

Pentafluorosulfanyl (SF₅): a robust and unique electron-withdrawing group for optoelectronic materials

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Abstract

π -Conjugated organic materials have gained much attention and proven useful in multiple optoelectronic applications such as nonlinear optics, organic light-emitting diodes, organic solar cells, and organic field-effect transistors due to their low cost, facile synthesis, light weight, fine tunability, high processibility and mechanical flexibility. Particularly, molecular designs of π -conjugated systems featuring electron donors and acceptors (donor-acceptor systems), or just electron-deficient moieties (acceptor materials) are essential and valuable in realizing critical properties that are desirable for a wide range of optoelectronic materials, such as nonlinear optical materials, thermally activated delayed fluorescence emitters, solar harvesting materials and organic n-type semiconductors. Pentafluorosulfanyl (SF_5) is a strong electron-withdrawing group that can certainly be applied in the structural designs of donor-acceptor systems and acceptor materials. Along with its strongly electron-withdrawing nature, SF_5 is also sterically bulky, chemically/thermally robust and hydrophobic/lipophilic, rendering it unique among electron-withdrawing groups and highly desirable in various optoelectronic materials. However, the SF_5 group was only adopted sporadically in a small number of optoelectronic materials and its potential in a wide range of other optoelectronic materials remained largely untapped.

Therefore, this thesis aims to investigate the potential of SF_5 in a wider variety of molecular designs for novel optoelectronic materials. Specifically, Chapter One provides a brief overview of optoelectronic materials and covers the potential and reported application of SF_5 in the molecular designs for different optoelectronic organic materials. Chapter Two will discuss the synthesis of five SF_5 -containing push-pull dyes and their photophysical properties, particularly their large two-photon absorption characters. In Chapter Three, two styrenic polymers bearing the polar SF_5 groups are synthesized and utilized as charge-storage electrets in nonvolatile organic field-effect transistor memory devices. Also, their superior memory device performance to other polar styrenic polymers will be revealed. Chapter Four elaborates the synthesis of a series of SF_5 -functionalized ullazine derivatives, with the success of synthesis ascribed to the chemical and thermal robustness of SF_5 . Additionally, the photophysical and electrochemical properties of these

SF₅-functionalized ullazine derivatives will be investigated, and their potential application in dye-sensitized solar cells will be examined. Finally, in Chapter Five, the work presented in Chapters Two through Four, as well as the previously reported work on SF₅-containing optoelectronic materials (in Chapter One), is summarized. In addition, the future scope of SF₅ in optoelectronic materials will be proposed as well.

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Table of contents

Abstract	II
Acknowledgments.....	IV
Table of contents.....	VI
List of Figures	VIII
List of Tables	XIV
List of Abbreviations	XVII
Statement of Contributions	XX
Chapter 1. Introduction	1
1.1 Organic materials for optoelectronic applications	1
1.2 π -Conjugated organic materials	3
1.2.1 Donor-Acceptor systems	4
1.2.2 Acceptor materials.....	8
1.3 Pentafluorosulfanyl (SF ₅): a robust and unique electron-withdrawing group.....	11
1.3.1 Chemical and physical properties of SF ₅	12
1.3.2 Comparison of SF ₅ with other electron-withdrawing groups and the substituent effects.....	15
1.3.3 CF ₃ Versus SF ₅	17
1.3.4 SF ₅ : an emerging functional group for optoelectronic materials.....	21
1.4 Outline of the thesis.....	30
1.5 References	31
Chapter 2. Large Two-Photon Absorption Cross-Sections by SF ₅ -Containing Push-Pull Dyes	39
2.1 Introduction	39
2.2 Results and Discussion.....	42
2.3 Conclusion.....	54
2.4 Experimental Section	55
2.5 References	61
Chapter 3. SF ₅ -Containing Polymers as Electrets in Nonvolatile OFET Memory Devices	67
3.1 Introduction	67

3.2 Results and Discussion.....	70
3.3 Conclusion.....	83
3.4 Experimental Section	83
3.5 References	86
Chapter 4. SF ₅ -Functionalized Ullazine Derivatives as Potential Dye-Sensitizer Solar Cell Materials	90
4.1 Introduction	90
4.2 Results and Discussion.....	92
4.3 Conclusion.....	104
4.4 Experimental Section	104
4.5 References	119
Chapter 5. Conclusion and Outlook.....	123
5.1 Conclusion.....	123
5.2 Outlook.....	125
5.3 References	129
Appendix.....	131
Crystallographic Data.....	131
Chapter 4.....	131
Theoretical Calculations.....	133
Chapter 2.....	133
Chapter 3.....	153
Chapter 4.....	157
NMR Spectra.....	176
Chapter 2.....	176
Chapter 3.....	190
Chapter 4.....	196
Copyright Permissions	234

List of Figures

Figure 1. 1 a) Laser device. b) Light-emitting diode. c) Solar cell. d) Field-effect transistor. e) Electronics-based optoelectronic devices. f) Flexible OLED display by Huawei Mate X2.	1
Figure 1. 2 Chart of best research-cell efficiencies for three representative photovoltaic technologies, plotted from 1976 to 2020. ^{9,10}	3
Figure 1. 3 Examples of a) small π -conjugated molecules and b) π -conjugated polymers.	3
Figure 1. 4 Examples of all sorts of D-A systems. Electron-donating and electron-accepting moieties are highlighted in red and blue, respectively.....	5
Figure 1. 5 MO diagram of different approaches for obtaining broad absorption (small HOMO-LUMO gap) by a) extending conjugation or b) donor-acceptor structure designs.....	5
Figure 1. 6 Comparison of electroluminescence mechanism of a) conventional fluorescent emitter (9,10-diphenylanthracene) and b) TADF emitter (4CzIPN) in OLED devices. ³² F, P, IC, RISC, ΔE_{ST} represent fluorescence (F), phosphorescence (P), internal conversion (IC), reverse intersystem crossing (RISC), and singlet-triplet energy gap (ΔE_{ST}), respectively.	7
Figure 1. 7 a) Band diagram and main processes in bulk heterojunction OSCs: 1. Light absorption followed by exciton formation; 2. Exciton diffusion to the donor-acceptor interface; 3. Exciton dissociation into free charges; 4. Charge collection. b) Acceptor materials including fullerene and non-fullerene molecules: Y6 and ITIC (electron-accepting moieties are highlighted in blue). ^{42,43}	10
Figure 1. 8 Structure and chemical/physical properties of SF ₅ group.....	12
Figure 1. 9 a) Representative chemical structures of methyl and CF ₃ substituted twisted donor-acceptor systems by Li's study. ⁹² b) Chemical structures of CN-QP and TFM-QP . ⁹⁶	18
Figure 1. 10 a) Power conversion efficiency improved by changing the donor material from PBZ1 (5.8%) to PBZ-m-CF3 (10.4%) while using ITIC as the acceptor material for bulk heterojunction OSCs. ¹⁰³ b) Efficiency improved by varying the acceptor material from ITIC (8.4%) to ITICF3 (13.3%) while using PM6 as the donor material for bulk heterojunction OSCs. ¹⁰⁶	21
Figure 1. 11 a) Chemical structures of N-phenyl imide derivatives. b) F $\cdots$ F interactions in Crystal packing of N1 . c) F $\cdots$ F interactions in Crystal packing of N2 . ¹¹⁰	23
Figure 1. 12 a) Ir(III) complexes showed blue-shifted emission upon fluorination, trifluoromethylation, and pentafluorosulfanylation. ¹¹⁵ b) Different SF ₅ positions on Pt(II) complexes displayed a red-shifted or blue-shifted emission relative to the no-SF ₅ analogue. ¹¹⁸	25
Figure 1. 13 Chemical structures of SF ₅ -containing azulenes. ¹²⁶	28
Figure 1. 14 a) Chemical structures of SF ₅ -containing push-pull dyes L1-L6 . b) crystal packing diagrams of L1-L6 . ¹²⁸	29

Figure 2. 1	Jablonski diagram of two-photon absorption.	39
Figure 2. 2	Cyanine dye (top), porphyrin dimer (bottom left), and a squaraine dye (bottom right), featuring resonance-stabilized cationic acceptors.	40
Figure 2. 3	Modified valence bond description of SF ₆ featuring ionic resonance contributors.	41
Figure 2. 4	a) Negative hyperconjugation and “no-bond” resonance in 4-(pentafluorosulfanyl)aniline, canonical structures featuring sulfur with ionic character. b) Resonance contributors of a two-photon chromophore featuring hypervalent sulfur with ionic character due to negative hyperconjugation.	41
Figure 2. 5	Two-photon absorbing molecules based on potent pentafluorosulfanyl acceptors.	42
Figure 2. 6	Normalized absorption and fluorescence spectra of D1-D5 as measured in chloroform.	46
Figure 2. 7	Molar absorptivities (ϵ) of D1-D5 as measured in chloroform.	46
Figure 2. 8	a-e) Emission spectra of D1-D5 in four different solvents with different polarities. f) Lippert-Mataga correlations for D1-D5	47
Figure 2. 9	a-e) Logarithmic plot of fluorescence output with the photoluminescent intensity of D1-D5 . f) Two-photon action spectra for SF ₅ -containing dyes D1-D5 in CHCl ₃	50
Figure 3. 1	Schematic configuration of an OFET memory device and molecular structures of charge storage polymer electrets.	67
Figure 3. 2	Absorption spectra of P1 and P2 in a) THF solutions and b) thin-film states.	72
Figure 3. 3	Fluorescence spectra of P1 and P2 in chloroform.	73
Figure 3. 4	Thermogravimetric analysis (TGA) of a) P1 and b) P2 . Differential scanning calorimetry (DSC) curves of c) P1 and d) P2	74
Figure 3. 5	Images of water droplet contact angles of a) P1 and b) P2 films. AFM topologies of c) P1 and d) P2 on the top of SiO ₂ surface. AFM topographic images of pentacene on e) P1 and f) P2 surface.	75
Figure 3. 6	Output characteristics of OEFT memories based on a) P1 and b) P2	76
Figure 3. 7	Transfer characteristics of OFET memories based on a) P1 and b) P2 electrets under initial, PGM ($V_g = 120$ V, 10 s), and ERS processes ($V_g = -120$ V, 10 s), with $V_d = -80$ V in all measurements.	77
Figure 3. 8	Data retention characteristics of OFET memories based on a) P1 and b) P2 electrets at the reading voltage of $V_g = -5$ V; $V_d = -80$ V, after PGM ($V_g = 120$ V, 10 s), and after ERS ($V_g = -120$ V, 10 s).	78
Figure 3. 9	I_d response for the repeated pulse bias of PRER operations of OFET memories based on a) P1 and b) P2 electrets.	79
Figure 3. 10	Cyclic endurance characteristics of OFET memories based on a) P1 and b) P2 electrets for PGM/ERS repeating cycles.	79

Figure 3. 11	A schematic energy band diagram during a) initial, b) PGM, and c) ERS operations for the charge trapping/detrapping mechanistic description.....	81
Figure 4. 1	Chemical structure and frontier molecular orbitals of ullazine.....	90
Figure 4. 2	a-g) Normalized absorption and photoluminescence spectra and h) molar absorptivities (ϵ) of U1–U3 and U7–U10 in chloroform.....	99
Figure 4. 3	a) Cyclic voltammograms of U1–U3 and U7–U10 in chloroform with 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu ₄ NPF ₆) as the supporting electrolyte. b) Potential energy diagram of conduction band (CB) of TiO ₂ , E _(S+/S) and E _(S+/S*) of U1–U3 , U7–U10 , and I [–] /I ₃ [–] redox couple.	101
Figure 4. 4	Working principle of dye-sensitized solar cells.	103
Figure 5. 1	The next generation of SF ₅ -functionalized two-photon absorption dye based on D2 with potential improved δ_{TPA} and $\delta_{\text{TPA}}\phi_f$ values.....	126
Figure 5. 2	a) Next generation of SF ₅ -functionalized styrenic polymer electret based on P2 . b) Example of donor-acceptor type small molecule electret for OFET memory devices. c) Molecular design of SF ₅ -functionalized donor-acceptor type small molecule electret.	127
Figure 5. 3	New SF ₅ -containing ullazine dyes based on U8 for DSSC applications.....	128
Figure A. 1	ORTEP view of U2 and the atom-labelling scheme. Thermal ellipsoids are plotted at the 50 % level.	131
Figure A. 2	Frontier molecular orbitals of dyes D1–D5 , as calculated using Gaussian09 at the B3LYP/6-31G** level for C, N, S, and H.....	134
Figure A. 3	Frontier molecular orbitals of U1–U3 and U7–U10 , calculated using Gaussian09 at the B3LYP/6-31G level for C, N, S, and H.	158
Figure A. 4	¹ H NMR spectrum of compound 2e	176
Figure A. 5	¹³ C NMR spectrum of compound 2e	176
Figure A. 6	¹ H NMR spectrum of compound 2f	177
Figure A. 7	¹³ C NMR spectrum of compound 2f	177
Figure A. 8	¹ H NMR spectrum of compound 2g	178
Figure A. 9	¹³ C NMR spectrum of compound 2g	178
Figure A. 10	¹ H NMR spectrum of compound 2j	179
Figure A. 11	¹³ C NMR spectrum of compound 2j	179
Figure A. 12	¹ H NMR spectrum of compound 2k	180
Figure A. 13	¹³ C NMR spectrum of compound 2k	180

Figure A. 14	^1H NMR spectrum of compound 2l	181
Figure A. 15	^{13}C NMR spectrum of compound 2l	181
Figure A. 16	^1H NMR spectrum of compound D1	182
Figure A. 17	^{13}C NMR spectrum of compound D1	182
Figure A. 18	^{19}F NMR spectrum of compound D1	183
Figure A. 19	^1H NMR spectrum of compound D2	183
Figure A. 20	^{13}C NMR spectrum of compound D2	184
Figure A. 21	^{19}F NMR spectrum of compound D2	184
Figure A. 22	^1H NMR spectrum of compound D3	185
Figure A. 23	^{13}C NMR spectrum of compound D3	185
Figure A. 24	^{19}F NMR spectrum of compound D3	186
Figure A. 25	^1H NMR spectrum of compound D4	186
Figure A. 26	^{13}C NMR spectrum of compound D4	187
Figure A. 27	^{19}F NMR spectrum of compound D4	187
Figure A. 28	^1H NMR spectrum of compound D5	188
Figure A. 29	^{13}C NMR spectrum of compound D5	188
Figure A. 30	^{19}F NMR spectrum of compound D5	189
Figure A. 31	^1H NMR spectrum of compound 3a	190
Figure A. 32	^{13}C NMR spectrum of compound 3a	190
Figure A. 33	^{19}F NMR spectrum of compound 3a	191
Figure A. 34	^1H NMR spectrum of compound 3b	191
Figure A. 35	^{13}C NMR spectrum of compound 3b	192
Figure A. 36	^{19}F NMR spectrum of compound 3b	192
Figure A. 37	^1H NMR spectrum of compound P1	193
Figure A. 38	^{13}C NMR spectrum of compound P1	193
Figure A. 39	^{19}F NMR spectrum of compound P1	194
Figure A. 40	^1H NMR spectrum of compound P2	194
Figure A. 41	^{13}C NMR spectrum of compound P2	195
Figure A. 42	^{19}F NMR spectrum of compound P2	195
Figure A. 43	^1H NMR spectrum of compound 4a	196
Figure A. 44	^{13}C NMR spectrum of compound 4a	196
Figure A. 45	^{19}F NMR spectrum of compound 4a	197
Figure A. 46	^1H NMR spectrum of compound 4b	197
Figure A. 47	^{13}C NMR spectrum of compound 4b	198
Figure A. 48	^{19}F NMR spectrum of compound 4b	198
Figure A. 49	^1H NMR spectrum of compound 4c	199
Figure A. 50	^{13}C NMR spectrum of compound 4c	199
Figure A. 51	^{19}F NMR spectrum of compound 4c	200
Figure A. 52	^1H NMR spectrum of compound 4d	200

Figure A. 53	^{13}C NMR spectrum of compound 4d	201
Figure A. 54	^{19}F NMR spectrum of compound 4d	201
Figure A. 55	^1H NMR spectrum of compound 4e	202
Figure A. 56	^{13}C NMR spectrum of compound 4e	202
Figure A. 57	^{19}F NMR spectrum of compound 4e	203
Figure A. 58	^1H NMR spectrum of compound 4f	203
Figure A. 59	^{13}C NMR spectrum of compound 4f	204
Figure A. 60	^{19}F NMR spectrum of compound 4f	204
Figure A. 61	^1H NMR spectrum of compound 4g	205
Figure A. 62	^{13}C NMR spectrum of compound 4g	205
Figure A. 63	^{19}F NMR spectrum of compound 4g	206
Figure A. 64	^1H NMR spectrum of compound 4h	206
Figure A. 65	^{13}C NMR spectrum of compound 4h	207
Figure A. 66	^{19}F NMR spectrum of compound 4h	207
Figure A. 67	^1H NMR spectrum of compound 4i	208
Figure A. 68	^{13}C NMR spectrum of compound 4i	208
Figure A. 69	^{19}F NMR spectrum of compound 4i	209
Figure A. 70	^1H NMR spectrum of compound 4j	209
Figure A. 71	^{13}C NMR spectrum of compound 4j	210
Figure A. 72	^{19}F NMR spectrum of compound 4j	210
Figure A. 73	^1H NMR spectrum of compound 4k	211
Figure A. 74	^{13}C NMR spectrum of compound 4k	211
Figure A. 75	^{19}F NMR spectrum of compound 4k	212
Figure A. 76	^1H NMR spectrum of compound 4l	212
Figure A. 77	^{13}C NMR spectrum of compound 4l	213
Figure A. 78	^{19}F NMR spectrum of compound 4l	213
Figure A. 79	^1H NMR spectrum of compound 4m	214
Figure A. 80	^{13}C NMR spectrum of compound 4m	214
Figure A. 81	^{19}F NMR spectrum of compound 4m	215
Figure A. 82	^1H NMR spectrum of compound 4n	215
Figure A. 83	^{13}C NMR spectrum of compound 4n	216
Figure A. 84	^{19}F NMR spectrum of compound 4n	216
Figure A. 85	^1H NMR spectrum of compound 4o	217
Figure A. 86	^{13}C NMR spectrum of compound 4o	217
Figure A. 87	^{19}F NMR spectrum of compound 4o	218
Figure A. 88	^1H NMR spectrum of compound 4p	218
Figure A. 89	^{13}C NMR spectrum of compound 4p	219
Figure A. 90	^{19}F NMR spectrum of compound 4p	219
Figure A. 91	^1H NMR spectrum of compound U1	220

Figure A. 92	^{13}C NMR spectrum of compound U1 .	220
Figure A. 93	^{19}F NMR spectrum of compound U1 .	221
Figure A. 94	^1H NMR spectrum of compound U2 .	221
Figure A. 95	^{13}C NMR spectrum of compound U2 .	222
Figure A. 96	^{19}F NMR spectrum of compound U2 .	222
Figure A. 97	^1H NMR spectrum of compound U3 .	223
Figure A. 98	^{13}C NMR spectrum of compound U3 .	223
Figure A. 99	^{19}F NMR spectrum of compound U3 .	224
Figure A. 100	^1H NMR spectrum of compound U5 .	224
Figure A. 101	^{13}C NMR spectrum of compound U5 .	225
Figure A. 102	^{19}F NMR spectrum of compound U5 .	225
Figure A. 103	^1H NMR spectrum of compound U6 .	226
Figure A. 104	^{13}C NMR spectrum of compound U6 .	226
Figure A. 105	^{19}F NMR spectrum of compound U6 .	227
Figure A. 106	^1H NMR spectrum of compound U7 .	227
Figure A. 107	^{13}C NMR spectrum of compound U7 .	228
Figure A. 108	^{19}F NMR spectrum of compound U7 .	228
Figure A. 109	^1H NMR spectrum of compound U8 .	229
Figure A. 110	^{13}C NMR spectrum of compound U8 .	229
Figure A. 111	^{19}F NMR spectrum of compound U8 .	230
Figure A. 112	^1H NMR spectrum of compound U9 .	230
Figure A. 113	^{13}C NMR spectrum of compound U9 .	231
Figure A. 114	^{19}F NMR spectrum of compound U9 .	231
Figure A. 115	^1H NMR spectrum of compound U10 .	232
Figure A. 116	^{13}C NMR spectrum of compound U10 .	232
Figure A. 117	^{19}F NMR spectrum of compound U10 .	233

List of Tables

Table 1. 1 Examples of n-type organic semiconductors and their OFET device data. Electron-withdrawing moieties are highlighted in blue.	11
Table 1. 2 Representative examples of CF ₃ -containing n-type semiconductors exhibiting high electron mobilities and good air stability.	19
Table 2. 1 Photophysical data from the solvatochromic studies of D1-D5	48
Table 2. 2 The one- and two-photon photophysical properties of dyes D1-D5	51
Table 2. 3 Comparison of two-photon absorption properties of D1 with previously reported analogues.	52
Table 2. 4 Comparison of two-photon absorption properties of D2 with previously reported analogues.	53
Table 3. 1 Examples of pendent polymer electrets that have been studied in memory devices based on pentacene field-effect transistor. ¹⁴	69
Table 3. 2 Polymerization results and physical properties of P1 and P2	71
Table 3. 3 Comparison of memory properties of P1 and P2 with other polar styrenic polymers. ¹⁴ All OFET memory devices were fabricated with a bottom-gate and top-contact architecture using pentacene as the semiconductor layer.	82
Table 4. 1 Mono- vs. double-cycloaromatization.	94
Table 4. 2 Photophysical and electrochemical properties of U1-U3 and U7-U10	100
Table 4. 3 Photophysical characteristics of ullazines A , B , and U1	102
Table A. 1 Crystal data and structure refinement for U2	131
Table A. 2 Atomic coordinates for structure of D1	134
Table A. 3 Atomic coordinates for structure of D2	137
Table A. 4 Atomic coordinates for structure of D3	140
Table A. 5 Atomic coordinates for structure of D4	144
Table A. 6 Atomic coordinates for structure of D5	148
Table A. 7 Atomic coordinates for the representative model structure of the P1 repeat unit.	153
Table A. 8 Atomic coordinates for the representative model structure of the P2 repeat unit.	154

Table A. 9 Atomic coordinates for structure of U1	158
Table A. 10 Atomic coordinates for structure of U2	160
Table A. 11 Atomic coordinates for structure of U3	162
Table A. 12 Atomic coordinates for structure of U7	165
Table A. 13 Atomic coordinates for structure of U8	167
Table A. 14 Atomic coordinates for structure of U9	170
Table A. 15 Atomic coordinates for structure of U10	173

List of Schemes

Scheme 1. 1 Landmark synthetic approaches of SF ₅ -functionalized arene. ^{59, 74, 77}	14
Scheme 1. 2 Representative synthesis of SF ₅ -substituted phthalocyanine. ¹¹²	24
Scheme 1. 3 Representative synthesis of SF ₅ -functionalized fullerene. ¹²³	27
Scheme 2. 1 Synthesis of olefin intermediates 2j-2l . Reagents and reaction conditions: a) Pd(OAc) ₂ , TBAB, K ₂ CO ₃ , DMF, 110 °C, 30 h; b) <i>t</i> -BuOK, CH ₃ PPh ₃ I, THF, rt, 36 h.....	44
Scheme 2. 2 Synthesis of two-photon dyes D1-D5 via Mizoroki-Heck coupling.....	44
Scheme 3. 1 Synthesis of pentafluorosulfanylated polymers P1 and P2 . Reagents and reaction conditions: a) Pd(PPh ₃) ₄ cat., Na ₂ CO ₃ , H ₂ O, PhMe, 100 °C, 18 h; b) (PhCO) ₂ O ₂ initiator, benzene, reflux, 4 h.	71
Scheme 4. 1 Synthesis of key intermediate 4d	92
Scheme 4. 2 Attempted synthesis of pentafluorosulfanylated ullazines U1-U3	93
Scheme 4. 3 Synthesis of iodinated pentafluorosulfanylated ullazines U5 and U6	96
Scheme 4. 4 Synthesis of U7-U10 . Reagents and conditions: a) InCl ₃ , 1,2-DCB, 145 °C, 24 h; b) CuCN, DMF, 110 °C, 16 h; c) InCl ₃ , 1,2-DCB, 180 °C, 24 h; d) Trimethylsilyl acetylene, PdCl ₂ (PPh ₃) ₂ , CuI, Et ₃ N, 50 °C, 24 h; e) KOH, THF/MeOH, 0 °C to rt, 2 h; f) 4-bromophenylsulfur pentafluoride, Pd(PPh ₃) ₄ , CuI, NEt ₃ , 80 °C, 24 h; g) 4-(pentafluorosulfanyl)phenylboronic acid, Pd(PPh ₃) ₄ , K ₂ CO ₃ , DMF, 110 °C, 16 h; h) InCl ₃ , 1,2-DCB, 150 °C, 24 h; i) 4-methoxyphenylboronic acid, Pd(PPh ₃) ₄ , K ₂ CO ₃ , DMF, 110 °C, 16 h; j) InCl ₃ , 1,2-DCB, 140 °C, 24 h.	97

List of Abbreviations

2PA	Two-Photon Absorption
A	Acceptor
Å	Angstrom
a.u.	Arbitrary Unit
ACQ	Aggregation Caused Emission Quenching
AFM	Atomic Force Microscopy
AIBN	Azoisobutyronitrile
BHJ	Bulk Heterojunction
CB	Conduction Band
CCD	Charge Coupled Device
CF ₃	Trifluoromethyl
CN	Cyano
D	Donor
<i>D</i>	Dispersity
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
DSSC	Dye-Sensitized Solar Cell
E	Energy
EQE	External Quantum Efficiency
E _r C _i	Irreversible Chemical Reaction
ERS	Erasing
EWG	Electron-Withdrawing Group
<i>f</i>	Solvent Orientation Polarizability Parameter
FET	Field-Effect Transistor
FF	Fill Factor
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
HRMS	High-Resolution Mass Spectrometry
IC	Internal Conversion

ICT	Intramolecular Charge Transfer
I_d	Drain Current
IQE	Internal Quantum Efficiency
LCD	Liquid Crystal Display
LED	Light-Emitting Diode
LEEC	Light-Emitting Electrochemical Cell
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
MW	Memory Window
NHE	Normal Hydrogen Electrode
NIR	Near-Infrared
NLO	Nonlinear Optics
NMR	Nuclear Magnetic Resonance
NO ₂	Nitro
N _{π}	The Total Number Of π -Electrons
OCF ₃	Trifluoromethoxy
OFET	Organic Field-Effect Transistor
OLED	Organic Light-Emitting Diode
ONVM	Organic Nonvolatile Memory
OSC	Organic Solar Cell
PCE	Power Conversion Efficiency
PGM	Programming
PRER	Program/Read/Erase/Read
RISC	Reverse Intersystem Crossing
S ₀	Ground State
S ₁	First Singlet Excited State
SALC	Symmetry-Adapted Linear Combination
SCF ₃	Trifluoromethylthio
SF ₅	Pentafluorosulfanyl
SF ₆	Sulfur Hexafluoride
S _n	Excited State

SOMO	Singly Occupied Molecular Orbital
T_1	First Triplet Excited State
TADF	Thermally Activated Delayed Fluorescence
T_d	Decomposition Temperature
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
UV-Vis	Ultraviolet-Visible
VB	Valence Bond
V_d	Drain Voltage
V_g	Gate Voltage
V_{oc}	Open Circuit Voltage
V_{read}	Reading Voltage
V_{th}	Threshold Voltage
XRD	X-Ray Diffraction
ΔE_{ST}	Singlet-Triplet Energy Gap
δ_{TPA}	Two-Photon Absorption Cross-Section
$\Delta\nu$	Stokes Shift
ε	Molar Extinction Coefficient
λ_{em}	Emission Peak
μ_e	Electron mobility
Φ_f	Fluorescence Quantum Yield
σ_P	Hammett Substituent Parameter
σ_I	Inductive Effect Constant
σ_R	Resonance Effect Constant

Statement of Contributions

Chapters 2, 3 and 4 are revised based on the previously published manuscripts to adapt to this thesis format. Figures, tables, and data have been reproduced with permissions from publishers.

Reference of Chapter 2: P. Gautam, Y. Wang, G. Zhang, H. Sun, and J. M. W. Chan. Using the Negative Hyperconjugation Effect of Pentafluorosulfanyl Acceptors to Enhance Two-Photon Absorption in Push–Pull Chromophores. *Chem. Mater.* **2018**, *30*, 7066.

Contributions of Chapter 2: The syntheses of all compounds, NMR characterizations, and DTF calculations were performed by Dr. Prabhat Gautam. The preparation of spectroscopically pure compounds (**D1-D5**), and one-photon photophysical studies and interpretation were performed by Guoxian Zhang. The two-photon photophysical studies of **D1-D5** were performed by Dr. Yue Wang. All authors contributed to the preparation and editing of the manuscript.

Reference of Chapter 3: G. Zhang, Y.-J. Lee, P. Gautam, C.-C. Lin, C.-L. Liu, and J. M. W. Chan. Pentafluorosulfanylated Polymers as Electrets in Nonvolatile Organic Field-Effect Transistor Memory Devices. *J. Mater. Chem. C* **2019**, *7*, 7865.

Contributions of Chapter 3: The syntheses of all compounds, characterizations including NMR, GPC, TGA, DSC, and DFT calculations were performed by Guoxian Zhang. The photophysical studies and interpretation were performed by Guoxian Zhang and Dr. Prabhat Gautam. The hydrophobicity characterization, AFM studies, and device fabrication and measurement of **P1** and **P2** were performed by Yu-Jung Lee and Chia-Chi Lin. Guoxian Zhang, Yu-Jung Lee, Dr. Cheng-Liang Liu, and Dr. Julian Chan contributed to the preparation and editing of the manuscript.

Reference of Chapter 4: G. Zhang, P. Gautam, and J. M. W. Chan. Symmetrical and Unsymmetrical Fluorine-rich Ullazines via Controlled Cycloaromatizations. *Org. Chem. Front.* **2020**, *7*, 787.

Contributions of Chapter 4: The syntheses and NMR characterizations of **4a-4d** were performed by Dr. Prabhat Gautam, while the rest of the compounds were performed by Guoxian Zhang. The DFT calculations of **U2** were performed by Dr. Prabhat Gautam,

while the rest of the compounds were performed by Guoxian Zhang. The HRMS and elemental analysis characterization, photophysical and electrochemical studies and interpretation were performed by Guoxian Zhang. The first draft of the manuscript was written by Guoxian Zhang and Dr. Julian Chan edited the final draft.

Additional publications that are not included in this thesis:

Wei Zhang, Wenqi Xu, **Guoxian Zhang**, Jie Kong, Xinmiao Niu, Julian M. W. Chan, Weimin Liu, and Andong Xia. *J. Phys. Chem. B* 2021, 125, 4456.

Guoxian Zhang, Pratap C. Naha, Prabhat Gautam, David P. Cormode, and Julian M. W. Chan. *ACS Appl. Bio Mater.* 2018, 1, 1918.

Prabhat Gautam, Craig P. Yu, **Guoxian Zhang**, Victoria E. Hillier, and Julian M. W. Chan. *J. Org. Chem.* 2017, 82, 11008.

Guoxian Zhang and Julian M. W. Chan. *J. Mater. Chem. C*, 2017, 5, 10007.

Tarunpreet Singh Virk, Niranjana V. Ilawe, **Guoxian Zhang**, Craig P. Yu, Bryan M. Wong, and Julian M. W. Chan. *ACS Omega* 2016, 1, 1336.

Chapter 1. Introduction

1.1 Organic materials for optoelectronic applications

Semiconducting materials such as silicon, gallium arsenide and indium phosphide can interact with light in a quantum mechanical manner, endowing them with fascinating properties that profoundly impact our daily lives by enabling all sorts of electronics through a variety of optoelectronic devices, e.g., lasers, light-emitting diodes (LEDs), solar cells, and field-effect transistors (FETs) (Figure 1.1).¹ While research on optoelectronic devices based on inorganic semiconductors continues to develop and prosper, since the 1980s, a new class of optoelectronic devices that worked on carbon-based materials, termed organic semiconductors or π -conjugated organic materials, gained significant attention due to the first successful demonstration of efficient organic thin-film light-emitting diode operated under low voltage by Tang and Van Slyke.² Since then, π -conjugated organic materials have been proven with practical significance in multiple optoelectronic applications such as nonlinear optics (NLOs), organic light-emitting diodes (OLEDs), organic solar cells (OSCs), and organic field-effect transistors (OFETs).³



Figure 1. 1 a) Laser device. b) Light-emitting diode. c) Solar cell. d) Field-effect transistor. e) Electronics-based optoelectronic devices. f) Flexible OLED display by Huawei Mate X2.

Thus far, the most successful application of π -conjugated organic materials is in the OLED display technique,^{4,5} which has been commercialized and becomes popular in high-quality displays for electronic devices such as iPhone Pro series by Apple, Mate X series by Huawei (Figure 1.1f), and Galaxy smartphone series by Samsung. However, in contrast to the current dominant display technique, i.e., liquid crystal display (LCD), OLED display generally suffers from a short device lifespan mainly due to the low stability of organic emitters.⁴ Nevertheless, it also demonstrates unrivalled advantages such as high quality and flexible display, low energy consumptions, easy fabrication, etc.⁶ In contrast to their application in OLEDs, π -conjugated organic materials have not achieved the same level of success in OSCs and OFETs. Still, great progress has been made in the past few decades.⁷ Figure 1.2 shows the best efficiencies for three representative research cells,^{9,10} with the best efficiencies for inorganic multijunction cells exceeding 47%, and single crystalline silicon and organic cells exceeding 27% and 18% efficiency,¹¹ respectively. Even though the efficiencies are still inferior to the inorganic solar cells, OSCs are constantly being improved and the results are encouraging.^{7,8} Also, low-cost manufacturing and lightweight organic molecules make OSCs more economically accessible and used as portable solar cells.⁷ Similarly, OFETs have great potential because of their low cost, light weight, and easy fabrication.¹² Even their performances can not compete with inorganic silicon-based FETs that enable sophisticated microprocessors such as chips, OFETs are still desired due to their potential to serve in inexpensive/disposable and flexible electronic circuits such as radio frequency identification tags and flexible display backplanes.¹³ These circuits can be potentially fabricated by simple printing methods without requiring the demanding techniques needed for silicon-based circuitry.

Overall, even though π -conjugated organic materials are still inferior to their inorganic counterparts in terms of efficiency or stability in optoelectronic applications such as OLEDs, OSCs, and OFETs, they display great potential as tremendous improvements and exciting results have been obtained over the past few decades.^{1, 3, 7-9, 12, 14-16} More importantly, they demonstrate unparalleled advantages such as low cost, facile synthesis, light weight, fine tunability, high processibility and mechanical flexibility compared to the inorganic semiconductors.

Best Research-Cell Efficiencies

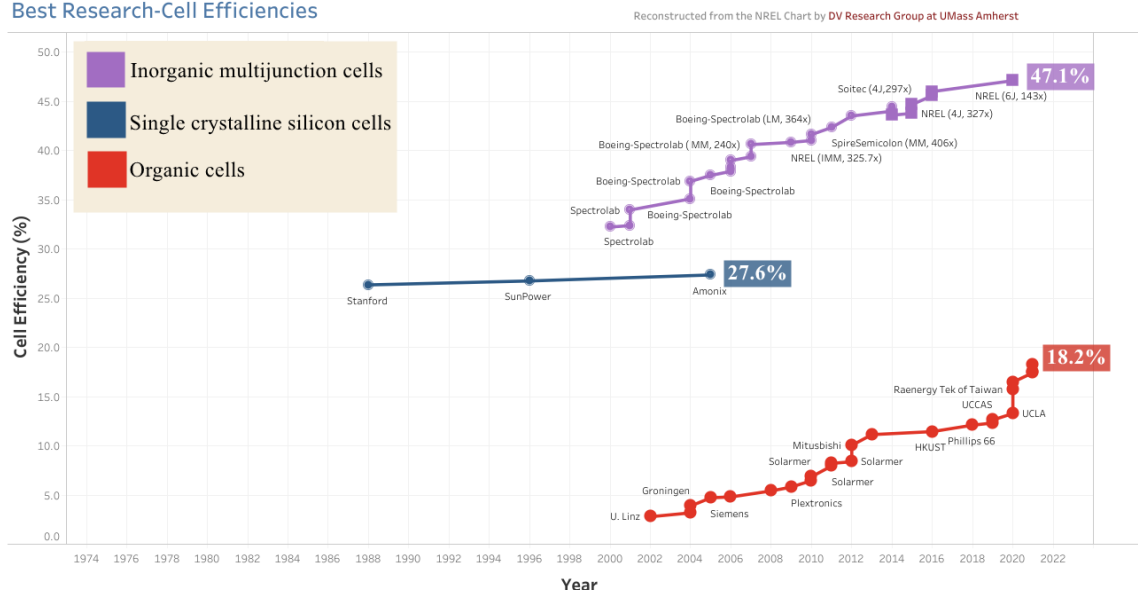


Figure 1. 2 Chart of best research-cell efficiencies for three representative photovoltaic technologies, plotted from 1976 to 2020.^{9,10}

1.2 π -Conjugated organic materials

There are two major types of π -conjugated organic materials for optoelectronic applications: π -conjugated small molecules (Figure 1.3a) and π -conjugated polymers (Figure 1.3b). Both have in common a sizable delocalized π -electron system formed by the sp^2 carbons in the structures, which gives them an optical band gap of 1 – 4 eV, allowing them to absorb and emit light in the spectral range from ultraviolet-visible to near-infrared (UV-Vis-NIR). Also, the closely aligned conjugated molecules allow the injected charges to move via the overlapping electron clouds in these molecules, giving them the semi-conductivity that is suitable for the operation in optoelectronic devices.¹

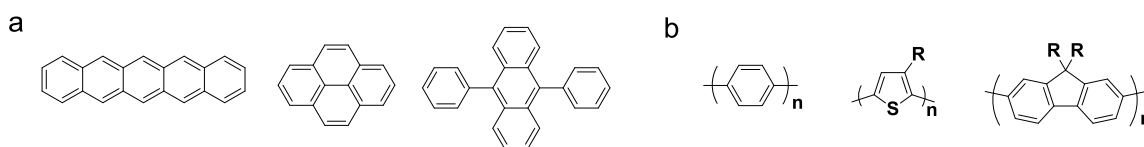


Figure 1. 3 Examples of a) small π -conjugated molecules and b) π -conjugated polymers.

Typically, it is nearly impossible to have a molecular design that displays desirable properties ideal for different optoelectronic applications at the same time. Instead, it is more

common to have a rational structure design suited to a specific optoelectronic application. For example, the light-harvesting material in OSCs should have a sizeable conjugated structure, such as a polymer, with a sufficiently broad and intense absorption spectrum to cover the UV-Vis-NIR region where solar light is the most intense.⁷ For another example, emitters are deposited in OLED devices with their solid form. To have high emission quantum yields and minimize undesired emission quenching effects in their solid states, emitters used in efficient OLEDs are more likely to adopt a non-planar structure to suppress the aggregation caused emission quenching (ACQ).¹⁷ π -Conjugated molecules with planar structures, on the other hand, are more favourable in yielding a closely intermolecular packing. As a result, electrons or holes can migrate more efficiently in their solid states, giving these planar molecules high charge mobilities. Organic semiconductors with high charge mobilities are highly desired for high-performance OFETs as they can reduce the power consumption of the devices.^{12, 16} Indeed, different molecular design ultimately results in different optoelectronic properties.³ Better knowledge of the structure-property relationships and the development of novel structural designs have significantly expanded the uses of π -conjugated organic materials in a broader range of optoelectronic applications. Notably, molecular designs of π -conjugated systems featuring electron donors/acceptors or both electron donors and acceptors play a pivotal role in the family of π -conjugated organic materials, and their intriguing properties are promising for a wide variety of optoelectronic applications.^{12, 15, 16, 18-25}

1.2.1 Donor-Acceptor systems

π -Conjugated molecules end-capped or functionalized with an electron donor(s) and an electron acceptor(s) represent a subclass of π -conjugated organic materials widely known as donor-acceptor (D-A) systems (Figure 1.4). They have been proven valuable and are commonly adopted in molecular designs for OSC, OLED, and NLO applications.^{15, 17-24, 26}

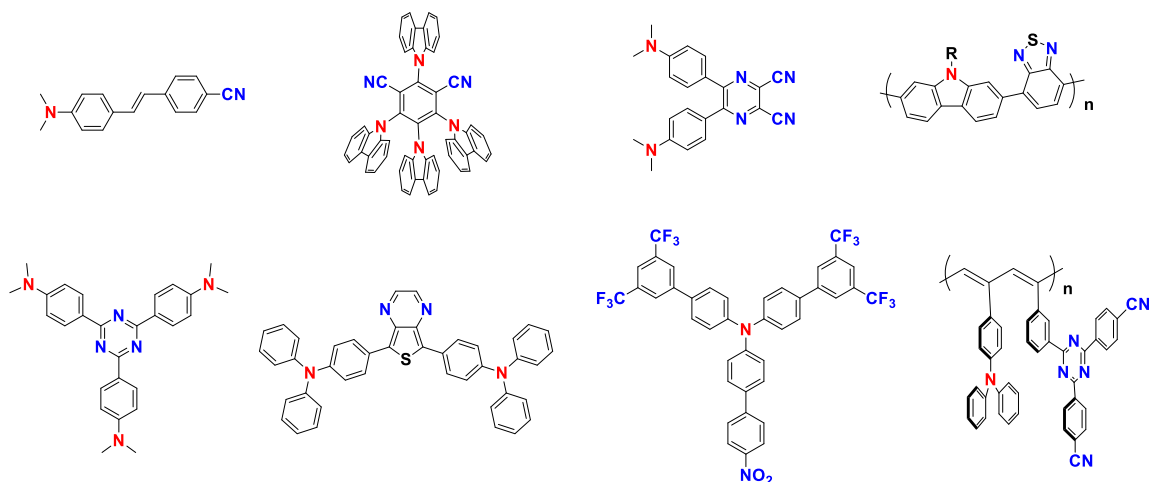


Figure 1. 4 Examples of all sorts of D-A systems. Electron-donating and electron-accepting moieties are highlighted in red and blue, respectively.

D-A systems for OSCs. For high-performance OSCs, the molecular design of an active material should display a broad and strong absorption band that covers the UV-Vis-NIR region of the solar spectrum. For this reason, conjugated polymers such as poly(3-hexylthiophene) (Figure 1.5a) are well suited to serve as the active material due to their satisfactory absorption properties.¹⁴ However, conjugated polymers also have the drawbacks of poor synthetic reproducibility and requiring arduous purification. As a result, the electronic properties of the polymers may vary from batch to batch.

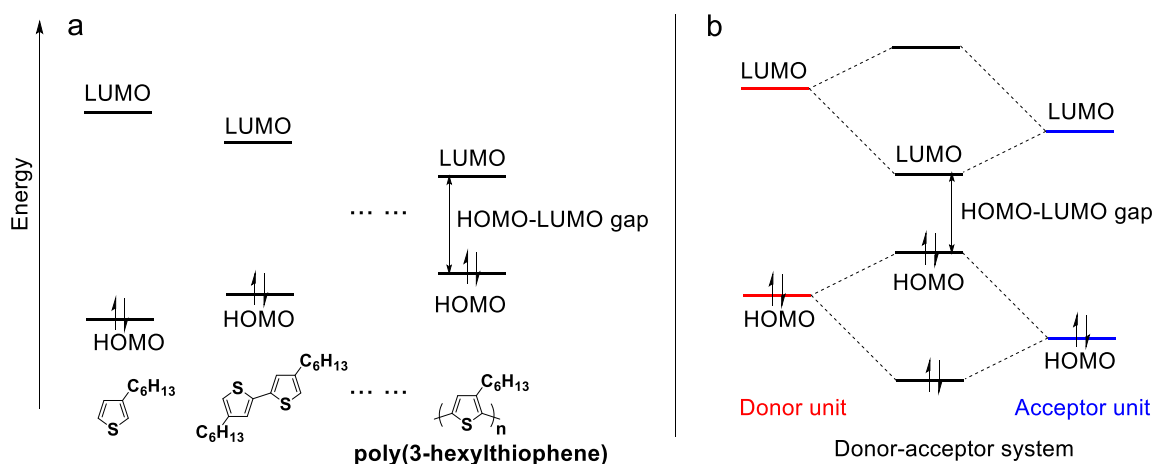


Figure 1. 5 MO diagram of different approaches for obtaining broad absorption (small HOMO-LUMO gap) by a) extending conjugation or b) donor-acceptor structure designs.

Alternatively, strong and broad absorption can also be obtained by small molecular weight D-A systems, which are widely recognized as push-pull dyes.^{25, 27} D-A interaction in a push-pull dye by intramolecular charge transfer (ICT) can produce a new molecular orbital (MO). As depicted in Figure 1.5b, the two highest occupied molecular orbitals (HOMOs) of the donor and acceptor moieties can interact with each other to generate two new occupied molecular orbitals after the two moieties are covalently bonded, with one of them higher and the other one lower than the two initial HOMOs of the donor and acceptor moieties. Meanwhile, two new unoccupied molecular orbitals would also be generated similarly when the two moieties are covalently bonded. The two new unoccupied molecular orbitals are lower or higher than the two initial lowest unoccupied molecular orbitals (LUMOs) of the donor and acceptor moieties. Consequently, the resultant frontier molecular orbitals form a higher-energy level HOMO and a lower energy level LUMO, leading to a narrower HOMO-LUMO gap. In comparison to polymers, small push-pull systems have well-defined molecular structure/weight and can be easily obtained in high purity, giving them consistent performance in optoelectronic devices. Moreover, increasing the conjugation length and fusing more aromatic rings in a polymer backbone indeed leads to a smaller energy bandgap, but the band gap shrinking becomes negligible when the polymer is larger than a certain point, typically 7-10 repeating units.²⁸ Thus, it is usually challenging to broaden a polymer's absorption, especially to the near-infrared region, by simply extending its conjugation. While in the case of the D-A molecule, the near-IR absorption can be attained easily by introducing more potent donor and acceptor moieties in the D-A molecular design, which in turn leads to a smaller band gap that covers the near-IR spectral region.

D-A systems for OLEDs. D-A molecules have also been shown to be excellent candidates for OLED devices due to their high efficiencies in converting electrical energy into light emission.^{17, 26, 29, 30} It is widely acknowledged that electrical excitation in OLED devices typically generates 25% singlet excitons and 75% triplet excitons.³⁰ Conventional fluorescent molecules such as 9,10-diphenylanthracene³¹ with a 100% fluorescence quantum yield in OLED devices can only harvest the 25% singlet excitons (Figure 1.6a), yielding a maximum internal quantum efficiency (IQE) of 25%. While the remaining 75% triplet excitons are dissipated via nonradiative decay as the triplet excited state to the

ground state (S_0) transition (phosphorescence) is forbidden for fluorescence emitters. Herein, conventional fluorescent emitters are not suitable for high-performance OLEDs due to their low efficiencies. In this regard, much effort had been spent in the quest for molecular designs capable of fully converting both the singlet and triplet excitons into light emission.

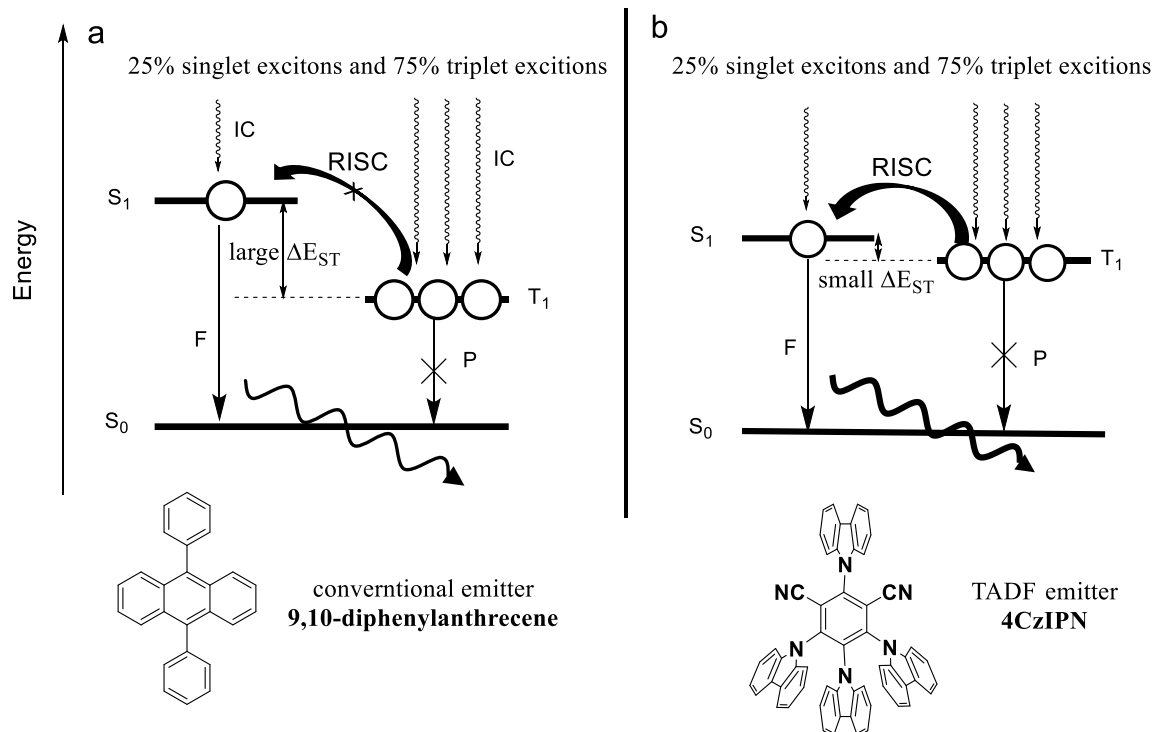


Figure 1. 6 Comparison of electroluminescence mechanism of a) conventional fluorescent emitter (9,10-diphenylanthracene) and b) TADF emitter (**4CzIPN**) in OLED devices.³² F, P, IC, RISC, ΔE_{ST} represent fluorescence (F), phosphorescence (P), internal conversion (IC), reverse intersystem crossing (RISC), and singlet-triplet energy gap (ΔE_{ST}), respectively.

In 2012, Adachi discovered that D-A systems with a separated HOMO/LUMO distribution caused by a twisted angle between the donor and acceptor, e.g., **4CzIPN** (Figure 1.6b),³² could yield a small singlet-triplet energy gap (ΔE_{ST}) between the first singlet excited state (S_1) and the first triplet excited state (T_1). These molecules featuring small ΔE_{ST} (typically <0.3 eV) are called thermally activated delayed fluorescence (TADF) emitters. The resulting small ΔE_{ST} can significantly boost the reverse intersystem crossing (RISC) channel, allowing the triplet excitons to be transferred into singlet excitons (Figure

1.6b). As a result, TADF emitters can potentially harvest both singlet and triplet excitons and convert them into fluorescent emission, displaying a theoretical maximum IQE of 100% that is much higher than that (25%) of a conventional emitter in OLEDs. Indeed, TADF emitters possessing high IQEs close to 100% are not rare.^{17, 33} Thanks to their high efficiencies in OLEDs and easily accessible structure designs, D-A type TADF emitters have become a hot topic of research since their discovery by Adachi in 2012.^{17, 32}

D-A systems for NLOs. When subjected to an intense laser pulse, organic molecules can get promoted to the excited states in a nonlinear optical manner by simultaneously absorbing two or more photons with energy lower than that of the S_0-S_1 transition.¹⁸ Thus, the two-photon absorption process allows molecules to convert two low-energy photons into one higher-energy photon, making them potentially valuable for applications such as optical data storage, photodynamic therapy, bioimaging, upconverted lasing, etc.³⁴⁻³⁸ In the quest for organic molecules with large two-photon absorption cross-sections, planar D-A molecules featuring intense ICT effect have been found to possess large two-photon absorption cross-sections, rendering them the most important class of NLO chromophores.^{18, 24, 39} In particular, a more in-depth investigation of D-A systems for two-photon absorption will be covered in Chapter Two.

1.2.2 Acceptor materials

Acceptor materials are defined as a type of electron-transporting materials in optoelectronic devices. They can serve as the non-fullerene acceptors in bulk-heterojunction OSCs,^{19, 23, 40} and function as the n-type organic semiconductor in OFETs.^{12, 16} Except for fullerene and its derivatives, acceptor materials are typically functionalized with electron-withdrawing moieties to provide good electron affinities and sufficiently low LUMO energy levels in order to possess the electron-transporting characteristics.

Acceptor materials as non-fullerene acceptors for bulk-heterojunction OSCs. In OSC devices, the photon-generated excitons need to be dissociated into free charge carriers in the active materials before being collected as electrical energy by the built-in circuit.¹⁹ However, excitons tend to recombine due to the existing exciton binding energy. The most adopted approach to splitting the excitons into free carriers is using a bilayer bulk-heterojunction (Figure 1.7a), where donor and acceptor materials are blended to create a

donor-acceptor interface.^{19, 23} Hence, excitons generated (step 1 of Figure 1.7a) from either the donor or the acceptor materials can diffuse (step 2 of Figure 1.7a) to the donor-acceptor interface. Subsequently, a sufficiently large energy difference between the LUMOs of the donor and acceptor materials can overcome the exciton binding energy, thus splitting the excitons into free charge carriers (step 3 of Figure 1.7a). Finally, the charges diffuse to the electrodes and are collected as electrical energy (step 4 of Figure 1.7a). There are two major types of bulk-heterojunction OSCs. They are either a blend of donor materials and fullerene type acceptors (Figure 1.7b),⁷ or a mixture of donor materials and non-fullerene acceptors.^{19, 23} For a long time, fullerene and its derivatives were the dominant acceptor materials for efficient bulk-heterojunction OSCs due to their exceptional high electron mobilities.¹⁹ However, fullerene and its derivatives have some significant drawbacks, such as weak light absorption, limited tunability of the energy levels to match different donor materials for efficient exciton dissociation, and high synthesis costs, limiting their potential for high-efficiency and low-cost OSCs.⁴¹ The situation has changed recently that new acceptor materials, termed non-fullerene acceptor materials, were developed and became popular for bulk-heterojunction OSC devices.^{23, 40, 42} In contrast to fullerene featuring a ball shape structure, non-fullerene acceptor materials are characteristic of planar structures and contain electron-deficient aromatics and electron-withdrawing groups, such as carbonyl and cyano (CN) groups (Figure 1.7b). Despite the structural differences from fullerenes, non-fullerene acceptor materials also possess favourable electron-transporting properties owing to their high electron affinities provided by the electron-withdrawing moieties and good electron mobilities resulting from close intermolecular packing.^{23, 40, 42} More importantly, non-fullerene acceptor materials are more attractive for OSC devices since they are more chemically accessible and display better light absorption properties and more manageable energy level tunability than fullerene type acceptor materials.⁴¹ Indeed, more state-of-the-art non-fullerene type OSCs with the highest PCEs had been reported recently.¹¹ The superior performance of non-fullerene type OSCs is mainly attributed to the vastly improved absorption, exemplified by two ultranarrow bandgap acceptor materials, **Y6** and **ITIC** (Figure 1.7b),^{42, 43} with the absorption edge reaching the near-infrared (NIR) region.

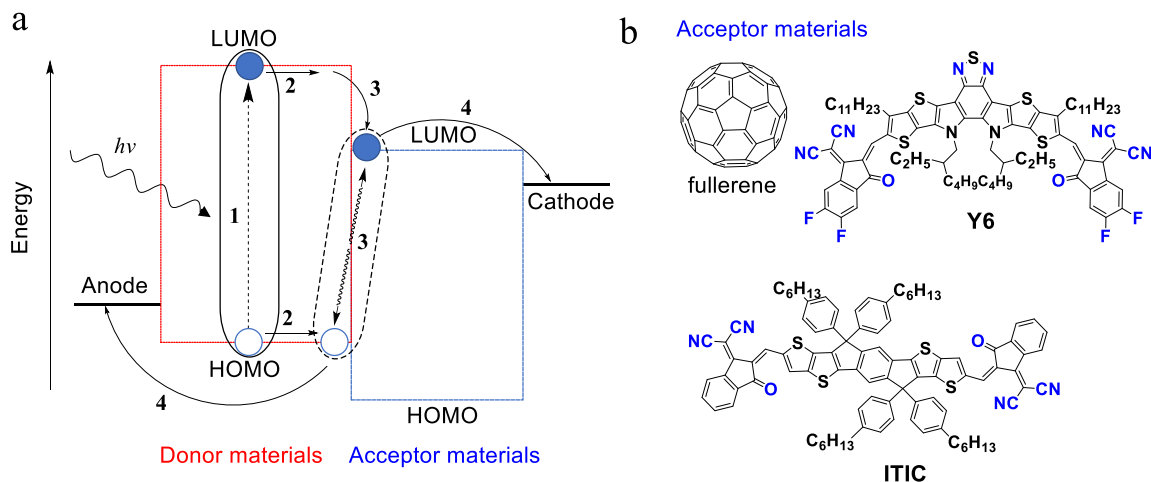
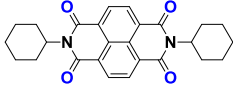
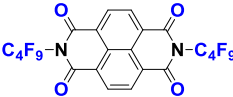
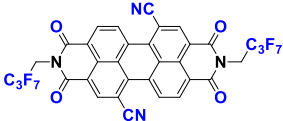
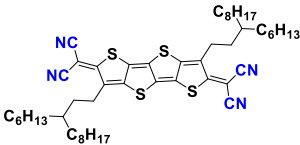


Figure 1. 7 a) Band diagram and main processes in bulk heterojunction OSCs: 1. Light absorption followed by exciton formation; 2. Exciton diffusion to the donor-acceptor interface; 3. Exciton dissociation into free charges; 4. Charge collection. b) Acceptor materials including fullerene and non-fullerene molecules: **Y6** and **ITIC** (electron-accepting moieties are highlighted in blue).^{42, 43}

Acceptor materials as organic n-type semiconductors for OFETs. The development of organic n-type semiconductors has been a hot topic in the past two decades as they are essential components for the construction of OFET based complementary circuits.^{12, 15, 16} Similar to the acceptor materials in OSCs, sufficiently low LUMO energy levels are required for the n-type semiconductors to warrant stable electron transport. More importantly, high electron mobility is necessary for n-type semiconductors as it directly impacts the performance of the corresponding OFET devices.⁴⁴ Consequently, organic n-type semiconductors (Table 1.1) are usually composed of planar backbone structures accompanying electron-withdrawing groups such as carbonyls and CN, etc.^{1, 12} In particular, electron-withdrawing groups can increase electron affinity of a material, while planar backbone structures favour dense packing in crystals, leading to high electron mobility.^{12, 16} However, compared to p-type (hole-transporting) semiconductors, n-type semiconductors generally suffer from air instability issues. For instance, even a record high electron mobility of 6.2 cm²/(V·s) was reported for the *N, N'*-bis(cyclohexyl) NDI (Table 1.1, NO. 1),⁴⁵ significant performance degradation was observed during the OFET device operation, which may be caused by the intrinsically poor stability of the *N, N'*-bis(cyclohexyl) NDI radical anions. More significantly, it is believed that the air instability

of n-type semiconductors mainly arises from the charge carrier trapping by oxygen and water molecules.¹² To overcome the instabilities of n-type semiconductors, lowering their LUMO energy levels below -4.0 eV is an effective approach, which not only enhances their intrinsic radical stabilities but also reduces the electron trapping sites by oxygen and water molecules.⁴⁶ Specifically, incorporating electron-withdrawing groups onto the planar π -system is one of the most adopted strategies to lower the LUMO energy levels for air-stable n-type organic semiconductors (Table 1.1, NO. 2-4).^{12, 47-49}

Table 1. 1 Examples of n-type organic semiconductors and their OFET device data. Electron-withdrawing moieties are highlighted in blue.

NO.	N-type organic semiconductor	Max μ_e^a (cm ² V ⁻¹ s ⁻¹)	LUMO (eV)	Morphology	Test condition	Ref.
1		6.2	Not reported	Thin-film	Argon	45
2		1.4	-4.0	Thin-film	Air	47
3		3.0	Not reported	Crystal	Air	48
4		0.9	-4.3	Thin-film	Air	49

^a μ_e : electron mobility.

1.3 Pentafluorosulfanyl (SF₅): a robust and unique electron-withdrawing group

Apparently, the pentafluorosulfanyl (SF₅) group possessing strong electron-withdrawing ability is potentially useful as an electron acceptor in the aforementioned molecular designs, i.e., D-A systems and acceptor materials. However, SF₅ is more than an electron-withdrawing group. It contains other features that may be conducive to a designed

structure, such as imparting the thermal stability of the target structure, improving its solubility, etc.^{50, 51} To further exploit the potential of SF₅ in π -conjugated organic materials, its chemical and physical properties will be discussed in depth in the following section.

1.3.1 Chemical and physical properties of SF₅

Electronic properties. The SF₅ group has an octahedral geometry with a central hypervalent sulfur (VI) atom surrounded by five fluorine atoms and a remaining axial position bonded to other fragments (Figure 1.8). Due to the presence of five fluorine atoms, the SF₅ group exhibits a strong electron-withdrawing ability that has an electronegativity of 3.65, higher than 3.36 for trifluoromethyl (CF₃).⁵² In terms of the electrophilic substitution effect, the Hammett substituent parameters (σ_p) for SF₅ and CF₃ are 0.68 and 0.54, respectively.^{53, 54} Specifically, the σ_p of SF₅ can be split into the components, with an inductive effect constant (σ_I) of 0.56 and a resonance effect constant (σ_R) of 0.12. Indeed, resonance effects exist in SF₅ due to the formation of negative hyperconjugation between the sulfur and fluorine atoms and its ability to afford "no-bond" resonance structures.^{55, 56}

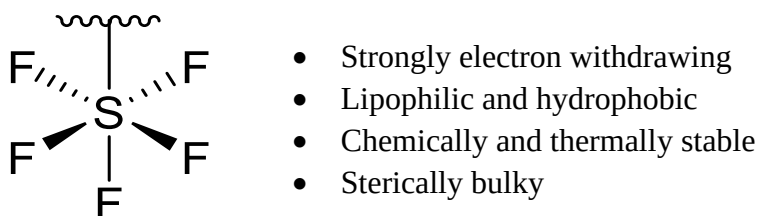


Figure 1. 8 Structure and chemical/physical properties of SF₅ group.

Lipophilicity and hydrophobicity. SF₅ is one of the rare functional groups that are strongly electron-withdrawing and hydrophobic at the same time, two characteristics that are usually mutually exclusive. CF₃, trifluoromethoxy (OCF₃), and trifluoromethylthio (SCF₃) are among the few other functional groups that display such exotic properties, while other common electron-withdrawing substitutes, e.g. CN, nitro (NO₂), and carbonyl, do not.⁵⁰ Interestingly, SF₅ is also highly lipophilic, in stark contrast to perfluoroalkyl that is oleophobic.^{57, 58}

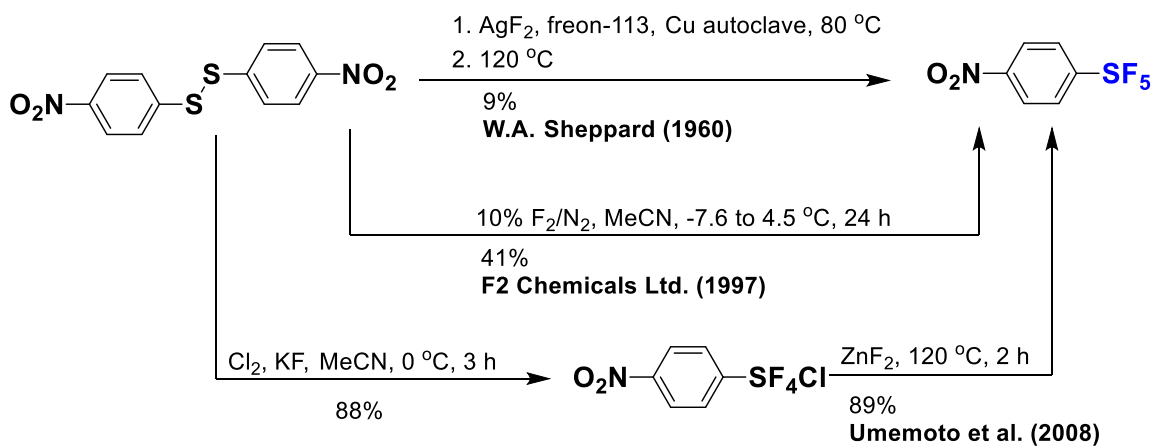
Chemical and thermal stability. The SF₅ group also possesses excellent chemical and thermal stability along with its large polarity and high hydrophobicity.⁵⁰ In particular, the SF₅ group has been shown to be hydrolytically stable, superior to that of CF₃,⁵⁹⁻⁶¹ which

makes it highly desirable to be used in drug and agrochemical compounds. In addition to its hydrolytic stability, the SF₅ group was also shown to be thermally stable at temperatures exceeding 300 °C and robust against a wide array of harsh chemical reagents and reaction conditions.⁶⁰ Owing to its excellent chemical and thermal stability, the SF₅ group was employed in energetic materials, exerting a good stabilizing effect.⁶² Also, because of its outstanding chemical compatibility, SF₅ can be introduced into a target molecule at any stage during the synthesis without concerning its negative impact in the subsequent reactions. It is not surprising that SF₅ has such thermal and chemical robustness when one relates it to its analogue of sulfur hexafluoride (SF₆).⁶³ SF₆ is a stable gaseous substance that is mainly used as an electrical insulator. It is highly inert, non-flammable, and nontoxic. However, owing to its high stability against chemical degradation, SF₆ has been shown to be a problem as a persistent long-lived greenhouse gas with an estimated atmospheric lifetime of 800–3200 years.⁶⁴ Thankfully, SF₅-containing substances are known to be photolytically degradable or biodegradable, and the decomposed products are environmentally friendly.⁶⁵

Steric bulk. In terms of size, the volume size of the SF₅ moiety is 49.2 cm³/mol, which is marginally smaller than a tertbutyl group⁵⁰ but substantially larger than the CF₃ group (20.5 cm³/mol).⁶⁶ The steric bulk of SF₅ renders it a valuable substituent for drug and agrochemical compounds.⁶⁷⁻⁶⁹ Similarly, the sterically bulky SF₅ substituent are especially beneficial in materials design for enhancing the solution processibility as well as suppressing the undesired ACQ.^{70, 71} Although the steric bulk of SF₅ in a planar system potentially prevents the intermolecular dense packing, the SF₅ can form CH $\cdots$ F intermolecular hydrogen-bonding interactions, which actually promotes crystal formation and is useful for crystal-engineering of a particular molecular design.⁷²

Accessibility. Even though the first synthesis of an SF₅ arene was reported 60 years ago,⁵⁹ it lay dormant for almost 40 years since its discovery due to the SF₅ chemistry being hindered by severe impediments such as low yields, dangerous procedures, and requiring sophisticated equipment and techniques. Starting from 1960, Sheppard introduced the first practical synthesis of pentafluorosulfanylated arenes,⁵⁹ involving the oxidative fluorination of diaryldisulfides with silver(II) fluoride (Scheme 1.1). Unfortunately, the reaction gave

a poor yield that was not amenable to scale-up, significantly impeding the development of SF₅ chemistry. In the subsequent decades, the synthesis of SF₅ moieties based on Sheppard reaction, albeit slightly improved, remained impractical for large-scale production.⁷³ It was not until 1997 that a methodological breakthrough on the synthesis of SF₅ was eventually developed by F2 Chemical Ltd.⁷⁴ They provided a reliable synthetic procedure via direct fluorination on bis(nitrophenyl)disulfides (Scheme 1.1), which not only largely simplified the reaction procedures but also significantly improve the reaction yields. As a result, o- and m-nitrophenyl(pentafluorosulfanyl)benzene became commercially available for the first time, which subsequently revived chemists' interest in the SF₅ chemistry and allowed new investigations of SF₅ in medicinal chemistry, agrochemistry, and materials science.^{51, 67, 75, 76} More recently, one of the most significant improvements in the SF₅ chemistry was a new method developed and patented by Umemoto in 2008 and subsequently published in 2012.⁷⁷ This new method, albeit involving two steps, gave an excellent overall yield of 78%. Initially, the thiol (e.g., ArSH) was treated with KF and Cl₂ to produce a tetrafluorosulfanyl chloride (–SF₄Cl) intermediate, which was then subjected to ZnF₂ at 120 °C for Cl–F exchange in the following step to afford ArSF₅ (Scheme 1.1). The advent of Umemoto's method had significantly lowered the synthesis cost and greatly facilitated the large-scale production of various SF₅-containing building blocks, making SF₅ moieties more accessible for its application in many research fields.⁵¹



Scheme 1. 1 Landmark synthetic approaches of SF₅-functionalized arene.^{59, 74, 77}

1.3.2 Comparison of SF₅ with other electron-withdrawing groups and the substituent effects

It is true that with the introduction of SF₅ as an electron-withdrawing group to a donor-acceptor system or an acceptor material, the SF₅ can display similar electronic effects, e.g., lowering both the HOMO and LUMO energy levels, like other commonly used strong electron-withdrawing groups such as CF₃, CN, and NO₂. However, for material designs, not only the electronic effect of a functional group on the HOMO and LUMO energy levels needs to be considered, but its effects on other properties, such as absorption, emission, charge transport, stability, and processibility, are also essential and needs to be carefully examined as well.^{1, 3}

Effects on absorption. In general, the effect of an electron-withdrawing group on absorption is the most pronounced when it is coupled to an electron donor moiety in a conjugated manner, resulting in a D-A system.⁷⁸ As explained earlier, the ICT effect of a D-A system can afford a red-shifted absorption charge transfer band. Increasing the donor and acceptor strength can exert a more prominent ICT effect, which in turn results in a more significant red-shifted of the absorption maximum. Hence, introducing CF₃, SF₅, CN, or NO₂ as an acceptor to the same D-A system at the same position is expected to result in the absorption maximum red-shifted in the following order: NO₂ > SF₅ > CN > CF₃, according to their Hammett substituent parameters.^{60, 61}

Effects on emission. For molecular designs of luminescent molecules, the NO₂ group is usually excluded as it has been notoriously known as a fluorescence quencher.^{79, 80} In fact, the rapid detection of nitro explosives by conjugated polymers works on the fluorescence quenching effect of nitro-containing substances on organic fluorophores.^{81, 82} Also, planar structure designs are often avoided for the luminescent materials as it generally results in ACQ.^{71, 83} Thus, the planar NO₂ and CN groups are less favourable than the sterically bulky CF₃ or SF₅ in luminescent materials to serve as a spacer to mitigate the ACQ where advantageous.

Effects on stability. In the selection of functional groups for organic materials, one has to consider whether the functional group has sufficient chemical stability to endure a wide array of reaction conditions in the process of synthesis. While SF₅ and CF₃ moieties

are known to impart good chemical and thermal stability to an organic system, the relatively labile NO₂ group is not compatible with an array of chemical reagents, such as alkyllithiums and Grignard reagents.⁸⁴ Similarly, the CN group is also susceptible to being attacked by nucleophilic organometallic reagents.⁸⁵ In contrast, SF₅ has been shown to be robust against a wide array of harsh chemical reagents, even Grignard reagents⁶⁰ and tert-butyllithium.⁷⁵ Also important is the operational stability that a molecule displays in response to the optoelectronic device environment, such as oxygen and moisture. Not only the chemical and thermal stabilities of CF₃- and SF₅-functionalized optoelectronic materials are expected to be beneficial in prolonging their corresponding devices lifetime, their hydrophobic nature, as well as their ability to form CF $\cdots$ H interactions, are also conducive to reducing the source of interference from the operating environment. It has been reported that materials end-capped with CF₃ groups displayed long-term air stability in OFET devices as the hydrophobic CF₃ groups can form self-passivation layers to prevent detrimental oxygen and moisture penetration.⁸⁶ Similarly, the hydrophobic SF₅ group is expected to exert the same effect when it is applied to the same structure.

Effects on charge transport. A molecule's charge transport property is governed by its intermolecular interactions and is quantified by its charge mobility, which describes how fast a charge carrier can diffuse in its solid states.^{1, 3} And molecules with high charge mobilities are desired in OSC and OFET applications. In general, a more compact and ordered molecular packing would result in higher charge mobility.⁴⁴ Consequently, planar molecular design is essential for achieving high charge mobilities. In this respect, integrating planar NO₂ and CN to planar π -conjugated systems would be more favourable than the nonplanar CF₃ and SF₅ for gaining high charge mobilities. Still, it is worth noting the ability of CF₃ and SF₅ to form CH $\cdots$ F intermolecular hydrogen-bonding interactions would also be used to facilitate crystal-engineering of a π -conjugated system that potentially exhibits high enough charge mobility for OSC and OFET applications.^{72, 87}

Effects on Processibility. Optoelectronic materials need to be carefully deposited onto device substrates to obtain optimal morphology that provides desirable electronic properties such as high charge mobility. Generally, the deposition of a material can be processed via vacuum evaporation or by spin-coating the solution of the studied material

in an organic solvent such as chloroform, tetrahydrofuran or chlorobenzene.¹ For vacuum deposition, the target material needs to be thermally stable, which is typically achieved by adopting an intrinsically stable structure design such as including fused rings or avoiding labile side chains. While for spin-coating, the solubility of the target material needs to be high, which can be obtained by a non-planar structure design or by introducing solubilizing groups such as side chains. In general, it appears the deposition of a material can only be accomplished by one of the processing techniques mentioned above. However, both CF₃ and SF₅ groups can impart thermal stability and enhanced solubility to the materials that contain them, potentially rendering the materials applicable for both processing techniques.⁵¹ In comparison, introducing NO₂ or CN into π -conjugated systems tends to decrease solubility, marking the compounds less amenable to solution processing techniques.

1.3.3 CF₃ Versus SF₅

As was discussed above, SF₅ displays a remarkable resemblance to CF₃ (among all sorts of electron-withdrawing groups) in terms of substituent effects for organic molecules. Indeed, SF₅ has the same peculiarity of fluorine as CF₃ and is often referred to as “super CF₃” due to its stronger electron-withdrawing ability, larger size, higher lipophilicity/hydrophobicity, and greater hydrolytically stability than CF₃.^{51, 66} Studies showed that replacing the CF₃ groups with SF₅ groups in some well-known drugs, e.g., fenfluramine, mefloquine, resulted in comparable and even enhanced potencies.^{76, 88} Given the attractive properties of CF₃-containing materials for optoelectronic applications (which will be discussed in the following context), this naturally raises the question of whether SF₅ may likewise be utilized in the same optoelectronic materials where CF₃ was introduced and afford comparable or better desirable properties.

CF₃-containing TADF emitters for OLEDs. Since 2015, there has been an increasing interest in using the CF₃ group as a strong acceptor in D-A type TADF emitters to tune the energy levels and emission colour.⁸⁹⁻⁹⁶ For instance, in Li’s quest for TADF emitters,⁹² they incorporated either methyl and CF₃ to the phenylene bridge between the donor and acceptor (Figure 1.9a) to produce a twisted structure in the hope of achieving a small ΔE_{ST} . Compared to methyl-substituted emitters, the emission spectra of CF₃

substituted emitter were remarkably red-shifted 31 – 62 nm. However, they found that only those with CF₃ groups closer to the donor side (**TrzCz-CF₃** and **TrzBuCz-CF₃**) displayed TADF characters. It appeared that the TADF characters of **TrzCz-CF₃** and **TrzBuCz-CF₃** were due to the collective electron affinity and steric bulk effect of CF₃, which not only enhanced the acceptor strength but also led to a large dihedral angle between the donor and acceptor. Both **TrzCz-CF₃** and **TrzBuCz-CF₃** displayed blue emission and moderate to good maximum external quantum efficiencies (EQE) of 9.4% and 14.2%, respectively. In another study by Jiang,⁹⁶ the steric bulk of CF₃ was highlighted and shown helpful in mitigating the ACQ. They found that **TFM-QP** with a non-planar CF₃ substitution displayed a higher EQE (14.1%) than that (9.7%) of **CN-QP** (Figure 1.9b). The lower EQE of **CN-QP** was due to serious ACQ resulting from the more planar structure of **CN-QP**, which bears a CN group. Apart from having a higher EQE, **TFM-QP** also possessed a decent EQE of 8.7% in a non-doped device, highlighting the advantageous effect of introducing the CF₃ group in reducing ACQ. On the whole, the CF₃ moiety was proven effective as an electron-withdrawing handle in adjusting the emission colour, reducing ACQ, and attaining TADF character when linked to a twisted donor, allowing for highly efficient TADF emitters for OLED applications.

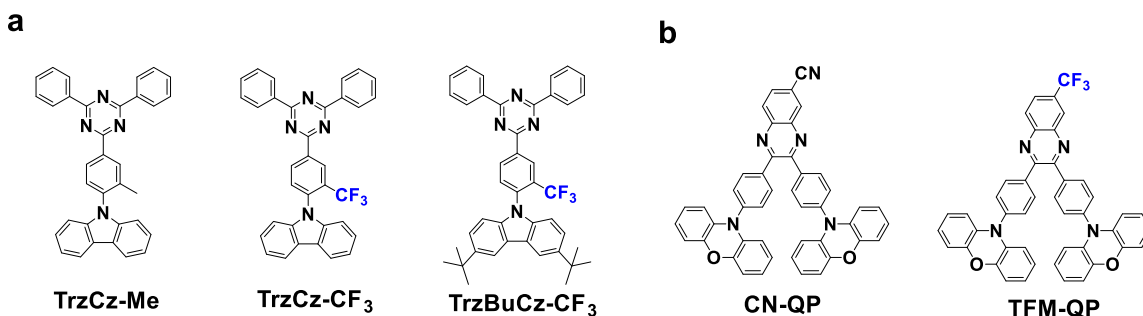
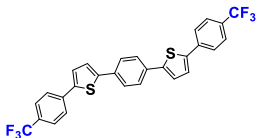
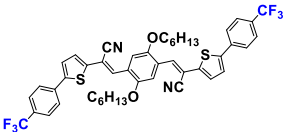
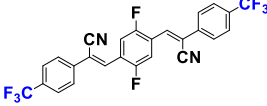
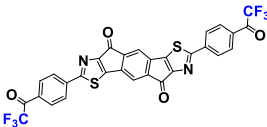


Figure 1. 9 a) Representative chemical structures of methyl and CF₃ substituted twisted donor-acceptor systems by Li's study.⁹² b) Chemical structures of **CN-QP** and **TFM-QP**.⁹⁶

CF₃-containing n-type semiconductors for OFETs. Substantial studies had shown that integrating CF₃ to planar π -conjugated small systems was an effective strategy in obtaining n-type semiconductors with high electron mobilities due to the resulting well-ordered molecular alignment and dense packing.^{87, 91, 94, 95, 97, 98} Even CF₃ is considered a bulky moiety, which may be unfavourable for close intermolecular packing, CF₃-

containing n-type semiconductors (Table 1.2, NO. 1-2) featuring high electron mobilities were still obtained due to the overall structure planarity and relatively close packing derived from the ability of CF₃ to form CH $\cdots$ F and F $\cdots$ S intermolecular interactions in solid states.^{97, 98}

Table 1. 2 Representative examples of CF₃-containing n-type semiconductors exhibiting high electron mobilities and good air stability.

NO.	N-type organic semiconductor	Max μ_e^a (cm ² V ⁻¹ s ⁻¹)	LUMO (eV)	Morphology	Test condition	Ref.
1		3.1	-3.1	Crystal	Vacuum	98
2		2.1	-3.9	Thin-film	Nitrogen	97
3		0.39 ~ 0.1	-3.7	Thin-film	Vacuum Exposed to air after 1 year	86
4		0.39 0.14	-3.8	Thin-film	Vacuum Exposed to air after 2 months	99

^a μ_e : electron mobility.

Aside from the high electron mobilities, CF₃-containing n-type semiconductors are also characterized with long-term air-exposed stability owing to the electron-withdrawing ability of CF₃ to lower the LUMO energy levels (Table 1.2, NO. 3-4).^{86, 99-101} Additionally, the enhanced electron affinity induced by CF₃ groups was also crucial for realizing electron transport. Yu reported three similar structures with one of them without CF₃ only displaying a hole-transporting character, but the other two featuring CF₃ groups demonstrated electron-transporting properties, even the energy differences between their

LUMO energy levels are only 0.14-0.22 eV.⁸⁷ A similar phenomenon was also observed for other fluorinated n-type semiconductors that lowering the LUMO is not sufficient for achieving electron transport character, but including extra F atoms does.¹⁰² Overall, these CF₃-containing n-type semiconductors displayed high electron mobilities and good air stability.

CF₃-containing donor or acceptor materials for bulk-heterojunction OSCs. Recently, CF₃-functionalized materials in the application of OSCs have received great attention due to the resulting high solar cell power conversion efficiencies (PCEs).¹⁰³⁻¹⁰⁸ Li and Zhang reported that bulk heterojunction OSC devices based on **PBZ-m-CF₃** (containing CF₃ moieties) as the donor material and **ITIC** as the acceptor material, displaying a much higher PCE of 10.4% than that of (5.8%) the OSC based on **PBZ1** (without CF₃ moieties, Figure 1.10a).¹⁰³ In contrast to **PBZ1**, the introduction of CF₃ to **PBZ-m-CF₃** was found to afford a lower HOMO energy level, leading to a higher open-circuit voltage (V_{OC}) and higher PCE when blended with **ITIC**. The higher extinction coefficient, hole mobility and fill factor (FF) compared to **PBZ1** also accounted for the higher performance of **PBZ-m-CF₃**. Similarly, Meng developed a new acceptor material, **ITIF3**, derived from the trifluoromethylation of **ITIC**. They observed that the bulk-heterojunction OSC based on **ITCF3** blended with the **PM6** polymer donor exhibited a notably improved PCE of 13.3% compared with the **ITIC**-based device (8.4%, Figure 1.10b).¹⁰⁶ The author ascribed the improved efficiency of **ITCF3** to the narrower band gap, stronger light absorption, lower molecular energy levels, better electron-transporting property, and better morphology in solid-state compared to the reference **ITIC**. Concurrently, He¹⁰⁴ and Tao¹⁰⁷ reported trifluoromethylated materials showing state-of-art OSCs with high PCEs exceeding 16%, which were among the best performance OSCs.¹⁰⁹ Overall, the introduction of CF₃ to an active material of OSCs was found to be beneficial in achieving higher performance in OSCs by improving the properties of the active material in various aspects such as absorption, charge mobility, V_{OC} , FF, and others. The improved properties are believed to be associated with the ability of CF₃ to lower the energy levels of the active material and improve its solid-state packing via short contacts interaction (e.g., CH $\cdots$ F).

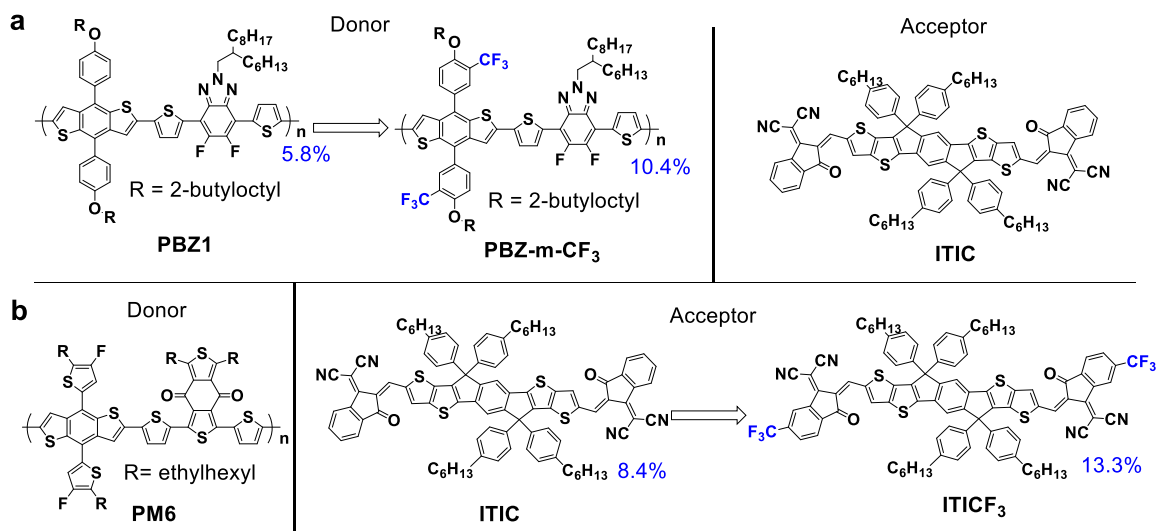


Figure 1. 10 a) Power conversion efficiency improved by changing the donor material from **PBZ1** (5.8%) to **PBZ-m-CF₃** (10.4%) while using **ITIC** as the acceptor material for bulk heterojunction OSCs.¹⁰³ b) Efficiency improved by varying the acceptor material from **ITIC** (8.4%) to **ITICF₃** (13.3%) while using **PM6** as the donor material for bulk heterojunction OSCs.¹⁰⁶

1.3.4 SF₅: an emerging functional group for optoelectronic materials

While the well-explored CF₃ had demonstrated its practicability in the structural designs for all sorts of optoelectronic applications, as stated above, the use of “super CF₃”-SF₅ had remained less active. Given its similar properties to CF₃ moiety yet superior performance in pharmaceutical design to CF₃-containing analogues,^{76, 88} the SF₅ group holds as much potential as the CF₃ group in molecular designs for the optoelectronic applications mentioned above. Apparently, the recent revitalization of SF₅ chemistry and the commercialization of SF₅-containing arenes have sparked a surge of interest in its application in medicinal and agrochemicals (as previously stated) research, and to a lesser extent, in optoelectronic applications. Nevertheless, numerous research studies have been conducted to investigate the application of SF₅ in molecular designs that are suited to or potentially interesting for different types of optoelectronic applications.

SF₅-substituted asymmetric N-phenyl imide as triboluminescent materials. One of the earliest applications of SF₅, reported by Nishida in 2012, was related to a type of unusual optoelectronic materials that displayed triboluminescence.¹¹⁰ Triboluminescent materials can display light emission when mechanical stress is applied to their solid states.

Despite the unclear mechanism behind this phenomenon, triboluminescence is generally believed to result from a dipolar structural design with noncentrosymmetric molecular arrangements in its crystal. In this regard, a series of asymmetric N-phenyl imides with different substituents (Figure 1.11a) were synthesized and investigated for their triboluminescent properties. Out of the five molecules depicted in Figure 1. 11a, both the CF₃- and SF₅- substituted N-phenyl imides (**1a-1b**) displayed relatively strong blue triboluminescence emission (λ_{em} : 444 – 448 nm) due to their sufficiently large dipole moments (5.71 and 7.53 debyes, respectively) and noncentrosymmetric crystal packings. In contrast, nonsubstituted **1d** and F-substituted **1e** have a center of symmetry in their crystals, resulting in non-triboluminescence characteristics. In the case of methyl-substituted **1c** featured a non-noncentrosymmetric crystal packing, only weak triboluminescence was observed due to its weak dipole (2.06 debye). The author attributed the different crystal arrangements of N-phenyl imides derivatives to the size of the substituents that bulkier substituents promoted the formation of noncentrosymmetric crystals. It is worth noting that both CF₃- and SF₅- substituted N-phenyl imides (**1a-1b**) are arranged parallelly in the same direction with a similar herringbone packing in their crystals (Figure 1.11b-c), which may result from the F $\cdots$ F interactions caused by the CF₃ or SF₅ groups, respectively. Specifically, the distances of the short-contact F $\cdots$ F interactions were 2.89 Å for CF₃ and 2.59-2.89 Å for SF₅. Notably, in the crystal of **N2**, the F $\cdots$ F interactions formed by the equatorial fluorine atoms of the SF₅ groups were in the same plane, thus giving the well-ordered alignments (Figure 1.11c). This is interesting as fluorine is generally more involved in F $\cdots$ H than in F $\cdots$ F interactions,¹¹¹ and F $\cdots$ F interactions are rarely reported for CF₃ or SF₅ groups, although F $\cdots$ F interactions do appear in long perfluoroalkyl chains.^{57, 58} In contrast, the methyl-substituted **1c**, despite the presence of bulky methyl groups, adopted a half-slipped herringbone crystal packing. All in all, the highly polar and bulky SF₅ group was shown useful for the molecular design of triboluminescent materials, where SF₅ could afford a large dipole moment to the structure and facilitate noncentrosymmetric crystal packing by possible F $\cdots$ F interactions.

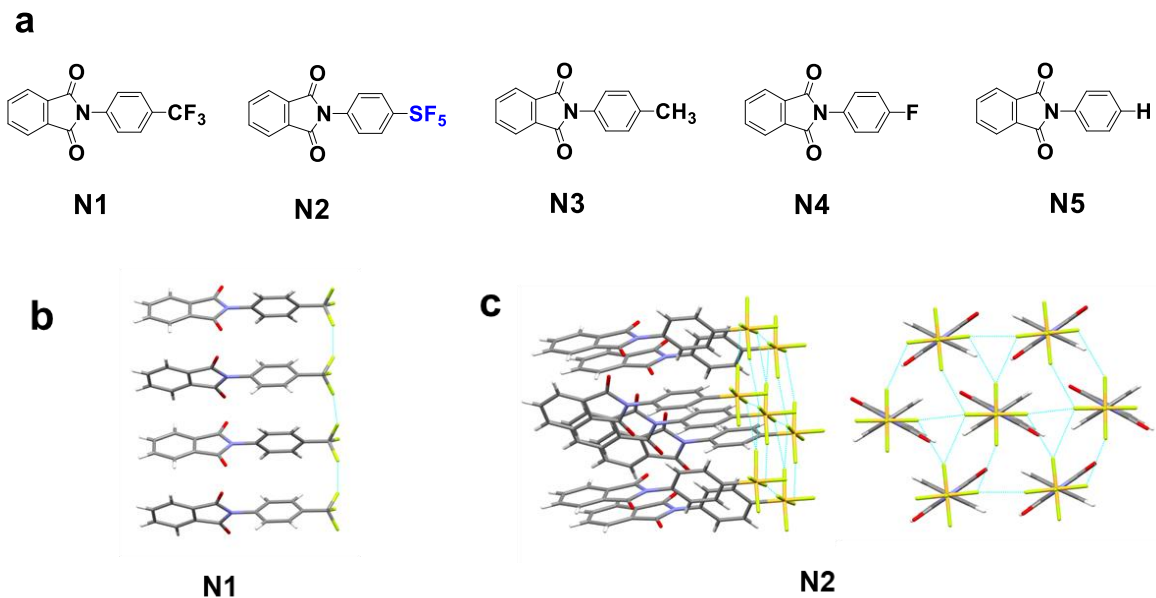
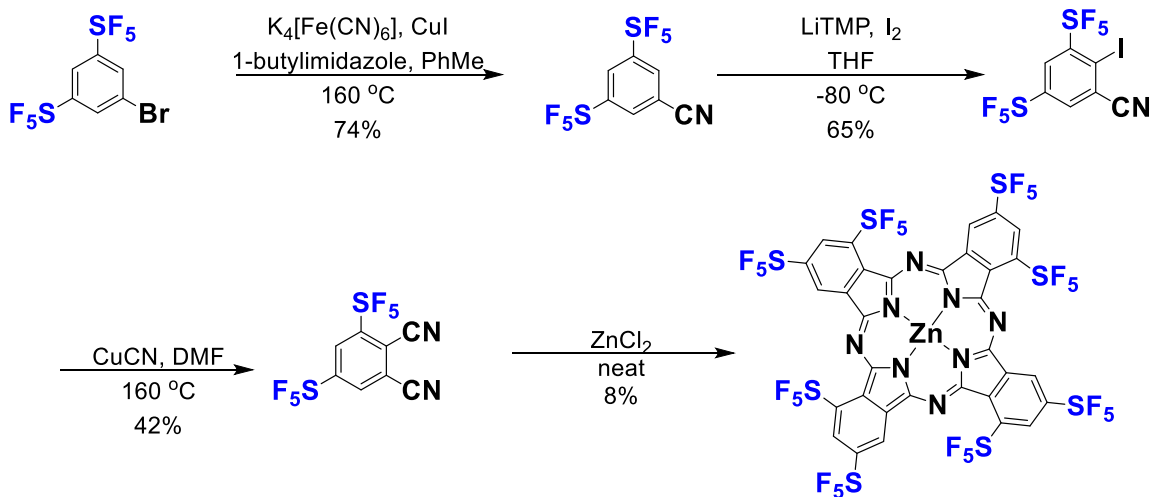


Figure 1. 11 a) Chemical structures of N-phenyl imide derivatives. b) F $\cdots$ F interactions in Crystal packing of **N1**. c) F $\cdots$ F interactions in Crystal packing of **N2**.¹¹⁰

SF₅-functionalized macrocycles. SF₅ was also used to adjust the electronic and photophysical properties of a few macrocycles, which are interesting for optoelectronic applications.¹¹²⁻¹¹⁴ In 2015, Shibata separately reported two types of SF₅-containing macrocycles with phthalocyanine and subphthalocyanine as the parent core, respectively.^{112, 113} In the former case,¹¹² the elegant syntheses of a series of phthalocyanines with SF₅ substituents different at positions were elaborated (Scheme 1. 2), where the introduction of the electronegative and bulky SF₅ groups was intended to enhance the macrocycles' resistance towards oxidation as well as improve the solubility of phthalocyanine in organic solvents. In the photophysical studies, SF₅ substituents at different regioposition of the phthalocyanine were found to not only result in different absorption and emission properties but also yield different aggregation behaviours in their solid states. Likewise, the SF₅ groups were employed in the later case of subphthalocyanine by Shibata for a similar reason, and the syntheses of SF₅-containing subphthalocyanine were detailed.¹¹³ Concurrently, Reissig and Wiehe also reported the syntheses of series SF₅-substituted BODIPYs, porphyrins, and corroles.¹¹⁴ In particular, the electron-deficient intermediates/precursor resulting from the highly electronegative SF₅ substituents were

shown beneficial in minimizing side reactions, undesirable polymerization, and decomposition.



Scheme 1. 2 Representative synthesis of SF₅-substituted phthalocyanine.¹¹²

Overall, the studies presented by Shibata, Reissig, and Wiehe had mainly focused on the synthesis of a variety of SF₅-substituted macrocycles, highlighting the chemical robustness and synthetic versatility of the SF₅ group in a wide array of chemical reagents and reaction conditions. However, these studies lacked the goal of designing specific optoelectronic materials for optoelectronic applications and only covered the basic photophysical studies such as absorption and fluorescence characterizations.

SF₅-containing transition metal complexes as phosphorescent emitters. In recent years, one of the most important applications of the SF₅ group in optoelectronic materials was mainly dedicated to phosphorescent emitters, in which SF₅ groups were applied to the ligands of the Ir(III) and Pt(II) complexes to adjust the frontier energy levels and manipulate the photophysical properties.¹¹⁵⁻¹²² The first SF₅-containing Ir(III) complexes were reported by Zysman-Colman in 2015.¹¹⁵ They synthesized a series of SF₅-functionalized heteroleptic cationic Ir(III) complexes (Fig. 1.13a), where the SF₅ groups were employed as strongly electron-withdrawing substituents on bidentate cyclometalating ligands. The introduction of SF₅ to molecular design was found to increase the oxidation potentials and redox gaps, resulting in more pronounced blue-shifted phosphorescent emissions than those with F or CF₃ substitutions. Specifically, the emission peak (λ_{em}) of

R2 and **R3** with the F and CF₃ substituents compared to reference **R1** was blue-shifted by 29 nm and 69 nm, respectively. In comparison, the most significant blue-shift λ_{em} by almost 100 nm was observed for one of the SF₅-containing Ir(III) complexes (**R5** in Figure 1.12a). These SF₅-containing iridium complexes exhibited green phosphorescence with high quantum yields ranging from 0.70 to 0.79. Additionally, the bulky SF₅ was shown useful in increasing solubilities of the metal complexes and minimizing unfavourable intermolecular interactions in the solid states. However, the introduction of SF₅ was also shown problematic that these SF₅-functionalized complexes exhibited irreversible reduction, which limited their applications in light-emitting electrochemical cells (LEECs). Nevertheless, these complexes displayed green to yellow-green electroluminescence (λ_{em} : 501-520 nm) with an EQE of up to 1.7% in OLED devices.

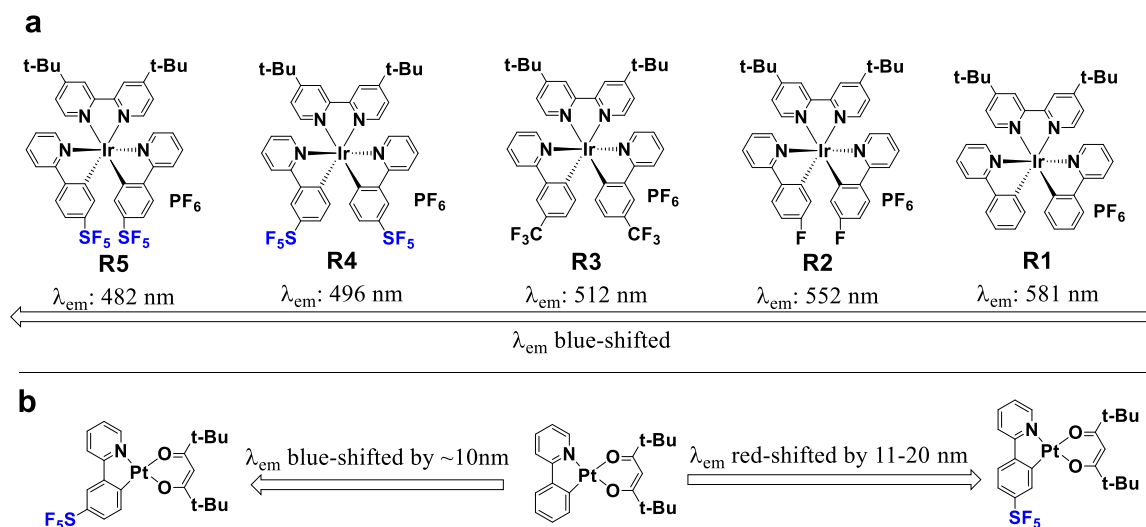


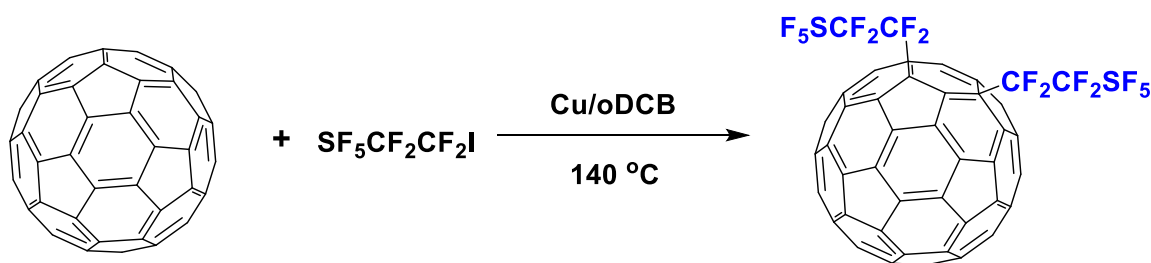
Figure 1. 12 a) Ir(III) complexes showed blue-shifted emission upon fluorination, trifluoromethylation, and pentafluorosulfanylation.¹¹⁵ b) Different SF₅ positions on Pt(II) complexes displayed a red-shifted or blue-shifted emission relative to the no-SF₅ analogue.¹¹⁸

Aside from the application of SF₅ in Ir(III) complexes, Zysman-Colman also incorporated SF₅ moieties into Pt(II) complexes (Figure 1.12b) for a similar reason to modify the photophysical and electrochemical properties.¹¹⁸ When substituted meta to the Pt-C bond, the SF₅ group could stabilize the lowest triplet excited state of the Pt(II) complex that led to peak emission (λ_{em}) red-shifted by 11-20 nm relative to parent complex. Whereas in the case where SF₅ was in a para position to the Pt-C bond, the triplet state

remained unaffected, and the metal-based orbitals were stabilized by SF₅, leading to a blue-shifted λ_{em} by around 10 nm. Overall, these studies by Zysman-Colman established the practicability of SF₅ as an effective tool for engineering the photophysical properties of transition metal complexes potentially interesting for phosphorescent OLEDs devices.^{116, 119-122} Additionally, their studies also showed that the potent electronegative SF₅ group provides other critical advantages to the metal complexes, including excellent chemical and thermal stability, enhanced solubility and processability, and reduced intermolecular aggregation in the solid-state. However, a potential disadvantage of SF₅-containing complexes, as previously mentioned, is that they are not suitable for LEECs due to their irreversible reduction nature resulting from the SF₅ group, which might decompose by releasing a fluoride upon receiving an electron.

SF₅-functionalized fullerene as acceptor materials. As mentioned before, fullerene C₆₀ and its derivatives are among the best acceptor materials for bulk-heterojunction OSCs. In a recent study by Strauss, Thrasher, and Boltalina, the electron-withdrawing SF₅ moieties were introduced to fullerene as a way to lower its HOMO/LUMO energy levels and enhance its electron affinities.¹²³ In particular, they reported the successful synthesis of SF₅-functionalized fullerenes, bis-adduct 1,7-C₆₀(CF₂CF₂SF₅)₂, by heating C₆₀ with SF₅CF₂CF₂I or SF₅CF₂I in the presence of copper powder at 140 °C (Scheme 1.3). However, during the optimization process of synthesis, the thermal stability of the SF₅CF₂CF₂ group was found to be lower than the perfluoroalkyl group that SF₅CF₂CF₂I tended to fragment above 150 °C due to relatively weak S–C bond. In comparison, fragmentation at that temperature was not observed for the perfluoroalkyl group. It needs to point out that the SF₅ group has been shown to possess high thermal stability at temperatures exceeding 300 °C and display higher hydrolytic stability than the CF₃ group,⁵⁹⁻⁶¹ where the sulfur in SF₅ is generally bonded to an sp² carbon in aryl moieties. While in the case of SF₅CF₂CF₂I, the sulfur is bonded to an sp³ carbon, which may account for the lower stability of the SF₅CF₂CF₂ group than the perfluoroalkyl group.¹²⁴ In the electrochemical studies, 1,7-C₆₀(CF₂CF₂SF₅)₂ displayed irreversible reduction behaviour, while perfluoroalkylfullerenes generally exhibit several reversible reductions,¹²⁵ which may further attest to the unstable nature of SF₅ upon receiving electrons. On the other hand,

the SF₅-functionalized fullerenes displayed superior solubility than most perfluoroalkylfullerenes, rendering them more suitable for solution processing. Nonetheless, the readily ionized nature of C₆₀(CF₂CF₂SF₅)₂ in the electrospray ion source indirectly implied the electron affinities of C₆₀(CF₂CF₂SF₅)₂ were comparable to those of perfluoroalkylfullerenes. In all, the introduction of SF₅ moieties to fullerenes was found to be advantageous in improving the solubility and leading to higher electron affinities of fullerene. However, the major drawback of SF₅-functionalized fullerenes was the irreversible reduction nature, which may limit their applications as the acceptor materials for bulk heterojunction OSCs.



Scheme 1. 3 Representative synthesis of SF₅-functionalized fullerene.¹²³

All-organic SF₅-containing chromophores. A very recent work by Lewis described the synthesis and spectroscopic characterization of SF₅-containing azulenes (Figure 1.13).¹²⁶ Azulene is a bicyclic aromatic compound featuring an unusual large dipole and visible light absorption that are interesting for colorimetric sensing and OSC application.¹²⁷ The author was interested in investigating the impact of SF₅ groups on azulene as the absorption properties of azulene are generally heavily influenced by the nature and position of the substituents. Herein, four regioisomeric azulenes bearing SF₅ substituents were synthesized. In the UV-vis spectroscopy studies, the four blue-coloured compounds (**A1-A4**) displayed similar absorption spectra in the green-to-red region (500–700 nm). Upon protonation by excessive trifluoroacetic acid, however, the four regioisomers responded differently in their absorption profiles. The spectroscopic change was most significant for 2-substituted [**A1**+H]⁺ and [**A2**+H]⁺ with the appearance of a new absorption band in the blue region (400–450 nm), resulting in the colour change from blue to yellow-brown and red, respectively. In contrast, 1-substituted [**A3**+H]⁺ and [**A4**+H]⁺ exhibited almost non-observable colour change and only a subtle increase in absorbance. Notably, all four SF₅-

substituted azulenes seemed to be completely stable under such a strongly acidic environment, again validating the chemical robustness of SF₅. On the whole, the 2-substituted SF₅-containing azulenes (**A1** and **A2**) were stable under strong acid solution and displayed a colour change to the stimulus of acids, indicative of their potential for chemical sensing.

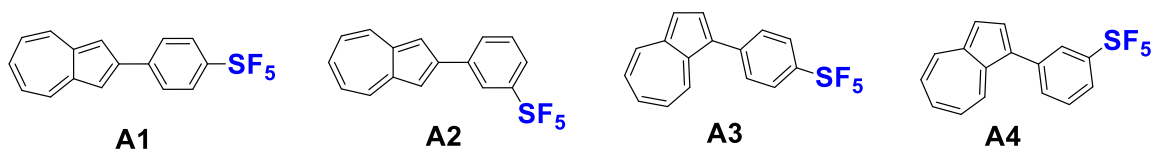


Figure 1. 13 Chemical structures of SF₅-containing azulenes.¹²⁶

SF₅-containing push-pull dyes. In 2017, our group reported the first application of SF₅ as a potent acceptor in donor-acceptor systems, giving six novel push-pull dyes **L1–L6** (Figure 1.14a).¹²⁸ The six dyes featured the electron acceptor SF₅-phenyl covalently bonded to the electron donor triphenylamine via different conjugated π -linkers or/and different bonding fashions (single, double, and triplet bond). And they were synthesized separately via the key Pd-catalyzed cross-coupling reactions, i.e., Suzuki, Heck, and Sonogashira couplings in good yields (52-80%). Owing to the electronic interactions between the strongly electron-withdrawing SF₅-phenyl and electron-donating triphenylamine moieties, all six SF₅-containing push-pull dyes exhibited strong ICT effects, resulting in an extended charge transfer band (320-480 nm) to the longer wavelength region with strong absorption [ϵ : $3.8\text{-}10.1 \times (10^4 \text{ L} \cdot \text{mol}^{-1})$] in their absorption spectra, respectively. The ICT effect in **L1–L6** was further corroborated by the solvatofluorochromic studies that the emission spectra of **L1–L6** were all more red-shifted accompanying a lower quantum yield with the increasing solvent polarity, which is characteristic of the presence of strong ICT effects in push-pull dyes. As a result of strong ICT effects along with the relatively flexible structures of **L1–L6**, large Stokes shifts ranging from 117–150 nm were observed for the six dyes. In terms of emission properties, **L1–L6** displayed intense blue to orange/green fluorescence emission in both solution (λ_{em} : 418-547 nm) and solid-state (λ_{em} : 425-487 nm) with moderate to good quantum yields ranging from 0.24-0.49 in toluene and 0.10-0.60 in thin films, respectively. Strongly fluorescent dyes associated with large Stokes shifts (i.e., >80 nm) are interesting for bioimaging applications,^{129, 130}

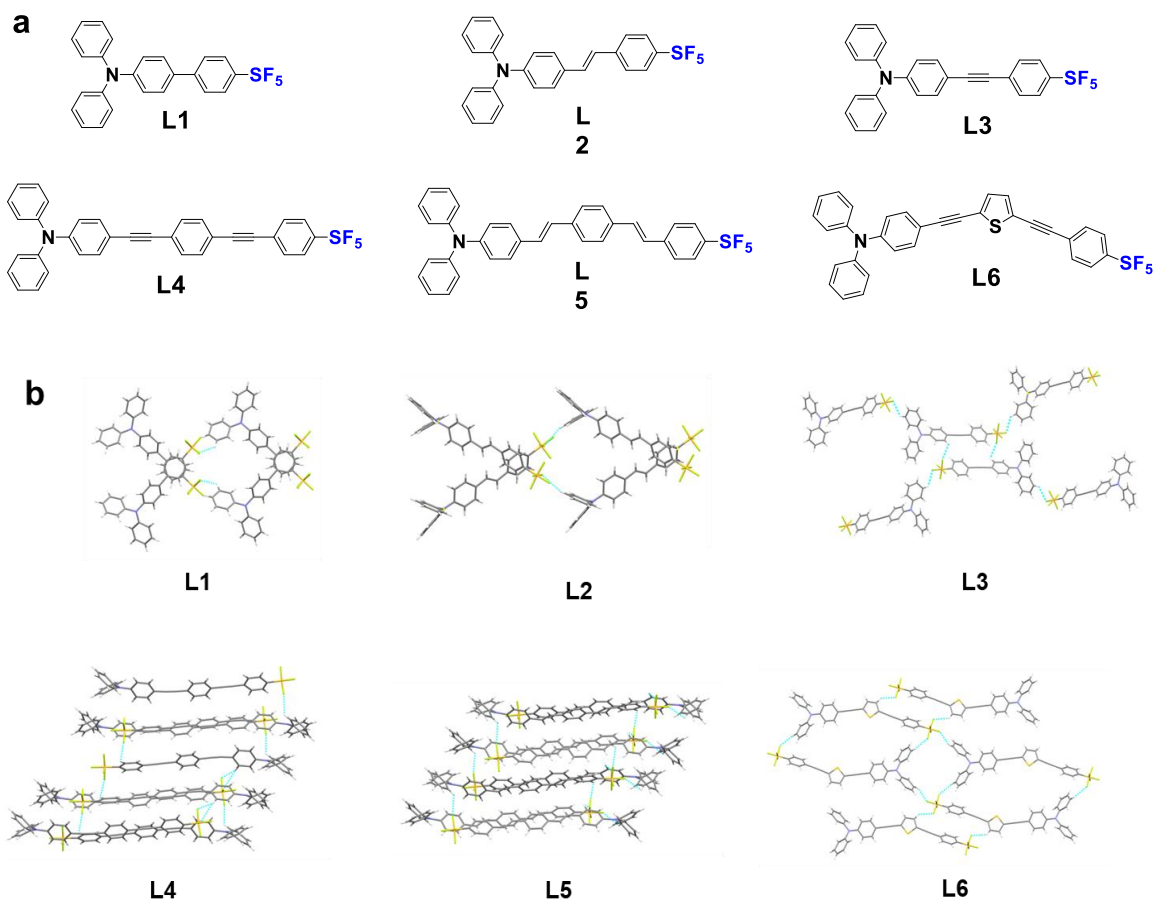


Figure 1. 14 a) Chemical structures of SF₅-containing push-pull dyes **L1-L6**. b) crystal packing diagrams of **L1-L6**.¹²⁸

Interestingly, **L5** displayed a visually observable mechanofluorochromism in that its emission was blue-shifted from orange emission ($\lambda_{\text{em}} = 567 \text{ nm}$) in pristine crystals to yellow emission ($\lambda_{\text{max}} = 545 \text{ nm}$) in fine powder after grinding the crystals. Single-crystal and powder X-ray diffraction (XRD) analyses of **L5** revealed that the blue-shifting of emission upon grinding was possibly derived from the disruption of intermolecular π - π stacking interactions in the crystals. Indeed, the single-crystal structure of **L5** displayed extensive π - π stacking interactions, which were facilitated by overall planar structure and the $\text{CH}\cdots\text{F}$ interactions mediated by the SF₅ groups. Similarly, short-contact $\text{CH}\cdots\text{F}$ interactions (2.45-2.65 Å) were observed in the crystals of **L1-L6** (Figure 1.14b). The mechanofluorochromism of **L5** was found to be reversible in the cycle of regrowing-grinding the crystals. Such properties rendered **L5** potentially applicable as smart inks and mechanical sensors.^{131, 132} Overall, a series of first examples of push-pull dyes featuring

the SF₅ acceptor were reported in this study. Our study showed that the SF₅ group is an excellent choice as an acceptor in donor-acceptor systems. Owing to the potent electron-accepting ability of SF₅, the resultant donor-acceptor systems, or push-pull dyes, possessed a pronounced ICT effect, leading to red-shifted absorption and emission spectra and large Stokes shifts. Also, the ability of SF₅ to form CH $\cdots$ F interactions may be useful as a tool for crystal engineering in other optoelectronic materials.

1.4 Outline of the thesis

As SF₅-containing reagents became more commercially available, there has been a surge of interest in utilizing SF₅ in research areas such as pharmaceutical design and, to a lesser extent, in optoelectronic materials. It is surprising that SF₅ still received not much attention in the molecular designs for optoelectronic applications, especially considering that the strongly electron-withdrawing SF₅ also possesses other unique features such as high hydrophobicity/lipophilicity, steric bulk, and chemical/thermal robustness. As stated in section 1.3.4, recent research has shown the effectiveness of the SF₅ group in manipulating the electronic and photophysical properties of a studied molecule, conferring them with desirable properties for a wide range of optoelectronic applications. However, half of the research efforts have been involved in applying SF₅ in metal-ligand complexes for phosphorescent OLED emitters. The other half of SF₅-containing optoelectronic materials mainly focused on reporting their syntheses and general photophysical properties such as UV-vis and fluorescence spectra, while the specific properties for a particular type of optoelectronic applications lacked in these studies. More importantly, the application of SF₅ remained unexplored in D-A systems or acceptor systems specifically designed for optoelectronic materials such as NLO materials, TADF emitters for OLEDs, donor or acceptor materials for OSCs, and n-type semiconductors for OFETs.

Therefore, the goal of this work was to explore the utilization of SF₅ in a wider range of molecular designs for specific optoelectronic materials.

In Chapter Two, the syntheses of five SF₅-containing push-pull dyes and their photophysical properties, including two-photon absorption characters, will be revealed.

In Chapter Three, two SF₅-containing polymers are synthesized and utilized as charge-storage electrets in nonvolatile OFET memory devices.

In Chapter Four, the syntheses of a series of SF₅-functionalized ullazine derivatives are elaborated, and their photophysical and electrochemical properties are investigated. Additionally, their potential for dye-sensitized solar cells will be examined.

1.5 References

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Chapter 2. Large Two-Photon Absorption Cross-Sections by SF₅-Containing Push-Pull Dyes

2.1 Introduction

Organic dyes can simultaneously absorb two low-energy photons from the ground state (S_0) to the excited state (S_n , $n \geq 1$) via a virtual state when exposed to high-intensity excitations such as laser beams (Figure 2.1).^{1, 2} On the one hand, the long wavelength of the two absorbed photons is advantageous for deep penetration.^{3, 4} The resulting excited states, on the other hand, can either emit photons with higher energies than that of the absorbed photons or transfer the high energy excited electrons to other species for other purposes such as photodynamic therapy.⁵ Two-photon dyes exhibiting large two-photon absorption (2PA) cross-sections are desirable in this context owing to their broad range of applications in bioimaging, upconverted lasing, 3D optical data storage, and photodynamic treatment, among others.^{3, 6-12} In terms of molecular designs, increasing the conjugation length of the two-photon dyes generally results in large two-photon absorption cross-sections (σ_{TPA}).^{1, 4} However, the large size of the two-photon dyes may limit their applications in a biological environment.^{13, 14} Large π -conjugated systems, for example, are not compatible with biological specimens that may be unable to reach the biological targets by crossing cell membranes. While for small molecules, they can be easily loaded into cells and detect biological targets with high sensitivity.¹⁵ In this regard, developing efficient two-photon dyes with small molecular weight and large 2PA cross-sections is necessary for practical applications.

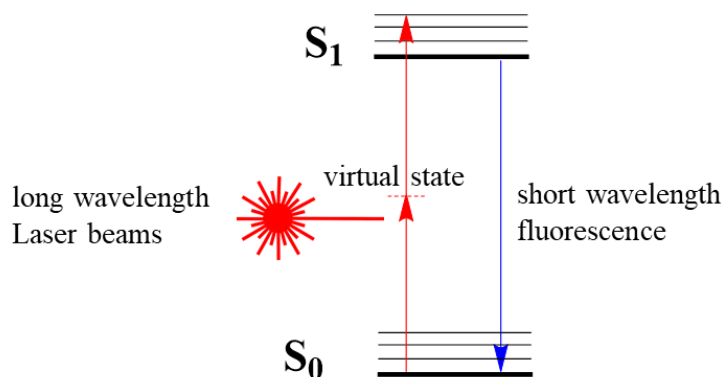


Figure 2. 1 Jablonski diagram of two-photon absorption.

In the context of designing small two-photon dyes, donor- π -acceptor systems have been found to possess large two-photon absorption cross-sections.^{4, 16, 17} Specifically, it was shown that a select number of two-photon dyes with cationic acceptors displayed exceptional large 2PA cross-sections due to their large transition dipole moment induced by the strong intramolecular charge transfer (ICT), as exemplified by some cyanine dyes, squaraine dyes, and porphyrin dimers with carbocation cores (Figure 2.2).^{2, 18-20}

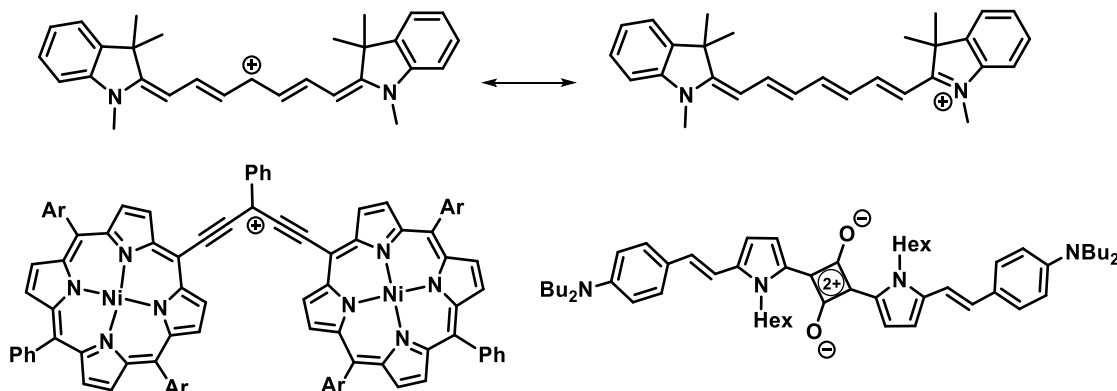


Figure 2. 2 Cyanine dye (top), porphyrin dimer (bottom left), and a squaraine dye (bottom right), featuring resonance-stabilized cationic acceptors.

The SF₅ functional group is fascinating for the features of its structure, bonding, and properties associated with it. The SF₅ group has a hypervalent sulfur(VI) in an octahedral environment, in which the axial SF bond is generally slightly longer than its four equatorial counterparts.^{21, 22} Chemical bonding in hypervalent sulfur systems such as -SF₅, or a more well-known structure SF₆, should be best described by ionic structures, e.g., structure **S2** and **S3** in Figure 2.3, that involve the concept of negative hyperconjugation.²³⁻²⁵ The ionic structures arising from negative hyperconjugation in SF₆ or other hypervalent molecules were found dominant over the covalent structure (**S1** in Figure 2.3) that uses sp³d² hybridization of the sulfur to rationalize hypervalency.²⁶ In particular, the existence of ionic bonding in SF₆ is supported by either a modified valence bond (VB) or a molecular orbital (MO) approach.²⁷ In the modified VB mode, it has been suggested that the electronegativity difference between sulfur and fluorine is sufficiently large to justify the presence of ionic canonical structures in the resonance hybrid (Figure 2.3). In this regard, the sulfur only forms four covalent bonds to avoid octet expansion.

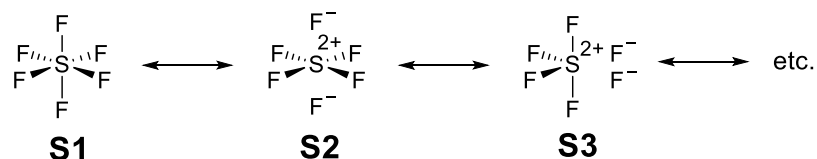


Figure 2. 3 Modified valence bond description of SF₆ featuring ionic resonance contributors.

While in the MO-based approach, the MO diagram, where participation of sulfur 3s and 3p electrons in the O_h point group and symmetry-adapted linear combinations (SALCs) from six fluorines are involved, also suggests that the overall bond order in SF₆ is approximately four (i.e., 3.84).²⁸ Also, it is shown that the four sigma-bonding MOs have a higher proportion of ligand (F-) character, providing further evidence to ionic canonical structures in the VB model. As a result, negative hyperconjugation stabilizes the ionic bonding in SF₆ that can be described by the ionic canonical structures via “no-bond resonance” in both models.²⁹ Additionally, both VB and MO descriptions give the sulphur atom of SF₆ a formal charge of +2 and +3.71, respectively,³⁰ rather than a neutral hypervalent sulphur that makes six covalent bonds.³¹ Similarly, the SF₅ group also contains ionic character³² like SF₆ and can be described by “no-bond resonance” structures (Figure 2.4a) as a result of negative hyperconjugation.^{26, 33} This is corroborated by the observation that S–F bonds in SF₅ are lengthened when coupled to an electron donor moiety,³⁴ as well as the resonance acceptor constants of SF₅-functionalized organic molecules.³¹ Overall, the exceptional powerful electron-accepting ability of SF₅ can attribute to not only its potent inductive effect but also the existence of a significant resonance effect.

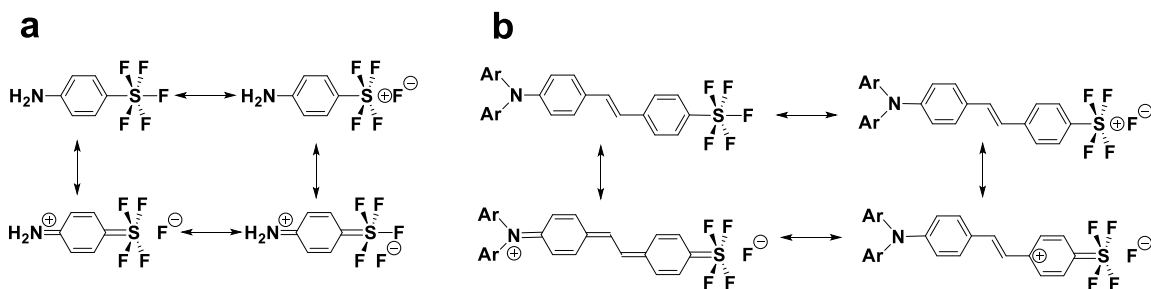


Figure 2. 4 a) Negative hyperconjugation and “no-bond” resonance in 4-(pentafluorosulfanyl)aniline, canonical structures featuring sulfur with ionic character. b) Resonance contributors of a two-photon chromophore featuring hypervalent sulfur with ionic character due to negative hyperconjugation.

To that end, I was interested in investigating the effect of the SF₅ moiety as an acceptor on the two-photon absorption (2PA) properties of a series of donor-acceptor systems. It was expected that molecules with large 2PA cross-sections could be obtained when SF₅ acceptors, which display ionic character resulting from negative hyperconjugation, were linked to proper donors in a conjugated manner (Figure 2.4b). Herein, five novel SF₅-containing push-pull molecules were designed and synthesized (Figure 2.5), and their photophysical properties, especially the 2PA properties, were investigated. To our delight, the 2PA cross-sections of the five molecules were found to be high, ranging from about 1100 to 2200 GM. The best two-photon absorber was **D2**, a tripodal (A- π -)₃D system composed of a core triphenylamine donor coupled to three-terminal SF₅ acceptors via π -linkers. Additionally, not only did **D2** display much larger 2PA cross-sections than most of the tripods in the (D- π -)₃A configuration,³⁵⁻³⁸ but it also performed on a par with or better than the majority of tripods in the (A- π -)₃D configuration.³⁹⁻⁴⁸

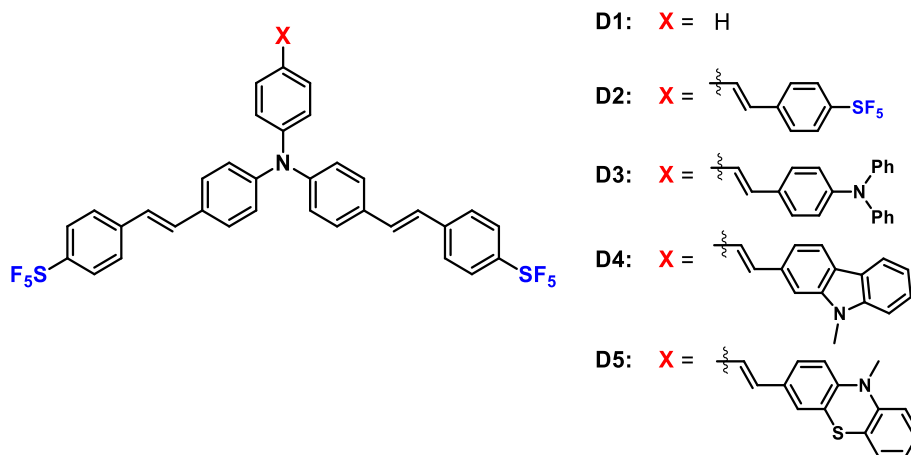


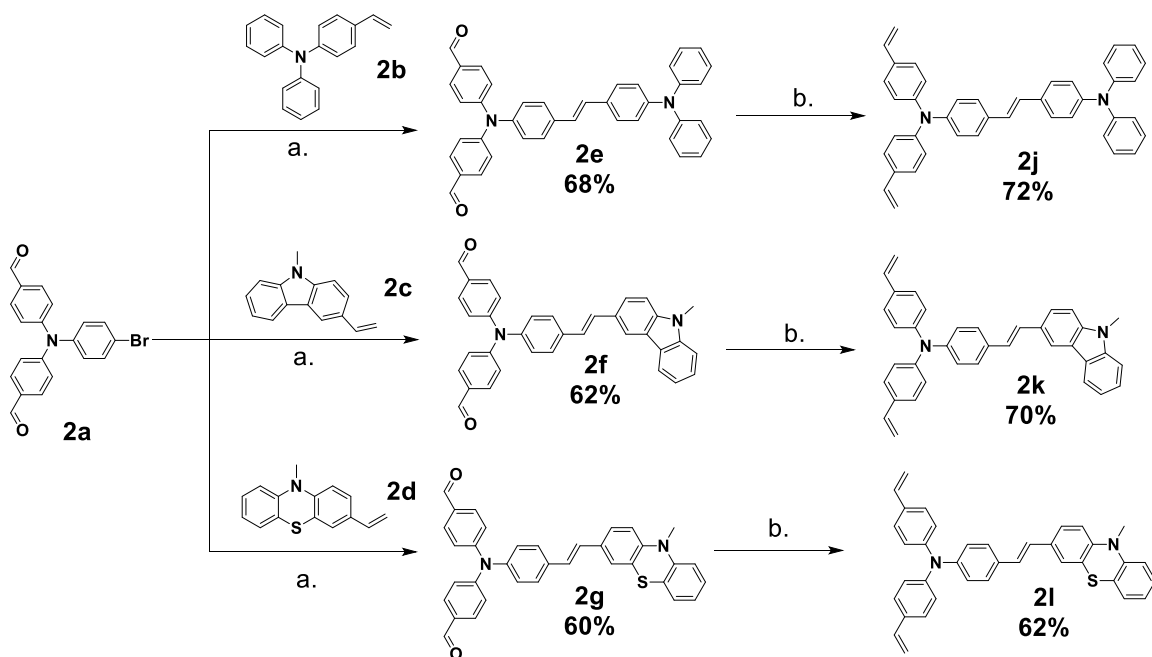
Figure 2. 5 Two-photon absorbing molecules based on potent pentafluorosulfanyl acceptors.

2.2 Results and Discussion

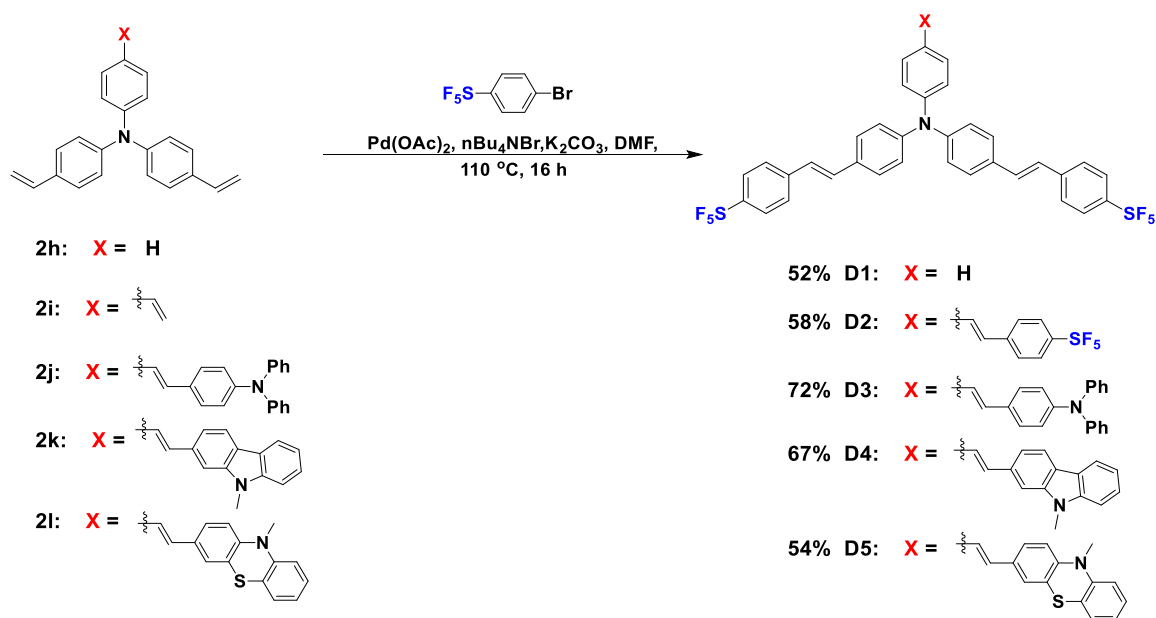
Molecular Design. It has been shown that some donor- π -acceptor dyes with cationic acceptors displayed large 2PA cross-sections due to the strong acceptor strength of the positively charged centers, such as cyanine, squaraine, porphyrin dyes, and molecules containing alkylpyridinium acceptors.^{2, 18-20, 47-49} Likewise, the ionic nature of sulfur in SF₅

is expected to promote large 2PA cross-sections (δ_{2PA}) values if it is used as the acceptor in a donor- π -acceptor design. Thus, the effectiveness of pentafluorosulfanyl moieties in increasing 2PA cross-sections was evaluated for the first time in this work. For better comparison to evaluate the effect of the SF₅ group thus minimizing unknown factors, I adopted a well-studied molecular design based on an electron-rich triphenylamine core connected to terminal acceptors through π -conjugated linkers (Figure 2.5). Also, the motivation behind such molecular design was three-fold: 1) The tripod system offered sufficient modularity at each of the three sidearms. In this study, SF₅ acceptors were installed on two arms while the third arm was varied with substituents possessing different electronic nature, i.e., X = H, electron-poor, electron-rich. 2) The triphenylamine-based tripods are small π -systems, which enables facile syntheses, yet providing high enough δ_{2PA}/N_π ratios (N_π : effective number of π electrons), a normalized figure of merit used to compare molecules with different structures and sizes for their two-photon absorption properties. 3) This work also sought to explore the performance and broaden the scope of this particular (A- π)-₃D type two-photon dyes, as it has shown that (A- π)-₃D systems³⁵⁻³⁸ are inferior to the (D- π)-₃A counterpart design.³⁹⁻⁴⁸ Furthermore, the exotic acceptor SF₅ would also impart added advantages to the design structures, such as conferring chemical and thermal stability and suppressing undesired self-aggregation by its steric bulk.⁵⁰⁻⁵²

Synthesis. The novel two-photon molecules **D1-D5** were prepared via 3-5 steps from triphenylamine (Scheme 2.1 and 2.2). First, **2a-2d**, **2h**, **2i** were prepared using previously reported procedures.⁵³⁻⁵⁹ Three new molecules, **2e-2g**, were then synthesized via Mizoroki-Heck couplings between **2a** and **2b-2d**, followed by Wittig reactions to convert them into olefins from corresponding aldehydes (Scheme 2.1). Finally, the target five molecules **D1-D5** were synthesized via Mizoroki-Heck reactions between **2h-2i** and commercial compound 4-bromo(pentafluorosulfanyl)benzene in 52-72% yields (Scheme 2.2), during which no compatibility issues were observed due to the excellent thermal and chemical stability of the SF₅ substituent. Molecules **D1-D5** were also found highly soluble in a variety of organic solvents, such as chloroform, acetone, tetrahydrofuran, and toluene thanks to the lipophilic nature of the SF₅ group. The five molecules were unambiguously characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy and high-resolution mass spectrometry (HRMS).



Scheme 2. 1 Synthesis of olefin intermediates **2j-2l**. Reagents and reaction conditions: a) $\text{Pd}(\text{OAc})_2$, TBAB, K_2CO_3 , DMF, 110°C , 30 h; b) $t\text{-BuOK}$, $\text{CH}_3\text{PPh}_3\text{I}$, THF, rt, 36 h.



Scheme 2. 2 Synthesis of two-photon dyes **D1-D5** via Mizoroki-Heck coupling.

Photophysical Properties (One-Photon). The one-photon photophysical properties of **D1-D5** were examined by UV-vis and fluorescence spectroscopy. The UV-vis spectra of all five dyes showed similar λ_{max} values between 405–410 nm even with different

electronic nature of substituents on X (Figure 2.6), i.e., a hydrogen atom (**D1**), an electron acceptor (**D2**), and electron donors (**D3-D5**). The absorption of **D1-D5** at around 400 nm can be attributed to the ICT absorption bands. The minor redshift with increased branching (from **D1** to **D2-D5**) implies the addition of a third branch does not increase the ICT effects among those five dyes, resulting in similar ICT absorption bands. In terms of one-photon absorption properties, it is evident that the one-photon absorptivity (molar extinction coefficient, ϵ) increased proportionally as the conjugation is extended (larger N_π , effective number of π electrons), with ϵ of **D1** and **D3** being the smallest and largest, respectively (Figure 2.7). Such a trend is normally expected in various types of dyes.^{60, 61} However, it was also observed that the extended conjugation on the X position promoted the nonradiative decays. Consequently, **D2-D5** showed lower quantum yields (Φ_f) (23-49%) than that of **D1** (83%), with **D3** being the lowest possibly due to the presence of the largest nonradiative decay channel that arises from the most flexible triphenylamine on the third arm (Table 2.2).

Regarding the fluorescence colour, the five dyes displayed blue to green emission with peak emission (λ_{em}) ranging from 475 to 509 nm (Figure 2.6, Table 2.2). Compared to **D1**, the emission spectrum of **D2** showed a minor red-shift of 7 nm mainly due to the extended conjugation. While **D3-D5** displayed a more pronounced red-shift ranging between 19-27 nm relative to **D2**, this can be explained by their larger conjugations (large N_π) as well as the greater geometric relaxation of their excited states prior to emission, as indicated by their larger Stokes shifts than that of **D2** (Table 2.2). The S_1 states of **D3-D5** could be the ^1CT states (charge-transfer excited states) that led to their greater geometric changes associated with the more substantial electron movement upon excitation, based on the observation that they have more separated HOMO/LUMO distributions compared to **D1** and **D2** (Figure A.2).⁶² Additionally, the easily perturbed structures of **D3-D5** at excited states also led to their moderate quantum yields (0.23-0.38) due to the high tendency of nonradiative decay via geometric relaxation. In contrast, **D2** and **D1** displayed higher Φ_f values of 49% and 83%, respectively (Table 2.2).

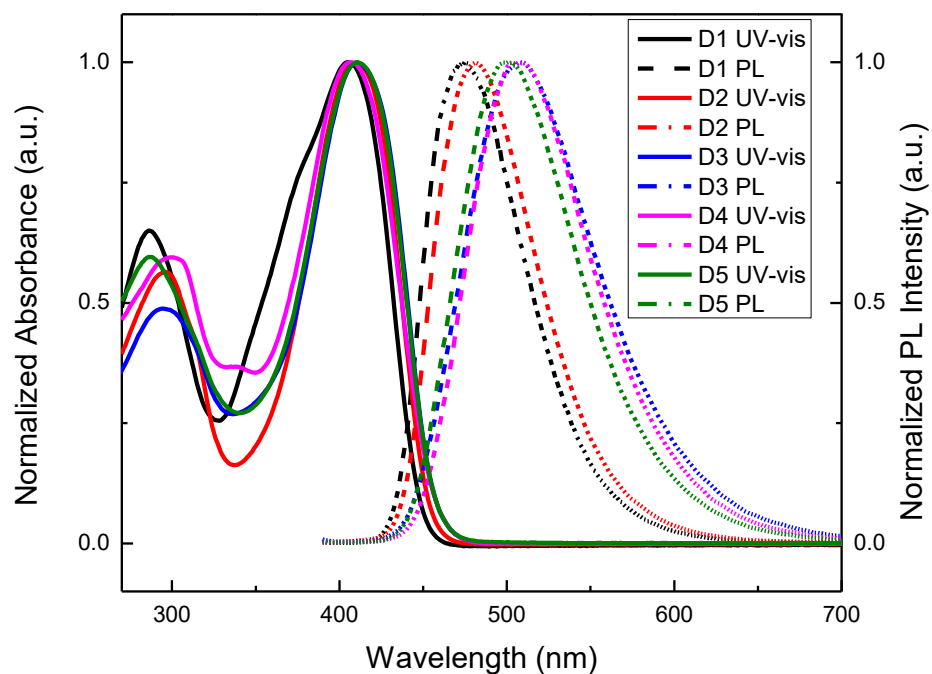


Figure 2. 6 Normalized absorption and fluorescence spectra of **D1-D5** as measured in chloroform.

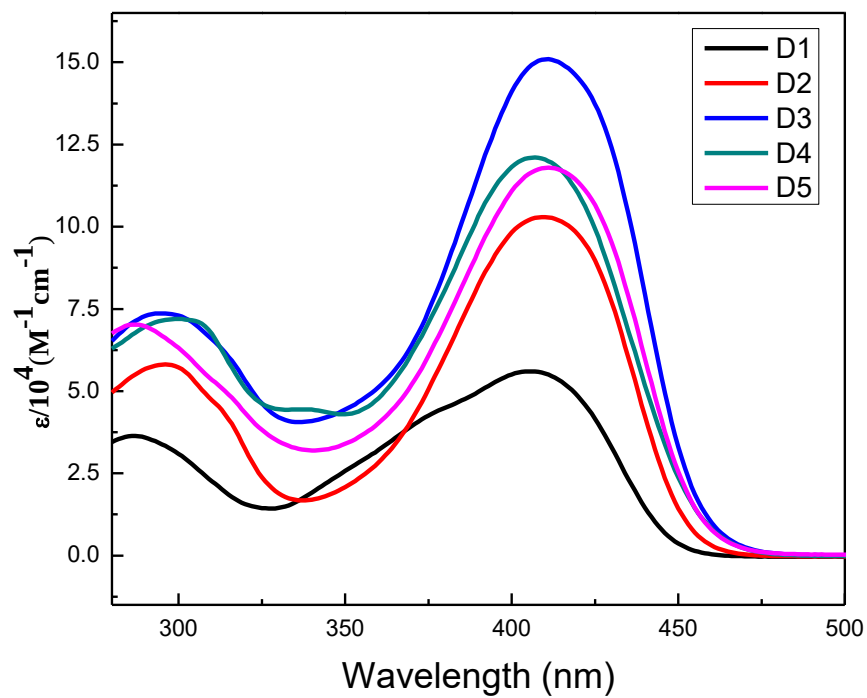


Figure 2. 7 Molar absorptivities (ϵ) of **D1-D5** as measured in chloroform.

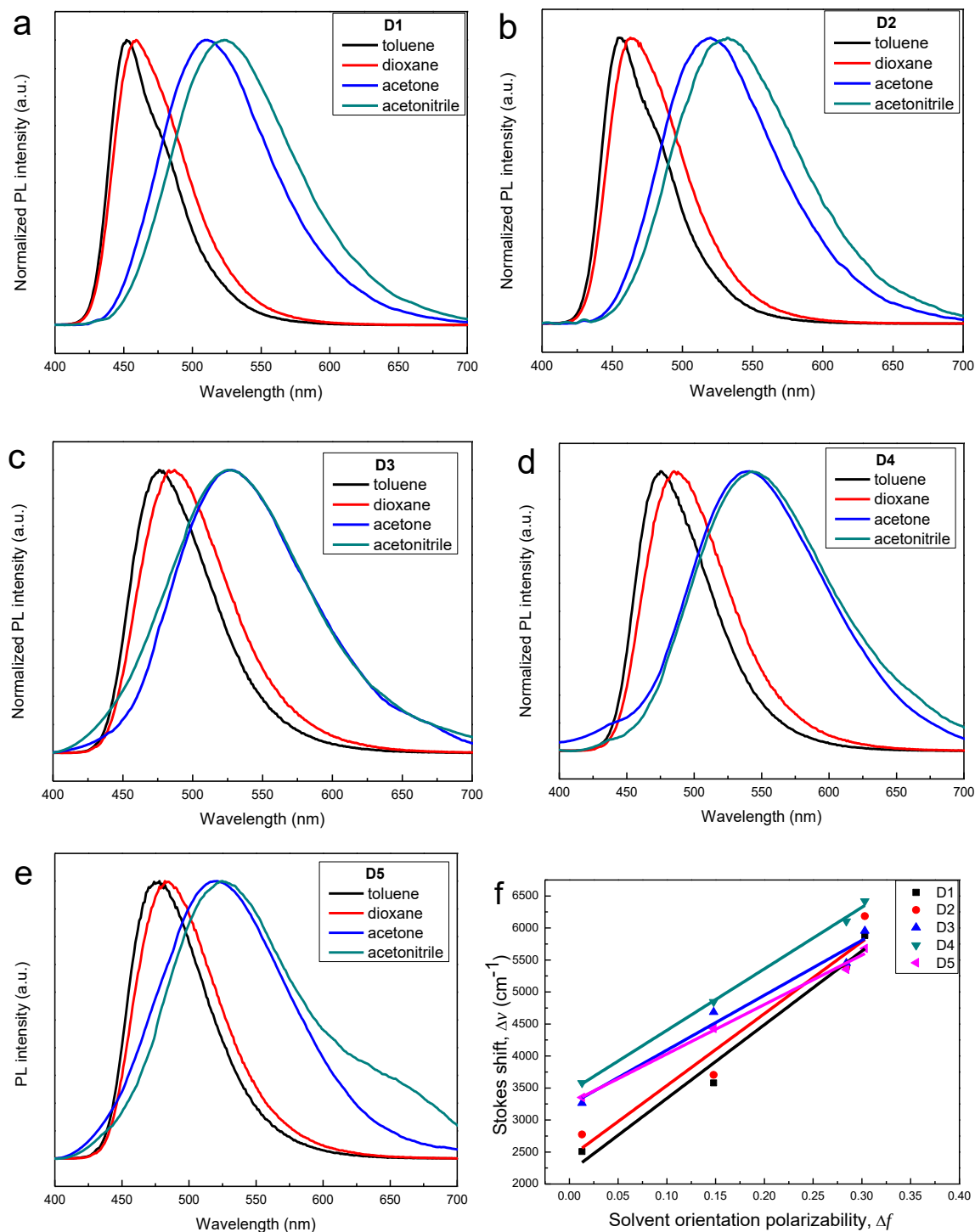


Figure 2.8 a-e) Emission spectra of **D1-D5** in four different solvents with different polarities.
f) Lippert-Mataga correlations for **D1-D5**.

Table 2. 1 Photophysical data from the solvatochromic studies of **D1-D5**.

Comd	solvent	λ_{abs} (nm)	λ_{em} (nm)	Stoke shift (nm)	Φ_f^a
D1	toluene	406	452	46	0.83
	dioxane	403	459	56	0.84
	acetone	400	510	110	0.19
	acetonitrile	400	523	123	0.08
D2	toluene	404	455	51	0.74
	dioxane	406	463	57	0.70
	acetone	406	520	114	0.19
	acetonitrile	402	535	133	0.09
D3	toluene	412	476	55	0.68
	dioxane	410	487	77	0.56
	acetone	407	523	116	0.008
	acetonitrile	404	532	128	0.005
D4	toluene	406	475	69	0.87
	dioxane	406	485	79	0.55
	acetone	401	531	130	0.014
	acetonitrile	401	540	139	0.005
D5	toluene	412	478	66	0.56
	dioxane	411	482	71	0.59
	acetone	408	522	114	0.005
	acetonitrile	405	526	121	0.004

^a Excited at 380 nm.

Solvatochromic Studies. To verify the presence of the strong ICT in the five push-pull dyes, solvatochromic studies were performed by investigating the solvent effects on their photophysical properties. Specifically, the emission spectra of **D1-D5** were obtained from four different solvents with increasing polarity, i.e., toluene, dioxane, acetone, and acetonitrile (Figure 2.8a-e). Even in the nonpolar toluene, the Stokes shifts ($\Delta\lambda$) of molecules **D1-D5** were found to be large (46-69 nm), indicating the presence of strong ICT effects. Furthermore, while there was no change in their absorption maxima as the solvent polarity was increased, the emission maxima were gradually red-shifted (Table 2.1). Meanwhile, the fluorescence quantum yield of each dye was also observed to gradually

decrease as the solvent became more polar (Table 2.1). The emission red-shift was most significant in acetonitrile, resulting in $\Delta\lambda$ ranging from 121 to 139 nm. The pronounced emission red-shifts of **D1-D5**, associated with fluorescence quenching as solvent polarity increases, are characteristic of push-pull dyes that demonstrate strong ICT effects. All five dyes exhibited solvatofluorochromic behaviour consistent with the Lippert-Mataga relationship (Figure 2.8f), with a linear dependency of the Stokes shift ($\Delta\nu$) on the solvent orientation polarizability parameter (f) for each dye.

Two-Photon Absorption Properties. Following the one-photon photophysical properties, the two-photon absorption cross-sections of the **D1-D5** were investigated. Logarithmic plots of fluorescence intensity (a.u.) versus excitation intensity (mW) were obtained for **D1-D5** (Figure 2.9a-e), all with approximate slope values of 2, indicating quadratic dependence on the laser power as a result of two-photon absorption. For **D1** with a hydrogen on X, the resulting quadrupolar system displayed δ_{2PA} values of 1133, 1100, and 1085 GM when excited at 780, 800, and 820 nm, respectively (Figure 2.9f). As in the case for **D3-D5**, with an additional electron-donating branch on X, their δ_{2PA} values ranged from 1515 to 1710 GM. The extended conjugation for **D3-D5** was expected to increase the corresponding δ_{2PA} values.^{1, 63-66} Hence, the δ_{2PA} values of **D3-D5** were about 35-55% higher than that of **D1**. It is worth noting, **D5** exhibited a noticeably lower δ_{2PA} value even with a larger N_π compared to **D4**, which might be caused by the smaller molecular dipole moment difference between S_0 and S_1 ($\Delta\mu_{ge}$) of **D5**. As was observed from the plots of the Lippert-Mataga relationship (Figure 2.8f), the smaller slope for the plot of **D5** compared to that of **D4** was indicative of a smaller $\Delta\mu_{ge}$,¹ thus, a smaller δ_{2PA} value. Aside from the extended conjugation of **D3-D5**, the cooperative enhancement effect derived from the extra branch (compared to **D1**) was also expected to increase the corresponding δ_{2PA} values, a well-recognized effect for other extended dendritic systems.^{1, 63-66} However, owing to the larger N_π in **D3-D5**, their δ_{2PA}/N_π values were about the same as that of **D1** (Table 2.2). Finally, in the case of **D2**, an extra phenylvinylene-linked SF_5 group was placed on X, resulting in a 3-fold symmetric tripodal octupolar molecule. **D2** displayed the highest δ_{2PA} of 2205 GM under 820 nm excitation among the five molecules. In addition to the strong ICT induced by the potent SF_5 acceptors, symmetrical intramolecular charge transfer

between dipolar branches^{47, 67} of **D2** may also account for its higher cross-section than those of **D3-D5**, as was observed for other symmetrical tribranched octupoles.

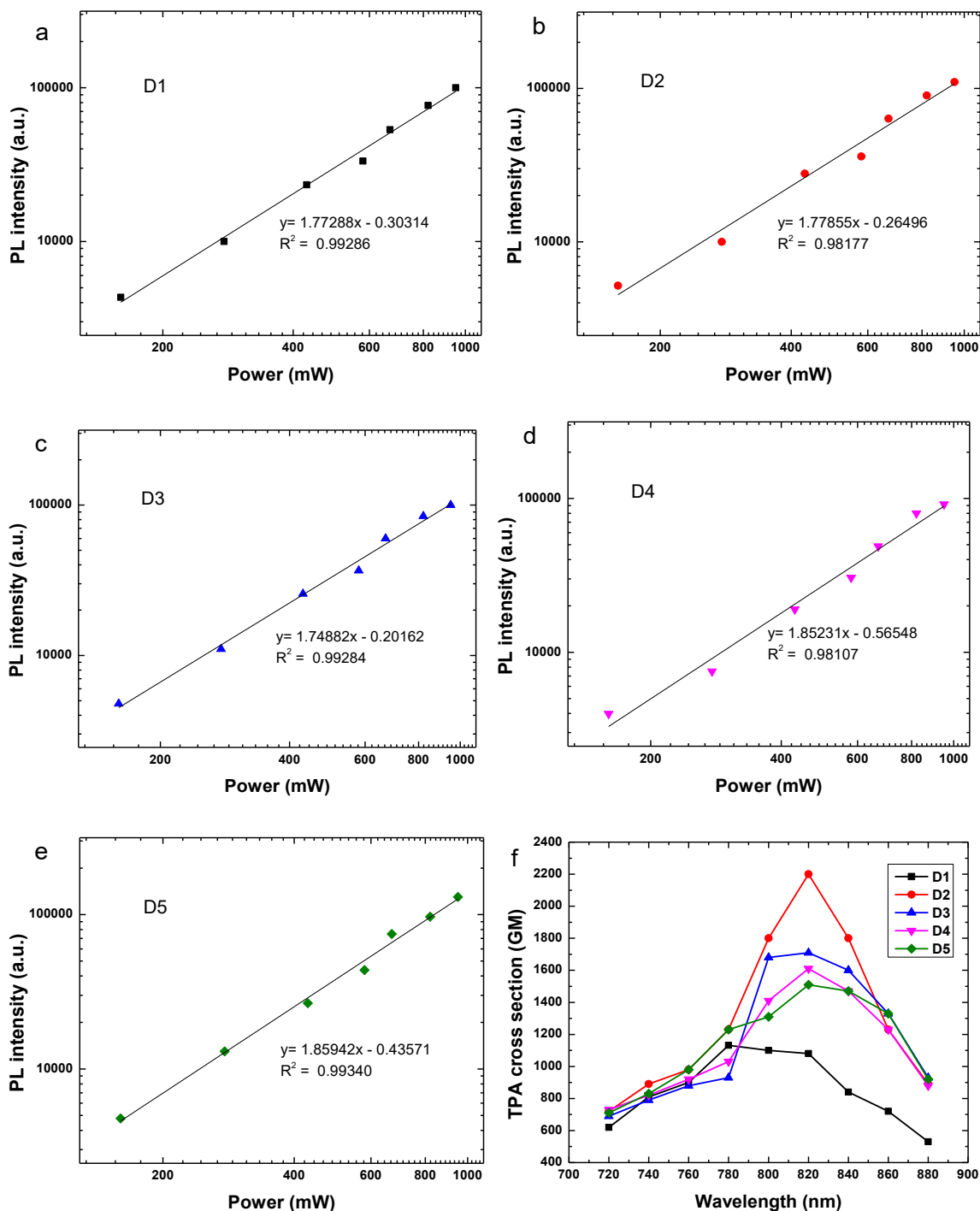


Figure 2. 9 a-e) Logarithmic plot of fluorescence output with the photoluminescent intensity of **D1-D5**. f) Two-photon action spectra for SF_5 -containing dyes **D1-D5** in CHCl_3 .

Table 2. 2 The one- and two-photon photophysical properties of dyes **D1-D5**.

Cmpd	$\lambda_{\max}$ (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	Φ_f^a	N_π^b	$\delta_{2\text{PA}}^c (\lambda_{\max})^d$ (GM) / (nm)	$\delta_{2\text{PA}}/N_\pi$ (GM)	$\delta_{2\text{PA}}\Phi_f$ (GM)
D1	406	475	69	0.83	36	1133 (780)	31.5	940
D2	409	482	73	0.49	44	2205 (820)	50.1	1080
D3	411	509	98	0.23	58	1710 (820)	29.5	393
D4	407	507	100	0.34	52	1614 (820)	31.0	549
D5	410	501	91	0.38	54	1515 (820)	28.1	576

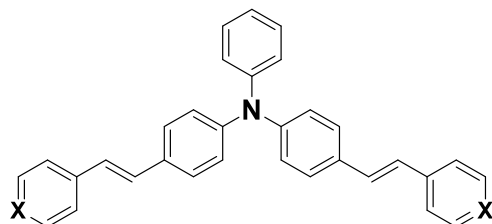
^a The fluorescence quantum yields (Φ_f) of dyes **D1-D5** were calculated with respect to a quinine sulfate standard in 0.5 M sulfuric acid ($\Phi_{\text{st}} = 0.546$). ^b N_π : the number of π electrons. ^c 1 GM = $1 \times 10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$. ^d $\lambda_{\max}$ of the two-photon excitation spectra.

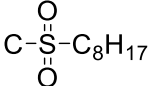
Although **D1** had the smallest $\delta_{2\text{PA}}$ value among the five dyes in this work, its $\delta_{2\text{PA}}$ was much larger than those of previously published analogues of **D1** that varied with benzene and pyridine at the two arms (Table 2.3, NO.2-3), or with different electron-withdrawing groups (Table 2.3, NO.4-7) at the same (X) positions.^{41, 42, 68-71} The 2PA cross-sections were moderate in situations where the electron-withdrawing group had an inductive impact only, such as the keto (Table 2.3, NO.5) or sulfone (Table 2.3, NO.7) groups. In the case of cyano substituents (Table 2.3, NO.3), a relatively high $\delta_{2\text{PA}}$ of 1050 GM was obtained. Aside from its analogues, the 2PA cross-sections of **D1** were also high when compared to other known two photon-absorbing quadrupoles of comparable molecular size and symmetry, which is noteworthy given the A- π -D- π -A systems' generally poor performance compared to the opposite D- π -A- π -D design.⁴

The $\delta_{2\text{PA}}$ of **D2** was consistently higher when compared to previously published tribranched analogues where SF_5 groups were replaced with various EWGs (Table 2.4).^{41, 42, 67-72} A reasonably high $\delta_{2\text{PA}}$ of 1050 GM was obtained in the case where three EWGs were substituted with cyano π -acceptors (Table 2.4, NO.2). When the peripheral EWGs were alkylsulfonyl (Table 2.4, NO.5-6) or perfluoroalkylsulfonyl (Table 2.4, NO.7-8) substituents featuring strong inductive effects, $\delta_{2\text{PA}}$ also reached values ranging from 1000–1430 GM. Still, **D2** showed a much higher $\delta_{2\text{PA}}$ value than both CN substituted

(Table 2.4, NO.2) and trifyl-substituted (Table 2.4, NO.7) analogues. Additionally, **D2** exhibited a significantly higher δ_{2PA} than octupolar systems, which are composed of triphenylamine cores connected through phenylethynylene bridges to peripheral super acceptors such as fluorinated sulfilimines and sulfoximines.⁷³

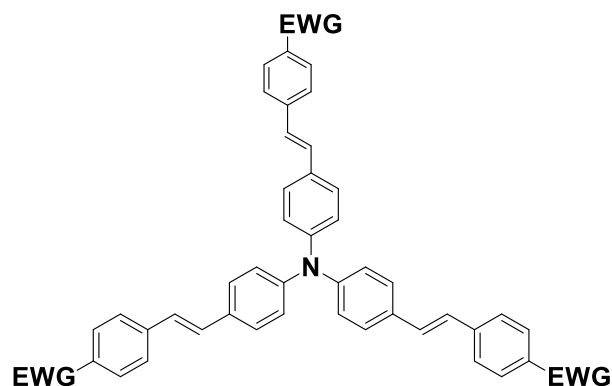
Table 2. 3 Comparison of two-photon absorption properties of **D1** with previously reported analogues.

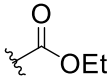
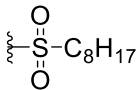
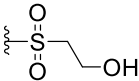
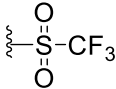
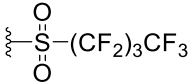


NO.	X	δ_{2PA}^a (GM)	δ_{2PA}^a/N_π (GM)	λ_{max}^b	Reference
1	C-SF ₅	1133	31.5	780	This work
2	C-H	219	6.1	700	68
3	N	102	2.8	820	42
4	C-CN	1050	26.3	750	41
5		57	1.1	800	69
6		358	8.1	780	70
7		420	11.7	740	71

^a Maximum δ_{2PA} value. ^b λ_{max} of the two-photon excitation spectra.

Table 2. 4 Comparison of two-photon absorption properties of **D2** with previously reported analogues.



NO.	EWG	δ_{2PA}^a (GM)	δ_{2PA}^a/N_π (GM)	λ_{max}^b	Reference
1	-SF ₅	2205	50.1	820	This work
2	-CN	1100	22.0	810	41
3		82	1.2	800	69
4		590	10.5	780	70
5		>995	22.6	705	71
6		1300	29.5	700	72
7		1340	30.5	740	67
8		1430	32.5	755	67

^a Maximum δ_{2PA} value. ^b λ_{max} of the two-photon excitation spectra.

Obtaining large 2PA cross-section values is not the only aspect to be considered for new two-photon dyes. Figures of merit such as δ_{2PA}/N_π and $\delta_{2PA}\Phi_f$ are also important.^{4, 16} For example, dyes with extended conjugation may have large δ_{2PA} values yet a large N_π as well. A normalized 2PA cross-section parameter, i.e., δ_{2PA}/N_π , is more suitable for comparing different dyes in applications such as biological imaging, where the size of the conjugated dye is crucial for fast transport across membranes.^{14, 15} Another important figure of merit is the two-photon excited fluorescence action cross-section ($\delta_{2PA}\Phi_f$). Extending the conjugation of dyes may yield large δ_{2PA} values, yet may simultaneously diminish the fluorescence quantum yields (Φ_f), as was observed for **D2-D5** (compared to **D1**) in this study. It was also found in the previous studies that lengthier and more strongly coupled porphyrin oligomers reached a threshold of diminishing returns when the increased δ_{2PA} began to be offset by a concomitant drop in Φ_f .^{74, 75} Hence, to achieve large $\delta_{2PA}\Phi_f$, it is important to balance the δ_{2PA} and Φ_f values with a suitable structure design. Out of the five molecules (**D1-D5**) in this work (Table 2.2), **D2** stood out as the best performer in terms of δ_{2PA} , δ_{2PA}/N_π , and $\delta_{2PA}\Phi_f$. As aforementioned, the high δ_{2PA} value of **D2** is mainly attributed to the strong ICT effects induced by the potent SF₅ acceptor, cooperative enhancement, as well as the symmetrical ICT effects between three branches, and a less significant contribution from the extended conjugation as in the case of **D3-D5**. Consequently, **D2** also possessed the largest δ_{2PA}/N_π , with 50 GM per π -electron against ~30 GM for the other four dyes. It should also be noted that, unlike other strong acceptors like CN, adding SF₅ groups does not enhance N_π . Both **D1** and **D2** performed well in terms of $\delta_{2PA}\Phi_f$ values of 901 and 1080 GM, respectively. Although the δ_{2PA} was less than half that of **D2**, **D1** still showed a comparable high $\delta_{2PA}\Phi_f$ owing to its high fluorescence quantum yield (83%). On the other hand, **D3-D5** exhibited smaller $\delta_{2PA}\Phi_f$ values due to their relatively low fluorescence quantum yields (23–38%). Overall, **D2** was the best two-photon dye among the five molecules in terms of $\delta_{2PA}\Phi_f$ as it showed an optimal trade-off between 2PA cross-section and fluorescence quantum yield.

2.3 Conclusion

In this study, a series of first-generation SF₅-containing push-pull dyes featuring large 2PA cross-sections were developed. The large δ_{TPA} values of these dyes hinged on

the molecular design that adopts the unique SF₅ groups as the electron acceptors. Apart from its potent inductive effect, the SF₅ group also possesses the “no-bond” resonance effect due to negative hyperconjugation, rendering it an exceptionally powerful electron-withdrawing group. The SF₅ groups featuring ionic character can act as strong electron acceptors and can be linked to a proper donor such as triarylamine core via π -linkers to generate donor- π -acceptor systems with large 2PA cross-sections. This is the first time that the fascinating yet little-studied SF₅ moiety is used for 2PA materials. The findings of this work can serve as a model for developing the next-generation 2PA dyes with superior properties. It is anticipated that our study will pique further interest in developing SF₅-functionalized two-photon dyes for biological imaging or other practical applications.

2.4 Experimental Section

Materials and Methods. All synthetic procedures were carried out in oven-dried glassware under an anhydrous nitrogen atmosphere using standard Schlenk techniques. Reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, TCI America, Ube Industries, and Fisher Scientific, and used without further purification. Reaction solvents were dried over activated 3 Å molecular sieves. Crude products were purified by flash column chromatography on silica gel 60–230 mesh. ¹H, ¹³C and ¹⁹F NMR spectra were obtained from a Bruker AVANCE II 400 MHz and Bruker AVANCE II 300 MHz NMR spectrometer. Chemical shifts are reported relative to tetramethylsilane (¹H: δ = 0.00 ppm), CDCl₃ (¹H: δ = 7.26 ppm; ¹³C: δ = 77.0 ppm), (CD₃)₂CO (¹H: δ = 2.05 ppm; ¹³C: δ = 29.84 ppm). HRMS were recorded on a Kratos Concept-Magnetic Sector Electron Impact mass spectrometer and Waters Global electrospray high-resolution Q-TOF mass spectrometer with lock spray accuracy. UV–visible spectra were recorded on a Cary 60 UV-Vis spectrophotometer. PL spectra were recorded on a Horiba Fluorolog-3 spectrofluorometer. The fluorescence quantum yields (Φ_f) of dyes **D1–D5** were calculated by the steady-state comparative method using quinine sulfate (QS) in 0.5 M sulfuric acid as a standard (Φ_{st} = 0.546). Density Functional Theory (DFT) calculations: The initial structures of the SF₅-containing molecules were constructed using the GaussView 5.0 visualization program. Geometry optimizations were performed using Gaussian09 at the B3LYP level of theory and the 6-31G(d) basis set. The two-photon absorption cross-sections of the samples were

measured by employing two-photon induced fluorescence techniques using Rhodamine 6G in methanol as a reference.⁷⁶ To measure the wavelength-dependent two-photon absorption cross-sections from 720 nm to 880 nm, a wavelength-tunable Ti-Sapphire femtosecond laser with pulse-width of 100 fs and repetition rate of 80 MHz was used as the excitation source. The two-photon excited PL signals were dispersed by a 320 mm-monochromator and detected by a charge coupled device (CCD).^{77, 78}

Compounds **2a-2b**, **2h**, and **2i** were synthesized by using previously published methods.⁵³⁻⁵⁹

Synthesis of compound 2e. To a mixture of **2b** (0.062 g, 0.23 mmol), **2a** (0.087 g, 0.23 mmol), Pd(OAc)₂ (1.5 mg, 0.0069 mmol), K₂CO₃ (0.32 g, 2.3 mmol), and tetra-*n*-butylammonium bromide (0.15 g, 0.46 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 30 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and ethyl acetate (7:3 v/v) as eluent to afford compound **2e** (0.089 g, 68%) as a greenish-yellow solid. ¹H NMR (400 MHz, (CD₃)₂CO): δ 9.94 (s, 2H), 7.89-7.86 (m, 4H), 7.69-7.65 (d, 2H, *J* = 9 Hz), 7.55-7.52 (d, 2H, *J* = 9 Hz), 7.35-7.17 (m, 12H), 7.10-7.00 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 190.5, 151.8, 147.6, 147.4, 144.3, 135.6, 131.4, 131.3, 131.0, 129.3, 128.8, 127.8, 127.4, 126.9, 125.6, 124.6, 123.3, 123.2, 122.9. HRMS (EI-magnetic sector) *m/z*: [M]⁺ calcd for C₄₀H₃₀N₂O₂ 570.2307, found 570.2294.

Synthesis of compound 2f. To a mixture of **2c** (0.048 g, 0.23 mmol), **2a** (0.087 g, 0.23 mmol), Pd(OAc)₂ (1.5 mg, 0.0069 mmol), K₂CO₃ (0.32 g, 2.3 mmol), and tetra-*n*-butylammonium bromide (0.15 g, 0.46 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 30 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and ethyl acetate (7:3 v/v) as eluent to afford compound **2f** (0.13 g, 62%) as a greenish-yellow solid. ¹H NMR (400 MHz, (CD₃)₂CO): δ 9.95 (s, 2H), 8.41-8.40 (d, 1H, *J* = 2 Hz), 8.19-8.17 (dd, 1H, *J* = 9 Hz, *J* = 1

Hz), 7.90-7.87 (m, 4H), 7.81-7.79 (dd, 1H, $J = 9$ Hz, $J = 1$ Hz), 7.74-7.70 (d, 2H, $J = 9$ Hz), 7.58-7.55 (m, 2H), 7.51-7.46 (m, 2H), 7.35-7.22 (m, 8H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.5, 151.9, 144.0, 141.4, 140.9, 131.3, 130.3, 128.3, 127.7, 127.4, 127.0, 126.2, 126.0, 124.6, 124.5, 123.2, 122.9, 122.7, 120.3, 119.2, 118.7, 108.7, 108.66, 29.2. HRMS (EI-magnetic sector) m/z : $[\text{M}]^+$ calcd for $\text{C}_{35}\text{H}_{26}\text{N}_2\text{O}_2$ 506.1994, found 506.1981.

Synthesis of compound 2g. To a mixture of **2d** (0.055 g, 0.23 mmol), **2a** (0.087 g, 0.23 mmol), $\text{Pd}(\text{OAc})_2$ (1.5 mg, 0.0069 mmol), K_2CO_3 (0.32 g, 2.3 mmol), and tetra-*n*-butylammonium bromide (0.15 g, 0.46 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 30 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and ethyl acetate (7:3 v/v) as eluent to afford compound **2g** (0.073 g, 60%) as a greenish-yellow solid. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.94 (s, 2H), 7.89-7.85 (dd, 4H, $J = 9$ Hz, $J = 2$ Hz), 7.68-7.64 (dd, 2H, $J = 9$ Hz, $J = 2$ Hz), 7.45-7.43 (m, 2H), 7.28-7.15 (m, 10H), 6.98-6.95 (m, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.5, 151.8, 145.4, 145.3, 144.4, 135.4, 131.7, 131.4, 131.3, 128.0, 127.8, 127.6, 127.5, 127.2, 126.9, 126.2, 125.7, 124.6, 123.8, 122.9, 122.6, 114.1, 114.08, 35.4. HRMS (EI-magnetic sector) m/z : $[\text{M}]^+$ calcd for $\text{C}_{35}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$ 538.1715, found 538.1726.

Synthesis of compound 2j. To a suspension of methyltriphenylphosphonium iodide (1.1 g, 2.6 mmol) in tetrahydrofuran (15 mL) cooled to 0 °C was added potassium *tert*-butoxide (0.32 g, 2.9 mmol). The reaction mixture was stirred at 0 °C for 20 min. The aldehyde **2e** (0.69 g, 1.2 mmol) was dissolved in THF (10 mL) and added to the reaction mixture and stirred at room temperature for 36 h before being poured into 50 mL of deionized water and extracted with dichloromethane. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to give compound **2j** (0.49 g, 72%) as a greenish-yellow solid. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.54-7.50 (m, 4H), 7.44-7.40 (d, 4H, $J = 9$ Hz), 7.34-7.30 (m, 4H), 7.14-7.00 (m, 16H), 6.76-6.69 (m, 2H), 5.75-5.71 (dd, 2H,), 5.18-5.16 (dd, 2H); ^{13}C NMR

(100 MHz, CDCl₃): δ 147.6, 147.1, 146.9, 146.5, 136.1, 132.4, 132.36, 131.8, 129.2, 127.2, 127.15, 127.12, 126.8, 126.4, 124.4, 124.16, 124.1, 123.7, 122.9, 112.4. HRMS (EI-magnetic sector) m/z : [M]⁺ calcd for C₄₂H₃₄N₂ 566.2722, found 566.2703.

Synthesis of compound 2k. To a suspension of methyltriphenylphosphonium iodide (1.1 g, 2.6 mmol) in tetrahydrofuran (15 mL) cooled to 0 °C was added potassium *tert*-butoxide (0.32 g, 2.99 mmol). The reaction mixture was stirred at 0 °C for 20 min. The aldehyde **2f** (0.61 g, 1.2 mmol) was dissolved in THF (10 mL) and added to the reaction mixture and stirred at room temperature for 36 h before being poured into 50 mL of deionized water and extracted with dichloromethane. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to give compound **2k** (0.42 g, 70%) as a greenish-yellow solid. ¹H NMR (400 MHz, (CD₃)₂CO): δ 8.36 (m, 1H), 8.19-8.16 (m, 1H), 7.77-7.75 (m, 1H), 7.59-7.35 (m, 10H), 7.27-7.20 (m, 2H), 7.10-7.04 (m, 6H), 6.77-6.70 (dd, 2H, J = 18 Hz, J = 12 Hz), 5.75-5.71 (d, 2H, J = 18 Hz), 5.19-5.16 (d, 2H, J = 12 Hz), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.0, 146.2, 141.4, 140.6, 136.2, 132.9, 132.3, 128.8, 128.4, 127.1, 127.06, 125.8, 125.4, 124.4, 124.37, 124.0, 123.1, 122.8, 120.4, 119.1, 118.4, 112.4, 108.6, 108.57, 29.1. HRMS (EI-magnetic sector) m/z : [M]⁺ calcd for C₃₇H₃₀N₂ 502.2409, found 502.2404.

Synthesis of compound 2l. To a suspension of methyltriphenylphosphonium iodide (1.1 g, 2.6 mmol) in tetrahydrofuran (15 mL) cooled to 0 °C was added potassium *tert*-butoxide (0.32 g, 2.9 mmol). The reaction mixture was stirred at 0 °C for 20 min. The aldehyde **2g** (0.65 g, 1.2 mmol) was dissolved in THF (10 mL) and added to the reaction mixture and stirred at room temperature for 36 h before being poured into 50 mL of deionized water and extracted with dichloromethane. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to give compound **2l** (0.40 g, 62%) as a greenish-yellow solid. ¹H NMR (400 MHz, (CD₃)₂CO): δ 7.53-7.50 (d, 2H, J = 9 Hz), 7.44-7.39 (m, 6H), 7.24-7.19 (m, 1H), 7.17-7.14 (m, 1H), 7.11 (d, 2H, J = 10 Hz), 7.06-7.03 (m, 6H), 6.98-6.94 (m, 3H), 6.76-

6.69 (dd, 2H, $J = 18$ Hz, $J = 12$ Hz), 5.75-5.71 (d, 2H, $J = 18$ Hz), 5.18-5.15 (d, 2H, $J = 12$ Hz), 3.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.9, 146.6, 145.5, 145.0, 136.1, 132.4, 132.3, 132.2, 132.18, 127.5, 127.2, 127.18, 127.1, 126.5, 126.1, 125.9, 124.5, 124.1, 124.08, 123.7, 123.0, 122.5, 114.1, 112.4, 35.4. HRMS (EI-magnetic sector) m/z : $[\text{M}]^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{F}_5\text{NS}$ 534.2130, found 534.2143.

Synthesis of compound D1. To a mixture of 4-bromophenylsulfur pentafluoride (0.13 g, 0.46 mmol), **2h** (0.068 g, 0.23 mmol), $\text{Pd}(\text{OAc})_2$ (3.0 mg, 0.013 mmol), K_2CO_3 (0.64 g, 4.6 mmol), and tetra-*n*-butylammonium bromide (0.30 g, 0.92 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 16 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to afford compound **D1** (0.083 g, 52%) as a yellow solid. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.87–7.84 (m, 4H), 7.80 (d, 4H, $J = 9$ Hz), 7.62–7.59 (m, 4H), 7.44 (d, 2H, $J = 16$ Hz), 7.39–7.35 (m, 2H), 7.26 (d, 2H, $J = 16$ Hz), 7.16–7.13 (m, 3H), 7.11–7.07 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.3 (apparent t, $J = 17.5$ Hz), 147.6, 146.9, 140.8, 131.3, 130.9, 129.5, 127.8, 126.3 (quintet, $J = 4.4$ Hz), 126.1, 125.2, 124.8, 124.0, 123.8; ^{19}F NMR (282 MHz, CDCl_3): δ 85.2 (quintet, 1F, $J = 148.8$ Hz), 63.13 (d, 4F, $J = 148.8$ Hz). HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{34}\text{H}_{25}\text{F}_{10}\text{NS}_2$ 701.1269, found 701.1259.

Synthesis of compound D2. To a mixture of 4-bromophenylsulfur pentafluoride (0.20 g, 0.69 mmol), **2i** (0.074 g, 0.23 mmol), $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.020 mmol), K_2CO_3 (0.95 g, 6.9 mmol), and tetra-*n*-butylammonium bromide (0.44 g, 1.4 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 24 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to afford compound **D2** (0.12 g, 58%) as a yellow solid. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.88-7.85 (m, 6H), 7.82-7.80 (d, 6H, $J = 9$ Hz), 7.66-7.63 (m, 6H), 7.46 (d, 3H, $J = 16$ Hz), 7.30 (d, 3H, $J = 16$ Hz), 7.17-7.13 (m, 6H); ^{13}C

NMR (100 MHz, CDCl₃): δ 152.5 (apparent t, J = 18.2 Hz), 147.1, 140.7, 131.6, 131.1, 127.9, 126.4 (quintet, J = 4.4 Hz), 126.1, 125.2, 124.3; ¹⁹F NMR (282 MHz, CDCl₃): δ 85.08 (quintet, 1F, J = 148.8 Hz), 63.11 (d, 4F, J = 148.8 Hz). HRMS (ESI-TOF) m/z : [M]⁺ calcd for C₄₂H₃₀F₁₅NS₃ 929.1301, found 929.1290.

Synthesis of compound D3. To a mixture of 4-bromophenylsulfur pentafluoride (0.13 g, 0.46 mmol), **2j** (0.13 g, 0.23 mmol), Pd(OAc)₂ (3.0 mg, 0.013 mmol), K₂CO₃ (0.64 g, 4.6 mmol), and tetra-*n*-butylammonium bromide (0.30 g, 0.92 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 30 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to afford compound **D3** (0.16 g, 72%) as a yellow solid. ¹H NMR (400 MHz, (CD₃)₂CO): δ 7.88–7.84 (m, 4H), 7.81 (d, 4H, J = 9 Hz), 7.65–7.61 (m, 4H), 7.59–7.56 (m, 2H), 7.54–7.50 (m, 2H), 7.45 (d, 2H, J = 16 Hz), 7.35–7.26 (m, 7H), 7.18–7.17 (m, 2H), 7.14–7.05 (m, 12H), 7.03–7.00 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 152.4 (apparent t, J = 16 Hz), 147.5, 147.4, 147.3, 145.9, 140.8, 133.2, 131.5, 131.2, 131.1, 129.3, 127.9, 127.4, 127.3, 127.2, 126.3 (quintet, J = 3.7 Hz), 126.2, 126.1, 125.0, 124.9, 124.5, 124.0, 123.6, 123.0; ¹⁹F NMR (282 MHz, CDCl₃): δ 85.14 (quintet, 1F, J = 148.8 Hz), 63.13 (d, 4F, J = 148.8 Hz). HRMS (ESI-TOF) m/z : [M]⁺ calcd for C₅₄H₄₀F₁₀N₂S₂ 970.2473, found 970.2491.

Synthesis of compound D4. To a mixture of 4-bromophenylsulfur pentafluoride (0.13 g, 0.46 mmol), **2k** (0.12 g, 0.23 mmol), Pd(OAc)₂ (3.0 mg, 0.014 mmol), K₂CO₃ (0.64 g, 4.6 mmol), and tetra-*n*-butylammonium bromide (0.30 g, 0.92 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 36 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to afford compound **D4** (0.14 g, 67%) as a yellow solid. ¹H NMR (400 MHz, (CD₃)₂CO): δ 8.38 (m, 1H), 8.18 (d, 1H, J = 8 Hz), 7.88–7.77 (m, 9H), 7.64–7.62 (m, 6H), 7.57–7.54 (m, 2H), 7.50–7.46 (m, 2H), 7.41 (d, 2H, J = 16 Hz), 7.31–

7.21 (m, 4H), 7.16-7.13 (m, 6H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.3 (apparent t, $J = 18.2$ Hz), 147.4, 145.7, 141.4, 140.8, 140.7, 133.7, 131.2, 131.1, 129.0, 128.6, 127.9, 127.2, 126.3 (quintet, $J = 4.4$ Hz), 126.1, 125.9, 125.2, 125.1, 124.9, 124.4, 123.9, 123.2, 122.8, 120.3, 119.1, 118.5, 108.7, 108.6, 29.1; ^{19}F NMR (282 MHz, CDCl_3): δ 85.18 (quintet, 1F, $J = 148.8$ Hz), 63.15 (d, 4F, $J = 148.8$ Hz). HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd. for $\text{C}_{49}\text{H}_{36}\text{F}_{10}\text{N}_2\text{S}_2$ 906.2160, found 906.2164.

Synthesis of compound D5. To a mixture of 4-bromophenylsulfur pentafluoride (0.13 g, 0.46 mmol), **21** (0.12 g, 0.23 mmol), $\text{Pd}(\text{OAc})_2$ (3.0 mg, 0.013 mmol), K_2CO_3 (0.64 g, 4.6 mmol), and tetra-*n*-butylammonium bromide (0.30 g, 0.92 mmol) was added anhydrous DMF (10 mL). The reaction mixture was stirred at 110 °C for 40 h before being poured into 50 mL of water and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:2 v/v) as eluent to afford compound **D5** (0.12 g, 54%) as a yellow solid. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.87–7.85 (m, 4H), 7.81 (d, 4H, $J = 9$ Hz), 7.64–7.61 (m, 4H), 7.58–7.56 (m, 2H), 7.47–7.41 (m, 4H), 7.28 (d, 2H, $J = 16$ Hz), 7.24–7.09 (m, 10H), 6.98–6.95 (m, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.4 (apparent t, $J = 16.4$ Hz), 147.3, 146.0, 145.4, 145.1, 140.8, 133.0, 132.0, 131.2, 131.16, 127.9, 127.5, 127.4, 127.2, 126.6, 126.3 (quintet, $J = 4.4$ Hz), 126.1, 126.0, 125.0, 124.9, 124.5, 124.0, 123.7, 122.9, 122.5, 114.1, 35.4; ^{19}F NMR (282 MHz, CDCl_3): δ 85.14 (quintet, 1F, $J = 148.8$ Hz), 63.13 (d, 4F, $J = 148.8$ Hz). HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd. for $\text{C}_{49}\text{H}_{36}\text{F}_{10}\text{N}_2\text{S}_3$ 938.1881, found 938.1866.

2.5 References

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Chapter 3. SF₅-Containing Polymers as Electrets in Nonvolatile OFET Memory Devices

3.1 Introduction

Organic nonvolatile memory (ONVM) devices have gained much attention in recent years owing to the attractive possibility of fabricating low-cost and lightweight memory devices on flexible substrates such as plastic and paper.¹⁻⁷ Among the different types of memory devices, the ones based on organic field-effect transistor (OFET) architectures are of particular interest by their non-destructive read-outs and amenability to integrated circuit design.⁸⁻¹² In essence, an OFET-based memory device possesses all the same components as a standard three-terminal OFET but also includes an additional charge storage layer that lies between the gate contact and the organic semiconductor (e.g., pentacene) channel (Figure 3.1). There are three main classes of OFET-based ONVM devices, namely: (i) polymer electret-based,¹³⁻³⁰ (ii) floating-gate memories,³¹⁻³⁸ and (iii) ferroelectric OFET memories.³⁹⁻⁴¹

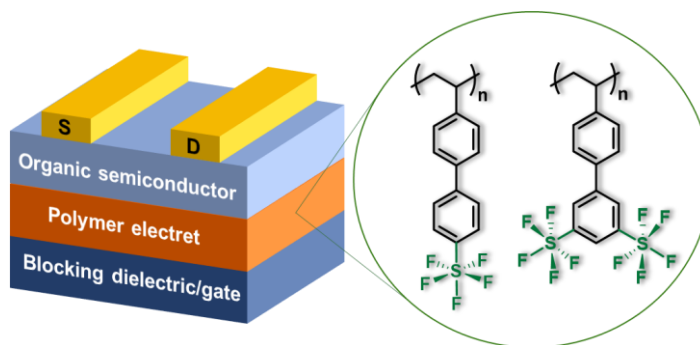


Figure 3. 1 Schematic configuration of an OFET memory device and molecular structures of charge storage polymer electrets.

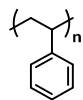
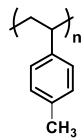
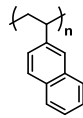
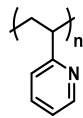
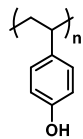
In this work, we focus exclusively on the first category of ONVM devices in which the charge storage layer is composed of a dielectric polymer that serves the function of reversibly trapping electrostatic charges, thereby setting up a quasi-permanent electric field. These trapped charges modulate the channel conductance within the organic semiconductor layer upon the application of a programming (PGM) or an erasing (ERS) gate voltage (V_g). Three key figures of merit relevant to such devices are the memory

window (MW), memory ratio, and retention time. The first important parameter refers to the V_g shift between PGM and ERS states, which is a measure of the level of information storage possible. The second parameter is the difference in drain current (I_d) between the PGM and ERS states at fixed reading voltage bias (V_{read}), which is typically held at ~ 0 V for non-destructive readout purposes. Third, the retention time measures the ability of the OFET memory device to preserve the PGM and ERS states without the trapped charges dissipating via various leakage pathways. A minimum of 10,000 seconds is typically required for a reliable function. The working principle of these OFET memory devices hinges on the charge storage ability of the polymer electret, which is in turn intimately dependent on the molecular structure of the polymer dielectric. Regarding pendent polymer electret systems (Table 3.1), it has previously been shown that the hydrophobic/hydrophilic nature of the pendent sidechains exerts a profound effect on the MW and retention time of the memory devices. More precisely, both parameters have been found to be inversely proportional to the hydrophilicity (water droplet contact angle) and polarity of the pendent moieties.¹⁴ For example, when hydrophilic and highly polar OH groups were present, as in poly(vinyl alcohol) (Table 3.1, NO.6), the MW was essentially non-existent.^{13, 14} Conversely, when large hydrophobic moieties such as naphthyl groups occupied the pendent positions, the resulting MWs and retention times were both improved. The inferior performance observed in these polar styrenic polymers is mainly due to the rapid charge dissipation through the conductive pathways formed from the moisture adsorption and ion solvation by the polar hydrophilic moieties.¹¹

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pathways formed from the moisture adsorption and ion solvation by the polar hydrophilic moieties.¹¹

Table 3. 1 Examples of pendent polymer electrets that have been studied in memory devices based on pentacene field-effect transistor.¹⁴

NO.	Electret	Water droplet contact angle (°)	MW (V)	Retention time (10 ⁵ s)	Memory ratio
1		100	~22	5.2	10 ⁵
2		110	~24	2.1	10 ⁵
3		115	~28	3.4	10 ⁶
4		70	~21	0.42	10 ⁵
5		55	~17	0.24	10 ⁵
6		15	Negligible	N/A	N/A

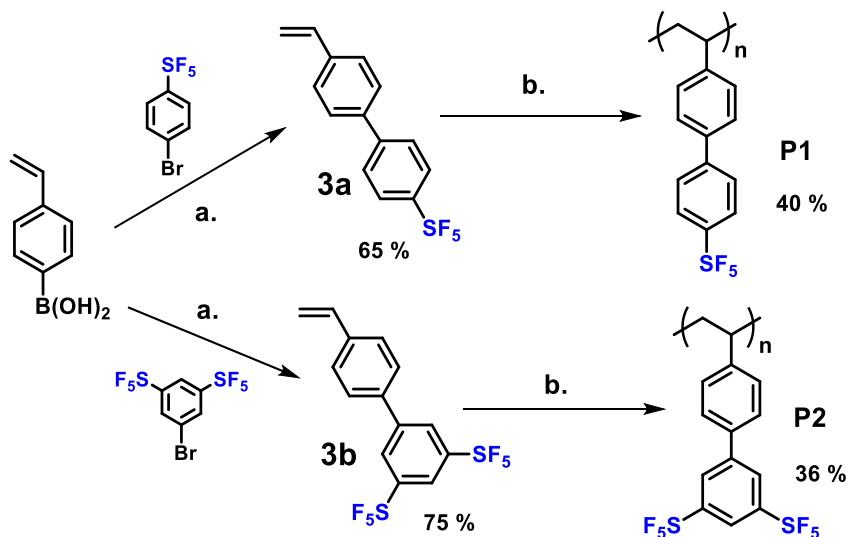
In the present study, I sought to investigate two styrenic polymers that feature the somewhat paradoxical SF₅ group, which is strongly dipolar yet highly hydrophobic.^{42, 43} The marked hydrophobicity of this unique functional group has been frequently employed in medicinal chemistry as a lipophilic handle to improve drug pharmacokinetics.^{44, 45} In

materials chemistry, on the other hand, the highly dipolar nature of the SF₅ group has been exploited in liquid crystalline molecules that respond strongly to electric fields.^{46, 47} It was also found that liquid crystal molecules with SF₅ substituents, unlike those molecules bearing CN groups, did not solvate and mobilize ionic impurities.⁴⁸ As such, the employment of SF₅ substituents in polymer electrets may be beneficial for minimizing conductive channels that lead to undesirable rapid charge dissipation. Herein, I report the synthesis and characterization of two styrene-type polymers containing pendent pentafluorosulfanylated biphenyl groups (Scheme 3.1) and study the effects on device characteristics upon their incorporation into OFET-based nonvolatile memory devices. To the best of our knowledge, this study represents the very first application of SF₅-containing organic polymers in memory device applications.

3.2 Results and Discussion

Synthesis and Characterization. The new polymers **P1** and **P2** were synthesized by free radical vinyl polymerization of monomers **3a** and **3b**, respectively. Both monomers were derived from the commercially available starting material, 4-vinylphenylboronic acid. Suzuki coupling of 4-vinylphenylboronic acid with 4-(pentafluorosulfanyl)-bromobenzene and bis-3,5-(pentafluorosulfanyl)-bromobenzene afforded the biphenyl molecules **3a** and **3b**, respectively (Scheme 3.1). The isolated yields of the target monomers resulting from the palladium-catalyzed cross-couplings were generally high, ranging from 65-75 %. Aside from the excellent chemical compatibility exhibited by SF₅, the high electronegativity of the functional group also likely played a favourable role in the oxidative addition step of the cross-coupling mechanism. For the polymerization step, we had initially attempted the anionic polymerization of **3a** and **3b** without much success. This was likely due to the incompatibility of the highly reducing alkyllithium initiators with the SF₅ group, with which undesirable single-electron transfer could conceivably occur. Our focus then shifted to the use of free radical vinyl polymerizations, with azoisobutyronitrile (AIBN) and benzoyl peroxide being the initiators of choice. Experimentally, I found that the use of the latter initiator in benzene (solvent) yielded the best results, successfully affording polymers **P1** and **P2** in good purity following post-reaction workup. Structural confirmation of the two polymers was provided by ¹H, ¹³C, and ¹⁹F NMR spectroscopy, while their molecular

weights were determined by gel permeation chromatography (GPC). The number-average molecular weights of **P1** and **P2** as determined by GPC were found to be 10.6 and 14.8 kDa, respectively, while their respective dispersities ($\bar{D}$) were relatively narrow at 1.45 and 1.22 (Table 3.2).



Scheme 3. 1 Synthesis of pentafluorosulfanylated polymers **P1** and **P2**. Reagents and reaction conditions: a) $\text{Pd(PPh}_3)_4$ cat., Na_2CO_3 , H_2O , PhMe , 100°C , 18 h; b) $(\text{PhCO})_2\text{O}_2$ initiator, benzene, reflux, 4 h.

Table 3. 2 Polymerization results and physical properties of **P1** and **P2**.

Polymer	M_n^a [kDa]	M_w^a [kDa]	$\bar{D}$	T_d [$^\circ\text{C}$]	T_g [$^\circ\text{C}$]	λ_{max} (solution) ^b [nm]	λ_{max} (film) ^c [nm]	E_g^d [eV]
P1	14.8	21.5	1.45	302	199.4	265	265	4.08
P2	10.6	12.9	1.22	334	190.2	262	262	4.12

^a Measured by gel permeation chromatography calibrated using polystyrene standards.

^b In dilute THF solution. ^c Spin-cast film on quartz slide. ^d Optical bandgaps calculated from the absorption edge.

Photophysical Properties. Polymers **P1** and **P2** were also studied by UV-vis and fluorescence spectroscopy to elucidate their photophysical properties (data summarized in

Table 3.2). The polymers showed peak absorptions at around 260 nm and were both weakly fluorescent despite being nonconjugated systems. Their estimated optical bandgaps based on the absorption edges were approximately 4.0 eV. In the thin-film state, the UV-vis absorption profile of both polymers remained essentially unchanged compared to that of the solution phase (Figure 3.2a-b). Specifically, in dilute THF solutions, polymers **P1** and **P2** showed absorption maxima at 265 and 262 nm, respectively, which is primarily due to the aromatic side-chain chromophores. The polymer film UV-vis spectra were nearly identical, indicating the absence of aggregation effects that would have bathochromically shifted the absorption profiles. This lack of aggregation even in the solid-state suggested that the chains of both polymers did not pack closely and efficiently, which could be due to diminished interchain interactions resulting from the presence of sterically bulky SF₅ substituents. Regarding the small degree of photoluminescence that was observed in both polymers, this could be attributed to intrachain excimer formation between the pendent aromatic moieties, a phenomenon that has also been previously observed in polystyrene.⁴⁹ Here, **P1** and **P2** exhibited emission maxima (λ_{em}) at 382 and 355 nm, respectively (Figure 3.3).

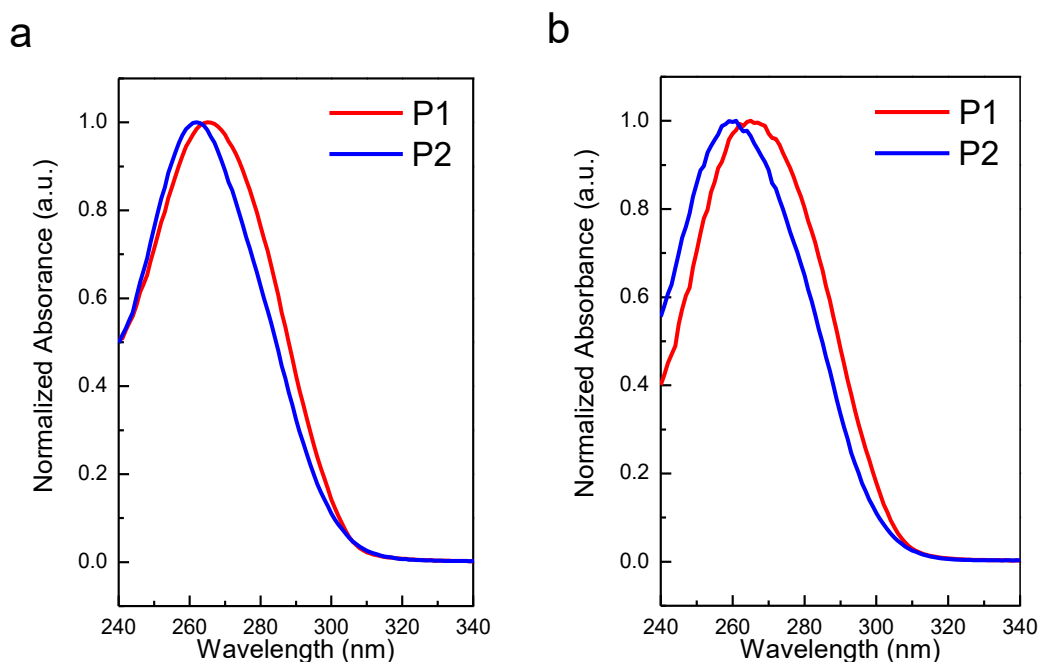


Figure 3. 2 Absorption spectra of **P1** and **P2** in a) THF solutions and b) thin-film states.

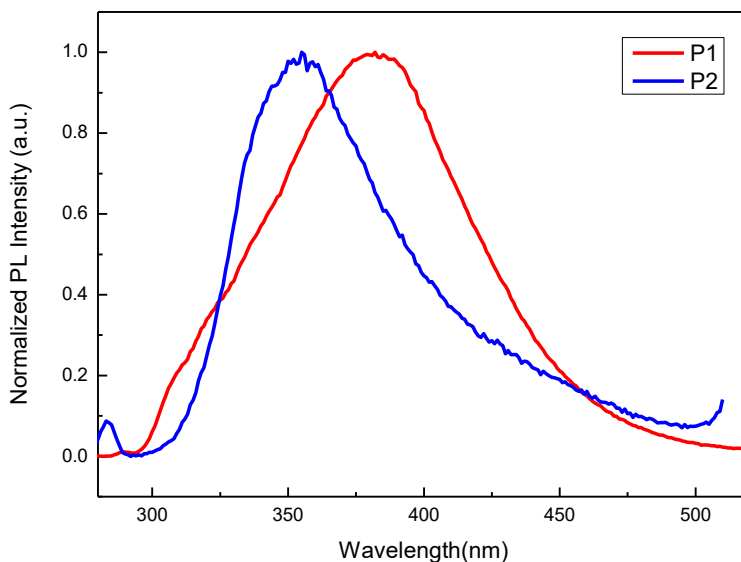


Figure 3. 3 Fluorescence spectra of **P1** and **P2** in chloroform.

Density Functional Theory (DFT) Studies. Molecular modelling was carried out on Gaussian09 at the B3LYP level of theory to estimate the dipole moments of model structures resembling the repeat units of polymers **P1** and **P2** (see Appendix for details). Each repeat unit of **P1** features a biphenyl sidechain with a strongly electron-withdrawing SF₅ group in a para- configuration, while the pendent sidechain of polymer **P2** features two SF₅ moieties in a mutually meta- relationship. Based on DFT calculations, the dipole moments of the **P1** and **P2** model repeat units were estimated to be 5.31 D and 5.45 D, respectively.

Thermal Stability and Surface Characterizations. The thermal stabilities of the polymers were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA indicated that both polymers possess excellent thermal stability in air, with decomposition temperatures (T_d , corresponding to 5% weight loss) measured at 302 °C and 334 °C for **P1** and **P2**, respectively (Figure 3.4a-b). Indeed, previous studies of SF₅-containing compounds have shown them to exhibit robust thermal stabilities.^{45, 50} Subsequent DSC characterization of polymers **P1** and **P2** showed their respective glass transition temperatures (T_g) to be 199.4 °C and 190.2 °C, respectively (Figure 3.4c-d), rendering them amenable to operating at relatively high device temperatures.

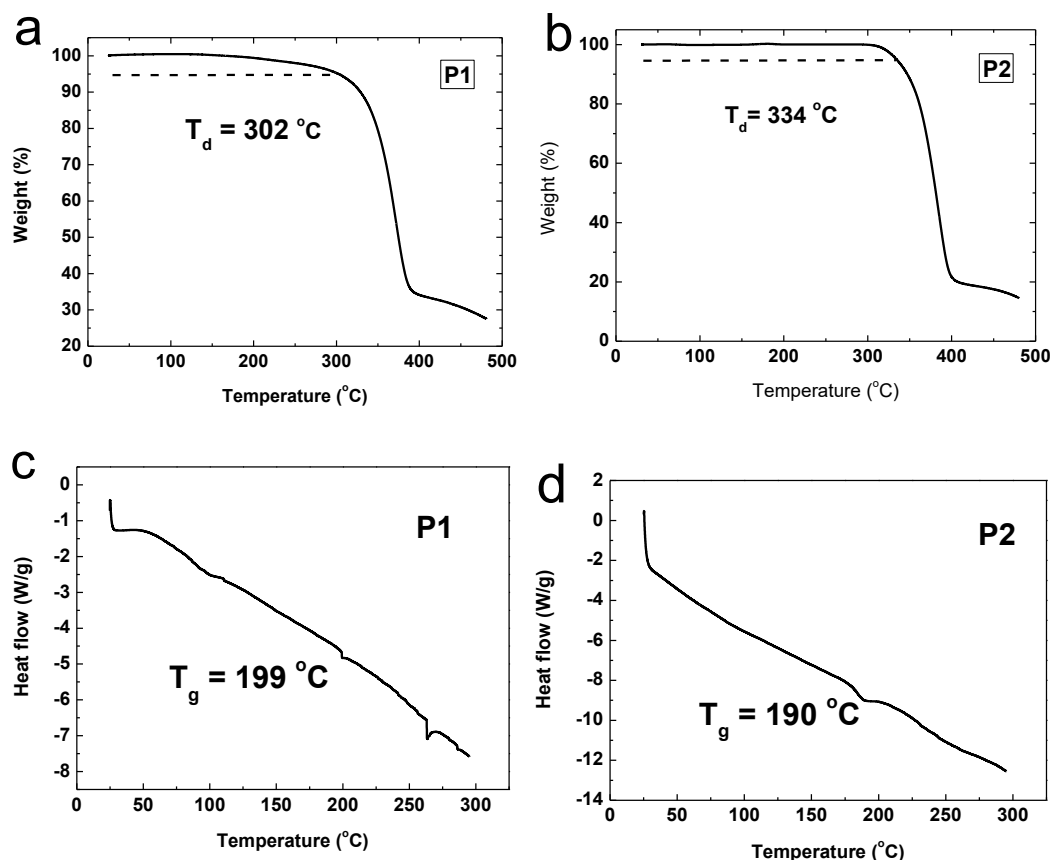


Figure 3. 4 Thermogravimetric analysis (TGA) of a) **P1** and b) **P2**. Differential scanning calorimetry (DSC) curves of c) **P1** and d) **P2**.

The surface topographies and properties of the charge-storage polymer electret films were investigated by atomic force microscopy (AFM) and water contact angle measurements, as shown in Figure 3.5. When spin-cast from polymer solutions onto bare SiO_2 substrates, both electret films were continuous and relatively uniform (root-mean-square roughness (R_{RMS}) ~ 3 nm) without notable aggregated clusters (Figure 3.5c-d). Photographs of the water droplet on both the **P1** and **P2** films (Figure 3.5a-b) indicated that the surfaces were markedly hydrophobic (water contact angle of $\sim 101^{\circ}$), likely due to the hydrophobic/lipophilic SF_5 groups on the polymer side-chains. The lipophilic nature of the surfaces facilitated subsequent deposition of the upper pentacene layer.⁵¹ The morphology of the pentacene layer was also characterized by AFM topographic images (Figure 3.5e-f). Interestingly, deposition of pentacene on **P1** and **P2** gave different morphologies of the pentacene layers (Figure 3.5e-f), with a larger grain size of pentacene on the **P2** film. The difference in grain size of pentacene was most likely caused by the different surface

energies of **P1** and **P2**,⁵² which could result in different charge mobility of the pentacene layer.^{17, 53, 54} However, there was no clear evidence that the altered charge mobility depending on the different grain sizes of pentacene had an effect on the memory characteristics.^{17, 55, 56} Hence, given the negligible differences in adsorption, thin-film morphologies, and surface hydrophobicity of **P1** and **P2**, any observed differences in their charge-trapping abilities and memory performance could thus be mainly attributed to intrinsic differences in their molecular-level parameters such as localized polarities, free volumes, and/or relative energy levels.

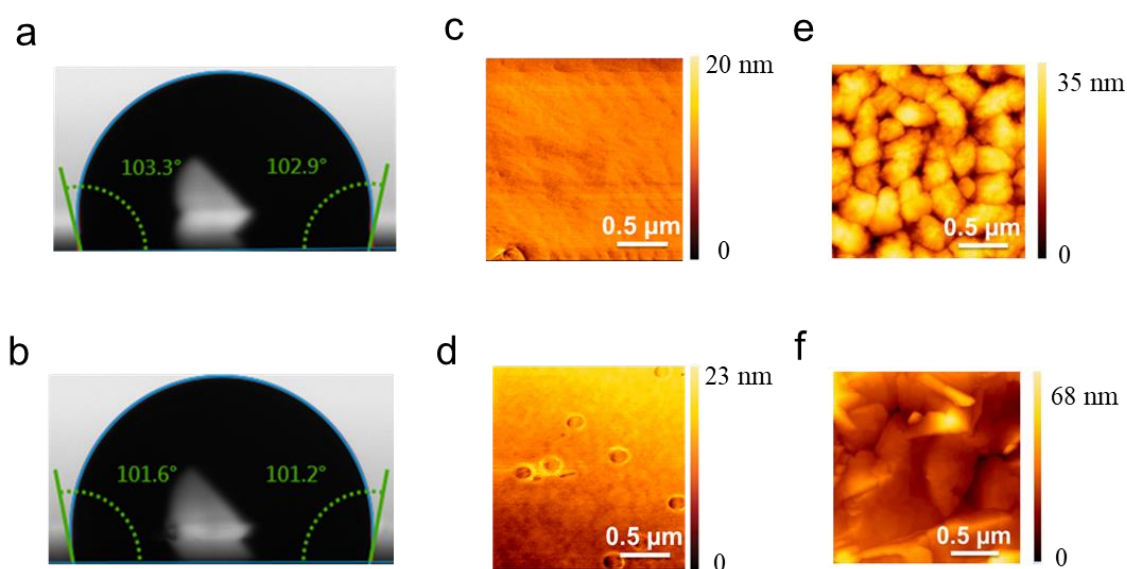


Figure 3. 5 Images of water droplet contact angles of a) **P1** and b) **P2** films. AFM topologies of c) **P1** and d) **P2** on the top of SiO₂ surface. AFM topographic images of pentacene on e) **P1** and f) **P2** surface.

OFET Memory Characteristics. To investigate the performance of the ONVM, pentacene-based OFET memory devices with **P1** and **P2** electret layers were fabricated and studied. Based on the thickness of the pentacene layer, the p-type channel of the OFET would likely be localized in the pentacene region directly above the electret-pentacene interface where induction occurs. The typical output characteristics of the **P1**- and **P2**-based OFET devices with respect to different V_g biases are shown in Figure 3.6. The conductance of the active pentacene channel increased monotonically as V_g was increased

from 0 to -100 V, thus demonstrating p-type behaviour. I_d values of $\sim 10^{-4}$ A in the saturated region were measured in both OFET devices.

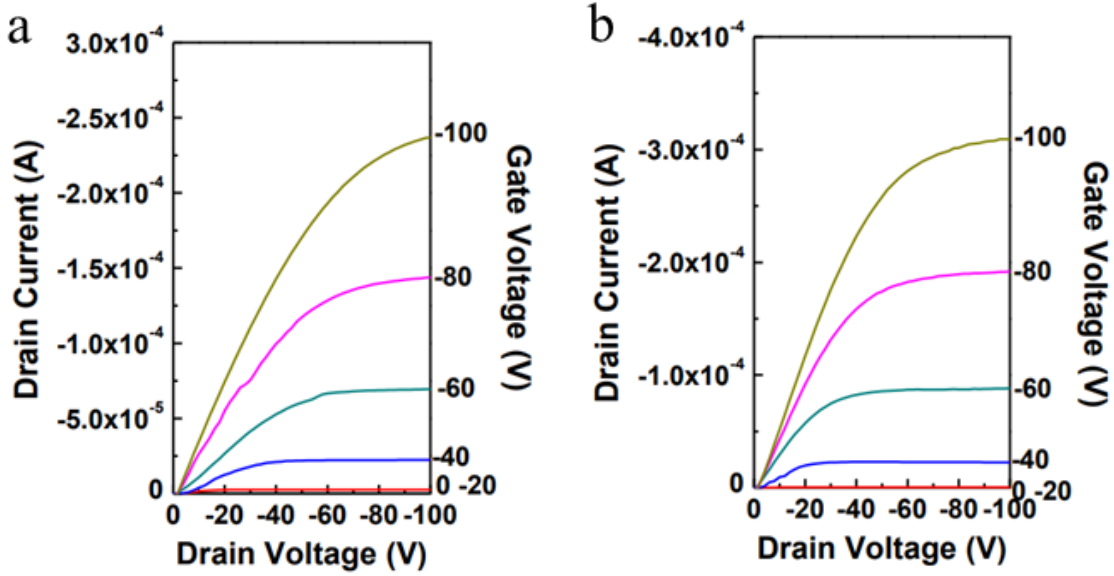


Figure 3. 6 Output characteristics of OEFT memories based on a) **P1** and b) **P2**.

Transfer characteristics curves were conducted in sweeps of V_g at a constant drain voltage (V_d) of -80 V under dark conditions (Figure 3.7). After the initial sweep in the transfer curve (black square/line), a V_g of -120 V was applied to the device for 10 s. Negligible shifts in the transfer curves could be observed with both OFET memory devices (cf. red curves in Figure 3.7a-b). Therefore, almost negligible charging/trapping of the charge carriers — especially for holes — occurred at the semiconductor-electret interface. The subsequent PGM/ERS operations were performed by applying a V_g of 120 V/-120 V for 10 s and the transfer curves were swept from 80 V/30 V to -80 V. Upon application of the positive V_g , the OFET memories exhibited a positive shift of transfer curves (Figure 3.7a-b, blue curves) relative to the initial ones. This is referred to as electrical PGM. The stored holes migrating from the pentacene layer to the polymer electret layer screen the gate and modulate the channel conductance. Following that, an intensive negative V_g causes a negative shift of the transfer curve (back to the initial curve) from the electrical ERS state (Figure 3.7a-b, orange curves), suggesting that the stored holes could be released under a reversed V_g bias. It should be noted here that the MW is defined as the magnitude of the threshold voltage (V_{th}) shift between the transfer curves following the application of

PGM/ERS bias pulses. The MWs obtained with the OFET memory devices based on the **P1** and **P2** electrets (Figure 3.7) were 31.4 ± 2.7 and 44.4 ± 2.6 V, respectively. Notably, the broadened MW of the **P2**-based OFET could be attributed to a larger number of trapped electrons during the memory operation, which will be discussed further below.

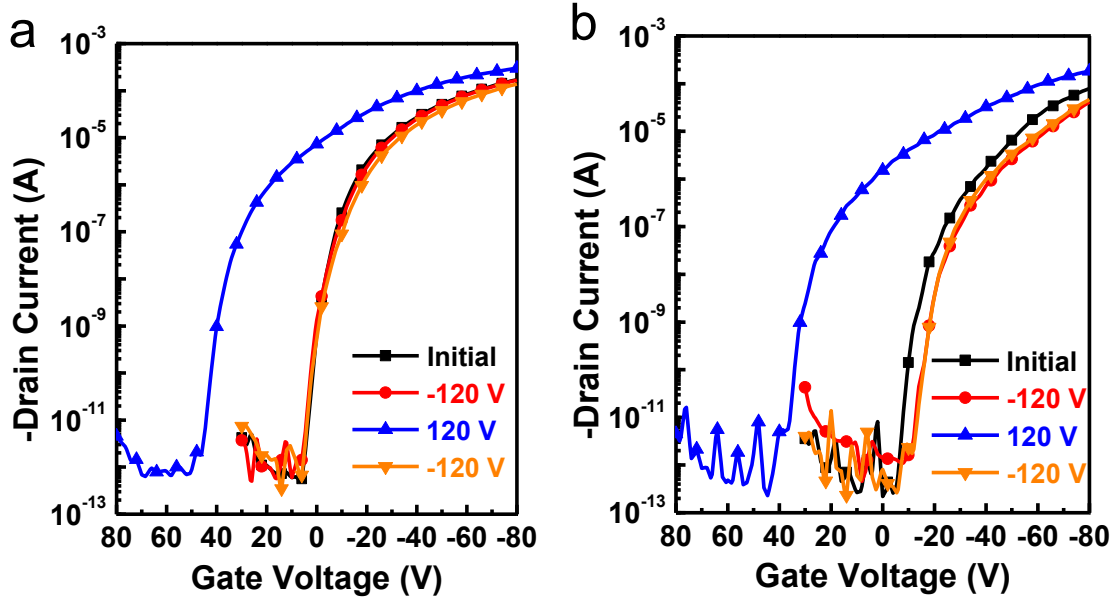


Figure 3. 7 Transfer characteristics of OFET memories based on a) **P1** and b) **P2** electrets under initial, PGM ($V_g = 120$ V, 10 s), and ERS processes ($V_g = -120$ V, 10 s), with $V_d = -80$ V in all measurements.

Data retention capability is another important factor for nonvolatile memory applications since it represents the data storage lifetime in the memory devices. Figure 3.8 shows that the **P1**- and **P2**-based OFET memories were programmed/erased by applying V_g of 120 V/-120 V with a pulse width of 10 s at $V_d = -80$ V, achieving perfectly trapped and detrapped states in the electret layers, and the I_d was recorded at a V_{read} of 5 V over a certain period of time. Both the PGM and ERS states were well-formed in the **P1** and **P2**-based OFETs over 10,000 s, and the extracted I_d at both memory states showed a memory ratio of $\sim 10^6$, indicating good retention characteristics. Slight I_d decay in the PGM state upon continuous reading, especially for the **P2**-based memory device, was probably due to the sustained application of low V_g bias or the low energy barrier/localized defect states

that cause the trapped charges to flow back to the semiconductor channel via a leakage path.^{57, 58}

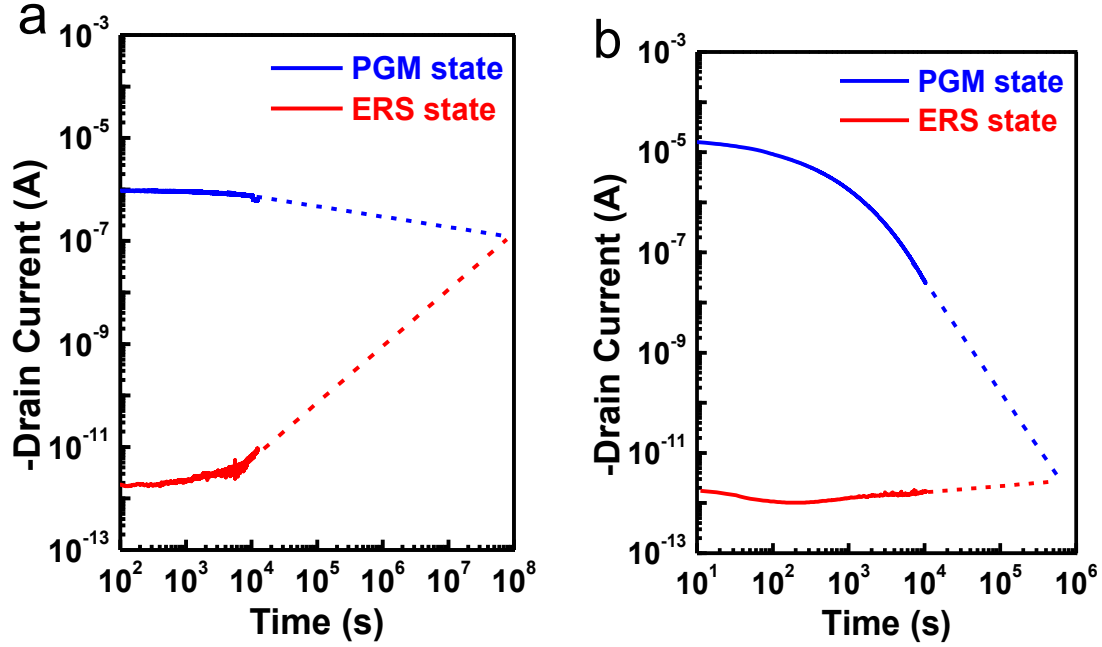


Figure 3. 8 Data retention characteristics of OFET memories based on a) **P1** and b) **P2** electrets at the reading voltage of $V_g = -5$ V; $V_d = -80$ V, after PGM ($V_g = 120$ V, 10 s), and after ERS ($V_g = -120$ V, 10 s).

Additionally, another important ONVM parameter is its reliability over repeated PGM and ERS steps, which is a measure of data storage stability for practical device applications. The dynamic switching ability was evaluated by a program/read/erase/read (PRER) endurance test. Figure 3.9 shows the process conditions of repeatable cycle tests in which a cycle consists of sequential PGM (V_g of 120 V), reading (5 V), ERS (-120 V), and reading (5 V). As shown in Figure 3.10, highly reproducible memory behaviour and well-separated PGM/ERS states over 100 repetition cycles could be observed, and the MWs for both **P1** and **P2** electret-based devices were preserved without visible degradation, which points toward their reliability for nonvolatile memory applications.

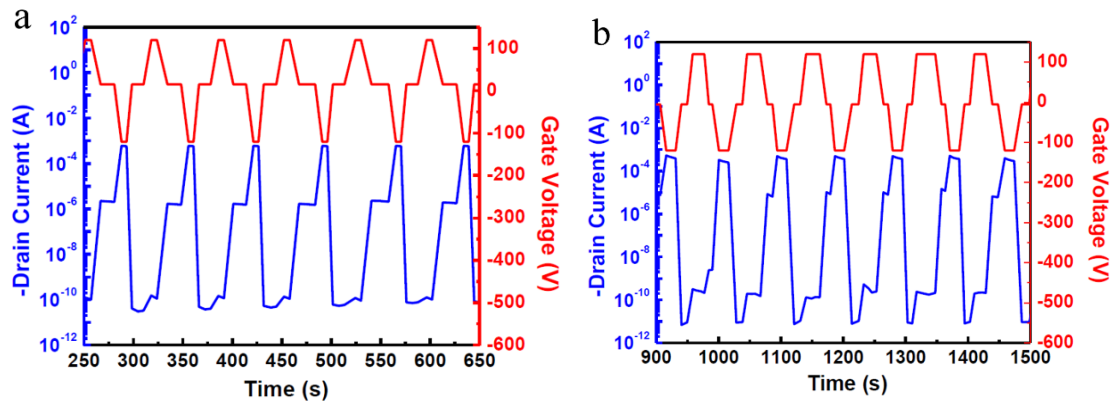


Figure 3. 9 I_d response for the repeated pulse bias of PRER operations of OFET memories based on a) **P1** and b) **P2** electrets.

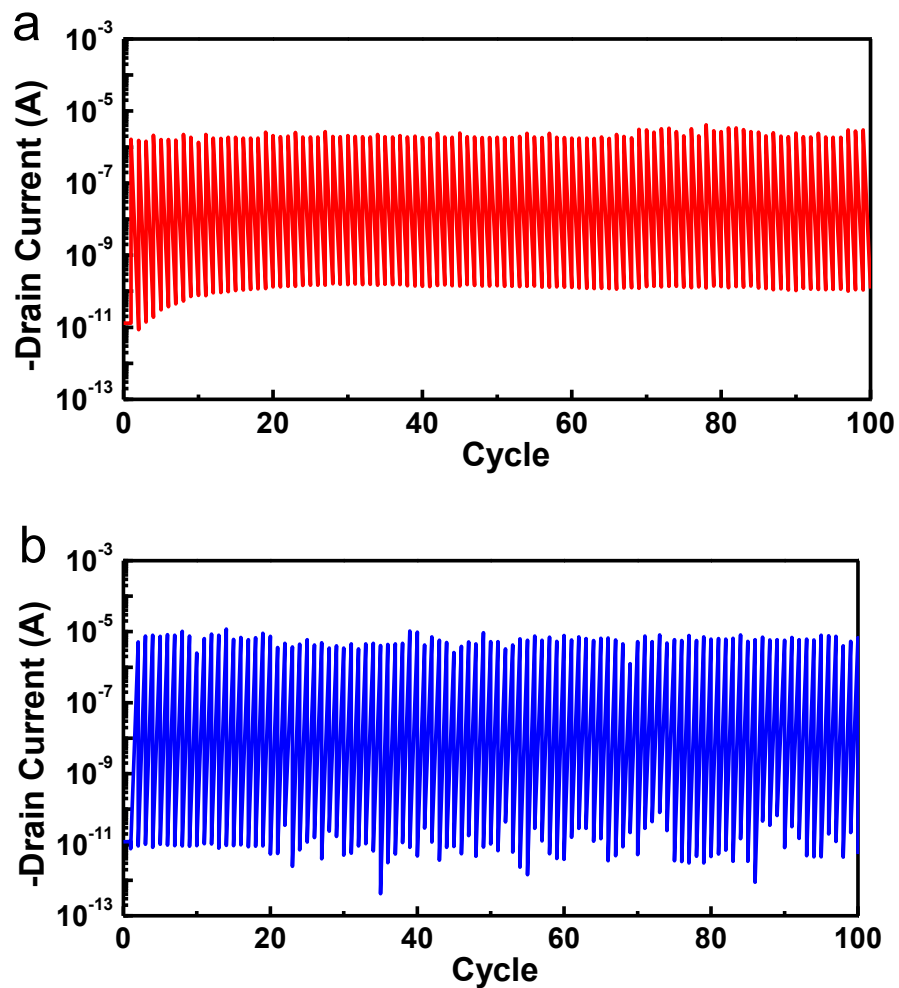


Figure 3. 10 Cyclic endurance characteristics of OFET memories based on a) **P1** and b) **P2** electrets for PGM/ERS repeating cycles.

The schematic band diagrams of heterostructured ONVMs illustrating the PGM/ERS operation states are given in Figure 3.11 to explain the charge-transfer process and memory operation mechanism. In polymer electret-based memories, information is stored by injecting/removing charges through Fowler-Nordheim tunnelling at the gate field;⁵⁹ therefore, the OFET requires a larger/smaller voltage to turn-ON the device, termed the PGM/ERS operation, respectively. The digital “0” and “1” memory status is determined by applying V_{read} to the gate between ERS and PGM states to read the corresponding I_d . In our case, the charge transport toward the SiO₂ blocking dielectric was assumed to be restricted since the thermally-deposited SiO₂ layer (~300 nm) was compact and sufficiently thick. When the V_g was applied toward a suitable positive value, electrons were driven from the pentacene into the polymer electret layer, which defines the PGM state of the memory device (Figure 3.11b). Hence, the **P1** and **P2** polymer electrets, featuring strong electron-withdrawing SF₅ groups in their structure, function as the electron-trapping layer. The trapped electrons would leave induced holes in their wake within the OFET semiconducting channel, which makes the OFET easier to turn-ON, i.e., the V_{th} is positively shifted. Conversely, electrons from the polymer electret are driven back into the pentacene layer if a reverse V_g were to be applied, which defines the ERS state of the memory device (Figure 3.11c). This release of electrons resulted in a negative shift of the V_{th} . It should be noted that the trapping of opposite-polarity charge carriers (electrons in our case) for recombination can be excluded. In other words, unipolar trapping behaviour is operative in our ONVMs, as reflected in the data depicted in Figure 3.7. Although holes were conducted through the *p*-type pentacene channel, the additional pentafluorosulfanylated polymer electret layer promotes the trapping of electrons as well as the shift/change in V_{th}/I_d . This is primarily the case since the energy barrier for electron transport between the LUMOs of pentacene, and the polymer electret is lower than the corresponding barrier for hole transport between their HOMOs. The applied V_g can precisely modulate the charge carriers stored in the electret to fulfill the PGM/ERS operation of the memory device, and only a fairly low V_{read} of 5V needs to be applied to distinguish between these two high/low conductance states.

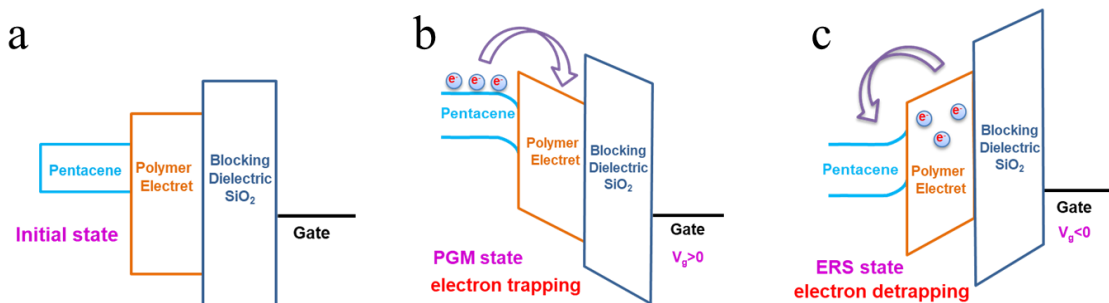


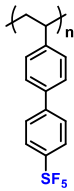
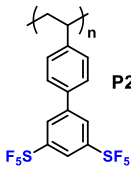
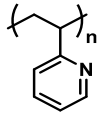
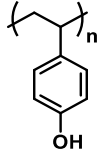
Figure 3. 11 A schematic energy band diagram during a) initial, b) PGM, and c) ERS operations for the charge trapping/detrapping mechanistic description.

Evidently, the electric dipole field of the polymer electret sandwiched between the blocking dielectric and pentacene layers plays an important role in the ONVM properties. In terms of structure-property-function relationships, the differing dipole moments of each molecular repeat unit of **P1** and **P2** could be correlated with the memory properties (especially for MW) of their corresponding devices. Specifically, **P2** features pendent sidechains that are doubly-substituted with highly electronegative SF₅ groups, resulting in a larger estimated local dipole moment (5.45 Debyes) within each repeat unit compared to the monosubstituted **P1** (5.31 Debyes). The enhanced polarization effect of the **P2** electret would conceivably result in more trapped electrons, and additional V_g would be required to compensate for the built-up electric field that opposes the external field. Consequently, the V_{th} of the **P2**-based OFET memory device was positively shifted to a greater degree, and a larger MW was achieved compared to the **P1**-based device. Another possible reason for the superior performance of the **P2**-based device could be attributed to the increased free volume afforded by double *meta*-substitution of the pendent group with sterically bulky SF₅, which is almost as large as a *tert*-butyl group.^{60, 61} Larger free volume within electrets has been associated with effective trapping of charges.⁶²

In contrast to the previously reported polar styrenic polymers (Table 3.3) as electrets for non-volatile OFET memory devices based on pentacene,¹⁴ both **P1** and **P2** displayed superior performance in terms of MW, retention time and memory ratio, owing to the polar yet hydrophobic and sterically bulky SF₅ groups. Specifically, Table 3.3 showed that the hydrophobicity of the electrets had a significant impact on the retention time. This is reasonable as the hydrophilic nature of conventional polar moieties, such as hydroxy group,

can adsorb moisture that creates conductive pathways for charge leakage.¹¹ As a result, the longer retention time of **P1** and **P2** could benefit from the hydrophobic nature of the SF₅ group. Additionally, the larger MW and memory ratio of P1 and P2 can be attributed to the larger dipole and steric bulkiness of the pendants that are imparted by the SF₅ group. Overall, the studies detailed herein have indicated that ONVM devices based on these pentafluorosulfanylated polymer electrets can be repetitively operated between PGM and ERS states, demonstrating non-destructive successive reading cycle capability.

Table 3. 3 Comparison of memory properties of **P1** and **P2** with other polar styrenic polymers.¹⁴ All OFET memory devices were fabricated with a bottom-gate and top-contact architecture using pentacene as the semiconductor layer.

Electret	Electret thickness (nm)	Pentacene thickness (nm)	Water droplet contact angle (°)	MW (V)	Retention time	Memory ratio
 P1	50-60	50	103	~31	10 ⁸	10 ⁶
 P2	50-60	50	101	~44	10 ⁶	10 ⁶
	30-35	50	70	~21	10 ⁴	10 ⁵
	30-35	50	55	~17	10 ⁴	10 ⁵
	30-35	50	15	negligible	N/A	N/A

3.3 Conclusion

In summary, two pentafluorosulfanylated styrenic polymers **P1** and **P2** have been synthesized, characterized, and evaluated as charge-storage electrets in ONVM applications. The memory characteristics of the OFET memory devices employing solution-cast polymer electret layers could be manipulated by varying the degree of SF₅ substitution on each polymer repeat unit. A maximum MW of 44.4±2.6 V was achieved with the **P2** electret-based memory device. Moreover, the memory characteristics in both the **P1**- and **P2**-based devices showed clearly separated bistable high/low conductance states with high memory ratios of ~10⁶ over a period of 10,000 s following PGM and ERS operations. These memories also exhibited excellent dynamic switching behaviour throughout the PRER endurance cycles. The overall superior properties of **P1** and **P2** over other polar styrenic polymers can be attributed to the cooperative effects of hydrophobicity, high electronegativity and bulkiness of the unique SF₅ groups. This study suggests that the unique combination of intrinsic properties afforded by the exotic SF₅ functional group may be exploited for the future design of novel polymer electrets for advanced ONVMs.

3.4 Experimental Section

Materials and Methods. The syntheses of all compounds were carried out in oven-dried glassware under nitrogen atmosphere using Schlenk techniques. Solvents and reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI America, Fisher Scientific, and Ube Industries, and used without further purification. Solvents for synthesis were dried over activated 3 Å molecular sieves. Crude products were purified by flash chromatography using silica gel 60–230 mesh. ¹H, ¹³C, and ¹⁹F NMR spectra were obtained on the Bruker AVANCE II 400 MHz and AVANCE II 300 MHz NMR spectrometers. Chemical shifts (δ) are reported with respect to tetramethylsilane (TMS) as a reference (¹H: δ = 0.00 ppm), CDCl₃ (¹H: δ = 7.26 ppm; ¹³C: δ = 77.0 ppm), (CD₃)₂CO (¹H: δ = 2.05 ppm; ¹³C: δ = 29.84 ppm). Thermogravimetric analysis was performed on a TGA Q500 (TA Instruments; New Castle, DE, USA) at the Centre for Self-Assembled Chemical Structures (CSACS) at McGill University. Both samples were heated in air from 25 °C to 500 °C, using a heating rate of 10 °C min⁻¹. Analysis of the TGA data was done using the Universal

Analysis 2000 Version 4.5 A from TA Instruments. For differential scanning calorimetry, samples were initially put in Tzero aluminum lids and pans, and the measurements were collected on a TA Instrument Q2000 V24.11 Build 124 using a heating rate of 10 °C min⁻¹ under a flow of nitrogen. UV-visible absorption spectra were acquired on a Cary 60 UV-vis spectrophotometer, while fluorescence spectra were obtained on a Fluorolog-3 spectrofluorometer (Horiba, Ltd.). The hydrophobicity characterization of the polymer electret-coated substrates was performed using the Dataphysics DSA10-MK2 (Krüss, Germany) contact angle measurement system under ambient conditions. Atomic force microscopy (AFM) was performed in tapping mode at room temperature on a Seiko SPA400 instrument. For DFT studies, initial structures of the SF₅-functionalized model structures were created on GaussView 5.0, and subsequent geometric optimizations were done on Gaussian09 using the B3LYP level of theory and the 6-31G(d) basis set.

Synthesis of Monomer 3a. To a mixture of 4-vinylphenylboronic acid (0.50 g, 3.4 mmol), 4-bromophenylsulfur pentafluoride (1.1 g, 3.7 mmol), Pd(PPh₃)₄ (0.12 g, 0.10 mmol), and NaCO₃ (0.54 g, 5.1 mmol) was added degassed toluene (70 mL) and deionized H₂O (10 mL). The reaction mixture was stirred at 100 °C for 18 h. Afterwards, the solvents were removed by rotary evaporation and the crude residue was purified by silica gel column chromatography using hexane as eluent to afford alkene **3a** as a white solid (0.67 g, 65 %). ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, 2H, *J* = 8 Hz), 7.67 (d, 2H, *J* = 8 Hz), 7.58 (d, 2H, *J* = 8 Hz), 7.53 (d, 2H, *J* = 8 Hz), 6.81 (dd, 1H, *J* = 20 Hz, *J* = 12 Hz), 5.86 (d, 2H, *J* = 20 Hz), 7.35 (d, 2H, *J* = 12 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 153.0 (quintet, *J* = 17 Hz), 144.1, 138.4, 137.9, 136.2, 127.5, 127.1, 127.0, 126.6 (quintet, *J* = 4 Hz), 114.9; ¹⁹F NMR (376 MHz, CDCl₃): δ 85.57 (quintet, 1F, *J* = 150.4 Hz), 63.37 (d, 4F, *J* = 150.4 Hz).

Synthesis of Monomer 3b. To a mixture of 4-vinylphenylboronic acid (0.30 g, 2.0 mmol), 4-bromophenylsulfur pentafluoride (0.91 g, 2.2 mmol), Pd(PPh₃)₄ (0.070 g, 0.060 mmol), and NaCO₃ (0.32 g, 3.1 mmol) was added degassed toluene (50 mL) and deionized H₂O (8 mL). The reaction mixture was stirred at 100 °C for 18 h. After this, the solvents were removed by rotary evaporation and the crude residue was purified by silica gel column chromatography using hexane as eluent to yield alkene **3b** as a white solid (0.66 g,

75 %). ^1H NMR (300 MHz, CDCl_3): δ 8.10 (s, 3H), 7.55 (s, 4H), 6.81 (dd, 1H, $J = 16$ Hz, $J = 8$ Hz), 5.88 (d, 2H, $J = 16$ Hz), 7.38 (d, 2H, $J = 8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 154.2 (quintet, $J = 19$ Hz), 143.3, 138.8, 137.0, 135.9, 127.6, 127.4, 122.7 (quintet, $J = 5$ Hz), 115.6; ^{19}F NMR (376 MHz, CDCl_3): δ 82.59 (quintet, 2F, $J = 150.4$ Hz), 63.11 (d, 8F, $J = 150.4$ Hz).

Synthesis of P1. To a solution of **3a** (0.50 g, 1.6 mmol) in degassed benzene (5 mL) was added benzoyl peroxide (34 mg, 0.14 mmol). The reaction mixture was refluxed with vigorous stirring under nitrogen atmosphere for 4 h, during which the reaction mixture became viscous. Afterwards, the viscous solution was cooled to room temperature and the polymer was precipitated by slowly pouring into methanol (300 mL). The resulting white precipitate was collected by filtration, washed three times with methanol (50 mL), and dried under high vacuum overnight, which resulted in the final polymer product **P1** as a white solid (0.20 g, 40%). ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.97-7.11 (m, 6H), 6.98-6.56 (m, 2H), 2.19-1.39 (m, 3H); ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ 152.3, 146.1, 145.5, 144.1, 135.9, 128.5, 126.9, 126.3, 40.3; ^{19}F NMR (282 MHz, $(\text{CD}_3)_2\text{CO}$): δ 85.67 (quintet, 1F, $J = 149.5$ Hz), 62.88 (d, 4F, $J = 149.5$ Hz).

Synthesis of P2. Polymer **P2** was synthesized using the same method as **P1** but using **3b** as the starting material in place of **3a**. **P2** was isolated as an off-white solid (0.18 g, 36%). ^1H NMR (300 MHz, THF-d_8): δ 8.37-8.10 (m, 1H), 8.10-7.63 (m, 2H), 7.55-6.45 (m, 4H), 2.01-1.34 (m, 3H); ^{13}C NMR (75 MHz, THF-d_8): δ 154.7, 146.8, 146.5, 143.8, 136.2, 129.3, 127.7, 123.2, 41.3; ^{19}F NMR (376 MHz, THF-d_8): δ 81.57 (quintet, 2F, $J = 146.6$ Hz), 62.13 (d, 8F, $J = 146.6$ Hz).

Device Fabrication and Measurement. The OFET memory devices were fabricated with a bottom-gate top-contact (BGTC) architecture. Heavily-doped silicon wafers passivated with a 300 nm thick SiO_2 layer were ultrasonically cleaned in acetone and then isopropanol for 10 min in each solvent. Polymer electret layers measuring ~50-60 nm thick were made by spin-coating films from a 10 mg mL^{-1} solution of **P1** in chlorobenzene (or a 20 mg mL^{-1} solution of **P2** in toluene) onto the substrate, followed by subsequent annealing at 100 °C for 1 h. After this, a 50 nm thick layer of pentacene was thermally deposited on top of the electret layer at a rate of 0.1~0.3 Å s^{-1} at a substrate temperature of 90 °C under

10^{-6} torr of pressure. Gold source/drain electrodes (50 nm) were thermally deposited in the evaporation chamber using a shadow mask with a channel length (L) of 50 μm and a channel width (W) of 1000 μm . All electrical characterizations were measured using a Keithley 4200-SCS semiconductor parameter analyzer in a nitrogen-filled glove box.

3.5 References

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Chapter 4. SF₅-Functionalized Ullazine Derivatives as Potential Dye-Sensitizer Solar Cell Materials

4.1 Introduction

There has been extensive research on polycyclic heteroaromatic arenes (PHAs) due to their relevance to organic electronics, e.g., organic light-emitting diodes (OLEDs), organic solar cells (OSCs), etc.¹ One class of PHAs, based on the nitrogen-containing 16 π -electron ullazine core that is isoelectronic with pyrene (Figure 4.1), has recently emerged as a hot topic due to its outstanding performance in dye-sensitized solar cells (DSSCs).²⁻⁷ Following its debut synthesis in 1983,⁸ scant attention was paid to the ullazines in subsequent decades because of their non-trivial synthesis and perceived lack of applications. However, the advent of new synthetic methods and the newfound ability of ullazines to harvest solar energy have resulted in their revival.⁹⁻¹⁴ Contemporary methods for constructing the ullazine framework include acid-promoted and metal-catalyzed cyclizations of 1-(2,6-dialkynylphenyl)-1*H*-pyrroles,^{2, 15-18} along with several annulation-based strategies.^{7, 17}

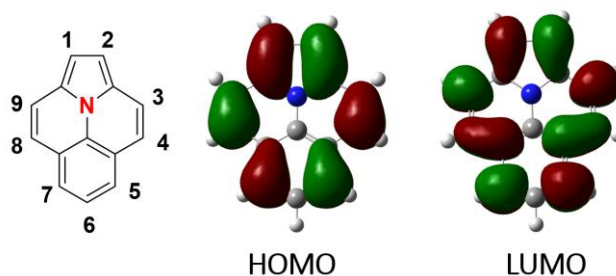


Figure 4. 1 Chemical structure and frontier molecular orbitals of ullazine.

Aside from an ongoing interest in ullazine core synthesis, substantial effort has also gone into developing methods to selectively functionalize various peripheral positions of the *N*-heterocycle,¹⁹ as this would enable rational tuning of its optoelectronic properties. Density functional theory (DFT) calculations indicate that both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) coefficients of ullazine are concentrated along the periphery (Figure 4.1).^{2, 13} Also noteworthy is a nodal

plane passing through C6, where substituents can be installed to confer solubility and stability without altering overall optoelectronic character.^{2, 7, 10, 18, 20} Functionalization of other positions has also been investigated recently,^{2, 9, 10, 14} with 1-, 2-, 5-, and 7-substituted ullazines receiving extra attention since the installation of strong acceptors at these positions produce strong intramolecular charge transfer (ICT) character that is beneficial to light-harvesting.^{2, 5, 9, 10} Similarly, ullazines bearing acceptors at C4 and C8 have also displayed strong ICT, though the overall molecular planarity could be compromised in these two cases.² Lastly, Gerson et al. have also shown that substitution at C3 and C9 can stabilize the resulting ullazines.^{2, 21}

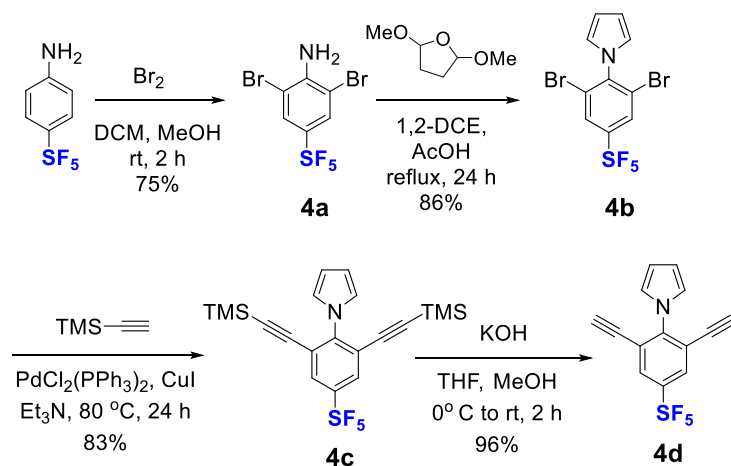
In regard to light-harvesting molecules for DSSCs, organic solar cells (OSCs), and perovskite solar cells, fluorinated π -conjugated systems have recently been shown to boost device efficiency.²²⁻³² Reasons for this remain unclear due to the wide diversity of structures and complexity of the underlying physics. However, contemporary hypotheses suggest that fluorination may lower HOMO energies to promote higher open-circuit voltages (V_{oc}) and power conversion efficiencies (PCEs).^{13, 24, 25, 32} It is also believed that enhanced efficiencies may be due to higher fill factors (FF) arising from the ability of F atoms to modulate aggregation morphologies and improve solid-state packing via intermolecular interactions (e.g., $F\cdots H$, $F\cdots \pi$, and $F\cdots S$).^{25, 33} Additionally, owing to the high hydrophobicity, fluorinated dyes have the potential to increase the DSSC device stability by reducing the desorption of dye from the TiO_2 surface caused by water penetration.^{34, 35} Nonetheless, the discovery of the “F effect” has sparked interest in the synthesis of fluorine-rich π -conjugated structures for light-harvesting applications.

This work sought to access fluorine-rich ullazines from readily available precursors containing the electron-withdrawing SF_5 group.³⁶⁻⁴² First introduced by Sheppard in the 1960s, the intriguing fluorine-rich SF_5 moiety has received widespread interest from organic, medicinal, and materials chemists.³⁶ From a materials perspective, SF_5 is an interesting acceptor to explore, especially given the renewed interest in unconventional electron-deficient molecular designs.⁴³ The main challenge encountered during the synthesis was the low reactivity of the electron-deficient SF_5 -substituted alkynes towards double 6-endo-trig cycloaromatizations and iodocyclization. In my efforts to address the

problem, I incidentally found the two cyclization steps could occur by raising the reaction temperatures thanks to the chemical and thermal robustness of the SF₅ group, which granted successful access to symmetrical (**U1–U3**) and unsymmetrical ullazines (**U5–U10**). The photophysical and electrochemical properties of these SF₅-functionalized ullazines were subsequently investigated in order to evaluate their potential for DSSC applications.

4.2 Results and Discussion

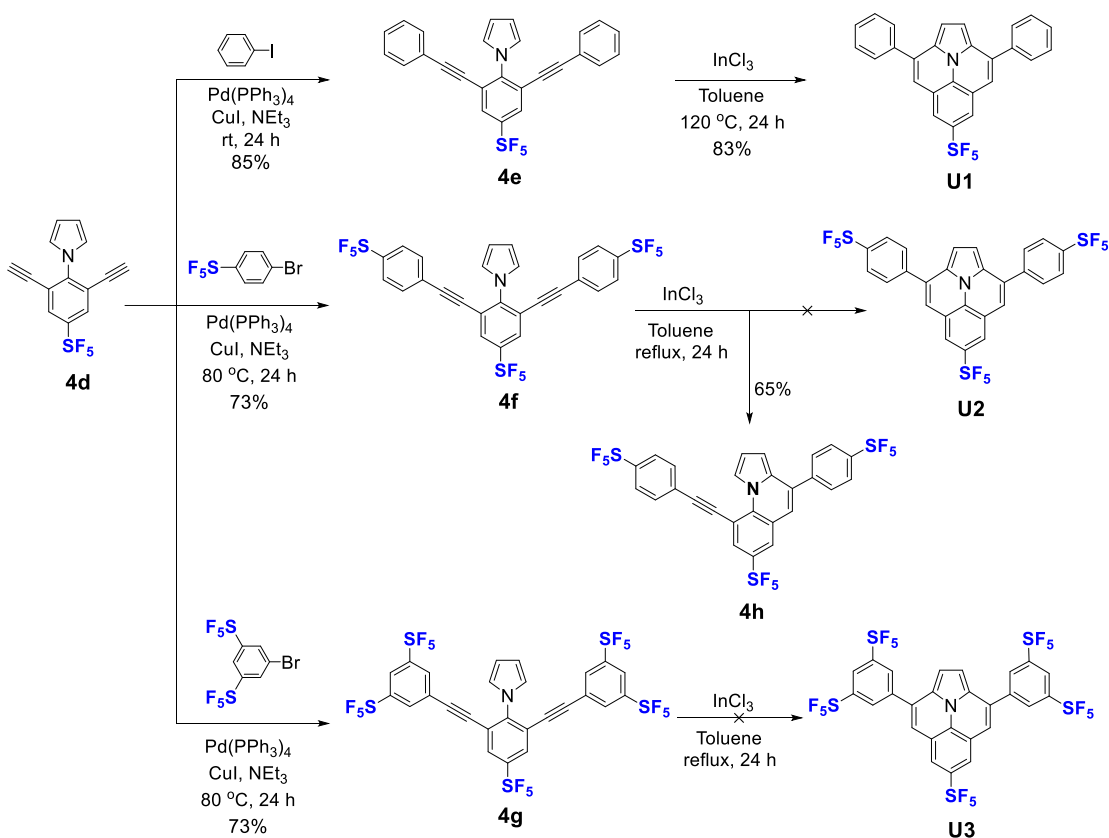
Synthesis. The six fluorine-rich ullazines were derived from a common intermediate **4d**, 1-(2,6-diethynylphenyl)-1*H*-pyrrole, synthesized from commercially available 4-(pentafluorosulfanyl)aniline (Scheme 4.1). Specifically, 4-(pentafluorosulfanyl)aniline underwent double *ortho*-bromination in the first step, followed by a Clauson-Kaas reaction with 2,5-dimethoxytetrahydrofuran to generate pyrrole **4b**, which was subjected to double Sonogashira coupling with (trimethylsilyl)acetylene and subsequent basic deprotection to afford **4d** in 52% yield over four steps.



Scheme 4. 1 Synthesis of key intermediate **4d**.

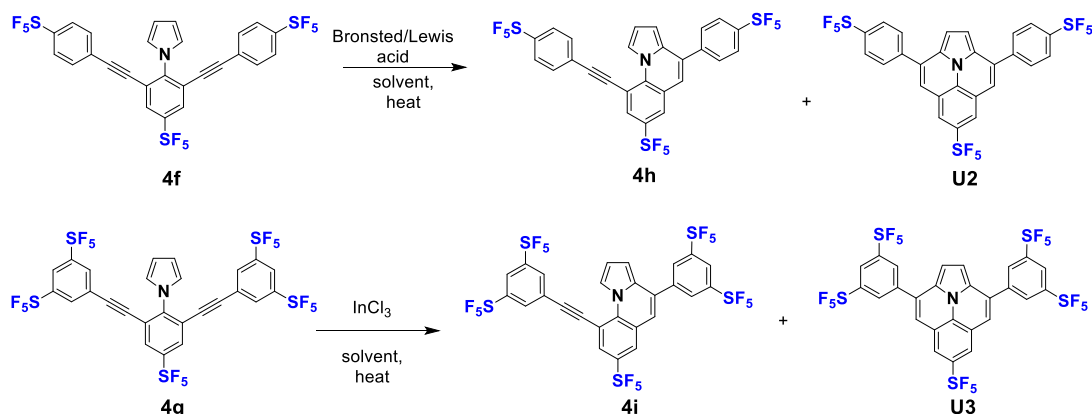
Dialkyne **4d** was further coupled with different aryl halides via Sonogashira reaction to yield intermediates **4e–4g**, which can undergo double electrophilic cyclizations to yield ullazines **U1–U3** (Scheme 4.2). While **U1** was obtained in 83% yield via facile InCl₃-promoted Fürstner-type cycloaromatization in refluxing toluene,² attempts to extend this methodology to the more highly fluorinated substrates **4f** and **4g** were unsuccessful (Scheme 4.2). When reaction temperatures between 100–120 °C were used, only moderate

yields of the mono-cyclized product **4h** were observed (Scheme 4.2, Table 4.1-entries 7). This was likely due to the additional electron-withdrawing SF₅ groups, which lower the nucleophilicity of the pyrrole following the first cyclization and subsequently render the second ring-closure impossible under the same conditions.



Scheme 4. 2 Attempted synthesis of pentafluorosulfanylated ullazines **U1–U3**.

To address this problem, various conditions for the double electrophilic cyclization were screened (Table 4.1). I initially adopted the Brønsted acid method by Langer,¹⁸ who had reported ullazines bearing electronegative groups (e.g., F and CF₃) at the same positions. In my case, the use of excess protic acid either failed to convert the SF₅-functionalized **4f**, or resulted in its decomposition (Table 4.1, entries 1–6). The lack of reactivity at 20 °C was again attributed to the electron-poor system, while decomposition at 120 °C in the presence of strong acids was likely due to the destruction of the SF₅ moiety.^{36, 44} It must be noted that even with F and CF₃ in the Langer case,¹⁸ observed yields were rather modest (30–40%), which highlighted the need for a feasible method to prepare electron-deficient ullazines.

Table 4. 1 Mono- vs. double-cycloaromatization.

^a SM: starting material, TFA: trifluoroacetic acid, MsOH: methanesulfonic acid, p-TsOH:

Entry	SM	Acid ^a	Solvent	T (°C)	t (h)	Yield (%)				Notes
						4h	U2	4i	U3	
1	4f	TFA (30 equiv.)	xylenes	120	36	-	-			no reaction
2	4f	MsOH (30 equiv.)	xylenes	20	36	-	-			no reaction
3	4f	MsOH (30 equiv.)	xylenes	120	24	-	-			decomposition
4	4f	p-TsOH (30 equiv.)	xylenes	20	36	-	-			no reaction
5	4f	p-TsOH (30 equiv.)	xylenes	120	24	-	-			decomposition
6	4f	TfOH (30 equiv.)	CH ₂ Cl ₂	20	24	-	-			decomposition
7	4f	InCl ₃ (2 equiv.)	toluene	100	24	65	0			
8	4f	InCl ₃ (2 equiv.)	xylenes	120	24	56	0			
9	4f	InCl ₃ (2 equiv.)	xylenes	140	24	25	58			
10	4f	InCl ₃ (2 equiv.)	mesitylene	160	24	0	73			
11	4f	InCl ₃ (2 equiv.)	o-DCB	160	24	0	81			
12	4f	InCl ₃ (0.6 equiv.)	o-DCB	160	24	0	77			
13	4g	InCl ₃ (2 equiv.)	xylenes	120	24			71	0	
14	4g	InCl ₃ (2 equiv.)	mesitylene	165	24			24	56	
15	4g	InCl ₃ (2 equiv.)	o-DCB	175	24			0	82	
16	4h	InCl ₃ (2 equiv.)	o-DCB	160	24	-	83			
17	4i	InCl ₃ (2 equiv.)	o-DCB	175	24			-	80	

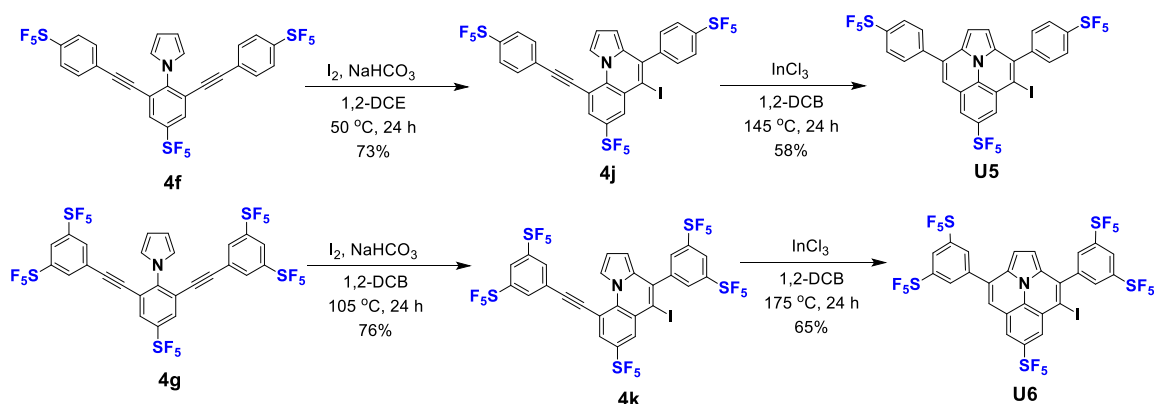
p-toluenesulfonic acid, TfOH: trifluoromethanesulfonic acid, o-DCB: 1,2-dichlorobenzene.

Following the lack of success with protic acids, I revisited the use of Lewis acid promoters for the cycloaromatization. Faced with a dearth of examples in the context of ullazine synthesis from electron-deficient alkyne precursors, I scoured the literature for methods involving other heterocycles as well as carbocycles.⁴⁵⁻⁴⁸ Indeed, in almost all cases featuring electronegative substituents (e.g., F, CF₃, CN, NO₂), isolated yields were

consistently low.^{47, 48} In the absence of promising precedents, I then entertained the option of modifying the InCl₃ method, which had cleanly afforded mono-SF₅-functionalized ullazine **U1** without incurring decomposition products. By carrying out the reaction at 140 °C in xylenes, the doubly-cyclized product **U2** was observed for the first time, accompanied by a small quantity of monocyclized product (Table 4.1, entry 9). Again, no decomposition products were observed. Gratifyingly, upon performing the reaction at 160 °C in mesitylene, the desired **U2** was obtained exclusively in 73% yield (Table 4.1, entry 10). Results were further improved by replacing the mesitylene solvent with *o*-dichlorobenzene, which afforded **U2** in 81% yield. Late-stage optimization also revealed that the InCl₃ could be used in substoichiometric quantities, with only minor detriment to the yield (Table 4.1, entry 12). The structure of **U2** was confirmed by NMR, mass spectrometry, and single-crystal X-ray diffraction analysis (Figure A.1 and Table A.1, CCDC NO. 1923328). Applying these new conditions to the heavily fluorinated **4g**, I was likewise successful in effecting twofold cyclization to **U3** in excellent yields (82%).

During the course of the above studies, I also discovered that **U2** and **U3** could be obtained in excellent yields from the mono-cyclized products **4h** and **4i** (Table 4.1, entries 16 and 17) when they were subjected to the same condition as **4f** and **4g** in entry 11 and 15 (Table 4.1), respectively. In this regard, I was especially interested in iodocyclization, which would provide an iodine handle for further functionalization and tuning of properties. I then applied the reported method developed by Rustag to **4f** for iodocyclization,⁴⁹ which raised a similar issue that no reaction occurred at 0 °C due to the electron-deficient nature of **4f**. In Rustag's studies, the iodine mediated cyclization only occurred for the electron-rich and electron-neutral substrates. While the only example of an electron-deficient substrate bearing NO₂ group underwent decomposition at such reaction condition. Herein, I applied a similar protocol as I did to the InCl₃ mediated double cyclization by raising the reaction temperature. To my delight, trace of **4j** was observed at room temperature. Surprisingly, compared to the substrates in Rustag's work that decomposed at room temperature, the SF₅-functionalized substrates (**4f** and **4g**) showed no sign of decomposition even under the high-temperature (50-105 °C) iodocyclization conditions that both **4j** and **4k** were obtained in excellent yields of 73% and 76%, respectively

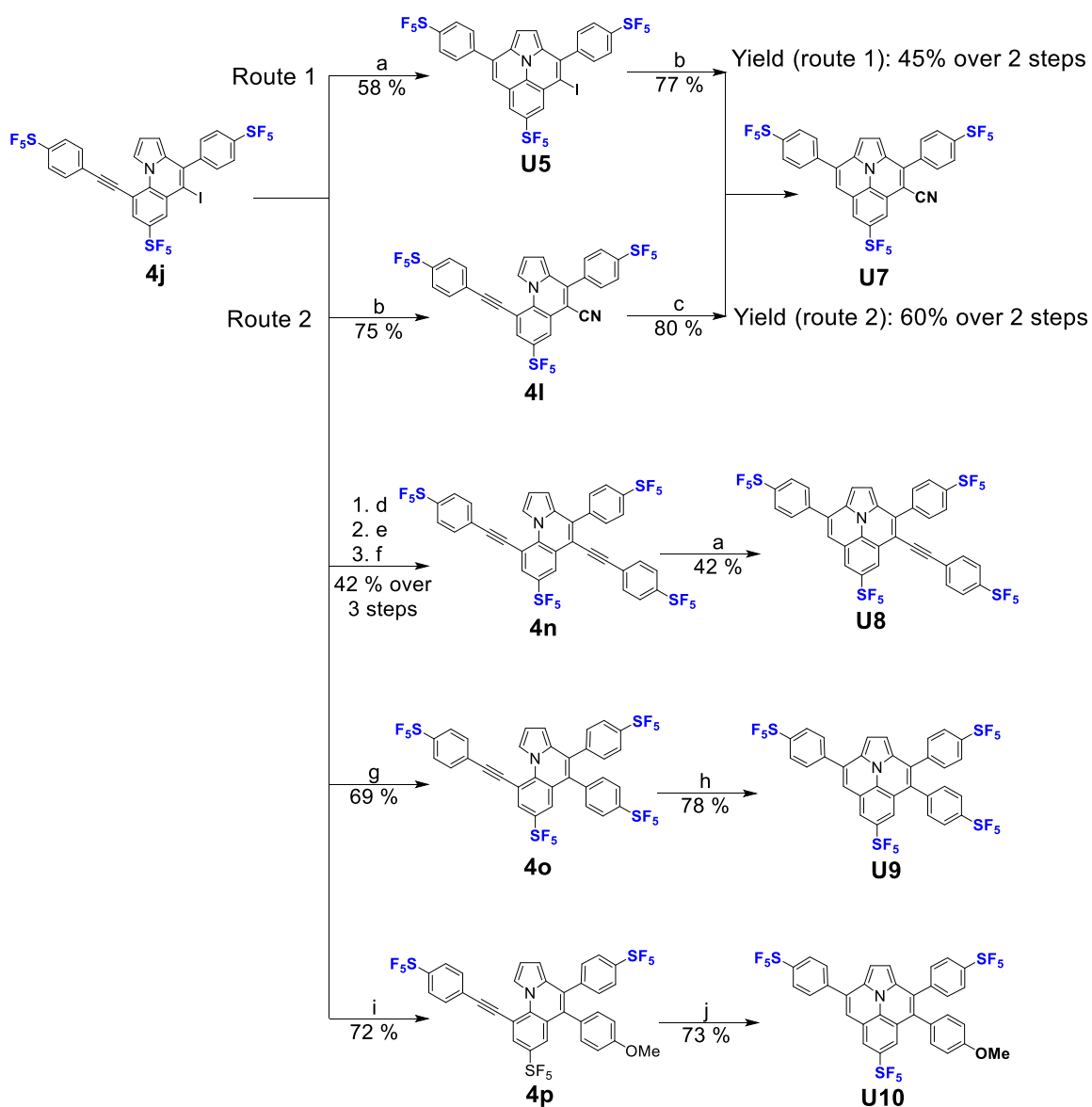
(Scheme 4.3). For practical reasons (e.g., chromatographic separation), I found that the two-stage double electrophilic cyclization was best achieved with iodocyclization as the first step and In(III)-catalyzed cycloisomerization in the second. Specifically, **4f** and **4g** were converted to mono-iodocyclized **4j** and **4k** with isolated yields >70% (Scheme 4.3). Compounds **4j** and **4k** were in turn cycloisomerized at high temperatures in the presence of InCl₃ to the unsymmetrical iodine-containing ullazines **U5** and **U6** in 58% and 65% yield, respectively (Scheme 4.3).



Scheme 4. 3 Synthesis of iodinated pentafluorosulfanylated ullazines **U5** and **U6**.

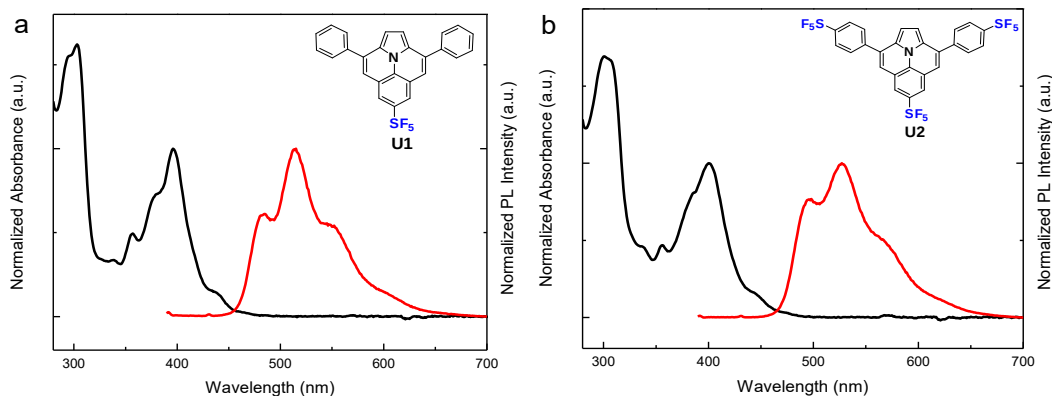
To expand the scope of these iodinated derivatives, I took compounds **4j** and **U5** and further investigated the possibility of subsequent synthetic elaboration, starting with an attempt to obtain the cyanated ullazine **U7** (Scheme 4.4). Here, two routes were examined, i.e., direct access via CuI-mediated substitution of the iodine atom in **U5** with CN, and a second route where substitution of I with CN in **4j** was carried out before the cycloisomerization step to the identical target **U7**. Experimentally, results revealed that the second pathway led to higher isolated yields over two steps (60% vs. 45%). This can be attributed to the lower observed yield (58%) of the high-temperature cycloisomerization step when the reaction was carried out on an iodine-containing substrate (Scheme 4.4). Conversely, when the iodine in **4j** was first substituted with CN, subsequent cycloisomerization to the ullazine proceeded in 80% yield. Using this two-step substitution/cycloisomerization approach, intermediate **4j** was also successfully converted to additional ullazine derivatives **U8–U10** (Scheme 4.4). Specifically, the iodine synthetic

handle was replaced with acceptor- or donor-bearing aryl and arylethynyl moieties via Pd-catalyzed Sonogashira and Suzuki couplings.



Scheme 4. 4 Synthesis of **U7–U10**. Reagents and conditions: a) InCl_3 , 1,2-DCB, 145 °C, 24 h; b) CuCN , DMF, 110 °C, 16 h; c) InCl_3 , 1,2-DCB, 180 °C, 24 h; d) Trimethylsilyl acetylene, $\text{PdCl}_2(\text{PPh}_3)_2$, CuI , Et_3N , 50 °C, 24 h; e) KOH , THF/MeOH, 0 °C to rt, 2 h; f) 4-bromophenylsulfur pentafluoride, $\text{Pd}(\text{PPh}_3)_4$, CuI , NEt_3 , 80 °C, 24 h; g) 4-(pentafluorosulfanyl)phenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , DMF, 110 °C, 16 h; h) InCl_3 , 1,2-DCB, 150 °C, 24 h; i) 4-methoxyphenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , DMF, 110 °C, 16 h; j) InCl_3 , 1,2-DCB, 140 °C, 24 h.

Photophysical studies. Seven ullazines **U1–U3** and **U7–U10** were studied by UV-Vis and fluorescence spectroscopy to determine their photophysical properties (Figure 4.2). The iodine-containing **U5** and **U6** were non-fluorescent. The UV-vis spectra of five of the ullazines (**U1–U3**, **U9**, and **U10**), which bear non-coplanar substitutions on the ullazine core at the C3, C9, or C4 positions, showed similar absorption bands between 360–470 nm, with corresponding estimated optical bandgaps [$E_{(0-0)}$] of 2.62–2.72 eV (Table 4.2). While the UV-vis spectra of **U7** and **U8** showed broader absorption spectra with strong ICT bands between 420–550 nm (Figure 4.2h) with smaller optical bandgaps [$E_{(0-0)}$] of 2.33–2.49 eV (Table 4.2) due to the strong electron-withdrawing effects exerted by the C4 cyano group and ethynylphenyl SF_5 group, which are coplanar with the ullazine core. Furthermore, due to the extended conjugation, **U8** had the most intense absorption with λ_{abs} at 472 and 503 nm showing a large molar extinction coefficient (ϵ) of 13598 and 9469 $\text{L}\cdot\text{mol}^{-1}\text{cm}^{-1}$, respectively. The seven compounds also displayed fluorescence maxima between 500–530 nm, with low quantum yields (0.03–0.12) that are characteristic of ullazines. In general, for the ullazines substituted at C3, C4, C8, and C9 (which do not reside in the nodal plane), substitution effects depend on the degree of coplanarity—and henceforth conjugation—between the substituents and the ullazine core. For example, compared to **U9** and **U10**, whose substituents at C3 and C4 are aryl-based, **U7** and **U8** feature substituents (CN, ethynyl) at C4 that are better coupled to the ullazine core and thus exert more pronounced effects on the $E_{(\text{S}^+/\text{S})}$ and $E_{(\text{S}^+/\text{S}^*)}$ potentials and other optoelectronic properties resulting therefrom (Table 4.2).



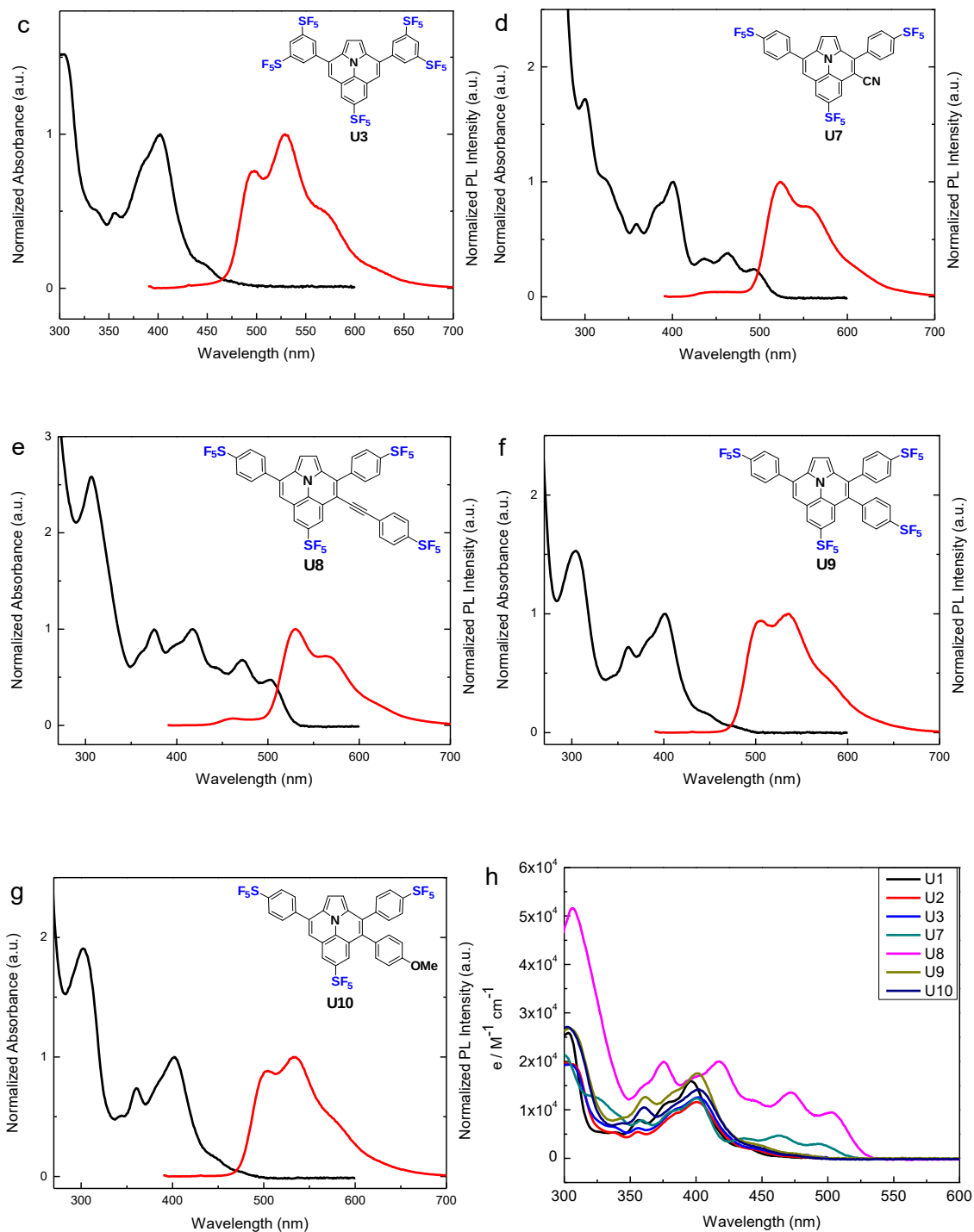


Figure 4. 2 a-g) Normalized absorption and photoluminescence spectra and h) molar absorptivities (ϵ) of U1–U3 and U7–U10 in chloroform.

Table 4. 2 Photophysical and electrochemical properties of **U1–U3** and **U7–U10**.

Cmpd	$\lambda_{\text{abs}}^{\text{a}} / \text{nm}$ ($\epsilon / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	$\lambda_{\text{em}}^{\text{b}} / \text{nm}$	Stokes shift ^c / cm^{-1}	Φ_{f}	$E_{(0-0)}^{\text{d}} / \text{eV}$	$E_{(\text{S+}/\text{S})}^{\text{e}} / \text{V}$	$E_{(\text{S+}/\text{S}^*)}^{\text{f}} / \text{V}$
U1	396 (15956), 438 (sh) ^g	485, 515, 551 (sh) ^g	2212	0.027	2.72	1.18	-1.54
U2	400 (11608), 448 (sh) ^g	498, 525, 564 (sh) ^g	2242	0.041	2.65	1.28	-1.37
U3	402 (12565), 453 (sh) ^g	498, 530, 567 (sh) ^g	1995	0.038	2.66	1.38	-1.28
U7	401 (12371), 436 (4117), 464 (4702), 493 (2989)	524, 558	1200	0.075	2.49	1.48	-1.01
U8	418 (19983), 444 (sh) ^g , 472 (13598), 503 (9469)	530, 567	1013	0.124	2.43	1.31	-1.12
U9	402 (17537), 451 (sh) ^g	503, 534	2298	0.054	2.62	1.26	-1.36
U10	402 (14211), 453 (sh) ^g	502, 531	2155	0.044	2.63	1.18	-1.45

^a Measured in chloroform and collected from 390–550 nm. ^b Measured in chloroform and excited at 380 nm. ^c Stokes shift (cm^{-1}) = $[1/\lambda_{\text{abs}} - 1/\lambda_{\text{em}}](10^7)$, e.g., Stokes shift of **U1** = $[1/(438) - 1/(485)](10^7)$.

^d Estimated from the intersection of normalized absorption and emission spectra measured in CHCl_3 .

^e Measured in chloroform with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte and ferrocene as internal standard, recorded using a scan rate of 100 mV/s.

^f $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{optical}}$. ^g sh = shoulder.

Electrochemical studies. Cyclic voltammetry was performed on **U1–U3** and **U7–U10** (Table 4.2 and Figure 4.3) to determine the ground-state oxidation potential $E_{(\text{S+}/\text{S})}$, which was calculated according to the reported method by setting the formal oxidative potential of Fc/Fc^+ vs. the normal hydrogen electrode (NHE) to 0.63V.⁵⁰ The $E_{(\text{S+}/\text{S})}$ values

of the seven ullazines ranged from 1.18 V to 1.48 V versus NHE, while excited state oxidation potential [$E_{(S+/S^*)}$] values were estimated from the $E_{(S+/S)}$ and optical gaps [i.e., $E_{(S+/S^*)} = E_{(S+/S)} - E_{(0-0)}$], ranging from -1.54 V to -1.10 V. Going from **U1** to **U3**, both the $E_{(S+/S)}$ and $E_{(S+/S^*)}$ potentials were observed to be driven larger from 1.18 V and -1.54 V to 1.38 V and -1.28 V upon successive SF₅-substitution of the pendent phenyls at C3 and C9. Despite being relatively distal from the ullazine core, the SF₅ groups were still able to remotely tune the electronic properties due to their exceptional electron-accepting ability. As expected, the ullazine (**U7**) that was simultaneously functionalized with both SF₅ and CN acceptors exhibited the largest $E_{(S+/S)}$ (1.48 V) and $E_{(S+/S^*)}$ (-1.01 V) potentials of the series.

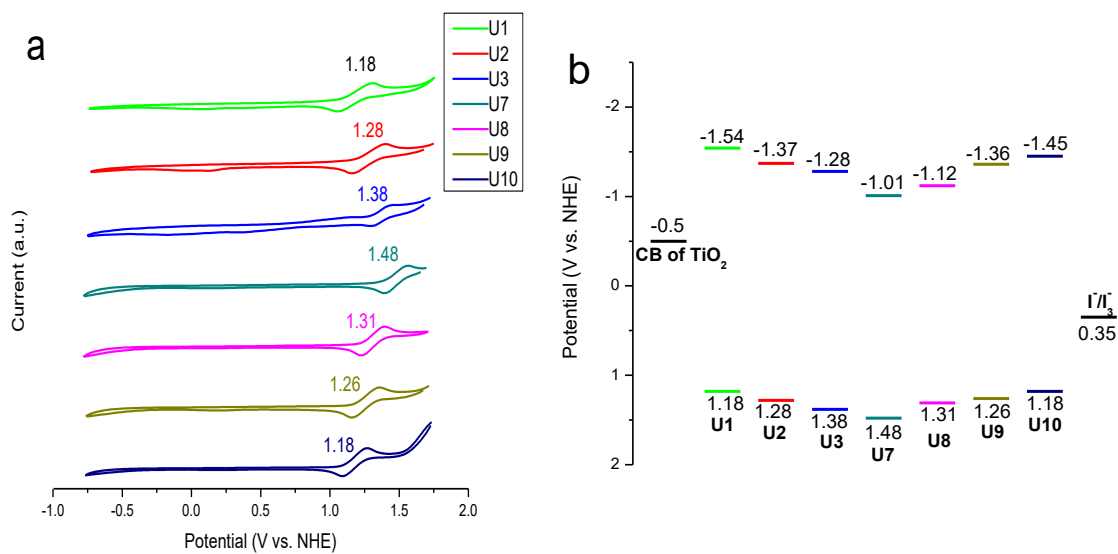
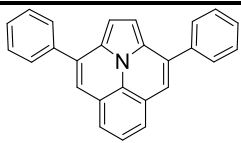
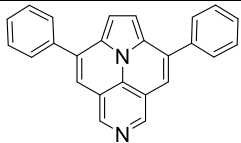
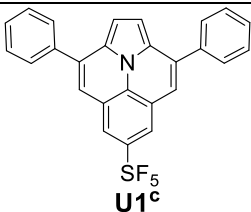


Figure 4.3 a) Cyclic voltammograms of **U1–U3** and **U7–U10** in chloroform with 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte. b) Potential energy diagram of conduction band (CB) of TiO₂, $E_{(S+/S)}$ and $E_{(S+/S^*)}$ of **U1–U3**, **U7–U10**, and I^-/I_3^- redox couple.

Compared to previously reported ullazine derivatives of analogous structures such as **A** and **B** (Table 4.3),^{10, 18} **U1** showed generally similar photophysical properties since the C6 substituent lies in the nodal plane of the frontier orbitals of the ullazine core (see Figure A.3). Interestingly, only **U1** and **B** exhibit reversible oxidation waves in electrochemical studies, while **A** showed irreversible oxidation, which involved a reversible electron

transfer followed by an irreversible chemical reaction (E_rC_i) mechanism. The reversible oxidation waves for **U1** and **B** indicate that the electron-withdrawing substituents could potentially stabilize the radical cations by lowering the singly occupied molecular orbitals (SOMO) of these ullazines, which render them less susceptible to nucleophilic attack (e.g. oxygen). For the same reason, the reversible oxidation waves (Figure 4.3a) of **U2**, **U3** and **U7-U10** can be attributed to the SF_5 substitutions at C6 of the ullazine core even the SF_5 groups lie at the nodes of their HOMOs and LUMOs (Figure A.3). Although the electron-withdrawing substitution at the C6 position of the ullazine core has a minimal effect on the photophysical properties of an ullazine derivative, it clearly exerts a stabilizing effect on its cationic form.

Table 4. 3 Photophysical characteristics of ullazines **A**, **B**, and **U1**.

Compound	λ_{abs}^d /nm	λ_{em} /nm	Stokes shift /cm ⁻¹	Reference
 A^a	391 438 (sh)	480 513 553	1997	10
 B^b	390 434 (sh)	477 508 543	2077	18
 U1^c	396 438 (sh)	485 515 551	2212	This work

^a Measured in cyclohexane. ^b Measured in dichloromethane. ^c Measured in chloroform. ^d Collected from 390–550 nm.

Evaluation of the SF_5 -ullazines as the photosensitizer for DSSCs. The operation of DSSC involves four main steps (Figure 4.4):^{34, 35} 1) The ground state (S^+/S) photosensitizer molecule gets photoexcited to the excited state (S^+/S^*) by absorbing solar energy; 2) Electrons are transferred from the excited state of photosensitizer to the

conduction band (CB) of titanium oxide (TiO_2); 3) Electrons diffuse from the conduction band of TiO_2 to the counter electrode through the external circuit. Meanwhile, the electrical energy is also collected; 4) The electrons reaching the counter electrode can reduce the triiodide to iodide in the electrolyte, and then ground state photosensitizer is regenerated by receiving an electron from the iodide/triiodide (I^-/I_3^-) redox couple when iodide is oxidized to triiodide again.

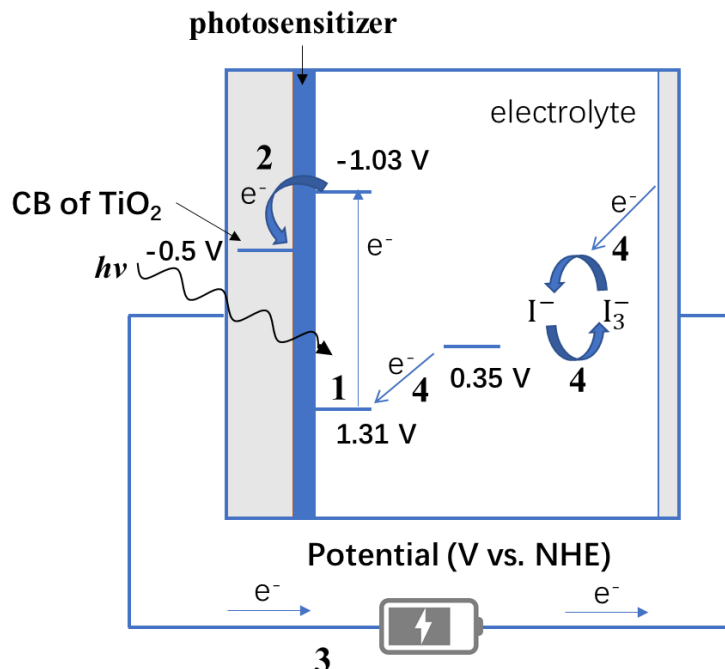


Figure 4. 4 Working principle of dye-sensitized solar cells.

Clearly, the photosensitizer is responsible for harvesting photon energy in DSSCs and should satisfy the following requirements:^{34, 35} 1) The photosensitizer should have an intense and broad absorption spectrum, ideally covering the whole visible and even the near-infrared region. 2) The excited-state oxidation potential [$E_{(S^+/S^*)}$] of the photosensitizer should be more negative than the conduction band (CB) potential of the semiconductor, e.g., titanium oxide (TiO_2) ($\sim -0.5\text{V}$ vs. NHE),^{51, 52} allowing electrons to be transferred from the excited photosensitizer to the CB of TiO_2 . 3) While the ground state oxidation potential [$E_{(S^+/S)}$] should be more positive than the redox electrolyte, such as I^-/I_3^- redox couple (0.35 V vs. NHE).⁵³ Hence, the ground state photosensitizer can be regenerated upon electron injection to the excited state from the redox electrolyte. 4) Both

the ground state and excited state of the photosensitizer should be sufficiently stable during the operation of the DSSCs in repeatable cycles.

Regarding the seven ullazines as the photosensitizers in this study, the $E_{(S+/S)}$ and $E_{(S+/S^*)}$ potentials of **U1-U3** and **U7-U10** are sufficiently positive and negative than the iodide/triiodide redox couple and the TiO_2 conduction band potential, respectively (Figure 4.3b), indicating that they are energetically favourable for DSSC application. Their reversible oxidative waves (Figure 4.3a) also show that their cation forms/ excited states are stable enough to revert back to the ground state forms during the DSSC device operation. In terms of absorption properties, **U8** is the best candidate as the photosensitizer for DSSCs among the seven ullazines since it has the most intense and broad absorption spectrum (Figure 4.2).

4.3 Conclusion

A series of SF_5 -functionalized ullazine derivatives were reported in this work. During the synthesis, two key cyclization steps, i.e., InCl_3 mediated double-cyclization and iodocyclization, were initially shown problematic due to electron-deficient alkynes induced by the SF_5 groups. To my delight, both cyclization steps can be resolved by raising the reaction temperature, and surprisingly, the SF_5 -substituted substrates showed no sign of decomposition under the harsh reaction conditions, which can be attributed to the chemical and thermal robustness of the SF_5 groups. In the subsequent photophysical and electrochemical studies, **U1-U3** and **U7-U10** displayed favourable properties, such as stable radical cations and favourable $E_{(S+/S)}$ and $E_{(S+/S^*)}$ potentials, as the photosensitizers for DSSC devices. Among them, **U8** was the best candidate as the photosensitizer due to its extra broad and intense absorption spectrum compared to other ullazines in this work.

4.4 Experimental Section

Materials and Methods. All synthetic procedures were performed in oven-dried glassware under an anhydrous nitrogen atmosphere using standard Schlenk techniques. Reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, TCI America, Ube Industries, and Fisher Scientific. The reagents were used without further purification, and

the reaction solvents were dried over activated 3 Å molecular sieves prior to use. Crude products were purified by flash column chromatography on silica gel 60–230 mesh or 230–400 mesh. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a Bruker AVANCE II 400 MHz and Bruker AVANCE II 300 MHz NMR spectrometer. Chemical shifts are reported relative to CDCl_3 (^1H : $\delta = 7.26$ ppm; ^{13}C : $\delta = 77.16$ ppm), $(\text{CD}_3)_2\text{CO}$ (^1H : $\delta = 2.05$ ppm; ^{13}C : $\delta = 206.26$ ppm), THF-d_8 (^{13}C : $\delta = 67.57$ ppm). HRMS were recorded on a Kratos Concept-Magnetic Sector Electron Impact mass spectrometer and Waters Global electrospray high-resolution Q-TOF mass spectrometer with lock spray accuracy. UV–visible spectra were obtained on a Cary 60 UV-Vis spectrophotometer. PL spectra were obtained on a Horiba Fluorolog-3 spectrofluorometer. The fluorescence quantum yields (Φ_f) of dyes U1–U4 and U7–U10 were calculated by the steady-state comparative method using quinine sulfate (QS) in 0.5 M sulfuric acid as a standard ($\Phi_{\text{st}} = 0.546$). Density Functional Theory (DFT) calculations: The initial structures of the SF_5 -containing molecules were constructed using the GaussView 5.0 visualization program. Geometry optimizations were performed using Gaussian09 at the B3LYP level of theory and the 6-31G(d) basis set. The single-crystal X-ray diffraction data was collected on a Bruker APEX II diffractometer with graphite-monochromatized Mo–K α radiation ($\lambda = 0.71073$ Å). The Bruker APEX II software package was used to collect and process the data. Semiempirical absorption corrections based on equivalent reflections were adopted. The structure was solved by direct methods and refined with full-matrix least-squares procedures using SHELX and WinGX. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated based on the geometry of related non-hydrogen atoms. No restraints or constraints were used during the refinement.

Synthesis of compound 4a. 4-(Pentafluorosulfanyl)aniline (2.2 g, 10 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (1:1, 25 mL), to which a solution of bromine (1.3 mL, 25 mmol) in mixed solvents of CH_2Cl_2 and MeOH (1:1, 25 mL) was added dropwise at rt. The reaction mixture was stirred at rt for 2 h before being poured into 50 mL of NaOH aqueous solution (20%) and extracted with Et_2O . The resulting organic layer was washed with water (3 x 50 mL) and dried over Na_2SO_4 . Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4a** as a light pink solid (2.8 g,

75%). Mp: 74.7-75.9 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.79 (s, 2H), 4.94 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 147.8, 143.6 (quintet, *J* = 19 Hz), 129.6 (quintet, *J* = 5 Hz), 106.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 84.8 (quintet, 1F, *J* = 150 Hz), 65.3 (d, 4F, *J* = 150 Hz). HRMS (EI-magnetic sector) *m/z*: [M]⁺ calcd for C₆H₄Br₂F₅NS 374.8351, found 374.8368.

Synthesis of compound 4b. To 2,6-dibromo-4-(pentafluorosulfanyl)aniline **4a** (2.3 g, 6.0 mmol) in a mixture of dichloroethane and acetic acid (1:1, 50 mL) was added dimethoxytetrahydrofuran (0.87 g, 6.6 mmol). The mixture was stirred under reflux for 24 hours. After cooling to room temperature, all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4b** as a light pink solid (2.2 g, 86%). Mp: 116.2-117.5 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.05 (s, 2H), 6.68 (d, 2H, *J* = 2 Hz), 6.41 (d, 2H, *J* = 2 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 153.4 (quintet, *J* = 5 Hz), 142.9, 130.0 (quintet, *J* = 6 Hz), 124.2, 121.1, 110.2; ¹⁹F NMR (282 MHz, CDCl₃): δ 84.8 (quintet, 1F, *J* = 150 Hz), 65.3 (d, 4F, *J* = 150 Hz). HRMS (EI-magnetic sector) *m/z*: [M]⁺ calcd for C₁₀H₆Br₂F₅NS 424.8508, found 424.8494.

Synthesis of compound 4c. To a mixture of 1-(2,6-dibromo-4-pentafluorosulfanylphenyl)-1*H*-pyrrole **4b** (2.1 g, 5.0 mmol), ethynyltrimethylsilane (1.5 g, 15.0 mmol), PdCl₂(PPh₃)₂ (175 mg, 0.25 mmol) and CuI (48 mg, 0.25 mmol) was added degassed NEt₃ (60 mL). The reaction mixture was stirred at 80 °C for 24 h. After cooling to room temperature, all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4c** as a white solid (1.9 g, 83%). Mp: 84.5-86.1 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.85 (s, 2H), 6.96 (t, 2H, *J* = 2 Hz), 6.26 (d, 2H, *J* = 2 Hz), 0.15 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ 151.1 (quintet, *J* = 19 Hz), 146.5, 130.8 (quintet, *J* = 4 Hz), 122.0, 121.7, 109.1, 102.4, 99.3, -0.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 82.5 (quintet, 1F, *J* = 150 Hz), 63.4 (d, 4F, *J* = 150 Hz). HRMS (EI-magnetic sector) *m/z*: [M]⁺ calcd for C₂₀H₂₄F₅NSSi₂ 461.1088, found 462.1097.

Synthesis of compound 4d. To 1-(4-(pentafluorosulfanyl)-2,6-bis((trimethylsilyl)ethynyl)phenyl)-1*H*-pyrrole **4c** (2.3 g, 5.0 mmol) in a mixture of THF

(25 mL) and MeOH (25 mL) was added KOH (0.8 g, 15.0 mmol) at 0 °C. The reaction mixture was allowed to warm to rt and stirred for 2 hours. Afterwards the mixture was poured into 50 mL of water and extracted with CH₂Cl₂. The organic layer was washed with brine (3× 20 mL), dried over anhydrous Na₂SO₄ and filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4d** as a white solid (1.5 g, 96%). Mp: 91.7-92.1 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.96 (s, 2H), 6.99 (t, 2H, *J* = 2 Hz), 6.36 (d, 2H, *J* = 2 Hz), 3.21 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 151.4 (quintet, *J* = 19 Hz), 146.5, 131.9 (quintet, *J* = 4 Hz), 122.2, 121.2, 109.7, 84.2, 79.1; ¹⁹F NMR (282 MHz, CDCl₃): δ 81.9 (quintet, 1F, *J* = 150 Hz), 63.2 (d, 4F, *J* = 150 Hz). HRMS (EI-magnetic sector) *m/z*: [M]⁺ calcd for C₁₄H₈F₅NS 317.0298, found 317.0283.

Synthesis of compound 4e. To a mixture of 1-(2,6-diethynyl-4-(pentafluorosulfanyl)-1H-pyrrole **4d** (0.32 g, 1.0 mmol), iodobenzene (0.43 g, 2.1 mmol), Pd(PPh₃)₄ (58 mg, 0.050 mmol), and CuI (4.0 mg, 0.02 mmol) was added degassed NEt₃ (20 mL). The reaction mixture was stirred at room temperature for 24 h. Afterwards all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4e** (0.40 g, 85%) as a white solid. Mp: 173.5-175.7 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.95 (s, 2H), 7.42-7.29 (m, 10H), 7.12 (d, 2H, *J* = 2 Hz), 6.42 (d, 2H, *J* = 2 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 151.5 (quintet, *J* = 19 Hz), 145.5, 131.8, 129.8 (quintet, *J* = 4 Hz), 129.3, 128.5, 122.6, 122.2, 122.1, 109.4, 95.8, 84.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 82.6 (quintet, 1F, *J* = 150 Hz), 63.3 (d, 4F, *J* = 150 Hz). HRMS (EI-magnetic sector) *m/z*: [M]⁺ calcd for C₂₆H₁₆F₅NS 469.0924, found 469.0897.

Synthesis of compound 4f. To a mixture of 1-(2,6-diethynyl-4-(pentafluorosulfanyl)-1H-pyrrole **4d** (0.32 g, 1.0 mmol), 4-bromophenylsulfur pentafluoride (0.85 g, 3.0 mmol), Pd(PPh₃)₄ (58 mg, 0.050 mmol), and CuI (4 mg, 0.02 mmol) was added degassed NEt₃ (20 mL). The reaction mixture was stirred at 80 °C for 24 h. Afterwards all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4f** (0.53 g, 73%) as a greenish solid. Mp: 203.1-205.2 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.01

(s, 2H), 7.73 (d, 2H, $J = 6$ Hz), 7.45 (d, 2H, $J = 6$ Hz), 7.07 (t, 2H, $J = 2$ Hz), 6.44 (t, 2H, $J = 2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 153.9 (quintet, $J = 18$ Hz), 151.8 (quintet, $J = 19$ Hz), 146.3, 132.0, 130.6 (quintet, $J = 4$ Hz), 126.3 (quintet, $J = 5$ Hz), 125.6, 122.6, 121.8, 109.8, 93.7, 86.8; ^{19}F NMR (282 MHz, CDCl_3): δ 83.5 (quintet, 2F, $J = 150$ Hz), 82.0 (quintet, 1F, $J = 150$ Hz), 63.3 (d, 4F, $J = 150$ Hz), 62.8 (d, 8F, $J = 150$ Hz). HRMS (EI-magnetic sector) m/z : $[\text{M}]^+$ calcd for $\text{C}_{26}\text{H}_{14}\text{F}_{15}\text{NS}_3$ 721.0049, found 721.0037.

Synthesis of compound 4g. To a mixture of 1-(2,6-diethynyl-4-(pentafluorosulfanyl)-1H-pyrrole **4d** (0.32 g, 1.0 mmol), 1,3-bis(pentafluorosulfanyl)-5-bromobenzene (1.0 g, 2.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.050 mmol), and CuI (4 mg, 0.02 mmol) was added degassed NEt_3 (20 mL). The reaction mixture was stirred at 80°C for 24 h. Afterwards all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford compound **4g** (0.71 g, 72.9%) as a greenish solid. Mp: $206.7\text{--}208.9^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 8.09 (t, 2H, $J = 2$ Hz), 8.05 (s, 2H), 7.85 (d, 4H, $J = 3$ Hz), 7.03 (t, 2H, $J = 3$ Hz), 6.49 (t, 2H, $J = 3$ Hz); ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ 154.2 (quintet, $J = 20$ Hz), 152.5 (quintet, $J = 19$ Hz), 148.2, 133.4 (quintet, $J = 4$ Hz), 132.0 (quintet, $J = 5$ Hz), 125.7, 125.3 (quintet, $J = 5$ Hz), 124.1, 122.5, 110.5, 92.6, 88.8. ^{19}F NMR (282 MHz, CDCl_3): δ 81.5 (quintet, 1F, $J = 150$ Hz), 80.8 (quintet, 4F, $J = 150$ Hz), 63.3 (d, 4F, $J = 150$ Hz), 63.1 (quintet, 16F, $J = 150$ Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{12}\text{F}_{25}\text{NS}_5$: C, 32.07; H, 1.24; N, 1.44; S, 16.46. Found C, 32.58; H, 1.68; N, 1.46; S, 16.54.

Synthesis of compound 4h. To a mixture of 1-(4-(pentafluorosulfanyl)-2,6-bis((4-(pentafluorosulfanyl)phenyl)ethynyl)phenyl)-1H-pyrrole **4f** (0.10 g, 0.14 mmol), InCl_3 (62 mg, 0.28 mmol) was added toluene (25 mL). The reaction mixture was stirred at 100°C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4h** (65 mg, 65%) as a yellow solid. Mp: $225.6\text{--}227.2^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 9.49 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz), 8.13 (d, 1H, $J = 3$ Hz), 8.08 (d, 1H, $J = 3$ Hz), 7.95-7.82 (m, 4H), 7.82-8.71 (m, 4H), 6.98 (s, 1H), 6.90 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz), 6.68 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 154.1 (quintet, $J = 18$ Hz), 154.0 (quintet, $J = 17$ Hz), 148.2 (quintet, $J = 19$ Hz),

141.3, 134.0, 133.3, 131.8, 131.6, 131.5 (quintet, $J = 5$ Hz), 128.7, 128.6, 127.5 (quintet, $J = 5$ Hz), 126.6 (quintet, $J = 5$ Hz), 125.9, 125.4, 118.3, 118.2, 113.9, 110.7, 105.2, 94.8, 90.5; ^{19}F NMR (282 MHz, CDCl_3): δ 85.2 (quintet, 1F, $J = 150$ Hz), 85.1 (quintet, 1F, $J = 150$ Hz), 83.6 (quintet, 1F, $J = 150$ Hz), 64.0 (d, 4F, $J = 150$ Hz), 63.2 (d, 4F, $J = 150$ Hz), 62.9 (d, 4F, $J = 150$ Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{14}\text{F}_{15}\text{NS}_3$: C, 43.28; H, 1.96; N, 1.94; S, 13.33. Found C, 43.29; H, 2.19; N, 1.90; S, 13.31.

Synthesis of compound 4i. To a mixture of 1-(2,6-bis((3,5-bis(pentafluorosulfanyl)phenyl)ethynyl)-4-(pentafluorosulfanyl)phenyl)-1H-pyrrole **4g** (0.10 g, 0.10 mmol), InCl_3 (44 mg, 0.20 mmol) was added xylene (25 mL). The reaction mixture was stirred at 120°C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4i** (71 mg, 71%) as a yellow solid. Mp: $237.4\text{--}240.7^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 9.40 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz), 8.26 (s, 3H), 8.22–8.14 (m, 5H), 7.06 (s, 1H), 6.97 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz), 6.64 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 154.2 (quintet, $J = 19$ Hz), 154.0 (quintet, $J = 17$ Hz), 148.4 (quintet, $J = 17$ Hz), 139.7, 134.1, 132.3 (quintet, $J = 14$ Hz), 131.9 (quintet, $J = 5$ Hz), 131.7, 131.0, 129.0 (quintet, $J = 5$ Hz), 128.3 (quintet, $J = 5$ Hz), 125.1, 124.7 (quintet, $J = 5$ Hz), 124.5, 124.4 (quintet, $J = 4$ Hz), 118.8, 118.6, 114.6, 110.0, 105.1, 93.0, 91.1; ^{19}F NMR (282 MHz, CDCl_3): δ 83.0 (quintet, 1F, $J = 150$ Hz), 81.3 (quintet, 2F, $J = 150$ Hz), 80.6 (quintet, 2F, $J = 150$ Hz), 64.1 (d, 4F, $J = 150$ Hz), 63.4 (d, 8F, $J = 150$ Hz), 63.3 (d, 8F, $J = 150$ Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{12}\text{F}_{25}\text{NS}_5$: C, 32.07; H, 1.24; N, 1.44; S, 16.46. Found C, 32.24; H, 1.45; N, 1.46; S, 16.57.

Synthesis of compound 4j. To a mixture of 1-(4-(pentafluorosulfanyl)-2,6-bis((4-(pentafluorosulfanyl)phenyl)ethynyl)phenyl)-1H-pyrrole **4f** (0.30 g, 0.42 mmol), I_2 (0.85 g, 3.4 mmol), NaHCO_3 (0.56 g, 6.7 mmol) was added 1,2-dichloroethane (100 mL). The reaction mixture was stirred at 50°C for 24 h, after which the reaction mixture was quenched with saturated NaSO_3 solution (60 mL) and extracted with dichloromethane (200 mL). The resulting organic layer was washed with water (3×50 mL) and dried over Na_2SO_4 . Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4j** as a

yellow solid (0.26 g, 73%). Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.49 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz), 8.71 (d, 1H, *J* = 3 Hz), 8.20 (d, 1H, *J* = 3 Hz), 7.96 (d, 2H, *J* = 9 Hz), 7.87 (d, 2H, *J* = 9 Hz), 7.76 (d, 2H, *J* = 9 Hz), 7.50 (d, 2H, *J* = 9 Hz), 6.79 (t, 1H, *J* = 3 Hz), 6.13 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.0 (quintet, *J* = 18 Hz), 153.8 (quintet, *J* = 17 Hz), 148.6 (quintet, *J* = 19 Hz), 145.1, 140.0, 134.0, 133.7 (quintet, *J* = 5 Hz), 132.8, 132.6 (quintet, *J* = 5 Hz), 131.8, 129.9, 126.7, 126.7 (quintet, *J* = 4.5 Hz), 126.6, 126.1, 125.7, 118.6, 114.0, 111.1, 107.1, 95.1, 91.6, 90.1; ¹⁹F NMR (282 MHz, CDCl₃): δ 83.9 (quintet, 1F, *J* = 150 Hz), 83.4 (quintet, 1F, *J* = 150 Hz), 83.3 (quintet, 1F, *J* = 150 Hz), 64.0 (d, 4F, *J* = 150 Hz), 63.2 (d, 4F, *J* = 150 Hz), 62.8 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₂₆H₁₃F₁₅INS₃: C, 36.85; H, 1.55; N, 1.65; S, 11.35. Found C, 36.99; H, 1.78; N, 1.62; S, 11.48.

Synthesis of compound 4k. To a mixture of 1-(2,6-bis((3,5-bis(pentafluorosulfanyl)phenyl)ethynyl)-4-(pentafluorosulfanyl)phenyl)-1H-pyrrole **4g** (0.30 g, 0.31 mmol), I₂ (0.88 g, 3.1 mmol), NaHCO₃ (0.52 g, 6.2 mmol) was added dichlorobenzene (100 mL). The reaction mixture was stirred at 105 °C for 24 h, after which the reaction mixture was quenched with saturated NaSO₃ solution (60 mL) and extracted with dichloromethane (200 mL). The resulting organic layer was washed with water (3×50 mL) and dried over Na₂SO₄. Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4k** as a yellow solid (0.26 g, 76%). Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.40 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz), 8.74 (d, 1H, *J* = 3 Hz), 8.31 (t, 1H, *J* = 1.5 Hz), 8.25 (d, 1H, *J* = 3 Hz), 8.23-8.13 (m, 3H), 8.00 (d, 2H, *J* = 3 Hz), 6.86 (t, 1H, *J* = 3 Hz), 6.19 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.0 (quintet, *J* = 19 Hz), 154.0 (quintet, *J* = 19 Hz), 148.8 (quintet, *J* = 17 Hz), 143.2, 138.0, 134.5 (quintet, *J* = 5 Hz), 134.1, 133.3 (quintet, *J* = 4 Hz), 132.4, 131.9 (quintet, *J* = 5 Hz), 130.5 (quintet, *J* = 5 Hz), 125.9, 124.8 (quintet, *J* = 4 Hz), 124.6 (quintet, *J* = 4 Hz), 124.3, 118.9, 114.7, 110.3, 107.1, 93.3, 92.6, 90.7; ¹⁹F NMR (282 MHz, CDCl₃): δ 82.6 (quintet, 1F, *J* = 150 Hz), 81.1 (quintet, 2F, *J* = 150 Hz), 80.6 (quintet, 2F, *J* = 150 Hz), 64.0 (d, 4F, *J* = 150 Hz), 63.5 (d, 8F, *J* = 150 Hz), 63.2 (d, 8F, *J* = 150 Hz). Anal. Calcd for C₂₆H₁₂F₂₅NS₅: C, 28.40; H, 1.01; N, 1.27; S, 14.58. Found C, 28.48; H, 1.33; N, 1.28; S, 14.89.

Synthesis of ullazine U1. To a mixture of 1-(4-(pentafluorosulfanyl)-2,6-bis(phenylethynyl)phenyl)-1H-pyrrole **4e** (0.10 g, 0.21 mmol), InCl₃ (92 mg, 0.42 mmol) was added toluene (25 mL). The reaction mixture was stirred at 120 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **U1** (83 mg, 83%) as a yellow solid. Mp: 233.7- 236.2 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.89 (s, 2H), 7.82-7.76 (m, 4H), 7.60-7.46 (m, 6H), 7.32 (s, 2H), 7.20 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 149.9 (quintet, *J* = 17 Hz), 138.0, 135.1, 132.8, 129.0, 128.9, 128.3, 127.1, 125.6, 119.0, 116.5 (quintet, *J* = 5 Hz), 107.8; ¹⁹F NMR (282 MHz, CDCl₃): δ 85.2 (quintet, 1F, *J* = 150 Hz), 65.0 (d, 4F, *J* = 150 Hz). HRMS (ESI-TOF) *m/z*: [M]⁺ calcd for C₂₆H₁₆F₅NS 469.0924, found 469.0911.

Synthesis of ullazine U2. To a mixture of 1-(4-(pentafluorosulfanyl)-2,6-bis((4-(pentafluorosulfanyl)phenyl)ethynyl)phenyl)-1H-pyrrole **4f** (0.10 g, 0.14 mmol), InCl₃ (62 mg, 0.28 mmol) was added *o*-dichlorobenzene (25 mL). The reaction mixture was stirred at 160 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **U2** (81 mg, 81%) as a yellow solid. Mp: 245.8-247.1 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.99-7.93 (m, 6H), 7.92-7.85 (m, 4H), 7.35 (s, 2H), 7.18 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 154.1 (quintet, *J* = 18 Hz), 150.1 (quintet, *J* = 17 Hz), 141.2, 133.2, 128.6, 126.9 (quintet, *J* = 5 Hz), 126.7, 125.3, 120.0, 117.6 (quintet, *J* = 5 Hz), 107.9; ¹⁹F NMR (282 MHz, CDCl₃): δ 85.1 (quintet, 2F, *J* = 150 Hz), 84.0 (quintet, 1F, *J* = 150 Hz), 64.9 (d, 4F, *J* = 150 Hz), 63.2 (d, 8F, *J* = 150 Hz). Anal. Calcd for C₂₆H₁₄F₁₅NS₃: C, 43.28; H, 1.96; N, 1.94; S, 13.33. Found C, 43.88; H, 2.59; N, 1.77; S, 11.99.

Synthesis of ullazine U3. To a mixture of 1-(2,6-bis((3,5-bis(pentafluorosulfanyl)phenyl)ethynyl)-4-(pentafluorosulfanyl)phenyl)-1H-pyrrole **4g** (0.10 g, 0.10 mmol), InCl₃ (44 mg, 0.20 mmol) was added *o*-dichlorobenzene (25 mL). The reaction mixture was stirred at 175 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **U3** (82

mg, 82%) as a yellow solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.35 (d, 4H, *J* = 1.5 Hz), 8.29 (t, 2H, *J* = 1.5 Hz), 8.07 (s, 2H), 7.43 (s, 2H), 7.14 (s, 2H); ¹³C NMR (75 MHz, THF-d₈): δ 155.1 (quintet, *J* = 19 Hz), 151.1 (quintet, *J* = 17 Hz), 141.3, 134.4, 132.2, 130.3 (quintet, *J* = 4 Hz), 127.4, 126.3, 125.3 (quintet, *J* = 5 Hz), 122.4, 119.6 (quintet, *J* = 5 Hz), 108.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 84.4 (quintet, 1F, *J* = 150 Hz), 81.2 (quintet, 4F, *J* = 150 Hz), 64.9 (d, 4F, *J* = 150 Hz), 63.4 (d, 16F, *J* = 150 Hz). Anal. Calcd for C₂₆H₁₂F₂₅NS₅: C, 32.07; H, 1.24; N, 1.44; S, 16.46. Found C, 32.10; H, 2.07; N, 1.38; S, 18.47.

Synthesis of compound U5. To a mixture of 5-iodo-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4j** (0.10 g, 0.12 mmol), InCl₃ (53 mg, 0.24 mmol) was added dichlorobenzene (25 mL). The reaction mixture was stirred at 145 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **U5** (58 mg, 58%) as a yellow solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.39 (d, 1H, *J* = 1.5 Hz), 8.09 (d, 1H, *J* = 1.5 Hz), 8.03-7.91 (m, 4H), 7.89 (d, 2H, *J* = 9 Hz), 7.60 (d, 2H, *J* = 9 Hz), 7.50 (s, 1H), 7.12 (d, 1H, *J* = 3 Hz), 6.73 (d, 1H, *J* = 3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.2 (quintet, *J* = 19 Hz), 150.6 (quintet, *J* = 19 Hz), 149.5 (quintet, *J* = 19 Hz), 144.3, 140.9, 139.1, 133.0, 131.7, 130.1, 128.7, 127.8, 127.0 (quintet, *J* = 5 Hz), 126.8 (quintet, *J* = 5 Hz), 125.1, 123.6 (quintet, *J* = 4 Hz), 120.6, 119.0 (quintet, *J* = 4 Hz), 109.3, 108.0, 93.8; ¹⁹F NMR (282 MHz, CDCl₃): δ 84.6 (quintet, 1F, *J* = 150 Hz), 84.1 (quintet, 1F, *J* = 150 Hz), 83.9 (quintet, 1F, *J* = 150 Hz), 65.0 (d, 4F, *J* = 150 Hz), 63.2 (d, 4F, *J* = 150 Hz), 62.2 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₂₆H₁₃F₁₅INS₃: C, 36.85; H, 1.55; N, 1.65; S, 11.35. Found C, 36.71; H, 1.94; N, 1.61; S, 11.23.

Synthesis of compound U6. To a mixture of 4-(3,5-bis(pentafluorosulfanyl)-9-((3,5-bis(pentafluorosulfanyl)phenyl)ethynyl)-5-iodo-7-(pentafluorosulfanyl)pyrrolo[1,2a]quinoline **4k** (0.10 g, 0.090 mmol), InCl₃ (40 mg, 0.18 mmol) was added dichlorobenzene (25 mL). The reaction mixture was stirred at 175 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and

dichloromethane (9:1 v/v) as eluent to afford **U6** (65 mg, 65%) as a yellow solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.45 (d, 1H, *J* = 3 Hz), 8.37-8.27 (m, 4H), 8.19 (d, 1H, *J* = 1.5 Hz), 8.10 (d, 1H, *J* = 1.5 Hz), 7.58 (s, 1H), 7.09 (d, 1H, *J* = 3 Hz), 6.78 (d, 1H, *J* = 3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.4 (quintet, *J* = 19 Hz), 154.1 (quintet, *J* = 20 Hz), 150.8 (quintet, *J* = 19 Hz), 142.3, 139.3, 137.1, 131.8, 131.4, 130.7 (quintet, *J* = 4 Hz), 128.9 (quintet, *J* = 4 Hz), 127.6, 126.7, 126.5, 124.9, 124.8, 124.7, 124.6, 121.5, 120.0 (quintet, *J* = 4 Hz), 109.3, 107.9, 95.1; ¹⁹F NMR (282 MHz, CDCl₃): δ 83.9 (quintet, 1F, *J* = 150 Hz), 81.1 (quintet, 2F, *J* = 150 Hz), 81.1 (quintet, 2F, *J* = 150 Hz), 65.0 (d, 4F, *J* = 150 Hz), 63.4 (d, 8F, *J* = 150 Hz), 63.4 (d, 8F, *J* = 150 Hz). Anal. Calcd for C₂₆H₁₂F₂₅NS₅: C, 28.40; H, 1.01; N, 1.27; S, 14.58. Found C, 29.24; H, 1.66; N, 1.31; S, 14.46.

Synthesis of compound 4i. To a mixture of 5-iodo-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4j** (0.10 g, 0.12 mmol), CuCN (16 mg, 0.18 mmol) was added DMF (20 mL). The reaction mixture was stirred at 110 °C for 16 h, after which the reaction mixture was filtered. The filtrate was poured into dichloromethane (60 mL) and washed with brine (2 x 20 mL) and dried over Na₂SO₄. Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (4:1 v/v) as eluent to afford **4i** (67 mg, 75 %) as a yellow solid. Mp: 289.7-292.4 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.67 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz), 8.52 (d, 1H, *J* = 3 Hz), 8.25 (d, 1H, *J* = 3 Hz), 8.03-7.95 (m, 2H), 7.92-7.83 (m, 2H), 7.80 (m, 4H), 7.01 (dd, 1H, *J* = 6 Hz, *J* = 3 Hz), 6.73 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 155.1 (quintet, *J* = 18 Hz), 154.4 (quintet, *J* = 18 Hz), 149.2 (quintet, *J* = 20 Hz), 141.1, 137.7, 133.2, 133.0 (quintet, *J* = 5 Hz), 131.9, 130.7, 129.8, 127.0 (quintet, *J* = 5 Hz), 126.8 (quintet, *J* = 5 Hz), 125.6 (quintet, *J* = 5 Hz), 125.3, 122.6, 121.8, 115.9, 115.8, 111.7, 111.6, 99.6, 96.0, 89.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 83.2 (quintet, 1F, *J* = 150 Hz), 83.1 (quintet, 1F, *J* = 150 Hz), 82.2 (quintet, 1F, *J* = 150 Hz), 64.0 (d, 4F, *J* = 150 Hz), 63.0 (d, 4F, *J* = 150 Hz), 62.8 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₂₇H₁₃F₁₅N₂S₃: C, 43.44; H, 1.76; N, 3.75; S, 12.88. Found C, 43.42; H, 2.15; N, 3.61; S, 12.79.

Synthesis of compound U7. To a mixture of 7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)-9-((4-(pentafluorosulfanyl)ethynyl)pyrrolo[1,2-a]quinoline-5-

carbonitrile **4l** (0.10 g, 0.13 mmol), InCl₃ (57 mg, 0.26 mmol) was added dichlorobenzene (20 mL). The reaction mixture was stirred at 180 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (4:1 v/v) as eluent to afford **U7** (80 mg, 80%) as an orange solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.18 (s, 1H), 8.03 (s, 1H), 8.03-7.80 (m, 4H), 7.78 (d, 4H, *J* = 9 Hz), 7.18 (d, 1H, *J* = 3 Hz), 7.08 (d, 1H, *J* = 6 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 155.2 (quintet, *J* = 18 Hz), 154.4 (quintet, *J* = 18 Hz), 150.8 (quintet, *J* = 19 Hz), 140.8, 140.2, 137.4, 133.3, 132.6, 129.8, 129.4, 128.6, 127.2 (quintet), 127.1 (quintet), 126.1, 125.4, 123.2, 122.6, 119.4 (quintet, *J* = 4 Hz), 116.8 (quintet, *J* = 4 Hz), 115.9, 113.0, 110.3, 100.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 83.6 (quintet, 2F, *J* = 150 Hz), 83.1 (quintet, 1F, *J* = 150 Hz), 65.0 (d, 4F, *J* = 150 Hz), 63.1 (d, 4F, *J* = 150 Hz), 63.0 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₂₇H₁₃F₁₅N₂S₃: C, 43.44; H, 1.76; N, 3.75; S, 12.88. Found C, 42.97; H, 2.04; N, 3.57; S, 12.82.

Synthesis of compound U7. To a mixture of 4-iodo-6-(pentafluorosulfanyl)-3,9-bis(4-(pentafluorosulfanyl)phenyl)indolizino[6,5,4,3-*ija*]quinoline **U5** (0.10 g, 0.12 mmol), CuCN (16 mg, 0.18 mmol) was added DMF (20 mL). The reaction mixture was stirred at 110 °C for 16 h, after which the reaction mixture was filtered. The filtrate was poured into dichloromethane (60 mL) and washed with brine (2 x 20 mL) and dried over Na₂SO₄. Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (4:1 v/v) as eluent to afford **U7** (69 mg, 77 %) as an orange solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.18 (s, 1H), 8.03 (s, 1H), 8.03-7.80 (m, 4H), 7.78 (d, 4H, *J* = 9 Hz), 7.18 (d, 1H, *J* = 3 Hz), 7.08 (d, 1H, *J* = 6 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 155.2 (quintet, *J* = 18 Hz), 154.4 (quintet, *J* = 18 Hz), 150.8 (quintet, *J* = 19 Hz), 140.8, 140.2, 137.4, 133.3, 132.6, 129.8, 129.4, 128.6, 127.2 (quintet), 127.1 (quintet), 126.1, 125.4, 123.2, 122.6, 119.4 (quintet, *J* = 4 Hz), 116.8 (quintet, *J* = 4 Hz), 115.9, 113.0, 110.3, 100.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 83.6 (quintet, 2F, *J* = 150 Hz), 83.1 (quintet, 1F, *J* = 150 Hz), 65.0 (d, 4F, *J* = 150 Hz), 63.1 (d, 4F, *J* = 150 Hz), 63.0 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₂₇H₁₃F₁₅N₂S₃: C, 43.44; H, 1.76; N, 3.75; S, 12.88. Found C, 42.97; H, 2.04; N, 3.57; S, 12.82.

Synthesis of compound 4m. To a mixture of 5-iodo-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4j** (0.60 g, 0.71 mmol), ethynyltrimethylsilane (0.14 g, 1.42 mmol), PdCl₂(PPh₃)₂ (25 mg, 36 μmol) and CuI (7.0 mg, 36 μmol) was added degassed NEt₃ (60 mL). The reaction mixture was stirred at 50 °C for 24 h, after which all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to remove the minor impurities and afford a yellow solid. To the yellow solid in a mixture of THF (10 mL) and MeOH (10 mL) was added KOH (0.080 g, 1.4 mmol) at 0 °C. The reaction solution was allowed to warm to rt and stirred for 2 hours. Afterwards the reaction solution was poured into 50 mL of water and extracted with CH₂Cl₂. The organic layer was washed with brine (3× 20 mL), dried over anhydrous Na₂SO₄ and filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4m** as a yellow solid (0.36 g, 67%). Mp: 267.8-269.3 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.51 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz), 8.74 (d, 1H, *J* = 3 Hz), 8.18 (d, 1H, *J* = 3 Hz), 8.93-7.79 (m, 4H), 7.78-7.68 (m, 4H), 6.88 (dd, 1H, *J* = 6 Hz, *J* = 3 Hz), 6.46 (dd, 1H, *J* = 6 Hz, *J* = 3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.1 (quintet, *J* = 20 Hz), 148.6 (quintet, *J* = 19 Hz), 139.9, 137.4, 133.7, 132.2 (quintet, *J* = 4 Hz), 131.8, 130.2, 126.7 (quintet, *J* = 4 Hz), 126.7, 126.6, 126.3 (quintet, *J* = 5 Hz), 125.8, 124.8, 119.5, 114.6, 110.9, 108.8, 108.1, 95.0, 90.4, 87.2, 78.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 84.1 (quintet, 1F, *J* = 150 Hz), 83.4 (quintet, 1F, *J* = 150 Hz), 83.3 (quintet, 1F, *J* = 150 Hz), 64.0 (d, 4F, *J* = 150 Hz), 63.2 (d, 4F, *J* = 150 Hz), 62.9 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₂₈H₁₄F₁₅NS₃: C, 45.11; H, 1.89; N, 1.88; S, 12.90. Found C, 45.36; H, 2.17; N, 1.76; S, 12.76.

Synthesis of compound 4n. To a mixture of 5-ethynyl-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4m** (0.20 g, 0.27 mmol), 4-bromophenylsulfur pentafluoride (0.12 g, 0.41 mmol), Pd(PPh₃)₄ (16 mg, 14 μmol), and CuI (0.1 mg, 5 μmol) was added degassed NEt₃ (35 mL). The reaction mixture was stirred at 80 °C for 24 h. Afterwards all volatiles were evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **4n** (0.16 g, 63%) as a yellow solid. Mp: >

300 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.55 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz), 8.76 (d, 2H, *J* = 3 Hz), 8.21 (d, 2H, *J* = 3 Hz), 8.03-7.90 (m, 2H), 7.90-7.82 (m, 2H), 7.83-7.70 (m, 6H), 7.32 (d, 2H, *J* = 9 Hz), 6.92 (dd, 1H, *J* = 6 Hz, *J* = 3 Hz), 6.55 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz); ¹³C NMR (75 MHz, THF-d₈): δ 154.7 (quintet, *J* = 17 Hz), 154.7 (quintet, *J* = 18 Hz), 154.0 (quintet, *J* = 17 Hz), 149.0, 141.0, 138.0, 134.5, 132.7, 132.6 (quintet, *J* = 5 Hz), 132.5, 132.0, 131.3, 127.2 (quintet, *J* = 5 Hz), 127.0 (quintet, *J* = 5 Hz), 126.7, 126.6, 125.2, 120.8, 115.5, 111.9, 109.3, 109.3, 97.4, 96.1, 90.4, 88.2; ¹⁹F NMR (282 MHz, CDCl₃): δ 81.7 (quintet, F, *J* = 150 Hz), 81.3 (quintet, 1F, *J* = 150 Hz), 81.2 (quintet, 1F, *J* = 150 Hz), 80.9 (quintet, 1F, *J* = 150 Hz), 61.3 (d, 4F, *J* = 150 Hz), 60.5 (d, 4F, *J* = 150 Hz), 60.2 (d, 4F, *J* = 150 Hz), 60.2 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₃₄H₁₇F₂₀NS₄: C, 43.09; H, 1.81; N, 1.48; S, 13.53. Found C, 43.23; H, 1.94; N, 1.42; S, 13.52.

Synthesis of compound U8. To a mixture of 7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)-5,9-bis((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4n** (0.10 g, 0.11 mmol), InCl₃ (49 mg, 0.22 mmol) was added dichlorobenzene (20 mL). The reaction mixture was stirred at 145 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (9:1 v/v) as eluent to afford **U8** (42 mg, 42%) as an orange solid. Mp: > 300 °C. ¹H NMR (300 MHz, THF-d₈): δ 8.46 (d, 2H, *J* = 3 Hz), 8.34 (d, 2H, *J* = 3 Hz), 8.16-8.13 (m, 2H), 8.10-8.01 (m, 6H), 7.83-7.86 (m, 2H), 7.81 (s, 1H), 7.56 (d, 2H, *J* = 9 Hz), 7.41 (d, 1H, *J* = 6 Hz), 7.22 (d, 1H, *J* = 3 Hz); ¹³C NMR (75 MHz, THF-d₈): δ 154.8 (quintet, *J* = 17 Hz), 154.6 (quintet, *J* = 17 Hz), 154.1 (quintet, *J* = 17 Hz), 150.9 (quintet, *J* = 17 Hz), 141.9, 140.7, 137.4, 133.5, 133.3, 132.3, 131.4, 129.6, 128.7, 127.7, 127.5 (quintet, *J* = 5 Hz), 127.2 (quintet, *J* = 5 Hz), 127.1 (quintet, *J* = 5 Hz), 127.1 (quintet, *J* = 5 Hz), 126.4, 125.3, 122.1, 119.2 (quintet, *J* = 5 Hz), 117.0 (quintet, *J* = 5 Hz), 111.5, 110.8, 109.8, 98.1, 88.3; ¹⁹F NMR (282 MHz, THF-d₈): δ 82.6 (quintet, F, *J* = 150 Hz), 81.9 (quintet, 1F, *J* = 150 Hz), 81.8 (quintet, 1F, *J* = 150 Hz), 81.4 (quintet, 1F, *J* = 150 Hz), 62.3 (d, 4F, *J* = 150 Hz), 60.5 (d, 8F, *J* = 150 Hz), 60.3 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₃₄H₁₇F₂₀NS₄: C, 43.09; H, 1.81; N, 1.48; S, 13.53. Found C, 43.12; H, 1.98; N, 1.41; S, 13.65.

Synthesis of compound 4o. To a mixture of 5-iodo-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4j** (0.20 g, 0.24 mmol), (4-(pentafluorosulfanyl)phenyl)boronic acid (89 mg, 0.36 mmol), Pd(PPh₃)₄ (14 mg, 12 μmol), and K₂CO₃ (66 mg, 0.48 mmol) was added degassed DMF (20 mL). The reaction mixture was stirred at 110 °C for 16 h, after which the reaction mixture was filtered. The filtrate was poured into dichloromethane (60 mL) and washed with brine (2 x 20 mL) and dried over Na₂SO₄. Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (6:1 v/v) as eluent to afford **4o** (0.153 g, 69 %) as a yellow solid. Mp: > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.55 (dd, 1H, *J* = 3 Hz, *J* = 1.5 Hz), 8.17 (d, 2H, *J* = 3 Hz), 7.90-7.82 (d, 2H, *J* = 3 Hz), 7.81-7.63 (m, 7H), 7.35-7.21 (m, 4H), 6.88 (t, 1H, *J* = 4 Hz, *J* = 3 Hz), 6.33 (dd, 1H, *J* = 4 Hz, *J* = 1.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.2 (quintet, *J* = 18 Hz), 153.4 (quintet, *J* = 18 Hz), 153.4 (quintet, *J* = 18 Hz), 148.2 (quintet, *J* = 18 Hz), 140.0, 139.7, 134.2, 132.1, 132.1, 131.9 (quintet, *J* = 4 Hz), 131.8, 131.7, 130.3, 126.7 (quintet, *J* = 5 Hz), 126.4 (quintet, *J* = 5 Hz), 126.2 (quintet, *J* = 5 Hz), 126.0, 125.8, 125.5, 118.7, 114.3, 111.1, 107.0, 95.1, 90.5; ¹⁹F NMR (282 MHz, CDCl₃): δ 83.8 (quintet, F, *J* = 150 Hz), 83.6 (quintet, 1F, *J* = 150 Hz), 83.4 (quintet, 1F, *J* = 150 Hz), 83.3 (quintet, 1F, *J* = 150 Hz), 63.8 (d, 4F, *J* = 150 Hz), 63.1 (d, 4F, *J* = 150 Hz), 63.0 (d, 4F, *J* = 150 Hz), 62.9 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₃₂H₁₇F₂₀NS₄: C, 41.61; H, 1.86; N, 1.52; S, 13.88. Found C, 41.70; H, 2.14; N, 1.48; S, 13.76.

Synthesis of compound U9. To a mixture of 7-(pentafluorosulfanyl)-4,5-bis(4-(pentafluorosulfanyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4o** (0.10 g, 0.11 mmol), InCl₃ (49 mg, 0.22 mmol) was added dichlorobenzene (20 mL). The reaction mixture was stirred at 150 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by silica gel column chromatography using hexane and dichloromethane (6:1 v/v) as eluent to afford **U9** (78 mg, 78%) as a yellow solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.04 (d, 1H, *J* = 3 Hz), 7.99 (d, 2H, *J* = 9 Hz), 7.91 (d, 2H, *J* = 9 Hz), 7.81 (d, 2H, *J* = 8.8 Hz), 7.75 (d, 2H, *J* = 9 Hz), 7.55 (d, 1H, *J* = 3 Hz), 7.43 (s, 1H), 7.39 (d, 2H, *J* = 6 Hz), 7.35 (d, 2H, *J* = 6 Hz), 7.18 (d, 1H, *J* = 3 Hz), 6.89 (d, 1H, *J* = 6 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.2 (quintet, *J* = 17 Hz), 153.6 (quintet, *J* = 18 Hz), 153.5 (quintet, *J* = 18 Hz), 150.2 (quintet,

$J = 17$ Hz), 141.0, 139.6, 139.4, 133.2, 131.7, 131.0, 130.4, 128.6, 128.4, 127.7, 127.1 (quintet, $J = 5$ Hz), 127.0, 126.4 (quintet, $J = 4$ Hz), 125.5, 125.4, 120.2, 118.3 (quintet, $J = 5$ Hz), 116.4 (quintet, $J = 5$ Hz), 109.3, 108.0; ^{19}F NMR (282 MHz, CDCl_3): δ 84.8 (quintet, F, $J = 150$ Hz), 84.3 (quintet, 1F, $J = 150$ Hz), 84.0 (quintet, 1F, $J = 150$ Hz), 83.7 (quintet, 1F, $J = 150$ Hz), 64.7 (d, 4F, $J = 150$ Hz), 63.2 (d, 4F, $J = 150$ Hz), 63.0 (d, 4F, $J = 150$ Hz), 63.0 (d, 4F, $J = 150$ Hz). Anal. Calcd for $\text{C}_{32}\text{H}_{17}\text{F}_{20}\text{NS}_4$: C, 41.61; H, 1.86; N, 1.52; S, 13.88. Found C, 41.64; H, 2.16; N, 1.47; S, 14.02.

Synthesis of compound 4p. To a mixture of 5-iodo-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4j** (0.20 g, 0.24 mmol), (4-(pentafluorosulfanyl)phenyl)boronic acid (55 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (14 mg, 12 μmol), and K_2CO_3 (66 mg, 0.48 mmol) was added degassed DMF (20 mL). The reaction mixture was stirred at 110 °C for 16 h, after which the reaction mixture was filtered. The filtrate was poured into dichloromethane (60 mL) and washed with brine (2 x 20 mL) and dried over Na_2SO_4 . Afterwards, the volatiles were evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (4:1 v/v) as eluent to afford **4p** (0.143 g, 72 %) as a yellow solid. Mp: > 300 °C. ^1H NMR (300 MHz, CDCl_3): δ 9.51 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz), 8.13 (d, 2H, $J = 1.5$ Hz), 7.90-7.82 (m, 3H), 7.78 (d, 2H, $J = 9$ Hz), 7.68 (d, 2H, $J = 9$ Hz), 7.34 (d, 2H, $J = 6$ Hz), 7.04 (d, 2H, $J = 9$ Hz), 6.90-6.80 (m, 3H), 6.28 (dd, 1H, $J = 3$ Hz, $J = 1.5$ Hz), 3.85 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 159.1, 153.9 (quintet, $J = 18$ Hz), 152.8 (quintet, $J = 17$ Hz), 147.9 (quintet, $J = 19$ Hz), 140.8, 134.1, 132.5, 132.2, 131.6, 131.4 (quintet), 130.3, 128.0, 127.4, 126.8 (quintet, $J = 5$ Hz), 126.6, 126.5 (quintet, $J = 5$ Hz), 125.9, 125.7 (quintet, $J = 5$ Hz), 117.9, 114.1, 113.7, 110.5, 105.8, 94.5, 90.7, 55.2; ^{19}F NMR (282 MHz, CDCl_3): δ 84.5 (quintet, F, $J = 150$ Hz), 83.7 (quintet, 1F, $J = 150$ Hz), 83.5 (quintet, 1F, $J = 150$ Hz), 63.8 (d, 4F, $J = 150$ Hz), 63.1 (d, 4F, $J = 150$ Hz), 62.9 (d, 4F, $J = 150$ Hz). Anal. Calcd for $\text{C}_{33}\text{H}_{20}\text{F}_{15}\text{NOS}_3$: C, 47.89; H, 2.44; N, 1.69; S, 11.62. Found C, 46.89; H, 2.80; N, 1.58; S, 10.91.

Synthesis of compound U10. To a mixture of 5-(4-methoxyphenyl)-7-(pentafluorosulfanyl)-4-(4-(pentafluorosulfanyl)phenyl)-9-((4-(pentafluorosulfanyl)phenyl)ethynyl)pyrrolo[1,2-a]quinoline **4p** (0.10 g, 0.12 mmol),

InCl₃ (53 mg, 0.24 mmol) was added *o*-dichlorobenzene (20 mL). The reaction mixture was stirred at 140 °C for 24 h, after which the reaction mixture was filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (4:1 v/v) as eluent to afford **U10** (73 mg, 73%) as a yellow solid. Mp: > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.00-7.94 (m, 3H), 7.91 (d, 2H, *J* = 9 Hz), 7.75-7.64 (m, 3H), 7.43 (d, 2H, *J* = 9 Hz), 7.38 (s, 1H), 7.16-7.09 (m, 3H), 6.95-6.87 (d, 2H, *J* = 9 Hz), 6.86 (d, 1H, *J* = 6 Hz), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 159.4, 154.0 (quintet, *J* = 17 Hz), 153.1 (quintet, *J* = 17 Hz), 150.1 (quintet, *J* = 17 Hz), 141.3, 140.6, 133.2, 132.9, 131.6, 131.0, 130.8, 130.6, 128.6, 128.1, 127.4, 126.9 (quintet, *J* = 5 Hz), 126.5, 126.4, 126.0 (quintet, *J* = 5 Hz), 125.3, 119.8, 117.8 (quintet, *J* = 4 Hz), 117.2 (quintet, *J* = 5 Hz), 114.8, 108.5, 107.5, 55.4; ¹⁹F NMR (282 MHz, CDCl₃): δ 85.3 (quintet, *F*, *J* = 150 Hz), 84.4 (quintet, 1F, *J* = 150 Hz), 84.1 (quintet, 1F, *J* = 150 Hz), 67.8 (d, 4F, *J* = 150 Hz), 63.2 (d, 4F, *J* = 150 Hz), 63.2 (d, 4F, *J* = 150 Hz). Anal. Calcd for C₃₃H₂₀F₁₅NOS₃: C, 47.89; H, 2.44; N, 1.69; S, 11.62. Found C, 46.85; H, 2.88; N, 1.59; S, 11.05.

4.5 References

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Chapter 5. Conclusion and Outlook

5.1 Conclusion

Even though the synthesis of pentafluorosulfanyl (SF_5) arenes was first reported about 60 years ago,¹ it did not receive much attention for the following 40 years due to the challenging synthesis and low accessibility. The situation has changed in the past two decades.² New methods to prepare SF_5 arenes in large scales and diverse commercial SF_5 arenes have become available, which has significantly advanced the application of SF_5 , particularly in medicinal chemistry and agrochemicals,³⁻⁶ but to a lesser extent in optoelectronic materials. Nonetheless, recent research studies have employed SF_5 in various molecular designs to afford a variety of optoelectronically active materials such as phosphorescent emitters, triboluminescent materials, fullerene type acceptor materials and several types of organic dyes.⁷ And the SF_5 group had demonstrated its effectiveness as a strong electron-withdrawing group, which is also bulky, hydrophobic, chemically and thermally stable, in manipulating the electronic and photophysical properties of these molecules. However, SF_5 moieties remained unexplored in the structures designed for a large number of optoelectronic materials such as NLO materials, TADF emitters for OLEDs, donor and acceptor materials for OSCs, and n-type semiconductors for OFETs.

Herein, this thesis set out to explore the utilization of the SF_5 group in three different types of optoelectronic materials, i.e., two-photon absorption dyes, polymer electrets for nonvolatile OFET memory devices, and ullazine dyes as potential photosensitizers for DSSCs. To that end, SF_5 was employed in three different molecular designs to achieve the corresponding specific aims and these new materials were prepared and characterized herein.

Chapter Two applied the SF_5 arene as an acceptor in a series of multibranched triarylamine-based push-pull dyes and investigated the influence of SF_5 on their two-photon absorption properties. Owing to the exceptionally robust electron-withdrawing ability of SF_5 with its inductive and resonance effects, these SF_5 -containing push-pull dyes all displayed very large two-photon absorption cross-sections (δ_{TPA}) ranging from 1100–2200 GM. As was exemplified by **D1** and **D2**, their δ_{TPA} and $\delta_{\text{TPA}}/N_\pi$ (N_π : the

effective number of π -electrons) values were substantially higher than their corresponding analogues bearing other electron-withdrawing groups, such as carbonyl and cyano group. This work suggested that the SF₅ arene is an excellent choice as an acceptor in a relatively small π -conjugated donor-acceptor system in providing large two-photon absorption cross-sections.

In Chapter Three, the SF₅ groups were installed onto two styrenic polymers, which were used as the electron-trapping electrets in nonvolatile OFET memory devices. During the operation of the memory devices, both SF₅-functionalized polymer electrets displayed remarkable electron-trapping capabilities (with large memory windows), excellent thermal stability, long retention times and stable irreversibilities spanning multiple programming/erasing cycles. The overall superior properties of the two SF₅-functionalized polymers over other polar styrenic polymers can be attributed to the unique properties of the SF₅ group, which includes high electronegativity, hydrophobicity, and bulkiness. Such unique properties of SF₅ also distinguish it from other polar functional groups as these properties are usually exclusive. In view of the previously held belief that polar moieties were detrimental to the performance of polymer electrets in OFET memory devices, the findings of this study have provided fresh insight into the possibility of developing novel electrets with the polar SF₅ group.

In Chapter Four, a series of SF₅-functionalized ullazine dyes were designed with the expectation that the addition of SF₅ moieties to the ullazines would boost their efficiencies and stability as the photosensitizers in DSSC devices. Thanks to the chemical and thermal robustness of SF₅ groups, the SF₅-functionalized ullazine dyes were successfully synthesized via two critical cyclization steps in harsh conditions (high temperature) without showing any sign of decomposition. In the subsequent photophysical and electrochemical studies of these SF₅-functionalized ullazines, **U8** showed interesting properties that may be suited to DSSC applications due to the following reasons: 1) Owing to strong ICT effect resulting from the electronic interactions between the SF₅ arene acceptor and ullazine core donor, **U8** displayed a relatively strong and broad absorption which was critical for harvesting solar energy. 2) The observed reversible oxidation peak of **U8** in the electrochemical study indicated that its cation form (excited state) was sufficiently stable

to revert back to the ground state during the DSSC operation cycles, which could be attributed to the stabilization effects of pendent SF₅-phenyls at C3 and C9, as well as the direct substitution of SF₅ at the C6 of ullazine. 3) The oxidation and excited-state potentials of **U8** matched well with the conduction band potential of TiO₂ and redox potential of I⁻/I₃⁻ to complete the circuit. Overall, this study indicates that SF₅-functionalized ullazines are of interest for DSSC applications and their performance in DSSC devices needs to be further evaluated in the future study.

In conclusion, my studies again prove that the SF₅ group is an effective and versatile tool in manipulating the optoelectronic properties of different materials and further expand the utilization of SF₅ in the new fields that were not explored before.⁷ In all, the SF₅ moiety has the following attractive features: 1) strongly electron-withdrawing; 2) chemically and thermally stable; 3) lipophilic and hydrophobic; 4) sterically bulky; 5) able to form noncovalent contacts (e.g., CH $\cdots$ F interactions). In particular, the electron-withdrawing nature and the chemical/thermal stability of SF₅ have a more significant impact on the intrinsic electronic/photophysical properties and stability of a material at the molecular level, respectively. Impact of such includes lowering the HOMO/LUMO energy levels of an organic system, inducing a strong ICT effect in a donor-acceptor system, increasing the electron affinities, enhancing the overall stability of a material, etc. While the lipophilicity/hydrophobicity and steric bulk of the SF₅ and its ability to form noncovalent contacts mainly affect the intermolecular interactions of a material that governs its properties as a whole, such as charge mobility associated with the morphology, aggregation emission behaviour and processibility, etc. Taken together, these features of SF₅ render it highly adaptable for a wide range of optoelectronic materials as each feature may have a significant role in manipulating the optoelectronic properties of a studied material. However, one potential weakness of the SF₅, as stated in section 1.3.4, is its instability upon receiving electrons,⁸ which may pose a problem when employed in materials that transport electrons, such as organic n-type semiconductors for OFETs and acceptor materials for bulk-heterojunction OSCs.

5.2 Outlook

Regarding the future work based on two-photon absorption dyes in Chapter two, new SF₅-functional push-pull dyes can be modified to improve the two-photon absorption properties, such as the δ_{TPA} and $\delta_{\text{TPA}}\phi_f$ values. As shown in the work of Chapter two, the extra arm of tripodal push-pull dyes (**D2-D5**) compared to **D1** was detrimental to their emission properties that they all showed moderate fluorescence quantum yield (0.24 – 0.49) in chloroform. The low quantum yields may limit their practicability in applications like bioimaging.⁹ To improve the fluorescence quantum yield, a general approach is to reduce the nonradiative energy loss by using a more rigid donor- π -acceptor structure design.¹⁰ As depicted in Figure 5.1, benzotriindole is a planar rigid donor that is commonly employed in structure designs of solar cells and luminescent materials.¹¹ By replacing the triphenylamine core of **D2** with a more rigid benzotriindole donor, the fluorescence quantum yield is expected to be improved. Additionally, in contrast to **D2**, the more planar donor- π -acceptor structure resulting from the planar benzotriindole core would favourably enhance the electronic interaction between the donor and acceptor, hence a larger δ_{TPA} . Overall, novel SF₅-functional push-pull dyes should have a more rigid, planar, and strong electron donor coupled to the SF₅ acceptor to attain more desirable two-photon absorption properties, such as large δ_{TPA} , $\delta_{\text{TPA}}/N_\pi$, and $\delta_{\text{TPA}}\phi_f$ values.

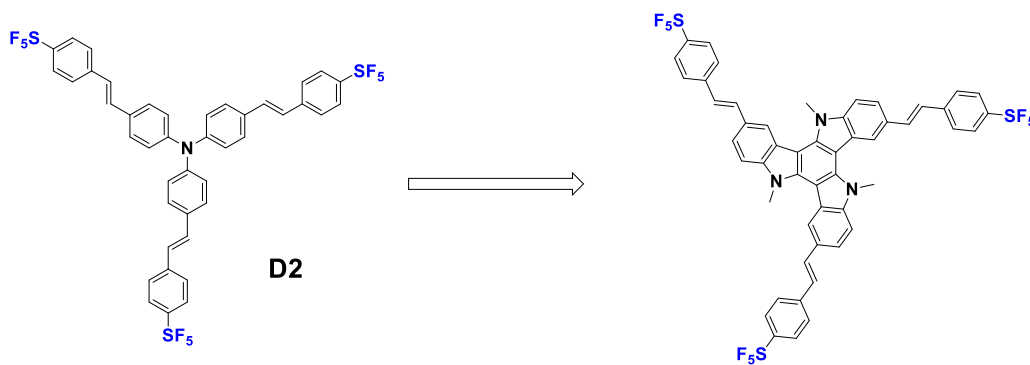


Figure 5. 1 The next generation of SF₅-functionalized two-photon absorption dye based on **D2** with potential improved δ_{TPA} and $\delta_{\text{TPA}}\phi_f$ values.

In terms of polymer electrets for nonvolatile OFET memory devices, it had been shown that the charge trapping ability and charge retention time could be substantially increased by introducing 1) a longer side chain; 2) more branching structures; 3) bulkier building blocks.¹² Herein, as shown in Figure 5.2a, the next generation of SF₅-

functionalized polymer electrets can be further modified based on **P2** according to those criteria. In addition to polymer type electrets, certain types of small molecules have also been found to display good charge trapping and retention abilities for OFET memory devices. Among them, donor-acceptor type small molecules with twisted structures are promising candidates for high-performance OFET memory devices.¹³⁻¹⁶ Lee reported that a larger steric hindrance between the donor and acceptor could enhance the charge trapping capability, resulting in a larger memory window.¹⁶ Similarly, in Huang's study, a donor-acceptor small molecule, TPA(PDAF)₃ with non-planar topologies (Figure 5.2b) was found to have a large memory window of 89 V.¹⁴ The separated HOMO and LUMO distributions resulting from the nonplanar structure were also found to not only produce both electron and hole trapping sites but also further strengthen the charge retention ability. Overall, the primary source of charge trapping sites is derived from the disorder of these twisted small molecules as they exhibit very weak intermolecular interactions in solid states that restrains the mobility of the trapped charges.¹⁷ Owing to the hydrophobic nature of SF₅, which inhibits moisture-induced conducting channels for charge leakage, and its steric bulkiness, which enables the formation of non-planar topologies, employing the electron-withdrawing SF₅ group is expected to impart beneficial memory characteristics to a non-planar donor-acceptor structure (Figure 5.2c).

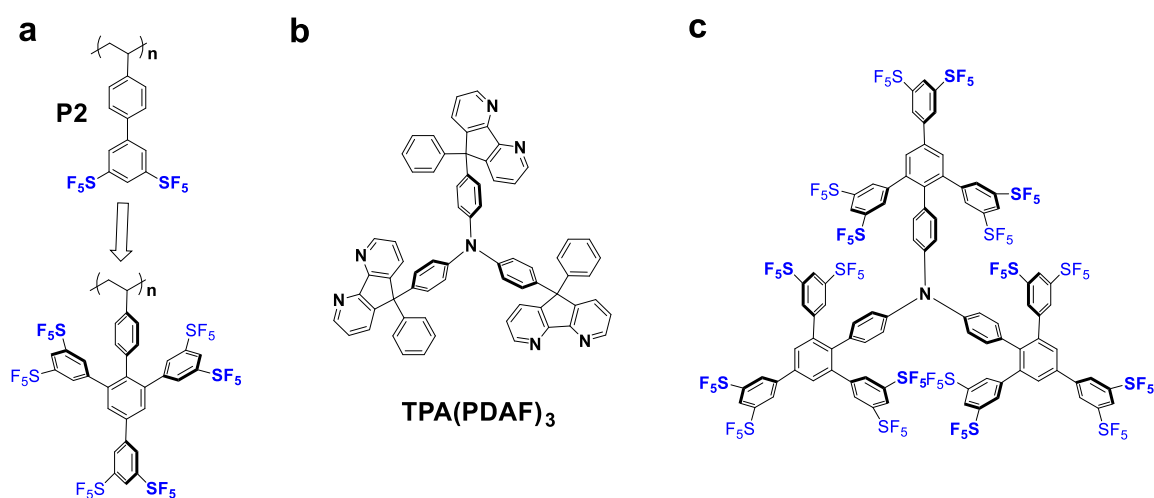


Figure 5. 2 a) Next generation of SF₅-functionalized styrenic polymer electret based on **P2**. b) Example of donor-acceptor type small molecule electret for OFET memory devices. c) Molecular design of SF₅-functionalized donor-acceptor type small molecule electret.

As was shown in Chapter Four, SF₅-functionalized ullazines exhibited favourable features for DSSC application, with **U8** being the best candidate. Yet, the absorption of **U8** remains moderate and its absorption spectrum only partially covers the ultraviolet-visible-near infrared spectrum, which may limit its performance as the photosensitizer in harvesting solar energy for DSSCs.^{18, 19} In this respect, the SF₅-functionalized ullazines should be further modified to improve the absorption properties for DSSC application. Thankfully, the weak and narrow absorption of a donor-acceptor system can be easily improved by extending the conjugation and enhancing the donor or acceptor strength.^{20, 21} For example, in figure 5.3, the introduction of electron-deficient benzothiadiazole in between the SF₅-phenylethynyl moiety and ullazine core is expected to afford a more intense and broader absorption spectrum. On the one hand, the lengthier conjugated structure relative to **U8** can increase the molar absorptivity. On the other hand, the enhanced acceptor strength brought by the additional benzothiadiazole can substantially red-shift the ICT band, resulting in a broader absorption spectrum. As was stated in the Introduction section of Chapter Four, fluorinated conjugated materials have been shown to boost the performance of solar cell devices. I would be particularly curious about the performance of these highly fluorinated SF₅-containing ullazine in DSSCs.

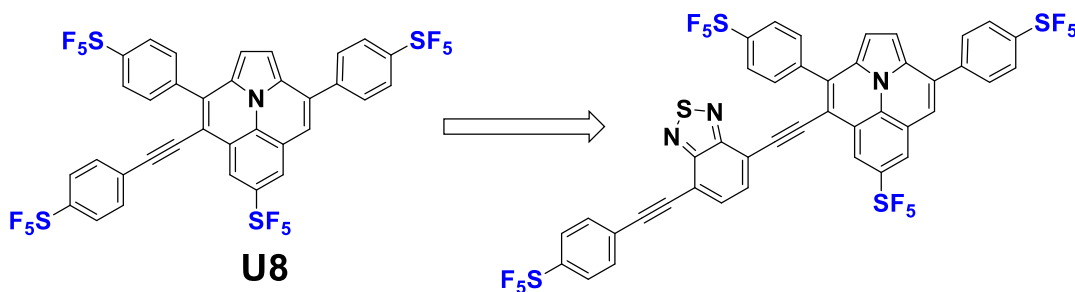


Figure 5. 3 New SF₅-containing ullazine dyes based on **U8** for DSSC applications.

Apart from extending my studies based on the previous work, it would also be exciting to investigate the effect of the “super CF₃”- SF₅ in the new optoelectronic materials such as TADF emitters, organic n-type semiconductors, and the active materials in OSCs as CF₃ (discussed in section 1.3.3) has shown its effectiveness in harnessing the electronic properties of these materials and demonstrating desirable properties in their corresponding applications. Importantly, it is necessary to systematically investigate the stability issue of

SF₅ upon accepting electrons to determine whether it is suitable for organic n-type semiconductors in future studies.

5.3 References

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Appendix

Crystallographic Data

Chapter 4

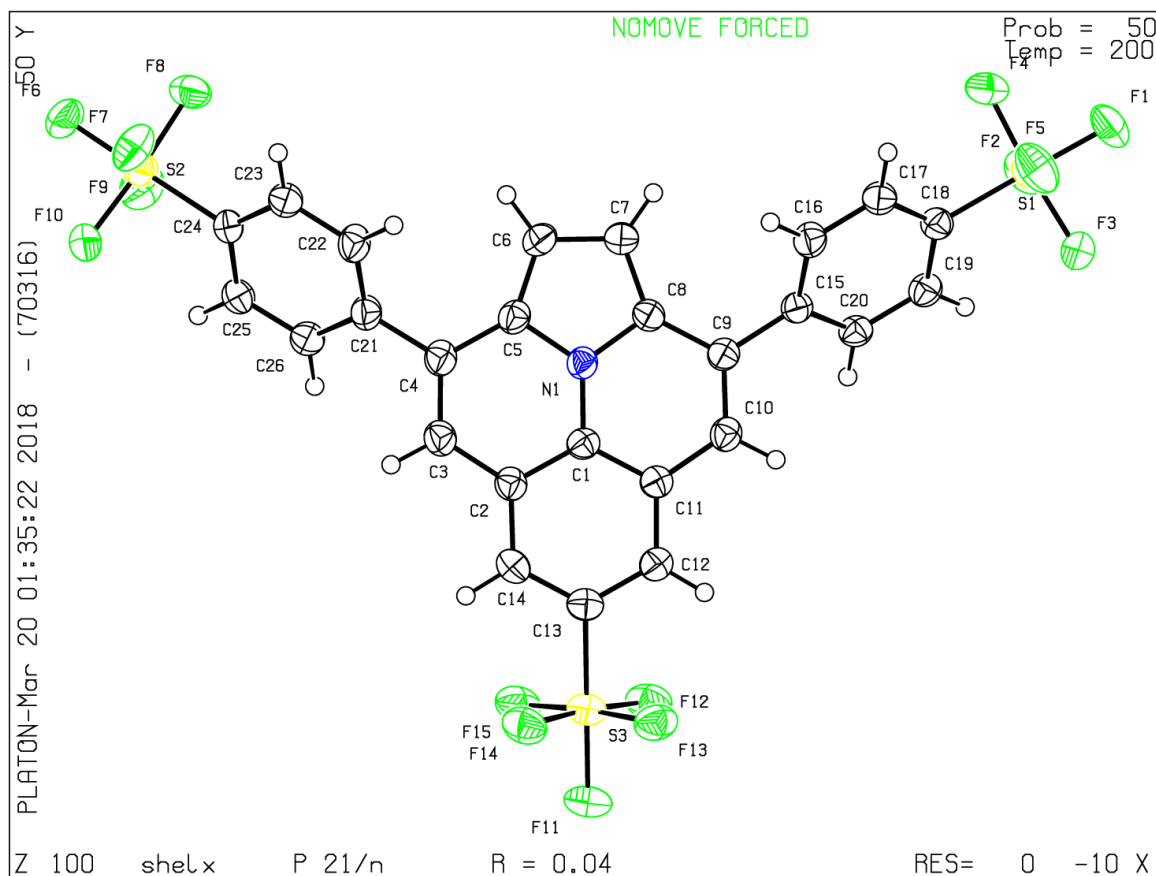


Figure A. 1 ORTEP view of U2 and the atom-labelling scheme. Thermal ellipsoids are plotted at the 50 % level.

Table A. 1 Crystal data and structure refinement for U2.

Identification code	shelx
Empirical formula	C ₂₆ H ₁₄ F ₁₅ N S ₃
Formula weight	721.56
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n

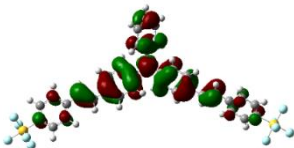
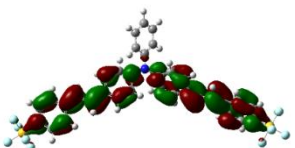
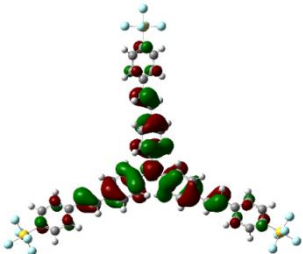
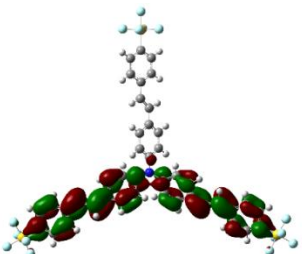
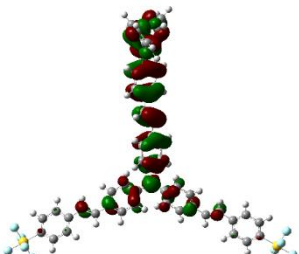
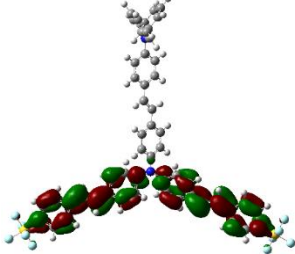
Unit cell dimensions	a = 4.8722(3) Å b = 26.0296(14) Å c = 20.8633(11) Å
Volume	2640.7(3) Å ³
Z	4
Density (calculated)	1.815 Mg/m ³
Absorption coefficient	0.408 mm ⁻¹
F(000)	1440
Crystal size	0.280 x 0.210 x 0.110 mm ³
Theta range for data collection	1.565 to 28.460°.
Index ranges	-6<=h<=6, -34<=k<=34, -27<=l<=27
Reflections collected	67852
Independent reflections	6658 [R(int) = 0.0714]
Completeness to theta = 25.242°	100.0 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6658 / 0 / 406
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0856
R indices (all data)	R1 = 0.0880, wR2 = 0.1079
Extinction coefficient	n/a
Largest diff. peak and hole	0.304 and -0.293 e.Å ⁻³

Structure of **U2** determined by single-crystal XRD and its crystal packing diagrams.

Theoretical Calculations

Chapter 2

Density functional theory (DFT) calculations were performed on dyes **D1–D5**. The calculated HOMO and LUMO of the five compounds are shown below in Figure A.2. The HOMO coefficients were mainly localized on the triarylamine donor moiety for dyes **D1–D5**, and extending around the additional donor triphenylamine, carbazole, and phenothiazine moieties for dyes **D3–D5**, respectively. The LUMO coefficients for all the dyes were concentrated in the region proximal to the SF₅ acceptor. The calculated energy values of HOMO/LUMO for dyes **D1–D5** were –5.21/–2.12 eV, –5.30/–2.24 eV, –4.86/–2.10 eV, –4.93/–2.08 eV, and –4.94/–2.11 eV, respectively.

Dye	HOMO	LUMO	HOMO–LUMO (eV)
D1	 –5.21 eV	 –2.12 eV	3.09
D2	 –5.30 eV	 –2.24 eV	3.06
D3	 –4.86 eV	 –2.10 eV	2.76

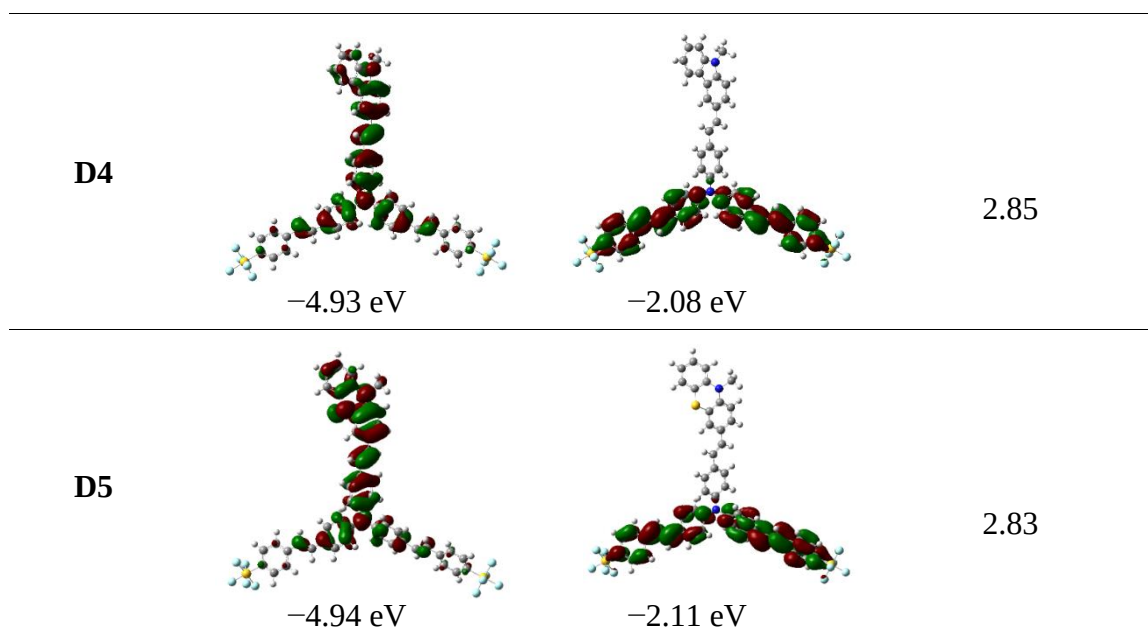


Figure A. 2 Frontier molecular orbitals of dyes **D1-D5**, as calculated using Gaussian09 at the B3LYP/6-31G** level for C, N, S, and H.

Table A. 2 Atomic coordinates for structure of **D1**.

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	6	0	-0.009373	7.286381	0.045114	
2	6	0	0.791673	6.596795	-0.867674	
3	6	0	0.790076	5.203336	-0.898409	
4	6	0	-0.005190	4.479518	0.002587	
5	6	0	-0.802575	5.173223	0.925116	
6	6	0	-0.808303	6.567001	0.936542	
7	7	0	-0.001655	3.052665	-0.019021	
8	6	0	-1.228215	2.347261	0.032073	
9	6	0	1.230496	2.357287	-0.085059	

10	6	0	1.367466	1.199120	-0.867873
11	6	0	2.582546	0.528592	-0.922003
12	6	0	3.714918	0.979577	-0.216686
13	6	0	3.563917	2.147986	0.557928
14	6	0	2.352740	2.818940	0.629122
15	6	0	-1.349593	1.158011	0.769732
16	6	0	-2.559412	0.477293	0.809314
17	6	0	-3.703272	0.950087	0.137661
18	6	0	-3.566706	2.146421	-0.595955
19	6	0	-2.360506	2.827533	-0.653917
20	1	0	1.412449	7.144743	-1.571442
21	1	0	1.402042	4.669052	-1.618417
22	1	0	-1.412571	4.615612	1.628916
23	1	0	-1.430551	7.091503	1.656690
24	1	0	0.519092	0.831680	-1.435806
25	1	0	2.665011	-0.363366	-1.538931
26	1	0	4.403962	2.535375	1.126696
27	1	0	2.263249	3.708976	1.243317
28	1	0	-0.493291	0.774232	1.314344
29	1	0	-2.629549	-0.438553	1.391810
30	1	0	-4.412480	2.543704	-1.149329
31	1	0	-2.281733	3.738190	-1.238618
32	6	0	-4.945618	0.188896	0.233612
33	6	0	-6.150747	0.517373	-0.280444
34	1	0	-4.854415	-0.738877	0.796810
35	6	0	-7.385474	-0.260971	-0.177659
36	1	0	-6.254109	1.453738	-0.825879
37	6	0	-8.572036	0.274600	-0.714367

38	6	0	-7.461260	-1.530237	0.430924
39	6	0	-9.781550	-0.409697	-0.647961
40	1	0	-8.544965	1.250441	-1.192224
41	6	0	-8.660099	-2.227097	0.506273
42	1	0	-6.571265	-1.988556	0.849673
43	6	0	-9.814743	-1.659544	-0.034840
44	1	0	-10.679313	0.026486	-1.067755
45	1	0	-8.693110	-3.201078	0.978192
46	16	0	-11.386322	-2.571346	0.059261
47	9	0	-11.135534	-2.978951	1.619379
48	9	0	-12.787879	-3.386944	0.144787
49	9	0	-11.757979	-2.233595	-1.493447
50	9	0	-10.683189	-3.967242	-0.410401
51	9	0	-12.209020	-1.245114	0.535630
52	6	0	4.962209	0.227441	-0.323685
53	6	0	6.130416	0.486239	0.302875
54	1	0	4.905121	-0.635102	-0.986308
55	6	0	7.374063	-0.275579	0.186851
56	1	0	6.188664	1.338246	0.977816
57	6	0	8.475404	0.102413	0.978668
58	6	0	7.541870	-1.374888	-0.679431
59	6	0	9.687437	-0.577873	0.922612
60	1	0	8.377183	0.947705	1.654794
61	6	0	8.745049	-2.065339	-0.748445
62	1	0	6.724761	-1.697617	-1.316449
63	6	0	9.811504	-1.660914	0.056029
64	1	0	10.517330	-0.266360	1.544466
65	1	0	8.850408	-2.906404	-1.422260

66	16	0	11.390166	-2.561442	-0.031278
67	9	0	11.367269	-2.583694	-1.662745
68	9	0	12.799085	-3.365141	-0.109308
69	9	0	11.533481	-2.607972	1.593402
70	9	0	10.643584	-4.012528	-0.009249
71	9	0	12.257569	-1.179412	-0.060057
72	1	0	-0.010982	8.372421	0.061638

Table A. 3 Atomic coordinates for structure of **D2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.270061	7.411623	0.175097
2	6	0	-3.386632	7.931808	0.856970
3	6	0	-3.700064	9.286755	0.824256
4	6	0	-2.883616	10.148770	0.096647
5	6	0	-1.767163	9.673113	-0.592690
6	6	0	-1.468783	8.317300	-0.548984
7	16	0	-3.275739	11.925206	0.048881
8	9	0	-3.019528	12.009562	-1.560438
9	9	0	-3.624559	13.509901	0.006544
10	9	0	-3.562214	11.975528	1.654489
11	9	0	-1.720711	12.344997	0.310789
12	9	0	-4.860183	11.639138	-0.216467
13	6	0	-2.002334	5.975372	0.257713
14	6	0	-1.008144	5.301004	-0.359230

15	6	0	-0.727369	3.869815	-0.275163
16	6	0	0.317360	3.331155	-1.050427
17	6	0	0.629844	1.977856	-1.023195
18	6	0	-0.088711	1.101426	-0.194592
19	6	0	-1.128995	1.626017	0.595553
20	6	0	-1.441588	2.975967	0.549086
21	7	0	0.228834	-0.280054	-0.147942
22	6	0	-0.807996	-1.245739	-0.072863
23	6	0	1.585331	-0.697470	-0.177585
24	6	0	1.981622	-1.802541	-0.946640
25	6	0	3.311403	-2.204634	-0.961948
26	6	0	4.303592	-1.522646	-0.231738
27	6	0	3.888864	-0.414798	0.535832
28	6	0	2.562285	-0.012861	0.568895
29	6	0	-0.683877	-2.371577	0.756290
30	6	0	-1.704580	-3.311760	0.818988
31	6	0	-2.894324	-3.169030	0.079332
32	6	0	-3.002291	-2.034266	-0.750595
33	6	0	-1.983928	-1.096657	-0.831686
34	1	0	-4.022857	7.258294	1.425181
35	1	0	-4.565027	9.659987	1.358030
36	1	0	-1.135962	10.349961	-1.154742
37	1	0	-0.594057	7.964368	-1.085561
38	1	0	-2.699717	5.425421	0.887164
39	1	0	-0.323142	5.851908	-1.002168
40	1	0	0.885556	3.989977	-1.702956
41	1	0	1.430346	1.592501	-1.646079
42	1	0	-1.684193	0.965077	1.253152

43	1	0	-2.242413	3.344029	1.183315
44	1	0	1.243950	-2.340413	-1.533263
45	1	0	3.596397	-3.060250	-1.569714
46	1	0	4.610934	0.133101	1.133701
47	1	0	2.268817	0.834465	1.180128
48	1	0	0.212925	-2.502438	1.353001
49	1	0	-1.588677	-4.172651	1.473298
50	1	0	-3.888884	-1.890254	-1.360747
51	1	0	-2.087732	-0.240882	-1.490902
52	6	0	-3.935656	-4.185629	0.208433
53	6	0	-5.160824	-4.175691	-0.359476
54	1	0	-3.662243	-5.023744	0.847887
55	6	0	-6.199040	-5.197742	-0.221819
56	1	0	-5.444819	-3.330327	-0.983764
57	6	0	-7.442460	-4.987117	-0.847727
58	6	0	-6.030276	-6.392368	0.506863
59	6	0	-8.477103	-5.912239	-0.753041
60	1	0	-7.601692	-4.076417	-1.419173
61	6	0	-7.052683	-7.326529	0.612237
62	1	0	-5.086635	-6.602607	0.999759
63	6	0	-8.272196	-7.077874	-0.019335
64	1	0	-9.424264	-5.723791	-1.242663
65	1	0	-6.900307	-8.236821	1.178427
66	16	0	-9.617372	-8.295473	0.121955
67	9	0	-9.371861	-8.481689	1.724364
68	9	0	-10.817444	-9.380950	0.249700
69	9	0	-9.964010	-8.201433	-1.469533
70	9	0	-8.610262	-9.545655	-0.169780

71	9	0	-10.725994	-7.136942	0.423696
72	6	0	5.685855	-1.990233	-0.306072
73	6	0	6.767903	-1.433541	0.279293
74	1	0	5.821126	-2.883871	-0.913680
75	6	0	8.150460	-1.906091	0.198601
76	1	0	6.637804	-0.533181	0.877126
77	6	0	9.154553	-1.170304	0.856365
78	6	0	8.544226	-3.062588	-0.504358
79	6	0	10.490333	-1.556463	0.818728
80	1	0	8.881078	-0.274752	1.408133
81	6	0	9.873568	-3.462511	-0.552677
82	1	0	7.805141	-3.664681	-1.022880
83	6	0	10.839032	-2.703545	0.110495
84	1	0	11.242706	-0.971251	1.332360
85	1	0	10.152863	-4.354328	-1.099691
86	16	0	12.583267	-3.219374	0.047736
87	9	0	12.509361	-3.513688	-1.555581
88	9	0	14.138959	-3.678502	-0.009117
89	9	0	12.788270	-2.964088	1.646189
90	9	0	12.205355	-4.778923	0.343371
91	9	0	13.093200	-1.698701	-0.252365

Table A. 4 Atomic coordinates for structure of **D3**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	5.269212	-1.339319	0.288922
2	6	0	4.186946	-1.723526	-0.423287
3	6	0	2.830485	-1.187807	-0.323397
4	6	0	1.832457	-1.686694	-1.183460
5	6	0	0.525287	-1.215776	-1.144809
6	6	0	0.157399	-0.227384	-0.221112
7	6	0	1.137179	0.276418	0.651709
8	6	0	2.442833	-0.189807	0.595055
9	7	0	-1.182943	0.252209	-0.161851
10	6	0	-1.425343	1.644423	-0.075308
11	6	0	-2.257243	-0.670478	-0.182819
12	6	0	-3.439737	-0.391779	-0.888015
13	6	0	-4.485068	-1.306352	-0.894152
14	6	0	-4.399162	-2.540515	-0.221491
15	6	0	-3.205139	-2.806632	0.479864
16	6	0	-2.160588	-1.895772	0.504499
17	6	0	-2.460535	2.152822	0.726852
18	6	0	-2.683812	3.521577	0.799991
19	6	0	-1.886229	4.445964	0.098126
20	6	0	-0.848051	3.920639	-0.698525
21	6	0	-0.623560	2.555786	-0.789491
22	1	0	5.155635	-0.538767	1.019112
23	1	0	4.301263	-2.514438	-1.163311
24	1	0	2.096159	-2.452506	-1.909215
25	1	0	-0.217361	-1.611682	-1.830491
26	1	0	0.863492	1.034276	1.379325
27	1	0	3.169152	0.217411	1.291955
28	1	0	-3.532752	0.542093	-1.432503

29	1	0	-5.388598	-1.069717	-1.451413
30	1	0	-3.098295	-3.732143	1.037797
31	1	0	-1.260086	-2.120994	1.066289
32	1	0	-3.084203	1.470751	1.295170
33	1	0	-3.488556	3.890538	1.431822
34	1	0	-0.212967	4.588420	-1.272979
35	1	0	0.174653	2.180465	-1.421296
36	6	0	-2.171798	5.871941	0.228682
37	6	0	-1.502069	6.896472	-0.342737
38	1	0	-3.025228	6.097381	0.866772
39	6	0	-1.800948	8.322173	-0.208092
40	1	0	-0.643677	6.676641	-0.974994
41	6	0	-0.974908	9.252035	-0.868457
42	6	0	-2.876905	8.829961	0.548055
43	6	0	-1.200537	10.622247	-0.786962
44	1	0	-0.136878	8.891341	-1.459138
45	6	0	-3.116855	10.194769	0.640466
46	1	0	-3.542425	8.152935	1.073746
47	6	0	-2.274714	11.083258	-0.030064
48	1	0	-0.549074	11.314077	-1.306003
49	1	0	-3.950481	10.560852	1.226607
50	16	0	-2.589288	12.871682	0.084101
51	9	0	-2.839079	12.796002	1.695124
52	9	0	-2.870808	14.467803	0.186106
53	9	0	-2.364003	13.084699	-1.517997
54	9	0	-4.190394	12.675859	-0.164963
55	9	0	-1.012587	13.204092	0.341973
56	6	0	-5.531260	-3.461184	-0.277406

57	6	0	-5.585001	-4.719450	0.211077
58	1	0	-6.407976	-3.059842	-0.784083
59	6	0	-6.730152	-5.628661	0.162609
60	1	0	-4.699719	-5.137314	0.687211
61	6	0	-6.565977	-6.950362	0.619631
62	6	0	-8.004487	-5.257204	-0.311829
63	6	0	-7.611887	-7.867268	0.603466
64	1	0	-5.595472	-7.265640	0.993786
65	6	0	-9.059969	-6.159758	-0.335316
66	1	0	-8.182883	-4.245077	-0.660219
67	6	0	-8.854825	-7.461747	0.123777
68	1	0	-7.457679	-8.877830	0.960350
69	1	0	-10.030739	-5.850097	-0.701782
70	16	0	-10.236704	-8.645261	0.106307
71	9	0	-10.693668	-8.197325	-1.394999
72	9	0	-11.470708	-9.700547	0.091150
73	9	0	-9.886910	-9.184486	1.606181
74	9	0	-11.270554	-7.552208	0.738573
75	9	0	-9.307963	-9.828482	-0.526841
76	6	0	6.624236	-1.877236	0.199970
77	6	0	7.638265	-1.319550	1.002367
78	6	0	6.996183	-2.940656	-0.648209
79	6	0	8.948518	-1.779068	0.960283
80	1	0	7.392140	-0.492608	1.664911
81	6	0	8.297635	-3.416851	-0.689252
82	1	0	6.250572	-3.419952	-1.275902
83	6	0	9.303005	-2.841868	0.112628
84	1	0	9.705987	-1.314955	1.583350

85	1	0	8.547591	-4.247120	-1.341675
86	7	0	10.631064	-3.326930	0.066640
87	6	0	11.197198	-3.751415	-1.168822
88	6	0	11.413230	-3.394213	1.254428
89	6	0	11.952320	-4.933001	-1.234791
90	6	0	11.013473	-2.992923	-2.335818
91	6	0	12.754551	-2.980376	1.245757
92	6	0	10.857900	-3.882659	2.447859
93	6	0	12.515371	-5.339920	-2.442885
94	1	0	12.093588	-5.525948	-0.336689
95	6	0	11.565595	-3.417295	-3.543060
96	1	0	10.438313	-2.073589	-2.288762
97	6	0	13.522517	-3.062526	2.405866
98	1	0	13.188059	-2.597297	0.327354
99	6	0	11.628541	-3.944081	3.607312
100	1	0	9.823834	-4.212517	2.459195
101	6	0	12.322443	-4.589392	-3.604687
102	1	0	13.097224	-6.257292	-2.476707
103	1	0	11.414290	-2.818290	-4.437271
104	6	0	12.965196	-3.539519	3.594102
105	1	0	14.559552	-2.738114	2.381592
106	1	0	11.183343	-4.325454	4.522569
107	1	0	12.757199	-4.913172	-4.546003
108	1	0	13.564805	-3.595926	4.498091

Table A. 5 Atomic coordinates for structure of **D4**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.617740	6.446566	-0.782195
2	6	0	-0.113935	5.588801	-0.038322
3	6	0	-0.056854	4.127788	-0.069344
4	6	0	-0.861277	3.391446	0.822363
5	6	0	-0.843065	2.001735	0.854232
6	6	0	-0.022413	1.285626	-0.028202
7	6	0	0.777486	2.002115	-0.934562
8	6	0	0.763498	3.389562	-0.947798
9	7	0	0.000606	-0.139225	-0.010641
10	6	0	1.242163	-0.818825	-0.045212
11	6	0	-1.216933	-0.859984	0.043020
12	6	0	-1.333721	-2.028339	0.814213
13	6	0	-2.533609	-2.726272	0.852779
14	6	0	-3.671775	-2.292223	0.146065
15	6	0	-3.540671	-1.114892	-0.618923
16	6	0	-2.344397	-0.416532	-0.675055
17	6	0	1.399789	-2.004013	-0.782877
18	6	0	2.624325	-2.658510	-0.805869
19	6	0	3.747990	-2.162138	-0.117080
20	6	0	3.575042	-0.970068	0.616002
21	6	0	2.354065	-0.314836	0.657050
22	1	0	1.339650	6.035712	-1.487080
23	1	0	-0.829510	5.992887	0.676383
24	1	0	-1.503247	3.926662	1.518182
25	1	0	-1.463673	1.464663	1.564838

26	1	0	1.408357	1.459744	-1.632121
27	1	0	1.390310	3.906669	-1.668066
28	1	0	-0.481534	-2.382679	1.384642
29	1	0	-2.600501	-3.625723	1.460681
30	1	0	-4.382404	-0.746882	-1.198107
31	1	0	-2.268736	0.478600	-1.283627
32	1	0	0.559734	-2.405080	-1.340203
33	1	0	2.722519	-3.571710	-1.388472
34	1	0	4.403632	-0.556420	1.183185
35	1	0	2.246819	0.592832	1.241808
36	6	0	5.007794	-2.895984	-0.194327
37	6	0	6.199236	-2.536045	0.330830
38	1	0	4.944476	-3.829274	-0.752333
39	6	0	7.452407	-3.286613	0.249567
40	1	0	6.274898	-1.592254	0.867937
41	6	0	8.622509	-2.713398	0.783713
42	6	0	7.562156	-4.564896	-0.334633
43	6	0	9.848288	-3.369593	0.736784
44	1	0	8.569312	-1.730044	1.243604
45	6	0	8.777707	-5.234181	-0.390264
46	1	0	6.685503	-5.052379	-0.748590
47	6	0	9.915183	-4.629238	0.146716
48	1	0	10.732701	-2.904477	1.153890
49	1	0	8.836640	-6.215803	-0.843499
50	16	0	11.508983	-5.503876	0.078159
51	9	0	11.275529	-5.950621	-1.473965
52	9	0	12.930905	-6.285975	0.015355
53	9	0	11.865591	-5.124525	1.624779

54	9	0	10.838728	-6.906663	0.574520
55	9	0	12.300788	-4.168002	-0.423165
56	6	0	-4.902120	-3.072646	0.238807
57	6	0	-6.100226	-2.785810	-0.315329
58	1	0	-4.807725	-3.978919	0.835515
59	6	0	-7.321103	-3.586047	-0.216368
60	1	0	-6.208444	-1.870195	-0.893992
61	6	0	-8.508792	-3.086146	-0.784257
62	6	0	-7.381889	-4.843880	0.417223
63	6	0	-9.705526	-3.793046	-0.723079
64	1	0	-8.492926	-2.120217	-1.282318
65	6	0	-8.567793	-5.562956	0.487686
66	1	0	-6.489728	-5.276077	0.858536
67	6	0	-9.724250	-5.030131	-0.083978
68	1	0	-10.604530	-3.383958	-1.166823
69	1	0	-8.589498	-6.527757	0.978702
70	16	0	-11.278246	-5.971938	0.003971
71	9	0	-11.045947	-6.340294	1.576762
72	9	0	-12.664083	-6.814531	0.084367
73	9	0	-11.630287	-5.676061	-1.561843
74	9	0	-10.539107	-7.363088	-0.422964
75	9	0	-12.136172	-4.653188	0.437043
76	6	0	0.571943	7.908964	-0.761037
77	6	0	1.451952	8.619014	-1.615295
78	6	0	-0.299499	8.646208	0.059804
79	6	0	1.490539	10.007039	-1.670218
80	1	0	2.122244	8.051053	-2.255992
81	6	0	-0.282479	10.038182	0.026438

82	1	0	-0.993044	8.135596	0.721721
83	6	0	0.621463	10.717260	-0.837422
84	1	0	2.174008	10.510817	-2.346980
85	6	0	-1.034225	11.063597	0.723183
86	7	0	0.461304	12.085725	-0.679293
87	6	0	-0.550902	12.312051	0.249935
88	6	0	-2.050402	11.037792	1.683762
89	6	0	1.168723	13.110157	-1.416750
90	6	0	-1.075182	13.522474	0.711293
91	6	0	-2.571691	12.241166	2.152776
92	1	0	-2.430381	10.090534	2.057747
93	1	0	0.640982	13.398631	-2.335618
94	1	0	1.290939	13.996615	-0.788346
95	1	0	2.164975	12.747541	-1.682414
96	6	0	-2.087209	13.467845	1.668404
97	1	0	-0.717350	14.477441	0.338398
98	1	0	-3.362171	12.233549	2.897651
99	1	0	-2.511302	14.395474	2.043113

Table A. 6 Atomic coordinates for structure of **D5**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.525588	5.973405	-0.406908
2	6	0	-1.081758	4.951548	0.279277
3	6	0	-0.719443	3.537270	0.197495

4	6	0	-1.344731	2.618289	1.062626
5	6	0	-1.038161	1.262604	1.040670
6	6	0	-0.096097	0.766165	0.128563
7	6	0	0.529858	1.666465	-0.750576
8	6	0	0.227333	3.019978	-0.710937
9	7	0	0.218894	-0.622543	0.087160
10	6	0	1.574567	-1.027265	0.018613
11	6	0	-0.823596	-1.580245	0.110748
12	6	0	-0.683604	-2.787979	0.814500
13	6	0	-1.715052	-3.718093	0.824248
14	6	0	-2.933362	-3.486941	0.157055
15	6	0	-3.058937	-2.269954	-0.544134
16	6	0	-2.031354	-1.340175	-0.572759
17	6	0	1.970223	-2.110651	-0.783140
18	6	0	3.304958	-2.490734	-0.839408
19	6	0	4.305401	-1.808623	-0.120230
20	6	0	3.892624	-0.721948	0.677968
21	6	0	2.561827	-0.341294	0.751824
22	1	0	0.294295	5.758478	-1.091136
23	1	0	-1.884213	5.167772	0.983098
24	1	0	-2.076548	2.982666	1.779762
25	1	0	-1.527224	0.581728	1.730349
26	1	0	1.251173	1.292547	-1.470667
27	1	0	0.721062	3.682484	-1.415481
28	1	0	0.234587	-2.990683	1.355773
29	1	0	-1.584331	-4.643094	1.381181
30	1	0	-3.967751	-2.054197	-1.098032
31	1	0	-2.151348	-0.419329	-1.133817

32	1	0	1.227918	-2.648287	-1.363858
33	1	0	3.587384	-3.329153	-1.472047
34	1	0	4.620987	-0.173172	1.267464
35	1	0	2.271819	0.490580	1.385229
36	6	0	5.691523	-2.253467	-0.235935
37	6	0	6.779266	-1.693952	0.337026
38	1	0	5.825714	-3.132490	-0.864990
39	6	0	8.165429	-2.145446	0.215984
40	1	0	6.650141	-0.808517	0.956926
41	6	0	9.174239	-1.411851	0.869537
42	6	0	8.559779	-3.280106	-0.521809
43	6	0	10.513647	-1.779285	0.795442
44	1	0	8.900996	-0.532990	1.447648
45	6	0	9.892731	-3.661259	-0.606837
46	1	0	7.817699	-3.879748	-1.038895
47	6	0	10.862301	-2.905224	0.053824
48	1	0	11.268936	-1.196278	1.307347
49	1	0	10.171618	-4.536589	-1.180110
50	16	0	12.610609	-3.397365	-0.055017
51	9	0	12.508093	-3.661807	-1.662190
52	9	0	14.170872	-3.835887	-0.152785
53	9	0	12.846791	-3.170477	1.543687
54	9	0	12.258766	-4.967350	0.217658
55	9	0	13.096629	-1.864979	-0.335767
56	6	0	-3.983344	-4.499777	0.221536
57	6	0	-5.243417	-4.399829	-0.254782
58	1	0	-3.687504	-5.417911	0.727537
59	6	0	-6.287075	-5.423039	-0.190516

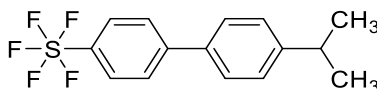
60	1	0	-5.554704	-3.470309	-0.728137
61	6	0	-7.587346	-5.092214	-0.617837
62	6	0	-6.068397	-6.735757	0.274035
63	6	0	-8.628767	-6.013461	-0.578879
64	1	0	-7.785959	-4.088648	-0.984795
65	6	0	-7.096714	-7.668416	0.319947
66	1	0	-5.078654	-7.041744	0.597261
67	6	0	-8.372996	-7.298553	-0.106901
68	1	0	-9.619814	-5.731096	-0.911368
69	1	0	-6.904261	-8.671553	0.679397
70	16	0	-9.723640	-8.516549	-0.051584
71	9	0	-9.299690	-9.024055	1.440223
72	9	0	-10.929506	-9.602980	-0.002603
73	9	0	-10.251870	-8.102946	-1.539104
74	9	0	-8.790442	-9.685250	-0.705254
75	9	0	-10.759255	-7.440878	0.606831
76	6	0	-0.891414	7.386907	-0.342164
77	6	0	-0.146935	8.323512	-1.076805
78	6	0	-1.972176	7.881115	0.416360
79	6	0	-0.455259	9.681268	-1.064222
80	1	0	0.685679	7.979723	-1.685748
81	6	0	-2.262517	9.237490	0.465357
82	1	0	-2.594051	7.201201	0.990387
83	6	0	-1.511934	10.171435	-0.282626
84	1	0	0.130022	10.358614	-1.675731
85	16	0	-3.535970	9.829432	1.563618
86	7	0	-1.830425	11.543440	-0.223124
87	6	0	-4.111856	11.204187	0.586865

88	6	0	-3.187537	11.943498	-0.177337
89	6	0	-0.846849	12.499680	-0.707440
90	6	0	-5.452740	11.582744	0.641661
91	6	0	-3.651113	13.069418	-0.874523
92	1	0	-1.070529	13.482352	-0.285911
93	1	0	0.143332	12.196522	-0.359351
94	1	0	-0.820084	12.587611	-1.804925
95	6	0	-5.894116	12.724462	-0.029647
96	1	0	-6.146366	10.985443	1.226744
97	1	0	-2.971421	13.641518	-1.495825
98	6	0	-4.987432	13.464049	-0.785109
99	1	0	-6.935873	13.024017	0.034734
100	1	0	-5.316046	14.347717	-1.325002

Chapter 3

Calculation Method: Gaussian09 at the B3LYP/6-31G(d) level for C, N, S, and H

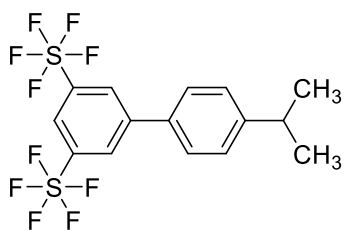
Table A. 7 Atomic coordinates for the representative model structure of the **P1** repeat unit.



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.124064	-0.906091	0.459260
2	6	0	-2.732954	-0.943278	0.482130
3	6	0	-1.971380	0.107299	-0.057122
4	6	0	-2.659831	1.192663	-0.619882
5	6	0	-4.052832	1.220889	-0.644708
6	6	0	-4.814585	0.176061	-0.107238
7	1	0	-4.679088	-1.732038	0.897165
8	1	0	-2.229347	-1.785050	0.949841
9	1	0	-2.100955	2.008818	-1.069824
10	1	0	-4.558861	2.069845	-1.099144
11	6	0	-0.488750	0.069676	-0.034332
12	6	0	0.260845	1.233126	0.208005
13	6	0	0.208835	-1.129500	-0.256803
14	6	0	1.652555	1.208497	0.227722
15	1	0	-0.251704	2.168752	0.409498
16	6	0	1.600275	-1.172907	-0.241200
17	1	0	-0.343367	-2.039158	-0.472069
18	6	0	2.309800	0.001160	0.001469

19	1	0	2.211040	2.115004	0.424558
20	1	0	2.118690	-2.105627	-0.424780
21	16	0	4.130587	-0.041819	0.021019
22	6	0	-6.335776	0.226406	-0.134686
23	1	0	-6.617136	1.143824	-0.669489
24	6	0	-6.939221	-0.961356	-0.907536
25	1	0	-8.029895	-0.867240	-0.966702
26	1	0	-6.544851	-1.012873	-1.928147
27	1	0	-6.715392	-1.914430	-0.413835
28	6	0	-6.927061	0.321483	1.285103
29	1	0	-6.528296	1.187989	1.823606
30	1	0	-8.018372	0.417943	1.242262
31	1	0	-6.694598	-0.573867	1.873858
32	9	0	4.203247	0.802076	1.415463
33	9	0	4.242462	1.352400	-0.819810
34	9	0	4.160075	-1.439344	0.863251
35	9	0	4.193704	-0.889045	-1.371836
36	9	0	5.753578	-0.079149	0.038020

Table A. 8 Atomic coordinates for the representative model structure of the **P2** repeat unit.



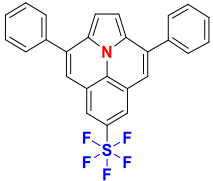
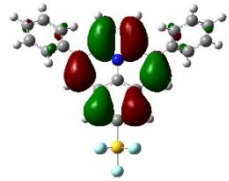
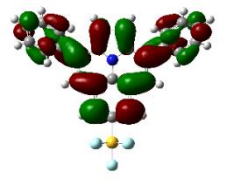
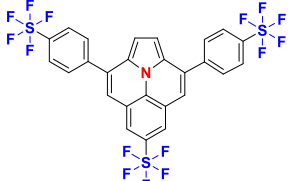
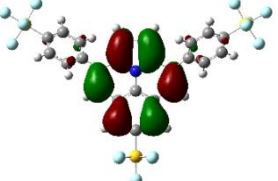
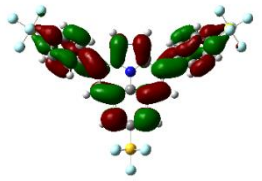
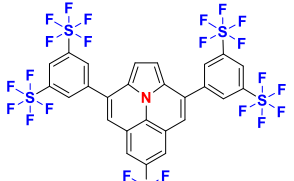
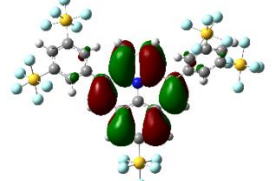
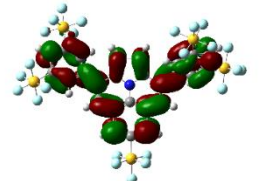
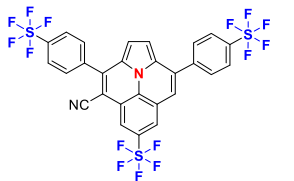
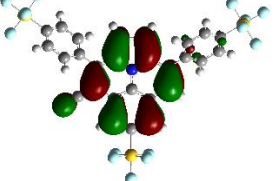
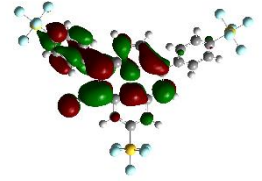
Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	1.317305	1.208146	-0.014111
2	6	0	-0.071400	1.161246	-0.045631
3	6	0	-0.732285	-0.077342	-0.043894
4	6	0	0.043246	-1.247174	-0.014488
5	6	0	1.430099	-1.161201	0.006470
6	6	0	2.099991	0.058193	0.009739
7	1	0	-0.646120	2.076806	-0.093673
8	1	0	-0.442666	-2.213537	0.013980
9	1	0	3.178432	0.109476	0.030240
10	6	0	-2.213690	-0.148211	-0.072376
11	6	0	-2.876194	-1.153801	-0.792069
12	6	0	-2.996299	0.790054	0.620965
13	6	0	-4.268022	-1.215300	-0.814643
14	1	0	-2.302046	-1.877917	-1.363787
15	6	0	-4.385692	0.721517	0.593803
16	1	0	-2.513682	1.564027	1.211715
17	6	0	-5.052359	-0.282892	-0.124292
18	1	0	-4.754667	-2.000449	-1.388670
19	1	0	-4.957479	1.459407	1.150295
20	6	0	-6.571958	-0.362942	-0.158904
21	1	0	-6.833725	-1.234769	-0.773596
22	6	0	-7.165768	-0.591882	1.244069
23	1	0	-8.254063	-0.709520	1.185341
24	1	0	-6.749876	-1.491665	1.710111
25	1	0	-6.958914	0.255583	1.908297

26	6	0	-7.193772	0.877624	-0.828424
27	1	0	-6.800830	1.022078	-1.840593
28	1	0	-8.282754	0.771616	-0.896301
29	1	0	-6.983708	1.788082	-0.254617
30	16	0	2.415423	-2.700503	0.046066
31	16	0	2.150843	2.835286	-0.018501
32	9	0	1.459525	-3.356615	1.191140
33	9	0	3.401003	-2.113582	1.202635
34	9	0	3.435008	-2.146106	-1.097189
35	9	0	3.287261	-4.064395	0.078228
36	9	0	1.493640	-3.389895	-1.108504
37	9	0	3.228314	2.350329	-1.139386
38	9	0	3.178046	2.378065	1.160272
39	9	0	2.887486	4.277416	-0.019536
40	9	0	1.126592	3.427959	1.102604
41	9	0	1.176749	3.399942	-1.196607

Chapter 4

Density functional theory (DFT) with Gaussian09 at the B3LYP/6-31G level was carried out to relate the optical and geometrical properties of **U1–3** and **U7–10** to their electronic ground states. The frontier molecular orbitals of **U1–3** and **U7–10** were calculated before their geometries were optimized.

Compound	HOMO	LUMO	HOMO-LUMO gap, ΔE_g (eV)
 U1	 -5.18 eV	 -1.57 eV	3.61
 U2	 -5.69 eV	 -2.22 eV	3.47
 U3	 -5.97 eV	 -2.57 eV	3.40
 U7	 -6.04 eV	 -2.71 eV	3.33

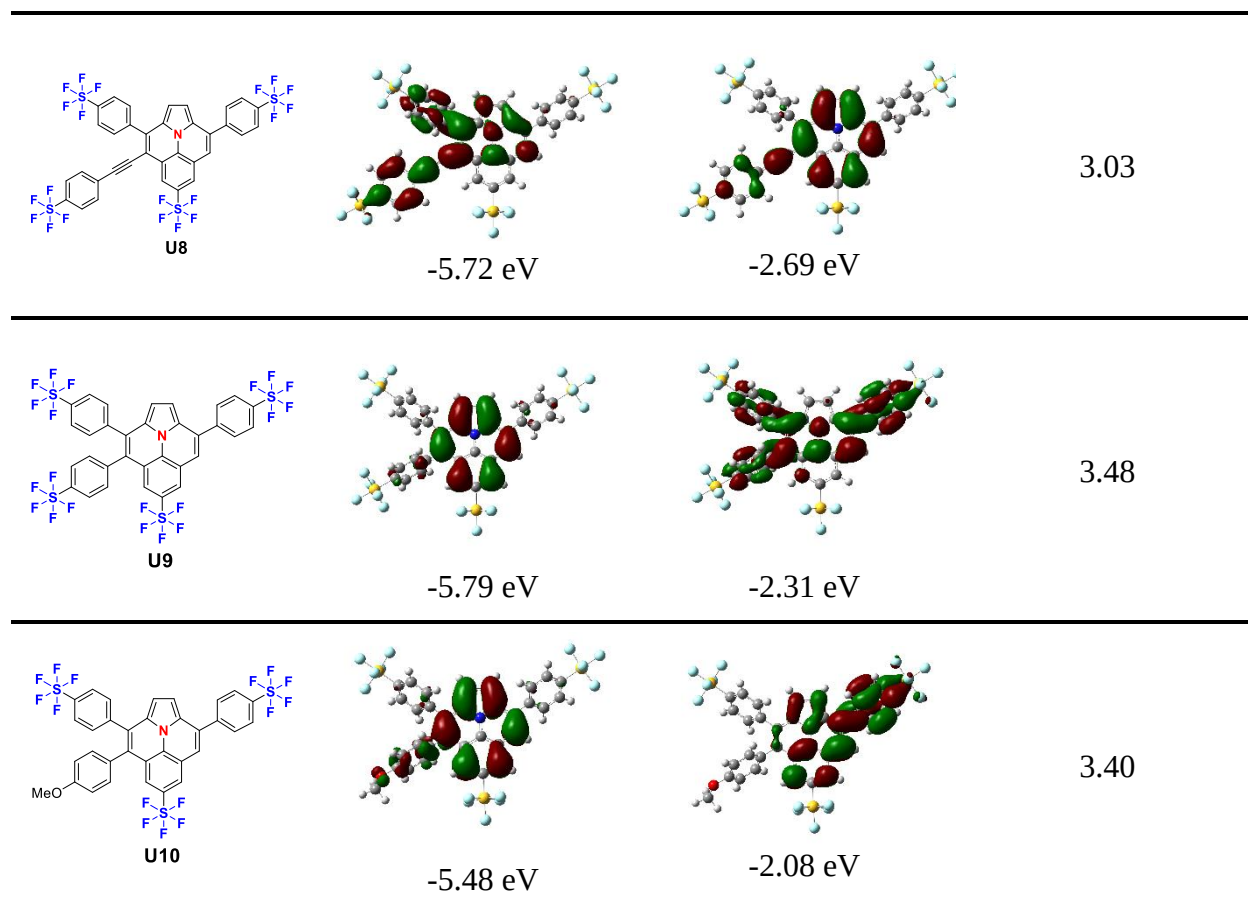


Figure A. 3 Frontier molecular orbitals of **U1–U3** and **U7–U10**, calculated using Gaussian09 at the B3LYP/6-31G level for C, N, S, and H.

Table A. 9 Atomic coordinates for structure of **U1**.

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	6	0	2.754271	-0.000119	-0.000002	
2	6	0	2.092132	1.224446	-0.014835	
3	6	0	0.686596	1.246149	-0.016798	
4	6	0	0.014015	-0.000006	0.000026	
5	6	0	0.686494	-1.246216	0.016826	
6	6	0	2.092032	-1.224631	0.014835	

7	1	0	2.642436	2.156370	-0.024089
8	1	0	2.642254	-2.156602	0.024093
9	7	0	-1.354010	0.000048	-0.000020
10	6	0	-2.148979	-1.146343	-0.009994
11	6	0	-2.148884	1.146507	0.009886
12	6	0	-3.477202	-0.701568	-0.001169
13	6	0	-3.477144	0.701843	0.000901
14	1	0	-4.346324	-1.342784	0.009597
15	1	0	-4.346211	1.343132	-0.009957
16	6	0	-0.108645	2.444052	-0.016326
17	6	0	-1.483747	2.417395	0.006194
18	6	0	-1.483952	-2.417286	-0.006212
19	6	0	-0.108845	-2.444054	0.016376
20	6	0	-2.271163	-3.676531	-0.029960
21	6	0	-3.337620	-3.851715	-0.927749
22	6	0	-1.939529	-4.734763	0.831752
23	6	0	-4.047458	-5.051309	-0.962884
24	1	0	-3.592029	-3.053033	-1.617882
25	6	0	-2.651616	-5.932825	0.797029
26	1	0	-1.130760	-4.604878	1.545426
27	6	0	-3.708665	-6.095415	-0.100222
28	1	0	-4.264753	-7.028516	-0.126603
29	6	0	-2.270852	3.676707	0.029963
30	6	0	-3.337296	3.851968	0.927749
31	6	0	-1.939059	4.734954	-0.831668
32	6	0	-4.047010	5.051635	0.962918
33	1	0	-3.591802	3.053286	1.617847
34	6	0	-2.651021	5.933090	-0.796910
35	1	0	-1.130262	4.605025	-1.545303
36	6	0	-3.708087	6.095742	0.100310
37	1	0	-4.264074	7.028904	0.126723

38	1	0	0.405580	-3.399894	-0.004997
39	1	0	0.405855	3.399851	0.005128
40	16	0	4.581014	-0.000190	-0.000004
41	9	0	4.653101	1.162521	1.142973
42	9	0	4.653484	1.145417	-1.160321
43	9	0	4.653400	-1.145801	1.160315
44	9	0	4.653015	-1.162901	-1.142985
45	9	0	6.206140	-0.000245	-0.000004
46	1	0	-4.862724	-5.172331	-1.671199
47	1	0	-2.384303	-6.737207	1.477020
48	1	0	-4.862278	5.172714	1.671222
49	1	0	-2.383593	6.737482	-1.476843

E(RB3LYP) = -1952.47321128 a.u.

Imaginary Freq = 0

Table A. 10 Atomic coordinates for structure of **U2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.223423	3.677278	0.032494
2	6	0	1.244873	2.272330	0.035607
3	6	0	0.000000	1.598466	-0.000065
4	6	0	-1.244848	2.272380	-0.035694
5	6	0	-1.223335	3.677331	-0.032522
6	6	0	0.000056	4.340818	-0.000005
7	1	0	2.155173	4.227598	0.055183
8	1	0	-2.155059	4.227697	-0.055179
9	16	0	0.000098	6.168322	0.000008

10	9	0	0.000139	7.790842	0.000019
11	9	0	1.172669	6.235552	-1.131757
12	9	0	-1.134336	6.236384	-1.170256
13	9	0	1.134537	6.236315	1.170272
14	9	0	-1.172469	6.235592	1.131774
15	7	0	-0.000017	0.230373	-0.000009
16	6	0	1.145834	-0.565154	0.008550
17	6	0	-1.145904	-0.565095	-0.008454
18	6	0	0.701678	-1.893171	0.010455
19	6	0	-0.701833	-1.893134	-0.010238
20	1	0	1.339799	-2.764392	0.033698
21	1	0	-1.340047	-2.764296	-0.033340
22	6	0	2.443349	1.477597	0.056043
23	6	0	2.414979	0.103236	0.033495
24	6	0	-2.443360	1.477701	-0.056146
25	6	0	-2.415026	0.103334	-0.033478
26	6	0	3.675875	-0.680515	0.026585
27	6	0	3.865848	-1.747727	-0.866088
28	6	0	4.721869	-0.345359	0.900505
29	6	0	5.063379	-2.458405	-0.891518
30	1	0	3.080185	-2.009819	-1.567109
31	6	0	5.924428	-1.047394	0.887695
32	1	0	4.585936	0.462089	1.613363
33	6	0	6.081455	-2.099853	-0.010907
34	1	0	5.198750	-3.271334	-1.593759
35	1	0	6.718141	-0.780378	1.573977
36	6	0	-3.675903	-0.680431	-0.026607
37	6	0	-3.865924	-1.747520	0.866201
38	6	0	-4.721857	-0.345358	-0.900611
39	6	0	-5.063455	-2.458199	0.891661
40	1	0	-3.080263	-2.009516	1.567274

41	6	0	-5.924407	-1.047405	-0.887785
42	1	0	-4.585873	0.462034	-1.613523
43	6	0	-6.081474	-2.099762	0.010935
44	1	0	-5.198862	-3.270979	1.594070
45	1	0	-6.718085	-0.780489	-1.574145
46	16	0	7.651433	-3.027847	-0.033172
47	16	0	-7.651485	-3.027761	0.033157
48	9	0	8.535049	-1.658766	0.026470
49	9	0	7.717806	-3.002456	-1.662071
50	9	0	6.877649	-4.462224	-0.094409
51	9	0	9.047350	-3.851889	-0.052709
52	9	0	7.695152	-3.119247	1.594282
53	9	0	-6.877780	-4.462187	0.094615
54	9	0	-7.695064	-3.119356	-1.594292
55	9	0	-8.535105	-1.658670	-0.026736
56	9	0	-9.047430	-3.851754	0.052666
57	9	0	-7.718029	-3.002182	1.662048
58	1	0	-3.398805	1.993186	-0.049587
59	1	0	3.398807	1.993051	0.049379

E(RB3LYP) = -3475.83241447 a.u.

Imaginary Freq = 0

Table A. 11 Atomic coordinates for structure of **U3**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000028	4.711563	-0.000044
2	6	0	-1.222945	4.047170	0.026643

3	6	0	-1.244420	2.642616	0.026046
4	6	0	0.000022	1.967640	-0.000015
5	6	0	1.244467	2.642612	-0.026106
6	6	0	1.222998	4.047166	-0.026728
7	1	0	-2.154740	4.597529	0.049020
8	1	0	2.154796	4.597519	-0.049125
9	7	0	0.000016	0.599453	-0.000019
10	6	0	1.144283	-0.196574	-0.048319
11	6	0	-1.144262	-0.196560	0.048252
12	6	0	0.701431	-1.524818	-0.024711
13	6	0	-0.701427	-1.524808	0.024702
14	1	0	1.335156	-2.399688	-0.038427
15	1	0	-1.335164	-2.399669	0.038464
16	6	0	-2.443174	1.848807	0.068398
17	6	0	-2.411947	0.475187	0.088462
18	6	0	2.411974	0.475159	-0.088571
19	6	0	2.443213	1.848797	-0.068473
20	6	0	3.668579	-0.311571	-0.161854
21	6	0	3.781726	-1.405017	-1.032656
22	6	0	4.772877	0.042718	0.626674
23	6	0	4.973141	-2.117618	-1.093358
24	1	0	2.948393	-1.678381	-1.665715
25	6	0	5.953043	-0.685353	0.528519
26	1	0	4.695405	0.869672	1.320458
27	6	0	6.080782	-1.778357	-0.322974
28	1	0	7.000572	-2.341739	-0.380408
29	6	0	-3.668552	-0.311549	0.161787
30	6	0	-3.781652	-1.404970	1.032619
31	6	0	-4.772876	0.042727	-0.626721
32	6	0	-4.973054	-2.117581	1.093345
33	1	0	-2.948304	-1.678300	1.665668

34	6	0	-5.953062	-0.685328	-0.528518
35	1	0	-4.695245	0.869604	-1.320582
36	6	0	-6.080719	-1.778344	0.322992
37	1	0	-7.000512	-2.341700	0.380653
38	1	0	3.396003	2.366191	-0.126653
39	1	0	-3.395963	2.366202	0.126571
40	16	0	0.000026	6.539579	-0.000032
41	9	0	-1.137555	6.604384	1.166368
42	9	0	-1.168746	6.603740	-1.135005
43	9	0	1.168797	6.603731	1.134943
44	9	0	1.137606	6.604412	-1.166430
45	9	0	0.000020	8.160482	-0.000019
46	16	0	-7.383204	-0.203811	-1.561794
47	16	0	-5.087451	-3.551673	2.221658
48	16	0	5.087581	-3.551711	-2.221671
49	16	0	7.383028	-0.203751	1.561893
50	9	0	-7.173020	1.373596	-1.209973
51	9	0	-8.647601	0.225902	-2.472663
52	9	0	-8.407990	-0.349544	-0.305477
53	9	0	-7.678882	-1.749540	-1.977255
54	9	0	-6.444006	-0.027244	-2.880812
55	9	0	-3.632647	-4.111083	1.738521
56	9	0	-4.363201	-2.732487	3.429096
57	9	0	-5.180832	-4.822386	3.216520
58	9	0	-6.544631	-3.080042	2.771050
59	9	0	-5.814930	-4.460292	1.083607
60	9	0	3.632712	-4.111096	-1.738669
61	9	0	5.180972	-4.822422	-3.216530
62	9	0	5.814924	-4.460375	-1.083584
63	9	0	6.544825	-3.080160	-2.770984
64	9	0	4.363450	-2.732505	-3.429152

65	9	0	7.680755	-1.749767	1.974877
66	9	0	8.647289	0.226098	2.472876
67	9	0	6.444151	-0.030327	2.881535
68	9	0	8.407413	-0.346355	0.304908
69	9	0	7.170789	1.373966	1.212588

E(RB3LYP) = -5539.16453969 a.u.

Imaginary Freq = 0

Table A. 12 Atomic coordinates for structure of **U7**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.337959	3.675316	-0.025381
2	6	0	-1.346199	2.271058	-0.032946
3	6	0	-0.095573	1.606690	-0.008709
4	6	0	1.141480	2.290661	0.018933
5	6	0	1.109068	3.692904	0.021894
6	6	0	-0.121065	4.346867	0.000859
7	1	0	-2.274555	4.217573	-0.039560
8	1	0	2.036401	4.250513	0.039662
9	16	0	-0.134973	6.175792	0.008742
10	9	0	-0.151876	7.796285	0.015844
11	9	0	-1.304009	6.223080	1.145688
12	9	0	1.001332	6.244245	1.173307
13	9	0	-1.277160	6.233936	-1.154944
14	9	0	1.028186	6.253987	-1.127991
15	7	0	-0.092148	0.238825	-0.012685
16	6	0	-1.227286	-0.562129	-0.019743

17	6	0	1.060307	-0.548926	-0.014661
18	6	0	-0.774151	-1.891311	-0.033055
19	6	0	0.625221	-1.883292	-0.019499
20	1	0	-1.408657	-2.764987	-0.057853
21	1	0	1.272496	-2.747950	-0.010324
22	6	0	-2.538753	1.467696	-0.048397
23	6	0	-2.503698	0.093815	-0.032994
24	6	0	2.362680	1.493765	0.027246
25	6	0	2.325336	0.104596	0.004783
26	6	0	-3.757259	-0.701375	-0.024362
27	6	0	-3.934557	-1.771158	0.867723
28	6	0	-4.807475	-0.374887	-0.896269
29	6	0	-5.124807	-2.493940	0.893746
30	1	0	-3.146142	-2.026029	1.568503
31	6	0	-6.002640	-1.089563	-0.882546
32	1	0	-4.681166	0.434637	-1.608603
33	6	0	-6.147477	-2.144838	0.014739
34	1	0	-5.251130	-3.308963	1.595212
35	1	0	-6.799979	-0.829910	-1.567416
36	6	0	3.557741	-0.727957	-0.003846
37	6	0	3.750758	-1.694415	-1.003346
38	6	0	4.539644	-0.570832	0.984781
39	6	0	4.896084	-2.486413	-1.019799
40	1	0	3.008836	-1.816852	-1.785981
41	6	0	5.686983	-1.360659	0.982714
42	1	0	4.406208	0.165491	1.770141
43	6	0	5.850390	-2.312253	-0.020372
44	1	0	5.038822	-3.221557	-1.801582
45	1	0	6.434830	-1.233404	1.754949
46	16	0	-7.707827	-3.090095	0.037477
47	16	0	7.345023	-3.360277	-0.022282

48	9	0	-8.604818	-1.730138	-0.019618
49	9	0	-7.771406	-3.066513	1.666179
50	9	0	-6.917039	-4.514960	0.096186
51	9	0	-9.093769	-3.928917	0.057362
52	9	0	-7.750586	-3.179235	-1.589782
53	9	0	6.472686	-4.706569	-0.318557
54	9	0	7.225983	-3.637017	1.580070
55	9	0	8.316744	-2.087982	0.274588
56	9	0	8.668427	-4.294173	-0.022107
57	9	0	7.562437	-3.157714	-1.624698
58	1	0	-3.497069	1.977709	-0.034960
59	6	0	3.604204	2.199389	0.013959
60	7	0	4.582624	2.831078	0.006735

E(RB3LYP) = -3838.06105139 a.u.

Imaginary Freq = 0

Table A. 13 Atomic coordinates for structure of **U8**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.210882	-3.503418	0.003981
2	6	0	-2.688609	-2.182699	0.006593
3	6	0	-1.732422	-1.136986	-0.035754
4	6	0	-0.338047	-1.364478	-0.072200
5	6	0	0.097996	-2.697031	-0.071334
6	6	0	-0.838947	-3.726186	-0.035398
7	1	0	-2.911595	-4.327969	0.031352
8	1	0	1.157823	-2.907480	-0.097223

9	16	0	-0.232090	-5.450186	-0.039521
10	9	0	0.306121	-6.980430	-0.042894
11	9	0	-1.333395	-5.905362	-1.152742
12	9	0	0.842332	-5.140431	-1.227400
13	9	0	-1.261685	-5.885185	1.148154
14	9	0	0.914349	-5.120819	1.073202
15	7	0	-2.189317	0.151749	-0.038977
16	6	0	-3.529393	0.526079	-0.024081
17	6	0	-1.367477	1.276966	-0.051802
18	6	0	-3.546866	1.929363	-0.022953
19	6	0	-2.224319	2.389452	-0.049391
20	1	0	-4.437356	2.540303	0.002617
21	1	0	-1.903012	3.420654	-0.068157
22	6	0	-4.081653	-1.826430	0.035978
23	6	0	-4.508756	-0.519754	0.011661
24	6	0	0.561231	-0.210648	-0.090605
25	6	0	0.043156	1.084073	-0.075450
26	6	0	-5.956354	-0.189621	0.019680
27	6	0	-6.497745	0.726411	-0.896415
28	6	0	-6.818930	-0.812603	0.934543
29	6	0	-7.861055	1.011176	-0.905285
30	1	0	-5.852013	1.203537	-1.626655
31	6	0	-8.183460	-0.533779	0.941107
32	1	0	-6.414755	-1.507854	1.663878
33	6	0	-8.689895	0.377904	0.018092
34	1	0	-8.266781	1.710330	-1.625535
35	1	0	-8.834381	-1.015547	1.659741
36	6	0	0.920475	2.285067	-0.064816
37	6	0	0.808987	3.234868	0.961840
38	6	0	1.872020	2.492180	-1.074476
39	6	0	1.634216	4.357201	0.993423

40	1	0	0.084966	3.085794	1.756705
41	6	0	2.698171	3.613473	-1.060457
42	1	0	1.962792	1.775055	-1.883300
43	6	0	2.572325	4.532179	-0.020439
44	1	0	1.548043	5.074617	1.799677
45	1	0	3.421765	3.766462	-1.851253
46	16	0	-10.475115	0.753316	0.021494
47	16	0	3.664147	5.993301	0.016766
48	9	0	-10.870885	-0.818087	0.202462
49	9	0	-10.575719	0.594427	-1.597843
50	9	0	-10.204633	2.351647	-0.159130
51	9	0	-12.060809	1.086958	0.024653
52	9	0	-10.496764	0.938483	1.641106
53	9	0	2.422888	6.992918	0.359484
54	9	0	3.452603	6.272191	-1.575636
55	9	0	4.981868	5.093057	-0.322946
56	9	0	4.635901	7.288808	0.050524
57	9	0	3.953237	5.815039	1.611416
58	1	0	-4.814009	-2.627983	0.041122
59	6	0	1.957852	-0.451017	-0.072709
60	6	0	3.149252	-0.702363	-0.046116
61	6	0	4.551402	-0.937110	-0.017957
62	6	0	5.065167	-2.248958	-0.045597
63	6	0	5.451174	0.146953	0.037357
64	6	0	6.436851	-2.473560	-0.019985
65	1	0	4.382524	-3.091365	-0.086956
66	6	0	6.823536	-0.072457	0.062464
67	1	0	5.065557	1.160888	0.061410
68	6	0	7.302405	-1.381738	0.033135
69	1	0	6.821711	-3.485244	-0.041378
70	1	0	7.506966	0.766112	0.105580

71	16	0	9.102213	-1.671830	0.066016
72	9	0	9.323508	-0.571699	1.249025
73	9	0	10.702321	-1.929624	0.095094
74	9	0	8.956886	-2.849095	1.184673
75	9	0	9.373895	-0.515168	-1.051021
76	9	0	9.008205	-2.792209	-1.115146

E(RB3LYP) = -4949.71032294 a.u.

Imaginary Freq = 0

Table A. 14 Atomic coordinates for structure of **U9**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.828848	-3.520341	-0.003008
2	6	0	2.200124	-2.166540	-0.018923
3	6	0	1.164785	-1.197819	-0.010183
4	6	0	-0.214426	-1.527133	-0.007795
5	6	0	-0.536848	-2.896090	0.027232
6	6	0	0.478663	-3.848093	0.024497
7	1	0	2.591668	-4.288110	-0.008906
8	1	0	-1.571006	-3.205806	0.059170
9	16	0	0.010237	-5.614880	0.056016
10	9	0	-0.403595	-7.182490	0.081134
11	9	0	1.123712	-5.958802	1.196980
12	9	0	-1.107046	-5.368773	1.217468
13	9	0	1.093987	-5.989354	-1.104884
14	9	0	-1.136579	-5.399532	-1.084679
15	7	0	1.525198	0.120314	-0.004784

16	6	0	2.834979	0.597172	-0.035819
17	6	0	0.621683	1.177449	-0.020651
18	6	0	2.742256	1.994201	-0.091779
19	6	0	1.385796	2.350613	-0.081812
20	1	0	3.581087	2.672253	-0.149199
21	1	0	0.984915	3.352730	-0.124386
22	6	0	3.562794	-1.706652	-0.031687
23	6	0	3.891397	-0.372018	-0.035631
24	6	0	-1.196517	-0.447114	-0.014372
25	6	0	-0.776385	0.872131	-0.013067
26	6	0	5.309968	0.065191	-0.031780
27	6	0	5.756246	1.077022	0.833674
28	6	0	6.243862	-0.548085	-0.881409
29	6	0	7.093129	1.466222	0.854871
30	1	0	5.057137	1.549351	1.515993
31	6	0	7.583775	-0.168544	-0.872532
32	1	0	5.914802	-1.316558	-1.574074
33	6	0	7.993899	0.838634	-0.002386
34	1	0	7.423891	2.240718	1.535233
35	1	0	8.289254	-0.645645	-1.541059
36	6	0	-1.714537	2.033061	-0.028726
37	6	0	-2.637143	2.212558	-1.069096
38	6	0	-1.661584	2.991059	0.995377
39	6	0	-3.492654	3.311808	-1.087570
40	1	0	-2.686414	1.489272	-1.876208
41	6	0	-2.513353	4.093669	0.993027
42	1	0	-0.953444	2.869143	1.809325
43	6	0	-3.421123	4.241122	-0.052560
44	1	0	-4.198033	3.438453	-1.899128
45	1	0	-2.467941	4.820172	1.794419
46	16	0	9.744457	1.351334	0.010888

47	16	0	-4.536411	5.685045	-0.067022
48	9	0	10.263947	-0.193797	0.003402
49	9	0	9.794901	1.362649	1.640460
50	9	0	9.346578	2.932750	0.019217
51	9	0	11.299189	1.807665	0.022883
52	9	0	9.815798	1.376196	-1.617702
53	9	0	-4.268300	5.956176	-1.652278
54	9	0	-3.321716	6.704916	0.313663
55	9	0	-4.879757	5.514613	1.518022
56	9	0	-5.525009	6.968438	-0.078269
57	9	0	-5.826458	4.766049	-0.447902
58	1	0	4.351605	-2.452090	-0.004502
59	6	0	-2.646820	-0.802403	0.005365
60	6	0	-3.228142	-1.499288	-1.066189
61	6	0	-3.458218	-0.456179	1.095574
62	6	0	-4.580950	-1.832616	-1.059800
63	1	0	-2.618956	-1.779517	-1.920777
64	6	0	-4.813087	-0.780985	1.116959
65	1	0	-3.026958	0.074550	1.938351
66	6	0	-5.360064	-1.466395	0.035313
67	1	0	-5.014823	-2.365284	-1.896623
68	1	0	-5.425820	-0.505653	1.966063
69	16	0	-7.132745	-1.897591	0.053118
70	9	0	-6.831364	-3.420061	-0.443953
71	9	0	-7.324636	-1.435697	-1.499336
72	9	0	-8.707217	-2.280469	0.067296
73	9	0	-7.555390	-0.404016	0.550461
74	9	0	-7.064164	-2.388285	1.605918

E(RB3LYP) = -4873.54684784 a.u.

Imaginary Freq = 0

Table A. 15 Atomic coordinates for structure of **U10**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.445534	3.575470	0.017498
2	6	0	-1.663805	2.189044	-0.002401
3	6	0	-0.526558	1.341882	0.015344
4	6	0	0.806857	1.822498	0.031206
5	6	0	0.975439	3.219115	0.068096
6	6	0	-0.139703	4.051345	0.056889
7	1	0	-2.289127	4.253488	0.005443
8	1	0	1.971470	3.635132	0.106632
9	16	0	0.125057	5.859054	0.094428
10	9	0	0.357961	7.465470	0.125147
11	9	0	-1.024783	6.073818	1.231883
12	9	0	1.259053	5.741721	1.260011
13	9	0	-0.989948	6.114641	-1.070342
14	9	0	1.293375	5.781877	-1.042554
15	7	0	-0.737019	-0.008406	0.018648
16	6	0	-1.986259	-0.629159	-0.023018
17	6	0	0.279249	-0.956383	0.010801
18	6	0	-1.736765	-2.006303	-0.077187
19	6	0	-0.348167	-2.207684	-0.055816
20	1	0	-2.493289	-2.774826	-0.140206
21	1	0	0.162896	-3.158465	-0.095041
22	6	0	-2.966626	1.579805	-0.027811
23	6	0	-3.143267	0.216612	-0.033133
24	6	0	1.908152	0.863315	0.034521
25	6	0	1.635157	-0.494301	0.028588
26	6	0	-4.504149	-0.375921	-0.040393

27	6	0	-4.841848	-1.430904	0.822745
28	6	0	-5.493861	0.127870	-0.898962
29	6	0	-6.126516	-1.968148	0.833032
30	1	0	-4.099281	-1.820995	1.511004
31	6	0	-6.782653	-0.399888	-0.901324
32	1	0	-5.246871	0.928260	-1.589623
33	6	0	-7.084528	-1.446462	-0.033367
34	1	0	-6.373486	-2.774846	1.511656
35	1	0	-7.531774	-0.005482	-1.576202
36	6	0	2.699656	-1.540200	0.012820
37	6	0	3.652903	-1.589996	-1.014625
38	6	0	2.743142	-2.520711	1.015663
39	6	0	4.627929	-2.583685	-1.042034
40	1	0	3.632726	-0.844162	-1.801687
41	6	0	3.715096	-3.519331	1.005107
42	1	0	2.014833	-2.497678	1.820504
43	6	0	4.648034	-3.538989	-0.028188
44	1	0	5.354957	-2.611247	-1.843737
45	1	0	3.741333	-4.263635	1.790930
46	16	0	-8.765604	-2.153124	-0.035172
47	16	0	5.920040	-4.845198	-0.056620
48	9	0	-9.457214	-0.676573	-0.064012
49	9	0	-8.836333	-2.156227	1.593756
50	9	0	-8.193454	-3.680164	-0.006248
51	9	0	-10.259820	-2.782584	-0.037064
52	9	0	-8.813811	-2.200171	-1.664329
53	9	0	5.709420	-5.107818	-1.652685
54	9	0	4.826369	-6.007972	0.279852
55	9	0	6.222325	-4.678340	1.537507
56	9	0	7.050775	-6.007861	-0.081908
57	9	0	7.104318	-3.776832	-0.394946

58	1	0	-3.834216	2.232265	-0.008441
59	6	0	3.306430	1.382297	0.086689
60	6	0	3.841017	2.135611	-0.966514
61	6	0	4.127107	1.140616	1.203366
62	6	0	5.147859	2.626953	-0.926669
63	1	0	3.230834	2.340620	-1.842611
64	6	0	5.426058	1.624361	1.259547
65	1	0	3.736305	0.567297	2.038956
66	6	0	5.949184	2.371853	0.193074
67	1	0	5.524266	3.201243	-1.765222
68	1	0	6.058121	1.440113	2.122419
69	8	0	7.231902	2.800414	0.344409
70	6	0	7.814941	3.571546	-0.696427
71	1	0	7.265373	4.507562	-0.859925
72	1	0	8.828702	3.801274	-0.364558
73	1	0	7.860350	3.008261	-1.637569

E(RB3LYP) = -4091.39615769 a.u.

Imaginary Freq = 0

NMR Spectra

Chapter 2

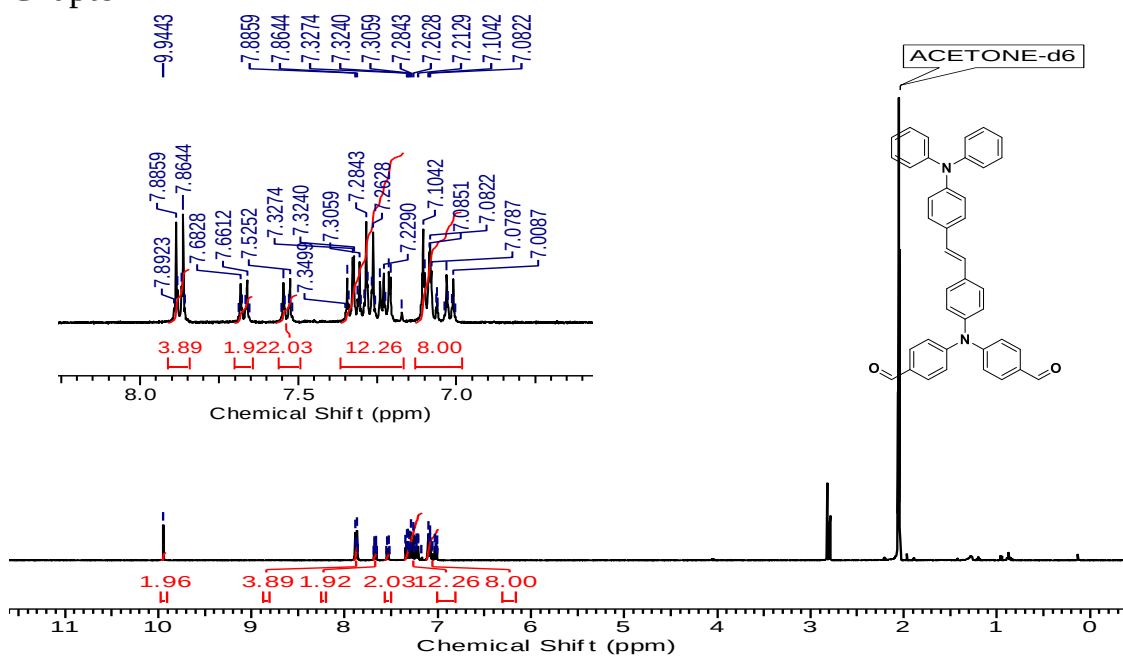


Figure A. 4 ¹H NMR spectrum of compound 2e.

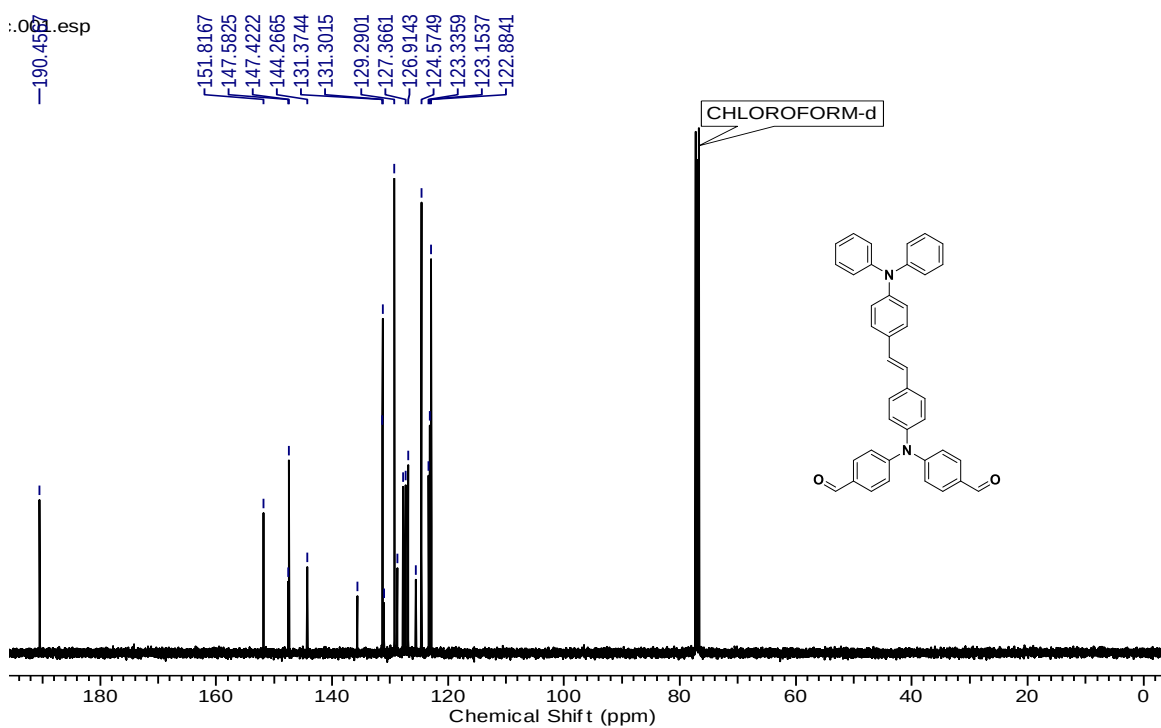


Figure A. 5 ¹³C NMR spectrum of compound 2e.

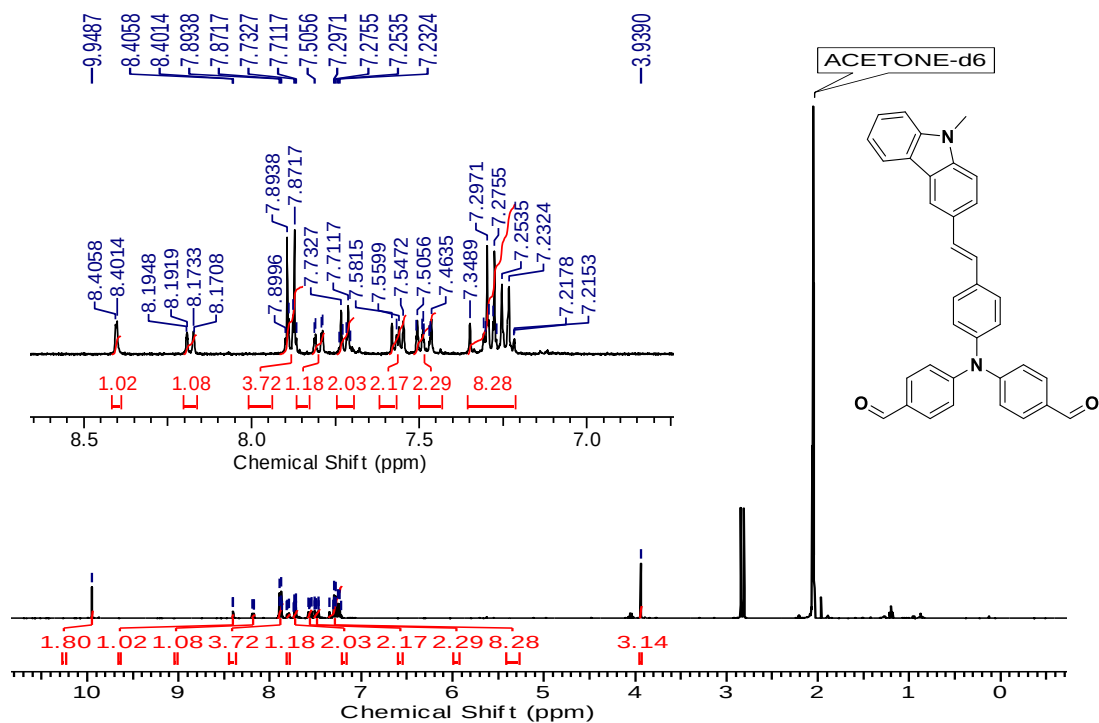


Figure A. 6 ¹H NMR spectrum of compound 2f.

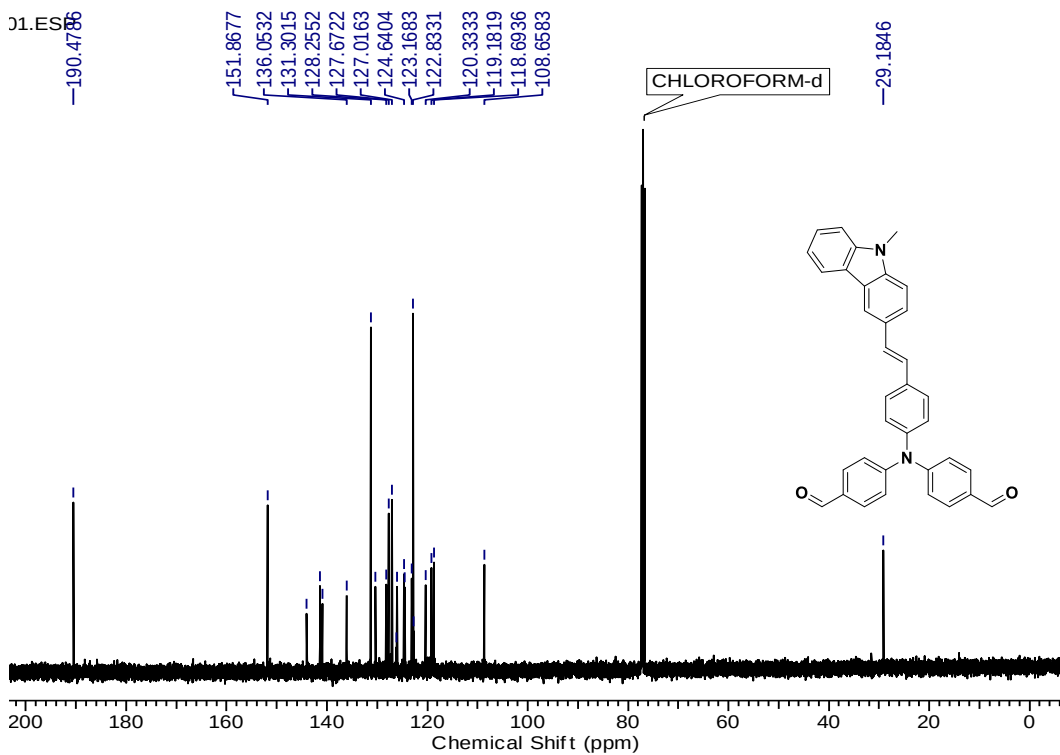


Figure A. 7 ¹³C NMR spectrum of compound 2f.

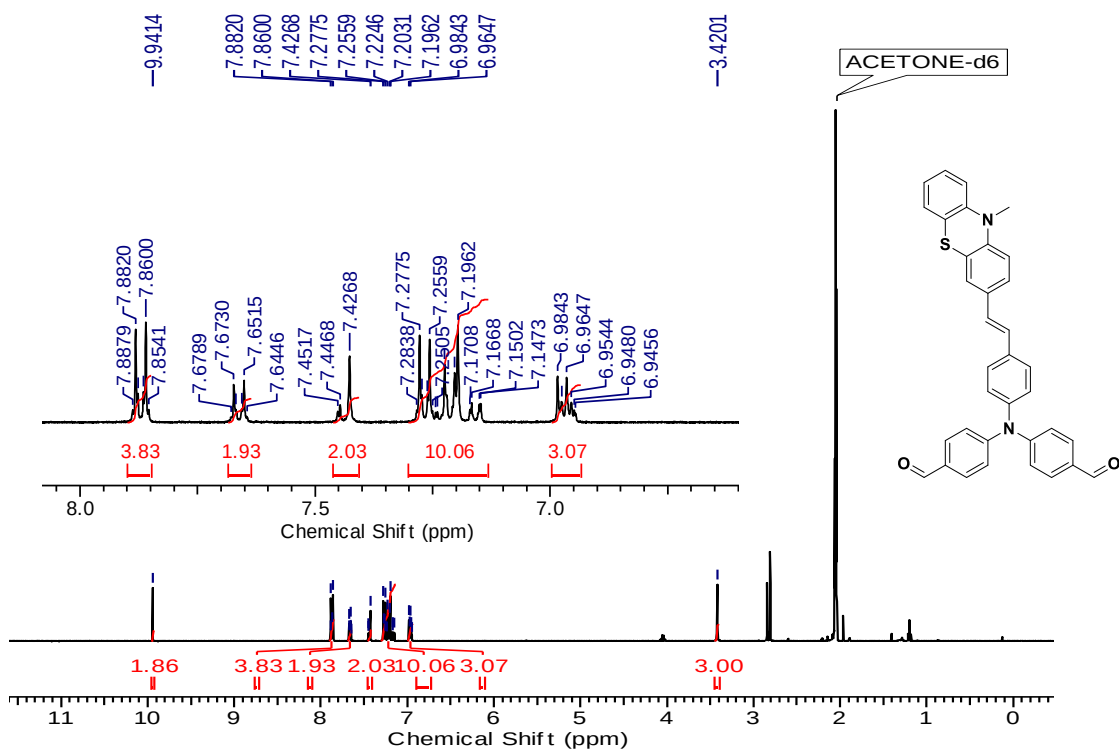


Figure A. 8 ¹H NMR spectrum of compound **2g**.

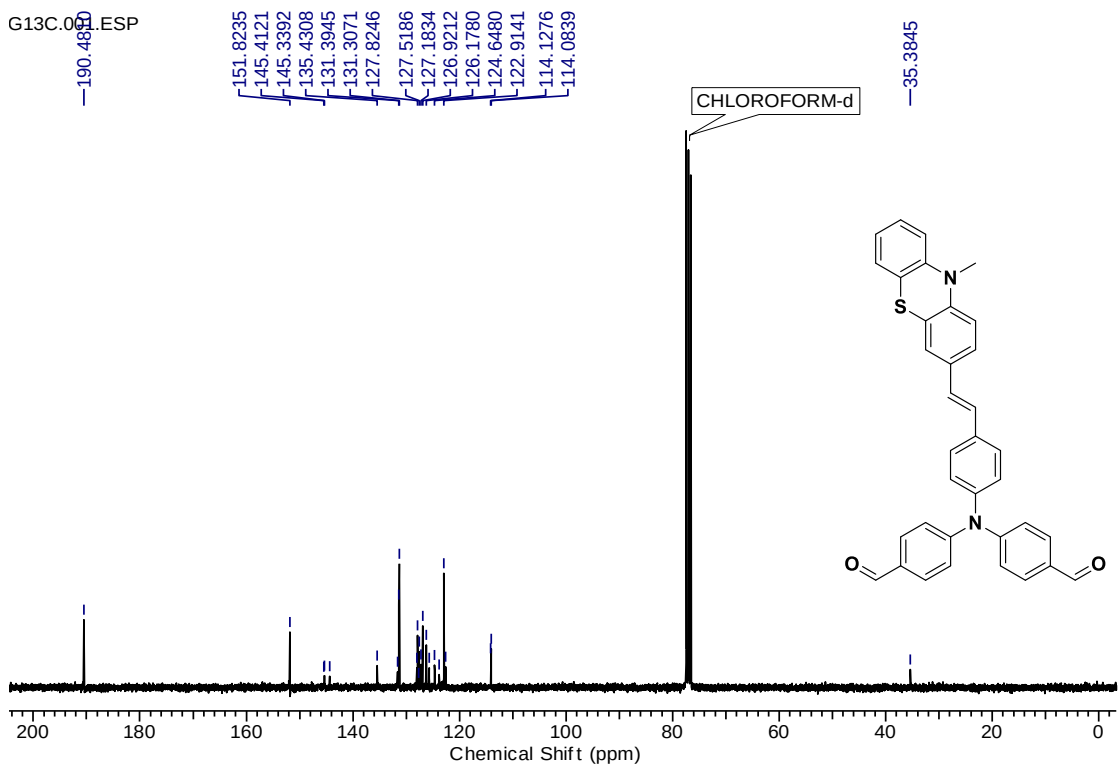


Figure A. 9 ¹³C NMR spectrum of compound **2g**.

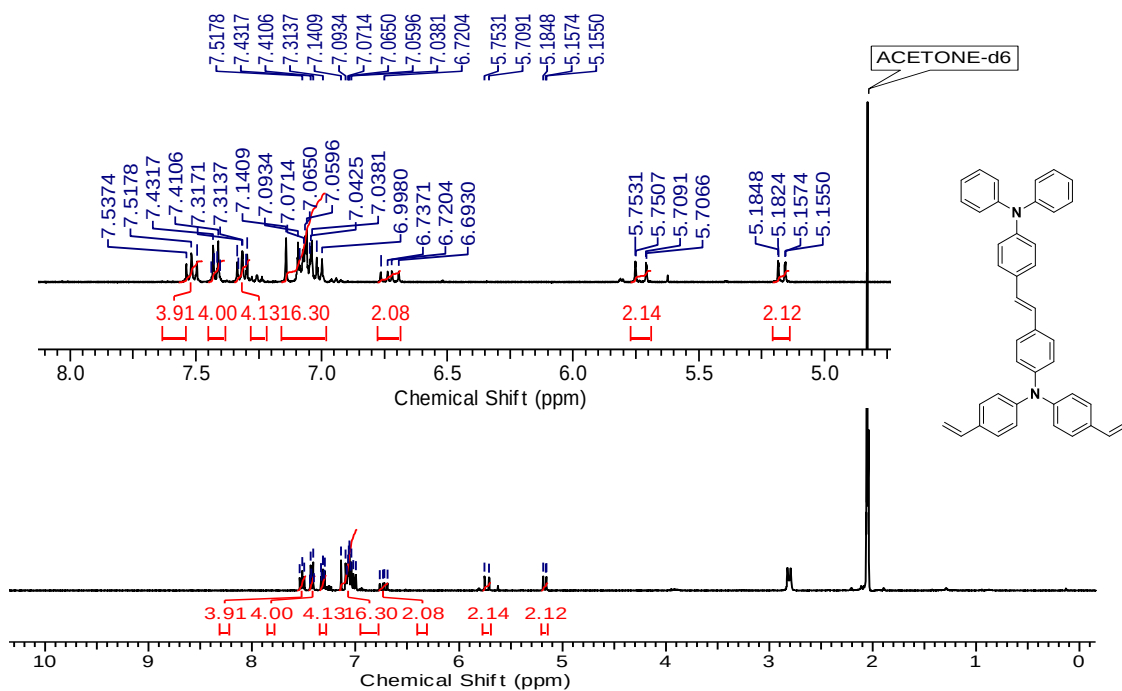


Figure A. 10 ¹H NMR spectrum of compound 2j.

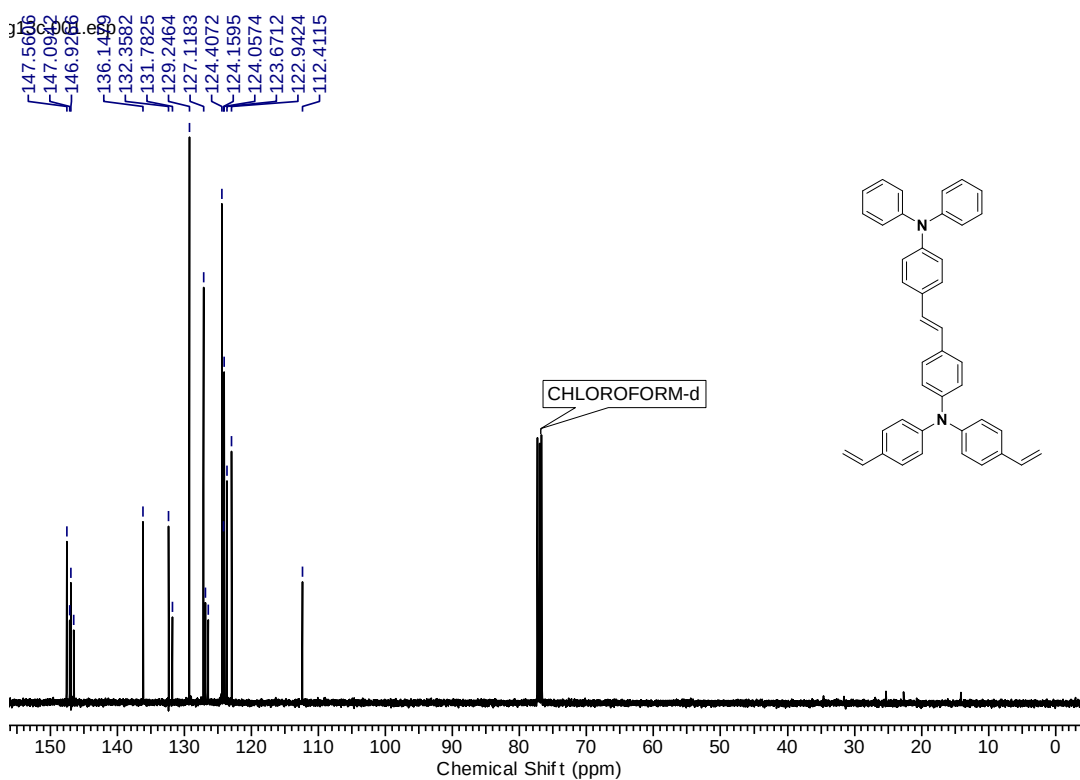


Figure A. 11 ¹³C NMR spectrum of compound 2j.

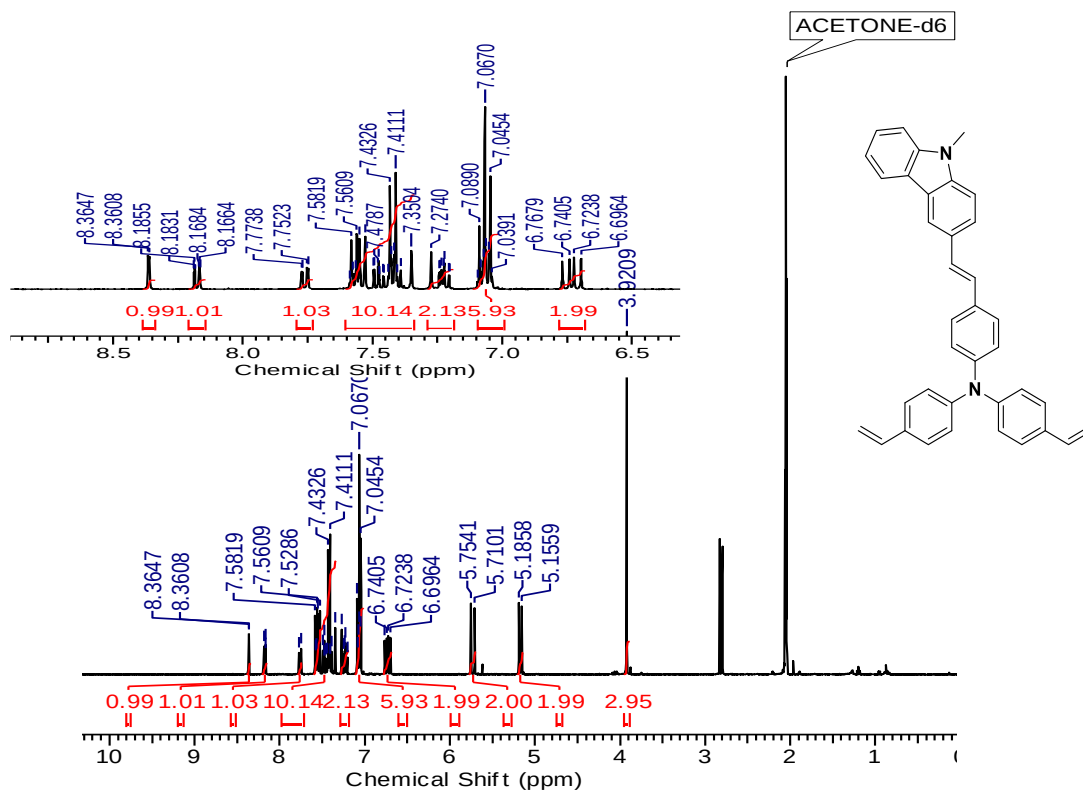


Figure A. 12 ¹H NMR spectrum of compound 2k.

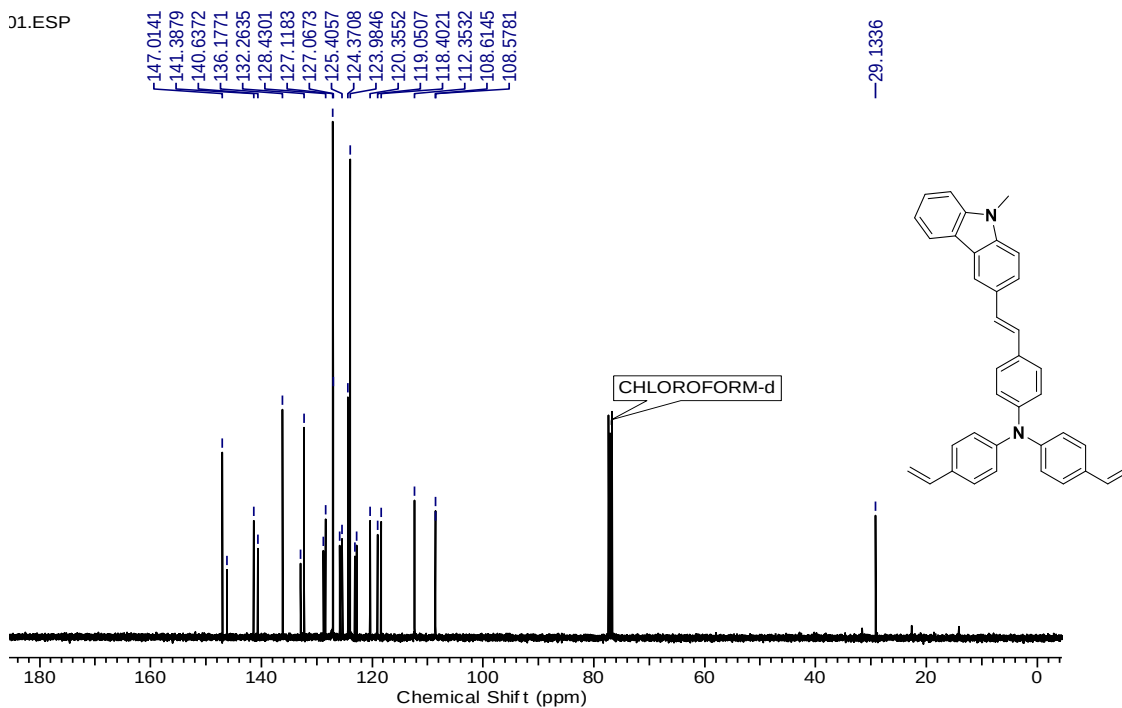


Figure A. 13 ¹³C NMR spectrum of compound 2k.

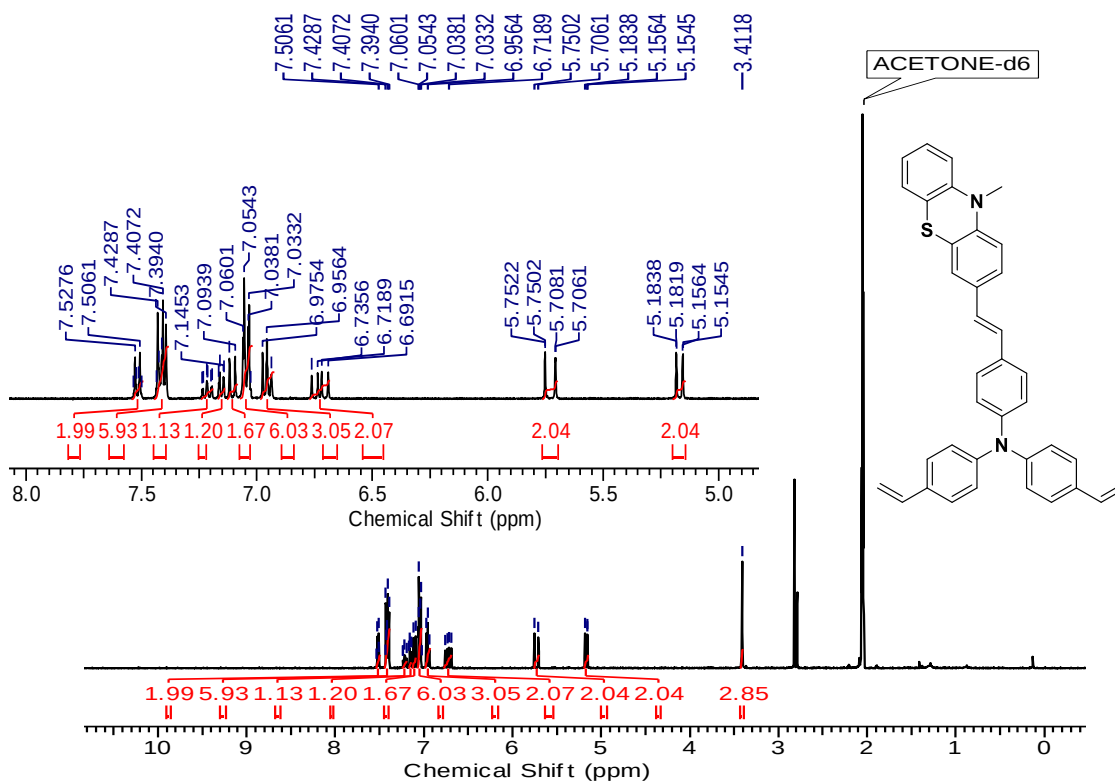


Figure A. 14 ¹H NMR spectrum of compound 2l.

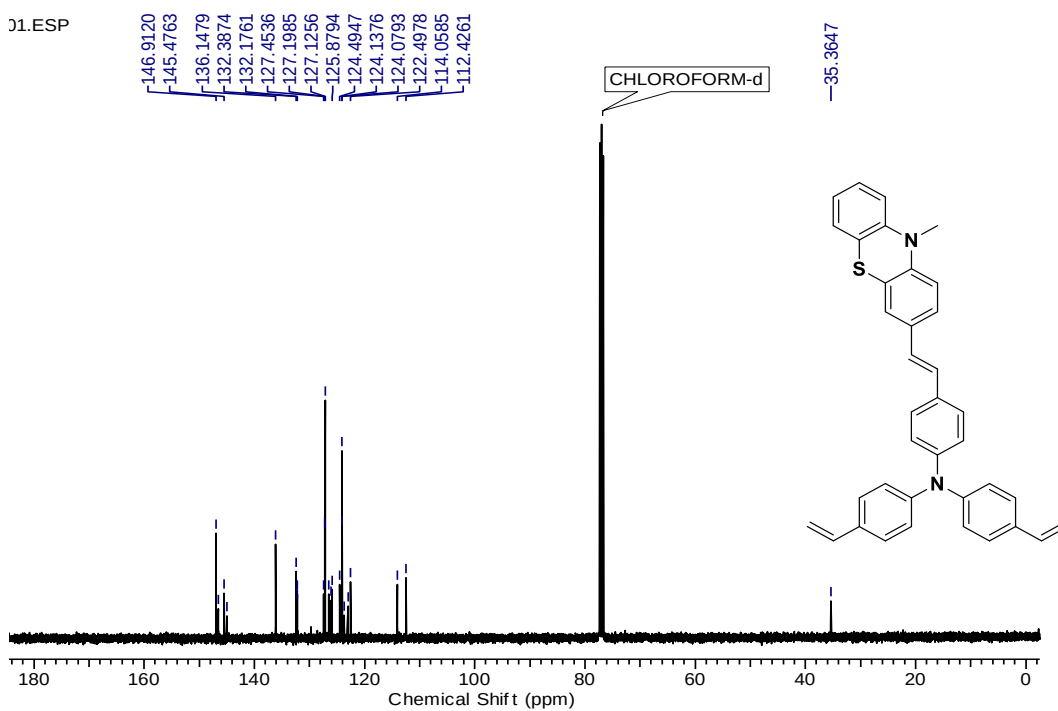


Figure A. 15 ¹³C NMR spectrum of compound 2l.

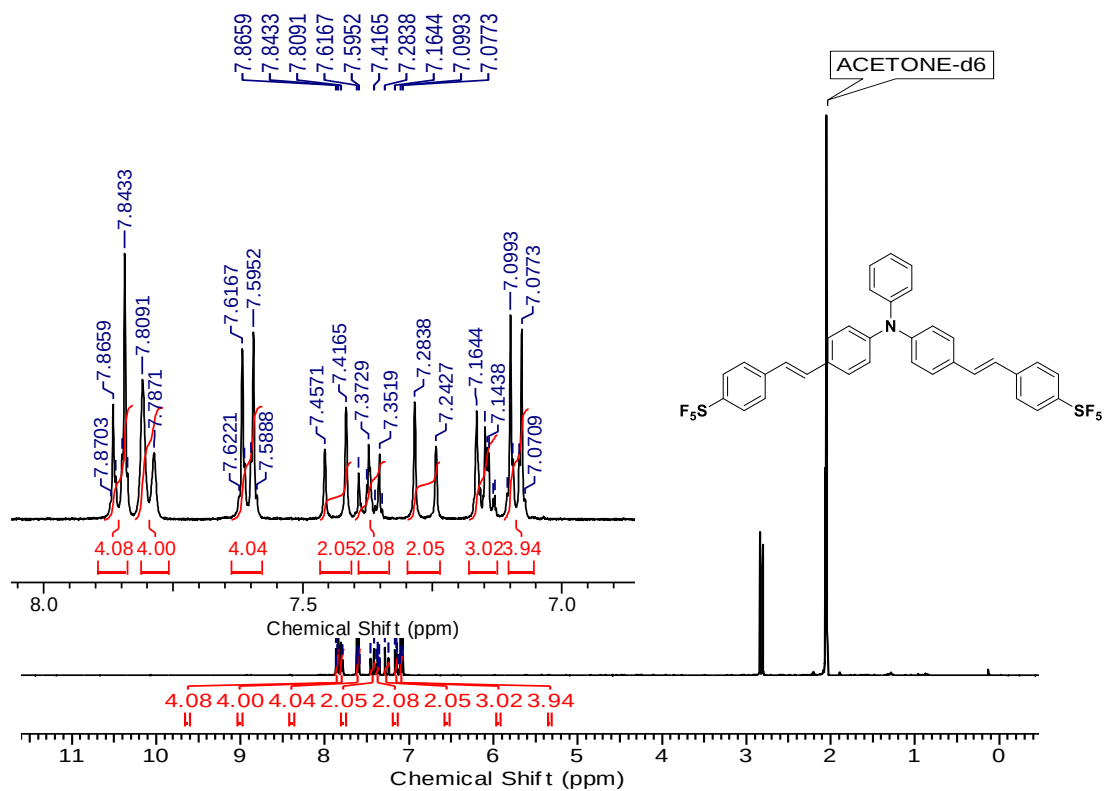


Figure A. 16 ¹H NMR spectrum of compound D1.

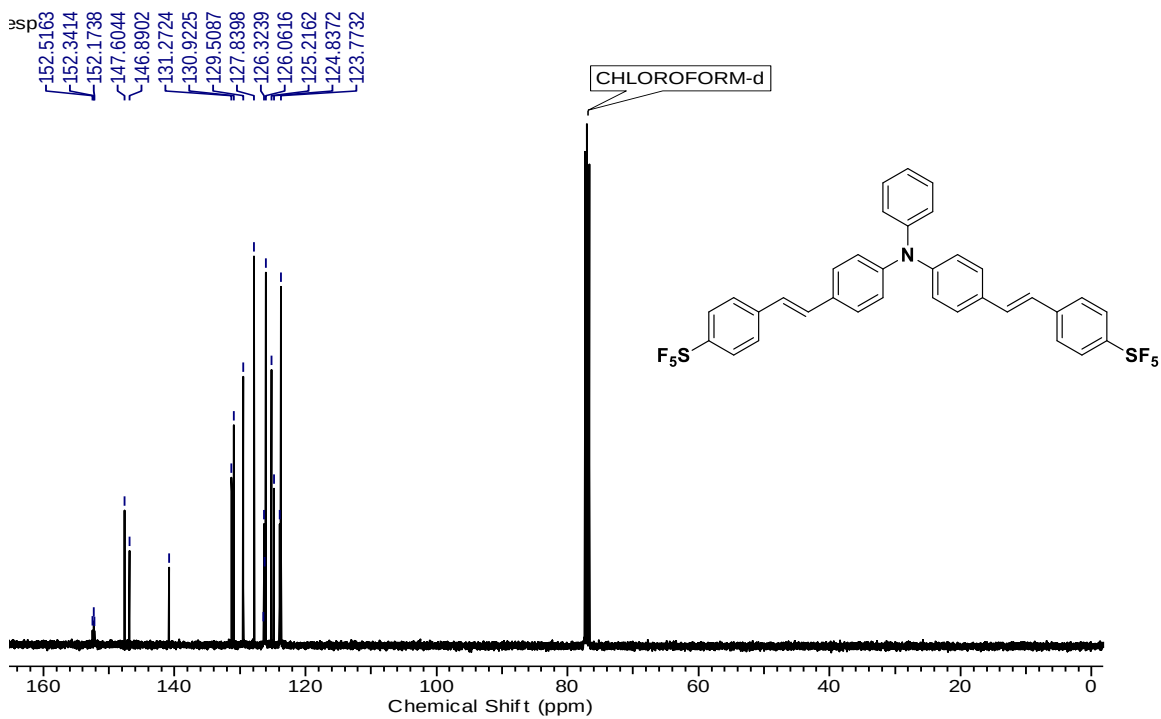


Figure A. 17 ¹³C NMR spectrum of compound D1.

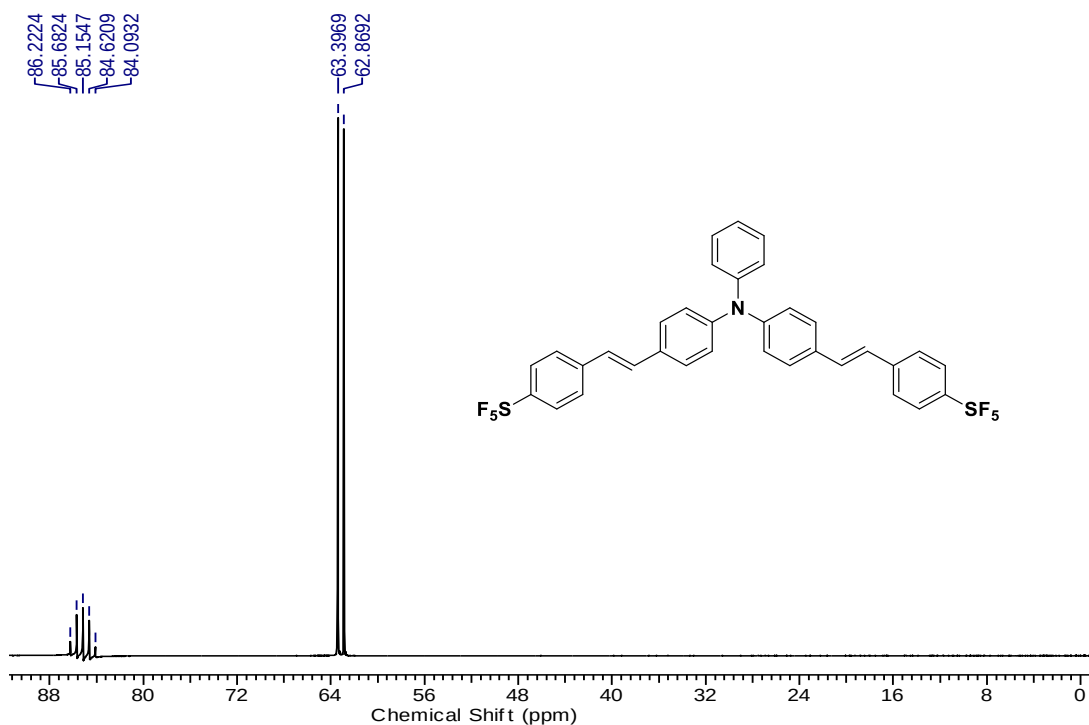


Figure A. 18 ¹⁹F NMR spectrum of compound **D1**.

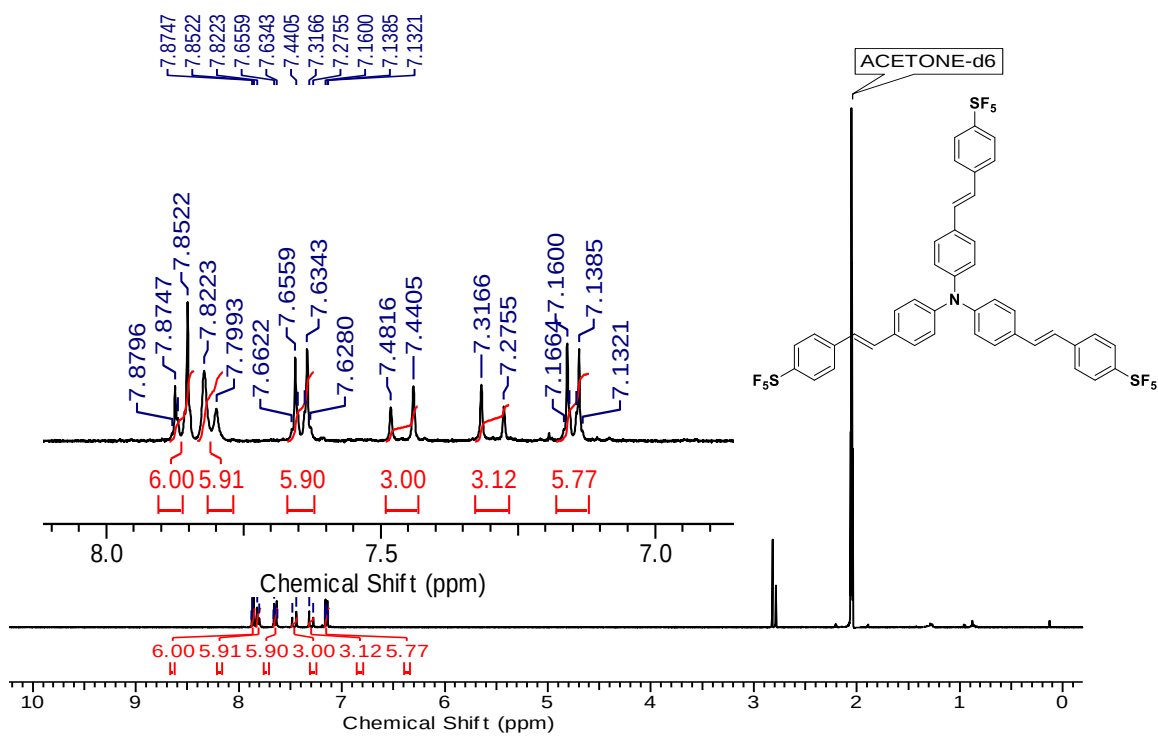


Figure A. 19 ¹H NMR spectrum of compound **D2**.

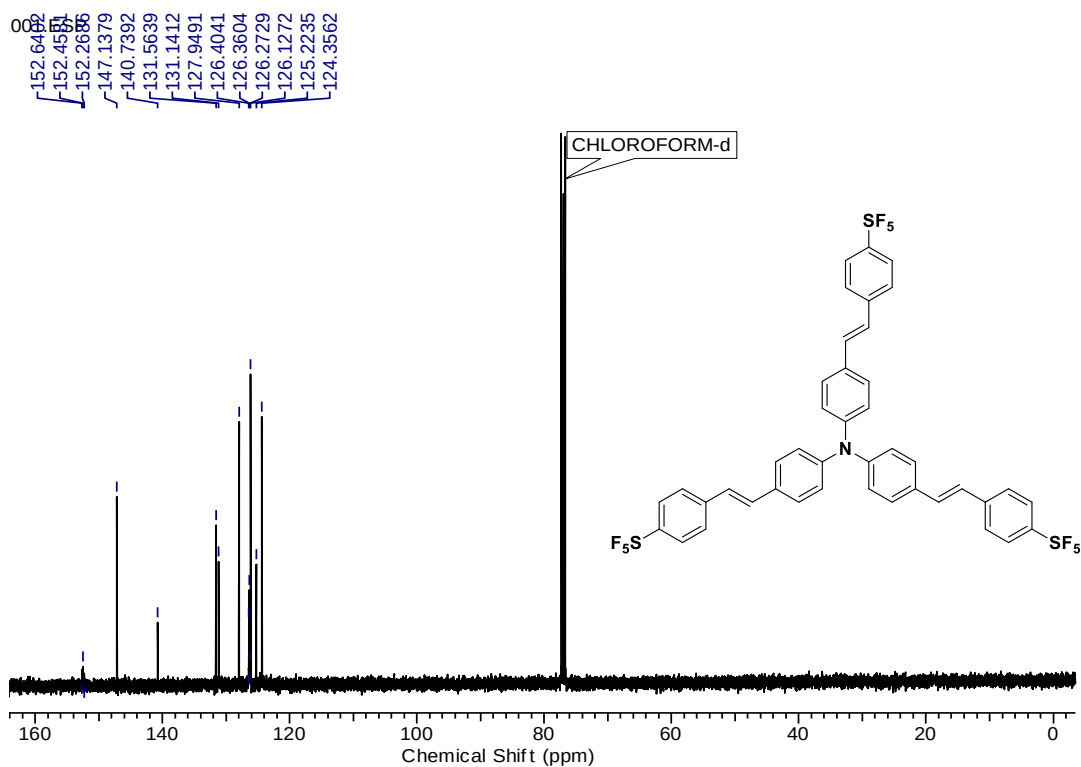


Figure A. 20 ¹³C NMR spectrum of compound **D2**.

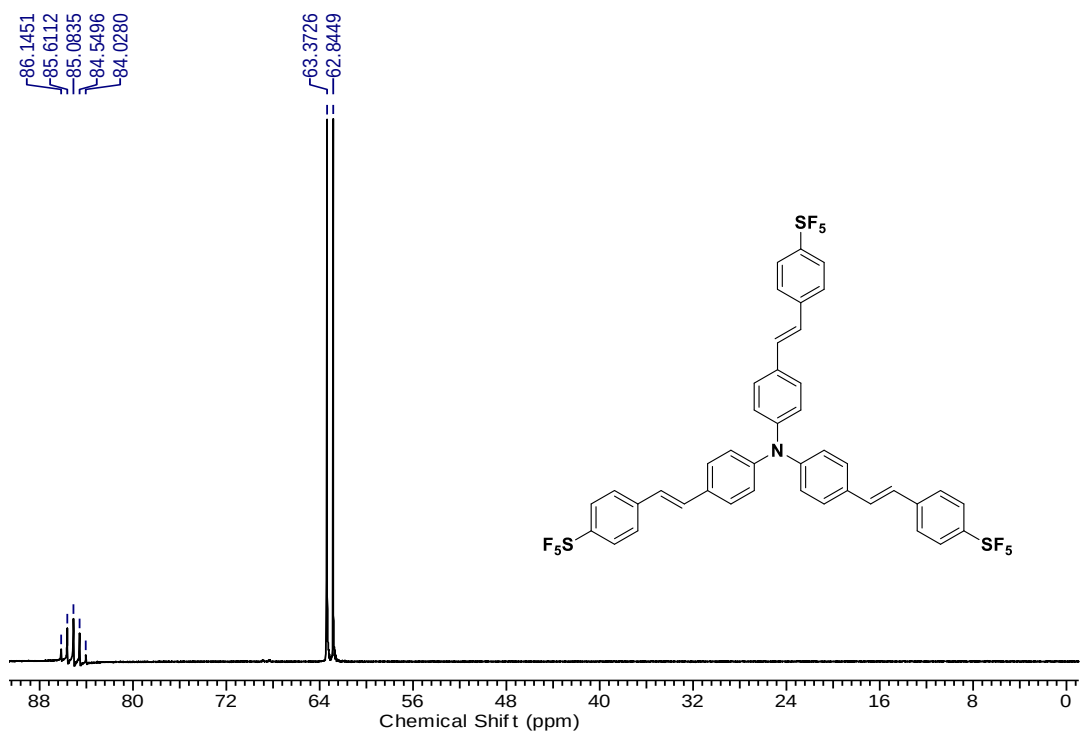


Figure A. 21 ¹⁹F NMR spectrum of compound **D2**.

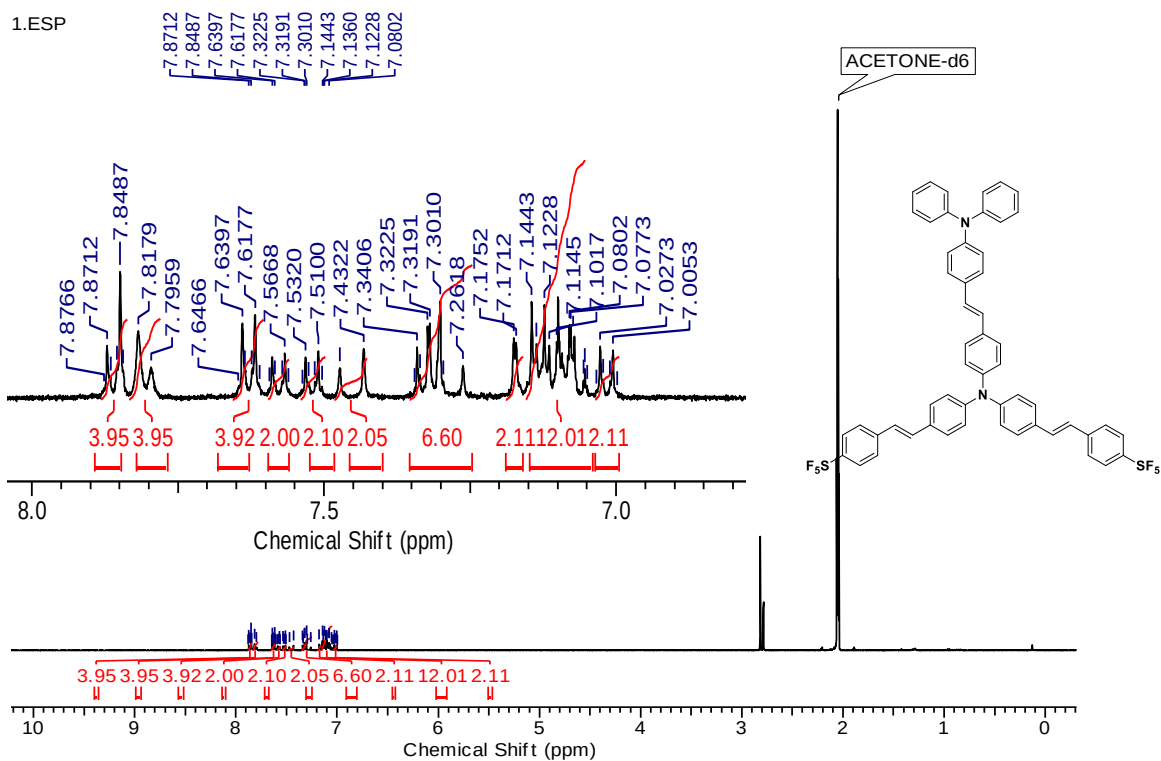


Figure A. 22 ^1H NMR spectrum of compound **D3**.

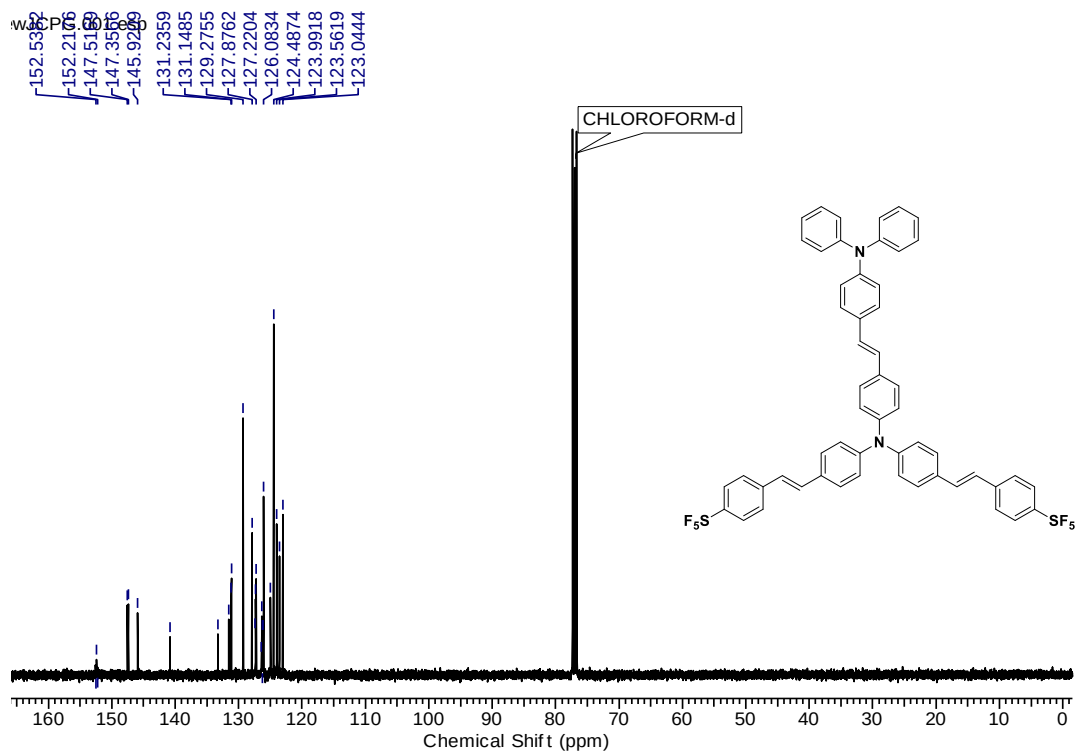


Figure A. 23 ^{13}C NMR spectrum of compound **D3**.

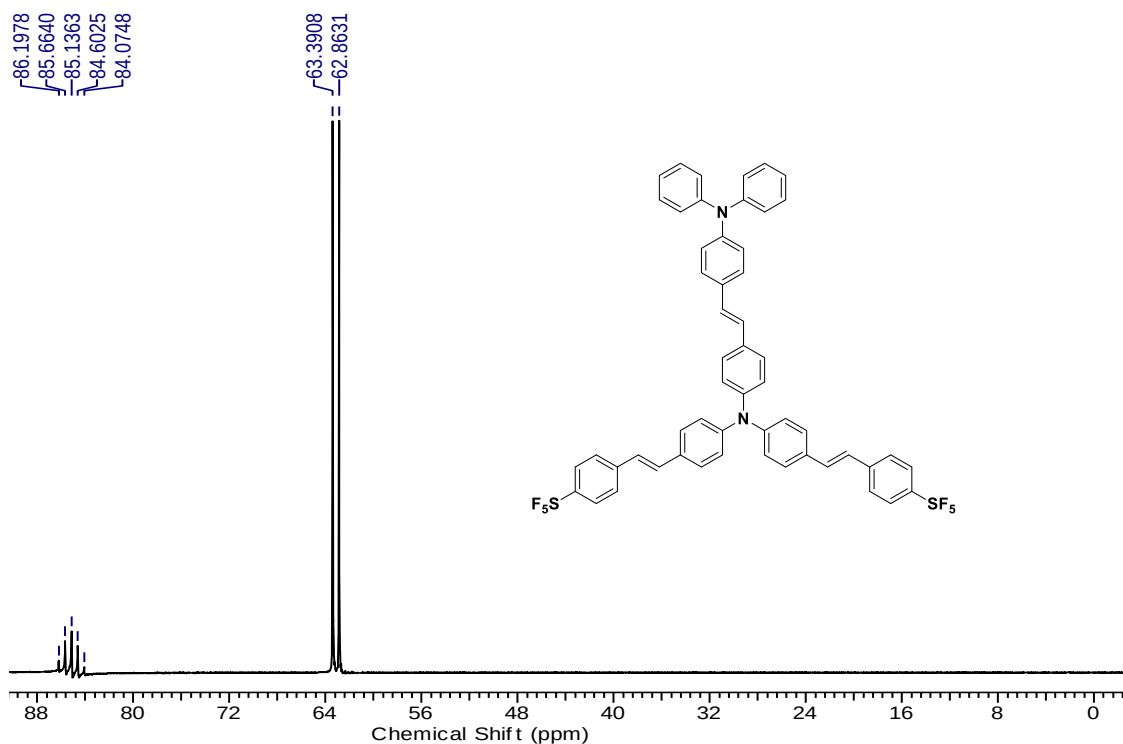


Figure A. 24 ¹⁹F NMR spectrum of compound **D3**.

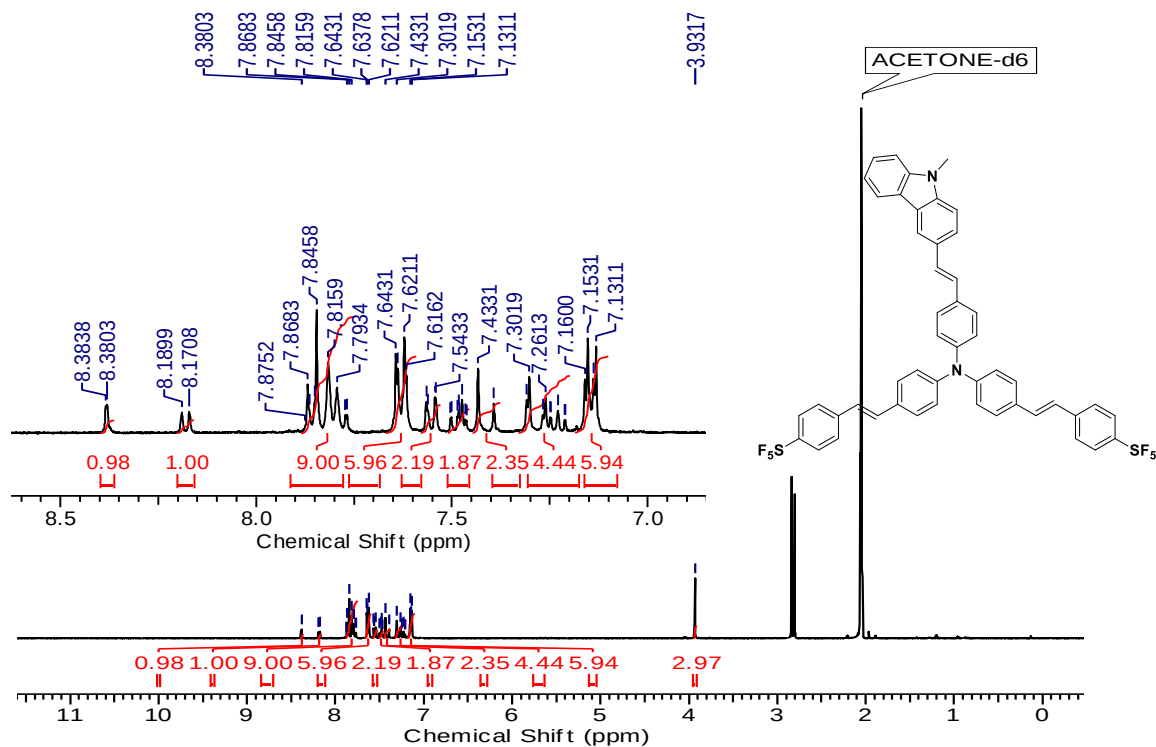


Figure A. 25 ¹H NMR spectrum of compound **D4**.

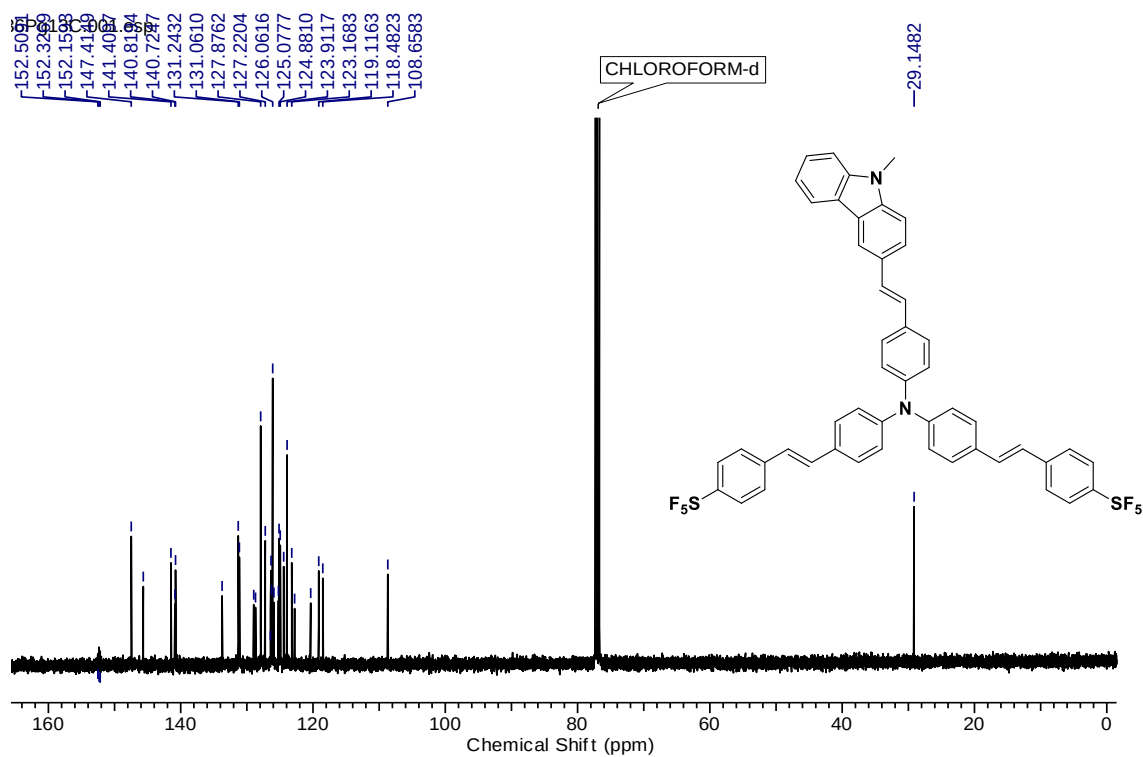


Figure A. 26 ¹³C NMR spectrum of compound **D4**.

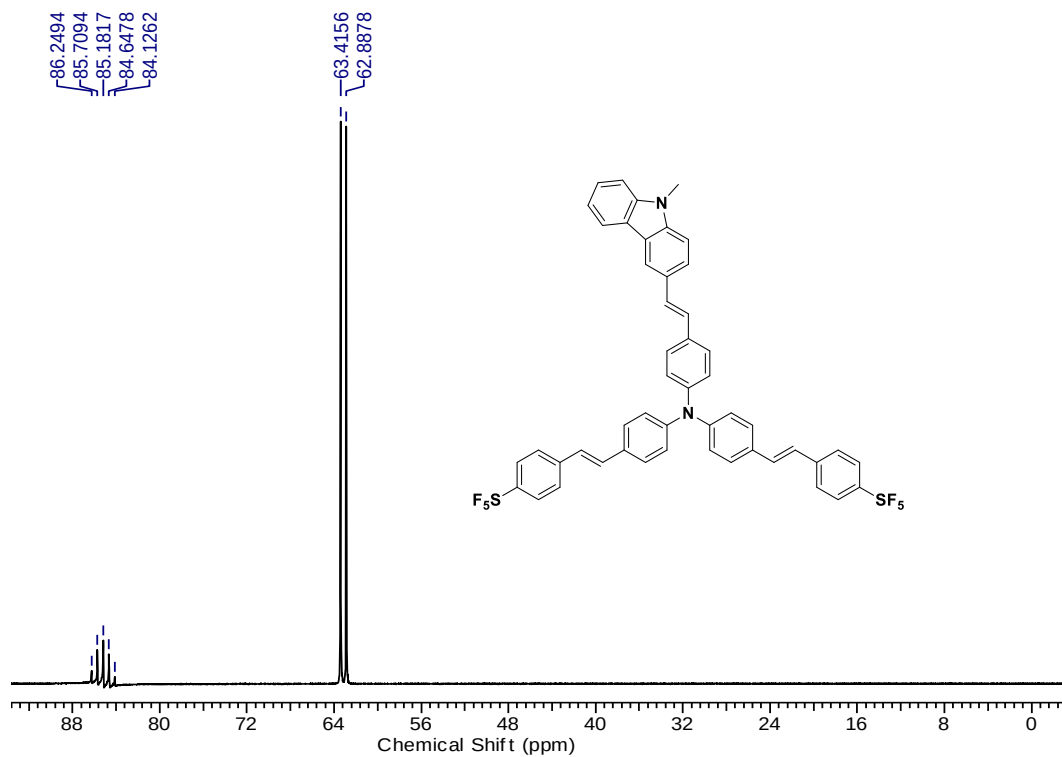


Figure A. 27 ¹⁹F NMR spectrum of compound **D4**.

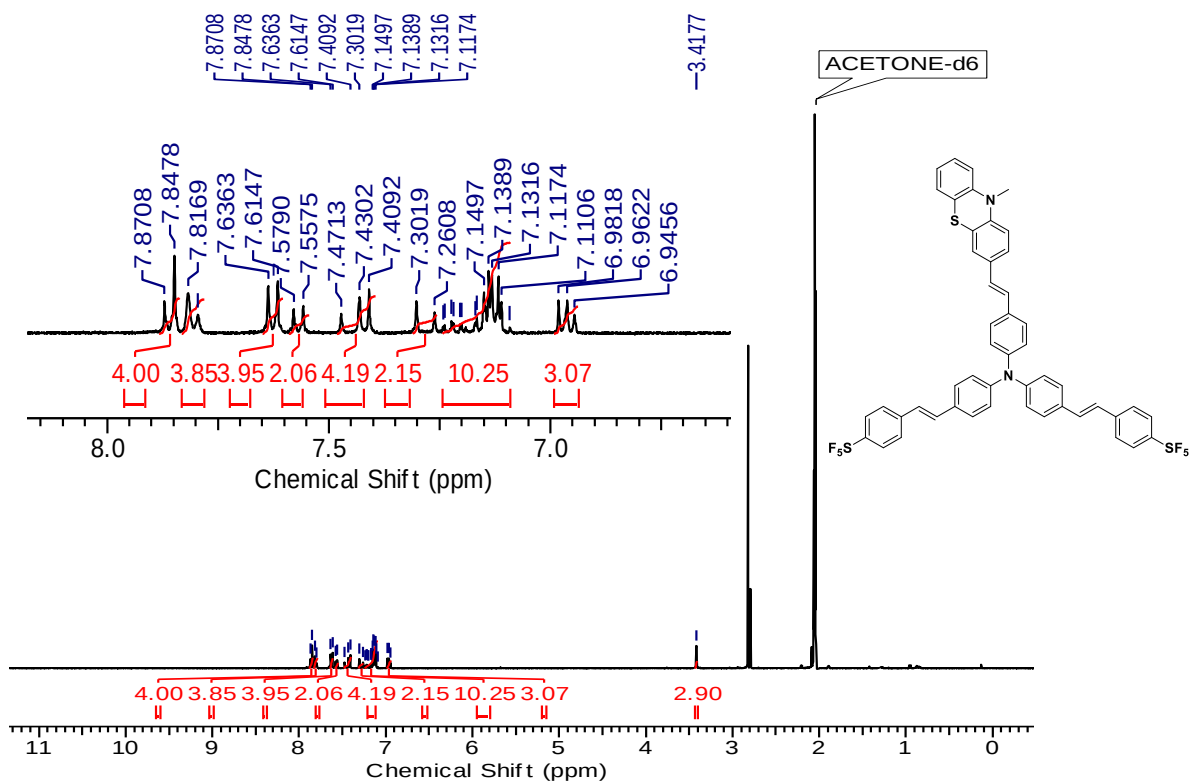


Figure A. 28 ¹H NMR spectrum of compound D5.

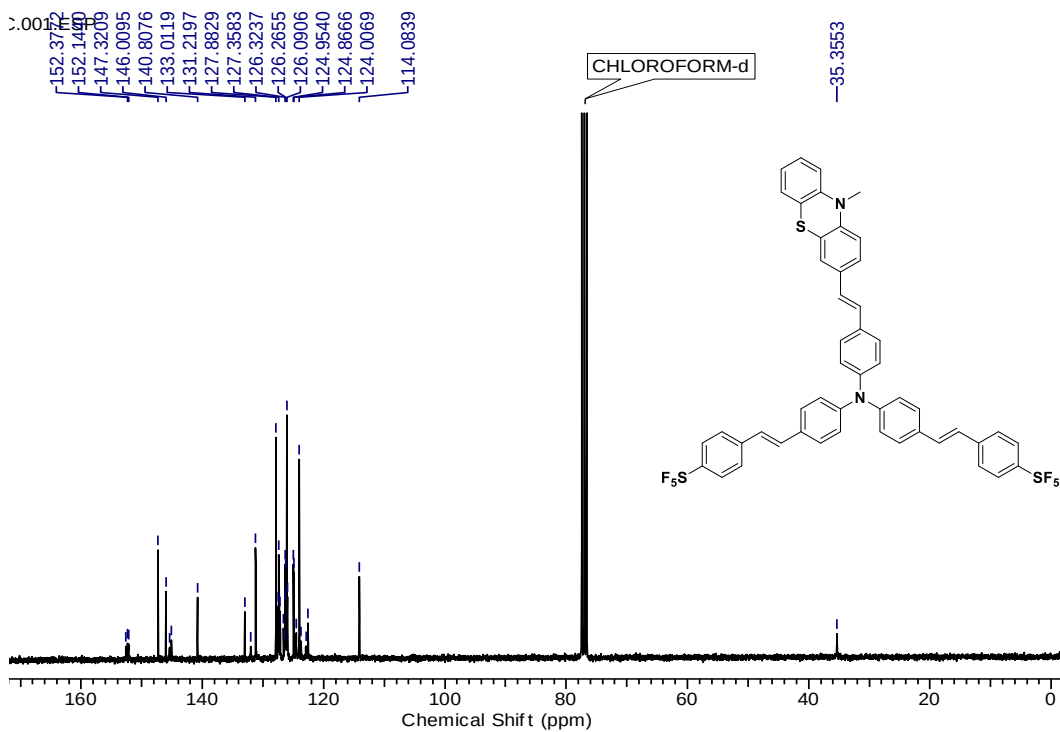


Figure A. 29 ¹³C NMR spectrum of compound D5.

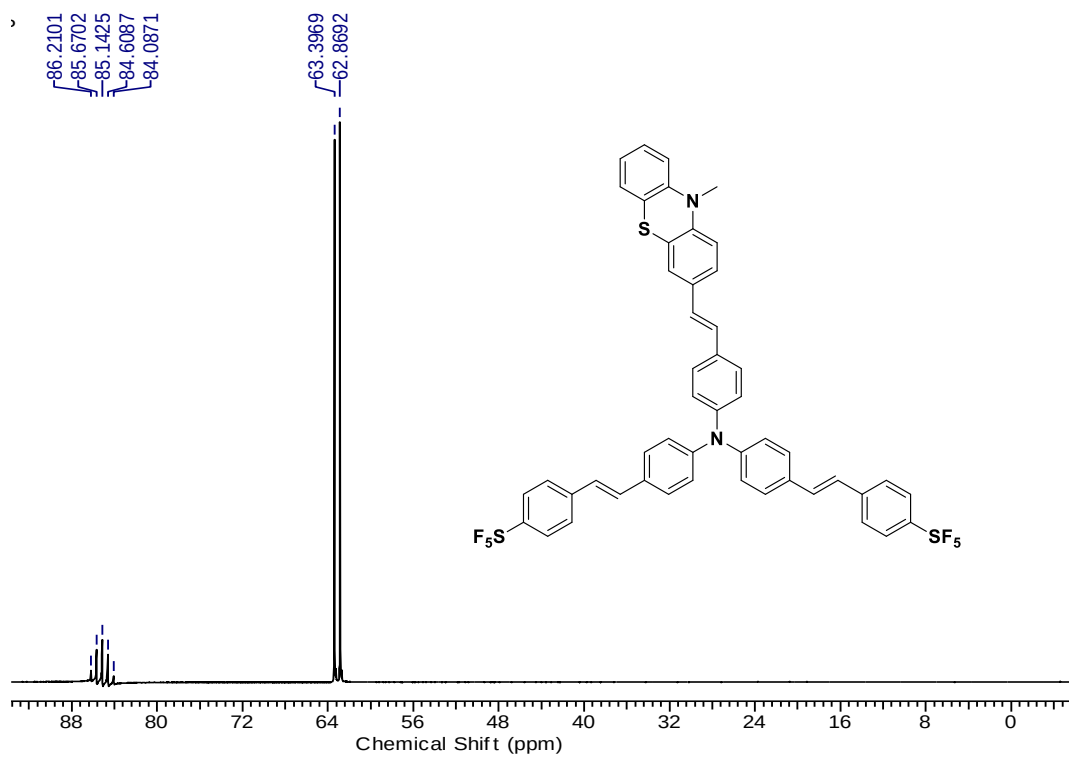


Figure A. 30 ¹⁹F NMR spectrum of compound **D5**.

Chapter 3

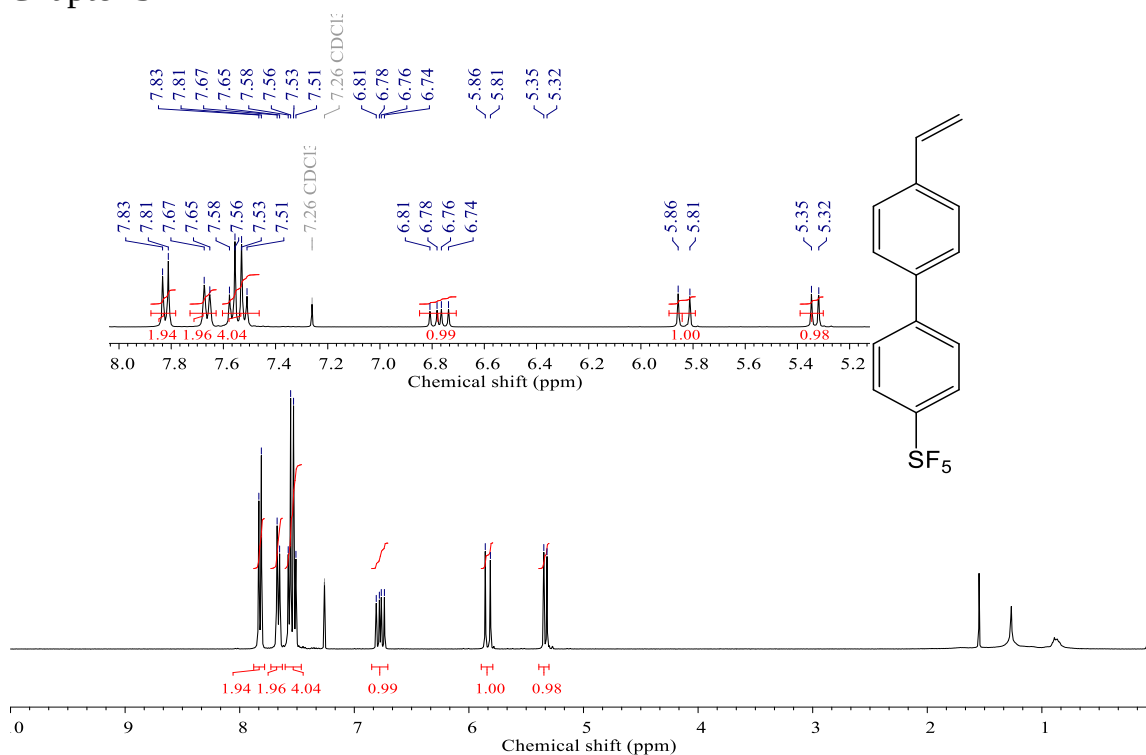


Figure A. 31 ¹H NMR spectrum of compound **3a**.

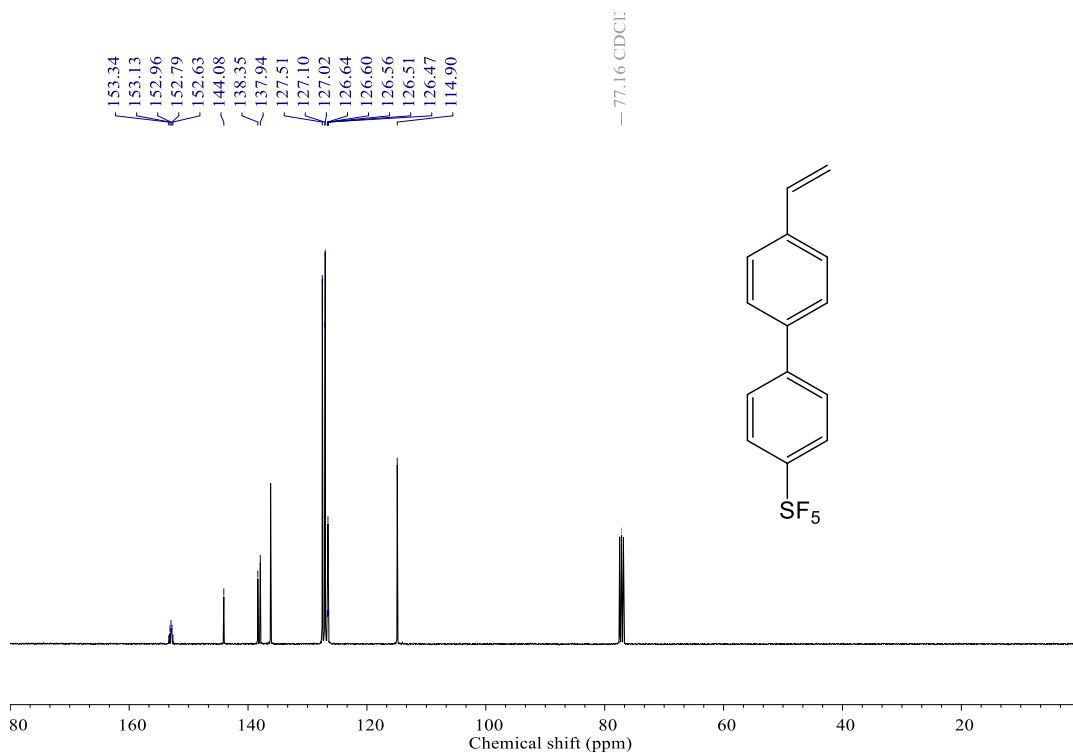


Figure A. 32 ¹³C NMR spectrum of compound **3a**.

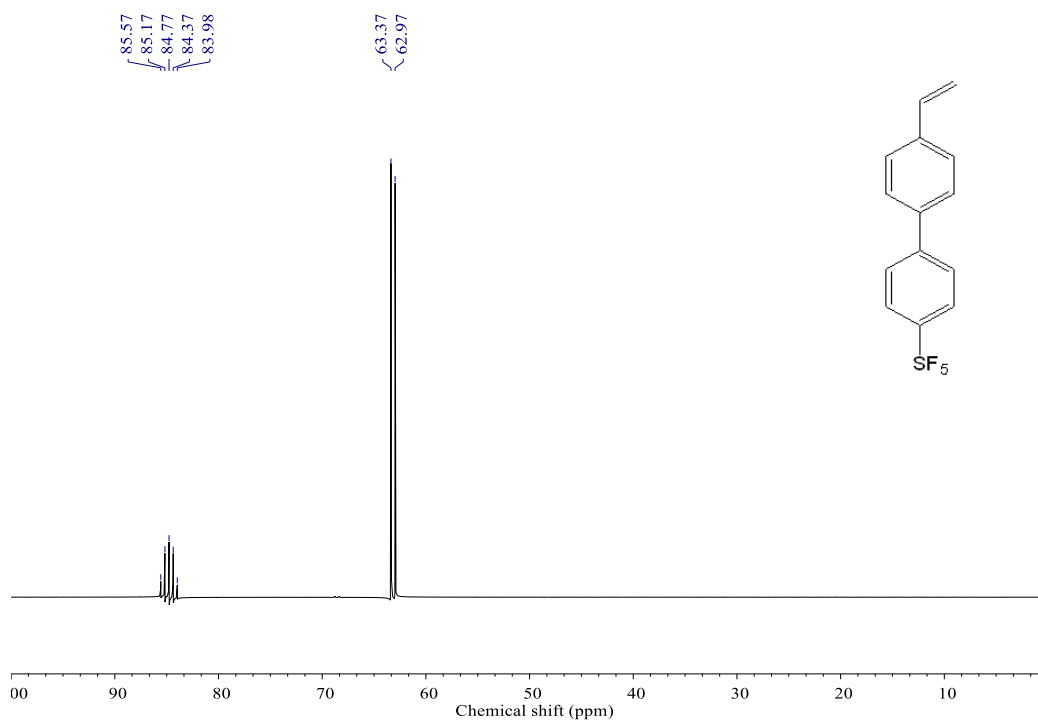


Figure A. 33 ¹⁹F NMR spectrum of compound **3a**.

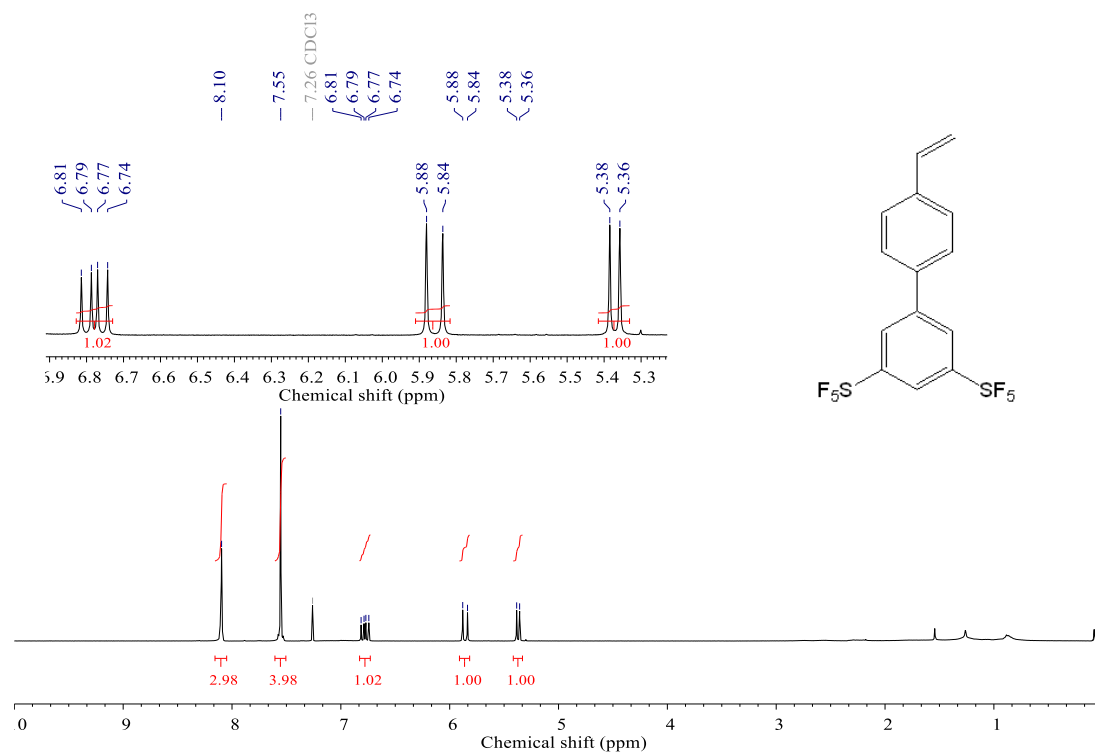


Figure A. 34 ¹H NMR spectrum of compound **3b**.

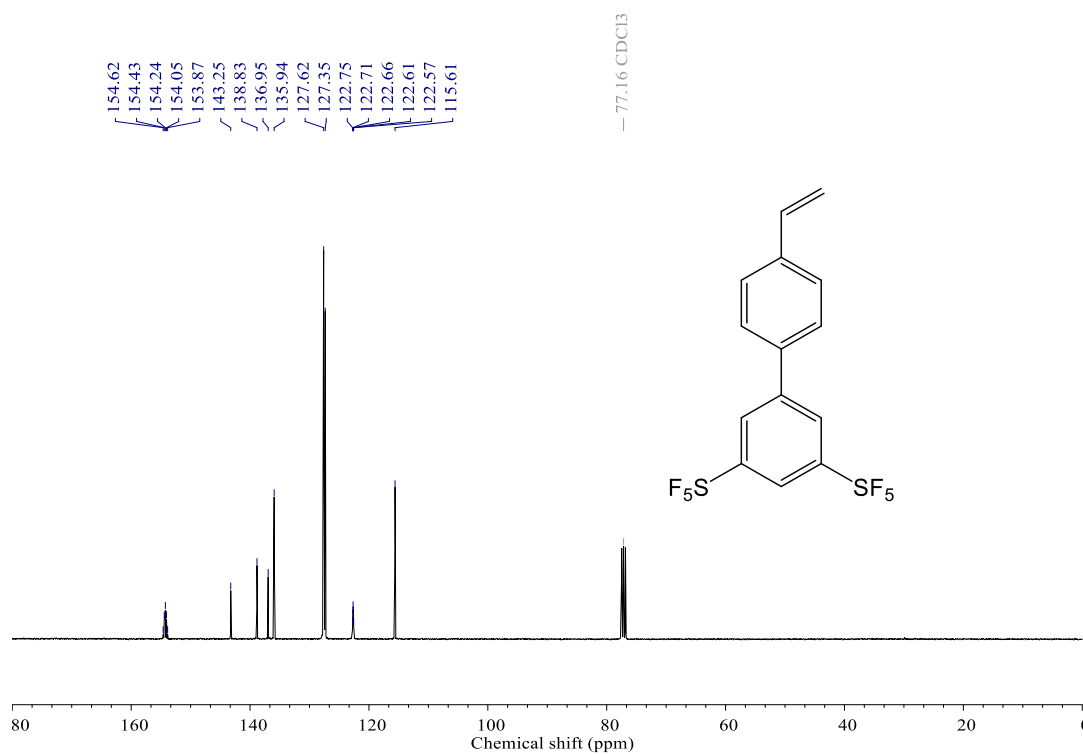


Figure A. 35 ¹³C NMR spectrum of compound **3b**.

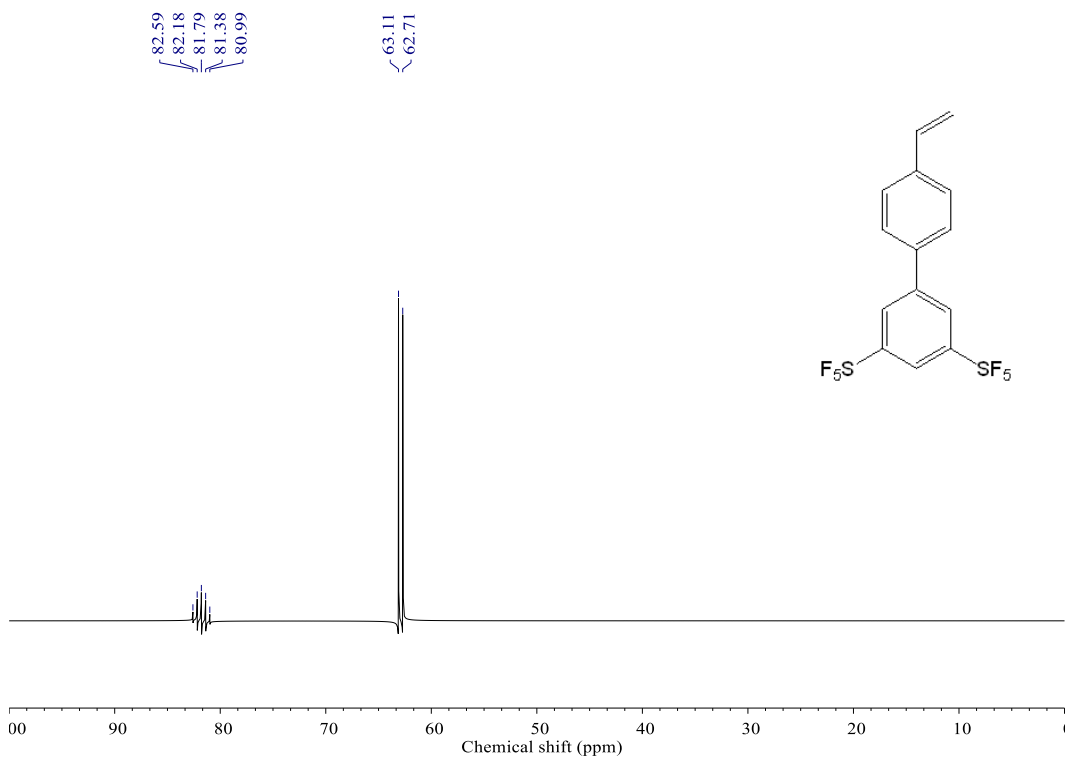


Figure A. 36 ¹⁹F NMR spectrum of compound **3b**.

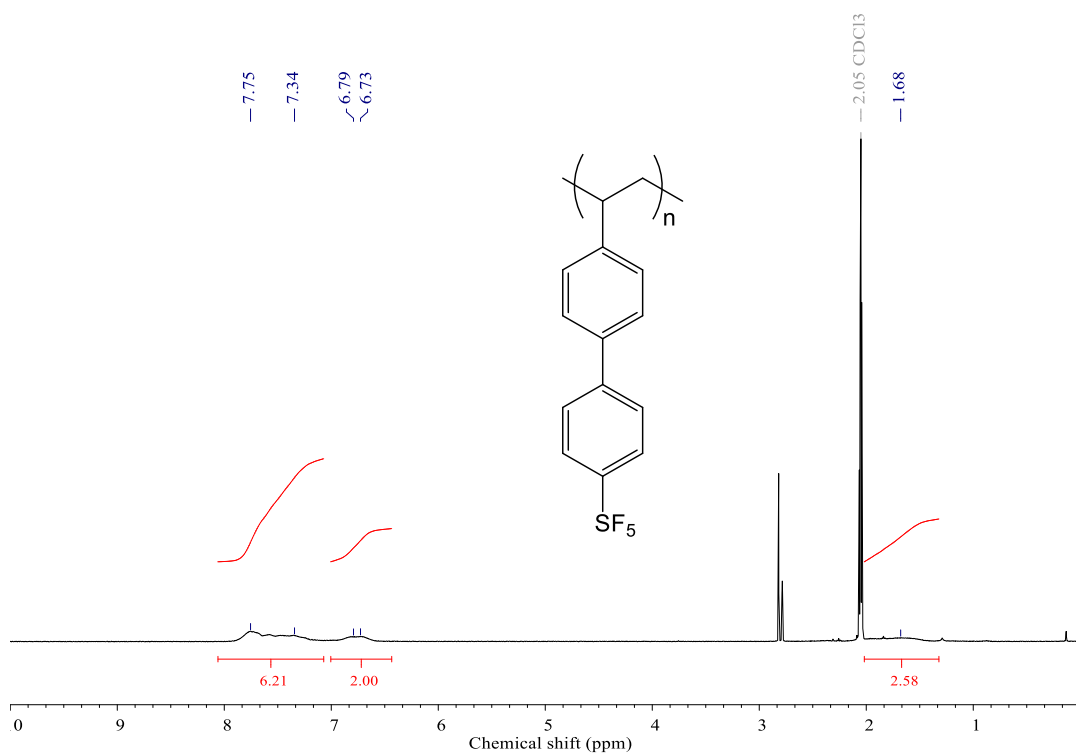


Figure A. 37 ¹H NMR spectrum of compound **P1**.

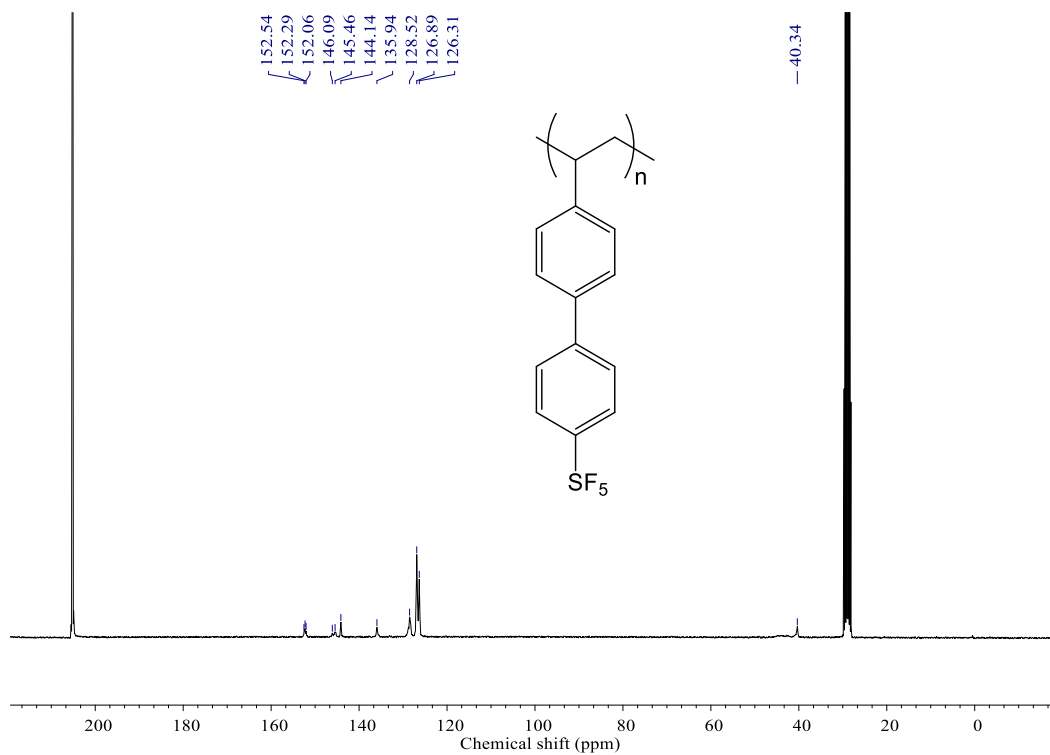


Figure A. 38 ¹³C NMR spectrum of compound **P1**.

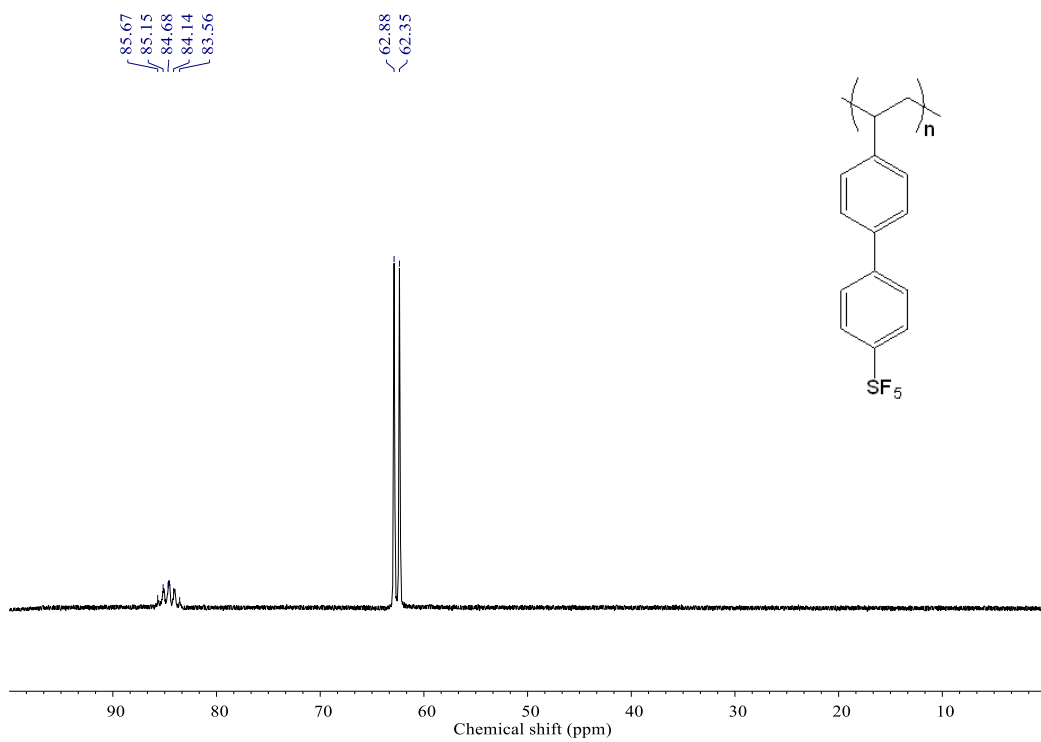


Figure A. 39 ¹⁹F NMR spectrum of compound **P1**.

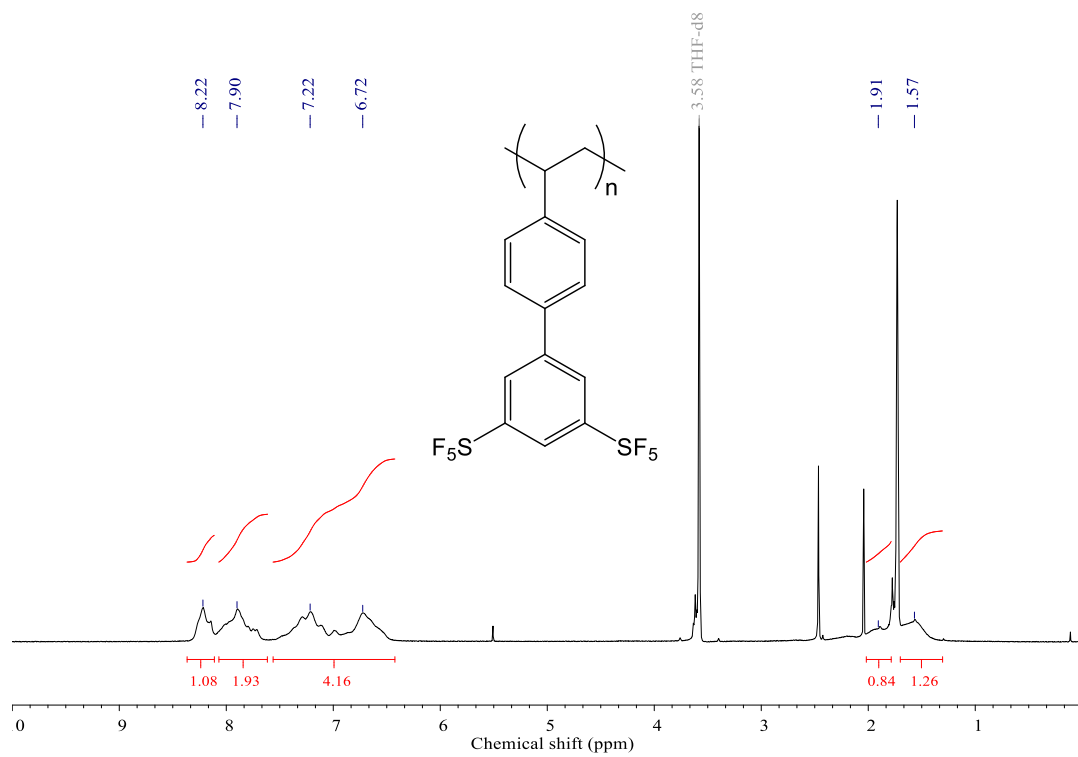


Figure A. 40 ¹H NMR spectrum of compound **P2**.

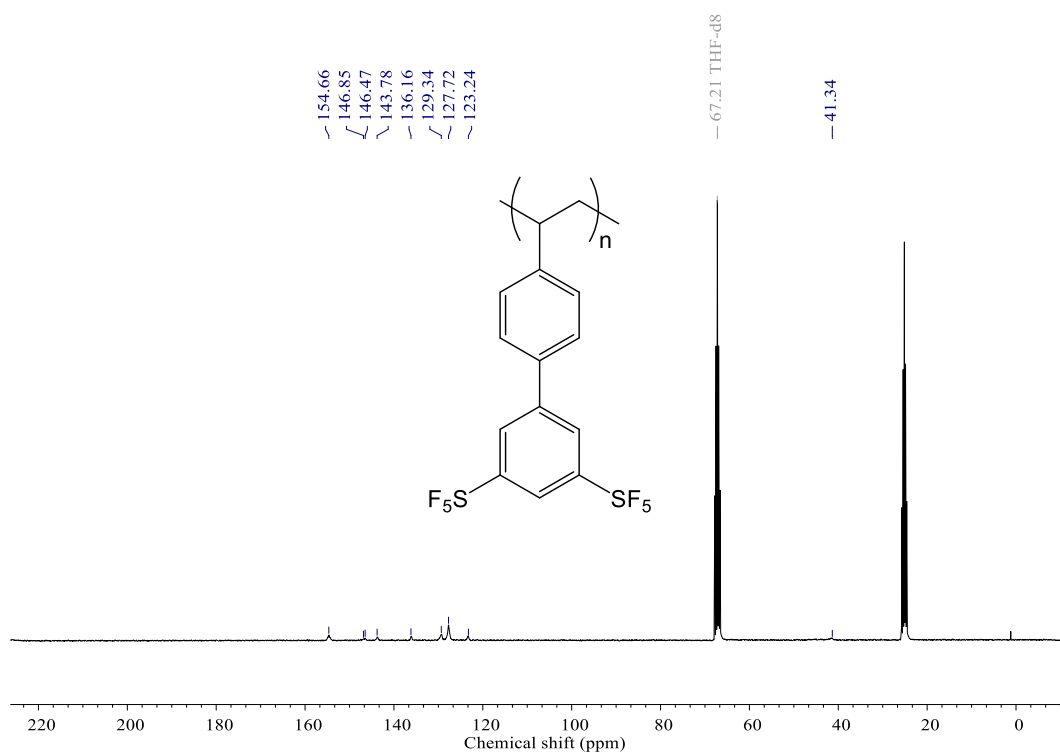


Figure A. 41 ¹³C NMR spectrum of compound **P2**.

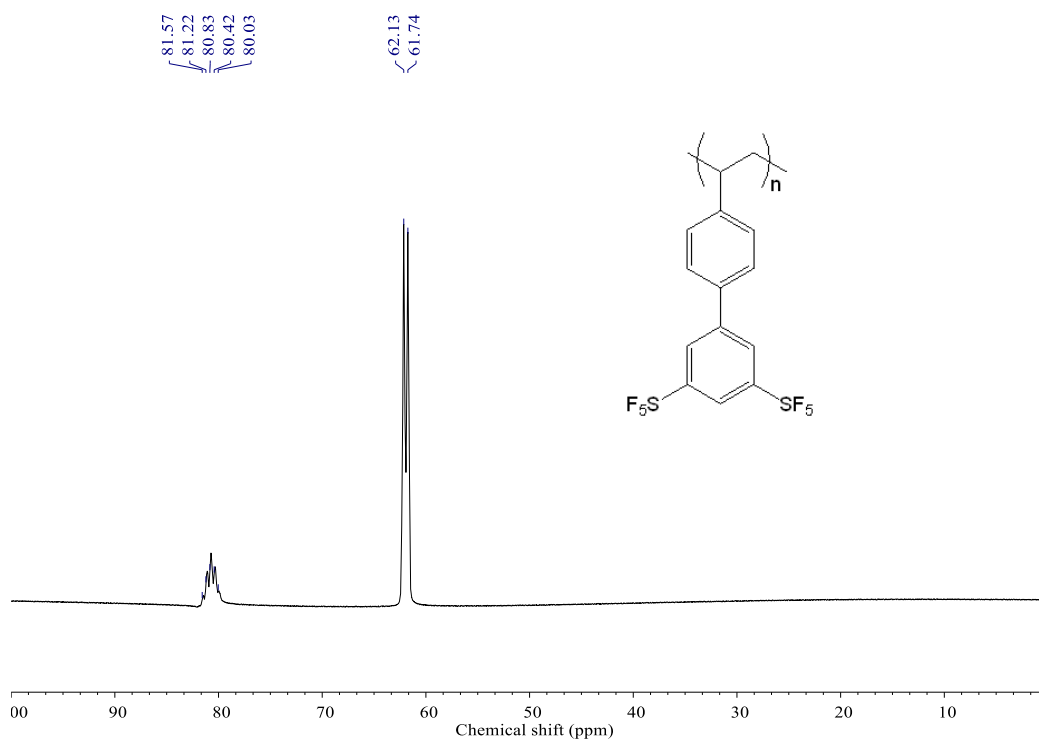


Figure A. 42 ¹⁹F NMR spectrum of compound **P2**.

Chapter 4

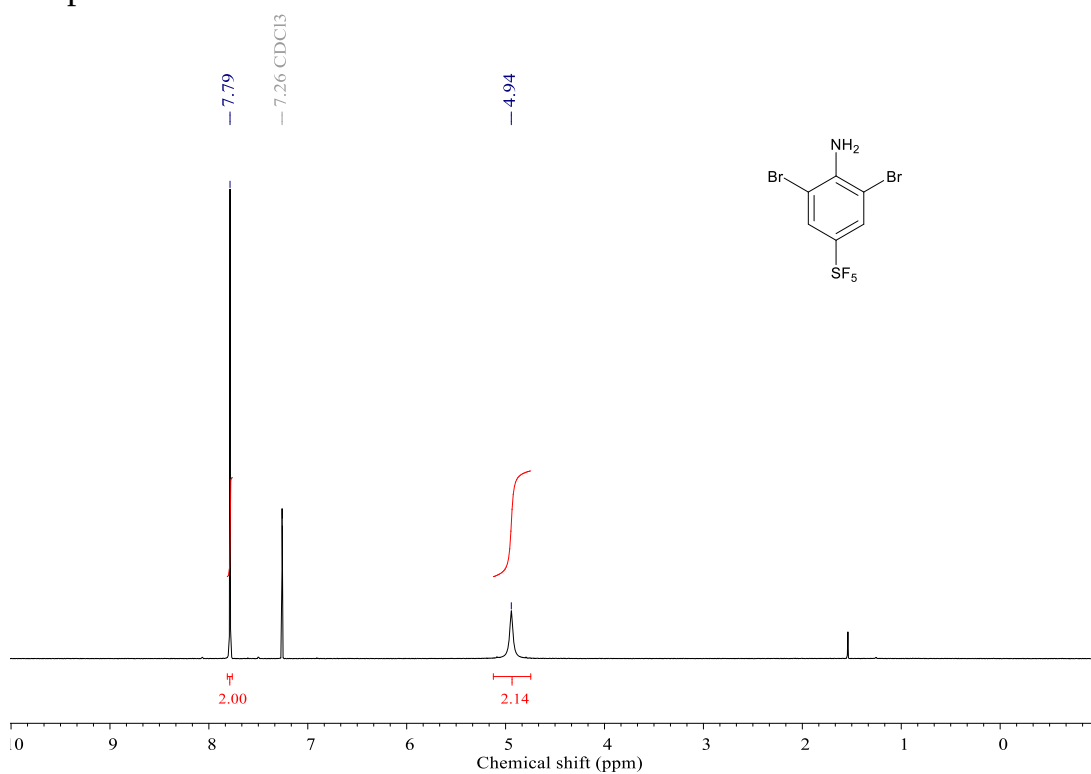


Figure A. 43 ¹H NMR spectrum of compound **4a**.

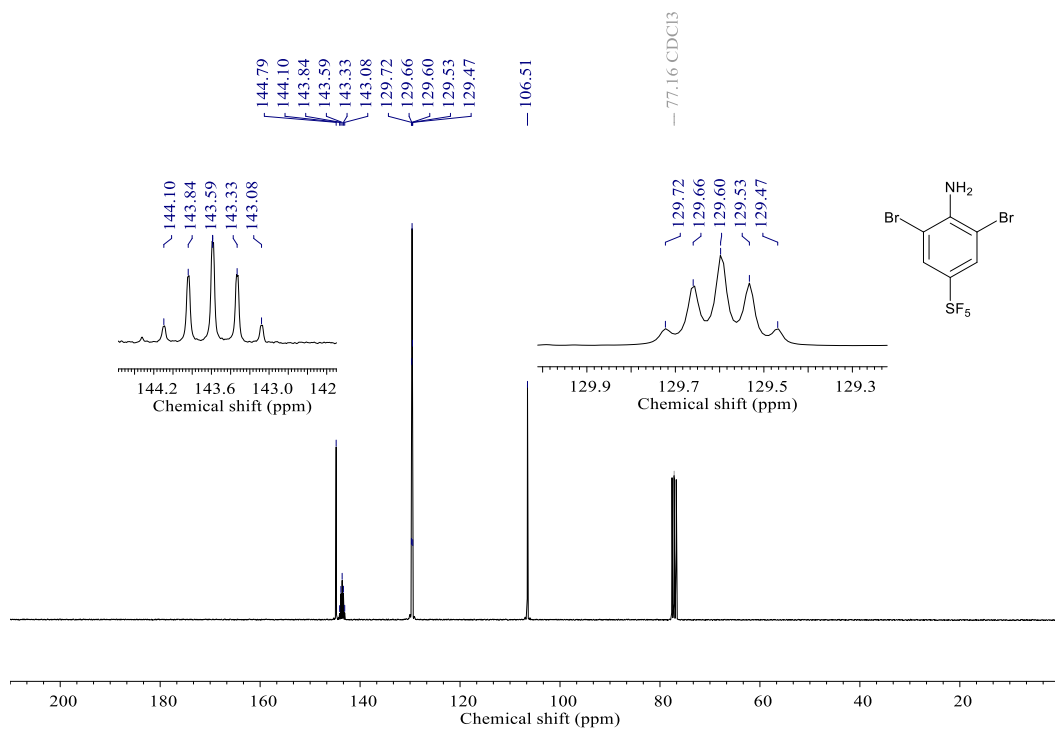


Figure A. 44 ¹³C NMR spectrum of compound **4a**.

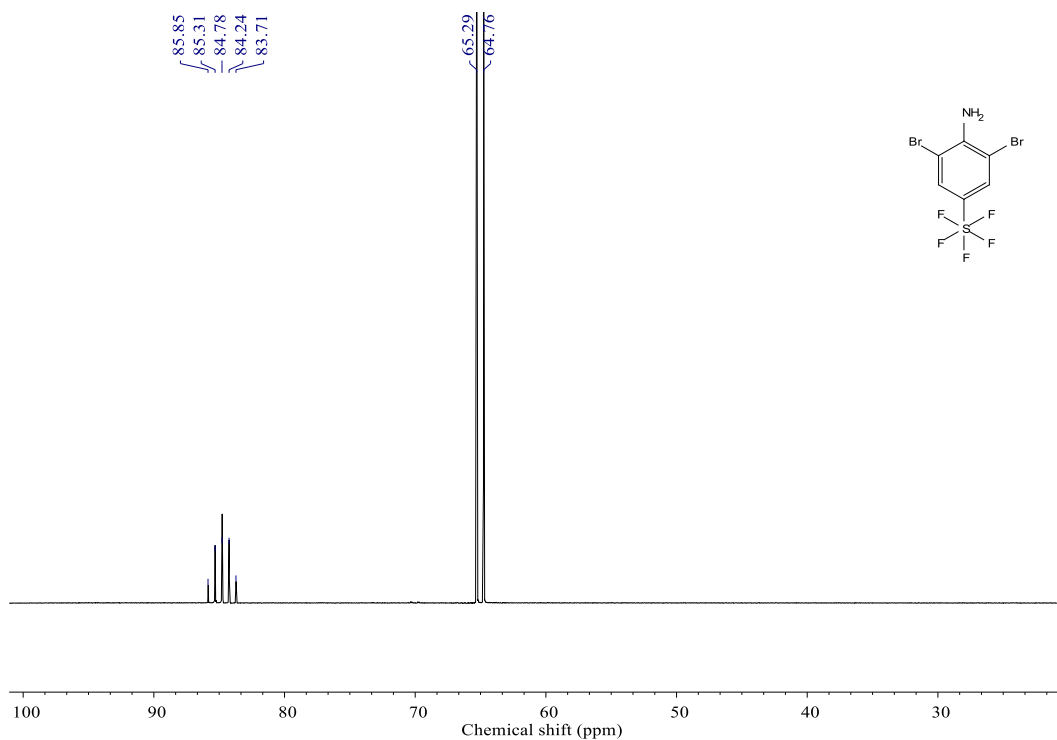


Figure A. 45 ¹⁹F NMR spectrum of compound **4a**.

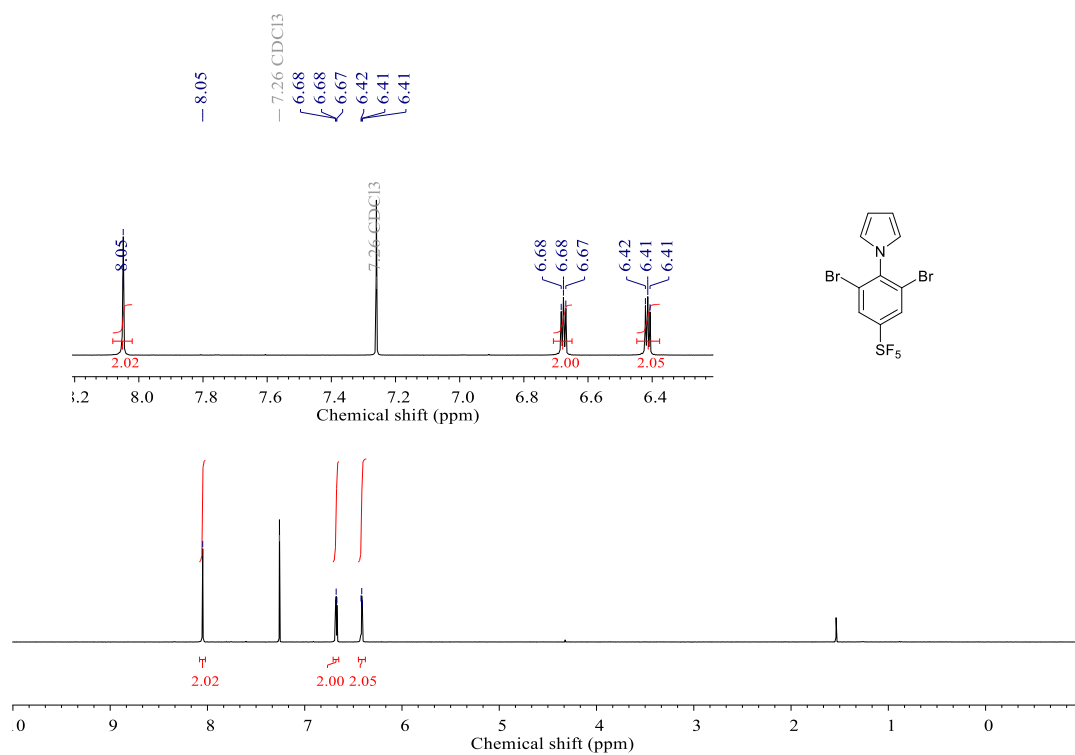


Figure A. 46 ¹H NMR spectrum of compound **4b**.

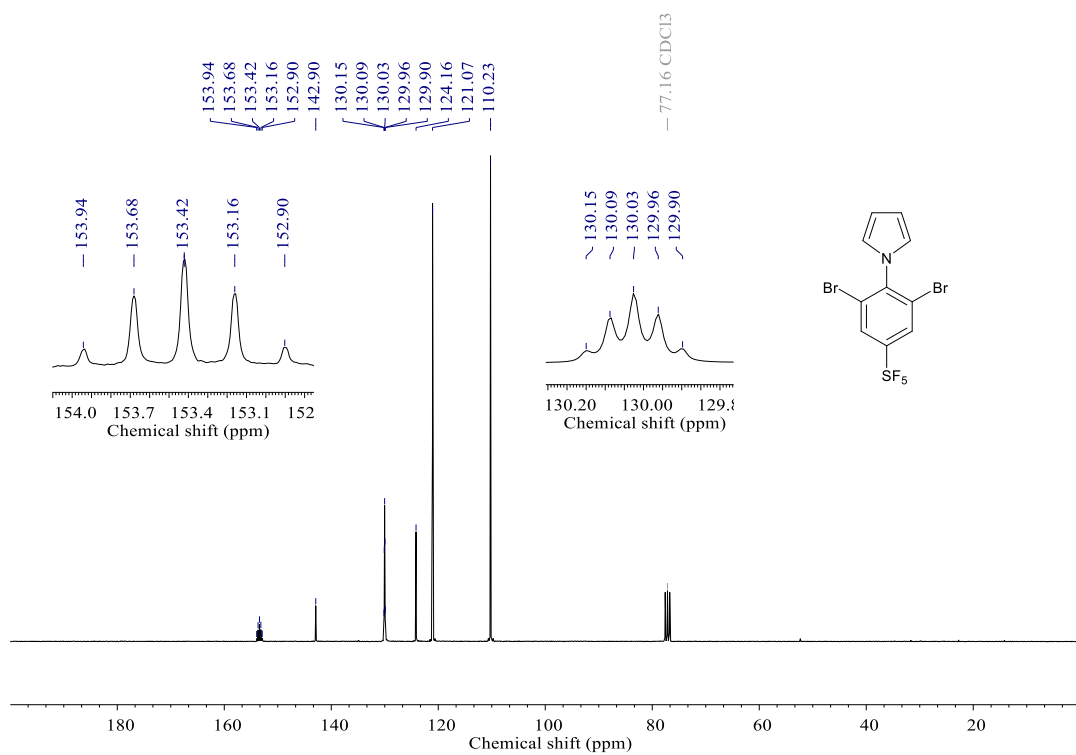


Figure A. 47 ¹³C NMR spectrum of compound **4b**.

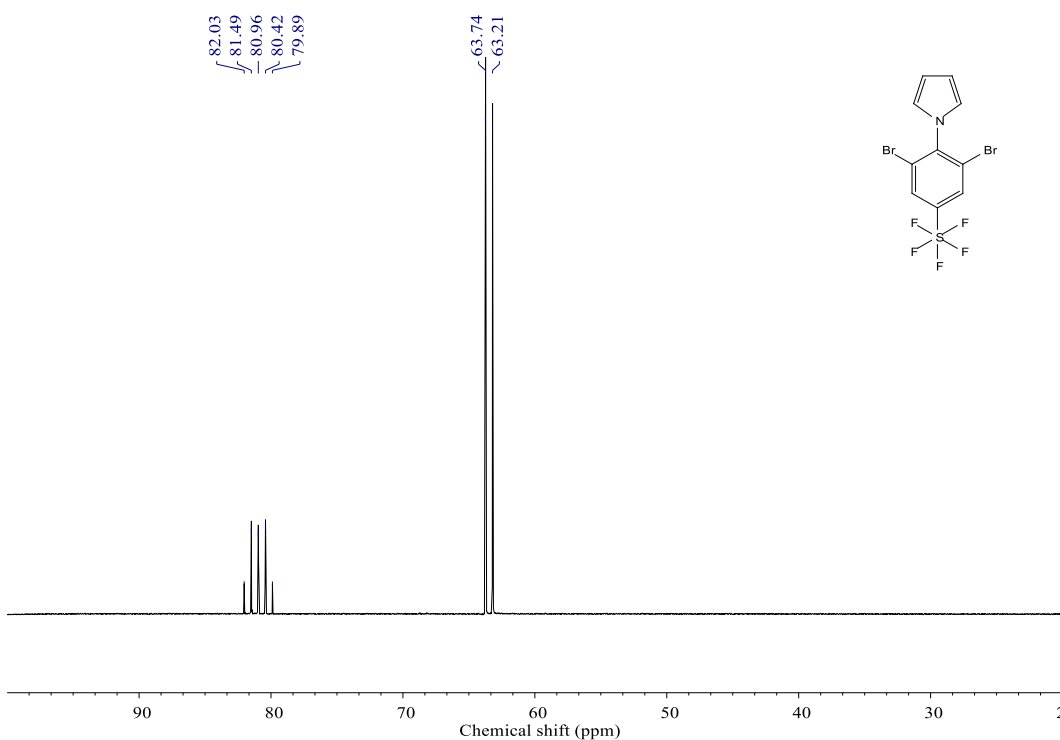


Figure A. 48 ¹⁹F NMR spectrum of compound **4b**.

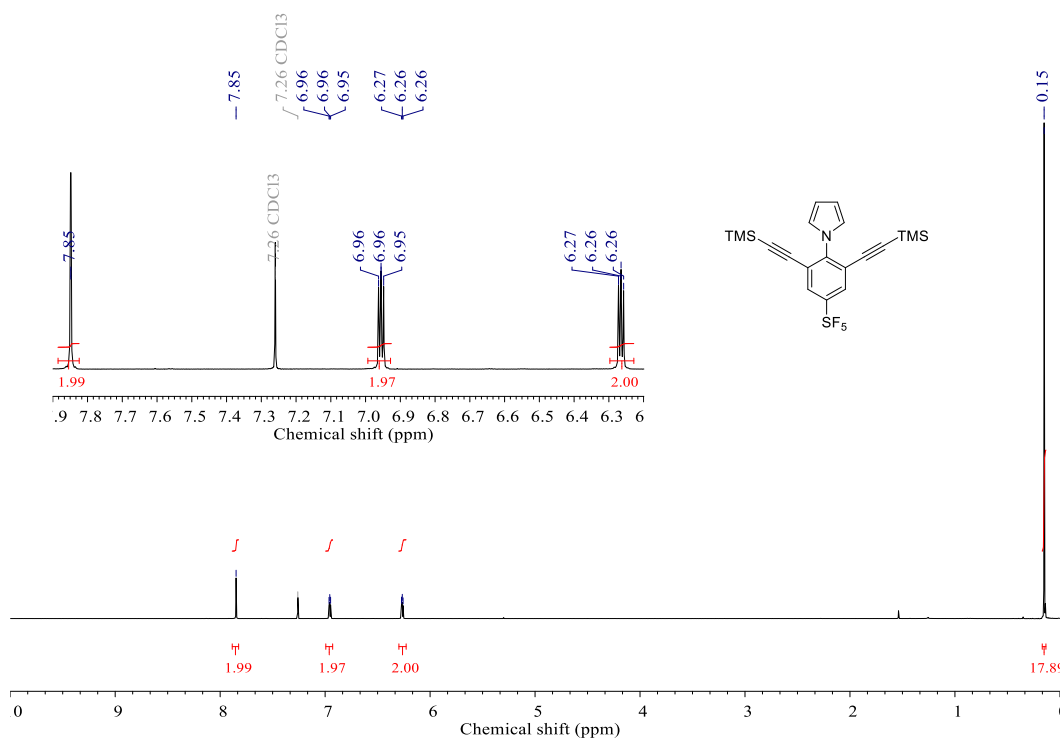


Figure A. 49 ^1H NMR spectrum of compound **4c**.

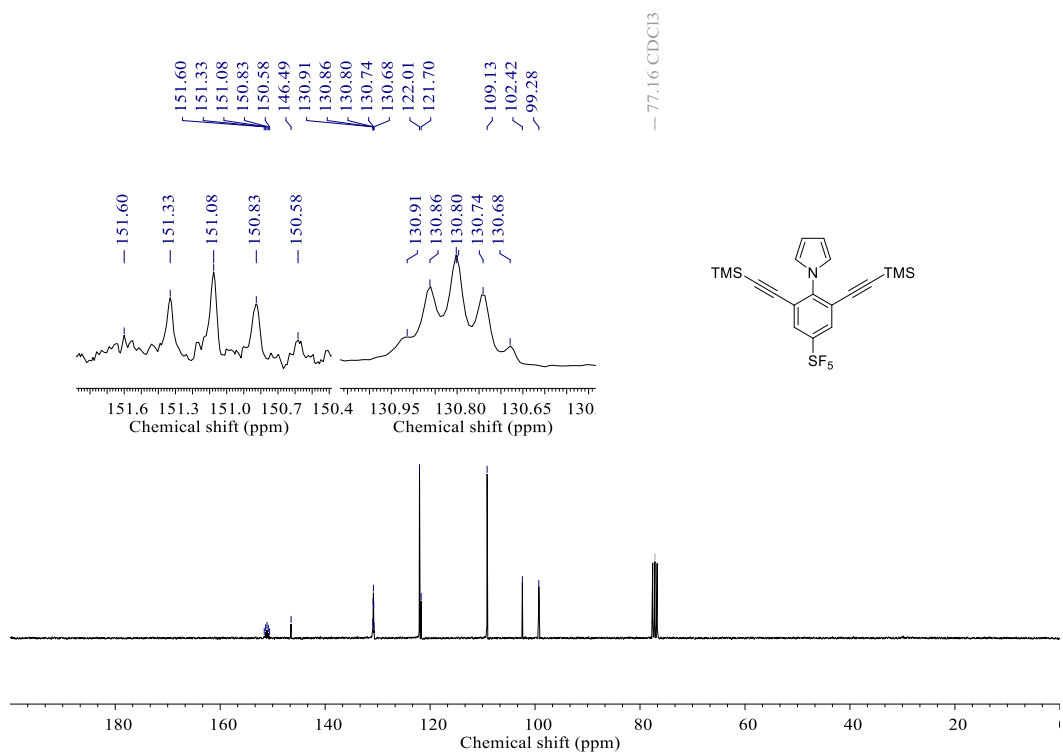


Figure A. 50 ^{13}C NMR spectrum of compound **4c**.

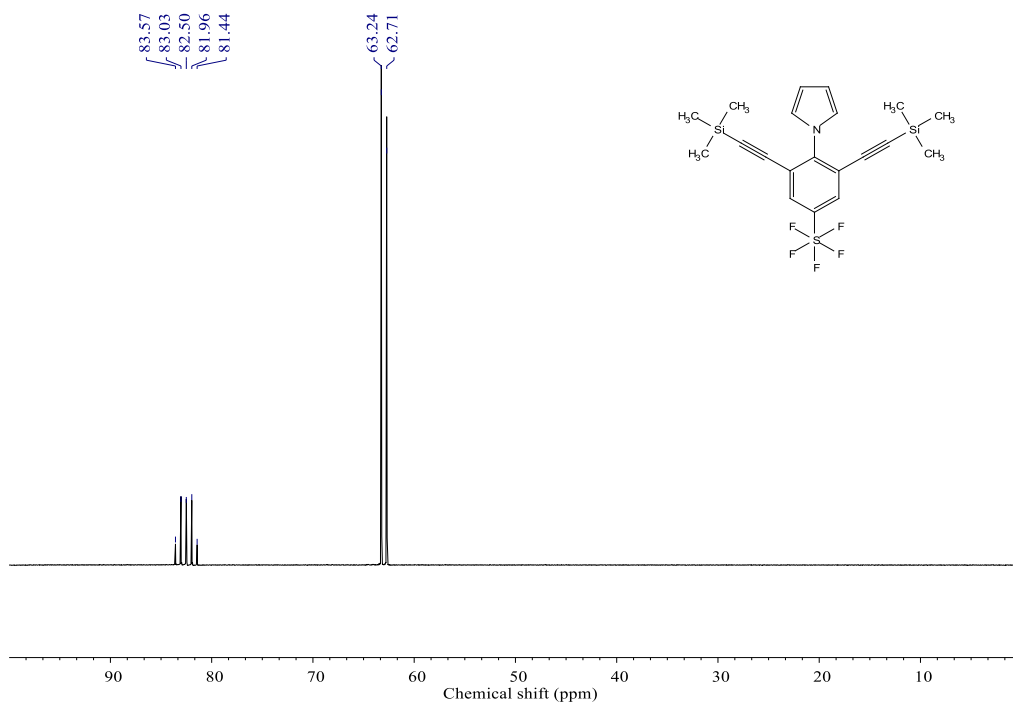


Figure A. 51 ¹⁹F NMR spectrum of compound **4c**.

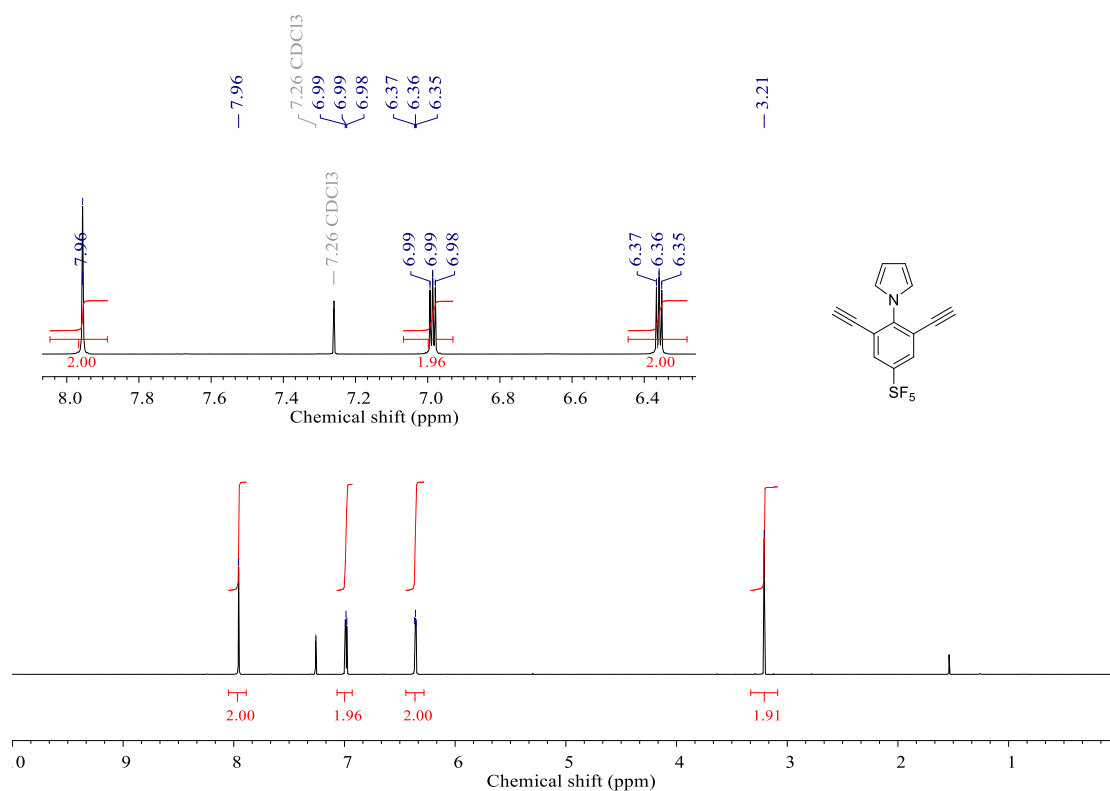


Figure A. 52 ¹H NMR spectrum of compound **4d**.

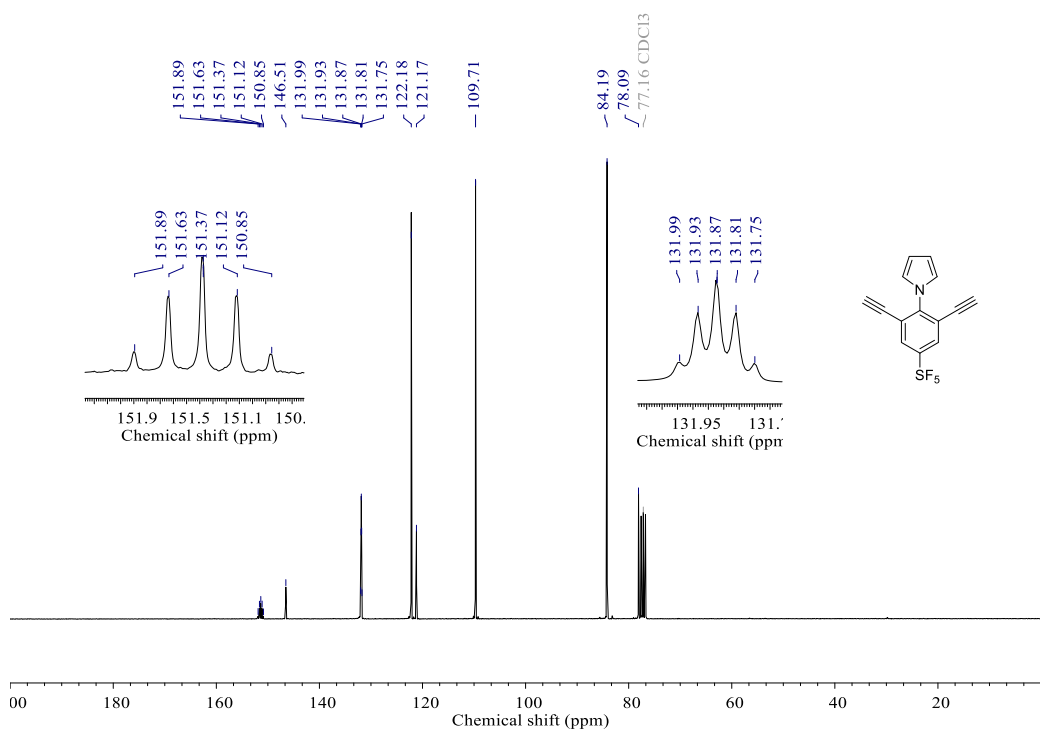


Figure A. 53 ^{13}C NMR spectrum of compound **4d**.

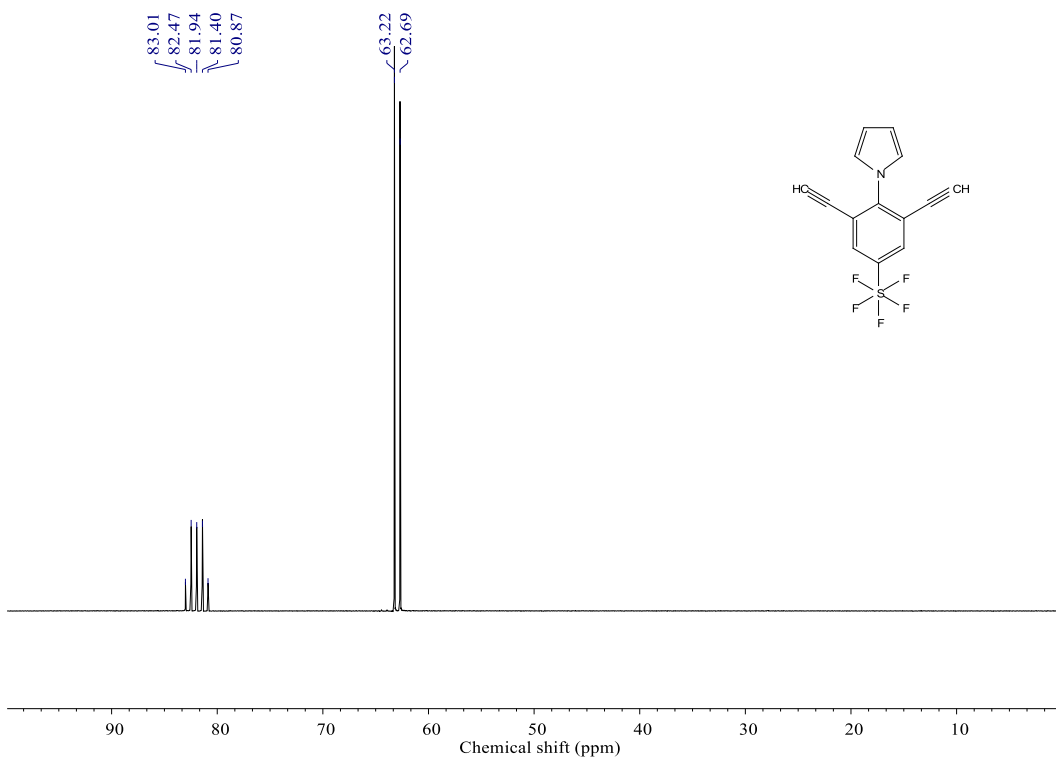


Figure A. 54 ^{19}F NMR spectrum of compound **4d**.

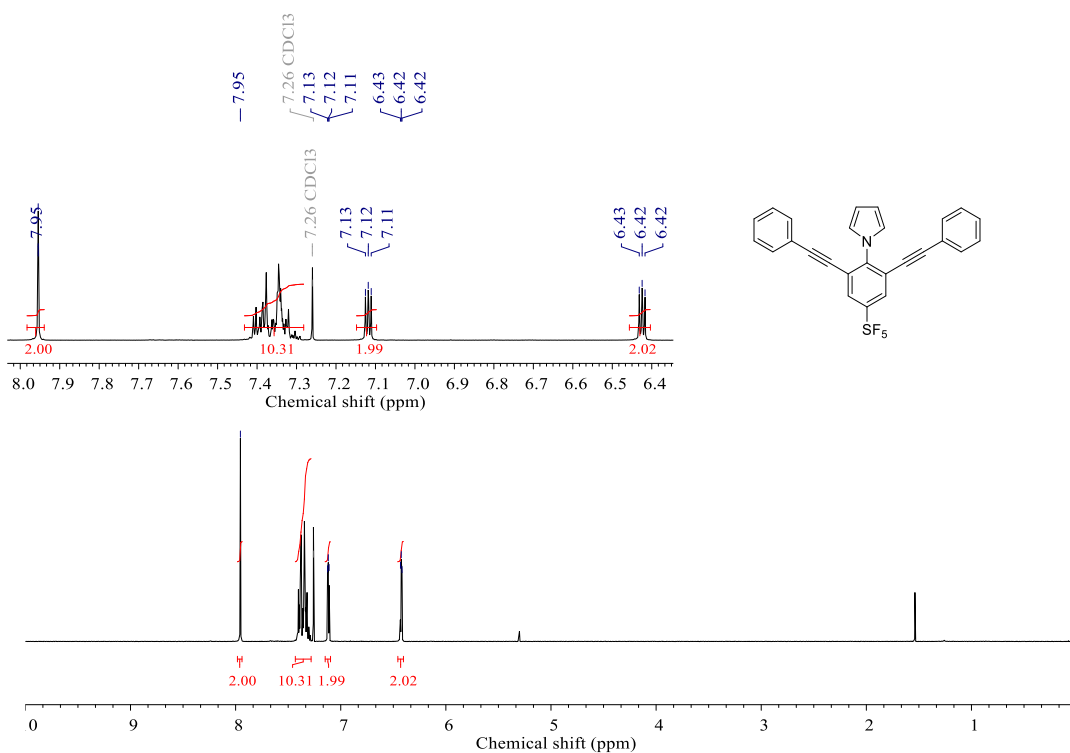


Figure A. 55 ¹H NMR spectrum of compound **4e**.

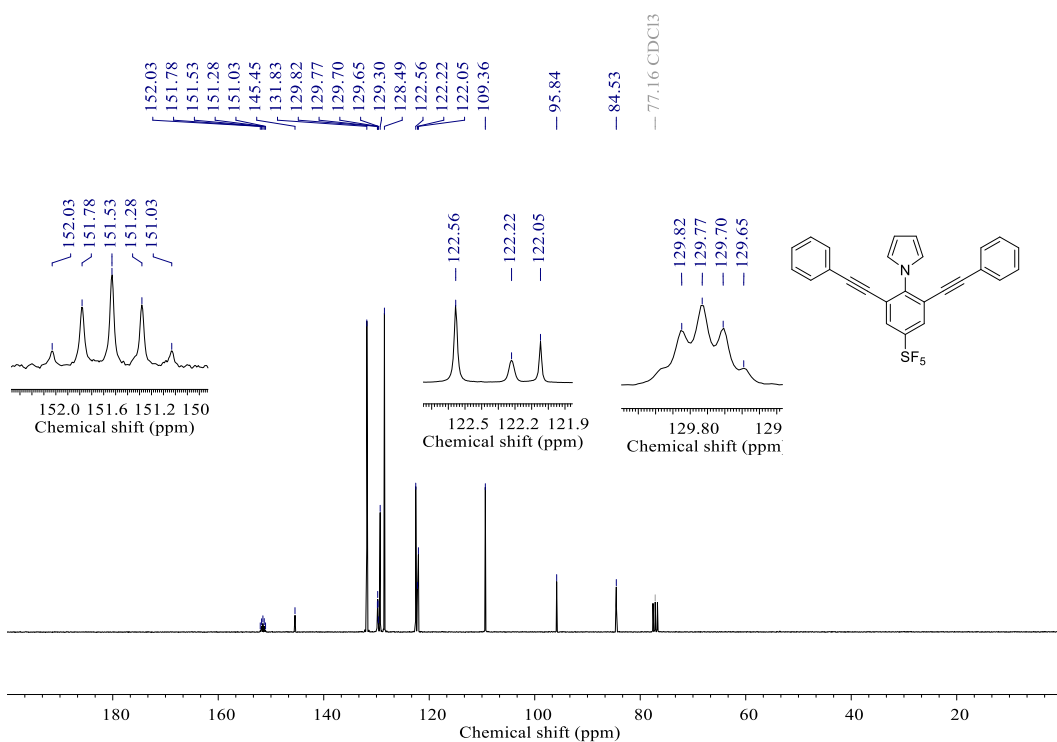


Figure A. 56 ¹³C NMR spectrum of compound **4e**.

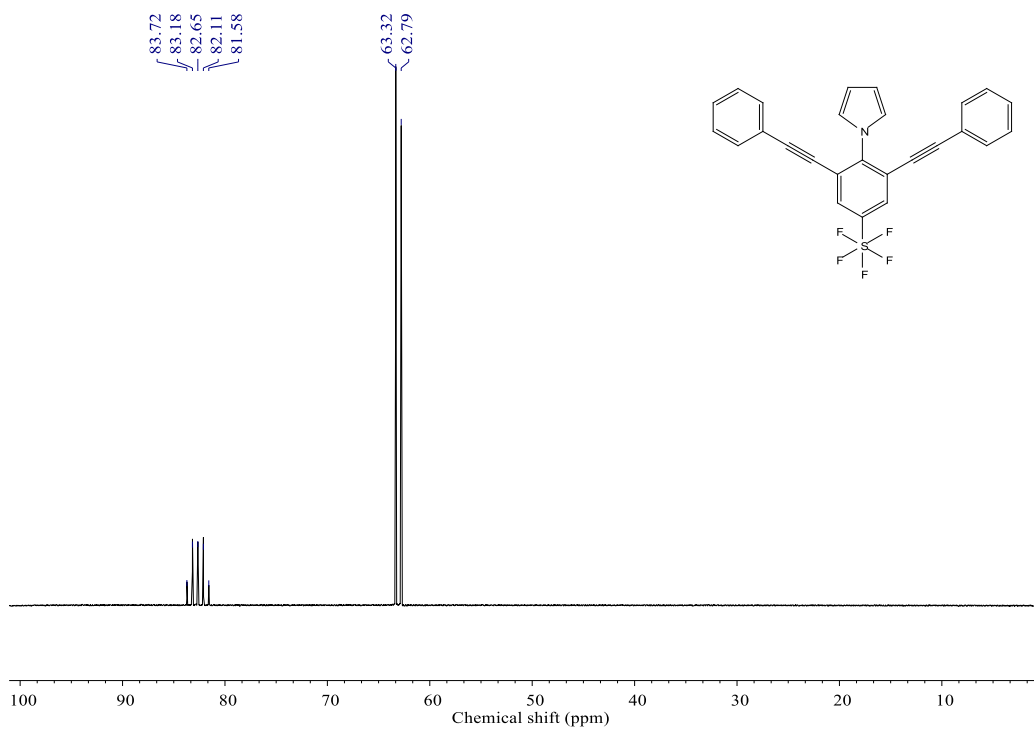


Figure A. 57 ¹⁹F NMR spectrum of compound **4e**.

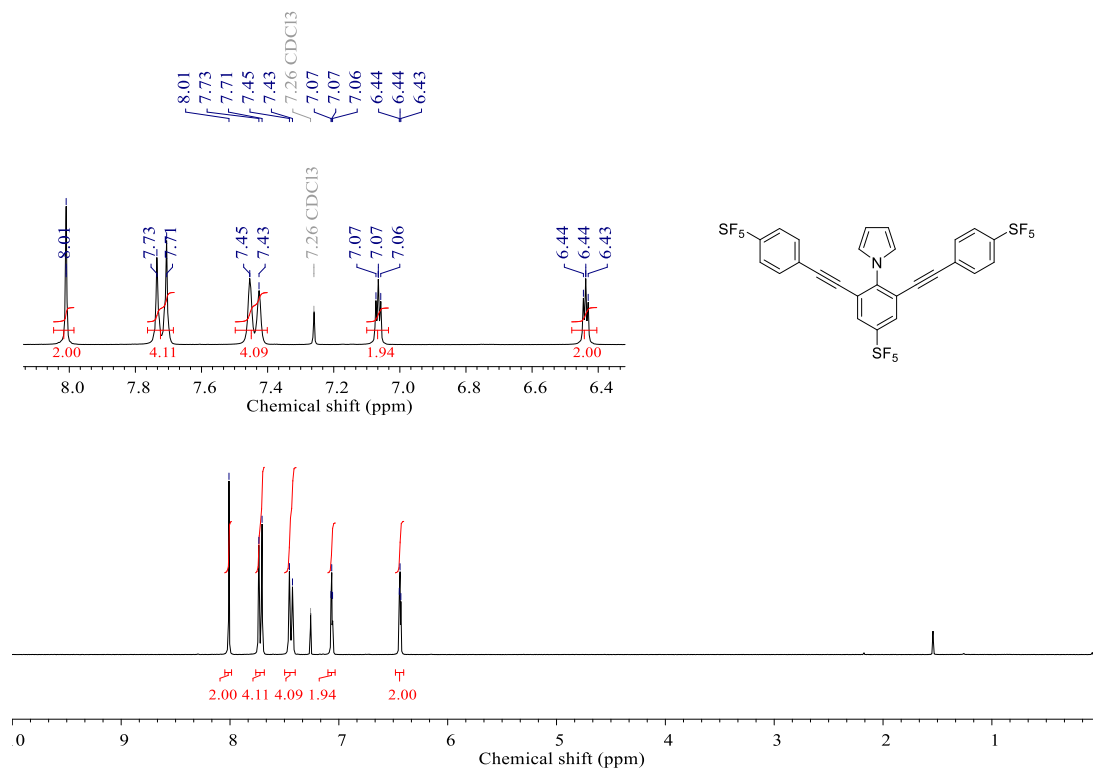


Figure A. 58 ¹H NMR spectrum of compound **4f**.

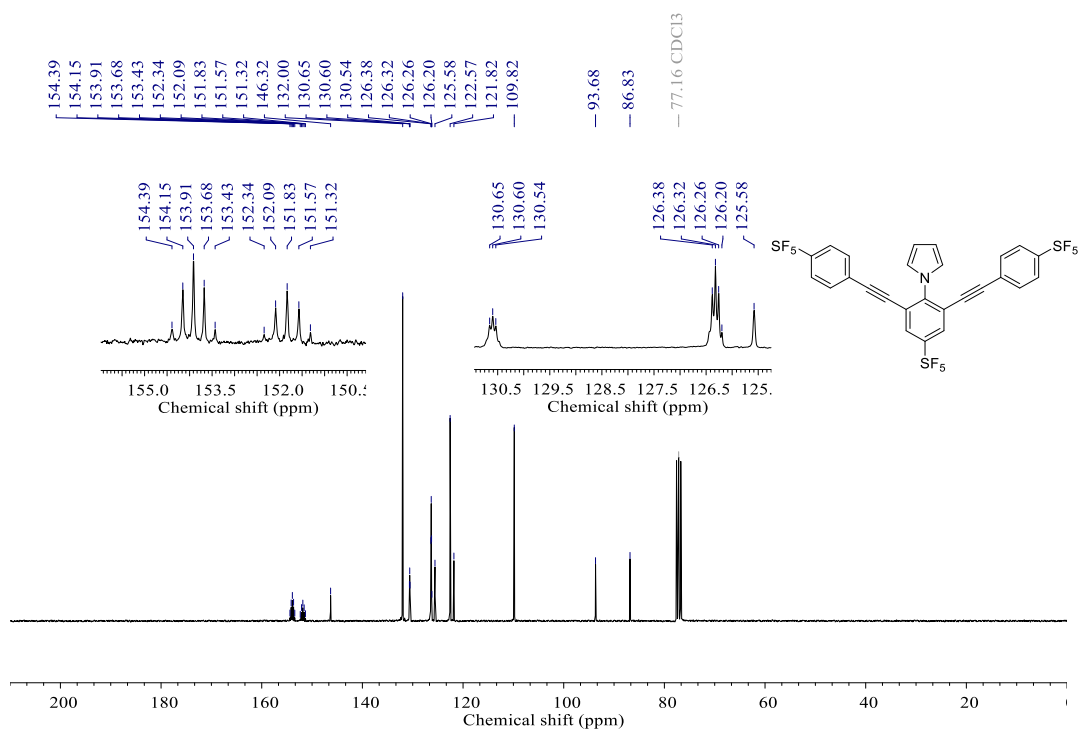


Figure A. 59 ¹³C NMR spectrum of compound **4f**.

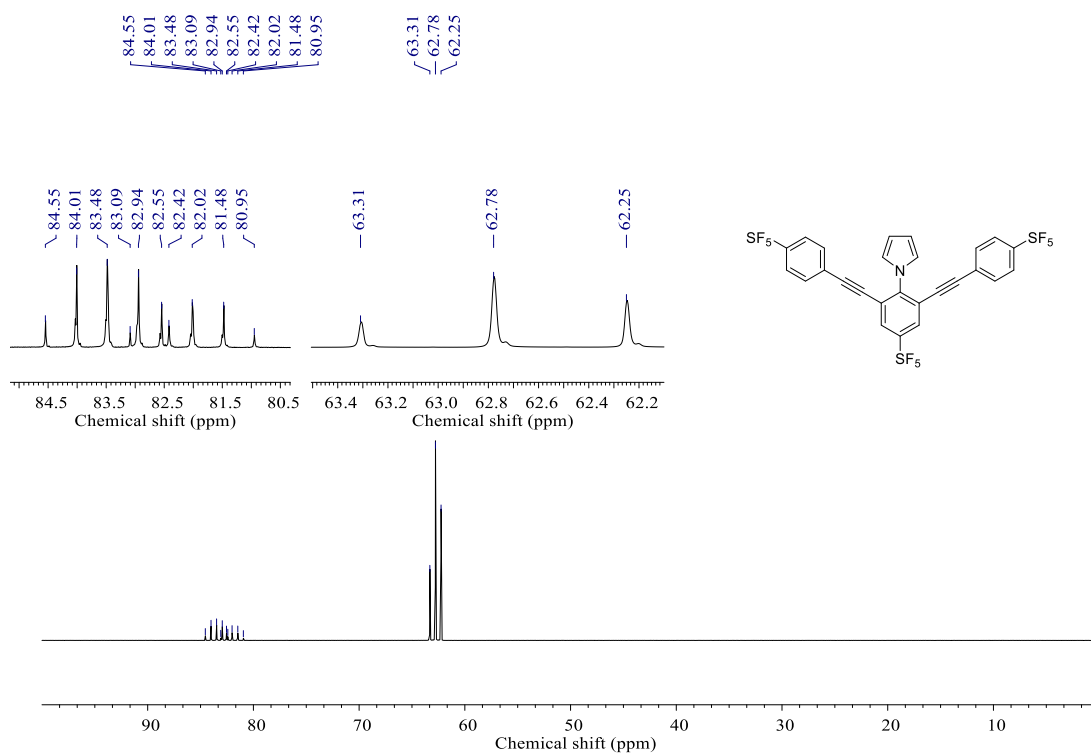


Figure A. 60 ¹⁹F NMR spectrum of compound **4f**.

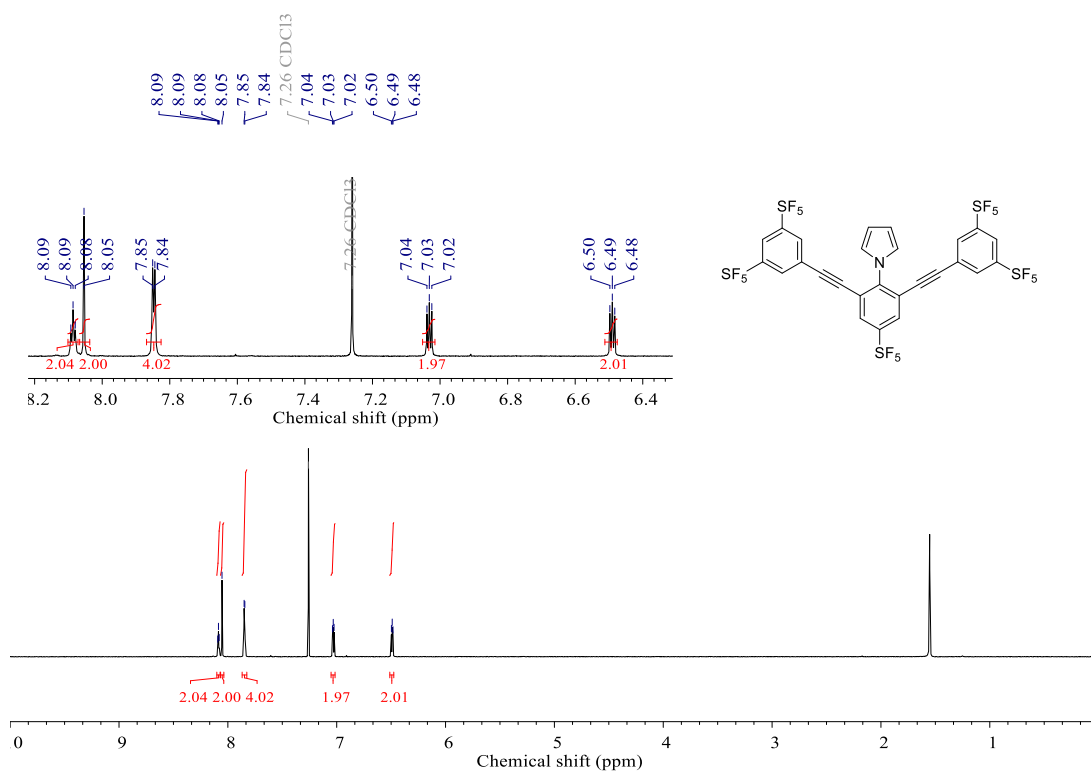


Figure A. 61 ¹H NMR spectrum of compound **4g**.

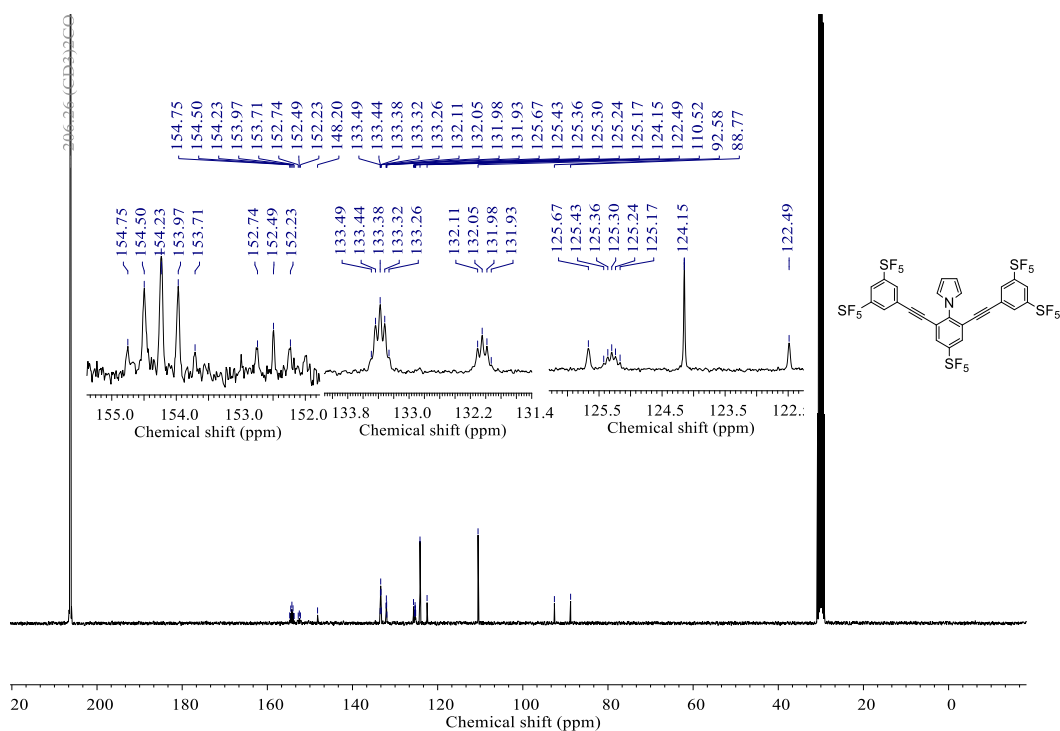


Figure A. 62 ¹³C NMR spectrum of compound **4g**.

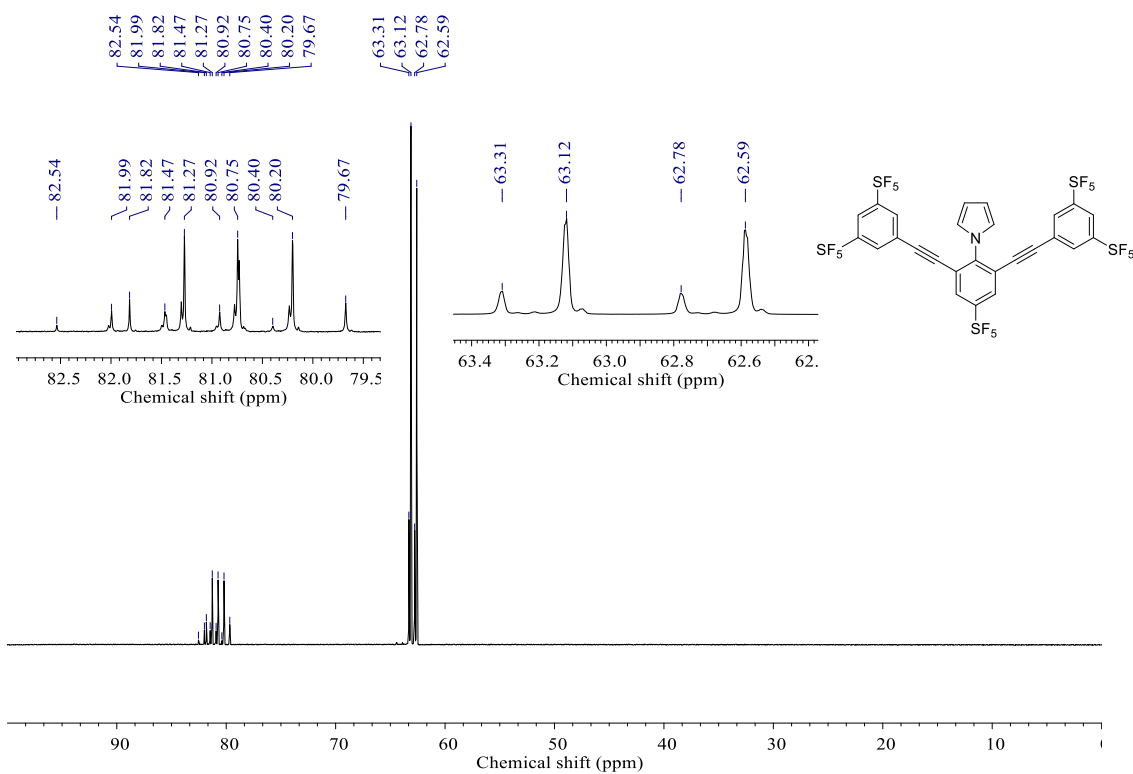


Figure A. 63 ^{19}F NMR spectrum of compound **4g**.

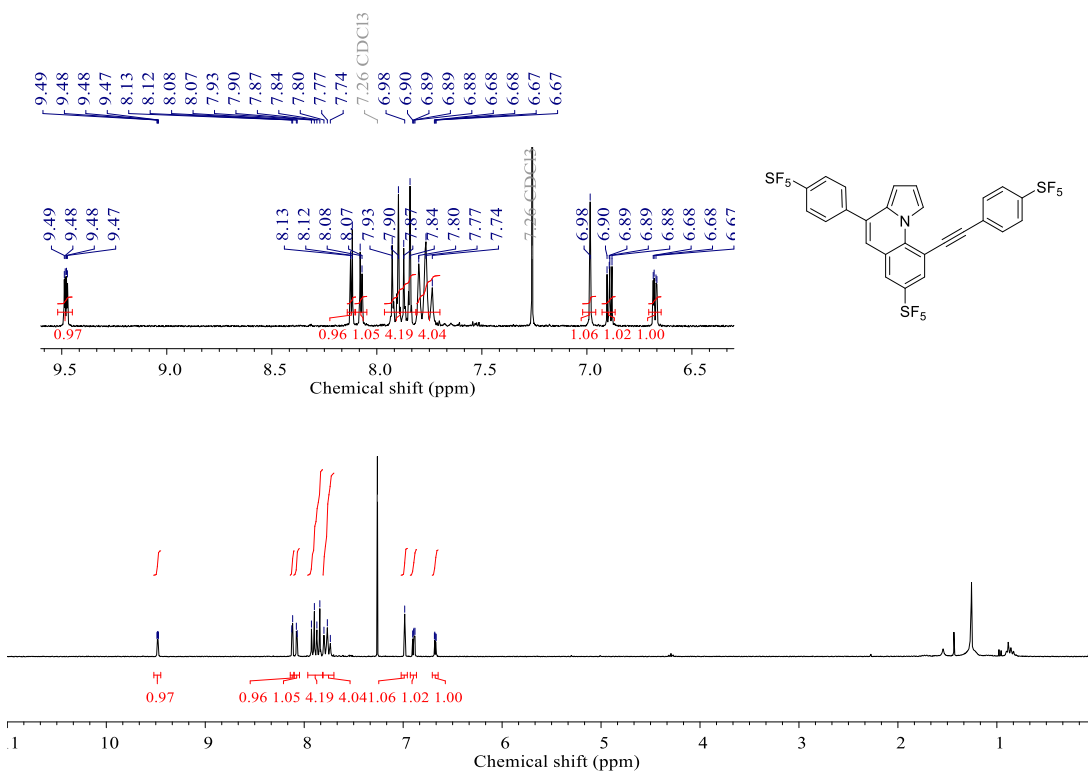


Figure A. 64 ^1H NMR spectrum of compound **4h**.

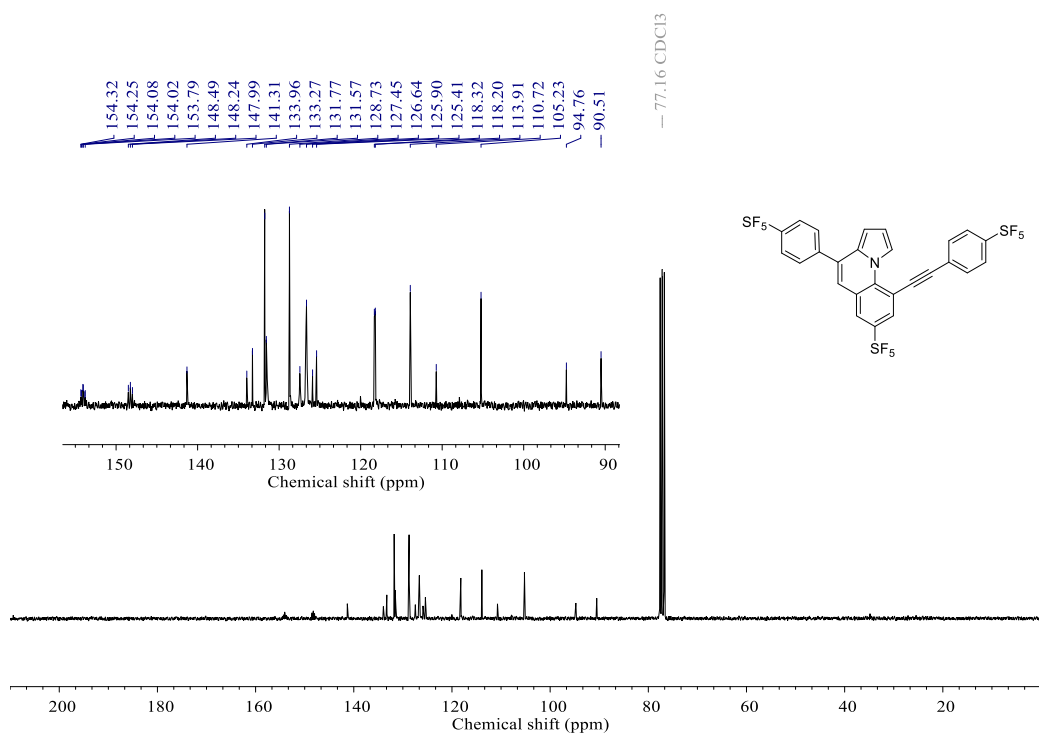


Figure A. 65 ^{13}C NMR spectrum of compound **4h**.

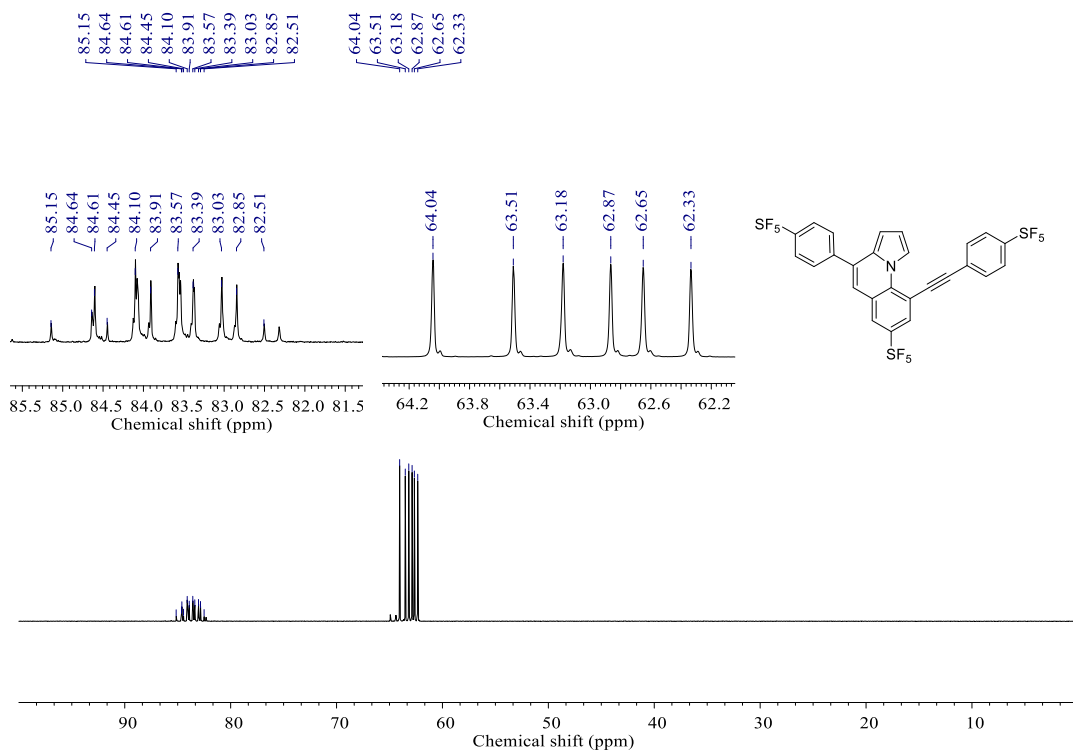


Figure A. 66 ^{19}F NMR spectrum of compound **4h**.

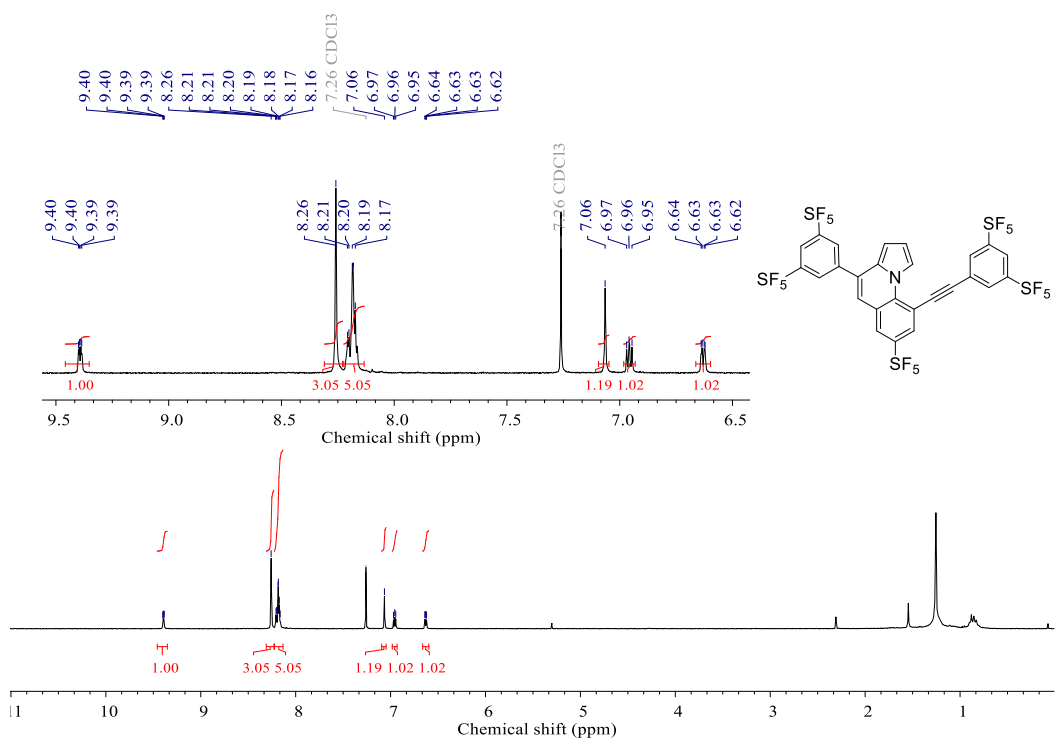


Figure A. 67 ¹H NMR spectrum of compound 4i.

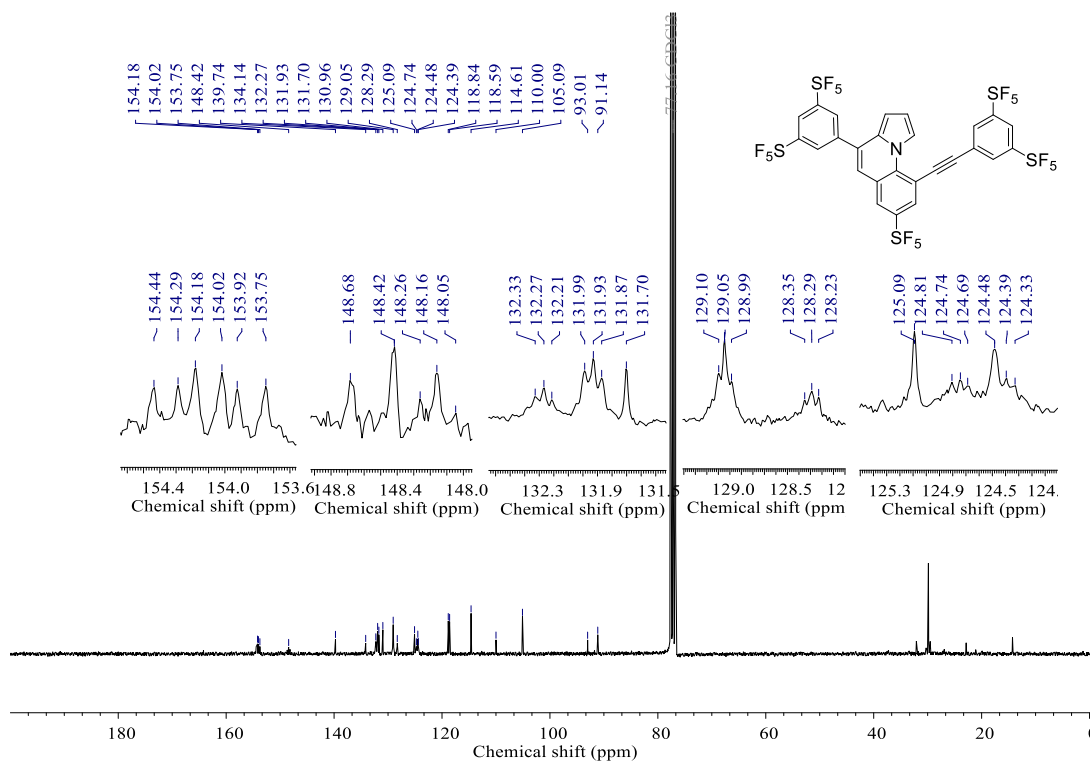


Figure A. 68 ¹³C NMR spectrum of compound 4i.

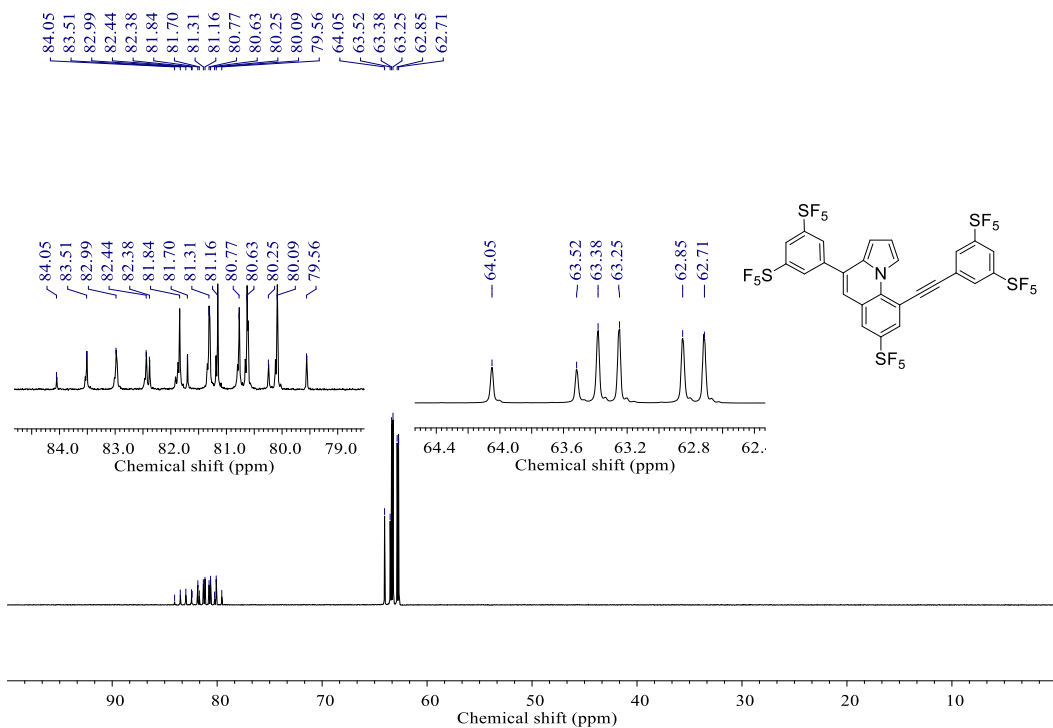


Figure A. 69 ¹⁹F NMR spectrum of compound **4i**.

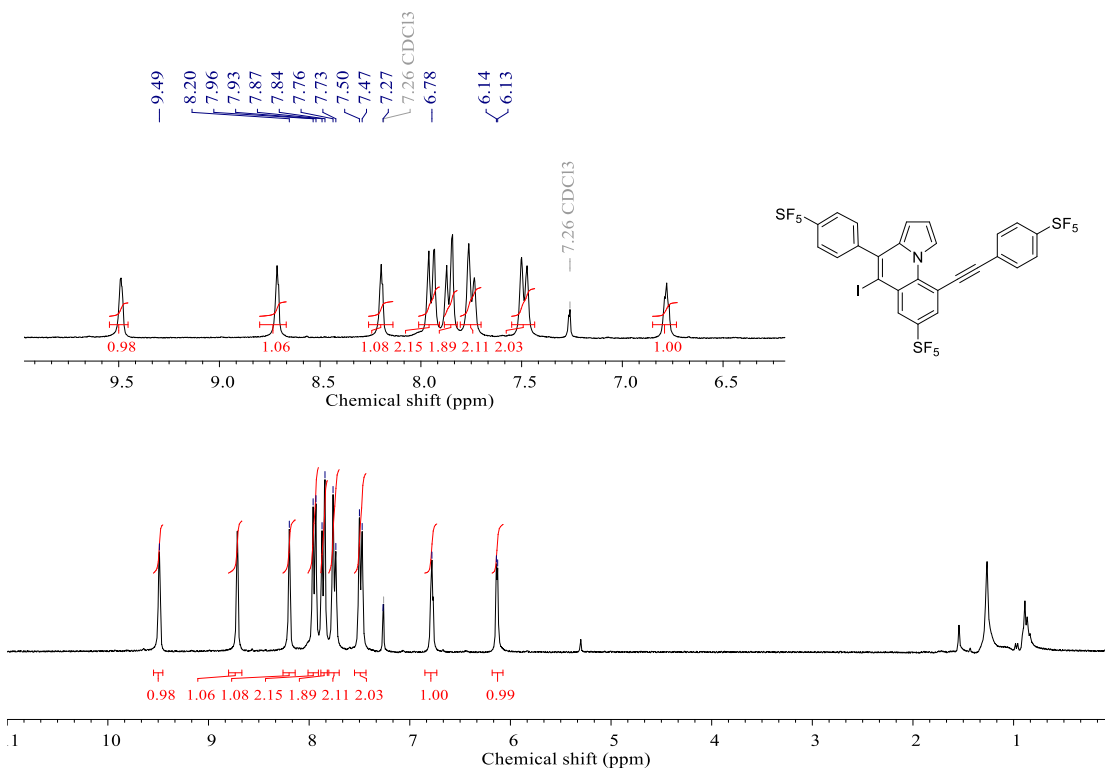


Figure A. 70 ¹H NMR spectrum of compound **4j**.

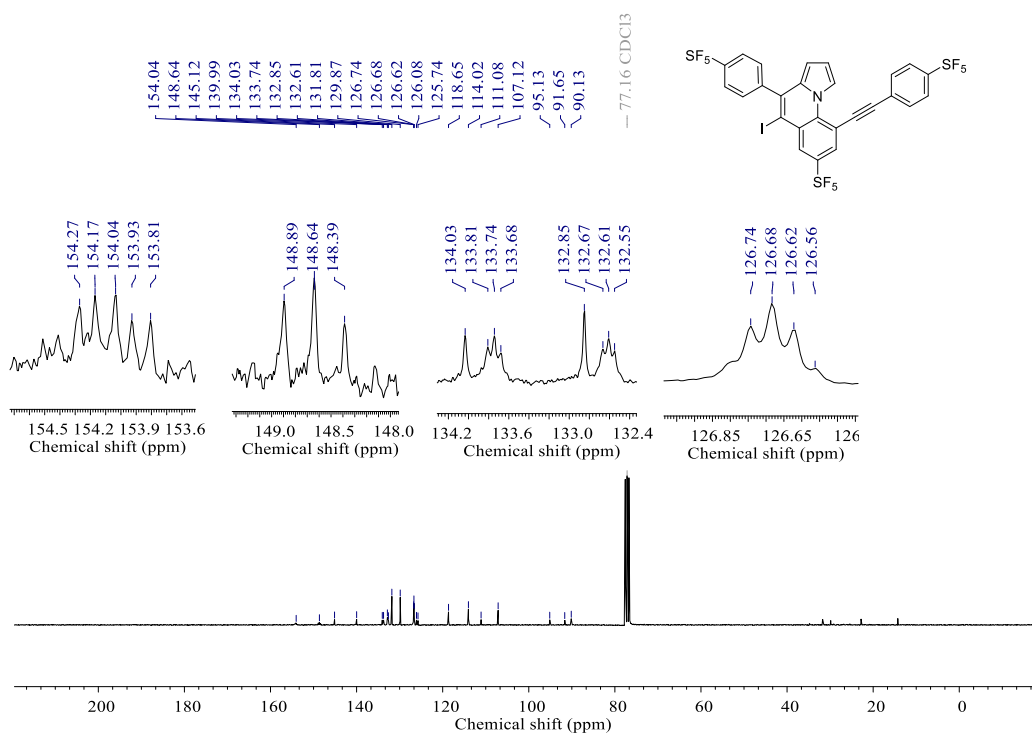


Figure A. 71 ¹³C NMR spectrum of compound **4j**.

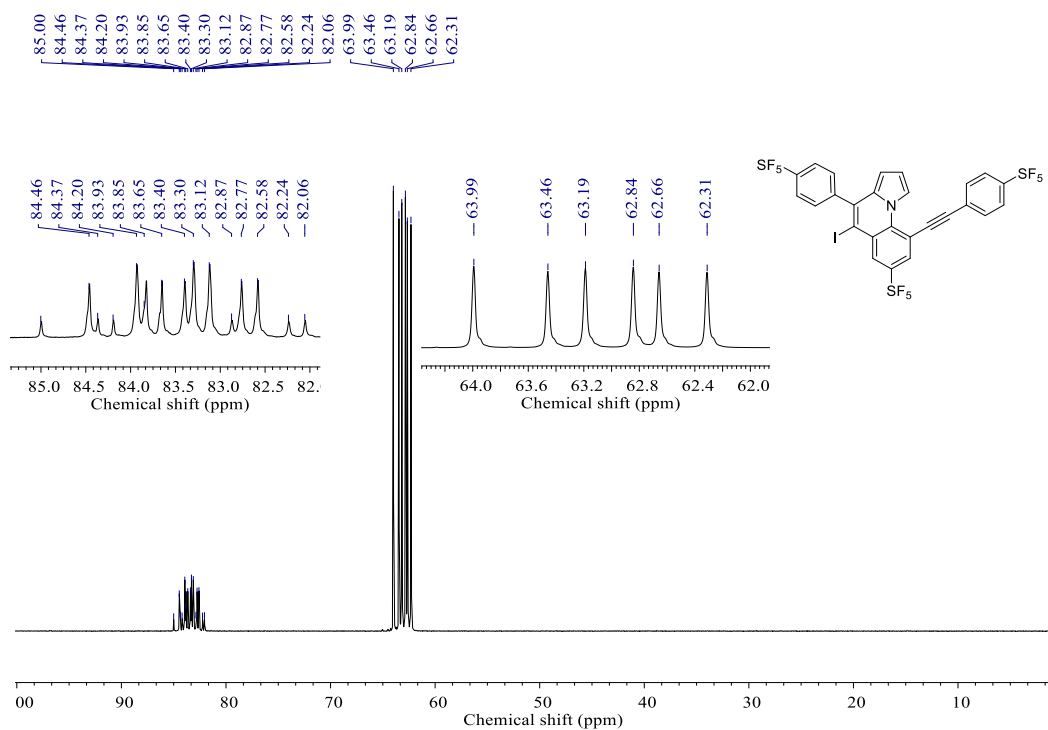


Figure A. 72 ¹⁹F NMR spectrum of compound **4j**.

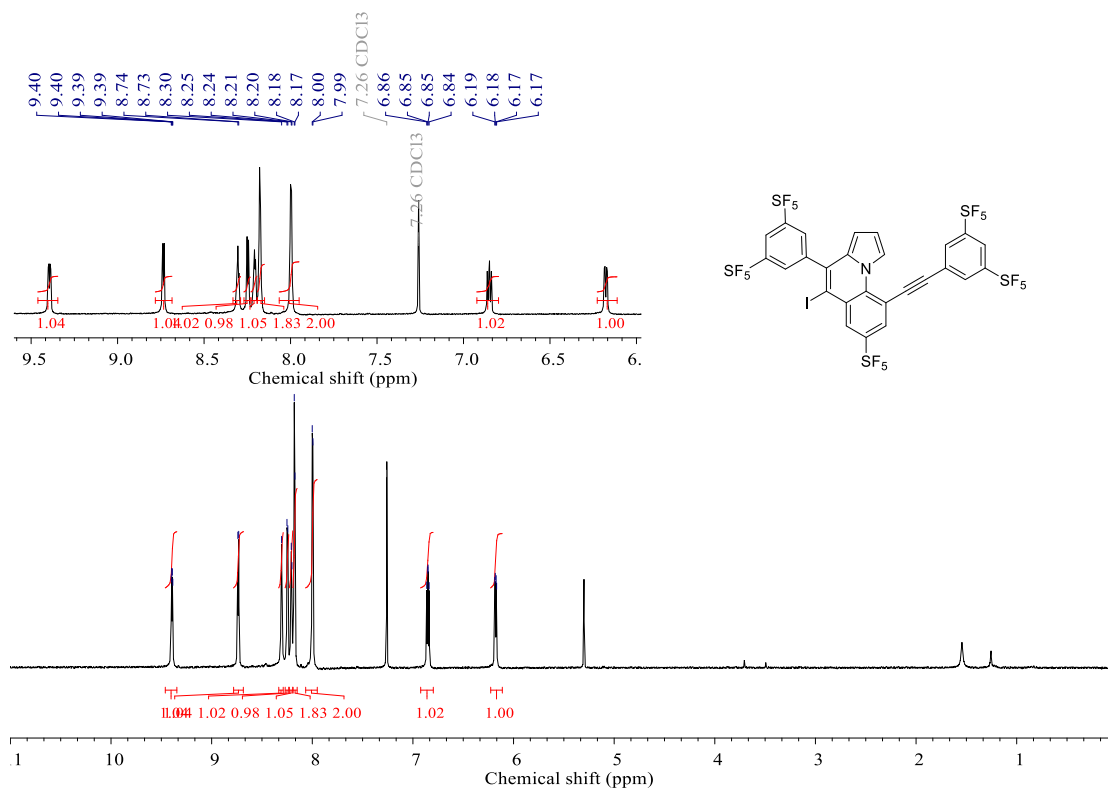


Figure A. 73 ¹H NMR spectrum of compound **4k**.

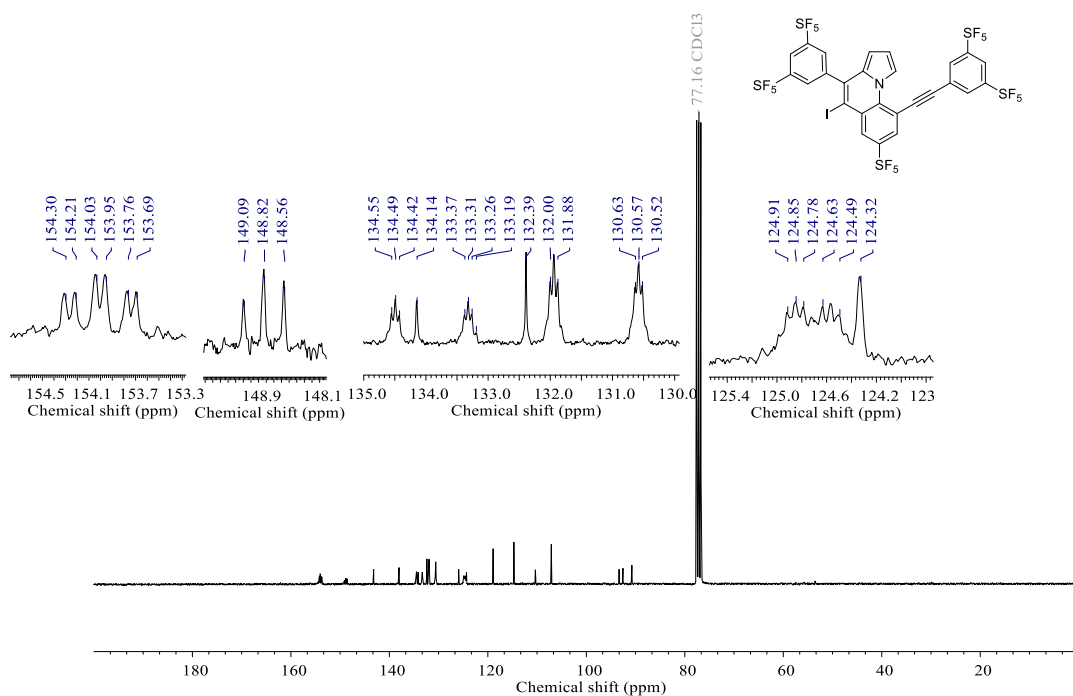


Figure A. 74 ¹³C NMR spectrum of compound **4k**.

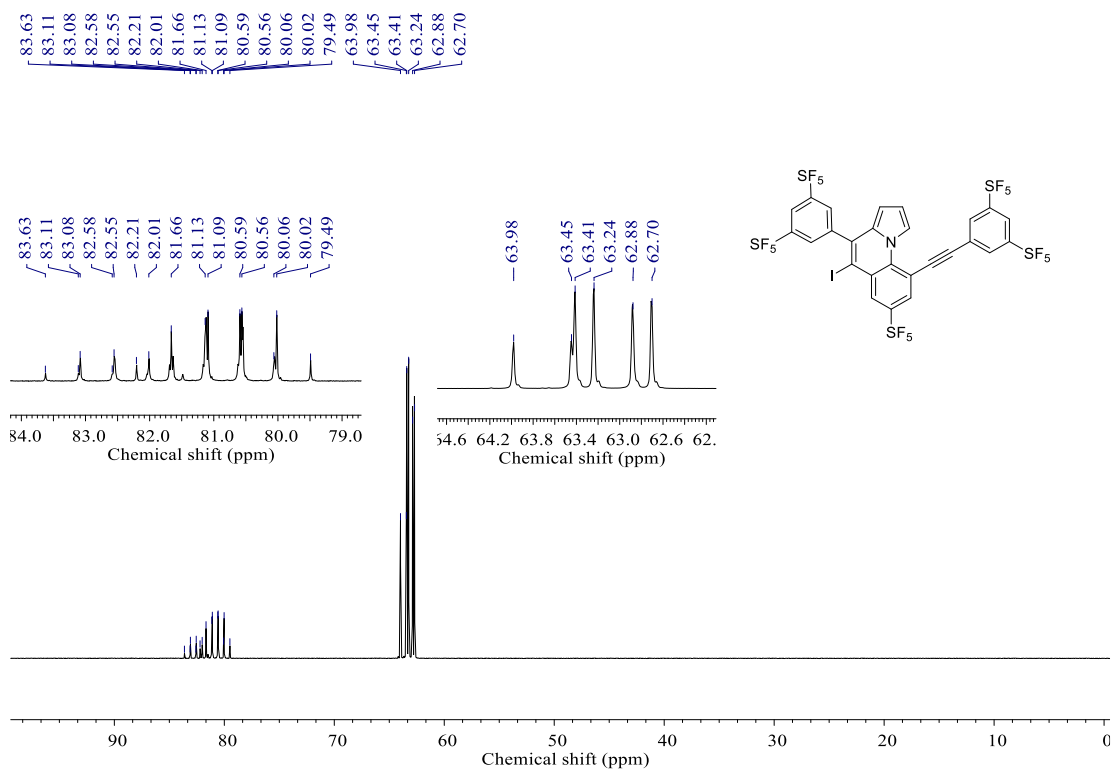


Figure A. 75 ¹⁹F NMR spectrum of compound **4k**.

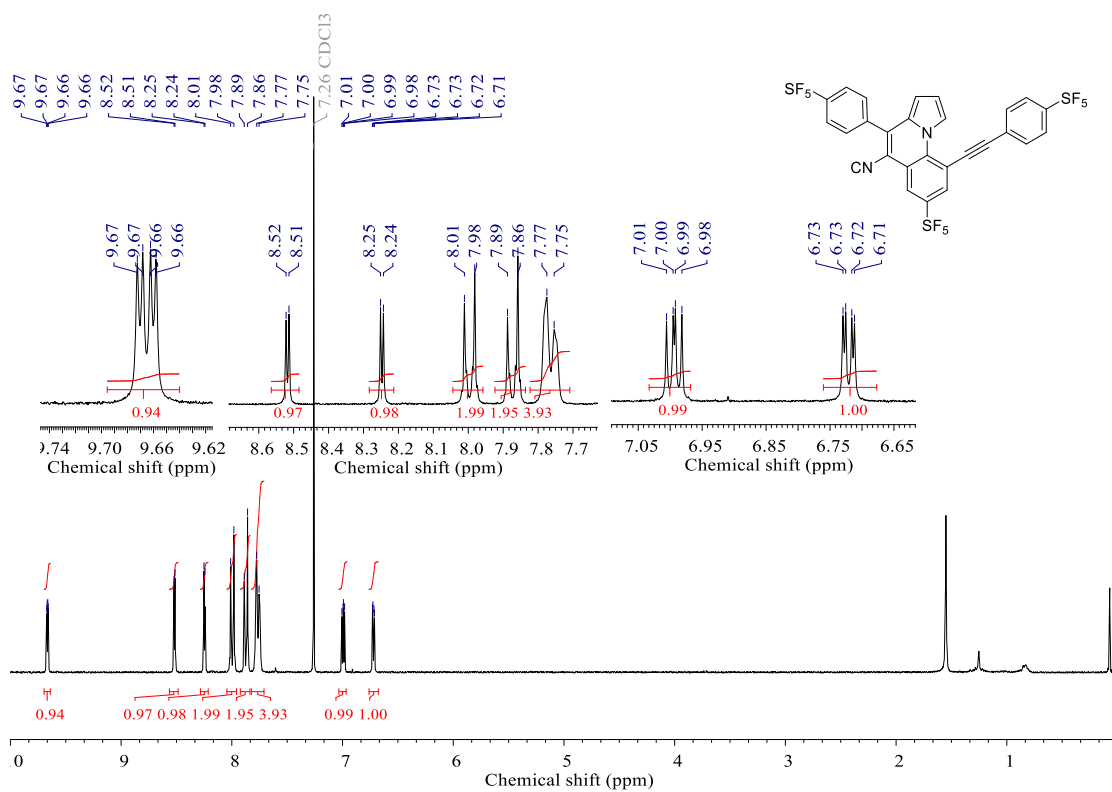


Figure A. 76 ¹H NMR spectrum of compound **4l**.

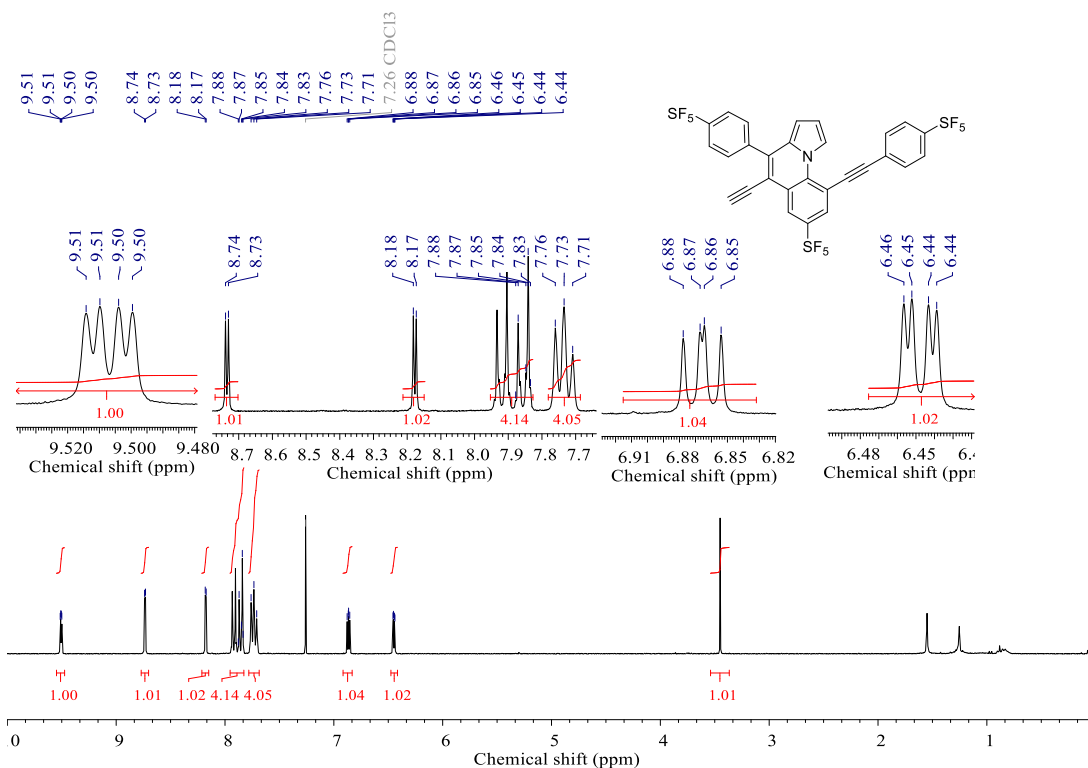


Figure A. 79 ¹H NMR spectrum of compound **4m**.

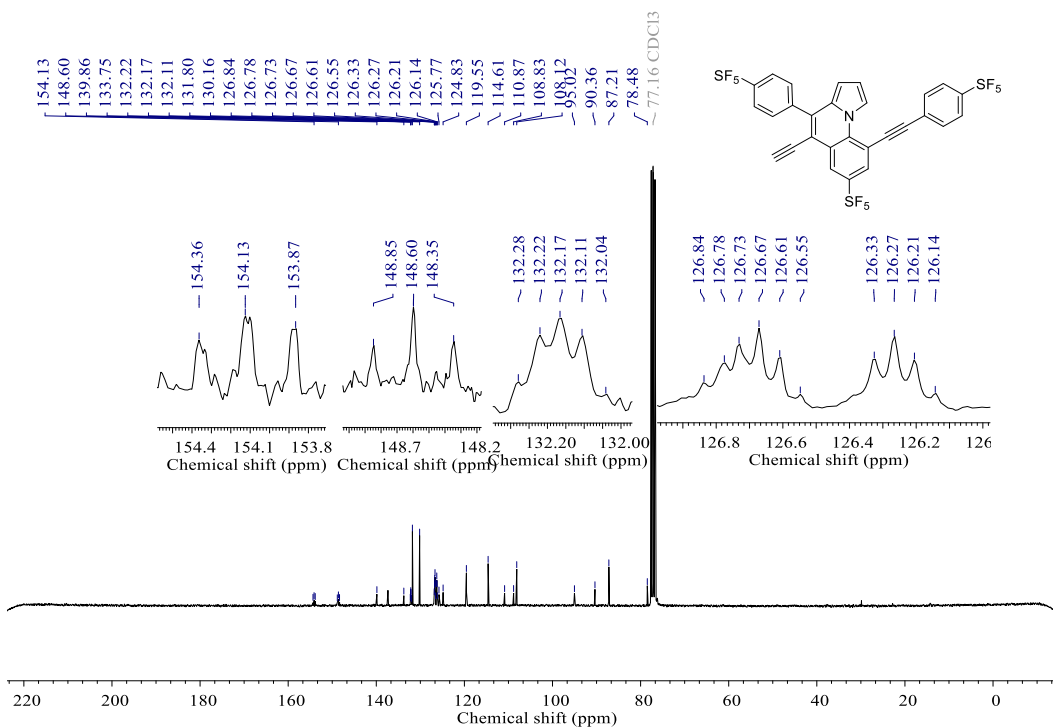


Figure A. 80 ¹³C NMR spectrum of compound **4m**.

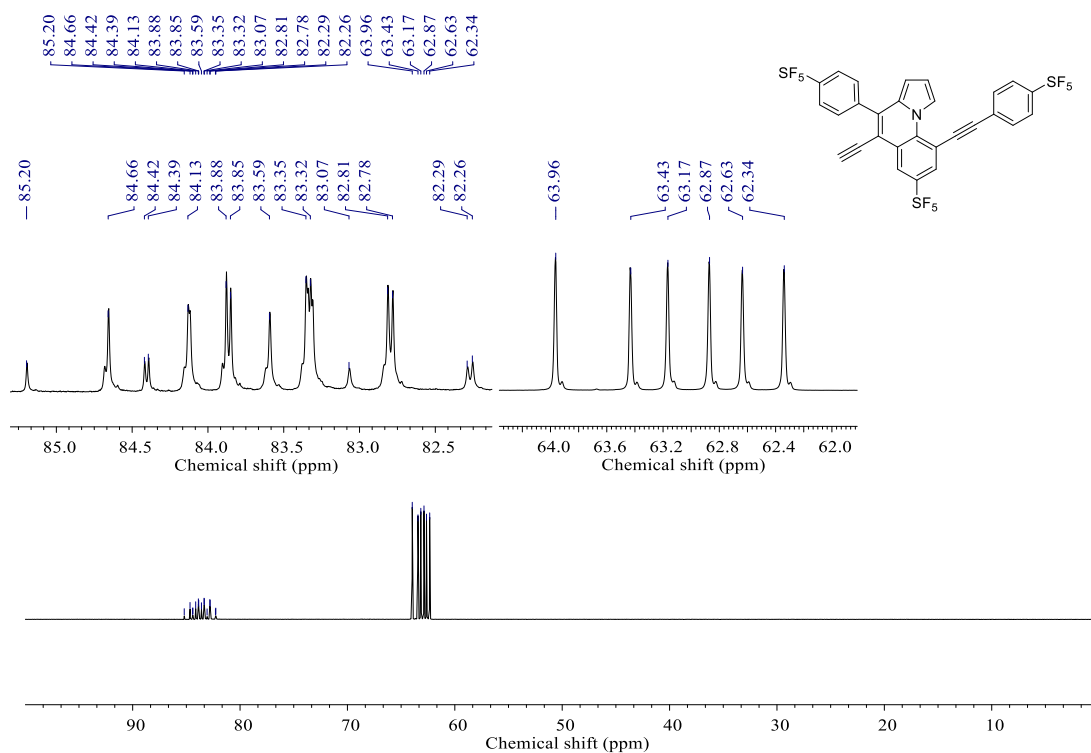


Figure A. 81 ^{19}F NMR spectrum of compound **4m**.

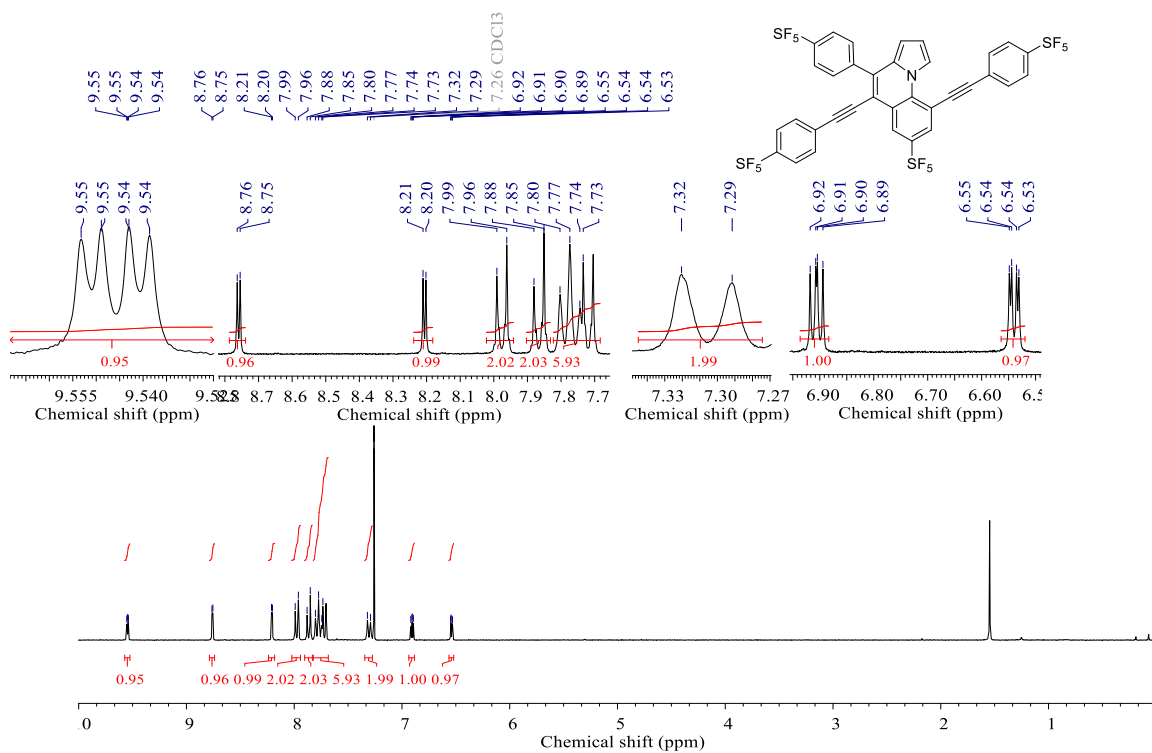


Figure A. 82 ^1H NMR spectrum of compound **4n**.

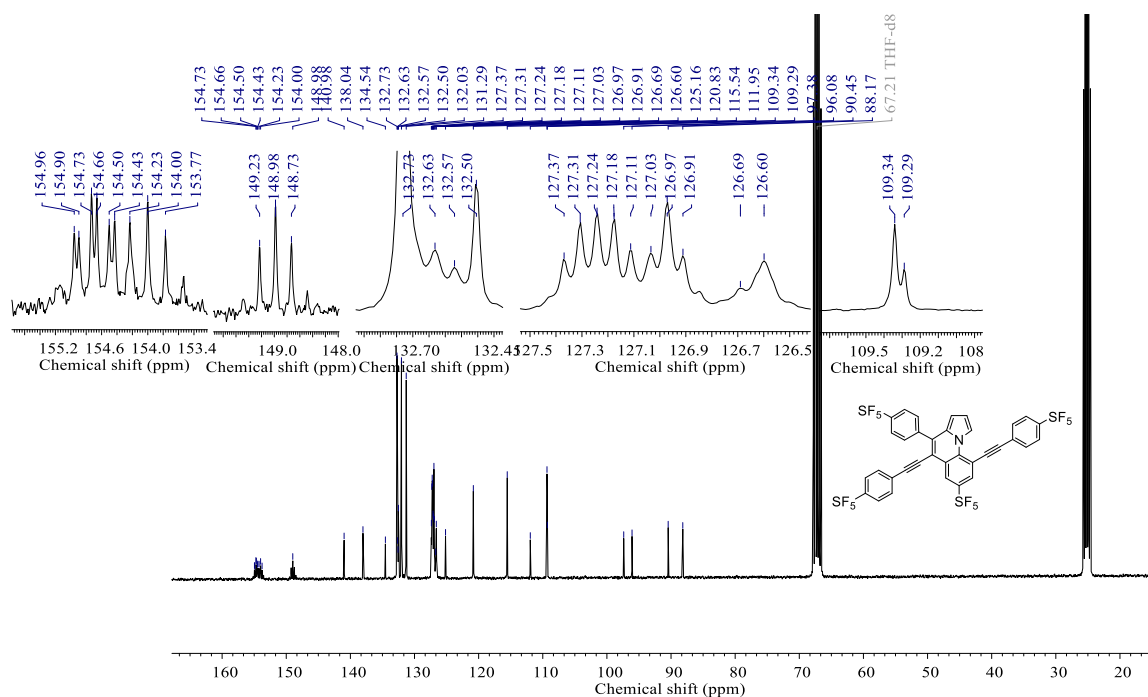


Figure A. 83 ^{13}C NMR spectrum of compound **4n**.

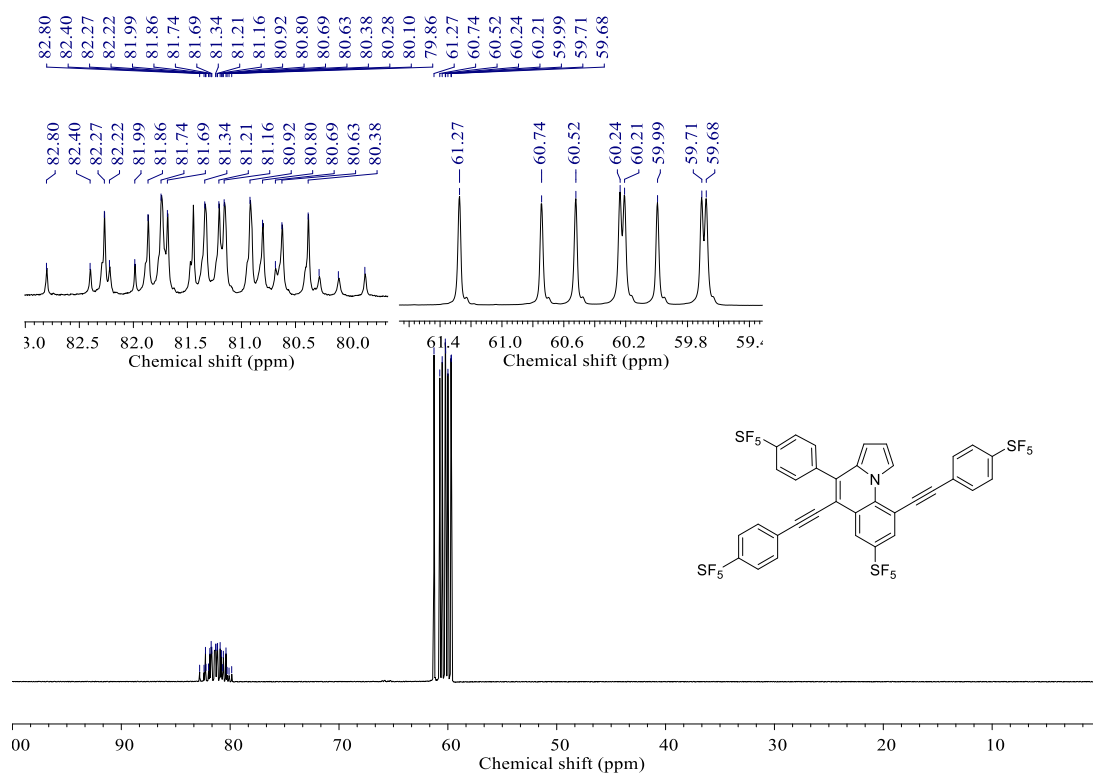


Figure A. 84 ^{19}F NMR spectrum of compound **4n**.

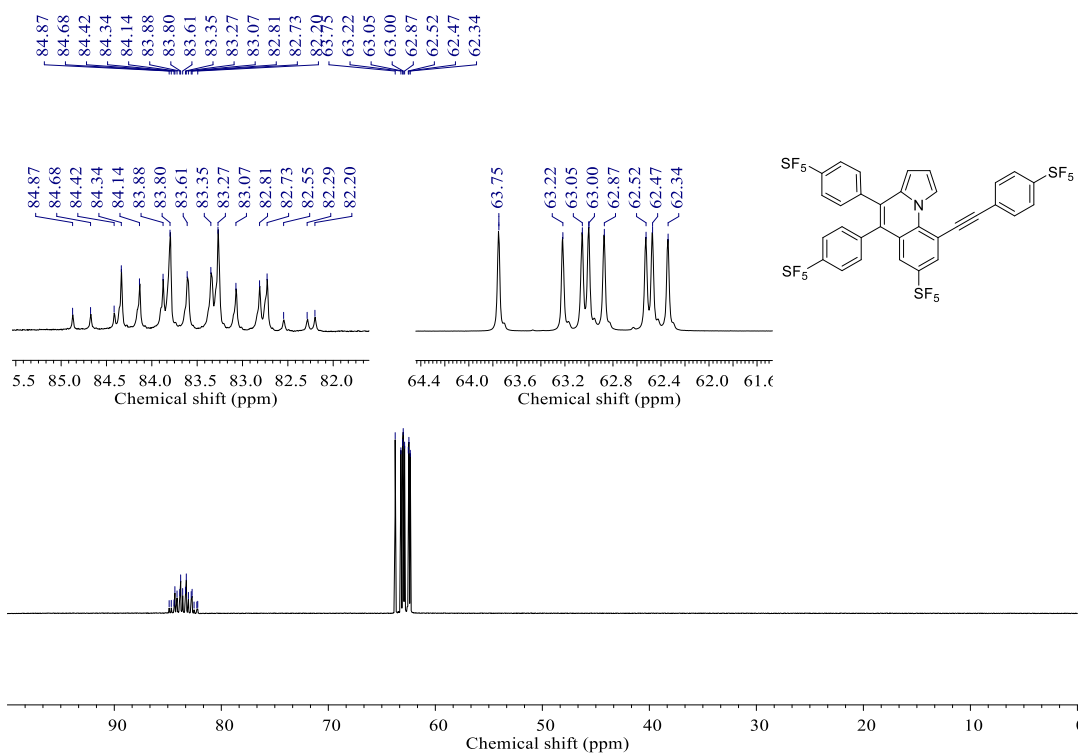


Figure A. 87 ¹⁹F NMR spectrum of compound **4o**.

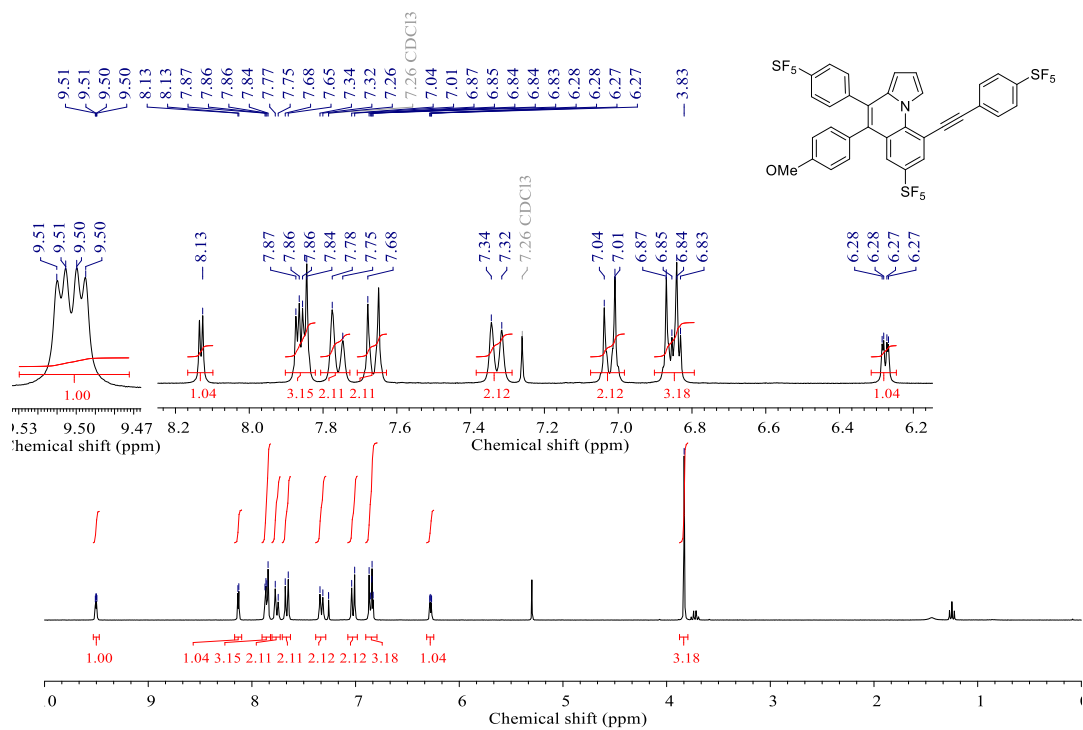


Figure A. 88 ¹H NMR spectrum of compound **4p**.

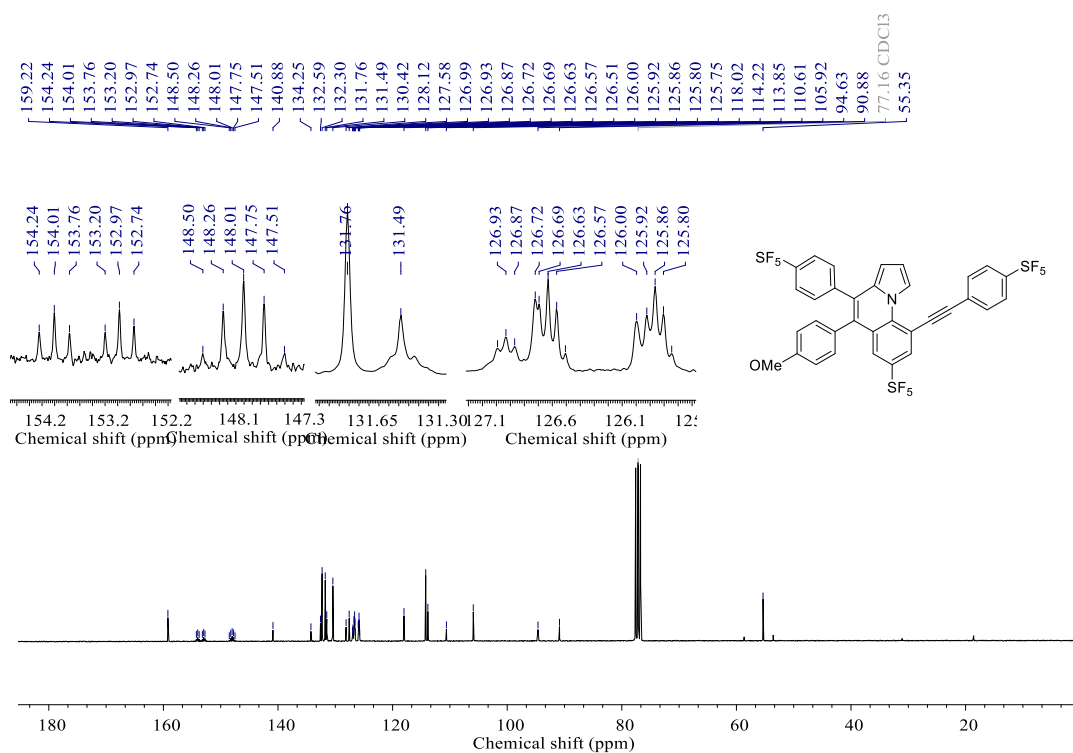


Figure A. 89 ¹³C NMR spectrum of compound **4p**.

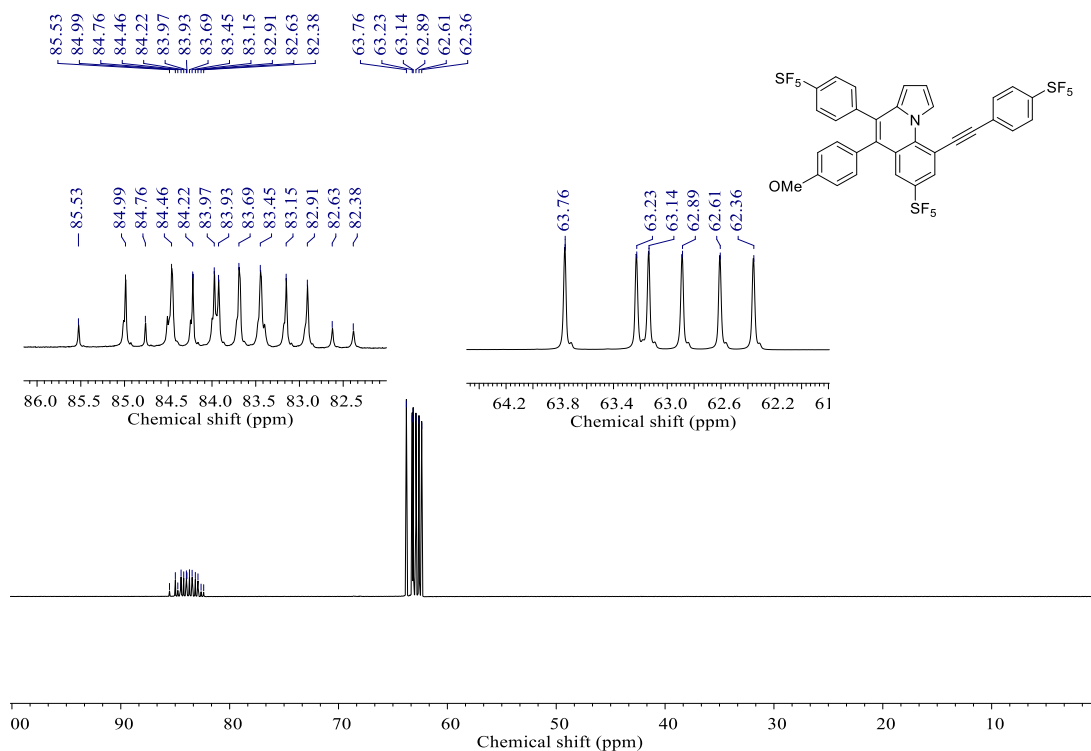


Figure A. 90 ¹⁹F NMR spectrum of compound **4p**.

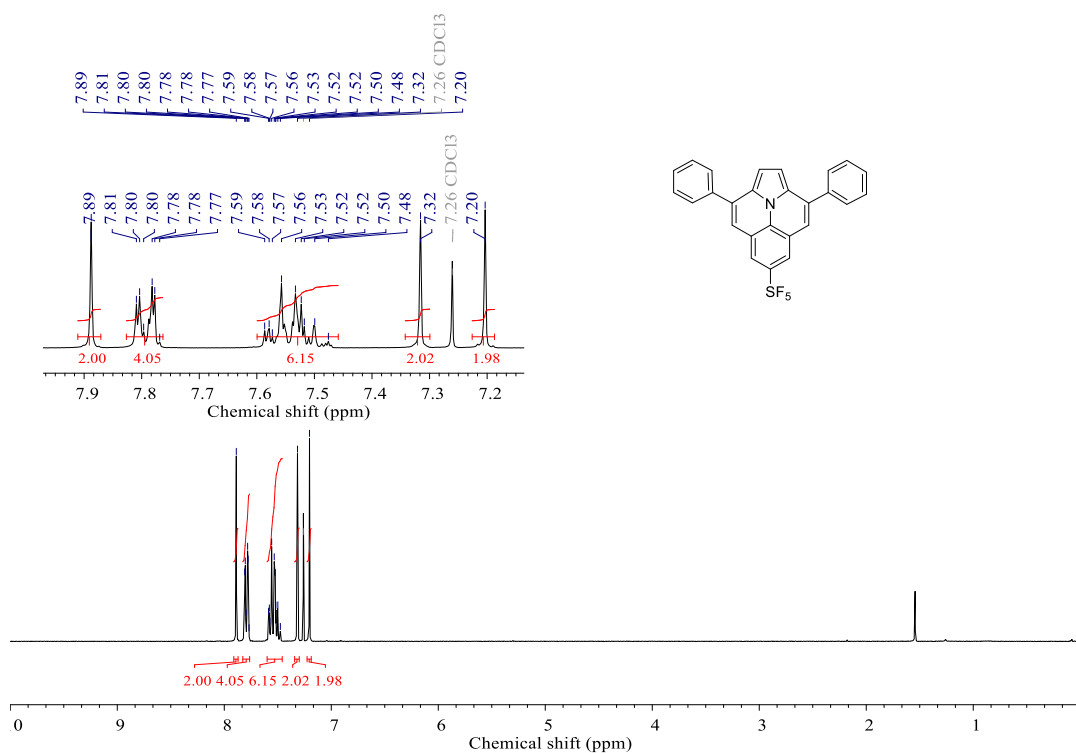


Figure A. 91 ¹H NMR spectrum of compound U1.

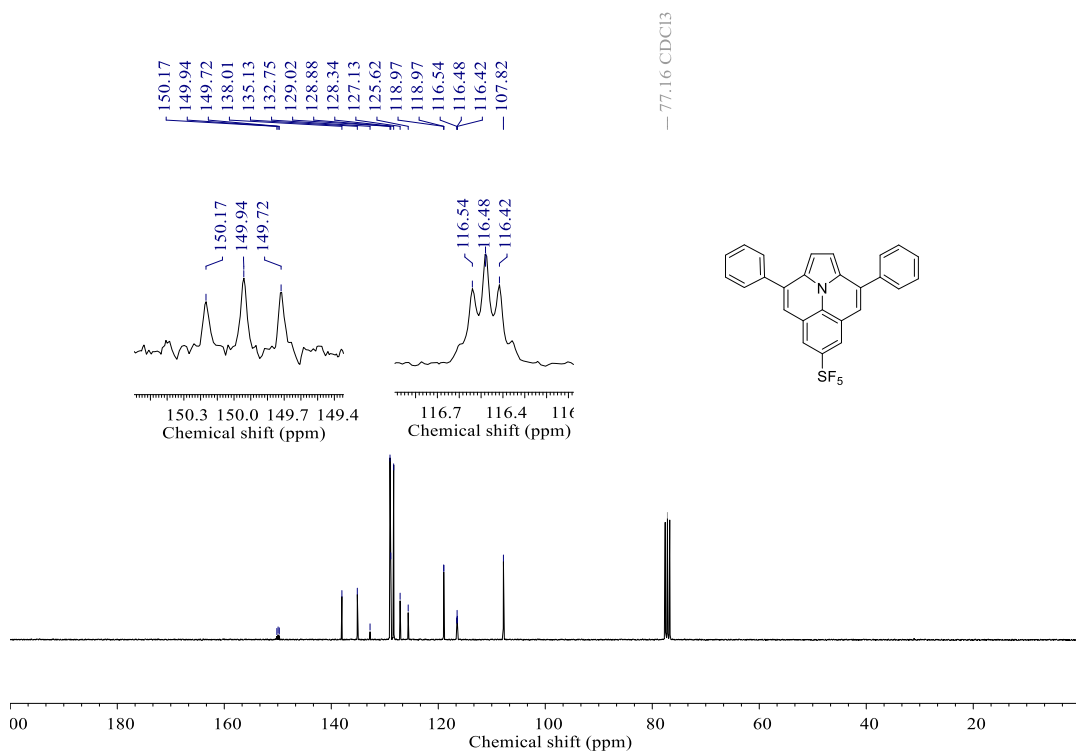


Figure A. 92 ¹³C NMR spectrum of compound U1.

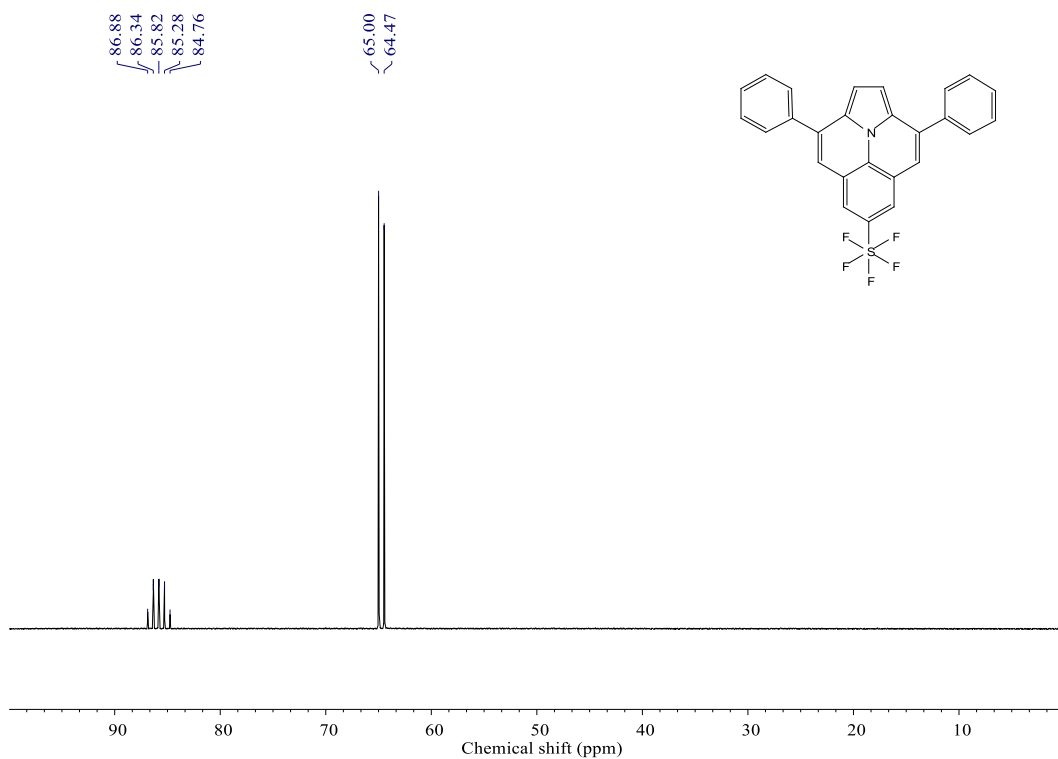


Figure A. 93 ¹⁹F NMR spectrum of compound U1.

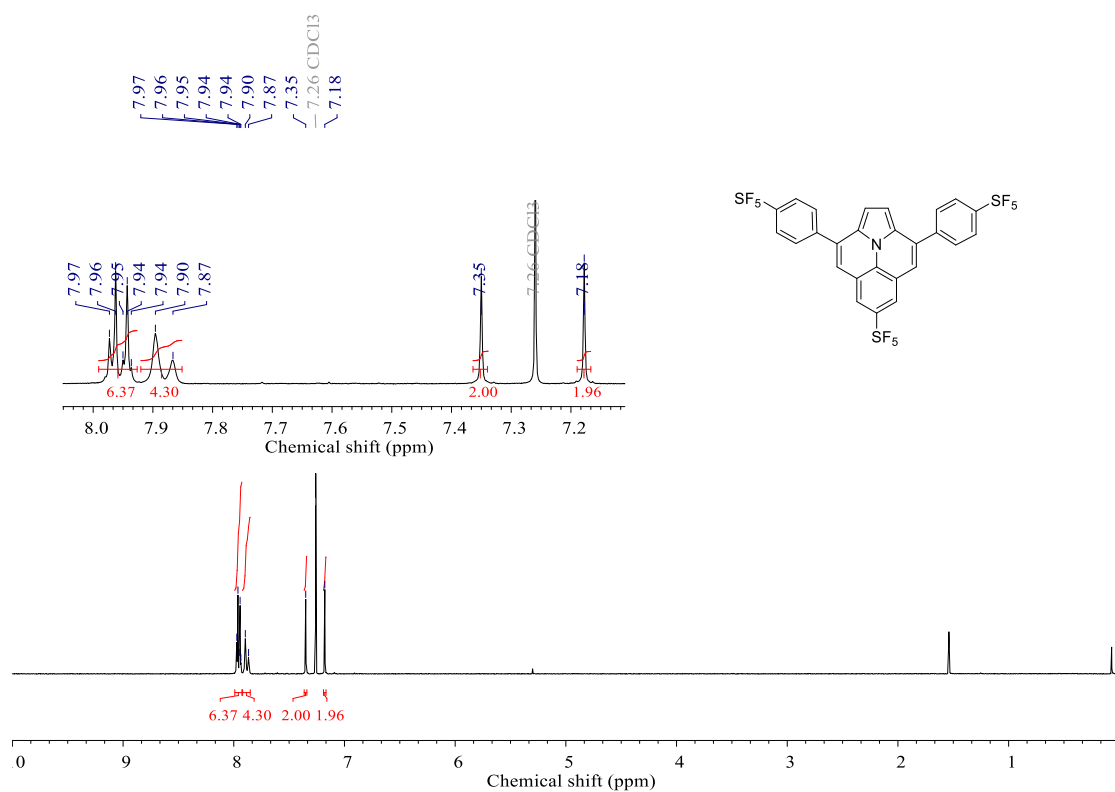


Figure A. 94 ¹H NMR spectrum of compound U2.

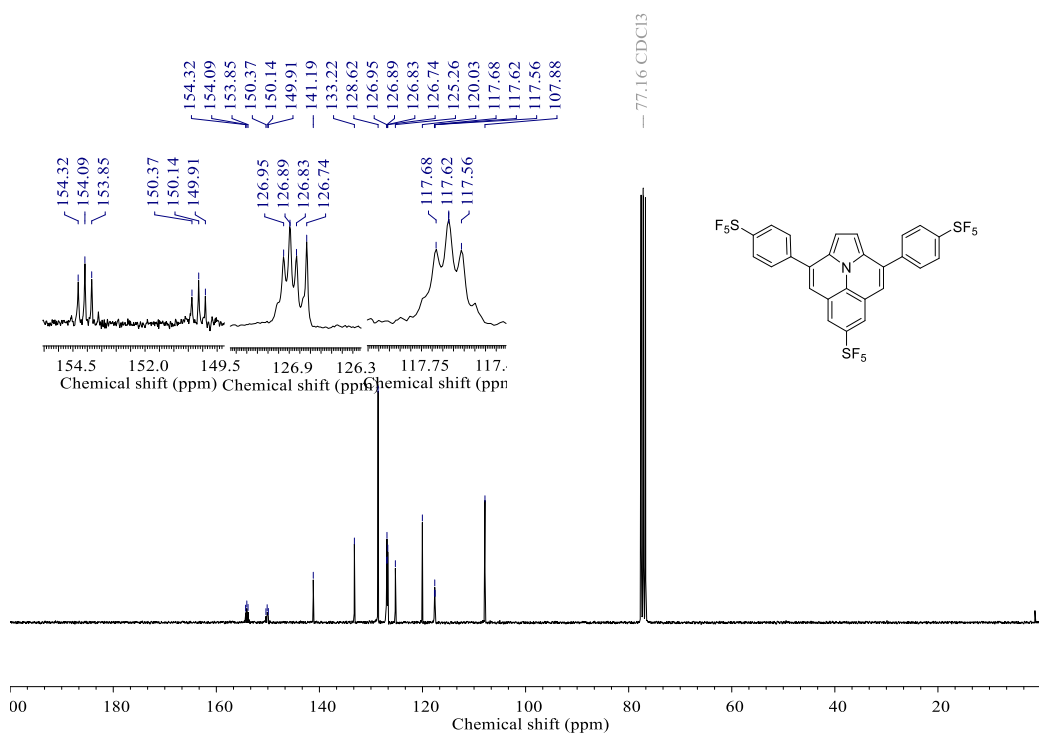


Figure A. 95 ^{13}C NMR spectrum of compound U2.

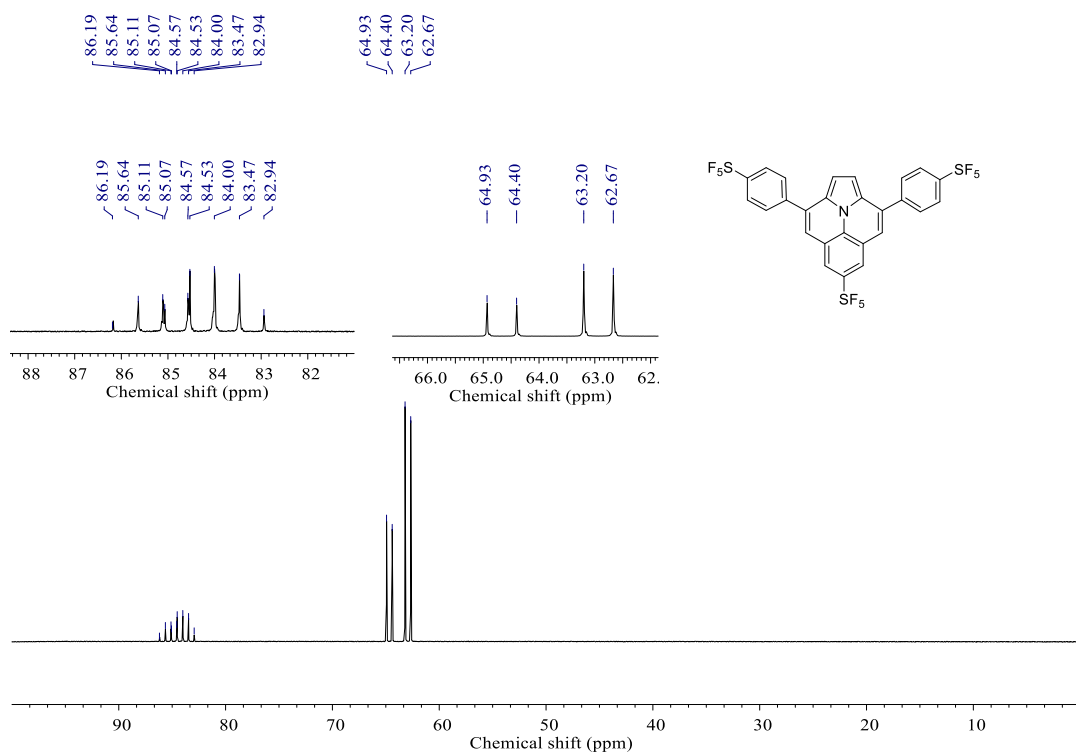


Figure A. 96 ^{19}F NMR spectrum of compound U2.

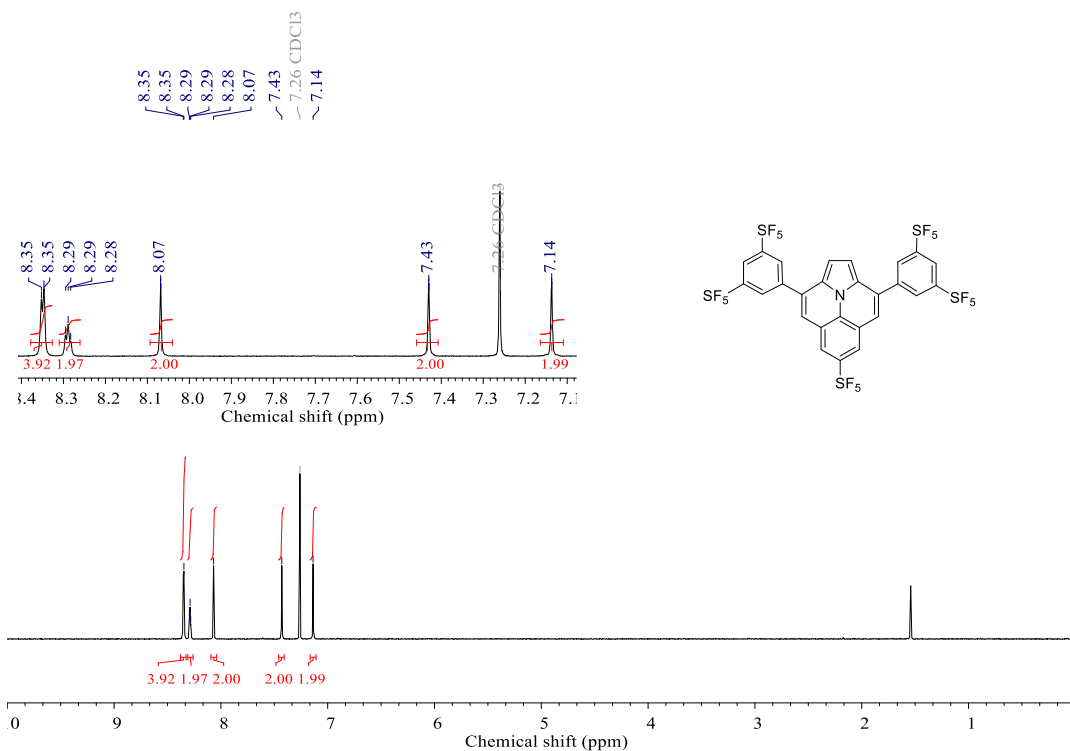


Figure A. 97 ¹H NMR spectrum of compound U3.

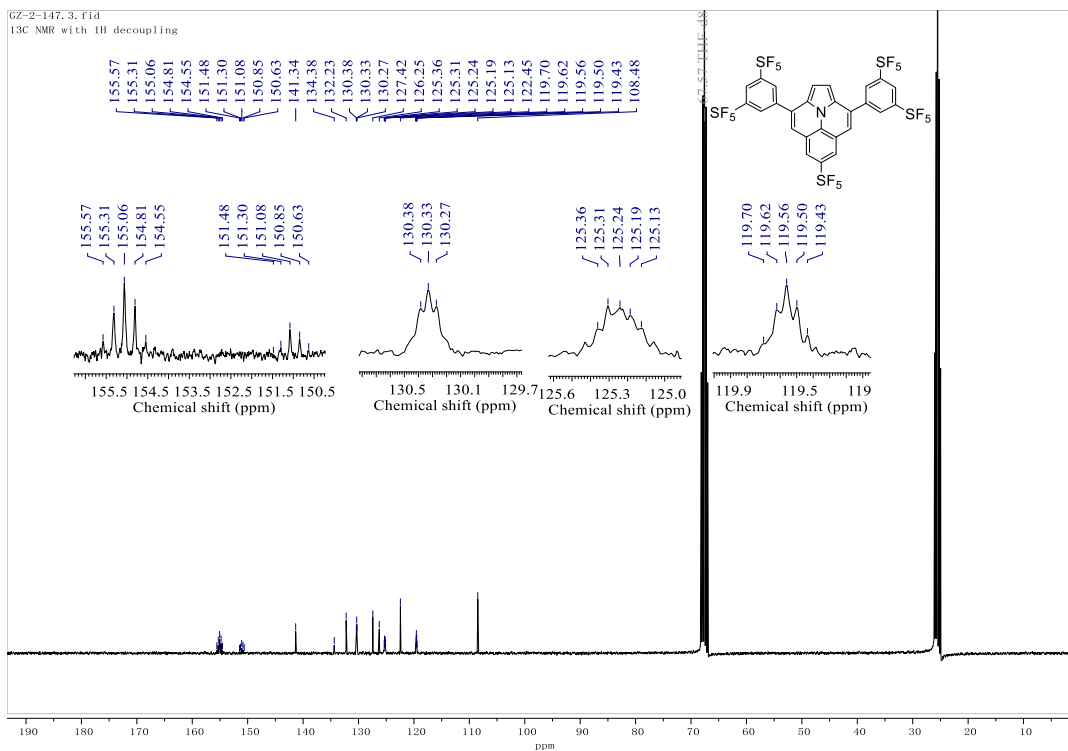


Figure A. 98 ¹³C NMR spectrum of compound U3.

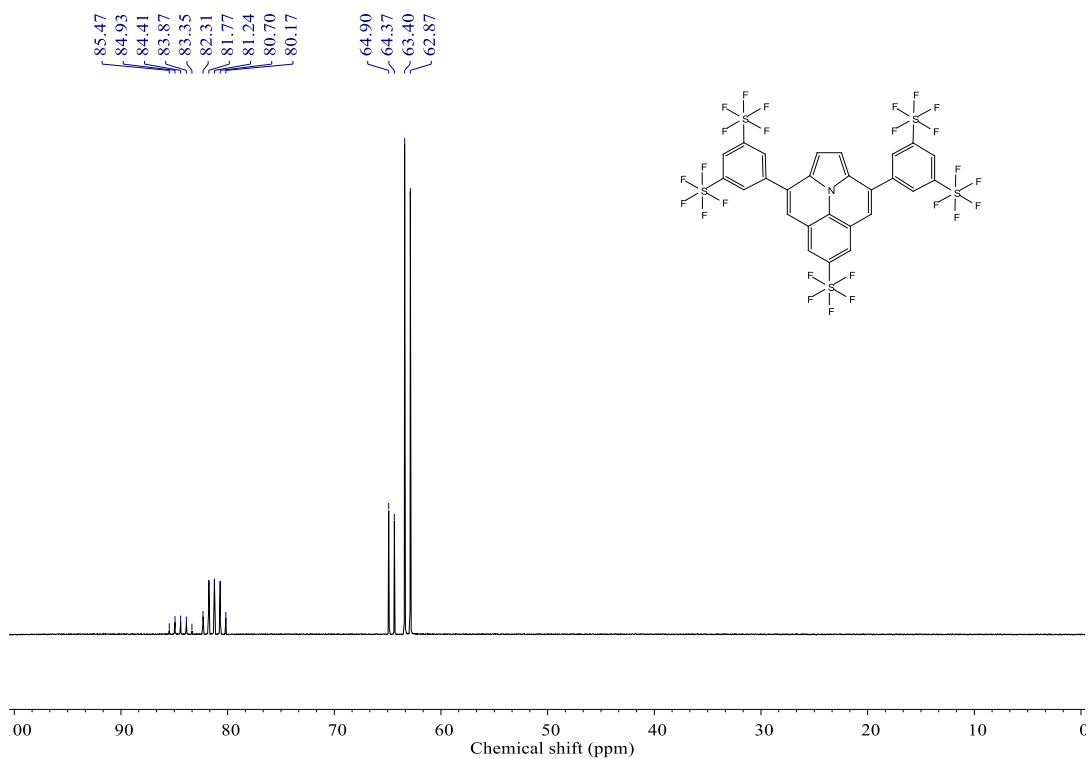


Figure A. 99 ¹⁹F NMR spectrum of compound U3.

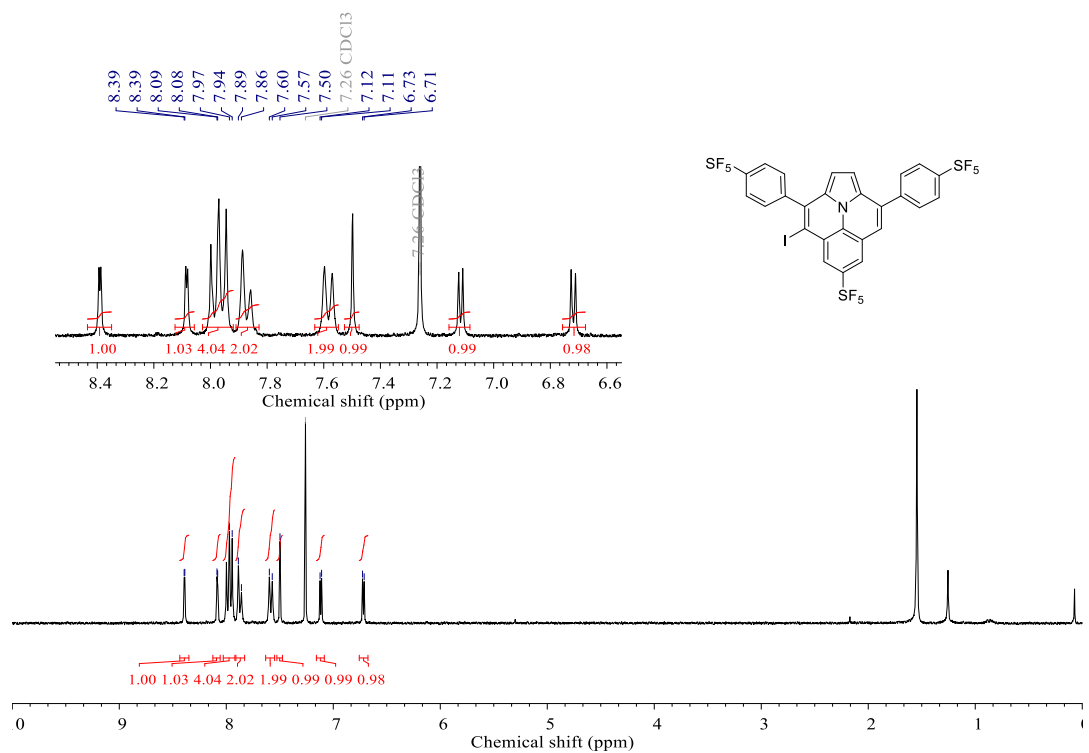


Figure A. 100 ¹H NMR spectrum of compound U5.

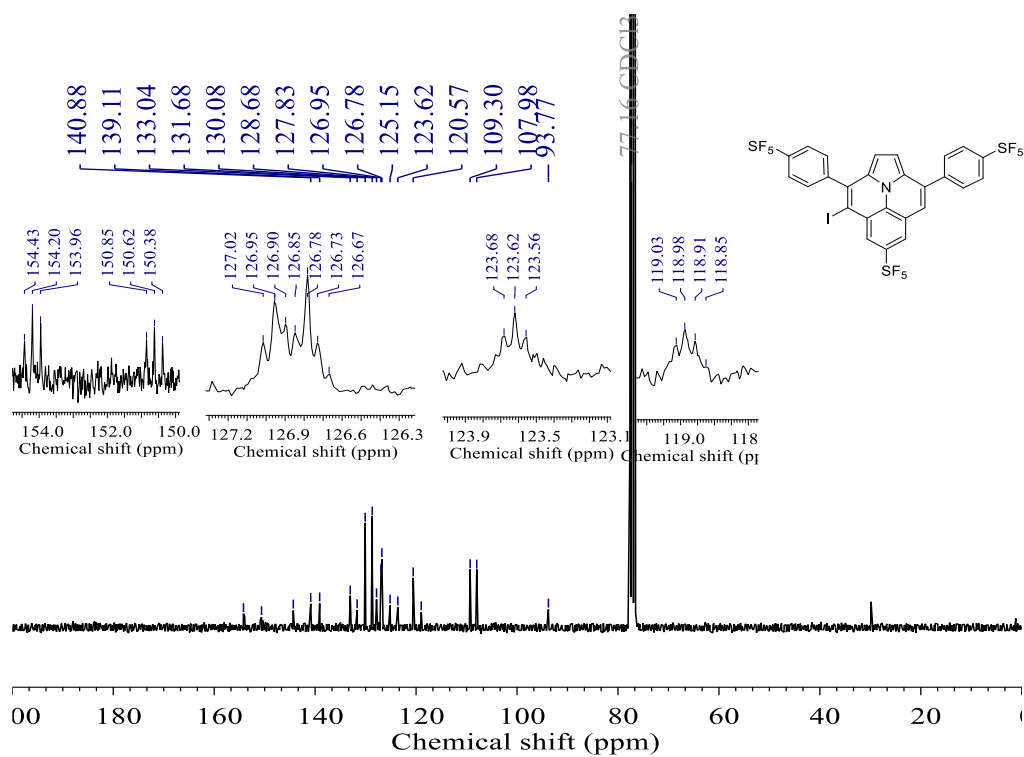


Figure A. 101 ¹³C NMR spectrum of compound U5.

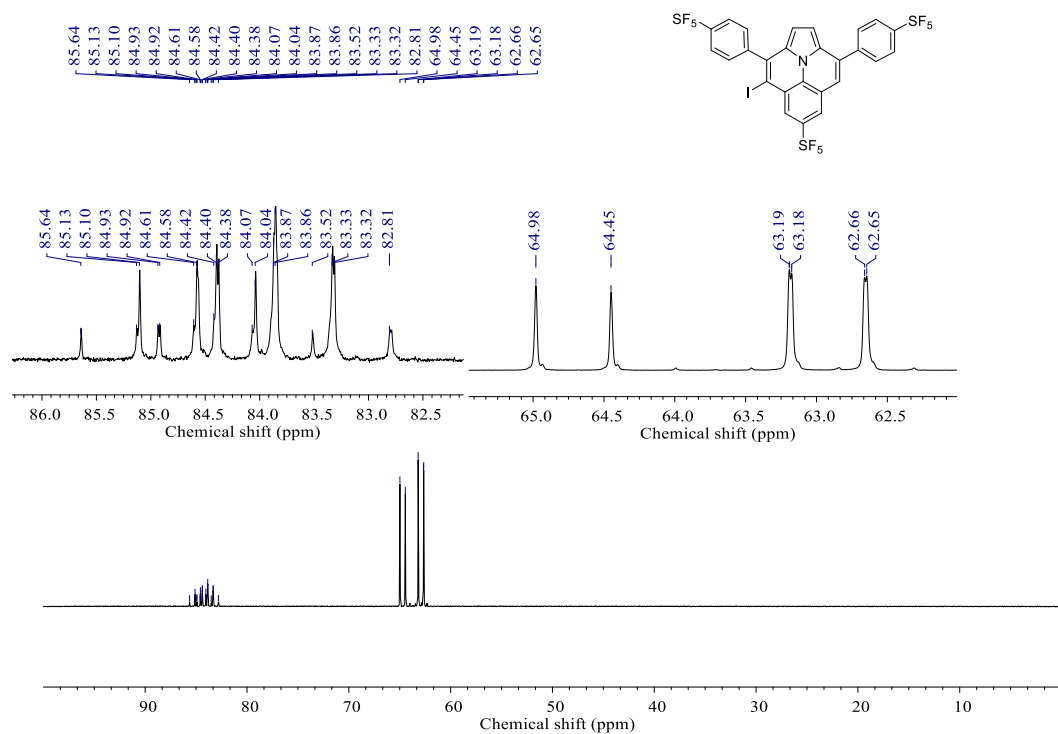


Figure A. 102 ¹⁹F NMR spectrum of compound U5.

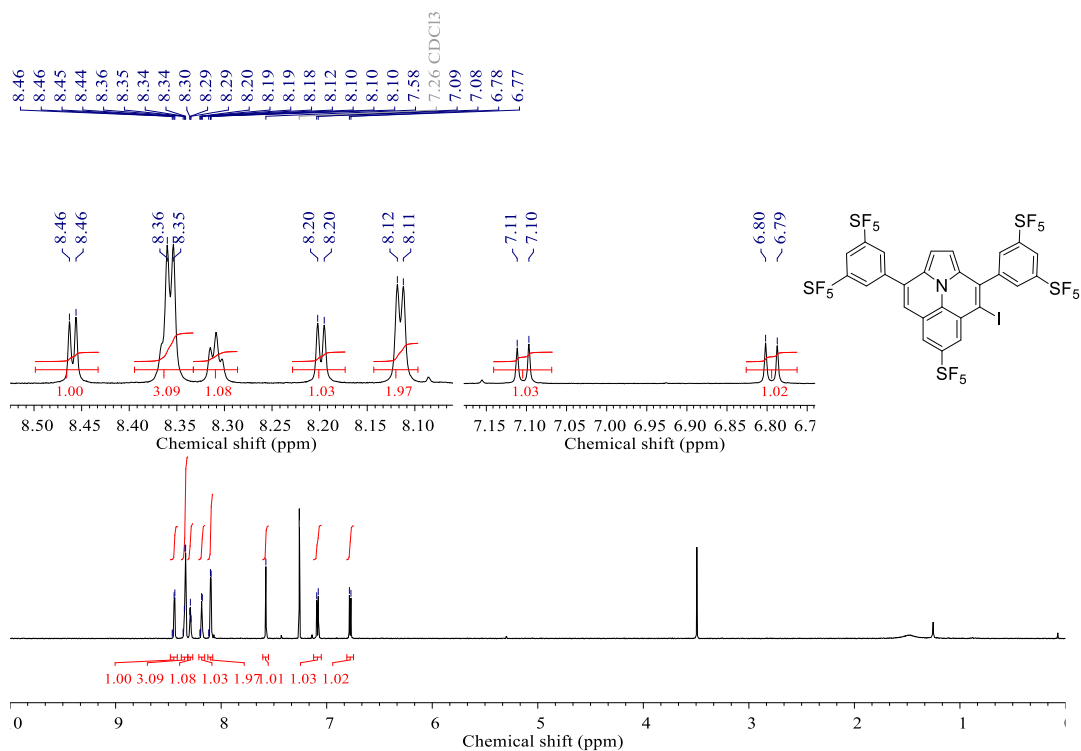


Figure A. 103 ¹H NMR spectrum of compound U6.

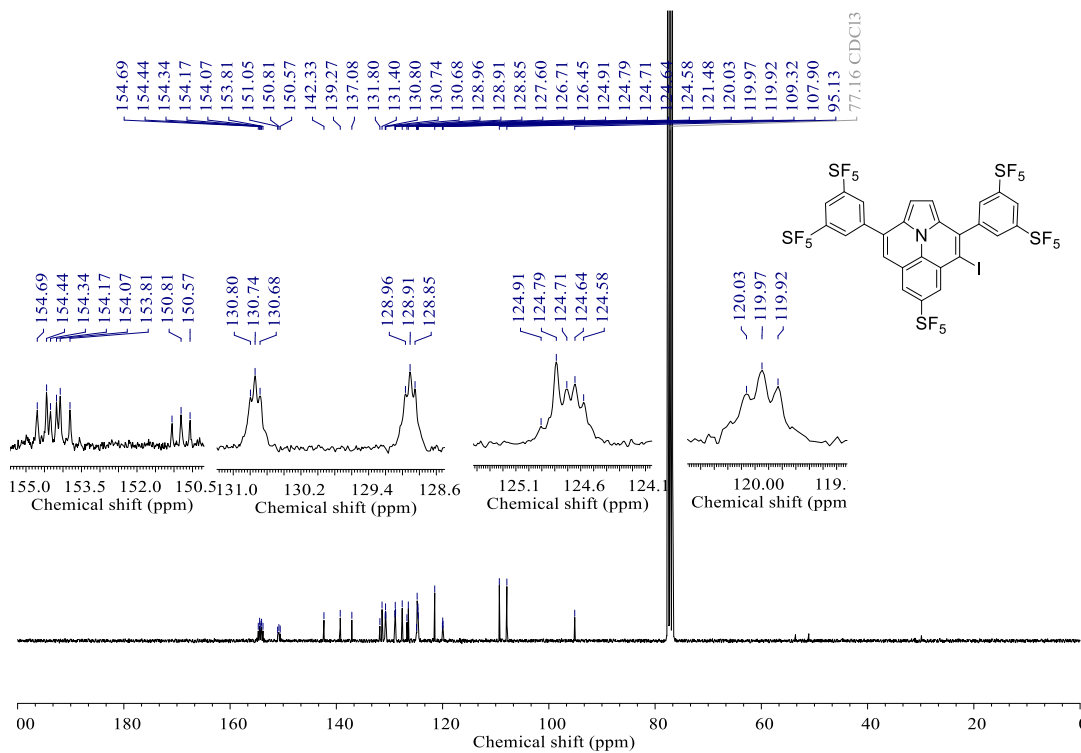


Figure A. 104 ¹³C NMR spectrum of compound U6.

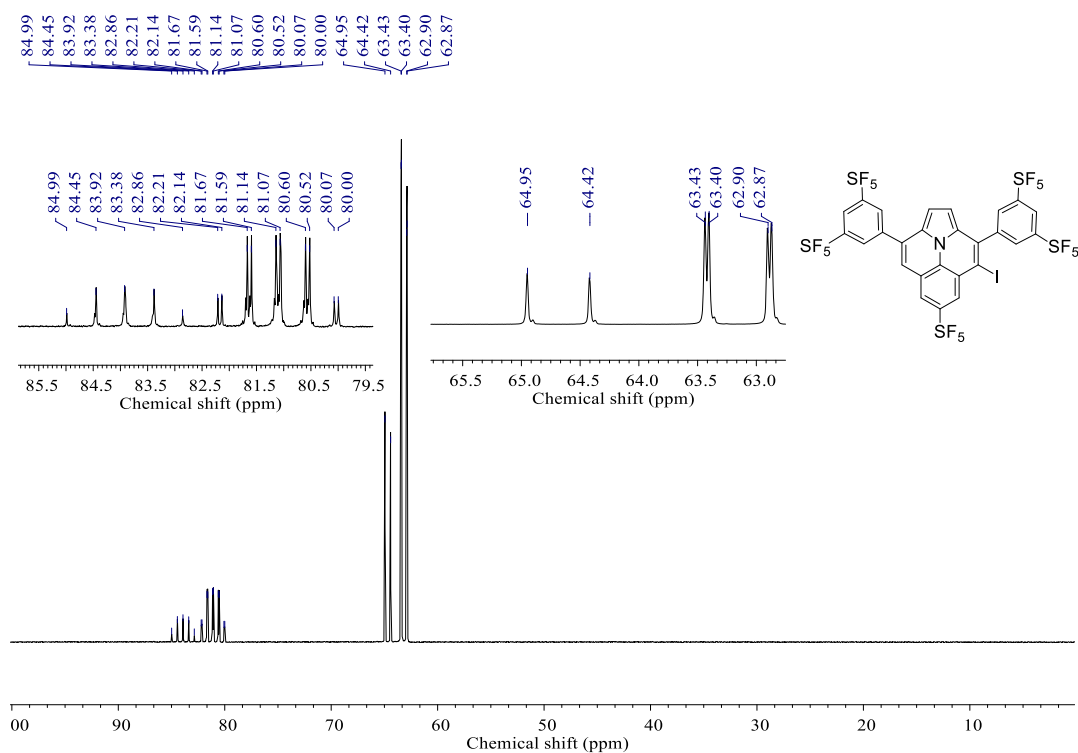


Figure A. 105 ^{19}F NMR spectrum of compound **U6**.

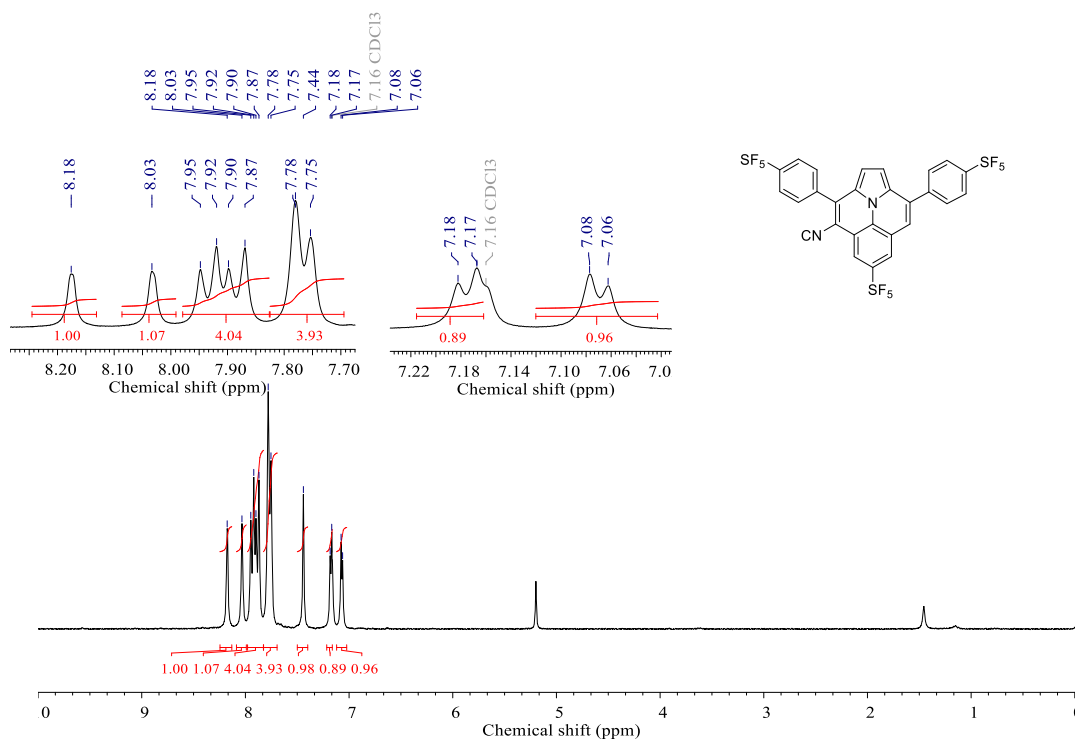


Figure A. 106 ^1H NMR spectrum of compound **U7**.

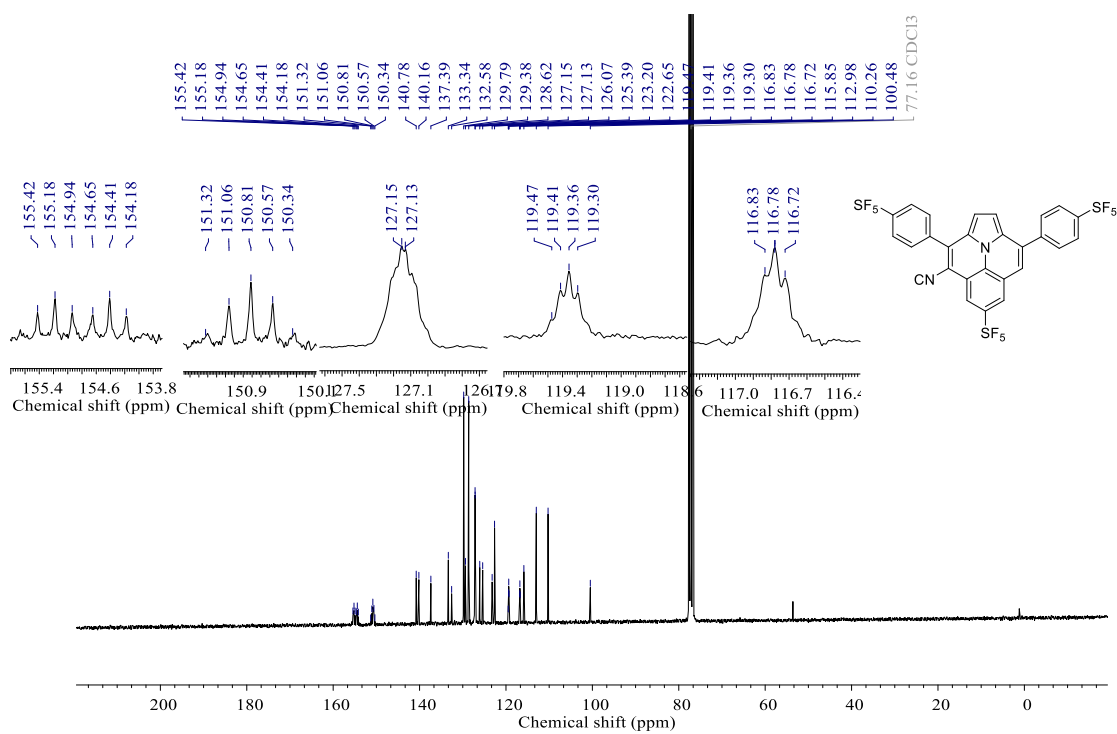


Figure A. 107 ¹³C NMR spectrum of compound U7.

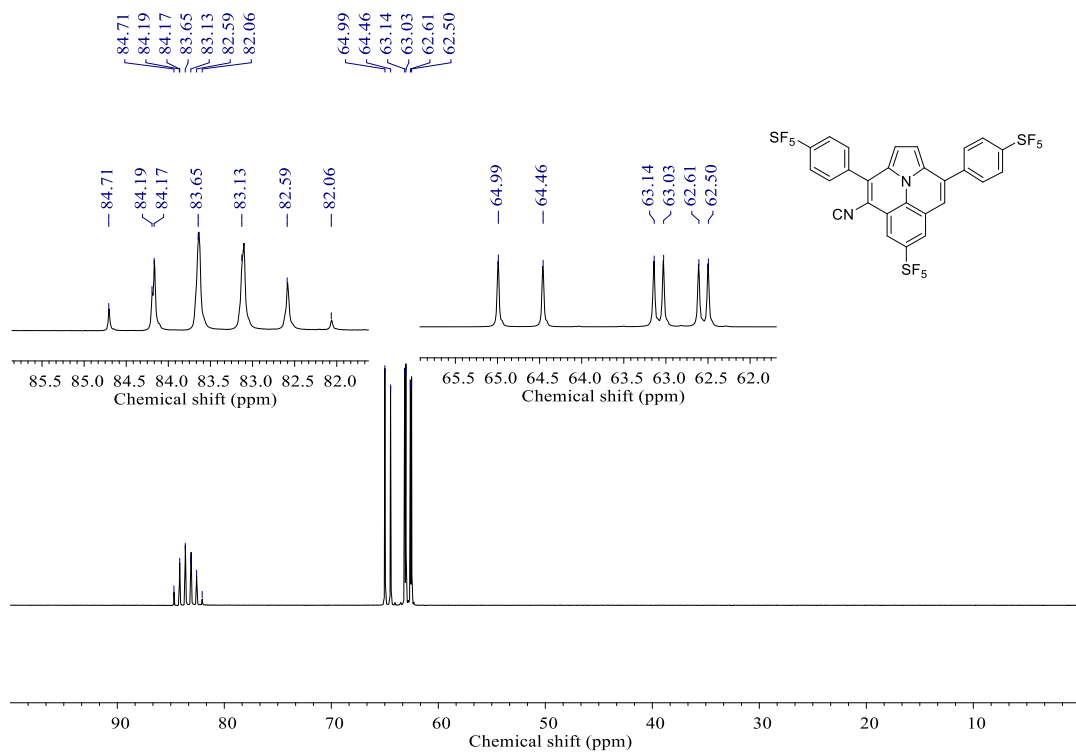


Figure A. 108 ¹⁹F NMR spectrum of compound U7.

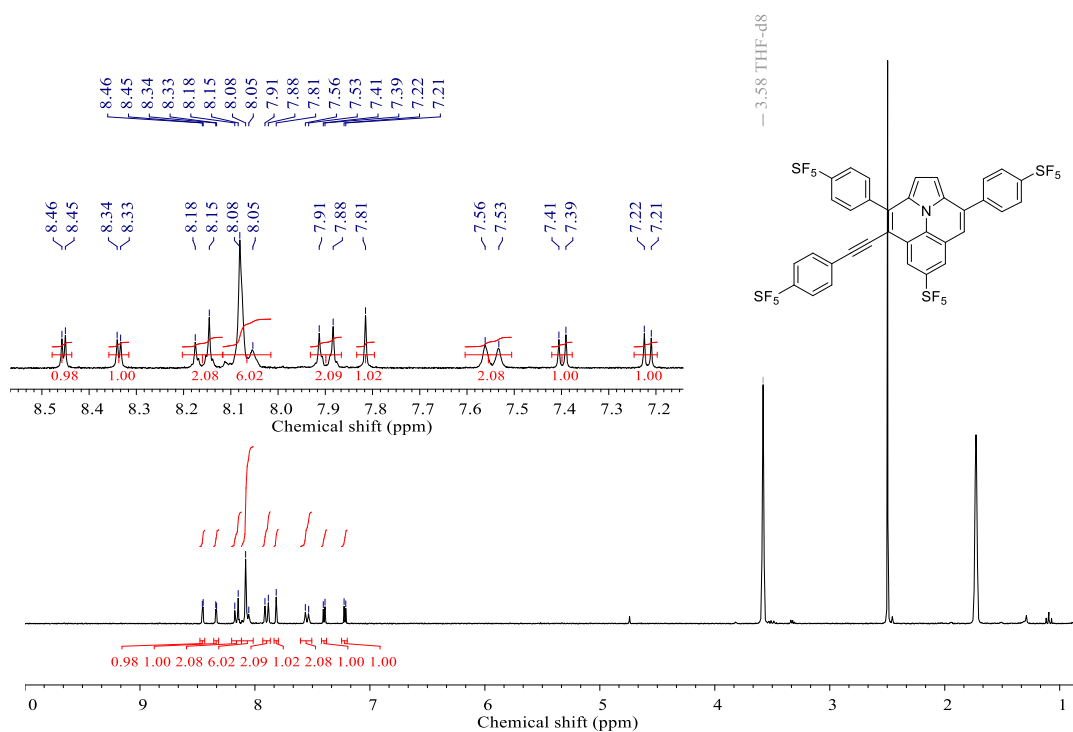


Figure A. 109 ¹H NMR spectrum of compound U8.

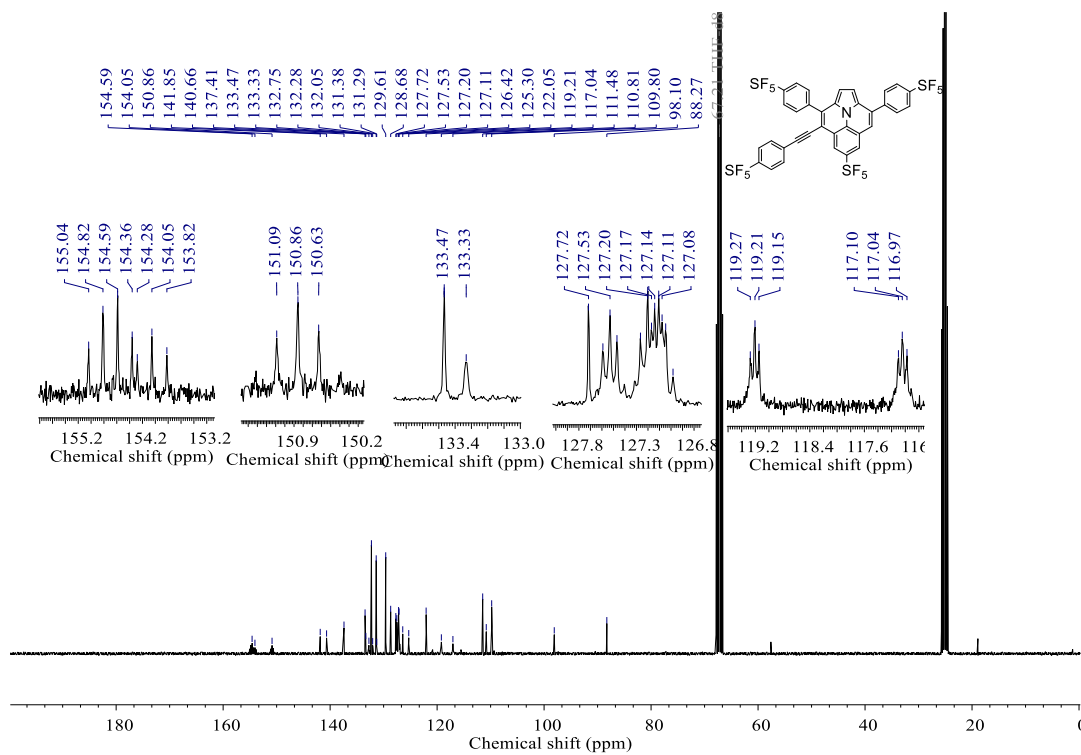


Figure A. 110 ¹³C NMR spectrum of compound U8.

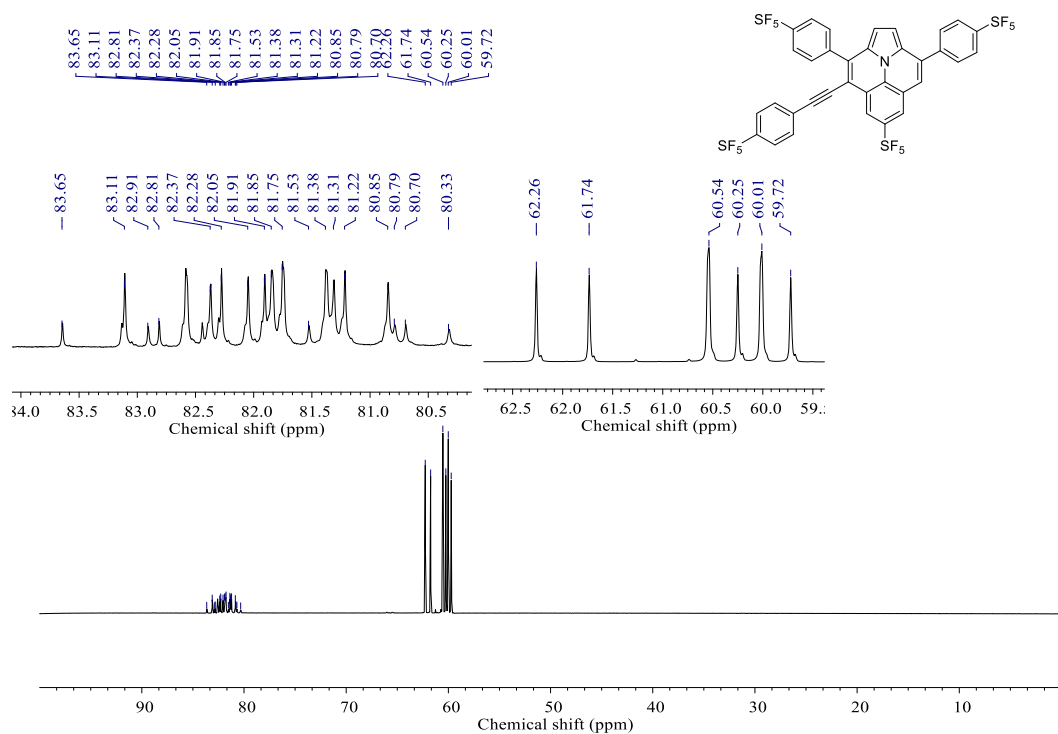


Figure A. 111 ¹⁹F NMR spectrum of compound **U8**.

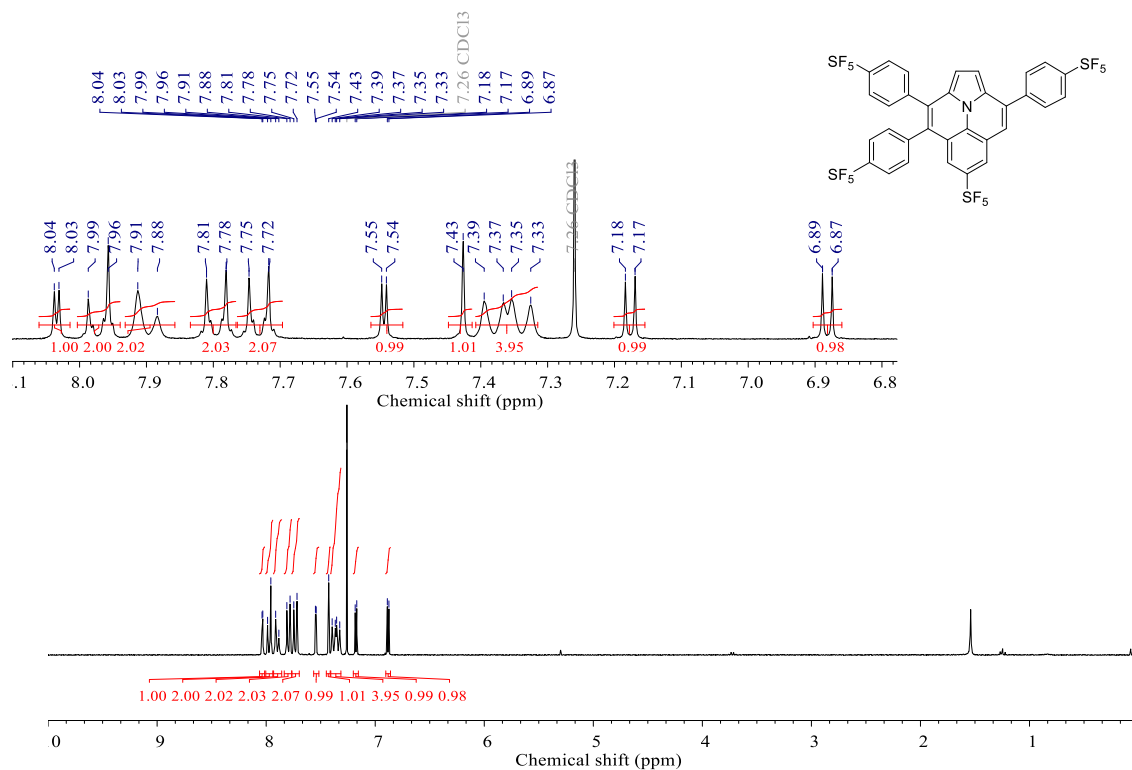


Figure A. 112 ¹H NMR spectrum of compound **U9**.

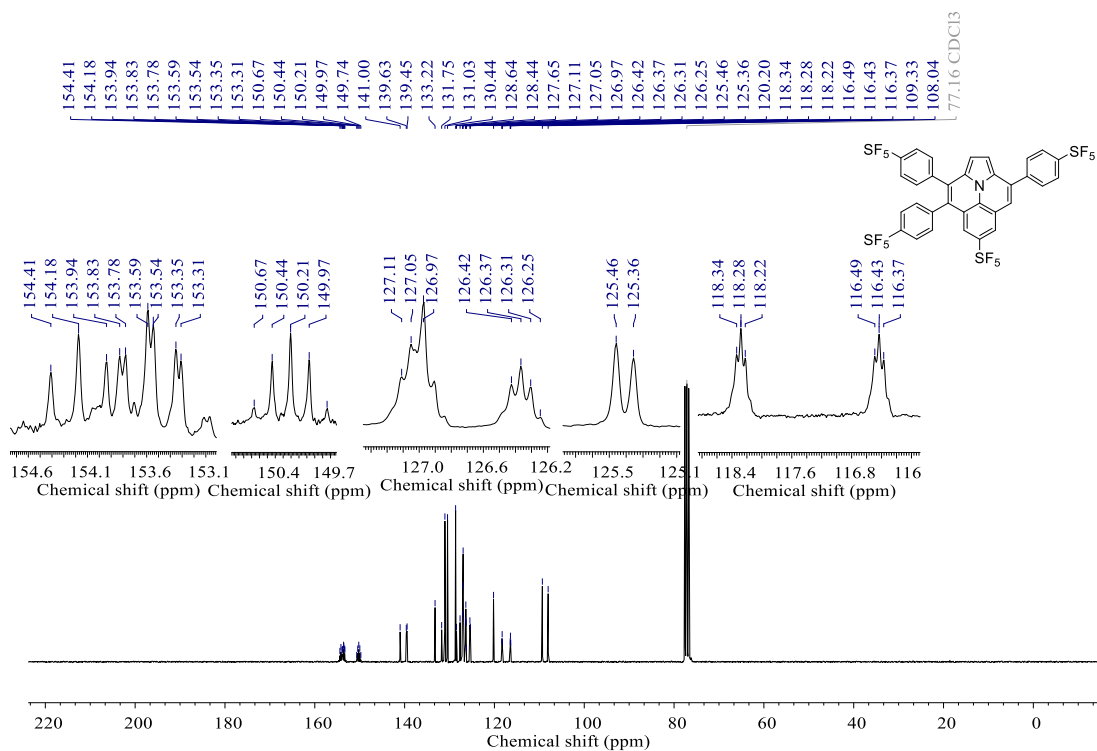


Figure A. 113 ^{13}C NMR spectrum of compound U9.

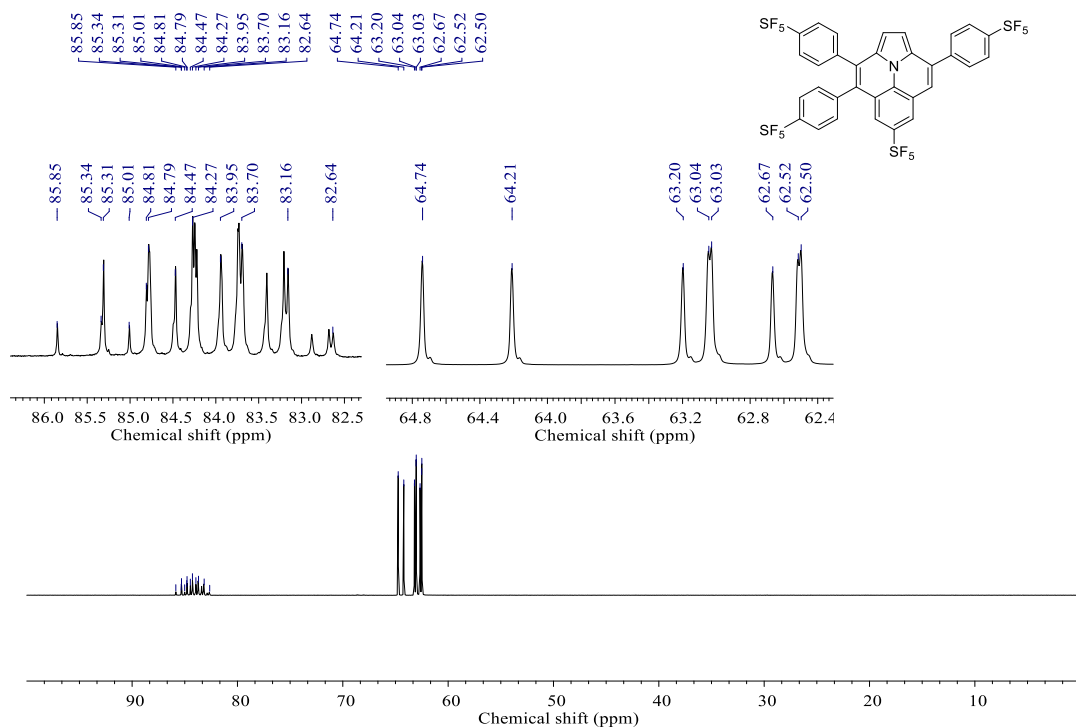


Figure A. 114 ^{19}F NMR spectrum of compound U9.

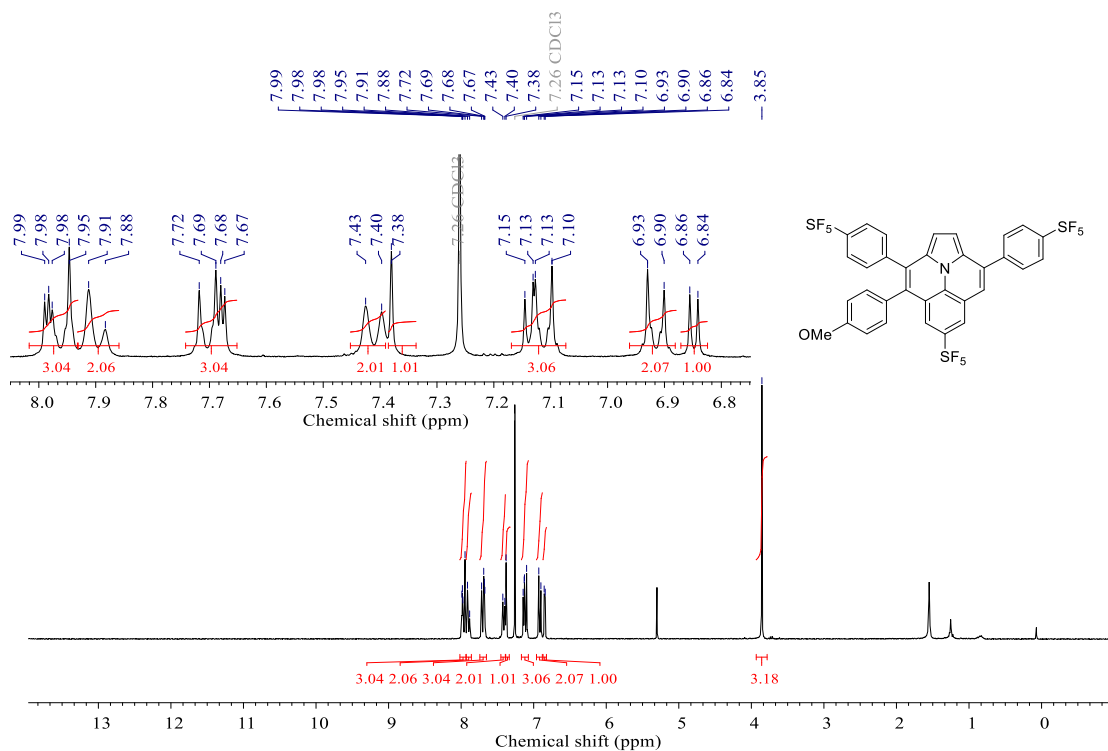


Figure A. 115 ¹H NMR spectrum of compound U10.

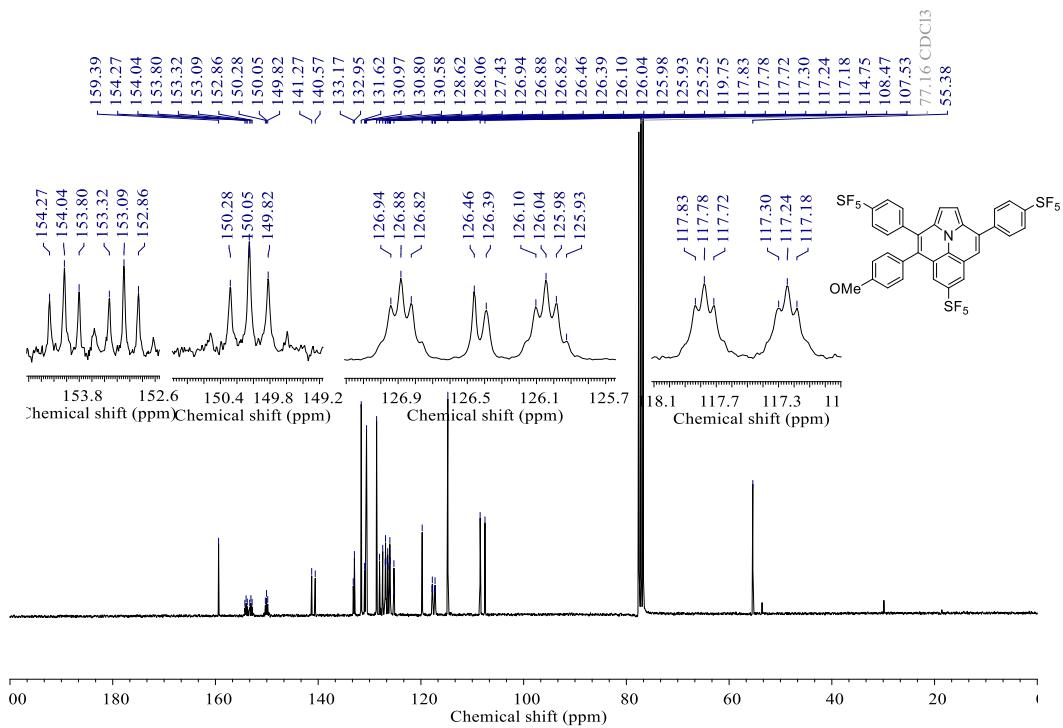


Figure A. 116 ¹³C NMR spectrum of compound U10.

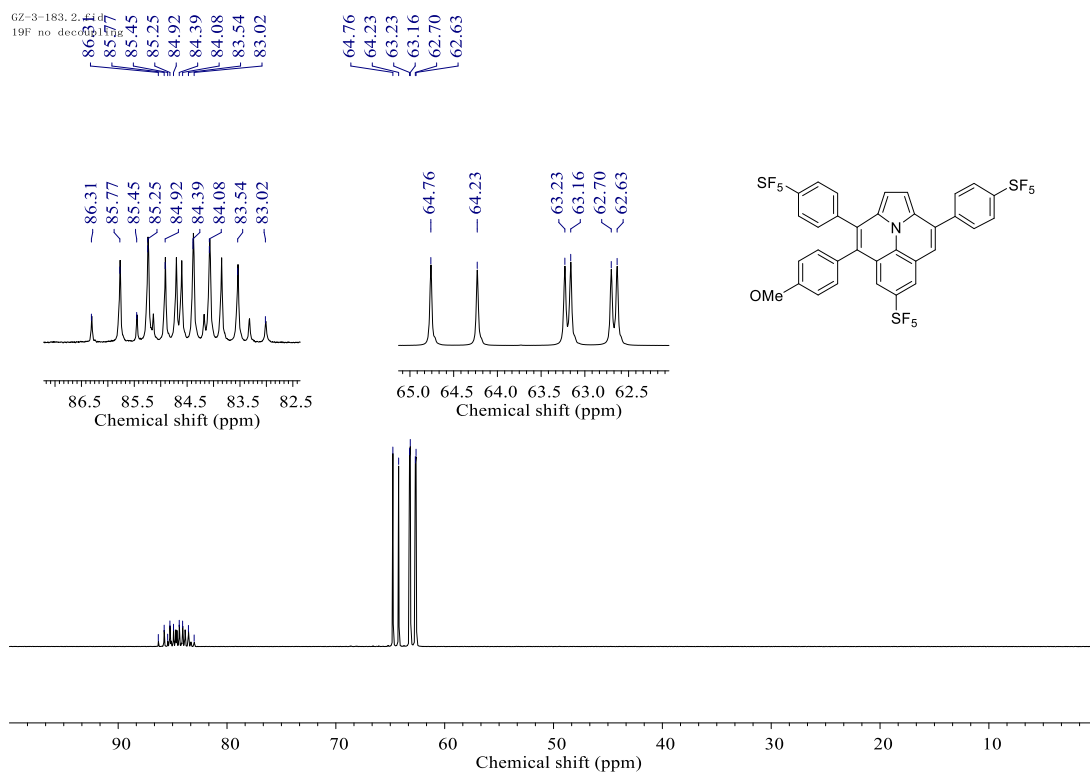


Figure A. 117 ¹⁹F NMR spectrum of compound **U10**.

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Crystal Structures and Triboluminescence Based on Trifluoromethyl and Pentafluorosulfanyl Substituted Asymmetric N-Phenyl Imide Compounds

Author: Hikaru Nakayama, Jun-ichi Nishida, Noriyuki Takada, et al

Publication: Chemistry of Materials

Publisher: American Chemical Society

Date: Feb 1, 2012

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