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TITRE DE LA THÈSE - TITLE OF THE THESIS

Design and Synthesis of Π-Conjugated Chromium and Boron Systems *en Route* to Fullerenes and Optical Materials

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Design and Synthesis of π-Conjugated Chromium and Boron Systems *en Route* to Fullerenes and Optical Materials

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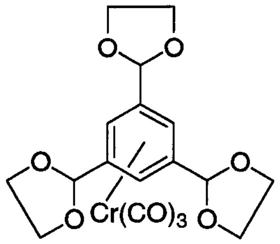
Abstract

Synthesis of several interrelated metallo-compounds is described. They are of intrinsic interest in their own right and were designed as intermediates and model studies for construction of various acetylene metal systems with interesting synthetic and optical potential. Synthesis of a triacetal and its η^6-tricarbonylchromium(0) complex **31** is described. Further transformations towards an eneyne derivative of **31** were complicated by the inherent instability of the complex towards oxidative decomplexation. Synthesis of a series of hexa-substituted η^6-tricarbonylchromium(0) complexes **39-47** (E = H, Me, $SiMe_3$, $SnMe_3$, Cl, Br, I, COH, CO_2Me) and **54-57** (E = H, Cl, Br, I) by di- or tri-lithiation of the parent compounds followed by quenching with a series of electrophiles is reported. Attempts to obtain alkynylated derivatives of the complexes by Sonagashira coupling reactions failed to produce the desired products. A novel tridurylborane **83**, incorporating three azulenyl substituents, was prepared and displayed unique photophysical properties with an absorption maximum nearly 80 nm longer than that of its precursor. A new class of heteroatom-containing triarylboranes **79** (R = OMe) and **96** (R = Me) were synthesized. Triarylborane **96** displayed broadened resonances in the ^{1}H NMR spectrum at room temperature and a low-temperature ^{1}H NMR study revealed that the borane existed as an approximate 10:1 ratio of two enantiomeric sets of conformational isomers. Triarylborane **96** was further extended by sequential Sonagashira coupling reactions to yield the highly fluorescent chromophore **110**, which exhibited intense and long-wave absorption and emission maxima.



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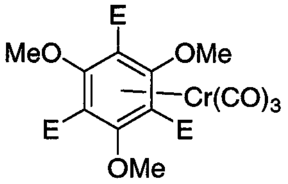

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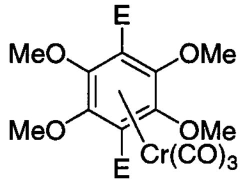

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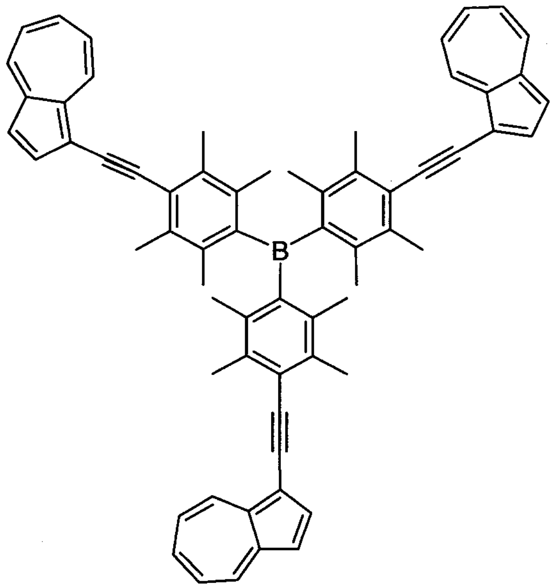

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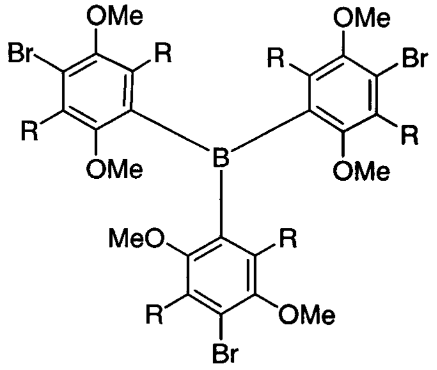
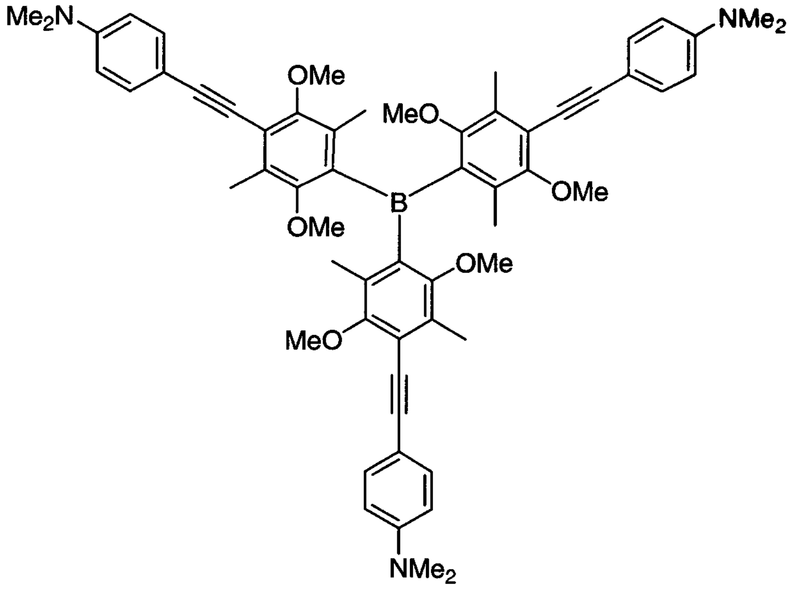


79 (R = OMe)
96 (R = Me)



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Finally, I would like to thank NSERC and the University of Ottawa for financial support.

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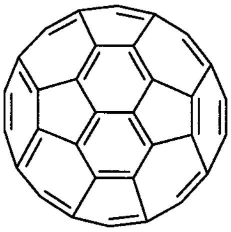
calcd	calculated
DMF	*N,N*-dimethylformamide
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DMSO	dimethyl sulfoxide
eq.	equivalent
EI (MS)	electron impact mass spectrometry
ES (MS)	electrospray mass spectrometry
FAB (MS)	fast atom bombardment mass spectrometry
GC-MS	gas chromatography-mass spectrometry
HOMO	highest occupied molecular orbital
HMPA	hexamethylphosphoramide
HRMS	high resolution mass spectrometry
IBX	1-hydroxy-1,2-benziodoxol-3(1H)-one
IR	infrared spectroscopy
J	coupling constant
LUMO	lowest unoccupied molecular orbital
m.p.	melting point
NIS	*N*-iodosuccinimide
NMR	Nuclear Magnetic Resonance
ppm	parts per million
R_f	retention factor
rt	room temperature
TBAF	tetrabutylammonium fluoride
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TMEDA	*N,N,N',N'*-tetramethylethylenediamine
TMS	trimethylsilyl
UV-VIS	ultraviolet-visible

Chapter 1: Aryl Chromium Tricarbonyl Compounds as Precursors to Fullerenes

Introduction

1.1 Fullerenes

Until the mid 1980's graphite and diamond were the only known allotropic forms of carbon. Kroto and Smalley[1] discovered the existence of a third allotrope comprised of 60 carbon atoms in 1985. The structure of this new elementary form of carbon was determined to be a closed shell polyhedron with 60 vertices, 32 faces, 12 pentagons and 20 hexagons (Figure 1). The shape of C_{60} resembles the geodesic dome design of the famous inventor and architect Buckminster Fuller and in fact, knowledge of these material constructs was instrumental in the elucidation of the structure. Accordingly, C_{60} was dubbed 'Buckminsterfullerene' or 'buckyball' for short and the generic name fullerene was applied to the entire family of C_n closed shell compounds.



1

Figure 1. Buckminsterfullerene (C_{60}).

Following the discovery of **1**, several preparative procedures based on graphite vaporization were developed.[2] This breakthrough fostered an avalanche of interest in the chemistry of fullerenes and hundreds of journal articles relating the properties and reactivity of buckyball followed. C_{60} also represents a formidable synthetic challenge

---

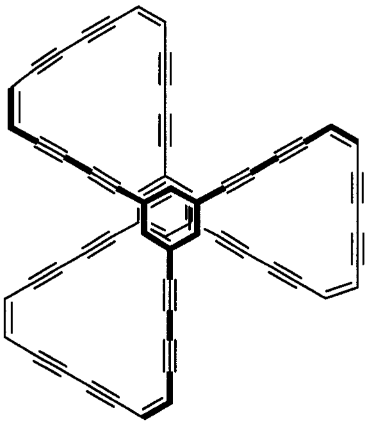
[1] Kroto, H. W.; Heath, J. R.; O'Brien, R. F.; Curl, R. E.; Smalley, E. *Nature* **1985**, *318*, 162.

[2] Haufler, R. E.; Conceicao, J.; Chibante, L. P.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O' Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.*, **1990**, *94*, 8634.

and several research groups have become interested in the development of a controlled laboratory synthesis of **1** and related compounds. At present, evaporation of graphite rods remains the only feasible route to gram quantities of **1**, and strategies toward a laboratory synthesis continue to be actively pursued.

1.1.2 Strained Cycloalkynes as Precursors to Fullerenes

A plausible synthetic route to buckyball is by way of a highly strained intermediate containing all of the requisite 60 carbon atoms. Such a structure can be envisioned to fall into a potential energy well driven by the thermodynamic stability of **1**. Strained cycloalkynes have become the precursor of choice for construction of C_{60} and related fullerenes. Rubin designed a $C_{60}H_{18}$ cyclophane (Figure 2) comprised of two 1,3,5 -trisubstituted benzene rings joined together by eneyne linkages.[3] Although the acetylenic cyclophane underwent coalescence to C_{60} in the gas phase, transformation of the double bonds to triple bonds was not possible in solution. The difficulty Rubin encountered in manipulating the central double bond of the eneyne linkage is not altogether surprising. Previous reports have illustrated the inert character of this double bond towards functionalization due to π orbital overlap with the adjacent triple bonds.[4]



2

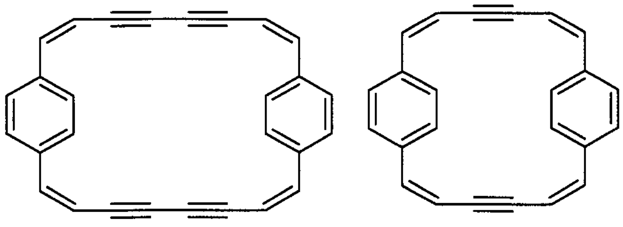
Figure 2. Rubin's acetylenic cyclophane, $C_{60}H_{18}$.

---

[3] Rubin, Y.; Parker, T. C.; Khan, S. I.; Holliman, C. L.; McElvany, S. W. *J. Am. Chem. Soc.* **1996**, *118*, 5308.

[4] Lu, Y. F.; Harwig, C. W.; Fallis, A. G. *Can. J. Chem.* **1995**, *73*, 2253.

A novel class of enediyne cyclophanes have been developed and synthesized in our laboratory (Figure 3).[5] In these structures, the olefinic component of the eneyne unit is situated in the more reactive benzylic position.



3 **4**

Figure 3. Eneyne Cyclophanes

The related, albeit more complex hexasubstituted eneyne cyclophane **6** (Figure 4) has the potential to serve as a precursor to C_{60}. In contrast to **2**, the reactive nature of the styrenyl double bonds of **6** should facilitate installation of the remaining acetylenes by a bromination-dehydrobromination protocol generating the highly strained intermediate **5**. Thermal rearrangement of this species should then give rise to the spherical C_{60} system. The key feature of this route is construction of the $C_{60}H_{24}$ species, **6**, by an intermolecular oxidative dimerization of the acetylenic substituents of the two C_{30} subunits in **7**. For this approach to be successful, the freely rotating enediyne 'arms' of the two subunits have to be oriented on the same face of the aromatic ring to reduce polymerization. It was postulated that such a requirement could be fulfilled by use of a labile organometallic group that would occupy one face of the aromatic ring and control the facial orientation of the substituent arms to facilitate intermolecular coupling. The chromium tricarbonyl moiety appears to be the most promising candidate due to its robust nature in (η^6-arene)$Cr(CO)_3$ complexes as well as the ease with which the arene can be released from complexation following reaction. A wide variety of arene complexes of chromium are known and the chemistry of these organometallic compounds has been extensively developed, particularly in relation to their applicability in synthetic organic chemistry.

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[5] Romero, M. A.; Fallis, A. G. *Tetrahedron Lett.* **1994**, *35*, 471.

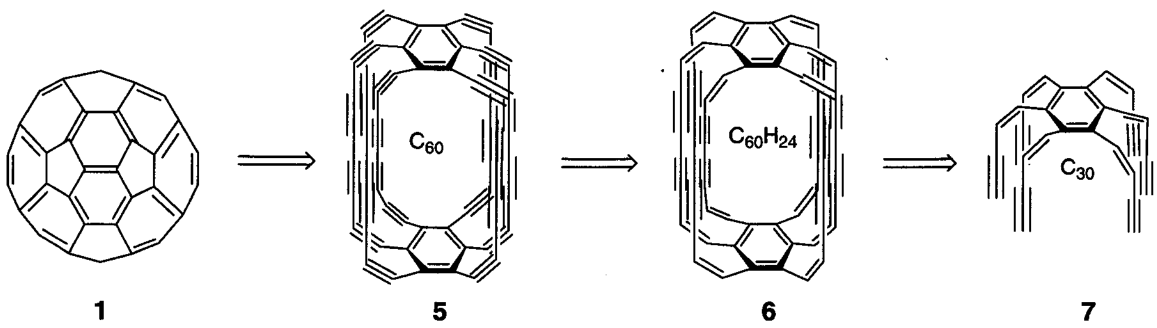


Figure 4. Retrosynthetic plan for synthesis of C_{60} (Buckminsterfullerene).

1.2 η^6-Arene Chromium Tricarbonyl Complexes

1.2.1 General Characteristics

The arene ligand in arene chromium tricarbonyl compounds is bound to the chromium in the six-electron, η^6-form. η represents the *hapticity* of the arene and is defined as the number of atoms in the ligand bound to the metal.

Chromium tricarbonyl complexes are bright yellow, air-stable, crystalline solids. Although they are stable to air oxidation in the solid state, solutions of the complexes are moderately air-sensitive. Decomposition in solution is an autocatalytic process and formation of the green/brown precipitates of Cr_2O_3 progresses until the metal oxide is removed by filtration. While arene chromium solutions are best handled under inert atmosphere conditions, manipulation in the open atmosphere is possible when done expediently.

Binding the chromium tricarbonyl moiety to an arene significantly alters the spectroscopic and physical properties of the ring.[6] Binding is accompanied by a dramatic 1-2.5 ppm upfield shift of the aryl proton resonances in the ^1H NMR spectrum as well as a 20-40 ppm shift of the metal bound carbon atoms to higher field in the ^{13}C NMR spectrum. The IR spectra of the complexes show two characteristic carbonyl stretching frequencies between 1940-2000 and 1850-1940 cm^{-1} and stepwise loss of the CO ligands is usually detected in the mass spectrum.

---

[6] Gibson, E. S. *Transition Metals in Organic Synthesis: A Practical Approach*; Gibson, S. E., Oxford University Press: Oxford, 1997.

Chromium tricarbonyl bound aryl rings also exhibit markedly different chemical reactivity compared to their uncomplexed counterparts (Figure 5).[7] The tricarbonyl moiety has a net electron withdrawing effect on the arene ring, which makes it susceptible to nucleophilic attack. This depletion of electron density in the aromatic ring also facilitates deprotonation of both the aryl ring protons as well as those in the benzylic position. Aside from altering the chemical reactivity of the arene, the $Cr(CO)_3$ group is a steric encumbrance, which can be used to block one face of the ring and direct incoming reagents to the opposite face.

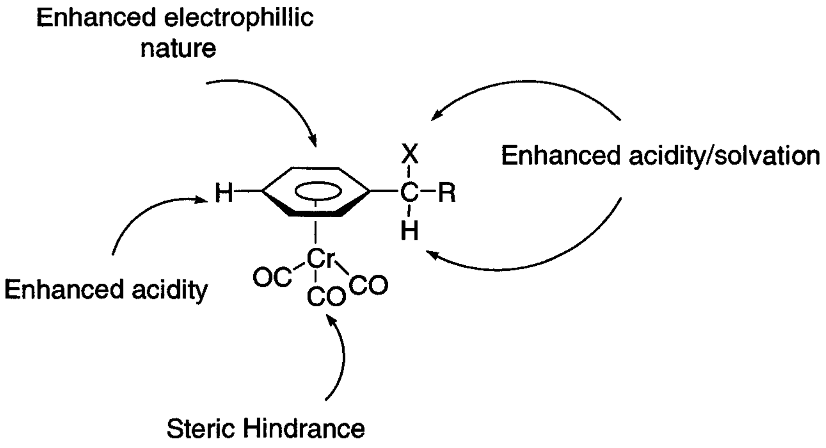


Figure 5. Altered reactivity of arene chromium tricarbonyl complexes

1.2.2 Synthesis

A number of methods exist for the synthesis of arene chromium tricarbonyl complexes.[8] Generally, only two methods are widely utilized and include direct thermal complexation and indirect formation by functional group manipulation. The most common and straight forward thermal method for preparation of η^6-arene chromium tricarbonyl compounds is by heating a high boiling ethereal solution of the arene and $Cr(CO)_6$.[9] A mixture of dibutyl ether/THF (10:1) is the most effective and routinely sited

---

[7] Hegadus, Louis, S. *Transition Metals in the Synthesis of Complex Organic Molecules;* University Science Books: Mill Valley, Calif., 1994.

[8] Watts. W. E. In *Comprehensive Organometallic Chemistry;* Pergamon Press: Oxford, U.K., 1982; Vol.8, 1013.

[9] Mahaffy, C.A.L.; Pauson, P.L. *Inorg. Synth.* **1979**, *19*, 154.

solvent system for thermal complexation reported in the literature (Scheme 1).[9] Preformed amine complexes of the metal such as $Cr(CO)_3(NH_3)_3$[10] and $Cr(CO)_3(CH_3CN)_3$[11] can also be used in direct complexation. Although these complexes require milder reaction conditions, synthesis of the reagents is not trivial and it is more convenient to use the commercially available $Cr(CO)_6$ (Aldrich).

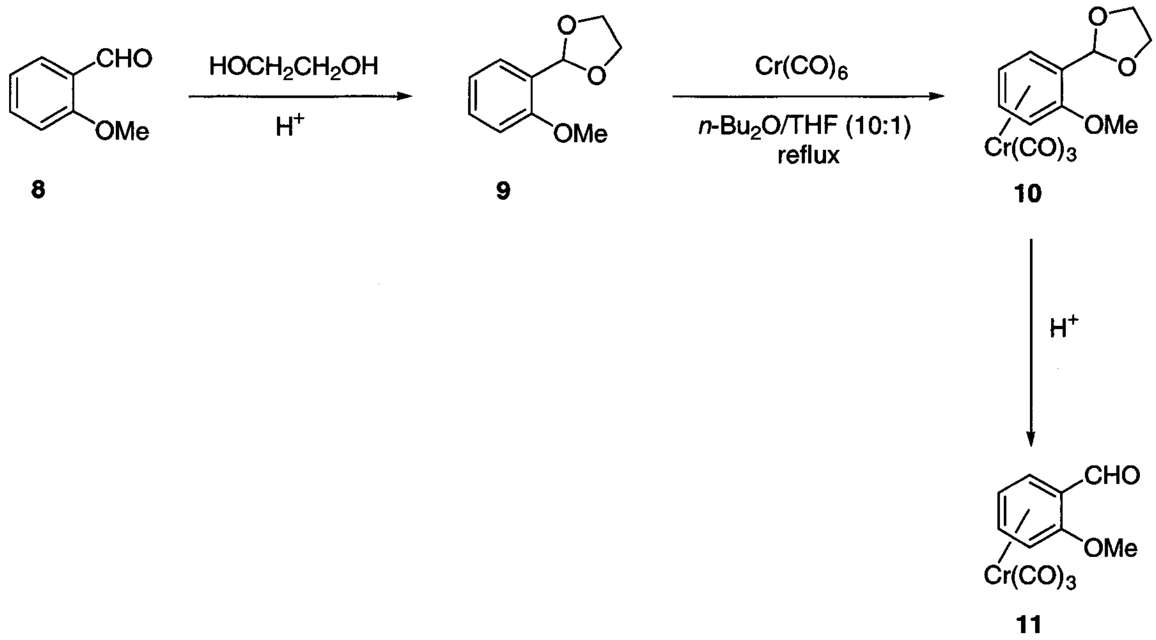
$$\text{Arene} + Cr(CO)_6 \xrightarrow{n\text{-}Bu_2O/\ THF\ (10:1)} (\text{Arene})Cr(CO)_3 + 3CO$$

Scheme 1. Direct thermal complexation of an arene ligand

Only certain functional groups are tolerated on the arene ring during direct thermal complexation. Electron-donating groups (OH, OR, NR_2, R, etc) accelerate complex formation, while electron-withdrawing substituents (X, CHO, CO_2H, C≡C, etc.) impede it.[7] In order to obtain complexes of arenes bearing electron-withdrawing functionalities, the metal carbonyl can first be bound to an arene ring containing electron-donating or neutral substituents, which can then undergo further synthetic manipulation. For example, a ketone or aldehyde function can be protected as an acetal prior to complexation of the chromium tricarbonyl moiety (Scheme 2).[12] Subsequent hydrolysis yields the otherwise inaccessible aryl chromium tricarbonyl compound.

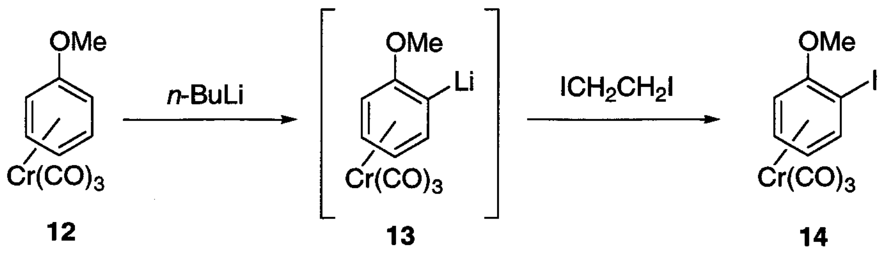
---

[10] Morley, J. A.; Woolsey, N. F. *J. Org. Chem.* **1992**, *57*, 6487.
[11] Moran, M.; Cuadrado, I.; Pascual, M. C.; Casado, C. M.; Losado, J. *Organometallics* **1992**, *11*, 1210.
[12] Bromley, L. A.; Davies, S. G.; Goodfellow, C. L. *Tetrahedron: Asymmetry* **1991**, *2*, 139.



Scheme 2. ***Indirect synthesis of a chromium tricarbonyl- complexed benzaldehyde***

Alternatively, electron-withdrawing substituents can be installed directly onto the ring following formation of the complex. The special reactivity of the complexed arene can be exploited in this situation and substituents can be introduced via a number of methods including nucleophilic substitution, electrophilic quenching of a carbanion, and palladium-catalyzed cross-coupling. For instance, halogenated chromium tricarbonyl complexes are difficult to prepare directly by thermal reaction due to their electron-withdrawing character. Compounds of this nature are frequently prepared by electrophilic quenching of an *in-situ*-generated carbanion of the arene complex (Scheme 3).[13]



Scheme 3. Indirect synthesis of a chromium tricarbonyl- complexed aryl halide

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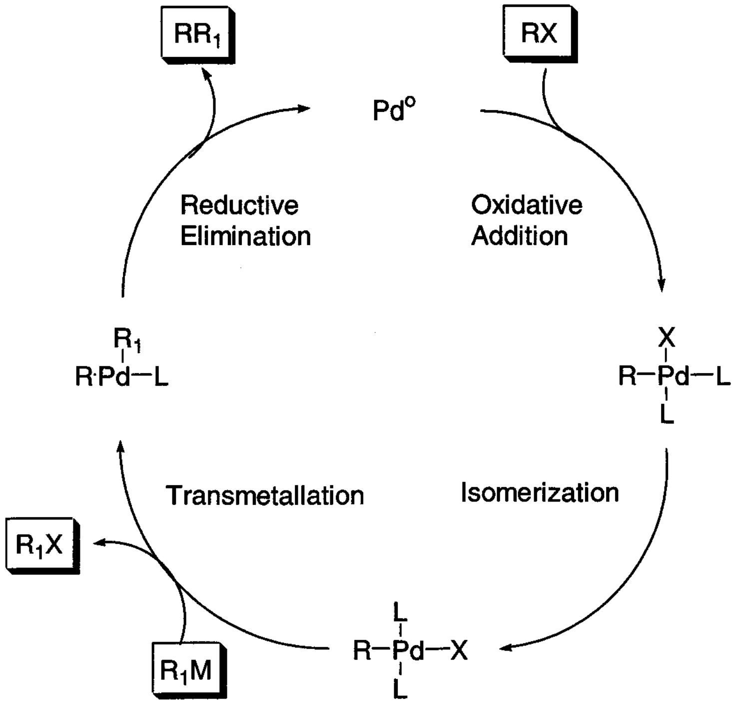
[13] Sebhat, I. K.; Tan, Y-L.; Widdowson, D. A.; Wilhelm, R.; White, A. J. P.; Williams, D.J. *Tetrahedron* **2000**, *56*, 6121.

The $Cr(CO)_3$ group can be removed by a variety of mild oxidative procedures including treatment with oxygen, light, I_2, $FeCl_3$, or $(NH_4)_2Ce(NO_3)_6$ (CAN). Consequently, the chromium tricarbonyl group is sensitive to oxidative decomplexation and usually will not withstand oxidation of the arene substituents.

1.2.3 Palladium-Catalyzed Cross-Coupling Reactions of Arene Chromium Tricarbonyl Complexes

Palladium is used extensively in organic synthesis as a catalyst in formation of carbon-carbon bonds. Connection of Csp^2-Csp^2, and Csp-Csp^2 carbon centers is catalyzed by Pd(0). A Pd(0) complex can be utilized directly in the cross-coupling reaction or the active catalytic species can be generated *in situ* by reduction of a Pd(II) salt. Generally speaking, the palladium catalytic cycle is comprised of four parts: oxidative addition, isomerization, transmetallation, and reductive elimination (Scheme 4).



Scheme 4. The catalytic cycle of palladium catalyzed cross-coupling reactions

Csp^2-Csp^2 bond formation involves an alkenyl or aryl halide and an organometallic derivative of an alkene or arene. Organozincates,[14] -stannanes,[15] and

---

[14] Reviews: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.; Erdik, E. *Tetrahedron* **1992**, *48*, 9577.

–boranes[16] are particularly effective as the organometallic component in the cross-coupling and reactions involving these metals/metalloids are called the Negishi, Stille and Suzuki couplings, respectively, after the chemists who discovered their application in this context. *Csp-Csp*^{2} bond formation is catalyzed by palladium in the presence of a co-catalyst such as copper iodide and an organic base. This type of reaction most often involves coupling of an aryl or alkenyl halide with a terminal alkyne and is named after its originator, Sonagashira (Figure 6).[17] Both Pd(0) complexes ($Pd(PPh_3)_4$) and Pd(II) salts ($Pd(PPh_3)_2Cl_2$) can be utilized in the Sonagashira coupling, although the latter is more commonly employed due to its lower cost and increased stability. When a Pd(II) salt is used, the active Pd(0) catalyst is generated by homocoupling of two acetylene units. The first step of the catalytic cycle is oxidative insertion of Pd(0) into the carbon-halide bond and is accelerated by electron withdrawing groups on the organic halide. Copper iodide and base are needed in the next step to generate a copper acetylide, which undergoes transmetallation with the organopalladium halide to form a dialkylpalladium species, followed by reductive elimination to form the new carbon-carbon bond. The most commonly employed bases include NEt_3 and $HNEt_2$ although a wide variety of amines are effective. A co-solvent such as THF or DMF is often utilized in the coupling reaction as well.

Oxidative insertion of Pd(0) into the vinyl or aryl halide carbon-halide bond is the rate-determining step of the catalytic cycle and the rate of reactivity decreases as follows: vinyl iodide ≈ vinyl bromide > aryl iodide > vinyl chloride >> aryl bromide >>> aryl chloride. Aryl iodides generally undergo facile reaction at room temperature while aryl bromides require more severe conditions such as heating. Aryl chlorides are essentially inert under normal coupling conditions.

---

[15] Reviews: Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178.; Suzuki, A. *Pure Appl. Chem.* **1985**, *66*, 213.
[16] Reviews: Stille, J. K. *Angew. Chem. Int. Ed.* **1986**, *25*, 508.; Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.
[17] (a) Sonagashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975,** 4467. (b) Tohda, Y.; Sonagashira, K.; Hagihara, N. *Synthesis* **1977**, 777.

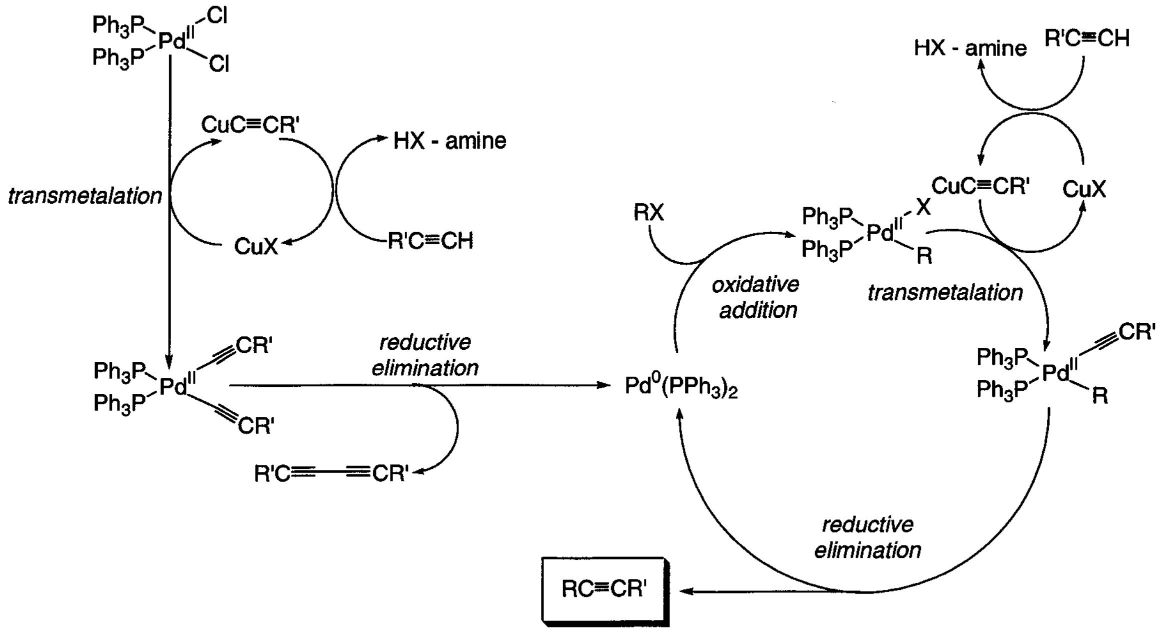


Figure 6. The catalytic cycle of the Sonagashira coupling

Aryl chlorides are activated towards oxidative addition by coordination of the strongly electron-withdrawing $Cr(CO)_3$ moiety. Oxidative addition is analogous to nucleophilic substitution in this respect. Chloroaryl chromium tricarbonyl complexes readily undergo palladium catalyzed coupling with all of the most common organometallic derivatives of alkenes, alkynes and arenes. Complexed aryl chlorides, for example, have been used in the Stille,[18] Negishi,[19] Suzuki,[20] and Sonagashira[21] reactions.

---

[18] (a) Scott, W.J. *Chem. Commun.* **1987**, 1755. (b) Clough, J.M.; Mann, I.S.; Widdowson, D.A. *Tetrahedron Lett.* **1987**, *28*, 2645.

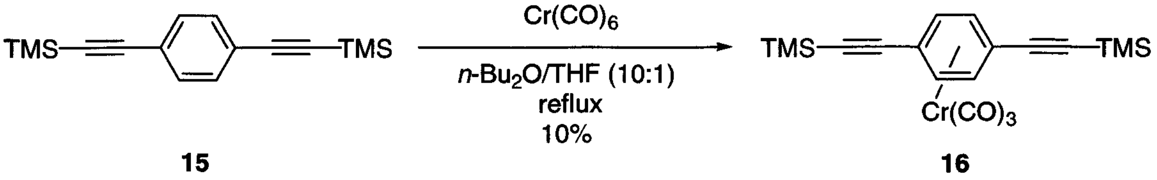
[19] Uemura, M.; Nishimura, H.; Kamikawa, K.; Nakayama, K.; Hayashi, Y. *Tetrahedron Lett*, **1994**, *35*, 1909.

[20] (a) Uemura, M.; Kamikawa, K. *J. Chem. Soc., Chem. Commun.* **1994**, 269. (b) Uemura, M.; Daimon, A.; Yoshinori, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1943.

[21] (a) Muller, T.J.J; Lindner, H, J. *Chem. Ber.* **1996**, *129*, 607. (b) Muller, T.J.J.; Ansorge, M.; Polborn, K. *J. Organomet. Chem.* **1999**, *578*, 252.

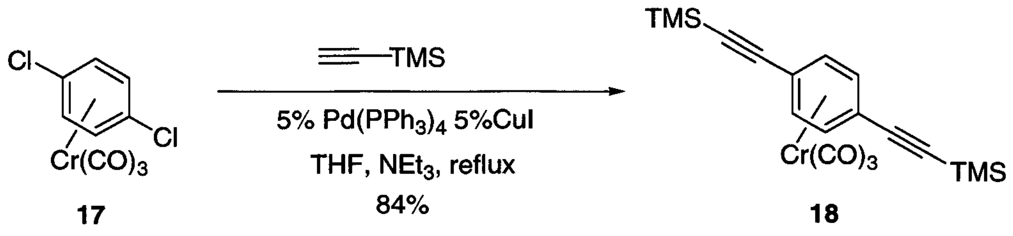
1.2.4 Alkynyl Aryl Chromium Tricarbonyl Complexes

Only certain functional groups are tolerated on the arene ring during direct thermal complexation of the chromium tricarbonyl group. Although we have seen that a wide variety of functional groups can be introduced following complexation of the metal to an appropriate precursor, this method requires a certain amount of planning. For our purposes, the arene ring of the complex must contain unsaturated side chains capable of being transformed into the eneyne linkages of **7** (Figure 4). A survey of the literature revealed that both vinyl and alkynyl substituents, which are electron- withdrawing, impede direct thermal complexation. A representative example is shown in Scheme 5, where the dialkynylated complex, **16**, was obtained in only 10% yield.[21]



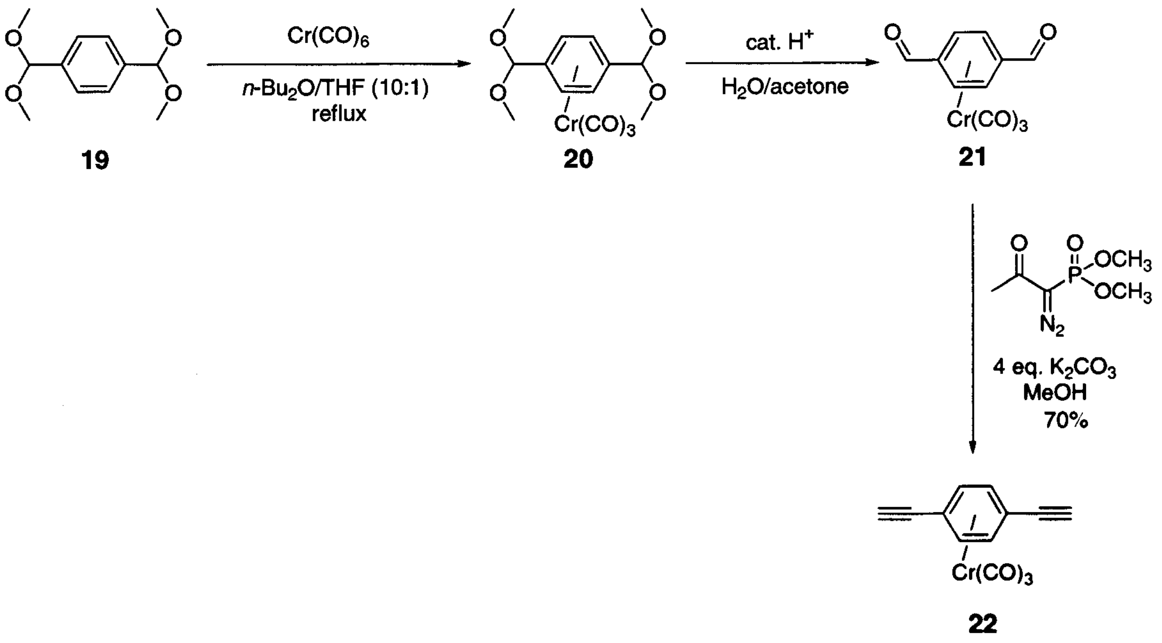
Scheme 5. Direct thermal complexation of a dialkynylated arene

As mentioned, an alternative route to alkynylated arene complexes is by Sonagashira coupling between chloroaryl chromium tricarbonyl complexes and terminal alkynes. Muller *et al.* used this method to prepare the dialkynylated arene complex shown in Scheme 6.[21] This route is flawed, however, as the chloride substituents in **17** are also electron-withdrawing and the 1,4-dichlorobenzene complex itself was obtained in only 10% yield by direct thermal complexation.



Scheme 6. Sonagashira coupling of a dichloro benzene complex

Muller *et al.*[21] acknowledged this limitation and opted to prepare the deprotected dialkynylated complex by making use of the Horner-Emmons-Wadsworth type conversion of aldehydes to acetylenes with Ohira's[22] reagent (Scheme 7). Thus, bisacetal complex, **20**, was prepared in high yield by thermal complexation and subsequently hydrolyzed to yield dialdehyde **21**, which was converted to the corresponding dialkyne **22** with Ohira's reagent.



Scheme 7. Horner-Emmons-Wadsworth type synthesis of a dialkynylated complex

Of the three approaches mentioned, this last method is the most feasible route to alkynylated aryl chromium tricarbonyl compounds.

1.3 Research Objective for the Synthesis of Polyalkynylated Aryl Chromium Tricarbonyl Complexes

1.3.1 Retrosynthetic Plan

Ultimately, we sought to utilize the chromium tricarbonyl group as a steric control element in the oxidative dimerization of two C_{30} monomers (**24**) in a potential route to C_{60} (Figure 7). As a model, the more simplistic tri-substituted eneyne monomer, **26**, was chosen to first establish the validity of our approach. In the retrosynthetic plan (Figure 8), the oxidative dimerization precursor, **26**, is derived from triacetylene **29**, which is itself prepared by a Horner-Emmons-Wadsworth transformation of trialdehyde **30** in a

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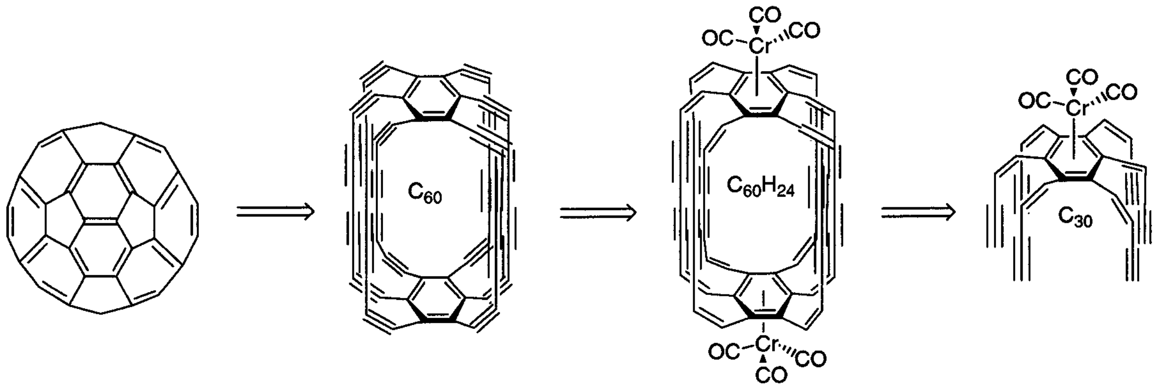
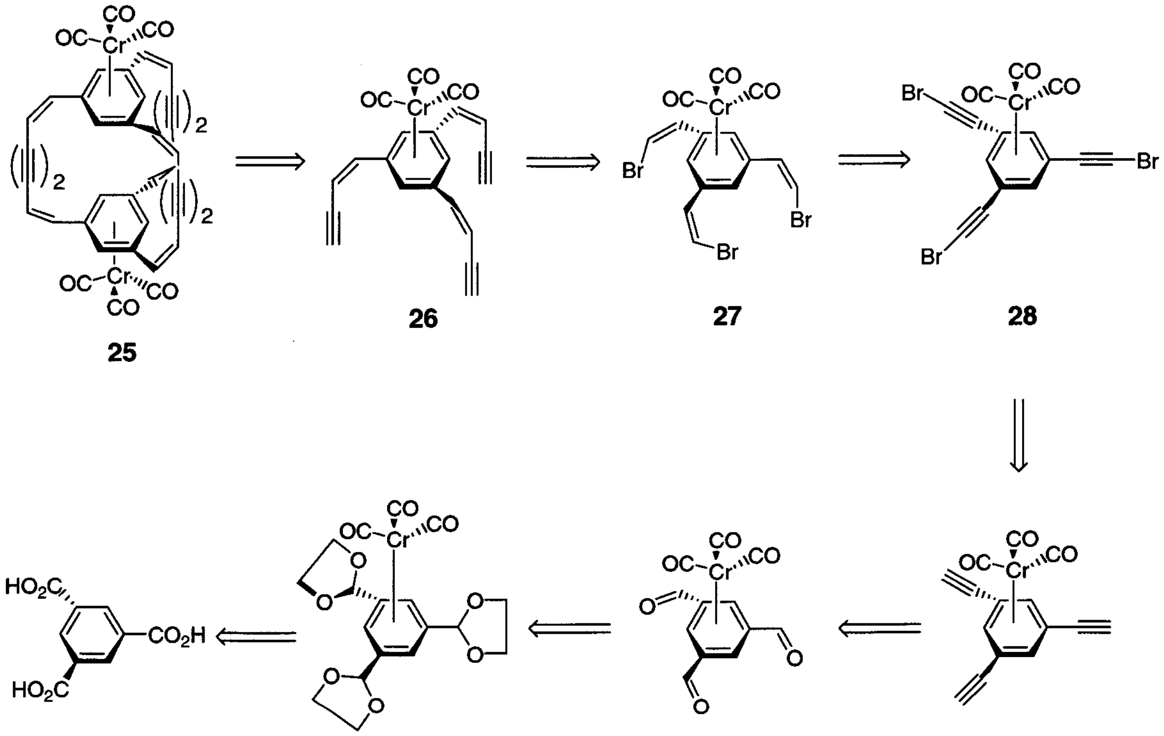
[22] Ohira, S. *Synth. Commun.* **1989**, *3*, 561.

strategy analogous to that presented previously in Scheme 7. This route necessitates the protection of the three aldehyde functionalities as their dioxolane acetals prior to complexation of the chromium tricarbonyl group. The uncomplexed triacetal precursor is readily prepared from commercially available benzene-1,3,5-tricarboxylic acid.



1 **5** **23** **24**

Figure 7. Retrosynthetic plan for synthesis of C_{60} (Buckminsterfullerene)



25 **26** **27** **28**

32 **31** **30** **29**

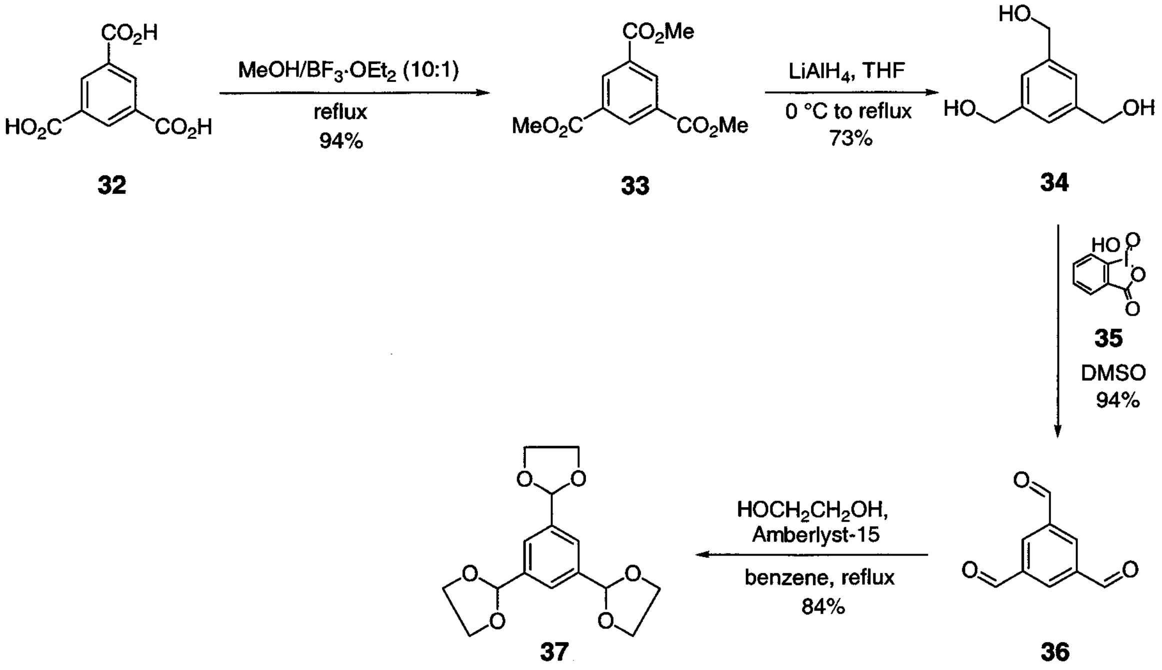
Figure 8. Retrosynthetic plan for synthesis of model dimer 25

Results and Discussion

1.4 Synthesis of the Chromium Tricarbonyl-Complexed Triacetal 31

1.4.1 Preparation of the Triacetal

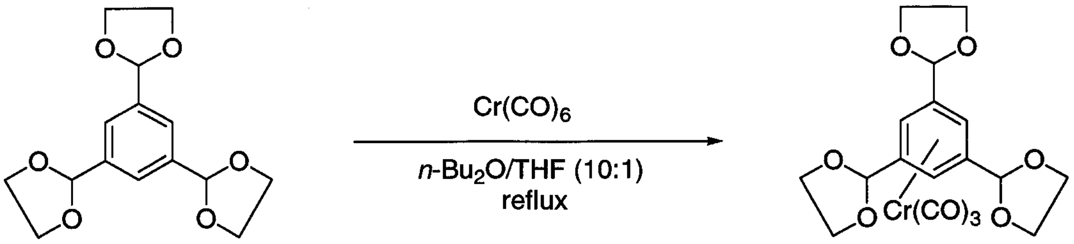
Synthesis of triacetal **37** is outlined in Scheme 8 below. Commercially available triacid **32** was converted to triester **33** to ease the purification of the reduction product in the following step. Incidentally, the triester is also commercially available at a considerably higher cost. Triester **33** was reduced to triol **34** with lithium aluminum hydride. Attempts to stop the reduction at the trialdehyde failed. Triol **34** was oxidized cleanly to the trialdehyde in only a few minutes with IBX (**35**). Protection of the three aldehyde functionalities in **36** as their dioxolane acetals afforded the precursor **37** for complexation of the chromium tricarbonyl group.



Scheme 8. Synthesis of the triacetal precursor to complex 31

1.4.2 Complexation of Chromium Tricarbonyl

Acetal **37** was subjected to thermolysis under standard conditions in the presence of $Cr(CO)_6$ in a 10:1 mixture of *n*-dibutyl ether and THF (Scheme 9). Unfortunately, a fine brown precipitate indicative of decomposition of the complex began to form after only 20 hours of reflux. Filtration and work-up yielded an inseparable mixture of the starting material and the metal-complexed acetal.



37 **31**

Scheme 9. Synthesis of the Cr(CO)$_3$-complexed acetal 31

The air-sensitivity of the chromium complexes quickly became evident following this preliminary reaction. Although solid arene chromium tricarbonyl complexes are stable to air oxidation, solutions of the complexes decompose rather rapidly under normal synthetic conditions. Acetal **31**, for example, starts to decompose after several minutes in an ordinary NMR tube. For this reason, column chromatography of the complexes and other manipulations that required extended periods of air exposure were avoided. Thus, the mixture of **37** and **31** was not submitted to rigorous separation by column chromatography or otherwise.

1.5 Attempted Synthesis of Alkynylated Aryl Chromium Tricarbonyl Complexes by Sonagashira Coupling

In light of the difficulty binding chromium tricarbonyl efficiently to triacetal **37**, a new strategy employing electron-donating methoxy groups was adopted. As mentioned, electron-donating substituents on an aryl ring ease the complexation of the metal carbonyl and the complexes are considerably more stable towards oxidative decomplexation. A commercially available, symmetrically substituted compound, 1,3,5-trimethoxybenzene, was chosen as a substrate. The intention was to functionalize this substrate at the remaining three positions by exploiting the enhanced acidity of the aryl protons in a lithiation-electrophilic quench strategy. Ultimately, cleavage of the methoxy groups could be achieved by nucleophilic hydride displacement.[23]

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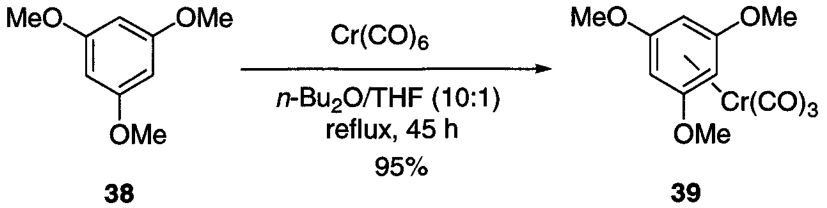
[23] Djukic, J-P.; Rose-Munch, F.; Rose, E.; Simon, F. *Organometallics* **1995**, *14*, 2027.

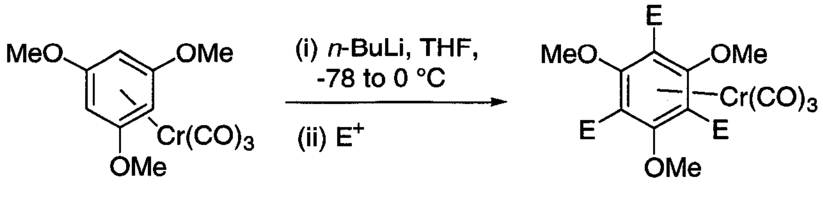
Complexation of the chromium tricarbonyl group under standard conditions was facile as expected and yielded the desired product, **39**, in excellent yield.



38 **39**

Scheme 10. Thermal complexation of $Cr(CO)_3$ to 1,3,5-trimethoxybenzene

The efficacy of the subsequent three-fold lithiation and electrophilic quench was preliminarily investigated with methyl iodide. The remaining electrophilic quenches shown in Table 1 were chosen to install functionalities which could be synthetically useful precursors to unsaturated linkages. The best results were obtained when a slight excess of *n*-BuLi (3.3 eq.) was added to a THF solution of **39** at –78 °C and stirred at 0 °C for 15 minutes before addition of the electrophile. Stirring of **39** in the presence of the base for excessive periods of time at –78 °C failed to yield satisfactory results. It was also necessary to warm the solution to 0 °C for a period following addition of the electrophile to ensure complete reaction of the anion. Although these conditions yielded reasonably pure compound following work-up, the compounds could be further purified by column chromatography with no appreciable decrease in yield.



39 **40-47**

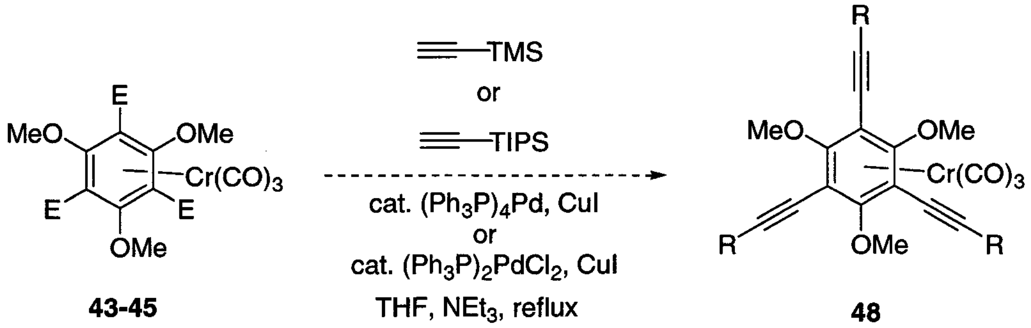
Table 1. Deprotonation-electrophilic quench of complex 39

No.	Reagent	E	% Yield
40	MeI	Me–	100
41	Me_3SiCl	Me_3Si–	87
42	Me_3SnCl	Me_3Sn–	90
43	Cl_3CCCl_3	Cl–	100
44	$BrCF_2CF_2Br$	Br–	56
45	I_2	I–	not isolated
46	DMF	CHO	not isolated
47	$ClCO_2Et$	CO_2Et	100

It was our intention to restrict the choice of electrophiles to those which could serve as useful substrates for further synthetic manipulations. Thus, aryl halides **43-45** could serve as useful palladium coupling partners, while the aldehyde function of **46** could be elaborated by a Horner-Emmons-Wadsworth type transformation.

Unfortunately, Sonagashira coupling of compounds **43-45** (Scheme 11) with silylacetylenes yielded complicated mixtures of $Cr(CO)_3$-complexed and uncomplexed products. Attempts to separate and characterize the products failed, largely due to the impracticality of submitting these air-sensitive compounds to column chromatography for a complex separation. Proton NMR of the crude reaction mixtures, however, showed resonances in the 4-6.5 ppm region indicative of complexed and uncomplexed dehalogenated compounds arising from protodehalogenation. Compound **45** was particularly air-sensitive and was used directly in the coupling reaction without isolation.

In view of the success of the lithiation-electrophilic quench strategy in triply functionalizing **39**, it was decided to abandon the palladium catalyzed coupling strategy and utilize the former method to generate the desired unsaturated moieties. This too, however, turned out to be quite challenging. Lithiation of **39** followed by quenching with anhydrous DMF yielded a bright orange compound, which was very unstable and underwent decomplexation of the $Cr(CO)_3$ group, even under strictly inert conditions. Characterization of the product by proton NMR was unsuccessful as attempts to properly shim the magnet failed and resulted in excessively broadened lines. The instability of **46** was initially attributed to steric congestion in the hexa-substituted product. However, one further experiment revealed a similar compound, triester **47**, could be prepared and isolated in high yield without $Cr(CO)_3$ decomplexation. Thus, the nature of the instability of **46** is likely electronic. The ester substituents of **47** are less electron-withdrawing than the aldehyde functionalities of **46** and presumably do not compete as strongly with the $Cr(CO)_3$ group for electron density.



Scheme 11. Attempted Sonagashira coupling of compounds 43-45

At this point, the initial goal of incorporating chromium tricarbonyl into synthesis of a fullerene precursor was amended to coincide with an ongoing interest in our laboratory in the chemistry of acetylenic cyclophanes. A new target closely resembling 1,3,5-trimethoxybenzene was chosen as a potential building block in construction of cyclophane **49**. Thus, following complexation of chromium tricarbonyl, 1,2,4,5-tetramethoxybenzene would be suitably functionalized and used as a key intermediate in construction of the cyclophane as outlined in Figure 9.

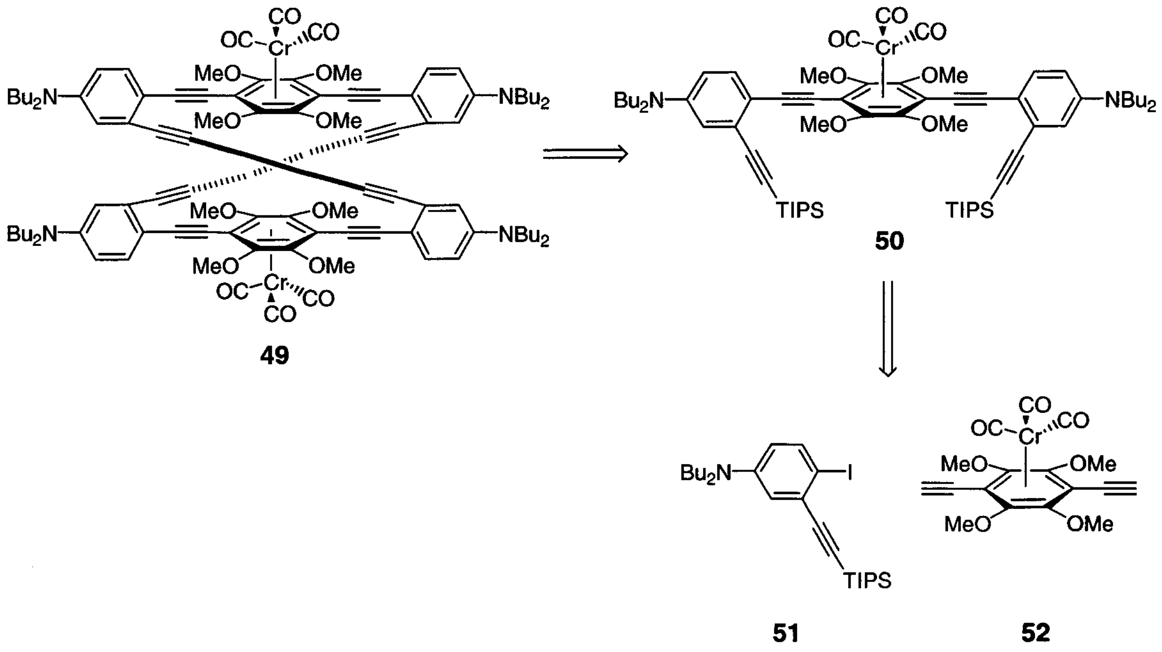
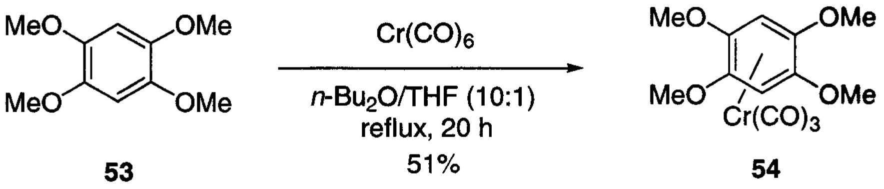
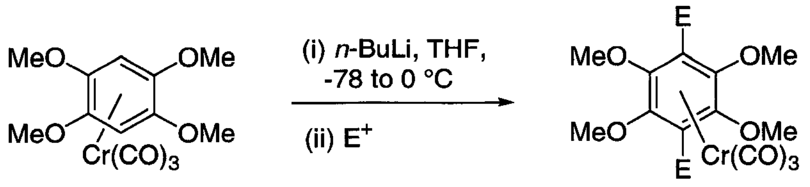


Figure 9. Retrosynthetic plan for construction of cyclophane 49 with an electron-rich aryl chromium tricarbonyl complex

Standard thermolysis of **53** in the presence of $Cr(CO)_6$ yielded complex **54**. The reaction conditions were not optimized and extending the reaction time should improve the yield considerably as thermal complexation generally requires heating in excess of 20 hours.



Scheme 12. Thermal complexation of $Cr(CO)_3$ to 1,2,4,5-tetramethoxybenzene



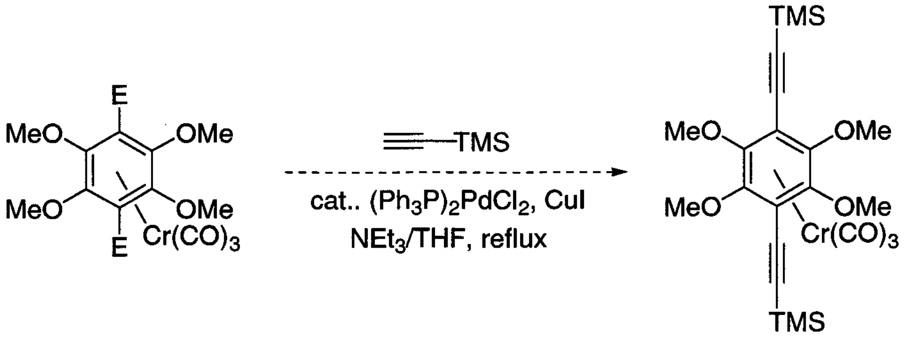
54 **55-57**

Table 2. Deprotonation-electrophilic quench of compound 54

No.	Reagent	E	% Yield
55	Cl_3CCl_3	Cl–	100
56	$BrCF_2CF_2Br$	Br–	96
57	I_2	I–	92

Aryl halides **55-57** were obtained in excellent yield from di-lithiation of compound **54** with *n*-BuLi and subsequent quenching with the electrophiles presented in Table 2.

Compounds **56** and **57** were subsequently exposed to trimethylsilylacetylene under Sonagashira coupling conditions (Scheme 13). Unfortunately, the coupling reactions produced complex mixtures of products, which could not be separated.



56, 57 **58**

Scheme 13. Attempted Sonagashira coupling of compounds 56 and 57

Conclusions

The ultimate goal of this research project was to investigate the efficacy of utilizing the $Cr(CO)_3$ moiety to establish a geometry among the eneyne substituent arms of **26** that would be conducive to intermolecular dimerization. It was proposed that the $Cr(CO)_3$ moiety could be utilized to occupy one face of the aromatic ring and force all three eneyne substituents to assume a position on the opposite face. Such an arrangement would be expected to reduce polymerization and enhance intermolecular dimerization of two **26** subunits. If successful, this approach could be extended to the intermolecular dimerization of two C_{30} subunits (**24**) *en route* to C_{60} (Buckminsterfullerene).

Synthesis of triacetal precursor **37** from commercially available 1,3,5-benzene tricarboxylic acid was straight-forward and was achieved in four steps. Attempts to synthesize the dimerization precursor **26** were thwarted by incomplete complexation of the $Cr(CO)_3$ group to triacetal **37** and the inherent instability of the complex to air oxidation. A new strategy incorporating electron-donating substituents to facilitate the complexation of the $Cr(CO)_3$ unit was undertaken and $Cr(CO)_3$ was subsequently complexed to 1,3,5-trimethoxybenzene to yield **39**. Complex **39** was functionalized at the remaining three positions by a three-fold lithiation and electrophilic quench sequence to install substituents which would be useful synthetic precursors to unsaturated linkages. Unfortunately, Sonagashira coupling reactions of halide derivatives **43-45** and silylacetylenes failed and trialdehyde **46** was not sufficiently stable to undergo a Horner-Emmons-Wadsworth type transformation. One final attempt to obtain an alkynylated $Cr(CO)_3$ compound was undertaken and involved the synthesis of tetramethoxybenzene complex **52**, a building block in the $Cr(CO)_3$-containing cyclophane, **49**. Tetramethoxybenzene complex **54** was synthesized and underwent a two-fold lithiation and electrophilic quench sequence. Analogous to the tri-substituted derivatives **43-45**, dihalides **55-57** were subjected to Sonagashira coupling reactions with trimethylsilylacetylene. The couplings were unsuccessful and there was no evidence for formation of the expected diacetylated complex, **58**.

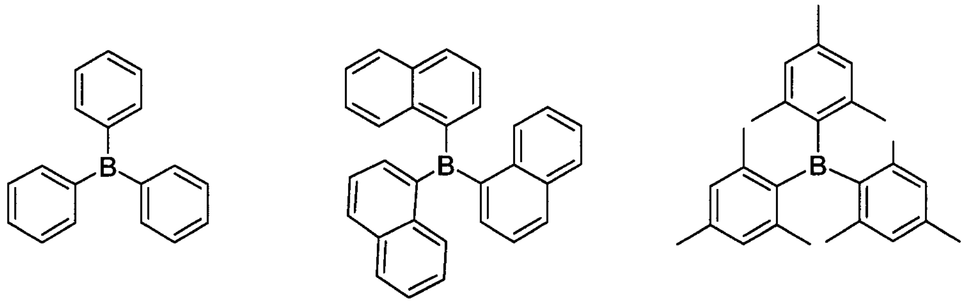
Although arene chromium tricarbonyl compounds are only moderately air-sensitive in relation to other organometallic complexes, typical synthetic manipulations were frustrated by the constant, albeit slow, decomplexation of the chromium tricarbonyl group. For this reason, further attempts towards an organometallic precursor to C_{60} and related structures were abandoned.

Chapter 2: Synthesis of Novel Conjugated Triarylboranes

Introduction

2.1 Triarylboranes

Triarylboranes have been the subject of numerous studies since the first synthesis of triphenylborane (**59**) was reported by Krauss and Nitsche in 1922.[24] Given the existence of an empty p orbital on the boron atom of such compounds, many of these studies have been designed to examine their reactivity towards nucleophilic attack. Triphenylborane and tri-α-naphthylborane (**60**), for example, have been found to undergo reaction with a variety of compounds including amines, water, oxygen, and bases.[25] Increasing the steric bulk of the aryl component greatly diminishes the reactivity of such compounds toward reaction with nucleophiles, allowing for easy handling and manipulation. Thus the methyl groups at the 2 and 6 positions of trimesitylborane (**61**) provide sufficient steric bulk around the boron atom to completely impede approach of an incoming molecule.[25] Sterically hindered boranes are generally air- and water-stable and can be manipulated under normal synthetic conditions.



59 **60** **61**

Figure 10. Some representative triaryl boranes

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[24] Krause, E.; Nitsche, R. Ber. **1922**, *55*, 1261.
[25] Brown, H. C.; Dodson, V.H. *J. Am. Chem. Soc.* **1957**, *79*, 2302.

The three-dimensional structures of several hindered triarylboranes have been determined by X-ray crystallography.[26] Generally, a propeller-like conformation is adopted in the solid state with the aryl planes offset from the trigonal planar boron by angles of 45-55°.[27] Evidence suggests that the triarylboranes maintain this propeller geometry in solution and isomerization is achieved by a concerted ring flip mechanism.[27] This isomerization process is often slow on the NMR timescale and causes peak broadening of the proton resonances in the ^{1}H NMR spectra of hindered triarylboranes such as tris-1-(2-methylnapthyl)borane.[27] Ring flipping can be slowed in many cases by cooling to low temperatures. Variable-temperature NMR studies can then be performed to establish the ground state conformation of the boranes in solution and the mechanism by which they isomerize.

As an example, a simple triarylborane would be expected to adopt four isomeric propeller conformations in solution, which are made up of two diastereomeric sets of enantiomers (Figure 11). In the first set of enantiomers, the sense of twist in each aryl ring is the same and all of the methyl groups are equivalent. In the second set of enantiomers, one of the aryl rings is twisted in an opposite sense to that of the other two. In this case, all three methyl groups are non-equivalent. Thus, a mixture of both sets of diastereoisomers would be expected to yield four methyl signals in the ^{1}H NMR spectrum. Isomerization at ambient temperatures produces a coalescence of these resonances, which are generally not observed as discrete singlets. In the case of tris-1-(2-methylnapthyl)borane, cooling to –70 °C slowed the isomerization sufficiently to allow for observation of all four methyl resonances in a ratio of 1:1:1:2.7.[27] Thus, the triarylborane presumably exists as an approximate 3.0:2.7 ratio of the two sets of diastereoisomers in the ground-state configuration.[27]

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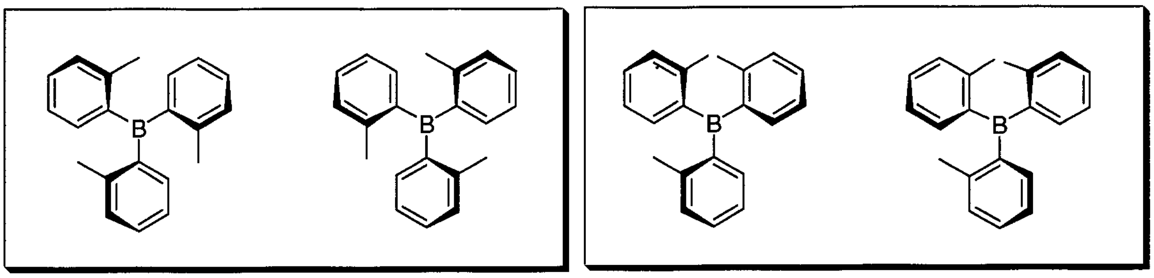
[26] For example see: (a) Wada, M.; Kanzaki, M.; Ogura, H.; Hayase, S.; Erabi, T. *J. Organomet. Chem.* **1995**, *485*, 127. (b) Kahr, B.; Jackson, J. E.; Ward, D. L. Jang, S.; Blount, J. F.; *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, *B48*, 324. (c) Stoudt, S. J.; Gopalan, P.; Kahr, B.; Jackson, J. E. *Struct. Chem.* **1994**, *5*, 335. (d) Yamaguchi, S.; Akiyama, S. Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6335. (e) Blount, J.F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019. (f) Yamaguchi, S.; Shirasaka, T.; Tamao, K. *Org. Lett.* **2000**, *2*, 4129.

[27] Blount, J.F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.



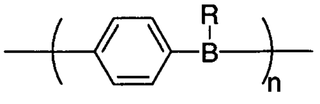
Pair of Enantiomers
Same Twist

Pair of Enantiomers
Staggered Twist

Figure 11. Possible propellar conformations of a methyl-substituted triarylborane

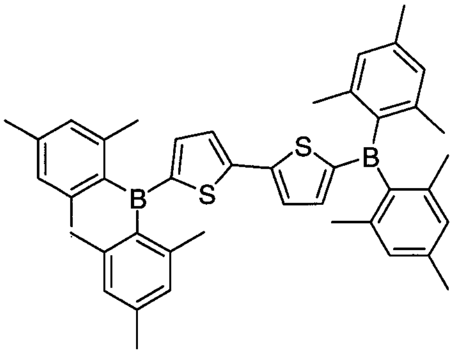
2.2 Extensively Conjugated Arylboranes

The empty p orbital of the boron atom makes it a particularly interesting candidate for use in π-conjugated systems. Indeed, boron has recently been incorporated into a number of extensively conjugated polymers[28] and amorphous materials[29] (Figure 12). Extension of the π-conjugation through the vacant p orbital of boron results in a low-lying LUMO, which is responsible for some very intense UV absorption and emission bands. Accordingly, materials with such unique photophysical properties may be useful in opto-electronics, non-linear optics and as light emitting diodes.



polymer

62



amorphous material

63

Figure 12. Boron-containing systems with extensive π-conjugation

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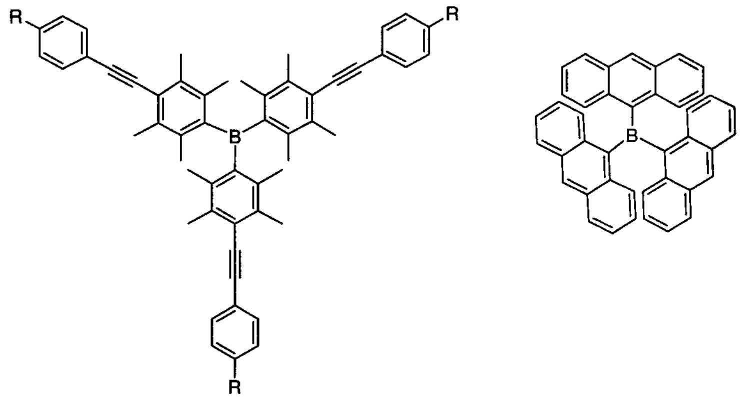
[28] (a) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112. (b) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776.

[29] Noda, T. Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714.

A new class of highly fluorescent, divergently extended π-electron systems (Figure 13) was recently developed by Yamaguchi et al.[30] These novel boranes feature durene and anthracene rings which are sufficiently bulky to offer steric protection of the central boron atom in **64** and **65**, respectively. The triduryl core of **64** (Scheme 14) is further extended by three functionalized arylethynyl groups, resulting in a significant lengthening of the π- conjugation, as evidenced by the long wavelength absorption and emission bands.[30b] By suitable choice of R groups, the flow of electrons in **64** can be directed from the outside edges in towards the empty p orbital of the boron. Such a push-pull or donor-acceptor effect forms the basis of non-linear optical materials and this new class of compounds is likely to find application in this area.[31]

Yamaguchi and coworkers have also demonstrated the applicability of the trianthrylborane **65** in calorimetric sensing of fluoride ions. A number of mixed anthryl- and mesityl boranes (including **65**) were found to undergo drastic colour changes upon selective complexation of a fluoride ion.[32] For instance, the fluorescent orange color of **65** faded to colorless upon addition of a TBAF solution of the anion.



64 **65**

Figure 13. Yamaguchi's divergently extended triarylboranes

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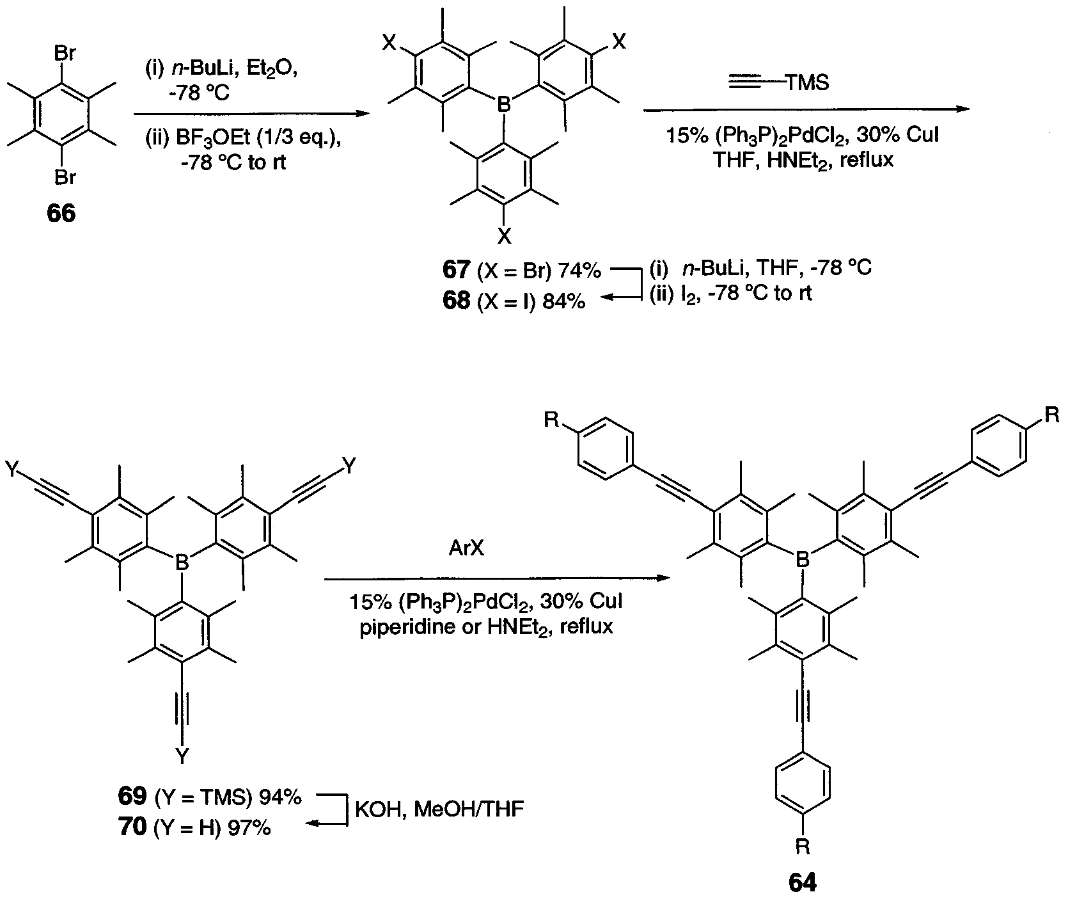
[30] (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6335. (b) Yamaguchi, S.; Shirasaka, T.; Tamao, K. *Org. Lett.* **2000**, *2*, 4129.

[31] Nonlinear optics is concerned with the modification of optical characteristics of some material systems upon exposure to very high intensity light (lasers). As opposed to linear optics, in which the relationship between the electrical field of light (E) and the resulting polarization (P) of the electrons in a molecule are linear ($P = \alpha E$), nonlinear optical effects are governed by a more complex, nonlinear relationship with higher order terms including the second (β)- and third (γ)-order hyperpolarizabilities ($P = \alpha E + \beta E^2 + \gamma E^3 + \ldots$). Generally, organic materials possessing large polarisable π-systems exhibit large nonlinear hyperpolarizabilites.

[32] Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372.



Scheme 14. Synthesis of a class of extended tridurylboranes, 64

2.3 Design of Novel π-Conjugated Triarylboranes

2.3.1 Research Objective for Modification of the Existing Tridurylborane System

A number of extended π systems have been developed in our laboratory including novel phenylyne and enediyne cyclophanes.[33] A new class of cyclophanes incorporating 1,10-phenanthroline units have very recently been added to this collection (Figure 14).[34] Aside from their interesting structures, many of these cyclophanes exhibit striking optical characteristics due to extended π-conjugation.

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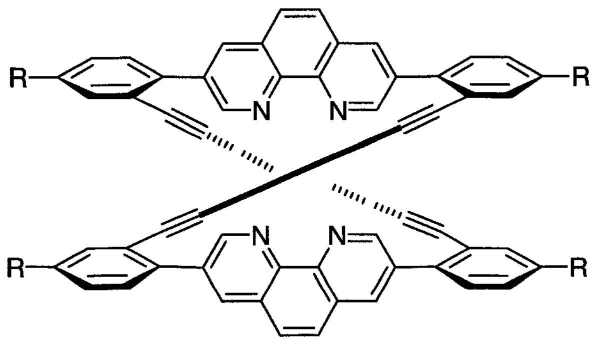
[33] (a) Collins, S. K.; Yap, G.P.A.; Fallis, A. G. *Angew. Chem. Int. Ed.* **2000**, *39*, 385. (b) Collins S. K., Yap G.P.A.; Fallis, A. G. *Org. Lett.* **2000**, *20*, 3189. (c) Romero, M. A.; Fallis, A. G. *Tetrahedron Lett.* **1994**, *35*, 471.

[34] Heuft, M.; Fallis, A. G. *Angew. Chem. Int. Ed.* **2002**, *41*, 4520.

Our initial interest in triarylboranes originated with an idea to incorporate the 1,10-phenanthroline unit intoYamaguchi's tridurylborane system. Functionalized 1,10-phenanthroline compounds are known to be highly fluorescent and their optical properties can be mediated by complexation with transition metal ions.[35]



71 (R = H)
72 (R = NBu_2)

Figure 14. Phenanthroline cyclophanes, 71 and 72

Our interest in functionalizing the tridurylborane system was further bolstered by recent developments in the chemistry of azulene and its potential application in extended π-systems.[36] Azulene (**73**) is an intensely blue aromatic compound with marked polarizability, a characteristic which is exploited in stabilization of both radical cations and anions.[37] Surprisingly, azulene has been scarcely employed as a building block in extended π-electron systems, largely due to the lack of efficient procedures, until very recently, for preparation of ethynylazulenes. Hafner and coworkers, have helped to fill this void with the publication of several mild and effective routes to mono-, di- and triethynylazulenes (Figure 15).[38]

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[35] (a) Loren, J. C.; Siegel, J. S. *Angew. Chem. Int. Ed.* **2001**, *40*, 754. (b) Hurley, D. J.; Tor, Y. *J. Am. Chem. Soc.* **1998**, *120*, 2194. (c) Joshi, H. S.; Jamshidi, R.; Tor, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 2722. (d) Felder, D.; Nierengarten, J-F.; Barigelletti, F.; Ventura, B.; Armoroli, N. *J. Am. Chem. Soc.* **2001**, *123*, 6291.

[36] (a) Elwahy, A.H.M.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 2859. (b) Colby, D.A.; Lash, T.D. *J.Org. Chem.* **2002**, *67*, 1031. (c) Ito, S.; Haruki, I.; Tetsuo, O.; Morita, N.; Watanabe, M.; Harada, N.; Imafuku, K. *J.Org. Chem.* **2001**, *66*, 7090.

[37] For eg. : Ito, S.; Kikuchi, S.; Okujima, T.; Morita, N. Asao, T. *J. Org. Chem.* **2001**, *66*, 2470.

[38] Fabian, K.H.H.; Elwahy, A.H.M.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 2855.

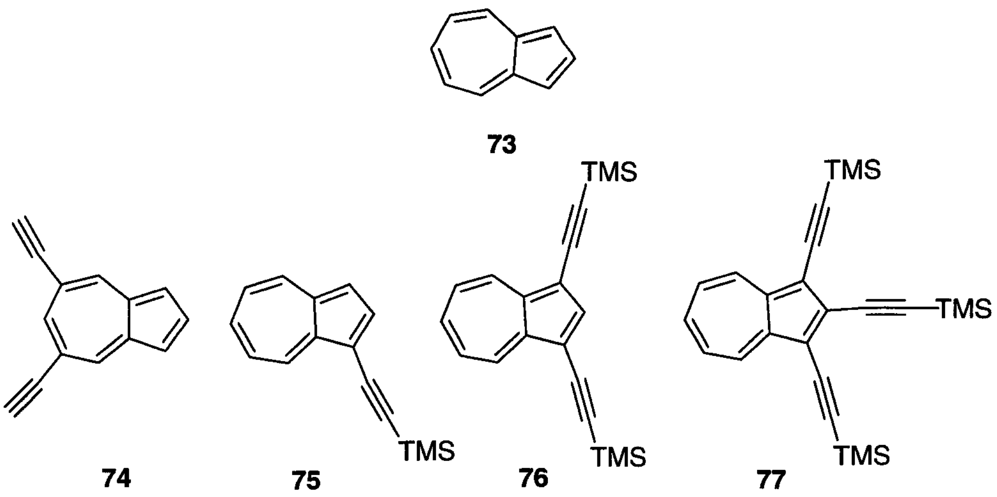

Figure 15. Structures of some recently synthesized ethynylazulenes

Compounds **75-77** were synthesized by Sonagashira coupling of the corresponding iodo- and bromoazulenes with trimethylsilylacetylene, while compound **74** was prepared by a Corey-Fuchs transformation of the corresponding dialdehyde precursor.

2.3.2 Research Objective for Generation of Novel Triarylboranes

Although a variety of aromatic compounds have been utilized in the construction of triarylboranes, few examples have incorporated heteroatom substituents on the ring.[39] This is surprising given the potential for augmentation of the electronic and photophysical properties that exists when electron-donating or –withdrawing functionalities are incorporated into this type of compound. It was our goal to generate a family of π-extended heteroatom-containing triarylboranes, which would have the potential to display novel and interesting electronic characteristics. Triarylboranes bearing electron-donating methoxy substituents were preliminarily chosen. We envisioned incorporation of a tetra-substituted aryl compound analogous to durene, which eliminated the necessity for selectively functionalizing the aryl ring in the presence of other reactive sites. Thus, a symmetrically functionalized compound, 1,2,4,5-tetramethoxybenzene was chosen as the aryl component of the novel triarylborane system. Once formed, the tris(tetramethoxyphenyl)borane would be further elaborated by

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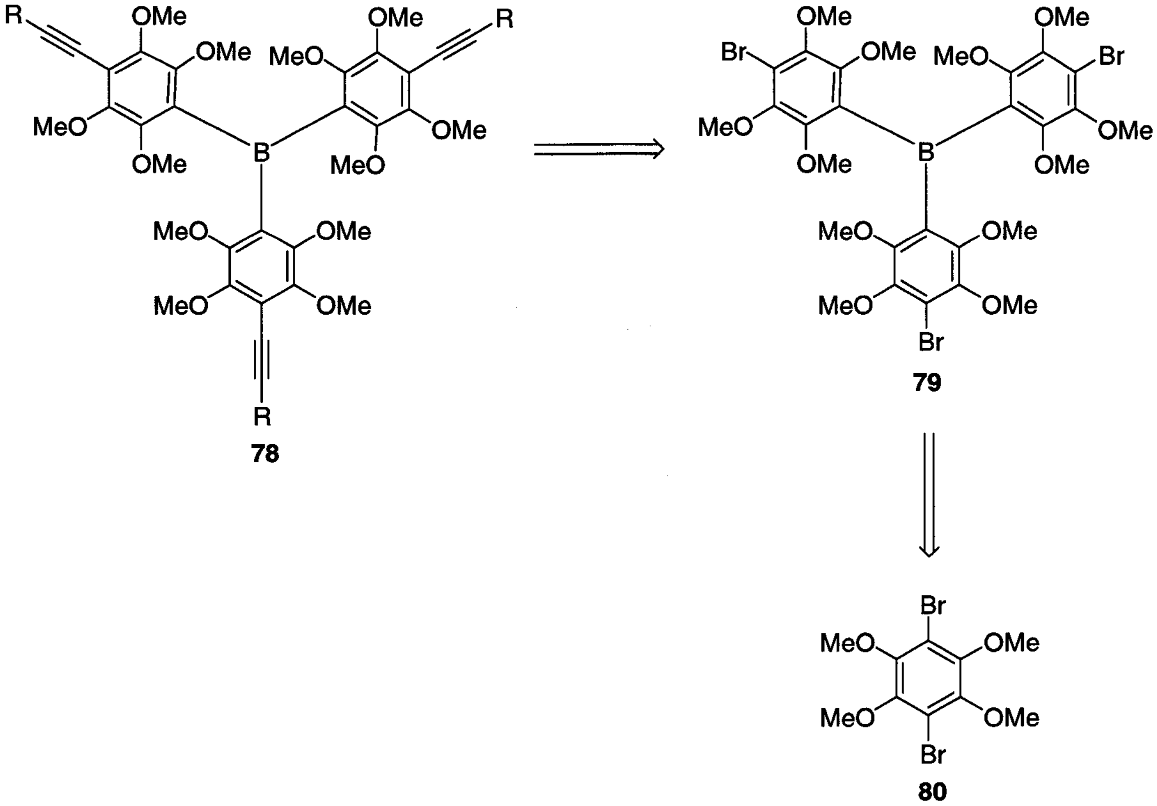
[39] Wada, M.; Kanzaki, M.; Ogura, H.; Hayase, S.; Erabi, T. *J. Organomet. Chem.* **1995**, *485*, 127.

Sonagashira coupling in a manner analogous to that of the tridurylborane system. This is depicted in the retrosynthetic plan shown below (Scheme 15). Both 1,10-phenanthroline and azulene would be potential end-groups (R), allowing for a direct measure of the effect of replacing methyl groups with ether functionalities in the tridurylborane system.



Scheme 15. Retrosynthetic plan for the synthesis of extended triarylborane 78

Results and Discussion

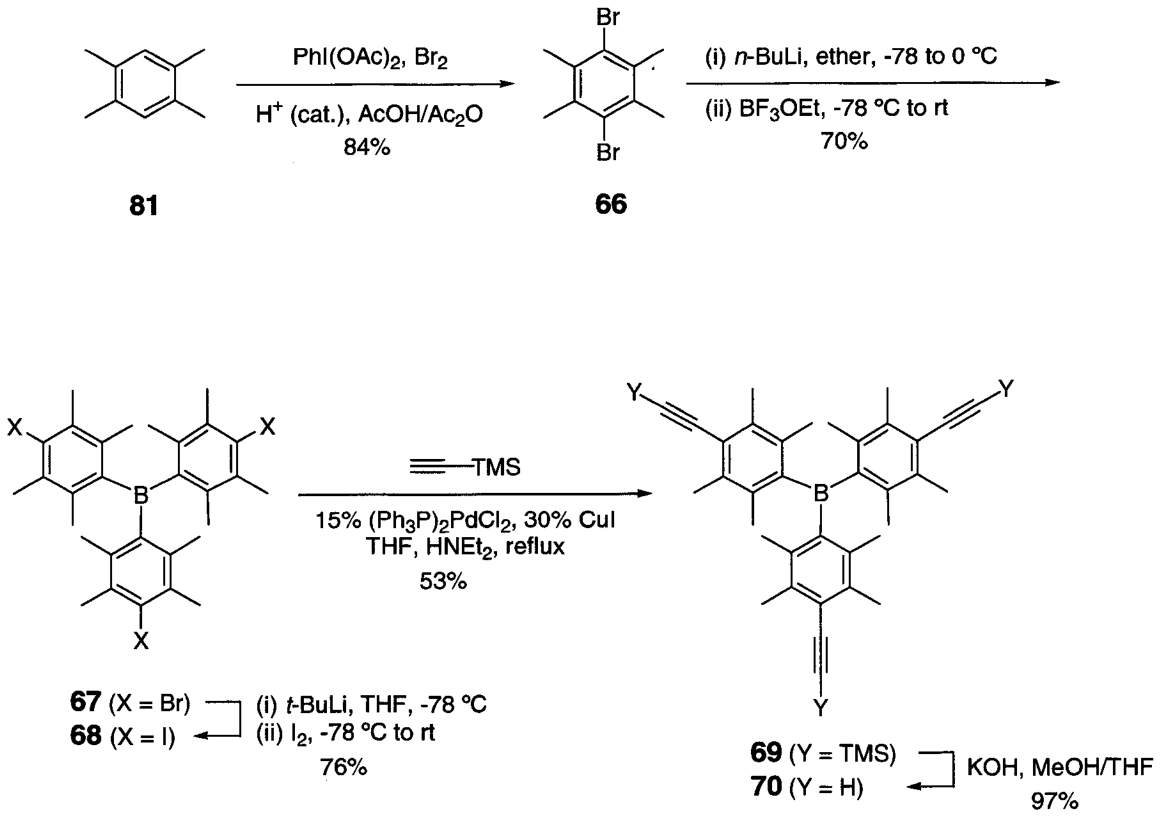
2.4 Modification of the Existing Tridurylborane System

2.4.1 Synthesis of Tris(ethynylduryl)borane 70

The extended durylborane **70** was synthesized in essentially the same manner as that described by Yamaguchi *et. al.*(Scheme 14). [30b] Acid-catalyzed bromination of durene (**81**) with a mixture of iodobenzene diacetate ($PhI(OAc)_2$) and bromine yielded a colourless suspension of dibromodurene (**66**) in less than 5 minutes. Replacement of bromine with iodine yielded pure diiododurene under the same reaction conditions. Lithium-halogen exchange of dibromodurene with *n*-BuLi in ether at –78 °C afforded the mono-lithiated species, which reacted with $BF_3{\cdot}OEt_2$ (1/3 eq.) to yield tridurylborane **67**.

Yamaguchi and coworkers determined that tribromide **67** was not a sufficiently reactive substrate for palladium-catalyzed Sonagashira coupling. Thus, tribromide **67** was converted to the corresponding triiodide, **68**. Attempts to circumvent the iodination step by generating the mono-anion of diiododurene with *n*-BuLi and quenching with $BF_3{\cdot}OEt_2$ (1/3 eq.) yielded only 20% yield of the desired tris(iododuryl)borane, **68**. Regardless, triiodide **68** was obtained in good yield from **67** by lithium-halogen exchange with 6 equivalents of *t*-BuLi in THF followed by quenching with excess iodine.

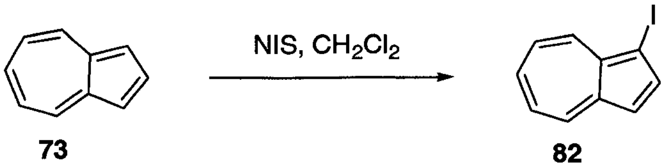
Sonagashira coupling between **68** and trimethylsilylacetylene proved to be quite sluggish. Although the reaction mixture was heated at reflux for a prolonged period in the presence of an excess of trimethylsilylacetylene and a large amount of catalyst, the reaction did not go to completion and partially iodinated products were recovered following work-up. Yamaguchi *et. al.* reportedly obtained the coupled product, **67**, in 94% yield following just 10 hours at reflux, albeit with a high catalyst loading (15% palladium, 30% copper). Despite this contradiction, the remainder of our results are in good agreement with those reported by Yamaguchi. Deprotection of tridurylborane **69** with KOH in a mixture of MeOH and THF was facile and produced the desilylated product, **70**, in high yield.



Scheme 16. Synthesis of Tris(ethynylduryl)borane

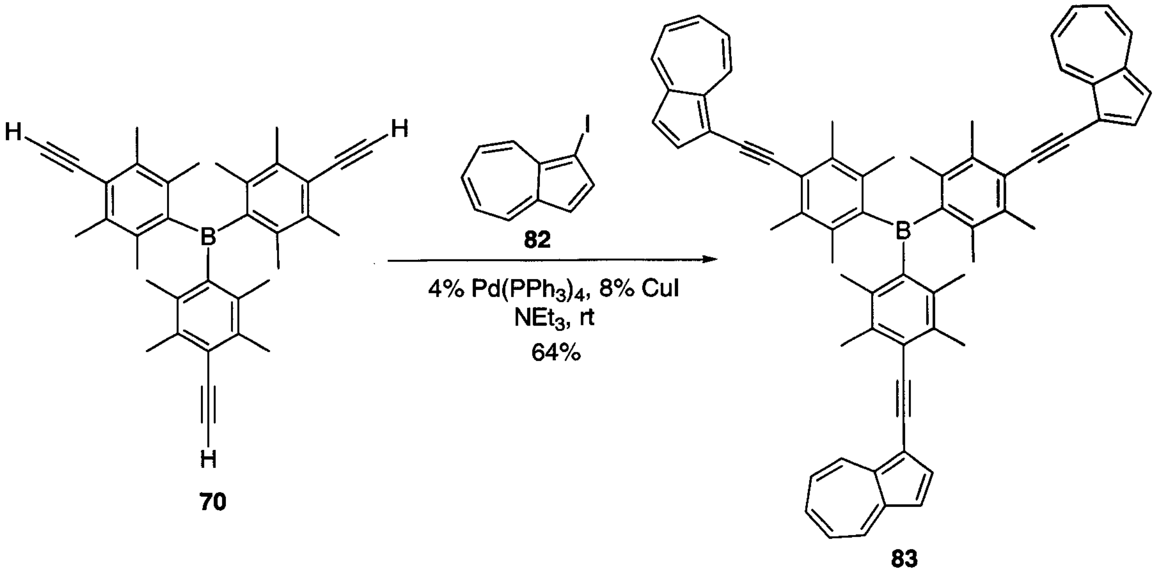
2.4.2 Sonagashira Coupling of the Tris(ethynylduryl)borane 70 and Iodoazulene

Iodoazulene was prepared according to the method of Hafner *et al.*[38] Thus, commercially obtained azulene was iodinated with *N*-iodosuccinimide in CH_2Cl_2 at room temperature (Scheme 17). The reaction was complete within several minutes and was worked-up immediately. The purple 2-iodoazulene would decompose to yield an insoluble, shiny black solid if the solution was stirred at room temperature for more than a few hours. Thus, following purification, **82** was immediately dissolved in NEt_3, palladium and copper catalysts were added, and the mixture was de-gassed for several minutes before addition of tris(ethynylduryl)borane (**70**).



Scheme 17. Synthesis of 2-Iodoazulene

The cross-coupling of **82** and **70** using $PdCl_2(PPh_3)_2$ as catalyst afforded a mixture of the desired product (**83**) and what appeared to be a homo-coupled dimer. Exhaustive separation by column chromatography afforded **83** in only 12% yield. However, when the coupling reaction was carried out with $Pd(PPh_3)_4$, **83** was easily isolated as the major product in 64% yield (Scheme 18).



Scheme 18. Synthesis of tris(azulenylethynylduryl)borane 83

Tris(azulenylethynylduryl)borane (**83**) is a green solid which dissolves to yield a beautiful blue-green solution. The UV-visible absorption spectrum of **83** in THF is shown in Figure 16a, together with the precursors, azulene (**73**) and tris(ethynylduryl)borane (**70**), for comparision. Compound **83** displays two maxima in the 300-700 nm region. The maxima at short-wave (Figure 16a) and long-wave (Figure 16b) of the UV-visible spectra are shown separately for clarification. In the short-wave region of the spectrum, the λ_{max} of compound **83** is red-shifted 78 nm from its precursor **70**. This bathochromic shift can be attributed to an extension of π-conjugation in **70** upon incorporation of the three azulenyl substituents. The long-wave absorption maximum of

83 is similarly red-shifted in comparison to azulene (**73**) by 37 nm. Although triarylborane **70** is highly fluorescent, azulene derivative **83** did not exhibit any substantial fluorescence.

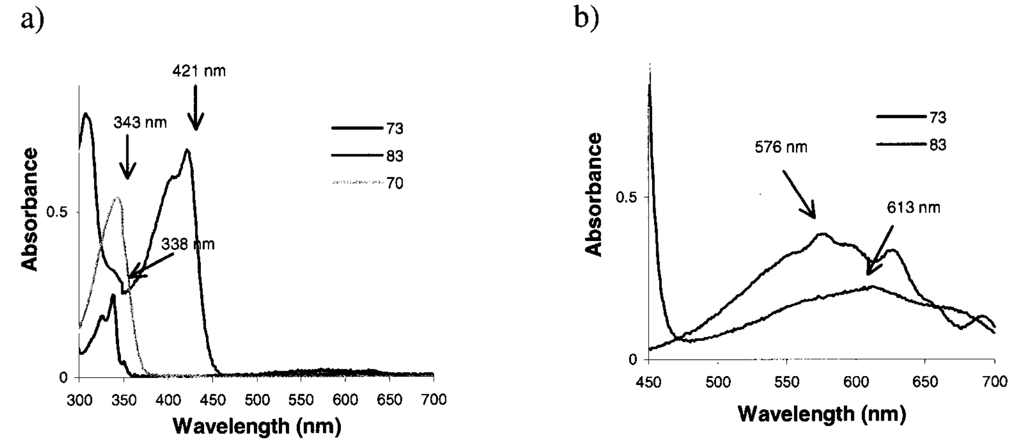


Figure 16. (a) UV-vis spectra of azulene (73), tris(azulenylethynylduryl)borane (83), and tris(ethynylduryl)borane (70); (b) visible spectra of a more concentrated solution of azulene (73) and tris(azulenylethynylduryl)borane (83) in THF at room temperature.

2.4.3 Sonagashira Coupling of the Tris(ethynylduryl)borane 70 and 3-Bromophenanthroline (84)

Our success in synthesizing the azulenyl system encouraged us to undertake the analogous coupling with 3-bromophenanthroline (Scheme 19). Thus, **84**, obtained as a side-product from formation of 3,8-dibromophenanthroline, was dissolved in a 1:1 mixture of DMF and THF.[40] Phenanthroline derivatives have limited solubility in ethereal solvents and the DMF was necessary for complete dissolution. Palladium and copper catalysts, NEt_3 and borane **70** were subsequently added to the reaction and the solution was stirred at room temperature overnight. The following morning, the reaction mixture had become heterogenous and all of the starting material had been consumed. Unfortunately, DMF and triphenylphosphine oxide were the only isolatable organic-soluble products. However, a substantial amount of yellow solid was collected by filtration of the organic and aqueous phases. Despite repeated washings, the yellow solid did not dissolve in any common organic or aqueous solvents including diethyl ether

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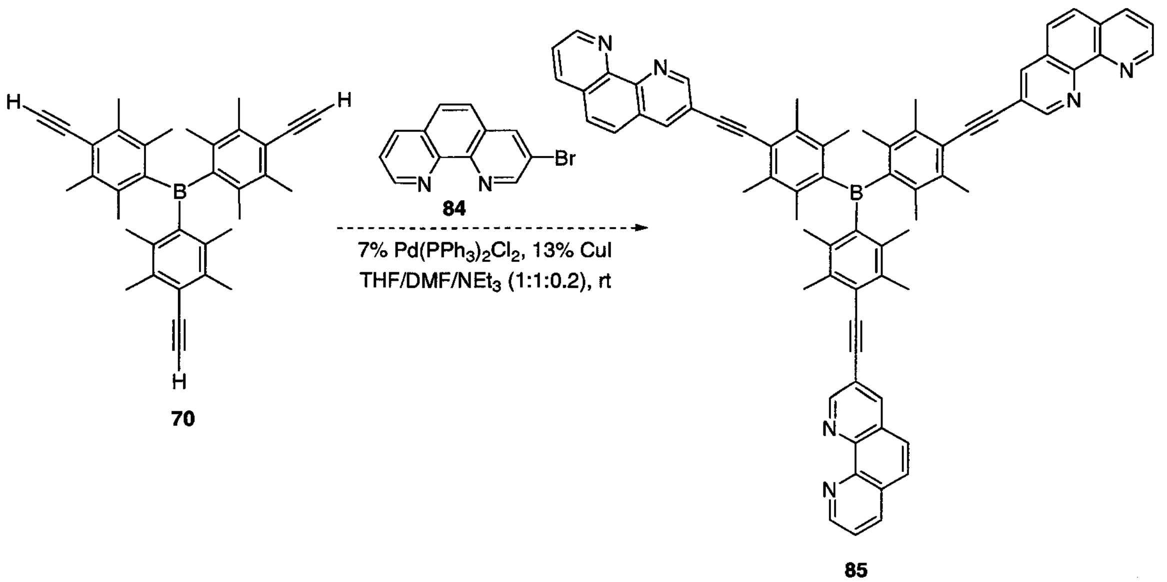
[40] Yutaka, S.; Take-aki, K.; Kohtaro, O.; Yamamoto, T. *Can. J. Chem.* **1997**, *75*, 1336.

CH_2Cl_2, ethylacetate, acetone, MeOH, DMSO, acetonitrile, benzene, H_2O, 1 M HCl, or AcOH.



Scheme 19. Attempted synthesis of tris(phenanthrenylethynylduryl)borane 85

In hindsight, it is not altogether surprising that **85** had poor solubility. As alluded to earlier, substituted phenanthroline compounds are notoriously insoluble in all but a select few, very polar solvents. In fact, the phenanthroline cyclophane, **71**, previously constructed in our laboratory, (Figure 14) also displayed very limited solubility. This problem was eventually overcome by introduction of four dibutylamine substituents in **72**. Incidentally, the solubility of the parent phenanthroline cyclophane was greatly enhanced by complexation of a Cu(I) ion between the two phenanthroline units. Unfortunately, attempts to synthesize an analogous compound with **85** by stirring a suspension of the solid in a very dilute solution of CH_2Cl_2 and $Cu(NCMe)_4PF_6$ failed and the insoluble yellow solid was recovered.

2.5 Synthesis of a Tris(Tetramethoxyphenyl)borane

2.5.1 Synthesis of 1,2,4,5-Tetramethoxybenzene (53)

Tetramethoxybenzene **53** was prepared from the inexpensive and commercially available 1,4-benzoquinone according to known literature procedure (Scheme 20).[41]

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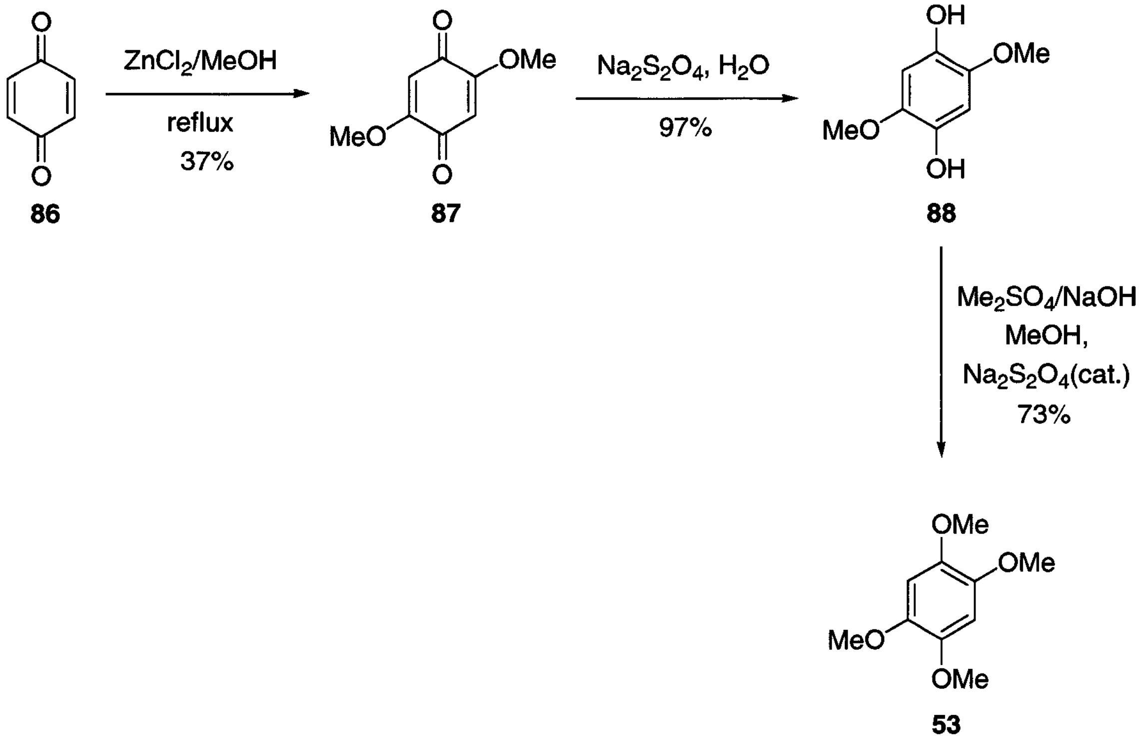
[41] Benington, F.; Morin, R.D.; Leland, C.C. *J. Org. Chem.* **1957**, *22*, 331.

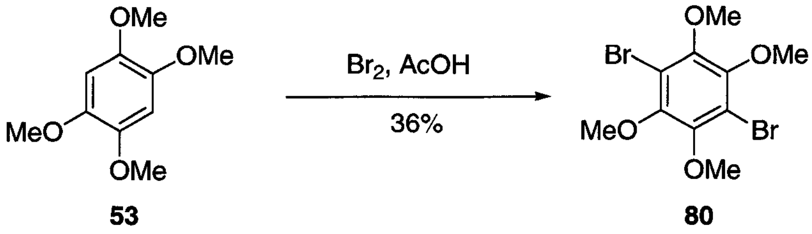
Although the tetramethoxybenzene can be obtained in higher yield by a variety of other procedures, this particular method is efficient, amenable to scale-up and does not require purification of the intermediates. In fact, the entire procedure can be carried out from start to finish in one day. Conjugate addition of MeOH to *para*-benzoquinone afforded quinone **87** as a dark brown solid after 30 minutes of heating with $ZnCl_2$. Reduction of **87** was accomplished by vigorous shaking of a suspension of the solid in a solution of $Na_2S_2O_4$ in boiling water for one minute. Alkylation of the resulting diol **88** with an alkaline solution of Me_2SO_4 and MeOH afforded pure tetramethoxybenzene, **53**.



Scheme 20. Synthesis of 1,2,4,5-tetramethoxybenzene (53)

2.5.2 Bromination of Tetramethoxybenzene

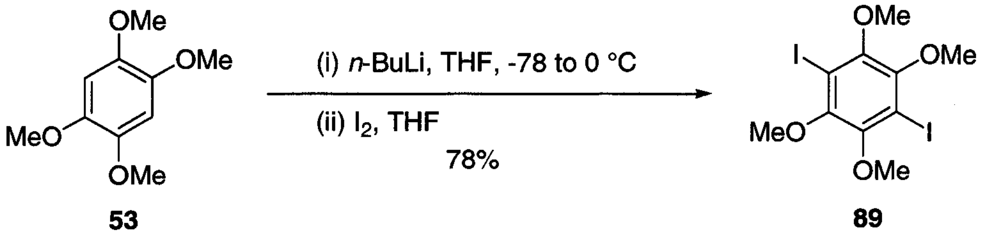
Bromination of **53** was carried out with an excess of bromine in acetic acid (Scheme 21). Although all of the starting material had been converted to dibromide **80** by GC-MS, only 36% of the desired product could be isolated by recrystallization and/or chromatography. The remaining material was lost as a bright red, crystalline substance, which did not could not be eluted from the column following chromatography.



Scheme 21. Bromination of 1,2,4,5-tetramethoxybenzene

2.5.3 Iodination of Tetramethoxybenzene

Staab *et al.* obtained the diiodide **89** in only 35% yield by lithiation of **53** with an excess of *n*-BuLi and subsequent reaction with excess iodine.[42] The yield of **89** could be considerably improved by decreasing the reaction time between *n*-BuLi and **53** from four to one hours. Furthermore, following addition of *n*-BuLi at –78 °C, the reaction temperature was maintained at 0 °C rather than room temperature and dropwise addition of iodine was prolonged from 30 minutes to two hours. Under these conditions, the diiodotetramethoxybenzene **89** was obtained in 78% yield (Scheme 22).



Scheme 22. Iodination of 1,2,4,5-tetramethoxybenzene

2.5.4 Synthesis of Tris(bromotetramethoxyphenyl)borane 79

Table 3 outlines the various reaction conditions utilized to obtain a tris(tetramethoxyphenyl)borane. When the conditions used to obtain the tridurylborane **70** were applied to compound **80** (Table 3, entry 1), a complex mixture of products resulted including starting material (**53**) and 1-bromo-2,3,5,6-tetramethoxybenzene. Likewise, the diiodide **89** gave an equally complex mixture under the same conditions (Table 3, entry 5). The best results were eventually obtained by heating a benzene/ether solution of the mono anion of **80** and $BF_3 \cdot OEt_2$ for 48 hours to give **79** in only 14% yield

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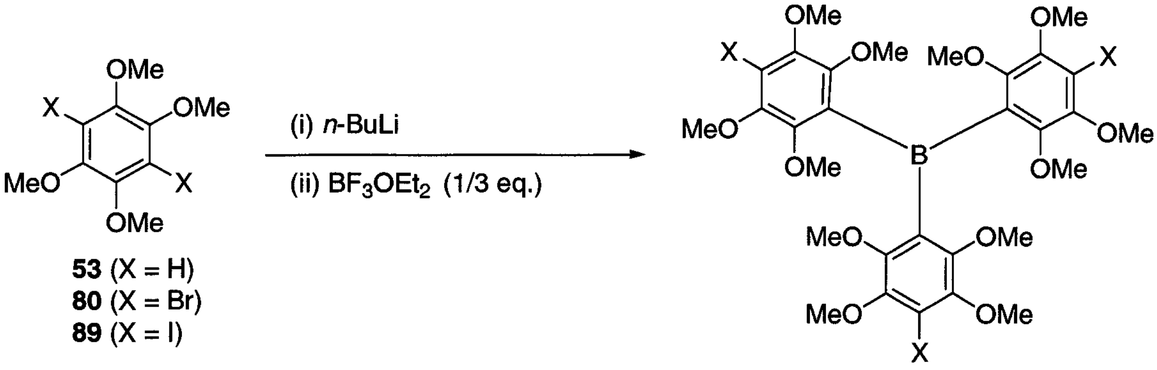
[42] Staab, H.A.; Weiser, J.; Futscher, M.; Voit, G.; Ruckemann, A.; Anders, C. *Chem. Ber.* **1992**, *125*, 2285.

(Table 3, entry 4). Unfortunately, the reaction could not be reliably reproduced on a large scale.



53 (X = H)
80 (X = Br)
89 (X = I)

90 (X = H) 0%
79 (X = Br) 14%
91 (X = I) 0%

Table 3. Attempted Synthesis of a Tris(tetramethoxyphenyl)borane

Substrate	Solvent	Temp. b/f $BF_3 \cdot OEt_2$ (° C)	Time (min)	Temp.[a] after $BF_3 \cdot OEt_2$[b] (° C)	Triarylborane
80	Et_2O	-78 to 0	20	rt	trace
80	Et_2O	-78	20	reflux	6%
80	Et_2O	-78	60	rt	trace
80	Et_2O	-78	60	reflux	14%
89	Et_2O	-78 to 0	30	rt	trace
89	Et_2O	-78 to 0	60	reflux	trace
53	Et_2O	-78 to 0	120	reflux	trace
53	Et_2O	-78 to 0	240	reflux	trace
53	THF	-40 to –10	180	rt	trace

[a] benzene was added to the reaction mixtures immediately prior to reflux to yield an approximately 1:1 mixture of benzene/ether

[b] all solutions were stirred at the specified temperature overnight

In order to ascertain whether the difficulty in obtaining the desired product originated from incomplete formation of the mono anion, the reaction between **80** and *n*-BuLi was quenched with water (in place of $BF_3 \cdot OEt_2$) and submitted to GC-MS analysis.

The analysis showed an approximate 1:1 mixture of starting material (**80**) and monobrominated tetramethoxybenzene (**94**).

A suitable interpretation of these results is shown in Scheme 23, below. In this proposal, dibromide **80** reacts with mono-lithiated species **92**, as it is formed, to yield 10-X-2[43] ate complex **93** as a stable intermediate. The existence of such ate complexes, in which the central halogen atom bears a formally negative charge, have been implicated as intermediates/transition states in all lithium-halogen exchange reactions.[44] Recent evidence suggests that the stability of ate complexes in solution is related to the availability of a Lewis basic site to remove the cationic lithium from the anionic halogen center.[45] This basic site can be provided intramolecularly by substituents in the ortho position of the aryl ring or intermolecularly by a solvent molecule such as TMEDA.[46] With four potential coordinating sites for lithium, ate complex **93** is presumably a stable intermediate. Although ate complex formation is a reversible process, dibromide **80** is conceivably tied up in ate complex **93** long enough for the remaining *n*-butyllithium to be consumed by reaction with *n*-butylbromide. Complex **93** yields the observed product mixture upon quenching.

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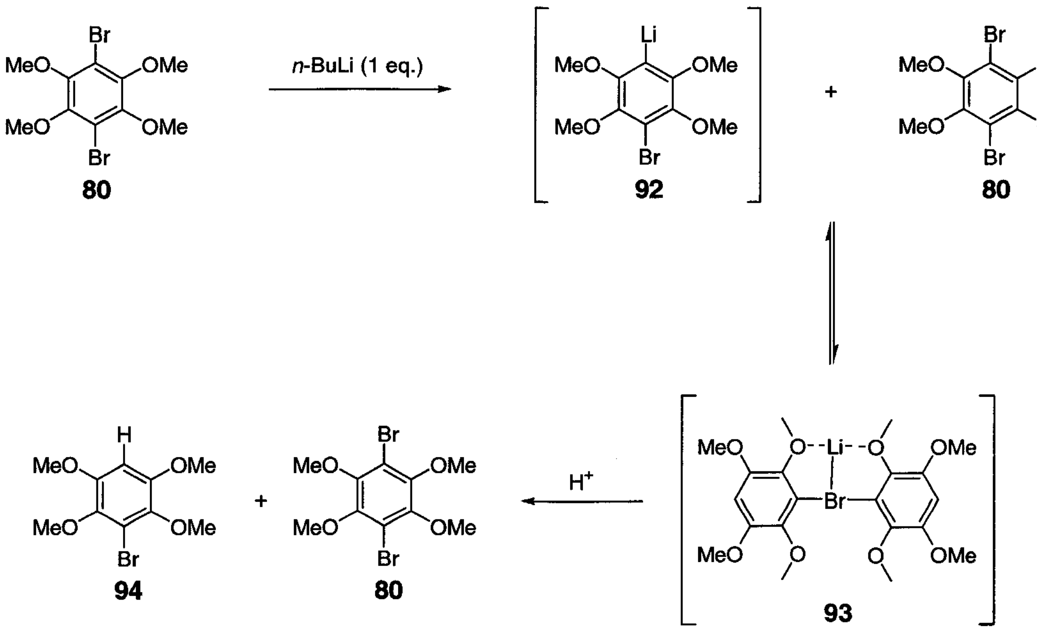
[43] This nomenclature is derived from a general classification of hypervalent N-X-L speciesm see Perkins, C. W. ; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

[44] Bailey, W. F.; Carson, M. W. *J. Org. Chem.* **1998**, *63*, 9960.

[45] Wilberg, K. B.; Sklenak, S. *J. Org. Chem.* **2000**, *65*, 2014.

[46] Reich, H. J.; Phillips, N. H.; Reich, I.L. *J. Am. Chem. Soc.* **1985**, *107*, 4101.



Scheme 23. Plausible mechanism to explain formation of 80 and 94

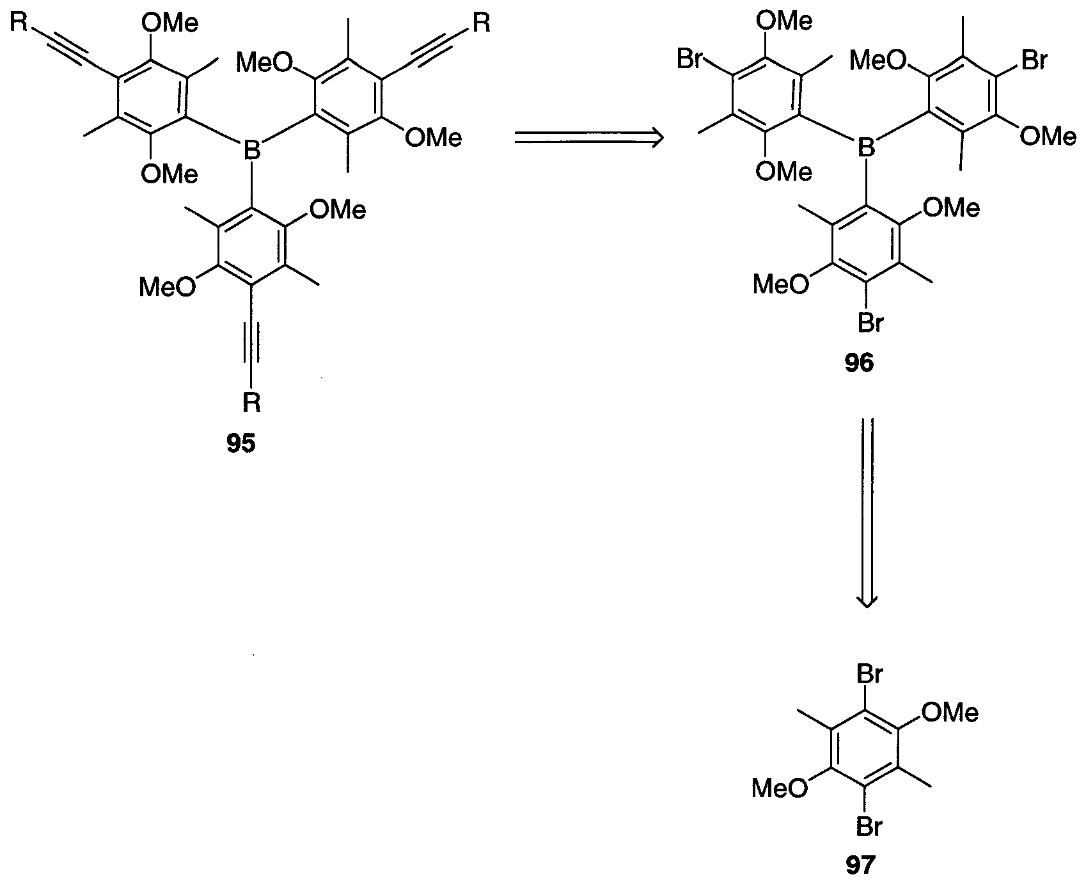
In order to circumvent this inevitable ate formation, **80** and **89** were replaced with the parent compound, **53**, in several additional attempts to obtain a triarylborane (Table 3, entries 7-9). Unfortunately, even in the presence of a catalytic amount of TMEDA or HMPA, the proton NMR spectra of the crude reaction mixture did not show any evidence for formation of the corresponding triarylborane **90**.

Although a sufficient amount of the triaryl borane **79** was isolated to permit full characterization, the low yield made further manipulations toward the ethynyl-extended derivative **78** impractical.

Clearly, the synthesis of a triarylborane composed of three tetramethoxybenzene substituents is not trivial. We had predicted that anion stabilization afforded by the neighbouring methoxy groups in **80** and **89** would aid lithiation and subsequent reaction with the lewis acid. On the contrary, this stabilization presumably resulted in formation of stable ate intermediates which are known to be unreactive towards electrophiles such as $BF_3{\cdot}OEt_2$.

2.6 Synthesis of a Tris(ethynylmethoxymethylphenyl)borane

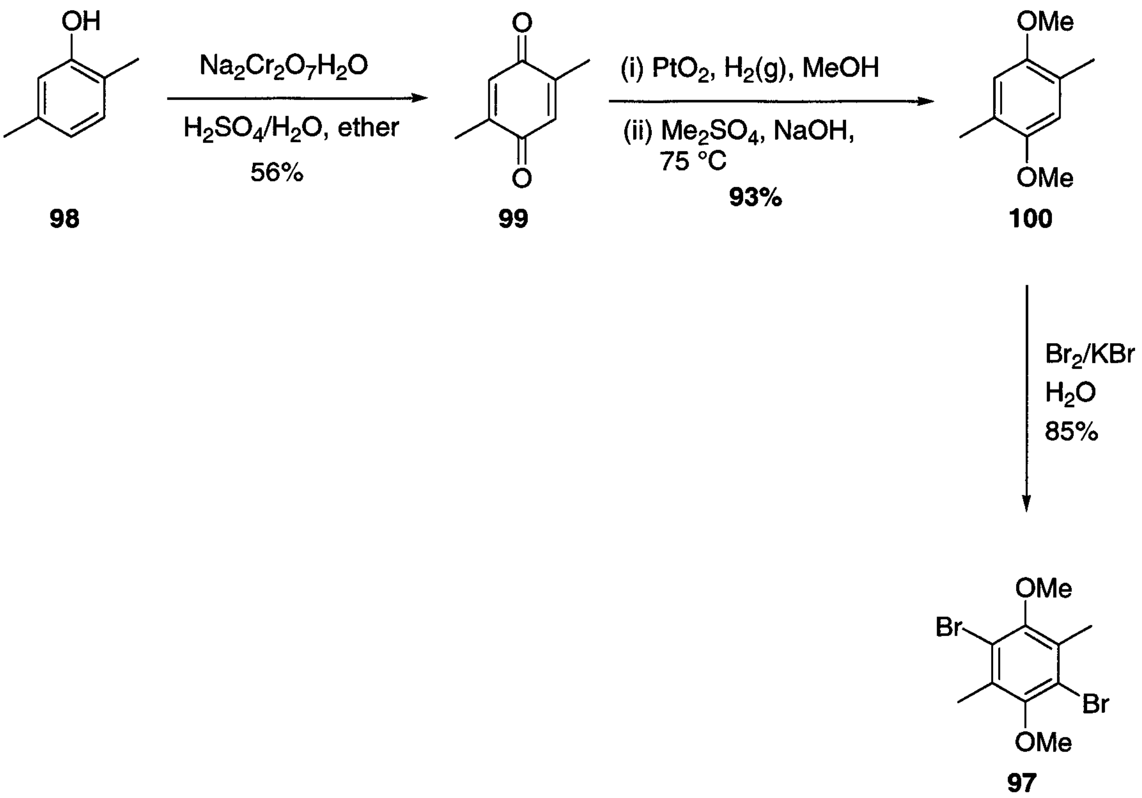
Necessarily, the plan to synthesize a novel heteroatom-containing triarylborane was reassessed. To this point, we had established that tetramethylbenzene was a suitable aromatic precursor to a triarylborane while tetramethoxybenzene was not. Another aromatic target, 1,4-dimethoxy-2,5-dimethylbenzene (**97**), was envisioned as a compromise between these two compounds. It was believed that dibromide **97** would be less reactive towards lithium-halogen exchange and less likely to form intermolecular associations due to the reduction in the number of methoxy substituents. The revised retrosynthetic analysis for formation of a triarylborane composed of **97** is outlined below (Scheme 24).



Scheme 24. Retrosynthetic plan for synthesis of extended triarylborane, 95

2.6.1 Synthesis of 1,4-Dibromo-2,5-dimethoxy-3,6-dimethylbenzene (97)

Aryl ether **100** was derived from reduction and alkylation of the quinone in a manner analogous to tetramethoxybenzene **53** (Scheme 25).

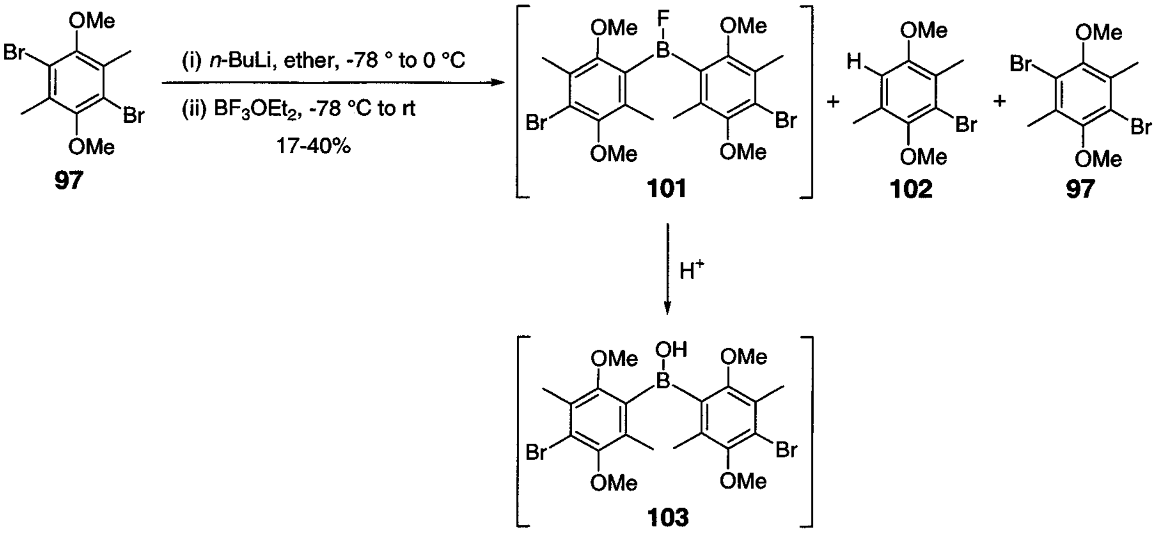


Scheme 25. Synthesis of 1,4-dibromo-2,5-dimethoxy-3,6-dimethylbenzene

Commercially available phenol **98** was oxidized to the corresponding bright yellow dimethyl quinone, **99**, with chromic acid (Jones Reagent) in ether according to a known literature procedure.[50] Incidentally, this procedure was derived from an article entitled "A Simple, Inexpensive Procedure for the Large-Scale Production of Alkyl Quinones", which accurately reflects the reason for employing it here. Catalytic hydrogenation of quinone **99** in methanol gave a colourless solution of the phenol in less than 1 hour. Dimethylsulfate was added and the phenol was alkylated in the same pot by dropwise addition of NaOH. Following a short period of heating and cooling, a thick colourless suspension of pure **100** crystallized from the solution and was collected by filtration. The best conditions for the bromination of **100** involved addition of bromine to a vigorously stirred suspension of diether **100** in an aqueous solution of potassium bromide. The pure ether **100** was cleanly converted to dibromide **97** under these conditions. When the bromination was performed in a solution of bromine in acetic acid, side-chain bromination often occurred as well as ether cleavage.

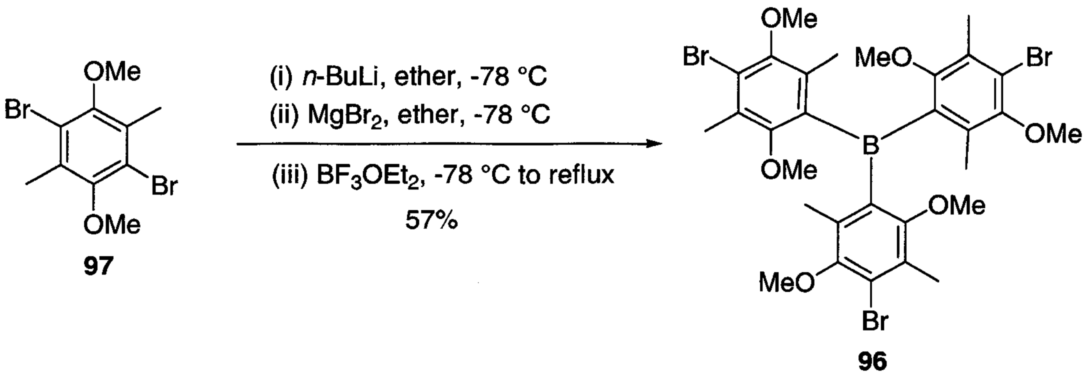
2.6.2 Synthesis of Triarylborane 96

Mono-lithiation of dibromide **97** with *n*-butyllithium and subsequent quenching with BF_3·OEt_2 (performed analogously to the preparation of the tridurylborane **67**), resulted in a mixture of compounds including starting material (**97**), monobromide **102**, and **103**, derived from hydrolysis of the corresponding diarylfluoroborane **101** (Scheme 26). The structure of **103** was confirmed by X-ray crystallographic analysis. Although the target triarylborane **96** was not generated, the formation of fluoroborane **101** was encouraging. Despite numerous attempts to push the reaction to completion, however, **103** was the only arylborane isolated under these conditions.



Scheme 26. Attempted synthesis of the triarylborane 96

A new strategy towards the synthesis of **96** was developed based on literature examples in which several triarylboranes, including trimesitylborane (**61**), were derived from the corresponding Grignard reagents. Dibromide **97** underwent mono-lithiation with *n*-BuLi followed by transmetallation with $MgBr_2$ (generated *in situ*) at –78 °C (Scheme 27). The exchange was visualized by the dissolution of the lithium salt of **97**. Addition of BF_3·OEt_2 yielded the desired triarylborane, **96**, in a modest 57% yield.



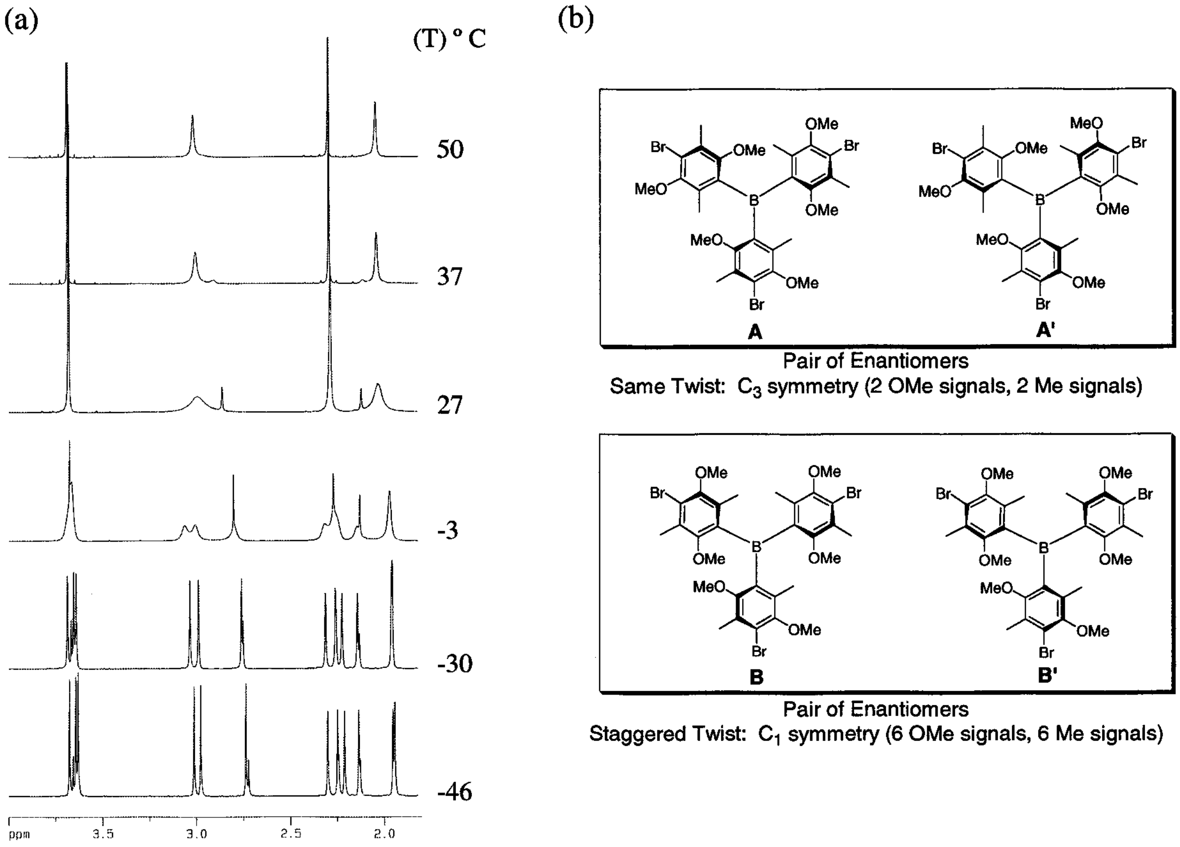
Scheme 27. Synthesis of the triarylborane 96

2.6.3 NMR Characteristics of Triarylborane 96

The ^1H NMR spectrum of **96** was complicated by excessive broadening of two of the four methyl and methoxy signals at room temperature. Analogous to the methyl-substituted triarylborane mentioned in the introduction, the broadening was attributed to restricted motion of the propellar-like molecule in solution. A temperature-dependent ^1H NMR investigation was undertaken to confirm this assumption (Figure 17a).

Assuming that compound **96** adopts a propellar conformation in solution, there are four possible conformational isomers, which are represented in Figure 17b. A and A' are enantiomers as are B and B' and are therefore indistinguishable from one another in the NMR spectrum. Conformers A and A' are C_3 symmetric and will give rise to only four signals in the ^1H NMR spectrum, corresponding to two methyl groups and two methoxy groups. Conformers B and B', however, are C_1 symmetric and each methyl and methoxy group is nonequivalent, giving rise to 12 signals in the NMR spectrum, corresponding to six methyl groups and six methoxy groups. In the absence of conformational exchange, a mixture of the two sets of enantiomers would theoretically yield 16 signals in the ^1H NMR spectrum.

At 50 °C, there are four signals in the ^1H NMR spectrum of **96** corresponding to two methyl groups and two methoxy groups. Presumably at this temperature, interconversion of the four isomeric conformations is fast and undetectable on the NMR time-scale. Upon cooling, the signals begin to broaden and separate into a series of single resonance peaks. At –46 °C, the spectrum consists of sixteen signals (four clusters of four signals). Thus, at this temperature, each of the original four resonance peaks have been resolved into an additional four signals. Within each region, the peaks integrate to a ratio of 1:1:1:0.3. For clarification, we will just focus on the downfield cluster of peaks corresponding to the methoxy group at C5 of **96.** The three equal intensity resonances correspond to the three non-equivalent methoxy groups of B and B' and the smaller intensity peak is assigned to the equivalent methoxy groups of A and A'. Following this reasoning, it appears as though the unsymmetrical conformation of B and B' is favored in the ground-state and the ratio of AA' to BB' in solution at this low temperature is 1:10 (0.3:3).



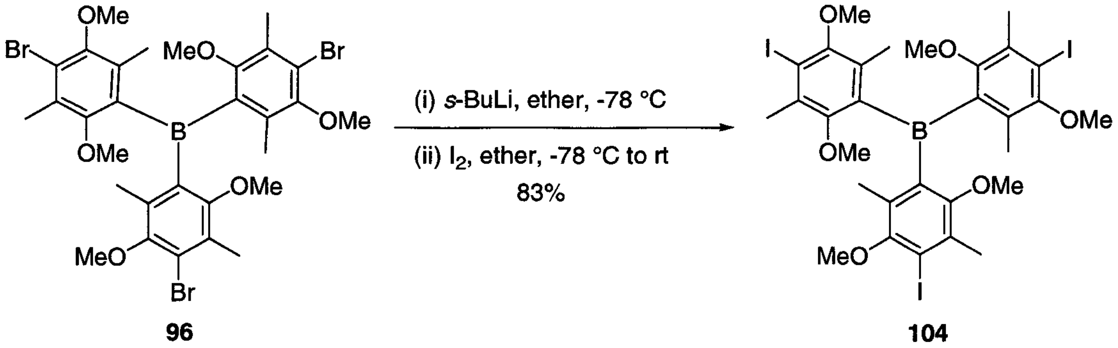
Pair of Enantiomers
Same Twist: C_3 symmetry (2 OMe signals, 2 Me signals)

Pair of Enantiomers
Staggered Twist: C_1 symmetry (6 OMe signals, 6 Me signals)

Figure 17. (a) The 500 MHz ^1H NMR spectrum of 96 at various temperatures; (b) diagrams depicting the possible propellar conformations of 96 and the number of signals expected in the ^1H NMR spectrum

2.6.4 Extension of Triarylborane 96

In line with our objective to synthesize a conjugated system analogous to tris(ethynylduryl)borane (**70**), tribromide **96** was converted to the more reactive triiodide, **104** (Scheme 28).



Scheme 28. Synthesis of triiodide 104

Preliminary attempts to prepare triiodide **104** resulted in a complex mixture of products when tribromide **96** was lithiated with *t*-BuLi and quenched with an excess of iodine. Curiously, despite prolonged reaction times and an obvious excess of iodine, aryl proton resonances could be seen in the ^{1}H NMR spectrum of the crude reaction mixture. An even more complex mixture was obtained when *n*-BuLi was employed as the base. After considerable experimentation, optimized conditions were determined to be those shown above (Scheme 28). Thus, lithiation with *s*-BuLi in ether at –78 °C followed by dropwise addition of a concentrated solution of excess iodine in ether afforded triiodide **104** in good yield.

Unfortunately, the subsequent Sonagashira coupling of triiodide **104** with trimethylsilylacetylene proved to be quite difficult (Scheme 29). The desired product, **105**, was eventually obtained in only 28% yield when a large excess of catalyst and terminal acetylene were used. In fact, the reaction mixture was recycled when the first reaction failed to produce a sufficient amount of product. In total, close to 20 equivalents of trimethylsilylacetylene, 45 mol % of $Pd(PPh_3)_4$, and 83 mol % of CuI were required to produce the desired product in only 28% yield. The reaction was monitored by TLC and the R_f value of the mono-, di- and tri-ethynyl substituted compounds increased with the number of ethynyl substituents from the starting compound **104** (Figure 18). Generally, the reaction progressed until a black precipitate developed on the inside walls of the flask and the reaction mixture became almost completely colourless. At this point, it was necessary to add additional palladium and copper catalysts and trimethylsilylacetylene to drive the reaction further. Despite repeated attempts with a variety of bases including NEt_3, $HNEt_2$, and piperidine, and catalysts, $PdCl_2(PPh_3)_2$, and $Pd(PPh_3)_4$, the yield of compound **105** could not be improved beyond 28%.

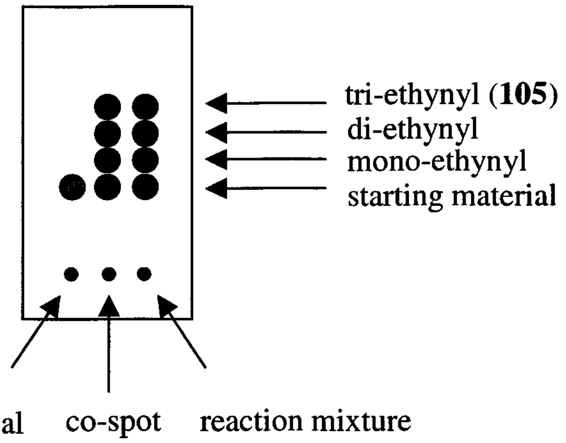
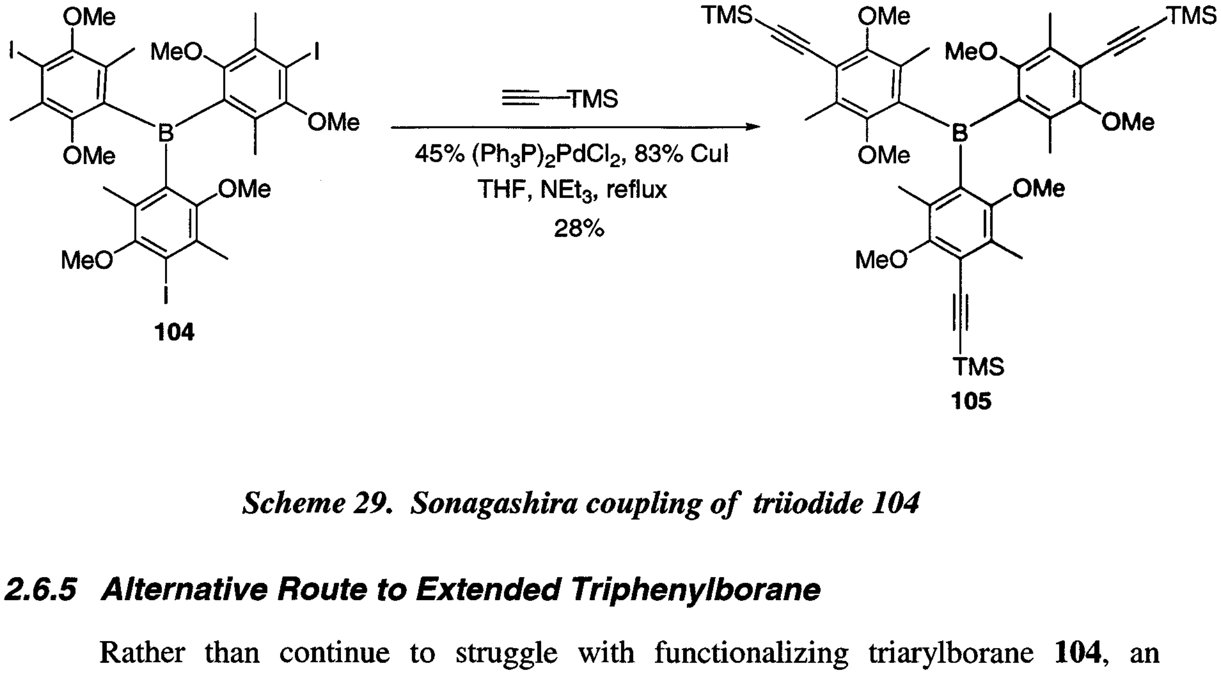


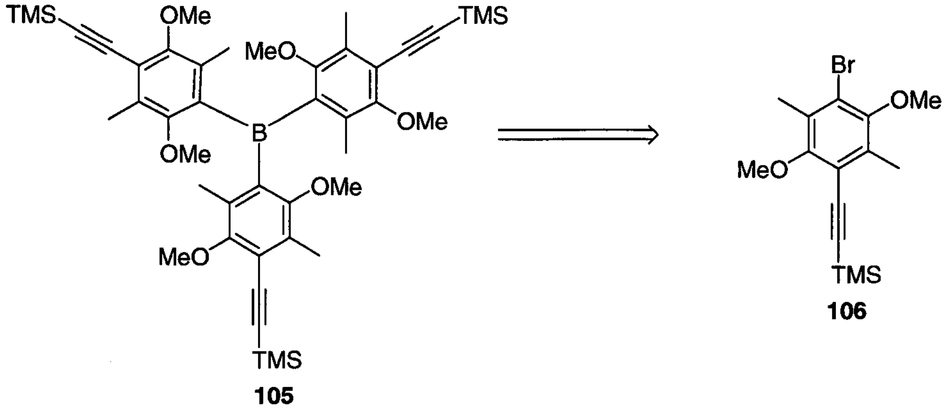
Figure 18. Depiction of the TLC obtained from the reaction shown in Scheme 29



Scheme 29. Sonagashira coupling of triiodide 104

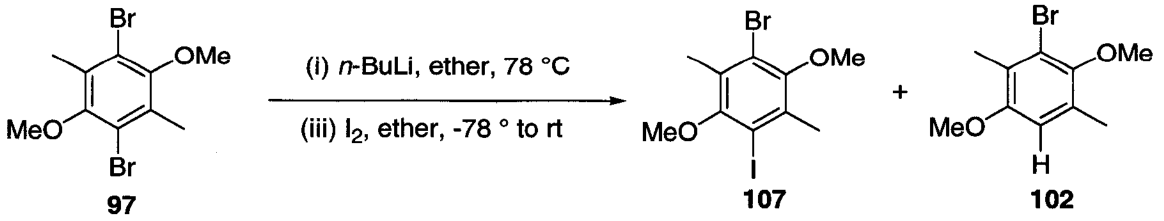
2.6.5 Alternative Route to Extended Triphenylborane

Rather than continue to struggle with functionalizing triarylborane **104**, an alternative route to **105** was developed starting from arylacetylene **106** (Scheme 30). In this new strategy, lithiation of arylacetylene **106** followed by quenching with $BF_3{\cdot}OEt_2$ would yield **105** directly. This route would also help to establish whether the reluctance of **104** in undergoing the Sonagashira coupling reaction with trimethylsilylacetylene was specific to **104** or whether the 1,4-dimethoxy-2,5-dimethylbenzene unit is a poor substrate for palladium coupling in general.

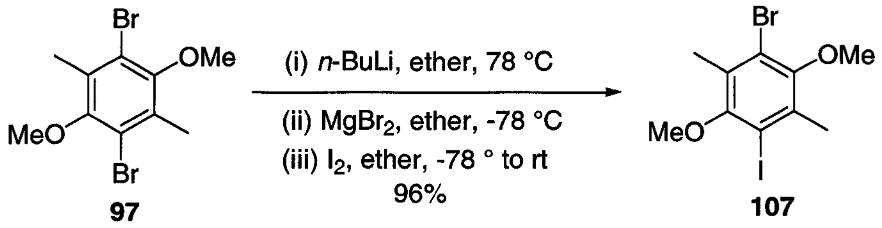


Scheme 30. Alternative route to the extended triphenylborane, 105

In accord with the established reactivity of arylhalides towards palladium coupling, dibromide **97** was converted to the more reactive bromoiodide, **107**. Treatment of **97** with one equivalent of *n*-BuLi and subsequent quenching with iodine gave a mixture of starting material (**97**), bromide **102** and the desired product, **107** (Scheme 31). Further experiments revealed that the formation of the quenched intermediate, bromide **102**, could be completely suppressed by transmetallation of the mono-lithium to the corresponding Grignard with $MgBr_2$ prior to quenching with iodine. In this case, iodide **108**, was obtained in 96% yield with minor amounts of dibromide **97**, that could not be separated by chromatography (Scheme 32).

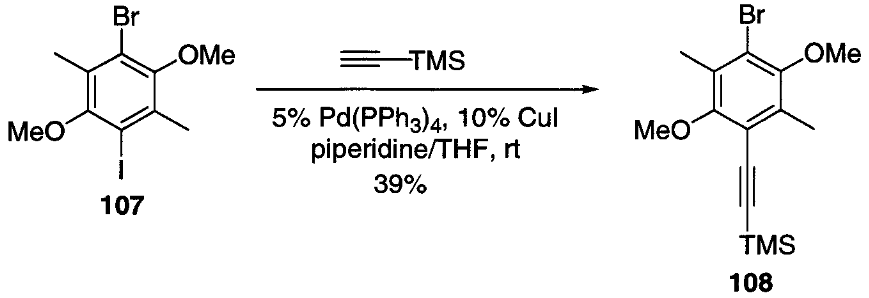


Scheme 31. Initial attempt toward synthesis of bromoiodide 107



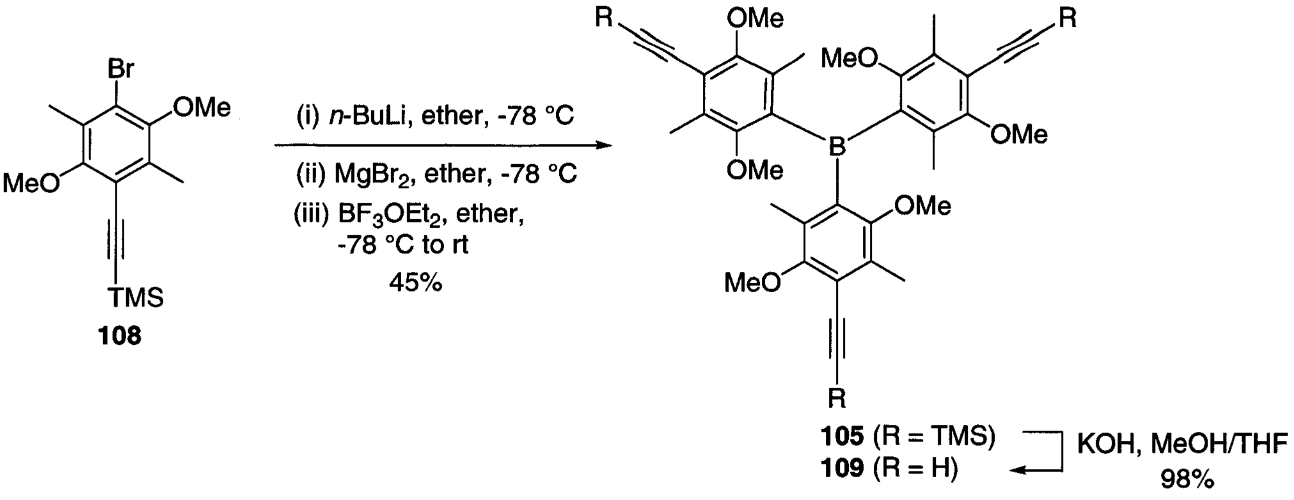
Scheme 32. Optimized conditions for synthesis of bromoiodide 107

Optimized conditions for the subsequent Sonagashira coupling reaction of **107** with trimethylsilylacetylene are presented below (Scheme 33). When piperidine was used as the base, GC-MS analysis showed complete conversion of iodide **107** to acetylene **108** after the reaction was stirred at room temperature for 2 days. Use of piperidine was essential to avoid formation of inseparable side products, which resulted when the reaction was performed in triethylamine. Despite the absence of any other peaks in the GC-MS, the desired product was isolated as a mixture with the dibromide **97** (a component of the starting material) in only 39% yield.



Scheme 33. Sonagashira coupling of bromoiodide 107

With **108** in hand, triarylborane **105** could be synthesized. In a manner analogous to preparation of tribromide **96**, **108** was converted to the corresponding magnesium bromide by lithium-halogen exchange with *n*-BuLi and subsequent transmetallation with $MgBr_2$. Quenching with $BF_3{\cdot}OEt_2$ afforded the desired product in 45% yield.

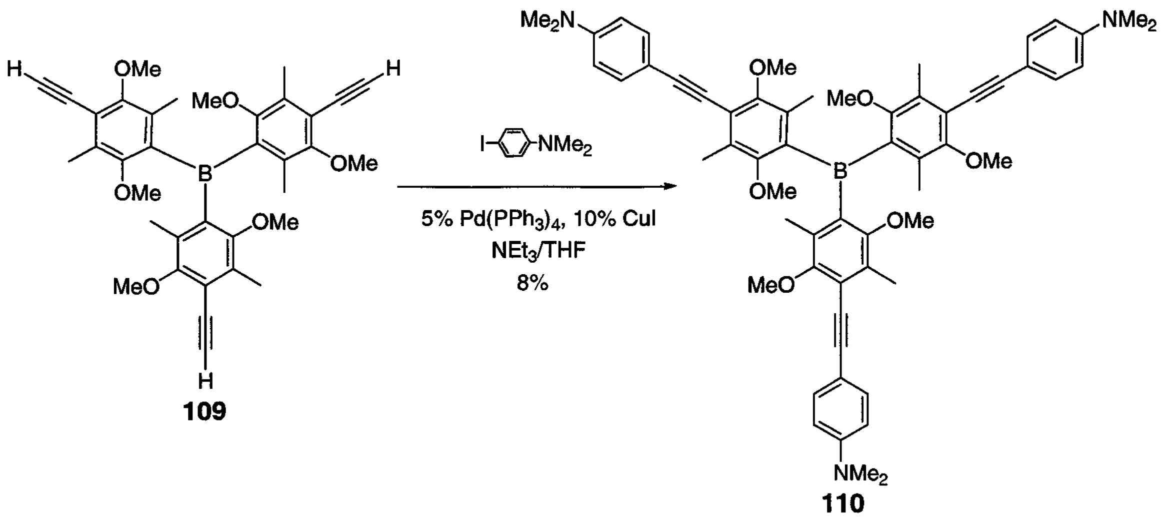


Scheme 34. Synthesis of extended triphenylborane 105

Desilylation of **105** with KOH in methanol afforded the deprotected compound, **109**, allowing for subsequent Sonagashira coupling reactions with aryl halides (Scheme 34).

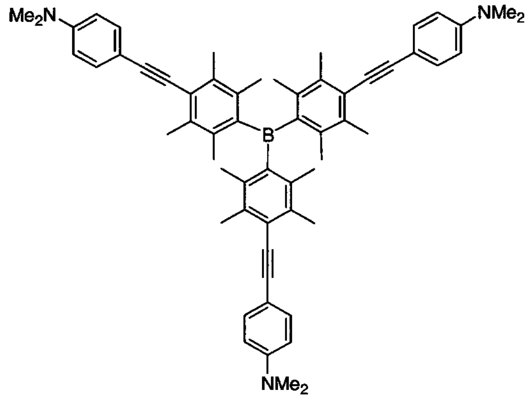
2.6.6 Sonagashira Coupling of Tris(ethynylphenyl)borane 109

Due to time constraints, our original goal to incorporate azulene into the novel triphenylborane was revised. A more simplistic end-group that would still display interesting photophysical properties was chosen. Yamaguchi *et al.* found that the *N,N*-dimethylaniline derivative of tris(ethynylduryl)borane **70** displayed the most intense and longest wavelength absorptions due to the strong electron-donating power of the para-amino group to the electron-deficient boron center.[30] Accordingly, triarylborane **109** was coupled with (4-iodo-phenyl)-dimethylamine under Sonagashira reaction conditions (Scheme 35). A solution of **109** in THF was added to a mixture of the (4-iodo-phenyl)-dimethylamine, 5% $Pd(PPh_3)_4$ and 10% CuI in triethylamine and was stirred at room temperature for several days. Column chromatography produced a streaky yellow band from which the desired product was eventually isolated in 8% yield.



Scheme 35. Synthesis of the extended chromophore, 110

The optical properties of **110** in THF are summarized in Table 4, along with its precursor **109**, and Yamaguchi's dimethylaniline derivative, **64a**. Figure 20a represents the UV-vis absorption spectrum of **110**, in which the λ_{max} is red-shifted by 54 nm in comparison to its precursor **109**. Again, this result can be rationalized as the extension of π-conjugation upon incorporation of the strongly electron-donating dimethylaniline substituents. The absorption maximum of **64a** is 26 nm longer than that of **110**. Both **109** and the extended chromophore **110** were highly fluorescent. The emission spectra are shown in Figure 20b and the data is summarized in Table 4. The emission maximum of **110** is approximately equal to the analogous durylborane, **64a**, and is red-shifted by about 11 nm in comparison to its precursor **109**.



64a

Figure 19. Yamaguchi's analogous tridurylborane 64a

Table 4. Optical properties of compound 109 and 110

Compound	**UV-Vis,[a] λ_{max} (nm)**	**Fluorescence,[a] λ_{max} (nm)**
109	313	500
110	367	511
64a	393	512

[a] In THF

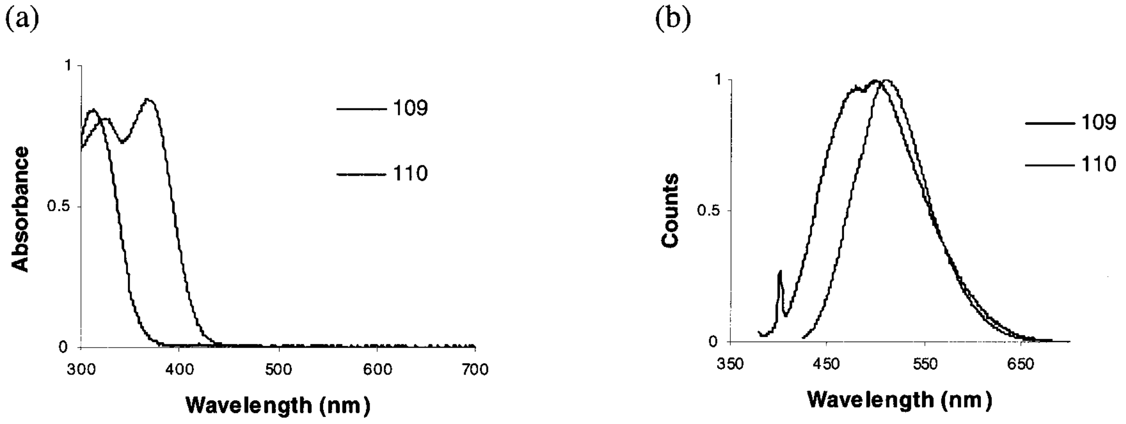


Figure 20. (a) UV-Vis absorption spectra of 109 and 110; (b) Fluorescence spectra of 109 and 110

Conclusions

The primary objective of this research project was to synthesize novel π-conjugated triarylboranes. Azulene was successfully incorporated into an existing class of tridurylboranes and a new class of π-conjugated triarylboranes containing heteroatom substituents was prepared.

The known tris(ethynylduryl)borane **70** was prepared in accordance to a literature procedure[30b] and underwent a Sonagashira coupling reaction with 2-iodoazulene to afford the novel borane, **83**. Triazulene **83** was a green solid, which displayed unique photophysical properties with an absorption maximum of 421 nm, bathochromic shifted by nearly 80 nm from its precursor, **70**. A Sonagashira coupling reaction of **70** with 3-bromophenanthroline yielded a yellow solid, which could not be characterized due to its insolubility in organic solvents.

Tris(tetramethoxyphenyl)borane **79** was prepared in low yield from mono-lithiation of 1,4-dibromo-2,3,5,6-tetramethoxybenzene (**80**) and quenching with $BF_3{\cdot}OEt_2$. Dibromotetramethoxybenzene **80** was itself prepared in four steps from 1,4-benzoquinone. Attempts to obtain the corresponding triarylboranes **90** and **91** from mono-lithiation of tetramethoxybenzene **53** or diiodotetramethoxybenzene **89**, respectively, followed by a $BF_3{\cdot}OEt_2$ quench failed to produce the desired products. The inability to form a triarylborane from these starting materials was attributed to the intermolecular association of the lithium anions with methoxy functionalities on neighbouring molecules. A reduction in electron density on the aromatic ring was proposed as a potential solution to this problem.

Thus, tris(dimethyldimethoxyphenyl)borane **96** was prepared by mono-lithiation of 1,4-dibromo-2,5-dimethoxy-3,6-dimethylbenzene (**97**), transmetallation with $MgBr_2$, and quenching with $BF_3{\cdot}OEt_2$. Borane **96** displayed restricted motion in solution at room temperature and a variable-temperature ^1H NMR study revealed that the borane existed as an approximately 10:1 ratio of the staggered propellar BB' conformation to the symmetrical propellar AA' conformation at low temperature. Borane **96** was subsequently converted to the more reactive triiodide **104** which underwent Sonagashira coupling with trimethylsilylacetylene to afford tris(ethynylphenyl)borane **105** in low yield. An alternative pathway to **105** was devised from ethynylbenzene **108**, itself constructed from dibromobenzene **97**. Deprotection of **105** followed by Sonagashira coupling with (4-iodophenyl)-dimethylamine afforded chromophore **110**. Borane **110** displayed intense UV-vis and fluorescence maxima, which were significantly red-shifted in comparison to the precursor **109**, due to the extension of π-conjugation.

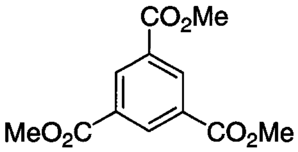
Chapter 3: Experimental

Proton magnetic resonance (^{1}H NMR) and proton-decoupled carbon magnetic resonance spectra (^{13}C NMR) were measured at 500 MHz (Bruker AMX500 spectrometer), 300 MHz (Bruker Avance300 spectrometer) or 200 MHz (Varian Gemini 200 spectrometer). Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (δ scale) and the temperature of the probe is indicated where appropriate in Kelvin (unless otherwise indicated, NMR spectra were obtained at room temperature). The multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad), number of protons, and coupling constants (reported in Hz) are indicated in parentheses. Electron impact mass spectra (EI (MS)) were determined on a Kratos Concept 2H instrument using an ionization energy of 70 eV. Electrospray mass spectra (ES (MS)) were determined on a Micromass Quattro LC with a pump rate of 20 μL/min. The masses of the most naturally abundant isotopes of each element (ie. Br^{79}, Cl^{35}, Sn^{118}, Si^{28}, Cr^{52}, and B^{11}) were used to calculate M^+.

All non-aqueous reactions were performed under an atmosphere of dry nitrogen or dry argon in flame or oven dried glassware equipped with a magnetic stir bar and a rubber septum. Room temperature corresponds to 23 °C. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. Reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminum sheets pre-coated (0.2 mm layer thickness) with silica gel 60 F_{254} (E. Merck). Organic layers after separations were dried over anhydrous magnesium sulfate unless otherwise specified. Concentration of organic layers was performed *in vacuo* at pressures obtained by a water aspirator drawing on a rotoevaporator. Trace and high boiling solvents were removed on a vacuum pump. Product purification by chromatography refers to flash column chromatography performed using E. Merck Silica Gel (70-230 or 230-400 mesh).

Petroleum ether refers to a mixture of hydrocarbons with a boiling range of 30 – 60 °C. Anhydrous diethyl ether (ether), and tetrahydrofuran (THF) were freshly distilled from benzophenone ketal/sodium. Anhydrous benzene, toluene, dichloromethane, and triethylamine were distilled from NaH or CaH. Dibutyl ether was used as an anhydrous solvent from Aldrich Chemical Company without drying. *n*-BuLi, *s*-BuLi, and *t*-BuLi were used as commercially available solutions in hexanes from Aldrich Chemical Company and titrated prior to use against diphenylacetic acid. All commercial starting materials were purchased from Aldrich Chemical Company unless otherwise stated.

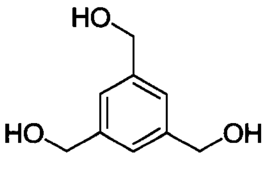
Trimethyl-1,3,5-benzenetricarboxylate



33

$BF_3 \cdot OEt_2$ (6 mL) was added to a suspension of 1,3,5-benzenetricarboxylic acid (4.02 g, 0.0191 mol) in MeOH (60 mL) and the reaction mixture was heated to reflux overnight (~20 h). After cooling, the reaction mixture was quenched with water (160 mL) and extracted with ether. The extract was washed with brine, dried, and concentrated to afford triester **33** as a colourless solid (4.52 g, 94%). m.p. 143-145 °C (lit. m.p.[47] 145-147 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 3H, ArH), 3.95 (s, 9H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 134.5, 131.1, 52.6; MS (EI) *m/z* (relative intensity) 252 (M^+, 19), 221 (M^+-OMe, 100), 75 ($C_6H_3^+$, 23).

(3,5-Bis-hydroxymethyl-phenyl)-methanol



34

Triester **33** (4.98 g, 0.0197 mol) was dissolved in THF (50 mL) and added dropwise to a cooled (0 °C) suspension of $LiAlH_4$ (2.52 g, 0.0665 mol) in THF (175 mL) over ~15 minutes. The reaction mixture was warmed to room temperature and then heated to reflux overnight (~20 h). The solution was then cooled to 0 °C and quenched with H_2O (2.5 mL), 15% NaOH (2.5 mL), and H_2O (7.5 mL) and stirred at room temperature overnight. The solution was filtered through celite and the insoluble suspension washed with ether (3 x 225 mL). The ether extract was concentrated and the resulting oil was

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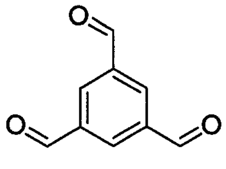
[47] Aldrich Chemical Catalog, 2001-2002.

recrystallized from hot ethyl acetate to yield the triol **34** as a colourless solid (2.44 g, 74%). m.p. 74-75 °C (lit. m.p.[48] 77 °C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.11 (s, 3H, ArH), 5.15 (t, J = 6Hz, 3H, OH), 4.46 (d, J = 6Hz, 6H, OCH_2); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.1, 122.9, 63.0; MS (EI) *m/z* (relative intensity) 168 (M^+, 62), 137 (M^+-CH_2OH, 59), 91 ($C_7H_7^+$, 100).

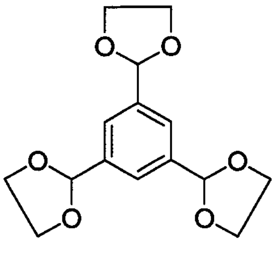
Benzene-1,3,5-tricarbaldehyde



36

Triol **36** (2.02 g, 0.0120 mol) was dissolved in DMSO (5 mL) and added dropwise to a cooled (0 °C) solution of IBX (11.0 g, 0.0392 mol) in DMSO (25 mL). The reaction was extremely exothermic and complete within several minutes. The reaction mixture was diluted with water (20 mL) and filtered. The filter cake was washed with water and ethyl acetate and the two layers were separated. The water layer was extracted with ethyl acetate and the organic extracts were washed several times with water to remove residual DMSO. The extracts were dried and concentrated to yield trialdehyde **36** as a colourless solid (1.84 g, 94%). m.p. 155-159 °C (lit. m.p.[48] 155.5-160 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 10.19 (s, 3H, CHO), 8.62 (s, 3H, ArH) MS (EI) *m/z* (relative intensity) 162 (M^+, 100), 133 (M^+-CHO, 35).

1,3,5-(tri(1',3'-dioxolano)benzene carbaldehyde



37

Trialdehyde **36** (101 mg, 0.624 mmol), ethylene glycol (1.5 mL, 0.0217 mol) and Amberlyst-15 ion-exchange resin (100 mg) in benzene (19 mL) were heated to reflux in a Dean-Stark trap overnight (~24 h). The solution was diluted with water and ethyl acetate,

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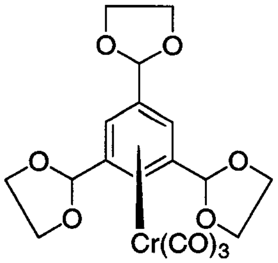
[48] Cochrane, W.P.; Pauson, P.L.; Stevens, T.S. *J. Chem. Soc. (C)*. **1968**, 630.

filtered and the two layers were separated. The water layer was extracted with ethyl acetate. The organic extracts were washed with brine, dried, and concentrated to yield triacetal **37** as a colourless solid (155 mg, 84%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.50 (s, 3H, ArH), 5.75 (s, 3H, CH), 3.91-4.07 (m, 12H, OCH_2); ^{13}C NMR (75 MHz, DMSO-d_6) δ 138.4, 125.5, 102.3, 64.9; MS (EI) *m/z* (relative intensity) 294 (M^+, 16), 293 (M^+-H, 92), 249 (M^+-OCH_2CH_2, 37) 221 (M^+-H-OCH_2CH_2-CO, 56), 73 (100).

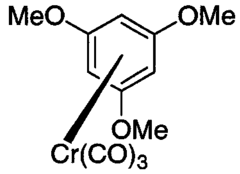
Tricarbonyl(η^6-1,3,5-(tri(1',3'-dioxolano)benzene carbaldehyde)chromium(0)



31

$Cr(CO)_6$ (83 mg, 0.376 mmol) was added to a suspension of acetal **37** (103 mg, 0.340 mmol) in a mixture of degassed dibutyl ether/THF (5 mL/0.5 mL) and the reaction mixture was heated to reflux overnight (~23 h). The solution became homogeneous at reflux temperature and gradually turned bright yellow. A brown precipitate developed after approximately 20 hours at reflux and became progressive until the reaction was eventually discontinued. After cooling, the solution was filtered through Celite and washed with THF. The yellow solution was concentrated to yield an inseparable mixture of acetal **37** and complexed acetal **31** as a yellow solid (115 mg). Acetal **31**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.77 (s, 3H, ArH), 5.58 (s, 3H, CH) 3.91-4.07 (m, 12H, OCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 231.2, 104.3, 101.3, 90.3, 65.8; MS (EI) *m/z* (relative intensity) 430 (M^+, 4), 346 (M^+-3CO, 12), 73 (100); HRMS exact mass calcd. for $C_{18}H_{18}O_9Cr_1$ 430.0356, found 430.0341.

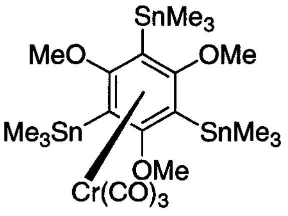
Tricarbonyl(η^6-1,3,5-trimethoxybenzene)chromium(0)



39

A solution of 1,3,5-trimethoxybenzene (**38**) (5.00 g, 0.0297 mol) and $Cr(CO)_6$ (7.20 g, 0.0327 mol) in a mixture of degassed dibutyl ether/THF (100 mL/10 mL) was heated to reflux for 2 days (~45 h). Subliming $Cr(CO)_6$ was returned to the flask periodically by shaking. A yellow solid crystallized from the solution upon cooling and was collected by filtration to yield **39** as a bright yellow solid (8.63 g, 95%). m.p. 145 °C (dec.); ^{1}H NMR ($CDCl_3$, 300 MHz) δ ^{13}C NMR ($CDCl_3$, 75 MHz) δ 234.1, 142.6, 64.6, 55.8; MS (EI) *m/z* (relative intensity) 304 (M^+, 11), 220 (M^+-3CO, 48), 168 (M^+-3CO-Cr, 100); HRMS exact mass calcd. for $C_{12}H_{12}O_6Cr_1$ 304.0039, found 304.0004.

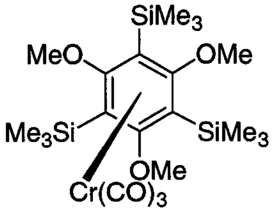
Tricarbonyl(η^6-1,3,5-trimethoxy-2,4,6-trimethylstannylbenzene)chromium(0)



42

n-BuLi (0.5 mL, 2.5 M) was added to a solution of **39** (111 mg, 0.365 mmol) in THF (5 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to –78 °C, $SnMe_3Cl$ (1.2 mL, 1 M) was added and the solution stirred at 0 °C for 1.75 hours. The reaction mixture was quenched with sodium bicarbonate and extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated to yield **42** as a bright yellow solid (260 mg, 90%). m.p. >250 °C (slow dec. >150 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.63 (s, 9H, OMe), 0.42 (s, 27H, $SnMe_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 235.2, 152.5, 86.4, 63.6, -5.6; IR ($CHCl_3$) ν/cm^{-1} 1961, 1887(C=O); MS (EI) *m/z* (relative intensity) 790 (M^+, 14), 708 (100).

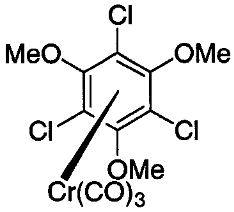
Tricarbonyl(η^6-1,3,5-trimethoxy-2,4,6-trimethylsilylbenzene)chromium(0)



41

n-BuLi (0.9 mL, 2.5 M) was added to a solution of **39** (211 mg, 0.694 mmol) in THF (5 mL) at –78 °C and the reaction mixture warmed to 0 °C for 20 minutes. The yellow suspension was then re-cooled to -78 °C, $SiMe_3Cl$ (0.85 mL, 6.70 mol) was added and the solution stirred at -78 °C for 2.5 hours. The reaction mixture was quenched with sodium bicarbonate and extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated to yield **41** as a bright yellow solid (315 mg, 87%). m.p. >250 °C (slow dec. >150 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.70 (s, 9H, OMe), 0.41 (s, 27H, $SiMe_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 234.7, 154.1, 86.6, 64.7, 3.0; IR ($CHCl_3$) ν/cm^{-1} 1968, 1896 (C=O); MS (EI) *m/z* (relative intensity) 520 (M^+, 10), 436 (M^+-3CO, 100), 384 (M^+-3CO-Cr, 6).

Tricarbonyl(η^6-1,3,5-trichloro-2,4,6-trimethoxybenzene)chromium(0)

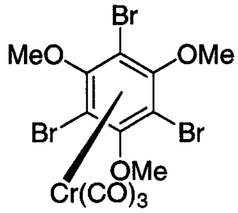


43

n-BuLi (0.4 mL, 2.5 M) was added to a solution of **39** (103 mg, 0.338 mmol) in THF (5 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to -78 °C, a solution of Cl_3CCCl_3 (257 mg, 1.09 mmol) in THF (1 mL) was added and the solution was stirred at 0 °C for 1.5 hours. The reaction mixture was quenched with sodium bicarbonate and extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated to yield **43** as a bright yellow solid (135 mg, 98%). m.p. 134-135 °C (dec.); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.94 (s, 9H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 229.1, 128.4, 102.2, 64.7; IR ($CHCl_3$) ν/cm^{-1} 1988, 1926 (C=O); MS (EI) *m/z* (relative intensity) 410 (M^+ + 4, 12), 408 (M^+ + 2, 39), 406

(M^+, 36), 350 (M^+-2CO, 18), 322 (M^+-3CO,100); HRMS exact mass calcd. for $C_{12}H_9O_6Cl_3Cr_1$ 405.8870, found 405.8957.

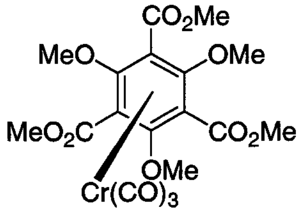
Tricarbonyl(η⁶-1,3,5-tribromo-2,4,6-trimethoxybenzene)chromium(0)



44

n-BuLi (2.2 mL, 2.5 M) was added to a solution of **39** (504 mg, 1.66 mmol) in THF (15 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to -78 °C, $BrCF_2CF_2Br$ (0.65 mL, 5.44 mmol) was added and the solution was stirred at 0 °C for 2 hours. The reaction mixture was quenched with sodium bicarbonate and extracted with ethyl acetate. The extract was washed with brine, dried and concentrated to yield **44** as a bright yellow solid (400 mg, 45%). m.p. 148 °C (slow dec.); ^1H NMR ($CDCl_3$, 200 MHz) δ 3.94 (s, 9H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 229.2, 131.9, 86.8, 63.7; IR ($CHCl_3$) ν/cm^{-1} 1994, 1930 (C=O); MS (EI) *m/z* (relative intensity) 542 (M^+ + 4, 27), 540 (M^+ + 2, 28), 538 (M^+, 11), 484 (M^+-2CO, 17), 456 (M^+-3CO, 100); HRMS exact mass calcd. for $C_{12}H_9O_6Br_3Cr_1$ 537.7354, found 537.7390.

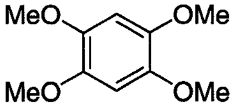
Tricarbonyl(η⁶-1,3,5-trimethoxy-2,4,6-trimethylbenzenetricarboxylate)chromium(0)



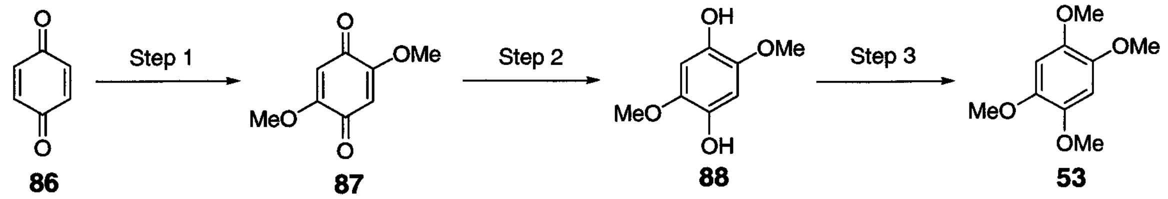
47

n-BuLi (0.45 mL, 2.5 M) was added to a solution of **39** (104 mg, 0.343 mmol) in THF (5 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to -78 °C, CO_2MeCl (0.1 mL, 1.29 mmol) was added and the solution was stirred at 0 °C for 1 hour. The reaction mixture was quenched with sodium bicarbonate and extracted with CH_2Cl_2. The extract was washed with brine, dried and concentrated to yield **47** as a bright yellow solid (167 mg, 100%). ^1H NMR ($CDCl_3$, 200 MHz) δ 3.89 (s, 9H, OMe), 3.83 (s, 9H, CO_2Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 229.0, 163.8, 135.5, 84.6, 63.3, 53.9; IR ($CHCl_3$) $\dot{\nu}$/cm^{-1} 1996, 1925 (C=O); MS (EI) *m/z* (relative intensity) 478 (M^+, 12), 304 (100); HRMS exact mass calcd. for $C_{18}H_{18}O_{12}Cr_1$ 478.0203, found 478.0188.

1,2,4,5-Tetramethoxybenzene



53



The following procedure was adapted from Benington *et al.*[41]

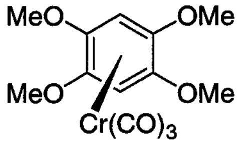
Step 1: A solution of *para*-benzoquinone (21.58 g, 0.200 mol) and $ZnCl_2$ (24.59 g, 0.180 mol) in MeOH (120 mL) was heated to reflux for 30 minutes. The red reaction mixture was then cooled in an ice-water bath for several hours. The resulting solid was collected by filtration, washed with cold MeOH and air-dried to afford **87** as a dark brown solid (9.83 g, 29%). The benzoquinone was used directly in the next step.

Step 2: Boiling water (100 mL) was added in one portion to a round bottom flask containing a mixture of quinone **87** (9.83 g, 0.058 mol) and $Na_2S_2O_4$ (1 g, 5.80 mmol) and the solution shaken vigorously for 1 minute. The solid suspension turned colourless during this time. The reaction mixture was then submersed in an ice-water bath and shaken for another 30 seconds and subsequently allowed to sit in the cold for several hours. The resulting solid was collected by filtration, washed with cold water, and air-dried to afford **88** as a colourless solid (9.65 g, 97%), which was used directly in the next step.

Step 3: Diol **88** (9.65 g, 0.057 mol), $Na_2S_2O_4$ (1.02 g, 5.86 mmol), and Me_2SO_4 (35 mL, 0.493 mol) were dissolved in MeOH (25 mL) and the reaction mixture was cooled in an ice-water bath. A solution of NaOH (14.40 g, 0.360 mol) in water (32 mL) was added dropwise by addition funnel over approximately 30 minutes and the reaction mixture was subsequently warmed to 80 °C for 30 minutes. Water (100 mL) was added and the heterogeneous solution was cooled in an ice-water bath for several hours. The resulting precipitate was collected by filtration, washed with cold water, and dried to yield **53** (8.23 g, 73%) as a colourless solid. m.p. 102 °C (lit. m.p.[41] 103 °C); ^{1}H NMR ($CDCl_3$, 200

MHz) δ 6.58 (s, 2H, ArH), 3.83 (s, 12H, OMe); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.0, 112.8, 61.0; MS (EI) *m/z* (relative intensity) 198 (M^+, 100), 183 (M^+-15, 49).

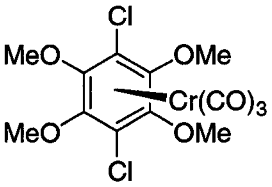
Tricarbonyl(η^6-1,2,4,5-tetramethoxybenzene)chromium(0)



54

A solution of 1,2,4,5-tetramethoxybenzene (2.04 g, 0.0103 mol) and $Cr(CO)_6$ (2.26 g, 0.0103 mol) in degassed dibutyl ether/THF (80 mL/8 mL) was heated to reflux overnight (~ 20 h). After cooling, the bright yellow solution was filtered through celite and concentrated. Excess $Cr(CO)_6$ sublimed during the removal of the solvent. Column chromatography (25% petroleum ether/CH_2Cl_2) afforded **54** as a bright yellow solid (1.72 g, 50%). m.p. 134-137 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.41 (s, 2H, ArH), 3.80 (s, 12H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 234.2, 126.8, 68.7, 58.5; IR ($CHCl_3$) ν/cm^{-1} 1960, 1874 (C=O); MS (EI) *m/z* (relative intensity) 334 (M^+, 7), 250 (M^+-3CO, 26), 198 (M^+-3CO-Cr, 100); HRMS exact mass calcd. for $C_{13}H_{14}O_7Cr_1$ 334.0145, found 334.0140.

Tricarbonyl(η^6-1,4-dichloro-2,3,5,6-tetramethoxybenzene)chromium(0)

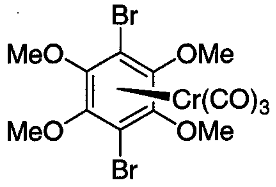


55

n-BuLi (0.53 mL, 2.5 M) was added to a solution of **54** (200 mg, 0.600 mmol) in THF (4.5 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to -78 °C, a solution of Cl_3CCCl_3 (351 mg, 1.48 mmol) in THF (2.5 mL) was added and the solution was stirred at –78 °C for 2 hours. The reaction mixture was warmed to room temperature, quenched with sodium bicarbonate and extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated to yield **55** as a bright yellow solid (240 mg, 99%). m.p. 85-87 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.94 (s, 12H, OMe); ^{13}C NMR ($CDCl_3$, 125 MHz) 230.7, 127.7, 68.0, 64.3; IR ($CHCl_3$) ν/cm^{-1} 1981, 1916 (C=O); MS (EI) *m/z* (relative intensity) 404 (M^+ + 2, 22), 402

(M^+, 34), 346 (M^+-2CO, 20), 318 (M^+-3CO, 100); HRMS exact mass calcd. for $C_{13}H_{12}O_7Cl_2Cr_1$ 401.9365, found 401.9351.

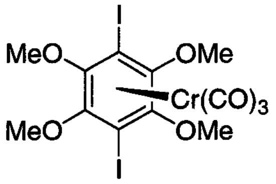
Tricarbonyl(η^6-1,4-dibromo-2,3,5,6-tetramethoxybenzene)chromium(0)



56

n-BuLi (0.79 mL, 2.5 M) was added to a solution of **54** (300 mg, 0.899 mmol) in THF (4 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to -78 °C, $BrCF_2CF_2Br$ (0.24 mL, 2.01 mmol) was added and the solution was stirred at -78 °C for 1.5 hours. The reaction mixture was warmed to room temperature, quenched with sodium bicarbonate, and extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated to yield **56** as a bright yellow solid (425 mg, 96%). m.p. 120-123 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (s, 9H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 230.8, 128.5, 89.6, 64.2; IR ($CHCl_3$) *ν*/cm^{-1} 1981, 1916 (C=O); MS (EI) *m/z* (relative intensity) 494 (M^+ +4,4), 492 (M^+ + 2, 10), 490 (M^+, 4), 408 (M^+-3CO, 40), 28 (100); HRMS exact mass calcd. for $C_{13}H_{12}O_7Br_2Cr_1$ 491.8336, found 491.8373.

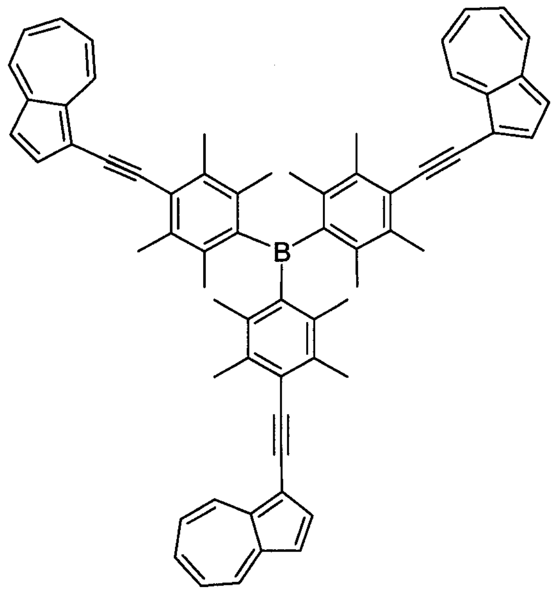
Tricarbonyl(η^6-1,4-diiodo-2,3,5,6-tetramethoxybenzene)chromium(0)



57

n-BuLi (0.79 mL, 2.5 M) was added to a solution of **54** (303 mg, 0.908 mmol) in THF (4 mL) at –78 °C and the reaction mixture warmed to 0 °C for 15 minutes. The yellow suspension was then re-cooled to -78 °C, a solution of I_2 (683 mg, 2.69 mmol) in THF (3.5 mL) was added and the solution was stirred at -78 °C for 6 hours. The reaction mixture was warmed to room temperature, quenched with sodium bicarbonate, and extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated to yield **57** as a bright yellow solid (491 mg, 92%). m.p. 145 °C (dec.); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.86 (s, 9H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 231.7, 129.9, 64.0, 62.1; IR ($CHCl_3$) ν/cm^{-1} 1977, 1914 (C=O); MS (EI) *m/z* (relative intensity) 586 (M^+, 17), 502 (M^+-3CO, 24), 450 (M^+-3CO-Cr, 100); HRMS exact mass calcd. for $C_{13}H_{12}O_7I_2Cr_1$ 585.8078, found 585.8066.

Tris[(2-azulenylethynyl)duryl]borane



83

The following procedure was adapted from Yamaguchi et.al.[30]

Step 1 (**66**)*:* Br_2 (2.0 mL, 0.039 mol) was added to a solution of durene (4.98 g, 0.037 mol) and $PhI(OAc)_2$ (13.29 g, 0.041 mol) in a mixture of AcOH (56 mL) and Ac_2O (56 mL). A catalytic amount of concentrated H_2SO_4 (4 drops) was then added. The bromination was complete within a few minutes by TLC and could be visualized by discoloration of the reaction mixture and formation of a thick precipitate. The mixture was poured into a stirred 5% Na_2SO_3 solution and buffered with $(NH_4)_2CO_3$. The precipitate was collected by filtration, washed with cold water and air-dried. Recrystallization from hot ethanol afforded **66** (8.44 g, 78%) as a colourless solid. m.p. 202 °C (lit. m.p.[30] 202 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 12H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.0, 128.1, 22.2; MS (EI) *m/z* (relative intensity) 294 (M^+ + 4, 53), 292 (M^+ + 2, 100), 290 (M^+, 60), 211 (M^+-Br, 62).

Step 2 (**67**)*:* *n*-BuLi (12.3 mL, 2.5 M) was added dropwise to a solution of dibromodurene (**66**) (8.87 g, 0.03 mol) in ether (150 mL) at –78 °C and the reaction mixture was warmed to 0 °C and stirred for 20 minutes. $BF_3 \cdot OEt_2$ (1.3 mL, 0.010 mol) was then added and the solution warmed to room temperature and stirred overnight (~20 h). After addition of water, the reaction mixture was extracted with ether. The ether extract was washed with brine, dried, and concentrated . The solid was dissolved in ether and MeOH was added to induce precipitation. The insoluble part was collected by filtration and washed with MeOH to afford **67** (4.59 g, 70%) as a colourless solid. m.p. 287 °C (lit. m.p.[30] 292 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.32 (s, 18H, Me), 1.98 (s, 18H, Me).

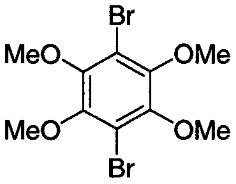
Step 3 (**68**)*:* *t*-BuLi (16.6 mL, 1.7 M) was added dropwise to a suspension of **67** (3.01 g, 4.66 mmol) in THF (100 mL) at –78° C and the reaction mixture was stirred for 50 minutes. A solution of I_2 (5.42 g, 0.021 mol) in THF (50 mL) was then added by cannula to the cold solution and the reaction mixture was warmed to room temperature and stirred overnight. After addition of water, the THF was removed and the reaction mixture was extracted with dichloromethane. The extract was washed with $Na_2S_2O_3$ and brine, dried, and concentrated to yield **68** as a colourless solid (2.77 g, 76%). m.p. 262° C (lit. m.p.[30] 262 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.42 (s, 18H, Me), 2.02 (s, 18H, Me).

Step 4 (**69**)*:* Triiodide **68** (3.58 g, 4.54 mmol), $PdCl_2(PPh_3)_4$ (478 mg, 0.681 mmol), and CuI (261 mg, 1.4 mmol) were dissolved in Et_2NH (50 mL) and the solution was degassed with nitrogen for several minutes. A solution of TMS-acetylene (2.8 mL, 0.020 mol) in Et_2NH (10 mL) was then added dropwise and the mixture was heated at reflux for 48 hours. Another aliquot of TMS-acetylene (1.4 mL, 0.01 mol) was necessary following 24 hours at reflux. The reaction was difficult to follow by TLC and so was cooled to room temperature and concentrated. After addition of water, the mixture was extracted with ether. The ether extract was washed with 1 M HCl and brine, dried, and concentrated. Purification by column chromatography (petroleum ether) yielded **69** (1.68 g, 53%) as a colourless solid. Despite the large excess of TMS-acetylene, partially iodinated compound was recovered which indicated that the reaction had not gone to completion. It should be noted that Yamaguchi et al. reported to have achieved a 94% yield of **69** after only 10 hours at reflux. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.31 (s, 18H, Me), 1.87 (s, 18H, Me), 0.246 (s, 27H, $SiMe_3$).

Step 5 (**70**)*:* A solution of powdered KOH (326 mg, 5.81 mol) and **69** (326 mg, 0.466 mmol) in a mixture of MeOH (26 mL) and THF (13 mL) was stirred for 2 hours. After addition of water, the solution was concentrated and the water layer was extracted with ether. The ether extract was washed with 1 M HCl, and brine, dried, and concentrated to yield a colourless solid, which was suspended in hexanes and collected by filtration to afford **70** (215 mg, 97%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.51 (s, 3H, C≡C–H), 2.33 (s, 18H, Me), 1.91 (s, 18H, Me).

Step 6 (**83**)*:* 2-Iodoazulene was obtained by the method of Hafner *et al.*[38] Special care was taken to work expediently to avoid decomposition, which occurs readily at room temperature. 2-Iodoazulene (296 mg, 1.16 mmol) was dissolved in Et_3N (50 mL) and degassed for several minutes before addition of $Pd(PPh_3)_4$ (19 mg, 0.016 mmol), and CuI (9 mg, 0.047 mmol). Triarylborane **70** (138 mg, 0.287 mmol) was then added and the reaction mixture was stirred overnight. The color of the reaction mixture changed from blue-purple to blue-green almost immediately. Water was added and the organic layer was concentrated. The residue was extracted with dichloromethane and the extract was washed with 1 M HCl and brine, dried, and concentrated. Purification by column chromatography (20% CH_2Cl_2/petroleum ether) yielded **83** (158 mg, 64%) as a green solid. m.p. >250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.69 (d, J = 9.6 Hz, 1H, AzH), 8.28 (d, J = 9.4 Hz, 1H, AzH), 8.05 (d, J = 4.0 Hz, 1H, AzH), 7.61 (t, J = 9.8 Hz, 1H, AzH), 7.35 (d, J = 4.0 Hz), 7.24 (t, J = 9.7 Hz, 1H, AzH), 7.18 (t, J = 9.7 Hz, 1H, AzH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.4, 141.4, 140.8, 139.3, 138.6, 137.2, 136.4, 135.8, 135.0, 125.3, 124.4, 123.8, 117.9, 111.7, 94.3, 93.8, 20.3, 18.7; IR ($CHCl_3$) ν/cm^{-1} 3056 (C=C–H), 2994, 2926, 2859 (C–H), 2186 (C≡C), 1572, 1498, 1455 (C=C); MS (FAB) *m/z* 860 (M^+).

1,4-Dibromo-2,3,5,6-tetramethoxybenzene



80

This method was adapted from Keegstra *et al.*[49] A solution of bromine (6.4 mL, 0.125 mol) in acetic acid (83 mL) was added dropwise to a suspension of 1,2,4,5-tetramethoxybenzene (**53**) (8.23 g, 0.042 mol) in acetic acid (83 mL). The reaction

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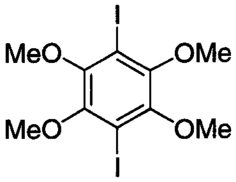
[49] Keegstra, E.M.D.; Huisman, B-H.; Paardekooper, E.M.; Hoogesteger, F.J.; Zwikker, J.W.; Jenneskens, L.W.; Kooijman, H.; Schouten, A.; Veldman, N.; Spek, A.L. *J. Chem. Soc., Perkin Trans. 2.* **Year**, *Volume*, 229.

mixture was heated to reflux for 15 minutes and stirred at room temperature overnight (~20 hours). All of the starting material had been converted to product by GC-MS. The excess bromine and acetic acid were removed (high vacuum) and the residue was recrystallized from acetone (-20 °C). Only a small portion of the desired product could be recovered by recrystallization (3.40 g). Purification by column chromatography (8% ether/petroleum ether) afforded more of the desired product, **80** (2.01 g, 5.41 g total, 37%). A large portion of the crude reaction mixture formed bright red crystals, which could not be eluted from the column. Keegstra *et al.* claimed this compound to be a charge-transfer complex between the starting material and excess bromine. m.p. 131 °C (lit. m.p.[49] 132 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.86 (s, 12 H, OMe); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.0, 112.9, 61.0; MS (EI) *m/z* (relative intensity) 358 (M^+ + 4, 49), 356 (M^+ + 2, 100), 354 (M^+, 52), 339 (M^+-CH_3, 48); HRMS exact mass calcd. for $C_{10}H_{12}O_4Br_2$ 353.9102, found 353.9076.

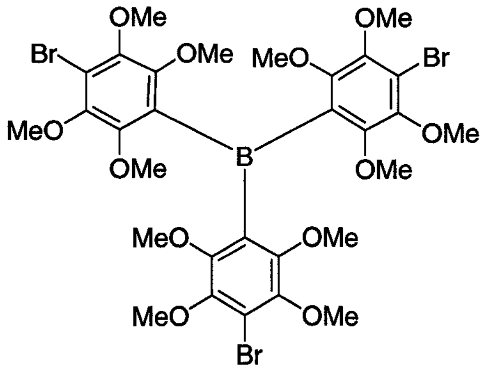
1,4-Diiodo-2,3,5,6-tetramethoxybenzene



89

n-BuLi (25 mL, 2.5 M) was added to a solution of **53** (5.00 g, 0.025 mol) in THF (300 mL) at −78 °C and the reaction mixture was warmed to 0 °C for 1 hour. A solution of I_2 (19.93 g, 0.078 mol) in THF (100 mL) was then added by cannula at −78 °C over 2 hours and the solution was warmed to room temperature and stirred overnight. Following addition of $Na_2S_2O_3$, the reaction mixture was extracted with ethyl acetate. The extract was washed with brine, dried, and concentrated. Purification by column chromatography (10% ethyl acetate/petroleum ether) afforded **89** as a colourless solid (8.83 g, 78%). m.p. 134 °C (lit. m.p.[42] 133-136 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.83 (s, 12H, OMe); MS (EI) *m/z* (relative intensity) 450 (M^+, 100); HRMS exact mass calcd. for $C_{10}H_{12}O_4I_2$ 449.8825, found 449.8812.

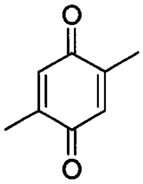
Tris(4-bromo-2,3,5,6-tetramethoxyphenyl)borane



79

n-BuLi (0.24 mL, 2.5 M) was added to a solution of dibromide **80** (200 mg, 0.563 mmol) in ether (5 mL) at –78 °C and the reaction mixture was stirred for 1 hour. $BF_3{\cdot}OEt_2$ (24 μL, 0.189 mmol) was then added and the solution warmed to room temperature. After addition of benzene (8 mL), the reaction mixture was heated at reflux for 48 hours. Following cooling and addition of water, the mixture was extracted with ether. The ether extract was washed with brine, dried, and concentrated. Purification by column chromatography (10% acetone/petroleum ether) yielded **79** as an oily film (21 mg, 13%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.81 (s, 18H, OMe), 3.38 (s, 18H, OMe); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.2, 146.7, 115.2, 60.41, 60.40; IR ($CHCl_3$) ν/cm^{-1} 3023 (C=C–H), 2938, 2849 (C–H), 1549, 1456 (C=C); MS (ES) *m/z* (relative intensity) 879 ($M^+ + K^+ + 4$, 16), 877 ($M^+ + K^+ + 2$, 14), 875 ($M^+ + K^+$, 4), 39 (100).

2,5-Dimethyl-1,4-benzoquinone



99

This method was adapted from Liotta *et al.*[50] 2,5-Dimethylphenol (30.01 g, 0.246 mol) was dissolved in 350 mL ether and the solution was cooled to 0 °C. A solution of $Na_2Cr_2O_7{\cdot}2H_2O$ (161.09 g, 0.540 mol) in H_2SO_4 (100 mL H_2O:230 mL H_2SO_4) was added dropwise by addition funnel over approximately 2 hours. The reaction mixture

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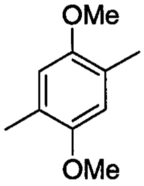
[50] Liotta, D.; Arbiser, J.; Short, J.W.; Saindane, M. *J. Org. Chem.* **1983**, *48*, 2932-2933.

immediately darkened and a thick, green gum formed. The gummy substance eventually impeded stirring and the reaction mixture was shaken periodically and allowed to sit for 72 hours. Following this time, two layers were apparent. A thick green gum had settled on the bottom and the top layer was clear and bright orange. Typical extraction procedures failed to separate the solid material from the ethereal layer. The desired product was most easily recovered by carefully decanting the ethereal layer from the gum. The gum was then repeatedly extracted with large portions of ether and the two layers allowed to settle again before the ether layer was separated by decantation. The combined extracts were washed with sodium bicarbonate and water, dried, and concentrated to yield **99** as a bright orange solid (18.5 g, 56%). m.p. 122-124 °C (lit. m.p.[50] 123.5-125 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.57 (q, J = 1.6 Hz, 2H), 2.01 (d, J = 1.6 Hz, 6H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.9, 145.7, 133.2, 15.3; MS (EI) *m/z* (relative intensity) 136 (M^+, 100).

1,4-Dimethoxy-2,5-dimethylbenzene



100

A bright yellow solution of **99** (488 mg, 3.58 mmol) and PtO_2 (11 mg, 0.048 mmol) in MeOH (5 mL) was subjected to hydrogenation [$P(H_2)$ 1 atm] with vigorous stirring. The reduction was complete by TLC within an hour and could be visualized by discoloration of the solution. The hydrogen atmosphere was replaced with nitrogen, Me_2SO_4 (2.1 mL, 0.0222 mol) was added and the reaction mixture was cooled in an ice-water bath. A solution of NaOH (909 mg, 0.0227 mol) in H_2O (5 mL) was added by addition funnel over approximately 15 minutes and the reaction mixture was subsequently warmed to 75 °C for 30 minutes. Following this time, the heterogeneous solution was cooled in an ice-water bath for several hours. The resulting precipitate was collected by filtration and washed with cold water to yield **100** as a colourless solid (552 mg, 93%). m.p. 106 °C (lit. m.p.[51] 105 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.64 (s, 2H, ArH), 3.76 (s, 6H, OMe),

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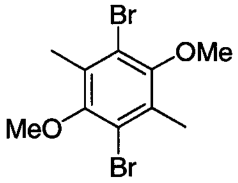
[51] Staab, H.A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3333.

2.18 (s, 6H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.4, 124.2, 113.7, 56.0, 16.0; MS (EI) *m/z* (relative intensity) 166 (M^+, 75), 151 (M^+-CH_3, 100); HRMS exact mass calcd. for $C_{10}H_{14}O_2$ 166.0994, found 166.1002.

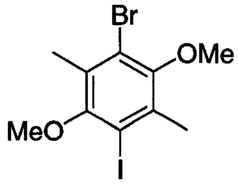
1,4-Dibromo-2,5-dimethoxy-3,6-dimethylbenzene



97

Diether **100** (202 mg, 1.22 mmol) was added to a solution of bromine (0.14 mL, 2.73 mmol) and KBr (862 mg, 7.24 mmol) in H_2O (5 mL). The heterogeneous solution was stirred vigorously at room temperature for approximately 5 hours. Following this time, the, **100** was cleanly converted to **97** by GC-MS. The solid was collected by filtration, dissolved in ether, dried, and concentrated to yield **97** as a fluffy, colourless solid (337 mg, 85%). m.p. 124-125 °C (lit. m.p[51] 125-126 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.73 (s, 6H, OMe), 2.38 (s, 6H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.1, 131.0, 119.8, 60.4, 17.1; MS (EI) *m/z* (relative intensity) 326 (M^+ + 4, 46), 324 (M^+ + 2, 100), 322 (M^+, 50), 307 (M^+-15, 79); HRMS exact mass calcd. for $C_{10}H_{12}O_2Br_2$ 321.9204, found 321.9179.

1-Bromo-4-iodo-2,5-dimethoxy-3,6-dimethylbenzene

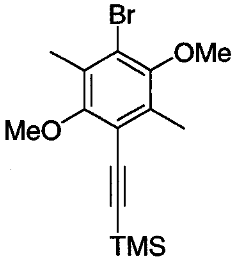


107

n-BuLi (0.62 mL, 2.5 M) was added to a solution of dibromide **97** (504 mg, 1.55 mmol) in ether (30 mL) at –78 °C and the reaction mixture stirred for 30 minutes. A solution of $MgBr_2$ (prepared in situ from 59 mg Mg turnings and 130 μL) in ether (8 mL) was transferred to the cold solution by cannula and the reaction mixture was stirred for 20 minutes. A solution of I_2 (481 mg, 1.89 mmol) in ether (5 mL) was then added dropwise over approximately 10 minutes and the reaction mixture warmed to room temperature. GC-MS indicated presence of both starting material and product. The reaction was quenched with $Na_2S_2O_3$ and extracted with ether. The extract was washed with brine, dried, and concentrated to yield an inseparable mixture of **107** and **97** as a colourless solid (540 mg, 96% assuming ~14 mol% **97**). After several optimization experiments, this procedure was found to produce the highest product/starting material ratio. ^{1}H NMR

($CDCl_3$, 200 MHz) δ 3.73 (s, 3H, OMe), 3.71 (s, 3H, OMe), 2.44 (s, 3H, Me), 2.39 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.7, 151.6, 134.4, 130.3, 121.3, 98.9, 60.45, 60.38, 22.7, 17.8; MS (EI) *m/z* (relative intensity) 372 (M^+ + 2, 92), 370 (M^+, 100), 355 (M^+-CH_3, 60); HRMS exact mass calcd. for $C_{10}H_{12}O_2BrI$ 369.9065, found 369.9073.

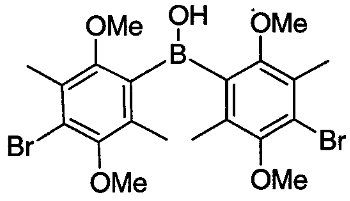
1-Bromo-2,5-dimethoxy-3,6-dimethyl-4-(trimethylsilylethynyl)benzene



108

Iodide **107** (313 mg, 0.757 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), and CuI (16 mg, 0.084 mmol) were dissolved in a mixture of piperidine (10 mL) and THF (5 mL) and the solution was degassed with nitrogen for several minutes. TMS-acetylene (0.14 mL, 0.991 mmol) was added and the reaction mixture was stirred at room temperature overnight. GC-MS indicated the presence of both starting material and product. Another aliquot of TMS-acetylene (0.06 mL, 0.424 mmol) was added and the reaction mixture was stirred at room temperature for another night. All of the starting material had been converted to product by GC-MS and the reaction mixture was concentrated. Water was added and the solution was extracted with ether. The ether extract was washed with 1 M HCl, and brine, dried, and concentrated. Purification of the reddish-brown residue by column chromatography (2% ether/petroleum ether) afforded an inseparable mixture of **108** and **97** (132 mg, 39% assuming ~20mol% **97**) as a semi-solid. ^1H NMR ($CDCl_3$, 200 MHz) δ 3.82 (s, 3H, OMe), 3.71 (s, 3H, OMe), 2.37 (s, 3H, Me), 2.30 (s, 3H, Me), 0.250 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.3, 151.5, 133.0, 130.2, 121.7, 119.8, 117.4, 103.6, 99.4, 60.6, 60.1, 16.3, 14.7, -0.12; MS (EI) *m/z* (relative intensity) 342 (M^+ + 2, 100), 340 (M^+, 93), 325 (M^+ - Me, 40), 310 (M^+ - 2Me, 25); HRMS exact mass calcd. for $C_{15}H_{21}O_2SiBr$ 340.0494, found 340.0503.

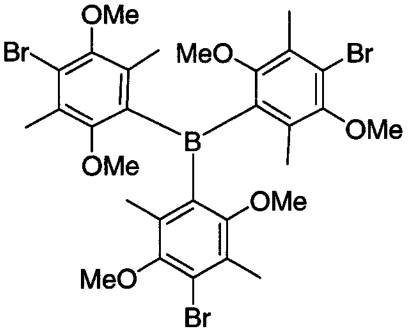
Hydroxy-di(1,4-dimethoxy-2,5-dimethyl-3-bromo)phenyl borane



103

n-BuLi (0.27 mL, 2.5 M) was added to a solution of dibromide **97** (204 mg, 0.630 mmol) in ether (10 mL) at –78 °C and the reaction mixture was warmed to 0 °C for 15 minutes. $BF_3 \cdot OEt_2$ (26 μL, 0.205 mmol) was then added at –78 °C and the solution was warmed to room temperature and stirred overnight. Following cooling and addition of water, the mixture was extracted with ether. The ether extract was washed with brine, dried, and concentrated. Purification by column chromatography (40% ether/petroleum ether) yielded **103** as an oily film (72 mg, 44%). ^1H NMR ($CDCl_3$, 500 MHz) δ 8.54 (s, 1H, OH), 3.71 (s, 6H, OMe), 3.54 (s, 6H, OMe), 2.32 (s, 6H, Me), 2.17 (s, 6H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.8, 152.4, 133.6, 129.8, 123.2, 61.3, 60.0, 16.6, 15.6; IR ($CHCl_3$) *v*/cm^{-1} 3389 (–OH); MS (ES) *m/z* (relative intensity) 554.9 (M^+ + K^+ + 4, 7), 552.9 (M^+ + K^+, 4), 115 (100).

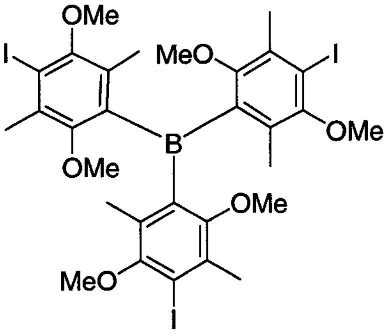
Tris(4-bromo-2,5-dimethoxy-3,6-dimethylphenyl)borane



96

n-BuLi (0.5 mL, 2.5 M) was added to a suspension of **97** (403 mg, 1.24 mmol) in ether (10 mL) at -78 °C and the reaction mixture was stirred for 15 minutes. A solution of $MgBr_2$ (prepared *in situ* from 45 mg Mg turnings and 107 μL $BrCH_2CH_2Br$) in ether (4 mL) was transferred to the cold solution by cannula and the reaction mixture stirred for 20 minutes. $BF_3 \cdot OEt_2$ (57 μL, 0.500 mmol) was then added and the solution warmed to room temperature. THF (10 mL) was added and the reaction mixture heated at reflux for approximately 48 hours. The solution was then allowed to cool to room temperature and concentrated. After addition of water, the mixture was extracted with ether. The extract was washed with 1 M HCl, and brine, dried, and concentrated. Purification by column chromatography (10% petroleum ether/ether) afforded **96** as a colourless foamy solid (175 mg, 57%). ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K) δ 3.68 (s, 9H, OMe) 2.98, 2.85 (br s, 9H, OMe), 2.29 (s, 9H, Me), 2.12, 2.03 (br s, 9H, Me); ^{1}H NMR (C_6D_6, 500 MHz, 300 K) δ 3.49 (s, 9H, OMe), 2.81 (s, 9H, OMe), 2.26 (s, 18 H, Me); ^{1}H NMR (C_6D_6, 500 MHz, 323 K) δ 3.51 (s, 9H, OMe), 2.85 (s, 9H, OMe), 2.27 (s, 9H, Me), 2.23 (s, 9H, Me); ^{13}C NMR (C_6D_6, 125 MHz, 323 K) 156.4, 152.8, 140.6, 132.4, 129.7, 123.4, 60.1, 59.8, 17.3, 15.2; IR ($CHCl_3$) ν/cm^{-1} 2955, 2923, 2839 (C–H), 1564, 1551, 1448, 1416 (C=C); MS (ES) *m/z* (relative intensity) 783 ($M^+ + K^+ + 4$, 3), 781 ($M^+ + K^+ + 2$, 3), 779 ($M^+ + K^+$, 1), 724 (4), 39 (100).

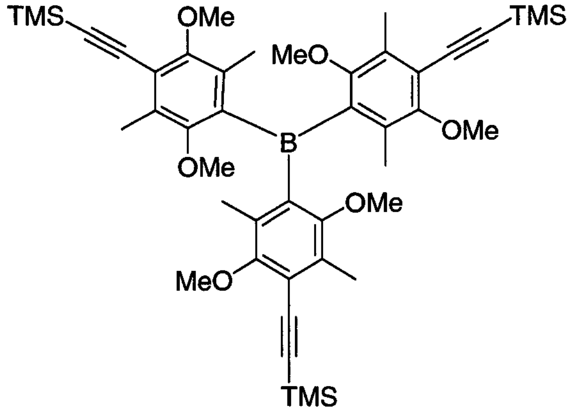
Tris(4-iodo-2,5-dimethoxy-3,6-dimethylphenyl)borane



104

s-BuLi (2.0 mL, 1.2 M) was added dropwise to a solution of **104** (579 mg, 0.779 mmol) in ether (40 mL) at –78 °C and the reaction mixture was stirred for 15 minutes. A solution of I_2 (660 mg, 2.60 mmol) in ether (15 mL) was added dropwise over 15 minutes and the reaction mixture was stirred at –78 °C for approximately 1 hour. Despite the obvious accumulation of I_2, TLC indicated the reaction had not gone to completion so two more equivalents of I_2 (416 mg, 1.64 mmol) in ether (5 mL) were added. The reaction mixture was warmed slowly to room temperature and quenched with $Na_2S_2O_3$. The solution was concentrated and extracted with CH_2Cl_2. The extract was washed with water, dried, and concentrated. Purification by column chromatography (10% petroleum ether/ether) yielded **104** as a colourless solid (570 mg, 83%). m.p. 196-198 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K); δ 3.65 (s, 9H, OMe), 2.96, 2.82 (br s, 9H, OMe), 2.34 (s, 9H, Me), 2.15, 2.05 (br s, 9H, Me); ^{13}C NMR (C_6D_6, 125 MHz, 323 K) δ 155.8, 155.3, 141.5, 132.9, 131.5, 103.0, 59.9, 59.7, 22.8, 15.6; IR ($CHCl_3$) ν/cm^{-1} 2958, 2936, 2842 (C–H), 1553, 1536, 1450, 1408 (C=C); MS (ES) *m/z* (relative intensity) 923 (M^+ + K^+, 5), 39 (100).

Tris(2,5-dimethoxy-3,6-dimethyl-4-trimethylsilylethynylphenyl)borane

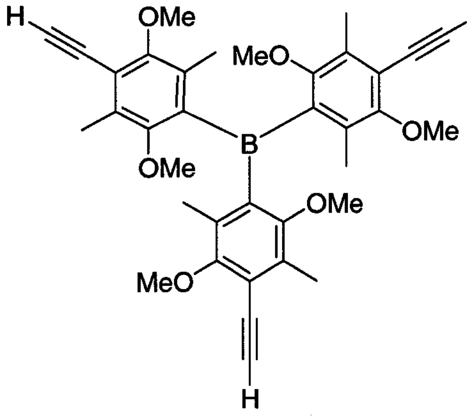


105

From **108**: *n*-BuLi (0.7 mL, 2.1 M) was added dropwise to a solution of **108** (494 mg, 1.43 mmol) in ether (30 mL) at –78 °C and the mixture was stirred for 1 hour. A solution of $MgBr_2$ (prepared *in situ* from 52 mg Mg turnings and 130 μL $BrCH_2CH_2Br$) in ether (5 mL) was transferred to the cold solution by cannula and the reaction mixture was stirred for 15 minutes. $BF_3 \cdot OEt_2$ (61 μL, 0.48 mmol) was then added and the solution stirred at room temperature overnight. After addition of water, the mixture was extracted with ether. The ether extract was washed with 1 M HCl, brine, dried, and concentrated. Purification by column chromatography (10%ether/petroleum ether) yielded **105** as a clear film (170 mg, 45%).

^{1}H NMR ($CDCl_3$, 500 MHz, 300 K) δ 3.75 (s, 9H, OMe), 3.00, 2.82 (br s, 9H, OMe), 2.29 (s, 9H, Me), 2.02, 1.92 (s, 9H, Me), 0.24 (s, 27 H, $SiMe_3$); ^{13}C NMR (C_6D_6, 125 MHz, 323 K) δ157.2, 155.9, 131.5, 128.5, 120.2, 103.6, 102.0, 60.1, 59.9, 15.0, 14.5, 0.12; IR ($CHCl_3$) ν/cm^{-1} 2955, 2929, 2839 (C–H), 2144 (C≡C), 1577, 1461, 1421 (C=C); MS (ES) *m/z* (relative intensity) 833 (M^+ + K^+, 0.25), 56 (100).

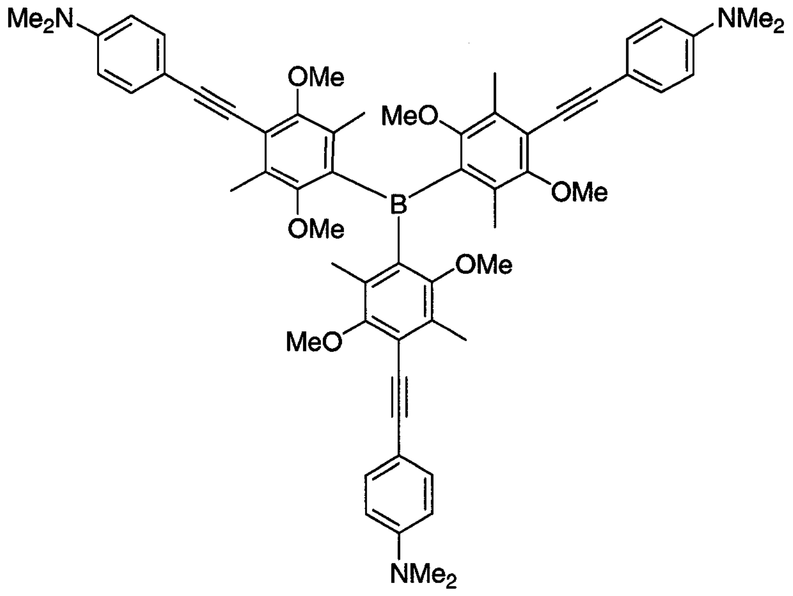
Tris(4-ethynyl-2,5-dimethoxy-3,6-dimethylphenyl)borane



109

A solution of powdered KOH (100 mg, 1.78 mol) and **109** (117 mg, 0.147 mmol) in a mixture of MeOH (6.5 mL) and THF (3.5 mL) was stirred for 5 hours. After addition of water, the solvents were removed. The reaction mixture was extracted with ether. The ether extract was washed with 1 M HCl, and brine, dried and concentrated to afford **109** (85 mg, 100%) as a colourless solid. m.p. 204-206 °C; ^{1}H NMR (CDCl$_3$, 500 MHz, 300 K) δ 3.74 (s, 9H, OMe), 3.50 (s, 3H, C≡C–H), 2.98, 2.84 (br s, 9H, OMe), 2.30 (s, 9H, Me), 2.06, 1.96 (br s, 9H, Me); ^{13}C NMR (C$_6$D$_6$, 125 MHz, 300 K) δ 157.4, 155.9, 143.11, 131.8, 131.6, 119.4, 86.1, 79.8, 60.2, 59.8, 14.9, 14.5; IR (CHCl$_3$) *v*/cm^{-1} 2962, 2923, 2846 (C–H), 2253, 2092 (C≡C), 1577, 1532, 1456, 1423 (C=C); MS (ES) *m/z* (relative intensity) 578 (M$^+$, 100), 74 (24).

Tris{[4-(dimethylamino)phenylethynyl]-2,5-dimethoxy-3,6-dimethylphenyl}borane



110

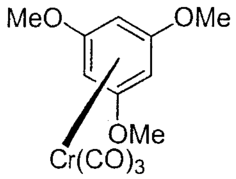
(4-Iodophenyl)-dimethylamine (136 mg, 0.548 mmol), $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), and CuI (2 mg, 0.010 mmol) were dissolved in Et_3N (20 mL) and the solution was degassed with nitrogen for several minutes. A solution of **109** (80 mg, 0.138 mmol) in THF (5 mL) was then added dropwise and the reaction mixture was stirred at room temperature for 7 days. Borane **110** had been consumed and several spots were evident by TLC. Following addition of water, the reaction mixture was concentrated and extracted with dichloromethane. The extract was washed with 1 M HCl, and brine, dried, and concentrated. Purification of the residue by column chromatography (50% ether/petroleum ether) yielded **110** (8 mg, 6%) as a pale yellow film. ^1H NMR ($CDCl_3$, 200 MHz, 300 K) δ 7.41 (d, J = 8.9 Hz, 6H, ArH), 6.65 (d, J = 8.9 Hz, 6H, ArH), 3.83, 3.77 (br s, 9H, OMe), 3.05, 2.89 (br s, 9H, OMe), 2.38, 2.30 (br s, 9H, Me), 2.10, 1.99 (br s, 9H, Me); ^{13}C NMR (C_6D_6, 125 MHz, 323 K) δ 156.5, 156.3, 150.5, 133.0, 131.6, 131.0, 121.2, 112.5, 112.0, 111.8, 100.3, 84.6, 60.2, 60.0, 39.7, 15.2, 14.8; IR ($CHCl_3$) ν/cm^{-1} 3696, 3599 (C≡C–H), 2936, 3852 (C–H), 2240, 2202 (C≡C), 1609, 1577, 1526, 1448 (C=C); MS (ES) *m/z* (relative intensity) 974 ($M^+ + K^+$, 4), 936 (M^+, 16), 151 (100).

Claims to Original Research

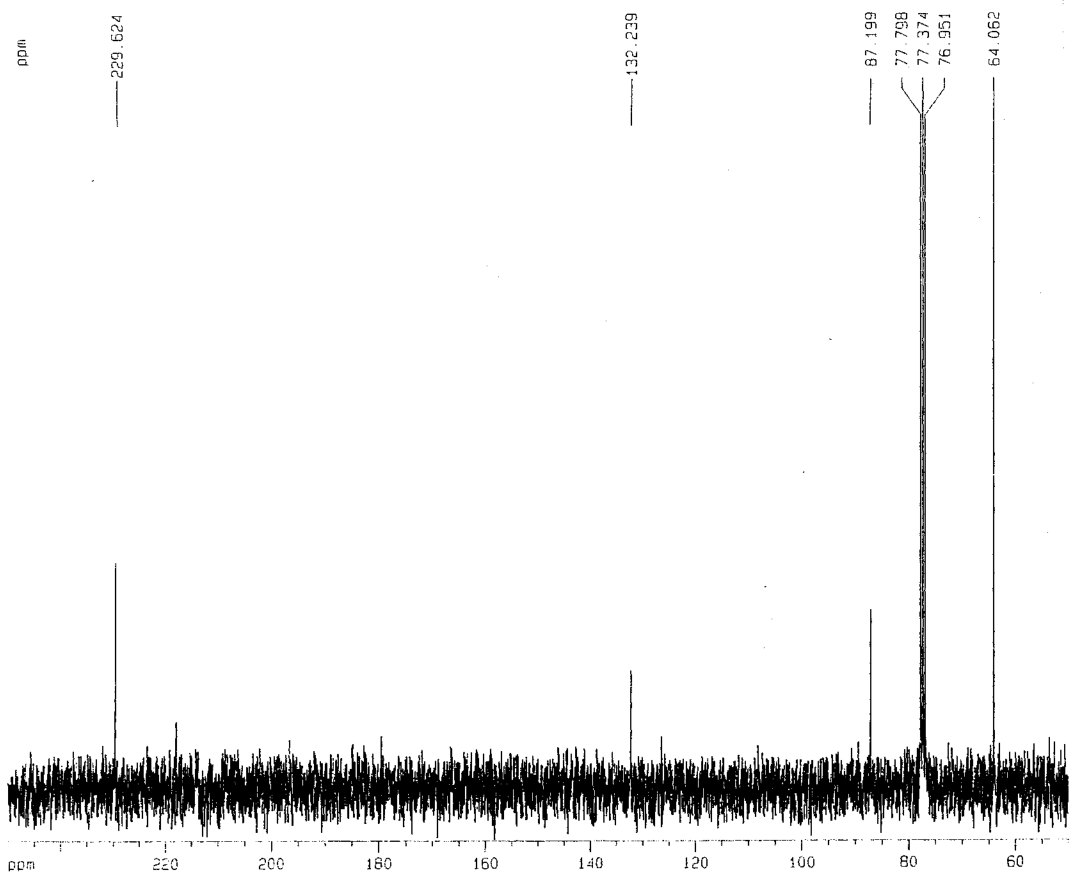
1. Investigated the efficacy of utilizing the $Cr(CO)_3$ group as a facial control element under normal synthetic conditions.
2. Prepared a number of novel $Cr(CO)_3$-complexed arenes and examined their ability to undergo Sonagashira coupling reactions with terminal silylacetylenes.
3. Prepared a novel triarylborane chromophore incorporating azulene, which displayed unique photophysical properties.
4. Designed and synthesized a novel class of heteroatom-containing triarylboranes and investigated their conformational dynamics and optical properties.

Appendix I

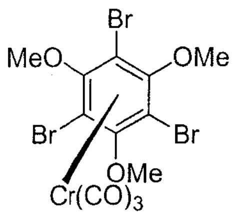
Selected Spectra



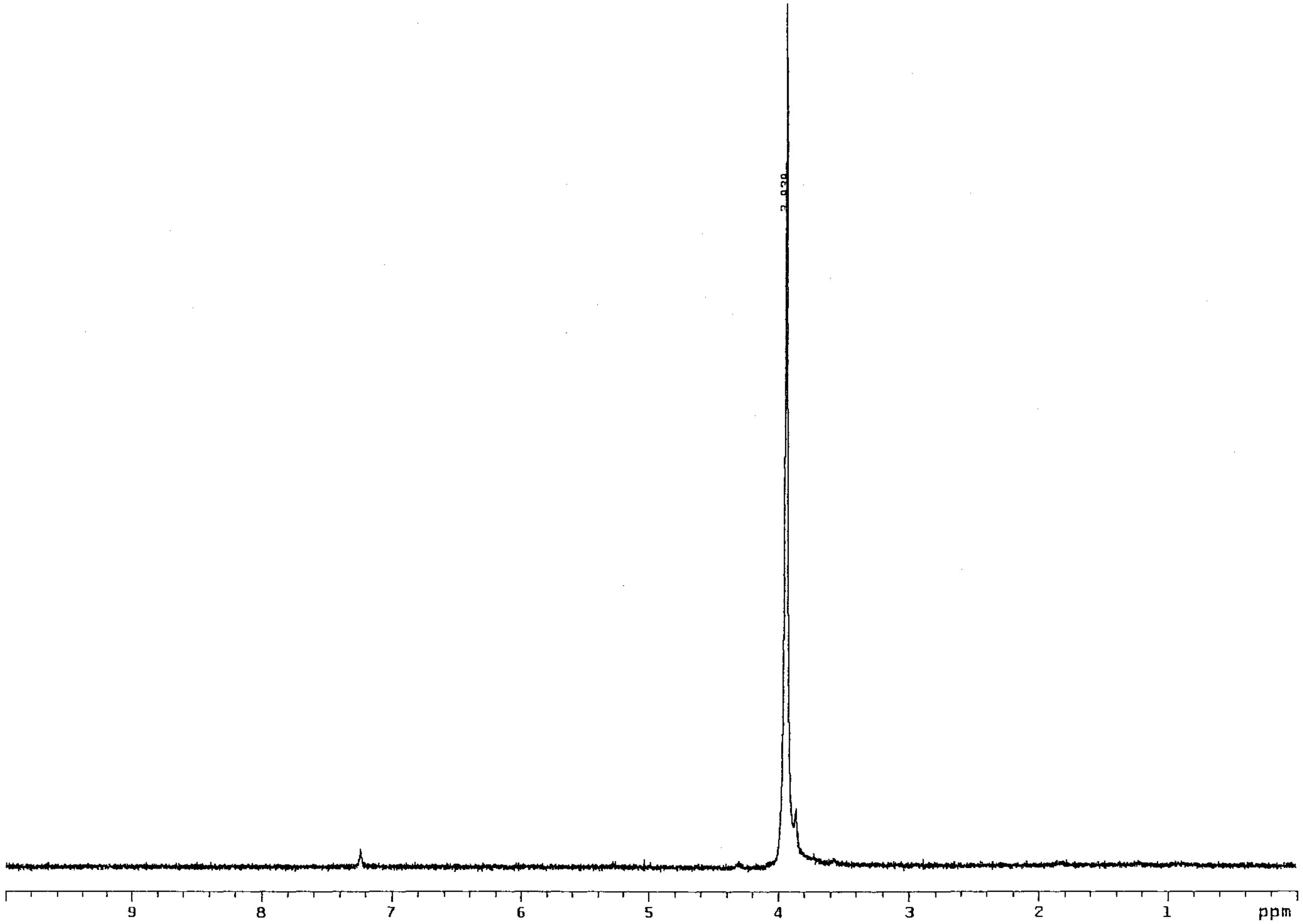
39



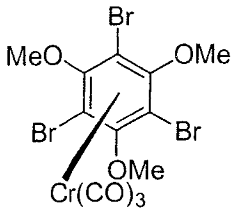
^{13}C NMR Spectrum (75 MHz, CDCl$_3$) of **39**



44



^{1}H NMR Spectrum (200 MHz, $CDCl_3$) of **44**



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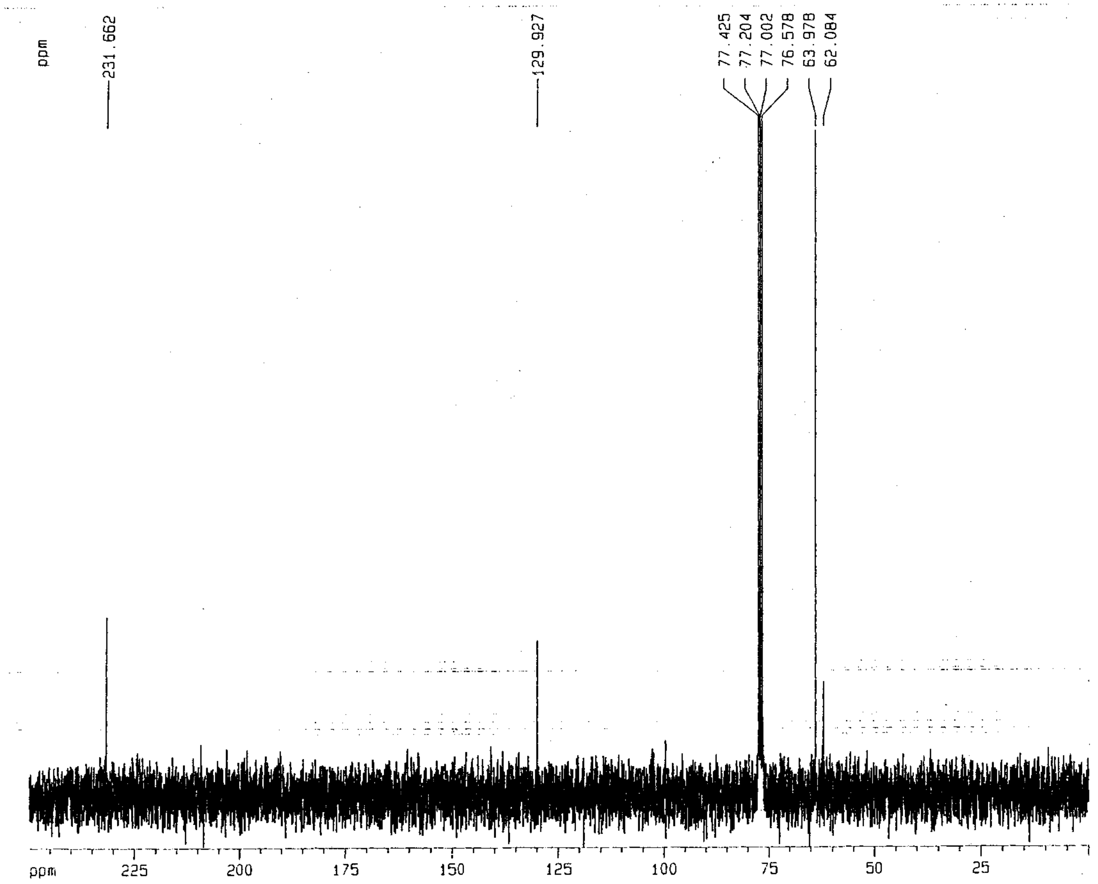
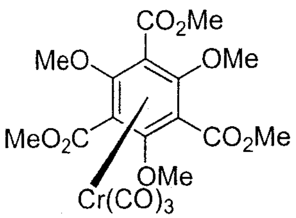


^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of **44**



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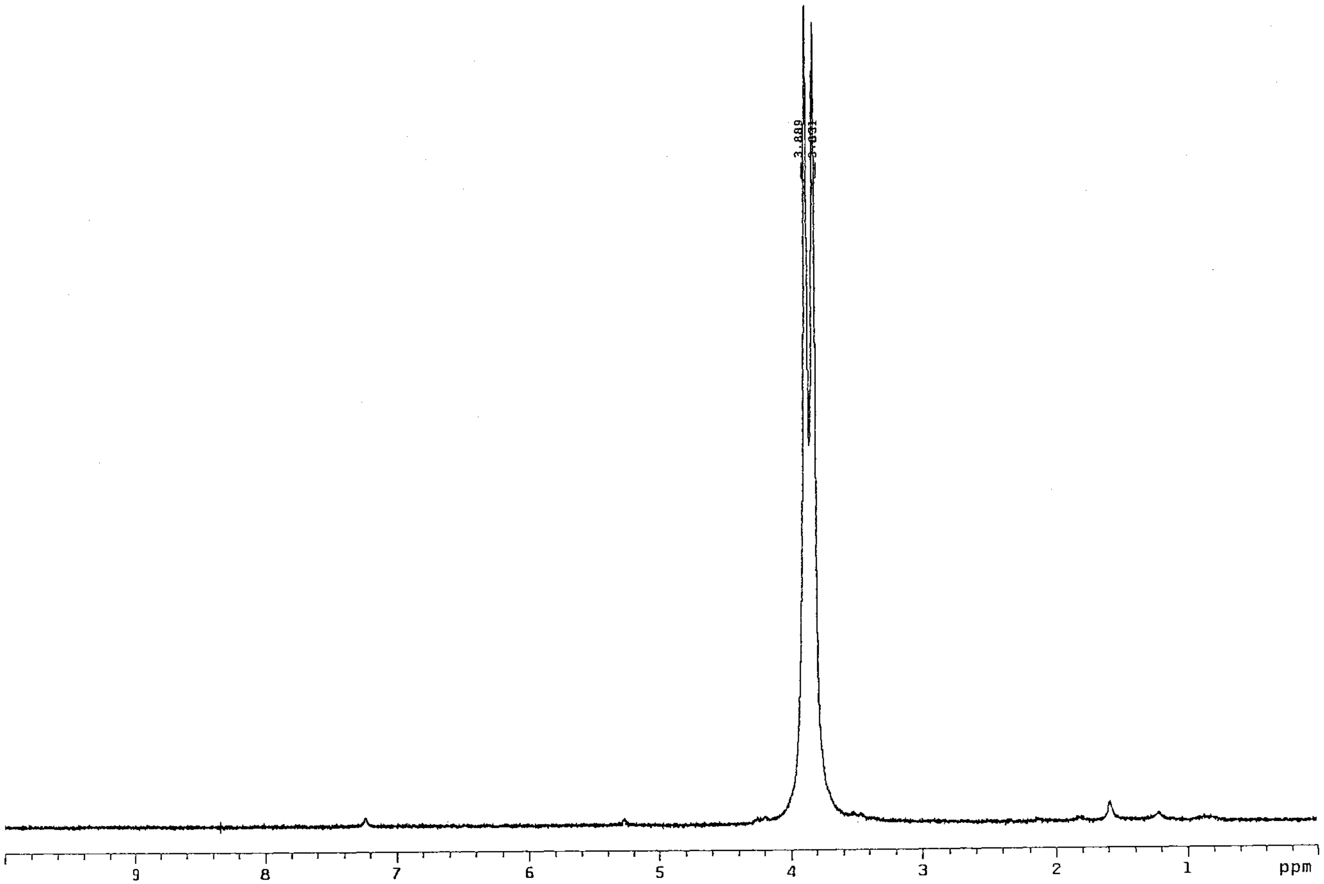
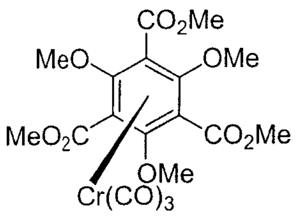


^{1}H NMR Spectrum (200 MHz, CDCl$_3$) of **47**



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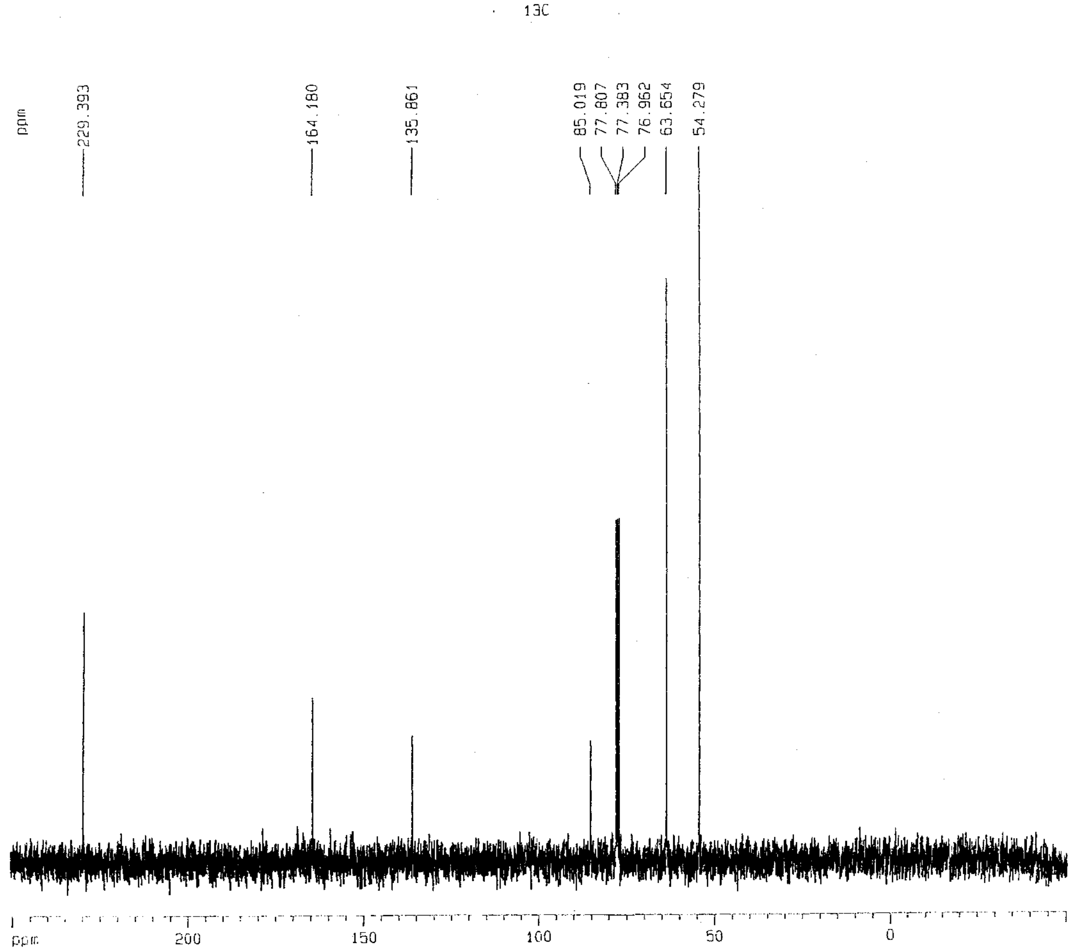
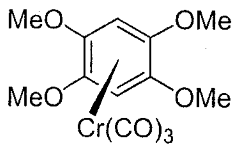


^{13}C NMR Spectrum (75 MHz, CDCl$_3$) of **47**



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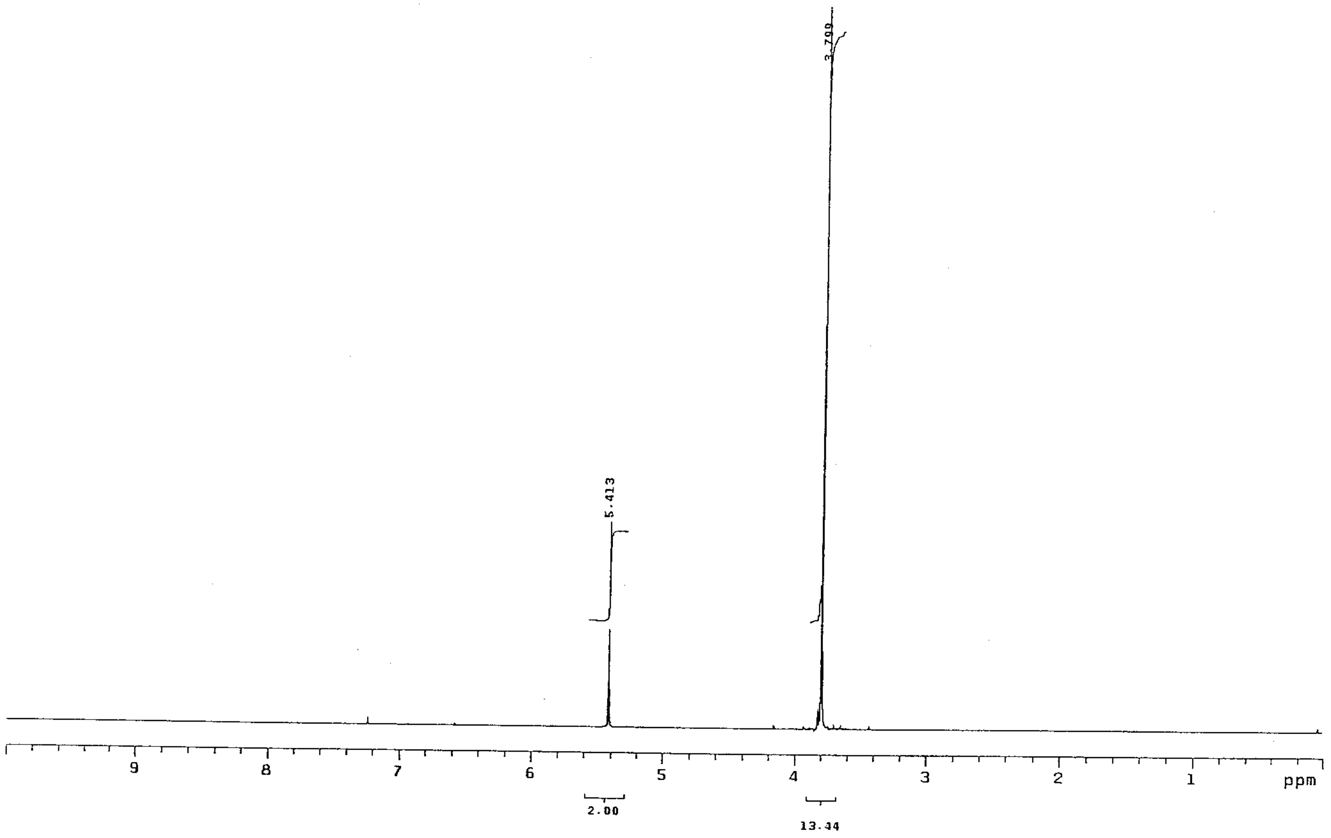
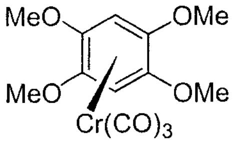


^{1}H NMR Spectrum (200 MHz, $CDCl_3$) of **54**



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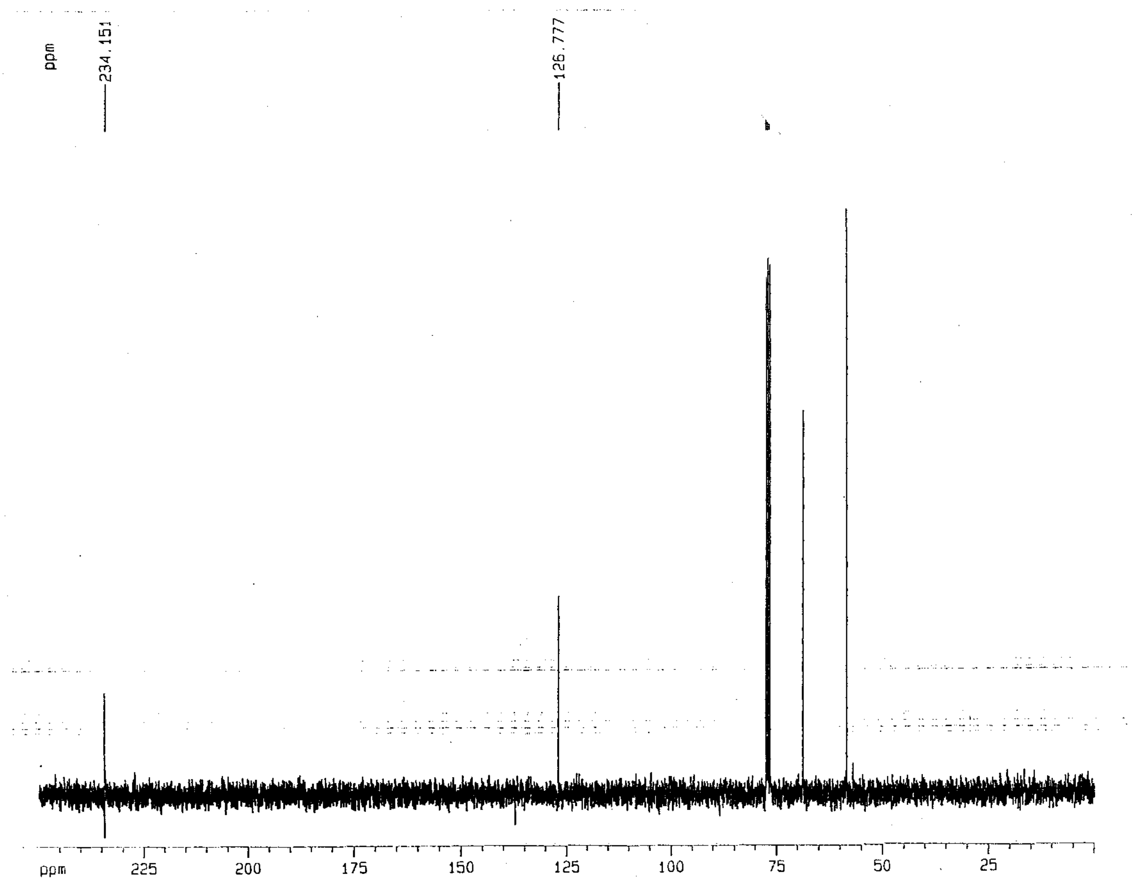
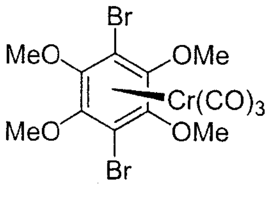
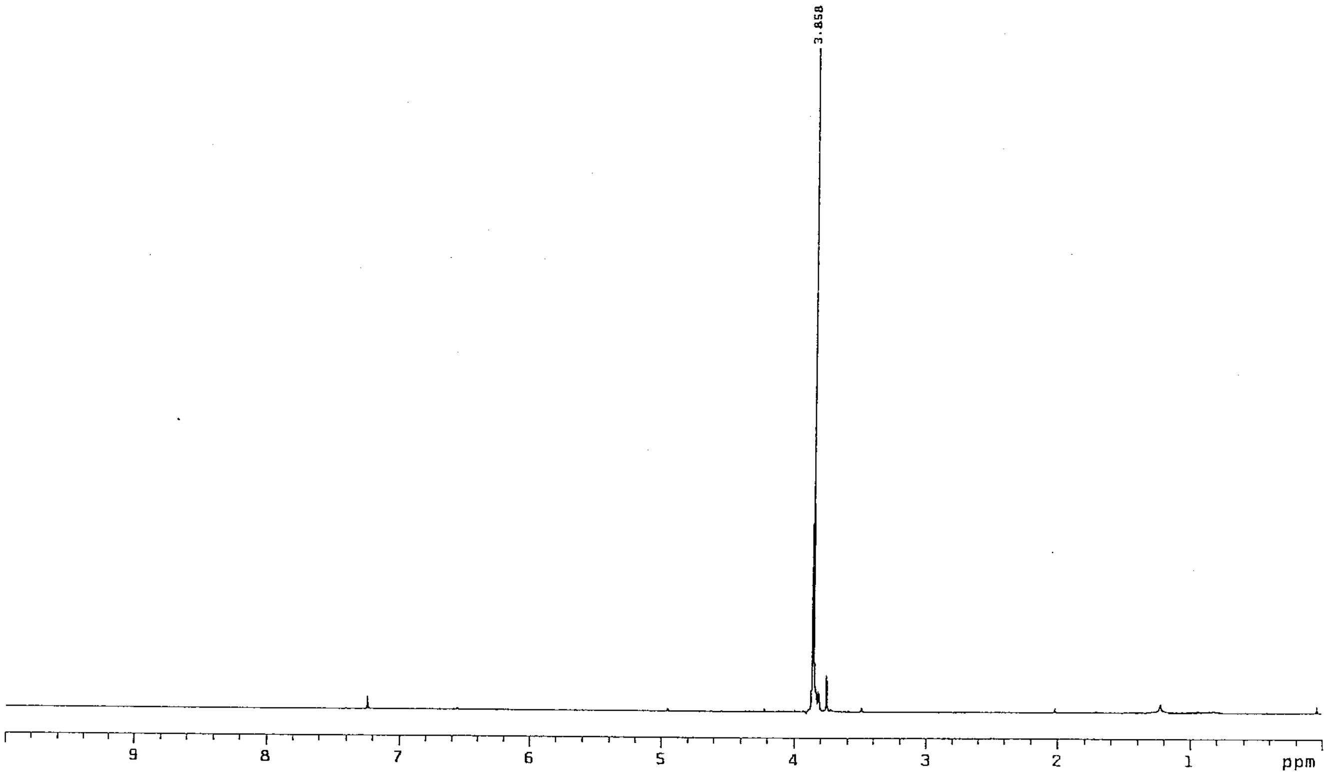


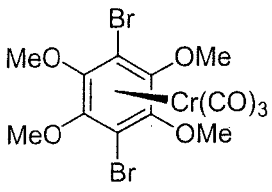
^{13}C NMR Spectrum (75 MHz, CDCl$_3$) of **54**



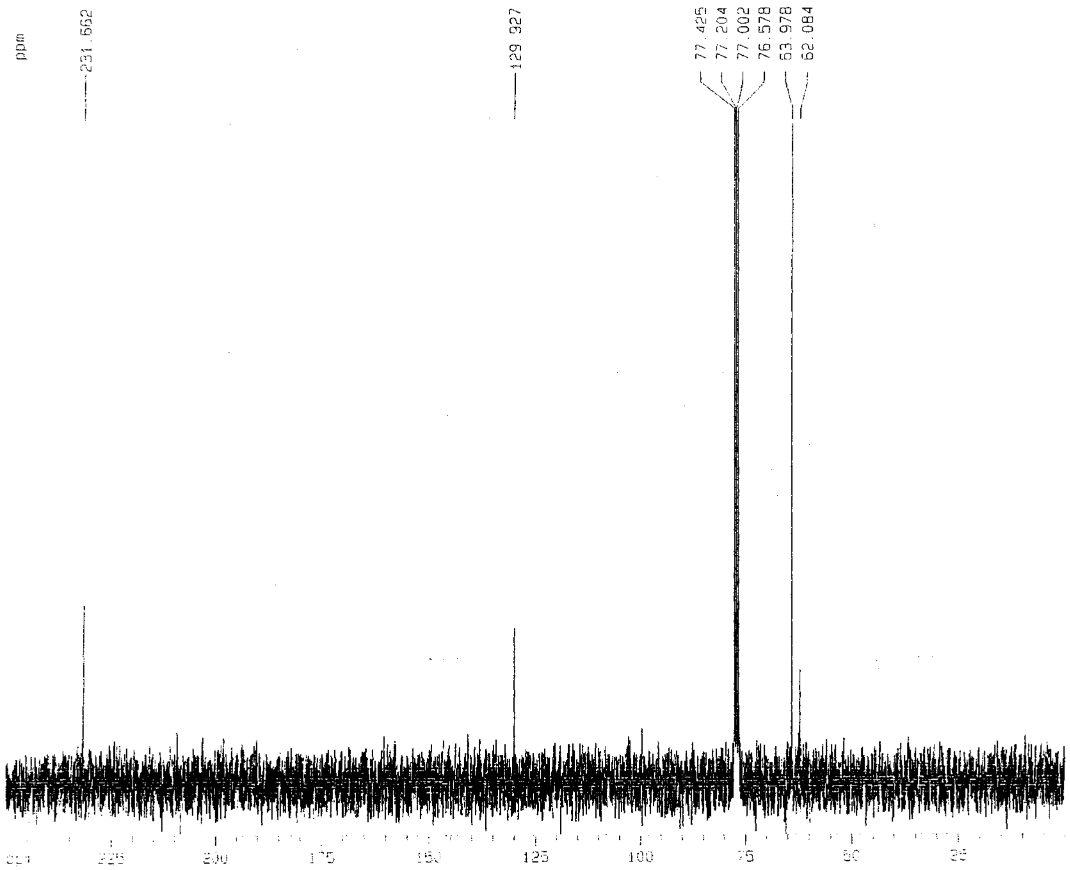
56



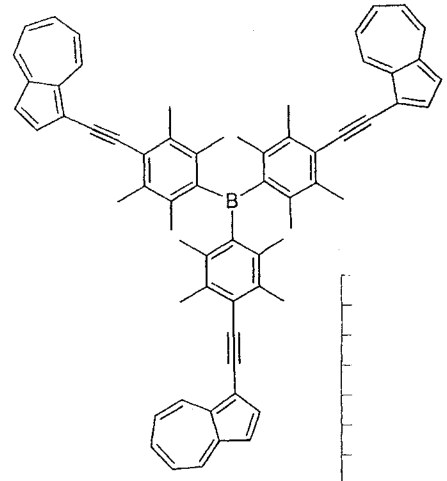
^{1}H NMR Spectrum (200 MHz, CDCl$_3$) of **56**



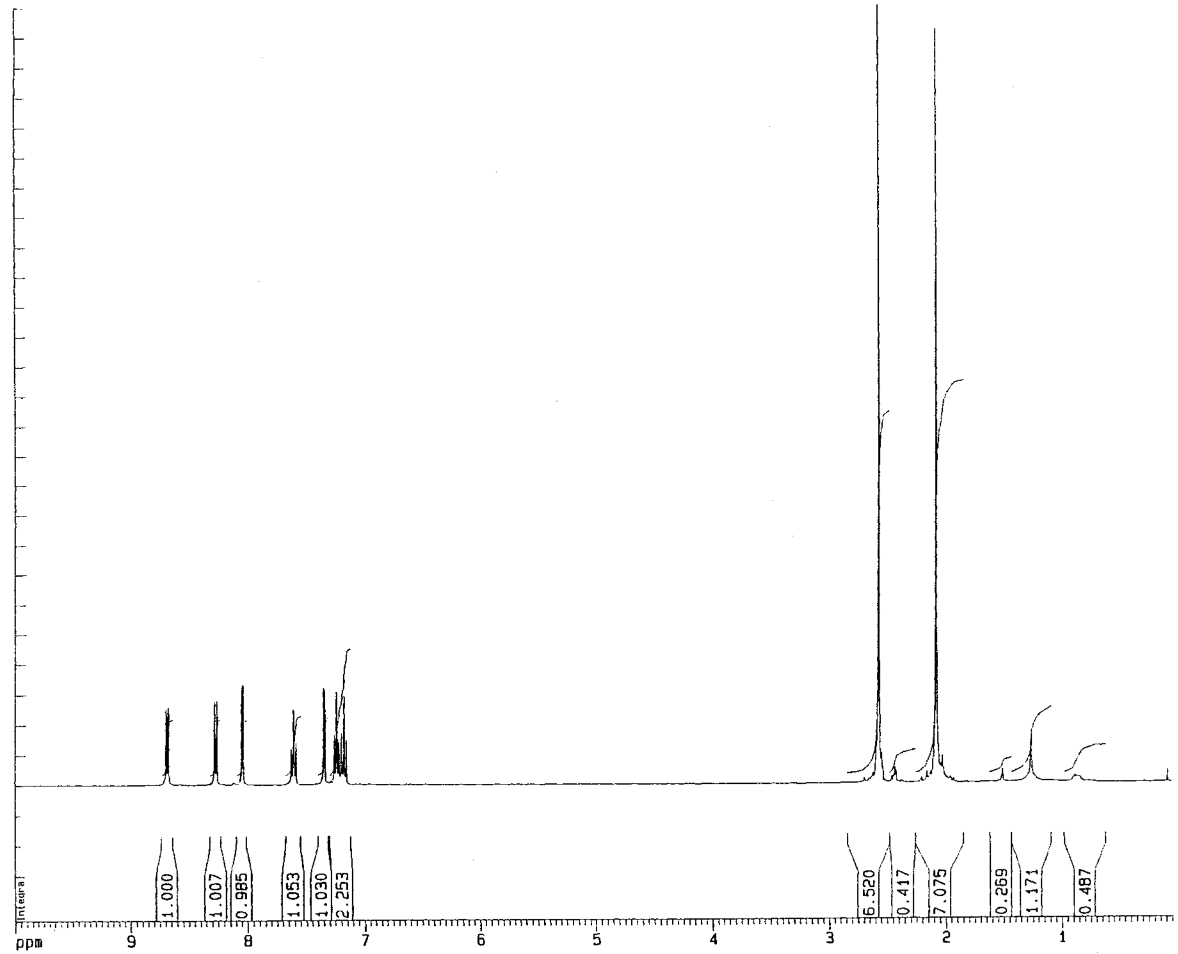
56



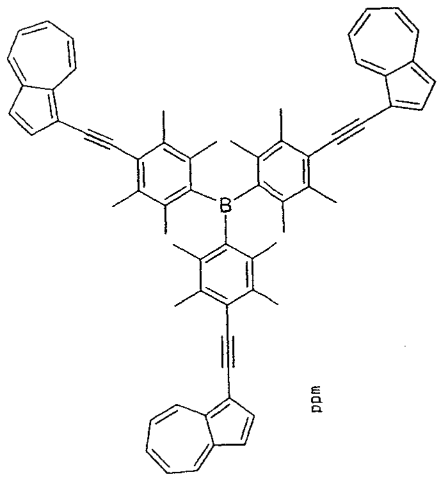
^{13}C NMR Spectrum (75 MHz, CDCl$_3$) of **56**



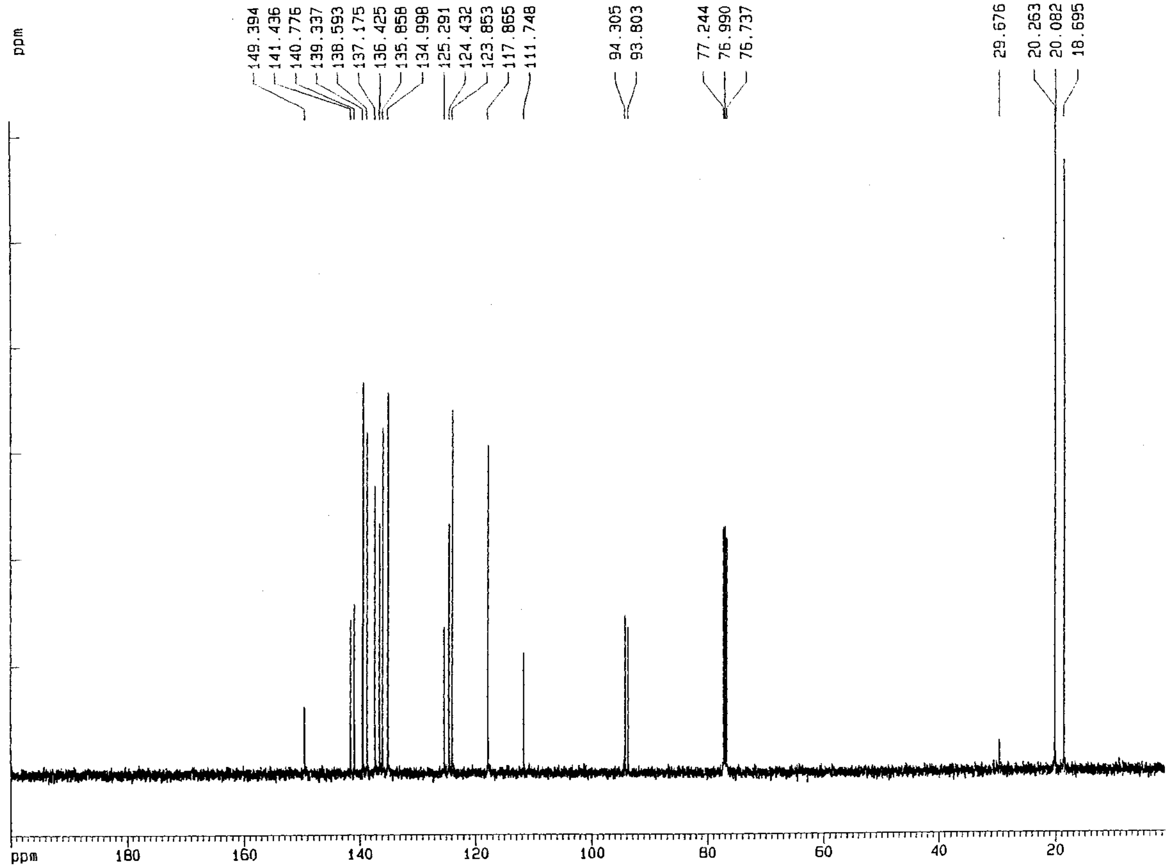
83



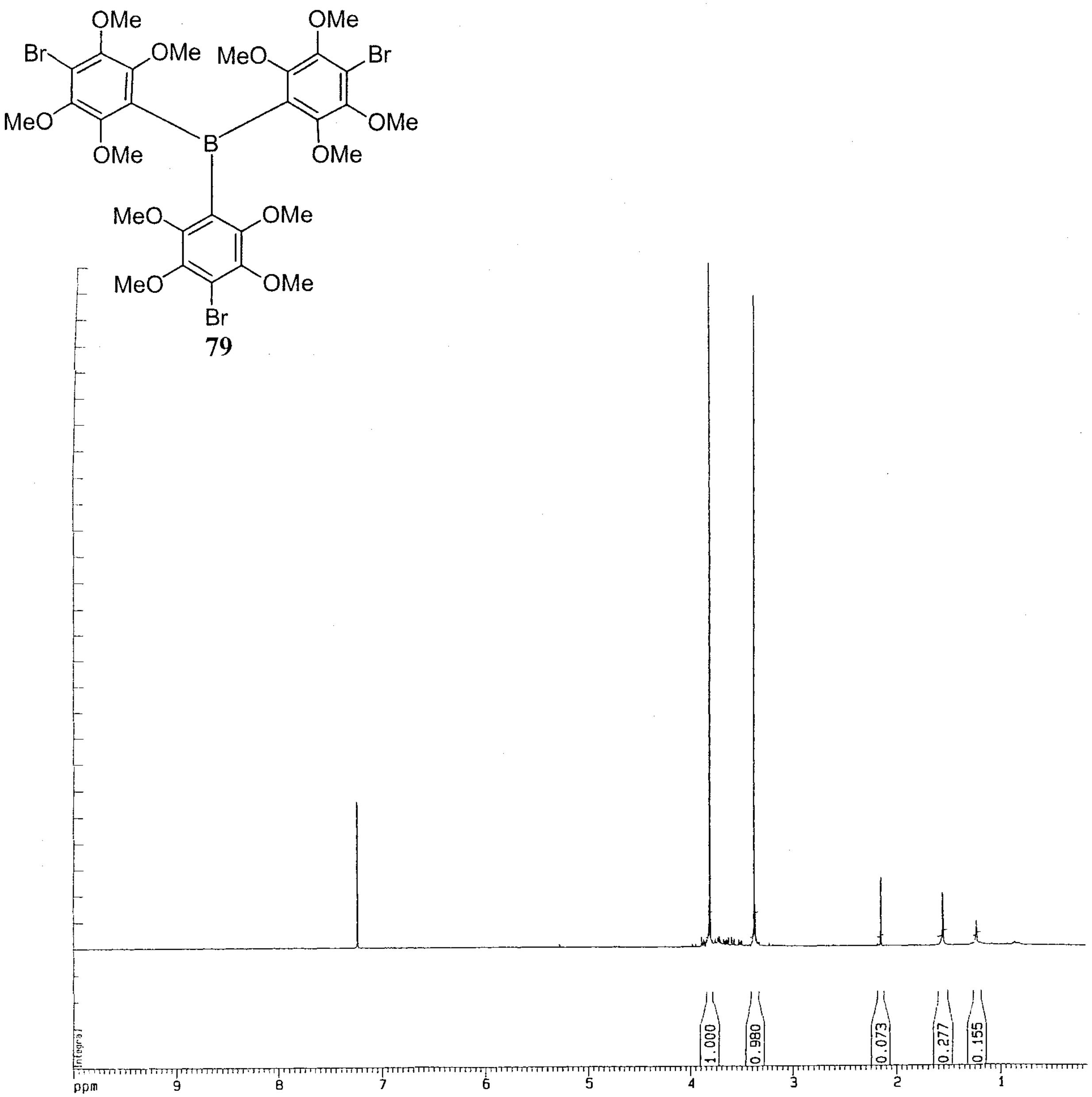
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of **83**



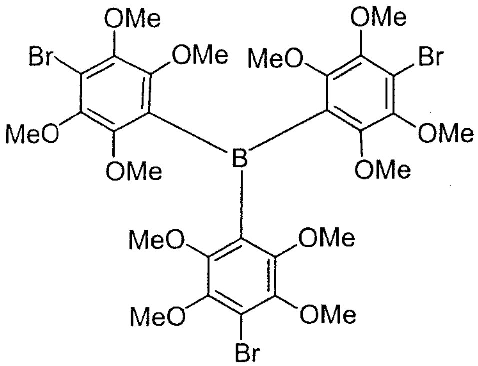
83



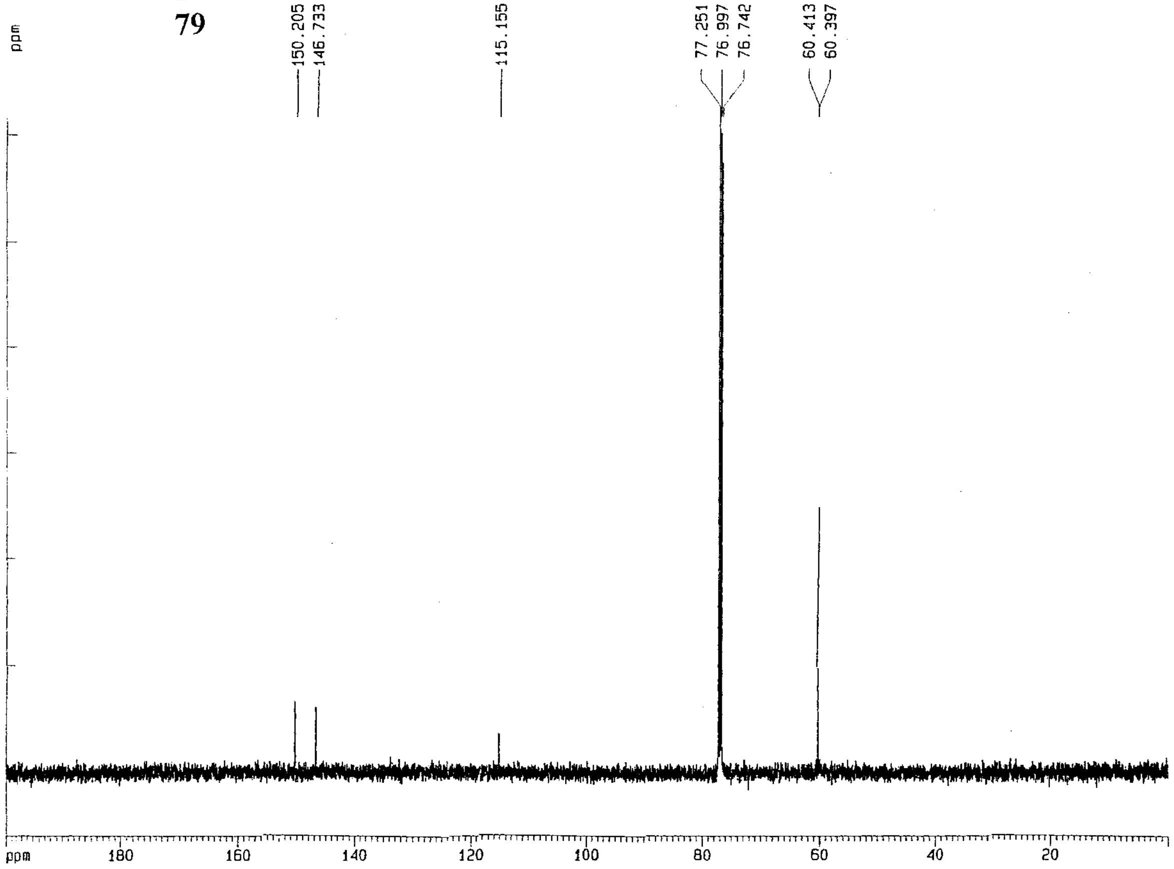
^{13}C NMR Spectrum (75 MHz, CDCl$_3$) of **83**



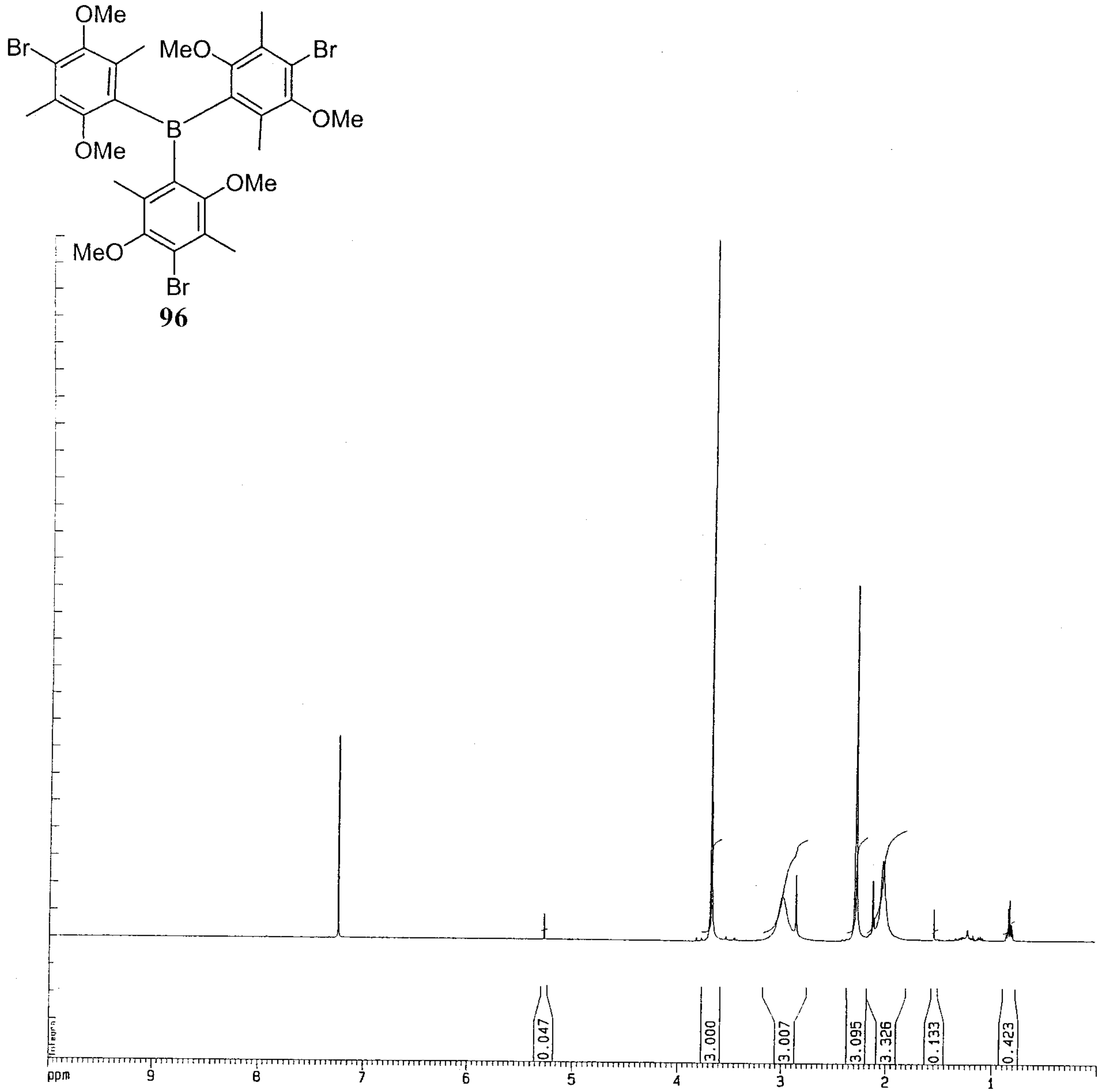
¹H NMR Spectrum (500 MHz, CDCl$_3$) of **79**



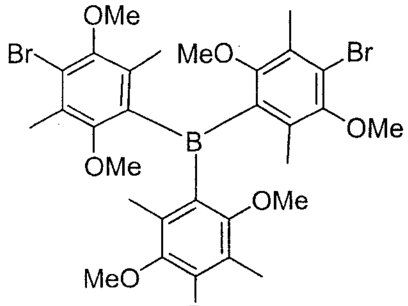
79



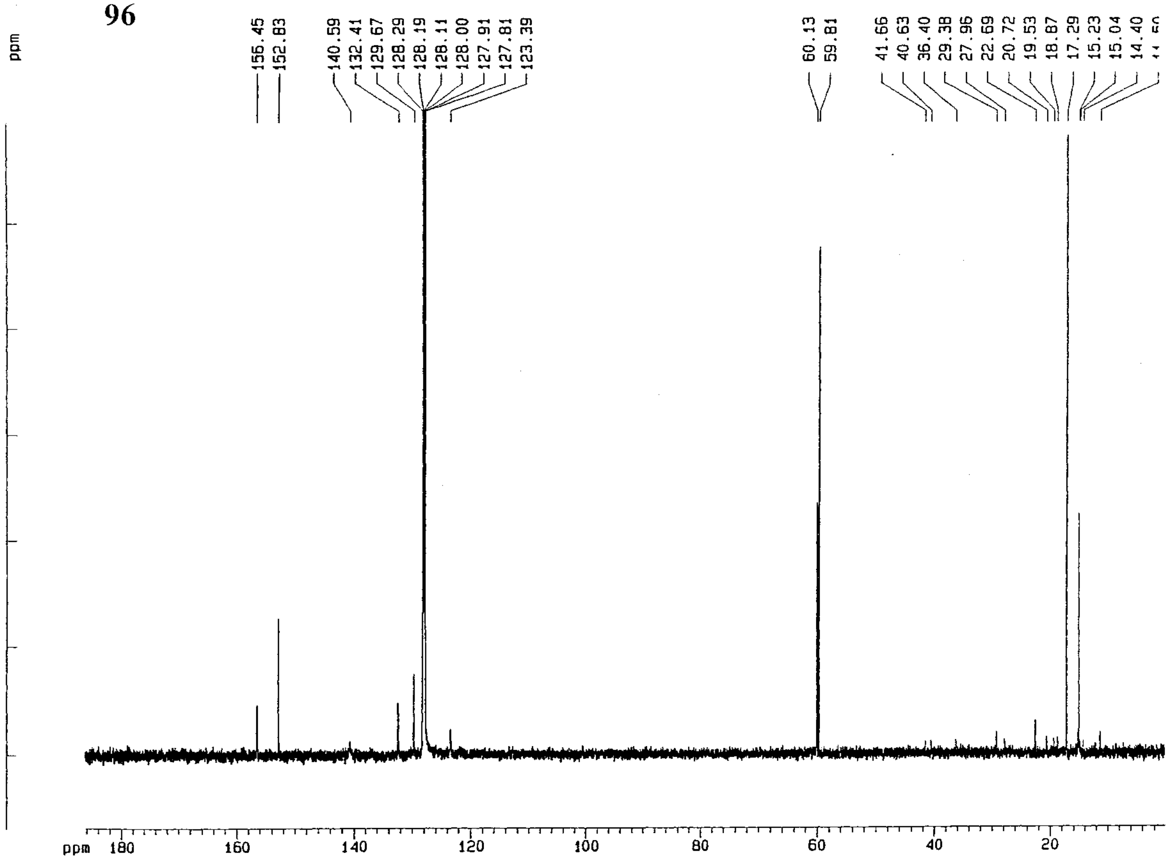
^{13}C NMR Spectrum (75 MHz, CDCl$_3$) of **79**


96

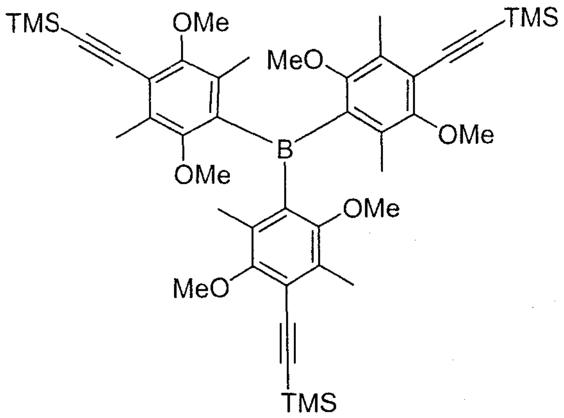
^{1}H NMR Spectrum (500 MHz, CDCl$_3$, 300 K) of **96**



96

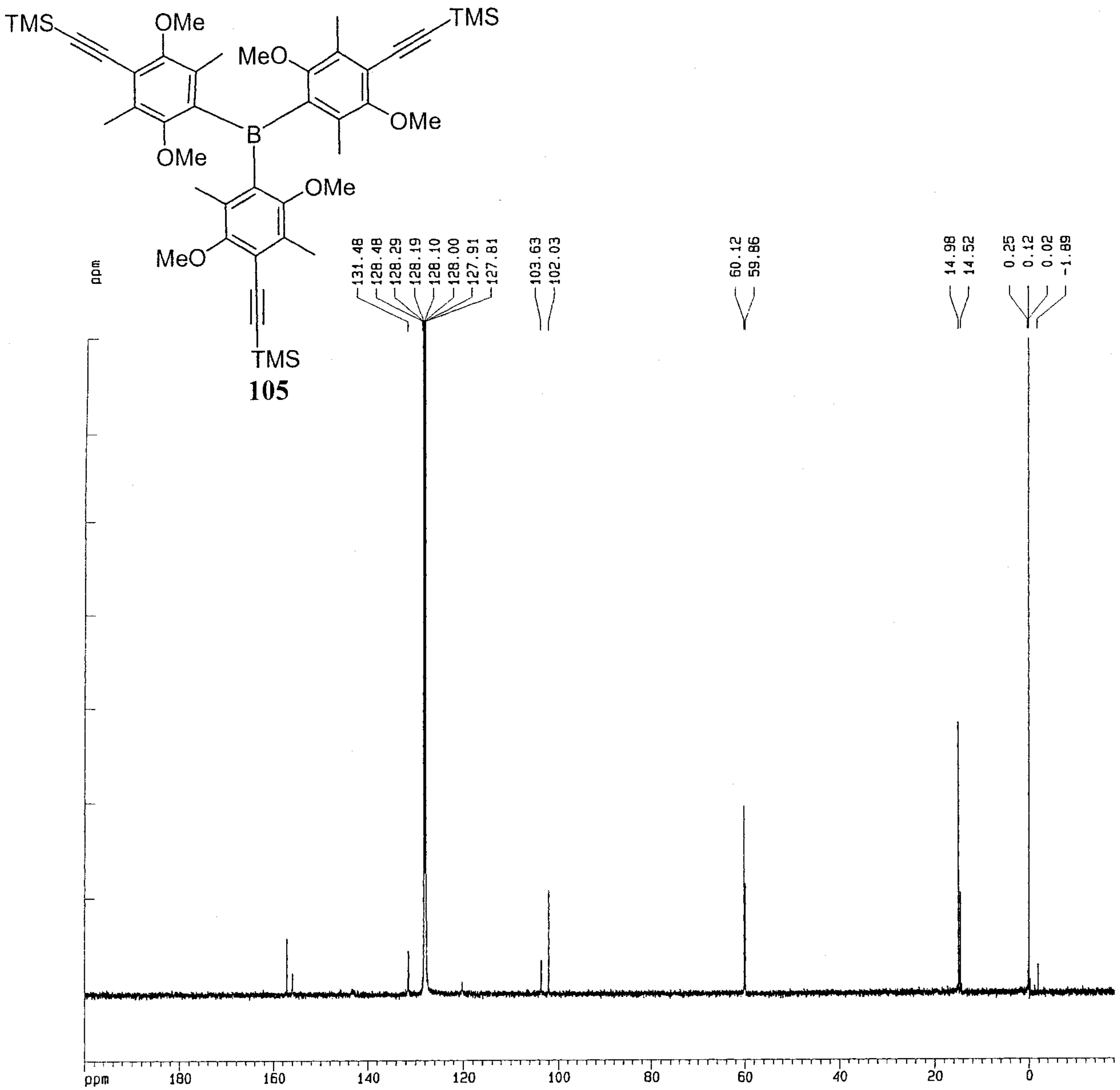


^{13}C NMR Spectrum (75 MHz, C_6D_6, 323 K) of **96**



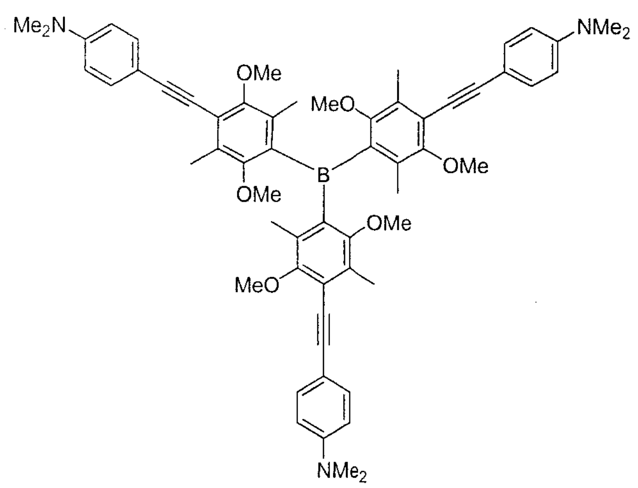
105

^{1}H NMR Spectrum (500 MHz, $CDCl_3$, 300 K) of **105**

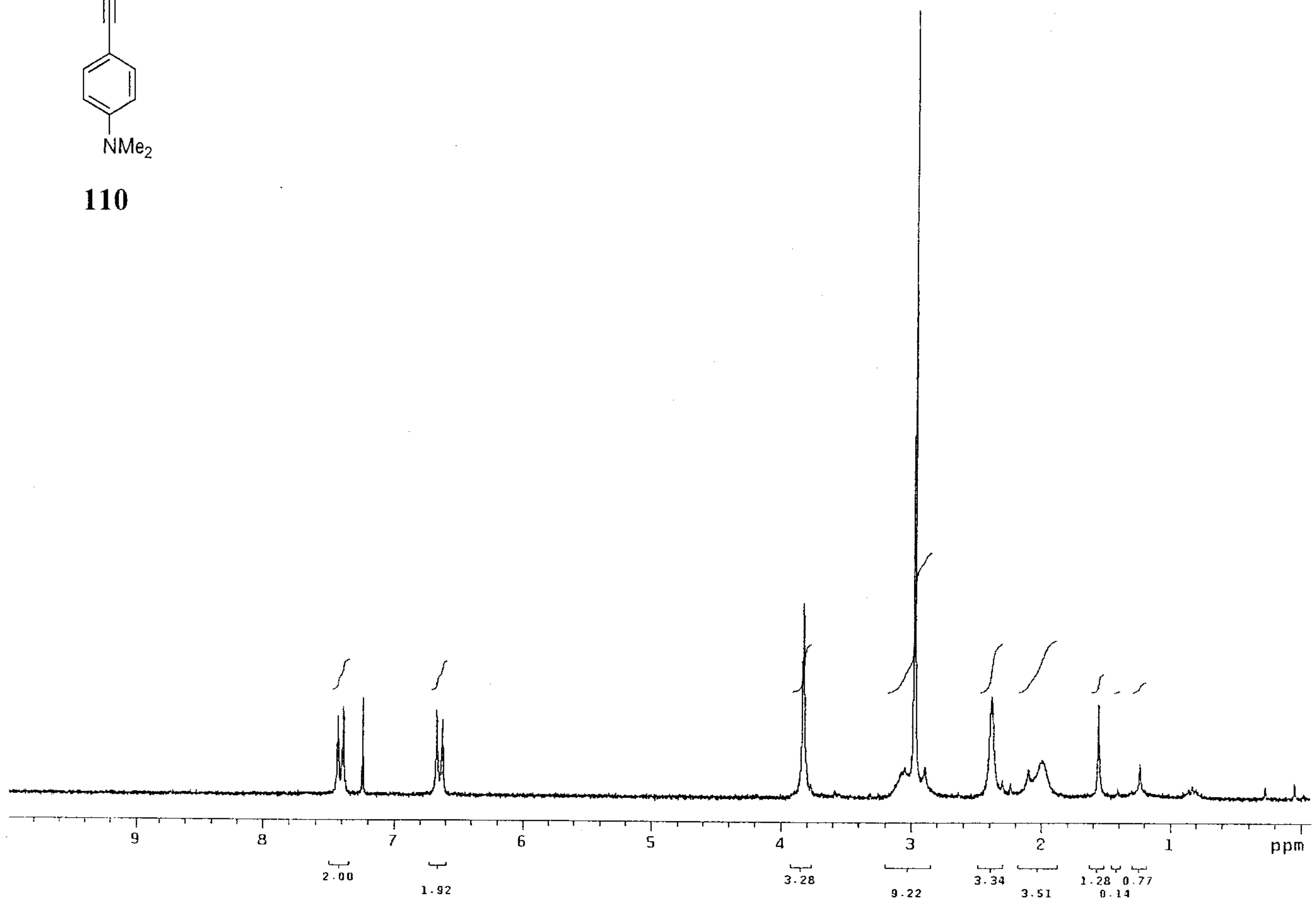


105

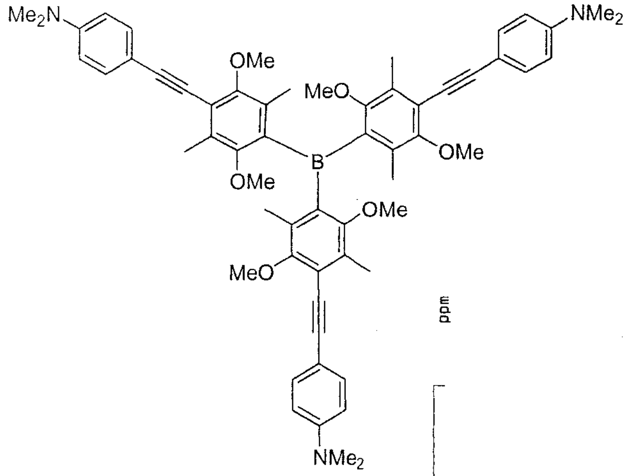
^{13}C NMR Spectrum (75 MHz, C_6D_6, 323 K) of **105**



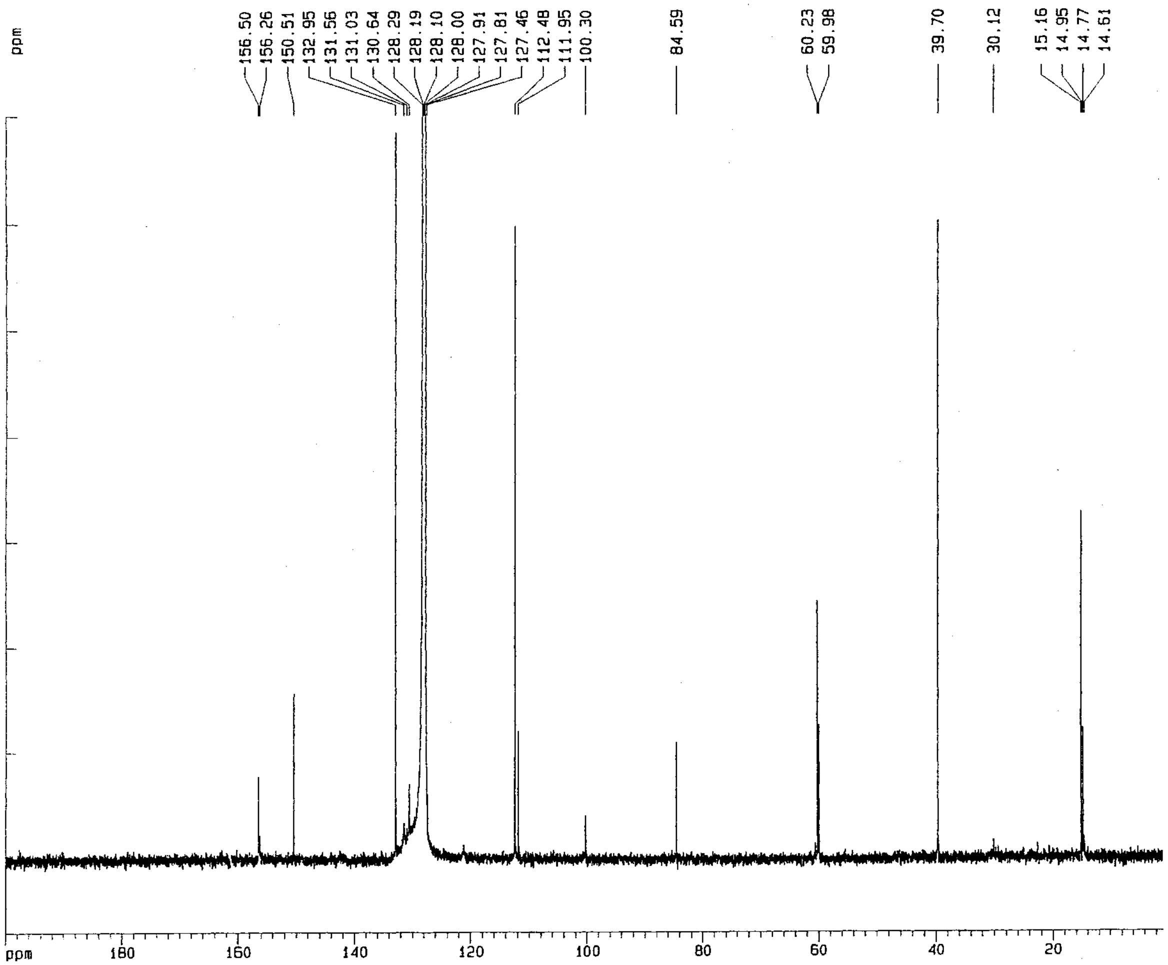
110



^{1}H NMR Spectrum (500 MHz, CDCl$_3$, 300 K) of **110**



110



^{13}C NMR Spectrum (75 MHz, C_6D_6, 323 K) of **110**

Appendix II

X-ray Data of Compound 103

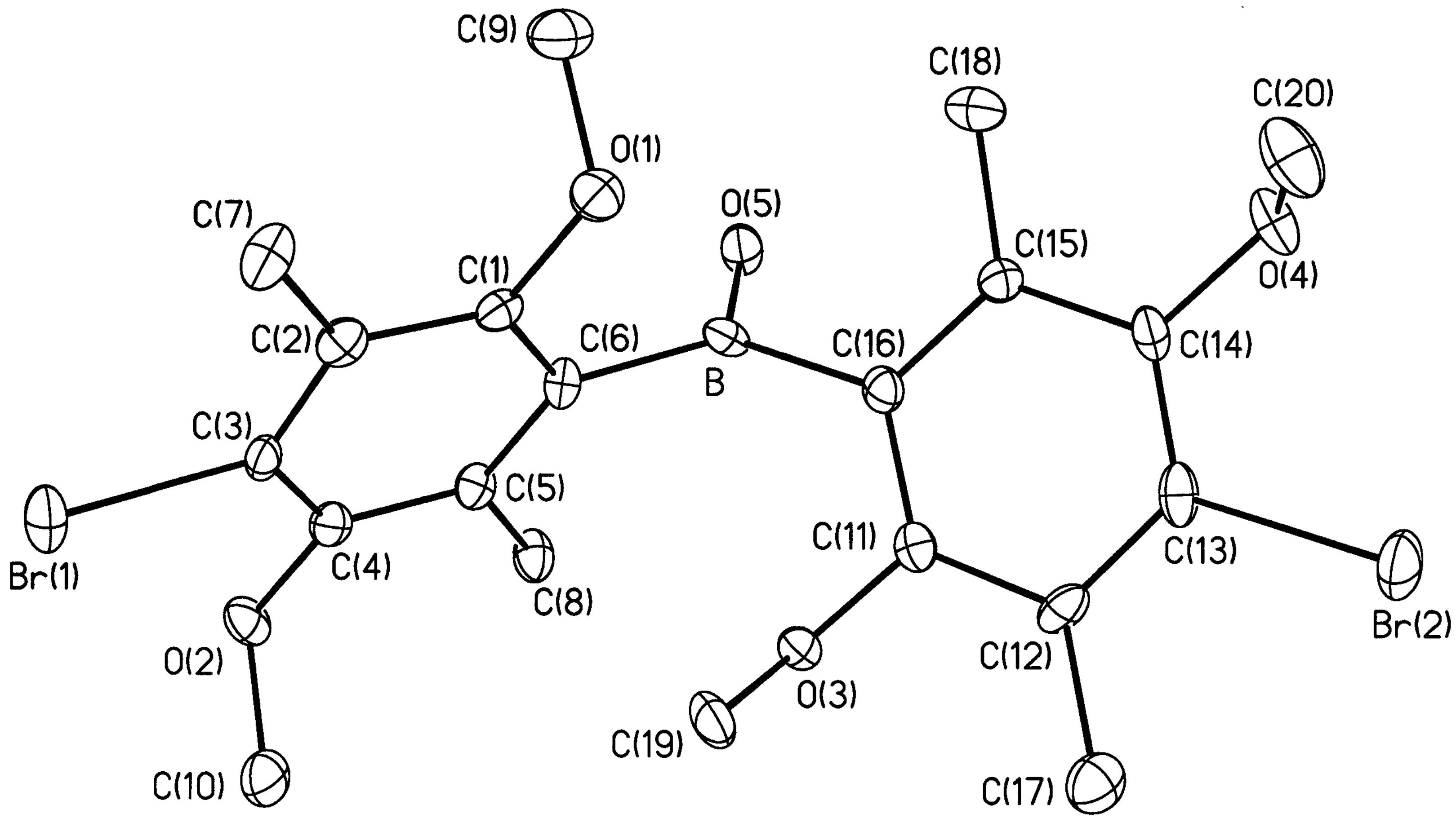

C(9)
C(18)
C(20)
O(1)
O(5)
C(7)
C(15)
O(4)
C(1)
C(2)
C(6)
C(16)
C(14)
B
C(3)
C(5)
C(11)
C(13)
Br(1)
C(4)
C(8)
Br(2)
O(2)
C(12)
O(3)
C(19)
C(10)
C(17)

Table 1. Crystal data and structure refinement for af2004.

Identification code	af2004
Empirical formula	C20 H25 B Br2 O5
Formula weight	516.03
Temperature	203(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.712(5) A alpha = 90 deg. b = 9.098(3) A beta = 110.565(6) deg c = 18.665(6) A gamma = 90 deg.
Volume	2180.0(12) A^3
Z, Calculated density	4, 1.572 Mg/m^3
Absorption coefficient	3.746 mm^-1
F(000)	1040
Crystal size	0.15 x 0.10 x 0.10 mm
Theta range for data collection	1.60 to 24.99 deg.
Limiting indices	-16<=h<=15, 0<=k<=10, 0<=l<=22
Reflections collected / unique	9051 / 3470 [R(int) = 0.0838]
Completeness to theta = 24.99	90.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.646453
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3470 / 0 / 253
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.2013
R indices (all data)	R1 = 0.1125, wR2 = 0.2210
Largest diff. peak and hole	0.900 and -0.925 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for af2004.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	4528(1)	5620(1)	880(1)	41(1)
Br(2)	-1949(1)	13756(1)	-1060(1)	45(1)
B	2455(8)	11354(11)	-873(5)	25(2)
O(1)	1841(5)	8560(7)	-1425(4)	34(2)
O(2)	5131(5)	8779(7)	1350(4)	32(2)
O(3)	1872(5)	11850(7)	445(3)	27(1)
O(4)	-1217(5)	12971(7)	-2367(4)	39(2)
O(5)	2919(5)	12186(7)	-1273(4)	32(2)
C(1)	2675(7)	8576(9)	-723(5)	24(2)
C(2)	3092(7)	7225(10)	-373(5)	27(2)
C(3)	3893(7)	7365(10)	331(5)	26(2)
C(4)	4283(7)	8718(10)	657(5)	26(2)
C(5)	3865(7)	10028(10)	288(5)	24(2)
C(6)	3022(7)	9946(10)	-411(5)	27(2)
C(7)	2640(8)	5766(11)	-724(6)	37(2)
C(8)	4302(8)	11496(10)	661(6)	34(2)
C(9)	2183(9)	8377(13)	-2070(6)	46(3)
C(10)	4836(8)	8854(13)	2014(6)	44(3)
C(11)	1077(7)	12119(9)	-259(5)	25(2)
C(12)	120(7)	12711(10)	-258(5)	30(2)
C(13)	-611(7)	12955(10)	-985(6)	32(2)
C(14)	-449(7)	12684(10)	-1663(5)	29(2)
C(15)	528(7)	12163(10)	-1644(5)	27(2)
C(16)	1320(7)	11884(9)	-928(5)	26(2)
C(17)	-57(8)	13049(12)	470(6)	43(2)
C(18)	682(9)	11870(14)	-2393(5)	45(3)
C(19)	1718(8)	10466(11)	787(6)	39(2)
C(20)	-1894(9)	11732(13)	-2673(7)	53(3)

Table 3. Bond lengths [A] and angles [deg] for af2004.

Br(1)-C(3)	1.923(8)
Br(2)-C(13)	1.933(9)
B-O(5)	1.368(12)
B-C(6)	1.587(13)
B-C(16)	1.597(14)
O(1)-C(1)	1.404(11)
O(1)-C(9)	1.447(13)
O(2)-C(4)	1.405(11)
O(2)-C(10)	1.434(13)
O(3)-C(11)	1.404(11)
O(3)-C(19)	1.460(12)
O(4)-C(14)	1.390(11)
O(4)-C(20)	1.445(13)
C(1)-C(6)	1.387(13)
C(1)-C(2)	1.416(13)
C(2)-C(3)	1.392(13)
C(2)-C(7)	1.513(13)
C(3)-C(4)	1.394(13)
C(4)-C(5)	1.395(13)
C(5)-C(6)	1.408(13)
C(5)-C(8)	1.528(13)
C(11)-C(16)	1.417(13)
C(11)-C(12)	1.420(13)
C(12)-C(13)	1.393(14)
C(12)-C(17)	1.494(14)
C(13)-C(14)	1.381(14)
C(14)-C(15)	1.409(13)
C(15)-C(16)	1.418(13)
C(15)-C(18)	1.510(13)

O(5)-B-C(6)	120.7(8)
O(5)-B-C(16)	115.4(8)
C(6)-B-C(16)	124.0(8)
C(1)-O(1)-C(9)	112.4(7)
C(4)-O(2)-C(10)	113.8(7)
C(11)-O(3)-C(19)	112.0(7)
C(14)-O(4)-C(20)	113.3(7)
C(6)-C(1)-O(1)	116.7(8)
C(6)-C(1)-C(2)	124.2(8)
O(1)-C(1)-C(2)	119.1(7)
C(3)-C(2)-C(1)	114.4(8)
C(3)-C(2)-C(7)	123.8(8)
C(1)-C(2)-C(7)	121.6(8)
C(2)-C(3)-C(4)	123.2(8)
C(2)-C(3)-Br(1)	119.1(7)
C(4)-C(3)-Br(1)	117.7(7)
C(3)-C(4)-C(5)	120.8(8)
C(3)-C(4)-O(2)	120.2(8)
C(5)-C(4)-O(2)	119.0(8)
C(4)-C(5)-C(6)	118.2(8)
C(4)-C(5)-C(8)	119.6(8)
C(6)-C(5)-C(8)	122.1(8)
C(1)-C(6)-C(5)	119.1(8)
C(1)-C(6)-B	117.8(8)
C(5)-C(6)-B	123.1(8)
O(3)-C(11)-C(16)	116.9(7)

O(3)-C(11)-C(12)	118.7(8)
C(16)-C(11)-C(12)	124.2(8)
C(13)-C(12)-C(11)	114.1(8)
C(13)-C(12)-C(17)	124.2(8)
C(11)-C(12)-C(17)	121.7(9)
C(14)-C(13)-C(12)	124.9(8)
C(14)-C(13)-Br(2)	117.1(7)
C(12)-C(13)-Br(2)	118.0(7)
C(13)-C(14)-O(4)	121.3(8)
C(13)-C(14)-C(15)	119.6(8)
O(4)-C(14)-C(15)	119.0(8)
C(14)-C(15)-C(16)	119.4(8)
C(14)-C(15)-C(18)	118.5(8)
C(16)-C(15)-C(18)	122.1(8)
C(11)-C(16)-C(15)	117.6(8)
C(11)-C(16)-B	121.0(8)
C(15)-C(16)-B	121.4(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for af2004. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	41(1)	28(1)	52(1)	10(1)	14(1)	10(1)
Br(2)	26(1)	52(1)	59(1)	9(1)	18(1)	11(1)
B	24(5)	32(6)	17(5)	3(4)	5(4)	-2(4)
O(1)	24(3)	41(4)	31(3)	-8(3)	2(3)	-2(3)
O(2)	22(3)	41(4)	27(3)	5(3)	2(3)	1(3)
O(3)	28(3)	28(3)	22(3)	1(2)	6(3)	3(3)
O(4)	27(4)	39(4)	38(4)	11(3)	-4(3)	1(3)
O(5)	28(3)	33(4)	35(4)	7(3)	10(3)	5(3)
C(1)	21(5)	27(5)	25(4)	-6(4)	10(4)	-2(3)
C(2)	25(5)	29(5)	33(5)	-1(4)	17(4)	-3(4)
C(3)	30(5)	24(5)	32(5)	9(4)	20(4)	11(4)
C(4)	18(4)	34(5)	27(5)	0(4)	8(4)	3(4)
C(5)	16(4)	25(4)	30(5)	-2(4)	7(4)	-1(3)
C(6)	24(5)	23(4)	34(5)	2(4)	10(4)	6(4)
C(7)	30(5)	31(5)	51(6)	-8(5)	15(5)	2(4)
C(8)	31(5)	24(5)	39(5)	-2(4)	4(5)	3(4)
C(9)	56(7)	48(7)	33(5)	-7(5)	14(5)	0(5)
C(10)	34(6)	52(7)	37(6)	-4(5)	4(5)	13(5)
C(11)	24(5)	18(4)	29(5)	1(3)	6(4)	-2(3)
C(12)	33(5)	26(5)	41(5)	1(4)	27(5)	-1(4)
C(13)	14(4)	28(5)	47(6)	4(4)	4(4)	0(4)
C(14)	22(5)	30(5)	31(5)	9(4)	4(4)	7(4)
C(15)	28(5)	29(5)	26(5)	2(4)	12(4)	3(4)
C(16)	29(5)	20(4)	27(5)	2(3)	8(4)	3(4)
C(17)	34(6)	47(6)	47(6)	-6(5)	15(5)	-3(5)
C(18)	50(7)	60(7)	26(5)	-1(5)	14(5)	5(5)
C(19)	39(6)	42(6)	35(5)	19(4)	11(5)	14(5)
C(20)	37(6)	52(7)	52(7)	7(5)	-6(6)	-8(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for af2004.

	x	y	z	U(eq)
H(5A)	3475	11793	-1253	48
H(7A)	3026	4972	-401	56
H(7B)	2691	5679	-1228	56
H(7C)	1915	5712	-769	56
H(8A)	4873	11319	1137	50
H(8B)	3758	12044	763	50
H(8C)	4552	12058	318	50
H(9A)	1583	8382	-2541	69
H(9B)	2549	7449	-2023	69
H(9C)	2646	9177	-2078	69
H(10A)	5456	8892	2470	65
H(10B)	4430	7992	2033	65
H(10C)	4422	9731	1987	65
H(17A)	554	12774	902	64
H(17B)	-655	12500	487	64
H(17C)	-186	14094	494	64
H(18A)	51	12123	-2814	68
H(18B)	838	10838	-2425	68
H(18C)	1255	12462	-2422	68
H(19A)	2287	10315	1267	59
H(19B)	1700	9662	441	59
H(19C)	1065	10500	878	59
H(20A)	-2415	12001	-3160	79
H(20B)	-2235	11450	-2318	79
H(20C)	-1486	10912	-2747	79

Table 6. Torsion angles [deg] for af2004.

C(9)-O(1)-C(1)-C(6)	98.3(9)
C(9)-O(1)-C(1)-C(2)	-83.1(10)
C(6)-C(1)-C(2)-C(3)	0.5(12)
O(1)-C(1)-C(2)-C(3)	-178.0(7)
C(6)-C(1)-C(2)-C(7)	176.7(9)
O(1)-C(1)-C(2)-C(7)	-1.9(12)
C(1)-C(2)-C(3)-C(4)	-2.2(12)
C(7)-C(2)-C(3)-C(4)	-178.3(9)
C(1)-C(2)-C(3)-Br(1)	179.5(6)
C(7)-C(2)-C(3)-Br(1)	3.4(12)
C(2)-C(3)-C(4)-C(5)	1.1(13)
Br(1)-C(3)-C(4)-C(5)	179.5(7)
C(2)-C(3)-C(4)-O(2)	-176.4(8)
Br(1)-C(3)-C(4)-O(2)	1.9(11)
C(10)-O(2)-C(4)-C(3)	-92.5(10)
C(10)-O(2)-C(4)-C(5)	89.9(10)
C(3)-C(4)-C(5)-C(6)	1.8(13)
O(2)-C(4)-C(5)-C(6)	179.3(8)
C(3)-C(4)-C(5)-C(8)	179.5(8)
O(2)-C(4)-C(5)-C(8)	-2.9(12)
O(1)-C(1)-C(6)-C(5)	-179.2(8)
C(2)-C(1)-C(6)-C(5)	2.2(13)
O(1)-C(1)-C(6)-B	-0.4(12)
C(2)-C(1)-C(6)-B	-179.0(8)
C(4)-C(5)-C(6)-C(1)	-3.3(13)
C(8)-C(5)-C(6)-C(1)	179.0(8)
C(4)-C(5)-C(6)-B	178.0(8)
C(8)-C(5)-C(6)-B	0.3(14)
O(5)-B-C(6)-C(1)	-104.1(10)
C(16)-B-C(6)-C(1)	74.3(12)
O(5)-B-C(6)-C(5)	74.6(12)
C(16)-B-C(6)-C(5)	-107.0(11)
C(19)-O(3)-C(11)-C(16)	-104.0(9)
C(19)-O(3)-C(11)-C(12)	80.9(10)
O(3)-C(11)-C(12)-C(13)	179.1(7)
C(16)-C(11)-C(12)-C(13)	4.4(13)
O(3)-C(11)-C(12)-C(17)	-0.1(13)
C(16)-C(11)-C(12)-C(17)	-174.8(9)
C(11)-C(12)-C(13)-C(14)	-1.0(13)
C(17)-C(12)-C(13)-C(14)	178.3(9)
C(11)-C(12)-C(13)-Br(2)	179.8(6)
C(17)-C(12)-C(13)-Br(2)	-1.0(12)
C(12)-C(13)-C(14)-O(4)	-179.4(8)
Br(2)-C(13)-C(14)-O(4)	-0.2(12)
C(12)-C(13)-C(14)-C(15)	-2.1(14)
Br(2)-C(13)-C(14)-C(15)	177.1(7)
C(20)-O(4)-C(14)-C(13)	-90.6(12)
C(20)-O(4)-C(14)-C(15)	92.1(11)
C(13)-C(14)-C(15)-C(16)	1.9(14)
O(4)-C(14)-C(15)-C(16)	179.3(8)
C(13)-C(14)-C(15)-C(18)	179.8(9)
O(4)-C(14)-C(15)-C(18)	-2.9(13)
O(3)-C(11)-C(16)-C(15)	-179.4(7)
C(12)-C(11)-C(16)-C(15)	-4.7(13)
O(3)-C(11)-C(16)-B	-0.6(12)
C(12)-C(11)-C(16)-B	174.2(8)

C(14)-C(15)-C(16)-C(11)	1.3(13)
C(18)-C(15)-C(16)-C(11)	-176.5(9)
C(14)-C(15)-C(16)-B	-177.5(8)
C(18)-C(15)-C(16)-B	4.6(14)
O(5)-B-C(16)-C(11)	-128.0(9)
C(6)-B-C(16)-C(11)	53.5(12)
O(5)-B-C(16)-C(15)	50.8(12)
C(6)-B-C(16)-C(15)	-127.7(9)

Symmetry transformations used to generate equivalent atoms: