Cover Page for Supporting Information

Trisyl-based multidentate ligands: synthesis and their transition-metal complexes

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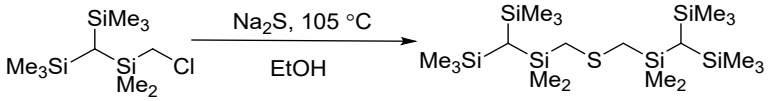
1) Experimental procedures and characterization data for 1-2

Preparation of $(Me_3Si)_2CH(SiMe_2CH_2Cl)$ 1

To a solution of $(Me_3Si)_2CHBr$ (28 g, 117 mmol) in dry Et_2O (230 mL) was added dropwise a solution of ^{n}BuLi (73 mL, 1.6 M solution in hexanes, 117 mmol) at -78 °C under nitrogen. The mixture was stirred for additional 30 min at -78 °C. $ClSiMe_2CH_2Cl$ (16.7 g, 117 mmol) was then added dropwise at -78 °C. The reaction mixture was stirred for another 24 h at room temperature. The solution was filtered through Celite, and the solvent was removed and dried *in vacuo* to give light yellow liquid. Distillation under reduced pressure at 120 °C under 2.5 mbar, obtaining a colorless liquid compound **1** (25 g), yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.51 (s, 1H, CH), 0.12 (s, 18H, $SiMe_3$), 0.23 (s, 6H, $SiMe_2$), 2.83 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 1.7 ($SiMe_2$), 3.6 (CH), 33.8 (CH_2). HRMS (EI-MS): calculated m/z for $C_9H_{25}Si_3$ [M-CH_2Cl]: 217.12641, found: 217.12567.

Preparation of 2a

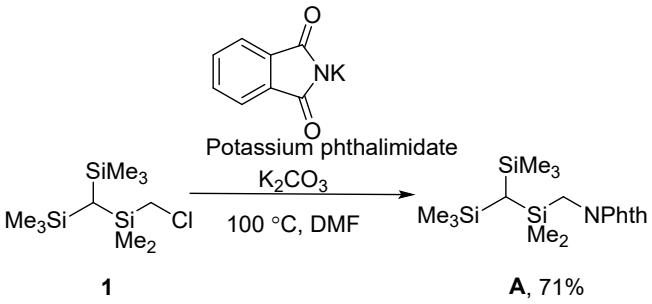


1 **2a**, 65%

The reaction of **1** (5.34 g, 20 mmol) and Na_2S (780 mg, 10 mmol) was processed at 105 °C for 12 h. The unreacted compound **1** is removed by distillation at 200 °C/2.5 mbar. The residue was then purified by column chromatography over silica gel (eluent: PE, monitored by TLC under $KMnO_4$) to afford 3.24 g (65%) of **2a** as a pale colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.55 (s, 2H, CH), 0.12 (s, 36H, $SiMe_3$), 0.19 (s, 12H, $SiMe_2$), 1.87 (s, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 1.1 ($SiMe_2$), 2.1 (CH), 25.1 (CH_2). HRMS (ESI) calcd for $C_{20}H_{55}SSi_6$ $[M+H]^+$ 495.26401, found: 495.26261.

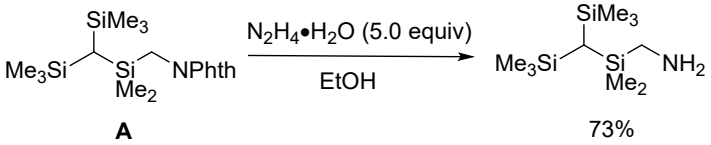
Preparation of 2b

Step 1: Preparation of $(Me_3Si)_2CH(SiMe_2CH_2NPhth)$ A



1 (2.0 g, 7.5 mmol) was added to a stirring mixture of potassium phthalimide (1.7 g, 9.4 mol) and anhydrous K_2CO_3 (207 mg, 1.5 mmol) in anhydrous DMF (15 mL). The mixture was brought to 100°C and stirred for 12 h. After cooling to room temperature, H_2O was added, extracted by diethyl ether. The ethereal layer was separated from the aqueous layer and washed with brine. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using PE : EA = 10:1 as eluent to afford the pure $(Me_3Si)_2CH(SiMe_2CH_2NPhth)$ **A** as white solid (2.0 g, 71% yield). ^1H NMR (500 MHz, $CDCl_3$) δ -0.46 (s, 1H, CH), 0.15 (s, 6H, $SiMe_2$), 0.16 (s, 18H, $SiMe_3$), 3.26 (s, 2H, CH_2), 7.67 (d, J = 4.1 Hz, 2H, Phth), 7.80 (d, J = 3.2 Hz, 2H, Phth). ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 2.0 ($SiMe_2$), 2.5 (CH), 30.4 (CH_2), 122.1 (Ar), 131.5 (Ar), 132.8 (Ar), 167.8 (CO). HRMS (ESI) calcd for $C_{18}H_{32}NO_2Si_3$ $[M+H]^+$ 378.17408, found: 378.17275.

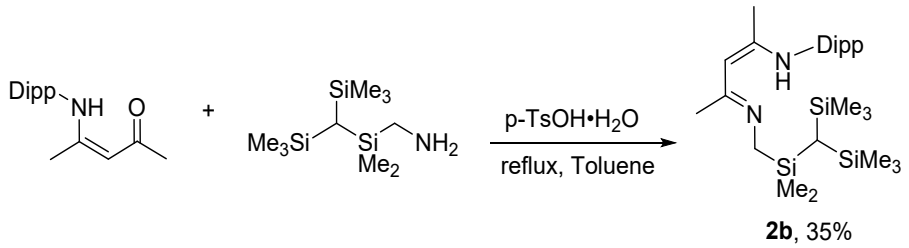
Step 2: Preparation of $(Me_3Si)_2CH(SiMe_2CH_2NH_2)$



$(Me_3Si)_2CH(SiMe_2CH_2NPhth)$ **A** (15.13 g, 40 mmol) was dissolved in anhydrous EtOH (280 mL) with mechanical stirring. Hydrazine monohydrate (10.27 g, 201 mol, 98% w/w) was added in one portion to the EtOH solution, and the temperature of the solution was brought to 90°C. During the reaction, phthalylhydrazide formation was evidenced by a cloudy-gel-like precipitate. After 8 hours of reaction, the solution was filtered under vacuum and washed with diethyl ether. The solvent was removed and dried *in vacuo*. Distillation under reduced pressure at 180 °C under 2.5 mbar, obtaining a light

yellow liquid **$(Me_3Si)_2CH(SiMe_2CH_2NH_2)$** (7.2 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.69 (s, 1H, CH), 0.11 (s, 18H, $SiMe_3$), 0.15 (s, 6H, $SiMe_2$), 2.22 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 1.9 ($SiMe_2$), 3.8 (CH), 33.5 (CH_2). HRMS (ESI) calcd for $C_{10}H_{30}NSi_3$ $[M+H]^+$ 248.16860, found: 248.16789.

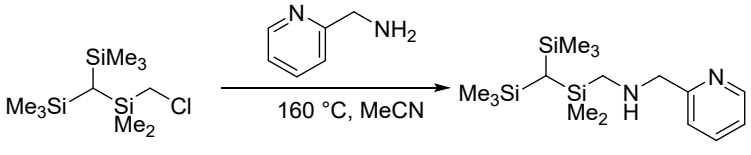
Step 3: Preparation of 2b



2b, 35%

$(Me_3Si)_2CH(SiMe_2CH_2NH_2)$ (1.24 g, 5.0 mmol), 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one[1] (1.30 g, 5.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (10 mL) were combined and heated at reflux for 24 h. The solvent was removed and dried *in vacuo*. The unreacted 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one and formed $DippNH_2$ are removed by distillation at 200 °C/2.5 mbar to give brown oil **2b** without other purification, yielding at least 35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.70 (s, 1H, CH), 0.07 (s, 18H, $SiMe_3$), 0.13 (s, 6H, $SiMe_2$), 1.10 (d, J = 6.9 Hz, 6H, $CH(\underline{CH_3})_2$), 1.13 (d, J = 7.0 Hz, 6H, $CH(\underline{CH_3})_2$), 1.60 (s, 3H, MeC(N)), 2.00 (s, 3H, MeC(N)), 2.75 (s, 2H, $SiMe_2\underline{CH_2}$), 2.93 (dt, J = 13.4, 6.6 Hz, 2H, $\underline{CH}(CH_3)_2$), 4.65 (s, 1H, MeC(N)$\underline{CH}$), 7.02 (d, J = 6.9 Hz, 1H, ArH), 7.08 (d, J = 7.2 Hz, 2H, ArH), 10.65 (br s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 1.8 ($SiMe_2$), 3.3 (CH), 19.8 ($CH(\underline{C}H_3)_2$), 21.7 ($CH(\underline{C}H_3)_2$), 23.4 (MeC(N)), 24.1 (MeC(N)), 27.9 ($\underline{C}H(CH_3)_2$), 35.3 ($SiMe_2\underline{C}H_2$), 92.6 (MeC(N)$\underline{CH}$), 122.4 (Ar), 122.7 (Ar), 138.5 (Ar), 147.2 (Ar), 157.8 (imine C), 166.2 (imine C). HRMS (ESI) calcd for $C_{27}H_{53}N_2Si_3$ $[M+H]^+$ 489.35165, found: 489.35070.

Preparation of B

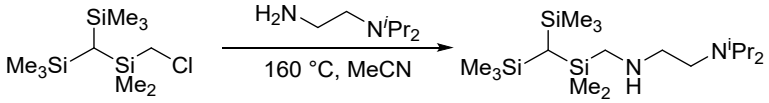


1 **B**, 73%

To a 250 mL Schlenk tube containing a magnetic stirring bar were added MeCN (60

mL), $(Me_3Si)_2CH(SiMe_2CH_2Cl)$ **1** (2.67 g, 10 mmol, 1.0 equiv) and 2-aminomethylpyridine (3.24 g, 3.0 equiv, 30 mmol). The reaction mixture was stirred at 160 °C for 18 h. The reaction was allowed to cool to rt, quenched with H_2O and extracted with DCM. The combined organics were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography over silica gel (eluent: DCM : MeOH = 20:1) afford the title compound **B** as yellow oil (2.46 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.68 (s, 1H, CH), 0.07 (s, 18H, $SiMe_3$), 0.16 (s, 6H, $SiMe_2$), 2.08 (s, 2H, $SiMe_2CH_2$), 3.89 (s, 2H, pyridineCH_2)), 7.18 – 7.11 (m, 1H, pyridine), 7.30 (d, J = 7.7 Hz, 1H, pyridine), 7.63 (t, J = 6.8 Hz, 1H, pyridine), 8.55 (d, J = 4.0 Hz, 1H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 1.4 ($SiMe_2$), 3.1 (CH), 41.1 ($SiMe_2CH_2$), 59.1 (pyridineCH_2), 121.6 (prydine), 122.2 (prydine), 135.9 (prydine), 149.1 (prydine), 160.0 (prydine). HRMS (ESI) calcd for $C_{16}H_{35}N_2Si_3$ $[M+H]^+$ 339.21080, found: 339.21001.

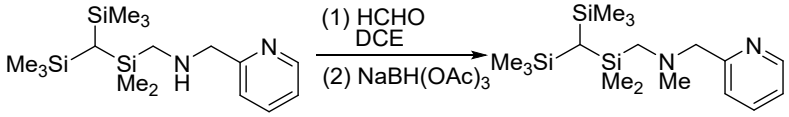
Preparation of C



1 **C**, 40%

To a 100 mL Schlenk tube containing a magnetic stirring bar were added MeCN (30 mL), $(Me_3Si)_2CH(SiMe_2CH_2Cl)$ **1** (2.67 g, 10 mmol, 1.0 equiv) and N',N'-diisopropyl-ethane-1,2-diamine (4.33 g, 3.0 equiv, 30 mmol). The reaction mixture was stirred at 160 °C for 18 h. The reaction was allowed to cool to rt, quenched with H_2O and extracted with DCM. The combined organics were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography over silica gel (eluent: PE :EA = 5:1 to DCM : MeOH = 20:1) afford the title compound **C** as light yellow oil (1.49 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.69 (s, 1H, CH), 0.10 (s, 18H, $SiMe_3$), 0.15 (s, 6H, $SiMe_2$), 0.98 (d, J = 6.6 Hz, 12H, $CH(\underline{CH_3})_2$), 2.09 (s, 2H, $SiMe_2CH_2$), 2.56 (s, 4H, CH_2CH_2), 2.99 (dt, J = 13.2, 6.6 Hz, 2H, $\underline{CH}(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 1.5 ($SiMe_2$), 2.9 (CH), 20.5 ($CH(\underline{CH_3})_2$), 41.9 ($SiMe_2CH_2$), 43.6 (CH_2CH_2), 47.4 ($\underline{C}H(CH_3)_2$), 53.6 (CH_2CH_2). HRMS (ESI) calcd for $C_{18}H_{47}N_2Si_3$ $[M+H]^+$ 375.30470, found: 375.30367.

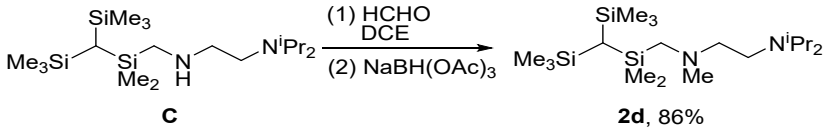
Preparation of 2c



B **2c**, 79%

Aqueous formaldehyde (423 mg, 5.6 mmol, 2.0 equiv, 40% in water) was added to a solution of **B** (944 mg, 2.8 mmol, 1.0 equiv) in 1,2-dichloroethane (15 mL). After 15 min, $NaBH(OAc)_3$ (1.2 g, 5.6 mmol, 2.0 equiv) was added portion-wise to the reaction mixture and stirring was continued for 24 h at room temperature. The reaction was quenched by the addition of an aqueous solution of 2 M NaOH (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using gradient hexane/ethyl acetate/Et_3N to DCM/MeOH mixture as eluent to afford the pure **2c** as yellow oil (776 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.66 (s, 1H, CH), 0.07 (s, 18H, $SiMe_3$), 0.19 (s, 6H, $SiMe_2$), 1.99 (s, 2H, $SiMe_2CH_2$), 2.22 (s, 3H, NMe), 3.60 (s, 2H, pyridineCH_2), 7.13 (dd, J = 6.8, 5.5 Hz, 1H, pyridine), 7.48 (d, J = 7.8 Hz, 1H, pyridine), 7.64 (td, J = 7.7, 1.7 Hz, 1H, pyridine), 8.56–8.44 (m, 1H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.1 ($SiMe_3$), 0.0 ($SiMe_2$), 1.5 (CH), 44.6 (NMe), 49.6 ($SiMe_2CH_2$), 66.3 (pyridineCH_2), 120.0 (prydine), 121.2 (prydine), 134.5 (prydine), 147.1 (prydine), 158.4 (prydine). HRMS (ESI) calcd for $C_{17}H_{37}N_2Si_3$ $[M+H]^+$ 353.22645, found: 353.22610.

Preparation of 2d

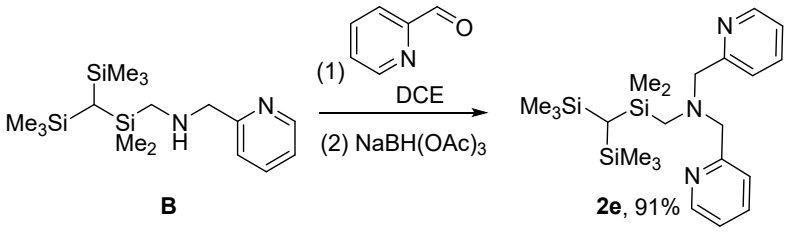


C **2d**, 86%

Aqueous formaldehyde (601 mg, 8.0 mmol, 2.0 equiv, 40% in water) was added to a solution of **C** (1.49 g, 4.0 mmol, 1.0 equiv) in 1,2-dichloroethane (20 mL). After 15 min, $NaBH(OAc)_3$ (1.7 g, 8.0 mmol, 2.0 equiv) was added portion-wise to the reaction mixture, and stirring was continued for 24 h at room temperature. The reaction was quenched by the addition of an aqueous solution of 2 M NaOH (15 mL). The organic

layer was separated, and the aqueous layer was extracted with DCM. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using gradient hexane/ethyl acetate/Et_3N mixture as eluent to afford the pure **2d** as light yellow oil (1.33 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.67 (s, 1H, CH), 0.11 (s, 18H, $SiMe_3$), 0.18 (s, 6H, $SiMe_2$), 1.00 (d, J = 6.5 Hz, 12H, $CH(\underline{CH_3})_2$), 1.90 (s, 2H, $SiMe_2CH_2$), 2.20 (s, 3H, NMe), 2.35–2.26 (m, 2H, CH_2CH_2), 2.50–2.43 (m, 2H, CH_2CH_2), 3.03–2.87 (m, 2H, $\underline{CH}(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 0.1 ($SiMe_2$), 1.6 (CH), 18.9 ($CH(\underline{CH_3})_2$), 42.3 ($SiMe_2CH_2$), 45.1 ($\underline{C}H(CH_3)_2$), 47.6 (NMe), 50.3 (CH_2CH_2), 62.4 (CH_2CH_2). HRMS (ESI) calcd for $C_{19}H_{49}N_2Si_3$ $[M+H]^+$ 389.32035, found: 389.31931.

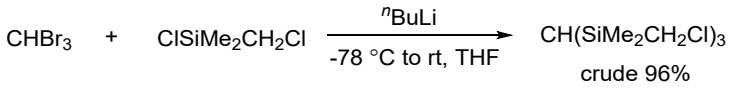
Preparation of $(Me_3Si)_2CH\{SiMe_2CH_2N(CH_2\text{-}_2\text{-}C_5H_3N)_2\}$ 2e



Pyridine-2-carbaldehyde (675 mg, 6.3 mmol, 2.1 equiv) was added to a solution of **B** (1.02 g, 3 mmol, 1.0 equiv) in 1,2-dichloroethane (20 mL). After 15 min, $NaBH(OAc)_3$ (1.27 g, 6.0 mmol, 2.0 equiv) was added portion-wise to the reaction mixture and stirring was continued for 24 h at room temperature. The reaction was quenched by the addition of an aqueous solution of 2 M NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with DCM. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using gradient hexane/ethyl acetate/Et_3N to DCM/MeOH mixture as eluent to afford the pure **2e** as orange yellow oil (1.17 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.79 (s, 1H, CH), 0.00 (s, 18H, $SiMe_3$), 0.16 (s, 6H, $SiMe_2$), 2.14 (s, 2H, $SiMe_2CH_2$), 3.71 (s, 4H, pyridineCH_2), 7.18–7.11 (m, 2H, pyridine), 7.57 (d, J = 7.6 Hz, 2H, pyridine), 7.67 (t, J = 7.1 Hz, 2H, pyridine), 8.51 (d, J = 4.0 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_3$), 0.6 ($SiMe_2$), 1.5 (CH), 45.8 ($SiMe_2CH_2$), 62.3 (pyridineCH_2), 120.2 (prydine), 121.2 (prydine), 134.6 (prydine), 147.2 (prydine), 158.2 (prydine). HRMS (ESI) calcd for $C_{22}H_{40}N_3Si_3$

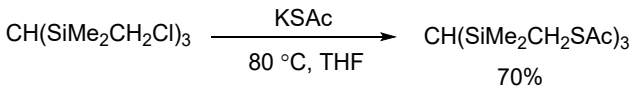
$[M+H]^+$ 430.25300, found: 430.25314.

Preparation of $HC(SiMe_2CH_2Cl)_3$



A 2.4 M solution of ^{n}BuLi in hexane (54 mL cm3, 131 mmol), cooled to - 78°C was added dropwise with vigorous stirring to a mixture of $ClSiMe_2CH_2Cl$ (17 g, 119 mmol) and $CHBr_3$ (10 g, 40 mmol) in THF (80 mL) maintained at -78 °C. When the addition was completed, the mixture was stirred at -78 °C for 1 h and was allowed to warm to room temperature, then cautiously treated with water. The organic layer was washed with dilute hydrochloric acid until the washings were colorless, then extracted by ethyl acetate, dried (Na_2SO_4), and filtered. The solvent was removed under vacuum to give colorless liquid (12.9 g, 96%) used without other purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 1H, CH), 0.28 (s, 18H, $SiMe_2$), 2.83 (s, 6H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.0 ($SiMe_2$), 32.8 (CH_2). (The signal from the central carbon atom was difficult to identify in this crude product). HRMS (EI-MS): calculated m/z for $C_9H_{23}Cl_2Si_3$ [M-CH_2Cl]: 285.04846, found: 285.04794.

Preparation of $HC(SiMe_2CH_2SAc)_3$



To a stirred solution of **$HC(SiMe_2CH_2Cl)_3$** (1.68 g, 5 mmol) in THF (40 mL) was added potassium thioacetate (3.43 g, 30 mmol), and the mixture was stirred at 80 °C for 24 h. And the solvent was evaporated to dryness in *vacuo*, and then added water, and the organic materials were extracted with ethyl acetate. The combined extracts were washed with water and brine, dried over anhydrous Na_2SO_4. The organic layer was purified by column chromatography over silica gel (eluent: PE :EA = 20:1) afford the title compound **$HC(SiMe_2CH_2SAc)_3$** as orange oil (1.59 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.33 (s, 1H, CH), 0.17 (s, 18H, $SiMe_2$), 2.13 (s, 6H, CH_2), 2.30 (s, 9H, SAc). ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.0 ($SiMe_2$), 0.0 (CH), 15.1 (CH_2), 29.3 ($COCH_3$), 195.3 (CO). HRMS (ESI) calcd for $C_{16}H_{35}O_3S_3Si_3$ $[M+H]^+$ 455.10561, found: 455.10444; HRMS (ESI) calcd for $C_{16}H_{38}NO_3S_3Si_3$ $[M+NH_4]^+$ 472.13216, found:

472.13046.

2) Copies of NMR Spectra

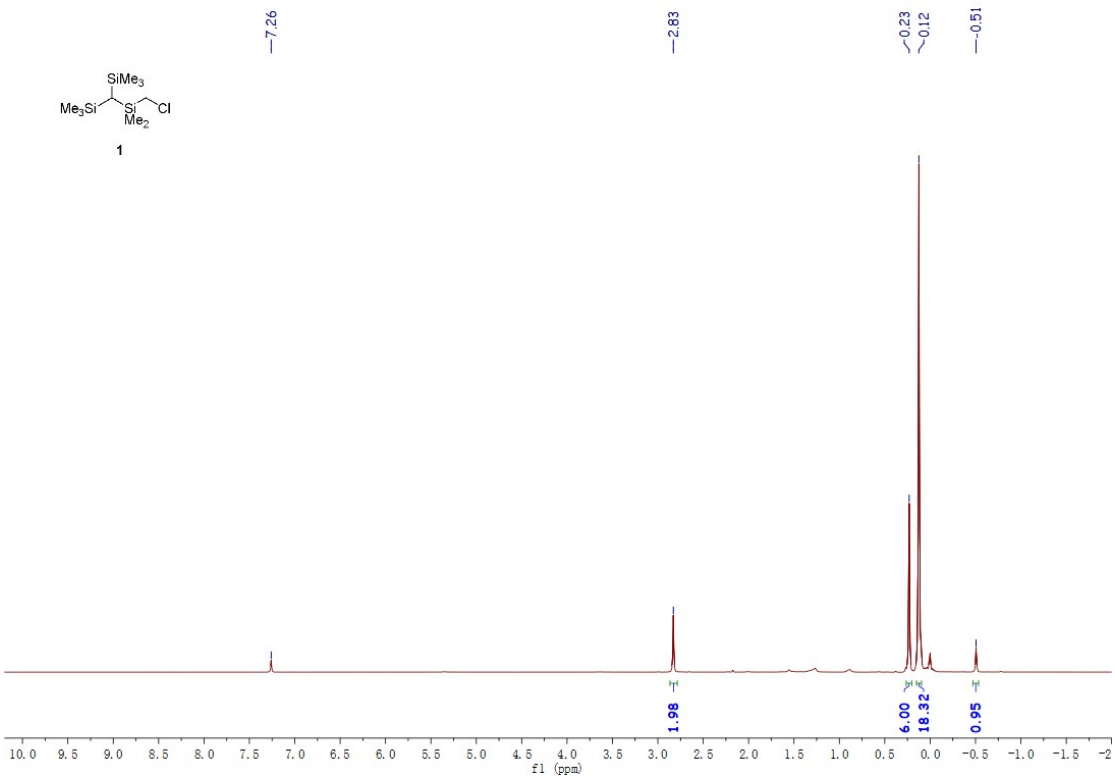


Figure S1 ^{1}H NMR of **1** at room temperature.

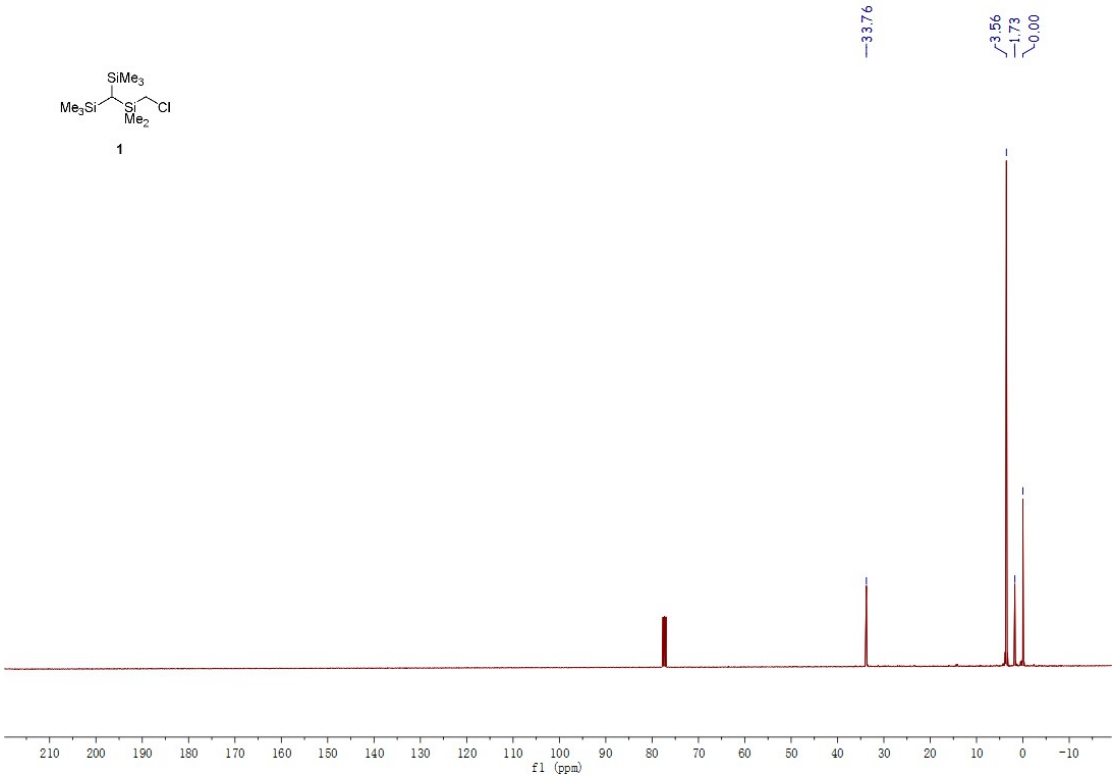


Figure S2 ^{13}C NMR of **1** at room temperature.

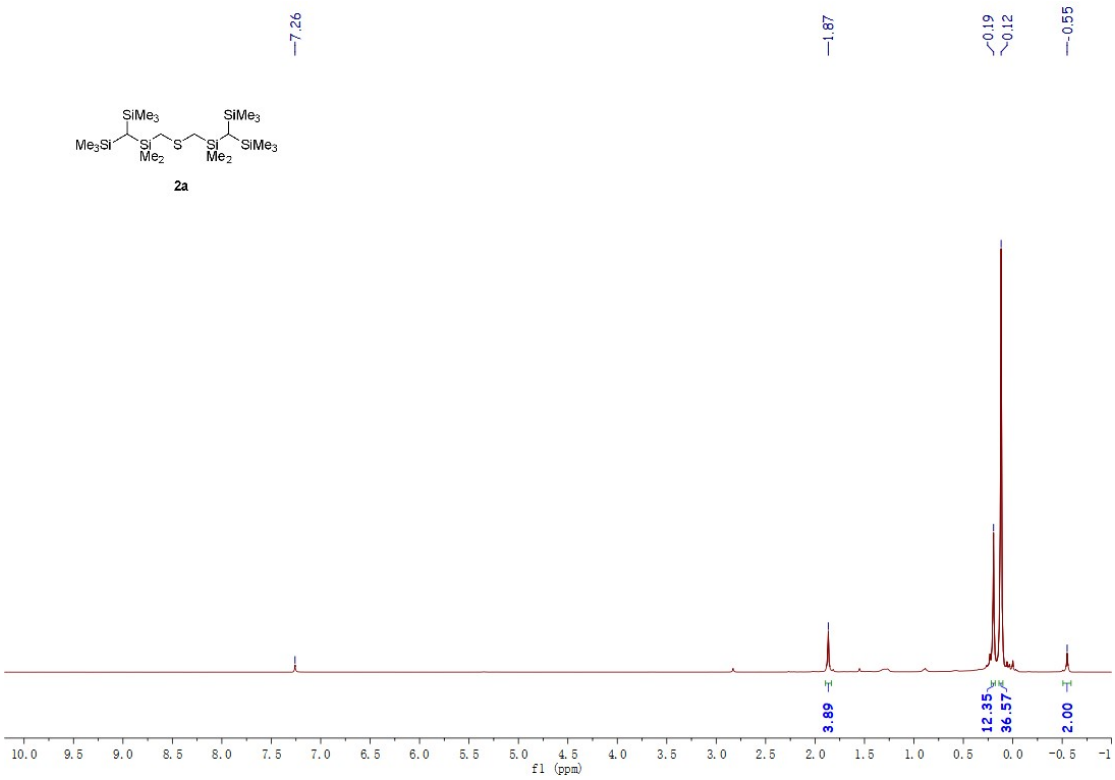


Figure S3 ^{1}H NMR of **2a** at room temperature.

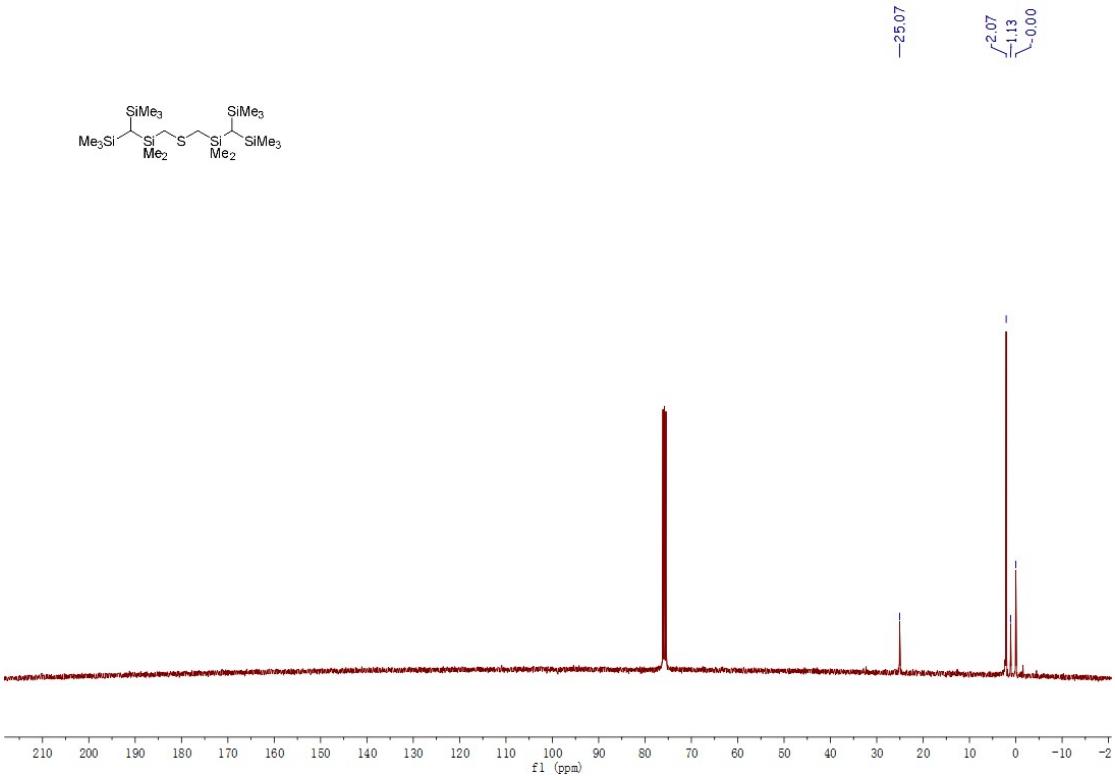


Figure S4 ^{13}C NMR of **2a** at room temperature.

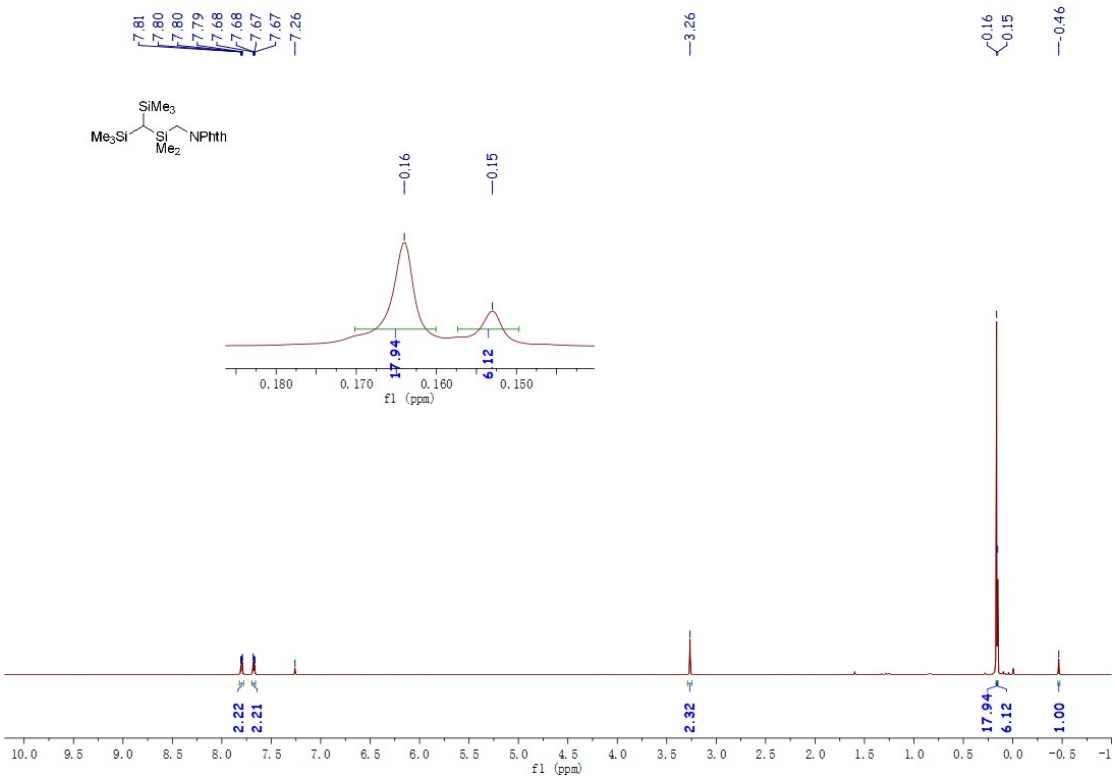


Figure S5 ^{1}H NMR of **A** at room temperature.

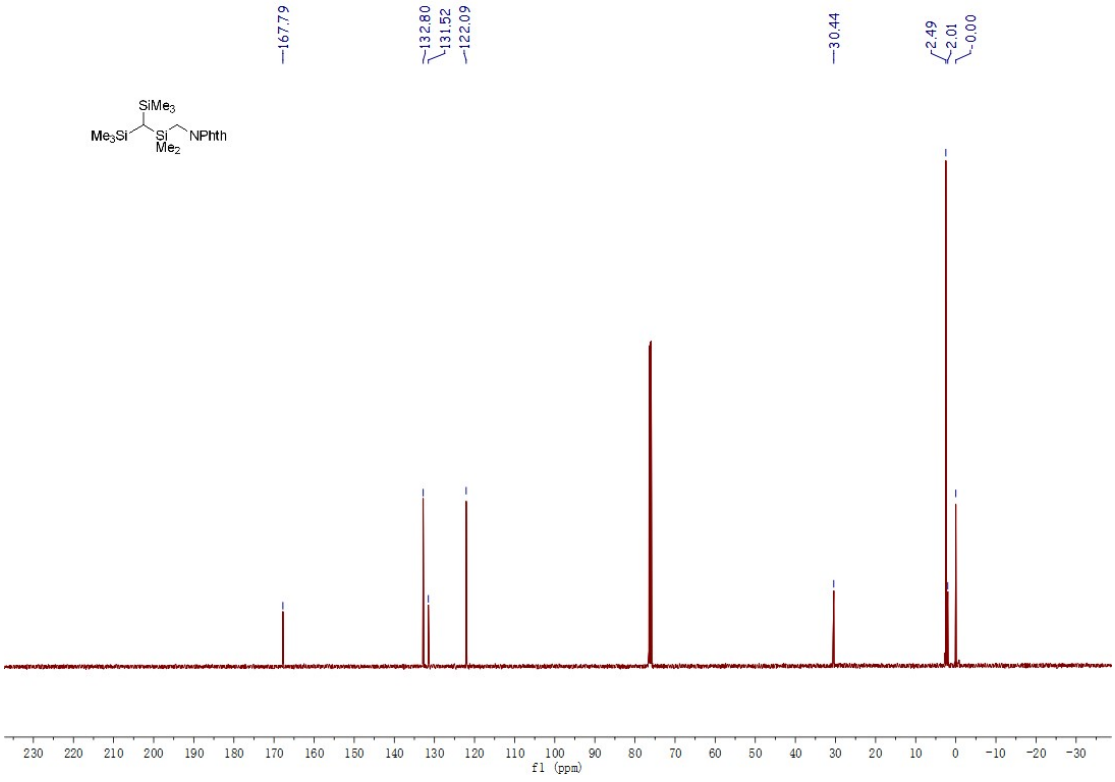


Figure S6 ^{13}C NMR of **A** at room temperature.

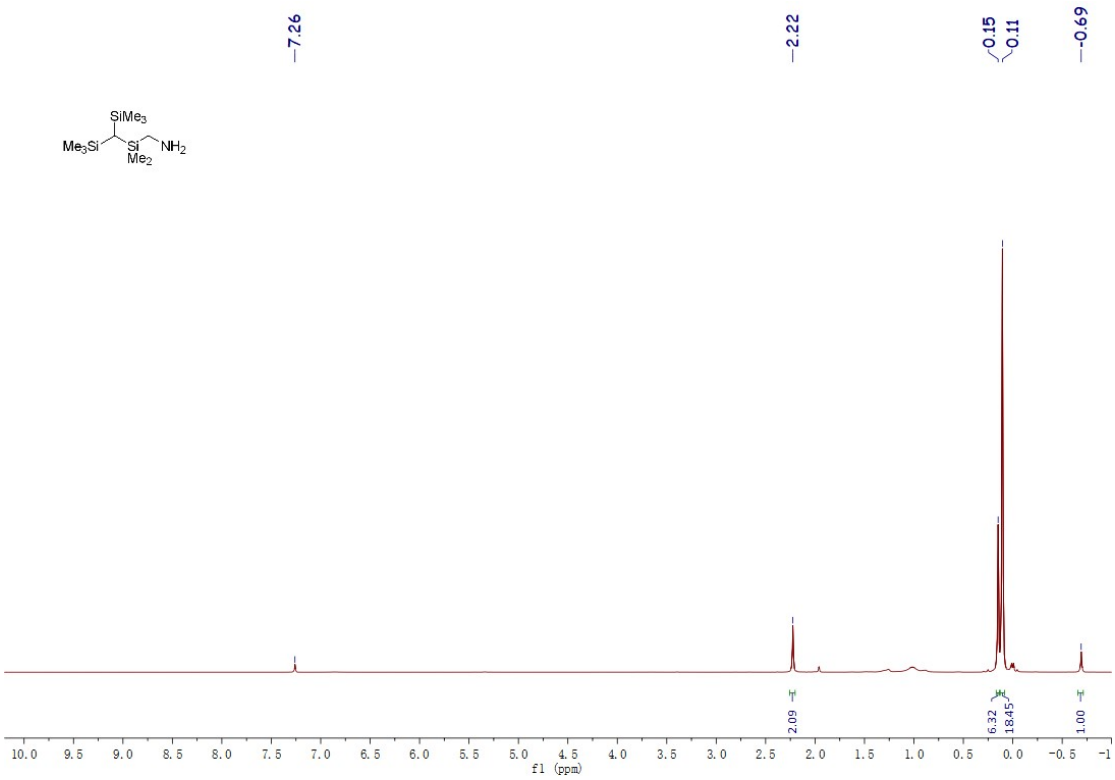


Figure S7 ^{1}H NMR of **$(Me_3Si)_2CH(SiMe_2CH_2NH_2)$** at room temperature.

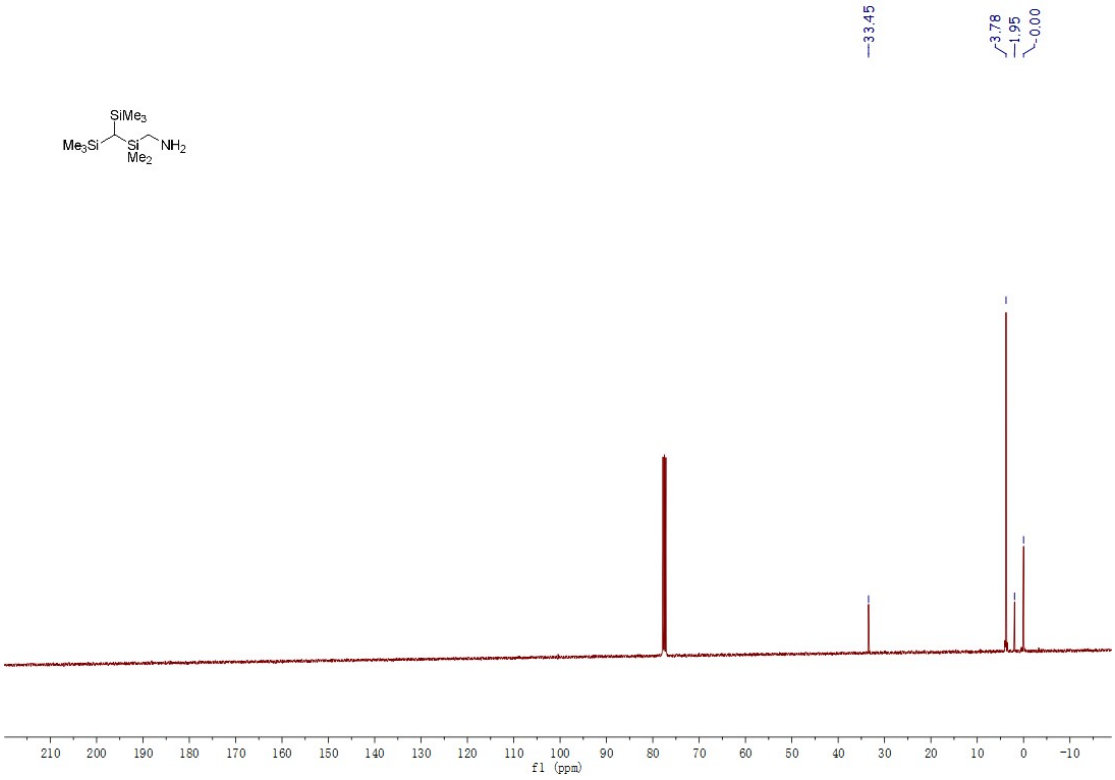


Figure S8 ^{13}C NMR of **$(Me_3Si)_2CH(SiMe_2CH_2NH_2)$** at room temperature.

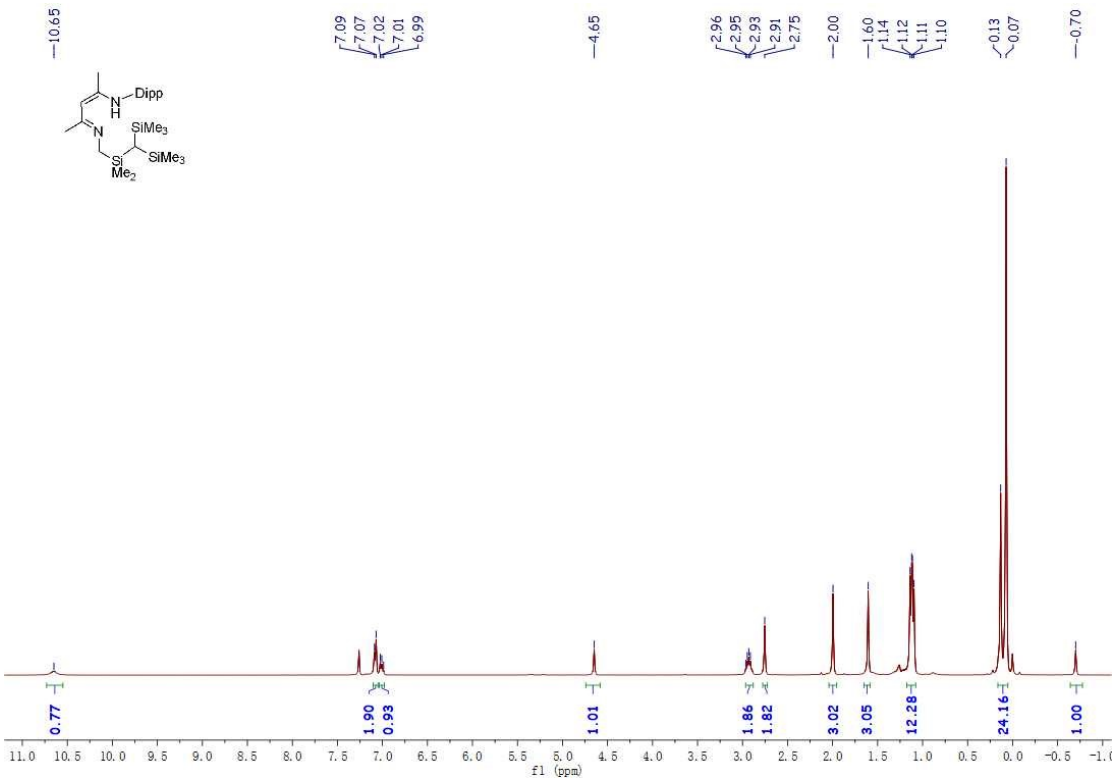


Figure S9 ^{1}H NMR of **2b** at room temperature.

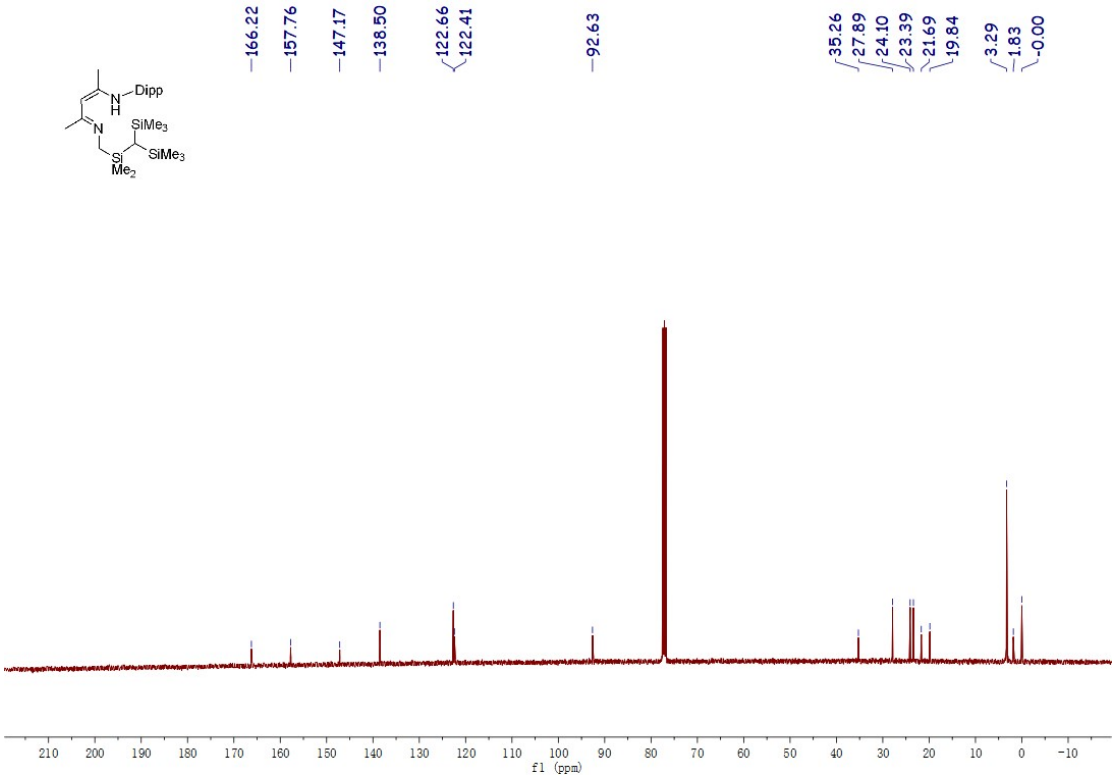


Figure S10 ^{13}C NMR of **2b** at room temperature.

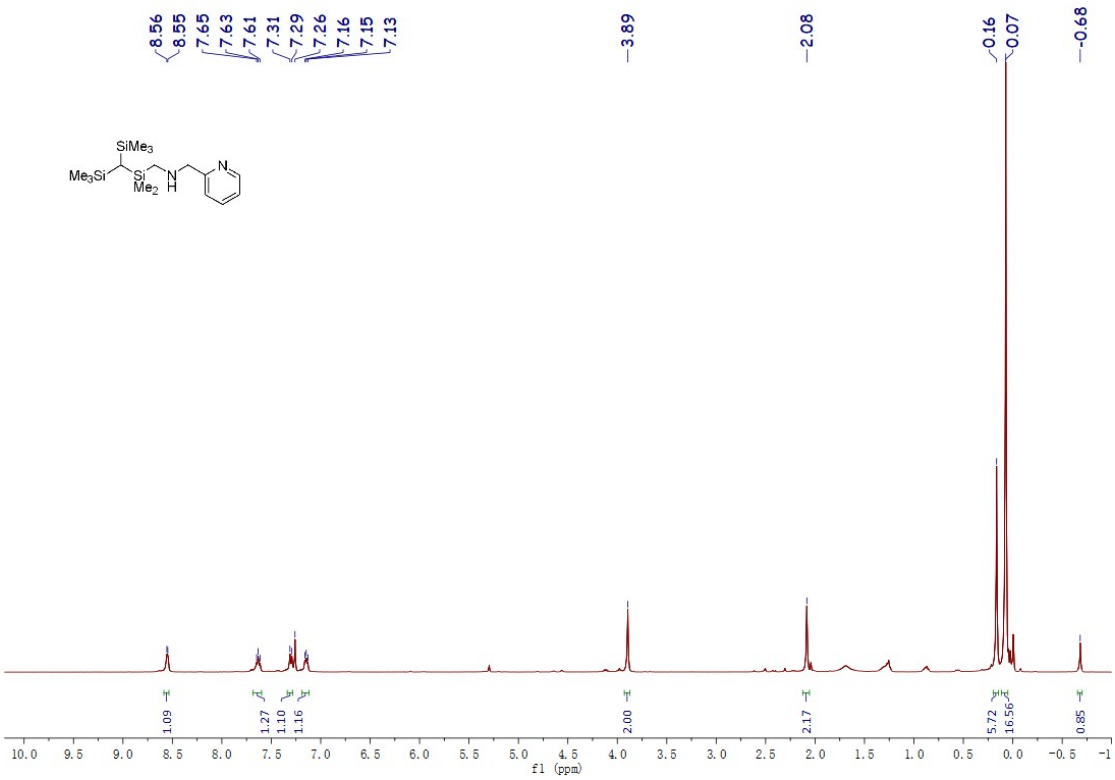


Figure S11 ^{1}H NMR of **B** at room temperature.

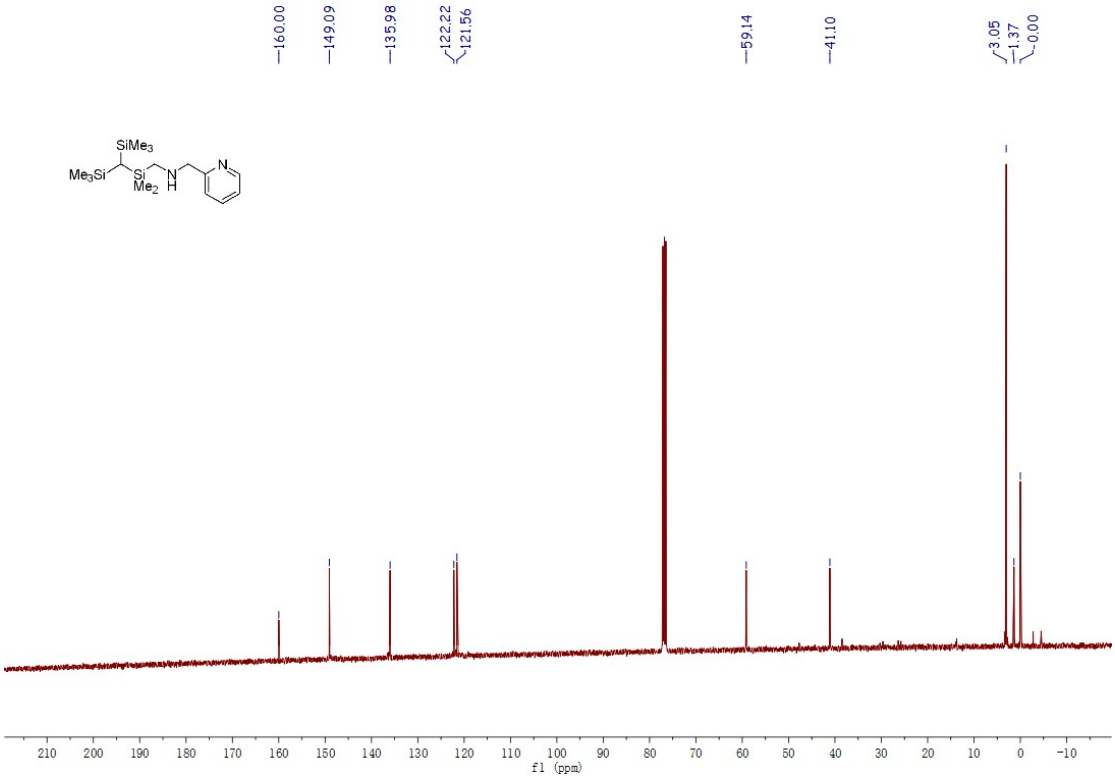


Figure S12 ^{13}C NMR of **B** at room temperature.

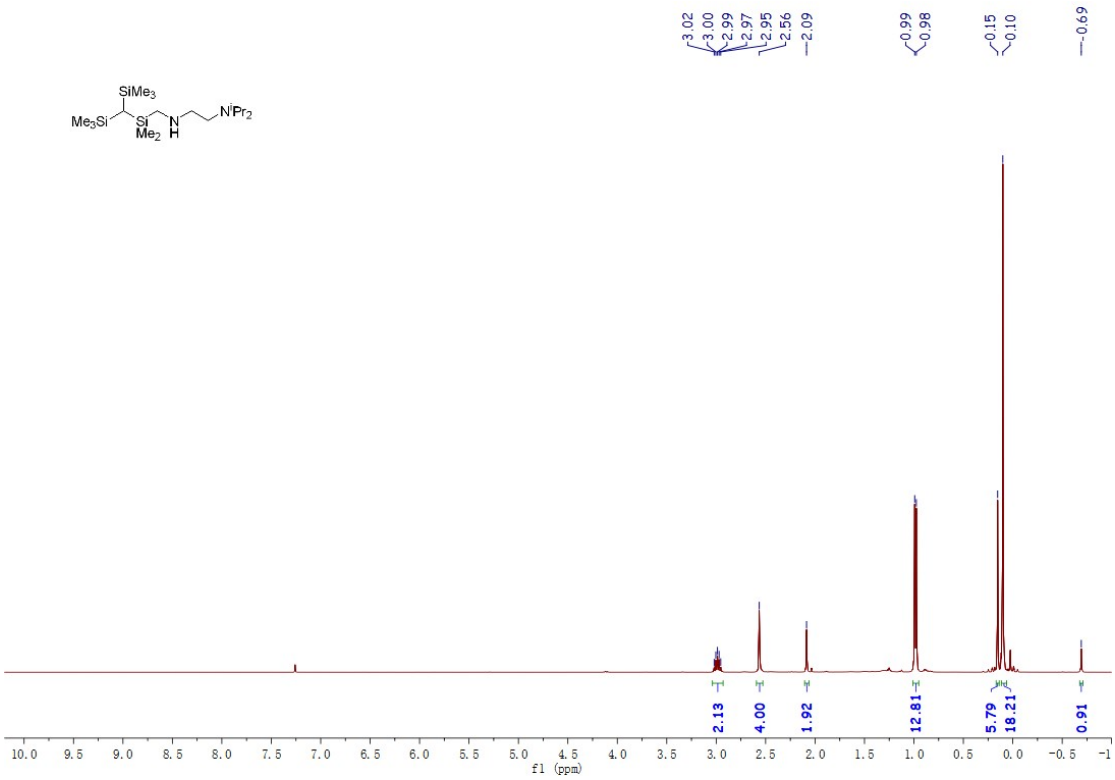


Figure S13 ^{1}H NMR of **C** at room temperature.

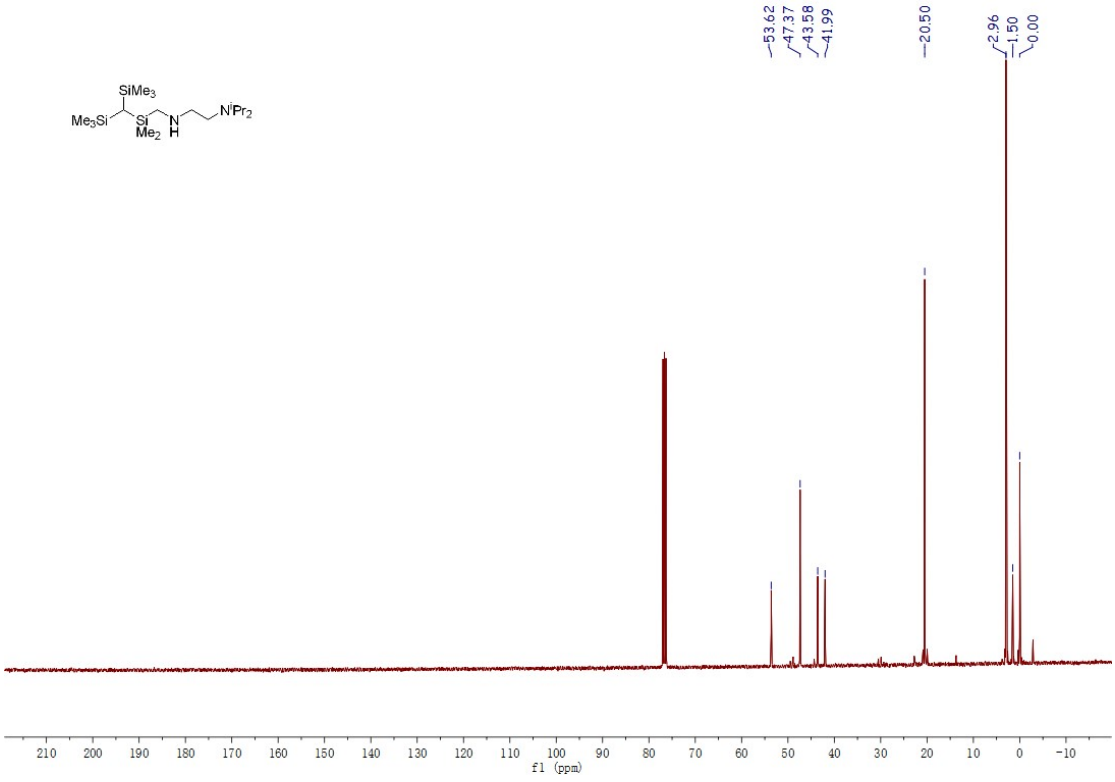


Figure S14 ^{13}C NMR of **C** at room temperature.

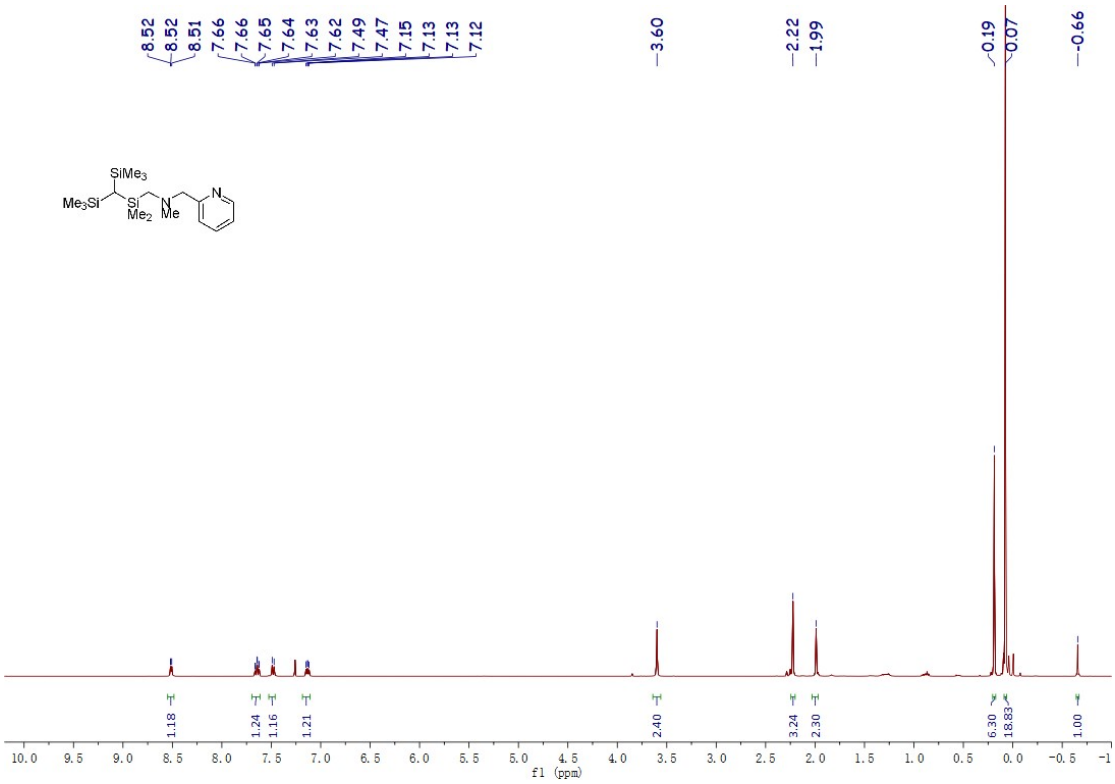


Figure S15 ^{1}H NMR of **2c** at room temperature.

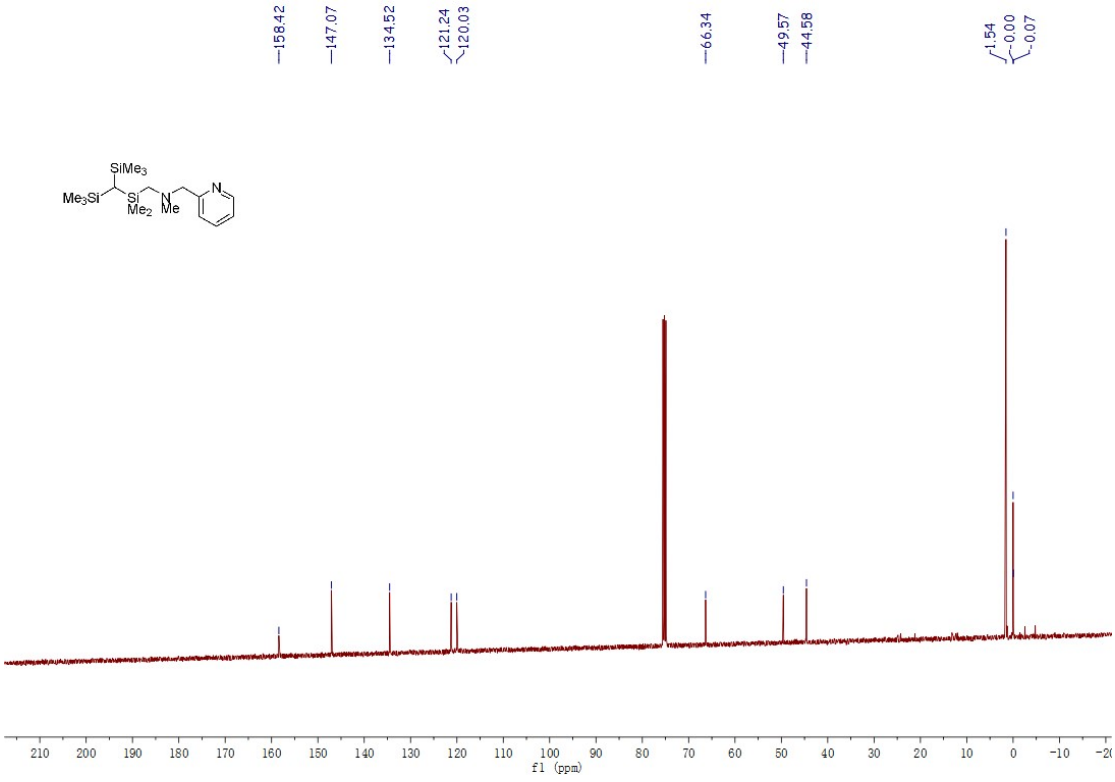


Figure S16 ^{13}C NMR of **2c** at room temperature.

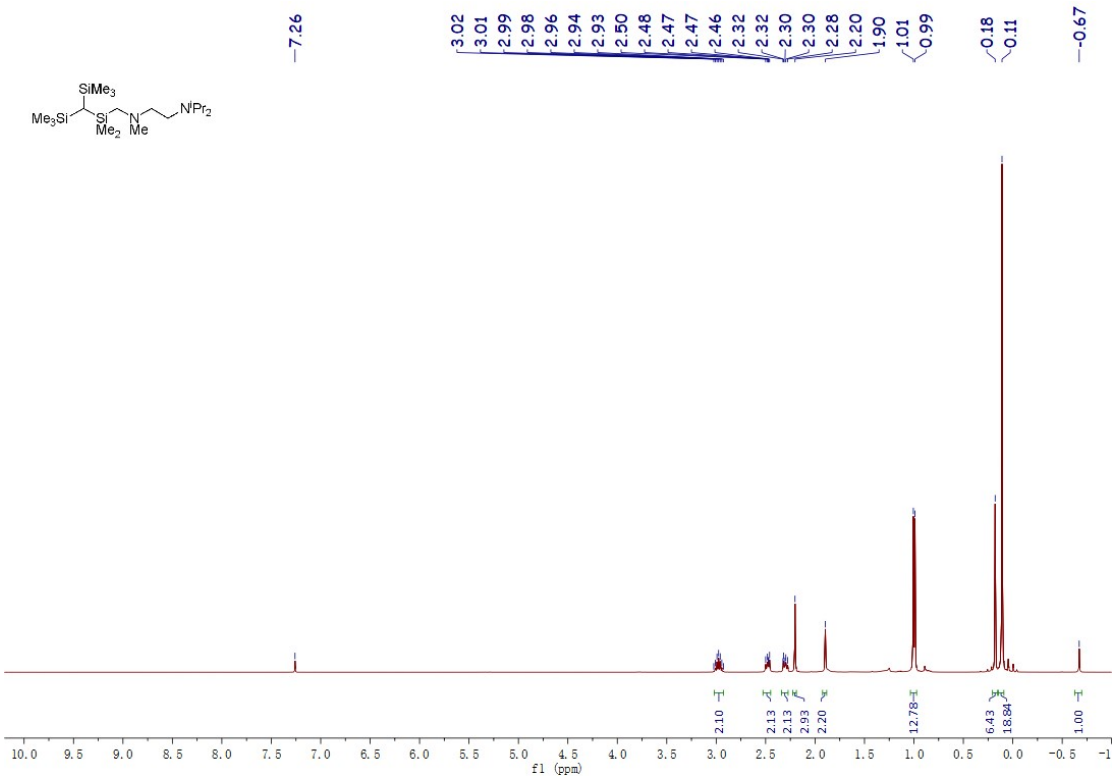


Figure S17 ^{1}H NMR of **2d** at room temperature.

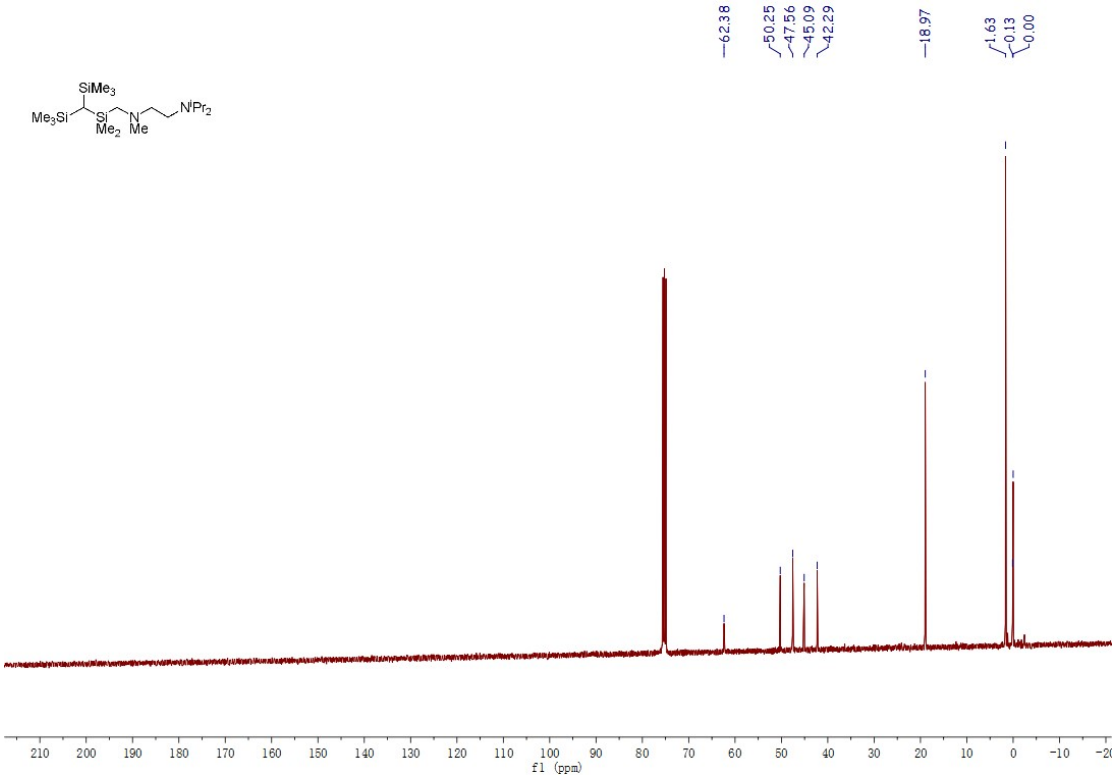


Figure S18 ^{13}C NMR of **2d** at room temperature.

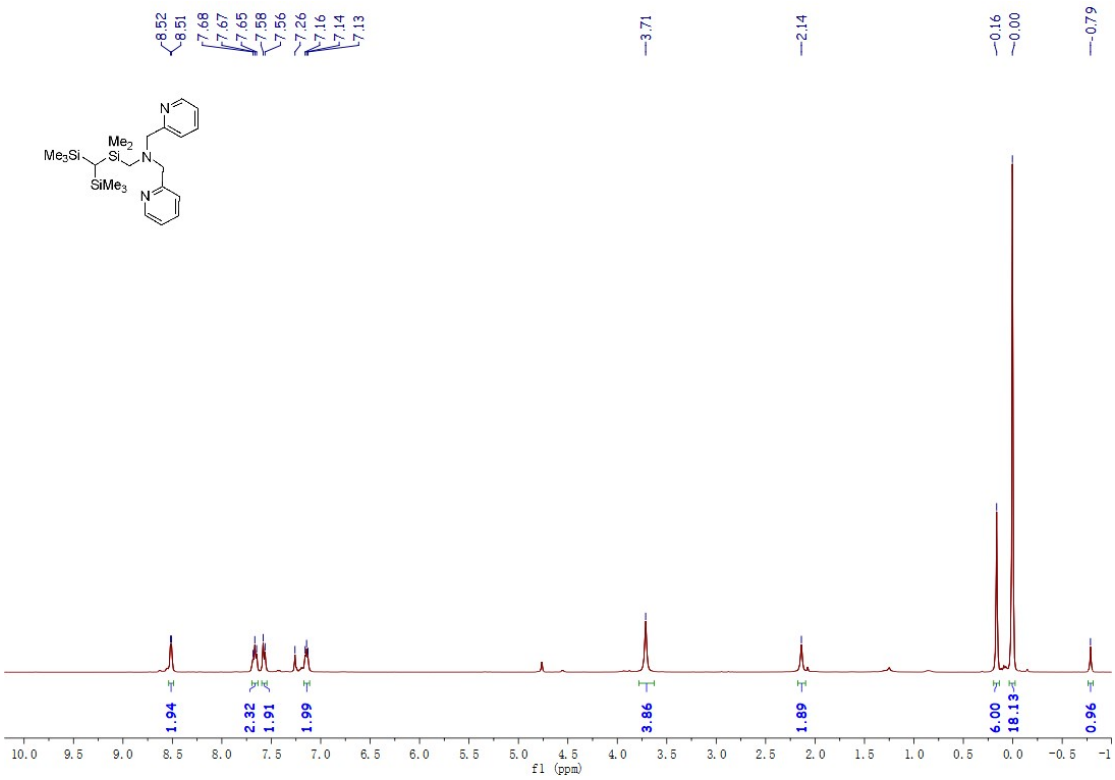


Figure S19 ^{1}H NMR of **2e** at room temperature.

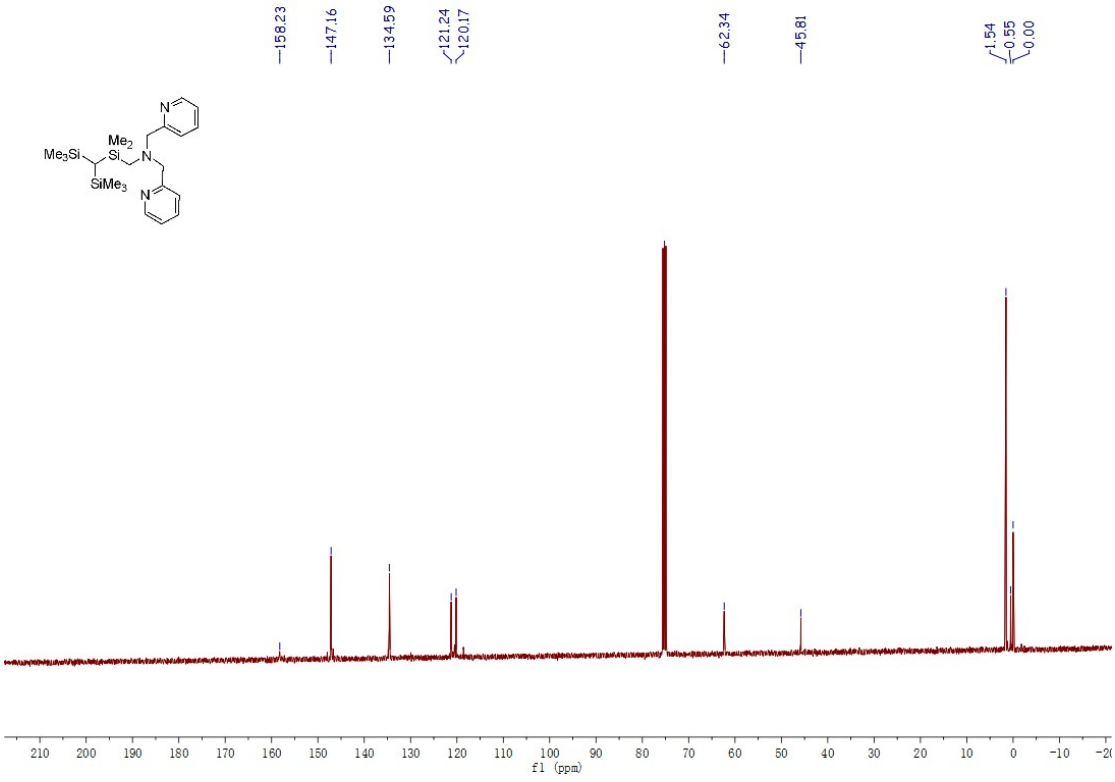


Figure S20 ^{13}C NMR of **2e** at room temperature.

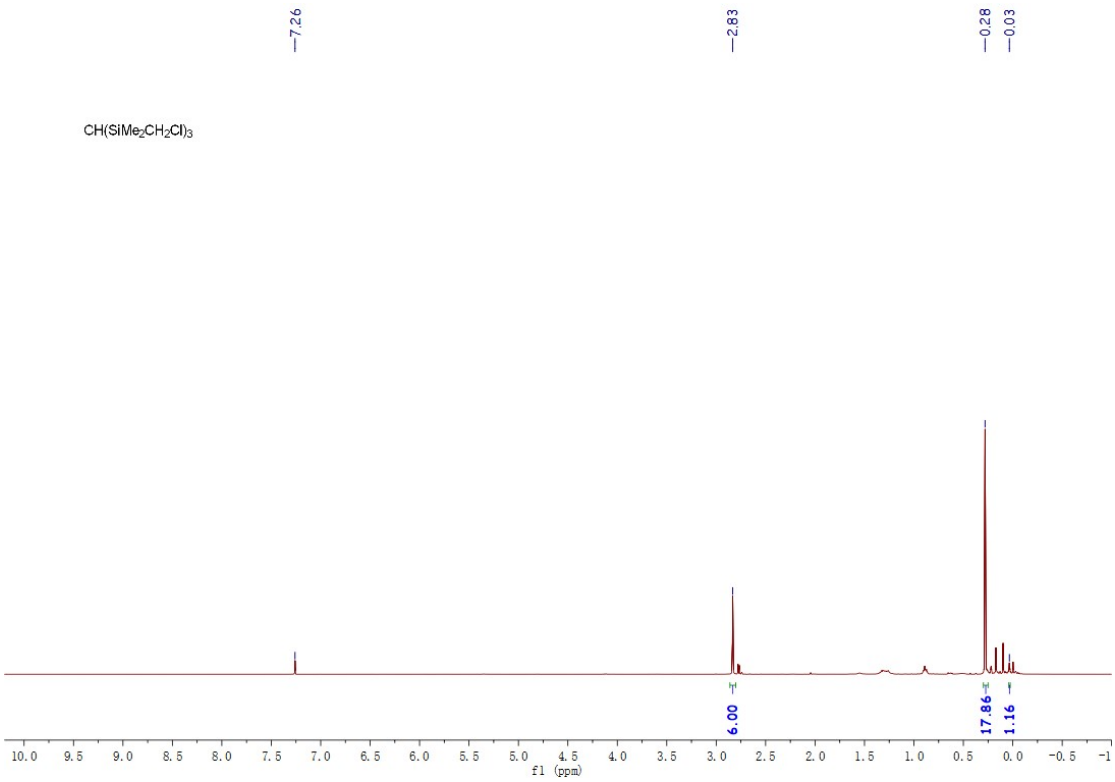


Figure S21 Crude ^{1}H NMR of **HC(SiMe$_2$CH$_2$Cl)$_3$** at room temperature.

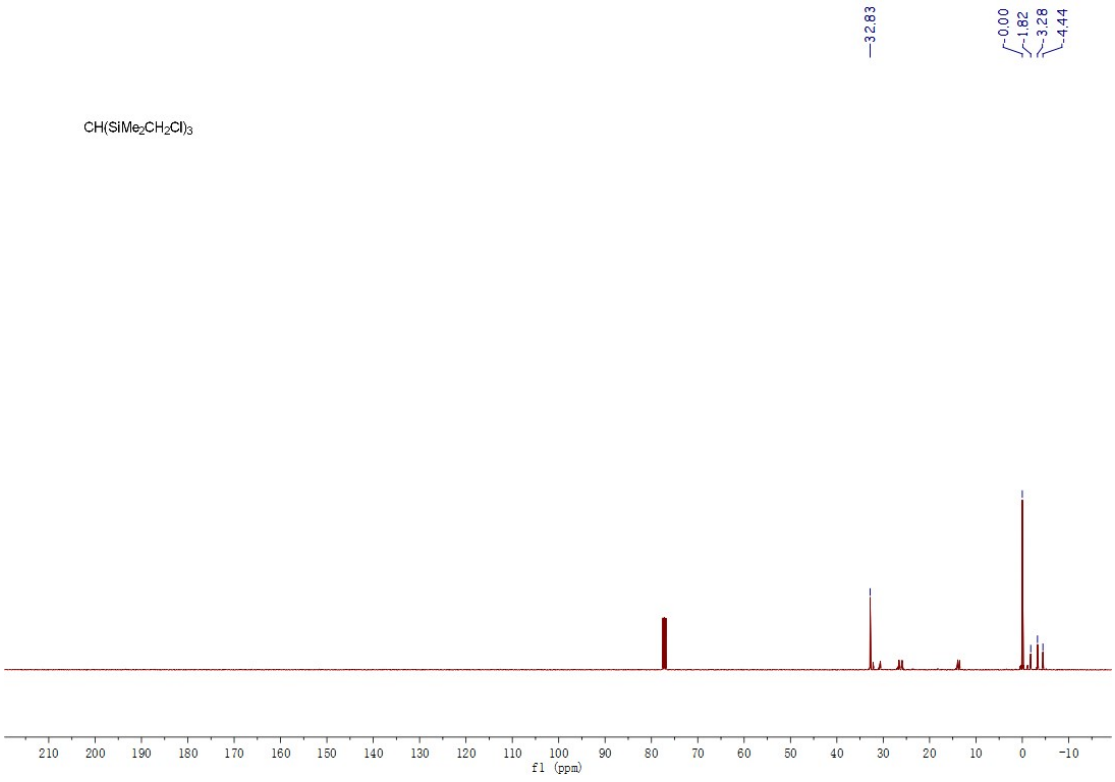


Figure S22 Crude ^{13}C NMR of **HC(SiMe$_2$CH$_2$Cl)$_3$** at room temperature.

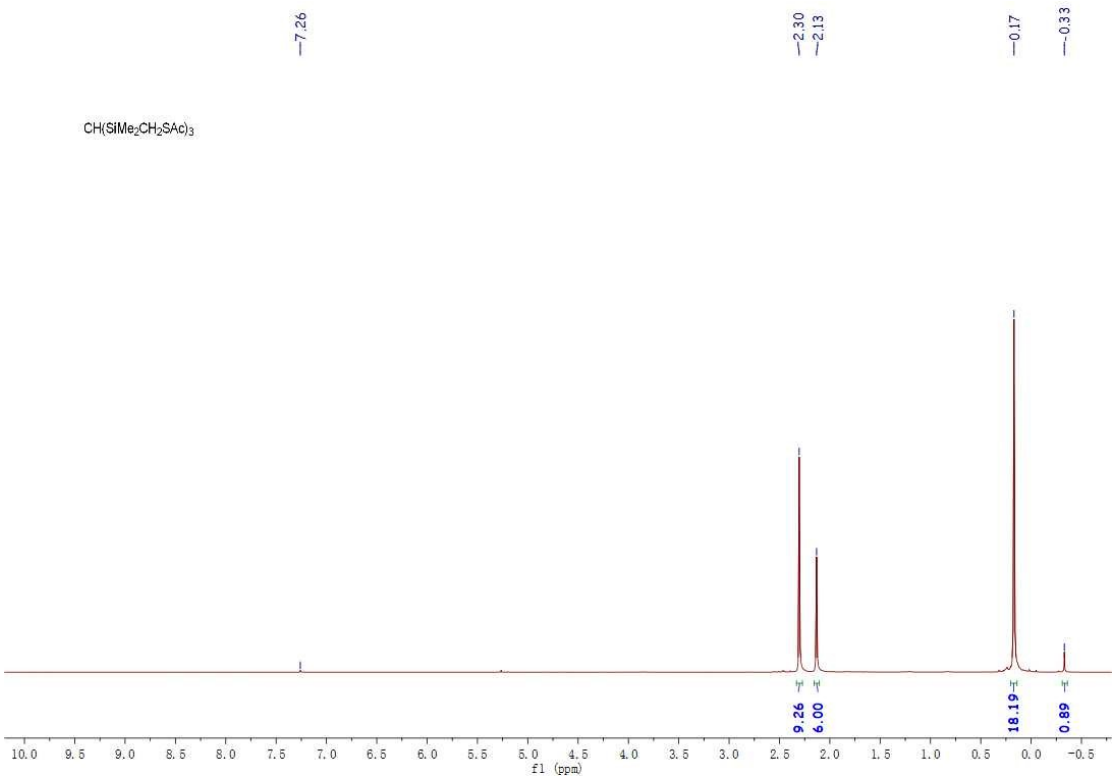


Figure S23 ^{1}H NMR of **HC(SiMe$_2$CH$_2$SAc)$_3$** at room temperature.

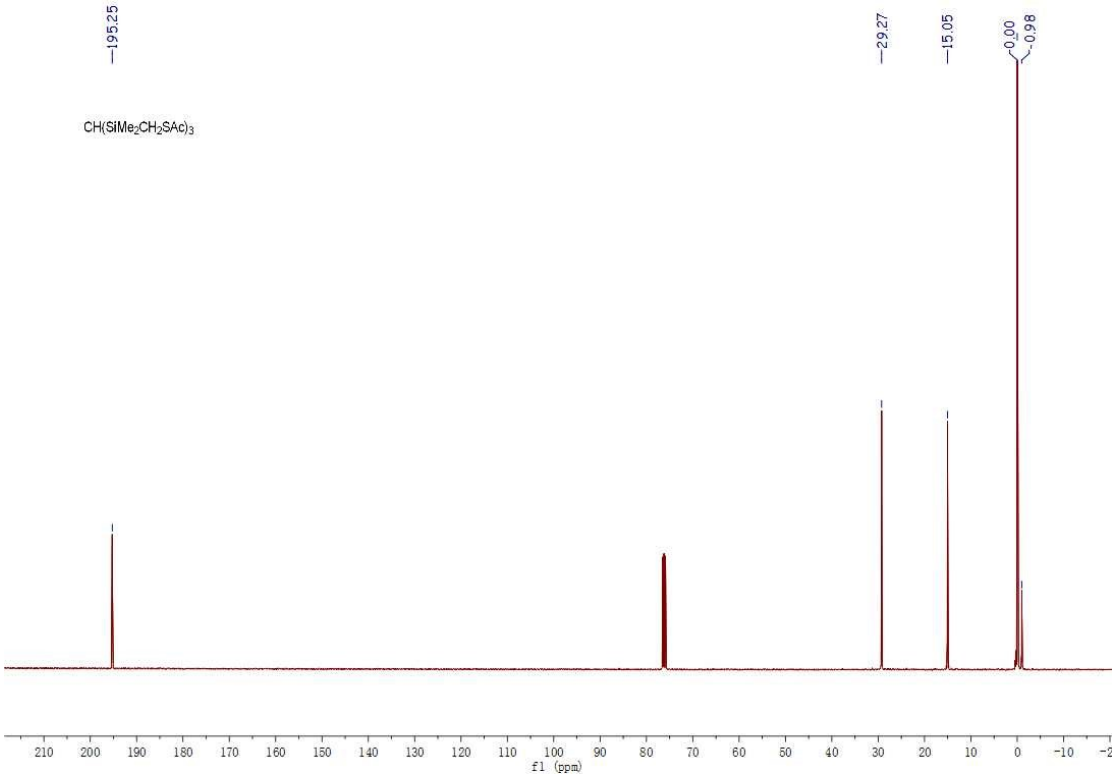


Figure S24 ^{13}C NMR of **HC(SiMe$_2$CH$_2$SAc)$_3$** at room temperature.

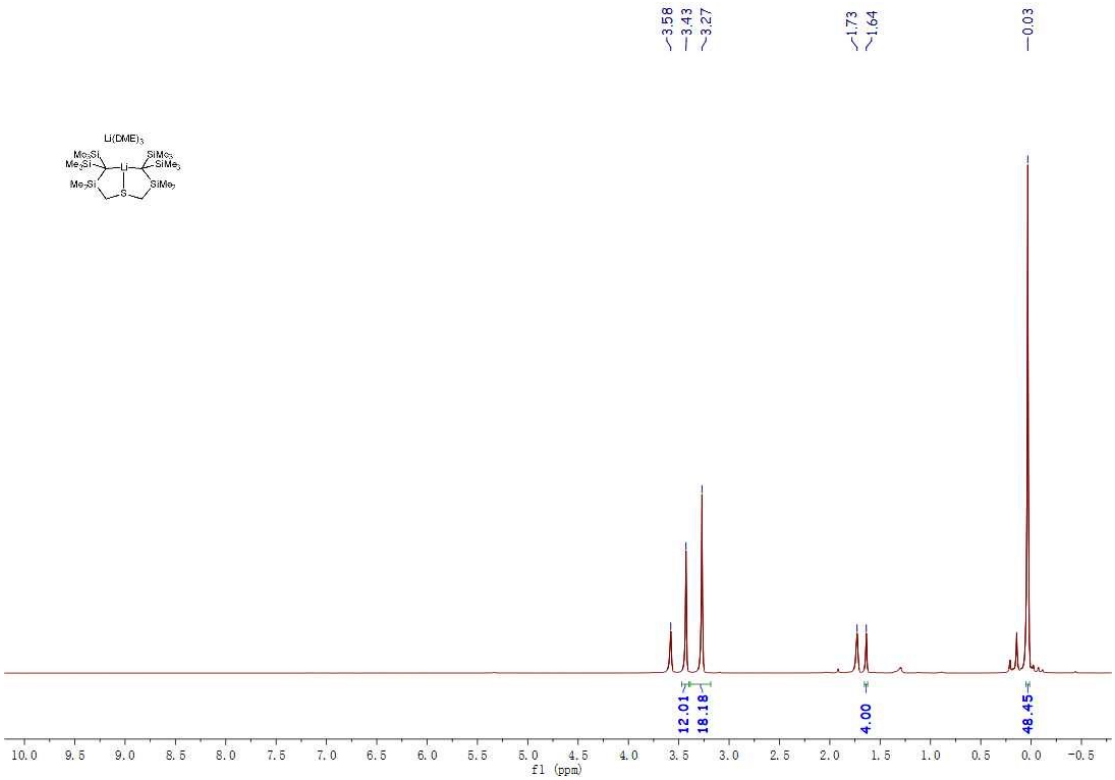


Figure S25 ^{1}H NMR of **3a** at room temperature.

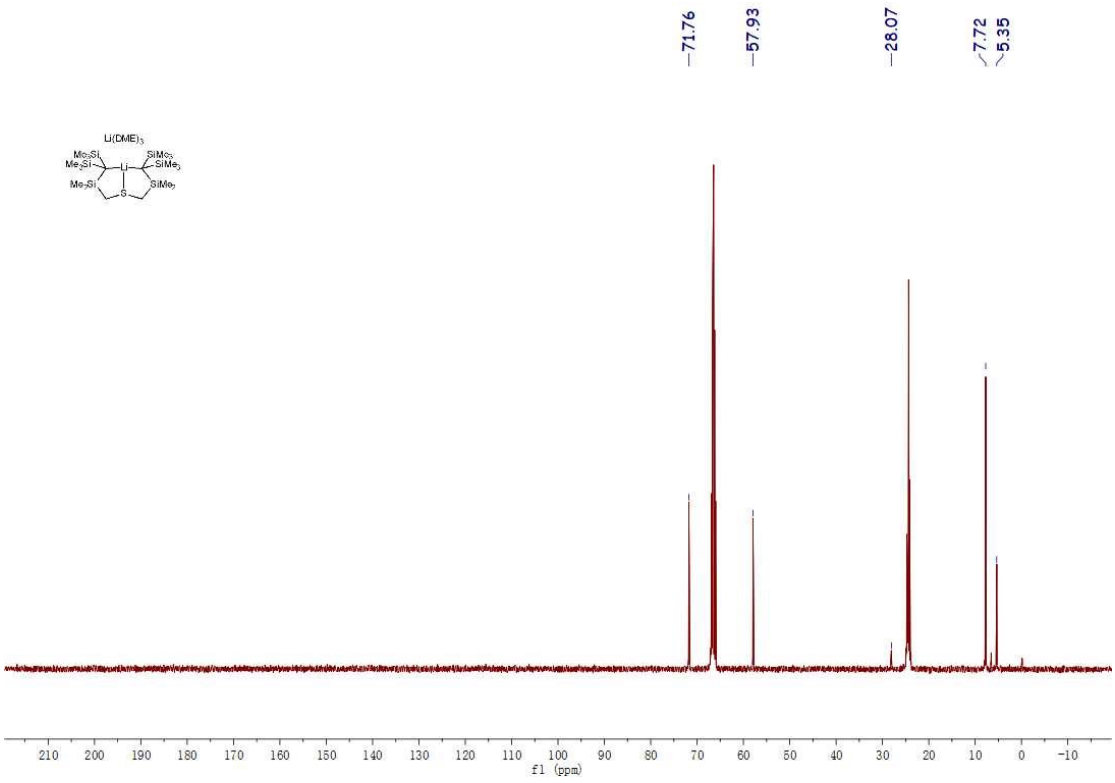


Figure S26 ^{13}C NMR of **3a** at room temperature.

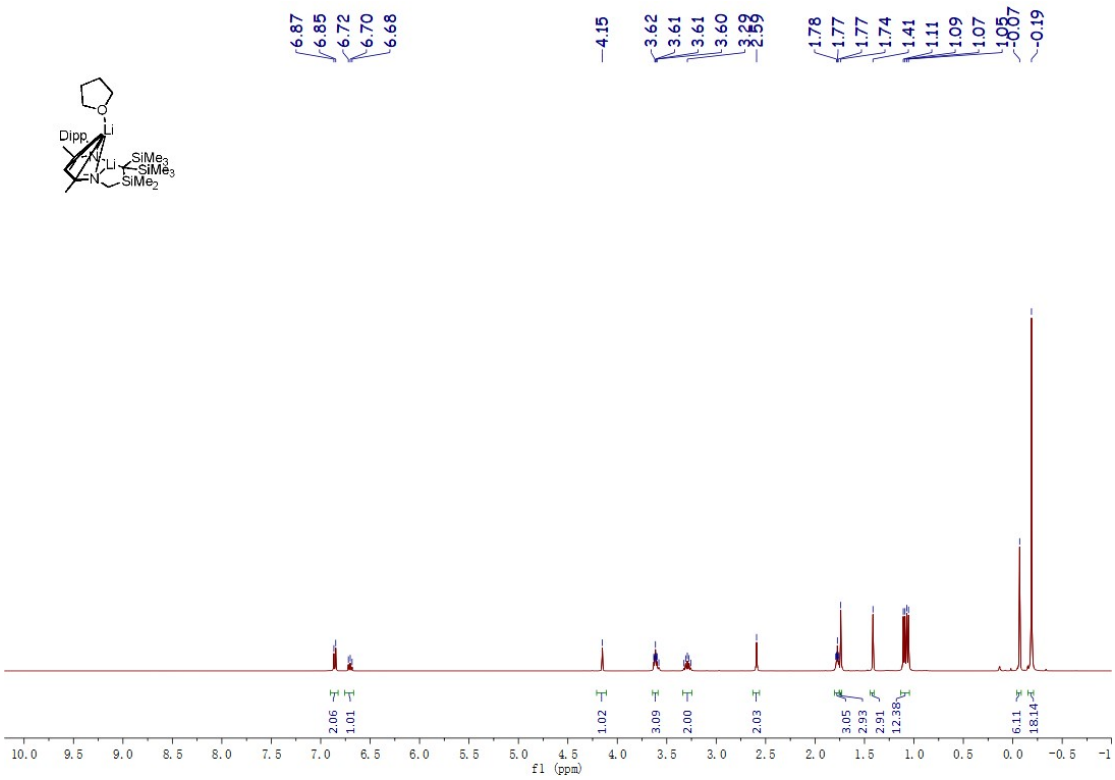


Figure S27 ^{1}H NMR of **3b** at room temperature.

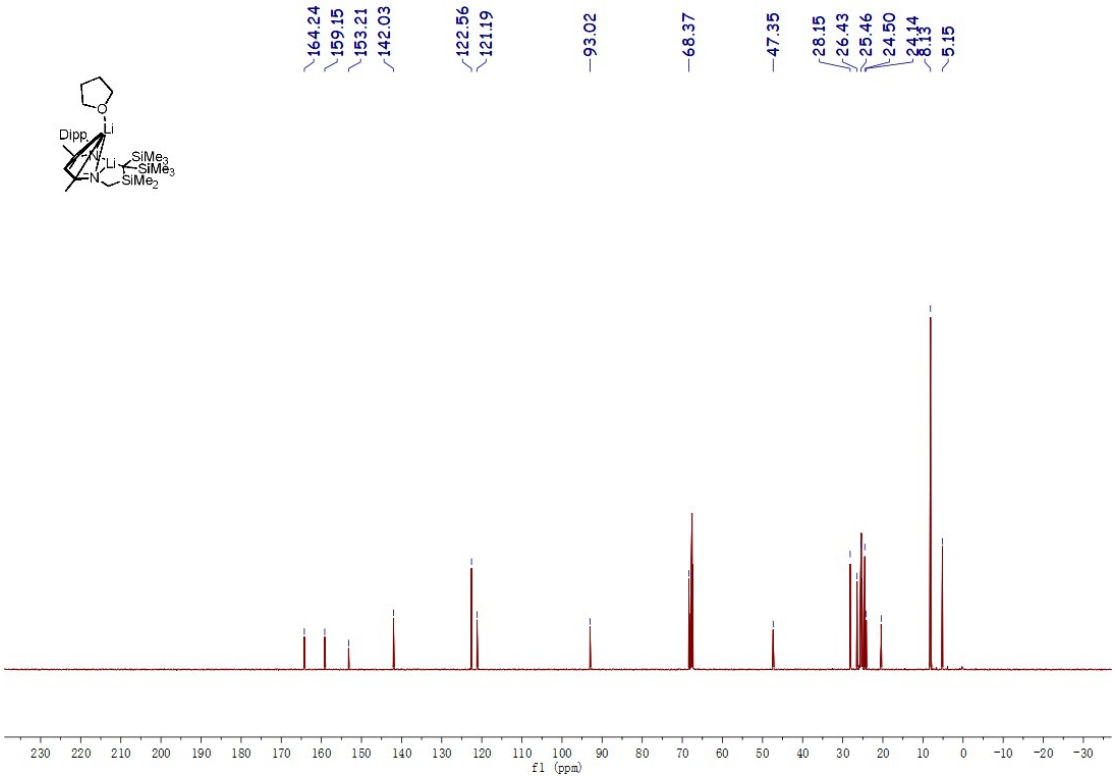


Figure S28 ^{13}C NMR of **3b** at room temperature.

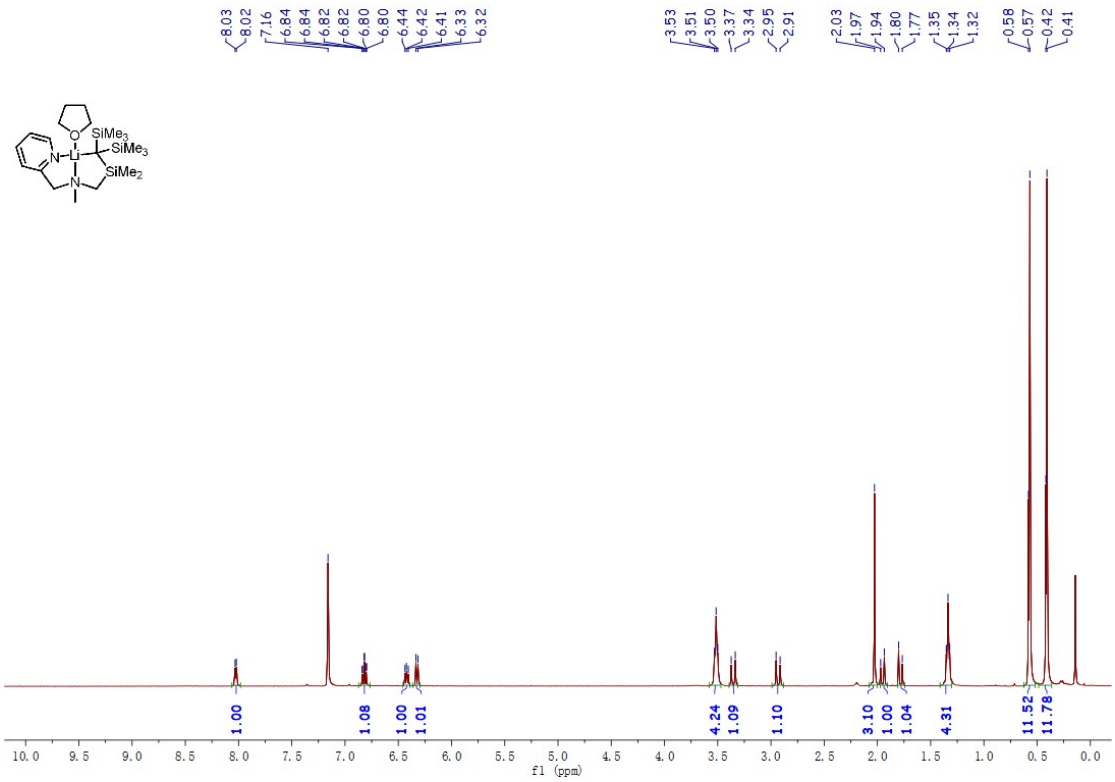


Figure S29 ^{1}H NMR of **3c** at room temperature.

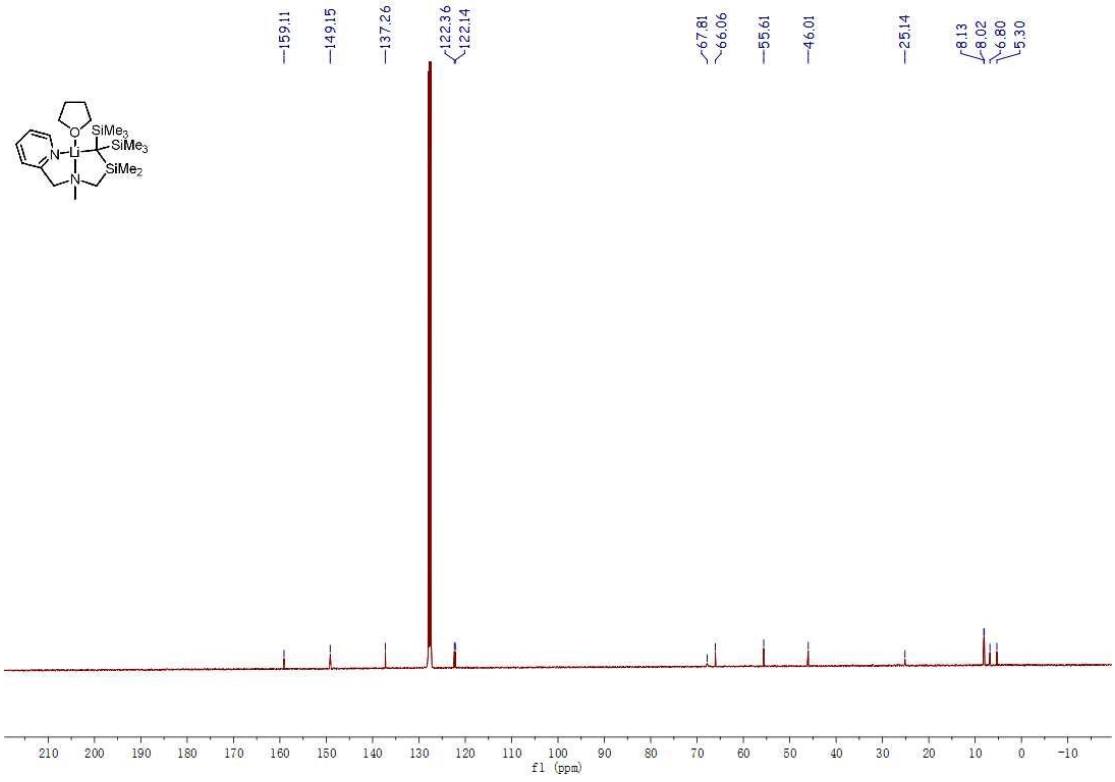


Figure S30 ^{13}C NMR of **3c** at room temperature.

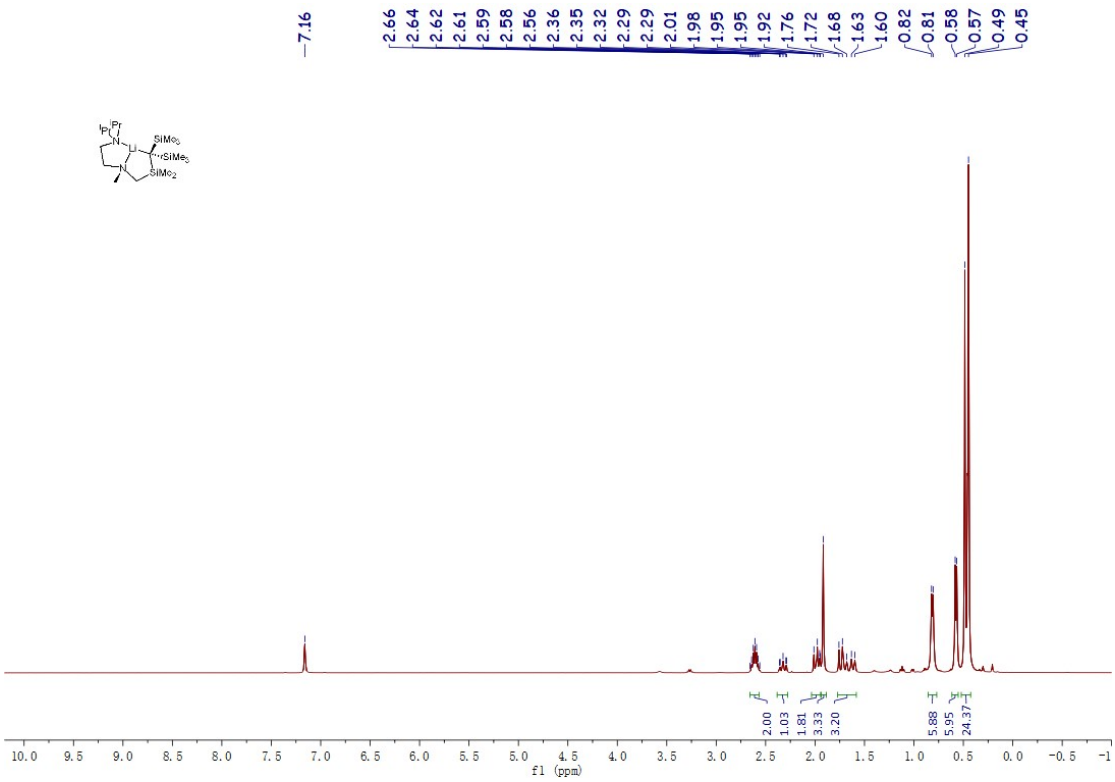


Figure S31 ^{1}H NMR of **3d** at room temperature.

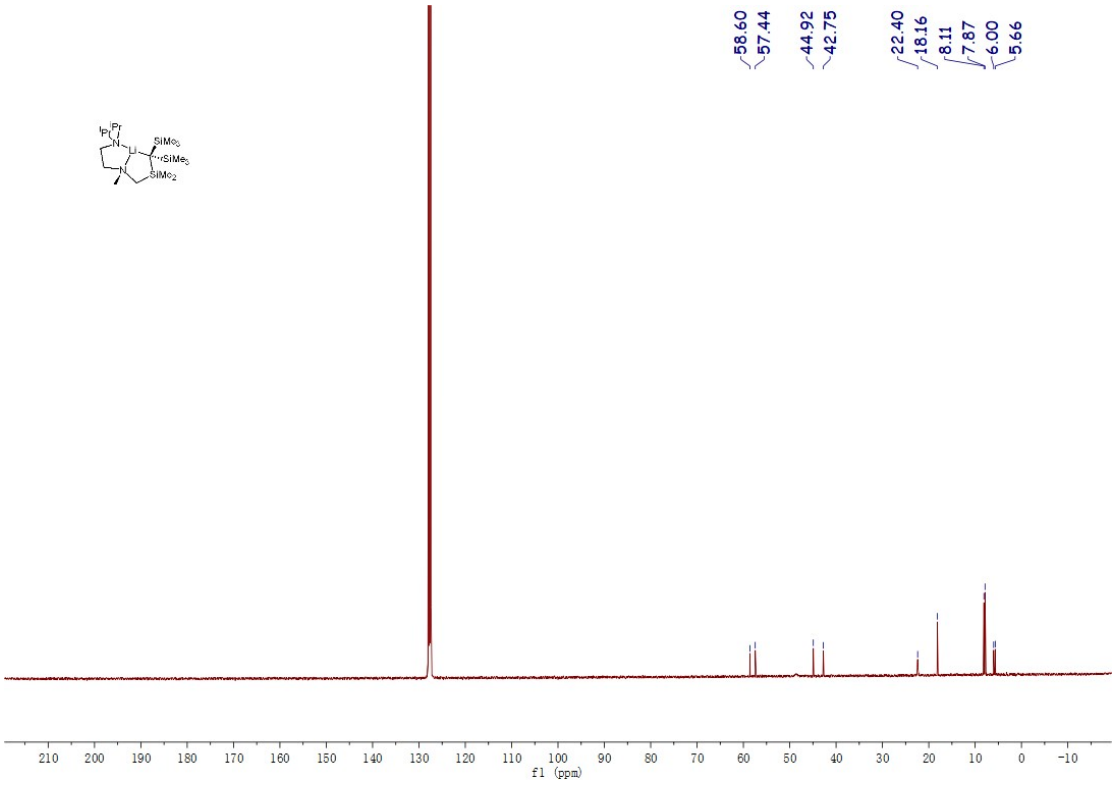


Figure 32 ^{13}C NMR of **3d** at room temperature.

(3) X-ray Crystallographic Studies for 3a', 3b-d, 4-8, S1-3

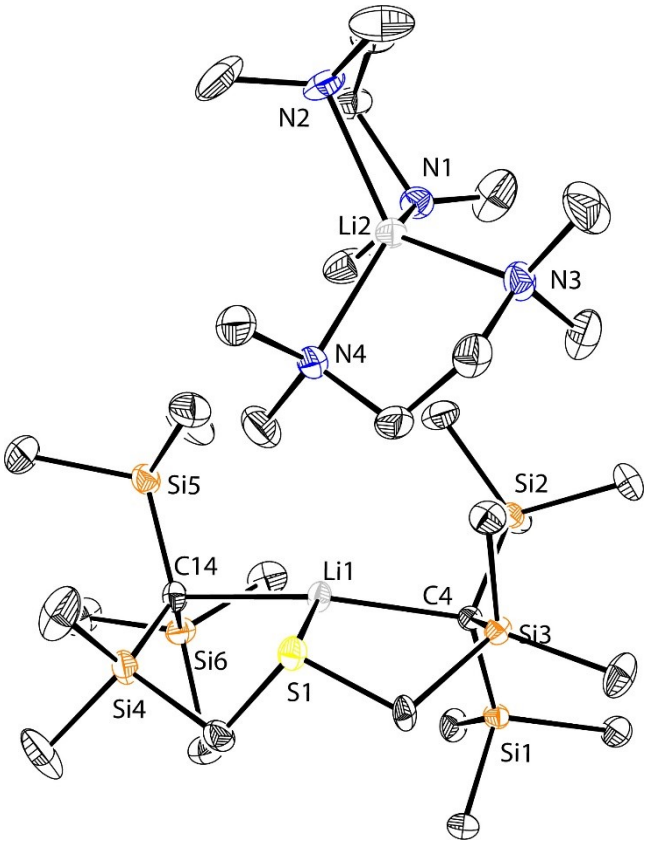


Figure S33 ORTEP drawing of **3a'**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S1 Selected Bond Lengths (Å) and Angles (deg) for **3a'**.

C(4)——Li(1)	2.275(10)
C(14)——Li(1)	2.227(10)
S(1)——Li(1)	2.534(8)
C(4)——Li(1)——S(1)	98.6(3)
C(14)——Li(1)——C(4)	162.4(4)
C(14)——Li(1)——S(1)	93.5(3)

Table S2 X-ray crystallographic data for **3a'**.

	3a'
CCDC number	2125715
Empirical formula	$C_{32}H_{84}Li_2N_4SSi_6$
Formula weight	739.51
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4284(2)
b/Å	17.4514(4)
c/Å	29.3718(6)
α/°	90
β/°	92.695(2)
γ/°	90
Volume/Å^3	4827.45(18
Z	4
ρ_{calc}, g/cm^3	1.017
μ/mm^{-1}	0.240
F(000)	1640.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.604 to 54.966
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -38 ≤ l ≤
Reflections collected	99372
Independent reflections	11070 [R_{int} = 0.0370, R_{sigma} = 0.02
Data/restraints/parameters	11070/482/622
Goodness-of-fit on F^2	1.071
R_1 [I>=2δ (I)]	0.0379
wR_2 [all data]	0.0961
Largest diff. peak/hole / e Å^{-3}	0.28/-0.30

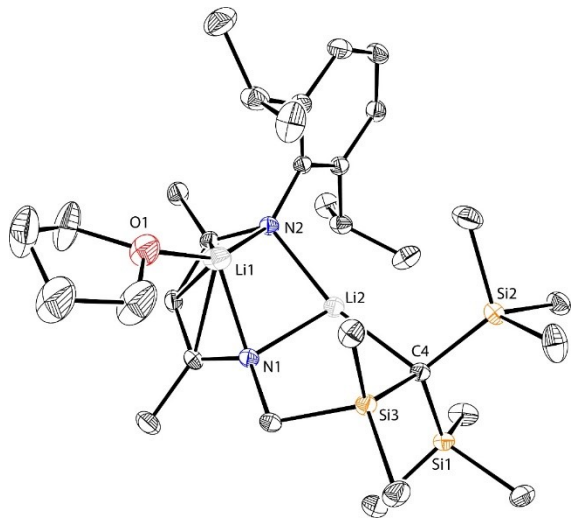


Figure S34 ORTEP drawing of **3b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S3 Selected Bond Lengths (Å) and Angles (deg) for **3b**.

C(4)——Li(2)	2.193(3)
N(1)——Li(2)	2.033(3)
N(2)——Li(2)	2.088(3)
N(2)——Li(2)——C(4)	163.75(16)
N(1)——Li(2)——C(4)	101.10(12)
N(1)——Li(2)——N(2)	87.64(11)

Table S4 X-ray crystallographic data for **3b**.

	3b
CCDC number	2125716
Empirical formula	$C_{62}H_{116}Li_4N_4O_2Si_6$
Formula weight	1145.88
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.0442(3)
b/Å	16.4938(4)
c/Å	22.9493(5)
α/°	77.906(2)
β/°	84.578(2)
γ/°	75.704(2)
Volume/Å^3	3598.77(16)
Z	2
ρ_{calc}, g/cm^3	1.057
μ/mm^{-1}	0.155
F(000)	1256.0
Crystal size/mm^3	0.2 x 0.2 x 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.384 to 52.044
Index ranges	$-9 \leq h \leq 12$, $-20 \leq k \leq 20$, $-28 \leq l \leq 27$
Reflections collected	51412
Independent reflections	14186 [R_{int} = 0.0246, R_{sigma} = 0.0247]
Data/restraints/parameters	14186/0/852
Goodness-of-fit on F^2	1.019
R_1 [I>=2δ (I)]	0.0478
wR_2 [all data]	0.1486
Largest diff. peak/hole / e Å^{-3}	0.53/-0.44

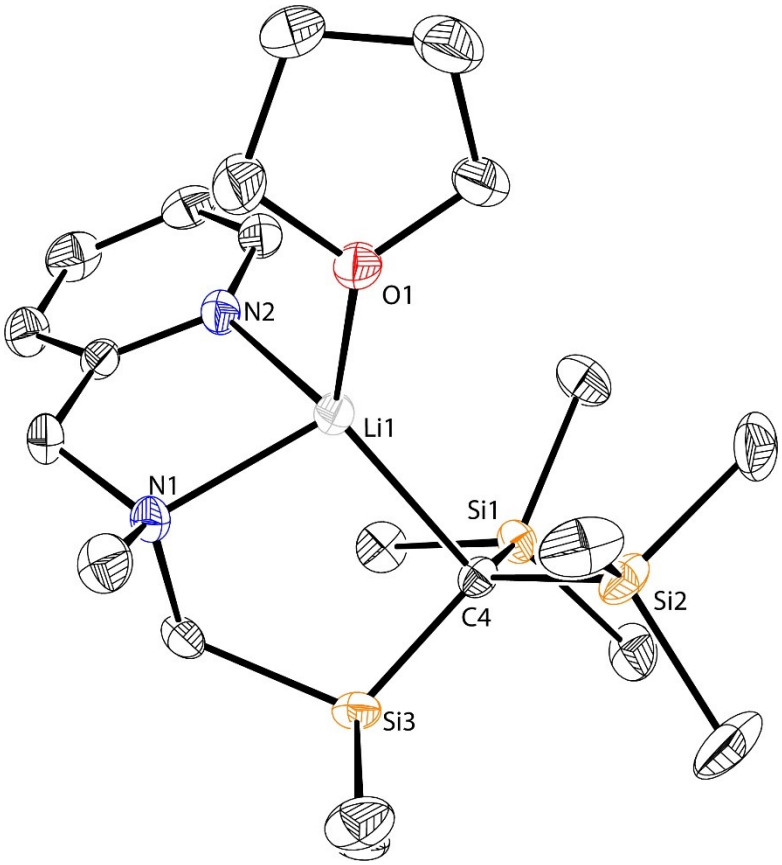


Figure S35 ORTEP drawing of **3c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S5 Selected Bond Lengths (Å) and Angles (deg) for **3c**.

C(4)——Li(1)	2.252(3)
N(1)——Li(1)	2.107(3)
N(2)——Li(1)	2.121(3)
N(2)——Li(1)——C(4)	124.70(13)
N(1)——Li(1)——C(4)	102.93(12)
N(1)——Li(1)——N(2)	82.19(11)

Table S6 X-ray crystallographic data for **3c**.

	3c
CCDC number	2125717
Empirical formula	$C_{21}H_{43}LiN_2OSi_3$
Formula weight	430.78
Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.1787(2)
b/Å	16.4316(4)
c/Å	31.9451(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5342.9(2)
Z	8
ρ_{calc}, g/cm^3	1.071
μ/mm^{-1}	0.191
F(000)	1888.0
Crystal size/mm^3	0.2 x 0.2 x 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.746 to 54.958
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 21$, $-41 \leq l \leq 41$
Reflections collected	70677
Independent reflections	6106 [R_{int} = 0.0426, R_{sigma} = 0.0232]
Data/restraints/parameters	6106/0/270
Goodness-of-fit on F^2	1.023
R_1 [I>=2δ (I)]	0.0425
wR_2 [all data]	0.1191
Largest diff. peak/hole / e Å^{-3}	0.51/-0.28

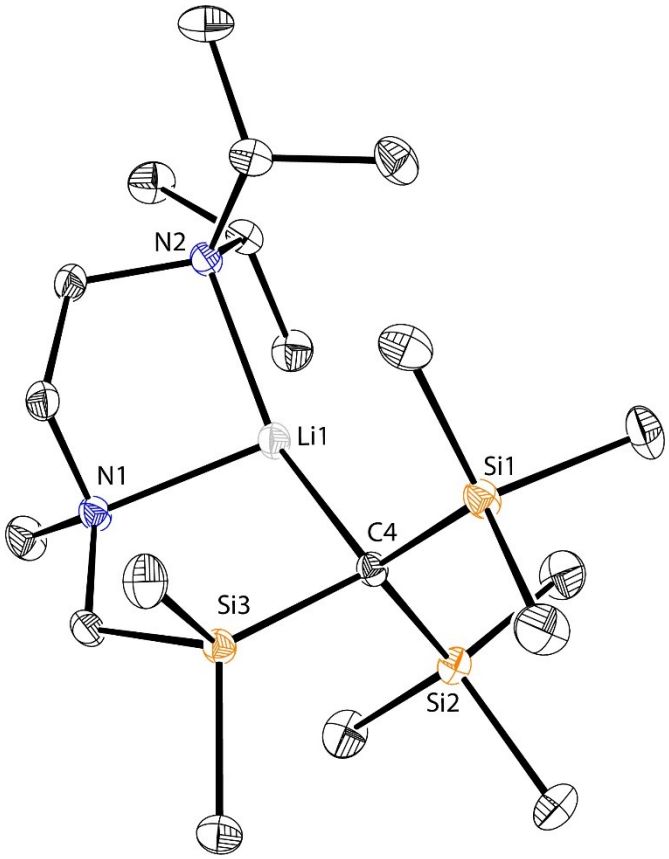


Figure S36 ORTEP drawing of **3d**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S7 Selected Bond Lengths (Å) and Angles (deg) for **3d**.

C(4)——Li(1)	2.172(3)
N(1)——Li(1)	2.073(2)
N(2)——Li(1)	2.146(2)
N(1)——Li(1)——C(4)	105.04(10)
N(2)——Li(1)——C(4)	149.13(12)
N(1)——Li(1)——N(2)	90.35(9)

Table S8 X-ray crystallographic data for **3d**.

	3d
CCDC number	2125718
Empirical formula	$C_{19}H_{47}LiN_2Si_3$
Formula weight	394.79
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.8100(9)
b/Å	10.4149(4)
c/Å	16.2663(9)
α/°	90
β/°	108.524(6)
γ/°	90
Volume/Å^3	2539.6(2)
Z	4
ρ_{calc}, g/cm^3	1.033
μ/mm^{-1}	0.192
F(000)	880.0
Crystal size/mm^3	0.2 x 0.2 x 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.762 to 54.968
Index ranges	$-20 \leq h \leq 20$, $-12 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	28387
Independent reflections	5804 [R_{int} = 0.0418, R_{sigma} = 0.0330]
Data/restraints/parameters	5804/0/239
Goodness-of-fit on F^2	1.040
R_1 [I>=2δ (I)]	0.0348
wR_2 [all data]	0.0993
Largest diff. peak/hole / e Å^{-3}	0.29/-0.20

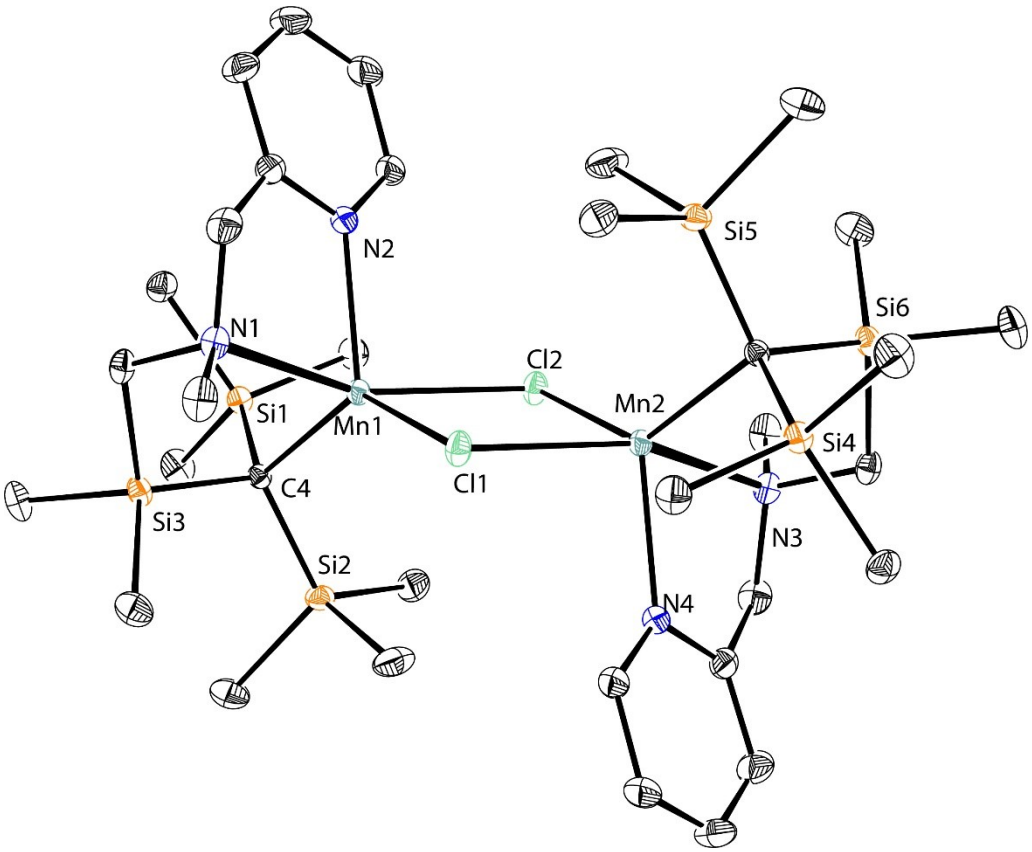


Figure S37 ORTEP drawing of **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S9 Selected Bond Lengths (Å) and Angles (deg) for **4**.

Mn(1)——Cl(1)	2.4810(6)
Mn(1)——Cl(2)	2.5474(6)
Mn(1)——N(1)	2.3895(17)
Mn(1)——N(2)	2.2366(16)
Mn(1)——C(4)	2.2274(19)
Cl(1)——Mn(1)——Cl(2)	83.34(2)

Table S10 X-ray crystallographic data for **4**.

	4
CCDC number	2125719
Empirical formula	$C_{34}H_{70}Cl_2Mn_2N_4Si_6$
Formula weight	884.26
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0194(6)
b/Å	10.6298(5)
c/Å	13.1801(8)
α/°	74.912(5)
β/°	73.834(6)
γ/°	77.514(4)
Volume/Å^3	1157.67(13)
Z	1
ρ_{calc}, g/cm^3	1.268
μ/mm^{-1}	0.844
F(000)	470.0
Crystal size/mm^3	0.2 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.11 to 54.97
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$
Reflections collected	9187
Independent reflections	9187 [R_{int} = ?, R_{sigma} = 0.0449]
Data/restraints/parameters	9187/0/227
Goodness-of-fit on F^2	0.985
R_1 [I>=2δ (I)]	0.0313
wR_2 [all data]	0.0738
Largest diff. peak/hole / e Å^{-3}	0.33/-0.28

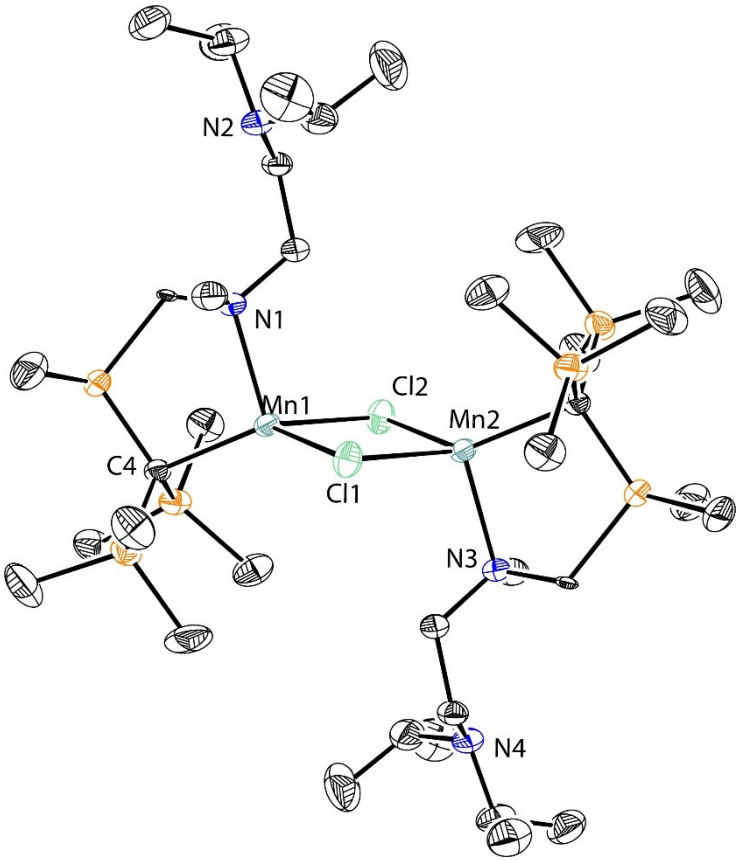


Figure S38 ORTEP drawing of **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S11 Selected Bond Lengths (Å) and Angles (deg) for **5**.

Mn(1)——Cl(1)	2.4274(8)
Mn(1)——Cl(2)	2.4468(9)
Mn(1)——N(1)	2.204(5)
Mn(1)——C(4)	2.160(3)
Cl(1)——Mn(1)——Cl(2)	89.87(3)

Table S12 X-ray crystallographic data for **5**.

	5
CCDC number	2125720
Empirical formula	$C_{38}H_{94}Cl_2Mn_2N_4Si_6$
Formula weight	956.49
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.1109(4)
b/Å	12.3473(5)
c/Å	12.7686(6)
α/°	101.770(4)
β/°	92.549(4)
γ/°	99.528(3)
Volume/Å^3	1382.24(11)
Z	1
ρ_{calc}, g/cm^3	1.149
μ/mm^{-1}	0.711
F(000)	518.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.182 to 54.964
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 16$, $-16 \leq l \leq 16$
Reflections collected	25253
Independent reflections	6323 [R_{int} = 0.0287, R_{sigma} = 0.0244]
Data/restraints/parameters	6323/96/324
Goodness-of-fit on F^2	1.071
R_1 [I>=2δ (I)]	0.0543
wR_2 [all data]	0.1504
Largest diff. peak/hole / e Å^{-3}	1.40/-0.36

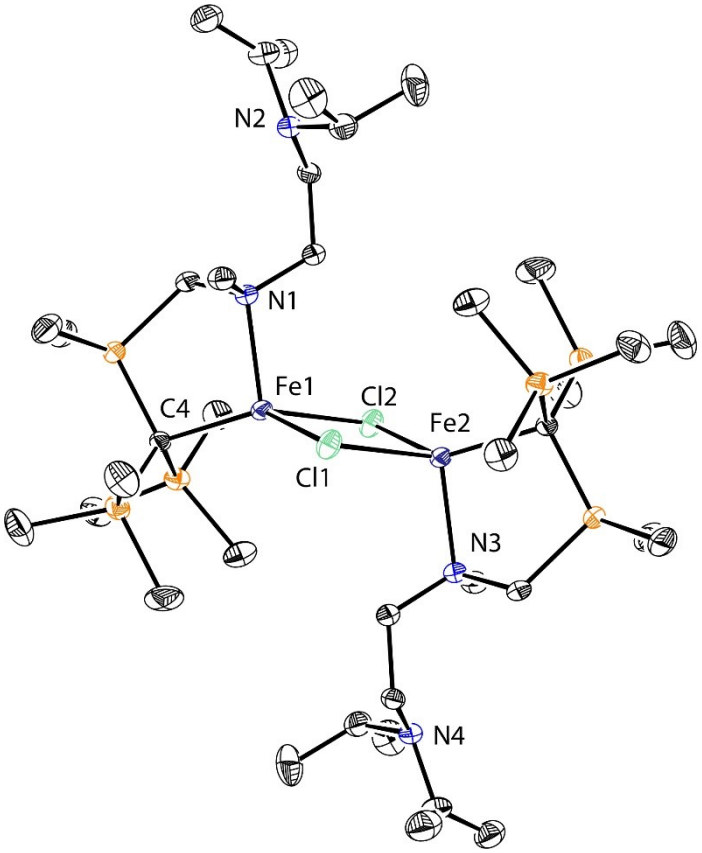


Figure S39 ORTEP drawing of **6**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S13 Selected Bond Lengths (Å) and Angles (deg) for **6**.

Fe(1)——Cl(1)	2.3871(6)
Fe(1)——Cl(2)	2.4140(6)
Fe(1)——N(1)	2.154(3)
Fe(1)——C(4)	2.084(2)
Cl(1)—— Fe(1)——Cl(2)	87.50(2)

Table S14 X-ray crystallographic data for **6**.

	6
CCDC number	2125721
Empirical formula	$C_{38}H_{94}Cl_2Fe_2N_4Si_6$
Formula weight	958.31
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0648(5)
b/Å	12.2798(7)
c/Å	12.6473(7)
α/°	100.964(5)
β/°	92.641(4)
γ/°	99.343(5)
Volume/Å^3	1359.48(13)
Z	1
ρ_{calc}, g/cm^3	1.171
μ/mm^{-1}	0.792
F(000)	520.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.21 to 54.968
Index ranges	$-10 \leq h \leq 11$, $-15 \leq k \leq 14$, $-16 \leq l \leq 16$
Reflections collected	23073
Independent reflections	6225 [R_{int} = 0.0438, R_{sigma} = 0.0457]
Data/restraints/parameters	6225/138/307
Goodness-of-fit on F^2	1.037
R_1 [I>=2δ (I)]	0.0395
wR_2 [all data]	0.0918
Largest diff. peak/hole / e Å^{-3}	0.42/-0.42

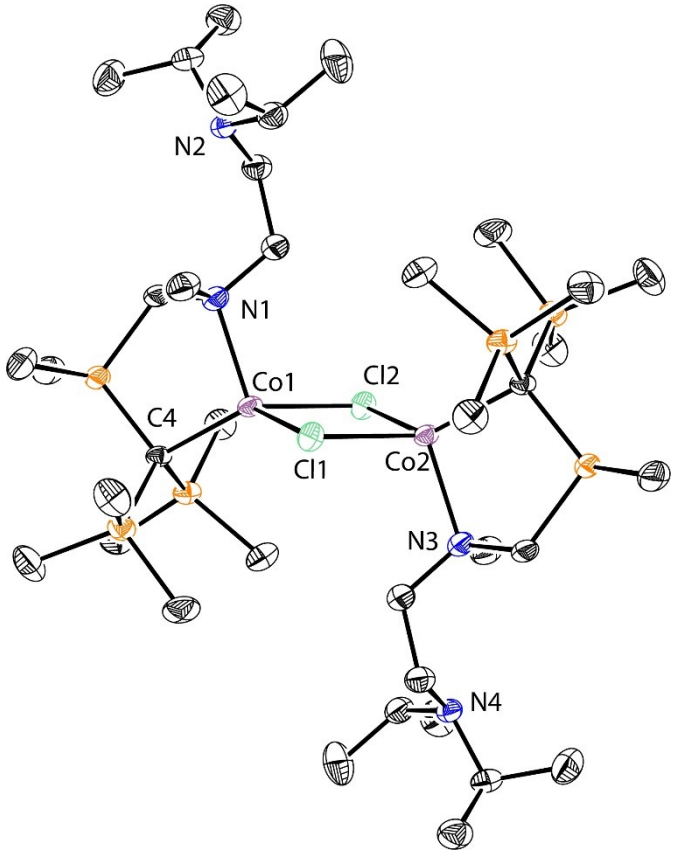


Figure S40 ORTEP drawing of **7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S15 Selected Bond Lengths (Å) and Angles (deg) for **7**.

Co(1)——Cl(1)	2.3484(10)
Co(1)——Cl(2)	2.3640(12)
Co(1)——N(1)	2.087(4)
Co(1)——C(4)	2.071(4)
Cl(1)——Co(1)——Cl(2)	88.41(4)

Table S16 X-ray crystallographic data for **7**.

	7
CCDC number	2125722
Empirical formula	$C_{38}H_{94}Cl_2Co_2N_4Si_6$
Formula weight	964.47
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0540(6)
b/Å	12.2175(7)
c/Å	12.6523(8)
α/°	100.857(5)
β/°	92.800(5)
γ/°	99.344(5)
Volume/Å^3	1351.71(15)
Z	1
ρ_{calc}, g/cm^3	1.185
μ/mm^{-1}	0.874
F(000)	522.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.218 to 54.968
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	24454
Independent reflections	6194 [R_{int} = 0.0543, R_{sigma} = 0.0424]
Data/restraints/parameters	6194/0/248
Goodness-of-fit on F^2	1.070
R_1 [I>=2δ (I)]	0.0678
wR_2 [all data]	0.1819
Largest diff. peak/hole / e Å^{-3}	1.27/-0.44

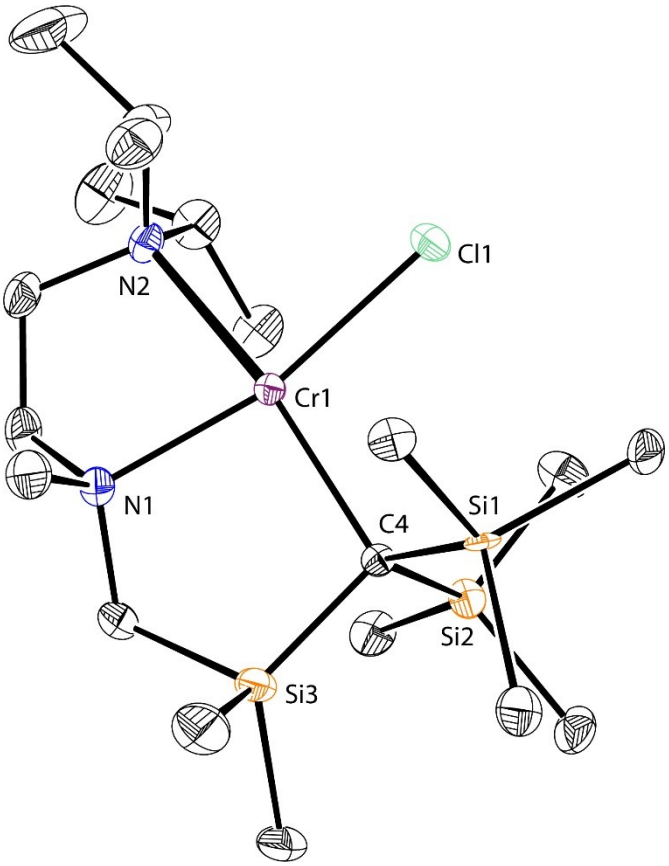


Figure S41 ORTEP drawing of **8**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S17 Selected Bond Lengths (Å) and Angles (deg) for **8**.

C(4)——Cr(1)	2.221(3)
N(1)——Cr(1)	2.139(3)
N(2)——Cr(1)	2.293(3)
Cr(1)——Cl(1)	2.3478(10)
N(1)——Cr(1)——Cl(1)	165.94(9)
N(1)——Cr(1)——C(4)	92.36(12)
N(2)——Cr(1)——C(4)	168.35(12)
N(1)——Cr(1)——N(2)	80.91(11)
N(2)——Cr(1)——Cl(1)	89.15(9)
C(4)——Cr(1)——Cl(1)	99.00(9)

Table S18 X-ray crystallographic data for **8**.

	8
CCDC number	2125723
Empirical formula	$C_{19}H_{47}ClCrN_2Si_3$
Formula weight	475.30
Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	Pca21
a/Å	14.9573(6)
b/Å	12.5606(4)
c/Å	14.2562(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2678.35(17)
Z	4
ρ_{calc}, g/cm^3	1.179
μ/mm^{-1}	0.668
F(000)	1032.0
Crystal size/mm^3	0.2 x 0.2 x 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.448 to 54.96
Index ranges	$-19 \leq h \leq 17$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	20081
Independent reflections	6010 [R_{int} = 0.0337, R_{sigma} = 0.0345]
Data/restraints/parameters	6010/258/318
Goodness-of-fit on F^2	1.050
R_1 [I>=2δ (I)]	0.0413
wR_2 [all data]	0.1074
Largest diff. peak/hole / e Å^{-3}	1.05/-0.28
Flack parameter	0.48(3)

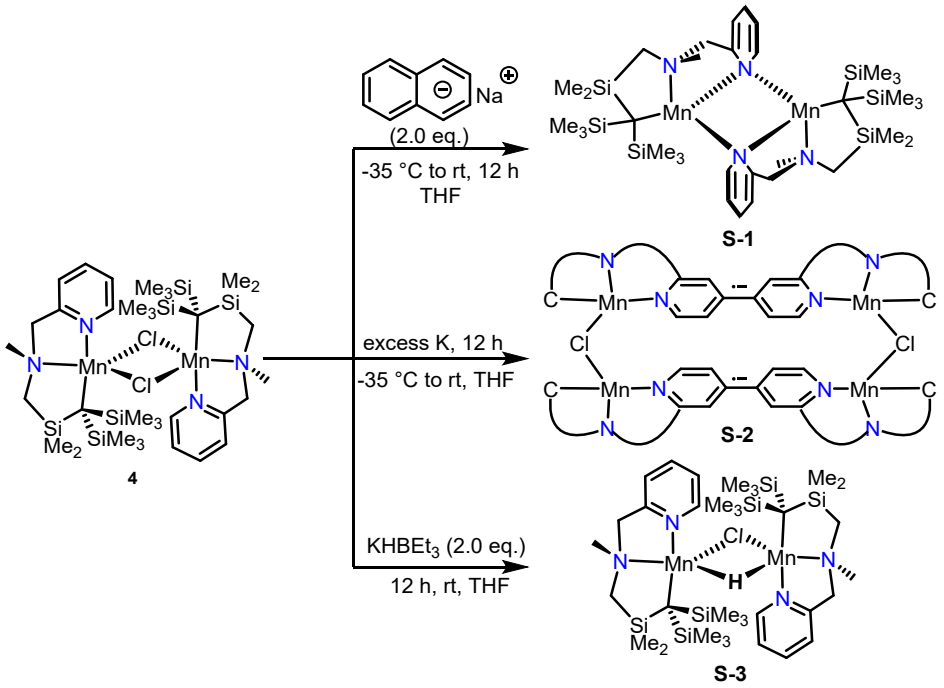


Figure S42 Preliminary applications of **4**.

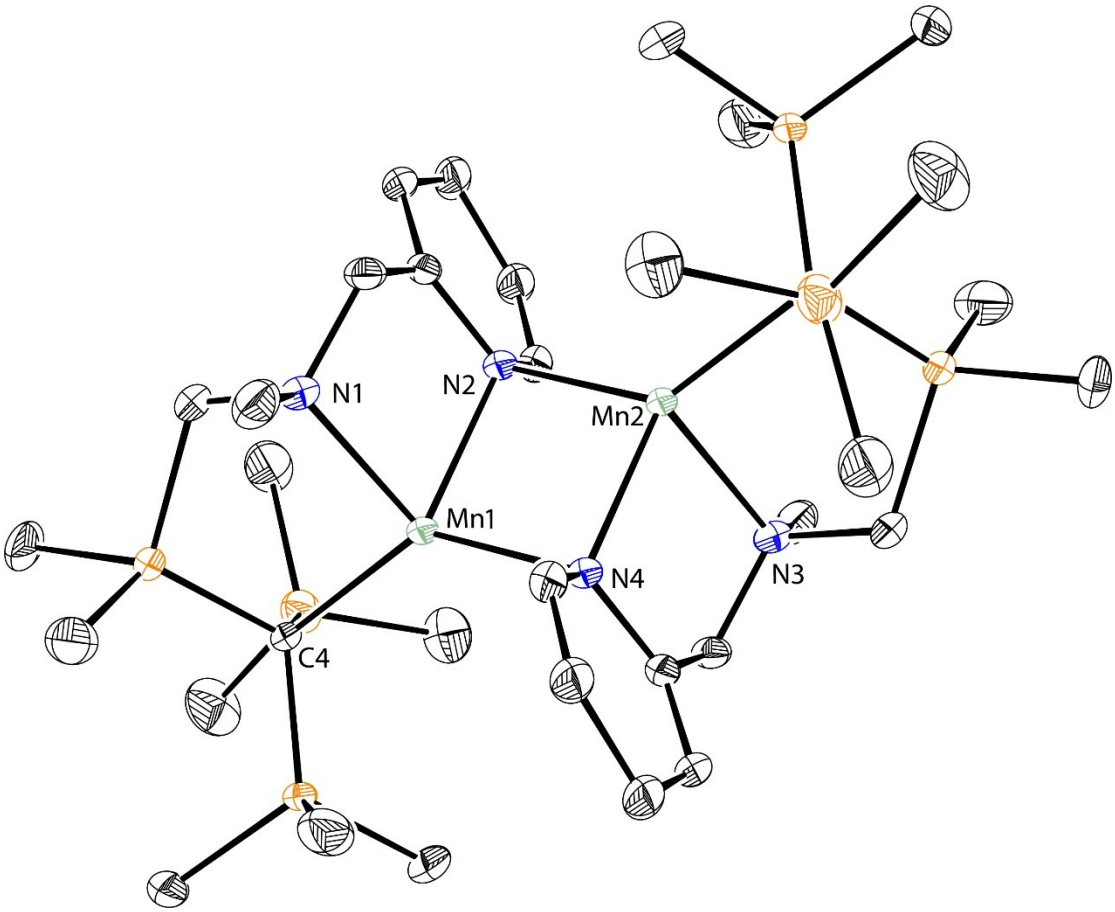


Figure S43 ORTEP drawing of **S-1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S19 Selected Bond Lengths (Å) and Angles (deg) for **S-1**.

Mn(1)——N(1)	2.287(4)
Mn(1)——N(2)	2.180(4)
Mn(1)——Mn(2)	3.0387(17)
Mn(1)——C(4)	2.186(4)

Table S20 X-ray crystallographic data for **S-1**.

	S-1
CCDC number	2150103
Empirical formula	$C_{34}H_{70}Mn_2N_4Si_6$
Formula weight	813.36
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.5513(10)
b/Å	10.1949(9)
c/Å	12.0621(11)
α/°	90.403(7)
β/°	102.656(8)
γ/°	103.957(8)
Volume/Å^3	1109.94(19)
Z	1
ρ_{calc}, g/cm^3	1.217
μ/mm^{-1}	0.758
F(000)	436.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.22 to 52.038
Index ranges	$-11 \leq h \leq 10$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$
Reflections collected	13545
Independent reflections	4357 [R_{int} = 0.0483, R_{sigma} = 0.0494]
Data/restraints/parameters	4357/0/217
Goodness-of-fit on F^2	1.127
R_1 [I>=2δ (I)]	0.0665
wR_2 [all data]	0.1669
Largest diff. peak/hole / e Å^{-3}	1.39/-0.43

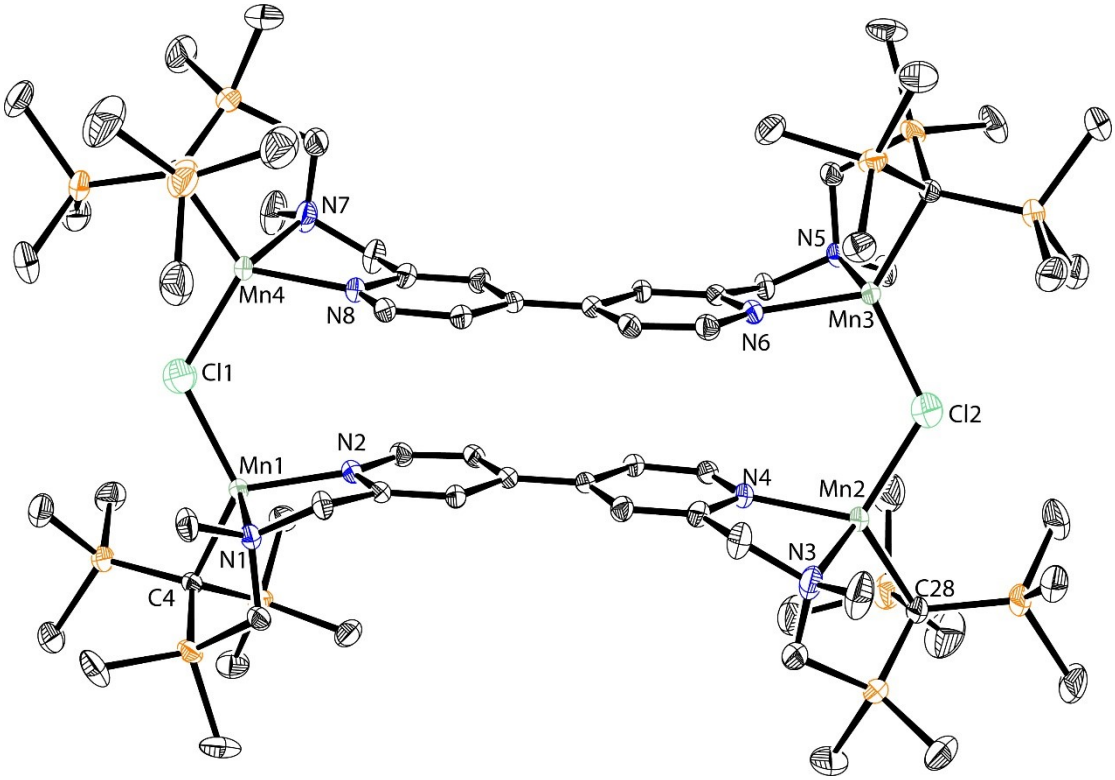


Figure S44 ORTEP drawing of **S-2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S21 Selected Bond Lengths (Å) and Angles (deg) for **S-2**.

Mn(1)——N(1)	2.225(3)
Mn(1)——N(2)	2.115(3)
Mn(1)——Cl(1)	2.346(15)
Mn(1)——C(4)	2.174(3)
Mn(2)——N(3)	2.220(4)
Mn(2)——N(4)	2.131(3)
Mn(2)——Cl(2)	2.307(14)
Mn(2)——C(28)	2.158(4)

Table S22 X-ray crystallographic data for **S-2**.

	S-2
CCDC number	2150104
Empirical formula	$C_{80}H_{164}Cl_2Mn_4N_8Si_{12}$
Formula weight	1865.92
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.4374(6)
b/Å	15.6526(8)
c/Å	18.7151(10)
α/°	107.997(5)
β/°	105.323(5)
γ/°	101.251(5)
Volume/Å^3	2673.9(3)
Z	1
ρ_{calc}, g/cm^3	1.159
μ/mm^{-1}	0.686
F(000)	1002.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.624 to 54.968
Index ranges	$-11 \leq h \leq 13$, $-20 \leq k \leq 20$, $-23 \leq l \leq 24$
Reflections collected	51851
Independent reflections	12256 [R_{int} = 0.0597, R_{sigma} = 0.0475]
Data/restraints/parameters	12256/102/545
Goodness-of-fit on F^2	1.053
R_1 [I>=2δ (I)]	0.0719
wR_2 [all data]	0.2100
Largest diff. peak/hole / e Å^{-3}	1.60/-0.65

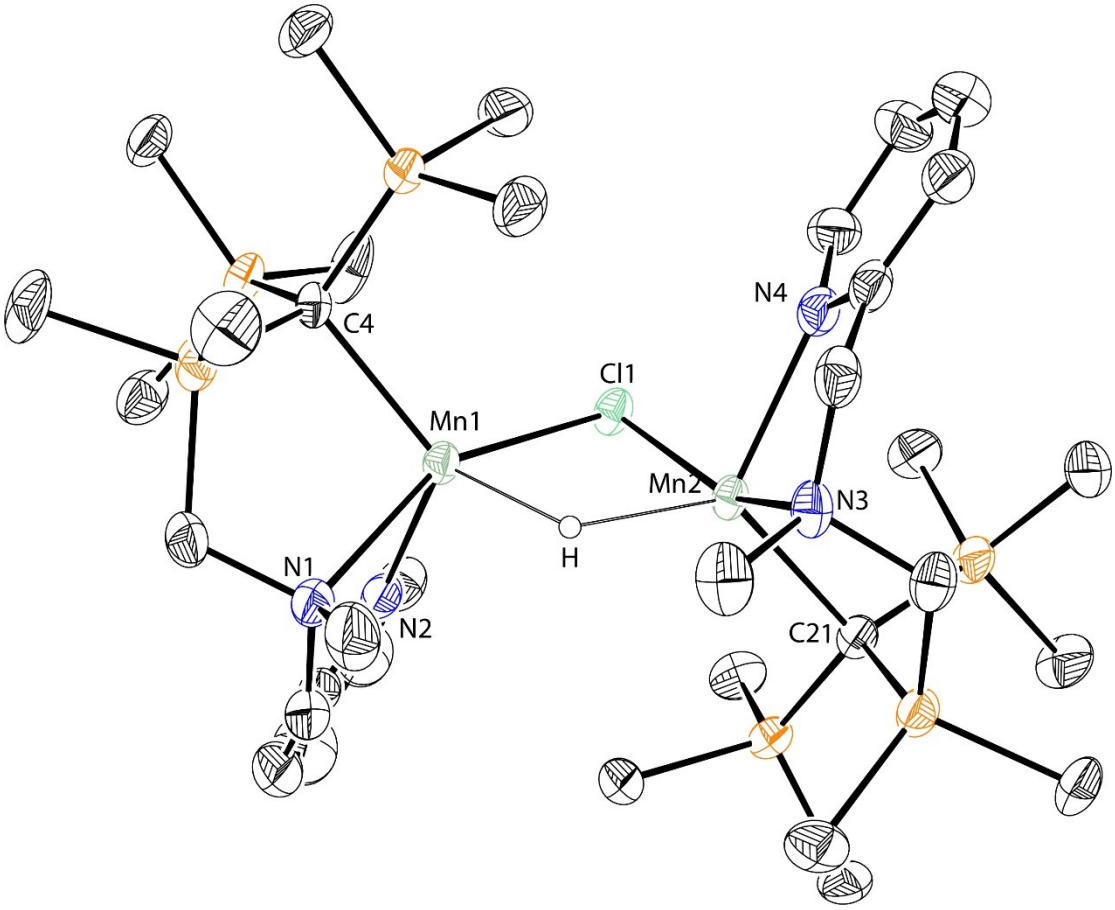


Figure S45 ORTEP drawing of **S-3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S23 Selected Bond Lengths (Å) and Angles (deg) for **S-3**.

Mn(1)——N(1)	2.365(5)
Mn(1)——N(2)	2.236(5)
Mn(1)——Cl(1)	2.5824(16)
Mn(1)——C(4)	2.240(6)
Mn(2)——N(3)	2.357(5)
Mn(2)——N(4)	2.268(5)
Mn(2)——Cl(1)	2.5376(17)
Mn(2)——C(21)	2.255(6)

Table S24 X-ray crystallographic data for **S-3**.

	S-3
CCDC number	2150105
Empirical formula	$C_{34}H_{71}ClMn_2N_4Si_6$
Formula weight	849.81
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.3689(9)
b/Å	14.5884(11)
c/Å	21.1472(12)
α/°	69.939(6)
β/°	86.262(7)
γ/°	74.947(7)
Volume/Å^3	2620.9(4)
Z	2
ρ_{calc}, g/cm^3	1.077
μ/mm^{-1}	0.694
F(000)	908.0
Crystal size/mm^3	0.2 x 0.2 x 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.9 to 50.054
Index ranges	$-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-25 \leq l \leq 25$
Reflections collected	39170
Independent reflections	9248 [R_{int} = 0.0771, R_{sigma} = 0.0615
Data/restraints/parameters	9248/0/446
Goodness-of-fit on F^2	1.075
R_1 [I>=2δ (I)]	0.0828
wR_2 [all data]	0.2237
Largest diff. peak/hole / e Å^{-3}	0.94/-0.76

4) IR Spectra for 3a-d, 4-8

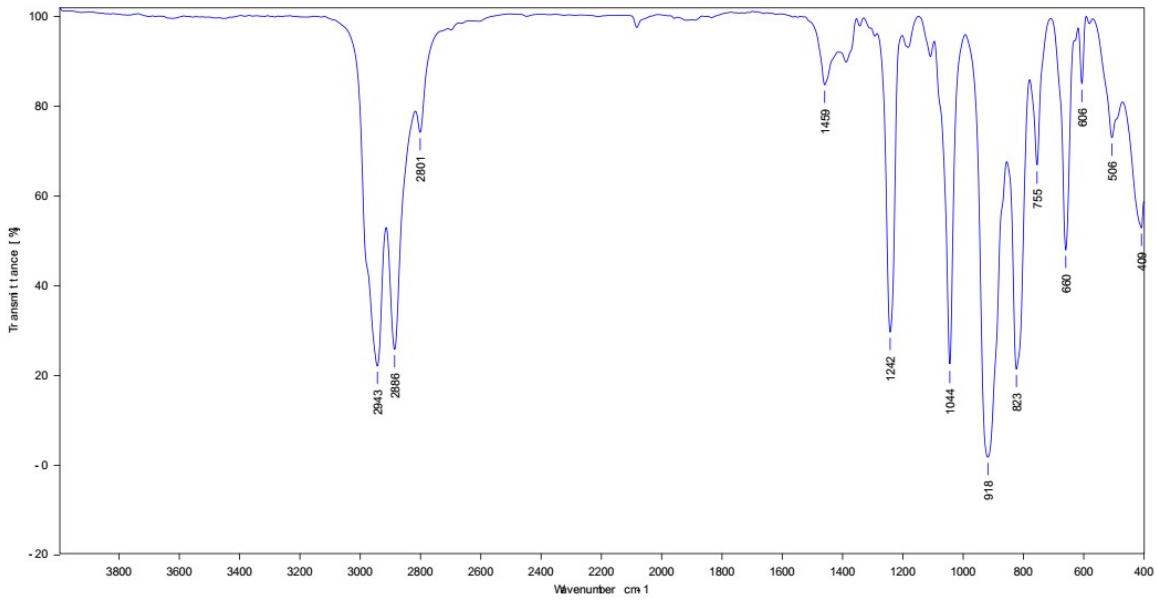


Figure S46 IR spectrum of **3a** in KBr pellet at room temperature.

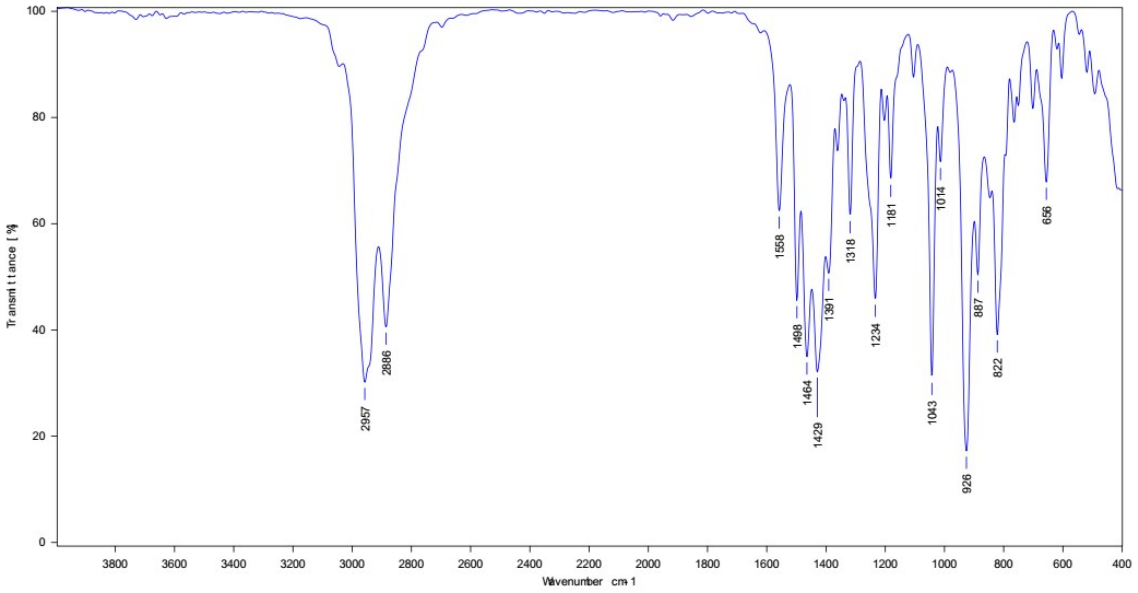


Figure S47 IR spectrum of **3b** in KBr pellet at room temperature.

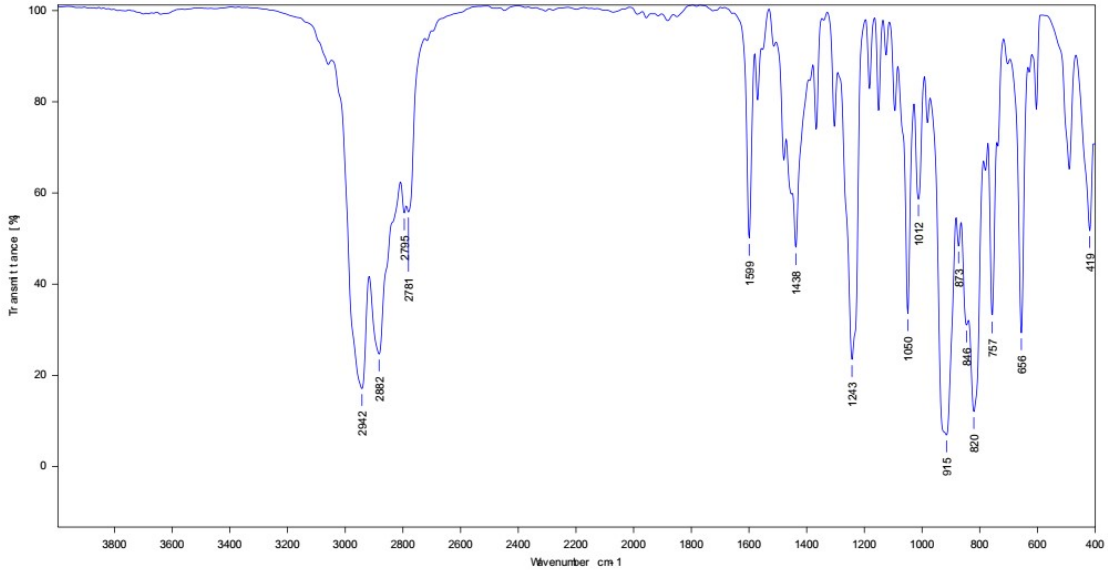


Figure S48 IR spectrum of **3c** in KBr pellet at room temperature.

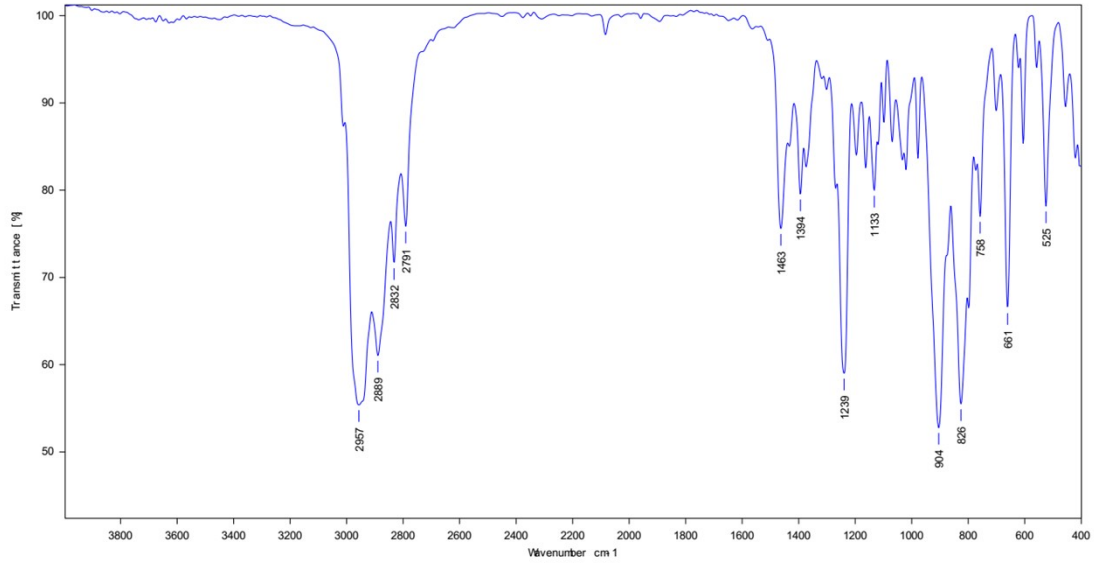


Figure S49 IR spectrum of **3d** in KBr pellet at room temperature.

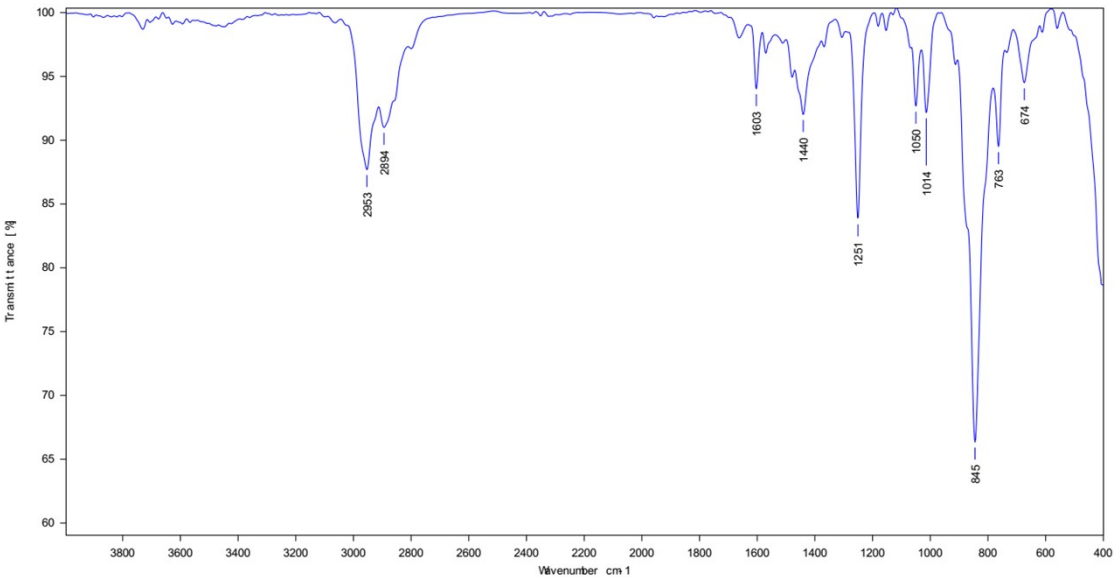


Figure S50 IR spectrum of **4** in KBr pellet at room temperature.

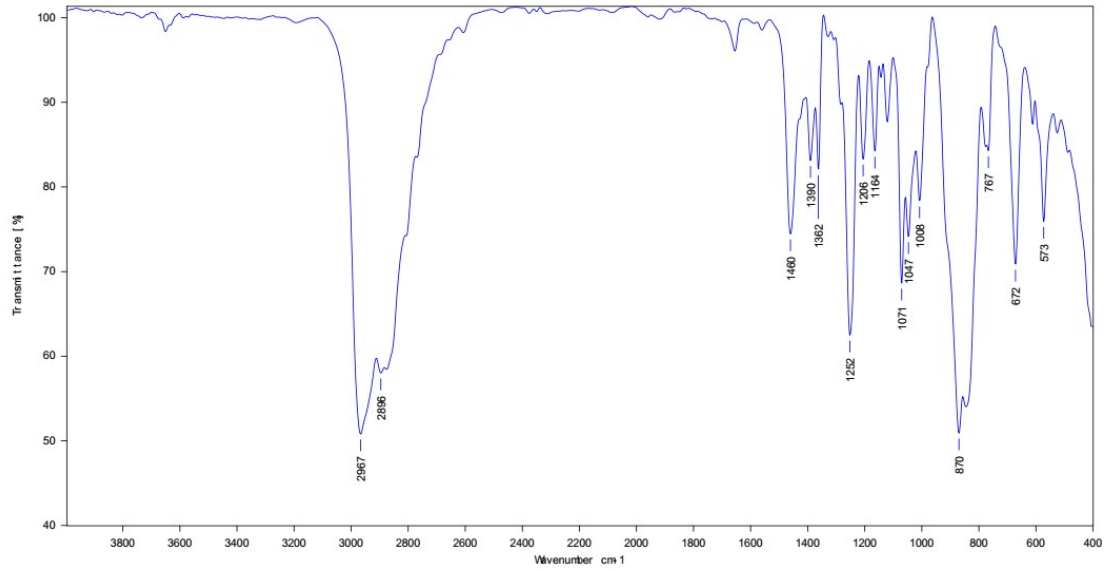


Figure S51 IR spectrum of **5** in KBr pellet at room temperature.

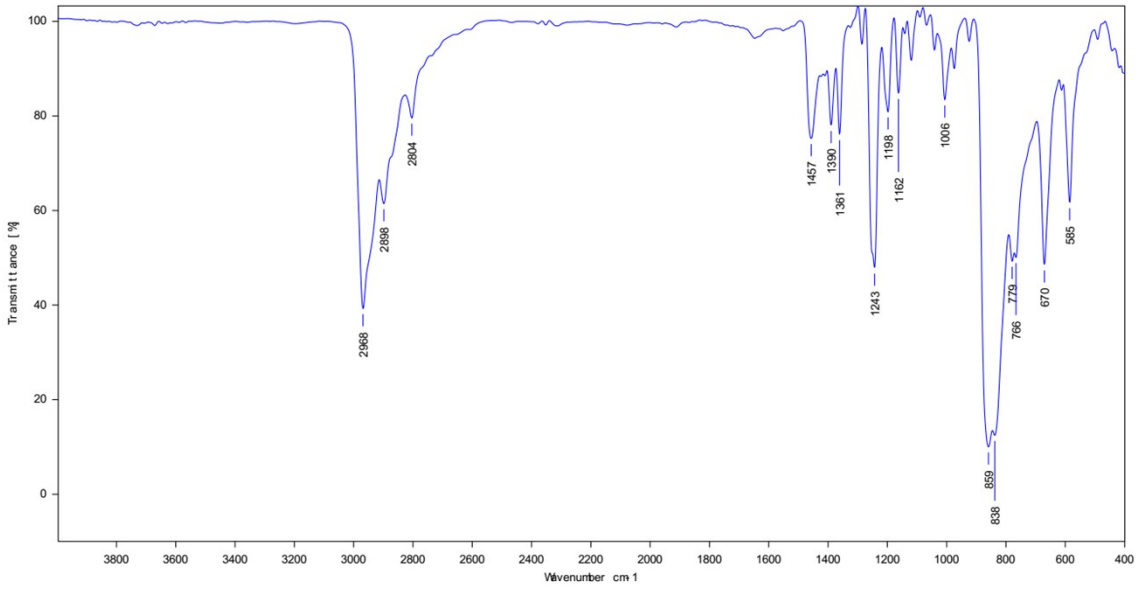


Figure S52 IR spectrum of **6** in KBr pellet at room temperature.

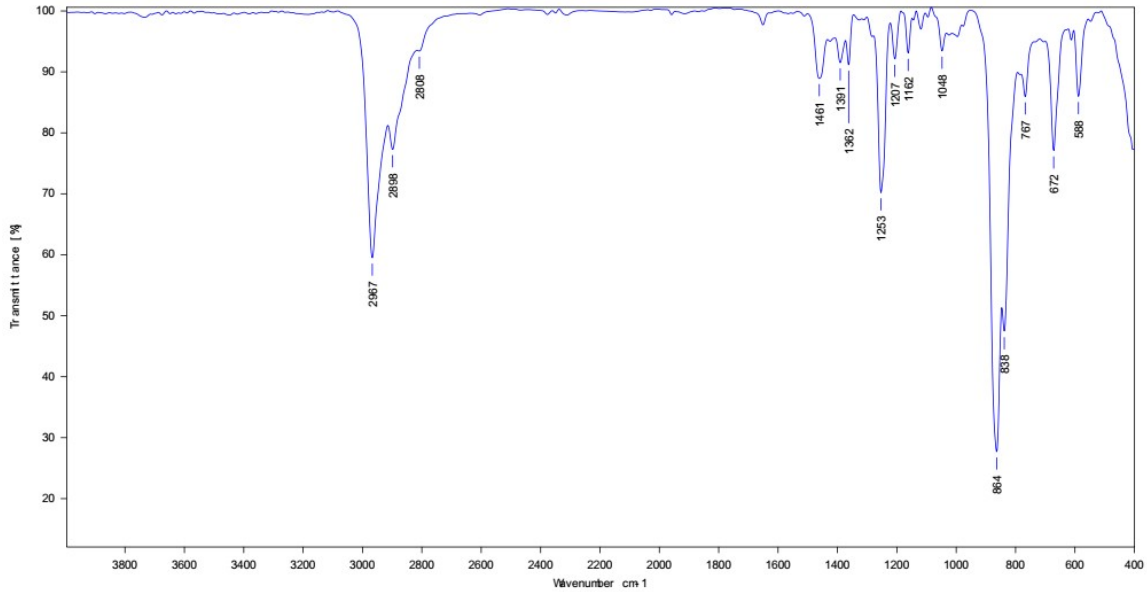


Figure S53 IR spectrum of **7** in KBr pellet at room temperature.

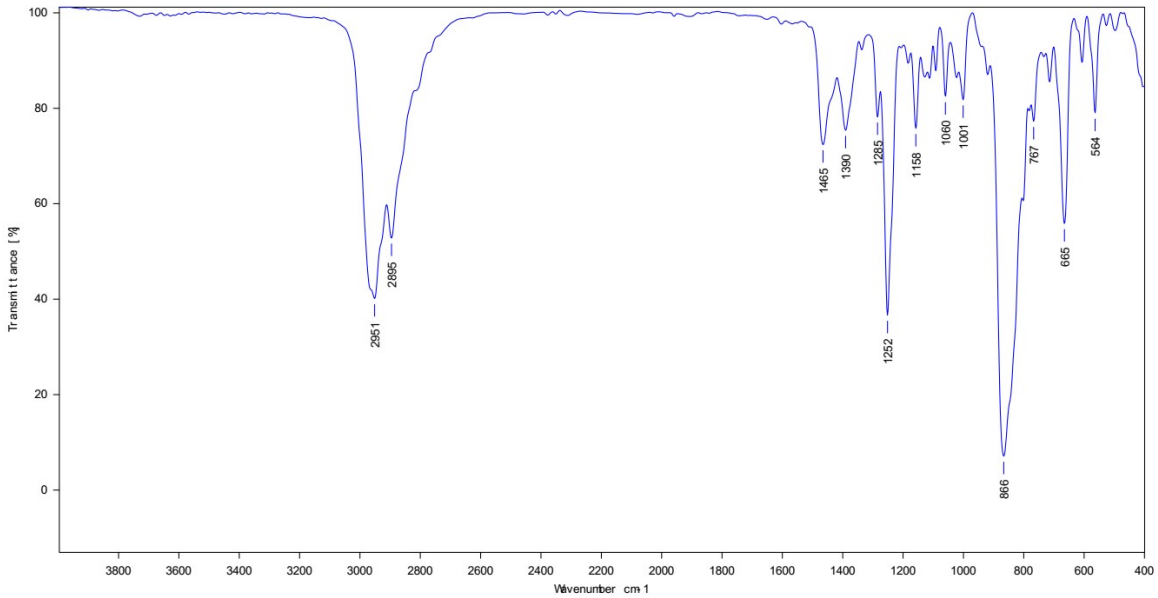


Figure S54 IR spectrum of **8** in KBr pellet at room temperature.

5) References

(1) X. H. He, Y. Z. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang and Q. Wu, *Organometallics*, 2003, **22**, 4952-4957.