Supporting Information (SI)

Synthesis and Characterization of a Boron–Nitrogen–Boron Zigzag–Edged Benzo[*fg*]tetracene Motif

Michael Fingerle,[a] Cäcilia Maichle-Mössmer,[b] Simon Schundelmeier,[a] Bernd Speiser,[a]

Holger F. Bettinger[a,*]

[a] Institut für Organische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany;
[b] Institut für Anorganische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-Mail: Holger.Bettinger@uni-tuebingen.de

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1. GENERAL

All reactions were done under dry and inert conditions by flaming all glassware with a heat gun under vacuum and purging with argon. Chemicals and solvents were purchased in anhydrous form from commercial suppliers. Deuterated dichloromethane was dried over 4 Å molecular sieve and degassed by three freeze-pump-thaw cycles. For working under inert conditions, a MBraun UNILab Glovebox was used. Column chromatography was done with a medium pressure liquid chromatography (MPLC) system (PuriFlash 430 evo, Interchim) using Si-HP 20 µm columns. Thin layer chromatography (TLC) was conducted on pre-coated polyester sheets (40 x 80 mm) from Machery-Nagel (POLYGRAM® SIL G/UV254) with 0.2 mm silica gel 60 with fluorescent indicator. For visualization, a UV light source (254 nm and 366 nm) was used. Nuclear magnetic resonance spectroscopy (NMR) was measured on a Bruker Avance III HD 400 or on a Bruker Avance III HDX 600 both equipped with a dual ($^{1}H/^{13}C$) probe head. Chemical shifts (δ) are given in ppm, coupling constants *J* in Hertz (Hz) and the multiplicities of the signals are designated as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, and m = multiplet. Reference for ^{1}H and ^{13}C is tetramethylsilane (TMS) and for ^{11}B $BF_3{\cdot}OEt_2$ in $CDCl_3$. The solvent signal of CD_2Cl_2 was calibrated on 5.32 ppm for ^{1}H-NMR and 53.84 ppm for ^{13}C spectra. High resolution electron spray ionization time of flight mass spectrometry (ESI-TOF-MS) was measured on a maXis 4G Bruker system. Low resolution electron impact mass spectrometry was measured on a MSD 5977 (Agilent Technology) with a DIP (direct inlet probe, SIM) system (EI-MS, 70 eV). Elemental analyses were determined using the Euro EA 3000 system (HEKAtech GmbH).

1.1 UV/VIS ABSORPTION AND FLUORESCENCE SPECTROSCOPY

Optical spectra were recorded on a PerkinElmer Lambda 1050 spectrometer with a PerkinElmer 3D WB Det Module. Emission and excitation spectra were measured on a Cary Varian SPVF spectrometer using Hellma Analytics quartz cuvettes. All spectra were recorded in spectroscopic grade solvents.

The fluorescence quantum yield of **5** in dichloromethane was also recorded with an excitation wavelength λ_{ex} = 373 nm. The reference was anthracene in ethanol (φ_{Fl} = 0.27).[1]

1.2 CRYSTAL STRUCTURE DETERMINATION

Compound **5** was crystallized from *n*-hexane as colorless needles. A serviceable crystal was selected under an optical microscope and mounted on a Bruker SMART APEX II instrument equipped with a fine focus sealed tube and curved graphite monochromator using MoK_α radiation (λ = 0.71073 Å). The crystal was kept at *T* = 100 K during data collection. The data collection strategy was determined using COSMO[2] employing ω and ϕ scans. Raw data were processed using APEX[3] and SAINT,[4] corrections for absorption effects were applied using SADABS.[5]

The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using SHELXTL[6] and Shelxle.[7] The data were refined with the following twin law (Twin 0 0 1 0 -1 0 1 0 0) and additionally as an inversion twin. The CCDC reference number is 1557246.

1.3 COMPUTATIONAL METHODS

Geometry optimizations on the S_0 and S_1 potential energy surfaces were performed using the hybrid density functional B3LYP[8,9] as implemented in Gaussian 09[10] in conjunction with the 6-311+G** basis set.[11] The time-dependent version of DFT was employed for computing vertical excitation energies and for geometry optimization on the S_1 PES.[12] Computation of second derivatives either analytically (S_0) or by finite differences (S_1) confirmed that minima and transition states have no or only one imaginary vibrational frequency. The harmonic vibrational frequencies were employed in the standard approximation for obtaining Gibbs free energies at 298.15 K.

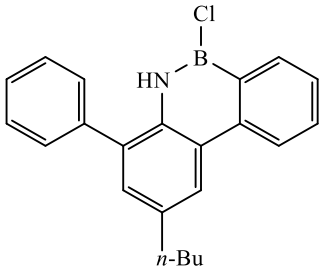
1.4 CYCLIC VOLTAMMETRY

Solvents used for electrochemical experiments were purified by distillation under an argon atmosphere. Amylene free dichloromethane was distilled over P_2O_5 and K_2CO_3 and stored over dried basic Al_2O_3. It was used within the next 5 days without deterioration of quality. Acetonitrile was distilled successively over P_2O_5, CaH_2, and P_2O_5 again. NBu_4PF_6 was recrystallized four times from ethanol/water 3:1 and dried at ≈ 2 mbar and 120 °C for three days.

Electroanalytical experiments were performed at 17 °C under an argon atmosphere with an ECO-Autolab PGSTAT100 (Metrohm) with GPES-Software 4.9.007. As the working electrode, a Pt disk electrode tip (Metrohm part No. 6.1204.310; nominal diameter 3 mm) was used. The electrode was polished with alumina (0.3 µm; Buehler Micropolish) prior to experiments. The counter electrode consisted of a Pt wire with 1 mm diameter. A Haber-Luggin double reference electrode with a potential determining Ag/Ag^+ redox system (0.01 M $AgClO_4$ in 0.1 M NBu_4PF_6/CH_3CN)[13] was used as the potential standard. *iR* drop was compensated by positive feedback under control of the GPES software. Cyclic voltammetric experiments were performed at a scan rate of 0.2 V s^{-1}. The potentials are referenced to an external ferrocene standard ($E^0(Fc/Fc^+)$ vs. Ag/Ag^+ = +209 mV).

2. SYNTHETIC PROCEDURES

SYNTHESIS OF 2-BUTYL-6-CHLORO-5,6-DIHYDRO-4-PHENYLDIBENZO[*C,E*][1,2]AZABORININE (2)

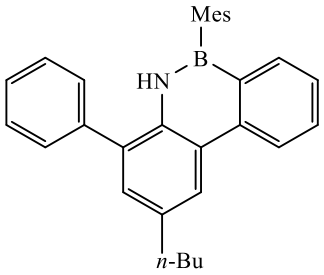


To an ice cooled solution of 1.0 g (3.3 mmol, 1 eq) 4-*n*-butyl-2,6-diphenylbenzenamine in 40 mL dry toluene was added dropwise 5.9 mL (1 M in *n*-hexane, 5.9 mmol, 1.8 eq) BCl_3. After stirring for ½ h, the solution was warmed to room temperature and stirred for 1 h. The resulting mixture was stirred for 6 h under reflux. After being cooled to room temperature, 88 mg (0.7 mmol, 0.2 eq) $AlCl_3$ was added and the suspension was stirred for 18 h under reflux. After the reaction was finished, all solvents were removed under vacuum to obtain the crude product of **2** (1.5 g) as a grey solid.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.51-8.55 (m, 1H), 8.24-8.29 (m, 2H), 7.99 (bs, 1H), 7.80-7.86 (m, 1H), 7.44-7.67 (m, 6H), 7.27 (s, 1H), 2.77-2.83 (m, 2H), 1.67-1.77 (m, 2H), 1.39-1.50 (m, 2H), 0.93-1.02 (m, 3H).

^{11}B NMR (128 MHz, CD_2Cl_2, δ): 34.4.

SYNTHESIS OF 2-BUTYL-5,6-DIHYDRO-6-MESITYL-4-PHENYLDIBENZO[*C,E*][1,2]AZABORININE (3)



To a solution of 1.5 g **2** (crude product) in 50 mL dry benzene was added 4.5 g MesMgBr. Solid MesMgBr was obtained by removing the solvent from 20 mL of a 1 M solution in diethyl ether. After transferal into a glovebox, the appropriate amount was taken from the solid. The resulting suspension was stirred for 1 h at room temperature. All solid materials were filtered and washed with 2 x 15 mL *n*-hexane and 3 x 10 mL dichloromethane. The combined organic layers were washed with 3 x 30 mL water and dried over $MgSO_4$. All solvents were removed in vacuum and the obtained yellow oil was purified by column chromatography (silica gel, *n*-hexane/DCM 19:1, R_f = 0.4) yielding 949 mg (2.21 mmol, 67 % over 2 steps) **3** as colorless solid.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.57-8.62 (m, 1H), 8.33-8.36 (m, 1H), 7.94 (bs, 1H), 7.75-7.80 (m, 1H), 7.66-7.69 (m, 1H), 7.48-7.55 (m, 4H), 7.39-7.45 (m, 2H), 7.26-7.28 (m, 1H), 6.87 (s, 2H), 2.84 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 2.09 (s, 6H), 1.71-1.81 (m, 2H), 1.43-1.52 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H).

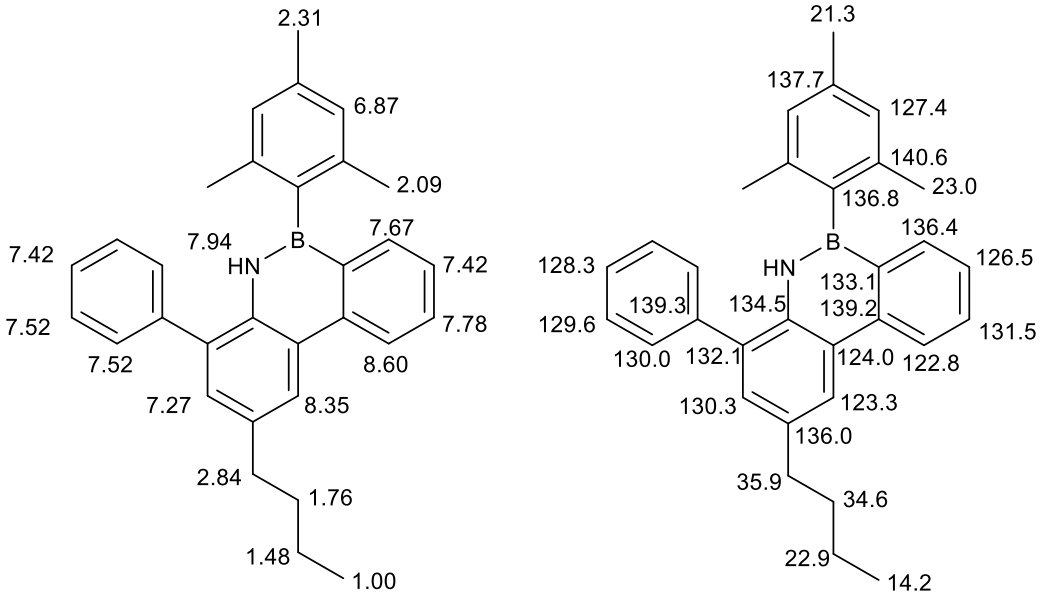


Figure S1: Assignments to **3** of ^{1}H (left) and ^{13}C signals (right).

^{13}C NMR (151 MHz, CD_2Cl_2, δ): 140.6, 139.3, 139.2, 137.7, 136.8, 136.4, 136.0, 134.5, 133.1, 132.1, 131.5, 130.3, 130.0, 129.6, 128.3, 127.4, 126.5, 124.0, 123.3, 122.8, 35.9, 34.6, 23.0, 22.9, 21.3. 14.2.

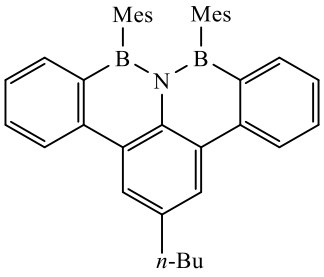
^{11}B NMR (128 MHz, CD_2Cl_2, δ): 39.0.

EA: calcd. for $C_{31}H_{32}BN$: C 86.71 %, H 7.51 %, N 3.26 %; found: C 86.75 %, H 7.56 %, N 3.13 %.

HRMS (ESI): m/z calcd. for $[C_{31}H_{32}BKN, M+K]^+$: 468.2259; found: 468.2266.

Melting point: 115 °C.

SYNTHESIS OF 2-BUTYL-8,9-DIMESITYL-8*H*,9*H*-8A-AZA-8,9-DIBORABENZO[*FG*]TETRACENE (5)



To a solution of 180 mg (0.42 mmol, 1 eq) **3** in 5 mL dry toluene was added 0.84 mL (0.5 M in toluene, 0.42 mmol, 1 eq) KHMDS dropwise. After stirring for ½ h, all volatile compounds were removed in vacuum at 50 °C. The resulting solid was suspended in 15 mL dry toluene. To the suspension was added dropwise 1.26 mL (1 M in *n*-hexane, 1.26 mmol, 3 eq) BCl_3 at -10 °C and the reaction mixture was stirred for 1 h at room temperature. After

adding 11 mg (84 µmol, 0.2 eq) $AlCl_3$, the suspension was stirred for 18 h under reflux. After being cooled to room temperature, all volatile compounds were removed in vacuum. The resulting solid was suspended in 10 mL dry benzene, to the suspension was added 1.2 g MesMgBr as a solid. Solid MesMgBr was obtained by removing the solvent from 20 mL of a 1 M solution in diethyl ether. After transferal into a glovebox, the appropriate amount was taken from the solid. and the reaction mixture was stirred for 1 h at room temperature. All solid materials removed by filtration with a frit (P3) and washed with 4 x 10 mL dichloromethane. The combined organic layers were washed with 3 x 15 mL water and dried over $MgSO_4$. All solvents were removed in vacuum and the obtained yellow oil was purified by column chromatography (silica gel, *n*-hexane/DCM 19:1, R_f = 0.4). The amorphous solid can be crystallized in *n*-hexane yielding 152 mg (0.27 mmol, 65 %) **5** as colorless crystals.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.49-8.56 (m, 4H), 7.74-7.80 (m, 2H), 7.51-7.54 (m, 2H), 7.33-7.39 (m, 2H), 6.52 (s, 4H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.25 (s, 3H), 1.84-1.93 (m, 2H), 1.72 (s, 12H), 1.50-1.61 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

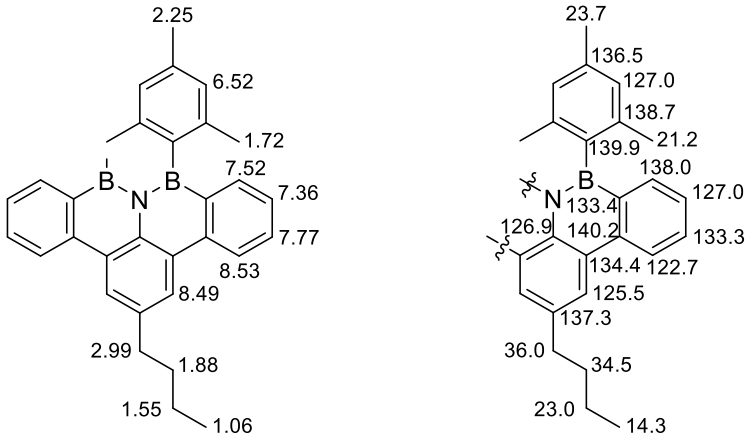


Figure S2: Assignments to **5** of ^{1}H (left) and ^{13}C signals (right).

^{13}C NMR (151 MHz, CD_2Cl_2, δ): 140.2, 139.9, 138.7, 138.0, 137.3, 136.5, 134.4, 133.4, 133.3, 127.0, 127.0, 126.9, 125.5, 122.7, 36.0, 34.5, 23.7, 23.0, 21.2, 14.3.

^{11}B NMR (128 MHz, CD_2Cl_2, δ): 51.1.

EA: calcd. for $C_{40}H_{41}B_2N$: C 86.19 %, H 7.41 %, N 2.51 %; found: C 86.10 %, H 7.45 %, N 2.47 %.

HRMS (ESI): m/z calcd. for $[C_{40}H_{41}B_2NNa, M+Na]^+$: 580.3317; found: 580.3333.

Melting point: 229 °C.

Fluorescence quantum yield: φ_{Fl} = 0.21.

UV/Vis (CH_2Cl_2, c ≈ 10^{-5} M) λ_{max}/nm (ε): 285 (10620), 295 (9300), 338 (13570), 349 (12490), 366 (10240).

3. CYCLIC VOLTAMMETRY

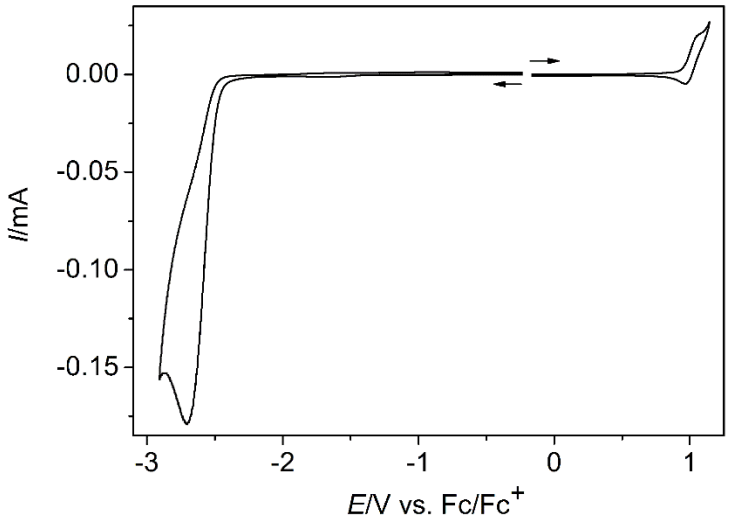


Figure S3: Cyclic voltammograms of **5** in CH_2Cl_2/ 0.1 M NBu_4PF_6, scan rate v = 0.2 Vs^{-1}, bulk concentration c = 0.66 mM; recorded separately for oxidation and reduction.

4. X-RAY CRYSTALLOGRAPHIC DATA

Empirical formula	C40 H41 B2 N
Formula weight	557.36
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21
Unit cell dimensions	a = 11.8877(2) Å α= 90°.
	b = 24.3685(4) Å β= 115.5680(10)°.
c = 11.9282(2) Å	γ = 90°.
Volume	3117.05(9) $Å^3$
Z	4
Density (calculated)	1.188 Mg/m^3
Absorption coefficient	0.067 mm^{-1}
F(000)	1192
Crystal size	0.438 x 0.176 x 0.142 mm^3
Theta range for data collection	1.671 to 29.238°.
Index ranges	-16<=h<=16, -33<=k<=33, -16<=l<=16
Reflections collected	61660
Independent reflections	16724 [R(int) = 0.0356]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.7096
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	16724 / 1 / 792
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.0995
R indices (all data)	R1 = 0.0521, wR2 = 0.1046
Absolute structure parameter	?
Extinction coefficient	n/a
Largest diff. peak and hole	0.358 and -0.250 e.Å^{-3}

5. CARTESIAN COORDINATES OF STATIONARY POINTS IN ÅNGSTRÖM

5.1 S_0 POTENTIAL ENERGY SURFACE, B3LYP/6-311+G**

a) Compound **5*** (C_1), S_0

```
 72
scf done: -1496.6921586
6       -0.457441      3.778154     -0.614592
6       -1.131170      4.858781     -1.159836
6       -1.095082      2.537088     -0.412926
6       -2.474936      4.713417     -1.520586
6       -2.469053      2.419453     -0.717048
6       -3.136226      3.515567     -1.298705
5       -0.315555      1.283788      0.047112
7       -1.019414     -0.000037      0.000016
6       -2.443651     -0.000135     -0.000015
6       -3.165305      1.173017     -0.362966
1        0.586336      3.881031     -0.342995
1       -0.622540      5.803640     -1.314739
1       -3.008659      5.542615     -1.972605
1       -4.174640      3.438407     -1.593090
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6       -4.566562      1.142878     -0.343545
6       -5.267441     -0.000362     -0.000147
6       -4.566412     -1.143485      0.343340
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1       -6.351101     -0.000451     -0.000211
1       -5.119714     -2.039542      0.587713
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6       -1.094737     -2.537158      0.413041
6       -3.135767     -3.515854      1.298845
6       -0.456926     -3.778117      0.614819
6       -2.474311     -4.713591      1.520844
6       -1.130517     -4.858795      1.160135
1       -4.174197     -3.438806      1.593207
1        0.586873     -3.880867      0.343260
1       -3.007924     -5.542825      1.972927
1       -0.621756     -5.803568      1.315131
5       -0.315380     -1.283774     -0.047051
6        1.122550     -1.472615     -0.679038
6        2.280220     -1.787753      0.057982
6        1.190817     -1.529970     -2.094761
6        3.466960     -2.117349     -0.607971
6        2.386672     -1.875996     -2.723902
6        3.544624     -2.166577     -1.997244
1        4.349854     -2.352629     -0.019406
6        1.122381      1.472791      0.679040
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6        2.279992      1.788037     -0.058046
6        2.386588      1.876248      2.723833
6        3.466733      2.117718      0.607841
6        3.544473      2.166920      1.997121
1        2.413867      1.928015      3.809070
6        2.299647     -1.761241      1.569828
1        1.298490     -1.827091      1.999322
1        2.889030     -2.592154      1.968169
1        2.748122     -0.832726      1.932801
6        4.834823     -2.511921     -2.701449
1        5.542718     -2.992724     -2.022629
1        4.660756     -3.186978     -3.543975
1        5.319244     -1.613987     -3.100893
6       -0.027916      1.251783      2.951324
1       -0.350893      0.209196      2.875526
1        0.180973      1.457553      4.003044
1       -0.880761      1.872313      2.657120
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1        4.660501      3.184872      3.545551
1        5.320630      1.613819      3.098000
1        5.541551      2.995522      2.023049
1        4.349574      2.353089      0.019229
6        2.299332      1.761549     -1.569896
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1        2.413898     -1.927763     -3.809141
6       -0.027892     -1.251752     -2.951273
1        0.180950     -1.457550     -4.002997
1       -0.880672     -1.872335     -2.656994
1       -0.350944     -0.209188     -2.875499
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b) Compound **5*** (C_S), S_0

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   72
scf done: -1496.6854168
6        0.342545     -2.760668     -4.945303
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5        0.026466     -0.417859     -1.291012
7        0.005202     -1.128533      0.000000
6       -0.073919     -2.563602      0.000000
6       -0.125329     -3.299565     -1.223705
1        0.228316      0.454281     -3.905876
1        0.436680     -0.866566     -5.979229
1        0.458151     -3.354254     -5.845904
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6       -0.125329     -3.299565      1.223705
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6        0.205503     -3.396507      3.722965
6        0.219490     -0.627440      3.855191
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1        0.228316      0.454281      3.905876
1        0.458151     -3.354254      5.845904
1        0.436680     -0.866566      5.979229
5        0.026466     -0.417859      1.291012
6       -0.008705      1.152122     -1.509825
6       -1.240008      1.799524     -1.745036
6        1.178610      1.879131     -1.734874
6       -1.267220      3.153880     -2.083691
6        1.118093      3.233426     -2.072828
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1       -2.819815      0.731442      2.750950
```

c) Compound **C** (R = H; C_{2V}), S_0

```
   34
scf done: -795.5191236
6        0.000000     -2.536310     -0.255246
6        0.000000     -2.558574      1.159076
6        0.000000     -3.790840      1.841176
6        0.000000     -4.992360      1.153686
6        0.000000     -4.969619     -0.246047
6        0.000000     -3.768829     -0.939587
1        0.000000     -3.784696      2.926294
```

```
1        0.000000     -5.937187      1.685126
1        0.000000     -5.901979     -0.800525
1        0.000000     -3.808131     -2.020332
6        0.000000      1.197096     -2.359532
6        0.000000      0.000000     -3.055591
6        0.000000     -1.197096     -2.359532
6        0.000000     -1.237093     -0.958465
6        0.000000      0.000000     -0.247011
6        0.000000      1.237093     -0.958465
1        0.000000      2.119158     -2.923031
1        0.000000      0.000000     -4.139282
1        0.000000     -2.119158     -2.923031
6        0.000000      4.992360      1.153686
6        0.000000      3.790840      1.841176
6        0.000000      2.558574      1.159076
6        0.000000      2.536310     -0.255246
6        0.000000      3.768829     -0.939587
6        0.000000      4.969619     -0.246047
1        0.000000      5.937187      1.685126
1        0.000000      3.784696      2.926294
1        0.000000      3.808131     -2.020332
1        0.000000      5.901979     -0.800525
7        0.000000      0.000000      1.166084
5        0.000000     -1.234987      1.912044
5        0.000000      1.234987      1.912044
1        0.000000     -1.174221      3.098030
1        0.000000      1.174221      3.098030
```

d) Compound **D** (C_{2V}), S_0

```
  34
scf done: -808.0658955
6        0.282936      3.538378      0.935748
6        0.919499      4.713069      1.246467
6        1.035190      2.369628      0.626648
6        2.328510      4.750761      1.256493
6        2.472311      2.406005      0.636334
6        3.084535      3.629380      0.959931
6        0.380746      1.173373      0.310199
6        1.081225     -0.000026     -0.000080
6        2.519306     -0.000136     -0.000030
6        3.218913      1.195862      0.316313
1       -0.799587      3.481809      0.920736
1        0.351384      5.604141      1.482124
1        2.833739      5.677851      1.501720
1        4.161861      3.716141      0.982925
6        3.218750     -1.196242     -0.316323
6        4.623770      1.165419      0.308345
6        5.312020     -0.000352      0.000068
6        4.623612     -1.166017     -0.308257
1        5.193128      2.054130      0.543424
1        6.395018     -0.000436      0.000106
1        5.192849     -2.054816     -0.543295
6        2.471984     -2.406271     -0.636395
6        1.034868     -2.369672     -0.626809
6        3.084042     -3.629741     -0.959949
6        0.282456     -3.538307     -0.935959
6        2.327865     -4.751005     -1.256561
6        0.918859     -4.713096     -1.246632
```

```
1        4.161356     -3.716668     -0.982868
1       -0.800060     -3.481571     -0.921022
1        2.832968     -5.678174     -1.501752
1        0.350623     -5.604082     -1.482327
6        0.380586     -1.173315     -0.310408
1       -0.704951     -1.153458     -0.305218
1       -0.704794      1.153681      0.304939
```

5.2 S_1 POTENTIAL ENERGY SURFACE, B3LYP/6-311+G**

a) Compound **5*** (C_1), S_1

```
  72
scf done: -1496.5723232
6       -0.576010      3.848995     -0.098962
6       -1.282604      5.007685     -0.326202
6       -1.200518      2.568583     -0.091953
6       -2.667474      4.934905     -0.572870
6       -2.617933      2.513508     -0.264404
6       -3.311635      3.711900     -0.536871
5       -0.443565      1.273597      0.051964
7       -1.155326     -0.000065      0.000023
6       -2.583097     -0.000211      0.000107
6       -3.303705      1.229945     -0.128294
1        0.492510      3.916006      0.076922
1       -0.778496      5.968369     -0.327940
1       -3.231591      5.835666     -0.787756
1       -4.374936      3.692415     -0.736559
6       -3.303475     -1.230494      0.128599
6       -4.713328      1.190757     -0.097523
6       -5.406454     -0.000405      0.000630
6       -4.713124     -1.191472      0.098440
1       -5.271540      2.114538     -0.140142
1       -6.491118     -0.000478      0.000910
1       -5.271228     -2.115299      0.141369
6       -2.617452     -2.513984      0.264229
6       -1.200026     -2.568719      0.091816
6       -3.310910     -3.712644      0.536182
6       -0.575205     -3.848970      0.098608
6       -2.666468     -4.935505      0.571888
6       -1.281542     -5.007894      0.325456
1       -4.374255     -3.693529      0.735645
1        0.493355     -3.915673     -0.077144
1       -3.230426     -5.836466      0.786351
1       -0.777201     -5.968455      0.327034
5       -0.443325     -1.273548     -0.051965
6        1.123091     -1.331552     -0.373672
6        2.112771     -1.686290      0.598955
6        1.536181     -1.282487     -1.755914
6        3.442228     -1.817971      0.220187
6        2.867003     -1.438633     -2.091868
6        3.849188     -1.681825     -1.113930
1        4.186395     -2.063827      0.971411
6        1.122828      1.331877      0.373749
6        1.535871      1.282857      1.756008
6        2.112509      1.686743     -0.598845
6        2.866663      1.439125      2.092010
6        3.441942      1.818519     -0.220031
```

6	3.848867	1.682367	1.114100
1	3.163471	1.393535	3.135535
6	1.735498	-2.003166	2.023067
1	0.797455	-1.537757	2.316468
1	1.594067	-3.083438	2.133728
1	2.520963	-1.698820	2.718533
6	5.289011	-1.844548	-1.510607
1	5.930507	-2.022502	-0.646513
1	5.407885	-2.685324	-2.202229
1	5.653953	-0.954005	-2.032513
6	0.501687	1.155159	2.844055
1	-0.242067	0.389349	2.621719
1	0.963173	0.933104	3.808127
1	-0.048383	2.097445	2.937758
6	5.288708	1.844887	1.510791
1	5.407389	2.683953	2.204495
1	5.654203	0.953185	2.030361
1	5.929890	2.025203	0.646956
1	4.186116	2.064467	-0.971215
6	1.735244	2.003670	-2.022943
1	1.593332	3.083895	-2.133443
1	2.520916	1.699786	-2.718375
1	0.797429	1.537901	-2.316509
1	3.163849	-1.392973	-3.135380
6	0.502046	-1.154867	-2.844020
1	0.963549	-0.932511	-3.808014
1	-0.047738	-2.097300	-2.937951
1	-0.241948	-0.389314	-2.621608

6. COMPUTED STRUCTURES OF 5*

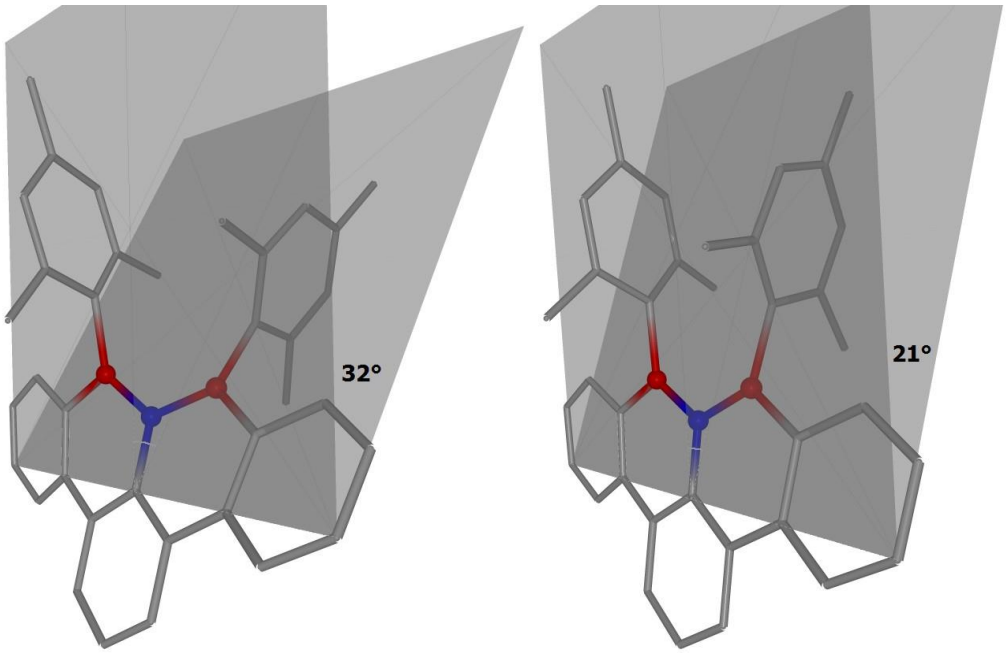
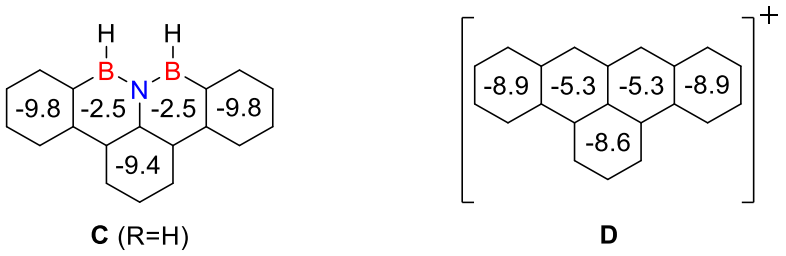


Figure S4: Optimized structure of **5*** (S_0, hydrogens are omitted for clarity) with measured torsion angle at the B3LYP/6-311+G** level of theory (left) and the optimized S_1 state structure (right) at the TD-B3LYP/6-311+G** level of theory.

7. COMPUTED NICS(1) VALUES



C (R=H) **D**

Figure S5: NICS(1) values of **C** (R = H) and **D** computed on the B3LYP/6-311+G** level of theory. NICS(1) of benzene is -10.2.

8. SPECTRA

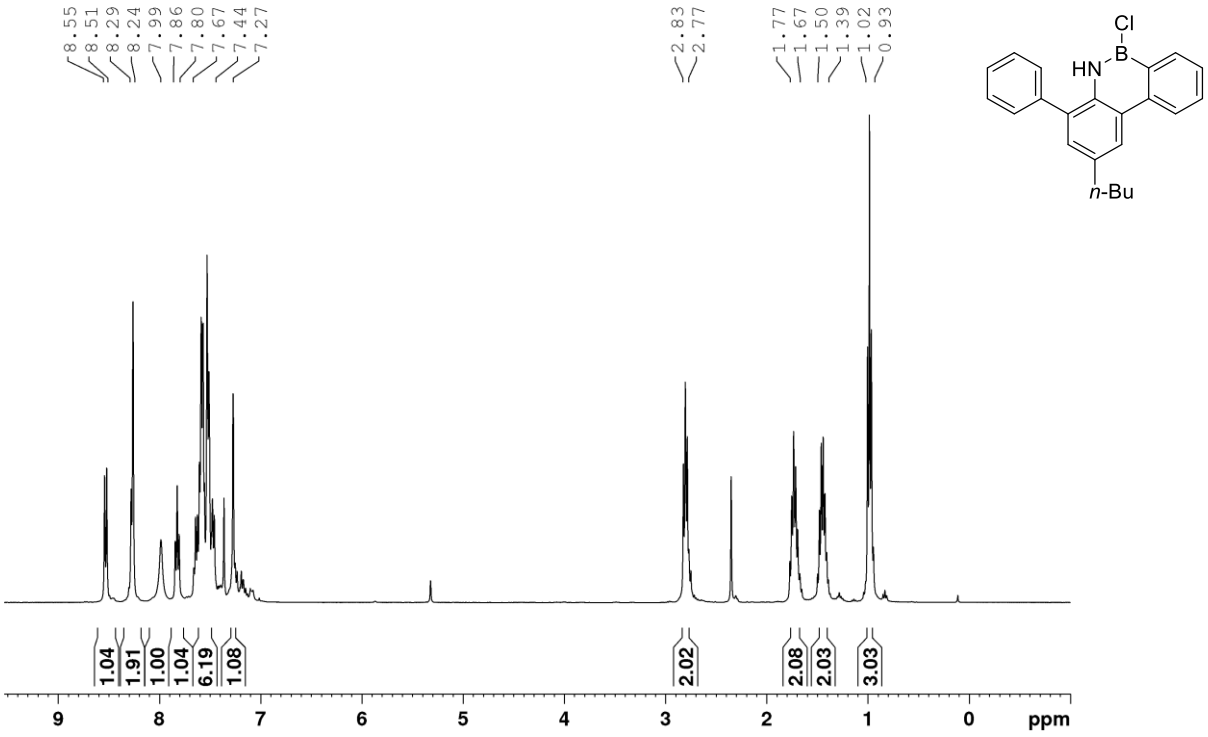


Figure S6: ^{1}H-NMR of **2** in CD_2Cl_2

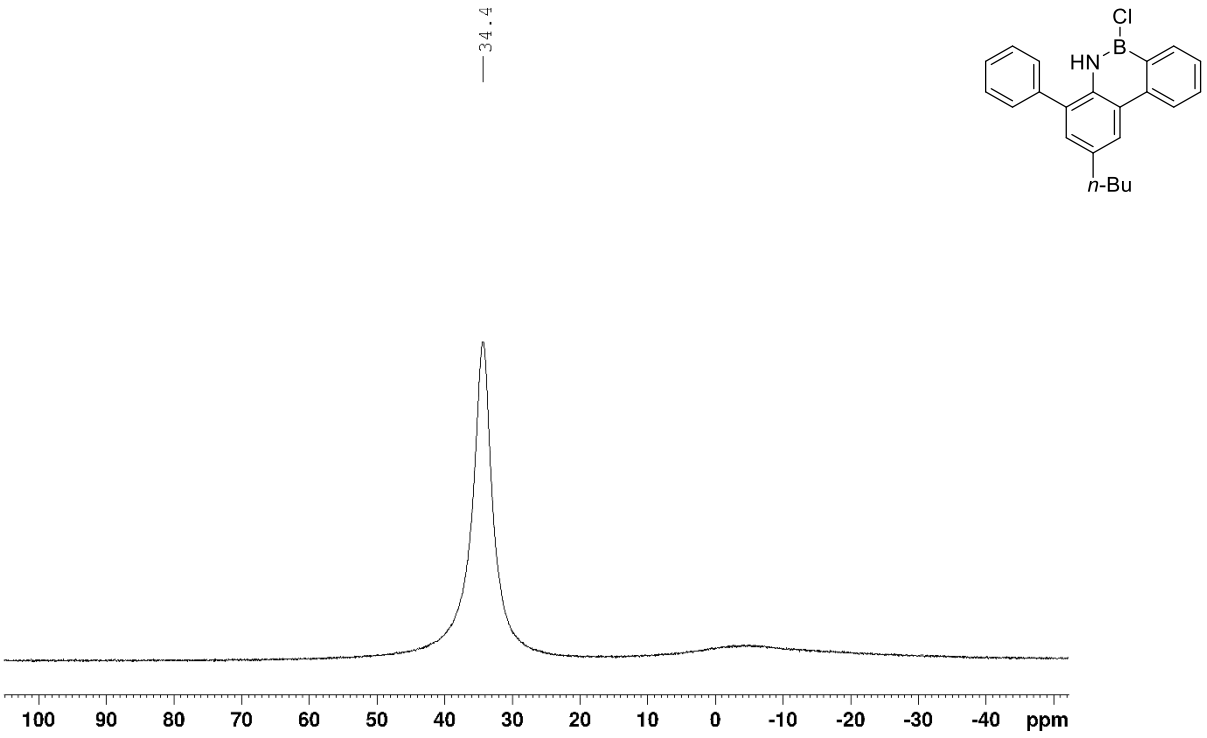


Figure S7: ^{11}B-NMR of **2** in CD_2Cl_2

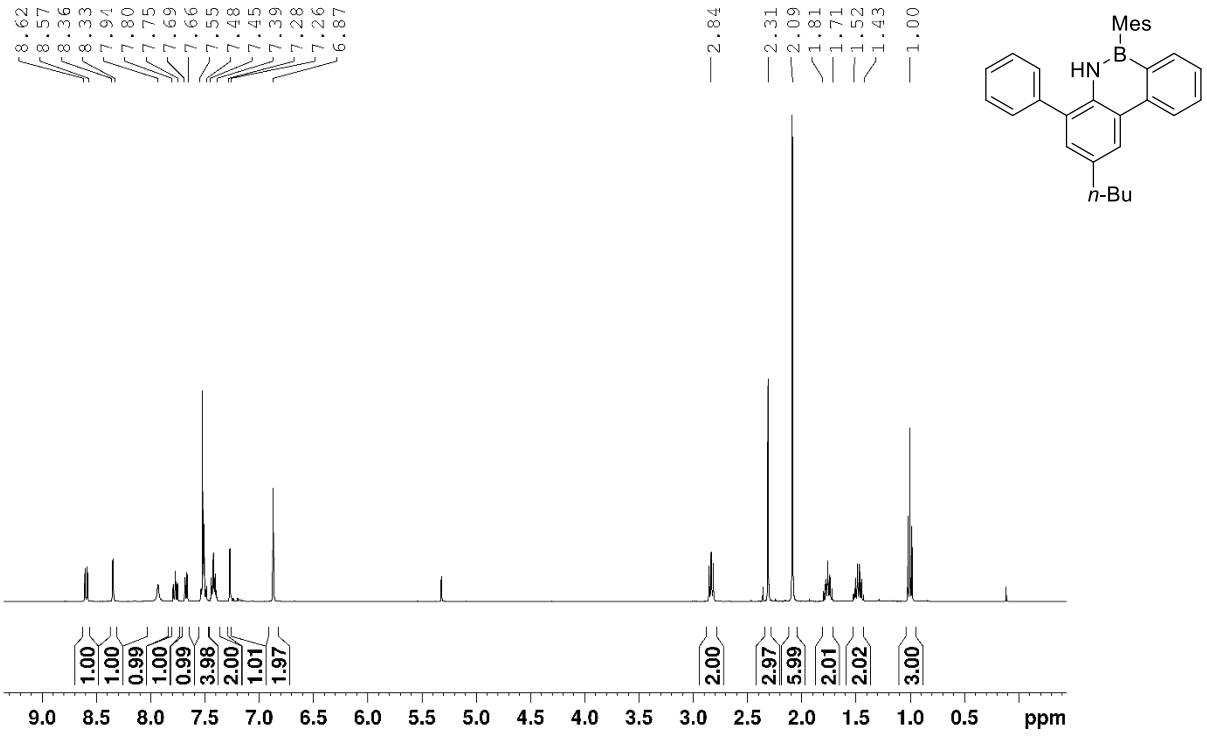


Figure S8: ^{1}H-NMR of **3** in CD_2Cl_2

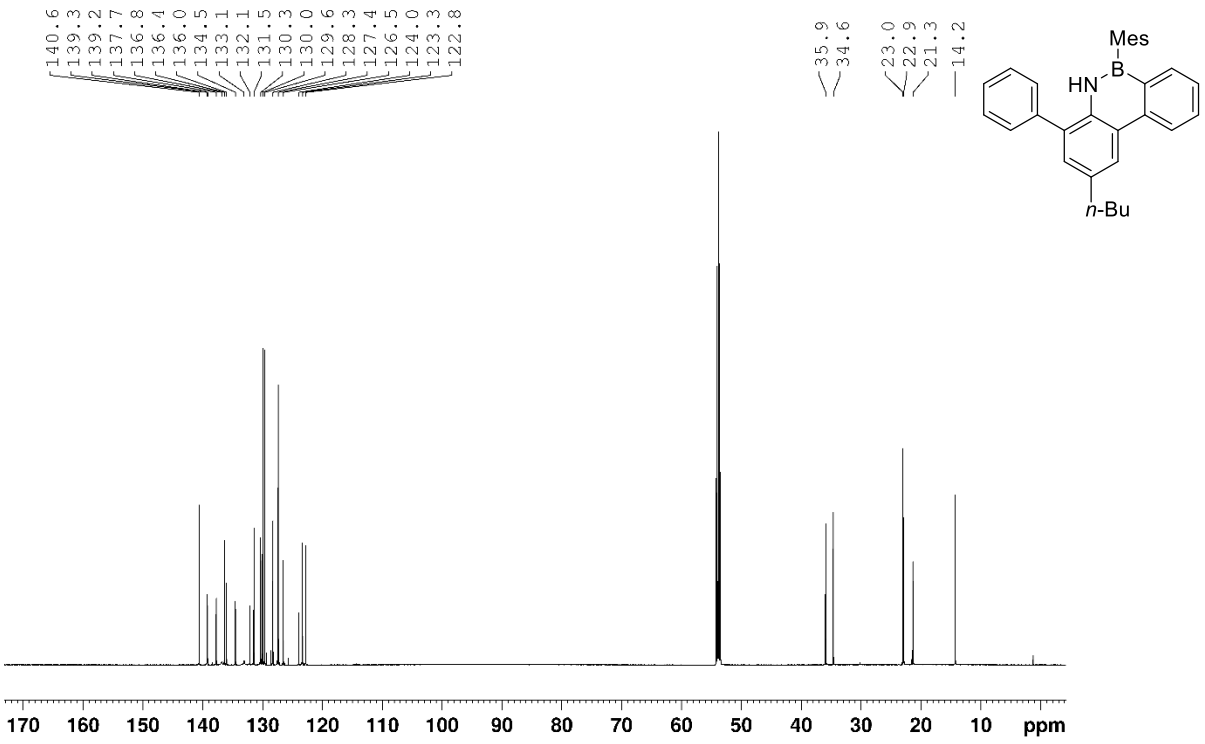


Figure S9: ^{13}C-NMR of **3** in CD_2Cl_2

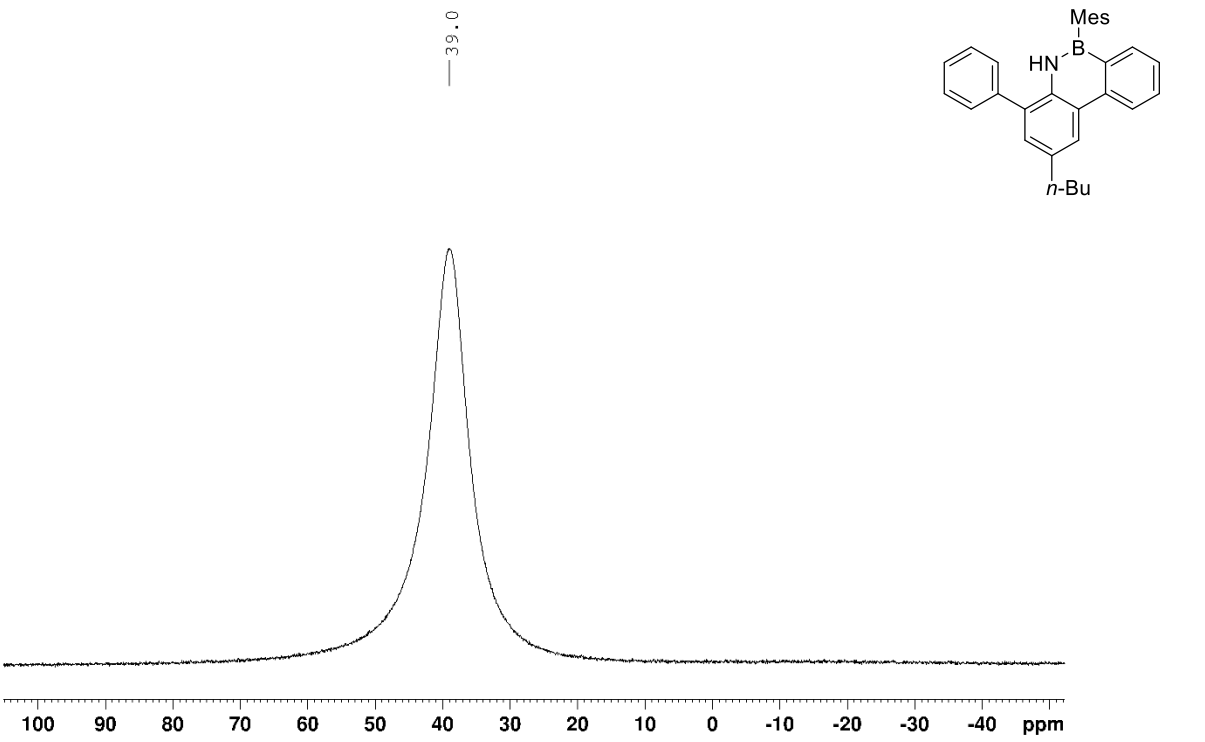


Figure S10: ^{11}B-NMR of **3** in CD_2Cl_2

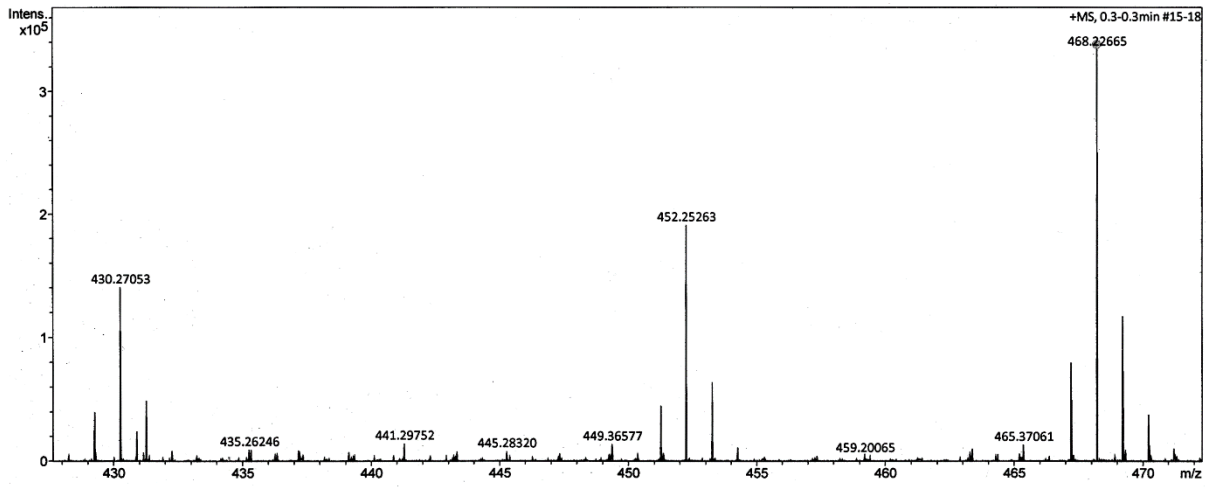


Figure S11: HR-ESI of **3** in acetonitrile

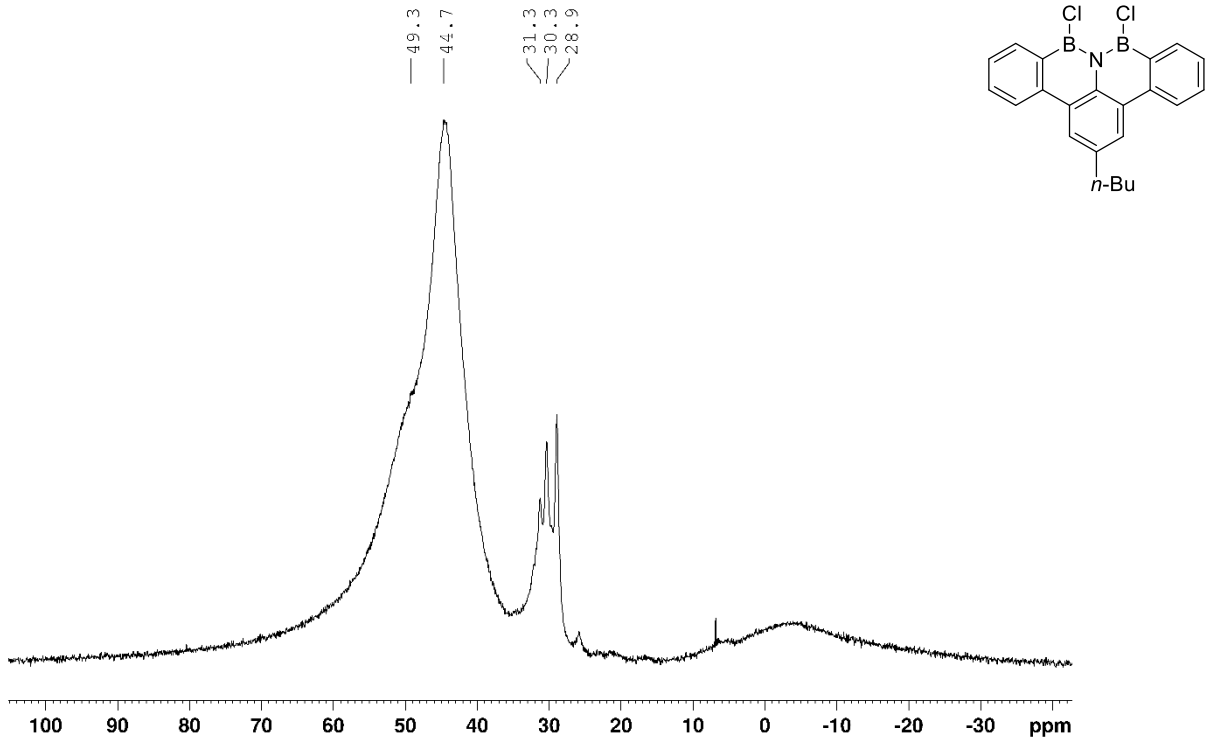


Figure S12: ^{11}B-NMR of **4** (crude product) in CD_2Cl_2

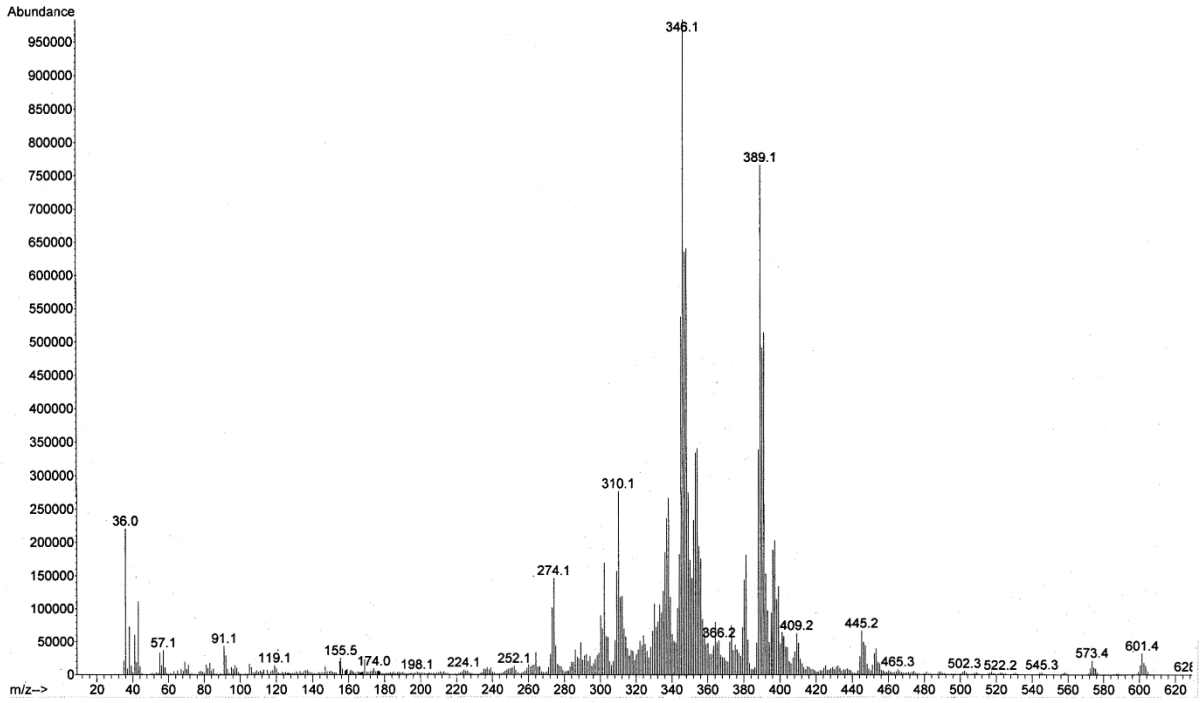


Figure S13: EI-MS of **4** (crude product)

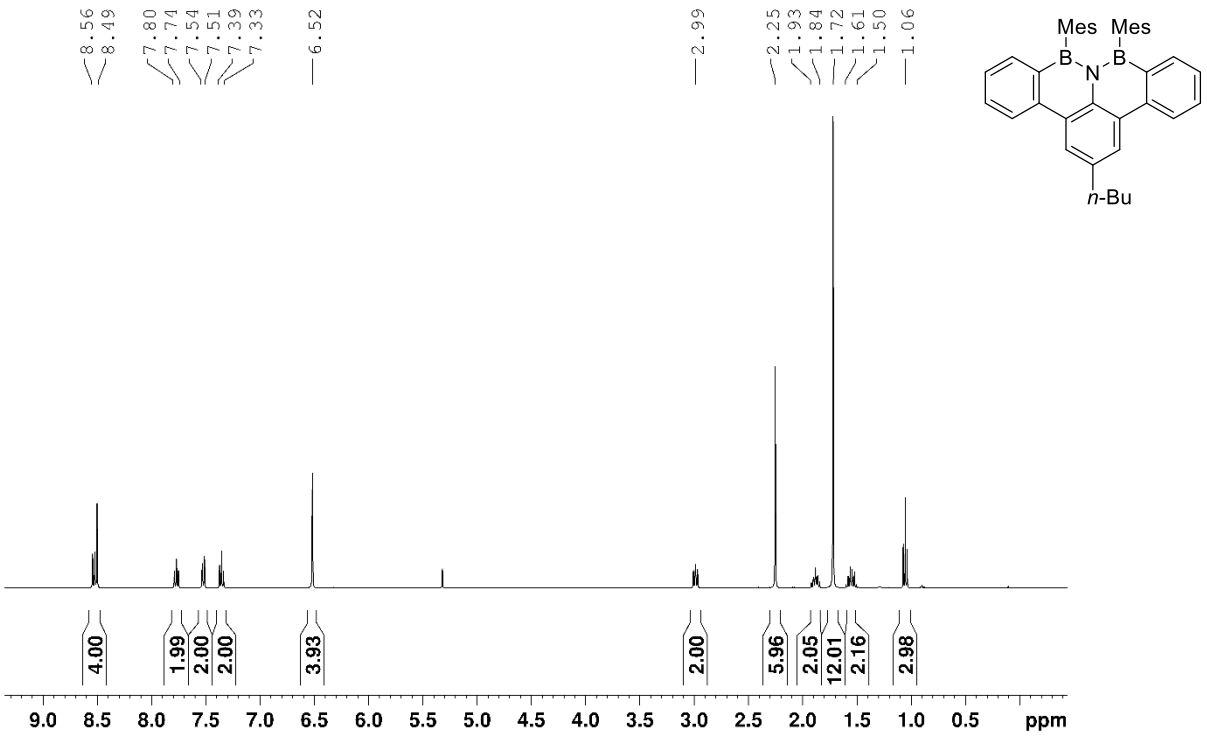


Figure S14: ^{1}H-NMR of **5** in CD_2Cl_2

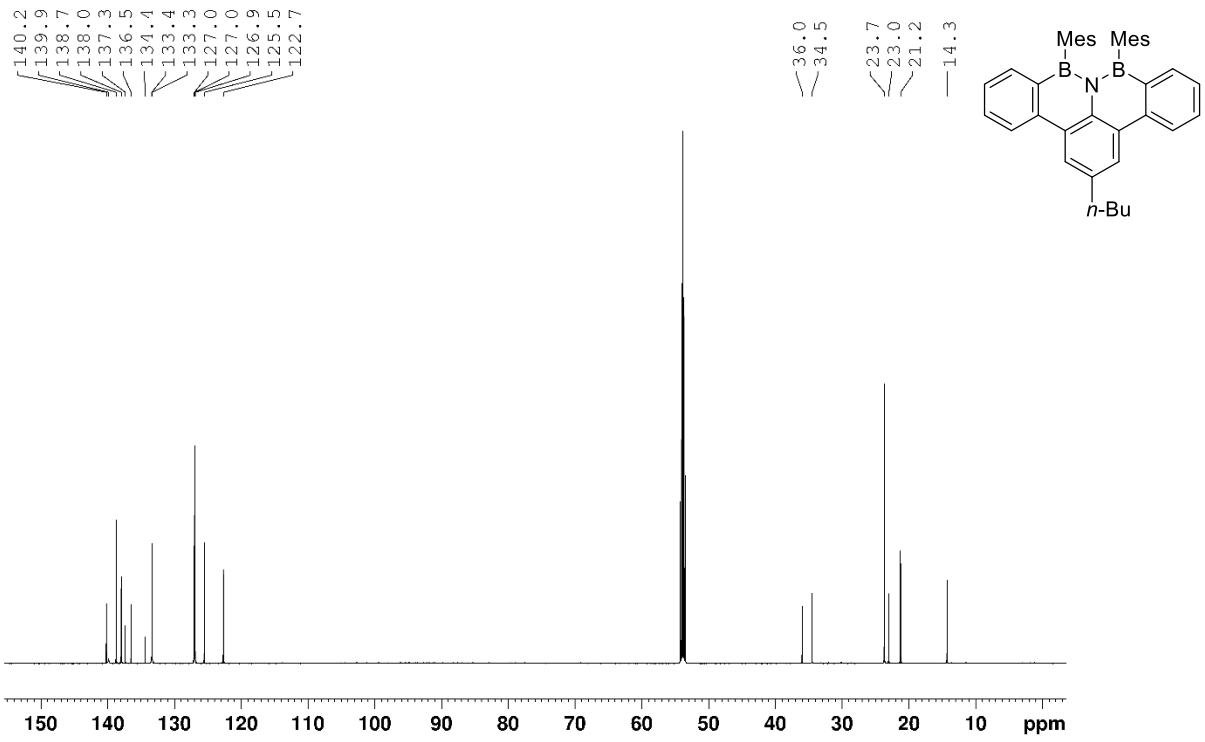


Figure S15: ^{13}C-NMR of **5** in CD_2Cl_2

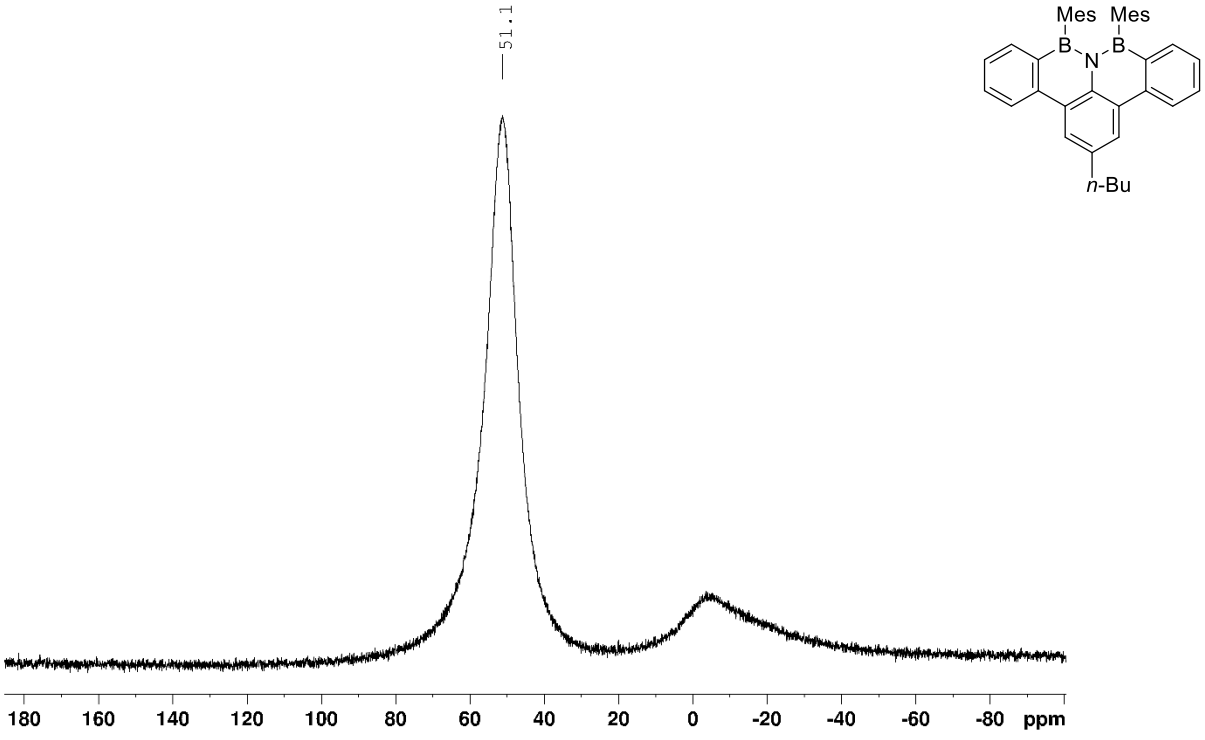


Figure S16: ^{11}B-NMR of **5** in CD_2Cl_2

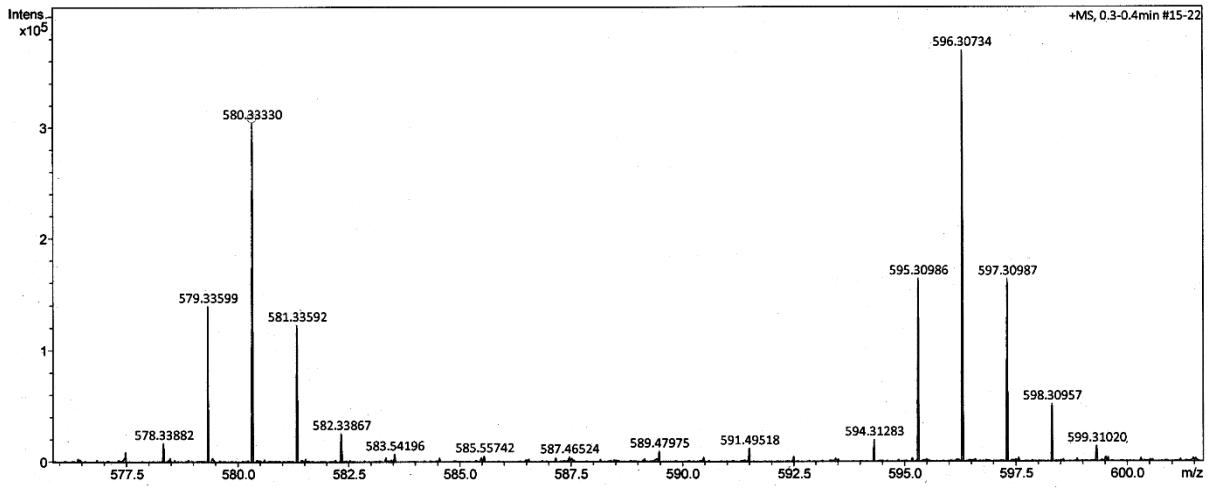


Figure S17: HR-ESI of **5** in acetonitrile

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