

**Development of well-defined, bench-stable Ni-NHC precatalysts for
challenging C-N bond formation reactions**

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Abstract

Transition-metal-catalyzed C–N bond formation represents one of the most powerful synthetic methods for constructing aromatic amines and nitrogen-containing heterocycles. While palladium has historically dominated this field, nickel has recently emerged as a sustainable and cost-effective alternative due to its earth abundance, unique redox flexibility, and capacity to engage in both two-electron and single-electron processes. However, despite its potential, the development of well-defined, air- and moisture-stable nickel complexes capable of promoting challenging amination reactions remains limited. This thesis describes the systematic design, synthesis, and catalytic evaluation of new generations of bench-stable Ni–NHC precatalysts that overcome longstanding challenges in nickel-catalyzed C–N cross-coupling. The work focused on enhancing catalyst stability and reactivity through rational modification of the NHC ligand's steric and electronic properties.

A first-generation Ni–NHC–IPr complex synthesized by Organ group shown to promote the amination of aryl chlorides under mild conditions while maintaining excellent air and moisture stability. The reactivity is consistent with in-situ reduction of Ni(II) to a catalytically active Ni(0) species operating through a conventional Ni(0)/Ni(II) cycle. Although its activity diminished with sterically hindered or electronically deactivated substrates, the results confirmed that well-defined Ni–NHC complexes can serve as reliable precatalysts for cross-coupling applications. Interestingly, an unusual halide reactivity trend was observed: aryl chlorides afforded higher yields than their bromide or iodide analogues. This behavior was attributed to catalyst poisoning by bromide and iodide species, which divert the Ni complex off-cycle and terminate productive catalysis. These findings emphasize the distinctive oxidative-addition behavior of the Ni–NHC system and the critical role of halide identity in determining catalytic efficiency and stability.

Building on these results, the Ni–NHC–IPr complex was further explored under visible-light irradiation in combination with an iridium-based photoredox co-catalyst. The resulting dual [Ni]/[Ir] system enabled cross-coupling under milder conditions via high-valent Ni(I)/Ni(III) intermediates, accelerating reductive elimination. This photochemically assisted platform demonstrated enhanced performance with select substrates, highlighting the potential of redox modulation to extend nickel’s reactivity window. However, the need for an external photosensitizer and diminished performance with demanding substrates underscore the need for further refinement. To advance catalyst performance, a range of sterically and electronically tuned NHC ligands, including IPent, IHept, IPr^{*OMe}, IPr^{Cl}, IPent^{Cl}, and IHept^{Cl}, were developed and incorporated into new generations of Ni–NHC complexes. Comparative catalytic studies revealed that increasing ligand bulk accelerates reductive elimination against β -hydride elimination but can also hinder substrate coordination, highlighting the need for fine steric balance. Backbone chlorination enhanced reactivity and selectivity in certain reactions but did not universally improve yields. The introduction of π -allyl ligands replaced the bulky stabilizing ligand with a more compact π -allyl group, opening greater coordination flexibility to accommodate bulkier NHC ligands on nickel; however, this modification came at the expense of reduced air stability.

Collectively, this work establishes a comprehensive framework for the development of well-defined Ni–NHC precatalysts that are not only bench-stable but also tunable across electronic and steric dimensions to meet diverse synthetic challenges. Through rational ligand design and systematic evaluation, it delivers a versatile platform for promoting challenging C–N bond formation with reliable performance under mild conditions, advancing both mechanistic understanding and practical applicability, and ultimately bridging the gap between academic discovery and industrial application.

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Statement of Contributions

All work presented in this thesis is original and was performed by the author of this dissertation unless otherwise noted below. The work discussed in Sections 2.2 and 2.3 of Chapter 2 resulted from a collaboration with Dr. Jurgen Schulmeister, who led the design and synthesis of the first-generation Ni–NHC precatalyst (**83**).

Publications and presentations

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Table of Contents

Abstract.....	ii
Acknowledgements	iv
Statement of Contributions	vi
Publications and presentations	vi
Table of Contents	vii
List of figures.....	xii
List of schemes.....	xxi
List of tables.....	xxiii
List of abbreviations	xxv
1. Chapter 1: Introduction	1
1.1 Brief History of Nickel in Catalysis.....	1
1.2 Nickel vs Palladium	2
1.3 Catalyst design	5
1.3.1 Phosphine ligands	5
1.3.2 <i>N</i> -Heterocyclic Carbenes (NHCs) ligands	9
1.3.3 NHC as a ligand in nickel chemistry	15
1.4 C-N Cross-Coupling	16
1.4.1 Nickel-Catalyzed C-N Cross-Coupling	19
1.4.2 Nickel-NHC Catalyzed C-N Cross-Coupling.....	22
1.4.3 Mechanism of Ni-catalyzed amination reaction	33
1.4.4 Mechanism of Ni ⁰ /Ni ^{II} amination reaction	33
1.4.4.1 Oxidative Addition (OA)	34
1.4.4.2 Amine Coordination/Deprotonation steps	35
1.4.4.3 Reductive Elimination (RE).....	35
1.4.5 Ni ⁰ /Ni ^{II} <i>versus</i> Ni ^I /Ni ^{III} catalytic cycles in C–N cross-coupling	36

1.5	Plan of study	38
2.	Chapter 2: Development of well-defined, bench-stable Ni–NHC precatalysts for challenging C–N bond formation reactions.....	40
2.1	Background	40
2.2	Designing an air-stable Ni(II)–NHC precatalyst (1 st Generation).....	41
2.2.1	The nickel precursor	42
2.2.2	The ligand framework (NHC design)	43
2.2.3	Stabilizing (throw-away) ligand	44
2.3	Synthesis and characterization of air-stable Ni(II)–NHC precatalyst (1 st Generation)	44
2.4	Proposed mechanism for Ni(II)–NHC precatalyst activation.....	46
2.5	Activity of Ni–NHC–IPr in C–N bond formation reaction	46
2.6	<i>N</i> -arylation of morpholine.....	50
2.6.1	<i>N</i> -arylation of morpholine – Optimization studies	52
2.6.2	Ar–Cl <i>versus</i> Ar–Br in <i>N</i> -arylation of morpholine	55
2.6.3	Silver tetrafluoroborate as halide scavenger	64
2.7	Ni–NHC–IPr-catalyzed C–N bond formation reaction: Substrate scope.....	65
2.8	Conclusion	70
3.	Chapter 3: C–N cross-coupling reactions using a Ni–NHC/photoredox dual catalytic system	72
3.1	Proposed mechanism for Ni–NHC catalyzed C–N cross-coupling reactions	72
3.2	Nickel-catalyzed amination reaction using “Photoredox Catalysis”	75
3.3	Ni–NHC-catalyzed amination reaction using “Photoredox Catalysis”	79
3.3.1	Catalyst activation screening	83
3.3.2	Catalyst deactivation screening.....	84
3.3.3	Study the electrophile scope	85
3.3.4	Optimization studies	86

3.3.5	Expand the substrate scope	88
3.4	Conclusion	90
4.	Chapter 4: Enhancing reactivity and selectivity through ligand bulk: development of sterically demanding Ni–NHC precatalysts.....	92
4.1	Increasing the steric bulk of NHC ligand by extending the alkyl side chains.....	92
4.1.1	Synthesis and characterization of air-stable Ni–NHC–IPent and Ni–NHC–IHept precatalysts.....	94
4.1.2	Synthesis and characterization of air-stable Ni–NHC–IPr ^{*OMe} precatalyst.....	96
4.1.3	Evaluation of bulky Ni–NHC pr-catalysts in <i>N</i> -arylation of morpholine.....	98
4.1.4	Evaluation of bulky Ni–NHC pr-catalysts in monoarylation of primary alkyl amines	99
4.2	Increasing the steric bulk of NHC ligand via backbone functionalization.....	103
4.3	Backbone-chlorinated ligands: 2nd generation Ni–NHC precatalysts.....	104
4.3.1	Synthesis and characterization of air-stable Ni–NHC–IPr ^{Cl} precatalyst	105
4.3.2	Evaluation of Ni–NHC–IPr ^{Cl} in monoarylation of primary alkyl amines	107
4.3.3	Control experiment to confirm β -hydride elimination.....	108
4.3.4	Ni–NHC–IPr <i>versus</i> Ni–NHC–IPr ^{Cl} : A comparison study with different substrates	109
4.3.5	Synthesis and characterization of air-stable Ni–NHC–IPent ^{Cl} and Ni–NHC–IHept ^{Cl} precatalysts.....	111
4.3.6	Ni–NHC precatalysts <i>versus</i> in-situ formation Ni–NHC catalysts in C–N bond formation reaction.....	115
4.4	π-allyl as a less bulky stabilizing ligand: 3rd generation Ni–NHC precatalysts...	119
4.4.1	Synthesis and characterization of (NHC)Ni(π -allyl)Cl precatalysts	120
4.4.2	Evaluation of (NHC)Ni(π -allyl)Cl precatalysts in monoarylation of octylamine	121
4.4.3	Evaluation of (NHC)Ni(π -allyl)Cl precatalysts in <i>N</i> -arylation of morpholine ..	122
4.4.4	The impact of substrate steric bulk on catalytic performance of Ni(allyl)Cl(IPent ^{Cl})	123

4.4.5	Is bigger ligand always better?	125
4.4.6	Evaluation the stability of (NHC)Ni(π -allyl)Cl precatalysts in air atmosphere.	127
4.5	Conclusion	128
5.	Chapter 5: Conclusions and outlook.....	130
5.1	Summary of key findings	130
5.2	Conceptual Advances	131
5.3	Limitations and Challenges.....	132
5.4	Outlook	132
5.5	Broader Implications	133
6.	Chapter 6: Experimental procedures (by chapter).....	134
6.1	General experimental	134
6.2	Experimental procedures for chapter 2.....	136
6.2.1	Precatalyst preparation.....	136
6.2.1.1	Preparation of the stabilizing ligand	136
6.2.1.2	Preparation of the NHC–IPr ligand.....	139
6.2.1.3	Ligation of the ligands to the nickel	140
6.2.2	General procedure for C–N cross-coupling reaction.....	142
6.2.3	Spectral data.....	143
6.3	Experimental procedures for chapter 3.....	153
6.3.1	General procedure for C–N cross-coupling reaction using photoredox catalysis	153
6.3.2	Experimental procedures for catalyst deactivation screening.....	154
6.3.3	Spectral data.....	154
6.4	Experimental procedures for chapter 4.....	157
6.4.1	Catalyst preparation	157
6.4.1.1	Preparation of the Ni–NHC–IPent precatalyst.....	157
6.4.1.2	Preparation of the Ni–NHC–IHept precatalyst	165
6.4.1.3	Preparation of the Ni–NHC–IPr ^{*OMe} precatalyst.....	172
6.4.1.4	Preparation of the Ni–NHC–IPr ^{Cl} precatalyst.....	177
6.4.1.5	Preparation of the Ni–NHC–IPent ^{Cl} precatalyst	181

6.4.1.6	Preparation of the Ni–NHC–IHept ^{Cl} precatalyst	184
6.4.1.7	Preparation of the (NHC)Ni(π -allyl)Cl precatalysts	188
6.4.2	General procedure for monoarylation of primary alkyl amines.....	191
6.4.3	Spectral data.....	192
6.5	X-ray crystallographic data	195
6.5.1	X-ray crystallographic data for Ni–NHC–IPr and Ni–NHC–IPr ^{Cl}	195
6.5.2	X-ray crystallographic data for Ni–NHC–IPent, Ni–NHC–IPr* ^{OMe} , Ni(allyl)Cl(IPr), Ni(allyl)Cl(IPr ^{Cl}), Ni(allyl)Cl(IPent ^{Cl}), and Ni(allyl)Cl(IHept ^{Cl})	196
7.	References.....	197
	Appendix.....	223
	Appendix for chapter 2.....	223
	Appendix for chapter 3.....	270
	Appendix for chapter 4.....	280
	X-ray diffraction data.....	323
	X-ray diffraction data for Ni–NHC–IPr.....	325
	X-ray diffraction data for Ni–NHC–IPent	332
	X-ray diffraction data for Ni–NHC–IPr* ^{OMe}	346
	X-ray diffraction data for Ni–NHC–IPr ^{Cl}	359
	X-ray diffraction data for Ni(allyl)Cl(IPr).....	366
	X-ray diffraction data for Ni(allyl)Cl(IPr ^{Cl})	372
	X-ray diffraction data for Ni(allyl)Cl(IPent ^{Cl}).....	382
	X-ray diffraction data for Ni(allyl)Cl(IHept ^{Cl})	390
	Permission for Figures.....	400

List of figures

Figure 1. Periodic table of the elements.....	3
Figure 2. (a) Tolman cone angle analysis in phosphine ligands. (b) Cone angle in selected phosphine ligands.....	6
Figure 3. (a) Tolman electronic parameter (TEP) diagram, and table of selected examples. (b) schematic representation of the bonding situation in phosphine-metal-CO complexes.	7
Figure 4. Examples of state-of-the-art phosphine ligands used in cross-coupling	9
Figure 5. Synergistic push-pull electronic effect of NHC	10
Figure 6. Examples of state-of-the-art imidazole and imidazoline-based NHCs used in cross-coupling.....	12
Figure 7. Nolan's correlation of average ν_{CO} values for $[(\text{L})\text{Ir}(\text{CO})_2\text{Cl}]$ complexes with the Tolman electronic parameter (TEP). (■) Experimental values for phosphines; (•) Experimental values for NHCs; (Δ) Values obtained by linear regression.	13
Figure 8. A comparison of the steric topographies of the two ligand classes.....	14
Figure 9. (a) Schematic representation of the sphere used for the %VBur calculation. (b) Comparison of %VBur some of common NHC ligands with two popular phosphines.	15
Figure 10. Main fields of application of C–N cross-coupling reactions.....	17
Figure 11. Proposed mechanism for the Ni-catalyzed amination reaction	34
Figure 12. DFT-computed (a) $\text{Ni}^0/\text{Ni}^{\text{II}}$ and (b) $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ catalytic cycles for the C–N cross-coupling of chlorobenzene and ammonia, $\text{L} = \text{PAd-DalPhos}$	37
Figure 13. Representative examples of Ni–NHC precatalysts developed over the past two decades.	41
Figure 14. Attributes of the 1 st generation of Ni–NHC complex (83) made by Organ group	42
Figure 15. Structure of the $\text{Ni}(\text{cod})_2$ precursor	42
Figure 16. SC-XRD analysis of the Ni–NHC–IPr (83) complex from two different view	46
Figure 17. Optimization studies – Catalyst loading.....	53
Figure 18. Optimization studies – temperature and time screening.....	54
Figure 19. Optimization studies – Time screening..	55
Figure 20. Oxidative addition of various aryl halides with palladium and nickel catalysts	57
Figure 21. Salt effect in nickel-catalyzed N-arylation of morpholine using 4-chloroanisole as electrophile partner	58

Figure 22. Salt effect in nickel-catalyzed N-arylation of morpholine using 4-bromoanisole as electrophile partner	59
Figure 23. Salt effect in nickel-catalyzed N-arylation of morpholine using 4-Methoxyphenyl Trifluoromethanesulfonate as electrophile partner	60
Figure 24. Triflate salt effect in nickel-catalyzed N-arylation of morpholine using 4-chloroanisole as electrophile partner	61
Figure 25. Proposed mechanism for the Ni–NHC-catalyzed C–N cross-coupling reactions	73
Figure 26. High-energy triplet state of iridium-based photocatalyst acting as a potent single-electron oxidant or reductant	76
Figure 27. Proposed mechanism reported by Buchwald for the amination reaction using photoredox/nickel dual catalyst system.	78
Figure 28. [Ni]/[Ir] as dual photoredox catalytic system for C–N bond formation reaction	79
Figure 29. Photoredox reaction set-up for [Ni]/[Ir]-catalyzed C–N bond formation reaction.....	80
Figure 30. Catalyst activation screening	84
Figure 31. Catalyst deactivation screening	85
Figure 32. Optimization studies – Ni–NHC–IPr (83) loading	87
Figure 33. Optimization studies – [Ir] photocatalyst (145) loading.....	87
Figure 34. Optimization studies – base screening.....	88
Figure 35. UV-150 photochemical reactor developed by Vapourtec company.....	90
Figure 36. Increasing the steric bulk of NHC ligand from isopropyl (83) to isopentyl (165) and isoheptyl (174)	93
Figure 37. SC-XRD analysis of the Ni–NHC–IPent (165) complex from two different view	96
Figure 38. Increasing the steric bulk of NHC ligand from isopropyl (83) to diphenylmethyl (181)	97
Figure 39. SC-XRD analysis of the Ni–NHC–IPr*OMe (181) complex from two different view	98
Figure 40. Proposed mechanism for the Ni–NHC-catalyzed monoarylation of octylamine	102
Figure 41. SC-XRD analysis of the Ni–NHC–IPr ^{Cl} (188) complex from two different view ...	106
Figure 42. Increasing the steric bulk of chlorinated NHC ligand from chlorinated isopropyl (188) to chlorinated isopentyl (203) and isoheptyl (206)	111
Figure 43. SC-XRD structure of the isolated material indicating no coordination between Ni and the NHC–IPent ^{Cl} ligand.....	113

Figure 44. Formation of nickel black due to thermal decomposition of the Ni(cod) ₂ at 60 °C .	114
Figure 45. The development of (NHC)Ni(π -allyl)Cl precatalysts	119
Figure 46. SC-XRD analysis of the Ni(allyl)Cl(IPr) 207 , Ni(allyl)Cl(IPr ^{Cl}) 208 , Ni(allyl)Cl(IPent ^{Cl}) 209 , and Ni(allyl)Cl(IHept ^{Cl}) 210 complexes from two different view	120
Figure 47. Evaluation of Ni(allyl)Cl(IPr) (207), Ni(allyl)Cl(IPr ^{Cl}) (208), Ni(allyl)Cl(IPent ^{Cl}) (209), and Ni(allyl)Cl(IHept ^{Cl}) (210) precatalysts in monoarylation of octylamine	121
Figure 48. Evaluation of Ni(allyl)Cl(IPr) (207), Ni(allyl)Cl(IPr ^{Cl}) (208), Ni(allyl)Cl(IPent ^{Cl}) (209), and Ni(allyl)Cl(IHept ^{Cl}) (210) precatalysts in N-arylation of morpholine	122
Figure 49. Evaluating the stability of Ni(allyl)Cl(IPent ^{Cl}) precatalyst in air atmosphere, (a) solid state, (b) solution (deuterated benzene)	127
Figure 50. Schematic representation of the enhanced stability of first-generation Organ-type Ni–NHC complexes compared to (NHC)Ni(π -allyl)Cl precatalysts	128
Figure 51. Calibration curve for the N-arylation of morpholine determined by GC-FID analysis (refer to Figures 17–19).	143
Figure A1. ¹ H NMR spectrum of 76 (500 MHz, CDCl ₃).....	223
Figure A2. ¹ H NMR spectrum of 77 (500 MHz, CDCl ₃)	223
Figure A3. ¹ H NMR spectrum of 78 (500 MHz, CDCl ₃)	224
Figure A4. ¹³ C NMR spectrum of 78 (125 MHz, CDCl ₃)	224
Figure A5. ¹ H NMR spectrum of 80 (500 MHz, CDCl ₃)	225
Figure A6. ¹³ C NMR spectrum of 80 (125 MHz, CDCl ₃)	225
Figure A7. ¹ H NMR spectrum of 81 (500 MHz, CDCl ₃)	226
Figure A8. ¹³ C NMR spectrum of 81 (125 MHz, CDCl ₃)	226
Figure A9. ¹ H NMR spectrum of 82 (600 MHz, C ₆ D ₆).....	227
Figure A10. ¹³ C NMR spectrum of 82 (150 MHz, C ₆ D ₆).....	227
Figure A11. ¹ H NMR spectrum of 83 (400 MHz, CDCl ₃)	228
Figure A12. ¹³ C NMR spectrum of 83 (100 MHz, C ₆ D ₆).....	228
Figure A13. ¹ H NMR spectrum of 88 (400 MHz, CDCl ₃)	229
Figure A14. ¹³ C NMR spectrum of 88 (100 MHz, CDCl ₃)	229
Figure A15. ¹ H NMR spectrum of 90 (400 MHz, CDCl ₃)	230
Figure A16. ¹³ C NMR spectrum of 90 (100 MHz, CDCl ₃)	230
Figure A17. ¹ H NMR spectrum of 97 (400 MHz, CDCl ₃)	231

Figure A18. ^{13}C NMR spectrum of 97 (100 MHz, CDCl_3)	231
Figure A19. ^1H NMR spectrum of 98 (400 MHz, CDCl_3)	232
Figure A20. ^{13}C NMR spectrum of 98 (100 MHz, CDCl_3)	232
Figure A21. ^1H NMR spectrum of 99 (400 MHz, CDCl_3)	233
Figure A22. ^{13}C NMR spectrum of 99 (100 MHz, CDCl_3)	233
Figure A23. ^1H NMR spectrum of 107 (400 MHz, CDCl_3)	234
Figure A24. ^{13}C NMR spectrum of 107 (100 MHz, CDCl_3)	234
Figure A25. ^1H NMR spectrum of 108 (400 MHz, CDCl_3)	235
Figure A26. ^{13}C NMR spectrum of 108 (100 MHz, CDCl_3)	235
Figure A27. ^1H NMR spectrum of 109 (400 MHz, CDCl_3)	236
Figure A28. ^{13}C NMR spectrum of 109 (100 MHz, CDCl_3)	236
Figure A29. ^1H NMR spectrum of 110 (400 MHz, CDCl_3)	237
Figure A30. ^{13}C NMR spectrum of 110 (100 MHz, CDCl_3)	237
Figure A31. ^1H NMR spectrum of 111 (400 MHz, CDCl_3)	238
Figure A32. ^{13}C NMR spectrum of 111 (100 MHz, CDCl_3)	238
Figure A33. ^1H NMR spectrum of 112 (400 MHz, CDCl_3)	239
Figure A34. ^{13}C NMR spectrum of 112 (100 MHz, CDCl_3)	239
Figure A35. ^1H NMR spectrum of 113 (400 MHz, CDCl_3)	240
Figure A36. ^{13}C NMR spectrum of 113 (100 MHz, CDCl_3)	240
Figure A37. ^1H NMR spectrum of 114 (400 MHz, CDCl_3)	241
Figure A38. ^{13}C NMR spectrum of 114 (100 MHz, CDCl_3)	241
Figure A39. ^1H NMR spectrum of 115 (400 MHz, CDCl_3)	242
Figure A40. ^{13}C NMR spectrum of 115 (100 MHz, CDCl_3)	242
Figure A41. ^1H NMR spectrum of 116 (400 MHz, CDCl_3)	243
Figure A42. ^{13}C NMR spectrum of 116 (100 MHz, CDCl_3)	243
Figure A43. ^1H NMR spectrum of 117 (400 MHz, CDCl_3)	244
Figure A44. ^{13}C NMR spectrum of 117 (100 MHz, CDCl_3)	244
Figure A45. ^1H NMR spectrum of 118 (400 MHz, CDCl_3)	245
Figure A46. ^{13}C NMR spectrum of 118 (100 MHz, CDCl_3)	245
Figure A47. ^1H NMR spectrum of 119 (400 MHz, CDCl_3)	246
Figure A48. ^{13}C NMR spectrum of 119 (100 MHz, CDCl_3)	246

Figure A49. ^1H NMR spectrum of 120 (400 MHz, CDCl_3)	247
Figure A50. ^{13}C NMR spectrum of 120 (100 MHz, CDCl_3)	247
Figure A51. ^1H NMR spectrum of 121 (400 MHz, CDCl_3)	248
Figure A52. ^{13}C NMR spectrum of 121 (100 MHz, CDCl_3)	248
Figure A53. ^1H NMR spectrum of 122 (400 MHz, CDCl_3)	249
Figure A54. ^{13}C NMR spectrum of 122 (100 MHz, CDCl_3)	249
Figure A55. ^1H NMR spectrum of 123 (400 MHz, CDCl_3)	250
Figure A56. ^{13}C NMR spectrum of 123 (100 MHz, CDCl_3)	250
Figure A57. ^1H NMR spectrum of 124 (400 MHz, CDCl_3)	251
Figure A58. ^{13}C NMR spectrum of 124 (100 MHz, CDCl_3)	251
Figure A59. ^1H NMR spectrum of 125 (400 MHz, CDCl_3)	252
Figure A60. ^{13}C NMR spectrum of 125 (100 MHz, CDCl_3)	252
Figure A61. ^1H NMR spectrum of 126 (400 MHz, CDCl_3)	253
Figure A62. ^{13}C NMR spectrum of 126 (100 MHz, CDCl_3)	253
Figure A63. ^1H NMR spectrum of 127 (400 MHz, CDCl_3)	254
Figure A64. ^{13}C NMR spectrum of 127 (100 MHz, CDCl_3)	254
Figure A65. ^1H NMR spectrum of 128 (400 MHz, CDCl_3)	255
Figure A66. ^{13}C NMR spectrum of 128 (100 MHz, CDCl_3)	255
Figure A67. ^1H NMR spectrum of 129 (400 MHz, CDCl_3)	256
Figure A68. ^{13}C NMR spectrum of 129 (100 MHz, CDCl_3)	256
Figure A69. ^1H NMR spectrum of 101 (400 MHz, CDCl_3)	257
Figure A70. ^{13}C NMR spectrum of 101 (100 MHz, CDCl_3)	257
Figure A71. ^1H NMR spectrum of 130 (400 MHz, CDCl_3)	258
Figure A72. ^{13}C NMR spectrum of 130 (100 MHz, CDCl_3)	258
Figure A73. ^1H NMR spectrum of 131 (400 MHz, CDCl_3)	259
Figure A74. ^{13}C NMR spectrum of 131 (100 MHz, CDCl_3)	259
Figure A75. ^1H NMR spectrum of 136 (400 MHz, CDCl_3)	260
Figure A76. ^{13}C NMR spectrum of 136 (100 MHz, CDCl_3)	260
Figure A77. ^1H NMR spectrum of 137 (400 MHz, CDCl_3)	261
Figure A78. ^{13}C NMR spectrum of 137 (100 MHz, CDCl_3)	261
Figure A79. ^1H NMR spectrum of 138 (400 MHz, CDCl_3)	262

Figure A80. ^{13}C NMR spectrum of 138 (100 MHz, CDCl_3)	262
Figure A81. ^1H NMR spectrum of 139 (400 MHz, CDCl_3)	263
Figure A82. ^{13}C NMR spectrum of 139 (100 MHz, CDCl_3)	263
Figure A83. ^1H NMR spectrum of 140 (400 MHz, CDCl_3)	264
Figure A84. ^{13}C NMR spectrum of 140 (100 MHz, CDCl_3)	264
Figure A85. ^1H NMR spectrum of 141 – monoarylated product (400 MHz, CDCl_3)	265
Figure A86. ^{13}C NMR spectrum of 141 – monoarylated product (100 MHz, CDCl_3)	265
Figure A87. ^1H NMR spectrum of 142 – diarylated product (400 MHz, CDCl_3)	266
Figure A88. ^{13}C NMR spectrum of 142 – diarylated product (100 MHz, CDCl_3)	266
Figure A89. ^1H NMR spectrum of 141,142/mono– and diarylated products (400 MHz, CDCl_3)	267
Figure A90. ^1H NMR spectrum of 143 – monoarylated product (400 MHz, CDCl_3)	267
Figure A91. ^{13}C NMR spectrum of 143 – monoarylated product (100 MHz, CDCl_3)	268
Figure A92. ^1H NMR spectrum of 144 – diarylated product (400 MHz, CDCl_3)	268
Figure A93. ^{13}C NMR spectrum of 144 – diarylated product (100 MHz, CDCl_3)	269
Figure A94. ^1H NMR spectrum of 143,144/mono– and diarylated products (400 MHz, CDCl_3)	269
Figure A95. ^1H NMR spectrum of 148 (400 MHz, CDCl_3)	270
Figure A96. ^{13}C NMR spectrum of 148 (100 MHz, CDCl_3)	270
Figure A97. ^1H NMR spectrum of 149 (400 MHz, CDCl_3)	271
Figure A98. ^{13}C NMR spectrum of 149 (100 MHz, CDCl_3)	271
Figure A99. ^1H NMR spectrum of 150 (400 MHz, CDCl_3)	272
Figure A100. ^{13}C NMR spectrum of 150 (100 MHz, CDCl_3)	272
Figure A101. ^1H NMR spectrum of 151 (400 MHz, CDCl_3)	273
Figure A102. ^{13}C NMR spectrum of 151 (100 MHz, CDCl_3)	273
Figure A103. ^1H NMR spectrum of 152 (400 MHz, CDCl_3)	274
Figure A104. ^{13}C NMR spectrum of 152 (100 MHz, CDCl_3)	274
Figure A105. ^1H NMR spectrum of 153 (400 MHz, CDCl_3)	275
Figure A106. ^{13}C NMR spectrum of 153 (100 MHz, CDCl_3)	275
Figure A107. ^1H NMR spectrum of 154 (400 MHz, CDCl_3)	276
Figure A108. ^{13}C NMR spectrum of 154 (100 MHz, CDCl_3)	276

Figure A109. ^1H NMR spectrum of 155 (400 MHz, CDCl_3)	277
Figure A110. ^{13}C NMR spectrum of 155 (100 MHz, CDCl_3)	277
Figure A111. ^1H NMR spectrum of 156 (400 MHz, CDCl_3)	278
Figure A112. ^{13}C NMR spectrum of 156 (100 MHz, CDCl_3)	278
Figure A113. ^1H NMR spectrum of 157 (400 MHz, CDCl_3)	279
Figure A114. ^{13}C NMR spectrum of 157 (100 MHz, CDCl_3)	279
Figure A115. ^1H NMR spectrum of 161 (300 MHz, CDCl_3)	280
Figure A 116. ^1H NMR spectrum of 162 (500 MHz, CDCl_3)	281
Figure A117. ^{13}C NMR spectrum of 162 (125 MHz, CDCl_3)	281
Figure A118. ^1H NMR spectrum of 163a (500 MHz, CDCl_3)	282
Figure A119. ^{13}C NMR spectrum of 163a (125 MHz, CDCl_3)	282
Figure A120. ^1H NMR spectrum of 163b (500 MHz, CDCl_3)	283
Figure A121. ^{13}C NMR spectrum of 163b (125 MHz, CDCl_3)	283
Figure A122. ^1H NMR spectrum of 164 (600 MHz, C_6D_6).....	284
Figure A123. ^{13}C NMR spectrum of 164 (150 MHz, C_6D_6).....	284
Figure A124. ^1H NMR spectrum of 165 (400 MHz, C_6D_6).....	285
Figure A125. ^{13}C NMR spectrum of 165 (100 MHz, C_6D_6).....	285
Figure A126. ^1H NMR spectrum of 167 (500 MHz, CDCl_3)	286
Figure A127. ^{13}C NMR spectrum of 167 (125 MHz, CDCl_3)	286
Figure A128. ^1H NMR spectrum of 168 (500 MHz, CDCl_3)	287
Figure A129. ^{13}C NMR spectrum of 168 (125 MHz, CDCl_3)	287
Figure A130. ^1H NMR spectrum of 170 (500 MHz, CDCl_3)	288
Figure A131. ^{13}C NMR spectrum of 170 (125 MHz, CDCl_3)	288
Figure A132. ^1H NMR spectrum of 171 (500 MHz, CDCl_3)	289
Figure A133. ^{13}C NMR spectrum of 171 (125 MHz, CDCl_3)	289
Figure A134. ^1H NMR spectrum of 172 (500 MHz, CDCl_3)	290
Figure A135. ^{13}C NMR spectrum of 172 (125 MHz, CDCl_3)	290
Figure A136. ^1H NMR spectrum of 173 (600 MHz, C_6D_6).....	291
Figure A137. ^{13}C NMR spectrum of 173 (150 MHz, C_6D_6).....	291
Figure A138. ^1H NMR spectrum of 174 (400 MHz, C_6D_6).....	292
Figure A139. ^{13}C NMR spectrum of 174 (100 MHz, C_6D_6).....	292

Figure A140. ^1H NMR spectrum of 177 (500 MHz, CDCl_3)	293
Figure A141. ^{13}C NMR spectrum of 177 (125 MHz, CDCl_3)	293
Figure A142. ^1H NMR spectrum of 178 (500 MHz, CDCl_3)	294
Figure A143. ^{13}C NMR spectrum of 178 (125 MHz, CDCl_3)	294
Figure A144. ^1H NMR spectrum of 179 (500 MHz, CDCl_3)	295
Figure A145. ^{13}C NMR spectrum of 179 (125 MHz, CDCl_3)	295
Figure A146. ^1H NMR spectrum of 180 (600 MHz, C_6D_6).....	296
Figure A147. ^{13}C NMR spectrum of 180 (150 MHz, C_6D_6).....	296
Figure A148. ^1H NMR spectrum of 181 (500 MHz, CDCl_3)	297
Figure A149. ^{13}C NMR spectrum of 181 (100 MHz, C_6D_6).....	297
Figure A150. ^1H NMR spectrum of 186 (500 MHz, CDCl_3)	298
Figure A151. ^{13}C NMR spectrum of 186 (125 MHz, CDCl_3)	298
Figure A152. ^1H NMR spectrum of 187 (600 MHz, C_6D_6).....	299
Figure A153. ^{13}C NMR spectrum of 187 (150 MHz, C_6D_6).....	299
Figure A154. ^1H NMR spectrum of 188 (500 MHz, CDCl_3)	300
Figure A155. ^{13}C NMR spectrum of 188 (100 MHz, C_6D_6).....	300
Figure A156. ^1H NMR spectrum of 201 (500 MHz, CDCl_3)	301
Figure A157. ^{13}C NMR spectrum of 201 (125 MHz, CDCl_3)	301
Figure A158. ^1H NMR spectrum of 202 (600 MHz, C_6D_6).....	302
Figure A159. ^{13}C NMR spectrum of 202 (150 MHz, C_6D_6).....	302
Figure A160. ^1H NMR spectrum of 203 (400 MHz, C_6D_6).....	303
Figure A161. ^{13}C NMR spectrum of 203 (100 MHz, C_6D_6).....	303
Figure A162. ^1H NMR spectrum of 204 (500 MHz, CDCl_3)	304
Figure A163. ^{13}C NMR spectrum of 204 (125 MHz, CDCl_3)	304
Figure A164. ^1H NMR spectrum of 205 (600 MHz, C_6D_6).....	305
Figure A165. ^{13}C NMR spectrum of 205 (150 MHz, C_6D_6).....	305
Figure A166. ^1H NMR spectrum of 206 (400 MHz, C_6D_6).....	306
Figure A167. ^{13}C NMR spectrum of 206 (100 MHz, C_6D_6).....	306
Figure A168. ^1H NMR spectrum of 207 (500 MHz, C_6D_6).....	307
Figure A169. ^{13}C NMR spectrum of 207 (125 MHz, C_6D_6).....	307
Figure A170. ^1H NMR spectrum of 208 (500 MHz, C_6D_6).....	308

Figure A171. ^{13}C NMR spectrum of 208 (125 MHz, C_6D_6).....	308
Figure A172. ^1H NMR spectrum of 209 (500 MHz, C_6D_6).....	309
Figure A173. ^{13}C NMR spectrum of 209 (125 MHz, C_6D_6).....	309
Figure A174. ^1H NMR spectrum of 210 (500 MHz, C_6D_6).....	310
Figure A175. ^{13}C NMR spectrum of 210 (125 MHz, C_6D_6).....	310
Figure A176. ^1H NMR spectrum of 102 (500 MHz, CDCl_3)	311
Figure A177. ^{13}C NMR spectrum of 102 (125 MHz, CDCl_3)	311
Figure A178. ^1H NMR spectrum of 191 (400 MHz, CDCl_3)	312
Figure A179. ^{13}C NMR spectrum of 191 (100 MHz, CDCl_3)	312
Figure A180. ^1H NMR spectrum of 192 (400 MHz, CDCl_3)	313
Figure A181. ^{13}C NMR spectrum of 192 (100 MHz, CDCl_3)	313
Figure A182. ^1H NMR spectrum of 193 (400 MHz, CDCl_3)	314
Figure A183. ^{13}C NMR spectrum of 193 (100 MHz, CDCl_3)	314
Figure A184. ^1H NMR spectrum of 194 (400 MHz, CDCl_3)	315
Figure A185. ^{13}C NMR spectrum of 194 (100 MHz, CDCl_3)	315
Figure A186. ^1H NMR spectrum of 195 (400 MHz, CDCl_3)	316
Figure A187. ^{13}C NMR spectrum of 195 (100 MHz, CDCl_3)	316
Figure A188. ^1H NMR spectrum of 196 (400 MHz, CDCl_3)	317
Figure A189. ^{13}C NMR spectrum of 196 (100 MHz, CDCl_3)	317
Figure A190. ^1H NMR spectrum of 197 (400 MHz, CDCl_3)	318
Figure A191. ^{13}C NMR spectrum of 197 (100 MHz, CDCl_3)	318
Figure A192. ^1H NMR spectrum of 198 (400 MHz, CDCl_3)	319
Figure A 193. ^{13}C NMR spectrum of 198 (100 MHz, CDCl_3)	319
Figure A194. ^1H NMR spectrum of 199 (400 MHz, CDCl_3)	320
Figure A195. ^{13}C NMR spectrum of 199 (100 MHz, CDCl_3)	320
Figure A196. ^1H NMR spectrum of 212 (400 MHz, CDCl_3)	321
Figure A197. ^{13}C NMR spectrum of 212 (100 MHz, CDCl_3)	321
Figure A198. ^1H NMR spectrum of 213 (400 MHz, CDCl_3)	322
Figure A199. ^{13}C NMR spectrum of 213 (100 MHz, CDCl_3)	322

List of schemes

Scheme 1. The first C-N Pd-catalyzed coupling	18
Scheme 2. The Buchwald–Hartwig C–N cross-coupling reactions.	18
Scheme 3. Ni-catalyzed amination of amines with bromoarenes under Cristau’s and Desmurs’ conditions	19
Scheme 4. Ni-catalyzed amination of aryl chlorides developed by Buchwald’s group.	20
Scheme 5. Ni-catalyzed amination of aryl chlorides with 1-substituted piperazines developed by Fort’s group.....	21
Scheme 6. Fort’s modified conditions for Ni-catalyzed amination of (hetero)-aryl chlorides	23
Scheme 7. Aryl Amination Catalyzed with Ni(NHC)CpCl Complexes as Precatalysts.....	24
Scheme 8. [Ni(IPr)Cl ₂ (PPh ₃)]-catalyzed amination of bromoarenes with anilines.....	25
Scheme 9. First room-temperature Ni-catalyzed amination of (hetero)aryl chlorides	26
Scheme 10. Aryl amination catalyzed with Ni(NHC)CpCl Complexes as precatalysts	27
Scheme 11. Aryl amination catalyzed with that [Ni(allyl)(IPr* ^{OMe})Cl] Complex (55) as precatalyst	28
Scheme 12. First Ni-catalyzed arylation of indoles and carbazoles with heteroaryl chlorides....	30
Scheme 13. Aryl amination catalyzed with well-defined Ni(0)-NHC Complex as precatalyst..	31
Scheme 14. (a) Novel Ni-NHC precatalysts made by Jamison. (b) Aryl amination with precatalyst 71	32
Scheme 15. Hypothesized mechanism of activation for Jamison type Ni-NHC precatalyst	33
Scheme 16. Comparison of palladium- and nickel-catalyzed C–N cross-coupling	33
Scheme 17. Representative synthesis of an NHC from its protonated salt form	43
Scheme 18. Methylation of 2-Chlorophenethylamine (75) to 2-Chlorophenethyl N-methylamine (78) through three-step process (protection, methylation, deprotection).....	44
Scheme 19. General procedure for synthesis Ni–NHC–IPr (83) precatalyst (1 st Generation)	45
Scheme 20. Proposed mechanism of precatalyst activation	46
Scheme 21. Substrate scope of amination reactions catalyzed by Ni–NHC–IPr (83) (a) electrophile scope, (b) nucleophile scope, ^[a] Isolated yield, average of two runs.....	49
Scheme 22. Formation of nickel halide-bridged complex (105) in N-arylation of morpholine...	63
Scheme 23. Substrate scope of amination reactions catalyzed by Ni–NHC–IPr (83).....	69

Scheme 24. New strategy to use four different oxidation states of nickel (0, +1, +2, and +3) to facilitate the reductive elimination in C–N cross-coupling reactions catalyzed by Ni–NHC	75
Scheme 25. Using bromobenzene, and bromotoluene (ortho, meta and para) in N-arylation of pyrrolidine.....	86
Scheme 26. Substrate scope of C–N bond formation catalyzed by nickel/photoredox dual catalytic system.	89
Scheme 27. Increasing the steric bulk of NHC ligand facilitate the reductive elimination step..	93
Scheme 28. General procedure for synthesis Ni–NHC–IPent (165) precatalyst.....	94
Scheme 29. General procedure for synthesis Ni–NHC–IHept (174) precatalyst.....	95
Scheme 30. General procedure for synthesis Ni–NHC–IPr ^{*OMe} (181) precatalyst.....	97
Scheme 31. Monoarylation of primary alkyl amines	100
Scheme 32. Evaluation of Ni–NHC–IPr (83) in selective monoarylation of octylamine	101
Scheme 33. Functionalization of the NHC ligand backbone	104
Scheme 34. Backbone chlorination: 2 nd generation of air-stable Ni–NHC complexes.....	105
Scheme 35. General procedure for synthesis Ni–NHC–IPr ^{Cl} (188) precatalyst.....	106
Scheme 36. Ni-catalyzed C–N bond-forming reaction using (a) aniline and (b) benzylamine as nucleophilic coupling partner	109
Scheme 37. General procedure for synthesis Ni–NHC–IPent ^{Cl} (203) and Ni–NHC–IHept ^{Cl} (206)	112
Scheme 38. Minimizing the steric bulk of the stabilizing ligand using π -allyl.....	119
Scheme 39. The impact of substrate steric bulk on catalytic performance of Ni(allyl)Cl(IPent ^{Cl})..	124
Scheme 40. General procedure for synthesis Ni–NHC–IPr (83) precatalyst	136
Scheme 41. General procedure for synthesis Ni–NHC–IPent (165) precatalyst.....	157
Scheme 42. General procedure for synthesis Ni–NHC–IHept (174) precatalyst.....	165
Scheme 43. General procedure for synthesis Ni–NHC–IPr ^{*OMe} (181) precatalyst.....	172
Scheme 44. General procedure for synthesis Ni–NHC–IPr ^{Cl} (188) precatalyst.....	177
Scheme 45. General procedure for synthesis Ni–NHC–IPent ^{Cl} (203) precatalyst	181
Scheme 46. General procedure for synthesis Ni–NHC–IHept ^{Cl} (206) precatalyst.....	184
Scheme 47. General procedure for synthesis (NHC)Ni(π -allyl)Cl precatalysts.....	188

List of tables

Table 1. Comparison of basic characteristics of nickel and palladium	4
Table 2. Representative examples of into Ni(0) and Ni(II) precursors	43
Table 3. The first evaluation of Ni–NHC–IPr (83) in C–N cross-coupling reaction	47
Table 4. Evaluation of Ni–NHC–IPr (83) in the cross-coupling of 4-chloroanisole as an electron-rich electrophile	48
Table 5. Evaluation of ligand on the catalytic efficiency of nickel in N-arylation of morpholine	51
Table 6. Optimization studies – base and solvent screening.....	52
Table 7. BDE Values for Aryl Halides (X = F, Cl, Br, I)	56
Table 8. Ar–Cl versus Ar–Br in N-arylation of morpholine.....	57
Table 9. Aryl halides effect in N-arylation of morpholine.....	62
Table 10. Investigate the effect of AgBF ₄ as halide scavenger in N-arylation of morpholine	65
Table 11. Control experiments to evaluate the necessity of each reaction component in the ligand-free nickel (74)/iridium (145) dual catalytic system for C–N bond formation.....	81
Table 12. Control experiments to evaluate the necessity of each reaction component in the Ni–NHC–IPr (83)/iridium (145) dual catalytic system for C–N bond formation	82
Table 13. Evaluation of Ni–NHC–IPent (165), Ni–NHC–IHept (174) and Ni–NHC–IPr*OMe (181) precatalysts in N-arylation of morpholine	99
Table 14. Evaluation of Ni–NHC–IPr (83), Ni–NHC–IPent (165), Ni–NHC–IHept (174) and Ni–NHC–IPr*OMe (181) precatalysts in monoarylation of octylamine	103
Table 15. Catalytic comparison of Ni–NHC–IPr ^{Cl} (188) with non-chlorinated analogues in the monoarylation of octylamine	108
Table 16. Ni–NHC–IPr versus Ni–NHC–IPr ^{Cl} : A comparison study with different substrates	110
Table 17. The ligation of nickel by bulky NHC–IPent ^{Cl} and NHC–IHept ^{Cl} ligands – Optimization studies	114
Table 18. Ni–NHC precatalysts versus in-situ formation Ni–NHC catalysts in N-arylation of morpholine.	117
Table 19. Ni–NHC precatalysts versus in-situ formation Ni–NHC catalysts in monoarylation of octylamine.....	118

Table 20. Comparison of Ni–NHC–IPr (83), Ni–NHC–IPr ^{Cl} (188), and Ni–NHC–IPent ^{Cl} (209) complexes in C–N bond formation reactions.....	126
Table A1. X-ray crystallographic data collection and refinement details for Ni–NHC–IPr (83), Ni–NHC–IPr ^{Cl} (188), Ni–NHC–IPent (165), and Ni–NHC–IPr* ^{OMe} (181).....	323
Table A2. X-ray crystallographic data collection and refinement details for Ni(allyl)Cl(IPr) (207), Ni(allyl)Cl(IPr ^{Cl}) (208), Ni(allyl)Cl(IPent ^{Cl}) (209), and Ni(allyl)Cl(IHept ^{Cl}) (210)	324
Table A3. Bond lengths for Ni–NHC–IPr (83)	325
Table A4. Bond angles for Ni–NHC–IPr (83)	327
Table A5. Bond lengths for Ni–NHC–IPent (165)	332
Table A6. Bond angles for Ni–NHC–IPent (165).....	335
Table A7. Bond lengths for Ni–NHC–IPr* ^{OMe} (181).....	346
Table A8. Bond angles for Ni–NHC–IPr* ^{OMe} (181)	350
Table A9. Bond lengths for Ni–NHC–IPr ^{Cl} (188)	359
Table A10. Bond angles for Ni–NHC–IPr ^{Cl} (188).....	361
Table A11. Bond lengths for Ni(allyl)Cl(IPr) (207)	366
Table A12. Bond angles for Ni(allyl)Cl(IPr) (207).....	368
Table A13. Bond lengths for Ni(allyl)Cl(IPr ^{Cl}) (208).....	372
Table A14. Bond angles for Ni(allyl)Cl(IPr ^{Cl}) (208)	374
Table A15. Bond lengths for Ni(allyl)Cl(IPent ^{Cl}) (209)	382
Table A16. Bond angles for Ni(allyl)Cl(IPent ^{Cl}) (209)	385
Table A17. Bond lengths for Ni(allyl)Cl(IHept ^{Cl}) (210)	390
Table A18. Bond angles for Ni(allyl)Cl(IHept ^{Cl}) (210).....	393

List of abbreviations

α	Alpha position, or angle label (X-ray crystallography)
%Vbur	Percentage of buried volume
Å	Angstrom
Ad	Adamantyl
Ar	Aryl
Atm	Atmospheric pressure
BHE	β -hydride elimination
BHT	3,5-Di-tert-4-butyl-4-methylphenol (butylated hydroxytoluene)
BippyPhos	5-(Di-tert-butylphosphino)-1', 3', 5'-triphenyl-1'H-[1,4']bipyrazole
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene
Boc	<i>tert</i> -butyloxycarbonyl
BOP	(Benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate
Br	Bromine
BrettPhos	2-Dicyclohexylphosphino-3,6-dimethoxy-2',4',6'-triisopropylbiphenyl
β	Beta position, or angle label (X-ray crystallography)
br	Broad (NMR spectroscopy)
Bu	Butyl
°C	Degree Celsius
cm ⁻¹	Wavenumbers
¹³ C	Carbon-13
C ₆ D ₆	Deuterated benzene
CDCl ₃	Deuterated chloroform
cod	Cyclooctadiene
CPent	1,3-bis(2,6-dicyclopentylphenyl)imidazole-2-ylidene
Cy	Cyclohexyl
δ	Chemical shift
Δ	Delta (difference between variables)
D	Deuterium, 2H

d	Doublet (NMR spectroscopy)
dd	Doublet of doublets (NMR spectroscopy)
ddd	Doublet of doublet of doublets (NMR spectroscopy)
ddt	Doublet of doublet of triplets (NMR spectroscopy)
deg (or °)	Degrees
DCM	Dichloromethane
DFT	Density Functional Theory
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DPPF	Bis(diphenylphosphino)ferrocene
EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
EDG	Electron-donating group
EI-MS	Electron impact mass spectroscopy
equiv.	Equivalents
ESI-MS	Electron spray ionization mass spectroscopy
Et	Ethyl
EWG	Electron-withdrawing group
<i>F</i>	Structure factors (X-ray crystallography)
γ	Gamma, angle label (X-ray crystallography)
<i>g</i>	Gram
ΔG	Gibbs free energy
$\Delta G^\ddagger$	Gibbs free energy of activation
GC-FID	Gas chromatography flame ionization detection
GC-MS	Gas chromatography mass spectrometry detection
h	Hour(s)
HRMS	High-resolution mass spectrometry
^1H	Proton
Hz	Hertz
ΔH	Enthalpy
$\Delta H^\ddagger$	Enthalpy of activation

HOMO	Highest occupied molecular orbital
IAd	1,3-diadamantylimidazol-2-ylidene
IBiox	Bisoxazolinium-derived NHC
IEt	1,3-bis(2,6-diethylphenyl)imidazol-2-ylidene
IHept	1,3-bis(2,6-di(4-heptyl)phenyl)imidazole-2-ylidene
IHept ^{Cl}	1,3-bis(2,6-di(4-heptyl)phenyl)-4,5-dichloroimidazol-2-ylidene
IHept ^{Me}	1,3-Bis(2,6-di(4-heptyl)phenyl)-4,5-dimethylimidazol-2-ylidene
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPent	1,3-bis(2,6-di(3-pentyl)phenyl)imidazole-2-ylidene
IPent ^{Cl}	1,3-bis(2,6-di(3-pentyl)phenyl)-4,5-dichloroimidazol-2-ylidene
IPent ^{Me}	1,3-Bis(2,6-di(3-pentyl)phenyl)-4,5-dimethylimidazol-2-ylidene
IPr	1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene
IPr*	1,3-bis(2,6-bis(di-para-tolylmethyl)phenyl)imidazole-2-ylidene
IPr ^{Cl}	1,3-bis(2,6-diisopropylphenyl)-4,5-dichloroimidazol-2-ylidene
IPr ^{Me}	1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethylimidazol-2-ylidene
IR	Infrared spectroscopy
Ir	Iridium
IS	Internal standard
J	Joules
ⁿ J _{AB}	n-bond scalar coupling constant between nuclei A and B
Josiphos	(R)-1-[(SP)-2-(Diphenylphosphino)ferrocenyl]ethylidicyclohexylphosphine
<i>k</i>	Rate constant
K	Kelvin
kcal	Kilocalorie
kJ	Kilojoules
λ	Wavelength
L	Neutral ligand donor
LiHMDS	Lithium bis(trimethylsilyl)amide
LUMO	Lowest unoccupied molecular
μ	Bridging ligand or absorption coefficient (X-ray crystallography)
M	Central metal atom (or molar when referring to concentration)

M ⁺	Parent ion (mass spectrometry)
m	Multiplet
Me	Methyl
mg	Milligram
MHz	Megahertz
MI	Migratory insertion
min	Minutes
mL	Milliliter
MLCT	Metal to ligand charge transfer
mmol	Millimoles
mol	Moles
MW	Molecular weight
MorDalPhos	Di(1-adamantyl)-2-morpholinophenylphosphine
<i>n</i> Bu	<i>n</i> -butyl
NHC	<i>N</i> -heterocyclic carbene
Ni	Nickel
NMR	Nuclear magnetic resonance
OA	Oxidative addition
OMe	Methoxy group, –OCH ₃
π	pi-bonding or orbital
p	Pentet (NMR spectroscopy)
Pd	Palladium
Pd[(<i>o</i> -tol) ₃ P] ₂	bis(tris(<i>o</i> -tolyl)phosphine)palladium(0)
Pd(PPh ₃) ₄	Tetrakis(triphenylphosphine)palladium(0)
Pd(dba) ₂	Bis(dibenzylideneacetone)palladium(0)
Pd ₂ (dba) ₃	Tris(dibenzylideneacetone)dipalladium(0)
Pd(PtBu ₃) ₂	Bis(tri- <i>tert</i> -butylphosphine)palladium(0)
PEPPSI	Pyridine-enhanced pre-catalyst preparation, stabilization, and initiation
Ph	Phenyl group, –C ₆ H ₅
pK _a	Negative logarithmic acid dissociation constant
ppm	Parts per million

q	Quartet (NMR spectroscopy)
R	Alkyl group
<i>R</i>	Reliability factor (X-ray crystallography)
Reflns	Reflections (X-ray crystallography)
rt	Room temperature
RE	Reductive elimination
RuPhos	dicyclohexy 1(2',6' -diisopropoxybiphenyl-2-yl)phosphine
σ	Estimated standard deviation (X-ray crystallography)
s	Singlet (NMR spectroscopy)
SIMes	1,3-bis(2,4,6-trimethylphenyl)imidazolidine-2-ylidene
SIPr	1,3-bis(2,6-diisopropylphenyl)imidazolidine-2-ylidene
SPhos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl
T	Temperature
<i>t</i> Bu	<i>tert</i> -butyl
TEP	Tolman's electronic parameter
TMEDA	Tetramethylethylenediamine
Tf	Trifluoromethanesulfonyl
THF	Tetrahydrofuran
TMS	Trimethylsilyl
TLC	Thin-layer chromatography
tr	Triplet (NMR spectroscopy)
TS	Transition state
X	Halide substituent (or anionic ligand donor)
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
XPhos	2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl
Z	Number of formula units per unit cell (X-ray crystallography)

Chapter 1

1. Chapter 1: Introduction

This section explores the fundamental concepts and unique properties that establish nickel as an important element in catalysis. It begins with an introduction to distinctive properties of nickel and catalytic potential, emphasizing the critical role ligands play in shaping its behavior. To provide a comprehensive understanding, key descriptors for assessing ligand properties in the context of nickel catalysis are introduced, highlighting their critical influence on reaction mechanisms and outcomes.

The discussion further explores the impact of ligands on the stabilization of nickel intermediates, demonstrating their role in enhancing both the efficiency and selectivity of catalytic processes. Representative examples of ligand-dependent nickel catalysis are presented to underscore how varying ligand environments can direct reaction pathways and diversify product formation. Additionally, this section concludes with an overview of nickel's broad applications, spanning its essential role in the total synthesis of complex natural products to its expanding utility in industrial-scale processes.

1.1 Brief History of Nickel in Catalysis

Nickel, discovered in 1751 by Axel Fredrik Cronstedt in Sweden, has a long and rich history in organometallic chemistry, predating many advancements in transition metal catalysis.¹ Its name, derived from the German term *kupfernickel*—meaning "devil's copper"—reflects the frustration of miners who mistook nickel ores for copper, only to find them barren of the desired metal.^{1,2} The first pure samples of nickel were isolated in 1775 by Torbern Bergman, and its reactivity gained significant attention in the 1890s when Ludwig Mond discovered its ability to form $\text{Ni}(\text{CO})_4$, a

toxic, low-boiling liquid used for nickel purification.³ Nickel's catalytic capabilities were further demonstrated in 1912 when Paul Sabatier, awarded the Nobel Prize in Chemistry, utilized nickel for the first hydrogenation of ethylene.⁴ Contributions by Wilke and his group at the Max Planck Institute later advanced the field by synthesizing important nickel complexes, such as Ni(cod)₂ (1,5-cyclooctadiene), and exploring their applications in olefin and diene oligomerization.³ These breakthroughs laid the foundation for industrial processes like the Shell Higher Olefins Process (SHOP) and the hydrocyanation of butadiene to adiponitrile, a precursor to nylon-6,6.^{5,6} Despite this legacy, nickel is often viewed as the "impoverished younger sibling"⁷ of palladium in transition metal catalysis, given palladium's dominance in cross-coupling reactions—a field recognized with the 2010 Nobel Prize in chemistry. Palladium's widespread applications, from natural product synthesis to drug discovery and manufacturing, have overshadowed nickel's capabilities. However, as a group 10 metal, nickel shares many fundamental reaction pathways with palladium and platinum and has proven to be far more than a low-cost substitute. Homogeneous nickel catalysis is currently experiencing a renaissance, with numerous innovative and diverse nickel-catalyzed reactions challenging longstanding misconceptions and expanding the frontiers of transition metal catalysis.⁷

1.2 Nickel vs Palladium

Nickel, positioned just above palladium in the periodic table ([Figure 1](#)), possesses unique reactivity that distinguishes it within transition metal catalysis. Nickel, as a relatively electropositive late transition metal, readily undergoes oxidative addition, resulting in a significant loss of electron density around the metal center.⁸ While reductive elimination is comparatively more challenging for nickel,⁹ its efficient oxidative addition enables the activation of cross-coupling electrophiles

that are typically less reactive under palladium catalysis, including phenol derivatives,^{10–12} aromatic nitriles,¹³ and even aryl fluorides.¹⁴

Figure 1 shows the periodic table of elements. A callout box highlights the element Nickel (Ni) with the following details:

- Atomic Number: 28
- Name: Nickel
- Symbol: Ni
- Atomic Weight: 58.693
- Electronic configuration: $[Ar] 3d^8 4s^2$

The periodic table includes elements from Hydrogen (1) to Oganesson (118), with Lanthanide and Actinide series at the bottom.

Figure 1. Periodic table of the elements

Moreover, nickel's ability to access multiple oxidation states (e.g., Ni(0), Ni(I), Ni(II), and Ni(III)) allows for a diverse range of catalytic cycles, including both polar and radical mechanisms. This flexibility supports unique reactivity patterns, such as Ni(0)/Ni(II), Ni(I)/Ni(III), Ni(0)/Ni(II)/Ni(III)/Ni(I) cycles, and even cycles in which nickel remains in the Ni(I) state for the entire catalytic cycle.¹⁵ These capabilities allow nickel to perform transformations that palladium cannot easily achieve, broadening its applicability across various chemical reactions.

Nickel complexes have long been recognized as effective catalysts for reactions involving alkenes and alkynes, such as oligomerization and reductive coupling.¹⁶ Their strong olefin bonding arises from nickel's ability to efficiently donate d-electrons to π -acceptors.¹⁷ Furthermore, β -hydride elimination is notably slower with nickel compared to palladium, as the energy barrier for Ni–C

bond rotation, a prerequisite for β -hydride elimination, is significantly higher in nickel complexes.¹⁸ This slower elimination can offer distinct advantages in catalytic selectivity.

Beyond its reactivity and selectivity, nickel differs from its group 10 counterparts in several notable ways. Economically, elemental nickel is approximately 2,000 times cheaper than palladium and 10,000 times less expensive than platinum on a mole-for-mole basis.¹⁹ Additionally, as a first-row transition metal, nickel features a small atomic radius, resulting in relatively short Ni–ligand bond lengths.²⁰ These unique characteristics have been used by researchers to develop innovative reactions, as illustrated by the examples discussed in the following sections.

Table 1. Comparison of basic characteristics of nickel and palladium⁷

Aspect	Nickel	Palladium
Oxidation States ^[a]	-1 0 +1 +2 +3 +4	0 +1 +2 +3 +4
Electronegativity	Less electronegative (1.91)	More electronegative (2.2)
Size	Smaller atomic radius	Larger atomic radius
Hard/Soft character	Harder	Softer
Mechanisms	Capable of radical and polar mechanisms	Mostly polar mechanisms
Reactivity	Facile oxidative addition	Facile reductive elimination
β-Hydride Elimination	Slower, improving selectivity in catalytic cycles	Faster, which can be beneficial in alkene functionalization
Bond Activation	Activates C–O, C–N, and even strong aryl-fluorine bonds effectively	Excellent at activating aryl-halide and C–H bonds
Cost	Significantly less expensive (nickel's cost is roughly 1/2000th that of palladium)	Expensive and increasingly scarce
Environmental Impact	Favorable due to lower cost and increasing focus on green chemistry	Less favorable due to higher cost and limited availability

^[a]The oxidation states in bold are more commonly involved in catalysis

1.3 Catalyst design

Catalyst design has played a crucial role in advancing nickel chemistry, and the major role in tuning the reactivity of a nickel center is played by ligands. The choice of ligand can significantly influence the stability, electronic properties, and steric environment of the nickel catalyst and thus control the course of the reaction. Ligands can modulate the electronic properties of the nickel center. Electron-donating ligands can enhance the nucleophilicity of the nickel, while electron-withdrawing ligands can increase its electrophilicity. The steric bulk of ligands influences the accessibility of substrates and reagents to the active catalytic center. Steric considerations are also crucial in determining the regio- and stereoselectivity of nickel-catalyzed reactions. In addition, ligands can stabilize the active nickel species, increasing their stability and preventing degradation. Some ligands can significantly influence the catalytic cycle by facilitating substrate activation or stabilization of reaction intermediates. The design and selection of appropriate ligands is therefore a cornerstone in the advancement of nickel catalysis and enables the fine-tuning of catalytic systems to achieve the desired reactivity and selectivity profile.

To date, many ligands have been introduced, but phosphine and N-heterocyclic carbene (NHC) ligands stand out as the two most intensively studied. They maintain their status as “blockbuster” ligand classes due to their proven effectiveness, versatility, and relative ease of handling, which make them essential in various catalytic applications.

1.3.1 Phosphine ligands

Phosphine ligands were the first and most commonly employed class of ligands in nickel chemistry. The steric and electronic characteristics of phosphine ligands can be systematically tuned by modifying the substituents on the phosphorus atom. Tolman introduced key parameters to evaluate these characteristics, including the Tolman cone angle, which assesses steric effects,

and the Tolman electronic parameter, which quantifies electron-donating ability. These metrics provide a comprehensive framework for understanding and optimizing the behavior of phosphine ligands in catalytic systems.^{21–23}

The Tolman cone angle (θ) quantifies the steric bulk of a ligand by measuring the space it occupies around the metal center. It is determined as the angle of a cone with the metal at its apex, using a fixed metal-phosphorus bond distance of 2.28 Å and extending the cone's edges to the van der Waals radii of the outermost ligand atoms (Figure 2a). The Tolman cone angle increases predictably with the size of the substituents on the phosphorus atom (e.g., R = *t*Bu versus R = Et, as shown in Figure 2b).²³ This predictable relationship offers a reliable means to evaluate and compare the steric bulk of phosphine ligands.

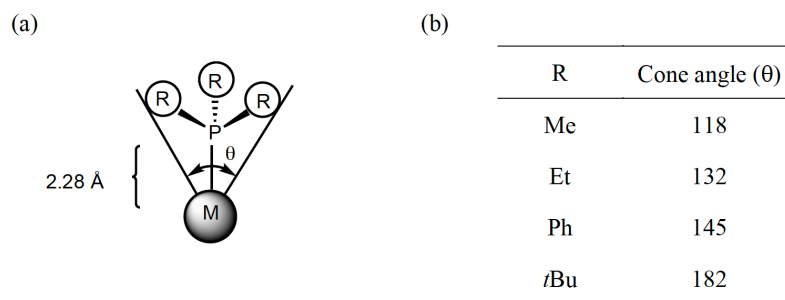


Figure 2. (a) Tolman cone angle analysis in phosphine ligands. (b) Cone angle in selected phosphine ligands²³

The Tolman Electronic Parameter (TEP) is a measure of the σ -donating properties of phosphine ligands. It is determined by analyzing the A_1 -symmetric CO stretching frequency of the complex $\text{LNi}(\text{CO})_3$, where L represents the phosphine ligand under study (Figure 3a).²⁴ Phosphine ligands (PR_3) primarily act as σ -donors, although they can also function as π -acceptors depending on the nature of the R substituent. Their σ -donor strength is highest when R is an electron-donating group, such as an alkyl group, and decreases with electron-withdrawing substituents like aryl groups. When a strong σ -donor phosphine binds to the metal center, it increases the electron density at the metal. This, in turn, enhances metal-to-carbonyl π -back donation into the π^* orbital of the CO

ligand, weakening the CO bond and lowering the $\nu(\text{CO})$ stretching frequency (Figure 3b). Conversely, with π -acceptor phosphines, electron density is pushed from the metal into the phosphine's σ^* orbital through π -back donation, leading to higher $\nu(\text{CO})$ stretching frequencies.^{22,23} By comparing these CO stretching frequencies across different complexes, the Lewis basicity and electronic properties of various phosphine ligands can be effectively assessed.

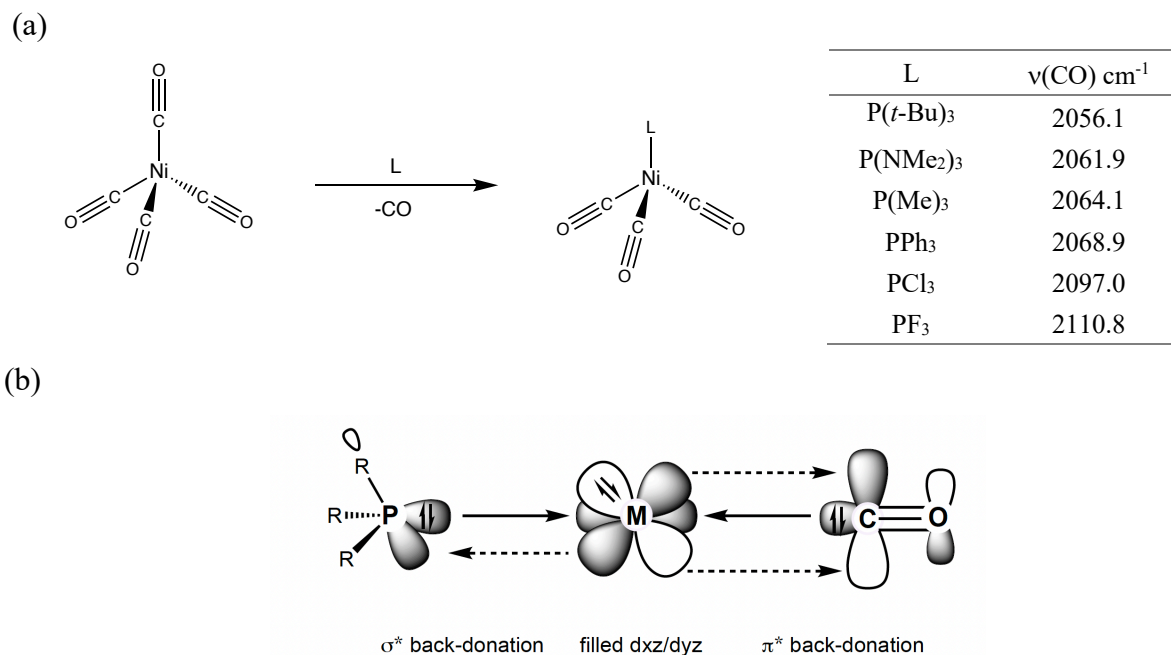


Figure 3. (a) Tolman electronic parameter (TEP) diagram, and table of selected examples. (b) schematic representation of the bonding situation in phosphine-metal-CO complexes.

Since the first report of nickel-mediated cross-coupling using phosphine ligands,²⁵ significant efforts have been dedicated to developing new phosphine ligands. This has led to the invention of numerous mono- and bidentate ligands designed to enhance the efficiency of these reactions (Figure 4). These advancements in ligand design have enabled remarkable progress, particularly in accommodating challenging substrates in cross-coupling and improving functional group compatibility. These innovations also allow for the use of increasingly milder reaction conditions, broadening the scope of cross-coupling applications. Notable contributions to ligand development, including trialkylphosphines (e.g., $\text{P}(t\text{Bu})_3$ (**1**), $\text{P}(i\text{Pr})_3$ (**2**), $\text{P}(\text{Cy})_3$ (**3**),²⁶ cataCXium A (**4**),²⁷),

(hetero)biaryl monophosphines (e.g., RuPhos (**5**),^{28,29} BrettPhos (**6**),²⁹ BippyPhos (**7**),^{30,31}), bisphosphines (e.g., BINAP (**8**)³², DPEPhos (**9**)³³), large bite angle bisphosphines (e.g., XantPhos (**10**),³⁴ CyPF-tBu JosiPhos (**11**),^{35–37} dppf (**12**),^{38,39}), mixed P,N donors (e.g., Mor-DalPhos (**13**),^{40–43} Me-DalPhos (**14**),⁴⁴), N-heterocyclic phosphine (e.g., NHP-DalPhos (**15**)⁴⁵), ortho-phenylene bisphosphine (e.g., PAd-DalPhos (**16**)⁴⁶, CyPAd-DalPhos (**17**)⁴⁷), and ortho-phenylene bisphosphine (e.g., DCYPBz (**18**)⁴⁸, PS-DPPBz, (**19**)⁴⁹) are highlighted in [Figure 4](#).

Although phosphines have proven to be highly effective ligands for palladium and nickel catalysis, their use is accompanied by several drawbacks. First, the steric bulk of phosphines typically projects away from the metal center, reducing its direct impact on catalytic performance. Additionally, trialkyl phosphines are pyrophoric and prone to oxidation in air, requiring handling under an inert atmosphere. They are also susceptible to degradation at high temperatures, necessitating the use of excess ligand to maintain catalytic activity. These limitations have driven the search for alternative ligands, with *N*-heterocyclic carbenes (NHCs) emerging as a promising option. NHCs offer high thermal stability, and ease of steric and electronic customization, making them an attractive replacement for phosphines in nickel-catalyzed reactions.⁵⁰

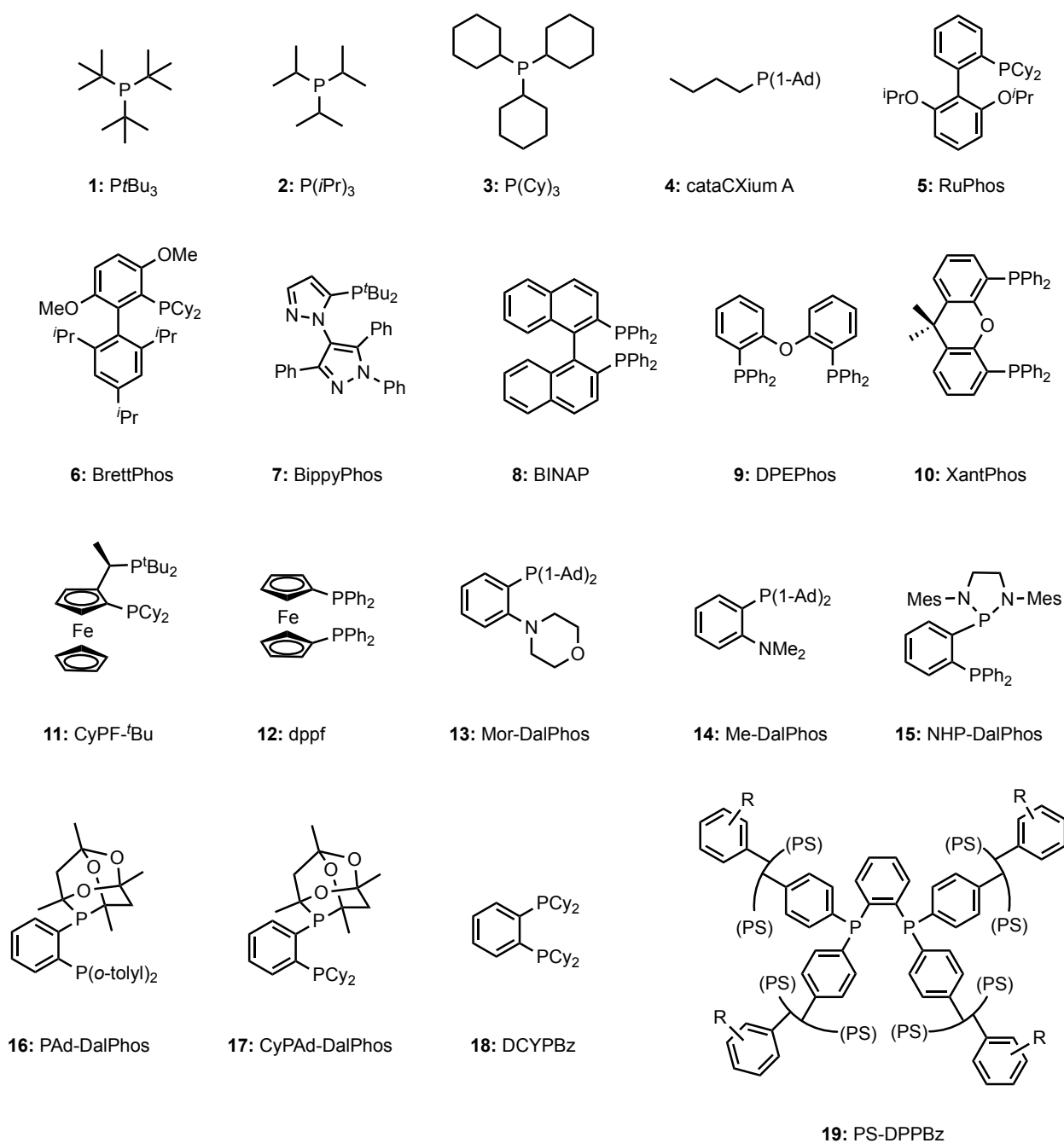


Figure 4. Examples of state-of-the-art phosphine ligands used in cross-coupling

1.3.2 *N*-Heterocyclic Carbenes (NHCs) ligands

N-Heterocyclic carbenes (NHCs), initially prepared independently by Wanzlick⁵¹ and Öfele⁵² in 1968 and later isolated by Arduengo⁵³ in 1991 (**28**), have attracted significant attention as versatile ligands in catalysis. They have emerged as valuable alternatives to phosphines, particularly in

transition-metal-catalyzed cross-coupling reactions. In 1995, Herrmann and colleagues first demonstrated the use of NHCs as ligands for palladium-catalyzed reactions, including the Heck coupling.⁵⁴ This breakthrough sparked considerable interest in the catalysis community, leading to the synthesis and development of a wide array of NHC ligands⁵⁵ (Figure 6). Structurally, NHCs are nitrogen-containing heterocyclic compounds featuring a divalent carbene center, whose remarkable stability arises from the electronic influence of the two adjacent nitrogen atoms.⁵⁶ These nitrogen atoms exert a synergistic push-pull electronic effect on the carbene center, significantly impacting its electronic properties (Figure 5).⁵⁷ In this push-pull system, the nitrogen atoms inductively withdraw σ -electrons while simultaneously mesomerically donating π -electrons to the imidazolium ring. The inductive electron withdrawal lowers the highest occupied molecular orbital (HOMO) energy level occupied by the p-orbital, thereby increases the energy gap between HOMO and lowest unoccupied molecular orbital (LUMO) levels of NHC. Hence, the second electron gets paired in the HOMO level resulting in the singlet form of carbene.^{57,58} Additionally, the mesomeric donation of non-bonding electrons from the p-orbital of the nitrogen overlaps with the empty p-orbitals of the carbene center, further reinforcing its stability. Unlike acyclic carbenes, which typically exist in the triplet state, the cyclic structure of NHCs enforces a bent geometry, locking them into a singlet state. This singlet-state stabilization enhances the σ -donor and π -acceptor capabilities of NHCs,^{56,59} enabling them to form strong and stable bonds with transition metals.

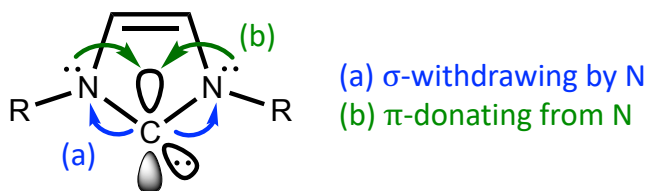


Figure 5. Synergistic push-pull electronic effect of NHC

While free NHCs can be isolated and characterized, they are typically synthesized and stored as their protonated HX salt forms for ease of handling. Advances in NHC ligand design have focused on modifying both the nitrogen substituents and the backbone of the imidazolium ring to enhance steric and electronic properties. For example, di-ortho-substituted aryl groups on the nitrogen atoms, such as those found in IMes (**20**) and IPr (**21**), are optimal for increasing reactivity and stability.⁶⁰

Recent advancements by researchers such as Organ^{61–63} and Nolan^{64–66} have significantly expanded the steric bulk of NHC ligands. For example, the size of the ortho substituents on IPr has been increased up to isononane (**22,23,24**) and IPr* (**25**). Similarly, substituting the N-aryl rings with bulkier groups such as naphthalene (**26,27**)^{67,68} and adamantyl (**28**)⁵³ has been explored to enhance ligand performance. Beyond modifications to N-substituents, considerable attention has been given to altering the backbone of NHC ligands. Notable examples include the saturation of the alkene to create SIMes (**29**) and SIPr (**30**),⁶⁰ as well as substitutions with functional groups like NMe₂ (**31**),⁶⁰ methyl (**32, 34, 36**),⁶⁰ and chlorine (**33, 35, 37**).^{61,69} Additionally, the development of chiral NHC ligands, such as IMes* (**38**) and others (**39,40**), has facilitated various asymmetric transformations, further broadening the scope of NHC applications in catalysis.^{70,71}

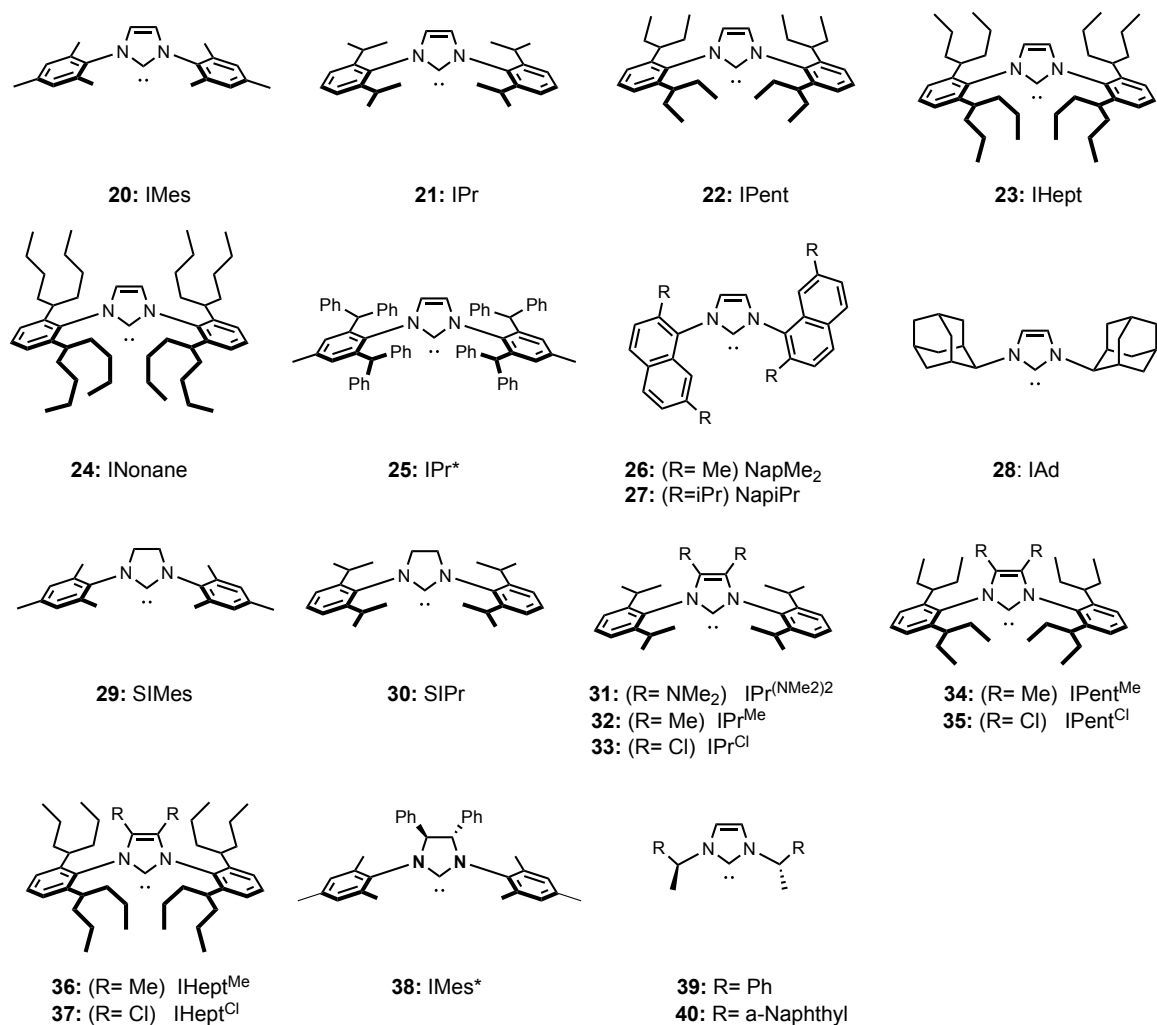


Figure 6. Examples of state-of-the-art imidazole and imidazoline-based NHCs used in cross-coupling

NHCs are exceptionally strong σ -donor ligands, and their electron-donating properties can be effectively measured by examining the carbonyl stretching frequencies (ν) in complexes of the type $[(L)Ir(CO)_2Cl]$, where L represents NHCs or various phosphines like PR_3 , or $P(OR)_3$. This method, independently introduced by Crabtree^{72,73} and Nolan,⁷⁴ revealed that NHCs provide far greater electron donation than even highly electron-rich trialkyl phosphines like PCy_3 . The difference in electron-donating strength is reflected in the observed carbonyl stretching frequencies. For phosphine ligands, these values typically range from 2085 to 2072 cm^{-1} , whereas

NHCs show significantly lower frequencies between 2072 and 2063 cm^{-1} , demonstrating their stronger σ -donating character.⁷⁴ This greater electron donation enhances the strength of the metal-ligand (M–L) bond when compared to phosphine-based ligands. Importantly, these studies also established that the electron-donating ability of NHCs is not influenced by changes to the *ortho*-substituents on the N-aryl ring (Figure 7). This characteristic contrasts with phosphine ligands and indicates that the electronic and steric properties of NHCs can be modified independently, offering greater flexibility in ligand design.

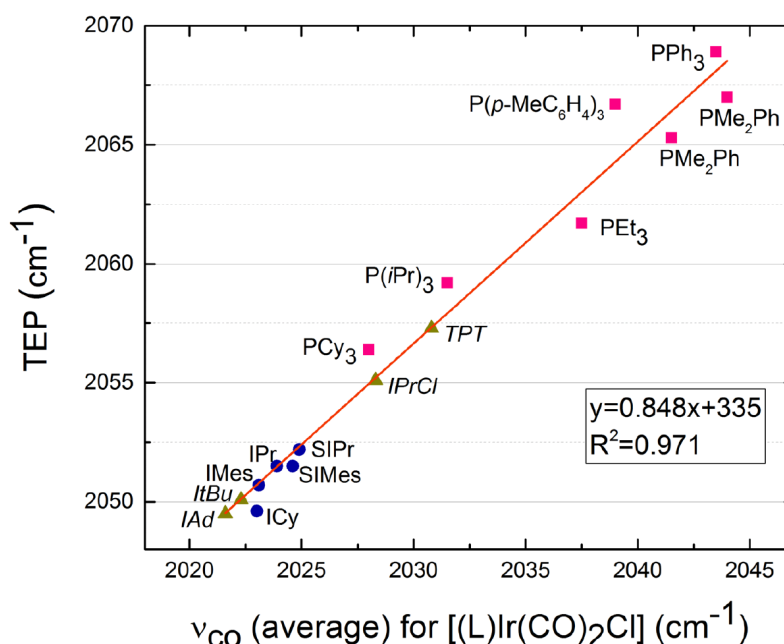


Figure 7. Nolan's correlation of average ν_{CO} values for $[(\text{L})\text{Ir}(\text{CO})_2\text{Cl}]$ complexes with the Tolman electronic parameter (TEP).⁷⁴ (■) Experimental values for phosphines; (•) Experimental values for NHCs; (Δ) Values obtained by linear regression.

A key factor contributing to the effectiveness of NHC ligands is the directed steric bulk provided by *ortho*-substituted N-aryl rings. In the case of phosphine ligands, the steric impact is often evaluated using Tolman's cone angle method (Figure 2), which assumes that the three substituents on the phosphorus atom are pointing away from the metal (M) center (i.e., contributing to the cone shape). This assumption is reasonable for phosphines due to their sp^3 hybridization and bulky

groups that project away from the lone electron pair. In contrast, NHC ligands exhibit a distinct steric bulk distribution around the metal center. Structural analyses through X-ray crystallography have demonstrated that the R substituents on the nitrogen atoms of NHCs are pointing towards the metal center, creating a compact and localized steric pocket around the metal (Figure 8).⁵³ Moreover, the R substituents on the nitrogen atoms are pushed even closer to the metal center due to steric interactions with the R' groups on the imidazole-based NHC backbone. This interaction creates additional steric pressure on the metal center, further enhancing the ligand's ability to influence the coordination environment and reaction pathway.

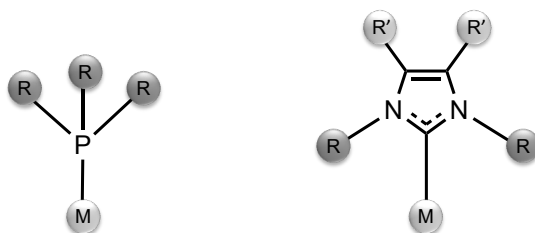


Figure 8. A comparison of the steric topographies of the two ligand classes

Due to the distinct steric topology of NHCs compared to phosphines, Tolman's cone angle cannot effectively quantify their steric properties. To address this limitation, Nolan and Cavallo developed a method for evaluating the steric demand of NHC ligands by calculating the percentage of a spherical volume around the metal center occupied by the ligand, a metric known as the percent buried volume (%Vbur).⁷⁵ This parameter has been extensively measured and cataloged for many common NHC ligands using [(NHC)Ir(CO)₂Cl] complexes (Figure 9a). The %Vbur can also be used to quantify the steric properties of phosphines, thus allowing a direct comparison between the two ligand classes (Figure 9b). More recently, Ogoshi refined this approach by incorporating ligand flexibility into the analysis. Using DFT calculations, the change in %Vbur during a catalytic transformation was quantified, introducing a new metric, $\Delta\%$ Vbur.⁷⁶ This parameter measures the

flexibility of bulky ligands throughout a reaction. The interplay between steric bulk and flexibility is crucial, as bulky ligands can enhance catalyst activity but must remain sufficiently flexible to facilitate interactions between the reactants and the metal center. Striking this balance between steric demand and flexibility represents a key challenge for chemists designing ligands in this field.

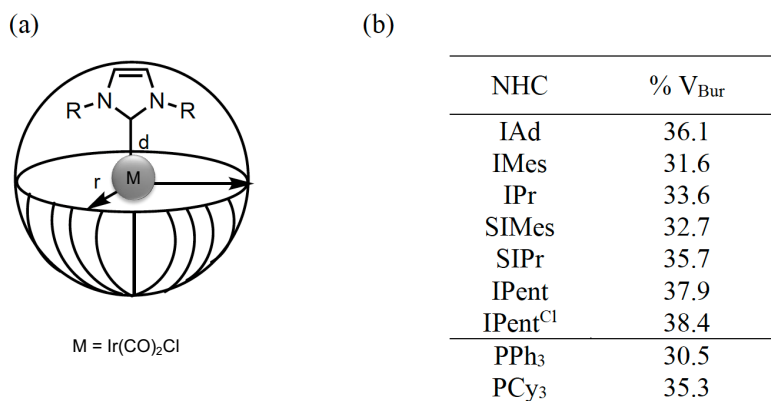


Figure 9. (a) Schematic representation of the sphere used for the %VBur calculation. (b) Comparison of %VBur some of common NHC ligands with two popular phosphines.⁷⁷

1.3.3 NHC as a ligand in nickel chemistry

As mentioned previously, NHCs have transformed organometallic chemistry in various aspects, a success attributed to several key factors. First, NHCs are derived from cost-effective and air-stable imidazolium salt precursors, making them readily accessible and easier to use.⁷⁸ Second, their strong σ -donor properties enable the formation of robust metal-ligand bonds, surpassing the strength of those formed with many traditional ligands, including trialkylphosphines.^{79–82} Additionally, NHCs provide significant steric protection to metal centers in metal-NHC complexes while offering exceptional tunability of steric and electronic properties through modifications to the ligand backbone and N-bound substituents. These attributes have driven the rapid adoption of NHC ligands in nickel chemistry over the past two decades in a variety of catalytic processes.^{56,83,84} The versatility of NHCs has expanded their applications to include catalytic cross-couplings, C–H bond functionalization, three-component couplings involving unsaturated hydrocarbons,

aldehydes, and silyl derivatives, [2 + 2 + 2] cycloadditions, olefin oligo- and polymerization, dehalogenation of aryl halides, and hydrosilylation of internal alkynes.^{85–89} Among these, cross-coupling reactions have emerged as a preferred method for constructing C–C and C–heteroatom bonds. This methodology enables the selective coupling of alkyl and aryl halides with a variety of nucleophiles under mild conditions.^{90,91} The classification of these reactions is based on the nucleophile employed, including organoboron reagents (Suzuki–Miyaura coupling),⁹² organozinc reagents (Negishi coupling),⁹³ Grignard reagents (Kumada coupling),^{25,94} alkenes (Heck couplings),^{95,96} and amines (Buchwald–Hartwig couplings).⁹¹ These advancements have revolutionized the synthesis of complex organic molecules, including biologically active compounds and advanced materials.^{91,97–100} The significance of these reactions was recognized in 2010 when Ei-ichi Negishi, Richard Heck, and Akira Suzuki were awarded the Nobel Prize in Chemistry for their work on palladium-catalyzed cross-coupling in organic synthesis. Nickel-NHC complexes, either generated in situ or as well-defined catalysts, have been widely employed in cross-coupling reactions, particularly in C–N (amination) and C–C (Negishi) cross-couplings, as explored in the following sections.

1.4 C-N Cross-Coupling

The transition metal-catalyzed cross-coupling of amines with aryl halides and pseudohalides has become a widely adopted and versatile method for forming C–N bonds, facilitating the synthesis of aromatic amines across various domains of basic and applied research.^{90,101,102} This process has found extensive application due to the prevalence of arylated amines in pharmaceuticals, natural products, organic materials, and catalysts. Continuous advancements in ligand and precatalyst design have led to increasingly robust and reliable protocols, significantly expanding the scope of this transformation.^{103–106} Over the past two decades, the utility and adaptability of transition-

metal-catalyzed C–N cross-coupling have been thoroughly demonstrated in numerous studies spanning diverse areas of chemical research. A summary of its major applications is presented in Figure 10.

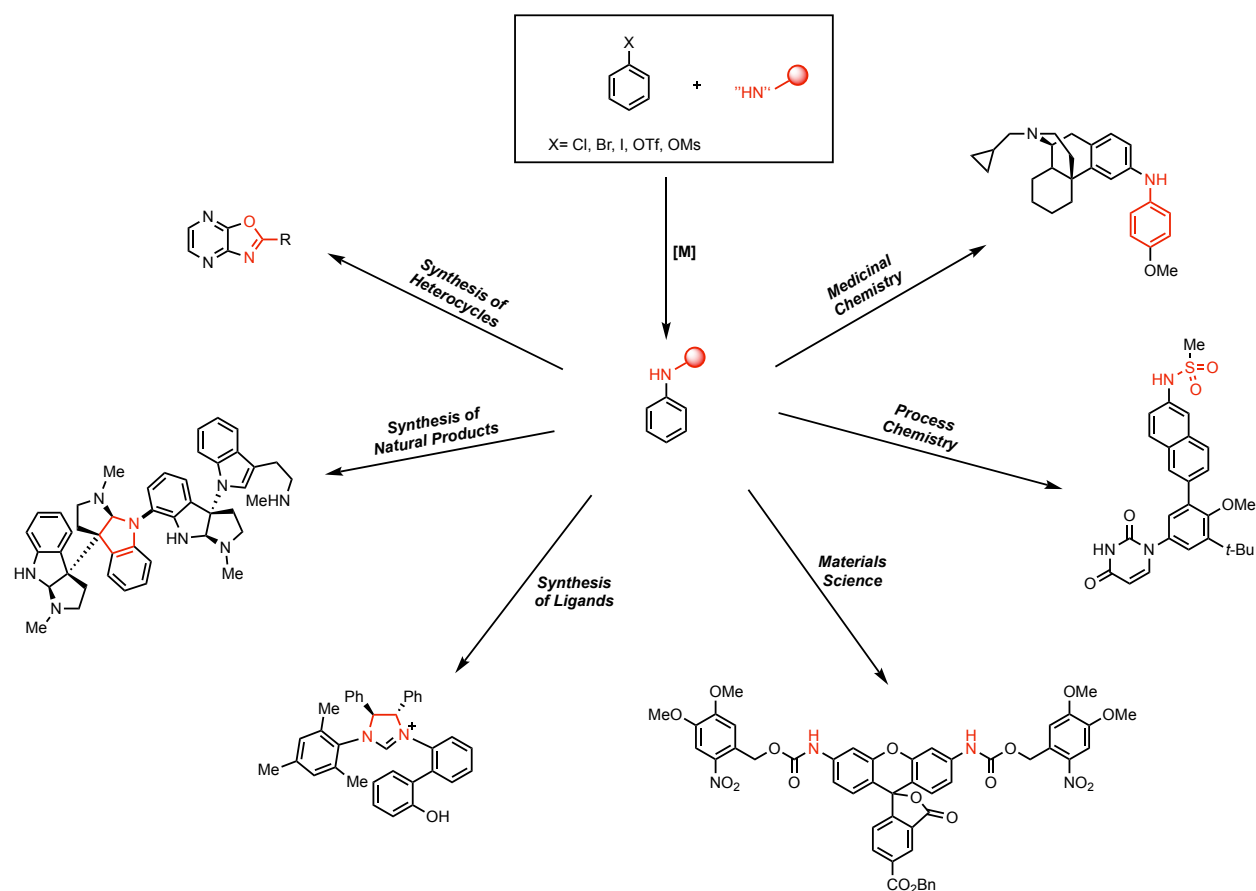
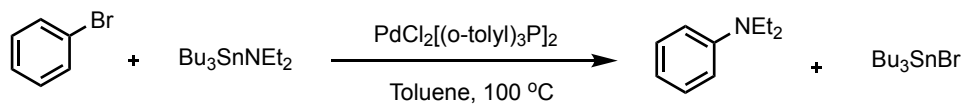


Figure 10. Main fields of application of C–N cross-coupling reactions.⁹¹

The formation of aromatic C–N bonds was first reported over a century ago, in 1903, by Ullmann¹⁰⁷ and Goldberg.¹⁰⁸ Their method utilized stoichiometric amounts of copper salts to activate aryl (pseudo)halides for reaction with amine nucleophiles. However, the synthetic utility of this approach was limited by the production of stoichiometric copper waste and the requirement for harsh reaction conditions.

In 1983, Migita and co-workers reported C–N coupling reaction in the presence of catalytic amount of palladium catalyst featuring a sterically hindered monodentate phosphine ligand. This

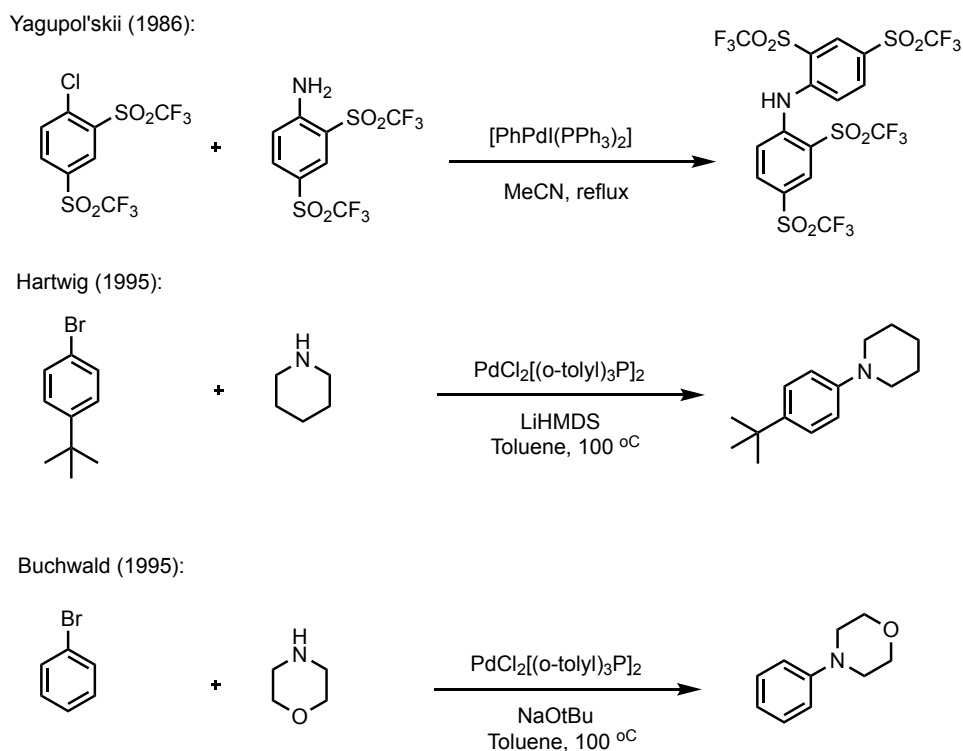
ground-breaking study employed tin amides as nucleophiles, which were successfully coupled with aryl bromides (Scheme 1).¹⁰⁹



Scheme 1. The first C-N Pd-catalyzed coupling.¹⁰⁹

The use of free amines in metal-catalyzed amination reactions was first demonstrated by Yagupol'skii and co-workers in 1985.¹¹⁰ Since that work was published in a Russian journal it remained unknown to most working in the field for years.

Following this work, in 1995, Buchwald¹¹¹ and Hartwig¹¹² independently reported the Pd-catalyzed coupling of free amines with aryl halides in the presence of a strong base such as lithium hexamethyldisilazide (LiHMDS) or sodium tert-butoxide (NaOtBu), as shown in Scheme 2.



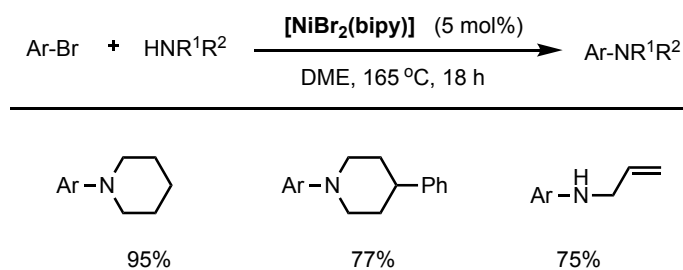
Scheme 2. The Buchwald–Hartwig C–N cross-coupling reactions.

1.4.1 Nickel-Catalyzed C-N Cross-Coupling

The first example of using a nickel salt as a catalyst for an amination reaction dates back to 1950.¹¹³ Researchers from The Standard Oil Company investigated the reaction between methylamine and chlorobenzene using catalytic amounts of various metal salts. While Cu(I) and Cu(II) chlorides proved to be the most effective, achieving 50% conversion within 30 minutes, nickel(II) chloride (NiCl_2) also demonstrated catalytic activity under the tested conditions (200 °C, 20 mol% catalyst, and a 5:1 methylamine-to-chlorobenzene ratio).

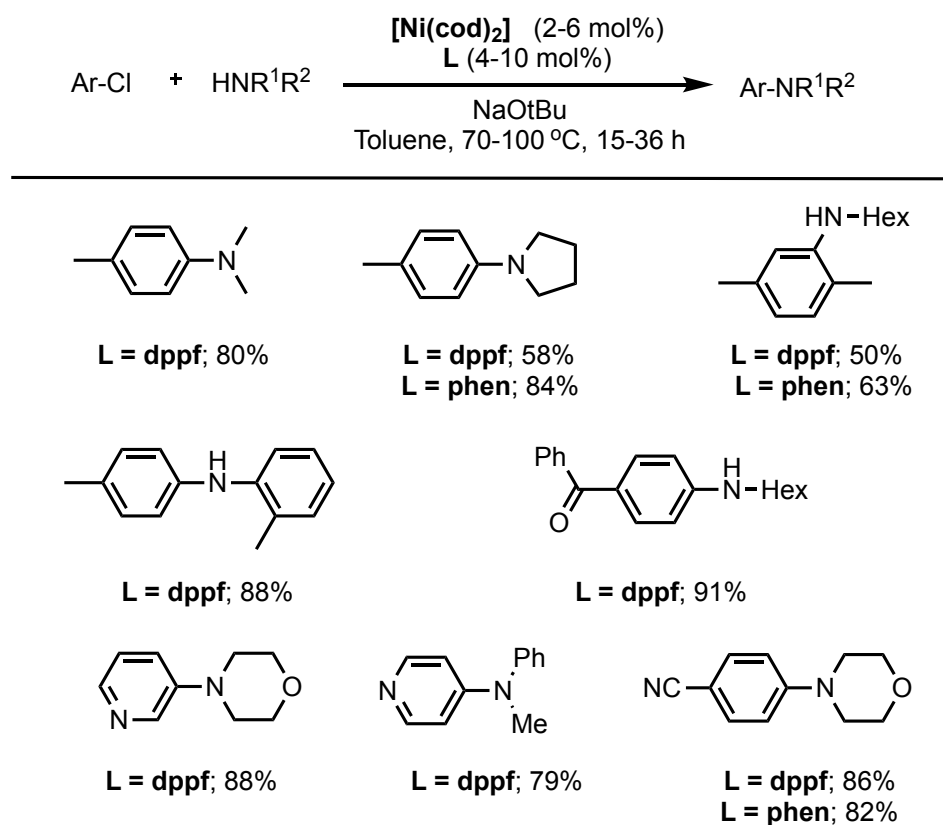
Fifteen years later, Cramer and Coulson conducted a comprehensive investigation into the impact of reaction conditions and catalyst composition on nickel-catalyzed amination reactions.¹¹⁴ Notably, their findings revealed that Ni(0) complexes, such as $[\text{Ni}(\text{CO})_2(\text{dppe})]$ and $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane), were almost as effective as NiBr_2 in catalyzing the amination of piperidine with bromobenzene.

In 1995, Cristau and Desmurs conducted a study comparing the catalytic performance of copper, nickel, and palladium in the arylation of hard nucleophiles with bromoarenes.¹¹⁵ Notably, the nickel catalyst $[\text{NiBr}_2(\text{bipy})_2]$ (bipy = 2,2'-bipyridine) demonstrated exclusive selectivity for C–N coupling when used with amines other than primary and secondary benzylamines. In contrast, palladium catalysts such as Pd/C, $[\text{Pd}(\text{PPh}_3)_4]$, and $[\text{PdCl}_2(\text{PPh}_3)_2]$ primarily facilitated the dehalogenation of bromoarenes. These results underscore the unique reactivity and selectivity of nickel in these transformations (Scheme 3).



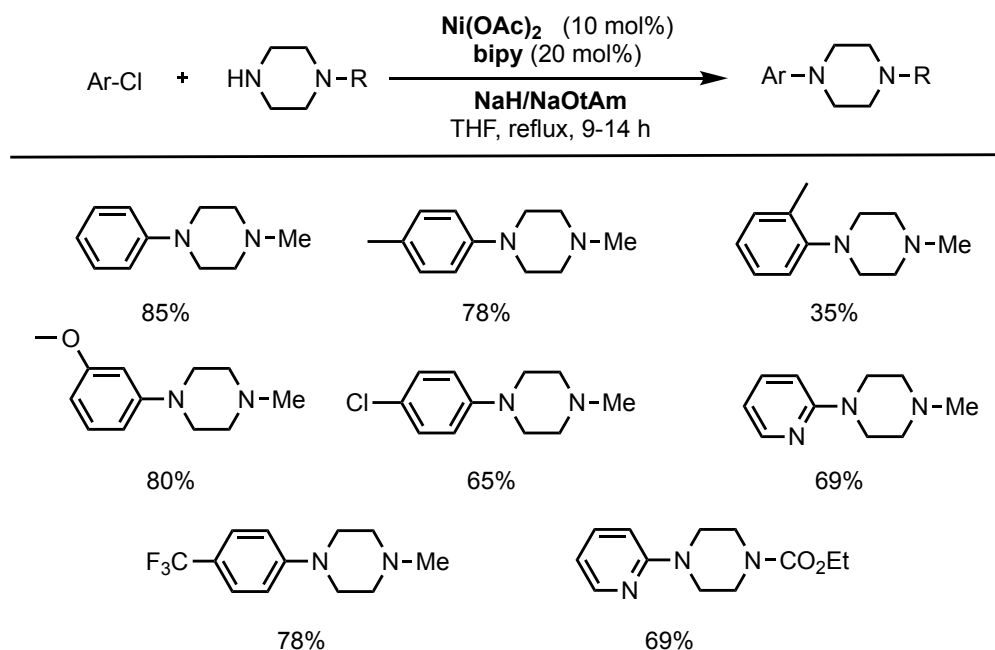
Scheme 3. Ni-catalyzed amination of amines with bromoarenes under Cristau's and Desmurs' conditions.¹¹⁵

In 1997, Wolfe and Buchwald made significant advancements in the reaction conditions and substrate scope of nickel-catalyzed amination reactions.¹¹⁶ They used a 1:2 mixture of $\text{Ni}(\text{cod})_2$ (cod = 1,5-cyclooctadiene) and dppf (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as the catalyst to achieve C–N coupling of aryl chlorides with a range of primary and secondary amines in good yields using NaOtBu as the base at 100 °C (Scheme 4). One of the highlights of this work was the ability to use catalyst loadings as low as 2 mol% for certain substrate combinations while still achieving excellent yields. Furthermore, they demonstrated that air-stable precatalysts of the type $[\text{NiCl}_2(\text{L-L})]$ (L-L = dppf or 1,10-phenanthroline), when combined with a reductant such as MeMgBr , showed catalytic behavior comparable to in situ-generated $\text{Ni}(0)$ catalysts in several reactions, offering a more practical and efficient alternative.



Scheme 4. Ni-catalyzed amination of aryl chlorides developed by Buchwald's group.¹¹⁶

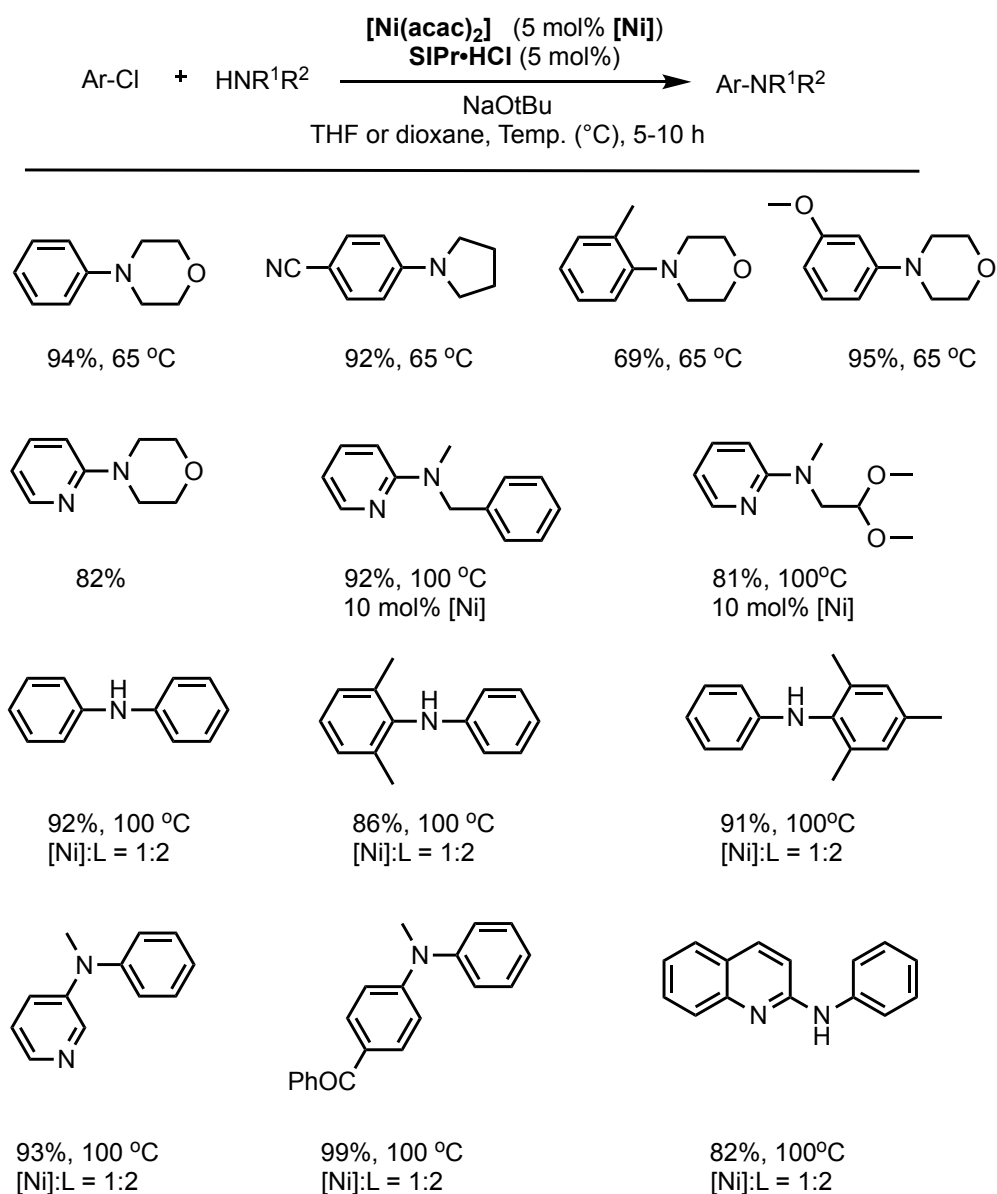
In 1998, Brenner and Fort introduced a mild catalytic procedure for coupling aryl chlorides with secondary amines or piperazines.¹¹⁷ The reaction occurred in two stages. Initially, the Ni(0) catalyst was generated in situ by reducing Ni(OAc)₂ with an excess of NaH in the presence of 2,2-bipyridine, the amine, and the base (NaOtAm). Once the catalyst was formed, the aryl chloride was introduced, and the reaction was carried out in THF under reflux (Scheme 5). A key requirement for the reaction's success was the presence of the amine, which facilitated the formation of the active catalytic species during the reduction.¹¹⁸ However, a large excess of NaH required to reduce the Ni(II) precursor led to some challenges. Specifically, it caused partial hydrogenolysis of the C–Cl bonds, generating unwanted arene by-products. To mitigate this side reaction, styrene was added to the mixture as a hydrogen acceptor. Moreover, the strong basicity of NaH limited the scope of the protocol. Fort's group later expanded on this methodology, successfully applying it to the selective synthesis of mono-, di-, and triaminobenzenes, diaminopyridines,^{119–122} and the monoarylation or diarylation of piperazines.^{123,124}



Scheme 5. Ni-catalyzed amination of aryl chlorides with 1-substituted piperazines developed by Fort's group.^{117,118}

1.4.2 Nickel-NHC Catalyzed C-N Cross-Coupling

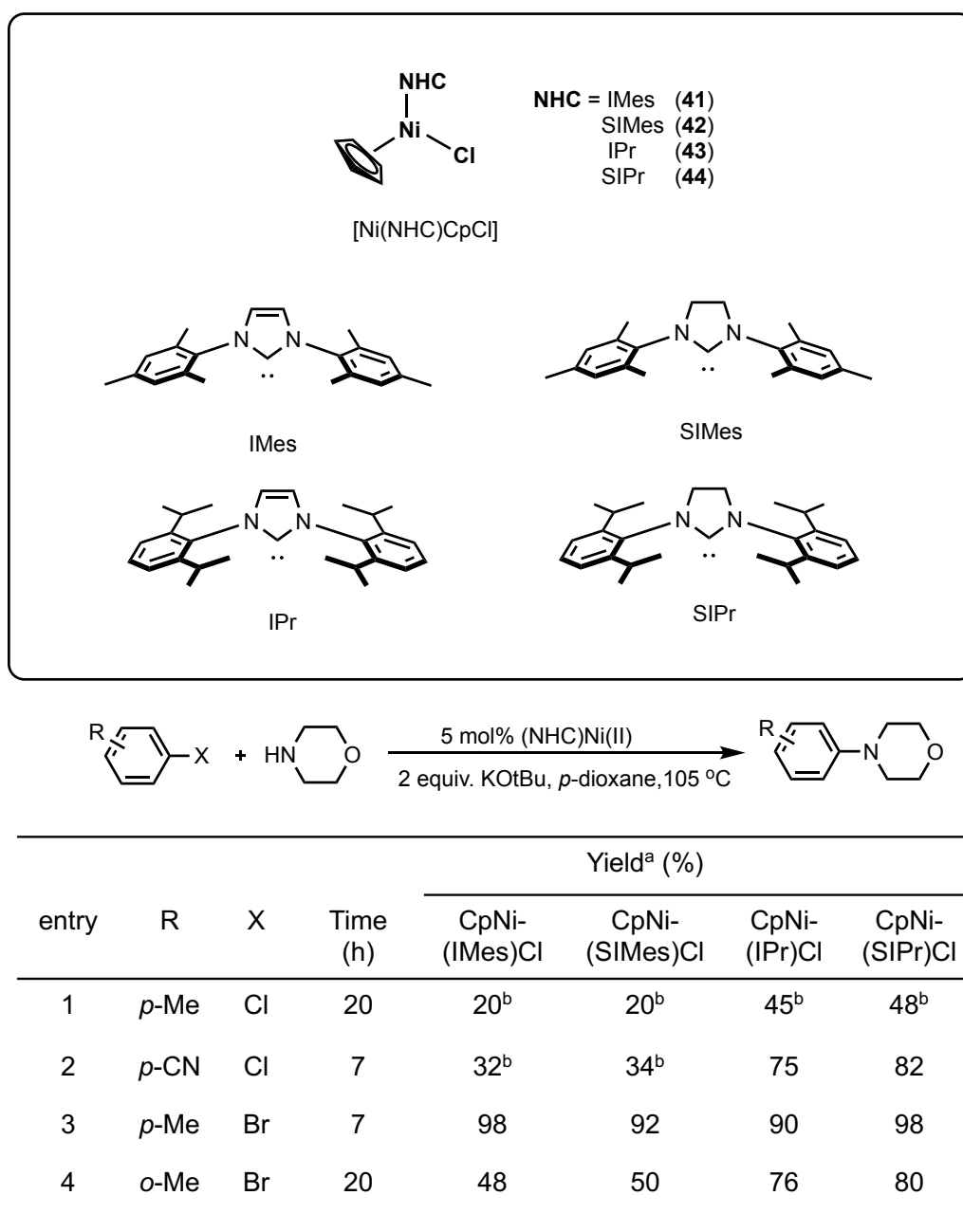
In 2001, Fort and co-workers introduced significant advancements to their catalytic system by implementing several strategic modifications. The first improvement involved employing *N*-heterocyclic carbenes (NHCs) as ligands to stabilize the nickel catalyst.¹²⁵ Next, the choice of the nickel precursor shifted to [Ni(acac)₂], and the original base (NaOtAm) was replaced with in situ generated NaOtBu through the addition of *t*BuOH. Additionally, the amount of NaH was carefully calibrated to reduce Ni(II) to Ni(0) and to convert *t*BuOH into NaOtBu. Among the carbene ligands tested, SIPr (1,3-bis(2,6-diisopropylphenyl)dihydroimidazol-2-ylidene) delivered the most effective results. This optimized system allowed catalyst loading to be reduced to as low as 2 mol%, although a 5 mol% loading was ideal for most of the substrates evaluated.¹²⁶ The optimal Ni/ligand ratio was found to be 1:1 for coupling (hetero)aryl chlorides with secondary cyclic and acyclic amines. However, for aniline substrates, a higher ligand ratio (1:2) was required, accompanied by an increase in reaction temperature (Scheme 6).¹²⁶ This refined protocol was successfully employed to synthesize a variety of compounds, including conjugated tetraarylamines¹²⁷ and mono- and diarylated aromatic diamines.¹²⁸ Furthermore, both catalytic approaches were successfully applied to the intramolecular aryl amination, facilitating the preparation of five-, six-, and seven-membered nitrogen-containing heterocycles.¹²⁹



Scheme 6. Fort's modified conditions for Ni-catalyzed amination of (hetero)-aryl chlorides.^{125,126}

In 2005, Nolan's group introduced a series of well-defined Ni(II) complexes supported by N-heterocyclic carbene (NHC) ligands as air-stable precatalysts for aryl amination reactions.¹³⁰ These complexes, represented by the formula [Ni(NHC)CpCl] (**41-44**), were synthesized with various NHC ligands, including IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), SIMes (1,3-bis(2,4,6-trimethylphenyl)dihydroimidazol-2-ylidene), IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), and SIPr as shown in [Scheme 7](#). Although these compounds featured robust ligand

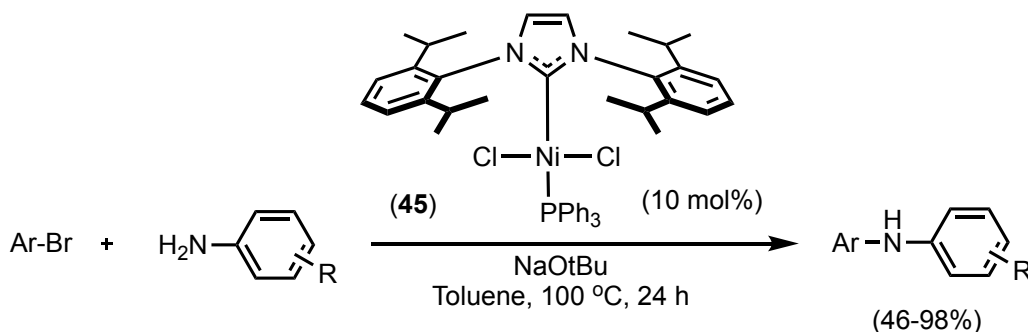
frameworks, their catalytic efficiency was limited, particularly when aryl chlorides served as the substrates. The reactions, carried out at 105 °C without the addition of external reducing agents, exhibited only moderate activity, reflecting the constraints of the system under these specific reaction conditions.



^a Isolated yields. ^b Conversion determined by ¹H NMR of the crude product.

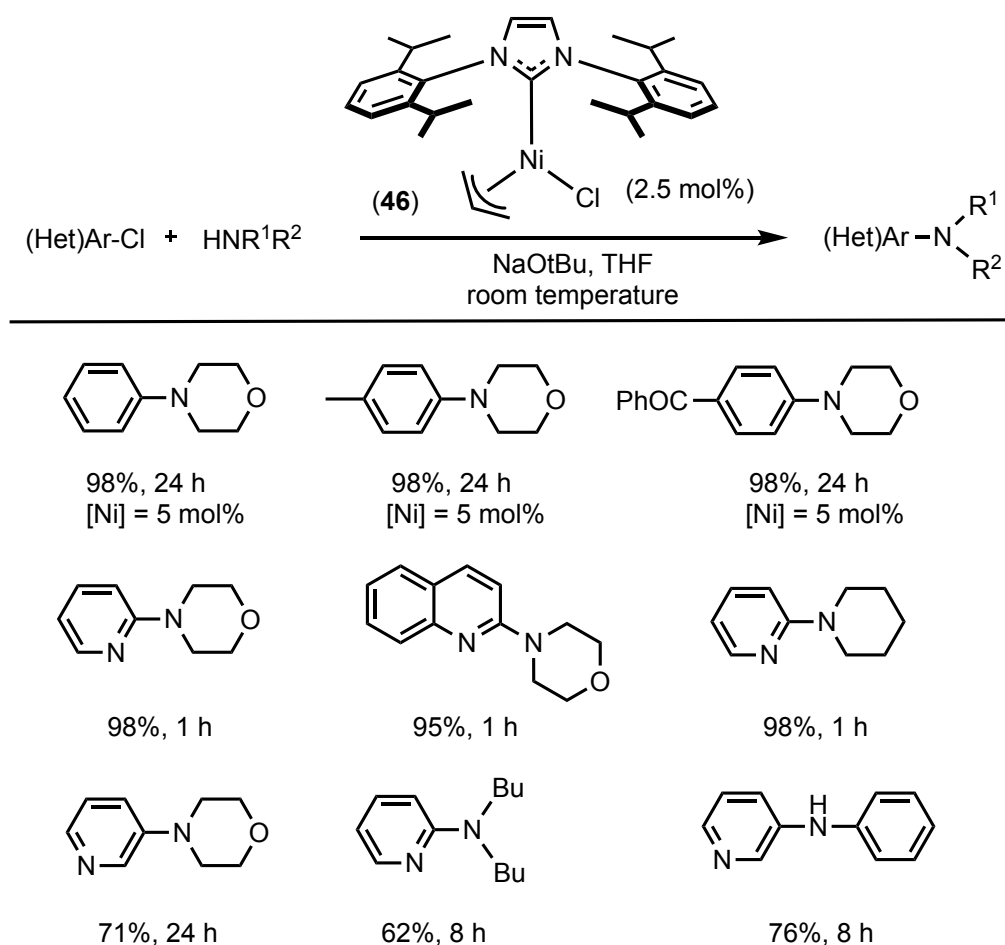
Scheme 7. Aryl Amination Catalyzed with Ni(NHC)CpCl Complexes as Precatalysts.¹³⁰

In 2007, Matsubara and collaborators explored the catalytic properties of a mixed PPh_3/NHC Ni(II) complex, $\text{trans}[\text{Ni}(\text{IPr})\text{Cl}_2(\text{PPh}_3)]$ (**45**),¹³¹ for the amination of aryl bromides¹³² (Scheme 8). The Ni(II) complex was activated during the coupling process, and operated at 100 °C with a catalyst loading of 10 mol%. The reaction demonstrated higher efficiency when using less basic arylamines compared to more basic alkylamines. Later, the same group developed Ni(0) species with unsaturated coordination frameworks, such as $[\text{Ni}(\text{NHC})_2]$ (where NHC = IPr or IMes).¹³³ The performance of $[\text{Ni}(\text{IPr})_2]$ as a precatalyst in the arylation of aniline with chlorobenzene was then compared to the catalyst generated in situ using Fort's methodology.^{125,126} The results showed that $[\text{Ni}(\text{IPr})_2]$ produced better yields of the desired amination product, highlighting the significance of employing a well-defined precatalyst to control the formation of active catalytic species and enhance reaction outcomes.



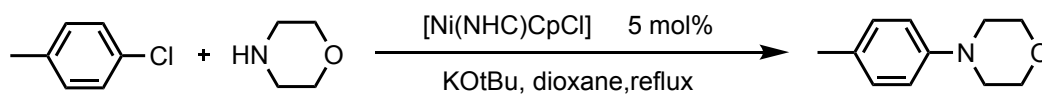
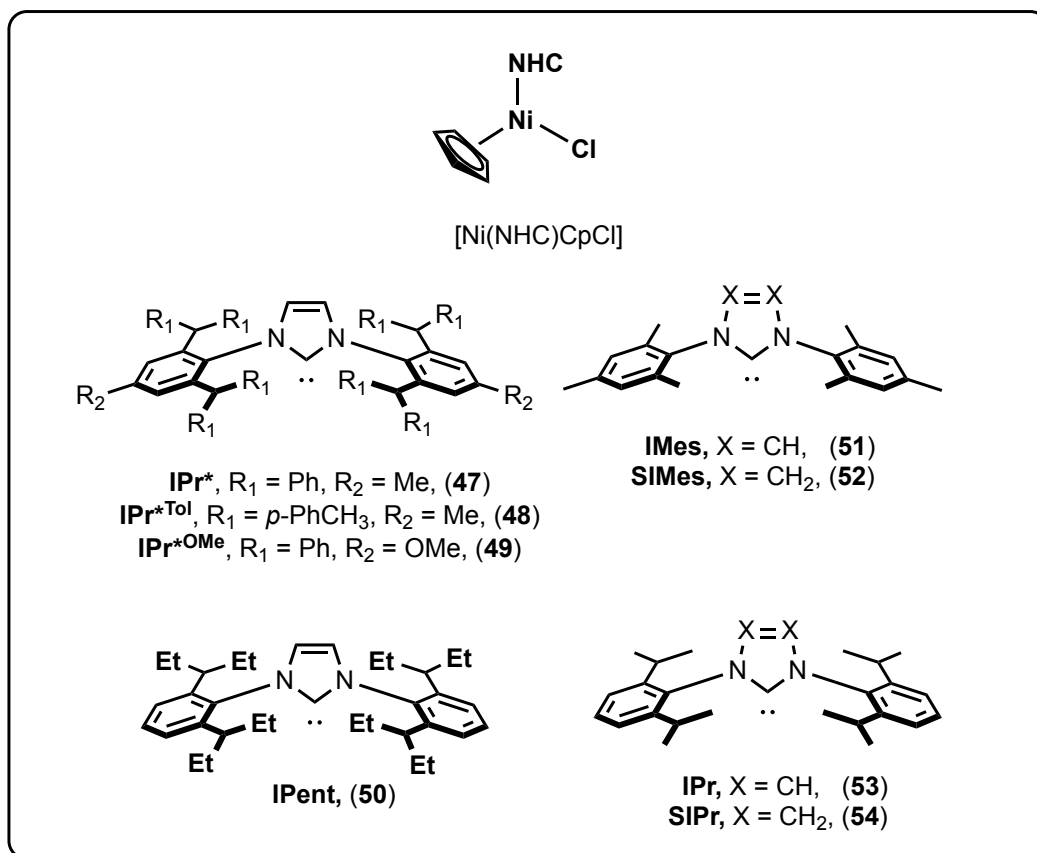
Scheme 8. $[\text{Ni}(\text{IPr})\text{Cl}_2(\text{PPh}_3)]$ -catalyzed amination of bromoarenes with anilines.¹³²

In 2010, Nicasio introduced the first example of nickel-catalyzed amination of aryl chlorides that could be conducted at room temperature.¹³⁴ The process employed $[\text{Ni}(\text{allyl})(\text{IPr})\text{Cl}]$ (**46**) as the catalytic species.^{135,136} The reactions were typically performed in THF at 60 °C over 2–4 hours, but similar results could be achieved at room temperature by extending the reaction time to 24 hours. The method was particularly effective for the amination of heteroaryl chlorides, which, in most cases, proceeded rapidly at room temperature with a catalyst loading of only 2.5 mol% (Scheme 9).



Scheme 9. First room-temperature Ni-catalyzed amination of (hetero)aryl chlorides.¹³⁴

Nolan and his team proposed that enhancing the steric flexibility of NHC ancillary ligands could boost the catalytic performance of [Ni(NHC)CpCl] precatalysts (**47-54**). To explore this, they developed a series of CpNi(II) complexes incorporating various ligands, including IPr* (**47**), IPr*^{Tol} (**48**), IPr*^{OMe} (**49**), and IPent (**50**) (Scheme 10).^{137,138} The catalytic activity of these new precatalysts was strongly influenced by the bulkiness of the NHC ligands, with the IPr*^{OMe}-Ni(II) complex (**49**) demonstrating the highest activity in the amination of hetero(aryl) chlorides.

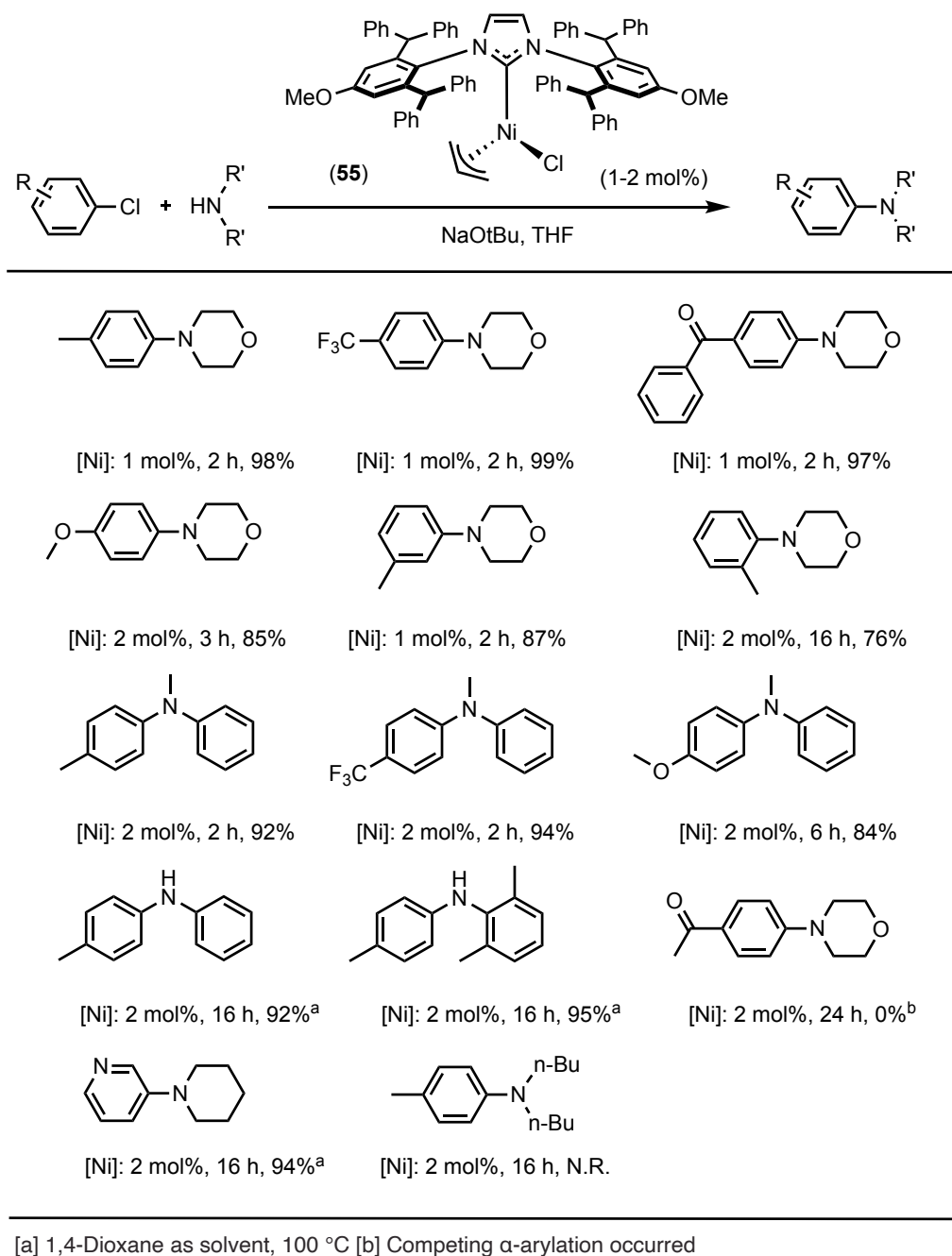


Pre-catalyst	Conversion ^[a] (%)
[Ni(IPr*)CpCl] (47)	75
[Ni(IPr* ^{Tol})CpCl] (48)	51
[Ni(IPr* ^{OMe})CpCl] (49)	90
[Ni(IPent)CpCl] (50)	23
[Ni(IMes)CpCl] (51)	17
[Ni(SIMes)CpCl] (52)	16
[Ni(IPr)CpCl] (53)	28
[Ni(SIPr)CpCl] (54)	32

[a] Conversion to coupling product based on starting material determined by GC; average of two runs.

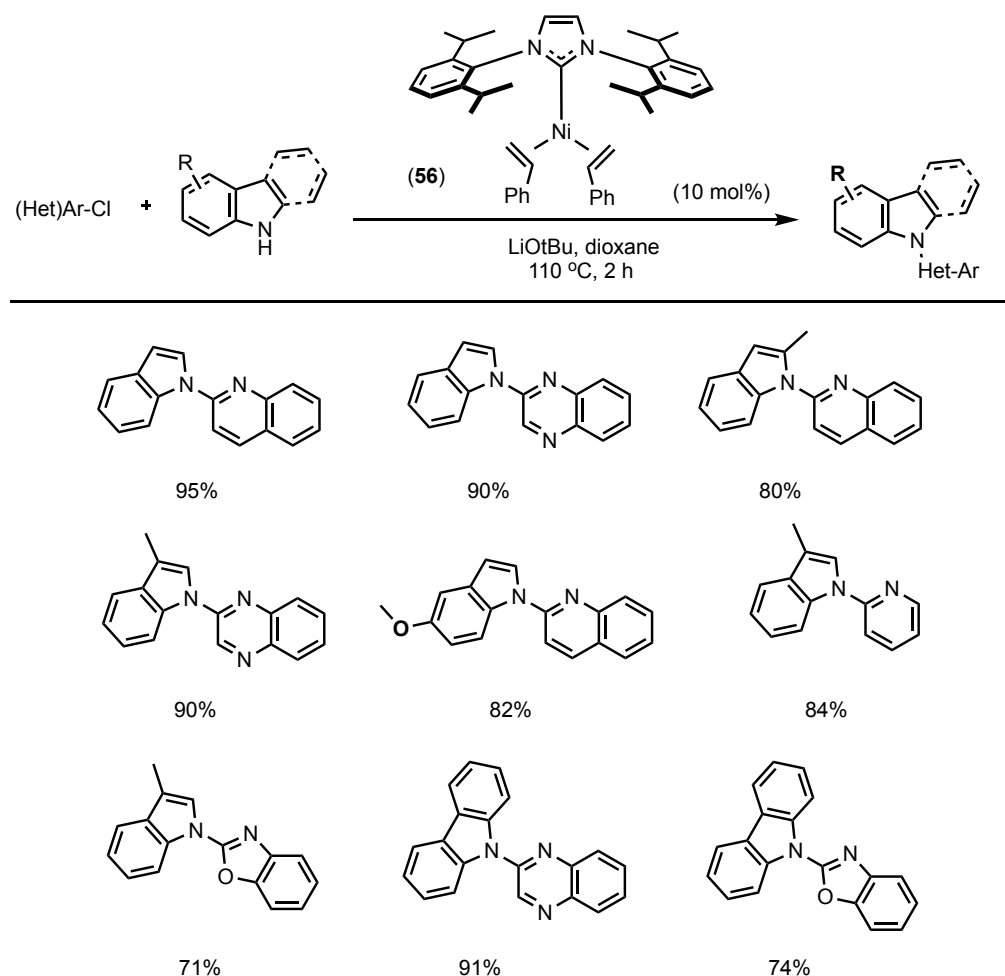
Scheme 10. Aryl amination catalyzed with Ni(NHC)CpCl complexes as precatalysts.¹³⁷

In subsequent studies, they demonstrated that $[\text{Ni}(\text{allyl})(\text{IPr}^{\text{OMe}})\text{Cl}]$ (**55**) exhibited superior catalytic performance compared to the original IPr-based precatalyst in Buchwald-Hartwig amination reactions, highlighting the impact of ligand modifications on catalytic efficiency (Scheme 11).¹³⁸



Scheme 11. Aryl amination catalyzed with that $[\text{Ni}(\text{allyl})(\text{IPr}^{\text{OMe}})\text{Cl}]$ complex (**55**) as precatalyst.¹³⁸

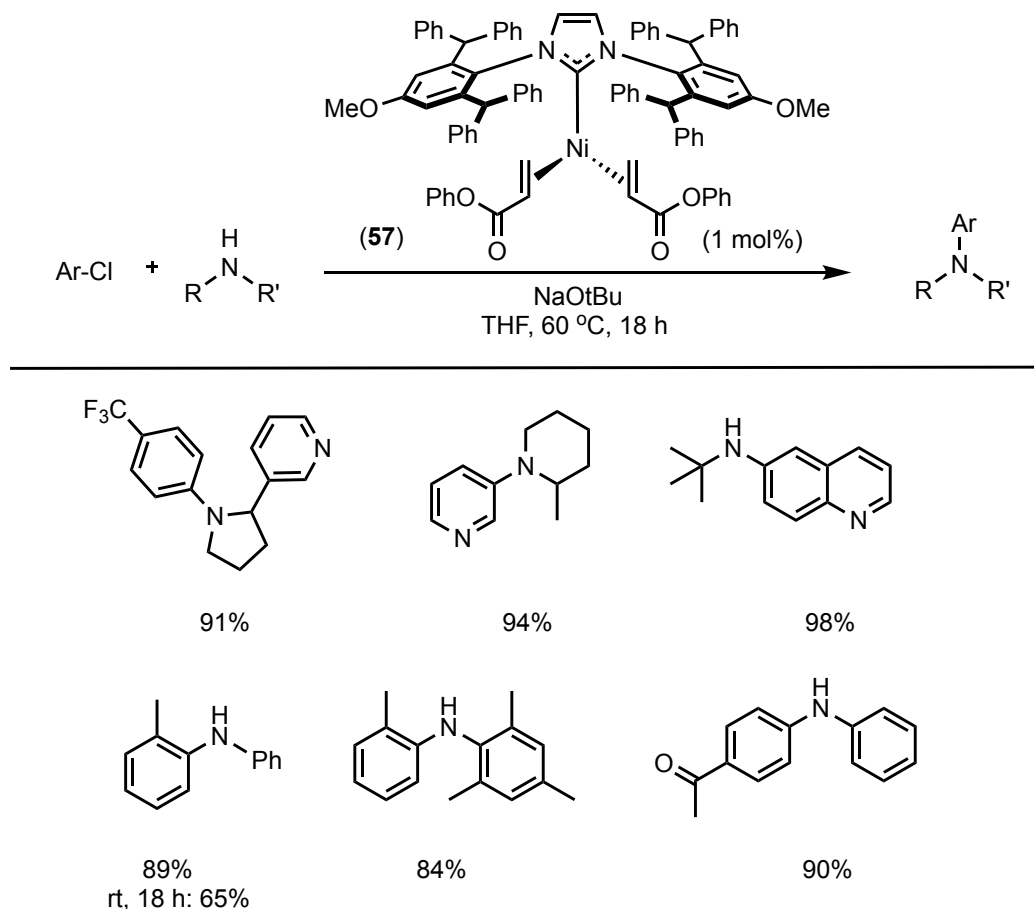
The Nicasio group reported the synthesis of $[\text{Ni}(\text{IPr})(\text{styrene})_2]$ (**56**), a novel monoligated NHC-Ni(0) complex stabilized through olefin coordination.¹³⁹ This complex proved to be a versatile precatalyst for challenging C–N cross-coupling reactions, particularly with NH heterocycles that often present significant challenges in palladium-catalyzed C–N coupling due to their low nucleophilicity, high acidity, and the strong coordinating ability of the NH group.^{31,38,140,141} Focusing on the arylation of indoles, $[\text{Ni}(\text{IPr})(\text{styrene})_2]$ efficiently facilitated the C–N coupling of indoles with chloroarenes at 110 °C, achieving excellent results within a short reaction time of 2 hours.¹⁴² The scope of the reaction was extended to include heteroaryl chlorides, although these more demanding substrates required an increased catalyst loading of up to 10 mol% to achieve high yields ([Scheme 12](#)). Notably, no competing C-arylation was observed under any of the reaction conditions tested. This method provided selective access to N-(hetero)aryl indoles in good to high yields, with short reaction times, and without the need for excess ligands.



Scheme 12. First Ni-catalyzed arylation of indoles and carbazoles with heteroaryl chlorides.¹⁴²

In 2018, Montgomery and co-workers reported a novel class of highly reactive and stable Ni(0) precatalysts incorporating NHC donor ligands and π -acceptor stabilizing groups, such as electron-withdrawing fumarate and acrylate alkenes.¹⁴³ These precatalysts were designed to provide practical and adaptable catalysts for a wide range of chemical transformations. The series included analogues featuring SIPr, IPr, and IPr*^{OMe} ligands, which were successfully synthesized and applied in C–N bond formation reactions, as illustrated in [Scheme 13](#). Notably, the Montgomery Ni(0)-NHC precatalysts remain the only commercially available Ni-NHC precatalysts, listed under

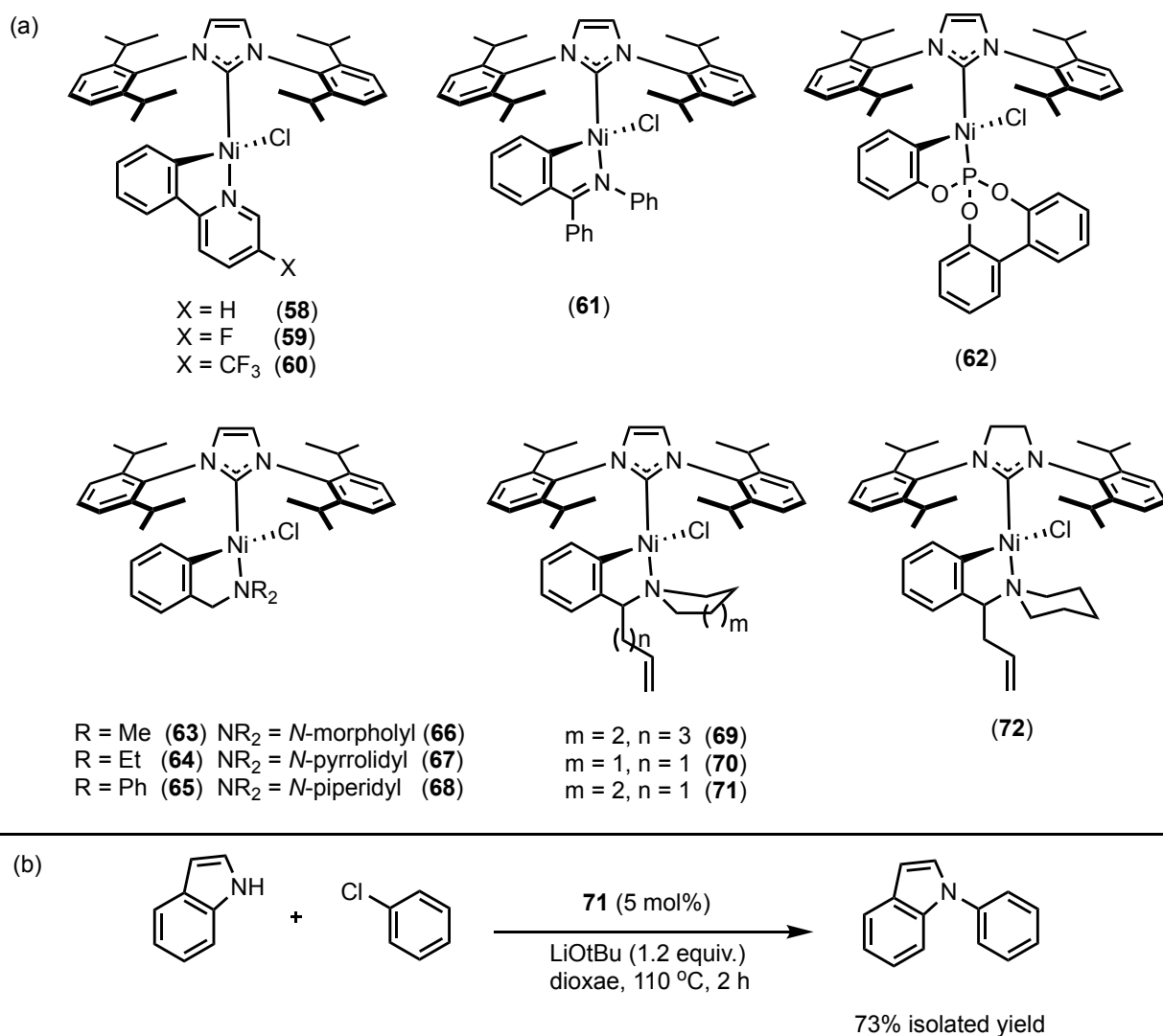
CAS number [2230140-52-8](#),¹⁴⁴ and [2230140-59-5](#).¹⁴⁵ Their combination of stability, reactivity, and accessibility make them valuable tools for challenging catalytic applications.



Scheme 13. Aryl amination catalyzed with well-defined Ni(0)-NHC Complex as precatalyst.¹⁴³

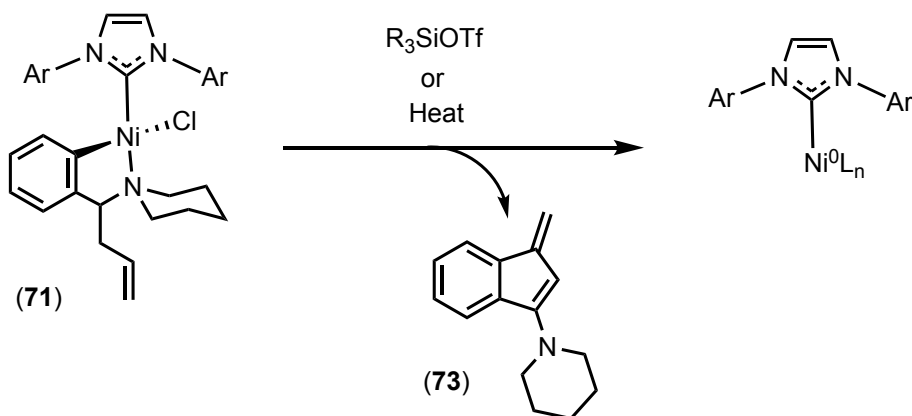
In 2018, the Jamison group introduced a novel series of bench-stable nickel(II) precatalysts incorporating N-heterocyclic carbene (NHC) ligands.¹⁴⁶ Initially, these complexes were synthesized with π -acceptor ligands positioned trans to the strongly σ -donating NHC, as this arrangement was believed to be essential for achieving stability. As shown in [Scheme 14](#), ligands such as pyridines (**58–60**), imines (**61**), and phosphites (**62**) were utilized. Interestingly, stable complexes were also attainable in the absence of strong π -acceptors by using amine ligands trans to the NHC. While attempts with acyclic amines (**63–65**) failed to yield stable complexes, cyclic

amines such as morpholine (**66**), pyrrolidine (**67**), and piperidine (**68**) successfully formed stable complexes, albeit in low to moderate yields. However, complexes **66** and **67** could not be isolated in a pure form. Additionally, similar complexes incorporating tethered olefins with varying carbon linker lengths (**69–71**) were synthesized, with yields ranging from 38% to 43%. Lastly, in addition to IPr, complex **72** was synthesized with the SIPr ligand.¹⁴⁶



Scheme 14. (a) Novel Ni-NHC precatalysts made by Jamison. (b) Aryl amination with precatalyst **71**.¹⁴⁶

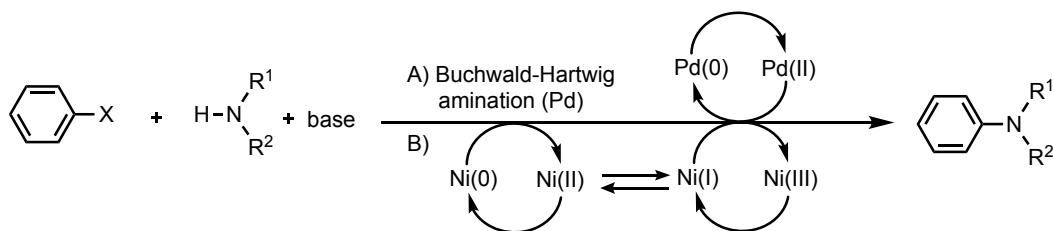
The incorporation of the olefin functionality aimed to evaluate the potential for in situ reduction of Ni(II) to Ni(0) via an intramolecular Heck-type reaction,¹⁴⁶ thus facilitating catalytic activation (Scheme 15).



Scheme 15. Hypothesized mechanism of activation for Jamison type Ni-NHC precatalyst.¹⁴⁶

1.4.3 Mechanism of Ni-catalyzed amination reaction

Mechanistic studies for nickel-catalysed amination have not been investigated to the same level of detail as those for Pd.¹⁴⁷ The easy access to different nickel oxidation states make such studies more challenging and both Ni⁰/Ni^{II} and Ni^I/Ni^{III} cycles have been proposed (Scheme 16).¹⁴⁸



Scheme 16. Comparison of palladium- and nickel-catalyzed C–N cross-coupling.¹⁴⁸

1.4.4 Mechanism of Ni⁰/Ni^{II} amination reaction

The typical mechanism of Ni-catalyzed amination proceeds through a three-step sequence as shown in Figure 11; The catalytic cycle begins with the oxidative addition (OA) of the aryl halide,

where the carbon-halide bond adds into the L_nNi^0 complex. This step is followed by the coordination and subsequent deprotonation (DEP) of the amine, which is followed by reductive elimination (RE), yielding the desired product while simultaneously restoring the L_nNi^0 catalyst for the next catalytic cycle.^{32,148,149}

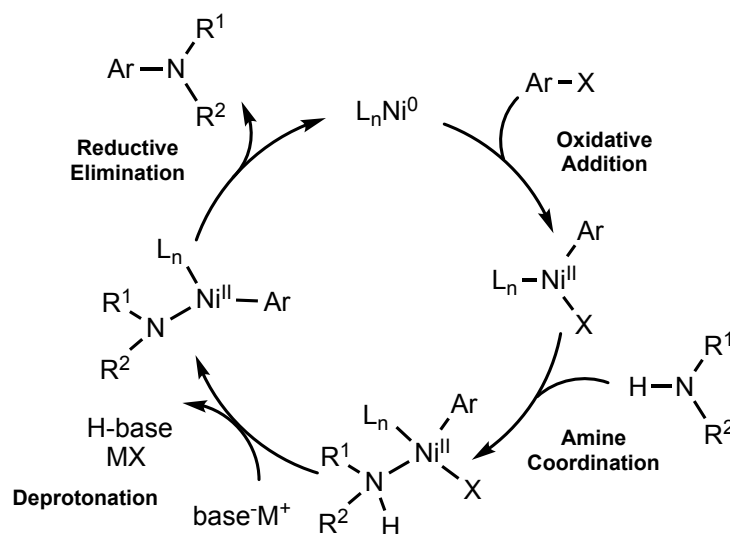


Figure 11. Proposed mechanism for the Ni-catalyzed amination reaction

1.4.4.1 Oxidative Addition (OA)

The catalytic cycle begins with the oxidative addition (OA) of the carbon-halide ($C-X$) bond, where X can be Cl , Br , I , or OSO_2R , to the L_nNi^0 complex. This step involves the oxidation of the metal center, making electron-deficient arenes more susceptible to OA than their electron-rich counterparts due to the higher electrophilicity of the $C-X$ bond. The reactivity of aryl halides in this step follows the trend: $ArI \gg ArBr > ArCl$. This trend is primarily attributed to the bond dissociation energies, with $C-I$ bonds (64 kcal mol^{-1}) being the easiest to cleave, while $C-Cl$ bonds (95 kcal mol^{-1}) is the most challenging.^{150–152} One of the key advantages of nickel catalysts in this field is their lower calculated energy barriers for oxidative addition,^{8,18} which enable the use of a broader variety of leaving groups.^{11,13,153–156} In addition to halides, pseudohalides such as triflates,

mesylates, and sulfamates¹⁵⁷ have also been demonstrated to participate in oxidative addition during amination reactions. In general, electron-rich metal centers facilitate OA more effectively than electron-deficient ones, as the oxidation state of nickel increases from Ni⁰ to Ni^{II} during this step. Consequently, electron-donating ligands can promote the oxidative addition process.¹⁵⁸ From the electrophile perspective, substrates that are electron-poor and sterically unhindered exhibit the highest reactivity.¹⁵⁷

1.4.4.2 Amine Coordination/Deprotonation steps

The sequence in which amine coordination and deprotonation occur is largely dependent on the reaction conditions. However, it is widely acknowledged that effective deprotonation of the amine nucleophile—such as alkyl amines, ammonia, or anilines—by bases commonly used in amination reactions (e.g., NaOtBu, LiHMDS, Cs₂CO₃) can only take place after the amine has coordinated to the metal center.³² Alkyl amines and ammonia exhibit relatively high pK_a values of approximately 40, while anilines have lower pK_a values, ranging from 21 to 32, depending on the substituents present on the aromatic ring (all values in DMSO).¹⁵⁹ The most commonly used bases in amination reactions include alkoxides such as *tert*-butoxide (pK_a of *tert*-butyl alcohol $\approx$ 29), carbonates (pK_a of HCO₃[−] $\approx$ 18), and phenoxides (pK_a of phenol $\approx$ 18). A comparison of these values suggests that direct deprotonation of the amine by these bases is unlikely due to the significant difference in pK_a. Instead, coordination of the amine to the metal center is necessary to lower its pK_a by approximately 20 units, thereby facilitating effective deprotonation under the reaction conditions.

1.4.4.3 Reductive Elimination (RE)

The final step of the catalytic cycle, which involves C–N bond formation, occurs through reductive elimination (RE) and is accompanied by the regeneration of the active L_nNi⁰ species. The

efficiency of this step is largely dictated by the steric and electronic characteristics of the ancillary ligand, with steric factors playing a more significant role. Unlike the oxidative addition (OA) step, where electron-donating ligands are beneficial, electron-withdrawing ligands have been shown to accelerate the RE process.⁷ Regarding steric effects, it is now well established that sterically bulky ligands significantly enhance the rate of RE. This effect is likely due to the spatial constraints imposed by the bulky ligands, which push the aryl and amine substituents into an optimal orientation, facilitating effective orbital overlap for bond formation while relieving steric congestion around the metal center.^{138,143}

The electronic and steric properties of the coupling partners significantly influence the rate of reductive elimination (RE). Complexes bearing electron-rich amido substituents typically exhibit faster RE rates. Additionally, the presence of electron-withdrawing groups on the electrophile has been shown to accelerate this step.^{32,149} Furthermore, steric effects play a crucial role, as bulky substituents on either the amine nucleophile or the electrophile can further accelerate RE by promoting a favorable spatial arrangement for bond formation.

1.4.5 $\text{Ni}^0/\text{Ni}^{\text{II}}$ versus $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ catalytic cycles in C–N cross-coupling

In 2017, Mark Stradiotto and his team at Dalhousie University conducted an extensive investigation combining experimental and computational approaches to explore the influence of nickel oxidation states on the mechanistic pathways of Ni-catalyzed C–N cross-coupling reactions, particularly focusing on the $\text{Ni}^0/\text{Ni}^{\text{II}}$ and $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ catalytic cycles (Figure 12).^{148,160} Through rigorous computational studies, they demonstrated that both cycles are viable under appropriate conditions, with distinct rate-limiting steps influencing the overall efficiency and reactivity of the system. The $\text{Ni}^0/\text{Ni}^{\text{II}}$ cycle was shown to feature rate-limiting C–N reductive elimination, a critical step for forming the desired C–N bond. This cycle is commonly observed in reactions where two-

electron processes dominate, and ligand design often focuses on facilitating this key reductive elimination step to improve catalytic performance.

In parallel, the $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ cycle was found to involve a fundamentally different mechanistic landscape, characterized by rate-limiting C–Cl oxidative addition. This pathway is driven by single-electron transfer (SET) processes, which introduce unique reactivity profiles and access to challenging substrates that are less reactive under conventional $\text{Ni}^0/\text{Ni}^{\text{II}}$ conditions.¹⁶⁰ The investigation highlighted the interplay between these cycles and underscored how subtle changes in reaction conditions, ligands, or substrates can shift the mechanistic preference. By bridging experimental data with computational insights, Stradiotto's study provided a deeper understanding of the catalytic behavior of nickel and set the stage for designing more efficient systems tailored to exploit the strengths of both the $\text{Ni}^0/\text{Ni}^{\text{II}}$ and $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ pathways. This dual mechanistic understanding also opened new avenues for exploring nickel's potential in catalyzing complex transformations that demand fine-tuning of electronic and steric parameters.

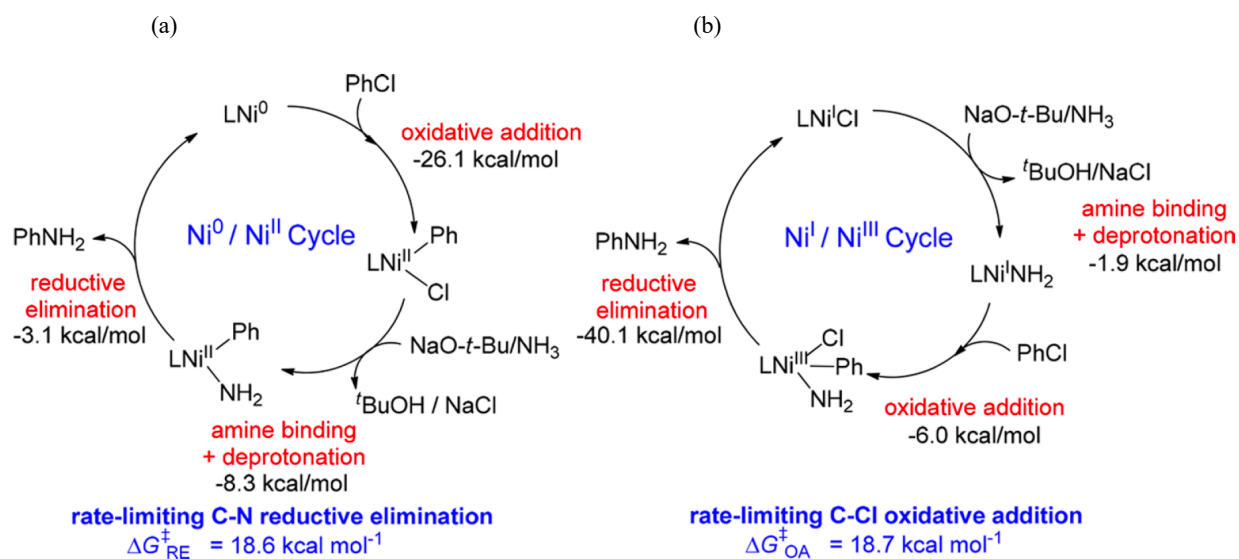


Figure 12. DFT-computed (a) $\text{Ni}^0/\text{Ni}^{\text{II}}$ and (b) $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ catalytic cycles for the C–N cross-coupling of chlorobenzene and ammonia, L = PAd-DalPhos. Figure taken directly from Ref. [148] with permission.

1.5 Plan of study

Despite the significant advancements in Ni-NHC precatalysts for cross-coupling reactions, several challenges remain unaddressed. Many of these catalysts exhibit sensitivity to air and moisture, necessitating careful handling and storage under inert conditions. Additionally, their activation often requires harsh reagents such as strong bases (e.g., NaH), which are incompatible with base-sensitive functional groups, or aggressive additives such as organomagnesium species at elevated temperatures. Another significant drawback, particularly from an industrial perspective, is the high catalyst loading required in most Ni-catalyzed cross-coupling applications. These limitations restrict the scope of cross-coupling reactions and hinder their broader applicability. Furthermore, no universal nickel catalyst system exists that can efficiently and selectively mediate both C–C and C–heteroatom cross-coupling reactions across a truly diverse range of substrates. Therefore, designing a novel, all-purpose, and user-friendly nickel precatalyst that is air-stable and easily activated while maintaining high selectivity and efficiency in cross-coupling reactions is crucial. The central objective of this thesis is to address these unmet needs by developing next-generation Ni–NHC precatalysts and systematically evaluating their structural features, reactivity patterns, and mechanistic pathways. The study will begin with the synthesis and characterization of air-stable nickel complexes, establishing reliable structural and spectroscopic benchmarks that ensure reproducibility and stability. Once defined, these systems will be applied to the C–N cross-coupling transformations to probe their catalytic behavior across a spectrum of substrates, ranging from electronically activated to more sterically and electronically challenging coupling partners. This strategy allows the systematic identification of the key limitations that govern catalytic turnover, such as slow reductive elimination or difficulties in oxidative addition, and provides a framework for targeted improvements. A particular focus will be placed on understanding how

NHC ligands modulate nickel's unique redox flexibility, as the accessibility of multiple oxidation states (Ni(0), Ni(I), Ni(II), and Ni(III)) underlies both the opportunities and challenges of nickel catalysis. By examining how steric and electronic parameters of the NHC ligand influence the stability of these oxidation states and their participation in elementary catalytic steps, the work seeks to uncover guiding principles that can be applied broadly across cross-coupling chemistry. Insights from these mechanistic studies will then be leveraged to design and implement ligands with tailored steric profiles, particularly those that can accelerate slow steps such as reductive elimination while simultaneously enhancing selectivity in challenging transformations.

Overall, this thesis aims to advance Ni–NHC catalysis by developing next-generation precatalysts that overcome the traditional barriers of air sensitivity, harsh activation, and narrow substrate scope. By integrating structural characterization, mechanistic investigation, and rational ligand design, the work establishes clear connections between ligand architecture, oxidation-state control, and catalytic performance. These insights not only enable the creation of more robust Ni–NHC systems for challenging C–N bond formation but also provide broadly applicable design principles that will extend the utility of nickel-catalyzed cross-coupling reactions in synthetic chemistry.

Chapter 2

2. Chapter 2: Development of well-defined, bench-stable Ni–NHC precatalysts for challenging C–N bond formation reactions

2.1 Background

In recent years, highly active nickel-based catalytic systems have been developed for amination reactions. Notably, due to its greater electropositivity compared to palladium, nickel facilitates the oxidative addition of electrophiles that are typically less reactive under Pd catalysis, such as aryl fluorides,^{14,161} aryl chlorides,^{162,163} and phenol derivatives.^{155,157,164} Despite the rapid expansion of the role of nickel in cross-coupling chemistry, mechanistic studies on these transformations remain relatively underexplored.^{165–167} One challenge lies in the diverse oxidation states accessible to nickel (ranging from 0 to +3), which complicates the analysis of reaction pathways. Additionally, the limited availability of efficient nickel-based catalysts may be attributed to the difficulty in reducing stable Ni(II) precursors to catalytically active Ni(0) species (NaH used as reducing agent), resulting in low reactivity,^{117,125,126,168} or to the challenges associated with handling air-sensitive Ni(0).¹¹⁶

In the past two decades, significant efforts have been made to overcome these limitations. As a result, several novel air-stable Ni–NHC precatalysts have been developed by researchers such as Nolan (**43,55**),^{130,138} Matsubara (**45**),¹³² Nicasio (**46,56**),^{134,139} Montgomery (**57**),¹⁴³ and Jamison (**71**)¹⁴⁶ (Figure 13), demonstrating high activity in C–N cross-coupling reactions. Although many of these catalytic systems have shown remarkable efficiency, no universal catalyst has yet been identified that can selectively couple a broad range of aryl halides with both simple and functionalized aryl or alkyl amines.

Recognizing the need for a readily accessible and efficient Ni–NHC precatalyst for both routine and advanced cross-coupling reactions, particularly C–N bond formation, we aimed to develop a universal well-defined catalyst that could streamline these transformations. In pursuit of this goal, we recently synthesized a new class of Ni–NHC complex (**83**; [Figure 13](#)) and demonstrated its superior performance compared to catalysts generated in situ from the corresponding imidazolium salt and a standard Ni source (Ni[cod]₂) in amination reactions. Building on this work, we now present a comprehensive evaluation of complex **83** across a broad scope of C–N cross-coupling reactions.

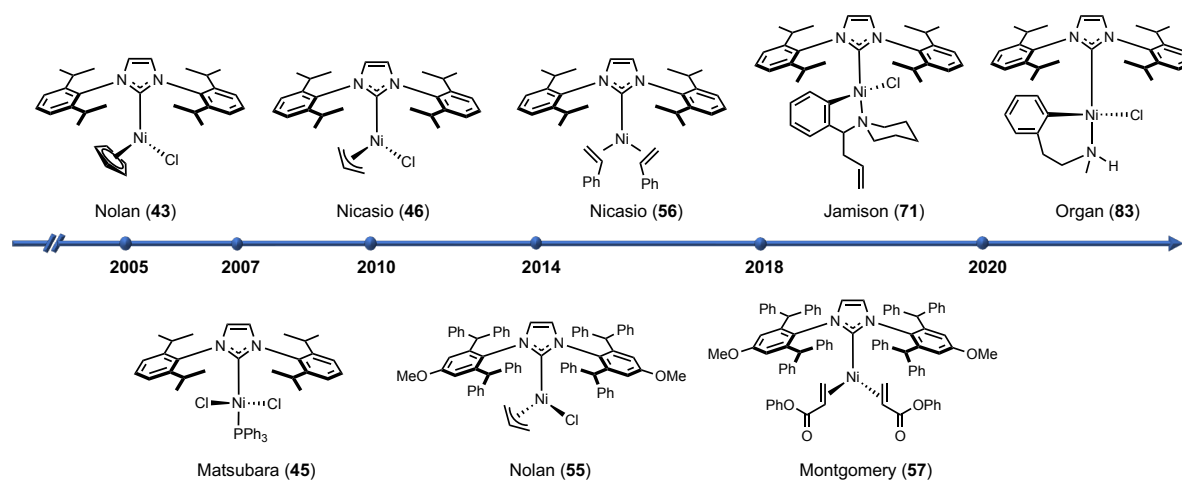


Figure 13. Representative examples of Ni–NHC precatalysts developed over the past two decades.

2.2 Designing an air-stable Ni(II)–NHC precatalyst (1st Generation)

The design of an efficient Ni–NHC catalytic system for C–N coupling relies on three key considerations: the nickel precursor, the ligand framework (NHC design), and designing a stabilizing (throw-away) ligand ([Figure 14](#)).

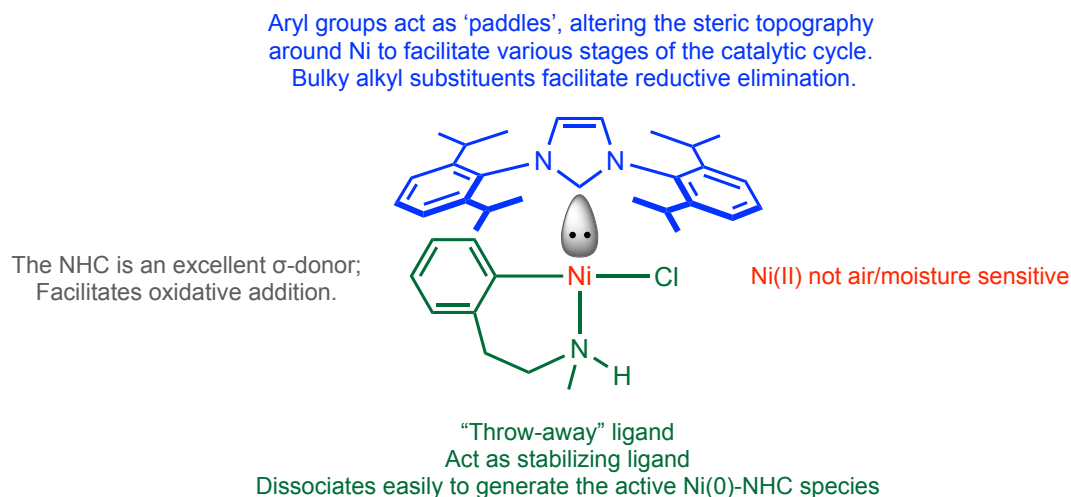


Figure 14. Attributes of the 1st generation of Ni–NHC complex (**83**) made by Organ group

2.2.1 The nickel precursor

Nickel precursors fall into Ni(0) and Ni(II) complexes. While Ni(0) complexes require strict air-free handling due to their sensitivity to oxygen and moisture, they exhibit high reactivity. Among them, bis(cyclooctadiene)nickel(0) [Ni(cod)₂] stands out as the most commonly used and cost-effective Ni(0) source. It is highly soluble in various organic solvents and readily coordinates with a wide range of ligands.¹⁶⁹ Notably, Ni(cod)₂ efficiently releases cod under reaction conditions without interfering with other components, making it an ideal precursor for catalysis. Given these advantages, Ni(cod)₂ was selected as the best nickel precursor for our research (Figure 15).

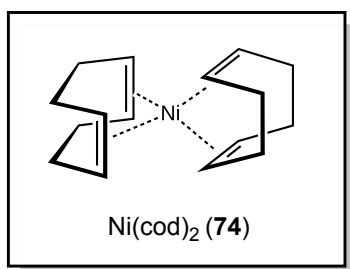


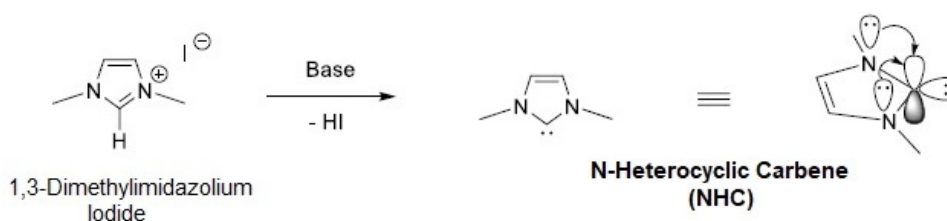
Figure 15. Structure of the Ni(cod)₂ precursor

Table 2. Representative examples of Ni(0) and Ni(II) precursors

Ni(II) precursors		Ni(0) precursors	
NiCl ₂	NiBr ₂	Ni(cod) ₂	Ni(cod)(dmpe)
Ni(OAc) ₂	Ni(acac) ₂	Ni(CO) ₄	Ni(PPh ₃) ₄
Ni(OTf) ₂	Ni(cod)Cl ₂		

2.2.2 The ligand framework (NHC design)

1,3-Imidazolium salts serve as simple and stable precursors for NHCs and can generate them either through heating or by deprotonation with a base (Scheme 17).⁵⁴

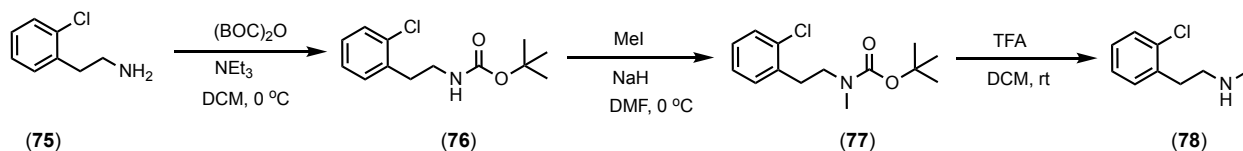
**Scheme 17.** Representative synthesis of an NHC from its protonated salt form

NHCs are nitrogen-containing heterocycles featuring a divalent carbene center stabilized by the adjacent nitrogen atoms through a synergistic push–pull electronic effect.^{56,57} This effect combines inductive σ -electron withdrawal and mesomeric π -electron donation, resulting in a singlet ground state with enhanced stability.^{56,58} The cyclic structure of NHCs enforces this singlet state, distinguishing them from less stable acyclic carbenes, which typically exist in a triplet state.⁵⁹ These electronic characteristics enhance the σ -donor and π -acceptor abilities of NHCs, making them excellent ligands for transition metal complexes, particularly nickel. In addition to the unique electronic features, the structural versatility of NHCs is another key factor that attracted the attention of chemists. The ability to tune the ring size, ranging from four- to seven-membered structures, along with the flexibility to introduce substituents at either the N-atom or on the C-atom of the ring, has significantly expanded the diversity and applicability of NHC

ligands.¹⁷⁰ This structural tunability directly influences both the electronic and steric properties of NHCs, providing a powerful means to modulate reaction mechanism. By carefully designing NHC ligands, it is possible to control key catalytic steps, such as oxidative addition and reductive elimination, ultimately enhancing reaction efficiency and selectivity.¹⁷¹

2.2.3 Stabilizing (throw-away) ligand

Ni(0)–NHC is a highly reactive catalyst but lacks stability in air, necessitating the incorporation of an additional ligand to stabilize the nickel center and create a well-defined and bench-stable catalyst structure.¹⁷¹ Beyond providing stability to the nickel center, this stabilizing ligand functions as a "throw-away" ligand, meaning it dissociates under reaction conditions to generate the active Ni(0)–NHC species. To achieve enhanced stability in both solution and solid-state, we selected a Buchwald-type ligand (phenethylamine)¹⁷² with a modified amine group, substituting the primary amine (**75**) with an *N*-methylamine (**78**), as shown in Scheme 18. This modification improves the stability of the Ni(0)–NHC system.

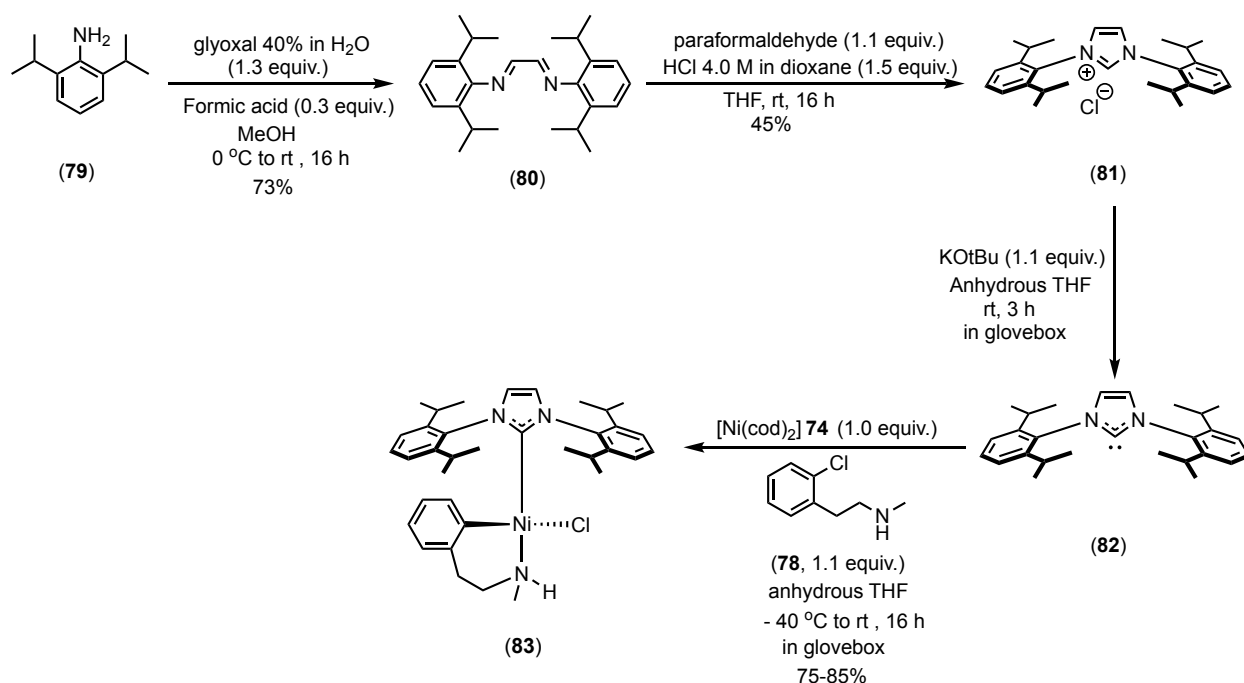


Scheme 18. Methylation of 2-Chlorophenethylamine (**75**) to 2-chlorophenethyl *N*-methylamine (**78**) through three-step process (protection, methylation, deprotection)

2.3 Synthesis and characterization of air-stable Ni(II)–NHC precatalyst (1st Generation)

As illustrated in Scheme 19, the IPr•HCl ligand (**81**) was synthesized following literature procedures.¹⁷³ First, the condensation of 2,6-diisopropylaniline (**79**) produced bisimine intermediate (**80**) in quantitative yield. This was followed by cyclization to afford NHC salt (**81**) in high purity. In the final step, free IPr carbene (**82**) was generated and subsequently ligated to

the nickel precursor, along with the stabilizing ligand (**78**), to furnish the first-generation (Organ type) air- and moisture-stable Ni(II)–NHC precatalyst (**83**).



Scheme 19. General procedure for synthesis Ni–NHC–IPr (**83**) precatalyst (1st generation)

To confirm the structure of complex (**83**), a series of analytical techniques were employed, including single-crystal X-ray diffraction (SC-XRD), nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). As shown in [Figure 16](#), the molecular structure of Ni–NHC–IPr (**83**) was unambiguously determined by SC-XRD analysis. The crystallographic data confirm the coordination environment around the nickel center and are provided in the appendix for reference.

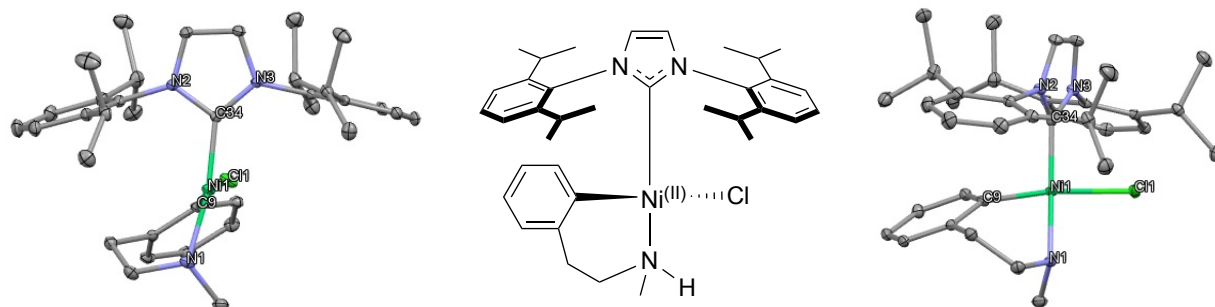
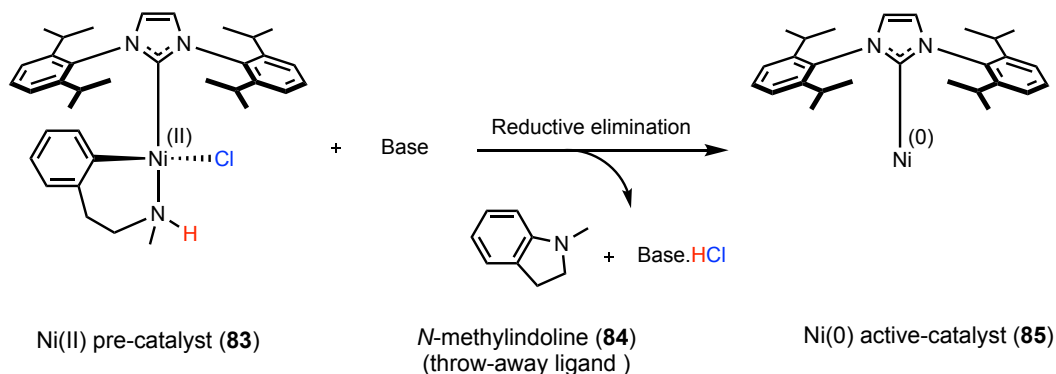


Figure 16. SC-XRD analysis of the Ni–NHC–IPr (**83**) complex from two different view

2.4 Proposed mechanism for Ni(II)–NHC precatalyst activation

As shown in Scheme 20, the air- and moisture-stable Ni(II)–NHC precatalyst (**83**) offers the key advantage of forming the active Ni(0)–NHC species without requiring external aggressive additives. In the presence of a mild base, the Ni(II)–NHC precatalyst (**83**) undergoes reductive elimination to generate the active Ni(0)–NHC catalyst (**85**), while *N*-methylindoline (**84**), derived from ligand dissociation, acts as the throw-away ligand. Notably, this transformation proceeds efficiently at room temperature.



Scheme 20. Proposed mechanism of precatalyst activation

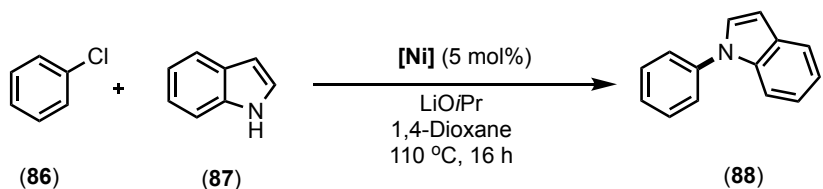
2.5 Activity of Ni–NHC–IPr in C–N bond formation reaction

To evaluate the catalytic activity of the Ni–NHC–IPr precatalyst (**83**), we employed 5 mol% of this complex in a C–N bond formation reaction using chlorobenzene as the electrophile, indole as

the nucleophile, and LiOtBu as the base in dioxane at 110 °C for 16 hours. As shown in Table 3, no reaction occurred in the absence of a nickel catalyst (entry 1). Similarly, using 5 mol% Ni(cod)₂ alone resulted in no detectable conversion (entry 2). However, when 5 mol% of Ni–NHC–IPr (**83**) was applied, the cross-coupled product was obtained in 75% yield (entry 3). Based on mass balance, the remaining material was unreacted starting material.

These findings confirm that Ni–NHC–IPr (**83**) is active for C–N cross-coupling and highlight the critical role of the NHC ligand in enhancing the catalytic efficiency of nickel in such transformations. Furthermore, when comparing this result (entry 3) with the same reaction reported by Jamison in 2018 using a Jamison-type Ni–NHC–IPr catalyst (**71**) (entry 4)¹⁴⁶, our Ni–NHC–IPr precatalyst (**83**) demonstrates competitive activity, underscoring its effectiveness relative to other Ni–NHC–IPr systems.

Table 3. The first evaluation of Ni–NHC–IPr (**83**) in C–N cross-coupling reaction

		
Entry	Catalyst	% Isolated Yield (88)
1	No catalyst	NR
2	Ni(cod) ₂ (74)	NR
3	Ni–NHC–IPr (83)	75
4*	Ni–NHC–IPr (Jamison, 71) ¹⁴⁶	73

Reagents and conditions: Chlorobenzene (1 mmol, 1 equiv.), Indole (1.2 equiv.), [Ni] 5 mol%, LiOtBu (1.1 equiv.), 1,4-Dioxane (1 ml), 110 °C, 16 h. *using LiOtBu (1.5 equiv.), 2 h.

Employing an electron-rich aryl chloride further increases the challenge of C–N cross-coupling. Electron-rich electrophiles impact all three key steps—oxidative addition, amine coordination, and reductive elimination—by altering the electronic properties of the reaction. However, oxidative

addition is particularly affected, as the increased electron density in electron-rich aryl chlorides makes it more difficult for nickel to insert into the C–Cl bond. To investigate this effect, we replaced chlorobenzene (**86**) with 4-chloroanisole (**89**). As shown in Table 4 (entry 2), using 5 mol% of Ni–NHC–IPr (**83**) in the cross-coupling reaction between 4-chloroanisole (**89**) and indole (**87**) led to the complete conversion of the starting material (**89**) and a 65% yield of the cross-coupled product (**90**). Additionally, a comparative study was conducted to evaluate the catalytic activity of the Ni–NHC–IPr (**83**) precatalyst against its in situ-generated counterpart. As shown in entry 3, the in situ-formed Ni–NHC–IPr catalyst exhibited similar activity to the precatalyst (entry 2), demonstrating that both approaches are comparably effective for this transformation.

Table 4. Evaluation of Ni–NHC–IPr (**83**) in the cross-coupling of 4-chloroanisole as an electron-rich electrophile

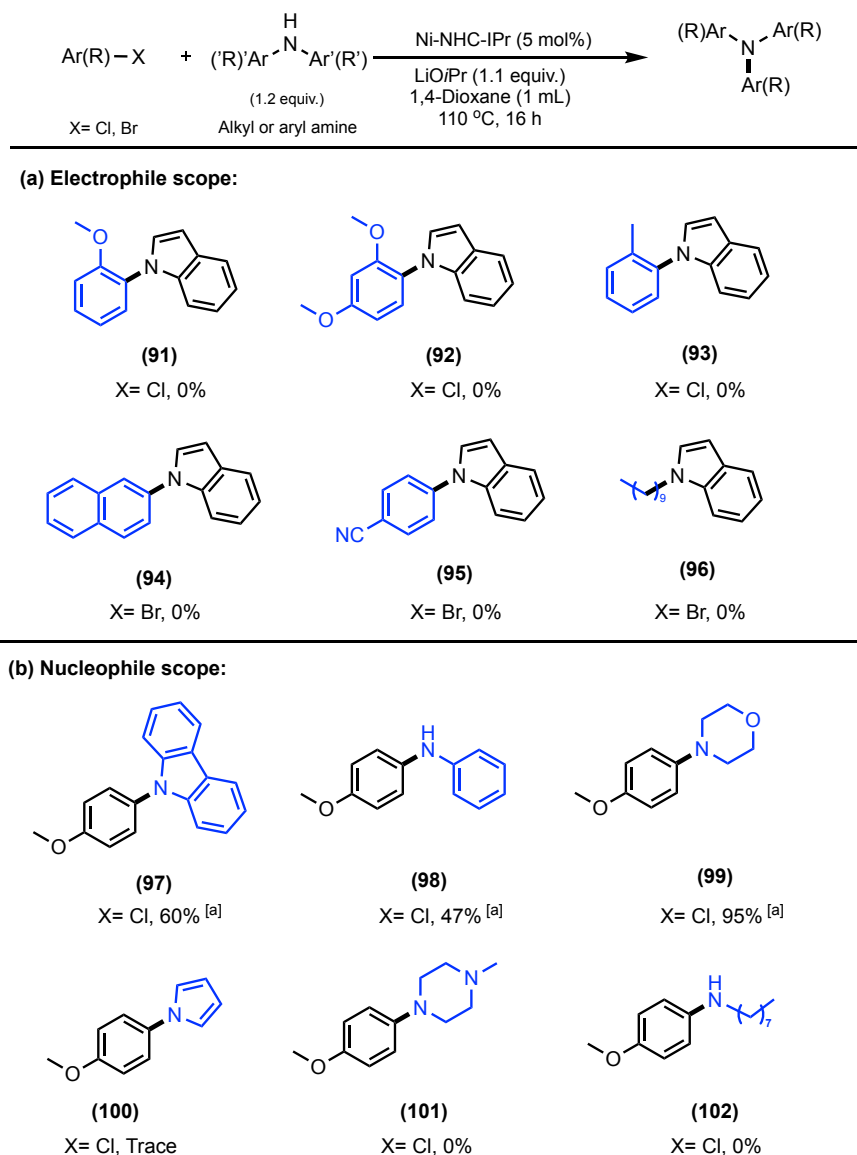
(89) + (87) $\xrightarrow[\text{LiO/Pr, 1,4-Dioxane, 110 °C, 16 h}]{\text{[Ni] (5 mol\%)}}$ (90)

Entry	Catalyst	% Isolated Yield (90)
1	Ni(cod) ₂	NR
2	Ni-NHC-IPr	65
3*	Ni(cod) ₂ + NHC-IPr.HCl	68

Reagents and conditions: Chlorobenzene (1 mmol, 1 equiv.), Indole (1.2 equiv.), [Ni] 5 mol%, LiO/Pr (1.1 equiv.), 1,4-Dioxane (1 ml), 110 °C, 16 h. *In-situ preparation of Ni-NHC catalyst using 5 mol% Ni(cod)₂ and 5 mol% NHC-IPr.HCl ligand

To explore the substrate scope, a variety of bulky and/or electron-rich electrophiles were tested in the C–N bond formation reaction with indole (Scheme 21a). These particular aryl halides were selected because bulky and electron-rich aryl halides are known to undergo oxidative addition slowly and also lead to a more difficult reductive elimination step;^{32,149} no conversion to the desired cross-coupled products was observed.

To complete the substrate scope, a variety of aliphatic and aromatic amines, including carbazole, aniline, morpholine, *1H*-pyrrole, 1-methylpiperazine, and octylamine, were tested for coupling with 4-chloroanisole (**Scheme 21b**). Among these, only carbazole, aniline and morpholine successfully formed the C–N bond, achieving moderate to high yields.



Scheme 21. Substrate scope of amination reactions catalyzed by Ni–NHC–IPr (**83**) (a) electrophile scope, (b) nucleophile scope, ^[a] Isolated yield, average of two runs.

2.6 N-arylation of morpholine

Based on the above results, Ni–NHC–IPr (**83**) demonstrates catalytic activity in C–N bond formation but exhibits substrate specificity. To gain a deeper understanding of the reaction mechanism, we selected one highly successful reaction for further investigation. Given the successful cross-coupling between 4-chloroanisole and morpholine, this reaction was chosen as the primary model for detailed mechanistic studies.

In the first study, the effect of the ligand on the catalytic efficiency of nickel was investigated. To assess this, ligand-free nickel [Ni(cod)₂], an in situ-generated Ni–NHC–IPr catalyst, and the Ni–NHC–IPr precatalyst (**83**) were applied in the C–N bond formation reaction using 4-chloroanisole (0.5 mmol, 1 equiv.), morpholine (1 equiv.), and NaOtBu (1.2 equiv.) in THF (1 mL), with the reaction mixture stirred at 60 °C overnight (16 h). These conditions were selected based on the optimized protocols reported by Nicasio¹³⁴ and Nolan¹³⁸ for the same reaction using complexes (**46**) and (**55**), respectively.

According to Table 5, using 5 mol% of ligand-free nickel [Ni(cod)₂] resulted in only a trace amount of the cross-coupled product (**99**) (entry 2). In contrast, when the catalyst was generated in situ by adding 5 mol% NHC–IPr to a solution of 5 mol% Ni(cod)₂ in THF, the yield increased significantly to 89% (entry 3). The highest efficiency was observed with the Ni–NHC–IPr precatalyst (**83**), which achieved a 98% yield under the same conditions (entry 4). Since the reaction showed negligible conversion with ligand-free nickel but proceeded efficiently with both the in situ-generated and pre-formed Ni–NHC catalysts, this study confirms the crucial role of the NHC ligand in enhancing the catalytic efficiency of nickel in C–N coupling.

Furthermore, the reaction with the Ni–NHC–IPr precatalyst (**83**) achieved an 88% yield at **room temperature** (22 °C), demonstrating that the precatalyst can be effectively activated under mild conditions (entry 4). The ability to activate at room temperature is a significant breakthrough,

broadening the scope of challenging reactions that are sensitive to elevated temperatures.¹³⁴ This makes our Ni–NHC precatalyst highly versatile and user-friendly, enhancing its applicability across a wider range of transformations.

Additionally, Nicasio and Nolan previously conducted the same C–N cross-coupling reaction under identical conditions, reporting yields of 72%¹³⁴ and 85%¹³⁸ for the coupled product (**99**) using complexes (**46**) and (**55**), respectively (entries 5–6). These results highlight the improved catalytic performance of our Ni–NHC–IPr precatalyst (**83**) compared to other precatalysts.

Table 5. Evaluation of ligand on the catalytic efficiency of nickel in N-arylation of morpholine

(**89**) + (**103**) $\xrightarrow[\text{THF, 60 } ^\circ\text{C, 16 h}]{[\text{Ni}] (5 \text{ mol\%}), \text{NaOtBu}}$ (**99**)

Entry	Catalyst	% Isolated Yield (99)
1	No catalyst	NR
2	Ni(cod) ₂	Trace
3[a]	Ni(cod) ₂ + NHC-IPr.HCl	89
4	Ni-NHC-IPr (83)	98 (88) ^[b]
5	[Ni(allyl)(IPr)Cl] (Nicasio, 46) ¹³⁴	72
6	Ni(allyl)(IPr ^{*OMe})Cl] (Nolan, 55) ¹³⁸	85 ^[c]

Reagents and conditions: 4-chloroanisole (0.5 mmol, 1 equiv.), morpholine (1.2 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), THF (1 ml), 60 °C, 16 h. [a] In-situ preparation of Ni-NHC catalyst using 5 mol% Ni(cod)₂ and 5 mol% NHC-IPr.HCl
 [b] T= room temperature (22 °C). [c] [Ni] 2 mol%, 3 h.

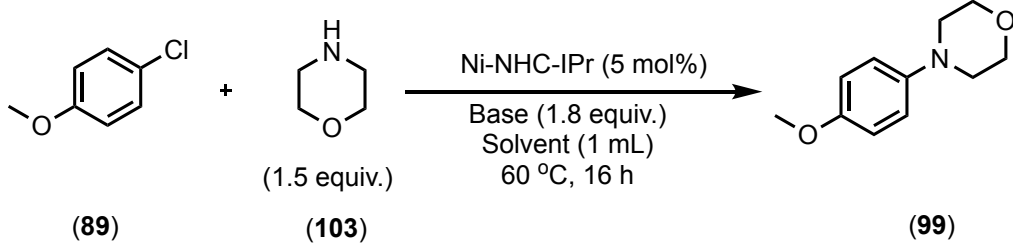
Several studies have been conducted to evaluate the impact of reaction conditions on the catalytic performance of the Ni–NHC–IPr (**83**) precatalyst. Key parameters, including catalyst loading, base selection, solvent choice, and reaction time were experimentally examined to determine the optimal conditions for maximum efficiency.

2.6.1 N-arylation of morpholine – Optimization studies

As shown in Table 6, various bases, were tested in the C–N bond formation between 4-chloroanisole and morpholine, while all other reaction conditions remained unchanged. Among them, NaOtBu and LiHMDS provided the highest conversion to the coupled product (99).

Additionally, different solvents were screened to identify the most suitable medium for the reaction. The best results were seen in THF, toluene and 1,4-dioxane (Table 6, entry 10-12).

Table 6. Optimization studies – base and solvent screening

			
(89)	(103)		(99)
Entry	Solvent	Base	% Conversion to (99) ^[a]
1	THF	Cs ₂ CO ₃	0
2	THF	Na ₂ CO ₃	0
3	THF	K ₂ CO ₃	0
4	THF	NaBHT	0
5	THF	DBU	0
6	THF	LiHMDS	89
7	THF	LiO ^t Pr	0
8	THF	LiO ^t Bu	22
9	THF	KO ^t Bu	79
10	THF	NaO ^t Bu	92
11	Toluene	NaO ^t Bu	92
12	1,4-dioxane	NaO ^t Bu	90
13	DME	NaO ^t Bu	68
14	DCM	NaO ^t Bu	0

Reagents and conditions: 4-chloroanisole (0.5 mmol), morpholine (0.75 mmol), base (0.9 mmol), Ni-NHC-IPr (5 mol%), Solvent (1 mL), 60 °C, 16 h. [a] Conversion into coupling product, as determined by GC analysis using dodecane as an internal standard.

To determine the ideal catalyst loading, varying amounts of the Ni–NHC–IPr (**83**) precatalyst were tested in the same C–N bond formation reaction, keeping all other parameters constant. As shown in Figure 17, 2 mol% was the lowest catalyst loading to obtain good results, and reducing the catalyst amount to 1 mol% led to a significant decrease in conversion to the coupled product (**99**).

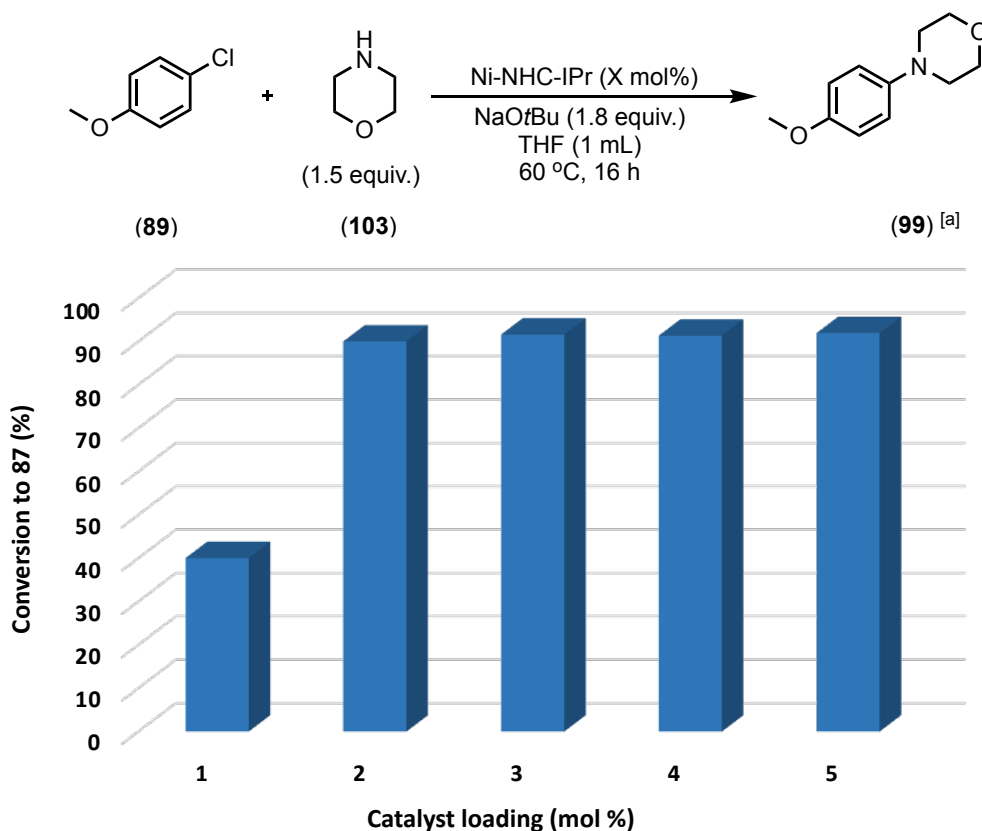


Figure 17. Optimization studies – Catalyst loading. [a] Conversion to **99**, as determined by GC-FID analysis using dodecane as an internal standard.

Screening the reaction time and temperature provides valuable insights into induction period and the reaction rate. As shown in Figure 18, the reaction was performed at two different temperatures: 60 °C and room temperature (22 °C). At 60 °C, the reaction reached maximum conversion within 5 minutes, whereas at room temperature, it required 180 minutes to achieve the same result. This

study highlights Ni–NHC–IPr (**83**) precatalyst activates at room temperature, but additional time is required to complete the coupling when compared to running the reactions at 60 °C.

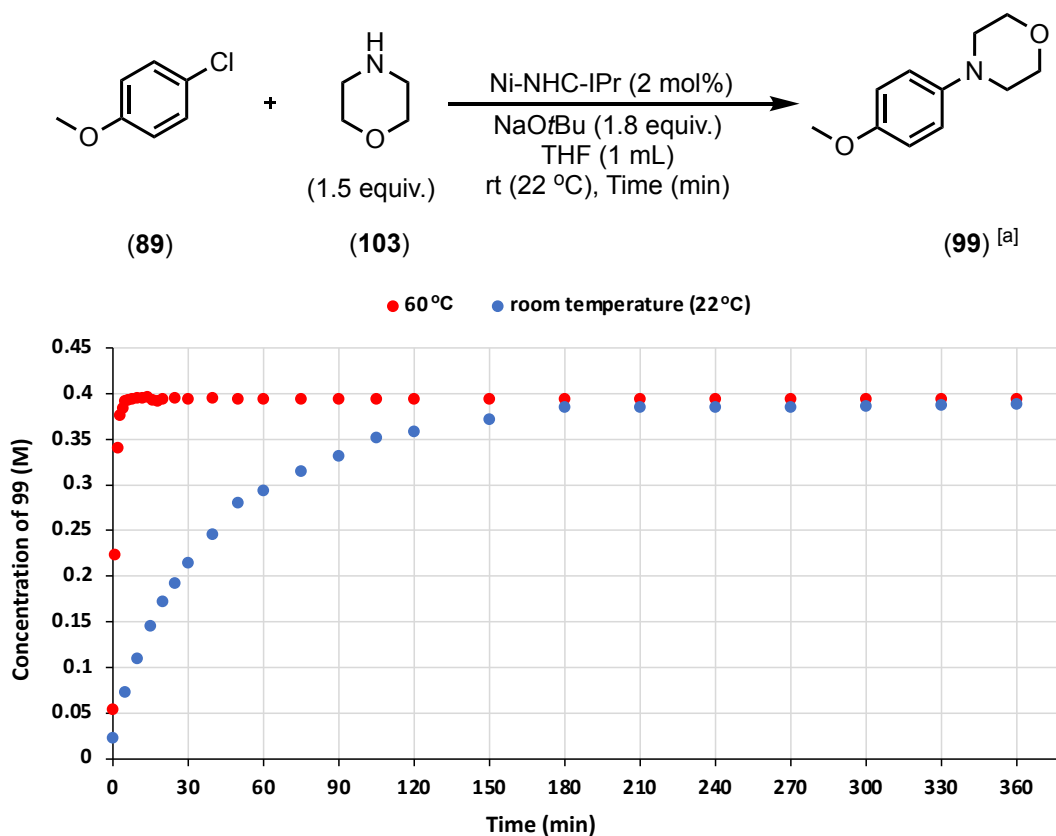


Figure 18. Optimization studies – temperature and time screening. [a] Concentration of coupling product, as determined by GC-FID analysis using dodecane as an internal standard.

In Figure 19, the consumption of 4-chloroanisole (**89**) and the corresponding formation of the product (**99**) at room temperature are plotted. The reaction reached maximum conversion at 180 minutes, after which no significant changes in 4-chloroanisole consumption or product formation were observed. Therefore, the optimum reaction conditions for this C–N bond formation involve using 2 mol% of Ni–NHC–IPr (**83**) in THF at room temperature for 3 hours.

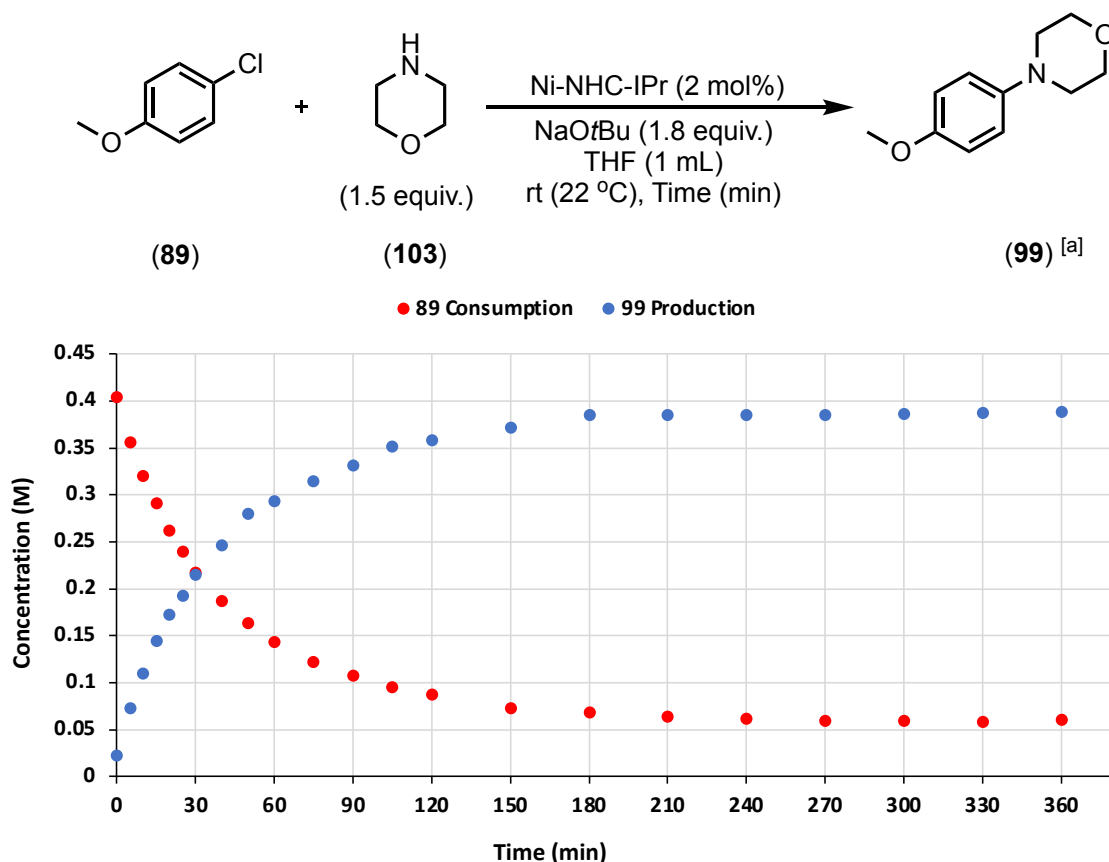


Figure 19. Optimization studies – Time screening. [a] Concentration of coupling product, as determined by GC-FID analysis using dodecane as an internal standard.

2.6.2 Ar–Cl versus Ar–Br in *N*-arylation of morpholine

In cross-coupling reactions, the reactivity of aryl halides (X = F, Cl, Br, I) varies significantly, influencing both the reaction mechanism and overall efficiency. This variation is primarily attributed to the strength of the carbon-halide (C–X) bond and the energy barrier associated with the oxidative addition step, both of which are influenced by the electronic and steric features of the C–X bond, and the orbital interactions between the halogen and carbon.¹⁷⁴ The general reactivity trend follows the order: aryl iodides are the most reactive, followed by aryl bromides, while aryl chlorides and aryl fluorides are significantly less reactive (Figure 20).¹⁷⁴ This trend is closely linked to the bond dissociation energy (BDE) of the C–X bond, which plays a crucial role in determining the ease of oxidative addition, a key step in the cross-coupling mechanism. BDE

represents the energy required to homolytically cleave the bond, forming two radicals. The BDE values for aryl halides typically follow the pattern $\text{C-F} > \text{C-Cl} > \text{C-Br} > \text{C-I}$, with approximate values of ~130 kcal/mol for C-F, ~100 kcal/mol for C-Cl, ~85 kcal/mol for C-Br, and ~65 kcal/mol for C-I.¹⁷⁵

Table 7. BDE Values for Aryl Halides (X = F, Cl, Br, I)¹⁷⁵

Aryl Halide	BDE (kcal/mol)	Oxidative Addition Difficulty	Reactivity in Cross-Coupling
C-F	~130	Very Difficult	Least Reactive
C-Cl	~100	Moderate	Less Reactive
C-Br	~85	Relatively Easy	More Reactive
C-I	~65	Easiest	Most Reactive

The high BDE of the C-F bond is attributed to the strong orbital overlap between the fluorine 2p orbital and the 2sp^2 carbon orbital, which leads to exceptional bond stability.¹⁷⁴ This strength makes oxidative addition of aryl fluorides highly challenging, requiring specialized catalysts for successful coupling.¹⁷⁵ Aryl chlorides, with a moderately strong C-Cl bond (BDE ~100 kcal/mol), also present challenges in oxidative addition. However, their lower cost and greater commercial availability make them attractive substrates when paired with appropriate catalysts featuring electron-rich or sterically demanding ligands.¹⁷⁵

In contrast, aryl bromides, with a BDE of approximately 85 kcal/mol, offer a favorable balance between reactivity and stability, making them widely employed in standard cross-coupling protocols. Aryl iodides, possessing the weakest C-I bond (BDE ~65 kcal/mol), are the most reactive in cross-coupling reactions as oxidative addition occurs with minimal energy input. Despite their superior reactivity, aryl iodides are less frequently used in large-scale synthesis due to their higher cost and lower stability.¹⁷⁴

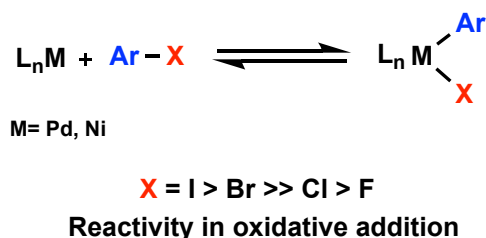
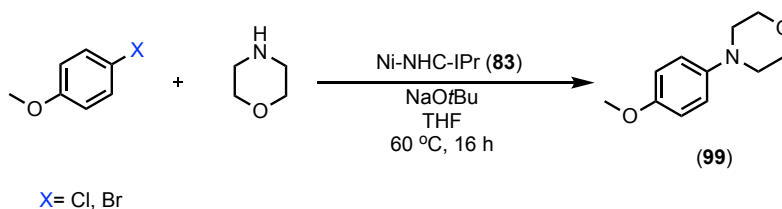


Figure 20. Oxidative addition of various aryl halides with palladium and nickel catalysts

Based on the aforementioned discussion, we initially expected aryl bromide to be more reactive than aryl chloride in the *N*-arylation of morpholine. However, our results revealed the opposite trend. In the nickel-catalyzed *N*-arylation of morpholine, a high yield of the cross-coupled product was obtained when using aryl chloride, whereas the reaction with aryl bromide resulted in a significantly lower yield of the desired product, as shown in Table 8.

Table 8. Ar–Cl versus Ar–Br in *N*-arylation of morpholine



Entry	X	% Isolated Yield (99)
1	Cl	92 [a]
2	Br	30 [b]

Reagents and conditions: 4-chloroanisole (0.5 mmol), morpholine (0.75 mmol), NaOtBu (0.9 mmol), Ni-NHC-IPr (5 mol%), THF (2 mL), 60 °C, 16 h. [a] The remaining consisted of unreacted starting material, [b] The remaining consisted of unreacted starting material and its reduced form, both of which were identified by GC-MS analysis.

To investigate the effect of bromine, a series of control experiments were conducted. In the first study, 4-chloroanisole was used as the electrophile partner in the nickel-catalyzed *N*-arylation of morpholine, and LiBr (1 equivalent) was added to the reaction mixture. As shown in Figure 21, the yield of the cross-coupled product decreased to 62%. Increasing the amount of LiBr to 3

equivalents resulted in the complete suppression of the reaction. In a subsequent experiment, LiCl was added to the *N*-arylation of morpholine with 4-chloroanisole. The addition of 1 equivalent of LiCl resulted in no significant change in the yield of the cross-coupled product. Increasing the amount of LiCl to 3 equivalents led to a slight decrease in product yield.

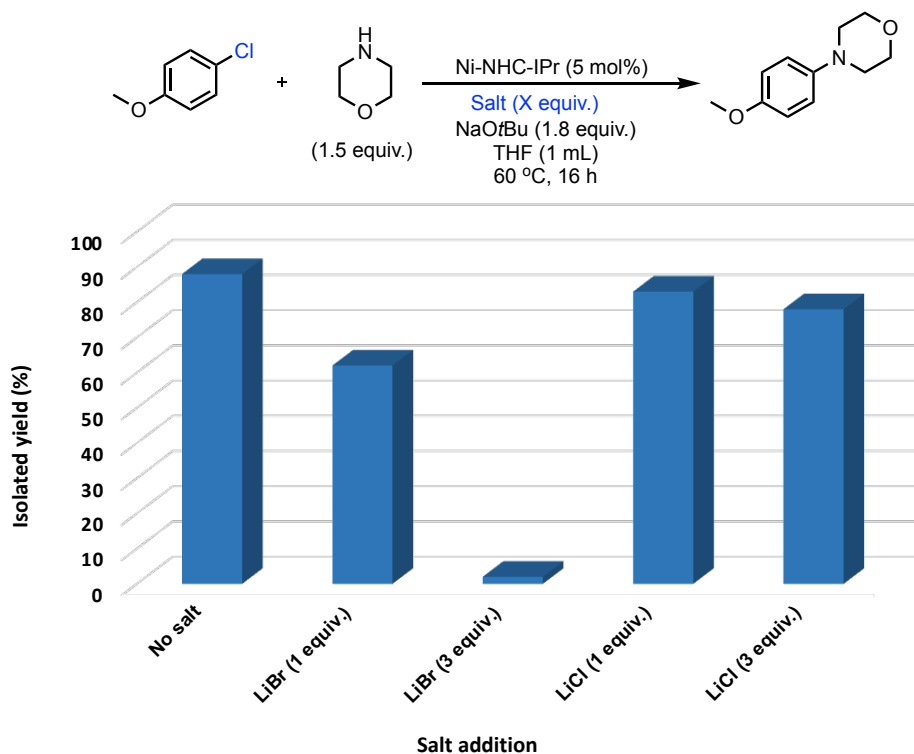


Figure 21. Salt effect in nickel-catalyzed *N*-arylation of morpholine using 4-chloroanisole as electrophile partner

Next, a series of salt effect studies were conducted in the nickel-catalyzed *N*-arylation of morpholine using 4-bromoanisole as the electrophile partner. As shown in Figure 22, the reaction without any salt additive yielded 30% of the desired product. The addition of LiCl, at both 1 and 3 equivalents, had no noticeable impact on the product yield. To examine the effect of a bromide-based additive, LiBr was introduced into the reaction since it shares the same counter ion (Br) as the electrophile. Adding 1 equivalent of LiBr produced no significant change in the product yield;

however, increasing the amount of LiBr to 3 equivalents resulted in a substantial decline in product yield.

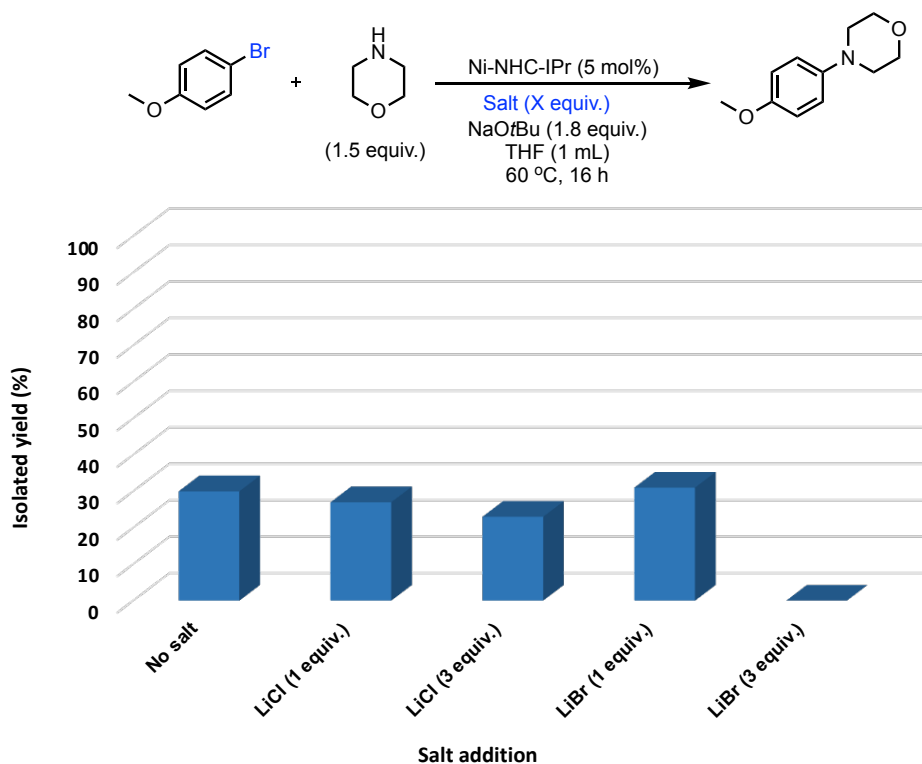


Figure 22. Salt effect in nickel-catalyzed *N*-arylation of morpholine using 4-bromoanisole as electrophile partner

To further investigate the observed effects, a series of control experiments were conducted. In one experiment, an aryl triflate was selected as the electrophile partner for the nickel-catalyzed *N*-arylation of morpholine, and the influence of LiBr and LiCl additives was examined. As shown in Figure 23, the reaction without any salt additive yielded 65% of the desired product. The addition of LiCl (1 equivalent) had no noticeable impact on the product yield, whereas adding LiBr (1 equivalent) reduced the yield to 20%, further highlighting the detrimental effect of bromide in this type of nickel-catalyzed amination reaction. These results also revealed that aryl triflate derivatives are more reactive than aryl bromides but less reactive than aryl chlorides in nickel-catalyzed *N*-arylation of morpholine.

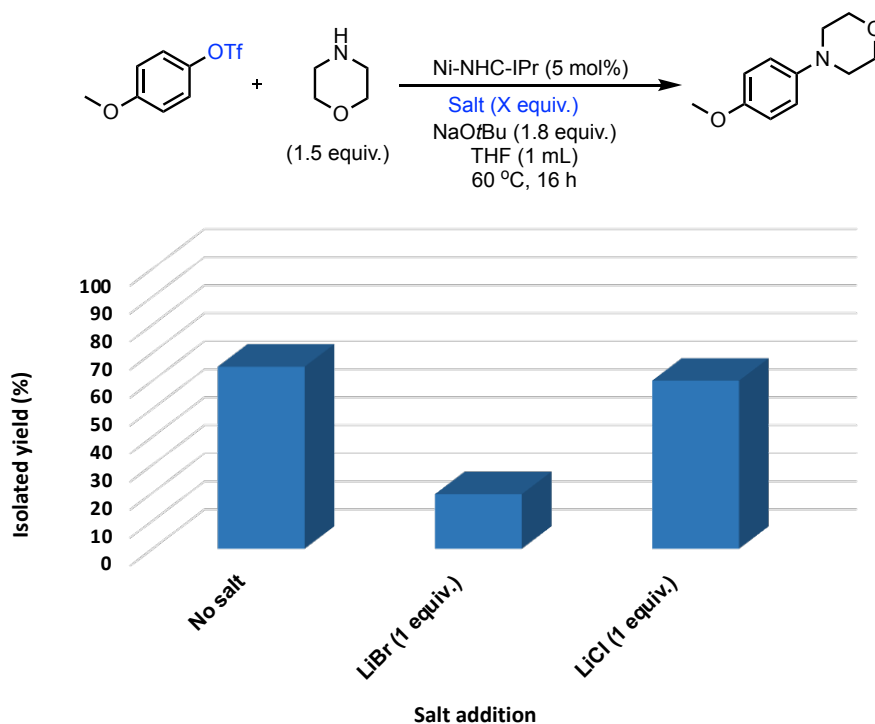


Figure 23. Salt effect in nickel-catalyzed *N*-arylation of morpholine using 4-Methoxyphenyl Trifluoromethanesulfonate as electrophile partner

To confirm whether triflate interferes with the *N*-arylation of morpholine, a series of control experiments were conducted by adding triflate salts to the nickel-catalyzed *N*-arylation of morpholine using 4-chloroanisole as the electrophile partner. As shown in [Figure 24](#), the addition of LiOTf (1 equivalent) or NaOTf (1 equivalent) had no significant impact on the product yield, indicating that triflate salts do not notably influence this amination reaction. However, when the amount of triflate salt was increased to 3 equivalents, both LiOTf and NaOTf had a negative effect on the product yield, suggesting that an excessive amount of triflate salt interferes with product formation.

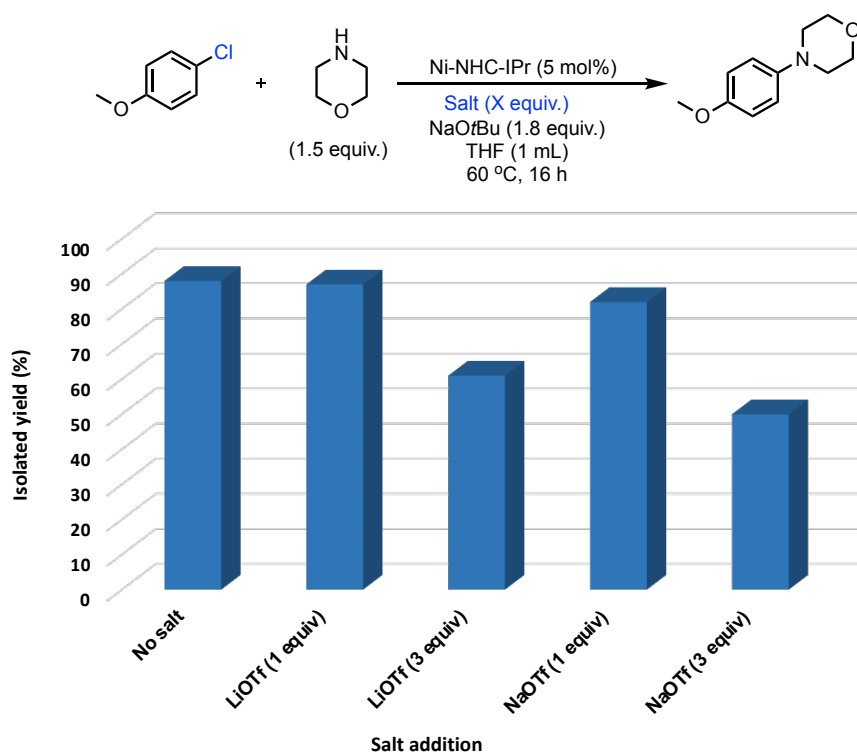
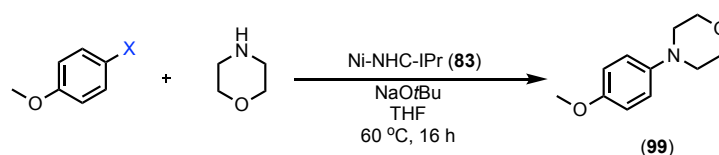


Figure 24. Triflate salt effect in nickel-catalyzed N-arylation of morpholine using 4-chloroanisole as electrophile partner

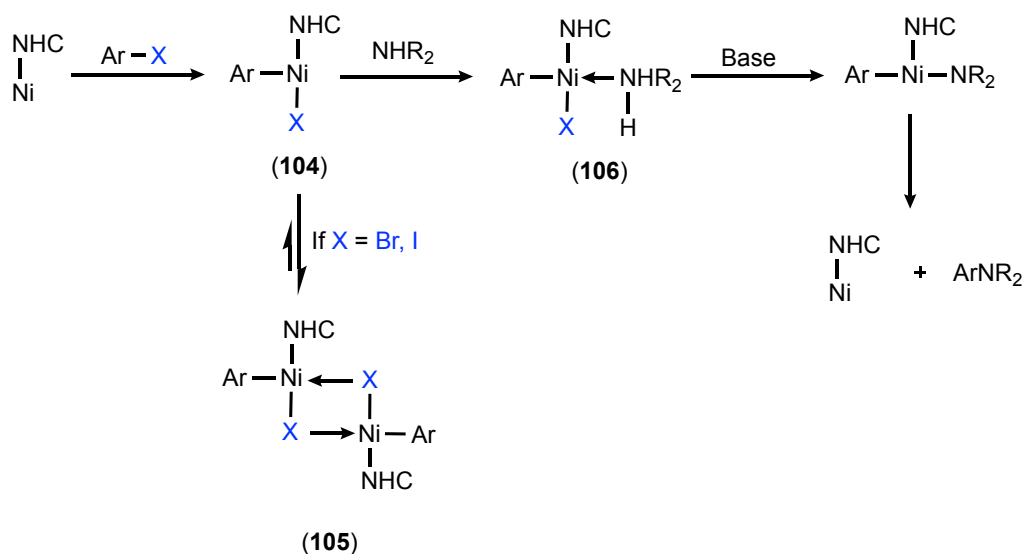
To complete this investigation into the effect of halides on nickel-catalyzed *N*-arylation of morpholine, 4-iodoanisole was selected as a coupling partner to directly compare its reactivity with that of 4-chloroanisole and 4-bromoanisole. However, as shown in Table 9 (entry 3), the reaction with 4-iodoanisole afforded only a low yield of the desired product, indicating that a lower bond dissociation energy (BDE) of the C–I bond does not guarantee improved coupling efficiency under the current catalytic conditions.

Table 9. Aryl halides effect in N-arylation of morpholine

Entry	X	% Isolated Yield (99)
1	Cl	92 [a]
2	Br	30 [b]
3	I	27 [b]

Reagents and conditions: 4-chloroanisole (0.5 mmol), morpholine (0.75 mmol), NaOtBu (0.9 mmol), Ni-NHC-IPr (5 mol%), THF (2 mL), 60 °C, 16 h. [a] The remaining consisted of unreacted starting material, [b] The remaining consisted of unreacted starting material and its reduced form, both of which were identified by GC-MS analysis.

Based on these results, it appears that bromine and iodine have a detrimental effect on the nickel-catalyzed *N*-arylation of morpholine. This negative impact is attributed to the formation of a nickel halide-bridged dimer complex (**105**), which effectively terminates the catalytic cycle. As shown in [Scheme 22](#), after the oxidative addition of Ar–X, a T-shaped intermediate (**104**) is initially formed, featuring an open coordination site that is crucial for amine binding. However, this intermediate readily dimerizes to form the nickel halide-bridged complex (**105**), which blocks the coordination site. As a result, for the amine to access the nickel center, it must first cleave the halide bridge, introducing an additional energetic barrier that significantly hampers the efficiency of the reaction.



Scheme 22. Formation of nickel halide-bridged complex (105) in N-arylation of morpholine

A review of the existing literature on Ni–NHC catalyzed amination reactions reveals no reported examples involving aryl bromides and aryl iodides; instead, all documented reactions exclusively feature aryl chloride derivatives. Consequently, no mechanistic studies have been conducted to explore the influence of halides in nickel-catalyzed amination reactions. However, in 1996, Buchwald et al. investigated the effect of halides in palladium-catalyzed amination reactions.¹⁷⁶ According to their findings, palladium's tendency to form Pd-(μ-halogen) bridged dimers follows the order: Cl < Br < I. Additionally, the strength of the dative Pd-(μ-halogen) bond is expected to correlate with the halide's polarizability and donicity, which increases in the same order: Cl < Br < I. By calculating the enthalpy and equilibrium constant, they demonstrated that the bridge cleavage of the palladium iodide dimer by an amine to form the corresponding 1:1 palladium amine adduct is significantly less favorable than the analogous reactions involving palladium bromide and chloride dimers. This halide-dependent equilibrium effect explains the lower efficiency observed for aryl iodides compared to aryl bromides and chlorides in palladium-catalyzed amination reactions.¹⁷⁷

Building on the insights gained from Buchwald's work, we concluded that bromine and iodine act as poisons to the nickel complex by promoting the formation of a nickel halide-bridged dimer complex (**105**), which exists in equilibrium with the mono-nickel halide complex (**104**). Given the low product conversion observed, we believe this equilibrium heavily favors the formation of the nickel iodide- or bromide-bridged dimer, effectively driving the nickel catalyst out of the catalytic cycle. In contrast, since nickel is less prone to form a bridged dimer with chloride, the equilibrium in this case likely favors the mono-nickel chloride complex, which remains in the catalytic cycle with an open coordination site available for amine binding.

2.6.3 Silver tetrafluoroborate as halide scavenger

To remove bromide ions from the reaction mixture, silver tetrafluoroborate (AgBF_4) was employed in the nickel-catalyzed *N*-arylation of morpholine. AgBF_4 is a well-established halide scavenger in organometallic and catalytic chemistry, commonly employed for its ability to abstract halide ions such as Cl^- , Br^- , and I^- .¹⁷⁸ The silver ion (Ag^+) exhibits a strong affinity for these halides, forming highly insoluble silver halide salts (AgX) that precipitate out of solution. This precipitation is thermodynamically favorable and serves as the driving force for halide removal. By effectively shifting the equilibrium toward halide abstraction, AgBF_4 eliminates halide ions that could otherwise interfere with catalytic activity, thereby helping to maintain the metal center in its active form throughout the reaction. Additionally, the accompanying tetrafluoroborate anion (BF_4^-) is weakly coordinating, ensuring that it does not disrupt the coordination environment of the metal center. As a result, AgBF_4 promotes the formation of cationic nickel species that are more reactive and less prone to forming off-cycle, halide-bridged dimeric complexes. Thus, the use of AgBF_4 helps maintain the nickel catalyst in its active form and enhances the efficiency of the cross-coupling reaction by preventing catalyst deactivation.

To evaluate the effect of AgBF₄ on bromide ion abstraction, a series of experiments were conducted, as summarized in Table 10. In all cases, no product formation was observed in the presence of AgBF₄, and the immediate formation of metal black suggested rapid catalyst decomposition. These results suggest that AgBF₄ is incompatible with the Ni–NHC–IPr complex (**83**) under the conditions employed in this study. To further investigate the role of bromide, alternative mild halide scavengers are being considered to effectively trap bromide ions without deactivating the catalyst. Additionally, computational studies are warranted to calculate bond dissociation energies, thermodynamic parameters, and equilibrium constants, which would help support the proposed formation of the nickel halide-bridged dimer complex (**105**) during reactions involving aryl bromides and aryl iodides in the nickel-catalyzed *N*-arylation of morpholine.

Table 10. Investigate the effect of AgBF₄ as halide scavenger in *N*-arylation of morpholine

Entry	X	Additive	% Isolated Yield (99)
1	Br	-	0
2	Cl	-	0
3	Cl	LiBr (1 equiv.)	0

Reagents and conditions: Ar-X (0.5 mmol), morpholine (0.75 mmol), AgBF₄ (0.5 mmol), NaOtBu (0.9 mmol), Ni-NHC-IPr (5 mol%), THF (1 mL), 60 °C, 16 h.

2.7 Ni–NHC–IPr-catalyzed C–N bond formation reaction: Substrate scope

Following the promising results obtained in the nickel-catalyzed *N*-arylation of morpholine with 4-chloroanisole, a series of aryl chlorides were evaluated under the optimal conditions (Scheme 23). A wide variety of aryl chlorides, including electron-neutral, electron-rich, and electron-

deficient derivatives, proved to be effective coupling partners, delivering the corresponding *N*-arylated products in excellent yields (Scheme 23, green box, 107–117). Notably, comparable conversions could also be achieved by performing the reactions at room temperature, highlighting the mild and efficient nature of this catalytic system.

While the electronic nature of the aryl chloride had minimal impact on the reaction outcome, as demonstrated by the efficient coupling of both electron-rich and electron-deficient substrates (99, 107–109), steric effects played a more significant role. Moving from 4- to 3- and 2-chlorotoluene (109–111) led to a noticeable decrease in conversion. Although 4-chlorotoluene coupled efficiently under standard conditions, a slight drop in yield was observed for 3- and 2-substituted analogues. A similar trend was noted when comparing 4-, 3-, and 2-chloroanisole (99, 114, and 115). Further increasing the steric bulk of the aryl chloride, as in 2-chloro-1,3-dimethylbenzene (112), 4-tertbutylchlorobenzene (113), 1-chloro-2,4-dimethoxybenzene (116), and 1-chloronaphthalene (117) rendered the *N*-arylation of morpholine more challenging.

After examining the steric and electronic effects of aryl chlorides, we turned our attention to the amine coupling partner. As previously demonstrated, morpholine—a cyclic dialkylamine—readily undergoes *N*-arylation with a variety of aryl chlorides. To explore the amine scope, 4-chlorobenzotrifluoride was selected as a reactive electrophile, and a range of alkyl and aryl amines were evaluated for their steric and electronic influence on the reaction outcome (Scheme 23, blue box). Piperidine, another cyclic dialkylamine, coupled efficiently to deliver the corresponding *N*-arylated product in quantitative yield (118), while 1-methylpiperazine provided a noticeably lower yield under the same conditions (119). *N*-Methylaniline, despite being a less nucleophilic amine, afforded a high yield (120), whereas the use of even less nucleophilic aniline proved more challenging, resulting in reduced conversion (121). To probe steric effects on the amine side, 2,6-

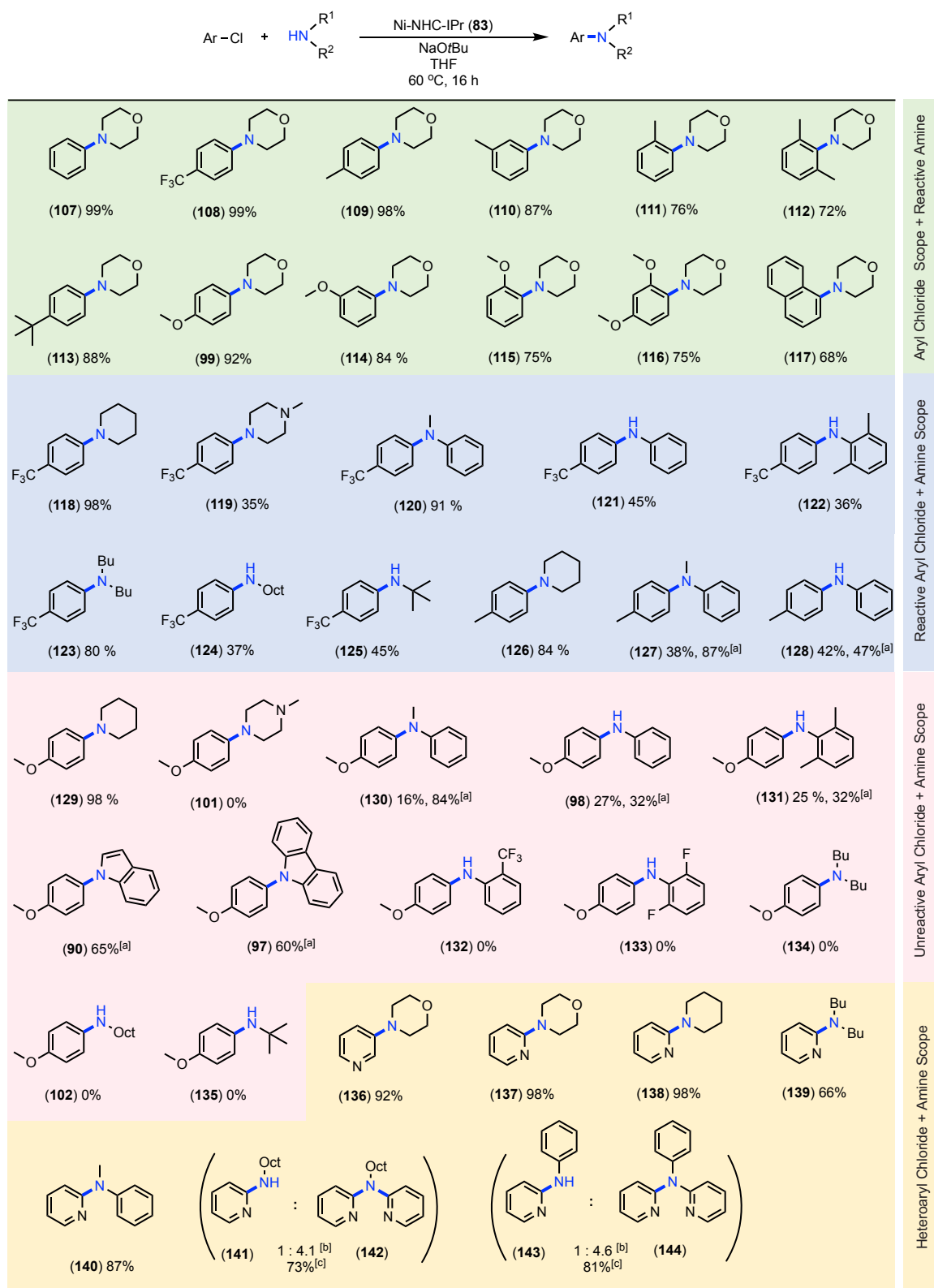
dimethylaniline was tested and afforded moderate yield of the desired product (**122**). Among acyclic alkyl amines, dibutylamine—though sterically bulky—gave high yields (**123**), whereas *n*-octylamine and *tert*-butylamine led to significantly diminished conversions (**124** and **125**), underscoring the sensitivity of the reaction to amine steric bulk.

By slightly increasing the electron density of the aryl chloride through the use of 4-chlorotoluene as the electrophilic coupling partner, the C–N bond formation proceeded smoothly with piperidine, affording the desired product in high yield (**126**). In contrast, *N*-methylaniline, a less nucleophilic amine, gave a noticeably lower yield under the same conditions (**127**). However, this reduced reactivity could be mitigated by switching the solvent to 1,4-dioxane and raising the reaction temperature, while maintaining a reaction time of 16 hours. Under these modified conditions, the *N*-arylated product was obtained in high yield. The use of aniline, an even less nucleophilic coupling partner, was also problematic (**128**), and no significant improvement in yield was observed despite performing the reaction in 1,4-dioxane at 100 °C.

To further challenge the nickel-catalyzed amination reaction, 4-chloroanisole—an electron-rich aryl chloride—was employed as the electrophilic coupling partner. As shown in [Scheme 23](#), (yellow box), high yields were achieved with piperidine (**129**) and morpholine (**99**), whereas no conversion was observed with 1-methylpiperazine (**101**). Reactions with less nucleophilic amines, such as *N*-methylaniline, aniline, 2,6-dimethylaniline, indole, and carbazole, also afforded moderate to low yields (**130–131**, **90**, **97–98**). Although switching the solvent to 1,4-dioxane and increasing the reaction temperature to 100 °C improved the yield for *N*-methylaniline, similar modifications failed to enhance the outcomes for aniline and 2,6-dimethylaniline. Furthermore, the use of even less nucleophilic substrates—such as 2-(trifluoromethyl)aniline and 2,6-difluoroaniline—resulted in no detectable product formation (**132** and **133**). Similarly, sterically

hindered acyclic alkyl amines, including dibutylamine, octylamine, and *tert*-butylamine, failed to undergo *N*-arylation (**134**,**102**), highlighting a clear limitation of this catalytic system under the current conditions.

Given the catalytic capabilities of Ni–NHC–IPr (**83**) for the amination of a wide range of aryl chlorides, we sought to extend this system to heteroaromatic substrates. To this end, a series of N-containing heteroaromatic chlorides were evaluated as coupling partners. The reactions of 3- and 2-chloropyridine with morpholine proceeded to full conversion in THF at 60 °C, affording the desired products in excellent yields (**136** and **137**). Under the same conditions, piperidine, a cyclic secondary amine, also coupled efficiently with 2-chloropyridine to give the product in quantitative yield (**138**). In contrast, the more sterically hindered di-butylamine resulted in only moderate yield (**139**). *N*-Methylaniline, despite its lower nucleophilicity, delivered the *N*-arylated product in acceptable yield (**140**). However, reactions involving n-octylamine and aniline led predominantly to undesired diarylated products (**142** and **144**), highlighting a limitation of this system when using alkyl and aryl primary amines with highly reactive heteroaryl halides.



Reagents and conditions: Ar-Cl (0.5 mmol), HN(R¹)(R²) (0.75 mmol), NaOtBu (0.9 mmol), Ni-NHC-IPr (5 mol%), THF (1 mL), 60 °C, 16 h. [a] 1,4-dioxane, 100 °C, [b] the ratio of monoarylated product to diarylated product were determined using ¹HNMR spectral analysis of the crude reaction. [c] The yield obtained for both mono- and di-arylated product

Scheme 23. Substrate scope of amination reactions catalyzed by Ni-NHC-IPr (**83**)

2.8 Conclusion

In summary, this chapter presents the design, synthesis, characterization, and comprehensive evaluation of a well-defined, bench-stable Ni–NHC–IPr precatalyst (**83**) for C–N bond-forming cross-coupling reactions. This precatalyst is catalytically active across a range of aryl chlorides and amine substrates, with excellent functional group tolerance under mild conditions. Mechanistic investigations confirmed the essential role of the NHC ligand in enhancing catalytic efficiency of nickel as ligand-free nickel showed negligible activity. Importantly, the precatalyst was effectively activated even at room temperature, highlighting its practicality for temperature-sensitive substrates.

A detailed analysis of halide effects revealed a distinct reactivity trend in the order Ar–Cl > Ar–Br > Ar–I, contradicting classical bond dissociation energy expectations. The formation of off-cycle nickel halide-bridged dimer complexes is hypothesized as the key deactivation pathway for aryl bromides and iodides. Control experiments and salt effect studies further emphasized the detrimental role of bromide and iodide ions, offering mechanistic insight into halide-dependent reactivity in nickel-catalyzed amination.

Optimization of key reaction parameters, including catalyst loading, base, solvent, and temperature, enabled the development of a robust and efficient protocol for Ni–NHC–IPr (**83**)-catalyzed amination reactions. Under these optimized conditions, the catalyst demonstrated high efficiency in coupling a variety of aryl chlorides with both alkyl and aryl amine nucleophiles. The compatibility of this catalytic system with heteroaryl chlorides further highlighted its versatility and synthetic utility.

Despite its broad applicability, substrate scope studies revealed that the catalytic performance of Ni–NHC–IPr (**83**) is strongly influenced by the electronic and steric properties of the coupling partners. High efficiency was observed when both the aryl chloride and the amine were

electronically activated and/or sterically accessible. The catalyst also maintained high activity when one of the substrates was unreactive, i.e., when the oxidative addition partner was electron-poor or when the amine was suitably nucleophilic with only moderate hindrance present. However, when both coupling partners were electronically deactivated or sterically hindered, a significant drop in reaction efficiency was observed. These results underscore the critical role of substrate selection in achieving optimal outcomes with this catalytic system.

Collectively, these results demonstrate that Ni–NHC–IPr (**83**) is a powerful air-stable precatalyst for C–N bond formation, capable of addressing several long-standing challenges associated with nickel-catalyzed cross-coupling chemistry. This work lays a strong foundation for future developments aimed at expanding the substrate scope, improving selectivity, and enabling milder and more sustainable synthetic methodologies—topics that will be explored in greater detail in the following chapter.

Chapter 3

3. Chapter 3: C–N cross-coupling reactions using a Ni–NHC/photoredox dual catalytic system

3.1 Proposed mechanism for Ni–NHC catalyzed C–N cross-coupling reactions

As discussed in Chapter 2, a new class of Ni–NHC precatalyst (complex **83**) developed by the Organ group exhibits exceptional air stability. The first batch, synthesized in 2020 and stored under ambient bench conditions, retained its catalytic activity over five years without any decomposition or change in physical appearance. Notably, this complex can be activated easily at room temperature, making it especially suitable for thermally sensitive substrates and broadening its applicability to challenging C–N bond-forming reactions. Studies on its catalytic performance in C–N cross-coupling demonstrate its strong activity, positioning it as a highly effective alternative to previously reported Ni–NHC precatalysts.

Although Ni–NHC–IPr (**83**) demonstrates broad utility, substrate scope studies indicate that its catalytic efficiency is significantly affected by the electronic and steric characteristics of the coupling partners. Notably, when both the aryl halide and amine are electronically deactivated or sterically hindered, a marked decrease in reaction efficiency was observed. To address these limitations, investigating the underlying mechanism of the nickel-catalyzed C–N cross-coupling reaction is essential. The proposed catalytic mechanism for this transformation is illustrated in [Figure 25](#).

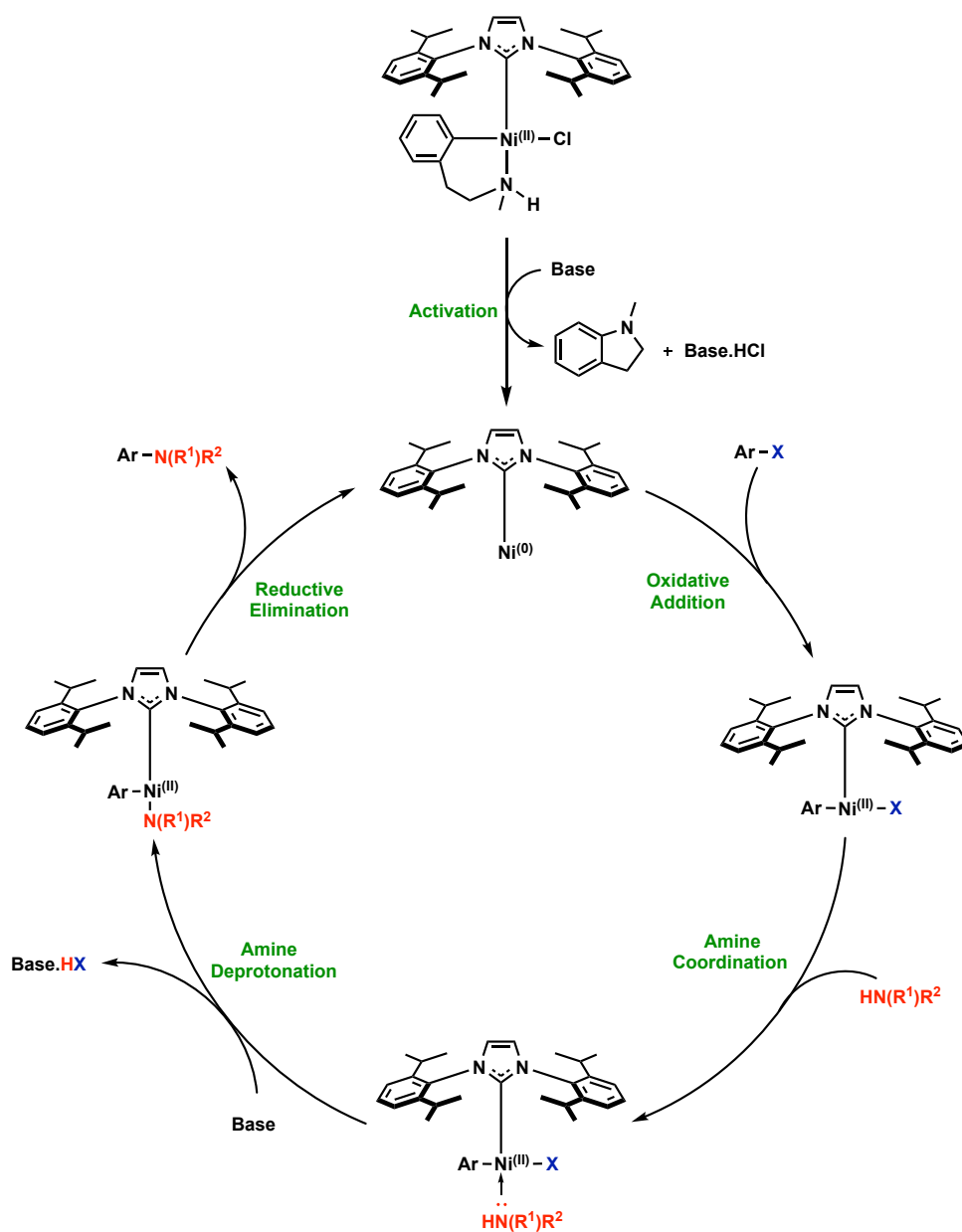


Figure 25. Proposed mechanism for the Ni-NHC-catalyzed C-N cross-coupling reactions

The catalytic cycle begins with the activation of the NHC-Ni^{II} pre-catalyst via a reductive elimination process in the presence of base, generating the active NHC-Ni⁰ species. This is followed by oxidative addition of the aryl halide, in which the carbon-halide bond oxidatively adds into the Ni⁰ center, increasing the oxidation state of nickel from 0 to +2. Electron-poor and sterically unhindered aryl halides typically undergo this step most efficiently. However, given that

nickel is more electropositive than palladium (electronegativity: Ni = 1.9, Pd = 2.2),⁷ it readily undergoes oxidative addition even with electron-rich aryl halides. This behavior aligns well with our experimental findings, as shown in [Scheme 23](#) (green box).

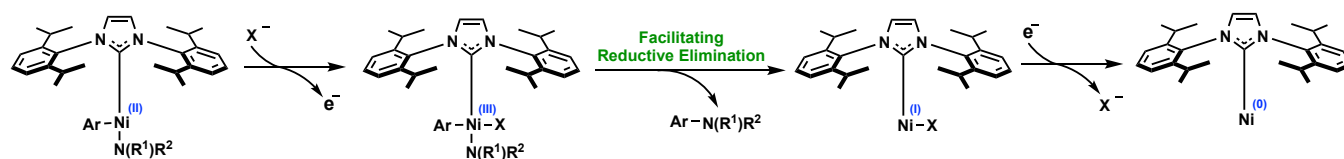
Following oxidative addition, the next key steps are amine coordination to the nickel center and subsequent deprotonation. Coordination is essential, as it lowers the amine's pKa, enabling efficient deprotonation under the reaction conditions. Both the nucleophilicity of the amine and the basicity of the base are critical in determining the success of this step. Electron-rich and sterically accessible amines generally display the highest reactivity, while electron-deficient or sterically hindered amines lead to reduced efficiency (see [Scheme 23](#), blue box). Thus, the electronic and steric properties of the amine coupling partner play a pivotal role in influencing the overall reaction outcome.

Finally, the catalytic cycle concludes with the reductive elimination step, which forms the desired C–N bond and regenerates the active NHC–Ni⁰ species for the next cycle. The rate of this step is significantly influenced by the electronic and steric properties of the coupling partners. Since nickel undergoes a formal reduction from Ni^{II} to Ni⁰ during the reductive elimination step, electron-rich amine partners and electron-poor aryl halides (oxidative addition partners) tend to accelerate the reaction (see [Scheme 23](#), blue box).

In 2017, Mark Stradiotto and co-workers conducted a comprehensive study using both experimental and computational methods to investigate the rate-determining step in Ni-catalyzed C–N cross-coupling reactions.^{148,150} Their findings revealed that, within the Ni⁰/Ni^{II} catalytic cycle, reductive elimination is the rate-limiting step ([Figure 12](#)). This is largely due to the inherently electropositive nature of nickel, which does not readily undergo reduction from Ni^{II} to Ni⁰ without an additional driving force. One effective strategy to promote this step is to render the

nickel center more electron-deficient, thereby enhancing its ability to accept electrons and undergo reduction.

As discussed in Chapter 1, nickel readily accesses multiple oxidation states, including 0, +1, +2, and +3.⁷ In this chapter, we take advantage of nickel's unique ability to access multiple oxidation states by exploring how the conversion of Ni^{II} to the more electron-deficient Ni^{III} species can be employed to accelerate the reductive elimination step, as illustrated in [Scheme 24](#).



Scheme 24. New strategy to use four different oxidation states of nickel (0, +1, +2, and +3) to facilitate the reductive elimination in C–N cross-coupling reactions catalyzed by Ni–NHC

3.2 Nickel-catalyzed amination reaction using “Photoredox Catalysis”

In 2016, Stephen L. Buchwald (MIT) and David W. C. MacMillan (Princeton University) published a landmark study in *Science*, introducing the use of photoredox catalysis in nickel-catalyzed amination reactions for the first time.¹⁷⁹ In this work, photoredox catalysis plays a pivotal mechanistic role in facilitating ligand-free C–N bond formation. The core function of the photoredox catalyst is to mediate single-electron transfer (SET) processes, enabling nickel to readily access multiple oxidation states throughout the catalytic cycle. The iridium-based photocatalyst (Ir^{III}) exhibits strong redox capabilities and, upon visible-light irradiation, is excited to a long-lived triplet state (*Ir^{III}) that serves as a powerful single-electron oxidant or reductant, as illustrated in [Figure 26](#).

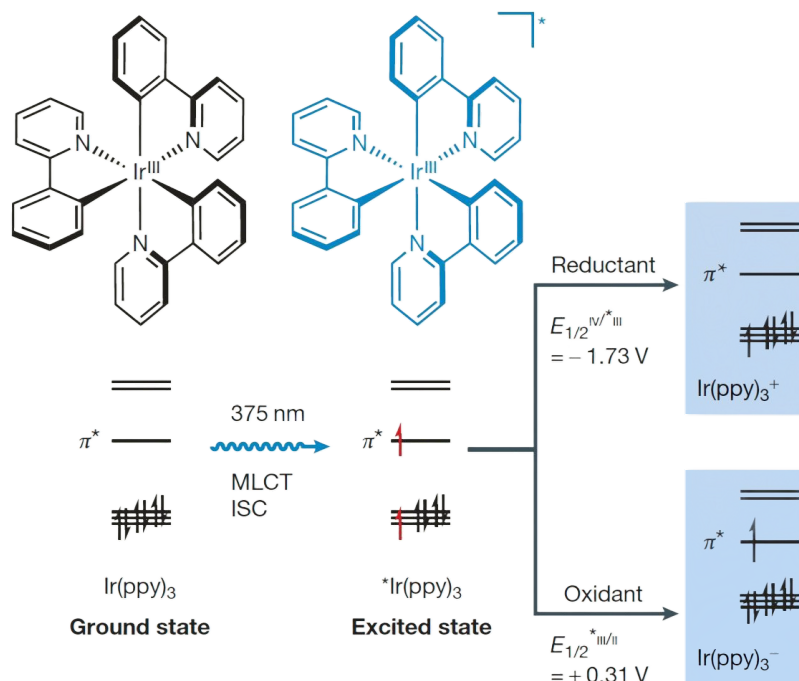


Figure 26. High-energy triplet state of iridium-based photocatalyst acting as a potent single-electron oxidant or reductant. Figure taken directly from Ref. [180] with permission.

Buchwald and MacMillan demonstrated that the excited state of the photocatalyst enables two critical steps in the nickel-catalyzed amination reaction. First, it facilitates the generation of the catalytically active Ni⁰ species from a simple Ni^{II} salt. In traditional nickel-catalyzed cross-coupling, air-sensitive Ni⁰ precursors such as Ni(cod)₂ are typically required. However, in this system, the *Ir^{III} photocatalyst, in conjunction with a mild organic reductant such as DABCO, promotes a reduction of Ni^{II} to Ni⁰, initiating the catalytic cycle under ambient conditions. This approach not only simplifies the transformation but also enhances operational practicality by eliminating the need for glovebox conditions or stoichiometric reducing agents. The resulting Ni⁰ complex then undergoes oxidative addition into an aryl bromide, forming a Ni^{II}–aryl–bromide intermediate as shown in Figure 27.

Next, the amine coupling partner coordinates to this Ni^{II} species and undergoes deprotonation by the base, forming a Ni^{II}–aryl–amido complex. This intermediate is known to be

thermodynamically uphill due to the stability of the square-planar Ni^{II} center, so it is unreactive toward reductive elimination. However, in this system, a second SET event is triggered by the interaction between the Ni^{II} –amido complex and the photoexcited $^*\text{Ir}^{\text{III}}$ species. This electron transfer oxidizes Ni^{II} to Ni^{III} , forming a highly reactive Ni^{III} –aryl–amido species. This oxidation dramatically changes the electronic environment of the metal center, lowering the barrier for reductive elimination. The Ni^{III} intermediate rapidly undergoes reductive elimination, forging the desired C–N bond, yielding the arylamine product alongside a Ni^{I} –Br species.

To complete the cycle, the reduced Ir^{II} photocatalyst, generated during the oxidation step, transfers an electron back to the Ni^{I} species, regenerating the active Ni^0 catalyst and restoring the Ir^{III} photocatalyst to its ground state. This orchestrated electron exchange between the iridium and nickel species ensures that both catalytic cycles remain operational throughout the reaction.

This finding not only establishes the feasibility of ligand-free aryl amination under mild conditions but also offering a powerful and general strategy using photoredox catalysis in promoting reductive elimination in nickel-catalyzed C–N bond formation reactions.

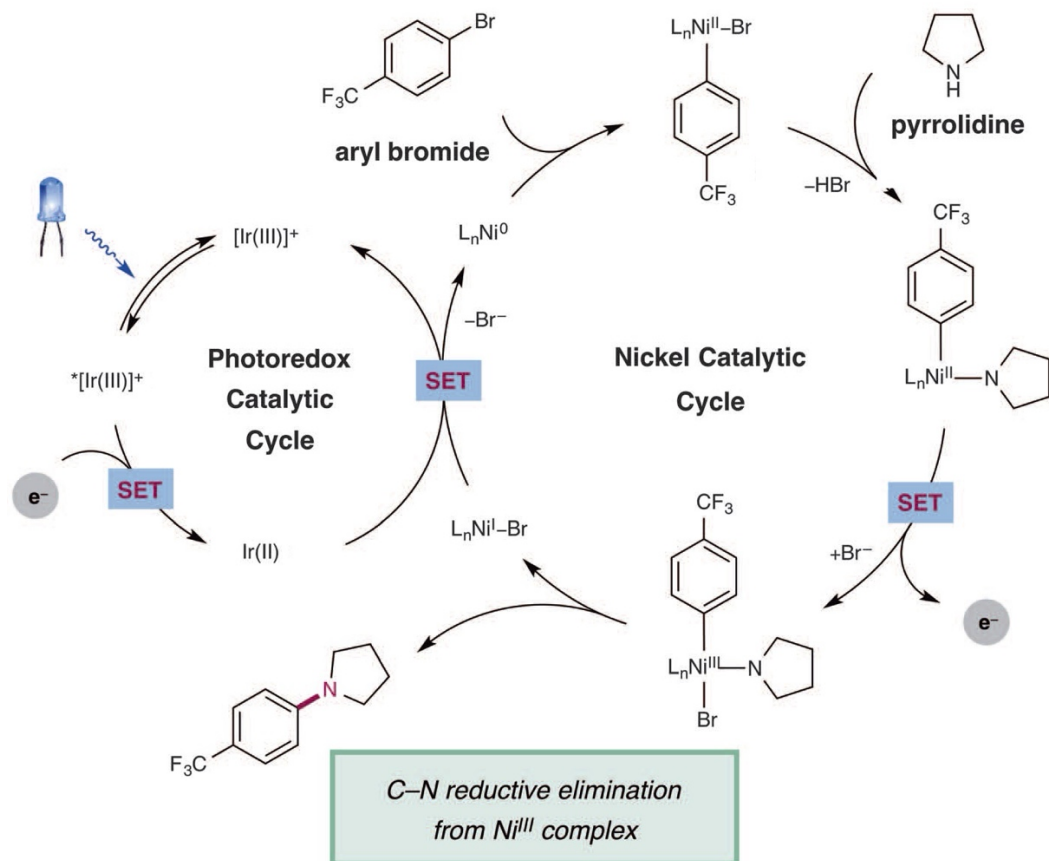


Figure 27. Proposed mechanism reported by Buchwald for the amination reaction using photoredox/nickel dual catalyst system. Figure taken directly from Ref. [179] with permission.

Building on the insights from Buchwald and MacMillan's work, we pursued C–N bond formation using a dual photoredox/nickel catalytic system. Our goal was to promote the challenging reductive elimination step by combining the bench-stable $\text{Ni}^{\text{II}}-\text{NHC}-\text{IPr}$ complex (**83**) with an Ir^{III} -based photoredox catalyst, thereby enhancing the overall efficiency of the C–N cross-coupling reaction.

3.3 Ni-NHC-catalyzed amination reaction using “Photoredox Catalysis”

The C–N bond-forming reaction selected as the case study to evaluate the catalytic activity of the Ni–NHC–IPr precatalyst (**83**) in combination with photoredox catalysis was the same previously studied by Buchwald using ligand-free nickel [Figure 28](#). To this end, we employed 5 mol% of nickel catalyst in combination with 0.02 mol% of the Ir^{III} photocatalyst (**145**) in the coupling of 4-bromobenzotrifluoride (**146**) as the electrophile and pyrrolidine (**147**) as the nucleophile, using 1,4-diazabicyclo[2.2.2]octane (DABCO) as the base in dimethylacetamide (DMA). The reaction was conducted under blue LED irradiation (Kessil-PR160L, 456 nm), as illustrated in [Figure 29](#). The temperature during the reaction ranged from 35°C to 40°C, which resulted from the heat generated by the LED light around the reaction vial over the 16-hour reaction period.

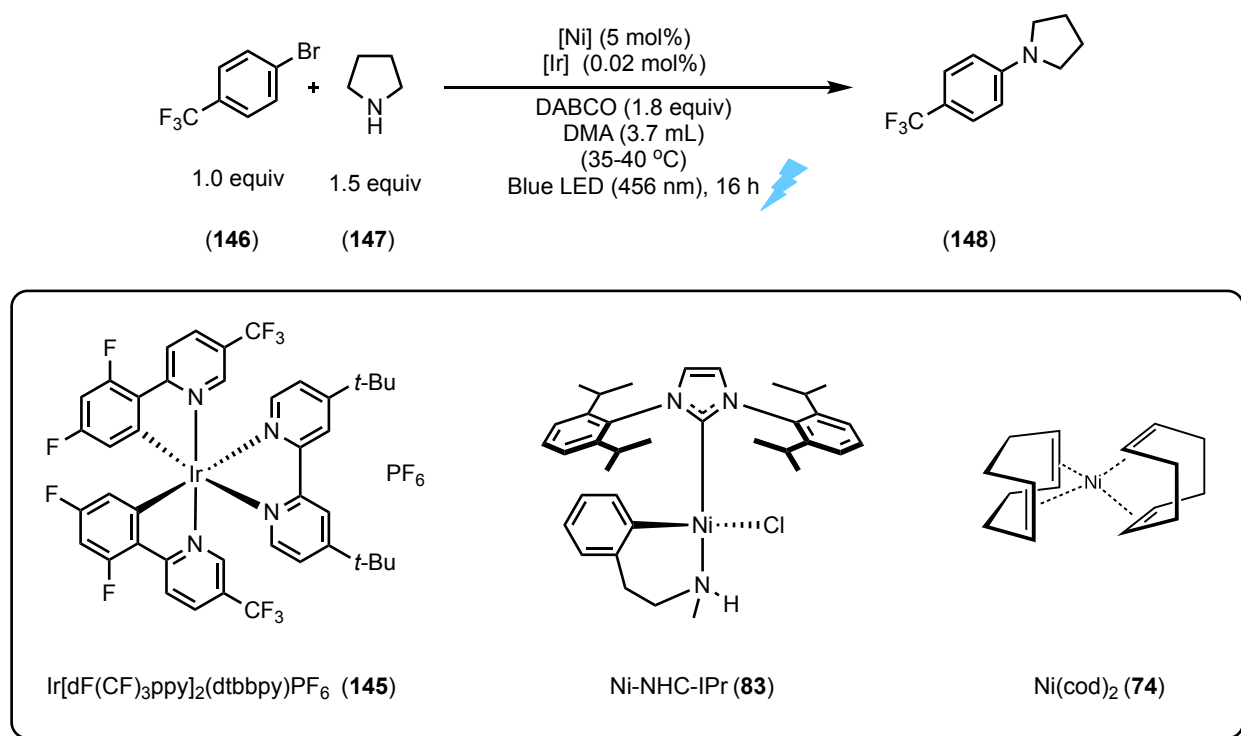


Figure 28. [Ni]/[Ir] as dual photoredox catalytic system for C–N bond formation reaction

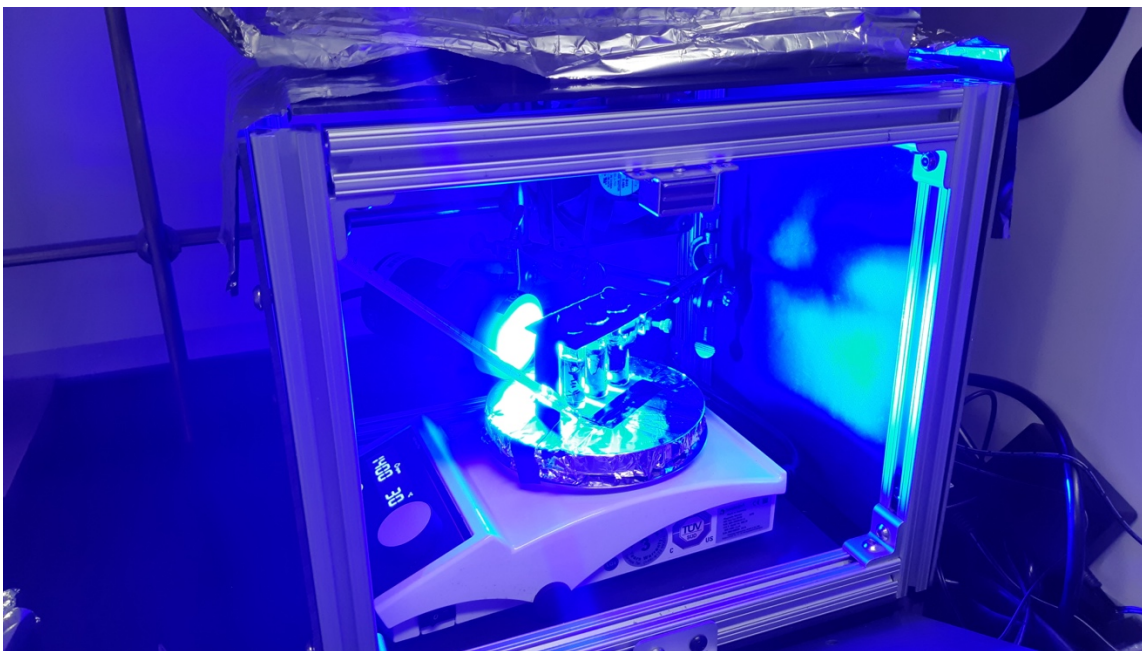


Figure 29. Photoredox reaction set-up for [Ni]/[Ir]-catalyzed C–N bond formation reaction

For the initial study, $\text{Ni}(\text{cod})_2$ (**74**) and Ir^{III} photocatalyst (**145**) were selected as the dual catalytic system for C–N bond formation. Table 11 presents a series of control experiments designed to evaluate the necessity of each reaction component in this photoredox/nickel dual catalytic system. Under standard conditions (entry 1), where all components are present, the reaction affords a high isolated yield of 93%, confirming the efficiency of the full catalytic system. When the light source is omitted (entry 2), the yield drops dramatically to 9%, demonstrating that visible-light irradiation is critical for activating the photocatalyst and enabling the reaction. Similarly, omission of the Ir-photocatalyst alone (entry 3) leads to a sharp decrease in yield to 27%, indicating that while a minor background reaction may occur, the photocatalyst is essential for optimal performance. The combination of removing both the Ir-photocatalyst and light (entry 4) further reduces the yield to 7%, reinforcing that photoredox activation is crucial. When nickel is omitted (entry 5), no product formation is observed (0% yield), confirming that nickel is indispensable for catalysis. Omitting nickel, Ir- photocatalyst, and light simultaneously (entry 6) also results in no reaction, as expected.

Finally, when DABCO, the sacrificial reductant and base, is excluded (entry 7), the yield decreases to 58%, highlighting its important but not absolutely critical role: some product formation still occurs, but efficiency is significantly compromised. Overall, these results clearly demonstrate that light, the Ir photocatalyst, the nickel source, and DABCO are all essential to achieve high yields in this photoredox-mediated nickel-catalyzed C–N coupling system.

Table 11. Control experiments to evaluate the necessity of each reaction component in the ligand-free nickel (**74**)/iridium (**145**) dual catalytic system for C–N bond formation

Entry	Reaction component omitted	% Isolated Yield (148)
1	None	93
2	Light	9
3	[Ir]	27
4	[Ir] and Light	7
5	[Ni]	0
6	[Ni] and [Ir] and Light	0
7	DABCO	58

Reagents and conditions: 4-bromobenzotrifluoride (1.0 mmol), pyrrolidine (1.5 mmol), DABCO (1.8 mmol), Ni(cod)₂ (5 mol%), [Ir] photocatalyst (0.02 mol%), DMA (3.7 mL), blue LED (456 nm), 35–40 °C, 16 h.

Table 12 presents a series of control experiments investigating the role of each component in the photoredox/nickel dual catalytic system, this time using the well-defined Ni–NHC–IPr complex (**83**) instead of the ligand-free Ni(cod)₂ precursor (**74**). Under standard reaction conditions, using Ni–NHC–IPr (**83**) and the Ir-photocatalyst (**145**), the C–N bond formation between 4-bromobenzotrifluoride (**146**) and pyrrolidine (**147**) proceeds with an outstanding 99% isolated yield (entry 1). When light is omitted (entry 2) or when the iridium photocatalyst is removed (entry

3), the yield drops dramatically to 2% and 6%, respectively, confirming again that visible-light irradiation and photoredox catalysis are crucial to initiate and drive the catalytic cycle. In the absence of both the iridium and light (entry 4), the yield remains negligible (2%), highlighting that no significant thermal background reactivity is taking place. Omission of the nickel catalyst (entry 5) or removal of both the nickel, iridium catalyst, and light (entry 6) leads to complete suppression of product formation (0% yield), underscoring the necessity of the Ni–NHC–IPr complex for catalysis. Interestingly, when DABCO is excluded (entry 7), the yield drops to 68%, showing a notable decrease compared to the full system, although some product formation still occurs similar to observations in the ligand-free system.

Table 12. Control experiments to evaluate the necessity of each reaction component in the Ni–NHC–IPr (**83**)/iridium (**145**) dual catalytic system for C–N bond formation

Fc1ccc(Br)cc1 (**146**) + C1CCNC1 (**147**) $\xrightarrow[\text{DABCO, DMA, (35-40 }^\circ\text{C), Blue LED (456 nm), 16 h}]{\text{Ni-NHC-IPr (83), [Ir] (145)}}$ Fc1ccc(NC1CCCN1)cc1 (**148**)

Entry	Reaction component omitted	% Isolated Yield (148)
1	None	99
2	Light	2
3	[Ir]	6
4	[Ir] and Light	2
5	[Ni]	0
6	[Ni] and [Ir] and Light	0
7	DABCO	68

Reagents and conditions: 4-bromobenzotrifluoride (1.0 mmol), pyrrolidine (1.5 mmol), DABCO (1.8 mmol), Ni–NHC–IPr (5 mol%), [Ir] photocatalyst (0.02 mol%), DMA (3.7 mL), blue LED (456 nm), 35–40 °C, 16 h.

The data presented in Table 11 and 12 clearly highlight the essential role of the iridium photocatalyst in enhancing the catalytic activity of nickel systems by promoting reductive

elimination. By mediating the transition of nickel from Ni^{II} to Ni^{III}, the photoredox catalyst directly facilitates the key C–N bond-forming step, thereby significantly boosting the efficiency and overall effectiveness of the nickel-catalyzed coupling reaction.

3.3.1 Catalyst activation screening

Screening the reaction time provides valuable insights into both the induction period—the time required for activation of the nickel precatalyst and the iridium photocatalyst—and the overall reaction rate. The reaction involves the coupling of 4-bromobenzotrifluoride and pyrrolidine in the presence of DABCO as the base and DMA as the solvent. As shown in [Figure 30](#), the reaction progresses rapidly during the initial hours. After 2 hours, a 20% yield is achieved, and by 3 hours, a significant yield of 65% is obtained, indicating meaningful activation of both the nickel precatalyst and the iridium photocatalyst. The reaction approaches near-complete conversion by 6 hours, reaching its maximum isolated yield. Extending the reaction time to 24 hours does not lead to any substantial further increase in yield, confirming that the reaction effectively reaches completion within approximately 6 hours. This kinetic profile highlights the rapid activation and high efficiency of the Ni–NHC–IPr catalytic system under photoredox conditions, enabling efficient C–N bond formation within a relatively short reaction time.

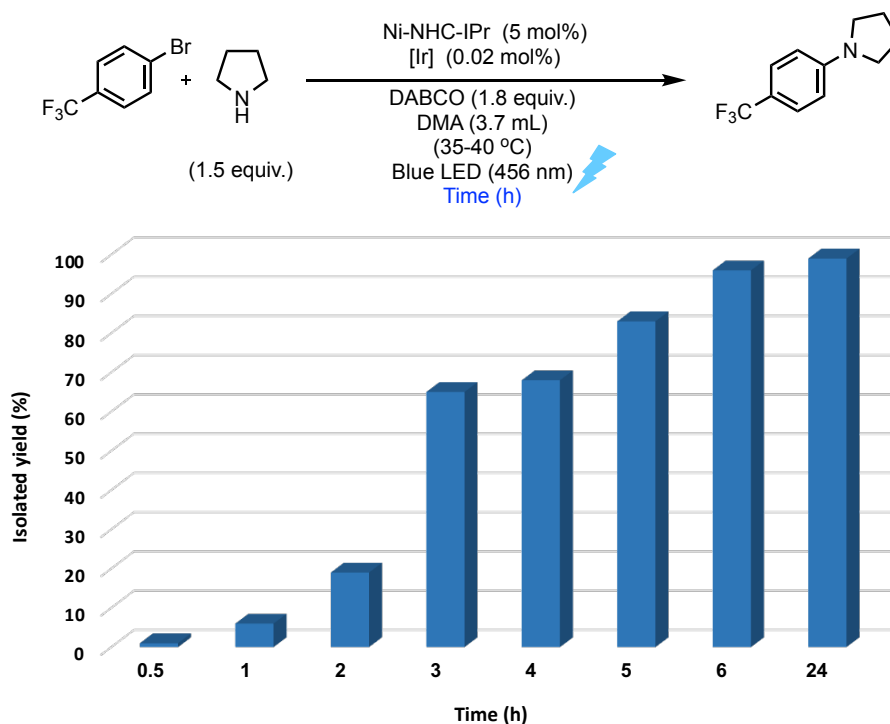


Figure 30. Catalyst activation screening

3.3.2 Catalyst deactivation screening

In order to evaluate the stability of the catalysts within the reaction mixture, a C–N bond formation between 4-bromobenzotrifluoride and pyrrolidine was performed under optimized conditions. After allowing the reaction to proceed for 6 hours, during which the reaction reached completion, the process was temporarily stopped. At this point, an additional 1.0 mmol of 4-bromobenzotrifluoride, 1.5 mmol of pyrrolidine, and 1.8 mmol of DABCO were added directly to the reaction mixture, and the reaction was allowed to continue under the same conditions for another 6 hours. If the [Ni]/[Ir] dual catalytic system remained active after the initial 6-hour period, further product formation should occur during the second reaction phase, theoretically doubling the amount of product.

As shown in [Figure 31](#), the reaction performed efficiently in both cycles. In the first 6 hours, the expected product mass was 215.22 mg, and the actual isolated mass was 191.9 mg, corresponding

to an 89% yield. After the second addition and an additional 6 hours of reaction, the cumulative expected product mass was 430.44 mg, and the isolated product mass was 391.7 mg, corresponding to a 91% overall yield. These results clearly demonstrate that the Ni–NHC–IPr (**77**)/Ir^{III} (**132**) dual catalytic system remains highly stable and active under the reaction conditions, showing no significant deactivation over the 12-hour total reaction period.

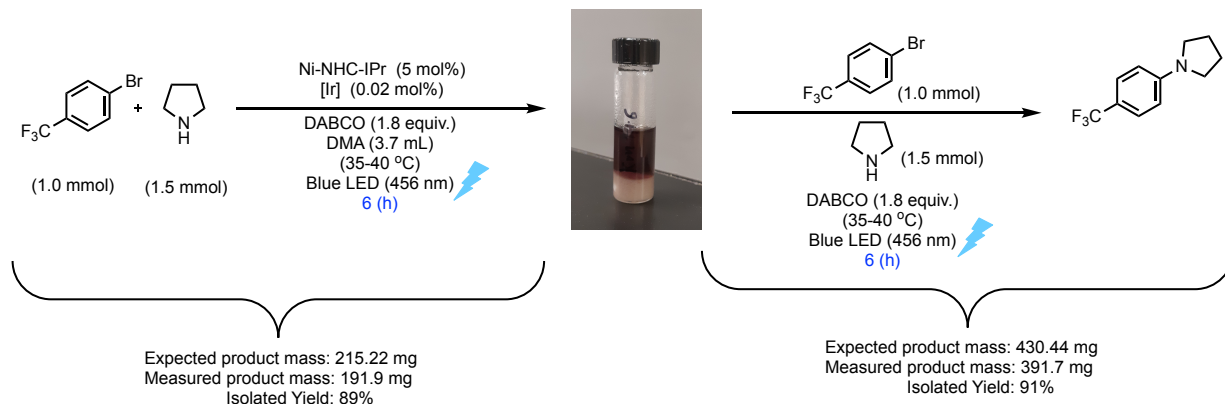
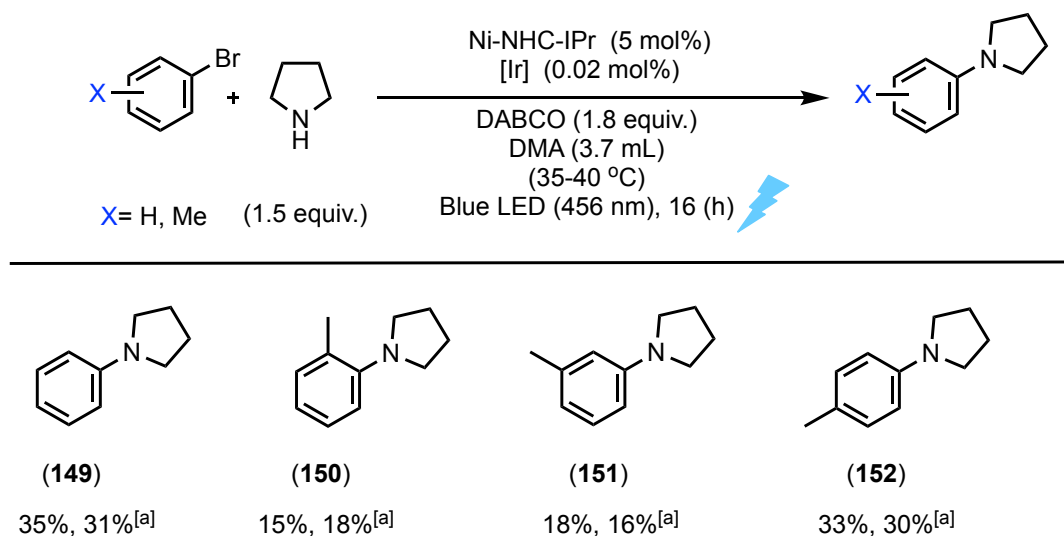


Figure 31. Catalyst deactivation screening

3.3.3 Study the electrophile scope

It is evident that 4-bromobenzotrifluoride acts as a highly reactive electrophilic coupling partner. To reduce its electron-deficient character, we decided to replace it with less activated electrophiles, specifically bromobenzene and bromotoluene (ortho-, meta-, and para-substituted), while keeping all other reaction conditions and reagents unchanged. As shown in [Scheme 25](#), the *N*-arylation of pyrrolidine with bromobenzene afforded only a 35% yield of the desired product (**149**). Furthermore, reactions using ortho-, meta-, and para-bromotoluene gave unsatisfactory yields (**150–152**), and no significant improvements were observed even when the reactions were performed in THF.



Scheme 25. Using bromobenzene, and bromotoluene (ortho, meta and para) in *N*-arylation of pyrrolidine, [a] in THF

3.3.4 Optimization studies

Several studies were conducted to improve the catalytic performance of the Ni–NHC–IPr (**83**)/Ir^{III} (**145**) dual catalytic system in the *N*-arylation of pyrrolidine. Key parameters, including catalyst loading and base selection, were experimentally examined to identify the optimal conditions for maximum efficiency. For this purpose, the *N*-arylation of pyrrolidine with bromobenzene was selected as the model reaction. To determine the ideal catalyst loading, different amounts of the Ni–NHC–IPr (**83**) precatalyst were tested while keeping all other reaction parameters constant. As shown in Figure 32, using 2 mol% of Ni–NHC–IPr (**83**) delivered the highest yield. Reducing the catalyst loading to 1 mol% led to a significant decrease in the yield of the coupling product (**149**), whereas increasing the loading to 5 mol% offered no substantial improvement. Further increasing the nickel loading to 10 mol% resulted in a slight decline in yield, suggesting that excessive catalyst amounts may negatively impact the reaction outcome.

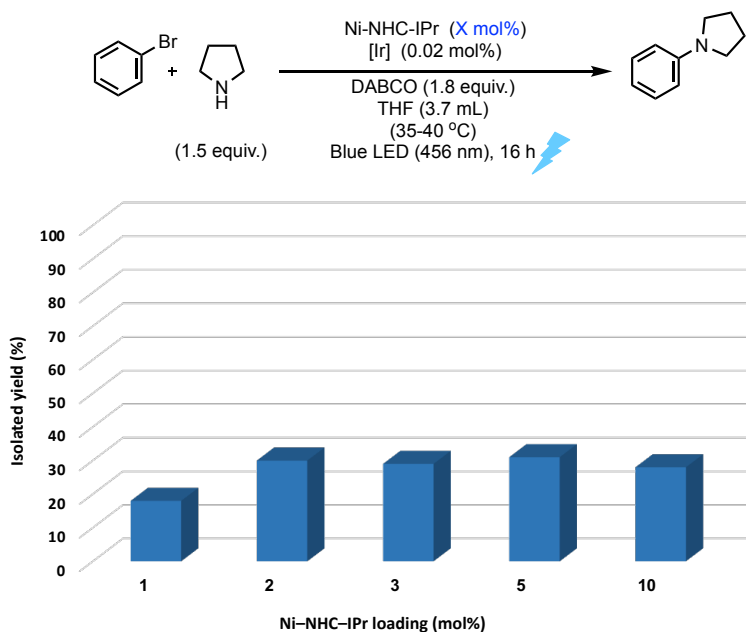


Figure 32. Optimization studies – Ni-NHC-IPr (**83**) loading

In the next study, the amount of Ir^{III} photocatalyst was increased from 0.02 mol% to 0.2 mol%, while the loading of Ni-NHC-IPr (**83**) and all other reaction parameters were kept constant. As shown in Figure 33, increasing the amount of iridium photocatalyst resulted in a dramatic decrease in the conversion to the coupled product.

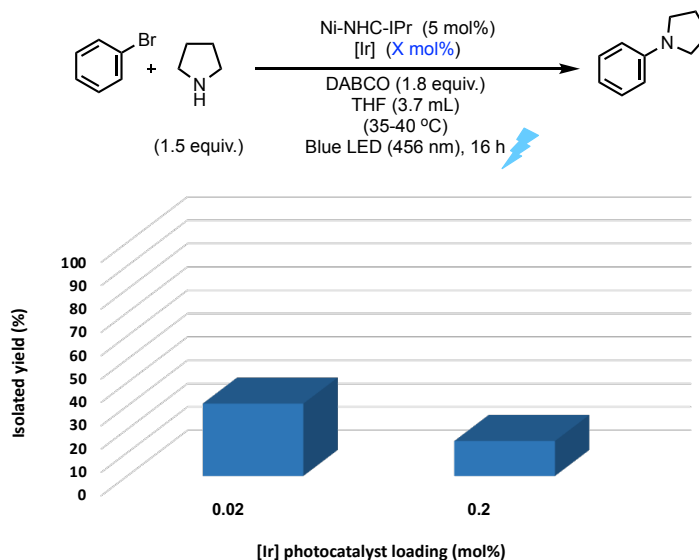


Figure 33. Optimization studies – [Ir] photocatalyst (**145**) loading

Additionally, various bases, including KO t Bu, NaO t Bu, LiO i Pr, and NaBHT, were evaluated to investigate the effect of the base on the *N*-arylation of pyrrolidine with bromobenzene and ortho-bromobenzene. As shown in Figure 34, DABCO proved to be the most effective base, delivering significantly higher yields than KO t Bu, NaO t Bu, LiO i Pr, and NaBHT.

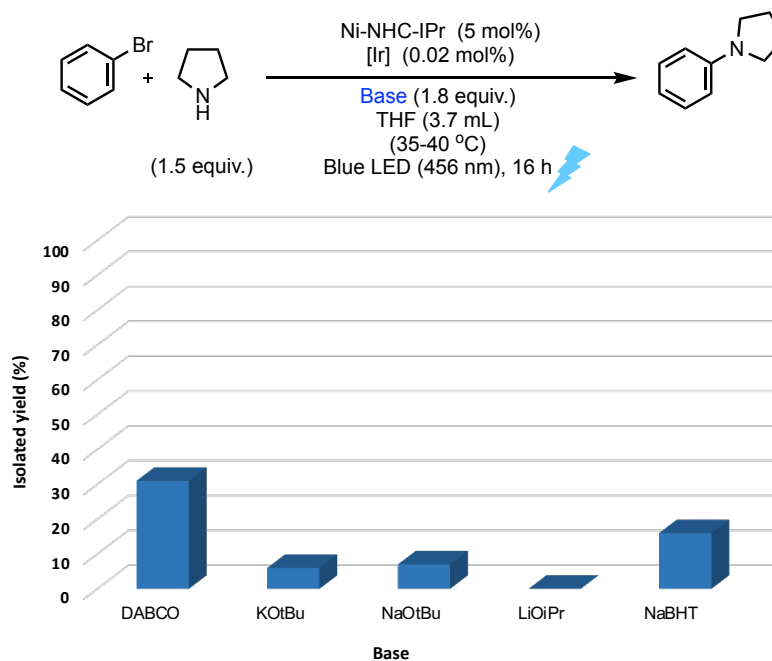
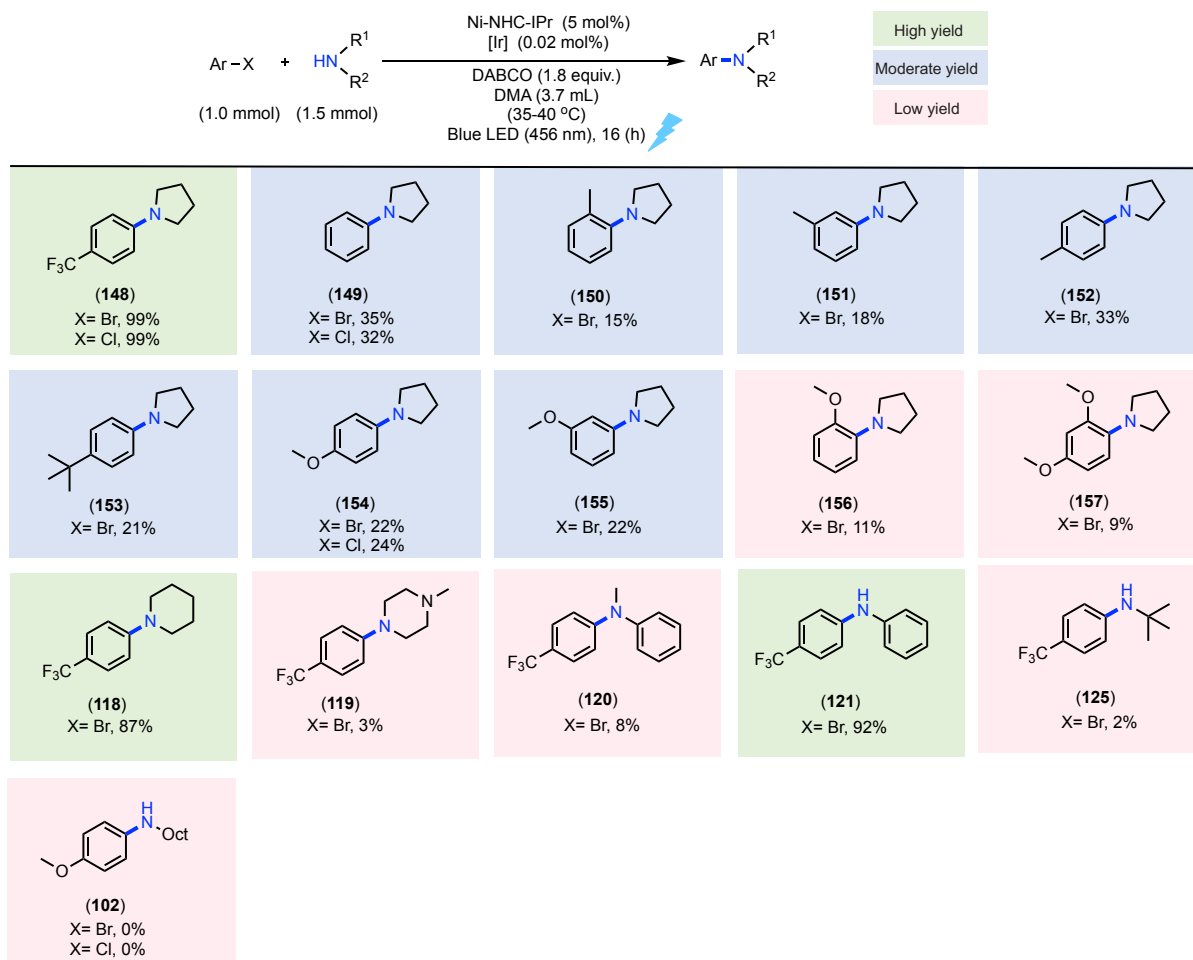


Figure 34. Optimization studies – base screening

3.3.5 Expand the substrate scope

To expand the substrate scope of the C–N bond formation catalyzed by the nickel/photoredox dual catalytic system (Ni–NHC–IPr (**83**)/Ir^{III} (**145**)), a variety of aryl bromides and amine derivatives including electronically deactivated and sterically hindered substrates were evaluated. As shown in Scheme 26, high yields of the coupled products were obtained with electronically activated and/or sterically less hindered substrates (green boxes). In contrast, moderate to low yields were observed when using electronically deactivated and/or sterically hindered substrates (blue and pink boxes), highlighting the sensitivity of the catalytic system to electronic and steric effects.



Scheme 26. Substrate scope of C–N bond formation catalyzed by nickel/photoredox dual catalytic system; yields are average of two runs.

One parameter that can significantly influence the yield of the amination reaction is temperature. However, under batch conditions, it is challenging to control the reaction temperature while maintaining consistent blue LED light exposure. Using conventional heating methods such as oil or water baths alters the light intensity as it passes through these media, potentially affecting the efficiency of photoredox activation. A practical solution to this limitation is to conduct the reaction under flow conditions, where both temperature and light intensity can be precisely controlled. As shown in the [Figure 35](#), a commercially available photoreactor, previously employed by Buchwald and MacMillan for [Ni]/[Ir]-catalyzed amination in flow, enables such control. Therefore, for

future studies, it would be valuable to collaborate with a chemical engineering team to design and build a similar photoreactor and conduct this reaction under flow conditions. This approach would allow precise temperature control to systematically investigate its effect on the [Ni]/[Ir]-catalyzed amination reaction.



Figure 35. UV-150 photochemical reactor developed by Vapourtec company

3.4 Conclusion

This chapter presents a comprehensive investigation into the use of a dual photoredox/nickel catalytic system employing the air-stable Ni–NHC–IPr precatalyst (**83**) in combination with an Ir^{III} photocatalyst (**145**) for C–N bond formation. Inspired by the pioneering work of Buchwald and MacMillan, this study demonstrates that photoredox catalysis plays a critical role in promoting reductive elimination step through single-electron oxidation of Ni^{II} to Ni^{III}. This strategic oxidation enables efficient C–N bond formation under mild condition that would otherwise be inaccessible via traditional Ni^{II}-based pathways.

Through systematic investigations, we demonstrated that the Ni–NHC–IPr/Ir^{III} system exhibits catalytic activity, rapid activation, and excellent operational stability under mild conditions. Time-

course and deactivation studies confirmed that the system remains active over extended reaction periods without notable loss in performance, even over successive reaction cycles. Control experiments confirmed that light, the iridium photocatalyst, nickel, and DABCO are all essential for achieving high yields. While the system performs efficiently with electronically activated and sterically accessible substrates, its reactivity decreases notably toward more challenging coupling partners, such as electron-neutral or electron-rich aryl bromides and sterically hindered amines. Reaction optimization showed that catalyst loading, and base selection are critical parameters. An optimal Ni–NHC–IPr loading of 2 mol% was identified, while DABCO emerged as the most effective base. Notably, increasing the Ir^{III} photocatalyst loading above 0.02 mol% led to reduced efficiency, suggesting that excessive oxidant concentration may disrupt the delicate redox balance of the dual catalytic cycle.

Although temperature is known to influence reaction performance, its effect could not be systematically evaluated due to technical limitations inherent to batch photoreactors, where external heating interferes with light penetration. The use of continuous flow photoreactors, which allow for precise control of both light intensity and temperature, presents a promising direction for future exploration.

In summary, this study establishes the Ni–NHC–IPr/Ir^{III} system as a platform for visible-light-driven C–N bond formation. By emphasizing the interplay between redox control, ligand architecture, and catalyst stability, it provides key mechanistic insights into running amination reaction under mild conditions. These findings not only expand the understanding of dual photoredox/nickel catalysis but also lay a strong foundation for future development of more broadly applicable and sustainable nickel catalysts.

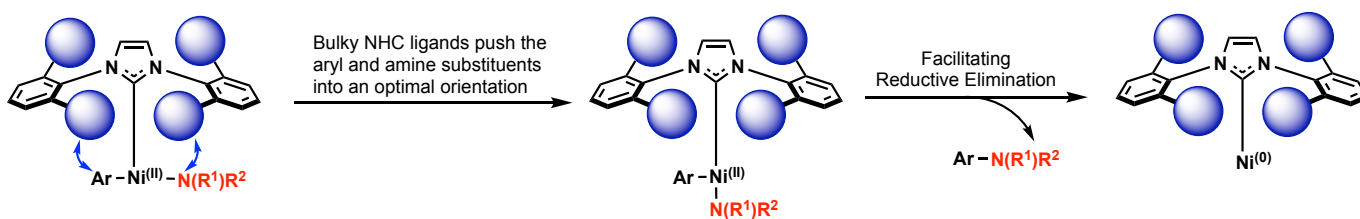
Chapter 4

4. Chapter 4: Enhancing reactivity and selectivity through ligand bulk: development of sterically demanding Ni–NHC precatalysts

4.1 Increasing the steric bulk of NHC ligand by extending the alkyl side chains

Despite the many advantages offered by the first-generation Ni–NHC precatalyst (complex **83**) developed by the Organ group, it exhibits limitations when applied to challenging C–N cross-coupling reactions. As discussed in Chapter 3, mechanistic studies of nickel-catalyzed C–N bond formation suggest that reductive elimination can serve as the rate-limiting step. The efficiency of this step is highly influenced by both the electronic and steric properties of the NHC ligand. Electronically, Ni^{II} does not readily undergo reductive elimination to form Ni⁰ without an additional driving force. In this context, photoredox catalysis plays a crucial role by promoting single-electron oxidation of Ni^{II} to Ni^{III}, thereby altering the electronic environment of the nickel center. This oxidation significantly lowers the activation barrier for reductive elimination, facilitating the efficient formation of the aryl–amine product.

It is now well established that the use of sterically bulky NHC ligands significantly enhances the rate of reductive elimination. This effect is likely due to the spatial constraints imposed by the bulky ligands, which push the aryl and amine substituents into an optimal orientation, facilitating effective orbital overlap for bond formation while relieving steric congestion around the metal center ([Scheme 27](#)).



Scheme 27. Increasing the steric bulk of NHC ligand facilitate the reductive elimination step

Therefore, to enhance the rate of reductive elimination, we strategically increased the steric bulk of the NHC ligand by extending the alkyl side chains on the imidazole ring. Specifically, the isopropyl substituents in complex (**83**) were replaced with isopentyl (**165**) and isoheptyl (**174**) groups, as illustrated in Figure 36.

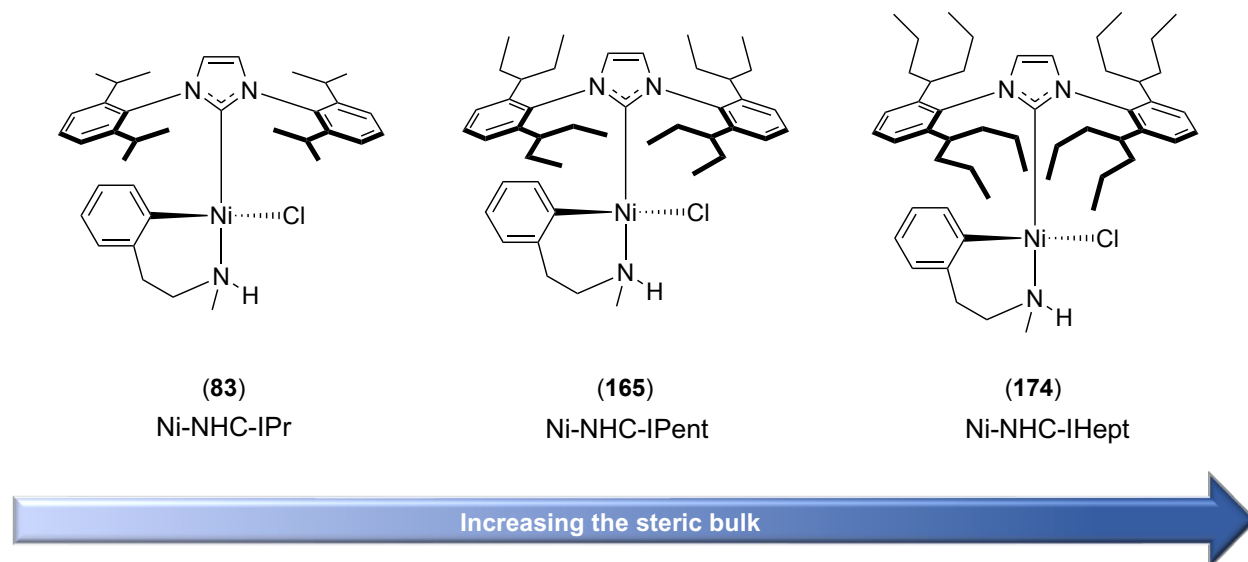
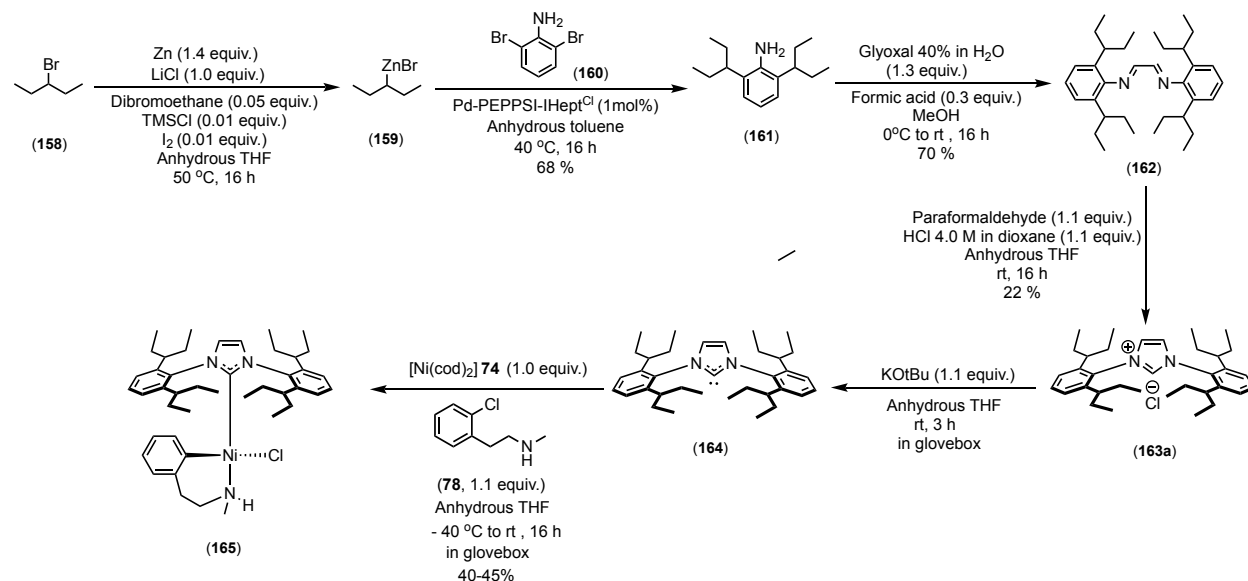


Figure 36. Increasing the steric bulk of NHC ligand from isopropyl (**83**) to isopentyl (**165**) and isoheptyl (**174**)

4.1.1 Synthesis and characterization of air-stable Ni–NHC–IPent and Ni–NHC–IHept precatalysts

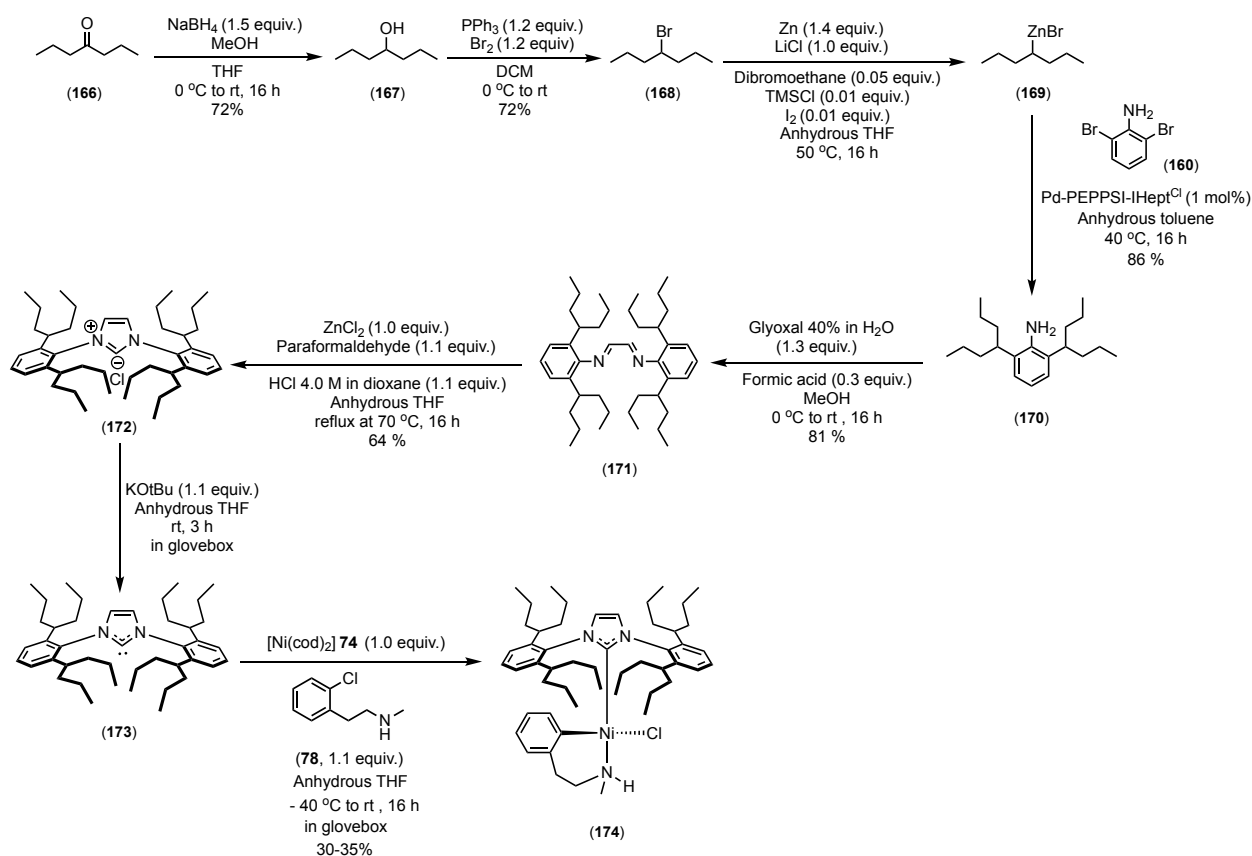
To synthesize the Ni–NHC–IPent (**165**) precatalyst, the corresponding NHC–IPent ligand (**163a**) was first prepared according to literature procedures.¹⁷³ As illustrated in [Scheme 28](#), the 3-pentylzinc bromide (**159**) was prepared from 3-bromopentane (**158**) and subjected to Negishi cross-coupling with 2,6-dibromoaniline (**160**) to afford 2,6-di(3-pentyl)aniline (**161**). Subsequent condensation yielded the bisimine intermediate (**162**) in quantitative yield. Cyclization of this intermediate furnished the IPent•HCl salt (**163a**) in high purity. In the final step, the free IPent carbene (**164**) was generated and ligated to the nickel precursor, together with the stabilizing ligand (**78**), to produce the air- and moisture-stable Ni(II)–NHC precatalyst (**165**).



Scheme 28. General procedure for synthesis of Ni–NHC–IPent (**165**) precatalyst

To synthesize the Ni–NHC–IHept (**174**) precatalyst, the corresponding NHC–IHept ligand (**172**) was first prepared according to literature procedures.¹⁷³ As illustrated in [Scheme 29](#), heptan-4-ol (**167**) was obtained by reduction of heptan-4-one (**166**), followed by bromination to afford 4-

bromoheptane (**168**). Reaction of 4-bromoheptane with zinc provided 4-heptylzinc bromide (**169**), which then underwent Negishi cross-coupling with 2,6-dibromoaniline (**160**) to yield 2,6-di(4-heptyl)aniline (**170**). Subsequent condensation furnished the bisimine intermediate (**171**) in quantitative yield, which upon cyclization afforded the IHept•HCl salt (**172**) in high purity. In the final step, the free IHept carbene (**173**) was generated and ligated to the nickel precursor, along with the stabilizing ligand (**78**), to produce the air- and moisture-stable Ni(II)–NHC precatalyst **174**.



Scheme 29. General procedure for synthesis of Ni–NHC–IHept (**174**) precatalyst

The resulting Ni–NHC–IPent (**165**) and Ni–NHC–IHept (**174**) complexes are fully characterized using NMR spectroscopy, high-resolution mass spectrometry (HRMS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and single-crystal X-ray diffraction. Structural

analysis confirmed the successful formation of the Ni–NHC bond and clearly showed coordination of the bulky NHC ligands to the nickel center, along with the steric influence of the extended *N*-alkyl side chains on the metal’s coordination environment (Figure 37).

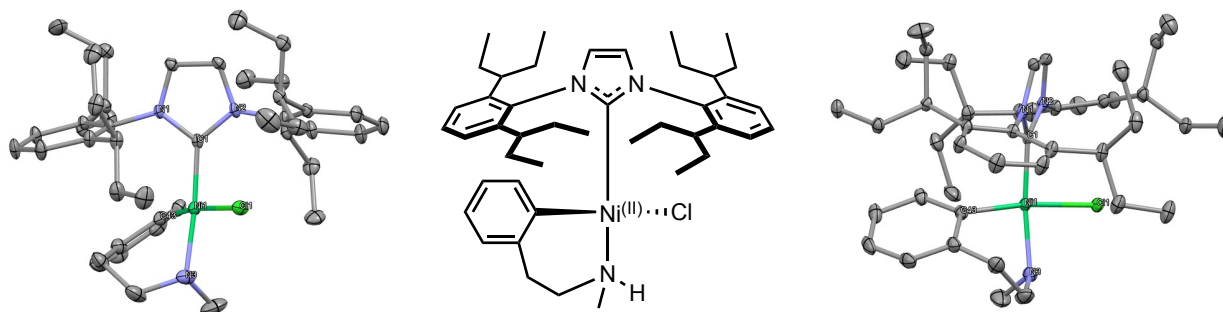


Figure 37. SC-XRD analysis of the Ni–NHC–IPent (**165**) complex from two different view

4.1.2 Synthesis and characterization of air-stable Ni–NHC–IPr*^{OMe} precatalyst

To further explore the impact of steric and electronic tuning on catalyst performance, we investigated a class of expanded NHC ligands known as IPr* derivatives. Unlike the conventional IPr ligand, which features isopropyl groups on the *N*-aryl substituents to confer steric bulk, IPr* introduces a more rigid and extended architecture by incorporating diphenylmethyl groups in the ortho positions of the aryl rings. In the IPr*^{OMe} variant, methoxy groups are introduced at the para positions, further fine-tuning both electronic and solubility properties.

This structural modification leads to an NHC ligand with a high percent buried volume (%V_{Bur}), 39.8 for IPr*^{OMe} versus 33.6 for IPr,¹⁸¹ but with enhanced rigidity and more uniform steric distribution around the metal center (Figure 38).

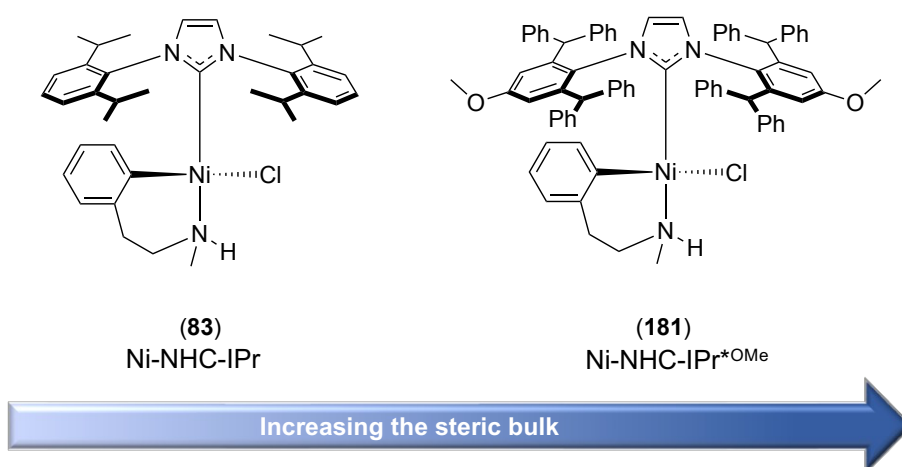
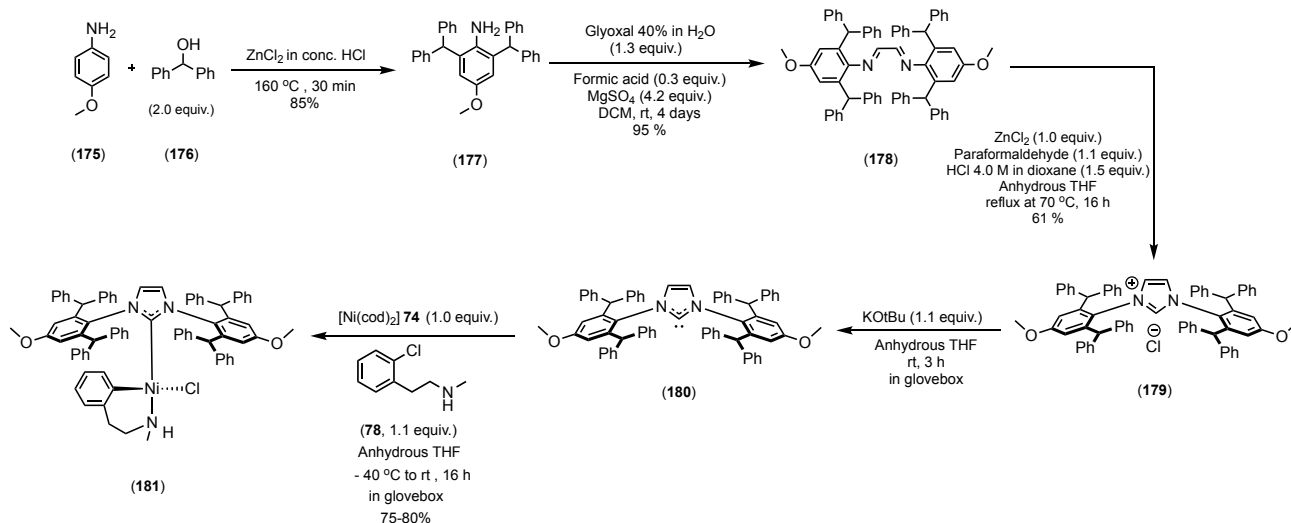


Figure 38. Increasing the steric bulk of NHC ligand from isopropyl (**83**) to diphenylmethyl (**181**)

To synthesize the Ni-NHC-IPr*OMe precatalyst (**181**), the corresponding NHC-IPr*OMe ligand (**179**) was first prepared according to literature procedures.¹⁸¹ As illustrated in [Scheme 30](#), *p*-anisidine (**175**) was reacted with diphenylmethanol (**176**) to yield 2,6-bis(diphenylmethyl)-4-methoxyaniline (**177**). Subsequent condensation gave bisimine intermediate **178** in quantitative yield, which underwent cyclization to afford the IPr*OMe•HCl salt (**179**) in high purity. In the final step, the free IPr*OMe carbene (**180**) was generated and ligated to the nickel precursor, together with the stabilizing ligand (**78**), to furnish the air- and moisture-stable Ni(II)-NHC precatalyst (**181**).



Scheme 30. General procedure for synthesis Ni-NHC-IPr*OMe (**181**) precatalyst

The resulting Ni–NHC–IPr*^{OMe} (**181**) complex is fully characterized using NMR spectroscopy, HRMS-ESI, ICP-AES, and SC-XRD. As shown in Figure 39, structural analysis confirmed the successful coordination of the NHC–IPr*^{OMe} ligand to the nickel center.

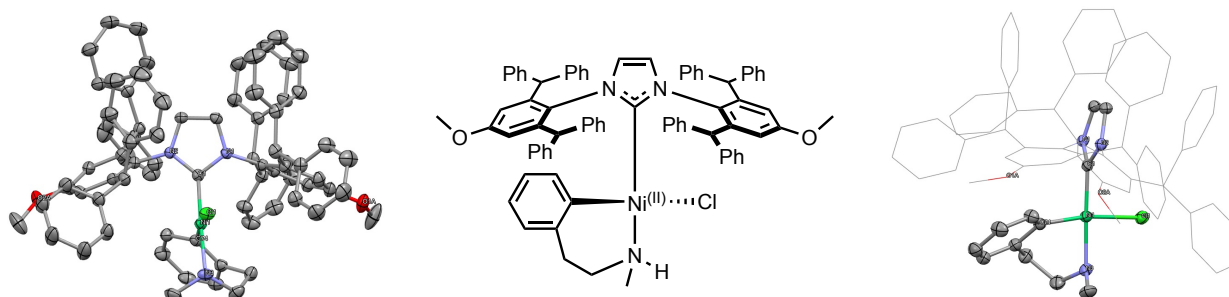


Figure 39. SC-XRD analysis of the Ni–NHC–IPr*^{OMe} (**181**) complex from two different view

4.1.3 Evaluation of bulky Ni–NHC pr-catalysts in *N*-arylation of morpholine

In order to quickly evaluate the catalytic activity of the Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**) and Ni–NHC–IPr*^{OMe} (**181**) in C–N bond formation, we selected the *N*-arylation of morpholine as the case study reaction. To this end, we employed 5 mol% of the nickel precatalyst in C–N bond formation using 4-chloroanisole as the electrophile, and morpholine as the nucleophile. As illustrated in Table 13, similar to Ni–NHC–IPr (**83**), the Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**), and Ni–NHC–IPr*^{OMe} (**181**) precatalysts, show high activity in *N*-arylation of morpholine, and highlight the critical role of the NHC ligand in enhancing the catalytic efficiency of nickel in such transformations.

Table 13. Evaluation of Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**) and Ni–NHC–IPr*^{OMe} (**181**) precatalysts in N-arylation of morpholine

COc1ccc(Cl)cc1 (**89**) + C1CCNCC1 (**103**) $\xrightarrow[60\text{ }^{\circ}\text{C, 16 h}]{\text{[Ni] (5 mol\%), NaOtBu, THF}}$ COc1ccc(NC2CCOCC2)cc1 (**99**)

Entry	Catalyst	% Isolated Yield (99) ^[a]
1	No catalyst	NR
2	Ni(cod) ₂	Trace
3	Ni–NHC–IPr (83)	92
4	Ni–NHC–IPent (165)	92
5	Ni–NHC–IHept (174)	94
6	Ni–NHC–IPr* ^{OMe} (181)	95

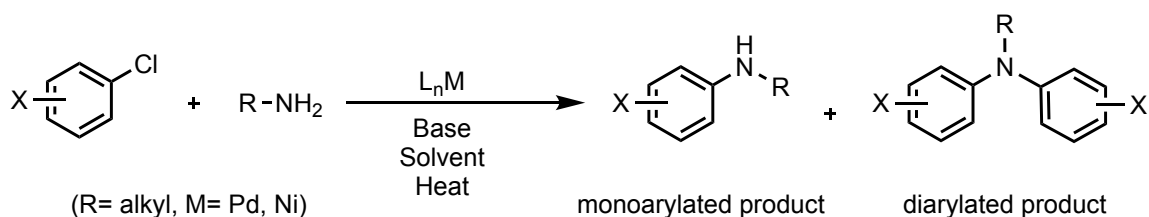
Reagents and conditions: 4-chlorobenzene (0.5 mmol, 1 equiv.), morpholine (1.2 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), THF (1 ml), 60 °C, 16 h. [a] Average of two runs

Having confirmed the catalytic efficiency of these bench-stable Ni–NHC precatalysts in the *N*-arylation of morpholine, we turned our attention to more challenging C–N bond formation reactions. As illustrated in [Scheme 23](#) (Section 2.7), one particularly challenging transformation is the monoarylation of primary alkyl amines, such as octylamine, with electronically rich aryl halides like 4-chloroanisole. Under standard conditions, Ni–NHC–IPr (**83**) failed to catalyze this reaction, affording 0% yield of the desired product (**102**). In this chapter, we conduct an in-depth investigation of this transformation, with a focus on how increasing the steric bulk of the NHC ligand can enhance both the reactivity and selectivity of nickel catalysts in this class of reactions.

4.1.4 Evaluation of bulky Ni–NHC pr-catalysts in monoarylation of primary alkyl amines

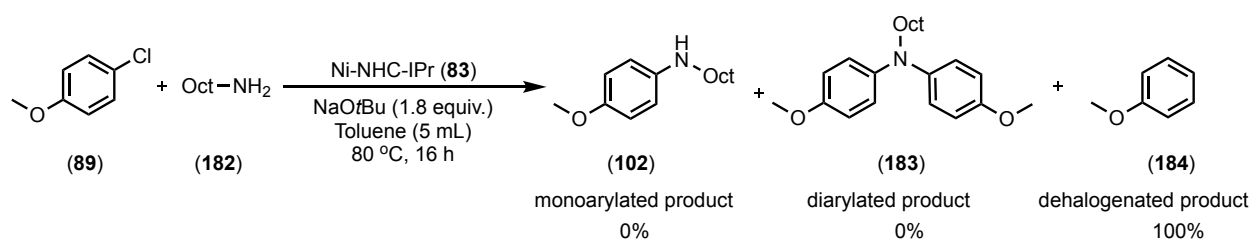
The difficulty of selective monoarylation of primary amines arises from the inherent tendency of primary amines to undergo both mono- and diarylation, resulting in a mixture of secondary and tertiary anilines ([Scheme 31](#)). Such mixtures not only complicate product purification but also

diminish the overall efficiency of the reaction by reducing the yield of the desired monoarylated product. The selectivity between mono- and diarylation is fundamentally governed by the catalyst's ability to discriminate between the starting primary amine and the secondary aniline formed in the initial catalytic cycle. In many cases, the catalyst fails to effectively differentiate between these two nucleophiles, leading to overarylation. To address this issue, considerable effort has been devoted to tuning the steric and electronic properties of ancillary ligands in order to favor selective binding and activation of the primary amine while disfavoring further coupling of the secondary amine. This ligand-based strategy has proven essential for enhancing monoarylation selectivity and improving the practicality of such transformations in synthetic applications.¹⁸²



Scheme 31. Monoarylation of primary alkyl amines

Building upon these insights, our work focused on developing a nickel-based catalytic system capable of achieving selective monoarylation of primary amines using well-defined Ni-NHC precatalysts. As an initial study, we employed 5 mol% of Ni-NHC-IPr (**83**) in the coupling of octylamine with 4-chloroanisole, an electron-rich aryl chloride known to be challenging in cross-coupling chemistry. As shown in [Scheme 32](#), complete consumption of the starting material (**89**) was observed; however, no monoarylated product (**102**) or diarylated product (**183**) was detected. Instead, the reaction exclusively produced the dehalogenated byproduct (**184**), indicating that the catalyst was unable to facilitate C–N bond formation under these conditions.



Scheme 32. Evaluation of Ni-NHC-IPr (**83**) in selective monoarylation of octylamine

As illustrated in Figure 40, the mechanism of Ni-NHC-catalyzed C–N bond formation between 4-chloroanisole (**89**) and octylamine (**182**) begins with the activation of the bench-stable Ni^{II}-NHC precatalyst (**83**). Following activation and oxidative addition of the aryl chloride, amine binding and deprotonation steps lead to the formation of intermediate (**iv**), a key Ni^{II}-amido-aryl complex poised for reductive elimination. However, instead of undergoing productive C–N bond formation, this intermediate primarily follows a competing β -hydride elimination pathway.

The β -hydride elimination occurs due to the presence of β -hydrogens on the alkyl chain adjacent to the coordinated amine. In this process, the nickel center abstracts a β -hydrogen from the bound octyl group, forming a hydrido-alkyl Ni^{II} species (**v**) and releasing imine by-product **185**. Subsequent reductive elimination of this complex then yields the dehalogenated (reduced) side product (**184**), which was observed as the major product in our experimental study.

These observations suggest that the barrier to reductive elimination for the desired C–N coupling is significantly higher than that of β -hydride elimination under the given conditions. As a result, the reaction pathway is diverted toward formation of the undesired dehalogenated product. This mechanistic insight highlights a critical limitation in using Ni-NHC-IPr (**83**) for the monoarylation of primary amines and underscores the need for catalyst systems that can more effectively suppress β -hydride elimination and favor productive C–N bond formation.

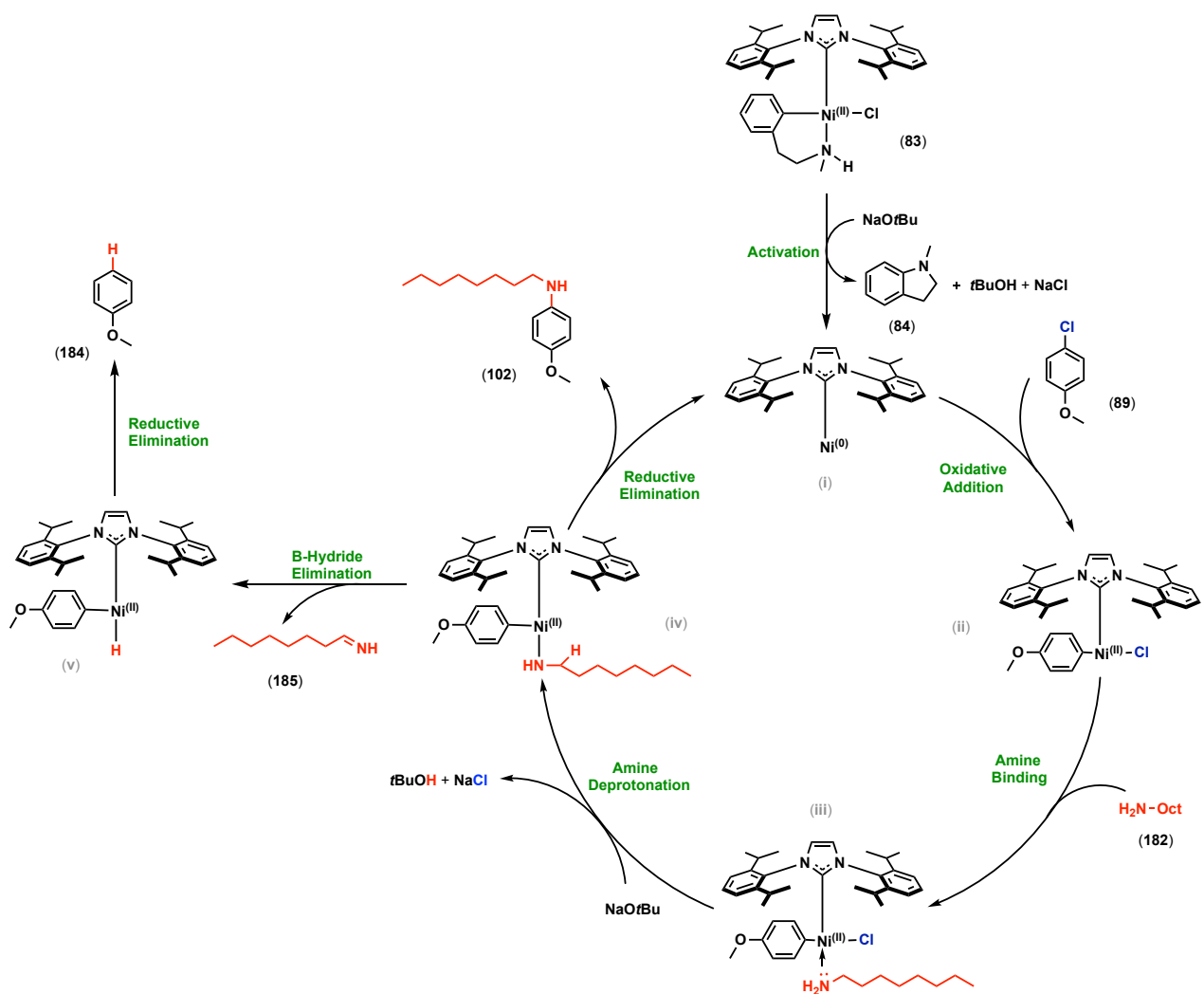


Figure 40. Proposed mechanism for the Ni–NHC-catalyzed monoarylation of octylamine

Recognizing that steric control plays a critical role in suppressing β -hydride elimination and promoting productive C–N bond formation, we investigated the effect of ligand bulk by employing Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**) and Ni–NHC–IPr*OMe (**181**) as catalysts. These sterically demanding complexes were evaluated in the coupling of octylamine with 4-chloroanisole, as summarized in Table 14 (entry 2 and 3). We observed that increasing the steric bulk of the NHC ligand could enhanced the rate of reductive elimination. This improvement is attributed to the spatial constraints imposed by the bulky ligands, which force the aryl and amine substituents into an optimal geometry, facilitating effective orbital overlap for bond formation.

These results demonstrate that sterically demanding Ni–NHC complexes represent a promising strategy for promoting reductive elimination over β -hydride elimination, thereby enabling selective C–N bond formation with primary amines.

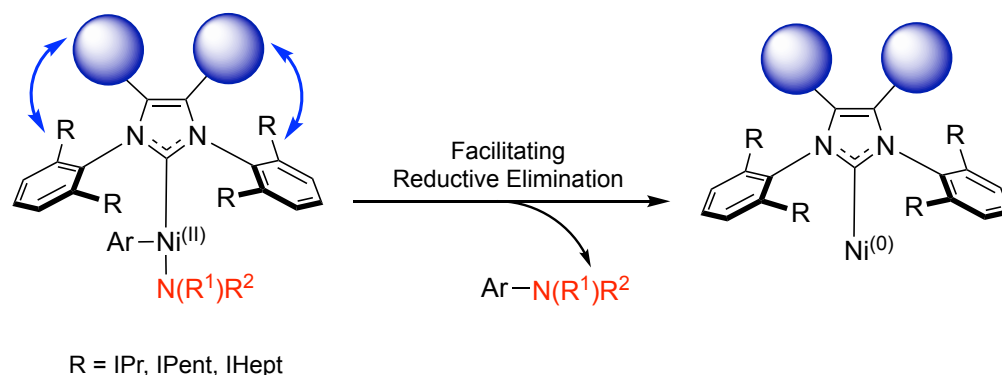
Table 14. Evaluation of Ni–NHC–IPr (**83**), Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**) and Ni–NHC–IPr*OMe (**181**) precatalysts in monoarylation of octylamine ^[a]

Entry	Catalyst	% Isolated Yield (102)	% Isolated Yield (183)	% Conversion to (184) ^[b]
1	Ni–NHC–IPr (83)	0	0	100
2	Ni–NHC–IPent (165)	10	0	remaining
3	Ni–NHC–IHept (174)	14	0	remaining
4	Ni–NHC–IPr*OMe (181)	0	0	remaining

Reagents and conditions: 4-chloroanisole (0.5 mmol, 1 equiv.), octylamine (1.1 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), Toluene (5 mL), 80 °C, 16 h. [a] Complete consumption of 4-chloroanisole (**89**) was observed in all three reactions. [b] Compound (**184**) could not be isolated due to its volatility; conversion was monitored by GC–MS.

4.2 Increasing the steric bulk of NHC ligand via backbone functionalization

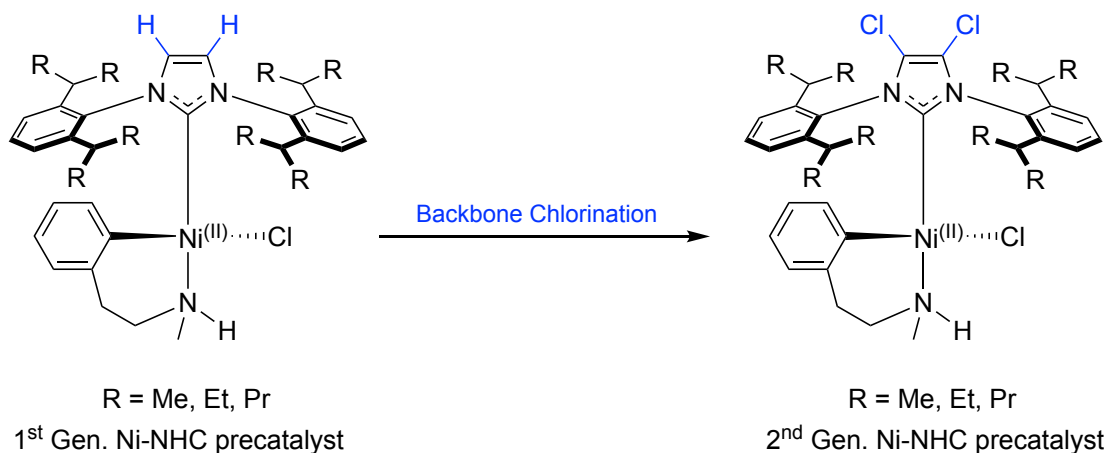
The steric bulk provided by Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**) and Ni–NHC–IPr*OMe (**181**) was insufficient to achieve high yields of the desired monoarylated product (**102**). To further increase the steric hindrance around the nickel center, we explored an alternative approach: functionalization of the NHC ligand backbone. As illustrated in Scheme 33, the introduction of substituents on the backbone forces the two *N*-substituted side arms to bend downward, effectively increasing the steric congestion around the metal center. This conformational change favors reductive elimination over β -hydride elimination, providing a new design element for enhancing selectivity in Ni-catalyzed C–N bond-forming reactions.



Scheme 33. Functionalization of the NHC ligand backbone

4.3 Backbone-chlorinated ligands: 2nd generation Ni–NHC precatalysts

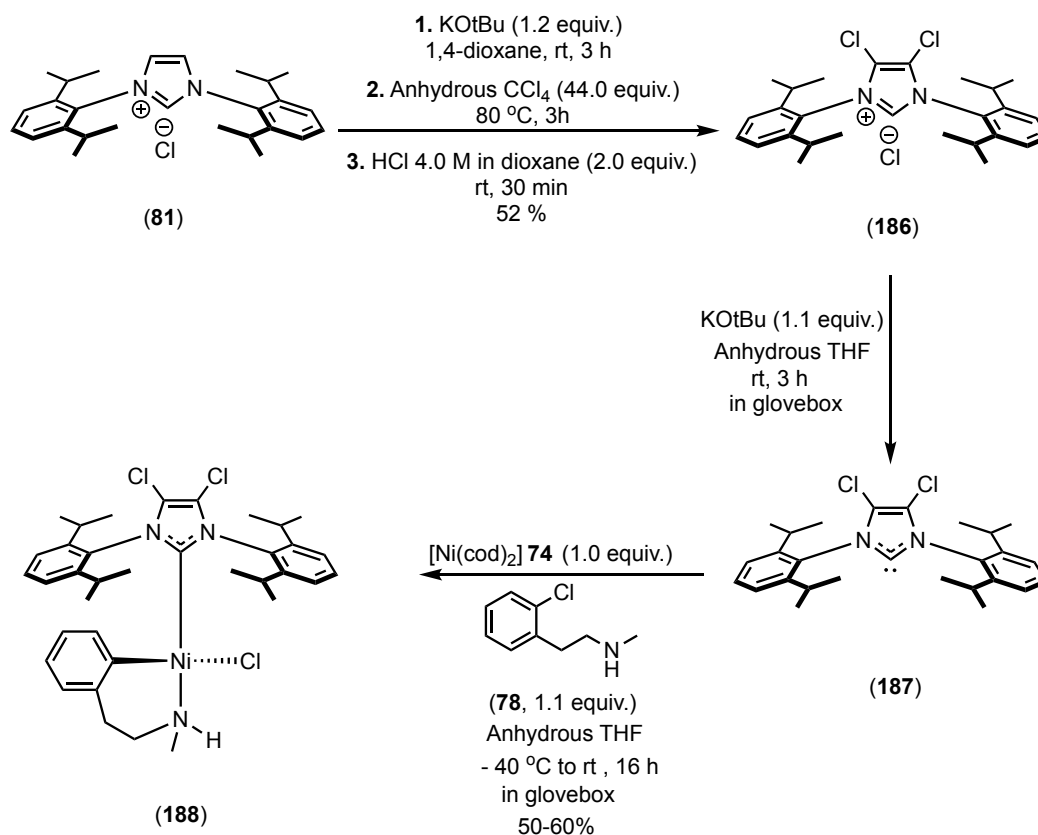
To test the preceding hypothesis, we synthesized the 2nd generation of Ni–NHC precatalysts incorporating chlorine substituents at the 4- and 5-positions of the imidazole backbone. This modification was designed to enhance both the steric and electronic environment around the nickel center. From a steric standpoint, the introduction of backbone chlorine atoms induces a downward tilt of the *N*-aryl side arms, effectively increasing steric congestion near the metal center. This conformational change restricts access to reactive intermediates and disfavors undesired β -hydride elimination pathways. More importantly, the electron-withdrawing nature of the chlorine substituents plays a critical electronic role by withdrawing electron density from the nickel center, rendering it more electron-deficient. This electronic modulation is particularly beneficial for facilitating reductive elimination, a step that often requires a high degree of metal electrophilicity. By lowering the energetic barrier for C–N bond formation, these electron-deficient Ni^{II} species are better poised to undergo productive reductive elimination over competing side reactions.



Scheme 34. Backbone chlorination: 2nd generation of air-stable Ni-NHC complexes

4.3.2 Synthesis and characterization of air-stable Ni-NHC-IPr^{Cl} precatalyst

To synthesize the Ni-NHC-IPr^{Cl} precatalyst (**188**), the corresponding NHC-IPr^{Cl} ligand (**186**) was first prepared according to literature procedures.¹⁷³ As illustrated in [Scheme 35](#), backbone chlorination of the IPr•HCl salt (**81**) was carried out using KO^{*t*}Bu/CCl₄ to afford the chlorinated NHC salt (**186**). The free IPr^{Cl} carbene (**187**) was then generated and ligated to the nickel precursor, along with the stabilizing ligand (**78**), to furnish the air- and moisture-stable Ni-NHC-IPr^{Cl} precatalyst **188**. The detailed experimental procedure is provided in Chapter 6.



Scheme 35. General procedure for synthesis Ni-NHC-IPr^{Cl} (**188**) precatalyst

The resulting Ni-NHC-IPr^{Cl} (**188**) complex was fully characterized using NMR spectroscopy, HRMS-ESI, ICP-AES, and SC-XRD. As shown in Figure 41, structural analysis confirmed the successful incorporation of chlorine atoms on the NHC backbone.

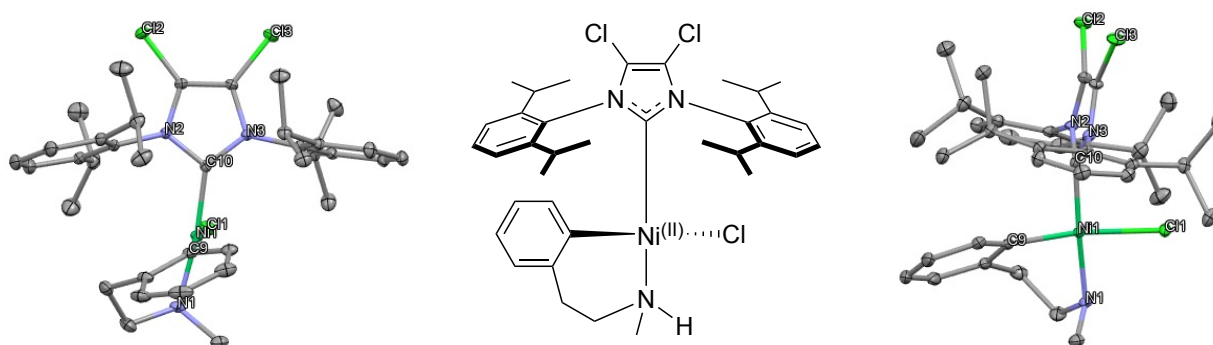


Figure 41. SC-XRD analysis of the Ni-NHC-IPr^{Cl} (**188**) complex from two different view

4.3.3 Evaluation of Ni–NHC–IPr^{Cl} in monoarylation of primary alkyl amines

To assess the effectiveness of this design, Ni–NHC–IPr^{Cl} (**188**) was compared with non-chlorinated analogues Ni–NHC–IPr (**83**), Ni–NHC–IPent (**165**), Ni–NHC–IHept (**174**) and Ni–NHC–IPr*^{OMe} (**181**) in the monoarylation of octylamine with 4-chloroanisole (Table 15). Ni–NHC–IPr and Ni–NHC–IPr*^{OMe} showed no catalytic activity, leading exclusively to the dehalogenated side product (**184**). The bulkier complexes Ni–NHC–IPent and Ni–NHC–IHept yielded 10% and 14% of the monoarylated product (**102**), respectively, with no diarylation observed in either case. Ultimately, Ni–NHC–IPr^{Cl} (**188**) afforded a notably improved 30% isolated yield of the desired monoarylated product. In all reactions, complete consumption of 4-chloroanisole (**89**) was observed, and the volatile reduction by-product (**184**) was detected by GC–MS. These results clearly demonstrate that backbone chlorination enhances both the reactivity and selectivity of Ni–NHC complexes, validating this dual steric–electronic ligand design as an effective strategy for improving catalytic outcomes and suppressing undesired pathways in challenging C–N bond-forming reactions involving primary amines.

Table 15. Catalytic comparison of Ni-NHC-IPr^{Cl} (**188**) with non-chlorinated analogues in the monoarylation of octylamine ^[a]

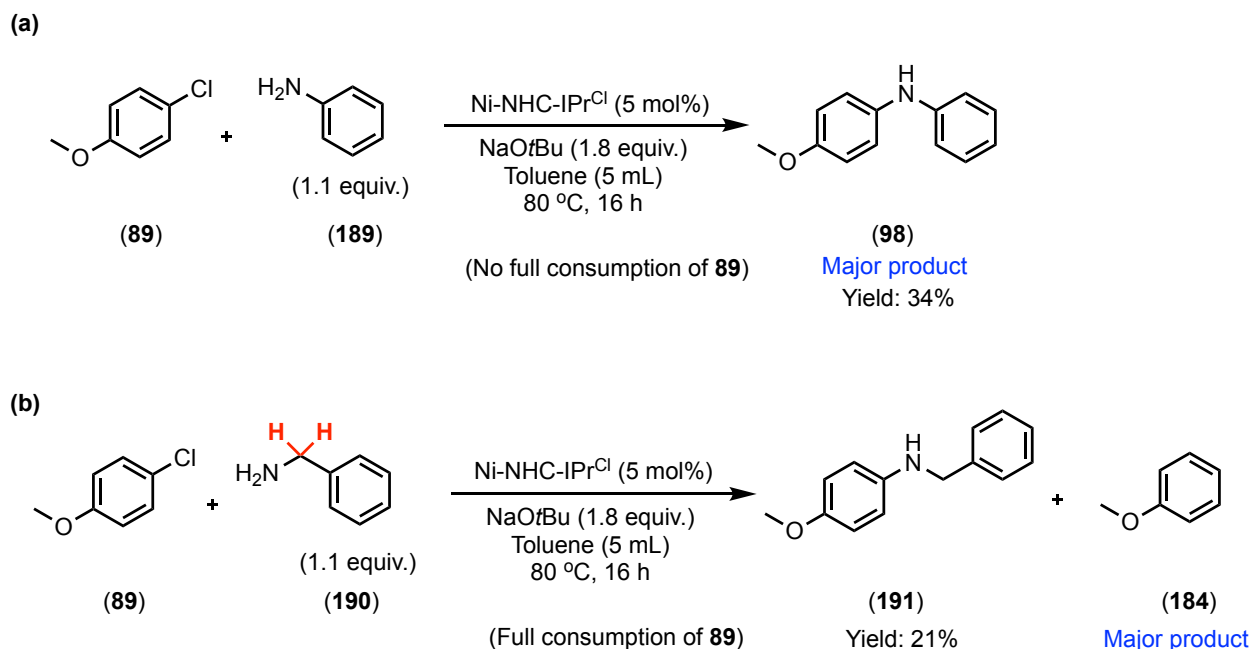
Reaction scheme: 4-chloroanisole (**89**) + Oct-NH₂ (**182**) $\xrightarrow[\text{Toluene (5 mL), 80 °C, 16 h}]{\text{[Ni] (5 mol%), NaOtBu (1.8 equiv.)}}$ monoarylated product (**102**) + diarylated product (**183**) + dehalogenated product (**184**)

Entry	Catalyst	% Isolated Yield (102)	% Isolated Yield (183)	% Conversion to (184) ^[b]
1	Ni-NHC-IPr (83)	0	0	100
2	Ni-NHC-IPent (165)	10	0	remaining
3	Ni-NHC-IHept (174)	14	0	remaining
4	Ni-NHC-IPr ^{*OMe} (181)	0	0	remaining
5	Ni-NHC-IPr ^{Cl} (188)	30	0	remaining

Reagents and conditions: 4-chlorobenzene (0.5 mmol, 1 equiv.), octylamine (1.1 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), Toluene (5 ml), 80 °C, 16 h. [a] Complete consumption of 4-chloroanisole (**89**) was observed in all three reactions. [b] Compound (**184**) could not be isolated due to its volatility; conversion was monitored by GC-MS.

4.3.4 Control experiment to confirm β-hydride elimination

To confirm the origin of the hydride involved in the β-hydride elimination pathway, aniline and benzylamine were employed as nucleophiles in C–N bond-forming reactions with 4-chloroanisole. Benzylamine possesses α-hydrogens that, upon coordination to nickel, enable β-hydride elimination, whereas aniline, lacking such hydrogens, is inherently unable to engage in this pathway. As shown in Scheme 36, no β-hydride elimination product was detected in the reaction with aniline, while the reaction with benzylamine yielded the β-hydride elimination product as the major product. These results clearly demonstrate that the hydride originates from the β-position of the amine substrate, supporting the proposed mechanistic pathway for the formation of the undesired by-product in this Ni-catalyzed C–N bond-forming reaction.



Scheme 36. Ni-catalyzed C–N bond-forming reaction using (a) aniline and (b) benzylamine as nucleophilic coupling partner

4.3.5 Ni–NHC–IPr *versus* Ni–NHC–IPr^{Cl}: A comparison study with different substrates

A comparative substrate scope study was conducted to evaluate the performance of Ni–NHC–IPr (**83**) and its backbone-chlorinated analogue Ni–NHC–IPr^{Cl} (**188**) in the arylation of various aryl chlorides with primary and secondary alkyl amines. As shown in Table 16, in most cases, the chlorinated catalyst delivered notably higher yields of the desired products, with improvements ranging from moderate (entries 1 and 9) to substantial (entries 2, 3, 5, and 7). In reactions where Ni–NHC–IPr showed no activity (entries 4, 6, and 8), Ni–NHC–IPr^{Cl} facilitated moderate product formation, highlighting the crucial role of backbone chlorination in expanding substrate compatibility and enhancing reactivity. These results demonstrate that the electronic and steric modifications introduced by backbone functionalization significantly improve the catalyst's performance in challenging C–N bond-forming reactions.

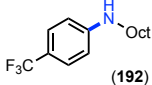
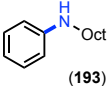
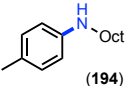
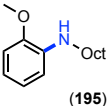
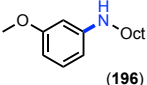
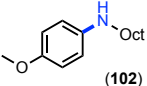
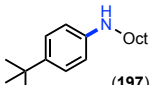
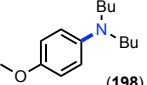
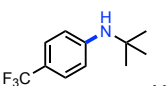
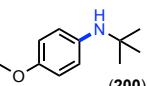
Table 16. Ni–NHC–IPr versus Ni–NHC–IPr^{Cl}: A comparison study with different substrates

$$\text{Ar-Cl} + \text{HN} \begin{matrix} \text{R}^1 \\ \text{R}^2 \end{matrix} \xrightarrow[\text{NaOtBu (1.8 equiv.)}]{[\text{Ni}] (5 \text{ mol\%})} \text{Ar-N} \begin{matrix} \text{R}^1 \\ \text{R}^2 \end{matrix}$$

(1.0 mmol) (1.1 mmol)

Toluene (5 mL)
80 °C, 16 h

R¹, R² = H or alkyl

		Ni–NHC–IPr (83)	Ni–NHC–IPr ^{Cl} (188)
Entry	Product	% Isolated Yield ^[a]	% Isolated Yield ^[a]
1	 (192)	47	94
2	 (193)	21	90
3	 (194)	15	88
4	 (195)	0	32
5	 (196)	15	84
6	 (102)	0 ^{[a][b][c][d]}	30
7	 (197)	6	75
8	 (198)	0	21
9	 (199) ^[e]	45	72
10	 (200)	0	0

Reagents and conditions: [a] Ar-Cl (0.5 mmol, 1 equiv.), amine (1.1 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), Toluene (5 ml), 80 °C, 16 h. [b] Toluene, 100 °C, 40 h. [c] 1,4-dioxane, 100 °C, 40 h. [d] using 5 mol% Ni(cod)₂. [e] No product was observed in the absence of [Ni] catalyst

4.3.6 Synthesis and characterization of air-stable Ni–NHC–IPent^{Cl} and Ni–NHC–IHept^{Cl} precatalysts

Encouraged by the enhanced reactivity and selectivity observed with Ni–NHC–IPr^{Cl} (**188**), we next turned our attention to backbone-chlorinated variants of more sterically demanding ligands: Ni–NHC–IPent^{Cl} (**203**) and Ni–NHC–IHept^{Cl} (**206**). These complexes were designed to integrate both the steric bulk introduced by extended N-substituted alkyl chains and the steric and electronic influence of chlorine atoms on the imidazole backbone. The combined steric and electronic tuning was expected to further suppress undesired β -hydride elimination and promote efficient reductive elimination, particularly in monoarylation of primary alkyl amines.

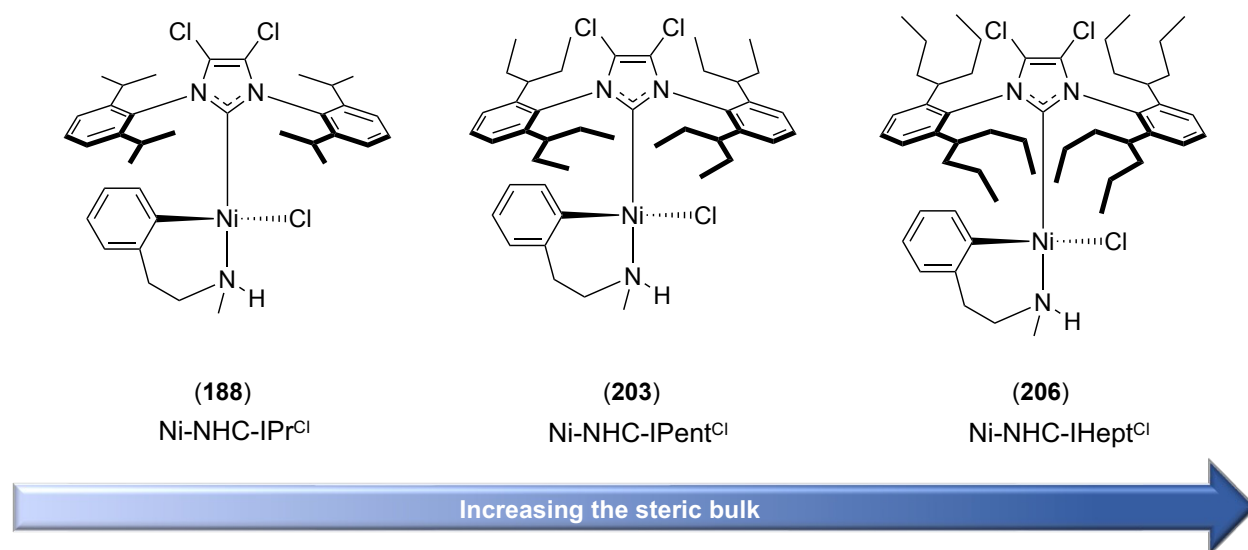
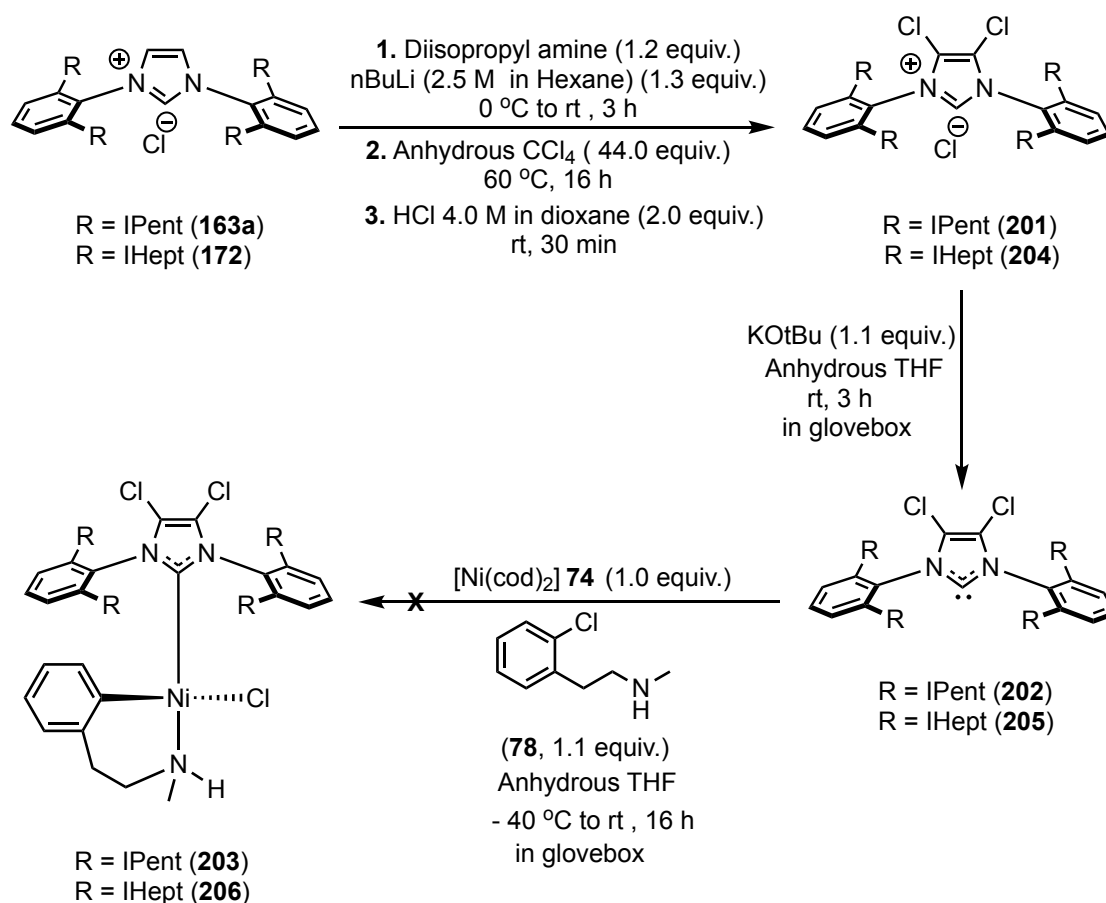


Figure 42. Increasing the steric bulk of chlorinated NHC ligand from chlorinated isopropyl (**188**) to chlorinated isopentyl (**203**) and isoheptyl (**206**)

To synthesize the Ni–NHC–IPent^{Cl} (**203**) and Ni–NHC–IHept^{Cl} (**206**) precatalysts, the corresponding chlorinated NHC ligands, NHC–IPent^{Cl} (**201**) and NHC–IHept^{Cl} (**204**), were first prepared according to literature procedures.¹⁷³ As illustrated in [Scheme 37](#), backbone chlorination of the IPent•HCl (**163a**) and IHept•HCl (**172**) salts was performed using LDA/CCl₄ to afford the respective chlorinated NHC salts (**201** and **204**). The resulting salts were then converted to the free

carbenes IPent^{Cl} (**202**) and IHept^{Cl} (**205**), which were subjected to ligation with the nickel precursor. However, initial attempts to synthesize the Ni–NHC–IPent^{Cl} and Ni–NHC–IHept^{Cl} complexes were unsuccessful, as detailed in Chapter 6.



Scheme 37. General procedure for synthesis Ni–NHC–IPent^{Cl} (**203**) and Ni–NHC–IHept^{Cl} (**206**)

Single-crystal X-ray diffraction (SC-XRD) analysis of the isolated material revealed no coordination between the nickel center and the NHC–IPent^{Cl} ligand (Figure 43). Additionally, the high-resolution electrospray ionization spectrum (HRMS-ESI) of the isolated product displayed an $[\text{M} - \text{Cl}]^+$ peak at $m/z = 569.3478$, closely matching the calculated value of 569.3424 for the NHC–IPent^{Cl} ligand (C₃₅H₅₁Cl₂N₂). These data confirm the presence of the unbound NHC ligand and the absence of any nickel-containing species.

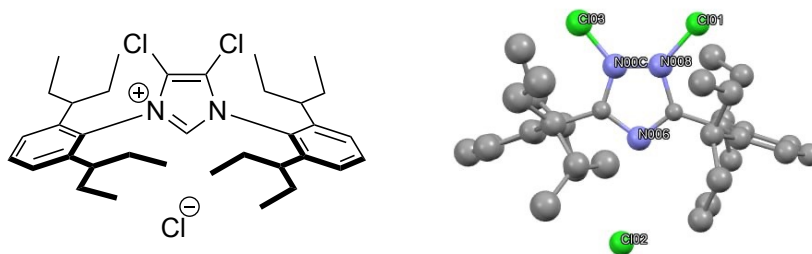
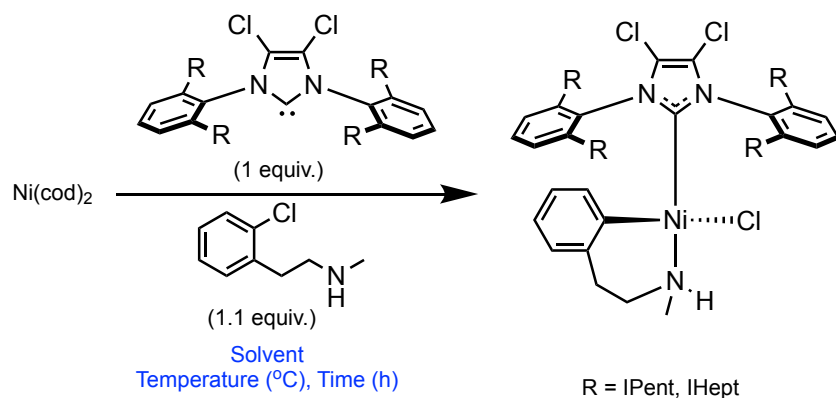


Figure 43. SC-XRD structure of the isolated material indicating no coordination between Ni and the NHC–IPent^{Cl} ligand

It appears that NHC–IPent^{Cl} and NHC–IHept^{Cl} are too sterically bulky to effectively coordinate to the nickel center under standard conditions. To overcome this challenge, we attempted to increase both the reaction time and temperature. As shown in [Table 17](#), stirring the reaction at room temperature for 3 to 4 days did not result in the formation of the desired Ni–NHC complex. Moreover, increasing the temperature to 35, 60, and 90 °C led to visible decomposition of the nickel precursor, resulting in the formation of a black precipitate identified as metallic nickel ([Figure 44](#)). This outcome is attributed to the thermal sensitivity of the nickel precursor; heating the reaction mixture accelerates its decomposition, thereby preventing successful complex formation.

Table 17. The ligation of nickel by bulky NHC-IPent^{Cl} and NHC-IHept^{Cl} ligands – Optimization studies (room temp. = 22 °C)



Entry	NHC free carbene	Solvent	Temperature (°C)	Time (h)	Product formation
1	NHC-IPent ^{Cl}	THF	room temp.	16	Failed
2	NHC-IPent ^{Cl}	THF	room temp.	72	Failed
3	NHC-IPent ^{Cl}	THF	35	16	Failed
4	NHC-IPent ^{Cl}	THF	60	16	Failed
5	NHC-IHept ^{Cl}	THF	room temp.	16	Failed
6	NHC-IHept ^{Cl}	THF	room temp.	72	Failed
7	NHC-IHept ^{Cl}	THF	60	72	Failed
8	NHC-IHept ^{Cl}	1,4-dioxane	90	96	Failed



Figure 44. Formation of nickel black due to thermal decomposition of the Ni(cod)₂ at 60 °C

These results suggest that the extreme steric bulk introduced by both the extended *N*-alkyl side chains and the backbone chlorine substituents severely hinders metal–ligand coordination. Moreover, in our precatalyst design, nickel is coordinated not only to the bulky NHC ligand but also to an additional ancillary ligand, referred to as the stabilizing ligand, which itself carries

significant steric bulk. The combination of the extended *N*-alkyl side chains and the backbone chlorine substituents on the NHC ligand, together with the spatial demands of the stabilizing ligand, creates an extremely crowded coordination environment. This severe steric hindrance may obstruct effective metal–ligand bonding, thereby preventing the successful formation of the desired Ni–NHC complexes. In addition to steric effects, electronic factors might also contribute to the instability of these complexes. The chlorine atoms on the backbone of the NHC ligand are strongly electron-withdrawing, which reduces the electron density at the carbene carbon and weakens its σ -donating ability toward the nickel center. This diminished donor strength may lead to a weaker metal–ligand interaction, ultimately resulting in a less stable Ni–NHC bond. Taken together, both the extreme steric hindrance and the electronically attenuated donor strength of the NHC–IPent^{Cl} and NHC–IHept^{Cl} ligands contribute to the failure in forming stable nickel complexes. This outcome highlights a structural limitation in the design of excessively bulky ligands and underscores the delicate balance between steric protection and effective metal coordination in Ni–NHC catalyst development.

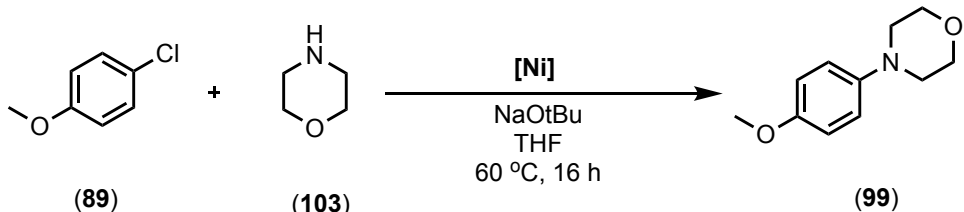
4.3.7 Ni–NHC precatalysts *versus* in-situ formation Ni–NHC catalysts in C–N bond formation reaction

To gain deeper insight into the factors influencing bond formation between nickel and sterically bulky NHC ligands, we conducted a series of control experiments comparing in-situ generated Ni–NHC species with their pre-formed counterparts under identical catalytic conditions. In the *in-situ* approach, the free NHC ligand was generated from its corresponding imidazolium salt in the presence of a base and reacted directly with a nickel(0) precursor, such as Ni(cod)₂, under standard C–N cross-coupling conditions. Parallel reactions were carried out using well-defined, isolated Ni–NHC precatalysts to assess differences in reactivity, stability, and overall catalytic

performance. *In-situ* ligation is known to work with the IPr ligand (Chapter 2), thus the absence of the additional ancillary ligand will instruct us on whether no complex can form at all with the larger chlorinated NHCs, or it can/does form, but simply cannot form the Ni(II) complex.

As shown in Table 18, both catalyst types were evaluated in the *N*-arylation of morpholine while all other reaction parameters were kept constant. For less sterically demanding NHC ligands, the in-situ and pre-formed systems displayed comparable catalytic activity. However, when bulkier ligands such as NHC–IPent^{Cl} and NHC–IHept^{Cl} were used, significantly diminished activity was observed in the in-situ systems. These results suggest that although Ni–NHC(bulky) species may form under in situ conditions, the extent of ligation remains uncertain. The observation of the cross-coupled product (**99**) confirms that at least some catalytically active Ni–NHC(bulky) species are generated under in situ conditions, even in the absence of a stabilizing ligand. However, the pronounced steric demand of NHC–IPent^{Cl} and NHC–IHept^{Cl} likely limits the extent of ligation and hinders effective coordination of the aryl halide and amine substrates to the nickel center. Consequently, catalytic efficiency is reduced, leading to diminished overall product yields.

Table 18. Ni–NHC precatalysts versus in-situ formation Ni–NHC catalysts in N-arylation of morpholine.

			
Entry	Catalyst	% Isolated Yield (99) using Pre-catalyst	% Isolated Yield (99) using In-situ catalyst ^[a]
1	Ni-NHC-IPr	89	89
2	Ni-NHC-IPent	91	90
3	Ni-NHC-IHept	94	90
4	Ni-NHC-IPr ^{*OMe}	95	92
5	Ni-NHC-IPr ^{Cl}	72	74
6	Ni-NHC-IPent ^{Cl}	-	19
7	Ni-NHC-IHept ^{Cl}	-	12

Reagents and conditions: 4-chlorobenzene (0.5 mmol, 1 equiv.), morpholine (1.2 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), THF (1 ml), 60 °C, 16 h. [a] In-situ preparation of Ni-NHC catalyst using 5 mol% Ni(cod)₂ and 5 mol% NHC-IPr.HCl ligand

Similarly, the same control experiments were conducted for the monoarylation of octylamine with 4-chloroanisole. As summarized in Table 19, less bulky NHC ligands performed comparably well in both in-situ and pre-formed catalyst systems. However, in the case of highly sterically hindered ligands such as NHC–IPent^{Cl} and NHC–IHept^{Cl}, in-situ catalyst generation led to the formation of the desired product, albeit in low yield. This result indicates that despite the steric bulk, Ni–NHC bond formation is still possible under in-situ conditions, although the overall catalytic efficiency remains limited.

Table 19. Ni–NHC precatalysts versus in-situ formation Ni–NHC catalysts in monoarylation of octylamine.^{[a][b]}

COc1ccc(Cl)cc1 (88) + CCCCCCCCN (182) $\xrightarrow[\text{NaOtBu, Toluene, 80 } ^\circ\text{C, 16 h}]{[\text{Ni}]}$ COc1ccc(NCCCCCCCC)cc1 (102) + COc1ccccc1 (184)

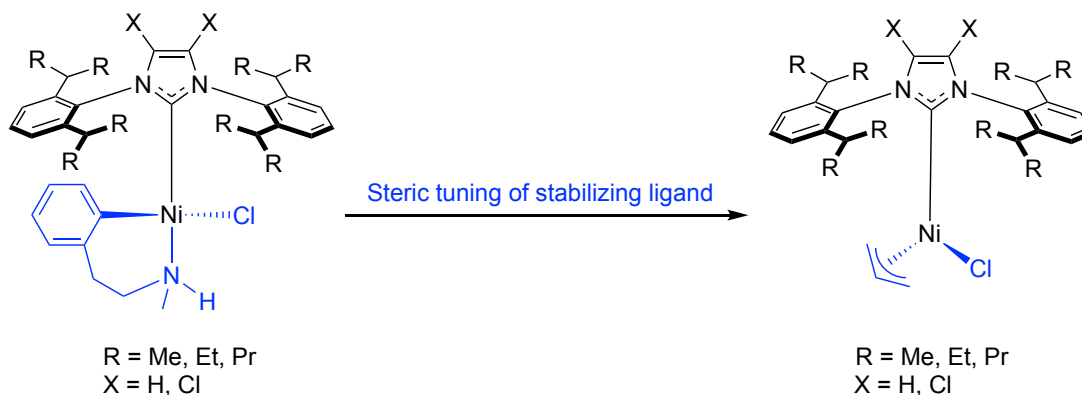
Entry	Catalyst	% Isolated Yield (102) using Pre-catalyst	% Isolated Yield (102) using In-situ catalyst ^[c]
1	Ni-NHC-IPr	0	0
2	Ni-NHC-IPent	10	8
3	Ni-NHC-IHept	14	13
4	Ni-NHC-IPr ^{*OMe}	0	0
5	Ni-NHC-IPr ^{Cl}	30	30
6	Ni-NHC-IPent ^{Cl}	-	15
7	Ni-NHC-IHept ^{Cl}	-	25

Reagents and conditions: 4-chlorobenzene (0.5 mmol, 1 equiv.), octylamine (1.1 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), Toluene (5 ml), 80 °C, 16 h. [a] Complete consumption of 4-chloroanisole (**89**) was observed in all seven reactions. [b] The remaining was side-product (**184**) and could not be isolated due to its volatility and just monitored by GC–MS. [c] In-situ preparation of Ni–NHC catalyst using 5 mol% Ni(cod)₂ and 5 mol% NHC-IPr.HCl ligand.

This outcome suggests that Ni–NHC bond formation with bulky ligands may occur under *in-situ* conditions. However, its formation may be limited by the steric demand of the NHC ligand. In contrast, attempts to pre-form the corresponding Ni–NHC complexes in the presence of a stabilizing ligand were unsuccessful. This failure is likely due to the combined steric demands of both the bulky NHC ligand and the stabilizing ligand, which together create excessive congestion around the nickel center and hinder complex formation. To address this, our next strategy focused on reducing the steric bulk of the stabilizing ligand in order to provide sufficient spatial flexibility for the bulky NHC ligand to coordinate effectively to nickel.

4.4 π -allyl as a less bulky stabilizing ligand: 3rd generation Ni–NHC precatalysts

To minimize steric congestion around the nickel center, we designed a new system in which the previous stabilizing ligand is replaced with a less bulky π -allyl group, as illustrated in Scheme 38.



Scheme 38. Minimizing the steric bulk of the stabilizing ligand using π -allyl

The Ni(allyl)Cl(IPr) complex (**207**) is a known compound first reported by Nicasio in 2010.¹³⁴ We developed this system further by replacing the IPr ligand with bulkier NHC ligands, including NHC–IPr^{Cl}, NHC–IPent^{Cl}, and NHC–IHept^{Cl}, in order to evaluate their coordination behavior and catalytic performance.

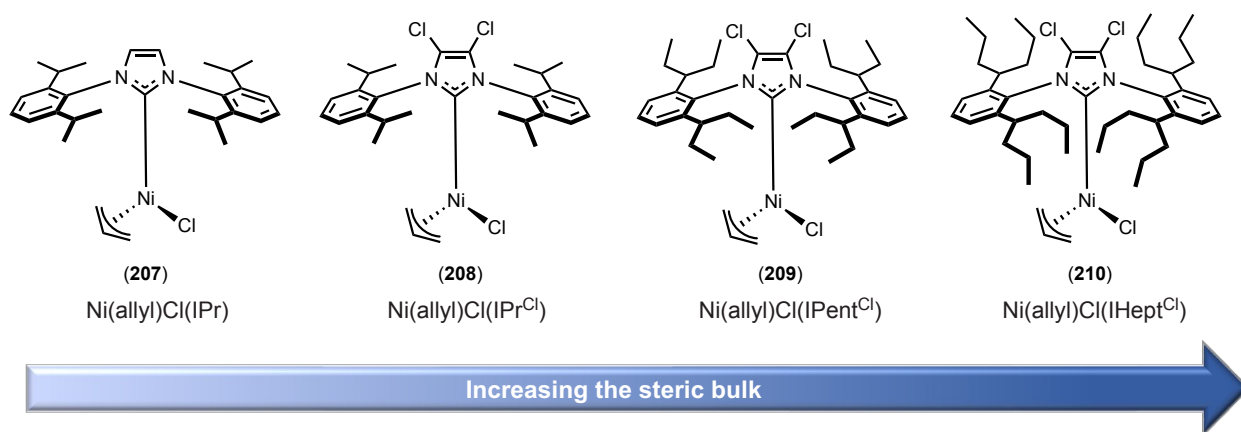


Figure 45. The development of (NHC)Ni(π -allyl)Cl precatalysts

4.4.2 Synthesis and characterization of (NHC)Ni(π -allyl)Cl precatalysts

The Ni(allyl)Cl(IPr) **207**, Ni(allyl)Cl(IPr^{Cl}) **208**, Ni(allyl)Cl(IPent^{Cl}) **209**, Ni(allyl)Cl(IHept^{Cl}) **210** complexes were synthesized according to the literature procedures for **207**¹⁸³ and fully characterized using NMR spectroscopy, HRMS, and SC-XRD.

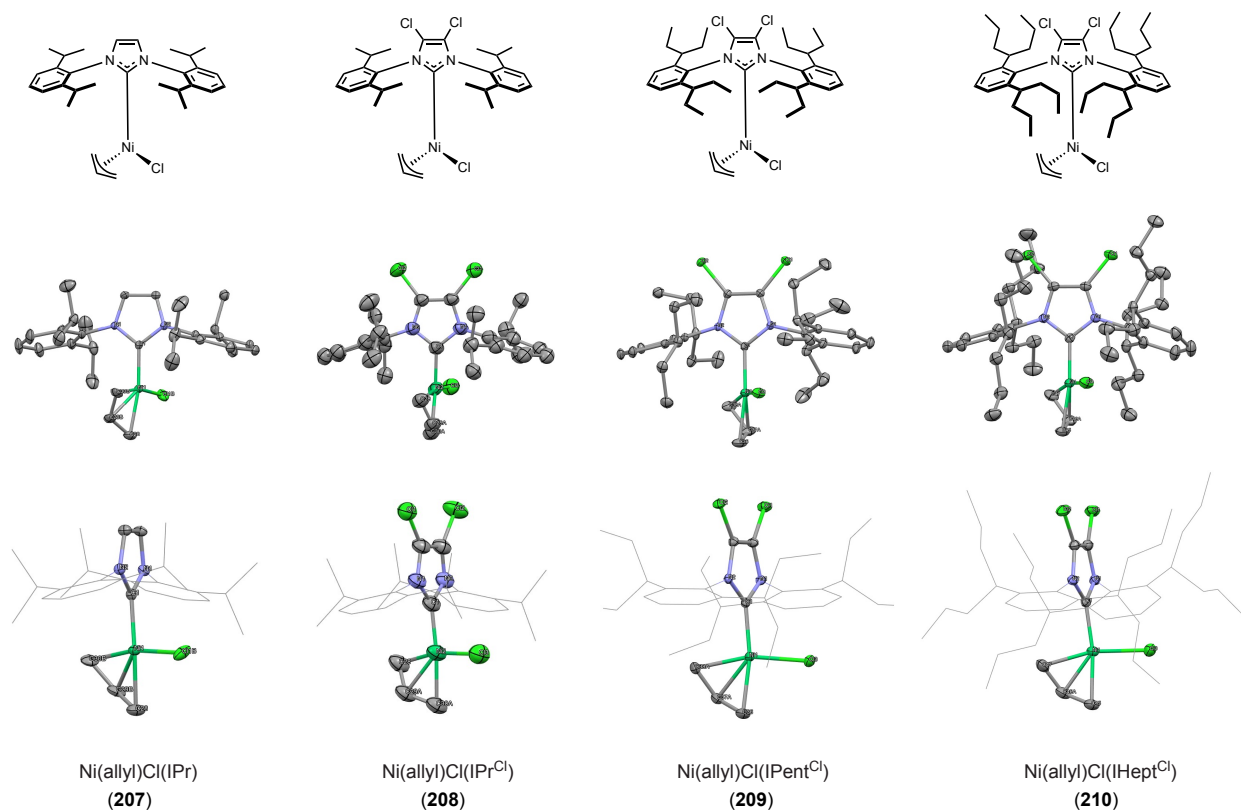


Figure 46. SC-XRD analysis of the Ni(allyl)Cl(IPr) **207**, Ni(allyl)Cl(IPr^{Cl}) **208**, Ni(allyl)Cl(IPent^{Cl}) **209**, and Ni(allyl)Cl(IHept^{Cl}) **210** complexes from two different view

Structural analysis confirmed successful formation of the Ni–NHC bond and clearly demonstrated coordination of the bulky NHC ligands to the nickel center. These results validate our initial hypothesis: reducing the steric bulk of the stabilizing ligand provides sufficient spatial flexibility to enable effective coordination of highly hindered NHC ligands such as IPent^{Cl} and IHept^{Cl} to the nickel center.

4.4.3 Evaluation of (NHC)Ni(π -allyl)Cl precatalysts in monoarylation of octylamine

These newly developed complexes were evaluated in the monoarylation of octylamine with 4-chloroanisole, a transformation previously shown to benefit from the use of bulky Ni–NHC catalysts. As illustrated in Figure 47, increasing the steric bulk of the NHC ligand across the series Ni(allyl)Cl(IPr) (**207**), Ni(allyl)Cl(IPr^{Cl}) (**208**), Ni(allyl)Cl(IPent^{Cl}) (**209**), and Ni(allyl)Cl(IHept^{Cl}) (**210**) led to a notable improvement in reaction yield. Among them, Ni(allyl)Cl(IPent^{Cl}) (**209**), and Ni(allyl)Cl(IHept^{Cl}) (**210**) delivered the highest performance, affording the monoarylated product in approximately 60% yield.

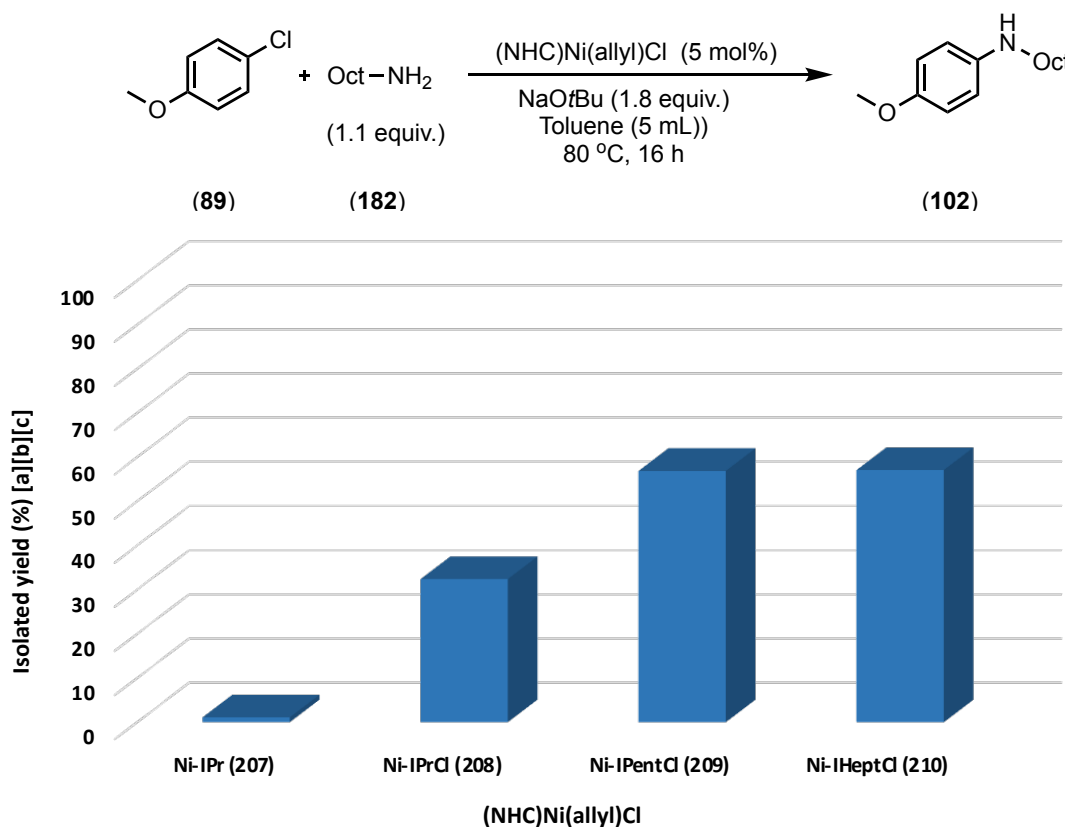


Figure 47. Evaluation of Ni(allyl)Cl(IPr) (**207**), Ni(allyl)Cl(IPr^{Cl}) (**208**), Ni(allyl)Cl(IPent^{Cl}) (**209**), and Ni(allyl)Cl(IHept^{Cl}) (**210**) precatalysts in monoarylation of octylamine. [a] yields are average of two runs. [b] Complete consumption of 4-chloroanisole (**89**) was observed in all reactions. [c] Based on mass balance, the remaining material was dehalogenated (reduced) side product.

4.4.4 Evaluation of (NHC)Ni(π -allyl)Cl precatalysts in *N*-arylation of morpholine

The catalytic activity of Ni(allyl)Cl(IPr) (**207**), Ni(allyl)Cl(IPr^{Cl}) (**208**), Ni(allyl)Cl(IPent^{Cl}) (**209**), and Ni(allyl)Cl(IHept^{Cl}) (**210**) was also evaluated in the *N*-arylation of morpholine using 4-chloroanisole as the electrophilic coupling partner. As illustrated in Figure 48, Ni(allyl)Cl(IPr) (**207**) exhibited high catalytic activity, affording the desired cross-coupled product in excellent yield. Employing the more sterically demanding Ni(allyl)Cl(IPr^{Cl}) (**208**) complex resulted in a slight decrease in yield, while the bulkier Ni(allyl)Cl(IPent^{Cl}) (**209**) and Ni(allyl)Cl(IHept^{Cl}) (**210**) complexes furnished the product in significantly lower yields. These results indicate that excessive steric congestion around the nickel center hinders effective coordination of the sterically demanding amine substrate, such as morpholine, thereby diminishing overall catalytic efficiency.

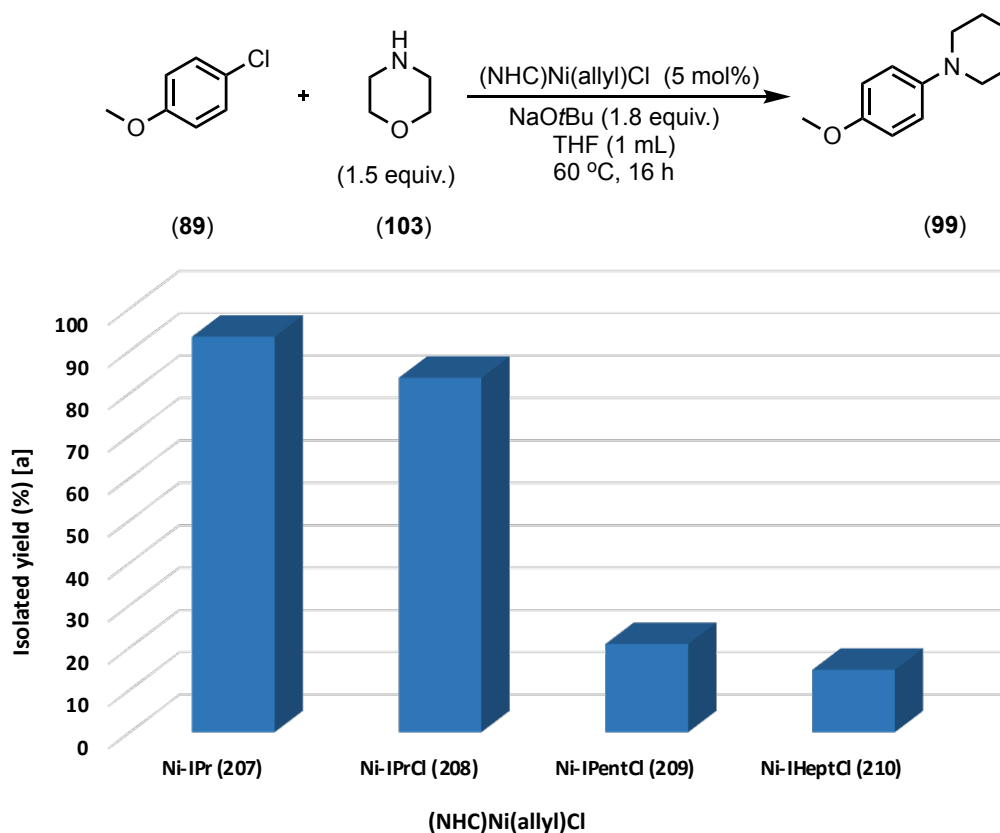
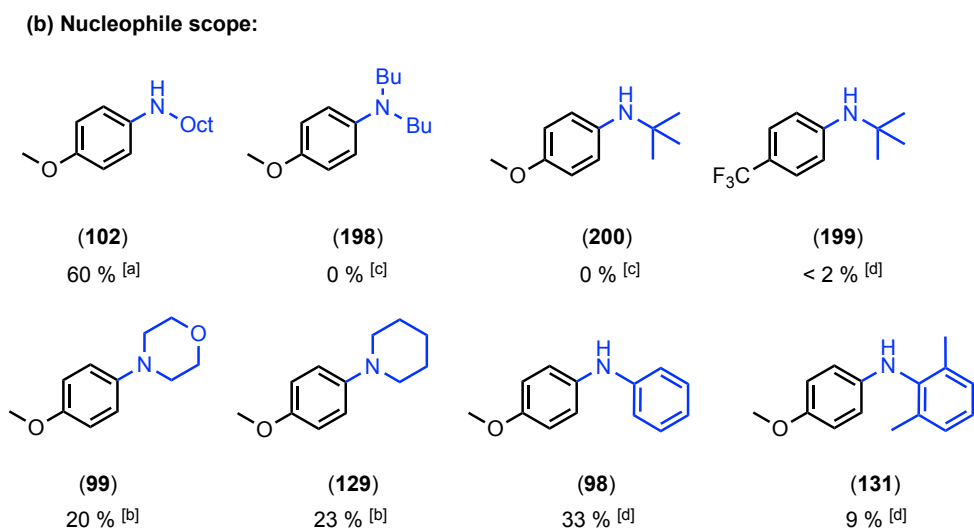
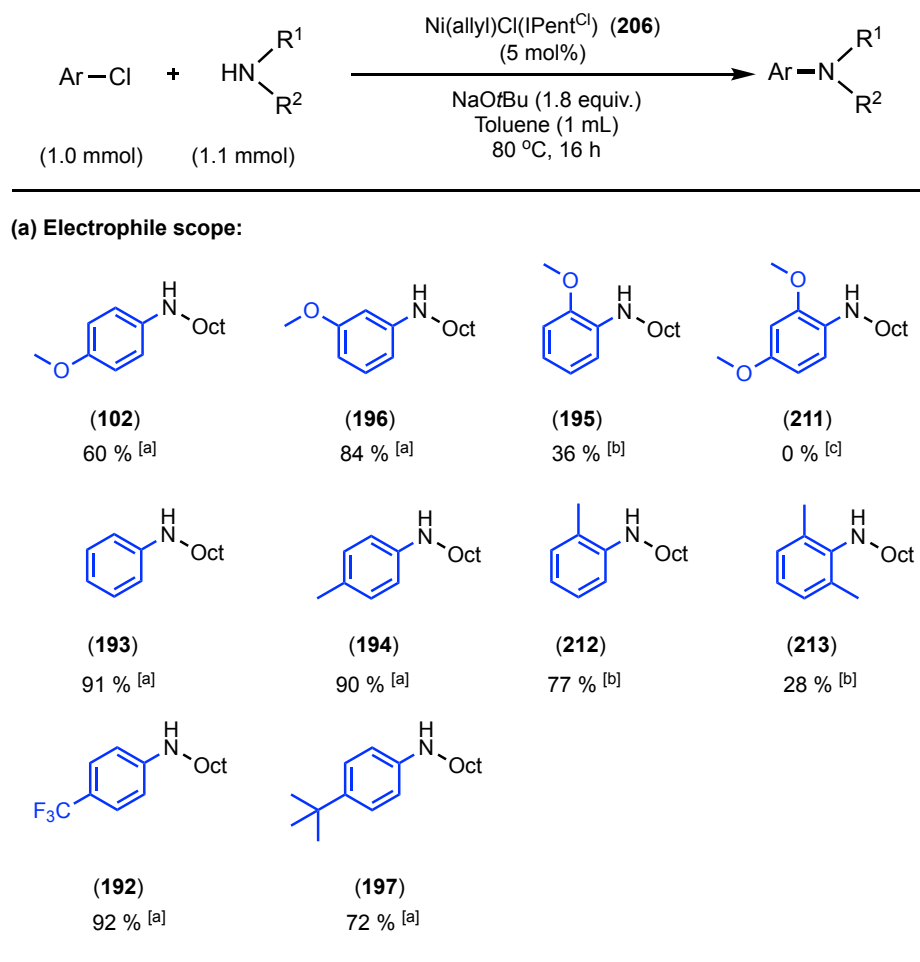


Figure 48. Evaluation of Ni(allyl)Cl(IPr) (**207**), Ni(allyl)Cl(IPr^{Cl}) (**208**), Ni(allyl)Cl(IPent^{Cl}) (**209**), and Ni(allyl)Cl(IHept^{Cl}) (**210**) precatalysts in *N*-arylation of morpholine, [a] average of two runs

4.4.5 The impact of substrate steric bulk on catalytic performance of Ni(allyl)Cl(IPent^{Cl})

To assess the impact of substrate steric bulk on catalytic performance, a series of sterically demanding coupling partners were examined in the C–N bond formation reaction using Ni(allyl)Cl(IPent^{Cl}) (**209**). As shown in [Scheme 39a](#), increasing the steric bulk of the aryl chloride from 4-chloroanisole to 2-chloroanisole led to a pronounced decline in yield, dropping from 60% to 36% (**102** and **195**, respectively). A similar trend was observed for the chlorotoluene derivatives, where greater ortho-substitution resulted in markedly lower product yields (**194**, **212**, and **213**). Subsequently, the steric influence of the amine coupling partner was evaluated ([Scheme 39b](#)). While the coupling of 4-chloroanisole with octylamine afforded a 60% yield (**102**), the reaction with the more sterically hindered dibutylamine produced no detectable product (**198**). Likewise, the arylation of *tert*-butylamine, a bulky primary amine, showed no product formation with either electron-rich or electron-deficient aryl chlorides (**200** and **199**). The *N*-arylation of cyclic secondary amines such as morpholine and piperidine proceeded in low yields of approximately 20% (**99** and **129**). Moreover, the coupling of aniline, a primary aryl amine, afforded the corresponding product in 33% yield (**98**), whereas increasing steric hindrance on the aniline substrate further reduced product formation (9%, **131**).

Collectively, these results indicate that the congested coordination environment around the nickel center, imposed by the bulky NHC–IPent^{Cl} ligand, limits the approach and binding of sterically demanding substrates, thereby diminishing overall catalytic efficiency.



Scheme 39. The impact of substrate steric bulk on catalytic performance of Ni(allyl)Cl(IPent^{Cl}). [a] Complete consumption of the aryl chloride was observed, the remaining material was reduced product; [b] Unreacted aryl chloride and reduced product were obtained; [c] All aryl chloride recovered; [d] the remaining material was unreacted aryl chloride.

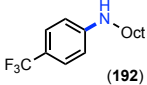
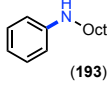
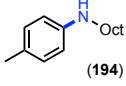
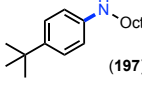
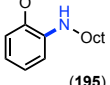
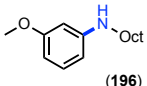
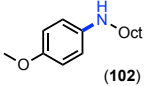
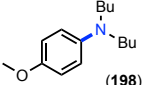
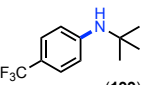
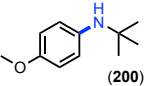
4.4.6 Is bigger ligand always better?

To better understand the influence of NHC ligand steric bulk on the catalytic performance of nickel in C–N bond formation reactions, a series of amination reactions were performed with Ni–NHC–IPr (**83**), Ni–NHC–IPr^{Cl} (**188**), and Ni–NHC–IPent^{Cl} (**209**) using representative substrates, as summarized in Table 20. As shown, in the arylation of octylamine with reactive aryl chlorides, Ni–NHC–IPr^{Cl} exhibited higher activity than Ni–NHC–IPr, while its performance was comparable to that of Ni–NHC–IPent^{Cl}, (entries 1–4). When 4-chloroanisole, an electron-rich coupling partner, was employed, Ni–NHC–IPent^{Cl} afforded the highest yield (entry 7). However, increasing the steric hindrance of the aryl chloride led to a notable decline in yield with Ni–NHC–IPent^{Cl} (entry 5). In contrast, when more sterically hindered amines such as dibutylamine and tert-butylamine were used, Ni–NHC–IPr^{Cl} outperformed Ni–NHC–IPent^{Cl}, suggesting that excessive ligand bulk can impede substrate coordination.

Overall, these findings demonstrate that although sterically demanding Ni–NHC systems can enhance selectivity and minimize side reactions, they are not universally effective across all substrate classes. The combined results from the coupling reactions with hindered aryl chlorides and amines emphasize the importance of maintaining an optimal balance between the steric protection imparted by the NHC ligand and the steric requirements of the substrates to achieve maximum catalytic efficiency.

Table 20. Comparison of Ni-NHC-IPr (**83**), Ni-NHC-IPr^{Cl} (**188**), and Ni-NHC-IPent^{Cl} (**209**) complexes in C–N bond formation reactions

$$\begin{array}{c}
 \text{Ar-Cl} + \text{HN} \begin{array}{l} \text{R}^1 \\ \text{R}^2 \end{array} \xrightarrow[\text{NaOtBu (1.8 equiv.)}]{[\text{Ni}] (5 \text{ mol\%})} \text{Ar-N} \begin{array}{l} \text{R}^1 \\ \text{R}^2 \end{array} \\
 (1.0 \text{ mmol}) \quad (1.1 \text{ mmol}) \quad \text{Toluene (5 mL)} \\
 \quad \quad \quad 80^\circ\text{C, 16 h} \\
 \text{R}^1, \text{R}^2 = \text{H or alkyl}
 \end{array}$$

Entry	Product	Ni-IPr (83) % Isolated Yield	Ni-IPr ^{Cl} (188) % Isolated Yield	Ni-IPent ^{Cl} (209) % Isolated Yield
1	 (192)	47	94	92
2	 (193)	21	90	91
3	 (194)	15	88	90
4	 (197)	6	75	72
5	 (195)	0	32	36
6	 (196)	15	84	84
7	 (102)	0	30	60
8	 (198)	0	21	0
9	 (199)	45	72	Trace
10	 (200)	0	0	0

Reagents and conditions: Ar-Cl (0.5 mmol, 1 equiv.), amine (1.1 equiv.), [Ni] 5 mol%, NaOtBu (1.8 equiv.), Toluene (5 ml), 80 °C, 16 h.

4.4.7 Evaluation the stability of (NHC)Ni(π -allyl)Cl precatalysts in air atmosphere

Although the (NHC)Ni(π -allyl)Cl precatalysts demonstrated catalytic activity in C–N bond formation reactions, they exhibited poor stability when exposed to air, both in the solid state and in solution. As shown in Figure 49, the precatalysts underwent visible decomposition after being left in air for 48 h in their solid form. In solution, the complexes decomposed within 2 h upon exposure to air. These observations highlight a key limitation of this precatalyst class, underscoring the need for further structural modification to enhance air stability without compromising catalytic performance.

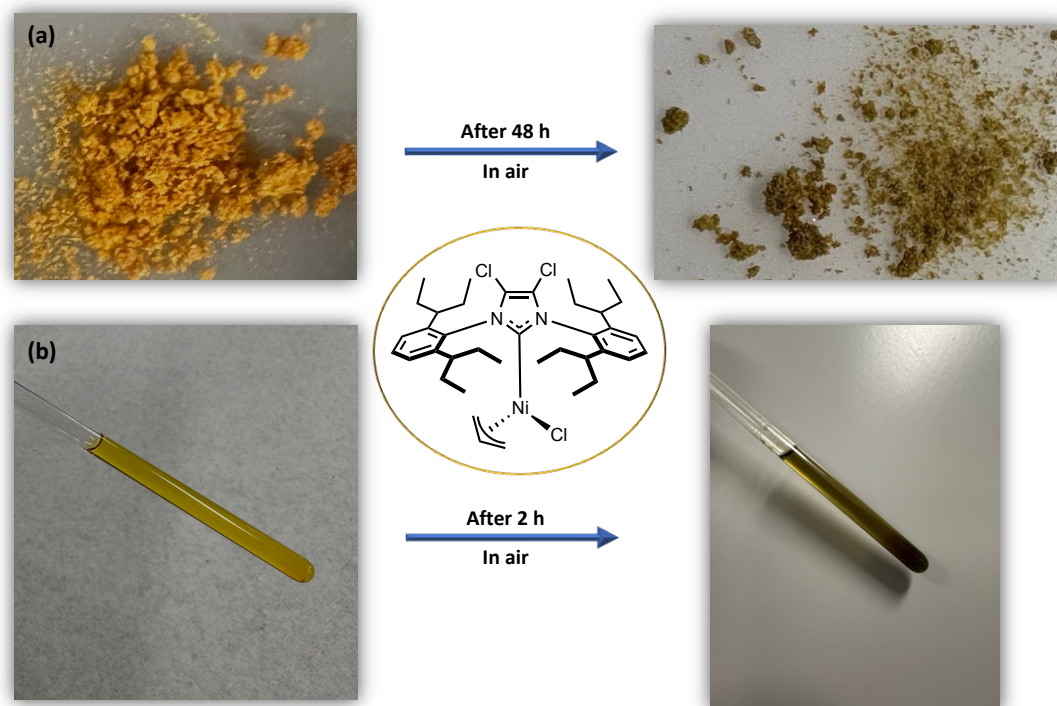


Figure 49. Evaluating the stability of Ni(allyl)Cl(IPent^{Cl}) precatalyst in air atmosphere, (a) solid state, (b) solution (deuterated benzene)

To compare the stability of (NHC)Ni(π -allyl)Cl precatalysts with the first-generation Organ-type Ni–NHC complexes, it is evident that the first-generation complexes exhibit greater air stability, likely due to their chelating ligand framework. In these first-generation systems, nickel is

coordinated to a six-membered ring, which enhances complex stability through chelation. This structural feature appears to play a key role in protecting the metal center from air-induced decomposition. Guided by this insight, we are now aiming to design a new generation of air-stable Ni–NHC precatalysts by fine-tuning both the steric properties of the ligand and the coordination environment of the nickel center.

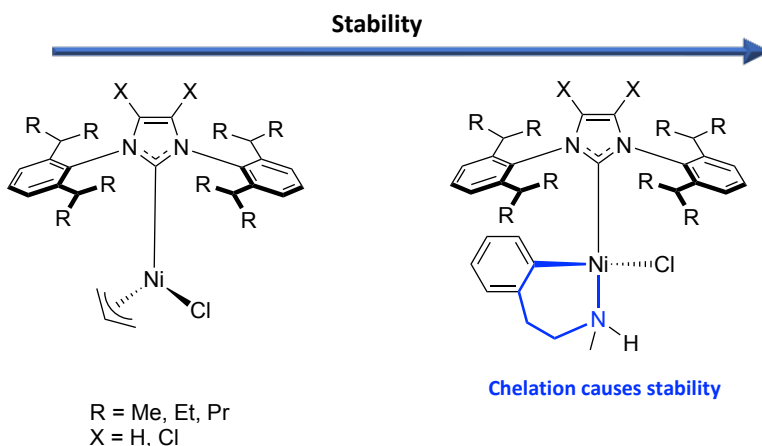


Figure 50. Schematic representation of the enhanced stability of first-generation Organ-type Ni–NHC complexes compared to (NHC)Ni(π -allyl)Cl precatalysts

4.5 Conclusion

In this chapter, we explored the development of sterically demanding Ni–NHC precatalysts to address key limitations in nickel-catalyzed C–N bond formation reactions, particularly in the selective monoarylation of primary alkyl amines. Building upon first-generation Ni–NHC–IPr complex **83**, we systematically increased the steric bulk of the NHC ligand through two complementary strategies: (1) extending the *N*-alkyl side chains (e.g., Ni–NHC–IPent (**165**) and Ni–NHC–IHept (**174**)), and (2) introducing backbone substituents (e.g., chlorine atoms) to create a second generation of more rigid and electronically modulated ligands (e.g., Ni–NHC–IPr^{Cl} (**188**)). All newly synthesized complexes exhibited excellent performance in the *N*-arylation of morpholine, confirming their catalytic competence under standard conditions. However, when

applied to the more demanding monoarylation of octylamine with 4-chloroanisole, marked differences in reactivity and selectivity were observed. The backbone-chlorinated complex Ni–NHC–IPr^{Cl} outperformed non-chlorinated analogues, providing a significantly higher yield of the monoarylated product and effectively suppressing β -hydride elimination. These findings highlight the synergistic role of steric hindrance and electronic modulation in facilitating the key reductive elimination step while minimizing competing side reaction.

Attempts to further increase steric protection by combining backbone chlorination with longer *N*-alkyl chains (as in Ni–NHC–IPent^{Cl} (**203**) and Ni–NHC–IHept^{Cl} (**206**)) were unsuccessful. Structural and spectroscopic analyses confirmed that these ligands failed to coordinate to nickel, likely due to excessive steric congestion around the nickel center. To address this limitation, we explored an alternative strategy: reducing the steric bulk of the stabilizing ligand to create sufficient spatial flexibility for the bulky NHC ligand to coordinate effectively to nickel. Guided by this approach, a new class of complexes was synthesized using π -allyl as a less hindered stabilizing ligand. Although these (NHC)Ni(π -allyl)Cl precatalysts demonstrated high catalytic activity in C–N bond-forming reactions with less hindered substrates, they suffered from poor air stability, decomposing readily in both solid and solution states.

Overall, this study highlights the critical balance between steric bulk and electronic properties in the design of Ni–NHC precatalysts. Fine-tuning these parameters is essential for promoting efficient reductive elimination while maintaining structural integrity under ambient conditions. The insights gained here lay the groundwork for the rational development of next-generation, air-stable Ni–NHC precatalysts with optimized ligand architectures and coordination environments tailored for challenging C–N cross-coupling reactions.

Chapter 5

5. Chapter 5: Conclusions and outlook

The work presented in this thesis advances the field of nickel–NHC catalysis by addressing one of its most persistent challenges: developing well-defined, bench-stable precatalysts that retain high activity toward demanding C–N bond formation reactions. Through systematic ligand design, mechanistic analysis, and exploration of activation strategies, this study delivers new structural and conceptual tools for catalyst development, providing a foundation for future innovations in both academic and industrial contexts.

5.1 Summary of key findings

In **Chapter 2**, the first-generation Ni–NHC–IPr precatalyst stabilized by a chelating “throw-away” ligand was developed. This design overcame the air and moisture sensitivity that has historically limited Ni–NHC applications, allowing the catalyst to be handled outside a glovebox and activated under ambient conditions. The complex proved effective for the amination of aryl chlorides with a variety of primary and secondary amines, outperforming analogous phosphine-based systems under mild conditions. Mechanistic studies revealed that the nature of the aryl halide significantly influences catalyst speciation, with aryl bromides and iodides promoting the formation of thermodynamically stable nickel halide-bridged dimers that produces a catalytically inactive form of metal complex. In contrast, aryl chlorides are less prone to dimerization, leaving more monomeric nickel species available for productive amine coordination, resulting in higher turnover efficiency

In **Chapter 3**, we expanded the mechanistic studies by coupling Ni–NHC–IPr with photoredox catalysis, enabling access to high-valent Ni^{III} species that facilitate otherwise challenging reductive

elimination steps. The dual Ni/Ir catalytic system showed high efficiency for electronically activated and sterically accessible aryl halides but diminished activity for electron-rich and sterically hindered substrates. This limitation, coupled with constraints of batch photochemistry, underscored the importance of engineering both light delivery and thermal control to fully exploit photochemical activation in nickel catalysis.

In **Chapter 4**, we pursued ligand modifications to enhance selectivity in C–N couplings, particularly for the monoarylation of primary alkyl amines where β -hydride elimination competes. Increasing steric bulk via *N*-alkyl chain extension and backbone chlorination improved product selectivity and suppressed side pathways. Among the complexes synthesized, backbone-chlorinated Ni–NHC–IPr^{Cl} emerged as the most effective, delivering good yields and selectivity with challenging electrophiles. However, combining long *N*-alkyl chains with backbone chlorination proved counterproductive, as excessive steric congestion hindered ligand coordination. To address this, a third-generation system using a less hindered π -allyl ligand as a stabilizer was developed. This design restored coordination and enhanced catalytic activity but sacrificed air stability, highlighting the delicate balance between stability and reactivity in catalyst design.

5.2 Conceptual Advances

Collectively, these findings contribute to a deeper understanding of how steric and electronic properties of NHC ligands interact with nickel's coordination environment to determine both stability and catalytic performance. The progression from the first-generation system to backbone-chlorinated (2nd Gen.) and π -allyl-stabilized complexes (3rd Gen.) demonstrates that no single design parameter—steric protection, electronic modulation, or ligand lability—can be optimized

in isolation. Instead, catalyst performance emerges from a finely tuned compromise between these factors.

Mechanistic insights from this work also clarify the roles of off-cycle species, halide effects, and competing side reactions. By identifying conditions and ligand features that minimize catalyst deactivation, this thesis provides guiding principles for rational catalyst design that extend beyond amination reactions.

5.3 Limitations and Challenges

While notable advances were achieved, limitations remain. The poor air stability of the π -allyl-stabilized systems restricts their practical utility. The reduced reactivity observed with electron-rich and sterically demanding aryl electrophiles points to unresolved challenges in oxidative addition and reductive elimination steps. Additionally, the scope of nucleophiles examined—primarily alkyl and aryl amines—leaves open questions about performance with other heteroatom nucleophiles or highly functionalized substrates.

5.4 Outlook

Future research inspired by this work should focus on:

1. **Hybrid steric–electronic designs** – Incorporating moderate steric bulk with electron-withdrawing or -donating substituents to create ligands that balance air-stability and reactivity.
2. **Expanded substrate scope** – Testing the catalysts against heteroaryl halides, unprotected amines, alcohols, and thiols to evaluate versatility.
3. **Mechanistic refinement** – Using in-situ spectroscopic tools (EPR, operando NMR, XAS) and computational studies to dissect the interplay between Ni(0)/Ni(II) and Ni(I)/Ni(III) cycles, especially in photochemical regimes.

4. **Industrial translation** – Lowering catalyst loading, heterogenization of catalyst and enabling recycling, enhancing compatibility with pharmaceutical process constraints to move these systems toward practical continuous-flow and large-scale applications.

5.5 Broader Implications

The strategies and principles developed in this thesis are not confined to C–N bond formation. The design concepts, particularly those surrounding ligand sterics/electronics and activation modes, can be extended to C–C and C–O cross-coupling reactions, alkene functionalization, and other transformations where nickel catalysis offers distinct advantages over palladium. As the field moves toward more sustainable and cost-effective transition-metal catalysis, Ni–NHC systems such as those described here will play a pivotal role in bridging the gap between laboratory innovation and industrial adoption.

In summary, this thesis delivers both practical catalysts and fundamental insight into Ni–NHC design, laying the groundwork for the next generation of user-friendly, bench-stable and all-purpose nickel precatalysts. The ongoing challenge, and opportunity, will be to translate these molecular-level optimizations into catalysts that perform robustly under the demanding conditions of real-world chemical synthesis.

Chapter 6

6. Chapter 6: Experimental procedures (by chapter)

6.1 General experimental

All experiments were conducted under an atmosphere of dry nitrogen in oven or flame dried glassware using standard Schlenk techniques unless noted otherwise. Experiments performed in an oil bath were done using Fisher Scientific silicone oil in a Pyrex crystallizing dish on top of an Hei-PLATE Mix 'n' Heat Core+ basic model magnetic hotplate stirrer equipped with an Pt1000 electronic contact thermometer. Glovebox manipulations were performed in an MBraun Unilab glovebox under a dry nitrogen atmosphere. All reagents were purchased from Sigma-Aldrich, Oakwood chemicals, Combi-Blocks or Alfa Aesar and were used without further purification, unless noted otherwise. All reaction vials (8 mL, 20 mL and 40 mL disposable scintillation vials) were purchased from VWR. Analytical thin layer chromatography (TLC) was performed on EMD 60 F254 pre-coated aluminum plates and spots were visualized with UV light (254 nm). Column chromatography was performed using either standard flash chromatography on EMD silica gel 60 (230–400 mesh) or a Biotage Isolera Four system equipped with 5-250 g Santai cartridges. NMR spectra were recorded on a Bruker 400 AVANCE II, Bruker 500 AVANCE III or Bruker 600 AVANCE III spectrometer; The chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent; coupling constants (J) are given in Hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal(s) of the deuterated solvent. The following abbreviations are used to describe peak multiplicities: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, tt = triplet of triplets, qt = quartet of triplets, qd = quartet of doublets, and m = multiplet.

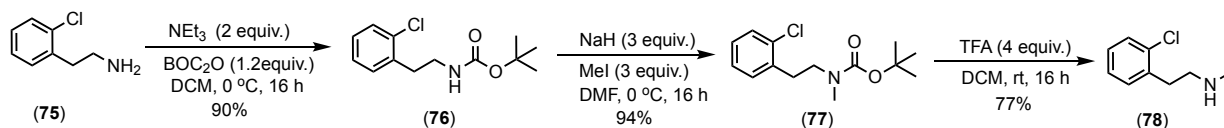
Gas chromatography with flame ionization detection (GC-FID) was performed on a Agilent 6850 Series II instrument. The progress of the reactions was monitored with Agilent 5977C single quadrupole GC/MS instrument. High resolution mass spectrometry (HRMS) analysis was performed by the John L. Holmes Mass Spectrometry Facility at the University of Ottawa. Single-crystal X-ray diffraction data were collected using a Bruker SMART (or Venture Metaljet k-geometry) diffractometer equipped with an APEXII CCD (or CMOS Photon III) detector and a sealed-tube Mo K α radiation source, $\lambda = 0.71073 \text{ \AA}$ (or Ga K α radiation source, $\lambda = 1.34139 \text{ \AA}$).

6.2 Experimental procedures for chapter 2

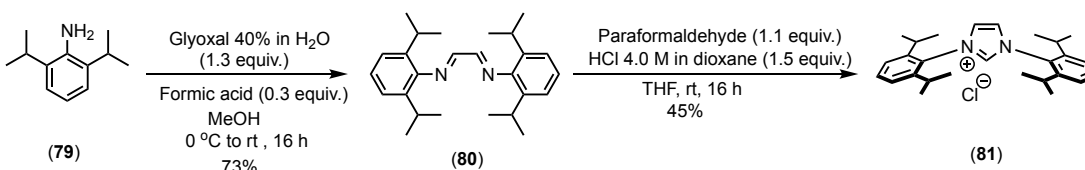
6.2.1 Precatalyst preparation

As illustrated in [Scheme 40](#), the precatalyst **83** was prepared in three key steps: (i) preparation of the stabilizing ligand, (ii) preparation of the NHC–IPr ligand, and (iii) ligation of the ligands to the nickel.

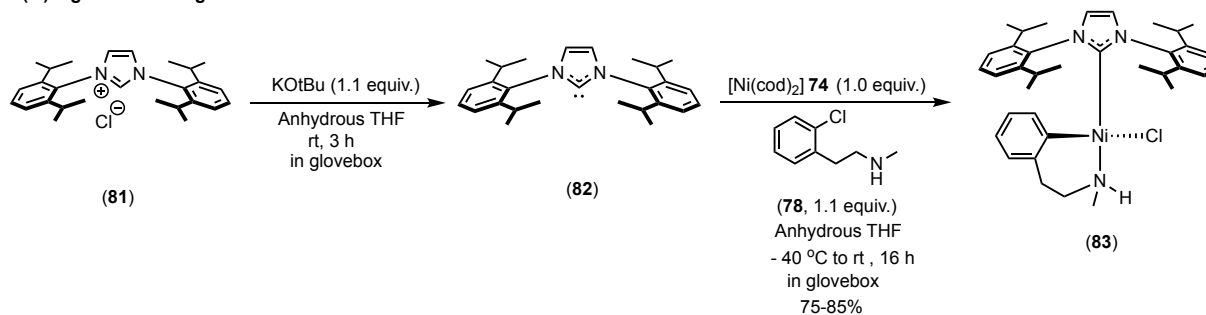
(i) Preparation of the stabilizing ligand



(ii) Preparation of the NHC–IPr ligand



(iii) Ligation of the ligands to the nickel

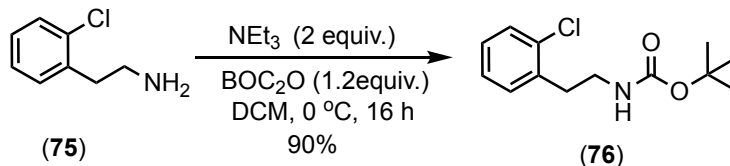


Scheme 40. General procedure for synthesis Ni–NHC–IPr (**83**) precatalyst

6.2.1.1 Preparation of the stabilizing ligand

As shown in [Scheme 40\(i\)](#), the preparation of the stabilizing ligand involves three main steps: Boc-protection, methylation, and subsequent Boc-deprotection.

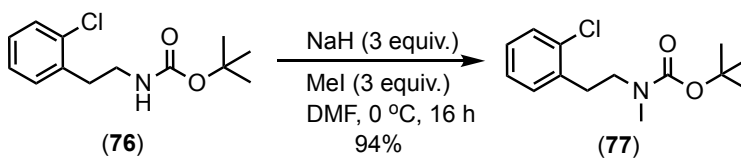
***tert*-butyl (2-chlorophenethyl)carbamate (76)**



To a 250 mL round-bottom flask equipped with a magnetic stir bar were added 2-(2-chlorophenyl)ethan-1-amine (**75**) (7.04 mL, 50 mmol) and anhydrous dichloromethane (80 mL). The reaction mixture was cooled to 0 °C, and triethylamine (13.9 mL, 2 equiv., 100 mmol) was added dropwise while stirring. After 5 minutes, a solution of di-*tert*-butyl dicarbonate (13.09 g, 1.2 equiv., 60 mmol) in DCM (20 mL) was added, and the reaction mixture was stirred overnight while gradually warmed to room temperature. The reaction was then quenched with H₂O and extracted with DCM (2 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford the crude product. Purification by flash silica gel chromatography (EtOAc/hexanes) provided *tert*-butyl (2-chlorophenethyl)carbamate (**76**) as a pure product (11.5 g, 90% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.12 (m, 3H), 4.58 (s, 1H), 3.39 (q, *J* = 7.0 Hz, 2H), 2.94 (t, *J* = 6.5 Hz, 2H), 1.43 (s, 9H) ppm.

***tert*-butyl (2-chlorophenethyl)(methyl)carbamate (77)**



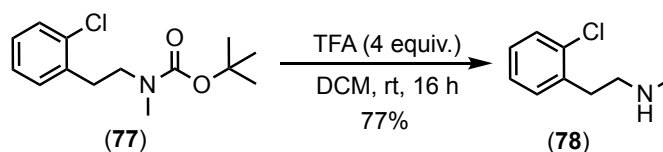
To a 200 mL round-bottom flask equipped with a magnetic stir bar were added Boc-protected amine **76** (11.5 g, 44.95 mmol) and DMF (45 mL). The reaction mixture was cooled to 0 °C, and NaH (60% dispersion in mineral oil, 5.4 g, 3.0 equiv., 134.85 mmol) was added slowly over 30

minutes with stirring. MeI (8.4 mL, 3.0 equiv., 134.85 mmol) was then added dropwise, and the reaction mixture was allowed to warm gradually to room temperature while stirring overnight.

The reaction was quenched with water (40 mL) and extracted with ethyl acetate (EtOAc, 3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (EtOAc/hexanes) to afford the *tert*-butyl (2-chlorophenethyl)(methyl)carbamate (**77**) as a pure product (11.4 g, 94%).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.12 (m, 3H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.81 (s, 3H), 1.35 (s, 9H) ppm.

2-(2-chlorophenyl)-*N*-methylethan-1-amine (**78**)



To a 200 mL round-bottom flask equipped with a magnetic stir bar were added *tert*-butyl (2-chlorophenethyl)(methyl)carbamate **77** (11.3 g, 41.9 mmol) and dichloromethane (DCM, 85 mL). Trifluoroacetic acid (TFA, 12.8 mL, 4.0 equiv., 167.6 mmol) was added slowly to the reaction mixture, which was then stirred at room temperature for 3 hours.

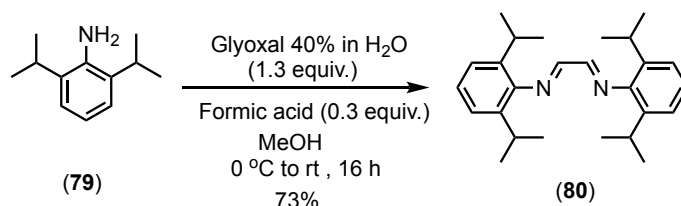
The solvent was removed under reduced pressure, and the residue was treated with H₂O (20 mL) followed by aqueous NaOH solution (1 N, 10 mL). The resulting aqueous phase was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford 2-(2-chlorophenyl)-*N*-methylethan-1-amine (**78**) as an orange-yellow oily product (5.49 g, 77% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.34 (dd, J = 7.6, 1.6 Hz, 1H), 7.23 (d, J = 7.3, 1.9 Hz, 1H), 7.21 – 7.12 (m, 2H), 3.71 (s, 1H), 2.98 (t, J = 7.0 Hz, 2H), 2.91 (t, J = 7.0 Hz, 2H), 2.50 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 136.98, 134.10, 130.85, 129.65, 127.90, 126.93, 50.94, 35.70, 33.29 ppm.

6.2.1.2 Preparation of the NHC–IPr ligand

The NHC–IPr ligand was prepared following the procedures shown in [Scheme 40\(ii\)](#).

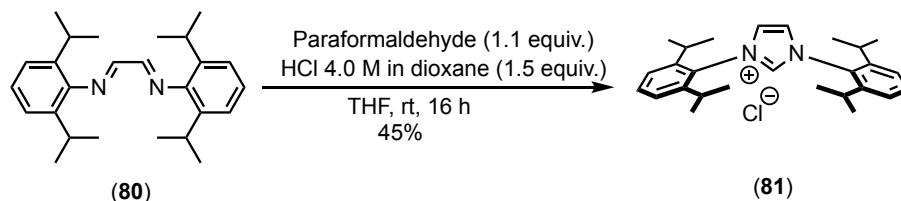
N,N'-bis(2,6-diisopropylphenyl)diazabutadiene (**80**)



In a 500 mL round-bottom flask equipped with a magnetic stir bar were added 2,6-diisopropylaniline **79** (20 mL, 2.0 equiv., 106.1 mmol) and reagent-grade methanol (100 mL). To this solution, glyoxal (40% in H₂O, 7.9 mL, 1.3 equiv., 68.9 mmol) was added, followed by formic acid (0.6 mL, 0.3 equiv., 15.9 mmol) at 0 °C. A yellow precipitate of the bisimine began to form during addition. The reaction mixture was stirred overnight at room temperature, then transferred to a –20 °C freezer for 2 hours to complete precipitation. The resulting solid was collected by vacuum filtration and washed with a small volume of cold methanol. The filtrate was concentrated, and the combined solids were recrystallized from methanol. After drying under high vacuum, the bisimine (**80**) was obtained as a bright yellow crystalline powder (14.7 g, 73% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.11 (s, 2H), 7.22 – 7.13 (m, 6H), 2.95 (hept, J = 6.9 Hz, 4H), 1.22 (d, J = 6.9 Hz, 24H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.98, 147.90, 136.60, 125.01, 123.07, 27.94, 23.28 ppm.

1,3-bis(2,6-diisoprylphenyl)imidazolium chloride (**81**)

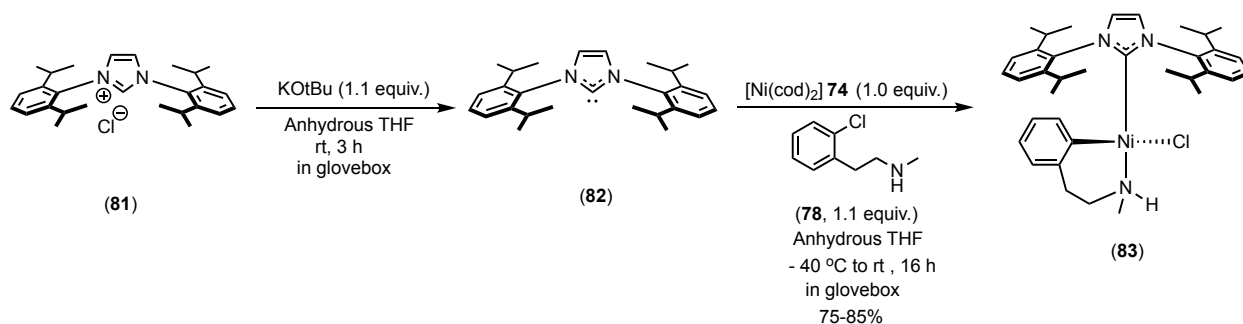


In a 200 mL round-bottom flask equipped with a magnetic stir bar were added *N,N'*-bis(2,6-diisopropylphenyl)diazabutadiene **80** (14.2 g, 1.0 equiv., 37.67 mmol) and THF (350 mL). *para*-Formaldehyde (1.24 g, 1.1 equiv., 41.44 mmol) was added in one portion, and the solution was stirred for 1 minute. HCl (4 M in dioxane, 14.1 mL, 1.5 equiv., 56.50 mmol) was then added dropwise via syringe, and the reaction mixture was stirred at room temperature overnight.

The reaction mixture was placed in a -20°C freezer for 2 hours to induce precipitation. The resulting solid was collected by filtration and triturated three times with diethyl ether/pentane (1:1), followed by two washes with pure pentane. The product was dried overnight under high vacuum to afford the imidazolium chloride salt (**81**) as an off-white solid (7.2 g, 45% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 10.14 (s, 1H), 8.14 (d, $J = 1.6$ Hz, 2H), 7.57 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 4H), 2.44 (hept, $J = 6.8$ Hz, 4H), 1.28 (d, $J = 6.8$ Hz, 12H), 1.24 (d, $J = 6.9$ Hz, 12H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.41, 138.70, 132.56, 130.27, 127.21, 125.12, 29.54, 25.16, 24.14 ppm.

6.2.1.3 Ligation of the ligands to the nickel



In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with NHC–IPr ligand (**81**) (463.60 mg, 1.0 equiv., 1.09 mmol), KO^tBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**82**) in THF, were added dropwise to a precooled (–35 °C) slurry of Ni(cod)₂ **74** (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL), which immediately turned blood-red upon addition. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine **78** (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, resulting in a color change to an orange-brown solution (Scheme 40(iii)). The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The resulting red-brown residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The red-brown oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the desired yellow solid product (**83**) (554.6 mg, 82%).

Free carbene (**82**): ¹H NMR (600 MHz, Benzene-*d*₆) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 4H), 6.61 (s, 2H), 2.95 (hept, *J* = 6.9 Hz, 4H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 7.0 Hz, 12H) ppm; ¹³C NMR (150 MHz, Benzene-*d*₆) δ 219.45, 146.29, 138.85, 129.08, 123.72, 121.59, 28.81, 24.82, 23.66 ppm.

Product (**83**): ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.32 (m, 4H), 6.99 (s, 2H), 6.73 (d, *J* = 7.0 Hz, 1H), 6.64 (t, *J* = 7.1 Hz, 1H), 6.57 (t, *J* = 7.1 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 4.02 – 3.87 (m, 1H), 3.67 – 3.51 (m, 1H), 3.06 – 2.74 (m, 3H), 2.23 (dd, *J* = 11.5, 5.4 Hz, 1H), 2.04 (dd,

$J = 10.9, 3.3$ Hz, 1H), 1.72 – 0.82 (m, 20H), 0.32 (d, $J = 5.9$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 181.19, 151.80, 143.24, 137.43, 125.57, 125.04, 124.67, 124.25, 124.07, 123.61, 123.31, 46.95, 39.25, 38.98, 29.13, 26.86, 26.54, 24.35, 23.91 ppm. MS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{36}\text{H}_{48}\text{ClN}_3\text{Ni}$, 615.2890; found, 615.2918. HRMS-ESI (m/z): $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_{36}\text{H}_{48}\text{N}_3\text{Ni}$, 580.3202; found, 580.3206. ICP-AES: 91237 ppm nickel in a 10 mg sample.

6.2.2 General procedure for C-N cross-coupling reaction

A vial equipped with a magnetic stir bar was charged with NaOtBu (86.49 mg, 0.9 mmol, 1.8 equiv.) and Ni–NHC–IPr complex **83** (15.42 mg, 5 mol%). The vial was sealed with a screw cap fitted with a septum, evacuated, and backfilled with nitrogen ($\times 2$). Anhydrous THF (1 mL) was then added via syringe. The aryl halide (0.5 mmol, 1.0 equiv.) and amine (0.75 mmol, 1.5 equiv.) were added by syringe. If either the aryl halide or amine was a solid at room temperature, it was added directly to the vial with the catalyst prior to evacuation. The reaction mixture was stirred at the specified temperature (either room temperature or 60 °C) for the designated time (1–16 h).

Upon completion of the reaction, as determined by GC-MS or when no further conversion was observed, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (unless noted otherwise) to yield product of >95% purity.

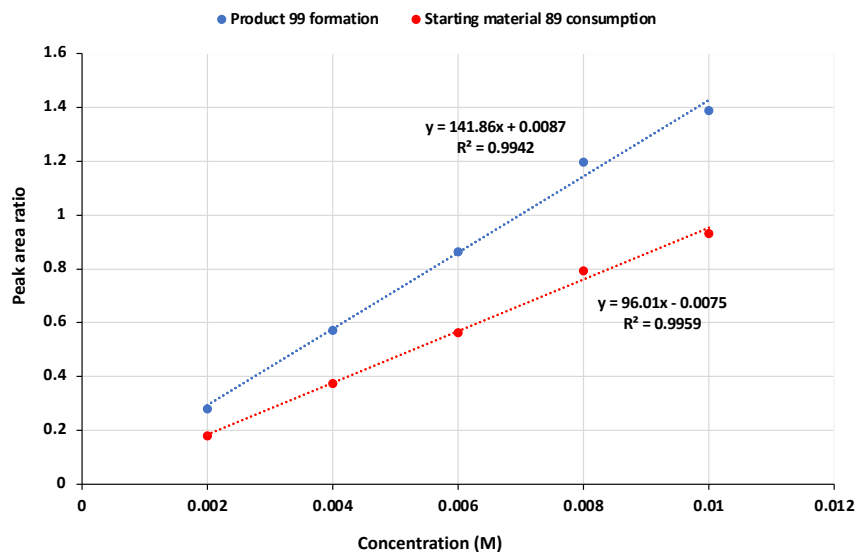
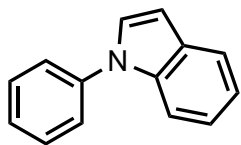


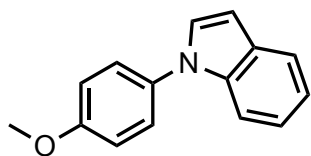
Figure 51. Calibration curve for the N-arylation of morpholine determined by GC-FID analysis (refer to Figures 17–19).

6.2.3 Spectral data



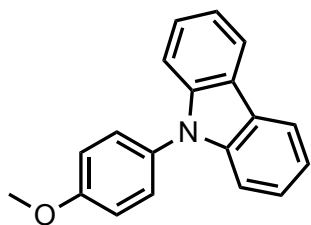
1-phenyl-1H-indole (88) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.43 (d, $J = 4.4$ Hz, 4H),

7.31 – 7.24 (m, 2H), 7.19 – 7.06 (m, 2H), 6.61 (d, $J = 3.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.95, 135.97, 129.73, 129.44, 128.07, 126.55, 124.49, 122.47, 121.25, 120.47, 110.63, 103.69 ppm.

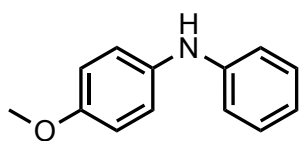


1-(4-methoxyphenyl)-1H-indole (90) Following General Coupling Procedure, the title compound was isolated as an off-white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, $J = 7.4$ Hz, 1H), 7.46 (d, $J =$

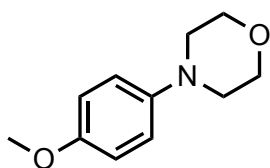
8.3 Hz, 1H), 7.41 (d, $J = 8.9$ Hz, 2H), 7.29 (d, $J = 3.2$ Hz, 1H), 7.23 – 7.14 (m, 2H), 7.04 (d, $J = 8.9$ Hz, 2H), 6.66 (d, $J = 3.2$ Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.38, 136.46, 132.98, 129.07, 128.42, 126.13, 122.27, 121.14, 120.20, 114.86, 110.50, 103.01, 55.74 ppm.



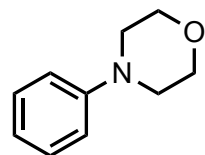
9-(4-methoxyphenyl)-9H-carbazole (97) Following General Coupling Procedure, the title compound was isolated as an off-white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, J = 7.7 Hz, 2H), 7.46 (d, J = 8.9 Hz, 2H), 7.41 (td, J = 7.6, 7.1, 1.1 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.12 (d, J = 8.9 Hz, 2H), 3.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.00, 141.51, 130.45, 128.72, 125.97, 123.24, 120.38, 119.77, 115.20, 109.83, 55.75 ppm.



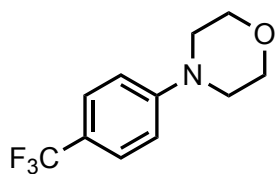
4-methoxy-N-phenylaniline (98) Following General Coupling Procedure, the title compound was isolated as an off-white solid. ^1H NMR (400 MHz, Benzene-*d*₆) δ 7.15 – 7.10 (m, 2H), 6.88 – 6.83 (dd, J = 8.9, 2.2 Hz, 2H), 6.82 – 6.76 (m, 3H), 6.76 – 6.71 (dd, J = 8.9, 2.3 Hz, 2H), 4.83 (s, 1H), 3.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, Benzene-*d*₆) δ 155.90, 145.80, 136.15, 129.58, 122.67, 119.76, 116.01, 114.96, 55.09 ppm.



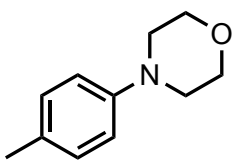
4-(4-methoxyphenyl)morpholine (99) Following General Coupling Procedure, the title compound was isolated as a white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.93 – 6.81 (m, 4H), 3.86 (d, J = 4.7 Hz, 4H), 3.77 (s, 3H), 3.06 (d, J = 4.7 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.15, 145.76, 117.98, 114.65, 67.17, 55.71, 50.99 ppm.



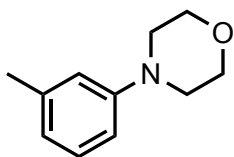
4-phenylmorpholine (107) Following General Coupling Procedure, the title compound was isolated as a pale-yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 6.94 – 6.87 (m, 3H), 3.87 (t, J = 4.7 Hz, 4H), 3.17 (t, J = 4.9 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.40, 129.33, 120.21, 115.87, 67.09, 49.54 ppm.



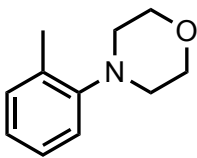
4-(4-(trifluoromethyl)phenyl)morpholine (108) Following General Coupling Procedure, the title compound was isolated as a pale-yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.87 (t, J = 4.8 Hz, 4H), 3.24 (t, J = 5.0 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.47, 126.58, 126.14, 123.45, 114.49, 66.79, 48.35 ppm.



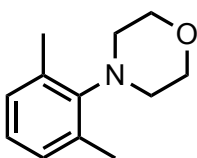
4-(*p*-tolyl)morpholine (109) Following General Coupling Procedure, the title compound was isolated as a pale-yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 3.87 (t, J = 4.7 Hz, 4H), 3.11 (t, J = 4.9 Hz, 4H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.32, 129.84, 129.71, 116.18, 67.12, 50.08, 20.56 ppm.



4-(*m*-tolyl)morpholine (110) Following General Coupling Procedure, the title compound was isolated as a pale-yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.18 (t, J = 7.7 Hz, 1H), 6.78 – 6.70 (m, 3H), 3.86 (t, J = 4.7 Hz, 4H), 3.16 (t, J = 4.9 Hz, 4H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.49, 139.04, 129.16, 121.11, 116.71, 113.02, 67.12, 49.64, 21.92 ppm.

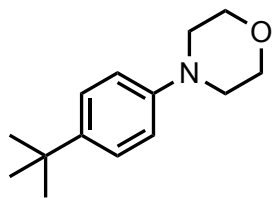


4-(*o*-tolyl)morpholine (111) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, J = 7.2 Hz, 2H), 7.08 – 6.98 (m, 2H), 3.86 (t, J = 4.7 Hz, 4H), 2.92 (t, J = 4.5 Hz, 4H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.39, 132.76, 131.30, 126.79, 123.55, 119.08, 67.59, 52.39, 18.01 ppm.

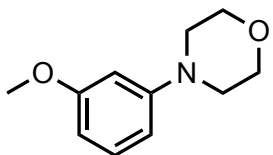


4-(2,6-dimethylphenyl)morpholine (112) Following General Coupling Procedure, the title compound was isolated as an off-white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.02 – 6.95 (m, 3H), 3.81 (t, J = 4.5 Hz, 4H), 3.11 (t, J

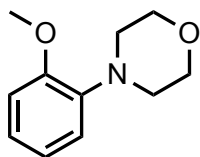
= 4.6 Hz, 4H), 2.36 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.96, 137.10, 129.20, 125.51, 68.31, 50.17, 19.75 ppm.



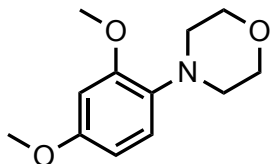
4-(4-(*tert*-butyl)phenyl)morpholine (113) Following General Coupling Procedure, the title compound was isolated as a yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.86 (t, J = 4.7 Hz, 4H), 3.14 (t, J = 4.9 Hz, 4H), 1.30 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.03, 142.95, 126.12, 115.56, 67.15, 49.73, 34.12, 31.58 ppm.



4-(3-methoxyphenyl)morpholine (114) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, J = 8.3 Hz, 1H), 6.54 (d, J = 9.3 Hz, 1H), 6.45 (d, J = 7.6 Hz, 2H), 3.85 (t, J = 4.8 Hz, 4H), 3.80 (s, 3H), 3.16 (t, J = 4.9 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.75, 152.82, 129.98, 108.59, 104.84, 102.34, 67.01, 55.31, 49.41 ppm.

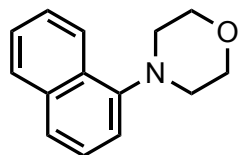


4-(2-methoxyphenyl)morpholine (115) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.02 (dt, J = 8.3, 4.5 Hz, 1H), 6.94 (d, J = 4.3 Hz, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 7.6 Hz, 2H), 3.90 (t, J = 4.6 Hz, 4H), 3.87 (s, 3H), 3.16 (t, J = 4.6 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.37, 141.24, 123.27, 121.16, 118.12, 111.42, 67.34, 55.48, 51.29 ppm.



4-(2,4-dimethoxyphenyl)morpholine (116) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.85 (d, J = 8.6 Hz, 1H), 6.49 (d, J = 2.7 Hz, 1H), 6.43 (dd, J = 8.6, 2.7 Hz, 1H), 3.88 (t, J = 4.6 Hz, 4H), 3.84 (s, 3H), 3.78 (s, 3H), 2.99 (t, J = 4.6

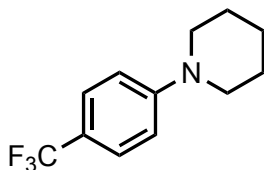
Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.37, 153.49, 135.13, 118.48, 103.49, 100.06, 67.39, 55.55, 51.81 ppm.



4-(naphthalen-1-yl)morpholine (117) Following General Coupling

Procedure, the title compound was isolated as a yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.18 (m, 1H), 7.83 (dt, J = 6.2, 3.7 Hz, 1H),

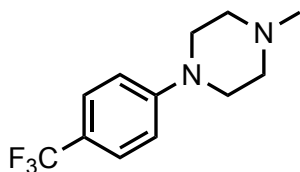
7.58 (d, J = 8.2 Hz, 1H), 7.49 (qd, J = 6.9, 3.4 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 4.00 (t, J = 4.5 Hz, 4H), 3.13 (t, J = 4.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.51, 134.94, 128.91, 128.61, 126.04, 125.99, 125.62, 123.98, 123.53, 114.83, 67.61, 53.66 ppm.



1-(4-(trifluoromethyl)phenyl)piperidine (118) Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.8

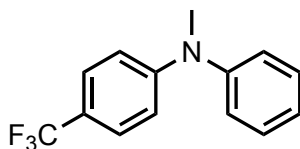
Hz, 2H), 3.28 (t, J = 5.1 Hz, 4H), 1.74 – 1.58 (m, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.94, 129.07, 126.44, 123.69, 114.71, 49.44, 25.57, 24.42 ppm.



1-methyl-4-(4-(trifluoromethyl)phenyl)piperazine (119) Following

General Coupling Procedure, the title compound was isolated as an off-white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.7 Hz,

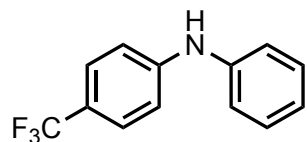
2H), 6.92 (d, J = 8.8 Hz, 2H), 3.31 (t, J = 5.0 Hz, 4H), 2.59 (t, J = 5.1 Hz, 4H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.33, 126.56, 126.20, 123.52, 114.72, 54.90, 48.00, 46.17 ppm.



N-methyl-N-phenyl-4-(trifluoromethyl)aniline (120) Following

General Coupling Procedure, the title compound was isolated as a pale-yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.35 (m, 4H),

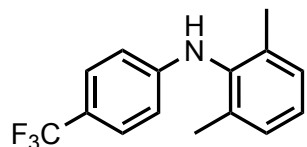
7.23 – 7.17 (m, 3H), 6.86 (d, $J = 8.7$ Hz, 2H), 3.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 151.63, 147.88, 129.93, 126.36, 125.42, 125.08, 123.68, 114.95, 40.32 ppm.



***N*-phenyl-4-(trifluoromethyl)aniline (121)** Following General

Coupling Procedure, the title compound was isolated as an off-white powder. ^1H NMR (400 MHz, Chloroform- d) δ 7.48 (d, $J = 8.5$ Hz, 2H),

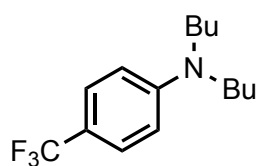
7.34 (td, $J = 7.5, 1.9$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 2H), 7.06 (td, $J = 8.5, 2.4$ Hz, 3H), 5.92 (s, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 146.91, 141.28, 129.68, 126.81, 126.09, 123.40, 123.08, 120.19, 115.47 ppm.



2,6-dimethyl-*N*-(4-(trifluoromethyl)phenyl)aniline (122) Following

General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.39 (d, $J = 8.5$ Hz, 2H), 7.17

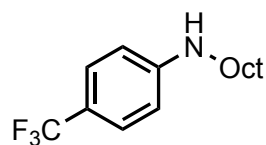
– 7.12 (m, 3H), 6.50 (d, $J = 8.4$ Hz, 2H), 5.42 (s, 1H), 2.21 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 149.25, 136.96, 136.63, 128.84, 126.88, 126.78, 126.38, 123.70, 112.56, 18.40 ppm.



***N,N*-dibutyl-4-(trifluoromethyl)aniline (123)** Following General

Coupling Procedure, the title compound was isolated as a colorless oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.41 (d, $J = 8.8$ Hz, 2H), 6.63 (d, $J = 8.8$

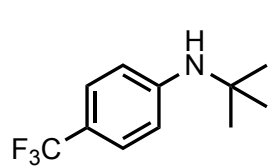
Hz, 2H), 3.30 (t, $J = 7.6$ Hz, 4H), 1.58 (p, $J = 7.6$ Hz, 4H), 1.37 (sext, $J = 7.5$ Hz, 4H), 0.97 (t, $J = 7.3$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 150.30, 129.44, 126.63, 124.08, 110.68, 50.87, 29.34, 20.44, 14.11 ppm.



***N*-(4-(trifluoromethyl)phenyl)octanamide (124)** Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.39 (d, $J = 8.5$ Hz, 2H), 6.58 (d, $J = 8.6$

Hz, 2H), 3.96 (s, 1H), 3.13 (t, $J = 7.1$ Hz, 2H), 1.63 (p, $J = 7.1$ Hz, 2H), 1.46 – 1.25 (m, 10H), 0.9 (t, $J = 7.1$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 150.99, 131.47, 126.69, 123.86, 111.78, 43.67, 31.96, 29.49, 29.39, 28.49, 27.23, 22.80, 14.24 ppm.

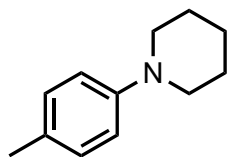


***N*-(*tert*-butyl)-4-(trifluoromethyl)aniline (125)** Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H

NMR (400 MHz, Chloroform- d) δ 7.37 (d, $J = 8.6$ Hz, 2H), 6.69 (d, $J = 8.6$

Hz, 2H), 3.98 (s, 1H), 1.39 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 149.69, 131.17, 126.46, 123.83, 114.48, 51.39, 29.83 ppm.

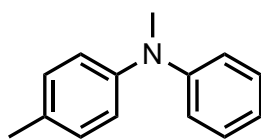


1-(*p*-tolyl)piperidine (126) Following General Coupling Procedure, the title

compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ

7.08 (d, $J = 8.3$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 3.11 (t, $J = 5.4$ Hz, 4H),

2.28 (s, 3H), 1.73 (p, $J = 5.7$ Hz, 4H), 1.57 (p, $J = 5.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 150.41, 129.65, 128.86, 117.09, 51.46, 26.09, 24.43, 20.55 ppm.

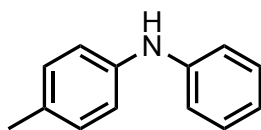


***N*,4-dimethyl-*N*-phenylaniline (127)** Following General Coupling

Procedure, the title compound was isolated as a blood red oil. ^1H NMR (400

MHz, Chloroform- d) δ 7.26 – 7.21 (m, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.03

– 6.97 (m, 2H), 6.96 – 6.90 (m, 2H), 6.90 – 6.83 (m, 1H), 3.29 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 149.51, 146.73, 132.18, 130.04, 129.15, 122.70, 119.91, 118.32, 40.47, 20.89 ppm.

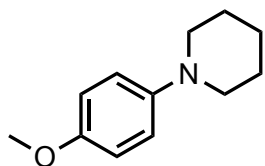


4-methyl-*N*-phenylaniline (128) Following General Coupling Procedure,

the title compound was isolated as an off-white solid. ^1H NMR (400 MHz,

Benzene- d_6) δ 7.15 – 7.06 (m, 2H), 6.93 (d, $J = 8.1$ Hz, 2H), 6.88 – 6.78

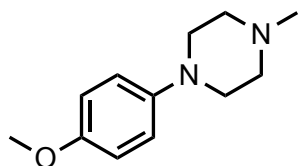
(m, 5H), 4.95 (s, 1H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 144.50, 140.90, 130.75, 130.10, 129.56, 120.52, 119.37, 117.29, 20.77 ppm.



1-(4-methoxyphenyl)piperidine (129) Following General Coupling

Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 6.92 (dd, $J = 9.1, 2.3$ Hz, 2H), 6.83 (dd, $J = 9.1, 2.4$

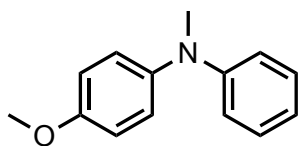
Hz, 2H), 3.77 (s, 3H), 3.03 (t, $J = 5.4$ Hz, 4H), 1.73 (p, $J = 5.7$ Hz, 4H), 1.55 (p, $J = 5.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 153.68, 147.04, 118.87, 114.43, 55.68, 52.43, 26.27, 24.32 ppm.



1-(4-methoxyphenyl)-4-methylpiperazine (101) Following General

Coupling Procedure, the title compound was isolated as an off-white solid. ^1H NMR (400 MHz, Chloroform- d) δ 6.90 (dd, $J = 9.2, 2.4$ Hz,

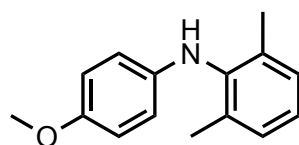
2H), 6.84 (dd, $J = 9.2, 2.5$ Hz, 2H), 3.77 (s, 3H), 3.11 (t, $J = 4.9$ Hz, 4H), 2.60 (t, $J = 5.0$ Hz, 4H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 153.95, 145.79, 118.34, 114.58, 55.71, 55.39, 50.68, 46.22 ppm.



4-methoxy-N-methyl-N-phenylaniline (130) Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.25 – 7.18 (m, 2H), 7.11 (dd, $J = 9.0,$

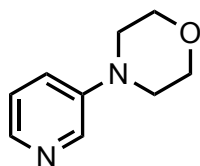
2.3 Hz, 2H), 6.91 (dd, $J = 9.0, 2.3$ Hz, 2H), 6.84 – 6.76 (m, 3H), 3.83 (s, 3H), 3.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 156.40, 149.87, 142.37, 129.04, 126.33, 118.46, 115.86, 114.90, 55.63, 40.60 ppm.



N-(4-methoxyphenyl)-2,6-dimethylaniline (131) Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.12 (d, $J = 7.4$ Hz, 2H), 7.05 (dd, J

= 8.5, 6.3 Hz, 1H), 6.76 (dd, J = 8.9, 2.2 Hz, 2H), 6.51 (dd, J = 8.9, 2.1 Hz, 2H), 5.04 (s, 1H), 3.76 (s, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 152.86, 140.24, 139.38, 135.01, 128.71, 125.14, 115.41, 114.84, 55.83, 18.50 ppm.

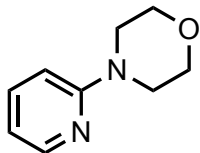


4-(pyridin-3-yl)morpholine (136) Following General Coupling Procedure, the

title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-

d) δ 8.29 (s, 1H), 8.11 (s, 1H), 7.19 – 7.15 (m, 2H), 3.86 (t, J = 4.8 Hz, 4H), 3.17

(t, J = 4.9 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 147.05, 141.04, 138.24, 123.68, 122.29, 66.77, 48.69 ppm.

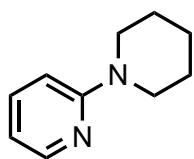


4-(pyridin-2-yl)morpholine (137) Following General Coupling Procedure, the

title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d)

δ 8.20 (dd, J = 6.1, 1.2 Hz, 1H), 7.49 (ddd, J = 8.8, 7.2, 2.0 Hz, 1H), 6.68 – 6.60

(m, 2H), 3.82 (t, J = 4.8 Hz, 4H), 3.49 (t, J = 5.0 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 159.72, 148.07, 137.65, 113.94, 107.07, 66.89, 45.74 ppm.

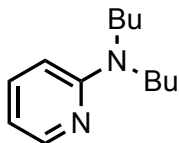


2-(piperidin-1-yl)pyridine (138) Following General Coupling Procedure, the

title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d)

δ 8.17 (dd, J = 6.1, 1.2 Hz, 1H), 7.43 (ddd, J = 8.8, 7.1, 2.0 Hz, 1H), 6.64 (d, J =

8.6 Hz, 1H), 6.54 (dd, J = 6.8, 5.2 Hz, 1H), 3.52 (s, 4H), 1.64 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 159.87, 148.04, 137.41, 112.50, 107.22, 46.45, 25.65, 24.87 ppm.



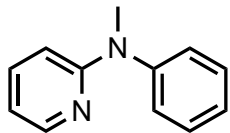
***N,N*-dibutylpyridin-2-amine (139)** Following General Coupling Procedure, the

title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ

8.12 (dd, J = 4.9, 1.3 Hz, 1H), 7.37 (ddd, J = 8.9, 7.1, 2.0 Hz, 1H), 6.48 – 6.38 (m,

2H), 3.42 (t, J = 7.6 Hz, 4H), 1.57 (p, J = 7.5 Hz, 4H), 1.36 (sext, J = 7.5 Hz, 4H), 0.95 (t, J = 7.3

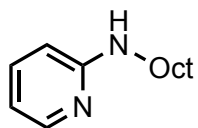
Hz, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.09, 148.19, 136.96, 110.76, 105.64, 48.53, 29.96, 20.49, 14.19 ppm.



***N*-methyl-*N*-phenylpyridin-2-amine (140)** Following General Coupling

Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, J = 5.1, 2.0 Hz, 1H), 7.44 – 7.36 (m, 2H),

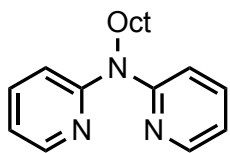
7.35 – 7.16 (m, 4H), 6.61 (ddd, J = 7.0, 5.0, 0.7 Hz, 1H), 6.54 (d, J = 8.6 Hz, 1H), 3.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.97, 147.91, 146.97, 136.66, 129.81, 126.44, 125.55, 113.23, 109.29, 38.52 ppm.



***N*-octylpyridin-2-amine (141)** Following General Coupling Procedure, the title

compound was isolated as an off-white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, J = 5.1, 1.8 Hz, 1H), 7.41 (ddd, J = 8.8, 7.3, 1.9 Hz, 1H), 6.54 (ddd,

J = 7.1, 5.1, 0.8 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 4.56 (s, 1H), 3.23 (q, J = 6.9 Hz, 2H), 1.61 (p, J = 7.1 Hz, 2H), 1.44 – 1.20 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.02, 148.14, 137.65, 112.70, 106.45, 42.48, 31.96, 29.70, 29.51, 29.40, 27.22, 22.80, 14.24.

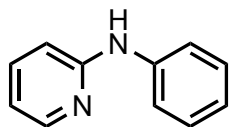


***N*-octyl-*N*-(pyridin-2-yl)pyridin-2-amine (142)** Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR

(400 MHz, Chloroform-*d*) δ 8.33 (dd, J = 6.2, 3.6 Hz, 2H), 7.50 (ddd, J = 9.0,

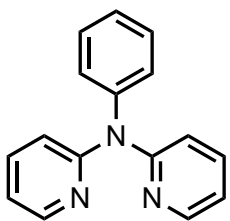
7.3, 2.0 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.83 (dd, J = 7.1, 5.0 Hz, 2H), 4.16 (t, 2H), 1.68 (p, J = 7.6 Hz, 2H), 1.40 – 1.16 (m, 10H), 0.86 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.66, 148.43, 137.17, 116.90, 114.85, 48.54, 31.96, 29.55, 29.42, 28.44, 27.20, 22.78, 14.23 ppm.



N-phenylpyridin-2-amine (143) Following General Coupling Procedure, the

title compound was isolated as a yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, J = 3.9, 1.1 Hz, 1H), 7.49 (ddd, J = 8.9, 7.2, 1.9 Hz,

1H), 7.33 (d, J = 4.5 Hz, 4H), 7.11 – 6.99 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.74 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 6.64 (s, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.11, 148.52, 140.58, 137.84, 129.44, 122.98, 120.48, 115.19, 108.37 ppm.



N-phenyl-N-(pyridin-2-yl)pyridin-2-amine (144) Following General

Coupling Procedure, the title compound was isolated as a white solid. ^1H

NMR (400 MHz, Chloroform-*d*) δ 8.34 (dd, J = 3.6, 1.9 Hz, 2H), 7.55 (ddd, J = 8.4, 7.4, 2.0 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.25 – 7.16 (m, 3H), 6.98 (d,

J = 8.3 Hz, 2H), 6.92 (dd, J = 7.2, 5.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.26, 148.61, 145.05, 137.69, 129.85, 127.43, 125.82, 118.25, 117.08 ppm.

6.3 Experimental procedures for chapter 3

6.3.1 General procedure for C-N cross-coupling reaction using photoredox catalysis

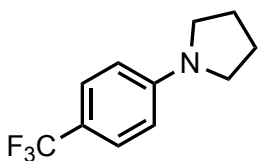
A vial equipped with a magnetic stir bar was charged with DABCO (201.92 mg, 1.8 equiv.) and Ni–NHC–IPr complex **83** (30.85 mg, 0.05 equiv.). The vial was sealed with a screw cap fitted with a septum, evacuated, and backfilled with nitrogen ($\times 3$). Anhydrous DMA (2.7 mL) was then added via syringe. The aryl halide (1.0 mmol, 1.0 equiv.) and amine (1.5 equiv.) and a solution of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (224.39 μg , 0.0002 equiv.) in DMA (1 mL) were added by syringe. If either the aryl halide or amine was a solid at room temperature, it was added directly to the vial with the catalyst prior to evacuation. Then the vial was placed 6 cm in front of one blue LED (Kessil-PR160L, 456 nm), and irradiated either under fan cooling (to maintain ambient temperature) or without fan cooling (to heat to approximately 35–40 °C). Upon completion of the

reaction, as determined by GC-MS or when no further conversion was observed, the mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (unless noted otherwise) to yield product of >95% purity.

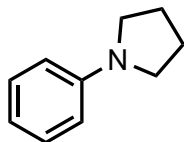
6.3.2 Experimental procedures for catalyst deactivation screening

Following the general coupling procedure, two parallel reactions were conducted under identical conditions. After 6 hours, both reactions had reached completion, at which point they were stopped. One reaction mixture was purified by flash chromatography, affording the desired product in 89% yield (191.9 mg). To the second reaction mixture, an additional 1.0 mmol of 4-bromobenzotrifluoride, 1.5 mmol of pyrrolidine, and 1.8 mmol of DABCO were added. The reaction was then allowed to proceed under the same conditions for an additional 6 hours. After purification by flash chromatography, the yield was 91% (391.7 mg).

6.3.3 Spectral data

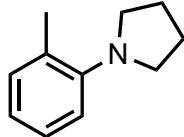


1-(4-(trifluoromethyl)phenyl)pyrrolidine (148) Following General Coupling Procedure, the title compound was isolated as a white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 8.7 Hz, 2H), 6.55 (d, J = 8.7 Hz, 2H), 3.32 (t, J = 6.6 Hz, 4H), 2.03 (p, J = 3.3 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.88, 126.82, 126.50, 124.14, 110.99, 47.69, 25.62 ppm.

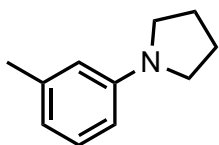


1-phenylpyrrolidine (149) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, J = 7.9 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 8.3 Hz, 2H), 3.32 (t,

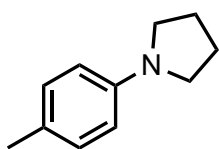
$J = 6.5$ Hz, 4H), 2.03 (p, $J = 3.5$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 148.10, 129.25, 115.48, 111.76, 47.70, 25.60 ppm.



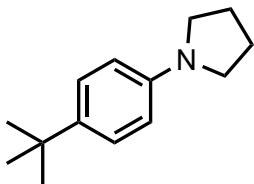
1-(*o*-tolyl)pyrrolidine (150) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.14 (ddd, $J = 7.3, 6.1, 1.8$ Hz, 2H), 6.91 (dd, $J = 8.5, 1.2$ Hz, 1H), 6.86 (td, $J = 7.4, 1.2$ Hz, 1H), 3.21 (t, $J = 6.5$ Hz, 4H), 2.35 (s, 3H), 1.96 (p, $J = 3.3$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 149.54, 131.77, 128.84, 126.38, 120.35, 115.87, 51.13, 25.07, 20.70 ppm.



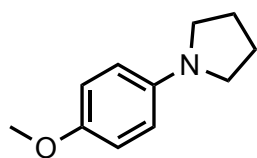
1-(*m*-tolyl)pyrrolidine (151) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.15 (dd, $J = 8.8, 7.5$ Hz, 1H), 6.52 (d, $J = 7.4$ Hz, 1H), 6.46 – 6.38 (m, 2H), 3.30 (t, $J = 6.6$ Hz, 4H), 2.35 (s, 3H), 2.01 (p, $J = 3.4$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 148.20, 138.90, 129.11, 116.48, 112.50, 109.03, 47.72, 25.58, 21.98 ppm.



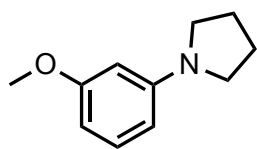
1-(*p*-tolyl)pyrrolidine (152) Following General Coupling Procedure, the title compound was isolated as a white solid. ^1H NMR (400 MHz, Chloroform- d) δ 7.05 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 8.4$ Hz, 2H), 3.27 (t, $J = 6.6$ Hz, 4H), 2.26 (s, 3H), 2.00 (p, $J = 3.3$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 146.25, 129.75, 124.56, 111.91, 47.96, 25.55, 20.42 ppm.



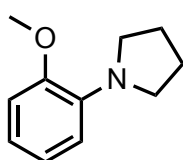
1-(4-(*tert*-butyl)phenyl)pyrrolidine (153) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.19 (dd, $J = 8.7, 2.0$ Hz, 2H), 6.46 (d, $J = 8.6$ Hz, 2H), 3.19 (t, $J = 6.5$ Hz, 4H), 2.00 (p, $J = 3.2$ Hz, 4H), 1.22 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 146.02, 138.07, 126.04, 111.45, 47.83, 33.87, 31.74, 25.61 ppm.



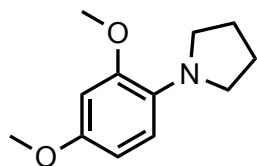
1-(4-methoxyphenyl)pyrrolidine (154) Following General Coupling Procedure, the title compound was isolated as a white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.85 (dd, J = 9.0, 2.3 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 3.24 (t, J = 6.0 Hz, 4H), 1.99 (p, J = 3.3 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.90, 143.36, 115.16, 112.73, 56.16, 48.38, 25.52 ppm.



1-(3-methoxyphenyl)pyrrolidine (155) Following General Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 (t, J = 8.1 Hz, 1H), 6.24 (ddd, J = 16.6, 8.1, 2.2 Hz, 2H), 6.14 (t, J = 2.3 Hz, 1H), 3.82 (s, 3H), 3.29 (t, J = 6.6 Hz, 4H), 2.00 (p, J = 3.3 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.85, 149.39, 129.91, 105.05, 100.59, 98.04, 55.20, 47.77, 25.57 ppm.



1-(2-methoxyphenyl)pyrrolidine (156) Following General Coupling Procedure, the title compound was isolated as a pink oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.93 – 6.78 (m, 4H), 3.85 (s, 3H), 3.30 (t, J = 6.6 Hz, 4H), 1.95 (p, J = 3.3 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.58, 140.08, 121.21, 119.70, 115.55, 111.81, 55.68, 50.56, 24.81 ppm.



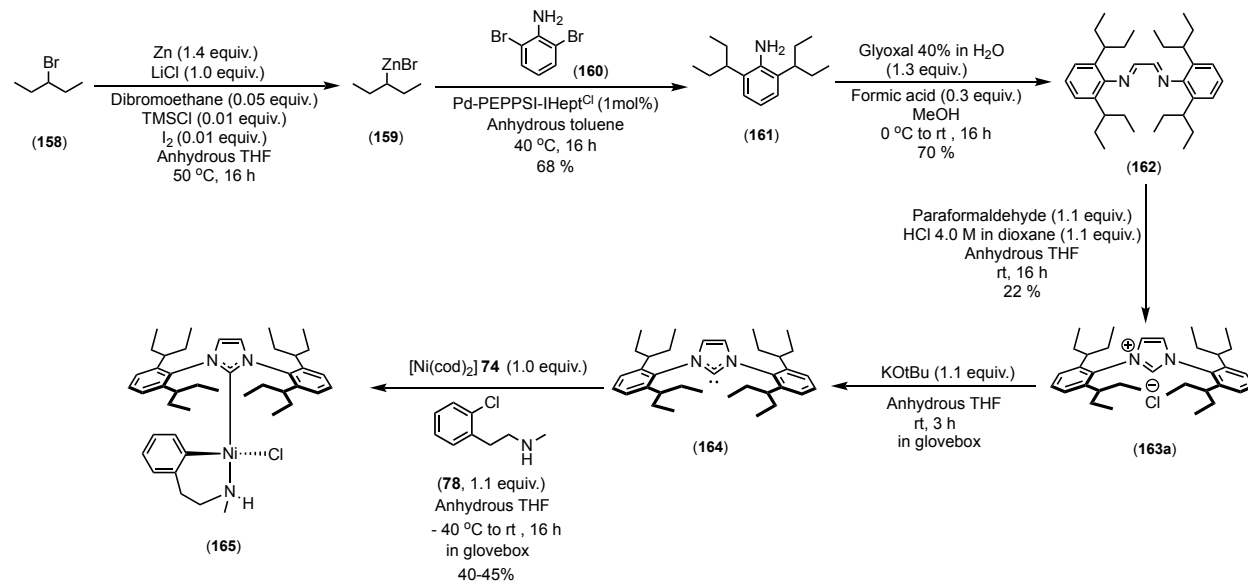
1-(2,4-dimethoxyphenyl)pyrrolidine (157) Following General Coupling Procedure, the title compound was isolated as a blood red oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.77 (d, J = 8.4 Hz, 1H), 6.49 (d, J = 2.7 Hz, 1H), 6.41 (dd, J = 8.6, 2.7 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.17 (t, J = 5.9 Hz, 4H), 1.93 (p, J = 3.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.62, 152.32, 134.01, 116.17, 103.45, 100.11, 55.67, 55.48, 50.95, 24.33 ppm.

6.4 Experimental procedures for chapter 4

6.4.1 Catalyst preparation

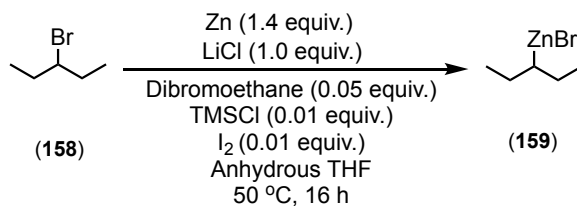
6.4.1.1 Preparation of the Ni–NHC–IPent precatalyst

The Ni–NHC–IPent (**165**) precatalyst was prepared following below procedures (Scheme 41):



Scheme 41. General procedure for synthesis Ni–NHC–IPent (**165**) precatalyst

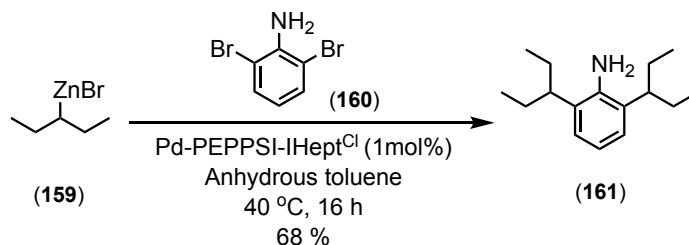
3-pentylzinc bromide (**159**)



In a glovebox, a 1 L round-bottom flask equipped with a magnetic stir bar was charged with LiCl (13.65 g, 322.02 mmol) and zinc dust (29.48 g, 450.83 mmol) after which it sealed with a rubber septum and moved outside the glovebox. Under high vacuum, the flask was heated with a heat gun for 15 min with occasional stirring every 3 min. The flask was back filled with nitrogen and allowed to come to room temperature. After repeating the process once more, THF (322 mL) and the reaction mixture was heated at 60 °C for 5 min. Then the 1,2-dibromoethane (1.4 mL, 16.1

mmol) were added slowly via syringe and the reaction mixture stirred at 60 °C for 15 min. After cooling to rt, TMSCl (0.41 mL, 3.22 mmol) and a solution of iodine (817.32 mg, 3.22 mmol) in THF (1 mL) was added via syringe. The reaction mixture was heated at 60 °C for 20 min and then cooled to rt. Then 3-bromopentane **158** (40 mL, 322.02 mmol) was added dropwise over 5 min and the flask was heated at 50 °C under a constant flow of nitrogen with stirring for 20 – 24 h at which time it was cooled to rt and allowed to stand without stirring for 24 h. The concentration of the organozinc solution (**159**) was 0.63 M and determined by iodometric titration of the resulting supernatant using Knochel's procedure.¹⁸⁴

2,6-Di(3-pentyl)aniline (**161**)

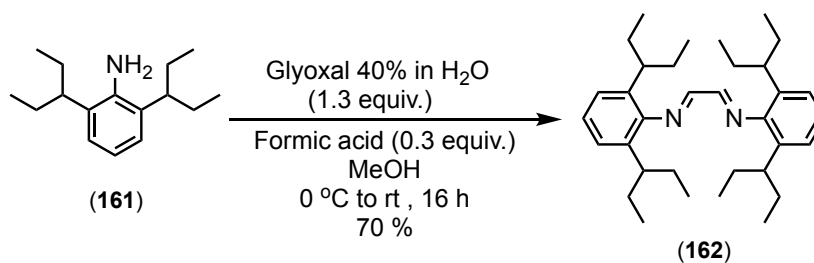


An oven-dried 2 L round-bottom flask equipped with a stir bar was added 2,6-dibromoaniline **160** (23.08 g, 92.0 mmol, 1.0 equiv.) followed by Pd-PEPPSI-IHeptCl precatalyst (447.94 mg, 1.0 mol%) and sealed with a rubber septum. Then the flask was evacuated and refilled with nitrogen 3 times. Anhydrous toluene (460 mL) was cannulated into the flask and the mixture was stirred for 5 min. 3-Pentylzinc bromide (**159**) in THF (350.5 mL, 220.8 mmol, 2.4 equiv., 0.63 M) was added via syringe at room temperature. Once the addition was complete (ca. 30 min) the flask was immersed in a pre-heated 40 °C oil bath and the reaction mixture was stirred overnight. The reaction mixture was cooled to room temperature and concentrated to ca. 100 mL in a rotary evaporator at which time the solution was diluted with 300 mL of ethyl acetate and washed with water (5 × 200 mL) and brine (100 mL). The organic phase was dried over anhydrous magnesium

sulfate, filtered, and concentrated in vacuo to provide a dark-brown oil. The crude product was then passed through a 5-cm pad of silica gel washing with pentane. The filtrate was concentrated to yield a light-brown oil **161** (14.6 g, 68 %).

^1H NMR (300 MHz, Chloroform-*d*) δ 6.90 (d, J = 7.2 Hz, 2H), 6.78 (t, J = 6.8 Hz, 1H), 3.64 (s, 2H), 2.49 (p, J = 8.0, 2H), 1.81 – 1.50 (m, 8H), 0.84 (t, J = 7.4 Hz, 12H) ppm.

N,N'-Bis(di(3-pentyl))diazabutadiene (**162**)

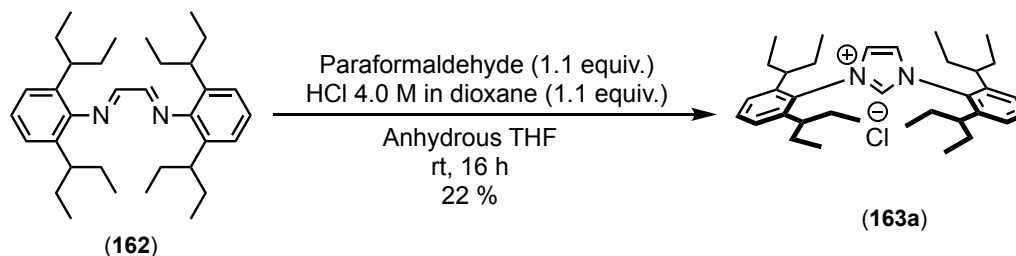


In a 500 mL round-bottom flask equipped with a magnetic stir bar were added 2,6-di(3-pentyl)aniline **161** (14.6 g, 2.0 equiv., 62.55 mmol) and reagent-grade methanol (62 mL). To this solution, glyoxal (40% in H₂O, 4.7 mL, 1.3 equiv., 40.66 mmol) was added, followed by formic acid (0.35 mL, 0.3 equiv., 9.38 mmol) at 0 °C. A yellow precipitate of the bisimine began to form during addition. The reaction mixture was stirred overnight at room temperature, then transferred to a –20 °C freezer for 2 hours to complete precipitation. The resulting solid was collected by vacuum filtration and washed with a small volume of cold methanol. The filtrate was concentrated, and the combined solids were recrystallized from methanol. After drying under high vacuum, the bisimine (**162**) was obtained as a bright yellow crystalline powder (10.6 g, 70% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.02 (s, 2H), 7.14 (t, J = 7.5 Hz, 2H), 7.07 (d, J = 7.5 Hz, 4H), 2.50 (p, J = 7.8 Hz, 4H), 1.72 – 1.48 (m, 16H), 0.80 (t, J = 7.3 Hz, 24H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 164.02, 151.06, 133.98, 124.94, 124.03, 42.67, 29.06, 12.34 ppm.

1,3-Bis(2,6-di(3-pentyl)phenyl)imidazolium chloride (163a)

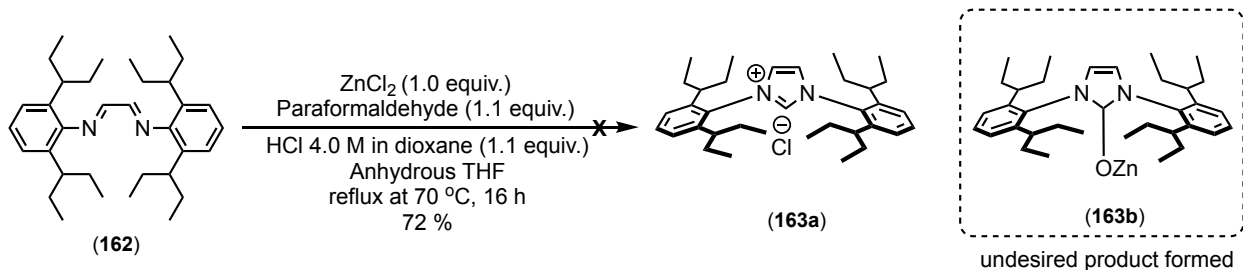
Protocol 1 (without ZnCl₂):



In a 200 mL round-bottom flask equipped with a magnetic stir bar were added N,N'-bis(di(3-pentyl))diazabutadiene **162** (10.6 g, 1.0 equiv., 21.68 mmol) and THF (45 mL). Paraformaldehyde (0.716 g, 1.1 equiv., 23.85 mmol) was added in one portion, and the solution was stirred for 1 minute. HCl (4 M in dioxane, 8.3 mL, 1.5 equiv., 32.52 mmol) was then added dropwise via syringe, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was placed in a -20 °C freezer for 2 hours to induce precipitation. The resulting solid was collected by filtration and triturated three times with diethyl ether/pentane (1:1), followed by two washes with pure pentane. The product was dried overnight under high vacuum to afford the imidazolium chloride salt (**163a**) as an **off-white** solid (2.56 g, 22 % yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 8.30 (s, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 1.94 (p, *J* = 7.0 Hz, 4H), 1.79 – 1.56 (m, 16H), 0.83 (t, *J* = 7.3 Hz, 12H), 0.76 (t, *J* = 7.3 Hz, 12H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 142.65, 136.32, 132.81, 132.11, 128.39, 125.48, 43.62, 29.30, 28.57, 12.60, 12.43 ppm.

Protocol 2 (with ZnCl₂):

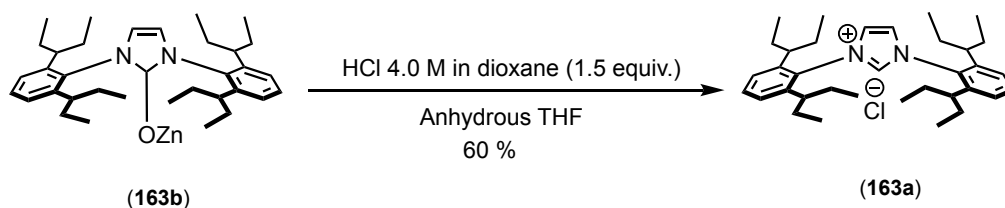


A 2-neck 150 mL round bottom flask equipped with a stir bar and reflux condenser was oven dried and cooled under nitrogen. To this was added N,N'-bis(di(3-pentyl))diazabutadiene **162** (4.4 g, 1.0 equiv. 9.0 mmol) in one portion under positive nitrogen pressure and the flask was evacuated and refilled with nitrogen (x3). Anhydrous THF (45 mL) was added via syringe into to the flask and the stirred mixture was heated to 70°C in an oil bath. ZnCl₂ (1.23 g, 1.0 equiv., 9.0 mmol) was added quickly in one portion under positive nitrogen pressure and the mixture stirred at the same temperature for 5 min. Paraformaldehyde (297.26 mg, 1.1 equiv., 9.9 mmol) was added in one portion under positive nitrogen pressure and the solution stirred for 1 min. HCl (4M in Dioxane, 3.4 mL, 1.5 equiv., 13.5 mmol) was added dropwise via a syringe and the mixture stirred overnight at 70 °C. The reaction mixture was cooled to room temperature, transferred to a 200 mL round bottom flask, and concentrated in a rotary evaporator. After diluting with 300 mL of EtOAc and washing with water (3 × 100 mL) and brine (100 mL), the combined aqueous phases were extracted with EtOAc (100 mL). The combined organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated to provide dark brown solid. The crude product was triturated (3 times) with Et₂O/Pentane (1:1) and pentane (2 times). The solids were dried overnight under high vacuum to yield the undesired imidazolium product **163b** (3.5 g, 72%) as **brown** solid.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.65 (s, 2H), 7.88 (s, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 10.6 Hz, 4H), 2.03 (p, *J* = 6.9 Hz, 4H), 1.80 – 1.53 (m, 16H), 0.89 (t, *J* = 7.3 Hz, 12H), 0.75

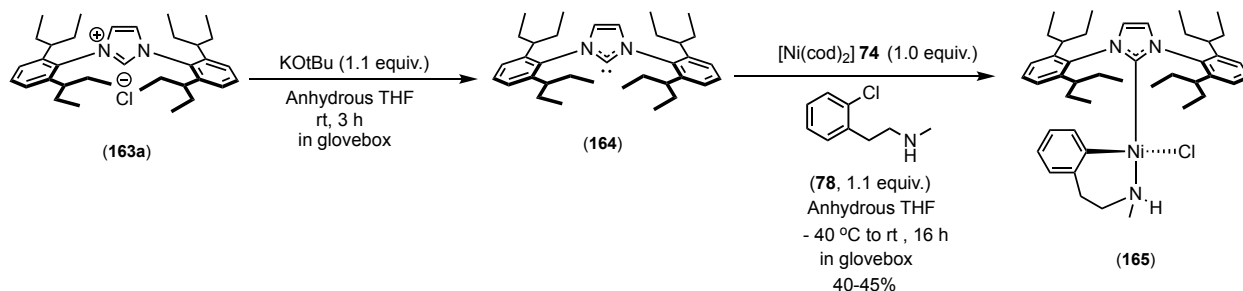
(t, $J = 7.3$ Hz, 12H) ppm; ^{13}C NMR (125 MHz, Chloroform- d) δ 142.90, 133.72, 133.03, 131.75, 129.89, 125.27, 43.33, 29.51, 28.43, 12.56, 12.33 ppm.

Conversion of imidazolium intermediate (**163b**) to imidazolium chloride salt (**163a**)



The undesired brown imidazolium compound (**163b**) was converted to the desired off-white imidazolium chloride salt (**163a**) by treatment with an excess of hydrochloric acid. To a 100 mL round-bottom flask equipped with a magnetic stir bar were added imidazolium compound **163b** (3.27 g, 1.0 equiv., 5.6 mmol) and anhydrous THF (40 mL). HCl (4 M in dioxane, 2.1 mL, 1.5 equiv., 8.4 mmol) was added dropwise via syringe, and the reaction mixture was stirred at room temperature overnight. The mixture was then concentrated under reduced pressure using a rotary evaporator. The resulting residue was diluted with ethyl acetate (50 mL) and washed sequentially with water (3×20 mL) and brine (20 mL). The combined aqueous layers were back-extracted with EtOAc (100 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated to afford an off-white solid. The resulting solid was triturated three times with a 1:1 mixture of diethyl ether and pentane, followed by two washes with pure pentane. The resulting product was dried overnight under high vacuum to yield the imidazolium chloride salt **163a** as an off-white solid (1.82 g, 60% yield).

Ligation of the NHC–IPent (**163a**) ligand to the nickel



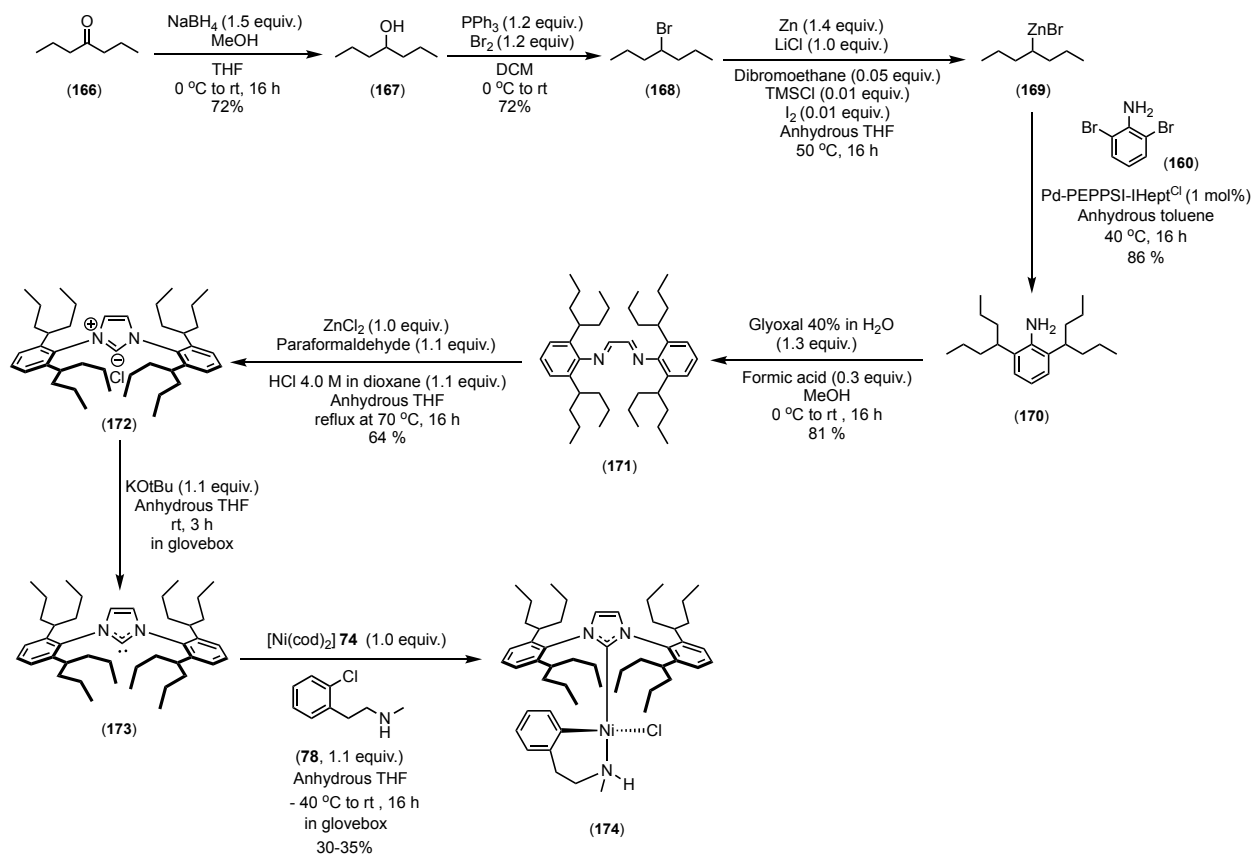
In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with 1,3-Bis(2,6-di(3-pentyl)phenyl)imidazolium chloride **163a** (585.99 mg, 1.0 equiv., 1.09 mmol), KOtBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**164**) in THF, were added dropwise to a precooled (–35 °C) slurry of Ni(cod)₂ (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL), which immediately turned blood-red upon addition. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine (**72**) (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, resulting in a color change to an orange-yellow solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The resulting red-brown residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The red-brown oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the desired yellow solid product (**165**) (350.7 mg, 44%).

Free carbene (**164**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.32 (t, $J = 7.7$ Hz, 2H), 7.11 (d, $J = 7.7$ Hz, 4H), 6.73 (s, 2H), 2.60 (p, $J = 7.4$ Hz, 4H), 1.79 – 1.43 (m, 16H), 0.93 (t, $J = 7.4$ Hz, 12H), 0.83 (t, $J = 7.4$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 221.11, 143.70, 141.77, 128.60, 124.20, 122.58, 42.41, 29.54, 29.30, 12.89, 12.26 ppm.

Product (**165**): ^1H NMR (400 MHz, Benzene- d_6) δ 7.32 – 7.26 (m, 4H), 6.86 – 6.78 (m, 2H), 6.58 (s, 2H), 6.49 (d, $J = 6.6$ Hz, 1H), 3.69 – 3.52 (m, 2H), 3.10 (q, $J = 7.4$ Hz, 1H), 2.99 (q, $J = 7.3$ Hz, 1H), 2.89 – 2.47 (m, 3H), 2.41 – 2.34 (m, 1H), 2.20 – 2.11 (m, 4H), 1.84 – 1.16 (m, 21H), 1.07 (d, $J = 6.2$ Hz, 4H), 0.98 (t, $J = 7.2$ Hz, 2H), 0.93 – 0.56 (m, 16H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 178.46, 152.11, 143.20, 137.01, 124.58, 124.10, 123.94, 123.09, 47.03, 43.19, 41.05, 39.41, 38.97, 29.72, 28.79, 13.59, 12.96 ppm. HRMS-ESI (m/z): $[\text{M-Cl}]^+$ calcd. for $\text{C}_{44}\text{H}_{64}\text{N}_3\text{Ni}$, 692.4454; found, 692.4451. ICP-AES: 73055 ppm nickel in a 10 mg sample.

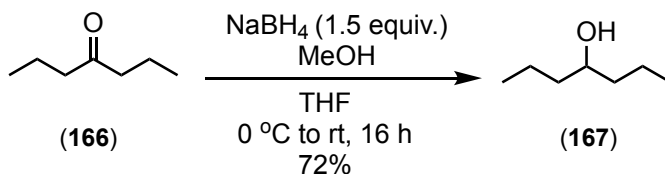
6.4.1.2 Preparation of the Ni–NHC–IHept precatalyst

The Ni–NHC–IHept (**174**) precatalyst was prepared following below procedures (Scheme 42):



Scheme 42. General procedure for synthesis Ni–NHC–IHept (**174**) precatalyst

Heptan-4-ol (**167**)

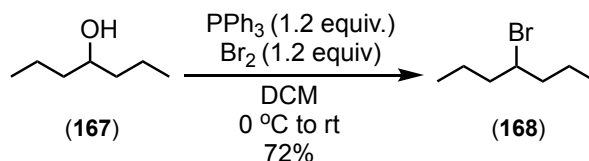


In air, a 3 L round-bottom flask equipped with a magnetic stir bar was charged with NaBH_4 (52.5 g, 1.39 mol) in THF (1 L), followed by the addition of heptan-4-one **166** (105.62 g, 0.925 mol). The flask was cooled to 0 °C, and MeOH (200 mL) was added slowly with dropping funnel while stirring. The reaction mixture was then stirred at room temperature for 16 hours. The reaction was

quenched with 2 M aqueous HCl, and the organic components were extracted with Et₂O (1 L). The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The resulting crude oil was passed through a plug of silica gel, eluting with pentane. Concentration of the eluent afforded the product, compound **167**, as a colorless oil (78.0 g, 72% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 3.60 (s, 1H), 1.51 – 1.28 (m, 9H), 0.91 (t, *J* = 7.0 Hz, 6H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 71.52, 39.81, 18.94, 14.22 ppm.

4-bromoheptane (**168**)

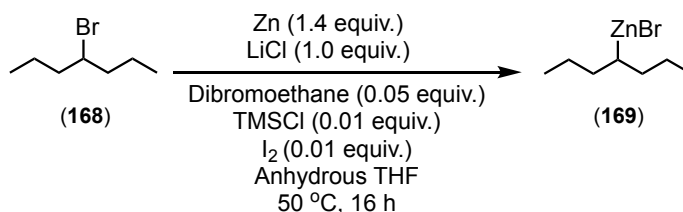


In air, a three-neck 3 L round-bottom flask equipped with a magnetic stir bar was charged with triphenylphosphine (210.57 g, 802.80 mmol) in DCM (1.3 L) and cooled to 0 °C. Bromine (41.1 mL, 802.80 mmol) was added dropwise via a pressure-equalizing dropping funnel (caution: exothermic), and the resulting suspension was stirred for 1 hour at 0 °C. Heptan-4-ol **167** (77.74 g, 669.0 mmol) was then added in one portion, and the reaction mixture was allowed to warm to room temperature and stirred for 16 hours. The reaction was quenched with water (500 mL) and stirred for an additional 30 minutes at room temperature. The mixture was transferred to a 3 L separatory funnel and extracted. The organic phase was washed sequentially with water (2 × 300 mL) and brine (200 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was triturated with pentane (3 × 300 mL), and the resulting solid was discarded. The remaining organic solution was concentrated and further purified by passage through a silica gel plug, eluting with pentane. Final concentration of the eluate at 55–60 °C

afforded the 4-bromoheptane (**168**), as a colorless oil (86.5 g, 72%). (Note: alkene side-products may be removed at this temperature by azeotrope with chloroform.)

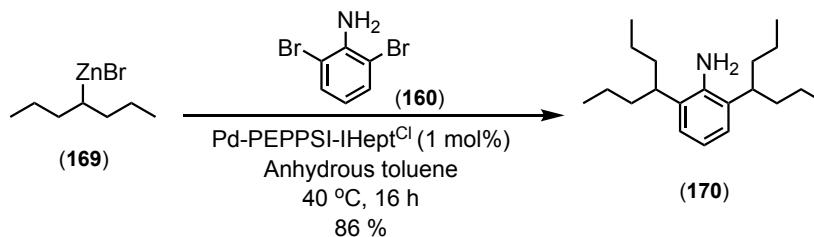
^1H NMR (500 MHz, Chloroform-*d*) δ 4.05 (tt, J = 8.7, 4.6 Hz, 1H), 1.79 (m, 4H), 1.65 – 1.37 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 58.42, 41.41, 20.95, 13.62 ppm.

4-heptylzinc bromide (**169**)



In a glovebox, a 1 L round-bottom flask equipped with a magnetic stir bar was charged with LiCl (13.65 g, 322.02 mmol) and zinc dust (29.47 g, 450.80 mmol) after which it sealed with a rubber septum and moved outside the glovebox. Under high vacuum, the flask was heated with a heat gun for 15 min with occasional stirring every 3 min. The flask was back filled with nitrogen and allowed to come to room temperature. After repeating the process once more, THF (322 mL) and the reaction mixture was heated at 60 °C for 5 min. Then the 1,2-dibromoethane (1.4 mL, 16.1 mmol) were added slowly via syringe and the reaction mixture stirred at 60 °C for 15 min. After cooling to rt, TMSCl (0.41 mL, 3.22 mmol) and a solution of iodine (817.26 mg, 3.22 mmol) in THF (1 mL) was added via syringe. The reaction mixture was heated at 60 °C for 20 min and then cooled to rt. Then 4-bromoheptane **168** (57.67 g, 322.0 mmol) was added dropwise over 5 min and the flask was heated at 50 °C under a constant flow of nitrogen with stirring for 20 – 24 h at which time it was cooled to rt and allowed to stand without stirring for 24 h. The concentration of the organozinc solution (**169**) was 0.74 M and determined by iodometric titration of the resulting supernatant using Knochel's procedure.¹⁸⁴

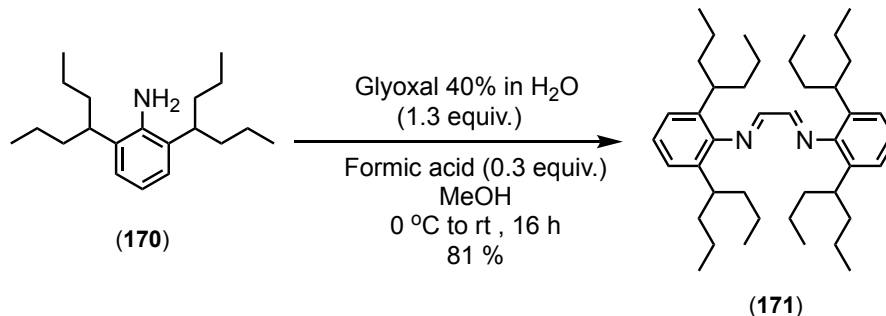
2,6-Di(4-heptyl)aniline (**170**)



An oven-dried 2 L round-bottom flask equipped with a stir bar was added 2,6-dibromoaniline **160** (25.09 g, 100.0 mmol, 1.0 equiv.) followed by Pd-PEPPSI-IHept^{Cl} precatalyst (486.39 mg, 1.0 mol%) and sealed with a rubber septum. Then the flask was evacuated and refilled with nitrogen 3 times. Anhydrous toluene (500 mL) was cannulated into the flask and the mixture was stirred for 5 min. 4-Heptylzinc bromide (**169**) in THF (324.3 mL, 240.0 mmol, 2.4 equiv., 0.74 M) was added via syringe at room temperature. Once the addition was complete (ca. 30 min) the flask was immersed in a pre-heated 40 °C oil bath and the reaction mixture was stirred overnight. The reaction mixture was cooled to room temperature and concentrated to ca. 100 mL in a rotary evaporator at which time the solution was diluted with 300 mL of ethyl acetate and washed with water (5 × 200 mL) and brine (100 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to provide a dark-brown oil. The crude product was then passed through a 5-cm pad of silica gel washing with pentane. The filtrate was concentrated to yield a light-brown oil **170** (25.1 g, 86 %).

¹H NMR (500 MHz, Chloroform-*d*) δ 6.91 (d, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 7.6 Hz, 1H), 3.63 (s, 2H), 2.66 (p, *J* = 8.0, 2H), 1.71 – 1.48 (m, 8H), 1.33 – 1.19 (m, 8H), 0.87 (t, *J* = 7.3 Hz, 12H) ppm;
¹³C NMR (125 MHz, Chloroform-*d*) δ 142.25, 130.80, 123.98, 118.57, 38.36, 23.12, 20.90, 14.48 ppm.

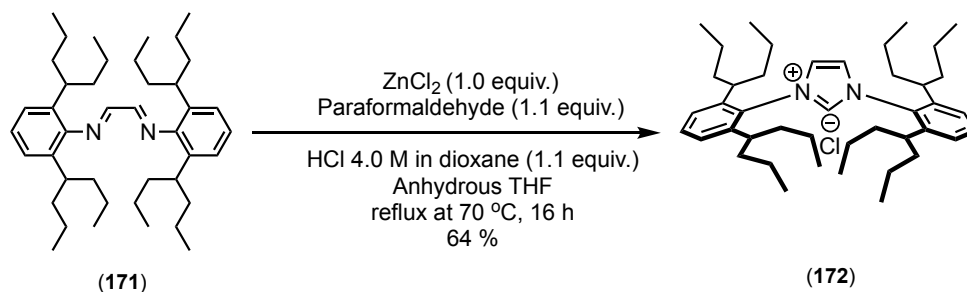
N,N'-Bis(di(4-heptyl)diazabutadiene (171)



In a 500 mL round-bottom flask equipped with a magnetic stir bar were added 2,6-di(4-heptyl)aniline **170** (25.1 g, 2.0 equiv., 86.7 mmol) and reagent-grade methanol (87 mL). To this solution, glyoxal (40% in H₂O, 6.5 mL, 1.3 equiv., 56.36 mmol) was added, followed by formic acid (0.49 mL, 0.3 equiv., 13.0 mmol) at 0 °C. A yellow precipitate of the bisimine began to form during addition. The reaction mixture was stirred overnight at room temperature, then transferred to a -20 °C freezer for 2 hours to complete precipitation. The resulting solid was collected by vacuum filtration and washed with a small volume of cold methanol. The filtrate was concentrated, and the combined solids were recrystallized from methanol. After drying under high vacuum, the bisimine (**171**) was obtained as a bright yellow crystalline powder (21.1 g, 81 % yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.99 (s, 2H), 7.12 (t *J* = 6.4 Hz, 2H), 7.07 (d, *J* = 6.9 Hz, 4H), 2.67 (p, *J* = 8.0 Hz, 4H), 1.62 – 1.43 (m, 16H), 1.26 – 1.10 (m, 16H), 0.83 (t, *J* = 7.3 Hz, 24H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 163.89, 150.68, 134.50, 124.94, 123.98, 39.24, 38.61, 20.91, 14.44 ppm.

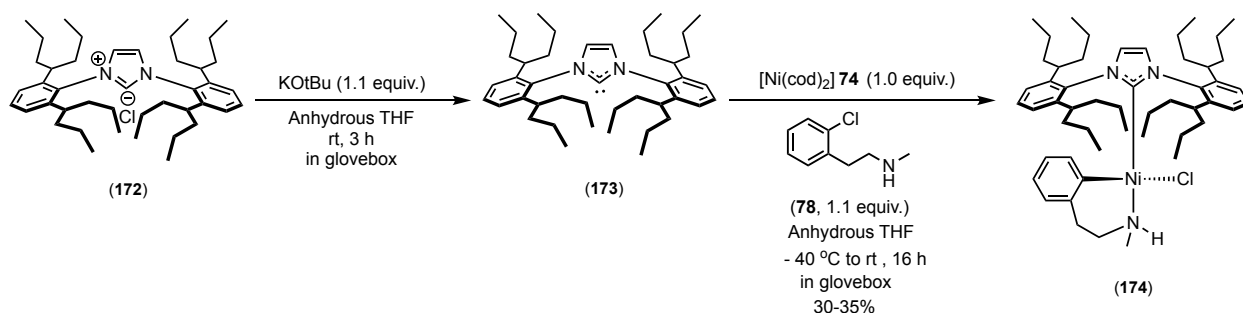
1,3-Bis(2,6-di(4-heptyl)phenyl)imidazolium chloride (**172**)



A 2-neck 250 mL round bottom flask equipped with a stir bar and reflux condenser was oven dried and cooled under nitrogen. To this was added N,N'-bis(di(4-heptyl))diazabutadiene **171** (7.0 g, 1.0 equiv. 11.65 mmol) in one portion under positive nitrogen pressure and the flask was evacuated and refilled with nitrogen (x3). Anhydrous THF (58 mL) was added via syringe into to the flask and the stirred mixture was heated to 70°C in an oil bath. ZnCl₂ (1.59 g, 1.0 equiv., 11.65 mmol) was added quickly in one portion under positive nitrogen pressure and the mixture stirred at the same temperature for 5 min. p-Formaldehyde (384.78 mg, 1.1 equiv., 12.82 mmol) was added in one portion under positive nitrogen pressure and the solution stirred for 1 min. HCl (4M in Dioxane, 4.4 mL, 1.5 equiv., 17.48 mmol) was added dropwise via a syringe and the mixture stirred overnight at 70 °C. The reaction mixture was cooled to room temperature, transferred to a 250 mL round bottom flask, and concentrated in a rotary evaporator. After diluting with 300 mL of EtOAc and washing with water (3 × 100 mL) and brine (100 mL), the combined aqueous phases were extracted with EtOAc (100 mL). The combined organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated to provide dark brown solid. The crude product was triturated (3 times) with Et₂O/Pentane (1:1) and pentane (2 times). The solids were dried overnight under high vacuum to yield the imidazolium chloride salt (**172**) as an **off-white** solid (4.9 g, 64 % yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.92 (s, 2H), 7.56 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 3.3 Hz, 4H), 2.17 – 2.06 (m, 4H), 1.72 – 1.46 (m, 16H), 1.37 – 1.28 (m, 4H), 1.20 – 0.97 (m, 12H), 0.87 (t, J = 7.3 Hz, 12H), 0.83 (t, J = 7.3 Hz, 12H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 143.35, 133.92, 132.30, 131.91, 129.65, 125.30, 40.62, 39.60, 38.49, 21.46, 21.06, 14.67, 14.42 ppm.

Ligation of the NHC–IHept (**172**) ligand to the nickel



In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with 1,3-Bis(2,6-di(4-heptyl)phenyl)imidazolium chloride **172** (708.38 mg, 1.0 equiv., 1.09 mmol), KO^tBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**173**) in THF, were added dropwise to a precooled (−35 °C) slurry of Ni(cod)₂ (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL), which immediately turned blood-red upon addition. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine (**78**) (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, resulting in a color change to an orange-yellow solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The

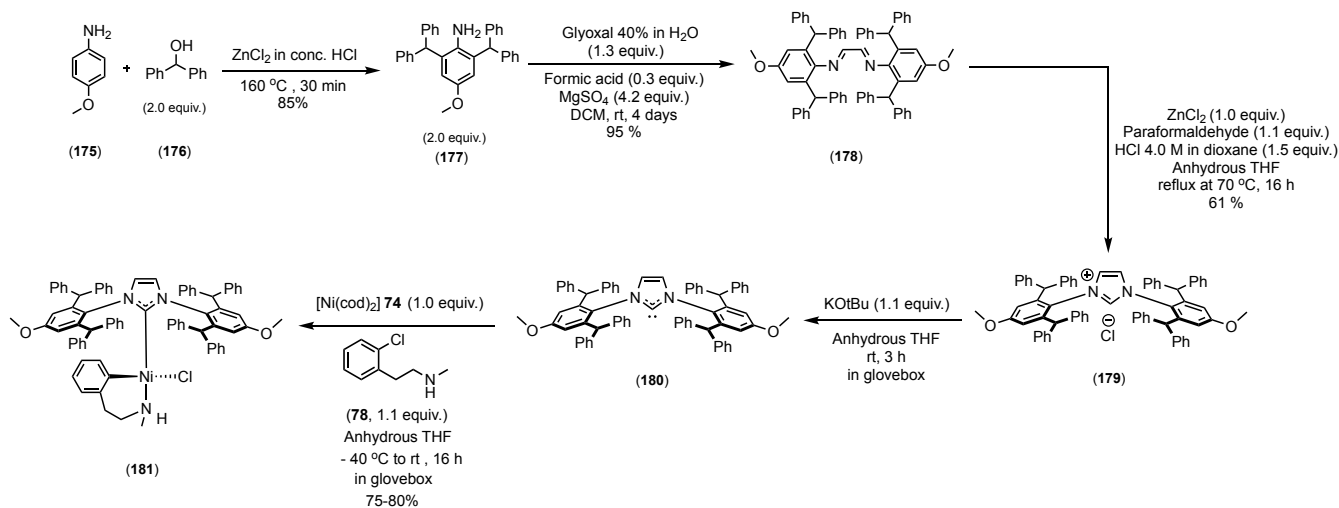
resulting red-brown residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The red-brown oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the desired yellow solid product (**174**) (305.1 mg, 33%).

Free carbene (**173**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.34 (t, $J = 7.7$ Hz, 2H), 7.17 (d, $J = 2.1$ Hz, 4H), 6.72 (s, 2H), 2.77 (p, $J = 7.2$ Hz, 4H), 1.77 – 1.52 (m, 16H), 1.50 – 1.45 (m, 4H), 1.33 – 1.20 (m, 12H), 0.87 (t, $J = 7.3$ Hz, 12H), 0.84 (t, $J = 7.2$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 220.22, 143.94, 140.73, 137.54, 128.98, 125.35, 123.91, 122.34, 39.81, 39.08, 21.27, 20.80, 14.63, 14.35 ppm.

Product (**174**): ^1H NMR (400 MHz, Benzene- d_6) δ 7.43 – 7.18 (m, 7H), 6.98 (d, $J = 7.9$ Hz, 1H), 6.79 (q, $J = 7.0$ Hz, 3H), 6.49 (d, $J = 6.7$ Hz, 1H), 4.04 – 0.28 (m, 68H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 178.54, 152.03, 143.53, 143.14, 137.02, 123.98, 123.86, 123.25, 47.15, 40.88, 40.27, 39.50, 39.06, 38.66, 21.62, 21.44, 14.94 ppm. HRMS-ESI (m/z): $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_{52}\text{H}_{80}\text{N}_3\text{Ni}$, 804.5706; found, 804.5719. ICP-AES: 63293 ppm nickel in a 10 mg sample.

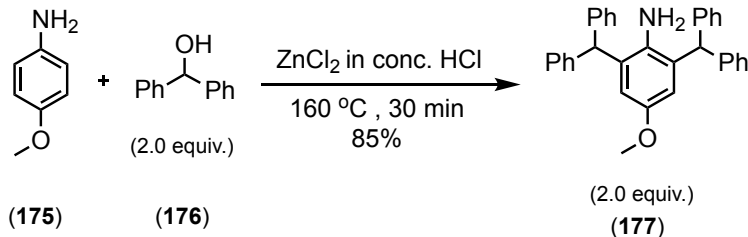
6.4.1.3 Preparation of the Ni–NHC–IPr*OMe precatalyst

The Ni–NHC–IPr*OMe (**181**) precatalyst was prepared following below procedures (Scheme 43):



Scheme 43. General procedure for synthesis Ni–NHC–IPr*OMe (**181**) precatalyst

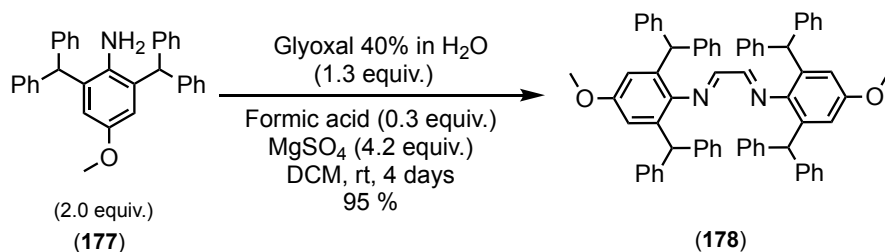
2,6-Bis(diphenylmethyl)-4-methoxyaniline (**177**)



A 250 mL round-bottom flask was loaded with p-anisidine **175** (7.45 g, 60 mmol, 1.0 equiv.) and diphenylmethanol **176** (22.3 g, 12 mmol, 2.0 equiv.) and heated to 160 °C. The eutectic homogeneous liquid was then treated with a premade solution of anhydrous zinc chloride (4.04 g, 30 mmol, 0.5 equiv.) in conc. hydrochloric acid (37% in H₂O, 5.1 mL, 60 mmol, 1.0 equiv.) (exothermic + intense bubbling). The reaction darkened and got more and more viscous until it turned completely solid within 30 min. The reaction was placed under high vacuum at 160 °C for 15 min before the crude solid was dissolved in hot DCM (150 mL). The DCM layer was washed with water (3 × 200 mL), then dried over anhydrous Na₂SO₄. The solvent was evaporated, and the resulting purple viscous oil was dissolved in the minimum amount of hot toluene. Crystallization was initiated by addition of pentane, and the process was repeated until no more crystals formed. The pure desired aniline (**177**) was obtained as a white crystalline solid (23.2 g, 84%).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 10H), 7.25 – 7.18 (m, 4H), 7.14 – 7.05 (m, 8H), 6.20 (s, 2H), 5.52 (s, 2H), 3.42 (s, 3H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 142.57, 129.64, 128.67, 126.86, 114.55, 55.27, 52.59 ppm.

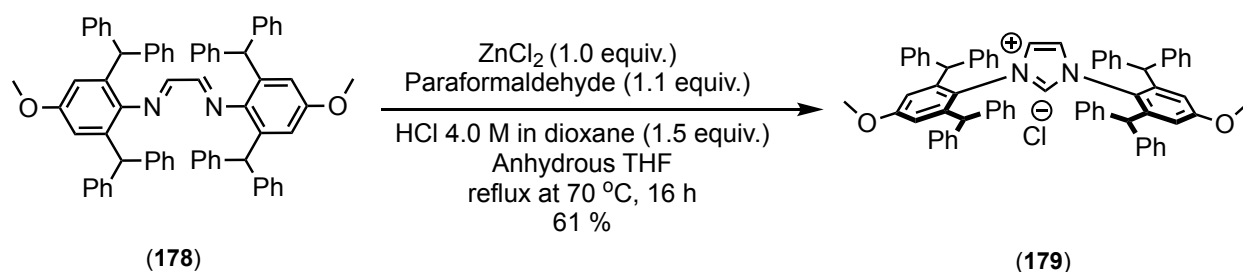
N,N'-Bis(2,6-bis(diphenylmethyl)-p-anisidyl)diazabutadiene (**178**)



A solution of aniline **177** (7.43 g, 16.3 mmol, 2.0 equiv.) in regular DCM (180 mL) was treated with anhydrous magnesium sulfate (4.12 g, 34.23 mmol, 4.2 equiv.), followed by an aqueous solution of glyoxal (40% in H₂O, 1.2 mL, 10.6 mmol, 1.3 equiv.) and formic acid (0.1 mL, 2.44 mmol, 0.3 equiv.). The reaction was stirred at room temperature until complete consumption of the starting aniline (± 4 days). The magnesium sulfate was filtered off, and the filtrate was concentrated under vacuum to afford a brownish solid. The crude solid was recrystallized from boiling toluene to provide the pure bisimine (**178**) as a bright yellow solid (7.2 g, 95 %).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.09 (m, 26H), 7.04 – 6.96 (m, 16H), 6.43 (s, 4H), 5.28 (s, 4H), 3.52 (s, 6H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 164.27, 156.31, 143.69, 142.92, 133.88, 129.59, 128.43, 126.55, 114.30, 55.18, 51.35 ppm.

IPr*OMe•HCl (**179**)

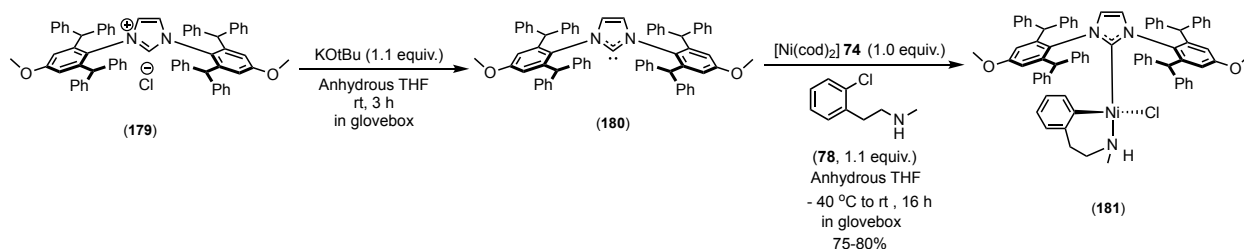


A 2-neck 500 mL round bottom flask equipped with a stir bar and reflux condenser was oven dried and cooled under nitrogen. To this was added N,N'-Bis(2,6-bis(diphenylmethyl)-p-anisidyl)diazabutadiene **178** (7.19 g, 7.7 mmol, 1.0 equiv.) in one portion under positive nitrogen

pressure and the flask was evacuated and refilled with nitrogen (x3). Anhydrous THF (260 mL) was added via syringe into to the flask and the stirred mixture was heated to 70°C in an oil bath. Anhydrous ZnCl₂ (1.05 g, 7.7 mmol, 1.0 equiv.) was added quickly in one portion under positive nitrogen pressure and the mixture stirred at the same temperature for 5 min. p-Formaldehyde (254.32 mg, 8.47 mmol, 1.1 equiv.) was added in one portion under positive nitrogen pressure and the solution stirred for 1 min. HCl (4.0 M in dioxane, 2.89 mL, 11.55 mmol, 1.50 equiv.) was added dropwise via a syringe and the mixture stirred overnight at 70 °C. The reaction mixture was cooled to room temperature, transferred to a 500 mL round bottom flask, and concentrated in a rotary evaporator. After diluting with 300 mL of EtOAc and washing with water (3 × 100 mL) and brine (100 mL), the combined aqueous phases were extracted with EtOAc (100 mL). The combined organic phase was dried over anhydrous magnesium sulfate, filtered and partially evaporated under reduced pressure until the formation of a white solid, and the remaining solution was diluted in pentane (300 mL). The off-white solid was isolated by filtration and triturated (3 times) with Et₂O/Pentane (1:1) and pentane (2 times). The solids were dried overnight under high vacuum to yield the imidazolium chloride salt (**179**) as an **off-white** solid (4.6 g, 61 % yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 12.94 (s, 1H), 7.33 – 7.16 (m, 18H), 7.21 – 7.10 (m, 16H), 6.82 – 6.80 (m, 8H), 6.46 (s, 4H), 5.40 (s, 2H), 5.30 (s, 4H), 3.51 (s, 6H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 160.93, 142.81, 142.53, 141.85, 130.19, 129.29, 128.82, 128.70, 127.11, 125.42, 123.57, 115.76, 55.34, 51.69 ppm.

Ligation of the NHC– IPr*OMe (179) ligand to the nickel



In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with IPr*OMe•HCl **179** (1.07 g, 1.0 equiv., 1.09 mmol), KOtBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**180**) in THF, were added dropwise to a precooled (–35 °C) slurry of Ni(cod)₂ (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL), which immediately turned blood-red upon addition. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine (**78**) (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, resulting in a color change to an orange-yellow solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The resulting red-brown residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The red-brown oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the desired yellow solid product (**181**) (994.0 mg, 77 %).

Free carbene (**180**): ¹H NMR (600 MHz, Benzene-*d*₆) δ 7.34 (d, *J* = 7.6 Hz, 8H), 7.07 – 6.89 (m, 32H), 6.90 (s, 4H), 6.01 (s, 4H), 5.76 (s, 2H), 3.09 (s, 6H) ppm; ¹³C NMR (150 MHz, Benzene-

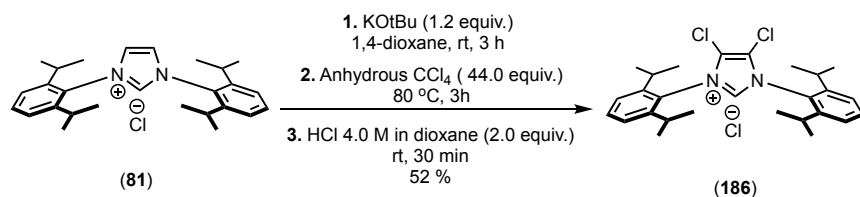
d_6) δ 220.95, 159.64, 144.84, 143.75, 143.56, 137.90, 133.97, 130.18, 129.90, 129.33, 126.56, 125.70, 122.70, 114.88, 54.66, 51.76 ppm.

Product (**181**): ^1H NMR (500 MHz, Chloroform- d) δ 7.75 (s, 1H), 7.60 (dd, $J = 12.5, 7.7$ Hz, 4H), 7.23 – 6.94 (m, 21H), 6.91 (t, $J = 7.0$ Hz, 6H), 6.88 – 6.83 (m, 3H), 6.78 (t, $J = 6.8$ Hz, 1H), 6.72 (t, $J = 2.5$ Hz, 2H), 6.65 (d, $J = 7.2$ Hz, 1H), 6.63 – 6.57 (m, 3H), 6.53 (s, 1H), 6.43 – 6.37 (m, 2H), 6.20 (d, $J = 7.5$ Hz, 3H), 4.97 (s, 1H), 4.75 – 4.64 (m, 2H), 4.20 (d, $J = 2.0$ Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.55 (s, 1H), 3.39 – 3.36 (m, 1H), 3.23 – 3.17 (m, 1H), 3.06 – 2.94 (m, 1H), 2.41 (dd, $J = 12.8, 4.7$ Hz, 1H), 1.51 (d, $J = 6.3$ Hz, 5H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 159.84, 159.60, 147.56, 145.42, 145.08, 145.01, 144.94, 144.76, 144.57, 144.49, 144.33, 144.10, 143.44, 142.80, 132.28, 131.54, 131.26, 130.06, 129.85, 129.51, 129.33, 129.12, 128.98, 126.23, 55.79, 54.42, 54.31, 52.29, 52.13, 51.95, 51.46, 50.85, 38.93 ppm. HRMS-ESI (m/z): $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_{78}\text{H}_{68}\text{N}_3\text{NiO}_2$, 1136.4665; found, 1136.4646. ICP-AES: 34857 ppm nickel in a 10 mg sample.

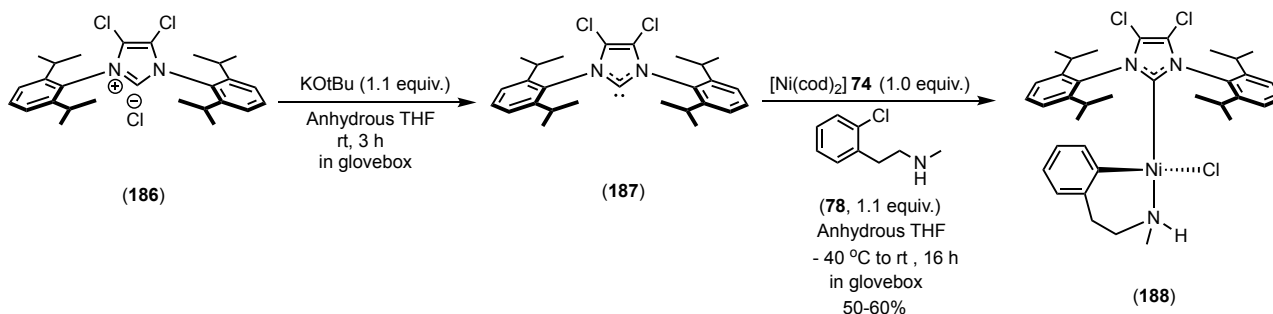
6.4.1.4 Preparation of the Ni–NHC–IPr^{Cl} precatalyst

The Ni–NHC–IPr^{Cl} (**188**) precatalyst was prepared following below procedures (Scheme 44):

(i) Backbone chlorination of NHC-IPr ligand

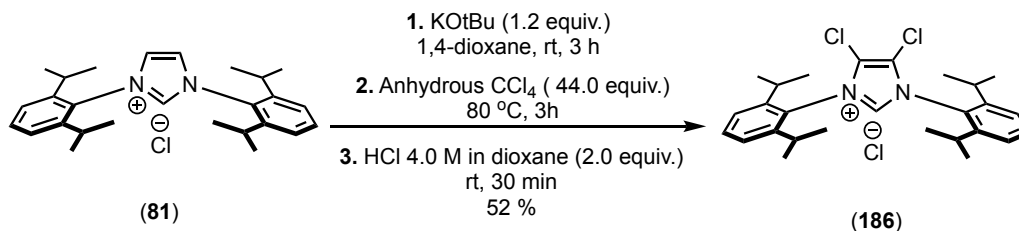


(ii) Ligation of the ligands to the nickel



Scheme 44. General procedure for synthesis Ni–NHC–IPr^{Cl} (**188**) precatalyst

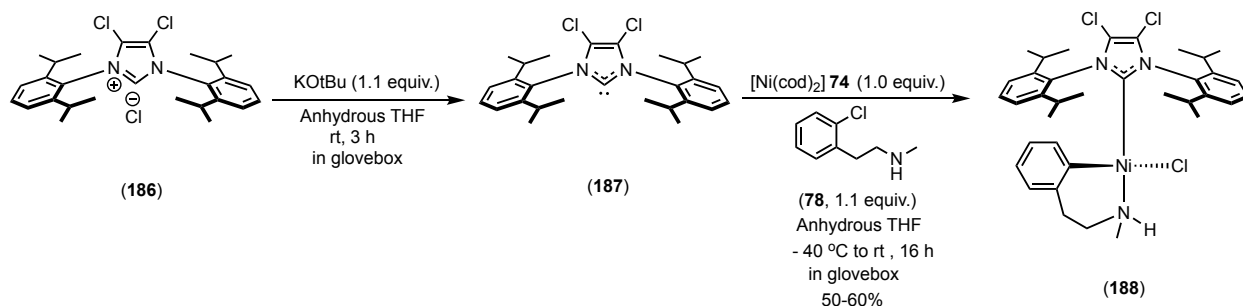
4,5-dichloro-1,3-bis(2,6-diisoprylphenyl)imidazolium chloride (**186**)



An oven-dried 250 mL round bottom flask equipped with a stir bar was charged with KOtBu (2.22 g, 1.2 equiv., 19.8 mmol) and 1,3-bis(2,6-diisoprylphenyl)imidazolium chloride **81** (7.01 g, 1.0 equiv., 16.5 mmol). The flask was evacuated and backfilled with nitrogen (x3). Anhydrous 1,4-dioxane (88 mL) was added via a syringe and resulting suspension was stirred at rt for 3 h. To this was added anhydrous CCl₄ (70.1 mL) and the flask was immersed in a pre-heated 80°C oil bath and the solution was stirred at this temperature under a static nitrogen atmosphere for 3 h. The mixture was then cooled to rt and HCl (4M in dioxane, 8.2 mL, 2.0 equiv., 33.0 mmol) was added slowly to the brown solution via a syringe while stirring vigorously for 30 min. The mixture was diluted with DCM (100 mL) and filtered through a pad of celite washing with DCM until the filtrate was colorless. The filtrate was concentrated and the resulting brownish solid was triturated (2x) with Et₂O/Pentane (1:1) and pentane (3x). The solids were dried overnight under high vacuum to yield the desired chlorinated imidazolium chloride salt **186** (4.3 g, 52 %) as an off-white solid.

¹H NMR (500 MHz, Chloroform-*d*) δ 13.43 (s, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 4H), 2.34 (hept, *J* = 6.8 Hz, 4H), 1.37 (d, *J* = 6.9 Hz, 12H), 1.30 (d, *J* = 6.8 Hz, 12H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 145.64, 132.95, 127.27, 125.07, 121.05, 29.91, 25.02, 23.27 ppm.

Ligation of the NHC–IPr^{Cl} (**186**) ligand to the nickel



In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with NHC–IPr^{Cl} ligand (**186**) (538.72 mg, 1.0 equiv., 1.09 mmol), KOtBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**187**) in THF, were added dropwise to a precooled (–35 °C) slurry of Ni(cod)₂ (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL), which immediately turned blood-red upon addition. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine (**78**) (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, resulting in a color change to an orange-brown solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The resulting red-brown residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The red-brown oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the desired yellow-orange solid product (**188**) (421.1 mg, 56%).

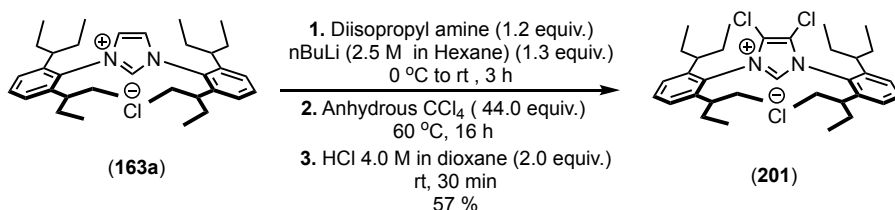
Free carbene (**187**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.28 (t, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 6.7$ Hz, 4H), 2.92 (hept, $J = 6.8$ Hz, 4H), 1.27 (d, $J = 6.9$ Hz, 12H), 1.22 (d, $J = 6.9$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 220.84, 146.85, 135.32, 130.06, 124.00, 117.06, 29.20, 24.82, 23.06 ppm.

Product (**188**): ^1H NMR (500 MHz, Chloroform- d) δ 7.72 – 7.53 (m, 3H), 7.39 (d, $J = 7.4$ Hz, 1H), 7.14 (d, $J = 3.7$ Hz, 1H), 6.61 (t, $J = 7.0$ Hz, 1H), 6.45 (dd, $J = 15.0, 7.1$ Hz, 2H), 6.35 (d, $J = 7.2$ Hz, 1H), 4.02 – 3.92 (m, 1H), 3.65 – 3.59 (m, 1H), 3.08 (s, 1H), 2.82 – 2.70 (m, 1H), 2.53 – 2.38 (m, 1H), 2.19 (d, $J = 11.4$ Hz, 2H), 1.69 (d, $J = 5.9$ Hz, 2H), 1.63 – 1.50 (m, 6H), 1.40 – 1.06 (m, 16H), 0.77 (d, $J = 6.5$ Hz, 3H), 0.21 (d, $J = 5.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 150.70, 150.07, 149.77, 147.61, 142.58, 138.12, 131.35, 131.07, 126.27, 125.87, 124.44, 124.31, 124.10, 124.03, 123.49, 47.26, 39.20, 38.74, 29.71, 29.41, 29.32, 29.14, 27.02, 26.50, 25.99, 25.76, 25.37, 24.38, 21.42 ppm. HRMS-ESI (m/z): $[\text{M-Cl}]^+$ calcd. for $\text{C}_{36}\text{H}_{46}\text{Cl}_2\text{N}_3\text{Ni}$, 648.2422; found, 648.2402. ICP-AES: 82031 ppm nickel in a 10 mg sample.

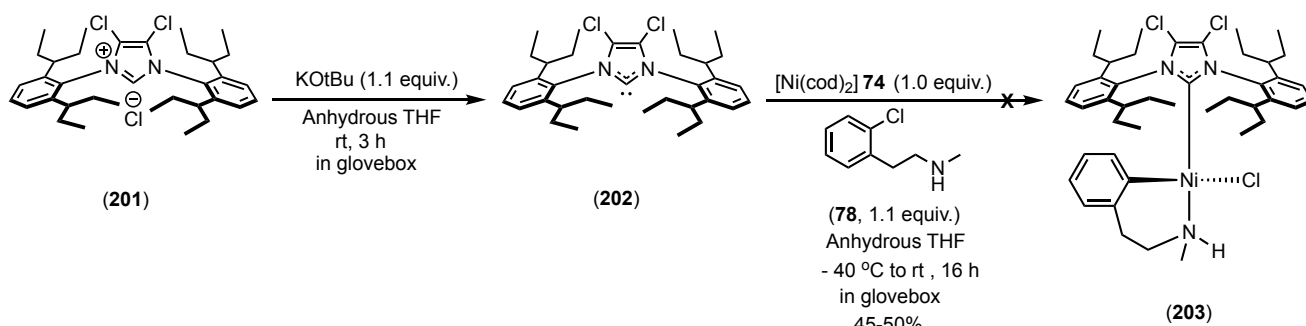
6.4.1.5 Preparation of the Ni–NHC–IPent^{Cl} precatalyst

The Ni–NHC–IPent^{Cl} (**203**) precatalyst was prepared following below procedures ([Scheme 45](#)):

(i) Backbone chlorination of NHC-IPent ligand

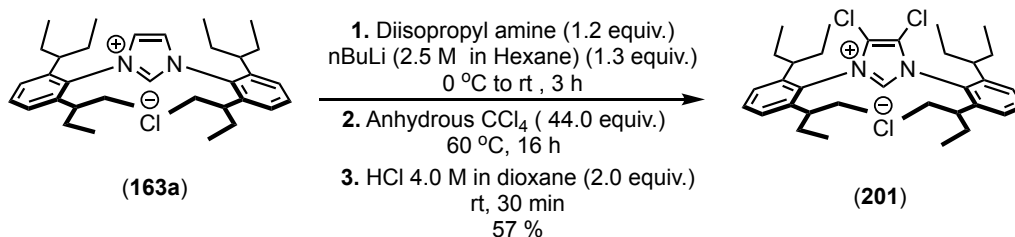


(ii) Ligation of the ligands to the nickel



Scheme 45. General procedure for synthesis Ni–NHC–IPent^{Cl} (**203**) precatalyst

4,5-dichloro-1,3-bis(2,6-di(3-pentyl)phenyl)imidazolium chloride (**201**)

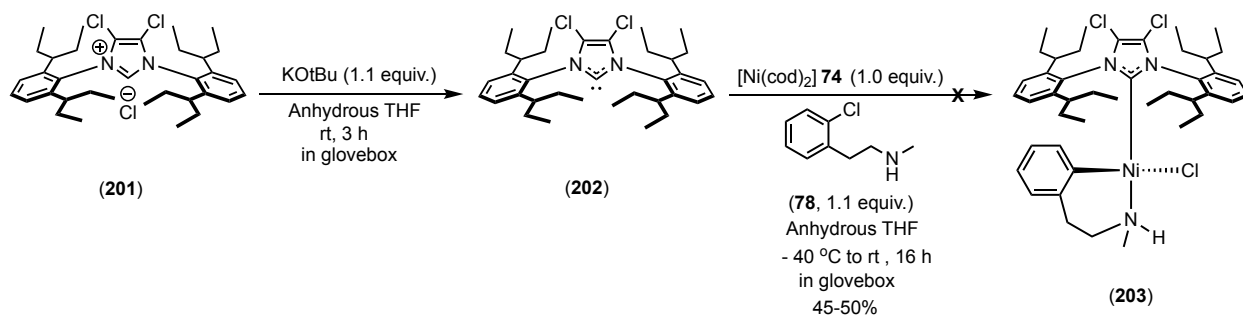


An oven-dried 200 mL round bottom flask equipped with a stir bar was evacuated and refilled with nitrogen (x3). To this was added anhydrous THF (25 mL) followed by diisopropyl amine (0.75 mL, 1.2 equiv., 5.35 mmol) and the flask and its contents were cooled to 0 °C. To the stirring solution was added nBuLi (2.5 M in Hexane, 2.32 mL, 1.3 equiv., 5.8 mmol) drop-wise via a syringe and the resultant solution stirred for 20 min. at 0 °C. 1,3-Bis(2,6-di(3-

pentyl)phenyl)imidazolium chloride **163a** (2.4 g, 1.0 equiv., 4.46 mmol) in anhydrous THF (25 mL) was added via syringe and the solution was further stirred for 5 min. after which it was warmed to rt and stirred for 3 h. Anhydrous CCl₄ (9.5 mL) was added via syringe and the flask was immersed in a pre-heated 60 °C oil bath and the solution was stirred for 16 h at this temperature under static nitrogen atmosphere. The mixture was then cooled to rt and HCl (4M in dioxane, 2.23 mL, 2.0 equiv., 8.92 mmol) was added slowly to the brown solution via syringe and the resultant mixture was stirred vigorously for 30 min, then concentrated in vacuo. After diluting with 50 mL of EtOAc and washing sequentially with water (3 × 25 mL) and brine (25 mL), the combined aqueous phases were extracted with EtOAc (50 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a dark brown solid. The crude product was triturated (3x) with Et₂O/Pentane (1:1) and pentane (2x). The solids were dried overnight under high vacuum to yield the desired chlorinated imidazolium chloride salt **201** (1.54 g, 57 %) as off-white solid.

¹H NMR (500 MHz, Chloroform-*d*) δ 13.15 (s, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 1.99 (p, *J* = 6.7 Hz, 4H), 1.89 – 1.73 (m, 8H), 1.66 (p, *J* = 7.2 Hz, 8H), 0.90 (t, *J* = 7.4 Hz, 12H), 0.86 (t, *J* = 7.4 Hz, 12H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 143.48, 143.11, 132.01, 129.75, 126.03, 121.52, 43.41, 28.25, 27.19, 12.45, 11.81 ppm.

Ligation of the NHC–IPent^{Cl} (**201**) ligand to the nickel



In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with NHC–IPent^{Cl} ligand (**201**) (661.11 mg, 1.0 equiv., 1.09 mmol), KO^tBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**202**) in THF, were added dropwise to a precooled (–35 °C) slurry of Ni(cod)₂ (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL). We expected the solution to turn blood-red immediately upon addition; however, no color change was observed. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine (**78**) (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, but no color change was observed. The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The resulting yellow-green residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The yellow-green oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the **undesired** pale yellow solid product **203** (410.2 mg, 47 %).

Free carbene (**202**): ¹H NMR (600 MHz, Benzene-*d*₆) δ 7.30 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 4H), 2.61 (p, *J* = 6.9 Hz, 4H), 1.77 – 1.69 (m, 8H), 1.70 – 1.51 (m, 8H), 0.92 (t, *J* = 7.4 Hz, 12H), 0.87 (t, *J* = 7.4 Hz, 12H) ppm; ¹³C NMR (150 MHz, Benzene-*d*₆) δ 222.30, 144.44, 137.69, 129.34, 124.78, 117.59, 42.38, 28.74, 28.21, 12.79, 11.62 ppm.

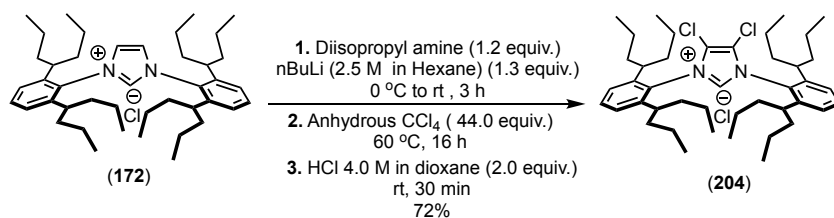
Product (**203**): ¹H NMR (400 MHz, Benzene-*d*₆) δ 15.45 (s, 1H), 7.39 – 6.81 (m, 10H), 5.41 (s, 1H), 3.93 (s, 1H), 3.78 – 3.53 (m, 1H), 3.33 (s, 1H), 2.35 – 0.56 (m, 47H) ppm; ¹³C NMR (100

MHz, Benzene-*d*₆) δ 143.66, 132.00, 130.34, 126.05, 120.97, 43.61, 28.58, 27.47, 23.90, 12.56, 12.13 ppm. HRMS-ESI (*m/z*): [M-Cl]⁺ calcd. for C₄₄H₆₂Cl₂N₃Ni, 760.3674; found, 569.3478.

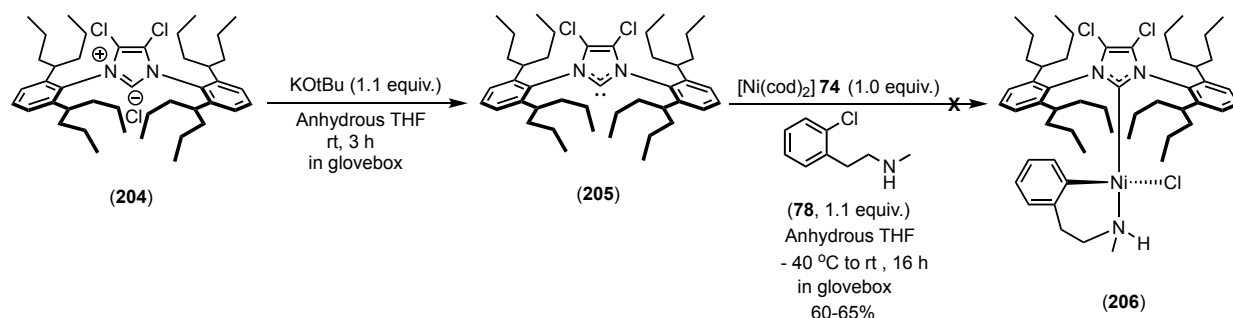
6.4.1.6 Preparation of the Ni–NHC–IHept^{Cl} precatalyst

The Ni–NHC–IHept^{Cl} (**206**) precatalyst was prepared following below procedures (Scheme 46):

(i) Backbone chlorination of NHC-I₂Pent ligand

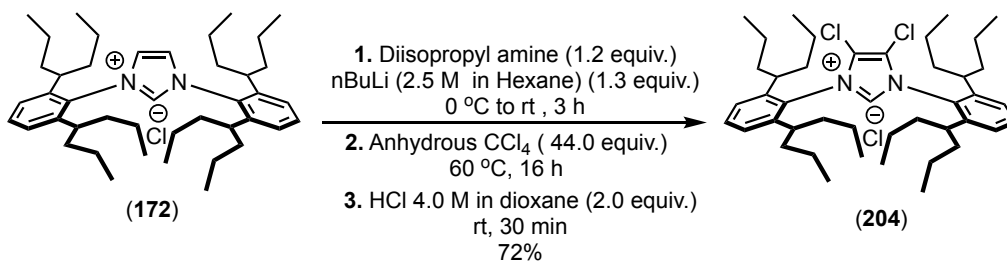


(ii) Ligation of the ligands to the nickel



Scheme 46. General procedure for synthesis Ni–NHC–IHept^{Cl} (**206**) precatalyst

4,5-dichloro-1,3-bis(2,6-di(4-heptyl)phenyl)imidazolium chloride (**204**)

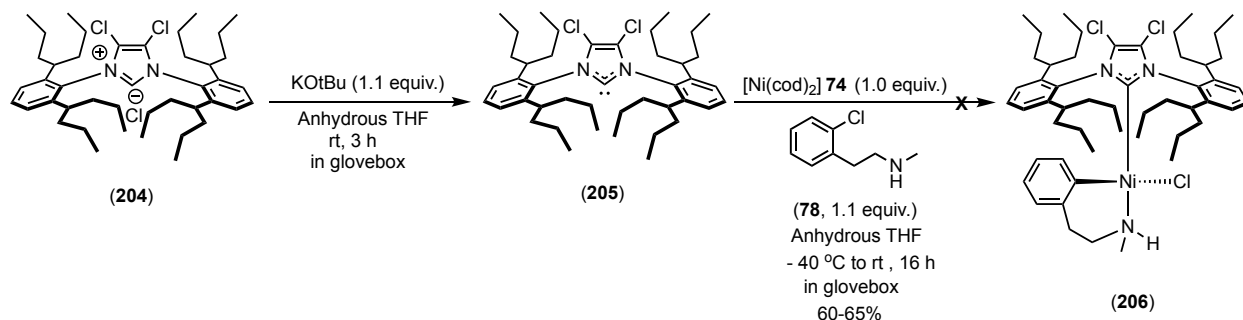


An oven-dried 500 mL round bottom flask equipped with a stir bar was evacuated and refilled with nitrogen (x3). To this was added anhydrous THF (70 mL) followed by diisopropyl amine (2.0 mL, 1.2 equiv., 14.78 mmol) and the flask and its contents were cooled to 0 °C. To the stirring solution

was added nBuLi (2.5 M in Hexane, 6.41 mL, 1.3 equiv., 16.02 mmol) drop-wise via a syringe and the resultant solution stirred for 20 min. at 0 °C. 1,3-Bis(2,6-di(4-heptyl)phenyl)imidazolium chloride **172** (8.0 g, 1.0 equiv., 12.32 mmol) in anhydrous THF (70 mL) was added via syringe and the solution was further stirred for 5 min. after which it was warmed to rt and stirred for 3 h. Anhydrous CCl₄ (26.2 mL) was added via syringe and the flask was immersed in a pre-heated 60 °C oil bath and the solution was stirred for 16 h at this temperature under static nitrogen atmosphere. The mixture was then cooled to rt and HCl (4M in dioxane, 6.2 mL, 2.0 equiv., 24.64 mmol) was added slowly to the brown solution via syringe and the resultant mixture was stirred vigorously for 30 min, then concentrated in vacuo. After diluting with 100 mL of EtOAc and washing sequentially with water (3 × 50 mL) and brine (50 mL), the combined aqueous phases were extracted with EtOAc (100 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a dark brown solid. The crude product was triturated (3x) with Et₂O/Pentane (1:1) and pentane (2x). The solids were dried overnight under high vacuum to yield the desired chlorinated imidazolium chloride salt **204** (6.36 g, 72 %) as off-white solid.

¹H NMR (500 MHz, Chloroform-*d*) δ 13.23 (s, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 2.15 (p, *J* = 6.7 Hz, 4H), 1.74 – 1.56 (m, 16H), 1.33 – 1.18 (m, 16H), 0.88 (d, *J* = 6.5 Hz, 12H), 0.85 (d, *J* = 6.8 Hz, 12H) ppm; ¹³C NMR (125 MHz, Chloroform-*d*) δ 143.95, 131.93, 129.35, 126.04, 121.58, 40.49, 37.88, 37.62, 21.04, 20.37, 14.69, 14.36 ppm.

Ligation of the NHC-IHept^{Cl} (**204**) ligand to the nickel



In a nitrogen-filled glovebox, an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with NHC-IHept^{Cl} ligand (**204**) (783.50 mg, 1.0 equiv., 1.09 mmol), KOtBu (134.63 mg, 1.1 equiv., 1.20 mmol), and anhydrous THF (5.5 mL). The mixture was stirred at room temperature for 1 hour. The resulting suspension was filtered through a pad of Celite and washed with anhydrous THF (5 × 2 mL). The filtrate, containing the free carbene (**205**) in THF, were added dropwise to a precooled (−35 °C) slurry of Ni(cod)₂ (300 mg, 1.0 equiv., 1.09 mmol) in THF (6 mL). We expected the solution to turn blood-red immediately upon addition; however, no color change was observed. Next, a solution of 2-(2-chlorophenyl)-N-methylethan-1-amine (**78**) (203.54 mg, 1.1 equiv., 1.20 mmol) in THF (3 mL) was added, but no color change was observed. The reaction mixture was allowed to warm to room temperature and stirred overnight. The vial was then opened to air and stirred for an additional 30 minutes. The mixture was transferred to a 100 mL round-bottom flask and concentrated under reduced pressure using a rotary evaporator. The resulting yellow-green residue was purified by flash column chromatography on neutral aluminum oxide (eluting first with 100% hexanes, followed by 100% ethyl acetate). The yellow-green oily product was solidified by trituration with pentane and evaporated under rapid reduced pressure to afford the **undesired** pale yellow solid product **206** (643.4 mg, 65 %).

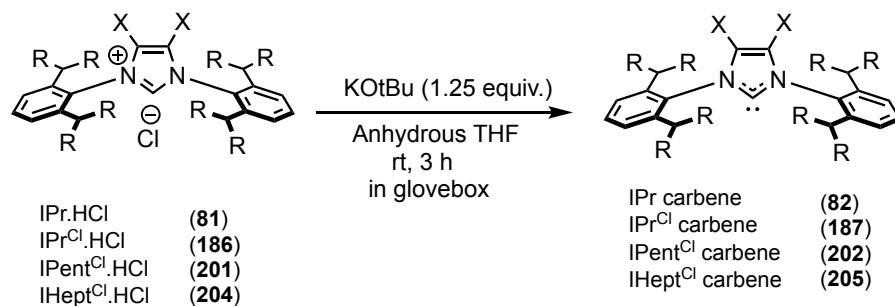
Free carbene (**205**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.33 (t, $J = 7.7$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 4H), 2.78 (p, $J = 6.0$, 4H), 1.82 – 1.65 (m, 8H), 1.61 – 1.51 (m, 8H), 1.48 – 1.16 (m, 16H), 0.91 (t, $J = 7.3$ Hz, 12H), 0.79 (t, $J = 7.3$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 222.11, 150.10, 139.70, 129.32, 124.84, 117.79, 39.29, 38.81, 38.69, 21.49, 20.46, 14.95, 14.61 ppm.

Product (**206**): ^1H NMR (400 MHz, Benzene- d_6) δ 15.98 (s, 1H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.21 – 7.12 (m, 4H), 2.79 (p, $J = 5.4$, 4H), 1.82 – 1.66 (m, 8H), 1.66 – 1.48 (m, 8H), 1.48 – 1.31 (m, 12H), 1.30 – 1.15 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 12H), 0.80 (t, $J = 7.1$ Hz, 12H) ppm; ^{13}C NMR (100 MHz, Benzene- d_6) δ 145.00, 137.08, 129.32, 124.84, 117.79, 39.29, 38.81, 38.69, 21.49, 20.46, 14.95, 14.61 ppm.

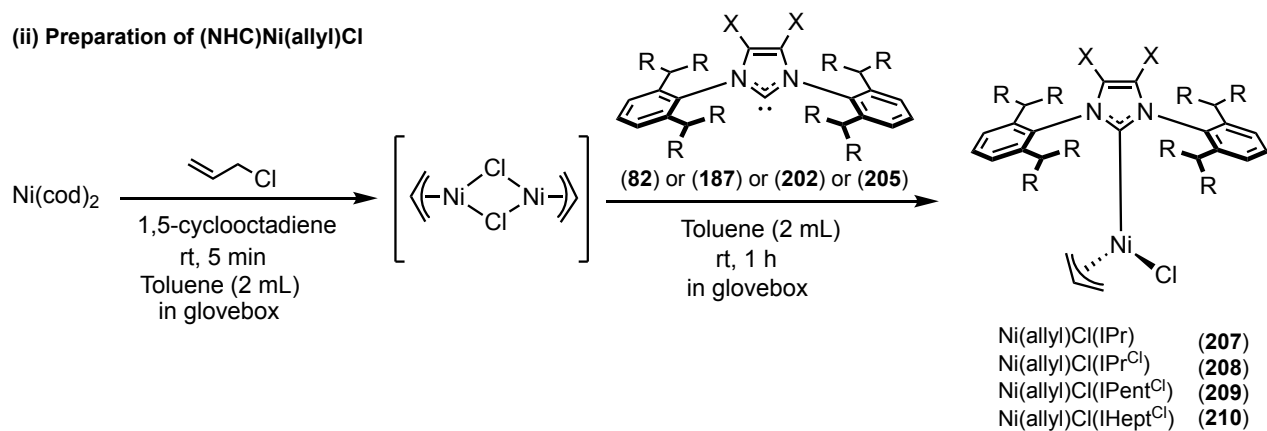
6.4.1.7 Preparation of the (NHC)Ni(π -allyl)Cl precatalysts

The (NHC)Ni(π -allyl)Cl precatalysts were prepared following literature procedures,¹⁸³ as illustrated in Scheme 47.

(i) Preparation of NHC free carbene from the corresponding NHC.HCl salt:



(ii) Preparation of (NHC)Ni(allyl)Cl



Scheme 47. General procedure for synthesis (NHC)Ni(π -allyl)Cl precatalysts

Preparation of NHC free carbene from the corresponding NHC•HCl salt

In a nitrogen-filled glovebox, an 8 mL vial was charged with NHC•HCl salt (0.5 mmol) and KOtBu (70.13 mg, 0.63 mmol), then suspended in THF (5 mL) and stirred magnetically for 6 hours in (Scheme 47-i). After completion, the THF was removed under reduced pressure to afford a yellow-orange solid. To this solid, toluene (1 mL) was added, dissolving most of the material. Pentane (10 mL) was then added to precipitate excess KOtBu and unreacted starting material. The mixture was filtered through a fritted funnel (10 mL), and the precipitate was washed with two 1 mL portions

of pentane. The combined filtrate was concentrated and dried under vacuum to yield the free NHC carbene as a flocculent white solid.

IPr carbene (**82**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.29 (t, $J = 7.7$ Hz, 2H), 7.18 (d, $J = 7.7$ Hz, 4H), 6.61 (s, 2H), 2.95 (hept, $J = 6.9$ Hz, 4H), 1.29 (d, $J = 6.9$ Hz, 12H), 1.19 (d, $J = 7.0$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 219.45, 146.29, 138.85, 129.08, 123.72, 121.59, 28.81, 24.82, 23.66 ppm.

IPr^{Cl} carbene (**187**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.28 (t, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 6.7$ Hz, 4H), 2.92 (hept, $J = 6.8$ Hz, 4H), 1.27 (d, $J = 6.9$ Hz, 12H), 1.22 (d, $J = 6.9$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 220.84, 146.85, 135.32, 130.06, 124.00, 117.06, 29.20, 24.82, 23.06 ppm.

IPent^{Cl} carbene (**202**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.30 (d, $J = 7.7$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 4H), 2.61 (p, $J = 6.9$ Hz, 4H), 1.77 – 1.69 (m, 8H), 1.70 – 1.51 (m, 8H), 0.92 (t, $J = 7.4$ Hz, 12H), 0.87 (t, $J = 7.4$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 222.30, 144.44, 137.69, 129.34, 124.78, 117.59, 42.38, 28.74, 28.21, 12.79, 11.62 ppm.

IHept^{Cl} carbene (**205**): ^1H NMR (600 MHz, Benzene- d_6) δ 7.33 (t, $J = 7.7$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 4H), 2.78 (p, $J = 6.0$, 4H), 1.82 – 1.65 (m, 8H), 1.61 – 1.51 (m, 8H), 1.48 – 1.16 (m, 16H), 0.91 (t, $J = 7.3$ Hz, 12H), 0.79 (t, $J = 7.3$ Hz, 12H) ppm; ^{13}C NMR (150 MHz, Benzene- d_6) δ 222.11, 150.10, 139.70, 129.32, 124.84, 117.79, 39.29, 38.81, 38.69, 21.49, 20.46, 14.95, 14.61 ppm.

Preparation of (NHC)Ni(π -allyl)Cl

Ni(cod)₂ (123.8 mg, 0.45 mmol) was suspended in approximately 910 μL of 1,5-cyclooctadiene. Allyl chloride (36.7 μL , 0.45 mmol) was then added dropwise. The resulting slurry was stirred for 5 minutes, during which a blood-red allylnickel(II) chloride dimer rapidly formed. Toluene (2 mL)

was added to dissolve the material completely, followed by the addition of a solution of free NHC carbene (0.45 mmol) in toluene (2 mL). The mixture was stirred for 1 hour, during which the color changed from dark maroon to a dark orange-brown solution ([Scheme 47-ii](#)). The reaction mixture was filtered through Celite and concentrated under reduced pressure. The resulting orange solid was washed with three 1 mL portions of cold pentane and dried under vacuum to afford (NHC)Ni(π -allyl)Cl as an orange powder.

Ni(allyl)Cl(IPr) (**207**): ^1H NMR (500 MHz, Benzene- d_6) δ 7.28 – 7.18 (m, 4H), 7.13 (dd, J = 7.5, 1.7 Hz, 2H), 6.59 (s, 2H), 4.64 – 4.51 (m, 1H), 3.43 (p, J = 6.8 Hz, 2H), 3.36 (dd, J = 7.4, 2.2 Hz, 1H), 2.97 (hept, J = 6.8 Hz, 2H), 2.46 (d, J = 14.1 Hz, 1H), 2.27 (ddd, J = 6.7, 2.7, 1.4 Hz, 1H), 1.49 (d, J = 6.8 Hz, 6H), 1.41 (d, J = 6.7 Hz, 6H), 1.04 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (125 MHz, Benzene- d_6) δ 189.00, 146.79, 146.66, 136.52, 130.27, 128.35, 124.41, 124.23, 124.11, 107.72, 70.27, 43.76, 28.88, 28.86, 26.64, 26.18, 23.02, 22.99 ppm. MS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{30}\text{H}_{41}\text{ClN}_2\text{Ni}$, 522.2312; found, 522.2336.

Ni(allyl)Cl(IPr $^{\text{Cl}}$) (**208**): ^1H NMR (500 MHz, Benzene- d_6) δ 7.26 – 7.17 (m, 4H), 7.12 (dd, J = 7.6, 1.7 Hz, 2H), 4.50 – 4.39 (m, 1H), 3.40 – 3.27 (m, 3H), 2.94 (p, J = 6.7 Hz, 2H), 2.45 (d, J = 14.1 Hz, 1H), 2.41 (ddd, J = 6.7, 2.8, 1.2 Hz, 1H), 1.49 (d, J = 6.7 Hz, 6H), 1.42 (d, J = 6.6 Hz, 6H), 1.14 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.9 Hz, 6H) ppm; ^{13}C NMR (125 MHz, Benzene- d_6) δ 193.44, 147.66, 147.58, 133.39, 131.20, 128.35, 124.97, 124.73, 119.85, 108.09, 71.25, 45.46, 29.10, 29.04, 25.49, 25.30, 24.46, 24.04 ppm. MS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{30}\text{H}_{39}\text{Cl}_3\text{N}_2\text{Ni}$, 590.1533; found, 590.1524.

Ni(allyl)Cl(IPent $^{\text{Cl}}$) (**209**): ^1H NMR (500 MHz, Benzene- d_6) δ 7.23 (t, J = 7.8 Hz, 2H), 7.18 – 7.03 (m, 4H), 4.76 – 4.68 (m, 1H), 3.58 – 3.50 (m, 1H), 3.19 – 3.14 (m, 1H), 2.75 (d, J = 14.2 Hz, 1H), 2.71 – 2.66 (m, 2H), 2.27 (d, J = 5.8 Hz, 1H), 2.11 – 2.01 (m, 4H), 1.98 – 1.51 (m, 13H), 1.19 (t,

$J = 7.3$ Hz, 6H), 1.14 (t, $J = 7.3$ Hz, 6H), 0.85 (td, $J = 7.5, 4.6$ Hz, 12H) ppm; ^{13}C NMR (125 MHz, Benzene- d_6) δ 189.04, 145.57, 144.77, 134.64, 129.76, 128.35, 126.72, 126.28, 120.22, 108.23, 73.33, 44.02, 41.54, 41.36, 27.61, 27.15, 26.69, 26.17, 12.92, 12.45, 11.07, 11.02 ppm. HRMS-ESI (m/z): $[\text{M-Cl}]^+$ calcd. for $\text{C}_{38}\text{H}_{55}\text{Cl}_2\text{N}_2\text{Ni}$, 667.3096; found, 569.3574. HRMS-MALDI (m/z): $[\text{M-Cl}]^+$ calcd. for $\text{C}_{38}\text{H}_{55}\text{Cl}_2\text{N}_2\text{Ni}$, 667.309; found, 569.321.

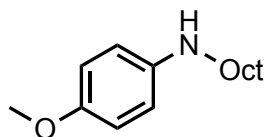
Ni(allyl)Cl(IHept^{Cl}) (**210**): ^1H NMR (500 MHz, Benzene- d_6) δ 7.26 (t, $J = 7.7$ Hz, 2H), 7.17 (dd, $J = 7.8, 1.2$ Hz, 2H), 7.13 (dd, $J = 7.8, 1.2$ Hz, 2H), 4.79 – 4.70 (m, 1H), 3.54 (d, $J = 7.3$ Hz, 1H), 3.19 – 3.14 (m, 2H), 2.82 – 2.71 (m, 3H), 2.26 – 2.18 (m, 1H), 2.07 – 2.00 (m, 4H), 1.94 – 1.47 (m, 20H), 1.35 – 1.27 (m, 8H), 1.04 (td, $J = 7.2, 3.4$ Hz, 12H), 0.87 (dt, $J = 9.7, 7.3$ Hz, 12H) ppm; ^{13}C NMR (125 MHz, Benzene- d_6) δ 188.87, 146.18, 145.43, 134.27, 129.91, 128.35, 126.46, 126.15, 120.18, 108.22, 73.09, 43.97, 39.81, 39.62, 38.66, 37.93, 37.87, 22.19, 21.65, 20.82, 20.54, 15.19, 15.12, 14.78, 14.74 ppm. HRMS-ESI (m/z): $[\text{M-Cl}]^+$ calcd. for $\text{C}_{46}\text{H}_{71}\text{Cl}_2\text{N}_2\text{Ni}$, 779.4348; found, 681.4803. HRMS-MALDI (m/z): $[\text{M-Cl}]^+$ calcd. for $\text{C}_{46}\text{H}_{71}\text{Cl}_2\text{N}_2\text{Ni}$, 779.434; found, 681.459.

6.4.2 General procedure for monoarylation of primary alkyl amines

A vial equipped with a magnetic stir bar was charged with NaOtBu (86.49 mg, 0.9 mmol, 1.8 equiv.) and Ni–NHC precatalyst (5 mol%). The vial was sealed with a screw cap fitted with a septum, evacuated, and backfilled with nitrogen ($\times 2$). Anhydrous toluene (5 mL) was then added via syringe. The aryl halide (0.5 mmol, 1.0 equiv.) and amine (0.55 mmol, 1.1 equiv.) were added by syringe. If either the aryl halide or amine was a solid at room temperature, it was added directly to the vial with the catalyst prior to evacuation. The reaction mixture was stirred at the specified temperature (usually 80 °C) for the designated time (1–16 h). Upon completion of the reaction, as determined by GC-MS or when no further conversion was observed, the mixture was cooled to

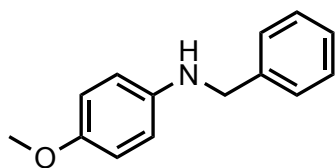
room temperature, diluted with ethyl acetate (10 mL), and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (unless noted otherwise) to yield product of >95% purity.

6.4.3 Spectral data



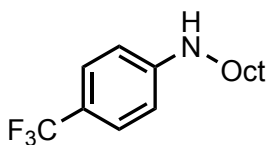
4-methoxy-*N*-octylaniline (102) Following General Coupling Procedure,

the title compound was isolated as a yellow oil. ^1H NMR (500 MHz, Chloroform-*d*) δ 6.79 (d, J = 8.6 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H), 3.75 (s, 3H), 3.32 (s, 1H), 3.06 (t, J = 7.1 Hz, 2H), 1.61 (p, J = 7.2 Hz, 2H), 1.44 – 1.21 (m, 10H), 0.90 (t, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.06, 143.02, 115.02, 114.12, 55.95, 45.16, 31.97, 29.84, 29.58, 29.40, 27.35, 22.80, 14.23 ppm.



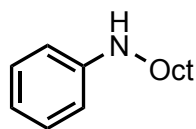
***N*-benzyl-4-methoxyaniline (191)** Following General Coupling

Procedure, the title compound was isolated as a yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H), 6.80 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 4.30 (s, 2H), 3.80 (s, 1H), 3.76 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.30, 142.58, 139.82, 128.71, 127.66, 127.28, 115.03, 114.22, 55.92, 49.36 ppm.



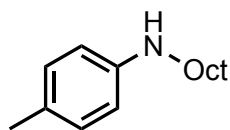
***N*-octyl-4-(trifluoromethyl)aniline (192)** Following General Coupling

Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 3.94 (s, 1H), 3.13 (t, J = 7.1 Hz, 2H), 1.63 (p, J = 7.1 Hz, 2H), 1.44 – 1.23 (m, 10H), 0.89 (t, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.00, 126.73, 126.54, 123.86, 111.78, 43.67, 31.96, 29.51, 29.47, 29.39, 27.24, 22.80, 14.24 ppm.



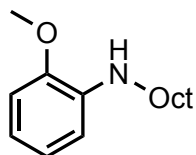
N-octylaniline (193) Following General Coupling Procedure, the title compound

was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.18 (t, J = 7.9 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 8.3 Hz, 2H), 3.58 (s, 1H), 3.11 (t, J = 7.1 Hz, 2H), 1.63 (p, J = 7.2 Hz, 2H), 1.47 – 1.23 (m, 10H), 0.90 (t, J = 5.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.68, 129.35, 117.21, 112.83, 44.16, 31.98, 29.74, 29.57, 29.42, 27.34, 22.81, 14.25 ppm.



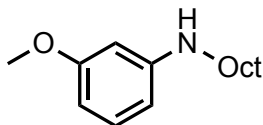
4-methyl-N-octylaniline (194) Following General Coupling Procedure, the

title compound was isolated as a yellow solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.99 (d, J = 8.3 Hz, 2H), 6.54 (d, J = 8.3 Hz, 2H), 3.49 (s, 1H), 3.08 (t, J = 7.1 Hz, 2H), 2.24 (s, 3H), 1.61 (p, J = 7.1 Hz, 2H), 1.48 – 1.20 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.43, 129.83, 126.45, 113.07, 44.57, 31.98, 29.78, 29.58, 29.42, 27.35, 22.81, 20.51, 14.25 ppm.



2-methoxy-N-octylaniline (195) Following General Coupling Procedure, the

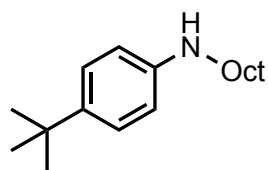
title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.88 (td, J = 7.7, 1.3 Hz, 1H), 6.77 (dd, J = 7.9, 1.0 Hz, 1H), 6.69 – 6.59 (m, 2H), 4.19 (s, 1H), 3.85 (s, 3H), 3.12 (t, J = 7.2 Hz, 2H), 1.66 (p, J = 7.1 Hz, 2H), 1.48 – 1.21 (m, 10H), 0.90 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.87, 138.64, 121.44, 116.21, 109.90, 109.47, 55.53, 43.90, 31.99, 29.70, 29.59, 29.42, 27.41, 22.82, 14.25 ppm.



3-methoxy-N-octylaniline (196) Following General Coupling Procedure,

the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.07 (t, J = 8.1 Hz, 1H), 6.24 (ddd, J = 13.6, 8.1, 2.1 Hz, 2H), 6.16 (t, J = 2.2 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 1H), 3.09 (t, J = 7.1 Hz, 2H), 1.61 (p, J = 7.0 Hz, 2H), 1.46 – 1.20 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*)

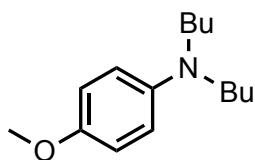
δ 160.99, 150.07, 130.05, 106.07, 102.30, 98.74, 55.21, 44.15, 31.97, 29.69, 29.55, 29.41, 27.32, 22.80, 14.24 ppm.



4-(*tert*-butyl)-*N*-octylaniline (197) Following General Coupling

Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, J = 8.6 Hz, 2H), 6.58 (d, J = 8.6 Hz, 2H),

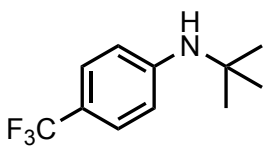
3.44 (s, 1H), 3.10 (t, J = 7.1 Hz, 2H), 1.62 (p, J = 7.0 Hz, 2H), 1.49 – 1.21 (m, 19H), 0.90 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.23, 139.85, 125.98, 112.44, 44.27, 44.16, 33.84, 31.86, 31.58, 31.36, 29.71, 29.45, 29.30, 27.23, 22.69, 14.13 ppm.



***N,N*-dibutyl-4-methoxyaniline (198)** Following General Coupling

Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.82 (dd, J = 9.1, 2.2 Hz, 2H), δ 6.66 (dd, J = 9.0,

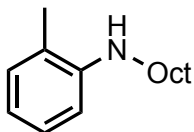
2.1 Hz, 2H), 3.76 (s, 3H), 3.18 (t, J = 7.5 Hz, 4H), 1.52 (p, J = 7.5 Hz, 4H), 1.34 (dq, J = 14.7, 7.3 Hz, 4H), 0.94 (t, J = 7.3 Hz, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.14, 143.50, 114.96, 114.52, 55.99, 51.83, 29.62, 20.57, 14.18 ppm.



***N*-(*tert*-butyl)-4-(trifluoromethyl)aniline (199)** Following General

Coupling Procedure, the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.6

Hz, 2H), 3.96 (s, 1H), 1.39 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.72, 126.43, 123.83, 118.68, 114.46, 51.37, 29.84 ppm.

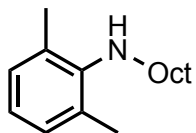


2-methyl-*N*-octylaniline (212) Following General Coupling Procedure, the

title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 (td, J = 7.7, 1.6 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 6.69 – 6.62 (m,

2H), 3.50 (s, 1H), 3.17 (t, J = 7.2 Hz, 2H), 2.15 (s, 3H), 1.69 (p, J = 7.1 Hz, 2H), 1.51 – 1.24 (m,

10H), 0.91 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 146.49, 130.13, 127.26, 121.82, 116.77, 109.79, 44.14, 31.98, 29.75, 29.58, 29.42, 27.40, 22.81, 17.59, 14.25 ppm.



2,6-dimethyl-N-octylaniline (213) Following General Coupling Procedure,

the title compound was isolated as a yellow oil. ^1H NMR (400 MHz, Chloroform- d) δ 6.99 (d, $J = 7.4$ Hz, 2H), 6.81 (t, $J = 7.5$ Hz, 1H), 2.98 (t, $J = 7.2$ Hz, 2H), 2.29 (s, 6H), 1.59 (p, $J = 7.6, 7.1$ Hz, 2H), 1.43 – 1.22 (m, 10H), 0.90 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 146.52, 129.24, 128.92, 121.70, 48.87, 31.98, 31.35, 29.65, 29.43, 27.35, 22.80, 18.72, 14.24 ppm.

6.5 X-ray crystallographic data

6.5.1 X-ray crystallographic data for Ni–NHC–IPr and Ni–NHC–IPr^{Cl}

Crystallographic data were collected from single crystals mounted on goniometer. Data were collected from a shock-cooled single crystal at 100 K on a Bruker Smart ApexII single crystal diffractometer equipped with a graphite monochromator. The instrument was equipped with a sealed tube Mo K α source ($\lambda = 0.71073$ Å), an ApexII CCD detector and a dry compressed air-cooling system. All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.^{185,186} The initial structural solutions were determined using ShelXT direct methods, and refined with full-matrix least-squares procedures based on F^2 using ShelXL.^{187,188} All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-bound hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.¹⁸⁹

6.5.2 X-ray crystallographic data for Ni–NHC–IPent, Ni–NHC–IPr*^{OMe}, Ni(allyl)Cl(IPr), Ni(allyl)Cl(IPr^{Cl}), Ni(allyl)Cl(IPent^{Cl}), and Ni(allyl)Cl(IHept^{Cl})

Crystallographic data were collected from single crystals mounted on goniometer. Data were collected from a shock-cooled single crystal at 150 K on a Bruker Venture Metaljet k-geometry diffractometer with a Metal Jet using a Helios MX Mirror Optics as monochromator and a Bruker CMOS Photon III detector. The instrument was equipped with a sealed tube Ga K α source ($\lambda = 1.34139$ Å). All data were integrated with SAINT and a multi-scan absorption correction using TWINABS or SADABS was applied.^{185,186} The structure was solved by dual methods with ShelXT and refined by full-matrix least-squares methods against F^2 using ShelXL.^{187,188} All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with isotropic displacement parameters. Some of their coordinates were refined freely and some on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints.

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Appendix

Appendix for chapter 2

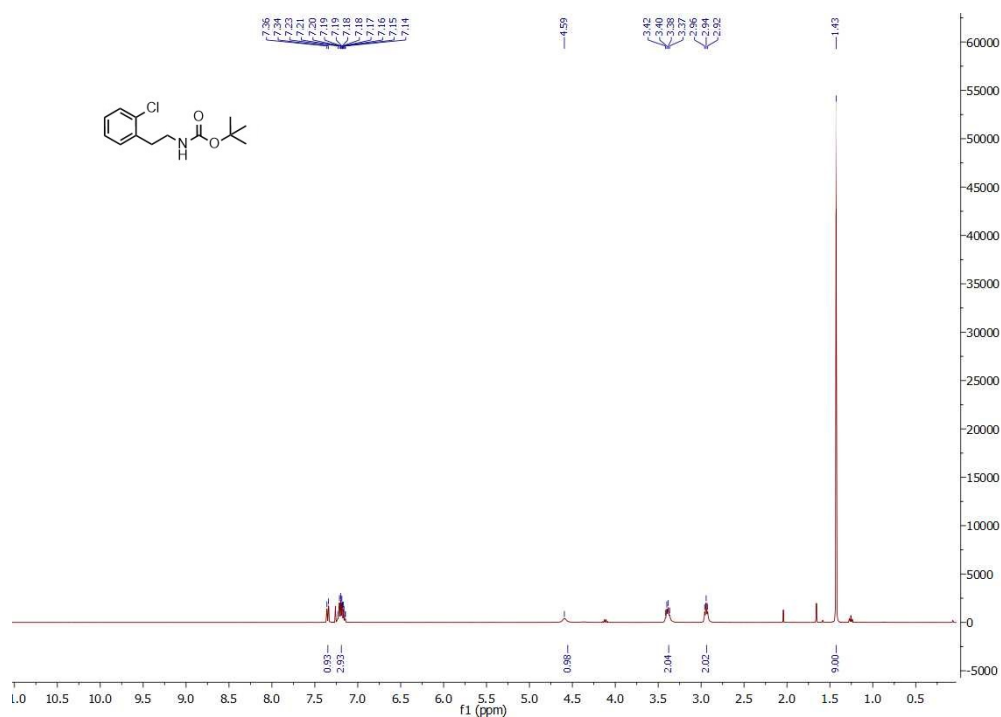


Figure A1. ¹H NMR spectrum of 76 (500 MHz, CDCl₃)

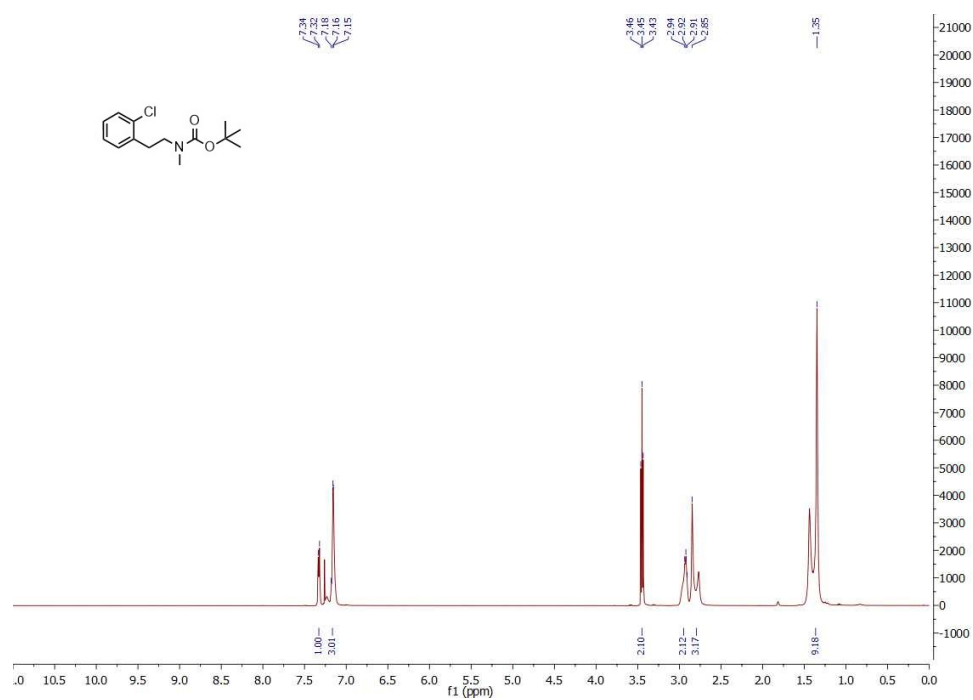


Figure A2. ¹H NMR spectrum of 77 (500 MHz, CDCl₃)

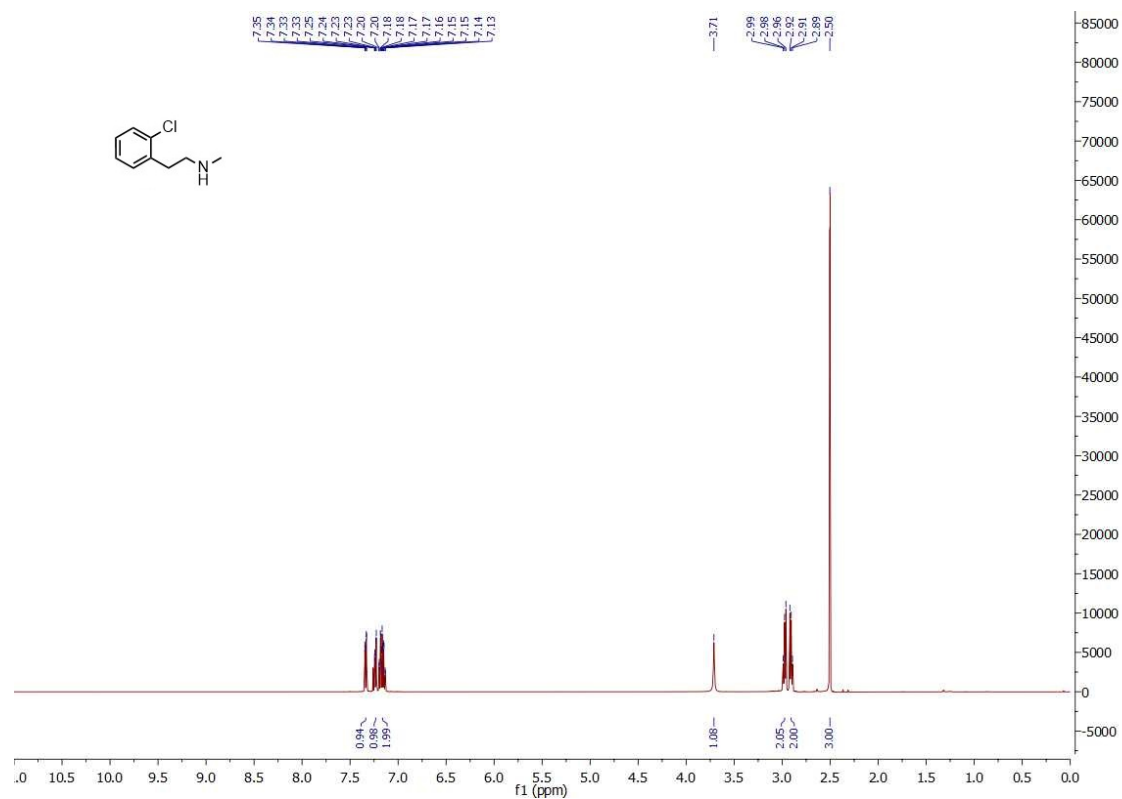


Figure A3. ¹H NMR spectrum of **78** (500 MHz, CDCl₃)

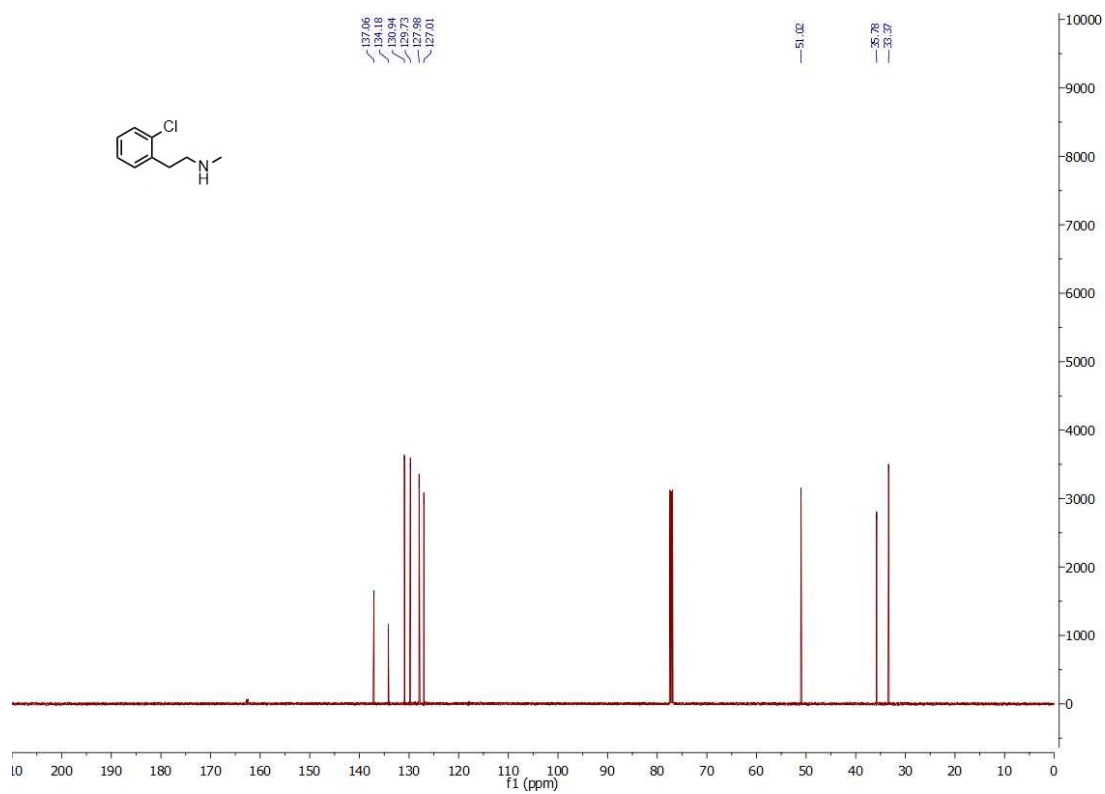


Figure A4. ¹³C NMR spectrum of **78** (125 MHz, CDCl₃)

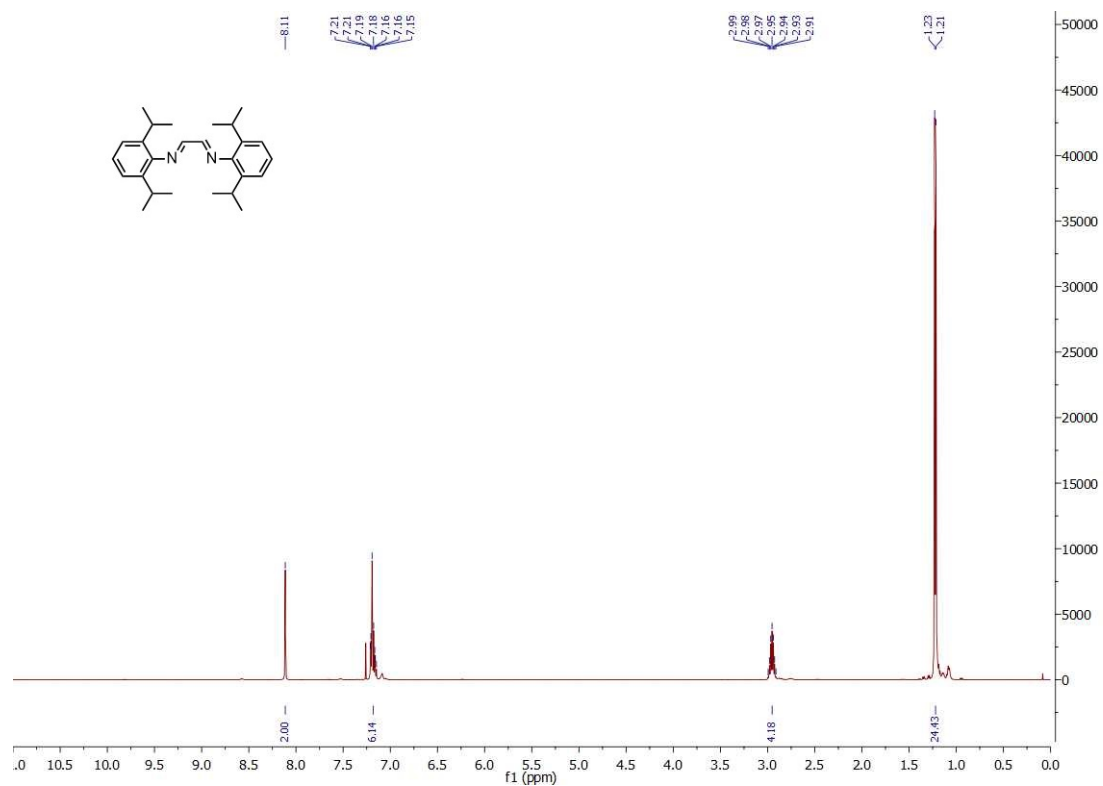


Figure A5. ¹H NMR spectrum of **80** (500 MHz, CDCl₃)

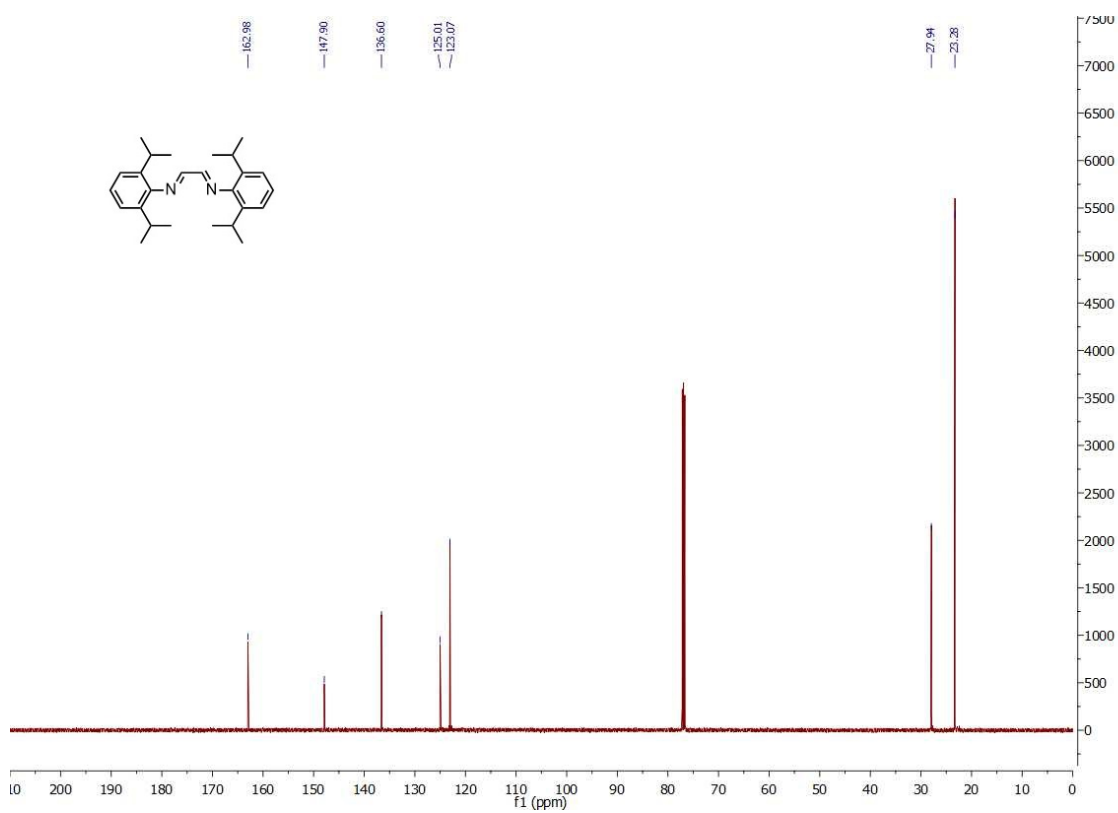


Figure A6. ¹³C NMR spectrum of **80** (125 MHz, CDCl₃)

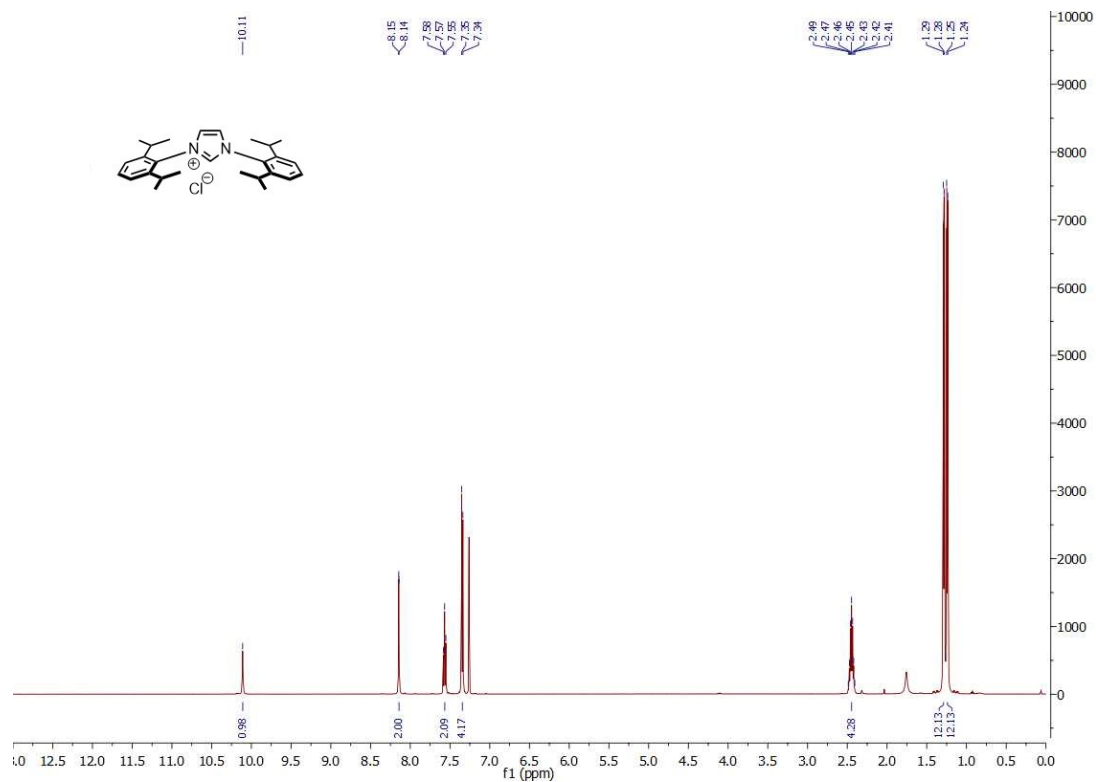


Figure A7. ¹H NMR spectrum of **81** (500 MHz, CDCl₃)

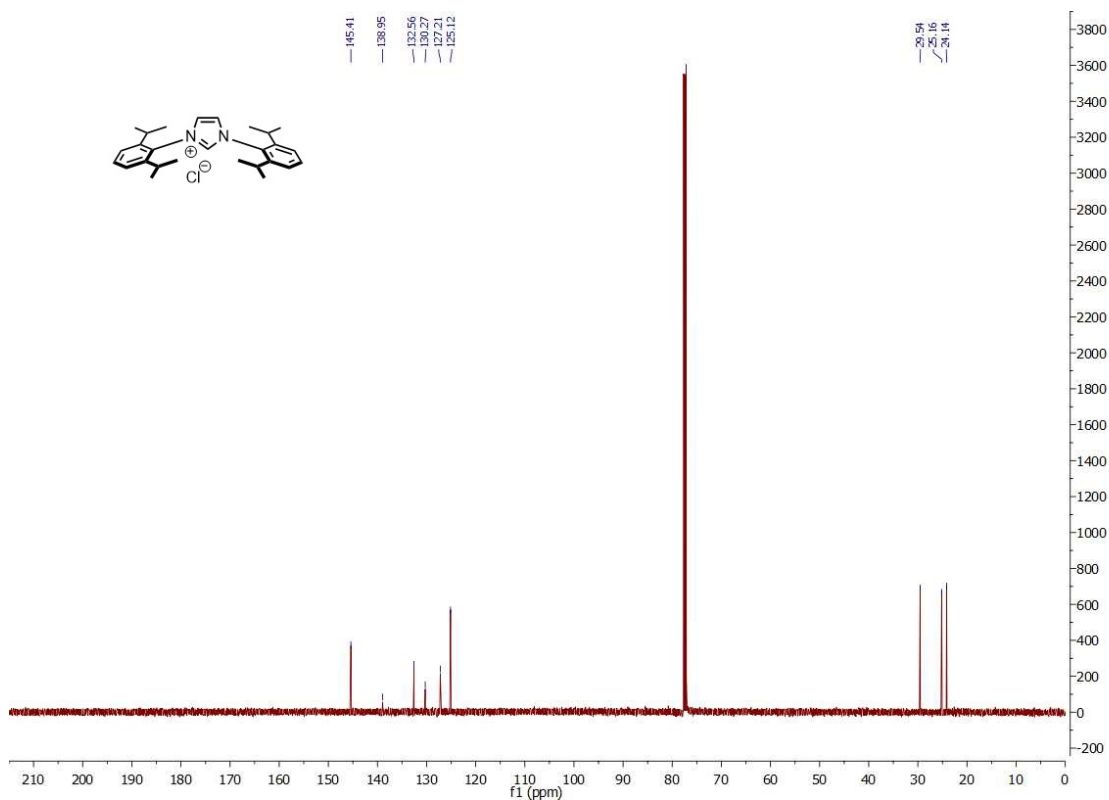


Figure A8. ¹³C NMR spectrum of **81** (125 MHz, CDCl₃)

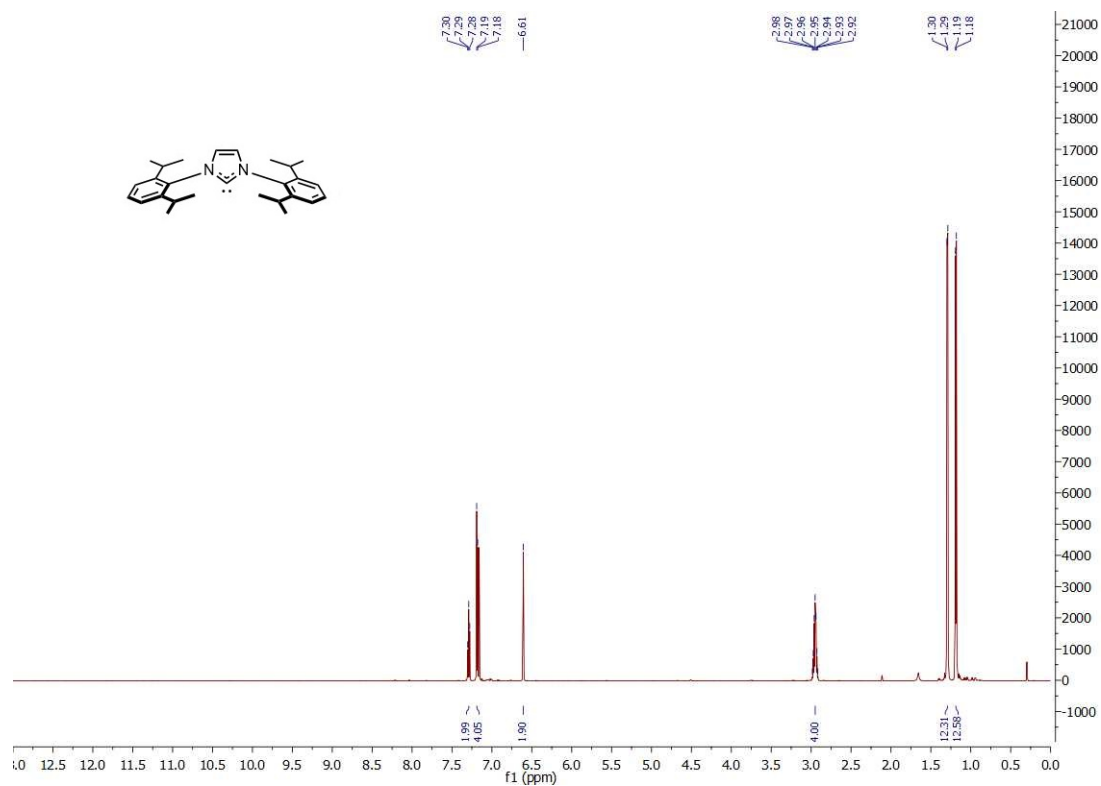


Figure A9. ^1H NMR spectrum of **82** (600 MHz, C_6D_6)

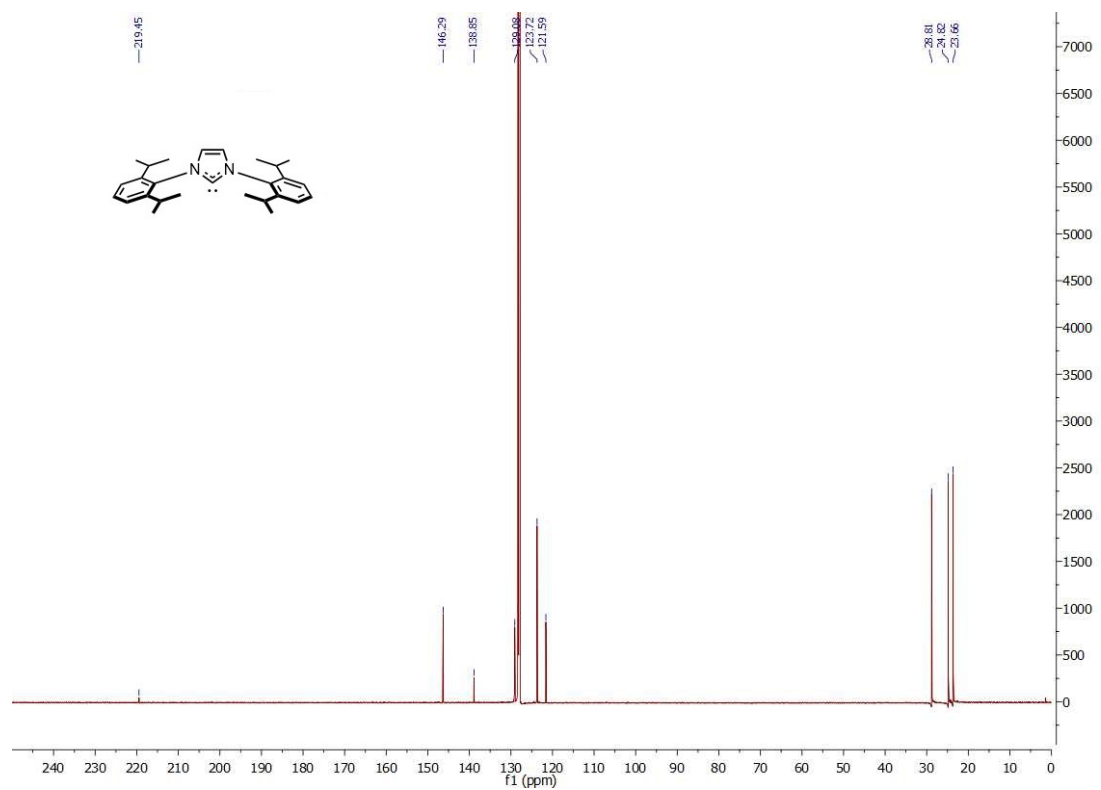


Figure A10. ^{13}C NMR spectrum of **82** (150 MHz, C_6D_6)

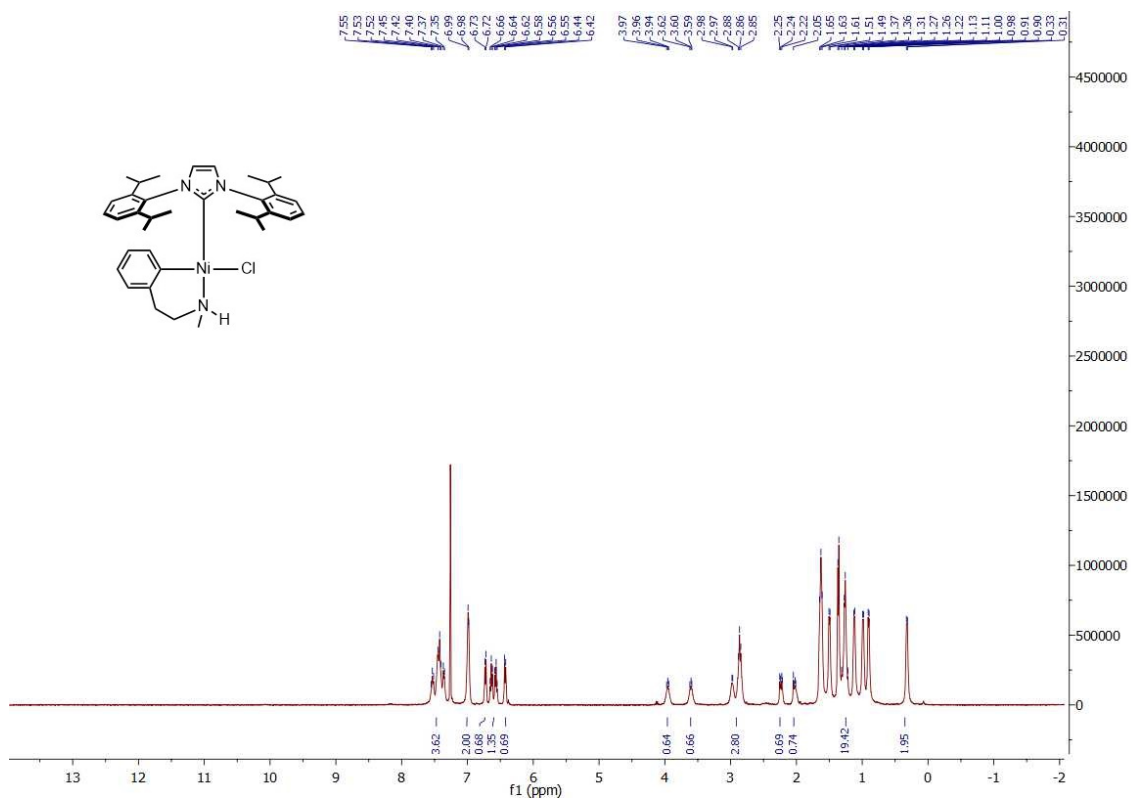


Figure A11. ¹H NMR spectrum of **83** (400 MHz, CDCl₃)

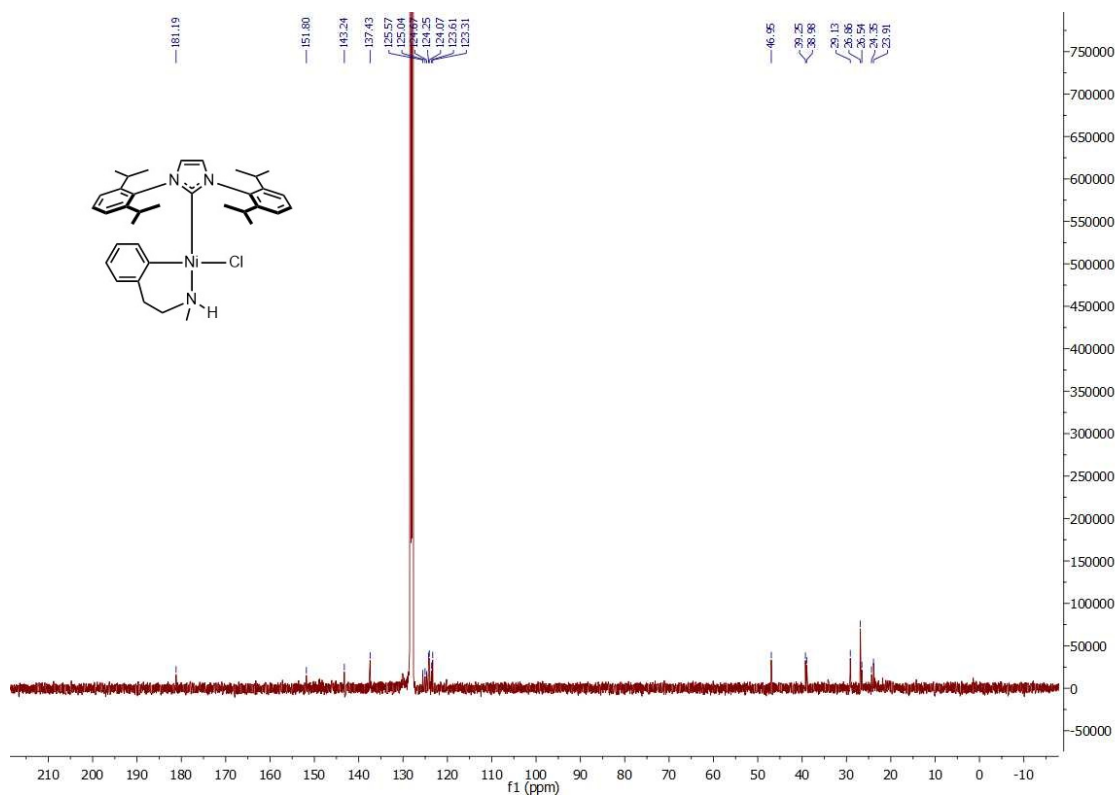


Figure A12. ¹³C NMR spectrum of **83** (100 MHz, C₆D₆)

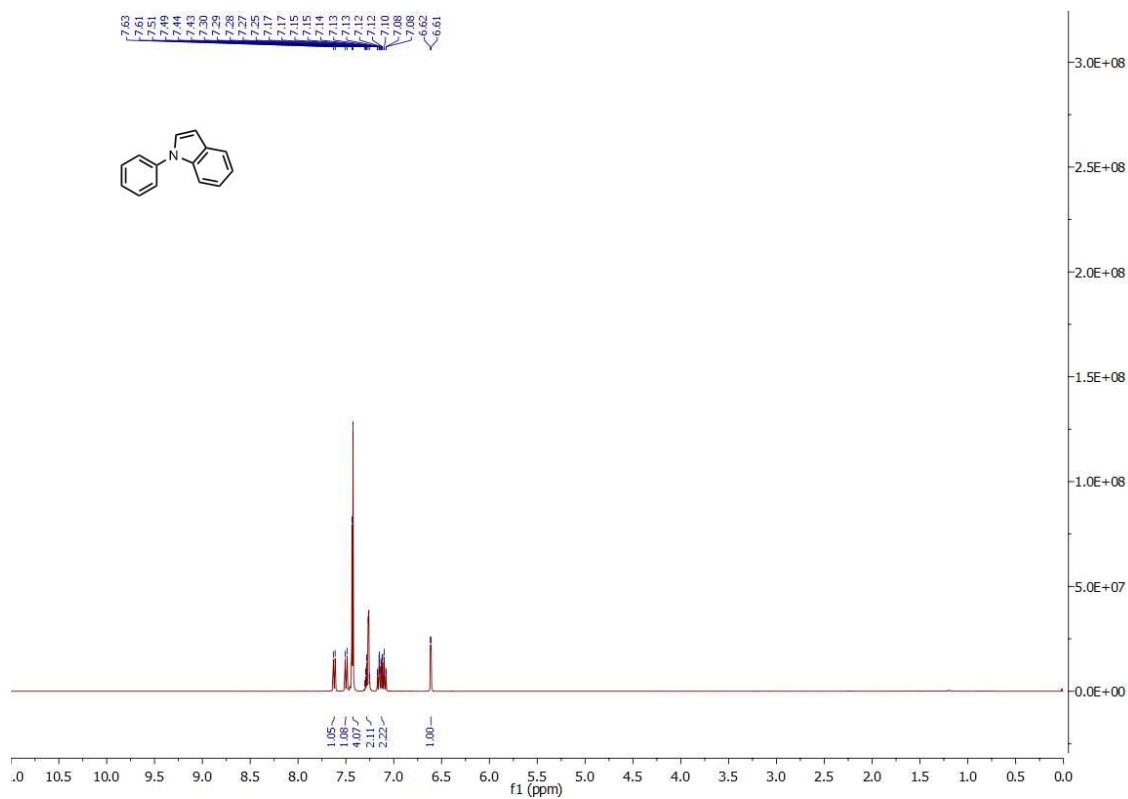


Figure A13. ¹H NMR spectrum of **88** (400 MHz, CDCl₃)

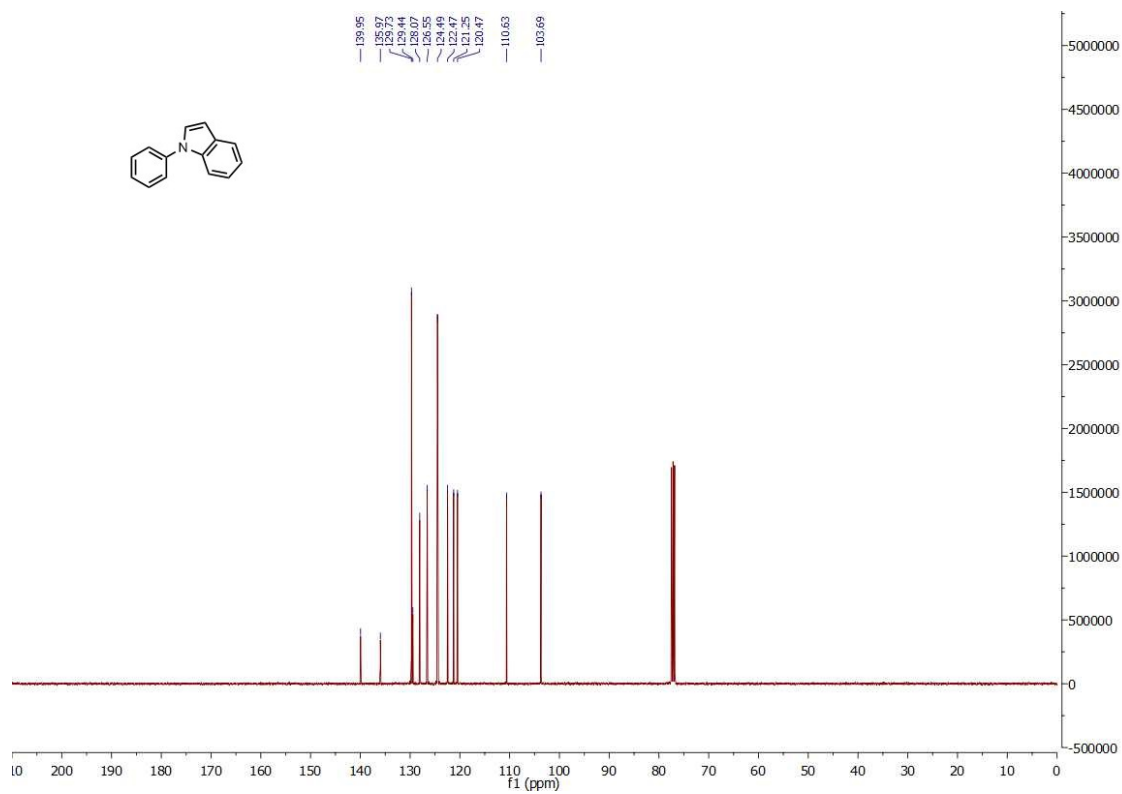


Figure A14. ¹³C NMR spectrum of **88** (100 MHz, CDCl₃)

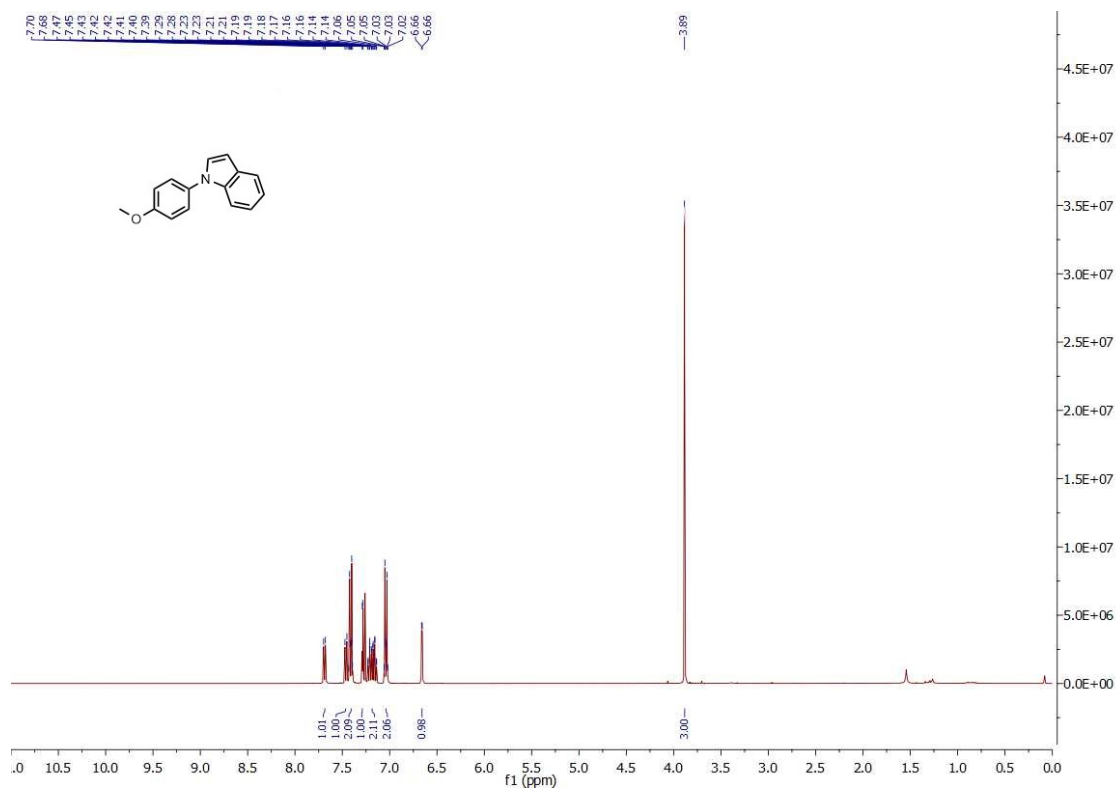


Figure A15. ¹H NMR spectrum of **90** (400 MHz, CDCl₃)

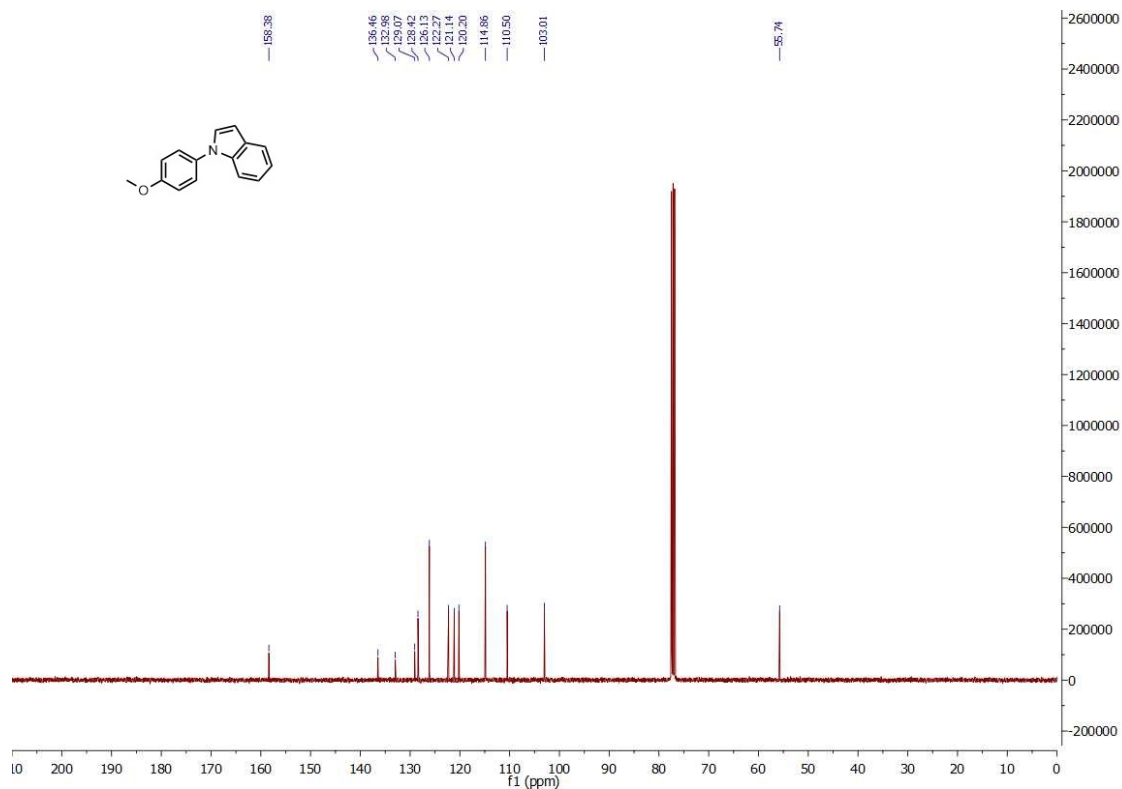


Figure A16. ¹³C NMR spectrum of **90** (100 MHz, CDCl₃)

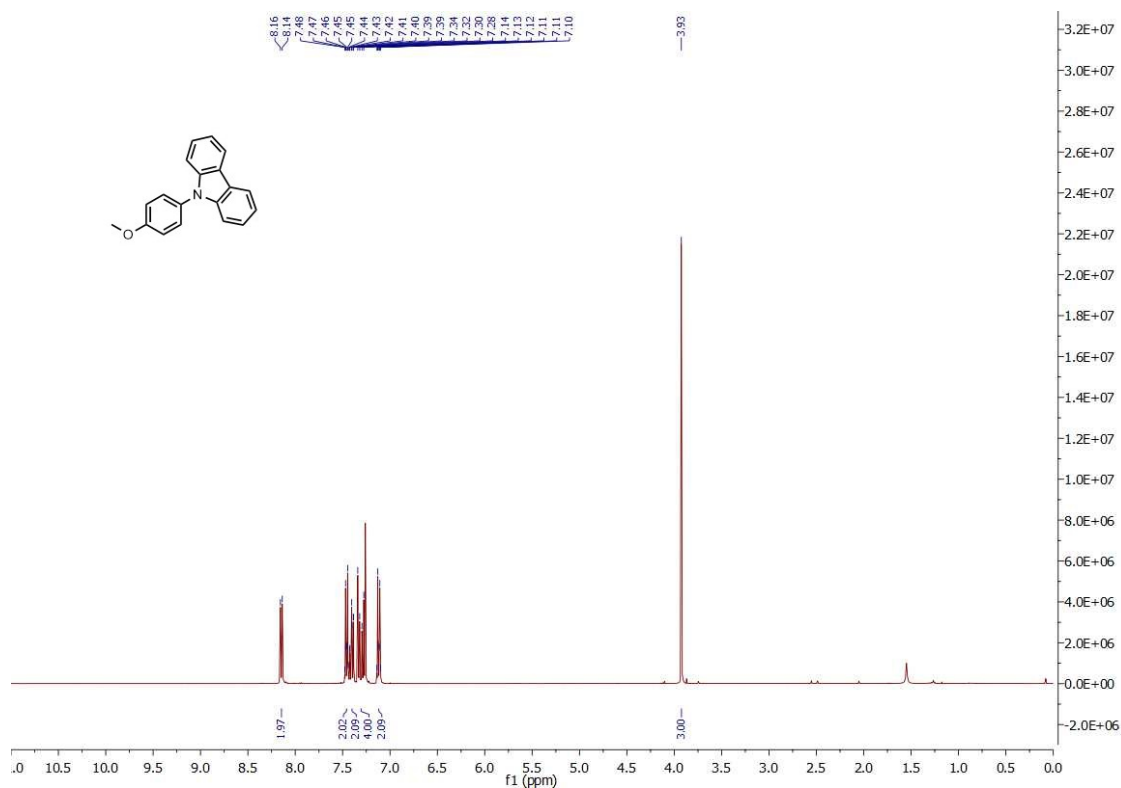


Figure A17. ¹H NMR spectrum of **97** (400 MHz, CDCl₃)

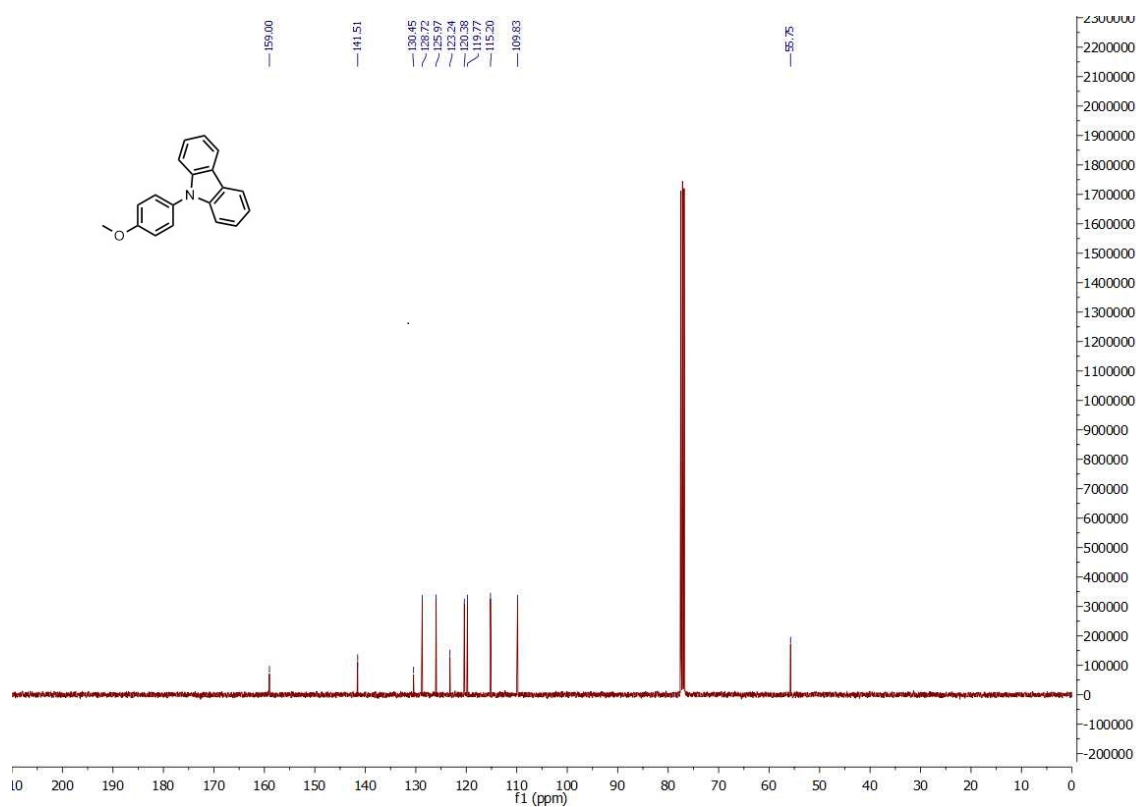


Figure A18. ¹³C NMR spectrum of **97** (100 MHz, CDCl₃)

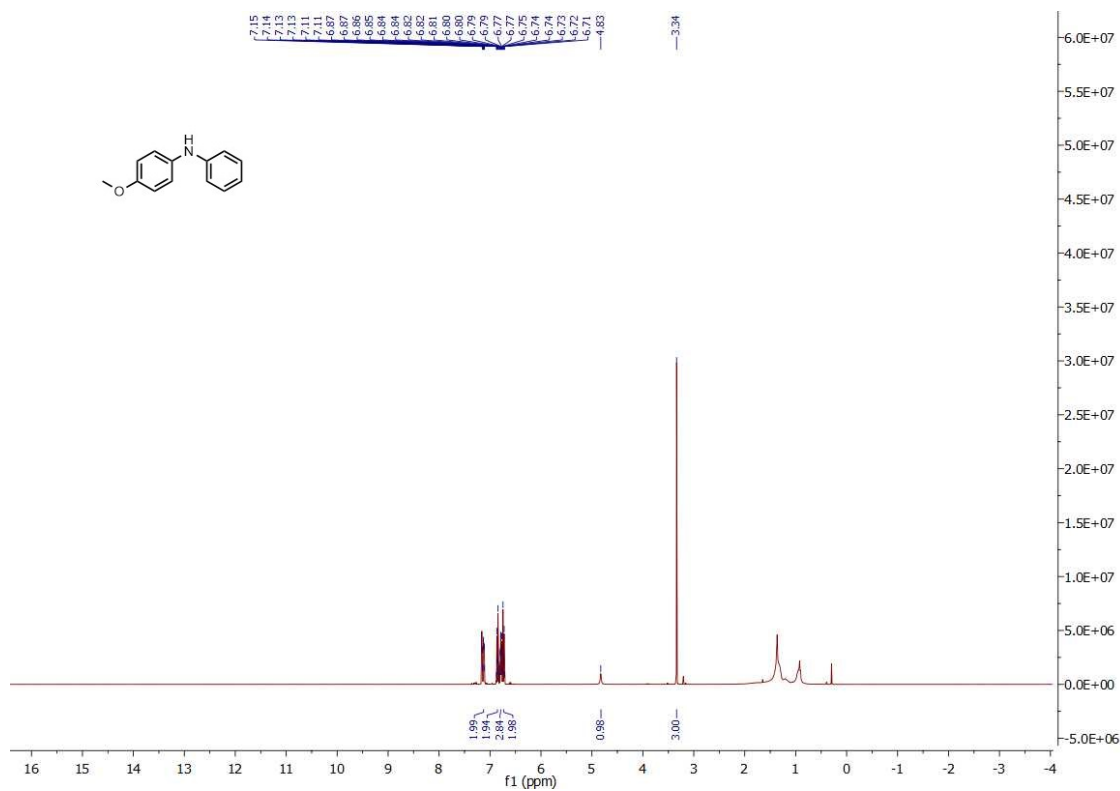


Figure A19. ¹H NMR spectrum of **98** (400 MHz, CDCl₃)

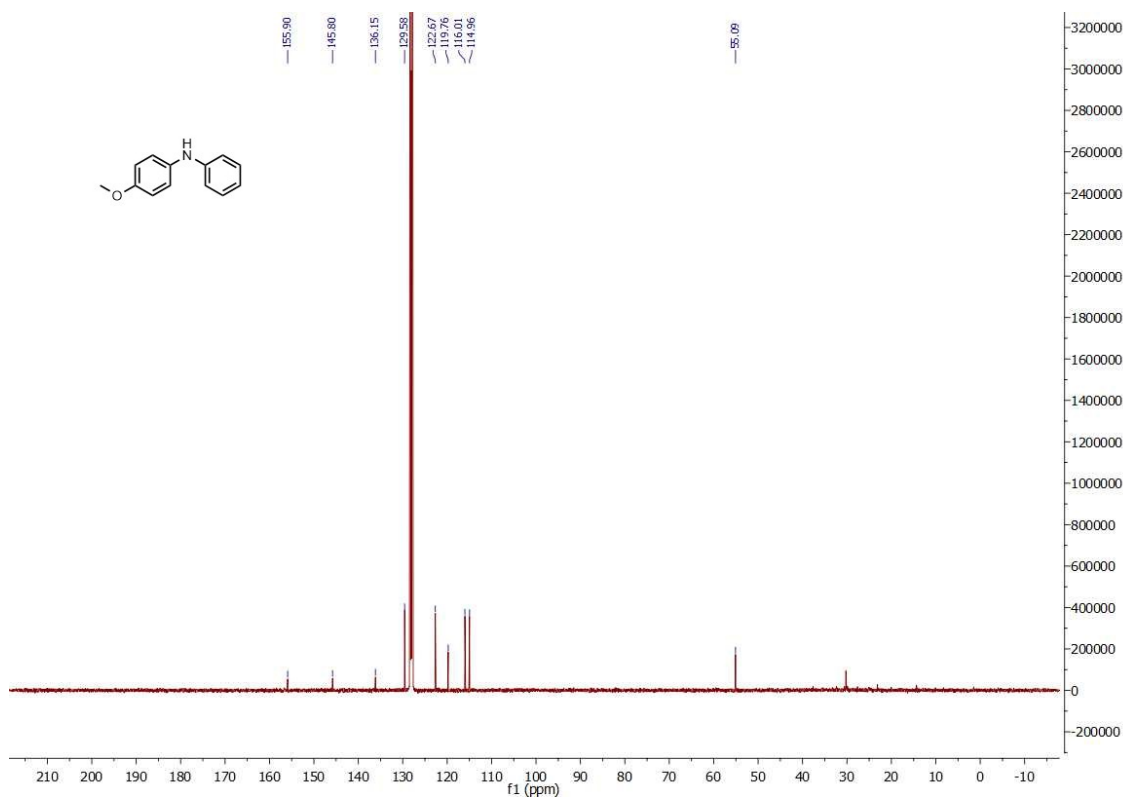


Figure A20. ¹³C NMR spectrum of **98** (100 MHz, CDCl₃)

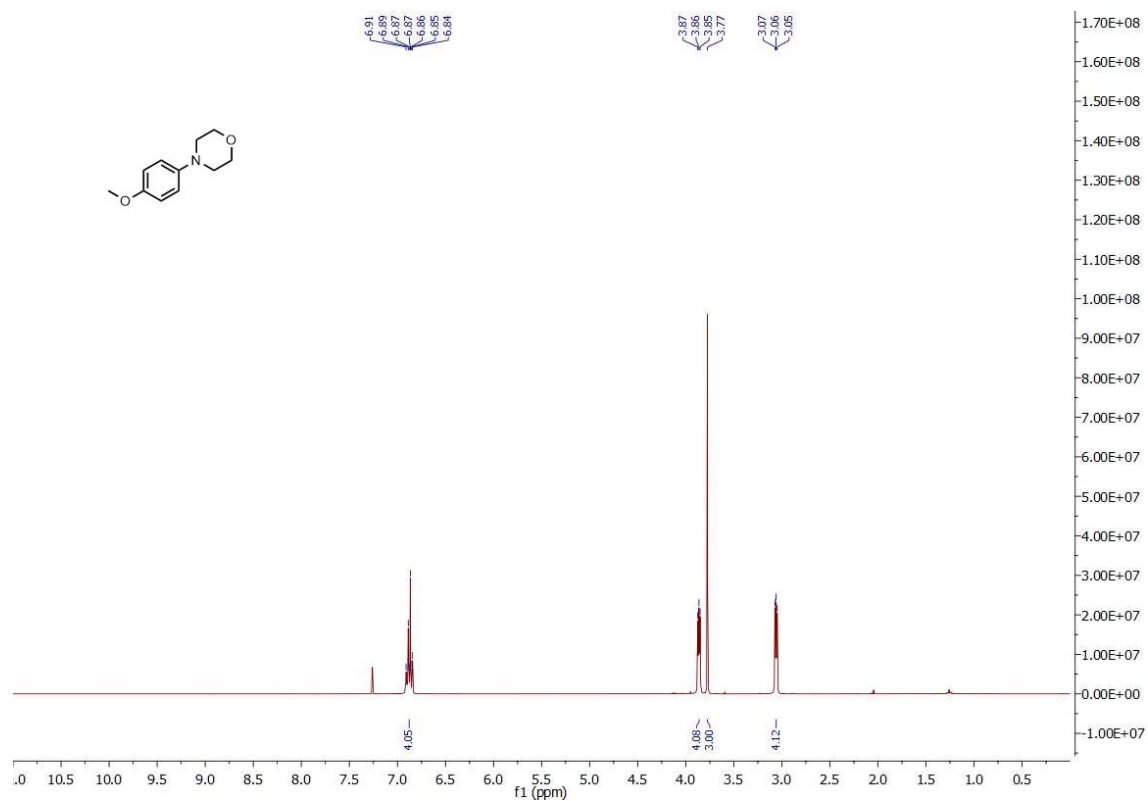


Figure A21. ^1H NMR spectrum of **99** (400 MHz, CDCl_3)

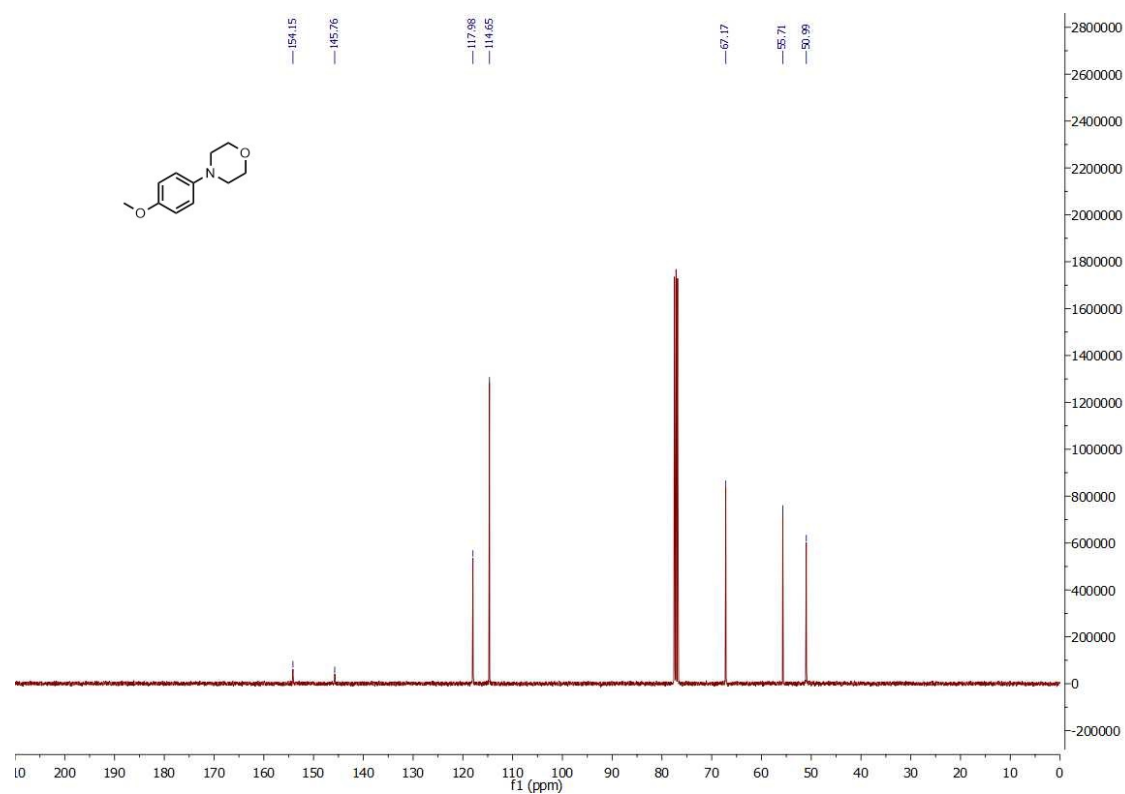


Figure A22. ^{13}C NMR spectrum of **99** (100 MHz, CDCl_3)

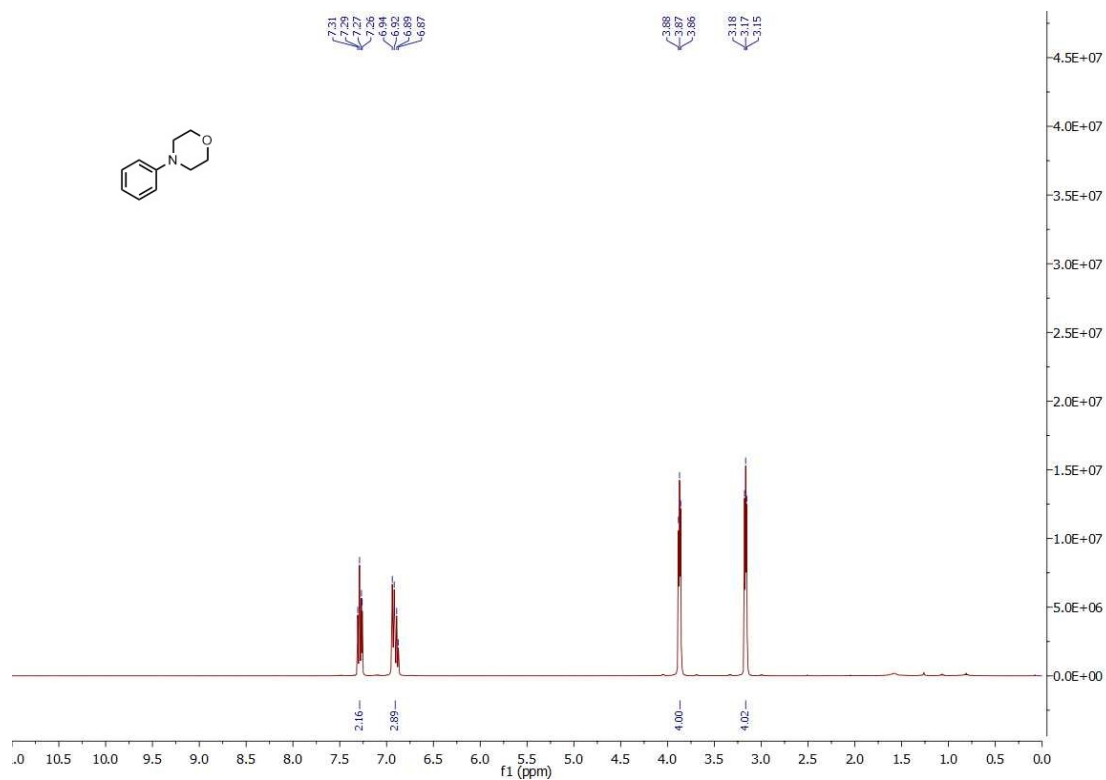


Figure A23. ^1H NMR spectrum of **107** (400 MHz, CDCl_3)

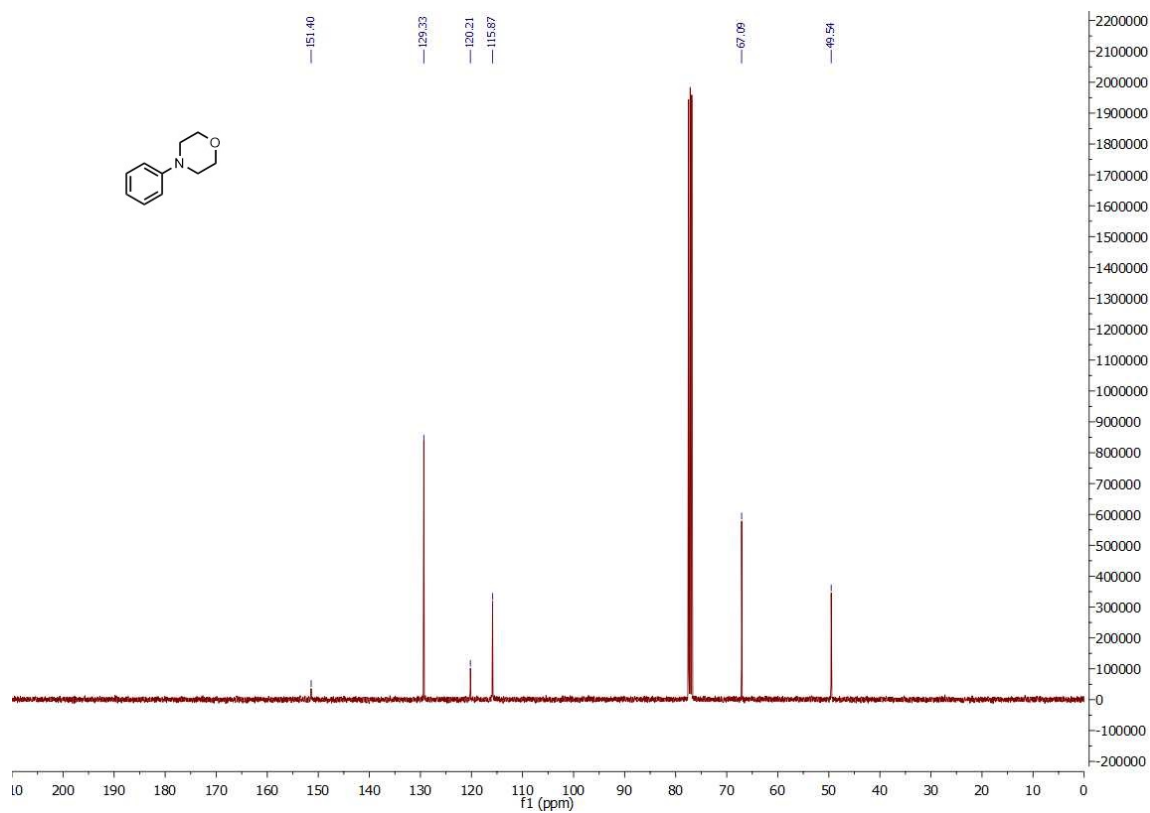


Figure A24. ^{13}C NMR spectrum of **107** (100 MHz, CDCl_3)

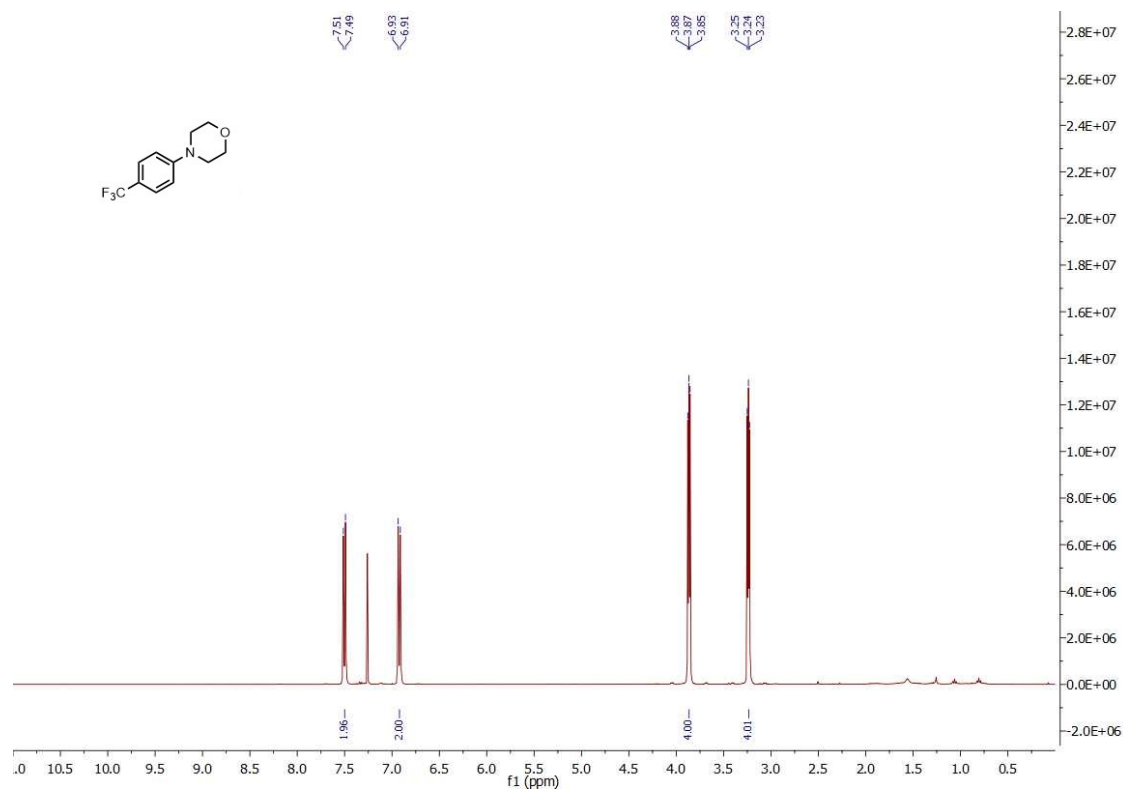


Figure A25. ¹H NMR spectrum of **108** (400 MHz, CDCl₃)

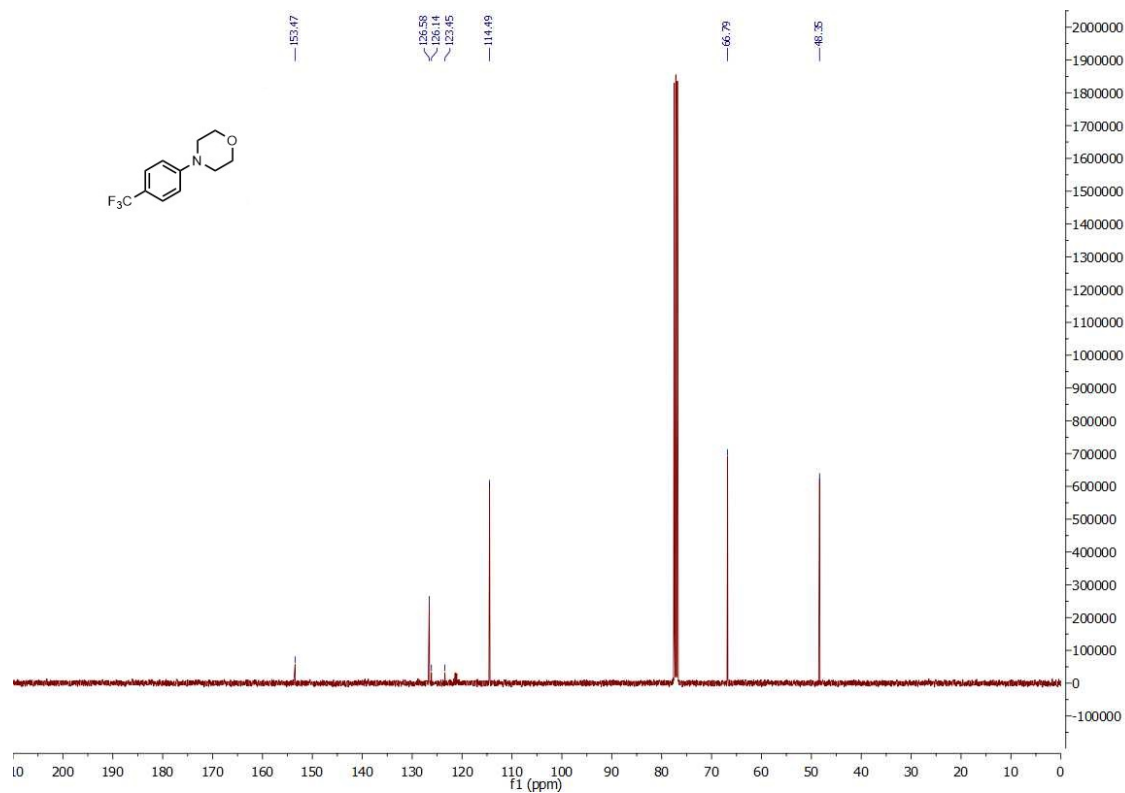


Figure A26. ¹³C NMR spectrum of **108** (100 MHz, CDCl₃)

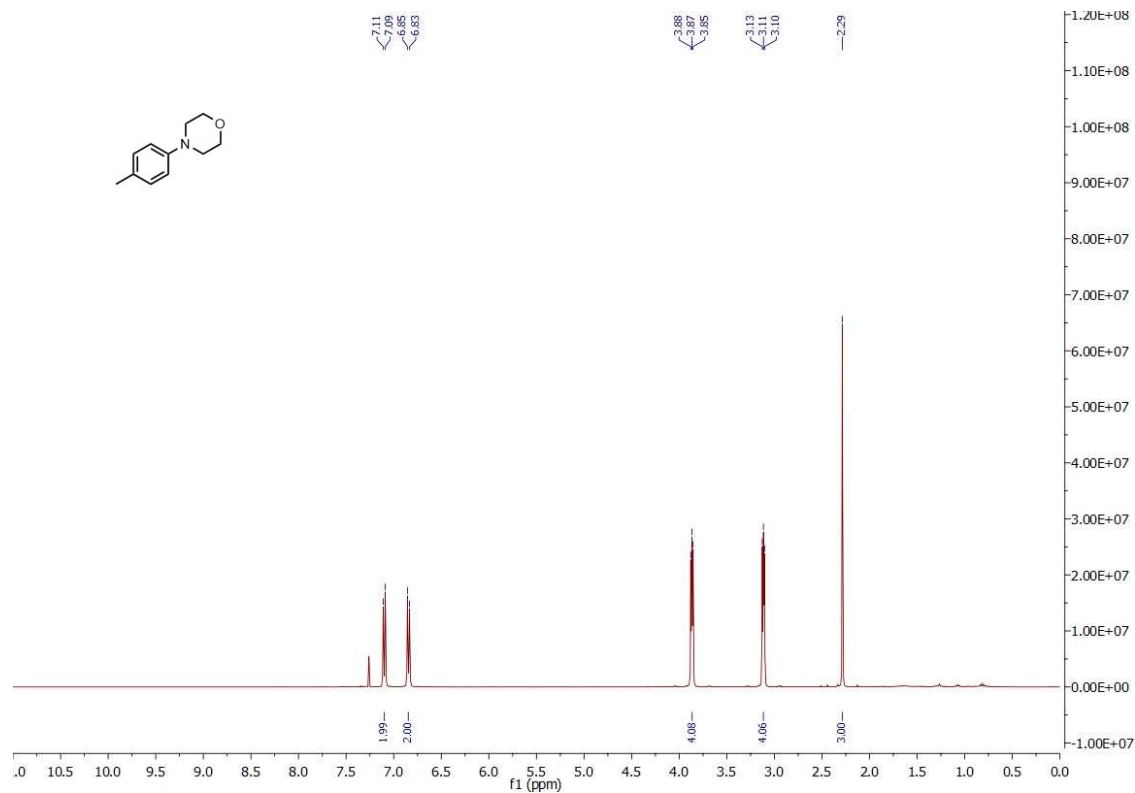


Figure A27. ^1H NMR spectrum of **109** (400 MHz, CDCl_3)

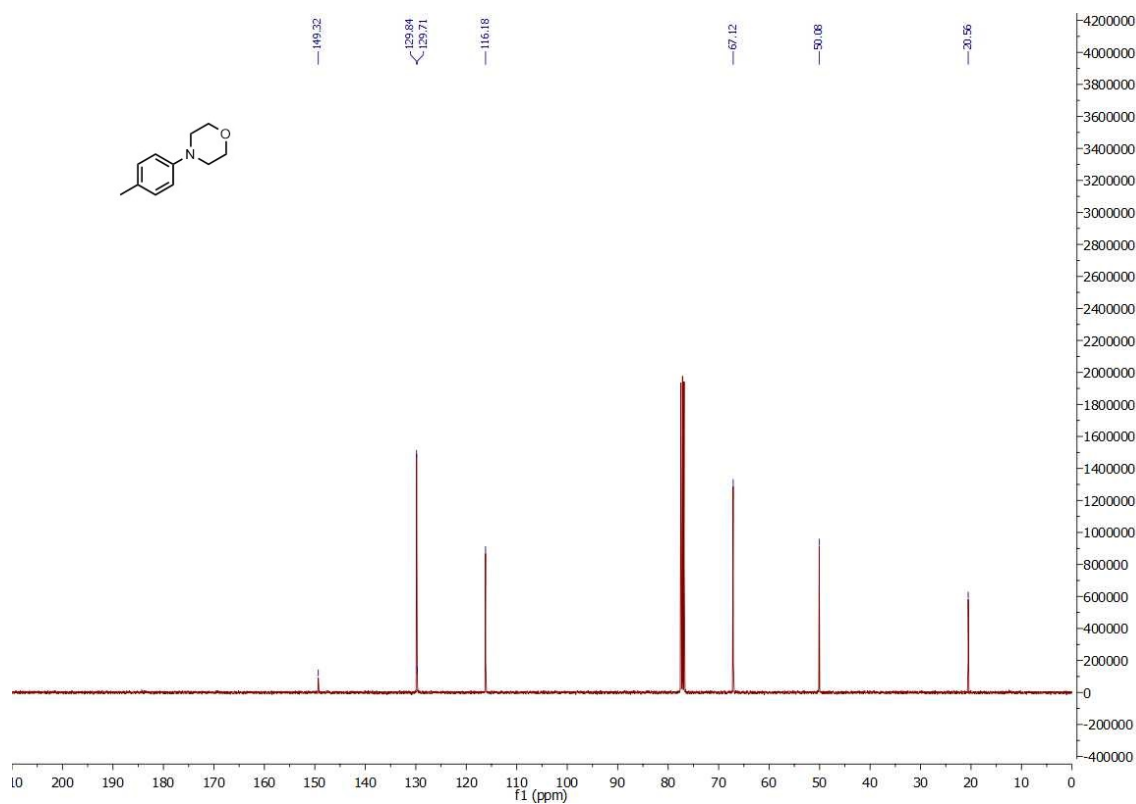


Figure A28. ^{13}C NMR spectrum of **109** (100 MHz, CDCl_3)

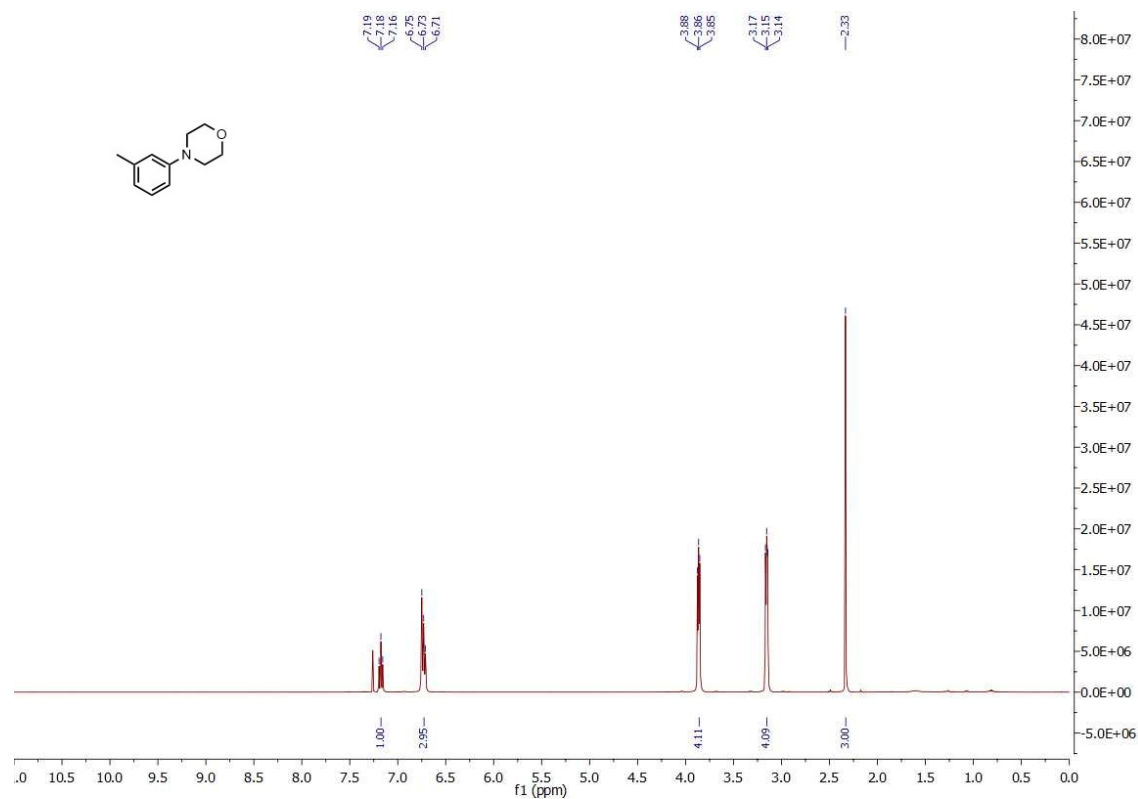


Figure A29. ^1H NMR spectrum of **110** (400 MHz, CDCl_3)

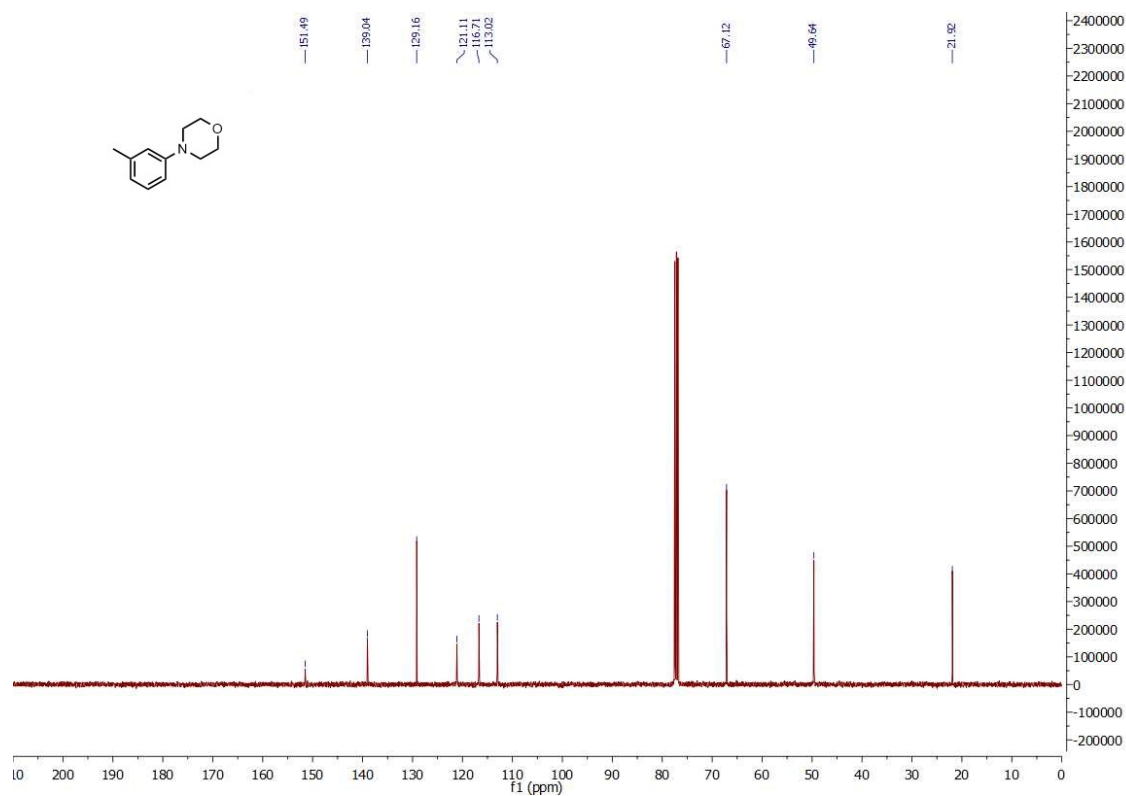


Figure A30. ^{13}C NMR spectrum of **110** (100 MHz, CDCl_3)

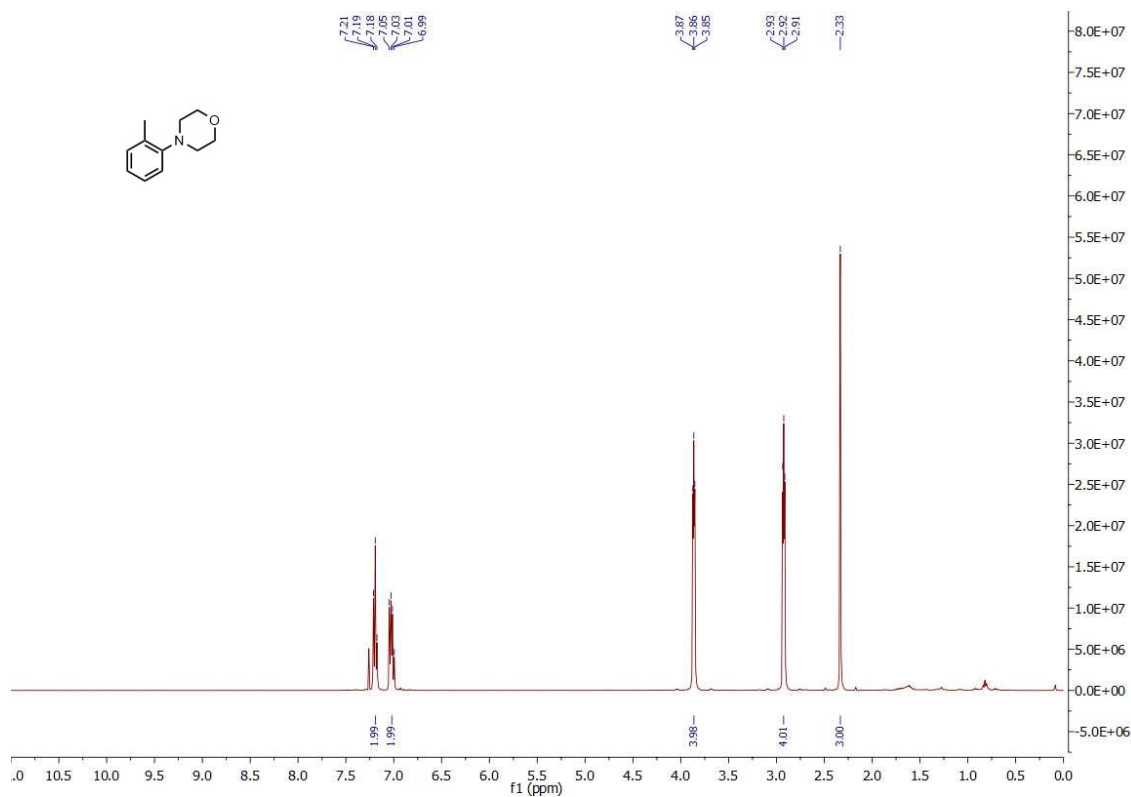


Figure A31. ¹H NMR spectrum of **111** (400 MHz, CDCl₃)

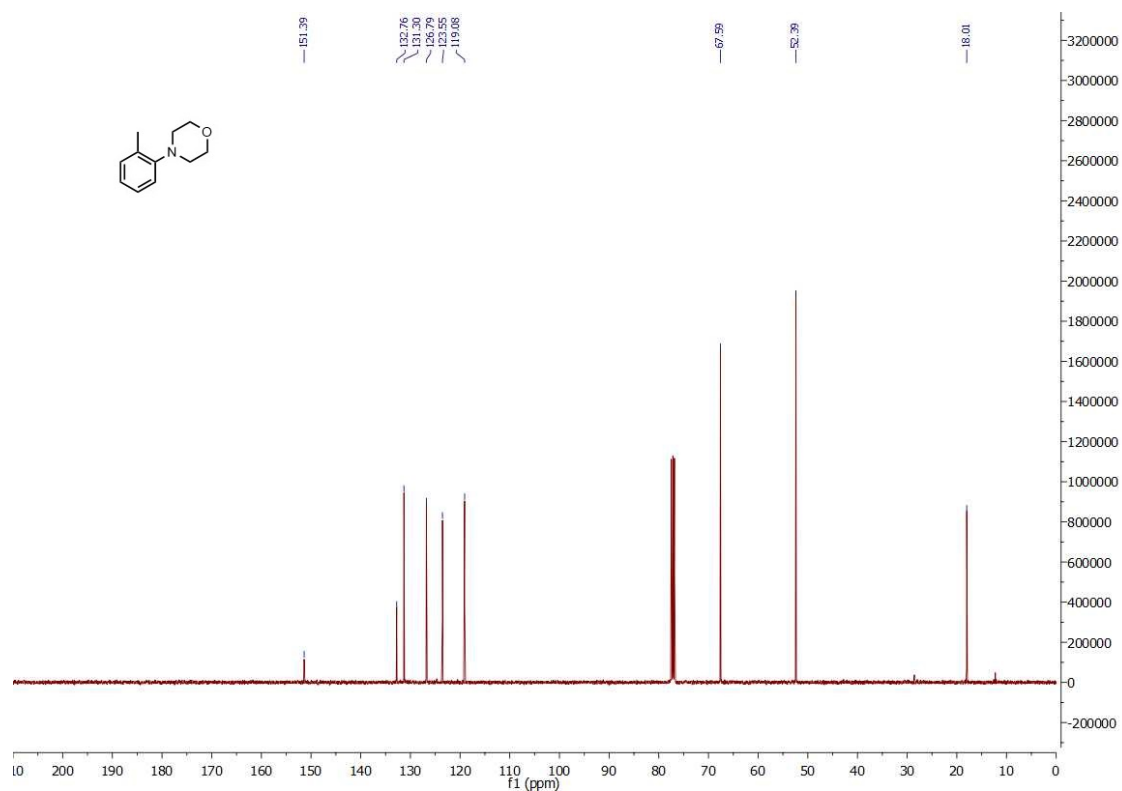


Figure A32. ¹³C NMR spectrum of **111** (100 MHz, CDCl₃)

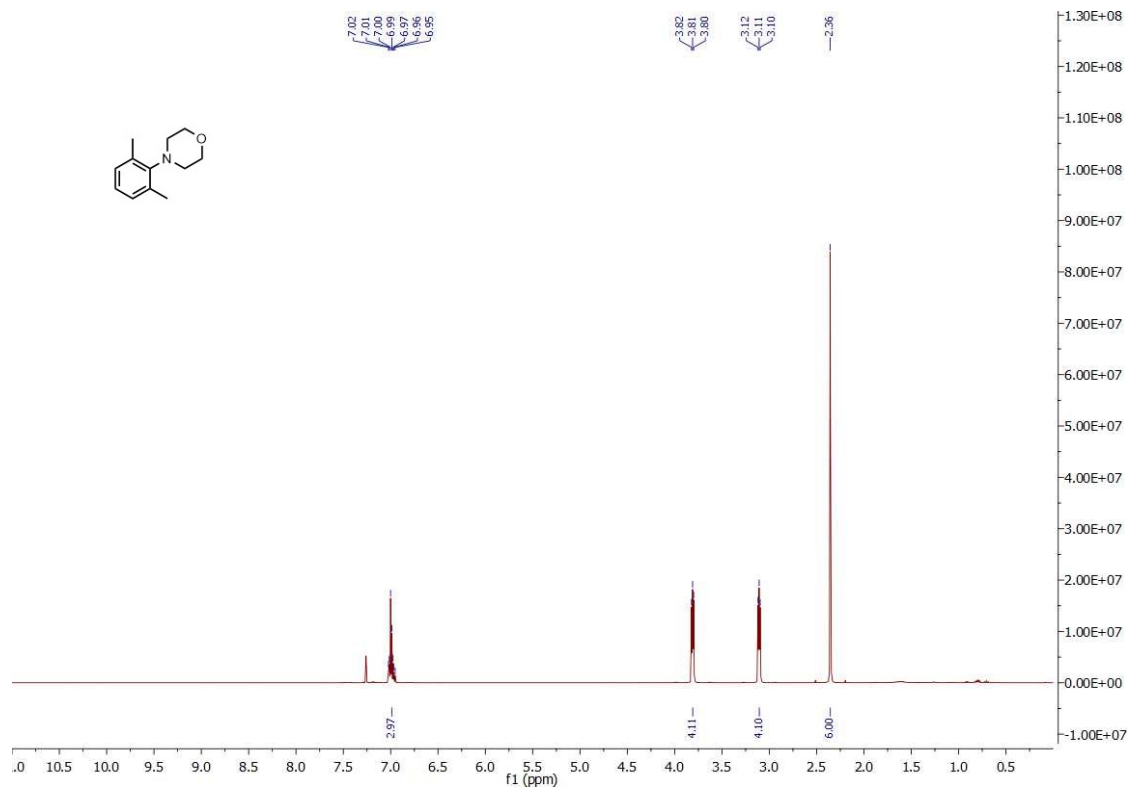


Figure A33. ¹H NMR spectrum of **112** (400 MHz, CDCl₃)

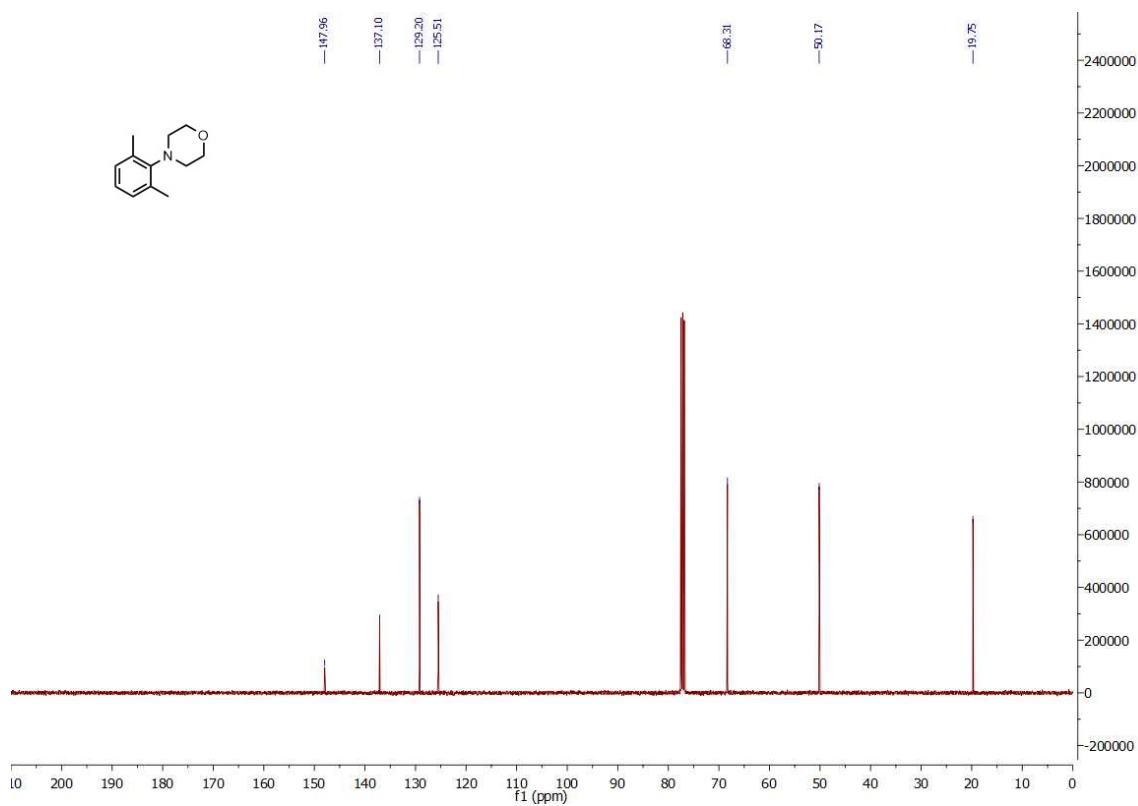


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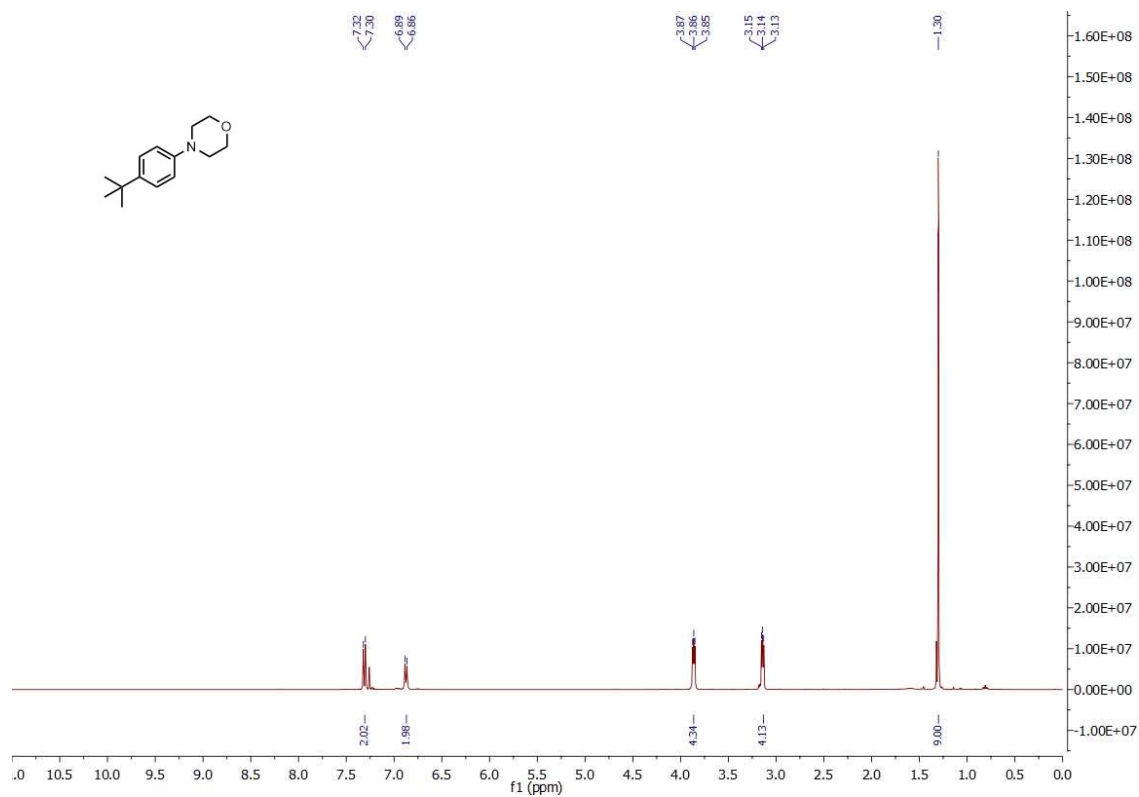


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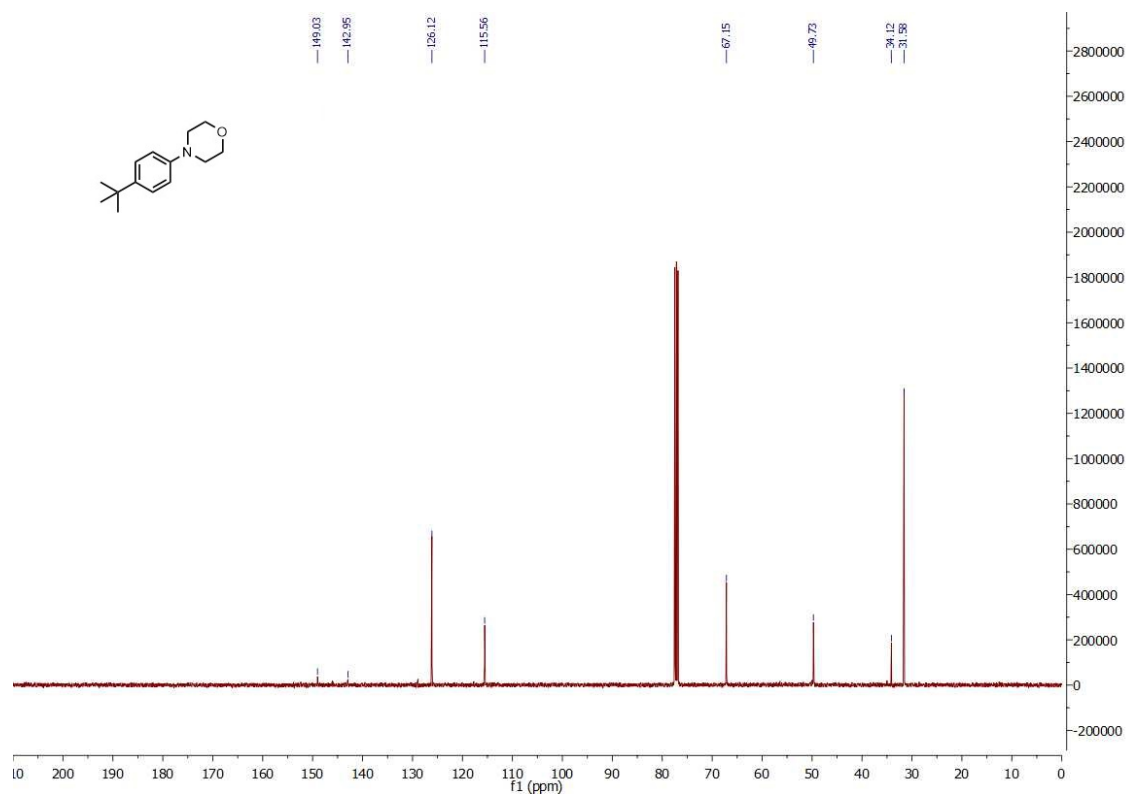


Figure A36. ^{13}C NMR spectrum of **113** (100 MHz, CDCl_3)

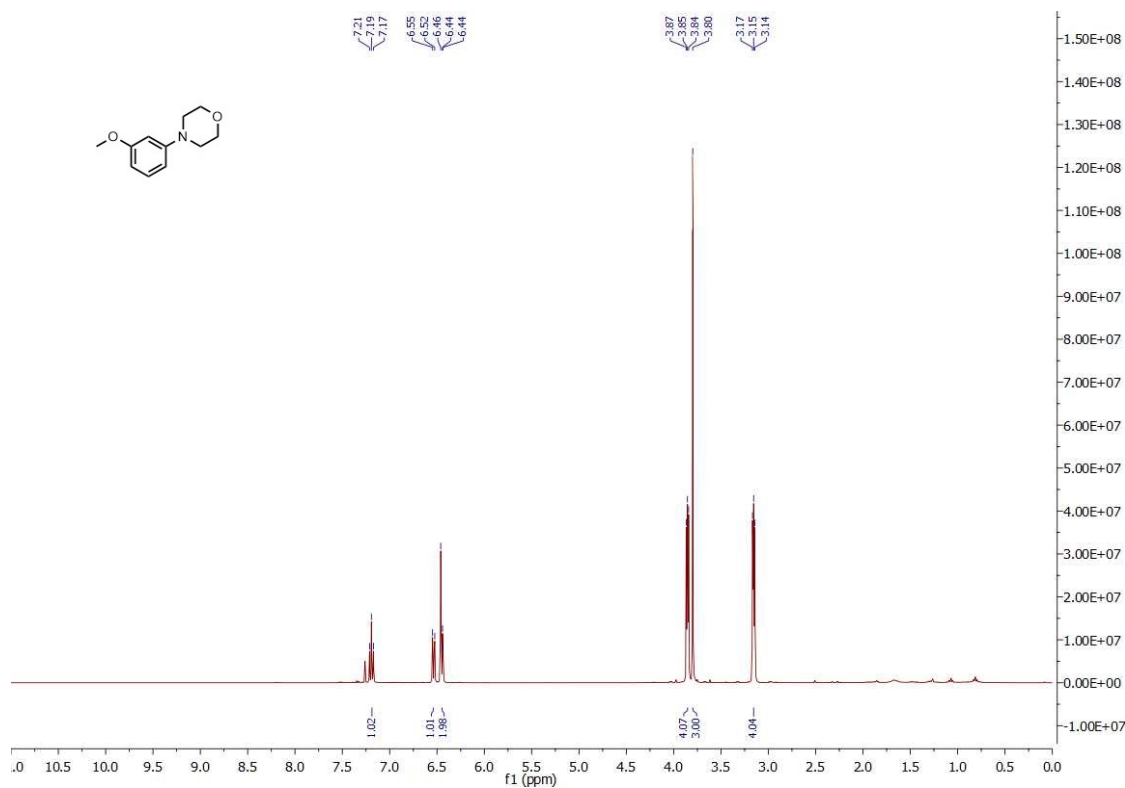


Figure A37. ^1H NMR spectrum of **114** (400 MHz, CDCl_3)

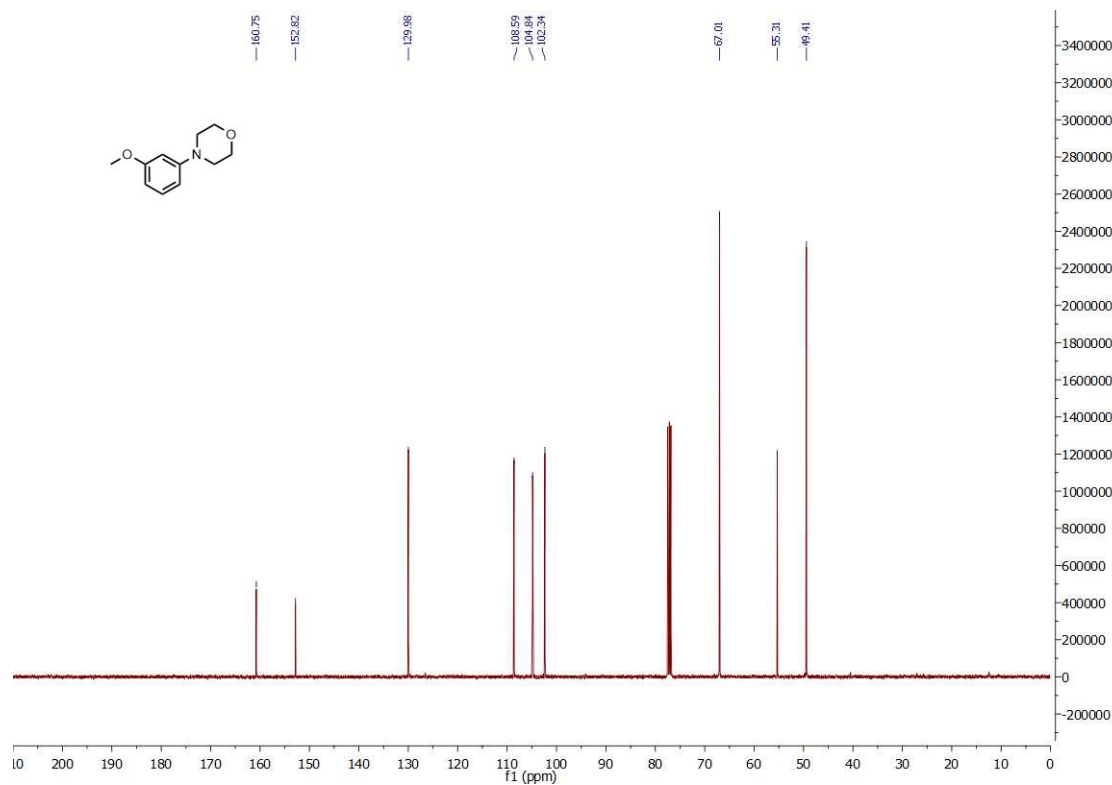


Figure A38. ^{13}C NMR spectrum of **114** (100 MHz, CDCl_3)

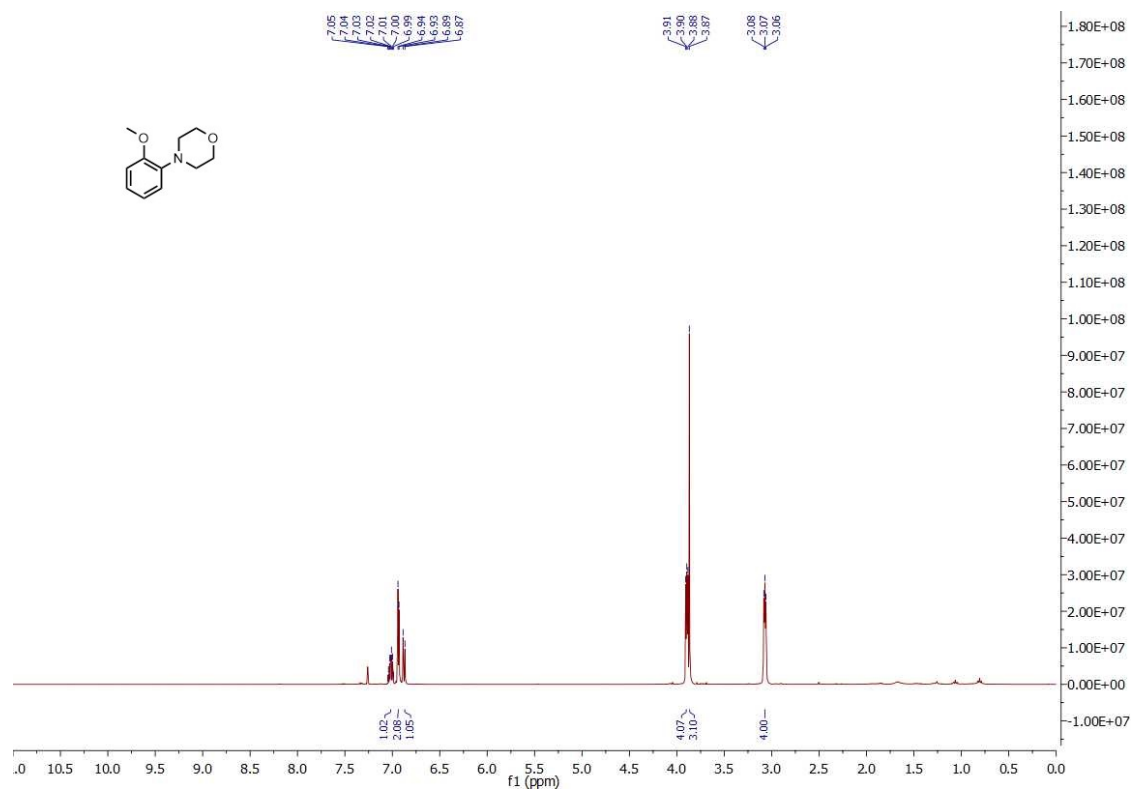


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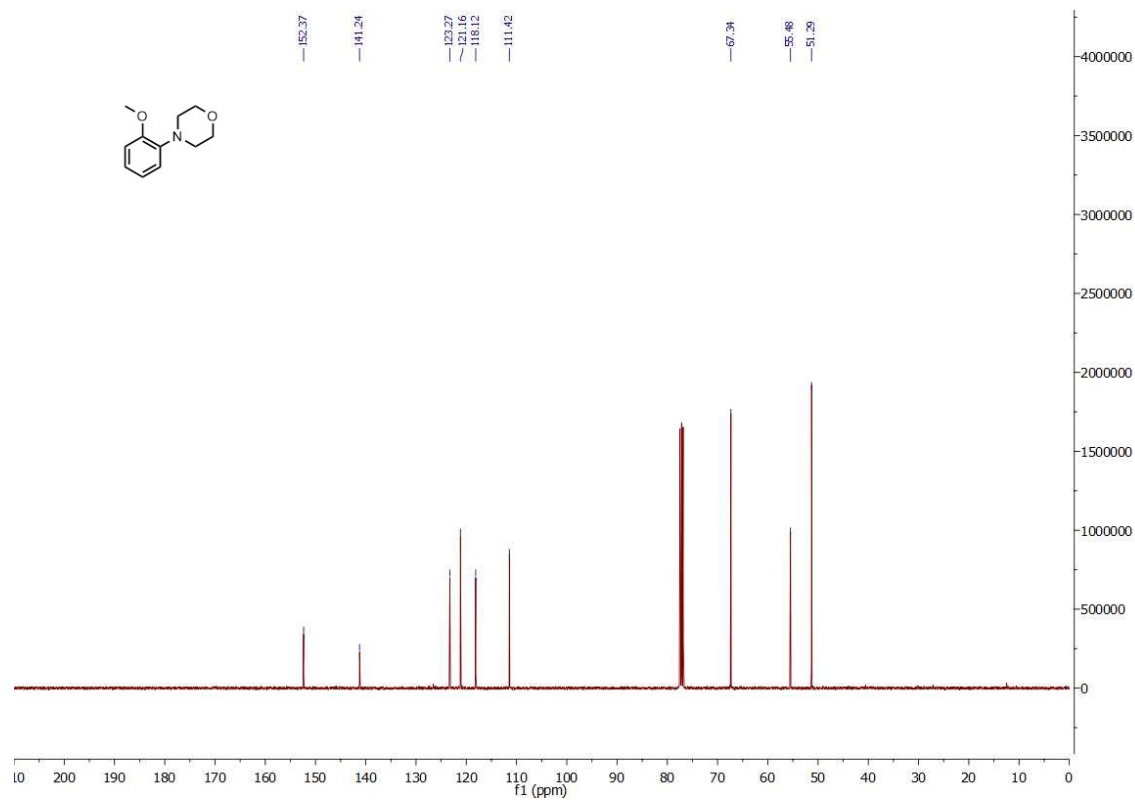


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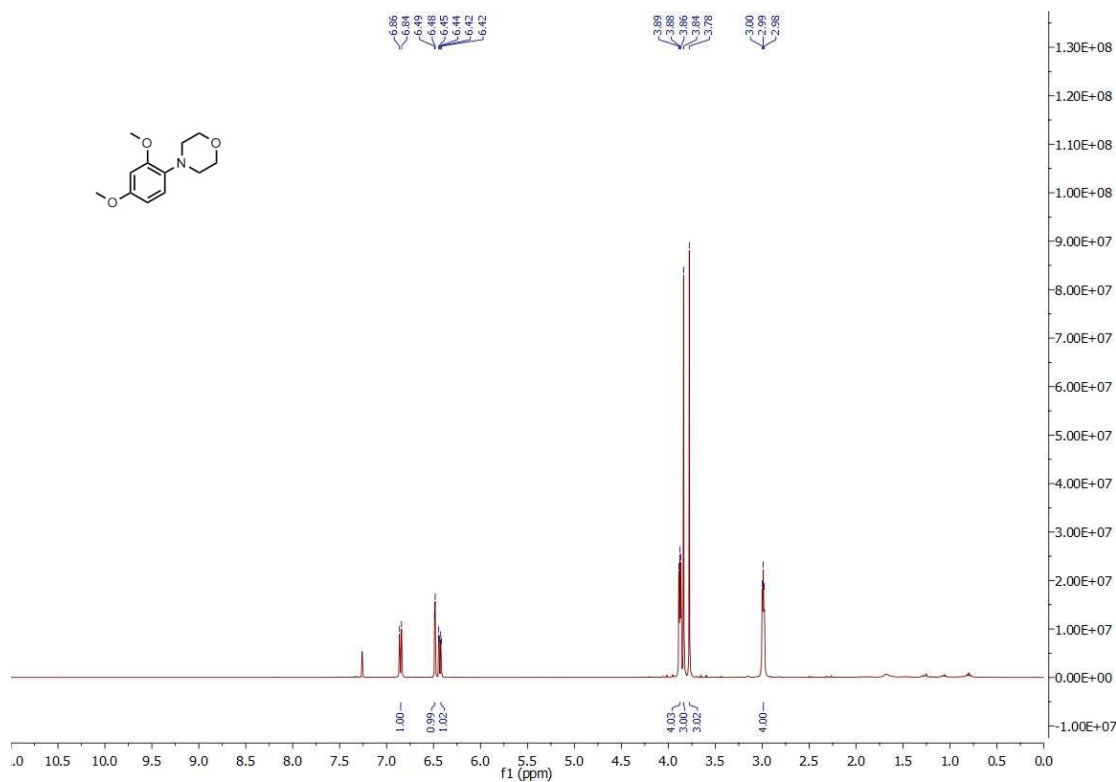


Figure A41. ¹H NMR spectrum of **116** (400 MHz, CDCl₃)

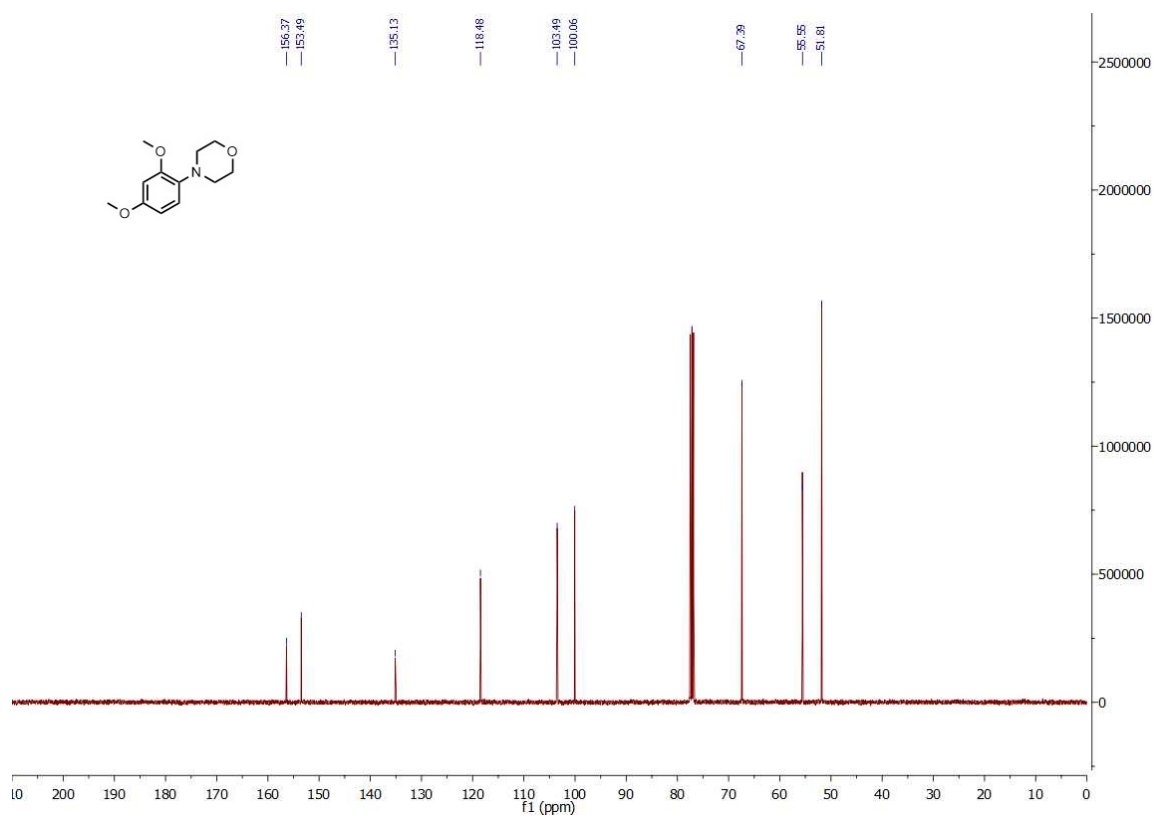


Figure A42. ¹³C NMR spectrum of **116** (100 MHz, CDCl₃)

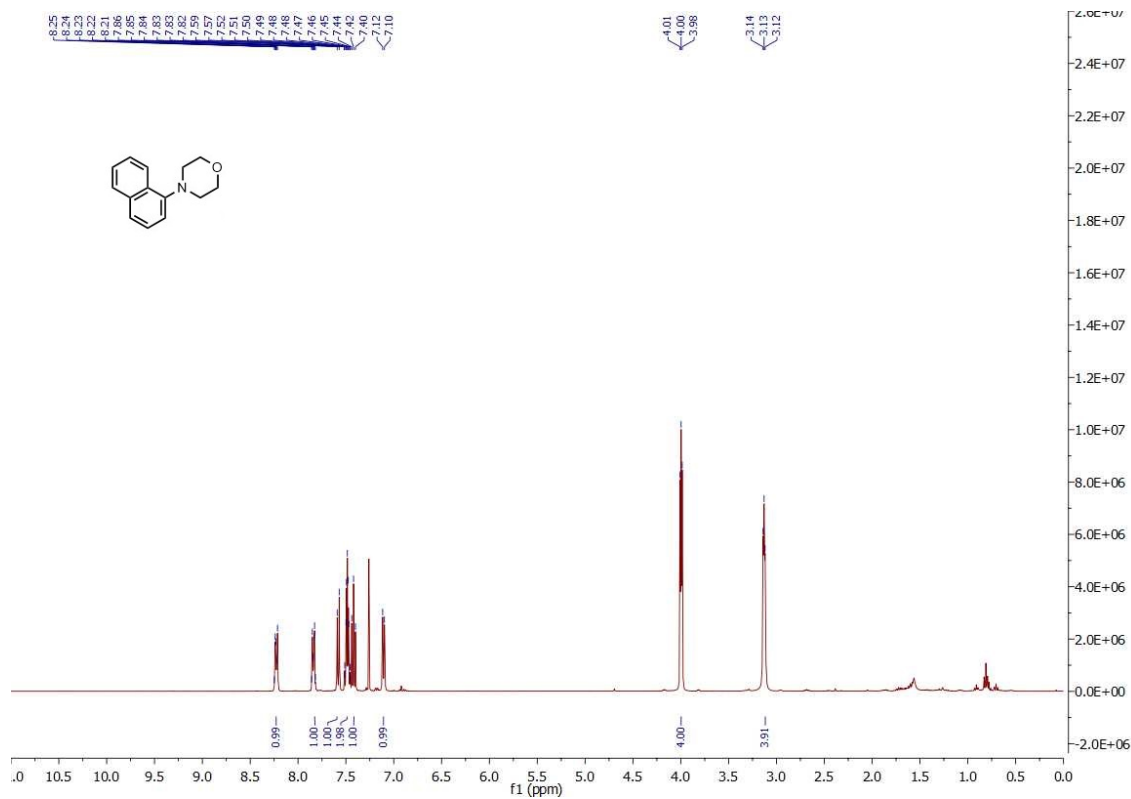


Figure A43. ¹H NMR spectrum of **117** (400 MHz, CDCl₃)

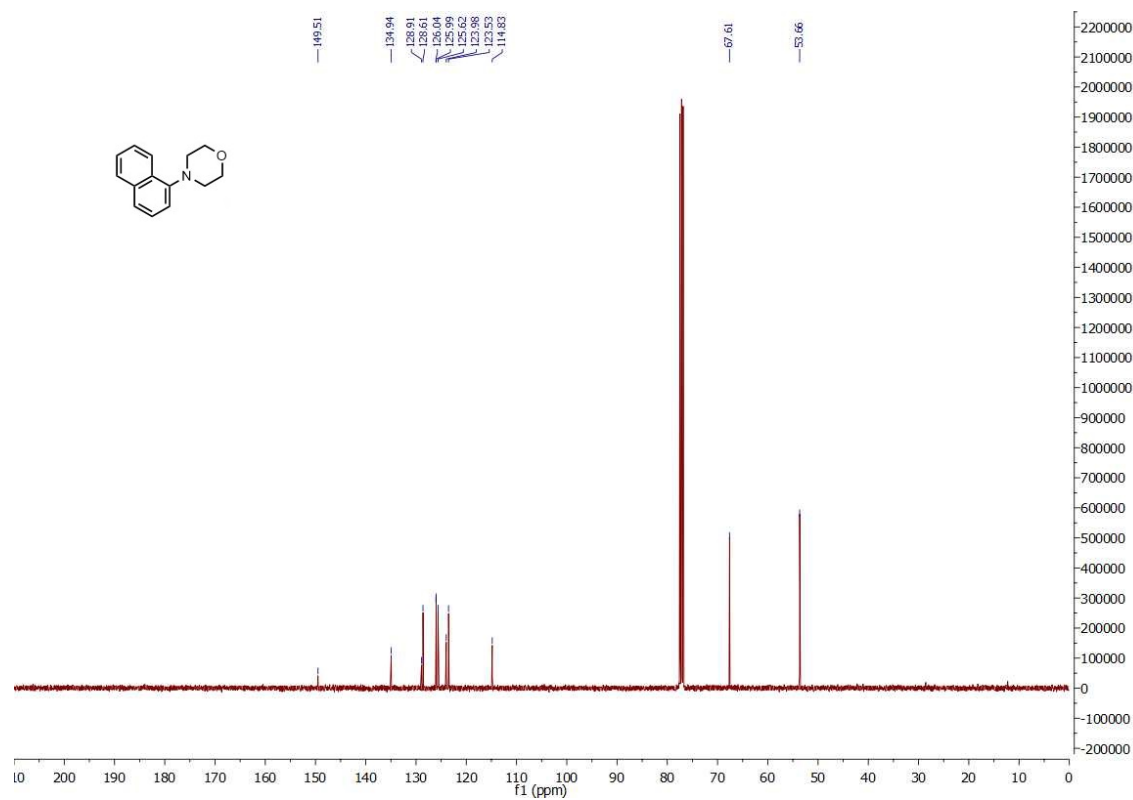


Figure A44. ¹³C NMR spectrum of **117** (100 MHz, CDCl₃)

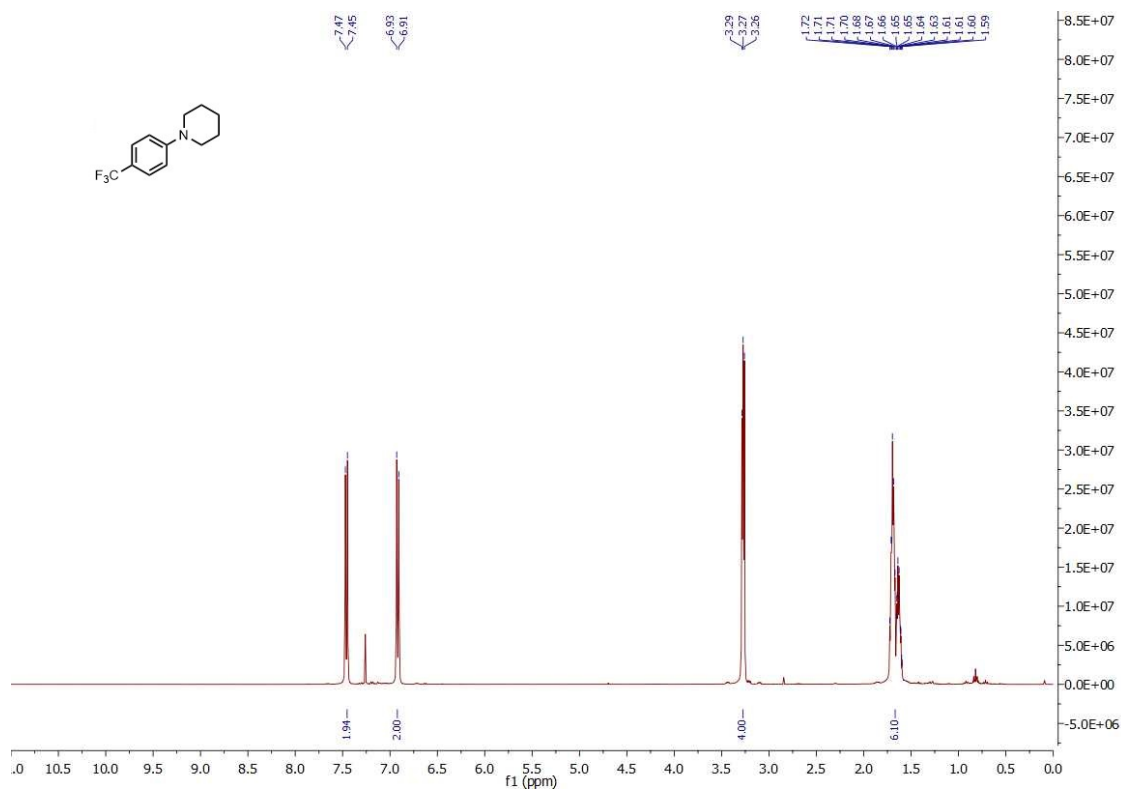


Figure A45. ¹H NMR spectrum of **118** (400 MHz, CDCl₃)

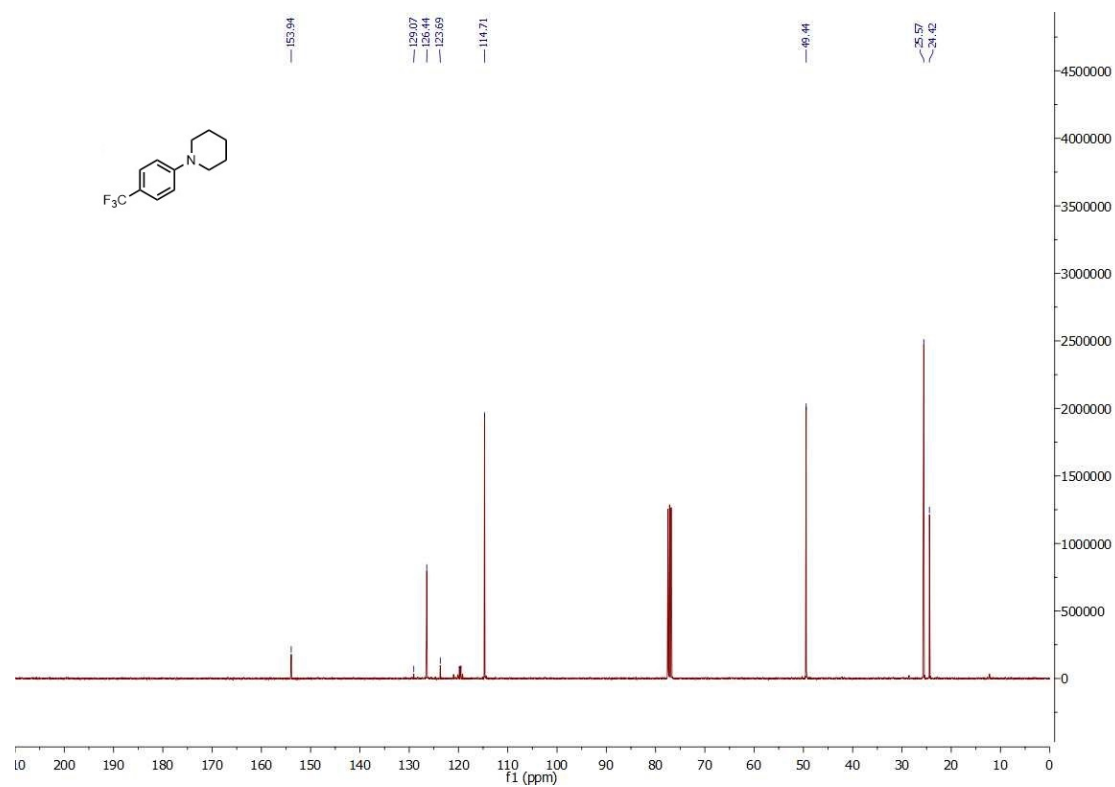


Figure A46. ¹³C NMR spectrum of **118** (100 MHz, CDCl₃)

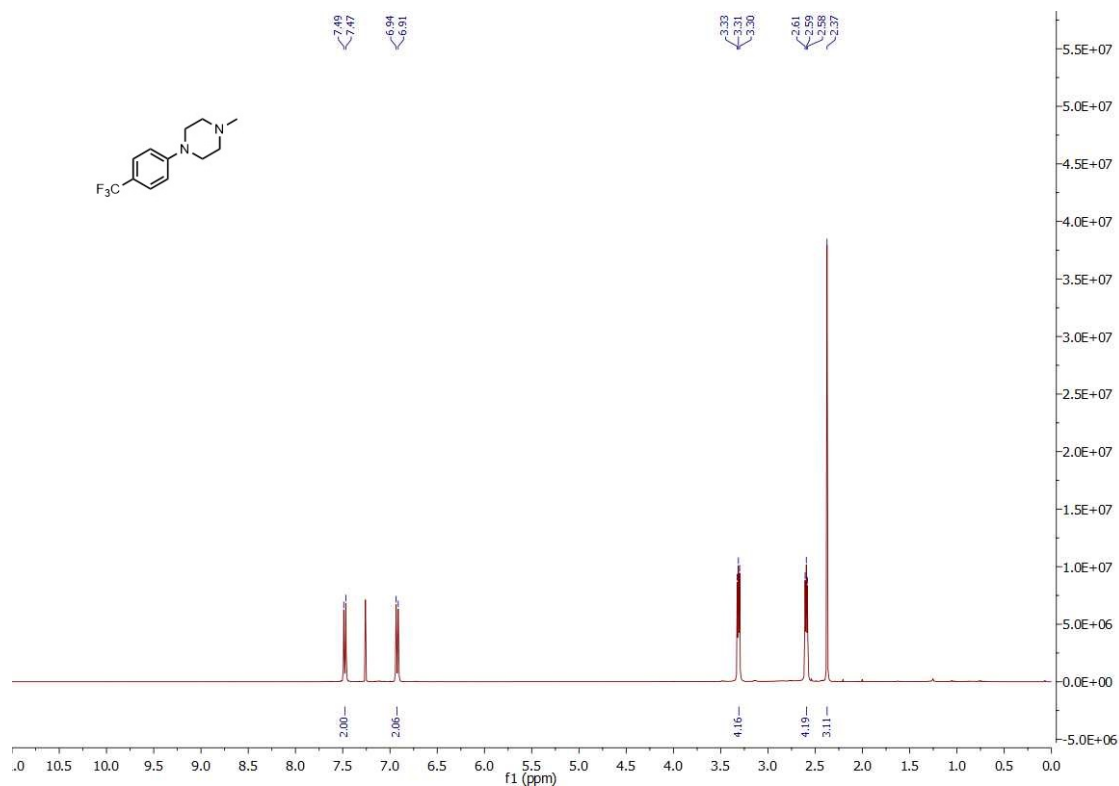


Figure A47. ¹H NMR spectrum of **119** (400 MHz, CDCl₃)

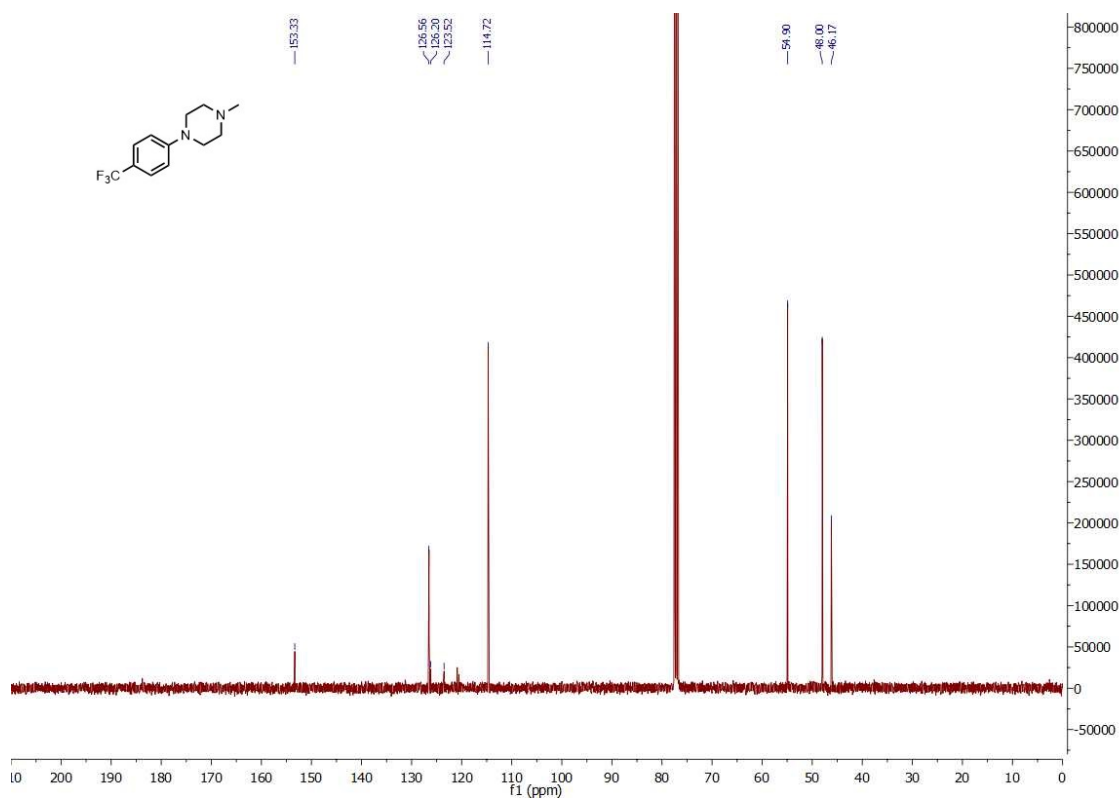


Figure A48. ¹³C NMR spectrum of **119** (100 MHz, CDCl₃)

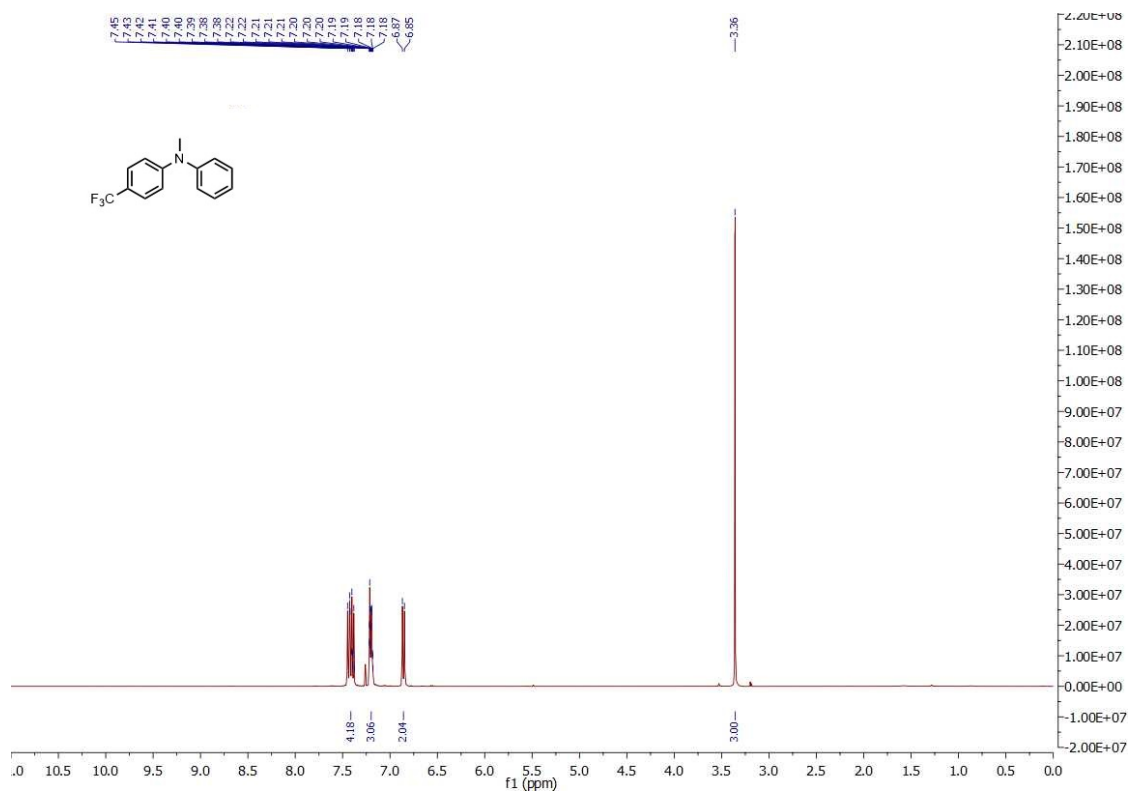


Figure A49. ¹H NMR spectrum of **120** (400 MHz, CDCl₃)

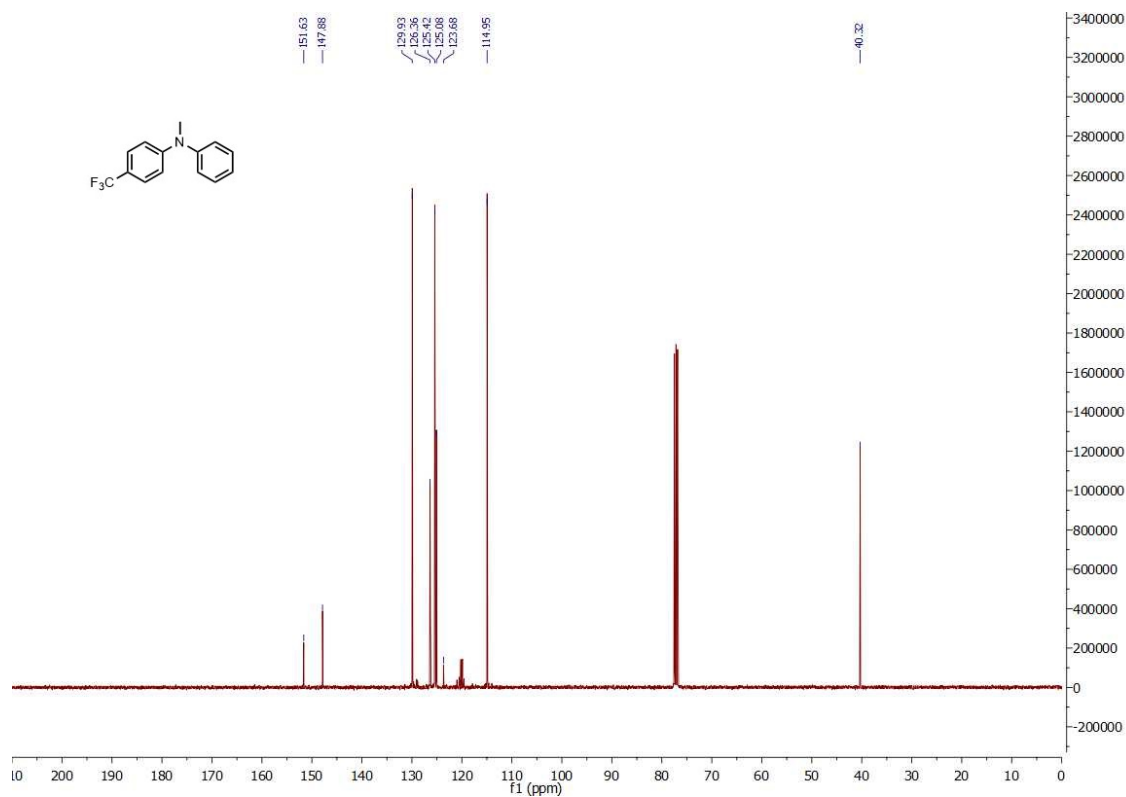


Figure A50. ¹³C NMR spectrum of **120** (100 MHz, CDCl₃)

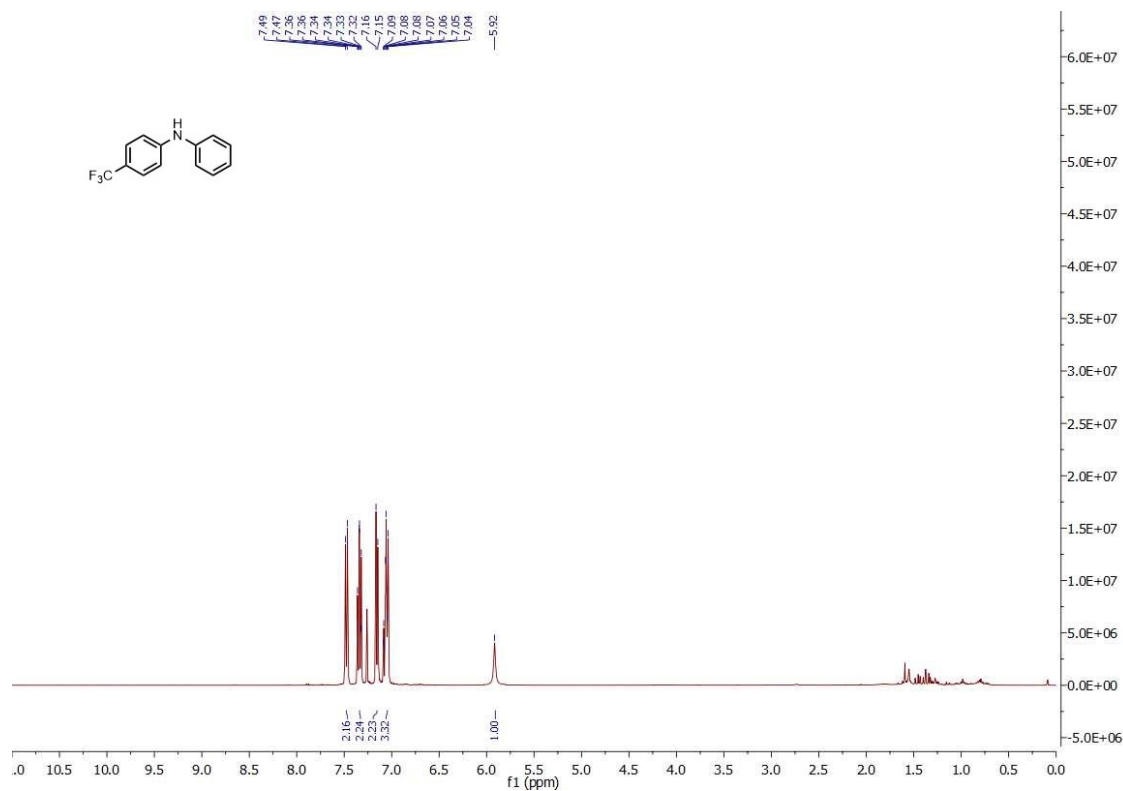


Figure A51. ¹H NMR spectrum of **121** (400 MHz, CDCl₃)

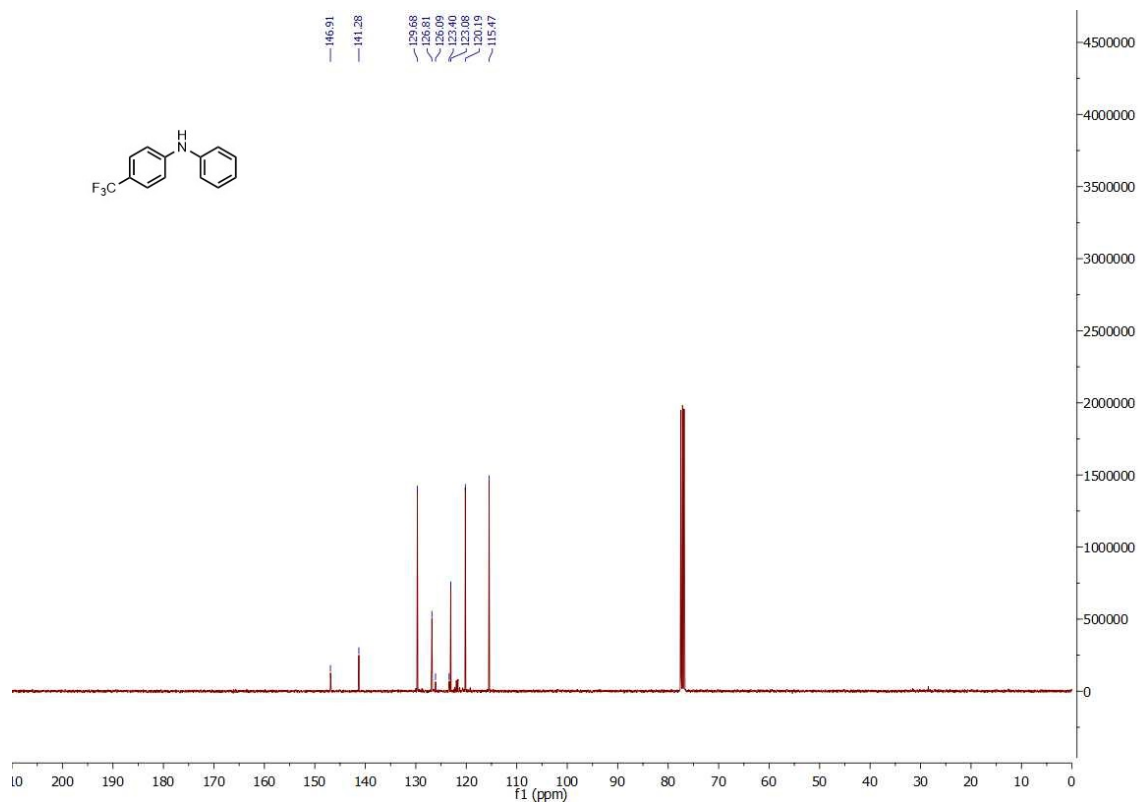


Figure A52. ¹³C NMR spectrum of **121** (100 MHz, CDCl₃)

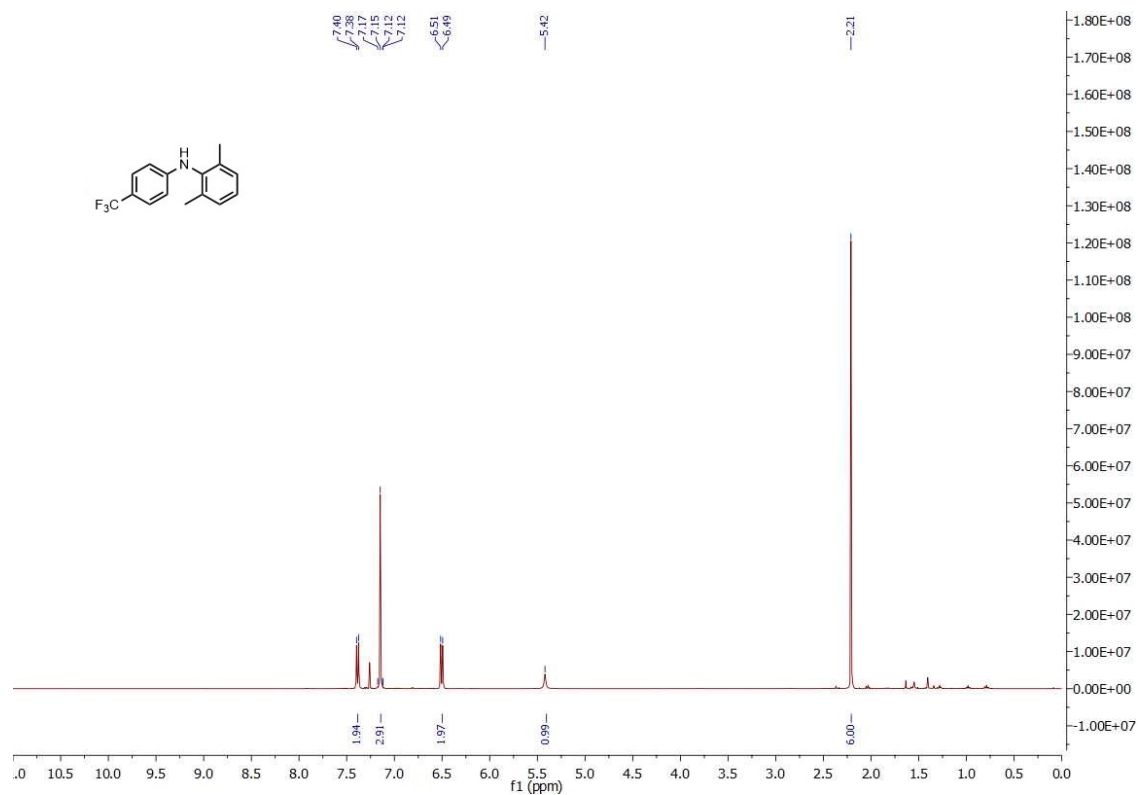


Figure A53. ^1H NMR spectrum of **122** (400 MHz, CDCl_3)

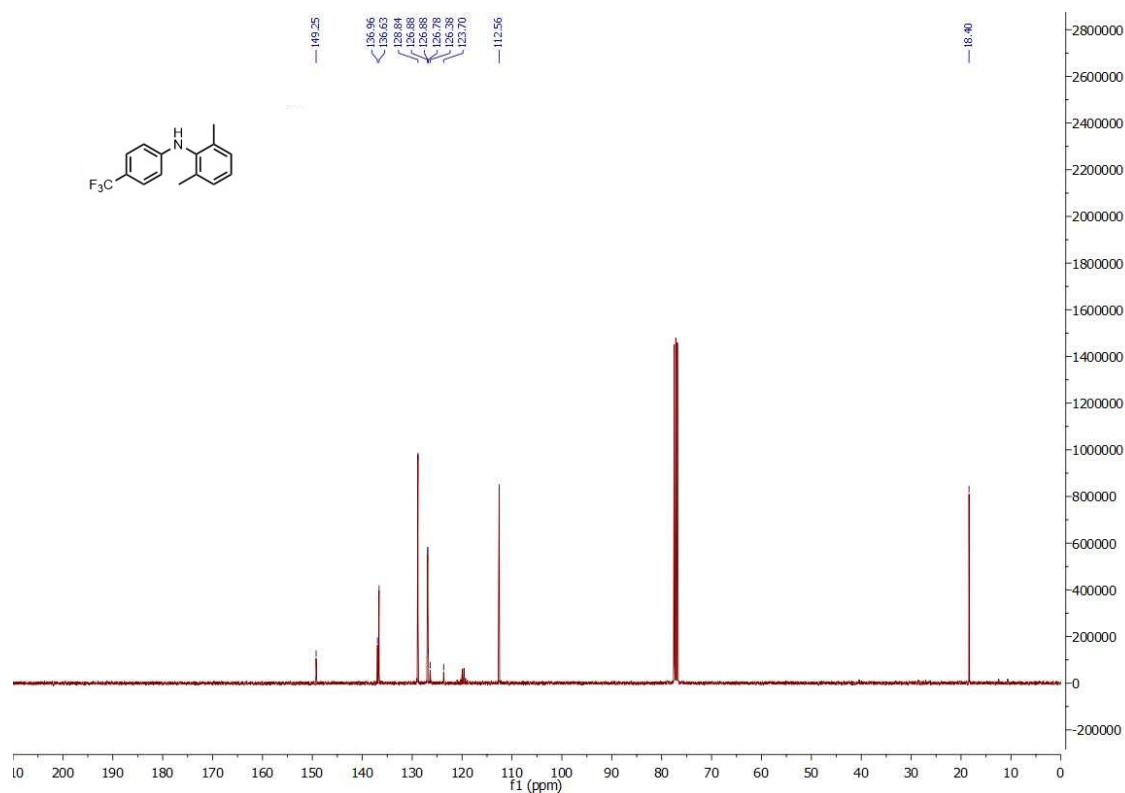


Figure A54. ^{13}C NMR spectrum of **122** (100 MHz, CDCl_3)

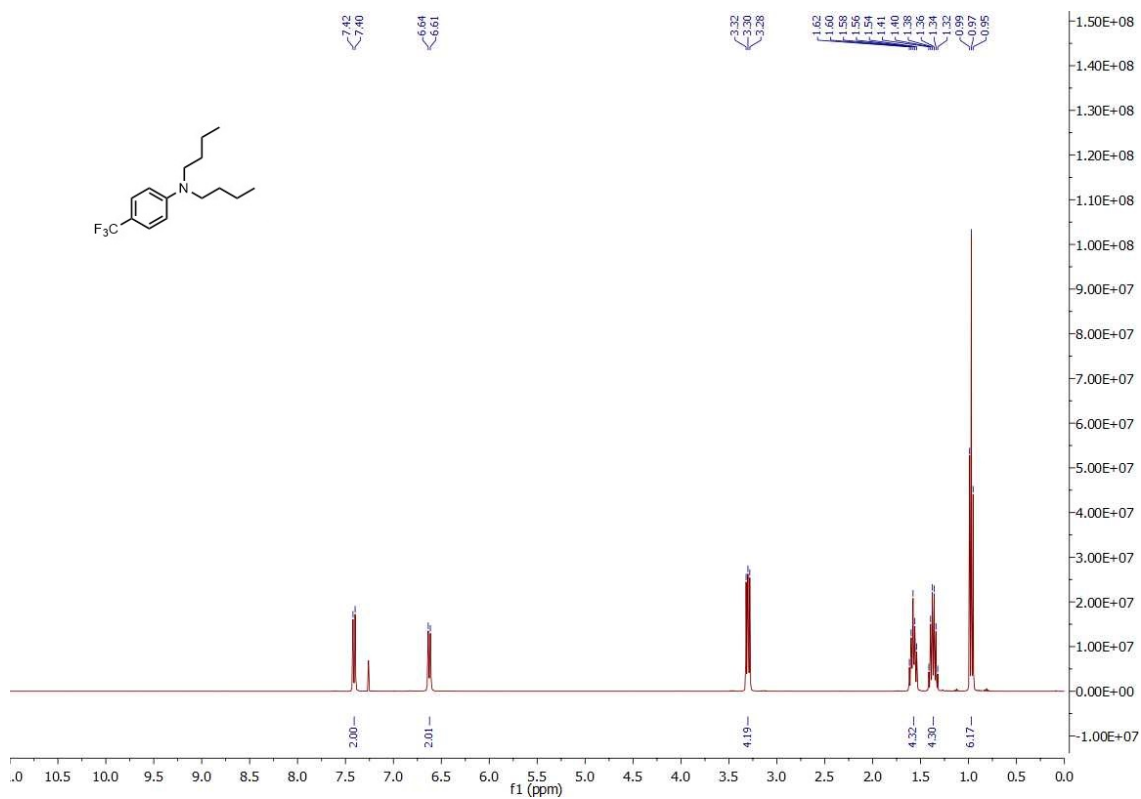


Figure A55. ¹H NMR spectrum of **123** (400 MHz, CDCl₃)

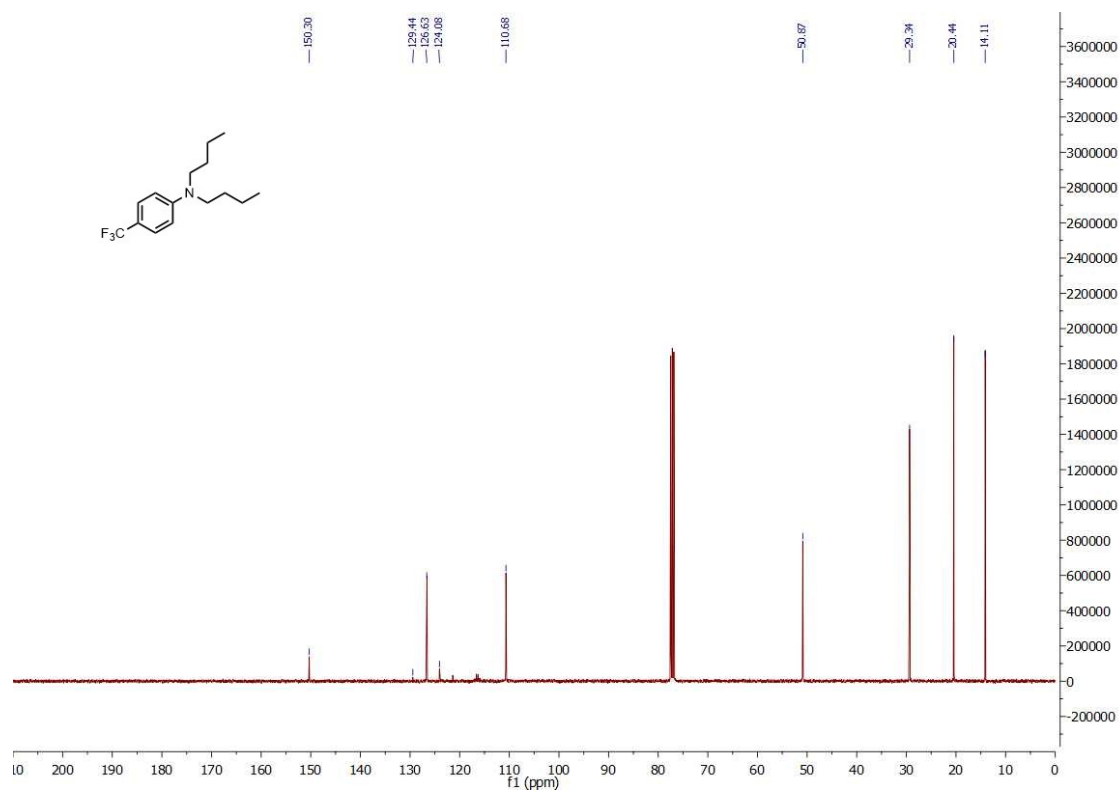


Figure A56. ¹³C NMR spectrum of **123** (100 MHz, CDCl₃)

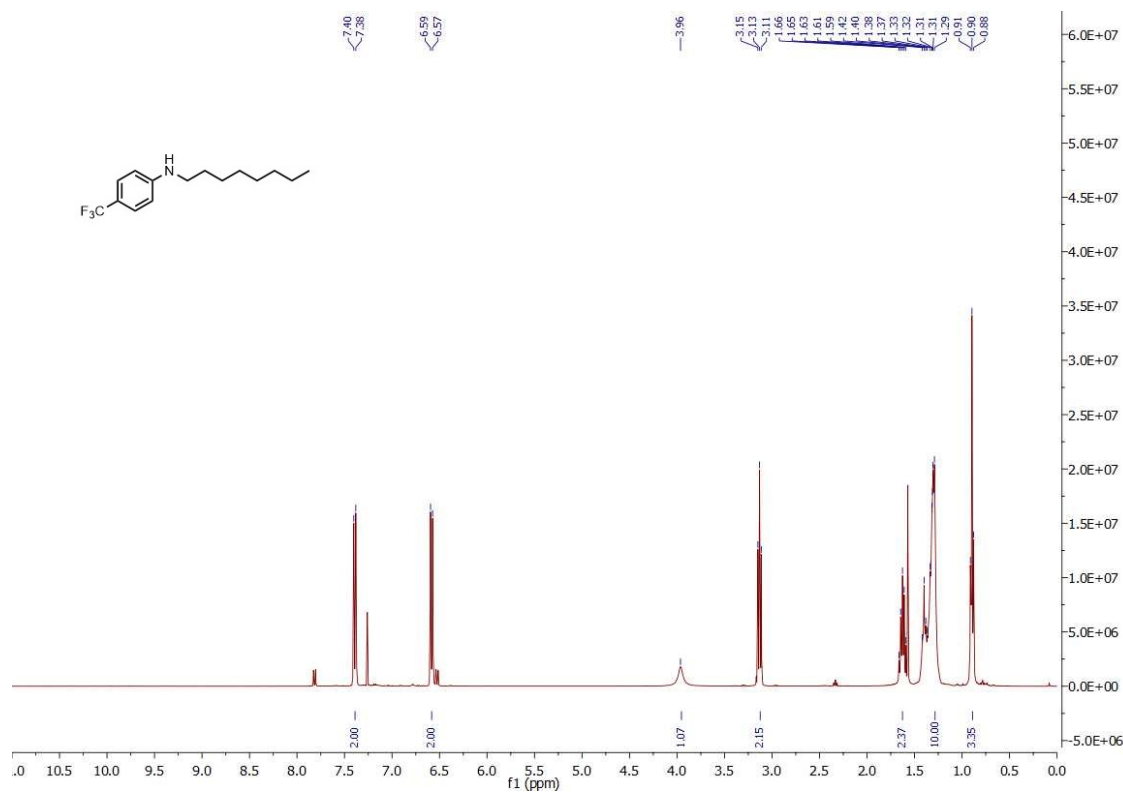


Figure A57. ¹H NMR spectrum of **124** (400 MHz, CDCl₃)

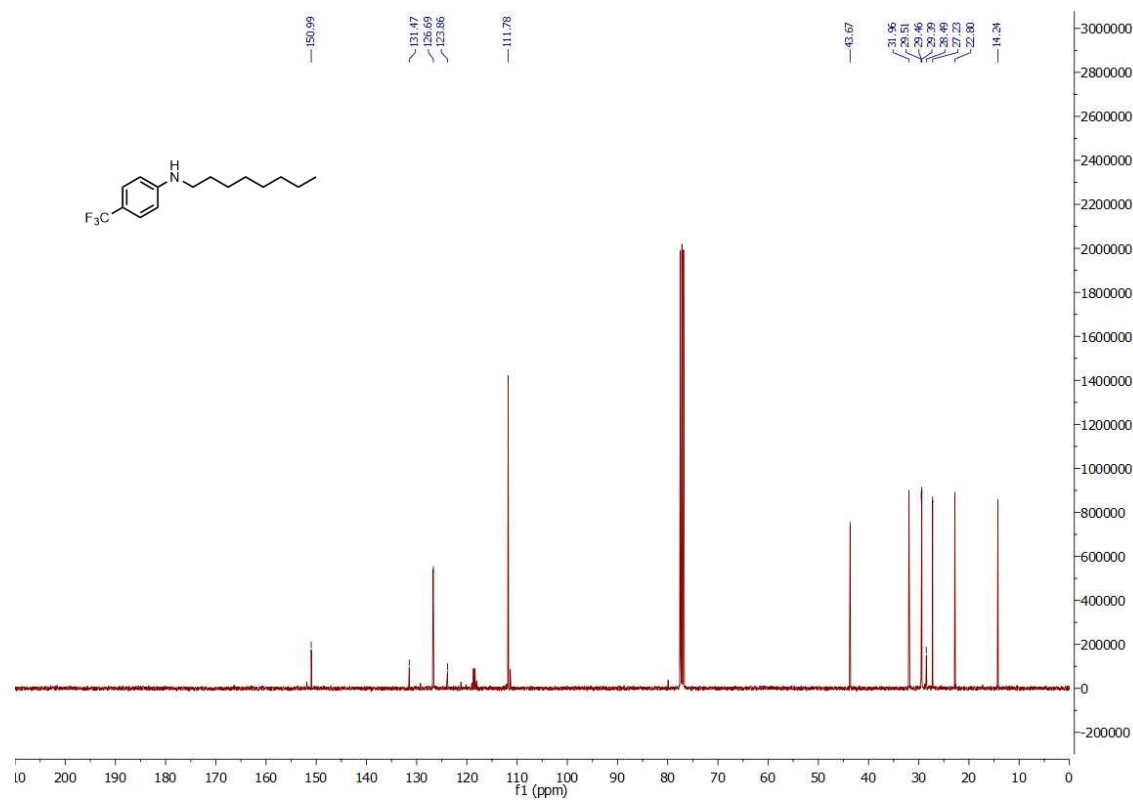


Figure A58. ¹³C NMR spectrum of **124** (100 MHz, CDCl₃)

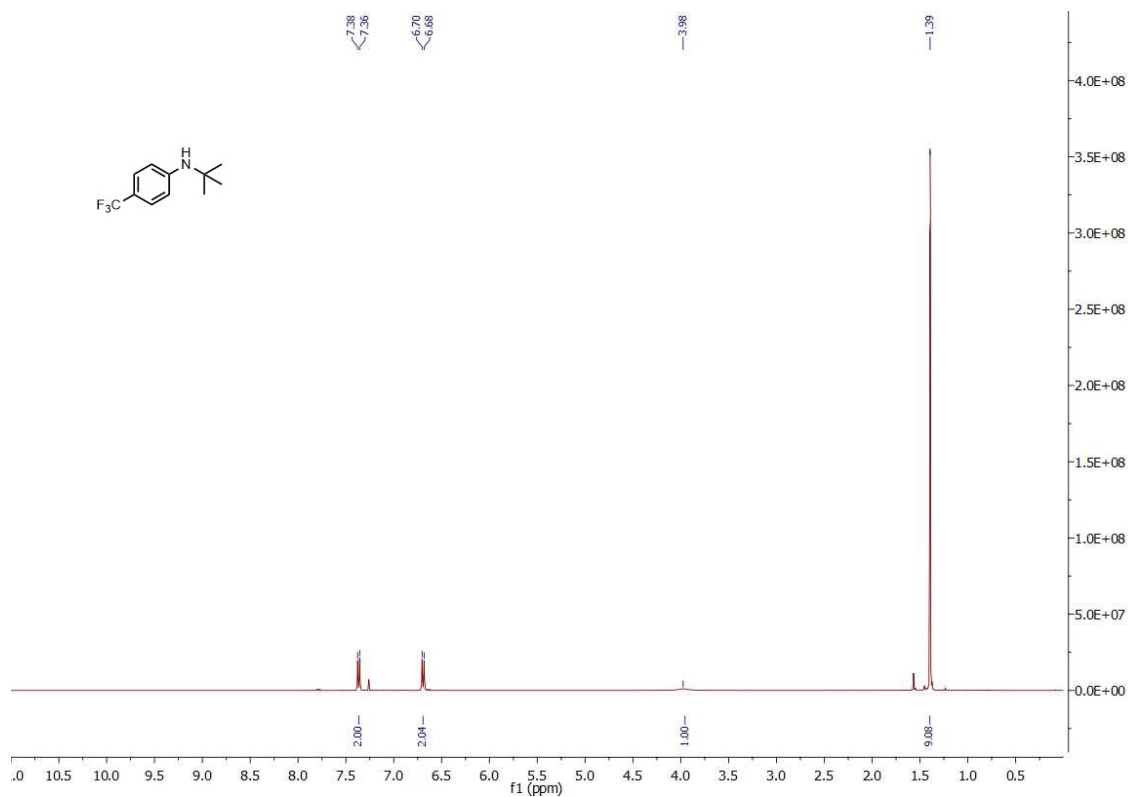


Figure A59. ¹H NMR spectrum of **125** (400 MHz, CDCl₃)

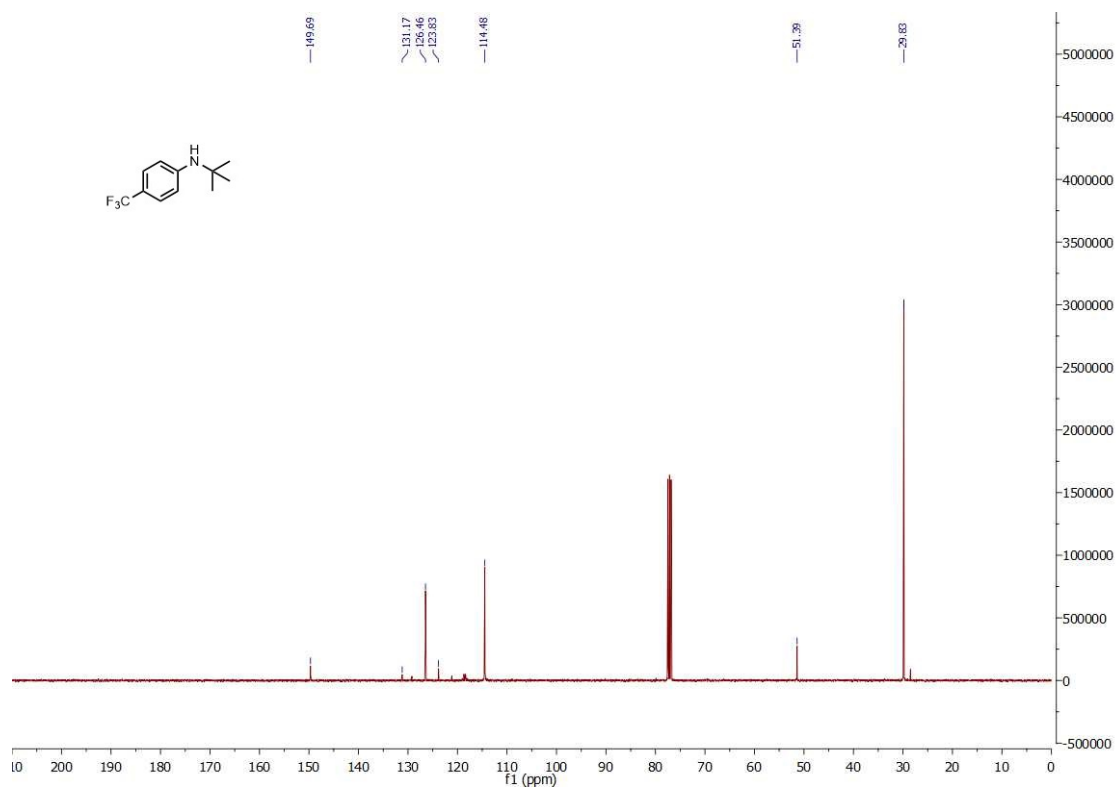


Figure A60. ¹³C NMR spectrum of **125** (100 MHz, CDCl₃)

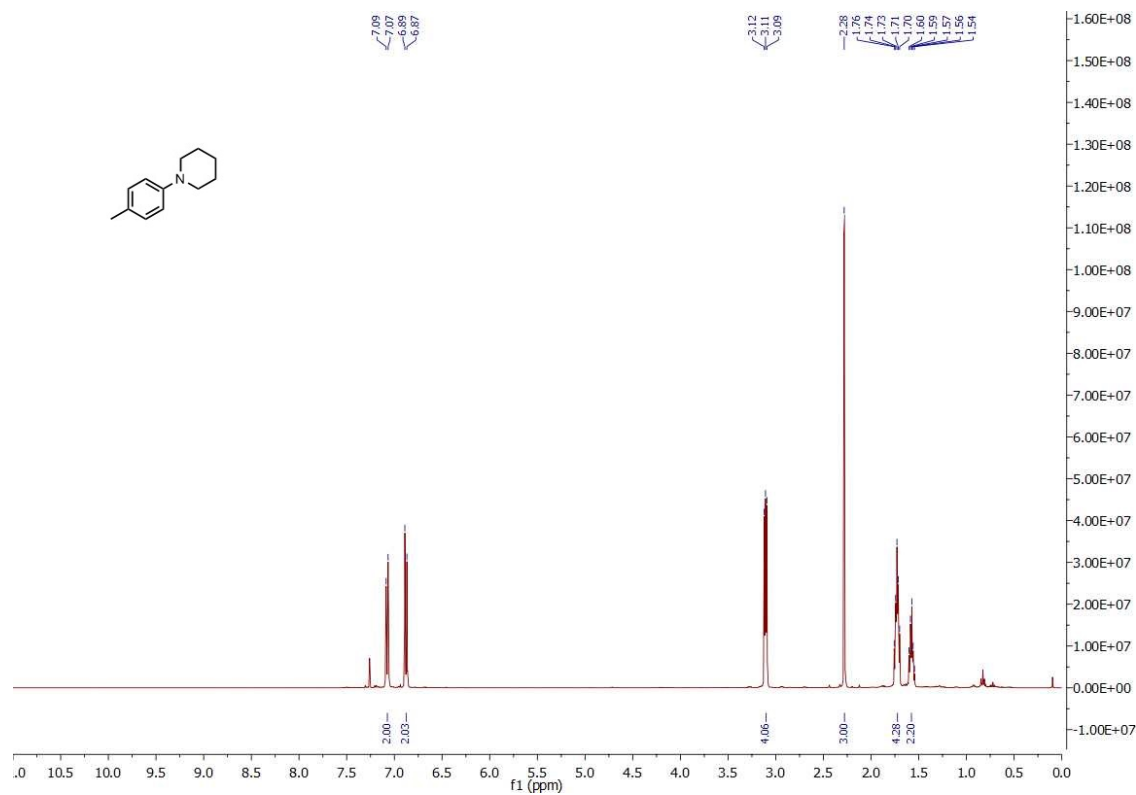


Figure A61. ¹H NMR spectrum of **126** (400 MHz, CDCl₃)

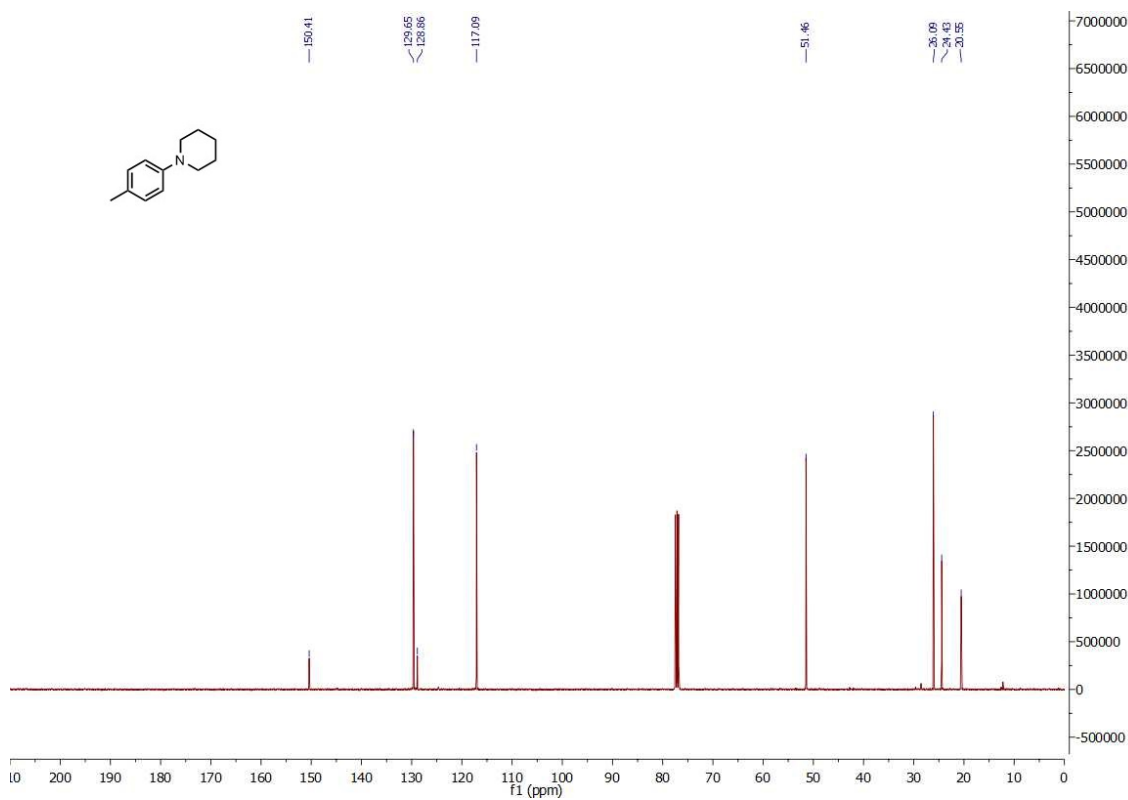


Figure A62. ¹³C NMR spectrum of **126** (100 MHz, CDCl₃)

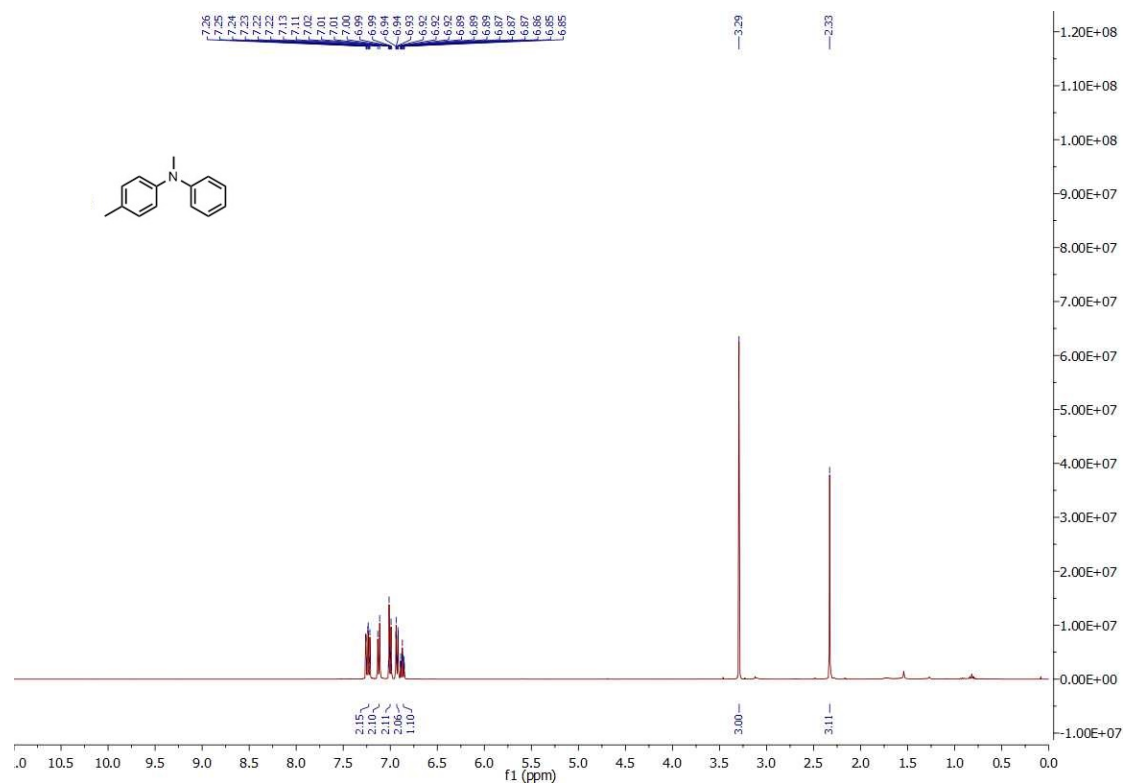


Figure A63. ¹H NMR spectrum of **127** (400 MHz, CDCl₃)

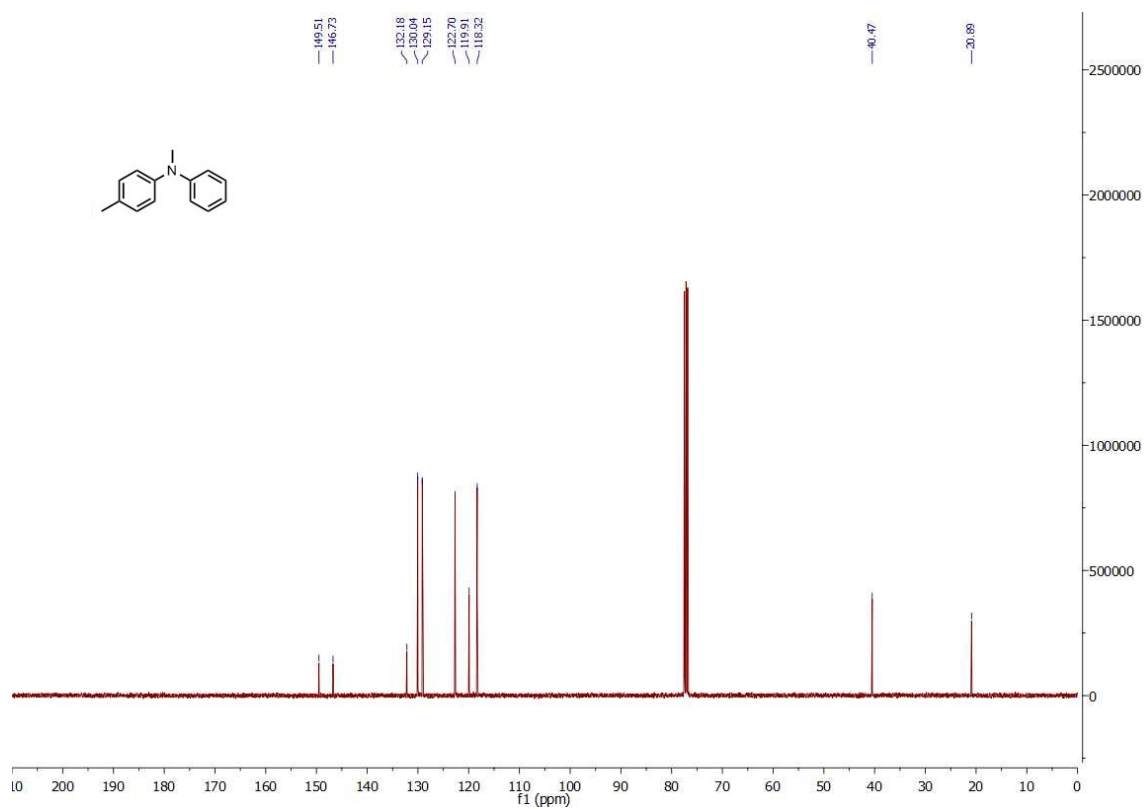


Figure A64. ¹³C NMR spectrum of **127** (100 MHz, CDCl₃)

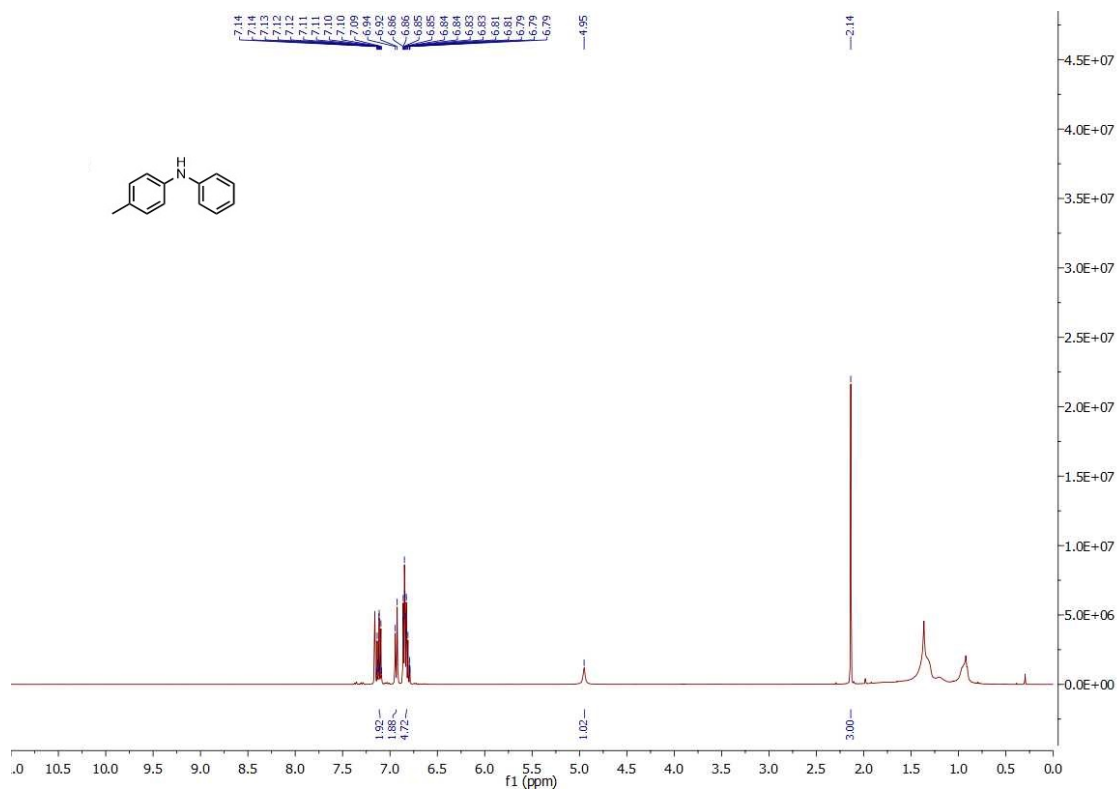


Figure A65. ¹H NMR spectrum of **128** (400 MHz, CDCl₃)

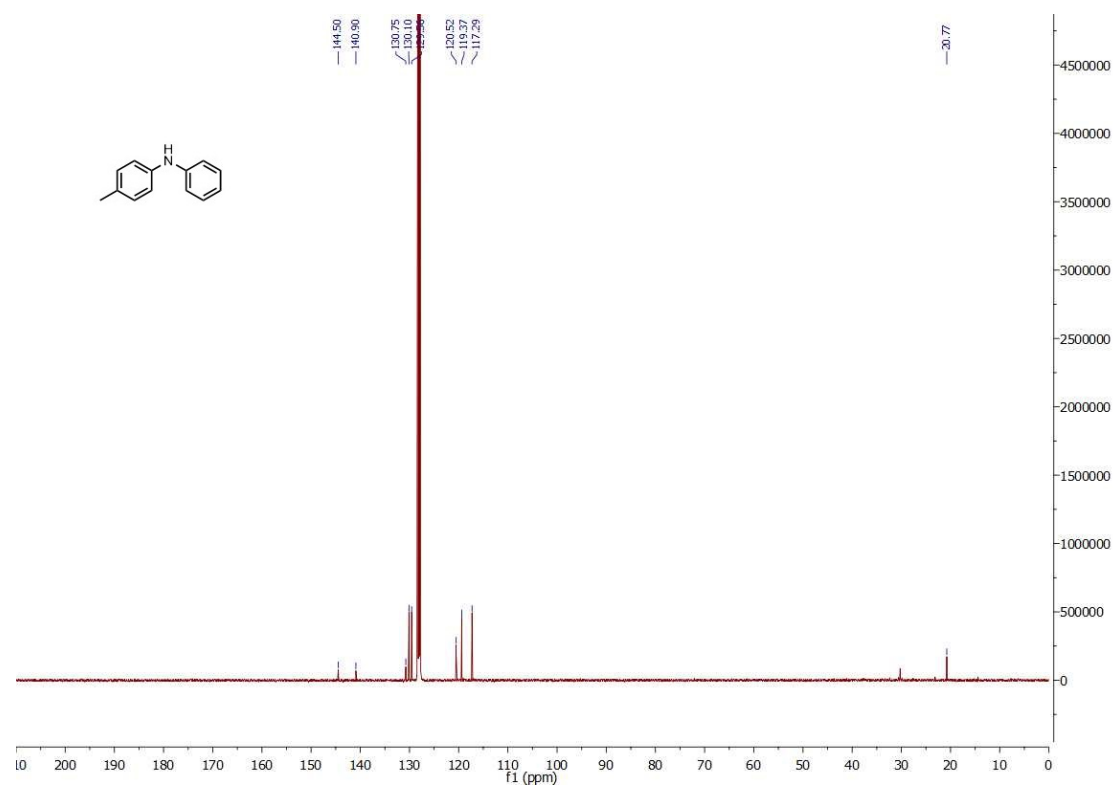


Figure A66. ¹³C NMR spectrum of **128** (100 MHz, CDCl₃)

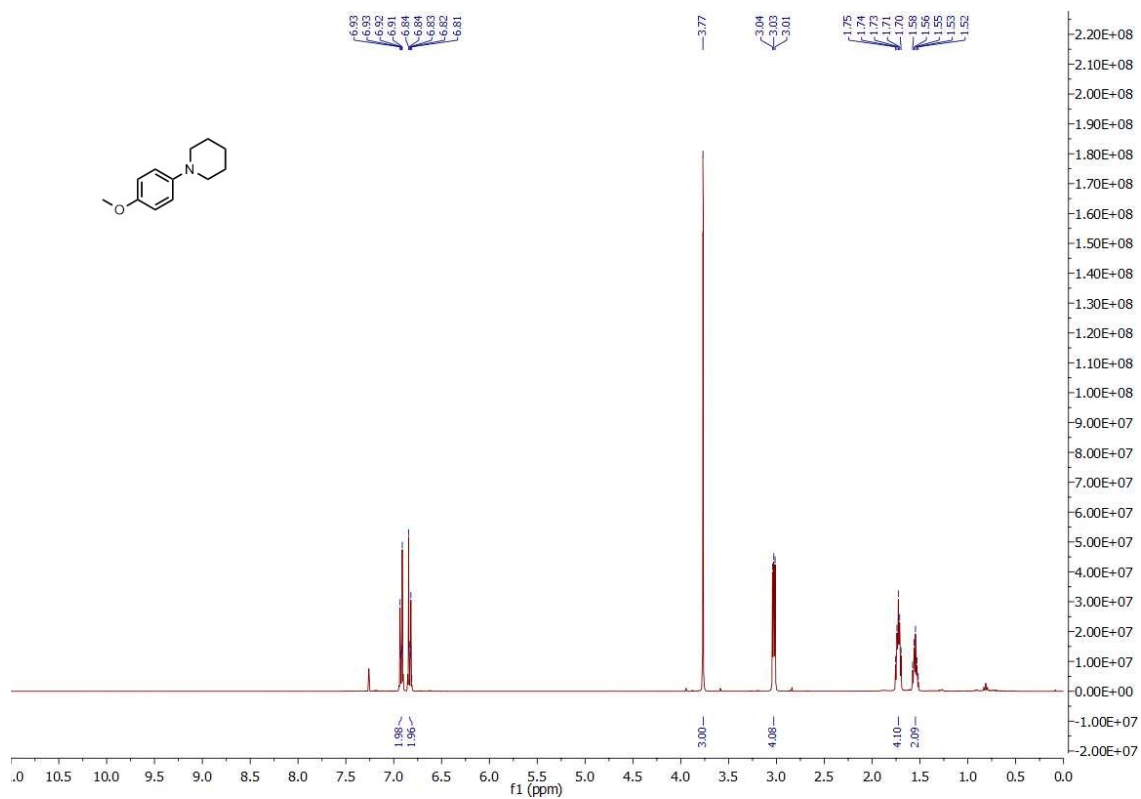


Figure A67. ^1H NMR spectrum of **129** (400 MHz, CDCl_3)

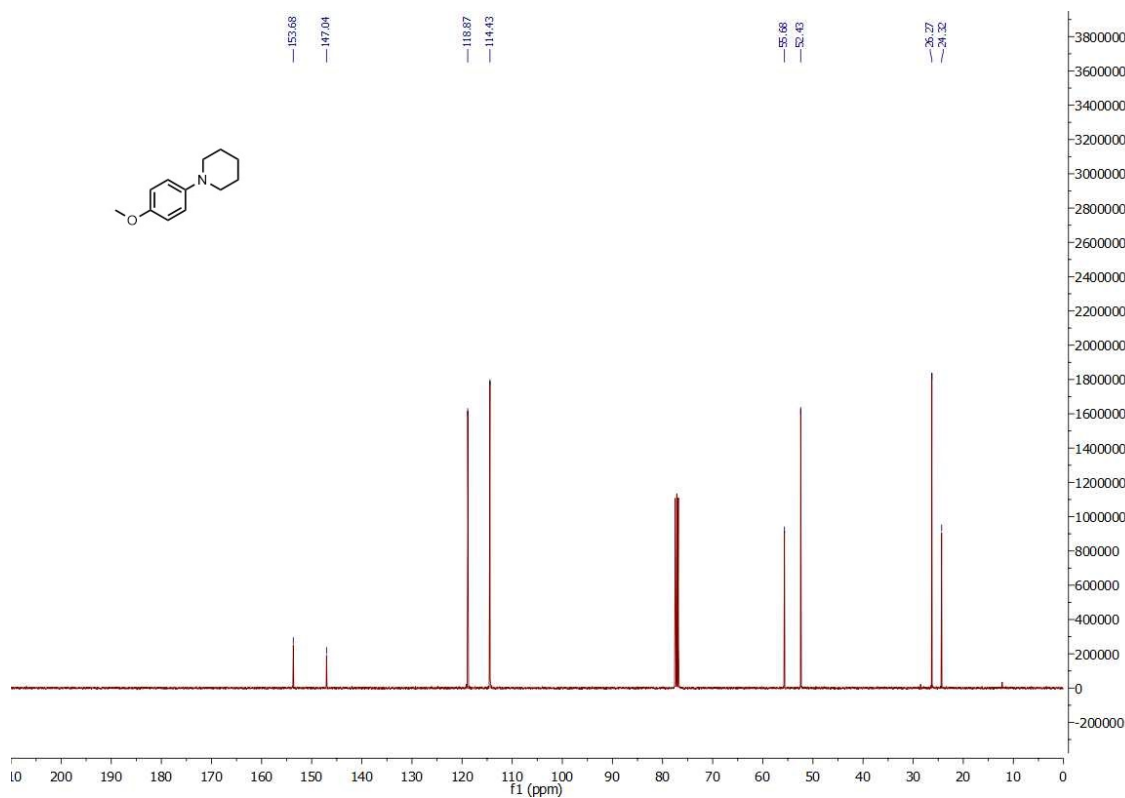


Figure A68. ^{13}C NMR spectrum of **129** (100 MHz, CDCl_3)

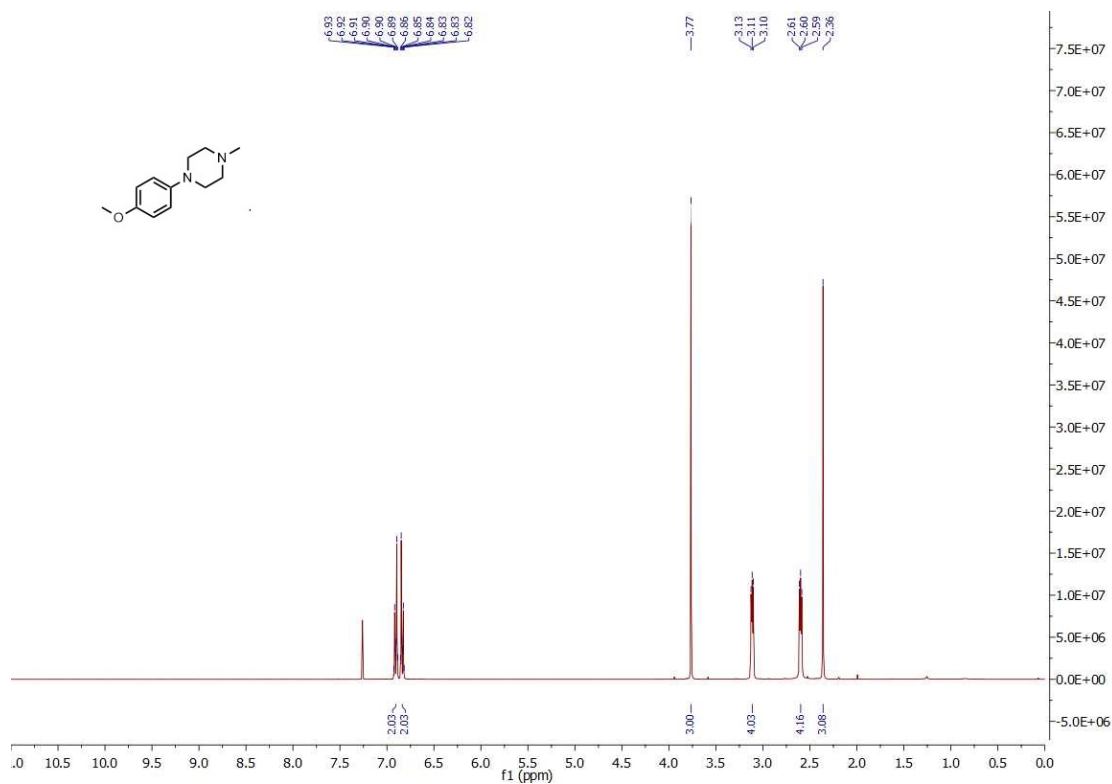


Figure A69. ^1H NMR spectrum of **101** (400 MHz, CDCl_3)

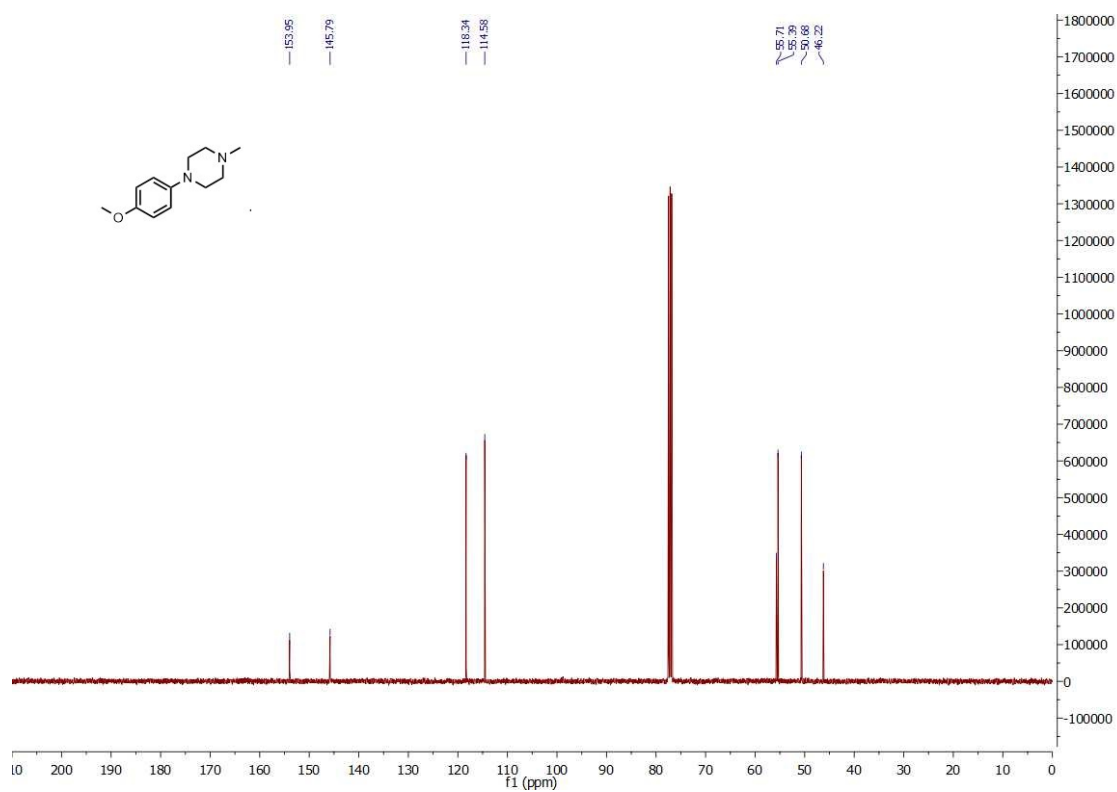


Figure A70. ^{13}C NMR spectrum of **101** (100 MHz, CDCl_3)

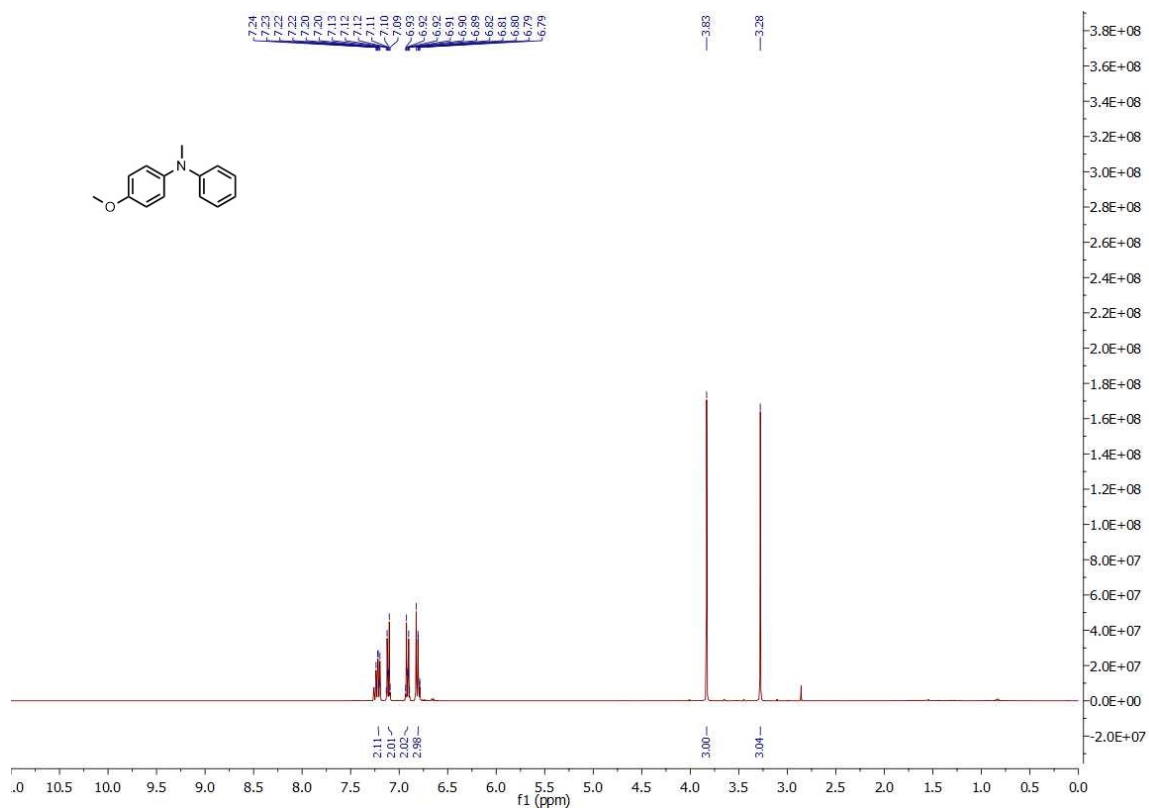


Figure A71. ¹H NMR spectrum of **130** (400 MHz, CDCl₃)

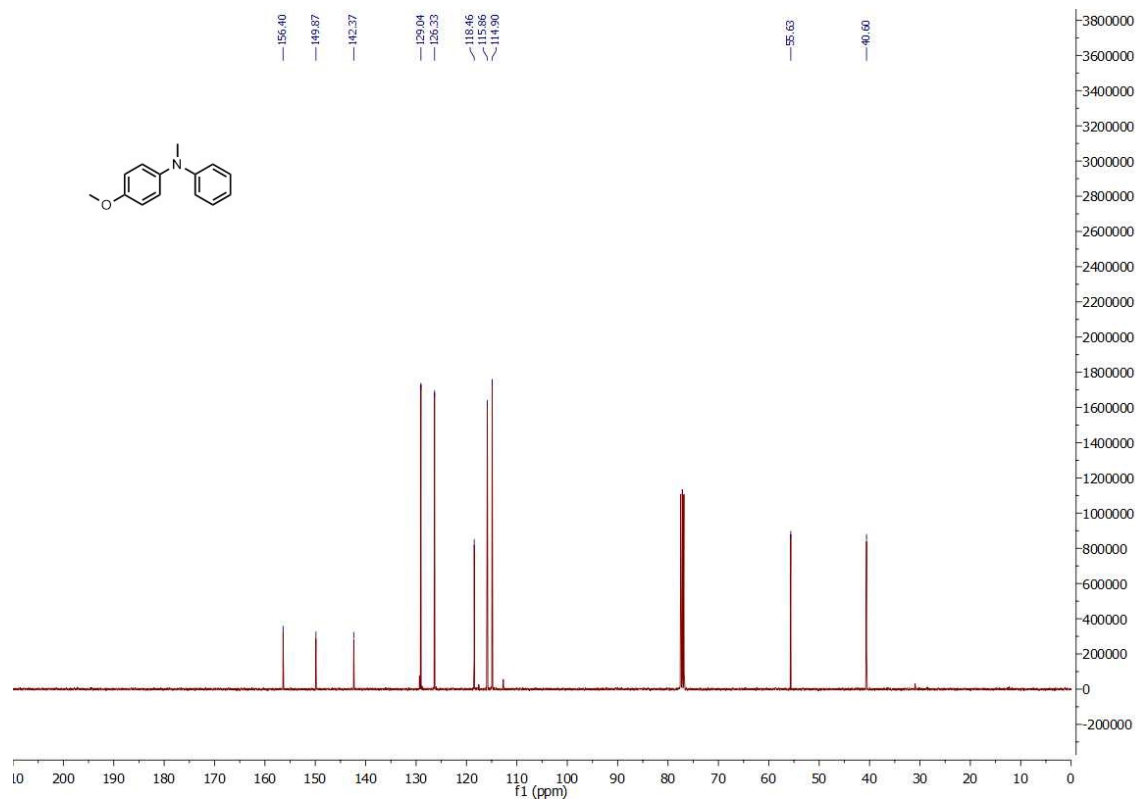


Figure A72. ¹³C NMR spectrum of **130** (100 MHz, CDCl₃)

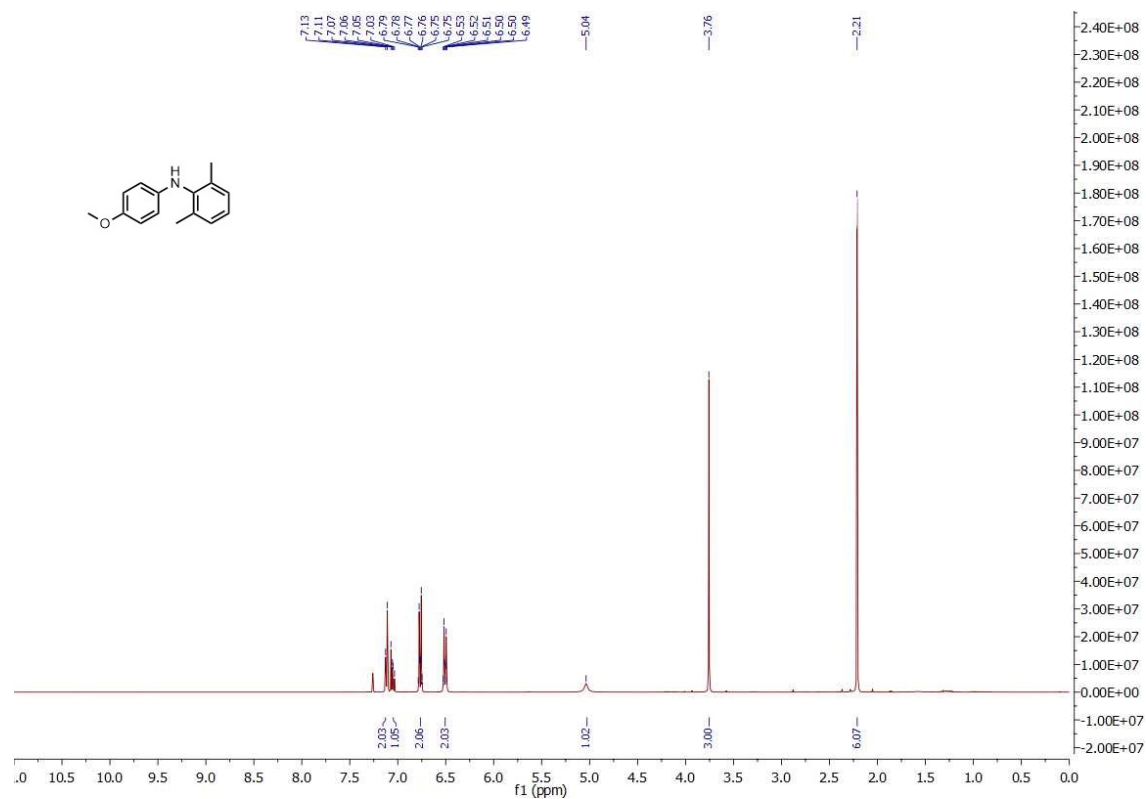


Figure A73. ¹H NMR spectrum of **131** (400 MHz, CDCl₃)

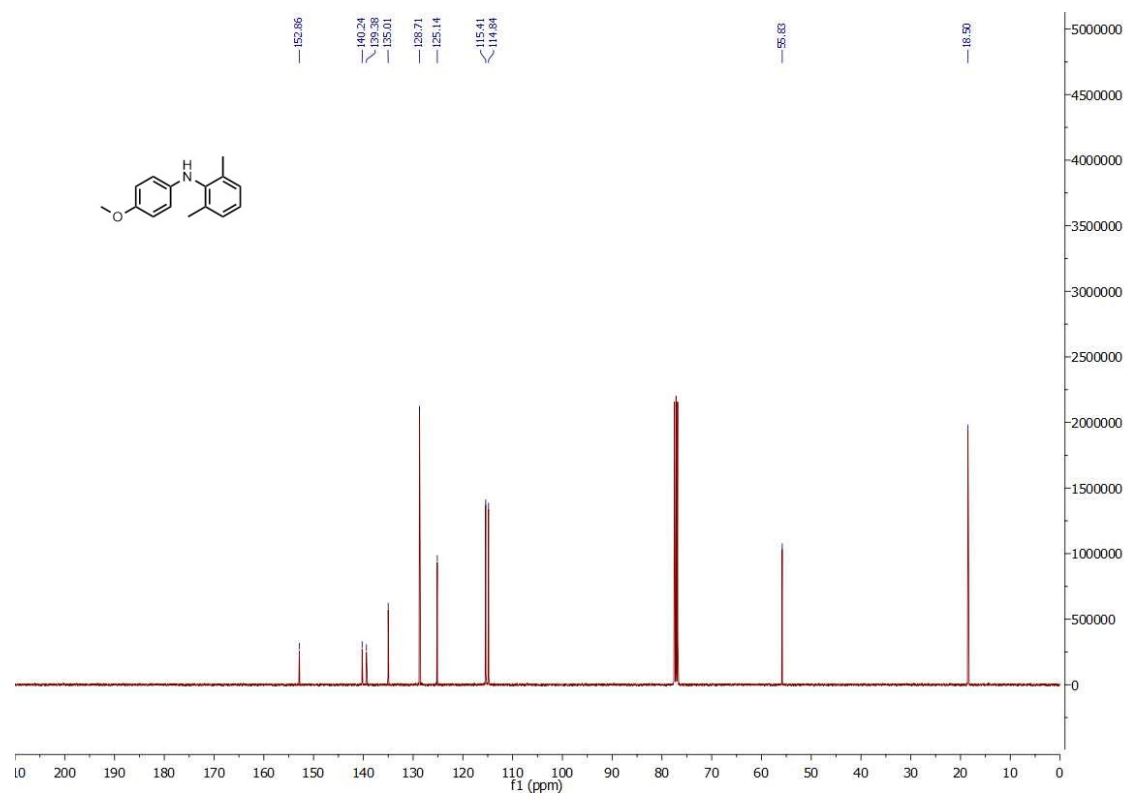


Figure A74. ¹³C NMR spectrum of **131** (100 MHz, CDCl₃)

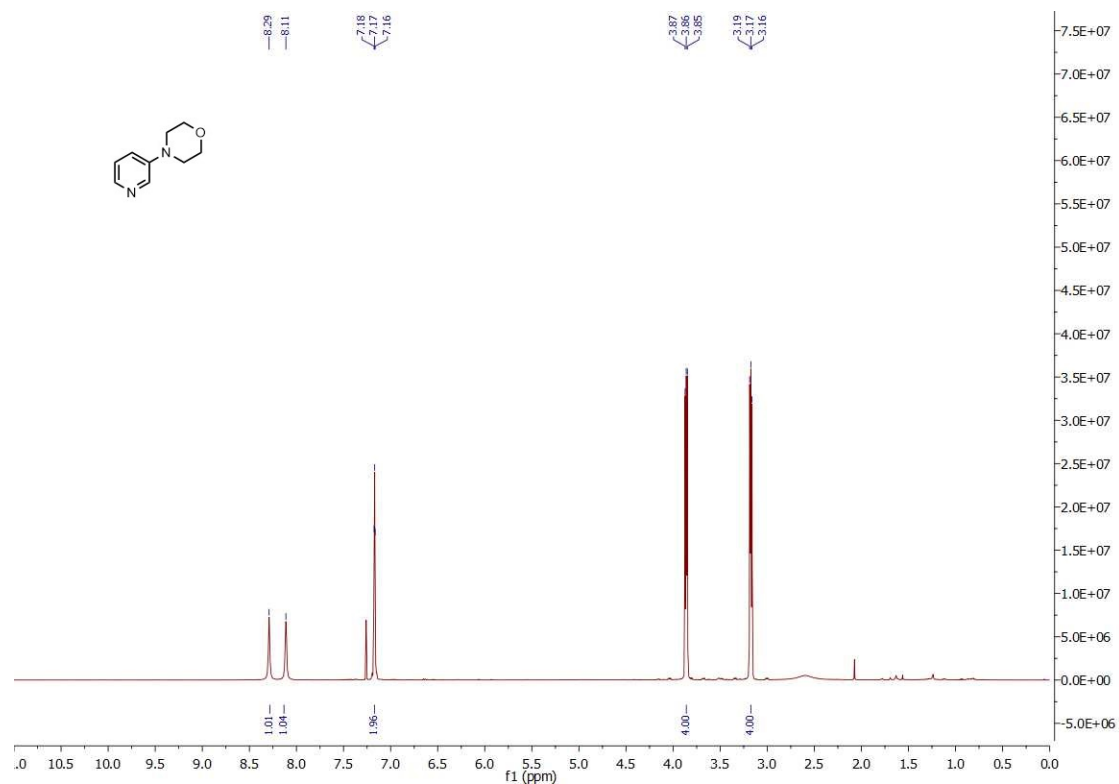


Figure A75. ^1H NMR spectrum of **136** (400 MHz, CDCl_3)

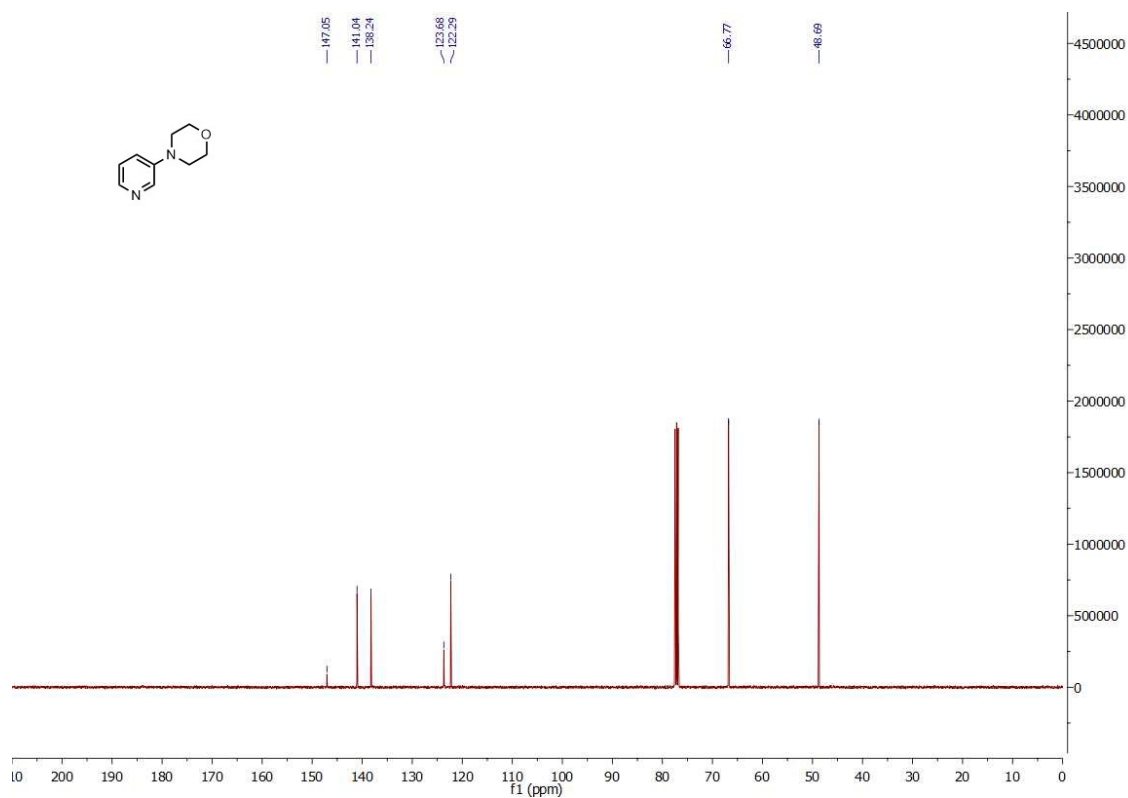


Figure A76. ^{13}C NMR spectrum of **136** (100 MHz, CDCl_3)

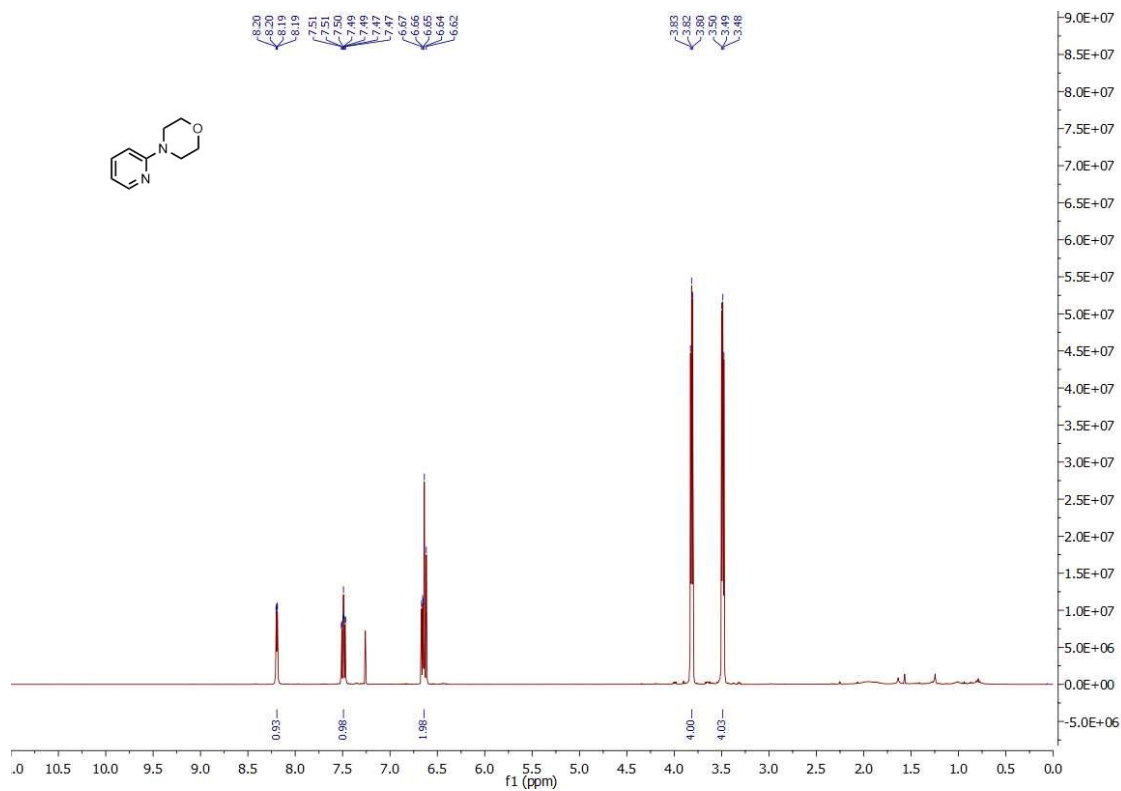


Figure A77. ¹H NMR spectrum of **137** (400 MHz, CDCl₃)

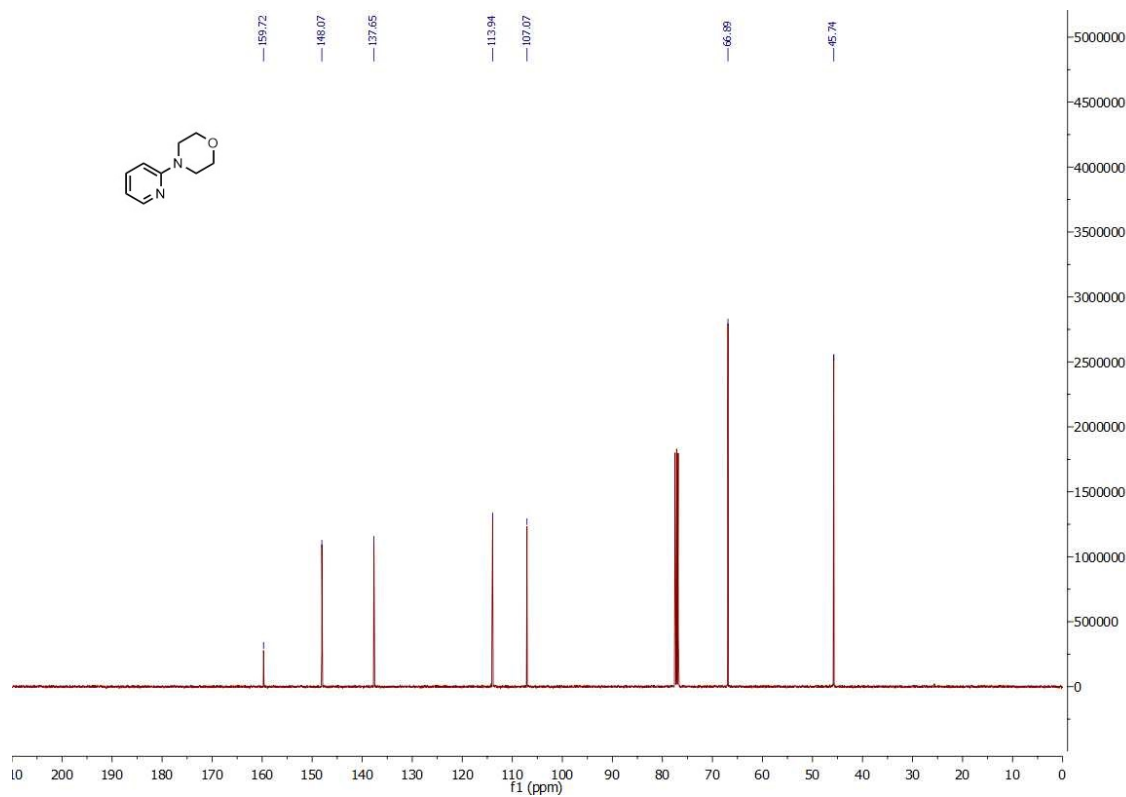


Figure A78. ¹³C NMR spectrum of **137** (100 MHz, CDCl₃)

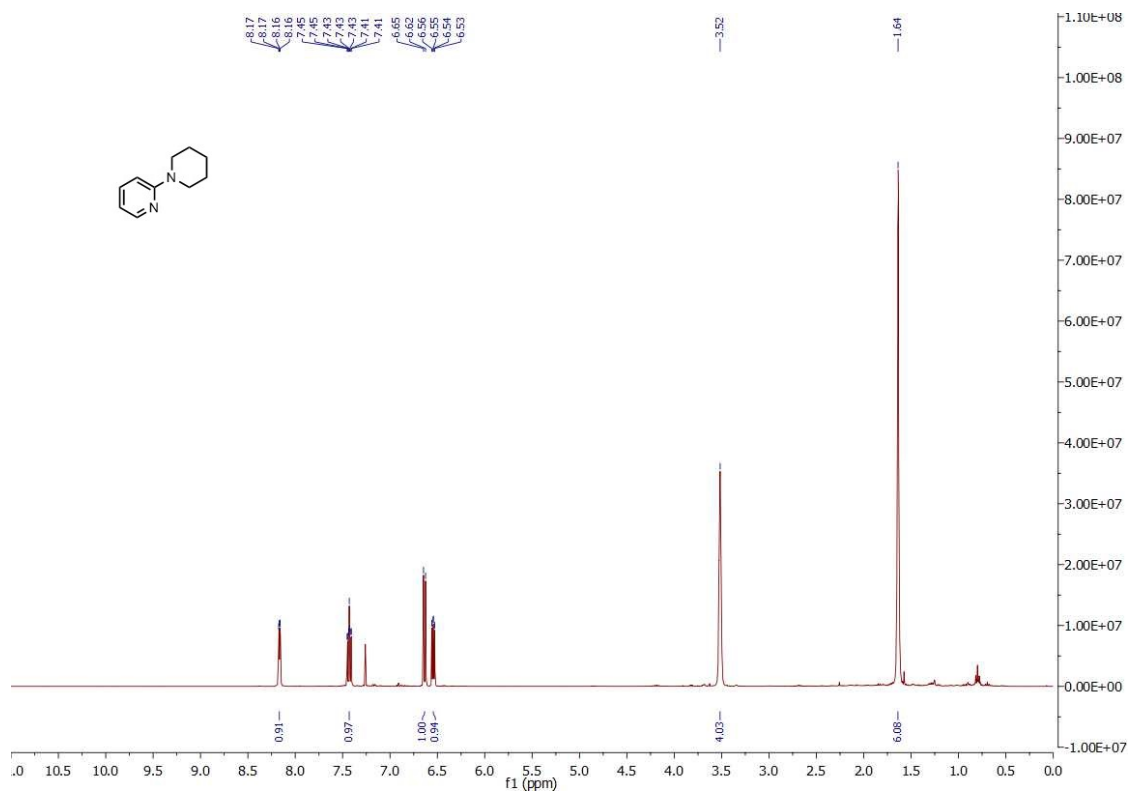


Figure A79. ¹H NMR spectrum of **138** (400 MHz, CDCl₃)

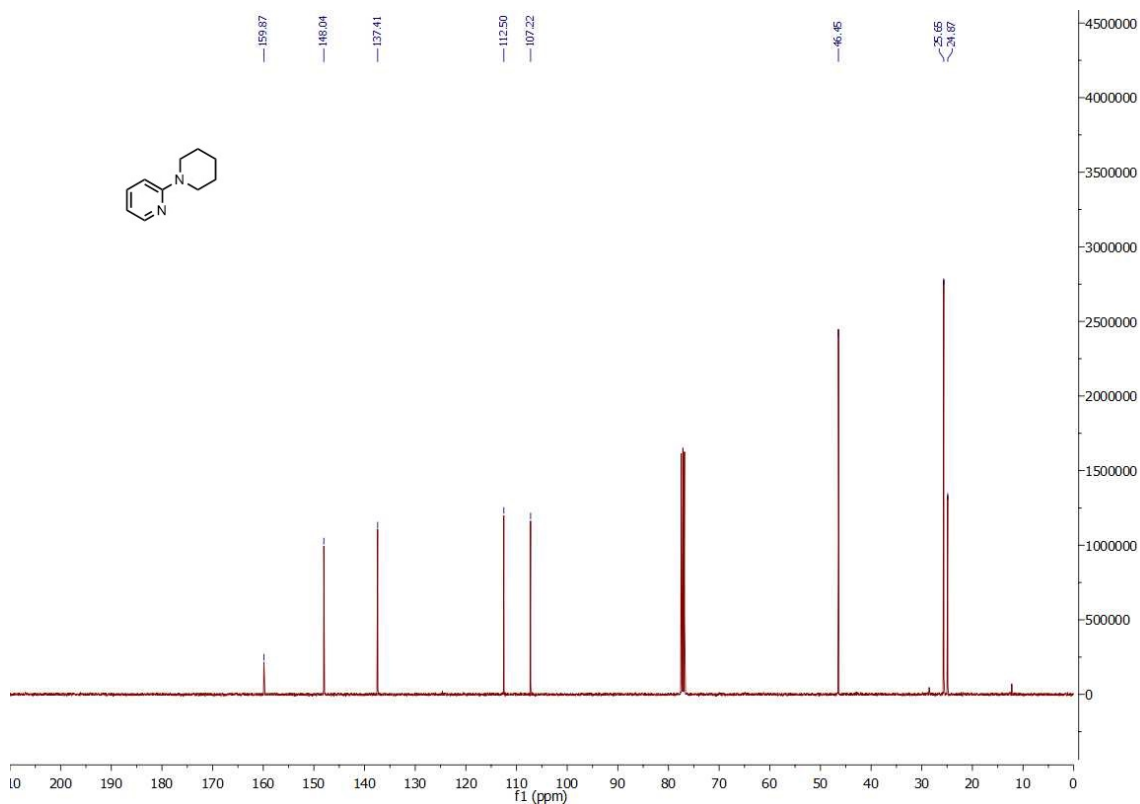


Figure A80. ¹³C NMR spectrum of **138** (100 MHz, CDCl₃)

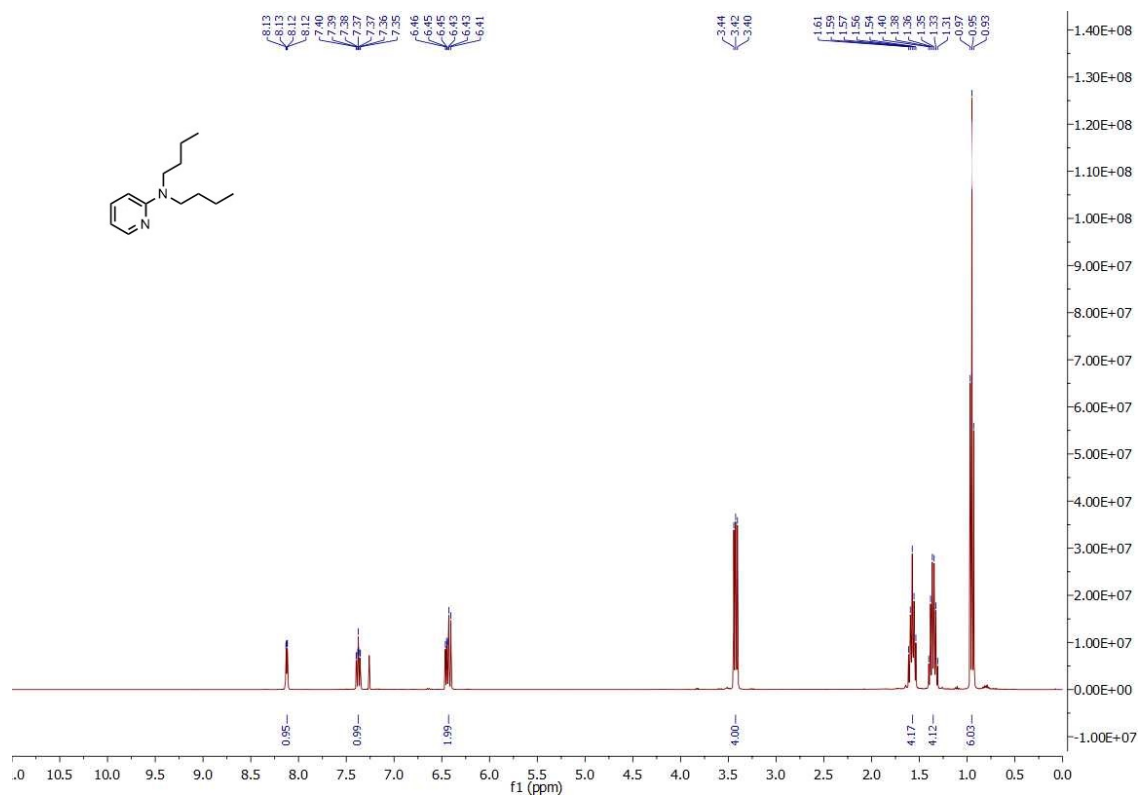


Figure A81. ¹H NMR spectrum of **139** (400 MHz, CDCl₃)

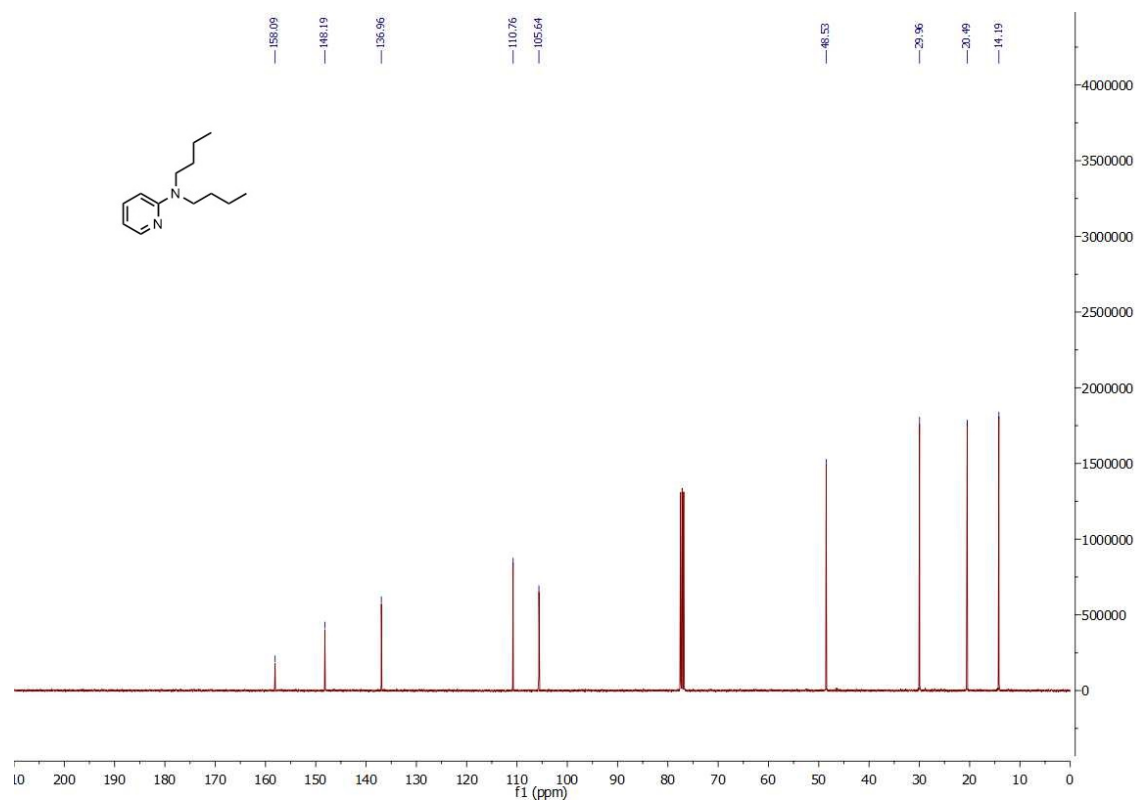


Figure A82. ¹³C NMR spectrum of **139** (100 MHz, CDCl₃)

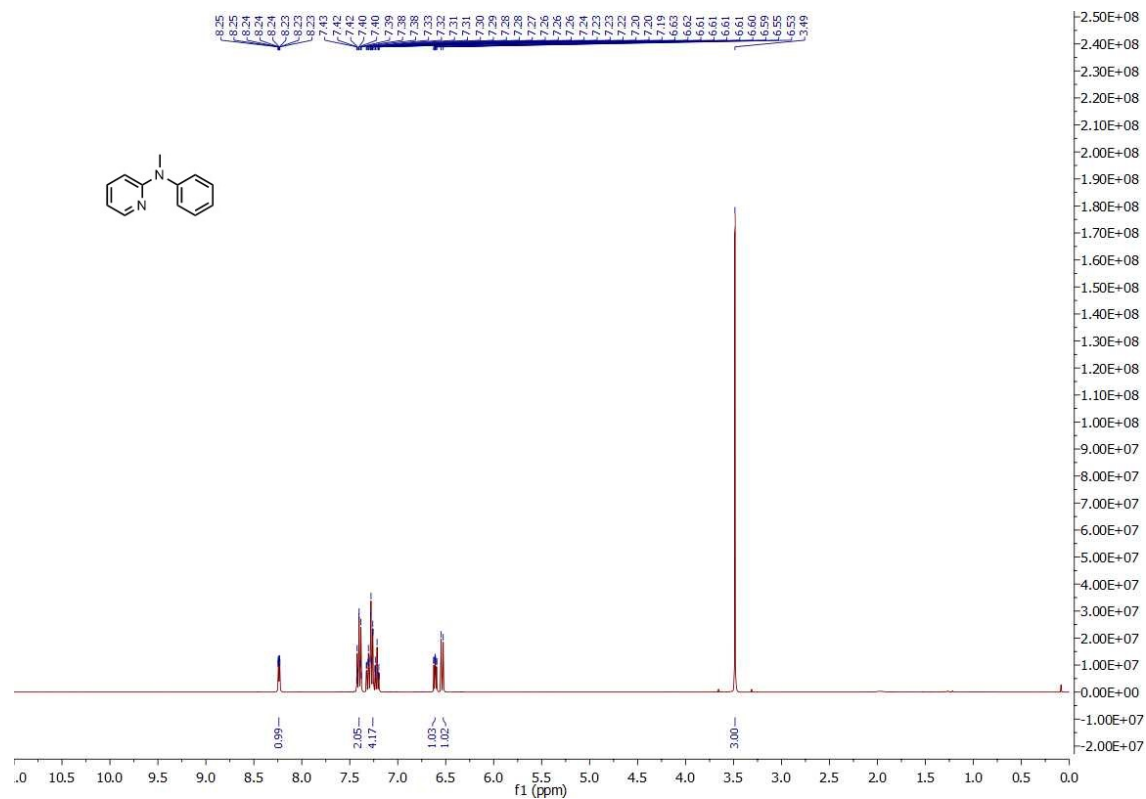


Figure A83. ¹H NMR spectrum of **140** (400 MHz, CDCl₃)

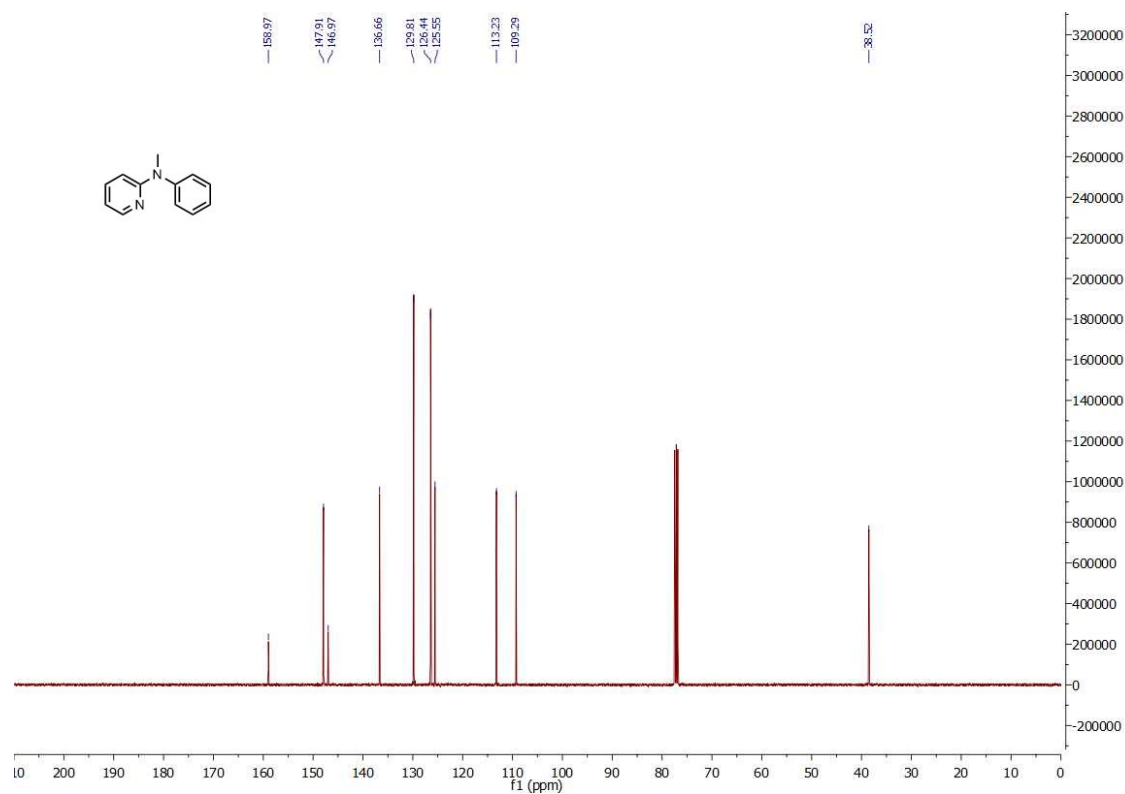


Figure A84. ¹³C NMR spectrum of **140** (100 MHz, CDCl₃)

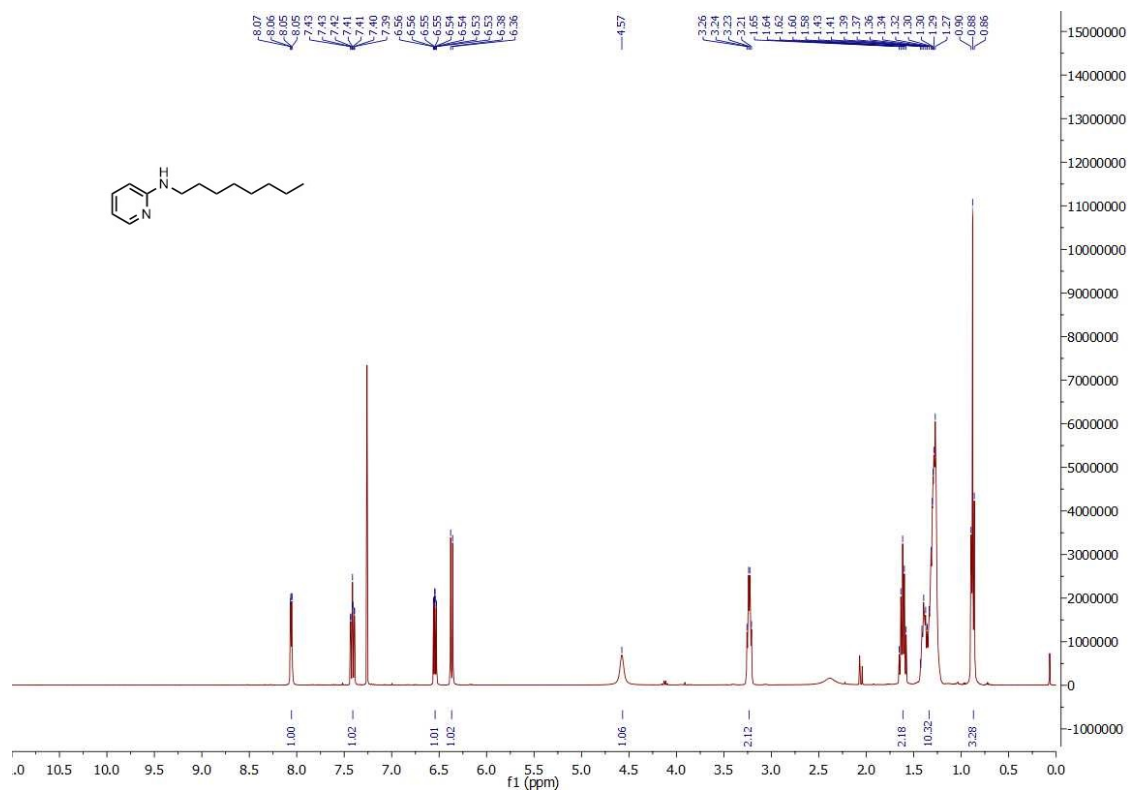


Figure A85. ¹H NMR spectrum of **141** – monoarylated product (400 MHz, CDCl₃)

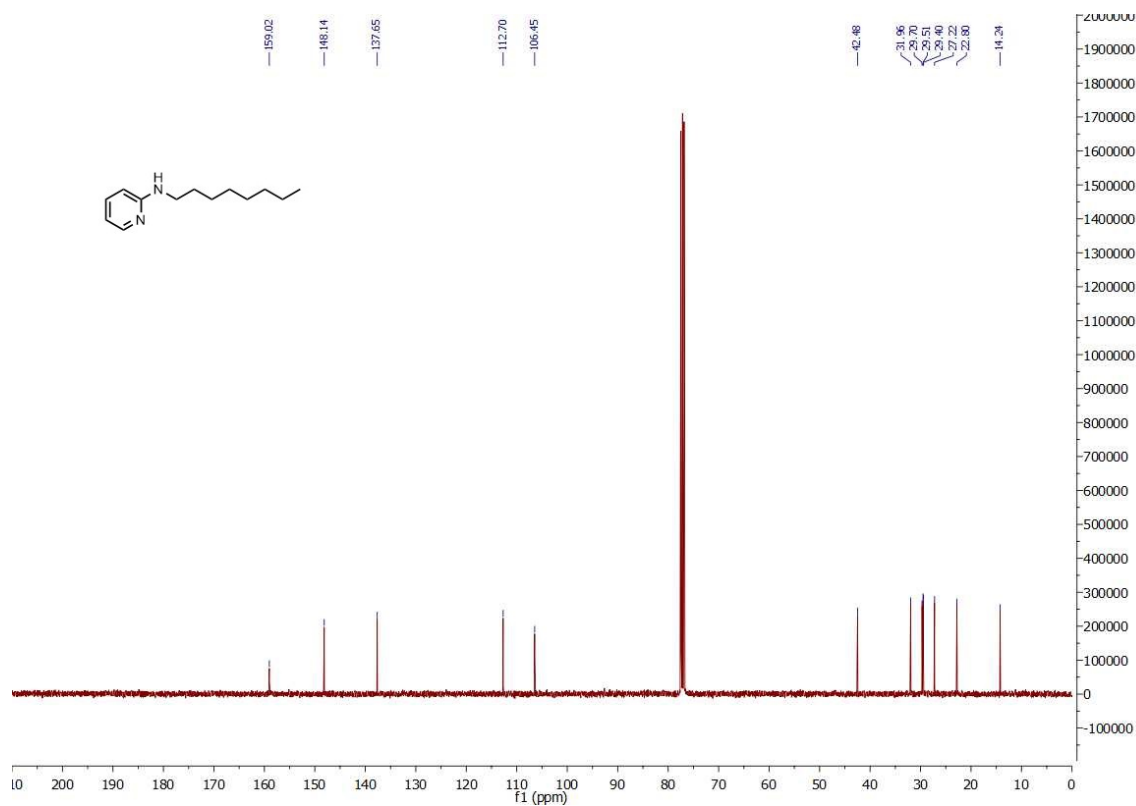


Figure A86. ¹³C NMR spectrum of **141** – monoarylated product (100 MHz, CDCl₃)

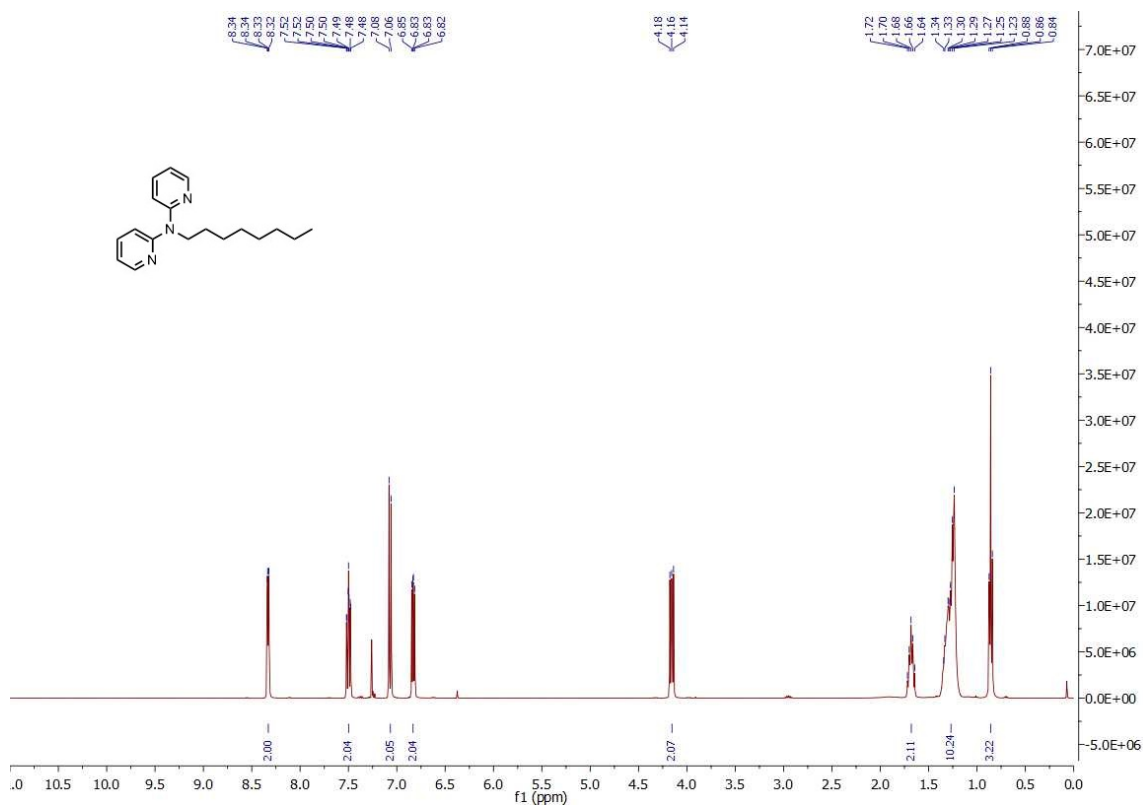


Figure A87. ¹H NMR spectrum of **142** – diarylated product (400 MHz, CDCl₃)

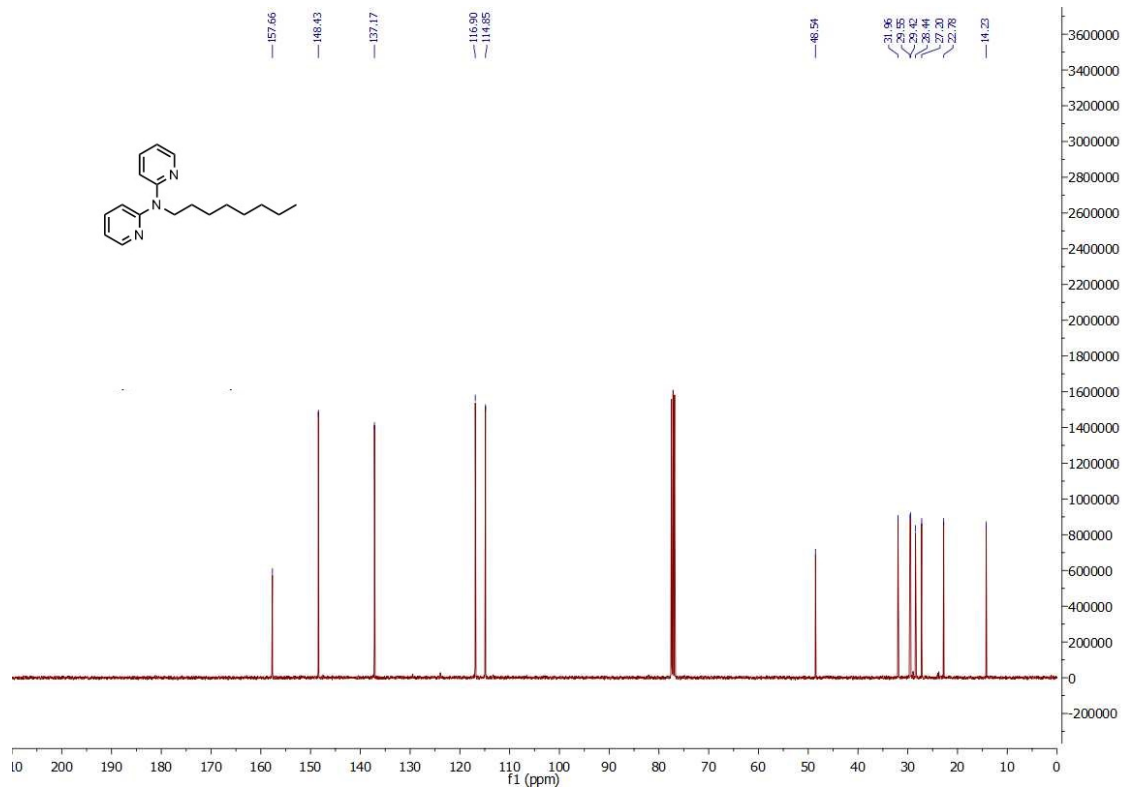


Figure A88. ¹³C NMR spectrum of **142** – diarylated product (100 MHz, CDCl₃)

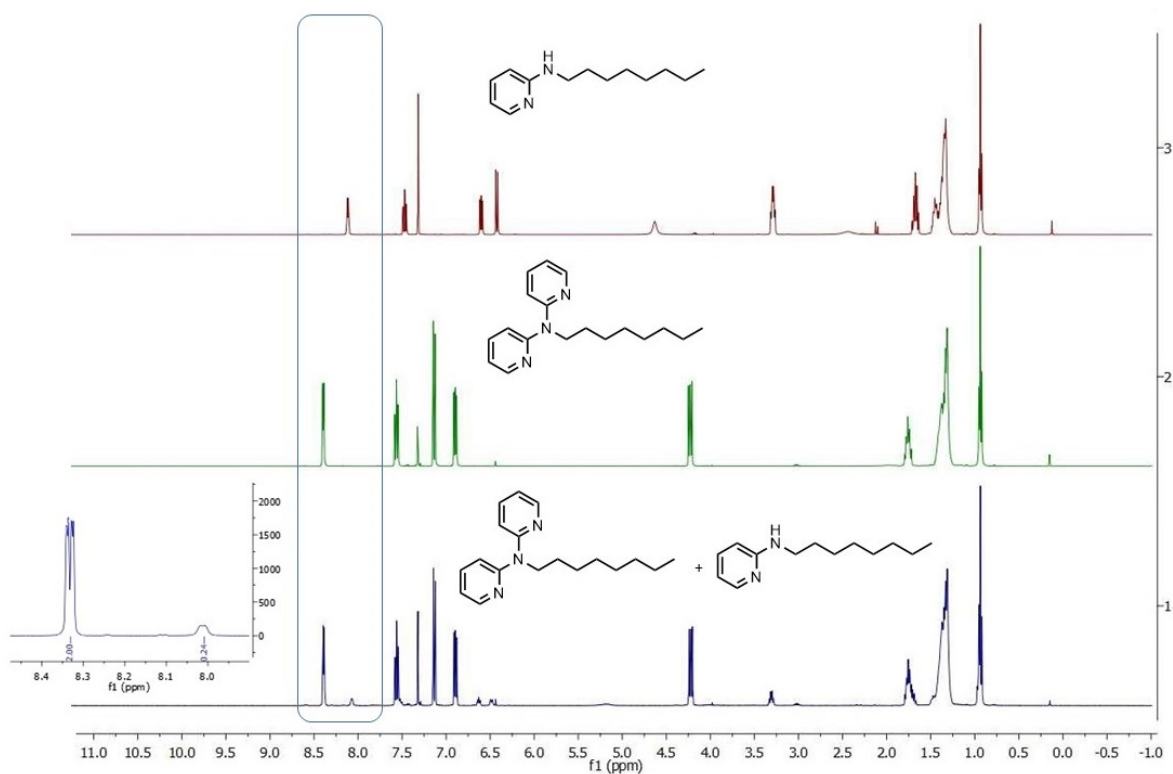


Figure A89. ^1H NMR spectrum of **141,142/mono- and diarylated products** (400 MHz, CDCl_3)

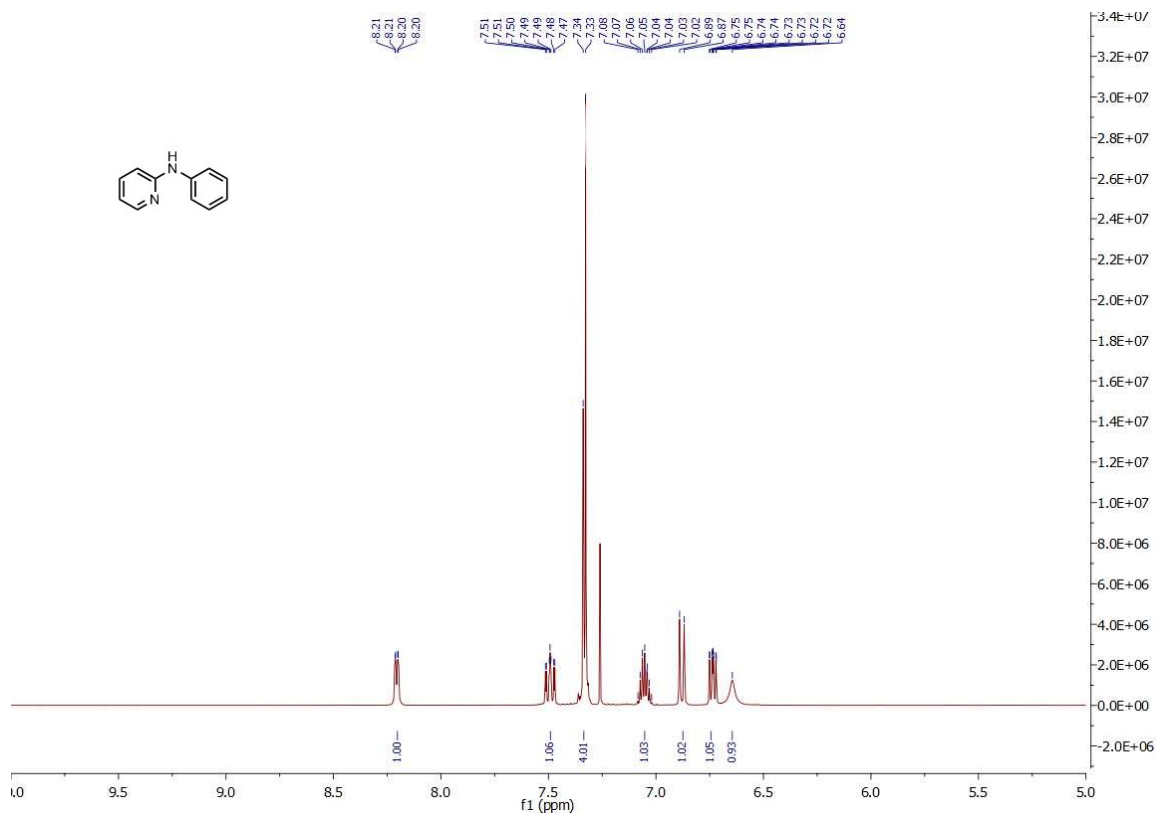


Figure A90. ^1H NMR spectrum of **143 – monoarylated product** (400 MHz, CDCl_3)

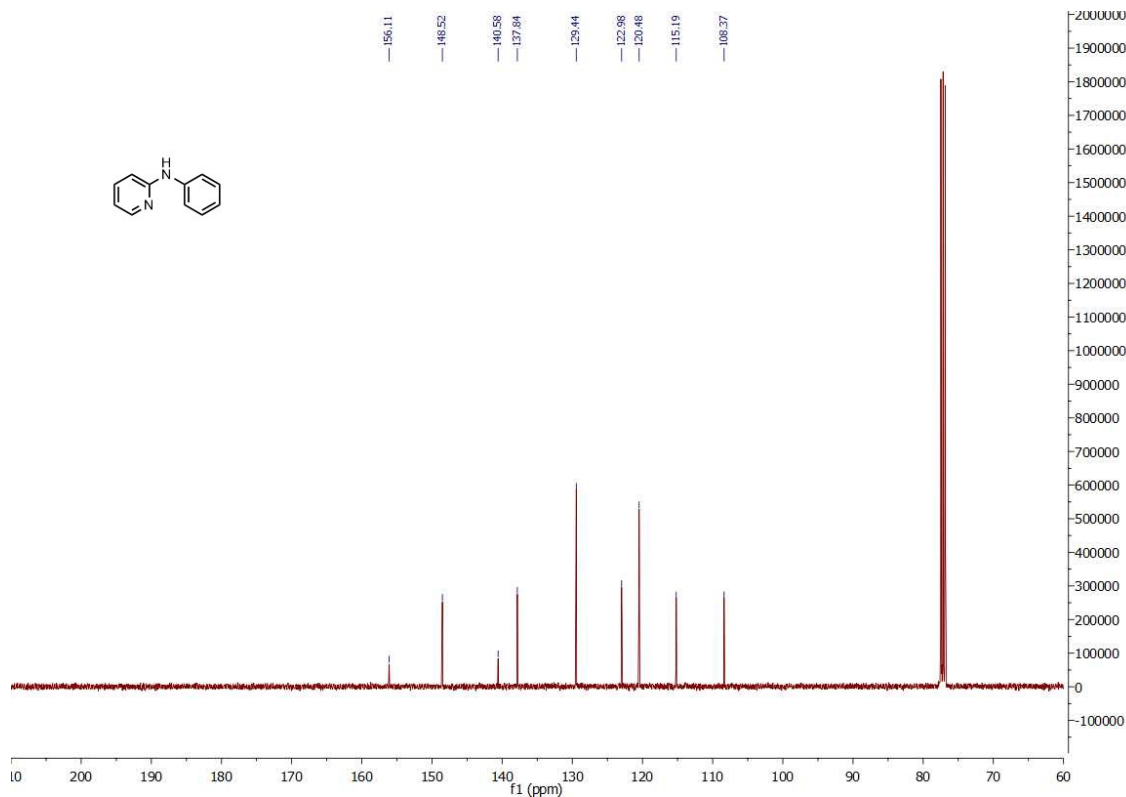


Figure A91. ¹³C NMR spectrum of **143** – monoarylated product (100 MHz, CDCl₃)

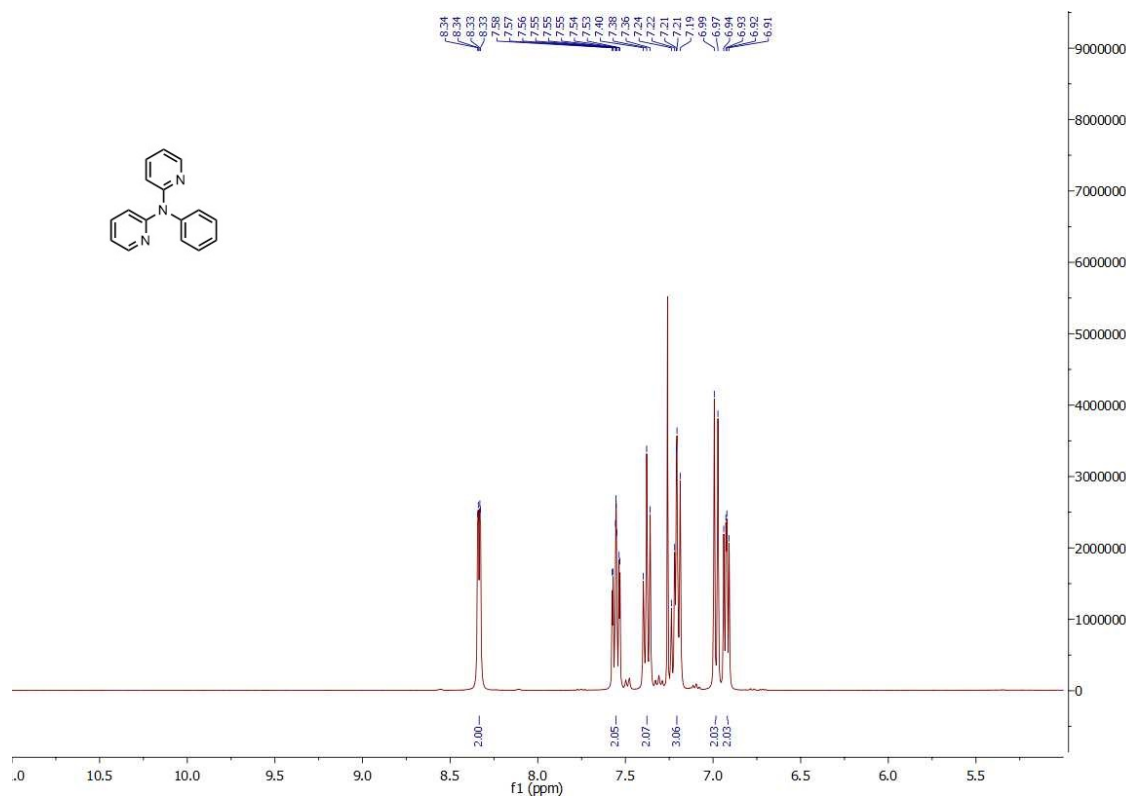


Figure A92. ¹H NMR spectrum of **144** – diarylated product (400 MHz, CDCl₃)

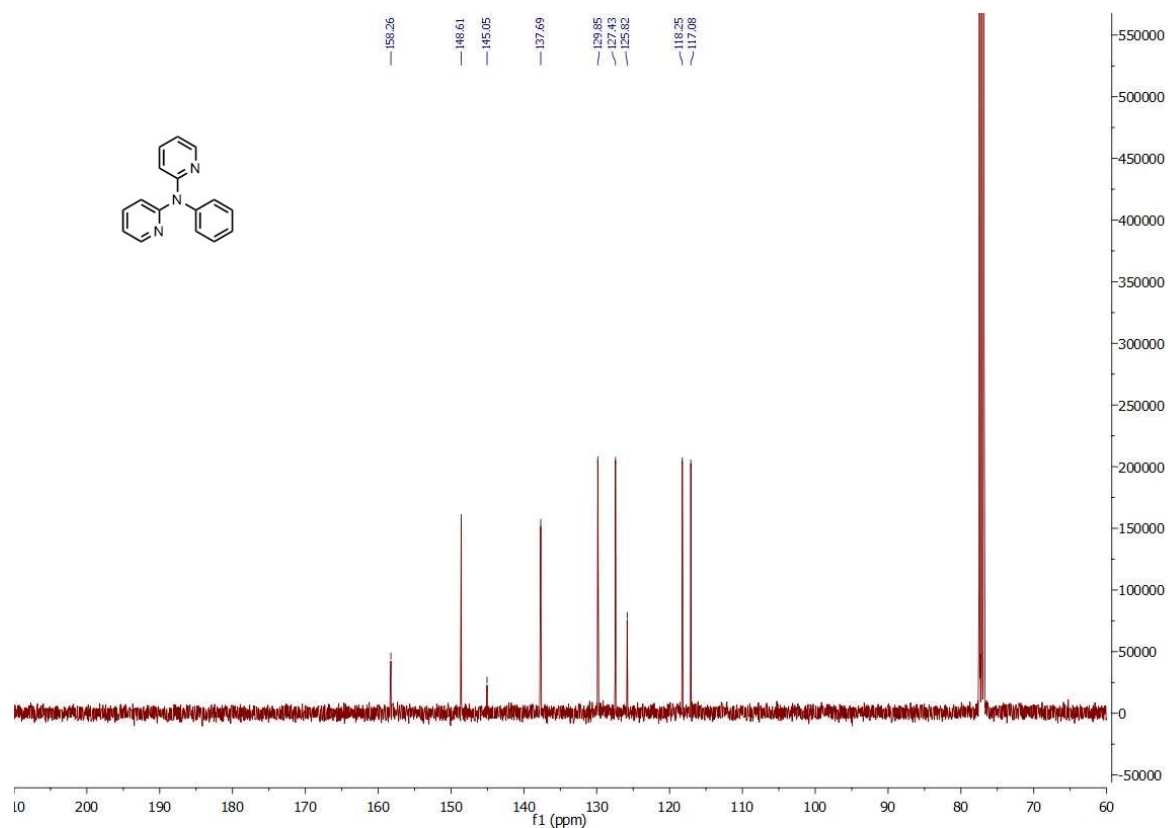


Figure A93. ¹³C NMR spectrum of **144** – diarylated product (100 MHz, CDCl₃)

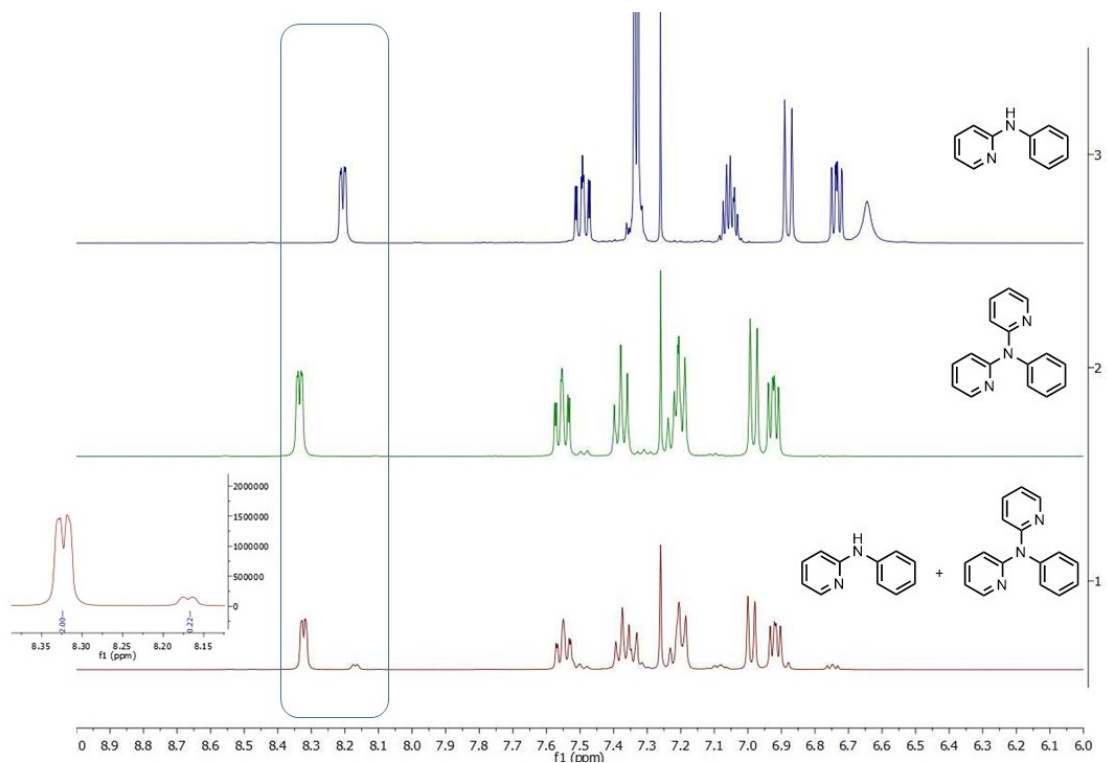


Figure A94. ¹H NMR spectrum of **143,144/mono– and diarylated products** (400 MHz, CDCl₃)

Appendix for chapter 3

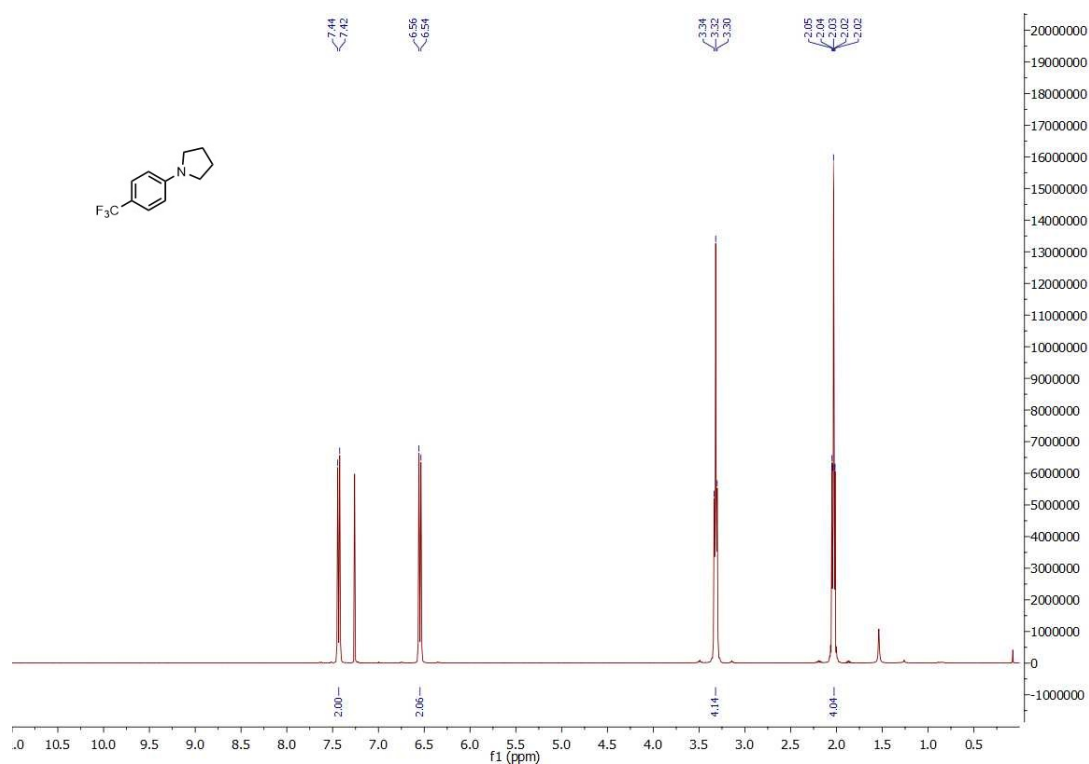


Figure A95. ¹H NMR spectrum of **148** (400 MHz, CDCl₃)

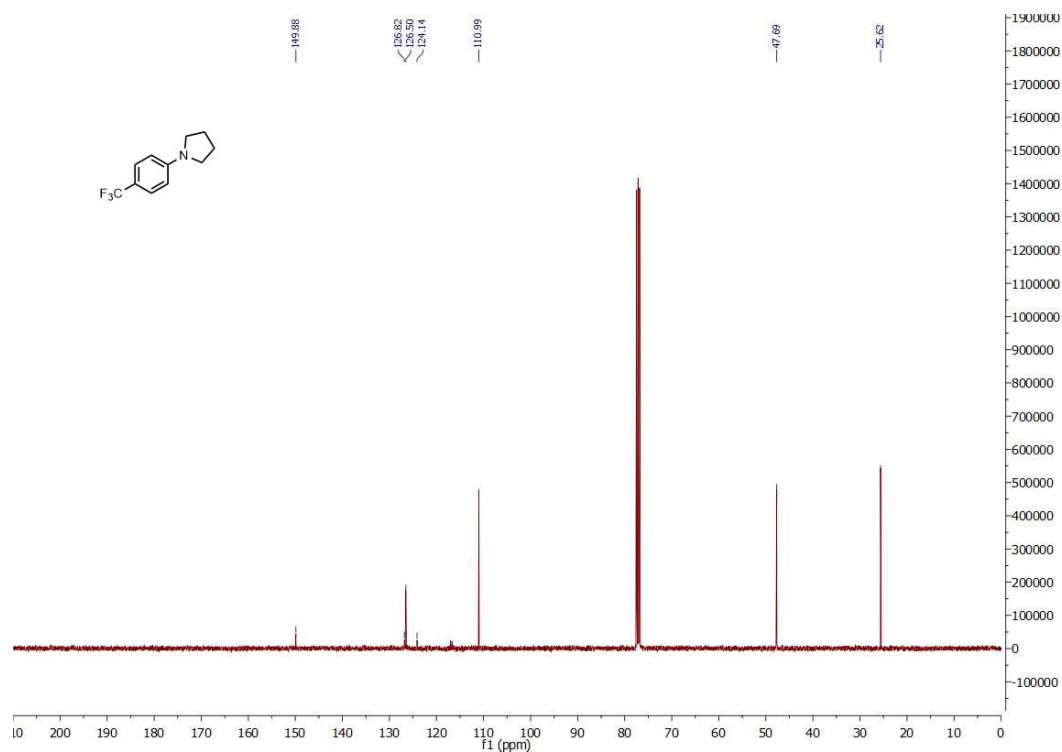


Figure A96. ¹³C NMR spectrum of **148** (100 MHz, CDCl₃)

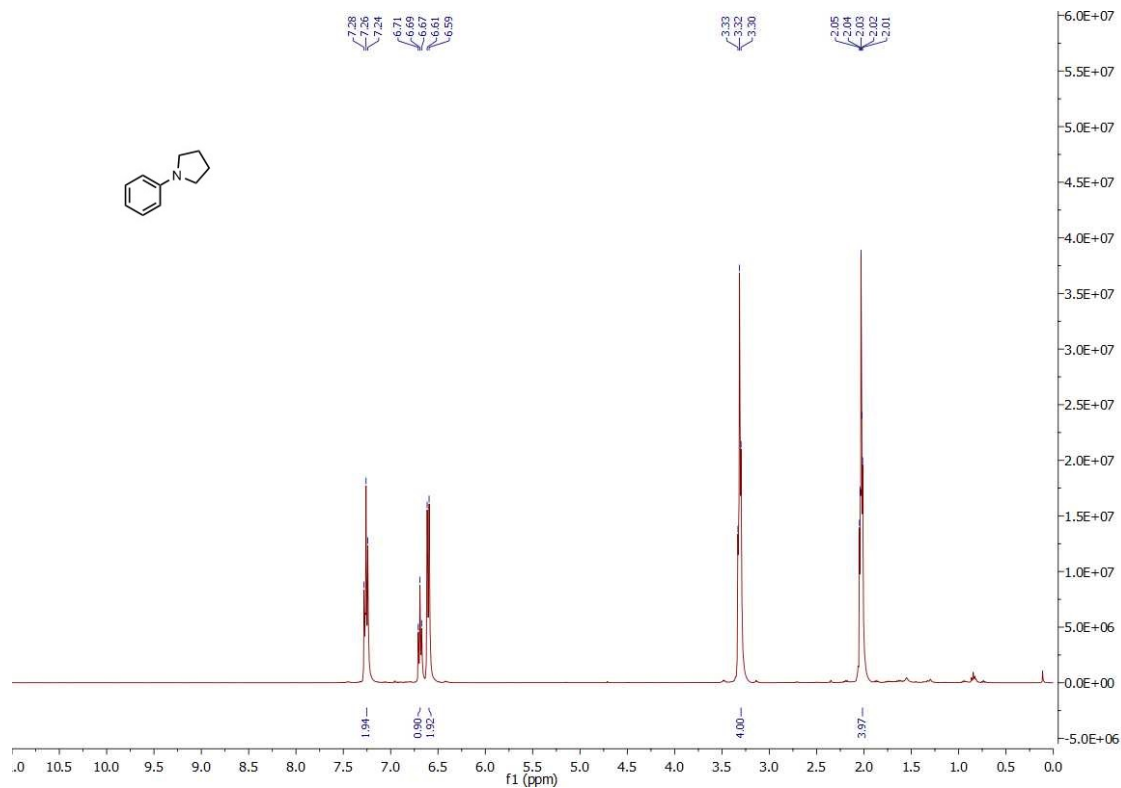


Figure A97. ^1H NMR spectrum of **149** (400 MHz, CDCl_3)

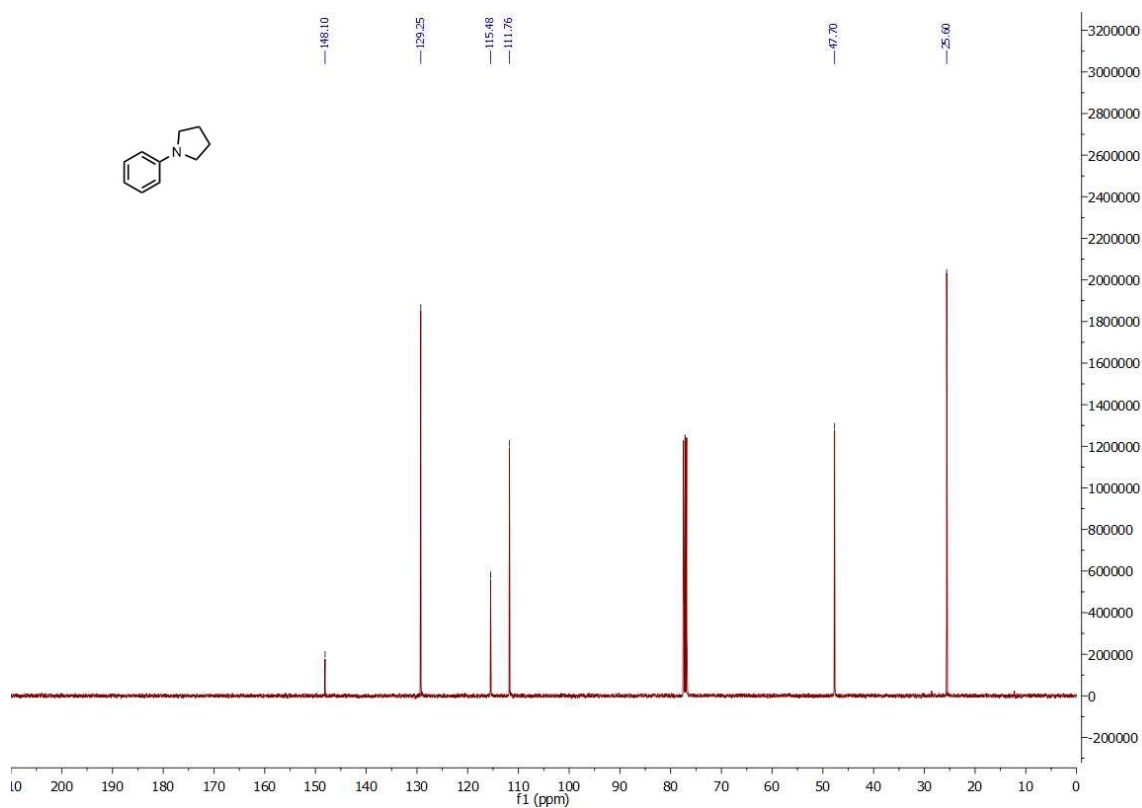


Figure A98. ^{13}C NMR spectrum of **149** (100 MHz, CDCl_3)

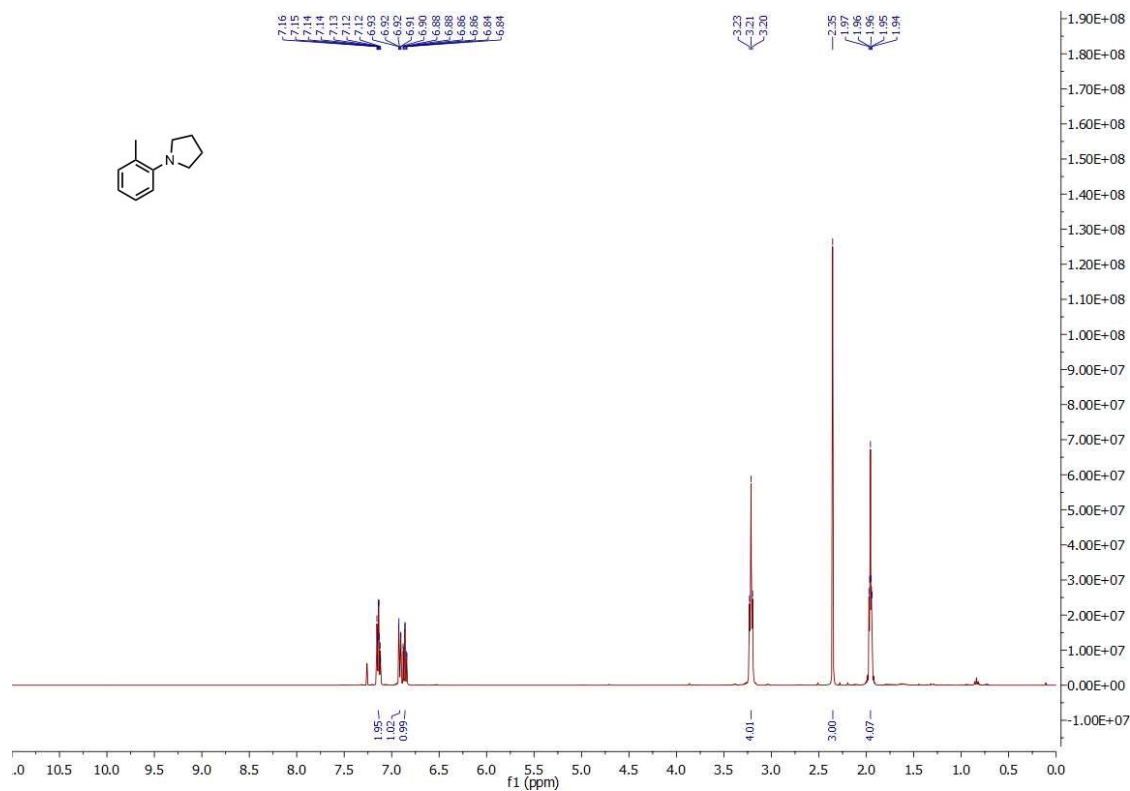


Figure A99. ^1H NMR spectrum of **150** (400 MHz, CDCl_3)

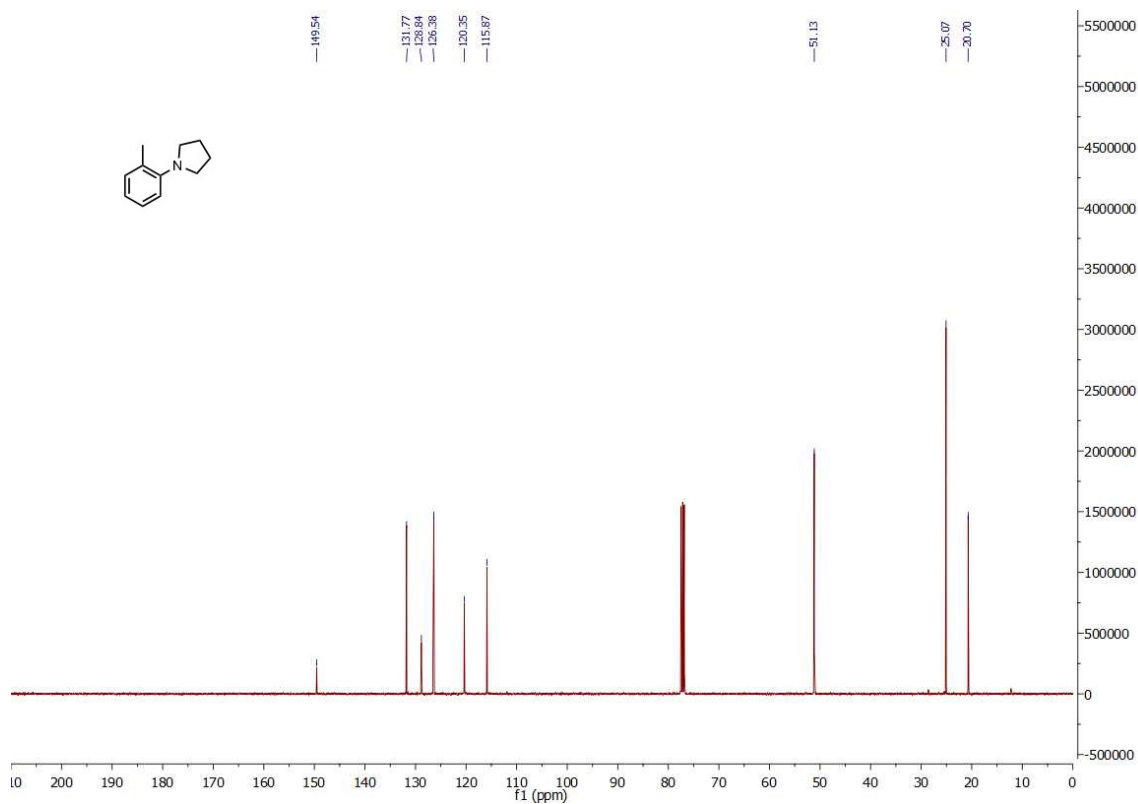


Figure A100. ^{13}C NMR spectrum of **150** (100 MHz, CDCl_3)

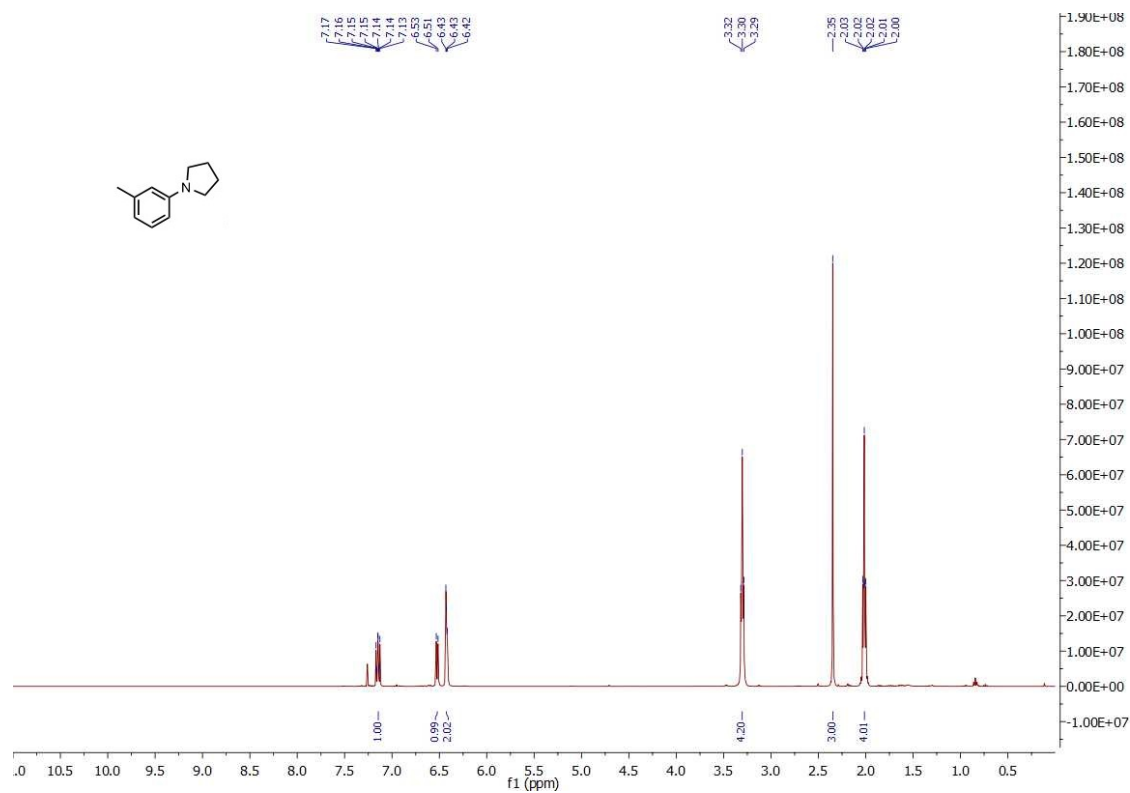


Figure A101. ¹H NMR spectrum of **151** (400 MHz, CDCl₃)

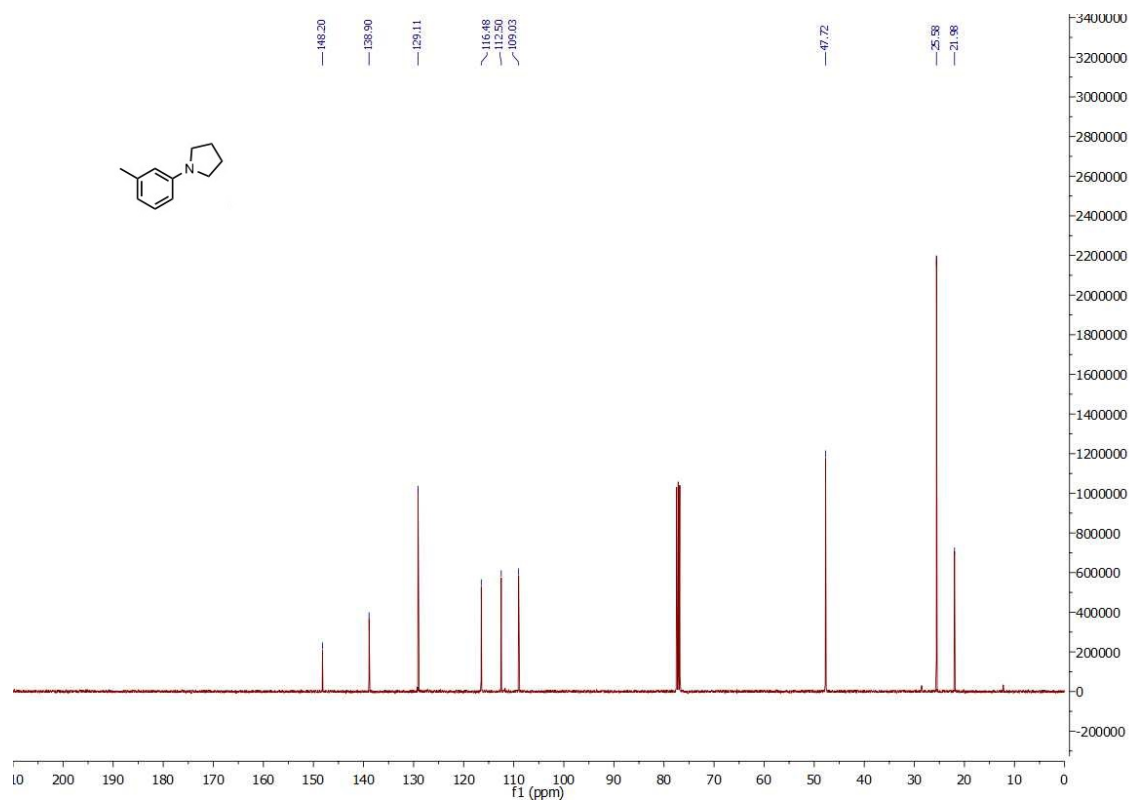


Figure A102. ¹³C NMR spectrum of **151** (100 MHz, CDCl₃)

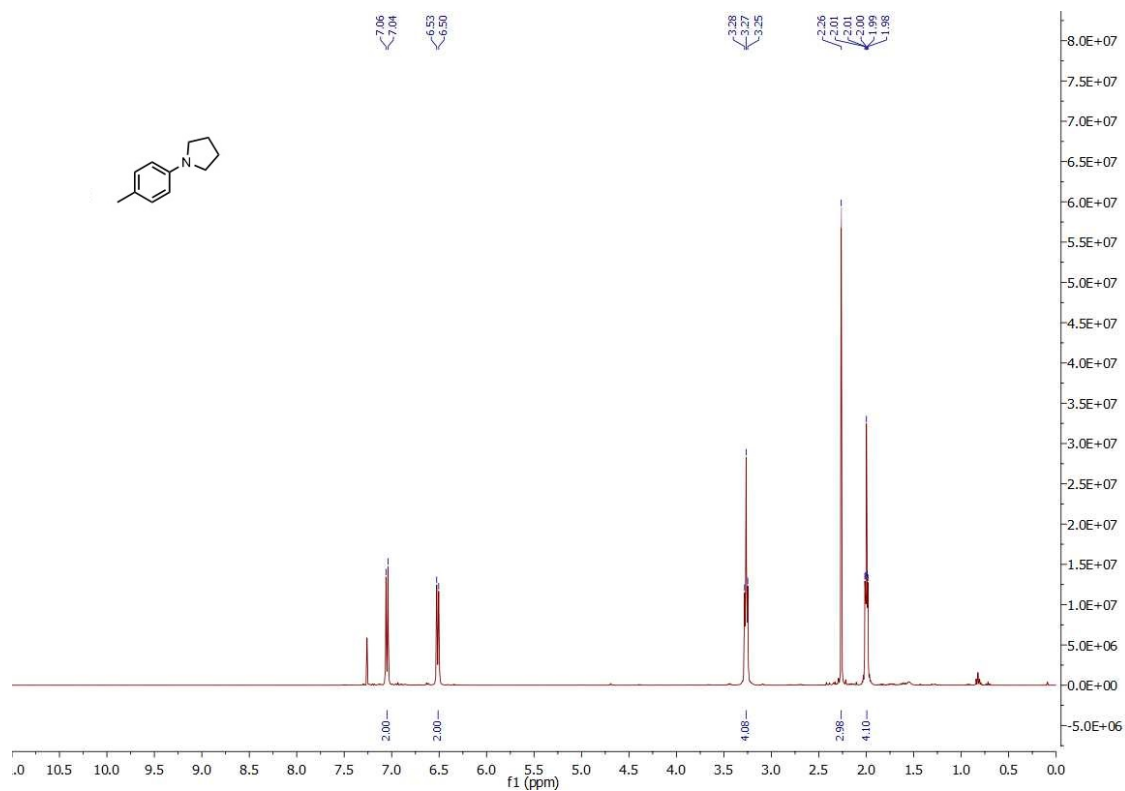


Figure A103. ^1H NMR spectrum of **152** (400 MHz, CDCl_3)

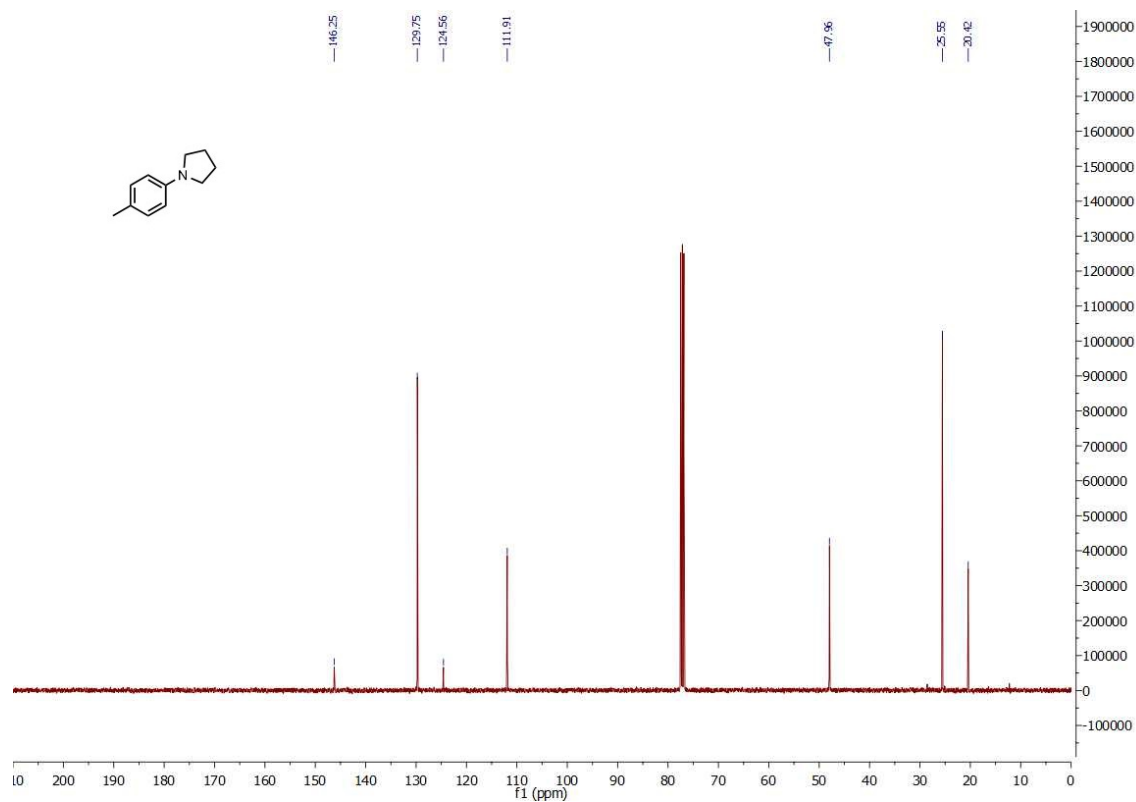


Figure A104. ^{13}C NMR spectrum of **152** (100 MHz, CDCl_3)

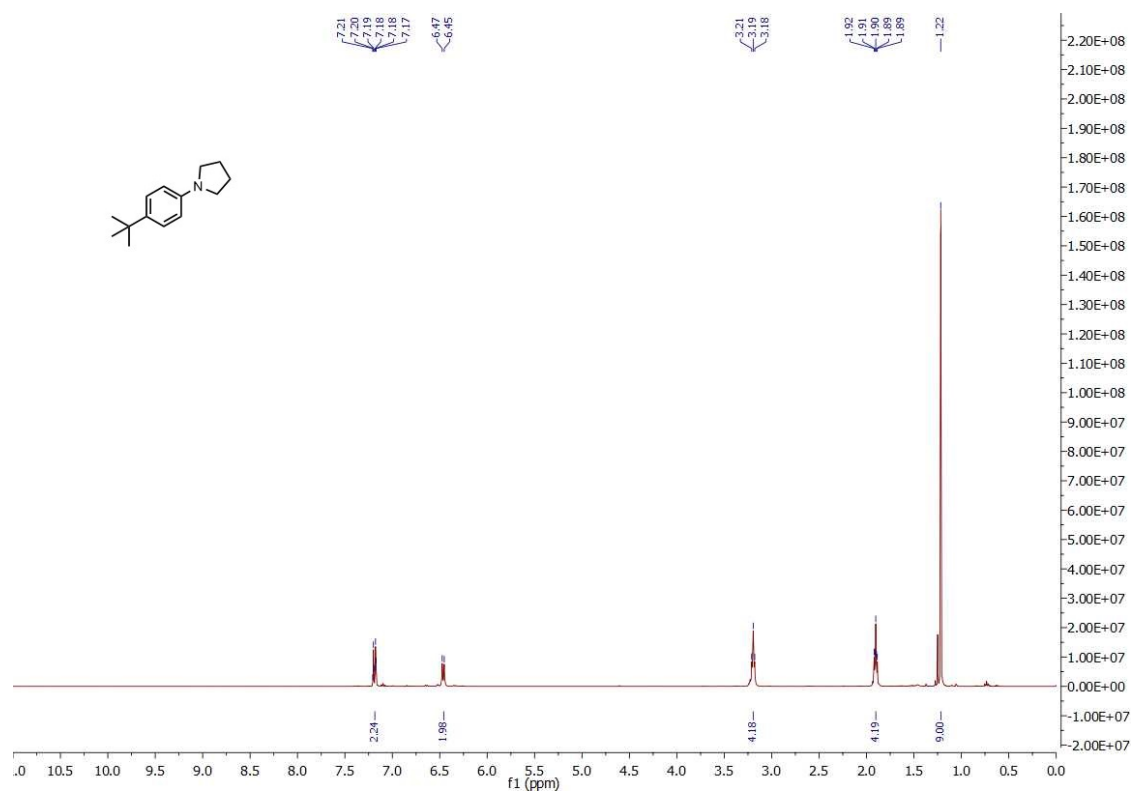


Figure A105. ¹H NMR spectrum of **153** (400 MHz, CDCl₃)

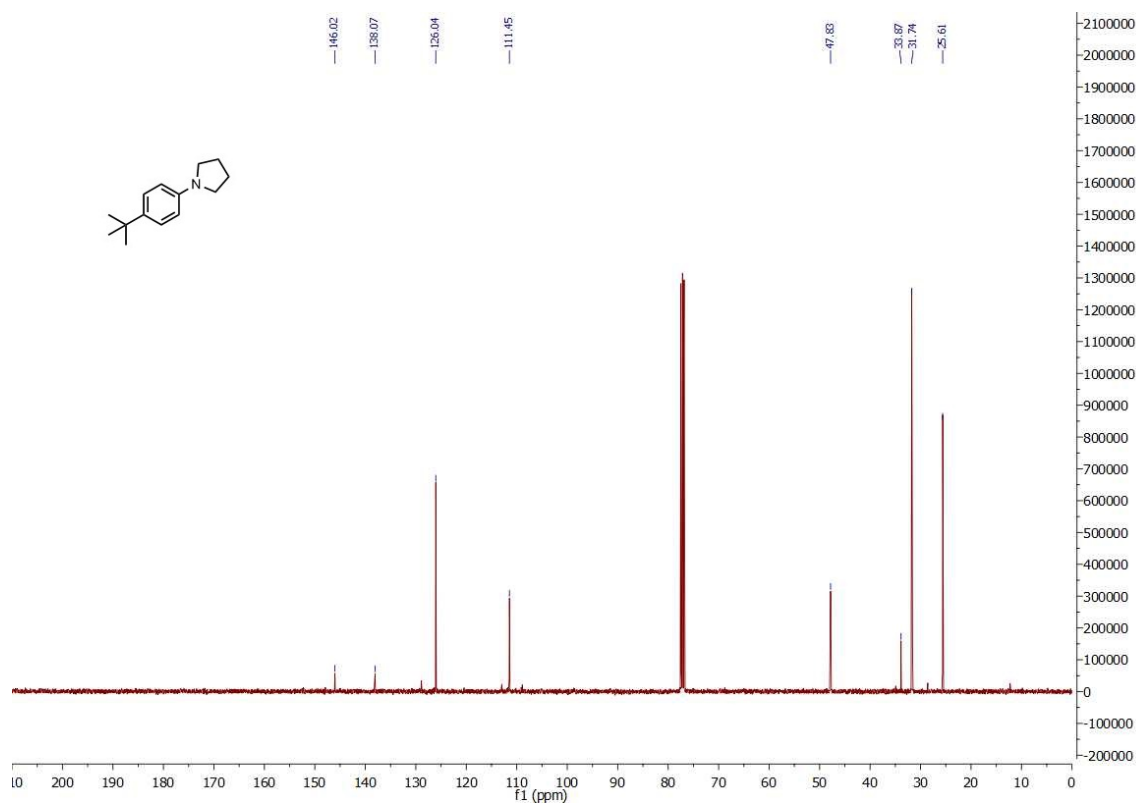


Figure A106. ¹³C NMR spectrum of **153** (100 MHz, CDCl₃)

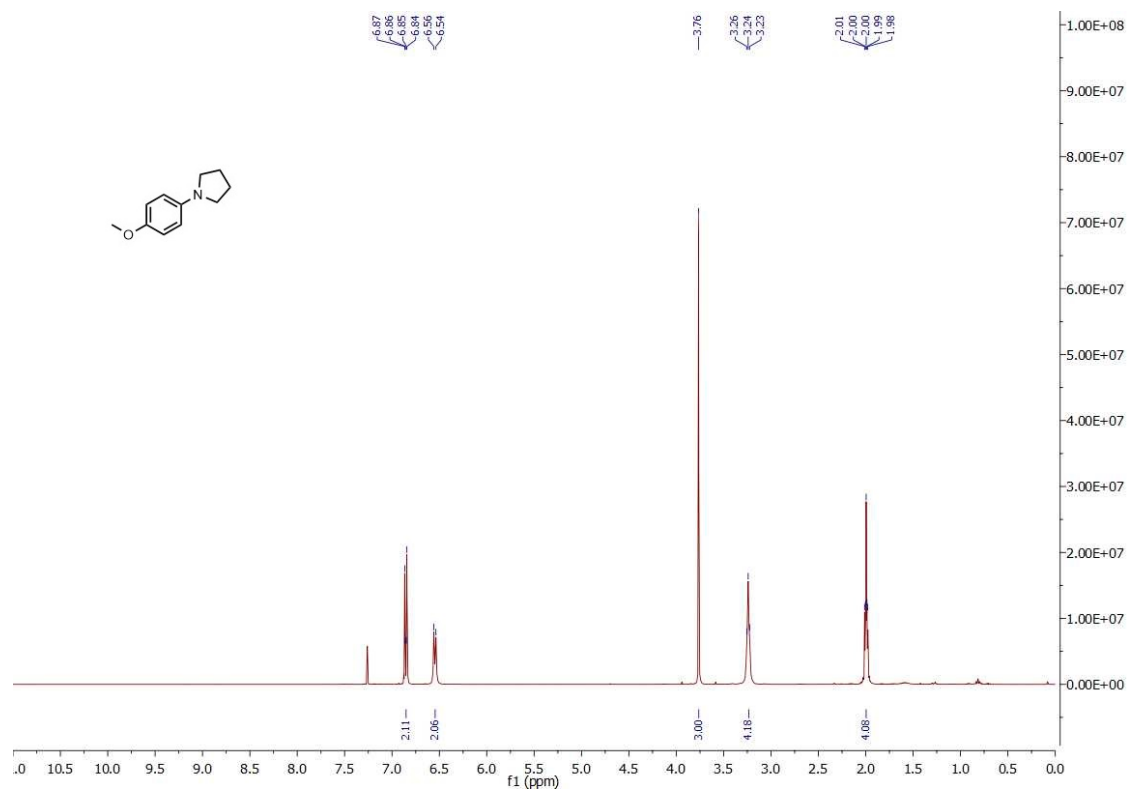


Figure A107. ^1H NMR spectrum of **154** (400 MHz, CDCl_3)

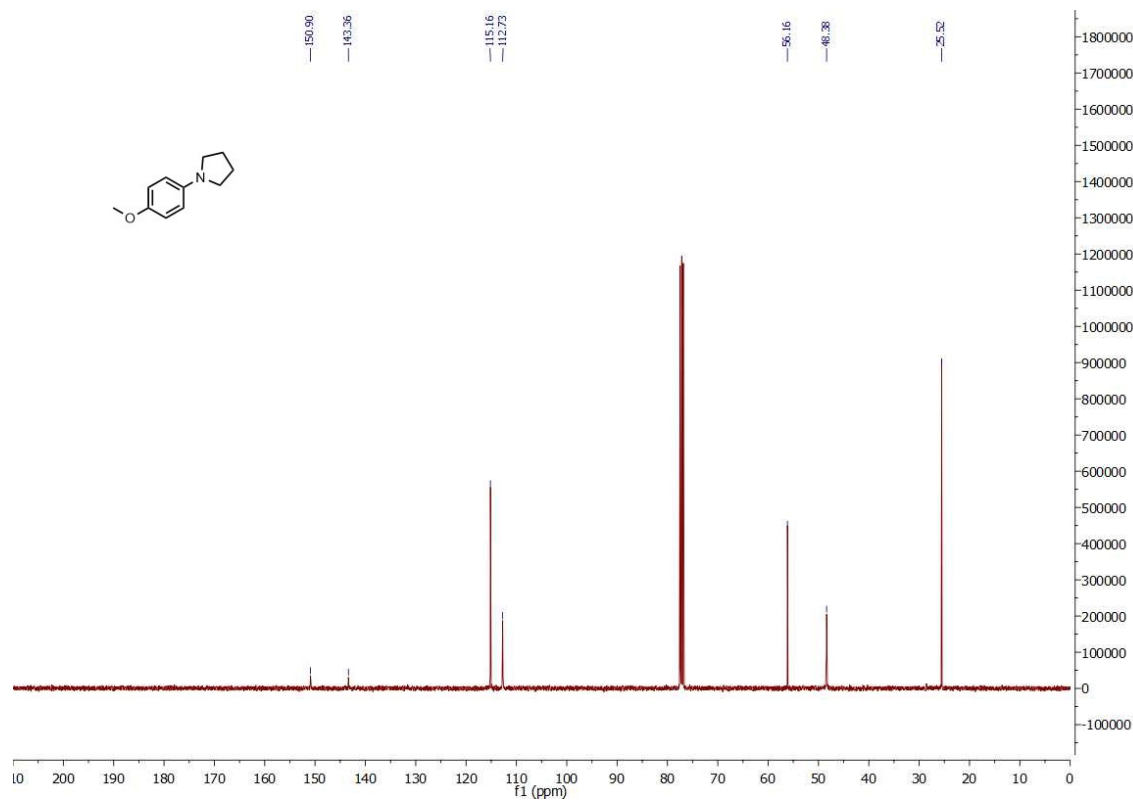


Figure A108. ^{13}C NMR spectrum of **154** (100 MHz, CDCl_3)

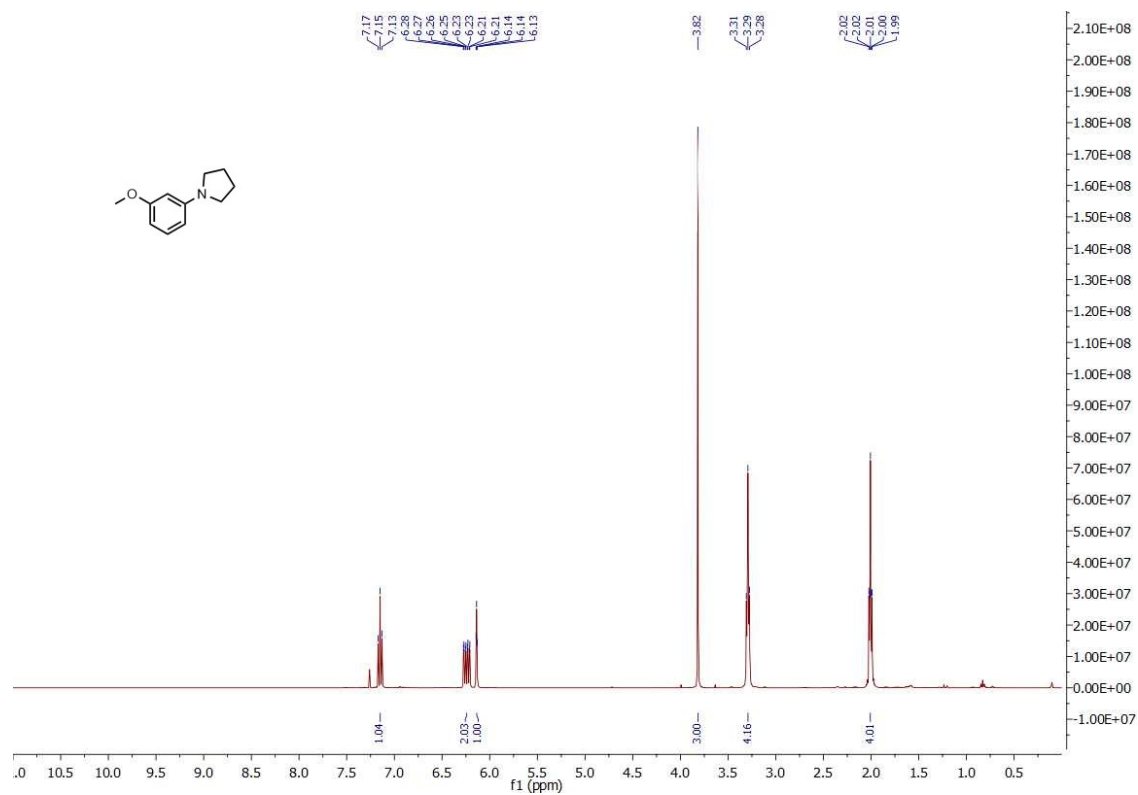


Figure A109. ^1H NMR spectrum of **155** (400 MHz, CDCl_3)

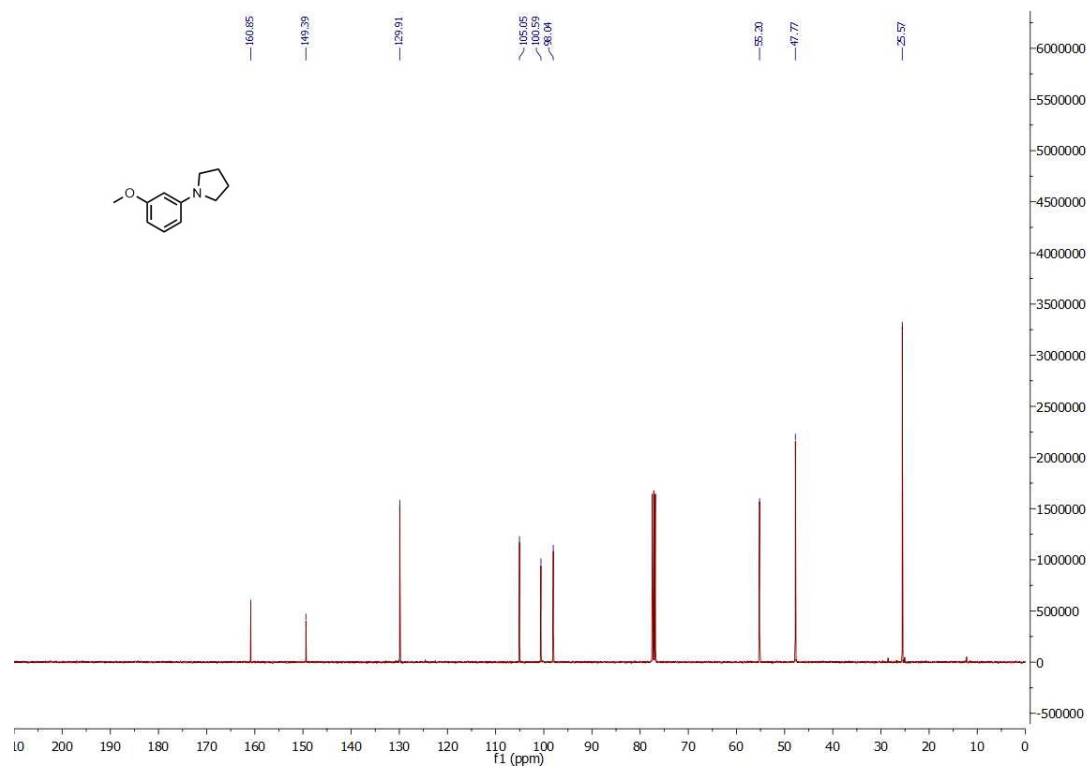


Figure A110. ^{13}C NMR spectrum of **155** (100 MHz, CDCl_3)

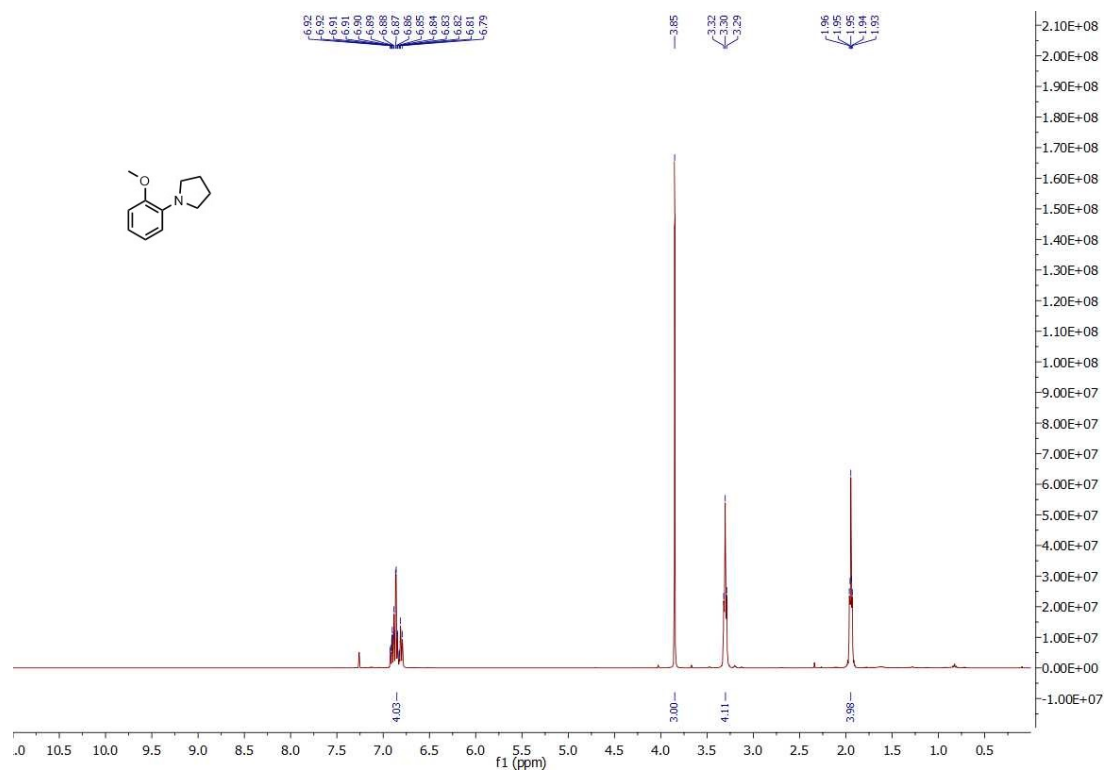


Figure A111. ^1H NMR spectrum of **156** (400 MHz, CDCl_3)

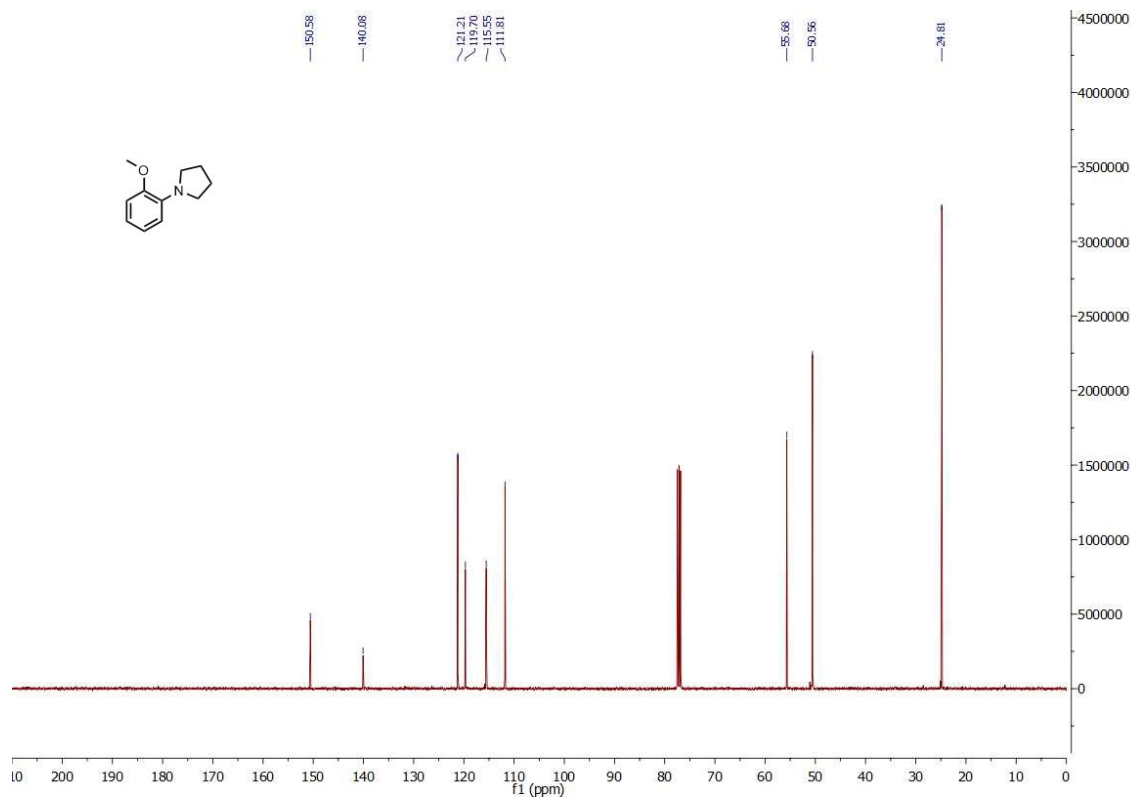


Figure A112. ^{13}C NMR spectrum of **156** (100 MHz, CDCl_3)

Figure A113. ^1H NMR spectrum of **(157)** (400 MHz, CDCl_3)

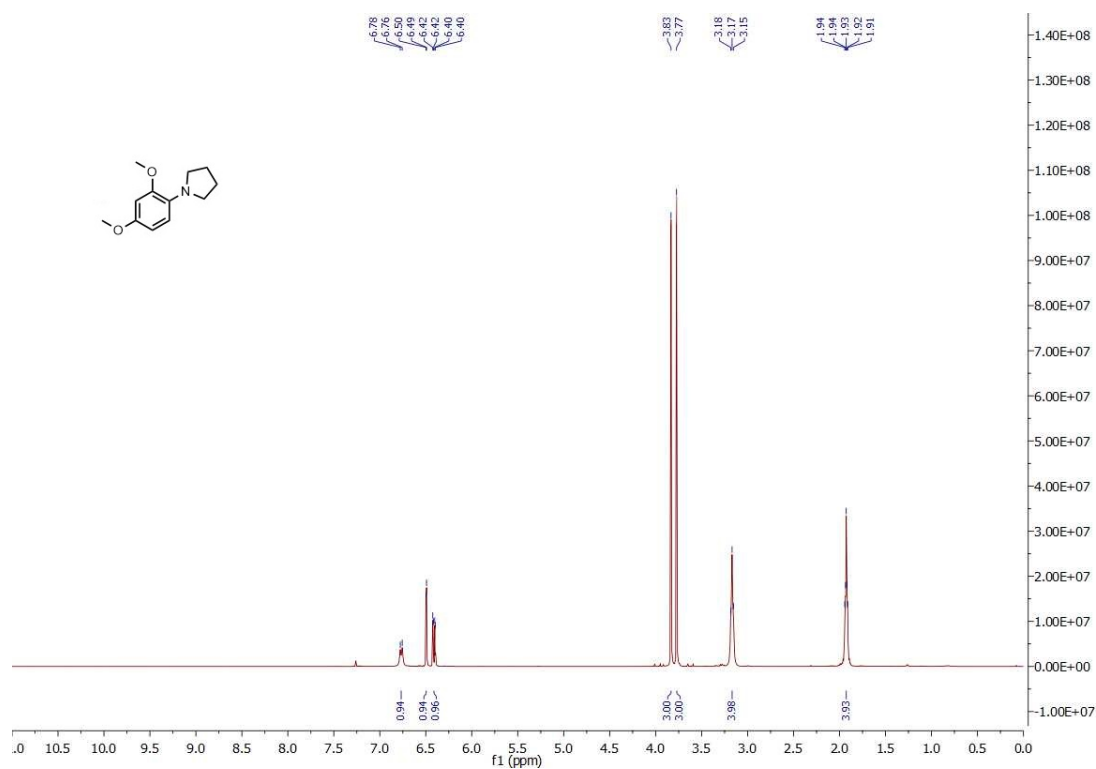


Figure A113. ^1H NMR spectrum of **157** (400 MHz, CDCl_3)

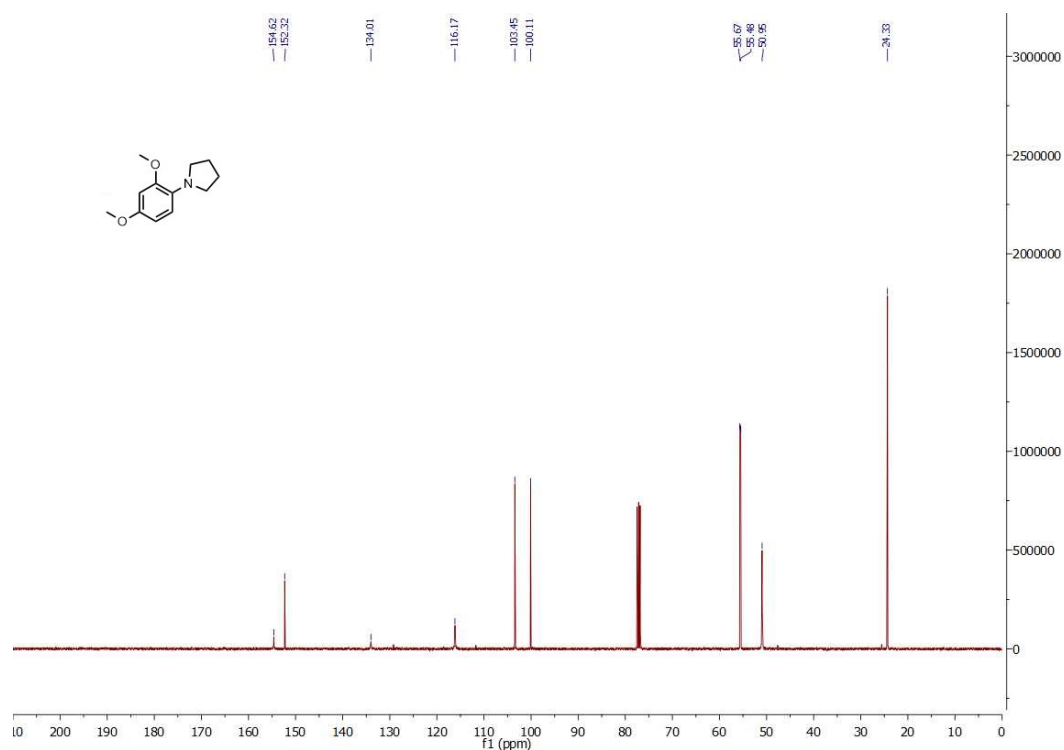


Figure A114. ^{13}C NMR spectrum of **157** (100 MHz, CDCl_3)

Appendix for chapter 4

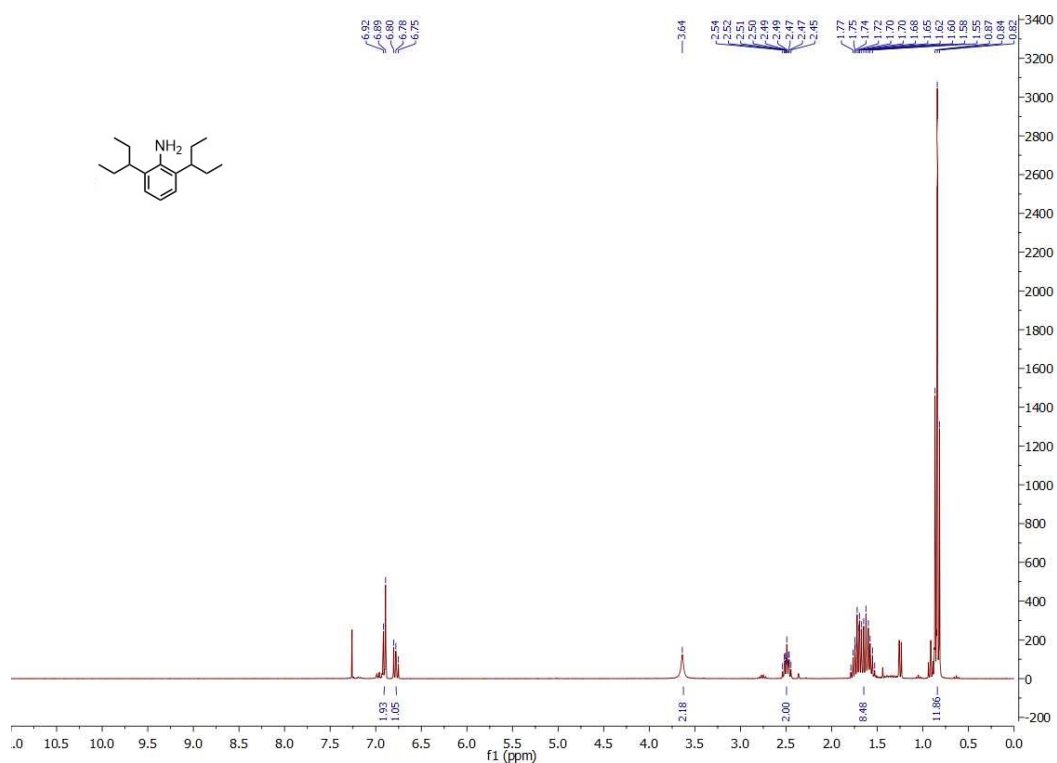


Figure A115. ¹H NMR spectrum of **161** (300 MHz, CDCl₃)

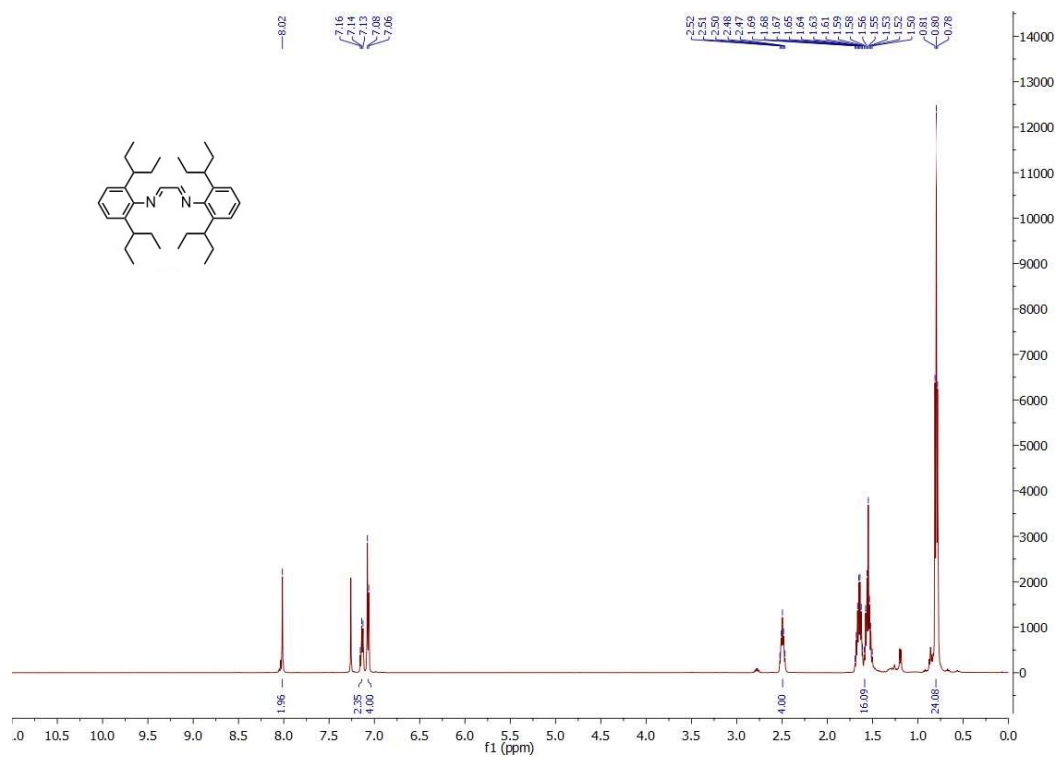


Figure A 116. ¹H NMR spectrum of **162** (500 MHz, CDCl₃)

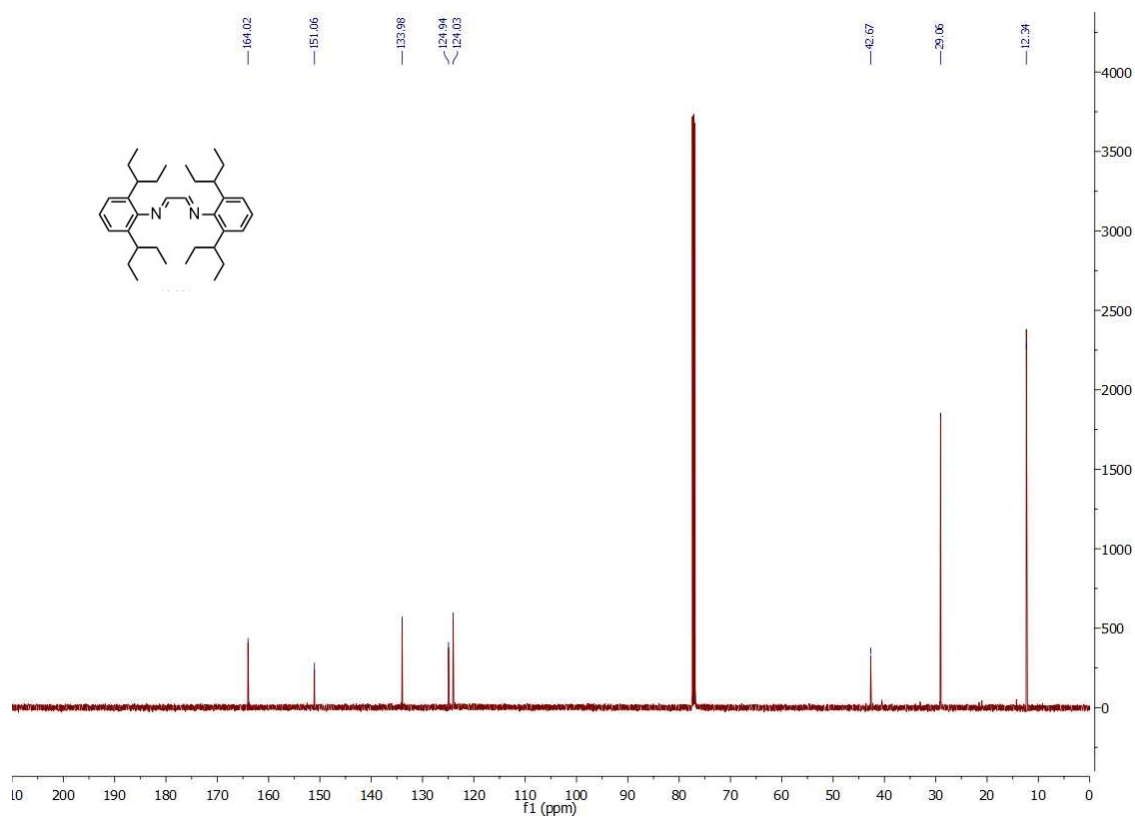


Figure A117. ¹³C NMR spectrum of **162** (125 MHz, CDCl₃)

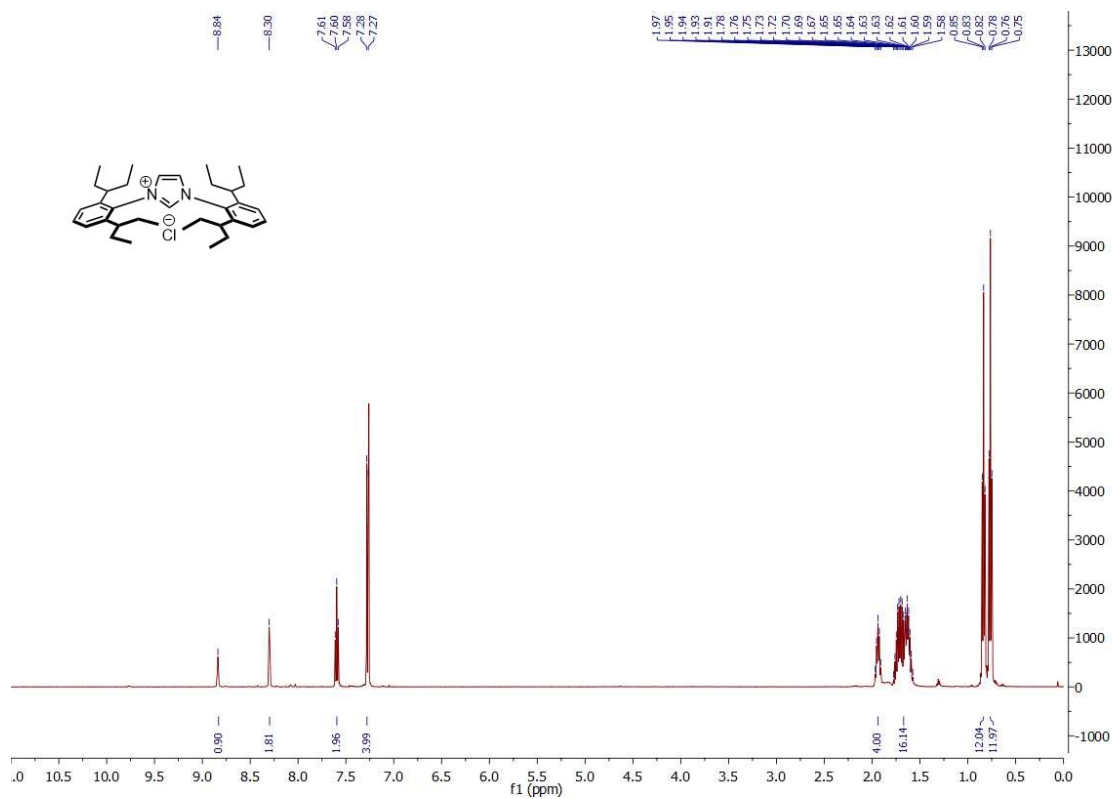


Figure A118. ¹H NMR spectrum of **163a** (500 MHz, CDCl₃)

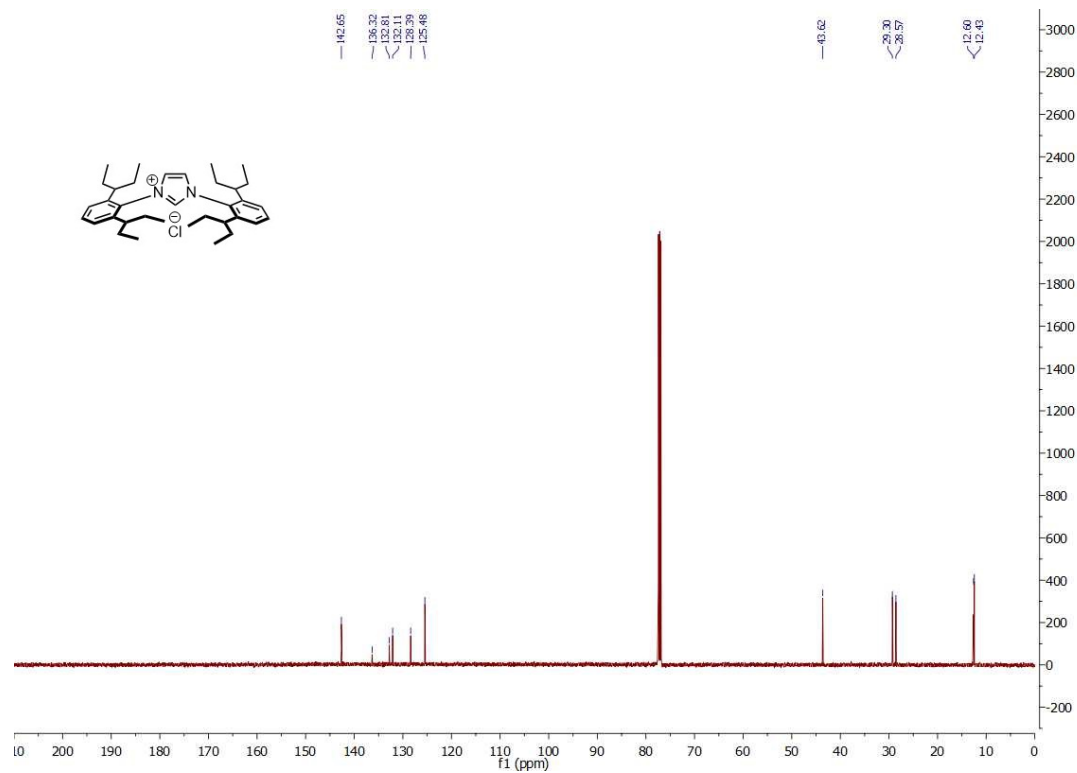


Figure A119. ¹³C NMR spectrum of **163a** (125 MHz, CDCl₃)

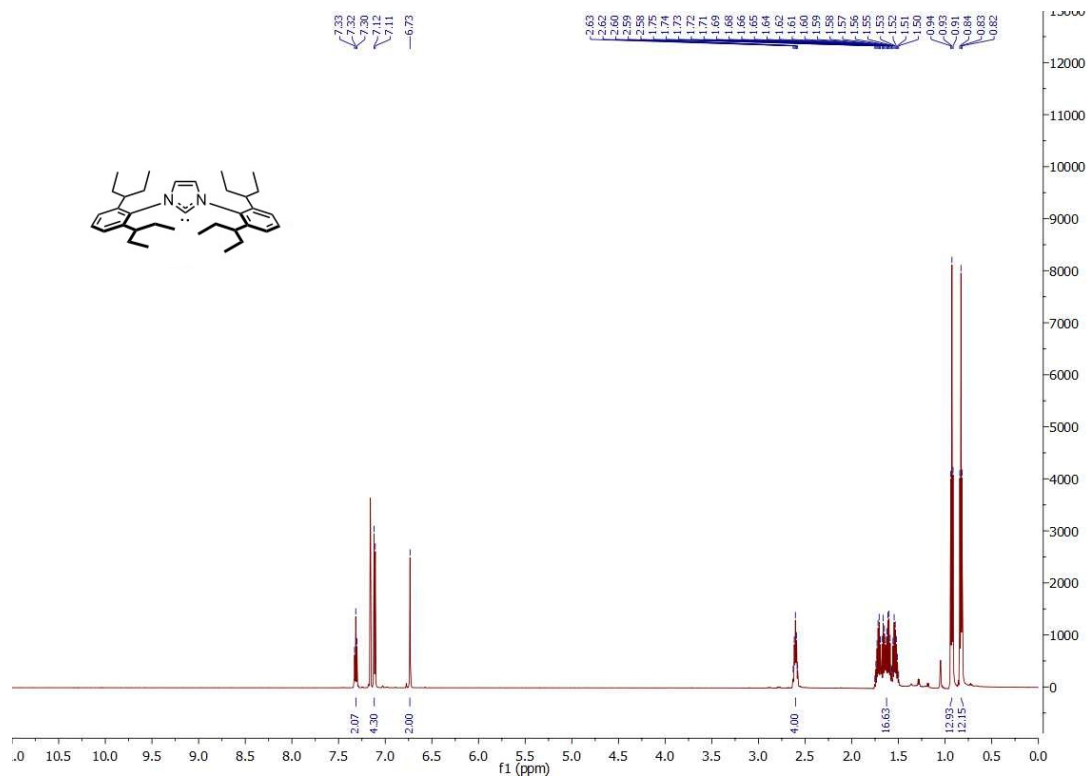


Figure A122. ¹H NMR spectrum of **164** (600 MHz, C₆D₆)

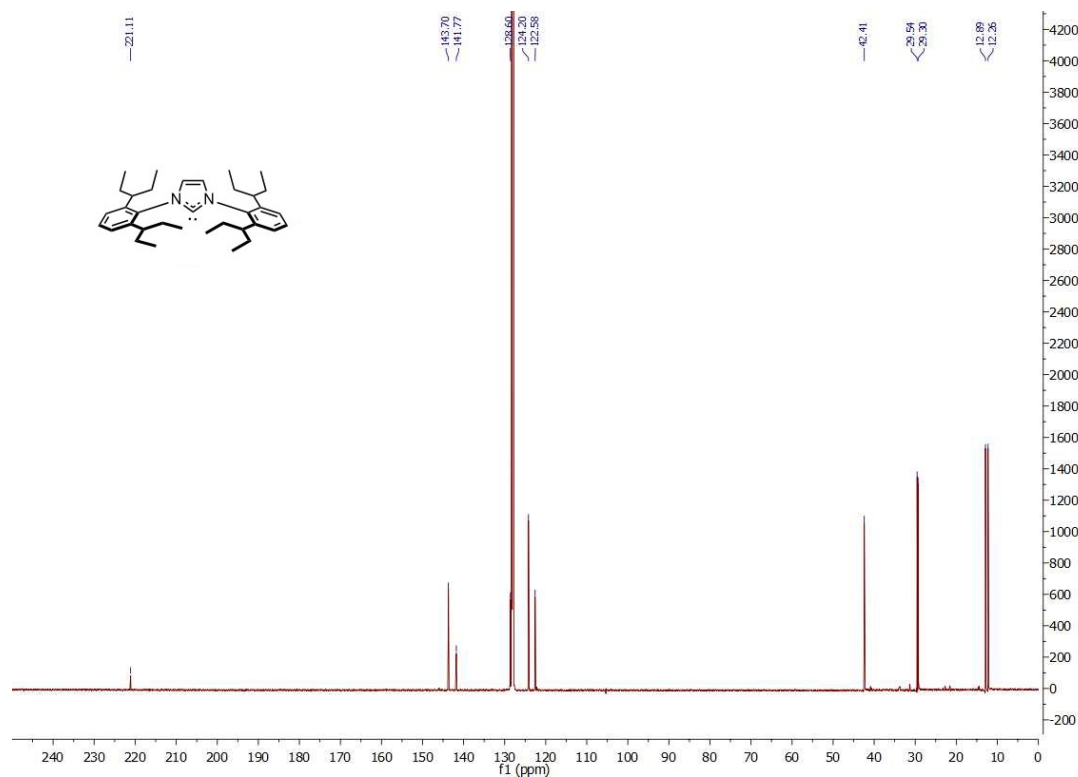


Figure A123. ¹³C NMR spectrum of **164** (150 MHz, C₆D₆)

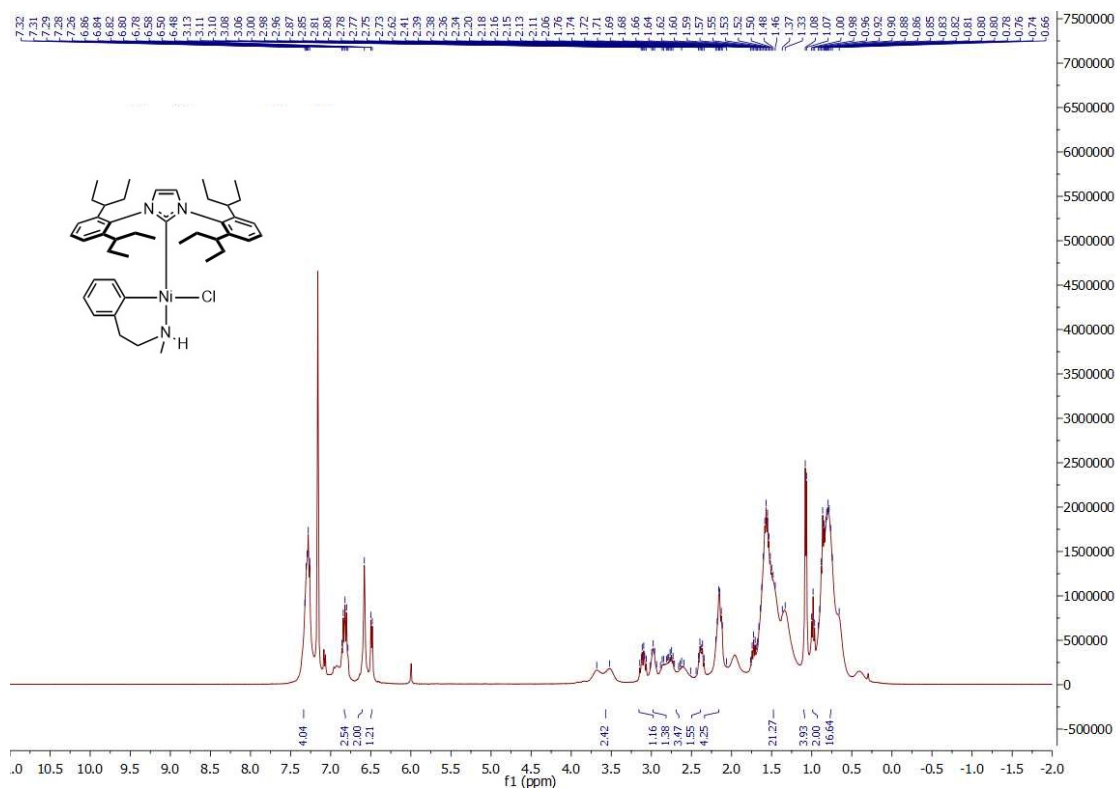


Figure A124. ^1H NMR spectrum of **165** (400 MHz, C_6D_6)

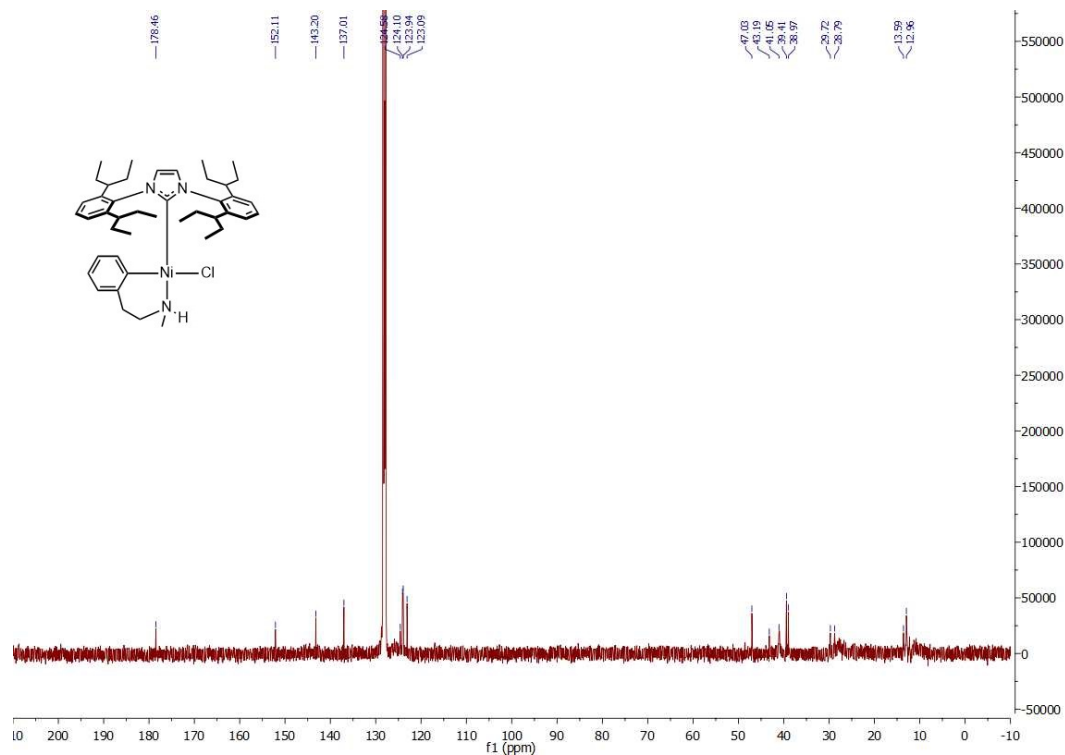


Figure A125. ^{13}C NMR spectrum of **165** (100 MHz, C_6D_6)

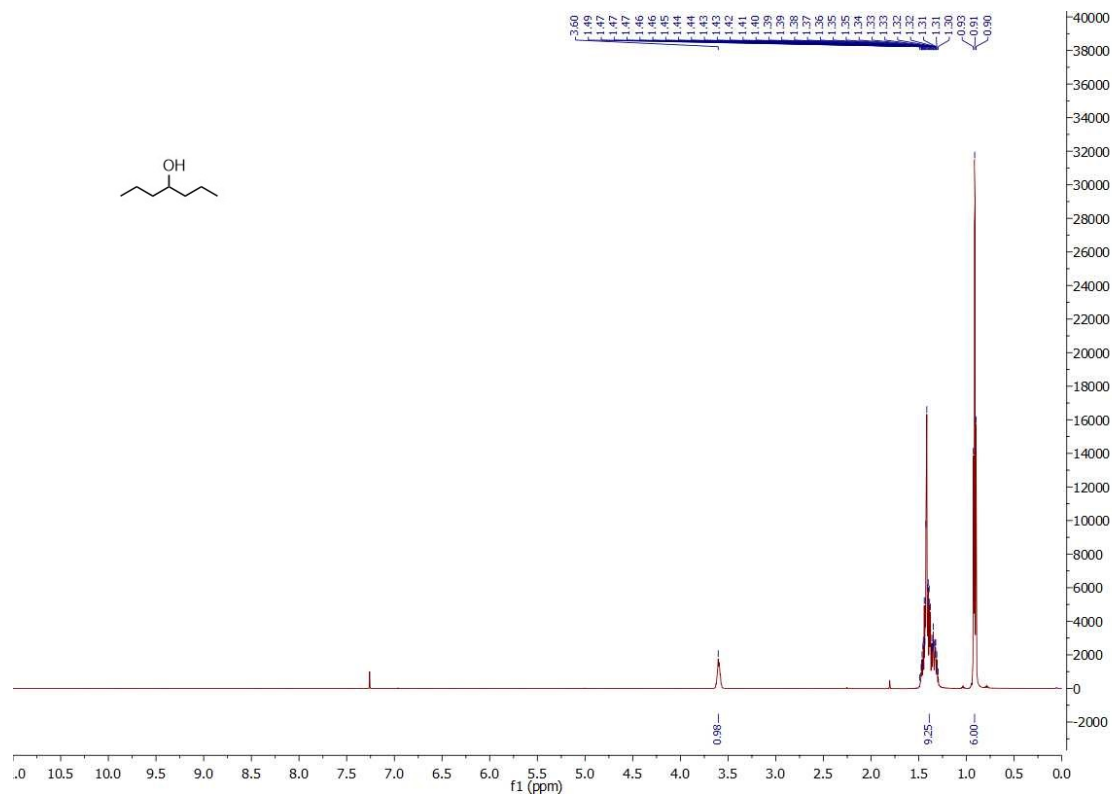


Figure A126. ¹H NMR spectrum of **167** (500 MHz, CDCl₃)

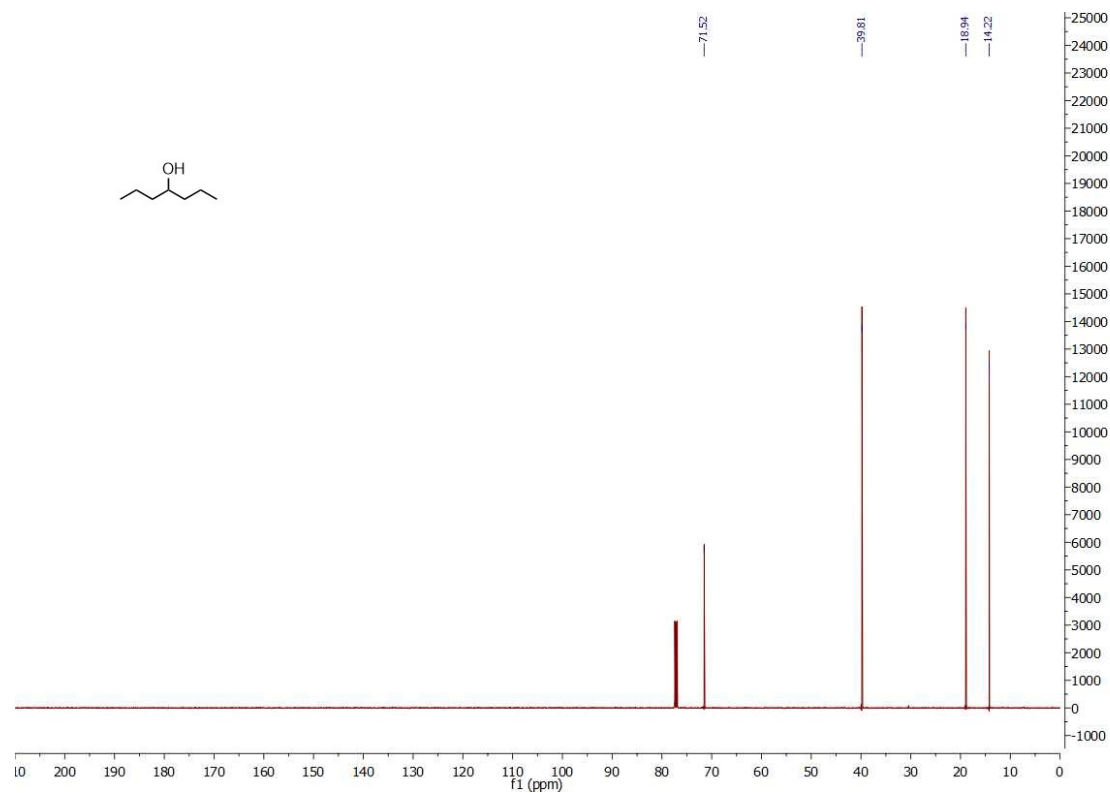


Figure A127. ¹³C NMR spectrum of **167** (125 MHz, CDCl₃)

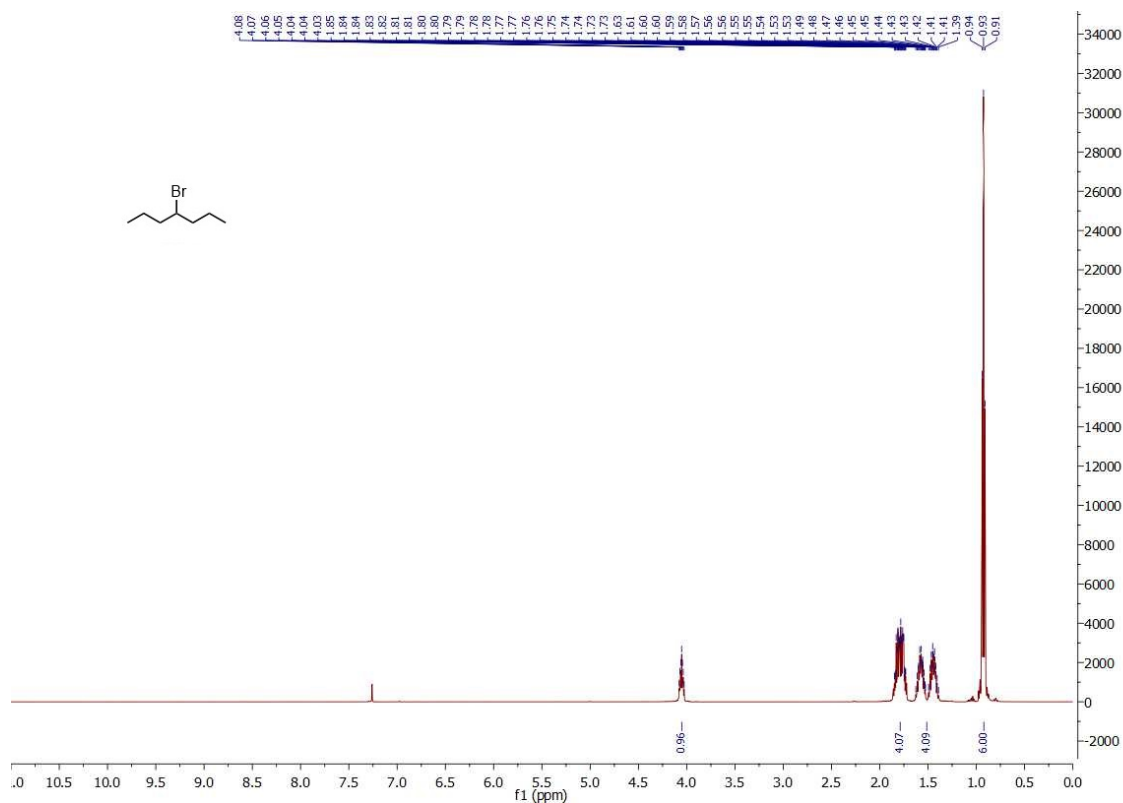


Figure A128. ¹H NMR spectrum of **168** (500 MHz, CDCl₃)

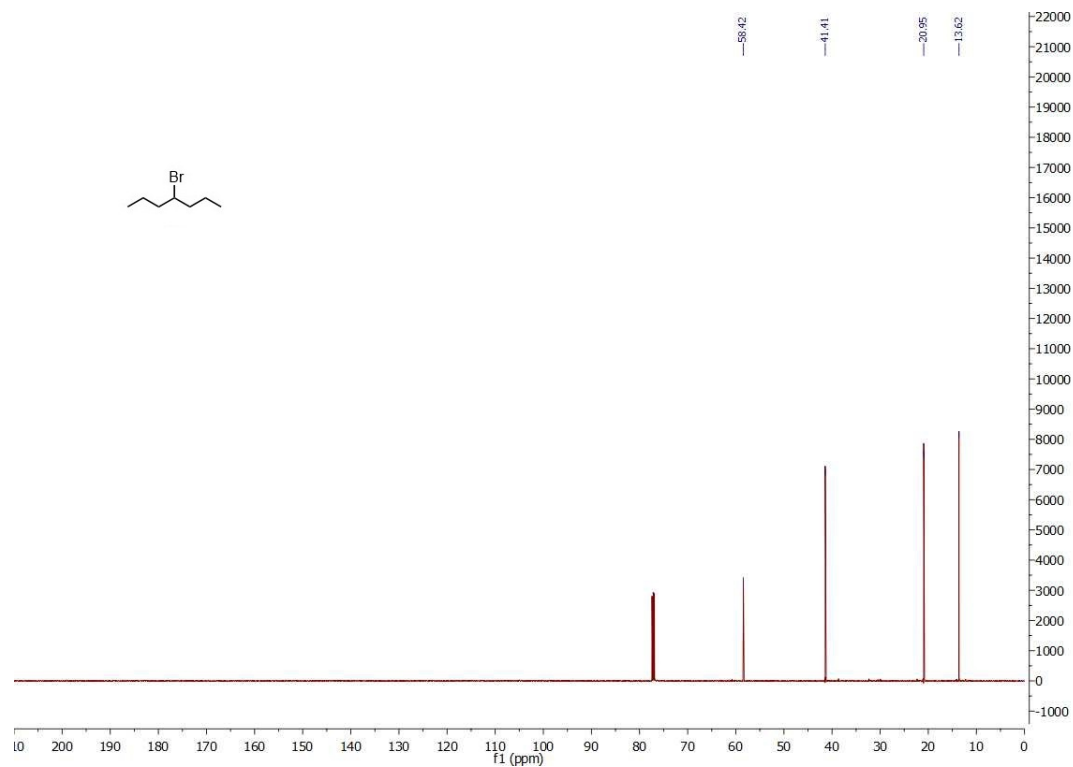


Figure A129. ¹³C NMR spectrum of **168** (125 MHz, CDCl₃)

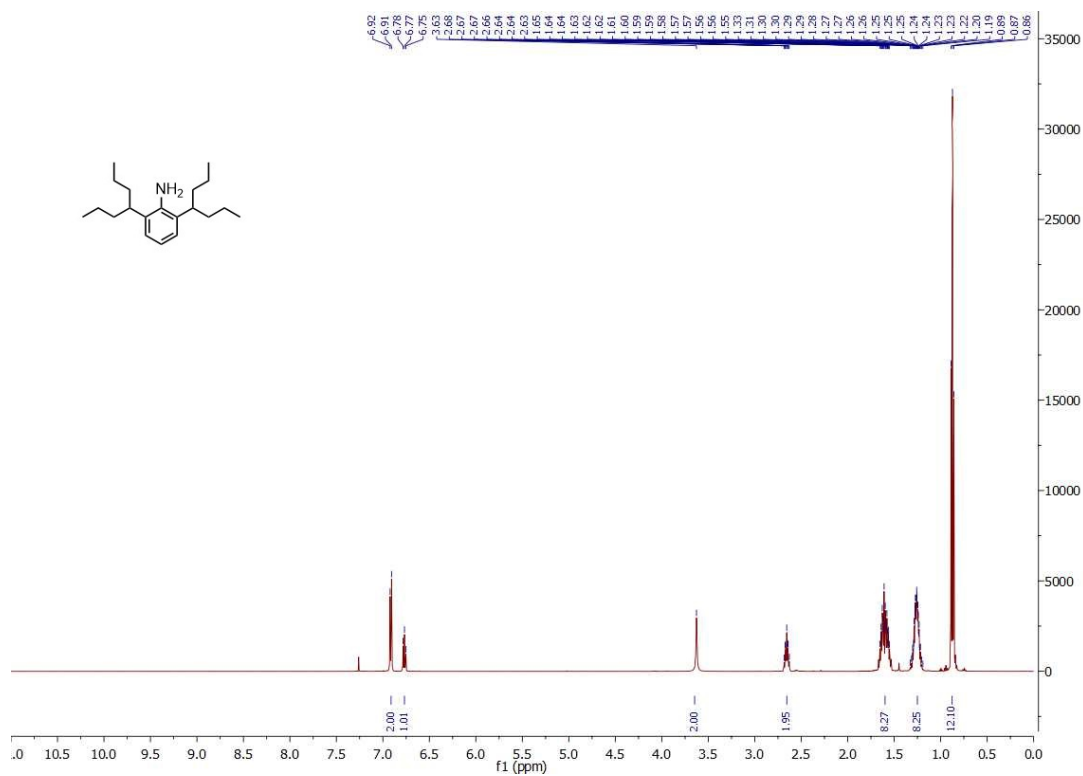


Figure A130. ¹H NMR spectrum of **170** (500 MHz, CDCl₃)

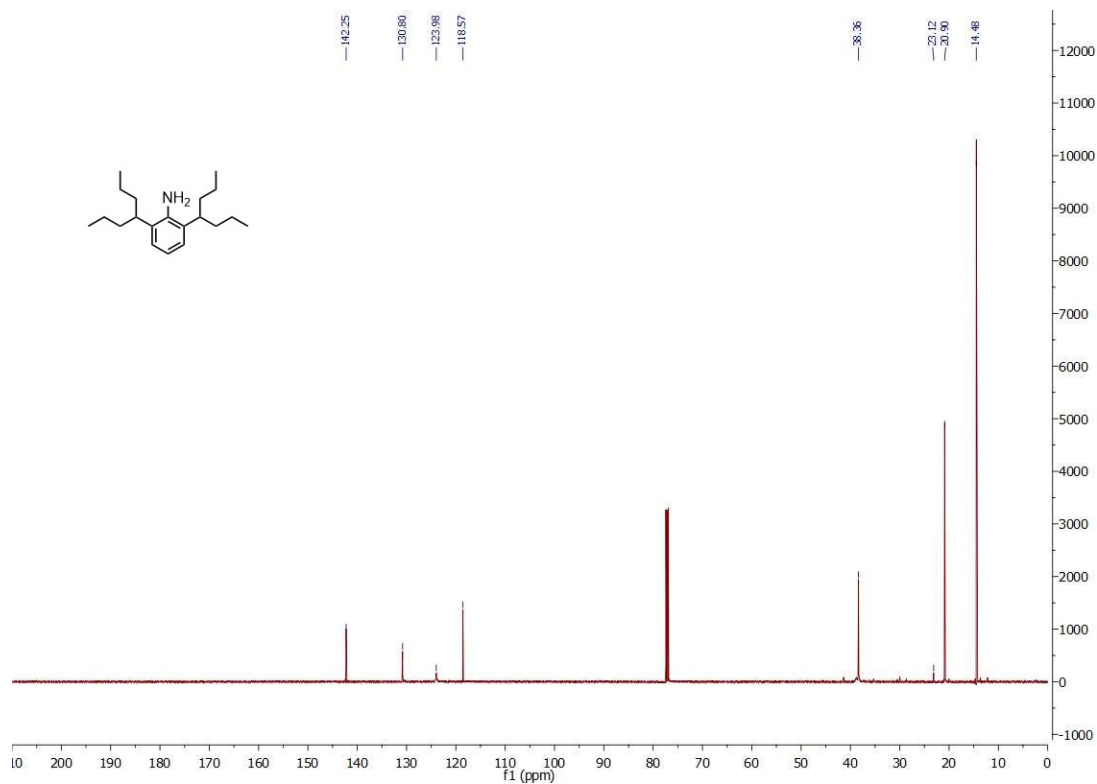


Figure A131. ¹³C NMR spectrum of **170** (125 MHz, CDCl₃)

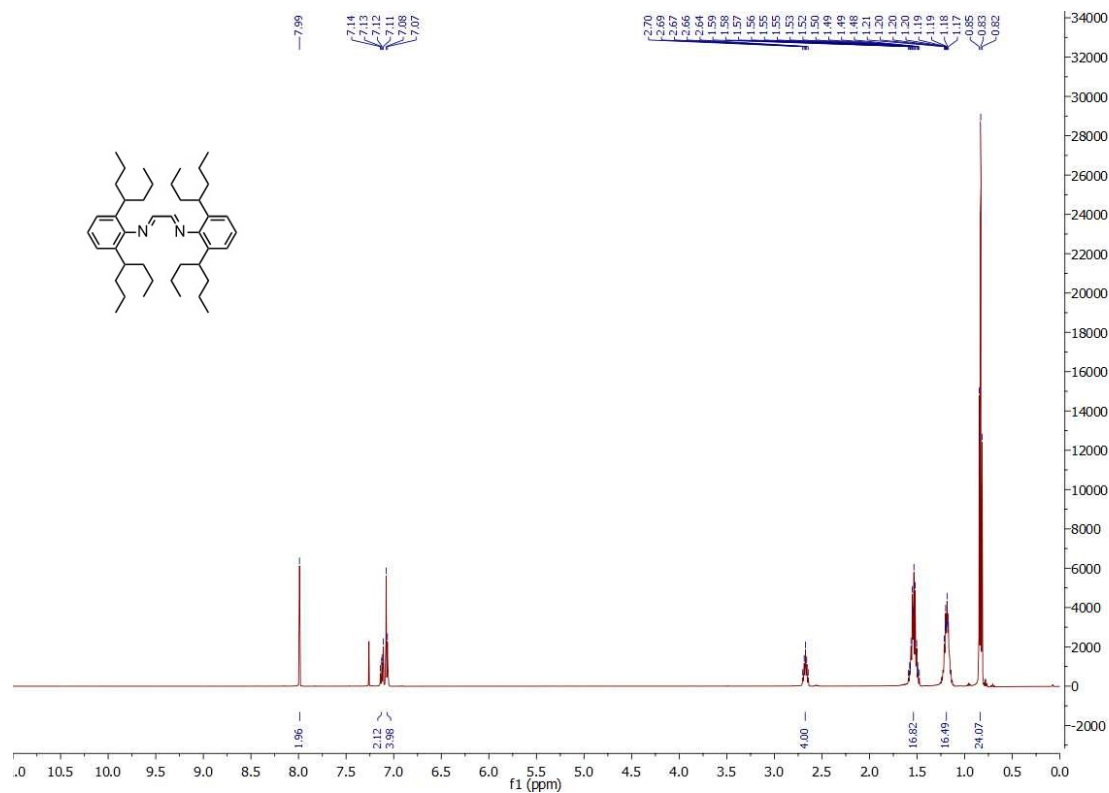


Figure A132. ¹H NMR spectrum of **171** (500 MHz, CDCl₃)

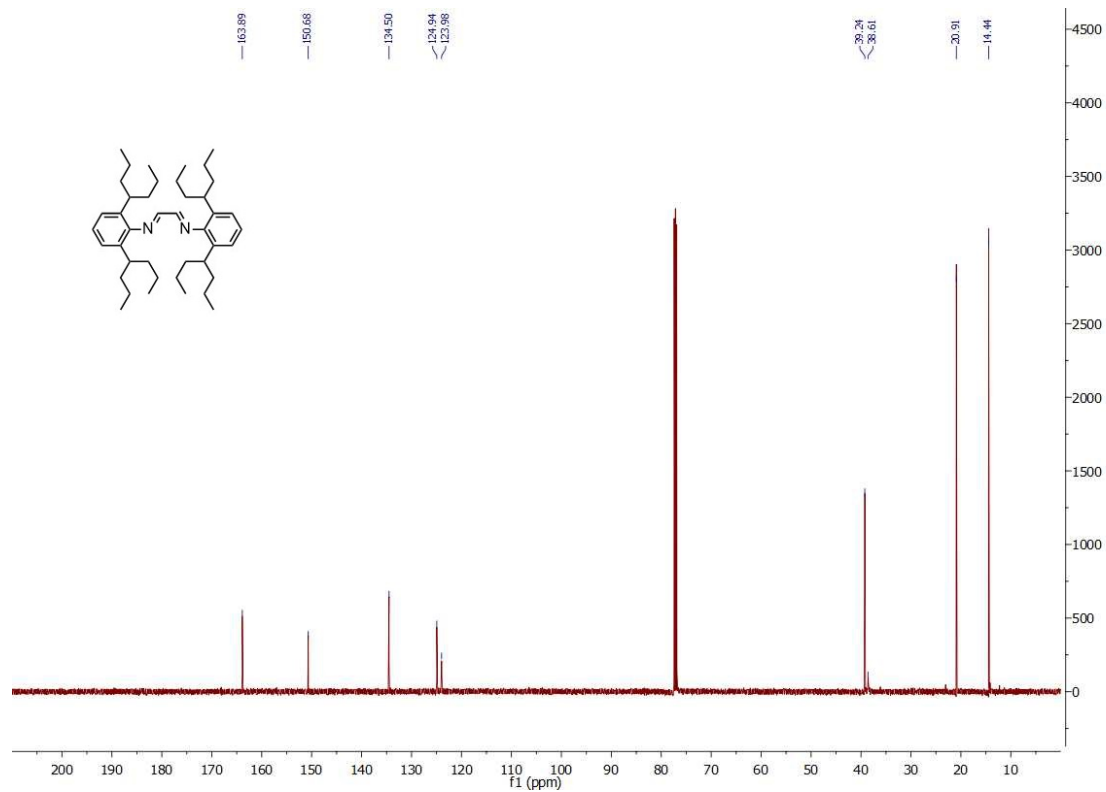


Figure A133. ¹³C NMR spectrum of **171** (125 MHz, CDCl₃)

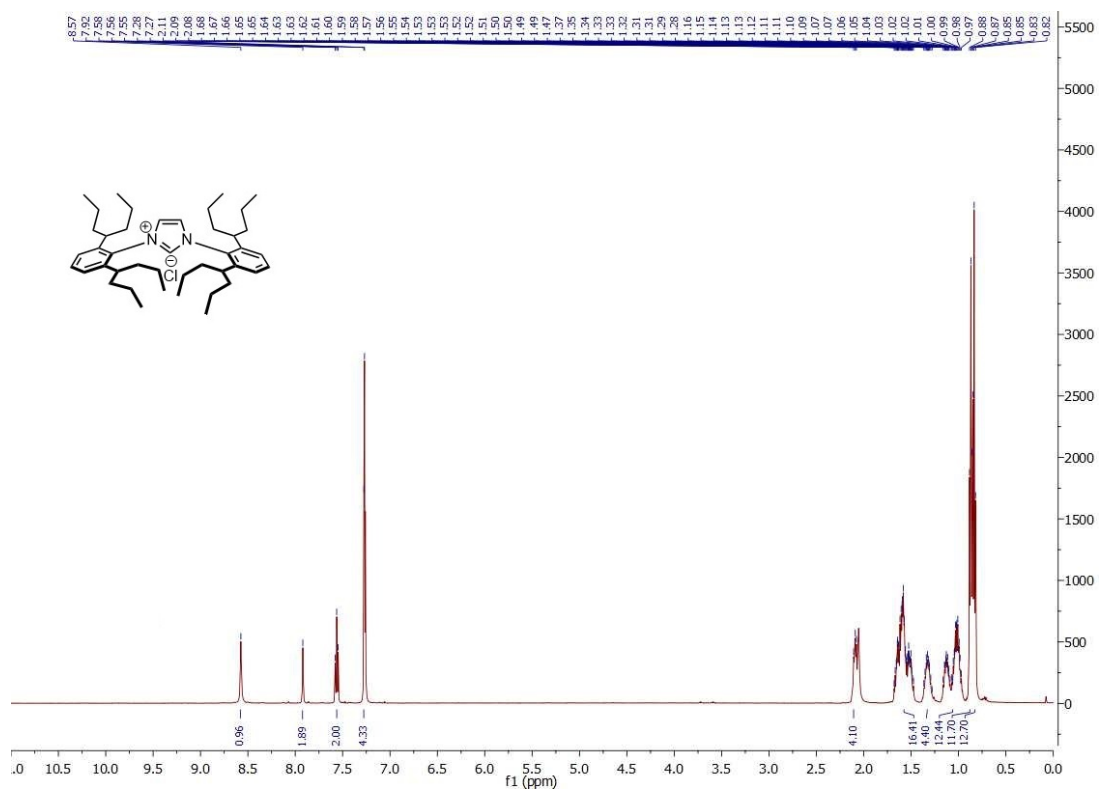


Figure A134. ^1H NMR spectrum of **172** (500 MHz, CDCl_3)

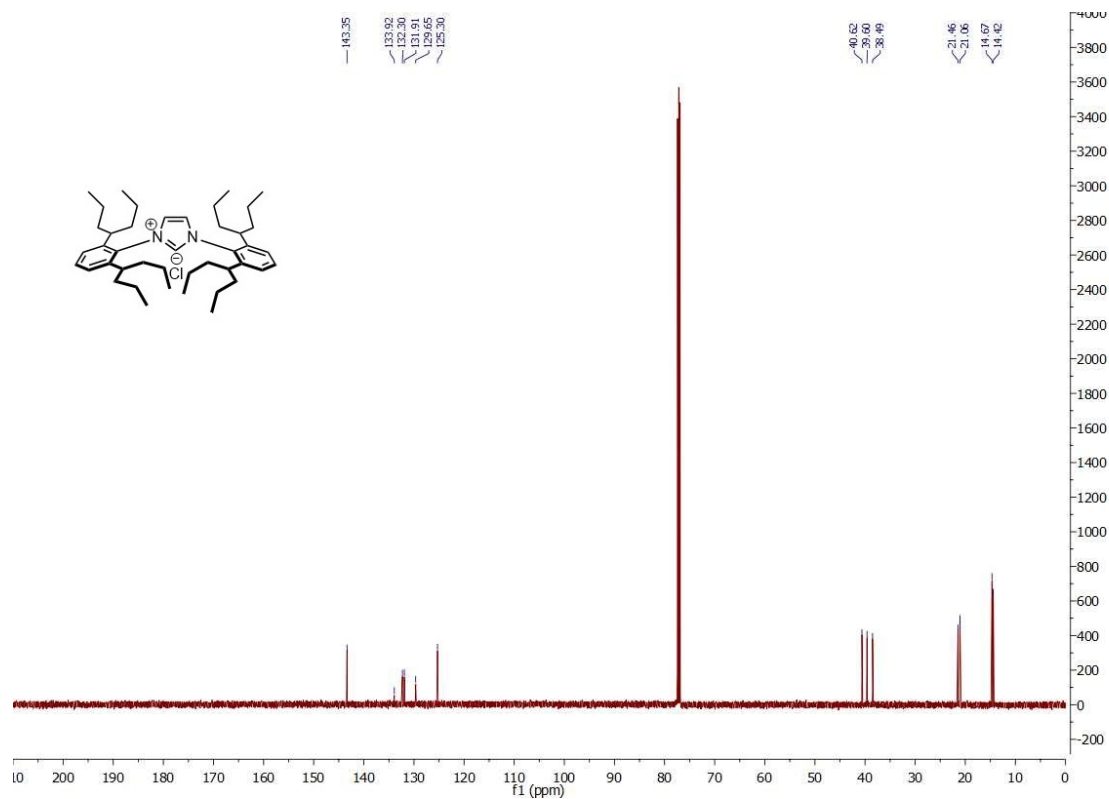


Figure A135. ^{13}C NMR spectrum of **172** (125 MHz, CDCl_3)

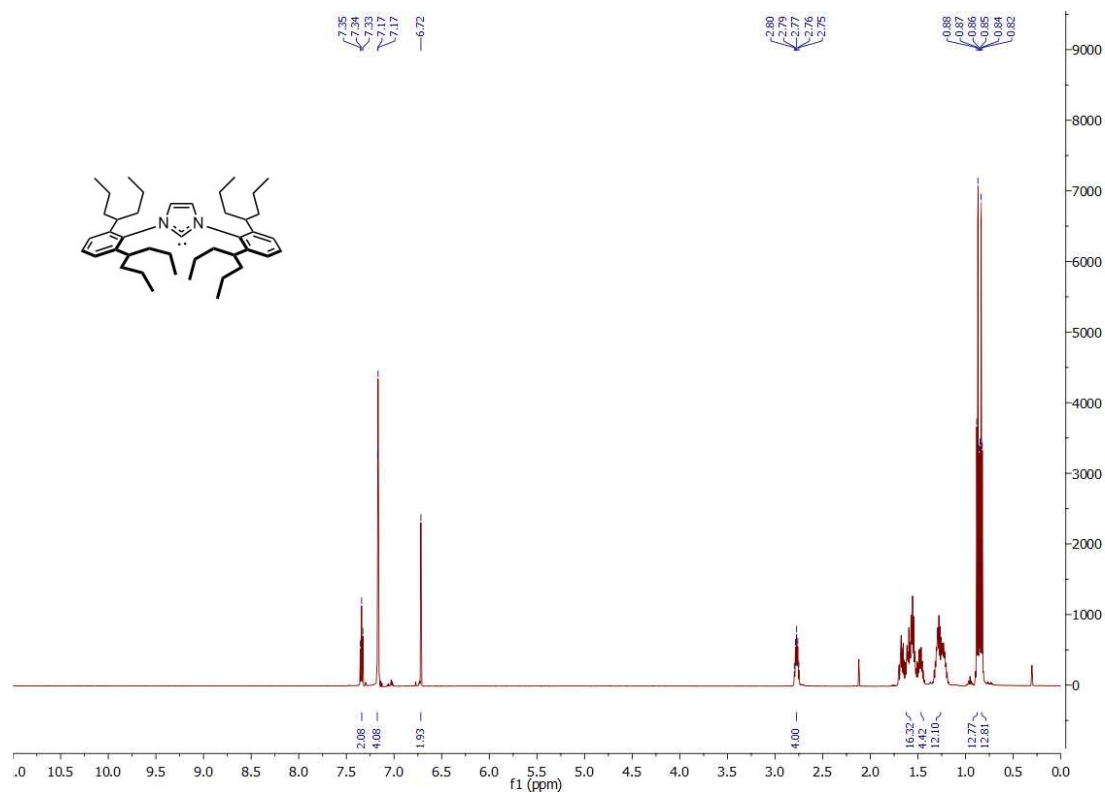


Figure A136. ^1H NMR spectrum of **173** (600 MHz, C_6D_6)

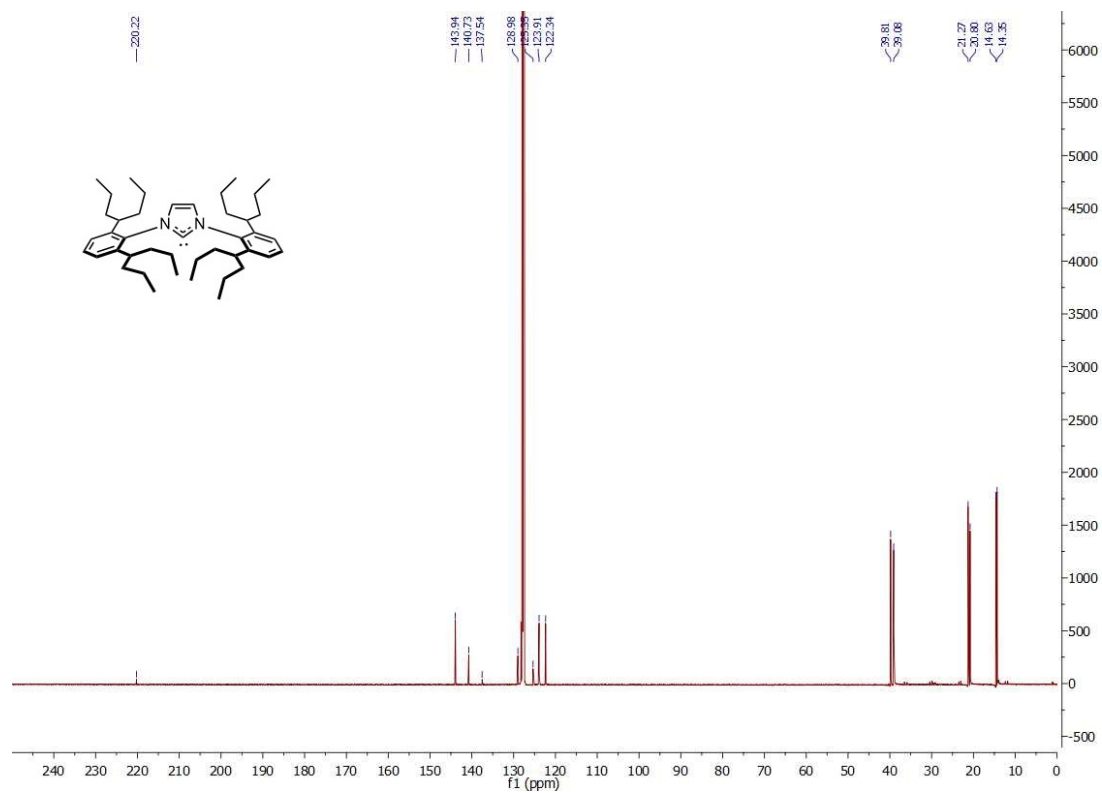


Figure A137. ^{13}C NMR spectrum of **173** (150 MHz, C_6D_6)

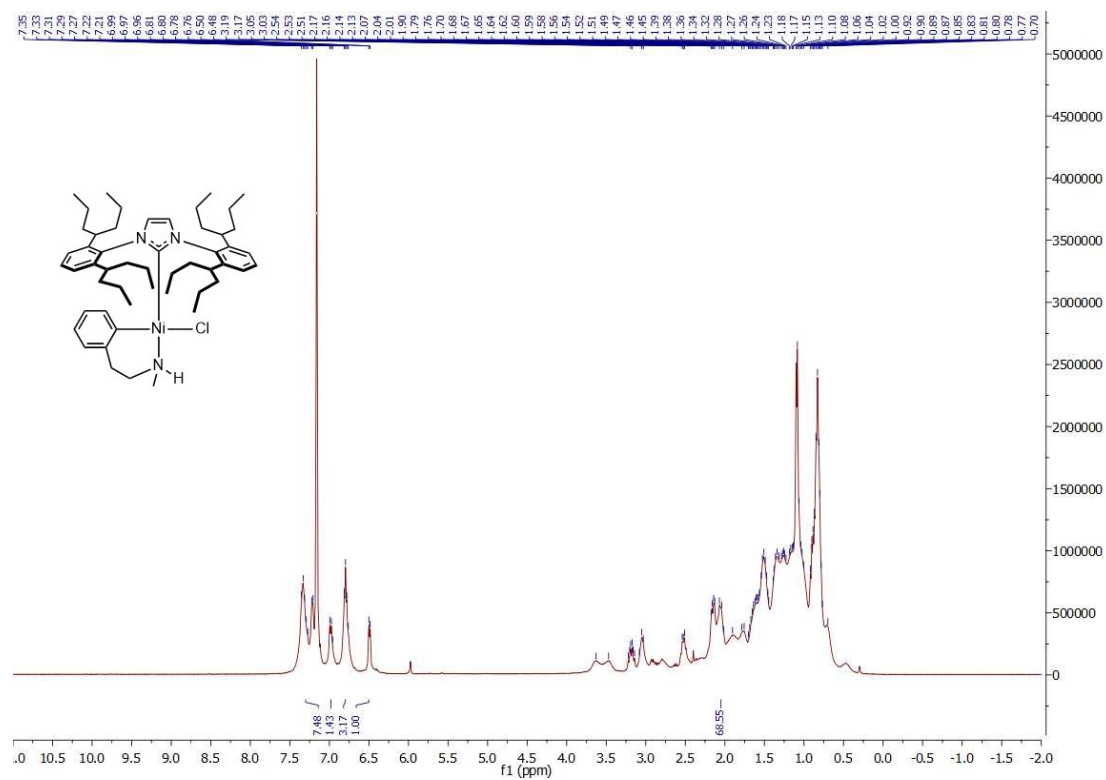


Figure A138. ¹H NMR spectrum of **174** (400 MHz, C₆D₆)

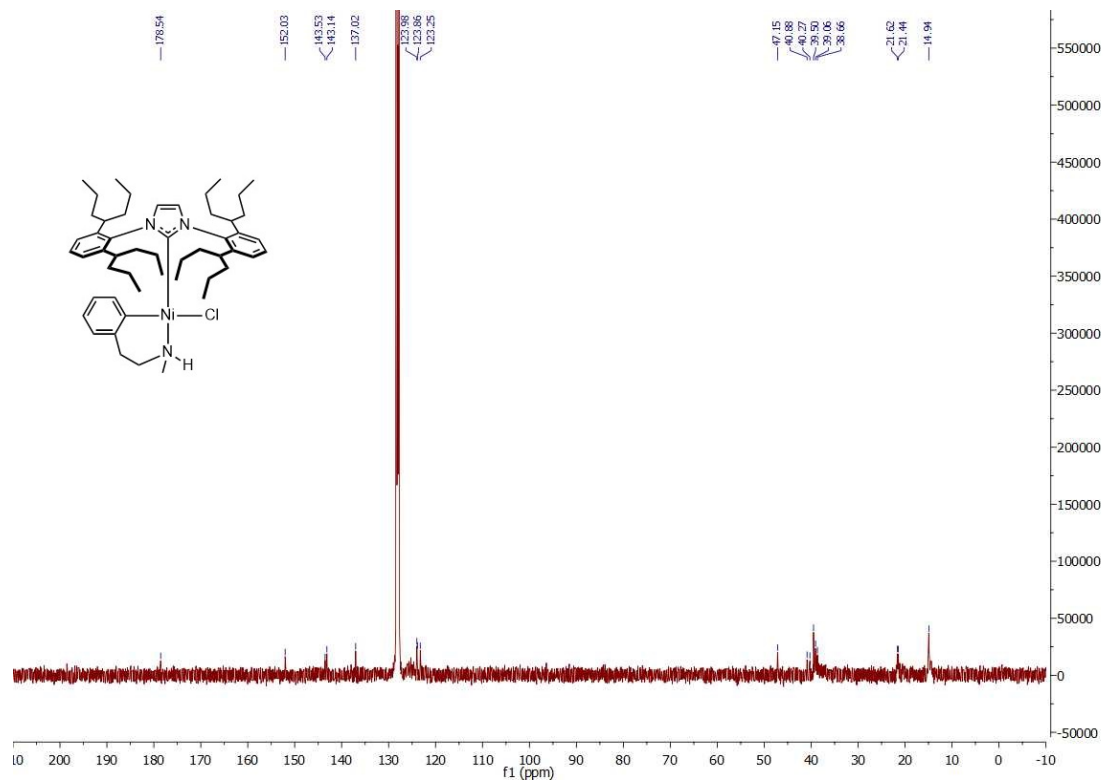


Figure A139. ¹³C NMR spectrum of **174** (100 MHz, C₆D₆)

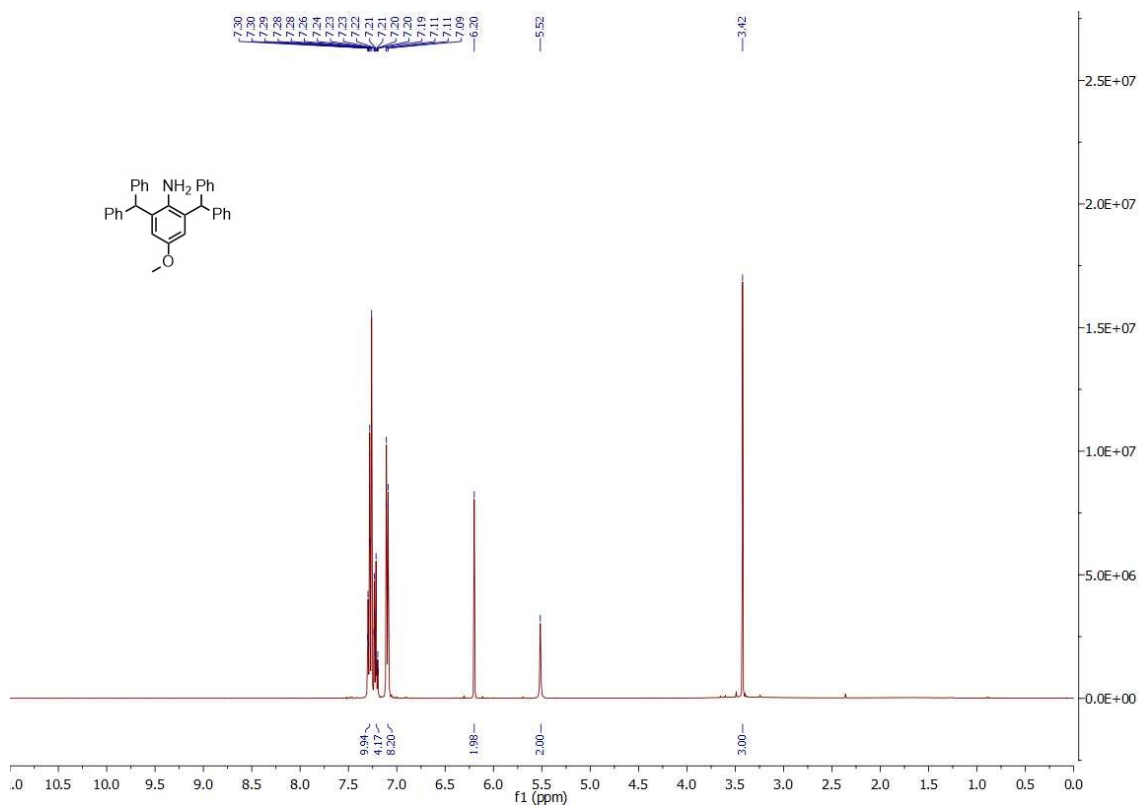


Figure A140. ¹H NMR spectrum of **177** (500 MHz, CDCl₃)

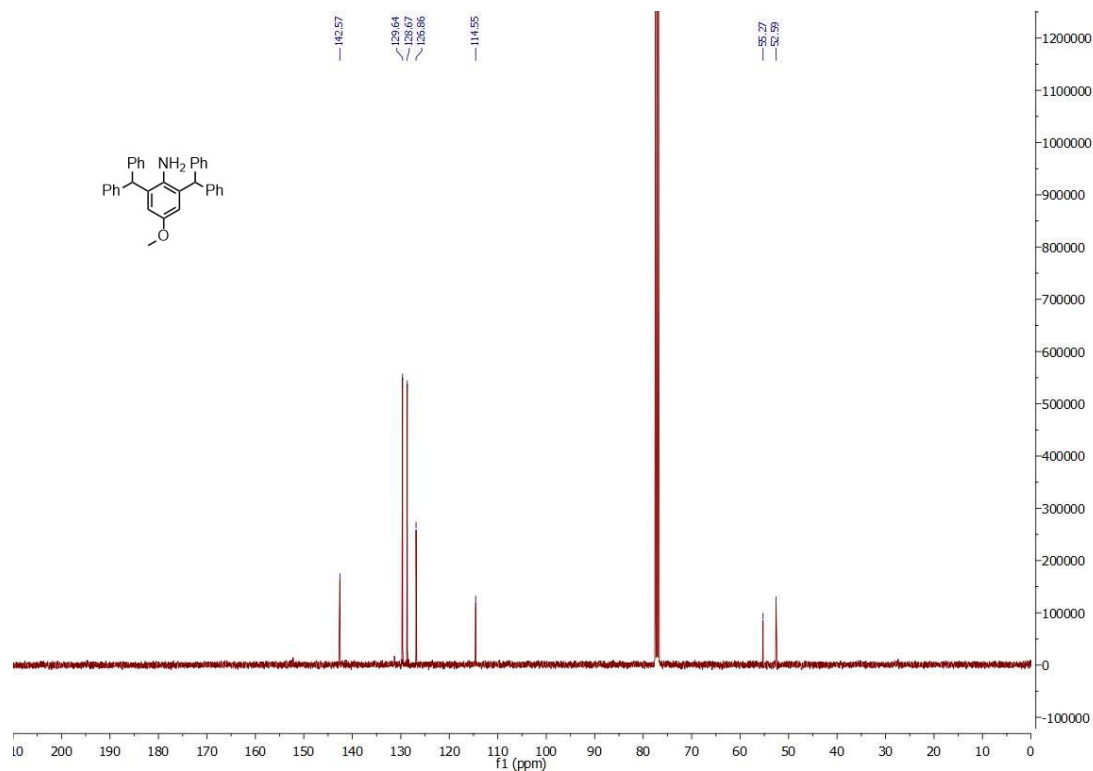


Figure A141. ¹³C NMR spectrum of **177** (125 MHz, CDCl₃)

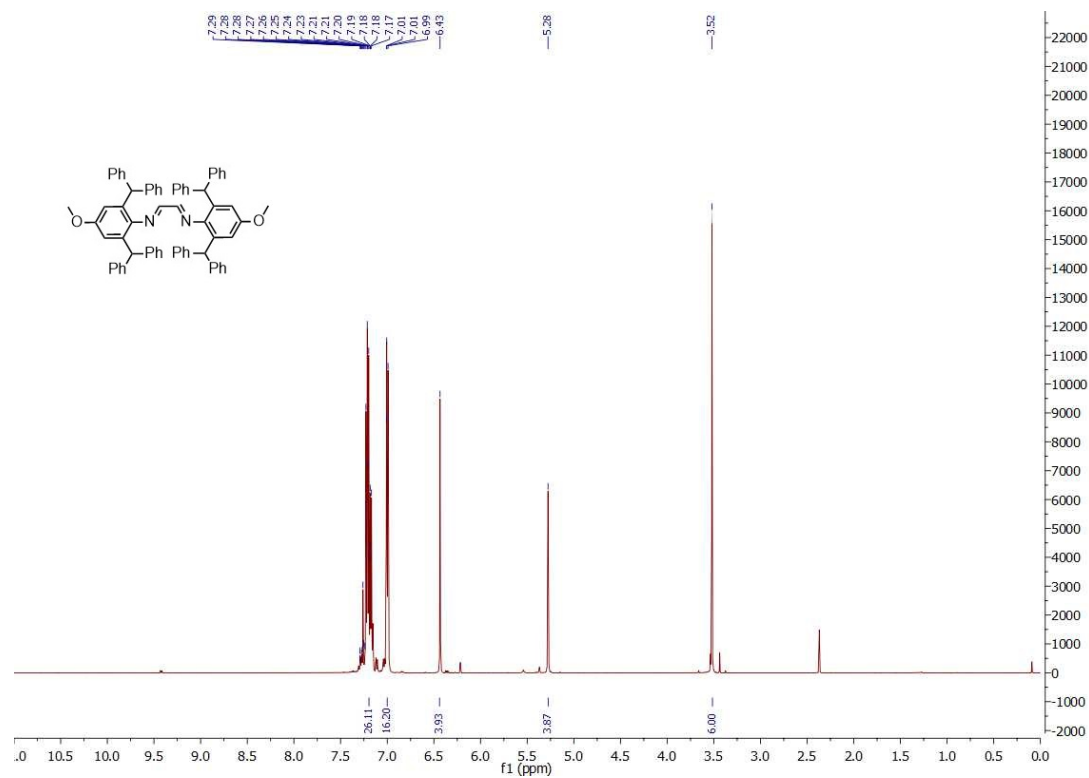


Figure A142. ¹H NMR spectrum of **178** (500 MHz, CDCl₃)

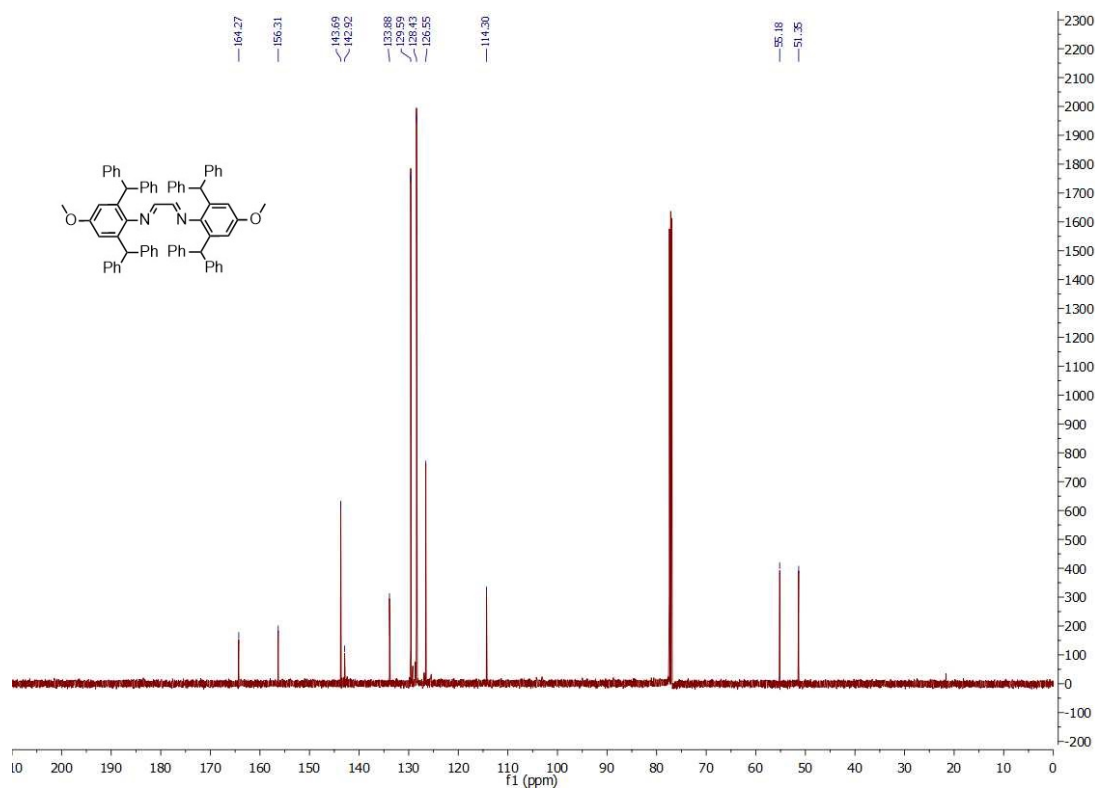


Figure A143. ¹³C NMR spectrum of **178** (125 MHz, CDCl₃)

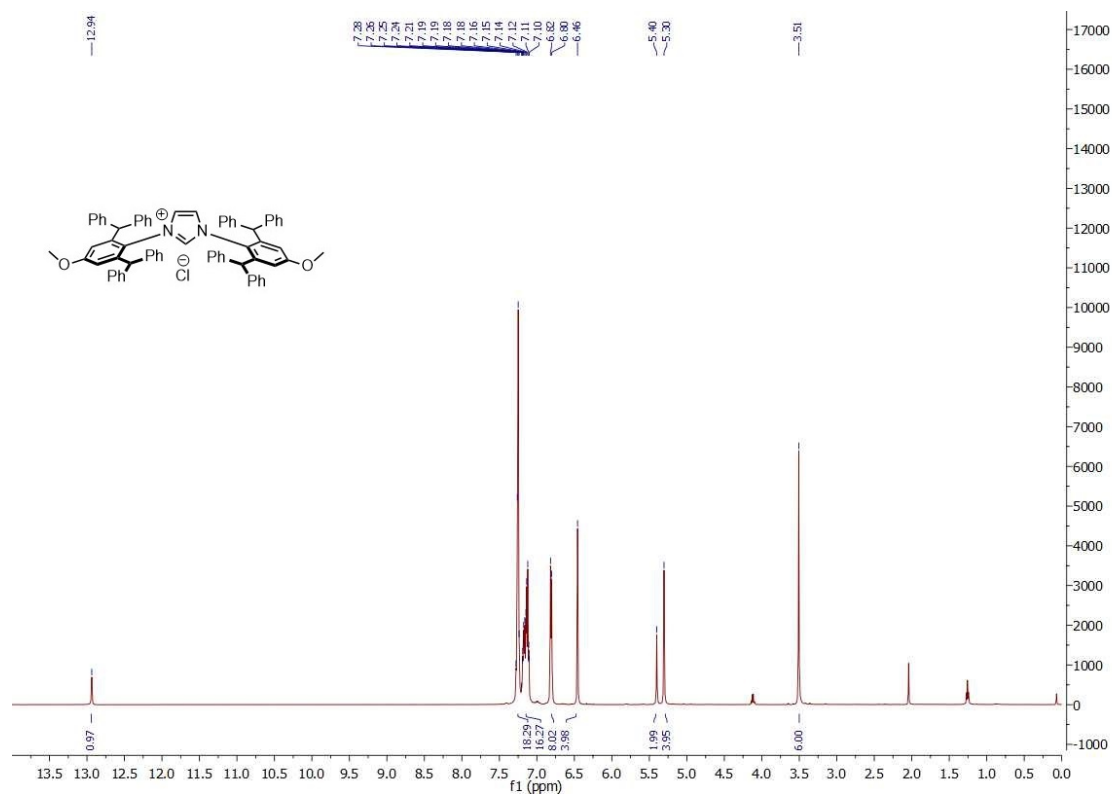


Figure A144. ¹H NMR spectrum of **179** (500 MHz, CDCl₃)

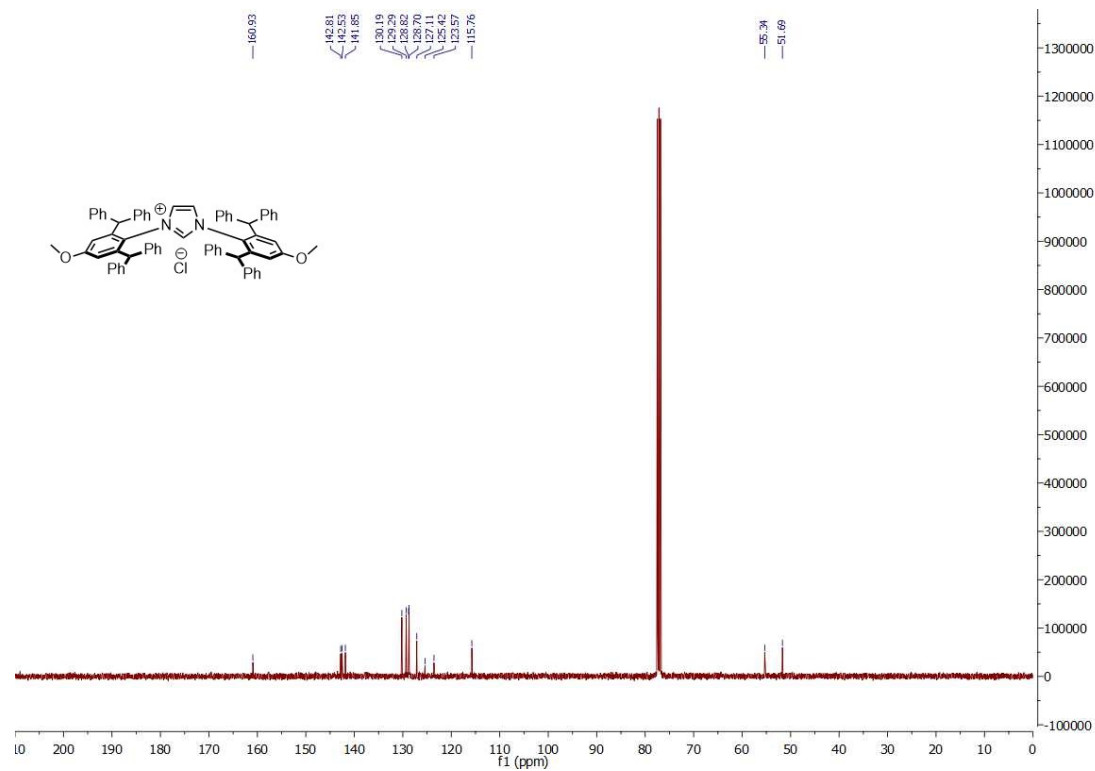


Figure A145. ¹³C NMR spectrum of **179** (125 MHz, CDCl₃)

Figure A146. ^1H NMR spectrum of **(180)** (600 MHz, C_6D_6)

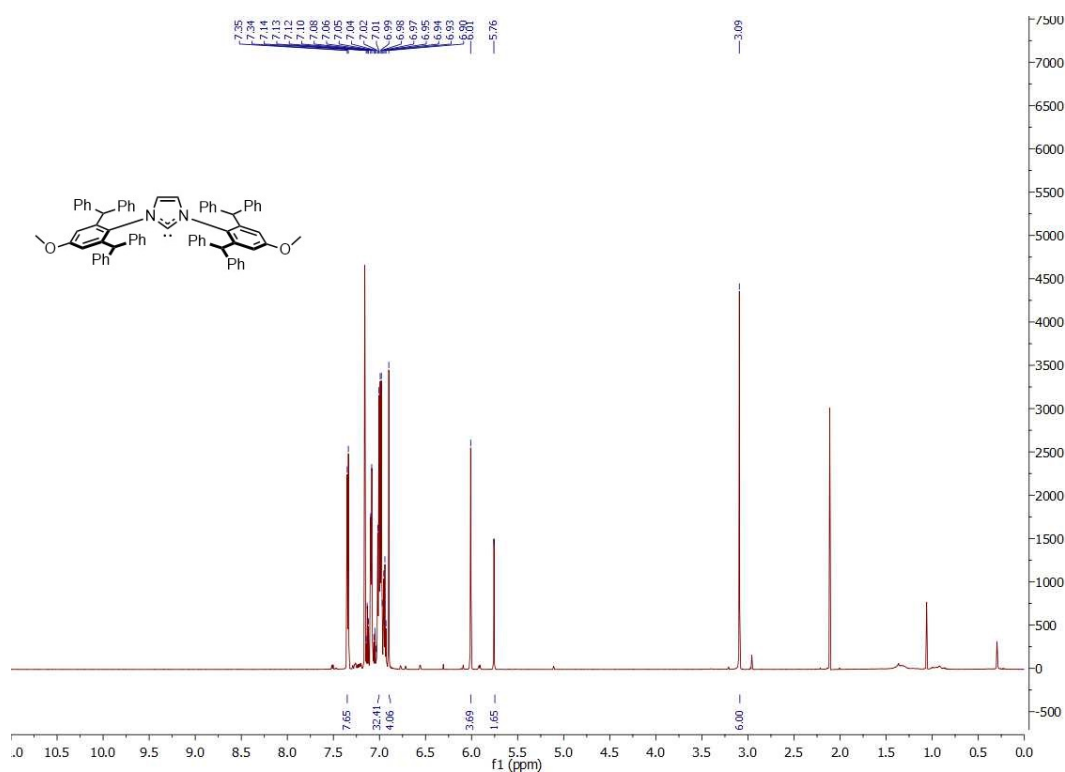


Figure A146. ^1H NMR spectrum of **180** (600 MHz, C_6D_6)

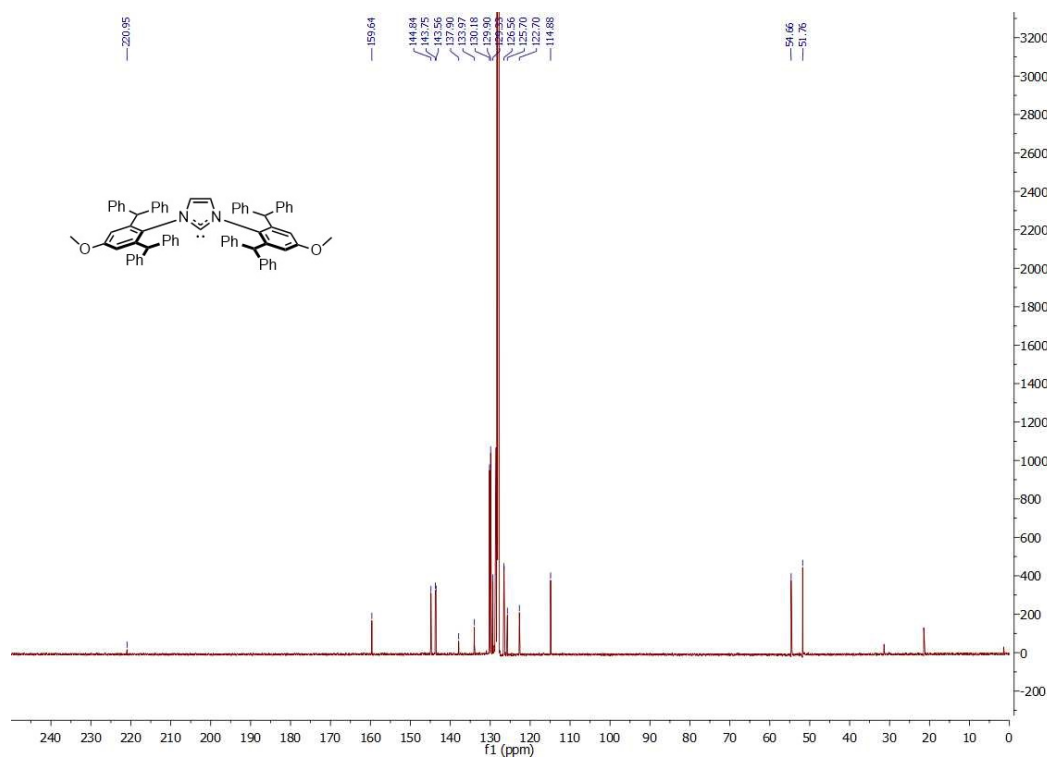


Figure A147. ^{13}C NMR spectrum of **180** (150 MHz, C_6D_6)

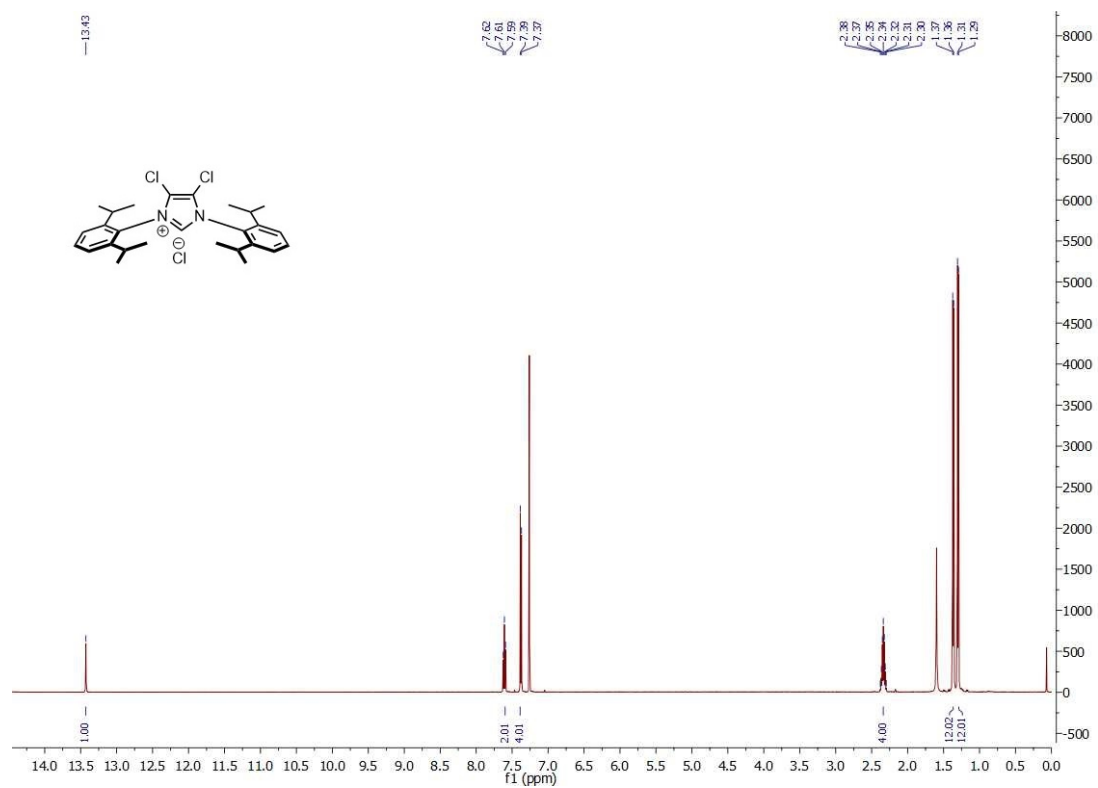


Figure A150. ¹H NMR spectrum of **186** (500 MHz, CDCl₃)

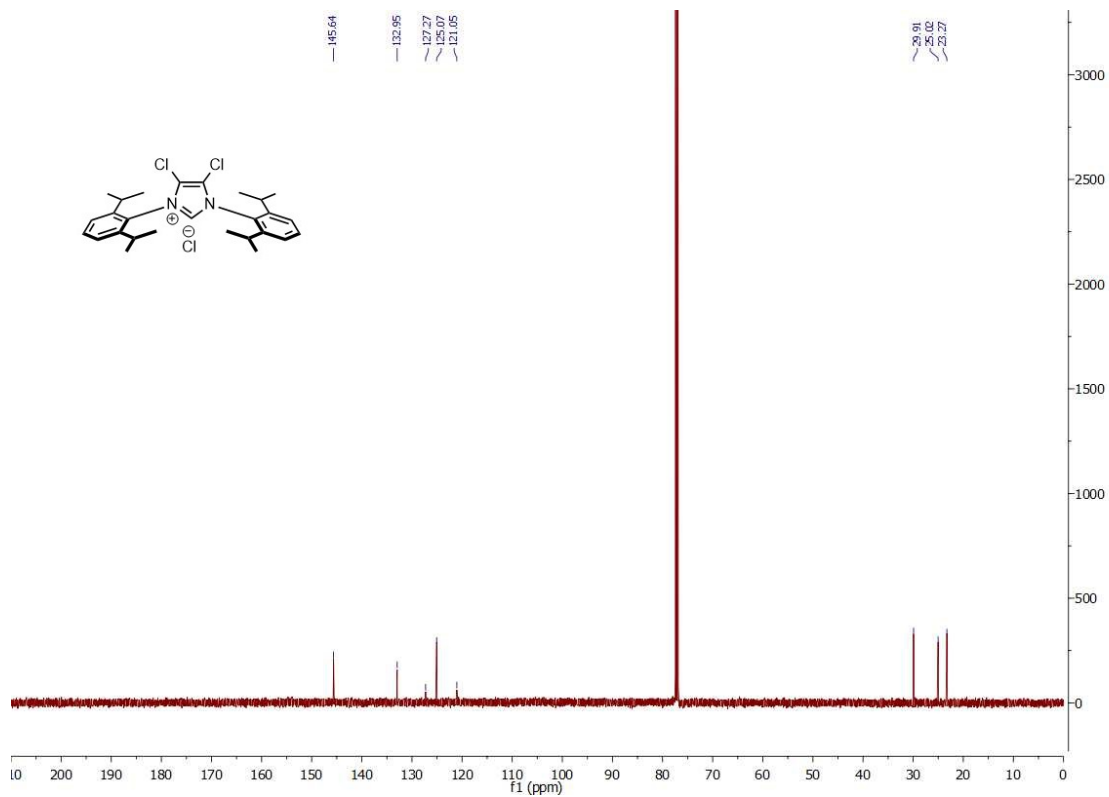


Figure A151. ¹³C NMR spectrum of **186** (125 MHz, CDCl₃)

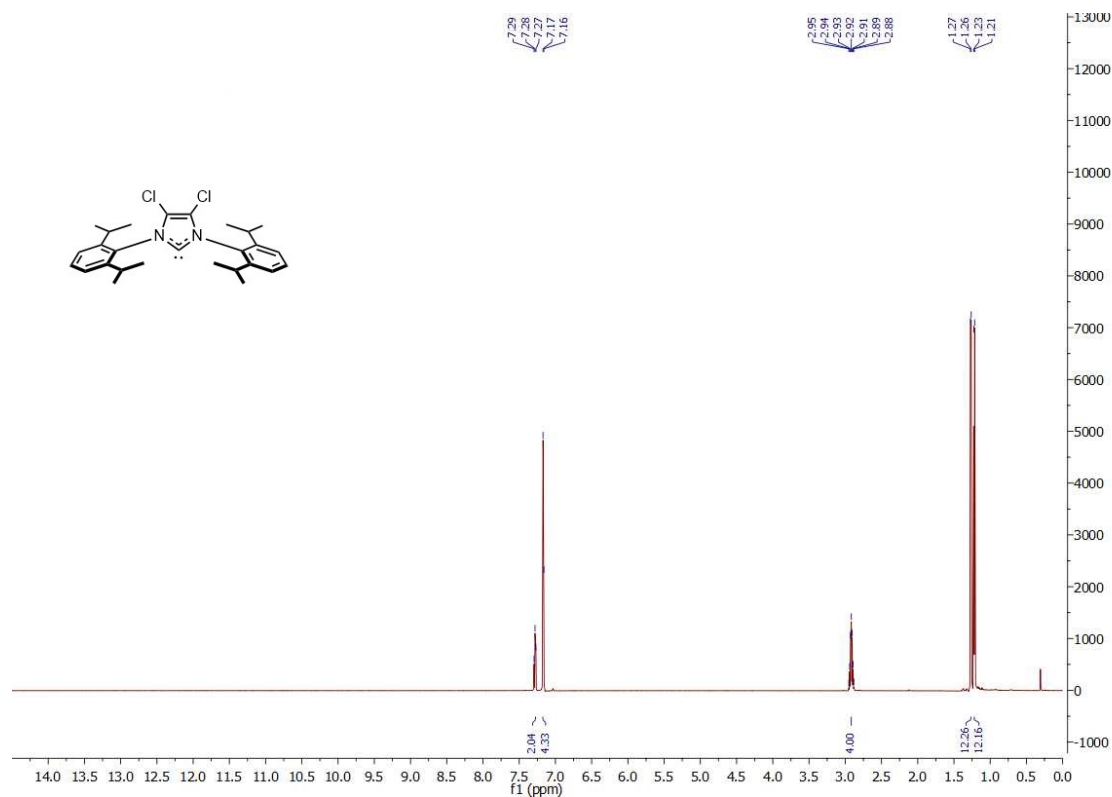


Figure A152. ¹H NMR spectrum of **187** (600 MHz, C₆D₆)

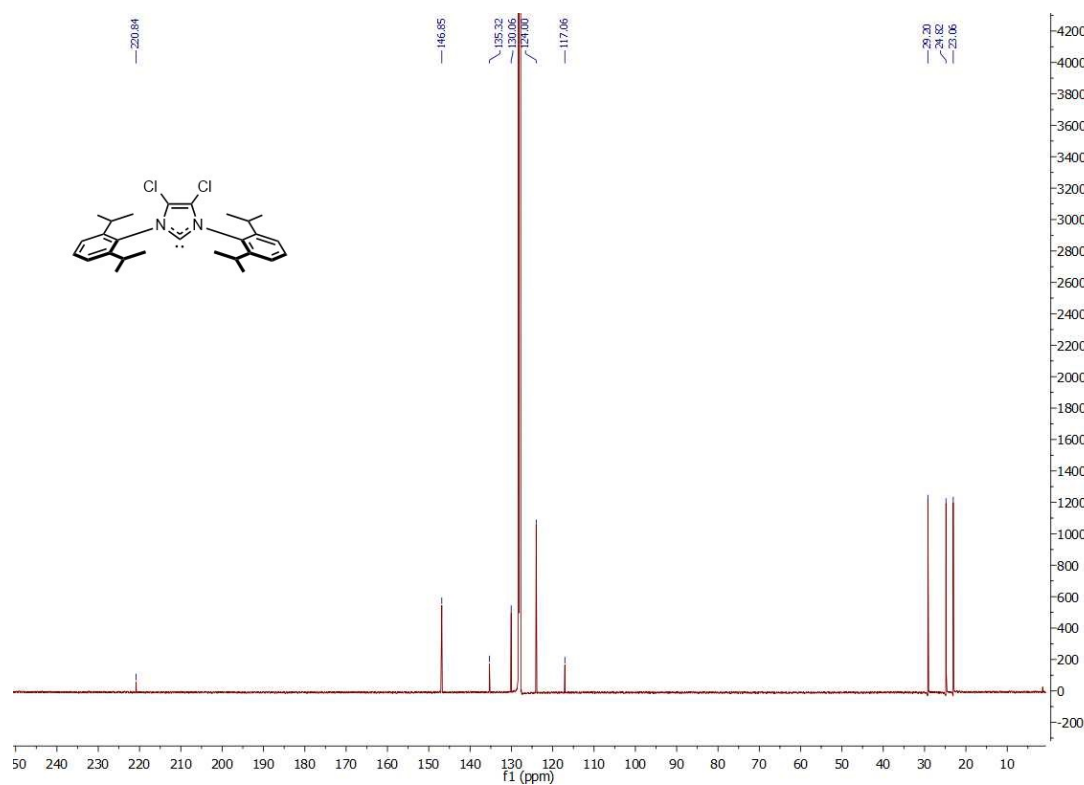


Figure A153. ¹³C NMR spectrum of **187** (150 MHz, C₆D₆)

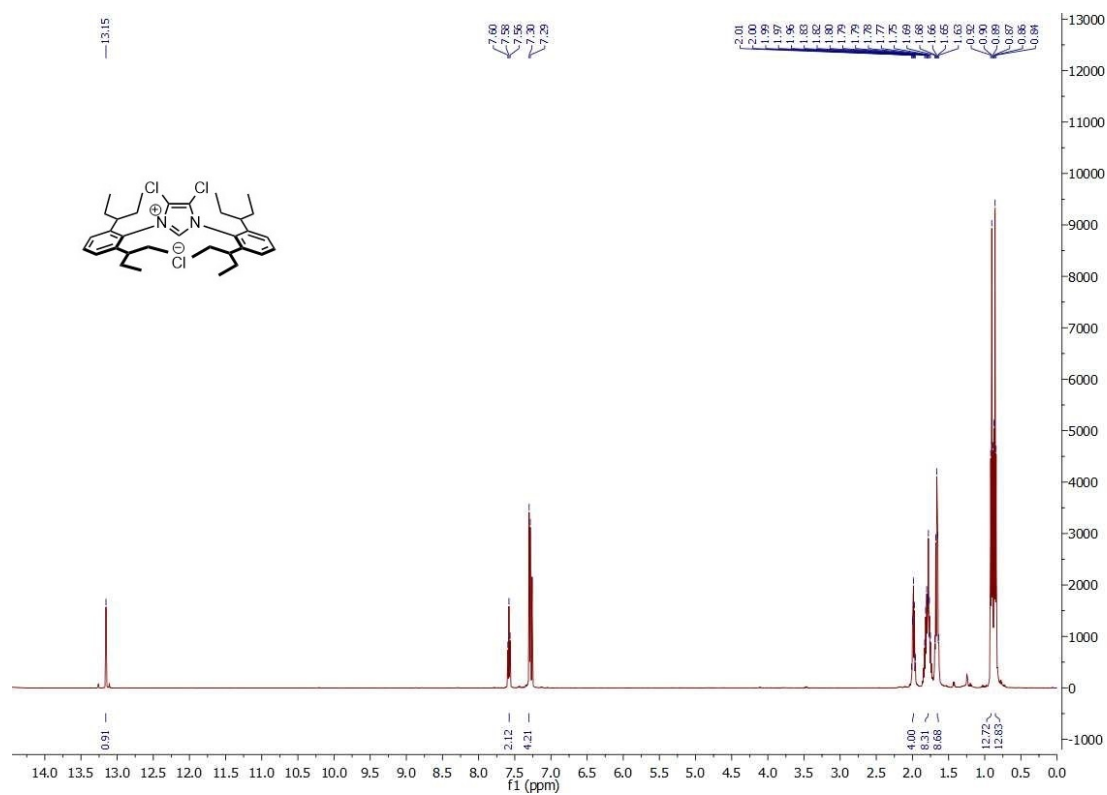


Figure A156. ^1H NMR spectrum of **201** (500 MHz, CDCl_3)

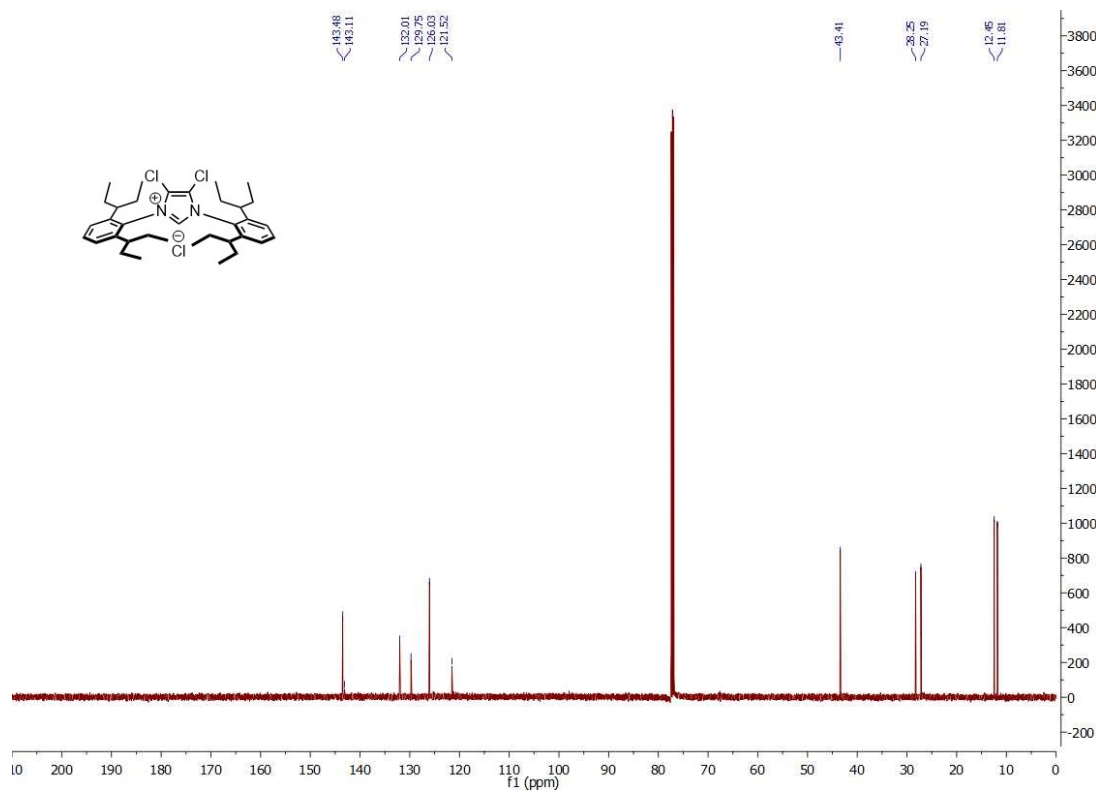


Figure A157. ^{13}C NMR spectrum of **201** (125 MHz, CDCl_3)

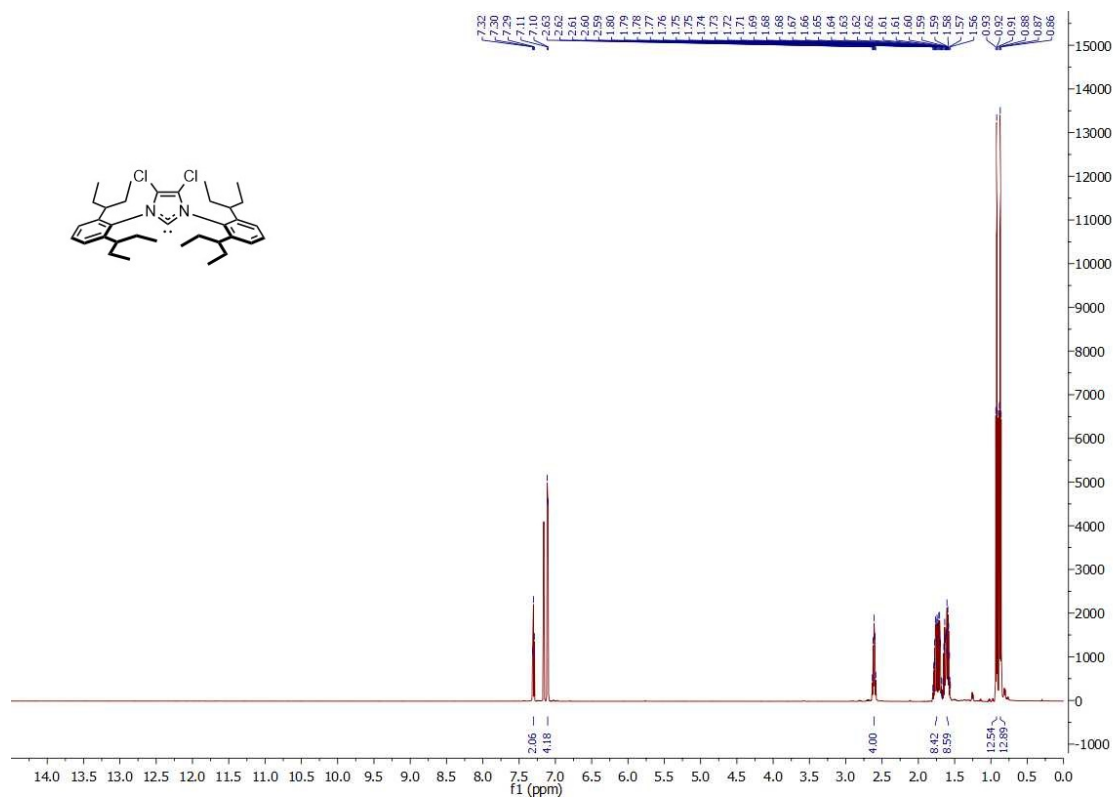


Figure A158. ¹H NMR spectrum of **202** (600 MHz, C₆D₆)

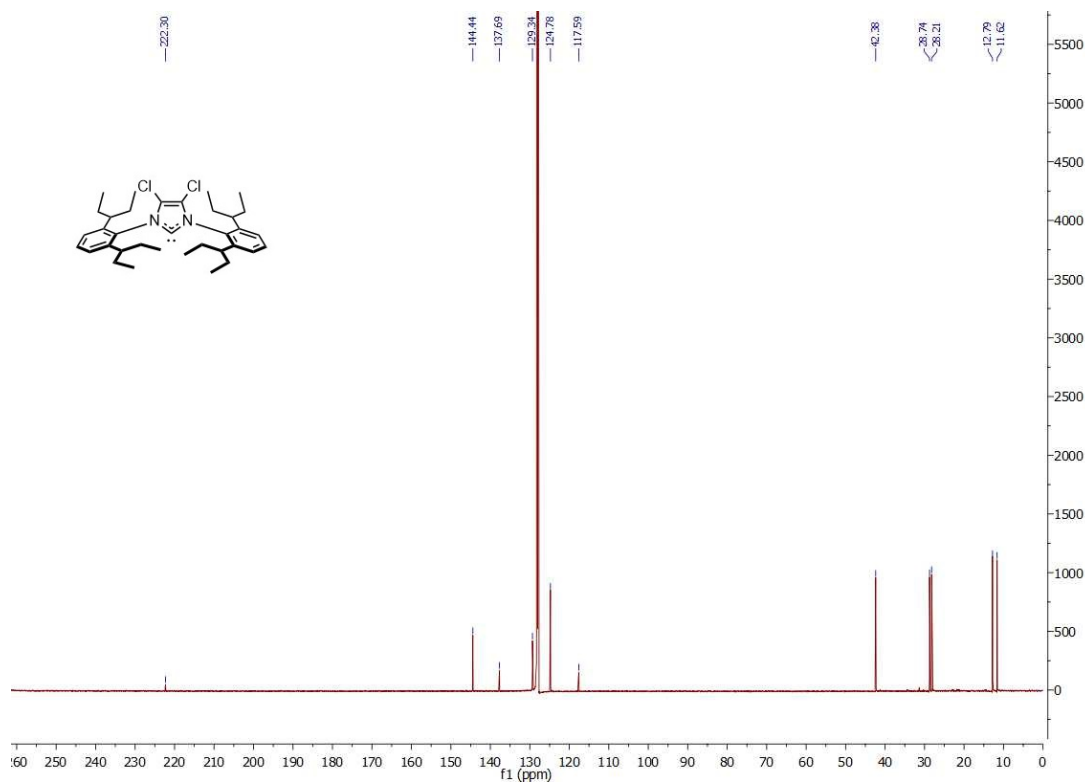


Figure A159. ¹³C NMR spectrum of **202** (150 MHz, C₆D₆)

Figure A160. ^1H NMR spectrum of **(203)** (400 MHz, C_6D_6)

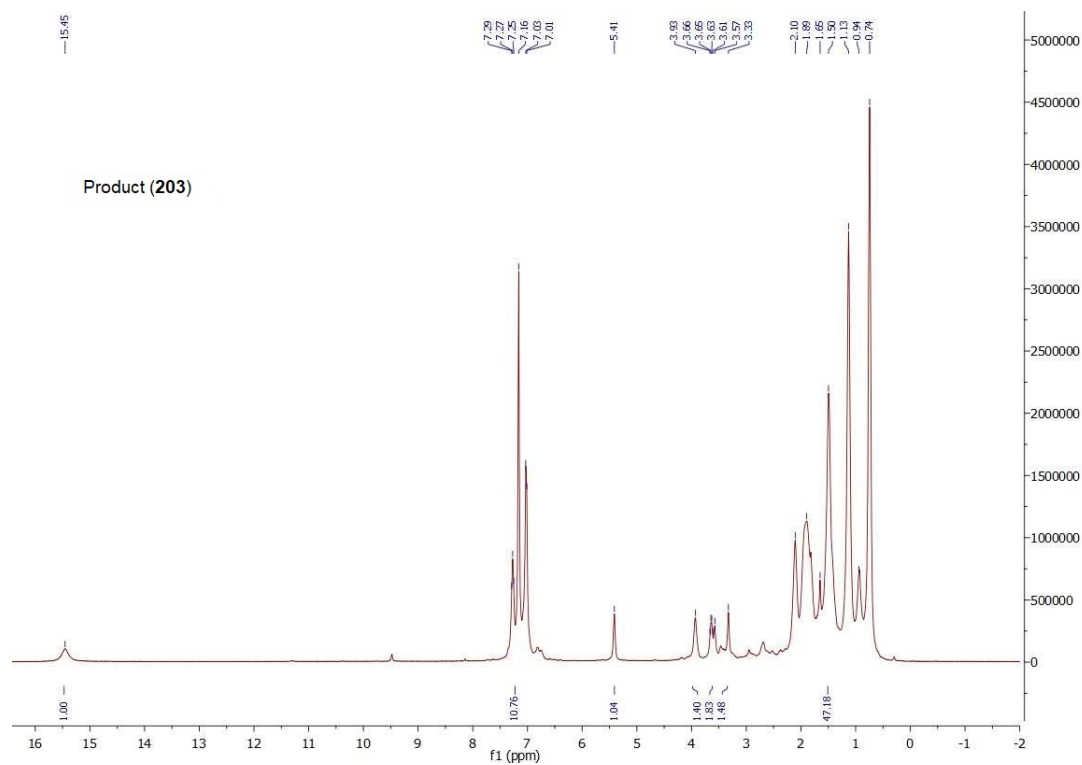


Figure A160. ^1H NMR spectrum of **203** (400 MHz, C_6D_6)

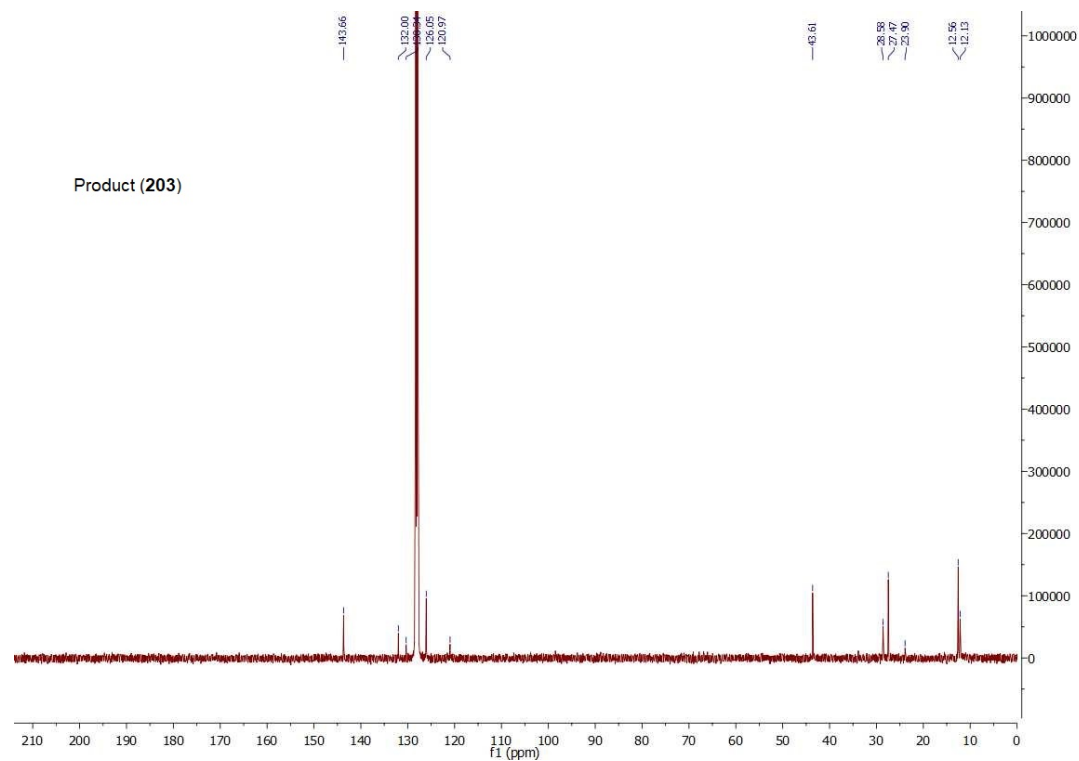


Figure A161. ^{13}C NMR spectrum of **203** (100 MHz, C_6D_6)

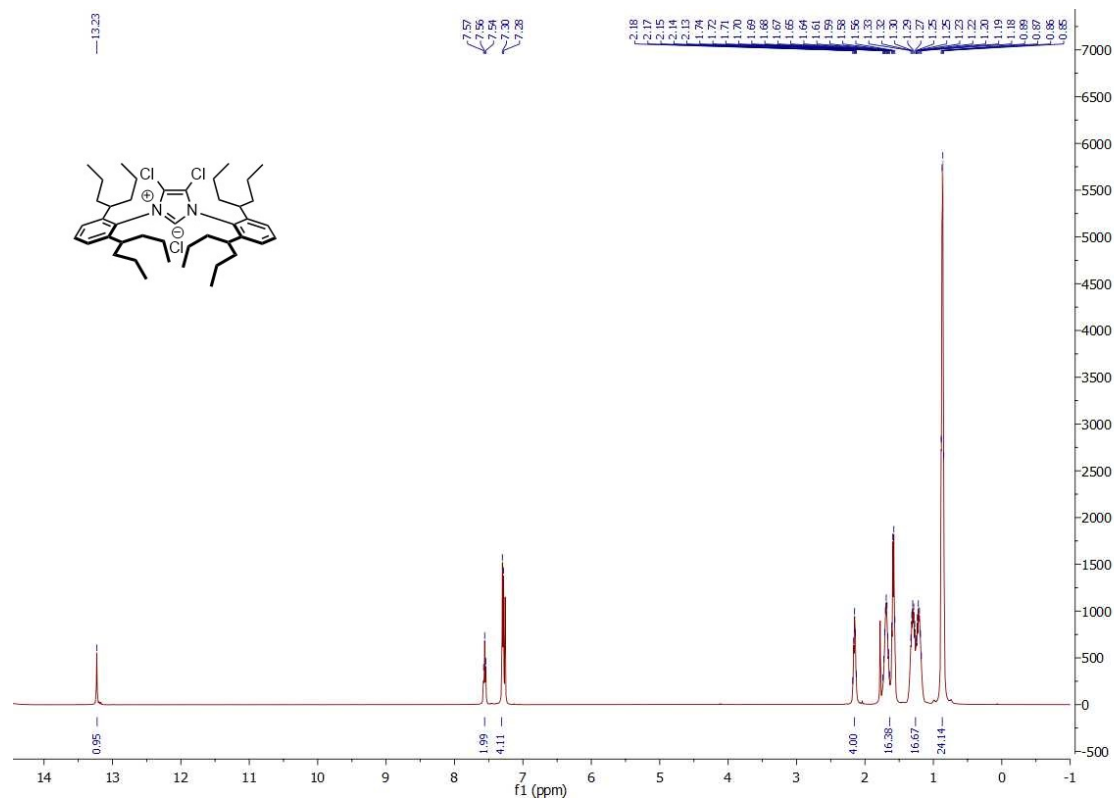


Figure A162. ^1H NMR spectrum of **204** (500 MHz, CDCl_3)

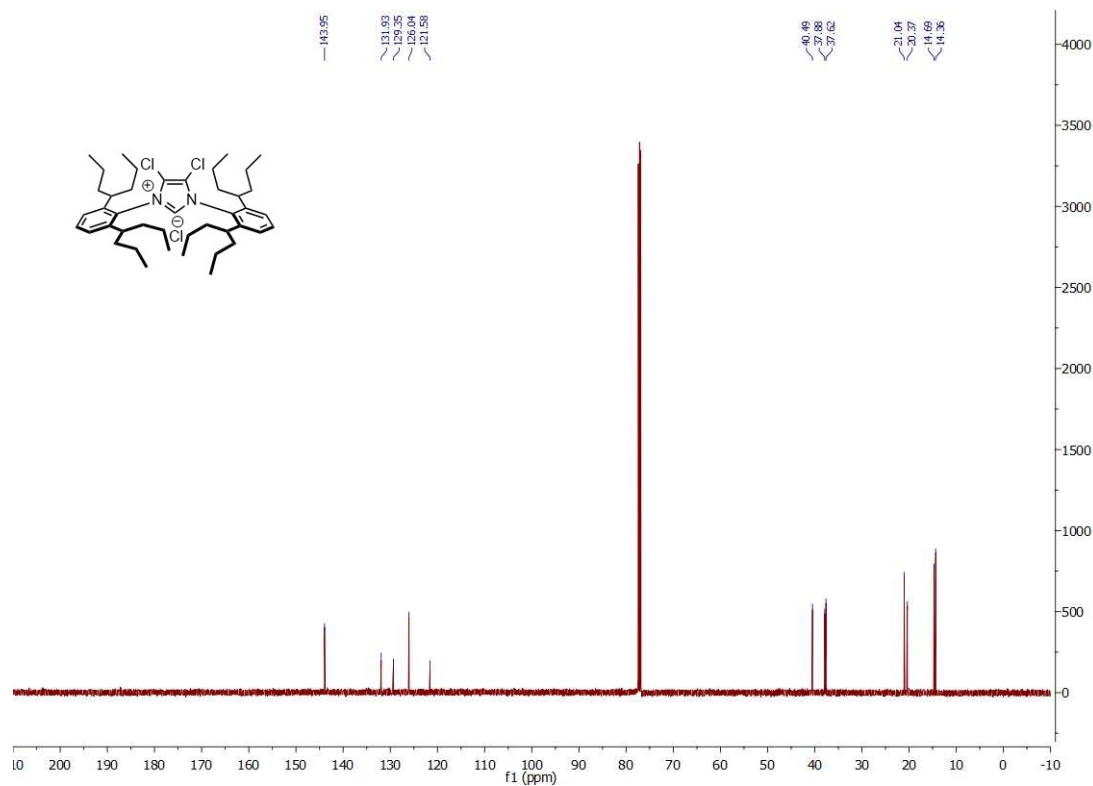
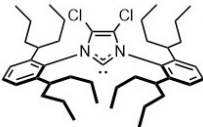


Figure A163. ^{13}C NMR spectrum of **204** (125 MHz, CDCl_3)



Chemical structure of the macrocyclic ligand is shown in the top left. The spectrum displays peaks from -10 to 250 ppm. Key peaks are labeled: 222.11, 145.00, 145.00, 137.08, 137.08, 129.32, 124.84, 117.79, 38.29, 38.11, 38.09, 21.49, 20.46, 14.95, and 14.61.

305

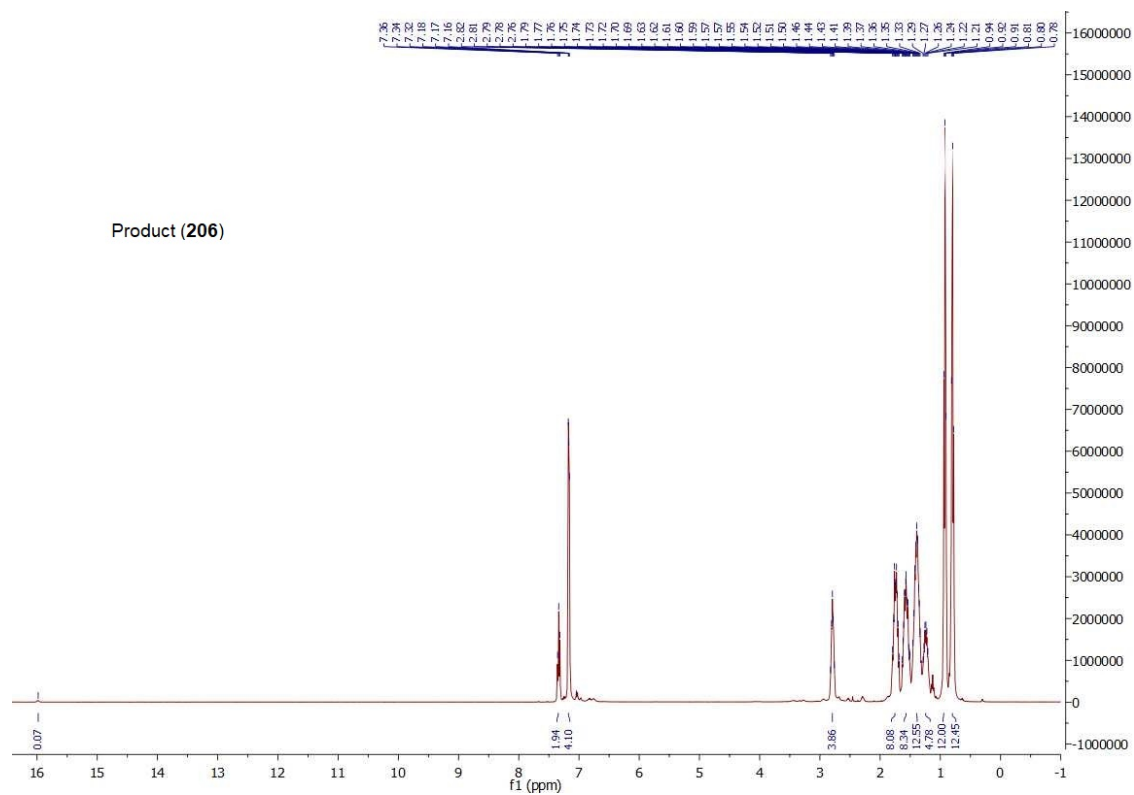


Figure A166. ^1H NMR spectrum of **206** (400 MHz, C_6D_6)

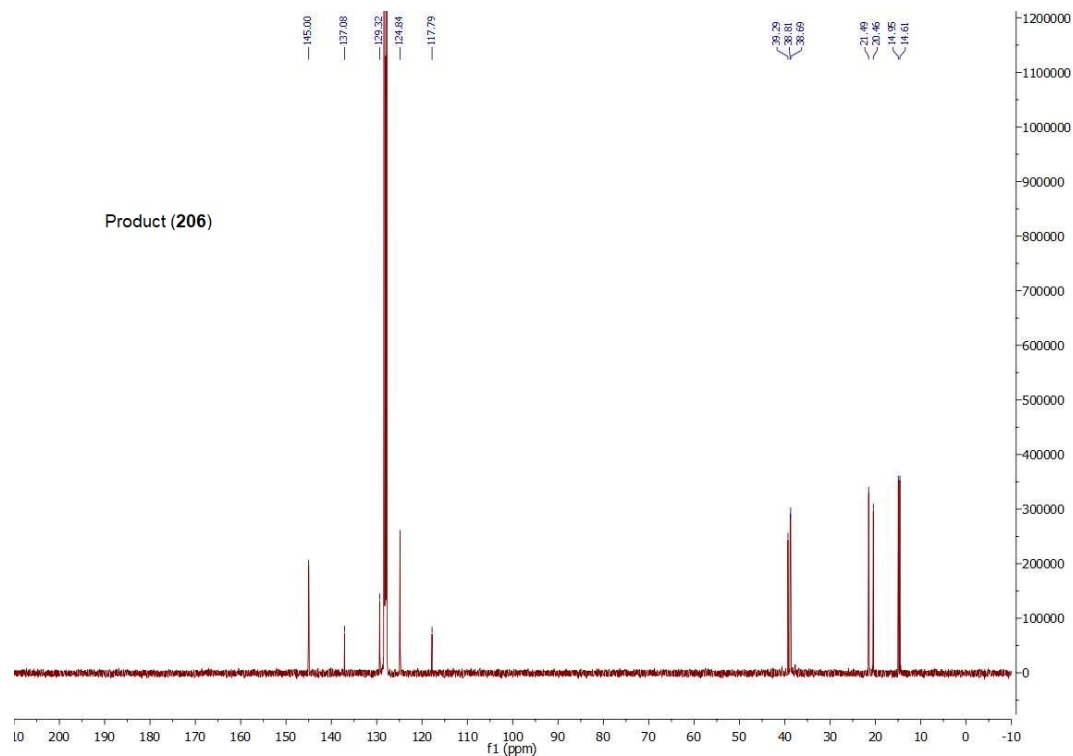


Figure A167. ^{13}C NMR spectrum of **206** (100 MHz, C_6D_6)

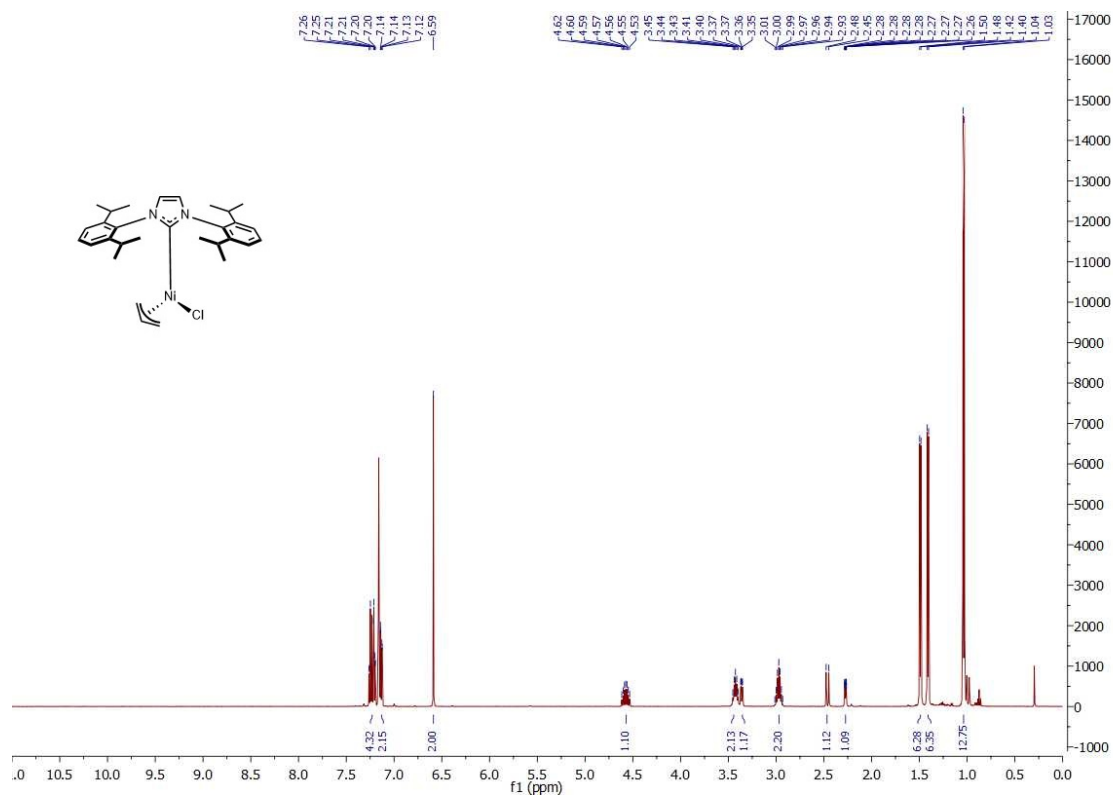


Figure A168. ^1H NMR spectrum of **207** (500 MHz, C_6D_6)

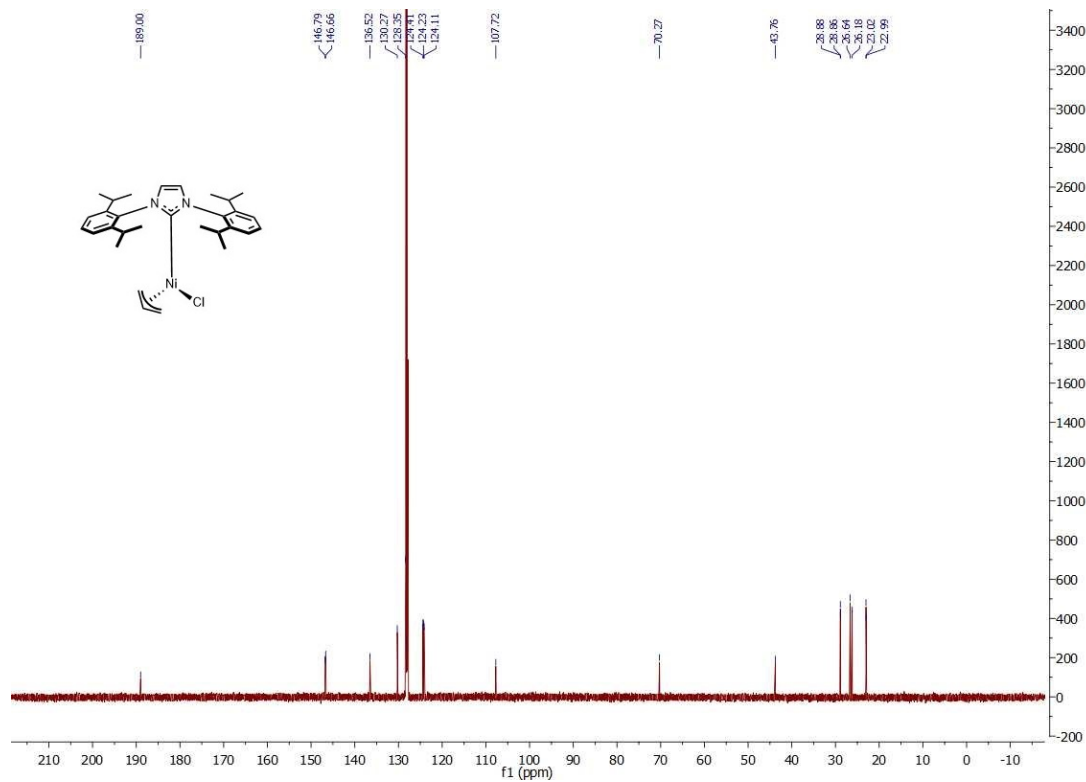


Figure A169. ^{13}C NMR spectrum of **207** (125 MHz, C_6D_6)

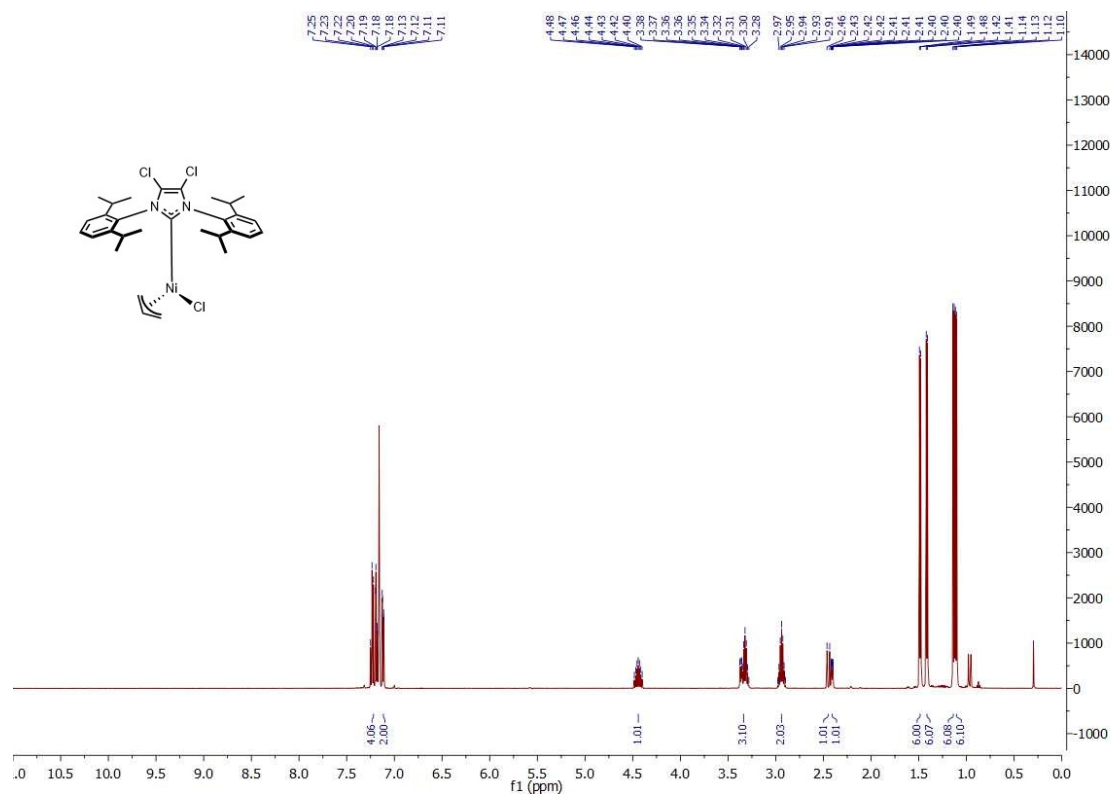


Figure A170. ¹H NMR spectrum of **208** (500 MHz, C₆D₆)

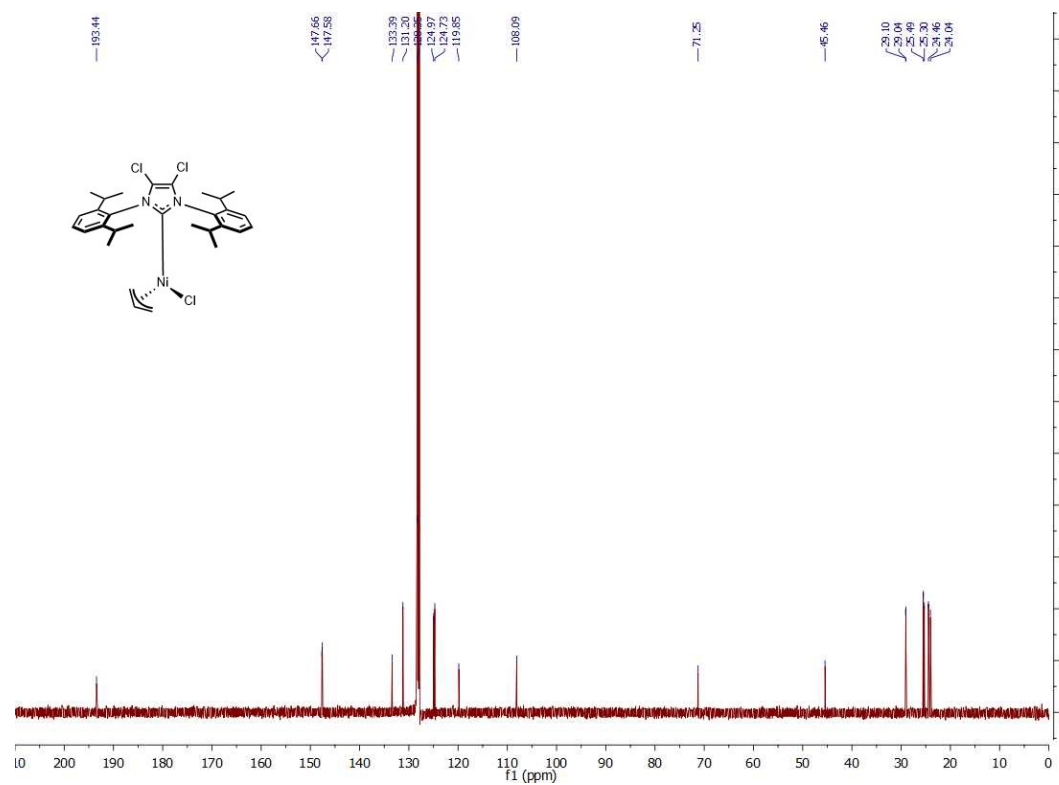


Figure A171. ¹³C NMR spectrum of **208** (125 MHz, C₆D₆)

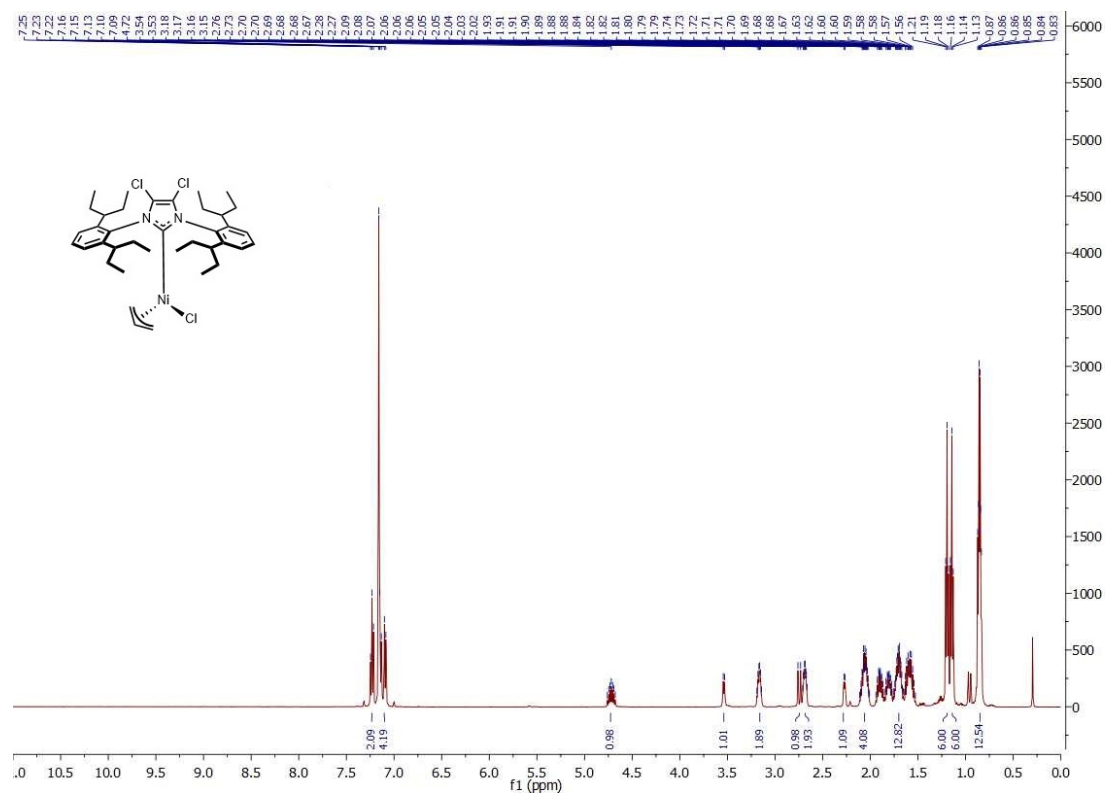


Figure A172. ¹H NMR spectrum of **209** (500 MHz, C₆D₆)

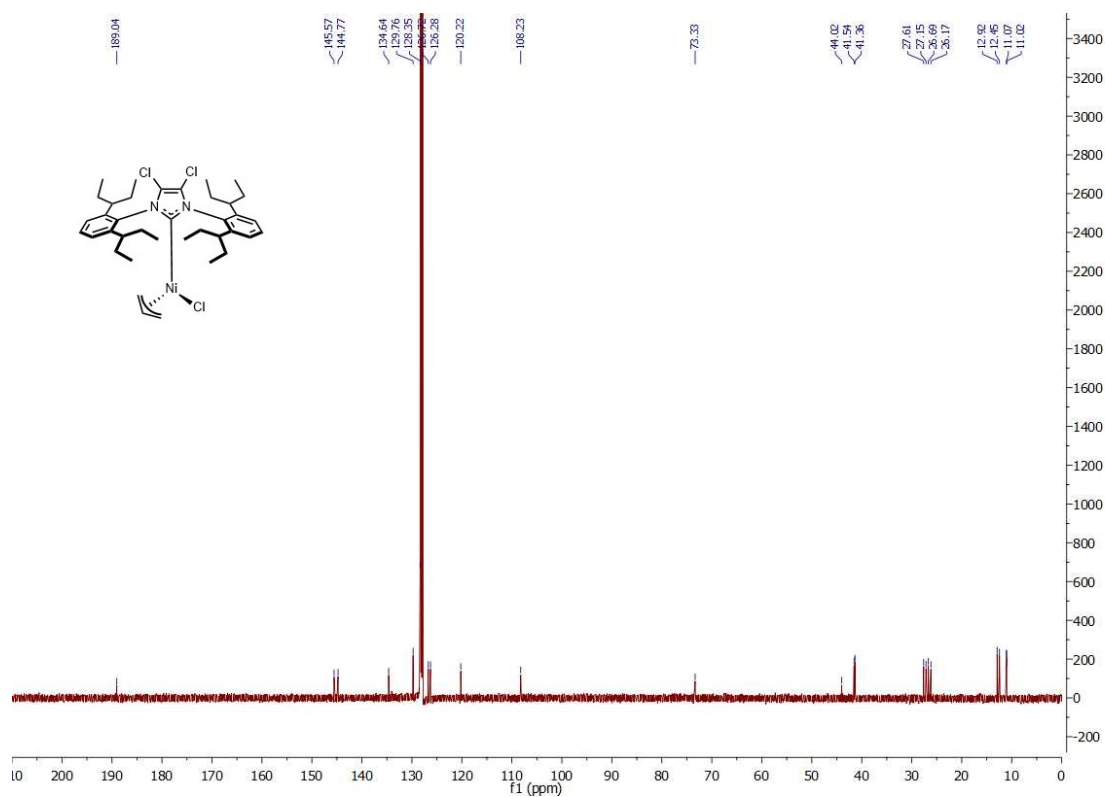


Figure A173. ¹³C NMR spectrum of **209** (125 MHz, C₆D₆)

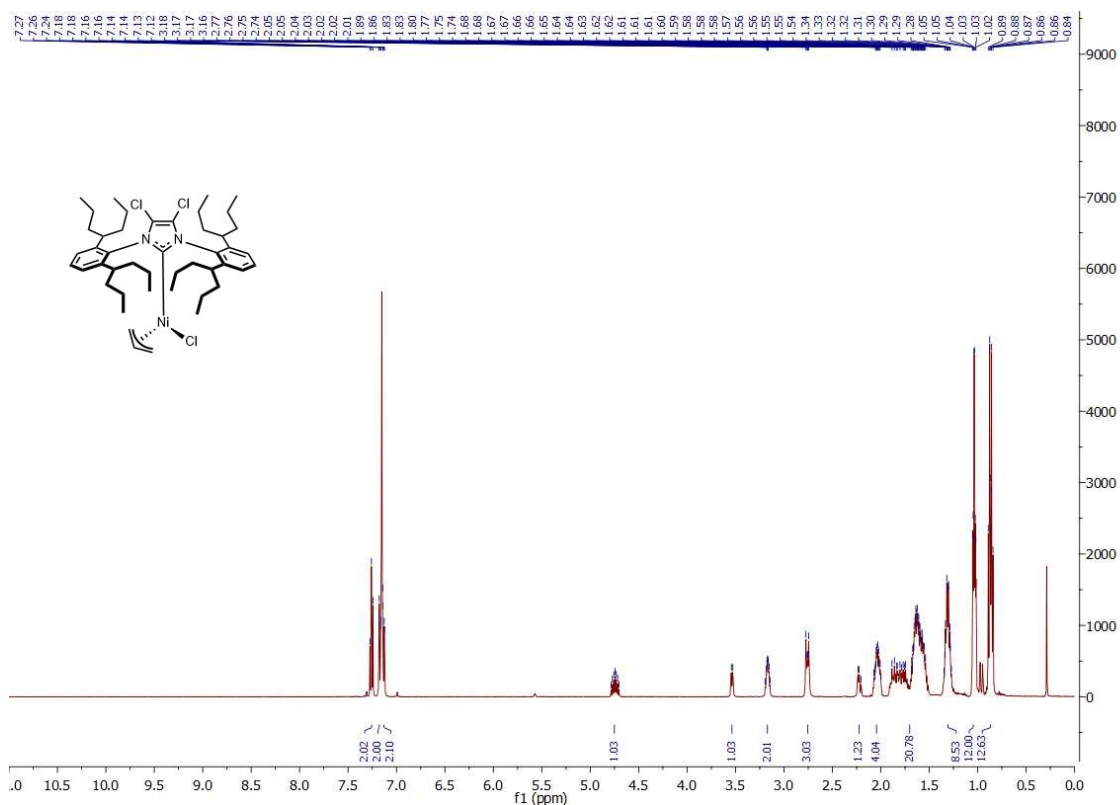


Figure A174. ^1H NMR spectrum of **210** (500 MHz, C_6D_6)

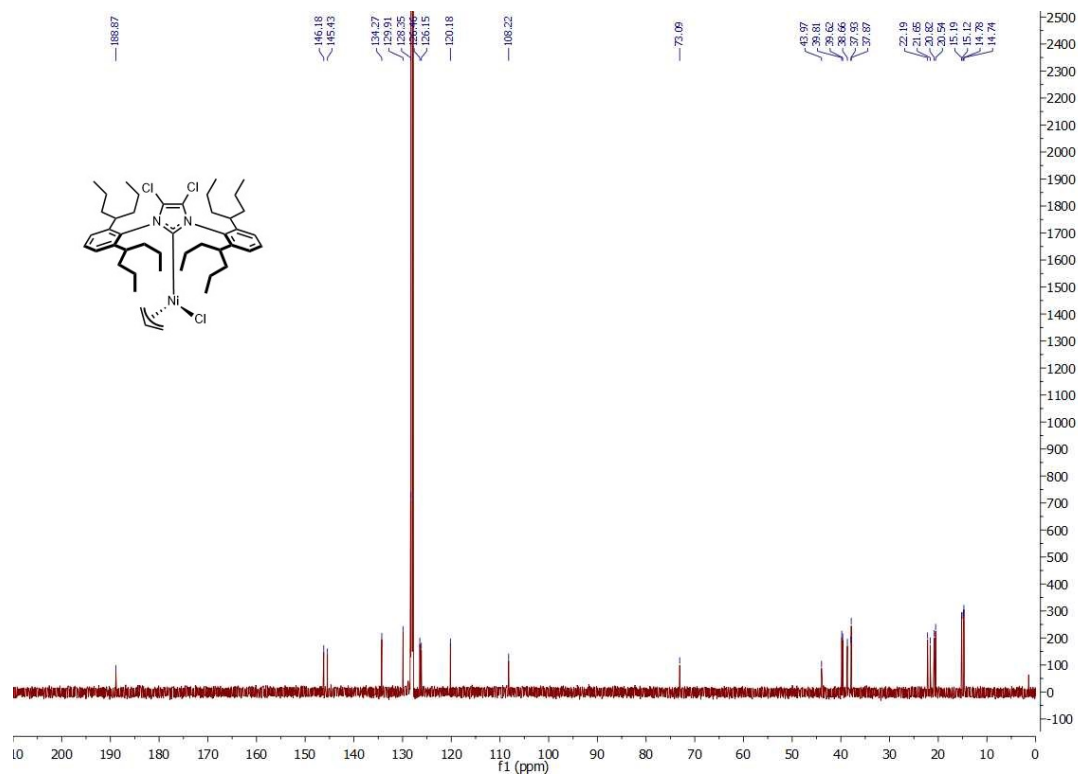


Figure A175. ^{13}C NMR spectrum of **210** (125 MHz, C_6D_6)

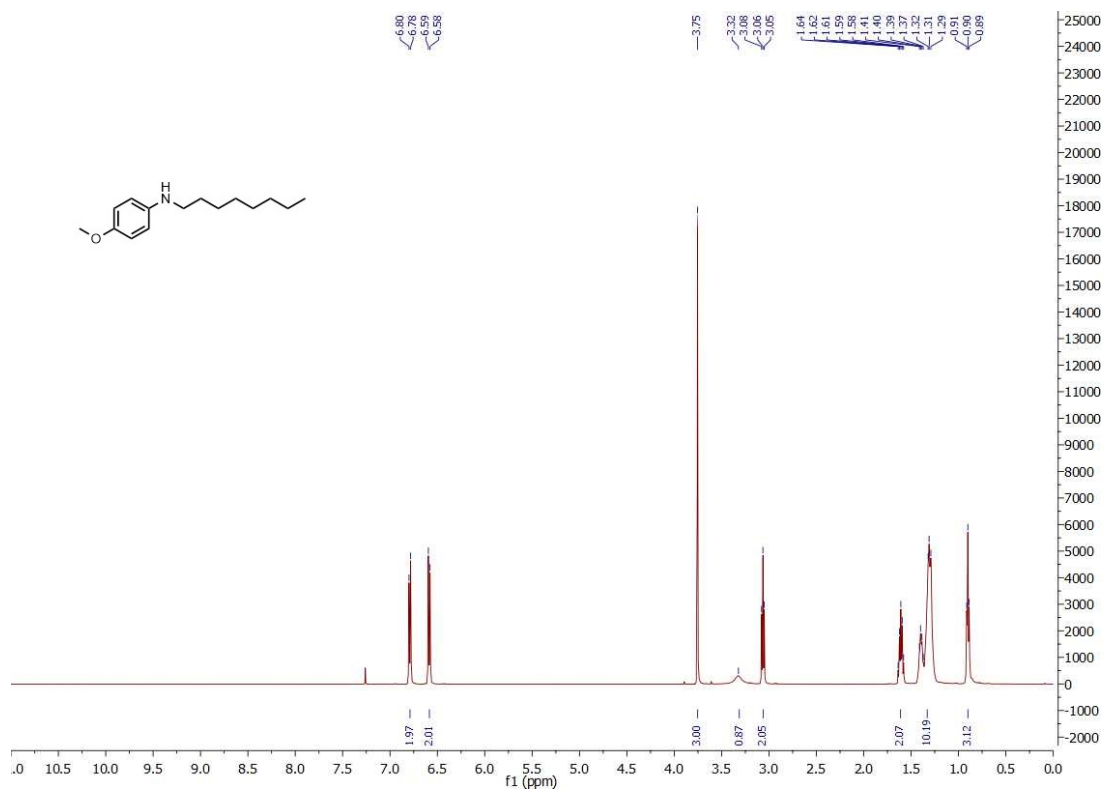


Figure A176. ^1H NMR spectrum of **102** (500 MHz, CDCl_3)

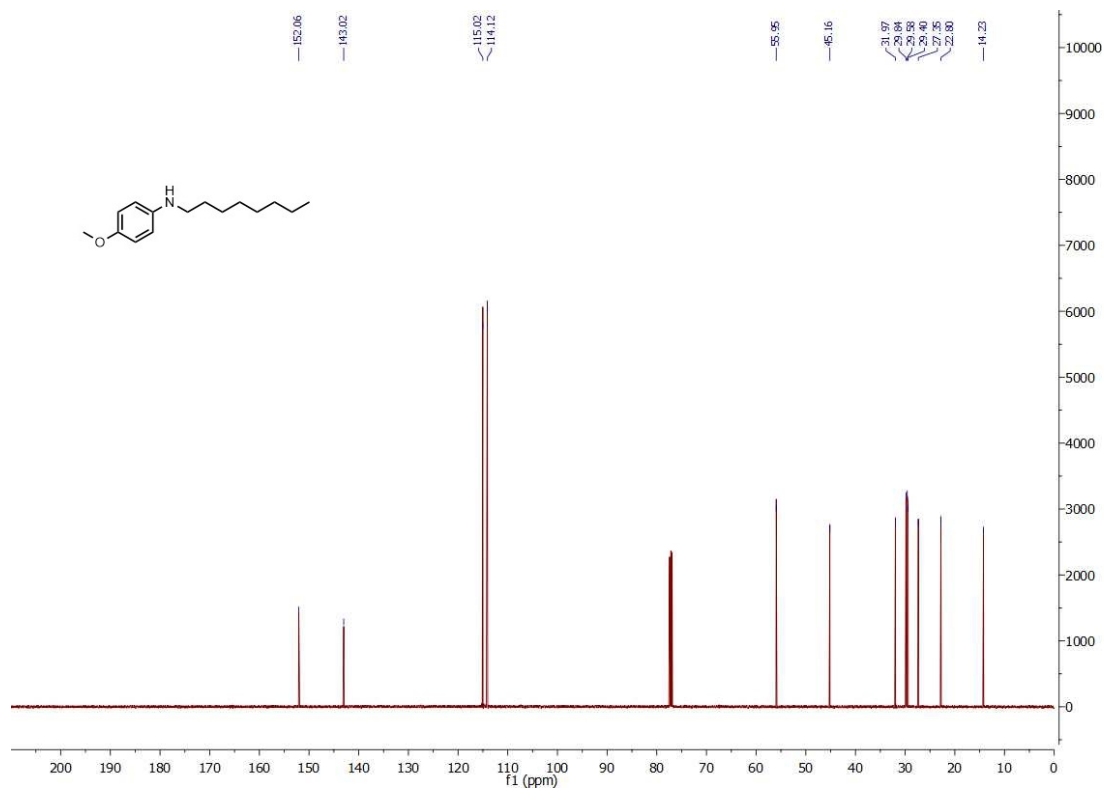


Figure A177. ^{13}C NMR spectrum of **102** (125 MHz, CDCl_3)

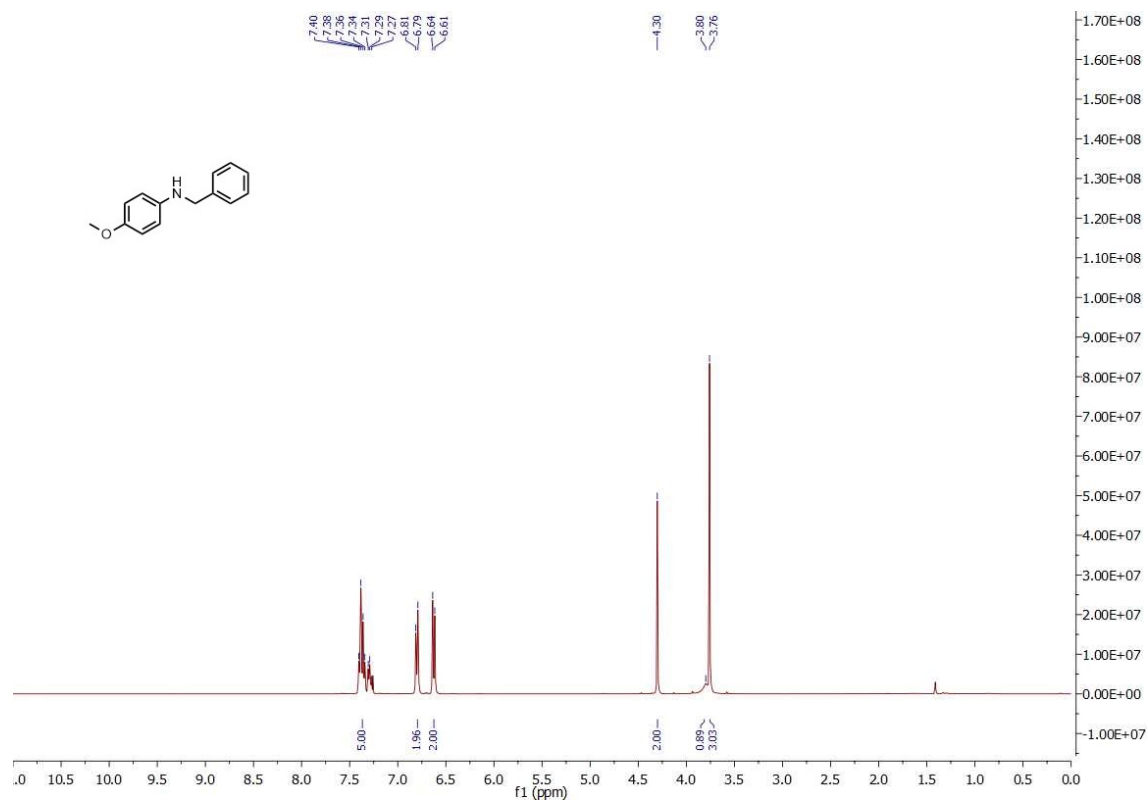


Figure A178. ¹H NMR spectrum of **191** (400 MHz, CDCl₃)

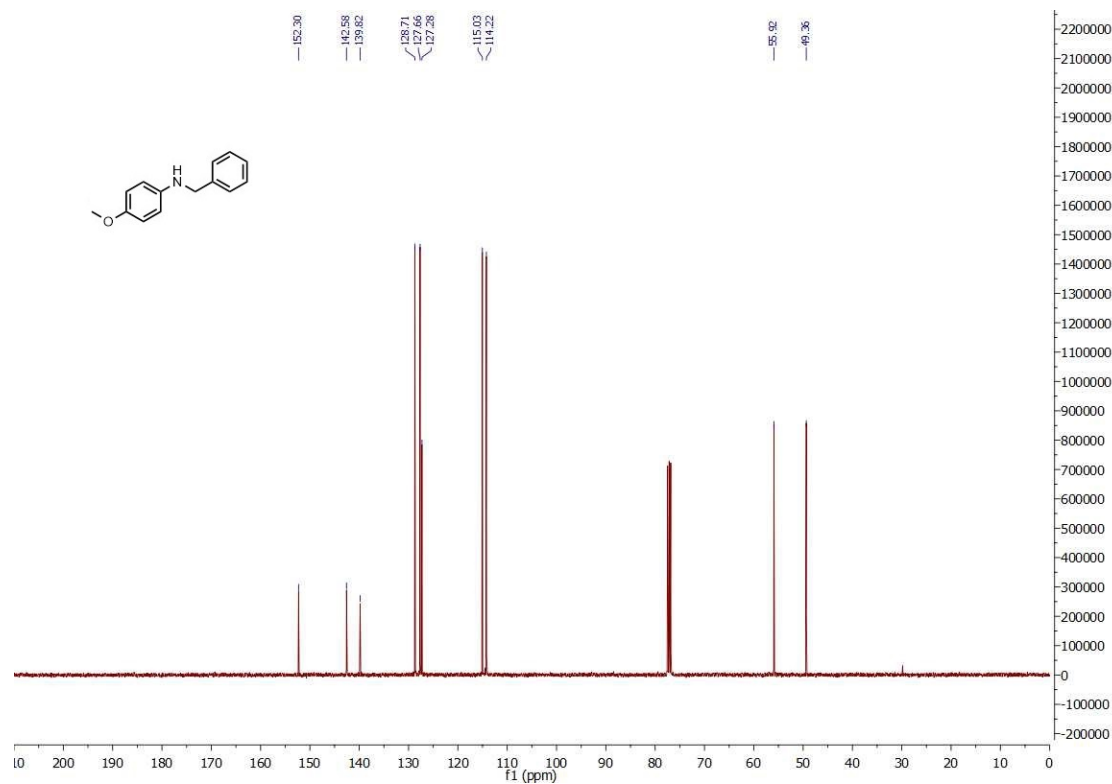


Figure A179. ¹³C NMR spectrum of **191** (100 MHz, CDCl₃)

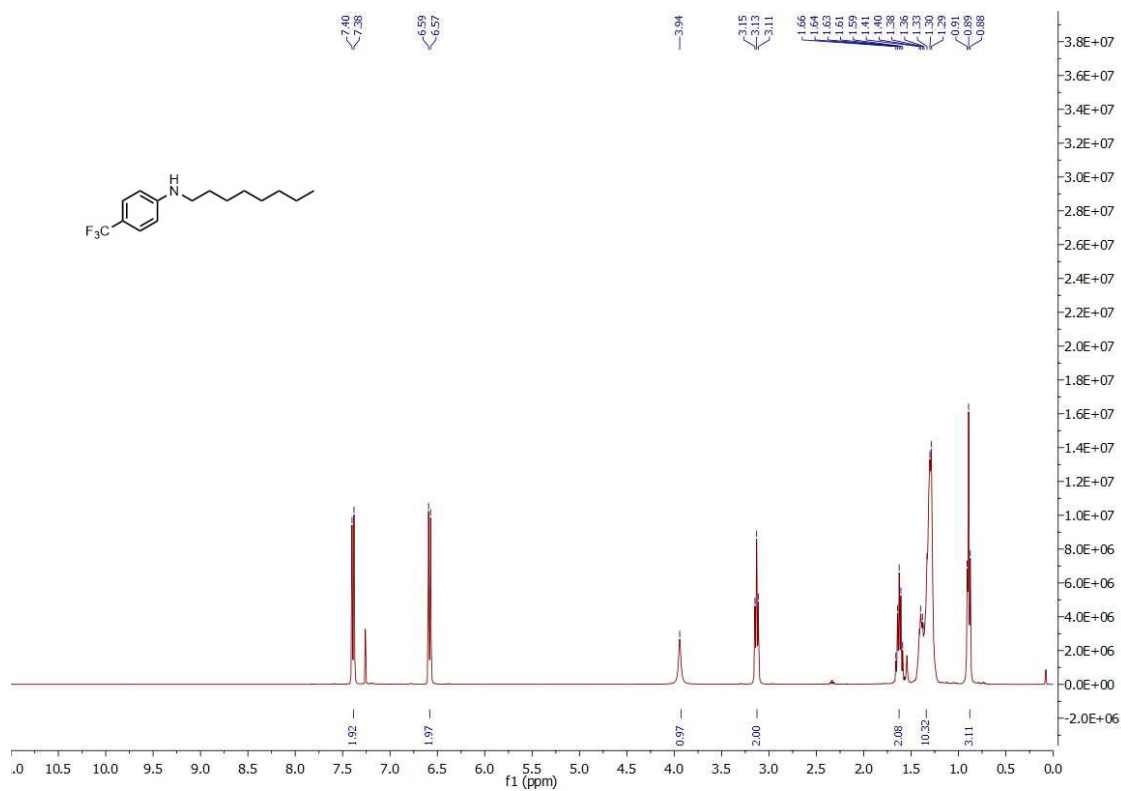


Figure A180. ¹H NMR spectrum of **192** (400 MHz, CDCl₃)

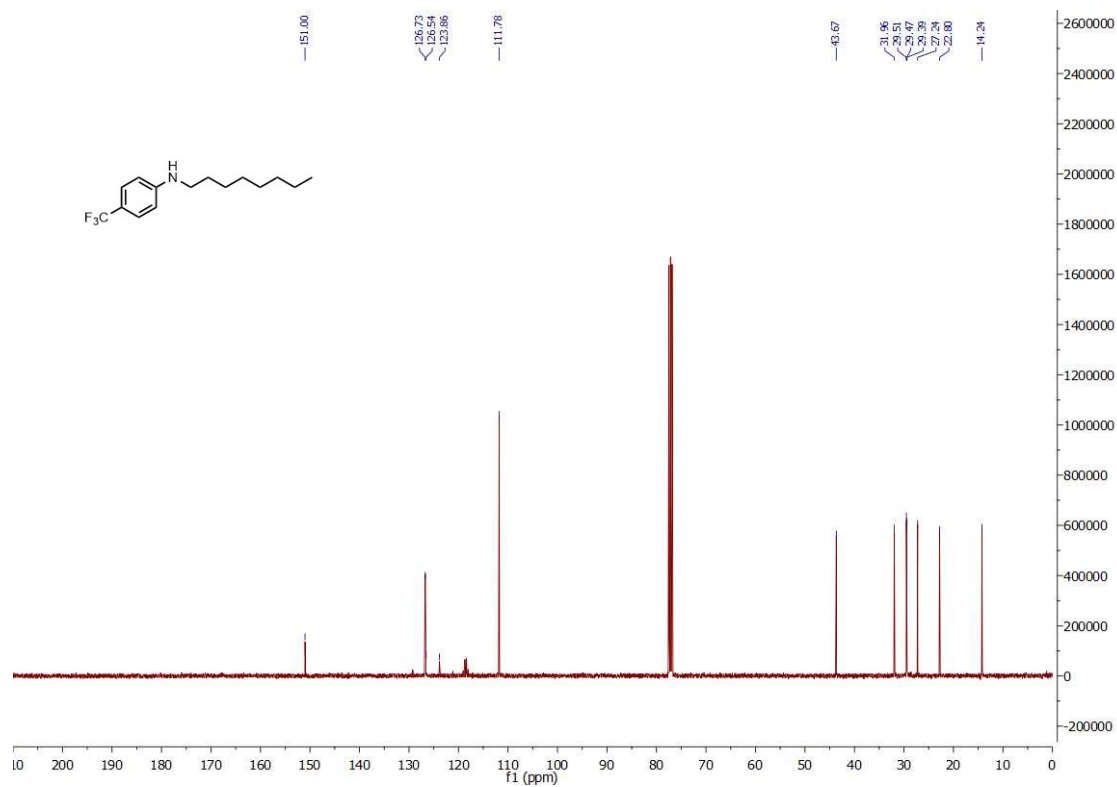


Figure A181. ¹³C NMR spectrum of **192** (100 MHz, CDCl₃)

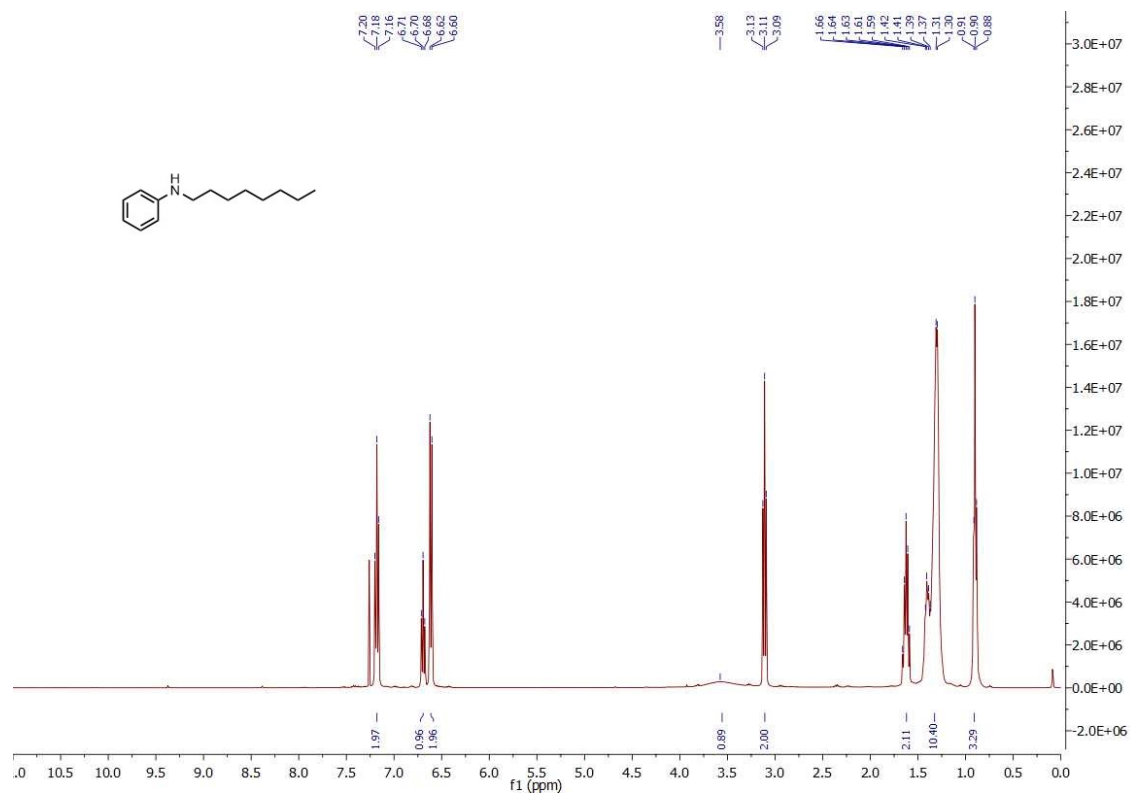


Figure A182. ¹H NMR spectrum of **193** (400 MHz, CDCl₃)

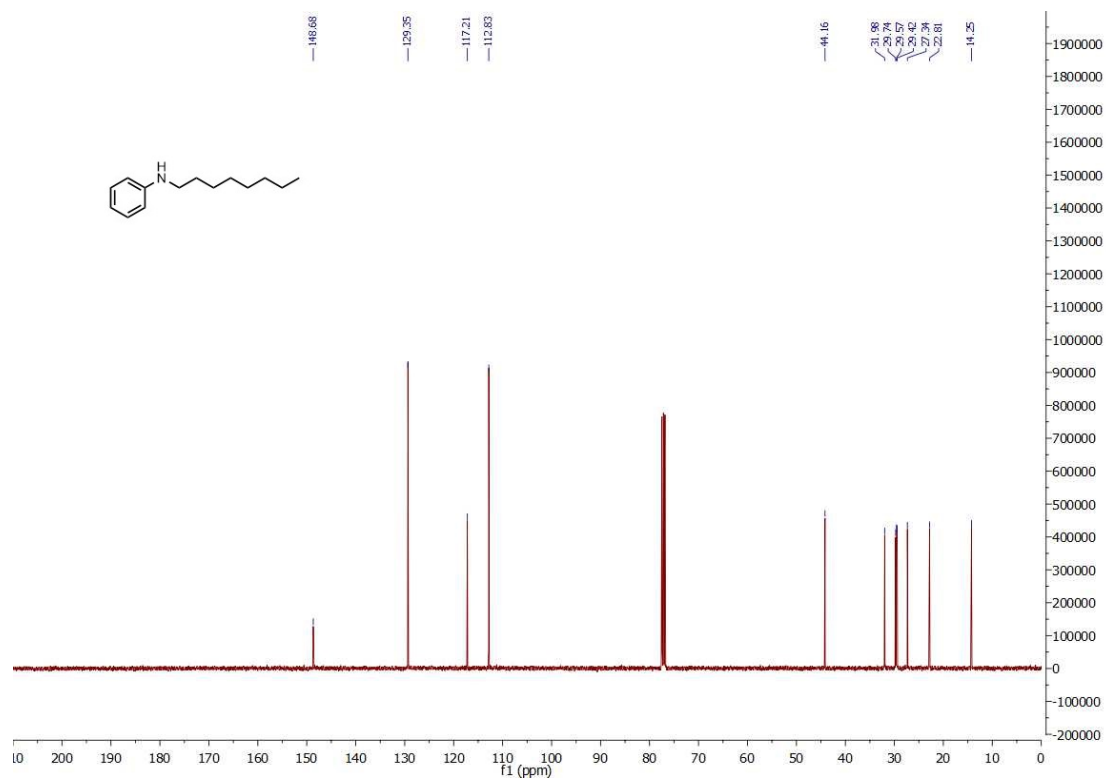


Figure A183. ¹³C NMR spectrum of **193** (100 MHz, CDCl₃)

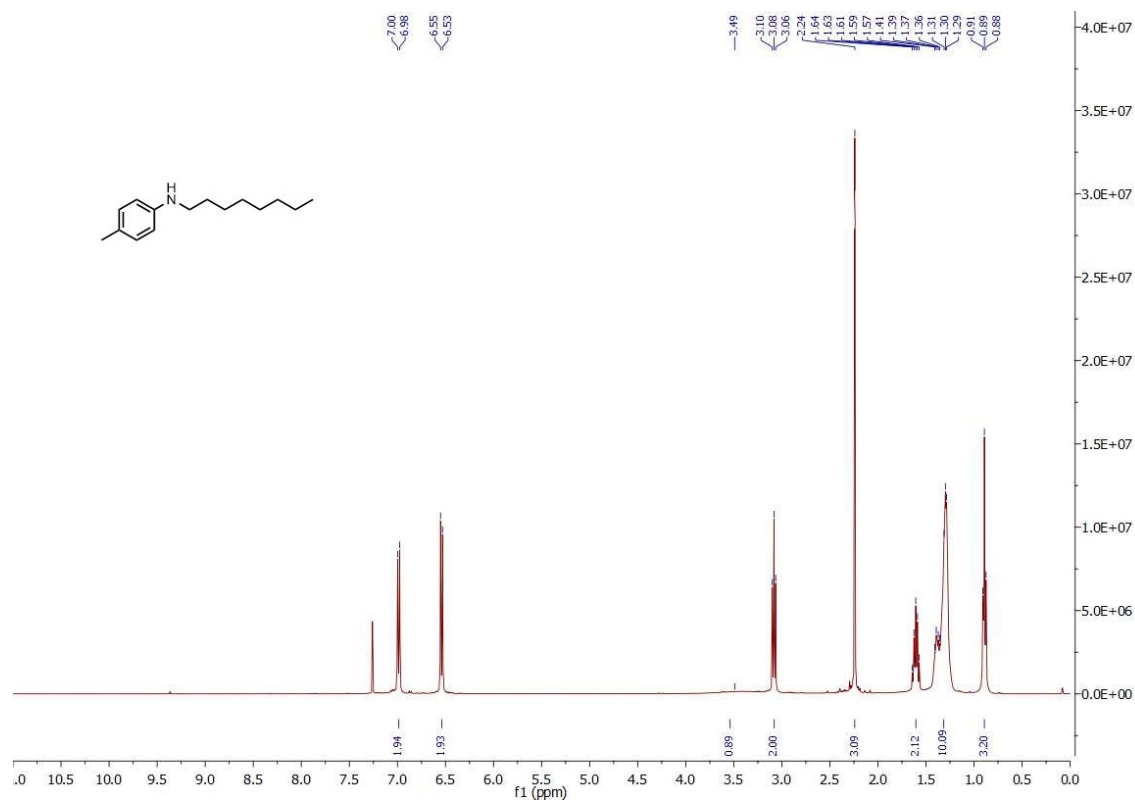


Figure A184. ¹H NMR spectrum of **194** (400 MHz, CDCl₃)

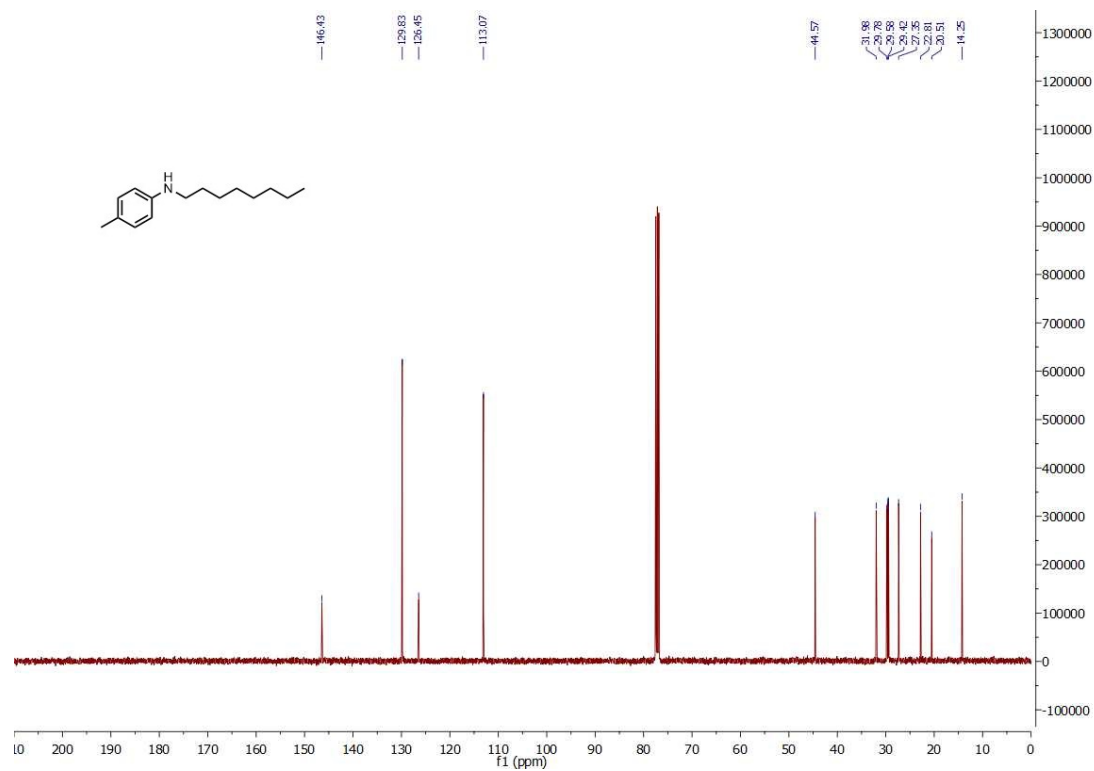


Figure A185. ¹³C NMR spectrum of **194** (100 MHz, CDCl₃)

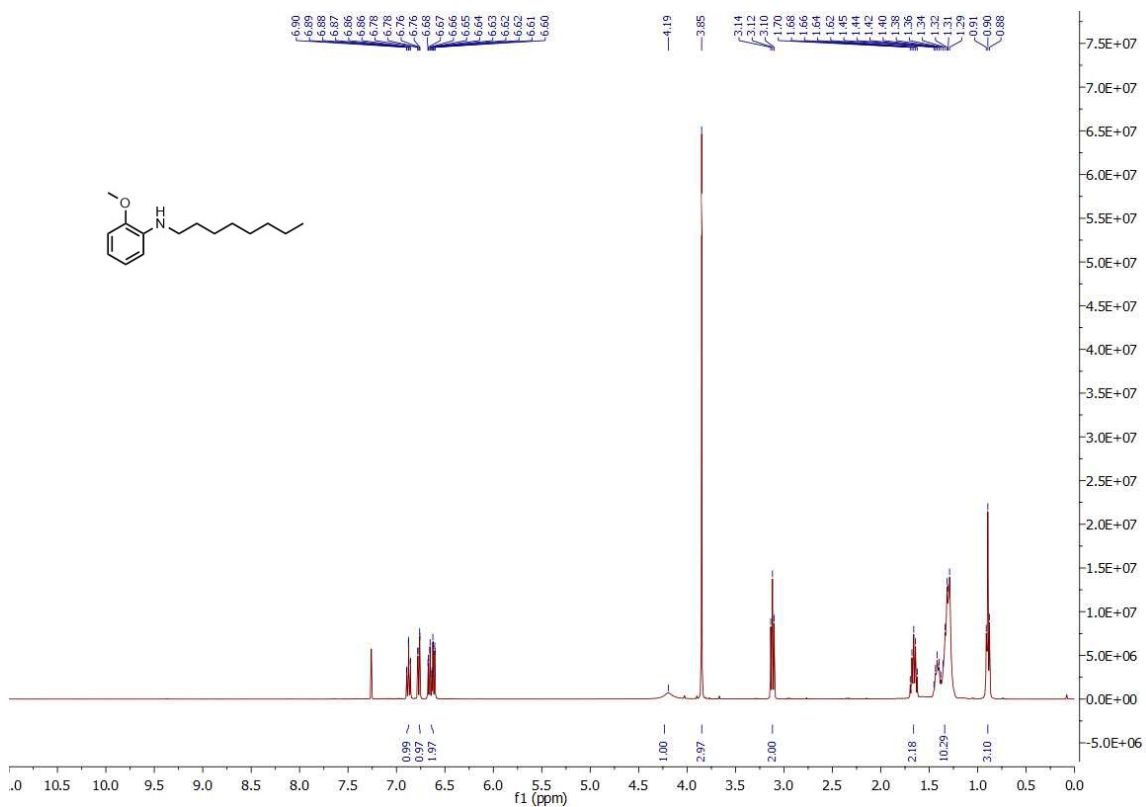


Figure A186. ¹H NMR spectrum of **195** (400 MHz, CDCl₃)

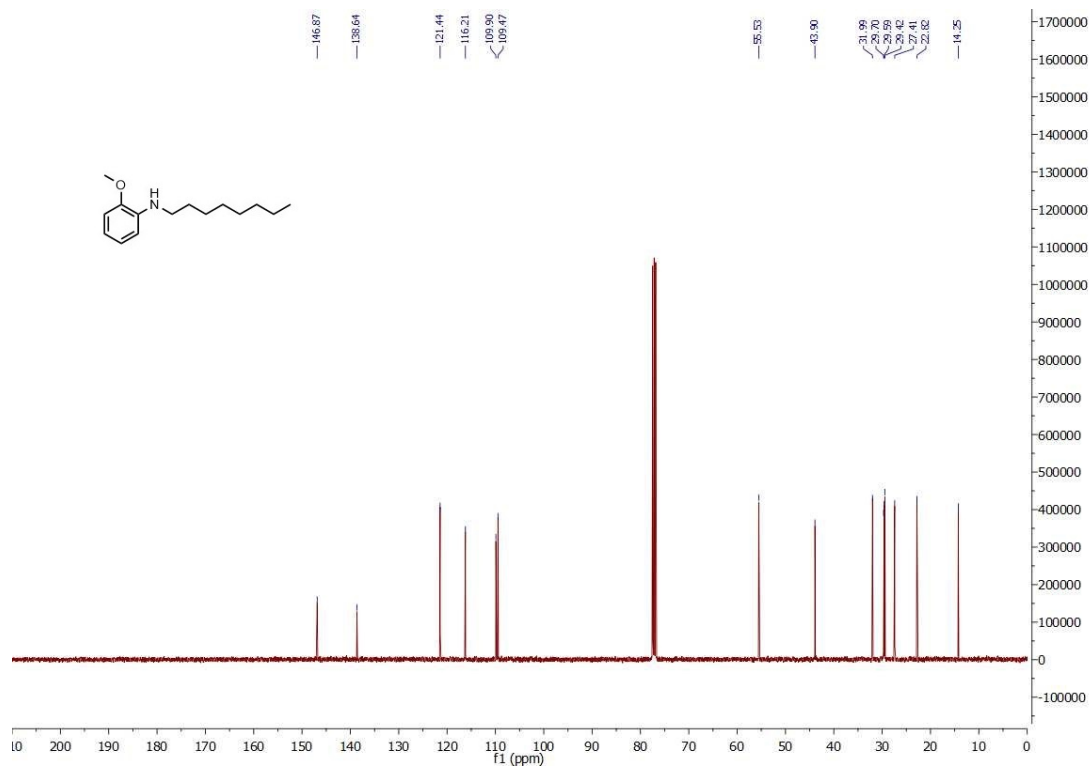


Figure A187. ¹³C NMR spectrum of **195** (100 MHz, CDCl₃)

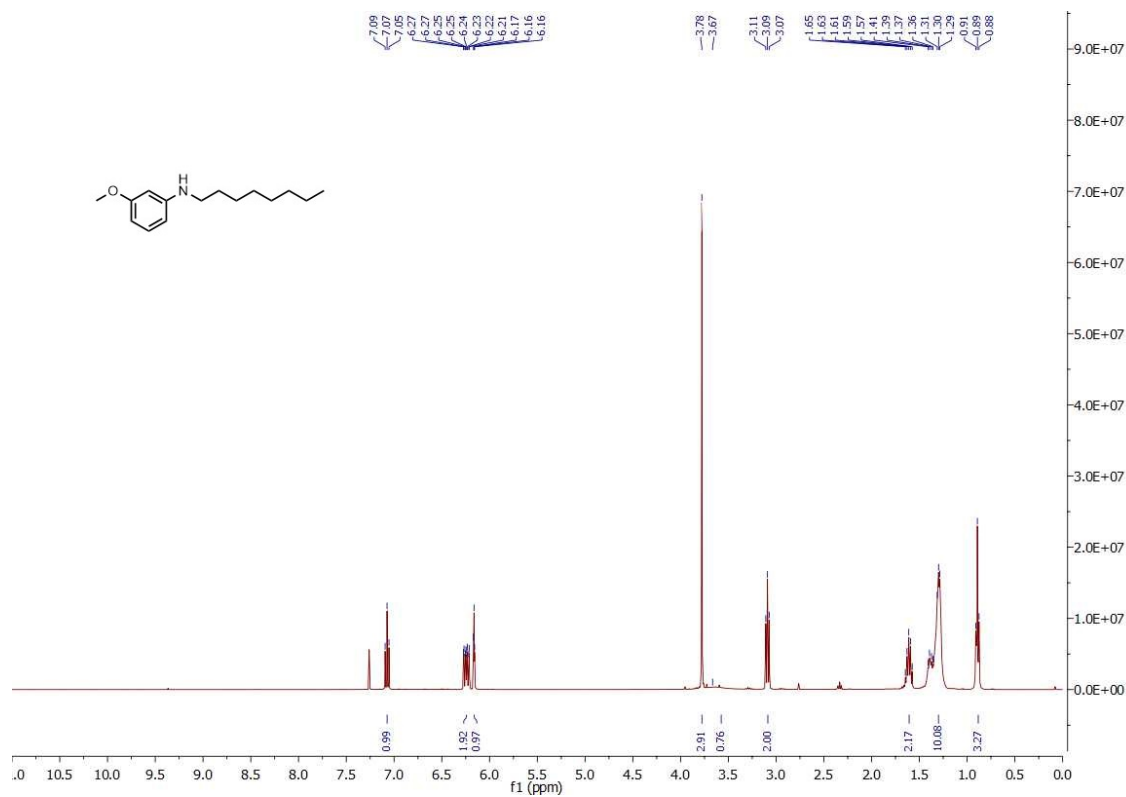


Figure A188. ^1H NMR spectrum of **196** (400 MHz, CDCl_3)

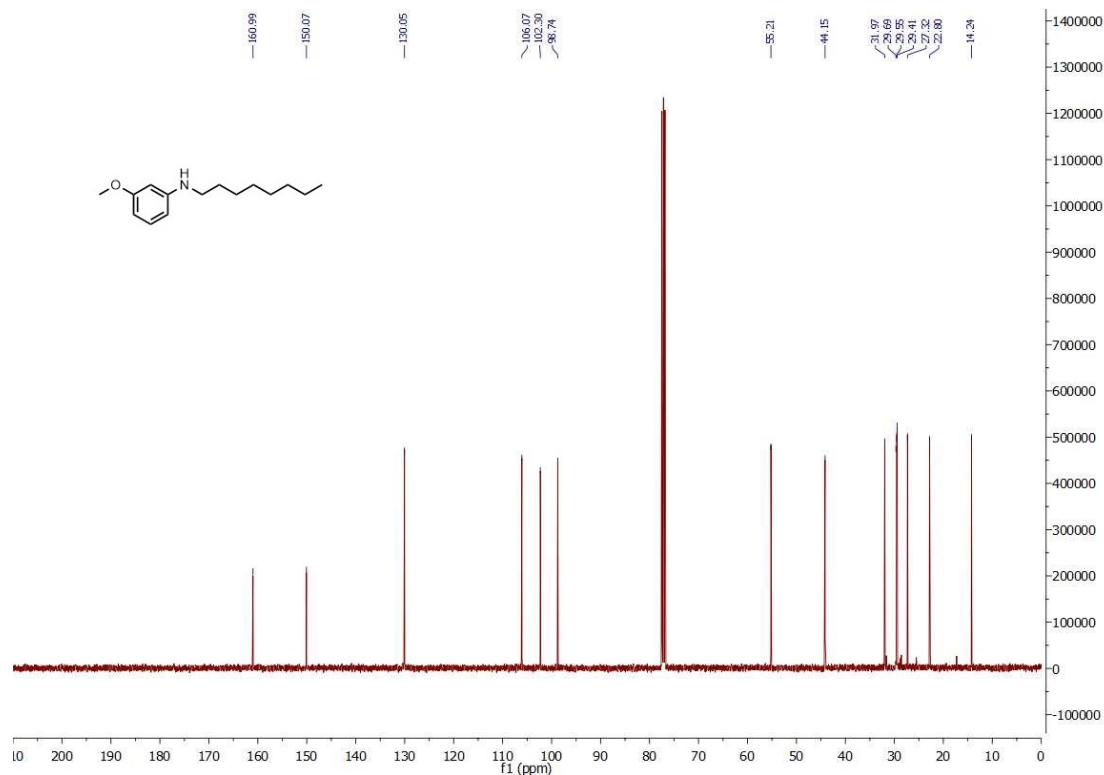


Figure A189. ^{13}C NMR spectrum of **196** (100 MHz, CDCl_3)

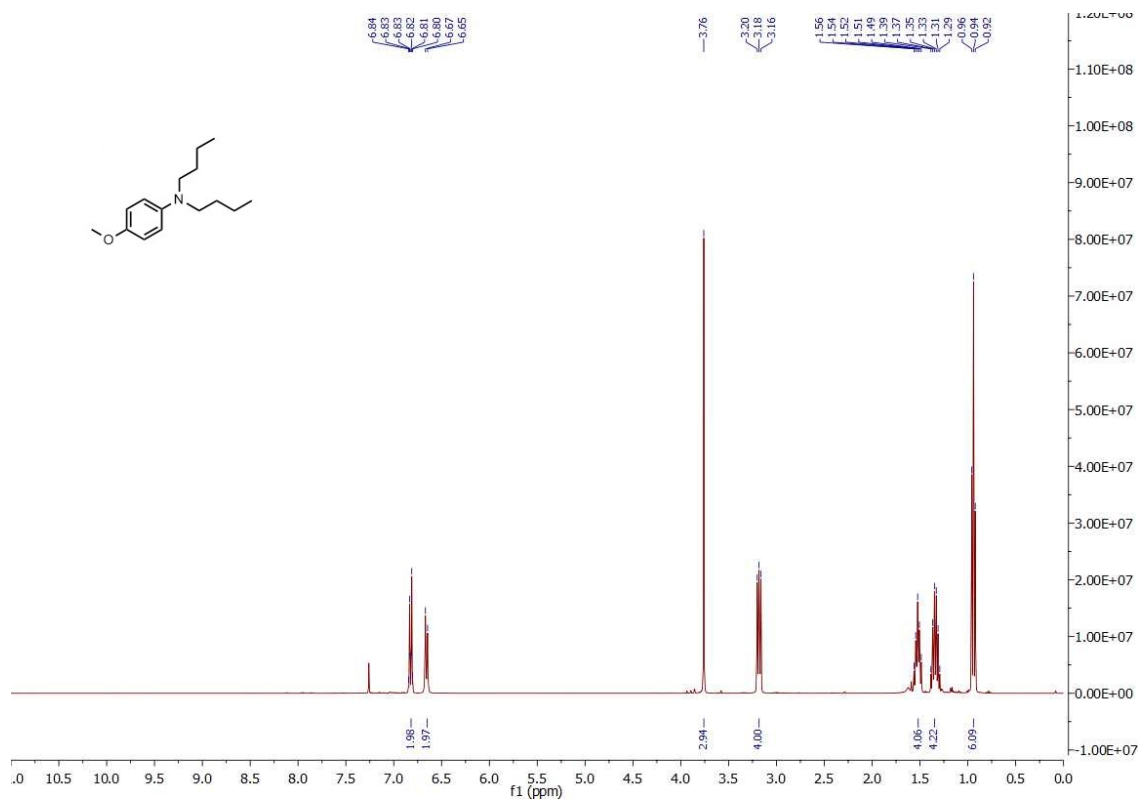


Figure A192. ^1H NMR spectrum of **198** (400 MHz, CDCl_3)

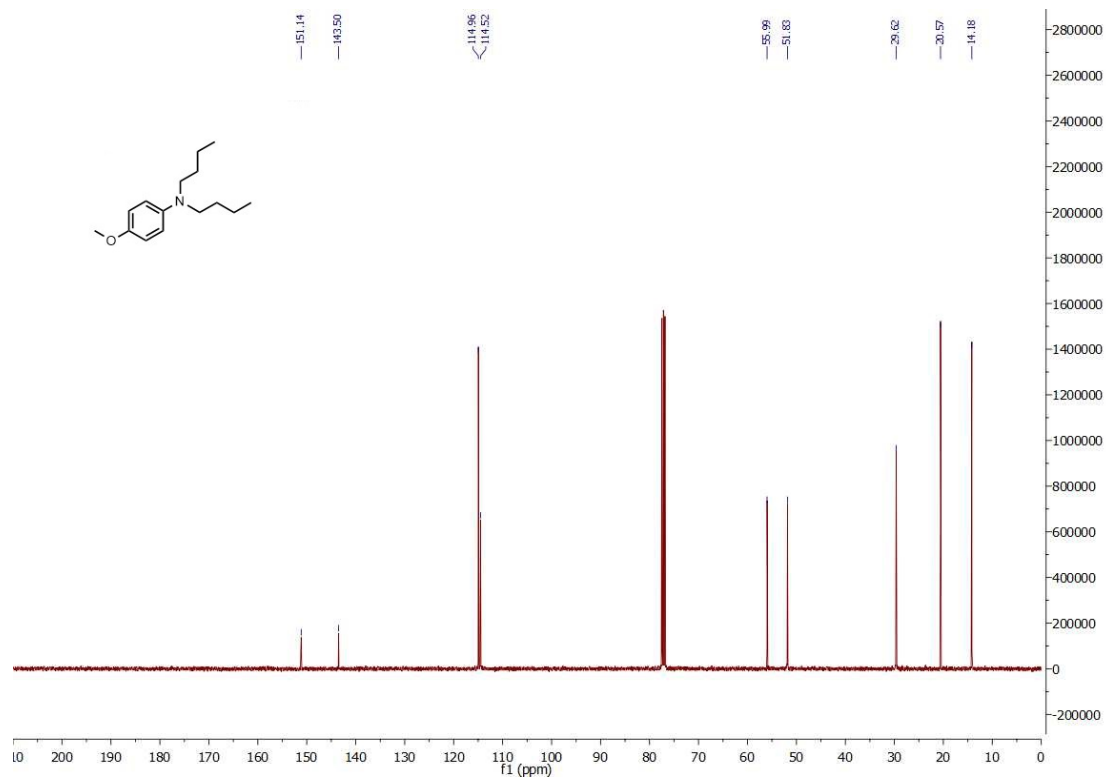


Figure A193. ^{13}C NMR spectrum of **198** (100 MHz, CDCl_3)

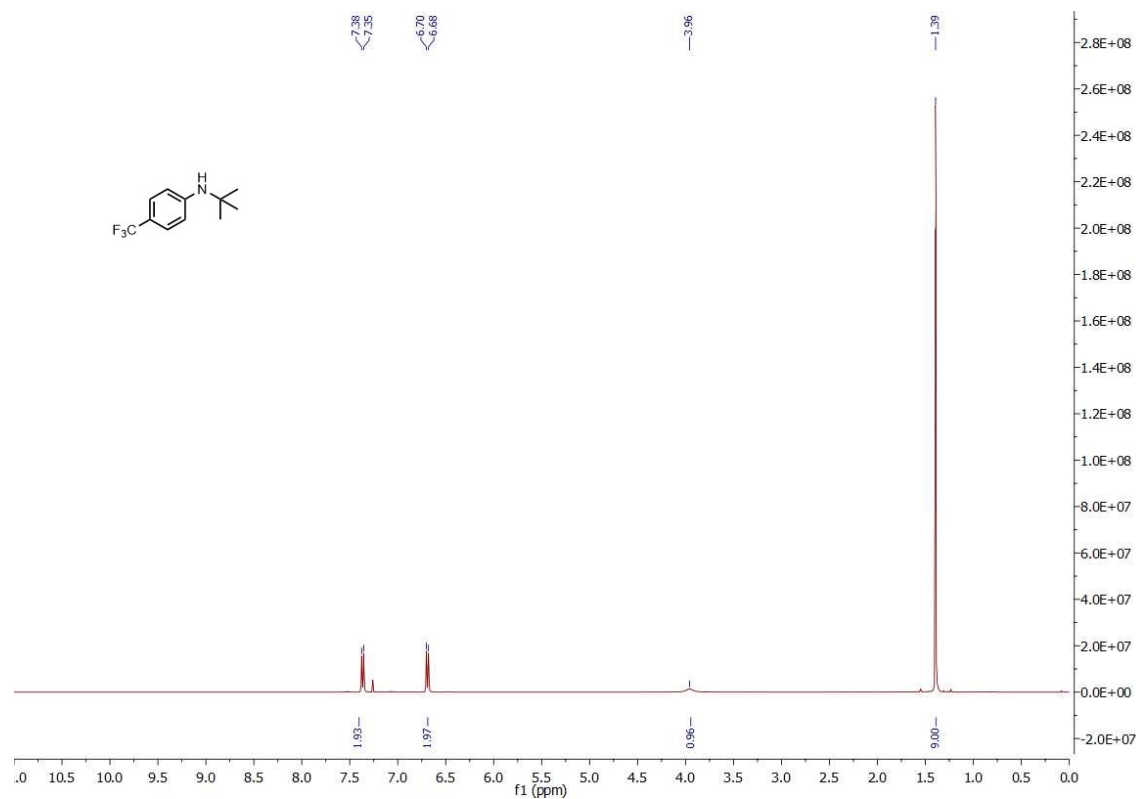


Figure A194. ¹H NMR spectrum of **199** (400 MHz, CDCl₃)

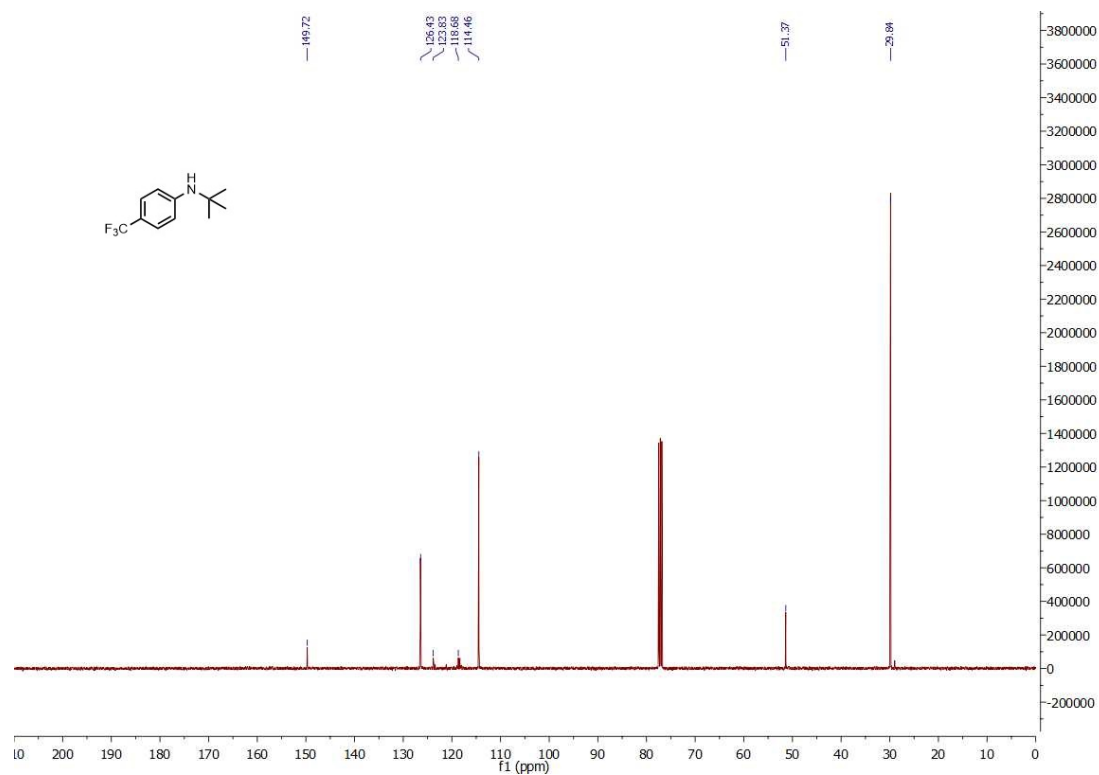


Figure A195. ¹³C NMR spectrum of **199** (100 MHz, CDCl₃)

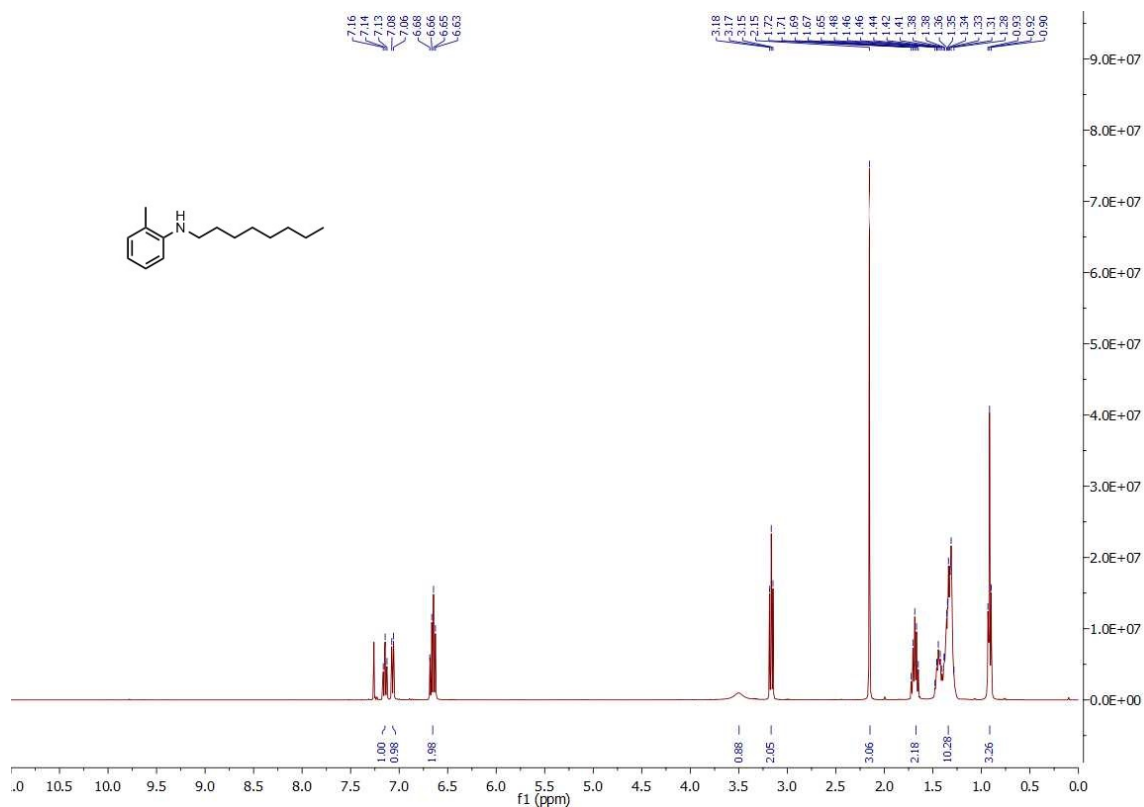


Figure A196. ¹H NMR spectrum of **212** (400 MHz, CDCl₃)

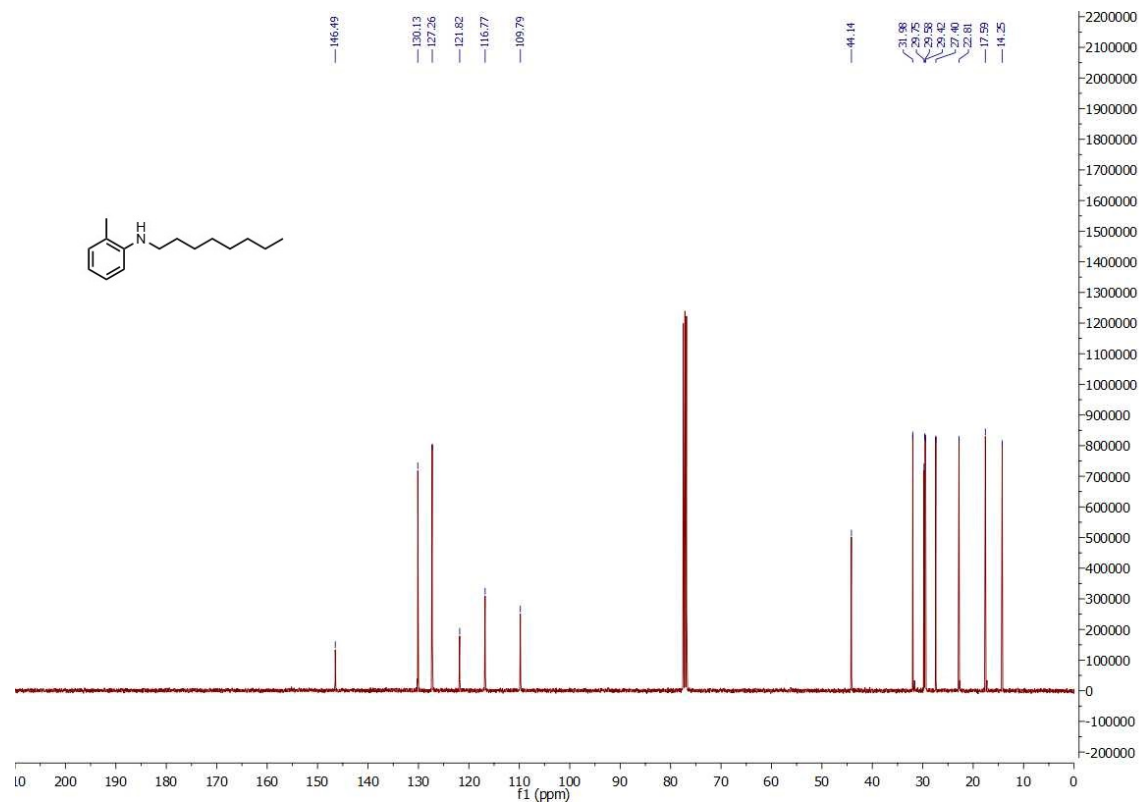


Figure A197. ¹³C NMR spectrum of **212** (100 MHz, CDCl₃)

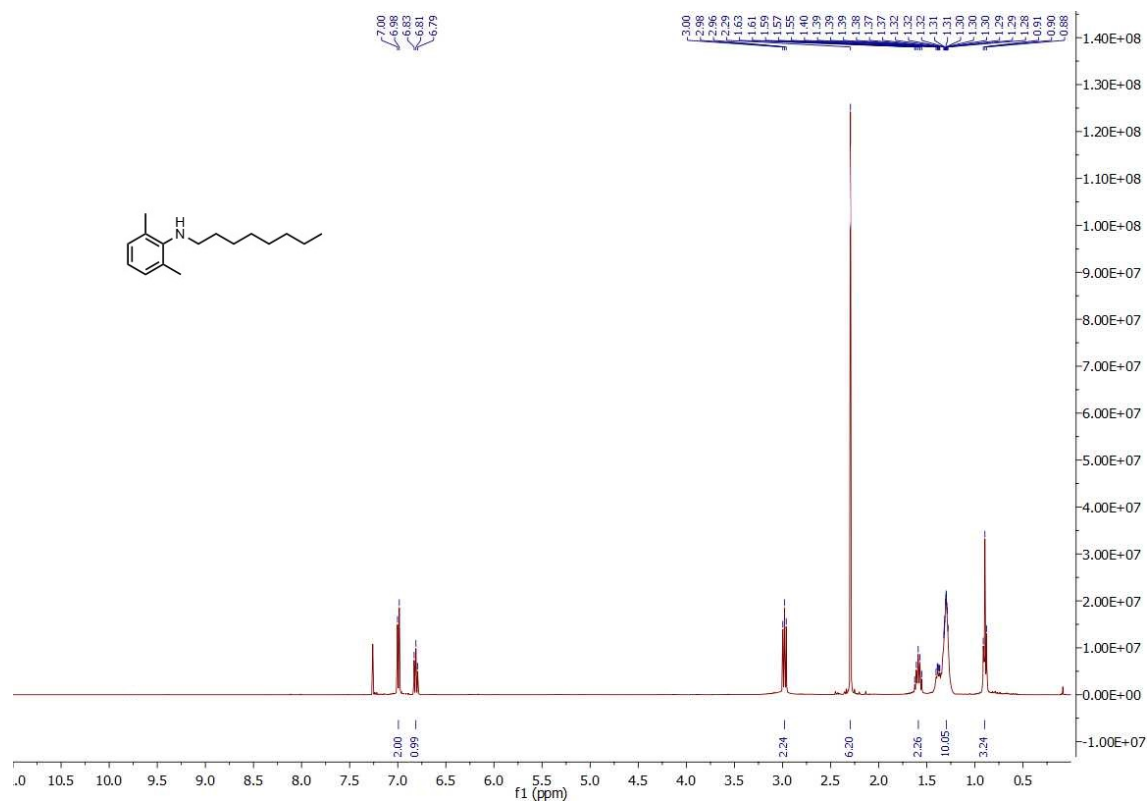


Figure A198. ¹H NMR spectrum of **213** (400 MHz, CDCl₃)

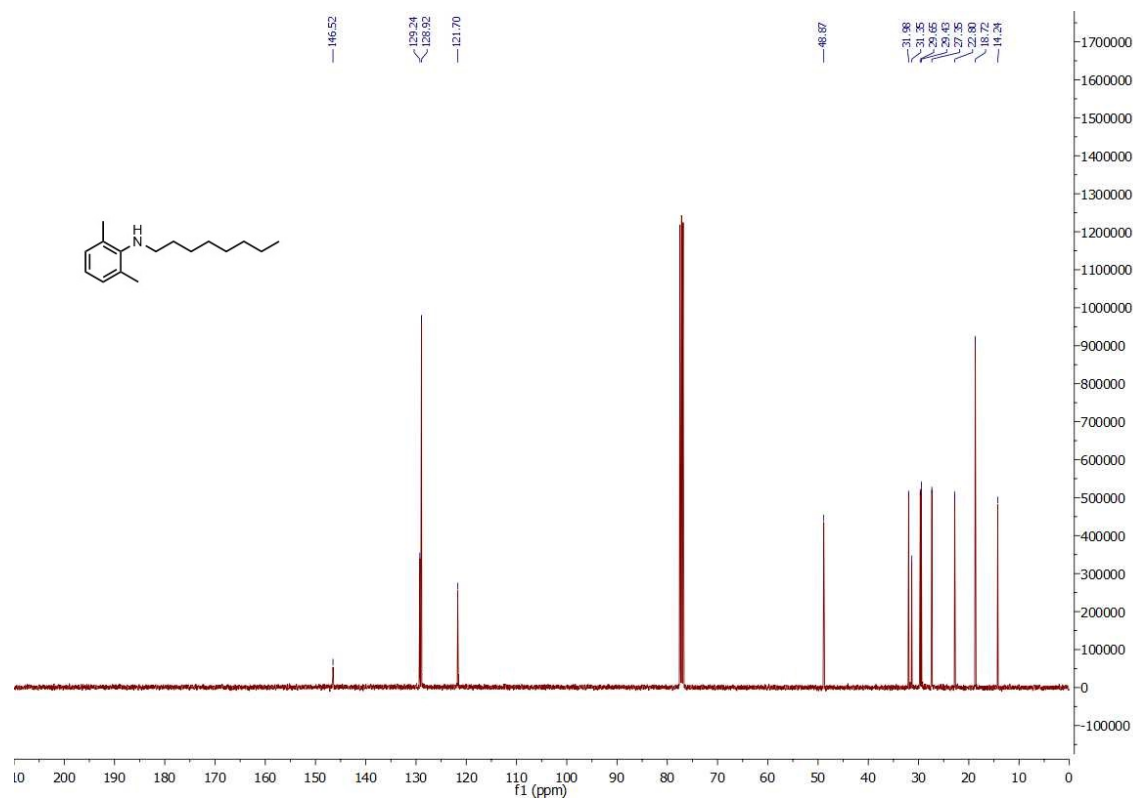


Figure A199. ¹³C NMR spectrum of **213** (100 MHz, CDCl₃)

X-ray diffraction data

Table A1. X-ray crystallographic data collection and refinement details for Ni–NHC–IPr (**83**), Ni–NHC–IPr^{Cl} (**188**), Ni–NHC–IPent (**165**), and Ni–NHC–IPr*^{OMe} (**181**)

Complex	Ni–NHC–IPr (83)	Ni–NHC–IPr ^{Cl} (188)	Ni–NHC–IPent (165)	Ni–NHC–IPr* ^{OMe} (181)
Empirical formula	C ₄₀ H ₅₆ ClN ₃ NiO	C ₃₆ H ₄₆ Cl ₃ N ₃ Ni	C ₄₄ H ₆₄ ClN ₃ Ni	C _{86.25} H _{86.75} ClN ₃ NiO _{2.50}
Formula weight	689.03	685.82	729.14	1299.49
Temperature [K]	100(2)	100(2)	150	150
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group (number)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>C</i> 2/ <i>c</i> (15)
a [Å]	9.674(3)	10.4654(6)	12.0891(3)	18.7655(4)
b [Å]	12.389(3)	12.8785(7)	12.4139(3)	18.9451(4)
c [Å]	16.323(5)	13.0688(8)	31.1879(8)	42.2477(8)
α [°]	104.642(4)	88.9930(10)	89.138(2)	90
β [°]	94.036(5)	87.4910(10)	84.135(2)	102.7140(10)
γ [°]	90.822(3)	88.0760(10)	62.221(2)	90
Volume [Å ³]	1886.9(9)	1758.49(18)	4116.55(19)	14651.4(5)
Z	2	2	4	8
ρ_{calc} [gcm ^{−3}]	1.213	1.295	1.176	1.178
μ [mm ^{−1}]	0.618	0.808	3.109	1.912
F(000)	740	724	1576	5522
Crystal size [mm ³]	0.06×0.147×0.29	0.064×0.111×0.296	0.05×0.1×0.1	0.08×0.12×0.18
Crystal colour	orange	yellow	clear light yellow	clear light yellow
Crystal shape	block	block	prism	chunk
Radiation	Mo K α (λ =0.71073 Å)	Mo K α (λ =0.71073 Å)	Ga K α (λ =1.34139 Å)	Ga K α (λ =1.34139 Å)
2 θ range [°]	2.59 to 64.39 (0.67 Å)	3.12 to 61.28 (0.70 Å)	2.48 to 122.58 (0.76 Å)	5.84 to 131.74 (0.73 Å)
Index ranges	−14 ≤ h ≤ 14 −18 ≤ k ≤ 18 −24 ≤ l ≤ 23	−12 ≤ h ≤ 15 −18 ≤ k ≤ 18 18 ≤ l ≤ 18	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 0 ≤ l ≤ 40	−23 ≤ h ≤ 25 −24 ≤ k ≤ 24 −56 ≤ l ≤ 57
Reflections collected	44735	33639	18725	120231
Independent reflections	12966 $R_{\text{int}} = 0.0611$ $R_{\text{sigma}} = 0.0692$	10829 $R_{\text{int}} = 0.0480$ $R_{\text{sigma}} = 0.0550$	18725 $R_{\text{int}} = ?$ $R_{\text{sigma}} = 0.0415$	18674 $R_{\text{int}} = 0.0558$ $R_{\text{sigma}} = 0.0426$
Completeness to $\theta = 25.242^\circ$	99.80%	100.0 %	100.0 %	99.9 %
Data / Restraints / Parameters	12966 / 232 / 470	10829 / 338 / 397	18725 / 103 / 969	18674 / 1887 / 1260
Absorption correction $T_{\text{min}}/T_{\text{max}}$ (method)	0.6846 / 0.7463 (multi-scan)	0.6976 / 0.7461 (multi-scan)	0.4274 / 0.7520 (multi-scan)	0.6493 / 0.7527 (multi-scan)
Goodness-of-fit on F^2	1.003	1.040	1.023	1.035
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0572$ $wR_2 = 0.1397$	$R_1 = 0.0445$ $wR_2 = 0.0816$	$R_1 = 0.0491$ $wR_2 = 0.1241$	$R_1 = 0.0594$ $wR_2 = 0.1665$
Final R indexes [all data]	$R_1 = 0.0924$ $wR_2 = 0.1578$	$R_1 = 0.0716$ $wR_2 = 0.0924$	$R_1 = 0.0595$ $wR_2 = 0.1318$	$R_1 = 0.0935$ $wR_2 = 0.1893$
Largest peak/hole [eÅ ^{−3}]	1.19/−0.71	0.44/−0.33	0.97/−0.59	0.71/−0.45

Table A2. X-ray crystallographic data collection and refinement details for Ni(allyl)Cl(IPr) (**207**), Ni(allyl)Cl(IPr^{Cl}) (**208**), Ni(allyl)Cl(IPent^{Cl}) (**209**), and Ni(allyl)Cl(IHept^{Cl}) (**210**)

Complex	Ni(allyl)Cl(IPr) (207)	Ni(allyl)Cl(IPr ^{Cl}) (208)	Ni(allyl)Cl(IPent ^{Cl}) (209)	Ni(allyl)Cl(IHept ^{Cl}) (210)
Empirical formula	C ₃₀ H ₄₁ ClN ₂ Ni	C ₆₀ H ₇₈ Cl ₆ N ₄ Ni ₂	C ₃₈ H ₅₅ Cl ₃ N ₂ Ni	C ₄₆ H ₇₁ Cl ₃ N ₂ Ni
Formula weight	523.81	1185.38	704.90	817.10
Temperature [K]	150	150	150	150
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	12.4413(3)	10.6688(16)	11.1309(3)	16.8204(5)
<i>b</i> [Å]	14.6987(4)	17.103(3)	20.4043(6)	17.0807(5)
<i>c</i> [Å]	16.5217(5)	17.199(3)	16.9408(5)	16.3724(4)
α [°]	90	76.877(10)	90	90
β [°]	103.821(2)	84.424(10)	106.2180(10)	104.874(2)
γ [°]	90	89.291(10)	90	90
Volume [Å ³]	2933.86(14)	3041.7(8)	3694.45(18)	4546.2(2)
<i>Z</i>	4	2	4	4
ρ_{calc} [gcm ⁻³]	1.186	1.294	1.267	1.194
μ [mm ⁻¹]	4.231	5.191	4.327	3.559
<i>F</i> (000)	1120	1248	1504	1760
Crystal size [mm ³]	0.2×0.3×0.4	0.002×0.017×0.061	0.1×0.1×0.2	0.04×0.1×0.14
Crystal colour	clear light orange	clear light bronze	clear light orange	clear light yellow
Crystal shape	chunk	needle	chunk	plate
Radiation	Ga <i>K</i> α (λ =1.34139 Å)	Ga <i>K</i> α (λ =1.34139 Å)	Ga <i>K</i> α (λ =1.34139 Å)	Ga <i>K</i> α (λ =1.34139 Å)
2 θ range [°]	7.10 to 132.59 (0.73 Å)	7.23 to 110.29 (0.82 Å)	6.05 to 132.41 (0.73 Å)	4.73 to 132.59 (0.73 Å)
Index ranges	-16 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 19 0 ≤ <i>l</i> ≤ 22	-8 ≤ <i>h</i> ≤ 12 -20 ≤ <i>k</i> ≤ 20 -21 ≤ <i>l</i> ≤ 20	-12 ≤ <i>h</i> ≤ 14 -27 ≤ <i>k</i> ≤ 27 -23 ≤ <i>l</i> ≤ 19	-22 ≤ <i>h</i> ≤ 22 -22 ≤ <i>k</i> ≤ 21 -21 ≤ <i>l</i> ≤ 20
Reflections collected	7633	10845	57471	70958
Independent reflections	7633 <i>R</i> _{int} = ? <i>R</i> _{sigma} = 0.0256	6836 <i>R</i> _{int} = 0.1024 <i>R</i> _{sigma} = 0.2781	9490 <i>R</i> _{int} = 0.0449 <i>R</i> _{sigma} = 0.0317	11698 <i>R</i> _{int} = 0.0495 <i>R</i> _{sigma} = 0.0352
Completeness to θ = 25.242°	99.7 %	59.8 %	99.9 %	100.0 %
Data / Restraints / Parameters	7633 / 86 / 380	6836 / 1398 / 728	9490 / 236 / 502	11698 / 173 / 621
Absorption correction <i>T</i> _{min} / <i>T</i> _{max} (method)	0.4208 / 0.7528 (multi-scan)	0.3349 / 0.7508 (multi-scan)	0.5626 / 0.7528 (multi-scan)	0.3756 / 0.5199 (multi-scan)
Goodness-of-fit on <i>F</i> ²	1.057	1.161	1.055	1.054
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0342 <i>wR</i> ₂ = 0.0836	<i>R</i> ₁ = 0.1686 <i>wR</i> ₂ = 0.4125	<i>R</i> ₁ = 0.0332 <i>wR</i> ₂ = 0.0881	<i>R</i> ₁ = 0.0394 <i>wR</i> ₂ = 0.0961
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0432 <i>wR</i> ₂ = 0.0880	<i>R</i> ₁ = 0.3566 <i>wR</i> ₂ = 0.4962	<i>R</i> ₁ = 0.0362 <i>wR</i> ₂ = 0.0901	<i>R</i> ₁ = 0.0530 <i>wR</i> ₂ = 0.1037
Largest peak/hole [eÅ ⁻³]	0.27/-0.27	1.35/-0.53	0.33/-0.61	0.52/-0.49

X-ray diffraction data for Ni–NHC–IPr

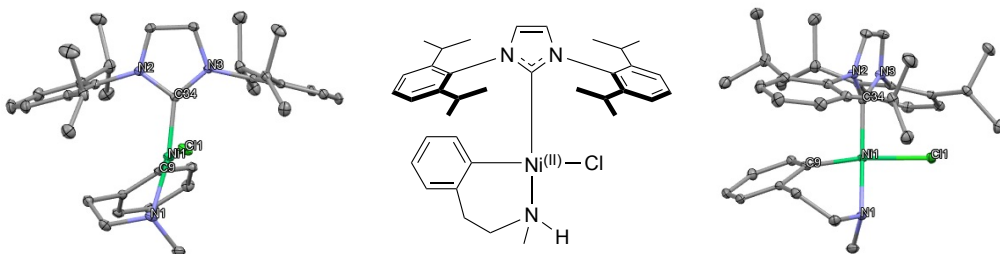


Table A3. Bond lengths for Ni–NHC–IPr (**83**)

Entry	Atom1	Atom2	Length
1	Ni1	Cl1	2.258(1)
2	Ni1	N1	1.977(2)
3	Ni1	C9	1.886(3)
4	Ni1	C34	1.891(2)
5	N1	H1	1
6	N1	C1	1.477(3)
7	N1	C2	1.491(3)
8	N2	C18	1.451(3)
9	N2	C34	1.368(3)
10	N2	C35	1.392(3)
11	N3	C30	1.447(3)
12	N3	C34	1.371(3)
13	N3	C36	1.392(3)
14	C1	H1A	0.98
15	C1	H1B	0.98
16	C1	H1C	0.98
17	C2	H2A	0.989
18	C2	H2AB	0.99
19	C2	C3	1.533(4)
20	C3	H3A	0.99
21	C3	H3AB	0.99
22	C3	C4	1.507(4)
23	C4	C5	1.395(3)
24	C4	C9	1.405(3)
25	C5	H5	0.951
26	C5	C6	1.390(4)
27	C6	H6	0.95
28	C6	C7	1.387(4)
29	C7	H7	0.95

30	C7	C8	1.395(4)
31	C8	H8	0.95
32	C8	C9	1.395(4)
33	C10	H10A	0.98
34	C10	H10B	0.98
35	C10	H10C	0.98
36	C10	C11	1.527(5)
37	C11	H11	1
38	C11	C12	1.522(5)
39	C11	C13	1.511(4)
40	C12	H12A	0.98
41	C12	H12B	0.98
42	C12	H12C	0.98
43	C13	C14	1.402(3)
44	C13	C18	1.396(4)
45	C14	H14	0.95
46	C14	C15	1.382(4)
47	C15	H15	0.95
48	C15	C16	1.382(4)
49	C16	H16	0.95
50	C16	C17	1.395(3)
51	C17	C18	1.402(4)
52	C17	C20	1.523(4)
53	C19	H19A	0.979
54	C19	H19B	0.98
55	C19	H19C	0.98
56	C19	C20	1.541(4)
57	C20	H20	1
58	C20	C21	1.528(4)
59	C21	H21A	0.98
60	C21	H21B	0.98
61	C21	H21C	0.98
62	C22	H22A	0.98
63	C22	H22B	0.98
64	C22	H22C	0.98
65	C22	C23	1.537(4)
66	C23	H23	1
67	C23	C24	1.530(4)
68	C23	C25	1.529(4)
69	C24	H24A	0.98

70	C24	H24B	0.981
71	C24	H24C	0.979
72	C25	C26	1.390(3)
73	C25	C30	1.417(4)
74	C26	H26	0.95
75	C26	C27	1.386(4)
76	C27	H27	0.95
77	C27	C28	1.384(4)
78	C28	H28	0.95
79	C28	C29	1.399(3)
80	C29	C30	1.398(3)
81	C29	C32	1.516(4)
82	C31	H31A	0.98
83	C31	H31B	0.98
84	C31	H31C	0.98
85	C31	C32	1.536(4)
86	C32	H32	1
87	C32	C33	1.531(4)
88	C33	H33A	0.98
89	C33	H33B	0.98
90	C33	H33C	0.98
91	C35	H35	0.949
92	C35	C36	1.341(3)
93	C36	H36	0.95

Table A4. Bond angles for Ni–NHC–IPr (**83**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl1	Ni1	N1	87.51(6)
2	Cl1	Ni1	C9	171.43(7)
3	Cl1	Ni1	C34	90.92(7)
4	N1	Ni1	C9	86.67(9)
5	N1	Ni1	C34	169.00(9)
6	C9	Ni1	C34	96.0(1)
7	Ni1	N1	H1	105.1
8	Ni1	N1	C1	116.9(2)
9	Ni1	N1	C2	112.6(2)
10	H1	N1	C1	105.1
11	H1	N1	C2	105.1
12	C1	N1	C2	110.9(2)
13	C18	N2	C34	125.6(2)

14	C18	N2	C35	122.1(2)
15	C34	N2	C35	111.7(2)
16	C30	N3	C34	126.4(2)
17	C30	N3	C36	121.9(2)
18	C34	N3	C36	111.2(2)
19	N1	C1	H1A	109.5
20	N1	C1	H1B	109.5
21	N1	C1	H1C	109.5
22	H1A	C1	H1B	109.5
23	H1A	C1	H1C	109.4
24	H1B	C1	H1C	109.5
25	N1	C2	H2A	108.9
26	N1	C2	H2AB	108.8
27	N1	C2	C3	113.5(2)
28	H2A	C2	H2AB	107.8
29	H2A	C2	C3	108.9
30	H2AB	C2	C3	108.8
31	C2	C3	H3A	109.0
32	C2	C3	H3AB	109.0
33	C2	C3	C4	112.9(2)
34	H3A	C3	H3AB	107.8
35	H3A	C3	C4	109.0
36	H3AB	C3	C4	109.0
37	C3	C4	C5	121.6(2)
38	C3	C4	C9	118.1(2)
39	C5	C4	C9	120.2(2)
40	C4	C5	H5	119.4
41	C4	C5	C6	121.1(2)
42	H5	C5	C6	119.5
43	C5	C6	H6	120.6
44	C5	C6	C7	119.0(2)
45	H6	C6	C7	120.5
46	C6	C7	H7	119.8
47	C6	C7	C8	120.2(2)
48	H7	C7	C8	119.9
49	C7	C8	H8	119.2
50	C7	C8	C9	121.5(2)
51	H8	C8	C9	119.3
52	Ni1	C9	C4	118.9(2)
53	Ni1	C9	C8	121.8(2)

54	C4	C9	C8	118.0(2)
55	H10A	C10	H10B	109.5
56	H10A	C10	H10C	109.5
57	H10A	C10	C11	109.5
58	H10B	C10	H10C	109.4
59	H10B	C10	C11	109.5
60	H10C	C10	C11	109.5
61	C10	C11	H11	107.7
62	C10	C11	C12	110.2(3)
63	C10	C11	C13	109.7(3)
64	H11	C11	C12	107.7
65	H11	C11	C13	107.7
66	C12	C11	C13	113.6(2)
67	C11	C12	H12A	109.4
68	C11	C12	H12B	109.5
69	C11	C12	H12C	109.5
70	H12A	C12	H12B	109.5
71	H12A	C12	H12C	109.5
72	H12B	C12	H12C	109.5
73	C11	C13	C14	120.9(2)
74	C11	C13	C18	121.8(2)
75	C14	C13	C18	117.2(2)
76	C13	C14	H14	119.6
77	C13	C14	C15	120.7(3)
78	H14	C14	C15	119.6
79	C14	C15	H15	119.6
80	C14	C15	C16	120.7(3)
81	H15	C15	C16	119.7
82	C15	C16	H16	119.5
83	C15	C16	C17	121.0(2)
84	H16	C16	C17	119.5
85	C16	C17	C18	117.2(2)
86	C16	C17	C20	120.4(2)
87	C18	C17	C20	122.3(2)
88	N2	C18	C13	119.4(2)
89	N2	C18	C17	117.3(2)
90	C13	C18	C17	123.1(2)
91	H19A	C19	H19B	109.5
92	H19A	C19	H19C	109.5
93	H19A	C19	C20	109.5

94	H19B	C19	H19C	109.5
95	H19B	C19	C20	109.4
96	H19C	C19	C20	109.4
97	C17	C20	C19	109.7(2)
98	C17	C20	H20	107.8
99	C17	C20	C21	113.3(2)
100	C19	C20	H20	107.8
101	C19	C20	C21	110.4(2)
102	H20	C20	C21	107.8
103	C20	C21	H21A	109.5
104	C20	C21	H21B	109.5
105	C20	C21	H21C	109.5
106	H21A	C21	H21B	109.5
107	H21A	C21	H21C	109.5
108	H21B	C21	H21C	109.4
109	H22A	C22	H22B	109.5
110	H22A	C22	H22C	109.5
111	H22A	C22	C23	109.5
112	H22B	C22	H22C	109.5
113	H22B	C22	C23	109.5
114	H22C	C22	C23	109.5
115	C22	C23	H23	107.9
116	C22	C23	C24	108.5(2)
117	C22	C23	C25	110.8(2)
118	H23	C23	C24	108.0
119	H23	C23	C25	108.0
120	C24	C23	C25	113.4(2)
121	C23	C24	H24A	109.5
122	C23	C24	H24B	109.4
123	C23	C24	H24C	109.5
124	H24A	C24	H24B	109.4
125	H24A	C24	H24C	109.5
126	H24B	C24	H24C	109.5
127	C23	C25	C26	120.6(2)
128	C23	C25	C30	121.9(2)
129	C26	C25	C30	117.4(2)
130	C25	C26	H26	119.4
131	C25	C26	C27	121.2(2)
132	H26	C26	C27	119.4
133	C26	C27	H27	120.0

134	C26	C27	C28	120.0(2)
135	H27	C27	C28	120.0
136	C27	C28	H28	119.3
137	C27	C28	C29	121.4(2)
138	H28	C28	C29	119.3
139	C28	C29	C30	117.3(2)
140	C28	C29	C32	119.6(2)
141	C30	C29	C32	122.9(2)
142	N3	C30	C25	117.9(2)
143	N3	C30	C29	119.7(2)
144	C25	C30	C29	122.2(2)
145	H31A	C31	H31B	109.5
146	H31A	C31	H31C	109.5
147	H31A	C31	C32	109.5
148	H31B	C31	H31C	109.5
149	H31B	C31	C32	109.4
150	H31C	C31	C32	109.5
151	C29	C32	C31	109.9(2)
152	C29	C32	H32	108.0
153	C29	C32	C33	113.0(2)
154	C31	C32	H32	107.9
155	C31	C32	C33	110.0(2)
156	H32	C32	C33	107.9
157	C32	C33	H33A	109.5
158	C32	C33	H33B	109.4
159	C32	C33	H33C	109.5
160	H33A	C33	H33B	109.5
161	H33A	C33	H33C	109.5
162	H33B	C33	H33C	109.4
163	Ni1	C34	N2	120.1(2)
164	Ni1	C34	N3	134.4(2)
165	N2	C34	N3	103.3(2)
166	N2	C35	H35	126.7
167	N2	C35	C36	106.6(2)
168	H35	C35	C36	126.7
169	N3	C36	C35	107.1(2)
170	N3	C36	H36	126.4
171	C35	C36	H36	126.4

X-ray diffraction data for Ni–NHC–IPent

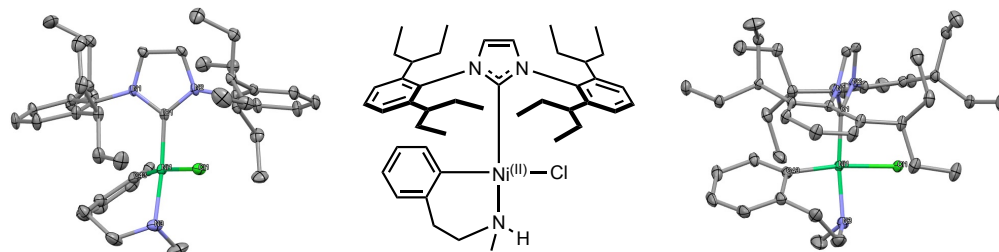


Table A5. Bond lengths for Ni–NHC–IPent (**165**)

Entry	Atom1	Atom2	Length
1	Ni11	Cl11	2.2463(7)
2	Ni11	N13	1.991(3)
3	Ni11	C51	1.887(3)
4	Ni11	C89	1.918(2)
5	N11	C51	1.368(3)
6	N11	C52	1.383(3)
7	N11	C54	1.453(3)
8	N12	C51	1.375(3)
9	N12	C53	1.384(4)
10	N12	C70	1.456(3)
11	N13	H13	0.88(3)
12	N13	C86	1.495(4)
13	N13	C94	1.462(5)
14	C52	H52	0.949
15	C52	C53	1.341(3)
16	C53	H53	0.950
17	C54	C55	1.400(3)
18	C54	C59	1.403(3)
19	C55	C56	1.404(4)
20	C55	C65	1.514(4)
21	C56	H56	0.950
22	C56	C57	1.376(5)
23	C57	H57	0.950
24	C57	C58	1.373(4)
25	C58	H58	0.950
26	C58	C59	1.399(4)
27	C59	C60	1.520(3)
28	C60	H60	1.000
29	C60	C61	1.558(5)

30	C60	C63	1.534(4)
31	C61	H61A	0.990
32	C61	H61B	0.990
33	C61	C62	1.513(6)
34	C62	H62A	0.980
35	C62	H62B	0.980
36	C62	H62C	0.980
37	C63	H63A	0.990
38	C63	H63B	0.990
39	C63	C64	1.524(6)
40	C64	H64A	0.980
41	C64	H64B	0.980
42	C64	H64C	0.980
43	C65	H65	1.000
44	C65	C66	1.550(5)
45	C65	C68	1.538(4)
46	C66	H66A	0.990
47	C66	H66B	0.991
48	C66	C67	1.526(6)
49	C67	H67A	0.980
50	C67	H67B	0.980
51	C67	H67C	0.980
52	C68	H68A	0.990
53	C68	H68B	0.990
54	C68	C69	1.515(6)
55	C69	H69A	0.980
56	C69	H69B	0.980
57	C69	H69C	0.980
58	C70	C71	1.421(3)
59	C70	C75	1.392(4)
60	C71	C72	1.403(4)
61	C71	C79	1.515(5)
62	C72	H72	0.950
63	C72	C73	1.365(6)
64	C73	H73	0.949
65	C73	C74	1.382(5)
66	C74	H74	0.949
67	C74	C75	1.409(4)
68	C75	C76	1.510(4)
69	C76	H76	1.000

70	C76	C77	1.529(6)
71	C76	C84A	1.555(6)
72	C77	H77A	0.990
73	C77	H77B	0.990
74	C77	C78	1.517(6)
75	C78	H78A	0.979
76	C78	H78B	0.980
77	C78	H78C	0.980
78	C79	H79	0.999
79	C79	C80	1.559(5)
80	C79	C82	1.555(4)
81	C80	H80A	0.990
82	C80	H80B	0.989
83	C80	C81	1.481(4)
84	C81	H81A	0.980
85	C81	H81B	0.980
86	C81	H81C	0.980
87	C82	H82A	0.990
88	C82	H82B	0.990
89	C82	C83	1.525(7)
90	C83	H83A	0.980
91	C83	H83B	0.980
92	C83	H83C	0.980
93	C84A	H84C	0.99
94	C84A	H84D	0.990
95	C84A	C85A	1.520(9)
96	C85A	H85D	0.980
97	C85A	H85E	0.980
98	C85A	H85F	0.98
99	C86	H86A	0.990
100	C86	H86B	0.989
101	C86	C87	1.530(4)
102	C87	H87A	0.990
103	C87	H87B	0.990
104	C87	C88	1.501(4)
105	C88	C89	1.415(3)
106	C88	C93	1.399(4)
107	C89	C90	1.393(4)
108	C90	H90	0.950
109	C90	C91	1.387(5)

110	C91	H91	0.950
111	C91	C92	1.388(4)
112	C92	H92	0.949
113	C92	C93	1.380(5)
114	C93	H93	0.950
115	C94	H94A	0.980
116	C94	H94B	0.980
117	C94	H94C	0.980

Table A6. Bond angles for Ni–NHC–IPent (**165**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl1	Ni1	N3	86.82(7)
2	Cl1	Ni1	C1	89.90(7)
3	Cl1	Ni1	C43	170.82(8)
4	N3	Ni1	C1	171.3(1)
5	N3	Ni1	C43	86.3(1)
6	C1	Ni1	C43	97.8(1)
7	C1	N1	C2	112.2(2)
8	C1	N1	C4	126.4(2)
9	C2	N1	C4	120.7(2)
10	C1	N2	C3	111.1(2)
11	C1	N2	C20	130.5(2)
12	C3	N2	C20	118.4(2)
13	Ni1	N3	H3	102(2)
14	Ni1	N3	C36	116.2(2)
15	Ni1	N3	C44	112.6(2)
16	H3	N3	C36	104(2)
17	H3	N3	C44	109(2)
18	C36	N3	C44	112.3(3)
19	Ni1	C1	N1	124.9(2)
20	Ni1	C1	N2	131.4(2)
21	N1	C1	N2	102.8(2)
22	N1	C2	H2	126.8
23	N1	C2	C3	106.5(2)
24	H2	C2	C3	126.8
25	N2	C3	C2	107.5(2)
26	N2	C3	H3A	126.3
27	C2	C3	H3A	126.3
28	N1	C4	C5	118.7(2)
29	N1	C4	C9	117.6(2)

30	C5	C4	C9	123.4(2)
31	C4	C5	C6	116.7(2)
32	C4	C5	C15	122.4(2)
33	C6	C5	C15	120.9(2)
34	C5	C6	H6	119.3
35	C5	C6	C7	121.3(2)
36	H6	C6	C7	119.3
37	C6	C7	H7	119.7
38	C6	C7	C8	120.6(2)
39	H7	C7	C8	119.7
40	C7	C8	H8	119.5
41	C7	C8	C9	121.0(2)
42	H8	C8	C9	119.5
43	C4	C9	C8	116.9(2)
44	C4	C9	C10	124.1(2)
45	C8	C9	C10	119.0(2)
46	C9	C10	H10	107.9
47	C9	C10	C11	110.2(2)
48	C9	C10	C13	110.7(2)
49	H10	C10	C11	107.9
50	H10	C10	C13	107.9
51	C11	C10	C13	112.1(2)
52	C10	C11	H11A	108.5
53	C10	C11	H11B	108.5
54	C10	C11	C12	115.0(2)
55	H11A	C11	H11B	107.5
56	H11A	C11	C12	108.5
57	H11B	C11	C12	108.5
58	C11	C12	H12A	109.4
59	C11	C12	H12B	109.5
60	C11	C12	H12C	109.5
61	H12A	C12	H12B	109.5
62	H12A	C12	H12C	109.5
63	H12B	C12	H12C	109.5
64	C10	C13	H13A	108.6
65	C10	C13	H13B	108.6
66	C10	C13	C14	114.5(3)
67	H13A	C13	H13B	107.6
68	H13A	C13	C14	108.6
69	H13B	C13	C14	108.7

70	C13	C14	H14A	109.5
71	C13	C14	H14B	109.5
72	C13	C14	H14C	109.5
73	H14A	C14	H14B	109.4
74	H14A	C14	H14C	109.4
75	H14B	C14	H14C	109.5
76	C5	C15	H15	106.8
77	C5	C15	C16	112.2(2)
78	C5	C15	C18	112.3(2)
79	H15	C15	C16	106.9
80	H15	C15	C18	106.8
81	C16	C15	C18	111.4(2)
82	C15	C16	H16A	108.4
83	C15	C16	H16B	108.3
84	C15	C16	C17	115.9(2)
85	H16A	C16	H16B	107.4
86	H16A	C16	C17	108.3
87	H16B	C16	C17	108.3
88	C16	C17	H17A	109.5
89	C16	C17	H17B	109.5
90	C16	C17	H17C	109.5
91	H17A	C17	H17B	109.4
92	H17A	C17	H17C	109.5
93	H17B	C17	H17C	109.5
94	C15	C18	H18A	108.8
95	C15	C18	H18B	108.8
96	C15	C18	C19	113.8(2)
97	H18A	C18	H18B	107.7
98	H18A	C18	C19	108.8
99	H18B	C18	C19	108.9
100	C18	C19	H19A	109.4
101	C18	C19	H19B	109.4
102	C18	C19	H19C	109.4
103	H19A	C19	H19B	109.5
104	H19A	C19	H19C	109.5
105	H19B	C19	H19C	109.5
106	N2	C20	C21	118.5(2)
107	N2	C20	C25	118.8(2)
108	C21	C20	C25	122.3(2)
109	C20	C21	C22	116.8(2)

110	C20	C21	C26	123.5(2)
111	C22	C21	C26	119.7(2)
112	C21	C22	H22	119.1
113	C21	C22	C23	121.8(2)
114	H22	C22	C23	119.1
115	C22	C23	H23	120.0
116	C22	C23	C24	120.1(2)
117	H23	C23	C24	120.0
118	C23	C24	H24	119.6
119	C23	C24	C25	120.9(2)
120	H24	C24	C25	119.5
121	C20	C25	C24	118.1(2)
122	C20	C25	C31A	119.9(2)
123	C24	C25	C31A	121.7(2)
124	C21	C26	H26	107.7
125	C21	C26	C27	111.2(2)
126	C21	C26	C29	110.5(2)
127	H26	C26	C27	107.7
128	H26	C26	C29	107.7
129	C27	C26	C29	111.9(2)
130	C26	C27	H27A	108.4
131	C26	C27	H27B	108.5
132	C26	C27	C28	115.3(2)
133	H27A	C27	H27B	107.5
134	H27A	C27	C28	108.4
135	H27B	C27	C28	108.4
136	C27	C28	H28A	109.5
137	C27	C28	H28B	109.4
138	C27	C28	H28C	109.5
139	H28A	C28	H28B	109.5
140	H28A	C28	H28C	109.5
141	H28B	C28	H28C	109.4
142	C26	C29	H29A	108.6
143	C26	C29	H29B	108.6
144	C26	C29	C30	114.6(3)
145	H29A	C29	H29B	107.5
146	H29A	C29	C30	108.7
147	H29B	C29	C30	108.7
148	C29	C30	H30A	109.5
149	C29	C30	H30B	109.5

150	C29	C30	H30C	109.5
151	H30A	C30	H30B	109.5
152	H30A	C30	H30C	109.4
153	H30B	C30	H30C	109.5
154	C25	C31A	H31A	107.3
155	C25	C31A	C32A	110.7(3)
156	C25	C31A	C34A	111.8(3)
157	H31A	C31A	C32A	107.3
158	H31A	C31A	C34A	107.3
159	C32A	C31A	C34A	112.2(3)
160	C31A	C32A	H32C	108.9
161	C31A	C32A	H32D	108.8
162	C31A	C32A	C33A	113.6(4)
163	H32C	C32A	H32D	107.7
164	H32C	C32A	C33A	108.8
165	H32D	C32A	C33A	108.8
166	C32A	C33A	H33A	109.5
167	C32A	C33A	H33B	109.5
168	C32A	C33A	H33C	109.5
169	H33A	C33A	H33B	109.4
170	H33A	C33A	H33C	109.5
171	H33B	C33A	H33C	109.5
172	C31A	C34A	H34A	108.8
173	C31A	C34A	H34B	108.8
174	C31A	C34A	C35A	114.0(4)
175	H34A	C34A	H34B	107.6
176	H34A	C34A	C35A	108.7
177	H34B	C34A	C35A	108.8
178	C34A	C35A	H35A	109.5
179	C34A	C35A	H35B	109.5
180	C34A	C35A	H35C	109.5
181	H35A	C35A	H35B	109.5
182	H35A	C35A	H35C	109.5
183	H35B	C35A	H35C	109.4
184	N3	C36	H36A	109.1
185	N3	C36	H36B	109.1
186	N3	C36	C37	112.6(3)
187	H36A	C36	H36B	107.8
188	H36A	C36	C37	109.0
189	H36B	C36	C37	109.1

190	C36	C37	H37A	109.6
191	C36	C37	H37B	109.6
192	C36	C37	C38	110.3(3)
193	H37A	C37	H37B	108.2
194	H37A	C37	C38	109.5
195	H37B	C37	C38	109.5
196	C37	C38	C39	121.0(2)
197	C37	C38	C43	118.1(2)
198	C39	C38	C43	120.6(2)
199	C38	C39	H39	119.4
200	C38	C39	C40	121.4(3)
201	H39	C39	C40	119.3
202	C39	C40	H40	120.5
203	C39	C40	C41	118.9(3)
204	H40	C40	C41	120.5
205	C40	C41	H41	119.8
206	C40	C41	C42	120.4(3)
207	H41	C41	C42	119.8
208	C41	C42	H42	119.1
209	C41	C42	C43	121.9(2)
210	H42	C42	C43	119.0
211	Ni1	C43	C38	117.6(2)
212	Ni1	C43	C42	124.2(2)
213	C38	C43	C42	116.8(2)
214	N3	C44	H44A	109.5
215	N3	C44	H44B	109.5
216	N3	C44	H44C	109.5
217	H44A	C44	H44B	109.5
218	H44A	C44	H44C	109.5
219	H44B	C44	H44C	109.5
220	Cl11	Ni11	N13	86.82(7)
221	Cl11	Ni11	C51	91.79(8)
222	Cl11	Ni11	C89	172.46(8)
223	N13	Ni11	C51	175.3(1)
224	N13	Ni11	C89	86.5(1)
225	C51	Ni11	C89	95.2(1)
226	C51	N11	C52	111.8(2)
227	C51	N11	C54	125.5(2)
228	C52	N11	C54	122.2(2)
229	C51	N12	C53	111.4(2)

230	C51	N12	C70	128.9(2)
231	C53	N12	C70	119.0(2)
232	Ni11	N13	H13	105(2)
233	Ni11	N13	C86	114.5(2)
234	Ni11	N13	C94	114.5(2)
235	H13	N13	C86	106(2)
236	H13	N13	C94	104(2)
237	C86	N13	C94	112.3(2)
238	Ni11	C51	N11	125.8(2)
239	Ni11	C51	N12	131.2(2)
240	N11	C51	N12	103.0(2)
241	N11	C52	H52	126.6
242	N11	C52	C53	106.8(2)
243	H52	C52	C53	126.6
244	N12	C53	C52	107.0(2)
245	N12	C53	H53	126.5
246	C52	C53	H53	126.5
247	N11	C54	C55	118.7(2)
248	N11	C54	C59	117.8(2)
249	C55	C54	C59	123.3(2)
250	C54	C55	C56	116.8(2)
251	C54	C55	C65	123.4(2)
252	C56	C55	C65	119.8(2)
253	C55	C56	H56	119.5
254	C55	C56	C57	120.9(3)
255	H56	C56	C57	119.5
256	C56	C57	H57	119.6
257	C56	C57	C58	120.8(3)
258	H57	C57	C58	119.6
259	C57	C58	H58	119.3
260	C57	C58	C59	121.5(3)
261	H58	C58	C59	119.3
262	C54	C59	C58	116.5(2)
263	C54	C59	C60	122.9(2)
264	C58	C59	C60	120.4(2)
265	C59	C60	H60	107.4
266	C59	C60	C61	110.3(2)
267	C59	C60	C63	113.9(2)
268	H60	C60	C61	107.3
269	H60	C60	C63	107.4

270	C61	C60	C63	110.2(3)
271	C60	C61	H61A	108.2
272	C60	C61	H61B	108.2
273	C60	C61	C62	116.2(3)
274	H61A	C61	H61B	107.4
275	H61A	C61	C62	108.3
276	H61B	C61	C62	108.3
277	C61	C62	H62A	109.5
278	C61	C62	H62B	109.5
279	C61	C62	H62C	109.5
280	H62A	C62	H62B	109.5
281	H62A	C62	H62C	109.5
282	H62B	C62	H62C	109.5
283	C60	C63	H63A	108.7
284	C60	C63	H63B	108.7
285	C60	C63	C64	114.3(3)
286	H63A	C63	H63B	107.6
287	H63A	C63	C64	108.7
288	H63B	C63	C64	108.7
289	C63	C64	H64A	109.5
290	C63	C64	H64B	109.4
291	C63	C64	H64C	109.5
292	H64A	C64	H64B	109.5
293	H64A	C64	H64C	109.5
294	H64B	C64	H64C	109.5
295	C55	C65	H65	106.9
296	C55	C65	C66	111.5(2)
297	C55	C65	C68	112.3(2)
298	H65	C65	C66	106.9
299	H65	C65	C68	106.9
300	C66	C65	C68	111.9(2)
301	C65	C66	H66A	108.1
302	C65	C66	H66B	108.1
303	C65	C66	C67	116.7(3)
304	H66A	C66	H66B	107.3
305	H66A	C66	C67	108.2
306	H66B	C66	C67	108.1
307	C66	C67	H67A	109.4
308	C66	C67	H67B	109.4
309	C66	C67	H67C	109.5

310	H67A	C67	H67B	109.5
311	H67A	C67	H67C	109.5
312	H67B	C67	H67C	109.5
313	C65	C68	H68A	109.0
314	C65	C68	H68B	109.0
315	C65	C68	C69	113.2(3)
316	H68A	C68	H68B	107.7
317	H68A	C68	C69	108.9
318	H68B	C68	C69	108.9
319	C68	C69	H69A	109.5
320	C68	C69	H69B	109.5
321	C68	C69	H69C	109.5
322	H69A	C69	H69B	109.4
323	H69A	C69	H69C	109.5
324	H69B	C69	H69C	109.4
325	N12	C70	C71	117.2(2)
326	N12	C70	C75	118.8(2)
327	C71	C70	C75	123.8(2)
328	C70	C71	C72	115.8(3)
329	C70	C71	C79	124.0(2)
330	C72	C71	C79	120.2(3)
331	C71	C72	H72	119.1
332	C71	C72	C73	121.9(3)
333	H72	C72	C73	119.1
334	C72	C73	H73	119.5
335	C72	C73	C74	121.0(3)
336	H73	C73	C74	119.5
337	C73	C74	H74	119.6
338	C73	C74	C75	120.8(3)
339	H74	C74	C75	119.6
340	C70	C75	C74	116.8(3)
341	C70	C75	C76	122.4(3)
342	C74	C75	C76	120.7(3)
343	C75	C76	H76	108.2
344	C75	C76	C77	114.0(3)
345	C75	C76	C84A	106.9(4)
346	H76	C76	C77	108.1
347	H76	C76	C84A	108.2
348	C77	C76	C84A	111.2(4)
349	C76	C77	H77A	108.6

350	C76	C77	H77B	108.6
351	C76	C77	C78	114.8(3)
352	H77A	C77	H77B	107.5
353	H77A	C77	C78	108.5
354	H77B	C77	C78	108.6
355	C77	C78	H78A	109.5
356	C77	C78	H78B	109.4
357	C77	C78	H78C	109.4
358	H78A	C78	H78B	109.5
359	H78A	C78	H78C	109.5
360	H78B	C78	H78C	109.4
361	C71	C79	H79	106.3
362	C71	C79	C80	114.5(2)
363	C71	C79	C82	112.5(2)
364	H79	C79	C80	106.3
365	H79	C79	C82	106.3
366	C80	C79	C82	110.4(3)
367	C79	C80	H80A	108.1
368	C79	C80	H80B	108.1
369	C79	C80	C81	116.6(3)
370	H80A	C80	H80B	107.4
371	H80A	C80	C81	108.1
372	H80B	C80	C81	108.2
373	C80	C81	H81A	109.4
374	C80	C81	H81B	109.5
375	C80	C81	H81C	109.5
376	H81A	C81	H81B	109.5
377	H81A	C81	H81C	109.5
378	H81B	C81	H81C	109.5
379	C79	C82	H82A	108.7
380	C79	C82	H82B	108.8
381	C79	C82	C83	114.0(3)
382	H82A	C82	H82B	107.7
383	H82A	C82	C83	108.8
384	H82B	C82	C83	108.8
385	C82	C83	H83A	109.5
386	C82	C83	H83B	109.4
387	C82	C83	H83C	109.5
388	H83A	C83	H83B	109.5
389	H83A	C83	H83C	109.5

390	H83B	C83	H83C	109.5
391	C76	C84A	H84C	108.9
392	C76	C84A	H84D	108.9
393	C76	C84A	C85A	113.4(6)
394	H84C	C84A	H84D	107.7
395	H84C	C84A	C85A	108.9
396	H84D	C84A	C85A	108.8
397	C84A	C85A	H85D	109.4
398	C84A	C85A	H85E	109.4
399	C84A	C85A	H85F	109.5
400	H85D	C85A	H85E	109.4
401	H85D	C85A	H85F	109.5
402	H85E	C85A	H85F	109.5
403	N13	C86	H86A	109.2
404	N13	C86	H86B	109.2
405	N13	C86	C87	112.1(3)
406	H86A	C86	H86B	107.9
407	H86A	C86	C87	109.1
408	H86B	C86	C87	109.2
409	C86	C87	H87A	109.6
410	C86	C87	H87B	109.6
411	C86	C87	C88	110.5(3)
412	H87A	C87	H87B	108.1
413	H87A	C87	C88	109.6
414	H87B	C87	C88	109.6
415	C87	C88	C89	117.9(2)
416	C87	C88	C93	121.6(3)
417	C89	C88	C93	120.3(2)
418	Ni11	C89	C88	116.7(2)
419	Ni11	C89	C90	125.2(2)
420	C88	C89	C90	116.6(2)
421	C89	C90	H90	118.6
422	C89	C90	C91	122.8(3)
423	H90	C90	C91	118.6
424	C90	C91	H91	120.1
425	C90	C91	C92	120.0(3)
426	H91	C91	C92	119.9
427	C91	C92	H92	120.7
428	C91	C92	C93	118.7(3)
429	H92	C92	C93	120.6

430	C88	C93	C92	121.5(3)
431	C88	C93	H93	119.3
432	C92	C93	H93	119.2
433	N13	C94	H94A	109.5
434	N13	C94	H94B	109.5
435	N13	C94	H94C	109.5
436	H94A	C94	H94B	109.4
437	H94A	C94	H94C	109.4
438	H94B	C94	H94C	109.5

X-ray diffraction data for Ni–NHC–IPr*OMe

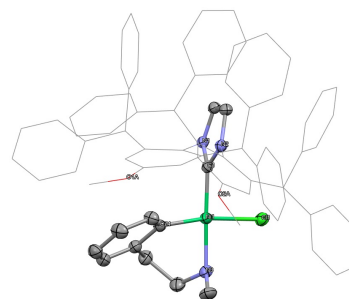
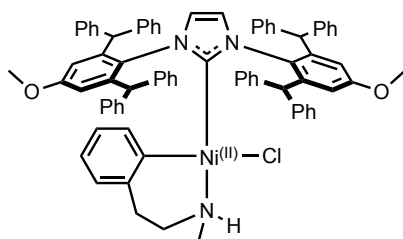
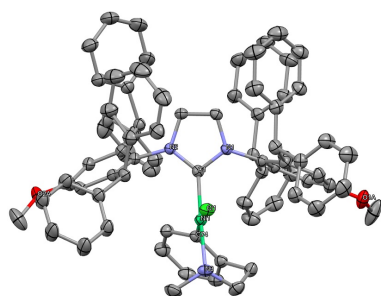


Table A7. Bond lengths for Ni–NHC–IPr*OMe (**181**)

Entry	Atom1	Atom2	Length
1	Ni1	Cl1	2.2957(7)
2	Ni1	N3	1.989(2)
3	Ni1	C1	1.905(2)
4	Ni1	C74	1.893(2)
5	O1A	C7	1.366(4)
6	O1A	C36A	1.408(7)
7	O2A	C40	1.386(4)
8	O2A	C69A	1.418(6)
9	N1	C1	1.367(3)
10	N1	C3	1.387(3)
11	N1	C4	1.450(3)
12	N2	C1	1.375(3)
13	N2	C2	1.397(3)
14	N2	C37	1.453(3)
15	N3	H3	0.93(2)
16	N3	C70	1.471(4)
17	N3	C71	1.478(4)

18	C2	H2	0.950
19	C2	C3	1.332(3)
20	C3	H3A	0.950
21	C4	C5	1.400(3)
22	C4	C9	1.405(3)
23	C5	C6	1.390(3)
24	C5	C23	1.533(3)
25	C6	H6	0.950
26	C6	C7	1.397(3)
27	C7	C8	1.381(4)
28	C8	H8	0.950
29	C8	C9	1.392(4)
30	C9	C10	1.519(4)
31	C10	H10	1.000
32	C10	C11	1.521(4)
33	C10	C17	1.545(7)
34	C11	C12	1.394(4)
35	C11	C16	1.382(4)
36	C12	H12	0.950
37	C12	C13	1.382(5)
38	C13	H13	0.950
39	C13	C14	1.369(5)
40	C14	H14	0.949
41	C14	C15	1.378(6)
42	C15	H15	0.950
43	C15	C16	1.381(6)
44	C16	H16	0.950
45	C17	C18	1.39(1)
46	C17	C22	1.38(1)
47	C18	H18	0.95
48	C18	C19	1.39(2)
49	C19	H19	0.95
50	C19	C20	1.38(2)
51	C20	H20	0.950
52	C20	C21	1.370(9)
53	C21	H21	0.949
54	C21	C22	1.388(8)
55	C22	H22	0.950
56	C23	H23	1.000
57	C23	C24	1.532(3)

58	C23	C30	1.535(4)
59	C24	C25	1.389(4)
60	C24	C29	1.383(3)
61	C25	H25	0.950
62	C25	C26	1.396(4)
63	C26	H26	0.950
64	C26	C27	1.379(4)
65	C27	H27	0.950
66	C27	C28	1.367(5)
67	C28	H28	0.950
68	C28	C29	1.386(4)
69	C29	H29	0.950
70	C30	C31	1.384(4)
71	C30	C35	1.387(3)
72	C31	H31	0.950
73	C31	C32	1.393(5)
74	C32	H32	0.950
75	C32	C33	1.359(5)
76	C33	H33	0.950
77	C33	C34	1.377(5)
78	C34	H34	0.950
79	C34	C35	1.385(4)
80	C35	H35	0.950
81	C36A	H36D	0.981
82	C36A	H36E	0.980
83	C36A	H36F	0.979
84	C37	C38	1.404(3)
85	C37	C42	1.396(3)
86	C38	C39	1.394(3)
87	C38	C56	1.522(3)
88	C39	H39	0.950
89	C39	C40	1.375(4)
90	C40	C41	1.381(4)
91	C41	H41	0.950
92	C41	C42	1.408(4)
93	C42	C43	1.522(3)
94	C43	H43	1.000
95	C43	C44	1.533(4)
96	C43	C50	1.526(4)
97	C44	C45	1.375(5)

98	C44	C49	1.398(5)
99	C45	H45	0.950
100	C45	C46	1.386(8)
101	C46	H46	0.950
102	C46	C47	1.388(7)
103	C47	H47	0.951
104	C47	C48	1.367(6)
105	C48	H48	0.950
106	C48	C49	1.383(5)
107	C49	H49	0.950
108	C50	C51	1.393(4)
109	C50	C55	1.384(5)
110	C51	H51	0.950
111	C51	C52	1.387(6)
112	C52	H52	0.949
113	C52	C53	1.384(7)
114	C53	H53	0.949
115	C53	C54	1.360(6)
116	C54	H54	0.950
117	C54	C55	1.383(6)
118	C55	H55	0.950
119	C56	H56	1.000
120	C56	C57	1.537(4)
121	C56	C63	1.535(3)
122	C57	C58	1.382(4)
123	C57	C62	1.381(4)
124	C58	H58	0.950
125	C58	C59	1.398(5)
126	C59	H59	0.950
127	C59	C60	1.356(5)
128	C60	H60	0.950
129	C60	C61	1.365(6)
130	C61	H61	0.950
131	C61	C62	1.392(7)
132	C62	H62	0.951
133	C63	C64	1.375(4)
134	C63	C68	1.384(4)
135	C64	H64	0.950
136	C64	C65	1.382(4)
137	C65	H65	0.950

138	C65	C66	1.381(5)
139	C66	H66	0.950
140	C66	C67	1.354(6)
141	C67	H67	0.950
142	C67	C68	1.393(5)
143	C68	H68	0.950
144	C69A	H69A	0.980
145	C69A	H69B	0.980
146	C69A	H69C	0.980
147	C70	H70A	0.980
148	C70	H70B	0.980
149	C70	H70C	0.980
150	C71	H71A	0.990
151	C71	H71B	0.990
152	C71	C72	1.529(4)
153	C72	H72A	0.990
154	C72	H72B	0.990
155	C72	C73	1.503(3)
156	C73	C74	1.406(4)
157	C73	C78	1.394(4)
158	C74	C75	1.395(3)
159	C75	H75	0.950
160	C75	C76	1.391(4)
161	C76	H76	0.950
162	C76	C77	1.380(5)
163	C77	H77	0.950
164	C77	C78	1.378(4)
165	C78	H78	0.950

Table A8. Bond angles for Ni–NHC–IPr*^{OMe} (**181**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl1	Ni1	N3	84.40(7)
2	Cl1	Ni1	C1	92.66(7)
3	Cl1	Ni1	C74	170.65(7)
4	N3	Ni1	C1	176.5(1)
5	N3	Ni1	C74	86.24(9)
6	C1	Ni1	C74	96.7(1)
7	C7	O1A	C36A	116.5(3)
8	C40	O2A	C69A	116.8(3)
9	C1	N1	C3	111.4(2)

10	C1	N1	C4	123.9(2)
11	C3	N1	C4	124.0(2)
12	C1	N2	C2	110.7(2)
13	C1	N2	C37	125.2(2)
14	C2	N2	C37	123.0(2)
15	Ni1	N3	H3	102(2)
16	Ni1	N3	C70	113.3(2)
17	Ni1	N3	C71	115.2(2)
18	H3	N3	C70	109(2)
19	H3	N3	C71	104(2)
20	C70	N3	C71	112.3(2)
21	Ni1	C1	N1	123.5(2)
22	Ni1	C1	N2	131.3(2)
23	N1	C1	N2	103.5(2)
24	N2	C2	H2	126.5
25	N2	C2	C3	107.0(2)
26	H2	C2	C3	126.5
27	N1	C3	C2	107.3(2)
28	N1	C3	H3A	126.4
29	C2	C3	H3A	126.4
30	N1	C4	C5	118.1(2)
31	N1	C4	C9	120.3(2)
32	C5	C4	C9	121.4(2)
33	C4	C5	C6	119.2(2)
34	C4	C5	C23	120.6(2)
35	C6	C5	C23	119.4(2)
36	C5	C6	H6	120.3
37	C5	C6	C7	119.4(2)
38	H6	C6	C7	120.3
39	O1A	C7	C6	124.4(3)
40	O1A	C7	C8	115.0(3)
41	C6	C7	C8	120.6(2)
42	C7	C8	H8	119.4
43	C7	C8	C9	121.3(2)
44	H8	C8	C9	119.3
45	C4	C9	C8	117.5(2)
46	C4	C9	C10	121.7(2)
47	C8	C9	C10	120.6(2)
48	C9	C10	H10	108.6
49	C9	C10	C11	110.8(2)

50	C9	C10	C17	109.8(3)
51	H10	C10	C11	108.6
52	H10	C10	C17	108.6
53	C11	C10	C17	110.3(3)
54	C10	C11	C12	123.1(2)
55	C10	C11	C16	119.3(2)
56	C12	C11	C16	117.5(3)
57	C11	C12	H12	119.6
58	C11	C12	C13	120.8(3)
59	H12	C12	C13	119.6
60	C12	C13	H13	119.5
61	C12	C13	C14	121.1(3)
62	H13	C13	C14	119.5
63	C13	C14	H14	120.6
64	C13	C14	C15	118.7(4)
65	H14	C14	C15	120.7
66	C14	C15	H15	119.6
67	C14	C15	C16	120.7(4)
68	H15	C15	C16	119.7
69	C11	C16	C15	121.3(3)
70	C11	C16	H16	119.3
71	C15	C16	H16	119.3
72	C10	C17	C18	118.3(7)
73	C10	C17	C22	123.5(6)
74	C18	C17	C22	118.0(8)
75	C17	C18	H18	120
76	C17	C18	C19	121(1)
77	H18	C18	C19	120
78	C18	C19	H19	120
79	C18	C19	C20	120(1)
80	H19	C19	C20	120
81	C19	C20	H20	120.4
82	C19	C20	C21	119.2(8)
83	H20	C20	C21	120.4
84	C20	C21	H21	119.8
85	C20	C21	C22	120.4(6)
86	H21	C21	C22	119.7
87	C17	C22	C21	121.2(6)
88	C17	C22	H22	119.4
89	C21	C22	H22	119.4

90	C5	C23	H23	107.2
91	C5	C23	C24	115.4(2)
92	C5	C23	C30	109.9(2)
93	H23	C23	C24	107.2
94	H23	C23	C30	107.2
95	C24	C23	C30	109.6(2)
96	C23	C24	C25	119.7(2)
97	C23	C24	C29	122.1(2)
98	C25	C24	C29	118.2(2)
99	C24	C25	H25	119.8
100	C24	C25	C26	120.4(3)
101	H25	C25	C26	119.8
102	C25	C26	H26	119.8
103	C25	C26	C27	120.4(3)
104	H26	C26	C27	119.8
105	C26	C27	H27	120.3
106	C26	C27	C28	119.3(3)
107	H27	C27	C28	120.3
108	C27	C28	H28	119.7
109	C27	C28	C29	120.6(3)
110	H28	C28	C29	119.7
111	C24	C29	C28	121.1(3)
112	C24	C29	H29	119.5
113	C28	C29	H29	119.5
114	C23	C30	C31	123.0(2)
115	C23	C30	C35	119.1(2)
116	C31	C30	C35	117.9(2)
117	C30	C31	H31	119.7
118	C30	C31	C32	120.6(3)
119	H31	C31	C32	119.7
120	C31	C32	H32	119.5
121	C31	C32	C33	120.9(3)
122	H32	C32	C33	119.6
123	C32	C33	H33	120.3
124	C32	C33	C34	119.4(3)
125	H33	C33	C34	120.4
126	C33	C34	H34	119.9
127	C33	C34	C35	120.3(3)
128	H34	C34	C35	119.8
129	C30	C35	C34	121.1(3)

130	C30	C35	H35	119.5
131	C34	C35	H35	119.5
132	O1A	C36A	H36D	109.4
133	O1A	C36A	H36E	109.5
134	O1A	C36A	H36F	109.5
135	H36D	C36A	H36E	109.4
136	H36D	C36A	H36F	109.5
137	H36E	C36A	H36F	109.5
138	N2	C37	C38	119.4(2)
139	N2	C37	C42	119.9(2)
140	C38	C37	C42	120.7(2)
141	C37	C38	C39	118.9(2)
142	C37	C38	C56	122.4(2)
143	C39	C38	C56	118.3(2)
144	C38	C39	H39	119.7
145	C38	C39	C40	120.5(2)
146	H39	C39	C40	119.7
147	O2A	C40	C39	114.0(3)
148	O2A	C40	C41	125.7(3)
149	C39	C40	C41	120.3(3)
150	C40	C41	H41	119.6
151	C40	C41	C42	120.8(3)
152	H41	C41	C42	119.6
153	C37	C42	C41	118.0(2)
154	C37	C42	C43	119.8(2)
155	C41	C42	C43	122.0(2)
156	C42	C43	H43	107.2
157	C42	C43	C44	112.9(2)
158	C42	C43	C50	110.8(2)
159	H43	C43	C44	107.2
160	H43	C43	C50	107.2
161	C44	C43	C50	111.2(2)
162	C43	C44	C45	120.4(3)
163	C43	C44	C49	120.9(3)
164	C45	C44	C49	118.6(3)
165	C44	C45	H45	119.3
166	C44	C45	C46	121.3(5)
167	H45	C45	C46	119.3
168	C45	C46	H46	120.3
169	C45	C46	C47	119.2(5)

170	H46	C46	C47	120.4
171	C46	C47	H47	120.0
172	C46	C47	C48	120.1(4)
173	H47	C47	C48	119.9
174	C47	C48	H48	119.7
175	C47	C48	C49	120.6(4)
176	H48	C48	C49	119.7
177	C44	C49	C48	120.1(3)
178	C44	C49	H49	120.0
179	C48	C49	H49	119.9
180	C43	C50	C51	119.9(3)
181	C43	C50	C55	122.1(3)
182	C51	C50	C55	118.0(3)
183	C50	C51	H51	119.8
184	C50	C51	C52	120.5(3)
185	H51	C51	C52	119.8
186	C51	C52	H52	119.9
187	C51	C52	C53	120.3(4)
188	H52	C52	C53	119.8
189	C52	C53	H53	120.2
190	C52	C53	C54	119.6(4)
191	H53	C53	C54	120.2
192	C53	C54	H54	119.7
193	C53	C54	C55	120.5(4)
194	H54	C54	C55	119.8
195	C50	C55	C54	121.2(3)
196	C50	C55	H55	119.4
197	C54	C55	H55	119.4
198	C38	C56	H56	107.1
199	C38	C56	C57	109.5(2)
200	C38	C56	C63	112.9(2)
201	H56	C56	C57	107.1
202	H56	C56	C63	107.1
203	C57	C56	C63	112.8(2)
204	C56	C57	C58	123.4(2)
205	C56	C57	C62	119.2(2)
206	C58	C57	C62	117.3(3)
207	C57	C58	H58	119.2
208	C57	C58	C59	121.6(3)
209	H58	C58	C59	119.2

210	C58	C59	H59	120.1
211	C58	C59	C60	119.9(3)
212	H59	C59	C60	120.1
213	C59	C60	H60	120.2
214	C59	C60	C61	119.6(4)
215	H60	C60	C61	120.2
216	C60	C61	H61	119.7
217	C60	C61	C62	120.8(4)
218	H61	C61	C62	119.5
219	C57	C62	C61	120.8(3)
220	C57	C62	H62	119.6
221	C61	C62	H62	119.6
222	C56	C63	C64	118.7(2)
223	C56	C63	C68	122.8(2)
224	C64	C63	C68	118.5(3)
225	C63	C64	H64	119.6
226	C63	C64	C65	120.8(3)
227	H64	C64	C65	119.6
228	C64	C65	H65	120.0
229	C64	C65	C66	120.0(3)
230	H65	C65	C66	120.0
231	C65	C66	H66	120.1
232	C65	C66	C67	119.8(3)
233	H66	C66	C67	120.1
234	C66	C67	H67	119.9
235	C66	C67	C68	120.4(4)
236	H67	C67	C68	119.8
237	C63	C68	C67	120.5(3)
238	C63	C68	H68	119.8
239	C67	C68	H68	119.8
240	O2A	C69A	H69A	109.5
241	O2A	C69A	H69B	109.5
242	O2A	C69A	H69C	109.5
243	H69A	C69A	H69B	109.5
244	H69A	C69A	H69C	109.5
245	H69B	C69A	H69C	109.5
246	N3	C70	H70A	109.5
247	N3	C70	H70B	109.5
248	N3	C70	H70C	109.5
249	H70A	C70	H70B	109.5

250	H70A	C70	H70C	109.5
251	H70B	C70	H70C	109.5
252	N3	C71	H71A	109.4
253	N3	C71	H71B	109.4
254	N3	C71	C72	111.3(2)
255	H71A	C71	H71B	108.0
256	H71A	C71	C72	109.4
257	H71B	C71	C72	109.4
258	C71	C72	H72A	109.7
259	C71	C72	H72B	109.7
260	C71	C72	C73	109.6(2)
261	H72A	C72	H72B	108.2
262	H72A	C72	C73	109.8
263	H72B	C72	C73	109.7
264	C72	C73	C74	118.0(2)
265	C72	C73	C78	121.7(2)
266	C74	C73	C78	120.1(2)
267	Ni1	C74	C73	116.0(2)
268	Ni1	C74	C75	125.0(2)
269	C73	C74	C75	117.9(2)
270	C74	C75	H75	119.3
271	C74	C75	C76	121.4(2)
272	H75	C75	C76	119.3
273	C75	C76	H76	120.0
274	C75	C76	C77	120.1(3)
275	H76	C76	C77	119.9
276	C76	C77	H77	120.2
277	C76	C77	C78	119.5(3)
278	H77	C77	C78	120.2
279	C73	C78	C77	121.0(3)
280	C73	C78	H78	119.5
281	C77	C78	H78	119.5
282	C112	O111	C115	116(1)
283	O111	C112	H11A	112
284	O111	C112	H11B	112
285	O111	C112	C113	100(2)
286	H11A	C112	H11B	110
287	H11A	C112	C113	112
288	H11B	C112	C113	112
289	C112	C113	H11C	112

290	C112	C113	H11D	111
291	C112	C113	C114	101(2)
292	H11C	C113	H11D	109
293	H11C	C113	C114	112
294	H11D	C113	C114	112
295	C113	C114	H11E	111
296	C113	C114	H11F	111
297	C113	C114	C115	102(2)
298	H11E	C114	H11F	109
299	H11E	C114	C115	111
300	H11F	C114	C115	111
301	O111	C115	C114	98(1)
302	O111	C115	H11G	112
303	O111	C115	H11H	112
304	C114	C115	H11G	112
305	C114	C115	H11H	112
306	H11G	C115	H11H	110
307	H13A	C131	H13B	109
308	H13A	C131	H13C	109
309	H13A	C131	C132	109
310	H13B	C131	H13C	110
311	H13B	C131	C132	110
312	H13C	C131	C132	109
313	C131	C132	H13D	110
314	C131	C132	H13E	110
315	C131	C132	C133	109(2)
316	H13D	C132	H13E	108
317	H13D	C132	C133	110
318	H13E	C132	C133	110
319	C132	C133	H13F	105
320	C132	C133	H13G	105
321	C132	C133	C134	131(2)
322	H13F	C133	H13G	106
323	H13F	C133	C134	105
324	H13G	C133	C134	105
325	C133	C134	H13H	108
326	C133	C134	H13I	108
327	C133	C134	C135	119(2)
328	H13H	C134	H13I	107
329	H13H	C134	C135	108

330	H13I	C134	C135	108
331	C134	C135	H13J	110
332	C134	C135	H13K	109
333	C134	C135	H13L	109
334	H13J	C135	H13K	110
335	H13J	C135	H13L	110
336	H13K	C135	H13L	109

X-ray diffraction data for Ni–NHC–IPr^{Cl}

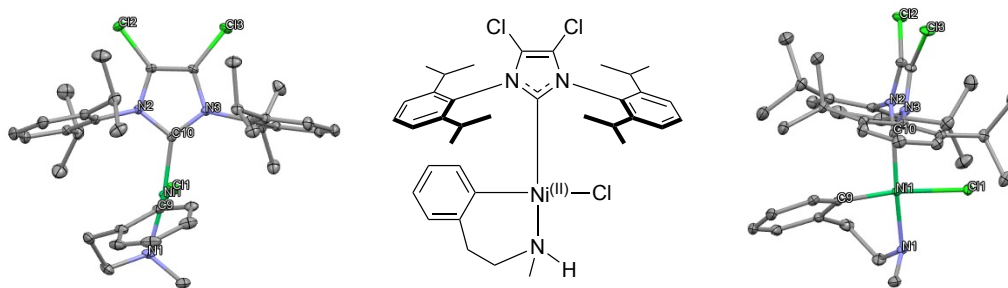


Table A9. Bond lengths for Ni–NHC–IPr^{Cl} (**188**)

Entry	Atom1	Atom2	Length
1	Ni1	Cl1	2.2624(6)
2	Ni1	N1	1.977(2)
3	Ni1	C9	1.892(2)
4	Ni1	C10	1.894(2)
5	Cl2	C23	1.694(2)
6	Cl3	C24	1.698(2)
7	N1	H1	1.000
8	N1	C1	1.480(3)
9	N1	C2	1.499(3)
10	N2	C10	1.373(2)
11	N2	C11	1.455(2)
12	N2	C23	1.390(2)
13	N3	C10	1.376(2)
14	N3	C24	1.396(2)
15	N3	C25	1.457(2)
16	C1	H1A	0.980
17	C1	H1B	0.980
18	C1	H1C	0.980
19	C2	H2A	0.990
20	C2	H2AB	0.990

21	C2	C3	1.530(3)
22	C3	H3A	0.990
23	C3	H3AB	0.990
24	C3	C4	1.503(3)
25	C4	C5	1.398(3)
26	C4	C9	1.408(3)
27	C5	H5	0.949
28	C5	C6	1.385(4)
29	C6	H6	0.950
30	C6	C7	1.383(3)
31	C7	H7	0.950
32	C7	C8	1.396(3)
33	C8	H8	0.950
34	C8	C9	1.393(3)
35	C11	C12	1.398(3)
36	C11	C19	1.406(3)
37	C12	C13	1.520(3)
38	C12	C16	1.404(3)
39	C13	H13	1.000
40	C13	C14	1.533(3)
41	C13	C15	1.529(3)
42	C14	H14A	0.980
43	C14	H14B	0.980
44	C14	H14C	0.979
45	C15	H15A	0.980
46	C15	H15B	0.980
47	C15	H15C	0.980
48	C16	H16	0.950
49	C16	C17	1.382(3)
50	C17	H17	0.950
51	C17	C18	1.376(3)
52	C18	H18	0.950
53	C18	C19	1.397(3)
54	C19	C20	1.521(3)
55	C20	H20	1.000
56	C20	C21	1.528(3)
57	C20	C22	1.538(3)
58	C21	H21A	0.979
59	C21	H21B	0.980
60	C21	H21C	0.980

61	C22	H22A	0.980
62	C22	H22B	0.980
63	C22	H22C	0.980
64	C23	C24	1.340(3)
65	C25	C26	1.403(3)
66	C25	C33	1.410(3)
67	C26	C27	1.520(3)
68	C26	C30	1.402(3)
69	C27	H27	1.000
70	C27	C28	1.534(3)
71	C27	C29	1.540(3)
72	C28	H28A	0.980
73	C28	H28B	0.980
74	C28	H28C	0.980
75	C29	H29A	0.980
76	C29	H29B	0.980
77	C29	H29C	0.980
78	C30	H30	0.950
79	C30	C31	1.381(3)
80	C31	H31	0.950
81	C31	C32	1.383(3)
82	C32	H32	0.950
83	C32	C33	1.395(3)
84	C33	C34	1.529(3)
85	C34	H34	1.000
86	C34	C35	1.535(3)
87	C34	C36	1.533(3)
88	C35	H35A	0.980
89	C35	H35B	0.980
90	C35	H35C	0.980
91	C36	H36A	0.980
92	C36	H36B	0.980
93	C36	H36C	0.980

Table A10. Bond angles for Ni–NHC–IPr^{Cl} (**188**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl1	Ni1	N1	86.32(5)
2	Cl1	Ni1	C9	171.91(6)
3	Cl1	Ni1	C10	91.20(6)
4	N1	Ni1	C9	86.60(7)

5	N1	Ni1	C10	171.71(7)
6	C9	Ni1	C10	96.35(8)
7	Ni1	N1	H1	104.9
8	Ni1	N1	C1	111.3(1)
9	Ni1	N1	C2	116.9(1)
10	H1	N1	C1	104.9
11	H1	N1	C2	104.9
12	C1	N1	C2	112.7(2)
13	C10	N2	C11	126.7(1)
14	C10	N2	C23	111.1(1)
15	C11	N2	C23	121.7(1)
16	C10	N3	C24	110.3(1)
17	C10	N3	C25	128.5(1)
18	C24	N3	C25	119.9(1)
19	N1	C1	H1A	109.5
20	N1	C1	H1B	109.5
21	N1	C1	H1C	109.5
22	H1A	C1	H1B	109.5
23	H1A	C1	H1C	109.5
24	H1B	C1	H1C	109.5
25	N1	C2	H2A	109.2
26	N1	C2	H2AB	109.2
27	N1	C2	C3	112.2(2)
28	H2A	C2	H2AB	107.9
29	H2A	C2	C3	109.2
30	H2AB	C2	C3	109.2
31	C2	C3	H3A	109.9
32	C2	C3	H3AB	109.9
33	C2	C3	C4	108.9(2)
34	H3A	C3	H3AB	108.3
35	H3A	C3	C4	109.9
36	H3AB	C3	C4	109.9
37	C3	C4	C5	121.6(2)
38	C3	C4	C9	118.0(2)
39	C5	C4	C9	120.1(2)
40	C4	C5	H5	119.7
41	C4	C5	C6	120.6(2)
42	H5	C5	C6	119.7
43	C5	C6	H6	120.1
44	C5	C6	C7	119.9(2)

45	H6	C6	C7	120.0
46	C6	C7	H7	120.1
47	C6	C7	C8	119.7(2)
48	H7	C7	C8	120.1
49	C7	C8	H8	119.3
50	C7	C8	C9	121.5(2)
51	H8	C8	C9	119.3
52	Ni1	C9	C4	117.8(1)
53	Ni1	C9	C8	123.2(1)
54	C4	C9	C8	118.1(2)
55	Ni1	C10	N2	121.5(1)
56	Ni1	C10	N3	132.1(1)
57	N2	C10	N3	104.0(1)
58	N2	C11	C12	119.3(2)
59	N2	C11	C19	117.1(2)
60	C12	C11	C19	123.4(2)
61	C11	C12	C13	122.7(2)
62	C11	C12	C16	116.8(2)
63	C13	C12	C16	120.4(2)
64	C12	C13	H13	107.6
65	C12	C13	C14	110.2(2)
66	C12	C13	C15	112.8(2)
67	H13	C13	C14	107.6
68	H13	C13	C15	107.7
69	C14	C13	C15	110.7(2)
70	C13	C14	H14A	109.4
71	C13	C14	H14B	109.5
72	C13	C14	H14C	109.5
73	H14A	C14	H14B	109.4
74	H14A	C14	H14C	109.5
75	H14B	C14	H14C	109.5
76	C13	C15	H15A	109.5
77	C13	C15	H15B	109.5
78	C13	C15	H15C	109.4
79	H15A	C15	H15B	109.5
80	H15A	C15	H15C	109.4
81	H15B	C15	H15C	109.5
82	C12	C16	H16	119.5
83	C12	C16	C17	121.1(2)
84	H16	C16	C17	119.5

85	C16	C17	H17	119.7
86	C16	C17	C18	120.5(2)
87	H17	C17	C18	119.7
88	C17	C18	H18	119.3
89	C17	C18	C19	121.4(2)
90	H18	C18	C19	119.3
91	C11	C19	C18	116.8(2)
92	C11	C19	C20	123.5(2)
93	C18	C19	C20	119.7(2)
94	C19	C20	H20	108.0
95	C19	C20	C21	112.3(2)
96	C19	C20	C22	110.7(2)
97	H20	C20	C21	108.0
98	H20	C20	C22	108.0
99	C21	C20	C22	109.5(2)
100	C20	C21	H21A	109.5
101	C20	C21	H21B	109.4
102	C20	C21	H21C	109.5
103	H21A	C21	H21B	109.5
104	H21A	C21	H21C	109.5
105	H21B	C21	H21C	109.4
106	C20	C22	H22A	109.5
107	C20	C22	H22B	109.5
108	C20	C22	H22C	109.5
109	H22A	C22	H22B	109.5
110	H22A	C22	H22C	109.4
111	H22B	C22	H22C	109.5
112	Cl2	C23	N2	124.5(1)
113	Cl2	C23	C24	128.5(2)
114	N2	C23	C24	107.0(2)
115	Cl3	C24	N3	124.4(1)
116	Cl3	C24	C23	128.0(2)
117	N3	C24	C23	107.6(2)
118	N3	C25	C26	119.3(2)
119	N3	C25	C33	117.6(2)
120	C26	C25	C33	122.7(2)
121	C25	C26	C27	123.8(2)
122	C25	C26	C30	117.1(2)
123	C27	C26	C30	119.1(2)
124	C26	C27	H27	108.3

125	C26	C27	C28	111.3(2)
126	C26	C27	C29	110.9(2)
127	H27	C27	C28	108.3
128	H27	C27	C29	108.3
129	C28	C27	C29	109.5(2)
130	C27	C28	H28A	109.5
131	C27	C28	H28B	109.5
132	C27	C28	H28C	109.5
133	H28A	C28	H28B	109.5
134	H28A	C28	H28C	109.5
135	H28B	C28	H28C	109.5
136	C27	C29	H29A	109.5
137	C27	C29	H29B	109.5
138	C27	C29	H29C	109.5
139	H29A	C29	H29B	109.5
140	H29A	C29	H29C	109.5
141	H29B	C29	H29C	109.5
142	C26	C30	H30	119.2
143	C26	C30	C31	121.6(2)
144	H30	C30	C31	119.2
145	C30	C31	H31	120.0
146	C30	C31	C32	120.0(2)
147	H31	C31	C32	120.0
148	C31	C32	H32	119.2
149	C31	C32	C33	121.5(2)
150	H32	C32	C33	119.2
151	C25	C33	C32	117.2(2)
152	C25	C33	C34	123.3(2)
153	C32	C33	C34	119.5(2)
154	C33	C34	H34	107.8
155	C33	C34	C35	112.6(2)
156	C33	C34	C36	112.2(2)
157	H34	C34	C35	107.8
158	H34	C34	C36	107.8
159	C35	C34	C36	108.4(2)
160	C34	C35	H35A	109.4
161	C34	C35	H35B	109.5
162	C34	C35	H35C	109.5
163	H35A	C35	H35B	109.5
164	H35A	C35	H35C	109.5

165	H35B	C35	H35C	109.5
166	C34	C36	H36A	109.5
167	C34	C36	H36B	109.5
168	C34	C36	H36C	109.5
169	H36A	C36	H36B	109.5
170	H36A	C36	H36C	109.5
171	H36B	C36	H36C	109.5

X-ray diffraction data for Ni(allyl)Cl(IPr)

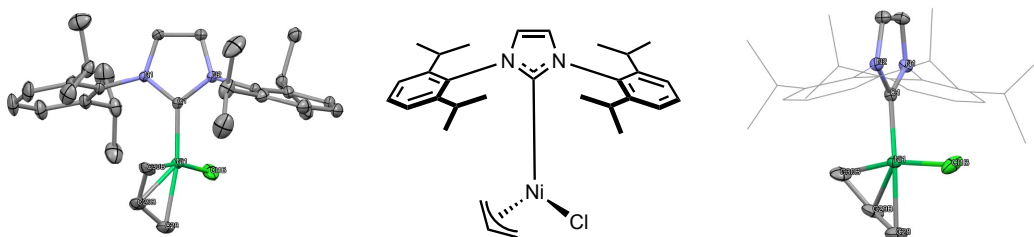


Table A11. Bond lengths for Ni(allyl)Cl(IPr) (**207**)

Entry	Atom1	Atom2	Length
1	Ni1	Cl1B	2.14(2)
2	Ni1	C1	1.905(1)
3	Ni1	C28	2.058(2)
4	Ni1	C29B	2.02(1)
5	Ni1	C30B	2.01(2)
6	N1	C1	1.361(2)
7	N1	C2	1.388(2)
8	N1	C4	1.444(2)
9	N2	C1	1.363(2)
10	N2	C3	1.387(2)
11	N2	C16	1.448(2)
12	C2	H2	0.950
13	C2	C3	1.340(2)
14	C3	H3	0.950
15	C4	C5	1.394(2)
16	C4	C9	1.404(2)
17	C5	C6	1.399(3)
18	C5	C10	1.516(2)
19	C6	H6	0.950
20	C6	C7	1.375(3)

21	C7	H7	0.950
22	C7	C8	1.379(3)
23	C8	H8	0.950
24	C8	C9	1.397(3)
25	C9	C13	1.520(3)
26	C10	H10	1.000
27	C10	C11	1.534(3)
28	C10	C12	1.527(3)
29	C11	H11A	0.980
30	C11	H11B	0.980
31	C11	H11C	0.980
32	C12	H12A	0.980
33	C12	H12B	0.980
34	C12	H12C	0.980
35	C13	H13	1.000
36	C13	C14	1.531(2)
37	C13	C15	1.528(3)
38	C14	H14A	0.980
39	C14	H14B	0.980
40	C14	H14C	0.980
41	C15	H15A	0.980
42	C15	H15B	0.980
43	C15	H15C	0.980
44	C16	C17	1.400(2)
45	C16	C21	1.400(2)
46	C17	C18	1.395(3)
47	C17	C22	1.518(2)
48	C18	H18	0.950
49	C18	C19	1.379(2)
50	C19	H19	0.950
51	C19	C20	1.378(3)
52	C20	H20	0.950
53	C20	C21	1.397(3)
54	C21	C25	1.511(3)
55	C22	H22	1.000
56	C22	C23	1.535(3)
57	C22	C24	1.537(2)
58	C23	H23A	0.980
59	C23	H23B	0.980
60	C23	H23C	0.980

61	C24	H24A	0.980
62	C24	H24B	0.980
63	C24	H24C	0.980
64	C25	H25	1.000
65	C25	C26	1.526(3)
66	C25	C27	1.537(3)
67	C26	H26A	0.980
68	C26	H26B	0.980
69	C26	H26C	0.980
70	C27	H27A	0.980
71	C27	H27B	0.980
72	C27	H27C	0.980
73	C28	H28C	0.97(4)
74	C28	H28D	0.98(2)
75	C28	C29B	1.39(2)
76	C29B	H29B	0.97(5)
77	C29B	C30B	1.39(3)
78	C30B	H30C	0.99(6)
79	C30B	H30D	0.98(6)

Table A12. Bond angles for Ni(allyl)Cl(IPr) (**207**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl1B	Ni1	C1	96.4(6)
2	Cl1B	Ni1	C28	91.8(6)
3	Cl1B	Ni1	C29B	129.1(7)
4	Cl1B	Ni1	C30B	167.7(9)
5	C1	Ni1	C28	169.64(7)
6	C1	Ni1	C29B	130.2(5)
7	C1	Ni1	C30B	95.8(7)
8	C28	Ni1	C29B	39.9(5)
9	C28	Ni1	C30B	76.2(7)
10	C29B	Ni1	C30B	40.5(9)
11	C1	N1	C2	111.4(1)
12	C1	N1	C4	126.2(1)
13	C2	N1	C4	122.4(1)
14	C1	N2	C3	111.7(1)
15	C1	N2	C16	125.4(1)
16	C3	N2	C16	122.6(1)
17	Ni1	C1	N1	128.0(1)
18	Ni1	C1	N2	128.2(1)

19	N1	C1	N2	103.5(1)
20	N1	C2	H2	126.5
21	N1	C2	C3	107.0(1)
22	H2	C2	C3	126.5
23	N2	C3	C2	106.4(1)
24	N2	C3	H3	126.8
25	C2	C3	H3	126.8
26	N1	C4	C5	119.1(1)
27	N1	C4	C9	117.7(1)
28	C5	C4	C9	123.1(1)
29	C4	C5	C6	117.4(2)
30	C4	C5	C10	122.8(2)
31	C6	C5	C10	119.8(2)
32	C5	C6	H6	119.5
33	C5	C6	C7	120.9(2)
34	H6	C6	C7	119.5
35	C6	C7	H7	119.8
36	C6	C7	C8	120.4(2)
37	H7	C7	C8	119.8
38	C7	C8	H8	119.2
39	C7	C8	C9	121.5(2)
40	H8	C8	C9	119.3
41	C4	C9	C8	116.6(2)
42	C4	C9	C13	122.6(1)
43	C8	C9	C13	120.8(2)
44	C5	C10	H10	107.9
45	C5	C10	C11	110.9(2)
46	C5	C10	C12	110.9(2)
47	H10	C10	C11	107.9
48	H10	C10	C12	107.9
49	C11	C10	C12	111.1(2)
50	C10	C11	H11A	109.5
51	C10	C11	H11B	109.4
52	C10	C11	H11C	109.5
53	H11A	C11	H11B	109.4
54	H11A	C11	H11C	109.5
55	H11B	C11	H11C	109.5
56	C10	C12	H12A	109.4
57	C10	C12	H12B	109.5
58	C10	C12	H12C	109.5

59	H12A	C12	H12B	109.5
60	H12A	C12	H12C	109.5
61	H12B	C12	H12C	109.5
62	C9	C13	H13	107.6
63	C9	C13	C14	112.7(2)
64	C9	C13	C15	111.6(2)
65	H13	C13	C14	107.6
66	H13	C13	C15	107.7
67	C14	C13	C15	109.4(2)
68	C13	C14	H14A	109.5
69	C13	C14	H14B	109.5
70	C13	C14	H14C	109.5
71	H14A	C14	H14B	109.5
72	H14A	C14	H14C	109.5
73	H14B	C14	H14C	109.5
74	C13	C15	H15A	109.5
75	C13	C15	H15B	109.5
76	C13	C15	H15C	109.4
77	H15A	C15	H15B	109.5
78	H15A	C15	H15C	109.4
79	H15B	C15	H15C	109.5
80	N2	C16	C17	119.3(1)
81	N2	C16	C21	117.8(1)
82	C17	C16	C21	122.9(1)
83	C16	C17	C18	117.0(1)
84	C16	C17	C22	122.5(1)
85	C18	C17	C22	120.5(1)
86	C17	C18	H18	119.2
87	C17	C18	C19	121.5(2)
88	H18	C18	C19	119.2
89	C18	C19	H19	119.9
90	C18	C19	C20	120.2(2)
91	H19	C19	C20	119.9
92	C19	C20	H20	119.4
93	C19	C20	C21	121.2(2)
94	H20	C20	C21	119.4
95	C16	C21	C20	117.2(2)
96	C16	C21	C25	122.4(1)
97	C20	C21	C25	120.3(2)
98	C17	C22	H22	107.9

99	C17	C22	C23	113.0(1)
100	C17	C22	C24	109.7(1)
101	H22	C22	C23	107.9
102	H22	C22	C24	107.9
103	C23	C22	C24	110.1(1)
104	C22	C23	H23A	109.5
105	C22	C23	H23B	109.5
106	C22	C23	H23C	109.5
107	H23A	C23	H23B	109.5
108	H23A	C23	H23C	109.5
109	H23B	C23	H23C	109.5
110	C22	C24	H24A	109.5
111	C22	C24	H24B	109.5
112	C22	C24	H24C	109.5
113	H24A	C24	H24B	109.5
114	H24A	C24	H24C	109.5
115	H24B	C24	H24C	109.5
116	C21	C25	H25	107.6
117	C21	C25	C26	112.3(2)
118	C21	C25	C27	109.8(2)
119	H25	C25	C26	107.6
120	H25	C25	C27	107.6
121	C26	C25	C27	111.6(2)
122	C25	C26	H26A	109.5
123	C25	C26	H26B	109.5
124	C25	C26	H26C	109.4
125	H26A	C26	H26B	109.5
126	H26A	C26	H26C	109.5
127	H26B	C26	H26C	109.5
128	C25	C27	H27A	109.5
129	C25	C27	H27B	109.5
130	C25	C27	H27C	109.5
131	H27A	C27	H27B	109.5
132	H27A	C27	H27C	109.5
133	H27B	C27	H27C	109.5
134	Ni1	C28	H28C	94(2)
135	Ni1	C28	H28D	122(2)
136	Ni1	C28	C29B	68.6(7)
137	H28C	C28	H28D	119(3)
138	H28C	C28	C29B	116(3)

139	H28D	C28	C29B	122(2)
140	Ni1	C29B	C28	71.6(7)
141	Ni1	C29B	H29B	111(3)
142	Ni1	C29B	C30B	69(1)
143	C28	C29B	H29B	112(3)
144	C28	C29B	C30B	129(2)
145	H29B	C29B	C30B	112(3)
146	Ni1	C30B	C29B	70(1)
147	Ni1	C30B	H30C	100(4)
148	Ni1	C30B	H30D	119(3)
149	C29B	C30B	H30C	120(4)
150	C29B	C30B	H30D	119(4)
151	H30C	C30B	H30D	117(5)

X-ray diffraction data for Ni(allyl)Cl(IPr^{Cl})

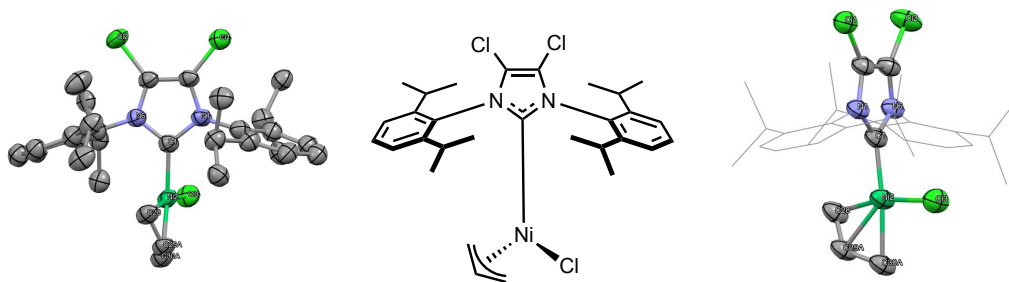


Table A13. Bond lengths for Ni(allyl)Cl(IPr^{Cl}) (**208**)

Entry	Atom1	Atom2	Length
1	Ni2	Cl3	2.154(8)
2	Ni2	C1	1.87(2)
3	Ni2	C28	1.98(3)
4	Ni2	C29A	2.03(3)
5	Ni2	C30A	2.00(2)
6	Cl1	C2	1.69(2)
7	Cl2	C3	1.73(2)
8	N1	C1	1.41(3)
9	N1	C2	1.37(3)
10	N1	C4	1.39(3)
11	N6	C1	1.38(3)
12	N6	C3	1.33(3)

13	N6	C16	1.40(3)
14	C2	C3	1.38(3)
15	C4	C5	1.45(4)
16	C4	C9	1.44(4)
17	C5	C6	1.36(4)
18	C5	C13	1.60(4)
19	C6	H6	0.93
20	C6	C7	1.36(4)
21	C7	H7	0.93
22	C7	C8	1.31(4)
23	C8	H8	0.93
24	C8	C9	1.35(4)
25	C9	C10	1.51(4)
26	C10	H10	0.98
27	C10	C11	1.54(3)
28	C10	C12	1.57(3)
29	C11	H11A	0.96
30	C11	H11B	0.96
31	C11	H11C	0.96
32	C12	H12A	0.96
33	C12	H12B	0.96
34	C12	H12C	0.96
35	C13	H13	0.98
36	C13	C14	1.56(3)
37	C13	C15	1.57(3)
38	C14	H14A	0.96
39	C14	H14B	0.96
40	C14	H14C	0.96
41	C15	H15A	0.96
42	C15	H15B	0.96
43	C15	H15C	0.96
44	C16	C17	1.40(4)
45	C16	C21	1.38(4)
46	C17	C18	1.47(4)
47	C17	C25B	1.55(5)
48	C18	H18	0.93
49	C18	C19	1.24(4)
50	C19	H19	0.93
51	C19	C20	1.33(4)
52	C20	H20	0.93

53	C20	C21	1.35(4)
54	C21	C22	1.55(3)
55	C22	H22	0.98
56	C22	C23	1.54(3)
57	C22	C24	1.56(4)
58	C23	H23A	0.96
59	C23	H23B	0.96
60	C23	H23C	0.96
61	C24	H24A	0.96
62	C24	H24B	0.96
63	C24	H24C	0.96
64	C25B	H25B	0.98
65	C25B	C26B	1.54(7)
66	C25B	C27B	1.55(7)
67	C26B	H26A	0.96
68	C26B	H26B	0.97
69	C26B	H26C	0.96
70	C27B	H27A	0.95
71	C27B	H27B	0.96
72	C27B	H27C	0.97
73	C28	H28C	0.97
74	C28	H28D	0.97
75	C28	C29A	1.34(3)
76	C29A	H29A	0.93
77	C29A	C30A	1.32(4)
78	C30A	H30A	0.98
79	C30A	H30B	0.97

Table A14. Bond angles for Ni(allyl)Cl(IPr^{Cl}) (**208**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl6	Ni1	C31	95.6(8)
2	Cl6	Ni1	C58	165(1)
3	Cl6	Ni1	C60	92(1)
4	C31	Ni1	C58	99(1)
5	C31	Ni1	C60	169(1)
6	C58	Ni1	C60	74(1)
7	C31	N3	C32	103(2)
8	C31	N3	C34	136(2)
9	C32	N3	C34	121(2)
10	C31	N4	C33	114(2)

11	C31	N4	C46	120(2)
12	C33	N4	C46	125(2)
13	Ni1	C31	N3	126(2)
14	Ni1	C31	N4	125(2)
15	N3	C31	N4	109(2)
16	Cl4	C32	N3	120(2)
17	Cl4	C32	C33	130(3)
18	N3	C32	C33	110(3)
19	Cl5	C33	N4	127(2)
20	Cl5	C33	C32	128(2)
21	N4	C33	C32	104(3)
22	N3	C34	C35	116(2)
23	N3	C34	C39	123(3)
24	C35	C34	C39	119(2)
25	C34	C35	C36	118(3)
26	C34	C35	C43A	111(2)
27	C36	C35	C43A	129(3)
28	C35	C36	H36	118
29	C35	C36	C37	124(3)
30	H36	C36	C37	118
31	C36	C37	H37	122
32	C36	C37	C38	116(2)
33	H37	C37	C38	122
34	C37	C38	H38	117
35	C37	C38	C39	126(3)
36	H38	C38	C39	117
37	C34	C39	C38	114(3)
38	C34	C39	C40	126(3)
39	C38	C39	C40	119(3)
40	C39	C40	H40	107
41	C39	C40	C41	113(2)
42	C39	C40	C42	110(2)
43	H40	C40	C41	107
44	H40	C40	C42	107
45	C41	C40	C42	112(2)
46	C40	C41	H41A	109
47	C40	C41	H41B	109
48	C40	C41	H41C	109
49	H41A	C41	H41B	110
50	H41A	C41	H41C	109

51	H41B	C41	H41C	109
52	C40	C42	H42A	110
53	C40	C42	H42B	109
54	C40	C42	H42C	110
55	H42A	C42	H42B	109
56	H42A	C42	H42C	110
57	H42B	C42	H42C	109
58	C35	C43A	H43A	108
59	C35	C43A	C44A	114(2)
60	C35	C43A	C45A	106(2)
61	H43A	C43A	C44A	108
62	H43A	C43A	C45A	108
63	C44A	C43A	C45A	112(2)
64	C43A	C44A	H44A	109
65	C43A	C44A	H44B	109
66	C43A	C44A	H44C	110
67	H44A	C44A	H44B	109
68	H44A	C44A	H44C	110
69	H44B	C44A	H44C	110
70	C43A	C45A	H45D	109
71	C43A	C45A	H45E	110
72	C43A	C45A	H45F	109
73	H45D	C45A	H45E	110
74	H45D	C45A	H45F	109
75	H45E	C45A	H45F	110
76	N4	C46	C47	114(2)
77	N4	C46	C51	125(2)
78	C47	C46	C51	120(2)
79	C46	C47	C48	116(2)
80	C46	C47	C55	123(2)
81	C48	C47	C55	121(2)
82	C47	C48	H48	118
83	C47	C48	C49	124(2)
84	H48	C48	C49	118
85	C48	C49	H49	120
86	C48	C49	C50	119(2)
87	H49	C49	C50	120
88	C49	C50	H50	121
89	C49	C50	C51	117(3)
90	H50	C50	C51	121

91	C46	C51	C50	123(3)
92	C46	C51	C52	116(2)
93	C50	C51	C52	121(3)
94	C51	C52	H52	109
95	C51	C52	C53	108(2)
96	C51	C52	C54	111(2)
97	H52	C52	C53	109
98	H52	C52	C54	110
99	C53	C52	C54	110(2)
100	C52	C53	H53A	110
101	C52	C53	H53B	110
102	C52	C53	H53C	109
103	H53A	C53	H53B	110
104	H53A	C53	H53C	109
105	H53B	C53	H53C	109
106	C52	C54	H54A	110
107	C52	C54	H54B	110
108	C52	C54	H54C	110
109	H54A	C54	H54B	109
110	H54A	C54	H54C	109
111	H54B	C54	H54C	109
112	C47	C55	H55	109
113	C47	C55	C56	109(2)
114	C47	C55	C57	113(2)
115	H55	C55	C56	109
116	H55	C55	C57	109
117	C56	C55	C57	107(2)
118	C55	C56	H56A	109
119	C55	C56	H56B	110
120	C55	C56	H56C	109
121	H56A	C56	H56B	110
122	H56A	C56	H56C	109
123	H56B	C56	H56C	110
124	C55	C57	H57A	110
125	C55	C57	H57B	110
126	C55	C57	H57C	109
127	H57A	C57	H57B	110
128	H57A	C57	H57C	109
129	H57B	C57	H57C	109
130	Ni1	C58	H58C	54

131	Ni1	C58	H58D	153
132	Ni1	C58	C59B	72(3)
133	H58C	C58	H58D	120
134	H58C	C58	C59B	120
135	H58D	C58	C59B	120
136	C58	C59B	H59B	112
137	C58	C59B	C60	137(5)
138	H59B	C59B	C60	112
139	Ni1	C60	C59B	72(3)
140	Ni1	C60	H60C	54
141	Ni1	C60	H60D	153
142	C59B	C60	H60C	120
143	C59B	C60	H60D	120
144	H60C	C60	H60D	119
145	Cl3	Ni2	C1	95.4(8)
146	Cl3	Ni2	C28	166.9(8)
147	Cl3	Ni2	C29A	128.9(8)
148	Cl3	Ni2	C30A	93(1)
149	C1	Ni2	C28	98(1)
150	C1	Ni2	C29A	134(1)
151	C1	Ni2	C30A	171(1)
152	C28	Ni2	C29A	39(1)
153	C28	Ni2	C30A	74(1)
154	C29A	Ni2	C30A	38(1)
155	C1	N1	C2	111(2)
156	C1	N1	C4	124(2)
157	C2	N1	C4	124(2)
158	C1	N6	C3	111(2)
159	C1	N6	C16	123(2)
160	C3	N6	C16	126(2)
161	Ni2	C1	N1	130(2)
162	Ni2	C1	N6	126(2)
163	N1	C1	N6	103(2)
164	Cl1	C2	N1	124(2)
165	Cl1	C2	C3	130(2)
166	N1	C2	C3	105(2)
167	Cl2	C3	N6	125(2)
168	Cl2	C3	C2	125(2)
169	N6	C3	C2	109(2)
170	N1	C4	C5	120(2)

171	N1	C4	C9	124(2)
172	C5	C4	C9	116(2)
173	C4	C5	C6	118(2)
174	C4	C5	C13	118(2)
175	C6	C5	C13	124(2)
176	C5	C6	H6	118
177	C5	C6	C7	124(2)
178	H6	C6	C7	118
179	C6	C7	H7	121
180	C6	C7	C8	119(2)
181	H7	C7	C8	121
182	C7	C8	H8	118
183	C7	C8	C9	124(3)
184	H8	C8	C9	118
185	C4	C9	C8	119(2)
186	C4	C9	C10	118(2)
187	C8	C9	C10	123(2)
188	C9	C10	H10	109
189	C9	C10	C11	113(2)
190	C9	C10	C12	108(2)
191	H10	C10	C11	109
192	H10	C10	C12	109
193	C11	C10	C12	107(2)
194	C10	C11	H11A	110
195	C10	C11	H11B	110
196	C10	C11	H11C	110
197	H11A	C11	H11B	109
198	H11A	C11	H11C	109
199	H11B	C11	H11C	109
200	C10	C12	H12A	110
201	C10	C12	H12B	110
202	C10	C12	H12C	109
203	H12A	C12	H12B	110
204	H12A	C12	H12C	109
205	H12B	C12	H12C	109
206	C5	C13	H13	110
207	C5	C13	C14	104(2)
208	C5	C13	C15	111(2)
209	H13	C13	C14	110
210	H13	C13	C15	110

211	C14	C13	C15	113(2)
212	C13	C14	H14A	109
213	C13	C14	H14B	109
214	C13	C14	H14C	109
215	H14A	C14	H14B	109
216	H14A	C14	H14C	109
217	H14B	C14	H14C	109
218	C13	C15	H15A	110
219	C13	C15	H15B	110
220	C13	C15	H15C	110
221	H15A	C15	H15B	109
222	H15A	C15	H15C	109
223	H15B	C15	H15C	109
224	N6	C16	C17	118(2)
225	N6	C16	C21	126(2)
226	C17	C16	C21	116(2)
227	C16	C17	C18	118(2)
228	C16	C17	C25B	128(3)
229	C18	C17	C25B	114(2)
230	C17	C18	H18	120
231	C17	C18	C19	121(2)
232	H18	C18	C19	120
233	C18	C19	H19	118
234	C18	C19	C20	124(3)
235	H19	C19	C20	118
236	C19	C20	H20	120
237	C19	C20	C21	119(2)
238	H20	C20	C21	120
239	C16	C21	C20	123(2)
240	C16	C21	C22	116(2)
241	C20	C21	C22	121(2)
242	C21	C22	H22	107
243	C21	C22	C23	114(2)
244	C21	C22	C24	108(2)
245	H22	C22	C23	107
246	H22	C22	C24	107
247	C23	C22	C24	113(2)
248	C22	C23	H23A	110
249	C22	C23	H23B	110
250	C22	C23	H23C	110

251	H23A	C23	H23B	109
252	H23A	C23	H23C	109
253	H23B	C23	H23C	109
254	C22	C24	H24A	109
255	C22	C24	H24B	109
256	C22	C24	H24C	109
257	H24A	C24	H24B	110
258	H24A	C24	H24C	109
259	H24B	C24	H24C	109
260	C17	C25B	H25B	103
261	C17	C25B	C26B	108(4)
262	C17	C25B	C27B	114(4)
263	H25B	C25B	C26B	104
264	H25B	C25B	C27B	103
265	C26B	C25B	C27B	123(4)
266	C25B	C26B	H26A	109
267	C25B	C26B	H26B	109
268	C25B	C26B	H26C	110
269	H26A	C26B	H26B	109
270	H26A	C26B	H26C	110
271	H26B	C26B	H26C	109
272	C25B	C27B	H27A	109
273	C25B	C27B	H27B	110
274	C25B	C27B	H27C	109
275	H27A	C27B	H27B	110
276	H27A	C27B	H27C	110
277	H27B	C27B	H27C	109
278	Ni2	C28	H28C	116
279	Ni2	C28	H28D	116
280	Ni2	C28	C29A	73(2)
281	H28C	C28	H28D	113
282	H28C	C28	C29A	117
283	H28D	C28	C29A	116
284	Ni2	C29A	C28	68(2)
285	Ni2	C29A	H29A	144
286	Ni2	C29A	C30A	69(2)
287	C28	C29A	H29A	116
288	C28	C29A	C30A	128(3)
289	H29A	C29A	C30A	116
290	Ni2	C30A	C29A	72(2)

291	Ni2	C30A	H30A	116
292	Ni2	C30A	H30B	117
293	C29A	C30A	H30A	116
294	C29A	C30A	H30B	117
295	H30A	C30A	H30B	113

X-ray diffraction data for Ni(allyl)Cl(IPent^{Cl})

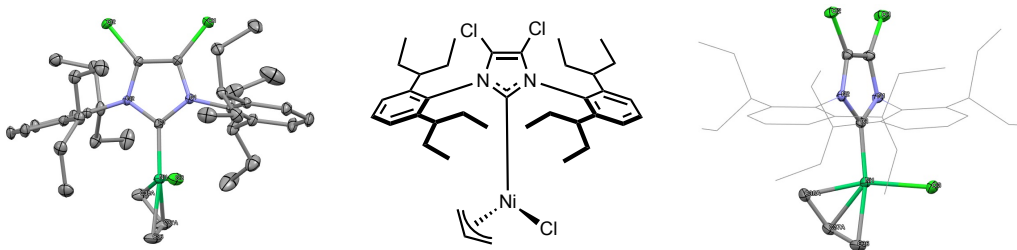


Table A15. Bond lengths for Ni(allyl)Cl(IPent^{Cl}) (**209**)

Entry	Atom1	Atom2	Length
1	Ni1	Cl3	2.1872(6)
2	Ni1	C1	1.919(1)
3	Ni1	C36	2.064(2)
4	Ni1	C37A	2.005(2)
5	Ni1	C38A	2.006(4)
6	Cl1	C2	1.695(1)
7	Cl2	C3	1.699(1)
8	N1	C1	1.368(2)
9	N1	C2	1.394(1)
10	N1	C4	1.452(2)
11	N2	C1	1.370(2)
12	N2	C3	1.389(1)
13	N2	C20	1.452(2)
14	C2	C3	1.343(2)
15	C4	C5	1.399(2)
16	C4	C9	1.404(2)
17	C5	C6	1.402(2)
18	C5	C15	1.533(4)
19	C6	H6	0.950
20	C6	C7	1.376(2)
21	C7	H7	0.950

22	C7	C8	1.380(2)
23	C8	H8	0.950
24	C8	C9	1.399(2)
25	C9	C10	1.521(2)
26	C10	H10	1.000
27	C10	C11	1.544(2)
28	C10	C13	1.545(2)
29	C11	H11A	0.990
30	C11	H11B	0.990
31	C11	C12	1.521(3)
32	C12	H12A	0.980
33	C12	H12B	0.980
34	C12	H12C	0.980
35	C13	H13A	0.990
36	C13	H13B	0.990
37	C13	C14	1.517(3)
38	C14	H14A	0.980
39	C14	H14B	0.980
40	C14	H14C	0.980
41	C15	H15	1.000
42	C15	C16A	1.538(9)
43	C15	C18A	1.528(6)
44	C16A	H16C	0.989
45	C16A	H16D	0.990
46	C16A	C17A	1.55(1)
47	C17A	H17D	0.98
48	C17A	H17E	0.981
49	C17A	H17F	0.98
50	C18A	H18C	0.990
51	C18A	H18D	0.990
52	C18A	C19A	1.494(7)
53	C19A	H19A	0.980
54	C19A	H19B	0.980
55	C19A	H19C	0.980
56	C20	C21	1.412(2)
57	C20	C25	1.402(2)
58	C21	C22	1.398(2)
59	C21	C31	1.527(2)
60	C22	H22	0.950
61	C22	C23	1.383(2)

62	C23	H23	0.950
63	C23	C24	1.385(2)
64	C24	H24	0.950
65	C24	C25	1.399(2)
66	C25	C26	1.524(2)
67	C26	H26	1.000
68	C26	C27	1.540(2)
69	C26	C29	1.543(2)
70	C27	H27A	0.990
71	C27	H27B	0.990
72	C27	C28	1.518(2)
73	C28	H28A	0.980
74	C28	H28B	0.980
75	C28	H28C	0.980
76	C29	H29A	0.990
77	C29	H29B	0.990
78	C29	C30	1.522(2)
79	C30	H30A	0.980
80	C30	H30B	0.980
81	C30	H30C	0.980
82	C31	H31	1.000
83	C31	C32	1.548(2)
84	C31	C34	1.539(2)
85	C32	H32A	0.990
86	C32	H32B	0.990
87	C32	C33	1.517(3)
88	C33	H33A	0.980
89	C33	H33B	0.980
90	C33	H33C	0.980
91	C34	H34A	0.990
92	C34	H34B	0.990
93	C34	C35	1.523(3)
94	C35	H35A	0.980
95	C35	H35B	0.980
96	C35	H35C	0.980
97	C36	H36A	0.99(4)
98	C36	H36B	1.00(2)
99	C36	C37A	1.391(3)
100	C37A	H37A	1.00(3)
101	C37A	C38A	1.410(5)

102	C38A	H38C	0.97(3)
103	C38A	H38D	0.97(2)

Table A16. Bond angles for Ni(allyl)Cl(IPent^{Cl}) (**209**)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl3	Ni1	C1	99.32(4)
2	Cl3	Ni1	C36	91.19(6)
3	Cl3	Ni1	C37A	125.53(6)
4	Cl3	Ni1	C38A	163.1(1)
5	C1	Ni1	C36	168.40(7)
6	C1	Ni1	C37A	132.37(7)
7	C1	Ni1	C38A	96.9(1)
8	C36	Ni1	C37A	39.93(8)
9	C36	Ni1	C38A	72.3(1)
10	C37A	Ni1	C38A	41.2(1)
11	C1	N1	C2	110.9(1)
12	C1	N1	C4	127.6(1)
13	C2	N1	C4	121.5(1)
14	C1	N2	C3	110.9(1)
15	C1	N2	C20	126.2(1)
16	C3	N2	C20	122.7(1)
17	Ni1	C1	N1	127.57(9)
18	Ni1	C1	N2	128.27(9)
19	N1	C1	N2	104.1(1)
20	Cl1	C2	N1	124.06(9)
21	Cl1	C2	C3	129.0(1)
22	N1	C2	C3	106.9(1)
23	Cl2	C3	N2	124.60(9)
24	Cl2	C3	C2	128.1(1)
25	N2	C3	C2	107.2(1)
26	N1	C4	C5	118.0(1)
27	N1	C4	C9	118.3(1)
28	C5	C4	C9	123.6(1)
29	C4	C5	C6	116.7(1)
30	C4	C5	C15	121.7(2)
31	C6	C5	C15	121.6(3)
32	C5	C6	H6	119.4
33	C5	C6	C7	121.2(2)
34	H6	C6	C7	119.4
35	C6	C7	H7	119.7

36	C6	C7	C8	120.6(2)
37	H7	C7	C8	119.7
38	C7	C8	H8	119.4
39	C7	C8	C9	121.3(1)
40	H8	C8	C9	119.4
41	C4	C9	C8	116.6(1)
42	C4	C9	C10	123.0(1)
43	C8	C9	C10	120.4(1)
44	C9	C10	H10	106.4
45	C9	C10	C11	110.7(1)
46	C9	C10	C13	114.4(1)
47	H10	C10	C11	106.4
48	H10	C10	C13	106.4
49	C11	C10	C13	112.0(1)
50	C10	C11	H11A	109.1
51	C10	C11	H11B	109.1
52	C10	C11	C12	112.6(1)
53	H11A	C11	H11B	107.8
54	H11A	C11	C12	109.1
55	H11B	C11	C12	109.1
56	C11	C12	H12A	109.5
57	C11	C12	H12B	109.5
58	C11	C12	H12C	109.5
59	H12A	C12	H12B	109.4
60	H12A	C12	H12C	109.5
61	H12B	C12	H12C	109.4
62	C10	C13	H13A	108.3
63	C10	C13	H13B	108.3
64	C10	C13	C14	116.0(1)
65	H13A	C13	H13B	107.4
66	H13A	C13	C14	108.3
67	H13B	C13	C14	108.3
68	C13	C14	H14A	109.5
69	C13	C14	H14B	109.5
70	C13	C14	H14C	109.5
71	H14A	C14	H14B	109.5
72	H14A	C14	H14C	109.5
73	H14B	C14	H14C	109.5
74	C5	C15	H15	107.6
75	C5	C15	C16A	110.6(5)

76	C5	C15	C18A	111.0(4)
77	H15	C15	C16A	107.5
78	H15	C15	C18A	107.5
79	C16A	C15	C18A	112.4(5)
80	C15	C16A	H16C	108.5
81	C15	C16A	H16D	108.4
82	C15	C16A	C17A	115.3(6)
83	H16C	C16A	H16D	107.5
84	H16C	C16A	C17A	108.4
85	H16D	C16A	C17A	108.4
86	C16A	C17A	H17D	109.5
87	C16A	C17A	H17E	109.5
88	C16A	C17A	H17F	109.5
89	H17D	C17A	H17E	109.5
90	H17D	C17A	H17F	109.5
91	H17E	C17A	H17F	109.4
92	C15	C18A	H18C	108.1
93	C15	C18A	H18D	108.1
94	C15	C18A	C19A	116.6(4)
95	H18C	C18A	H18D	107.3
96	H18C	C18A	C19A	108.1
97	H18D	C18A	C19A	108.2
98	C18A	C19A	H19A	109.5
99	C18A	C19A	H19B	109.4
100	C18A	C19A	H19C	109.4
101	H19A	C19A	H19B	109.5
102	H19A	C19A	H19C	109.5
103	H19B	C19A	H19C	109.5
104	N2	C20	C21	117.9(1)
105	N2	C20	C25	118.4(1)
106	C21	C20	C25	123.6(1)
107	C20	C21	C22	116.7(1)
108	C20	C21	C31	123.2(1)
109	C22	C21	C31	120.1(1)
110	C21	C22	H22	119.5
111	C21	C22	C23	121.1(1)
112	H22	C22	C23	119.5
113	C22	C23	H23	119.7
114	C22	C23	C24	120.6(1)
115	H23	C23	C24	119.7

116	C23	C24	H24	119.3
117	C23	C24	C25	121.4(1)
118	H24	C24	C25	119.3
119	C20	C25	C24	116.5(1)
120	C20	C25	C26	122.0(1)
121	C24	C25	C26	121.4(1)
122	C25	C26	H26	107.4
123	C25	C26	C27	112.6(1)
124	C25	C26	C29	111.1(1)
125	H26	C26	C27	107.4
126	H26	C26	C29	107.4
127	C27	C26	C29	110.7(1)
128	C26	C27	H27A	108.6
129	C26	C27	H27B	108.6
130	C26	C27	C28	114.6(1)
131	H27A	C27	H27B	107.6
132	H27A	C27	C28	108.6
133	H27B	C27	C28	108.6
134	C27	C28	H28A	109.5
135	C27	C28	H28B	109.5
136	C27	C28	H28C	109.5
137	H28A	C28	H28B	109.5
138	H28A	C28	H28C	109.5
139	H28B	C28	H28C	109.5
140	C26	C29	H29A	108.8
141	C26	C29	H29B	108.8
142	C26	C29	C30	113.8(1)
143	H29A	C29	H29B	107.7
144	H29A	C29	C30	108.8
145	H29B	C29	C30	108.8
146	C29	C30	H30A	109.5
147	C29	C30	H30B	109.5
148	C29	C30	H30C	109.5
149	H30A	C30	H30B	109.5
150	H30A	C30	H30C	109.5
151	H30B	C30	H30C	109.5
152	C21	C31	H31	106.8
153	C21	C31	C32	113.6(1)
154	C21	C31	C34	111.5(1)
155	H31	C31	C32	106.9

156	H31	C31	C34	106.9
157	C32	C31	C34	110.8(1)
158	C31	C32	H32A	108.3
159	C31	C32	H32B	108.3
160	C31	C32	C33	115.8(1)
161	H32A	C32	H32B	107.4
162	H32A	C32	C33	108.3
163	H32B	C32	C33	108.3
164	C32	C33	H33A	109.5
165	C32	C33	H33B	109.5
166	C32	C33	H33C	109.5
167	H33A	C33	H33B	109.5
168	H33A	C33	H33C	109.5
169	H33B	C33	H33C	109.5
170	C31	C34	H34A	109.0
171	C31	C34	H34B	109.0
172	C31	C34	C35	112.8(1)
173	H34A	C34	H34B	107.8
174	H34A	C34	C35	109.0
175	H34B	C34	C35	109.0
176	C34	C35	H35A	109.5
177	C34	C35	H35B	109.5
178	C34	C35	H35C	109.5
179	H35A	C35	H35B	109.5
180	H35A	C35	H35C	109.5
181	H35B	C35	H35C	109.4
182	Ni1	C36	H36A	93(2)
183	Ni1	C36	H36B	118(2)
184	Ni1	C36	C37A	67.8(1)
185	H36A	C36	H36B	120(2)
186	H36A	C36	C37A	117(2)
187	H36B	C36	C37A	122(2)
188	Ni1	C37A	C36	72.3(1)
189	Ni1	C37A	H37A	116(1)
190	Ni1	C37A	C38A	69.4(2)
191	C36	C37A	H37A	117(1)
192	C36	C37A	C38A	118.0(3)
193	H37A	C37A	C38A	123(1)
194	Ni1	C38A	C37A	69.4(2)
195	Ni1	C38A	H38C	93(1)

196	Ni1	C38A	H38D	119(1)
197	C37A	C38A	H38C	114(2)
198	C37A	C38A	H38D	116(1)
199	H38C	C38A	H38D	128(2)

X-ray diffraction data for Ni(allyl)Cl(IHept^{Cl})

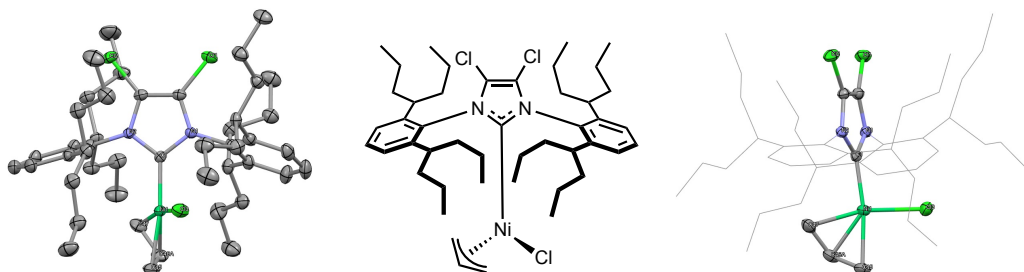


Table A17. Bond lengths for Ni(allyl)Cl(IHept^{Cl}) (210)

Entry	Atom1	Atom2	Length
1	Ni1	Cl3	2.1810(7)
2	Ni1	C1	1.905(2)
3	Ni1	C45	2.050(2)
4	Ni1	C46A	1.982(3)
5	Ni1	C47	1.988(3)
6	Cl1	C2	1.694(2)
7	Cl2	C3	1.700(2)
8	N1	C1	1.365(2)
9	N1	C2	1.391(2)
10	N1	C4	1.457(2)
11	N2	C1	1.369(2)
12	N2	C3	1.390(2)
13	N2	C24	1.450(2)
14	C2	C3	1.340(2)
15	C4	C5	1.403(3)
16	C4	C9	1.404(3)
17	C5	C6	1.401(3)
18	C5	C17A	1.445(7)
19	C6	H6	0.950
20	C6	C7	1.375(4)
21	C7	H7	0.950
22	C7	C8	1.378(3)

23	C8	H8	0.950
24	C8	C9	1.398(3)
25	C9	C10	1.528(3)
26	C10	H10	1.000
27	C10	C11	1.540(3)
28	C10	C14	1.543(3)
29	C11	H11A	0.990
30	C11	H11B	0.990
31	C11	C12	1.514(4)
32	C12	H12A	0.990
33	C12	H12B	0.990
34	C12	C13	1.527(4)
35	C13	H13A	0.980
36	C13	H13B	0.980
37	C13	H13C	0.980
38	C14	H14A	0.990
39	C14	H14B	0.990
40	C14	C15	1.514(3)
41	C15	H15A	0.990
42	C15	H15B	0.990
43	C15	C16	1.525(3)
44	C16	H16A	0.980
45	C16	H16B	0.980
46	C16	H16C	0.980
47	C17A	H17A	1.000
48	C17A	C18A	1.548(7)
49	C17A	C21	1.604(6)
50	C18A	H18C	0.990
51	C18A	H18D	0.990
52	C18A	C19A	1.507(5)
53	C19A	H19A	0.991
54	C19A	H19B	0.989
55	C19A	C20A	1.51(2)
56	C20A	H20A	0.98
57	C20A	H20B	0.98
58	C20A	H20C	0.98
59	C21	H21A	0.990
60	C21	H21B	0.990
61	C21	C22	1.512(3)
62	C22	H22A	0.990

63	C22	H22B	0.990
64	C22	C23	1.518(4)
65	C23	H23A	0.980
66	C23	H23B	0.980
67	C23	H23C	0.981
68	C24	C25	1.400(2)
69	C24	C29	1.406(3)
70	C25	C26	1.399(3)
71	C25	C30	1.510(3)
72	C26	H26	0.950
73	C26	C27	1.374(3)
74	C27	H27	0.950
75	C27	C28	1.374(3)
76	C28	H28	0.950
77	C28	C29	1.402(3)
78	C29	C37A	1.513(4)
79	C30	H30	1.000
80	C30	C31	1.560(3)
81	C30	C34	1.541(3)
82	C31	H31A	0.990
83	C31	H31B	0.990
84	C31	C32	1.507(4)
85	C32	H32A	0.990
86	C32	H32B	0.990
87	C32	C33	1.519(4)
88	C33	H33A	0.980
89	C33	H33B	0.980
90	C33	H33C	0.980
91	C34	H34A	0.990
92	C34	H34B	0.990
93	C34	C35	1.508(3)
94	C35	H35A	0.990
95	C35	H35B	0.990
96	C35	C36	1.534(3)
97	C36	H36A	0.980
98	C36	H36B	0.980
99	C36	H36C	0.980
100	C37A	H37A	0.999
101	C37A	C38A	1.552(4)
102	C37A	C41A	1.548(7)

103	C38A	H38A	0.991
104	C38A	H38B	0.990
105	C38A	C39A	1.526(4)
106	C39A	H39A	0.991
107	C39A	H39B	0.990
108	C39A	C40A	1.514(5)
109	C40A	H40D	0.980
110	C40A	H40E	0.980
111	C40A	H40F	0.981
112	C41A	H41A	0.990
113	C41A	H41B	0.991
114	C41A	C42A	1.519(6)
115	C42A	H42A	0.990
116	C42A	H42B	0.990
117	C42A	C43A	1.519(8)
118	C43A	H43A	0.980
119	C43A	H43B	0.980
120	C43A	H43C	0.980
121	C45	H45A	0.97(2)
122	C45	H45B	0.95(2)
123	C45	C46A	1.373(4)
124	C46A	H46A	0.98(2)
125	C46A	C47	1.394(3)
126	C47	H47A	0.96(2)
127	C47	H47B	0.96(2)

Table A18. Bond angles for Ni(allyl)Cl(IHept^{Cl}) (210)

Entry	Atom1	Atom2	Atom3	Angle
1	Cl3	Ni1	C1	96.76(5)
2	Cl3	Ni1	C45	92.27(7)
3	Cl3	Ni1	C46A	126.39(9)
4	Cl3	Ni1	C47	164.92(7)
5	C1	Ni1	C45	169.36(8)
6	C1	Ni1	C46A	134.2(1)
7	C1	Ni1	C47	97.88(9)
8	C45	Ni1	C46A	39.8(1)
9	C45	Ni1	C47	72.8(1)
10	C46A	Ni1	C47	41.1(1)
11	C1	N1	C2	110.4(1)
12	C1	N1	C4	124.8(1)

13	C2	N1	C4	124.8(1)
14	C1	N2	C3	110.4(1)
15	C1	N2	C24	125.2(1)
16	C3	N2	C24	124.2(1)
17	Ni1	C1	N1	127.9(1)
18	Ni1	C1	N2	127.3(1)
19	N1	C1	N2	104.7(1)
20	Cl1	C2	N1	124.0(1)
21	Cl1	C2	C3	128.5(1)
22	N1	C2	C3	107.3(2)
23	Cl2	C3	N2	123.7(1)
24	Cl2	C3	C2	129.1(1)
25	N2	C3	C2	107.1(2)
26	N1	C4	C5	118.6(2)
27	N1	C4	C9	118.1(2)
28	C5	C4	C9	123.2(2)
29	C4	C5	C6	116.4(2)
30	C4	C5	C17A	128.7(3)
31	C6	C5	C17A	114.8(3)
32	C5	C6	H6	119.2
33	C5	C6	C7	121.6(2)
34	H6	C6	C7	119.2
35	C6	C7	H7	119.7
36	C6	C7	C8	120.6(2)
37	H7	C7	C8	119.7
38	C7	C8	H8	119.5
39	C7	C8	C9	121.0(2)
40	H8	C8	C9	119.5
41	C4	C9	C8	117.1(2)
42	C4	C9	C10	122.5(2)
43	C8	C9	C10	120.3(2)
44	C9	C10	H10	106.7
45	C9	C10	C11	112.4(2)
46	C9	C10	C14	110.9(2)
47	H10	C10	C11	106.7
48	H10	C10	C14	106.7
49	C11	C10	C14	113.1(2)
50	C10	C11	H11A	108.6
51	C10	C11	H11B	108.6
52	C10	C11	C12	114.6(2)

53	H11A	C11	H11B	107.6
54	H11A	C11	C12	108.6
55	H11B	C11	C12	108.6
56	C11	C12	H12A	109.0
57	C11	C12	H12B	109.0
58	C11	C12	C13	112.8(2)
59	H12A	C12	H12B	107.8
60	H12A	C12	C13	109.0
61	H12B	C12	C13	109.0
62	C12	C13	H13A	109.5
63	C12	C13	H13B	109.5
64	C12	C13	H13C	109.5
65	H13A	C13	H13B	109.5
66	H13A	C13	H13C	109.5
67	H13B	C13	H13C	109.5
68	C10	C14	H14A	108.4
69	C10	C14	H14B	108.4
70	C10	C14	C15	115.5(2)
71	H14A	C14	H14B	107.5
72	H14A	C14	C15	108.4
73	H14B	C14	C15	108.4
74	C14	C15	H15A	109.0
75	C14	C15	H15B	109.0
76	C14	C15	C16	112.9(2)
77	H15A	C15	H15B	107.8
78	H15A	C15	C16	109.0
79	H15B	C15	C16	109.0
80	C15	C16	H16A	109.5
81	C15	C16	H16B	109.5
82	C15	C16	H16C	109.5
83	H16A	C16	H16B	109.5
84	H16A	C16	H16C	109.5
85	H16B	C16	H16C	109.5
86	C5	C17A	H17A	106.8
87	C5	C17A	C18A	110.6(4)
88	C5	C17A	C21	111.9(4)
89	H17A	C17A	C18A	106.9
90	H17A	C17A	C21	107.0
91	C18A	C17A	C21	113.2(4)
92	C17A	C18A	H18C	108.1

93	C17A	C18A	H18D	108.2
94	C17A	C18A	C19A	116.7(3)
95	H18C	C18A	H18D	107.3
96	H18C	C18A	C19A	108.1
97	H18D	C18A	C19A	108.1
98	C18A	C19A	H19A	109.0
99	C18A	C19A	H19B	109.1
100	C18A	C19A	C20A	112.5(6)
101	H19A	C19A	H19B	107.8
102	H19A	C19A	C20A	109.1
103	H19B	C19A	C20A	109.2
104	C19A	C20A	H20A	110
105	C19A	C20A	H20B	110
106	C19A	C20A	H20C	109
107	H20A	C20A	H20B	110
108	H20A	C20A	H20C	109
109	H20B	C20A	H20C	109
110	C17A	C21	H21A	107.5
111	C17A	C21	H21B	107.5
112	C17A	C21	C22	119.2(3)
113	H21A	C21	H21B	107.0
114	H21A	C21	C22	107.5
115	H21B	C21	C22	107.5
116	C21	C22	H22A	109.2
117	C21	C22	H22B	109.3
118	C21	C22	C23	111.9(2)
119	H22A	C22	H22B	107.9
120	H22A	C22	C23	109.2
121	H22B	C22	C23	109.3
122	C22	C23	H23A	109.5
123	C22	C23	H23B	109.5
124	C22	C23	H23C	109.5
125	H23A	C23	H23B	109.5
126	H23A	C23	H23C	109.4
127	H23B	C23	H23C	109.4
128	N2	C24	C25	118.6(1)
129	N2	C24	C29	118.4(1)
130	C25	C24	C29	122.9(2)
131	C24	C25	C26	117.1(2)
132	C24	C25	C30	121.8(2)

133	C26	C25	C30	120.9(2)
134	C25	C26	H26	119.4
135	C25	C26	C27	121.2(2)
136	H26	C26	C27	119.4
137	C26	C27	H27	119.6
138	C26	C27	C28	120.7(2)
139	H27	C27	C28	119.6
140	C27	C28	H28	119.4
141	C27	C28	C29	121.2(2)
142	H28	C28	C29	119.4
143	C24	C29	C28	116.8(2)
144	C24	C29	C37A	123.1(2)
145	C28	C29	C37A	120.1(2)
146	C25	C30	H30	107.8
147	C25	C30	C31	108.9(2)
148	C25	C30	C34	115.4(2)
149	H30	C30	C31	107.8
150	H30	C30	C34	107.8
151	C31	C30	C34	109.0(2)
152	C30	C31	H31A	108.6
153	C30	C31	H31B	108.6
154	C30	C31	C32	114.5(2)
155	H31A	C31	H31B	107.6
156	H31A	C31	C32	108.6
157	H31B	C31	C32	108.6
158	C31	C32	H32A	109.4
159	C31	C32	H32B	109.4
160	C31	C32	C33	111.2(2)
161	H32A	C32	H32B	108.0
162	H32A	C32	C33	109.4
163	H32B	C32	C33	109.4
164	C32	C33	H33A	109.5
165	C32	C33	H33B	109.5
166	C32	C33	H33C	109.5
167	H33A	C33	H33B	109.5
168	H33A	C33	H33C	109.5
169	H33B	C33	H33C	109.5
170	C30	C34	H34A	108.1
171	C30	C34	H34B	108.1
172	C30	C34	C35	116.7(2)

173	H34A	C34	H34B	107.3
174	H34A	C34	C35	108.1
175	H34B	C34	C35	108.1
176	C34	C35	H35A	109.4
177	C34	C35	H35B	109.4
178	C34	C35	C36	111.0(2)
179	H35A	C35	H35B	108.0
180	H35A	C35	C36	109.4
181	H35B	C35	C36	109.4
182	C35	C36	H36A	109.5
183	C35	C36	H36B	109.5
184	C35	C36	H36C	109.5
185	H36A	C36	H36B	109.5
186	H36A	C36	H36C	109.5
187	H36B	C36	H36C	109.5
188	C29	C37A	H37A	107.4
189	C29	C37A	C38A	109.4(2)
190	C29	C37A	C41A	114.1(3)
191	H37A	C37A	C38A	107.3
192	H37A	C37A	C41A	107.4
193	C38A	C37A	C41A	111.0(3)
194	C37A	C38A	H38A	108.5
195	C37A	C38A	H38B	108.6
196	C37A	C38A	C39A	115.0(3)
197	H38A	C38A	H38B	107.5
198	H38A	C38A	C39A	108.5
199	H38B	C38A	C39A	108.6
200	C38A	C39A	H39A	109.2
201	C38A	C39A	H39B	109.3
202	C38A	C39A	C40A	111.9(3)
203	H39A	C39A	H39B	107.9
204	H39A	C39A	C40A	109.2
205	H39B	C39A	C40A	109.3
206	C39A	C40A	H40D	109.5
207	C39A	C40A	H40E	109.5
208	C39A	C40A	H40F	109.4
209	H40D	C40A	H40E	109.5
210	H40D	C40A	H40F	109.5
211	H40E	C40A	H40F	109.4
212	C37A	C41A	H41A	108.9

213	C37A	C41A	H41B	109.0
214	C37A	C41A	C42A	113.4(4)
215	H41A	C41A	H41B	107.6
216	H41A	C41A	C42A	108.9
217	H41B	C41A	C42A	108.9
218	C41A	C42A	H42A	109.1
219	C41A	C42A	H42B	109.0
220	C41A	C42A	C43A	112.6(4)
221	H42A	C42A	H42B	107.9
222	H42A	C42A	C43A	109.1
223	H42B	C42A	C43A	109.1
224	C42A	C43A	H43A	109.5
225	C42A	C43A	H43B	109.5
226	C42A	C43A	H43C	109.5
227	H43A	C43A	H43B	109.5
228	H43A	C43A	H43C	109.5
229	H43B	C43A	H43C	109.5
230	Ni1	C45	H45A	95(2)
231	Ni1	C45	H45B	124(2)
232	Ni1	C45	C46A	67.4(2)
233	H45A	C45	H45B	111(2)
234	H45A	C45	C46A	117(2)
235	H45B	C45	C46A	130(2)
236	Ni1	C46A	C45	72.8(2)
237	Ni1	C46A	H46A	112(1)
238	Ni1	C46A	C47	69.7(2)
239	C45	C46A	H46A	119(1)
240	C45	C46A	C47	120.1(2)
241	H46A	C46A	C47	118(1)
242	Ni1	C47	C46A	69.2(2)
243	Ni1	C47	H47A	99(2)
244	Ni1	C47	H47B	130(2)
245	C46A	C47	H47A	118(2)
246	C46A	C47	H47B	127(2)
247	H47A	C47	H47B	108(2)

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