Supporting Information for:

Beryllium Bis(diazaborolyl): Old Neighbors Finally Shake Hands

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General synthetic considerations. All reactions were performed under an atmosphere of dry argon using standard Schlenk or glove box techniques. ^{1}H, ^{9}Be, ^{11}B and ^{13}C NMR spectroscopy data were obtained at ambient temperature using either a Bruker DRX-400 (operating at 400 MHz for ^{1}H, 56 MHz for ^{9}Be, 128 MHz for ^{11}B and 100 MHz for ^{13}C) or a Bruker Avance 500 NMR spectrometer (operating at 500 MHz for ^{1}H, 160 MHz for ^{11}B and 125 MHz for ^{13}C). ^{1}H NMR spectra were referenced via residual proton resonances of C_6D_6 (^{1}H, 7.16 ppm). ^{13}C spectra were referenced to C_6D_6 (^{13}C, 128.06 ppm). ^{9}Be NMR and ^{11}B NMR signals were referenced to $Be(H_2O)_4^{2+}$ (sulfate salt) and $BF_3{\cdot}OEt_2$, respectively. Elemental analyses were performed on a Elementar vario MICRO cube elemental analyzer.

Materials. $BeCl_2$ was purchased from Sigma-Aldrich and used as received. 1,3-Dimethylimidazol-2-ylidene (IMe)[1] and lithium diazaborolyl[2] were synthesized according to literature methods. Solvents (benzene, hexane, methanol) were purified by distillation using the appropriate drying agents, deoxygenated using the method of freeze-pump-thaw and stored over molecular sieves under dry argon prior to use. Deuterated solvents used for nuclear magnetic resonance spectroscopy were purchased from Cambridge Isotope Laboratories, deoxygenated by freeze-pump-thaw cycles and dried under an argon atmosphere over molecular sieves.

Beryllium bis(*N,N´*-bis(2,6-diisopropylphenyl)-1,3,2-diazaborolyl) (1). A solution of $BeCl_2$ (25 mg, 0.31 mmol) and lithium diazaborolyl (337 mg, 0.63 mmol) in benzene (5 mL) was stirred for ~12 h at room temperature. After 1 h, the formation of a white precipitate was observed. Upon completion, the mixture was filtered through Celite®, and the filtrate-solvent was evaporated under reduced pressure. The remaining solid was re-dissolved in a minimal amount of hexane and recrystallized at −30 °C, affording beryllium bis(*N,N´*-bis(2,6-di*iso*propylphenyl)-1,3,2-diazaborolyl) (**1**) as colorless crystals (170 mg, 70%). ^{9}Be NMR (C_6D_6, 56 MHz): δ = 44 (br-s). ^{11}B NMR (C_6D_6, 128 MHz): δ = 28 (br-s). ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.24 – 7.20 (m, 4H, *Ar-H*$_{para}$), 7.09 -7.07 (m, 8H, *Ar-H*$_{meta}$), 6.00 (s, 4H, *NCH*), 3.03 (sept., J_{HH} = 7.0 Hz, 8H, *CH*(*CH*$_3$)$_2$), 1.13 (d, J_{HH} = 7.0 Hz, 24H, *CH*(*CH*$_3$)$_2$), 0.98 (d, J_{HH} = 7.0 Hz, 24H, *CH*(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ = 146.1 (*C*$_q$), 141.8 (*NCq*), 127.4 (*CH*$_{para}$), 123.4 (*CH*$_{meta}$), 120.9 (*NCH*), 28.5 (*CH*(*CH*$_3$)$_2$), 25.2 (*CH*(*CH*$_3$)$_2$), 24.6 (*CH*(*CH*$_3$)$_2$).

Elemental analysis calcd (%) for $C_{52}H_{72}B_2BeN_4$: C 79.68, H 9.26, N 7.15; found: C 79.37, H 9.24, N 7.24.

Methanolysis of 1. A solution of **1** (16 mg, 0.02 mmol) in C_6D_6 (0.7 mL) was treated with MeOH (~10 eq.) inducing the immediate formation of a white solid, which was separated from the reaction mixture by filtration. The remaining solution was concentrated under reduced pressure, affording 1,3-bis(2,6-di*iso*propylphenyl)-2,3-dihydro-*1H*-1,3,2-diazaborole (**2**) as a colorless solid (8 mg, quant.). Both ^{1}H and ^{11}B NMR spectroscopy were in agreement with previously reported values for **2**.[3] Elemental analysis calcd (%) for $C_{26}H_{37}BN_2$: C 80.40, H 9.60, N 7.21; found: C 80.47, H 9.58, N 7.33.

When an equivalent experiment was carried out using ~10 eq. MeOD, identical results were obtained, save the disappearance of the 2-*H* resonance from the ^{1}H NMR spectrum of the products (Figs. S5 and S6), and the observance of a ^{2}H NMR resonance at 4.72 ppm, in agreement with the previously reported values for 1,3-bis(2,6-di*iso*propylphenyl)-2,3-dihydro-*1D*-1,3,2-diazaborole.[3]

Beryllium bis[*N,N´*-bis(2,6-diisopropylphenyl)-1,3,2-diazaborolyl](1,3-dimethylimidazole-2-ylidene) (3). A solution **1** (38 mg, 0.05 mmol) in C_6D_6 was treated with 1,3-dimethylimidazol-2-ylidene (IMe, 5 mg, 0.05 mmol). ^{11}B NMR indicated full conversion after 10 min, at which point the solution was concentrated under reduced pressure. The resultant solid was recrystallized by slow evaporation of benzene at room temperature and separation from the supernatant solution, affording **3**·C_6H_6 as colorless crystals (30 mg, 70%). ^{9}Be NMR (C_6D_6, 56 MHz): δ = 28 (br-s). ^{11}B NMR (C_6D_6, 128 MHz): δ = 38 (br-s). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.20 – 7.16 (m, 4H, *Ar-H*$_{para(borolyl)}$), 7.11 – 7.09 (m, 8H, *Ar-H*$_{meta(borolyl)}$), 6.17 (s, 4H, *NCH*$_{(borolyl)}$), 5.59 (s, 2H, *NCH*$_{(IMe)}$), 3.35 (brs, *C**H**(CH$_3$)$_{2(borolyl)}$), 2.13 (s, 6H, *CH*$_{3(IMe)}$), 1.23 (d, J_{HH} = 7 Hz, 24 H, *CH(C**H**$_3$)$_{2(borolyl)}$), 0.93 (d, J_{HH} = 7 Hz, 24 H, *CH(C**H**$_3$)$_{2(borolyl)}$). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ = 183.6 (*C*$_{q(IMe)}$), 147.4 (*C*$_{q(borolyl)}$), 145.0 (*C*$_{q(borolyl)}$), 128.4 (*CH*$_{(borolyl)}$), 126.7 (*CH*$_{(borolyl)}$), 123.5 (*CH*$_{(borolyl)}$), 122.3 (*NCH*$_{(borolyl)}$), 120.4 (*NCH*$_{(IMe)}$), 34.6 (*NCH*$_{3(IMe)}$), 28.2 (***C**H(CH$_3$)$_{2(borolyl)}$), 27.3 (*CH(**C**H$_3$)$_{2(borolyl)}$), 23.3 (*CH(**C**H$_3$)$_{2(borolyl)}$). Elemental analysis calcd (%) for $C_{57}H_{81}B_2BeN_6 \cdot C_6H_6$: C 78.90, H 9.14, N 8.76; found: C 78.97, H 9.14, N 8.84.

Crystallographic methods. The crystal data for **1** and **3** were collected on a Bruker X8-Apex II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_{Ka} radiation. The structures were solved using direct methods, refined with the Shelx software package[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for **1**: $C_{52}H_{72}B_2BeN_4$, M_r = 783.77, colorless block, 0.44×0.31×0.11 mm^3, monoclinic space group $P2_1/n$, a = 12.8550(9) Å, b = 27.0697(19) Å, c = 14.2004(10) Å, β = 92.555(2)°,

V = 4936.6(6) Å^3, Z = 4, ρ_{calcd} = 1.055 g·cm^{-3}, μ = 0.060 mm^{-1}, F(000) = 1704, T = 100(2) K,
R_1 = 0.0665, wR^2 = 0.1177, 10096 independent reflections [2θ≤52.74°] and 565 parameters.

Additional crystallographic Information for **1**: The displacement parameters of the disordered isopropyl-group atoms C56, C57, C58 and C156, C157, C158 as well as C41 C42 C43 and C141, C142, C143 were constrained to the same value. The coordinates of atoms C56-C156 and C41-C141 (isopropyl group) were constrained to the same position. The Uii displacement parameters of atoms C26, C27, C42, C43, C142 and C143 (isopropyl-groups) were restrained with ISOR keyword to approximate isotropic behavior.

Crystal data for **3**: $C_{63}H_{86}B_2BeN_6$, M_r = 958.01, colorless block, 0.25×0.13×0.10 mm^3, monoclinic space group $P2_1$, a = 12.3713(7) Å, b = 20.3783(11) Å, c = 12.4856(7) Å, β = 114.9190(19)°,
V = 2854.7(3) Å^3, Z = 2, ρ_{calcd} = 1.115 g·cm^{-3}, μ = 0.064 mm^{-1}, F(000) = 1040, T = 103(2) K,
R_1 = 0.0663, wR^2 = 0.1025, 12169 independent reflections [2θ≤53.6°] and 667 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1018058 (**1**) and CCDC-1018059 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Computational details. Compounds **1**, **3** and the free 1,3-di*iso*propylphenyl-1,3,2-diazaborolide anion were geometry-optimized with the Gaussian 09 software package[5] at the B3LYP/6-311G(d) level of theory. Frequency analysis confirmed the structures as true minima with no imaginary frequencies. Natural population analysis was carried out at the B3LYP/6-311G(d) level of theory with the NBO program[6] within Gaussian 09. Predictions of the ^{9}Be shifts were carried out with the NMR/GIAO option in Gaussian 09 at the B3LYP/6-311+G(2d,p) level of theory for Be and referenced to $Be(OH_2)_4^{2+}$ with an isotropic shielding constant of 108.9 ppm.[7] ^{11}B NMR shifts were calculated at the B3LYP/6-311G(d) level of theory and referenced against an isotropic shielding factor of 102.2 for BF_3-OEt_2.

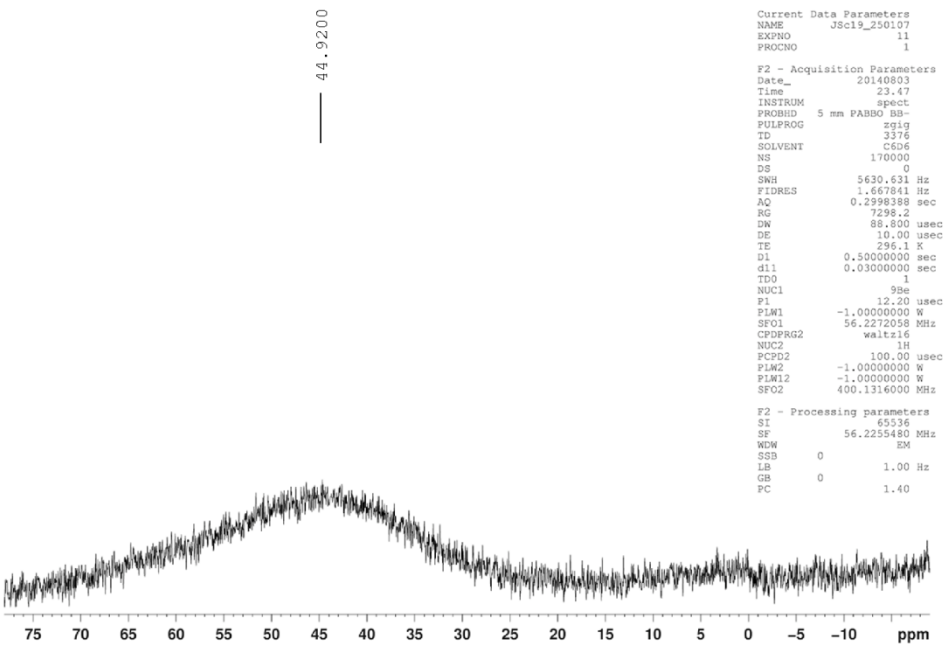


Figure S1. ^{9}Be NMR of **1** in C_6D_6.

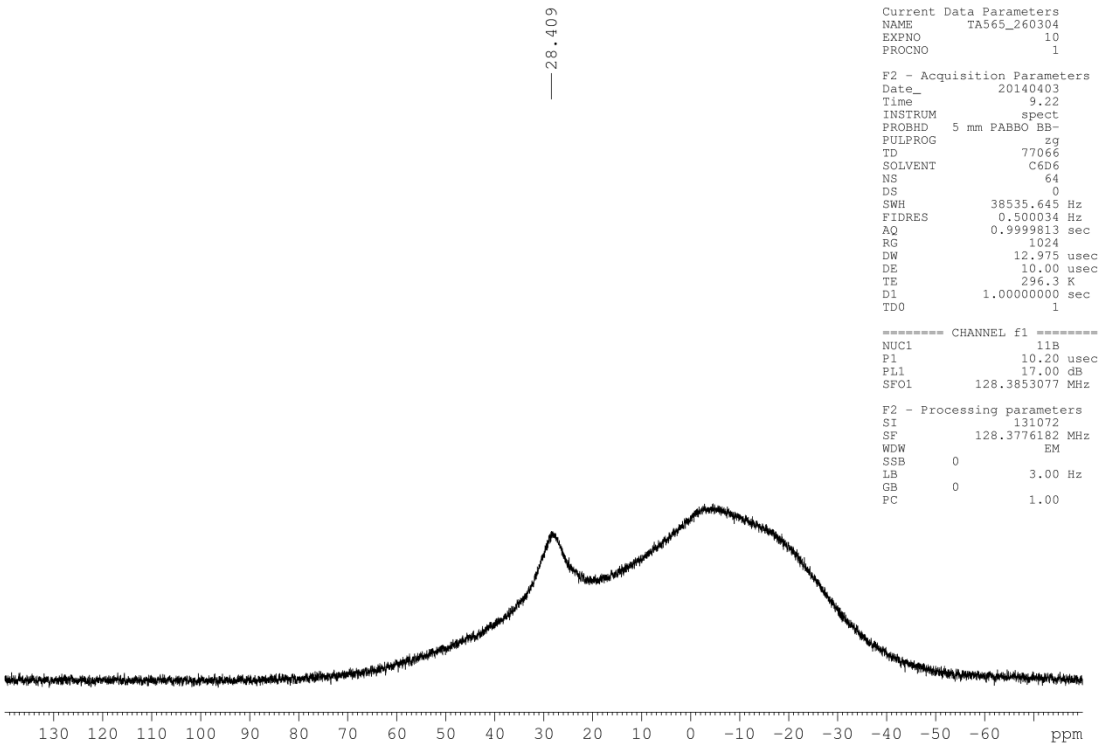


Figure S2. ^{11}B NMR of **1** in C_6D_6.

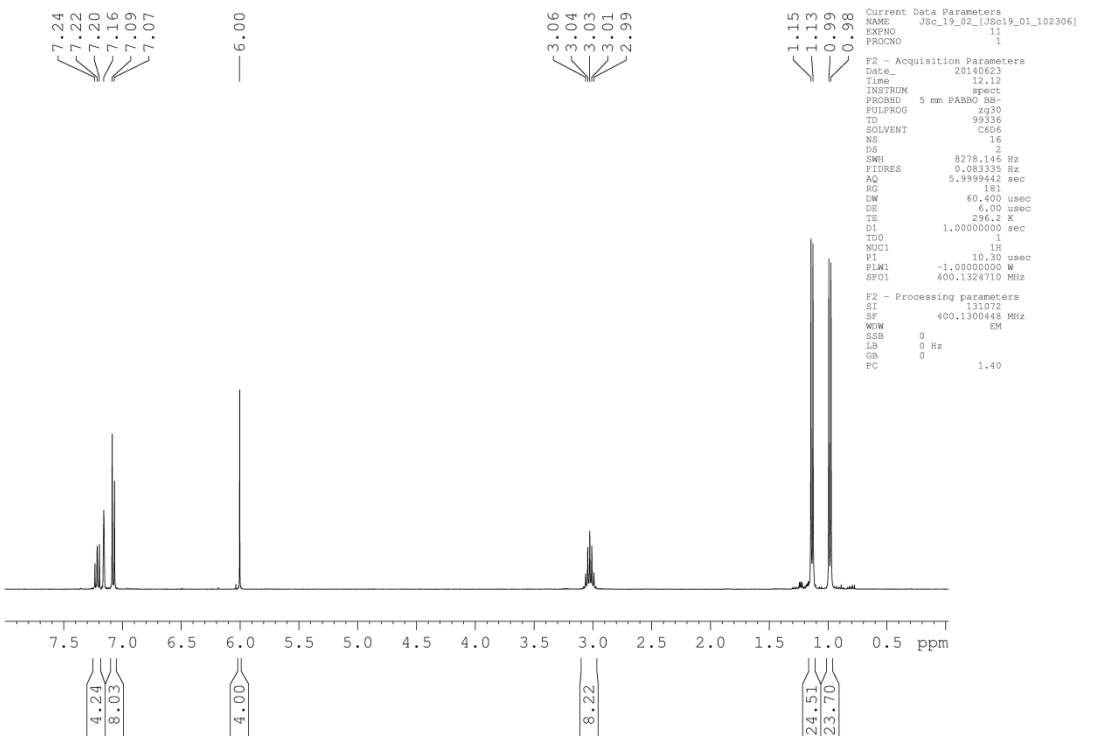
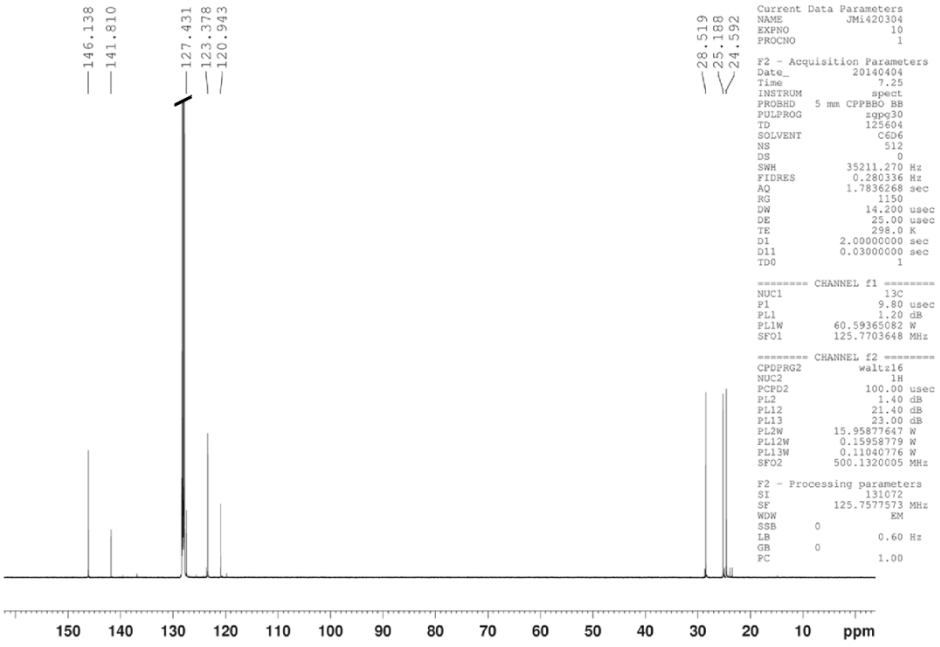


Figure S3. ^{1}H NMR of **1** in C_6D_6.



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FIDRES 0.280336 Hz
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DE 25.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

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PL1 1.20 dB
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SFO1 125.7703648 MHz

======== CHANNEL f2 ========
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PCPD2 100.00 usec
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PL12 21.40 dB
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F2 - Processing parameters
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Figure S4. $^{13}C\{^{1}H\}$ NMR of **1** in C_6D_6.

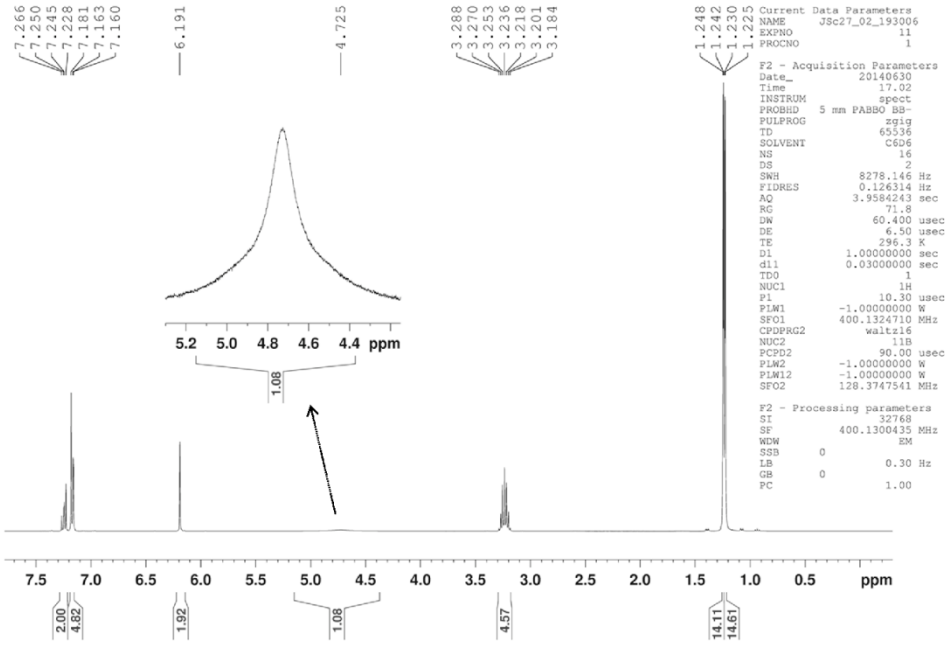
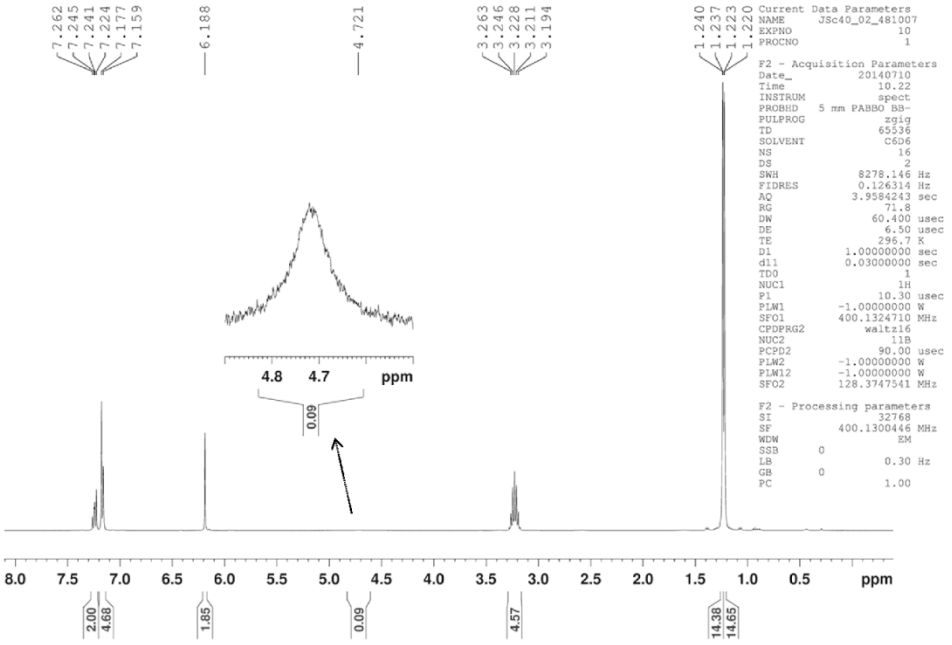


Figure S5. ^{1}H NMR of **2-H** in C_6D_6.



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DE 6.50 usec
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d11 0.03000000 sec
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Figure S6. ^{1}H NMR of **2-D** in C_6D_6.

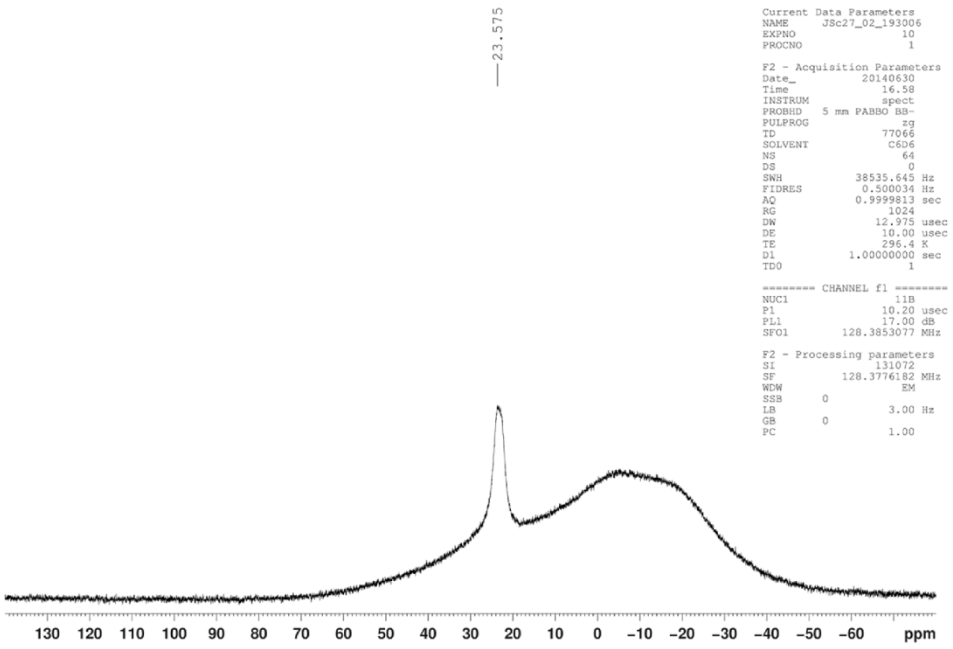

Figure S7. ^{11}B NMR of **2-H** in C_6D_6.

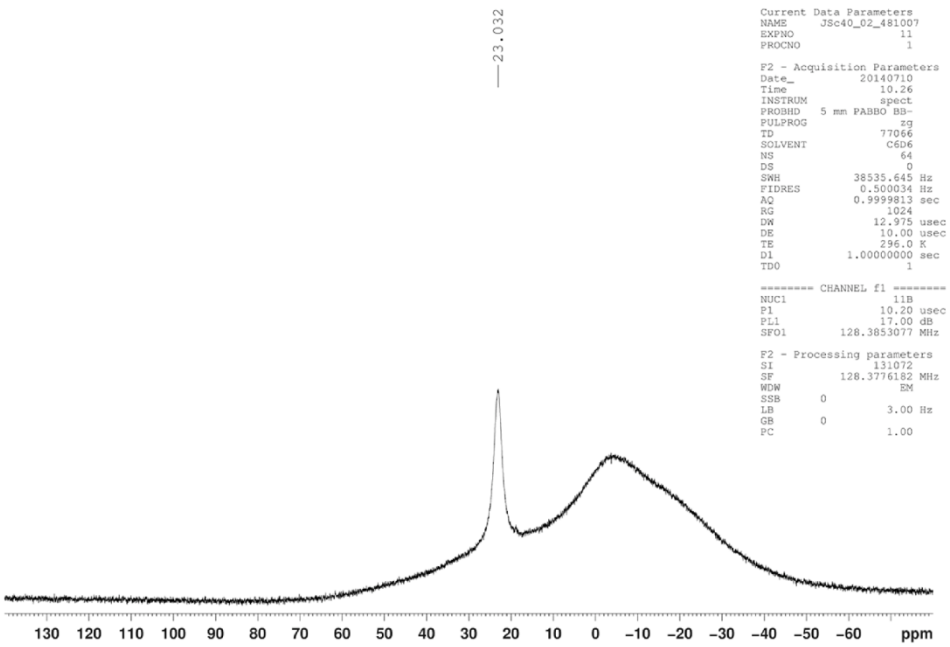

Figure S8. ^{11}B NMR of **2-D** in C_6D_6.

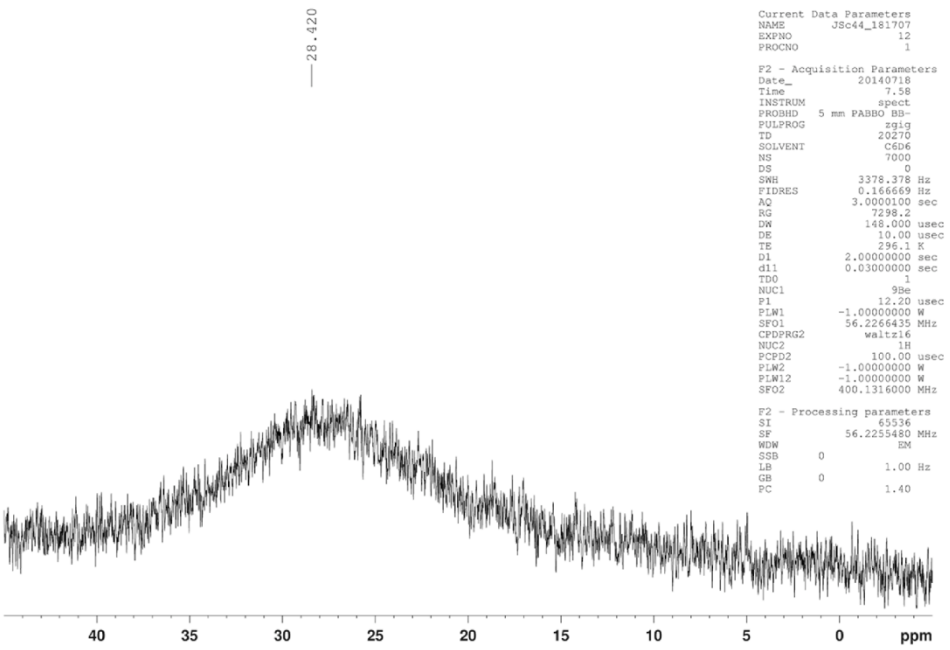

Figure S9. ^{9}Be NMR of **3** in C_6D_6.

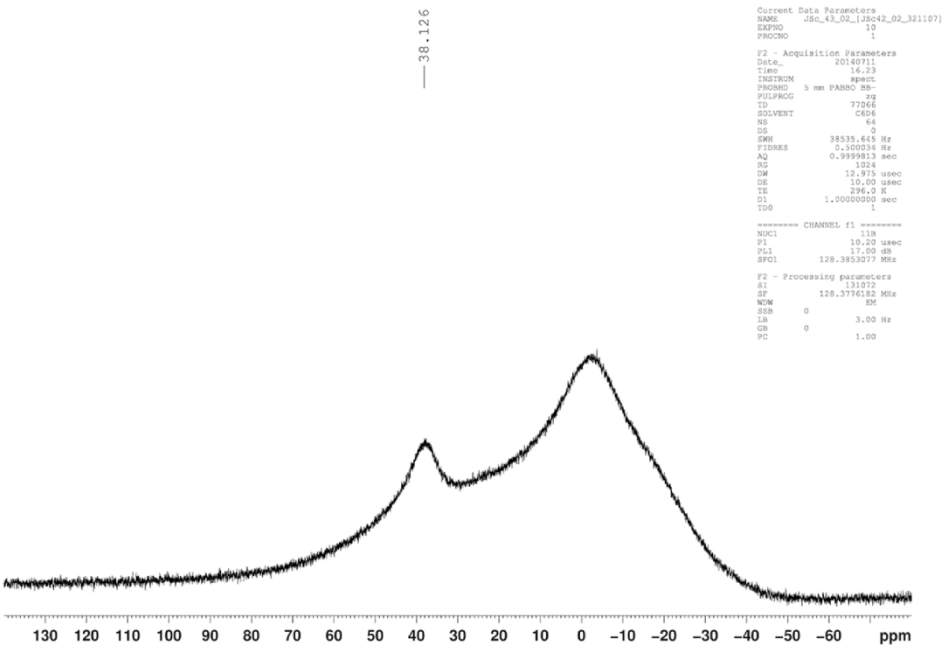

Figure S10. ^{11}B NMR of **3** in C_6D_6.

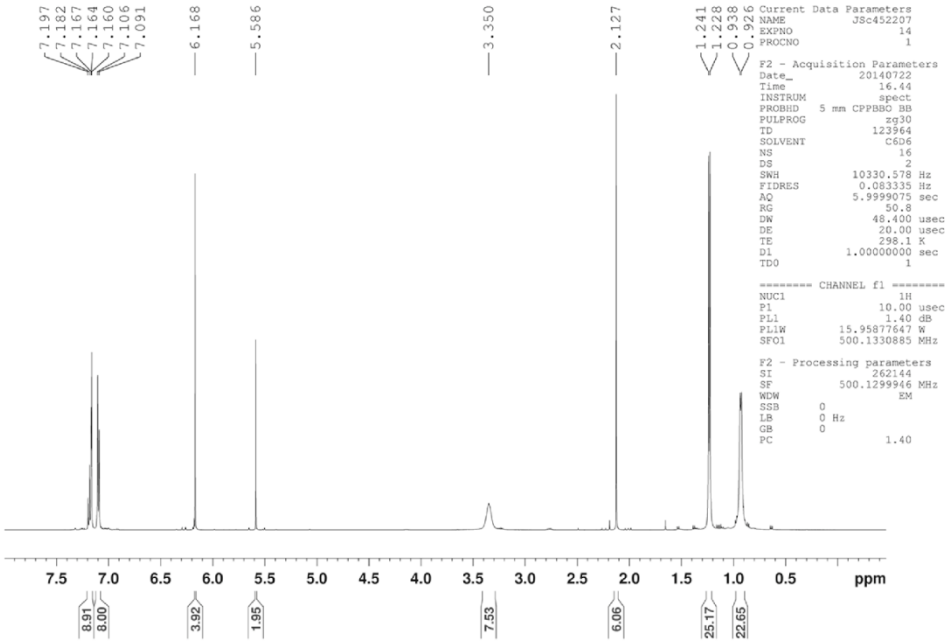

Figure S11. ^{1}H NMR of **3** in C_6D_6.

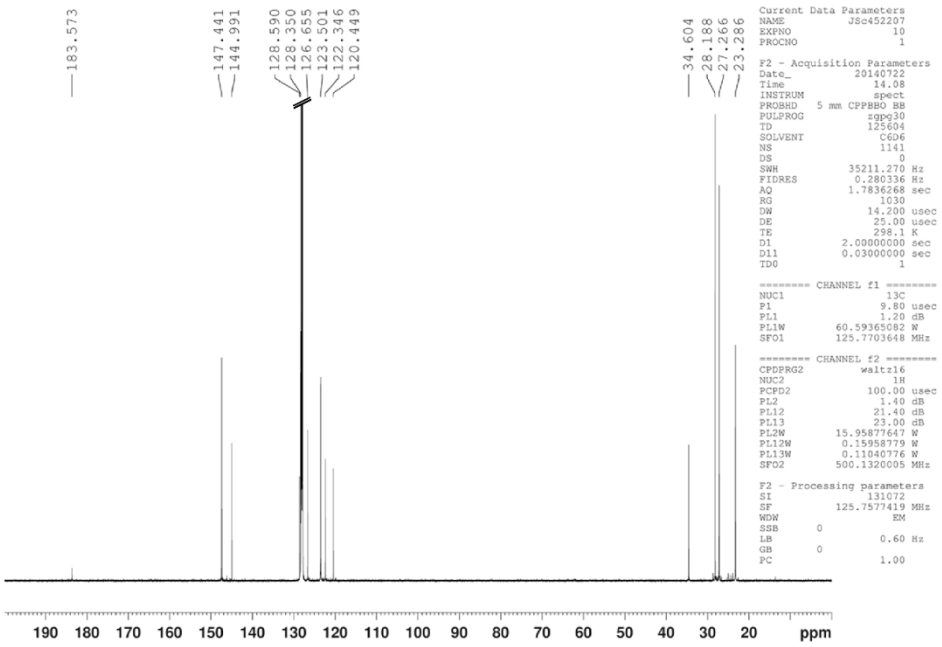

Figure S12. $^{13}C\{^{1}H\}$ NMR of **3** in C_6D_6.

Table S1. Coordinates for the optimized geometry of **1** (B3LYP/6-311G(d))

Atomic Number	X	Y	Z
7	1.045518	2.793733	-0.4387
6	0.622405	4.111671	-0.26206
1	1.250437	4.949766	-0.5226
6	-0.62479	4.1115	0.260052
1	-1.25327	4.94942	0.520063
7	-1.04721	2.79345	0.437469
7	1.0472	-2.7932	0.438648
6	0.624774	-4.11133	0.261895

1	1.253266	-4.94912	0.522302
6	-0.62244	-4.11176	-0.26016
1	-1.25048	-4.94999	-0.52026
7	-1.04555	-2.79392	-0.43748
6	2.362759	2.553771	-0.95935
6	2.549691	2.45648	-2.35468
6	3.851518	2.293045	-2.83804
1	4.019139	2.219432	-3.90748
6	4.937562	2.230206	-1.97476
1	5.940563	2.103633	-2.37076
6	4.737798	2.334982	-0.60468
1	5.593361	2.293985	0.061328
6	3.457175	2.504804	-0.06967
6	1.390888	2.580244	-3.33785
1	0.464469	2.523876	-2.76302
6	1.362705	1.43771	-4.36617
1	2.226144	1.465413	-5.03721
1	0.466934	1.509572	-4.98983
1	1.353015	0.460272	-3.87827
6	1.411233	3.948501	-4.04538
1	1.367326	4.770049	-3.32647
1	0.554625	4.048013	-4.71928
1	2.320648	4.075437	-4.64082
6	3.287493	2.688339	1.434474
1	2.217906	2.660886	1.650844
6	3.812917	4.065132	1.883517
1	4.887094	4.161435	1.697493
1	3.646612	4.210138	2.955489
1	3.310391	4.878356	1.354463
6	3.948874	1.56299	2.245555
1	3.600859	0.577276	1.931958
1	3.719509	1.678339	3.309382
1	5.038481	1.572911	2.148461
6	-2.3643	2.553055	0.958318
6	-2.55113	2.456422	2.353711
6	-3.85285	2.292491	2.837186
1	-4.0204	2.219394	3.906678

6	-4.93888	2.228524	1.973977
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6	-3.81518	4.062392	-1.88508
1	-4.88939	4.158316	-1.69903
1	-3.64899	4.207047	-2.95712
1	-3.31297	4.876039	-1.35637
6	-3.95016	1.560076	-2.24615
1	-3.60176	0.574611	-1.93221
1	-3.7209	1.675131	-3.31003
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6	2.551251	-2.45522	2.354627
6	3.853007	-2.29104	2.837926
1	4.020647	-2.2174	3.907368
6	4.938972	-2.22753	1.974607
1	5.941916	-2.10038	2.370563
6	4.739215	-2.33239	0.604522
1	5.59473	-2.29088	-0.06151
6	3.45867	-2.50294	0.069575
6	1.392568	-2.57972	3.337847
1	0.46609	-2.52384	2.763067
6	1.363833	-1.43727	4.36625

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1	0.46812	-1.50964	4.989941
1	1.35363	-0.4598	3.878434
6	1.413731	-3.948	4.045296
1	1.370232	-4.76953	3.326347
1	0.557222	-4.04802	4.719246
1	2.323254	-4.07447	4.640675
6	3.289017	-2.68665	-1.43456
1	2.219411	-2.65962	-1.65089
6	3.814954	-4.06328	-1.88349
1	4.889169	-4.15915	-1.69746
1	3.648705	-4.20844	-2.95545
1	3.31275	-4.87666	-1.35437
6	3.949964	-1.56113	-2.24576
1	3.601635	-0.57551	-1.93223
1	3.720585	-1.67665	-3.30956
1	5.039581	-1.57069	-2.14872
6	-2.36279	-2.55421	-0.95827
6	-2.54976	-2.45781	-2.35365
6	-3.8516	-2.29463	-2.83708
1	-4.01925	-2.22175	-3.90657
6	-4.9376	-2.23112	-1.97381
1	-5.94061	-2.10473	-2.36985
6	-4.7378	-2.335	-0.60365
1	-5.59333	-2.29345	0.06235
6	-3.45718	-2.5046	-0.06858
6	-1.39099	-2.58227	-3.33678
1	-0.46455	-2.5254	-2.76202
6	-1.36293	-1.44052	-4.36598
1	-2.22634	-1.46889	-5.03704
1	-0.46713	-1.51274	-4.98955
1	-1.35341	-0.4627	-3.87884
6	-1.41127	-3.95105	-4.04328
1	-1.36722	-4.77206	-3.32377
1	-0.55471	-4.05098	-4.71718
1	-2.32073	-4.07851	-4.63855
6	-3.28745	-2.68734	1.435652

1	-2.21787	-2.65935	1.652018
6	-3.81231	-4.06418	1.885256
1	-4.88644	-4.16098	1.699233
1	-3.64597	-4.20868	2.957291
1	-3.30944	-4.87742	1.35655
6	-3.94932	-1.56197	2.246289
1	-3.60178	-0.57622	1.932296
1	-3.71985	-1.67681	3.310149
1	-5.03893	-1.57245	2.149274
5	0.000575	-1.87228	0.000443
5	-0.00061	1.872319	-0.00034
4	-7.2E-05	0.000025	0.000075

Table S2. Coordinates for the optimized geometry of **3** (B3LYP/6-311G(d))

Atomic Number	X	Y	Z
7	2.468213	1.313342	1.085681
6	3.857238	1.185096	1.186053
1	4.457366	1.921289	1.697498
6	4.249784	0.063544	0.559849
1	5.249098	-0.31708	0.424101
7	3.130876	-0.59589	0.038292
7	-2.47091	1.30818	-1.08566
6	-3.85966	1.176986	-1.18607
1	-4.46134	1.911913	-1.69751
6	-4.24984	0.054573	-0.55993
1	-5.24834	-0.32819	-0.42423
7	-3.12954	-0.60248	-0.03833
6	1.948054	2.524929	1.657891
6	1.424372	2.5155	2.967918
6	1.093565	3.736522	3.563676
1	0.696992	3.750002	4.57352
6	1.287657	4.939529	2.897549
1	1.029662	5.877415	3.379971
6	1.816082	4.936387	1.614166
1	1.97574	5.88054	1.103142

6	2.162747	3.742549	0.974454
6	1.319978	1.229639	3.778574
1	1.378348	0.396973	3.075084
6	-0.0093	1.106519	4.534859
1	-0.1076	1.854834	5.326648
1	-0.08636	0.126298	5.014217
1	-0.86052	1.222525	3.860607
6	2.510692	1.09887	4.747981
1	3.462221	1.113691	4.212167
1	2.455517	0.159473	5.308384
1	2.520318	1.919282	5.472378
6	2.817892	3.800244	-0.40274
1	2.978026	2.774154	-0.73621
6	4.194291	4.489091	-0.34323
1	4.10661	5.536532	-0.03856
1	4.673124	4.471176	-1.32728
1	4.865933	3.99436	0.362324
6	1.917212	4.479416	-1.44309
1	0.952985	3.978745	-1.52048
1	2.390074	4.454823	-2.43022
1	1.727265	5.529093	-1.19918
6	3.409993	-1.84124	-0.62538
6	3.537704	-1.87701	-2.03617
6	3.869347	-3.09177	-2.6453
1	3.966754	-3.14125	-3.72331
6	4.104027	-4.23848	-1.89702
1	4.364405	-5.16934	-2.39217
6	4.037464	-4.17782	-0.51334
1	4.260944	-5.06753	0.065557
6	3.709095	-2.98985	0.148614
6	3.41794	-0.61287	-2.88896
1	2.638573	0.013468	-2.44564
6	3.042964	-0.88039	-4.3552
1	3.856597	-1.36582	-4.90205
1	2.840827	0.063973	-4.86474
1	2.153131	-1.50586	-4.45849
6	4.730491	0.199269	-2.85786

1	4.990419	0.517018	-1.84893
1	4.635461	1.09799	-3.47523
1	5.560192	-0.39359	-3.25622
6	3.770677	-2.9614	1.675602
1	3.22404	-2.07748	2.011933
6	5.226066	-2.83177	2.173216
1	5.824275	-3.68908	1.849234
1	5.254316	-2.79944	3.266954
1	5.709685	-1.92802	1.805013
6	3.140269	-4.19934	2.338122
1	2.152711	-4.42058	1.934731
1	3.048372	-4.04352	3.417364
1	3.756565	-5.0927	2.202069
6	-1.95335	2.52091	-1.65781
6	-1.42964	2.51266	-2.96784
6	-1.10146	3.734412	-3.56355
1	-0.70492	3.748782	-4.57339
6	-1.29814	4.936973	-2.89738
1	-1.04216	5.875432	-3.37976
6	-1.82656	4.932645	-1.614
1	-1.98825	5.876437	-1.10294
6	-2.17066	3.738043	-0.97433
6	-1.32252	1.227049	-3.77854
1	-1.37908	0.394249	-3.07506
6	0.006974	1.106777	-4.5349
1	0.103639	1.855321	-5.32667
1	0.086074	0.126737	-5.01429
1	0.85798	1.224554	-3.86069
6	-2.51301	1.093753	-4.74788
1	-3.46454	1.106549	-4.21202
1	-2.45587	0.154478	-5.30829
1	-2.52441	1.914146	-5.47228
6	-2.82602	3.794298	0.402827
1	-2.98377	2.767857	0.736358
6	-4.20402	4.479932	0.343181
1	-4.11874	5.527547	0.038421
1	-4.68287	4.460984	1.327197

1	-4.87446	3.983586	-0.36238
6	-1.92703	4.475652	1.443221
1	-0.96162	3.977286	1.520726
1	-2.39992	4.449978	2.430305
1	-1.73957	5.52577	1.19929
6	-3.40603	-1.84842	0.625318
6	-3.53367	-1.8845	2.036112
6	-3.86269	-3.09998	2.645216
1	-3.95998	-3.1497	3.723231
6	-4.09492	-4.24718	1.896907
1	-4.3533	-5.1786	2.392046
6	-4.02851	-4.18634	0.513235
1	-4.25009	-5.07651	-0.06569
6	-3.70269	-2.99766	-0.1487
6	-3.41664	-0.62012	2.888929
1	-2.63862	0.007914	2.445618
6	-3.04109	-0.88685	4.355159
1	-3.85367	-1.37406	4.902001
1	-2.84101	0.057945	4.864717
1	-2.1499	-1.51038	4.458448
6	-4.73095	0.189165	2.857837
1	-4.9916	0.506329	1.8489
1	-4.63788	1.088103	3.475191
1	-5.55935	-0.40549	3.256217
6	-3.76437	-2.96929	-1.67568
1	-3.21962	-2.0842	-2.01201
6	-5.22005	-2.84272	-2.17323
1	-5.81643	-3.70133	-1.84931
1	-5.24841	-2.81034	-3.26697
1	-5.7056	-1.94003	-1.80493
6	-3.13138	-4.20587	-2.33828
1	-2.14331	-4.42501	-1.935
1	-3.03993	-4.04983	-3.41753
1	-3.74575	-5.10054	-2.20218
5	-1.88483	0.170347	-0.34402
5	1.884535	0.174289	0.344026
4	0.000467	-0.39973	-9E-06

6	0.086347	-4.36662	-0.67104
6	-0.07718	-4.3668	0.671015
6	0.002321	-2.20404	0.000001
7	0.127527	-3.03678	-1.06406
1	0.185376	-5.17949	-1.37028
1	-0.1745	-5.17988	1.370252
7	-0.12114	-3.03706	1.06405
6	0.198865	-2.58489	-2.44503
1	0.873791	-3.22994	-3.00511
1	-0.79056	-2.5944	-2.90543
1	0.592233	-1.57213	-2.46638
6	-0.19336	-2.58534	2.445029
1	-0.86691	-3.23182	3.005127
1	0.796102	-2.59279	2.905393
1	-0.58885	-1.57341	2.466412

Table S3. Optimized geometry used for the GIAO calc of the NMR frequency for $[(CHN(dipp))_2B]^-$.

Atomic Number	X	Y	Z
7	-1.13015	-0.05691	0.362052
6	-0.69062	0.036456	1.693789
1	-1.36806	0.04078	2.538636
6	0.659166	0.110293	1.699126
1	1.327041	0.178896	2.548536
7	1.115362	0.076418	0.370355
6	-2.5193	-0.08238	0.062552
6	-3.12648	-1.28234	-0.37951
6	-4.5031	-1.29208	-0.61911
1	-4.98154	-2.20656	-0.95569
6	-5.27778	-0.15166	-0.43629
1	-6.34842	-0.18135	-0.62409
6	-4.67103	1.029906	-0.03017
1	-5.27567	1.925202	0.08122
6	-3.2953	1.089473	0.215589
6	2.509113	0.093067	0.092581
6	3.143574	1.300116	-0.27622
6	4.516886	1.289082	-0.542

1	5.010864	2.210588	-0.83778
6	5.261748	0.120795	-0.44167
1	6.328707	0.131532	-0.65104
6	4.630543	-1.06486	-0.08353
1	5.212773	-1.98036	-0.02782
6	3.259208	-1.10163	0.185163
5	0.000095	-0.04267	-0.61867
6	2.348369	2.588798	-0.43774
1	1.36667	2.411178	0.003948
6	2.571864	-2.43081	0.475506
1	1.597336	-2.20201	0.908412
6	-2.62995	2.426048	0.530067
1	-1.68345	2.213227	1.028826
6	-2.2853	-2.53731	-0.5742
1	-1.29796	-2.18387	-0.89167
6	-2.80686	-3.4692	-1.67529
1	-3.75294	-3.95644	-1.41095
1	-2.95515	-2.92797	-2.6138
1	-2.07831	-4.26477	-1.86246
6	-2.11343	-3.30075	0.751326
1	-1.65894	-2.66436	1.513376
1	-3.07814	-3.65661	1.133649
1	-1.46428	-4.17341	0.614361
6	-3.44789	3.32394	1.470497
1	-4.37188	3.685533	1.006942
1	-3.72175	2.798777	2.390713
1	-2.86425	4.207526	1.749829
6	-2.29098	3.153912	-0.78459
1	-1.75591	4.09033	-0.58652
1	-1.65585	2.522168	-1.41074
1	-3.20144	3.396041	-1.34521
6	2.986097	3.783247	0.290766
1	3.148078	3.563828	1.350532
1	3.951965	4.068515	-0.14025
1	2.332553	4.659953	0.225939
6	2.113618	2.891823	-1.92793
1	3.061016	3.034446	-2.46161

1	1.567634	2.06365	-2.38647
1	1.516359	3.803251	-2.0491
6	3.330988	-3.30695	1.484078
1	4.292676	-3.65771	1.094385
1	3.527915	-2.76634	2.414886
1	2.741504	-4.19624	1.731588
6	2.311224	-3.18319	-0.84239
1	1.707838	-2.56351	-1.51084
1	3.251312	-3.43223	-1.34866
1	1.768516	-4.11772	-0.65705

References.

[1] T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *24*, 4196-4206.

[2] Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc*. **2008**, *130*, 16069-16079.

[3] Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113-115.

[4] G. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112–122.

[5] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[6] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.

[7] P. G. Pleiger, K. D. John, T. S. Keizer, T. M. McClesky, A. K. Burrell, R. L. Martin, *J. Am. Chem. Soc*. **2004**, *126*, 14651-14658.