Supporting Information

for

Contrasting Reactivity of (Boryl)(Aryl)Lithium-Amide with Electrophiles: *N*- *vs* *p*-Aryl-*C*-Nucleophilic Substitution

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Experimental section:

All experiments were carried out under an argon atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox. *n*-Hexane, diethyl ether, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system. Mes_2BF was prepared according to a literature procedure.[S1] Benzene-d6 was dried and distilled over potassium under argon. NMR spectra were recorded with Bruker NanoBay 300 MHz NMR machine. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^{1}H) or the deuterated solvent itself. ($^{13}C\{^{1}H\}$). $^{7}Li\{^{1}H\}$, ^{29}Si, $^{29}Si\{^{1}H\}$, ^{31}P, and $^{31}P\{^{1}H\}$ NMR spectra were referenced to LiCl, $SiMe_4$, and H_3PO_4, respectively. Melting points were determined in closed NMR tubes under argon atmosphere and are uncorrected. Elemental analyses of compounds **4** and **7** were performed on a Leco CHN-900 analyzer. Elemental analyses of compounds **3**, **5**, and **6** were performed on a Perkin Elmer Analyser 240.

Synthesis of 3: About 30 mL of diethylether was added to a Schlenk flask containing 3 mL (15.90 mmol) of dry and distilled 2,6-diisopropylphenylamine, $DipNH_2$, and cooled at −78 °C. Then, *n*-BuLi (1.6 M solution in *n*-hexane, 11 mL, 17.6 mmol) was added to it and the reaction mixture was allowed to warm slowly to room temperature and stirred for another 4 hrs. After that, the reaction mixture was cooled again to −78 °C and slowly a diethylether solution of dimesitylboronfluoride, Mes_2BF, **2** (4.26 g, 15.90 mmol in 10 mL diethylether) was added. Then, the reaction mixture was slowly warmed to room temperature and stirred for another 12 hrs. After that all the volatilities including the solvent were removed under high vacuum affording a residue which was extracted with 30 mL of *n*-hexane. After concentrating to about 15 mL, it was kept for crystallization at room temperature. Colorless crystals of **3** were obtained within 6 hrs. After collection of the first crop of crystals the mother liquor was concentrated to 5 mL and kept at 0 °C for one day, giving a second crop of crystals. Total yield: 5 g (74 %). **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 0.86 (br, 6H, $(CH_3)_2CH$), 0.95 (d, $^{3}J_{(H, H)}$ = 6.35 Hz., $(CH_3)_2CH$), 2.08 (s, 3H, CH_3–Mes), 2.13 (s, 6H, CH_3–Mes), 2.17 (s, 6H, CH_3–Mes), 2.78 (S, 3H, CH_3–Mes), 3.37 (sep, $^{3}J_{(H, H)}$ = 6.95 Hz.), 6.11 (s, 1H, N-*H*), 6.64 (s, 2H, Ar–*H*), 6.73 (s, 1H, Ar–*H*), 6.96–7.09 (m, 4H, Ar–*H*) ppm. **^{11}B NMR** (96.5 MHz, C_6D_6, 298K): δ = 21.15 (s, br) ppm. **$^{13}C\{^{1}H\}$ NMR** (75.43 MHz, C_6D_6, 298K): δ = 21.45 (2C, CH_3), 21.53 (1C, CH_3), 22.02 (2C, CH_3), 22.78 (2C, CH_3), 25.80 (2C, CH_3). 29.23 (2C, $(CH_3)_2CH$), 124.18 (1C, Ar–CH), 126.33 (1C, Ar–CH), 128.68 (1C, Ar–CH), 129.10 (1C, Ar–CH), 129.31 (1C, Ar–CH), 129.50 (1C, Ar–CH), 129.67 (1C, Ar–CH), 138.02 (1C, C_{qua}), 138.14 (1C, C_{qua}), 138.15 (1C, C_{qua}), 140.16 (1C, C_{qua}), 141.48 (1C, C_{qua}), 141.95 (1C, C_{qua}), 143.12 (1C, C_{qua}) ppm. Elemental Analysis: Calcd. for $C_{30}H_{40}BN$ (425.47): C, 84.69; H, 9.48; N, 3.29. Found: C, 84.12; H, 9.05; N, 3.12.

Synthesis of 4: 15 mL THF was added to a 100 mL Schlenk flask containing 0.382 g (0.898 mmol) of **3**. Then 0.57 mL (0.9 mmol) of *n*-BuLi solution was added to it at −78 °C. Subsequently, the reaction mixture was allowed to slowly come to room temperature and then allowed to stir for another 2 hrs at this temperature. After that the reaction mixture was filtered and all the volatilities including solvents were removed under vacuum to get compound **4** whose molecular structure could be confirmed by NMR measurements. Suitable single crystals for X-ray diffraction study were obtained from a saturated

THF solution of **4** with slow diffusion of hexane at −35 °C over 15 days. **M.P.**: > 190 °C. **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 1.12−1.20 (m, 20H, 12H from $(CH_3)_2CH$ of Dip group, 8H from CH_2 THF), 2.17 (, 3H, CH_3−Mes), 2.20 (, 3H, CH_3−Mes), 2.40 (s, 3H, CH_3−Mes), 2.42 (s, 3H, CH_3−Mes), 2.57 (br, 6H, CH_3−Mes), 3.08 (t, $^{3}J_{(H, H)}$ = 6.50 Hz, 8H, O−CH_2 of THF), 3.85 (sep., $^{3}J_{(H, H)}$ = 6.60 Hz, $(CH_3)_2CH$), 6.74 (br, 3H, Ar−*H*), 6.82 (s, 1H, Ar−*H*), 6.95−7.07 (m, 1H, Ar−*H*), 7.20 (s, 1H, Ar−*H*), 7.22 (s, 1H, Ar−*H*) ppm. **^{7}Li{^{1}H} NMR** (116.59 MHz, C_6D_6, 298K): δ = −0.40 ppm. **^{11}B NMR** (96.5 MHz, C_6D_6, 298K): δ = 36.83 (s, br) ppm. **^{13}C{^{1}H} NMR** (75.43 MHz, C_6D_6, 298K): δ = 21.5 (1C, CH_3), 21.5(1C, CH_3), 21.6 (1C, CH_3), 22.0 (1C, CH_3), 22.8 (1C, CH_3), 23.4 (1C, CH_3), 24.3 (1C, CH_3), 24.7 (1C, CH_3), 22.6 (4C, CH_2 from THF), 25.8 (1C, CH_3), 26.3 (1C, CH_3), 28.0 (1C, $CH(CH_3)_2$), 29.2 (1C, $CH(CH_3)_2$), 68.5 (4C, O−CH_2, of THF), 118.3 (1C, Ar−*C*H), 123.8 (1C, Ar−*C*H), 124.2 (1C, Ar−*C*H), 126.3 (1C, Ar−*C*H), 128.2 (1C, Ar−*C*H), 129.0 (1C, Ar−*C*H), 129.1 (1C, Ar−*C*H), 135.1(2C, Ar−C_{qua}), 135.3 (2C, Ar−C_{qua}), 138.0 (1C, Ar−C_{qua}), 138.2 (2C, Ar−C_{qua}), 141.5 (2C, Ar−C_{qua}), 143.1 (1C, Ar−C_{qua}), 154.55 (1C, Ar−C_{qua}) ppm. Elemental Analysis: Calcd. for $C_{38}H_{55}BLiNO_2$ (575.61): C, 79.29; H, 9.63; N, 2.43. Found: C, 79.36; H, 9.15; N, 2.75.

Synthesis of 5: About 20 mL of THF was added to a Schlenk flask containing 0.690 g (1.60 mmol) of **3.** *n*-BuLi (1.6 M solution in *n*-hexane, 1.00 mL, 1.60 mmol) was added to this mixture at −78 °C. After that the reaction mixture was allowed to warm to room temperature slowly and stirred for another 2 hrs. Then, the reaction mixture was cooled to −78 °C. To this $SiCl_4$ (0.25 mL, 1.36 mmol) was added and slowly the reaction mixture was warmed to room temperature and stirred for another 12 hrs. Subsequently all the volatilities were removed under vacuum and the resulting residue was extracted with 40 mL of warm *n*-hexane. This was concentrated to about 10 mL and kept at 0 °C for one day to get the crystalline compound **5**. Yield: 0.590 g (65 %). **M.P.**: 132 °C. **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 0.86-0.97 (m, 12H, $(CH_3)_2CH$), 1.2 (s, 3H, CH_3−Mes), 2.05−2.18 (m, 12H, CH_3−Mes), 2.73 (s, 3H, CH_3−Mes), 3.3 (s, br, 2H, $(CH_3)_2CH$), 6.12 (s, 1H, N−*H*), 6.58−6.70 (m, 3H, Ar−*H*), 6.95−7.05 (2H, Ar−*H*), 7.74 (s, 1H, Ar−*H*) ppm. **^{11}B NMR** (96.5 MHz, C_6D_6, 298K): δ = 23.58 ppm. **^{13}C{^{1}H} NMR** (75.43 MHz, C_6D_6, 298K): δ = 14.68 (1C, CH_3), 21.40 (1C, CH_3), 21.51(1C, CH_3), 21.67(1C, CH_3), 22.01(1C, CH_3), 22.63 (1C, CH_3), 22.78 (1C, CH_3), 23.39(1C, CH_3), 23.40(1C, CH_3), 23.84 (1C, CH_3), 29.23(1c, $(CH_3)_2CH$), 29.44 (1c, $(CH_3)_2CH$), 126.33 (1C, Ar−*C*H), 128.68 (1C, Ar−*C*H), 129.10 (1C, Ar−*C*H), 129.28 (1C, Ar−*C*H), 129.63 (1C, Ar−*C*H), 129.78 (1C, Ar−*C*H), 138.01 (1C, Ar−C_{qua}), 138.13 (1C, Ar−C_{qua}), 138.54 (1C, Ar−C_{qua}), 138.61 (1C, Ar−C_{qua}), 140.07 (2C, Ar−C_{qua}), 141.24 (1C, Ar−C_{qua}), 141.47 (1C, Ar−C_{qua}), 142.05 (2C, Ar−C_{qua}), 143.17 (1C, Ar−C_{qua}), 143.83 (1C, Ar−C_{qua}), ppm. **^{29}Si{H} NMR** (59.59 MHz, C_6D_6, 295K): δ = −0.25 ppm. Elemental Analysis: Calcd. for $C_{30}H_{39}BCl_3NSi$ (558.89): C, 64.47; H, 7.03; N, 2.51. Found: C, 64.35; H, 6.95; N, 2.74.

Synthesis of 6: About 20 mL of THF was added to a Schlenk flask containing 0.500 g (1.17 mmol) of **3.** *n*-BuLi (1.6 M solution in *n*-hexane, 0.75 mL, 1.20 mmol) was added to it at −78 °C. After that the reaction mixture was allowed to warm to room temperature slowly and stirred for another 2 hrs. Then, the reaction mixture was cooled to −78 °C. To this, $MeSiHCl_2$ (0.12 mL, 1.20 mmol) was added and the

reaction mixture was slowly warmed to room temperature and stirred for another 12 hrs. Subsequently all the volatilities were removed under vacuum and the resulting residue was extracted with 50 mL of warm *n*-hexane. This was concentrated to about 15 mL and kept at 0 °C for one day to get crystals of **6**. Yield: 0.472 g (85 %). **M.P.**: 150 °C. **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 0.21 (d, $^{3}J_{(H,\ H)}$=2.66Hz. 3H, Si–CH_3), 0.98 –1.05 (m, 6H, (CH_3)$_2$CH), 1.28 (s, 3H (CH_3)$_2$CH), 1.30 (s, 3H (CH_3)$_2$CH), 1.98 (s, 3H, CH_3–Mes), 2.17 (s, 3H, CH_3–Mes), 2.26 (s, 6H, CH_3–Mes), 2.44 (s, 3H, CH_3–Mes), 2.56 (s, 3H, CH_3–Mes), 3.33 (sep, $^{3}J_{(H,\ H)}$= 6.43 Hz., 1H, (CH$_3$)$_2$C*H*), 3.54 (br, 1H, (CH$_3$)$_2$C*H*), 5.71 (q, $^{3}J_{(H,\ H)}$=2.66 Hz. 1H, Si–*H*), 6.52 (s, 2H, Ar–*H*), 6.75 (s, 1H, Ar–*H*), 6.78 (s, 1H, Ar–*H*), 7.00– 7.02 (m, 3H, Ar–*H*) ppm. **^{11}B NMR** (96.5 MHz, C_6D_6, 298K): δ = 51.17 ppm. **^{13}C{^{1}H} NMR** (75.43 MHz, C_6D_6, 298K): δ = 3.30 (1C, Si–*C*H$_3$), 21.05 (2C, *C*H$_3$), 21.45 (2C, *C*H$_3$), 23.40 (1C, *C*H$_3$), 23.85 (1C, *C*H$_3$), 24.54 (1C, *C*H$_3$), 26.26 (1C, *C*H$_3$), 26.86 (1C, *C*H$_3$), 27.17 (1C, *C*H$_3$), 29.83 (1c, (CH$_3$)$_2$*C*H), 30.06 (1C, (CH$_3$)$_2$*C*H), 125.16 (1C, Ar–*C*H), 125.25 (1C, Ar–*C*H), 127.05 (1C, Ar–*C*H), 128.69 (1C, Ar–*C*H), 129.07 (1C, Ar–*C*H), 129.32 (1C, Ar–*C*H), 129.60 (1C, Ar–*C*H), 138.25 (2C, C_{qua}), 138.42 (1C, C_{qua}), 141.14 (2c, C_{qua}), 141.50 (2C, C_{qua}), 142.04 (1C, C_{qua}), 142.22 (2C, C_{qua}), 145.21 (1C, C_{qua}), 145.37 (1C, C_{qua}). **^{29}Si{H} NMR** (59.59 MHz, C_6D_6, 295K): δ = –4.56 ppm. **^{29}Si NMR** (59.59 MHz, C_6D_6, 295K): δ = –4.56 (d, $^{1}J_{(H,\ Si)}$ = 270.50 Hz) ppm. Elemental Analysis: Calcd. for $C_{31}H_{43}BClNSi$ (504.04): C, 73.87; H, 8.60; N, 2.78. Found: C, 73.54; H, 8.34; N, 2.66.

Synthesis of 7: About 20 mL of THF was added to a Schlenk flask containing 0.586 g (1.37 mmol) of **3**. Then, *n*-BuLi (1.6 M solution in *n*-hexane, 0.87 mL, 1.39 mmol) was added to it at −78 °C. After that the reaction mixture was allowed to warm to room temperature slowly and stirred for another 2 hrs. Then, the reaction mixture was cooled again to −78 °C. Subsequently Ph_2PCl (0.25 mL, 1.36 mmol) was added after which the reaction mixture was warmed slowly to room temperature and stirred for another 12 hrs. Then, all the volatilities were removed under high vacuum and the resulting residue was extracted with 50 mL of *n*-hexane. This was concentrated to about 10 mL and kept at 0 °C for one day to obtain **7**. Yield: 0.580 g (70 %). **M.P.**: 135 °C). **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 0.73 (s, br, 6H, (CH_3)$_2$CH), 0 88 (d, ^{3}J=6.92 Hz., 6H, (CH_3)$_2$CH), 2.08 (s, 3H, CH_3-Mes), 2.15 (s, 6H, CH_3–Mes), 2.16 (s, 6H, CH_3–Mes), 2.75(s, 3H, CH_3–Mes), 3.32 (s, br, 2H, (CH$_3$)$_2$C*H*), 6.14 (s, 1H, N–*H*), 6.66 (s, 3H, Ar–*H*), 7.06 – 7.08 (m, 7H, Ar–*H*), 7.32 (d, ^{3}J=7.83 Hz., 2H, Ar–*H*), 7.41– 7.47 (m, 4H, Ar–*H*) ppm. ^{11}B NMR (96.5 MHz, C_6D_6, 298K): δ = 22.48 ppm. **^{13}C{^{1}H} NMR** (75.43 MHz, C_6D_6, 298K): δ = 21.67 (2C*,* *C*H$_{3,}$), 21.72 (2C*,* *C*H$_{3,}$), 22.00 (2C*,* *C*H$_3$), 23.00 (2C*,* *C*H$_{3,}$), 29.59 (2C, (CH$_3$)$_2$*C*H), 129.22 (4C, Ar–*C*H), 129.31 (4C, Ar–*C*H), 134.45 (4C, Ar–*C*H), 134.75, (4C, Ar–*C*H), 138.43(2C, Ar–C_{qua}), 138.46 (2C, Ar–C_{qua}), 139.20 (2C, Ar–C_{qua}), 139.26 (2C, Ar–C_{qua}), 139.37 (2C, Ar–C_{qua}), 141.65 (2C, Ar–C_{qua}), 143.57 (1C, Ar–C_{qua}), 143.65 (1C, Ar–C_{qua}) ppm. **^{31}P NMR** (121.5 MHz, C_6D_6, 298K): δ = –5.61 ppm. Elemental Analysis: Calcd. for $C_{42}H_{49}BNP$ (609.64): C, 82.75; H, 8.10; N, 2.30. Found: C, 82.85; H, 8.04; N, 2.21.

NMR Spectra

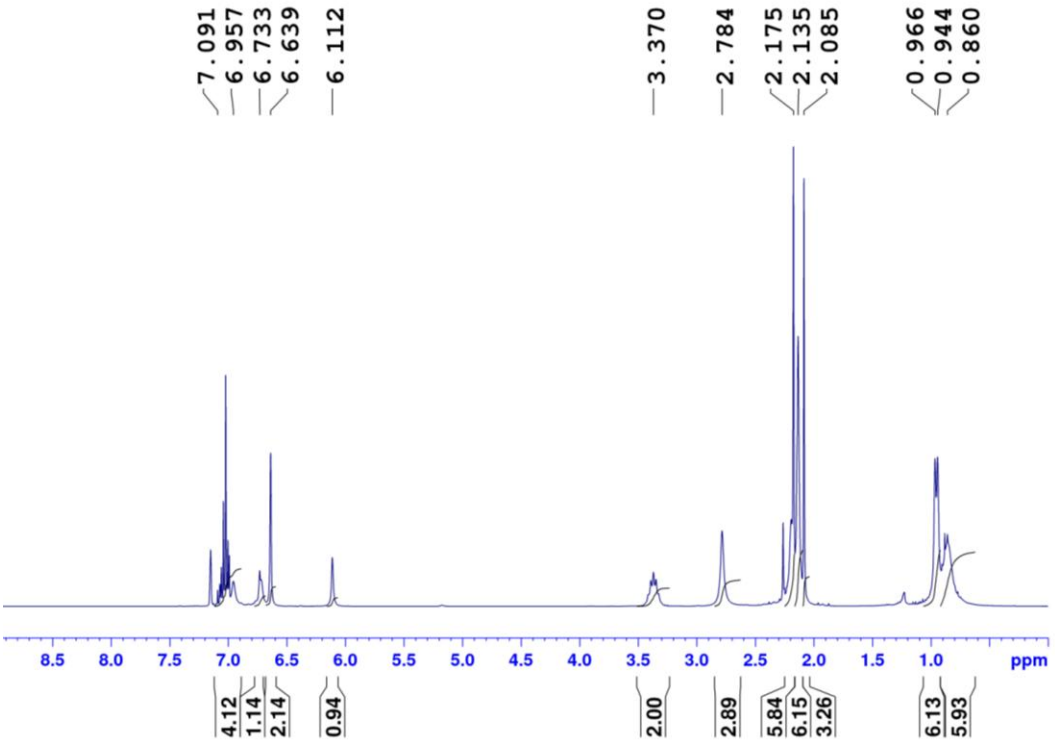

Figure S1 ^{1}H NMR spectrum of **3** in [D6]-benzene at RT.

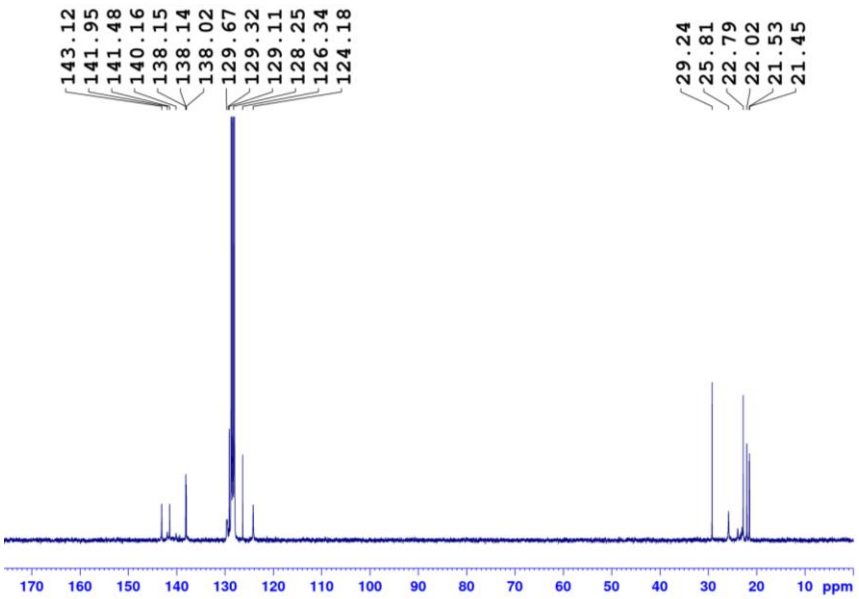

Figure S2 ^{13}C{^{1}H} NMR spectrum of **3** in [D6]-benzene at RT.

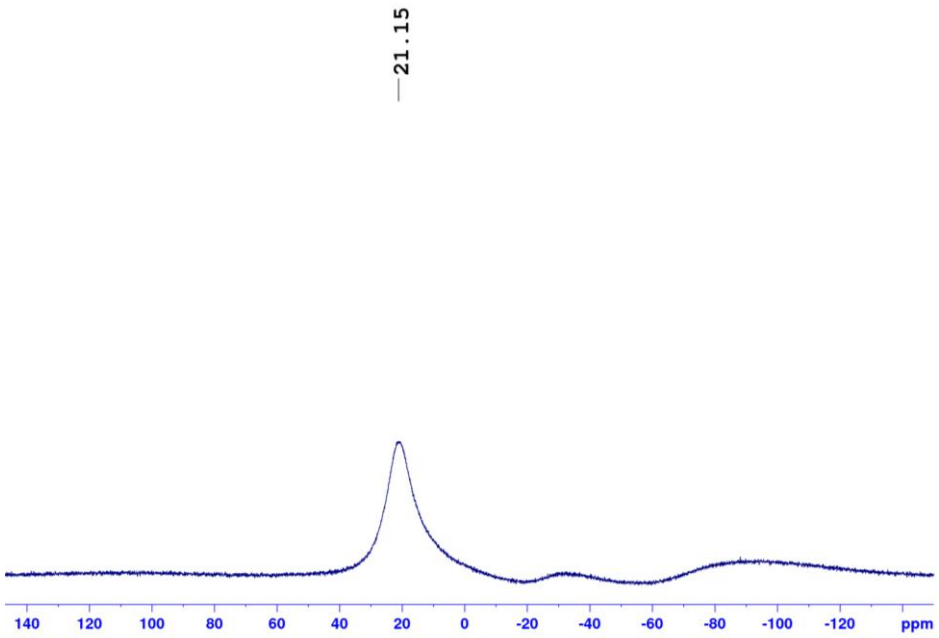

Figure S3 ^{11}B NMR spectrum of **3** in [D-6]-benzene at RT.

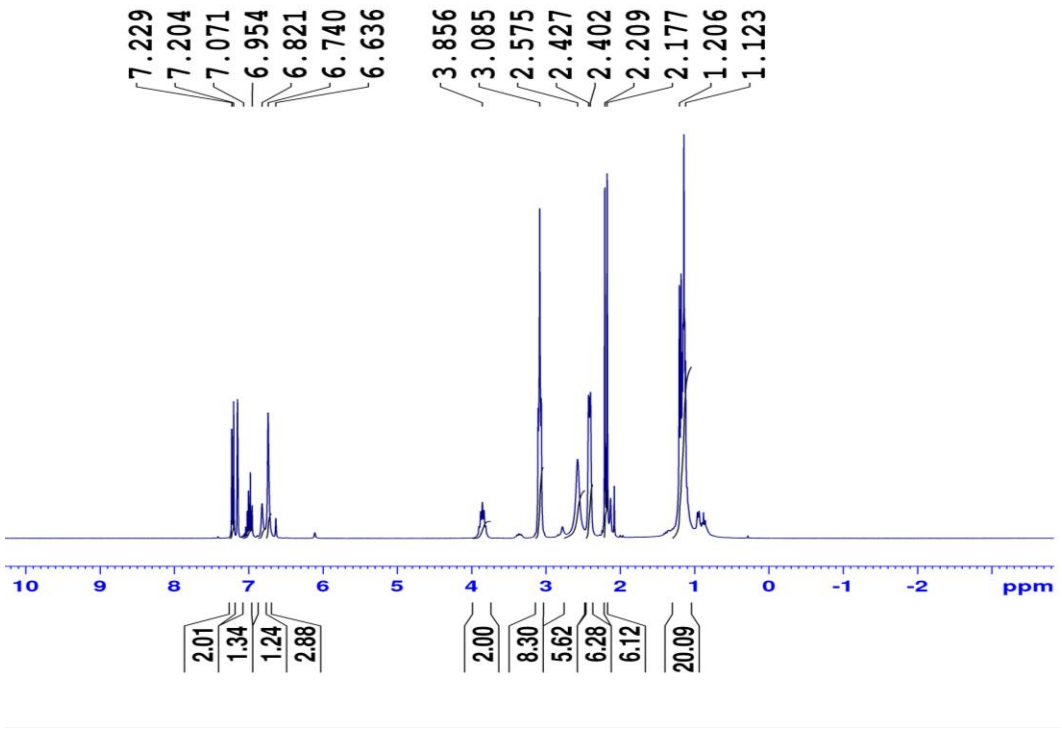

Figure S4 ^{1}H NMR spectrum of **4** in [D6]-benzene at RT.

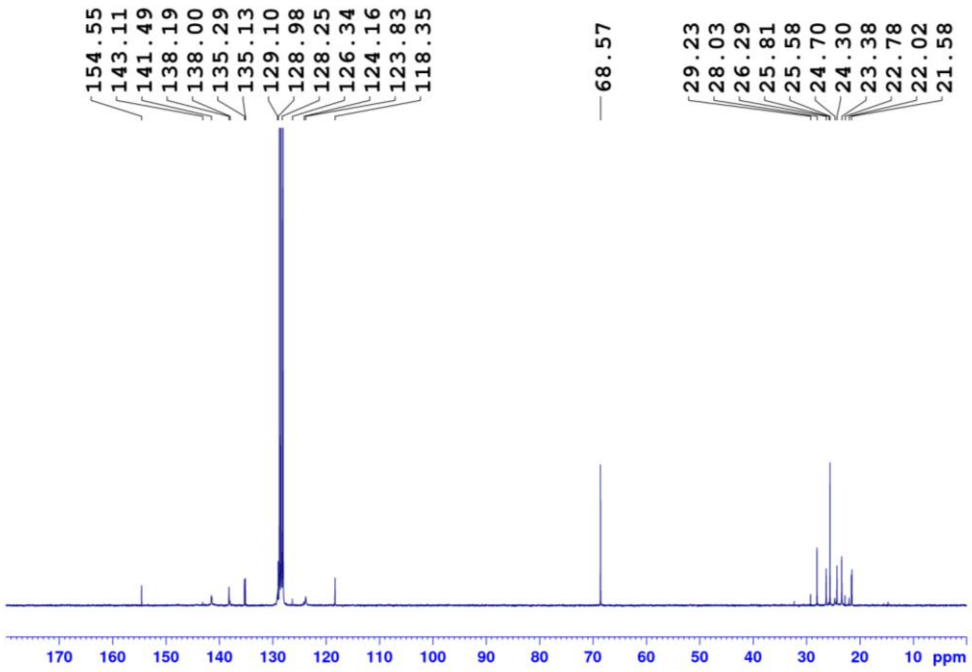

Figure S5 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in [D6]-benzene at RT.

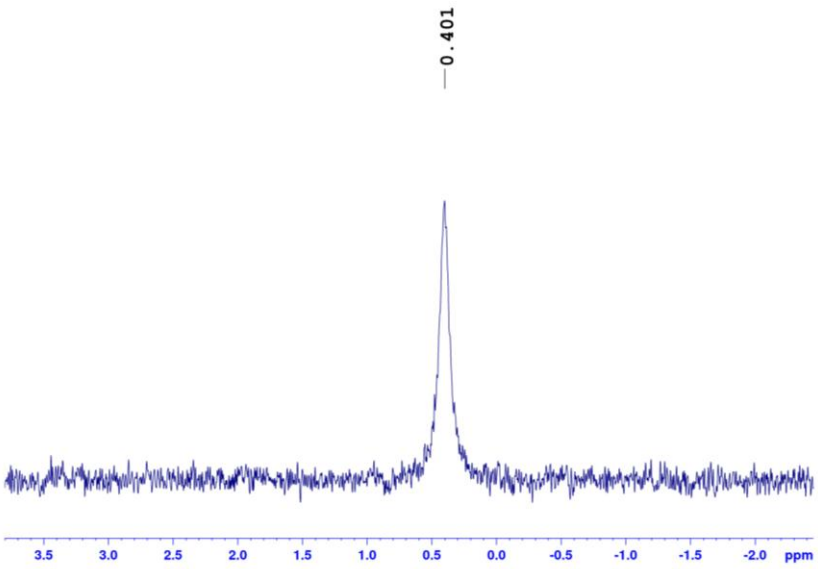

Figure S6 $^{7}Li\{^{1}H\}$ NMR spectrum of **4** in [D6]-benzene at RT.

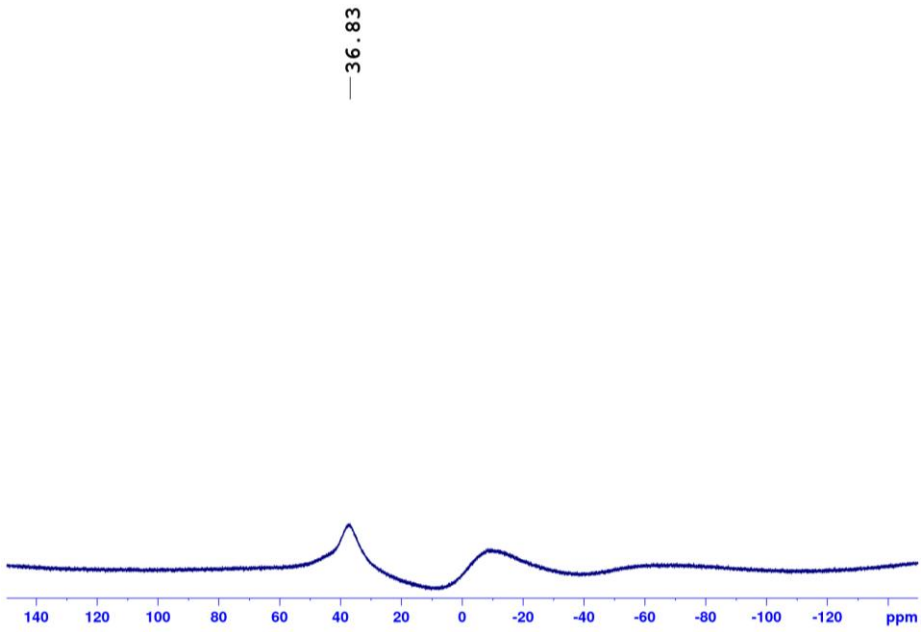

Figure S7 ^{11}B NMR spectrum of **4** in [D6]-benzene at RT.

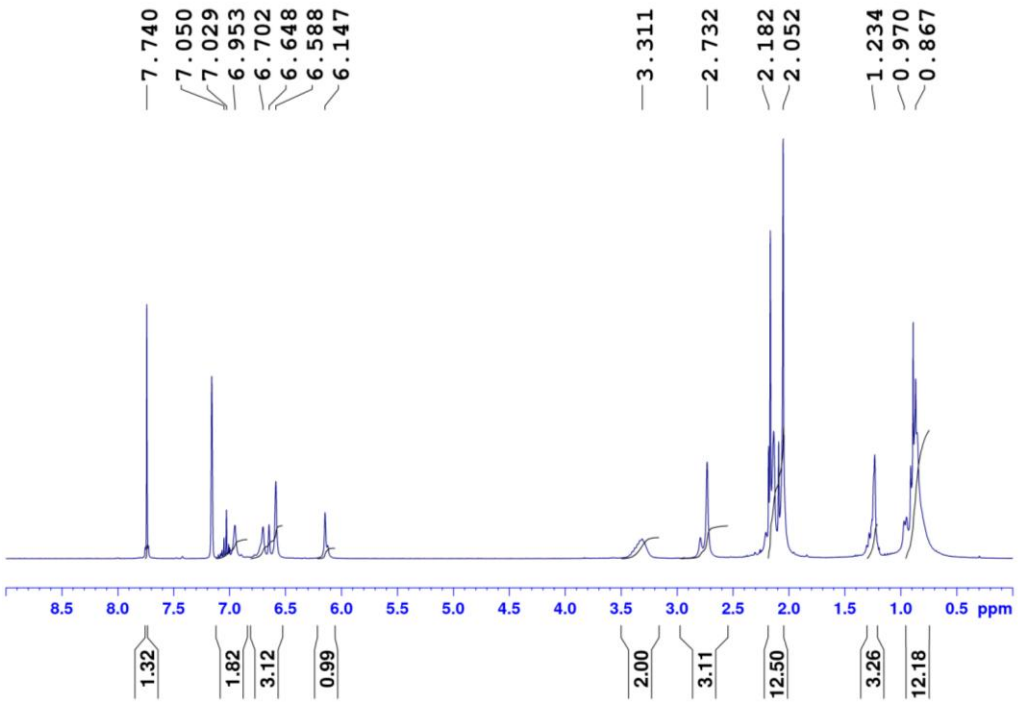

Figure S8 ^{1}H NMR spectrum of **5** in [D6]-benzene at RT.

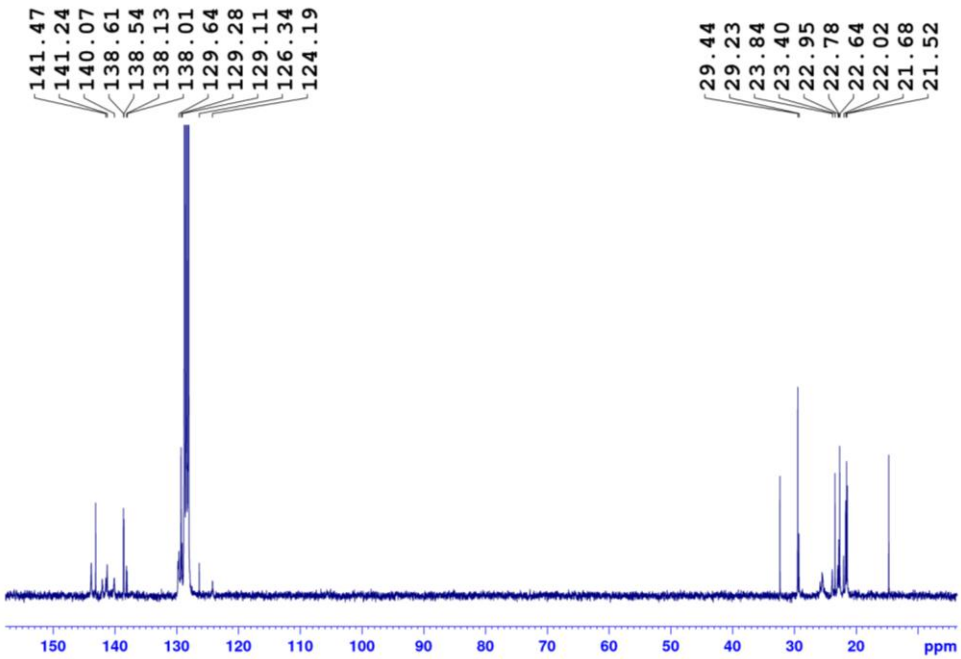

Figure S9 $^{13}C\{^{1}H\}$ NMR spectrum of **5** in [D6]-benzene at RT.

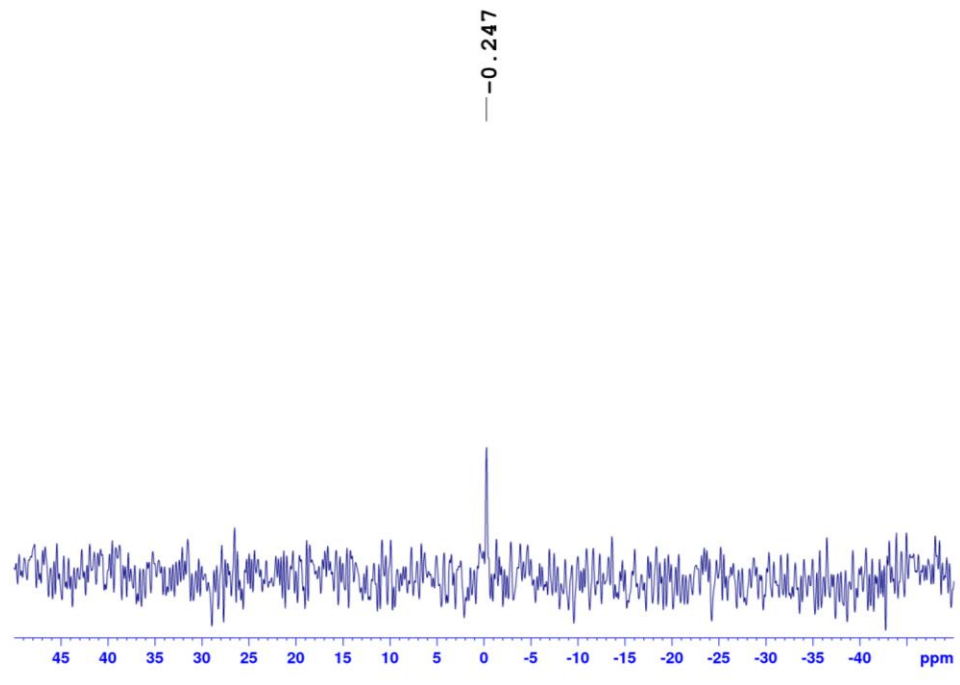

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Figure S10 $^{29}Si\{^{1}H\}$ NMR spectrum of **5** in [D6]-benzene at RT.

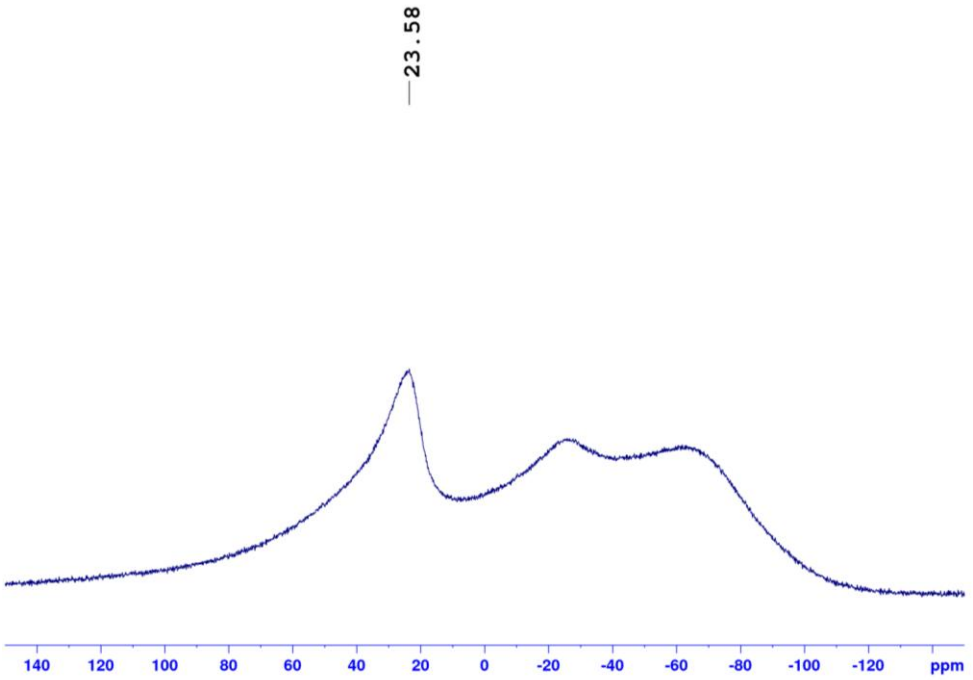


Figure S11 ^{11}B NMR spectrum of **5** in [D6]-benzene at RT.

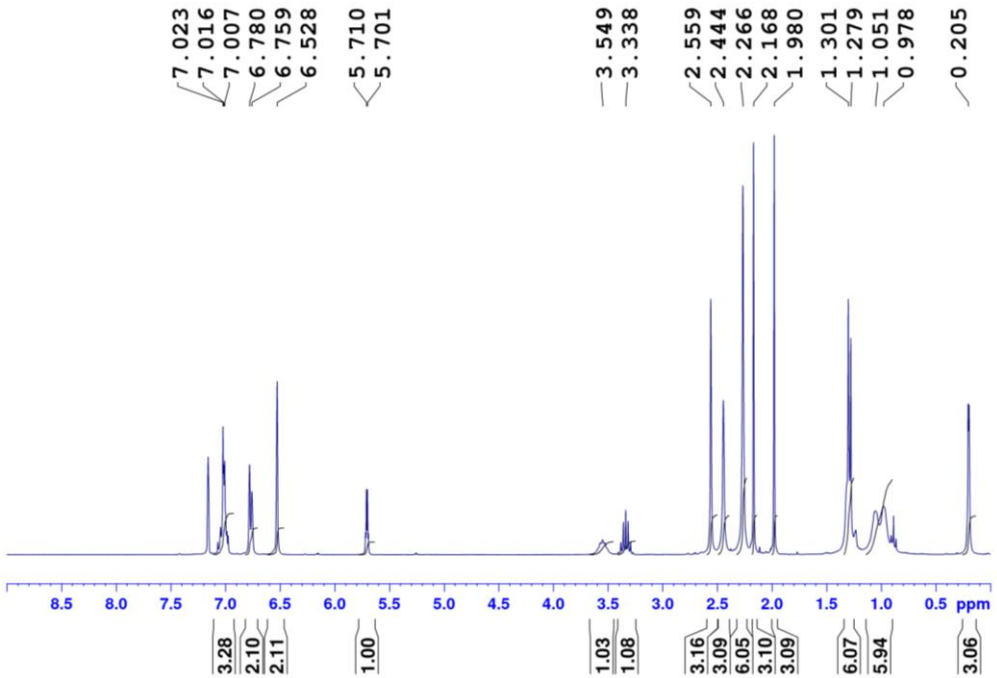


Figure S12 ^{1}H NMR spectrum of **6** in [D6]-benzene at RT.

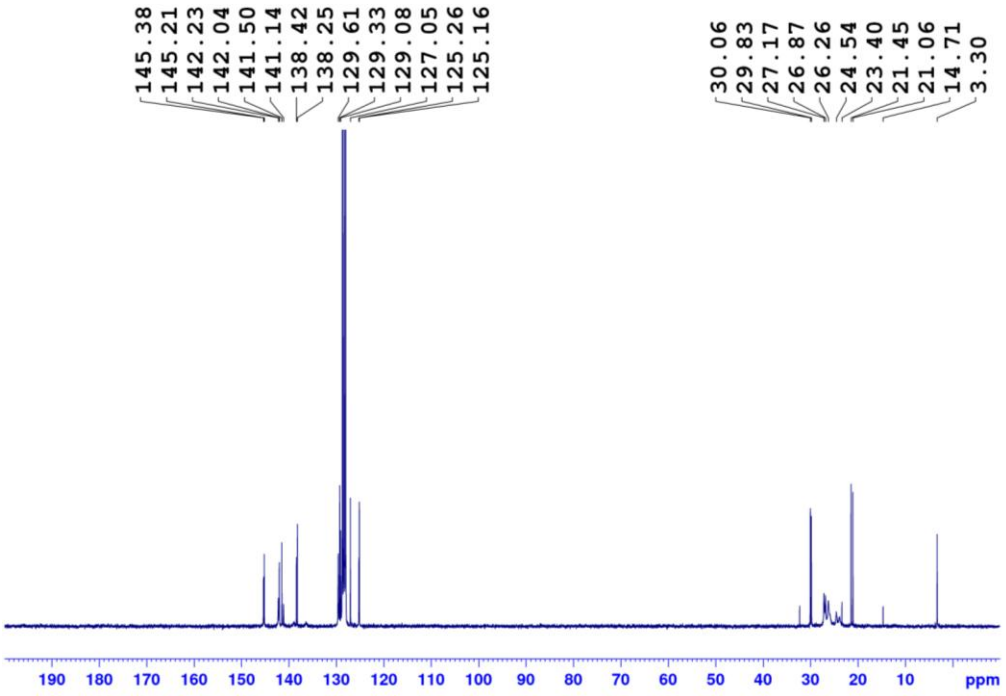


Figure S13 $^{13}C\{^{1}H\}$ NMR spectrum of **6** in [D6]-benzene at RT.

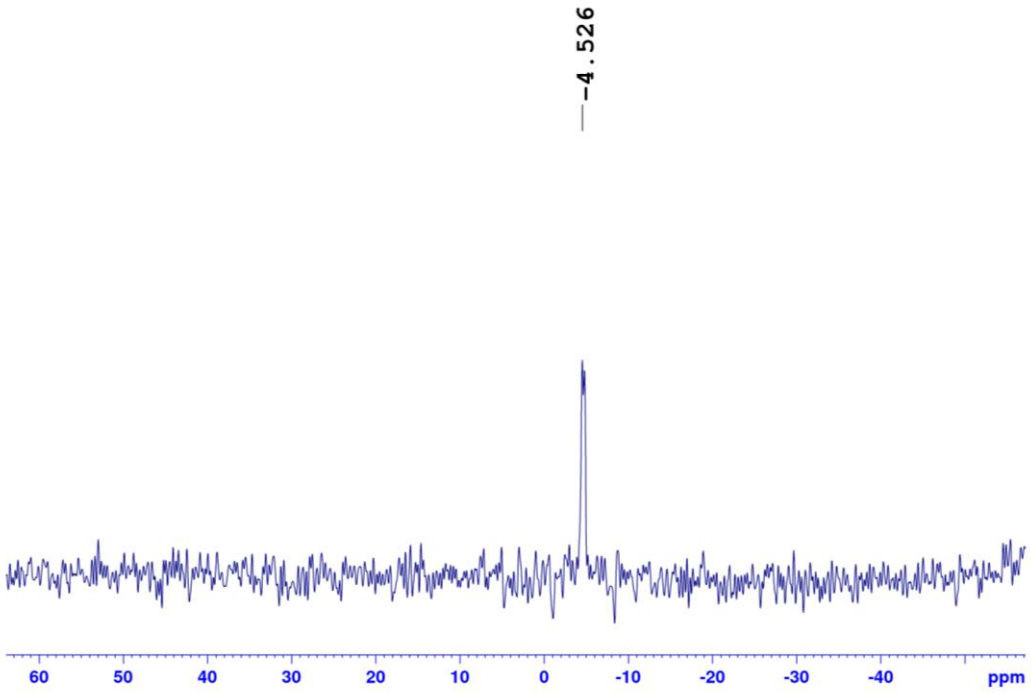


Figure S14 $^{29}Si\{^{1}H\}$ NMR spectrum of **6** in [D6]-benzene at RT.

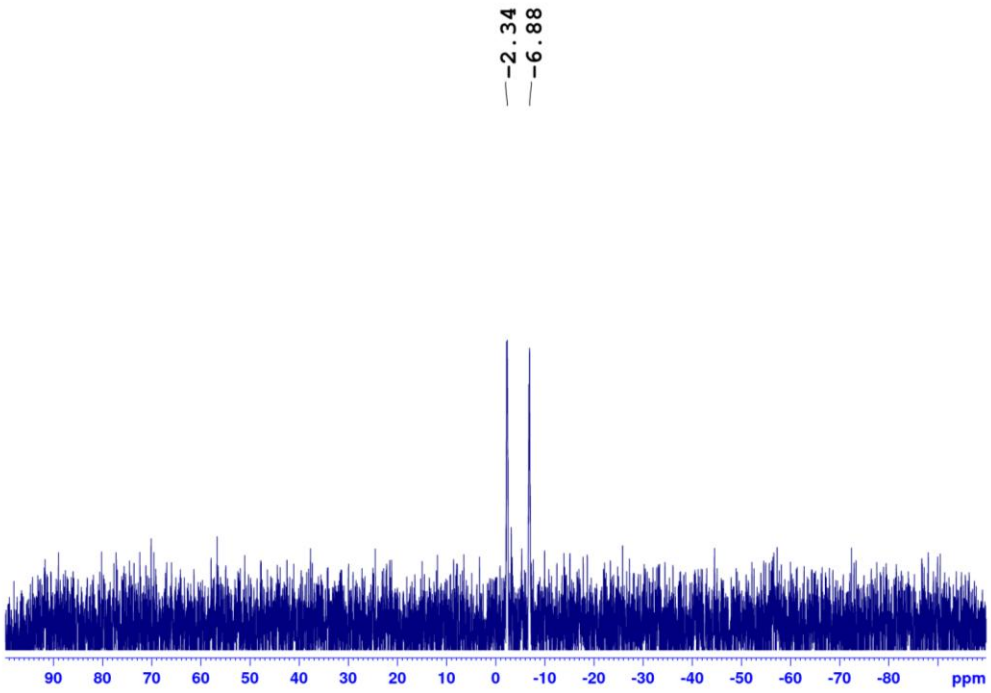


Figure S15 ^{29}Si NMR spectrum of **6** in [D6]-benzene at RT.

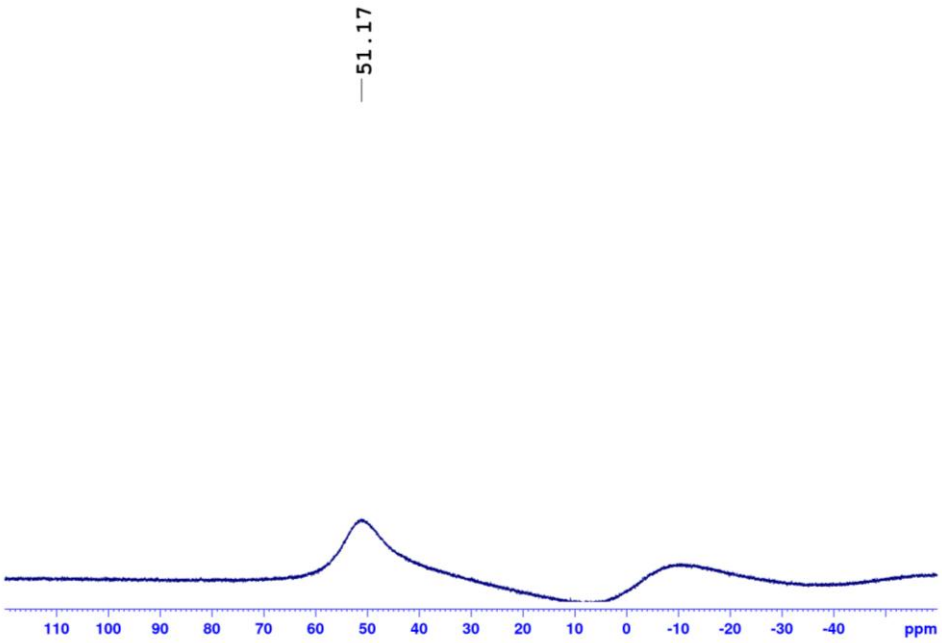


Figure S16 ^{11}B NMR spectrum of **6** in [D6]-benzene at RT.

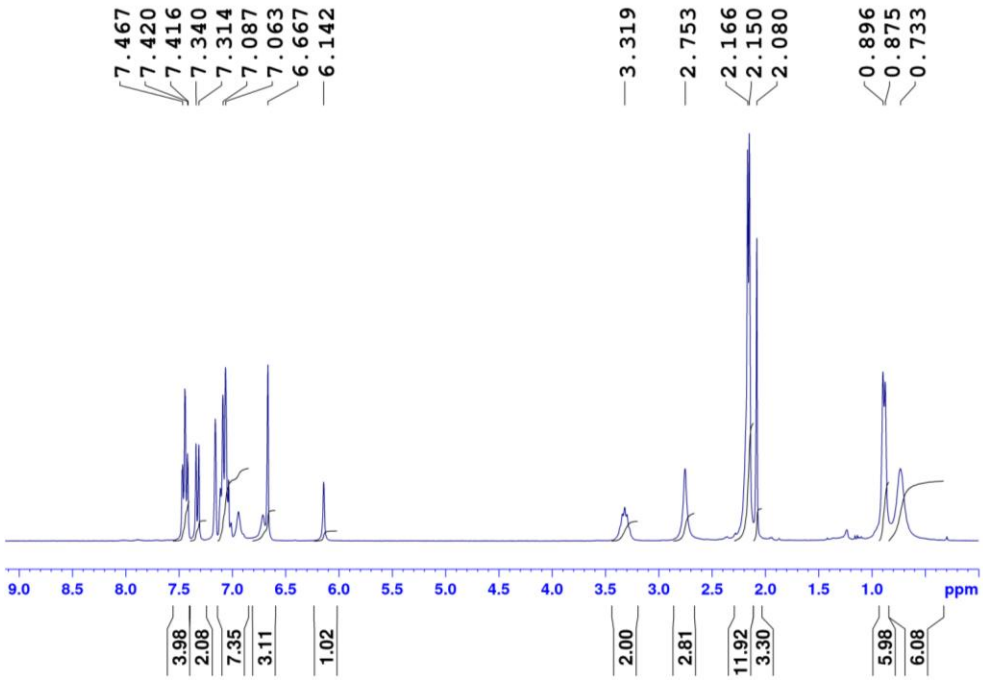


Figure S17 ^{1}H NMR spectrum of **7** in [D6]-benzene at RT.

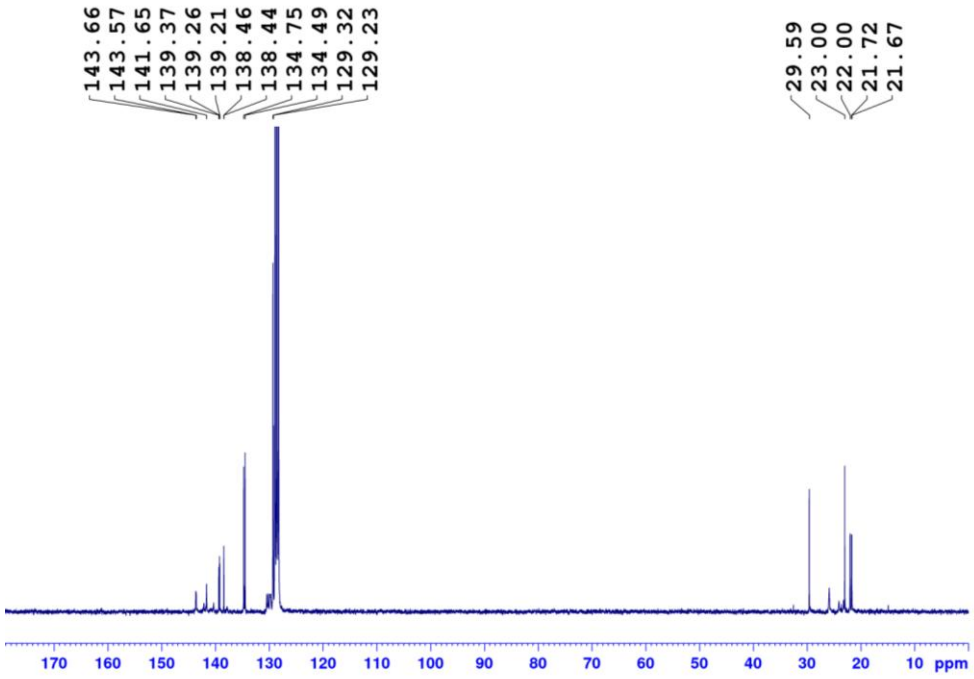


Figure S18 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in [D6]-benzene at RT.

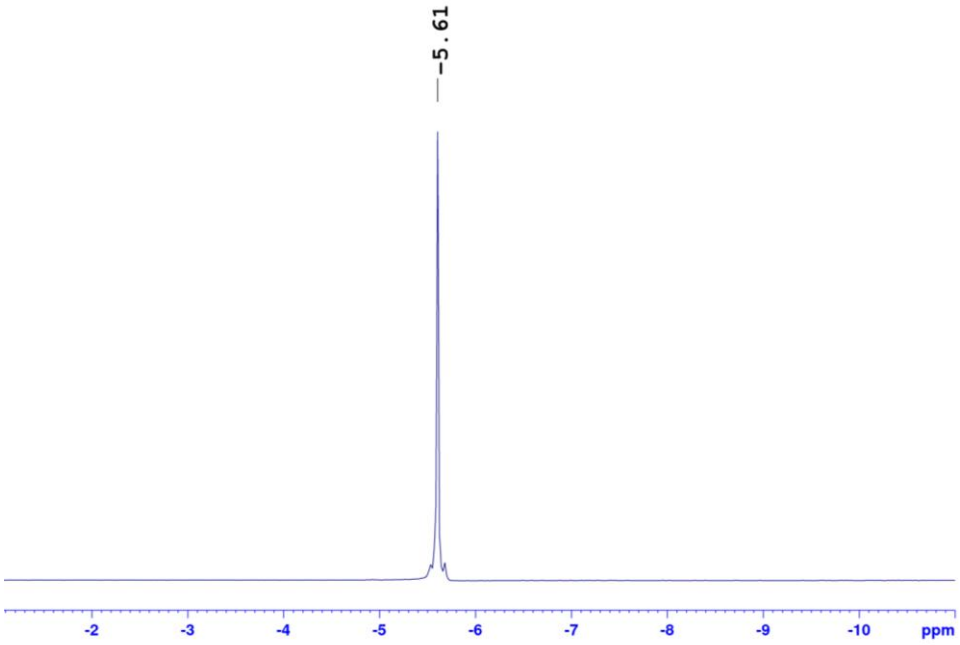


Figure S19 $^{31}P\{^{1}H\}$ NMR spectrum of **7** in [D6]-benzene at RT.

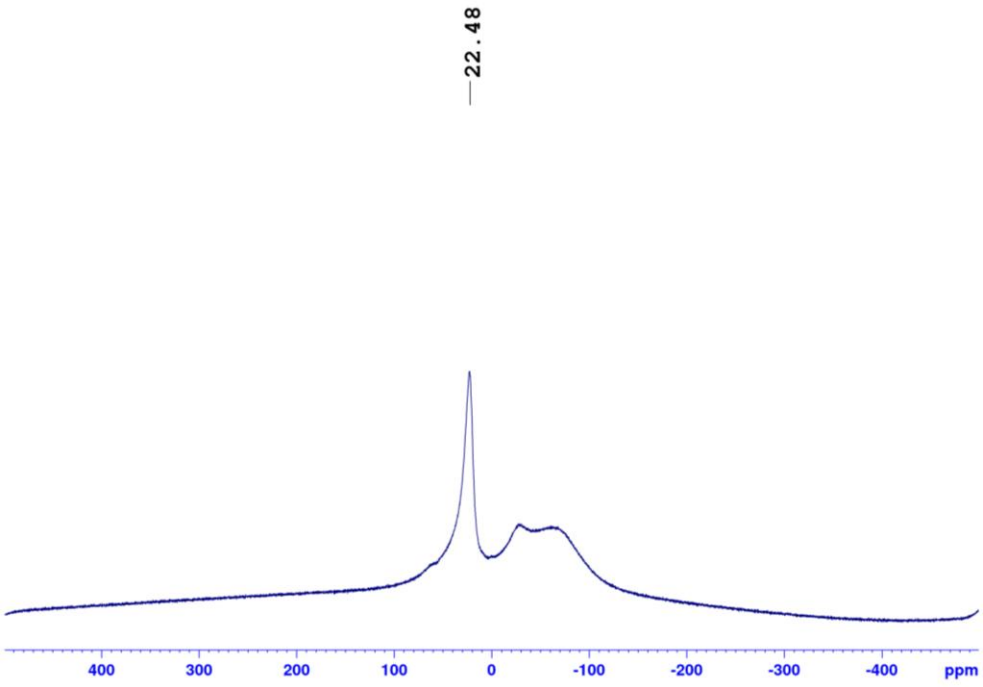


Figure S20 ^{11}B NMR spectrum of **7** in [D6]-benzene at RT.

Crystallographic Details

Diffraction data of **3**, **5**, **6**, and **7** were collected at low temperature (100.15 K) using a STOE-IPDS 2T diffractometer with graphite-monochromated molybdenum *Kα* radiation, λ = 0.71073 Å. Diffraction data of **4** was collected at low temperature (120 K) using a Rigaku XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite-monochromated molybdenum *Kα* radiation, *λ* = 0.71073 Å. Data integration and reduction were processed with CrysAlisPro software.[S2] An empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK integrated with CrysAlisPro. The structures were solved by direct methods using SHELXT[S3] program and refined by full matrix least-squares method based on F^2 by using SHELXL[S4] program through Olex2[S5] interface. All non-hydrogen-atoms were refined with anisotropic displacement parameters. Hydrogens atoms were fixed in their ideal geometries, and their contributions included in the refinement. The crystal and refinement data are summarized in Table S1. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. These data can be obtained free of charge on quoting the depository numbers CCDC 1542299 and 1542300 by FAX (+44-1223-336-033), email (deposit@ccdc.cam.ac.uk) or their web interface (at http://www.ccdc.cam.ac.uk).

Table S1 Crystal data and structure refinement for **3**, **4**, **5**, **6**, and **7**.

Compound	**3**	**4**	**5**	**6**	**7**
Chemical formula	$C_{30}H_{40}B_1N_1$	$C_{38}H_{55}BLiNO_2$	$C_{33}H_{46}BCl_3NSi$	$C_{31}H_{43}BClNSi$	$C_{42}H_{49}BNP$
CCDC No.	1847135	1847132	1847134	1847133	1847136
M_r	425.44	576.38	601.96	504.01	609.60
Crystal system, space group	Monoclinic, *P*21/*c*	Monoclinic, *P*21/*c*	Triclinic, *P*-1	Orthorhombic, *Pca*21	Triclinic, *P*-1
Temperature (K)	100(2)	119.97(10)	100.15	100.15	100(2)
a, *b*, *c* (Å)	a = 8.626(8), b = 21.45(2), c = 13.699(14)	a = 27.854(2), b = 18.5533(9), c = 21.3203(12)	a = 9.180(3), b = 13.123(4), c = 14.146(4)	a = 17.030(2), b = 10.4822(13), c = 16.225(2)	a = 12.418(7), b = 12.623(7), c = 13.822(7)
β (°)	α = 90 91.660(16) γ = 90	α = 90 107.399(7) γ = 90	α = 99.984(6), β = 99.791(6), γ = 93.044(8)	α = 90 β = 90 γ = 90	α = 68.521(12), β = 66.763(11), γ = 88.970(12)
V (Å^3)	2533(4)	10513.7(12)	1648.0(8)	2896.3(6)	1832.2(16)
Z	4	12	2	4	2
Radiation type	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
μ (mm^{-1})	0.063	0.064	0.337	0.193	0.104
Crystal size (mm)	0.15 x 0.11 x 0.08	0.40 x 0.33 x 0.2	0.13 × 0.13 × 0.09	0.19 × 0.13 × 0.1	0.17 × 0.11 × 0.09
Reflections collected	23792	21559	27921	50208	27556
GOOF on F^2	1.082	1.039	1.094	1.036	1.055
Unique reflections [R_{int}]	5825 [Rint = 0.0697]	21559 [Rint = 0.1484]	7616 [Rint = 0.0831]	5726 [Rint = 0.0447]	6444 [Rint = 0.0598]

No. of parameters	287	1193	364	331	421
No. of restraints	0	0	0	3	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, -0.45	0.41, -0.36	0.83, -0.89	0.22, -0.21	0.39, -0.53
Density (g cm^{-3})	1.115	1.091	1.213	1.156	1.105
Completeness to θ	99% (27.62º)	98.5% (26.32º)	98.9% (27.7º)	99% (28.16º)	99.3% (24.99º)
Limiting indices	-5 ≤ h ≤ 11, -27 ≤ k ≤ 26, -17 ≤ l ≤ 17	-34 ≤ h ≤ 34, -23≤ k ≤ 23, -23 ≤ l ≤ 26	-11 ≤ h ≤ 9, -13 ≤ k ≤ 17, -18 ≤ l ≤ 18	-22 ≤ h ≤ 22, -13 ≤ k ≤ 13, -14 ≤ l ≤ 21	-13 ≤ h ≤ 14, -15 ≤ k ≤ 12, -16 ≤ l ≤ 16
2ϑ range (°)	3.528 to 55.244	5.184 to 53	2.974 to 55.4	3.886 to 56.322	3.484 to 49.998
F (000)	928.0	3768.0	642.0	1088.0	656.0
Final R indices [I>2σ (I)]	R_1 = 0.0555, wR_2 = 0.1328	R_1 = 0.1441, wR_2 = 0.3650	R_1 = 0.0625, wR_2 = 0.1476	R_1 = 0.0434, wR_2 = 0.1196	R_1 = 0.0754, wR_2 = 0.1699
R indices [all data]	R_1 = 0.0876, wR_2 = 0.1637	R_1 = 0.2397, wR_2 = 0.4063	R_1 = 0.1150, wR_2 = 0.1694	R_1 = 0.0508, wR_2 = 0.1254	R_1 = 0.1155, wR_2 = 0.1987

Computational Details

All theoretical calculations were carried out using the Gaussian16 programs.[S6] The Full geometry optimizations and frequency analyses of **3-7** were performed at M062X/6-311G(d,p) level of theory with D3 dispersion correction.[S7, S8] Electrostatic potential map and natural bond orbital (NBO) analysis for **4** were predicted with using the optimized geometry at M062X-D3/6-311G(d,p) level of theory.[S9] The relative Gibbs free energies are given in kcal/mol. The GaussView 5.0 program was employed for visualization of the final geometries of the optimized structures.[S10]

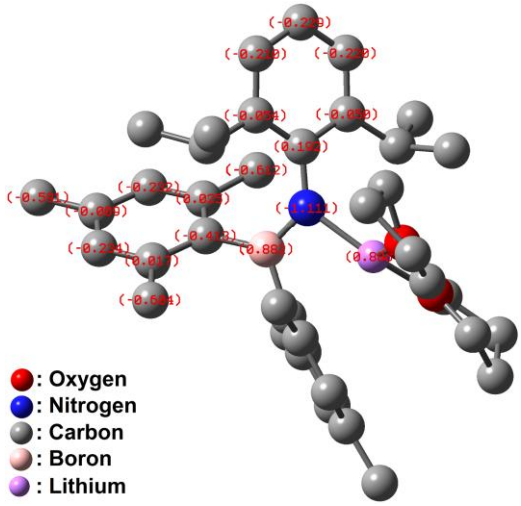
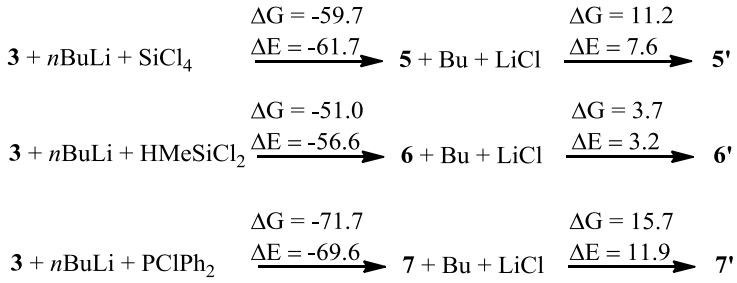


Figure S21 Calculated natural bond orbital (NBO) charges of **4**.



Scheme S1 Calculated relative Gibbs free and zero-point corrected energies of the title reactions at the M062X-D3/6-311G(d,p) level of theory (**5'** and **7'** are the corresponding *N*-substitution products, **6'** is the corresponding p-aryl-C-substitution product).

Table S2 Atomic coordinates and energies of **3** at the M062X-D3/6-311G(d,p) level of theory.

B,2.7307324724,7.4429165222,3.1707766756
C,5.3081351239,8.6160395892,4.9109966393
H,4.5104538765,8.8788185245,4.2193919113
C,4.889194482,9.0985305276,6.3036566681
H,4.6066966502,10.1539927225,6.2651755125
H,5.7107646677,9.0013306771,7.0187820395
H,4.0347120543,8.5303768183,6.6767421199
C,6.5785089767,9.3339495389,4.4366167286
H,6.8491349888,9.0235556099,3.4245276977
H,7.4222341359,9.1079640876,5.0942673694
H,6.4270876638,10.4166643245,4.4385685505
C,4.6208812286,4.0488879764,2.725760122
H,3.6316413744,4.4571194793,2.4986836396
C,5.4664479057,4.1176102295,1.4446065671
H,5.0003594466,3.5445036977,0.6394711596
H,6.4605484174,3.7036209391,1.6331607107
H,5.6037720111,5.1452330759,1.0968822941
C,4.4208926871,2.5929744242,3.1508843634
H,3.8371755816,2.0634505706,2.3948400719
H,3.8898475343,2.5293200711,4.103342455
H,5.3733182475,2.0672197843,3.2530643291
C,4.9182443228,6.288443619,3.8901342482
C,5.5120802337,7.1123028199,4.8584022778
C,6.3951557614,6.526213447,5.7690620306
H,6.8576445235,7.1482793415,6.527299285
C,6.7072089699,5.1786372281,5.7112538043
H,7.3969797322,4.7478231945,6.4271595293
C,6.1398014409,4.3829883918,4.723386552
H,6.3910234351,3.3302711975,4.6789928753
C,5.2389642337,4.91704114,3.8083286936
C,2.3547864882,5.3141828365,5.3729182998
H,2.448257544,5.0739973514,4.3136479158
H,1.5700765401,4.6823962034,5.7957070646
H,3.2992345663,5.0460544397,5.8562658131
C,0.6558410274,8.7748843298,8.5578343741
H,-0.2598580695,9.3661345944,8.4887133399
H,1.3931367135,9.3730262138,9.1000271227
H,0.4444374588,7.8835905818,9.1495990232
C,1.9018656517,10.205572771,3.9264560963
H,2.8733186277,10.218154844,3.424710731
H,1.7669455416,11.1721796901,4.4136757735
H,1.1442945509,10.1059850905,3.1446350635
C,3.9481395698,9.0722920255,0.8764491519
H,4.060158917,9.994158973,0.3034588936
H,4.6200796023,8.3326063614,0.4286631912

H,4.3051886972,9.2541384269,1.890464343
C,-0.3813034271,8.9629299032,-1.6345345839
H,0.1143220876,9.7477760423,-2.2071975424
H,-1.3760173518,9.3170909494,-1.3563906301
H,-0.5116182151,8.0987406097,-2.2916590714
C,-0.1321095421,6.6614277928,2.809594936
H,-1.0756255233,6.2631053754,2.4341224397
H,-0.3438539499,7.2780208704,3.6872179836
H,0.4766450575,5.8207581563,3.1510067477
C,1.7961981815,9.0850919165,4.9371074044
C,1.3081004052,9.3883851745,6.2022418444
H,1.0281751145,10.413415162,6.4300210346
C,1.169133916,8.4120474924,7.1888796224
C,1.5275392549,7.1110544754,6.8689938304
H,1.4122411295,6.328813356,7.614544609
C,2.0291866723,6.7717893587,5.6085256672
N,3.9707311914,6.8071866654,2.9601775215
H,4.1848154975,6.5739402132,1.9986625065
C,2.5074777936,8.602860824,0.8359793733
C,1.748178687,8.9690474675,-0.2774321854
H,2.2095627457,9.5709626741,-1.0554852096
C,0.4201462751,8.5877800842,-0.4152151073
C,-0.151934533,7.8293202645,0.6043870468
H,-1.190182043,7.5211403117,0.5153476535
C,0.5688936522,7.4636602133,1.7361459634
C,2.1828136774,7.7605638848,4.6221604567
C,1.9223376396,7.8442564598,1.8677545707

Zero-point correction= 0.632980 (Hartree/Particle)
Thermal correction to Energy= 0.667287
Thermal correction to Enthalpy= 0.668232
Thermal correction to Gibbs Free Energy= 0.567704
Sum of electronic and zero-point Energies= -1246.119217
Sum of electronic and thermal Energies= -1246.084910
Sum of electronic and thermal Enthalpies= -1246.083965
Sum of electronic and thermal Free Energies= -1246.184493

Table S3 Atomic coordinates and energies of **4** at the M062X-D3/6-311G(d,p) level of theory.

O,2.9127550415,-0.0132926655,1.2749082475
O,2.3259596644,-1.7794722837,-1.1872713077
N,-0.371792864,-0.5793831157,0.0719225101
C,-2.7194727251,2.1922563685,-0.9681784723
C,0.5799740287,1.6611971029,-0.5157103838
C,-3.9916078478,2.7358494587,-0.83008338
H,-4.4098641969,3.3211116893,-1.6450455584

C,-2.3028212906,-2.0364041836,-0.4143346451
C,-1.2199562053,-1.6319741617,0.4057830012
C,-2.148972406,1.4116793635,0.0660015768
C,-4.1850966922,1.7954821126,1.3467510424
H,-4.7477741482,1.6406710214,2.2639934332
C,1.3685398211,1.4095426297,-1.6618927153
C,-2.9101880609,1.2301909338,1.2354825129
C,-1.9925182874,2.4192798534,-2.2735556601
H,-2.5865358481,3.044981105,-2.9413369673
H,-1.8070956077,1.4707186802,-2.7870107712
H,-1.0245991669,2.9020696565,-2.1202326412
C,3.082175204,2.9636809818,-0.8941396112
C,-4.7482609865,2.5444246261,0.3250708794
C,2.598129179,2.0541199003,-1.829473886
H,3.1855970948,1.8501206845,-2.7229506473
C,2.2778618918,3.2542332343,0.2047643162
H,2.6214707186,3.984688638,0.9337271334
C,-2.6483429248,-1.3231458115,-1.7099903682
H,-2.0044623324,-0.4501974859,-1.7895255214
C,0.8816443658,0.5206526565,-2.7864408214
H,0.2171414668,-0.2653175059,-2.4253269996
H,1.720315844,0.0623424078,-3.3162207611
H,0.3308743201,1.1228450633,-3.5154207531
C,-4.098532612,-0.8271972969,-1.7285505069
H,-4.801025231,-1.6653928162,-1.7574143896
H,-4.2785046275,-0.2093645951,-2.6136062952
H,-4.3149893359,-0.225023054,-0.8434317554
C,-0.9369275064,-2.3941224687,1.573089245
C,-1.7135772714,-3.5017884698,1.8908734932
H,-1.4903030306,-4.0713017994,2.7870268312
C,1.0437817978,2.6320309417,0.3955820707
C,-3.0552803133,-3.156230282,-0.0552765397
H,-3.8814186949,-3.4572742046,-0.6923484528
C,-2.7773960221,-3.891712405,1.0855589385
H,-3.3777612434,-4.7552811095,1.3452387206
C,4.2638887447,0.0944681034,0.8017397035
H,4.2333128372,0.4247972659,-0.2381092652
H,4.7345403409,-0.8932410451,0.8609289836
C,-2.4172248165,0.4385734519,2.4253740009
H,-2.8796139609,-0.5531551142,2.4442703943
H,-2.6788051348,0.9505873773,3.355214619
H,-1.3389757733,0.2890938246,2.4014984966
C,0.2144639224,3.0042859814,1.6030822478
H,-0.7209134511,3.4798819562,1.2984837635
H,0.7573545334,3.6908190502,2.2559123422
H,-0.0643432557,2.1213071843,2.1853368117
C,2.7951818801,0.5520600475,2.5926258697

H,2.2469451918,-0.1508899436,3.2211059436
H,2.2342687808,1.4863017018,2.5146511345
C,-2.3579886659,-2.2137007894,-2.9248783678
H,-1.309896076,-2.5270936886,-2.9399106083
H,-2.5693188808,-1.678188497,-3.8553132521
H,-2.9740701084,-3.1171381387,-2.9066938591
C,0.2208684855,-1.9970826239,2.4730956452
H,0.4366500557,-0.9480412949,2.2574601963
C,1.484945036,-2.8740259539,-1.5891204448
H,0.4676360882,-2.637743109,-1.2752332882
H,1.8176309866,-3.7874512682,-1.0822935529
C,1.4764056473,-2.815682581,2.1422727033
H,1.2900338672,-3.876875917,2.3319090159
H,2.3289173828,-2.5020659907,2.7543063535
H,1.7606887842,-2.7088247422,1.092817402
C,3.4783541698,-1.7265216875,-2.0358659013
H,4.3573044452,-2.048202746,-1.4706670952
H,3.6153872955,-0.6839947577,-2.3332133693
B,-0.7034941612,0.74994815,-0.1235322318
C,-6.1343312969,3.1239902023,0.4415154704
H,-6.1467484937,4.1757231944,0.1465742888
H,-6.5077083157,3.0510180535,1.4638656934
H,-6.832655486,2.5916589803,-0.2101324985
C,4.4356519409,3.6033312083,-1.0714518099
H,4.5374288882,4.0409227827,-2.066874774
H,5.2368399855,2.8654753515,-0.9563458998
H,4.599252507,4.3923393767,-0.3357432174
C,4.9366032513,1.0923029398,1.7350383129
H,6.0174448435,0.9597163755,1.7799265777
H,4.7137902548,2.1112697117,1.4089372357
C,-0.105130959,-2.102386291,3.9653693915
H,-1.0291140097,-1.5709071008,4.2036154016
H,0.7046284005,-1.6718619346,4.5626910121
H,-0.2199999543,-3.1420217908,4.2821860512
C,4.2271699553,0.7946053595,3.0579757
H,4.2933913457,1.6089130546,3.7787514579
H,4.6391101012,-0.1093004439,3.5138796794
C,1.6916351164,-2.9698088043,-3.092296091
H,1.0863850674,-2.2186536083,-3.6016090836
H,1.4276971417,-3.9515036998,-3.4849455455
C,3.1890783378,-2.6567059144,-3.22880041
H,3.7748031649,-3.5734741298,-3.142803916
H,3.435612386,-2.1878860141,-4.1812644477
Li,1.5513996775,-0.5099324602,0.0299958885

Zero-point correction= 0.862076 (Hartree/Particle)
Thermal correction to Energy= 0.908440

Thermal correction to Enthalpy= 0.909384
Thermal correction to Gibbs Free Energy= 0.784015
Sum of electronic and zero-point Energies= -1717.735743
Sum of electronic and thermal Energies= -1717.689379
Sum of electronic and thermal Enthalpies= -1717.688435
Sum of electronic and thermal Free Energies= -1717.813804

Table S4 Atomic coordinates and energies of **5** at the M062X-D3/6-311G(d,p) level of theory.

Cl,5.6453737316,1.0067046343,1.4460230551
Si,4.8542657805,0.1228048751,-0.2196642329
Cl,5.1084934724,1.4267436326,-1.7789185459
Cl,5.9444435573,-1.5529324495,-0.6543644096
N,-1.0489883251,-1.0460861088,0.3128095658
H,-1.2815934129,-2.02385619,0.4324532083
C,0.9241693696,0.2271063951,1.0350618947
C,0.3468882748,-0.7978815653,0.2683669213
C,0.5040512114,-2.7507698875,-1.3523508285
H,-0.5176108998,-2.4503737253,-1.6043325479
C,-4.484292739,-0.7057560959,-0.9533027146
C,-3.5756687559,-0.8439622144,0.1183303014
C,-1.9287425081,1.3287428252,-0.3648356401
C,2.2893887141,0.4692183412,0.885464698
H,2.7385684089,1.2660635952,1.4694551482
C,-1.1031528033,1.738006833,-1.4256042884
C,1.1363777852,-1.6082193548,-0.5770067518
C,-3.9966507947,-1.5374001622,1.2697863681
C,-5.7584242343,-1.2561470927,-0.8618359516
H,-6.4431366285,-1.1475235467,-1.6984497518
C,-2.6259069068,2.32288461,0.3631342828
C,3.0829933262,-0.2944254991,0.0326569958
C,-6.1831024948,-1.9351947328,0.2783419171
C,2.4952444714,-1.3453043496,-0.6779854758
H,3.1041602251,-1.9564948423,-1.3345286874
C,-5.2897312835,-2.0593279944,1.3345849606
H,-5.6063987958,-2.573474786,2.2377778047
C,0.1610305949,1.0150051658,2.0848105097
H,-0.8999834587,0.8086927702,1.9639288959
C,-1.6283356686,4.0762786277,-0.9964964997
C,-2.4619325188,3.6650684661,0.0441794712
H,-2.9956601701,4.4152487054,0.6213372549
C,-0.9655851034,3.0977152091,-1.7220317068
H,-0.3248893916,3.3907213731,-2.5493806806
C,0.4293704308,-4.0088036373,-0.4722663764
H,-0.0830568127,-4.817978457,-0.9974178367
H,-0.0959604795,-3.8274111576,0.469556984

H,1.4383795863,-4.3452472409,-0.2202182425
C,-3.1076908288,-1.7345717327,2.4816340681
H,-3.7157953613,-1.8386690285,3.3814771171
H,-2.4114947416,-0.9092302273,2.6341304443
H,-2.5087012042,-2.6469120274,2.392472126
C,-0.360509381,0.7690626902,-2.3184911188
H,-0.4787567367,1.0610074042,-3.3645443331
H,-0.718043522,-0.2555305378,-2.21336591
H,0.7101942538,0.7744625919,-2.0911688018
C,-3.5574675599,1.9683529254,1.5008895736
H,-3.1051255652,1.2587474177,2.1993168007
H,-4.4753647261,1.5044782468,1.1304182029
H,-3.8281596173,2.8621001255,2.0644467862
C,-4.1097254819,0.0393260939,-2.2151149908
H,-4.8327922446,-0.1622179371,-3.0064328596
H,-3.1215698385,-0.2504443459,-2.5805139354
H,-4.0815192903,1.1185062307,-2.042087326
C,0.3576198866,2.5274034907,1.9402680353
H,1.3726524474,2.8245073806,2.2179545298
H,-0.3325046872,3.0569622221,2.6019002511
H,0.1662176812,2.8540438119,0.9162494807
C,1.2184784918,-3.067755651,-2.6671121834
H,1.3538027355,-2.1682557463,-3.2718640056
H,0.6282731603,-3.7831228881,-3.2431669697
H,2.1988018687,-3.5193816557,-2.4967706282
C,-7.5646511808,-2.5315593092,0.347714863
H,-7.6088767566,-3.4675234505,-0.2160001389
H,-8.3064501215,-1.8545177254,-0.0801212255
H,-7.850504132,-2.747803903,1.3778183739
C,0.5665726254,0.5337409462,3.4844714863
H,0.3772127708,-0.5359458134,3.6020993839
H,0.0008367491,1.0720501416,4.2491111826
H,1.6310051168,0.7088933077,3.6633635275
C,-1.4532204817,5.5402673639,-1.3038827621
H,-0.8817869319,6.0339313267,-0.5132848643
H,-2.4198544685,6.0436362995,-1.3738945054
H,-0.9213907445,5.6859105123,-2.2445969839
B,-2.1373449377,-0.1915555191,0.0198172409

Zero-point correction= 0.629015 (Hartree/Particle)
Thermal correction to Energy= 0.669409
Thermal correction to Enthalpy= 0.670353
Thermal correction to Gibbs Free Energy= 0.553252
Sum of electronic and zero-point Energies= -2915.766625
Sum of electronic and thermal Energies= -2915.726231
Sum of electronic and thermal Enthalpies= -2915.725287
Sum of electronic and thermal Free Energies= -2915.842388

Table S5 Atomic coordinates and energies of **6** at the M062X-D3/6-311G(d,p) level of theory.

N,8.2789343573,7.4412571603,8.0078511048
Si,7.8565206755,8.7741302775,6.9070215218
C,6.8733685398,4.8940270666,7.5179794161
H,7.7907746476,5.2336663379,7.0430594598
Cl,5.7810946932,8.9927045252,6.9841865458
B,9.5141610143,6.7429282022,7.7787767186
C,7.5760407113,9.1467329529,10.378781152
H,8.4577922952,9.2503847046,9.7415500367
C,5.7523762466,5.0179835816,6.478277569
H,5.6327207197,6.0525904956,6.1478418202
H,4.797858729,4.690471181,6.8991569461
H,5.9714287401,4.3953553845,5.6062511322
C,7.0948563193,3.4345656765,7.930889224
H,7.4870584945,2.8608470666,7.0863453196
H,6.1590414683,2.9628268734,8.241761954
H,7.80976083,3.3643595048,8.7535983528
C,11.6865045839,8.3276497991,8.8297636689
H,12.5711202308,8.9018666897,9.1061093189
H,11.7459424332,7.3505981603,9.3159011873
H,10.8118537802,8.8465653186,9.2374443323
C,8.0504916412,9.2235980853,11.8406268675
H,8.6778211494,8.3832379443,12.13048146
H,7.1985789458,9.2594835479,12.5234180147
H,8.6217822041,10.143456042,11.9885455636
C,6.6418125819,10.3443557818,10.1387937417
H,6.2747364809,10.4046246508,9.1168473001
H,7.1600021149,11.2771448693,10.3796832988
H,5.7705080637,10.269505696,10.7949581458
C,9.4106585091,6.6125631916,4.5791738671
H,8.9505181999,7.2527641344,3.8232750014
H,8.6147708103,6.2346735029,5.2219010863
H,9.8592766185,5.7616949865,4.060328278
C,13.4621855817,9.5110875353,4.2952712435
H,13.1493779689,9.5599156224,3.2517390361
H,14.4222553529,8.9896770151,4.335519538
H,13.6261975298,10.5297218857,4.6527276513
C,7.2584857325,7.0032587355,8.9428682209
C,9.6079121696,6.4547840711,10.8643589771
H,9.5068791788,7.3912334825,10.3257076375
H,10.4052147213,6.5767615766,11.603952193
H,8.6742737642,6.2697056963,11.4015757709
C,10.9656439301,1.6774833219,10.5868955529
H,10.9511135043,1.794108575,11.6709805404

H,11.9583248729,1.3286396922,10.2929627604
H,10.250347505,0.8954648334,10.3198286676
C,10.4238735867,4.1900765532,6.3291451157
H,9.4332546786,4.2852560485,5.8778898401
H,10.8352098808,3.2332414886,6.006449566
H,11.0569383975,4.9825337677,5.9300801127
H,8.0471394857,8.4138479149,5.5048677379
C,6.5911570903,5.7868087288,8.7136525065
C,5.5792258045,5.3996915092,9.5926746946
H,5.0605538182,4.4638773265,9.4187231918
C,5.2120066997,6.1939477362,10.6649980782
H,4.4152469137,5.8825724159,11.3298054483
C,5.8705332048,7.3945917562,10.8769886944
H,5.5812597552,8.0179414782,11.7155226532
C,6.9000255074,7.8199499733,10.0398624012
C,10.5333340829,7.4330542162,6.747252689
C,11.5792314207,8.1902541057,7.3301698437
C,12.5013125688,8.8544353652,6.5321138505
H,13.2901207479,9.4329141036,7.0050104917
C,12.4372105246,8.8006383042,5.1395112707
C,11.4121666149,8.0626543194,4.5694691369
H,11.3348405581,8.0088213397,3.4867483843
C,10.4654939045,7.3825488107,5.3430439258
C,9.9337676026,5.4001129354,8.5490199512
C,10.3499375885,4.242921145,7.833885976
C,10.6754505641,3.0711564156,8.5064409974
H,10.9761133901,2.2027644815,7.9271942542
C,10.6240076629,2.9699236824,9.8946317
C,10.2557135868,4.1028838511,10.5970068706
H,10.230008007,4.0749805093,11.6830791124
C,9.9238602816,5.2992670035,9.9535929453
C,8.6852005228,10.4026807558,7.2498766484
H,8.4641694731,10.824387151,8.2292167525
H,8.3583587894,11.1161671773,6.4889994158
H,9.767198644,10.2756421958,7.1484085476

Zero-point correction= 0.673077 (Hartree/Particle)
Thermal correction to Energy= 0.711522
Thermal correction to Enthalpy= 0.712466
Thermal correction to Gibbs Free Energy= 0.604901
Sum of electronic and zero-point Energies= -2035.741424
Sum of electronic and thermal Energies= -2035.702978
Sum of electronic and thermal Enthalpies= -2035.702034
Sum of electronic and thermal Free Energies= -2035.809600

Table S6 Atomic coordinates and energies of **7** at the M062X-D3/6-311G(d,p) level of theory.

N,-1.753514524,-1.2244630217,0.5979857511
C,-2.0467890771,1.1549061754,-0.4296491617
C,-0.9253732198,1.3361242095,-1.2582103604
C,-4.0949073915,-0.7144393155,-0.2823292763
C,-2.7098382931,2.3070235697,0.0533739966
C,-0.3664409899,-1.1065895765,0.9062370446
C,-0.2098186283,0.1941450259,-1.9437083836
H,0.8070073941,0.0755095451,-1.5570676856
H,-0.1363300832,0.3976242975,-3.0154302356
H,-0.7250898808,-0.7571567825,-1.817526504
C,-4.6683771301,-0.5527336663,-1.5624739
C,0.5398158326,-1.9862707097,0.2863022256
C,0.0913608963,-0.1032475695,1.7765164416
C,-3.9592034165,2.2058395897,0.8998097023
H,-3.8415017742,1.5022973041,1.7286299152
H,-4.8080806067,1.8540705517,0.307478455
H,-4.214503435,3.178352692,1.3226702487
C,-4.9010694647,-1.229162958,0.7516406884
B,-2.5926632232,-0.2815191705,-0.0321083925
C,1.9055816076,-1.7680107169,0.4451467067
H,2.6069090766,-2.398494296,-0.0862210443
C,-0.4576868902,2.6233772413,-1.5362629643
H,0.4054716368,2.7337349945,-2.1887076724
C,-0.8376043144,0.7846861019,2.5827721285
H,-1.8389880668,0.6952302722,2.1676489865
C,-5.9946922907,-0.9085914399,-1.7834920315
H,-6.4175262747,-0.785029613,-2.7767787379
C,2.3822011624,-0.7168979964,1.2247936369
C,0.0337160702,-3.1339433034,-0.5698643974
H,-0.8942724213,-2.8063161354,-1.0484058289
C,-2.2192651241,3.5743093505,-0.244697088
H,-2.7337390236,4.4464238714,0.1492059063
C,-3.8714564168,0.0100621467,-2.7180702308
H,-3.7020784517,1.083021053,-2.5945118594
H,-4.3996779073,-0.1475926947,-3.6592763394
H,-2.8889802571,-0.4607255079,-2.8008882817
C,1.4656962111,0.0557508552,1.9322188787
H,1.8307913198,0.8434467008,2.5849976209
C,3.028608718,2.0271969318,-0.0276852344
H,2.0599172129,1.5394589146,-0.0226368185
C,4.1452498899,1.4062811153,0.539343187
C,-6.2342771173,-1.5576700706,0.4985372561
H,-6.8476843274,-1.9355036298,1.3118282537
C,-0.4368856291,2.2622868968,2.5082120966
H,0.4585936161,2.4631216144,3.1024059808
H,-1.241042767,2.8896752259,2.9018335343

H,-0.2428655032,2.5645529682,1.4764358612
C,-6.7980527525,-1.4114179551,-0.762145986
C,-1.0791052031,3.7550990745,-1.0264863933
C,1.0005139238,-3.543475458,-1.6826922768
H,1.8974739962,-4.0234082823,-1.2831291093
H,1.3135062624,-2.6800174382,-2.2747886227
H,0.5149873373,-4.2605650039,-2.348006792
C,-4.3943696282,-1.4335146425,2.1653281453
H,-3.9415169937,-2.4228979578,2.2870836493
H,-5.2213966308,-1.371251237,2.8742979335
H,-3.6410290063,-0.7001759293,2.4541754768
C,-0.8957243933,0.2965884335,4.0358064396
H,0.0940183524,0.3445262149,4.4980581498
H,-1.2414518953,-0.7387319632,4.0876610514
H,-1.5767596034,0.9198434489,4.6214667058
C,4.3646136417,3.9502811553,-0.6202577383
H,4.4466664795,4.9358879925,-1.0628169523
C,3.1398592991,3.2946117041,-0.5945455657
H,2.2577518719,3.7667950393,-1.0126277871
H,-2.1370212367,-2.1495418759,0.7454997804
C,-8.2283880693,-1.8007760403,-1.0304169927
H,-8.2756228501,-2.7669655585,-1.5403667738
H,-8.7217645345,-1.0667332713,-1.6704395827
H,-8.7958770656,-1.8841866423,-0.1026926036
C,5.3703555016,2.0817423765,0.518063799
H,6.2436371869,1.6171928803,0.9656403607
C,-0.2975658378,-4.3419039758,0.320194365
H,0.6101221962,-4.7008402873,0.8122969767
H,-0.7151164345,-5.1588399899,-0.2732559472
H,-1.0150375502,-4.0871733873,1.1051107022
C,5.4840400576,3.3364016165,-0.0666680942
H,6.4431847707,3.8405485517,-0.0776293723
C,-0.5317047049,5.1335403541,-1.2898458132
H,0.0832357253,5.4690385826,-0.4492146568
H,-1.3359208912,5.8598561833,-1.4199142618
H,0.0904673599,5.1467362828,-2.1865107912
P,4.158764142,-0.2560047117,1.3573527034
C,4.8527245101,-1.2901709585,-0.0033005981
C,4.6953886013,-0.9790629267,-1.3569145354
H,4.201444584,-0.0562392875,-1.6423341445
C,5.4956874958,-2.477648501,0.3491029467
H,5.629842889,-2.7208980717,1.3980242157
C,5.958279285,-3.3510463055,-0.6316923936
H,6.4526384661,-4.2718401618,-0.3454901386
C,5.7925777306,-3.0358964574,-1.9749293996
H,6.1555195381,-3.7116312212,-2.7402889931
C,5.1644560662,-1.8463916393,-2.3357503401

H,5.0383872872,-1.5955677931,-3.3825028198

Zero-point correction= 0.807230 (Hartree/Particle)
Thermal correction to Energy= 0.852984
Thermal correction to Enthalpy= 0.853929
Thermal correction to Gibbs Free Energy= 0.726461
Sum of electronic and zero-point Energies= -2049.913091
Sum of electronic and thermal Energies= -2049.867337
Sum of electronic and thermal Enthalpies= -2049.866393
Sum of electronic and thermal Free Energies= -2049.993860

Table S7 Atomic coordinates and energies of **5'** at the M062X-D3/6-311G(d,p) level of theory.

N,-0.0494282257,-0.6497204103,0.1151608084
Si,1.1141319829,-1.8727118933,0.5697921216
C,-1.7335444198,0.2929531079,2.3124821796
H,-0.8034816173,0.744247353,1.9739149599
Cl,0.1025146908,-3.4659961001,1.3765796943
B,0.3070450258,0.7471966596,-0.1224253389
C,-1.1681192359,-2.6150631714,-1.9590929538
H,-0.2428871141,-2.0480728485,-2.077365706
C,-1.4140589285,-0.4821315028,3.5972173326
H,-0.6600077328,-1.2536315116,3.4211826226
H,-2.3104676345,-0.9745594197,3.9835114407
H,-1.037556984,0.1967492329,4.3671471275
C,-2.7122231185,1.4416523327,2.5782168925
H,-2.2350145726,2.2018008125,3.2027942002
H,-3.6024296316,1.0950813918,3.1089906431
H,-3.0240048775,1.9126929705,1.6434817416
C,1.4999073458,0.7718237403,-2.7196699972
H,2.0610816726,0.8357398597,-3.6520210104
H,0.6600848567,1.4691626467,-2.7801715122
H,1.0938535115,-0.2418206446,-2.6495715488
C,-1.9567902512,-2.4997446954,-3.2789020504
H,-2.3621432808,-1.5088309384,-3.4625613867
H,-2.7851777311,-3.2118765254,-3.2950488256
H,-1.2967548726,-2.7568965555,-4.1104541694
C,-0.8130413547,-4.1065040107,-1.8116795602
H,-0.1113274903,-4.3210818096,-1.0126012214
H,-0.3718263778,-4.4631406251,-2.7455027501
H,-1.720038876,-4.6878847075,-1.6248103127
C,2.3804980764,1.4988282706,2.2912343284
H,3.1172664415,0.9700434742,2.8958001437
H,1.4040224269,1.0637602165,2.5070270787
H,2.3735023863,2.5386064656,2.6243351312
C,6.0583767235,1.9486893433,-1.0284596404

H,6.5752459217,2.3020848605,-0.1357610527
H,6.1650179854,2.7052159854,-1.8090034688
H,6.5627552089,1.0434563735,-1.3760085924
C,-1.4387316246,-1.1118996422,0.1759178195
C,-1.8909752928,0.5938768512,-2.3395436987
H,-1.0642619763,-0.0995349644,-2.2437295569
H,-1.8990019432,0.9626685292,-3.3699016159
H,-2.821424894,0.0489180987,-2.1688599904
C,-3.8802522185,4.9365762848,-1.0157827976
H,-4.5560287341,4.6693908617,-1.8287005841
H,-3.4334450114,5.9065750298,-1.2460731405
H,-4.4730530293,5.0560394651,-0.1055107126
C,0.1980581529,3.4494225702,1.3870879798
H,0.1300007747,2.775495873,2.2425643473
H,0.0283685568,4.4605422837,1.7577558061
H,1.2104243005,3.4007819925,0.988407444
C,-2.2397258521,-0.6517888877,1.2351292657
C,-3.5447286801,-1.1312243897,1.3458006102
H,-4.1685604094,-0.781725724,2.1599026943
C,-4.0459870024,-2.0598289118,0.4508198042
H,-5.0571853454,-2.4333077554,0.5590024417
C,-3.2425905623,-2.5119923296,-0.583551028
H,-3.6388882792,-3.2405457702,-1.2813642521
C,-1.9372860611,-2.0545499428,-0.7565631997
C,1.8690201536,1.0957917837,-0.2180841071
C,2.3869277767,1.0873020116,-1.5396393485
C,3.7251995541,1.3639163564,-1.7793376053
H,4.0932614138,1.3406861287,-2.8010677504
C,4.6062775366,1.6704155868,-0.7441486491
C,4.0988744938,1.6937522817,0.5438460904
H,4.763044631,1.9299604195,1.3707884184
C,2.7581126351,1.413677421,0.8272956175
C,-0.8029360707,1.8827238336,-0.3989806056
C,-0.8164579519,3.1068601418,0.3310342865
C,-1.8052318795,4.0592792189,0.1169180553
H,-1.7859888253,4.9699237034,0.708388818
C,-2.816683282,3.8893239484,-0.8241149579
C,-2.781742724,2.729576722,-1.5731865587
H,-3.5293895834,2.567276977,-2.3448903753
C,-1.8023346652,1.7490115272,-1.3839241102
Cl,2.2290765469,-2.486964129,-1.0325731187
Cl,2.4728924424,-1.5065701822,2.044941916

Zero-point correction= 0.630945 (Hartree/Particle)
Thermal correction to Energy= 0.669893
Thermal correction to Enthalpy= 0.670837
Thermal correction to Gibbs Free Energy= 0.560882

Sum of electronic and zero-point Energies= -2915.754535
Sum of electronic and thermal Energies= -2915.715588
Sum of electronic and thermal Enthalpies= -2915.714643
Sum of electronic and thermal Free Energies= -2915.824598

Table S8 Atomic coordinates and energies of **6'** at the M062X-D3/6-311G(d,p) level of theory.

N,8.3208404053,7.3135784956,8.1230531155
C,6.9665932174,4.7043437052,7.6574691844
H,7.8599951482,5.0707381394,7.1565364996
B,9.5910841779,6.7223439178,7.9463312179
C,7.4056261318,9.2017288377,10.0425785117
H,8.4567962645,9.1075590647,9.7536741357
C,5.8330855779,4.6970241406,6.6230901352
H,5.6551618855,5.700573402,6.2291135593
H,4.9008575577,4.3403989928,7.0697252719
H,6.0837679282,4.0365470644,5.78894979
C,7.2660247267,3.2880464227,8.1591906112
H,7.660687554,2.6784691312,7.3421479428
H,6.3605671419,2.7988144791,8.528616587
H,8.0058924469,3.3025993713,8.9617981275
C,12.3720568138,7.3962217411,8.8115569888
H,13.304497718,7.9071702124,9.0549447783
H,12.543107586,6.3184624279,8.8778082114
H,11.6384743271,7.6498181852,9.580603191
C,7.3779458128,9.7664168584,11.4639657674
H,7.7749403951,9.0472423206,12.1837949396
H,6.3651275175,10.0371413189,11.772184722
H,7.9843782576,10.6731861475,11.5122928724
C,6.7313227099,10.1810573349,9.0688150089
H,6.7549144925,9.8213016131,8.0364031294
H,7.2197494624,11.1577718323,9.1002870972
H,5.68086879,10.3113488527,9.3421949963
C,8.8450172793,7.6038267299,5.1076700153
H,8.1546687235,8.4277741935,5.3168226951
H,8.3906408001,6.6974402521,5.5086570485
H,8.9055723092,7.505234686,4.0226686228
C,13.4054090499,9.5441500094,4.4034984602
H,13.0876372113,9.5147139292,3.3605459506
H,14.4005694154,9.1004066455,4.4721554481
H,13.4918636944,10.5935014858,4.6986197205
C,7.2273697097,6.9170788621,8.9405244307
C,9.4658859284,6.2467786537,10.9960190378
H,9.4597704853,7.2362042785,10.5383602475
H,10.1373107641,6.2779214788,11.857285375
H,8.4566065856,6.0453303378,11.3682804315

C,11.1101158163,1.5608161587,10.4229484294
H,11.1690120588,1.6263998084,11.5098373241
H,12.0748598482,1.2141157042,10.0464928065
H,10.3660400204,0.8003541022,10.1709774208
C,10.619377624,4.4270150165,6.3486817357
H,9.7226977939,4.8459975562,5.8835892307
H,10.8031245687,3.4515755385,5.8964080224
H,11.4490949226,5.0889745664,6.0872235694
C,6.6250597678,5.6601040348,8.7867898061
C,5.6040701984,5.3092566863,9.6739709093
H,5.1454217703,4.3303105139,9.569196077
C,5.151548207,6.1716054992,10.6686347996
C,5.7396021121,7.4377866561,10.76317242
H,5.4033496557,8.1253111254,11.5329807049
C,6.7732550322,7.8258527699,9.9225481864
C,10.5890059686,7.4953331911,6.9896393019
C,11.8978984799,7.7890079734,7.430164978
C,12.7855504733,8.4490988933,6.587027609
H,13.7866141669,8.6746408032,6.9443651655
C,12.4276060121,8.8211411227,5.2926878634
C,11.1427996145,8.5208100571,4.8594797384
H,10.8483074985,8.7906732396,3.8490537225
C,10.2193480657,7.8773092504,5.6856849236
C,9.9879511663,5.3590334865,8.6451974467
C,10.4756009713,4.2954107367,7.8487443439
C,10.8329478549,3.0888273884,8.437913106
H,11.1937083974,2.2791279317,7.8093584235
C,10.7385726293,2.8880572681,9.8153524706
C,10.2825200218,3.9407299019,10.5947287477
H,10.2165939892,3.815775357,11.6721780192
C,9.9091170979,5.1666236688,10.0350329512
H,8.2070466591,8.2336966849,7.7168445386
Si,3.8013420064,5.6577106346,11.8364016064
H,3.2882381462,4.3300160534,11.4429788849
Cl,4.6080940386,5.4294167066,13.7493572665
C,2.4529722795,6.935526195,11.969659843
H,1.9776955239,7.081551299,10.9967838734
H,1.6913151815,6.6299219493,12.6889059554
H,2.8629791477,7.8938655091,12.2958858627

Zero-point correction= 0.670352 (Hartree/Particle)
Thermal correction to Energy= 0.707018
Thermal correction to Enthalpy= 0.707962
Thermal correction to Gibbs Free Energy= 0.602967
Sum of electronic and zero-point Energies= -2035.736215
Sum of electronic and thermal Energies= -2035.699548
Sum of electronic and thermal Enthalpies= -2035.698604

Sum of electronic and thermal Free Energies= -2035.803599

Table S9 Atomic coordinates and energies of **7'** at the M062X-D3/6-311G(d,p) level of theory.

N,-0.1213015072,-0.1372866919,0.081249699
C,1.0067203006,-2.3039003587,-1.6378535893
H,1.0524325027,-1.2298894926,-1.8178359836
B,1.1009523437,0.6107474833,-0.0900614449
C,-1.3422375888,-0.8350303618,2.7582898374
H,-1.132014739,0.1641089143,2.3788257003
C,0.2045892547,-2.9359898476,-2.7840670815
H,-0.8163376635,-2.558339372,-2.8268954851
H,0.1580203716,-4.0222685251,-2.66927936
H,0.6936012201,-2.7239325988,-3.7389770068
C,2.4407886117,-2.8576606737,-1.6475119576
H,2.9843034804,-2.4857244964,-2.5206904
H,2.4258587965,-3.9495562736,-1.7077305546
H,2.9925444143,-2.5714796667,-0.7515862096
C,1.58008004,2.6032921659,1.9722632052
H,1.7065315425,3.4491131687,2.6488888888
H,2.4996042133,2.0128393259,1.9875537182
H,0.7817086963,1.9726994997,2.3775703769
C,-0.7888001644,-0.9237625581,4.1904948671
H,0.2800952666,-0.7329858258,4.2555232764
H,-0.9833349438,-1.9059251796,4.6277374635
H,-1.3016960029,-0.1851176434,4.8122585144
C,-2.866792561,-1.021209351,2.84954225
H,-3.3313277238,-1.1530686685,1.8754984309
H,-3.3276670771,-0.1498889224,3.3230031816
H,-3.0979473582,-1.9028244825,3.4547942388
C,0.4015118982,1.840730689,-2.9551893807
H,-0.583654515,2.0974044092,-3.3517924028
H,0.3966886087,0.7730309648,-2.736895838
H,1.1413233818,2.0247099021,-3.7398896243
C,0.8446574045,6.4613981198,-1.1305941742
H,0.6264123167,6.6984070657,-2.1724446842
H,1.795118677,6.9312474367,-0.866283728
H,0.0691097553,6.9165429687,-0.5095854425
C,-0.157031962,-1.5153052721,0.5415037039
C,2.0610538045,-0.6962871846,2.5577859049
H,1.1375286534,-0.1475251949,2.4100098293
H,2.5670374485,-0.2744457017,3.4320062659
H,1.8040185747,-1.7345806036,2.7837983588
C,6.5687672192,-1.6623055648,0.6742321286
H,6.72544601,-2.0243624686,1.6908821687
H,7.336274509,-0.9169659358,0.4534599694

H,6.7181817178,-2.5006807201,-0.0110425237
C,3.287857922,0.7020026209,-2.2220754963
H,2.4882537284,0.1795344112,-2.7520345047
H,4.1820321996,0.6394172501,-2.843048417
H,3.0055597148,1.7519265035,-2.1386164498
C,0.3488466011,-2.5386065316,-0.2879056475
C,0.2470223467,-3.8651497715,0.1358600063
H,0.6332808582,-4.650052517,-0.5043613041
C,-0.3399912753,-4.1988763293,1.3426888412
H,-0.4173068134,-5.2354780177,1.6486355643
C,-0.8218494782,-3.187863045,2.158737179
H,-1.279386576,-3.4433069629,3.1079138042
C,-0.7387382471,-1.8456989085,1.7908523929
C,1.0000348107,2.1640678998,-0.4732948753
C,1.2568502937,3.0807957314,0.5753193657
C,1.1962153925,4.4508213728,0.3472396447
H,1.3878847922,5.1319071073,1.1720243065
C,0.901317655,4.9722531737,-0.910672688
C,0.6594245935,4.0738392037,-1.9382547195
H,0.4235660894,4.4517527614,-2.9297409905
C,0.6975389509,2.691258838,-1.7412838852
C,2.5634894137,-0.0049851572,0.1495569761
C,3.5514271092,0.0861050637,-0.8703376208
C,4.8212569417,-0.4442978631,-0.6740277247
H,5.5484356405,-0.3687756398,-1.4775690387
C,5.1903538931,-1.0794106595,0.5094349573
C,4.2411612773,-1.1470938181,1.513420039
H,4.4955576848,-1.6126537431,2.4619423046
C,2.9573327597,-0.616674268,1.3535189869
P,-1.5491526886,0.5670402671,-0.7393086376
C,-2.7438409286,1.1441230521,0.5308635616
C,-4.1088398754,0.85906443,0.4551277799
C,-2.3099598197,2.1247124865,1.4313590262
C,-5.0113028515,1.4998751546,1.2993489832
H,-4.4710819312,0.1240583136,-0.2550825103
C,-3.2076275677,2.7467255724,2.2878510714
H,-1.261917886,2.4096261376,1.4489332117
C,-4.5637556244,2.4330527816,2.2261064777
H,-6.0664604705,1.2612832904,1.2346030604
H,-2.8523348733,3.4920319699,2.98980692
H,-5.2668883134,2.9255383982,2.8871208881
C,-2.4182404432,-0.8653188228,-1.5073390175
C,-2.8362410323,-2.0569383445,-0.898728022
C,-2.7028387129,-0.6774881154,-2.8645340174
C,-3.4942963234,-3.0319623714,-1.6371161982
H,-2.6372779896,-2.2423948809,0.1481249257
C,-3.3760813999,-1.6483690272,-3.6014485833

H,-2.3852984586,0.239693075,-3.3490227465
C,-3.764948141,-2.8318586075,-2.98877652
H,-3.7957515798,-3.9532473583,-1.1528192338
H,-3.5846554248,-1.481309703,-4.6513599396
H,-4.2784191707,-3.5971788806,-3.5588125928

Zero-point correction= 0.808744 (Hartree/Particle)
Thermal correction to Energy= 0.853143
Thermal correction to Enthalpy= 0.854087
Thermal correction to Gibbs Free Energy= 0.734057
Sum of electronic and zero-point Energies= -2049.894125
Sum of electronic and thermal Energies= -2049.849726
Sum of electronic and thermal Enthalpies= -2049.848782
Sum of electronic and thermal Free Energies= -2049.968812

Table S10 Atomic coordinates and energies of **$SiCl_4$** at the M062X-D3/6-311G(d,p) level of theory.

Si,1.0231800173,-1.4650253609,-0.0000005311
Cl,1.6981092967,-0.5109309448,1.6526361704
Cl,-1.0010178538,-1.4652387365,0.0000002438
Cl,1.6978982421,-3.3734556417,-0.0000002114
Cl,1.6981094776,-0.5109314762,-1.6526356718

Zero-point correction= 0.007515 (Hartree/Particle)
Thermal correction to Energy= 0.013908
Thermal correction to Enthalpy= 0.014852
Thermal correction to Gibbs Free Energy= -0.024907
Sum of electronic and zero-point Energies= -2130.449980
Sum of electronic and thermal Energies= -2130.443588
Sum of electronic and thermal Enthalpies= -2130.442644
Sum of electronic and thermal Free Energies= -2130.482403

Table S11 Atomic coordinates and energies of **$MeSiHCl_2$** at the M062X-D3/6-311G(d,p) level of theory.

Si,1.0425040336,-1.4514412858,-0.0393150751
Cl,1.7094280422,-0.4822004011,1.6494949246
Cl,-1.0156173836,-1.4457705226,-0.0193245013
H,1.4775430296,-2.8497988922,0.0577070627
C,1.6480414027,-0.5607491419,-1.5423914766
H,2.7397428495,-0.5464631989,-1.5585663833
H,1.2906918461,-1.0588619137,-2.4459748093
H,1.2870922838,0.4691344641,-1.5476625556

Zero-point correction= 0.049637 (Hartree/Particle)
Thermal correction to Energy= 0.055581

Thermal correction to Enthalpy= 0.056526
Thermal correction to Gibbs Free Energy= 0.019220
Sum of electronic and zero-point Energies= -1250.432993
Sum of electronic and thermal Energies= -1250.427049
Sum of electronic and thermal Enthalpies= -1250.426104
Sum of electronic and thermal Free Energies= -1250.463410

Table S12 Atomic coordinates and energies of **Ph_2PCl** at the M062X-D3/6-311G(d,p) level of theory.

P,-4.1058391711,0.4980834881,0.2490386067
C,-4.6995268602,-1.2361809058,0.2196214281
C,-4.4479999441,-2.1072747929,-0.8452580325
C,-5.4101304877,-1.6901245919,1.3292418027
C,-4.907154339,-3.4139179345,-0.7954981055
H,-3.8947251719,-1.7528343787,-1.7085238287
C,-5.8637075962,-3.0066772018,1.381228768
H,-5.6124300318,-1.0133990511,2.1526599306
C,-5.6131476141,-3.8650170297,0.3199457226
H,-4.715577425,-4.0856388639,-1.6236105537
H,-6.4141497753,-3.3552014205,2.246619146
H,-5.9682610606,-4.888098198,0.3559439819
C,-2.3609254981,0.2338957471,-0.2768401695
C,-1.707997006,1.1098991762,-1.1453597635
C,-1.6281059515,-0.7817551572,0.3453813341
C,-0.3510406223,0.95552501,-1.4058706475
H,-2.2606974081,1.9032854895,-1.6340468677
C,-0.2710074138,-0.9285150713,0.0863534136
H,-2.1200954677,-1.4723703232,1.0221342277
C,0.3703747847,-0.0616641014,-0.7916727443
H,0.1418697343,1.6332778055,-2.0925309512
H,0.283185093,-1.7257690343,0.5670510705
H,1.4274139951,-0.1795697355,-0.9973832925
Cl,-4.9118448825,1.1726896854,-1.5784176359

Zero-point correction= 0.185400 (Hartree/Particle)
Thermal correction to Energy= 0.197624
Thermal correction to Enthalpy= 0.198568
Thermal correction to Gibbs Free Energy= 0.144539
Sum of electronic and zero-point Energies= -1264.583896
Sum of electronic and thermal Energies= -1264.571672
Sum of electronic and thermal Enthalpies= -1264.570728
Sum of electronic and thermal Free Energies= -1264.624757

Table S13 Atomic coordinates and energies of ***n*BuLi** at the M062X-D3/6-311G(d,p) level of theory.

C,-0.781032721,-0.0368675989,0.0010882701
C,0.7469500883,-0.0659881529,0.0021032117
H,-1.1719080132,0.9834403122,0.003164468
H,-1.1782067026,-0.545049956,-0.8823982983
H,-1.1794412735,-0.5491151897,0.8816740764
C,1.3266933097,-1.4858017475,0.0002112245
H,1.130898307,0.470146416,-0.8730074333
H,1.1296748631,0.4672547569,0.8795079843
C,2.8624056469,-1.5584690184,0.0009677977
H,0.9176575586,-2.0144972141,0.8730192305
H,0.9186603142,-2.0117672164,-0.8747072028
H,3.2292561501,-0.9888196201,-0.8676201468
H,3.2282514492,-0.9916044285,0.8717966078
Li,3.7026661532,-3.3516276725,-0.0014169197

Zero-point correction= 0.120385 (Hartree/Particle)
Thermal correction to Energy= 0.127431
Thermal correction to Enthalpy= 0.128375
Thermal correction to Gibbs Free Energy= 0.090362
Sum of electronic and zero-point Energies= -165.162691
Sum of electronic and thermal Energies= -165.155645
Sum of electronic and thermal Enthalpies= -165.154701
Sum of electronic and thermal Free Energies= -165.192714

Table S14 Atomic coordinates and energies of **Butane** at the M062X-D3/6-311G(d,p) level of theory.

C,2.1521550167,-0.264769248,-0.0000027109
C,0.8410160451,0.516929738,-0.0000808185
H,3.0176977223,0.4003279427,-0.0001732206
H,2.221935249,-0.9060626329,0.8824679595
H,2.2218437128,-0.9063933508,-0.8822413033
C,-0.3866181082,-0.3923855635,0.0000422733
H,0.8009037626,1.1725814875,0.8765714677
H,0.8008820853,1.172376476,-0.876884486
C,-1.6973926581,0.3897595357,0.0000256789
H,-0.346582612,-1.0480649521,-0.8765754518
H,-0.346516613,-1.0479184875,0.8767667829
H,-1.7669476168,1.0312828318,0.8822809683
H,-1.7669956396,1.0311633806,-0.8823128874
H,-2.5632938661,-0.2750221974,0.0000940979

Zero-point correction= 0.132702 (Hartree/Particle)
Thermal correction to Energy= 0.138483
Thermal correction to Enthalpy= 0.139428
Thermal correction to Gibbs Free Energy= 0.104668
Sum of electronic and zero-point Energies= -158.271120

Sum of electronic and thermal Energies= -158.265339
Sum of electronic and thermal Enthalpies= -158.264394
Sum of electronic and thermal Free Energies= -158.299154

Table S15 Atomic coordinates and energies of **LiCl** at the M062X-D3/6-311G(d,p) level of theory.

Li,-5.011338845,1.15577888,0.
Cl,-7.032781575,1.15577888,0.

Zero-point correction= 0.001462 (Hartree/Particle)
Thermal correction to Energy= 0.003961
Thermal correction to Enthalpy= 0.004905
Thermal correction to Gibbs Free Energy= -0.019228
Sum of electronic and zero-point Energies= -467.792512
Sum of electronic and thermal Energies= -467.790013
Sum of electronic and thermal Enthalpies= -467.789069
Sum of electronic and thermal Free Energies= -467.813202

Table S16 Imaginary frequencies and vibrational frequencies (cm^{-1}) of optimized structures at the M062X-D3/6-311G(d,p) level of theory.

	3	**4**	**5**	**6**	**7**	**5'**	**6'**	**7'**
Freq.	24.51	23.97	7.19	25.24	11.45	17.80	13.05	23.40
I.F.	0	0	0	0	0	0	0	0

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