Supporting Information

for

The Least Stable Isomer of BN Naphthalene: Toward Predictive Trends for the Optoelectronic Properties of BN Acenes

Zhiqiang Liu[†], Jacob S. A. Ishibashi[†], Clovis Darrigan[‡], Alain Dargelos[‡], Anna Chrostowska[‡],* Bo Li[†], Monica Vasiliu[§], David A. Dixon[§], and Shih-Yuan Liu[†]*

[†] Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467 USA
[‡] Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Materiaux, UMR CNRS 5254, Universite de Pau et des Pays de l'Adour, Avenue de l'Universite, BP 1155, 64 013 Pau Cedex, France
[§] Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487 USA

General Considerations for Synthetic, Optical, and Electrochemical Experiments

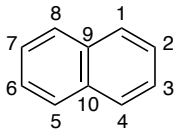
All oxygen- and moisture-sensitive manipulations were carried out under N_2 using either standard Schlenk techniques or a nitrogen-filled glovebox. THF, Et_2O, CH_2Cl_2, toluene, and pentane were dried with a solvent purification system consisting of columns of molecular sieves under argon. Cyclohexane and acetonitrile for photophysical characterizations and cyclic voltammetry, respectively, were dried over calcium hydride, distilled, and degassed via the freeze-pump-thaw method prior to use. All other chemicals were purchased (Acros, Sigma-Aldrich or TCI) and used as received.

NMR spectra were recorded on a Varian VNMRS 600 MHz, VNMRS 500 MHz, INOVA 500 MHz, or VNMRS 400 MHz spectrometer. ^{11}B NMR spectra were externally referenced to $BF_3 \bullet Et_2O$ (δ 0.0 ppm).

UV-vis absorption spectra were collected on an Agilent Cary 100 UV-Vis spectrometer. Emission spectra were collected on Photon Technology International spectrometer. Cyclic Voltammograms were collected using a BioLogic SP-200 potentiostat and the EC-Lab software package. Cathodic peak potentials are reported against an internally referenced ferrocene/ferrocenium couple. The CV were collected using a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire pseudoreference electrode in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

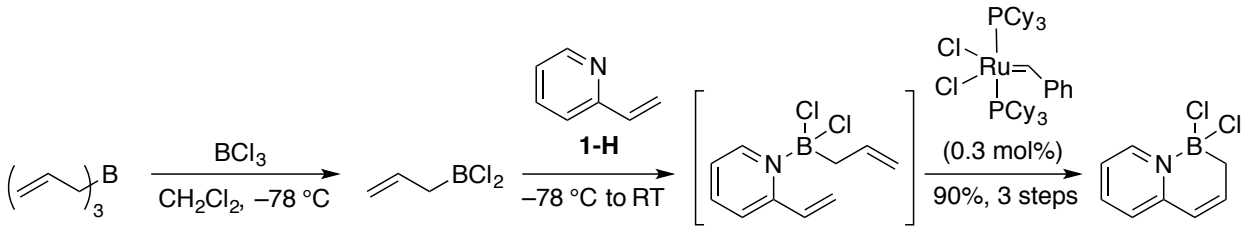
High-resolution mass spectra were collected by Marek Domin on a JEOL AccuTOF instrument (JEOL USA, Peabody, MA), equipped with a DART ion source (IonSense, Inc., Danvers, MA) in positive ion mode at the Boston College Center for Mass Spectrometry.

A note on nomenclature: Numbering refers to the positions on the naphthalene framework that are exchanged with heteroatoms. M. J. S. Dewar introduced non-standard numbering[1] of the bridging positions as 9 and 10 instead of 4a and 8a; we follow the former, non-standard system. Nitrogen is given priority over boron, so the number listed first corresponds to the position of the nitrogen and the second number corresponds to the position of the boron.



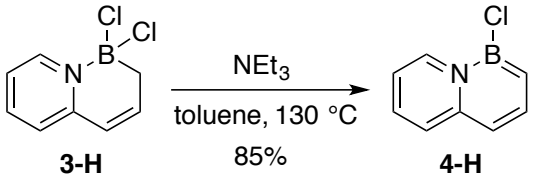
Synthetic Procedures

Compound 3-H



Triallylborane[2] (0.40 g, 3.0 mmol, 0.33 equiv) was dissolved in dry methylene chloride (20 mL). This solution was cooled to –78 °C and then a solution of boron trichloride (1.0 M in hexane, 6.0 mL, 6.0 mmol, 0.67 equiv) was added dropwise to the triallylborane solution *via* syringe over 5 minutes. The mixture was stirred at –78 °C for 30 minutes (the formation of **S1** may be monitored by ^{11}B NMR: δ 61 ppm (s)).[3] Then a solution of 2-vinylpyridine **1-H** (0.95 g, 9.0 mmol, 1.0 equiv) in methylene chloride (5.0 mL) was added dropwise to the *in-situ* generated allylborondichloride solution over 5 minutes at –78 °C, and the cooling bath was removed so the mixture could be allowed to warm to room temperature over 30 min. Once complete conversion to the pyridine-borane adduct **2-H** was judged complete by ^{11}B NMR (δ 9.2 (s)), Grubbs' 1st generation metathesis catalyst (20 mg, 0.024 mmol, 0.3 mol%) was added to the crude mixture as a solid, and the mixture was stirred at room temperature for 16 hours. Volatiles were removed under reduced pressure to afford **3-H** as a pale grey solid, which was carried forward without further purification. Yield: 1.62 g, 90%. ^{1}H NMR (500 MHz, C_6D_6) δ 9.04 (d, *J* = 6.1 Hz, 1H), 6.59 (td, *J* = 7.7, 1.4 Hz, 1H), 6.35 (brs, 1H), 6.18 (t, *J* = 6.8 Hz, 1H), 6.03 (d, *J* = 7.9 Hz, 1H), 5.70 (d, *J* = 9.7 Hz, 1H), 2.32 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 150.5, 145.2, 144.0, 143.1, 125.6, 123.5, 121.7. Carbon adjacent to boron not observed. ^{11}B NMR (160 MHz, CD_2Cl_2) δ 7.2 (s). FTIR (ATR thin film): 2932, 1638, 1486, 1152, 584. HRMS (DART+) calcd for C_8H_8BClN $[M+H–Cl]^+$: 164.04383; found: 164.04402.

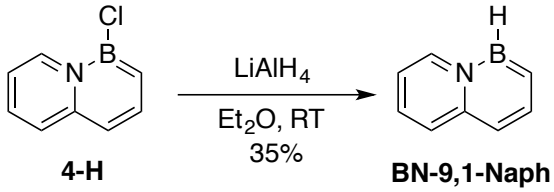
Compound 4-H



3-H **4-H**

Compound **3-H** (1.62 g, 8.11 mmol, 1.0 equiv) was dissolved in dry toluene (20 mL) and triethylamine (2.0 mL, 1.5 g, 14 mmol, 1.8 equiv) was added. The mixture was heated to reflux in a 130 °C oil bath until the reaction was judged to be complete by ^{11}B NMR (32.2 ppm (s)) (about 40 minutes). The reaction mixture was allowed to cool to room temperature, and subsequently passed through an acrodisc. The filtrate was concentrated to dryness, and the product **4-H**, a dark red oil, was carried forward without further purification. Yield: 1.13 g, 85%. ^{1}H NMR (500 MHz, C_6D_6) δ 8.18 (d, J = 7.3 Hz, 1H), 7.51 (app. t, 1H), 6.78 (d, J = 10.8 Hz, 1H), 6.54 (dd, J = 9.0, 1.4 Hz, 1H), 6.22 (d, J = 6.0 Hz, 1H), 6.14 (dd, J = 9.1, 6.4 Hz, 1H), 5.77 (dd, J = 7.5, 6.3 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 143.7, 142.2, 131.8, 125.9, 125.8, 121.2 (br), 113.0, 108.8. ^{11}B NMR (160 MHz, toluene) δ 32.2 (s). FTIR (ATR thin film): 3035, 1638, 1560, 1489, 1362, 1043, 800, 694.

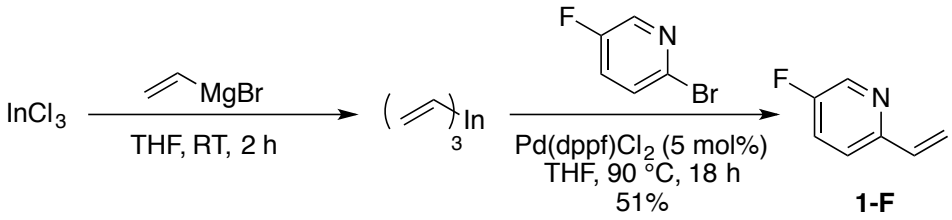
BN-9,1-Naph



4-H **BN-9,1-Naph**

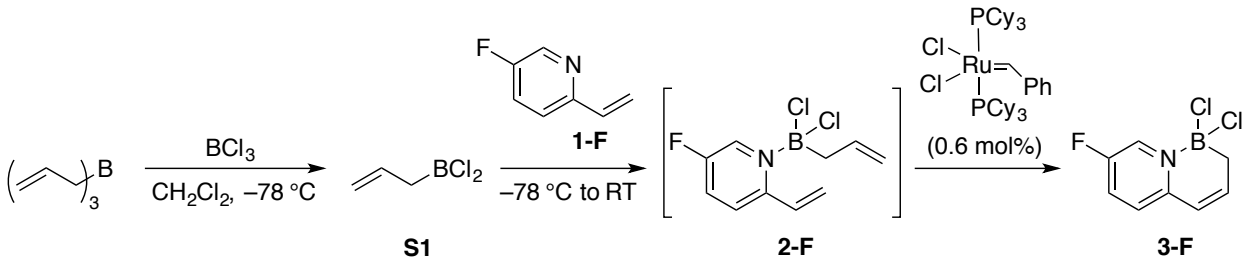
Compound **4-H** (0.81 g, 5.0 mmol, 1.0 equiv) was dissolved in dry ether (20 mL), and a solution of lithium aluminum hydride (1.0 M in ether, 1.5 mL, 1.5 mmol, 0.3 equiv) was added at room temperature. The mixture was stirred until the reaction was judged complete by ^{11}B NMR. Then, the reaction mixture was passed through an acrodisc, and the filtrate was concentrated to afford a pale yellow viscous liquid as the crude product (85% crude yield). The pure product was obtained as a pale yellow crystalline solid by sublimation. Yield: 226 mg (35%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.18 (d, J = 7.1 Hz, 1H), 7.94 (app. t, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.12 (ddd, J = 8.9, 6.5, 1.4 Hz, 1H), 6.84 (m, 2H), 6.66 (t, J = 6.8 Hz, 1H). The B–H proton is observed as a broad 1:1:1:1 quartet (6.0–4.9 ppm). ^{13}C NMR (126 MHz, C_6D_6) δ 143.1,142.3, 138.4, 125.9, 125.6, 112.2, 109.6. Carbon adjacent to boron not observed. ^{11}B NMR (160 MHz, C_6D_6) δ 34.0 (d, J = 134 Hz). FTIR (ATR thin film): 2940, 2517, 1635, 1560, 1362, 763, 452. HRMS (DART+) calcd for $C_{12}H_9BN$ $[M+H]^+$: 130.08280; found: 130.08299.

Compound 1-F



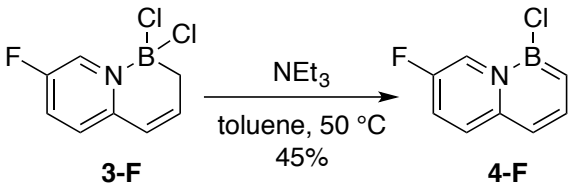
To a solution of indium trichloride (1.06 g, 4.77 mmol, 0.42 equiv) in 50 mL THF, a solution of vinylmagnesium bromide (14.5 mL, 14.5 mmol, 1.0 M, 1.27 equiv) was added dropwise over 10 minutes at room temperature. The mixture was stirred for 2 hours. This freshly prepared trivinylindium solution was brought into the glovebox, where 2-bromo-5-fluoropyridine (2.00 g, 11.4 mmol, 1 equiv) was added along with $Pd(dppf)Cl_2$ (470 mg, 0.57 mmol, 5 mol%). The reaction mixture was subsequently removed from the glovebox and heated to reflux with the heating bath at 90 °C for 18 hours. At the conclusion of the reaction, the reaction mixture was allowed to cool to room temperature, and the excess vinylindium species was quenched with 0.5 mL of ethanol. The solvent was removed using a rotary evaporator. The resulting residue was re-dissolved in ether with 5 mL dichloromethane and passed through a short plug of silica gel using ether as the mobile phase. Volatiles were removed using a rotary evaporator. Residual volatiles were carefully removed *in vacuo* to provide a colorless liquid. Yield: 717 mg (51%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.42 (d, J = 2.7 Hz, 1H), 7.44 – 7.30 (m, 2H), 6.80 (dd, J = 17.5, 10.8 Hz, 1H), 6.13 (dd, J = 17.5, 1.4 Hz, 1H), 5.45 (d, J = 10.8 Hz, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 158.7 (d, J = 255.9 Hz), 152.1, 137.5 (d, J = 23.6 Hz), 135.7, 122.9 (d, J = 18.7 Hz), 122.0 (d, J = 4.4 Hz), 117.5 (d, J = 2.6 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2) δ –129.0 (t, J = 6.0 Hz). FTIR (ATR thin film): 1578, 1477, 1220, 913, 837, 416. HRMS (DART+) $[M+H]^+$ Calcd. for C_7H_7NF 124.05625, found 124.05610.

Compound 3-F



Allylboron dichloride **S1** was prepared *in situ* (5.82 mmol) as described above for compound **3-H**. Compound **1-F** (717 mg, 5.82 mmol, 1.0 equiv) was dissolved in 5.0 mL CH_2Cl_2, and the solution was added to the cold (–78 °C) solution of **S1** over 5 minutes. The cooling bath was subsequently removed, and the reaction mixture was allowed to warm up to room temperature. When pyridine-borane adduct **2-F** was formed completely (judged by ^{11}B NMR δ 9.7 (s), 75 min.), Grubbs' 1st generation catalyst (30. mg, 0.040 mmol, 0.6 mol%) was added carefully to the crude mixture as a solution in 8 mL CH_2Cl_2. The mixture was stirred at room temperature for 16 hours, and the reaction was judged to be complete by ^{11}B NMR (δ 7.6 (s)). Subsequently, the crude mixture was passed through an acrodisc, and the filtrate was concentrated *in vacuo* to furnish **3-F** as a red solid that was carried forward without further purification. Yield: 1.15 g (quantitative). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.17 (d, J = 3.3 Hz, 1H), 7.88 (ddd, J = 9.2, 6.6, 2.8 Hz, 1H), 7.43 (dd, J = 8.9, 5.3 Hz, 1H), 6.89 – 6.78 (m, 1H), 6.50 (dd, J = 9.7, 1.9 Hz, 1H), 2.11 (s, 2H). Minor signals consistent with isomerized *B*-vinyl product visible at δ 6.04 (d, 17.2 Hz) and 5.86 (d, 11.3 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ –122.5 (m). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 158.2 (d, J = 252.7 Hz), 147.9, 144.8, 132.7 (d, J = 35.3 Hz), 131.1 (d, J = 18.9 Hz), 127.1 (d, J = 6.3 Hz), 120.7, 25.8 (br). FTIR (ATR thin film): 2925, 1499, 1346, 1251, 847, 648. HRMS (DART+) $[M–Cl+H]^+$ Calcd. for C_8H_7NBFCl 182.03441, found 182.03375.

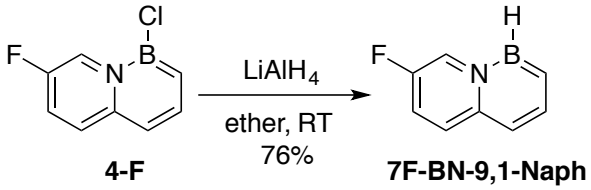
Compound 4-F



3-F **4-F**

Compound **3-F** (1.15 g, 5.82 mmol, 1.0 equiv) was dissolved in toluene, and triethylamine (1.30 mL, 9.31 mmol, 1.6 equiv) was added. The reaction mixture was stirred at 50 °C until the reaction was judged complete by ^{11}B NMR (δ 32.2 (s), 1 hour). Subsequently, the mixture was passed through an acrodisc, and the filtrate was concentrated to dryness *in vacuo*. This crude material was recrystallized from pentane at –30 °C to yield a crop of pale yellow crystals (479 mg, 45%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.48 (d, J = 4.2 Hz, 1H), 7.89 (app t, 1H), 7.44 (dd, J = 9.8, 6.0 Hz, 1H), 7.08 (ddd, J = 9.6, 6.9, 2.4 Hz, 1H), 6.88 (d, J = 7.4 Hz, 1H), 6.76 (d, J = 10.8 Hz, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 153.3 (d, J = 239.9 Hz), 143.2, 140.3, 128.5 (d, J = 8.0 Hz), 127.7 (br) 119.7 (d, J = 26.3 Hz), 117.0 (d, J = 38.9 Hz), 109.8. ^{19}F NMR (376 MHz, CD_2Cl_2) δ –140.07 (q, J = 6.2 Hz). ^{11}B NMR (160 MHz, toluene) δ 32.2 (s). FTIR (ATR thin film): 2921, 1642, 1502, 1299, 779, 693. HRMS (DART+) $[M+H]^+$ Calcd. for C_8H_7NBFCl 182.03441, found 182.03423.

Compound 7F-BN-9,1-Naph



4-F **7F-BN-9,1-Naph**

Compound **4-F** (479 mg, 2.64 mmol, 1.0 equiv) was dissolved in ether (50 mL), and lithium aluminum hydride was added at room temperature as a solid (100. mg, 2.64 mmol, 1.0 equiv). The reaction mixture was then stirred at room temperature for 5 hours. The mixture was then passed through a glass frit, and the filtrate was concentrated *in vacuo*. The residue was extracted into pentane, and the pentane mixture was passed through an acrodisc. The product **7F-BN-9,1-Naph** was isolated by placing a concentrated pentane solution of **7F-BN-9,1-Naph** in the glovebox freezer (–30 °C) and collecting the crystals that formed (pale yellow rods that were suitable for single-crystal X-ray diffraction analysis). Yield: 301 mg (76%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.12 – 7.99 (m, 1H), 7.93 (t, J = 9.0 Hz, 1H), 7.40 (dd, J = 9.8, 5.8 Hz, 1H), 7.06 (ddd, J = 9.7, 7.2, 2.5 Hz, 1H), 6.95 – 6.86 (m, 2H). The B–H proton is observed as a broad 1:1:1:1 quartet (6.0–5.0 ppm). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 153.2 (d, J = 239 Hz), 143.1, 141.0, 128.5 (d, J = 7.9 Hz), 125.3 (br) 123.6 (d, J = 36.3 Hz), 120.4 (d, J = 25.9 Hz), 110.9. ^{19}F NMR (CD_2Cl_2, 376 MHz) δ –139.04 (q, J = 6.0 Hz). ^{11}B NMR (128 MHz, CD_2Cl_2) δ 35.48 (d, J = 134.1 Hz). FTIR (ATR thin film): 3100, 2517, 1659, 1566, 1386, 1239, 829, 447. HRMS (DART+) calcd for C_8H_8BFN $[M+H]^+$ 148.07338; found: 148.07379.

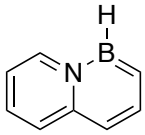
Computational Details

All calculations were performed using the Gaussian 09 program:

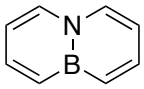
Full Reference for Gaussian 09
Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, 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.

The structures of **1**–**6**, naphthalene, **1-F**, anthracene, and the BN anthracenes were optimized at the CAM-B3LYP[4]/6-311G(d,p) level, and the coordinates are reproduced here. The coordinates for the G3MP2 calculations are also given.

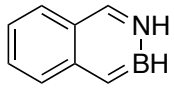
Naphthalenes: CAM-B3LYP/6-311G(d,p)



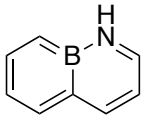
C	-2.39786	-0.71202	0.
C	-1.21696	-1.35757	0.
C	0.01836	0.69292	0.
C	-1.23622	1.38222	0.
C	-2.40947	0.71378	0.
H	-3.31825	-1.27900	0.
H	-1.13806	-2.43487	0.
C	1.22759	1.36242	0.
H	-1.20489	2.46411	0.
H	-3.35074	1.24886	0.
C	2.44601	0.67731	0.
H	1.20371	2.44414	0.
H	3.35638	1.27108	0.
B	1.24068	-1.47119	0.
H	1.11526	-2.65514	0.
N	0.00148	-0.69832	0.
C	2.50829	-0.69964	0.
H	3.48439	-1.17159	0.



C	0.00000	2.38559	-0.71841
C	0.00000	1.18721	-1.33971
C	0.00000	1.36931	1.48233
C	0.00000	2.48326	0.70679
H	0.00000	-1.10021	-2.41970
H	0.00000	3.28169	-1.32516
H	0.00000	1.10021	-2.41970
C	0.00000	-1.18721	-1.33971
C	0.00000	-1.36931	1.48233
H	0.00000	1.48891	2.56142
H	0.00000	3.47735	1.14440
C	0.00000	-2.48326	0.70679
C	0.00000	-2.38559	-0.71841
H	0.00000	-1.48891	2.56142
H	0.00000	-3.47735	1.14440
H	0.00000	-3.28169	-1.32516
N	0.00000	0.00000	-0.63668
B	0.00000	0.00000	0.82642

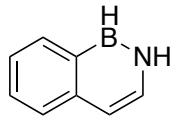


C	-1.241557	-1.437059	0.000000
C	-2.407433	-0.748842	0.000000
C	0.029226	-0.764829	0.000000
C	0.000000	0.677076	0.000000
C	-1.255422	1.365922	0.000000
C	-2.421605	0.680488	0.000000
C	1.239877	-1.444538	0.000000
B	2.521368	-0.690282	0.000000
N	2.372972	0.746020	0.000000
C	1.188274	1.376751	0.000000
H	3.188441	1.341687	0.000000
H	1.194502	-2.529251	0.000000
H	3.629529	-1.125371	0.000000
H	-1.241478	-2.521016	0.000000
H	-3.350449	-1.283313	0.000000
H	-1.251400	2.450695	0.000000
H	-3.368966	1.205031	0.000000
H	1.194008	2.461003	0.000000

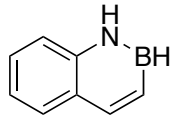


N	-1.293379	-1.372446	0.000004

C -2.434897 -0.653584 0.000007
B 0.010075 -0.758998 -0.000005
C 0.009716 0.761489 -0.000012
C -1.204108 1.421996 -0.000006
C -2.419906 0.717864 0.000002
C 1.342783 -1.486864 -0.000007
C 2.462283 -0.716099 0.000005
C 2.431347 0.723195 0.000003
C 1.274685 1.432872 -0.000030
H 3.380117 1.248765 0.000031
H 1.465470 -2.567293 -0.000004
H 3.445808 -1.179536 0.000020
H -1.397733 -2.377080 0.000010
H -3.367927 -1.204636 0.000015
H -1.237968 2.509836 -0.000011
H -3.363145 1.247209 0.000005
H 1.307236 2.519632 0.000155

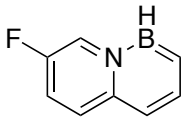


C 1.179269 1.444258 0.000000
C 2.409735 0.830430 0.000000
C 0.000000 0.677736 0.000000
C 0.086386 -0.734436 0.000000
C 1.360883 -1.328477 0.000000
C 2.506883 -0.566451 0.000000
C -1.295597 1.308611 0.000000
C -2.430062 0.585647 0.000000
N -2.407739 -0.793549 0.000000
B -1.208637 -1.543789 0.000000
H -3.307154 -1.248782 0.000000
H -1.271773 -2.733446 0.000000
H -1.358032 2.389383 0.000000
H -3.405955 1.055062 0.000000
H 1.109792 2.526659 0.000000
H 3.311807 1.431637 0.000000
H 1.432162 -2.410831 0.000000
H 3.481525 -1.039803 0.000000



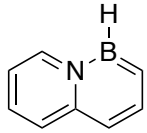
C   -2.40207   -0.83316   0.
C   -1.17857   -1.46032   0.
C   0.01994   -0.72818   0.

C	-0.05283	0.67813	0.
C	-1.30380	1.31018	0.
C	-2.45995	0.56471	0.
H	1.29949	-2.46230	0.
H	-3.31538	-1.41471	0.
H	-1.12012	-2.54339	0.
C	1.30716	-1.37444	0.
H	-1.34945	2.39432	0.
H	-3.42039	1.06625	0.
C	2.46875	-0.68182	0.
H	3.40109	-1.23652	0.
N	1.11906	1.40725	0.
H	0.99647	2.40957	0.
B	2.41579	0.84068	0.
H	3.35166	1.57704	0.



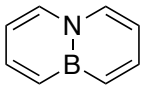
C	-4.139550	1.117849	0.000000
C	-5.241703	0.353891	0.000000
N	-2.871237	0.555750	0.000000
C	-2.740242	-0.829131	0.000000
C	-3.932693	-1.622085	0.000000
C	-5.160826	-1.061665	0.000000
C	-1.481162	-1.400042	0.000000
C	-0.322504	-0.618677	0.000000
C	-0.375382	0.758650	0.000000
B	-1.700881	1.427031	0.000000
F	-6.456508	0.925911	0.000000
H	-4.185242	2.196006	0.000000
H	-3.812078	-2.697328	0.000000
H	-6.069925	-1.648312	0.000000
H	-1.417642	-2.480082	0.000000
H	0.633339	-1.135465	0.000000
H	0.558518	1.309403	0.000000
H	-1.923012	2.595975	0.000000

Naphthalenes: G3MP2

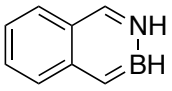


C	2.524083	0.646986	0.000000
C	0.000000	-0.694392	0.000000

C	1.206011	-1.394855	0.000000
C	2.437861	-0.742593	0.000000
H	-1.088654	2.471379	0.000000
H	3.515361	1.094933	0.000000
H	1.179607	2.648654	0.000000
C	-1.187496	1.392168	0.000000
C	-1.262541	-1.356561	0.000000
H	1.152028	-2.480035	0.000000
H	3.339346	-1.356058	0.000000
C	-2.439194	-0.662367	0.000000
C	-2.391396	0.758160	0.000000
H	-1.255067	-2.443596	0.000000
H	-3.392429	-1.183142	0.000000
H	-3.300092	1.351042	0.000000
N	0.020370	0.704677	0.000000
B	1.276668	1.456962	0.000000

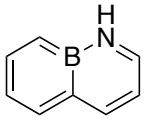


C	0.000000	2.396219	0.730052
C	0.000000	1.187213	1.364256
C	0.000000	1.367252	-1.468416
C	0.000000	2.497954	-0.688275
H	0.000000	-1.100267	2.448109
H	0.000000	3.291494	1.344917
H	0.000000	1.100267	2.448109
C	0.000000	-1.187213	1.364256
C	0.000000	-1.367252	-1.468416
H	0.000000	1.489845	-2.550647
H	0.000000	3.494393	-1.129075
C	0.000000	-2.497954	-0.688275
C	0.000000	-2.396219	0.730052
H	0.000000	-1.489845	-2.550647
H	0.000000	-3.494393	-1.129075
H	0.000000	-3.291494	1.344917
N	0.000000	0.000000	0.656161
B	0.000000	0.000000	-0.814228

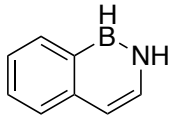


C	-2.426839	0.692077	0.000000
C	-1.242744	1.380578	0.000000
C	0.000000	0.679344	0.000000
C	0.017688	-0.762442	0.000000
C	-1.248645	-1.429354	0.000000
C	-2.428314	-0.730667	0.000000

H	1.224721	2.467500	0.000000
H	-3.370599	1.231379	0.000000
H	-1.234572	2.469630	0.000000
C	1.203046	1.379532	0.000000
C	1.236076	-1.456606	0.000000
H	-1.256366	-2.518046	0.000000
H	-3.375716	-1.264782	0.000000
H	1.175202	-2.544750	0.000000
H	3.640584	-1.158424	0.000000
H	3.208351	1.317120	0.000000
N	2.382168	0.723968	0.000000
B	2.530320	-0.716435	0.000000

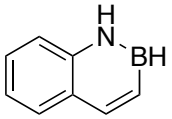


C	-2.455635	-0.614962	0.000000
C	0.027458	0.760932	0.000000
C	-1.187100	1.453826	0.000000
C	-2.407903	0.770079	0.000000
H	1.420345	-2.604063	0.000000
H	-3.399859	-1.153343	0.000000
H	-1.439755	-2.358676	0.000000
C	1.314001	-1.518447	0.000000
C	1.294763	1.414251	0.000000
H	-1.198013	2.546352	0.000000
H	-3.346710	1.315147	0.000000
C	2.450656	0.671634	0.000000
C	2.462598	-0.761484	0.000000
H	1.349267	2.504317	0.000000
H	3.408379	1.188985	0.000000
H	3.440410	-1.244960	0.000000
B	0.000000	-0.761404	0.000000
N	-1.318156	-1.348816	0.000000



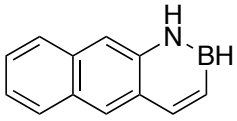
C	2.421948	0.828370	0.000000
C	1.186014	1.448729	0.000000
C	0.000000	0.681326	0.000000
C	0.079373	-0.740028	0.000000
C	1.357701	-1.340017	0.000000
C	2.511698	-0.575512	0.000000
H	-1.348151	2.402089	0.000000
H	3.329452	1.428183	0.000000

H	1.119435	2.535776	0.000000
C	-1.286888	1.316998	0.000000
H	1.427604	-2.426493	0.000000
H	3.488158	-1.054133	0.000000
C	-2.438207	0.595503	0.000000
H	-1.288707	-2.744109	0.000000
H	-3.320251	-1.242852	0.000000
H	-3.416272	1.068231	0.000000
N	-2.413934	-0.787184	0.000000
B	-1.216713	-1.549724	0.000000



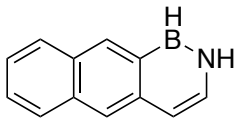
C	-2.410376	-0.725453	0.000000
C	-1.207111	-1.406437	0.000000
C	0.023745	-0.716326	0.000000
C	0.000000	0.698813	0.000000
C	-1.227910	1.383973	0.000000
C	-2.419243	0.679754	0.000000
H	1.235806	-2.502449	0.000000
H	-3.348453	-1.274023	0.000000
H	-1.192722	-2.495017	0.000000
C	1.280630	-1.411610	0.000000
H	-1.232178	2.473193	0.000000
H	-3.363482	1.218496	0.000000
C	2.477519	-0.752001	0.000000
H	1.115278	2.395904	0.000000
H	3.448894	1.480314	0.000000
H	3.387186	-1.348933	0.000000
B	2.484976	0.773205	0.000000
N	1.203039	1.383174	0.000000

Anthracenes: CAM-B3LYP/6-311G(d,p)

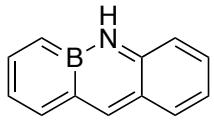


C	-3.62783200	0.72290300	-0.00000100
C	-2.44924700	1.40506200	-0.00000100
C	-1.20721600	0.71469800	0.00000000
C	-1.20862600	-0.70983100	0.00000000
C	-2.45740500	-1.38816600	-0.00000100
C	-3.62945200	-0.69368200	-0.00000100
C	0.02376700	1.38553100	0.00000000
C	0.01651800	-1.39467400	0.00000000
C	1.21589800	-0.71605800	0.00000100

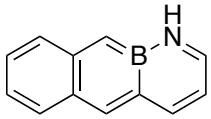
C	1.22915000	0.71138300	0.00000000
C	2.49251100	1.41500500	0.00000000
H	2.43534100	2.50100400	0.00000000
C	3.67974600	0.77614700	0.00000100
H	0.03113000	2.47066700	0.00000000
H	-4.56900300	1.25904300	-0.00000200
H	-2.44077100	2.48937600	-0.00000100
H	-2.46184900	-2.47239500	-0.00000100
H	-4.57360300	-1.22526600	-0.00000200
H	0.01498800	-2.48012200	0.00000000
H	4.58668400	1.37111800	0.00000100
B	3.69398800	-0.75317800	0.00000200
H	4.66495300	-1.44224200	0.00000100
N	2.43075200	-1.38353200	0.00000100
H	2.36006300	-2.39046000	0.00000100



C	-4.512524	2.692840	0.471682
C	-5.465405	1.911534	-0.107603
C	-3.213742	2.179453	0.743258
C	-2.929467	0.826926	0.396102
C	-3.949476	0.041873	-0.206957
C	-5.181857	0.565928	-0.452854
H	-4.730091	3.721781	0.735664
H	-6.450314	2.316207	-0.308692
H	-3.725487	-0.986489	-0.468395
H	-5.952109	-0.041098	-0.913033
C	-2.210584	2.959393	1.338599
C	-0.954167	2.443046	1.594427
C	1.304055	2.750445	2.458501
C	0.082070	3.245090	2.207524
H	-2.433408	3.988819	1.600848
H	2.077850	3.353138	2.917498
H	-0.134511	4.272516	2.471015
H	1.105934	-0.568727	1.303852
H	2.587750	1.168943	2.374358
H	-1.434743	-0.713859	0.396926
C	-1.648402	0.316908	0.662650
C	-0.659018	1.083153	1.248666
B	0.744065	0.540247	1.545042
N	1.645590	1.443939	2.145931

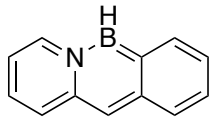


C	-4.500472	2.670879	0.468411
C	-5.469264	1.895986	-0.114108
C	-3.212557	2.163845	0.738499
C	-2.932676	0.819753	0.392694
C	-3.936771	0.036903	-0.204198
C	-5.178585	0.565137	-0.451974
H	-4.711179	3.700699	0.734957
H	-6.452080	2.303706	-0.313548
H	-3.715659	-0.992213	-0.466757
H	-5.940501	-0.052200	-0.912662
C	-2.204517	2.972733	1.345060
C	1.302204	2.757872	2.460372
C	0.082843	3.289737	2.222570
H	-2.475015	3.999014	1.590087
H	2.071579	3.367929	2.920347
H	-0.121312	4.322701	2.492168
H	1.120343	-0.482984	1.336690
H	2.652728	1.072308	2.364385
H	-1.558930	-0.660757	0.372408
B	-0.629813	1.045094	1.246027
C	0.772802	0.524879	1.549661
C	1.640536	1.389951	2.126415
C	-0.953298	2.497361	1.612575
N	-1.688394	0.303675	0.644933

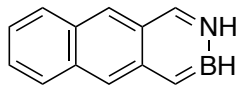


C	-4.493182	2.683039	0.475052
C	-5.455479	1.928889	-0.098808
C	-3.181148	2.161131	0.748468
C	-2.897645	0.774834	0.389994
C	-3.969357	0.024551	-0.219290
C	-5.183403	0.567595	-0.453055
H	-4.692567	3.714292	0.746027
H	-6.436365	2.344742	-0.295068
H	-3.768470	-1.006427	-0.489243
H	-5.965574	-0.025481	-0.912831
C	-2.224486	2.964782	1.335912
C	1.333411	2.751496	2.468687
C	0.063557	3.267246	2.208597
H	-2.490486	3.990667	1.582331
H	2.096200	3.365745	2.927702

H	-0.141226	4.301438	2.478285
H	1.066570	-0.311442	1.374717
H	2.631569	1.043435	2.347636
H	-1.538783	-0.836278	0.321897
B	-0.598947	1.045074	1.256634
C	1.645500	1.445651	2.146247
C	-0.927505	2.487022	1.618023
C	-1.661497	0.202760	0.621111
N	0.751326	0.627245	1.575984

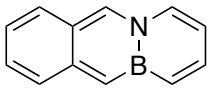


C	-4.4912220	2.6858810	0.4765020
C	-5.4630570	1.9148330	-0.1053210
C	-3.2094990	2.1484810	0.7340920
C	-2.9407310	0.8018240	0.3837330
C	-3.9676410	0.0399070	-0.2136120
C	-5.2059620	0.5773830	-0.4567090
N	-0.6026190	1.1236440	1.2802380
B	-1.5678040	0.2481310	0.6666890
H	-4.6974490	3.7162190	0.7446660
H	-6.4422340	2.3385960	-0.2979060
H	-3.7624700	-0.9908340	-0.4820370
H	-5.9854600	-0.0184600	-0.9158960
C	-2.1867630	2.9316110	1.3367630
C	-0.9362390	2.4509920	1.6023220
C	0.6789590	0.6585890	1.5615130
C	1.6234290	1.4212180	2.1314620
C	1.3133300	2.7798460	2.4719590
C	0.0842670	3.2622620	2.2137740
H	-2.3969420	3.9599690	1.6030320
H	2.0669050	3.4061540	2.9325480
H	-0.1821500	4.2825420	2.4581420
H	0.8465410	-0.3710370	1.2804680
H	2.6023350	1.0067170	2.3270120
H	-1.2155130	-0.8624660	0.4215760

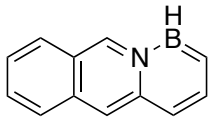


C	-4.503035	2.702541	0.478014
C	-5.446716	1.925358	-0.096673
C	-3.189918	2.190353	0.754732
C	-2.890415	0.819166	0.406555
C	-3.932195	0.037073	-0.202691
C	-5.152408	0.565255	-0.442972

H	-4.718600	3.731840	0.742765
H	-6.433850	2.321572	-0.301190
H	-3.713026	-0.991496	-0.465730
H	-5.925131	-0.039281	-0.902965
C	-2.209302	2.955834	1.337766
C	-0.924099	2.433329	1.601314
C	0.050584	3.228503	2.191510
H	-2.422450	3.986506	1.603782
H	1.912203	3.407891	2.879406
H	-0.163758	4.258003	2.456405
H	0.843905	-0.482016	1.243710
H	2.821119	1.116268	2.436231
H	-1.429734	-0.728767	0.393347
C	-1.641245	0.301196	0.659637
C	-0.607909	1.063497	1.259269
B	1.701051	1.400363	2.150610
C	0.666829	0.551940	1.522898
N	1.270107	2.757077	2.449281

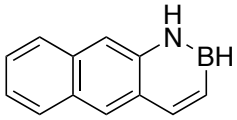


C	-4.457716	2.704963	0.494598
C	-5.440217	1.976779	-0.077878
C	-3.164376	2.131061	0.744605
C	-2.916360	0.753799	0.376774
C	-4.004680	0.030770	-0.229620
C	-5.205150	0.611529	-0.446354
H	-4.628288	3.738363	0.776180
H	-6.412100	2.417350	-0.262970
H	-3.831761	-1.001990	-0.509922
H	-6.007466	0.045041	-0.904473
C	-2.174650	2.881094	1.325720
C	1.253138	2.799943	2.456917
C	0.005172	3.222123	2.173840
H	-2.355232	3.913808	1.603285
H	1.938102	3.500251	2.917421
H	-0.325590	4.230219	2.392262
H	1.199091	-0.425004	1.383136
H	2.702971	1.195923	2.421512
H	-1.535301	-0.841265	0.321510
C	-1.678765	0.195517	0.613095
N	-0.933972	2.390473	1.584441
B	-0.584884	0.998126	1.246412
C	0.837158	0.577653	1.589215
C	1.682883	1.465483	2.165307



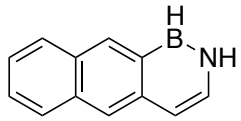
C	-4.528229	2.712582	0.472840
C	-5.448238	1.907109	-0.102725
C	-3.208549	2.224863	0.759352
C	-2.899282	0.861318	0.416984
C	-3.909209	0.042904	-0.193195
C	-5.136291	0.547538	-0.443103
N	-0.667182	1.147306	1.266011
H	-4.767924	3.738099	0.728254
H	-6.441332	2.284571	-0.315023
H	-3.664985	-0.982252	-0.446820
H	-5.898624	-0.068618	-0.903240
C	-2.226225	2.985312	1.341043
C	-0.938004	2.476020	1.609910
C	1.667773	1.418285	2.145013
C	1.325778	2.725747	2.458050
C	0.063786	3.243429	2.200503
H	-2.422264	4.015212	1.612600
H	2.054068	3.386465	2.921229
H	-0.177256	4.267043	2.454604
H	0.771537	-0.587922	1.183554
H	2.672245	1.081424	2.374553
C	-1.645163	0.392092	0.687504
H	-1.355453	-0.622785	0.452591
B	0.656022	0.549259	1.517509

Anthracenes (G3MP2)

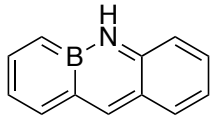


C	-4.501907	2.687774	0.473449
C	-5.457243	1.890391	-0.111302
C	-3.202549	2.180261	0.746824
C	-2.900829	0.818900	0.402641
C	-3.913275	0.025334	-0.200196
C	-5.160871	0.547077	-0.451391
H	-4.727549	3.720260	0.735572
H	-6.447614	2.290059	-0.315461
H	-3.686062	-1.007122	-0.461779
H	-5.925864	-0.072397	-0.913395
C	-2.202070	2.965575	1.342904
C	-0.930060	2.463304	1.608745
C	1.337624	2.805328	2.488385
C	0.088327	3.280097	2.221207

H	-2.425351	3.999963	1.606450
H	2.052286	3.482126	2.952152
H	-0.193235	4.306981	2.462571
H	0.771585	-0.354744	1.260794
H	2.726768	0.812588	2.305233
H	-1.386281	-0.720531	0.410541
C	-1.616778	0.313278	0.671440
C	-0.642606	1.106677	1.261281
N	0.628768	0.614840	1.530329
B	1.676794	1.355985	2.128018

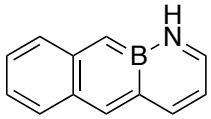


C	-4.515897	2.699887	0.472684
C	-5.479330	1.911997	-0.111696
C	-3.218413	2.184530	0.742845
C	-2.930622	0.820522	0.393111
C	-3.949970	0.034439	-0.209630
C	-5.193520	0.566762	-0.455983
H	-4.735516	3.733272	0.737134
H	-6.467296	2.319794	-0.312375
H	-3.727891	-0.998536	-0.473117
H	-5.965269	-0.044624	-0.917628
C	-2.214544	2.966276	1.338921
C	-0.947497	2.444547	1.596690
C	1.315740	2.754807	2.464418
C	0.079267	3.248428	2.207763
H	-2.437084	4.001197	1.602886
H	2.092360	3.358685	2.925253
H	-0.138513	4.280019	2.472263
H	1.119063	-0.579640	1.304652
H	2.600370	1.167158	2.378688
H	-1.430604	-0.726650	0.393543
C	-1.647192	0.308834	0.659667
C	-0.650270	1.082202	1.250668
B	0.752214	0.533533	1.545448
N	1.652422	1.444566	2.148805

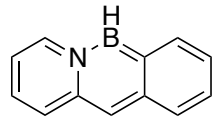


C	-4.507912	2.680750	0.469117
C	-5.477517	1.895980	-0.116335
C	-3.212256	2.172526	0.741005
C	-2.933886	0.819125	0.391531
C	-3.938580	0.030307	-0.207137

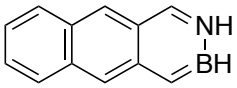
C	-5.188990	0.558613	-0.457131
H	-4.722501	3.714346	0.735346
H	-6.464410	2.304680	-0.316356
H	-3.715297	-1.002935	-0.470305
H	-5.953427	-0.061321	-0.919104
C	-2.211535	2.980494	1.344589
C	1.313010	2.751680	2.462464
C	0.079383	3.292361	2.222201
H	-2.478510	4.012496	1.592565
H	2.080011	3.370233	2.924845
H	-0.125097	4.329473	2.493004
H	1.127267	-0.493413	1.335714
H	2.671457	1.071980	2.371551
H	-1.557812	-0.667160	0.369994
B	-0.622780	1.043462	1.247265
C	0.776565	0.517148	1.548324
C	1.655963	1.390517	2.132287
C	-0.945203	2.496161	1.614399
N	-1.685933	0.304503	0.645179



C	-4.491219	2.683909	0.475797
C	-5.464799	1.917042	-0.105125
C	-3.186323	2.160314	0.745783
C	-2.908173	0.775429	0.385897
C	-3.967518	0.020897	-0.220008
C	-5.200991	0.562667	-0.459863
H	-4.696049	3.719025	0.745829
H	-6.447310	2.341568	-0.298479
H	-3.764185	-1.014653	-0.490689
H	-5.982692	-0.036708	-0.920932
C	-2.219989	2.978423	1.341052
C	1.336880	2.755848	2.471909
C	0.074494	3.280382	2.216618
H	-2.490243	4.008899	1.587420
H	2.106149	3.367970	2.932950
H	-0.129548	4.318972	2.488056
H	1.060396	-0.319720	1.370027
H	2.645384	1.028817	2.348577
H	-1.533960	-0.844730	0.319842
B	-0.599851	1.048741	1.256755
C	1.658228	1.438067	2.148643
C	-0.929948	2.494712	1.619086
C	-1.655987	0.198653	0.620608
N	0.749264	0.627482	1.575258

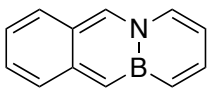


C	-4.497517	2.694723	0.477210
C	-5.476334	1.920467	-0.107900
C	-3.211008	2.153725	0.735267
C	-2.936928	0.797703	0.383468
C	-3.968488	0.033434	-0.216219
C	-5.213362	0.577776	-0.459091
N	-0.600722	1.117858	1.279106
B	-1.565226	0.235600	0.663418
H	-4.703985	3.729676	0.746634
H	-6.459216	2.345016	-0.301374
H	-3.764907	-1.001436	-0.486599
H	-5.995432	-0.020912	-0.920051
C	-2.195099	2.933851	1.334868
C	-0.929828	2.450636	1.604677
C	0.684828	0.651151	1.561198
C	1.634332	1.428662	2.137469
C	1.328266	2.782985	2.477896
C	0.081904	3.262683	2.213327
H	-2.402694	3.967880	1.603613
H	2.080180	3.416374	2.940039
H	-0.186613	4.287379	2.458395
H	0.856044	-0.381839	1.280476
H	2.615784	1.009341	2.332175
H	-1.211967	-0.880731	0.417007

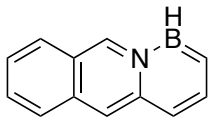


C	-4.505159	2.704197	0.477704
C	-5.458631	1.911719	-0.104795
C	-3.199479	2.191697	0.751643
C	-2.904226	0.821527	0.402312
C	-3.930170	0.032971	-0.203379
C	-5.170454	0.559246	-0.450646
H	-4.728039	3.737052	0.740884
H	-6.447930	2.315251	-0.307353
H	-3.706450	-0.999949	-0.466292
H	-5.941364	-0.052996	-0.912255
C	-2.208291	2.970584	1.342437
C	-0.927829	2.443655	1.603102
C	0.056101	3.242996	2.198169
H	-2.426052	4.006072	1.608231
H	1.928239	3.400880	2.883540
H	-0.145076	4.277638	2.469302

H	0.837548	-0.489153	1.239015
H	2.842203	1.105001	2.440131
H	-1.422743	-0.731408	0.394592
C	-1.636829	0.304188	0.661749
C	-0.612349	1.070431	1.259607
B	1.718444	1.393005	2.154226
C	0.671277	0.549872	1.523397
N	1.279265	2.747529	2.449690



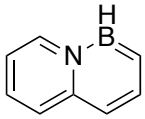
C	-4.457915	2.707000	0.494650
C	-5.453051	1.966136	-0.085046
C	-3.173598	2.129956	0.740143
C	-2.928544	0.755047	0.372317
C	-4.003996	0.027747	-0.230116
C	-5.224566	0.608968	-0.452664
H	-4.632877	3.744504	0.775580
H	-6.426419	2.414895	-0.267356
H	-3.829220	-1.009638	-0.511070
H	-6.026282	0.035601	-0.911983
C	-2.175655	2.895732	1.328955
C	1.268738	2.792117	2.460739
C	0.006775	3.228576	2.176721
H	-2.355987	3.933087	1.608021
H	1.951020	3.499778	2.923664
H	-0.321579	4.241215	2.397584
H	1.199562	-0.433435	1.379829
H	2.722715	1.193007	2.428569
H	-1.530119	-0.846393	0.320581
C	-1.672738	0.194856	0.613685
N	-0.932205	2.397009	1.586294
B	-0.579312	0.997217	1.246809
C	0.837256	0.572772	1.587091
C	1.700005	1.466252	2.172016

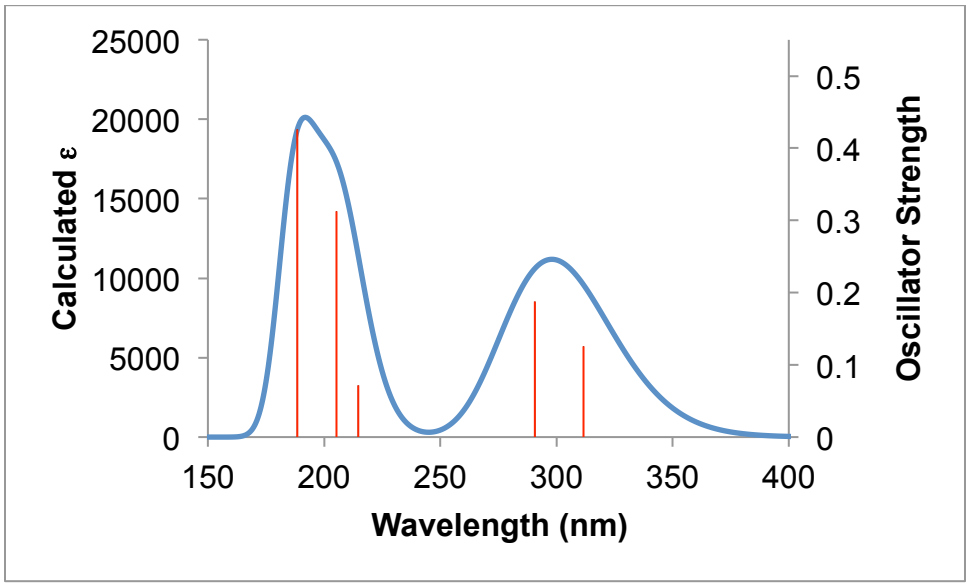


C	-4.527334	2.717420	0.474600
C	-5.466530	1.909770	-0.108141
C	-3.218427	2.219736	0.754298
C	-2.905807	0.856574	0.413088
C	-3.910001	0.039608	-0.194712
C	-5.151528	0.557474	-0.445032
N	-0.657209	1.135307	1.265495

```
H -4.764301  3.748268  0.732479
H -6.461236  2.294541 -0.318567
H -3.671608 -0.990673 -0.451924
H -5.913156 -0.065590 -0.907136
C -2.220393  2.981759  1.342034
C -0.936374  2.472444  1.609554
C  1.670559  1.422470  2.147498
C  1.331745  2.742704  2.465828
C  0.069063  3.250205  2.204922
H -2.417657  4.017376  1.614910
H  2.062216  3.405871  2.930551
H -0.183788  4.276841  2.456058
H  0.793659 -0.605329  1.185656
H  2.679842  1.089604  2.379917
C -1.639626  0.374629  0.683493
H -1.350300 -0.644808  0.447089
B  0.667016  0.536629  1.517323
```

TD-DFT Calculations *CAM-B3LYP/6-311G(d,p):*
The transition from orbital 34 -> 35 is the HOMO-LUMO transition in all cases.





Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 3.98 eV 311.65 nm f=0.1245 <S**2>=0.000
33 -> 36 0.10297
34 -> 35 0.68395
44 -> 36 0.10562

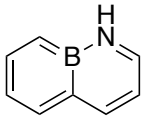
Excited State 2: Singlet-A' 4.26 eV 290.71 nm f=0.1874 <S**2>=0.000
33 -> 35 -0.16424
34 -> 36 0.67467

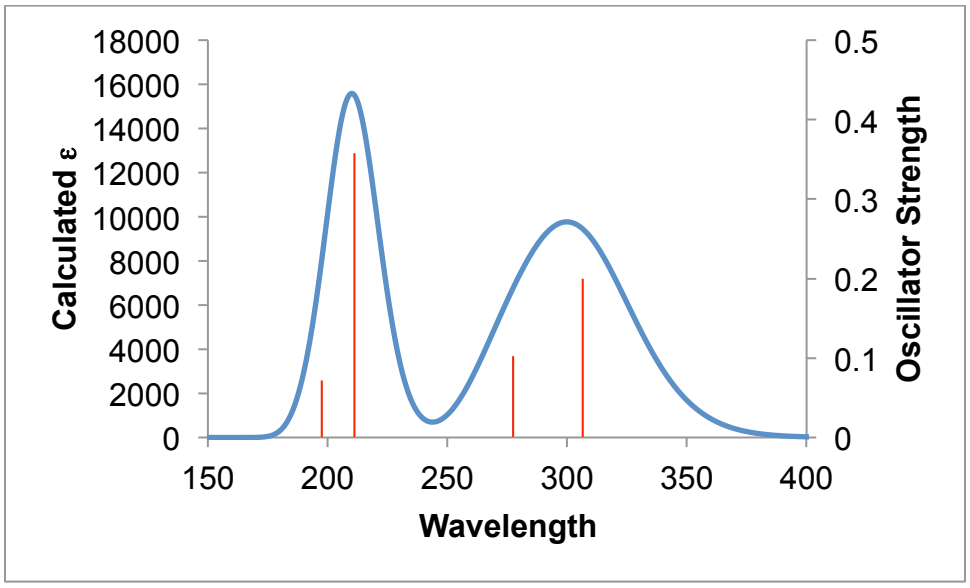
Excited State 3: Singlet-A' 5.77 eV 214.79 nm f=0.0720 <S**2>=0.000
33 -> 36 0.15821 34 -> 37 0.67357

Excited State 4: Singlet-A' 6.04 eV 205.34 nm f=0.3125 <S**2>=0.000
32 -> 36 -0.12640
33 -> 35 0.65043
34 -> 36 0.14655

Excited State 5: Singlet-A" 6.26 eV 198.08 nm f=0.0000 <S**2>=0.000
34 -> 38 0.66011
34 -> 39 0.19838

Excited State 6: Singlet-A' 6.58 eV 188.48 nm f=0.4260 <S**2>=0.000
32 -> 35 0.14423
33 -> 36 0.65667
34 -> 35 -0.11952
34 -> 37 -0.13527





Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 4.05 eV 306.50 nm f=0.1998 <S**2>=0.000
33 -> 36 -0.13576
34 -> 35 0.68767

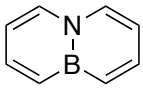
Excited State 2: Singlet-A 4.47 eV 277.55 nm f=0.1022 <S**2>=0.000
33 -> 35 0.66647
34 -> 36 0.21793

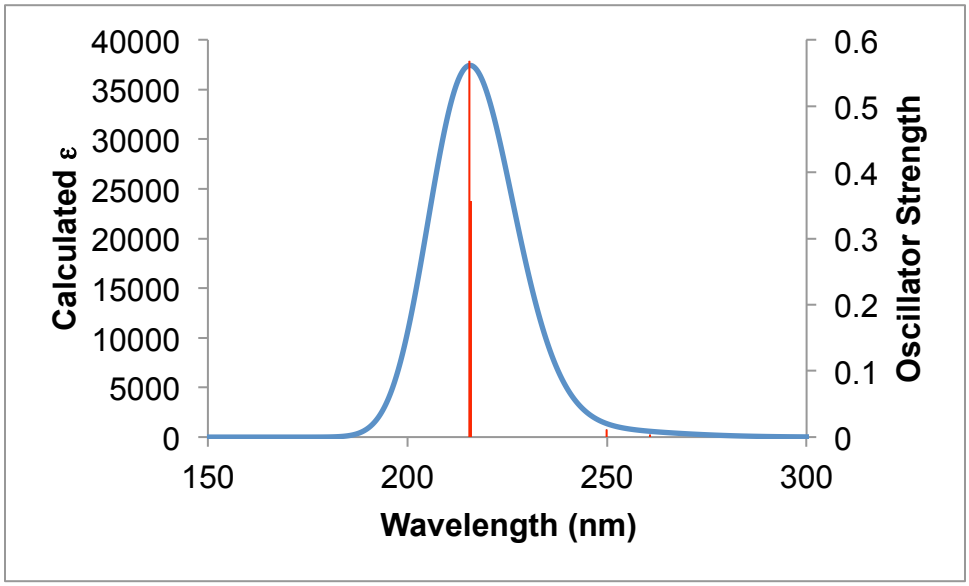
Excited State 3: Singlet-A 5.46 eV 226.96 nm f=0.0000 <S**2>=0.000
32 -> 35 0.69643

Excited State 4: Singlet-A 5.87 eV 211.20 nm f=0.3575 <S**2>=0.000
33 -> 35 -0.20388
33 -> 38 -0.10946
34 -> 36 0.64616

Excited State 5: Singlet-A 6.28 eV 197.54 nm f=0.0712 <S**2>=0.000
31 -> 35 0.41535
33 -> 36 0.46358
34 -> 38 0.29151

Excited State 6: Singlet-A 6.39 eV 194.17 nm f=0.0001 <S**2>=0.000
33 -> 37 0.28770
34 -> 37 0.63198





Excitation energies and oscillator strengths:
Excited State 1: Singlet-B2 4.75 eV 260.77 nm f=0.0036 <S**2>=0.000
33 -> 35 0.52107
34 -> 36 0.46503

Excited State 2: Singlet-A1 4.96 eV 249.91 nm f=0.0116 <S**2>=0.000
33 -> 36 -0.39761
34 -> 35 0.58005

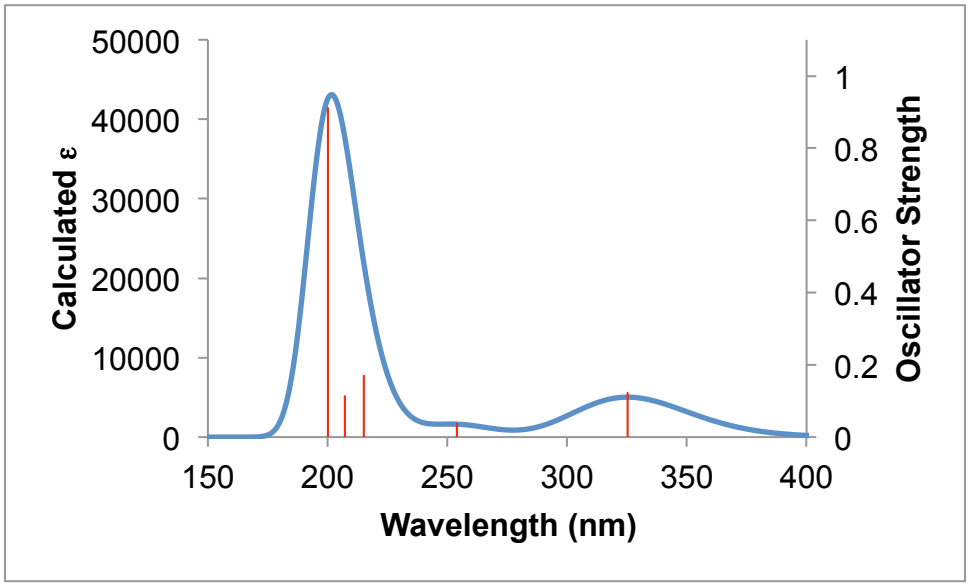
Excited State 3: Singlet-A1 5.74 eV 215.92 nm f=0.3562 <S**2>=0.000
33 -> 36 0.56803
34 -> 35 0.39854

Excited State 4: Singlet-B2 5.75 eV 215.52 nm f=0.5679 <S**2>=0.000
33 -> 35 -0.46236
34 -> 36 0.51827

Excited State 5: Singlet-B1 6.70 eV 184.95 nm f=0.0000 <S**2>=0.000
30 -> 36 -0.19307
31 -> 35 0.66280

Excited State 6: Singlet-A2 6.79 eV 182.59 nm f=0.0000 <S**2>=0.000
30 -> 35 -0.39375
31 -> 36 0.57202

As in naphthalene, the lowest energy transition does not correspond to the HOMO-LUMO gap. We have assigned, the 2nd-lowest energy transition (experimental optical gap: 4.13 eV) as the HOMO-LUMO transition.



Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 3.81 eV 325.25 nm f=0.1241 <S**2>=0.000
34 -> 35 0.69768

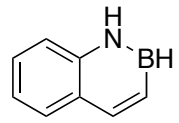
Excited State 2: Singlet-A' 4.88 eV 253.97 nm f=0.0386 <S**2>=0.000
33 -> 35 -0.40825
34 -> 36 0.56482

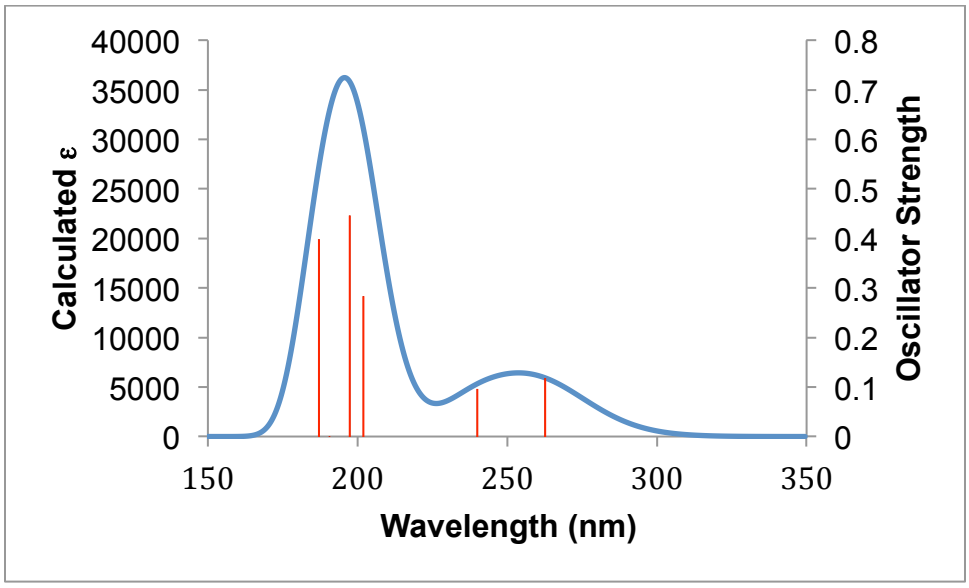
Excited State 3: Singlet-A' 5.76 eV 215.09 nm f=0.1717 <S**2>=0.000
32 -> 35 0.14574
33 -> 35 -0.32002
34 -> 36 -0.22934
34 -> 38 0.56153

Excited State 4: Singlet-A' 5.98 eV 207.19 nm f=0.1145 <S**2>=0.000
32 -> 35 0.53335
33 -> 35 -0.26617
34 -> 36 -0.12533
34 -> 38 -0.32723

Excited State 5: Singlet-A" 6.03 eV 205.64 nm f=0.0001 <S**2>=0.000
33 -> 37 -0.10437
34 -> 37 0.69158

Excited State 6: Singlet-A' 6.20 eV 200.11 nm f=0.9120 <S**2>=0.000
32 -> 35 0.39725
33 -> 35 0.38084
33 -> 36 -0.10800
34 -> 36 0.31975
34 -> 38 0.26265





Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 4.72 eV 262.72 nm f=0.1183 <S**2>=0.000
33 -> 35 -0.12885
33 -> 36 0.27062
34 -> 35 0.62951

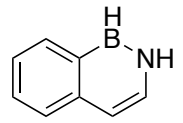
Excited State 2: Singlet-A' 5.17 eV 240.01 nm f=0.0966 <S**2>=0.000
33 -> 35 0.62099
34 -> 35 0.13368
34 -> 36 -0.28925

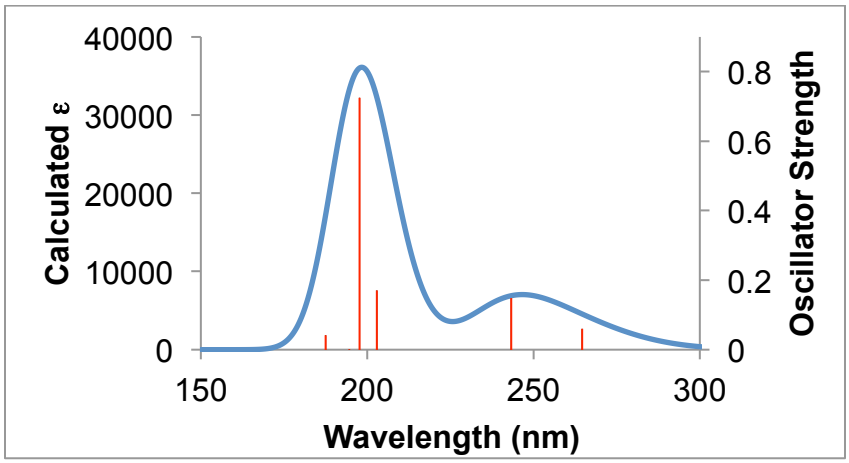
Excited State 3: Singlet-A' 6.14 eV 201.98 nm f=0.2834 <S**2>=0.000
29 -> 35 0.10008 32 -> 36 0.11860
33 -> 36 -0.42392 34 -> 35 0.21714
34 -> 37 0.48297

Excited State 4: Singlet-A' 6.28 eV 197.39 nm f=0.4456 <S**2>=0.000
33 -> 35 0.29134
33 -> 37 0.17274
34 -> 36 0.61147

Excited State 5: Singlet-A" 6.50 eV 190.65 nm f=0.0004 <S**2>=0.000
31 -> 35 0.66779
31 -> 37 0.19733

Excited State 6: Singlet-A' 6.63 eV 187.10 nm f=0.3981 <S**2>=0.000
32 -> 35 -0.13292
32 -> 36 0.10142
33 -> 36 0.46859
33 -> 37 -0.10541
34 -> 35 -0.15554
34 -> 37 0.45284





Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 4.69 eV 264.63 nm f=0.0605 <S**2>=0.000
33 -> 36 0.25569
34 -> 35 0.63495
34 -> 36 0.12051

Excited State 2: Singlet-A' 5.09 eV 243.35 nm f=0.1489 <S**2>=0.000
33 -> 35 -0.27872
34 -> 35 -0.14496
34 -> 36 0.62357

Excited State 3: Singlet-A' 6.11 eV 202.95 nm f=0.1702 <S**2>=0.000
32 -> 35 0.30401
32 -> 36 0.11993
33 -> 36 0.50827
33 -> 38 0.10528
34 -> 35 -0.24129
34 -> 38 -0.22598

Excited State 4: Singlet-A' 6.27 eV 197.73 nm f=0.7248 <S**2>=0.000
32 -> 35 0.11085
32 -> 36 -0.12743
33 -> 35 0.62312
34 -> 36 0.26868

Excited State 5: Singlet-A" 6.37 eV 194.63 nm f=0.0003 <S**2>=0.000
32 -> 37 -0.18024
34 -> 37 0.67529

Excited State 6: Singlet-A' 6.61 eV 187.59 nm f=0.0408 <S**2>=0.000
32 -> 35 -0.12338
32 -> 36 -0.11331
33 -> 36 0.31379
34 -> 35 -0.10327
34 -> 38 0.59006

Frontier Orbitals

Table S1. Calculated [CAM-B3LYP/6-311G(d,p)] Kohn-Sham HOMO and LUMO levels in eV for compounds **1–6** and naphthalene in addition to calculated (G3MP2) heats of formation.

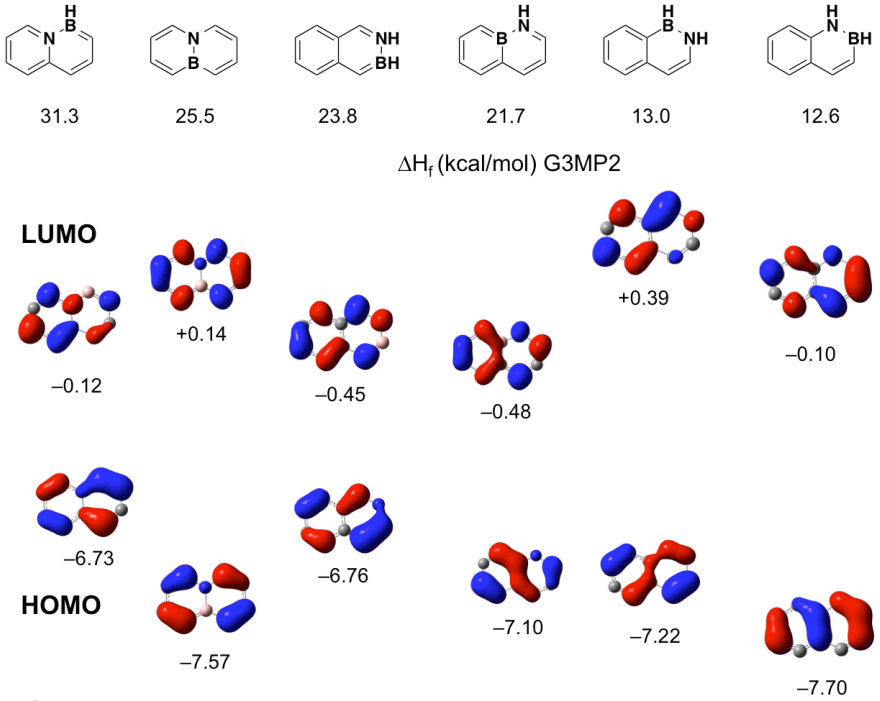


Table S2: Calculated [CAM-B3LYP/6-311G(d,p)] Kohn-Sham HOMO and LUMO levels in eV for BN anthracenes in addition to calculated (G3MP2) heats of formation.

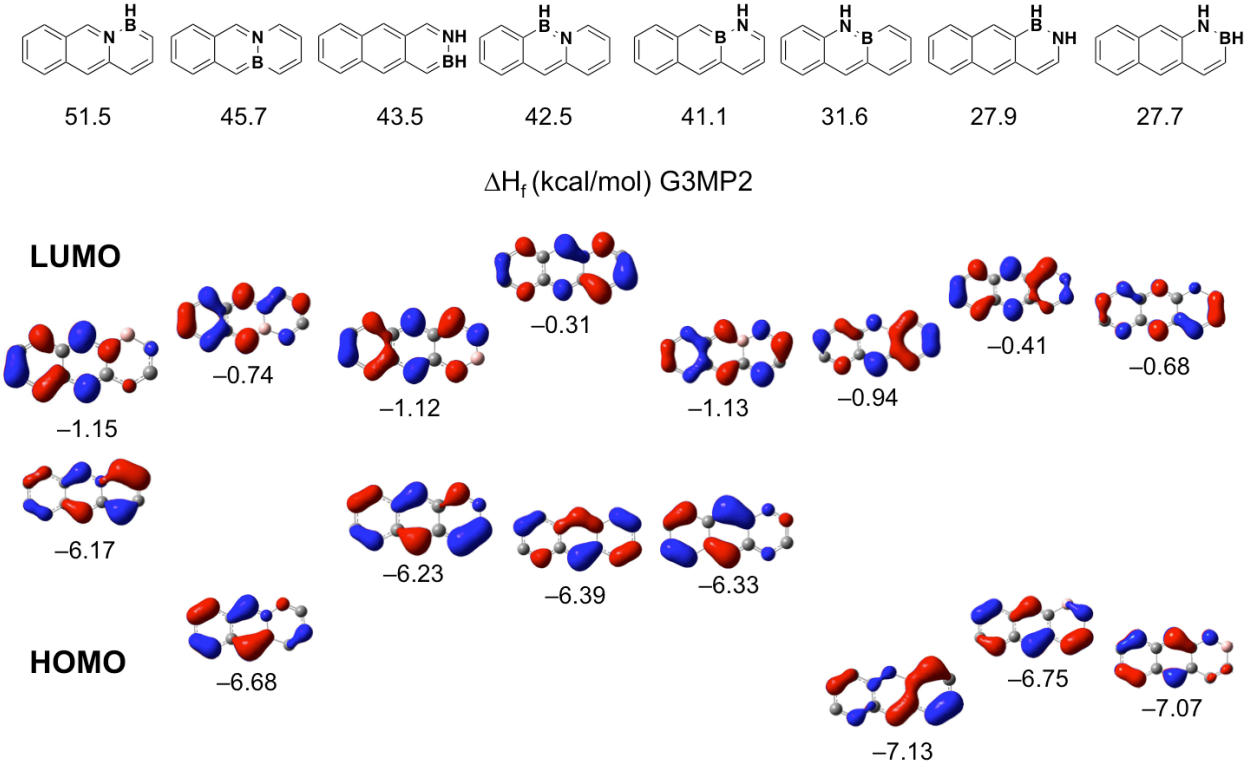
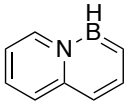
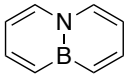
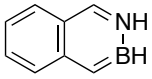
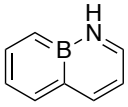
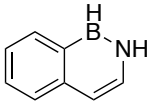
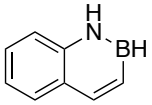
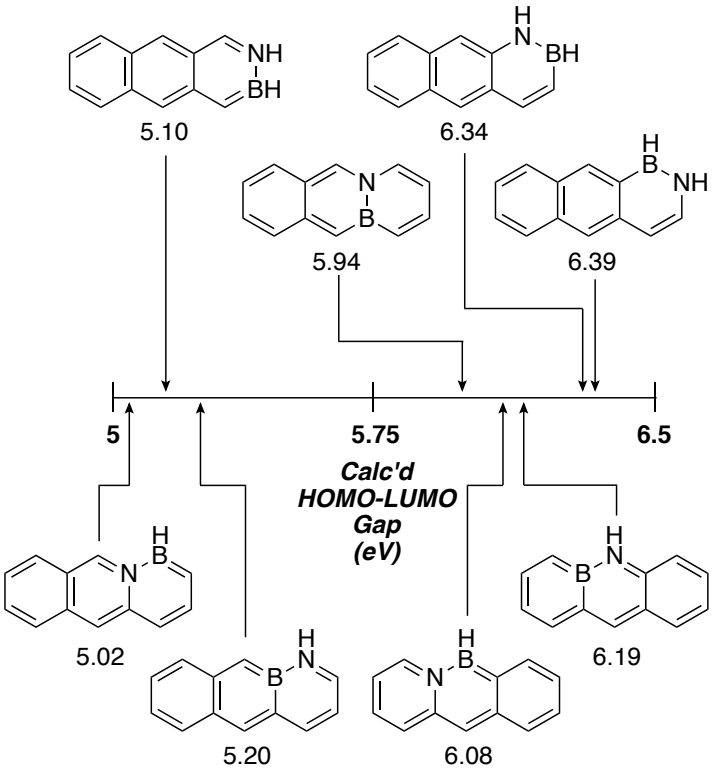


Table S3: G3MP2 Ionization energies and electron affinities (acetonitrile solution) in eV with experimental ionization energies (See Tables S4–S7) and experimental solution-phase reduction potential in V vs. Fc/Fc^{+} (see Figure S3)

	IP gas (eV, G3MP2)	IP MeCN (eV, G3MP2)	IP gas (eV, UV-PES)	EA gas (eV, G3MP2)	EA MeCN (eV, G3MP2)	E_{pc} MeCN (V vs. Fc/Fc^{+})
	7.55	5.63	7.44	0.08	2.13	–2.82
	8.45	6.54	8.42	–0.30	1.84	–3.34
	7.70	5.81	---	0.16	2.28	---
	8.03	6.20	7.78	0.32	2.49	–2.57
	8.10	6.14	---	–0.38*	1.89	---
	8.12	6.47	8.45	–0.11	2.03	–2.95

*G3MP2B3 value

Figure S1. Visualization of BN anthracene calculated Kohn-Sham HOMO-LUMO gap similarities between B/N inverted pairs



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.

For the reliable assignment of PE bands, different calculations of ionization energies using the 6-311G(d,p) basis set[5] have been carried out on optimized geometrical parameters of molecular structures under investigation. Tables S3–S7 contain calculated Kohn-Sham (CAM-B3LYP) energies of molecular orbitals (MO) ($-\varepsilon^{K-S}$)[6], ΔSCF+TD-DFT (CAM-B3LYP)[7], OVGF and P3[8], SAC-CI[9] and "corrected" ionization energies[7b], with the Molekel[10] MOs visualization of the investigated BN naphthalenes, and all-carbon naphthalene.

BN-9,1-Naph is characterized by the very intense and sharp low energy band at 7.44 eV, the next one is located at 9.36 eV and is followed by a much broad band at 11.10 eV with a left-side shoulder at 10.74 eV. The assignment of these first three, π symmetry (a″), ionizations follows the order of the low-energy MOs of naphthalene. The fourth (σ symmetry (a′)) and fifth (π symmetry (a″)) ionizations appear at 11.10 eV.

The most intense band of the PE spectrum of **BN-9,10-Naph** appears at low energy at 8.42 eV and the nature of this HOMO (a_2) corresponds to the π_1 of the naphthalene (as for **BN-9,1-Naph**). The HOMO-1 appears at the same energy (8.42 eV) and is attributed to the bonding combination of the nitrogen lone pair delocalized in the p boron vacant orbital in the antibonding interaction with the $\pi_{C=C}$ of two naphthalene rings (b_1). Another MO with $\pi_{C=C}$ of two naphthalene rings in antibonding interaction with nitrogen lone pair appears at nearly 2 eV higher energy ((b_1), 10.39 eV) and is followed by two σ symmetry (a′) ionizations: left-side shoulder ((b_2), 10.84 eV) of the band at 11.25 eV (a_1). HOMO-5 (right-side shoulder at 11.48 eV, (a_2)) looks like antibonding combination of π systems of two naphthalene rings. The higher energy bands are of σ symmetry and are located at 12.55 and 13.29 eV.

The PE spectrum of **BN-1,9-Naph** is characterized by the low-energy band at 7.78 eV (HOMO, a") followed by the more sharp and intense one at 8.46 eV (HOMO-1) and also attributed to the π MO. The third band at 10.20 eV contains two MO ionizations: the first one of σ-symmetry (a') and the second one of π-symmetry (a"). The next two ionizations appear at 11.28 eV (a') and 11.47 eV (a").

For **BN-1,2-Naph**, the HOMO of π symmetry (a″) is located at 8.45 eV and corresponds to the bonding combination of nitrogen lone pair delocalized in the p boron vacant orbital, and the $\pi_{C=C}$ antibonding interaction attributed to the π_2 of the naphthalene system. The two

following bands at 8.68 and 10.45 eV correspond to the HOMO-1 and HOMO-2, respectively, and are attributed to the π symmetry (a″), featuring nitrogen lone pair in the antibonding interaction with π_1 / bonding interaction with π_3 system of the naphthalene molecule, respectively. The band observed at 11.08 eV is representative of the σ symmetry (a’). The ionization at 11.35 eV of the π symmetry (a″) corresponds to the bonding combination of the nitrogen lone pair delocalized in the p boron vacant orbital in the antibonding interaction with the π_4 of naphthalene system. The last higher energy bands at 11.70 and 12.23 eV represent the ionizations of σ symmetry (a’) MOs.

Though the UV-PE spectra were truncated in the main text of this manuscript, the full spectra are reproduced below.

Figure S2: Full UV-PE spectra for the investigated compounds

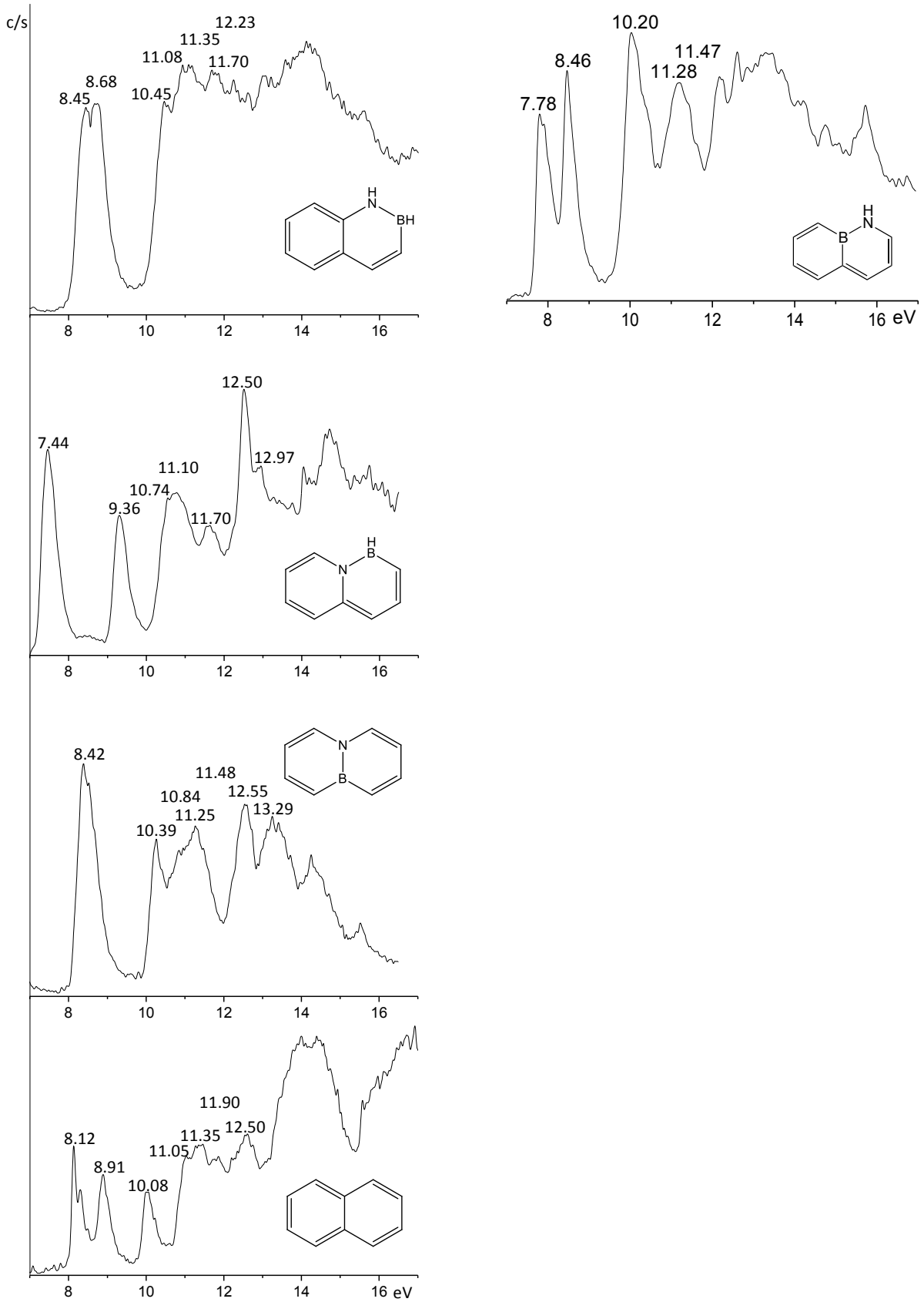


Table S4. Calculated Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF+TD-DFT (CAM-B3LYP), OVGF, P3, SAC-CI and "corrected" ionization energies with the Molekel MOs visualization of **BN-9,1-Naph** in comparison with experimental values (in eV). For all calculations 6-311G(d,p) basis set was applied.

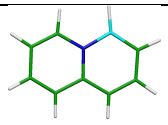
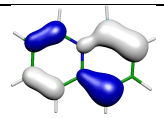
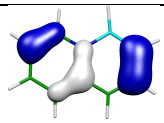
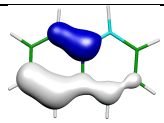
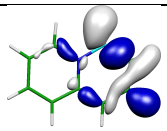
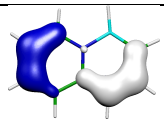
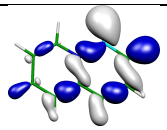
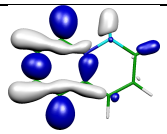
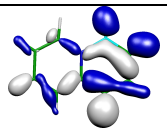
 Nature of MO	$-\varepsilon^{K-S}$	ΔSCF+ TD-DFT	OVGF	P3	SAC-CI	Corrected $x_{exp.}$=0.710	Exp.
 a"	6.73	7.34	7.18	7.31	6.78	7.44	**7.44**
 a"	8.81	9.45	9.16	9.34	8.92	9.52	**9.36**
 a"	10.30	10.70	10.62	10.75	10.45	11.01	**10.74**
 a'	10.32	10.96	11.06	11.04	10.73	11.03	**11.10**
 a"	10.82	11.06	11.11	11.13	10.94	11.53	**11.10**
 a'	10.96	11.61	11.77	11.78	11.44	11.67	**11.70**
 a'	12.02	12.72	12.78	12.85	12.58	12.73	**12.50**
 a'	12.37	12.96	13.20	13.15	12.90	13.08	**12.97**

Table S5. Calculated Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF+TD-DFT (CAM-B3LYP), OVGF, P3, SAC-CI and "corrected" ionization energies with the Molekel MOs visualization of **BN-9,10-Naph** in comparison with experimental values (in eV). For all calculations 6-311G(d,p) basis set was applied.

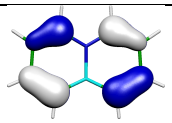
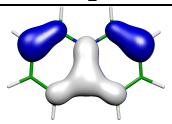
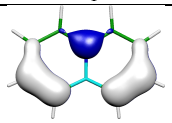
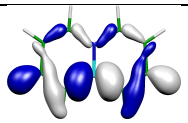
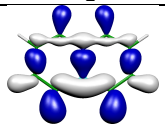
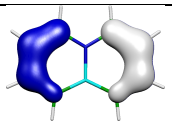
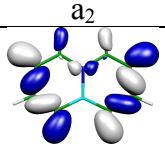
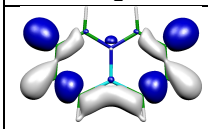
Nature of MO	$-\varepsilon^{K-S}$	ΔSCF+ TD-DFT	OVGF	P3	SAC-CI	Corrected $x_{exp.}$=0.847	Exp.
 a_2	7.57	8.26	8.17	8.26	7.94	8.42	**8.42**
 b_1	7.75	8.33	8.25	8.34	7.97	8.42	**8.42**
 b_1	9.72	10.40	10.13	10.23	10.03	10.57	**10.39**
 b_2	10.23	10.88	10.81	10.90	10.82	11.08	**10.84**
 a_1	10.55	11.23	11.28	11.31	11.11	11.40	**11.25**
 a_2	10.88	11.38	11.29	11.30	11.22	11.72	**11.48**
 b_2	11.80	12.55	12.59	12.60	12.59	12.64	**12.55**
 a_1	12.61	13.36	13.50	13.48	13.48	13.46	**13.29**

Table S6. Calculated Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF+TD-DFT (CAM-B3LYP), OVGF, P3, SAC-CI and "corrected" ionization energies with the Molekel MOs visualization of **BN-1,9-Naph** in comparison with experimental values (in eV). For all calculations 6-311G(d,p) basis set was applied.

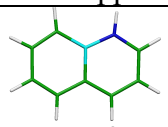
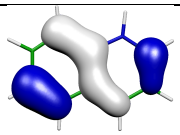
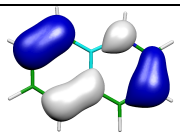
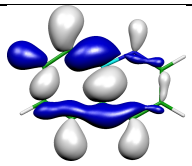
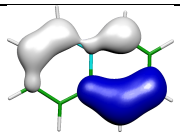
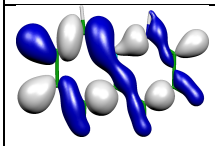
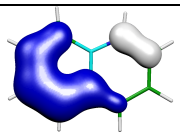
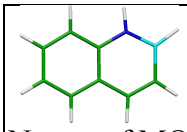
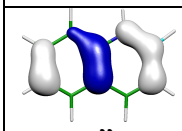
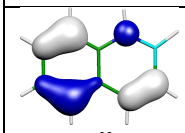
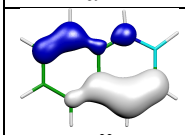
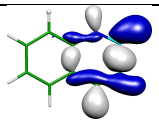
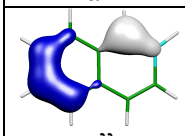
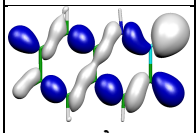
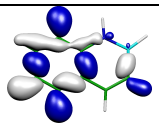
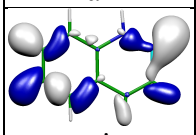
 Nature of MO	$-\varepsilon^{K-S}$	ΔSCF+TD-DFT	OVGF	P3	SAC-CI	Corrected x_{exp}= 0.679	Exp.
 a"	7.10	7.71	7.60	7.74	7.22	7.78	**7.78**
 a"	7.73	8.45	8.11	8.31	7.89	8.41	**8.46**
 a'	9.58	10.21	10.16	10.23	9.88	10.26	**10.20**
 a"	9.72	10.21	10.05	10.14	9.87	10.40	**10.20**
 a'	10.63	11.26	11.26	11.36	11.00	11.31	**11.28**
 a"	10.91	11.50	11.23	11.22	11.01	11.59	**11.47**

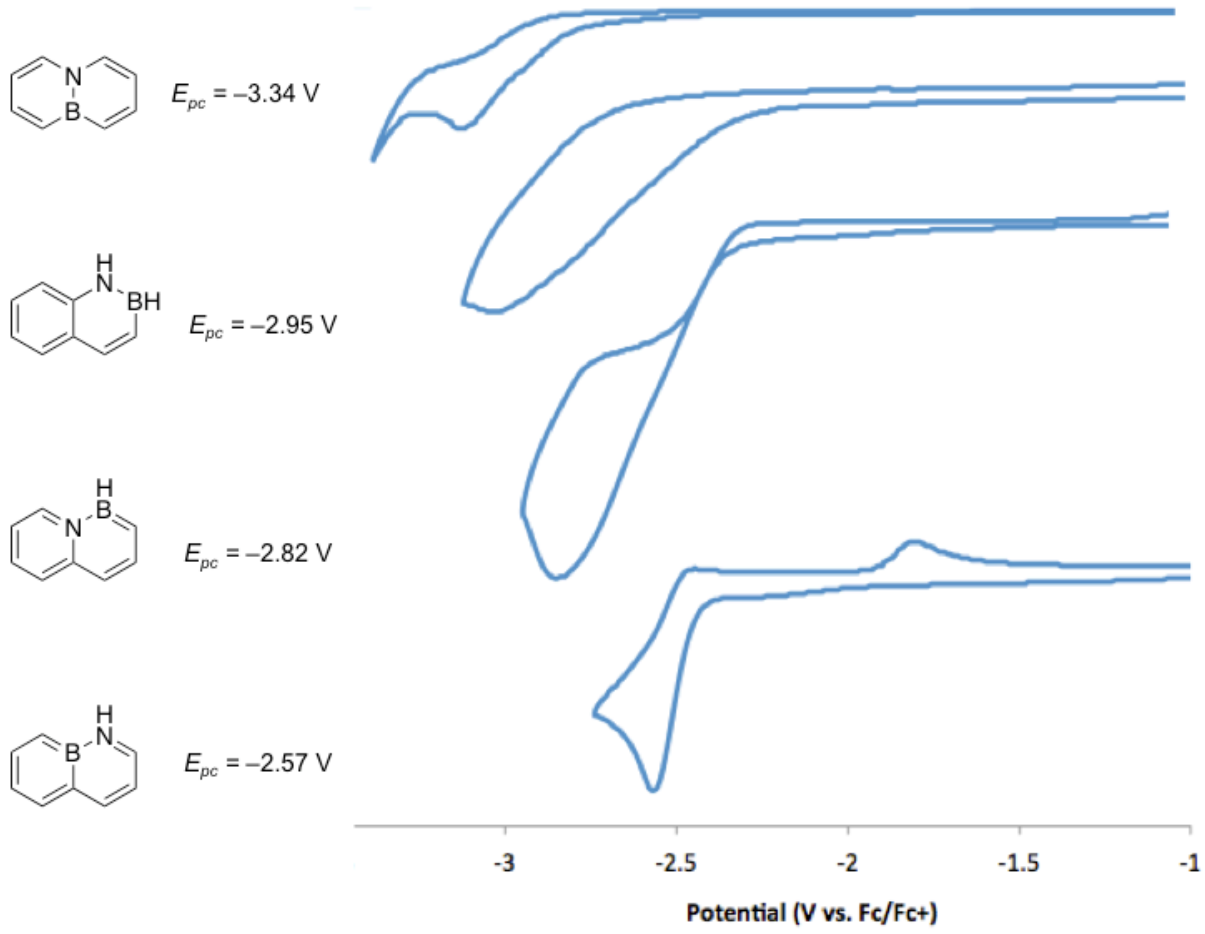
Table S7. Calculated Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF+TD-DFT (CAM-B3LYP), OVGF, P3, SAC-CI and "corrected" ionization energies with the Molekel MOs visualization of **BN-1,2-Naph** in comparison with experimental values (in eV). For all calculations 6-311G(d,p) basis set was applied.

 Nature of MO	$-\varepsilon^{K-S}$	ΔSCF+ TD-DFT	OVGF	P3	SAC-CI	Corrected x_{exp}=0.749	Exp.
 a"	7.70	8.32	8.16	8.04	7.79	8.45	**8.45**
 a"	7.96	8.67	8.47	8.57	8.164	8.71	**8.68**
 a"	10.05	10.65	10.46	10.57	10.28	10.74	**10.45**
 a'	10.32	11.04	11.06	11.07	10.84	11.07	**11.08**
 a"	10.97	11.35	11.31	11.27	11.14	11.72	**11.35**
 a'	10.97	11.69	11.78	11.84	11.54	11.72	**11.70**
 a'	11.55	12.28	12.28	12.36	12.07	12.30	**12.23**
 a'	12.35	13.08	13.33	13.27	13.11	13.10	**13.00**

Cyclic Voltammetry

Irreversible oxidation was observed for all BN naphthalene species. CVs were collected using 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with a scan rate of 150 mV/s. Potentials are reported against the ferrocene/ferrocenium redox couple used as an internal standard.

Figure S3: Cyclic voltammograms



Fluorescence Spectra of BN Naphthalenes

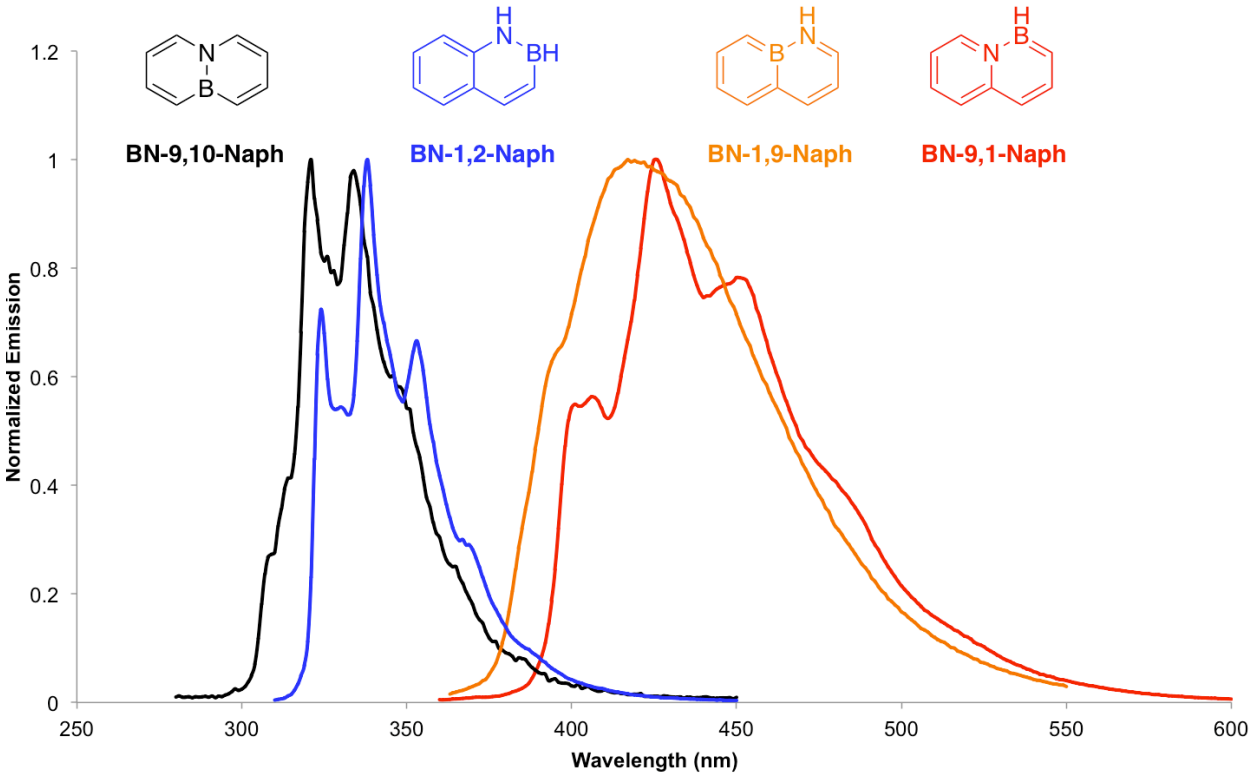


Figure S4: Emission spectra of BN naphthalenes in cyclohexane as the solvent.

Crystal data and structure refinement for BN-9,1-Naph.

Identification code	C8H8BN	
Empirical formula	C8 H8 B N	
Formula weight	128.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.850(2) Å	α= 90°
	b = 6.0119(16) Å	β= 112.370(4)°
	c = 7.995(2) Å	γ = 90°
Volume	348.89(16) $Å^3$	
Z	2	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	136	
Crystal size	0.510 x 0.320 x 0.260 mm^3	
Theta range for data collection	2.806 to 28.674°	
Index ranges	-10<=h<=10, -8<=k<=7, -10<=l<=9	
Reflections collected	5412	
Independent reflections	902 [R(int) = 0.0179]	
Completeness to theta = 25.242∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7082	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	902 / 0 / 62	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.1058	
R indices (all data)	R1 = 0.0395, wR2 = 0.1079	
Extinction coefficient	na	
Largest diff. peak and hole	0.335 and -0.211 $e.Å^{-3}$	

Crystal data and structure refinement for 7F-BN-9,1-Naph.

Identification code	C8H7BFN	
Empirical formula	C8 H7 B F N	
Formula weight	146.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Pc	
Unit cell dimensions	a = 7.465(3) Å	α= 90°
	b = 14.687(6) Å	β= 103.790(7)°
	c = 6.709(3) Å	γ = 90°
Volume	714.4(5) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	304	
Crystal size	0.600 x 0.380 x 0.320 mm^3	
Theta range for data collection	2.774 to 28.431°	
Index ranges	-10<=h<=8, -19<=k<=14, -8<=l<=6	
Reflections collected	3916	
Independent reflections	2294 [R(int) = 0.0217]	
Completeness to theta = 25.242∞	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6999	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2294 / 2 / 205	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1094	
R indices (all data)	R1 = 0.0468, wR2 = 0.1176	
Extinction coefficient	na	
Largest diff. peak and hole	0.246 and -0.218 $e.Å^{-3}$	

Crystal Packing of 7F-BN-9,1-Naph

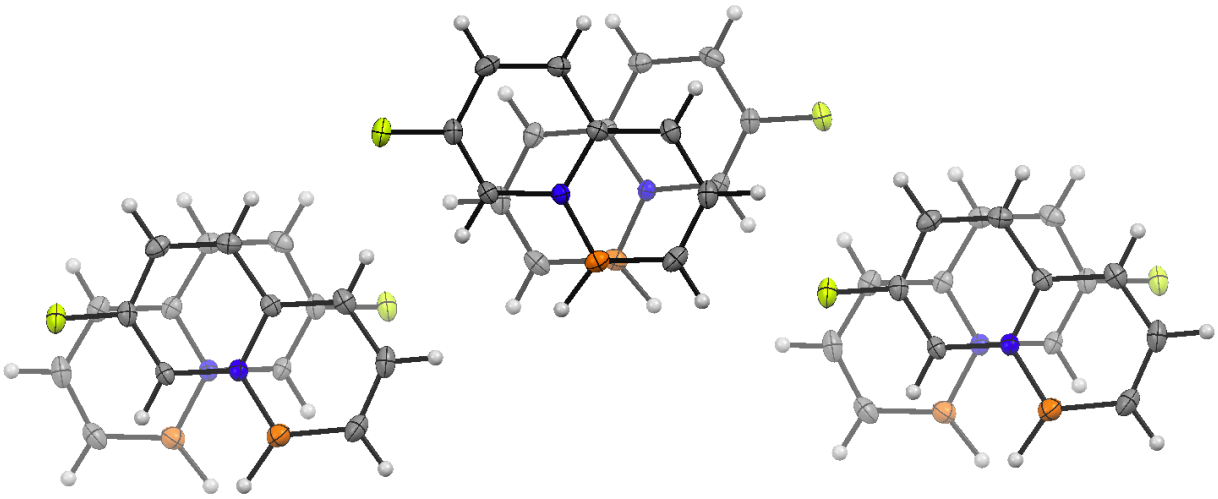


Figure S5. The crystal packing of **7F-BN-9,1-Naph** viewed along the crystallographic *c*-axis, with three consecutive stacks depicted. Two types of stacks alternate as shown.

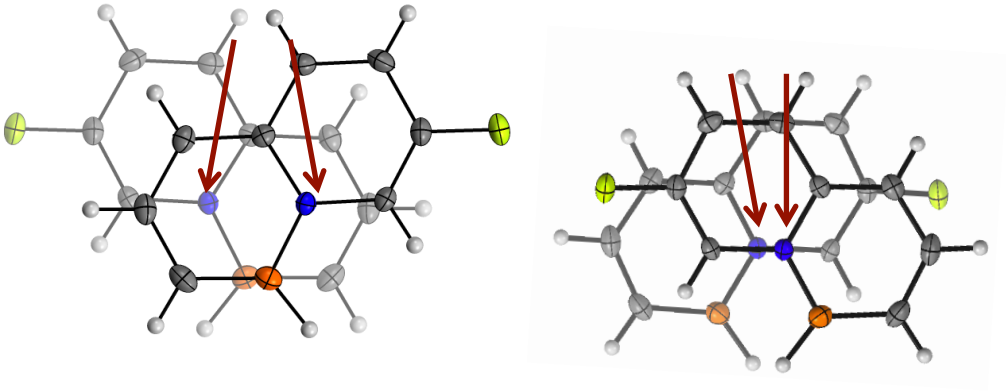


Figure S6. The packing of each type of is depicted with the calculated dipole moments of the constituent molecules drawn. Dipole moments within each π-stack do not cancel in the "down" direction, nor do they cancel between stacks.

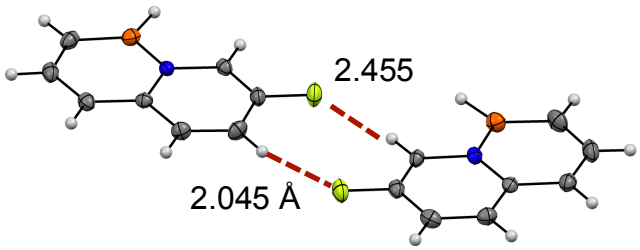


Figure S7. Asymmetric dimers of **7F-BN-9,1-Naph** in the solid state. Within each layer of molecules shown in Figure 2b of the main text there exists coplanar, asymmetric dimers as shown. The molecular dipoles do not cancel within these asymmetric dimers.

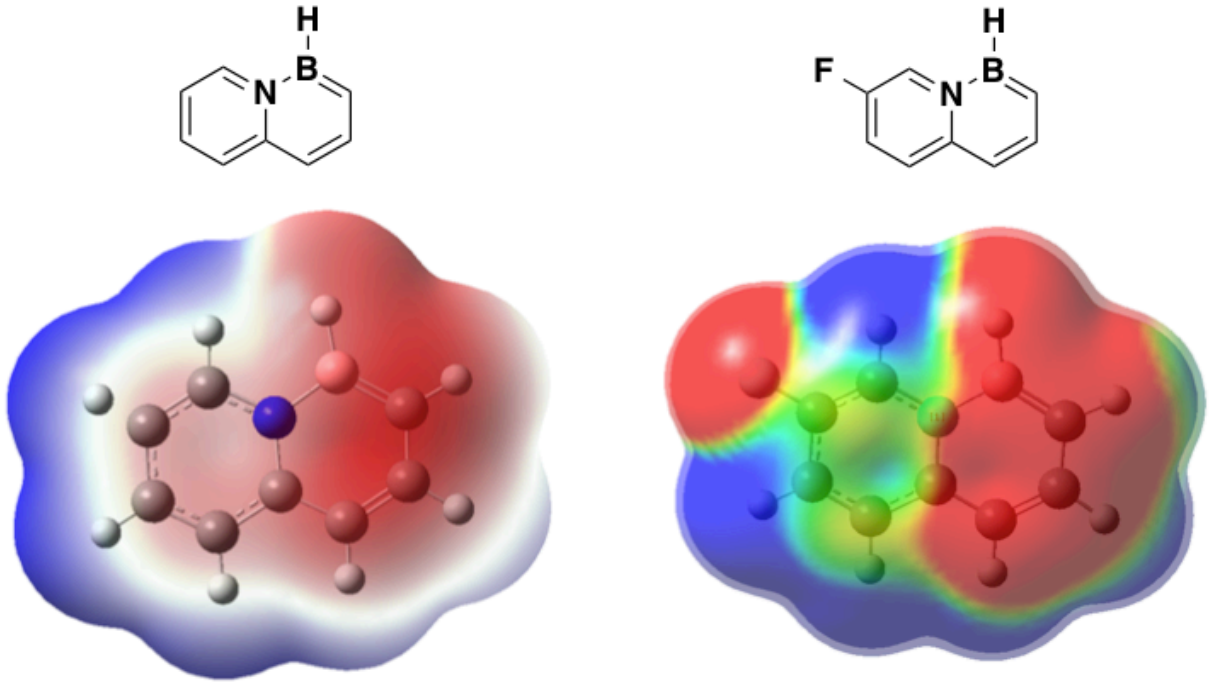


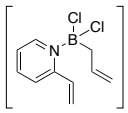
Figure S8. Calculated electrostatic potential (ESP) maps (CAM-B3LYP/6-311G(d,p), 0.0002 electron au isocontour level, +3.14 to –3.14 kcal/mol). Red is most negative, and blue is most positive. **7F-BN-9,1-Naph** shows an electron deficient pyridyl ring in **7F-BN-9,1-Naph** as compared to parent **BN-9,1-Naph**. The periphery of **7F-BN-9,1-Naph** is still mostly electron deficient, though it does contain the electron rich fluorine atom. Intermolecular H•••F interactions[11] help form coplanar dimers within the layers. These elements of the electronic structure of **7F-BN-9,1-Naph** diminish the impetus for edge-to-face π-stacking[12], which is normally thought of as a consequence of the electron deficient periphery of an aromatic system interacting with an adjacent molecule's electron rich π-cloud.

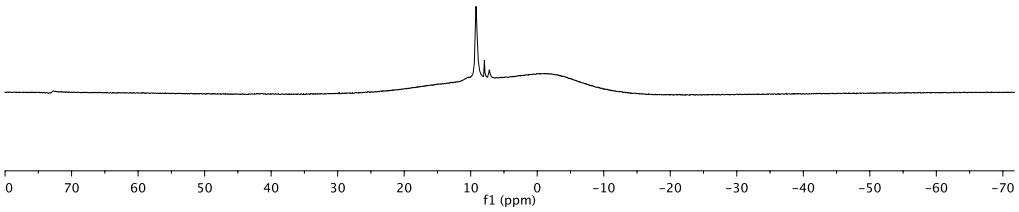
References

(1) Dewar, M. J. S.; Gleicher, G. J.; Robinson, B. P. *J. Am. Chem. Soc.* **1964**, *86*, 5698–5699.
(2) Brown, H. C.; Racherla, U. S. *J. Org. Chem.* **1986**, *51*, 427–432.
(3) Bubnov, Y. N.; Kuznetsov, N. Y.; Pastukhov, F. V.; Kublitsky, V. V. *Eur. J. Org. Chem.* **2005**, 4633–4639.
(4) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51–57.
(5) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.
(6) (a) Koopmans, T. *Physica* **1934**, *1*, 104–113. (b) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165–7168. (c) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691–1694. (d) Perdew, J. P.; Levy, M. *Phys. Rev. B-Condens. Matter* **1997**, *56*, 16021–16028. (e) Stowasser, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1999**, *121*, 3414–3420. (f) Baerends, E. J.; Gritsenko, O. V.; Meer, R. van. *Phys. Chem. Chem. Phys.* **2013**, *15*, 16408–16425.
(7) (a) Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997–1000. (b) Lemierre, V.; Chrostowska, A.; Dargelos, A.; Chermette, H. *J. Phys. Chem. A* **2005**, *109*, 8348–8355.
(8) Ortiz, J. V. *J. Chem. Phys.* **1996**, *104*, 7599–7605.
(9) (a) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68* (5), 2053–2065. (b) Nakatsuji, N. Cluster *Chem. Phys. Lett.* **1978**, *59*, 362–364.
(10) Vareto, U. Molekel, version 4.3, Swiss National Super- computing Centre, Manno, Switzerland.
(11) (a) Loader, J. R.; Libri, S.; Meijer, A. J. H. M.; Perutz, R. N.; Brammer, L. *CrystEngComm* **2014**, *16*, 9711–9720. (b) Taylor, R. *Cryst. Growth Des.* **2016**, *16*, 4165–4168. (c) Hallani, R. K.; Thorley, K. J.; Mei, Y.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. *Adv. Funct. Mater.* **2016**, *26*, 2341–2348.
(12) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887–10893.

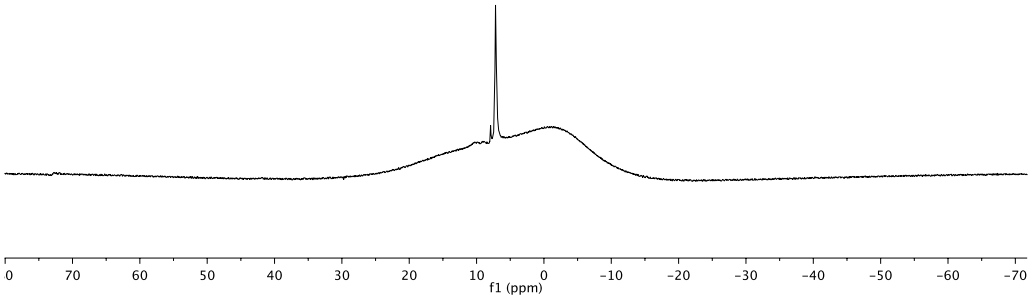
NMR Spectra

Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.1000
4 Acquisition Date	2015-07-22T15:48:25
5 Spectrometer Frequency	192.41
6 Nucleus	11B

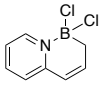


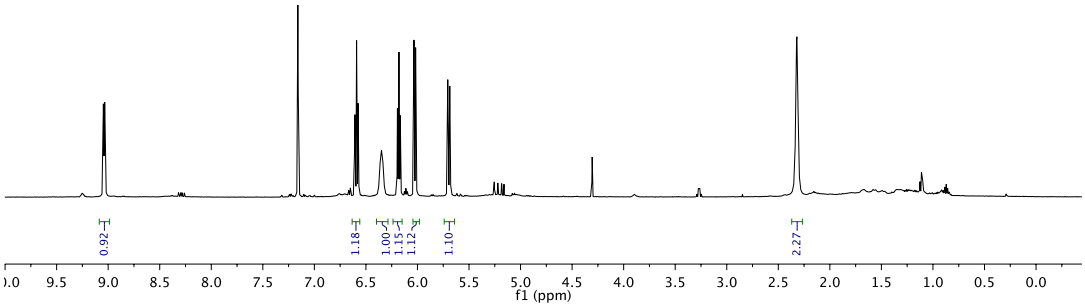


Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.1000
4 Acquisition Date	2015-07-22T15:50:58
5 Spectrometer Frequency	192.41
6 Nucleus	11B

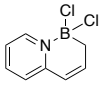


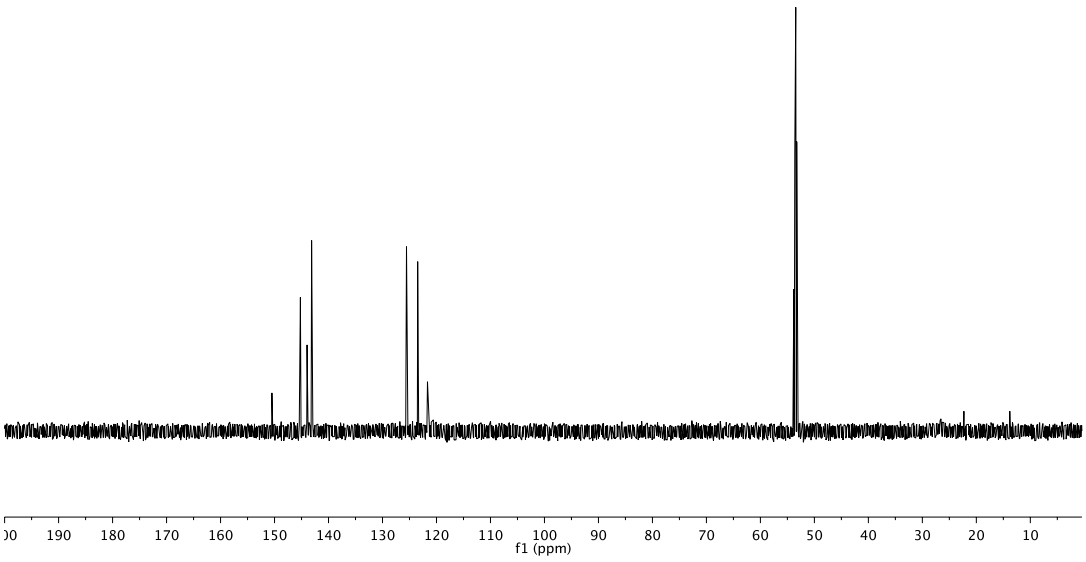
Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2015-03-27T16:53:52
5 Spectrometer Frequency	499.88
6 Nucleus	1H



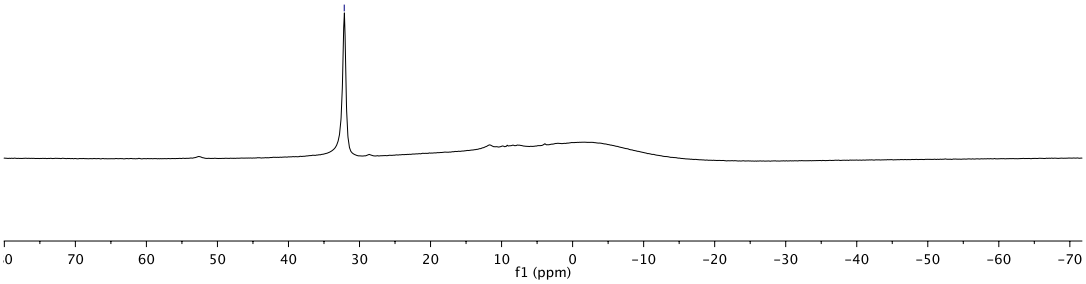


Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2015-11-02T14:37:06
5 Spectrometer Frequency	150.81
6 Nucleus	13C

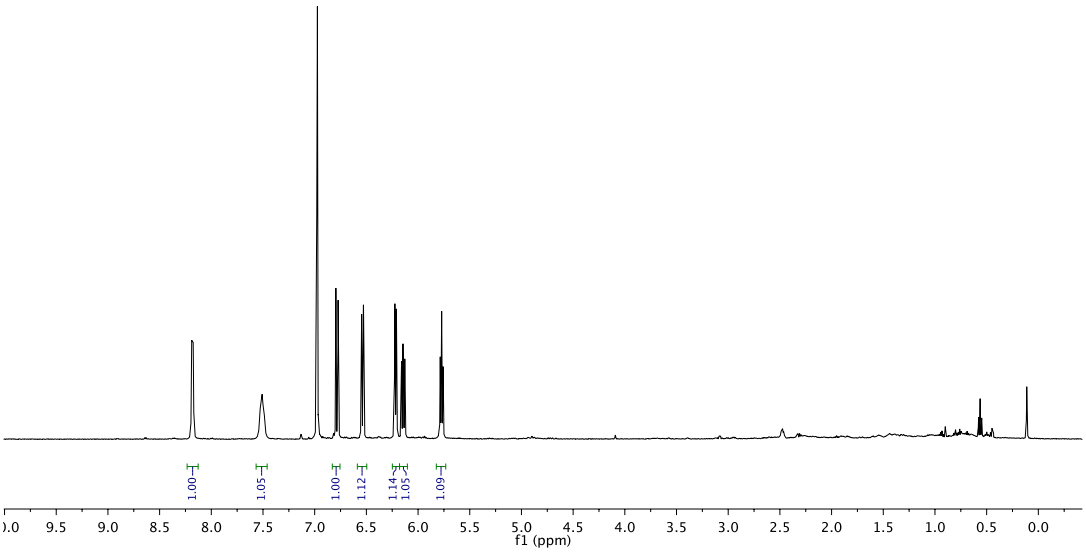




Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.1000
4 Acquisition Date	2015-07-23T11:38:11
5 Spectrometer Frequency	160.38
6 Nucleus	11B



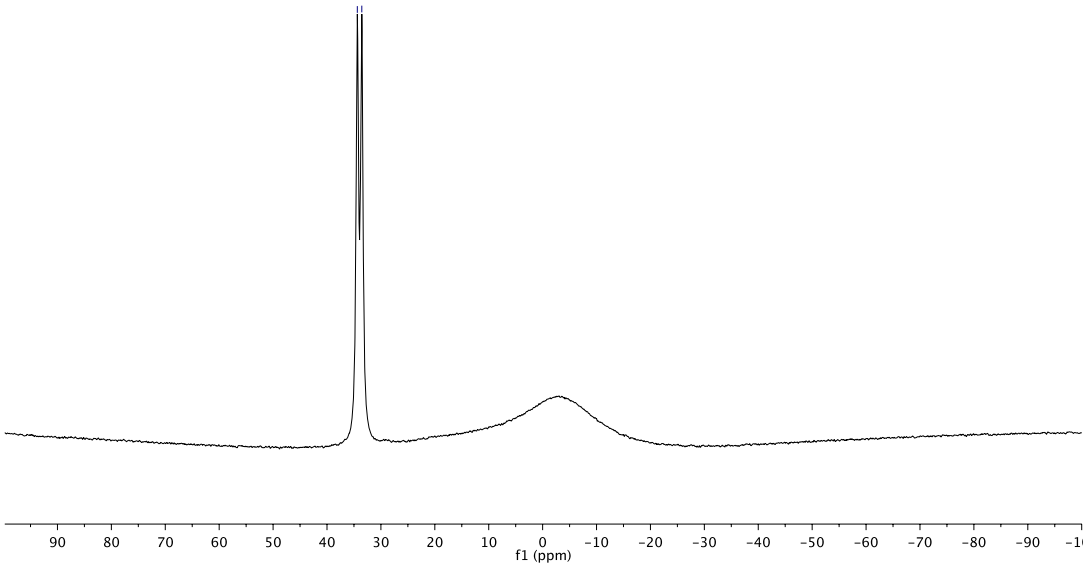
Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2015-04-18T19:42:16
5 Spectrometer Frequency	499.88
6 Nucleus	1H



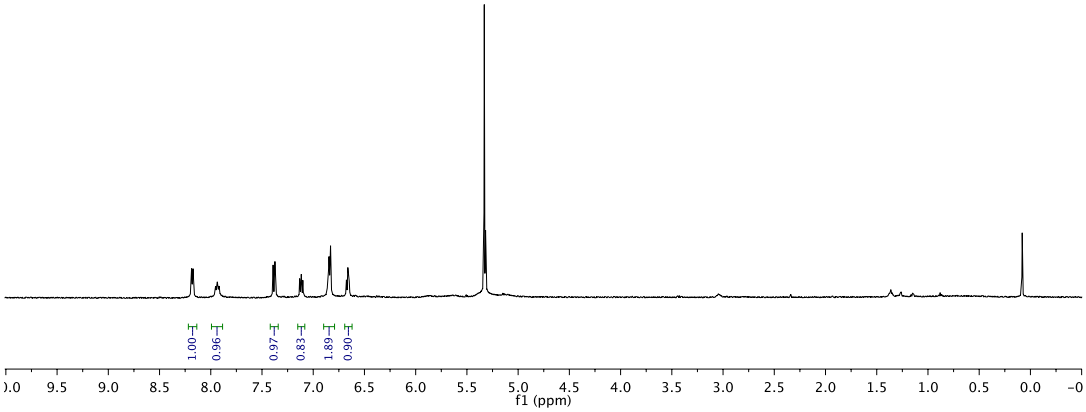
Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2015-04-18T22:08:52
5 Spectrometer Frequency	125.68
6 Nucleus	13C

Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	0.1000
4 Acquisition Date	2015-06-02T14:29:41
5 Spectrometer Frequency	160.38
6 Nucleus	11B

34.3
33.5

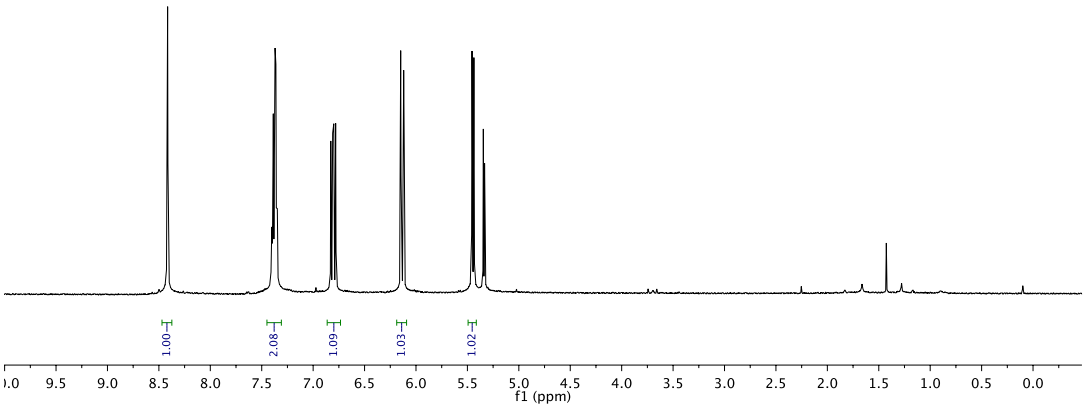


Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-01-13T14:06:07
5 Spectrometer Frequency	499.88
6 Nucleus	1H

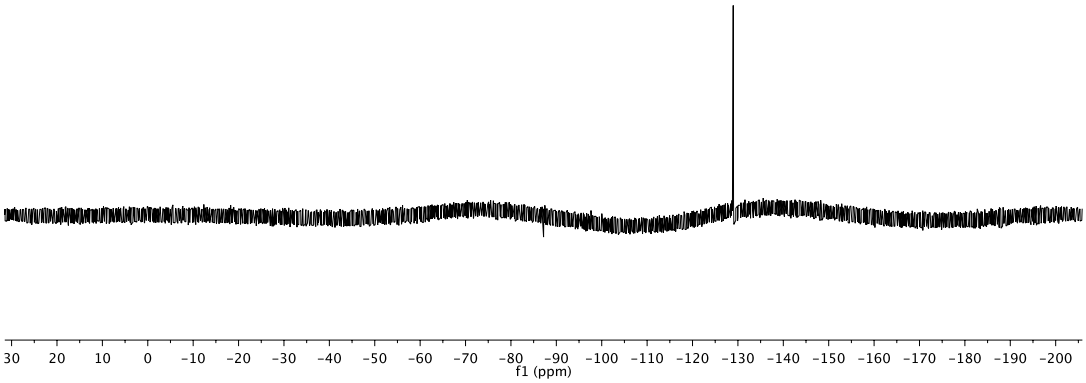


Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2015-06-02T20:13:44
5 Spectrometer Frequency	125.68
6 Nucleus	13C

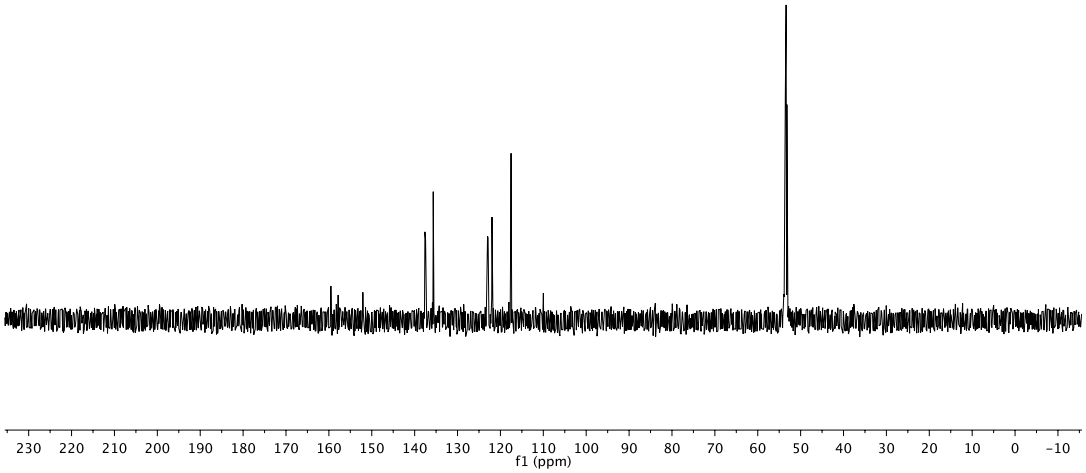
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-19T14:04:04
5 Spectrometer Frequency	599.69
6 Nucleus	1H



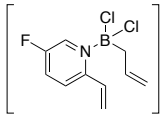
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-18T11:56:53
5 Spectrometer Frequency	376.12
6 Nucleus	19F

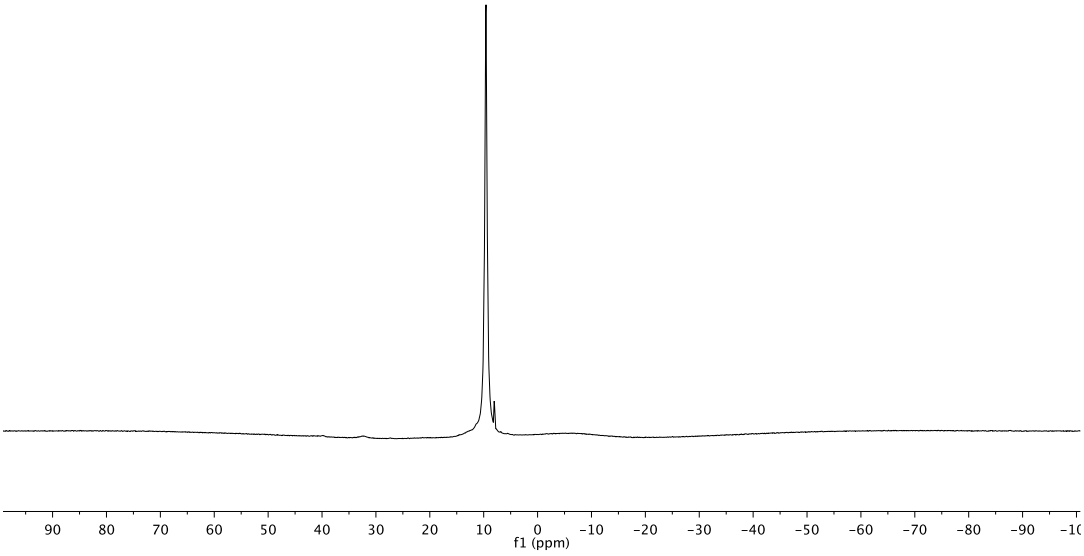


Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-19T14:06:09
5 Spectrometer Frequency	150.81
6 Nucleus	13C

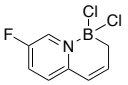


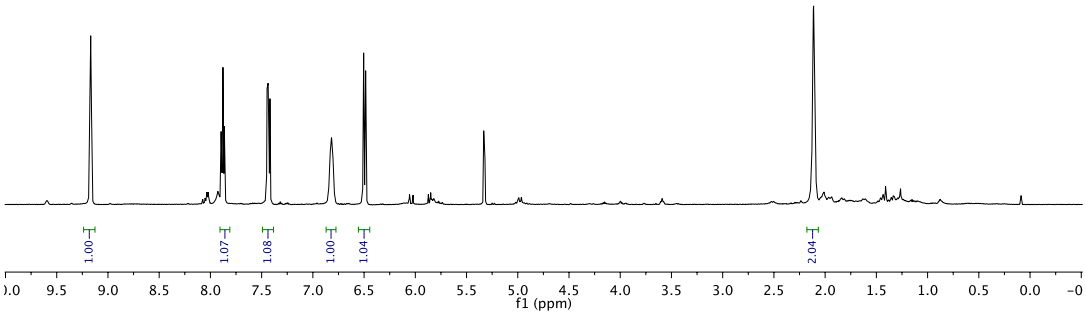
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-02-19T17:01:05
5 Spectrometer Frequency	160.35
6 Nucleus	11B



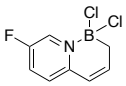


Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-20T12:49:45
5 Spectrometer Frequency	499.89
6 Nucleus	1H

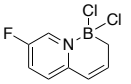


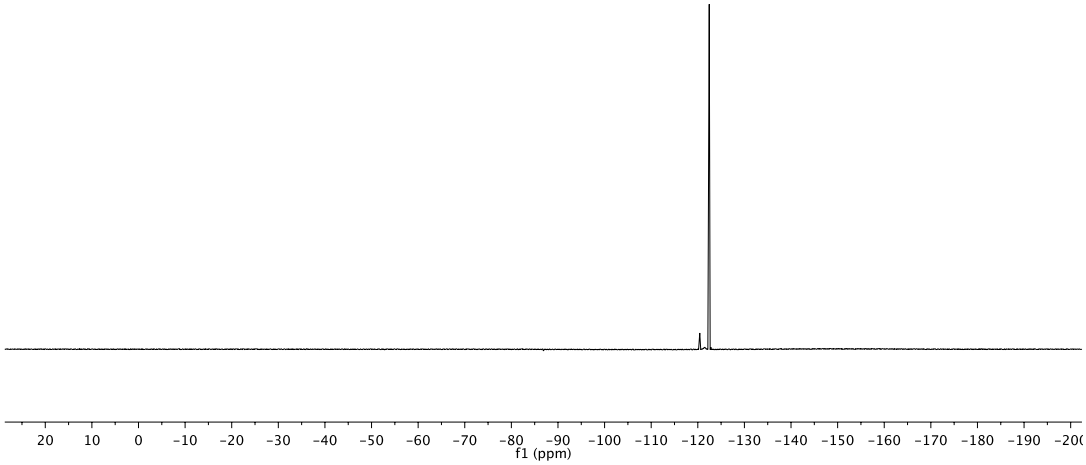


Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	5.0000
4 Acquisition Date	2016-02-20T13:35:45
5 Spectrometer Frequency	150.81
6 Nucleus	13C

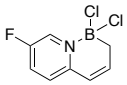


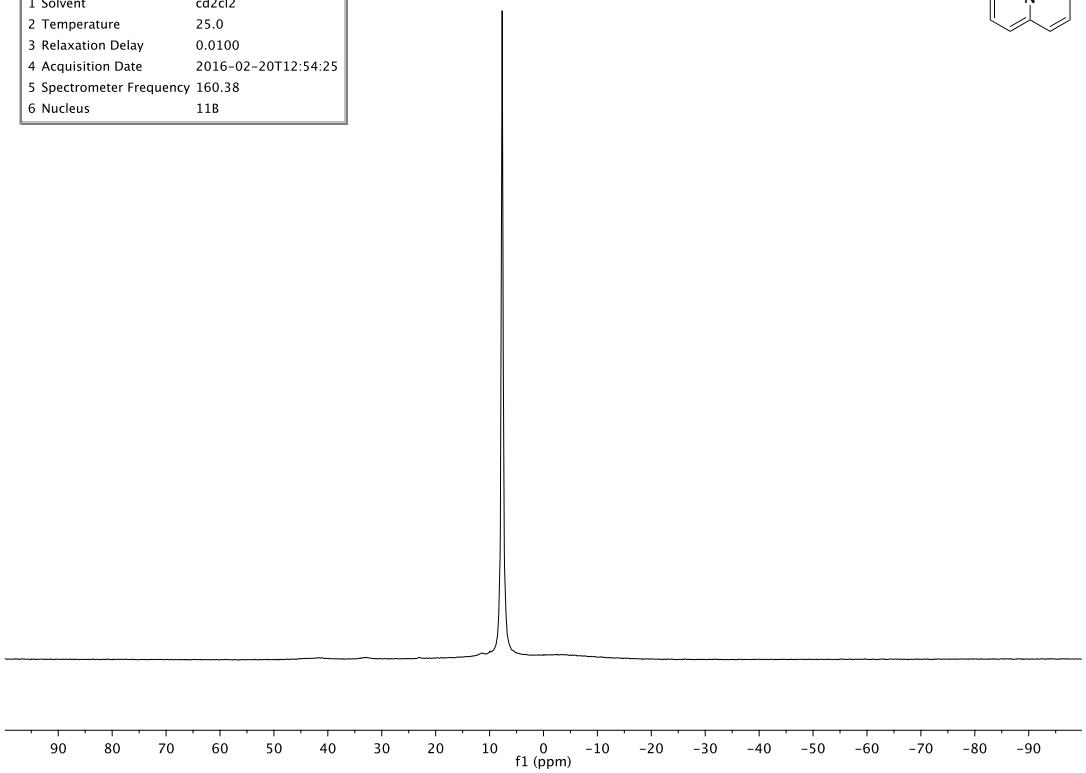
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-20T12:52:08
5 Spectrometer Frequency	470.32
6 Nucleus	19F



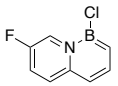


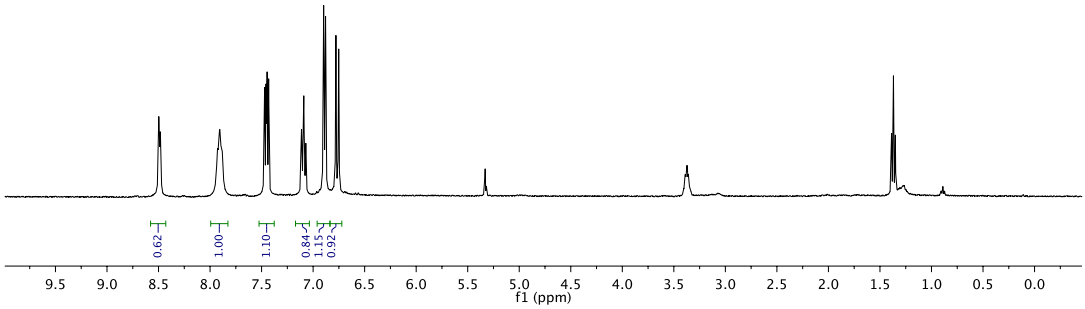
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-02-20T12:54:25
5 Spectrometer Frequency	160.38
6 Nucleus	11B



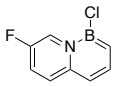


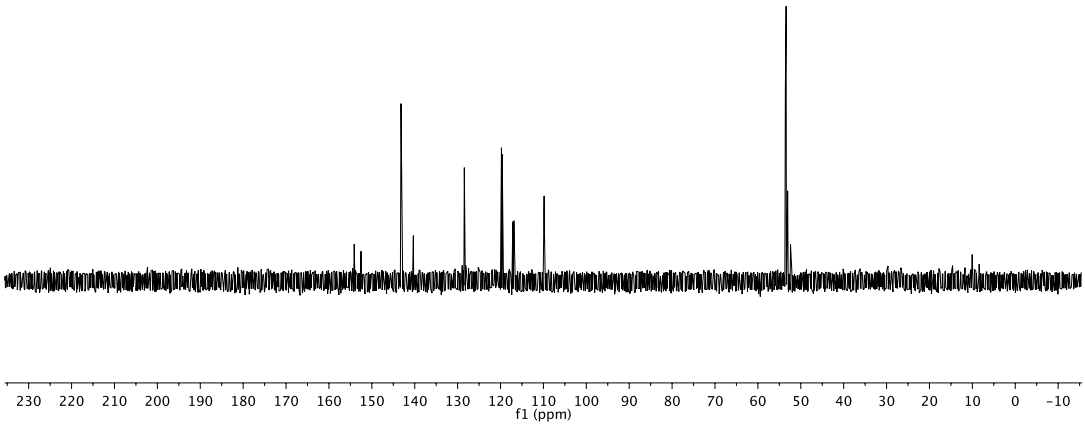
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-23T10:10:48
5 Spectrometer Frequency	399.77
6 Nucleus	1H



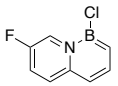


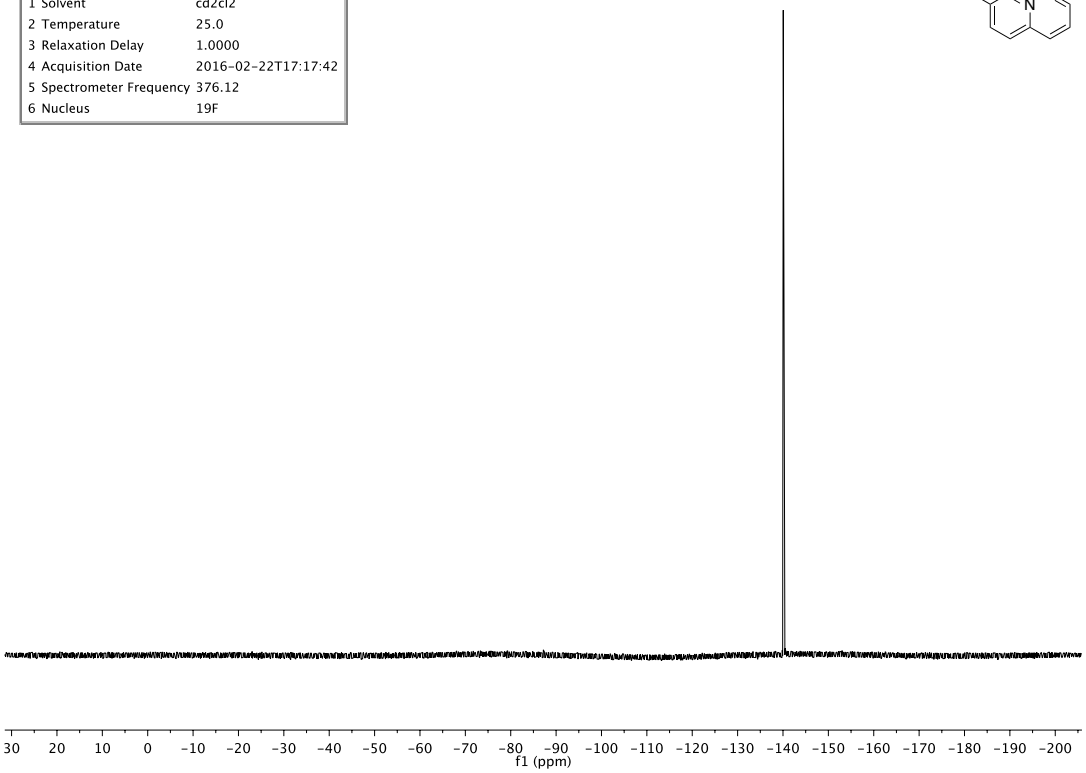
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-22T17:25:58
5 Spectrometer Frequency	150.81
6 Nucleus	13C



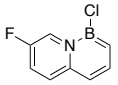


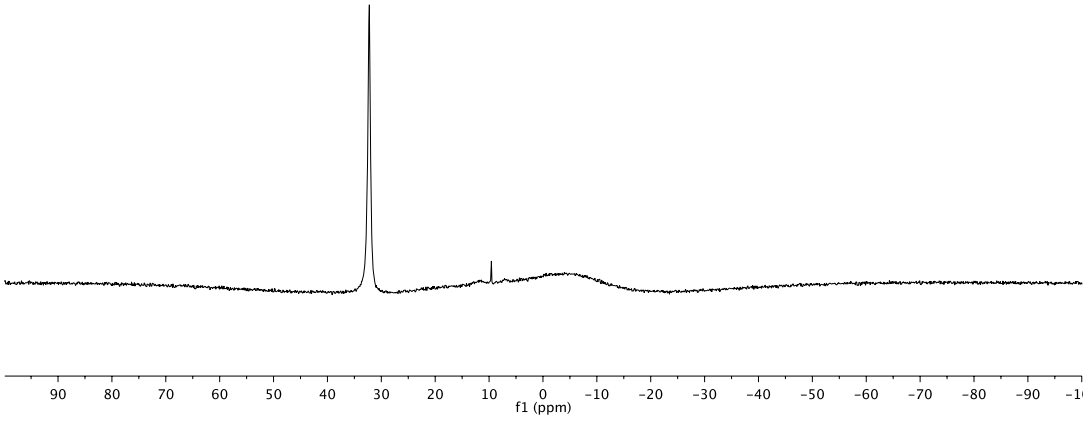
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-22T17:17:42
5 Spectrometer Frequency	376.12
6 Nucleus	19F



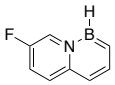


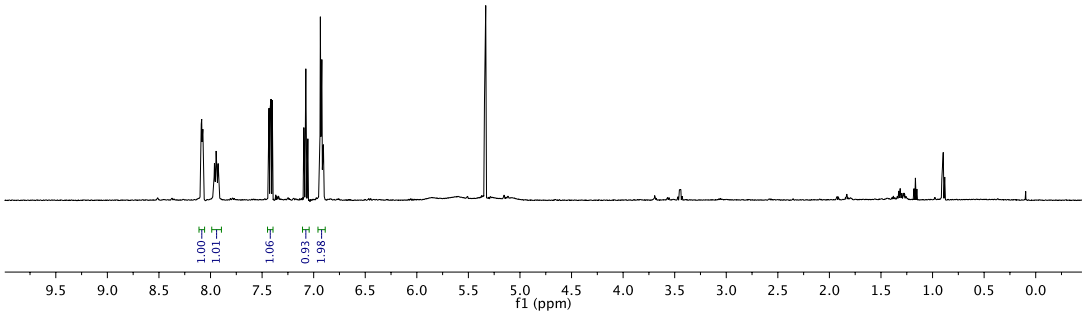
Parameter	Value
1 Solvent	toluene
2 Temperature	25.0
3 Relaxation Delay	0.1000
4 Acquisition Date	2016-02-22T13:40:36
5 Spectrometer Frequency	160.35
6 Nucleus	11B



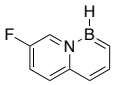


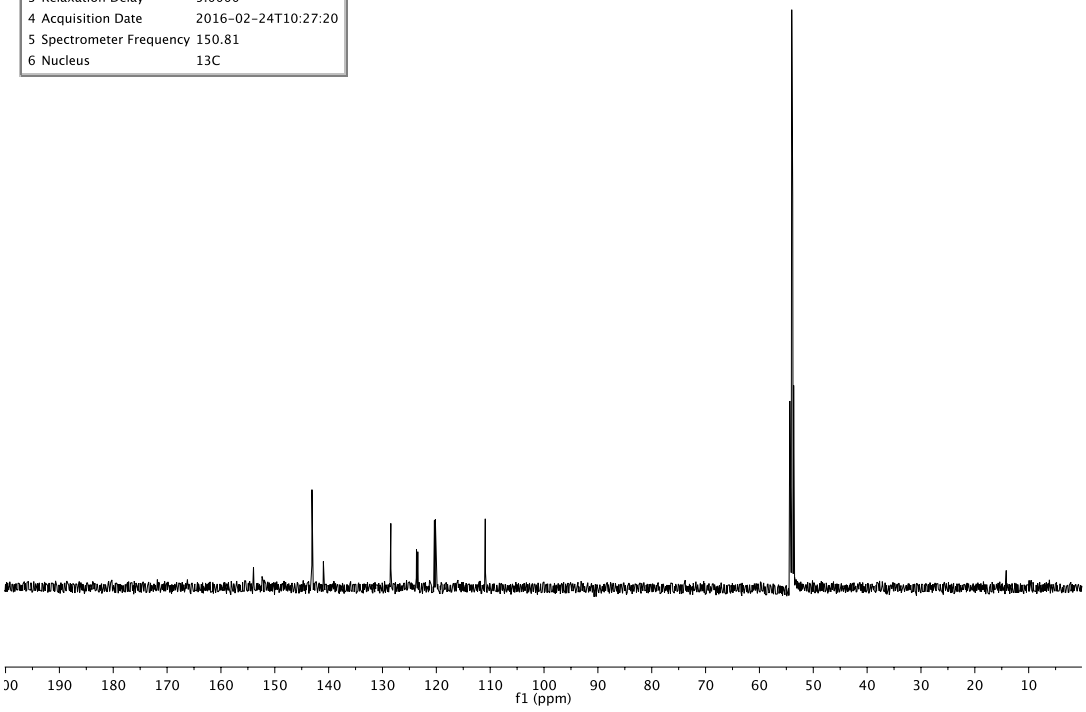
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	10.0000
4 Acquisition Date	2015-10-06T11:17:51
5 Spectrometer Frequency	499.88
6 Nucleus	1H



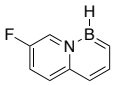


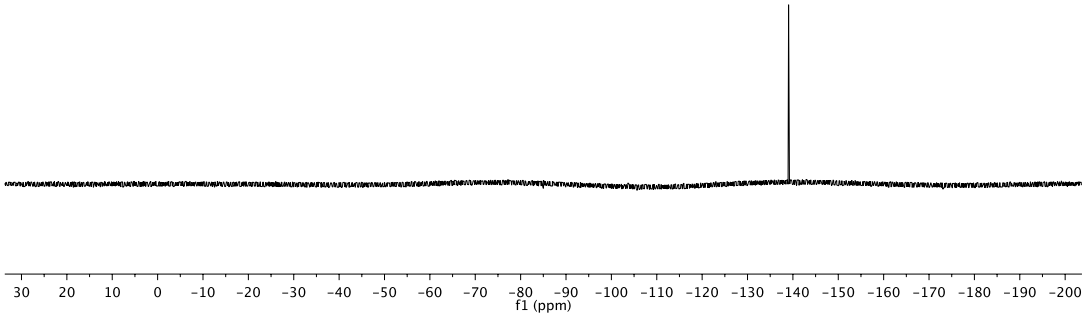
Parameter	Value
1 Solvent	cd2cl2
2 Temperature	25.0
3 Relaxation Delay	5.0000
4 Acquisition Date	2016-02-24T10:27:20
5 Spectrometer Frequency	150.81
6 Nucleus	13C





Parameter	Value
1 Solvent	“cd2cl2”
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2016-02-24T10:07:50
5 Spectrometer Frequency	376.12
6 Nucleus	19F





Parameter	Value
1 Solvent	cd2cl2”
2 Temperature	25.0
3 Relaxation Delay	0.0100
4 Acquisition Date	2016-02-24T10:11:23
5 Spectrometer Frequency	128.26
6 Nucleus	11B