# Supporting Information

# Complexation Behaviour of LiCl and $LiPF_6$ – Model Studies in the Solid-State and in Solution Using a Bidentate Picolyl-Based Ligand

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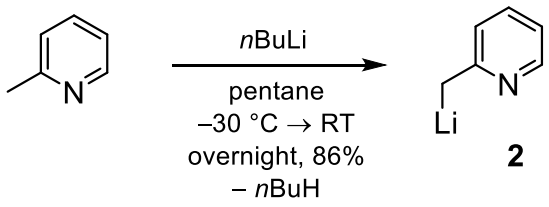
## 1. General Remarks

All experiments were performed under an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 140 °C prior to use. Diethyl ether, hexane, pentane, tetrahydrofuran (THF), acetonitrile, dichloromethane (DCM), and toluene were dried and degassed with a MBraun SP800 solvent purification system. 2-Picoline (98%, ABCR), 2,6-lutidine (98%, Sigma-Aldrich), dichlorodiphenylsilane (**1**) (97%, Sigma-Aldrich), *n*-Butyllithium (1.6 M or 2.5 M solution in hexane, Sigma-Aldrich), and thallium hexafluorophosphate ($TlPF_6$) (97%, Strem) were used without further purification. *tert*-Butylamine (98%, Sigma-Aldrich) was quickly dried over molecular sieves (MS-5Å) prior to use. 2-Picolyl-*N*-borane was synthesized according to a published procedure.[1] For NMR spectroscopy, benzene-$d_6$ (dried over Na/K amalgam), THF-$d_8$ (dried over Na), or DCM-$d_2$ (dried over CaH) were used. NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz). Chemical shifts ($\delta$) are reported in parts per million (ppm). $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra are referenced to tetramethylsilane ($SiMe_4$, $\delta$ = 0.0 ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. $^{29}Si\{^{1}H\}$ NMR spectra are referenced to $SiMe_4$ ($\delta$ = 0.0 ppm), $^{7}Li\{^{1}H\}$ NMR spectra to LiCl (1 M in $D_2O$, $\delta$ = 0.0 ppm), and $^{31}P\{^{1}H\}$ NMR spectra to $H_3PO_4$ (85% in $D_2O$, $\delta$ = 0.0 ppm) as external standard. Solid-state $^{7}Li$ NMR spectroscopy was performed on an $Infinity_{plus}$ spectrometer system (Agilent) operated at 7 T, equipped with a Chemagnetics–Varian 6 mm pencil magic angle spinning (MAS) probe. The spectra were recorded at the MAS rate of 5.5 kHz, a $\pi/16$ pulse of 4.0 μs, and a relaxation delay of 30 s. The spectra were indirectly referenced to LiCl (1 M in $H_2O$). For the assignment of the multiplicities the following abbreviations were used: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. $^{1}H$-diffusion-ordered NMR ($^{1}H$ DOSY) spectra were recorded on an Avance III 600 (600.13 MHz) spectrometer equipped with z-gradients, 5 mm TBI-F probe and BVTE 3900 unit at 300 K. The NMR spectra were processed with the Bruker program TopSpin® 3.2 and the diffusion coefficients were determined according to *Müller* and *Jerschow*[2] applying the Bruker software *T1/T2* relaxation module. High resolution mass spectrometry was carried out on a Jeol AccuTOF GCX or an Agilent Q-TOF 6540 UHD mass spectrometer. Elemental analyses were performed on a Vario MICRO cube apparatus.

## 2. Synthetic Procedures

### 2.1. Synthesis of 2-picolyllithium (2)




*n*-Butyllithium (25 ml of a 1.6 M solution in hexane, 40.0 mmol) was added dropwise to a solution of 2-picoline (3.72 g, 3.95 ml, 40.0 mmol) in pentane (120 ml) at –30 °C. The resulting orange suspension was allowed to slowly warm up to room temperature and kept stirring for 2 h. Then, the reaction mixture was stored overnight at room temperature for complete precipitation of the formed orange solid. The mother liquor was discarded *via* a PTFE cannula, the solid material washed with pentane and dried under vacuum yielding 2-picolyllithium (**2**) as an orange solid (3.40 g, 34.3 mmol, 86 %).

$^{1}$H NMR (400.13 MHz, THF-$d_8$, 25 °C): $\delta$ = 1.73 (m, $OCH_2CH_2$), 2.36 (bs, 1H, PyCH*H*), 2.51 (bs, 1H, PyC*H*H), 3.58 (m, $OCH_2CH_2$), 4.66 (ddd, $^{3}J_{HH}$ = 6.4 Hz, $^{3}J_{HH}$ = 5.7 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, $H_{m\text{-Py}}$), 5.50 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, $H_{m\text{-Py}}$), 5.89 (ddd, $^{3}J_{HH}$ = 9.0 Hz, $^{3}J_{HH}$ = 5.7 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, $H_{p\text{-Py}}$), 6.74 (dd, $^{3}J_{HH}$ = 5.7 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, $H_{o\text{-Py}}$).

$^{13}$C{$^{1}$H} NMR (100.62 MHz, THF-$d_8$, 25 °C): $\delta$ = 25.4 (s, $OCH_2CH_2$), 57.3 (s, Py$CH_2$), 67.3 (s, $OCH_2CH_2$), 94.9 (s, $C_{m\text{-Py}}$), 114.8 (s, $C_{m\text{-Py}}$), 130.0 (s, $C_{p\text{-Py}}$), 147.7 (s, $C_{o\text{-Py}}$), 162.9 (s, $C_{o\text{-Py}}$).

$^{7}$Li NMR (155.50 MHz, THF-$d_8$, 25 °C): $\delta$ = 0.2.

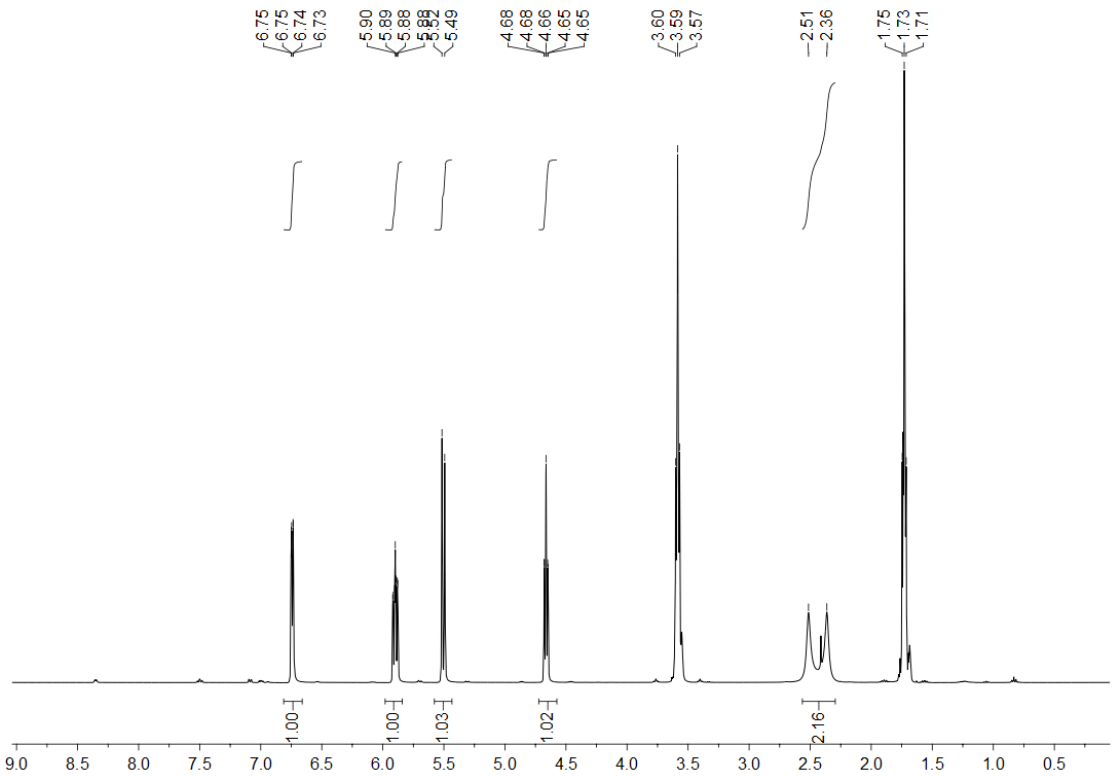



**Figure S1.** $^{1}$H NMR spectrum of 2-picolyllithium (**2**).

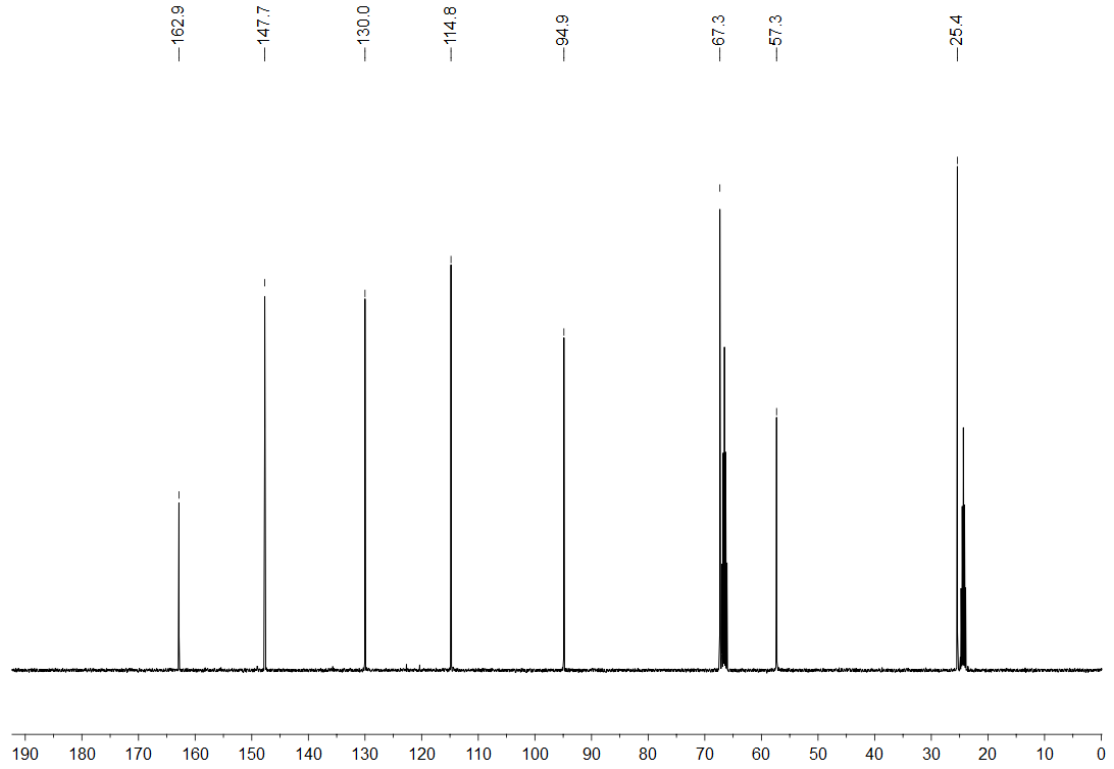



**Figure S2.** $^{13}$C{$^{1}$H} NMR spectrum of 2-picolyllithium (**2**).

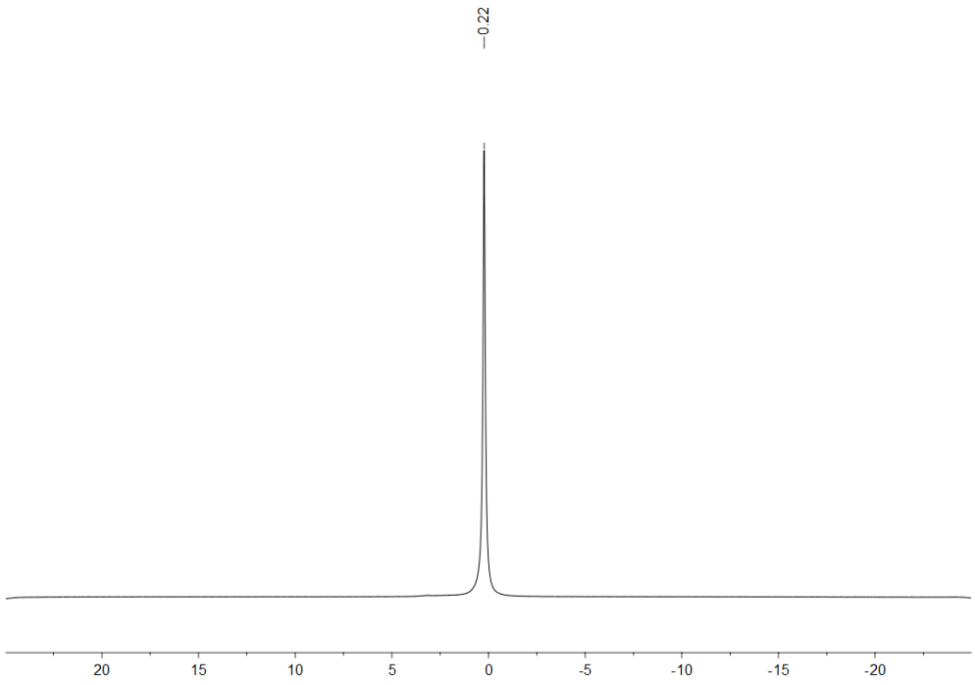
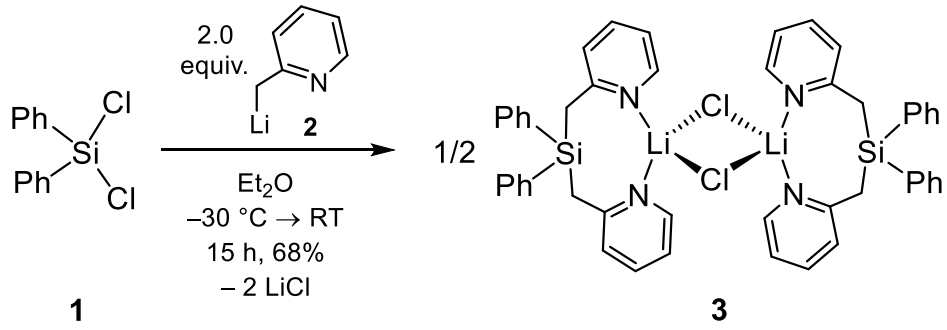



**Figure S3.** $^{7}$Li NMR spectrum of 2-picolyllithium (**2**).

### 2.2. Synthesis of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (3)




Dichlorodiphenylsilane (**1**) (2.55 g, 2.12 ml, 10.0 mmol) was added dropwise to a stirred solution of isolated 2-picolyllithium **2** (2.00 g, 20.0 mmol) in diethyl ether (60 ml) at –30 °C. The reaction mixture was allowed to slowly warm up to room temperature and kept stirring for 15 h. Then, the beige suspension was transferred to a fritted column layered with Celite® *via* a PTFE cannula, filtered and the remaining solids washed with diethyl ether (2 x 15 ml). The solids collected in the fritted column were carefully extracted with dichloromethane (6 x 20 ml). The filtrates were collected and all volatiles removed *in vacuo* yielding compound **3** as a colourless solid (2.80 g, 3.4 mmol, 68 %). Colourless crystals, suitable for single-crystal X-ray diffraction analysis were obtained after recrystallization of **3** from a hot, concentrated solution in acetonitrile/tetrahydrofuran.

HRMS (ESI+), Calcd. m/z for $C_{48}H_{44}LiN_4Si_2$ [(M – $LiCl_2$)$^+$]: 739.3259. Found: 739.3292.

Anal. Calcd. for $C_{48}H_{44}Cl_2Li_2N_4Si_2$: C 70.49, H 5.42, N 6.85. Found: C 69.53, H 5.63, N 6.74.

**Solution NMR spectroscopy of [$Ph_2Si(2\text{-}CH_2Py)_2$·LiCl]$_2$ (3) in DCM-$d_2$:**

$^1$H NMR (400.13 MHz, DCM-$d_2$, 25 °C): δ = 2.97 (s, 4H, Si(C$H_2$)$_2$), 6.77 (bd, $^3J_{HH}$ = 6.8 Hz, 2H, $H_{m\text{-Py}}$), 6.91 (bdd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 5.5 Hz, 2H, $H_{m\text{-Py}}$), 7.25 (m, 4H, $H_{Ph}$), 7.34 (m, 8H, $H_{Ph}$ and $H_{p\text{-Py}}$), 8.53 (bs, 2H, $H_{o\text{-Py}}$).

$^{13}$C{$^1$H} NMR (100.62 MHz, DCM-$d_2$, 25 °C): δ = 25.8 (bs, Si$C$H$_2$), 119.9 (s, $C_{m\text{-Py}}$), 123.9 (bs, $C_{m\text{-Py}}$), 128.0 (s, $C_{Ph}$), 129.8 (s, $C_{Ph}$), 134.5 (bs, $C_{Ph}$), 135.6 (s, $C_{Ph}$), 136.2 (bs, $C_{p\text{-Py}}$), 149.6 (bs, $C_{o\text{-Py}}$), 160.2 (s, $C_{o\text{-Py}}$).

$^{29}$Si{$^1$H} NMR (79.49 MHz, DCM-$d_2$, 25 °C): δ = –8.3.

$^7$Li NMR (155.50 MHz, DCM-$d_2$, 25 °C): δ = 2.5.

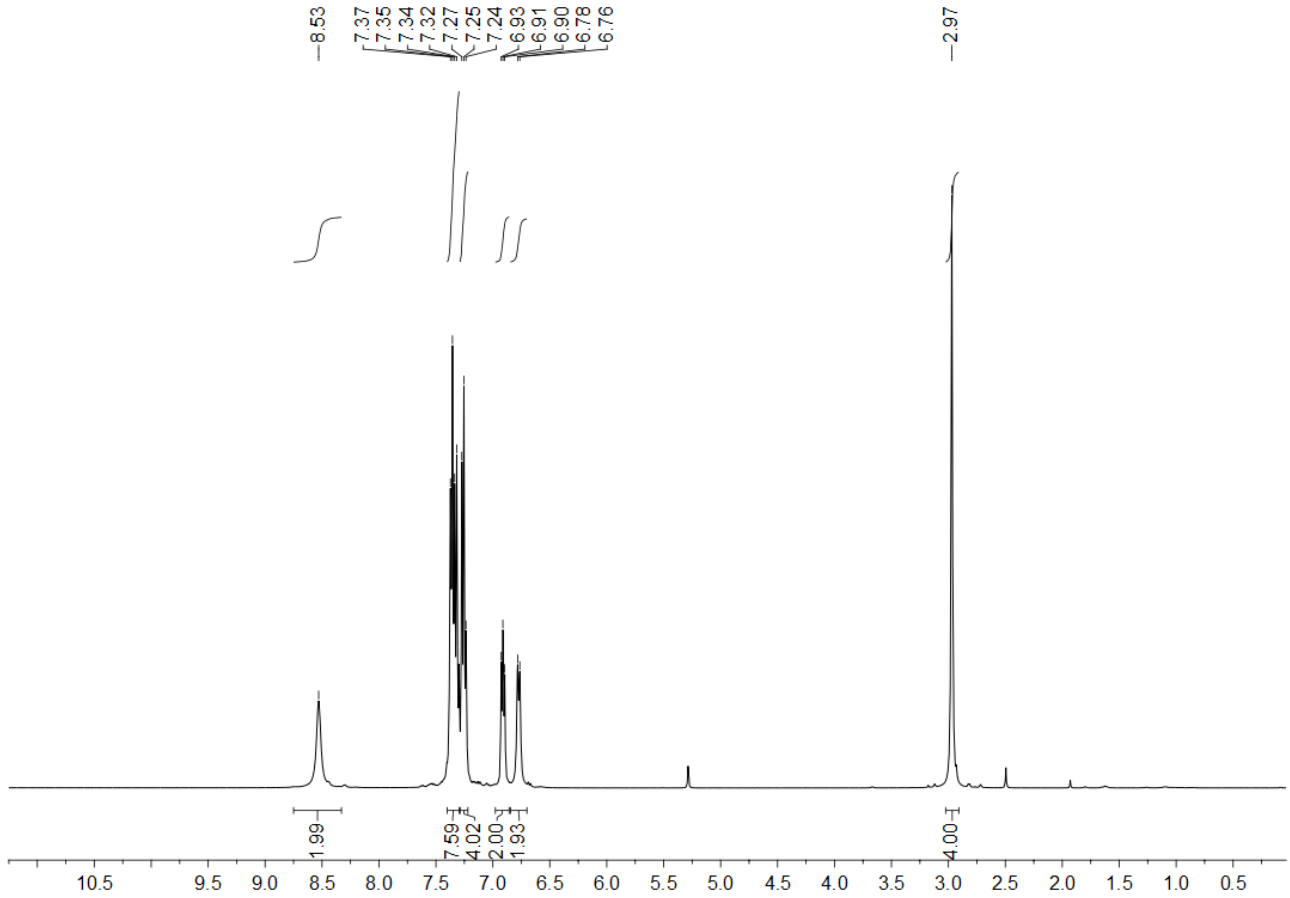



**Figure S4.** $^1$H NMR spectrum of [$Ph_2Si(2\text{-}CH_2Py)_2$·LiCl]$_2$ (**3**) in DCM-$d_2$.

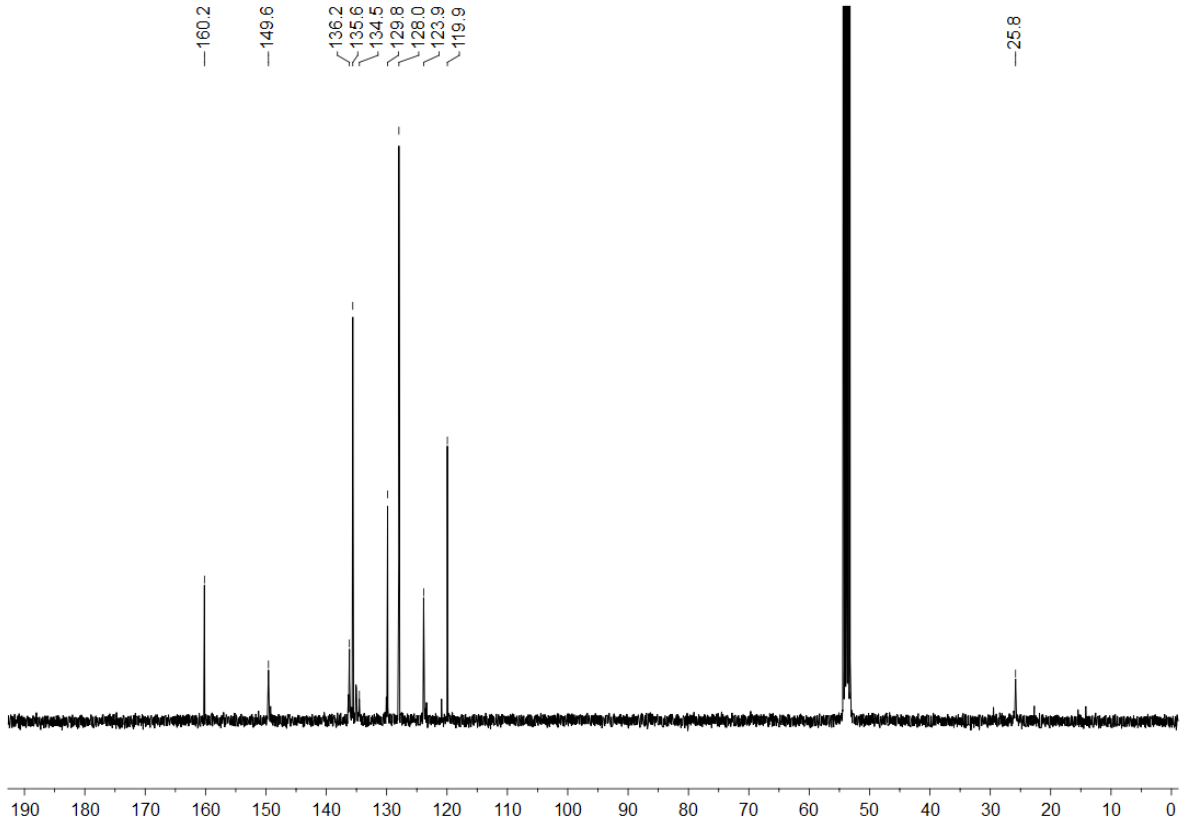



**Figure S5.** $^{13}C\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in DCM-$d_2$.

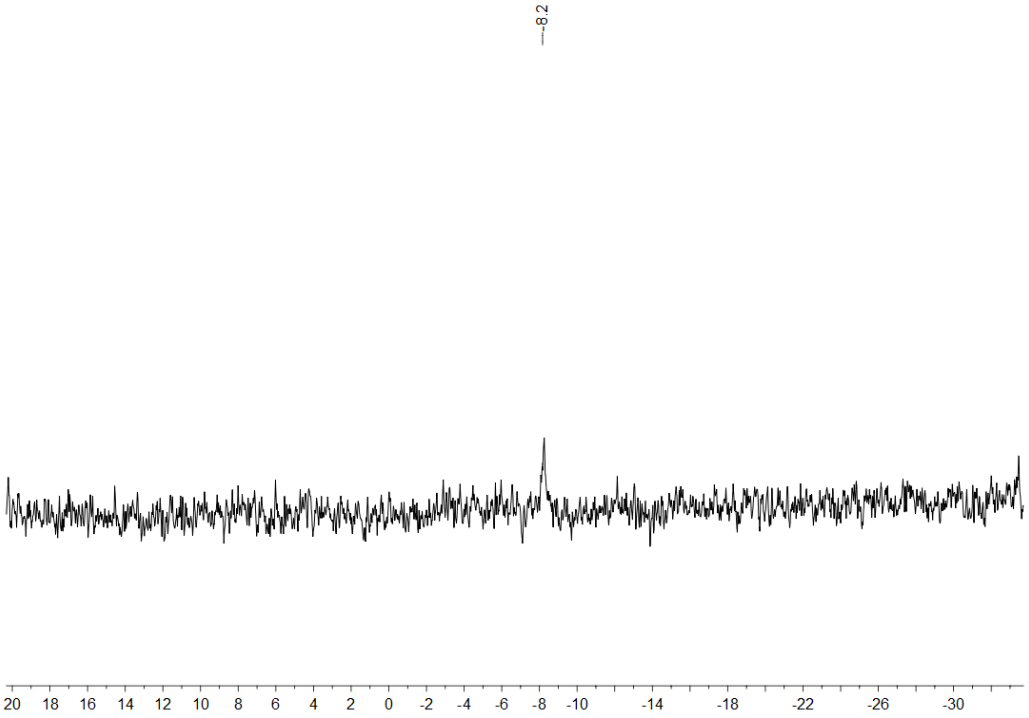



**Figure S6.** $^{29}Si\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in DCM-$d_2$.

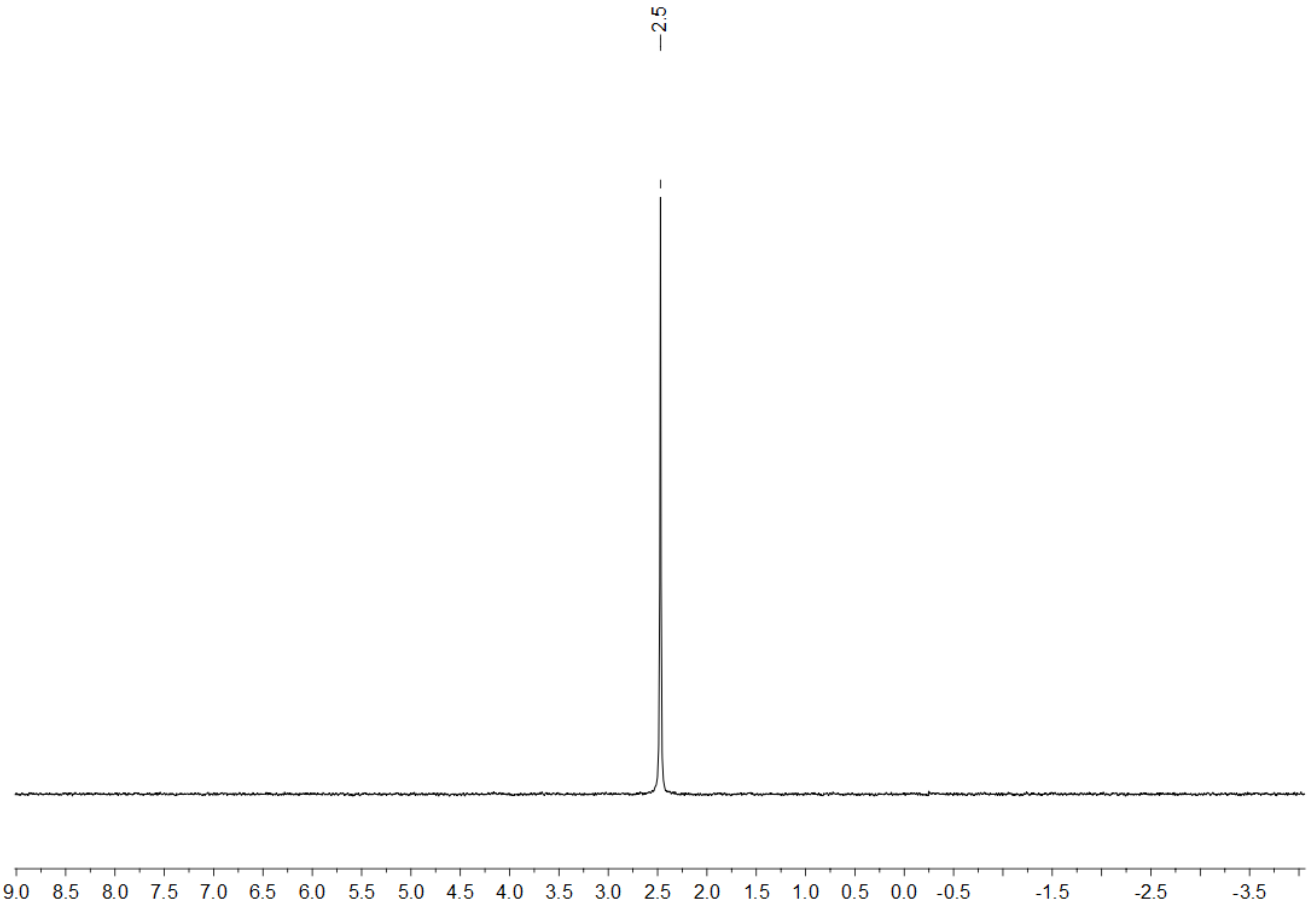



**Figure S7.** $^{7}$Li NMR spectrum of [$Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in DCM-$d^2$.

**Solution NMR spectroscopy of [$Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (3) in THF-$d_8$:**

$^{1}$H NMR (400.13 MHz, THF-$d_8$, 25 °C): $\delta$ = 3.00 (s, 4H, Si(C$H_2$)$_2$), 6.87 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, $H_{m\text{-}Py}$), 6.91 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 5.1 Hz, 2H, $H_{m\text{-}Py}$), 7.21 (m, 4H, $H_{Ph}$), 7.27 (m, 2H, $H_{Ph}$), 7.32 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, $H_{p\text{-}Py}$), 7.46 (m, 4H, $H_{Ph}$), 8.50 (bd, $^{3}J_{HH}$ = 4.2 Hz, 2H, $H_{o\text{-}Py}$).

$^{13}$C{$^{1}$H} NMR (100.62 MHz, THF-$d_8$, 25 °C): $\delta$ = 26.2 (s, Si$CH_2$), 120.0 (s, $C_{m\text{-}Py}$), 124.0 (s, $C_{m\text{-}Py}$), 128.1 (s, $C_{Ph}$), 129.8 (s, $C_{p\text{-}Py}$), 135.6 (s, $C_{Ph}$), 136.1 (m, $C_{Ph}$), 149.8 (s, $C_{o\text{-}Py}$), 160.9 (s, $C_{o\text{-}Py}$).

$^{29}$Si{$^{1}$H} NMR (79.49 MHz, THF-$d_8$, 25 °C): $\delta$ = –8.2.

$^{7}$Li{$^{1}$H} NMR (155.50 MHz, THF-$d_8$, 25 °C): $\delta$ = 0.8.

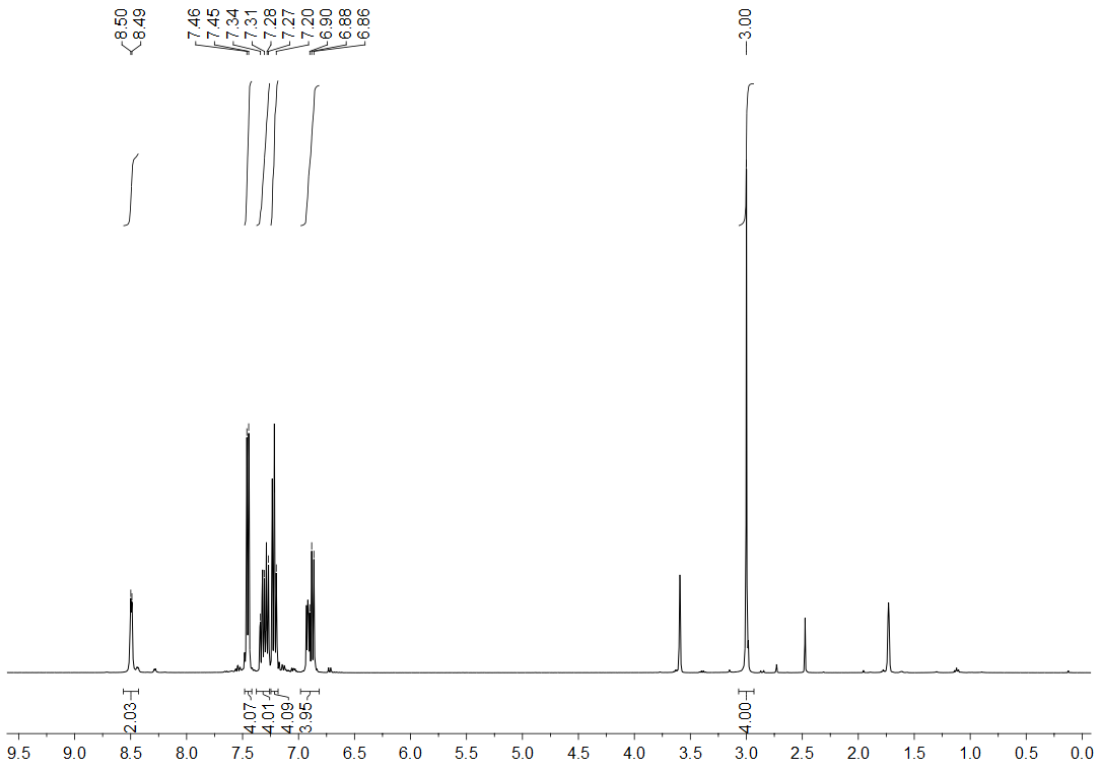



**Figure S8.** $^{1}$H NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in THF-$d_8$.

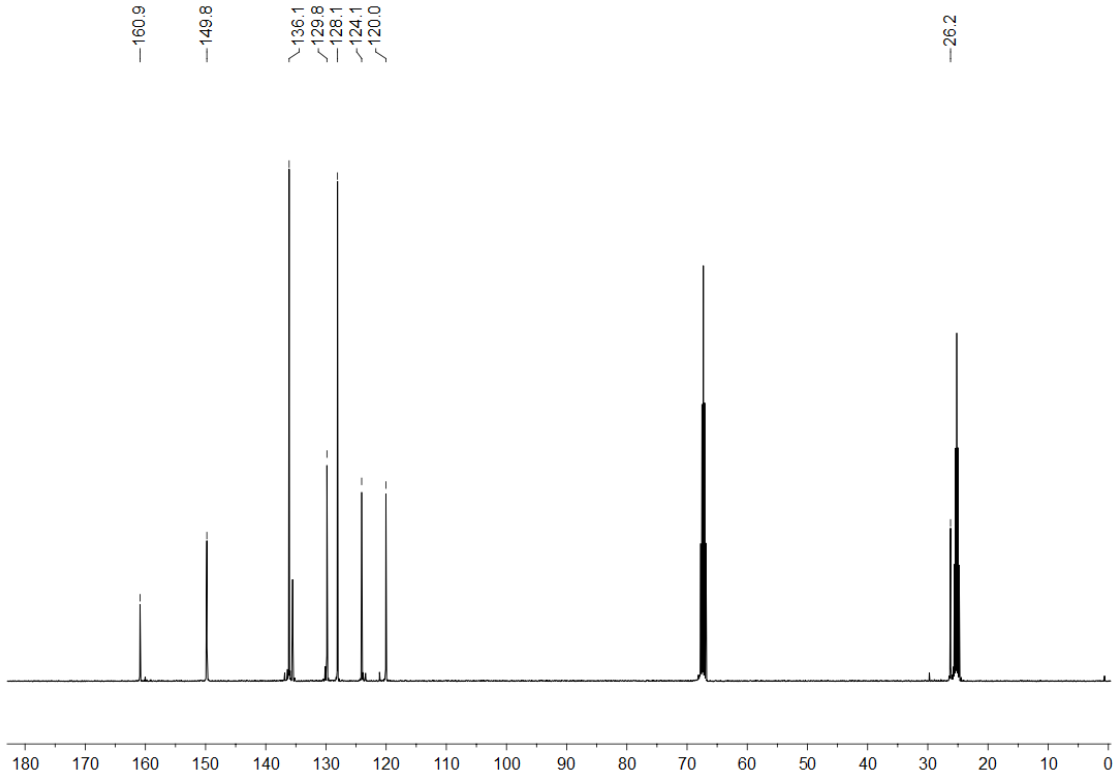



**Figure S9.** $^{13}$C{$^{1}$H} NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in THF-$d_8$.

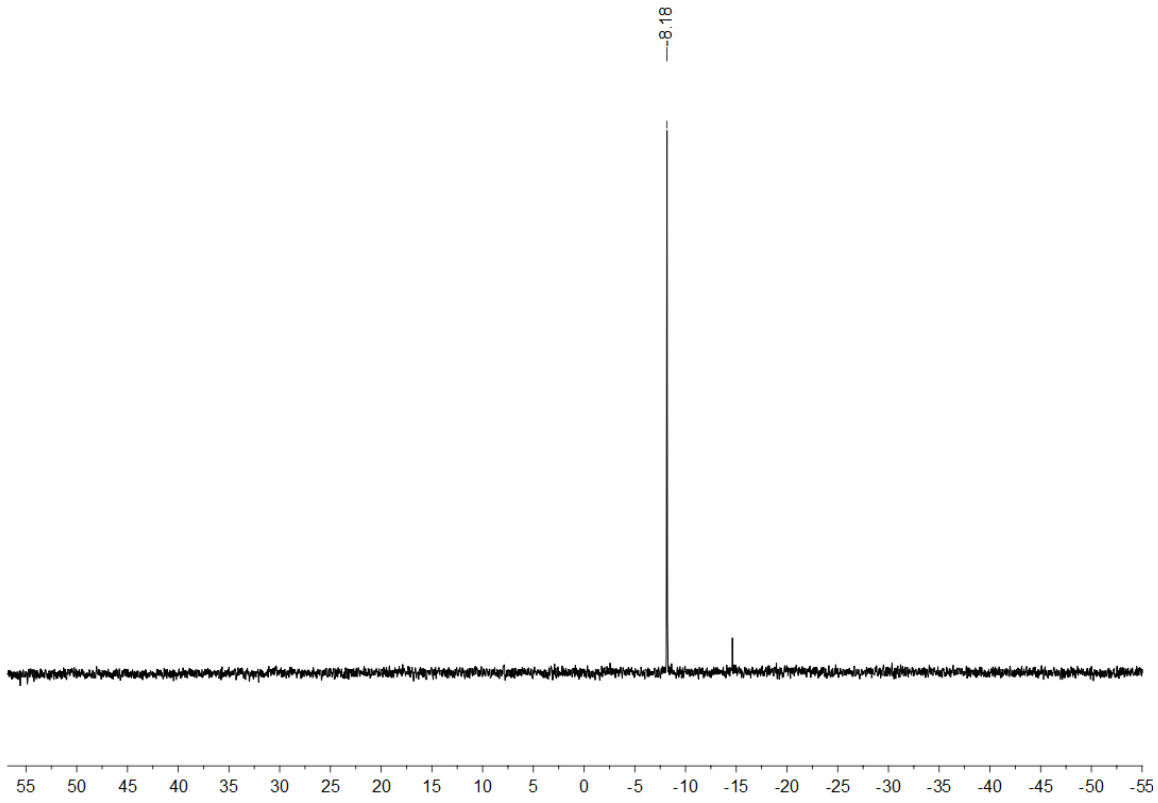



**Figure S10.** $^{29}Si\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in THF-$d_8$.

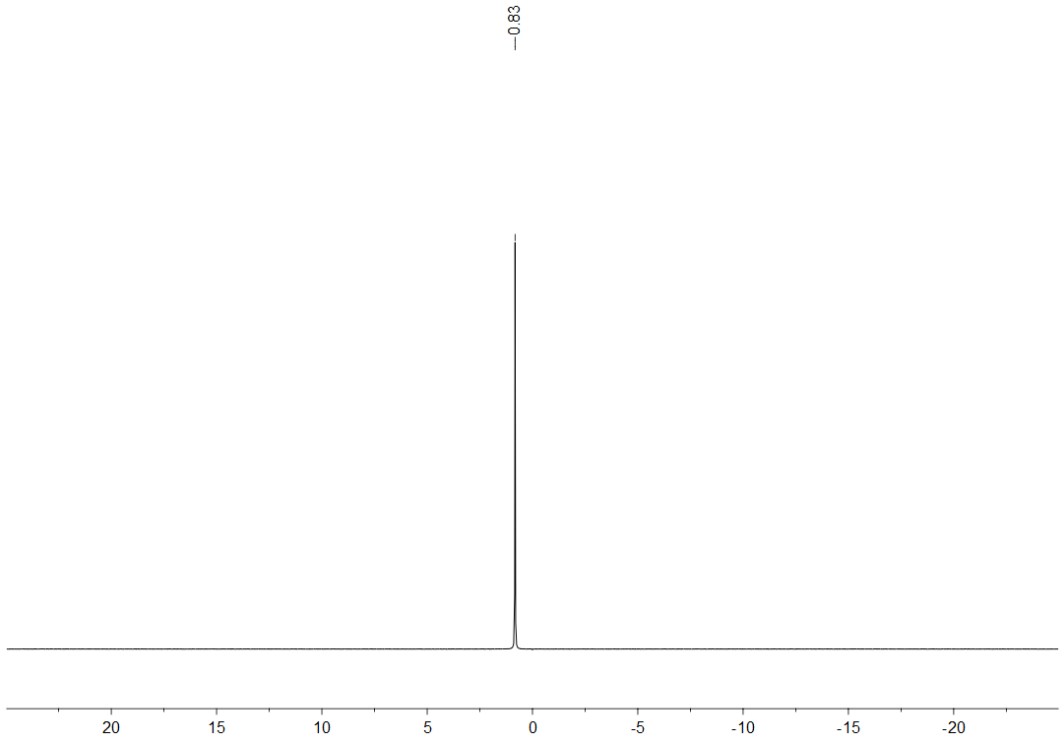



**Figure S11.** $^{7}Li$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) in THF-$d_8$.

**Solid-state $^{7}$Li NMR spectroscopy of [$Ph_2Si(2\text{-}CH_2Py)_2$·LiCl]$_2$ (3):**

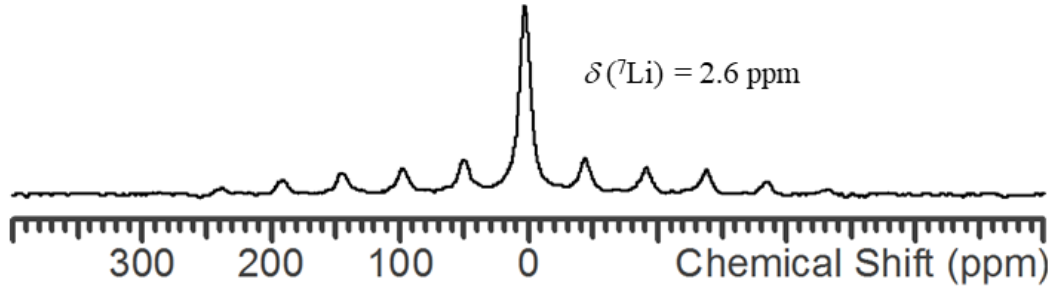
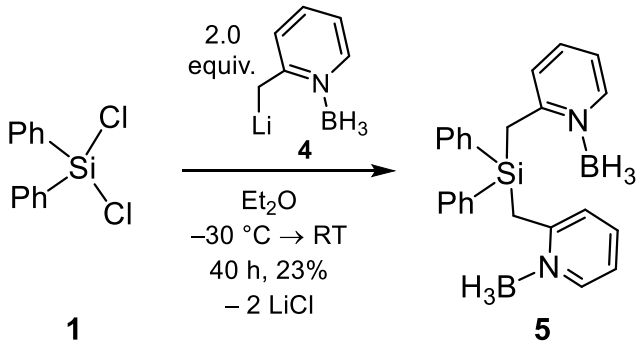



**Figure S12.** Solid-state $^{7}$Li NMR spectrum of [$Ph_2Si(2\text{-}CH_2Py)_2$·LiCl]$_2$ (**3**).

**2.3. Synthesis of $Ph_2Si[2\text{-}CH_2Py(N\text{-}BH_3)]_2$ (5)**




*n*-Butyllithium (40 ml of a 2.5 M solution in hexane, 100.0 mmol) was added dropwise to a solution of 2-picolyl-*N*-borane[1] (10.69 g, 100.0 mmol) in diethyl ether (160 ml) at –70 °C. The resulting red slightly cloudy reaction mixture was allowed to slowly warm up to at room temperature and kept stirring for 4 h yielding a clear red solution. Then, dichlorodiphenylsilane (**1**) (12.66 g, 10.51 ml, 50.0 mmol) was added dropwise under vigorous stirring at –30 °C to the freshly prepared lithiated 2-picolyl-*N*-borane (**4**). The reaction mixture was allowed to slowly warm up to room temperature and stirred over the period of 40 h. The white suspension was transferred to a fritted column layered with Celite® *via* a PTFE cannula, filtered and the remaining solids washed with diethyl ether (2 x 20 ml). The white solids collected in the fritted column were carefully extracted with dichloromethane (6 x 20 ml). The filtrates were collected and all volatiles removed *in vacuo* yielding compound **5** as a white solid (4.60 g, 11.65 mmol, 23 %).

$^{1}$H NMR (400.13 MHz, DCM-$d_2$, 25 °C): $\delta$ = 4.46 (bd, 6H, B$H_3$), 3.47 (s, 4H, Si(C$H_2$)$_2$), 7.07 (m, 4H, $H_{m\text{-Py}}$ and $H_{p\text{-Py}}$), 7.30 (m, 4H, $H_{Ph}$), 7.39 (tt, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 2.3 Hz, 2H, $H_{Ph}$), 7.48 (m, 4H, $H_{Ph}$), 7.56 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, $H_{m\text{-Py}}$), 8.52 (bd, $^{3}J_{HH}$ = 5.8 Hz, 2H, $H_{o\text{-Py}}$).

$^{13}C\{^{1}H\}$ NMR (100.62 MHz, DCM-$d_2$, 25 °C): $\delta$ = 23.7 (s, Si*C*H$_2$), 121.1 (s, $C_{m\text{-Py}}$), 126.5 (s, $C_{p\text{-Py}}$), 127.8 (s, $C_{\text{Ph}}$), 129.9 (s, $C_{\text{Ph}}$), 132.9 (s, $C_{\text{Ph}}$), 135.3 (s, $C_{\text{Ph}}$), 138.8 (s, $C_{m\text{-Py}}$), 148.5 (s, $C_{o\text{-Py}}$), 159.4 (s, $C_{o\text{-Py}}$).

$^{29}Si\{^{1}H\}$ NMR (79.49 MHz, THF-$d_8$, 25 °C): $\delta$ = –7.5.

$^{11}B\{^{1}H\}$ NMR (128.43 MHz, DCM-$d_2$, 25 °C): $\delta$ = –13.4.

HRMS (FDI+), Calcd. m/z for $C_{24}H_{27}N_2SiB_2$ [$M^+$]: 391.21968. Found: 391.21867.

Anal. Calcd. for $C_{24}H_{28}B_2N_2Si$: C 73.13, H 7.16, N 7.11. Found: C 72.56, H 6.96, N 7.00.

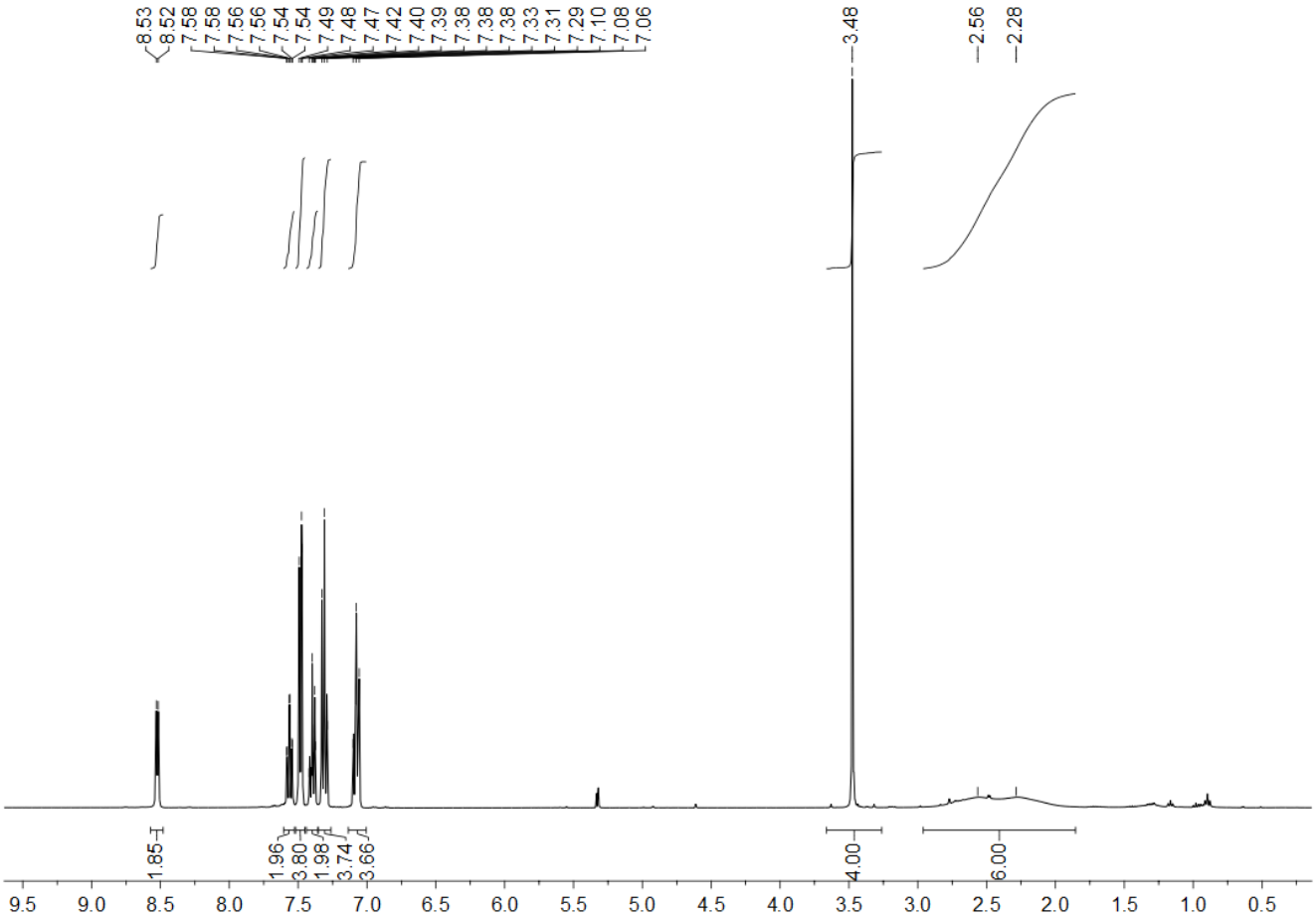



**Figure S13.** $^{1}H$ NMR spectrum of $Ph_2Si[2\text{-}CH_2Py(N\text{-}BH_3)]_2$ (**5**).

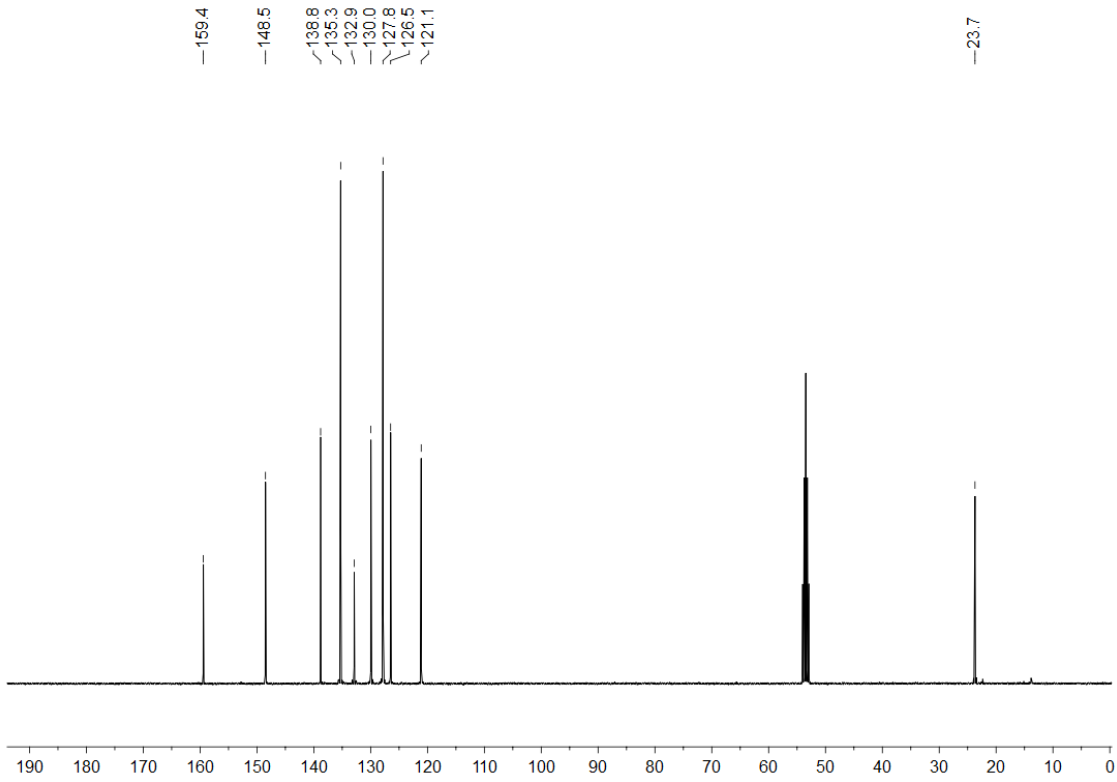



**Figure S14.** $^{13}C\{^{1}H\}$ NMR spectrum of $Ph_2Si[2\text{-}CH_2Py(N\text{-}BH_3)]_2$ (**5**).

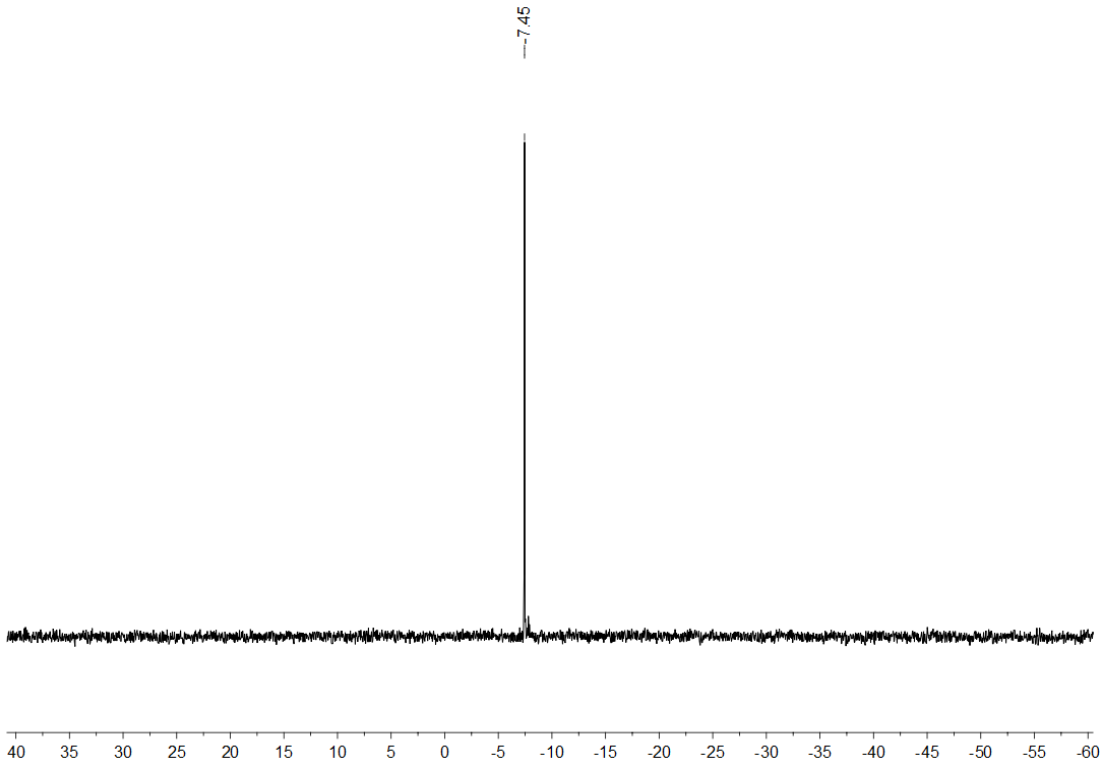



**Figure S15.** $^{29}Si\{^{1}H\}$ NMR spectrum of $Ph_2Si[2\text{-}CH_2Py(N\text{-}BH_3)]_2$ (**5**).

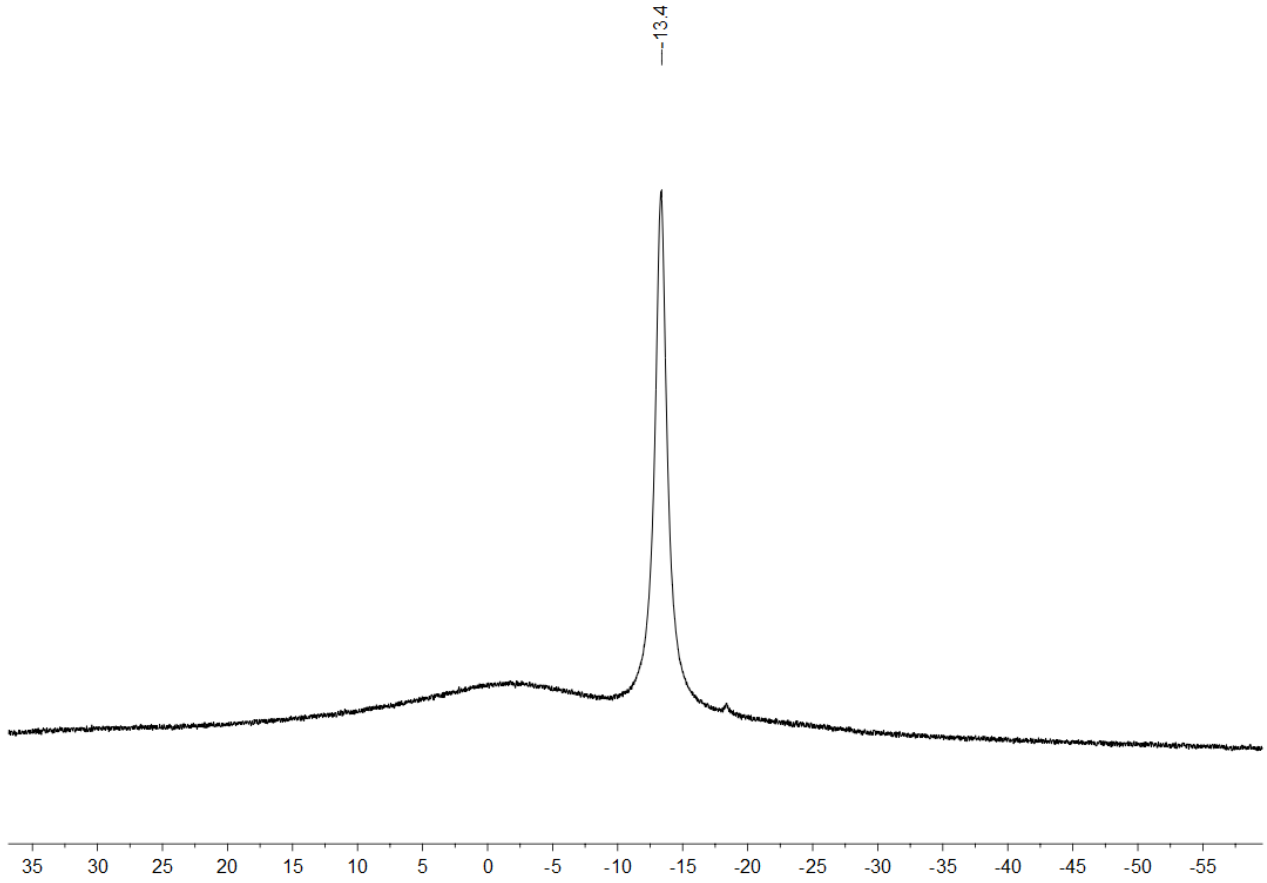
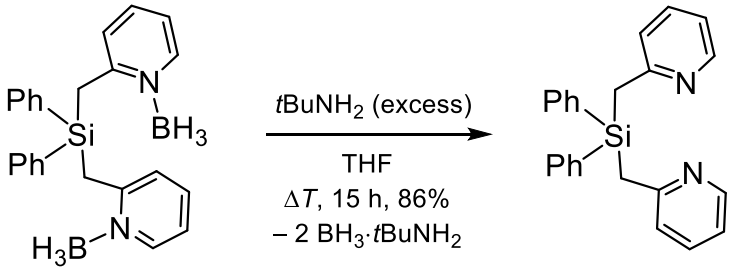



**Figure S16.** $^{11}B\{^{1}H\}$ NMR spectrum of $Ph_2Si[2\text{-}CH_2Py(N\text{-}BH_3)]_2$ (**5**).

### 2.4. Synthesis of $Ph_2Si(2\text{-}CH_2Py)_2$ (6)




**5** **6**

An excess of *tert*-butylamine (15 ml) was added to a solution of compound **5** (2.6 g, 6.60 mmol) in tetrahydrofuran (10 ml) in a thick-walled vessel with a stir bar and sealable TPFE valve at room temperature. The vessel was sealed and placed in an oil bath, maintained at 80 °C for 15 h. After cooling down to room temperature, all volatiles were removed *in vacuo*. The residue was extracted with pentane (30 ml) and the suspension transferred to a fritted column layered with Celite® *via* a PTFE cannula, filtered and the remaining solids washed with pentane (2 x 20 ml). The filtrates

were collected and all volatiles removed *in vacuo* yielding a pale beige oil. Compound **6** was isolated as colourless single-crystalline solid, suitable for single-crystal X-ray diffraction analysis, from pentane at –30 °C (2.08 g, 5.67 mmol, 86 %).

$^{1}$H NMR (400.13 MHz, THF-$d_8$, 25 °C): $\delta$ = 2.98 (s, 4H, Si(C$H_2$)$_2$), 6.89 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 5.2 Hz, 2H, $H_{m\text{-Py}}$), 6.95 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, $H_{m\text{-Py}}$), 7.21 (m, 4H, $H_{Ph}$), 7.28 (m, 2H, $H_{Ph}$), 7.33 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.8 Hz, 2H, $H_{p\text{-Py}}$), 7.49 (m, 4H, $H_{Ph}$), 8.34 (dd, $^{3}J_{HH}$ = 4.8 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, $H_{o\text{-Py}}$).

$^{13}$C{$^{1}$H} NMR (100.62 MHz, THF-$d_8$, 25 °C): $\delta$ = 25.6 (s, Si$C$H$_2$), 119.2 (s, $C_{m\text{-Py}}$), 123.1 (s, $C_{m\text{-Py}}$), 127.2 (s, $C_{Ph}$), 128.9 (s, $C_{Ph}$), 134.9 (s, $C_{Ph}$), 135.1 (s, $C_{p\text{-Py}}$), 135.3 (s, $C_{Ph}$), 148.7 (s, $C_{o\text{-Py}}$), 160.1 (s, $C_{o\text{-Py}}$).

$^{29}$Si{$^{1}$H} NMR (79.49 MHz, benzene-$d_6$, 25 °C): $\delta$ = –7.5.

HRMS (EI+), Calcd. m/z for $C_{24}H_{22}N_2Si$ [$M^+$]: 366.15468. Found 366.15500.

Anal. Calcd. for $C_{24}H_{22}N_2Si$: C 78.64, H 6.05, N 7.64. Found: C 78.11, H 5.92, N 7.13.

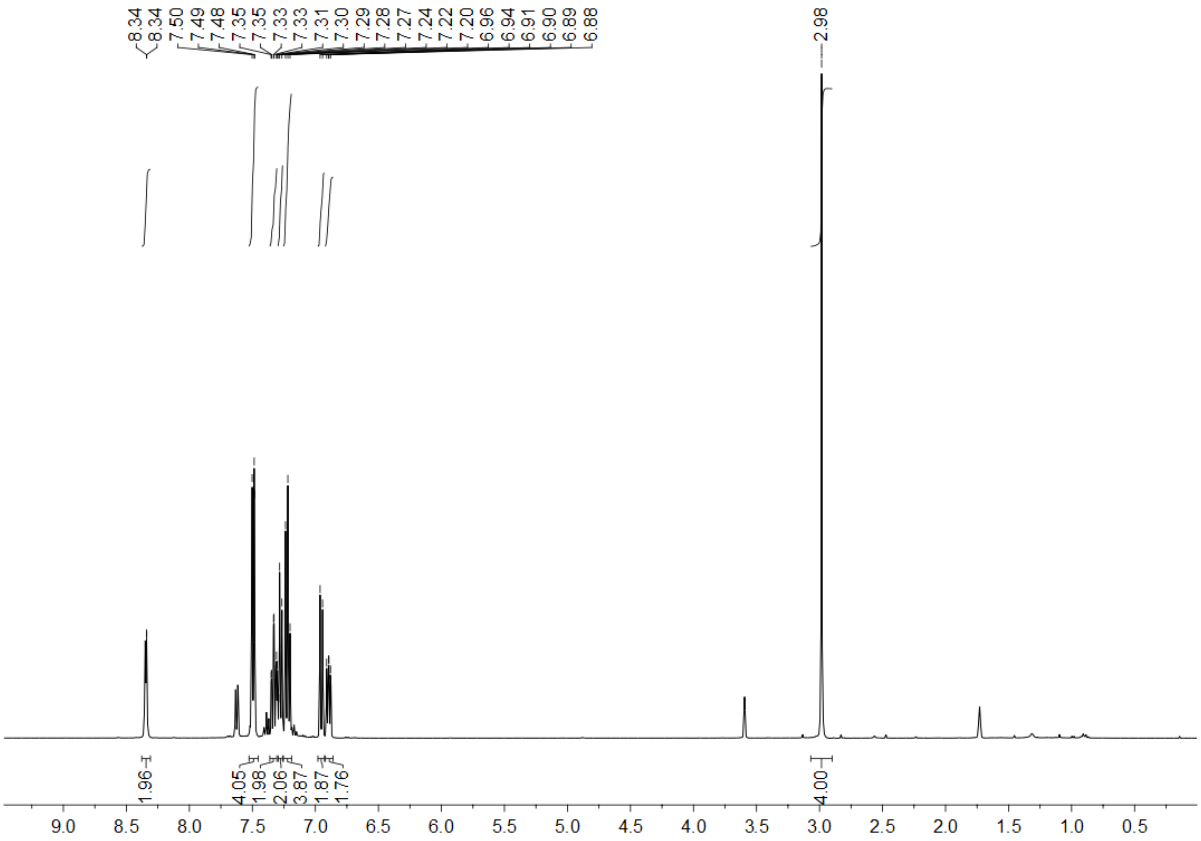



**Figure S17.** $^{1}$H NMR spectrum of $Ph_2Si(2\text{-}CH_2Py)_2$ (**6**).

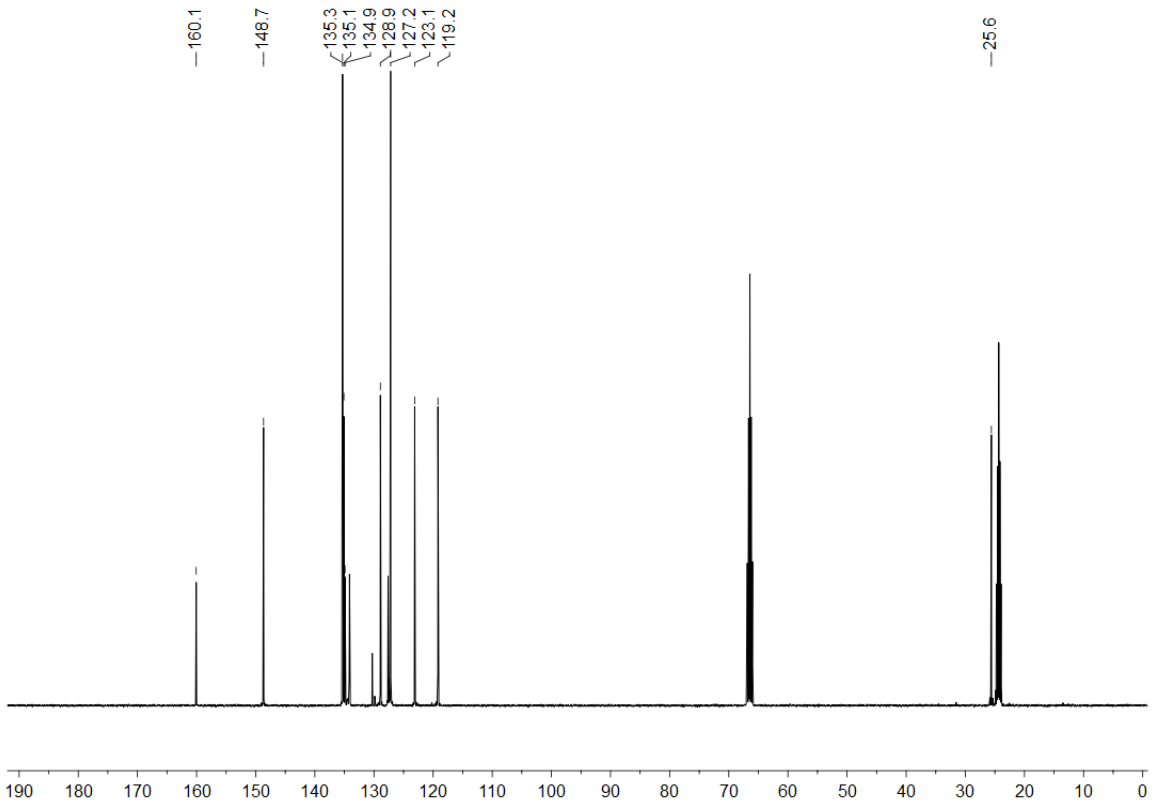



**Figure S18.** $^{13}C\{^{1}H\}$ NMR spectrum of $Ph_2Si(2\text{-}CH_2Py)_2$ (**6**).

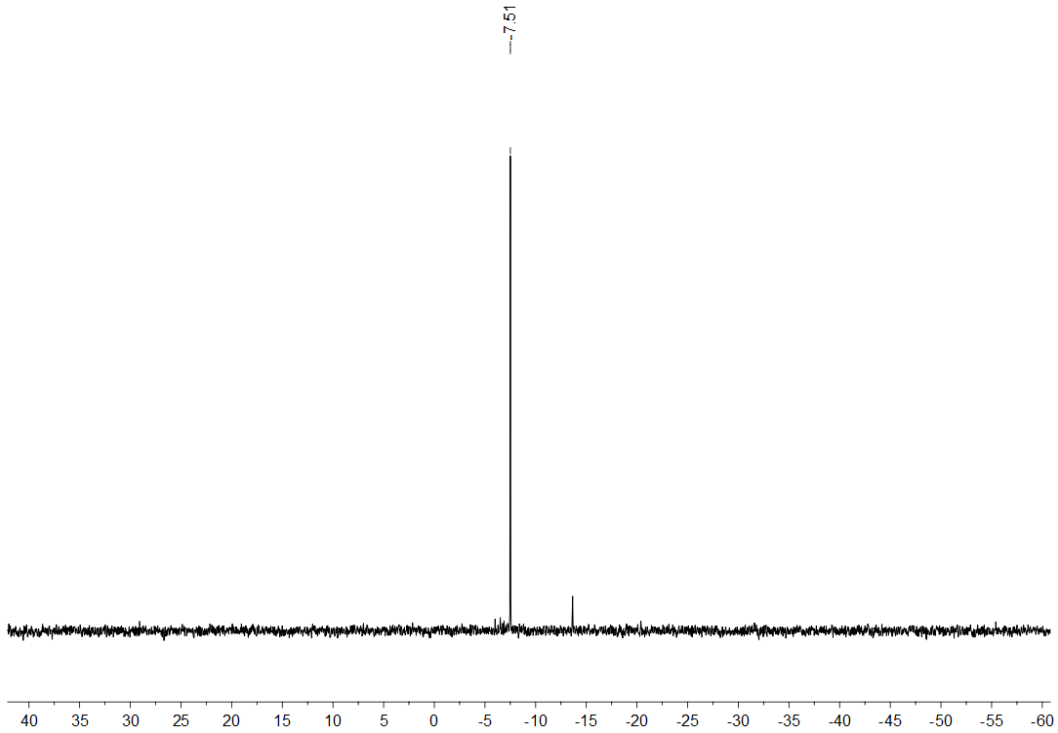
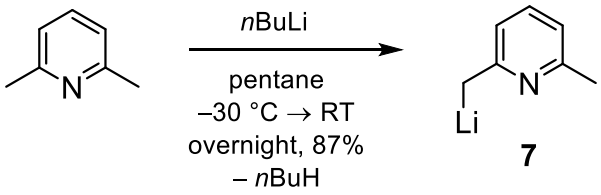



**Figure S19.** $^{29}Si\{^{1}H\}$ NMR spectrum of $Ph_2Si(2\text{-}CH_2Py)_2$ (**6**).

**2.5. Synthesis of 2,6-lutidyllithium (7)**




*n*-Butyllithium (25 ml of a 1.6 M solution in hexane, 40.0 mmol) was added dropwise to a solution of 2,6-lutidine (4.28 g, 4.64 ml, 40 mmol) in pentane (120 ml) at –30 °C. The resulting yellow suspension was allowed to slowly warm up to room temperature and kept stirring overnight. Then, the yellow suspension was transferred to a fritted column *via* a PTFE cannula, filtered and the solid material washed with pentane (20 ml). The mother liquor was discarded, the solid recovered from fritted column, and dried under vacuum yielding 2,6-lutidyllithium (**7**) as a yellow solid (3.93 g, 34.8 mmol, 87 %).

$^{1}$H NMR (400.13 MHz, THF-$d_8$, 25 °C): $\delta$ = 1.79 (s, 3H, C$H_3$), 2.44 (s, 2H, PyCH$H$), 4.85 (d, $^{3}J_{HH}$ = 6.3 Hz, 1H, $H_{m\text{-Py}}$), 5.57 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, $H_{m\text{-Py}}$), 6.09 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, $H_{p\text{-Py}}$).

$^{13}$C{$^{1}$H} NMR (100.62 MHz, THF-$d_8$, 25 °C): $\delta$ = 24.4 (s, Py$C$H$_3$), 54.2 (s, Py$C$H$_2$), 97.0 (s, $C_{m\text{-Py}}$), 112.5 (s, $C_{m\text{-Py}}$), 132.4 (s, $C_{p\text{-Py}}$), 155.6 (s, $C_{o\text{-Py}}$), 165.9 (s, $C_{o\text{-Py}}$).

$^{7}$Li NMR (155.50 MHz, THF-$d_8$, 25 °C): $\delta$ = 0.2.

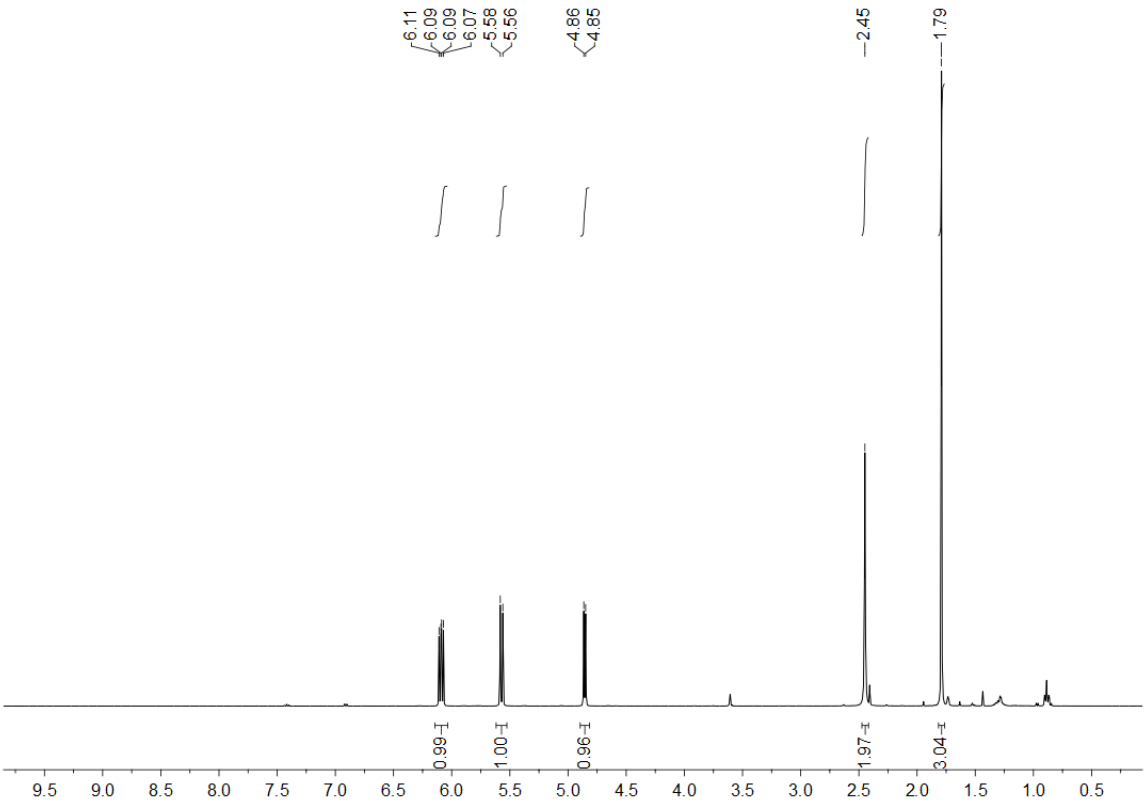



**Figure S20.** $^{1}$H NMR spectrum of 2,6-lutidyllithium (**7**).

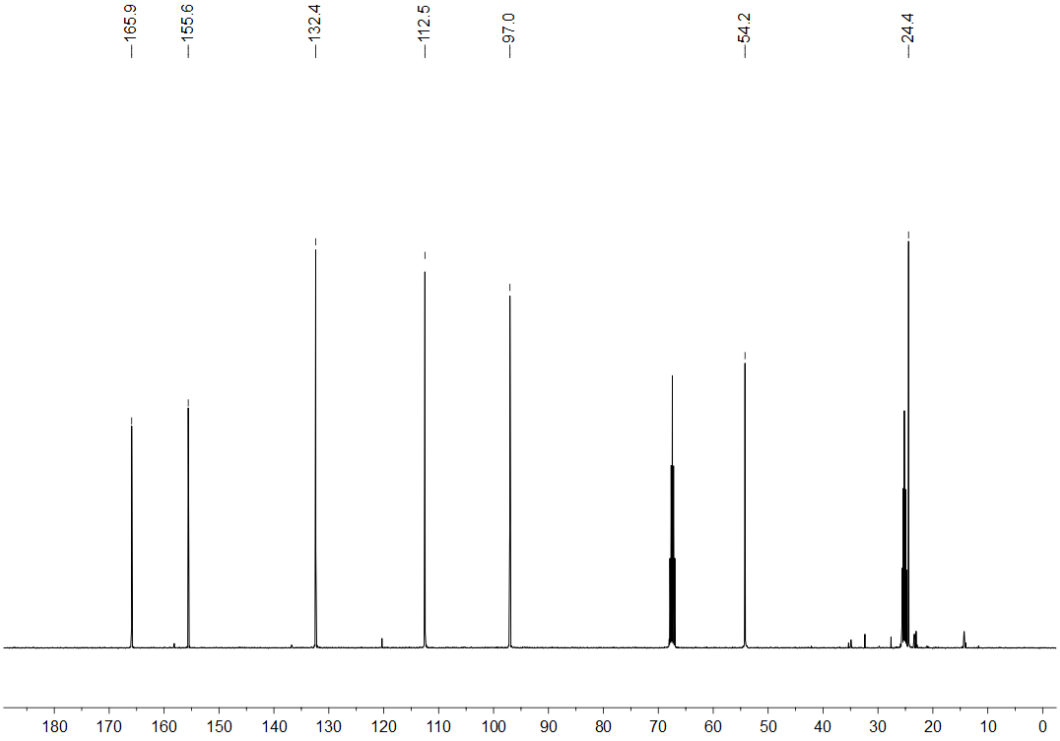



**Figure S21.** $^{13}$C{$^{1}$H} NMR spectrum of 2,6-lutidyllithium (**7**).

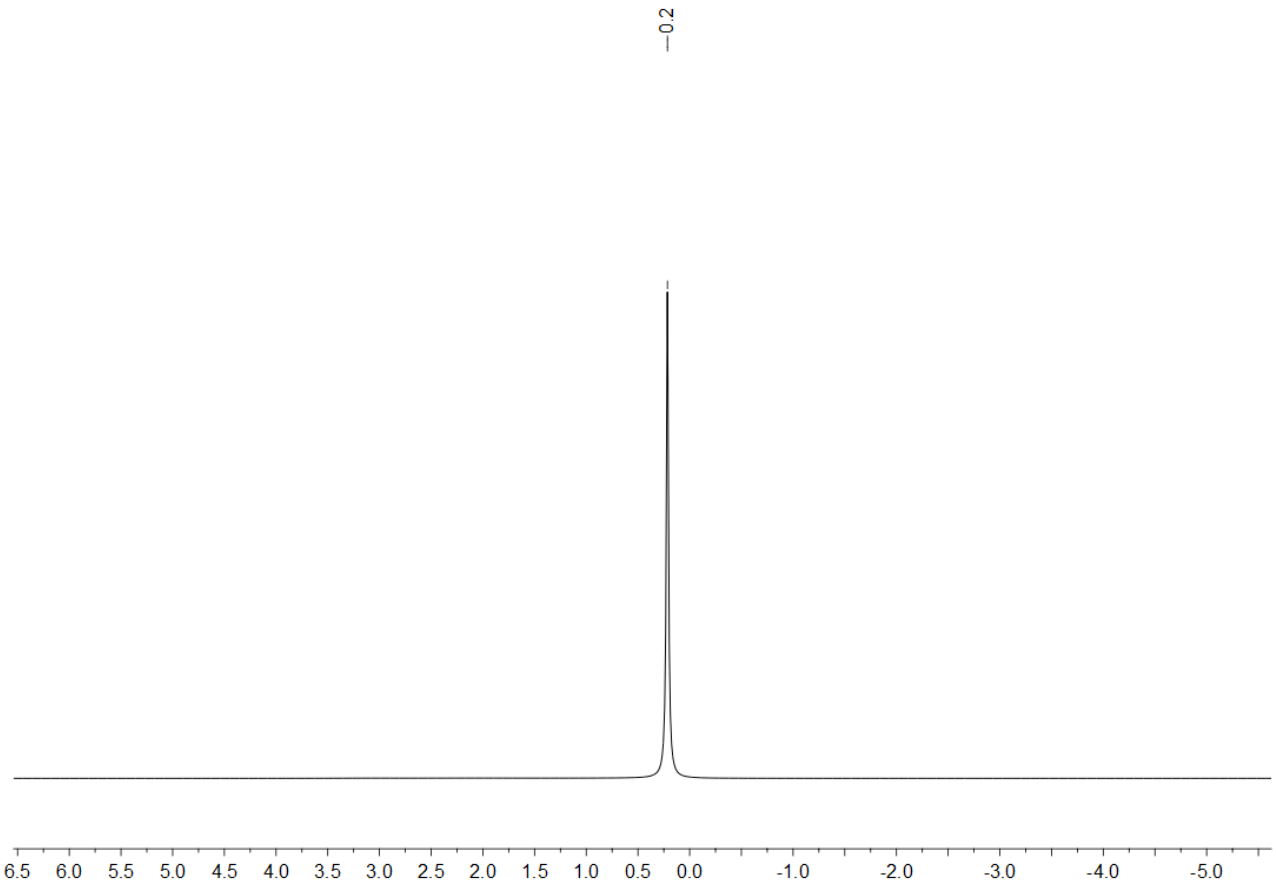
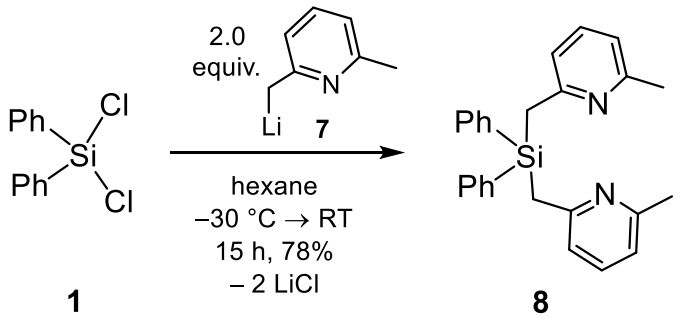



**Figure S22.** $^{7}$Li NMR spectrum of 2,6-lutidyllithium (**7**).

### 2.6. Synthesis of $Ph_2Si(Lut)_2$ (8)




Dichlorodiphenylsilane (**1**) (3.36 g, 2.8 ml, 13.3 mmol) was added dropwise to a stirred solution of isolated 2,6-lutidyllithium (**7**) (3.00 g, 26.5 mmol) in hexane (60 mL) at –30 °C. The reaction mixture was allowed to slowly warm up to room temperature and kept stirring for 15 h. Then, the white suspension was transferred to a fritted column *via* a PTFE cannula, filtered and the remaining solids washed with hexane (3 x 20 ml). The pale yellow clear filtrates were collected and all volatiles removed *in vacuo*. The yellow oily residue was purified by Kugelrohr distillation (190 °C

oven temperature, $2.5 \cdot 10^{-2}$ mbar) to give $Ph_2Si(Lut)_2$ (**8**) (4.1 g, 10.4 mmol, 78 %) as a viscous beige oil. Colourless crystals, suitable for single-crystal X-ray diffraction analysis were obtained after cooling down a concentrated solution of **8** in hexane at –30 °C.

$^1$H NMR (400.13 MHz, THF-$d_8$, 25 °C): $\delta$ = 2.39 (s, 6H, 2C$H_3$), 2.96 (s, 4H, Si(C$H_2$)$_2$), 6.77 (d, $^3J_{HH}$ = 7.4 Hz, 2H, $H_{m\text{-Py}}$), 6.79 (d, $^3J_{HH}$ = 7.4 Hz, 2H, $H_{m\text{-Py}}$), 7.25 (m, 8H, $H_{Ph}$ and $H_{p\text{-Py}}$), 7.54 (m, 2H, $H_{Ph}$).

$^{13}$C{$^1$H} NMR (100.62 MHz, THF-$d_8$, 25 °C): $\delta$ = 23.6 (s, $CH_3$), 25.6 (s, Si$CH_2$), 118.3 (s, $C_{m\text{-Py}}$), 119.9 (s, $C_{m\text{-Py}}$), 127.1 (s, $C_{Ph}$), 128.9 (s, $C_{p\text{-Py}}$), 135.2 (s, $C_{Ph}$), 135.4 (s, $C_{Ph}$), 135.5 (s, $C_{Ph}$), 156.9 (s, $C_{o\text{-Py}}$), 159.2 (s, $C_{o\text{-Py}}$).

$^{29}$Si{$^1$H} NMR (79.49 MHz, THF-$d_8$, 25 °C): $\delta$ = –8.7.

HRMS (EI+), Calcd. m/z for $C_{26}H_{26}N_2Si$ [$M^+$]: 394.18598. Found 394.18489.

Anal. Calcd. for $C_{26}H_{26}N_2Si$: C 79.14, H 6.64, N 7.10. Found: C 79.13, H 6.48, N 6.87.

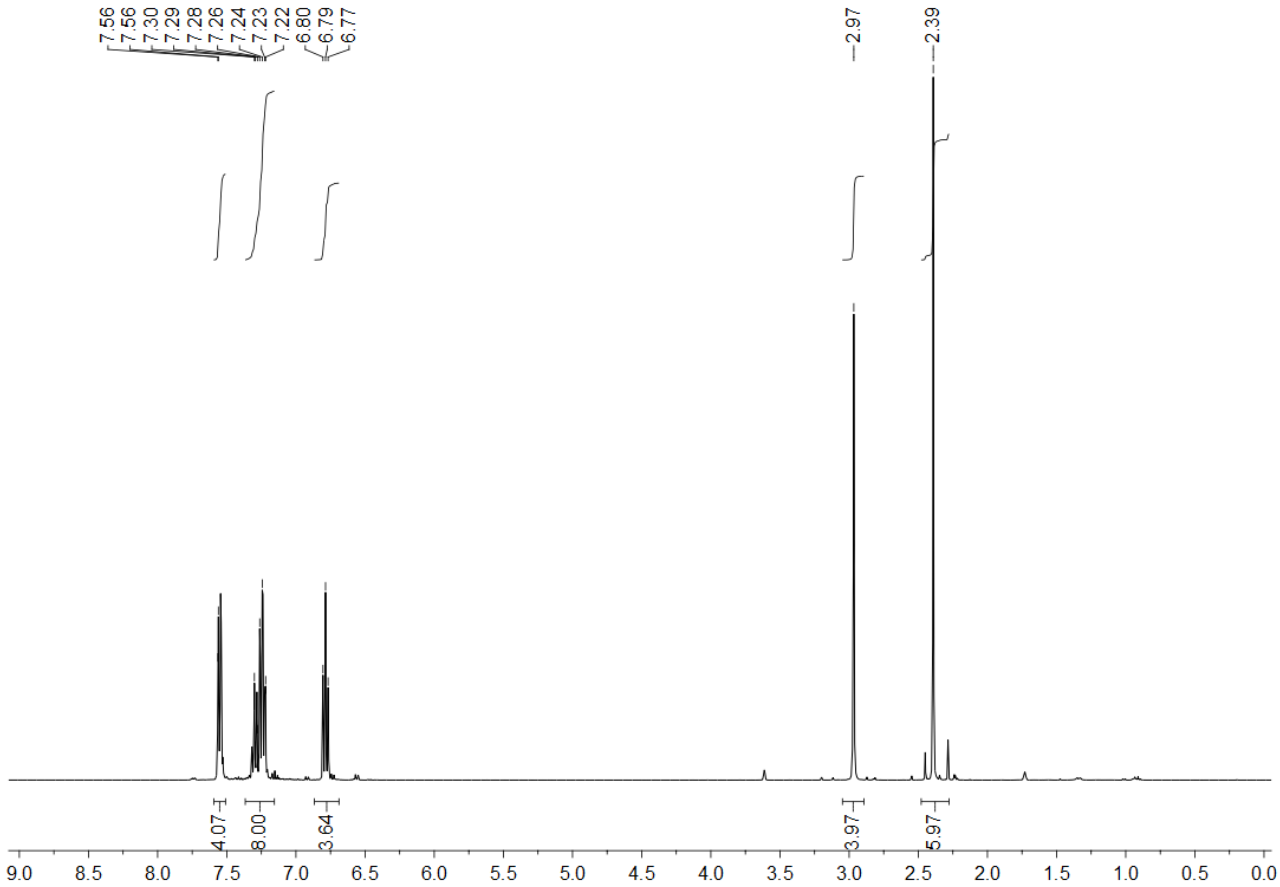



**Figure S23.** $^1$H NMR spectrum of $Ph_2Si(Lut)_2$ (**8**).

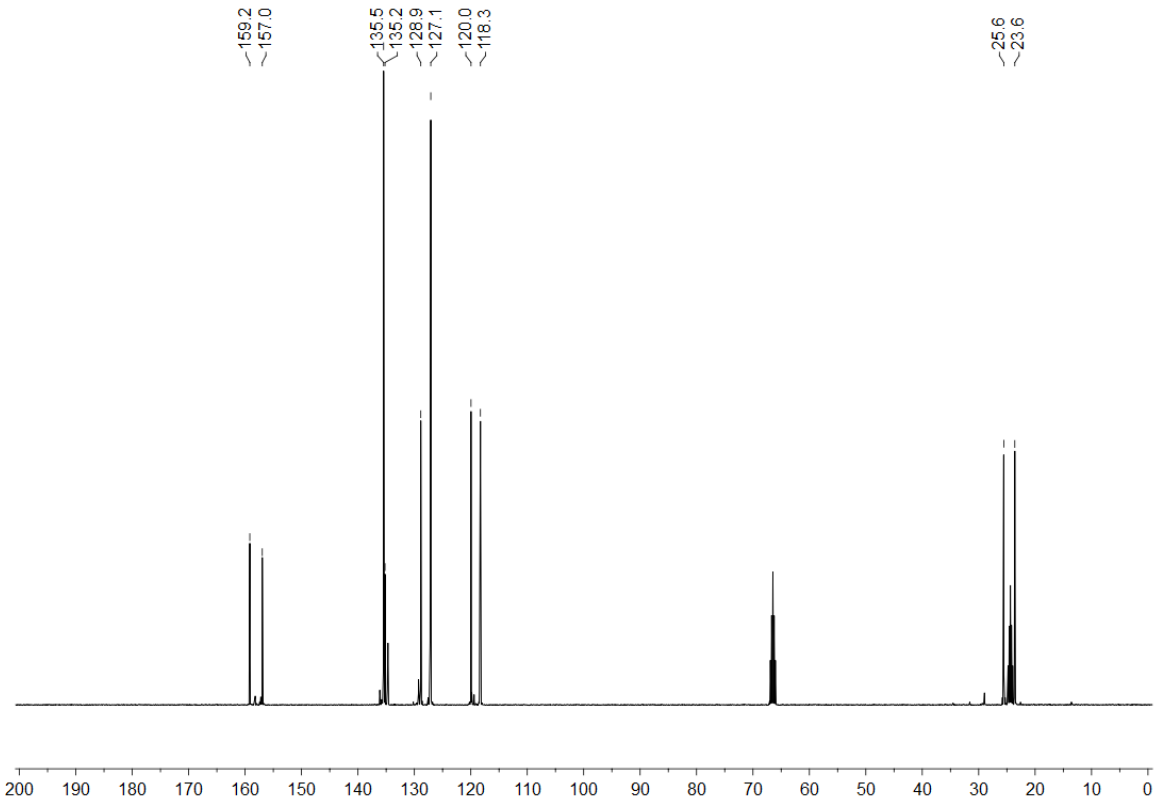



**Figure S24.** $^{1}$H NMR spectrum of $Ph_2Si(Lut)_2$ (**8**).

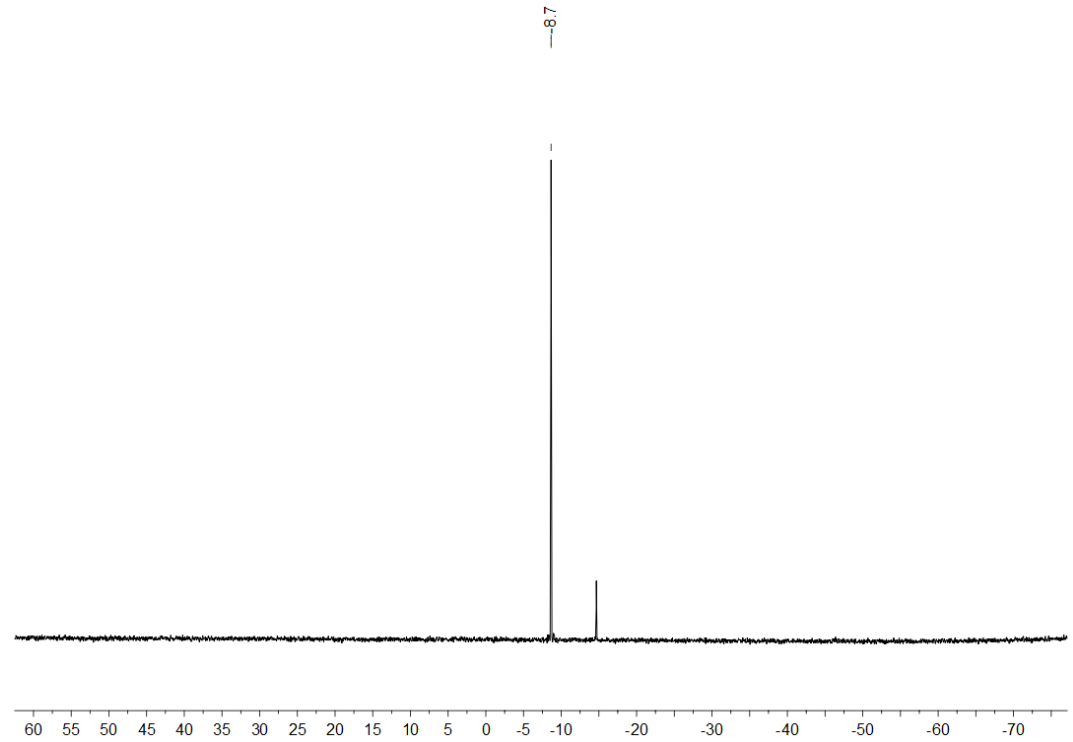
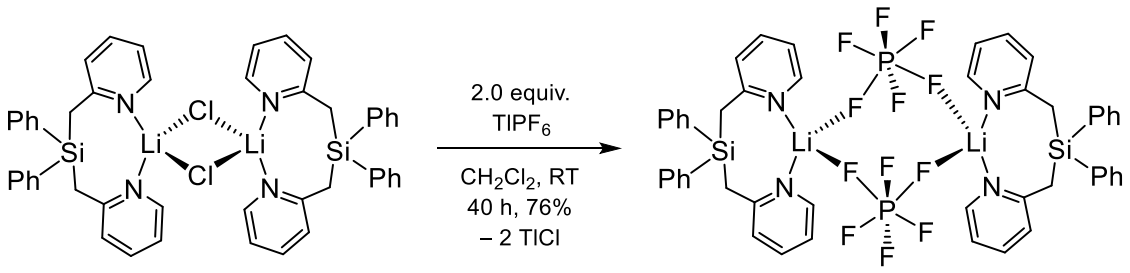



**Figure S25.** $^{29}$Si{$^{1}$H} NMR spectrum of $Ph_2Si(Lut)_2$ (**8**).

### 2.7. Synthesis of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (11)




**3** **11**

$[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiCl]_2$ (**3**) (2.53 g, 3.09 mmol) and $TlPF_6$ (2.16 g, 6.18 mmol) were loaded in a Schlenk flask, followed by the addition of dichloromethane (80 ml) at room temperature. The white suspension was stirred over the period of 40 h. Then, the beige suspension was transferred to a fritted column layered with Celite® *via* a PTFE cannula, filtered and the remaining solids carefully extracted with dichloromethane (2 x 15 ml). The filtrates were collected and all volatiles removed *in vacuo* yielding compound **11** as a pale yellow solid (2.43 g, 4.7 mmol, 76 %). Crystals, suitable for single-crystal X-ray diffraction analysis were obtained by layering a concentrated solution of compound **11** in dichloromethane with pentane.

HRMS (ESI+), Calcd. m/z for $C_{24}H_{22}N_2SiLi$ [$M^+$]: 373.1707. Found 373.1703.

Anal. Calcd. for $C_{24}H_{22}F_6LiN_2PSi_2$: C 55.60, H 4.28, N, 5.40. Found: C 54.96, H 4.63, N 5.34.

**Solution NMR spectroscopy of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (11) in DCM-$d_2$ at 25 °C:**

$^1$H NMR (400.13 MHz, DCM-$d_2$, 25 °C): $\delta$ = 2.93 (s, 4H, Si(C$H_2$)$_2$), 6.65 (bs, 2H, $H_{m\text{-Py}}$), 7.12 (bs, 2H, $H_{m\text{-Py}}$), 7.26 (m, 4H, $H_{Ph}$), 7.32 (m, 4H, $H_{Ph}$), 7.42 (m, 3H, $H_{Ph}$ and $H_{p\text{-Py}}$), 8.58 (bd, $^3J_{HH}$ = 4.8 Hz, 2H, $H_{o\text{-Py}}$).

$^{31}$P{$^1$H} NMR (162.04 MHz, DCM-$d_2$, 25 °C): $\delta$ = –143.4 (stp, $^1J_{PF}$ = 709.0 Hz).

$^{19}$F{$^1$H} NMR (376.66 MHz, DCM-$d_2$, 25 °C): $\delta$ = –73.9 (stp, $^1J_{PF}$ = 709.0 Hz).

$^{13}$C{$^1$H} NMR (100.62 MHz, DCM-$d_2$, 25 °C): $\delta$ = 23.8 (s, Si$CH_2$), 120.7 (bs, $C_{m\text{-Py}}$), 125.0 (bs, $C_{m\text{-Py}}$), 128.1 (bs, $C_{Ph}$), 130.3 (s, $C_{Ph}$), 131.9 (bs, $C_{Ph}$), 134.8 (s, $C_{Ph}$), 137.7 (bs, $C_{p\text{-Py}}$), 148.7 (s, $C_{o\text{-Py}}$), 159.5 (s, $C_{o\text{-Py}}$).

$^{29}$Si{$^1$H} NMR (79.49 MHz, DCM-$d_2$, 25 °C): $\delta$ = –6.4.

$^7$Li NMR (155.50 MHz, DCM-$d_2$, 25 °C): $\delta$ = 1.7 (major), 0.6 (bs, minor).

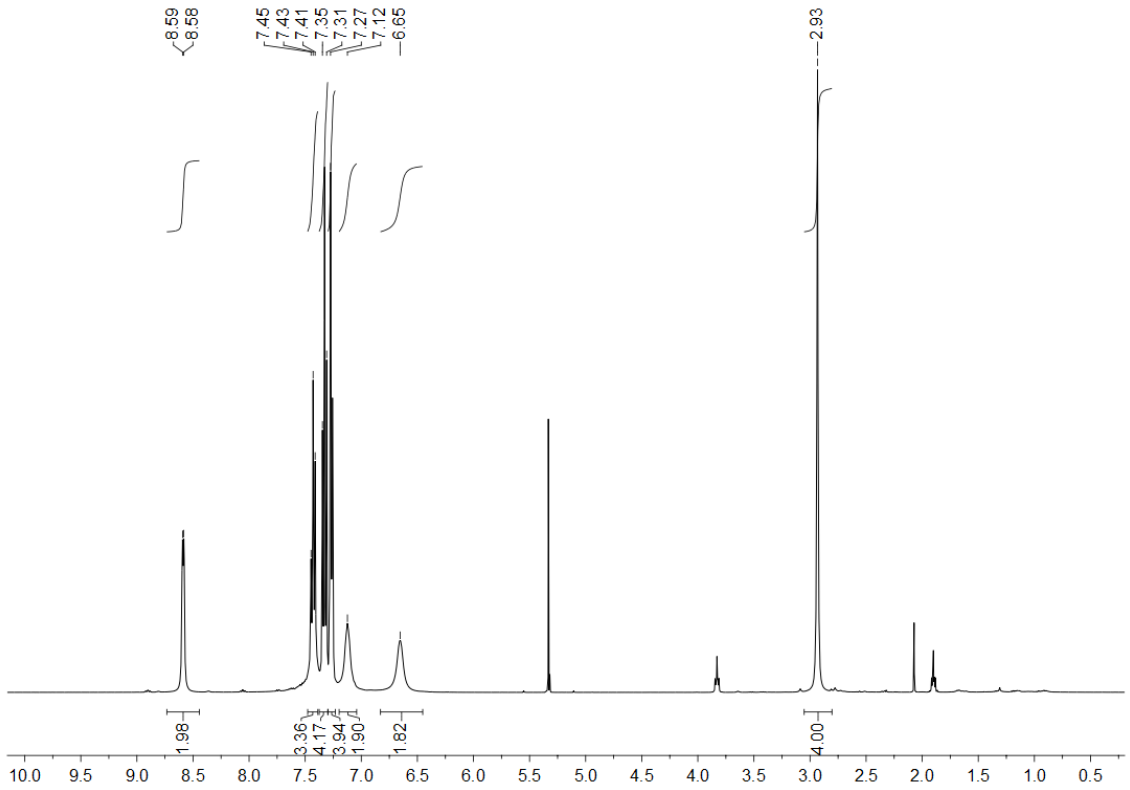



**Figure S26.** $^{1}$H NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at 25 °C.

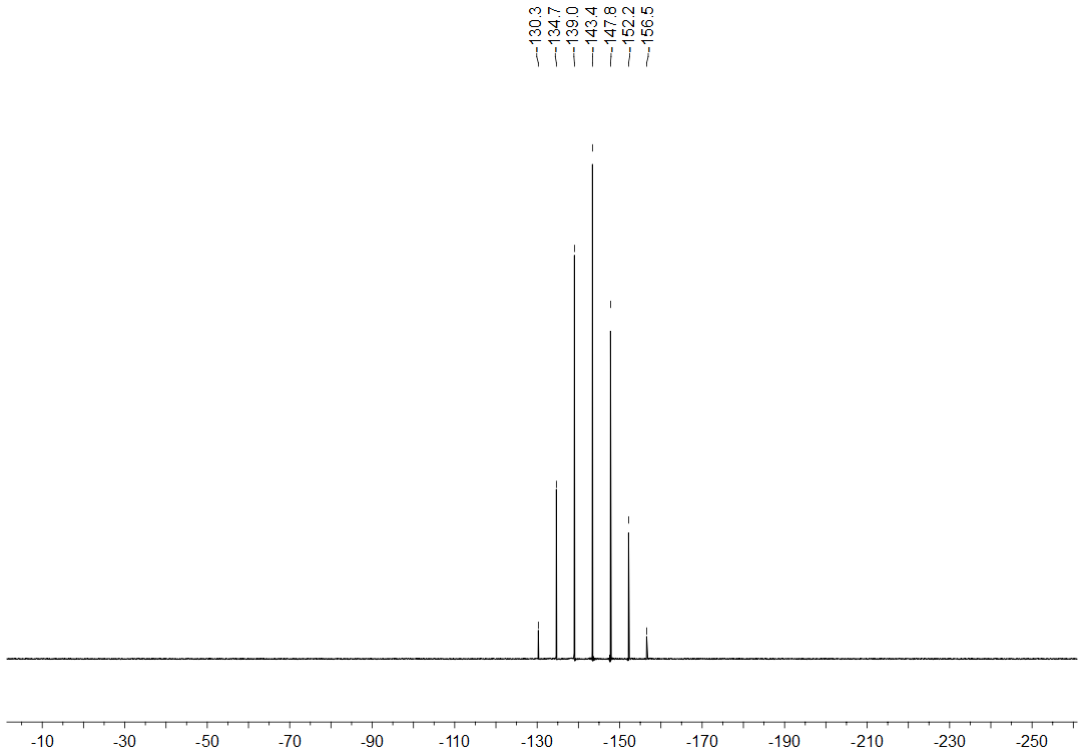



**Figure S27.** $^{31}$P{$^{1}$H} NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at 25 °C.

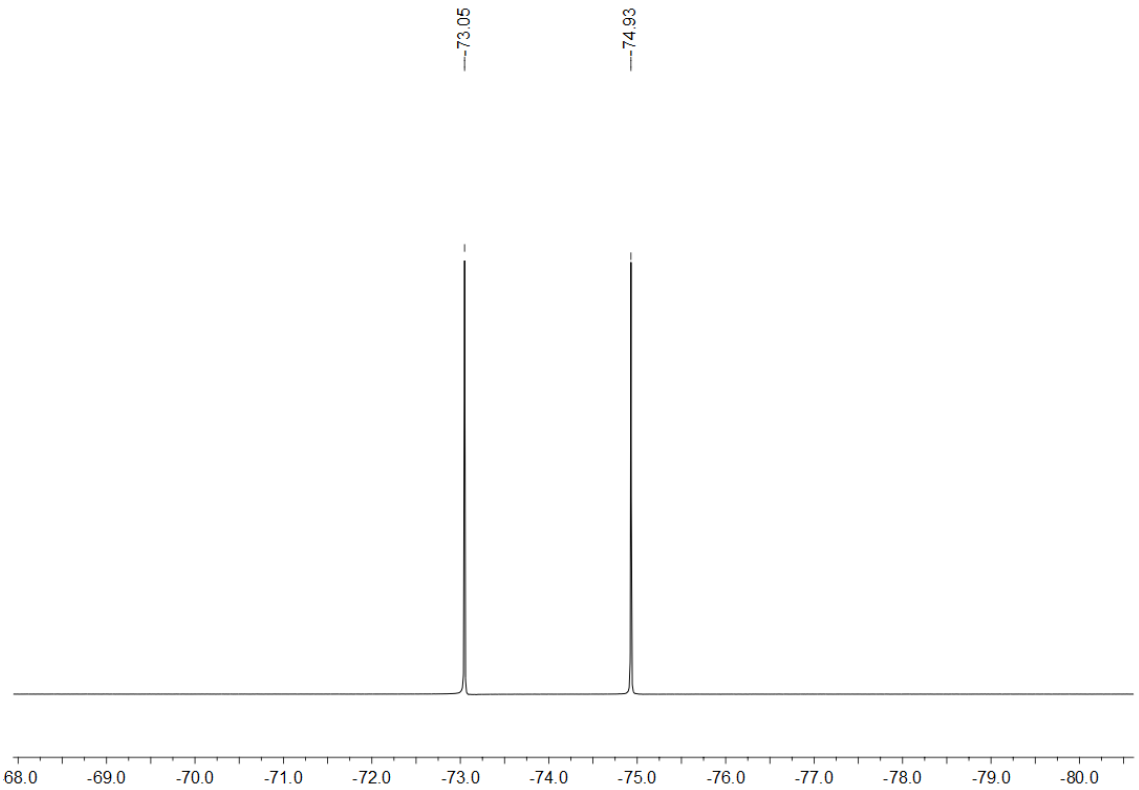



**Figure S28.** $^{19}F\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at 25 °C.

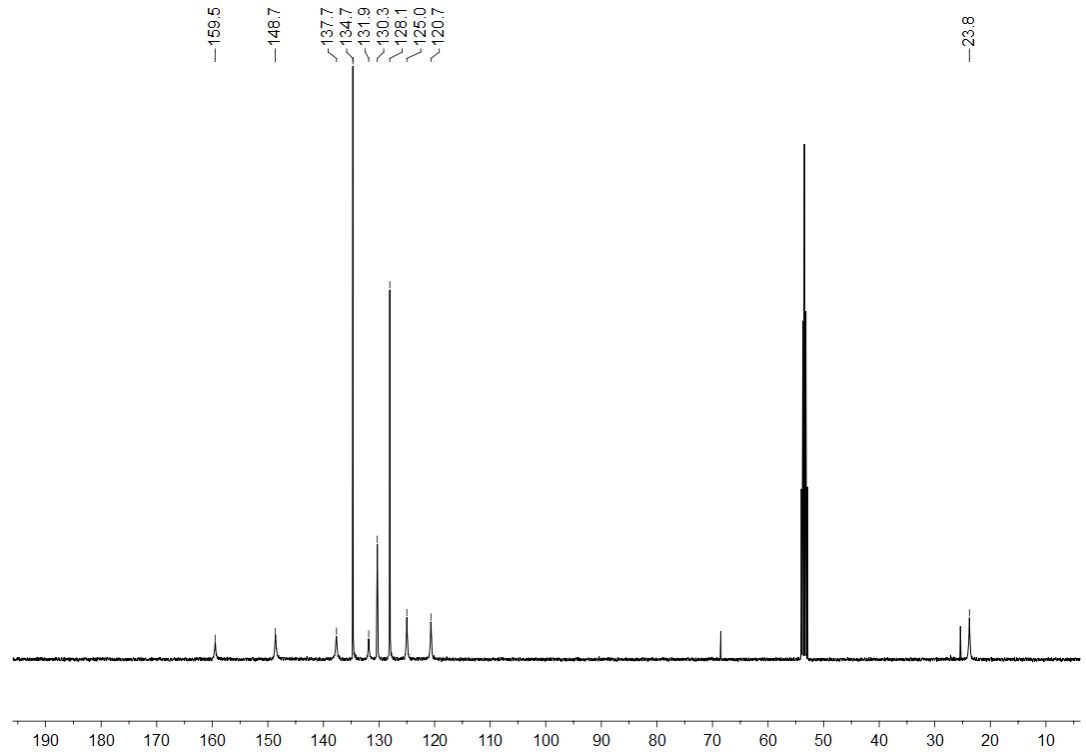



**Figure S29.** $^{13}C\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at 25 °C.

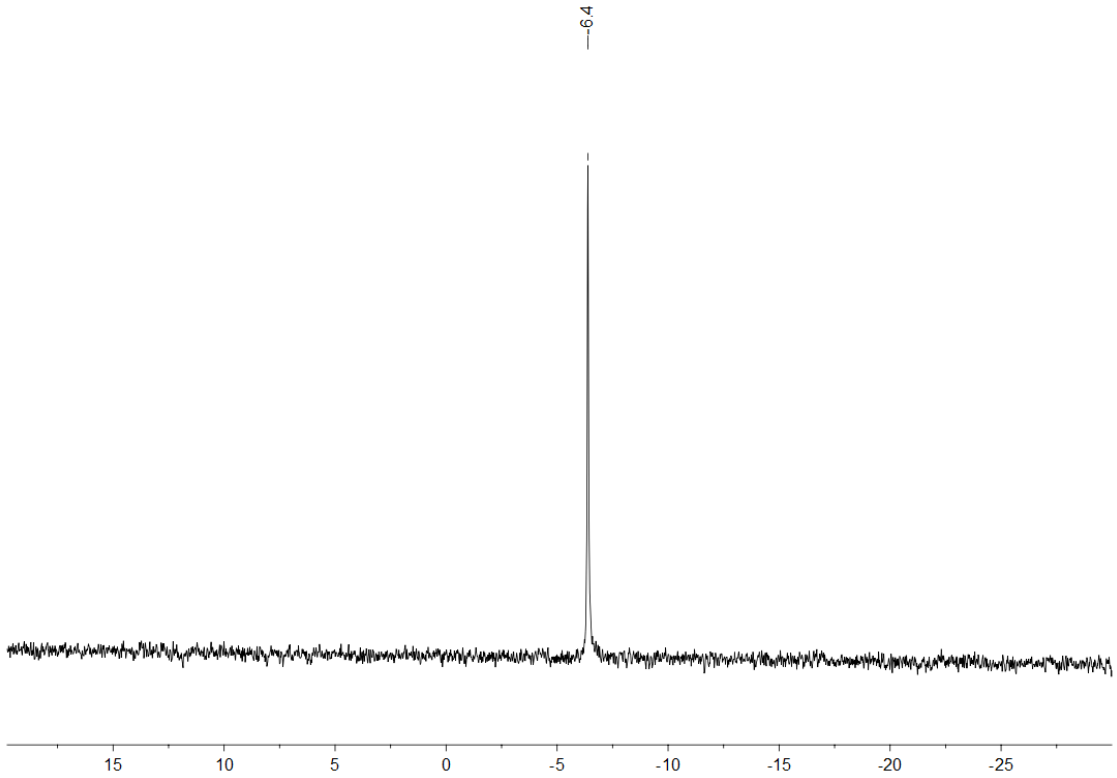



**Figure S30.** $^{29}Si\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at 25 °C.

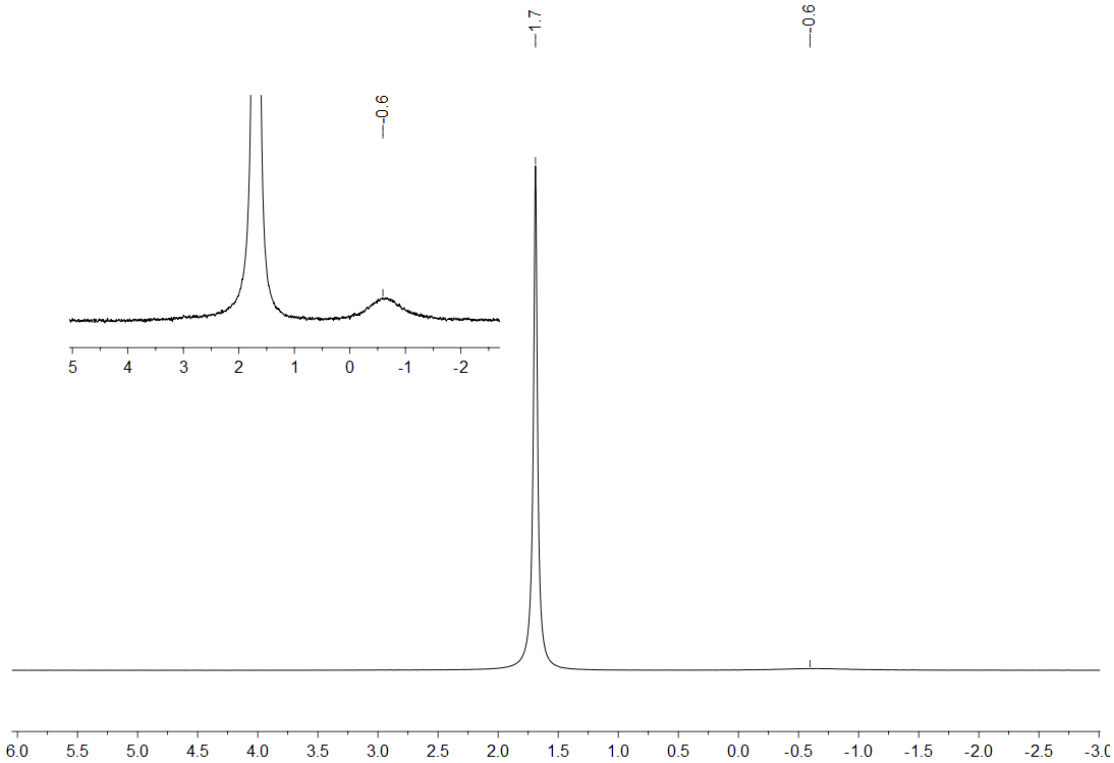



**Figure S31.** $^{7}Li$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at 25 °C.

**Solid-state $^{7}$Li NMR spectroscopy of [Ph$_2$Si(2-CH$_2$Py)$_2$·LiPF$_6$]$_2$ (11):**

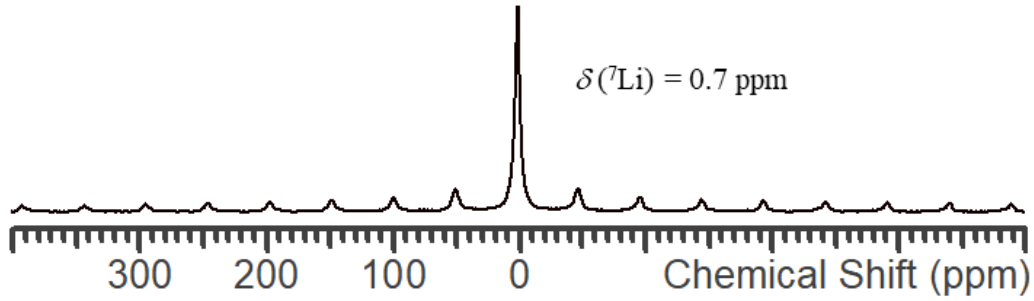



**Figure S32.** Solid-state $^{7}$Li NMR spectrum of [Ph$_2$Si(2-CH$_2$Py)$_2$·LiPF$_6$]$_2$ (**11**).

**Variable temperature NMR spectroscopy of [Ph$_2$Si(2-CH$_2$Py)$_2$·LiPF$_6$]$_2$ (11) in DCM-*d*$_2$:**

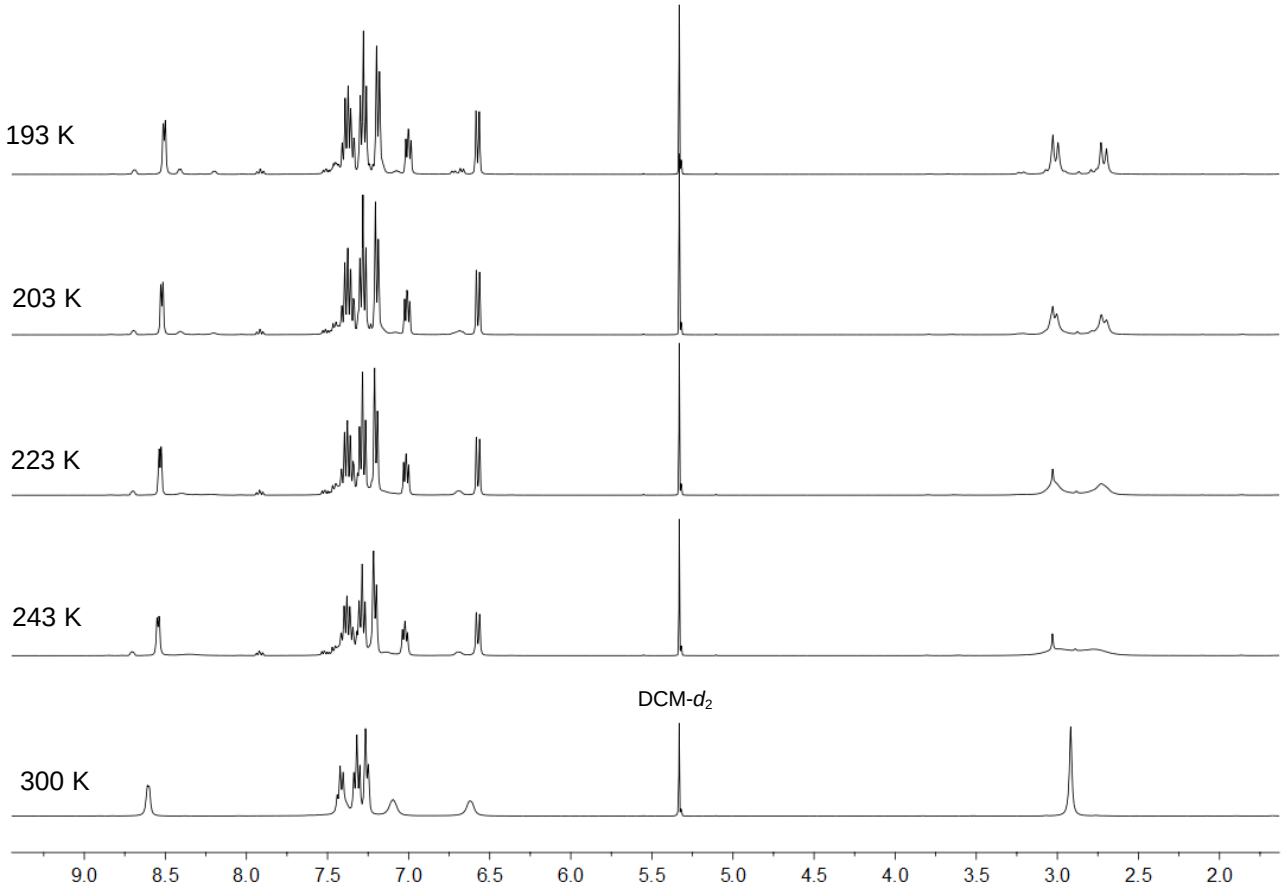



**Figure S33.** $^{1}$H NMR (400.13 MHz, DCM-*d*$_2$) spectrum of [Ph$_2$Si(2-CH$_2$Py)$_2$·LiPF$_6$]$_2$ (**11**) in DCM-*d*$_2$ at variable temperatures.

$^{1}$H NMR (600.03 MHz, DCM-$d_2$, –80 °C): $\delta$ = 2.75 (d, $^{2}J_{HH}$ = 13.3 Hz, 2H, Si(C$H_A H_B$)$_2$), 3.01 (d, $^{2}J_{HH}$ = 13.3 Hz, 2H, Si(C$H_A H_B$)$_2$), 6.61 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, $H_{m\text{-Py}}$), 7.05 (bt, $^{3}J_{HH}$ = 6.4 Hz, 2H, $H_{m\text{-Py}}$), 7.22 (bd, $^{3}J_{HH}$ = 7.2 Hz, 4H, $H_{Ph}$), 7.31 (bt, $^{3}J_{HH}$ = 7.2 Hz, 4H, $H_{Ph}$) 7.41 (m, 3H, $H_{Ph}$ and $H_{p\text{-Py}}$), 8.52 (bd, $^{3}J_{HH}$ = 5.0 Hz, 2H, $H_{o\text{-Py}}$).

$^{31}$P{$^{1}$H} NMR (242.86 MHz, DCM-$d_2$, –80 °C): $\delta$ = –144.8 (stp, $^{1}J_{PF}$ = 706.0 Hz).

$^{19}$F{$^{1}$H} NMR (564.54 MHz, DCM-$d_2$, –80 °C): $\delta$ = –74.4 (stp, $^{1}J_{PF}$ = 706.0 Hz).

$^{7}$Li NMR (155.50 MHz, DCM-$d_2$, –80 °C): $\delta$ = 1.2 (major), 3.3 (minor).

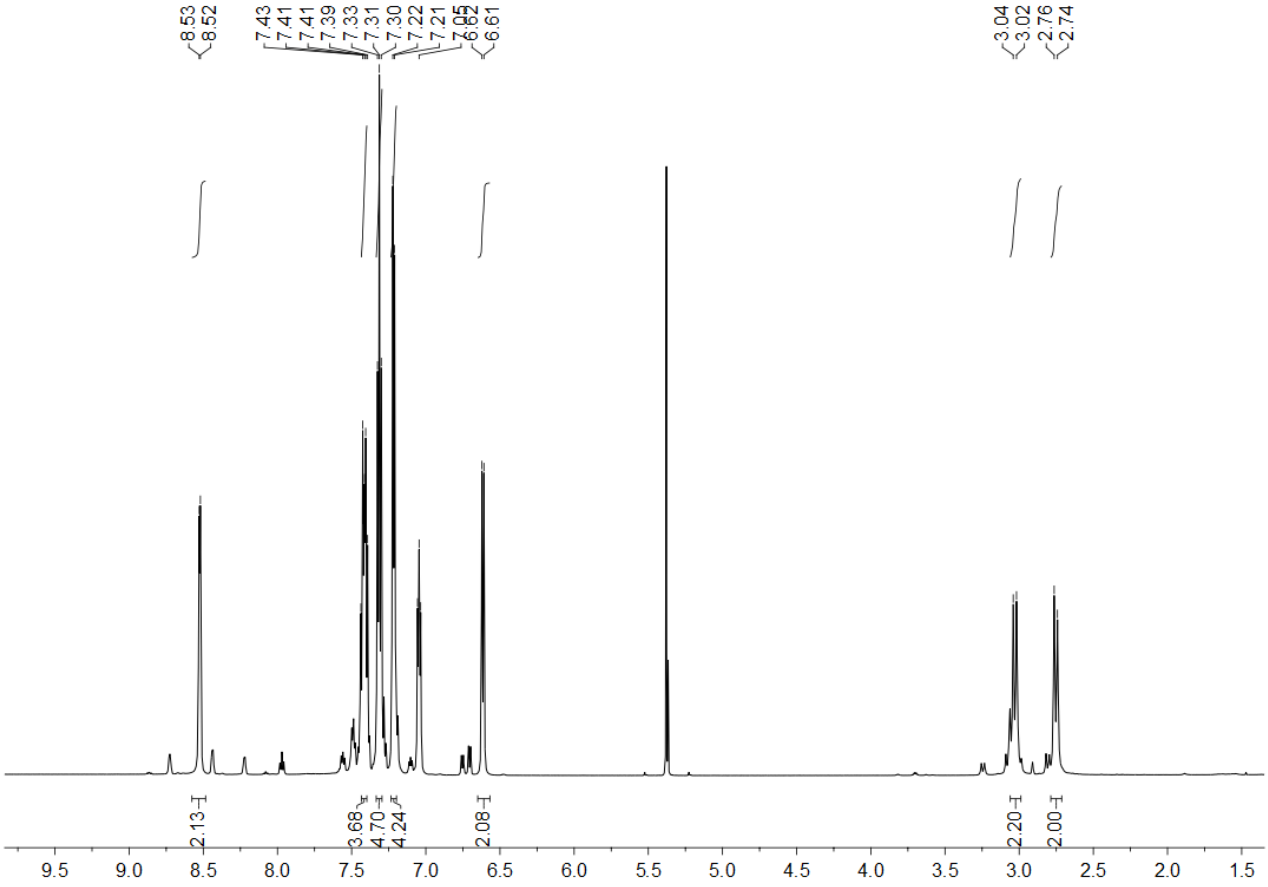



**Figure S34.** $^{1}$H NMR spectrum of [$Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at –80 °C.

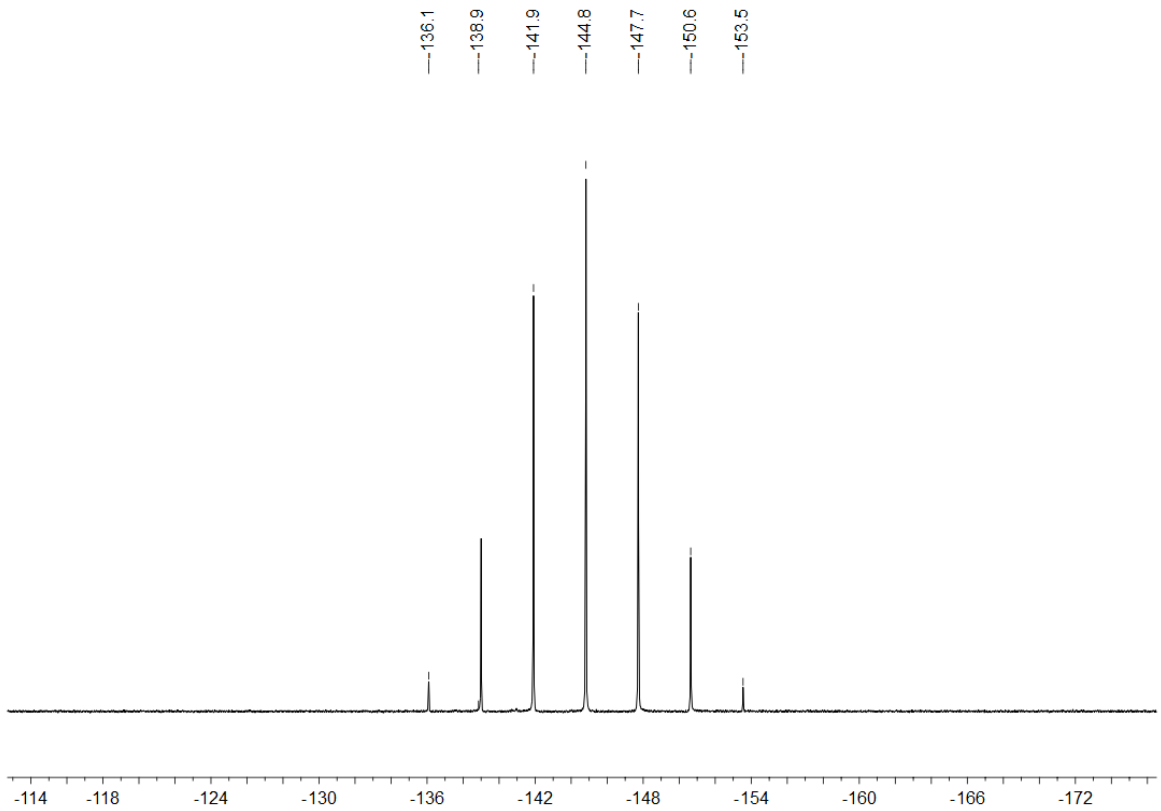



**Figure S35.** $^{31}P\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at –80 °C.

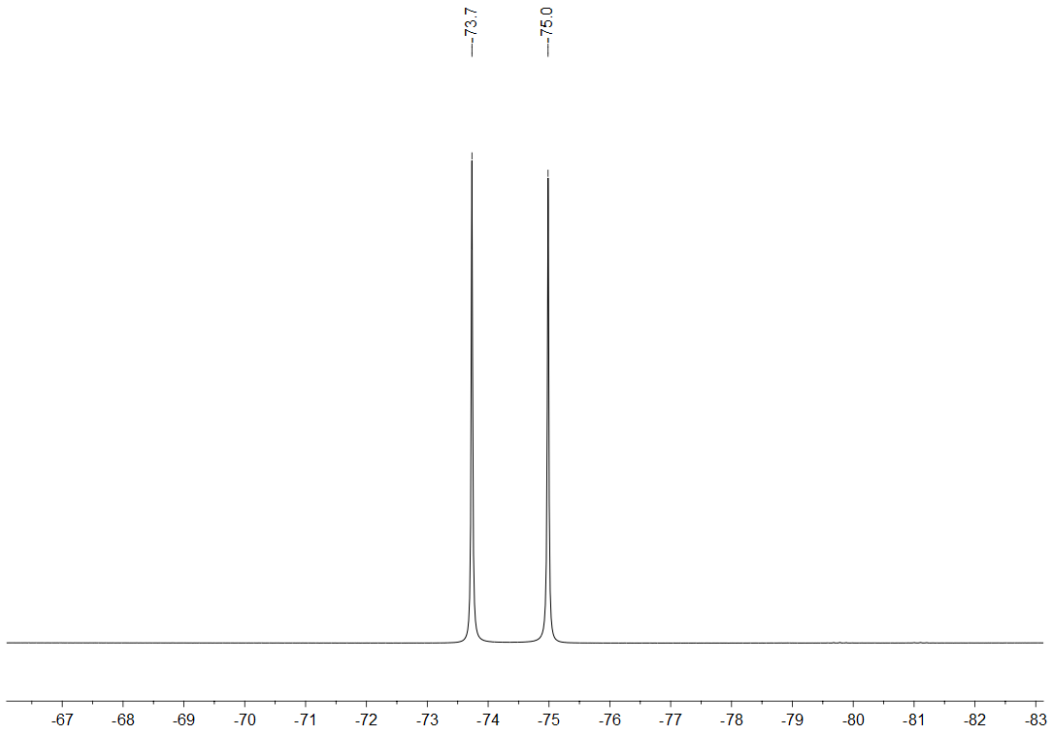



**Figure S36.** $^{19}F\{^{1}H\}$ NMR spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) in DCM-$d_2$ at –80 °C.

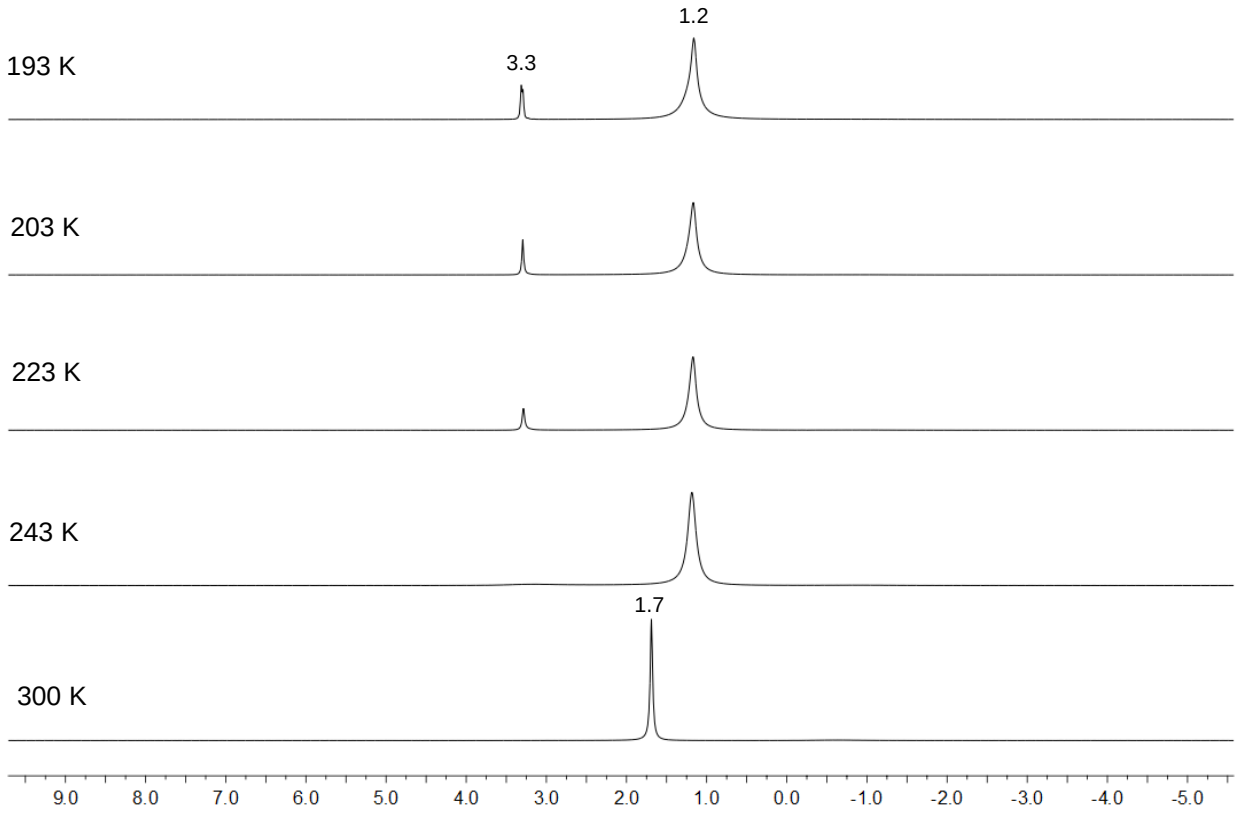



**Figure S37.** $^{7}$Li NMR (155.50 MHz, DCM-$d_2$) spectrum of $[Ph_2Si(2\text{-}CH_2Py)_2{\cdot}LiPF_6]_2$ (**11**) at variable temperature.

## 3. Summary of $^{7}$Li NMR Chemical Shifts in Solution and in the Solid-State

**Table S1.** List of the $^{7}$Li NMR chemical shifts in solution and in the solid-state.

| Compound | NMR method | $^{7}$Li NMR chemical shift $\delta$ [ppm] |
|---|---|---|
| **3** | solid-state | 2.6 |
| **3** | solution (DCM-$d_2$) | 2.5 |
| **3** | solution (THF-$d_8$) | 0.8 |
| **8** + 1.0 equiv. LiCl | solution (THF-$d_8$) | 0.5 |
| **11** | solid-state | 0.7 |
| **11** | solution (DCM-$d_2$) | 1.7 (major) / 0.6 (minor) |
| **LiCl** | solution (THF-$d_8$) | 0.5 |

## 4. $^1$H-Diffusion-Ordered NMR Spectroscopy ($^1$H DOSY)

**Spectroscopic details:**

The $^1$H-diffusion measurements were performed in THF-$d_8$ with the convection suppressing DSTE (double stimulated echo) pulse sequence, developed by *Müller* and *Jerschow* in a pseudo 2D mode.[2] Tetramethylsilane (TMS) was added as reference for the $^1$H chemical shifts and for temperature and viscosity corrections of the diffusion coefficients of the analytes.[3,4]

A set of 0 dummy scans/8 scans and 120 dummy scans/16 scans, respectively, were used with a relaxation delay of 2 s. Sinusoidal shapes were used for the gradient and a linear gradient ramp with 5 or 20 increments between 5 % and 95 % of the maximum gradient strength were applied. For the homospoil gradient strengths, values of 100, -13.17, 20 and -17.13 % were used. An effective diffusion time of 45 ms was applied. For each compound in the sample, the gradient pulses were adjusted in order to obtain optimized diffusion times $\Delta$ and gradient lengths $\delta$ according to the following correlation:

$$\Delta\,[ms] = D_{23} + \frac{\delta}{3}\,;\, P_{16}[ms] = \frac{\delta}{2}$$

**Size estimation:**

The experimental translational self-diffusion coefficients $D$ of the molecules in solution were determined according to the Stejskal-Tanner equation.[5-7] From the obtained diffusion coefficients, the hydrodynamic radii of the analytes $\boldsymbol{r_A}$ were estimated following the Stokes-Einstein equation (1), with $k$ = Boltzmann constant, $T$ = temperature, $\eta$ = viscosity of the sample, $c$ = correcting factor, $F$ = shape factor.[8]

$$D\,[m^2/s] = \frac{kT}{Fc\pi\eta\boldsymbol{r_A}} \quad (1)$$

For spherical shapes, $F$ is equal to 1. The correction factor $c$ of the Stokes-Einstein equation was calculated according to the semi-empirical modification (equation (2)) according to *Chen* using literature known values for the solvent ($r_{solv}$ = 2.58 Å for THF-$d^8$)[9].[10]

$$c_{Chen} = \frac{6F}{1 + 0.695\,(\frac{r_{solv}}{r_{ref}})^{2.234}};\;\; F = 1\; for\; spheres \quad (2)$$

The obtained diffusion coefficients $D$ for the analytes were calibrated by viscosity calculation using the literature known radius of TMS ($r_{ref}$ = 2.96 Å, calculated from hard-sphere increments)[11]

and the experimentally determined diffusion coefficient $D_{ref}$ of TMS for every sample (equation (3)).

$$\eta\ [kg/ms] = \frac{kT\ (1 + 0.695\ \left(\frac{r_{solv}}{r_{ref}}\right)^{2.234})}{6\pi D_{ref}\ r_{ref}} \quad (3)$$

Including all corrections and calibrations into the Stokes-Einstein equation (4), the hydrodynamic radii $\boldsymbol{r_A}$ were calculated. The corresponding volumes $V_A$ were calculated assuming a spherical shape.

$$D = \frac{kT(1 + 0.695\ \left(\frac{r_{solv}}{r_{ref}}\right)^{2.234})}{6\pi\eta \boldsymbol{r_A}} \quad (4)$$

Due to the assumption of spherical shapes, a deviation of the DOSY derived radii and related volumes from the effective volumes is feasible.

**Table S2.** Calculated hydrodynamic radii ($r_H$) for the measured systems.

| **Compound** | **Hydrodynamic radii $r_H$ [Å]** |
|---|---|
| **6** | 6.12 |
| **3** in THF | 4.70 |
| **8** | 4.08 |
| **8** + 1.0 equiv. LiCl | 4.88 |

## 5. X-Ray Crystallographic Details

The crystals were selected and measured on a Gemini Ultra diffractometer equipped with an AtlasS2 CCD detector. The crystals were kept at $T$ = 123(1) K during data collection. Data collection and reduction were performed with **CrysAlisPro** version 1.171.41.54a (**3**, **6**, and **8**) and version 1.171.41.76a (**11**), respectively.[12] For the compounds **3**, **6**, and **11** an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by *Clark* and *Reid*[13] and an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm has been applied. For compound **8** a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK has been applied. Using **Olex2**,[14] the structures were solved with **ShelXT**[15] and a least-square refinement

on $F^2$ was carried out with **ShelXL**[16]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at the carbon atoms have, unless otherwise noted, been located in idealized positions and refined isotropically according to the riding model.

The Figures in the SI were created with **Olex2**.[14] Figure 1 in the manuscript was created with **Mercury 4.1.0**.[17]

**Compound 3:** There is a single molecule of **3** and two acetonitrile solvent molecules in the asymmetric unit. Furthermore, compound **3** was refined as a 2-component inversion twin.

**Compound 6:** There is a single molecule of **6** in the asymmetric unit.

**Compound 8:** There are two separate molecules of **8** in the asymmetric unit.

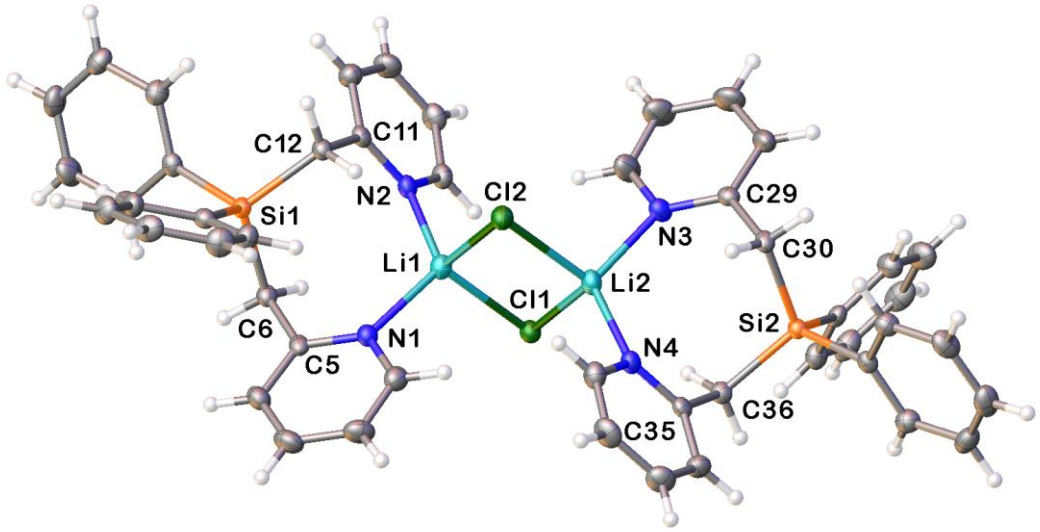
**Compound 11:** There is a single molecule of **11** and a partly occupied DCM molecule (0.7) in the asymmetric unit. Furthermore, a phenyl substituent at the Si1 atom is partly disordered (71:29). The restraints SADI and SIMU were applied to describe this disorder.

CCDC-2018220 (**3**), CCDC-2018218 (**6**), CCDC-2018217 (**8**), and CCDC-2018219 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Table S3.** Crystallographic data for compounds **3**, **6**, **8**, and **11**.

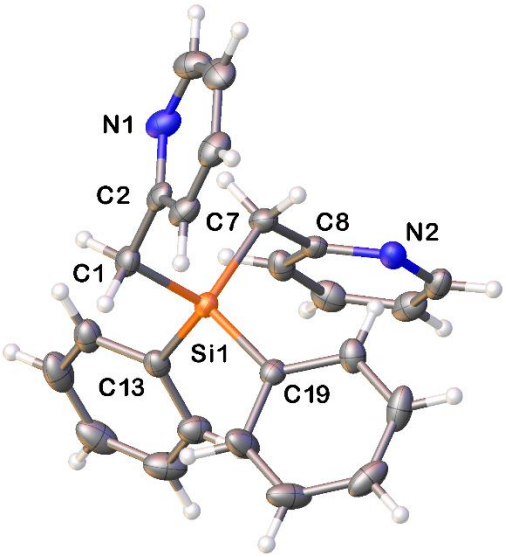
| **Compound** | **3** · 2 $CH_3CN$ | **6** | **8** | **11** · 0.7 DCM |
|---|---|---|---|---|
| Data set (internal naming) | **RX17DCM** | **RX_253** | **$Ph_2SiLut_2$** | **RX_318** |
| CCDC | 2018220 | 2018218 | 2018217 | 2018219 |
| Formula | $C_{52}H_{50}Cl_2Li_2N_6Si_2$ | $C_{24}H_{22}N_2Si$ | $C_{52}H_{52}N_4Si_2$ | $C_{48.7}H_{45.4}Cl_{1.4}F_{12}Li_2N_4P_2Si_2$ |
| $D_{calc.}$ / g · $cm^{-3}$ | 1.225 | 1.237 | 1.218 | 1.412 |
| $m$/$mm^{-1}$ | 0.224 | 1.115 | 1.054 | 2.600 |
| Formula Weight | 899.94 | 366.52 | 789.15 | 1096.32 |
| Colour | colourless | clear colourless | colourless | clear colourless |
| Shape | block | plate | block | plate |
| Size/$mm^3$ | 0.36×0.19×0.14 | 0.35×0.21×0.02 | 0.76×0.62×0.22 | 0.63×0.33×0.08 |
| $T$/K | 123(1) | 123(1) | 123(1) | 123.15 |
| Crystal System | triclinic | triclinic | triclinic | monoclinic |
| Space Group | $P1$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ |
| $a$/Å | 8.9867(2) | 9.8911(3) | 10.2134(2) | 10.57120(10) |
| $b$/Å | 11.6858(3) | 10.3035(2) | 14.0734(3) | 18.1992(2) |
| $c$/Å | 12.4491(3) | 10.8066(2) | 16.2616(3) | 27.2894(3) |
| α/° | 77.799(2) | 82.034(2) | 100.776(2) | 90 |
| β/° | 74.843(2) | 64.483(2) | 93.428(2) | 100.7840(10) |
| γ/° | 78.754(2) | 87.683(2) | 109.092(2) | 90 |
| V/$Å^3$ | 1219.77(5) | 984.09(4) | 2151.38(8) | 5157.42(10) |
| $Z$ | 1 | 2 | 2 | 4 |
| $Z'$ | 1 | 1 | 1 | 1 |
| Wavelength/Å | 0.71073 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | Mo$K_a$ | Cu $K_a$ | Cu $K_a$ | Cu $K_a$ |
| $Q_{min}$/° | 3.441 | 4.334 | 3.406 | 4.096 |
| $Q_{max}$/° | 32.457 | 72.377 | 71.507 | 71.860 |
| Measured Refl. | 28897 | 19425 | 17359 | 18202 |
| Independent Refl. | 15510 | 3796 | 8084 | 9665 |
| Reflections with I > 2(I) | 13734 | 3510 | 7390 | 8917 |
| $R_{int}$ | 0.0225 | 0.0222 | 0.0231 | 0.0171 |
| Parameters | 579 | 244 | 527 | 677 |
| Restraints | 3 | 0 | 0 | 51 |
| Largest Peak | 0.327 | 0.265 | 0.361 | 0.474 |
| Deepest Hole | -0.227 | -0.272 | -0.238 | -0.360 |
| GooF | 1.020 | 1.052 | 1.025 | 1.022 |
| $wR_2$ (all data) | 0.0850 | 0.0819 | 0.0969 | 0.0910 |
| $wR_2$ | 0.0807 | 0.0804 | 0.0937 | 0.0888 |
| $R_1$ (all data) | 0.0477 | 0.0341 | 0.0394 | 0.0376 |
| $R_1$ | 0.0387 | 0.0316 | 0.0359 | 0.0348 |

**Compound 3:**



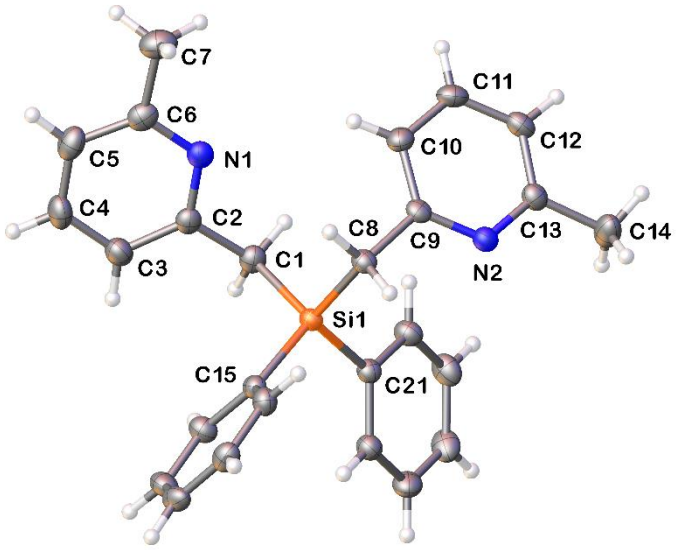

| Selected Bond Lengths [Å] | | Selected Bond Angles [°] | |
|---|---|---|---|
| **Si1–C6** | 1.884(2) | **C6–Si1–C12** | 110.29(10) |
| **Si1–C12** | 1.890(2) | **N1–Li1–N2** | 119.4(2) |
| **C11–C12** | 1.497(3) | **Cl1–Li1–Cl2** | 102.33(16) |
| **C5–C6** | 1.495(3) | **N1–Li1–Cl1** | 109.92(19) |
| **C5–N1** | 1.348(3) | **N1–Li1–Cl2** | 105.67(19) |
| **C11–N2** | 1.349(3) | **N2–Li1–Cl1** | 108.84(19) |
| **Li1–N1** | 2.078(5) | **N2–Li1–Cl2** | 109.32(18) |
| **Li1–N2** | 2.071(5) | **Cl1–Li2–Cl2** | 102.16(16) |
| **Li1–Cl1** | 2.357(4) | **N3–Li2–Cl1** | 105.60(19) |
| **Li1–Cl2** | 2.354(4) | **N3–Li2–Cl2** | 107.08(19) |
| **Li2–Cl1** | 2.361(4) | **N4–Li2–Cl1** | 110.10(19) |
| **Li2–Cl2** | 2.355(4) | **N4–Li2–Cl2** | 111.33(19) |
| **Li2–N3** | 2.059(5) | **N3–Li2–N4** | 119.1(2) |
| **Li2–N4** | 2.082(5) | **L1–Cl1–Li2** | 77.66(14) |
| **N3–C29** | 1.346(3) | **L1–Cl2–Li2** | 77.84(14) |
| **N4–C35** | 1.344(3) | **C30–Si2–C36** | 110.67(11) |
| **C29–C30** | 1.497(3) | | |
| **C35–C36** | 1.498(3) | | |
| **Si2–C30** | 1.884(2) | | |
| **Si2–C36** | 1.886(2) | | |

**Compound 6:**



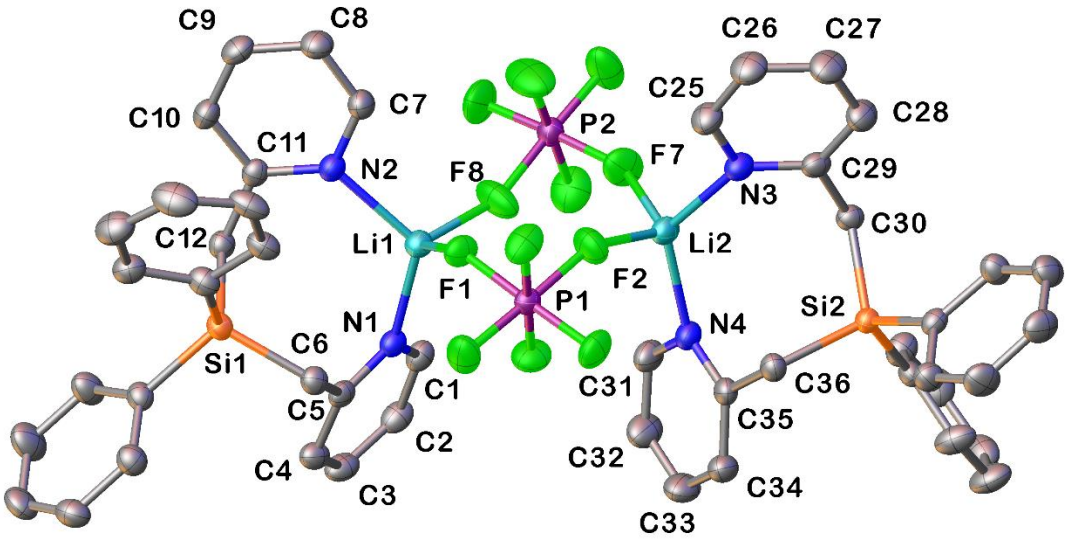

| Selected Bond Lengths [Å] | | Selected Bond Angles [°] | |
|---|---|---|---|
| **Si1–C1** | 1.8905(13) | **C1–Si1–C7** | 108.66(6) |
| **Si1–C7** | 1.8941(13) | **C1–Si1–C13** | 109.28(6) |
| **Si1–C13** | 1.8751(13) | **C7–Si1–C19** | 111.74(6) |
| **Si1–C19** | 1.8718(13) | **C13–Si1–C19** | 109.16(6) |
| **C1–C2** | 1.4946(19) | **C1–Si1–C19** | 109.99(6) |
| **C2–N1** | 1.3446(17) | **C13–Si1–C7** | 107.96(6) |
| **C7–C8** | 1.5024(17) | **Si1–C1–C2** | 112.67(8) |
| **C8–N2** | 1.3458(16) | **Si1–C7–C8** | 113.40(9) |

**Compound 8:**




| Selected Bond Lengths [Å] | | Selected Bond Angles [°] | |
|---|---|---|---|
| **Si1–C1** | 1.8912(14) | **C1–Si1–C8** | 109.65(6) |
| **Si1–C8** | 1.8925(13) | **C1–Si1–C15** | 111.97(6) |
| **Si1–C15** | 1.8782(13) | **C8–Si1–C21** | 114.69(6) |
| **Si1–C21** | 1.8767(13) | **C15–Si1–C21** | 108.54(6) |
| **C1–C2** | 1.4964(19) | **C1–Si1–C21** | 103.24(6) |
| **C2–N1** | 1.3483(18) | **C15–Si1–C8** | 108.72(6) |
| **C8–C9** | 1.5030(18) | **Si1–C1–C2** | 119.11(9) |
| **C9–N2** | 1.3462(17) | **Si1–C8–C9** | 114.26(9) |

**Compound 11:**




| Selected Bond Lengths [Å] | | Selected Bond Angles [°] | |
|---|---|---|---|
| **Si1–C6** | 1.8943(16) | **C6–Si1–C12** | 109.18(7) |
| **Si1–C12** | 1.8903(16) | **N1–Li1–N2** | 119.66(14) |
| **C11–C12** | 1.500(2) | **F1–Li1–F8** | 105.58(14) |
| **C5–C6** | 1.497(2) | **N1–Li1–F1** | 118.29(14) |
| **C5–N1** | 1.346(2) | **N1–Li1–F8** | 103.76(13) |
| **C11–N2** | 1.346(2) | **N2–Li1–F1** | 95.97(12) |
| **Li1–N1** | 2.026(3) | **N2–Li1–F8** | 113.17(14) |
| **Li1–N2** | 2.057(3) | **F2–Li2–F7** | 109.14(14) |
| **Li1–F1** | 1.925(3) | **N3–Li2–F2** | 96.46(13) |
| **Li1–F8** | 1.892(3) | **N3–Li2–F7** | 108.54(14) |
| **Li2–F2** | 1.888(3) | **N4–Li2–F2** | 107.84(14) |
| **Li2–F7** | 1.881(3) | **N4–Li2–F7** | 107.82(14) |
| **Li2–N3** | 2.032(3) | **N3–Li2–N4** | 125.80(14) |
| **Li2–N4** | 2.043(3) | **L1–F1–P1** | 136.10(10) |
| **N3–C29** | 1.344(2) | **L1–F8–P2** | 157.80(12) |
| **N4–C35** | 1.347(2) | **L2–F2–P1** | 148.62(11) |
| **C29–C30** | 1.501(2) | **L2–F7–P2** | 151.92(12) |
| **C35–C36** | 1.498(2) | **F1–P1–F2** | 88.21(6) |
| **Si2–C30** | 1.8935(15) | **F7–P2–F8** | 88.13(7) |

| | | | |
|---|---|---|---|
| **Si2–C36** | 1.8953(16) | **C30–Si2–C36** | 110.54(7) |
| **P1–F1** | 1.6304(10) | | |
| **P1–F2** | 1.6200(11) | | |
| **P2–F7** | 1.6223(11) | | |
| **P2–F8** | 1.6233(11) | | |

**Structural features of compound 3:**

The LiCl complex **3** crystallized from acetonitrile/THF as colourless blocks in the triclinic crystal system, space group *P*1. The LiCl core forms a dimeric rhombic structural unit in which each lithium atom is additionally coordinated by the two pyridyl nitrogen atoms of one ligand each (average N–Li bond length: 2.073(5) Å). An ideal tetrahedral geometry is retained around the silicon atom so that no significant structural changes of the bidentate ligand are required for an efficient coordination.

**Structural features of compound 11:**

**11** crystallized from DCM/pentane as colourless plates in the monoclinic crystal system, space group $P2_1/n$. The P–F–Li angles of the dinuclear eight-membered core in compound **11** range from 136.10(10)° [P(1)–F(1)–Li(1)] to 157.80(12)° [P(2)–F(8)–Li(1)] and differ greatly from an almost linear arrangement, as found in the [*N*,*N*,*N*',*N*",*N*"-pentamethyldiethylenetriamine • $LiPF_6$]$_2$ complex (mean P–F–Li angle: 175.5°).[18]

## 6. Quantum Chemical Calculations

Optimization and additional harmonic vibrational frequency analyses were performed with the software package Gaussian 09 (Revision E.01) on the B3LYP/6-31+G(d) level of theory without symmetry restrictions.[19] For thermodynamic considerations in tetrahydrofuran solution, the structures were optimized using the Polarizable Continuum Model (PCM) (solvent: THF). NMR calculations were performed with the software package Gaussian 09 (Revision E.01) on the B3LYP/6-311+G(2d,p) level of theory based on the B3LYP/6-31+G(d)-optimized structures. As reference for the calculated $^7$Li NMR chemical shifts, the calculated $^7$Li isotropic shielding (87.2921, 87.4177) [B3LYP/6-311+G(2d,p)] of the non-optimized, X-ray crystallographically determined molecular structure of compound **3** and the measured solid-state $^7$Li NMR chemical shift ($\delta$ = 2.6 ppm) of **3** were used. The GJF input files were created with the program GaussView 5.0. For the ground state structures, vibrational frequency analysis showed no imaginary frequency in the harmonical approximation. The relative enthalpies ($\Delta H$) were indicated

on the basis of the calculated zero-point-corrected energies (ZPE). The total (SCF) and zero-point-corrected (ZPE) energies of the calculated systems can be found in Table S4. The isotropic shieldings for lithium based on NMR calculations can be found in Table S5. The results on $^{7}$Li NMR calculations are shown in Table S5. The calculated standard orientations of the optimized structures can be found in Tables S6–S14. The Hartree units were converted as follows:[20] 1 Hartree = 2625.4995 kJ·mol$^{-1}$, 1 cal = 4.184 J

**Table S4.** Total (SCF) and zero-point-corrected (ZPE) energies of the optimized structures.

| Optimized structure | Method/Basis | SCF [Hartree] | ZPE [Hartree] |
|---|---|---|---|
| **3** | B3LYP/6-31+G(d) (PCM) | –3589.54794310 | – 3588.744780 |
| **3-g** | B3LYP/6-31+G(d) | –3589.51948727 | – 3588.715961 |
| **6** | B3LYP/6-31+G(d) (PCM) | –1326.88381636 | – 1326.486878 |
| **8** | B3LYP/6-31+G(d) (PCM) | –1405.52621866 | – 1405.074840 |
| **9** | B3LYP/6-31+G(d) (PCM) | –2027.23881562 | – 2026,719398 |
| **10** | B3LYP/6-31+G(d) (PCM) | –1865.63250666 | – 1865.153524 |
| **13** | B3LYP/6-31+G(d) (PCM) | –3746.80832466 | – 3745.895182 |
| **14** | B3LYP/6-31+G(d) (PCM) | –2105.87128691 | –2105.297010 |
| **THF** | B3LYP/6-31+G(d) (PCM) | –232.463025740 | –232.346064 |

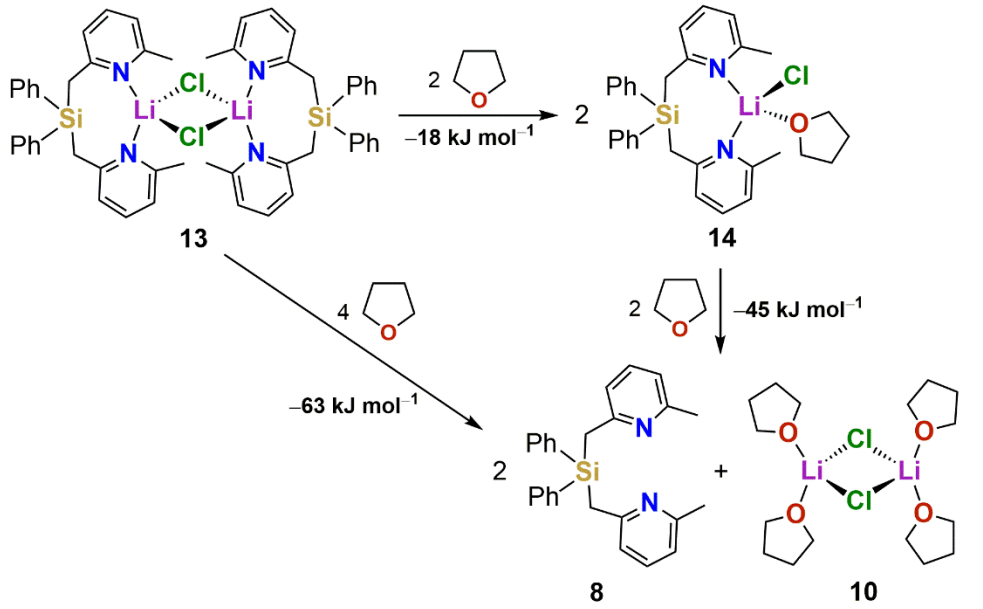



**Figure S38.** Calculated reaction enthalpies ($\Delta H$) for the dissociation of dimer **13** into the free ligand **8** and a dissolved LiCl • THF complex (**10**) *via* a monomeric LiCl complex (**14**) in THF [B3LYP/6-31+G(d)] (PCM calculations; solvent: THF).

**Table S5.** Isotropic shieldings for lithium based on NMR calculations.

| Structure | Method/Basis | $^{7}$Li Isotropic shielding [ppm] | $^{7}$Li NMR chemical shift ($\delta$) [ppm] |
|---|---|---|---|
| **Reference**[a] | B3LYP/6-311+G(2d,p) | 87.2921, 87.4177 | — |
| **3**[b] | B3LYP/6-311+G(2d,p) | 88.0794, 88.0796 | 1.9 |
| **3-g**[c] | B3LYP/6-311+G(2d,p) | 87.6814, 87.6833 | 2.3 |
| **9**[b] | B3LYP/6-311+G(2d,p) | 88.6253 | 1.3 |

[a] NMR calculation was performed based on the non-optimized, X-ray crystallographically determined molecular structure of **3**. [b] NMR calculations were performed based on the B3LYP/6-31+G(d)-optimized structures by using the Polarizable Continuum Model (PCM) (solvent: THF). [c] NMR calculation was performed based on the B3LYP/6-31+G(d)-optimized structure in the gas phase.

**Table S6.** Standard orientation of **3** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | –3.44259600 | 3.96356800 | 2.25174000 |
| C | –4.26873300 | 2.84344700 | 2.24061400 |
| C | –2.14601500 | 3.85039600 | 1.74496500 |
| C | 3.60249900 | 4.41857300 | 0.53720400 |
| C | –3.78951400 | 1.62729100 | 1.72507600 |
| C | –1.74494800 | 2.61321100 | 1.24888900 |
| C | 4.17401800 | 3.25768400 | 1.05145400 |
| C | 2.50123500 | 4.31027500 | –0.31576000 |
| C | –7.95855600 | 3.34323600 | –0.79957400 |
| C | –7.26687300 | 4.03116900 | –1.80231000 |
| C | –4.66523100 | 0.40542200 | 1.69729500 |
| C | –7.99210800 | –2.93628800 | 1.65879200 |
| C | –6.97536800 | –1.99276700 | 1.47436000 |
| C | –6.05456800 | 3.52389700 | –2.27857700 |
| C | –7.43756100 | 2.15443700 | –0.28075800 |
| C | 3.63533700 | 2.00613500 | 0.70891900 |
| C | 2.02038900 | 3.03555900 | –0.60450200 |
| C | –5.53735600 | 2.33511600 | –1.75224700 |
| C | –6.21600600 | 1.62441400 | –0.74351100 |
| C | 8.93188400 | 2.33187300 | 0.48579000 |
| C | 4.24423400 | 0.72615900 | 1.20696700 |
| C | –8.97366600 | –3.10772700 | 0.67855100 |
| C | 7.91359900 | 1.39061300 | 0.66182800 |

| | | | |
|---|---|---|---|
| C | –6.91288700 | –1.19879800 | 0.31304500 |
| C | 8.97350900 | 3.10817100 | –0.67736300 |
| C | 5.53687600 | –2.33455700 | 1.75307700 |
| C | 6.91280200 | 1.19906900 | –0.31233900 |
| C | 6.05397900 | –3.52322400 | 2.27977100 |
| C | –8.93214200 | –2.33156500 | –0.48469700 |
| C | –7.91382200 | –1.39039100 | –0.66097200 |
| C | 7.99208600 | 2.93678300 | –1.65774900 |
| C | 6.97538400 | 1.99317600 | –1.47355500 |
| C | –4.24486600 | –0.72588900 | –1.20725100 |
| C | 6.21574500 | –1.62406000 | 0.74434600 |
| C | –2.02071100 | –3.03599100 | 0.60294500 |
| C | 7.26639300 | –4.03058700 | 1.80388200 |
| C | –3.63597700 | –2.00605800 | –0.70968500 |
| C | 7.43740600 | –2.15417400 | 0.28197500 |
| C | 4.66593100 | –0.40558600 | –1.69729600 |
| C | –2.50184900 | –4.31057600 | 0.31411500 |
| C | 7.95829500 | –3.34286000 | 0.80115500 |
| C | –4.17497500 | –3.25745600 | –1.05227300 |
| C | 1.74579600 | –2.61374500 | –1.24977000 |
| C | 3.79039700 | –1.62758000 | –1.72529400 |
| C | –3.60344100 | –4.41853600 | –0.53846800 |
| C | 2.14723700 | –3.85092800 | –1.74555100 |
| C | 4.26999800 | –2.84372500 | –2.24049900 |
| C | 3.44402800 | –3.96396800 | –2.25181700 |
| H | –3.80306400 | 4.90753800 | 2.65214000 |
| H | –5.28041000 | 2.89851900 | 2.63130500 |
| H | –1.46131800 | 4.69255000 | 1.73484000 |
| H | 4.00996600 | 5.39202300 | 0.79740500 |
| H | 5.03249600 | 3.30912200 | 1.71437300 |
| H | –5.46238800 | 0.51106700 | 2.44271200 |
| H | 2.02224200 | 5.18597700 | –0.74262700 |
| H | –8.01621100 | –3.53525100 | 2.56602000 |
| H | –6.22388800 | –1.88235700 | 2.25282500 |
| H | –8.90389000 | 3.72926400 | –0.42555100 |
| H | –7.67140200 | 4.95419400 | –2.21035900 |
| H | –0.74575400 | 2.47467100 | 0.84538400 |

| | | | |
|---|---|---|---|
| H | –7.99796200 | 1.63013700 | 0.49089700 |
| H | –5.51048500 | 4.05098800 | –3.05854900 |
| H | 9.69249400 | 2.45687400 | 1.25282000 |
| H | 4.77400400 | 0.90157200 | 2.15131400 |
| H | –4.07572700 | –0.47696600 | 1.97359800 |
| H | 7.90577500 | 0.79260500 | 1.57112100 |
| H | –4.59141200 | 1.96489000 | –2.14003500 |
| H | 1.15827600 | 2.89288000 | –1.25146800 |
| H | –9.76591900 | –3.83881000 | 0.81974900 |
| H | 3.44959000 | –0.00161000 | 1.41090500 |
| H | 4.59083800 | –1.96426000 | 2.14056800 |
| H | 9.76573500 | 3.83931800 | –0.81837500 |
| H | 5.50972500 | –4.05015700 | 3.05973000 |
| H | –3.45019800 | 0.00183200 | –1.41126100 |
| H | –1.15834800 | –2.89357400 | 1.24963700 |
| H | –9.69285900 | –2.45660800 | –1.25161600 |
| H | 8.01626800 | 3.53585100 | –2.56490700 |
| H | –7.90607900 | –0.79248600 | –1.57033600 |
| H | 7.67083800 | –4.95352300 | 2.21221500 |
| H | 6.22400800 | 1.88280900 | –2.25212700 |
| H | –4.77495200 | –0.90101100 | –2.15147300 |
| H | 4.07643700 | 0.47667700 | –1.97401400 |
| H | 0.74643600 | –2.47531700 | –0.84663700 |
| H | –2.02283100 | –5.18643700 | 0.74062800 |
| H | 7.99797900 | –1.63003400 | –0.48966600 |
| H | –5.03370600 | –3.30863100 | –1.71488500 |
| H | 5.46344700 | –0.51123000 | –2.44233000 |
| H | 8.90371400 | –3.72896100 | 0.42742200 |
| H | –4.01114800 | –5.39187100 | –0.79871900 |
| H | 1.46266300 | –4.69318400 | –1.73558600 |
| H | 5.28183800 | –2.89869200 | –2.63078300 |
| H | 3.80478800 | –4.90793400 | –2.65196600 |
| Cl | 0.52825800 | –0.56666200 | 1.67384800 |
| Cl | –0.52807700 | 0.56580700 | –1.67515400 |
| Li | –1.49262600 | –0.13321200 | 0.44046400 |
| Li | 1.49278100 | 0.13264800 | –0.44159700 |
| N | –2.53570800 | 1.52381800 | 1.23239200 |

| | | | |
|---|---|---|---|
| N | 2.56422000 | 1.90786700 | –0.10993700 |
| N | –2.56455200 | –1.90811900 | 0.10880400 |
| N | 2.53638500 | –1.52423100 | –1.23310900 |
| Si | –5.51098300 | 0.03980700 | 0.01278000 |
| Si | 5.51089000 | –0.03962200 | –0.01245300 |

**Table S7.** Standard orientation of **3-g** [B3LYP /631+G(d)].

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | –3.18363800 | –3.60242000 | –2.89040100 |
| C | –4.09227900 | –2.57489700 | –2.65415100 |
| C | –1.84863700 | –3.41806200 | –2.52806400 |
| C | 3.63008500 | –4.53890400 | –0.01475800 |
| C | –3.65412700 | –1.38249100 | –2.05506800 |
| C | –1.49295400 | –2.21069500 | –1.93212100 |
| C | 4.15173400 | –3.40736200 | –0.63669100 |
| C | 2.49033100 | –4.41071800 | 0.78237000 |
| C | –7.04628500 | –3.67505300 | 1.21410800 |
| C | –6.00850900 | –4.33315100 | 1.88032800 |
| C | –4.61431800 | –0.25066200 | –1.80431900 |
| C | –8.46581300 | 2.40532600 | –1.23251700 |
| C | –7.29201900 | 1.64432600 | –1.22110400 |
| C | –4.75992700 | –3.71639600 | 1.99540700 |
| C | –6.83254100 | –2.40510600 | 0.67102300 |
| C | 3.52513200 | –2.16336700 | –0.45191100 |
| C | 1.92445100 | –3.14453100 | 0.91916200 |
| C | –4.54831800 | –2.44724100 | 1.44836900 |
| C | –5.58252700 | –1.76366300 | 0.77699400 |
| C | 8.91916000 | –1.72857200 | –1.03289800 |
| C | 4.04901900 | –0.90623600 | –1.08286500 |
| C | –9.28081400 | 2.45052600 | –0.09919300 |
| C | 7.74499600 | –0.97154000 | –1.03798200 |
| C | –6.90186000 | 0.91033100 | –0.08526300 |
| C | 9.28064000 | –2.45100900 | 0.10864100 |
| C | 4.55290600 | 2.44969200 | –1.44430400 |
| C | 6.90198800 | –0.91042400 | 0.09041200 |
| C | 4.76580600 | 3.71986500 | –1.98845600 |

| | | | |
|---|---|---|---|
| C | –8.91434200 | 1.73250800 | 1.04354800 |
| C | –7.74006000 | 0.97566200 | 1.04648700 |
| C | 8.46078300 | –2.41005600 | 1.23862500 |
| C | 7.28717600 | –1.64881800 | 1.22510900 |
| C | –4.04584000 | 0.90889200 | 1.08019300 |
| C | 5.58508400 | 1.76536900 | –0.77058600 |
| C | –1.92514200 | 3.14290900 | –0.93074100 |
| C | 6.01372900 | 4.33693800 | –1.86807000 |
| C | –3.52340500 | 2.16458500 | 0.44519800 |
| C | 6.83443600 | 2.40719600 | –0.65919900 |
| C | 4.60993200 | 0.24800800 | 1.80530100 |
| C | –2.49117300 | 4.40925700 | –0.79614300 |
| C | 7.04949200 | 3.67814900 | –1.19940300 |
| C | –4.15013100 | 3.40884100 | 0.62784600 |
| C | 1.49033400 | 2.21135800 | 1.92292900 |
| C | 3.64987600 | 1.38028100 | 2.05444700 |
| C | –3.62976900 | 4.53902500 | 0.00239000 |
| C | 1.84473800 | 3.41726000 | 2.52259200 |
| C | 4.08671300 | 2.57106800 | 2.65768800 |
| C | 3.17823400 | 3.59927800 | 2.89157600 |
| H | –3.51220700 | –4.52940200 | –3.35408900 |
| H | –5.13705700 | –2.68529800 | –2.93036100 |
| H | –1.09923900 | –4.18493800 | –2.69847400 |
| H | 4.10531500 | –5.50728300 | –0.15226000 |
| H | 5.03633300 | –3.47469100 | –1.26327100 |
| H | –5.48809700 | –0.37432000 | –2.45576200 |
| H | 2.04542000 | –5.26567800 | 1.28255600 |
| H | –8.74134700 | 2.96161300 | –2.12550200 |
| H | –6.67495100 | 1.63162900 | –2.11670200 |
| H | –8.02187700 | –4.14693000 | 1.12085300 |
| H | –6.17294400 | –5.31963800 | 2.30770700 |
| H | –0.46672600 | –2.01531000 | –1.63319100 |
| H | –7.65632600 | –1.90635700 | 0.16460200 |
| H | –3.94585600 | –4.22012500 | 2.51100100 |
| H | 9.55228000 | –1.75232000 | –1.91685400 |
| H | 4.58114700 | –1.14019700 | –2.01381400 |
| H | –4.13647900 | 0.69764500 | –2.07961500 |

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|---|---|---|---|
| H | 7.48826100 | –0.41070900 | –1.93496600 |
| H | –3.56175800 | –1.99950000 | 1.54753300 |
| H | 1.02746100 | –2.98218900 | 1.51254400 |
| H | –10.19498400 | 3.03926800 | –0.10546700 |
| H | 3.20417000 | –0.25951300 | –1.34812100 |
| H | 3.56688500 | 2.00170300 | –1.54756100 |
| H | 10.19470000 | –3.03990000 | 0.11657900 |
| H | 3.95328400 | 4.22414800 | –2.50594500 |
| H | –3.20041900 | 0.26267200 | 1.34484500 |
| H | –1.02902600 | 2.97939200 | –1.52512600 |
| H | –9.54366800 | 1.75956400 | 1.93011500 |
| H | 8.73240400 | –2.96982500 | 2.13063500 |
| H | –7.47942900 | 0.41830300 | 1.94451800 |
| H | 6.17920600 | 5.32422200 | –2.29319900 |
| H | 6.66629100 | –1.63940500 | 2.11811300 |
| H | –4.57569600 | 1.14498300 | 2.01190000 |
| H | 4.13043900 | –0.70035500 | 2.07751800 |
| H | 0.46530200 | 2.01788600 | 1.61875200 |
| H | –2.04727700 | 5.26313700 | –1.29906600 |
| H | 7.65667200 | 1.90798900 | –0.15071400 |
| H | –5.03384400 | 3.47741400 | 1.25554000 |
| H | 5.48178100 | 0.36990600 | 2.45964400 |
| H | 8.02454400 | 4.15029700 | –1.10197100 |
| H | –4.10509800 | 5.50758700 | 0.13824800 |
| H | 1.09552300 | 4.18480700 | 2.69076900 |
| H | 5.13036200 | 2.67974400 | 2.93880700 |
| H | 3.50577200 | 4.52502400 | 3.35845100 |
| Cl | 0.75560600 | 0.76021500 | –1.48732100 |
| Cl | –0.75578100 | –0.76225100 | 1.47890000 |
| Li | –1.34984800 | 0.26684600 | –0.58377800 |
| Li | 1.34923400 | –0.26777800 | 0.57566700 |
| N | –2.36554800 | –1.21614500 | –1.69235500 |
| N | 2.42550600 | –2.04686300 | 0.32552000 |
| N | –2.42493000 | 2.04652800 | –0.33363900 |
| N | 2.36276200 | 1.21609300 | 1.68560300 |
| Si | –5.27934900 | –0.07209400 | –0.00927200 |
| Si | 5.27984700 | 0.07233800 | 0.01178400 |

**Table S8.** Standard orientation of **6** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | 3.53121900 | 3.52467900 | –0.27199100 |
| C | 3.72992400 | 2.41868700 | –1.10294900 |
| C | 2.23897900 | 3.76316100 | 0.19491600 |
| C | 2.64143100 | 1.61038200 | –1.42162400 |
| C | 3.83578100 | –3.18152200 | –0.52342400 |
| C | 1.37049700 | 1.92365500 | –0.90540800 |
| C | 2.95436700 | –3.10358500 | –1.60667700 |
| C | 3.54700900 | –2.48262900 | 0.65239800 |
| C | 0.16388600 | 1.08082300 | –1.22679900 |
| C | 1.79303800 | –2.33087800 | –1.50913800 |
| C | 2.38257600 | –1.71249200 | 0.74244600 |
| C | 1.47903000 | –1.61807200 | –0.33399500 |
| C | –4.08511000 | 0.63016400 | –2.57191800 |
| C | –0.66951900 | 1.07642400 | 2.10509600 |
| C | –1.51002000 | –1.51416800 | –1.06765500 |
| C | –0.52578300 | –0.22084400 | 1.57645100 |
| C | –2.79260900 | –0.74519300 | –1.23688400 |
| C | –5.10369200 | 0.71649900 | –1.62249300 |
| C | –1.04113600 | 1.27864300 | 3.43980700 |
| C | –0.76952000 | –1.30877800 | 2.44097600 |
| C | –3.76892300 | –0.71263400 | –0.22477300 |
| C | –1.27931200 | 0.18539600 | 4.27684600 |
| C | –4.93498400 | 0.02423800 | –0.42042700 |
| C | –1.14150500 | –1.11319000 | 3.77368200 |
| H | 4.34845900 | 4.18459200 | 0.00355300 |
| H | 4.71687700 | 2.19053600 | –1.49732000 |
| H | 2.03538700 | 4.61580900 | 0.84084200 |
| H | 2.76586700 | 0.74380000 | –2.06442300 |
| H | 4.73852900 | –3.78318800 | –0.59523000 |
| H | 3.16919900 | –3.64450900 | –2.52525800 |
| H | 4.22592200 | –2.53736800 | 1.50011500 |
| H | 0.19575900 | 0.76764400 | –2.27868500 |
| H | 1.12727500 | –2.28776900 | –2.36890600 |
| H | –0.74087800 | 1.68727200 | –1.10849200 |

| | | | |
|---|---|---|---|
| H | 2.17713600 | –1.18094400 | 1.66859300 |
| H | –4.17514000 | 1.15026700 | –3.52427800 |
| H | –0.47609400 | 1.94178200 | 1.47659200 |
| H | –1.16374000 | –1.84357400 | –2.05397300 |
| H | –1.14295500 | 2.29110200 | 3.82366800 |
| H | –5.99556800 | 1.30302800 | –1.82191500 |
| H | –1.67911400 | –2.41423200 | –0.46316300 |
| H | –0.66588000 | –2.32925700 | 2.07549200 |
| H | –1.56864900 | 0.34177900 | 5.31326200 |
| H | –3.60904900 | –1.26189300 | 0.69862500 |
| H | –1.32292500 | –1.97059400 | 4.41753000 |
| H | –5.70006800 | 0.05610400 | 0.35108400 |
| N | 1.18144700 | 2.99401400 | –0.10805700 |
| N | –2.95806300 | –0.07701000 | –2.39672200 |
| Si | –0.07841300 | –0.54085900 | –0.23378800 |

**Table S9.** Standard orientation of **8** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | 3.69352700 | 3.07149600 | –0.88699000 |
| C | 3.71428400 | 1.92511300 | –1.68472300 |
| C | 2.50465200 | 3.41283000 | –0.23177800 |
| C | 2.55851000 | 1.15904800 | –1.80234600 |
| C | 3.61961100 | –3.66840700 | –0.96267900 |
| C | 1.40025700 | 1.56364300 | –1.11481400 |
| C | 2.54759600 | –3.61043000 | –1.85914300 |
| C | 3.59634000 | –2.88033500 | 0.19187700 |
| C | 0.11890600 | 0.77644800 | –1.21196200 |
| C | 1.46160600 | –2.76935800 | –1.59705100 |
| C | 2.50609100 | –2.04176000 | 0.44678700 |
| C | 1.41374400 | –1.96653300 | –0.43930800 |
| C | –4.36935300 | 0.55355700 | –1.68681400 |
| C | –0.21071900 | 0.93633700 | 2.20048000 |
| C | –1.64442300 | –1.70555400 | –0.66402100 |
| C | –0.15258100 | –0.38594900 | 1.71998500 |
| C | –2.90750700 | –0.88885100 | –0.59227300 |

| | | | |
|---|---|---|---|
| C | –5.18878800 | 0.65103200 | –0.55557000 |
| C | –0.34171800 | 1.20614500 | 3.56809800 |
| C | –0.22954400 | –1.42868100 | 2.66707000 |
| C | –3.68132700 | –0.83927100 | 0.58043400 |
| C | –0.41878500 | 0.15672800 | 4.48761700 |
| C | –4.83435400 | –0.05935700 | 0.59331300 |
| C | –0.36111400 | –1.16565100 | 4.03325600 |
| H | 4.57848000 | 3.69154200 | –0.77584600 |
| H | 4.62154100 | 1.63539800 | –2.20916100 |
| H | 2.54414700 | 0.26282000 | –2.41533200 |
| H | 4.46475900 | –4.32268400 | –1.16214800 |
| H | 2.55554600 | –4.21955100 | –2.75997000 |
| H | 4.42550400 | –2.91783000 | 0.89451900 |
| H | –0.02386900 | 0.42219700 | –2.24160700 |
| H | 0.64315500 | –2.74420800 | –2.31377900 |
| H | –0.72851600 | 1.43332100 | –0.98667400 |
| H | 2.50950800 | –1.43950400 | 1.35221300 |
| H | –0.13614500 | 1.76846400 | 1.50542400 |
| H | –1.50367500 | –2.04696300 | –1.69608700 |
| H | –0.38182700 | 2.23680000 | 3.91303900 |
| H | –6.08340700 | 1.26668300 | –0.57801700 |
| H | –1.73069500 | –2.59924000 | –0.03273300 |
| H | –0.18323300 | –2.46621600 | 2.33974700 |
| H | –0.52026800 | 0.36543400 | 5.54992000 |
| H | –3.37986700 | –1.40472300 | 1.45718300 |
| H | –0.41703000 | –1.98929000 | 4.74118200 |
| H | –5.45230500 | –0.00617700 | 1.48626500 |
| N | 1.38606000 | 2.67133500 | –0.35058200 |
| N | –3.25459400 | –0.20251500 | –1.69735100 |
| Si | –0.04322200 | –0.79353600 | –0.12402400 |
| C | 2.40736700 | 4.63895700 | 0.64332400 |
| C | –4.69179700 | 1.29220100 | –2.96303400 |
| H | 3.34931200 | 5.19566200 | 0.66147700 |
| H | 1.61519700 | 5.30674700 | 0.28419300 |
| H | 2.15172100 | 4.35826100 | 1.67233900 |
| H | –4.76862100 | 0.59251500 | –3.80371000 |
| H | –5.63346200 | 1.84359000 | –2.88190600 |

| | | | |
|---|---|---|---|
| H | –3.89398700 | 2.00432000 | –3.20708500 |

**Table S10.** Standard orientation of **9** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | –0.63278200 | 4.06654800 | 1.50657400 |
| C | 0.04017900 | 2.87610300 | 1.76799600 |
| C | –1.68207400 | 4.06076800 | 0.58448700 |
| C | –0.34794300 | 1.69667900 | 1.11017300 |
| C | –2.00811700 | 2.85281500 | –0.02687300 |
| C | 4.61297400 | 2.97719500 | 0.18742500 |
| C | 0.38149300 | 0.40374200 | 1.34974300 |
| C | 3.84096800 | 1.84009400 | 0.44289700 |
| C | 4.31798300 | 3.79059200 | –0.91178400 |
| C | 2.44640100 | –2.19105300 | 1.79535100 |
| C | 2.75650700 | 1.48720900 | –0.38572200 |
| C | 3.25690400 | –3.24402100 | 2.23445300 |
| C | 3.24933900 | 3.45918100 | –1.74964800 |
| C | 2.47936700 | 2.32121300 | –1.48649700 |
| C | 2.79042400 | –1.42167400 | 0.66760500 |
| C | 4.43533500 | –3.55263900 | 1.54930000 |
| C | 3.98439100 | –1.75165200 | –0.00577900 |
| C | 0.81168800 | –0.60355300 | –1.58895700 |
| C | 4.79829200 | –2.80275700 | 0.42526000 |
| C | –1.98631900 | –2.84082600 | –0.72696100 |
| C | –0.00152100 | –1.85536500 | –1.41418300 |
| C | –1.53118000 | –4.12438900 | –1.01667600 |
| C | 0.52975300 | –3.11707700 | –1.73064200 |
| C | –0.24023100 | –4.26002900 | –1.53343200 |
| H | –0.34154000 | 4.98359700 | 2.01206300 |
| H | 0.86300800 | 2.84984700 | 2.47626500 |
| H | –2.23402800 | 4.96359200 | 0.34259700 |
| H | 5.44497400 | 3.22514500 | 0.84227200 |
| H | 0.89591100 | 0.44417000 | 2.31704800 |
| H | 4.09577900 | 1.21604400 | 1.29719700 |
| H | –2.81028300 | 2.79327000 | –0.75837000 |

| | | | |
|---|---|---|---|
| H | –0.33293800 | –0.42712600 | 1.38952300 |
| H | 1.53411800 | –1.97519100 | 2.34683600 |
| H | 4.91822000 | 4.67417700 | –1.11439100 |
| H | 2.96722100 | –3.82109400 | 3.10937200 |
| H | 3.01368200 | 4.08429300 | –2.60747000 |
| H | 5.06728300 | –4.36964000 | 1.88862100 |
| H | 1.65386300 | 2.08942100 | –2.15520300 |
| H | 0.17095800 | 0.20879400 | –1.94988700 |
| H | –2.98503600 | –2.67815100 | –0.32964200 |
| H | 4.29162200 | –1.17711500 | –0.87773900 |
| H | 1.58920200 | –0.76343900 | –2.34565100 |
| H | 5.71465900 | –3.03396200 | –0.11251500 |
| H | –2.17128900 | –4.98464200 | –0.84770400 |
| H | 1.53692700 | –3.18954400 | –2.12971100 |
| H | 0.15929300 | –5.24000700 | –1.78071300 |
| Cl | –3.12984000 | 0.77678400 | –2.85972800 |
| Li | –2.35476800 | 0.07471300 | –0.75417200 |
| N | –1.36899300 | 1.69435900 | 0.22483200 |
| N | –1.25222800 | –1.72932300 | –0.91715600 |
| Si | 1.69204600 | –0.02510100 | 0.01331800 |
| O | –3.89689800 | –0.37248100 | 0.45191200 |
| C | –3.84074400 | –0.32364300 | 1.90165300 |
| C | –5.27911300 | –0.42698300 | 0.00824800 |
| C | –5.27920100 | –0.53061000 | 2.38668300 |
| H | –3.14887200 | –1.09957200 | 2.24516200 |
| H | –3.44696800 | 0.65703500 | 2.19337800 |
| C | –6.10535400 | 0.01974100 | 1.21222600 |
| H | –5.36643600 | 0.21398000 | –0.87129900 |
| H | –5.51270900 | –1.46113400 | –0.27901200 |
| H | –5.47270600 | –0.01456200 | 3.33210900 |
| H | –5.48736900 | –1.59742400 | 2.53200400 |
| H | –6.15762500 | 1.11425500 | 1.25645400 |
| H | –7.12677100 | –0.37213300 | 1.18329300 |

**Table S11.** Standard orientation of **10** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Li | –1.49842300 | –0.02544200 | –0.02256500 |
| Cl | 0.02711100 | 0.03670700 | –1.86557600 |
| Li | 1.52956800 | 0.01973400 | 0.00883700 |
| Cl | –0.01018200 | –0.15265200 | 1.84329700 |
| O | –2.75264200 | –1.56237600 | –0.09578000 |
| O | –2.71339800 | 1.53282300 | 0.08748800 |
| O | 2.59051300 | 1.69195100 | 0.03918700 |
| O | 2.78780500 | –1.52335800 | 0.00155000 |
| C | 2.70768800 | 2.64895600 | –1.04483900 |
| C | 3.09817000 | 3.96869400 | –0.38035700 |
| C | 3.94409900 | 3.48956000 | 0.81121200 |
| C | 3.20641200 | 2.21984800 | 1.24328200 |
| C | 2.90844800 | –2.51194300 | 1.05701900 |
| C | 3.27188600 | –3.81766300 | 0.35090800 |
| C | 4.10643300 | –3.31692800 | –0.83970300 |
| C | 3.38051700 | –2.02558400 | –1.22566700 |
| C | –3.39918100 | –2.02235300 | 1.12224900 |
| C | –3.89331300 | –3.44195400 | 0.82580000 |
| C | –2.90134600 | –3.92127100 | –0.24743700 |
| C | –2.67100800 | –2.64619000 | –1.05626300 |
| C | –3.75478000 | 1.75445200 | –0.89779200 |
| C | –4.37114200 | 3.10855000 | –0.54476300 |
| C | –3.16848700 | 3.86533700 | 0.04257900 |
| C | –2.43394300 | 2.76240200 | 0.80747300 |
| H | 1.75101900 | 2.67299100 | –1.57149300 |
| H | 3.48646200 | 2.29908300 | –1.73537700 |
| H | 3.64527500 | 4.62934000 | –1.06004800 |
| H | 2.20545200 | 4.49976300 | –0.02876700 |
| H | 4.00752500 | 4.22402400 | 1.61998900 |
| H | 4.96369200 | 3.25157800 | 0.48494800 |
| H | 3.86350600 | 1.44820000 | 1.65569400 |
| H | 2.41176300 | 2.43420500 | 1.96753000 |
| H | 1.95917900 | –2.53905200 | 1.59713900 |
| H | 3.70233200 | –2.19028600 | 1.74423700 |

| | | | |
|---|---|---|---|
| H | 3.82037000 | –4.50369300 | 1.00390100 |
| H | 2.36708800 | –4.32727500 | –0.00140100 |
| H | 4.14740100 | –4.02932400 | –1.66940800 |
| H | 5.13407800 | –3.10207700 | –0.52271800 |
| H | 4.04336500 | –1.25154700 | –1.62432900 |
| H | 2.57281800 | –2.20661200 | –1.94439500 |
| H | –4.20353500 | –1.32147100 | 1.36654600 |
| H | –2.65380500 | –2.00263200 | 1.92514000 |
| H | –3.89761300 | –4.07070800 | 1.72146900 |
| H | –4.91200500 | –3.41992500 | 0.42030000 |
| H | –3.29282300 | –4.73829400 | –0.86160400 |
| H | –1.96504000 | –4.25521800 | 0.21520900 |
| H | –1.69339000 | –2.58628200 | –1.54013700 |
| H | –3.45390000 | –2.50165100 | –1.81308600 |
| H | –4.45517300 | 0.91683100 | –0.83906900 |
| H | –3.29401700 | 1.76501300 | –1.89377200 |
| H | –4.80877400 | 3.60359500 | –1.41719700 |
| H | –5.15655800 | 2.98880800 | 0.21140800 |
| H | –3.45687200 | 4.69717500 | 0.69268000 |
| H | –2.53687900 | 4.26102400 | –0.76162100 |
| H | –1.34959500 | 2.89436900 | 0.84545500 |
| H | –2.81352600 | 2.65243800 | 1.83092800 |

**Table S12.** Standard orientation of **13** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | 3.86984700 | 3.96446000 | –2.64852300 |
| C | 4.63110800 | 2.83515300 | –2.37327600 |
| C | 2.48225100 | 3.87504900 | –2.55414600 |
| C | –3.76870400 | 4.47281800 | –0.56910300 |
| C | 3.98948300 | 1.64264700 | –1.99934100 |
| C | 1.90009400 | 2.66135400 | –2.17285400 |
| C | –4.12558400 | 3.25358900 | –1.13557400 |
| C | –2.93935400 | 4.47767100 | 0.55186200 |
| C | 7.15050800 | 3.50340600 | 1.72867000 |
| C | 6.08869200 | 4.14287100 | 2.37623000 |

| | | | |
|---|---|---|---|
| C | 4.81933100 | 0.41420300 | –1.73800700 |
| C | 8.62221700 | –2.33518800 | –1.10242800 |
| C | 7.46632100 | –1.54609500 | –1.12587700 |
| C | 4.81544700 | 3.56564600 | 2.34953700 |
| C | 6.93582400 | 2.29278600 | 1.06225000 |
| C | –3.61756800 | 2.06629700 | –0.58452300 |
| C | –2.46478400 | 3.26088200 | 1.05586000 |
| C | 4.60535000 | 2.35593400 | 1.67918700 |
| C | 5.66163000 | 1.69221900 | 1.02226000 |
| C | –8.86698200 | 1.86277600 | –1.22306500 |
| C | –4.05107000 | 0.72933600 | –1.11323800 |
| C | 9.30579800 | –2.54034600 | 0.09891300 |
| C | –7.74459400 | 1.03186100 | –1.16392000 |
| C | 6.96388800 | –0.94274800 | 0.04269700 |
| C | –9.20233500 | 2.66463600 | –0.12666000 |
| C | –4.80854800 | –2.55728600 | –1.43366400 |
| C | –6.92873800 | 0.97519900 | –0.01515400 |
| C | –5.09627800 | –3.82810900 | –1.94262200 |
| C | 8.82541000 | –1.95407000 | 1.27504100 |
| C | 7.67013400 | –1.16838700 | 1.24259100 |
| C | –8.40804700 | 2.62876300 | 1.02259500 |
| C | –7.28630400 | 1.79342600 | 1.07350600 |
| C | 4.02486000 | –0.94235200 | 0.98568800 |
| C | –5.78027900 | –1.81059200 | –0.73746500 |
| C | 2.56374900 | –3.14316100 | –1.59295100 |
| C | –6.36647000 | –4.38443600 | –1.76413600 |
| C | 3.64638700 | –2.19241500 | 0.24548600 |
| C | –7.05293400 | –2.39207900 | –0.56955000 |
| C | –4.73155100 | –0.24787300 | 1.79690000 |
| C | 3.07439700 | –4.40848800 | –1.28177300 |
| C | –7.34592000 | –3.66287800 | –1.07407800 |
| C | 4.18656900 | –3.43609800 | 0.60925300 |
| C | –1.90905200 | –2.60718300 | 2.27084700 |
| C | –3.94862500 | –1.48453400 | 2.14490800 |
| C | 3.88356700 | –4.55776900 | –0.15581800 |
| C | –2.52471500 | –3.74055900 | 2.81251500 |
| C | –4.62222500 | –2.59353500 | 2.68325400 |

| | | | |
|---|---|---|---|
| C | –3.90328900 | –3.73421900 | 3.01797100 |
| H | 4.34743400 | 4.89604300 | –2.94149500 |
| H | 5.71388000 | 2.86106500 | –2.45084700 |
| H | 1.85038500 | 4.73014300 | –2.77395600 |
| H | –4.14362800 | 5.40529100 | –0.98372100 |
| H | –4.79103600 | 3.20856600 | –1.99221800 |
| H | 5.73945000 | 0.48876300 | –2.32962800 |
| H | –2.66324000 | 5.40817200 | 1.03860200 |
| H | 8.98581000 | –2.78844200 | –2.02162400 |
| H | 6.95491600 | –1.40879400 | –2.07562900 |
| H | 8.14496500 | 3.94337800 | 1.74510900 |
| H | 6.25267200 | 5.08242100 | 2.89848100 |
| H | 7.77823500 | 1.80946400 | 0.57225000 |
| H | 3.98336400 | 4.05567100 | 2.84961100 |
| H | –9.47933300 | 1.88295900 | –2.12149300 |
| H | –4.48766200 | 0.84108200 | –2.11325000 |
| H | 4.28219300 | –0.47606500 | –2.08152400 |
| H | –7.50675100 | 0.41394000 | –2.02777400 |
| H | 3.60179400 | 1.93585100 | 1.67028700 |
| H | 10.20480300 | –3.15145000 | 0.11987400 |
| H | –3.18551500 | 0.06498600 | –1.21489200 |
| H | –3.81005900 | –2.15262000 | –1.58300400 |
| H | –10.07553300 | 3.31108900 | –0.16858100 |
| H | –4.32788700 | –4.38152700 | –2.47716300 |
| H | 3.14328900 | –0.31112200 | 1.14546900 |
| H | 9.35035600 | –2.10696000 | 2.21503700 |
| H | –8.65909300 | 3.24995400 | 1.87912200 |
| H | 7.31943200 | –0.71969000 | 2.17032300 |
| H | –6.59200700 | –5.37169900 | –2.16002700 |
| H | –6.68520000 | 1.79075000 | 1.97977400 |
| H | 4.42479500 | –1.19196800 | 1.97600300 |
| H | –4.12869000 | 0.64520900 | 1.99333300 |
| H | 2.84153400 | –5.25645100 | –1.91861100 |
| H | –7.83304000 | –1.84625200 | –0.04304100 |
| H | 4.83760500 | –3.50812900 | 1.47503900 |
| H | –5.61232200 | –0.19961900 | 2.44805200 |
| H | –8.33722600 | –4.08675400 | –0.93119600 |

| | | | |
|---|---|---|---|
| H | 4.28544800 | –5.53223100 | 0.11029200 |
| H | –1.92531600 | –4.60892400 | 3.06817000 |
| H | –5.69631900 | –2.54711200 | 2.83570900 |
| H | –4.40584900 | –4.60198800 | 3.43770600 |
| Cl | –0.82188500 | –0.89300500 | –1.34445100 |
| Cl | 0.86075200 | 0.79295100 | 1.31860400 |
| Li | 1.52162000 | –0.20531300 | –0.87572800 |
| Li | –1.46131400 | 0.13387800 | 0.79724000 |
| N | 2.64308200 | 1.56317400 | –1.88920000 |
| N | –2.77266600 | 2.07781500 | 0.47384300 |
| N | 2.81972200 | –2.06151200 | –0.81965100 |
| N | –2.61160200 | –1.49578900 | 1.93716200 |
| Si | 5.36606000 | 0.08041300 | 0.07478200 |
| Si | –5.37289100 | –0.11098100 | –0.01108100 |
| C | –0.42182700 | –2.58739700 | 2.04230400 |
| C | 1.73440600 | –2.92967900 | –2.83207600 |
| C | –1.61956900 | 3.22336100 | 2.30201900 |
| C | 0.40407600 | 2.53863700 | –2.06524300 |
| H | 0.04452500 | –1.74260900 | 2.55957400 |
| H | 0.03964300 | –3.51473300 | 2.39451400 |
| H | –0.19763900 | –2.46583500 | 0.97678400 |
| H | 0.74490100 | –2.53695700 | –2.57751600 |
| H | 2.21603200 | –2.19483300 | –3.48980000 |
| H | 1.61538400 | –3.86287800 | –3.39078200 |
| H | –0.08999300 | 3.44553900 | –2.42614400 |
| H | 0.03584200 | 1.68291100 | –2.64011100 |
| H | 0.10702000 | 2.36972300 | –1.02426000 |
| H | –2.13811500 | 2.66922000 | 3.09531400 |
| H | –0.66960700 | 2.71191000 | 2.11882000 |
| H | –1.41644500 | 4.23388600 | 2.66934000 |

**Table S13.** Standard orientation of **14** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | 0.56855400 | 4.11840200 | –1.47722300 |
| C | –0.10350300 | 2.93475200 | –1.76161200 |

| | | | |
|---|---|---|---|
| C | 1.60265500 | 4.09464000 | –0.54371000 |
| C | 0.27495300 | 1.75370000 | –1.10435100 |
| C | 1.94381700 | 2.88309100 | 0.06945300 |
| C | –4.49933600 | 3.30557100 | –0.07999500 |
| C | –0.48216300 | 0.48054500 | –1.36400500 |
| C | –3.80394900 | 2.13454200 | –0.39457100 |
| C | –4.17981000 | 4.01821200 | 1.08072200 |
| C | –2.68525300 | –1.98368800 | –1.87007500 |
| C | –2.77444700 | 1.64607100 | 0.43493700 |
| C | –3.56251400 | –2.95954100 | –2.35585800 |
| C | –3.16414200 | 3.55202000 | 1.92036800 |
| C | –2.47125200 | 2.38009400 | 1.59787100 |
| C | –3.00560700 | –1.20468600 | –0.74157600 |
| C | –4.78664600 | –3.17975500 | –1.71826200 |
| C | –4.24614600 | –1.44498400 | –0.11658300 |
| C | –0.93484800 | –0.60440800 | 1.51795200 |
| C | –5.12732100 | –2.41899000 | –0.59475000 |
| C | 1.33437200 | –3.27783400 | 0.35362600 |
| C | –0.34740000 | –1.97022600 | 1.29669800 |
| C | 0.71107800 | –4.45459200 | 0.78154100 |
| C | –1.01872300 | –3.11291200 | 1.75871700 |
| C | –0.47997100 | –4.36847900 | 1.50151000 |
| H | 0.28889700 | 5.04535300 | –1.97141900 |
| H | –0.91925800 | 2.91488200 | –2.47779400 |
| H | 2.14751900 | 4.99897500 | –0.29007200 |
| H | –5.29067300 | 3.65896100 | –0.73687100 |
| H | –0.98391400 | 0.54600500 | –2.33643500 |
| H | –4.07606900 | 1.59127300 | –1.29747800 |
| H | 0.20228700 | –0.37469400 | –1.40296700 |
| H | –1.73884400 | –1.83550400 | –2.38526600 |
| H | –4.72058800 | 4.92797700 | 1.32975000 |
| H | –3.28952200 | –3.54556600 | –3.23025500 |
| H | –2.91065800 | 4.09801800 | 2.82585700 |
| H | –5.47090100 | –3.93640900 | –2.09418000 |
| H | –1.68547300 | 2.04043900 | 2.26865500 |
| H | –0.15148800 | 0.09866200 | 1.82518200 |
| H | –4.53714200 | –0.85999500 | 0.75382600 |

| | | | |
|---|---|---|---|
| H | –1.66782800 | –0.64222700 | 2.33226200 |
| H | –6.07860400 | –2.58145900 | –0.09362600 |
| H | 1.15976800 | –5.41734500 | 0.55650300 |
| H | –1.94717200 | –3.00623400 | 2.31110900 |
| H | –0.98011600 | –5.26709400 | 1.85345500 |
| Cl | 2.74755600 | –0.32853200 | 2.94722100 |
| Li | 2.15840200 | –0.21728200 | 0.66010600 |
| N | 1.28861800 | 1.72992400 | –0.20748100 |
| N | 0.81623200 | –2.05574500 | 0.61320400 |
| Si | –1.81258600 | 0.08654900 | –0.03730700 |
| O | 3.81202800 | –0.21954800 | –0.48955800 |
| C | 3.83960500 | 0.09261400 | –1.90550400 |
| C | 5.16217300 | –0.42165100 | 0.00417800 |
| C | 5.28094600 | –0.15059100 | –2.36019000 |
| H | 3.10752300 | –0.54474500 | –2.41163000 |
| H | 3.54122700 | 1.14007900 | –2.03182000 |
| C | 6.08016400 | 0.14189800 | –1.07962300 |
| H | 5.23946400 | 0.07705300 | 0.97239800 |
| H | 5.32404100 | –1.49790500 | 0.14824800 |
| H | 5.56125100 | 0.48984200 | –3.20209200 |
| H | 5.41759100 | –1.19507900 | –2.66488000 |
| H | 6.21482600 | 1.22232000 | –0.94797100 |
| H | 7.06789300 | –0.32907500 | –1.07064400 |
| C | 3.08662400 | 2.82759100 | 1.04923600 |
| C | 2.63121100 | –3.33551200 | –0.41173100 |
| H | 2.56732100 | –2.75316600 | –1.33696900 |
| H | 3.44881500 | –2.91336600 | 0.18211000 |
| H | 2.89006900 | –4.36734300 | –0.66663000 |
| H | 2.86499300 | 2.15988600 | 1.88678100 |
| H | 3.98964400 | 2.43893200 | 0.56143300 |
| H | 3.31878100 | 3.82549900 | 1.43392100 |

**Table S14.** Standard orientation of **THF** [B3LYP /6-31+G(d)] (PCM calculations; solvent: THF).

| Atomic symbol | x | y | z |
|---|---|---|---|
| O | 0.00025400 | –1.25617700 | –0.00056000 |
| C | 1.17453000 | –0.42672500 | –0.13105900 |
| C | –1.17413600 | –0.42727600 | 0.13181400 |
| C | 0.73404200 | 0.99683700 | 0.22627500 |
| H | 1.95085200 | –0.82304500 | 0.53215500 |
| H | 1.53634100 | –0.48607500 | –1.16756100 |
| C | –0.73472000 | 0.99624900 | –0.22664700 |
| H | –1.95132600 | –0.82426300 | –0.52995800 |
| H | –1.53424000 | –0.48629400 | 1.16896000 |
| H | 1.34125800 | 1.75925100 | –0.27187100 |
| H | 0.80034200 | 1.15909500 | 1.30903200 |
| H | –0.80119500 | 1.15756800 | –1.30953700 |
| H | –1.34236500 | 1.75867400 | 0.27096300 |

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