Boron Heterocycles: from Aromaticity to Electronic Materials

by

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GO BLUE

To my family, relatives and all respected teachers

本论文献给我的家人,亲戚以及所有尊敬的师长

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Table of Contents

List of Figures

List of Appendices

List of Abbreviations

AN	acetonitrile
b.p.	boiling point
Bu	butyl
t-Bu	*tert*-butyl
Cp	cyclopentadienyl, $C_5H_5^-$
Cp*	pentamethylcyclopendienyl, $Me_5C_5^-$
Cy	cyclohexyl
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMAD	dimethyl acetylenedicarboxylate
DMSO	dimethyl sulfoxide
Et_2O	diethyl ether
HRMS	high resolution mass spectrometry
KHMDS	potassium hexamethyldisilazide
LDA	lithium diisopropylamide
m.p.	melting point
Me	methyl
Mes	mesityl or 2,4,6-trimethylphenyl
Ph	phenyl
i-Pr	isopropyl

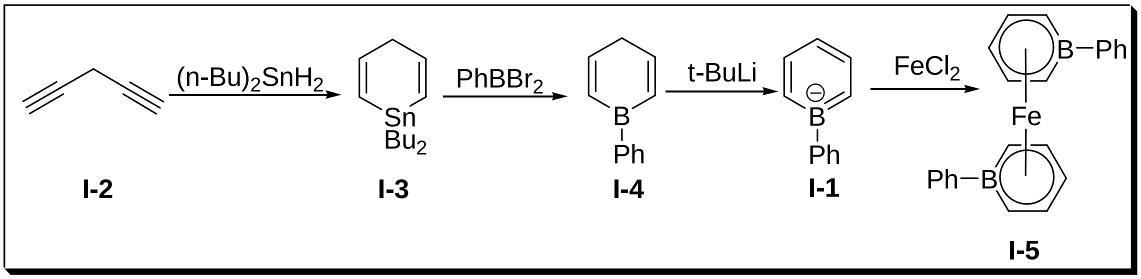
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMS	trimethylsilyl
TMSCl	chlorotrimethylsilane

Chapter I

Introduction

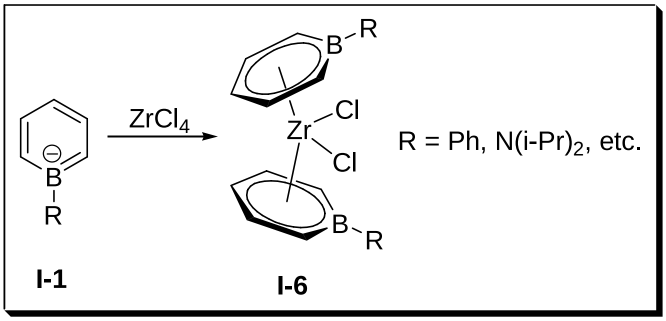
I.1. 6π-Electron Boron-Heterocyclic Aromatic Rings

Benzene and cyclopentadienyl (Cp) anion are the two most common and simplest 6π-electron aromatic rings. The rich chemistry of these two rings and their derivatives has driven chemists to explore the possible heteroaromatic rings by substitution of one or more CH groups with BH, P, or other heteroatom. The interest of boron-containing heterocycles in Ashe's group can be traced back to as early as in 1970's when Ashe and Shu prepared 1-phenylborabenzene anion (**I-1**).[1] Stannohydration of diethynylmethane (**I-2**) with dibutyltin dihydride gave 1,4-dihydro-1,1-dibutylstannabenzene (**I-3**). Reaction of **I-3** with phenylboron dibromide gave 1-phenyl-1,4dihydro-borabenzene (**I-4**), which was then converted to **I-1** by deprotonation with *tert*-butyllithium (Scheme I-1). The reaction of **I-1** with $FeCl_2$ afforded bis(1-phenylboratabenzene)iron (**I-5**), which has many ferrocene-like properties[2]. For example, it is air and moisture stable. It also has been shown to undergo electrophilic aromatic substitution reactions.

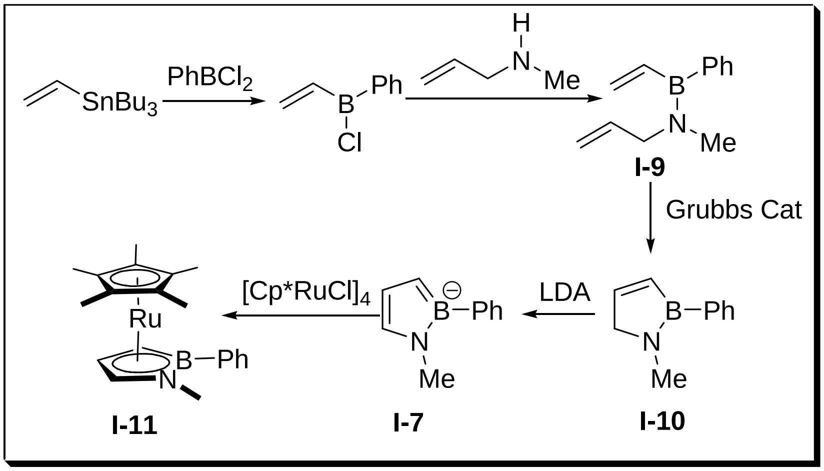


Scheme I-1

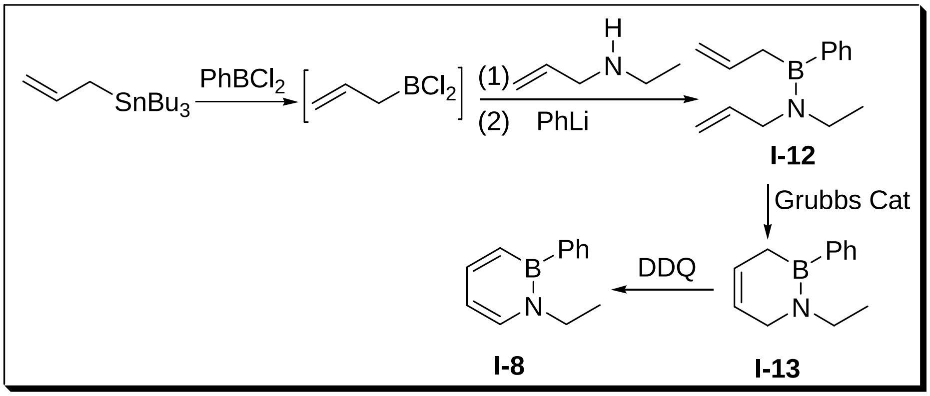
The development of metallocence-based homogeneous catalysts for the polymerization of olefins has attracted intense research.[3] While the design and synthesis of sterically modified metallocenes has been the center of the research, much less attention has been directed toward tuning the electronic properties of the catalytically active site by the substitution of heterocyclic ligands in place of the Cp ring. Ashe, Bazan and coworkers found that boratabenzenes could be converted to bis bis(boratabenzene)zirconium dichlorides (**I-6**) (Scheme I-2).[4] On activation by methylaluminoxane (MAO), **I-6** was a highly active catalyst for the polymerization of ethylene.



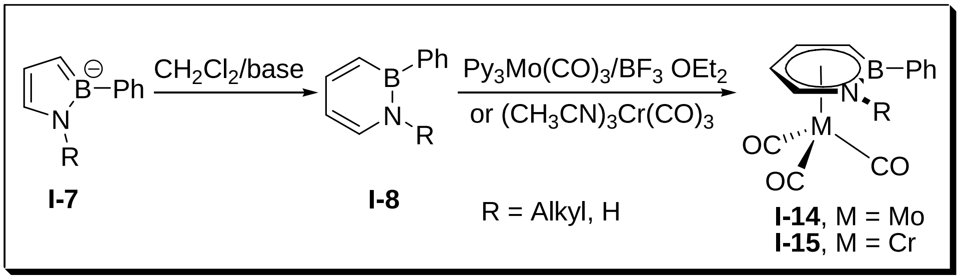
Scheme I-2



Scheme I-3



Scheme I-4



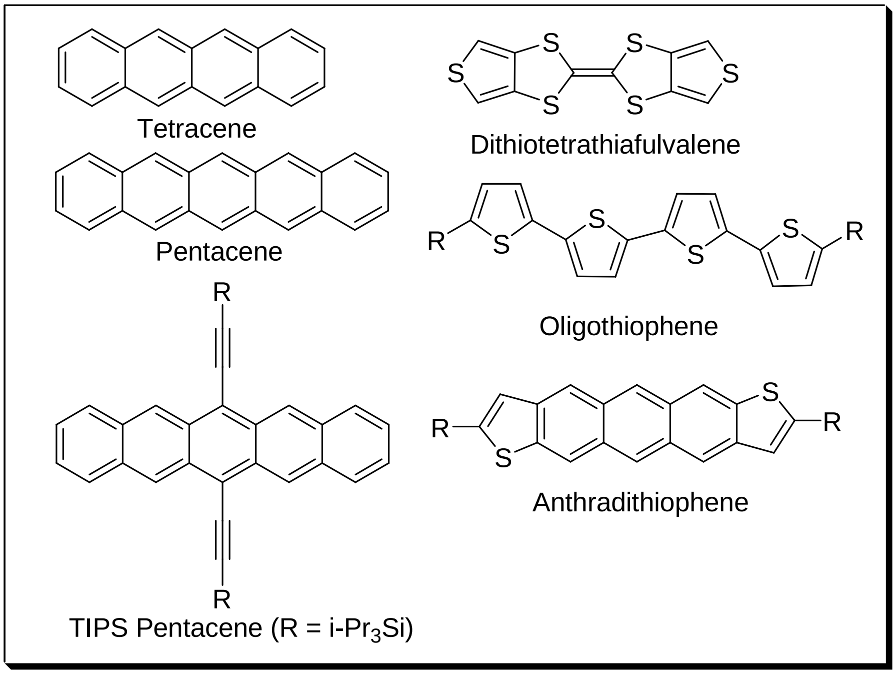
Scheme I-5

Inspired by the interesting results on **I-6**, research efforts were extended to other boron-heterocyclic systems. Likewise, replacement of an adjacent pair of carbon atoms of Cp and benzene by boron and nitrogen, 1,2-azaborolide (**I-7**) anion and 1,2-dihydro-1,2-azaborine (**I-8**), are isoelectronic with Cp and benzene, respectively (Scheme I-3).[5] **I-7** was prepared from the deprotonation of N-methyl-2-phenyl-1,2-azaborole (**I-10**), which can be obtained from the cyclization of **I-9** via ring closing metathesis (RCM) reaction using Grubbs catalyst, [PhCH=RuCl$_2$(PCy$_3$)$_2$]. Reaction of **I-7** with [Cp*RuCl]$_4$ afforded expected sandwich complex **I-11**. 1,2-Dihydro-1,2-azaborine **I-8** was prepared either by an analogous route (Scheme I-4),[5] or more generally a carbenoid ring expansion from 1,2-azaborolides **I-7** (Scheme I-5).[6] Mo(CO)$_3$ complex (**I-14**) or Cr(CO)$_3$ complex (**I-15**) can be prepared from the reaction of **I-8** with $Py_3Mo(CO)_3/BF_3{\cdot}OEt_2$ or $(CH_3CN)_3Cr(CO)_3$, respectively.

Since 1,2-azaborolide (**I-7**) anion and 1,2-dihydro-1,2-azaborine (**I-8**) are 6π-electron aromatic rings and good ligands to transition metals, we are now curious about the 1,2-oxaborolide and 1,2-dihydro-1,2-oxaborine systems. We hope to use the aforementioned experience and experimental technique to develop the synthetic routes for 1,2-oxaborolide and 1,2-oxaborine and explore their chemical properties such as aromaticity and coordination chemistry.

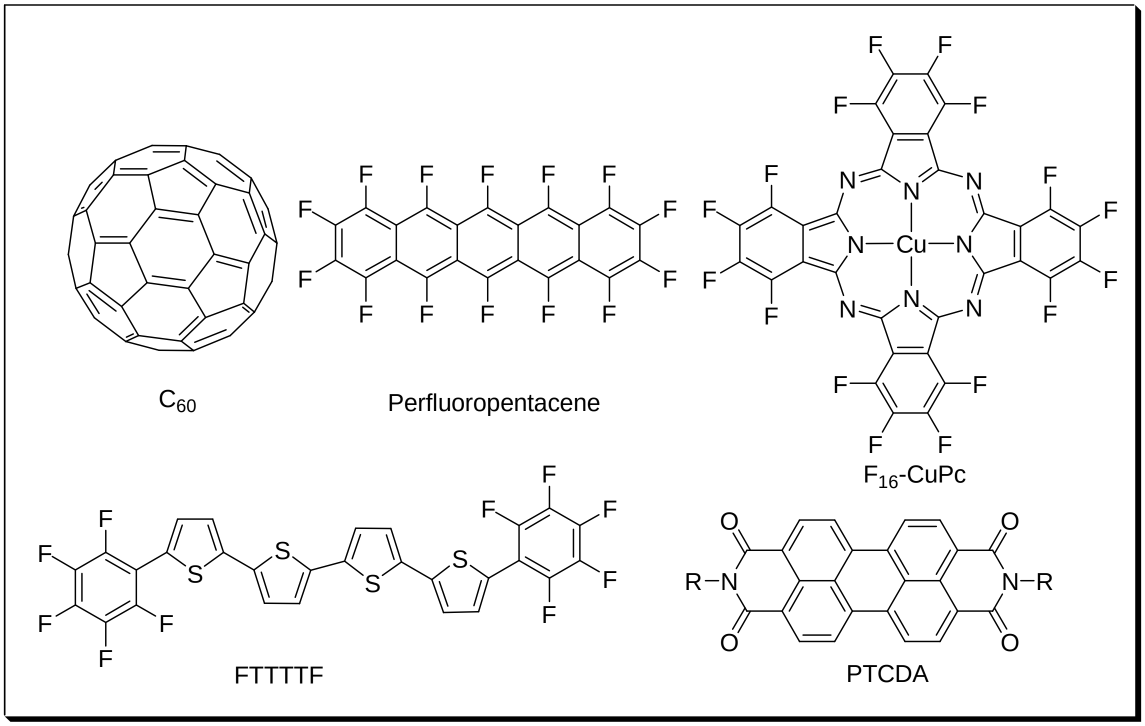
I.2. Polycyclic Aromatic Hydrocarbons and Diboraarenes

Semiconducting materials based upon small organic molecules and polymers have been the focus of intense investigation for the past decades.[7] The common feature of these structures, comprising molecular and polymeric units, are π-conjugated bonds giving rise to delocalized filled and empty π-orbitals that greatly impact the optical and electrical properties. Like traditional inorganic semiconductors, organic materials also can function either as p-type (hole transport) or n-type (electron transport). The most extensively studied organic semiconductors have been the p-type for its widely available candidates (See Scheme I-6 for some examples). There have been more examples of good p-type materials than n-type materials (see Scheme I-7 for some examples) for organic thin-film transistors (OTFTs). The motivation for seeking good n-channel OTFTs is that they enable complementary circuit design.[7b]



Scheme I-6 Examples of p-type organic semiconductors

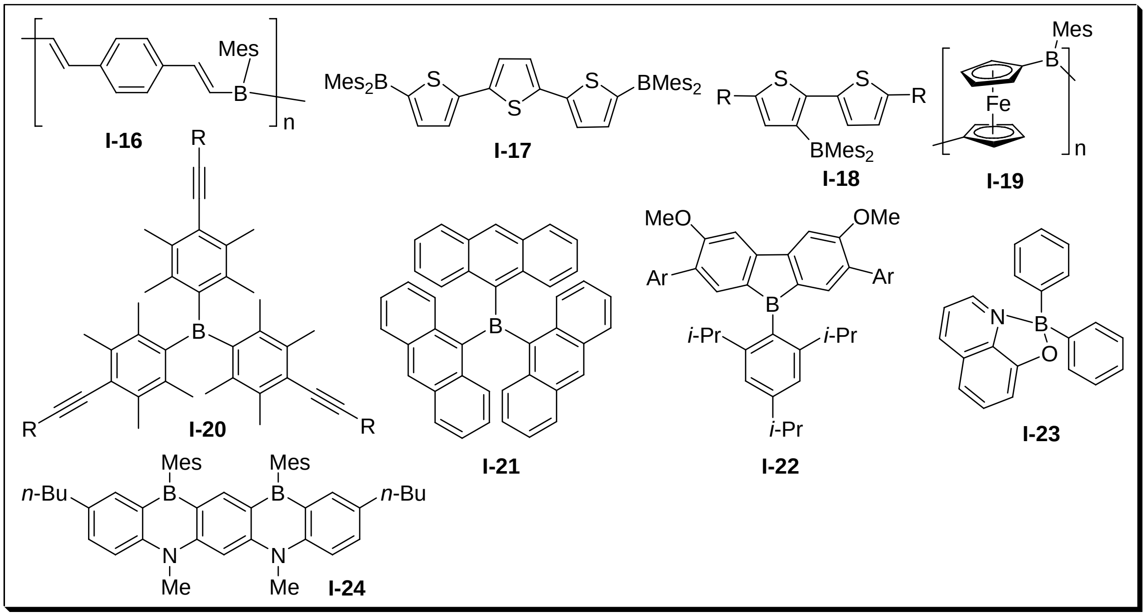
Among the fused aromatics, pentacene is one of the most commonly used p-type organic semiconducting materials for OTFTs due to its superior field effect mobility and reasonable environmental stability. Much efforts have been taken to modify the structure of pentacene in order to increase its processibility and change the solid-state packing pattern. An unsubstituted pentacene adopts a herringbone motif in the solid state. This aromatic edge-to-face interaction can be disrupted by adding silyl substitutents to the central ring of the pentacene molecule, leading to close cofacial π-stacking. A number of interesting pentacene derivatives have been synthesized and structurally characterized by X-ray crystallography. For instance, 6,13-disubstituted pentacene derivatives (TIPS pentacene (6,13-bis(triisopropylsilylethynyl)pentacene) in Scheme I-6) that are highly soluble in organic solvents have been prepared by Anthony and coworkers.[8]



Scheme I-7 Examples of n-type organic semiconductors

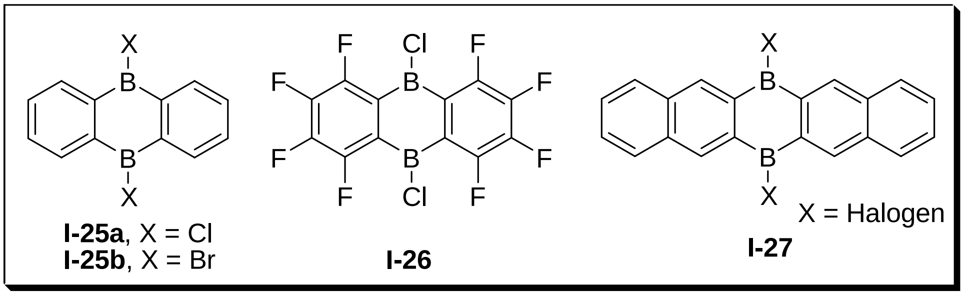
Another interesting derivative of pentacene, perfluoropentacene, which contains fluorine atoms in place of hydrogen, behaves like an n-type semiconductor while retaining almost the same molecular size as that of pentacene. Theoretical calculations indicate that fully replacing H with F atoms could decrease the HOMO-LUMO energy gap from 2.21 eV (pentacene) to 2.02 eV (perfluoropentacene).[9]

Boron-containing π-electron systems have recently attracted much attention (Scheme I-8).[10] Interest in boron-based functional materials is attributed to the characteristic features of the element boron. Three-coordinate boron is isoelectronic and isostructural with a positively charged carbocation. With its vacant p_z orbital, boron is inherently electron deficient and is a strong π-electron acceptor, allowing for conjugation of organic π-systems with and through boron and leading to the appearance of unique electronic and photophysical properties. With its Lewis acidity, boron readily forms unique complexes with Lewis bases or nucleophilic counterpart. This complexation is important for tuning the electronic structure or for constraining the three-dimensional molecular structure. Boron takes a trigonal planar geometry, which can be used as building block for constructing complex molecules.



Scheme I-8 Boron-Containing materials

However, at least one of the three substituents of open-chain boron (**I-16** to **I-21**) needs to be bulky to shield the vacant p_z-orbital to prevent it from water and oxygen attack. The disadvantage of this protection is that it affects boron’s conjugation with organic π-system, molecular packing, and intermolecular interactions which would transmit to the proficiency of electron transport of the materials when used as organic semiconductors. If boron is fused to a conjugate system (**I-22** to **I-24**), it will greatly increase the intramolecular electron delocalization and improve intermolecular interaction and packing pattern such as π-π stacking which is favorable by electronic materials.



Scheme 9

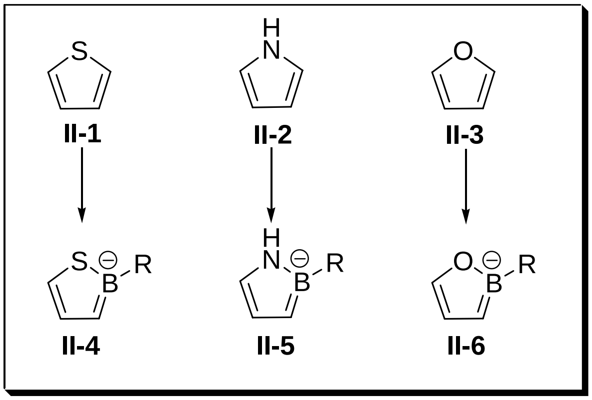
To extend our expertise in boron heterocycles, we turned to pick up a known diboracene system, 9,10-diboraanthracenes[11] (**I-25a,b, I-26**) (Scheme I-9) as a starting point and proposed to explore a system analogous to pentacene, 6,13-diborapentacenes (**I-27**). We would like to develop the synthetic methods, study molecular structures and investigate related electronic properties.

Chapter II

A Boron Analogue of Furan: The Synthesis and Coordination Chemistry of 2-Substituted-1,2-Oxaborolides

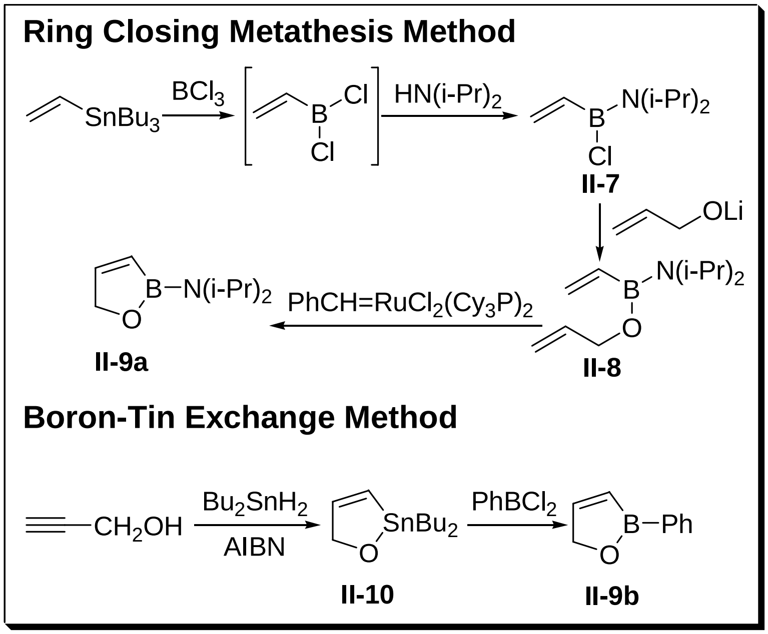
Although thiophene (**II-1**), pyrrole (**II-2**), and furan (**II-3**) are the best known and most important five-membered aromatic heterocycles (Scheme II-1),[1] they are not particularly good η^5-ligands toward transition metals. Thiophene[1] and pyrrole[2] form few stable π-coordinated transition metal complexes. To the best of our knowledge only one complex containing an η^5-furan ligand has been reported: the very labile $[Cp^*Ru(\eta^5\text{-}C_4H_4O)]Cl$.[4-6] We have been interested in anionic aromatic ligands, in which a CH group of a neutral aromatic is replaced by the isoelectronic BH^- group.[7-14] In this manner **II-1**, **II-2**, and **II-3** are converted to 1,2-thiaborolide (**II-4**),[10] 1,2-azaborolide (**II-5**),[11-14] and 1,2-oxaborolide (**II-6**), respectively (Scheme II-1). **II-4** and **II-5** are good ligands, which have been used to prepare Cp-like transition metal complexes.[10-14] Of particular significance is the observation that zirconium(IV) derivatives of **II-4**[10] and **II-5**[14] have high catalytic activity for the polymerization of olefins. Thus it is of considerable interest to prepare **II-6** so that its coordination chemistry can be explored. We now wish to report the first synthesis of the 1,2-oxaborolide ring system and on its facile conversion to late transition metal complexes.

The precursors to **II-6**, 2-substituted-2,5-dihydro-1,2-oxaboroles (**II-9**), may be easily prepared by either of the two synthetic methods summarized in Scheme II-2. In the first route, commercially available tributylvinyltin was treated with BCl_3 followed by diisopropylamine to obtain (N,N-diisopropylamino)vinylboron chloride (**II-7**).[10b] The reaction of **II-7** with lithium alloxide in THF gave (allyloxy)(N,N-diisopropylamino)vinylborane (**II-8**) in 87% yield. Upon addition of 2 mol% of Grubbs catalyst [$PhCH{=}RuCl_2(Cy_3P)_2$] to **II-8** in methylene chloride, cyclization took place smoothly to give **II-9a** in 92% yield. Alternatively, the reaction of 2,2-dibutyl-2,5-dihydro-1,2-oxastannole (**II-10**)[15] with $PhBCl_2$ afforded **II-9b** in 83% yield. Since **II-10** is available in large quantities from the reaction of Bu_2SnH_2 with propargyl alcohol, the latter preparation is particularly facile.

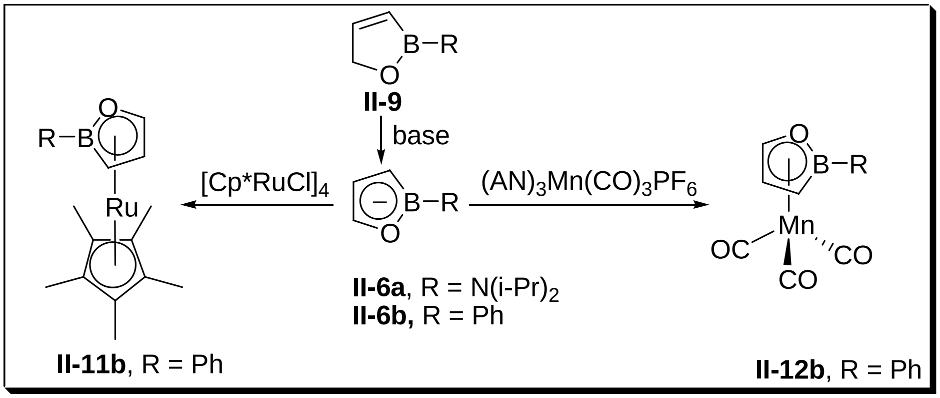


Scheme II-1

The reaction of **II-9a** with LDA in pentane at −78 °C gave a yellow powder, which after washing with excess pentane afforded pure Li-**II-6a** in 53% yield (Scheme II-3). Alternatively treatment of **II-9b** in ether with $KN(SiMe_3)_2$ gave a 86% yield of K-**II-6b**. The ^{1}H NMR spectra of **II-6a** and **II-6b** in THF-d_8 or DMSO-d_6 show first-order patterns, which are consistent with the assigned structures.



Scheme II-2



Scheme II-3

Of particular significance is the observation that the ^{1}H, ^{11}B, and ^{13}C NMR spectra of **II-6b** are extremely similar to those of **II-5b**, as is illustrated in Figure II-1. The spectra exhibit high-field ^{11}B chemical shift values, which are consistent with strong stabilization by π-bonding to boron.[16] The high-field ^{13}C NMR shifts for C(3) are consistent with appreciable carbanionic character, while the lower field chemical shift values of C(4) and C(5) suggest that these atoms bear little negative charge.[17] Overall the great similarity in spectra implies a similarity in the electronic structure of **II-5b** and **II-6b**. However, the greater upper field chemical shift for C(3) of **II-6a** might be due to the existence of partial external B=N bond that decreases the delocalization of anionic charge through the ring.

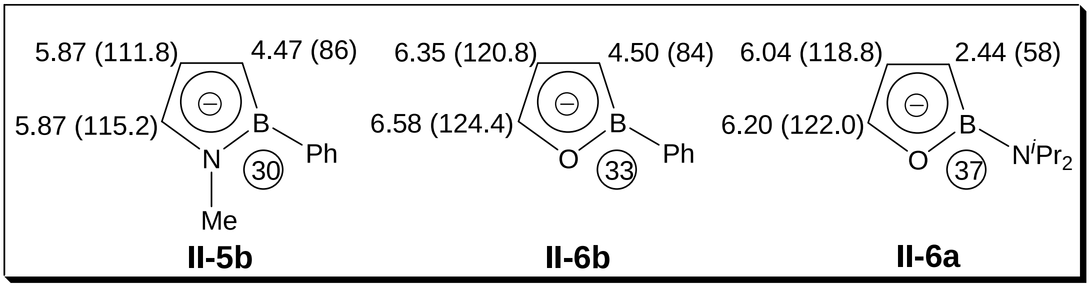


Figure II-1. Comparison of the ^{1}H NMR, ^{13}C NMR (in parentheses), and ^{11}B NMR (in circles) chemical shift values of **II-5b** and **II-6a,b** in THF-d_8.

Like 1,2-azaborolides, 1,2-oxaborolides readily form transition metal complexes. The reaction of **II-6b** with [Cp*RuCl]$_4$ gave **II-11b** as bright amber crystals in 70% yield. The crystal structure of **II-11b** shows that it is a diheteroruthenocene in which the oxaborolyl ring is η^5-bond to Ru in the same manner found for the corresponding complex of **II-4a** (See Figure II-2).

Unfortunately, a partial disorder limits the accuracy of the bond distances. **II-11b** is more robust than the isoelectronic furan complex, [Cp*Ru(η^5-C_4H_4O)]Cl, which was reported to be stable only in solutions of noncoordinating solvents at low temperature.[4]

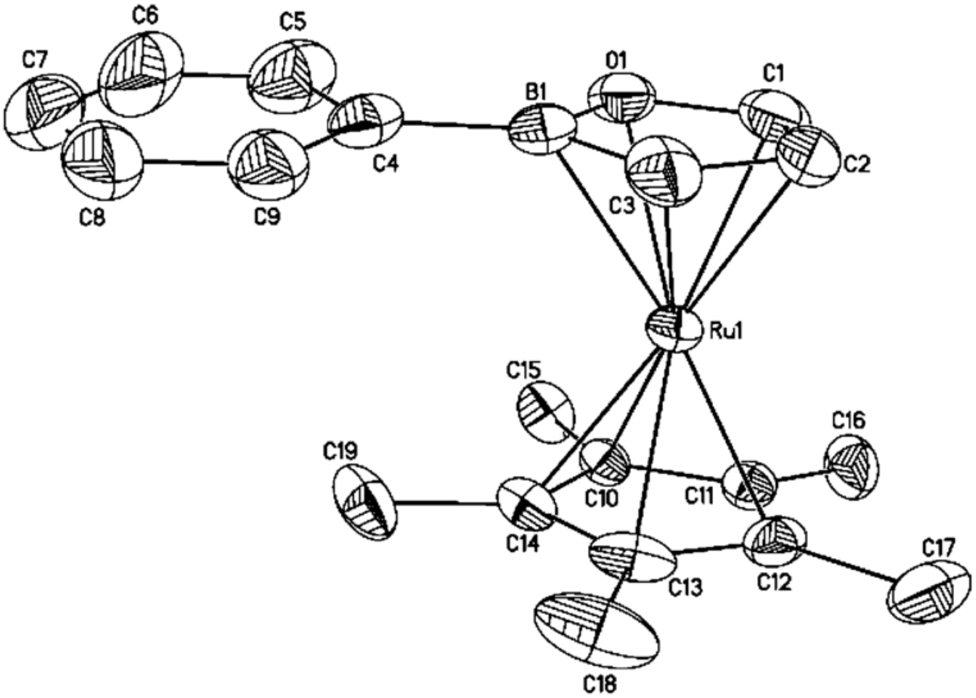


Figure II-2. Solid-state structure of **II-11b** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å): B(1)−C(3), 1.468(2); B(1)−O(1), 1.427(2); C(1)−C(2), 1.382(2); C(2)−C(3), 1.416(2); C(1)−O(1), 1.422(2); B(1)−Ru(1), 2.278(2); C(1)−Ru(1), 2.149(2); C(2)−Ru(1), 2.193(2); C(3)−Ru(1), 2.230(2); O(1)−Ru(1), 2.217(1); C(Cp)−Ru(1), 2.148(2)−2.186(2).

The reaction of **II-6b** with $(AN)_3Mn(CO)_3PF_6$ in THF afforded **II-12b** as a yellow crystalline solid in 63% yield. On recrystallization from pentane, **II-12b** was subject to single-crystal X-ray analysis. The molecular structure of **II-12b**, illustrated in Figure II-3, shows that the near planar oxaborolyl ring is η^5-bound to the $Mn(CO)_3$ group in a typical piano-stool fashion. The oxaborolyl ring shows a small deviation from planarity in that the boron atom is displaced away from Mn out of the plane defined by C(1)C(2)C(3)O(1) by 0.12(2) Å. The B−Mn distance (2.301(1) Å) is somewhat longer than the C−Mn distances (2.06−2.21 Å) and the Mn−O distance (2.111(1) Å). These observations are consistent with a somewhat weaker coordination to boron, and they conform to the pattern shown by complexes of other heterocyclic boron ligands.[7-12]

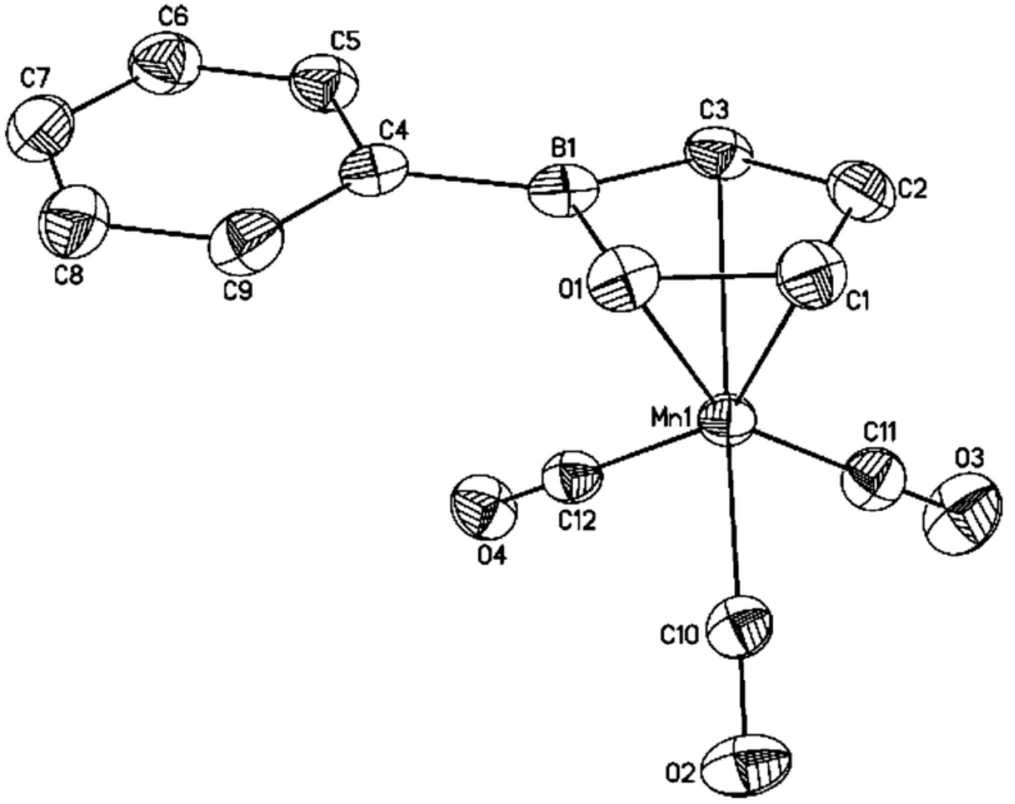


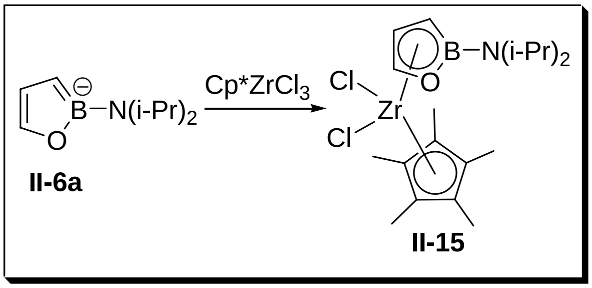
Figure II-3 Solid-state structure of **II-12b** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å): B(1)−C(3), 1.514(2); B(1)−O(1), 1.456(2); C(1)−C(2), 1.392(2); C(2)−C(3), 1.427(2); C(1)−O(1), 1.404(2); B(1)−Mn(1), 2.301(2); C(1)−Mn(1), 2.057(2); C(2)−Mn(1), 2.154(1); C(3)−Mn(1), 2.210(1); O(1)−Mn(1), 2.111(1).

The intra-ring C−C and B−C distances of the 1,2-oxaborolyl ligand of **II-12b** are typical of those found for similarly coordinated heteroaromatic ligands. The C−C bond distances (1.43−1.39 Å) of **II-12b** are only slightly different than those shown by (1-phenylboratabenzene)$Mn(CO)_3$ (**II-13**) (1.42−1.40 Å).[18] The intra-ring B−C distance of

II-12b (1.514(2) Å) is identical to that shown by **II-13**. However it is more difficult to draw conclusions about the B−O and C−O bonds due to the dearth of compounds with coordination similar to that of **II-12b**. The ring C−O bond of **II-12b** (1.404(2) Å) is somewhat longer than that of furan (1.368 Å).[19] On the other hand the B−O bond of **II-12b** (1.456(2) Å) is much longer than the range of the B−O bonds (1.34−1.38 Å) found for esters of borinic acids (R_2BOR') (**II-14**).[20] We speculate that hypothetical metal coordination to **II-3** or **II-14** might reasonably be expected to expand these bonds.

Finally we note that the CO stretching frequencies in the IR spectrum of **II-12b** in hexane are 2039, 1966, and 1948 cm^{-1}, which are virtually identical to those of **II-13** (2039, 1974, 1960 cm^{-1}),[21] but are slightly shifted from those of $CpMn(CO)_3$ (2028, 1944 cm^{-1}). This suggests that the boron heterocycles are weaker donors but better acceptors than Cp.[8b]

Z. Bajko of the Ashe group was able to convert **II-6a** to Cp^*ZrCl_2-complex (II) in a very low yield.[22] Apparently, the great oxophilicity of Zr(IV) leads to destruction of most of **II-6a** limiting the yield. For this reason this work was not progressed and no polymerization data were obtained for **II-15**.



Scheme II-4

In summary, we have developed two efficient syntheses of 1,2-oxaborolides from readily available starting materials. 1,2-Oxaborolides are diheterocyclopentadienides, which are also anionic boron analogues of furan. They are good ligands toward late transition metals. The way is now open for the development of new coordination chemistry of this Cp surrogate.

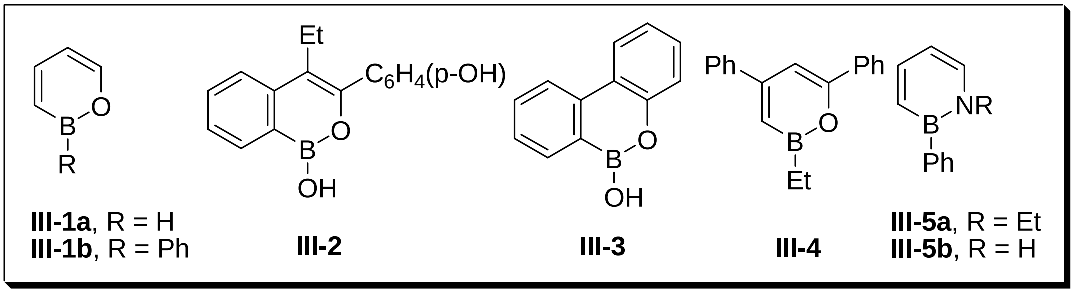
Table II-1. Crystal and data collection parameters for **II-11b** and **II-12b**

	II-11b	**II-12b**
empirical formula	$C_{19}H_{23}BORu$	$C_{12}H_8BMnO_4$
fw	379.25	281.93
temp,K	293(2)	150(2)
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	P2(1)/n	P2(1)/c
a, Å	8.7654(13)	8.4249(7)
b, Å	14.136(2)	17.0274(14)
c, Å	13.820(2)	8.2670(7)
β, deg	94.583(4)	98.110(2)
V, Å^3, Z	1706.9(4), 4	1174.07(17), 4
calcd density, Mg/m^3	1.476	1.595
abs coeff, mm^{-1}	0.917	1.124
F(000)	776	568
cryst size, mm	0.36 × 0.12 × 0.12	0.74 × 0.72 × 0.36
limiting indices	$-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$	$-11 \leq h \leq 11$, $-22 \leq k \leq 22$, $-11 \leq l \leq 11$
no. of reflns collected/ unique	23 160/22 728	13 720/2900
abs corr	semiempirical fr equivalents	semiempirical fr equivalents
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/ params	22 728/0/206	2900/0/163
GOF on F^2	1.043	1.058
final R indices (I>2σ(I))	R1 = 0.0350, wR2 = 0.0784	R1 = 0.0225, wR2 = 0.0634
R indices (all data)	R1 = 0.0534, wR2 = 0.0830	R1 = 0.0236, wR2 = 0.0641
largest diff peak and hole, e/A^3	0.772 and −0.790	0.377 and −0.282

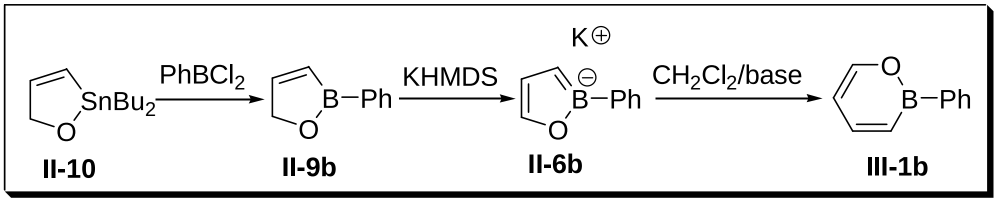
Chapter III

2-Substituted-1,2-Dihydro-1,2-Oxaborine: Boron−Oxygen Heterocycle Isoelectronic with Benzene

The boron−oxygen heterocycle 1,2-dihydro-1,2-oxaborine (**III-1**) is a potentially aromatic six-π-electron compound. Several fused-ring derivatives of **III-1**, isoelectronic with naphthalene,[1,2] e.g., **III-2**, and phenanthrene,[3-6] e.g., **III-3**, have been prepared (Scheme III-1). Structural data on **III-2** and **III-3** show that there are no significant differences between the B−O bond lengths which are exocyclic and endocyclic to the ring.[1,5,6] These B−O bond distances are also not significantly different from those of $PhB(OH)_2$.[7] Thus, the arylboronic acid derivatives **III-2** and **III-3** seem to have little π-delocalization over the heterocyclic rings. Unfortunately there are no structural data for compound **III-4**, which is the only reported non-fused-ring 1,2-dihydro-1,2-oxaborine.[8] Recently ab initio and DFT calculations on **III-1a** have suggested that 1,2-dihydro-1,2-oxaborines have considerable aromatic stabilization.[9] To experimentally test this hypothesis, a good synthesis of minimally substituted derivatives of **III-1** would be highly desirable. We report here on a synthesis of 1,2-dihydro-2-phenyl-1,2-oxaborine (**III-1b**). The availability of **III-1b** has allowed us to prepare its phenyl−$Cr(CO)_3$ complex **9,** which has been structurally characterized. These data clarify the potential aromaticity of the 1,2-dihydro-1,2-oxaborine ring system.

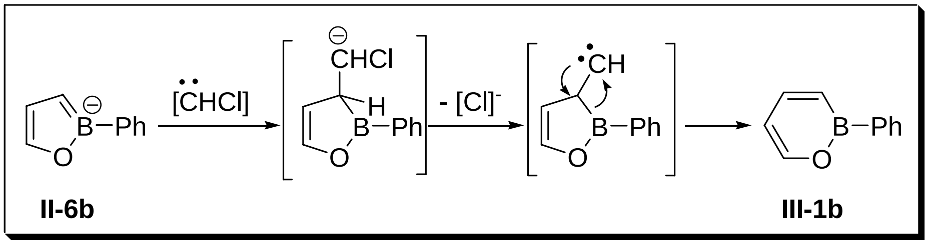


Scheme III-1



Scheme III-2

Our synthesis of **III-1b** involves an extension of the carbenoid ring-expansion route recently used to prepare the analogous boron−nitrogen heterocycle **III-5**.[10] The appropriate 1,2-oxaborolide (**II-6b**) needed for the ring expansion was prepared in two steps from the readily available 2,2-dibutyl-2,5-dihydro-1,2-oxastannole (**II-10**), as illustrated in Scheme III-2.[11] The reaction of **II-6b** with excess methylene chloride and $KN(SiMe_3)_2$ gave a 35% yield of **III-1b** as an air-sensitive colorless liquid. When the reaction was performed using methylene chloride-d_2, the deuterium in **III-1b** was exclusively at the 3-position. The reaction is consistent with an in situ formation of chlorocarbene, followed by addition of the carbene to the position adjacent to boron of **II-6b** and ultimately by ring expansion and loss of chloride as illustrated in Scheme III-3.[10,12]



Scheme III-3 Proposed Mechanism for Ring Expansion Reaction to **III-1b**

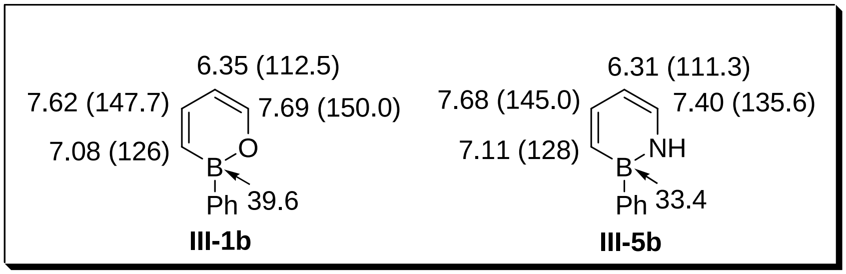
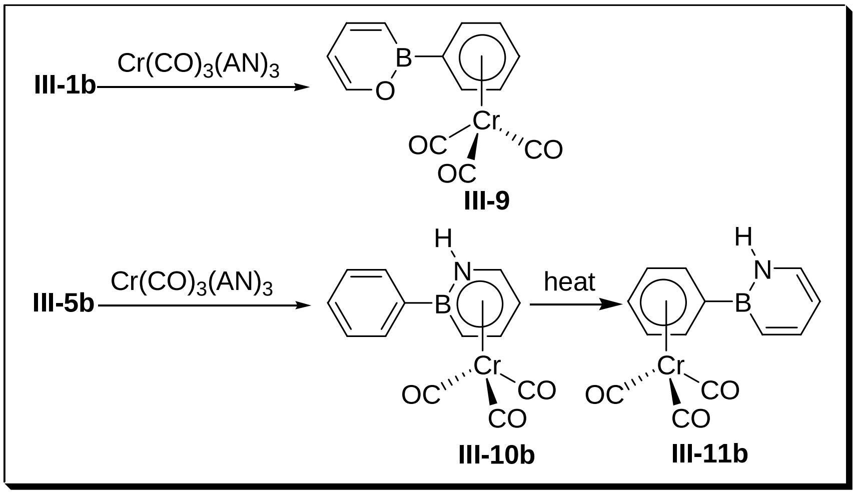


Figure III-1. Comparison of the ^1H NMR, ^{13}C NMR (in parentheses), and ^{11}B NMR (arrows) chemical shift values of **III-1b** and **III-5b** in THF-d_8.

The ^1H NMR spectrum of **III-1b** in THF-d_8 shows a first-order pattern, which is consistent with the assigned structure. The ^1H, ^{11}B, and ^{13}C NMR chemical shift values of **III-1b** are very similar to those of **III-5b**,[13] as illustrated in Figure III-1. There are only small differences in chemical shift values of the atoms near oxygen/nitrogen, which are consistent with the different electronegativities of those atoms. Overall the similarity of the spectra is consistent with a similarity in electronic structure of the two compounds. In this context it is important to emphasize that 1,2-dihydro-1,2-azaborine (**III-5a**) has classical aromatic properties.[14]

The reaction of **III-1b** with $(AN)_3Cr(CO)_3$ in THF at 70 °C gave yellow crystals of **III-9** (Scheme III-4). The molecular structure of **III-9**,[15] illustrated in Figure III-2, resembles that of **III-11**, the phenyl–$Cr(CO)_3$ complex of **III-5b**.[16] Apparently the 1,2-

dihydro-1,2-oxaborine ring is a poorer ligand than phenyl. Interestingly, the corresponding reaction of **III-5b** with $(AN)_3Cr(CO)_3$ initially forms **III-10**. Compound **III-10** is only converted to the phenyl-coordinated **III-11** on subsequent heating.[16] The uncoordinated 1,2-oxaborine ring of **III-9** is completely planar (±0.004 Å) and is canted by 5.7° relative to the phenyl ring. The intra-ring bond distances of the 1,2-oxaborine ring are close to those calculated by DFT for **III-1a** (average difference, ±0.02 Å). It is particularly noteworthy that the endocyclic B−C bond (1.481(8) Å) is significantly shorter than the exocyclic B−C bond (1.567(7) Å). Thus, the structural data for **9** are consistent with a delocalized π-bonding in the 1,2-dihydro-1,2-oxaborine ring.



Scheme III-4

It was of interest to explore possible aromatic substitution reactions of 1,2-dihydro-2-phenyl-1,2-oxaborine. We chose to examine the electrophilic aromatic substitution reaction, acid-catalyzed proton-deuterium exchange. A large number of data are available for the D-exchange of aromatic compounds in trifluoroacetic acid.[17]

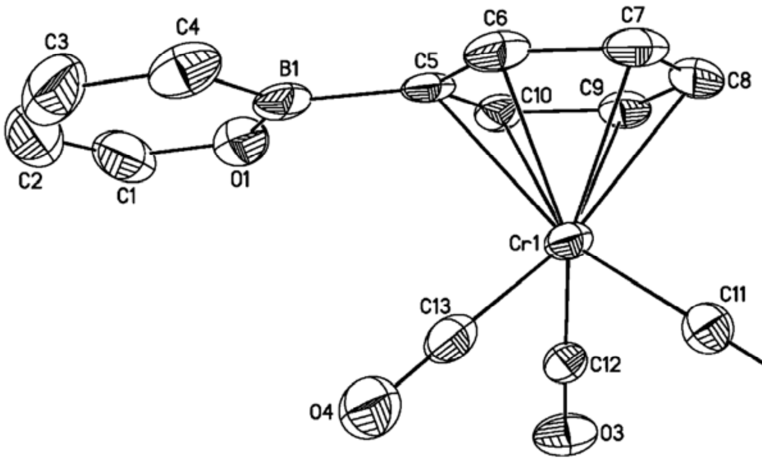
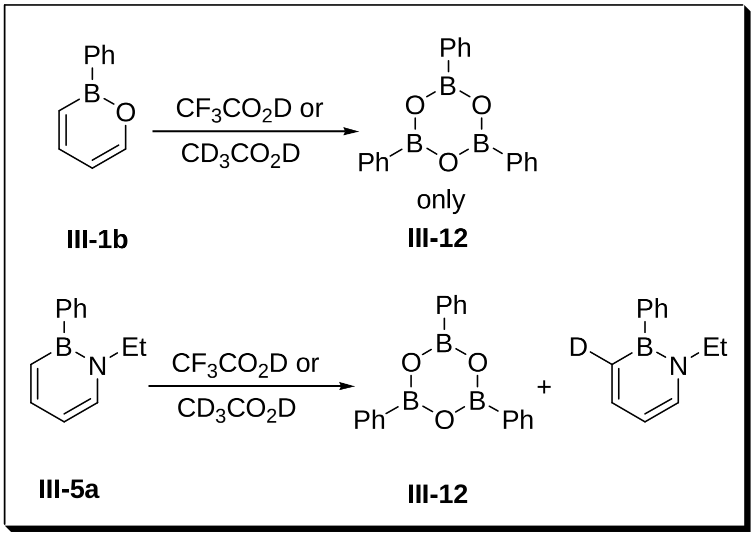
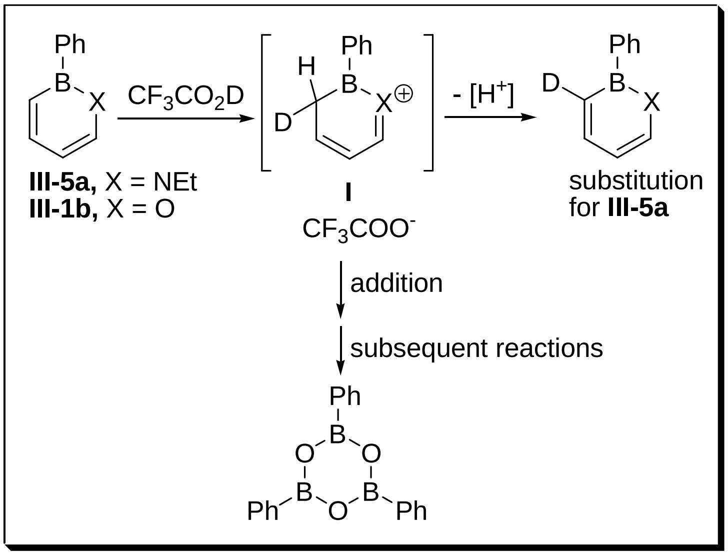


Figure III-2. Solid-state structure of **III-9** (ORTEP). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å): B(1)−C(5), 1.567(7); B(1)−C(4), 1.481(8); C(4)−C(3), 1.391(8); C(3)−C(2), 1.433(9); C(2)−C(1), 1.308(9); C(1)−O(1), 1.359(7); O(1)−B(1), 1.384(6).

In order to explore possible electrophilic hydrogen/deuterium exchange, **III-1b** was treated with CD_3CO_2D/CF_3CO_2D at 25 °C. This reaction led only to the formation of phenylboronic anhydride **III-12** and other unidentified products. Under identical conditions treatment of **III-5a** and with CF_3CO_2D led to H/D exchange but also **III -12**, as illustrated in Scheme III-5.



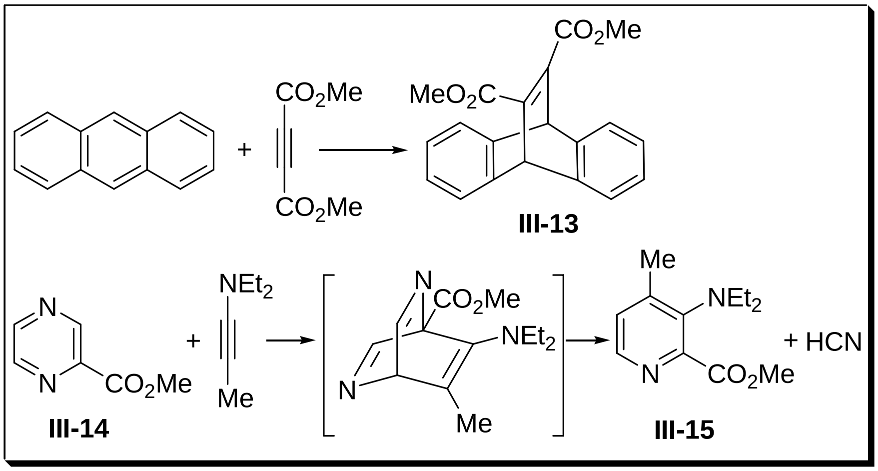
Scheme III-5



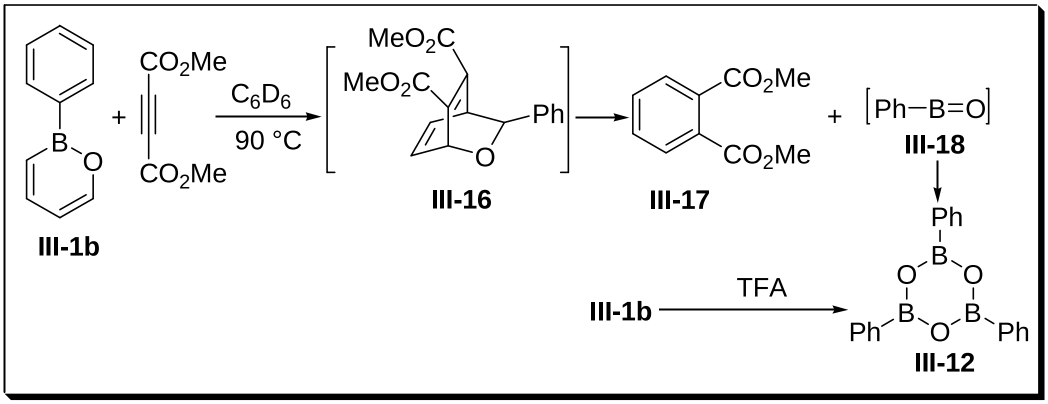
Scheme III-6 Proposed Mechanism for the CF_3CO_2D reaction

We speculate that reaction of **III-1b** and **III-5a** are initially similar, leading to putative intermediates **I** as illustrated in Scheme III-6. In the case of **III-5a** loss of a proton from **I** leads to D-substitution. However, in both cases, addition of trifluoroacetate to **I** followed by subsequent destructive reactions leads to phenylboronic anhydride and other unidentified products. The greater substitution rate for **III-5a** is consistent with the greater resonance energy of the B-N heterocycle.

Many carbocyclic and heterocyclic aromatic compounds behave as dienes in the Diels-Alder reaction. For example, anthracene will react with dimethylacetylene dicarboxylate at 25 °C yielding polycyclic product (**III-13**). In the case of many heteroaromatics, the initially formed adduct is unstable and the reaction is followed by a reverse Diels-Alder reaction (an Alder-Rickert cleavage) to give a new aromatic ring. A good example is reaction of pyrazine (**III-14**) with an acetylenic dienophile which gives pyridine (**III-15**) with loss of HCN. See Scheme III-7.



Scheme III-7



Scheme III-8

For these reasons we felt it would be interesting to examine the Diels-Alder reaction of **III-1b**. The reaction of **III-1b** with dimethyl acetylenedicarboxylate (DMAD) in benzene at 90 °C gave **III-12** and dimethyl phthalate (**III-17**)**.** These products are probably formed via a Diels−Alder reaction to give **III-16**,[18] followed by an Alder−Rickert cleavage, as illustrated in Scheme III-8. Phenyloxyborane (**III-18**) may be the precursor of **III-12**.[19] Under identical conditions **III-5** and DMAD do not react.

However, on heating **III-5a** to 150 °C, it also forms dimethyl phthalate and other unidentified products (J. Davidson, unpublished results).

We speculate that the higher reactivity of **III-1b** relative to **III-5a** is due to lower resonance energy of **III-1b**. Relative reactivity of benzocyclic compounds in the Diels-Alder reaction has been inversely correlated with the loss of resonance energy from isolating the 1 and 4 positions from the ring. The most familiar example of this effect is the higher reactivity of anthracene vs benzene.[20] [The loss of empirical resonance energies are 12 kcal/mol for anthracene and 36 kcal/mol for benzene.]

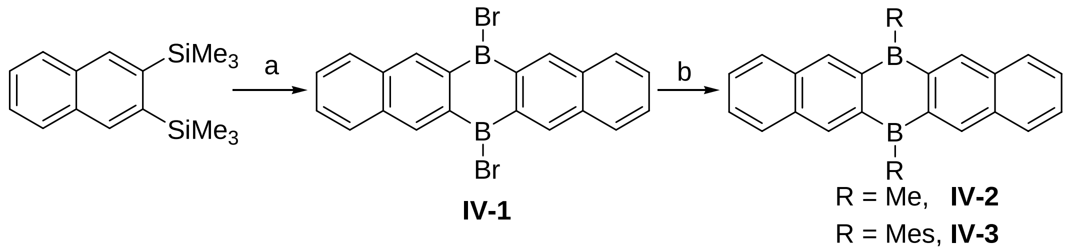
In summary, we have developed a new synthesis which allows the preparation of a minimally substituted 1,2-dihydro-1,2-oxaborine. Preliminary investigation of the chemistry of **III-1b** reveals that the 1,2-dihydro-1,2-oxaborine ring is readily cleaved under mild conditions. However, the molecular structure of **III-9** suggests that the 1,2-dihydro-1,2-oxaborine ring is aromatic, as had been predicted by DFT calculations.

Chapter IV

6,13-Dihydro-6,13-Diborapentacenes: Potential Building Blocks for n-Type Organic Semiconductors.

Organic semiconductors have potential applications as components of light-emitting diodes,[1] photovoltaics,[2] and organic thin-film transistors (OTFTs).[3] Intense research efforts have centered on the use of polycyclic aromatic hydrocarbons (PAHs),[3] e.g. pentacene, and their electron rich heterocyclic relatives [4] as p-type semiconductors for OTFTs. In the solid state many PAHs adopt a herringbone packing[5] which has less optimal intermolecular orbital overlap than a cofacial π stacking packing.[6] Although many of the factors which influence solid state packing are not well understood, it has been observed empirically that some substituted PAHs adopt a favorable cofacial stacking.[7] The search for other π-stacking materials continues. Improved n-type semiconductors structurally similar to PAHs but complementary in the type of charge carriers would also be highly desirable.[8] Promising preliminary investigations on PAHs with electron withdrawing substituents, particularly fluorine, have been reported.[9] The use of boron heterocycles has also been proposed.[10] Trivalent boron has a formally vacant 2p-orbital which might serve as an electron acceptor. Most of the prior work has involved compounds with bulky B-substituents.[11] Although these bulky substituents generally enhance the kinetic stability of boron compounds, they are also likely to prevent any possible intermolecular π-stacking important for high charge mobility in OTEFs.

We hypothesize that derivatives of the previously unknown 6,13-dihydro-6,13-diborapentacene ring system with small substituents at boron might circumvent these difficulties. Furthermore the anti-aromatic 4π-electron character of the central heterocyclic ring[12] should facilitate electron transfer to these compounds. We report here on the first syntheses 6,13-dihydro-6,13-diborapentacenes (**IV-1**, **IV-2**, and **IV-3**), the π-stacking structures of **IV-1** and **IV-2** and electrochemical data of **IV-3.**



Scheme IV-1 Synthesis of 6,13-dihydro-6,13-diborapentacenes
Conditions: (a) BBr_3/toluene, 110 ºC; (b) for **IV-2:** $SnMe_4$/ toluene, 110 ºC; for **IV-3**: Mesityllithium/THF, 0 ºC to r.t.

Our synthesis of **IV-1** relies on the known facile B/Si-exchange of arylsilanes with boron halides (Scheme IV-1).[13] The reaction of the readily available 2,3-bis(trimethylsilyl)naphthalene[14] with BBr_3 in toluene at 110 °C gave 22% of **IV-1** as a yellow crystalline solid. Like most organoboron bromides **IV-1** is quite moisture sensitive but can be handled using standard Schlenk techniques. It is thermally stable to at least its mp, 282 °C. 6,13-Dibromo-6,13-dihydro-6,13-diborapentacene **IV-1** has been fully characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy, high-resolution mass spectroscopy, elemental analysis and X-ray diffraction. The bromo groups of **IV-1** can be readily substituted for nucleophiles. Reaction of **IV-1** with Me_4Sn gave the crystalline yellow dimethyl derivative **IV-2** in 33% yield. The reaction of **IV-1** with mesityllithium afforded the dimesityl derivative **IV-3**, which like other mesitylboranes is much less sensitive to water and oxygen than **IV-1** and **IV-2.** It seems likely that **IV-1** could also be converted to a variety of other derivatives using the well-honed methods of organoboron chemistry.[15]

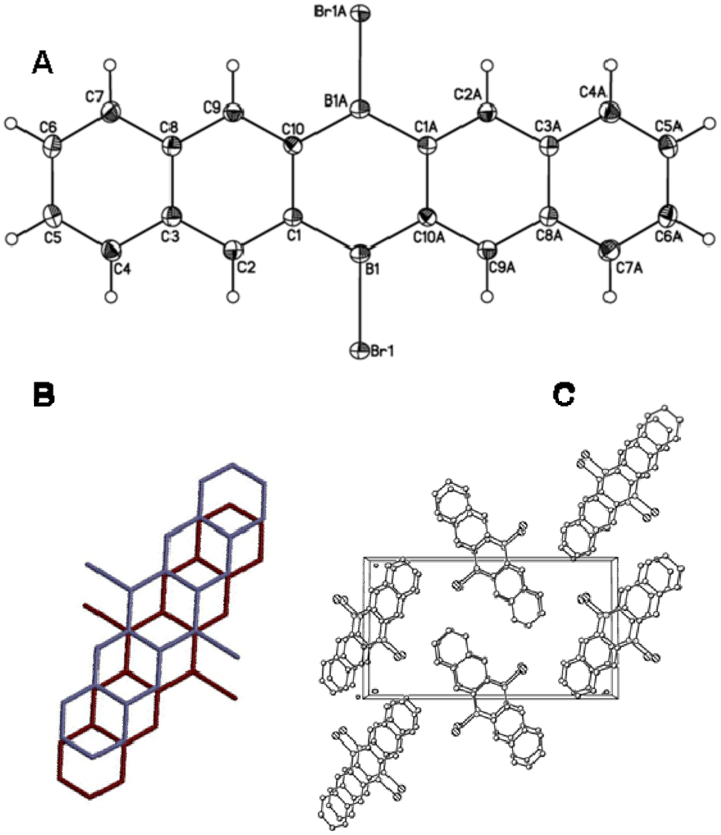


Figure IV-1. X-ray crystal structure of **IV-1** (A); a view along the axis perpendicular to the molecular plane showing slippage (B); a view of the packing along the a-axis showing π-stacking (C).

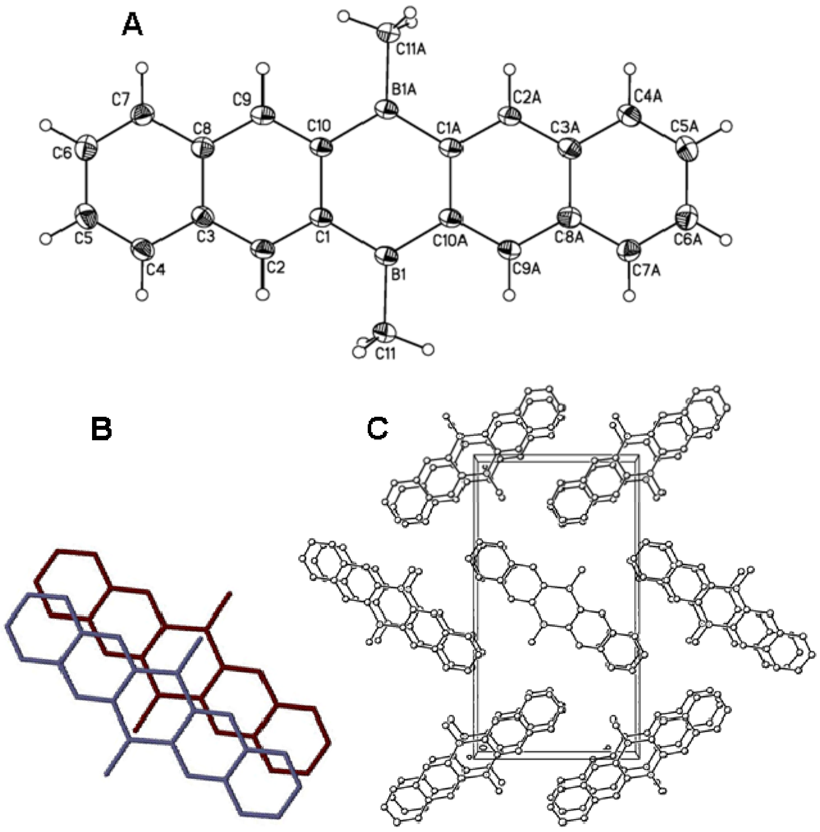
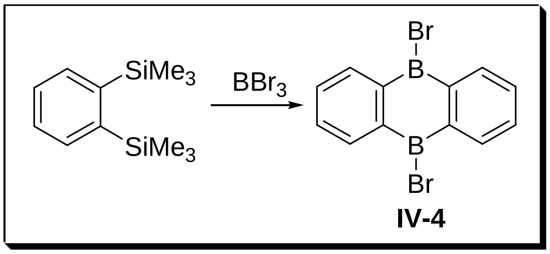


Figure IV-2. X-ray crystal structure of **IV-2** (A); a view along the axis perpendicular to the molecular plane showing slippage (B); a view of the packing along the a-axis showing π-stacking (C).

Single crystals of **IV-1**, **IV-2**, and **IV-3** were grown from toluene solutions. The molecular structures show that the 6,13-dihydro-6,13-diborapentacene core is planar for **IV-1**, **IV-2**, and **IV-3**. For **IV-3** the two mesityl groups are inclined to the core plane by approximately 85^{o} (see appendix W). For all three compounds the ring C-C bond distances range from 1.37-1.45 Å, quite similar to those of pentacene (1.34-1.46 Å).[5] However, the core B-C bond distances (1.54-1.56 Å) are longer than those found for neutral aromatic boron compounds (range 1.48-1.52 Å),[16] which is consistent with the antiaromatic character of the heterocyclic ring. None of the compounds pack in the familiar herringbone arrangement of pentacene. The packing of **IV-1**, illustrated in Figure IV-1, shows that the molecules form cofacial π stacks along the *a*-axis. The intermolecular face-to-face distance is 3.459 Å and the molecules are inclined to the *a*-axis by 29.0°. Viewed perpendicularly to the molecular plane (Figure IV-1B), the molecular packing is slipped along the long molecular axis by about 0.5 ring and along the short molecular axis about 0.25 ring. This brings the boron atom of one molecule vertically close (3.46 Å) to the α-carbon of its neighbor in the column. Figure IV-2 illustrates that the molecules of **IV-2** also form **π-π** stacks along the *a*-axis but in a somewhat less efficient manner. The intermolecular face-to-face distance is 3.50 Å and the molecules are inclined to the *a*-axis by 29.2°. Viewed perpendicularly to the molecular plane (Figure IV-2B), the molecular packing is slipped along the short molecular axis by about 0.75 ring. Since a smaller portion of each ring overlaps vertically and no ring atoms are vertically aligned, the π-interaction is less efficient. As had been anticipated, the large pendant mesityl groups of compound **IV-3** prevent it from stacking in the solid (see Appendix W).

In order to test the generality of π-stacking for dibora derivatives of PAHs, it would be desirable to examine other relative ring systems. The syntheses of novel fused ring compounds could be imagined, although these have not been pursued in this dissertation. Fortunately, the related 9,10-dihydro-9,10-diboraanthracene ring system is readily available. 9,10-Dibromo-dihydro-9,10-diboraanthracene has been prepared by the treatment of 1,2-bis(trimethylsilyl)benzene with BBr_3. This is the same general route which has been used to prepare **IV-1**, Scheme IV-2.



Scheme IV-2

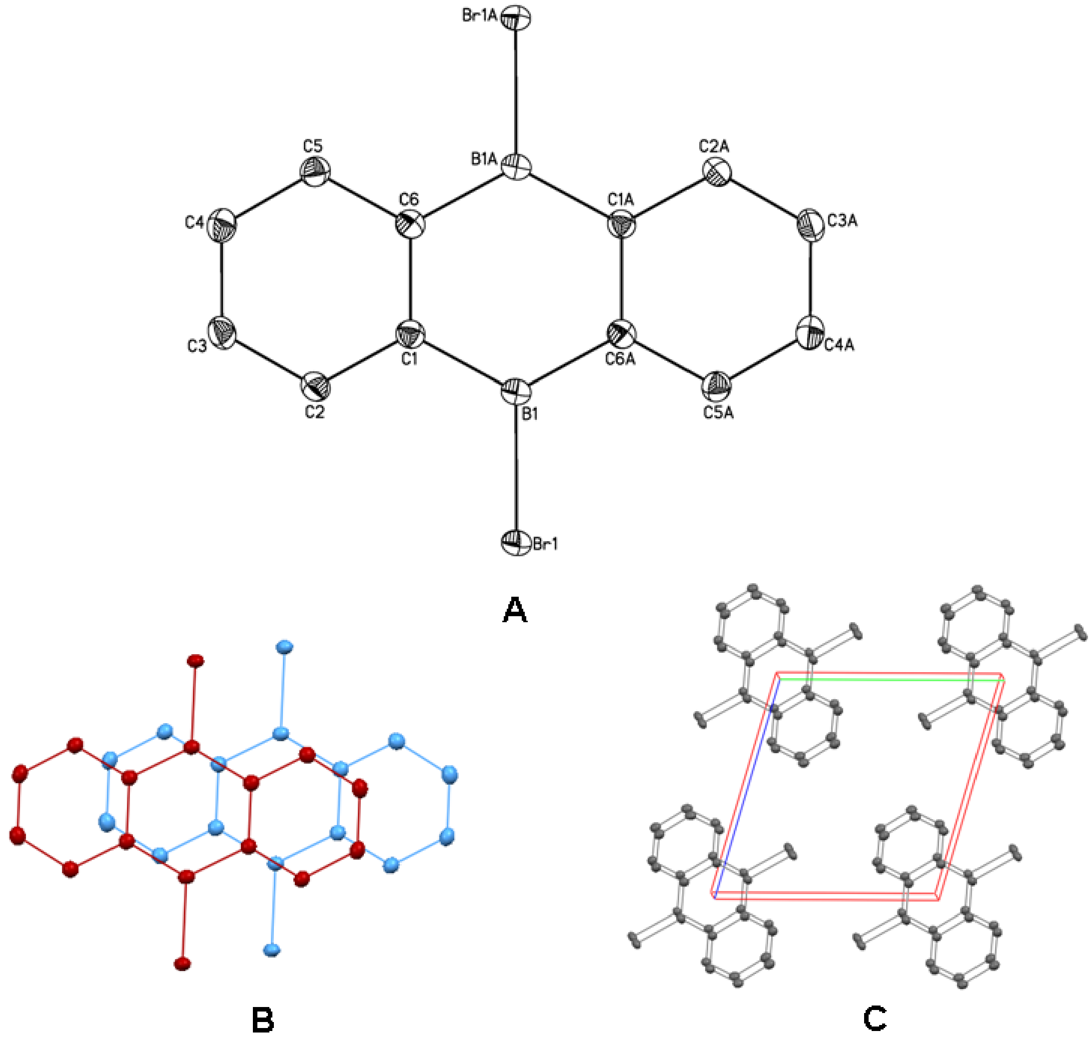


Figure IV-3. X-ray crystal structure of **IV-4** (A); a view along the axis perpendicular to the molecular plane showing slippage (B); a view of the packing along the a-axis showing π-stacking (C).

Although several other 9,10-dihydro-9,10-diboraanthracenes have been structurally characterized, there are no prior structural data on **IV-4**. Single crystals of **IV-4** were grown from toluene. The molecular structure of **IV-4**, illustrated in Figure IV-3A, shows that all of the atoms lie in a plane as expected. The C-C bond distances range from 1.396 to 1.422 Å and the B-C bond distances are close to 1.55 Å. The packing of **IV-4**, illustrated in Figure IV-4, shows that the molecules form cofacial π-stacks along the *a* axis. The intermolecular face-to-face distance is 3.453 Å and the molecules are inclined to the a axis by 63.4(1)^o. Viewed perpendicular to the molecular plane, the molecules are slipped along the long molecular axis by about 0.75 ring. The diboraheterocycle is closest to the terminal benzocyclic ring of the neighboring molecule of the stack.

As has been previously mentioned many of the factors which influence solid state packing are not completely understood. Based upon a very limited number of compounds described in this dissertation, empirical evidence suggests that the dibora- relatives of PAHs have a greater propensity to π-stack than do the corresponding PAHs. We speculate that an important factor may be the intermolecular π-interaction of the electron deficient diboraheterocycle with the relatively electron rich benzocyclic rings of the neighboring benzocyclic rings in the π-stack. Further investigation of this point from both computational and experimental standpoint would be highly desirable.

6,13-Dihydro-6,13-diborapentacenes **IV-1** and **IV-3** are all yellow solids. The UV-vis spectrum of **IV-1** in benzene shows a low energy maximum centered at 400 nm which has a marked vibronic fine structure (Appendix L). The HOMO-LUMO gaps obtained from the onset of absorption [2.8 eV (440 nm) for **IV-1**, 3.02 eV (410 nm) for **IV-2**, and 3.0 eV (415 nm) for **IV-3**] are significantly larger than the 2.07 eV for pentacene.

Electrochemical measurements on **IV-3** show the first reduction peak at -1.23 V (vs Fc/Fc$^+$) in acetonitrile (Figure IV-3). As expected the reduction peak is shifted positively relative to pentacene (-1.87 V).[9b] It is comparable in magnitude with the reduction of perfloropentacene (-1.13 V)[9b] and C_{60} (-1.14 V)[17] which are excellent n-type organic semiconductors.

In summary the novel 6,13-dihydro-6,13-diborapentacene ring system is easy to prepare. These compounds have molecular structures which are similar to pentacene but with two less π electrons, which makes them better electron acceptors. In the solid state both compounds **IV-1** and **IV-2** each form structures with cofacial π stacks but in a somewhat different manner. Thus the details of the packing are sensitive to B-substituents. Existing synthetic methodology should allow preparation of a variety of B-substituted dihydrodiborapentacenes.[15] In general boron atoms of boraheterocycles interact strongly with their exocyclic substituents,[18] thus electron density in the ring should also be tunable in a manner which is not as readily achievable in pentacenes. We believe that 6,13-dihydro-6,13-diborapentacenes may find innovative applications as n-type organic semiconductors that complement those of the p-type PAHs.

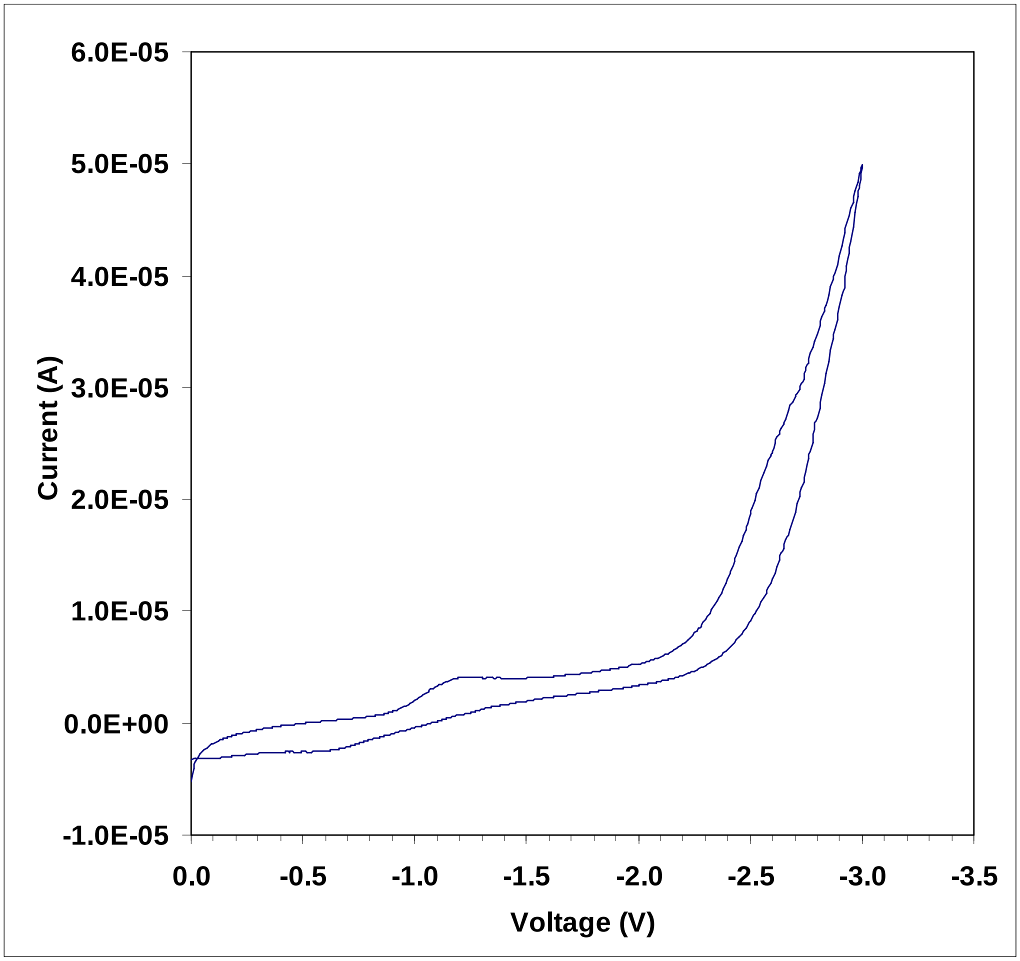


Figure IV-4 Cyclic voltammogram of **IV-3** in CH_3CN containing 0.1 M Bu_4NPF_6 (scan rate = 100 mV/s, Reference: Ferrocene)

Chapter V

Summary

Three new classes of organoboron heterocycles have been prepared. These include the boron-oxygen heterocycles, 1,2-oxaborolides and 1,2-dihydro-1,2-oxaborine and the diboron heterocycle, 6,13-dibora-6,13-dihydropentacenes and related derivatives.

1,2-Oxaborolides are dihetero-cyclopentadienides, which are anionic boron analogues of furan. 1,2-Oxaborolide anions were prepared from deprotonation of the precursors, 2-substituted-2,5-dihydro-1,2-oxaboroles with t-BuLi, LDA or KHMDS. Two synthetic methods were developed to prepare these precursors from ring-close metathesis of (allyloxy)(N,N-diisopropylamino)vinylborane or (allyloxy)(phenyl)vinylborane upon addition 2 mole% of Grubbs catalyst; alternatively, from boron-tin exchange reaction of 2,2-dibutyl-2,5-dihydro-1,2-oxastannole with $PhBCl_2$. Comparison of ^1H, ^{13}C, ^{11}B spectra chemical shift values of 2-phenyl-1,2-oxaborolide and previously published N-methyl-2-phenyl-1,2-azaborolide shows a great similarity which implies a similarity in the electronic structure. Treatment of $[Cp^*RuCl]_4$ and $(CH_3CN)_3Mn(CO)_3PF_6$, 2-phenyl-1,2-oxaborolide was converted to RuCp* and $Mn(CO)_3$ complexes, respectively. Structural characterization of both complexes by NMR spectra and single-crystal X-ray diffraction elucidated that the metals are η^5-bound to the ligand, similar to Cp ligand.

1,2-dihydro-1,2-oxaborine is a potentially aromatic six-π-electron compound. *ab initio* and DFT calculations suggested that 1,2-dihydro-1,2-oxaborines have considerable aromatic stabilization. To experimentally test this hypothesis, a good synthesis of minimally substituted derivatives of 1,2-dihydro-1,2-oxaborine would be highly desirable. 1,2-Dihydro-2-phenyl-1,2-oxaborine was obtained from the carbenoid ring-expansion reaction of potassium 2-phenyl-1,2-oxaborolide with methylene chloride and KHMDS, which was then used to prepare its phenyl-$Cr(CO)_3$ complex. The characterized data clarify the potential aromaticity of the 1,2-dihydro-1,2-oxaborine ring system.

Pentacene ($C_{22}H_{14}$) and its derivatives are the most promising materials for organic semiconducting materials. Replacing two CH groups (6- and 13-positions) of pentacene with BH^-, previously unknown 6,13-diborapentacenes were successfully synthesized. As a pentacene analogue, crystal structures of diborapentacene (6, 13-substituents R = Br or CH_3) show a π-π stacking pattern. Study of electronic property indicates diborapentacene has blue fluorescence with a quantum yield, $\phi = 0.25$ (R = CH_3) and 0.35 (R = Mes). Electrochemical measurements on diborapentacene (R = Mes) show the first reduction peak at -1.23 V (vs Fc/Fc^+), comparable to n-type semiconductors perfluoropentacene (-1.13 V) and C_{60} (-1.14 V). Derivative of 5,10-diboraanthracene, 5,10-distyryl-5,10-diboraanthracene was synthesized and structurally determined, which shows the promising potentials for extending to polymeric materials. 5,10-Dihydro-5,10-bis(8-quinolyloxy)-5,10-diboraanthracene (DBAq2) and 6,13-dihydro-6,13-bis(8-quinolyloxy)-6,13-diborapentacene (DBPq2) were also prepared and compared to aluminum tris(8-hydroxyquinoline) (Alq3), showing that both compounds have a higher quantum yield, $\phi = 0.22$ vs $\phi = 0.04$ (Alq3) in CH_2Cl_2 (see appendices).

Chapter VI

Experimental

General

^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian INOVA-400 or 500 MHz spectrometers. The solvents used were chloroform-d_1 ($CDCl_3$), methylene chloride-d_2 (CD_2Cl_2), cyclohexene-d_{12} (C_6D_{12}), benzene-d_6 (C_6D_6), dimethyl sulfoxide (DMSO-d_6), or tetrahydrofuran-d_8 (THF-d_8), as indicated. Chemical shifts (δ) are reported in parts per million (ppm). Proton and carbon chemical shifts are relative to respective solvent internal standards: 7.27 (for proton), 77.23 (for carbon) ($CDCl_3$); 5.32, 54.00 (CD_2Cl_2); 1.38, 26.43(C_6D_{12}); 7.16, 128.39 (C_6D_6); 2.50, 39.70 (DMSO-d_6); 3.58, 67.40 (THF-d_8). Boron-11 chemical shifts are relative to prospective external reference: δ 0.00 (BF_3/Et_2O 1.0 M LiCl in D_2O). The coupling constants (J) are reported in Hz. The following abbreviations are used to describe peak patterns: "s" for singlet, "d" for doublet", "t" for triplet, "q" for quartet, "m" for multiplet, and "br" for broad peak. Data are presented as follows: chemical shift (multiplicity, integrated intensity, coupling constant, and assignment). AA'XX' coupling pattern simulation was performed on a PC workstation by using MestRec (4.9.9.9 version, www.mestrec.com) program.

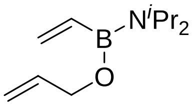
UV-visible absorption data were acquired on a Varian Cary 500 UV-vis/NIR spectrophotometer or a Shimadzu UV-160U spectrometer. The fluorescence data were measured on a Varian Cary Eclipse fluorescence spectrophotometer. Anthracene, used as the standard for determination of the quantum yields (Φ = 0.30 in cyclohexane), was adopted from the literature.[1] Quantum yields were calculated according to the reference method.[2]

Cyclic voltammetric measurements were carried out on an Electrochemical Impedance Analyzer, EG & G Instruments Model 6310 (Princeton Applied Research). All the three-electrode system consisted of Pt disk as the working electrode, a Pt wire as the secondary electrode and a Pt wire as a *quasi*-reference electrode. The voltammogram was recorded with about 1 mM solution (the setup was assembled in the glovebox) in anhydrous CH_3CN (Acros Oranics) containing 0.1 M Bu_4NPF_6 as supporting electrolyte. The scans were referenced after the addition of about 1 mM ferrocene (Fc) as internal standard. The potential is reported relative to Fc/Fc^+ redox couple (under the same conditions, $E_{1/2}(Fc/Fc^+) = 0.40$ V vs Pt) while in the literature, $E_{1/2}(Fc/Fc^+) = 0.667$ V vs NHE.[3]

Elemental analysis was conducted on a Perkin-Elmer 240 CHN analyzer by the analytical service in the Department of Chemistry at the University of Michigan, Ann Arbor. High-Resolution Mass spectrometry (HRMS) was performed on a VG (Micromass) 70-250-S Magnetic sector mass spectrometer. X-ray single crystal structure determination was performed on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube ($\lambda = 0.71073$ Å). Melting points were recorded on a Mel-Temp® 3.0 (laboratory device inc. USA) or a Laboratory Devices MEL-TEMP melting point apparatus and are given without correction.

Solvents were freshly distilled prior to use. Toluene, THF and diethyl ether were distilled from sodium and benzophenone ketyl under N_2. Pentane and hexane were distilled from sodium metal. Dichloromethane was dried by distillation from calcium hydride. Dibutyltin dihydride was prepared by reaction of dibutyltin dichloride with lithium aluminum hydride followed by vacuum distillation. 2,2-Dibutyl-1,2-dihydro-1,2-oxastannole,[4] and 2,3-Bis(trimethylsilyl)naphthalene[5] were prepared according to literature procedures. All other reagents were purchased from the commercial vendors and were used as received or distilled if necessary. All reactions were conducted under an inert atmosphere of argon or in the glove-box under nitrogen unless otherwise specified. were prepared according to the literature procedures.

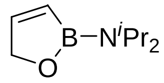
Caution! BBr_3 is toxic and highly corrosive and should be handled appropriately with great care. To successfully prepare these extremely moisture-sensitive compounds and avoid tedious purification, all of the air/moisture-sensitive reactions should be carried out by using a Schlenk flask or a Teflon screw-stoppered thick-walled glass reaction tube and manipulation of compounds should be handled in the glovebox. Pressured reactions should be performed behind a safety shield.



II-8a

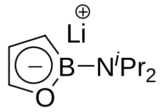
(*N*,*N*-Diisopropylamino)allyloxyvinylborane (II-8). A solution of *N*,*N*-diisopropylvinylboron chloride[7] (**II-7**) (21 g, 121 mmol) in 30 mL of THF was treated with a solution of lithium allyloxide (1.0 equiv) in 20 mL of THF at −78 °C. The mixture was stirred at −78 °C for 2 h and at 25 °C for 3 h. A white solid formed gradually. After filtration and removal of the solvent the residue was vacuum distilled to give the product as a clear colorless liquid (20.5 g, 87%), bp 32−34 °C at 0.05 Torr. ^1H NMR (C_6D_6, 400

MHz): δ 6.03 (dd, 1H, *J* = 20.5, 15.0 Hz, vinyl), 5.84 (m, 1H, vinyl), 5.34 (dq, 1H, *J* = 15.4, 2.2 Hz, vinyl), 5.04 (dq, 1H, *J* = 10.6, 1.8 Hz, vinyl), 135.7 (br, vinyl), 126.9 (vinyl), 113.7 (vinyl), 66.4 (CH_2O), 48.2 (NC), 44.2 (NC), 23.9 (Me), 22.9 (Me). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 29.9. HRMS (EI, *m*/*z*): calcd for $C_{11}H_{22}{}^{11}BNO$ (M^+), 195.1794; found, 195.1785. Anal. Calcd for $C_{11}H_{22}BNO$: C, 67.72; H, 11.36; N, 7.18. Found: C, 67.54; H, 11.52; N, 7.01.



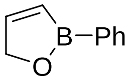
II-9a

***N*,*N*-Diisopropyl-2-amino-2,5-dihydro-1,2-oxaborole (II-9a).** A solution of **II-8** (16.7 g, 85.6 mmol) in 120 mL of CH_2Cl_2 was added to a solution of bis(tricyclohexylphosphine) benzylidene ruthenium(IV) dichloride (Grubb's catalyst) (1.4 g, 2 mol %) in 20 mL of CH_2Cl_2 at 25 °C for 10 h, after which the color had changed from purple-red to dark brown. The solvent was removed in vacuo at 0 °C, and the product (13.2 g, 92%) was obtained as a clear colorless liquid, bp 28 °C at 0.05 Torr. ^1H NMR (C_6D_6, 400 MHz): δ 6.78 (d, 1H, *J* = 7.7 Hz), 6.06 (d, 1H, *J* = 7.7 Hz), 4.40 (m, 2H), 3.64 (sept, 1H, *J* = 6.6 Hz), 3.46 (sept, 1H, *J* = 6.6 Hz), 1.27 (d, 6H, *J* = 6.6 Hz), 1.09 (d, 6H, *J* = 6.6 Hz). ^{13}C NMR (C_6D_6, 100.5 MHz): δ 152.2 (C=C), 53.3 (CH_2O), 47.2 (NCH), 45.2 (NCH), 24.0 (CH_3), 23.3 (CH_3). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 33.2. HRMS (EI, *m*/*z*): calcd for $C_9H_{18}{}^{11}BNO$, 167.1481; found, 167.1490. Anal. Calcd for $C_9H_{18}BNO$: C, 64.71; H, 10.86; N, 8.38. Found: C, 64.90; H, 10.78; N, 7.84.



II-6a

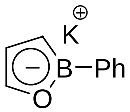
Lithium *N*,*N*-Diisopropyl-2-amino-1,2-oxaborolide (II-6a). A solution of **II-9a** (0.52 g, 3.11 mmol) in 12 mL of pentane was treated with a solution of t-BuLi (1.7 M, 1.8 mL) in pentane at −78 °C. The mixture was stirred at −78 °C for 1 h and at 25 °C for 15 min. A white solid formed gradually. After removal of the solvent and washing with cold pentane the residue was dried under vacuum to give the product as a light yellow powder (0.28 g, 53%). ^{1}H NMR (THF-d_8, 400 MHz): δ 6.2 (s, 1H, H_5), 6.04 (d, 1H, J = 4.8 Hz, H_4), 3.44 (sept, 2H, J = 6.6 Hz, NCH), 2.44 (d, 1H, J = 4.7 Hz, H_3), 1.11 (d, 12H, J = 6.6 Hz, Me). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 122.0, 118.8, 58 (br, C(3)), 46.3 (NC), 23.9 (Me). ^{11}B NMR (THF-d_8, 115.5 MHz): δ 37.0.



II-9b

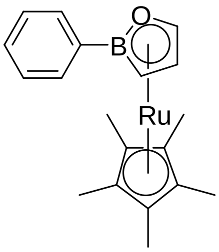
Synthesis of 2,5-Dihydro-2-phenyl-1,2-oxaborole (II-9b). A solution of dichlorophenylborane (7.87 g, 50 mmol) in 25 mL of pentane was added via cannula technique to a solution of 2,2-dibutyl-2,5-dihydro-1,2-oxastannole (**II-10**) (14.45 g, 50 mmol) in 60 mL of pentane at −78 °C. Upon the addition, the white oxastannole slurry dissolved and the solution turned light brown. The reaction mixture was gradually warmed and stirred at room temperature overnight. The solvent was removed under reduced pressure, and the product was obtained via vacuum distillation (bp 35−38 °C at 0.025 Torr) with a yield of 5.95 g (82.6%) as a colorless liquid. ^{1}H NMR (C_6D_6, 400

MHz): δ 8.13 (m, 2H, ArH), 7.28 (m, 3H, ArH), 7.01 (d, 1H, *J* = 8 Hz, H_3), 6.48 (d, 1H, *J* = 8 Hz, H_4), 4.44 (m, 2 H, H_5). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 158.94 (C_3), 136.29, 132.12, 128.63, 78.85 (C_5). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00 (m, 2H, ArH), 7.64 (d, 1H, *J* = 8 Hz, H_3), 7.54−7.45 (m, 3H, ArH), 6.68 (d, 1H, *J* = 8 Hz, H_4), 4.98 (d, 2H, *J* = 1.2 Hz, H_5). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 158. 54 (C_3), 135.56, 131.67, 128.14, 78.82 (C_5). ^{11}B NMR (C_6D_6, 160.4 MHz): δ 46.5. HRMS (EI, *m*/*z*): calcd for $C_9H_9{}^{11}BO$ (M^+), 144.0746; found, 144.0739. Anal. Calcd for C_9H_9BO: C, 75.08; H, 6.30. Found: C, 74.72; H, 6.28.



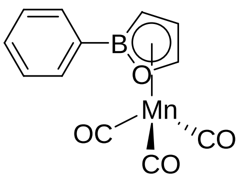
II-6b

Potassium 2-phenyl-1,2-oxaborolide (II-6b). A solution of potassium bis(trimethylsilyl)amide (5.95 g, 41.3 mmol) in 35 mL of diethyl ether was added slowly via cannula to a solution of **II-9b** (9.11 g, 43.4 mmol) in 15 mL of diethyl ether at −78 °C. Upon completion of addition, the solution turned light yellow. The reaction mixture was kept at −78 °C for 1 h and then slowly warmed to room temperature and stirred for 4 h. The liquid was removed via cannula filtration, and the residue was washed with diethyl ether (3 × 5 mL) to obtain the product (6.46 g, 85.9%) as a light yellow powder. ^1H NMR (DMSO-*d*$_6$, 400 MHz): δ 7.48 (m, 2H, ArH), 7.03 (m, 2H, ArH), 6.82 (m, 1H, ArH), 6.47 (t, 1H, *J* = 1.6 Hz, H_5), 6.11 (dd, 1H, *J* = 1.6 Hz, *J* = 4.4 Hz, H_4), 4.30 (d, 1H, *J* = 4.4 Hz, H_3). ^1H NMR (THF-*d*$_8$, 500 MHz): δ 7.61 (d, 2H, *J* = 9.5 Hz, ArH), 7.02 (t, 2H, *J* = 9.0 Hz, ArH), 6.84 (t, H, *J* = 9.0 Hz, ArH), 6.58 (s, 1H, H_5), 6.35 (d, 1H, *J* = 4.5 Hz, H_4), 4.50 (d, 1H, *J* = 4.5 Hz, H_3). ^{13}C NMR (DMSO-*d*$_6$, 100.6 MHz): δ 130.85, 126.23, 126.59, 122.55, 118.78, 85.50 (br). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 132.46, 128.72, 127.61, 124.44, 120.77, 84.19. ^{11}B NMR (DMSO-d_6, 160.4 MHz): δ 33.34.



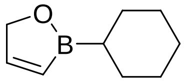
II-11b

[η^5-Pentamethylcyclopentadienyl] [η^5-2-phenyl-1,2-oxaborolyl] ruthenium (11b). A 40 mL portion of THF was added to a mixture of **II-6b** (0.728 g, 4.0 mmol) and [Cp*RuCl]$_4$ (1.087 g, 4.0 mmol) at −78 °C with magnetic stirring. The mixture was stirred at −78 °C for 2 h and allowed to warm to and maintained at room temperature for 20 h. The solvent was removed under reduced pressure, and the residue was dried in vacuo. The solid residue was then extracted with pentane (100 mL). The product was obtained as amber crystals (1.06 g, 70%) by cooling the extracts to −30 °C and slowly removing the solvent by vacuum. Mp = 84.7 °C (dec). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.84 (m, 2H, ArH), 7.32 (m, 2H, ArH), 7.22 (m, 1H, ArH), 6.31 (s, 1H, H_5), 4.64 (d, 1H, J = 4.8 Hz, H_4), 4.10 (d, 1H, J = 4.8 Hz, H_3), 1.61 (s, 15H, Cp*Me). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 132.79, 128.01, 127.69, 99.10, 85.32, 83.98, 11.30. ^{11}B NMR (C_6D_6, 160.4 MHz): δ 19.72. HRMS (EI, m/z): calcd for $C_{19}H_{23}{}^{11}BO^{102}Ru$ (M^+), 380.0885; found, 380.0886. Anal. Calcd for $C_{19}H_{23}BORu$: C, 60.17; H, 6.11. Found: C, 59.77; H, 5.98.



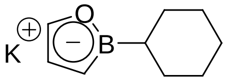
II-12b

Tricarbonyl[η^5-2-phenyl-1,2-oxaborolyl] manganese(I) (II-12b). THF (50 mL) was added to a mixture of **II-6b** (1.29 g, 7.0 mmol) and $Mn(CO)_3(NCCH_3)_3$ PF_6 (3.0 g, 7.0 mmol) at −78 °C with magnetic stirring. The mixture was stirred at −78 °C for 2 h and allowed to warm to and maintained at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was dried in vacuo. The solid residue was then extracted with pentane (100 mL). The product was obtained by recrystallization from pentane at −30 °C as yellow crystals (1.25 g, 62.5%). Mp = 64 °C. IR (hexane, film): 2039, 1966, 1948 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.56 (m, 2H, ArH), 7.17 (m, 3H, ArH), 5.79 (s, 1H, H_5), 4.65 (d, 1H, J = 4.8 Hz, H_4), 3.60 (d, 1H, J = 4.8 Hz, H_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 222.43, 134.24, 131.31, 128.71, 102.98, 98.23, 65.78. ^{11}B NMR (C_6D_6, 160.4 MHz): δ 24.68. HRMS (EI, *m/z*): calcd for $C_{12}H_8{}^{11}BOMn$ (M^+), 281.9896; found, 281.9902. Anal. Calcd for $C_{12}H_8BMnO_4$: C, 51.12; H, 2.86. Found: C, 51.49; H, 2.86.



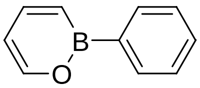
II-9c

1,2-Dihydro-2-cyclohexyl-1,2-oxaborole (**II-9c**). **II-9c** was prepared similar to **II-9b** except using $CyBCl_2$.^{1}H NMR (400 MHz, C_6D_6): δ 6.95 (d, 1H, J = 7.6 Hz, H_3), 6.16 (d, 1H, H_4), 4.31 (s, 2H, H_5). ^{13}C NMR (100 MHz, C_6D_6): δ 158.00, 78.37, 29.21, 28.22, 27.76. ^{11}B NMR ($CDCl_3$, 160.4 MHz): δ 50.99. HRMS (EI, *m*/*z*): calcd for $C_9H_{15}{}^{11}BO$ (M^+), 150.1216; found, 150.1217.



II-6c

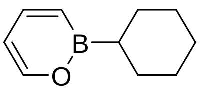
Potassium 1,2-dihydro-2-cyclohexyl-1,2-oxaborolide (**II-6c**). **II-6c** was prepared similar to **II-6b,** yield 82.9 %. ^{1}H NMR (400 MHz, THF-d_8): δ 6.43 (s, 1H, H_5), 6.26 (d, 1H, J = 4.8 Hz, H_4), 3.82 (d, 1H, H_3), 1.11-1.86 (m, 11H, cyclohexyl-H). ^{13}C NMR (100 MHz, THF-d_8): δ 125.89, 120.41, 79.00 (br), 33.74, 29.60, 28.89. ^{11}B NMR (THF-d_6, 160.4 MHz): δ 37.52.



III-1b

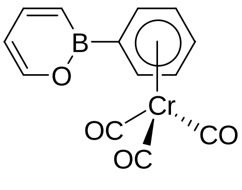
1,2-Dihydro-2-phenyl-1,2-oxaborine (III-1b). THF (20 mL) at −78 °C was added slowly via a cannula to a mixture of $KN(SiMe_3)_2$ (1.54 g, 7.70 mmol) and **II-6b** (1.33 g, 7.33 mmol) with stirring. Methylene chloride (10 mL) was added slowly at −78 °C. The mixture was stirred at −78 °C for 2 h and then warmed slowly to 25 °C for 10 h. The solvent was removed under reduced pressure, and the residue was extracted with pentane (2 × 25 mL). Removal of the solvent from the extracts gave a dark red oil, which was distilled (32 °C at 0.01 Torr) to afford **III-1b** as a colorless liquid (0.40 g, 35% yield). IR (film; cm^{-1}): 3075, 3014, 1617, 1504, 1435, 1388, 1266, 740, 697, 678. UV (hexane; λ_{max}, nm): 288, 231, 198. ^{1}H NMR (500 MHz, THF-d_8): δ 8.01 (dd, *J* = 7.5, 1.4 Hz, 2H, Ar H), 7.69 (d, *J* = 6.0 Hz, 1H, H(6)), 7.62 (dd, *J* = 11.0, 6.0 Hz, 1H, H(4)), 7.39 (m, 3H, Ar

H), 7.08 (d, J = 11.0 Hz, 1H, H(3)), 6.35 (t, J = 6.0 Hz, 1H, H(5)). ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 39.6. ^{13}C NMR (125.7 MHz, c-C_6D_{12}): δ 150.0 (C(6)), 147.7 (C(4)), 134.6 (C_o), 131.6 (C_p), 128.8 (C_m), 125.8 (br, C(3)), 112.5 (C(5)). HRMS (EI; *m*/*z*): calcd for $C_{10}H_9{}^{11}BO$, 156.0746 (M^+); found, 156.0753. Anal. Calcd for $C_{10}H_9BO$: C, 77.00; H, 5.82. Found: C, 76.97; H, 5.96. **III-1b**-*d*: When the above reaction was performed using methylene chloride-d_2, the isolated product had a deuterium atom at C(3), as shown by the ^{1}H NMR: no signal at δ 7.08 (H(3)), δ 7.62 signal now d (J = 6.0 Hz, H(4)), the rest of the spectrum unchanged.



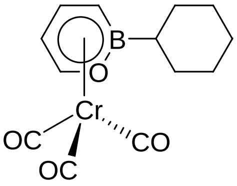
III-1c

1,2-Dihydro-2-cyclohexyl-1,2-oxaborine (III-1c). **III-1c** was prepared similarly as **III-1a** except LDA used instead as base. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.53 (d, 1H, J = 4.2 Hz, H_6), 7.48 (dd, 1H, J = 11.6, 6.4 Hz, H_4), 6.60 (d, 1H, J = 11.6 Hz, H_3). 6.23 (m, 1H, H_5). 1,31-1.85 (m, 11H, cyclohexyl). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 157.35, 148.70, 145.55, 127.0 (br), 28.96, 27.80, 27.24. UV-vis (in pentane): 267. IR (liquid thin film on salt plate): 2920, 2849, 1616, 1511, 1443, 1395, 1321, 1261, 755 cm^{-1}.

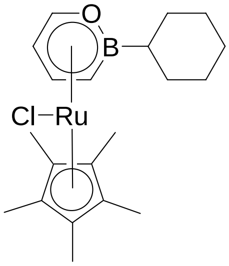


III-9

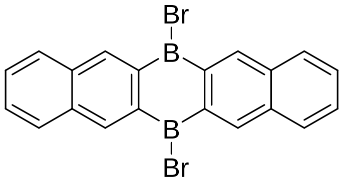
Tricarbonyl [η^6-(1,2-dihydro-1,2-oxaborinyl)benzene]chromium (III-9). A THF (3 mL) solution of **III-1b** (62.6 mg, 0.40 mmol) was added to $Cr(CO)_3(CH_3CN)_3$ (104 mg, 0.40 mmol). The resulting red solution was heated to 70 °C for 12 h. After removal of the solvent the crude product was extracted with hexanes to give a bright yellow solution. The solvent was removed, leaving a crystalline product (117 mg). The product was recrystallized from ether/hexanes to give yellow crystals. Mp: 116 °C. IR (hexane, film; cm^{-1}): 1981, 1916. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 11.2, 6.2 Hz, 1H, H(4)), 7.62 (d, *J* = 4.4 Hz, 1H, H(6)), 6.82 (d, *J* = 11.2 Hz, 1H, H(3)),6.40 (dd, *J* = 6.2, 4.4 Hz, 1H, H(5)), 5.96 (d, *J* = 6.4 Hz, 2H, Ph H), 5.61 (t, *J* = 6.4 Hz, 1H, Ph H), 5.30 (t, *J* = 6.4 Hz, 2H, Ph H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 233.0, 148.9, 147.8, 124 (br), 112.2, 99.3, 95.6, 91.4. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 46.5. HRMS (EI; *m*/*z*): calcd for $C_{13}H_9{}^{11}BCrO_4$ (M^+), 291.9987; found, 291.9999. Anal. Calcd for $C_{13}H_9BCrO_4$: C, 53.47; H, 3.11. Found: C, 53.37; H, 3.03.



Tricarbonyl [η^6-1,2-dihydro-2-cyclohexyl-1,2-oxaborinyl]chromium (III-9c) The reaction was carried out in an NMR tube with about 1:1 ratio of **III-9c** and **III-1c**. **III-9c** can only be identified by ^{1}H NMR, not other data available due to unstable of **III-9c**. ^{1}H NMR (400 MHz, C_6D_{12}): δ 6.55 (d, 1H, *J* = 2.4 Hz, H_6), 5.94 (dd, 1H, J = 9.2, 6.0 Hz, H_4), 5.30 (dd, 1H, H_5), 4.64 (d, 1H, H_3).



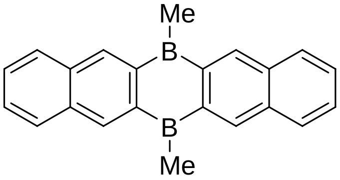
[η^5-Pentamethylcyclopentadienyl][η^6-1,2-dihydro-2-cyclohexyl-1,2-oxaborine]ruthenium(II) chloride (III-10c). A solution of **III-1c** (162 mg in 10 mL of CH_2Cl_2) was added to a solution of $[Cp^*RuCl]_4$ (272 mg in 15 mL of CH_2Cl_2) at room temperature. The reaction mixture was stirred at room temperature overnight. Then the reaction mixture was cooled down to -30 ºC and the solvent was slowly evaporated to obtain the product (**III-10c**) as amber powders (unstable). Only NMR data are available. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.18 (dd, 1H, J = 4.0, 1.6 Hz, H_6), 5.43 (m, 1H, H_4), 4.68 (m, 1H, H_5), 3.29 (d, 1H, H_3), 1.58 (s, 15H, C_5Me_5). ^{13}C NMR (100 MHz, CD_2Cl_2): δ ^{11}B NMR (CD_2Cl_2, 160.4 MHz): δ 44.33.



IV-1

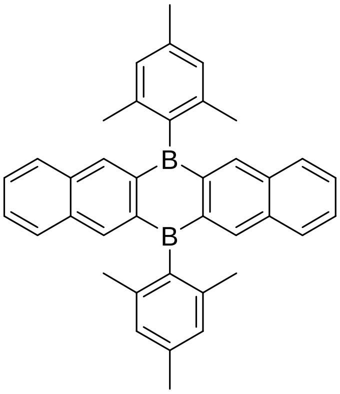
6,13-Dibromo-6,13-dihydro-6,13-diborapentacene (IV-1). 2,3-Bis(trimethysilyl) naphthalene (0.55 g, 2.0 mmol) and toluene (5 mL) were added to a Teflon screw-stoppered thick-walled glass reaction tube. After cooling to 0 °C, BBr_3 (0.6 mL, 6.3 mmol) was added with magnetically stirring and the valve was then closed. The mixture was next heated to 110 °C for 40 h, affording bright yellow crystals and a brown solution.

After the mixture was cooled to room temperature, the liquid was removed by cannula filtration. The solid residue was washed with toluene (2 mL) and dried *in vacuo* for 1 h to obtain analytically pure product **1** (yield: 0.168 g, 22%; m.p. = 282-284 °C). X-ray quality crystals were obtained by recrystallization from toluene. ^{1}H NMR (500 MHz, C_6D_6): δ 9.14 (s, 4H, H-5,7,12,14), 7.58, 7.17 (satisfactory computer simulation of AA′XX′ pattern was achieved using $\delta_1 = 7.588$, $\delta_2 = 7.174$, $J_{AB} = 8.1$ Hz, $J_{BB'} = 6.4$ Hz, $J_{AB'} = 1.8$ Hz, 8H, H-1,2,3,4,8,9,10,11). ^{13}C NMR (125.7 MHz, C_6D_6): δ 142.9, 136.5, 130.6, 129.8, *C*-B not observable. ^{11}B NMR (160.4 MHz, C_6D_6): 57.5. UV-vis (C_6D_6): λ_{max} = 423, 400, 380, 338 nm. HRMS (EI, *m/z*): calcd for $C_{20}H_{12}{}^{11}B_2{}^{79}Br_2$ (M+), 431.9492; found, 431.9501. Anal. Calcd for $C_{20}H_{12}B_2Br_2$: C, 55.38; H, 2.79. Found: C, 55.24; H, 2.76.



IV-2

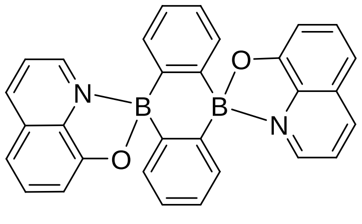
6,13-Dihydro-6,13-dimethyl-6,13-diborapentacene (IV-2). Excess amount of $SnMe_4$ (500 mg, 2.8 mmol) was added to a slurry of **IV-1** (150 mg, 0.346 mmol) in 5 mL toluene in a thick-walled glass reaction tube. The reaction tube was capped and heated to 110 °C overnight. After the mixture was cooled to room temperature, the liquid was removed in vacuo. The yellow residue was washed with hexane (2 mL) and then dried in vacuo. Purification was performed by recrystallization from toluene to obtain light yellow needle crystals **2** (35 mg, 33.3%; m.p. = 238-239 °C), which were also suitable for X-ray single crystallographic determination. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.78 (s, 4H, H-5,7,12,14), 8.03, 7.62 (satisfactory computer simulation of AA′XX′ pattern was achieved using δ_1 = 8.034, δ_2 = 7.624, J_{AB} = 8.2 Hz, $J_{BB'}$ = 6.0 Hz, $J_{AB'}$= 1.5 Hz, 8H, H-1,2,3,4,8,9,10,11), 1.66 (s, 6H, C**H**$_3$). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 138.2, 136.0, 129.9, 128.5, *C*-B not observable. ^{11}B NMR (160.4 MHz, CD_2Cl_2): 62.0. ^{1}H NMR (500 MHz, C_6D_6): δ 8.75 (s, 4H, H-5,7,12,14), 7.76, 7.31 (m, AA′XX′, 8H, H-1,2,3,4,8,9,10,11), 1.64 (s, 6H, C**H**$_3$). UV-vis (C_6D_6): 394, 375, 358 nm. HRMS (EI, m/z): calcd for $C_{22}H_{18}{}^{11}B_2$, 304.1595; found, 304.1603.



IV-3

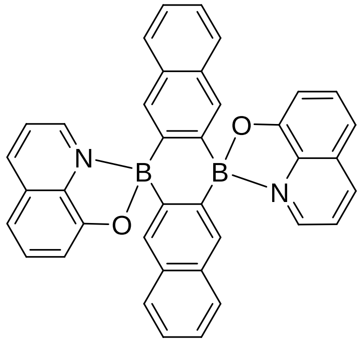
6,13-Dihydro-6,13-dimesityl -6,13-diborapentacene (IV-3). THF (10 mL) was added to a mixture of **IV-1** (80 mg, 0.184 mmol) and mesityllithium (52 mg, 2.2 equiv) at 0 °C in a thick-walled glass reaction tube. The reaction was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was extracted with toluene (15 mL). Removal of toluene afforded a light yellow powder. The product was further purified from concentrated toluene solution at 110 °C which was then cooled to room temperature and stored at -20 °C for 2 days, affording light yellow crystals **3** (yield, 23 mg, 24.4%; m.p. = 392-396 °C (dec)), which were also suitable for X-ray crystallographic determination. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 4H, H-5,7,12,14), 7.84, 7.52

(satisfactory computer simulation of AA′XX′ pattern was achieved using $\delta_1 = 7.843$, $\delta_2 = 7.519$, $J_{AB} = 8.2$ Hz, $J_{BB'} = 6.0$ Hz, $J_{AB'} = 1.5$ Hz, 8H, H-1,2,3,4,8,9,10,11), 7.03 (s, 4H, *m*-Mes-H), 2.49 (s, 6H, *p*-Mes-C**H**$_3$), 2.12 (s, 12H, *o*-Mes-C**H**$_3$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 141.7, 138.8, 136.9, 136.1, 129.9, 128.4, 127.2, 23.1, 21.6, *C*-B not observable. ^{11}B NMR (160.4 MHz, $CDCl_3$): 66.6. ^{1}H NMR (400 MHz, C_6D_6): δ 8.58 (s, 4H, H-5,7,12,14), 7.28, 7.04 (AA′XX′, 8H, H-1,2,3,4,8,9,10,11), 7.04 (s, 4H, *m*-Mes-H), 2.41 (s, 6H, *p*-Mes-C**H**$_3$), 2.26 (s, 12H, *o*-Mes-C**H**$_3$). ^{13}C NMR (100.58 MHz, C_6D_6): δ 142.7, 139.1, 137.4, 137.0, 130.3, 129.7, 128.9, 23.5, 21.8, *C*-B not observable.. UV-vis (*c*-C_6H_{12}): 407, 385, 366, 328, 302, and 268 nm. Fluorescence (*c*-C_6H_{12}): 464, 435, and 410 nm. CV: $E_{1/2}$(**3**) = -1.30 V (vs Fc/Fc$^+$, CH_3CN/0.1 M Bu_4NPF_6, scan = 100 mV/s). HRMS (EI, *m*/*z*): calcd for $C_{38}H_{34}{}^{11}B_2$ (M+), 512.2846; found, 512.2857. Anal. Calcd for $C_{38}H_{34}B_2$: C, 89.09; H, 6.69. Found: C, 89.21; H, 6.57.



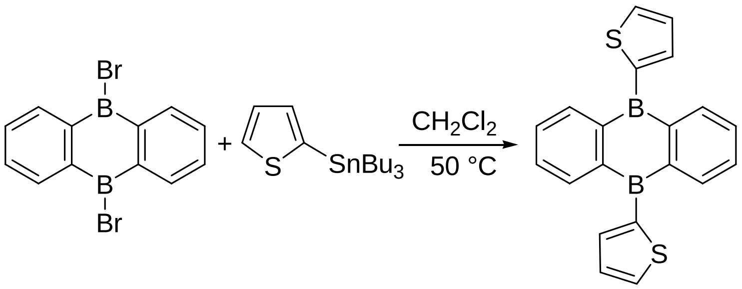
DBAq2

Pre-cooled Lithium 8-quinolinolate (250 mg) solution in 15 THF in ice-water bath was cannula-transferred to **IV-4** (260 mg, 0.78 mmol) also cooled in ice-water bath. The mixture was stirring at r.t. for 12 h. After filtration, the residue was washed with THF (2 × 10 mL). The residue was dissolved in 50 mL of CH_2Cl_2 and washed with water twice (20 mL each). After drying with anhydrous Na_2SO_4, CH_2Cl_2 was removed and dried in vacuo. ^{1}H NMR (500 MHz, CD_2Cl_2): 8.67 (dd, J = 5, 1 Hz, 2H), 8.46 (dd, J = 8,1 Hz, 2H), 7.74 (dd, J = 8 Hz, 2H), 7.64 (dd, J = 8, 5 Hz, 2H), 7.35 (dd, J = 3, 0.5 Hz, 2H), 7.22 (dd, J = 3, 0.5 Hz, 2H), 6.99 (m, 8 H).



DBPq2

IV-1 (60 mg, 0.138 mmol) and lithium 8-quinolinolate (51 mg, 0.338 mmol) were weighed to a Schlenk flask in the glove box. 10 mL of THF was added to the mixture with magnetically stirring at 0 °C, and the mixture was maintained at r.t. for 12 h. The solvent was then removed and dried in vacuo. 30 mL of CH_2Cl_2 was added to dissolve the crude product. The solution was washed twice with water (20 mL each), then brine (10 mL) and dried with anhydrous Na_2SO_4. After the filtration, CH_2Cl_2 was removed and dried in vacuo to obtain product 70 mg (90.2 %). ^{1}H NMR (500 MHz, CD_2Cl_2): 8.93 (dd, J = 1, 5 Hz, 4H), 8.52 (dd, J = 1, 8.5 Hz, 4H), 7,81 (dd, J = 7.5, 8.0 Hz, 4H), 7.68 (dd, J = 5, 8 Hz, 4H), 7.55 (s, 4H), 7.55 (dd, 8H), 7.42 (d, J = 8.5 Hz, 4H), 7.32 (d, J = 8 Hz, 4H), 7.23 (dd, J = 3.5, 6 Hz, 8H). ^{13}C NMR (125.7 MHz, CD_2Cl_2): 159.83, 141.63, 139.00, 138.54, 133.82, 133.26, 129.38, 129.27, 128.00, 125,14, 124.11, 112.97, 109.69, carbon next boron, not observable.



Tributylstannylthiophene (380 mg, 1.02 mmol) was dissolved in CH_2Cl_2 (5 mL) and then **IV-4** (157 mg, 0.47 mmol) was added to start the reaction. The reaction mixture was stirring at 50 °C overnight. After that, the solvent was removed and the residue was dried in vacuo. The residue was washed with pentane (7 mL, 3 times) and then dried to obtain a off-while powder. ^1H NMR (400 MHz, $CDCl_3$): 8.24 (dd, J = 3.2, 5.6 Hz, 4H), 8.04 (dd, J = 1.2, 3.6 Hz, 2H), 8.00 (dd, J = 1.2, 4.8 Hz, 2H), 7.56 (dd, 4H), 7.37 (dd, 2H).

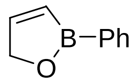
References:

(1) Hui, M. H.; Ware, W. R. *J. Am. Chem. Soc.* **1976,** *98*, 4718-4727.
(2) Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983,** *108*, 1067-1071.
(3) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985,** *89*, 2787-2794.
(4) Massol, M.; Satgé, J.; Bouyssières, B. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 1.
(5) (a)Kitamura, T.; Fukatsu, N.; Fujiwara, Y. *J. Org. Chem.* **1998,** *63*, 8579-8581. (b) Hart, H.; Bashirhashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986,** *42*, 1641-1654.

Appendices

Appendix A

^{1}H, and ^{13}C NMR Spectra of **II-9b**



II-9b

```
2-Phenyl-1,2-Oxaborole

exp1  std1h

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solvent      CDC13  dn              H1
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/vnmrsys/data/Inov~ dof              0
a.400/2-phenyl-oxa~ dm             nnn
borole-redistilled~ dmm              c
           -1f.fid  dmf          10400
   ACQUISITION      dseq
sfrq       399.967  dres           1.0
tn              H1  homo             n
at           2.666      PROCESSING
np           32000  lb            0.20
sw          6000.6  wtfile
fb            3000  proc            ft
bs               8  fn        not used
tpwr            57  math             f
pw             5.1
d1               0  werr
tof              0  wexp
nt               8  wbs
ct               8  wnt
alock            n
gain      not used
      FLAGS
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in               n
dp               y
hs              nn
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sp          -255.4
wp          4805.5
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sc               0
wc             250
hzmm         19.22
is          237.97
rfl          980.6
rfp              0
th               6
ins          2.000
ai    ph
```

```
INDEX    FREQUENCY  PPM      HEIGHT
  1       3205.267  8.014      25.0
  2       3203.802  8.010      37.3
  3       3202.703  8.007      26.3
  4       3199.407  7.999      14.7
  5       3197.576  7.995      34.7
  6       3195.745  7.990      34.1
  7       3061.698  7.655      14.6
  8       3053.274  7.634      14.8
  9       3020.678  7.552      10.0
 10       3019.213  7.549       7.8
 11       3016.283  7.541       7.7
 12       3013.353  7.534      23.3
 13       3010.790  7.528       9.8
 14       3009.325  7.524       5.9
 15       3007.493  7.519      15.3
 16       3006.028  7.516      29.1
 17       3004.563  7.512      15.2
 18       3003.098  7.508       6.1
 19       2996.506  7.492      32.0
 20       2995.773  7.490      40.6
 21       2994.675  7.487      26.4
 22       2993.210  7.484      10.7
 23       2989.914  7.475      34.4
 24       2988.449  7.472      45.4
 25       2986.984  7.468      24.4
 26       2982.955  7.458      11.5
 27       2981.856  7.455      20.8
 28       2980.025  7.451      17.4
 29       2978.926  7.448       6.1
 30       2676.406  6.692      11.0
 31       2668.348  6.671      10.3
 32       1992.621  4.982      83.7
 33       1990.790  4.977      98.7
 34       1989.325  4.974      80.6
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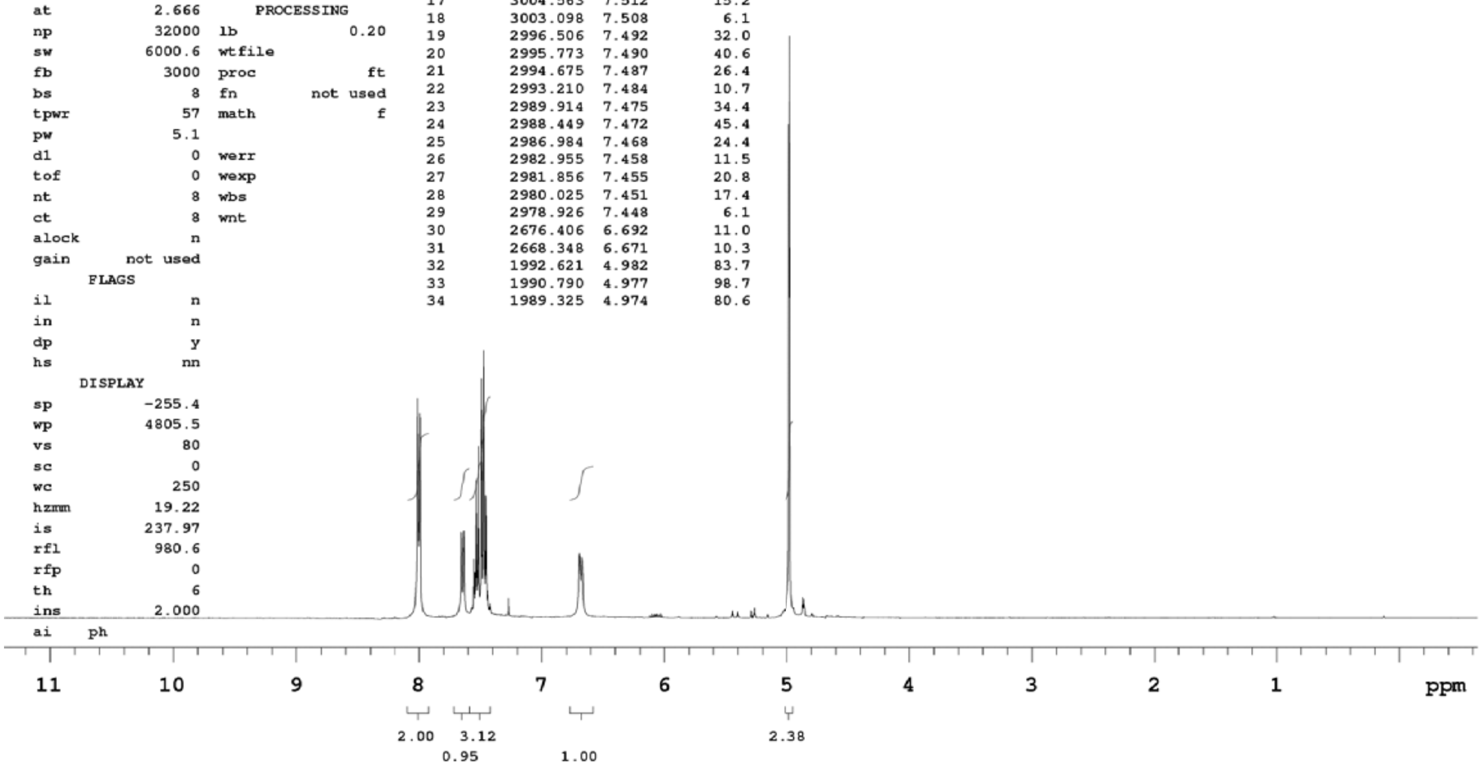
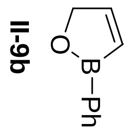
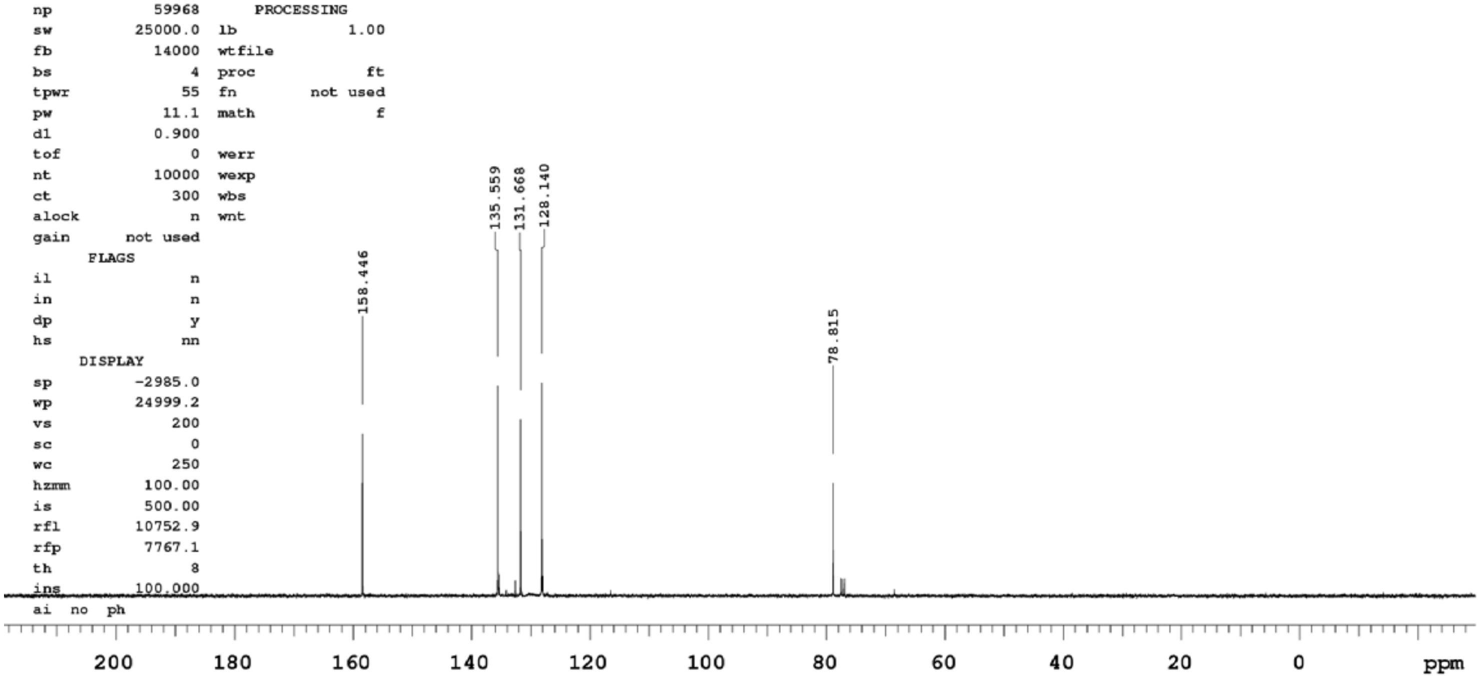




II-9b



```
2-Phenyl-1,2-Oxaborole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solvent      CDCl3  dn              H1
file /home/agostic~ dpwr            44
/vnmrsys/data/Inov~ dof              0
a.400/CDCl3-C13NMR~ dm             yyy
    -Oxaborole.fid  dmm              w
   ACQUISITION      dmf          10400
sfrq       100.581  dseq
tn             C13  dres           1.0
at           1.199  homo             n
np           59968     PROCESSING
sw         25000.0  lb            1.00
fb           14000  wtfile
bs               4  proc            ft
tpwr            55  fn        not used
pw            11.1  math             f
d1           0.900
tof              0  werr
nt           10000  wexp
ct             300  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
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wp         24999.2
vs             200
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10752.9
rfp         7767.1
th               8
ins        100.000
ai  no  ph
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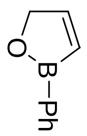
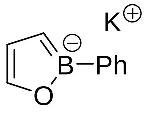


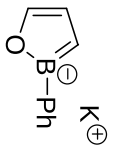
II-9b

Appendix B

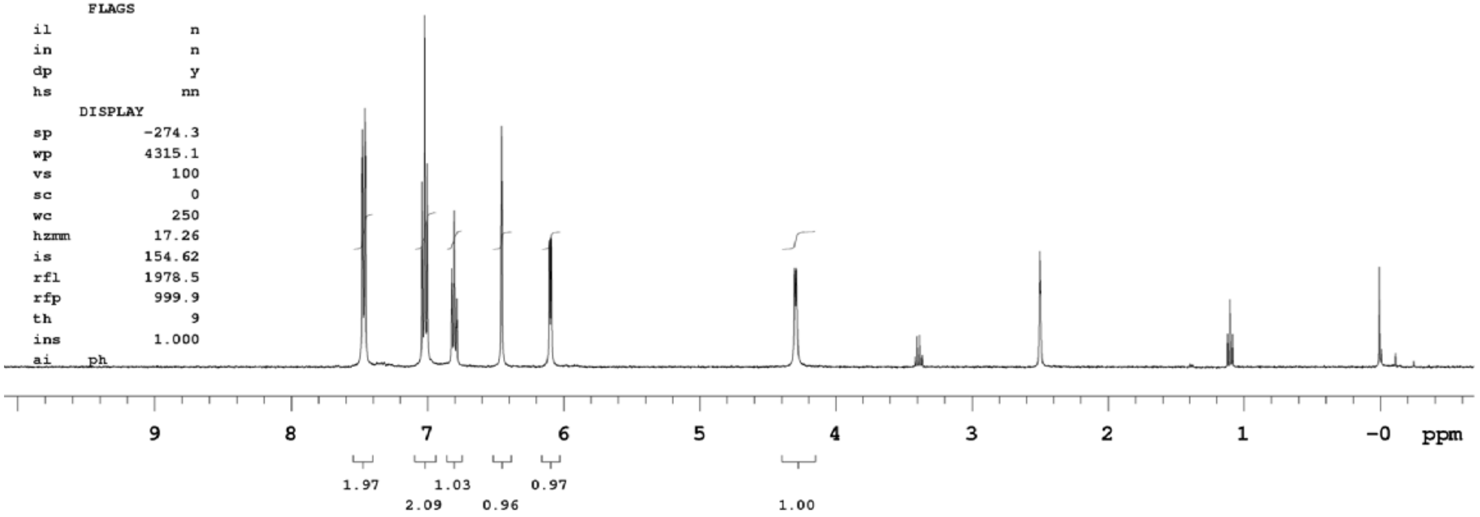
^{1}H, and ^{13}C NMR Spectra of **II-6b**



II-6b



II-6b



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                                              3     2984.613  7.462      44.0
                                              4     2815.406  7.039      31.5
      SAMPLE            DEC. & VT             5     2808.081  7.021      59.8
date   Feb  5 2004  dfrq        399.969      6     2800.390  7.002      34.6
solvent        DMSO  dn               H1      7     2729.704  6.825       9.9
file /home/agostic~ dpwr              44      8     2728.239  6.821      16.8
/vnmrsys/data/Inov~ dof                0      9     2726.774  6.818      10.0
a.400/K-oxaborolid~ dm               nnn     10     2720.914  6.803      26.6
   e-best-DMSO.fid  dmm                c     11     2713.956  6.785      11.6
   ACQUISITION      dmf            10400     12     2582.473  6.457      40.9
sfrq        399.969  dseq                    13     2442.200  6.106      21.3
tn               H1  dres            1.0     14     2441.101  6.103      21.6
at            2.666  homo              n     15     2437.073  6.093      21.9
np            32000      PROCESSING          16     2435.974  6.090      21.7
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bs                8  proc             ft     19     1001.748  2.505      14.4
tpwr             57  fn         not used     20      999.917  2.500      19.7
pw              5.1  math              f     21      998.086  2.495      14.7
d1                0                          22      440.657  1.102      11.5
tof               0  werr                    23        2.625  0.007      17.0
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ct                8  wbs
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ai    ph
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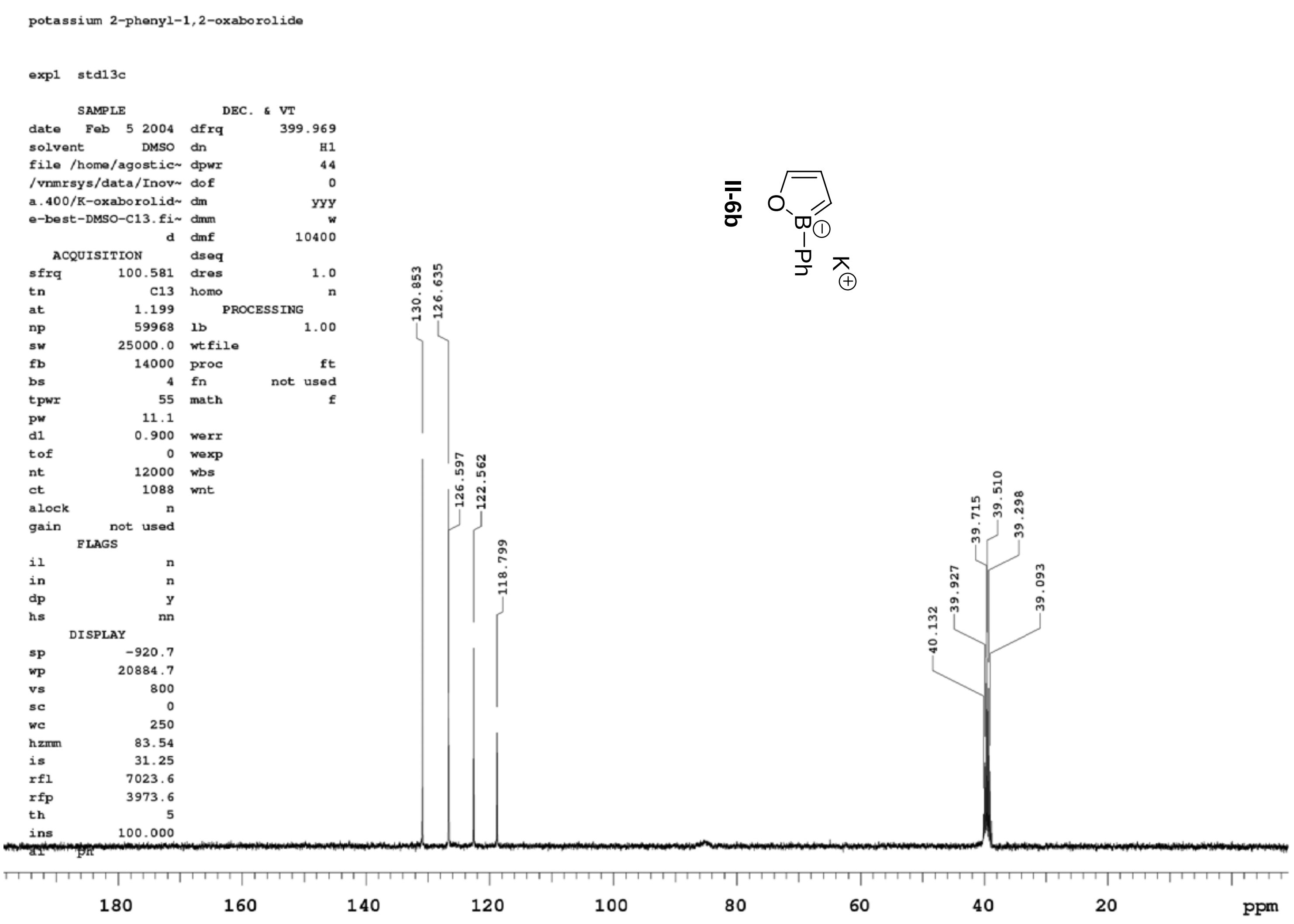

II-6b

```
potassium 2-phenyl-1,2-oxaborolide


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                 d  dmf           10400
   ACQUISITION      dseq
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tn             C13  homo              n
at           1.199       PROCESSING
np           59968  lb             1.00
sw         25000.0  wtfile
fb           14000  proc             ft
bs               4  fn         not used
tpwr            55  math              f
pw            11.1
d1           0.900  werr
tof              0  wexp
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alock            n
gain      not used
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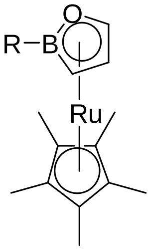
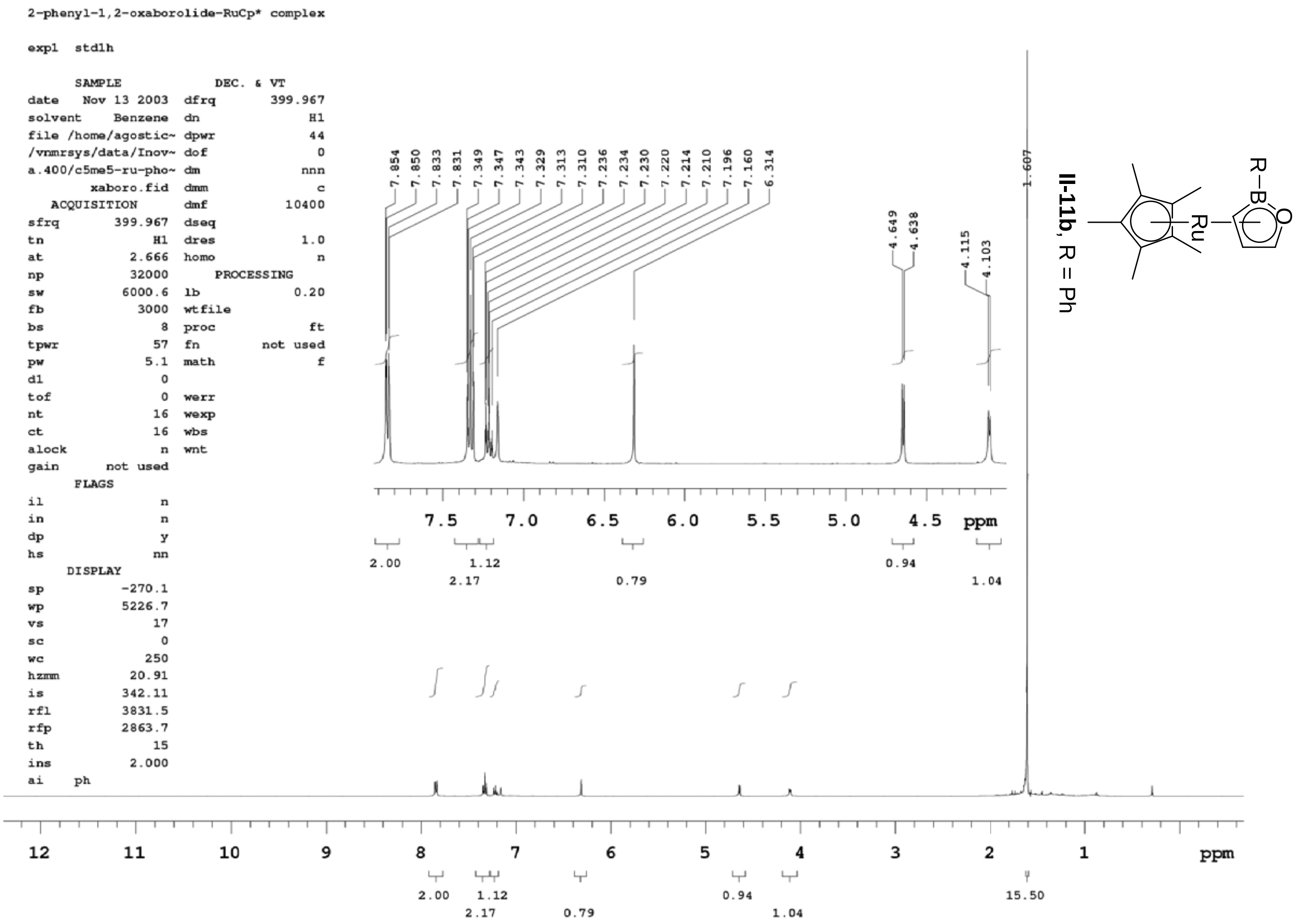
Appendix C

^{1}H, and ^{13}C NMR Spectra of **II-11b**



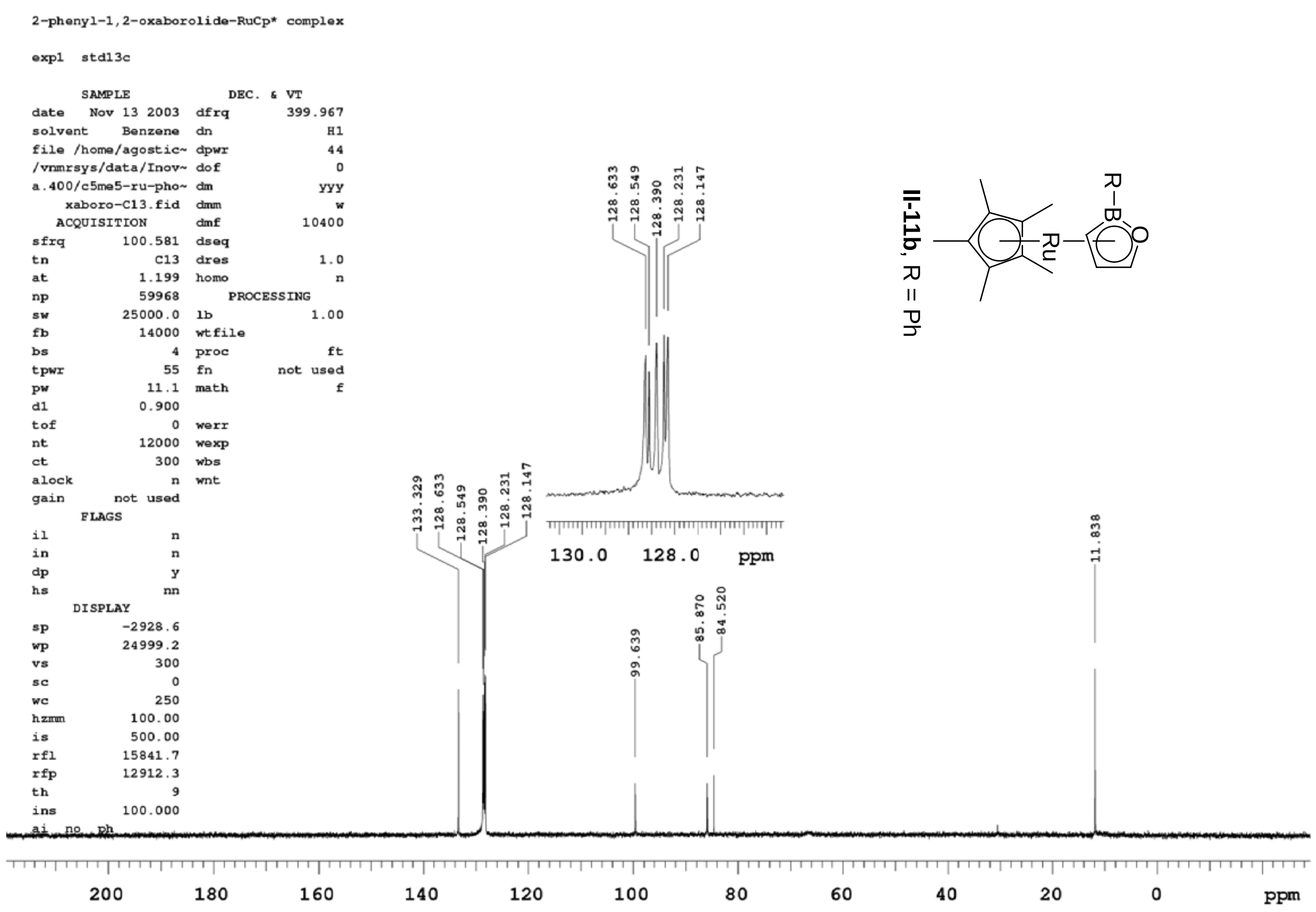
II-11b, R = Ph


II-11b, R = Ph

```
2-phenyl-1,2-oxaborolide-RuCp* complex

exp1  std1h

      SAMPLE            DEC. & VT
date   Nov 13 2003  dfrq       399.967
solvent    Benzene  dn              H1
file /home/agostic~ dpwr            44
/vnmrsys/data/Inov~ dof              0
a.400/c5me5-ru-pho~ dm             nnn
        xaboro.fid  dmm              c
   ACQUISITION      dmf          10400
sfrq       399.967  dseq
tn              H1  dres           1.0
at           2.666  homo             n
np           32000      PROCESSING
sw          6000.6  lb            0.20
fb            3000  wtfile
bs               8  proc            ft
tpwr            57  fn        not used
pw             5.1  math             f
d1               0
tof              0  werr
nt              16  wexp
ct              16  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -270.1
wp          5226.7
vs              17
sc               0
wc             250
hzmm         20.91
is          342.11
rfl         3831.5
rfp         2863.7
th              15
ins          2.000
ai    ph
```



```
2-phenyl-1,2-oxaborolide-RuCp* complex

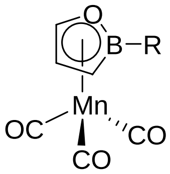
expl  std13c

      SAMPLE            DEC. & VT
date   Nov 13 2003  dfrq        399.967
solvent    Benzene  dn               H1
file /home/agostic~ dpwr             44
/vnmrsys/data/Inov~ dof               0
a.400/c5me5-ru-pho~ dm              yyy
   xaboro-C13.fid   dmm               w
   ACQUISITION      dmf           10400
sfrq       100.581  dseq
tn             C13  dres            1.0
at           1.199  homo              n
np           59968      PROCESSING
sw         25000.0  lb             1.00
fb           14000  wtfile
bs               4  proc             ft
tpwr            55  fn         not used
pw            11.1  math              f
d1           0.900
tof              0  werr
nt           12000  wexp
ct             300  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -2928.6
wp         24999.2
vs             300
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        15841.7
rfp        12912.3
th               9
ins        100.000
ai  no  ph
```

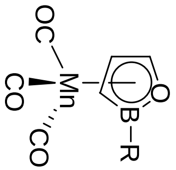
II-11b, R = Ph

Appendix D

^{1}H, and ^{13}C NMR Spectra of **II-12b**



II-12b, R = Ph

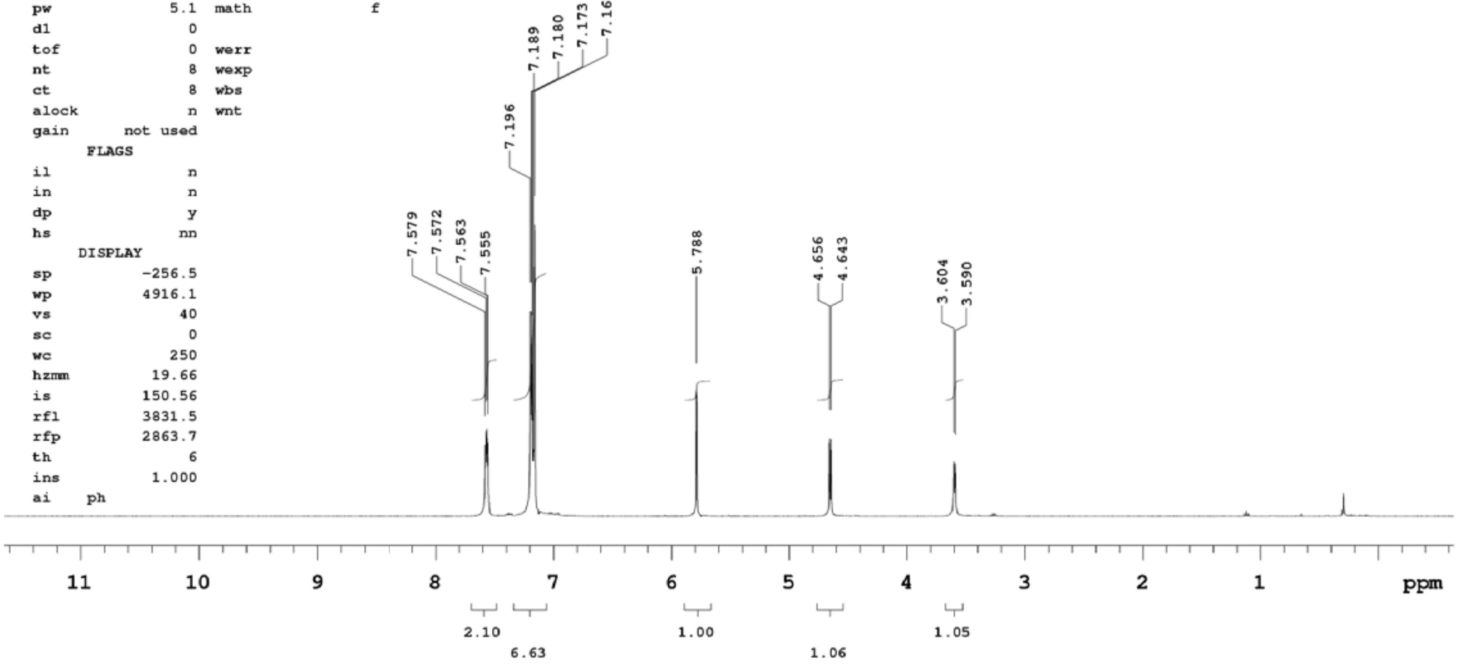


II-12b, R = Ph

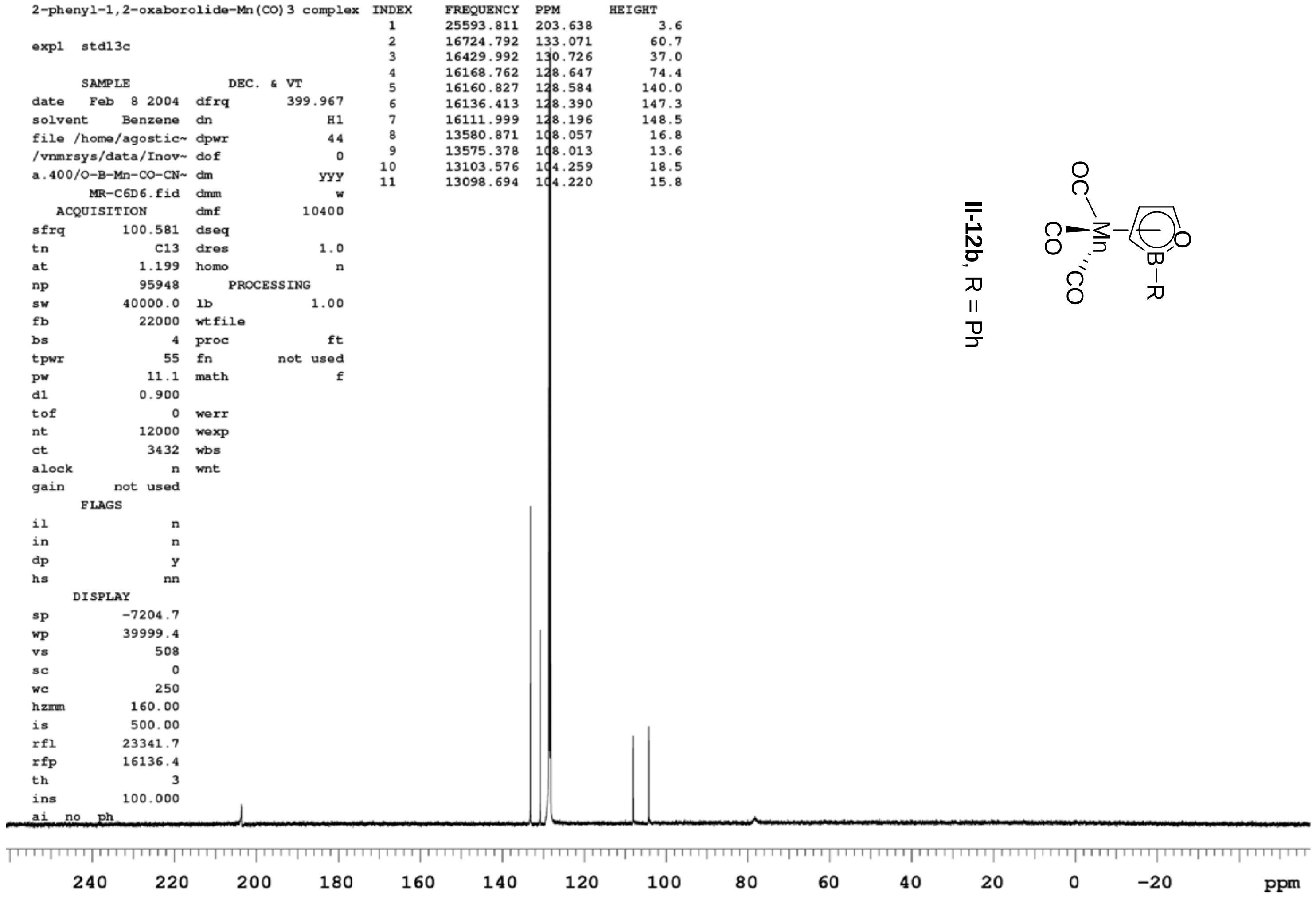
```
2-phenyl-1,2-oxaborolide-Mn(CO)3 complex

exp1  std1h

      SAMPLE           DEC. & VT
date   Feb  8 2004  dfrq       399.967
solvent    Benzene  dn              H1
file /home/agostic~ dpwr            44
/vnmrsys/data/Inov~ dof              0
a.400/O-B-Mn-CO-HN~ dm             nnn
      MR-C6D6.fid   dmm              c
   ACQUISITION      dmf          10400
sfrq       399.967  dseq
tn              H1  dres           1.0
at           2.666  homo             n
np           32000      PROCESSING
sw          6000.6  lb            0.20
fb            3000  wtfile
bs               8  proc            ft
tpwr            57  fn        not used
pw             5.1  math             f
d1               0
tof              0  werr
nt               8  wexp
ct               8  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -256.5
wp          4916.1
vs              40
sc               0
wc             250
hzmm         19.66
is          150.56
rfl         3831.5
rfp         2863.7
th               6
ins          1.000
ai    ph
```



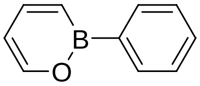
II-12b, R = Ph



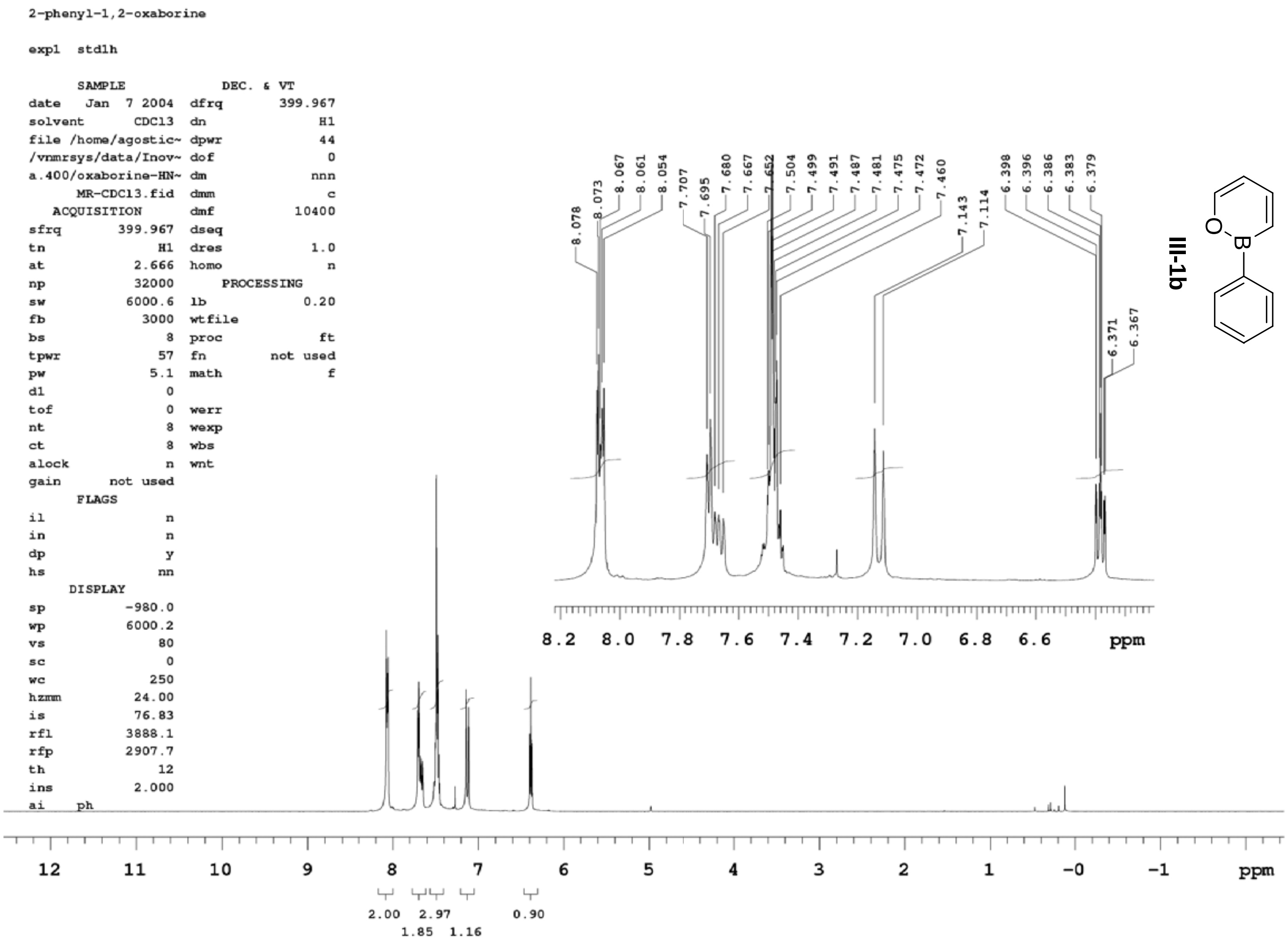
```
2-phenyl-1,2-oxaborolide-Mn(CO)3 complex INDEX    FREQUENCY  PPM      HEIGHT
                                             1    25593.811  203.638     3.6
expl  std13c                                 2    16724.792  133.071    60.7
                                             3    16429.992  130.726    37.0
      SAMPLE             DEC. & VT           4    16168.762  128.647    74.4
date   Feb  8 2004  dfrq       399.967       5    16160.827  128.584   140.0
solvent    Benzene  dn              H1       6    16136.413  128.390   147.3
file /home/agostic~ dpwr            44       7    16111.999  128.196   148.5
/vnmrsys/data/Inov~ dof              0       8    13580.871  108.057    16.8
a.400/O-B-Mn-CO-CN~ dm             yyy       9    13575.378  108.013    13.6
       MR-C6D6.fid  dmm              w      10    13103.576  104.259    18.5
   ACQUISITION      dmf          10400      11    13098.694  104.220    15.8
sfrq       100.581  dseq
tn             C13  dres           1.0
at           1.199  homo             n
np           95948      PROCESSING
sw         40000.0  lb            1.00
fb           22000  wtfile
bs               4  proc            ft
tpwr            55  fn        not used
pw            11.1  math             f
d1           0.900
tof              0  werr
nt           12000  wexp
ct            3432  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -7204.7
wp         39999.4
vs             508
sc               0
wc             250
hzmm        160.00
is          500.00
rfl        23341.7
rfp        16136.4
th               3
ins        100.000
ai  no  ph
```

Appendix E

^{1}H, and ^{13}C NMR Spectra of **III-1b**



III-1b

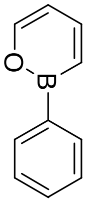


III-1b

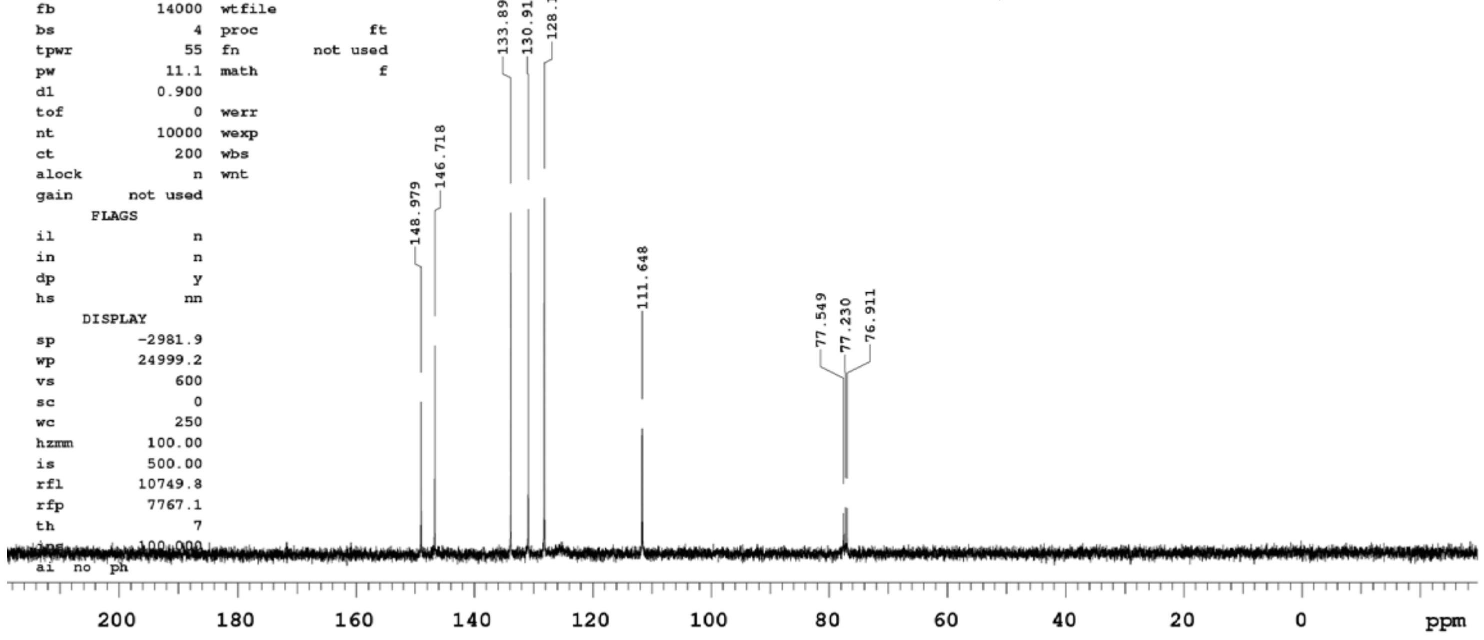
```
2-phenyl-1,2-oxaborine

exp1  std1h

      SAMPLE            DEC. & VT
date   Jan  7 2004  dfrq       399.967
solvent      CDC13  dn              H1
file /home/agostic~ dpwr            44
/vnmrsys/data/Inov~ dof              0
a.400/oxaborine-HN~ dm             nnn
     MR-CDC13.fid   dmm              c
   ACQUISITION      dmf          10400
sfrq       399.967  dseq
tn              H1  dres           1.0
at           2.666  homo             n
np           32000      PROCESSING
sw          6000.6  lb            0.20
fb            3000  wtfile
bs               8  proc            ft
tpwr            57  fn        not used
pw             5.1  math             f
d1               0
tof              0  werr
nt               8  wexp
ct               8  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -980.0
wp          6000.2
vs              80
sc               0
wc             250
hzmm         24.00
is           76.83
rfl         3888.1
rfp         2907.7
th              12
ins          2.000
ai    ph
```



III-1b



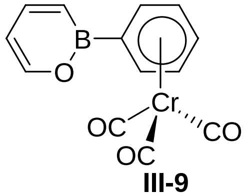
```
2-phenyl-1,2-oxaborine


expl  std13c

      SAMPLE            DEC. & VT
date   Jan  7 2004  dfrq       399.967
solvent      CDCl3  dn              H1
file /home/agostic~ dpwr            44
/vnmrsys/data/Inov~ dof              0
a.400/oxaborine-CN~ dm             yyy
      MR-CDCl3.fid  dmm              w
   ACQUISITION      dmf          10400
sfrq       100.581  dseq
tn             C13  dres           1.0
at           1.199  homo             n
np           59968      PROCESSING
sw         25000.0  lb            1.00
fb           14000  wtfile
bs               4  proc            ft
tpwr            55  fn        not used
pw            11.1  math             f
d1           0.900
tof              0  werr
nt           10000  wexp
ct             200  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -2981.9
wp         24999.2
vs             600
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10749.8
rfp         7767.1
th               7
ins        100.000
ai  no  ph
```

Appendix F

^{1}H, and ^{13}C NMR Spectra of **III-9**

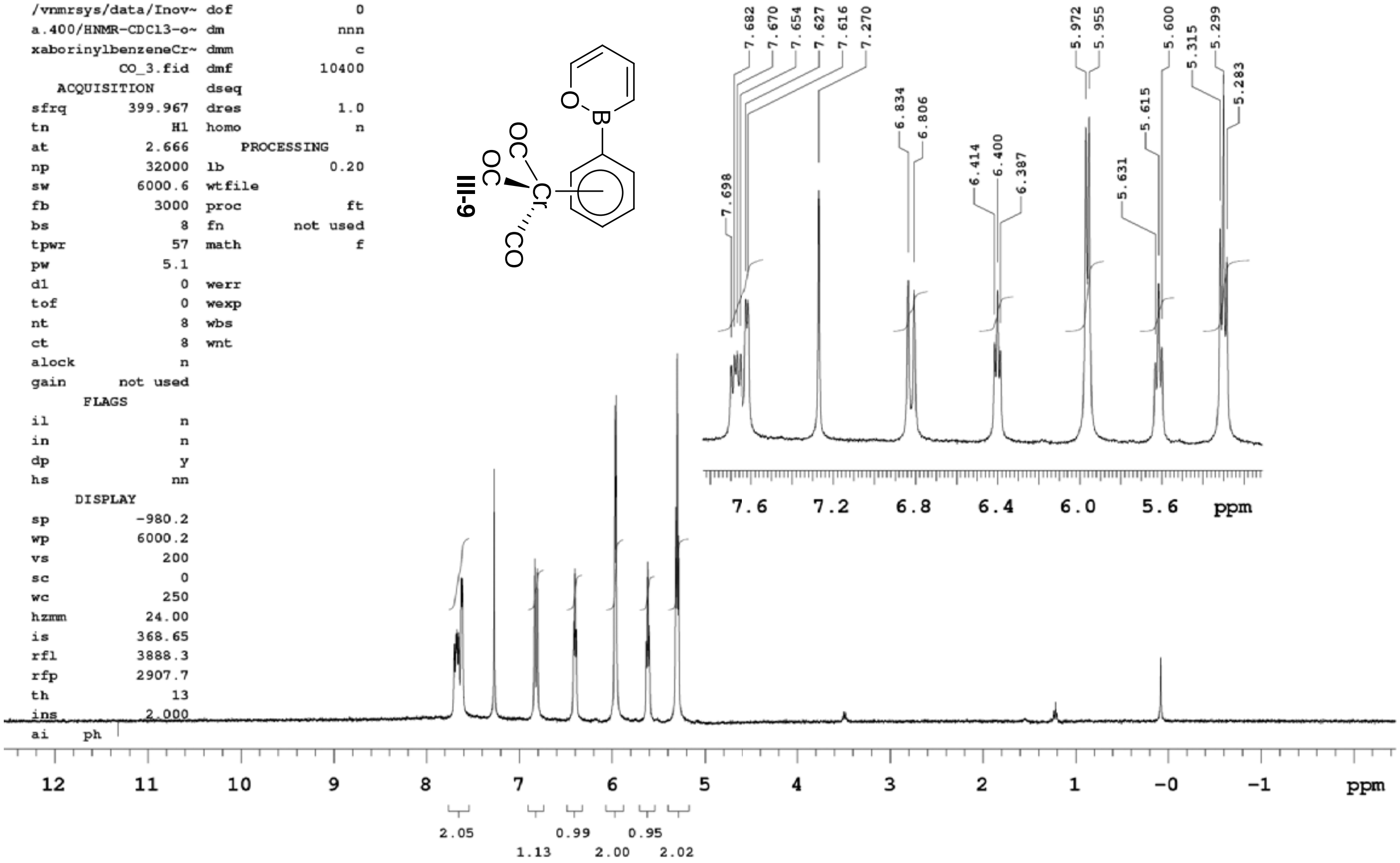


III-9

```
2-phenyl-1,2-oxaborine-Cr(CO)3 complex

expl  std1h

      SAMPLE              DEC. & VT
date   Jun 10 2004  dfrq        399.967
solvent      CDCl3  dn               H1
file /home/agostic~ dpwr             44
/vnmrsys/data/Inov~ dof               0
a.400/HNMR-CDCl3-o~ dm              nnn
xaborinylbenzeneCr~ dmm               c
         CO_3.fid   dmf           10400
   ACQUISITION      dseq
sfrq       399.967  dres            1.0
tn              H1  homo              n
at           2.666      PROCESSING
np           32000  lb             0.20
sw          6000.6  wtfile
fb            3000  proc             ft
bs               8  fn         not used
tpwr            57  math              f
pw             5.1
d1               0  werr
tof              0  wexp
nt               8  wbs
ct               8  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp          -980.2
wp          6000.2
vs             200
sc               0
wc             250
hzmm         24.00
is          368.65
rfl         3888.3
rfp         2907.7
th              13
ins          2.000
ai    ph
```

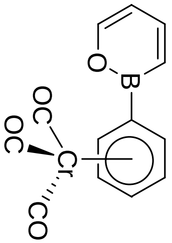


III-9

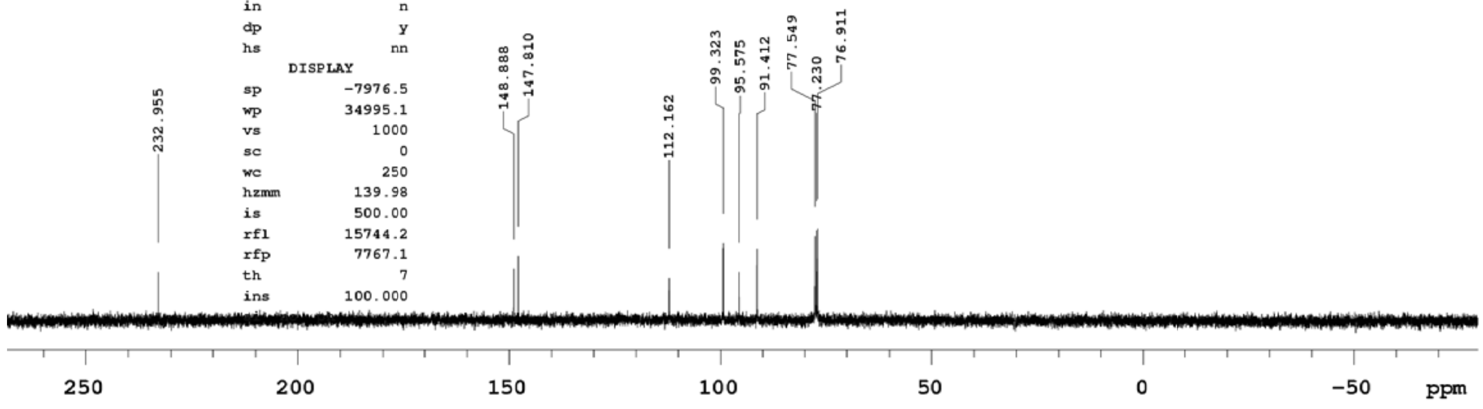
2-phenyl-1,2-oxaborine-Cr(CO)3 complex

```
exp1  std13c

      SAMPLE            DEC. & VT
date   Jun 11 2004  dfrq       399.967
solvent      CDC13  dn              H1
file /home/agostic~ dpwr            44
/vnmrsys/data/Inov~ dof              0
a.400/C13NMR-CDC13~ dm             yyy
-oxaborinylbenzene~ dmm              w
        CrCO_3.fid  dmf          10400
   ACQUISITION      dseq
sfrq       100.581  dres           1.0
tn             C13  homo             n
at           1.199      PROCESSING
np           83944  lb            1.00
sw         34995.6  wtfile
fb           19000  proc            ft
bs               4  fn        not used
tpwr            55  math             f
pw            11.1
d1           0.900  werr
tof              0  wexp
nt           10000  wbs
ct            1200  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -7976.5
wp         34995.1
vs            1000
sc               0
wc             250
hzmm        139.98
is          500.00
rfl        15744.2
rfp         7767.1
th               7
ins        100.000
```

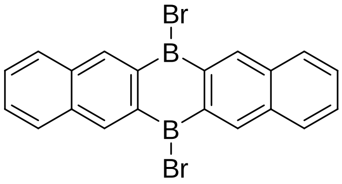


III-9

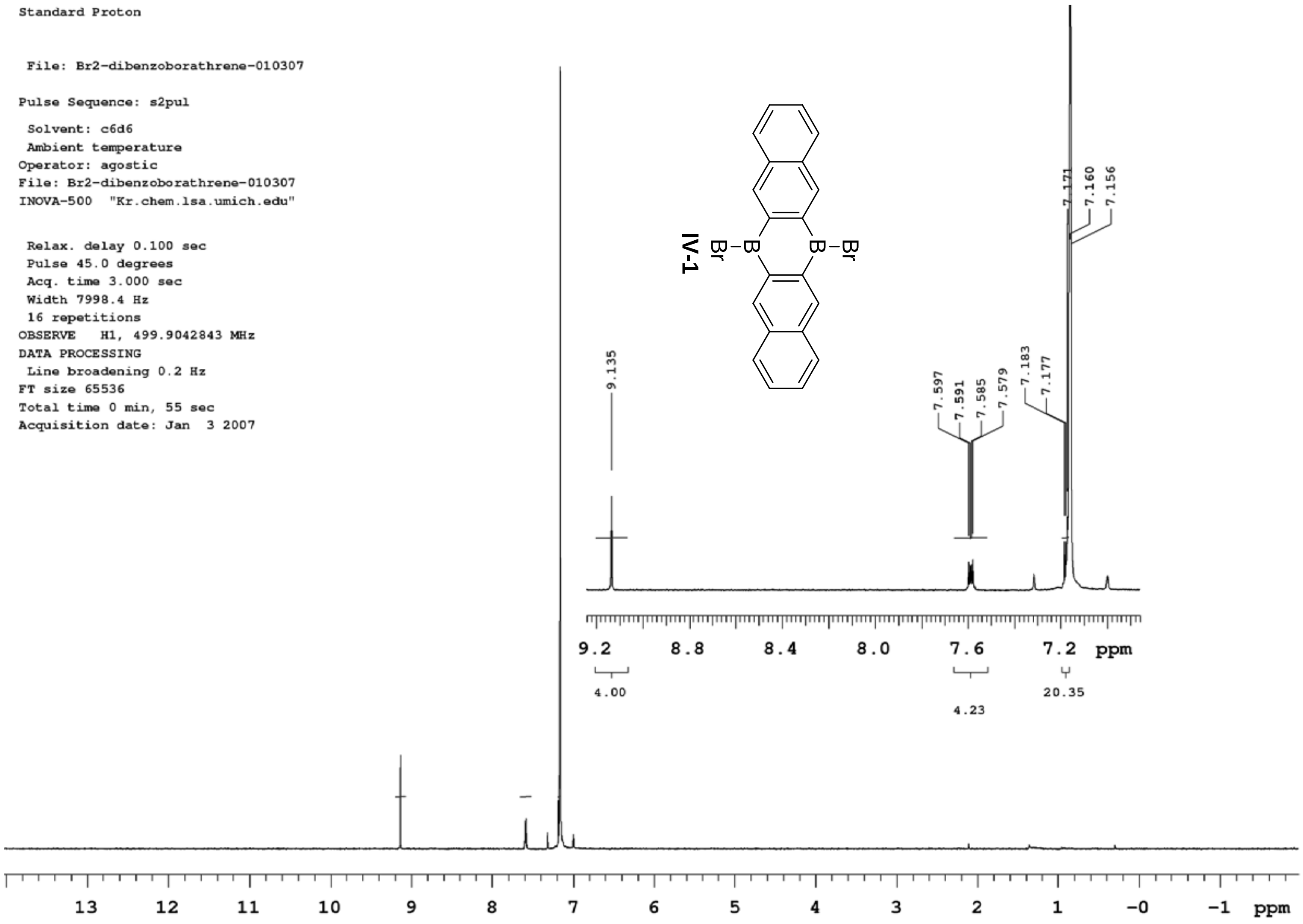


Appendix G

^{1}H, and ^{13}C NMR Spectra of **IV-1**



IV-1



```
Standard Proton

 File: Br2-dibenzoborathrene-010307

Pulse Sequence: s2pul
 Solvent: c6d6
 Ambient temperature
Operator: agostic
File: Br2-dibenzoborathrene-010307
INOVA-500  "Kr.chem.lsa.umich.edu"

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7998.4 Hz
 16 repetitions
OBSERVE   H1, 499.9042843 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 55 sec
Acquisition date: Jan  3 2007
```

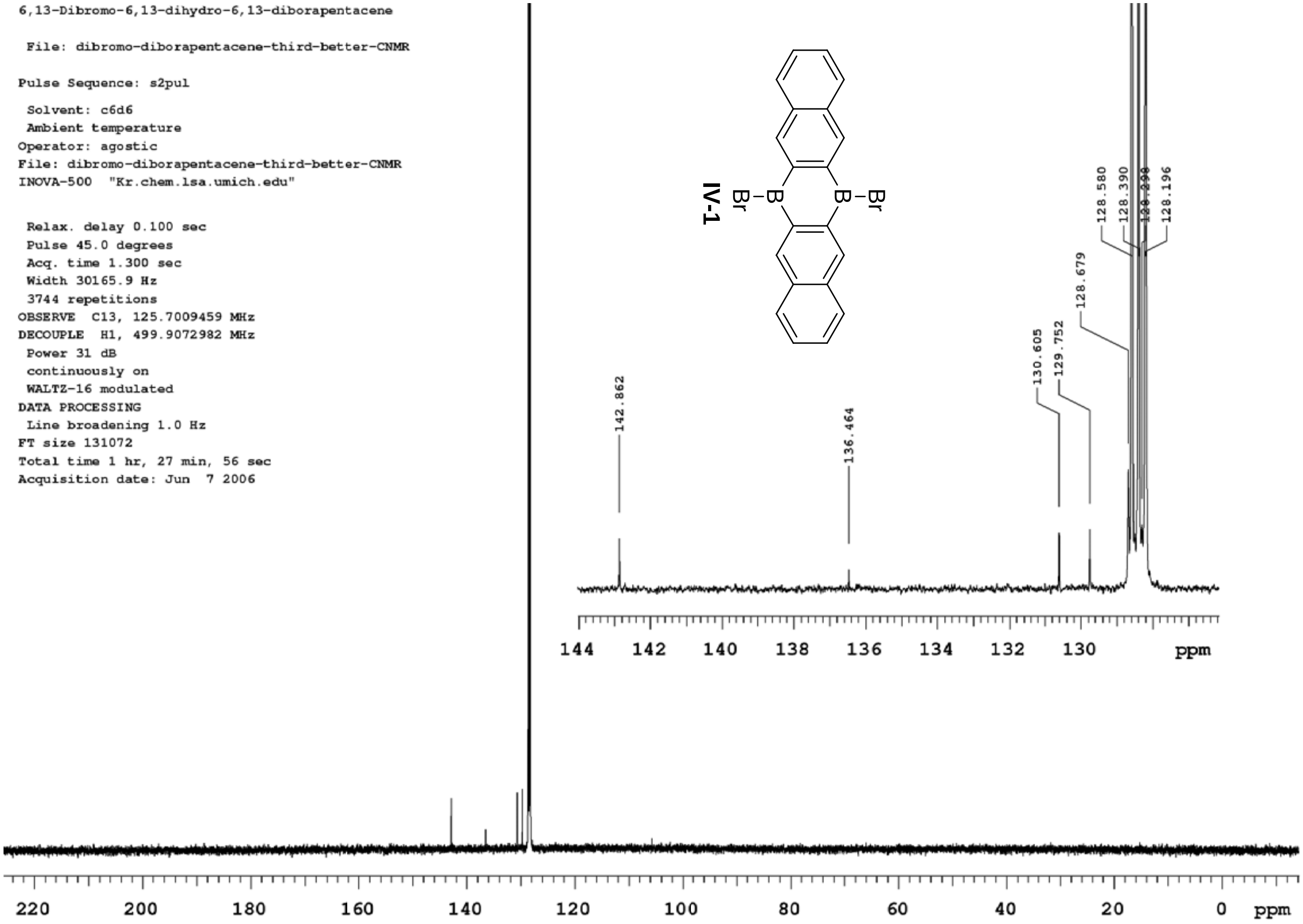
```
6,13-Dibromo-6,13-dihydro-6,13-diborapentacene

 File: dibromo-diborapentacene-third-better-CNMR

Pulse Sequence: s2pul

 Solvent: c6d6
 Ambient temperature
Operator: agostic
File: dibromo-diborapentacene-third-better-CNMR
INOVA-500  "Kr.chem.lsa.umich.edu"

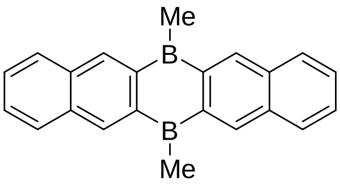
 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 30165.9 Hz
 3744 repetitions
OBSERVE  C13, 125.7009459 MHz
DECOUPLE  H1, 499.9072982 MHz
 Power 31 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 27 min, 56 sec
Acquisition date: Jun  7 2006
```



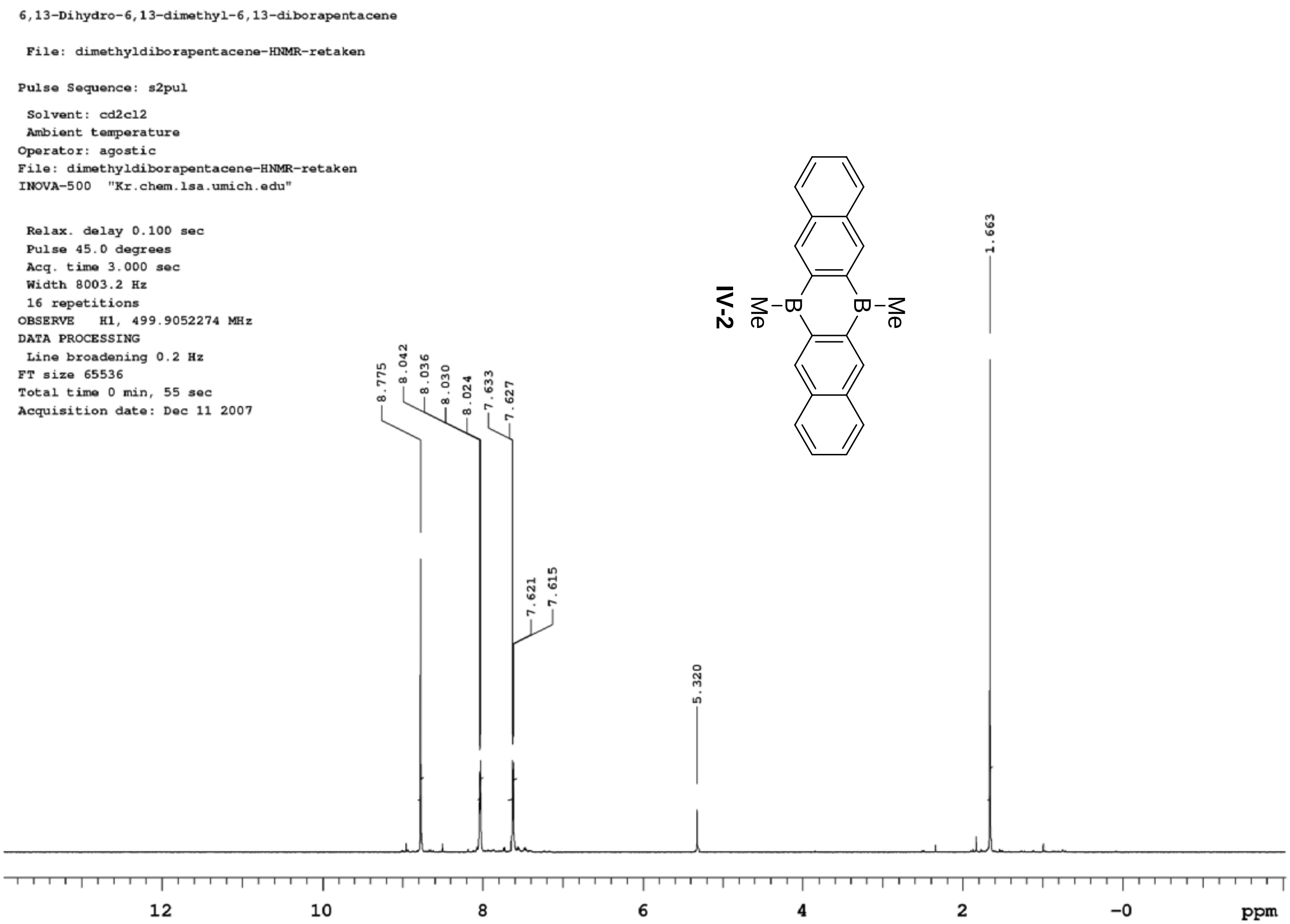
IV-1

Appendix H

^{1}H, and ^{13}C NMR Spectra of **IV-2**



IV-2



```
6,13-Dihydro-6,13-dimethyl-6,13-diborapentacene

 File: dimethyldiborapentacene-HNMR-retaken

Pulse Sequence: s2pul

 Solvent: cd2cl2
 Ambient temperature
Operator: agostic
File: dimethyldiborapentacene-HNMR-retaken
INOVA-500  "Kr.chem.lsa.umich.edu"

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 8003.2 Hz
 16 repetitions
OBSERVE   H1, 499.9052274 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 55 sec
Acquisition date: Dec 11 2007
```

IV-2

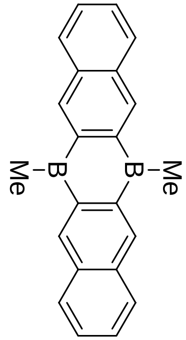
```
6,13-Dihydro-6,13-dimethyl-6,13-diborapentacene

 File: dimethyl-diborapentacene-crude-cd2cl2-CNMR

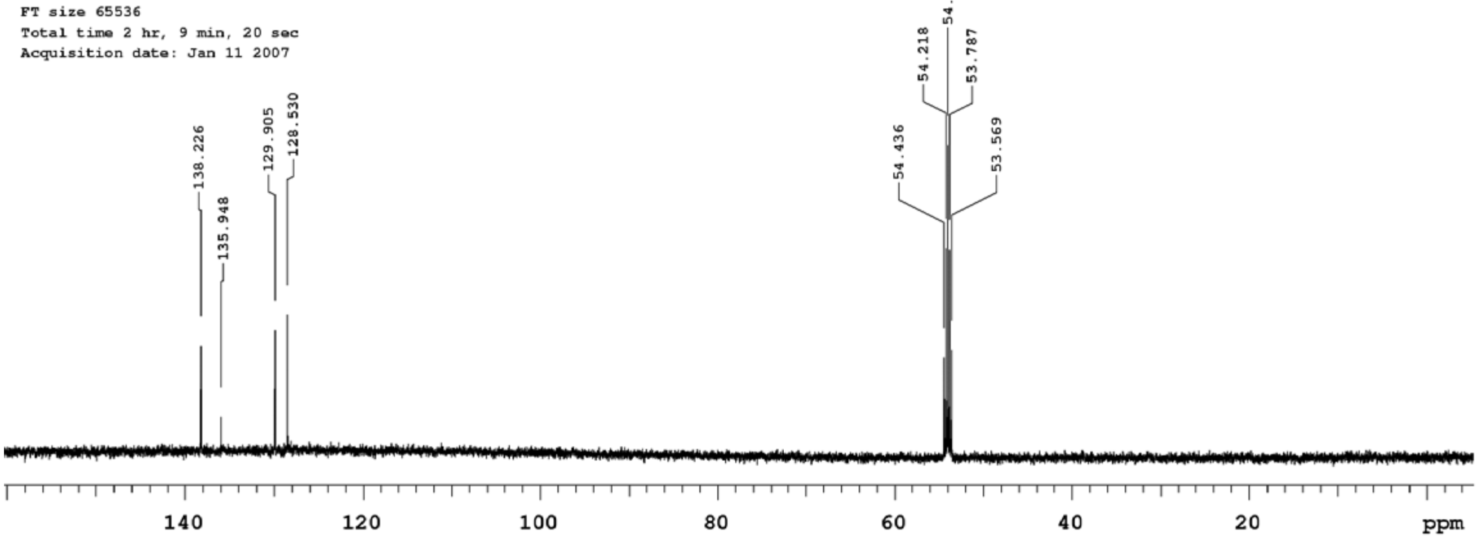
Pulse Sequence: s2pul

 Solvent: cd2cl2
 Ambient temperature
Operator: agostic
File: dimethyl-diborapentacene-crude-cd2cl2-CNMR
INOVA-500  "Kr.chem.lsa.umich.edu"

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 21367.5 Hz
 5504 repetitions
OBSERVE  C13, 125.7011949 MHz
DECOUPLE  H1, 499.9077131 MHz
 Power 31 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 9 min, 20 sec
Acquisition date: Jan 11 2007
```

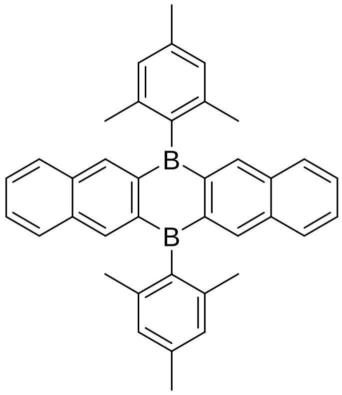


IV-2

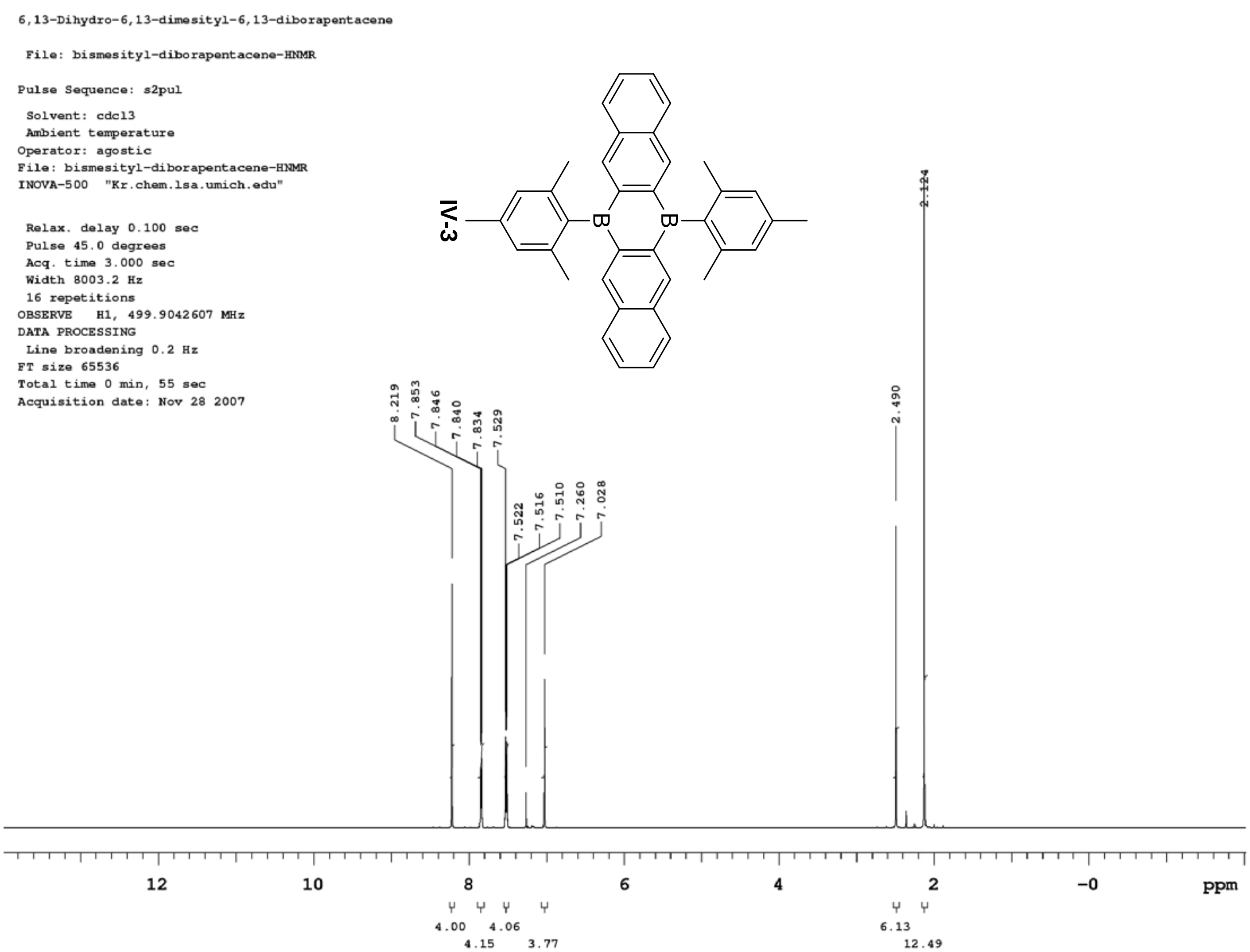


Appendix I

^{1}H, and ^{13}C NMR Spectra of **IV-3**



IV-3



6,13-Dihydro-6,13-dimesityl-6,13-diborapentacene

File: bismesityl-diborapentacene-HNMR

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: agostic
File: bismesityl-diborapentacene-HNMR
INOVA-500 "Kr.chem.lsa.umich.edu"

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 8003.2 Hz
16 repetitions
OBSERVE H1, 499.9042607 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 55 sec
Acquisition date: Nov 28 2007

IV-3

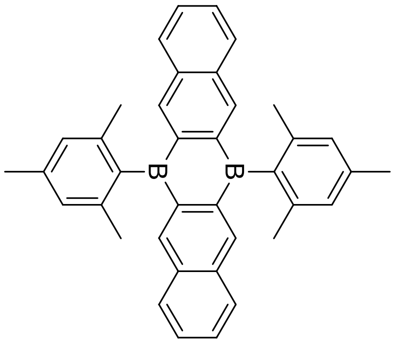
6,13-Dihydro-6,13-dimesityl-6,13-diborapentacene

File: bismesityldiborapentacene-CNMR

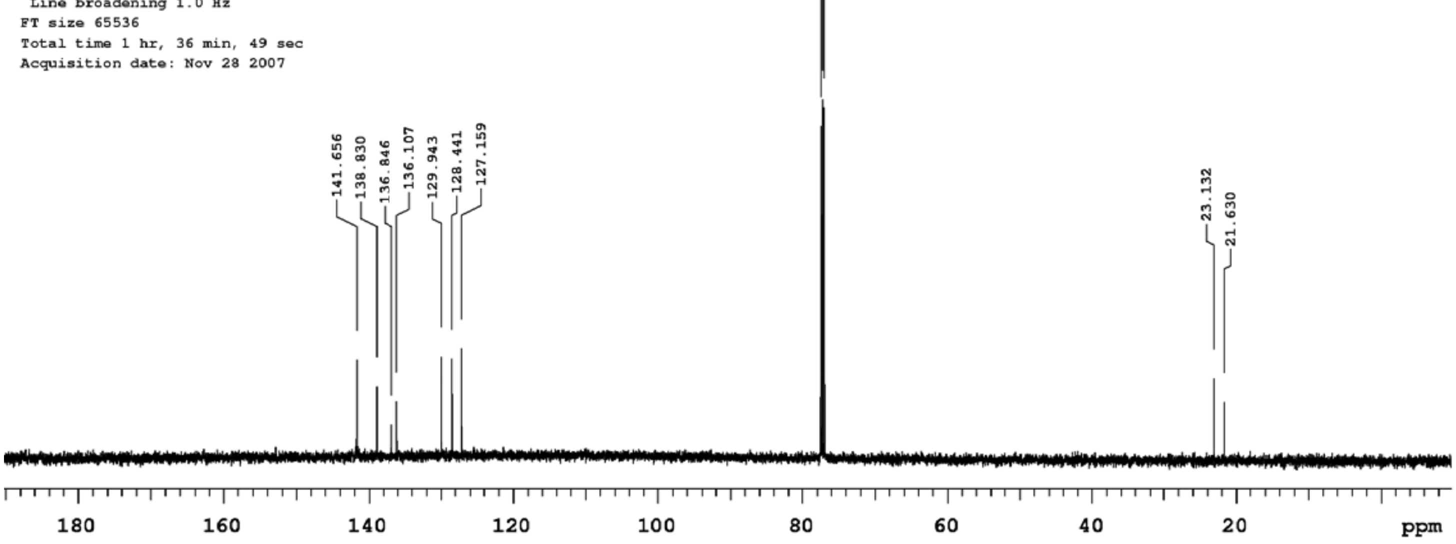
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: agostic
File: bismesityldiborapentacene-CNMR
INOVA-500 "Kr.chem.lsa.umich.edu"

Relax. delay 0.100 sec
Pulse 30.0 degrees
Acq. time 1.300 sec
Width 25141.4 Hz
4120 repetitions
OBSERVE C13, 125.7009971 MHz
DECOUPLE H1, 499.9067532 MHz
Power 31 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 36 min, 49 sec
Acquisition date: Nov 28 2007

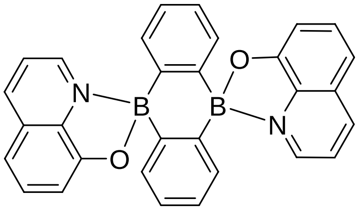


IV-3

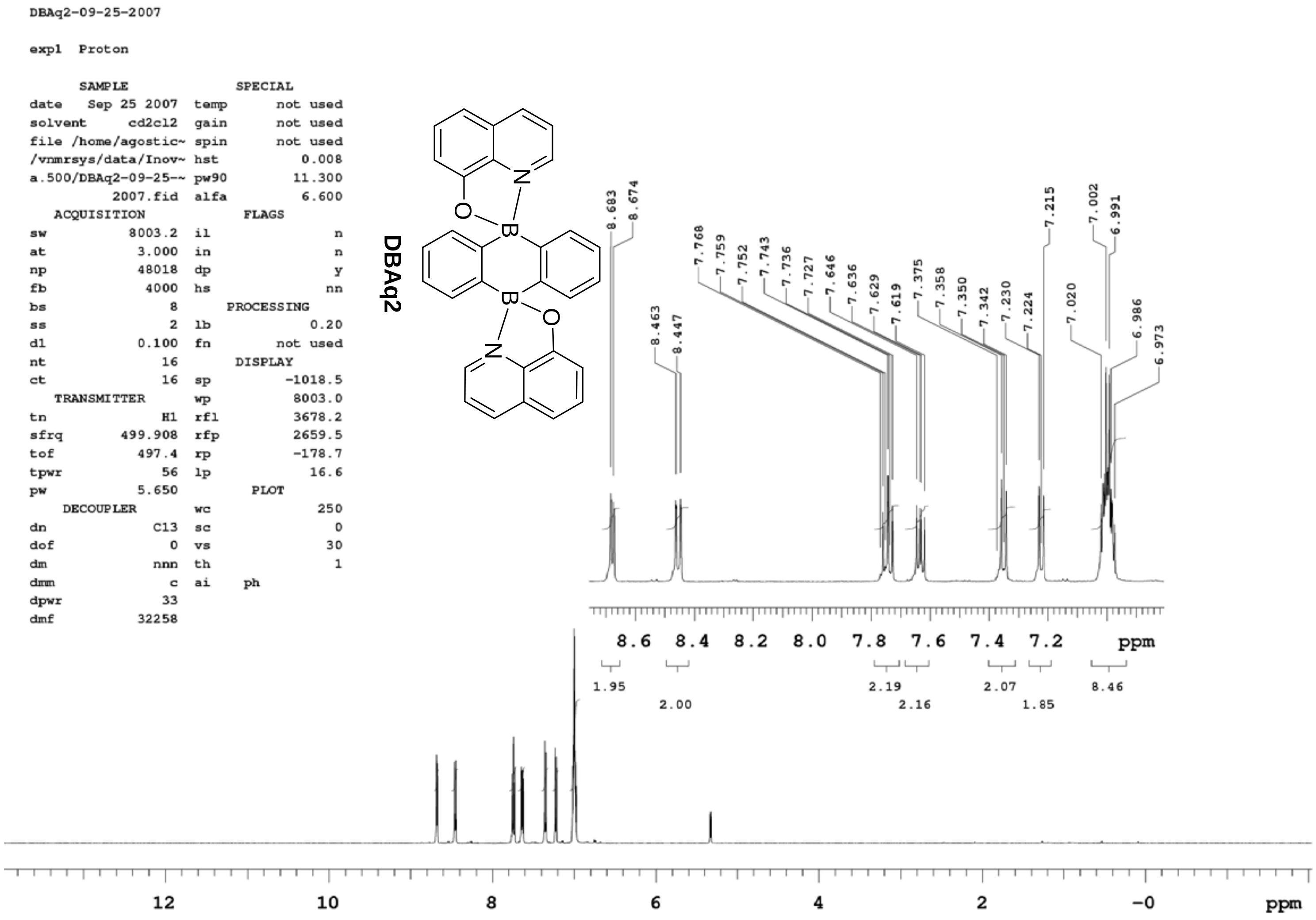


Appendix J

^{1}H, and ^{13}C NMR Spectra of **DBAq2**



DBAq2

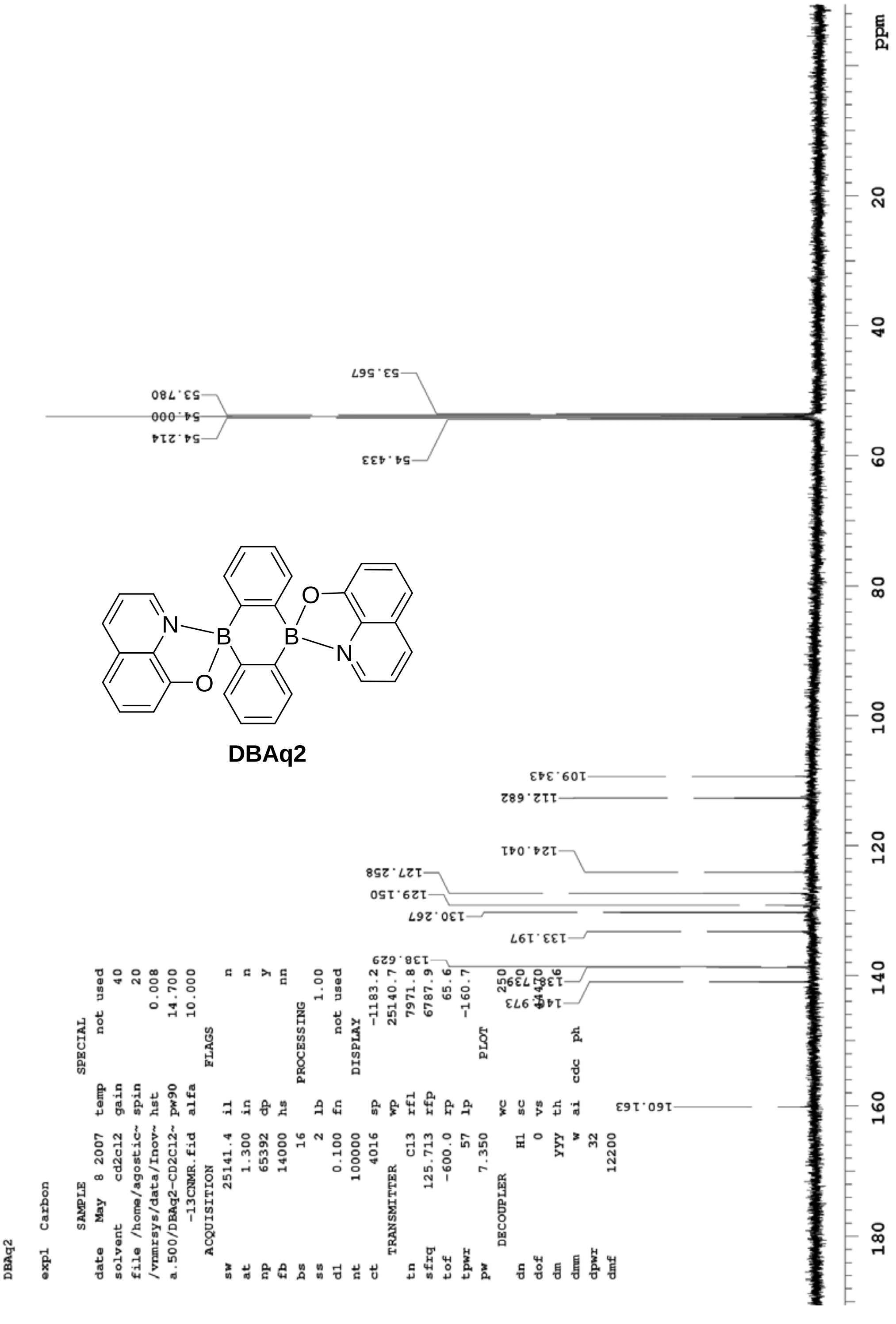


DBAq2

```
DBAq2-09-25-2007

exp1  Proton

      SAMPLE              SPECIAL
date   Sep 25 2007  temp      not used
solvent     cd2cl2  gain      not used
file /home/agostic~ spin      not used
/vnmrsys/data/Inov~ hst          0.008
a.500/DBAq2-09-25-~ pw90        11.300
          2007.fid  alfa         6.600
   ACQUISITION             FLAGS
sw          8003.2  il               n
at           3.000  in               n
np           48018  dp               y
fb            4000  hs              nn
bs               8      PROCESSING
ss               2  lb            0.20
d1           0.100  fn        not used
nt              16         DISPLAY
ct              16  sp         -1018.5
   TRANSMITTER      wp          8003.0
tn              H1  rfl         3678.2
sfrq       499.908  rfp         2659.5
tof          497.4  rp          -178.7
tpwr            56  lp            16.6
pw           5.650         PLOT
    DECOUPLER       wc             250
dn             C13  sc               0
dof              0  vs              30
dm             nnn  th               1
dmm              c  ai    ph
dpwr            33
dmf          32258
```



DBAq2

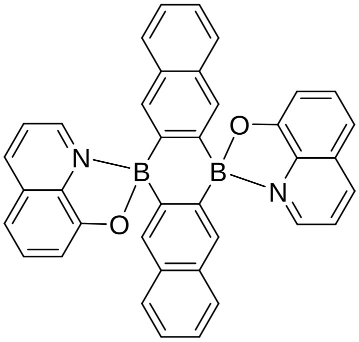
```
DBAq2

exp1  Carbon

      SAMPLE                    SPECIAL
date   May  8 2007   temp       not used
solvent     cd2cl2   gain             40
file /home/agostic~  spin             20
/vnmrsys/data/Inov~  hst           0.008
a.500/DBAq2-CD2Cl2~  pw90         14.700
   -13CNMR.fid       alfa         10.000
   ACQUISITION              FLAGS
sw         25141.4   il                n
at           1.300   in                n
np           65392   dp                y
fb           14000   hs               nn
bs              16      PROCESSING
ss               2   lb             1.00
d1           0.100   fn         not used
nt          100000       DISPLAY
ct            4016   sp          -1183.2
    TRANSMITTER      wp          25140.7
tn             C13   rfl          7971.8
sfrq       125.713   rfp          6787.9
tof         -600.0   rp             65.6
tpwr            57   lp           -160.7
pw           7.350          PLOT
    DECOUPLER        wc              250
dn              H1   sc                0
dof              0   vs             4470
dm             yyy   th                6
dmm              w   ai      cdc      ph
dpwr            32
dmf          12200
```

Appendix K

^{1}H, and ^{13}C NMR Spectra of **DBPq2**

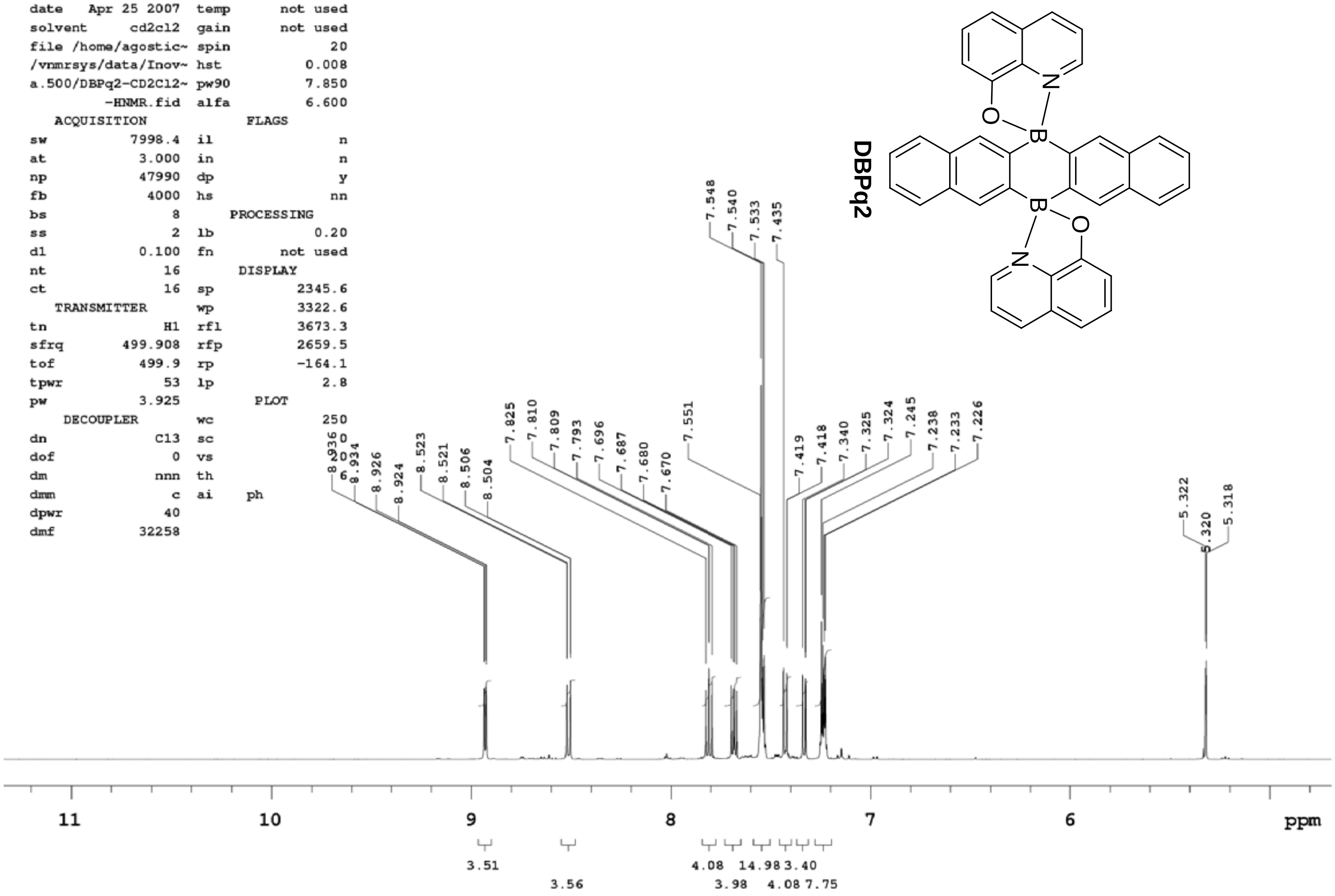


DBPq2

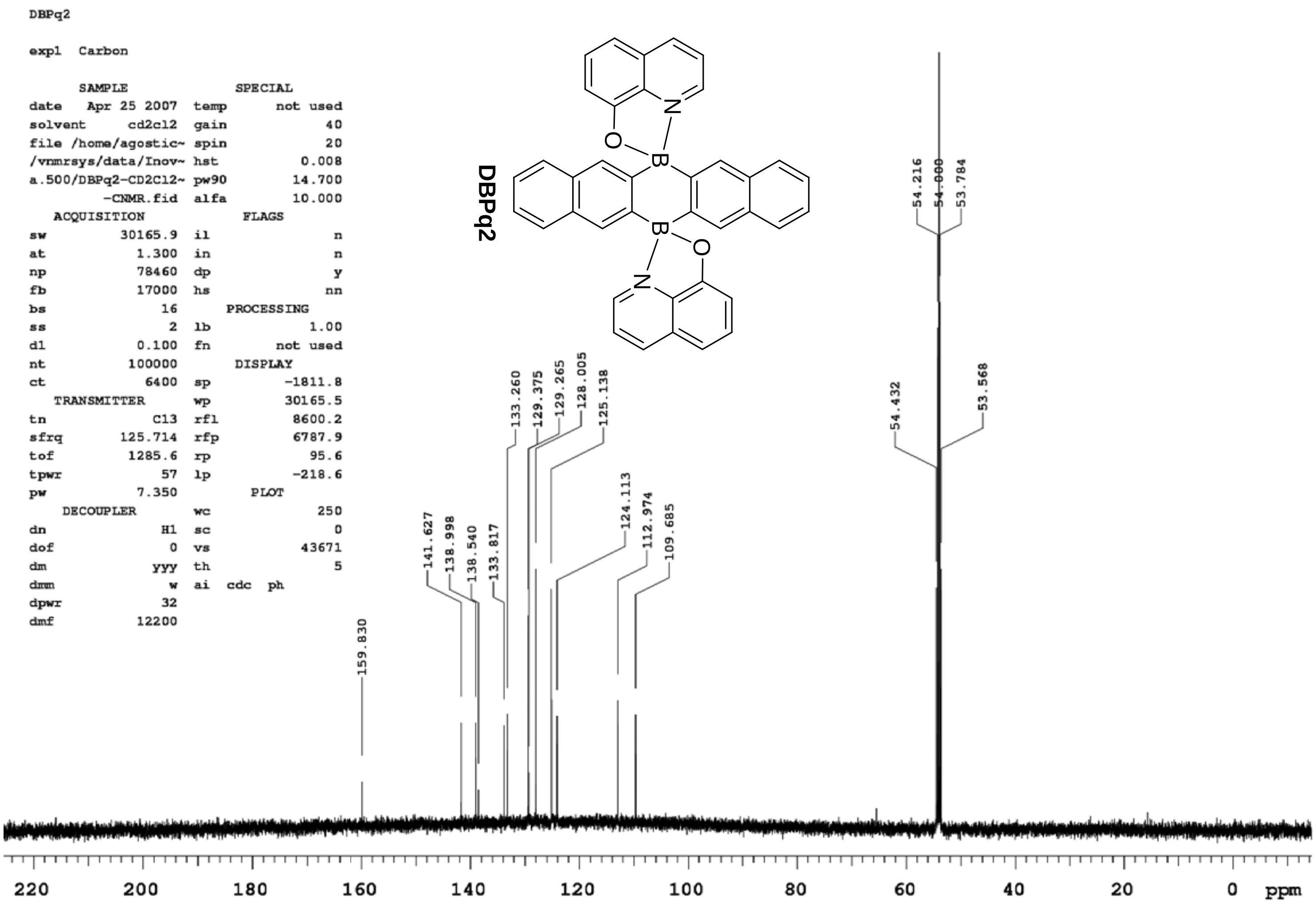
```
DBPq2

exp1  Proton

      SAMPLE             SPECIAL
date   Apr 25 2007  temp       not used
solvent     cd2cl2  gain       not used
file /home/agostic~ spin             20
/vnmrsys/data/Inov~ hst           0.008
a.500/DBPq2-CD2Cl2~ pw90          7.850
         -HNMR.fid  alfa          6.600
   ACQUISITION           FLAGS
sw          7998.4  il                n
at           3.000  in                n
np           47990  dp                y
fb            4000  hs               nn
bs               8       PROCESSING
ss               2  lb             0.20
d1           0.100  fn         not used
nt              16       DISPLAY
ct              16  sp           2345.6
   TRANSMITTER      wp           3322.6
tn              H1  rfl          3673.3
sfrq       499.908  rfp          2659.5
tof          499.9  rp           -164.1
tpwr            53  lp              2.8
pw           3.925         PLOT
    DECOUPLER       wc              250
dn             C13  sc                0
dof              0  vs
dm             nnn  th
dmm              c  ai    ph
dpwr            40
dmf          32258
```



DBPq2



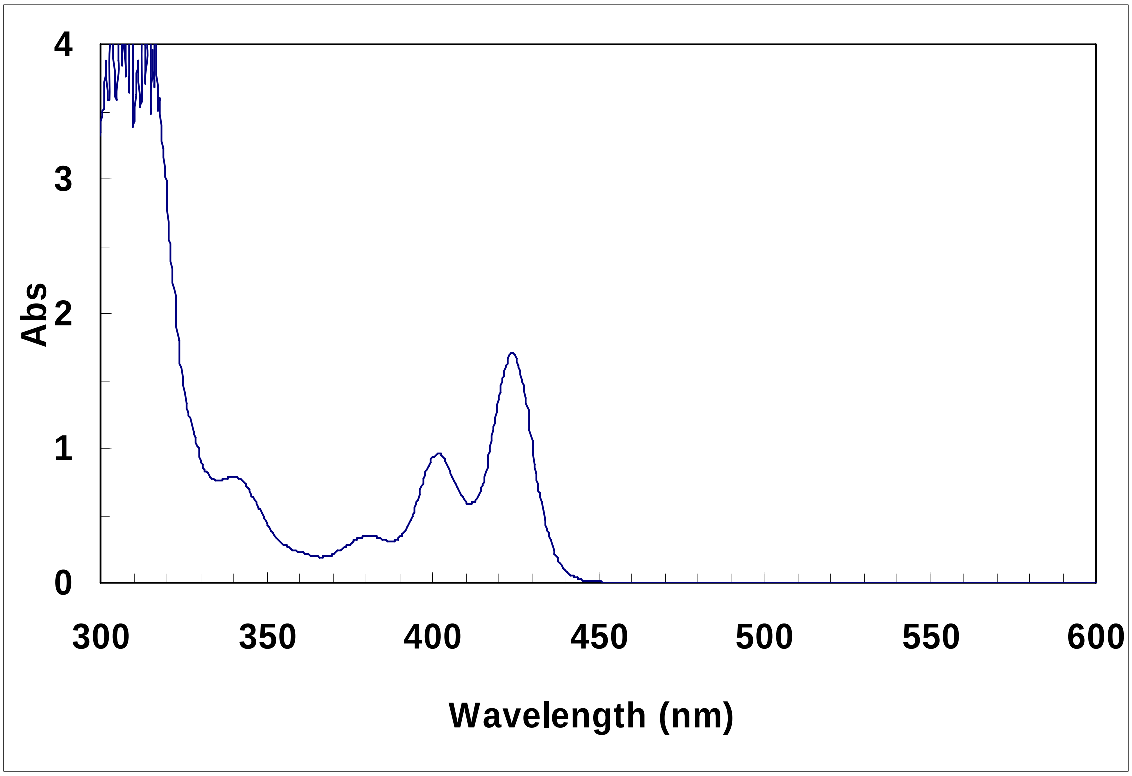
```
DBPq2

exp1  Carbon

      SAMPLE              SPECIAL
date   Apr 25 2007  temp       not used
solvent     cd2cl2  gain             40
file /home/agostic~ spin             20
/vnmrsys/data/Inov~ hst           0.008
a.500/DBPq2-CD2Cl2~ pw90         14.700
        -CNMR.fid   alfa         10.000
   ACQUISITION            FLAGS
sw         30165.9  il                n
at           1.300  in                n
np           78460  dp                y
fb           17000  hs               nn
bs              16       PROCESSING
ss               2  lb             1.00
d1           0.100  fn         not used
nt          100000         DISPLAY
ct            6400  sp          -1811.8
   TRANSMITTER      wp          30165.5
tn             C13  rfl          8600.2
sfrq       125.714  rfp          6787.9
tof         1285.6  rp             95.6
tpwr            57  lp           -218.6
pw           7.350          PLOT
    DECOUPLER       wc              250
dn              H1  sc                0
dof              0  vs            43671
dm             yyy  th                5
dmm              w  ai   cdc  ph
dpwr            32
dmf          12200
```

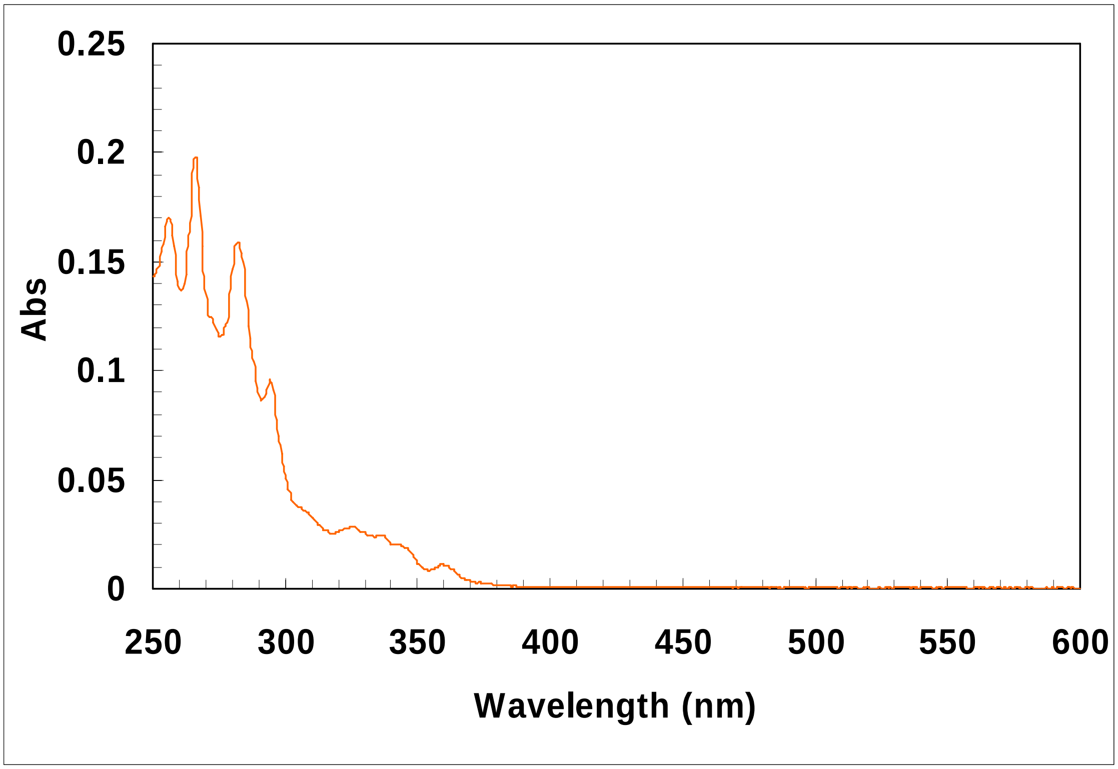
Appendix L

UV-vis Spectrum of **IV-1** in C_6D_6



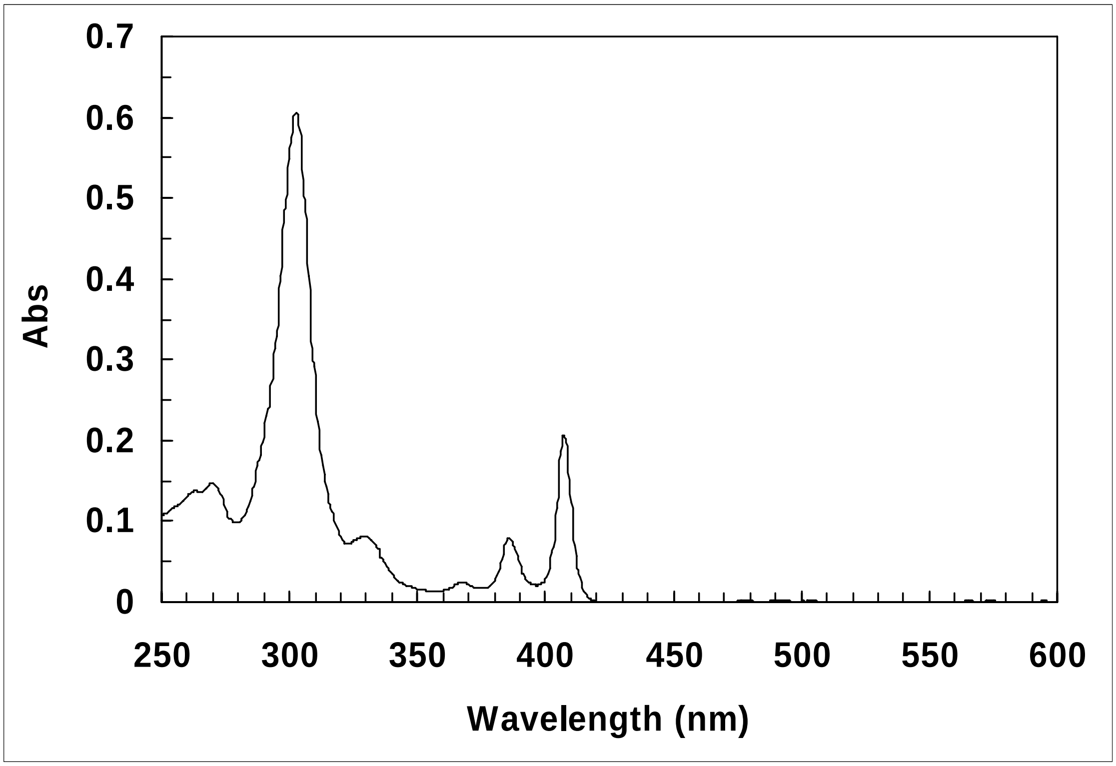
Appendix M

UV-vis Spectrum of **IV-2** in cyclohexane



Appendix N

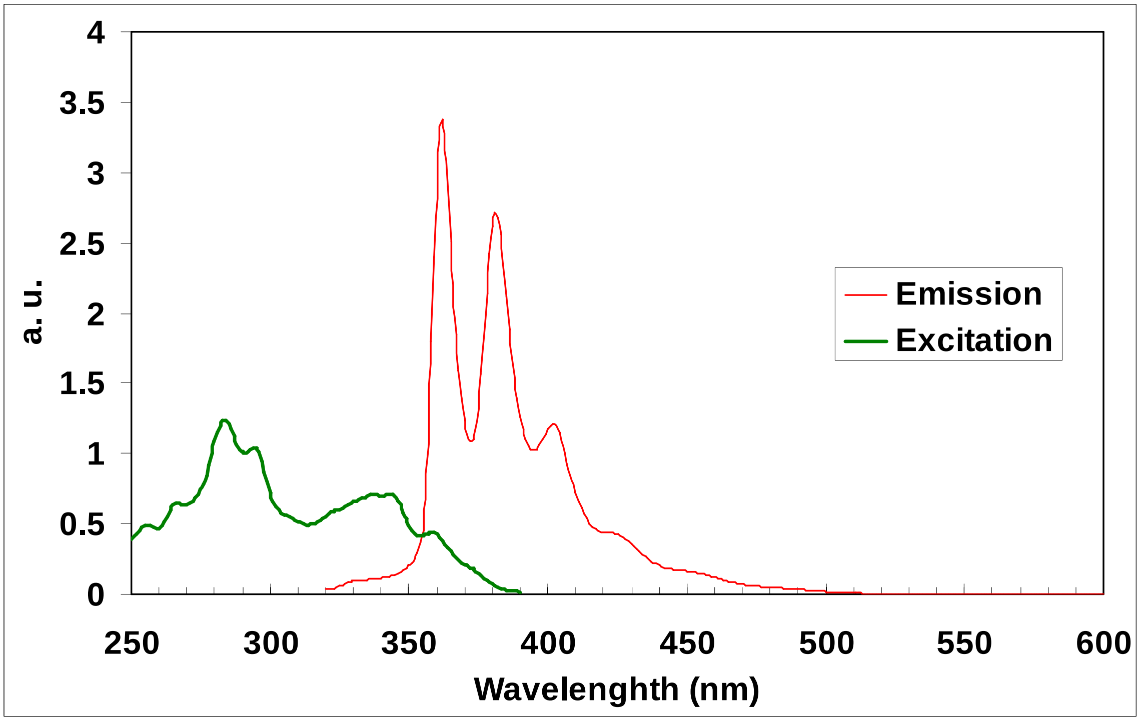
UV-vis Spectrum of **IV-3** in cyclohexane



Appendix O

Excitation and Emission Spectra of **IV-2**

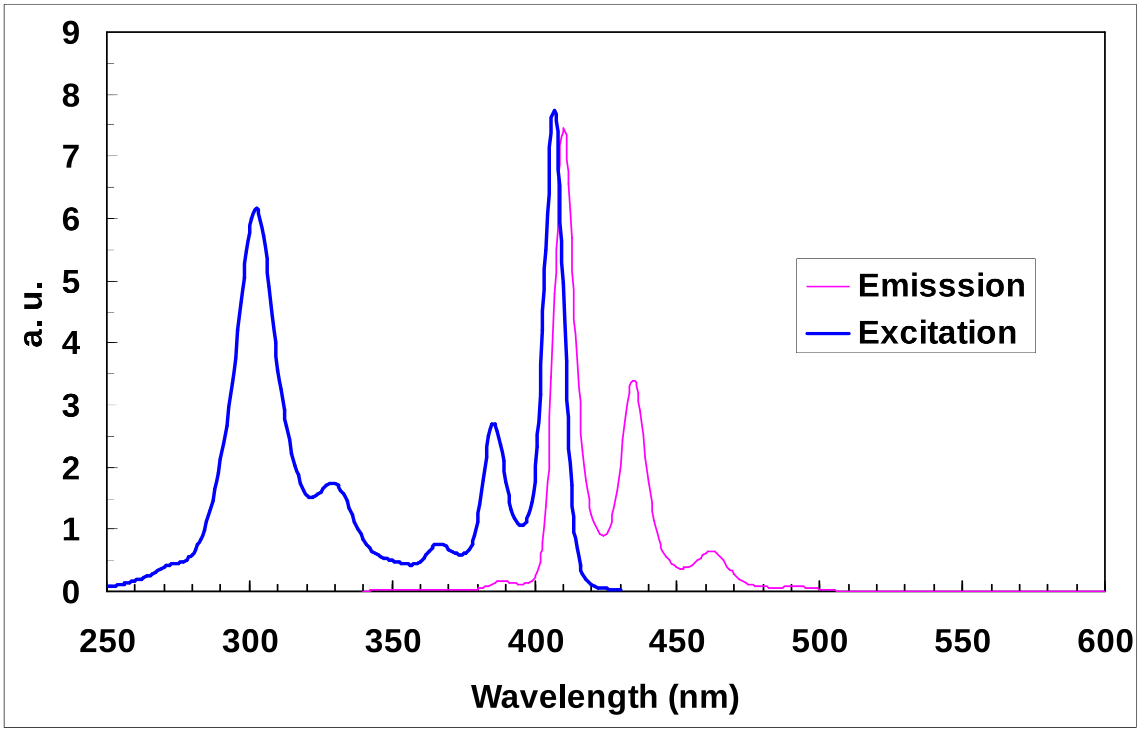
(λ_{Ex} = 300 nm; λ_{Em} = 410 nm)



Appendix P

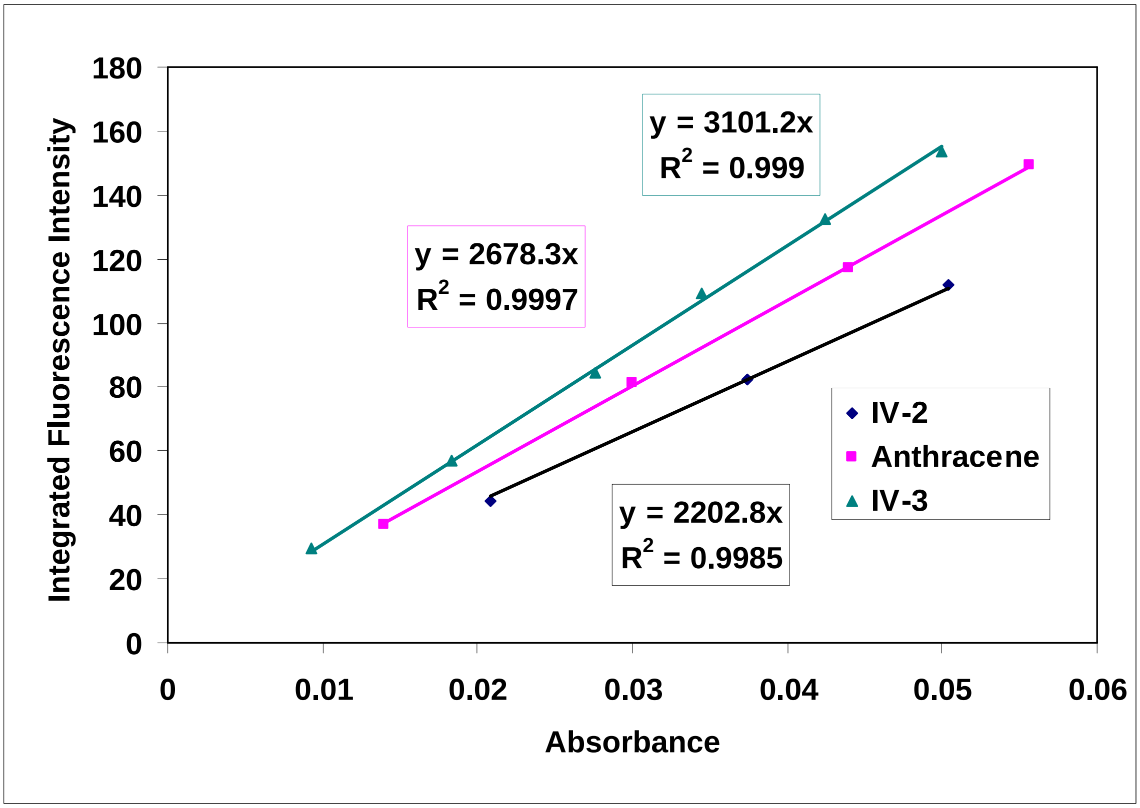
Excitation and Emission Spectra of **IV-3**

(λ_{Ex} = 330 nm; λ_{Em} = 430 nm)



Appendix Q

Quantum Yield of **IV-2** and **IV-3**



$$\boxed{\Phi_X = \Phi_{ST}\left(\frac{\mathrm{Grad}_X}{\mathrm{Grad}_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)}$$

Quantum Yield: Φ = 0.25 **(IV-2)**; Φ = 0.35 **(IV-3)**

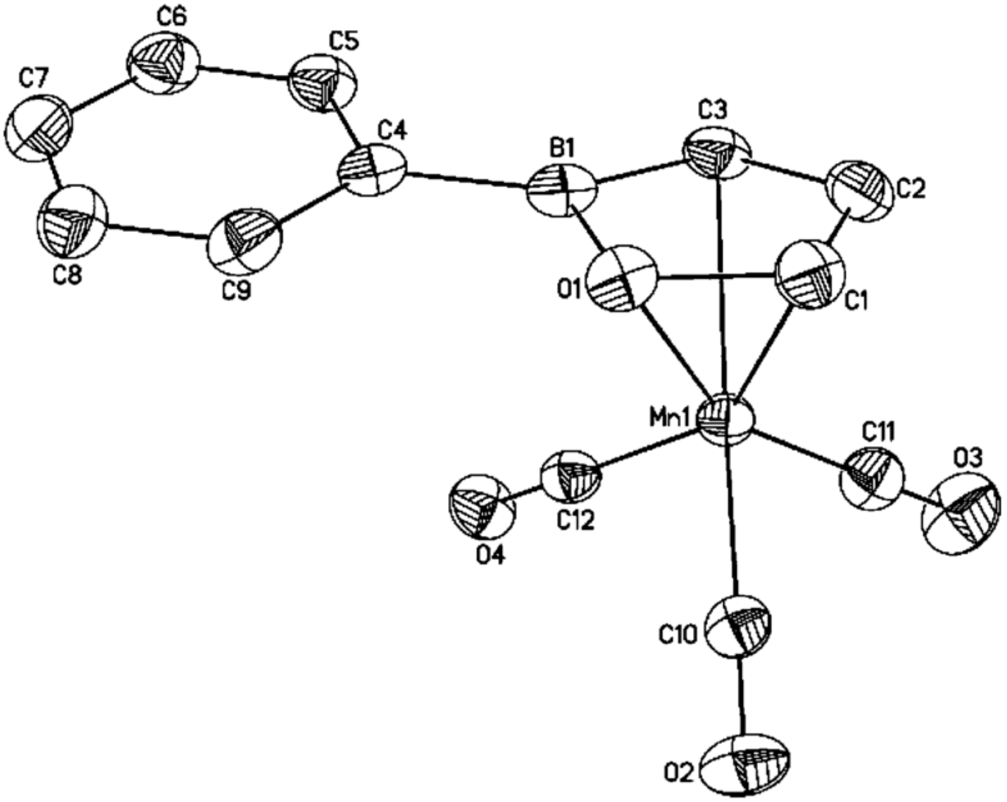
(Reference: Anthracene, Φ = 0.30 in cyclohexane)

Appendix R

Data collection and structure determination of **II-12b**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C6
C5
C7
C4
C3
B1
C2
C8
C9
O1
C1
Mn1
C11
O3
C12
O4
C10
O2

Structure Determination.

Orange plates of cj101 were crystallized from a pentane solution at 25 deg. C. A crystal of dimensions 0.74 x 0.72 x 0.36 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 150(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 3952 frames were collected with a scan width of 0.2° in ω and phi with an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 13720 reflections to a maximum 2θ value of 56.52° of which 2900 were independent and 2765 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 5370 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{12}H_8BO_4Mn$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0225 and wR2 = 0.0634 [based on I > 2sigma(I)], R1 = 0.0236 and wR2 = 0.0641 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.
Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction and Scaling of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.
Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table 1. Crystal data and structure refinement for cj101.

Identification code	cj101
Empirical formula	C12 H8 B Mn O4
Formula weight	281.93
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.4249(7) A alpha = 90 deg. b = 17.0274(14) A beta = 98.110(2) deg. c = 8.2670(7) A gamma = 90 deg.
Volume	1174.07(17) A^3
Z, Calculated density	4, 1.595 Mg/m^3
Absorption coefficient	1.124 mm^-1
F(000)	568
Crystal size	0.74 x 0.72 x 0.36 mm
Theta range for data collection	3.42 to 28.26 deg.
Limiting indices	-11<=h<=11, -22<=k<=22, -11<=l<=11
Reflections collected / unique	13720 / 2900 [R(int) = 0.0203]
Completeness to theta = 28.26	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6877 and 0.4901
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2900 / 0 / 163
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0225, wR2 = 0.0634

R indices (all data)	R1 = 0.0236, wR2 = 0.0641
Largest diff. peak and hole	0.377 and -0.282 e.Aˆ-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj101.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	8139(2)	5038(1)	8255(2)	25(1)
Mn(1)	6384(1)	4006(1)	7702(1)	20(1)
O(1)	6790(1)	5017(1)	9179(1)	26(1)
O(2)	2862(1)	4006(1)	7615(1)	35(1)
O(3)	6377(1)	2319(1)	6995(2)	47(1)
O(4)	6317(1)	4403(1)	4211(1)	34(1)
C(1)	6860(2)	4328(1)	10119(1)	28(1)
C(2)	8172(2)	3880(1)	9821(2)	29(1)
C(3)	8937(1)	4246(1)	8584(2)	27(1)
C(4)	8361(1)	5780(1)	7223(1)	25(1)
C(5)	9717(2)	5874(1)	6435(2)	30(1)
C(6)	9933(2)	6551(1)	5551(2)	35(1)
C(7)	8793(2)	7142(1)	5415(2)	36(1)
C(8)	7429(2)	7060(1)	6167(2)	36(1)
C(9)	7229(2)	6389(1)	7076(2)	31(1)
C(10)	4219(2)	3996(1)	7637(2)	25(1)
C(11)	6381(2)	2980(1)	7254(2)	29(1)
C(12)	6321(1)	4254(1)	5565(2)	24(1)

Table 3. Bond lengths [A] and angles [deg] for cj101.

B(1)-O(1)	1.4564(15)
B(1)-C(3)	1.5140(18)
B(1)-C(4)	1.5516(18)
B(1)-Mn(1)	2.3006(13)
Mn(1)-C(11)	1.7849(13)
Mn(1)-C(12)	1.8099(12)
Mn(1)-C(10)	1.8167(13)
Mn(1)-C(1)	2.0565(12)
Mn(1)-O(1)	2.1113(8)
Mn(1)-C(2)	2.1538(12)
Mn(1)-C(3)	2.2102(12)
O(1)-C(1)	1.4044(15)
O(2)-C(10)	1.1413(17)
O(3)-C(11)	1.1466(17)
O(4)-C(12)	1.1478(15)
C(1)-C(2)	1.3922(18)
C(2)-C(3)	1.4269(18)
C(4)-C(5)	1.4018(17)
C(4)-C(9)	1.4019(18)
C(5)-C(6)	1.3908(18)
C(6)-C(7)	1.385(2)
C(7)-C(8)	1.389(2)
C(8)-C(9)	1.3908(19)

O(1)-B(1)-C(3)	104.14(10)
O(1)-B(1)-C(4)	118.16(11)
C(3)-B(1)-C(4)	137.66(11)
O(1)-B(1)-Mn(1)	63.82(6)
C(3)-B(1)-Mn(1)	67.20(7)
C(4)-B(1)-Mn(1)	129.59(8)
C(11)-Mn(1)-C(12)	91.60(6)
C(11)-Mn(1)-C(10)	90.78(5)
C(12)-Mn(1)-C(10)	94.74(5)
C(11)-Mn(1)-C(1)	117.16(6)
C(12)-Mn(1)-C(1)	149.40(5)
C(10)-Mn(1)-C(1)	95.07(5)
C(11)-Mn(1)-O(1)	155.96(5)
C(12)-Mn(1)-O(1)	110.71(4)
C(10)-Mn(1)-O(1)	95.97(4)
C(1)-Mn(1)-O(1)	39.36(4)
C(11)-Mn(1)-C(2)	92.97(6)
C(12)-Mn(1)-C(2)	137.54(5)
C(10)-Mn(1)-C(2)	127.36(5)
C(1)-Mn(1)-C(2)	38.53(5)
O(1)-Mn(1)-C(2)	64.70(4)

C(11)-Mn(1)-C(3)	102.84(5)
C(12)-Mn(1)-C(3)	99.88(5)
C(10)-Mn(1)-C(3)	159.63(5)
C(1)-Mn(1)-C(3)	65.32(5)
O(1)-Mn(1)-C(3)	65.62(4)
C(2)-Mn(1)-C(3)	38.14(5)
C(11)-Mn(1)-B(1)	140.40(5)
C(12)-Mn(1)-B(1)	86.83(5)
C(10)-Mn(1)-B(1)	128.80(5)
C(1)-Mn(1)-B(1)	64.60(5)
O(1)-Mn(1)-B(1)	38.25(4)
C(2)-Mn(1)-B(1)	63.76(5)
C(3)-Mn(1)-B(1)	39.16(5)
C(1)-O(1)-B(1)	109.57(9)
C(1)-O(1)-Mn(1)	68.22(6)
B(1)-O(1)-Mn(1)	77.93(6)
C(2)-C(1)-O(1)	109.40(10)
C(2)-C(1)-Mn(1)	74.52(7)
O(1)-C(1)-Mn(1)	72.43(6)
C(1)-C(2)-C(3)	109.77(11)
C(1)-C(2)-Mn(1)	66.95(7)
C(3)-C(2)-Mn(1)	73.07(7)
C(2)-C(3)-B(1)	106.43(11)
C(2)-C(3)-Mn(1)	68.79(7)
B(1)-C(3)-Mn(1)	73.65(7)
C(5)-C(4)-C(9)	117.72(12)
C(5)-C(4)-B(1)	121.18(11)
C(9)-C(4)-B(1)	121.09(11)
C(6)-C(5)-C(4)	120.93(12)
C(7)-C(6)-C(5)	120.30(13)
C(6)-C(7)-C(8)	119.90(13)
C(7)-C(8)-C(9)	119.73(13)
C(8)-C(9)-C(4)	121.39(12)
O(2)-C(10)-Mn(1)	178.52(10)
O(3)-C(11)-Mn(1)	178.83(13)
O(4)-C(12)-Mn(1)	178.31(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj101. 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
B(1)	20(1)	31(1)	24(1)	-5(1)	2(1)	-3(1)
Mn(1)	18(1)	22(1)	21(1)	-1(1)	4(1)	1(1)
O(1)	26(1)	28(1)	24(1)	-4(1)	6(1)	-1(1)
O(2)	21(1)	41(1)	45(1)	-8(1)	8(1)	-2(1)
O(3)	50(1)	27(1)	65(1)	-8(1)	15(1)	2(1)
O(4)	35(1)	42(1)	24(1)	2(1)	5(1)	2(1)
C(1)	30(1)	32(1)	21(1)	-1(1)	5(1)	-2(1)
C(2)	24(1)	36(1)	25(1)	3(1)	-1(1)	1(1)
C(3)	18(1)	35(1)	27(1)	0(1)	1(1)	0(1)
C(4)	21(1)	28(1)	25(1)	-5(1)	1(1)	-5(1)
C(5)	23(1)	36(1)	30(1)	1(1)	3(1)	-1(1)
C(6)	28(1)	44(1)	33(1)	4(1)	5(1)	-6(1)
C(7)	40(1)	32(1)	35(1)	2(1)	0(1)	-8(1)
C(8)	36(1)	27(1)	44(1)	-4(1)	2(1)	0(1)
C(9)	27(1)	29(1)	37(1)	-6(1)	6(1)	-2(1)
C(10)	25(1)	24(1)	26(1)	-4(1)	5(1)	-1(1)
C(11)	27(1)	30(1)	32(1)	-1(1)	8(1)	2(1)
C(12)	20(1)	26(1)	28(1)	-2(1)	3(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj101.

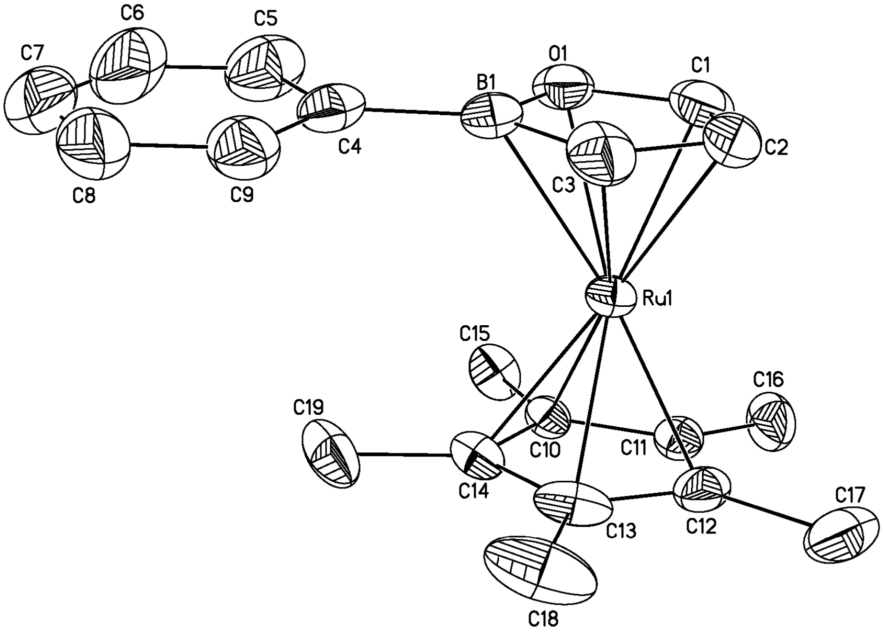
	x	y	z	U(eq)
H(1A)	6160	4209	10969	33
H(2A)	8508	3371	10368	35
H(3A)	9882	4042	8105	32
H(5A)	10499	5469	6506	36
H(6A)	10867	6608	5038	42
H(7A)	8944	7603	4807	43
H(8A)	6636	7460	6060	43
H(9A)	6305	6342	7609	37

Appendix S

Data collection and structure determination of **II-12b**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C6
C5
C7
O1
C1
B1
C2
C4
C3
C8
C9
Ru1
C15
C16
C19
C10
C11
C17
C14
C13
C12
C18

Structure Determination.

Amber needles of **cj102** were crystallized from a hexane/ether solution at -30 deg. C. A crystal of dimensions 0.36 x 0.12 x 0.12 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 150(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 2877 frames were collected with a scan width of 0.2° in ω with an exposure time of 15 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 23160 reflections to a maximum 2θ value of 56.74° of which 22728 were independent and 16562 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 8864 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The crystal was found to be a non-merohedral twin with the two components related by a rotation of 180 degrees about the (1 0 0) direct axis and refined twin volume fraction of 0.4141(3). The data were processed with TWINABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/ with Z = 4 for the formula $C_{19}H_{23}BORu$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The oxaborolyl group is disordered with two possible eta-5 bonding modes resulting in the superposition of carbon and oxygen site at a ratio of 0.798(7) / 0.202(7). Full matrix least-squares refinement based on F^2 converged at R1 = 0.0350 and wR2 = 0.0784 [based on I > 2sigma(I)], R1 = 0.0534 and wR2 = 0.0830 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. TWINABS, v. 1.05. Program for Empirical Absorption Correction and Scaling of Area Detector Data for Twinned Crystals , University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table 1. Crystal data and structure refinement for cj102.

Identification code	cj102
Empirical formula	C19 H23 B O Ru
Formula weight	379.25
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.7654(13) A alpha = 90 deg. b = 14.136(2) A beta = 94.583(4) deg. c = 13.820(2) A gamma = 90 deg.
Volume	1706.9(4) A^3
Z, Calculated density	4, 1.476 Mg/m^3
Absorption coefficient	0.917 mm^-1
F(000)	776
Crystal size	0.36 x 0.12 x 0.12 mm
Theta range for data collection	2.86 to 28.37 deg.
Limiting indices	-11<=h<=11, -18<=k<=18, -18<=l<=18
Reflections collected / unique	23160 / 22728 [R(int) = 0.0000]
Completeness to theta = 28.37	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8980 and 0.7338
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22728 / 0 / 206
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0784

R indices (all data)	R1 = 0.0534, wR2 = 0.0830
Largest diff. peak and hole	0.772 and -0.790 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj102. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ru(1)	6990(1)	2457(1)	3366(1)	24(1)
B(1)	5590(2)	3206(1)	2135(1)	32(1)
O(1)	5410(1)	2205(1)	2057(1)	36(1)
C(3A)	5410(1)	2205(1)	2057(1)	36(1)
C(3)	7232(2)	3379(1)	2078(1)	40(1)
O(1A)	7232(2)	3379(1)	2078(1)	40(1)
C(1)	6867(2)	1789(1)	1965(1)	41(1)
C(2)	7952(2)	2497(1)	1950(1)	38(1)
C(4)	4217(2)	3884(1)	2261(1)	36(1)
C(5)	2713(2)	3536(1)	2268(1)	58(1)
C(6)	1506(3)	4142(2)	2411(2)	80(1)
C(7)	1698(3)	5064(2)	2545(2)	81(1)
C(8)	3172(3)	5444(2)	2539(1)	63(1)
C(9)	4391(2)	4852(1)	2405(1)	45(1)
C(10)	6144(2)	1953(1)	4703(1)	23(1)
C(11)	7616(2)	1545(1)	4613(1)	27(1)
C(12)	8678(2)	2302(1)	4570(1)	32(1)
C(13)	7871(2)	3174(1)	4663(1)	35(1)
C(14)	6290(2)	2964(1)	4742(1)	28(1)
C(15)	4699(2)	1406(1)	4782(1)	35(1)
C(16)	7980(2)	510(1)	4631(1)	41(1)
C(17)	10387(2)	2202(1)	4507(1)	52(1)
C(18)	8557(2)	4150(1)	4710(1)	61(1)
C(19)	5017(2)	3655(1)	4879(1)	44(1)

Table 3. Bond lengths [A] and angles [deg] for cj102.

Ru(1)-C(12)	2.1479(15)
Ru(1)-C(13)	2.1485(15)
Ru(1)-C(1)	2.1491(16)
Ru(1)-C(10)	2.1662(14)
Ru(1)-C(14)	2.1665(15)
Ru(1)-C(11)	2.1862(14)
Ru(1)-C(2)	2.1933(15)
Ru(1)-O(1)	2.2173(11)
Ru(1)-C(3)	2.2304(14)
Ru(1)-B(1)	2.2782(18)
B(1)-O(1)	1.427(2)
B(1)-C(3)	1.468(2)
B(1)-C(4)	1.559(2)
O(1)-C(1)	1.422(2)
C(3)-C(2)	1.4159(19)
C(1)-C(2)	1.382(2)
C(4)-C(9)	1.389(2)
C(4)-C(5)	1.409(2)
C(5)-C(6)	1.387(3)
C(6)-C(7)	1.326(3)
C(7)-C(8)	1.399(3)
C(8)-C(9)	1.380(2)
C(10)-C(11)	1.428(2)
C(10)-C(14)	1.4362(19)
C(10)-C(15)	1.496(2)
C(11)-C(12)	1.4224(19)
C(11)-C(16)	1.4973(19)
C(12)-C(13)	1.432(2)
C(12)-C(17)	1.514(2)
C(13)-C(14)	1.430(2)
C(13)-C(18)	1.5045(19)
C(14)-C(19)	1.506(2)
C(12)-Ru(1)-C(13)	38.94(6)
C(12)-Ru(1)-C(1)	129.42(6)
C(13)-Ru(1)-C(1)	161.41(7)
C(12)-Ru(1)-C(10)	64.35(6)
C(13)-Ru(1)-C(10)	64.42(6)
C(1)-Ru(1)-C(10)	128.89(6)
C(12)-Ru(1)-C(14)	65.14(6)
C(13)-Ru(1)-C(14)	38.71(6)
C(1)-Ru(1)-C(14)	159.85(7)
C(10)-Ru(1)-C(14)	38.72(5)
C(12)-Ru(1)-C(11)	38.30(5)
C(13)-Ru(1)-C(11)	64.51(6)

C(1)-Ru(1)-C(11)	116.24(6)
C(10)-Ru(1)-C(11)	38.30(5)
C(14)-Ru(1)-C(11)	64.80(5)
C(12)-Ru(1)-C(2)	113.82(6)
C(13)-Ru(1)-C(2)	126.47(6)
C(1)-Ru(1)-C(2)	37.11(6)
C(10)-Ru(1)-C(2)	162.21(6)
C(14)-Ru(1)-C(2)	158.60(6)
C(11)-Ru(1)-C(2)	128.92(6)
C(12)-Ru(1)-O(1)	164.25(5)
C(13)-Ru(1)-O(1)	156.31(6)
C(1)-Ru(1)-O(1)	37.96(5)
C(10)-Ru(1)-O(1)	114.13(5)
C(14)-Ru(1)-O(1)	124.51(5)
C(11)-Ru(1)-O(1)	130.49(5)
C(2)-Ru(1)-O(1)	62.35(5)
C(12)-Ru(1)-C(3)	125.06(6)
C(13)-Ru(1)-C(3)	109.84(6)
C(1)-Ru(1)-C(3)	62.56(6)
C(10)-Ru(1)-C(3)	159.09(6)
C(14)-Ru(1)-C(3)	123.97(6)
C(11)-Ru(1)-C(3)	160.01(6)
C(2)-Ru(1)-C(3)	37.32(5)
O(1)-Ru(1)-C(3)	62.35(5)
C(12)-Ru(1)-B(1)	157.33(6)
C(13)-Ru(1)-B(1)	122.69(7)
C(1)-Ru(1)-B(1)	63.01(7)
C(10)-Ru(1)-B(1)	126.13(7)
C(14)-Ru(1)-B(1)	109.16(6)
C(11)-Ru(1)-B(1)	161.65(7)
C(2)-Ru(1)-B(1)	62.87(6)
O(1)-Ru(1)-B(1)	36.99(6)
C(3)-Ru(1)-B(1)	37.99(6)
O(1)-B(1)-C(3)	105.35(15)
O(1)-B(1)-C(4)	122.41(16)
C(3)-B(1)-C(4)	132.23(16)
O(1)-B(1)-Ru(1)	69.19(9)
C(3)-B(1)-Ru(1)	69.24(9)
C(4)-B(1)-Ru(1)	125.21(12)
C(1)-O(1)-B(1)	108.80(14)
C(1)-O(1)-Ru(1)	68.42(8)
B(1)-O(1)-Ru(1)	73.82(9)
C(2)-C(3)-B(1)	107.99(14)
C(2)-C(3)-Ru(1)	69.92(8)
B(1)-C(3)-Ru(1)	72.77(9)
C(2)-C(1)-O(1)	109.03(13)
C(2)-C(1)-Ru(1)	73.18(9)
O(1)-C(1)-Ru(1)	73.62(8)
C(1)-C(2)-C(3)	108.76(15)

C(1)-C(2)-Ru(1)	69.71(9)
C(3)-C(2)-Ru(1)	72.76(8)
C(9)-C(4)-C(5)	115.83(18)
C(9)-C(4)-B(1)	123.01(16)
C(5)-C(4)-B(1)	121.13(16)
C(6)-C(5)-C(4)	120.6(2)
C(7)-C(6)-C(5)	122.5(2)
C(6)-C(7)-C(8)	118.9(3)
C(9)-C(8)-C(7)	119.6(2)
C(8)-C(9)-C(4)	122.58(19)
C(11)-C(10)-C(14)	109.05(15)
C(11)-C(10)-C(15)	125.08(13)
C(14)-C(10)-C(15)	125.83(15)
C(11)-C(10)-Ru(1)	71.61(9)
C(14)-C(10)-Ru(1)	70.65(9)
C(15)-C(10)-Ru(1)	125.59(11)
C(12)-C(11)-C(10)	107.42(12)
C(12)-C(11)-C(16)	126.62(14)
C(10)-C(11)-C(16)	125.83(14)
C(12)-C(11)-Ru(1)	69.39(8)
C(10)-C(11)-Ru(1)	70.09(8)
C(16)-C(11)-Ru(1)	128.97(10)
C(11)-C(12)-C(13)	108.29(13)
C(11)-C(12)-C(17)	125.86(14)
C(13)-C(12)-C(17)	125.72(14)
C(11)-C(12)-Ru(1)	72.30(9)
C(13)-C(12)-Ru(1)	70.55(8)
C(17)-C(12)-Ru(1)	126.03(11)
C(14)-C(13)-C(12)	108.49(13)
C(14)-C(13)-C(18)	125.00(17)
C(12)-C(13)-C(18)	126.47(16)
C(14)-C(13)-Ru(1)	71.33(9)
C(12)-C(13)-Ru(1)	70.51(8)
C(18)-C(13)-Ru(1)	125.74(11)
C(13)-C(14)-C(10)	106.71(14)
C(13)-C(14)-C(19)	127.39(15)
C(10)-C(14)-C(19)	125.86(16)
C(13)-C(14)-Ru(1)	69.97(9)
C(10)-C(14)-Ru(1)	70.63(9)
C(19)-C(14)-Ru(1)	126.15(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj102.
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
Ru(1)	26(1)	26(1)	18(1)	0(1)	2(1)	-2(1)
B(1)	38(1)	38(1)	20(1)	4(1)	-2(1)	3(1)
O(1)	35(1)	49(1)	25(1)	-5(1)	-3(1)	-2(1)
C(3A)	35(1)	49(1)	25(1)	-5(1)	-3(1)	-2(1)
C(3)	50(1)	43(1)	28(1)	10(1)	12(1)	2(1)
O(1A)	50(1)	43(1)	28(1)	10(1)	12(1)	2(1)
C(1)	58(1)	41(1)	24(1)	-6(1)	-1(1)	8(1)
C(2)	38(1)	52(1)	23(1)	3(1)	6(1)	9(1)
C(4)	34(1)	48(1)	24(1)	6(1)	-2(1)	-4(1)
C(5)	42(1)	80(1)	50(1)	7(1)	0(1)	-8(1)
C(6)	35(1)	141(2)	62(2)	6(2)	6(1)	26(2)
C(7)	86(2)	117(2)	40(1)	5(1)	0(1)	52(2)
C(8)	90(2)	62(1)	38(1)	3(1)	6(1)	27(2)
C(9)	59(1)	43(1)	34(1)	3(1)	1(1)	4(1)
C(10)	27(1)	25(1)	19(1)	0(1)	5(1)	-1(1)
C(11)	29(1)	32(1)	20(1)	2(1)	3(1)	0(1)
C(12)	27(1)	49(1)	20(1)	1(1)	0(1)	-2(1)
C(13)	51(1)	34(1)	20(1)	-2(1)	2(1)	-21(1)
C(14)	38(1)	23(1)	23(1)	-2(1)	5(1)	-2(1)
C(15)	38(1)	30(1)	38(1)	-2(1)	13(1)	-5(1)
C(16)	47(1)	39(1)	37(1)	5(1)	7(1)	16(1)
C(17)	31(1)	95(2)	30(1)	4(1)	-2(1)	-12(1)
C(18)	95(2)	51(1)	39(1)	-11(1)	14(1)	-45(1)
C(19)	69(1)	28(1)	37(1)	0(1)	17(1)	11(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj102.

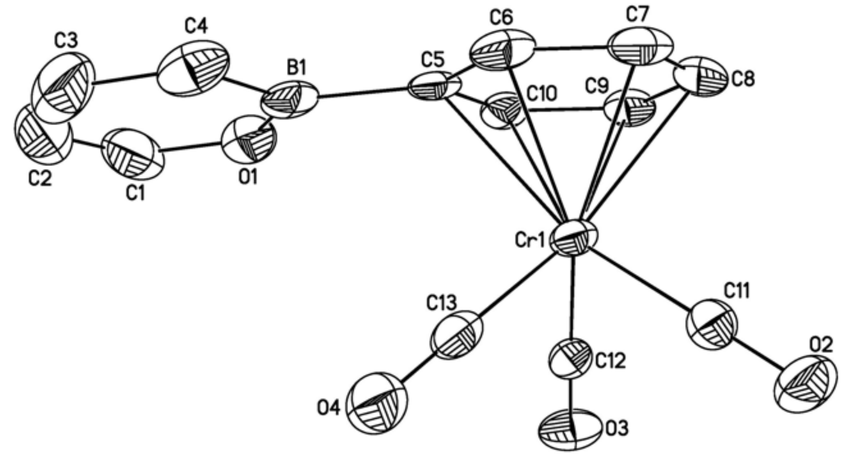
	x	y	z	U(eq)
H(3A)	4490	1879	2066	44
H(3)	7714	3966	2119	47
H(1)	7060	1144	1922	49
H(2)	8986	2408	1868	45
H(5A)	2527	2893	2177	69
H(6A)	525	3891	2412	95
H(7A)	868	5453	2642	98
H(8A)	3330	6090	2624	76
H(9A)	5366	5112	2412	55
H(15A)	4727	838	4403	52
H(15B)	3839	1784	4545	52
H(15C)	4602	1244	5449	52
H(16A)	8928	406	4344	61
H(16B)	7175	171	4270	61
H(16C)	8071	291	5290	61
H(17A)	10875	2088	5143	78
H(17B)	10785	2774	4248	78
H(17C)	10585	1681	4089	78
H(18A)	7778	4608	4524	92
H(18B)	9355	4188	4274	92
H(18C)	8974	4278	5360	92
H(19A)	4999	3802	5556	66
H(19B)	4056	3380	4645	66
H(19C)	5185	4224	4523	66

Appendix T

Data collection and structure determination of **III-9**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C3
C4
B1
C5
C6
C7
C8
C10
C9
C2
C1
O1
Cr1
C13
C11
C12
O2
O4
O3

Structure Determination.

Yelow needles of cj103 were crystallized from a diethyl ether solution at -30 deg. C. A crystal of dimensions 0.34 x 0.08 x 0.04 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 150(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 4017 frames were collected with a scan width of 0.2° in ω with an exposure time of 30 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 15689 reflections to a maximum 2θ value of 49.78° of which 2887 were independent and 1828 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 2000 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The crystal was found to be a non-merohedral twin with the two components related by a rotation of 180 degrees about the (1 0 0) direct axis and refined twin volume fraction of 0.142(2). The data were processed with TWINABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{13}H_9BO_4Cr$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0606 and wR2 = 0.1292 [based on I > 2sigma(I)], R1 = 0.1122 and wR2 = 0.1408 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. TWINABS, v. 1.05. Program for Empirical Absorption Correction and Scaling of Area Detector Data for Twinned Crystals , University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table 1. Crystal data and structure refinement for cj103.

Identification code	cj103
Empirical formula	C13 H9 B Cr O4
Formula weight	292.01
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.6721(17) A alpha = 90 deg. b = 7.1133(10) A beta = 107.503(8) deg. c = 15.635(2) A gamma = 90 deg.
Volume	1238.0(3) A^3
Z, Calculated density	4, 1.567 Mg/m^3
Absorption coefficient	0.928 mm^-1
F(000)	592
Crystal size	0.34 x 0.08 x 0.04 mm
Theta range for data collection	3.17 to 24.89 deg.
Limiting indices	-13<=h<=13, -8<=k<=8, -18<=l<=18
Reflections collected / unique	2824 / 2887 [R(int) = 0.0979]
Completeness to theta = 24.89	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9638 and 0.7432
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2887 / 0 / 173
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1292

R indices (all data)	R1 = 0.1122, wR2 = 0.1408
Largest diff. peak and hole	0.480 and -0.505 e.Aˆ-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj103.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	3063(5)	5223(8)	2986(4)	30(2)
Cr(1)	2139(1)	1603(1)	4034(1)	23(1)
O(1)	4267(3)	5026(5)	3054(2)	43(1)
O(2)	471(3)	-1416(5)	4265(3)	42(1)
O(3)	4030(3)	-1369(5)	4293(2)	37(1)
O(4)	1434(3)	715(5)	2073(3)	44(1)
C(1)	4689(6)	5579(8)	2373(5)	54(2)
C(2)	3995(7)	6319(9)	1633(5)	62(2)
C(3)	2736(7)	6615(9)	1491(4)	65(2)
C(4)	2249(5)	6081(7)	2164(4)	41(2)
C(5)	2672(4)	4523(6)	3806(3)	25(1)
C(6)	1445(4)	4515(7)	3785(4)	32(1)
C(7)	1090(5)	3771(7)	4485(4)	35(1)
C(8)	1943(5)	3027(7)	5244(4)	36(1)
C(9)	3159(5)	3028(7)	5297(3)	30(1)
C(10)	3517(4)	3790(6)	4584(3)	26(1)
C(11)	1106(4)	-243(7)	4172(3)	28(1)
C(12)	3298(4)	-199(7)	4187(3)	25(1)
C(13)	1701(5)	1076(6)	2836(4)	30(1)

Table 3. Bond lengths [A] and angles [deg] for cj103.

B(1)-O(1)	1.384(6)
B(1)-C(4)	1.481(8)
B(1)-C(5)	1.567(7)
Cr(1)-C(12)	1.826(5)
Cr(1)-C(13)	1.826(6)
Cr(1)-C(11)	1.839(5)
Cr(1)-C(7)	2.211(5)
Cr(1)-C(6)	2.216(5)
Cr(1)-C(10)	2.217(5)
Cr(1)-C(8)	2.217(5)
Cr(1)-C(9)	2.220(5)
Cr(1)-C(5)	2.228(5)
O(1)-C(1)	1.359(7)
O(2)-C(11)	1.154(5)
O(3)-C(12)	1.169(5)
O(4)-C(13)	1.168(6)
C(1)-C(2)	1.308(9)
C(2)-C(3)	1.433(9)
C(3)-C(4)	1.391(8)
C(5)-C(10)	1.415(6)
C(5)-C(6)	1.422(6)
C(6)-C(7)	1.386(7)
C(7)-C(8)	1.403(7)
C(8)-C(9)	1.397(6)
C(9)-C(10)	1.411(6)
O(1)-B(1)-C(4)	118.7(5)
O(1)-B(1)-C(5)	116.4(5)
C(4)-B(1)-C(5)	124.9(5)
C(12)-Cr(1)-C(13)	87.6(2)
C(12)-Cr(1)-C(11)	88.3(2)
C(13)-Cr(1)-C(11)	89.0(2)
C(12)-Cr(1)-C(7)	155.1(2)
C(13)-Cr(1)-C(7)	117.3(2)
C(11)-Cr(1)-C(7)	90.88(19)
C(12)-Cr(1)-C(6)	153.69(19)
C(13)-Cr(1)-C(6)	92.1(2)
C(11)-Cr(1)-C(6)	118.0(2)
C(7)-Cr(1)-C(6)	36.49(18)
C(12)-Cr(1)-C(10)	91.12(19)
C(13)-Cr(1)-C(10)	119.2(2)
C(11)-Cr(1)-C(10)	151.7(2)
C(7)-Cr(1)-C(10)	78.08(18)
C(6)-Cr(1)-C(10)	66.19(19)
C(12)-Cr(1)-C(8)	118.1(2)
C(13)-Cr(1)-C(8)	154.1(2)

C(11)-Cr(1)-C(8)	89.2(2)
C(7)-Cr(1)-C(8)	36.94(19)
C(6)-Cr(1)-C(8)	66.2(2)
C(10)-Cr(1)-C(8)	66.28(18)
C(12)-Cr(1)-C(9)	91.5(2)
C(13)-Cr(1)-C(9)	156.3(2)
C(11)-Cr(1)-C(9)	114.6(2)
C(7)-Cr(1)-C(9)	66.33(19)
C(6)-Cr(1)-C(9)	78.4(2)
C(10)-Cr(1)-C(9)	37.09(17)
C(8)-Cr(1)-C(9)	36.70(17)
C(12)-Cr(1)-C(5)	116.37(19)
C(13)-Cr(1)-C(5)	91.88(19)
C(11)-Cr(1)-C(5)	155.37(19)
C(7)-Cr(1)-C(5)	66.94(18)
C(6)-Cr(1)-C(5)	37.32(16)
C(10)-Cr(1)-C(5)	37.13(17)
C(8)-Cr(1)-C(5)	79.38(18)
C(9)-Cr(1)-C(5)	67.40(18)
C(1)-O(1)-B(1)	120.7(5)
C(2)-C(1)-O(1)	122.4(6)
C(1)-C(2)-C(3)	122.0(6)
C(4)-C(3)-C(2)	118.4(6)
C(3)-C(4)-B(1)	117.8(5)
C(10)-C(5)-C(6)	117.1(5)
C(10)-C(5)-B(1)	121.4(4)
C(6)-C(5)-B(1)	121.4(5)
C(10)-C(5)-Cr(1)	71.0(3)
C(6)-C(5)-Cr(1)	70.9(3)
B(1)-C(5)-Cr(1)	126.3(3)
C(7)-C(6)-C(5)	121.4(5)
C(7)-C(6)-Cr(1)	71.6(3)
C(5)-C(6)-Cr(1)	71.8(3)
C(6)-C(7)-C(8)	120.5(5)
C(6)-C(7)-Cr(1)	71.9(3)
C(8)-C(7)-Cr(1)	71.7(3)
C(9)-C(8)-C(7)	120.0(5)
C(9)-C(8)-Cr(1)	71.8(3)
C(7)-C(8)-Cr(1)	71.3(3)
C(8)-C(9)-C(10)	119.4(5)
C(8)-C(9)-Cr(1)	71.5(3)
C(10)-C(9)-Cr(1)	71.3(3)
C(9)-C(10)-C(5)	121.6(5)
C(9)-C(10)-Cr(1)	71.6(3)
C(5)-C(10)-Cr(1)	71.8(3)
O(2)-C(11)-Cr(1)	179.1(5)
O(3)-C(12)-Cr(1)	179.0(4)
O(4)-C(13)-Cr(1)	178.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj103.
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
B(1)	33(4)	15(3)	41(4)	-10(3)	11(3)	-9(3)
Cr(1)	24(1)	15(1)	30(1)	-3(1)	9(1)	-2(1)
O(1)	55(3)	31(2)	51(3)	-3(2)	25(2)	-3(2)
O(2)	41(2)	30(2)	61(3)	-5(2)	23(2)	-11(2)
O(3)	32(2)	25(2)	52(2)	-7(2)	7(2)	6(2)
O(4)	60(3)	36(2)	31(2)	1(2)	7(2)	-5(2)
C(1)	68(5)	45(4)	62(5)	-22(4)	42(4)	-18(4)
C(2)	101(6)	46(4)	53(5)	-14(4)	43(5)	-32(4)
C(3)	107(6)	39(4)	32(4)	2(3)	-3(4)	-15(4)
C(4)	36(3)	28(3)	51(4)	-2(3)	1(3)	-2(3)
C(5)	30(3)	12(2)	35(3)	-8(2)	11(3)	0(2)
C(6)	29(3)	18(3)	47(4)	-8(3)	9(3)	-3(2)
C(7)	30(3)	20(3)	59(4)	-13(3)	21(3)	-2(2)
C(8)	53(4)	24(3)	36(3)	-14(3)	22(3)	-6(3)
C(9)	38(3)	21(3)	32(3)	-10(2)	11(3)	-5(2)
C(10)	29(3)	18(3)	35(3)	-8(2)	13(2)	-8(2)
C(11)	27(3)	27(3)	32(3)	-1(2)	12(3)	1(3)
C(12)	26(3)	22(3)	29(3)	-6(2)	11(2)	-11(2)
C(13)	35(3)	19(3)	36(4)	3(2)	12(3)	-2(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj103.

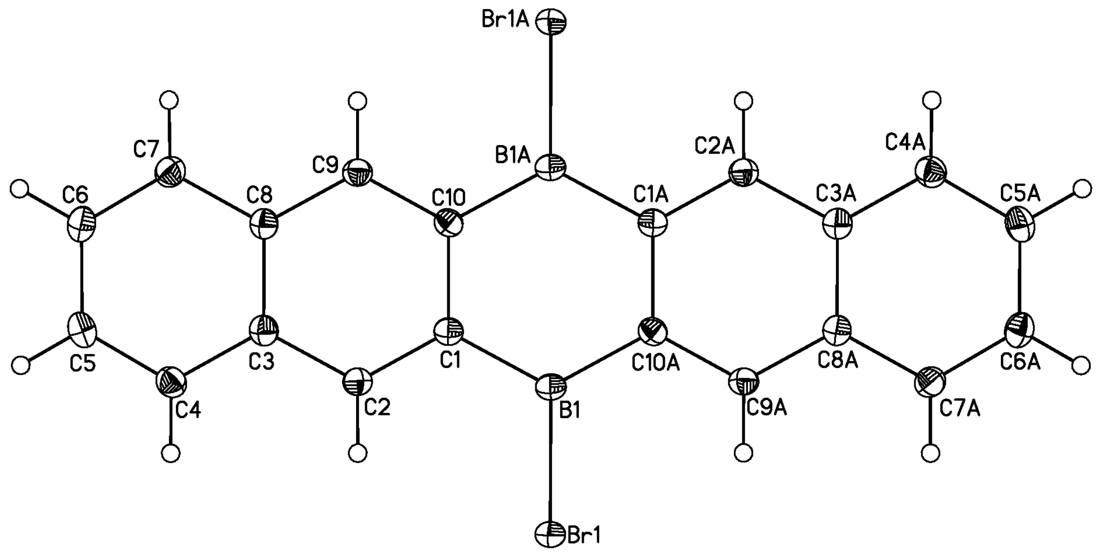
	x	y	z	U(eq)
H(1A)	5519	5423	2437	64
H(2A)	4334	6672	1175	75
H(3A)	2247	7162	950	78
H(4A)	1420	6261	2098	49
H(6A)	816	4802	3206	38
H(7A)	217	3552	4399	42
H(8A)	1667	2290	5690	43
H(9A)	3747	2299	5781	36
H(10A)	4357	3559	4571	32

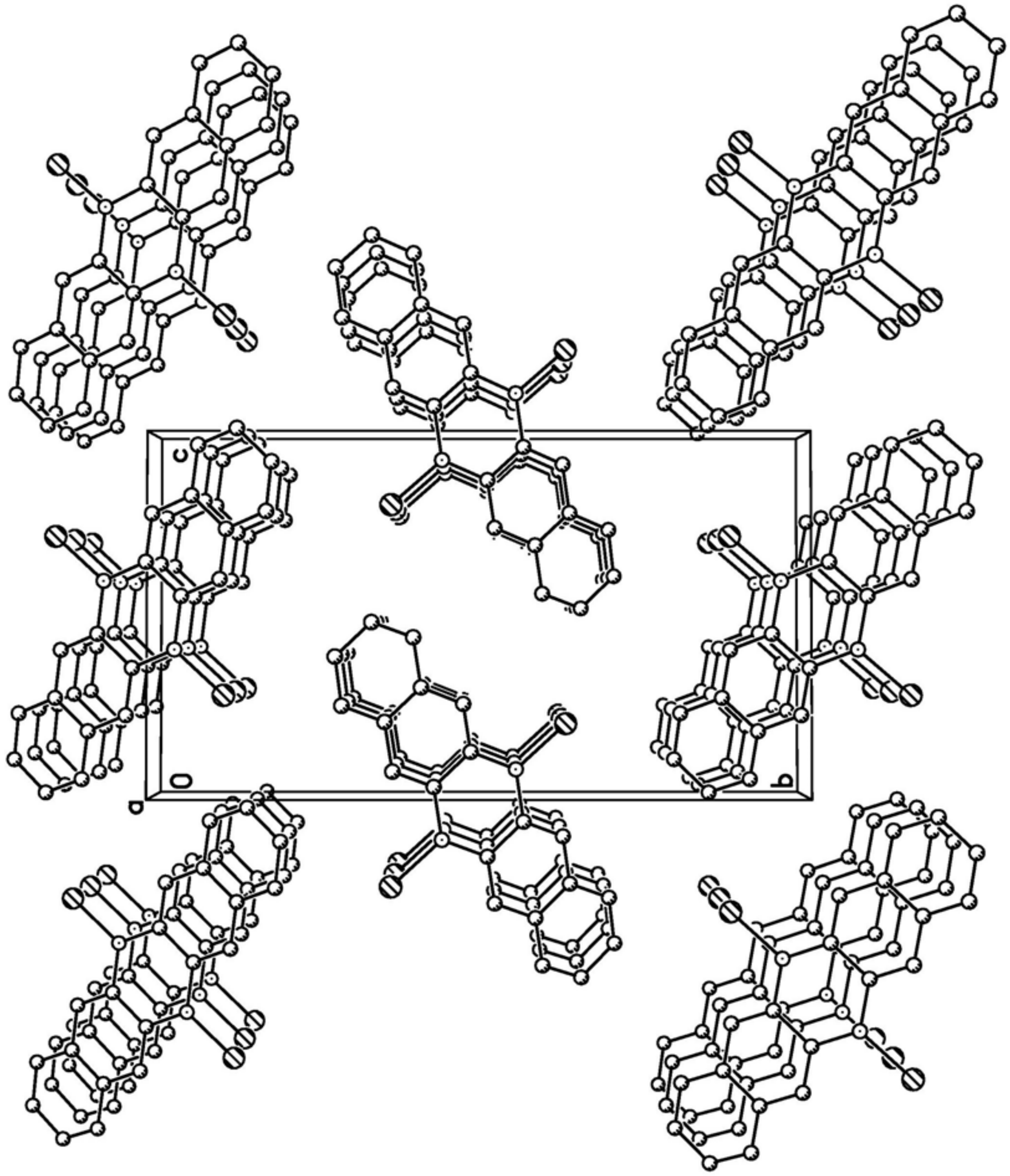
Appendix U

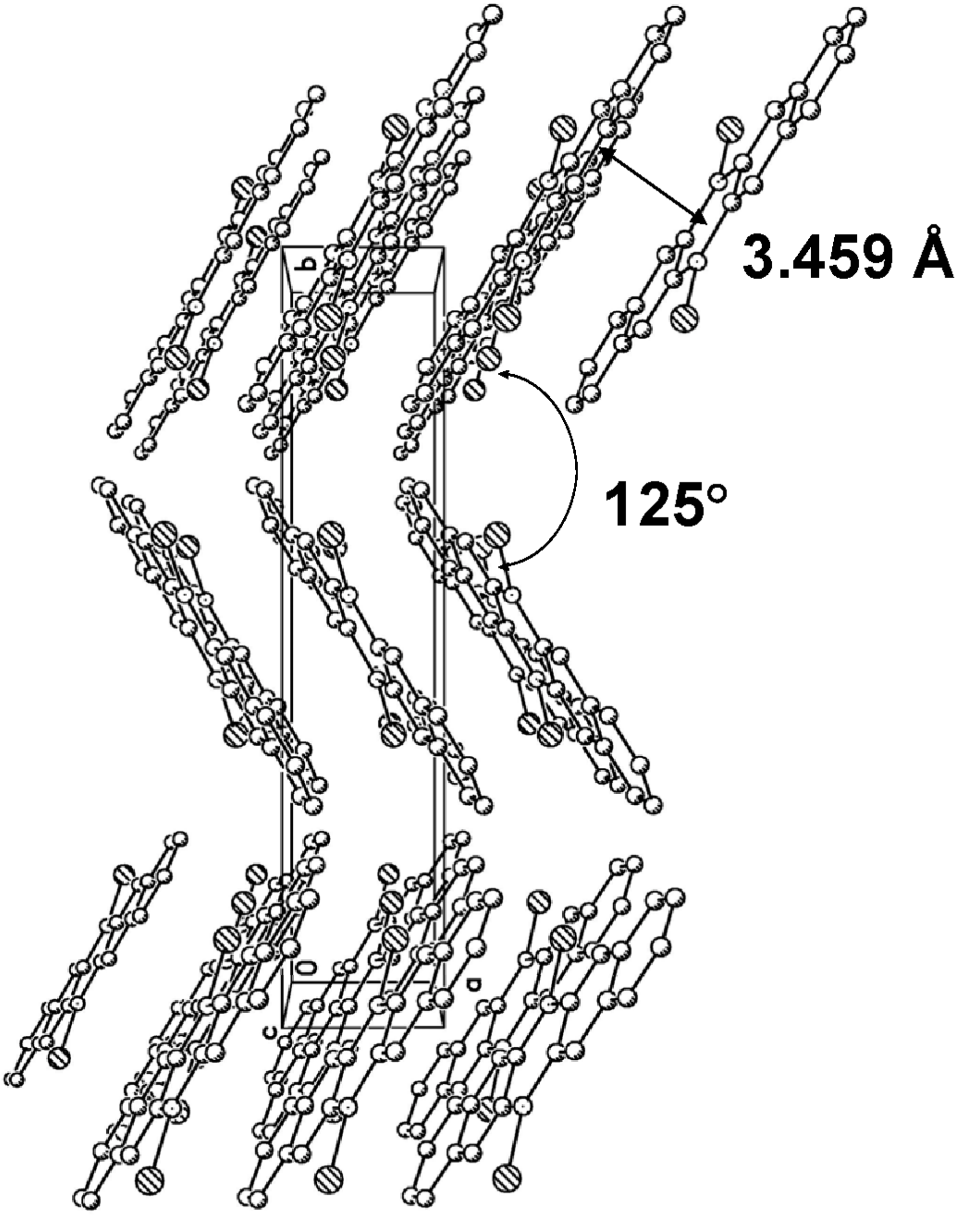
Data collection and structure determination of **IV-1**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


Br1A
C7
C9
B1A
C2A
C4A
C6
C8
C10
C1A
C3A
C5A
C5
C3
C1
C10A
C8A
C6A
C4
C2
B1
C9A
C7A
Br1


c
0
a
b


3.459 Å
125°
b
0
c
a

Structure Determination.

Slow cooling of a toluene solution from 120 deg. C to room temperature grew yellow needles of cj240. A crystal of dimensions 0.60 x 0.16 x 0.14 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 2456 frames were collected with a scan width of 0.5° in ω and phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 15304 reflections to a maximum 2θ value of 56.80° of which 1979 were independent and 1813 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9239 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 2 for the formula $C_{20}H_{12}B_2Br_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0182 and wR2 = 0.0461 [based on I > 2sigma(I)], R1 = 0.0209 and wR2 = 0.0472 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.
Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.
Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table 1. Crystal data and structure refinement for cj240.

Identification code	cj240
Empirical formula	C20 H12 B2 Br2
Formula weight	433.74
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 3.9318(15) A alpha = 90 deg. b = 19.055(7) A beta = 92.275(5) deg. c = 10.609(4) A gamma = 90 deg.
Volume	794.2(5) A^3
Z, Calculated density	2, 1.814 Mg/m^3
Absorption coefficient	5.100 mm^-1
F(000)	424
Crystal size	0.60 x 0.16 x 0.14 mm
Theta range for data collection	2.20 to 28.40 deg.
Limiting indices	-5<=h<=5, -25<=k<=25, -14<=l<=14
Reflections collected / unique	15304 / 1979 [R(int) = 0.0334]
Completeness to theta = 28.40	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5354 and 0.1498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1979 / 0 / 109
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0182, wR2 = 0.0461

R indices (all data)	R1 = 0.0209, wR2 = 0.0472
Largest diff. peak and hole	0.402 and -0.245 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj240.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	4123(4)	5542(1)	908(2)	14(1)
Br(1)	3072(1)	6282(1)	2103(1)	17(1)
C(1)	3120(4)	5659(1)	-502(2)	14(1)
C(2)	1400(4)	6250(1)	-937(2)	15(1)
C(3)	515(4)	6358(1)	-2236(2)	15(1)
C(4)	-1283(4)	6959(1)	-2673(2)	18(1)
C(5)	-2077(4)	7046(1)	-3938(2)	19(1)
C(6)	-1084(4)	6537(1)	-4820(2)	19(1)
C(7)	661(4)	5948(1)	-4423(2)	18(1)
C(8)	1482(4)	5838(1)	-3120(2)	15(1)
C(9)	3219(4)	5230(1)	-2670(2)	15(1)
C(10)	4029(4)	5123(1)	-1404(2)	14(1)

Table 3. Bond lengths [A] and angles [deg] for cj240.

B(1)-C(10)#1	1.543(2)
B(1)-C(1)	1.549(2)
B(1)-Br(1)	1.9504(18)
C(1)-C(2)	1.383(2)
C(1)-C(10)	1.454(2)
C(2)-C(3)	1.423(2)
C(3)-C(4)	1.415(2)
C(3)-C(8)	1.426(2)
C(4)-C(5)	1.375(2)
C(5)-C(6)	1.413(2)
C(6)-C(7)	1.374(2)
C(7)-C(8)	1.422(2)
C(8)-C(9)	1.418(2)
C(9)-C(10)	1.383(2)
C(10)-B(1)#1	1.543(2)
C(10)#1-B(1)-C(1)	123.04(14)
C(10)#1-B(1)-Br(1)	118.77(12)
C(1)-B(1)-Br(1)	118.18(12)
C(2)-C(1)-C(10)	118.87(14)
C(2)-C(1)-B(1)	122.72(14)
C(10)-C(1)-B(1)	118.41(13)
C(1)-C(2)-C(3)	122.53(14)
C(4)-C(3)-C(2)	122.32(15)
C(4)-C(3)-C(8)	119.27(15)
C(2)-C(3)-C(8)	118.41(14)
C(5)-C(4)-C(3)	120.56(15)
C(4)-C(5)-C(6)	120.36(15)
C(7)-C(6)-C(5)	120.38(15)
C(6)-C(7)-C(8)	120.60(15)
C(9)-C(8)-C(7)	122.33(15)
C(9)-C(8)-C(3)	118.86(14)
C(7)-C(8)-C(3)	118.81(14)
C(10)-C(9)-C(8)	122.54(14)
C(9)-C(10)-C(1)	118.77(14)
C(9)-C(10)-B(1)#1	122.69(14)
C(1)-C(10)-B(1)#1	118.54(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj240.
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
B(1)	14(1)	14(1)	15(1)	-2(1)	2(1)	-1(1)
Br(1)	21(1)	16(1)	15(1)	-3(1)	0(1)	4(1)
C(1)	14(1)	14(1)	15(1)	-1(1)	1(1)	-1(1)
C(2)	17(1)	15(1)	15(1)	-1(1)	1(1)	0(1)
C(3)	15(1)	14(1)	17(1)	1(1)	1(1)	-2(1)
C(4)	19(1)	15(1)	19(1)	0(1)	0(1)	0(1)
C(5)	19(1)	16(1)	22(1)	4(1)	-1(1)	1(1)
C(6)	21(1)	20(1)	16(1)	3(1)	-2(1)	-2(1)
C(7)	20(1)	17(1)	16(1)	0(1)	0(1)	-1(1)
C(8)	14(1)	14(1)	16(1)	1(1)	0(1)	-2(1)
C(9)	16(1)	14(1)	15(1)	-1(1)	1(1)	0(1)
C(10)	14(1)	13(1)	16(1)	0(1)	1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj240.

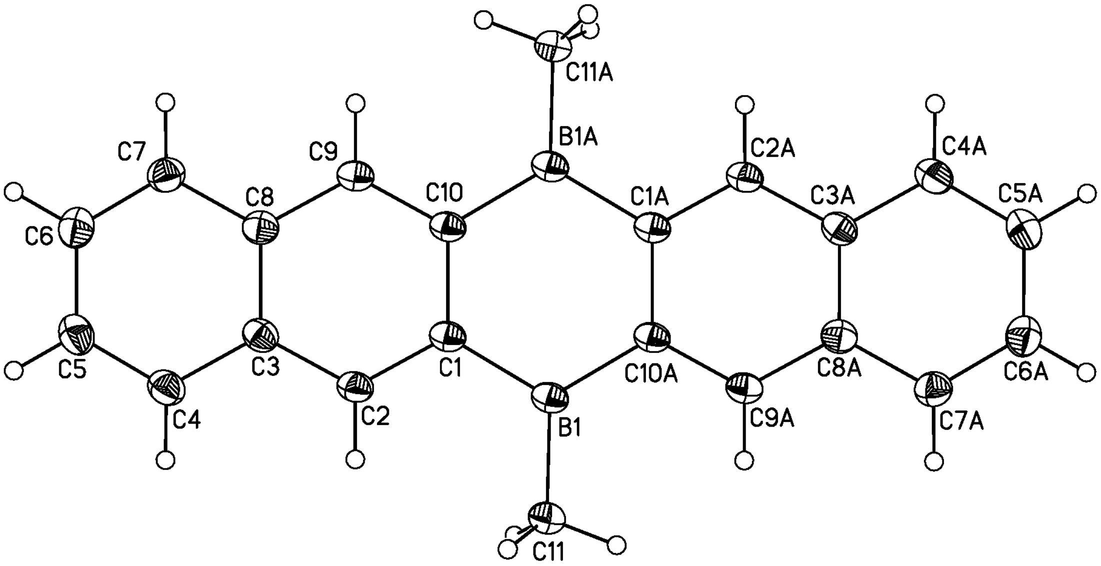
	x	y	z	U(eq)
H(2A)	787	6597	-345	18
H(4A)	-1948	7306	-2089	21
H(5A)	-3299	7450	-4220	23
H(6A)	-1626	6603	-5692	23
H(7A)	1326	5610	-5024	21
H(9A)	3852	4884	-3260	18

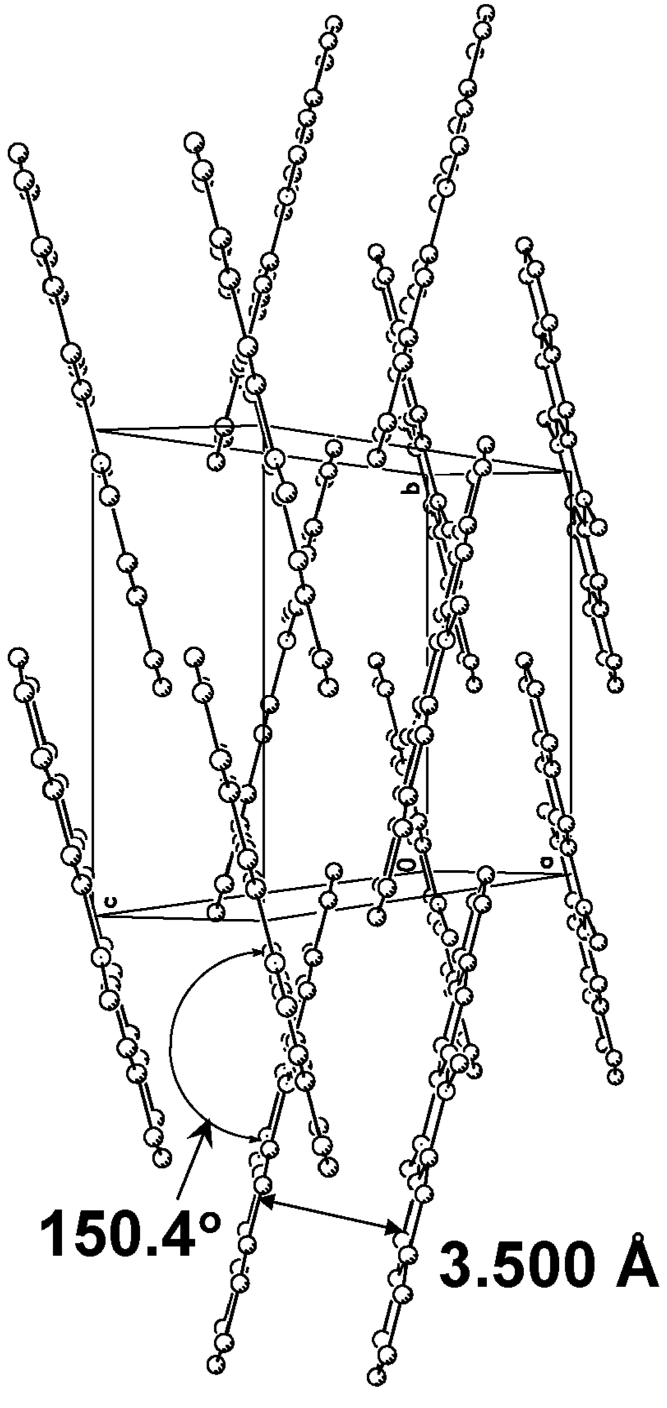
Appendix V

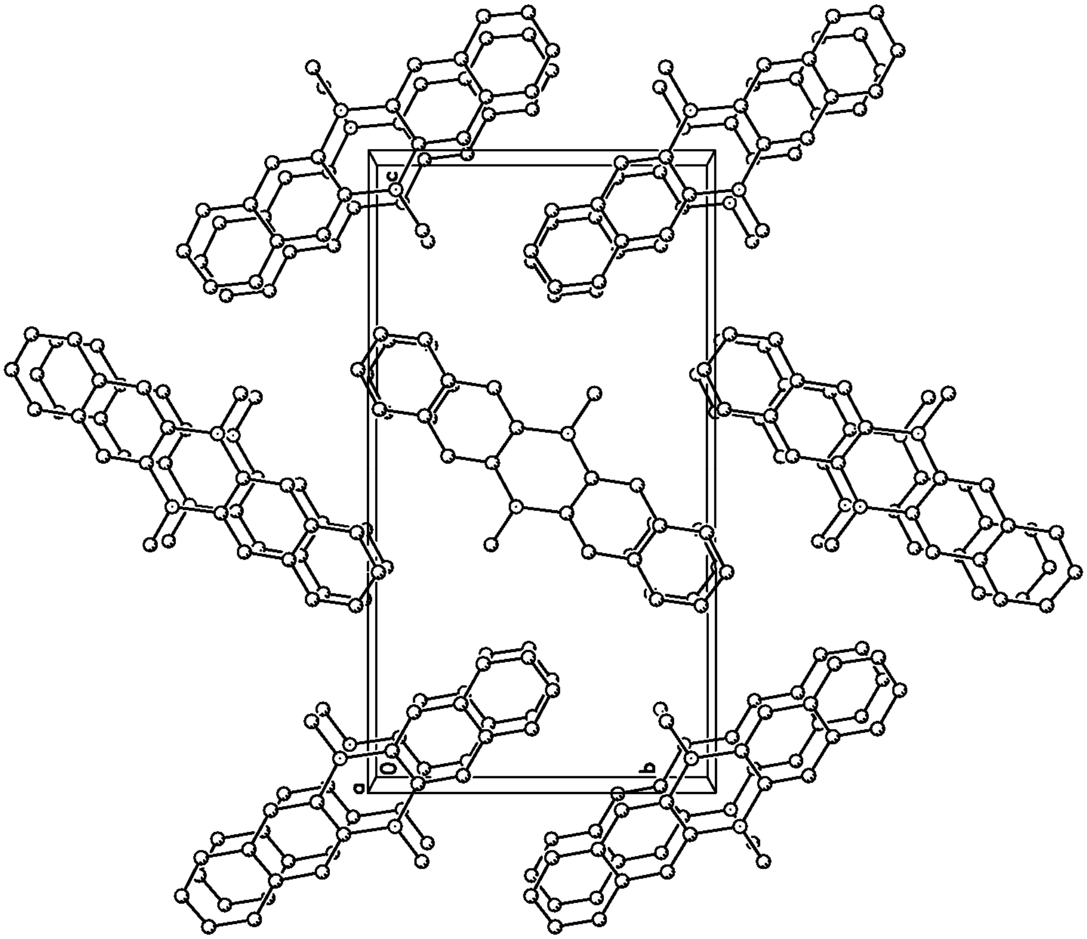
Data collection and structure determination of **IV-2**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C11A
B1A
C7
C9
C10
C1A
C2A
C3A
C4A
C5A
C8
C6
C5
C3
C2
C1
B1
C10A
C9A
C8A
C7A
C6A
C4
C11


b
0
a
c
150.4°
3.500 Å


c
0
a
b

Structure Determination.

Slow cooling of a toluene solution from 120 deg. C to room temperature grew yellow needles of cj282. A crystal of dimensions 0.50 x 0.20 x 0.20 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 108(2) K; the detector was placed at a distance 4.912 cm from the crystal. A total of 2690 frames were collected with a scan width of 0.5° in ω and phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 16010 reflections to a maximum 2θ value of 56.68° of which 1953 were independent and 1509 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 5141 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 2 for the formula $C_{22}H_{18}B_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The molecule lies on an inversion center in the crystal lattice. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0426 and wR2 = 0.01252 [based on I > 2sigma(I)], R1 = 0.0593 and wR2 = 0.1356 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.
Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.
Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Table 1. Crystal data and structure refinement for cj282.

Identification code	cj282
Empirical formula	C22 H18 B2
Formula weight	303.98
Temperature	108(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 3.9678(12) A alpha = 90 deg. b = 10.318(3) A beta = 91.268(4) deg. c = 19.103(6) A gamma = 90 deg.
Volume	781.8(4) A^3
Z, Calculated density	2, 1.291 Mg/m^3
Absorption coefficient	0.071 mm^-1
F(000)	320
Crystal size	0.50 x 0.20 x 0.20 mm
Theta range for data collection	2.13 to 28.34 deg.
Limiting indices	-5<=h<=5, -13<=k<=13, -25<=l<=25
Reflections collected / unique	16010 / 1953 [R(int) = 0.0403]
Completeness to theta = 28.34	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9859 and 0.9654
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1953 / 0 / 110
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.1252

R indices (all data)	R1 = 0.0593, wR2 = 0.1356
Largest diff. peak and hole	0.390 and -0.192 e.Aˆ-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj282.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	1880(3)	-745(1)	573(1)	20(1)
C(1)	989(3)	720(1)	670(1)	20(1)
C(2)	1875(3)	1360(1)	1282(1)	21(1)
C(3)	1130(3)	2683(1)	1397(1)	21(1)
C(4)	2046(3)	3332(1)	2026(1)	24(1)
C(5)	1282(3)	4615(1)	2115(1)	26(1)
C(6)	-418(3)	5310(1)	1580(1)	26(1)
C(7)	-1328(3)	4711(1)	964(1)	24(1)
C(8)	-576(3)	3384(1)	857(1)	21(1)
C(9)	-1495(3)	2725(1)	230(1)	21(1)
C(10)	-781(3)	1430(1)	122(1)	20(1)
C(11)	3837(3)	-1487(1)	1179(1)	24(1)

Table 3. Bond lengths [A] and angles [deg] for cj282.

B(1)-C(10)#1	1.5577(16)
B(1)-C(1)	1.5642(18)
B(1)-C(11)	1.5782(16)
C(1)-C(2)	1.3817(15)
C(1)-C(10)	1.4461(15)
C(2)-C(3)	1.4151(16)
C(3)-C(4)	1.4160(15)
C(3)-C(8)	1.4197(15)
C(4)-C(5)	1.3702(17)
C(5)-C(6)	1.4077(17)
C(6)-C(7)	1.3705(17)
C(7)-C(8)	1.4169(16)
C(8)-C(9)	1.4174(16)
C(9)-C(10)	1.3826(16)
C(10)-B(1)#1	1.5577(16)
C(10)#1-B(1)-C(1)	118.65(9)
C(10)#1-B(1)-C(11)	121.95(10)
C(1)-B(1)-C(11)	119.39(10)
C(2)-C(1)-C(10)	118.68(10)
C(2)-C(1)-B(1)	120.56(10)
C(10)-C(1)-B(1)	120.76(9)
C(1)-C(2)-C(3)	122.88(10)
C(2)-C(3)-C(4)	122.48(10)
C(2)-C(3)-C(8)	118.45(10)
C(4)-C(3)-C(8)	119.06(11)
C(5)-C(4)-C(3)	120.52(10)
C(4)-C(5)-C(6)	120.42(11)
C(7)-C(6)-C(5)	120.47(11)
C(6)-C(7)-C(8)	120.44(11)
C(7)-C(8)-C(9)	122.29(10)
C(7)-C(8)-C(3)	119.09(10)
C(9)-C(8)-C(3)	118.62(10)
C(10)-C(9)-C(8)	122.68(10)
C(9)-C(10)-C(1)	118.68(10)
C(9)-C(10)-B(1)#1	120.73(10)
C(1)-C(10)-B(1)#1	120.58(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj282.
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
B(1)	20(1)	23(1)	17(1)	4(1)	0(1)	-1(1)
C(1)	19(1)	22(1)	17(1)	3(1)	0(1)	-1(1)
C(2)	22(1)	23(1)	17(1)	4(1)	-2(1)	-1(1)
C(3)	21(1)	24(1)	17(1)	2(1)	1(1)	-2(1)
C(4)	27(1)	27(1)	19(1)	1(1)	-2(1)	-2(1)
C(5)	30(1)	28(1)	21(1)	-4(1)	1(1)	-3(1)
C(6)	29(1)	23(1)	27(1)	-2(1)	2(1)	0(1)
C(7)	26(1)	23(1)	23(1)	3(1)	1(1)	1(1)
C(8)	21(1)	22(1)	19(1)	2(1)	2(1)	-1(1)
C(9)	22(1)	23(1)	17(1)	4(1)	0(1)	0(1)
C(10)	20(1)	22(1)	16(1)	4(1)	0(1)	-1(1)
C(11)	30(1)	24(1)	20(1)	2(1)	-5(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj282.

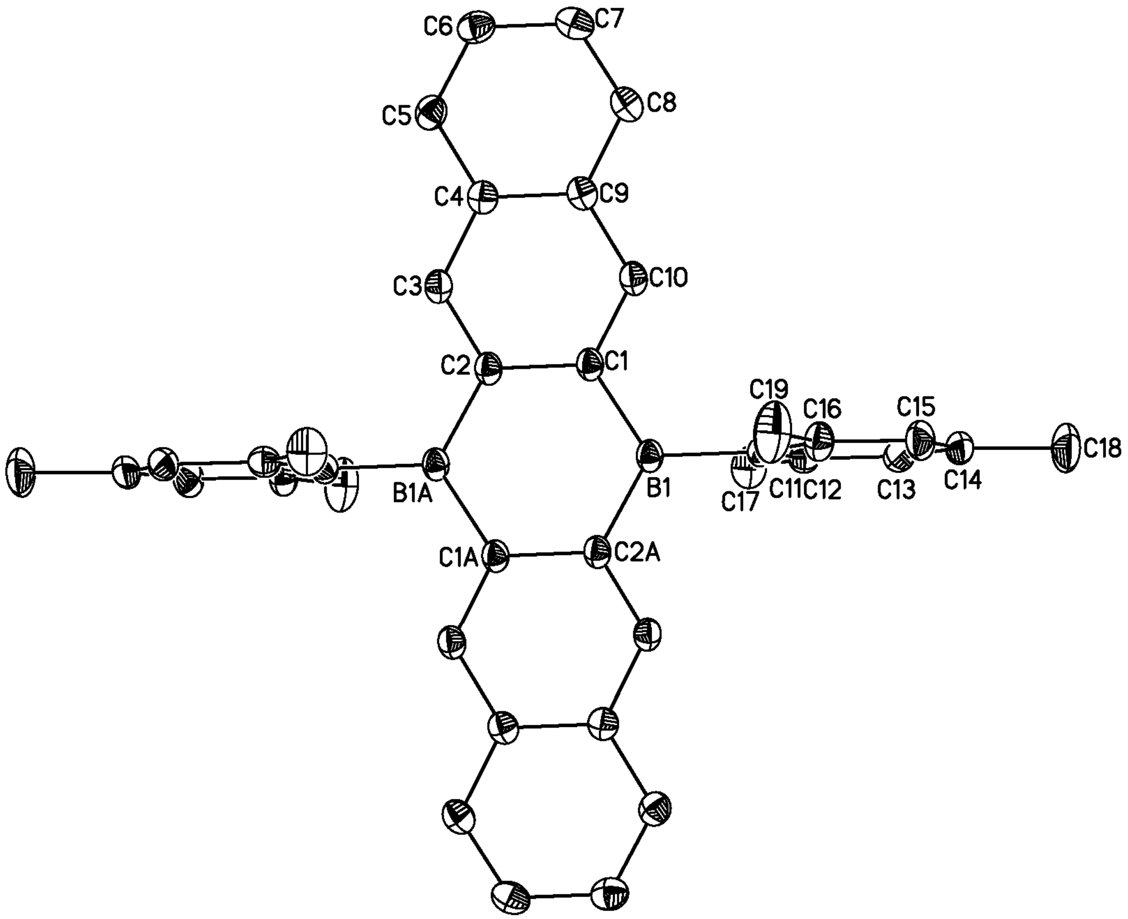
	x	y	z	U(eq)
H(2)	3034	892	1641	25
H(4)	3201	2873	2390	29
H(5)	1903	5040	2540	32
H(6)	-938	6199	1647	32
H(7)	-2470	5190	606	29
H(9)	-2648	3193	-130	25
H(11A)	4274	-2381	1032	37
H(11B)	2469	-1494	1600	37
H(11C)	5981	-1048	1282	37

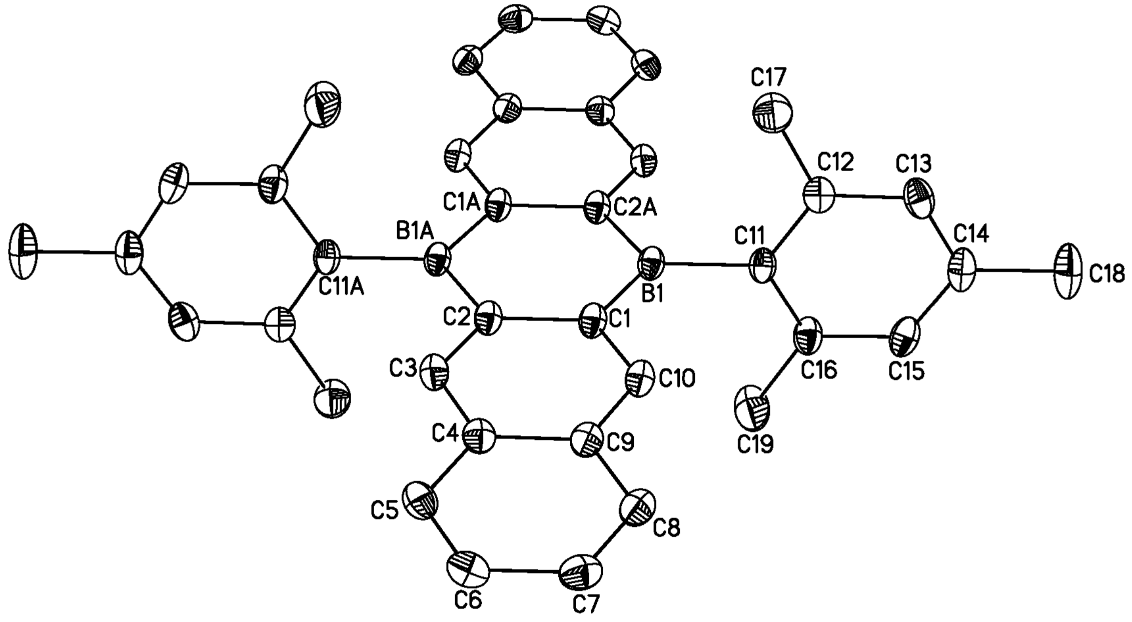
Appendix W

Data collection and structure determination of **IV-3**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C6
C7
C5
C8
C4
C9
C3
C10
C2
C1
C19
C16
C15
C18
B1A
B1
C17
C11C12
C13
C14
C1A
C2A


C17
C12
C13
C14
C18
C1A
C2A
B1A
C11
C11A
B1
C2
C1
C3
C10
C16
C15
C4
C9
C19
C5
C8
C6
C7

Structure Determination.

Yellow blocks of cj233 were grown from a toluene solution at -20 deg. C. A crystal of dimensions 0.32 x 0.26 x 0.15 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3265 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 15 s/frame. The integration of the data yielded a total of 62808 reflections to a maximum 2θ value of 56.74° of which 3738 were independent and 3275 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9886 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group R3bar with Z = 9 for the formula $C_{38}H_{34}B_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The molecule lies on an inversion center of the crystal lattice. The hydrogen atoms of one methyl group of the mesityl substituents are disordered. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0494 and wR2 = 0.1315 [based on I > 2sigma(I)], R1 = 0.0554 and wR2 = 0.1385 for all data.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2007/4. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2007.

Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Table 1. Crystal data and structure refinement for cj233.

Identification code	cj233
Empirical formula	C38 H34 B2
Formula weight	512.27
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Trigonal, R-3
Unit cell dimensions	a = 30.2192(12) A alpha = 90 deg. b = 30.2192(12) A beta = 90 deg. c = 8.4832(7) A gamma = 120 deg.
Volume	6709.0(7) A^3
Z, Calculated density	9, 1.141 Mg/m^3
Absorption coefficient	0.063 mm^-1
F(000)	2448
Crystal size	0.32 x 0.26 x 0.15 mm
Theta range for data collection	2.33 to 28.37 deg.
Limiting indices	-40<=h<=40, -40<=k<=40, -11<=l<=11
Reflections collected / unique	62808 / 3738 [R(int) = 0.0572]
Completeness to theta = 28.37	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9906 and 0.9800
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3738 / 0 / 207
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1315

R indices (all data) R1 = 0.0554, wR2 = 0.1385

Largest diff. peak and hole 0.422 and -0.296 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj233.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	2837(1)	1466(1)	744(1)	18(1)
C(1)	2905(1)	1123(1)	1979(1)	19(1)
C(2)	3379(1)	1313(1)	2849(1)	19(1)
C(3)	3423(1)	997(1)	3927(1)	20(1)
C(4)	3018(1)	496(1)	4249(1)	19(1)
C(5)	3060(1)	179(1)	5393(1)	22(1)
C(6)	2656(1)	-301(1)	5691(1)	24(1)
C(7)	2197(1)	-485(1)	4844(1)	25(1)
C(8)	2144(1)	-186(1)	3731(1)	22(1)
C(9)	2552(1)	312(1)	3407(1)	19(1)
C(10)	2511(1)	633(1)	2270(1)	20(1)
C(11)	2320(1)	1258(1)	-214(1)	18(1)
C(12)	2258(1)	1039(1)	-1716(1)	20(1)
C(13)	1801(1)	868(1)	-2537(1)	24(1)
C(14)	1400(1)	912(1)	-1916(2)	26(1)
C(15)	1461(1)	1127(1)	-432(2)	26(1)
C(16)	1912(1)	1297(1)	425(1)	24(1)
C(17)	2682(1)	985(1)	-2444(2)	31(1)
C(18)	912(1)	738(1)	-2833(2)	43(1)
C(19)	1964(1)	1526(1)	2037(2)	39(1)

Table 3. Bond lengths [A] and angles [deg] for cj233.

B(1)-C(1)	1.5577(15)
B(1)-C(2)#1	1.5583(15)
B(1)-C(11)	1.5839(14)
C(1)-C(10)	1.3817(14)
C(1)-C(2)	1.4503(14)
C(2)-C(3)	1.3766(14)
C(2)-B(1)#1	1.5584(15)
C(3)-C(4)	1.4181(14)

C(4)-C(5)	1.4140(15)
C(4)-C(9)	1.4214(14)
C(5)-C(6)	1.3732(16)
C(6)-C(7)	1.4077(16)
C(7)-C(8)	1.3691(16)
C(8)-C(9)	1.4157(14)
C(9)-C(10)	1.4162(15)
C(11)-C(16)	1.4039(15)
C(11)-C(12)	1.4042(15)
C(12)-C(13)	1.3955(15)
C(12)-C(17)	1.5008(16)
C(13)-C(14)	1.3881(17)
C(14)-C(15)	1.3858(18)
C(14)-C(18)	1.5101(16)
C(15)-C(16)	1.3969(15)
C(16)-C(19)	1.5051(17)

C(1)-B(1)-C(2)#1	118.29(9)
C(1)-B(1)-C(11)	120.90(9)
C(2)#1-B(1)-C(11)	120.81(9)
C(10)-C(1)-C(2)	119.02(9)
C(10)-C(1)-B(1)	120.23(9)
C(2)-C(1)-B(1)	120.74(9)
C(3)-C(2)-C(1)	118.80(9)
C(3)-C(2)-B(1)#1	120.23(9)
C(1)-C(2)-B(1)#1	120.96(9)
C(2)-C(3)-C(4)	122.50(9)
C(5)-C(4)-C(3)	122.25(9)
C(5)-C(4)-C(9)	119.10(10)
C(3)-C(4)-C(9)	118.64(9)
C(6)-C(5)-C(4)	120.64(10)
C(5)-C(6)-C(7)	120.14(10)
C(8)-C(7)-C(6)	120.61(10)
C(7)-C(8)-C(9)	120.56(10)
C(8)-C(9)-C(10)	122.23(10)
C(8)-C(9)-C(4)	118.95(10)
C(10)-C(9)-C(4)	118.82(9)
C(1)-C(10)-C(9)	122.18(9)
C(16)-C(11)-C(12)	118.26(9)
C(16)-C(11)-B(1)	120.07(9)
C(12)-C(11)-B(1)	121.66(9)
C(13)-C(12)-C(11)	120.09(10)
C(13)-C(12)-C(17)	119.61(10)
C(11)-C(12)-C(17)	120.30(10)
C(14)-C(13)-C(12)	121.71(10)
C(15)-C(14)-C(13)	118.14(10)
C(15)-C(14)-C(18)	120.64(12)
C(13)-C(14)-C(18)	121.22(12)
C(14)-C(15)-C(16)	121.41(11)

C(15)-C(16)-C(11)	120.38(10)
C(15)-C(16)-C(19)	119.90(10)
C(11)-C(16)-C(19)	119.72(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2/3,-y+1/3,-z+1/3

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj233. 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
B(1)	16(1)	18(1)	22(1)	-4(1)	-3(1)	11(1)
C(1)	16(1)	18(1)	23(1)	-3(1)	-4(1)	10(1)
C(2)	17(1)	18(1)	22(1)	-4(1)	-4(1)	10(1)
C(3)	19(1)	20(1)	21(1)	-4(1)	-5(1)	11(1)
C(4)	21(1)	19(1)	19(1)	-4(1)	-2(1)	11(1)
C(5)	26(1)	23(1)	19(1)	-3(1)	-3(1)	13(1)
C(6)	31(1)	23(1)	20(1)	1(1)	2(1)	14(1)
C(7)	25(1)	21(1)	24(1)	0(1)	5(1)	9(1)
C(8)	18(1)	21(1)	26(1)	-3(1)	1(1)	9(1)
C(9)	18(1)	19(1)	21(1)	-4(1)	-1(1)	10(1)
C(10)	17(1)	20(1)	24(1)	-4(1)	-4(1)	10(1)
C(11)	17(1)	16(1)	23(1)	-2(1)	-4(1)	9(1)
C(12)	22(1)	16(1)	24(1)	-1(1)	-3(1)	10(1)
C(13)	27(1)	17(1)	25(1)	-4(1)	-9(1)	10(1)
C(14)	21(1)	19(1)	35(1)	0(1)	-10(1)	8(1)
C(15)	18(1)	28(1)	36(1)	-1(1)	-4(1)	14(1)
C(16)	21(1)	26(1)	28(1)	-5(1)	-6(1)	14(1)
C(17)	31(1)	37(1)	31(1)	-8(1)	-2(1)	22(1)
C(18)	29(1)	44(1)	52(1)	-7(1)	-22(1)	16(1)
C(19)	36(1)	60(1)	36(1)	-19(1)	-9(1)	35(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj233.

	x	y	z	U(eq)

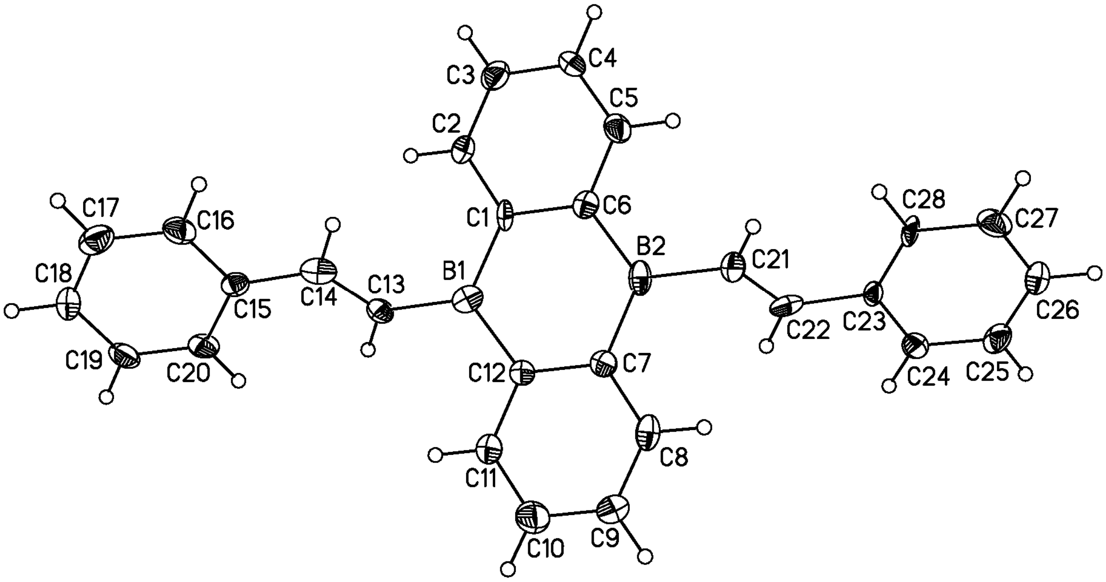
H(3A)	3737	1119	4476	23
H(5A)	3370	299	5960	26
H(6A)	2687	-509	6472	29
H(7A)	1921	-819	5045	30
H(8A)	1831	-315	3172	27
H(10A)	2203	507	1687	24
H(13A)	1764	718	-3548	28
H(15A)	1190	1160	13	32
H(17A)	2719	723	-1878	46
H(17B)	3002	1313	-2379	46
H(17C)	2601	886	-3552	46
H(18A)	975(13)	699(15)	-4040(40)	46(9)
H(18B)	810(16)	1017(16)	-2930(50)	51(10)
H(18C)	615(15)	420(15)	-2290(50)	46(9)
H(18D)	646(11)	795(12)	-2180(40)	41(7)
H(18E)	772(13)	393(13)	-3220(40)	41(8)
H(18F)	988(15)	972(16)	-3800(50)	49(10)
H(19A)	1642	1510	2326	59
H(19B)	2240	1883	2026	59
H(19C)	2043	1334	2807	59

Appendix X

Data collection and structure determination of **IV-4**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C3
C4
C5
C2
C17
C16
C1
C6
B2
C21
C28
C27
C18
C14
C13
B1
C15
C22
C23
C26
C19
C20
C12
C7
C24
C25
C8
C11
C10
C9

Structure Determination.

Slow cooling of a toluene/pentane solution from 110 deg. C to room temperature grew yellow needles of cj99. A crystal of dimensions 0.40 x 0.34 x 0.28 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 3000 frames were collected with a scan width of 0.5° in ω and phi with an exposure time of 30 s/frame. Unit cell determination was performed with use of the program CELL_NOW which revealed that the crystal was a non-merohedral twin. The two twin components are related by a rotation of 180 degrees about the (0 0 1) reciprocal axis. The integration of the data yielded a total of 98017 reflections to a maximum 2θ value of 57.46° of which 97011 were independent and 48777 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 1864 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with TWINABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group Pc with Z = 8 for the formula $C_{28}H_{22}B_2$. There are four crystalographically independent molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0662 and wR2 = 0.1410 [based on I > 2sigma(I)], R1 = 0.1420 and wR2 = 0.1593 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. CELL_NOW, Program for Indexing Twins and Other Problem Crystals, University of Gottingen: Gottingen, Germany, 2003.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. TWINABS, v. 1.05. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2005.

Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table 1. Crystal data and structure refinement for cj99.

Identification code	cj99
Empirical formula	C28 H22 B2
Formula weight	380.08
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, Pc
Unit cell dimensions	a = 7.387(5) A alpha = 90 deg. b = 22.449(14) A beta = 104.856(10) deg. c = 25.298(16) A gamma = 90 deg.
Volume	4055(4) A^3
Z, Calculated density	8, 1.245 Mg/m^3
Absorption coefficient	0.069 mm^-1
F(000)	1600
Crystal size	0.40 x 0.34 x 0.28 mm
Theta range for data collection	1.81 to 28.73 deg.
Limiting indices	-9<=h<=9, -30<=k<=30, -34<=l<=34
Reflections collected / unique	97011 / 97011 [R(int) = 0.0768]
Completeness to theta = 28.73	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9810 and 0.9730
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	97011 / 2 / 1082
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1410

R indices (all data)	R1 = 0.1420, wR2 = 0.1593
Absolute structure parameter	-1(2)
Largest diff. peak and hole	0.315 and -0.294 e.Aˆ-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj99.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-873(2)	3856(1)	4890(1)	19(1)
C(2)	-1743(2)	3368(1)	4597(1)	21(1)
C(3)	-1638(2)	2804(1)	4826(1)	29(1)
C(4)	-614(2)	2710(1)	5358(1)	24(1)
C(5)	257(2)	3188(1)	5661(1)	24(1)
C(6)	191(2)	3760(1)	5446(1)	17(1)
C(7)	1002(2)	4938(1)	5551(1)	19(1)
C(8)	2050(2)	5416(1)	5836(1)	26(1)
C(9)	2136(2)	5967(1)	5588(1)	31(1)
C(10)	1200(2)	6057(1)	5053(1)	34(1)
C(11)	161(2)	5588(1)	4763(1)	31(1)
C(12)	39(2)	5030(1)	4993(1)	21(1)
C(13)	-1774(2)	4593(1)	4012(1)	24(1)
C(14)	-1500(2)	4256(1)	3596(1)	26(1)
C(15)	-2025(2)	4358(1)	3018(1)	20(1)
C(16)	-1615(2)	3925(1)	2667(1)	24(1)
C(17)	-2081(2)	3991(1)	2107(1)	32(1)
C(18)	-3020(2)	4491(1)	1874(1)	28(1)
C(19)	-3485(2)	4927(1)	2213(1)	26(1)
C(20)	-3002(2)	4862(1)	2765(1)	22(1)
C(21)	1885(2)	4212(1)	6436(1)	25(1)
C(22)	1566(2)	4540(1)	6837(1)	24(1)
C(23)	2264(2)	4440(1)	7435(1)	18(1)
C(24)	1949(2)	4880(1)	7782(1)	23(1)
C(25)	2690(2)	4814(1)	8346(1)	25(1)
C(26)	3702(2)	4314(1)	8545(1)	30(1)
C(27)	3994(2)	3874(1)	8193(1)	29(1)
C(28)	3260(2)	3938(1)	7630(1)	20(1)
B(1)	-924(2)	4498(1)	4623(1)	19(1)
B(2)	1021(2)	4311(1)	5807(1)	19(1)
C(1A)	3604(2)	2472(1)	5013(1)	22(1)
C(2A)	2701(2)	1933(1)	4810(1)	29(1)
C(3A)	2726(2)	1432(1)	5139(1)	32(1)
C(4A)	3778(2)	1454(1)	5674(1)	30(1)
C(5A)	4778(2)	1974(1)	5882(1)	28(1)
C(6A)	4664(2)	2491(1)	5568(1)	24(1)
C(7A)	5291(2)	3659(1)	5449(1)	24(1)
C(8A)	5991(2)	4213(1)	5663(1)	26(1)

C(9A)	5619(2)	4731(1)	5370(1)	27(1)
C(10A)	4473(2)	4724(1)	4852(1)	32(1)
C(11A)	3743(2)	4182(1)	4618(1)	27(1)
C(12A)	4229(2)	3642(1)	4909(1)	24(1)
C(13A)	2766(2)	2951(1)	4001(1)	25(1)
C(14A)	3388(2)	3260(1)	3635(1)	19(1)
C(15A)	2866(2)	3171(1)	3031(1)	19(1)
C(16A)	3418(2)	3598(1)	2711(1)	22(1)
C(17A)	2945(2)	3538(1)	2149(1)	26(1)
C(18A)	1958(2)	3050(1)	1900(1)	30(1)
C(19A)	1402(2)	2618(1)	2212(1)	26(1)
C(20A)	1866(2)	2682(1)	2790(1)	25(1)
C(21A)	6712(2)	3164(1)	6419(1)	26(1)
C(22A)	6193(2)	2945(1)	6856(1)	22(1)
C(23A)	7140(2)	3049(1)	7428(1)	23(1)
C(24A)	6819(2)	2657(1)	7830(1)	23(1)
C(25A)	7676(2)	2731(1)	8374(1)	33(1)
C(26A)	8831(2)	3228(1)	8556(1)	28(1)
C(27A)	9117(2)	3630(1)	8167(1)	28(1)
C(28A)	8297(2)	3543(1)	7623(1)	26(1)
B(1A)	3467(2)	3043(1)	4637(1)	22(1)
B(2A)	5611(3)	3095(1)	5821(1)	32(1)
C(1B)	5023(2)	7492(1)	4995(1)	25(1)
C(2B)	5143(2)	6933(1)	4760(1)	28(1)
C(3B)	6185(2)	6460(1)	5053(1)	34(1)
C(4B)	7140(2)	6544(1)	5590(1)	29(1)
C(5B)	7037(2)	7100(1)	5840(1)	29(1)
C(6B)	6004(2)	7574(1)	5554(1)	24(1)
C(7B)	5179(2)	8739(1)	5455(1)	24(1)
C(8B)	5292(2)	9319(1)	5684(1)	24(1)
C(9B)	4378(2)	9796(1)	5379(1)	28(1)
C(10B)	3360(2)	9720(1)	4845(1)	25(1)
C(11B)	3287(2)	9150(1)	4615(1)	21(1)
C(12B)	4244(2)	8662(1)	4909(1)	22(1)
C(13B)	3161(2)	7930(1)	4015(1)	24(1)
C(14B)	3478(2)	8278(1)	3623(1)	19(1)
C(15B)	2847(2)	8183(1)	3017(1)	19(1)
C(16B)	3265(2)	8611(1)	2680(1)	25(1)
C(17B)	2752(2)	8532(1)	2120(1)	24(1)
C(18B)	1817(2)	8016(1)	1894(1)	27(1)
C(19B)	1370(2)	7590(1)	2232(1)	25(1)
C(20B)	1906(2)	7670(1)	2801(1)	22(1)
C(21B)	6836(2)	8300(1)	6441(1)	25(1)
C(22B)	6491(2)	7959(1)	6836(1)	22(1)
C(23B)	7136(2)	8052(1)	7428(1)	22(1)
C(24B)	6803(2)	7617(1)	7785(1)	24(1)
C(25B)	7385(2)	7671(1)	8340(1)	33(1)
C(26B)	8354(2)	8181(1)	8575(1)	31(1)
C(27B)	8675(2)	8623(1)	8234(1)	32(1)

C(28B)	8081(2)	8565(1)	7685(1)	28(1)
B(1B)	4055(3)	8045(1)	4644(1)	26(1)
B(2B)	6038(3)	8209(1)	5830(1)	28(1)
C(1C)	9142(2)	8838(1)	4916(1)	20(1)
C(2C)	8766(2)	8307(1)	4630(1)	28(1)
C(3C)	9495(2)	7766(1)	4855(1)	29(1)
C(4C)	10687(2)	7742(1)	5384(1)	28(1)
C(5C)	11023(2)	8266(1)	5682(1)	25(1)
C(6C)	10330(2)	8811(1)	5472(1)	19(1)
C(7C)	9670(2)	9986(1)	5582(1)	26(1)
C(8C)	9790(2)	10507(1)	5896(1)	29(1)
C(9C)	8825(2)	11030(1)	5689(1)	30(1)
C(10C)	7773(2)	11053(1)	5149(1)	33(1)
C(11C)	7742(2)	10549(1)	4824(1)	29(1)
C(12C)	8618(2)	10012(1)	5029(1)	26(1)
C(13C)	7705(2)	9525(1)	4028(1)	26(1)
C(14C)	8295(2)	9231(1)	3638(1)	24(1)
C(15C)	7755(2)	9328(1)	3055(1)	22(1)
C(16C)	8281(2)	8904(1)	2712(1)	24(1)
C(17C)	7813(2)	8966(1)	2144(1)	33(1)
C(18C)	6810(2)	9456(1)	1909(1)	29(1)
C(19C)	6254(2)	9880(1)	2243(1)	30(1)
C(20C)	6700(2)	9820(1)	2791(1)	23(1)
C(21C)	11651(2)	9331(1)	6444(1)	22(1)
C(22C)	11122(2)	9549(1)	6874(1)	25(1)
C(23C)	11916(2)	9444(1)	7459(1)	17(1)
C(24C)	11592(2)	9852(1)	7826(1)	24(1)
C(25C)	12349(2)	9765(1)	8384(1)	26(1)
C(26C)	13359(2)	9267(1)	8566(1)	28(1)
C(27C)	13709(2)	8852(1)	8196(1)	29(1)
C(28C)	12993(2)	8941(1)	7634(1)	22(1)
B(1C)	8464(2)	9461(1)	4647(1)	23(1)
B(2C)	10611(3)	9396(1)	5826(1)	22(1)

Table 3. Bond lengths [A] and angles [deg] for cj99.

C(1)-C(2)	1.383(2)
C(1)-C(6)	1.442(2)
C(1)-B(1)	1.588(2)
C(2)-C(3)	1.387(2)
C(3)-C(4)	1.381(2)
C(4)-C(5)	1.379(2)
C(5)-C(6)	1.391(2)
C(6)-B(2)	1.565(2)
C(7)-C(8)	1.407(2)
C(7)-C(12)	1.423(2)
C(7)-B(2)	1.548(2)
C(8)-C(9)	1.397(2)
C(9)-C(10)	1.367(2)
C(10)-C(11)	1.395(2)
C(11)-C(12)	1.393(2)
C(12)-B(1)	1.572(2)
C(13)-C(14)	1.353(2)
C(13)-B(1)	1.527(2)
C(14)-C(15)	1.431(2)
C(15)-C(16)	1.400(2)
C(15)-C(20)	1.405(2)
C(16)-C(17)	1.377(2)
C(17)-C(18)	1.371(2)
C(18)-C(19)	1.400(2)
C(19)-C(20)	1.359(2)
C(21)-C(22)	1.324(2)
C(21)-B(2)	1.571(2)
C(22)-C(23)	1.485(2)
C(23)-C(28)	1.368(2)
C(23)-C(24)	1.378(2)
C(24)-C(25)	1.398(2)
C(25)-C(26)	1.371(2)
C(26)-C(27)	1.383(2)
C(27)-C(28)	1.394(2)
C(1A)-C(2A)	1.413(2)
C(1A)-C(6A)	1.423(2)
C(1A)-B(1A)	1.584(2)
C(2A)-C(3A)	1.396(2)
C(3A)-C(4A)	1.379(2)
C(4A)-C(5A)	1.409(2)
C(5A)-C(6A)	1.398(2)
C(6A)-B(2A)	1.583(3)
C(7A)-C(12A)	1.390(2)
C(7A)-C(8A)	1.400(2)
C(7A)-B(2A)	1.560(3)

C(8A)-C(9A)	1.370(2)
C(9A)-C(10A)	1.366(2)
C(10A)-C(11A)	1.397(2)
C(11A)-C(12A)	1.418(2)
C(12A)-B(1A)	1.550(2)
C(13A)-C(14A)	1.329(2)
C(13A)-B(1A)	1.572(3)
C(14A)-C(15A)	1.489(2)
C(15A)-C(20A)	1.376(2)
C(15A)-C(16A)	1.383(2)
C(16A)-C(17A)	1.380(2)
C(17A)-C(18A)	1.375(2)
C(18A)-C(19A)	1.377(2)
C(19A)-C(20A)	1.420(2)
C(21A)-C(22A)	1.352(2)
C(21A)-B(2A)	1.529(3)
C(22A)-C(23A)	1.457(2)
C(23A)-C(28A)	1.409(2)
C(23A)-C(24A)	1.413(2)
C(24A)-C(25A)	1.369(2)
C(25A)-C(26A)	1.408(2)
C(26A)-C(27A)	1.391(2)
C(27A)-C(28A)	1.369(2)
C(1B)-C(2B)	1.402(2)
C(1B)-C(6B)	1.427(2)
C(1B)-B(1B)	1.587(2)
C(2B)-C(3B)	1.405(2)
C(3B)-C(4B)	1.375(2)
C(4B)-C(5B)	1.410(2)
C(5B)-C(6B)	1.399(2)
C(6B)-B(2B)	1.585(3)
C(7B)-C(12B)	1.387(2)
C(7B)-C(8B)	1.418(2)
C(7B)-B(2B)	1.553(3)
C(8B)-C(9B)	1.391(2)
C(9B)-C(10B)	1.377(2)
C(10B)-C(11B)	1.401(2)
C(11B)-C(12B)	1.409(2)
C(12B)-B(1B)	1.529(3)
C(13B)-C(14B)	1.330(2)
C(13B)-B(1B)	1.580(3)
C(14B)-C(15B)	1.500(2)
C(15B)-C(16B)	1.372(2)
C(15B)-C(20B)	1.382(2)
C(16B)-C(17B)	1.380(2)
C(17B)-C(18B)	1.395(2)
C(18B)-C(19B)	1.379(2)
C(19B)-C(20B)	1.403(2)
C(21B)-C(22B)	1.332(2)

C(21B)-B(2B)	1.520(3)
C(22B)-C(23B)	1.466(2)
C(23B)-C(24B)	1.394(2)
C(23B)-C(28B)	1.415(2)
C(24B)-C(25B)	1.363(2)
C(25B)-C(26B)	1.402(2)
C(26B)-C(27B)	1.374(2)
C(27B)-C(28B)	1.351(2)
C(1C)-C(2C)	1.384(2)
C(1C)-C(6C)	1.457(2)
C(1C)-B(1C)	1.580(3)
C(2C)-C(3C)	1.390(2)
C(3C)-C(4C)	1.401(2)
C(4C)-C(5C)	1.388(2)
C(5C)-C(6C)	1.379(2)
C(6C)-B(2C)	1.573(3)
C(7C)-C(8C)	1.405(2)
C(7C)-C(12C)	1.418(2)
C(7C)-B(2C)	1.548(3)
C(8C)-C(9C)	1.403(2)
C(9C)-C(10C)	1.388(2)
C(10C)-C(11C)	1.395(2)
C(11C)-C(12C)	1.402(2)
C(12C)-B(1C)	1.556(3)
C(13C)-C(14C)	1.348(2)
C(13C)-B(1C)	1.529(3)
C(14C)-C(15C)	1.443(3)
C(15C)-C(16C)	1.409(2)
C(15C)-C(20C)	1.416(2)
C(16C)-C(17C)	1.396(2)
C(17C)-C(18C)	1.372(2)
C(18C)-C(19C)	1.403(2)
C(19C)-C(20C)	1.347(3)
C(21C)-C(22C)	1.340(2)
C(21C)-B(2C)	1.561(3)
C(22C)-C(23C)	1.463(2)
C(23C)-C(24C)	1.370(2)
C(23C)-C(28C)	1.386(2)
C(24C)-C(25C)	1.393(2)
C(25C)-C(26C)	1.356(2)
C(26C)-C(27C)	1.390(3)
C(27C)-C(28C)	1.399(2)

C(2)-C(1)-C(6)	117.86(13)
C(2)-C(1)-B(1)	122.26(13)
C(6)-C(1)-B(1)	119.80(13)
C(1)-C(2)-C(3)	122.13(14)
C(4)-C(3)-C(2)	120.16(14)
C(5)-C(4)-C(3)	119.03(14)

C(4)-C(5)-C(6)	122.47(14)
C(5)-C(6)-C(1)	118.32(13)
C(5)-C(6)-B(2)	122.18(14)
C(1)-C(6)-B(2)	119.07(13)
C(8)-C(7)-C(12)	117.84(13)
C(8)-C(7)-B(2)	122.20(13)
C(12)-C(7)-B(2)	119.70(13)
C(9)-C(8)-C(7)	121.80(14)
C(10)-C(9)-C(8)	120.35(14)
C(9)-C(10)-C(11)	118.66(15)
C(12)-C(11)-C(10)	122.95(15)
C(11)-C(12)-C(7)	118.40(13)
C(11)-C(12)-B(1)	120.15(14)
C(7)-C(12)-B(1)	121.01(13)
C(14)-C(13)-B(1)	127.24(14)
C(13)-C(14)-C(15)	130.52(14)
C(16)-C(15)-C(20)	116.12(15)
C(16)-C(15)-C(14)	119.32(13)
C(20)-C(15)-C(14)	124.53(14)
C(17)-C(16)-C(15)	122.65(14)
C(18)-C(17)-C(16)	119.72(15)
C(17)-C(18)-C(19)	119.09(15)
C(20)-C(19)-C(18)	120.84(14)
C(19)-C(20)-C(15)	121.55(15)
C(22)-C(21)-B(2)	126.34(14)
C(21)-C(22)-C(23)	127.90(14)
C(28)-C(23)-C(24)	121.57(14)
C(28)-C(23)-C(22)	120.40(13)
C(24)-C(23)-C(22)	117.97(13)
C(23)-C(24)-C(25)	119.22(14)
C(26)-C(25)-C(24)	119.64(15)
C(25)-C(26)-C(27)	120.56(16)
C(26)-C(27)-C(28)	120.00(14)
C(23)-C(28)-C(27)	119.00(14)
C(13)-B(1)-C(12)	120.18(14)
C(13)-B(1)-C(1)	121.03(13)
C(12)-B(1)-C(1)	118.66(14)
C(7)-B(2)-C(6)	120.96(14)
C(7)-B(2)-C(21)	120.70(13)
C(6)-B(2)-C(21)	118.34(14)
C(2A)-C(1A)-C(6A)	118.37(14)
C(2A)-C(1A)-B(1A)	121.49(14)
C(6A)-C(1A)-B(1A)	120.14(13)
C(3A)-C(2A)-C(1A)	122.62(15)
C(4A)-C(3A)-C(2A)	118.40(15)
C(3A)-C(4A)-C(5A)	120.38(14)
C(6A)-C(5A)-C(4A)	121.78(14)
C(5A)-C(6A)-C(1A)	118.22(14)
C(5A)-C(6A)-B(2A)	121.72(15)

C(1A)-C(6A)-B(2A)	120.01(14)
C(12A)-C(7A)-C(8A)	117.74(14)
C(12A)-C(7A)-B(2A)	122.02(15)
C(8A)-C(7A)-B(2A)	120.14(15)
C(9A)-C(8A)-C(7A)	122.72(15)
C(10A)-C(9A)-C(8A)	119.91(15)
C(9A)-C(10A)-C(11A)	119.59(15)
C(10A)-C(11A)-C(12A)	120.38(15)
C(7A)-C(12A)-C(11A)	119.33(14)
C(7A)-C(12A)-B(1A)	120.74(14)
C(11A)-C(12A)-B(1A)	119.81(15)
C(14A)-C(13A)-B(1A)	124.23(14)
C(13A)-C(14A)-C(15A)	126.84(14)
C(20A)-C(15A)-C(16A)	119.86(15)
C(20A)-C(15A)-C(14A)	122.05(14)
C(16A)-C(15A)-C(14A)	118.09(13)
C(17A)-C(16A)-C(15A)	120.01(14)
C(18A)-C(17A)-C(16A)	120.98(15)
C(17A)-C(18A)-C(19A)	119.95(16)
C(18A)-C(19A)-C(20A)	119.28(15)
C(15A)-C(20A)-C(19A)	119.91(15)
C(22A)-C(21A)-B(2A)	125.45(16)
C(21A)-C(22A)-C(23A)	126.10(15)
C(28A)-C(23A)-C(24A)	115.91(15)
C(28A)-C(23A)-C(22A)	124.67(15)
C(24A)-C(23A)-C(22A)	119.31(14)
C(25A)-C(24A)-C(23A)	121.89(15)
C(24A)-C(25A)-C(26A)	120.70(16)
C(27A)-C(26A)-C(25A)	118.20(16)
C(28A)-C(27A)-C(26A)	120.68(15)
C(27A)-C(28A)-C(23A)	122.51(16)
C(12A)-B(1A)-C(13A)	123.75(15)
C(12A)-B(1A)-C(1A)	118.34(15)
C(13A)-B(1A)-C(1A)	117.56(14)
C(21A)-B(2A)-C(7A)	118.34(16)
C(21A)-B(2A)-C(6A)	123.65(16)
C(7A)-B(2A)-C(6A)	117.89(16)
C(2B)-C(1B)-C(6B)	117.74(14)
C(2B)-C(1B)-B(1B)	122.14(15)
C(6B)-C(1B)-B(1B)	119.70(14)
C(1B)-C(2B)-C(3B)	122.56(16)
C(4B)-C(3B)-C(2B)	119.44(15)
C(3B)-C(4B)-C(5B)	119.41(15)
C(6B)-C(5B)-C(4B)	121.81(15)
C(5B)-C(6B)-C(1B)	119.03(15)
C(5B)-C(6B)-B(2B)	120.81(15)
C(1B)-C(6B)-B(2B)	120.00(14)
C(12B)-C(7B)-C(8B)	118.95(15)
C(12B)-C(7B)-B(2B)	122.26(15)

C(8B)-C(7B)-B(2B)	118.74(15)
C(9B)-C(8B)-C(7B)	120.73(15)
C(10B)-C(9B)-C(8B)	120.87(15)
C(9B)-C(10B)-C(11B)	118.35(14)
C(10B)-C(11B)-C(12B)	122.00(15)
C(7B)-C(12B)-C(11B)	118.86(15)
C(7B)-C(12B)-B(1B)	121.10(15)
C(11B)-C(12B)-B(1B)	119.68(15)
C(14B)-C(13B)-B(1B)	123.12(15)
C(13B)-C(14B)-C(15B)	127.60(15)
C(16B)-C(15B)-C(20B)	120.61(15)
C(16B)-C(15B)-C(14B)	118.34(14)
C(20B)-C(15B)-C(14B)	121.03(14)
C(15B)-C(16B)-C(17B)	120.10(15)
C(16B)-C(17B)-C(18B)	120.31(15)
C(19B)-C(18B)-C(17B)	119.52(16)
C(18B)-C(19B)-C(20B)	119.98(15)
C(15B)-C(20B)-C(19B)	119.46(15)
C(22B)-C(21B)-B(2B)	125.86(15)
C(21B)-C(22B)-C(23B)	127.54(15)
C(24B)-C(23B)-C(28B)	114.85(16)
C(24B)-C(23B)-C(22B)	119.83(15)
C(28B)-C(23B)-C(22B)	125.31(15)
C(25B)-C(24B)-C(23B)	122.93(16)
C(24B)-C(25B)-C(26B)	120.14(17)
C(27B)-C(26B)-C(25B)	118.28(17)
C(28B)-C(27B)-C(26B)	120.93(17)
C(27B)-C(28B)-C(23B)	122.84(17)
C(12B)-B(1B)-C(13B)	123.92(15)
C(12B)-B(1B)-C(1B)	119.04(15)
C(13B)-B(1B)-C(1B)	116.59(15)
C(21B)-B(2B)-C(7B)	120.69(16)
C(21B)-B(2B)-C(6B)	121.78(15)
C(7B)-B(2B)-C(6B)	117.51(16)
C(2C)-C(1C)-C(6C)	117.38(15)
C(2C)-C(1C)-B(1C)	122.57(15)
C(6C)-C(1C)-B(1C)	119.89(15)
C(1C)-C(2C)-C(3C)	122.24(16)
C(2C)-C(3C)-C(4C)	120.53(15)
C(5C)-C(4C)-C(3C)	117.86(15)
C(6C)-C(5C)-C(4C)	123.14(15)
C(5C)-C(6C)-C(1C)	118.74(15)
C(5C)-C(6C)-B(2C)	122.64(15)
C(1C)-C(6C)-B(2C)	118.37(14)
C(8C)-C(7C)-C(12C)	117.53(15)
C(8C)-C(7C)-B(2C)	122.05(15)
C(12C)-C(7C)-B(2C)	120.41(15)
C(9C)-C(8C)-C(7C)	122.22(15)
C(10C)-C(9C)-C(8C)	120.15(15)

C(9C)-C(10C)-C(11C)	117.94(15)
C(10C)-C(11C)-C(12C)	122.97(16)
C(11C)-C(12C)-C(7C)	118.99(15)
C(11C)-C(12C)-B(1C)	120.03(15)
C(7C)-C(12C)-B(1C)	120.97(15)
C(14C)-C(13C)-B(1C)	126.94(16)
C(13C)-C(14C)-C(15C)	128.14(16)
C(16C)-C(15C)-C(20C)	116.31(16)
C(16C)-C(15C)-C(14C)	118.66(15)
C(20C)-C(15C)-C(14C)	125.03(16)
C(17C)-C(16C)-C(15C)	122.05(16)
C(18C)-C(17C)-C(16C)	119.30(17)
C(17C)-C(18C)-C(19C)	119.56(18)
C(20C)-C(19C)-C(18C)	121.24(16)
C(19C)-C(20C)-C(15C)	121.53(17)
C(22C)-C(21C)-B(2C)	127.45(16)
C(21C)-C(22C)-C(23C)	129.59(16)
C(24C)-C(23C)-C(28C)	120.90(16)
C(24C)-C(23C)-C(22C)	118.88(15)
C(28C)-C(23C)-C(22C)	120.21(15)
C(23C)-C(24C)-C(25C)	119.93(16)
C(26C)-C(25C)-C(24C)	120.13(17)
C(25C)-C(26C)-C(27C)	120.37(17)
C(26C)-C(27C)-C(28C)	120.09(16)
C(23C)-C(28C)-C(27C)	118.53(16)
C(13C)-B(1C)-C(12C)	120.75(16)
C(13C)-B(1C)-C(1C)	121.09(16)
C(12C)-B(1C)-C(1C)	118.16(16)
C(7C)-B(2C)-C(21C)	122.32(16)
C(7C)-B(2C)-C(6C)	120.42(15)
C(21C)-B(2C)-C(6C)	116.81(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj99.
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
C(1)	18(1)	26(1)	12(1)	4(1)	2(1)	5(1)
C(2)	20(1)	26(1)	16(1)	-3(1)	4(1)	0(1)
C(3)	42(1)	26(1)	22(1)	-6(1)	13(1)	-5(1)
C(4)	30(1)	18(1)	25(1)	3(1)	6(1)	-1(1)
C(5)	28(1)	23(1)	20(1)	2(1)	3(1)	7(1)
C(6)	13(1)	24(1)	12(1)	-6(1)	1(1)	2(1)
C(7)	19(1)	22(1)	17(1)	-1(1)	5(1)	-2(1)
C(8)	31(1)	33(1)	15(1)	-1(1)	4(1)	0(1)
C(9)	37(1)	26(1)	31(1)	-9(1)	9(1)	-6(1)
C(10)	47(1)	24(1)	31(1)	0(1)	6(1)	5(1)
C(11)	40(1)	26(1)	22(1)	1(1)	0(1)	-5(1)
C(12)	22(1)	20(1)	21(1)	-1(1)	3(1)	-1(1)
C(13)	23(1)	18(1)	26(1)	3(1)	1(1)	2(1)
C(14)	22(1)	20(1)	38(1)	4(1)	12(1)	2(1)
C(15)	16(1)	21(1)	22(1)	-4(1)	4(1)	-2(1)
C(16)	25(1)	19(1)	28(1)	6(1)	7(1)	4(1)
C(17)	39(1)	35(1)	24(1)	-6(1)	13(1)	-12(1)
C(18)	32(1)	32(1)	16(1)	3(1)	2(1)	2(1)
C(19)	35(1)	21(1)	24(1)	12(1)	9(1)	4(1)
C(20)	27(1)	10(1)	31(1)	6(1)	8(1)	10(1)
C(21)	25(1)	28(1)	18(1)	-3(1)	0(1)	0(1)
C(22)	23(1)	17(1)	31(1)	-6(1)	4(1)	-3(1)
C(23)	21(1)	21(1)	8(1)	-1(1)	-1(1)	-6(1)
C(24)	32(1)	17(1)	20(1)	-2(1)	8(1)	-3(1)
C(25)	32(1)	27(1)	17(1)	-11(1)	6(1)	-5(1)
C(26)	39(1)	31(1)	17(1)	-5(1)	2(1)	-4(1)
C(27)	36(1)	19(1)	31(1)	3(1)	8(1)	9(1)
C(28)	28(1)	27(1)	6(1)	-5(1)	4(1)	-1(1)
B(1)	19(1)	17(1)	24(1)	5(1)	12(1)	0(1)
B(2)	21(1)	31(1)	7(1)	-6(1)	6(1)	-3(1)
C(1A)	17(1)	25(1)	23(1)	2(1)	5(1)	-1(1)
C(2A)	28(1)	34(1)	24(1)	-4(1)	5(1)	-2(1)
C(3A)	40(1)	27(1)	28(1)	0(1)	8(1)	2(1)
C(4A)	42(1)	19(1)	34(1)	5(1)	18(1)	2(1)
C(5A)	37(1)	24(1)	21(1)	2(1)	6(1)	5(1)
C(6A)	28(1)	23(1)	21(1)	-1(1)	5(1)	6(1)
C(7A)	31(1)	24(1)	23(1)	-9(1)	15(1)	-1(1)
C(8A)	31(1)	34(1)	14(1)	5(1)	9(1)	6(1)
C(9A)	35(1)	24(1)	22(1)	-6(1)	6(1)	-2(1)

C(10A)	44(1)	24(1)	31(1)	2(1)	13(1)	3(1)
C(11A)	30(1)	36(1)	16(1)	4(1)	9(1)	7(1)
C(12A)	19(1)	24(1)	31(1)	11(1)	13(1)	7(1)
C(13A)	16(1)	37(1)	16(1)	5(1)	-5(1)	-3(1)
C(14A)	22(1)	24(1)	7(1)	-2(1)	-3(1)	1(1)
C(15A)	16(1)	23(1)	15(1)	1(1)	-1(1)	7(1)
C(16A)	17(1)	25(1)	22(1)	2(1)	-1(1)	1(1)
C(17A)	20(1)	23(1)	33(1)	8(1)	6(1)	-5(1)
C(18A)	30(1)	39(1)	18(1)	8(1)	2(1)	5(1)
C(19A)	23(1)	35(1)	19(1)	-7(1)	0(1)	0(1)
C(20A)	29(1)	32(1)	16(1)	12(1)	10(1)	10(1)
C(21A)	22(1)	30(1)	30(1)	8(1)	9(1)	4(1)
C(22A)	23(1)	22(1)	18(1)	-4(1)	2(1)	2(1)
C(23A)	19(1)	24(1)	28(1)	1(1)	11(1)	-1(1)
C(24A)	25(1)	21(1)	24(1)	2(1)	8(1)	-6(1)
C(25A)	39(1)	25(1)	34(1)	0(1)	11(1)	0(1)
C(26A)	25(1)	30(1)	25(1)	-10(1)	0(1)	-7(1)
C(27A)	24(1)	28(1)	25(1)	-2(1)	-3(1)	-5(1)
C(28A)	22(1)	19(1)	37(1)	0(1)	7(1)	-4(1)
B(1A)	15(1)	30(1)	23(1)	13(1)	11(1)	10(1)
B(2A)	23(1)	43(1)	34(1)	1(1)	15(1)	9(1)
C(1B)	26(1)	24(1)	26(1)	-4(1)	6(1)	1(1)
C(2B)	34(1)	26(1)	23(1)	-1(1)	6(1)	2(1)
C(3B)	43(1)	24(1)	34(1)	2(1)	11(1)	6(1)
C(4B)	32(1)	23(1)	31(1)	4(1)	3(1)	-1(1)
C(5B)	37(1)	27(1)	24(1)	0(1)	10(1)	1(1)
C(6B)	22(1)	27(1)	21(1)	4(1)	6(1)	1(1)
C(7B)	28(1)	23(1)	26(1)	-3(1)	14(1)	1(1)
C(8B)	28(1)	27(1)	21(1)	-5(1)	10(1)	-1(1)
C(9B)	40(1)	17(1)	27(1)	-2(1)	11(1)	-1(1)
C(10B)	31(1)	21(1)	25(1)	2(1)	10(1)	2(1)
C(11B)	25(1)	26(1)	13(1)	-1(1)	6(1)	5(1)
C(12B)	21(1)	19(1)	31(1)	8(1)	16(1)	2(1)
C(13B)	21(1)	26(1)	23(1)	0(1)	2(1)	-4(1)
C(14B)	22(1)	18(1)	12(1)	-5(1)	-2(1)	2(1)
C(15B)	16(1)	22(1)	16(1)	-6(1)	-1(1)	5(1)
C(16B)	23(1)	21(1)	31(1)	7(1)	10(1)	4(1)
C(17B)	22(1)	27(1)	24(1)	9(1)	5(1)	-1(1)
C(18B)	25(1)	41(1)	15(1)	-2(1)	3(1)	4(1)
C(19B)	23(1)	32(1)	19(1)	2(1)	1(1)	-3(1)
C(20B)	28(1)	27(1)	14(1)	8(1)	9(1)	7(1)
C(21B)	28(1)	16(1)	31(1)	-4(1)	8(1)	-4(1)
C(22B)	26(1)	25(1)	11(1)	-4(1)	0(1)	1(1)
C(23B)	19(1)	19(1)	30(1)	4(1)	11(1)	-1(1)
C(24B)	29(1)	19(1)	25(1)	-5(1)	7(1)	-5(1)
C(25B)	30(1)	30(1)	41(1)	2(1)	12(1)	-3(1)
C(26B)	27(1)	45(1)	24(1)	-1(1)	10(1)	1(1)
C(27B)	29(1)	43(1)	20(1)	-8(1)	0(1)	-1(1)
C(28B)	28(1)	19(1)	37(1)	-4(1)	9(1)	-4(1)

B(1B)	19(1)	34(1)	21(1)	13(1)	0(1)	−3(1)
B(2B)	17(1)	28(1)	39(1)	−8(1)	9(1)	−7(1)
C(1C)	15(1)	31(1)	15(1)	0(1)	4(1)	0(1)
C(2C)	30(1)	33(1)	19(1)	−1(1)	4(1)	3(1)
C(3C)	36(1)	24(1)	28(1)	−7(1)	10(1)	−9(1)
C(4C)	35(1)	24(1)	25(1)	−1(1)	11(1)	−3(1)
C(5C)	35(1)	26(1)	12(1)	2(1)	4(1)	1(1)
C(6C)	12(1)	32(1)	14(1)	−3(1)	5(1)	−2(1)
C(7C)	28(1)	26(1)	27(1)	−6(1)	14(1)	−5(1)
C(8C)	36(1)	28(1)	25(1)	−1(1)	13(1)	−8(1)
C(9C)	46(1)	20(1)	28(1)	−7(1)	17(1)	−9(1)
C(10C)	39(1)	22(1)	40(1)	1(1)	14(1)	4(1)
C(11C)	31(1)	30(1)	25(1)	−6(1)	3(1)	−3(1)
C(12C)	26(1)	26(1)	27(1)	−2(1)	6(1)	−1(1)
C(13C)	28(1)	22(1)	29(1)	0(1)	7(1)	3(1)
C(14C)	17(1)	20(1)	36(1)	−1(1)	8(1)	−2(1)
C(15C)	20(1)	22(1)	27(1)	−7(1)	11(1)	0(1)
C(16C)	22(1)	24(1)	26(1)	9(1)	6(1)	4(1)
C(17C)	39(1)	36(1)	27(1)	−10(1)	17(1)	−15(1)
C(18C)	26(1)	37(1)	24(1)	0(1)	6(1)	−6(1)
C(19C)	28(1)	25(1)	35(1)	4(1)	6(1)	2(1)
C(20C)	14(1)	17(1)	35(1)	4(1)	−1(1)	10(1)
C(21C)	22(1)	26(1)	17(1)	−9(1)	2(1)	−2(1)
C(22C)	21(1)	26(1)	29(1)	−7(1)	6(1)	−1(1)
C(23C)	11(1)	27(1)	12(1)	0(1)	0(1)	−6(1)
C(24C)	22(1)	25(1)	25(1)	−11(1)	7(1)	−2(1)
C(25C)	34(1)	36(1)	9(1)	−7(1)	5(1)	−4(1)
C(26C)	19(1)	43(1)	16(1)	1(1)	−6(1)	−9(1)
C(27C)	23(1)	24(1)	40(1)	−1(1)	6(1)	5(1)
C(28C)	19(1)	30(1)	16(1)	−10(1)	2(1)	−4(1)
B(1C)	16(1)	27(1)	26(1)	1(1)	5(1)	6(1)
B(2C)	22(1)	32(1)	11(1)	−3(1)	4(1)	−7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj99.

	x	y	z	U(eq)
H(2)	-2435	3422	4228	25
H(3)	-2273	2480	4615	35
H(4)	-511	2322	5513	29
H(5)	927	3125	6031	29
H(8)	2717	5361	6207	32
H(9)	2848	6282	5792	37
H(10)	1256	6431	4882	41
H(11)	-493	5652	4392	37
H(13)	-2586	4925	3913	28
H(14)	-853	3892	3704	31
H(16)	-989	3572	2822	28
H(17)	-1754	3691	1884	38
H(18)	-3350	4541	1489	33
H(19)	-4148	5273	2054	32
H(20)	-3332	5165	2986	27
H(21)	2716	3885	6538	30
H(22)	798	4881	6730	29
H(24)	1238	5223	7639	27
H(25)	2493	5115	8589	30
H(26)	4207	4269	8928	36
H(27)	4694	3529	8334	35
H(28)	3448	3636	7386	24
H(2A)	2050	1911	4434	35
H(3A)	2036	1085	4997	38
H(4A)	3828	1117	5904	36
H(5A)	5551	1973	6246	33
H(8A)	6755	4229	6027	31
H(9A)	6157	5095	5526	33
H(10A)	4175	5084	4651	39
H(11A)	2917	4177	4262	32
H(13A)	1838	2656	3870	30
H(14A)	4257	3570	3773	23
H(16A)	4124	3933	2877	27
H(17A)	3305	3837	1931	31
H(18A)	1660	3011	1514	36
H(19A)	715	2281	2042	32
H(20A)	1487	2388	3009	30
H(21A)	7857	3379	6489	32
H(22A)	5110	2700	6782	26
H(24A)	5985	2331	7721	28

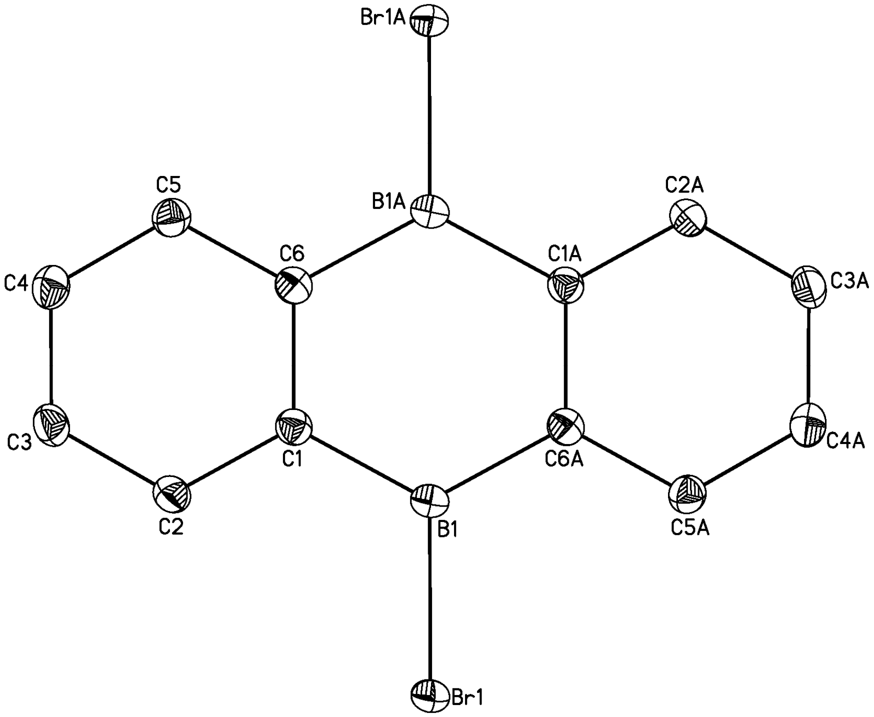
H(25A)	7488	2445	8632	39
H(26A)	9400	3287	8934	33
H(27A)	9890	3969	8281	33
H(28A)	8516	3826	7367	31
H(2B)	4495	6871	4388	34
H(3B)	6228	6086	4881	40
H(4B)	7863	6229	5791	35
H(5B)	7687	7153	6213	34
H(8B)	6000	9381	6050	29
H(9B)	4457	10181	5541	33
H(10B)	2724	10045	4638	30
H(11B)	2571	9091	4249	26
H(13B)	2359	7596	3912	29
H(14B)	4187	8629	3741	22
H(16B)	3908	8962	2832	29
H(17B)	3038	8831	1888	29
H(18B)	1490	7958	1509	33
H(19B)	699	7243	2081	30
H(20B)	1626	7374	3037	26
H(21B)	7654	8629	6552	30
H(22B)	5741	7616	6720	26
H(24B)	6140	7268	7635	29
H(25B)	7134	7361	8567	40
H(26B)	8778	8222	8961	38
H(27B)	9324	8973	8386	38
H(28B)	8306	8882	7462	33
H(2C)	7983	8313	4268	33
H(3C)	9182	7410	4648	35
H(4C)	11247	7377	5533	33
H(5C)	11766	8249	6049	30
H(8C)	10549	10506	6261	35
H(9C)	8893	11369	5918	36
H(10C)	7095	11402	5005	39
H(11C)	7098	10570	4448	35
H(13C)	6710	9801	3904	32
H(14C)	9178	8922	3763	29
H(16C)	8977	8564	2872	29
H(17C)	8185	8673	1922	39
H(18C)	6494	9506	1524	35
H(19C)	5550	10217	2079	36
H(20C)	6298	10115	3006	28
H(21C)	12789	9112	6524	27
H(22C)	10076	9810	6787	30
H(24C)	10851	10195	7700	29
H(25C)	12157	10054	8639	31
H(26C)	13830	9202	8947	34
H(27C)	14435	8508	8326	35
H(28C)	13239	8663	7378	27

Appendix Y

Data collection and structure determination of **DBBA**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


Br1A
C5
B1A
C2A
C6
C1A
C4
C3A
C3
C1
C6A
C4A
C2
B1
C5A
Br1

Structure Determination.

Colorless needles of cj253 were grown by slow cooling of a toluene solution from 110 deg. C to room temperature. A crystal of dimensions 0.31 x 0.09 x 0.09 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 4095 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 10 s/frame. The integration of the data yielded a total of 9962 reflections to a maximum 2θ value of 56.68° of which 1401 were independent and 1345 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 6805 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P1bar with Z = 1 for the formula $C_{12}H_8B_2Br_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0156 and wR2 = 0.0403 [based on I > 2sigma(I)], R1 = 0.0167 and wR2 = 0.0406 for all data.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2007/4. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2007.

Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Table 1. Crystal data and structure refinement for cj253.

Identification code	cj253
Empirical formula	C12 H8 B2 Br2
Formula weight	333.62
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 3.9616(3) A alpha = 106.255(1) deg. b = 8.4794(7) A beta = 90.874(1) deg. c = 8.6794(7) A gamma = 92.650(1) deg.
Volume	279.48(4) A^3
Z, Calculated density	1, 1.982 Mg/m^3
Absorption coefficient	7.212 mm^-1
F(000)	160
Crystal size	0.31 x 0.09 x 0.09 mm
Theta range for data collection	2.45 to 28.34 deg.
Limiting indices	-5<=h<=5, -11<=k<=11, -11<=l<=11
Reflections collected / unique	9962 / 1401 [R(int) = 0.0271]
Completeness to theta = 28.34	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5230 and 0.4133
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1401 / 0 / 73
Goodness-of-fit on F^2	1.131
Final R indices [I>2sigma(I)]	R1 = 0.0156, wR2 = 0.0403

R indices (all data)	R1 = 0.0167, wR2 = 0.0406
Largest diff. peak and hole	0.412 and -0.229 e.Aˆ-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj253.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	-340(4)	-1223(2)	878(2)	14(1)
Br(1)	-650(1)	-2893(1)	2008(1)	17(1)
C(1)	1635(4)	428(2)	1693(2)	14(1)
C(2)	3056(4)	794(2)	3246(2)	16(1)
C(3)	4836(4)	2286(2)	3943(2)	17(1)
C(4)	5238(4)	3434(2)	3087(2)	17(1)
C(5)	3827(4)	3102(2)	1540(2)	15(1)
C(6)	2010(4)	1619(2)	826(2)	14(1)

Table 3. Bond lengths [A] and angles [deg] for cj253.

B(1)-C(1)	1.549(2)
B(1)-C(6)#1	1.552(2)
B(1)-Br(1)	1.9358(17)
C(1)-C(2)	1.399(2)
C(1)-C(6)	1.422(2)
C(2)-C(3)	1.393(2)
C(3)-C(4)	1.385(2)
C(4)-C(5)	1.395(2)
C(5)-C(6)	1.396(2)
C(6)-B(1)#1	1.552(2)
C(1)-B(1)-C(6)#1	122.95(13)
C(1)-B(1)-Br(1)	118.69(11)
C(6)#1-B(1)-Br(1)	118.34(11)
C(2)-C(1)-C(6)	118.78(14)
C(2)-C(1)-B(1)	122.65(14)
C(6)-C(1)-B(1)	118.58(13)
C(3)-C(2)-C(1)	121.33(14)
C(4)-C(3)-C(2)	119.74(14)
C(3)-C(4)-C(5)	120.01(15)
C(4)-C(5)-C(6)	121.06(15)
C(5)-C(6)-C(1)	119.08(14)
C(5)-C(6)-B(1)#1	122.46(14)
C(1)-C(6)-B(1)#1	118.46(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj253.
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
B(1)	15(1)	14(1)	13(1)	6(1)	1(1)	1(1)
Br(1)	21(1)	16(1)	16(1)	9(1)	-3(1)	-3(1)
C(1)	15(1)	14(1)	13(1)	4(1)	1(1)	1(1)
C(2)	18(1)	16(1)	13(1)	4(1)	-1(1)	1(1)
C(3)	19(1)	18(1)	13(1)	2(1)	-2(1)	0(1)
C(4)	18(1)	16(1)	16(1)	1(1)	0(1)	-1(1)
C(5)	17(1)	14(1)	14(1)	3(1)	1(1)	1(1)
C(6)	14(1)	14(1)	13(1)	4(1)	1(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj253.

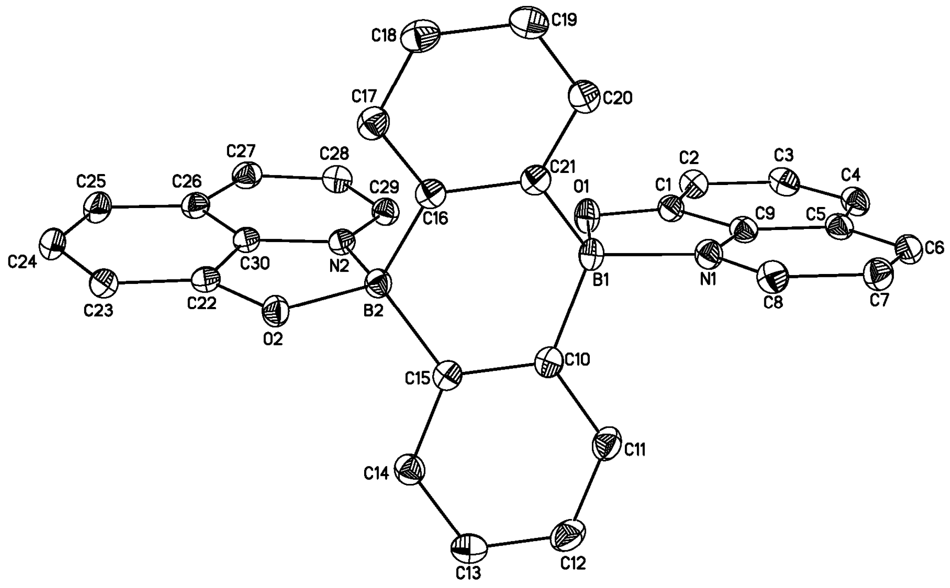
	x	y	z	U(eq)
H(2A)	2802	9	3837	19
H(3A)	5771	2516	5002	20
H(4A)	6474	4447	3553	21
H(5A)	4108	3897	962	18

Appendix Z

Data collection and structure determination of **DBAq2**

(Provided by Dr. Jeff W. Kampf of the University of Michigan)

Data were collected on a standard Bruker SMART CCD-based X-ray diffractometer. Structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are listed as follows.


C18
C19
C17
C20
C27
C28
C2
C3
C4
C25
C26
C29
C21
O1
C1
C9
C5
C6
C16
C24
C30
N2
B1
N1
C8
C7
C23
C22
B2
O2
C10
C15
C11
C14
C13
C12

Structure Determination.

Yellow blocks of cj225 were grown from a dichloromethane solution at 23 deg. C. A crystal of dimensions 0.52 x 0.26 x 0.17 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3000 frames were collected with a scan width of 0.5° in ω and phi with an exposure time of 15s/frame. The integration of the data yielded a total of 56777 reflections to a maximum 2θ value of 58.80° of which 5657 were independent and 5217 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9745 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{30}H_{20}B_2N_2O_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0442 and wR2 = 0.1137 [based on I > 2sigma(I)], R1 = 0.0474 and wR2 = 0.1168 for all data.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Table 1. Crystal data and structure refinement for cj225.

Identification code	cj225
Empirical formula	C30 H20 B2 N2 O2
Formula weight	462.10
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.5696(8) A alpha = 90 deg. b = 20.3329(17) A beta = 98.6450(10) deg. c = 11.8153(10) A gamma = 90 deg.
Volume	2272.9(3) A^3
Z, Calculated density	4, 1.350 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	960
Crystal size	0.52 x 0.26 x 0.17 mm
Theta range for data collection	2.00 to 28.35 deg.
Limiting indices	-12<=h<=12, -27<=k<=27, -15<=l<=15
Reflections collected / unique	56777 / 5657 [R(int) = 0.0411]
Completeness to theta = 28.35	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9859 and 0.9578
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5657 / 0 / 325
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1137

R indices (all data)	R1 = 0.0474, wR2 = 0.1168
Largest diff. peak and hole	0.266 and -0.188 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj225.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4167(1)	5551(1)	1430(1)	19(1)
O(2)	1482(1)	3611(1)	2783(1)	17(1)
N(1)	5528(1)	5849(1)	3222(1)	16(1)
N(2)	1684(1)	4234(1)	1094(1)	15(1)
C(1)	5105(1)	6019(1)	1294(1)	16(1)
C(2)	5349(1)	6334(1)	312(1)	18(1)
C(3)	6422(1)	6820(1)	417(1)	20(1)
C(4)	7224(1)	6995(1)	1436(1)	19(1)
C(5)	6974(1)	6682(1)	2462(1)	16(1)
C(6)	7629(1)	6800(1)	3601(1)	18(1)
C(7)	7210(1)	6449(1)	4491(1)	19(1)
C(8)	6149(1)	5967(1)	4282(1)	18(1)
C(9)	5917(1)	6201(1)	2341(1)	15(1)
C(10)	4967(1)	4588(1)	2796(1)	16(1)
C(11)	6418(1)	4449(1)	3004(1)	21(1)
C(12)	6921(1)	3807(1)	3070(1)	24(1)
C(13)	5975(1)	3286(1)	2924(1)	23(1)
C(14)	4531(1)	3413(1)	2716(1)	18(1)
C(15)	4002(1)	4056(1)	2650(1)	15(1)
C(16)	1938(1)	4865(1)	3061(1)	15(1)
C(17)	640(1)	4931(1)	3461(1)	18(1)
C(18)	270(1)	5512(1)	3965(1)	20(1)
C(19)	1205(1)	6036(1)	4094(1)	21(1)
C(20)	2510(1)	5977(1)	3712(1)	19(1)
C(21)	2895(1)	5400(1)	3190(1)	16(1)
C(22)	503(1)	3432(1)	1906(1)	16(1)
C(23)	-532(1)	2959(1)	1862(1)	19(1)
C(24)	-1460(1)	2873(1)	813(1)	22(1)
C(25)	-1354(1)	3227(1)	-160(1)	22(1)
C(26)	-271(1)	3707(1)	-140(1)	18(1)
C(27)	31(1)	4112(1)	-1046(1)	19(1)
C(28)	1136(1)	4550(1)	-853(1)	18(1)
C(29)	1957(1)	4607(1)	234(1)	17(1)
C(30)	610(1)	3791(1)	906(1)	16(1)
B(1)	4350(1)	5322(1)	2692(1)	16(1)
B(2)	2340(1)	4200(1)	2454(1)	15(1)

Table 3. Bond lengths [A] and angles [deg] for cj225.

O(1)-C(1)	1.3340(13)
O(1)-B(1)	1.5461(15)
O(2)-C(22)	1.3387(14)
O(2)-B(2)	1.5335(14)
N(1)-C(8)	1.3243(15)
N(1)-C(9)	1.3604(14)
N(1)-B(1)	1.6122(16)
N(2)-C(29)	1.3257(15)
N(2)-C(30)	1.3590(14)
N(2)-B(2)	1.6367(16)
C(1)-C(2)	1.3749(16)
C(1)-C(9)	1.4081(16)
C(2)-C(3)	1.4174(16)
C(3)-C(4)	1.3743(18)
C(4)-C(5)	1.4212(16)
C(5)-C(9)	1.3990(15)
C(5)-C(6)	1.4166(17)
C(6)-C(7)	1.3789(17)
C(7)-C(8)	1.4064(16)
C(10)-C(11)	1.4024(16)
C(10)-C(15)	1.4167(15)
C(10)-B(1)	1.6027(17)
C(11)-C(12)	1.3897(18)
C(12)-C(13)	1.3867(18)
C(13)-C(14)	1.3908(17)
C(14)-C(15)	1.3985(16)
C(15)-B(2)	1.5993(17)
C(16)-C(17)	1.4006(15)
C(16)-C(21)	1.4157(15)
C(16)-B(2)	1.6046(17)
C(17)-C(18)	1.3912(17)
C(18)-C(19)	1.3861(18)
C(19)-C(20)	1.3955(17)
C(20)-C(21)	1.4013(16)
C(21)-B(1)	1.5985(17)
C(22)-C(23)	1.3763(16)
C(22)-C(30)	1.4061(16)
C(23)-C(24)	1.4226(18)
C(24)-C(25)	1.3722(18)
C(25)-C(26)	1.4219(16)
C(26)-C(30)	1.3985(16)
C(26)-C(27)	1.4145(17)
C(27)-C(28)	1.3748(17)
C(28)-C(29)	1.4058(16)

C(1)-O(1)-B(1)	110.50(9)
C(22)-O(2)-B(2)	110.85(9)
C(8)-N(1)-C(9)	119.52(10)
C(8)-N(1)-B(1)	132.54(10)
C(9)-N(1)-B(1)	107.90(9)
C(29)-N(2)-C(30)	119.05(10)
C(29)-N(2)-B(2)	133.34(10)
C(30)-N(2)-B(2)	107.53(9)
O(1)-C(1)-C(2)	129.52(11)
O(1)-C(1)-C(9)	111.95(10)
C(2)-C(1)-C(9)	118.52(10)
C(1)-C(2)-C(3)	117.65(11)
C(4)-C(3)-C(2)	123.97(11)
C(3)-C(4)-C(5)	119.23(11)
C(9)-C(5)-C(6)	115.19(10)
C(9)-C(5)-C(4)	115.94(11)
C(6)-C(5)-C(4)	128.86(11)
C(7)-C(6)-C(5)	119.92(11)
C(6)-C(7)-C(8)	120.76(11)
N(1)-C(8)-C(7)	120.13(11)
N(1)-C(9)-C(5)	124.47(11)
N(1)-C(9)-C(1)	110.86(10)
C(5)-C(9)-C(1)	124.67(10)
C(11)-C(10)-C(15)	118.46(11)
C(11)-C(10)-B(1)	123.05(10)
C(15)-C(10)-B(1)	118.47(10)
C(12)-C(11)-C(10)	121.69(11)
C(13)-C(12)-C(11)	119.74(11)
C(12)-C(13)-C(14)	119.53(11)
C(13)-C(14)-C(15)	121.65(11)
C(14)-C(15)-C(10)	118.93(10)
C(14)-C(15)-B(2)	121.49(10)
C(10)-C(15)-B(2)	119.55(10)
C(17)-C(16)-C(21)	118.80(10)
C(17)-C(16)-B(2)	121.13(10)
C(21)-C(16)-B(2)	120.06(10)
C(18)-C(17)-C(16)	121.49(11)
C(19)-C(18)-C(17)	119.87(11)
C(18)-C(19)-C(20)	119.52(11)
C(19)-C(20)-C(21)	121.46(11)
C(20)-C(21)-C(16)	118.85(10)
C(20)-C(21)-B(1)	123.10(10)
C(16)-C(21)-B(1)	118.02(10)
O(2)-C(22)-C(23)	129.51(11)
O(2)-C(22)-C(30)	112.18(10)
C(23)-C(22)-C(30)	118.31(11)
C(22)-C(23)-C(24)	118.02(11)
C(25)-C(24)-C(23)	123.45(11)
C(24)-C(25)-C(26)	119.43(11)

C(30)-C(26)-C(27)	115.65(10)
C(30)-C(26)-C(25)	116.08(11)
C(27)-C(26)-C(25)	128.27(11)
C(28)-C(27)-C(26)	119.45(11)
C(27)-C(28)-C(29)	121.00(11)
N(2)-C(29)-C(28)	120.37(11)
N(2)-C(30)-C(26)	124.47(11)
N(2)-C(30)-C(22)	110.84(10)
C(26)-C(30)-C(22)	124.69(11)
O(1)-B(1)-C(21)	110.30(9)
O(1)-B(1)-C(10)	109.94(9)
C(21)-B(1)-C(10)	113.25(9)
O(1)-B(1)-N(1)	98.41(8)
C(21)-B(1)-N(1)	112.83(9)
C(10)-B(1)-N(1)	111.14(9)
O(2)-B(2)-C(15)	112.31(9)
O(2)-B(2)-C(16)	111.74(9)
C(15)-B(2)-C(16)	112.95(9)
O(2)-B(2)-N(2)	98.10(8)
C(15)-B(2)-N(2)	112.10(9)
C(16)-B(2)-N(2)	108.68(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj225.
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
O(1)	19(1)	20(1)	17(1)	1(1)	3(1)	-6(1)
O(2)	16(1)	17(1)	19(1)	2(1)	2(1)	-3(1)
N(1)	15(1)	16(1)	18(1)	1(1)	4(1)	-2(1)
N(2)	14(1)	15(1)	17(1)	-1(1)	3(1)	0(1)
C(1)	15(1)	15(1)	19(1)	-1(1)	4(1)	-1(1)
C(2)	20(1)	19(1)	18(1)	0(1)	5(1)	0(1)
C(3)	23(1)	17(1)	21(1)	2(1)	10(1)	0(1)
C(4)	19(1)	15(1)	25(1)	0(1)	9(1)	-2(1)
C(5)	15(1)	14(1)	21(1)	-1(1)	6(1)	1(1)
C(6)	16(1)	15(1)	24(1)	-3(1)	4(1)	-1(1)
C(7)	18(1)	19(1)	19(1)	-3(1)	2(1)	-1(1)
C(8)	18(1)	18(1)	18(1)	0(1)	4(1)	-1(1)
C(9)	15(1)	14(1)	17(1)	0(1)	5(1)	1(1)
C(10)	16(1)	18(1)	15(1)	0(1)	4(1)	-1(1)
C(11)	15(1)	23(1)	24(1)	-3(1)	4(1)	-2(1)
C(12)	16(1)	28(1)	28(1)	-3(1)	3(1)	4(1)
C(13)	22(1)	21(1)	26(1)	0(1)	4(1)	5(1)
C(14)	19(1)	18(1)	19(1)	1(1)	4(1)	0(1)
C(15)	15(1)	18(1)	13(1)	1(1)	3(1)	-1(1)
C(16)	16(1)	17(1)	14(1)	2(1)	2(1)	0(1)
C(17)	16(1)	20(1)	18(1)	3(1)	4(1)	-1(1)
C(18)	19(1)	24(1)	19(1)	3(1)	7(1)	4(1)
C(19)	23(1)	20(1)	20(1)	-1(1)	6(1)	4(1)
C(20)	20(1)	17(1)	20(1)	-1(1)	3(1)	-1(1)
C(21)	16(1)	17(1)	15(1)	2(1)	2(1)	0(1)
C(22)	14(1)	15(1)	20(1)	-1(1)	4(1)	2(1)
C(23)	16(1)	16(1)	26(1)	1(1)	6(1)	0(1)
C(24)	15(1)	19(1)	33(1)	-3(1)	4(1)	-3(1)
C(25)	16(1)	22(1)	26(1)	-4(1)	0(1)	-2(1)
C(26)	15(1)	17(1)	21(1)	-3(1)	2(1)	2(1)
C(27)	18(1)	21(1)	18(1)	-2(1)	1(1)	2(1)
C(28)	20(1)	19(1)	17(1)	1(1)	4(1)	2(1)
C(29)	17(1)	16(1)	18(1)	0(1)	4(1)	0(1)
C(30)	13(1)	14(1)	20(1)	-1(1)	4(1)	1(1)
B(1)	15(1)	17(1)	17(1)	0(1)	3(1)	-4(1)
B(2)	14(1)	15(1)	15(1)	2(1)	3(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj225.

	x	y	z	U(eq)
H(2A)	4817	6229	-410	22
H(3A)	6597	7038	-259	23
H(4A)	7939	7321	1454	23
H(6A)	8356	7120	3751	21
H(7A)	7642	6535	5254	22
H(8A)	5878	5725	4901	21
H(11A)	7074	4802	3101	25
H(12A)	7909	3725	3216	29
H(13A)	6311	2846	2965	27
H(14A)	3887	3055	2617	22
H(17A)	-3	4572	3386	21
H(18A)	-622	5548	4221	24
H(19A)	959	6433	4440	25
H(20A)	3151	6337	3807	23
H(23A)	-625	2697	2513	23
H(24A)	-2192	2555	785	26
H(25A)	-1999	3151	-841	26
H(27A)	-525	4082	-1781	23
H(28A)	1348	4818	-1463	22
H(29A)	2712	4915	352	20

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