Electronic Supporting Information for:

The Hydroboration of α-diimines

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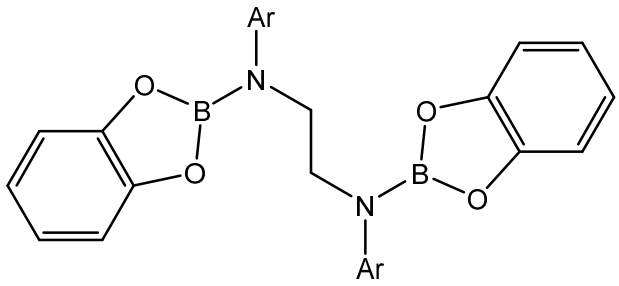
Experimental Section. Reagents and solvents used were obtained from Aldrich Chemicals. α-Diimines were prepared by condensation of aniline derivatives with glyoxal or 2,3-butanedione. NMR spectra were recorded on a JEOL JNM-GSX400 FT NMR (^{1}H: 400 MHz; ^{11}B: 128 MHz; ^{13}C: 100 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B)]. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m). Melting points were measured uncorrected with a Stuart SMP30 apparatus. Elemental analyses for C, H, and N were carried out at the University of Windsor. All reactions were carried out under an atmosphere of dinitrogen.

General Procedure for bis-Hydroboration Products 1-3. Catecholborane (50 mg, 0.42 mmol, 2.1 eq) was added to diimine (0.20 mmol) in toluene. Following 4 hours of stirring, the solvent was removed in vacuo and the residue washed with hexanes (3 x 5 mL).



Ar = 4-$MeOC_6H_4$ (**1**)
= 2,6-$Me_2C_6H_3$ (**2**)
= 2,6-*i*$Pr_2C_6H_3$ (**3**)

N^{1},*N*^{2}-Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-*N*^{1},*N*^{2}-bis(4-methoxyphenyl)ethane-1,2-diamine (**1**)

*Note: The ^{11}B NMR spectrum of the crude reaction mixture shows a resonance at 21.1 ppm in addition to the signal corresponding to **1**, suggesting that *B*O_3 environment(s) are also present in solution, possibly B_2cat_3 ((cat)*B*(cat)*B*(cat)) or (diamino)B(cat)*B*(cat).

Yield: 60 mg (59%, 0.12 mmol). M.P. = 180°C (decomp). Anal. calc. for $C_{28}H_{26}N_2B_2O_6$ (508.14 g/mol) (%): C 66.18, H 5.16, N 5.51. Found: C 66.35, H 5.04, N 5.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.78 (s, 4H), 3.79 (s, 6H), 6.82 (d, J = 9.2 Hz, 4H), 6.91-7.01 (m, 8H, cat), 7.05 (d, J = 8.7 Hz, 4H). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 24.5 (br). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 48.6, 55.5, 111.7, 114.3, 121.9, 125.6, 137.1, 148.7, 156.5.

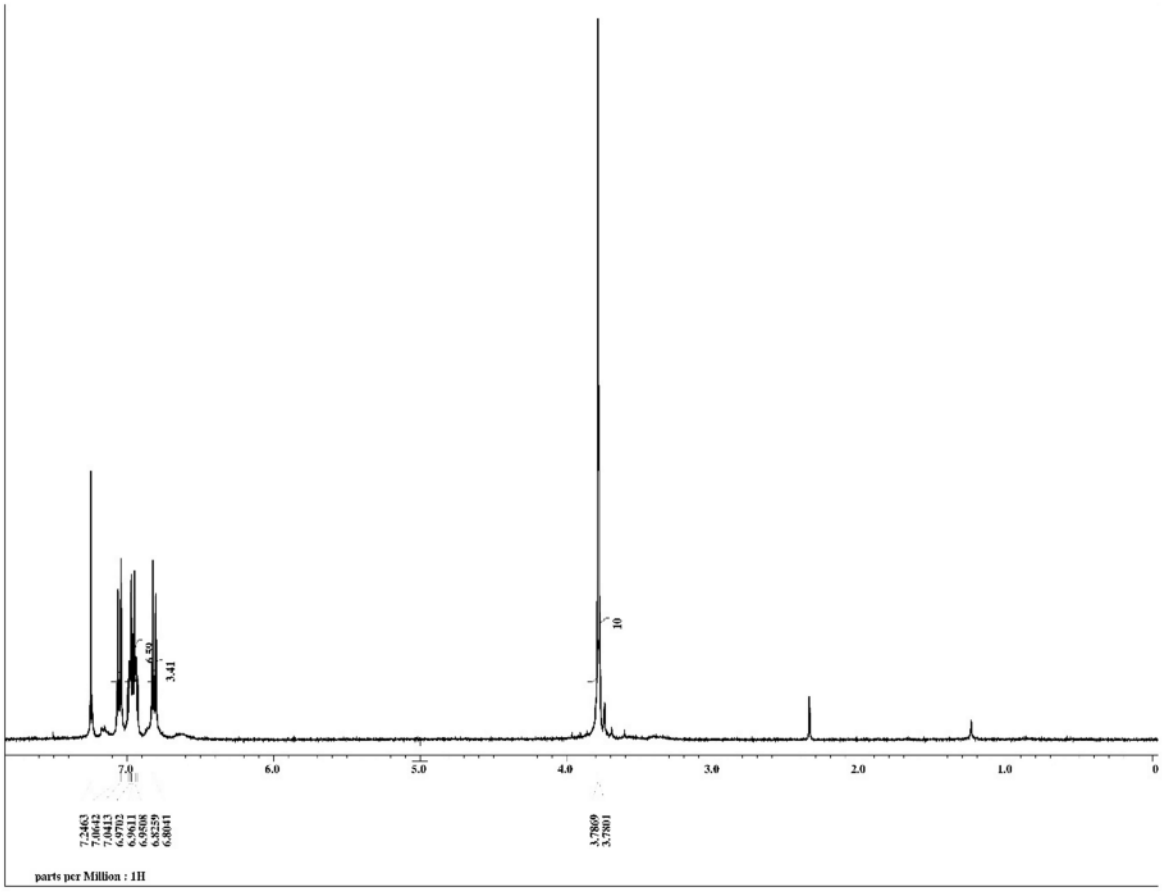


Figure S1. ^{1}H NMR of N^1,N^2-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-N^1,N^2-bis(4-methoxyphenyl)ethane-1,2-diamine (**1**) in $CDCl_3$.

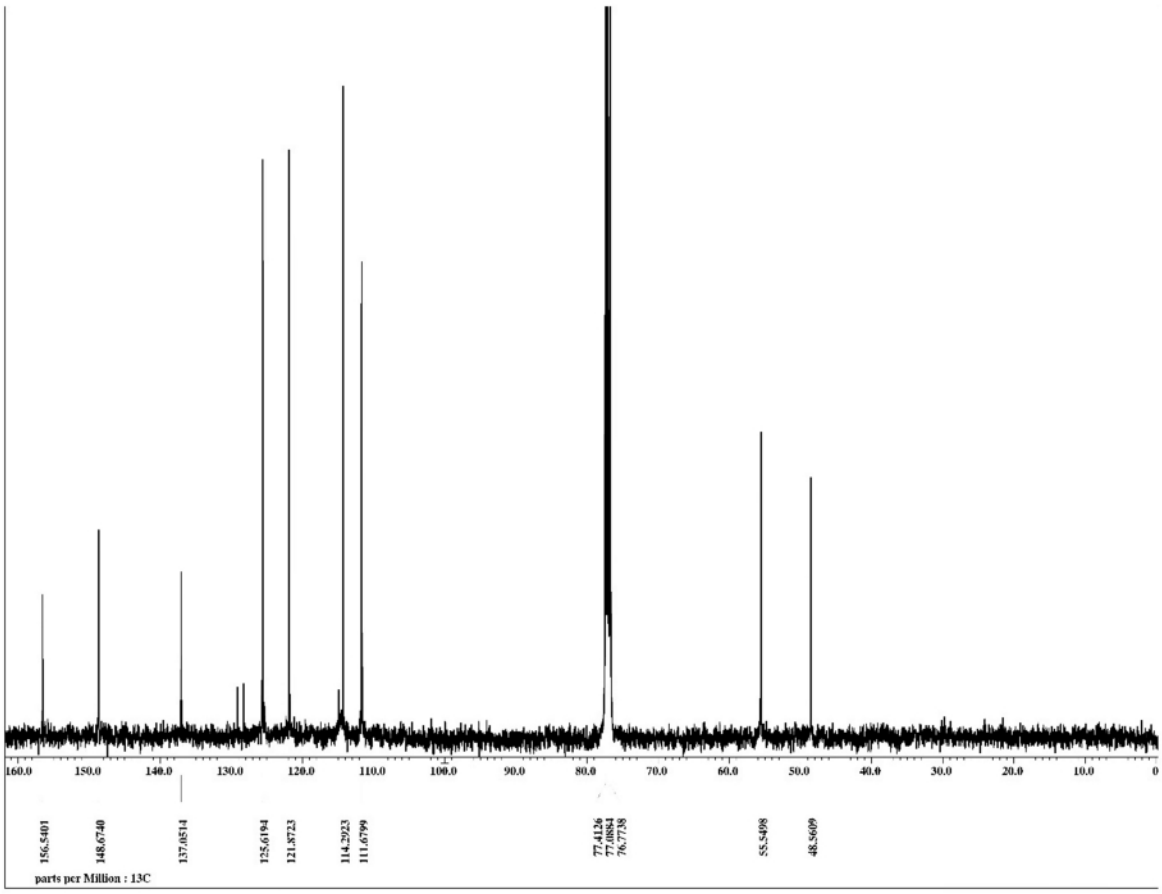


Figure S2. ^{13}C NMR of *N*^{1},*N*^{2}-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-*N*^{1},*N*^{2}-bis(4-methoxyphenyl)ethane-1,2-diamine (**1**) in $CDCl_3$.

N^{1},*N*^{2}-Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-*N*^{1},*N*^{2}-bis(2,6-dimethylphenyl)ethane-1,2-diamine (**2**)

Yield: 80 mg (79%, 0.16 mmol). M.P. = 147-149 (decomp). Anal. calc. Anal. calc. for $C_{30}H_{30}N_2B_2O_4 \cdot 1/4\ CH_2Cl_2$ (525.43 g/mol) (%): C 69.15, H 5.85, N 5.33. Found: C 69.72, H 5.57, N 5.00. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 12H), 3.62 (s, 4H), 6.95 (br s, 4H, cat), 6.98 (br s, 4H, cat), 7.11 (s, 4H), 7.20 (br, 1H), 7.35 (br, 1H) . ^{11}B NMR (128 MHz, $CDCl_3$) δ: 22.5 (br). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 18.8, 49.1, 111.7, 121.8, 126.7, 128.9, 136.1, 141.2, 149.0.

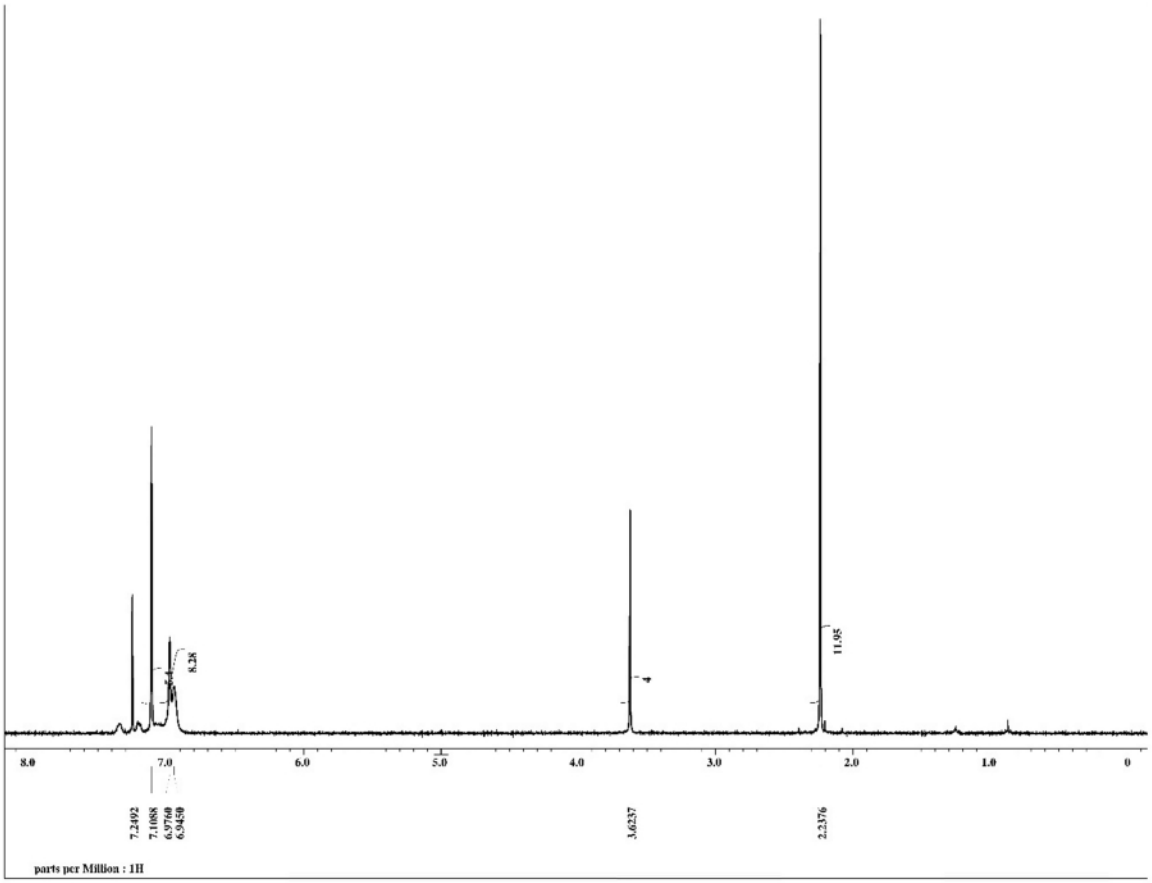


Figure S3. ^{1}H NMR of N^{1},N^{2}-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-N^{1},N^{2}-bis(2,6-dimethylphenyl)ethane-1,2-diamine (**2**) in $CDCl_3$.

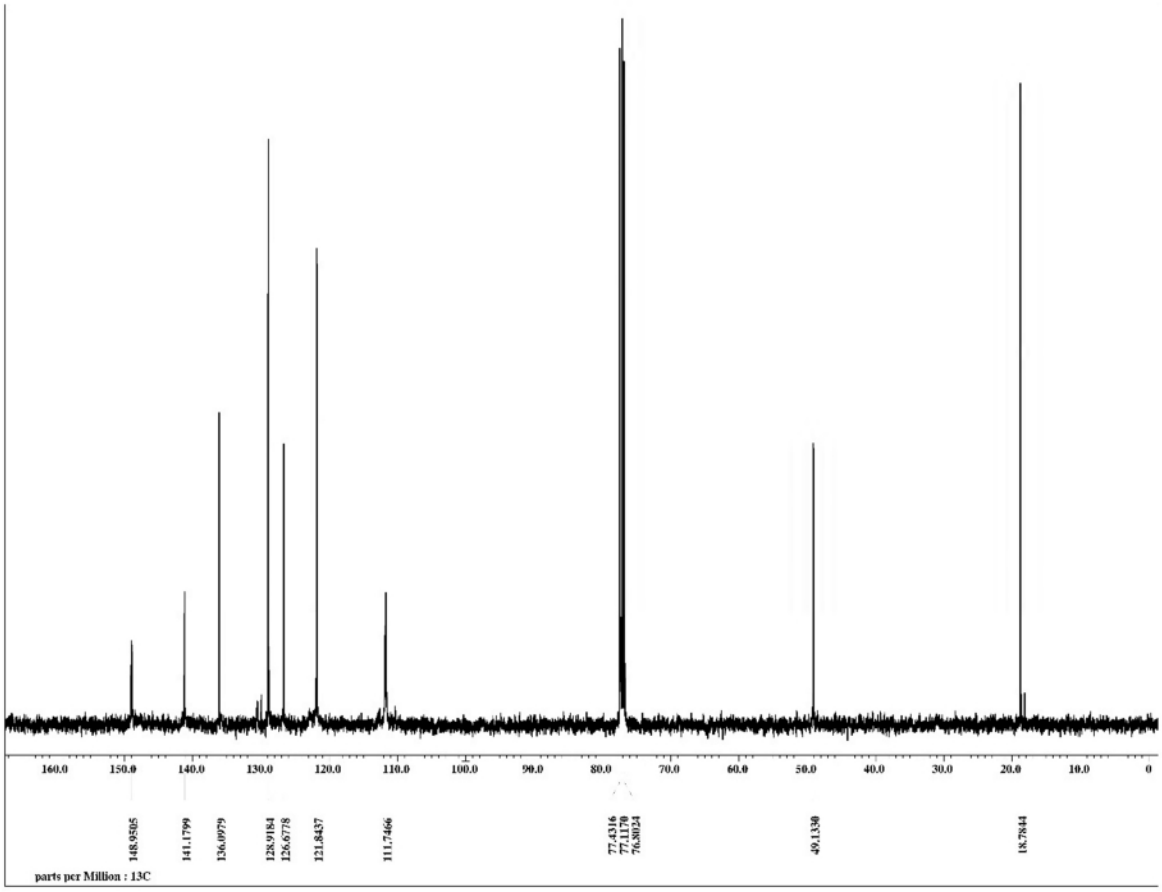


Figure S4. ^{13}C NMR of *N*^{1},*N*^{2}-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-*N*^{1},*N*^{2}-bis(2,6-dimethylphenyl)ethane-1,2-diamine (**2**) in $CDCl_3$.

N^{1},*N*^{2}-Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-*N*^{1},*N*^{2}-bis(2,6-diisopropylphenyl)ethane-1,2-diamine (**3**)

Yield: 104 mg (84%, 0.169 mmol). M.P. = 170°C (decomp). Anal. calc. for $C_{38}H_{46}N_2B_2O_4$ (616.42 g/mol) (%): C 74.04, H 7.52, N 4.54. Found: C 73.98, H 7.53, N 4.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10 (d, J = 6.9 Hz, 12H), 1.19 (d, J = 6.9 Hz, 12H), 3.19 (sept, J = 6.9 Hz, 4H), 3.64 (s, 4H), 6.93 (br s, 6H, cat), 7.17 (d, J = 7.8 Hz, 4H, *m*-C*H*), 7.28 (t, J = 7.8 Hz, 2H, *p*-C*H*). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 24.6 (br). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 23.8, 25.0, 28.2, 50.3, 111.7, 121.8, 124.3, 127.6, 137.8, 146.7, 148.9.

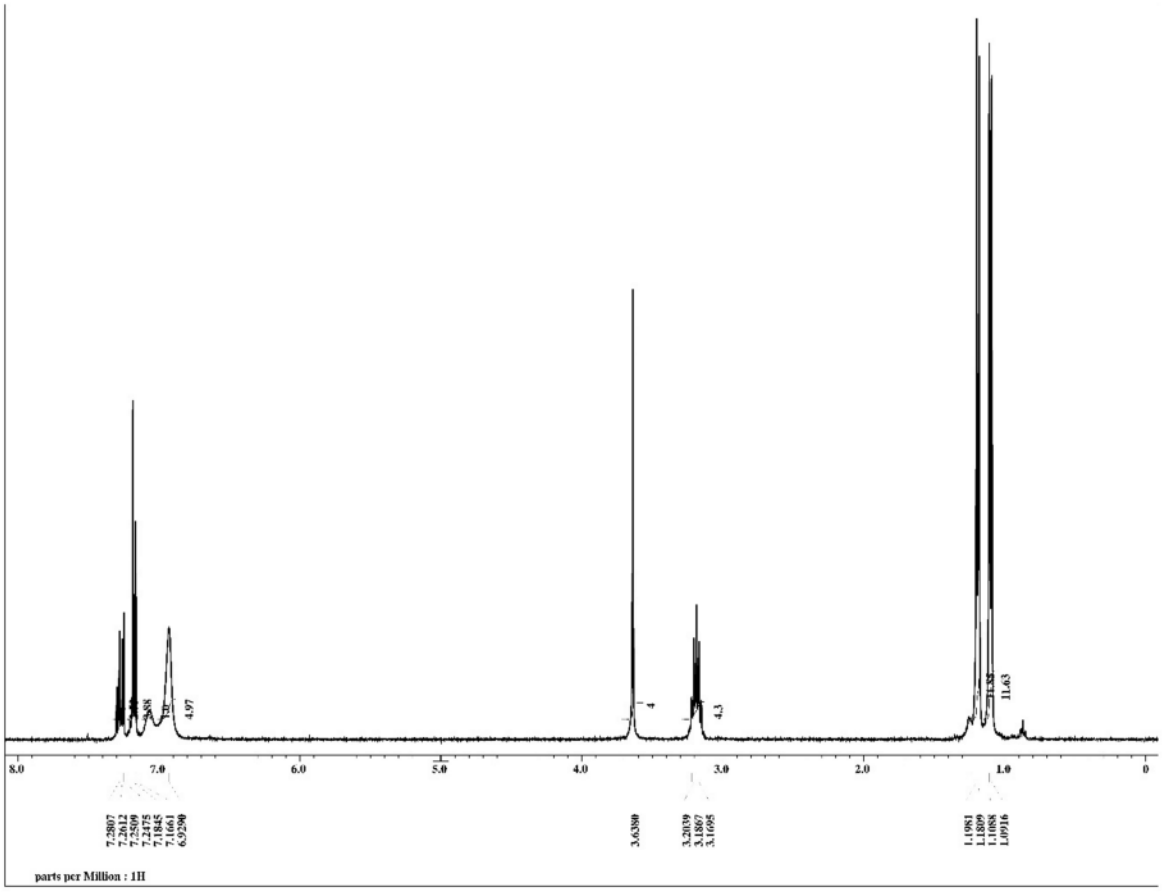


Figure S5. ^{1}H NMR of N^{1},N^{2}-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-N^{1},N^{2}-bis(2,6-diisopropylphenyl)ethane-1,2-diamine (**3**) in $CDCl_3$.

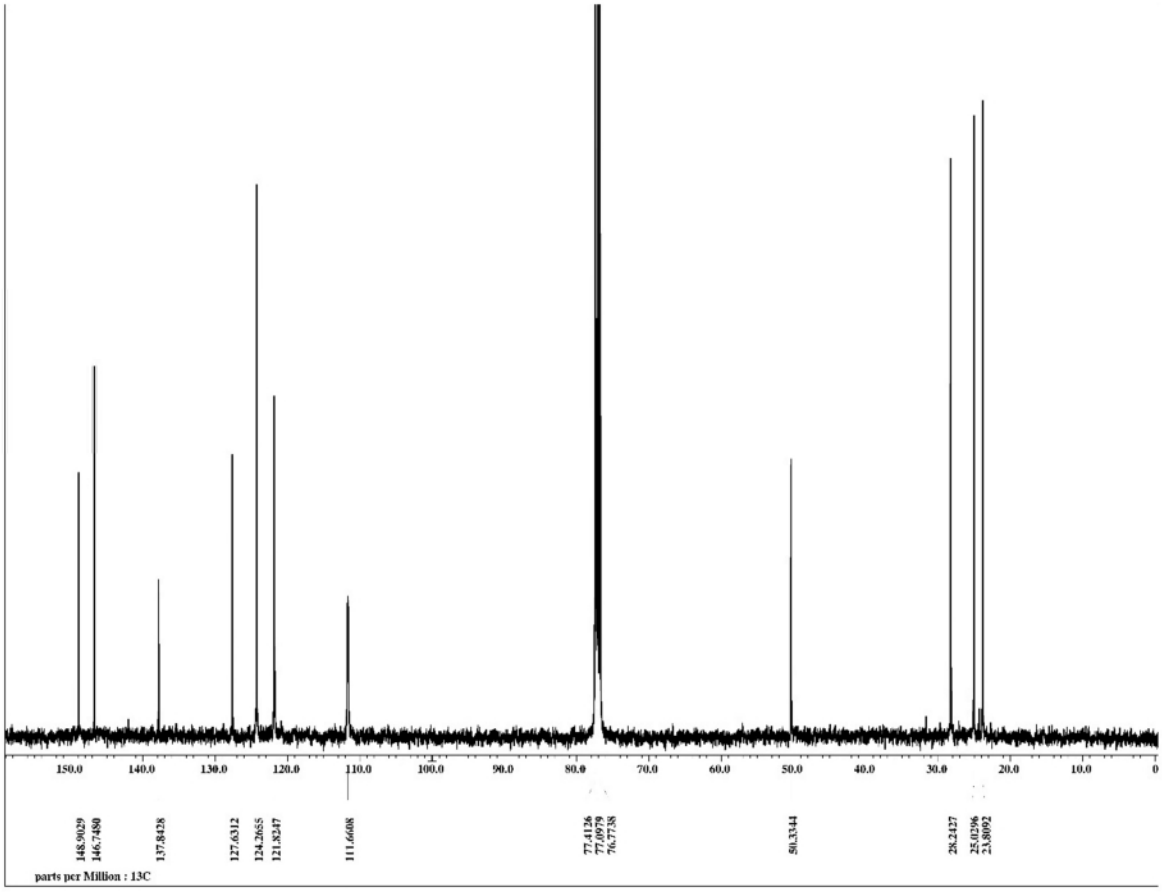
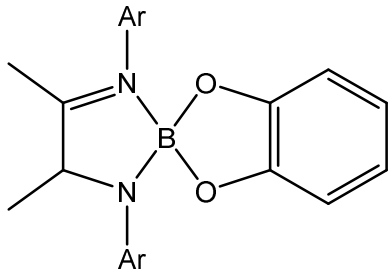


Figure S6. ^{13}C NMR of N^1,N^2-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-N^1,N^2-bis(2,6-diisopropylphenyl)ethane-1,2-diamine (**3**) in $CDCl_3$.

General Procedure for the Synthesis of 4-7. To 100 mg of diimine (0.34-0.42 mmol) in 10 mL of diethyl ether was added 1-1 mg catecholborane (0.37-0.47 mmol, 1.1 equivalents). Following 4 hours of stirring the mixture was filtered and the precipitate was washed with diethyl ether (3x5 mL) and dried *in vacuo*.



Ar = Ph (**4**)
= 4-MeC_6H_4 (**5**)
= 4-$MeOC_6H_4$ (**6**)
= 4-$MeOC_6H_4$ (**7**)

4',5'-Dimethyl-1',3'-diphenyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**4**)

Yield: 86 mg (57%, 0.24 mmol). M.P. = 128°C (decomp). Anal. calc. for $C_{22}H_{21}N_2BO_2$ • 1/4 Et_2O (374.76 g/mol) (%): C 73.71, H 6.32, N 7.48. Found: C 73.42, H 6.27, N 7.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.66 (d, J = 6.9 Hz, 3H), 2.23 (s, 3H), 4.83 (q, J = 6.9 Hz, 1H), 6.53-6.60 (ov m, 5H), 6.63-6.69 (m 2H), 7.10 (t, J = 8.2 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 7.27-7.33 (ov m, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 11.5 (br). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 16.0, 17.3, 59.6, 109.3, 109.5, 114.9, 117.1, 119.0, 124.0, 129.1, 129.2, 129.5, 137.2, 144.9, 151.2, 151.7, 187.0.

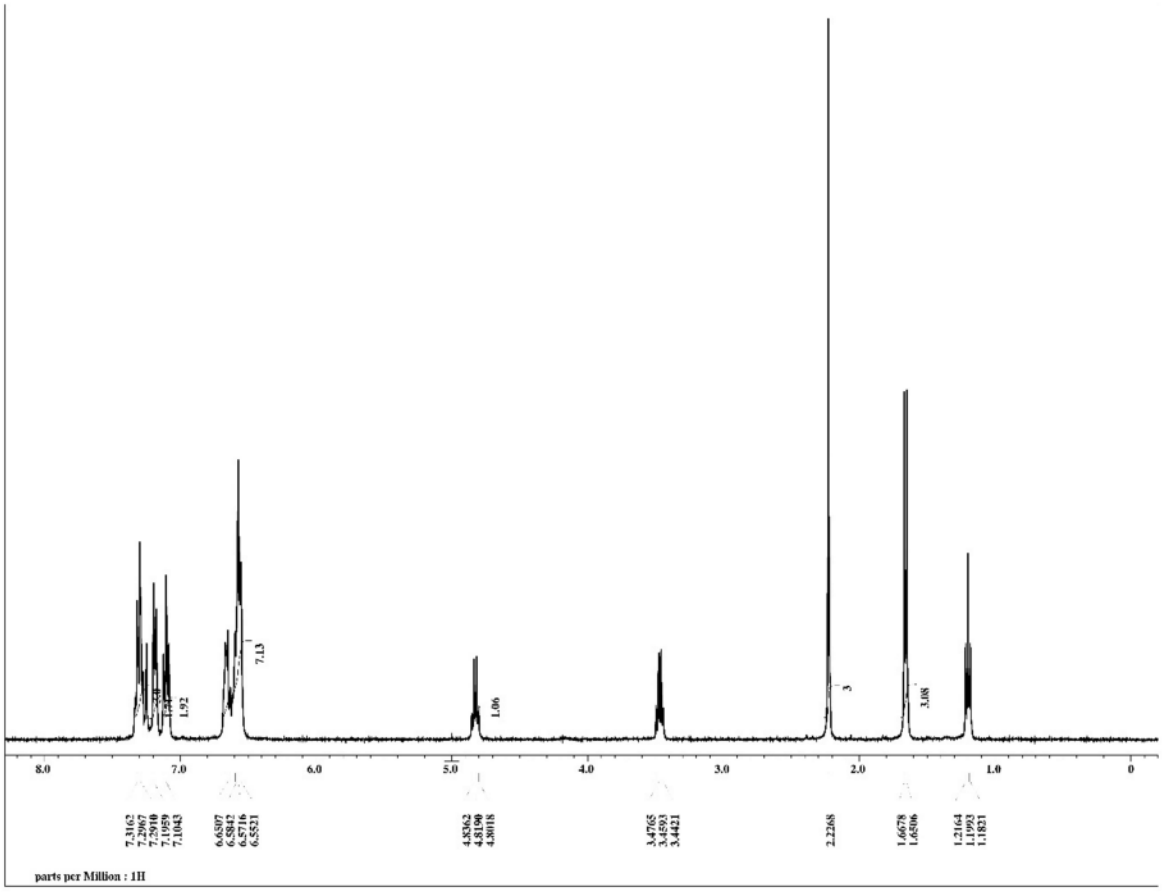


Figure S7. ^{1}H NMR of 4',5'-dimethyl-1',3'-diphenyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**4**) in $CDCl_3$.

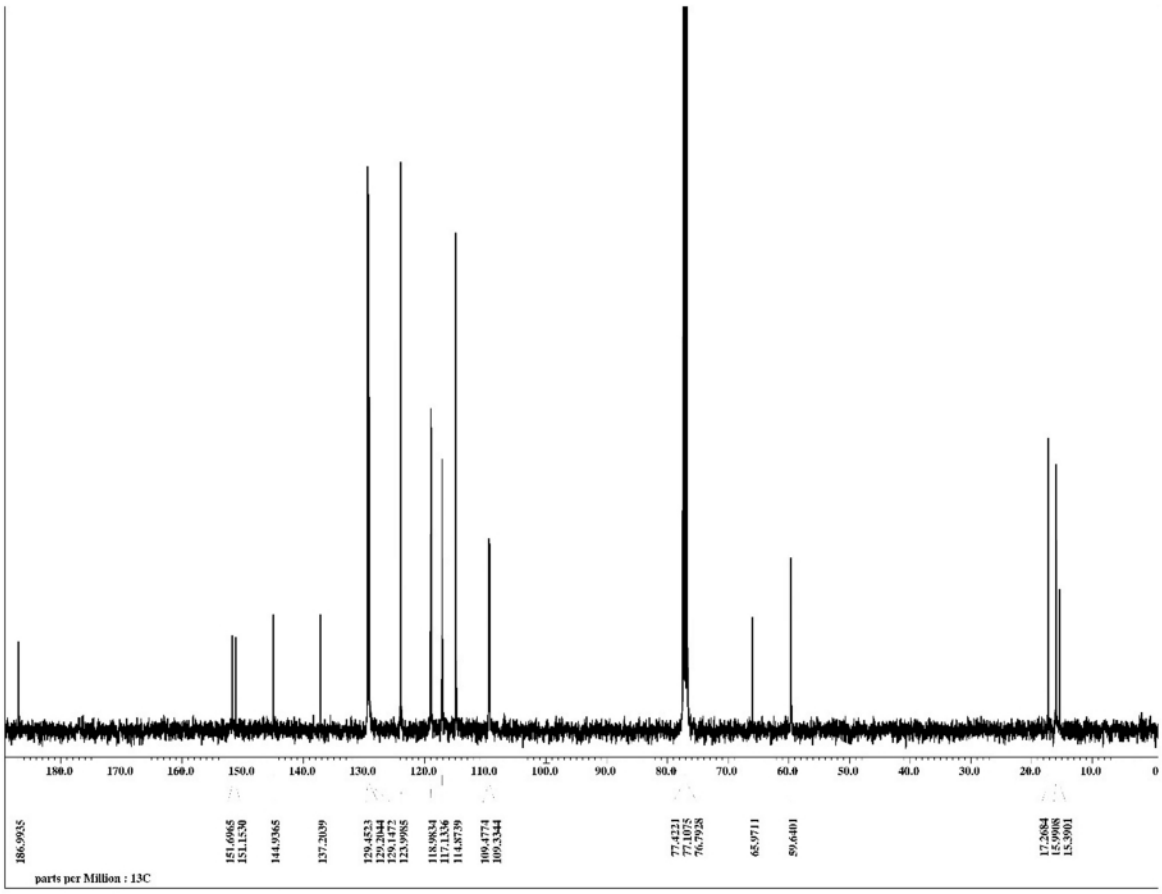


Figure S8. ^{13}C NMR of 4',5'-dimethyl-1',3'-diphenyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**4**) in $CDCl_3$.

4',5'-Dimethyl-1',3'-di-*p*-tolyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**5**)

Yield: 92 mg (63%, 0.24 mmol). M.P. = 160°C (decomp). Anal. calc. for $C_{24}H_{25}N_2BO_2$ (384.29 g/mol) (%): C 75.01, H 6.56, N 7.29. Found: C 74.48, H 6.55, N 7.17. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.62 (d, J = 6.9 Hz, 3H), 2.17 (s, 3H), 2.21 (s, 3H), 2.26 (s, 3H), 4.81 (q, J = 6.9 Hz, 1H), 6.48 (d, J = 8.2 Hz, 2H), 6.55-6.58 (ov m, 3H), 6.67 (d, J = 6.0 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 7.08 (ov m, 4H). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 11.6 (br). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 16.0, 17.1, 20.5, 21.2, 59.7, 109.2, 109.4, 115.1, 118.9, 123.8, 129.7, 130.1, 130.2, 134.7, 139.1, 150.6, 151.2, 151.9, 187.1.

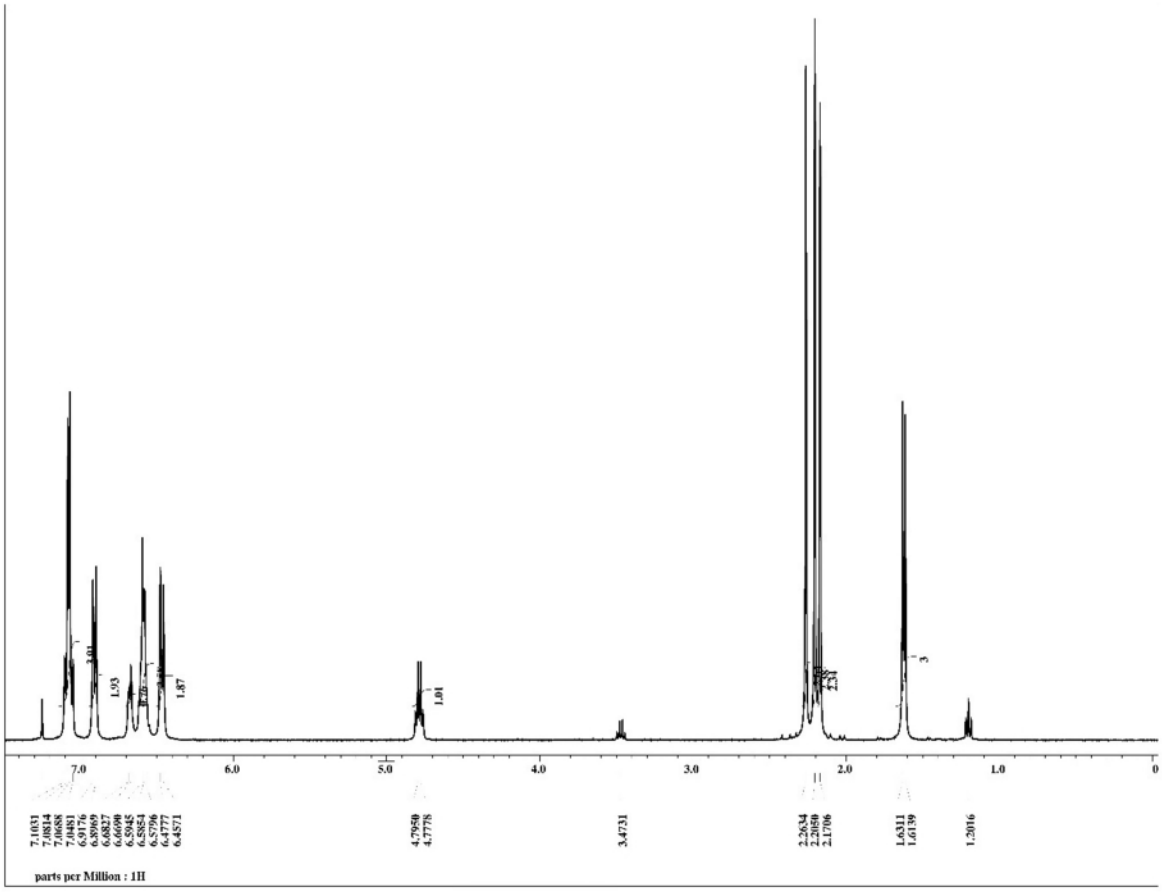


Figure S9. ^{1}H NMR of 4',5'-dimethyl-1',3'-di-*p*-tolyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**5**) in $CDCl_3$.

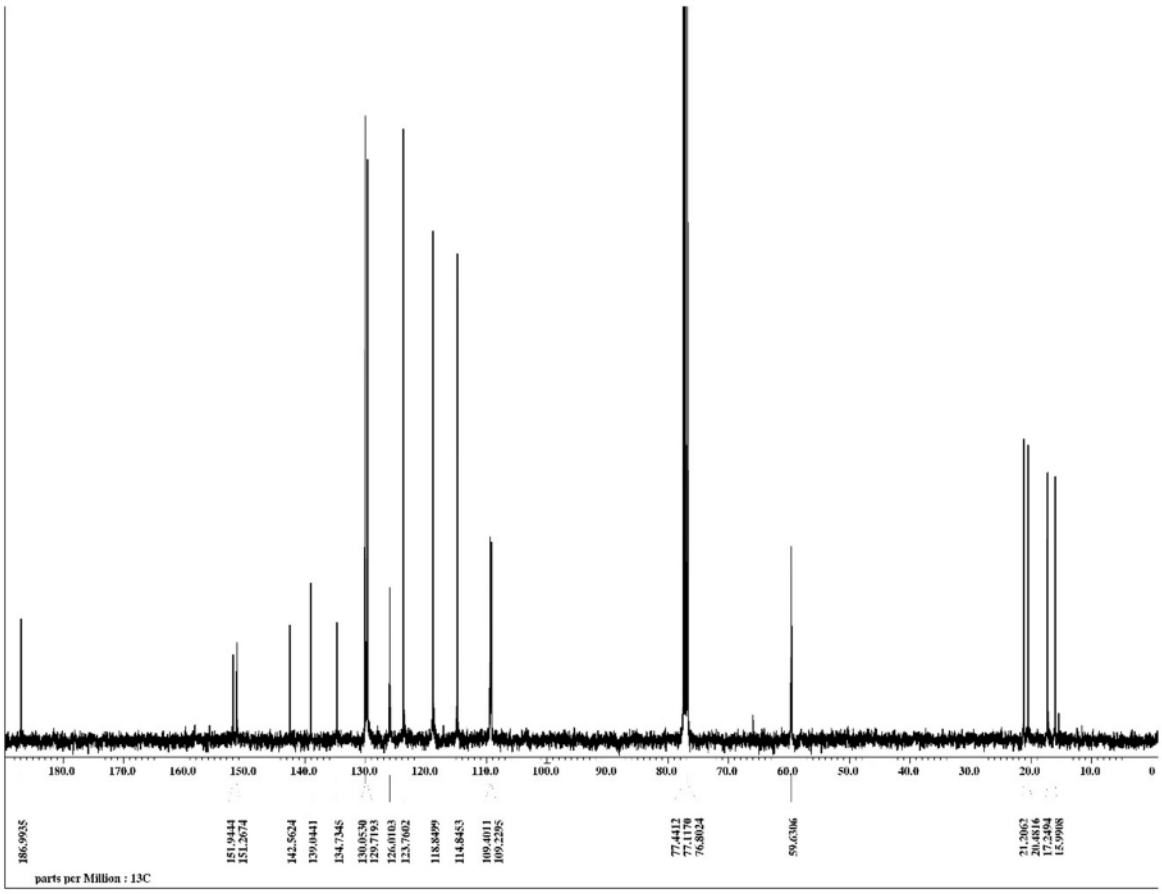


Figure S10. ^{13}C NMR of 4',5'-dimethyl-1',3'-di-*p*-tolyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**5**) in $CDCl_3$.

1',3'-bis(4-methoxyphenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**6**)

Yield: 110 mg (78%, 0.26 mmol). M.P. = 115°C (decomp). Anal. calc. for $C_{24}H_{25}N_2BO_4$ (416.28 g/mol) (%): C 69.25, H 6.05, N 6.73. Found: C 68.58, H 6.22, N 6.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.60 (d, J = 6.8 Hz, 3H), 2.22 (s, 3H), 3.68 (s, 3H), 3.73 (s, 3H), 4.76 (q, J = 6.8 Hz, 1H), 6.50 (d, J = 9.2 Hz, 2H), 6.55-6.61 (ov m, 3H), 6.70 (m, 3H), 6.79 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 11.5 (br). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 16.0, 17.3, 55.4, 55.8, 59.8, 109.2, 109.4, 114.6, 115.0, 115.6, 118.9, 125.2, 130.0, 139.0, 151.2, 151.5, 151.9, 159.7, 187.0.

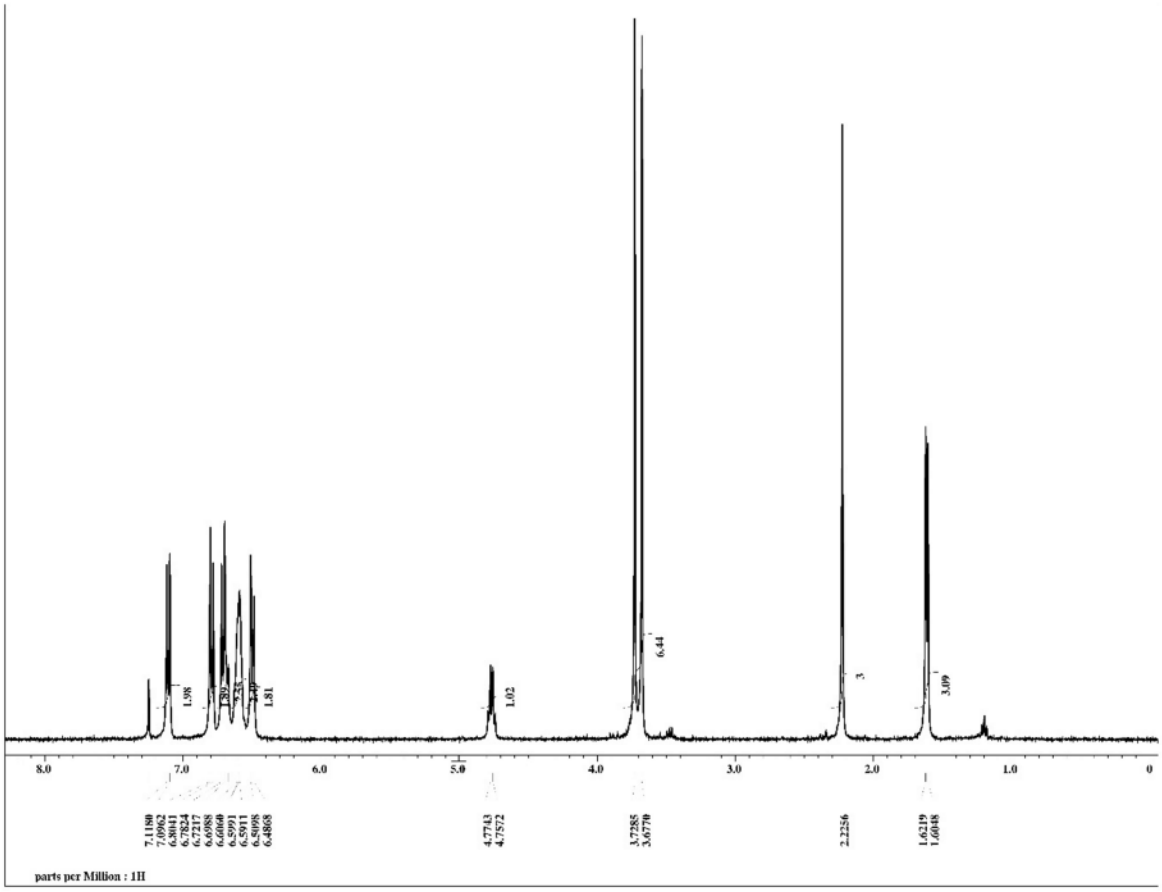


Figure S11. ^{1}H NMR of 1',3'-bis(4-methoxyphenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**6**) in $CDCl_3$.

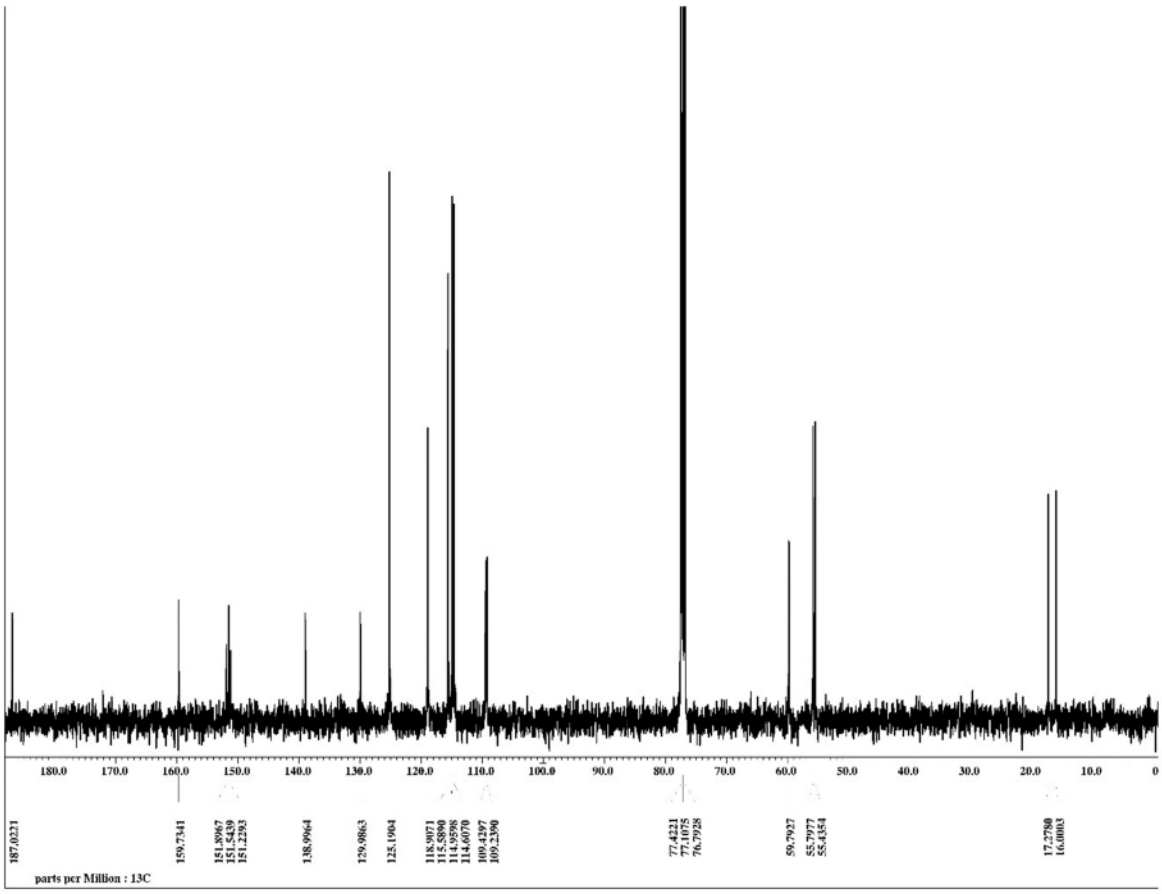


Figure S12. ^{13}C NMR of 1',3'-bis(4-methoxyphenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**6**) in $CDCl_3$.

1',3'-bis(4-fluorophenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**7**)

Yield: 86 mg (60%, 0.22 mmol). M.P. = 120°C (decomp). Anal. calc. for $C_{22}H_{19}N_2BO_4F_2$ (392.21 g/mol) (%): C 67.37, H 4.88, N 7.14. Found: C 67.04, H 4.97, N 7.12. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.63 (d, J = 6.9 Hz, 3H), 2.25 (s, 3H), 4.78 (q, J = 6.9 Hz, 1H), 6.47 (m, 2H), 6.58-6.62 (ov m, 3H), 6.68 (br, 1H), 6.82 (t, J = 8.7 Hz, 2H), 7.01 (t, J = 8.2 Hz, 2H), 7.18 (m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 11.6 (br). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 16.0, 17.1, 59.9, 109.4, 109.6, 115.4 (d, J_{C-F} = 10 Hz), 115.7 (d, J_{C-F} = 28 Hz), 116.7 (d, J_{C-F} = 29 Hz), 119.3, 125.9 (d, J_{C-F} = 12 Hz), 133.0 (d, J_{C-F} = 1.1 Hz), 141.0, 150.9, 151.5, 156.9, 163.8, 187.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.2 (t, J = 7.9 Hz), -128.7 (br).

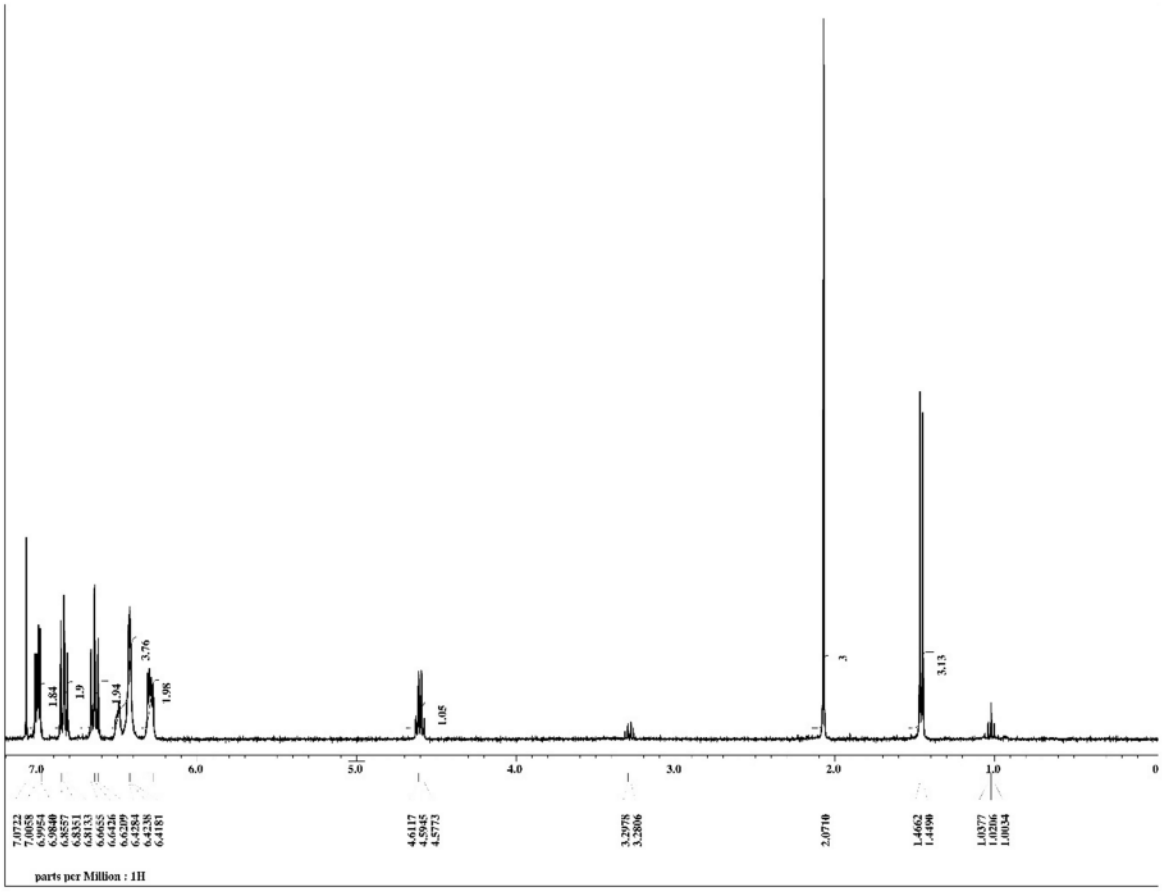


Figure S13. ^{1}H NMR of 1',3'-bis(4-fluorophenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**7**) in $CDCl_3$.

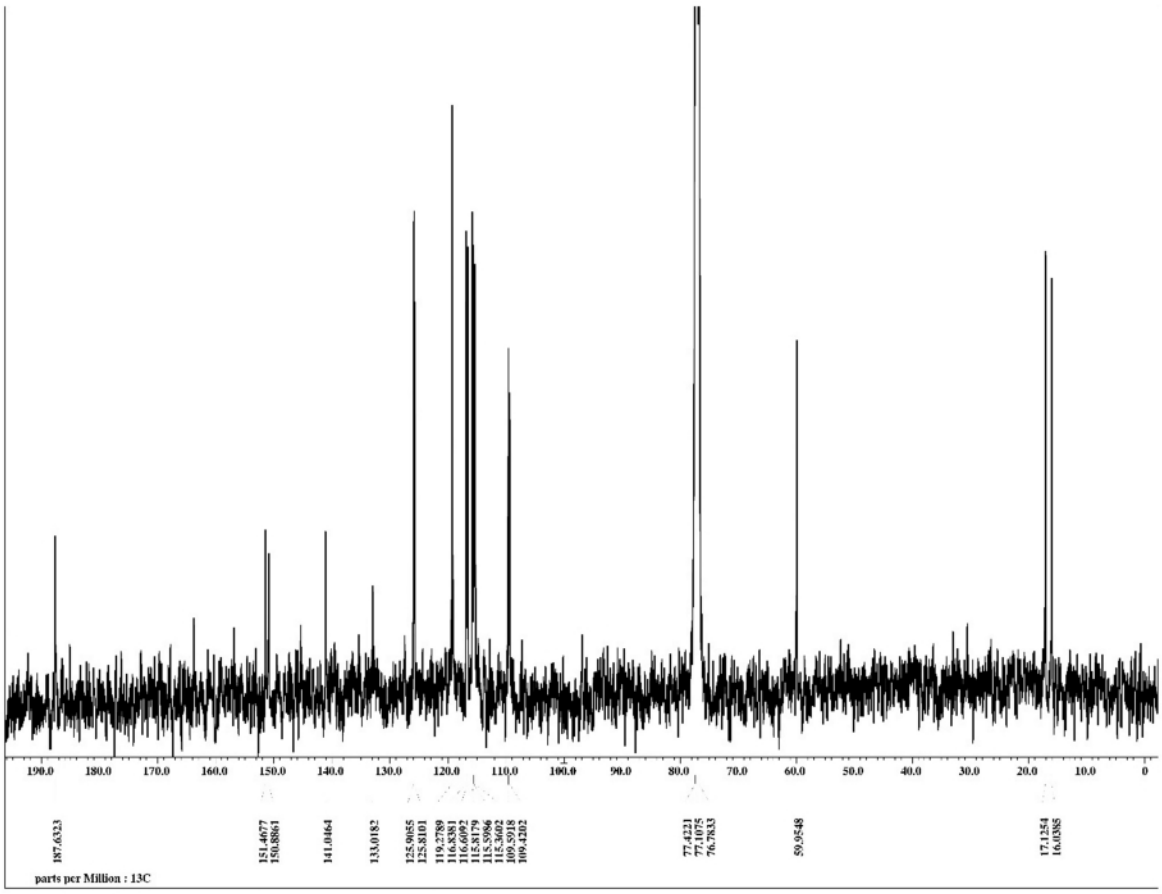


Figure S14. ^{13}C NMR of 1',3'-bis(4-fluorophenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**7**) in $CDCl_3$.

X-Ray Crystallography

Crystals were grown from dilute Et_2O solutions. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and ϕ scans with a scan width of 0.3 ° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)[1] and corrected for absorption (SADABS).[2] The structure was solved by direct methods and refined by full-matrix least squares on F2(SHELXTL)[3]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

1 SAINT 7.23A, 2006, Bruker AXS, Inc., Madison, Wisconsin, USA.
2 SADABS 2008, George Sheldrick, 2008, Bruker AXS, Inc., Madison, Wisconsin, USA.
3 Sheldrick, G.M. (2008). SHELXTL. Acta Cryst. A64, 112-122.

Table 1. Crystallographic Data-Collection Parameters

Complex	**3**	**6**	**7**
Formula	$C_{38}H_{46}B_2N_2O_4$	$C_{24}H_{25}BN_2O_4$	$C_{22}H_{19}BF_2N_2O_4$
Molecular weight	616.39	416.27	392.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/c	P2(1)/c
a/Å	28.1959(14)	10.4891(3)	9.9992(4)
b/Å	11.5570(6)	8.8508(3)	8.9229(4)
c/Å	22.0519(11)	22.8286(7)	21.8330(8)
α/°	90	90	90
β/°	101.603(2)	91.108(2)	99.004(2)
γ/°	90	90	90
V/Å^3	7039.0(6)	2118.94(11)	1923.98(14)
Z	8	4	4
$\rho_{calc.}$/Mg m^{-3}	1.163	1.305	1.354
Crystal size/mm^3	0.518 x 0.24 x 0.16	0.22 x 0.13 x 0.124	0.24 x 0.231 x 0.09
Temp/K	170.0	169.99	169.84

Radiation	Mo-K_α (λ=0.71073 Å)	Cu-K_α (λ=1.54178 Å)	Cu-K_α (λ=1.54178 Å)
μ/mm^{-1}	0.074	0.713	0.828
Total reflections	115455	40528	41998
Total unique reflections	7826	4028	3925
No. of variables	423	284	264
θ Range/^{o}	2.95 to 27.21	3.873 to 70.129	4.1 to 74.852
Largest difference peak/hole/e Å^{-3}	0.20 and -0.20	0.24 and -0.27	0.33 and -0.43
S (GoF) on F^2	1.089	1.046	1.052
$R1^a$ (I>2σ(I))	0.0491	0.0453	0.0578
w$R2^b$ (all data)	0.1062	0.1289	0.1652

^{a}) $R1 = \sum||F_o|-|F_c||/\sum|F_o|$. ^{b}) w$R2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0559 \cdot P)^2 + (0.0350 \cdot P]$ (**1**), $1/[\sigma^2(F_o^2) + (0.497 \cdot P)^2 + (1.8527 \cdot P)]$ (**3**), where $P = (\max(F_o^2, 0) + 2 \cdot F_c^2)/3$.