Supporting Information

For

A BN Anthracene Mimics the Electronic Structure of More Highly Conjugated Systems

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General Considerations

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk technique or a nitrogen-filled glovebox. For air- and moisture-sensitive techniques, tetrahydrofuran, diethyl ether, methylene chloride, pentane, and toluene were purified by passing through a neutral alumina column under argon. All other solvents for air- and moisture-sensitive work were distilled after drying over calcium hydride. For all chromatography involving air- and moisture-sensitive compounds, silica gel (240-300 mesh) was heated under vacuum in a 150 ˚C oil bath for 12 hours. Chromatography for those compounds was performed in a glovebox using the dry, degassed solvents previously mentioned.

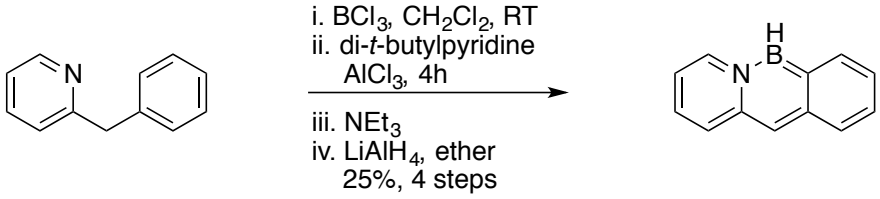
^{11}B NMR spectra were recorded on a Varian 500 spectrometer and externally referenced to neat $BF_3 \cdot Et_2O$. (δ 0). ^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 spectrometer, or a Varian 600 spectrometer. High-resolution mass spectrometry (HRMS) data were collected by Marek Domin at the Boston College Center for Mass Spectrometry using the Direct Analysis in Real Time (DART) technique.

UV-visible absorption spectra were acquired on a Cary 100 spectrometer. Emission spectra were acquired on a Quanta Master 40 spectrofluorimeter (Photon Technology International) in dry, degassed cyclohexane as solvent. Solution-phase quantum yields were determined using a PTI K-Sphere “petite” integrating sphere. Solid-state fluorescence spectra and quantum yield measurements were collected using the integrating sphere, and the solid was solution-cast from a CH_2Cl_2 solution onto a glass slide. The slide was oriented 72° from normal with respect to the detector, and excitation beam passed through the slide before reaching the sample.

Calculations were carried out using the Gaussian 09 program and the Linux cluster at Boston College.

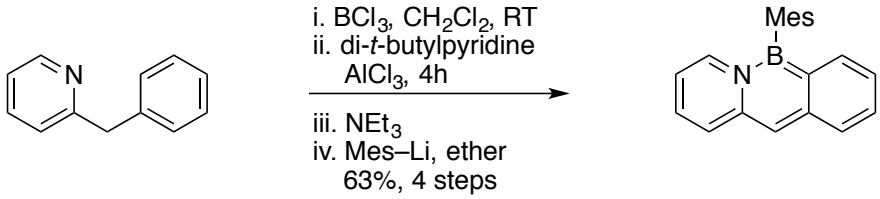
Synthetic Details

B-chloro-9a,9-BN-anthracene (1)



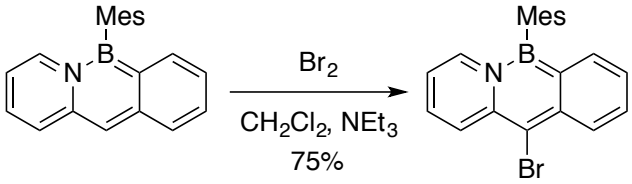
2-benzylpyridine (158 mg, 0.937 mmol, 1 equiv) and boron trichloride (0.94 mL 1M solution in hexanes, 0.94 mmol, 1 equiv) was stirred at room temperature in 10 mL CH_2Cl_2 for 10 minutes. Aluminum chloride (250. mg, 1.87 mmol 2 equiv) and 2,6-di-*tert*-butylpyridine (179 mg, 0.937 mmol, 1 equiv) were added and the mixture was stirred under inert gas for 6 hours. The solvent was removed *in vacuo,* and the residue was rinsed with pentane (Borenium ^{11}B NMR ∂ 45 (s)). The residue was suspended in 50 mL CH_2Cl_2 (some solid did not dissolve), and triethylamine (0.36 mL, 2.8 mmol, 3 equiv) was added. Pentane (20 mL) was added to the mixture, which was stirred vigorously. Two layers formed, and the mixture was allowed to sit at room temperature until the layers became clear. The upper, yellow phase contained the product, while the bottom, red phase contained triethylammonium salts. The top phase was collected, and its volatiles were removed to reveal a yellow powder, which contained intermediate **5**. ^{11}B NMR (160 MHz, CH_2Cl_2) δ 34.7 (s). HRMS (DART+) $[M]^+$ calcd for $C_{12}H_{10}BNCl$ 214.05948, found 214.05953. Crude **5** was suspended in 50 mL ether and cooled to –30 °C in the glovebox freezer. Lithium aluminum hydride (14 mg, 0.38 mmol, 0.4 equiv) was carefully added, and the reaction mixture was allowed to warm to room temperature over 4.5 hours. The mixture was passed through an acrodisc and concentrated *in vacuo*. The residue was recrystallized from ether at –30 °C to yield a yellow solid (42 mg, 25% over 2 steps). ^1H NMR (500 MHz, CD_2Cl_2) δ 8.25 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.69 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.37 (ddd, J = 7.8, 6.8, 1.1 Hz, 1H), 7.29 (d, J = 9.3 Hz, 1H), 7.05 (s, 1H), 6.86 (ddd, J = 9.4, 6.2, 1.2 Hz, 1H), 6.38 (ddd, J = 7.4, 6.2, 1.3 Hz, 1H). *B*–H can be observed as a broad signal from 6.5–5.5 ppm. ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.5 141.1, 138.1, 136.80, 131.3, 126.1, 125.93, 125.0, 122.6, 110.4, 107.4. Carbon adjacent to boron not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 37.5 (d, J = 133.5 Hz). FTIR (ATR thin film): 3049, 2546, 1622, 1515, 1361, 1262, 807. HRMS (DART+) $[M+H]^+$ calcd for $C_{12}H_{11}NB$ 180.09845, found 180.09886. X-ray quality crystals were obtained by crystallization from a saturated ether solution at –30 °C.

B-Mesityl-9,9a-BN-anthracene (6)



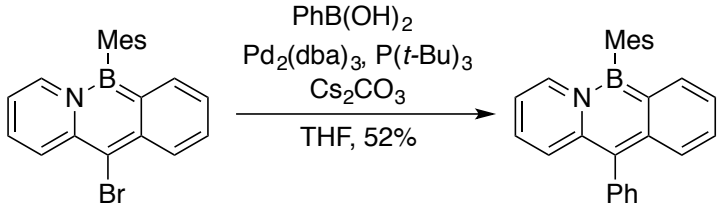
This procedure assumes a 100% yield of the *B*-Cl BN anthracene from an 11.8 mmol reaction of 2-benzylpyridine. Solid mesityllithium was used as the nucleophile, and it was added at room temperature until reaction was judged complete by ^{11}B NMR (1.42 g, 11.3 mmol, 0.96 equiv). Silica gel was added to the crude mixture, and the volatiles were removed under reduced pressure. The residue was filtered through a plug of silica gel using methylene chloride as the eluent, and the filtrate was concentrated under reduced pressure. The residue was rinsed with small amounts of pentane, yielding a bright yellow powder (yield: 2.20 g, 63%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.85 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.35 (d, J = 9.7 Hz, 1H), 7.29 (td, J = 7.4, 6.8, 1.1 Hz, 1H), 7.13 (s, 1H), 7.04 (s, 2H), 6.85 (td, J = 6.2, 3.1 Hz, 1H), 6.25 (t, J = 7.5 Hz, 1H), 2.44 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 141.3, 140.7, 139.5, 138.2, 136.3, 134.8, 131.5, 127.8, 127.2, 126.4, 125.0, 123.1, 110.9, 107.6, 22.6, 21.6. Carbons adjacent to boron not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 40.7. FTIR (ATR thin film): 2913, 1640, 1606, 1514, 907, 807. HRMS (DART+) $[M+H]^+$ calcd. for $C_{21}H_{21}NB$ 298.17670, found 298.17766. X-ray quality crystals were obtained from cooling a saturated ether solution to –30 °C.

10-bromo-9-mesityl-9,9a-BN-anthracene (7)



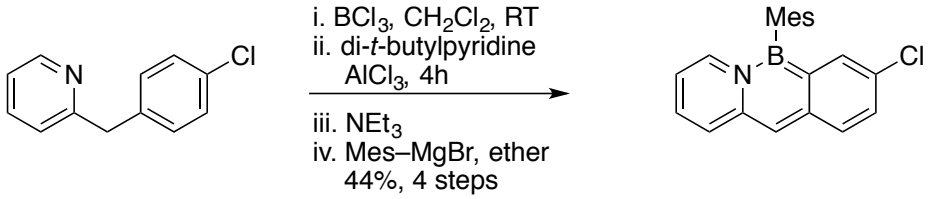
In a glovebox, compound **6** (301 mg, 1.01 mmol, 1 equiv) was dissolved in 50 mL CH_2Cl_2, and triethylamine (0.7 mL, 5.05 mmol, 5 equiv) was added. Bromine (52 µL, 1.01 mmol, 1 equiv) was separately dissolved in 10 mL CH_2Cl_2, and this solution was carefully added to the starting material. The reaction was monitored by ^{1}H NMR, and completion took approximately 20 minutes. The crude reaction mixture was passed through a short plug of silica gel with CH_2Cl_2as the eluent. The solvent was removed under reduced pressure to yield a yellow solid (yield: 283 mg, 75%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 9.6 Hz, 1H), 7.82 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.71 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.11 – 7.05 (m, 1H), 6.99 (s, 2H), 6.34 (ddd, *J* = 7.5, 6.2, 1.3 Hz, 1H), 2.39 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 140.6, 138.6, 136.7, 135.8, 132.9, 128.2, 128.0, 127.36, 127.35, 126.5, 126.1, 123.9, 111.0, 102.5, 22.6, 21.6. Carbons adjacent to boron were not observed. FTIR (ATR thin film): 2917, 1604, 1555, 1475, 1047, 750, 593. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 41.6 (s). HRMS (DART+) $[M+H]^+$ calcd. for $C_{21}H_{20}NBBr$ 376.08722, found 376.08552.

10-phenyl-9-mesityl-9,9a-BN-anthracene (8)



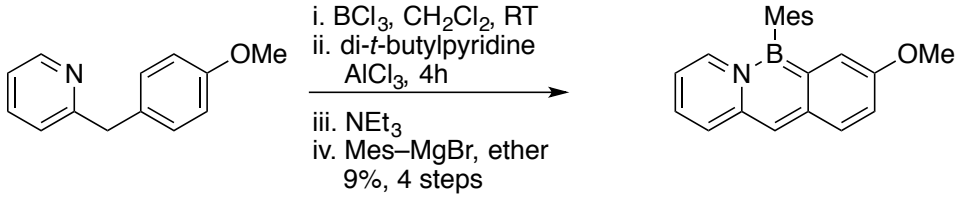
In a glovebox, compound **7** (134 mg, 0.356 mmol, 1 equiv) was combined in 6 mL THF with phenylboronic acid (65 mg, 0.53 mmol, 1.5 equiv), and cesium carbonate (232 mg, 0.712 mmol, 2 equiv). Separately in 2 mL THF, tris(dibenzylidineacetone)dipalladium(0) (8 mg, 0.009 mmol, 3 mol%) and tri-tert-butylphosphine (4 mg, 0.02 mmol, 6 mol%) were combined and stirred for 5 minutes. The palladium catalyst solution was added by pipet to the rest of the reaction mixture. The mixture was stirred at room temperature for 24 hours, and the mixture was subsequently filtered. The volatiles were removed under reduced pressure, and the residue was passed through a plug of silica gel using CH_2Cl_2 as the eluent. The filtrate was concentrated to a yellow-orange powder under reduced pressure. The powder was rinsed with small amounts of pentane (The filtrate was red in color.), and the final product was a bright yellow powder (Yield: 69 mg, 52%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.79 (d, *J* = 7.1 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.61 – 7.47 (m, 4H), 7.42 (app. d 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.24 (ddd, *J* = 7.8, 6.8, 1.1 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.02 (s, 2H), 6.71 (ddd, *J* = 9.5, 6.1, 1.3 Hz, 1H), 6.24 (ddd, *J* = 7.4, 6.0, 1.4 Hz, 1H), 2.41 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 141.1, 140.8, 140.0, 138.2, 136.9, 136.4, 135.1, 132.7, 131.4, 129.5, 127.9, 127.7, 125.7, 125.5, 124.9, 123.0, 118.7, 110.7, 22.7, 21.6. Carbons adjacent to boron were not observed. FTIR (ATR thin film): 2912, 1563, 1491, 1386, 852, 783. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 41.2 (s). HRMS (DART+) $[M+H]^+$ calcd. for $C_{27}H_{25}NB$ 374.20880, found 374.20899.

2-Chloro-BN-9a,9-anthracene (9)



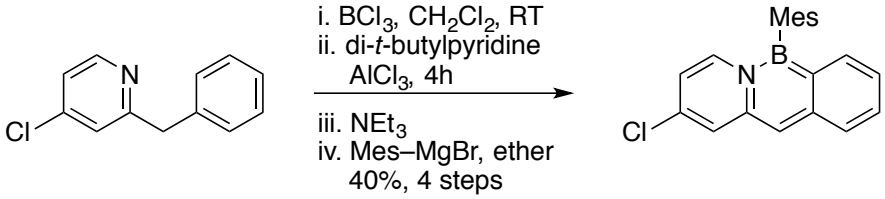
This procedure mirrors that of **6** and was performed at a 2.45 mmol scale using mesitylmagnesium bromide as the nucleophile. Yield: 359 mg, 44%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.76 (d, J = 8.7 Hz, 1H), 7.63 (s, 1H), 7.61 – 7.57 (m, 2H), 7.34 (dd, J = 9.3, 1.4 Hz, 1H), 7.09 (s, 1H), 6.98 (s, 2H), 6.88 (ddd, J = 9.3, 6.2, 1.3 Hz, 1H), 6.28 (ddd, J = 7.5, 6.2, 1.4 Hz, 1H), 2.39 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 140.7, 139.9, 139.5, 138.5, 134.77, 134.75, 132.0, 129.6, 128.4, 128.0, 127.2, 125.5, 111.5, 107.2, 22.6, 21.6. Carbons adjacent to boron were not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 40.7 (s). FTIR (ATR thin film) 2915, 1641, 1455, 1169, 846. HRMS (DART+) $[M+H]^+$ calcd. for $C_{21}H_{20}BNCl$ 332.13773, found 332.13760.

2-methoxy-B-mesityl-9a,9-BN-anthracene (10)



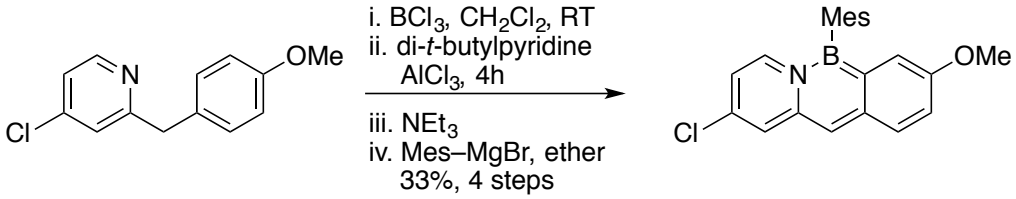
The procedure mirrors that of **6**, completed on a 2.76 mmol scale using mesitylmagnesium bromide as the nucleophile. Yield: 82 mg, 9%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.75 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 7.3 Hz, 1H), 7.33 (dd, J = 8.8, 2.7 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.08 (d, J = 2.8 Hz, 1H), 7.05 (s, 1H), 6.97 (s, 2H), 6.75 (dd, J = 9.3, 6.3 Hz, 1H), 6.19 (ddd, J = 7.5, 6.1, 1.6 Hz, 1H), 3.72 (s, 3H), 2.38 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.1, 140.7, 138.1, 137.9, 136.0, 134.4, 128.4, 127.9, 127.3, 123.8, 122.6, 115.2, 111.0, 107.5, 55.8, 22.5, 21.6. Carbons adjacent to boron were not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 39.9 (s). FTIR (ATR thin film): 2914, 1584, 1554, 1030, 798. HRMS (DART+) $[M+H]^+$ calcd. for $C_{22}H_{23}BNO$ 328.18727, found 328.18616.

3-Chloro-BN-9a-9-anthracene (11)



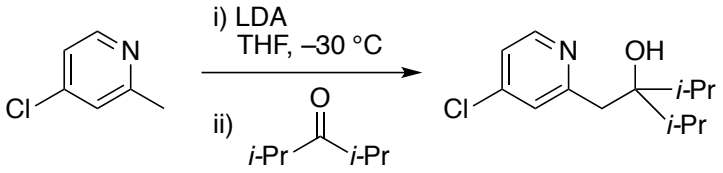
The procedure mirrors that of **6**, completed on a 3.91 mmol scale. Yield: 515 mg, 40%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.57 (d, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.31 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H), 7.05 (s, 1H), 7.01 (s, 2H), 6.21 (dd, *J* = 7.7, 2.2 Hz, 1H), 2.42 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 141.3, 140.7, 138.8, 138.5, 137.8, 136.4, 132.0, 131.1, 127.9, 126.5, 124.7, 123.7, 112.5, 107.5, 22.6, 21.6. Carbons adjacent to boron were not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 41.4 (s). FTIR (ATR thin film): 2913, 1631, 1607, 1519, 1334, 937, 751, 638. HRMS (DART+) $[M+H]^+$ calcd. for $C_{21}H_{20}BNCl$ 332.13773, found 332.13628.

3-Chloro-8-methoxy-B-mesityl-9a,9-BN-anthracene (12)



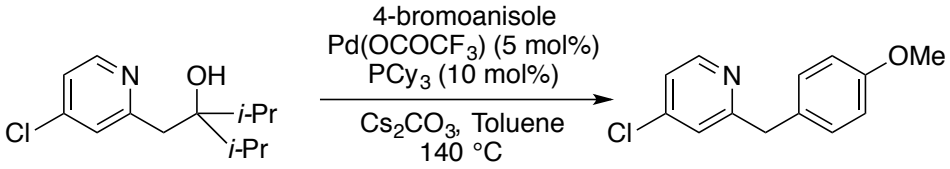
This procedure mirrors that of **6** and was performed on a 2.14 mmol scale using mesitylmagnesium bromide as the nucleophile. Yield: 255 mg, 33% ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.74 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.27 (d, *J* = 2.3 Hz, 1H), 7.08 (d, *J* = 2.7 Hz, 1H), 6.97 (app. s, 3H), 6.12 (dd, *J* = 7.8, 2.2 Hz, 1H), 3.72 (s, 3H), 2.37 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.6, 138.4, 137.2, 136.1, 135.9, 129.7, 128.4, 128.0, 124.8, 122.9, 115.5, 112.5, 110.6, 107.4, 55.8, 22.5, 21.6. Carbons adjacent to boron were not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 40.6 (s). FTIR (ATR thin film) 2961, 1630, 1557, 1285, 1068, 798. HRMS (DART+) $[M+H]^+$ calcd. for $C_{22}H_{22}ONBCl$ 362.14871, found 362.14846.

3-((4-chloropyridin-2-yl)methyl)-2,4-dimethylpentan-3-ol (S-1)



Diisopropylamine (6.35 mL, 45.1 mmol, 1.15 equiv) was cooled to –30 °C, and *n*-butyllithium (2.5 M in hexanes) (17.2 mL, 43.1 mmol, 1.1 equiv) was added dropwise at –30 °C. The mixture was stirred 10 minutes at this temperature, then 4-chloro-2-picoline (5.00 g, 39.2 mmol, 1 equiv) was added dropwise at –30 °C. After stirring 30 minutes at this temperature, diisopropyl ketone (5.37 g, 47.0 mmol, 1.2 equiv) was added dropwise, and then the bath was removed. The mixture was stirred for 2 hours more, whereupon it was poured into 30 mL water. The organics were extracted into ethyl acetate and washed with brine. The volatiles were removed using a rotary evaporator. The residue was purified using silica gel chromatography (3:1 hexane:ethyl acetate as the mobile phase). Yielded a pale yellow liquid which solidified upon further evacuation (9.37 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 5.4 Hz, 1H), 7.22 (s, 1H), 7.16 (dd, J = 5.4, 1.9 Hz, 1H), 5.86 (s, 1H), 2.89 (s, 2H), 1.91 (hept, J = 6.9 Hz, 2H), 0.90 (d, J = 6.6 Hz, 6H) 0.89 (d, J = 6.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.5, 149.0, 144.9, 124.9, 121.7, 78.3, 38.5, 35.3, 18.3, 18.1. FTIR (ATR thin film): 3362, 2961, 1678, 1469, 1029, 710. HRMS (DART+) $[M+H]^+$ calcd for $C_{13}H_{21}NOCl$ 242.13117, found 242.13162.

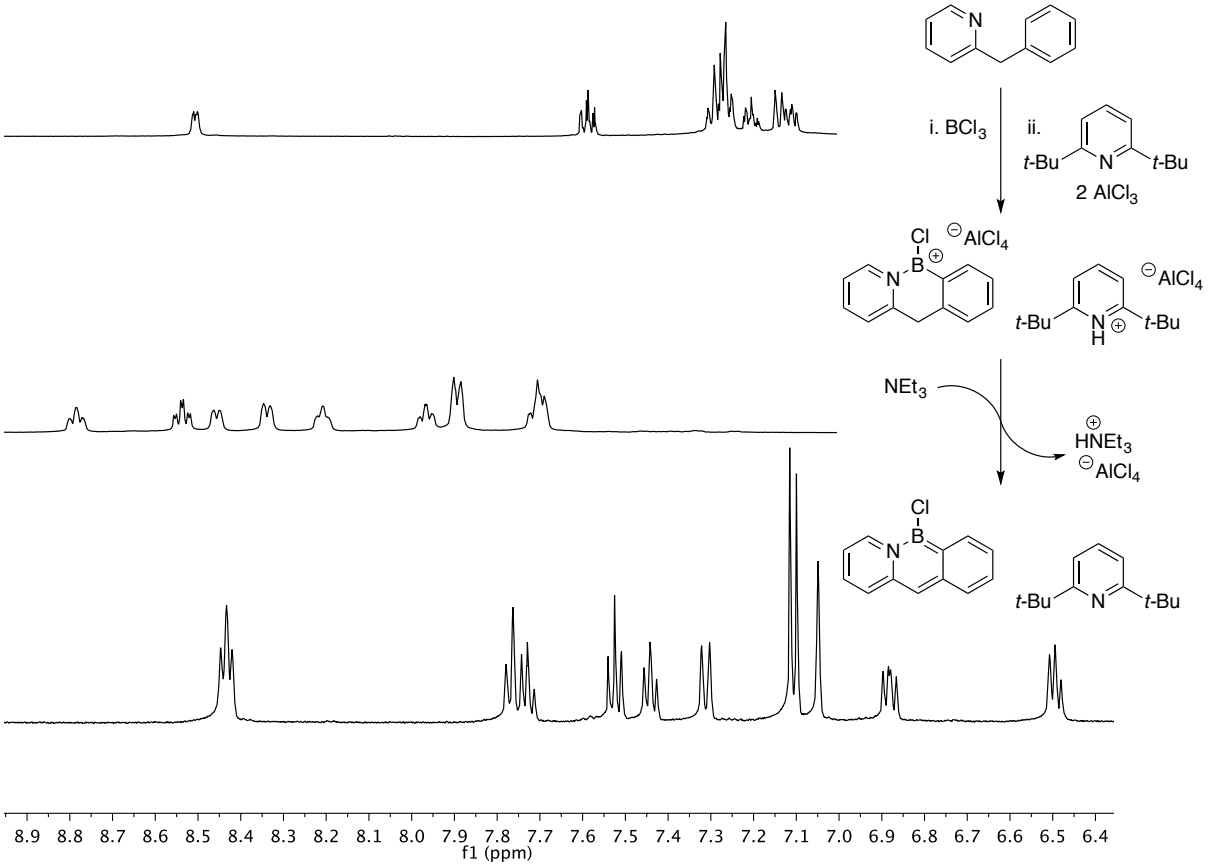
4-((4-chloropyridin-2-yl)methyl)phenol (S-2)



Compound **S-1** (3.21 g, 13.2 mmol, 1 equiv) was combined in a pressure vessel with 4-bromoanisole (2.72 g, 14.6 mmol, 1.1 equiv), cesium carbonate (5.19 g, 15.9 mmol, 1.2 equiv) Pd(TFA)2 (221 mg, 0.664 mmol, 5 mol%) and tricyclohexylphosphine (372 mg, 1.33 mmol, 10 mol%) and 10 mL toluene. The pressure vessel was sealed and heated to 140 °C for 16 hours. The mixture was cooled to room temperature, diluted with ethyl acetate, and the mixture was passed through a short plug of silica gel using ethyl acetate as the eluent. The filtrate was concentrated using a rotary evaporator. The residue was subjected to silica gel chromatography (10:1 hexane:ethyl acetate gradient to 3:1) to yield a yellow oil. Yield: 1.25 g, 40%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 5.4 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 5.5 Hz, 1H), 7.09 (s, 1H), 6.86 (d, J = 8.3 Hz, 2H), 4.08 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 158.6, 150.3, 144.6, 130.8, 130.3, 123.4, 121.8, 114.3, 55.4, 43.7. FTIR (ATR thin film): 2931, 2835, 1612, 1573, 1247, 1035, 885. HRMS (DART+) $[M+H]^+$ calcd for $C_{13}H_{13}NOCl$ 234.06857, found 234.06765.

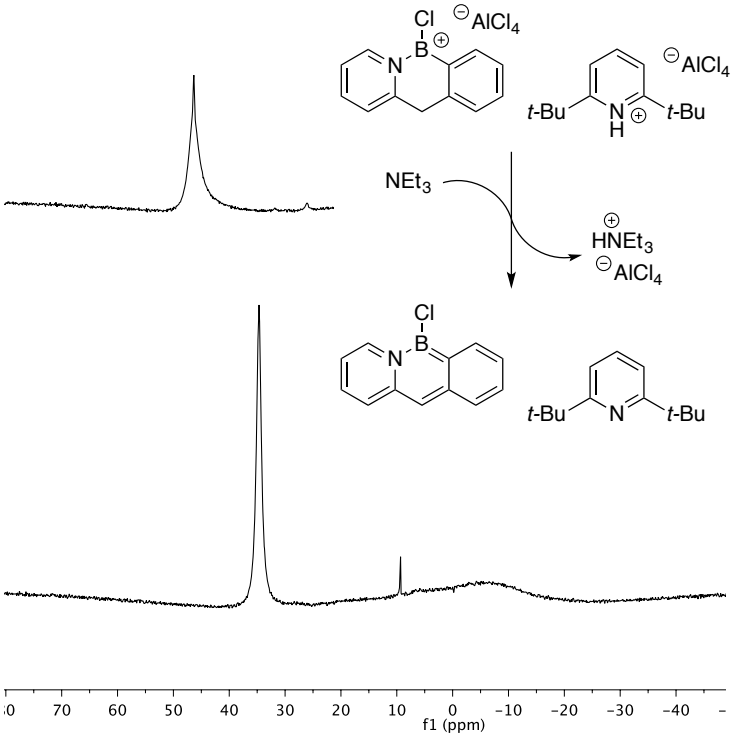
NMR Studies of the Borenium Formation and Aromatization

Figure S-1: ^{1}H NMR of the reaction sequence leading to 9,9a-BN anthracenes



Solvent: CD_2Cl_2

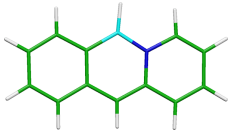
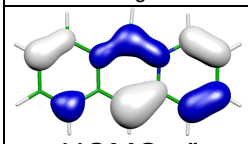
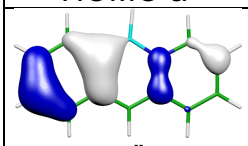
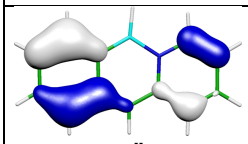
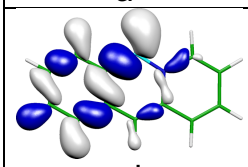
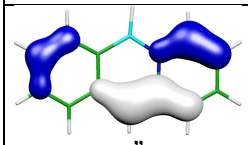
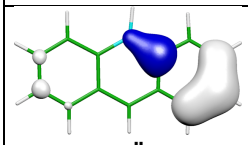
Figure S-2: ^{11}B NMR of the reaction sequence leading to 9,9a-BN anthracenes. The ^{11}B signal for boron trichloride also occurs at 46 ppm in methylene chloride, and this accounts for the unusual peak shape in the spectrum for the borenium species.



UV-Photoelectron Spectroscopy

The UV-PES spectra were recorded on a home-built (IPREM/ECP), three-part spectrometer equipped with a main body device, He-I radiation source (21.21 eV and/or 48 eV) and a 127° cylindrical analyzer. The spectrometer works at constant analyzer energy under $5x10^{-6}$ hPa working pressure and $\leq 10^{-7}$ hPa for channeltron (X914L) pressure. The monitoring is done by a microcomputer supplemented by a digital–analogue converter (AEI spectrum). The spectra resulting from a single scan are built from 2048 points and are accurate within 0.05 eV. Spectra are calibrated with lines of xenon (12.13 and 13.44 eV) and of argon (15.76 and 15.94 eV). The accuracy of the ionization energies is ± 0.03 eV for sharp peaks and ± 0.05 eV for broad and overlapping signals. Mass spectra were recorded on a modified quadrupole mass spectrometer (PFEIFFER Prisma QMS200) with an electron-impact at 50 eV (mass range: 200 amu; detection limit: $\leq 10^{-14}$ hPa; working pressure: $2x10^{-7}$ hPa; operating temperature: 200 °C; electronic amplifier in working conditions: 10^{-10} A, QUAD STAR422 software for recording and treatment of MS data). The samples were slowly vaporized under low pressure (10^{-6} Torr) inside a handmade three-valve injector (3/4 inch diameter; 10 cm length; working temperature: –190 °C $\leq T \leq$ +300 °C), and the gaseous flow was then continuously and simultaneously analyzed by both UV-photoelectron and mass spectrometers.

Table S-1. UV-PES and calculated ionization energies.

Nature of MO  C_s	$-\varepsilon^{K-S}$	ΔSCF+TD-DFT	OVGF	P3	SAC-CI	Corrected x_{exp}= 0.655	Exp.
 HOMO a”	6.385	6.893	6.768	6.931	6.180	7.04	**7.04**
 a”	8.371	8.937	8.600	8.856	8.284	9.026	**8.85**
 a”	8.613	9.119	8.907	9.080	8.600	9.268	**9.13**
 a’	10.194	10.505	10.444	10.503	10.150	10.849	**10.44**
 a”	10.210	10.734	10.730	10.869	10.275	10.865	**10.52**
 a”	10.365	10.691	10.652	10.738	10.427	11.020	**10.99**

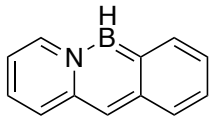
Computational Details

All calculations were performed using the Gaussian 09 program. TD-DFT single-point calculations were carried out at the CAM-B3LYP/6-311G(d,p) level using the PCM solvent model for cyclohexane. NICS calculations were performed at the B3LYP/6-311G(d,p) using B3LYP/6-311G(d,p) optimized geometries.

Full Reference for Gaussian 09

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*; Gaussian Inc., Wallingford, CT, 2010.

Optimized Coordinates



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C	1.303837	0.751100	0.000000
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H	2.567429	2.477991	0.000001
H	4.680814	1.186903	0.000004
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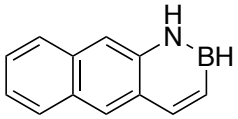

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H	0.01498800	-2.48012200	0.00000000
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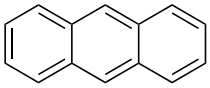

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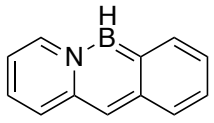

with dummy atoms for NICS(0)

C	-4.491	2.686	0.477
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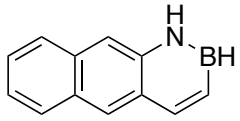
C	-2.941	0.802	0.384
C	-3.968	0.04	-0.214
C	-5.206	0.577	-0.457
N	-0.603	1.124	1.28
B	-1.568	0.248	0.667
H	-4.697	3.716	0.745
H	-6.442	2.339	-0.298
H	-3.762	-0.991	-0.482
H	-5.985	-0.018	-0.916
C	-2.187	2.932	1.337
C	-0.936	2.451	1.602
C	0.679	0.659	1.562
C	1.623	1.421	2.131
C	1.313	2.78	2.472
C	0.084	3.262	2.214
H	-2.397	3.96	1.603
H	2.067	3.406	2.933
H	-0.182	4.283	2.458
H	0.847	-0.371	1.28
H	2.602	1.007	2.327
H	-1.216	-0.862	0.422
Bq	-4.213	1.36133	0.1365
Bq	-1.90733	1.6175	1.00067
Bq	0.36	1.9495	1.87683



with dummy atoms for NICS(0)

C	-3.94500	0.36800	0.04500
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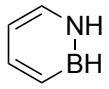
C	-6.30700	1.93400	-0.01300
C	-5.08200	2.56300	-0.02200
C	-3.86900	1.80900	0.00600
C	-2.59800	2.42000	-0.00300
C	-1.41500	1.68000	0.02500
C	-1.50400	0.24300	0.06400
C	-2.74700	-0.38100	0.07300
C	-0.11500	2.31800	0.01500
C	1.05100	1.60800	0.04200
B	0.99200	0.07800	0.08400
N	-0.31500	-0.49300	0.09100
H	1.93100	-0.65700	0.11000
H	-0.43400	-1.49900	0.11800
H	-0.11500	3.40800	-0.01500
H	1.99300	2.15200	0.03300
H	-2.80400	-1.46600	0.10200
H	-2.53600	3.50500	-0.03200
H	-5.01800	3.64700	-0.05200
H	-7.22200	2.51700	-0.03400
H	-7.35300	0.02900	0.03300
H	-5.29100	-1.33300	0.08300
Bq	-0.21767	0.90567	0.05350
Bq	-2.67967	1.02317	0.03500
Bq	-5.13617	1.15617	0.01600



with dummy atom for NICS(0)

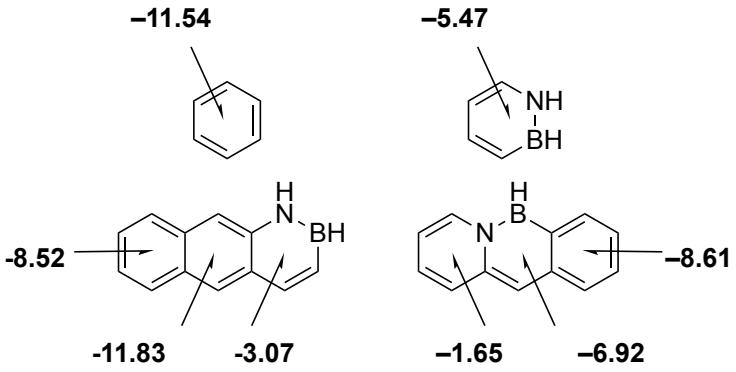
C	-2.795	2.87	0.
C	-3.99	2.209	0.
C	-4.021	0.787	0.
C	-2.868	0.037	0.
B	-1.534	0.747	0.
N	-1.616	2.18	0.
H	-2.735	3.952	0.
H	-4.909	2.78	0.
H	-4.997	0.306	0.
H	-0.778	2.745	0.
H	-2.961	-1.045	0.
H	-0.452	0.249	0.
Bq	-2.804	1.472	0.

 with dummy atom for NICS(0)

C	-2.995	1.914	0.
C	-4.214	1.231	0.
C	-1.795	1.201	0.
C	-1.813	-0.196	0.
C	-3.031	-0.879	0.
C	-4.231	-0.165	0.
H	-2.982	3.001	0.
H	-5.148	1.787	0.
H	-0.847	1.732	0.
H	-0.878	-0.751	0.
H	-3.045	-1.966	0.
H	-5.179	-0.697	0.
Bq	-3.01317	0.51767	0.

NICS(0) Results

Figure S-3: Results of the NICS(0) calculations



TD-DFT Results

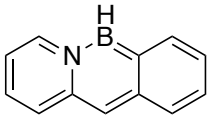
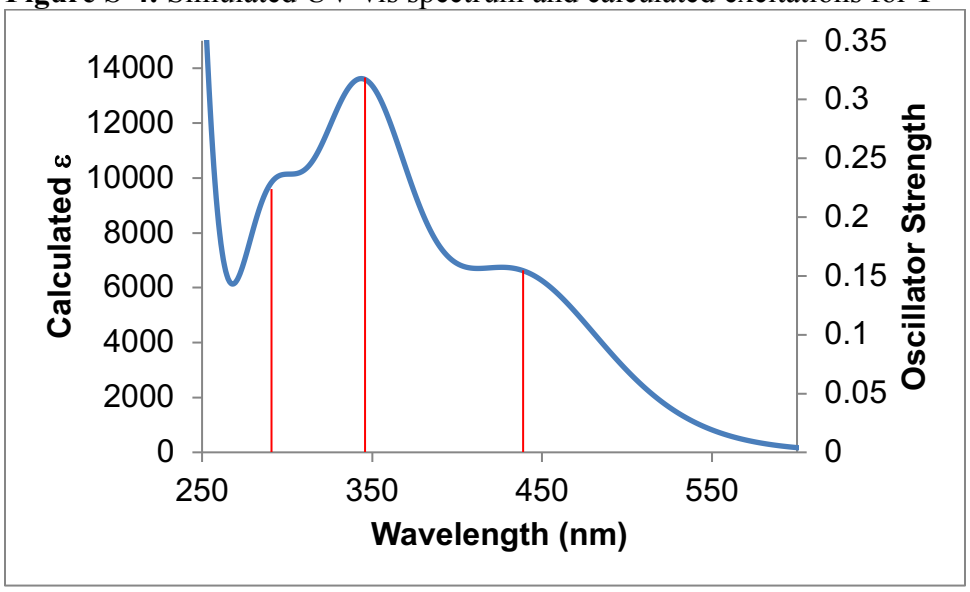


Figure S-4: Simulated UV-vis spectrum and calculated excitations for **1**



Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 2.8251 eV 438.87 nm f=0.1548 <S**2>=0.000
47 -> 48 -0.69996

Excited State 2: Singlet-A 3.58 eV 345.88 nm f=0.3187 <S**2>=0.000
46 -> 48 0.15213
47 -> 49 0.67809

Excited State 3: Singlet-A 4.26 eV 290.85 nm f=0.2239 <S**2>=0.000
47 -> 50 0.69036

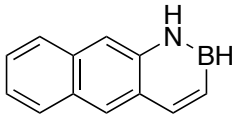
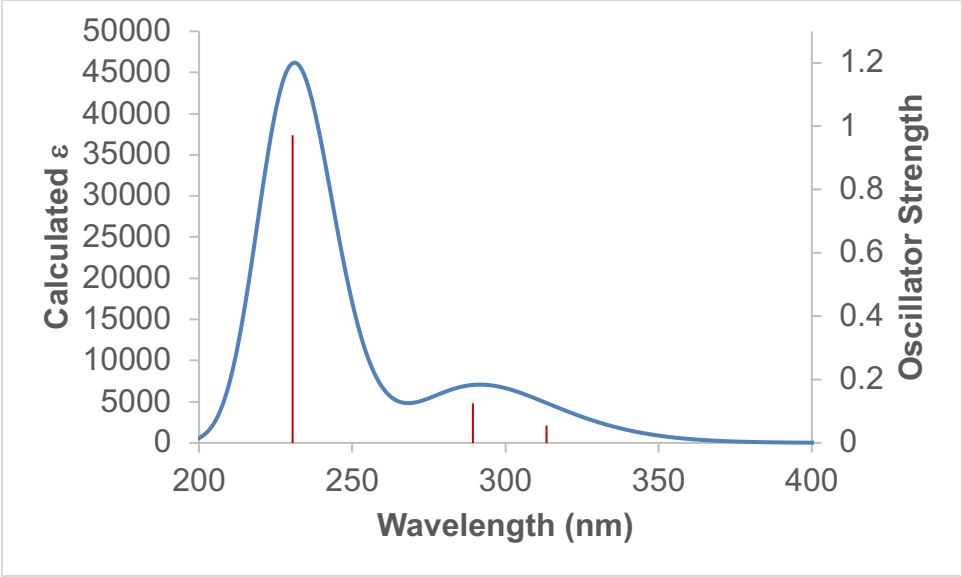


Figure S-5: Simulated UV-vis spectrum and calculated excitations for **X-H**



Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.96 eV 313.41 nm f=0.0542 <S**2>=0.000
46 -> 48 0.18060
46 -> 49 -0.14382
47 -> 48 0.65517

Excited State 2: Singlet-A 4.28 eV 289.37 nm f=0.1243 <S**2>=0.000
46 -> 48 0.55457
47 -> 48 -0.21359
47 -> 49 0.34890
47 -> 50 -0.10777

Excited State 3: Singlet-A 5.38 eV 230.53 nm f=0.9714 <S**2>=0.000
45 -> 48 0.12199
46 -> 48 -0.30517
46 -> 49 -0.10560
46 -> 50 -0.13452
47 -> 49 0.54097
47 -> 50 0.22829

Additional Optical Spectra

Figure S-6: Emission Spectra of **1** and **6** Compared with Anthracene and Tetracene

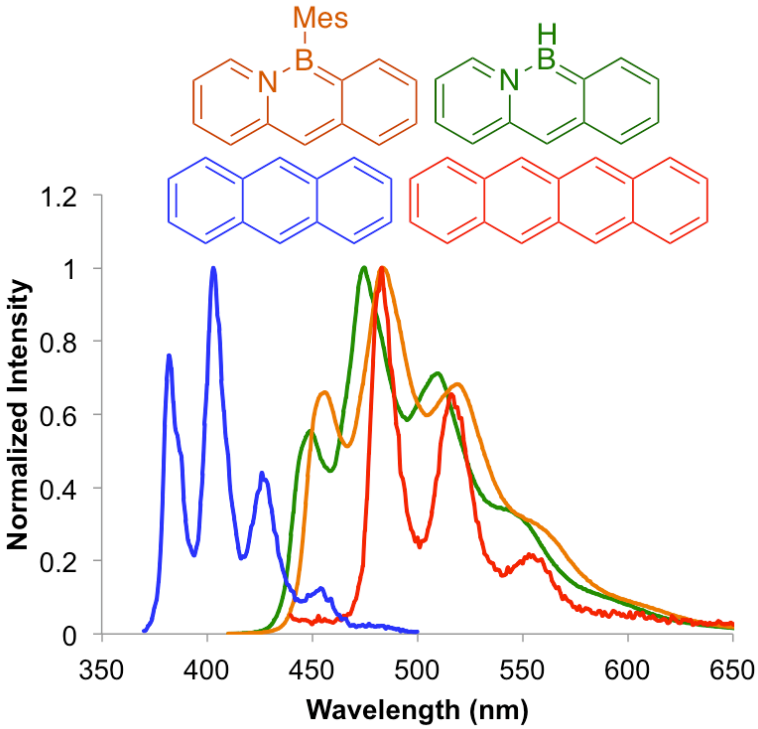


Figure S-7: Absorption Spectra of BN-9a,9 anthracenes

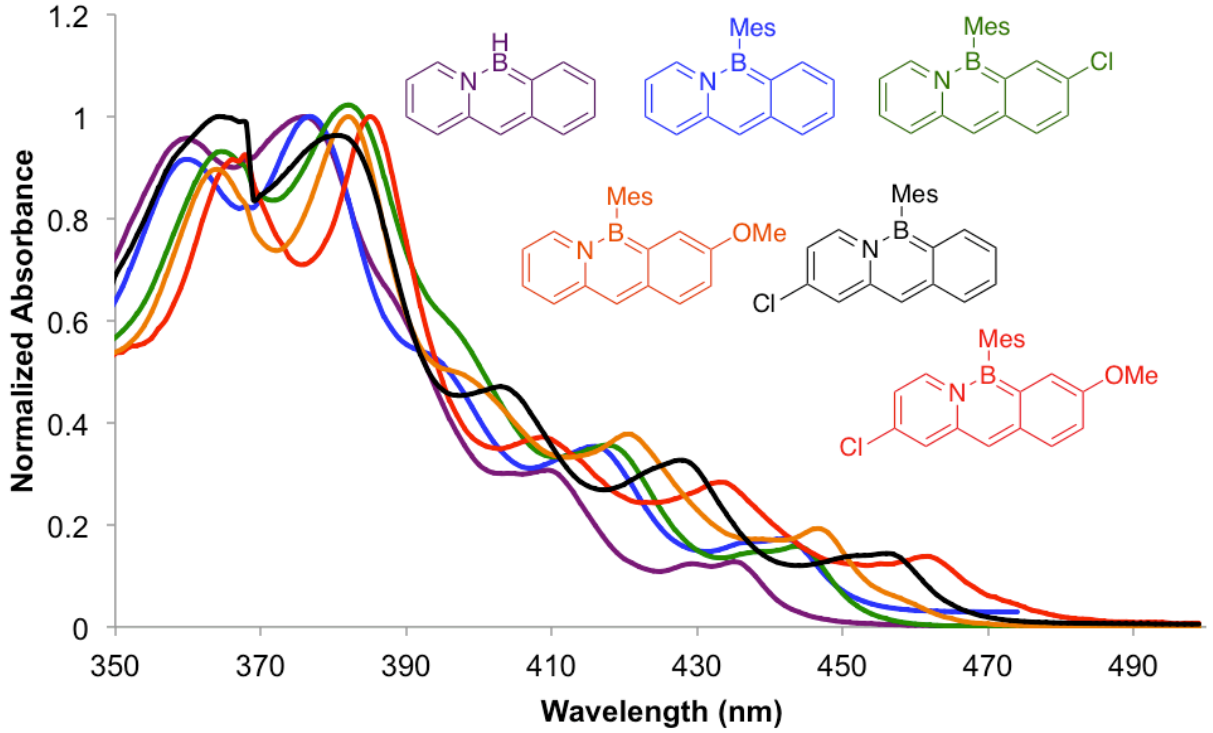


Figure S-8: Emission Spectra of BN-9a,9 anthracenes

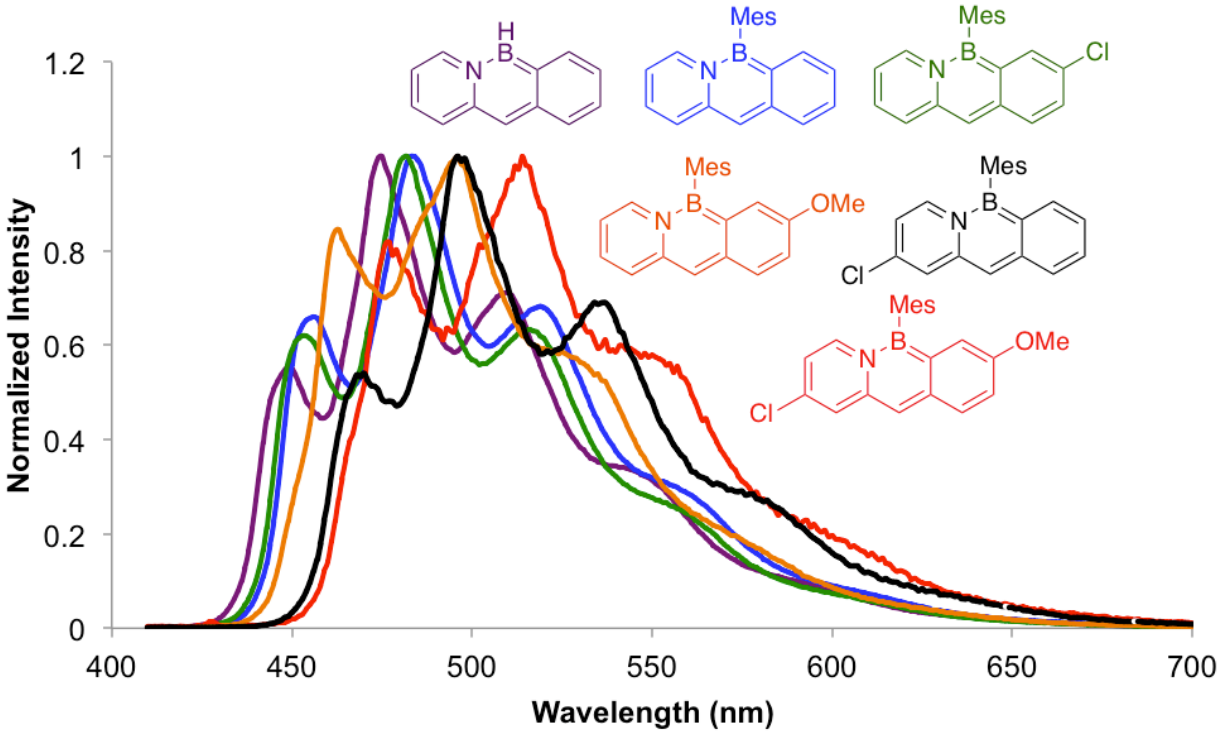
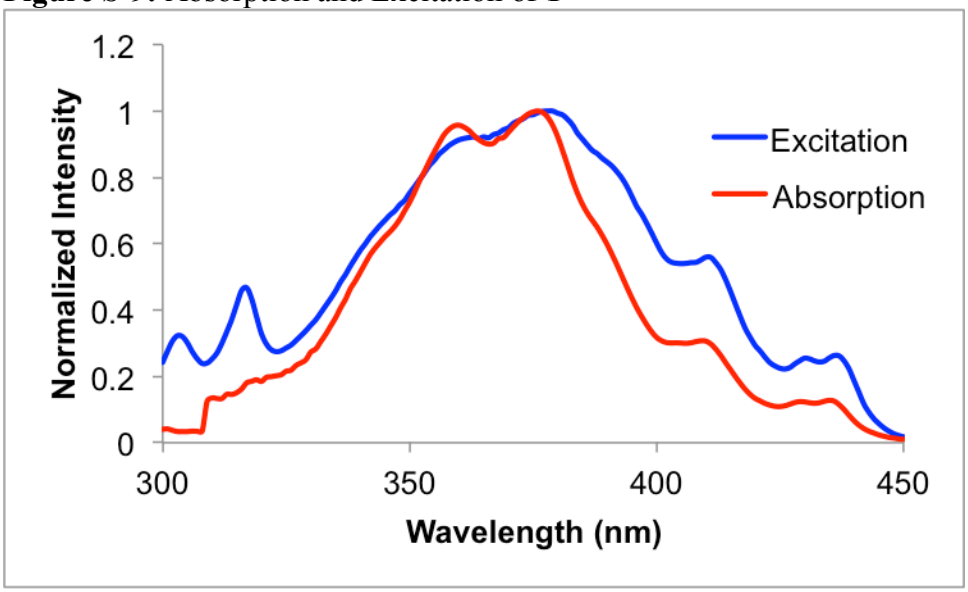


Figure S-9: Absorption and Excitation of **1**



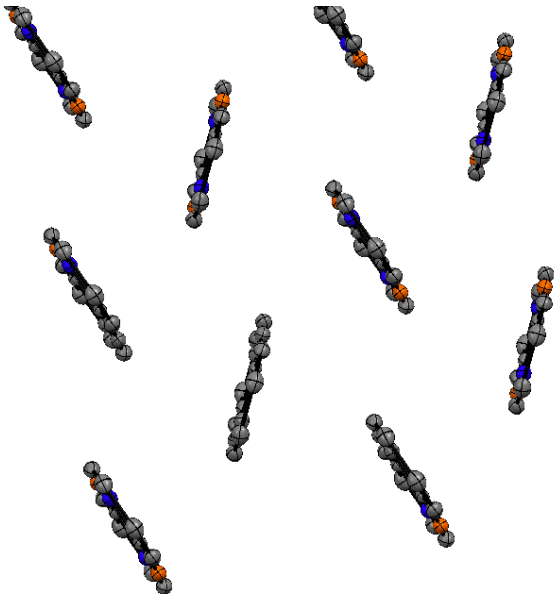
Crystal data and structure refinement for compound 1.

Identification code	C12H10BN	
Empirical formula	C12 H10 B N	
Formula weight	179.02	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.2912(5) Å	α= 90°.
	b = 6.0861(3) Å	β= 102.492(3)°.
	c = 8.3411(5) Å	γ = 90°.
Volume	460.50(4) $Å^3$	
Z	2	
Density (calculated)	1.291 Mg/m^3	
Absorption coefficient	0.565 mm^{-1}	
F(000)	188	
Crystal size	0.180 x 0.080 x 0.060 mm^3	
Theta range for data collection	4.875 to 67.325°.	
Index ranges	-11<=h<=10, -7<=k<=7, -9<=l<=9	
Reflections collected	3742	
Independent reflections	822 [R(int) = 0.0216]	
Completeness to theta = 67.325∞	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7529 and 0.6754	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	822 / 0 / 67	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.1028	
R indices (all data)	R1 = 0.0398, wR2 = 0.1048	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.220 and -0.201 $e.Å^{-3}$	

Crystal data and structure refinement for compound 6.

Identification code	C21H20BN	
Empirical formula	C21 H20 B N	
Formula weight	297.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.8660(6) Å	α= 82.031(2)°.
	b = 9.3604(7) Å	β= 82.674(2)°.
	c = 11.0495(8) Å	γ = 66.299(2)°.
Volume	828.93(10) $Å^3$	
Z	2	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	316	
Crystal size	0.600 x 0.370 x 0.240 mm^3	
Theta range for data collection	1.867 to 33.316°.	
Index ranges	-13<=h<=13, -14<=k<=14, -17<=l<=17	
Reflections collected	31412	
Independent reflections	11905 [R(int) = 0.0206]	
Completeness to theta = 25.242∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7465 and 0.7101	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11905 / 3 / 421	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1179	
R indices (all data)	R1 = 0.0492, wR2 = 0.1231	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.424 and -0.260 $e.Å^{-3}$	

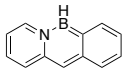
Figure S-10: Crystal packing of **1**. Hydrogen atoms omitted for clarity. Thermal ellipsoids depicted at the 50% probability level.

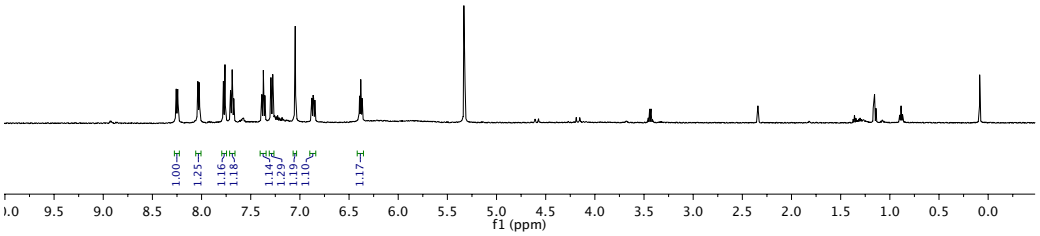


NMR Spectra of New Compounds

ji-VI-H227_D

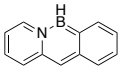
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-05-26T17:32:03
5 Spectrometer Frequency	499.78
6 Nucleus	1H

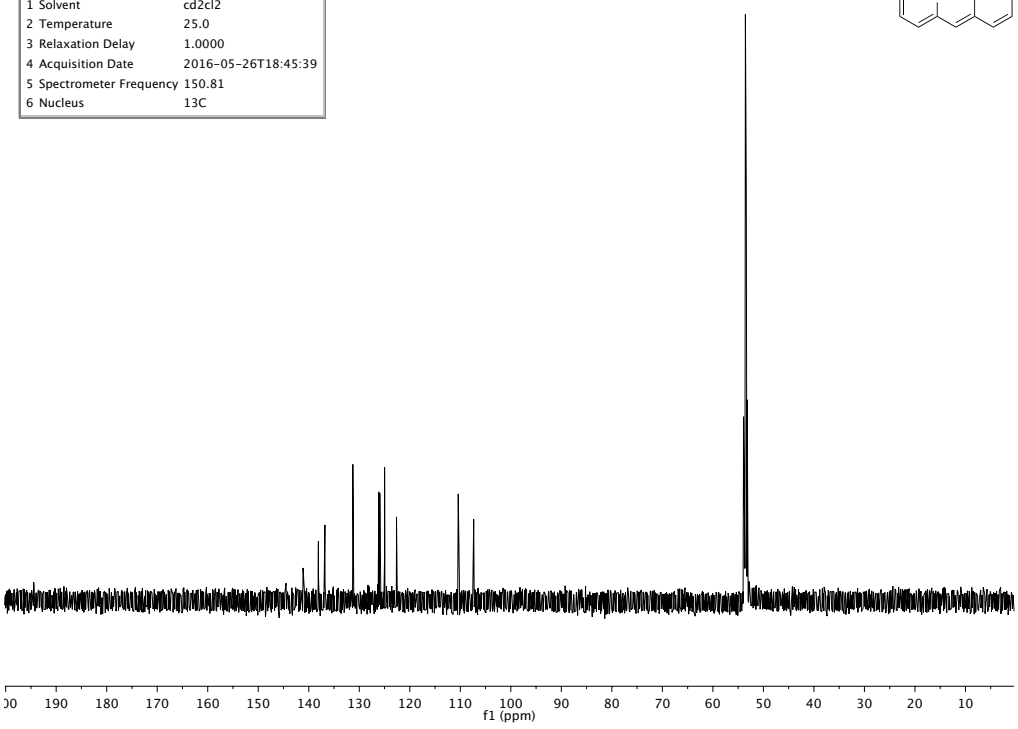




ji-VI-C227_C2

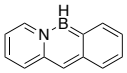
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-05-26T18:45:39
5 Spectrometer Frequency	150.81
6 Nucleus	13C

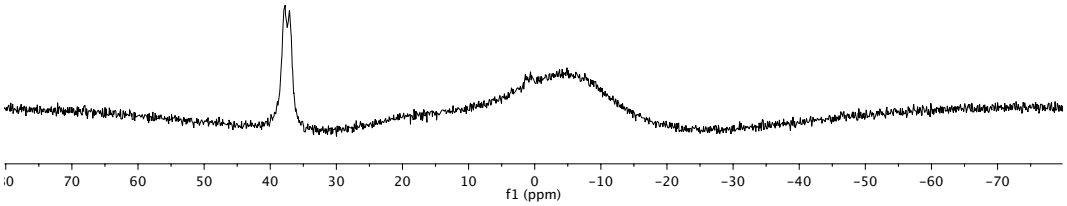




ji-VI-B227_D

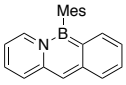
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-05-26T17:33:10
5 Spectrometer Frequency	160.35
6 Nucleus	11B

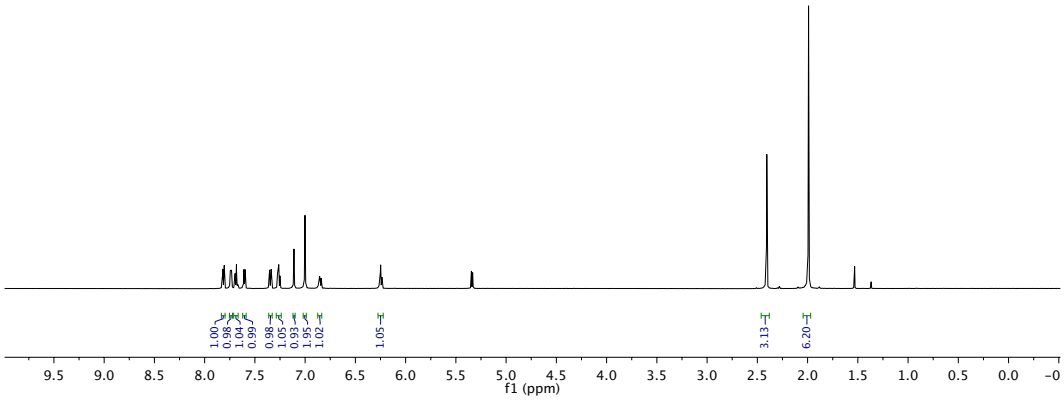




B-Mes_unsub_1H

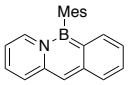
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-06-04T15:46:47
5 Spectrometer Frequency	599.69
6 Nucleus	1H

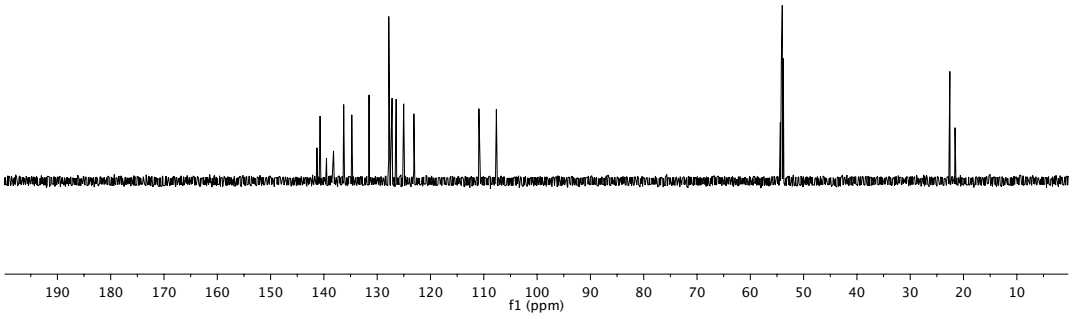




B-Mes_unsub_13C

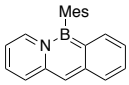
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-06-04T15:46:53
5 Spectrometer Frequency	150.81
6 Nucleus	13C

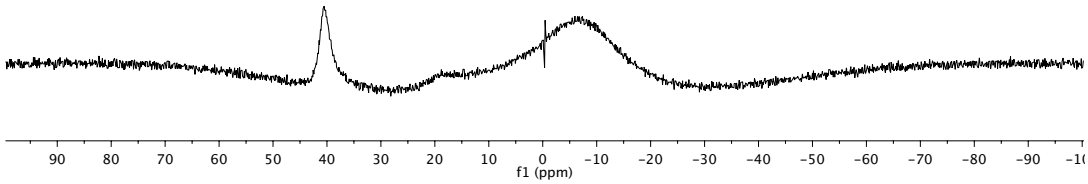




ji-1-B003_D

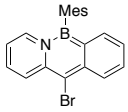
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-08-05T12:34:46
5 Spectrometer Frequency	160.35
6 Nucleus	11B

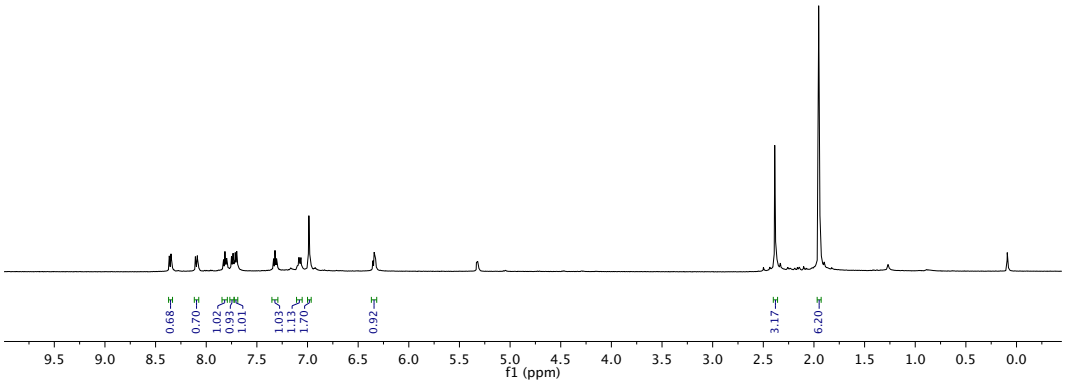




ji-1-015_1H_C

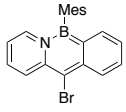
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-09-07T17:40:53
5 Spectrometer Frequency	499.78
6 Nucleus	1H

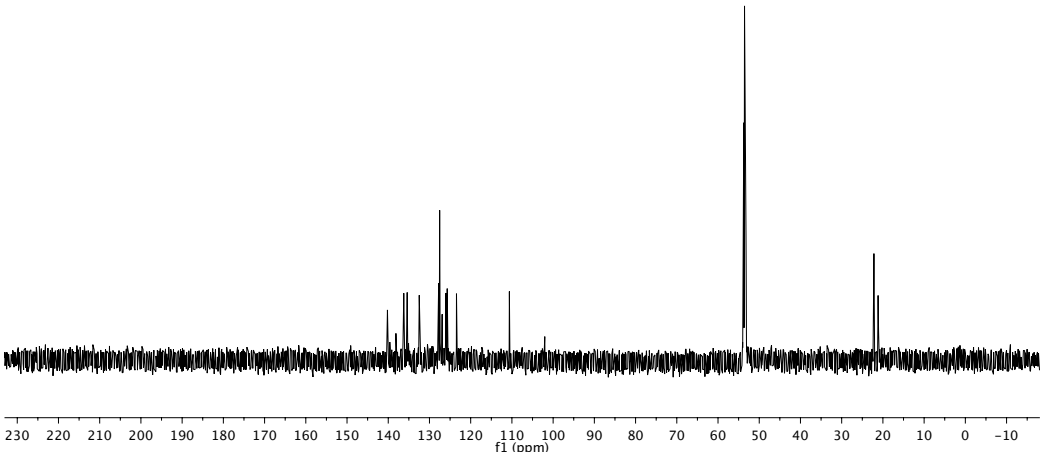




ji-1-015_13C_D

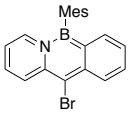
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-09-08T17:31:08
5 Spectrometer Frequency	150.81
6 Nucleus	13C

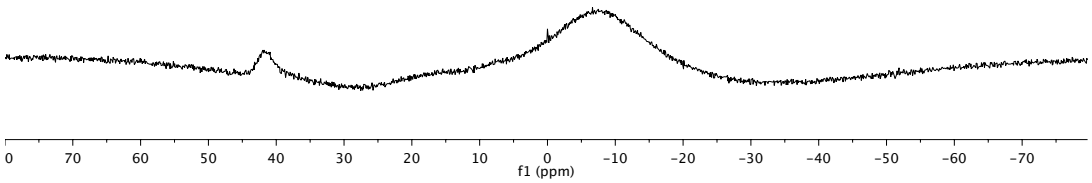




ji-1-015_11B_B

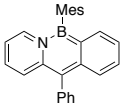
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-09-07T13:42:40
5 Spectrometer Frequency	160.35
6 Nucleus	11B

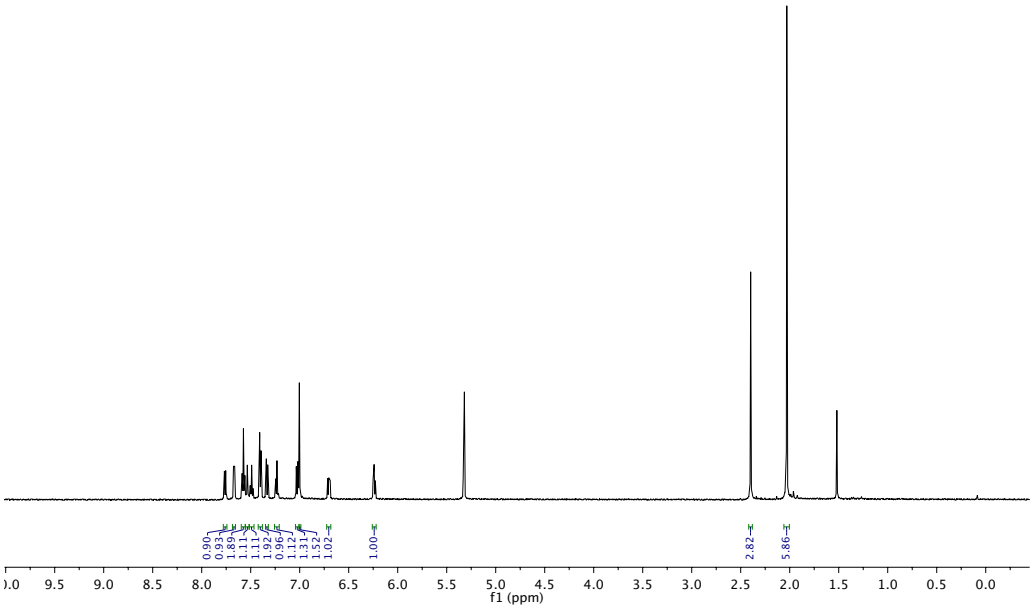




ji-1-009_1H_D

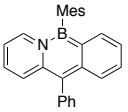
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-02-24T14:53:16
5 Spectrometer Frequency	599.69
6 Nucleus	1H





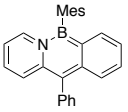
ji-1-009_13C_D

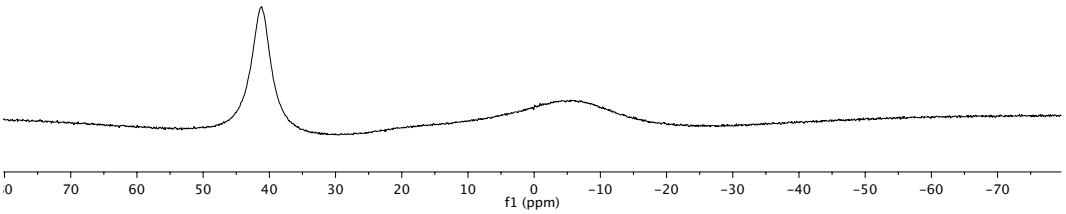
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-02-24T14:53:29
5 Spectrometer Frequency	150.81
6 Nucleus	13C



ji-1-B009_D

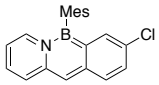
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-08-17T16:28:11
5 Spectrometer Frequency	160.35
6 Nucleus	11B

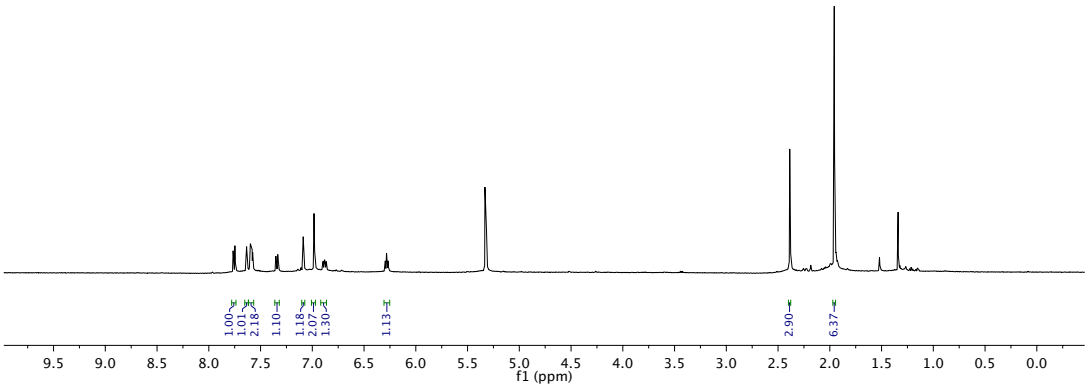




ji-2-067_1H_J

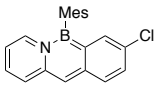
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-03-21T15:02:32
5 Spectrometer Frequency	499.78
6 Nucleus	1H

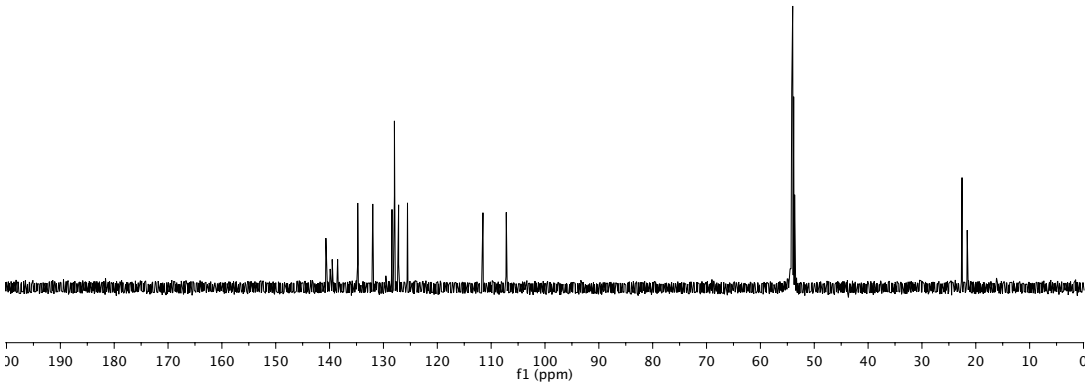




ji-2-067_13C_I2

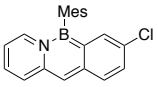
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-04-12T12:12:39
5 Spectrometer Frequency	150.81
6 Nucleus	13C

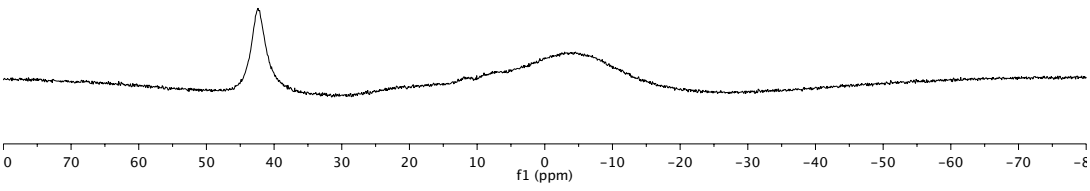




ji-2-066_11B_C

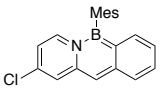
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2017-03-20T16:01:06
5 Spectrometer Frequency	160.35
6 Nucleus	11B

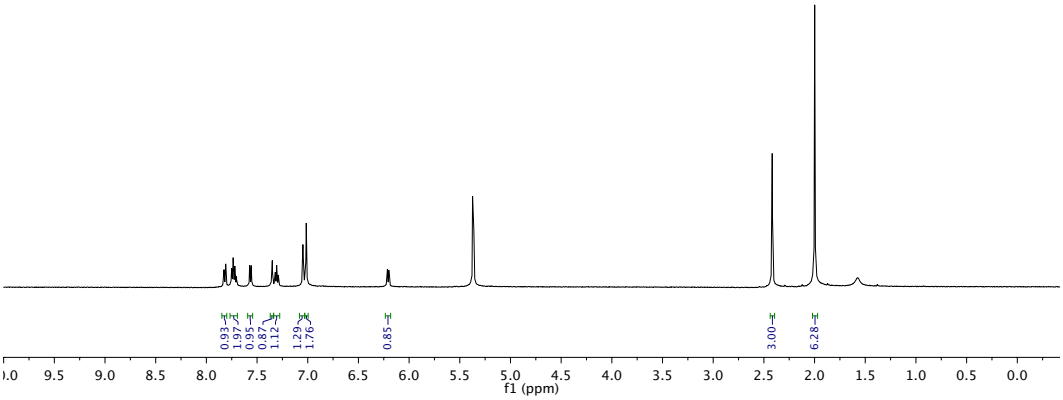




ji-2-130_1H_F

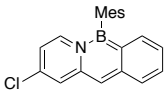
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-31T17:12:13
5 Spectrometer Frequency	499.78
6 Nucleus	1H





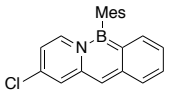
ji-2-130_13C_F

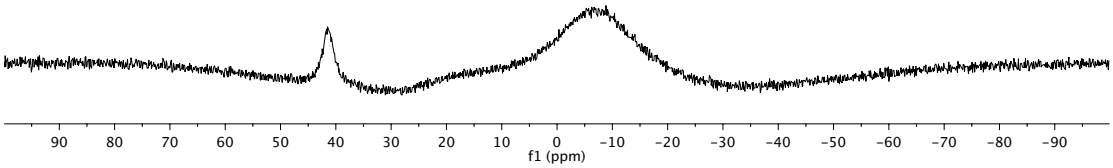
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-31T17:18:40
5 Spectrometer Frequency	150.81
6 Nucleus	13C



ji-2-130_11B_F

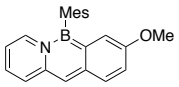
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2017-05-31T17:10:47
5 Spectrometer Frequency	160.35
6 Nucleus	11B

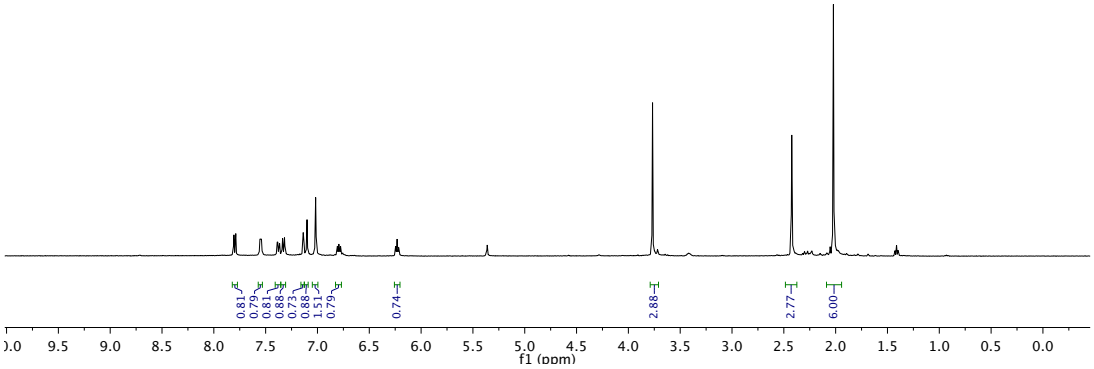




ji-2-132_1H_F

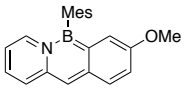
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-06-04T18:42:09
5 Spectrometer Frequency	499.78
6 Nucleus	1H

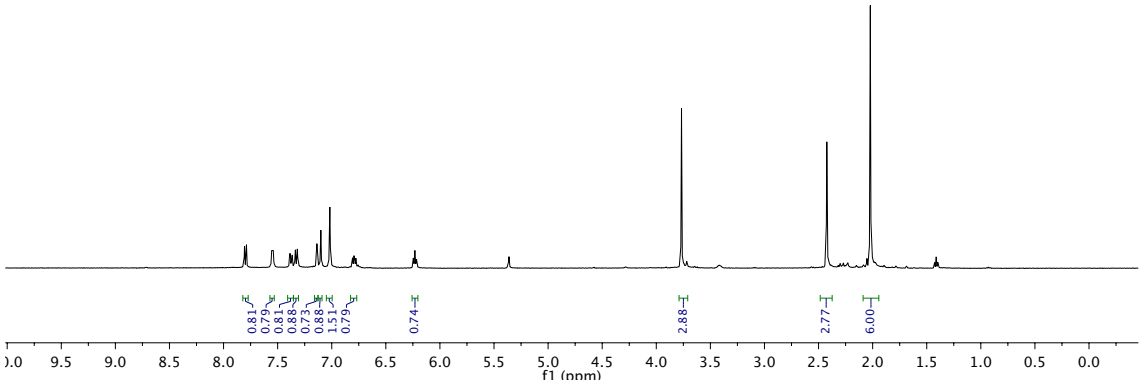




ji-2-132_1H_F

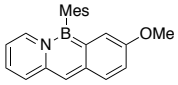
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-06-04T18:42:09
5 Spectrometer Frequency	499.78
6 Nucleus	1H

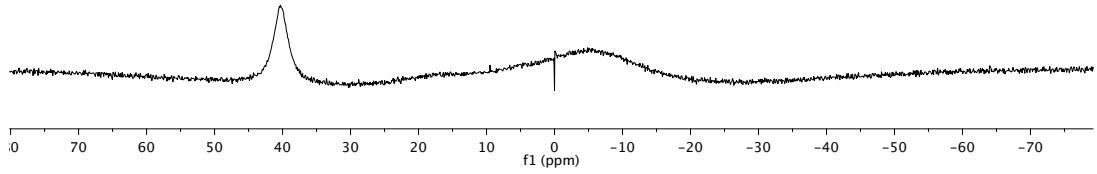




ji-2-132_11B_F

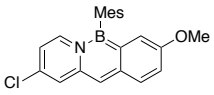
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2017-06-04T18:40:13
5 Spectrometer Frequency	160.35
6 Nucleus	11B

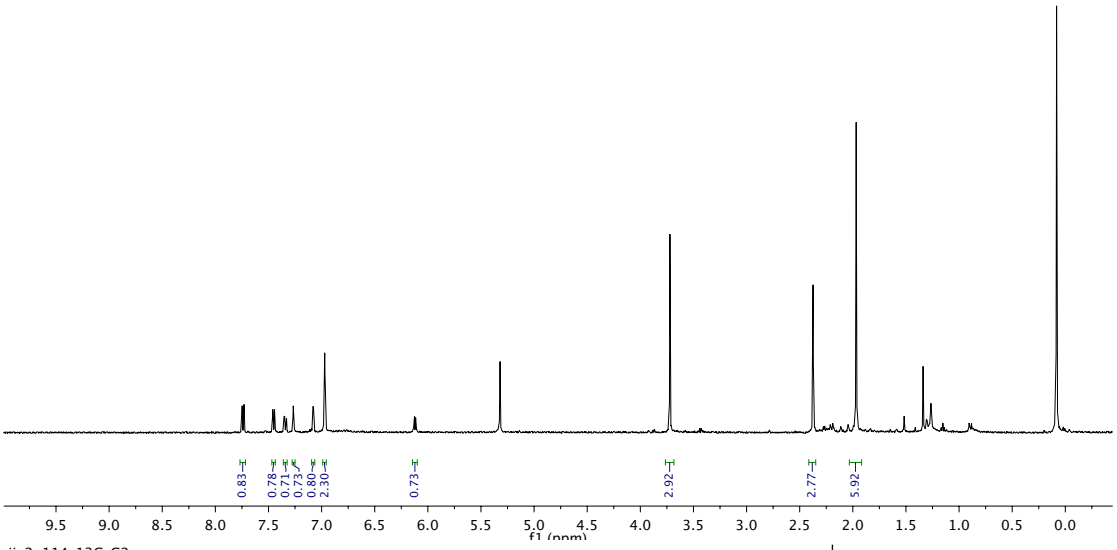




ji-2-114_1H_G

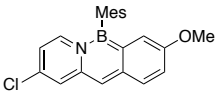
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-12T10:02:20
5 Spectrometer Frequency	499.78
6 Nucleus	1H





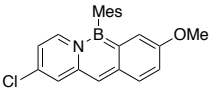
ji-2-114_13C_G2

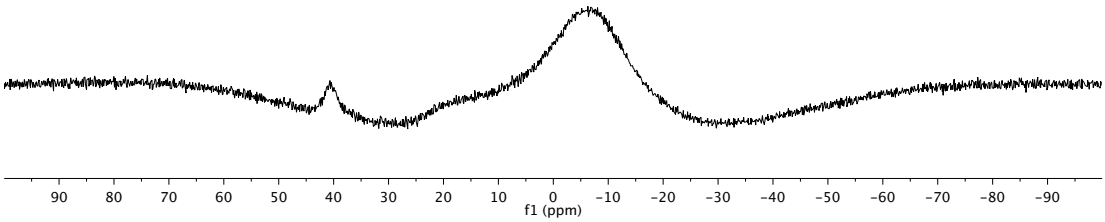
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-12T14:29:36
5 Spectrometer Frequency	125.71
6 Nucleus	13C



ji-2-114_11B_F

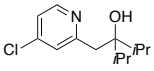
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2017-05-10T11:58:14
5 Spectrometer Frequency	160.35
6 Nucleus	11B





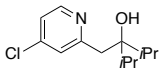
ji-2-102_1H_A

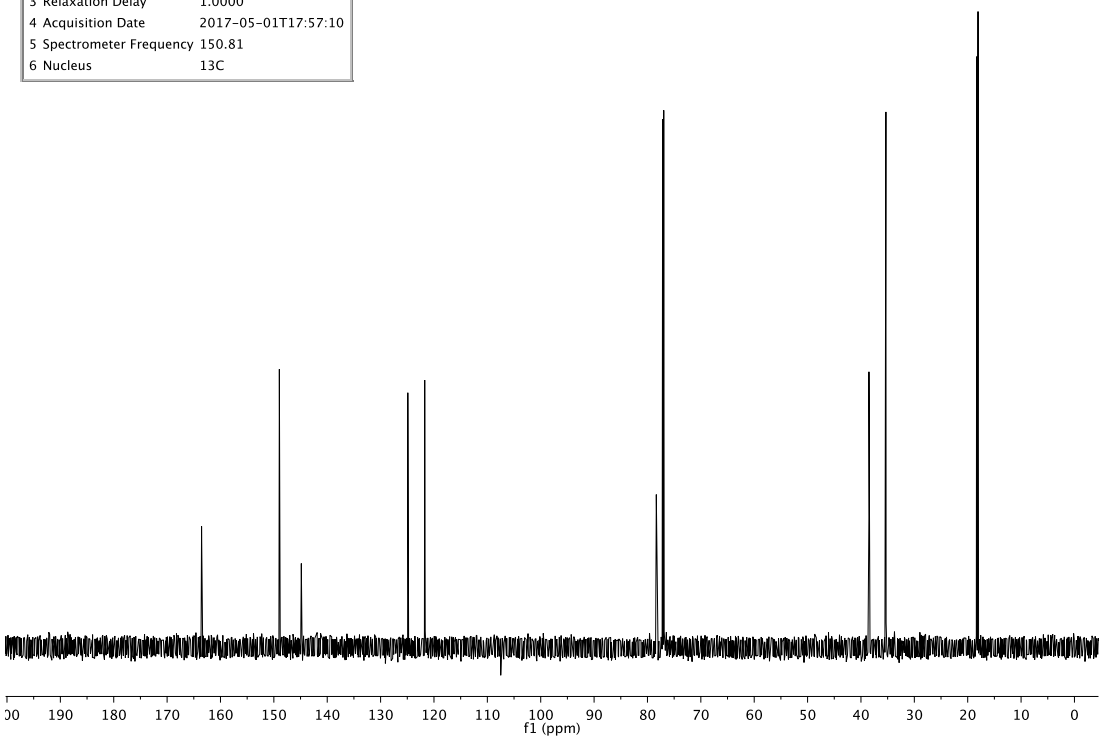
Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-04-29T13:37:28
5 Spectrometer Frequency	499.78
6 Nucleus	1H



ji-2-102_13C_D

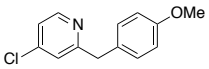
Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-01T17:57:10
5 Spectrometer Frequency	150.81
6 Nucleus	13C

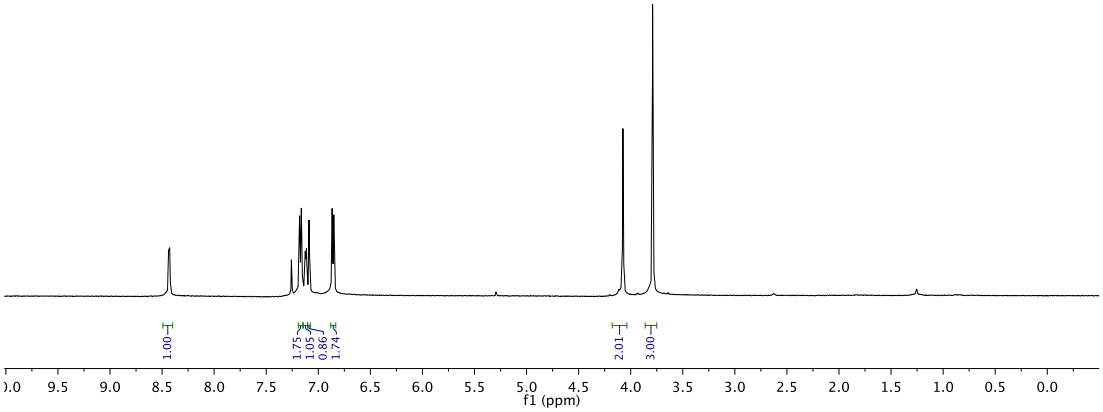




ji-2-110_1H_B

Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-05T19:14:29
5 Spectrometer Frequency	499.88
6 Nucleus	1H





ji-2-110_13C_B

Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2017-05-05T19:15:51
5 Spectrometer Frequency	125.71
6 Nucleus	13C