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Manuscript Title:

Diversified Two-Electron Reduction for Trivalent Scandium Complexes with Arene Ligands

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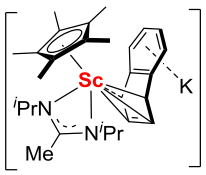
Contents:

1) Experimental Details and Characterization Data

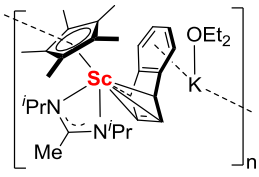
Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips and molecular sieves in a glovebox. d^8-THF was purchased from Cambridge Isotope Laboratory, degassed, and vacuum transferred to 4 Å molecular sieves. All reactions were operated under an argon atmosphere in a glovebox or under slightly positive dry nitrogen pressure using standard Schlenk line techniques. The argon in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure that both were always below 0.1 ppm.

Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox using J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz, 500 MHz or 600 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were reported with reference to solvent resonances of d^8-THF at 1.73 and 25.37 ppm, respectively. Elemental analyses were performed on a Vario MICRO cube elemental analyzer. HRMS were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI. Cyclic voltammetry measurement was performed on CHI660 electrochemical workstation with platinum as the working electrode and $Ag/AgNO_3$ (0.1 M in CH_3CN) as the reference electrode under a nitrogen atmosphere ($E_{1/2}$ (Fc^+/ Fc) = 0.14 V).

Compounds **1**-**3** were prepared following the literature procedures.[1,2]



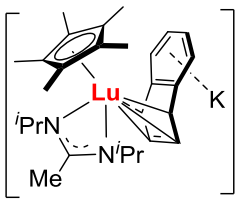
4



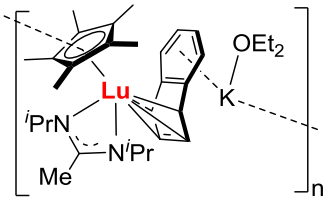
5

Synthesis of 4 and 5: In the glovebox, KC_8 (324.0 mg, 2.4 mmol) was added to a pre-cooled (−35 °C) THF (10 mL) solution of the mixture of **1** (356.9 mg, 0.5 mmol) and naphthalene (128.2 mg, 1.0 mol). The solution was stirred at room temperature for 1 h, then filtered by filter funnel with fritted disc. After that, the solvents were removed under reduced pressure and a large amount of purple solid was obtained. The solid was washed with hexane (5 mL x 3) thrice and dried under vacuum. The final purple powder was pure enough for NMR experiment without further purification. Yield: 85% (415.4 mg, 0.85 mmol). ^{1}H NMR of **4** (400 MHz, d^8-THF) δ 0.92 (d, J = 6.3 Hz, 6H, $(CH_3)_2CH$), 1.11 (d, J = 6.4 Hz, 6H, $(CH_3)_2CH$), 1.70 (s, 3H, CCH_3), 1.83 (s, 15H, C_5Me_5), 2.58-2.60 (m, 2H, naph), 3.44-3.51 (m, 2H, $(CH_3)_2CH$), 4.77-4.80 (m, 2H, naph), 5.68-5.71 (m, 2H, naph), 6.02-6.04 (m, 2H, naph). ^{13}C NMR of **4** (126

MHz, d^8-THF) δ 12.45 (C*C*H$_3$), 12.63 (C$_5$*Me*$_5$), 25.91 ((*C*H$_3$)$_2$CH), 26.95 ((*C*H$_3$)$_2$CH), 48.09 ((CH$_3$)$_2$*C*H), 70.06 (Sc*C*), 111.87 (naph), 114.78 (naph), 115.22 (*C*$_5$Me$_5$), 119.79 (naph), 150.68 (naph), 164.21 (N*C*N). After recrystallization in the mixed solvents of Et$_2$O/hexane (4:1) at −35 °C for 1 day, the single crystals of **5·0.5Et$_2$O** could be obtained. Yield: 73% (437.9 mg, 0.73 mmol). ^{1}H NMR of **5·0.5Et$_2$O** (400 MHz, d^8-THF) δ 0.92 (d, J = 6.3 Hz, 6H, (*CH*$_3$)$_2$CH), 1.10-1.13 (m, 15H, C*H*$_3$ of Et$_2$O, (*CH*$_3$)$_2$CH), 1.70 (s, 3H, C*CH*$_3$), 1.83 (s, 15H, C$_5$*Me*$_5$), 2.58-2.60 (m, 2H, naph), 3.39 (d, J = 7.0 Hz, 6H, C*H*$_2$ of Et$_2$O), 3.44-3.52 (m, 2H, (CH$_3$)$_2$*CH*), 4.77-4.79 (m, 2H, naph), 5.68-5.70 (m, 2H, naph), 6.01-6.03 (m, 2H, naph). Anal. Calcd for C$_{34}$H$_{55}$KN$_2$O$_{1.5}$Sc of **5·0.5Et$_2$O**: C, 68.08; H, 9.24; N, 4.67. Found: C, 68.30; H, 8.62; N, 5.30.

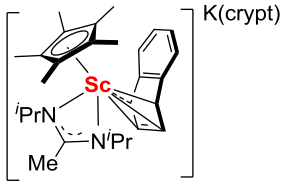


6



7

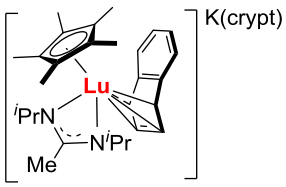
Synthesis of 6 and 7: This complex was prepared from the reaction of **3** (486.9 mg, 0.5 mmol), KC$_8$ (324.0 mg, 2.4 mmol) and naphthalene (128.2 mg, 1.0 mol) in THF (10 mL) by an analogous procedure as the synthesis of **4**. The final orange powder was pure enough for NMR experiment without further purification. Yield: 90% (556.8 mg, 0.90 mmol). ^{1}H NMR of **6** (400 MHz, d^8-THF) δ 0.91 (d, J = 6.3 Hz, 6H, (*CH*$_3$)$_2$CH), 1.09 (d, J = 6.2 Hz, 6H, (*CH*$_3$)$_2$CH), 1.71 (s, 3H, C*CH*$_3$), 1.90 (s, 15H, C$_5$*Me*$_5$), 2.43-2.45 (m, 2H, naph), 3.44-3.49 (m, 2H, (CH$_3$)$_2$*CH*), 4.64-4.66 (m, 2H, naph), 5.56-5.58 (m, 2H, naph), 5.97-6.00 (m, 2H, naph). ^{13}C NMR of **6** (126 MHz, d^8-THF) δ 12.24 (C$_5$*Me*$_5$), 12.32 (C*C*H$_3$), 25.97 ((*C*H$_3$)$_2$CH), 26.93 ((*C*H$_3$)$_2$CH), 48.10 ((CH$_3$)$_2$*C*H), 68.58 (Lu*C*), 111.44 (naph), 114.37 (*C*$_5$Me$_5$), 114.69 (naph), 119.42 (naph), 149.33 (naph), 166.99 (N*C*N). After recrystallization in the mixed solvents of Et$_2$O/hexane (4:1) at −35 °C for 1 day, the single crystals of **7** could be obtained. Yield: 70% (484.9 mg, 0.70 mmol). ^{1}H NMR of **7** (400 MHz, d^8-THF) δ 0.91 (d, J = 6.3 Hz, 6H, (*CH*$_3$)$_2$CH), 1.08-1.13 (m, 12H, C*H*$_3$ of Et$_2$O, *(CH*$_3$)$_2$CH), 1.70 (s, 3H, C*CH*$_3$), 1.90 (s, 15H, C$_5$*Me*$_5$), 2.43-2.45 (m, 2H, naph), 3.39 (d, J = 7.0 Hz, 4H, C*H*$_2$ of Et$_2$O), 3.41-3.50 (m, 2H, (CH$_3$)$_2$*CH*), 4.64-4.66 (m, 2H, naph), 5.56-5.58 (m, 2H, naph), 5.98-6.00 (m, 2H, naph). Anal. Calcd for C$_{32}$H$_{50}$KLuN$_2$O of **7**: C, 55.48; H, 7.27; N, 4.04. Found: C, 54.92; H, 6.90; N, 4.47.



8

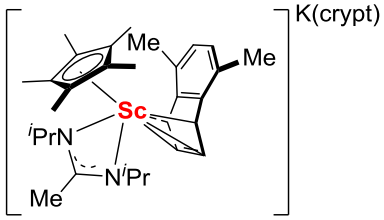
Synthesis of 8: In the glovebox, KC$_8$ (324.0 mg, 2.4 mmol) was added to a pre-cooled (−35 °C) THF (10 mL) solution of the mixture of **1** (356.9 mg, 0.5 mmol) and naphthalene (128.2 mg, 1.0 mol). The solution was stirred at room temperature for 1 h, then filtered by filter funnel with fritted disc. [2.2.2]cryptand (376.5 mg, 1.0 mmol) was

added to filtrate and the mixture was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure and a large amount of purple solid was obtained. The solid was washed with Et_2O (5 mL x 3) thrice and dried under vacuum. The final purple powder was pure enough for NMR experiment without further purification. Yield: 84% (726.7 mg, 0.84 mmol). ^{1}H NMR of **8** (500 MHz, d^8-THF) δ 0.94 (d, J = 6.3 Hz, 6H, (CH_3)$_2$CH), 1.10 (d, J = 6.2 Hz, 6H, (CH_3)$_2$CH), 1.68 (s, 3H, CCH_3), 1.82 (s, 15H, C_5Me_5), 2.50-2.52 (m, 12H, NCH_2CH$_2$O), 2.58-2.61 (m, 2H, naph), 3.43-3.46 (m, 2H, (CH$_3$)$_2$$CH$), 3.48-3.50 (m, 12H, NCH$_2$$CH_2$O), 3.54 (s, 12H, O$CH_2CH_2$O), 4.70-4.72 (m, 2H, naph), 5.61-5.63 (m, 2H, naph), 5.90-5.92 (m, 2H, naph). ^{13}C NMR of **8** (126 MHz, d^8-THF) δ 12.33 (CCH_3), 12.81 (C_5Me_5), 25.99 ((CH_3)$_2$CH), 27.10 ((CH_3)$_2$CH), 48.18 ((CH_3)$_2$$CH$), 54.99 (N$CH_2CH_2$O), 68.10 (Sc$C$), 68.69 (NCH$_2$$CH_2$O), 71.49 (O$CH_2CH_2$O), 112.52 (naph), 114.23 (C_5Me$_5$), 115.30 (naph), 118.64 (naph), 150.77 (naph), 163.75 (NCN). After recrystallization by slow diffusion of hexane into the THF solution of **8** for 3 days, the single crystals **8·0.5THF** suitable for X-ray analysis could be obtained. Anal. Calcd for $C_{48}H_{80}KN_4O_{6.5}Sc$ of **8·0.5THF**: C, 63.97; H, 8.95; N, 6.22. Found: C, 64.08; H, 9.33; N, 6.20.



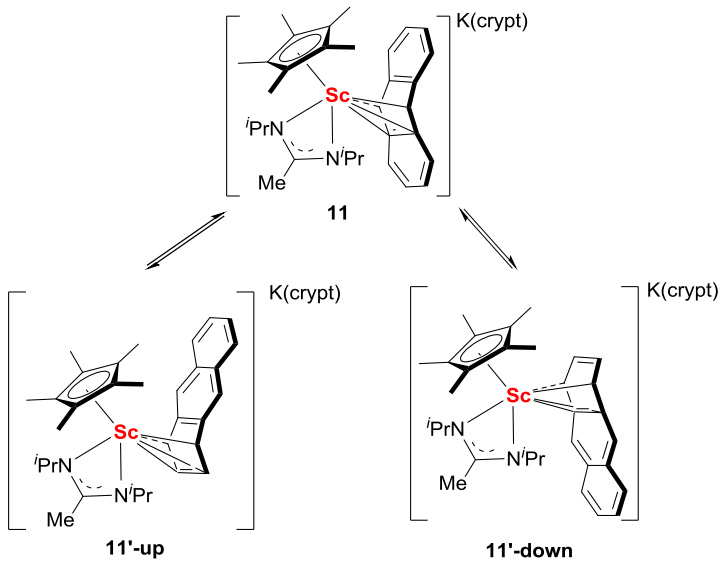
9

Synthesis of 9: This complex was prepared from the reaction of **3** (486.9 mg, 0.5 mmol), KC_8 (324.0 mg, 2.4 mmol) and naphthalene (128.2 mg, 1.0 mol) in THF (10 mL) by an analogous procedure as the synthesis of **8**. The final orange powder was pure enough for NMR experiment without further purification. Yield: 75% (746.4 mg, 0.75 mmol). ^{1}H NMR of **9** (500 MHz, d^8-THF) δ 0.94 (d, J = 6.3 Hz, 6H, (CH_3)$_2$CH), 1.08 (d, J = 6.2 Hz, 6H, (CH_3)$_2$CH), 1.67 (s, 3H, CCH_3), 1.88 (s, 15H, C_5Me_5), 2.46-2.47 (m, 2H, naph), 2.51-2.53 (m, 12H, NCH_2CH$_2$O), 3.40-3.45 (m, 2H, (CH$_3$)$_2$$CH$), 3.49-3.51 (m, 12H, NCH$_2$$CH_2$O), 3.55 (s, 12H, O$CH_2CH_2$O), 4.56 (br, 2H, naph), 5.51 (br, 2H, naph), 5.86-5.88 (m, 2H, naph). ^{13}C NMR of **9** (126 MHz, d^8-THF) δ 12.21 (CCH_3), 12.41 (C_5Me_5), 26.06 ((CH_3)$_2$CH), 27.08 ((CH_3)$_2$CH), 48.17 ((CH_3)$_2$$CH$), 55.01 (N$CH_2CH_2$O), 68.58 (Lu$C$), 68.71 (NCH$_2$$CH_2$O), 71.50 (O$CH_2CH_2$O), 111.86 (naph), 113.55 (C_5Me$_5$), 115.27 (naph), 118.20 (naph), 149.43 (naph), 166.33 (NCN). After recrystallization by slow diffusion of hexane into the THF solution of **9** for 3 days, the single crystals **9·1.5THF** suitable for X-ray analysis could be obtained. Anal. Calcd for $C_{48}H_{80}KLuN_4O_{6.5}$ of **9**: C, 55.91; H, 7.82; N, 5.43. Found: C, 55.46; H, 7.95; N, 5.73. The THF in **9·1.5THF** might be removed under reduced pressure to afford **9**.



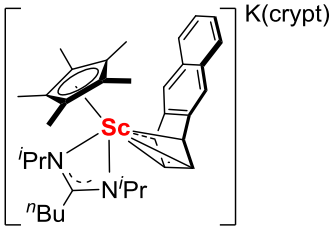
10

Synthesis of 10: This complex was prepared from the reaction of **1** (356.9 mg, 0.5 mmol), KC_8 (324.0 mg, 2.4 mmol) and 1,4-dimethylnaphthalene (156.2 mg, 1.0 mol) in THF (10 mL) by an analogous procedure as the synthesis of **8**. The final dark red powder was pure enough for NMR experiment without further purification. Yield: 85% (759.3 mg, 0.85 mmol). After recrystallization by slow diffusion of hexane into the THF solution of **10** for 3 days, the single crystals **10·0.5THF** suitable for X-ray analysis could be obtained. ^{1}H NMR of **10** (600 MHz, d^8-THF) δ 0.96 (d, J = 5.9 Hz, 6H, $(CH_3)_2$CH), 1.13 (d, J = 6.3 Hz, 6H, $(CH_3)_2$CH), 1.71 (s, 3H, CCH_3), 1.78 (s, 15H, C_5Me_5), 1.81 (br, 6H, ArCH_3), 2.47-2.49 (m, 12H, N$CH_2$$CH_2$O), 2.66-267 (m, 2H, naph), 3.46-3.48 (m, 12H, NCH$_2$$CH_2$O), 3.49-3.52 (m, 14H, $(CH_3)_2CH$, O$CH_2$$CH_2$O), 4.78-4.80 (br, 2H, naph), 5.83 (br, 2H, naph). ^{13}C NMR of **10** (151 MHz, d^8-THF) δ 12.41 (CCH_3), 12.73 (C_5Me_5), 20.62 (ArCH_3), 26.20 ((CH_3)$_2$CH), 27.00 ((CH_3)$_2$CH), 48.14 ((CH_3)$_2$CH), 54.95 (N$CH_2$$CH_2$O), 68.07 (Lu$C$), 68.68 (NCH$_2$$CH_2$O), 71.48 (O$CH_2$$CH_2$O), 112.96 (naph), 114.39 (C_5Me$_5$), 118.58 (naph), 120.82 (naph), 147.49 (naph), 163.41 (NCN). **10** was too sensitive to give satisfactory elemental analysis.



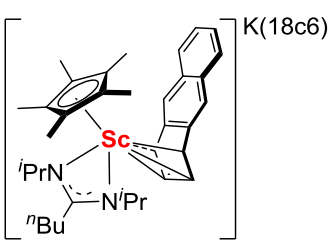
Synthesis of 11: In the glovebox, KC_8 (324.0 mg, 2.4 mmol) was added to a pre-cooled (−35 °C) THF (10 mL) solution of the mixture of **1** (356.9 mg, 0.5 mmol) and anthracene (178.2 mg, 1.0 mol). The solution was stirred at room temperature for 1 h, then filtered by filter funnel with fritted disc. [2.2.2]cryptand (376.5 mg, 1.0 mmol) was added to filtrate and the mixture was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure and a large amount of dark red solid was obtained. The solid was washed with Et_2O (5 mL x 3) thrice and dried under vacuum. The final dark red powder was pure enough for NMR experiment without further purification. Yield: 74% (677.3 mg, 0.74 mmol). In d^8-THF solution, **11** and **11'** are in a dynamic equilibrium. **11'** is the main isomer at low temperature while a rapid fluxional process between **11** and **11'** was observed at elevated

temperatures. ^{1}H NMR of **11** (500 MHz, d^{8}-THF, -40 °C) δ 0.88 (d, J = 6.1 Hz, 6H, (CH_3)$_2$CH), 1.16 (J = 6.4 Hz, 6H, (CH_3)$_2$CH), 1.23 (s, 3H, CCH_3), 1.76 (s, 15H, C_5Me_5), 2.38 (br, 12H, NCH_2CH$_2$O), 2.98 (s, 2H, anth), 3.01-3.06 (m, 2H, (CH$_3$)$_2$$CH$), 3.39 (m, 12H, NCH$_2$$CH_2$O), 3.43 (s, 12H, O$CH_2CH_2$O), 5.98 (br, 2H, anth), 6.09 (br, 2H, anth), 6.18 (br, 2H, anth), 6.28 (br, 2H, anth). ^{1}H NMR of **11** (400 MHz, d^{8}-THF, 25 °C) δ 0.95 (d, J = 5.6 Hz, 6H, (CH_3)$_2$CH), 1.12-1.14 (m, 6H, (CH_3)$_2$CH), 1.37 (br, 3H, CCH_3), 1.79 (s, 15H, C_5Me_5), 2.39-2.42 (m, 12H, NCH_2CH$_2$O), 3.10-3.24 (m, 2H, (CH$_3$)$_2$$CH$), 3.26-3.35 (m, 2H, anth), 3.38-3.41 (m, 12H, NCH$_2$$CH_2$O), 3.45 (s, 12H, O$CH_2CH_2$O), 5.59-6.41 (br, 8H, anth). ^{13}C NMR of **11** (126 MHz, d^{8}-THF, 25 °C) δ 12.54 (CCH_3), 12.63 (C_5Me_5), 15.86 (CH$_3$ of Et$_2$O), 25.98 ((CH_3)$_2$CH), 26.77 ((CH_3)$_2$CH), 47.29 ((CH$_3$)$_2$$C$H), 55.07 (N$CH_2CH_2$O), 66.48 ($CH_2$ of Et$_2$O), 68.10 (LuC), 68.82 (NCH$_2$$CH_2$O), 71.58 (O$CH_2CH_2$O), 108.82 (anth), 114.41 (anth), 116.20 (C_5Me$_5$), 120.63 (anth), 126.27 (anth), 126.57 (anth), 126.89 (anth), 128.15 (anth), 137.89 (anth), 146.03 (anth), 164.80 (NCN). After recrystallization by slow diffusion of hexane into the THF solution of **11** for 3 days, the single crystals **11** suitable for X-ray analysis could be obtained. Anal. Calcd for $C_{50}H_{78}KN_4O_6Sc$ of **11**: C, 65.62; H, 8.59; N, 6.12. Found: C, 65.22; H, 8.47; N, 6.09.



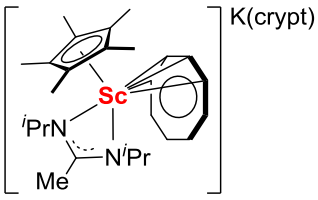
12

Synthesis of 12: This complex was prepared from the reaction of **2** (399.0 mg, 0.5 mmol), KC_8 (324.0 mg, 2.4 mmol), anthracene (178.2 mg, 1.0 mol) and [2.2.2]cryptand (376.5 mg, 1.0 mmol) in THF (10 mL) by an analogous procedure as the synthesis of **11**. The final purple oil was pure enough for NMR experiment without further purification. Yield: 53% (507.4 mg, 0.53 mmol). ^{1}H NMR of **12** (600 MHz, d^{8}-THF) δ 0.90-0.95 (m, 9H, (CH_3)$_2$CH, CH_3CH$_2$CH$_2$CH$_2$), 1.12 (d, J = 6.1 Hz, 6H, (CH_3)$_2$CH), 1.29-1.44 (br, 4H, CH$_3$$CH_2CH_2CH_2$), 1.88 (s, 15H, C_5Me_5), 2.03-2.10 (br, 2H, CH$_3$CH$_2$CH$_2$$CH_2$), 2.44 (m, 12H, N$CH_2CH_2$O), 2.76 (br, 2H, anth), 3.43 (m, 12H, NCH$_2$$CH_2$O), 3.47-3.53 (m, 14H, O$CH_2CH_2$O, (CH$_3$)$_2$$CH$), 4.64 (br, 2H, anth), 5.48 (br, 2H, anth), 6.25-6.27 (br, 2H, anth), 6.54-6.55 (br, 2H, anth). ^{13}C NMR of **12** (151 MHz, d^{8}-THF) δ 12.98 (C_5Me_5), 14.39 (CH$_3$CH$_2$CH$_2$CH$_2$), 24.63 (CH$_3$$CH_2CH_2CH_2$), 25.82 (($CH_3$)$_2$$C$H), 25.96 (($CH_3$)$_2$$C$H), 28.18 ($CH_3CH_2$$CH_2CH_2$), 30.64 ($CH_3CH_2CH_2$$CH_2$), 47.51 (($CH_3$)$_2$$C$H), 55.31 (N$CH_2CH_2$O), 69.04 (NCH$_2$$CH_2$O), 71.80 (O$CH_2$$CH_2$O), 73.98 (Sc$C$), 107.00 (anth), 115.65 (C_5Me$_5$), 118.93 (anth), 122.74 (anth), 126.20 (anth), 129.07 (anth), 129.84 (anth), 168.36 (NCN). **12** was too sensitive to give satisfactory elemental analysis.



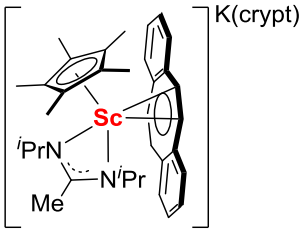
13

Synthesis of 13: This complex was prepared from the reaction of **2** (399.0 mg, 0.5 mmol), KC_8 (324.0 mg, 2.4 mmol), anthracene (178.2 mg, 1.0 mol) and 18c6 (264.3 mg, 1.0 mmol) in THF (10 mL) by an analogous procedure as the synthesis of **11**. The final purple oil was pure enough for NMR experiment without further purification. Yield: 68% (574.7 mg, 0.68 mmol). The crystals of **13·THF** were obtained by placing the Et_2O solution at −35 °C for 3 days. ^{1}H NMR of **13** (500 MHz, d^8-THF) δ 0.90-0.97 (m, 9H, $(CH_3)_2CH$, $CH_3CH_2CH_2CH_2$), 1.12 (d, J = 6.2 Hz, 6H, $(CH_3)_2CH$), 1.29-1.33 (br, 4H, $CH_3CH_2CH_2CH_2$), 1.88 (s, 15H, C_5Me_5), 2.04-2.06 (br, 2H, $CH_3CH_2CH_2CH_2$), 2.77 (br, 2H, anth), 3.38-3.48 (m, 26H, OCH_2CH_2O, $(CH_3)_2CH$), 4.65 (br, 2H, anth), 5.45 (br, 2H, anth), 6.27 (br, 2H, anth), 6.52 (br, 2H, anth). ^{13}C NMR of **13** (126 MHz, d^8-THF) δ 12.93 (C_5Me_5), 14.40 ($CH_3CH_2CH_2CH_2$), 24.65 ($CH_3CH_2CH_2CH_2$), 25.98 ($(CH_3)_2CH$), 26.31 ($(CH_3)_2CH$), 28.17 ($CH_3CH_2CH_2CH_2$), 30.52 ($CH_3CH_2CH_2CH_2$), 47.50 ($(CH_3)_2CH$), 71.62 (OCH_2CH_2O), 74.03 (Sc*C*), 115.89 (C_5Me_5), 119.19 (anth), 126.20 (anth), 126.88 (anth), 128.15 (anth), 129.07 (anth), 129.84 (anth), 167.10 (N*C*N). **13** was too sensitive to give satisfactory elemental analysis.



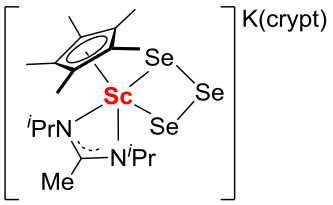
14

Synthesis of 14: In the glovebox, cyclooctatetraene (23.1 μL, 0.2 mmol) was added to a pre-cooled (−35 °C) THF (5 mL) solution of **8** (173.1 mg, 0.2 mmol) and the reaction mixture gradually turned to yellow. The solution was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure to afford yellow solid. The solid was washed with Et_2O (2 mL x 3) thrice and dried under vacuum affording yellow powder. This powder was pure enough for NMR experiment without further purification. Yield: 87% (146.4 mg, 0.17 mmol). Slowly diffusing hexane into the THF solution of **14** for 3 days afforded the yellow single crystals of **14**. ^{1}H NMR of **14** (600 MHz, d^8-THF) δ 0.82 (d, J = 6.1 Hz, 6H, $(CH_3)_2CH$), 1.30 (d, J = 6.4 Hz, 6H, $(CH_3)_2CH$), 1.71 (s, 3H, CCH_3), 1.92 (s, 15H, C_5Me_5), 2.31-2.32 (m, 12H, NCH_2CH_2O), 3.27-3.29 (m, 12H, NCH_2CH_2O), 3.33 (s, 12H, OCH_2CH_2O), 3.52-3.55 (m, 2H, $(CH_3)_2CH$), 5.38 (s, 8H, COT). ^{13}C NMR of **14** (126 MHz, d^8-THF) δ 12.59 (CCH_3), 12.99 (C_5Me_5), 26.67 ($(CH_3)_2CH$), 27.17 ($(CH_3)_2CH$), 48.07 ($(CH_3)_2CH$), 54.91 (NCH_2CH_2O), 68.57 (NCH_2CH_2O), 71.30 (OCH_2CH_2O), 97.68 (COT), 115.03 (C_5Me_5), 165.09 (N*C*N). Anal. Calcd for $C_{44}H_{76}KN_4O_6Sc$ of **14**: C, 62.83; H, 9.11; N, 6.66. Found: C, 62.79; H, 9.25; N, 6.68.



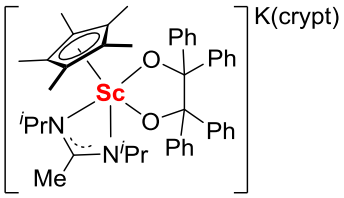
15

Synthesis of 15: In the glovebox, dibenzo[a,e]cyclooctene (40.9 mg, 0.2 mmol) was added to THF (5 mL) solution of **8** (173.1 mg, 0.2 mmol) and the reaction mixture was heated to 50 °C for 6 h. After that, the solvents were removed under reduced pressure to afford dark red solid. The solid was washed with Et_2O (2 mL x 3) thrice and dried under vacuum affording dark red powder. This powder was pure enough for NMR experiment without further purification. Yield: 81% (152.5 mg, 0.16 mmol). ^{1}H NMR of **15** (500 MHz, d^8-THF) δ 0.02 (d, J = 6.2 Hz, 6H, $(CH_3)_2CH$), 0.50 (d, J = 6.1 Hz, 6H, $(CH_3)_2CH$), 1.72 (s, 3H, CCH_3), 2.03 (s, 15H, C_5Me_5), 2.06-2.08 (m, 12H, NCH_2CH_2O), 2.69-2.74 (m, 2H, $(CH_3)_2CH$), 3.03-3.04 (m, 12H, NCH_2CH_2O), 3.10 (s, 12H, OCH_2CH_2O), 6.22-6.24 (m, 8H, Ar), 7.40-7.42 (m, 4H, Ar). ^{13}C NMR of **15** (126 MHz, d^8-THF) δ 12.67 (C_5Me_5), 14.71(CCH_3), 25.98 ($(CH_3)_2CH$), 26.02 ($(CH_3)_2CH$), 47.93 ($(CH_3)_2CH$), 54.86 (NCH_2CH_2O), 68.52 (NCH_2CH_2O), 71.24 (OCH_2CH_2O), 117.69 (C_5Me_5), 126.21 (dibenzo-COT), 127.69 (dibenzo-COT), 129.08 (dibenzo-COT), 129.84 (dibenzo-COT), 173.17 (NCN). Slowly diffusing hexane into the THF solution of **15** for 3 days afforded the dark red single crystals of **15·Et₂O**. Anal. Calcd for $C_{56}H_{90}KN_4O_7Sc$ of **15·Et₂O**: C, 66.24; H, 8.93; N, 5.52. Found: C, 65.98; H, 8.65; N, 5.74.



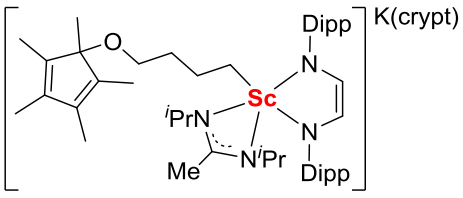
16

Synthesis of 16: In the glovebox, Se (63.2 mg, 0.8 mmol) was added to a pre-cooled (−35 °C) THF (5 mL) solution of **8** (173.1 mg, 0.2 mmol) and the reaction mixture gradually turned to red. The solution was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure to afford red solid. The solid was washed with Et_2O (2 mL x 3) thrice and dried under vacuum affording red powder. This powder was pure enough for NMR experiment without further purification. Yield: 78% (151.9 mg, 0.16 mmol). Slowly diffusing hexane into the THF solution of **16** for 3 days afforded the red single crystals of **16**. ^{1}H NMR of **16** (600 MHz, d^8-THF) δ 1.06 (d, J = 6.3 Hz, 6H, $(CH_3)_2CH$), 1.33 (d, J = 6.5 Hz, 6H, $(CH_3)_2CH$), 1.84 (s, 3H, CCH_3), 2.04 (s, 15H, C_5Me_5), 2.60-2.62 (m, 12H, NCH_2CH_2O), 3.56-3.57 (m, 2H, $(CH_3)_2CH$), 3.59-3.61 (m, 12H, NCH_2CH_2O), 3.65 (s, 12H, OCH_2CH_2O). ^{13}C NMR of **16** (151 MHz, d^8-THF) δ 12.19 (CCH_3), 14.17 (C_5Me_5), 25.82 ($(CH_3)_2CH$), 25.95 ($(CH_3)_2CH$), 49.10 ($(CH_3)_2CH$), 55.16 (NCH_2CH_2O), 68.82 (NCH_2CH_2O), 71.64 (OCH_2CH_2O), 117.54 (C_5Me_5), 171.49 (NCN). Anal. Calcd for $C_{40}H_{76}KN_4O_7ScSe_3$ of **16·THF**: C, 45.93; H, 7.32; N, 5.36. Found: C, 45.45; H, 7.39; N, 5.47. **16** might coordinate with a THF molecule to afford **16·THF**.



17

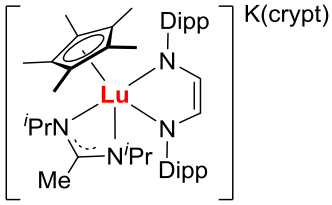
Synthesis of 17: In the glovebox, benzophenone (80.2 mg, 0.2 mmol) was added to a pre-cooled (−35 °C) THF (5 mL) solution of **8** (173.1 mg, 0.2 mmol) and the reaction mixture gradually turned to colorless. The solution was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure to afford colorless solid. The solid was washed with Et_2O (2 mL x 3) thrice and dried under vacuum affording white powder. Yield: 75% (165.2 mg, 0.15 mmol). ^{1}H NMR of **17** (500 MHz, d^8-THF) δ 0.94 (d, J = 6.1 Hz, 6H, $(CH_3)_2CH$), 1.18 (d, J = 6.3 Hz, 6H, $(CH_3)_2CH$), 1.67 (s, 3H, CCH_3), 1.93 (s, 15H, C_5Me_5), 2.50-2.52 (m, 12H, NCH_2CH_2O), 2.82-2.87 (m, 2H, $(CH_3)_2CH$), 3.48-3.50 (m, 12H, NCH_2CH_2O), 3.53 (s, 12H, OCH_2CH_2O), 6.58-6.67(m, 6H, Ph), 6.80-6.84 (m, 6H, Ph), 7.48-7.50 (m, 8H, Ph). ^{13}C NMR of **17** (126 MHz, d^8-THF) δ 13.33 (C_5Me_5), 13.55 (CCH_3), 26.44 ($(CH_3)_2CH$), 26.58 ($(CH_3)_2CH$), 47.71 ($(CH_3)_2CH$), 54.97 (NCH_2CH_2O), 68.39 (Sc-C), 68.68 (NCH_2CH_2O), 71.52 (OCH_2CH_2O), 114.04 (C_5Me_5), 125.83 (Ph), 126.67 (Ph), 128.76 (Ph), 131.78 (Ph), 168.64 (NCN). Slowly diffusing hexane into the THF solution of **17** for 3 days afforded the colorless crystals of **17·2THF**. Anal. Calcd for $C_{70}H_{104}KN_4O_{10}Sc$ of **17·2THF**: C, 67.50; H, 8.42; N, 4.50. Found: C, 67.13; H, 8.28; N, 4.50.



18

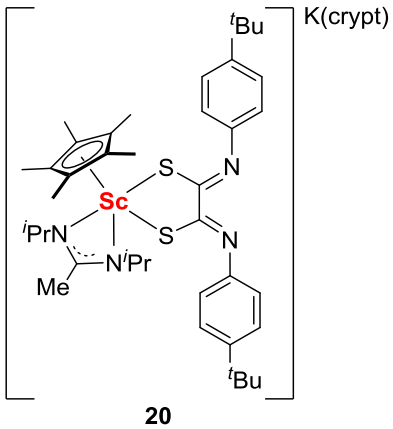
Synthesis of 18: In the glovebox, 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (75.3 mg, 0.2 mmol) was added to a pre-cooled (−35 °C) THF (5 mL) solution of **8** (173.1 mg, 0.2 mmol) and the reaction mixture gradually turned to yellow. The solution was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure to afford yellow solid. The solid was washed with Et_2O (2 mL x 3) thrice and dried under vacuum affording yellow powder. This powder was pure enough for NMR experiment without further purification. Yield: 53% (125.7 mg, 0.11 mmol). Slowly diffusing hexane into the THF solution of **18** for 3 days afforded the colorless crystals of **18**. ^{1}H NMR of **18** (500 MHz, d^8-THF) δ 0.67 (d, J = 6.4 Hz, 12H, $(CH_3)_2CH$), 0.82 (s, 3H, CCH_3), 1.14 (d, J = 6.8 Hz, 24H, $(CH_3)_2CH$), 1.29-1.42 (m, 6H, $OCH_2CH_2CH_2CH_2$), 1.66 (s, 6H, C_5Me_5), 1.70 (s, 3H, C_5Me_5), 1.71 (s, 6H, C_5Me_5), 2.52-2.53 (m, 12H, NCH_2CH_2O), 3.17-3.22 (m, 2H, $(CH_3)_2CH$), 3.50-3.52 (m, 12H, NCH_2CH_2O), 3.55 (s, 12H, OCH_2CH_2O), 3.80 (t, J = 7.1 Hz, 2H $OCH_2CH_2CH_2CH_2$), 4.04-4.09 (m, 4H, $(CH_3)_2CH$), 5.15 (s, 2H, N-CH=CH-N), 6.56 (t, J = 7.5 Hz, 2H, Ar), 6.78 (d, J = 7.5 Hz, 4H, Ar). ^{13}C NMR of **18** (126 MHz, d^8-THF) δ 10.18 (C_5Me_5), 10.70 (C_5Me_5), 11.29 (C_5Me_5), 21.59 ($OCH_2CH_2CH_2CH_2$), 23.21 (CCH_3), 25.82 ($(CH_3)_2CH$),

26.14 ((*C*H$_3$)$_2$CH), 28.11 ((CH$_3$)$_2$*C*H), 37.28 (OCH$_2$CH$_2$*C*H$_2$CH$_2$), 38.62 (OCH$_2$*C*H$_2$CH$_2$*C*H$_2$), 48.15 ((CH$_3$)$_2$*C*H), 54.95 (N*C*H$_2$CH$_2$O), 57.07 ((CH$_3$)$_2$*C*H), 68.10 (*C*$_5$Me$_5$), 68.64, (NCH$_2$*C*H$_2$O), 69.20 (OCH$_2$CH$_2$CH$_2$*C*H$_2$), 71.49 (O*C*H$_2$*C*H$_2$O), 117.73 (N-*C*H=*C*H-N), 119.27 (Ar), 122.61 (Ar), 133.94 (*C*$_5$Me$_5$), 141.33 (*C*$_5$Me$_5$), 144.91 (Ar), 157.31 (Ar), 171.18 (N*C*N). Anal. Calcd for C$_{66}$H$_{112}$KN$_6$O$_7$Sc of **18**: C, 66.86; H, 9.52; N, 7.09. Found: C, 66.94; H, 9.44; N, 7.12.



19

Synthesis of 19: This complex was prepared from the reaction of 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (75.3 mg, 0.2 mmol) and **9** (199.1 mg, 0.2 mmol) in THF (5 mL) by an analogous procedure as the synthesis of **18**. The final yellow powder was pure enough for NMR experiment without further purification. Yield: 65% (161.7 mg, 0.13 mmol). Slowly diffusing hexane into the THF solution of **19** for 3 days afforded the crystals of **19**. ^{1}H NMR of **19** (500 MHz, d^8-THF) δ 0.98-1.25 (m, 36H, (*CH*$_3$)$_2$CH), 1.78 (s, 15H, C$_5$*Me*$_5$), 1.83 (s, 3H, C*CH*$_3$), 2.50-2.51 (m, 12H, N*CH*$_2$CH$_2$O), 3.48-3.50 (m, 12H, NCH$_2$*CH*$_2$O), 3.53-3.55 (m, 14H, O*CH*$_2$*CH*$_2$O, (CH$_3$)$_2$*CH*), 3.62-3.67 (br, 4H, (CH$_3$)$_2$*CH*), 4.94 (s, 2H, N-*CH*=*CH*-N), 6.52 (t, *J* = 7.5 Hz, 2H, Ar), 6.77 (d, *J* = 7.5 Hz, 4H, Ar). ^{13}C NMR of **19** (126 MHz, d^8-THF) δ 12.82 (C$_5$*Me*$_5$), 16.78 (C*C*H$_3$), 25.98 ((*C*H$_3$)$_2$CH), 28.35 ((*C*H$_3$)$_2$CH), 48.11 ((CH$_3$)$_2$*C*H), 54.93 (N*C*H$_2$CH$_2$O), 68.10 ((CH$_3$)$_2$*C*H), 68.63 (NCH$_2$*C*H$_2$O), 71.47 (O*C*H$_2$*C*H$_2$O), 114.37 (*C*$_5$Me$_5$), 118.79 (N-*C*H=*C*H-N), 120.69 (Ar), 122.41 (Ar), 145.21 (Ar), 157.51 (Ar), 169.51 (N*C*N). **19** was too sensitive to give satisfactory elemental analysis.



20

Synthesis of 20: This complex was prepared from the reaction of 4-tert-butylphenyl isothiocyanate (84.2 mg, 0.2 mmol) and **8** (173.1 mg, 0.2 mmol) in THF (5 mL) by an analogous procedure as the synthesis of **18**. The final purple powder was pure enough for NMR experiment without further purification. Yield: 56% (125.4 mg, 0.11 mmol). Slowly diffusing hexane into the THF solution of **20** for 3 days afforded the colorless crystals of **20**. ^{1}H NMR of **20** (500 MHz, d^8-THF) δ1.00 (d, *J* = 6.3 Hz, 6H, (*CH*$_3$)$_2$CH), 1.08 (d, *J* = 6.4 Hz, 6H, (*CH*$_3$)$_2$CH), 1.30 (s, 18H, C(*CH*$_3$)$_3$), 1.87 (s, 3H, C*CH*$_3$), 1.97 (s, 15H, C$_5$*Me*$_5$), 2.45-2.47 (m, 12H, N*CH*$_2$CH$_2$O), 3.37-3.41 (m, 2H, (CH$_3$)$_2$*CH*), 3.45-3.46 (m, 12H, NCH$_2$*CH*$_2$O), 3.51 (s, 12H, O*CH*$_2$*CH*$_2$O), 6.94-6.95 (m, 4H, Ar), 7.15-7.16 (m, 4H, Ar). ^{13}C NMR of **20** (126 MHz, d^8-

THF) δ 12.27 (C*C*H$_3$), 13.43 (C$_5$*Me*$_5$), 25.98 ((*C*H$_3$)$_2$CH), 26.00 ((*C*H$_3$)$_2$CH), 32.55 (C(*C*H$_3$)$_3$), 34.87 (*C*(CH$_3$)$_3$), 48.68 ((CH$_3$)$_2$*C*H), 55.06 (N*C*H$_2$CH$_2$O), 68.69 (NCH$_2$*C*H$_2$O), 71.50 (OCH$_2$*C*H$_2$O), 118.86 (*C*$_5$Me$_5$), 122.73 (Ar), 124.72 (Ar), 143.12 (Ar), 153.06 (Ar), 171.02 (N*C*N), 178.17 (S*C*N). Anal. Calcd for C$_{58}$H$_{94}$KN$_6$O$_6$S$_2$Sc of **20**: C, 62.22; H, 8.46; N, 7.51. Found: C, 61.77; H, 8.42; N, 6.86.

2) Copies of ^{1}H NMR and ^{13}C NMR Spectra

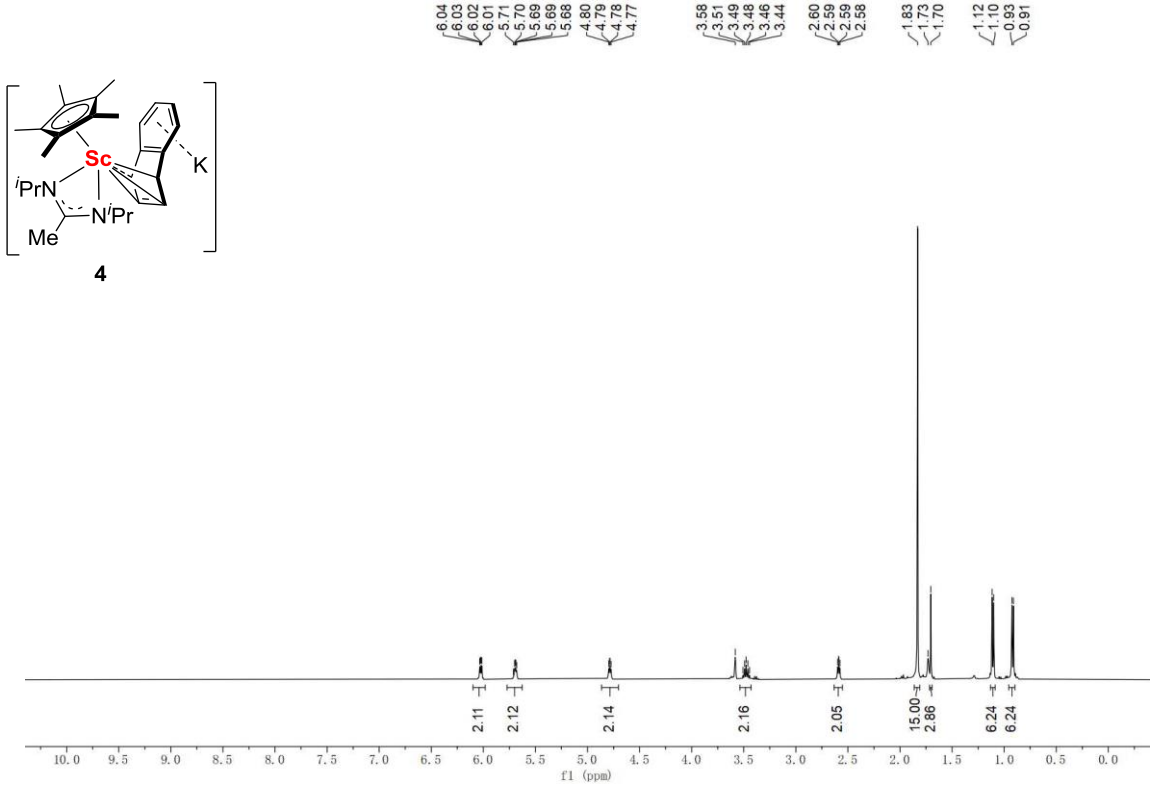


Figure S1. ^{1}H NMR spectrum of **4** (25 °C, 400 MHz, d^8-THF).

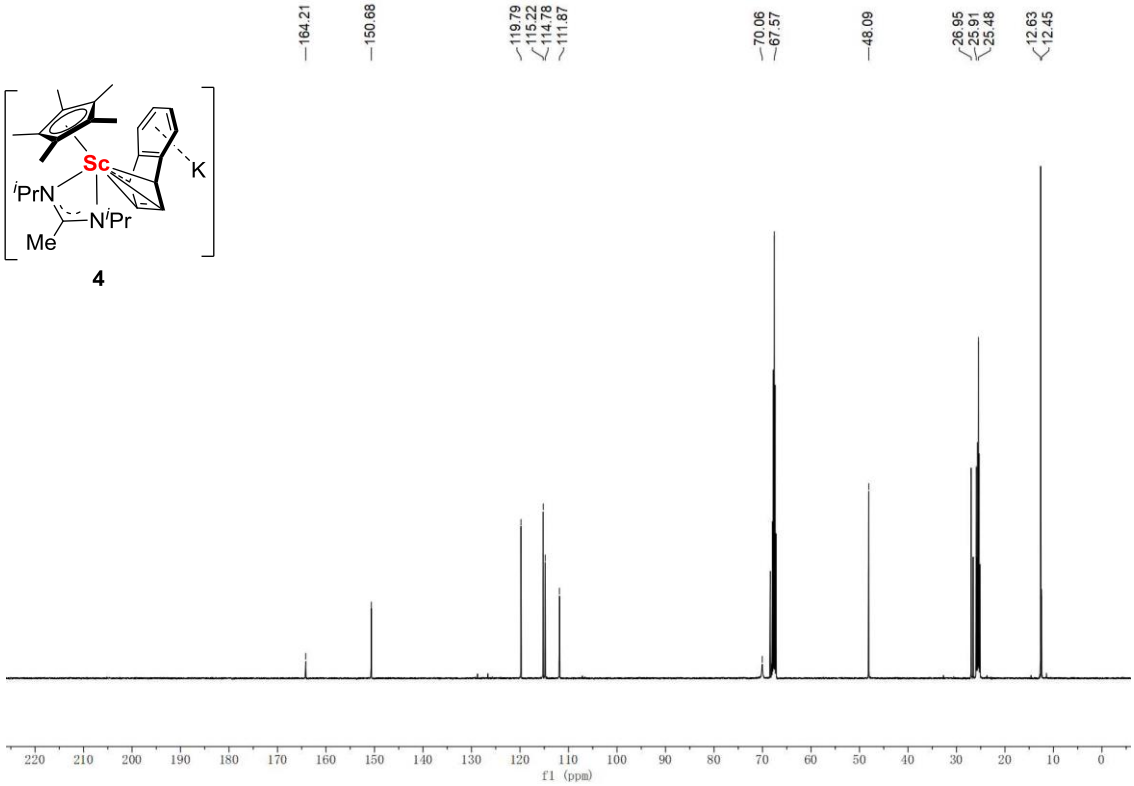


Figure S2. ^{13}C NMR spectrum of **4** (25 °C, 126 MHz, d^8-THF).

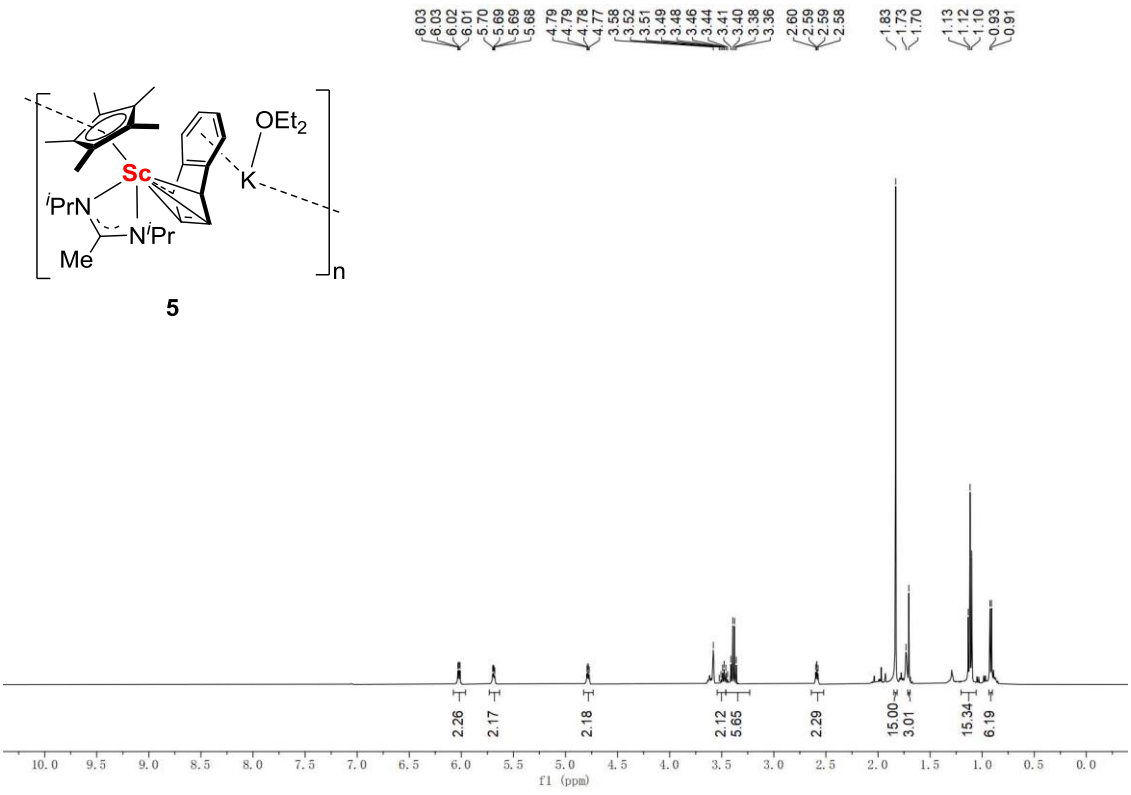


Figure S3. ^{1}H NMR spectrum of **5** (25 °C, 400 MHz, d^8-THF).

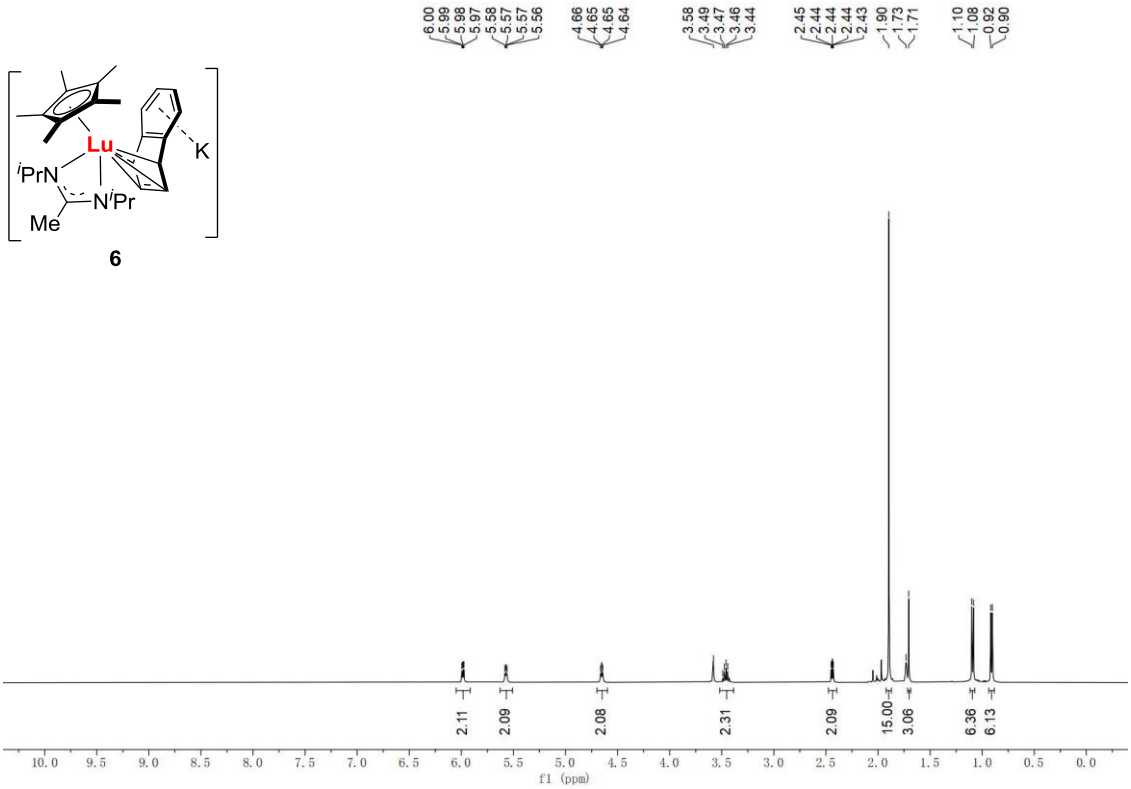


Figure S4. ^{1}H NMR spectrum of **6** (25 °C, 400 MHz, d^{8}-THF).

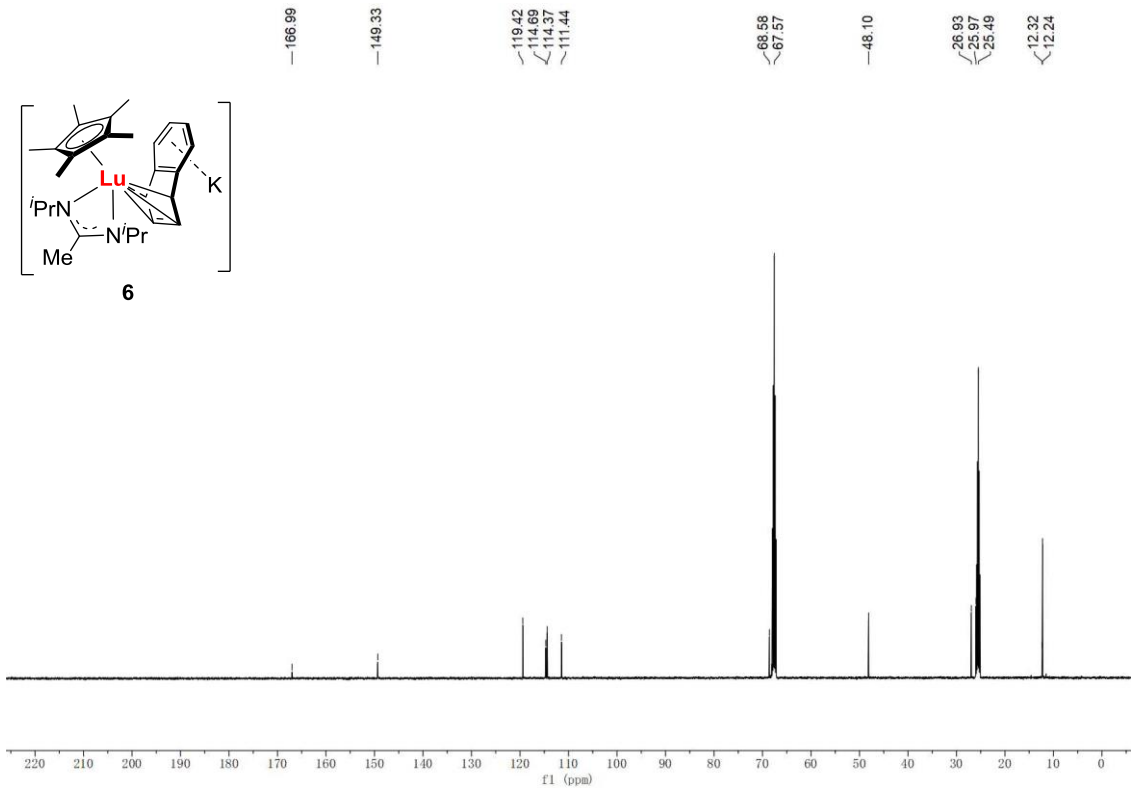


Figure S5. ^{13}C NMR spectrum of **6** (25 °C, 126 MHz, d^{8}-THF).

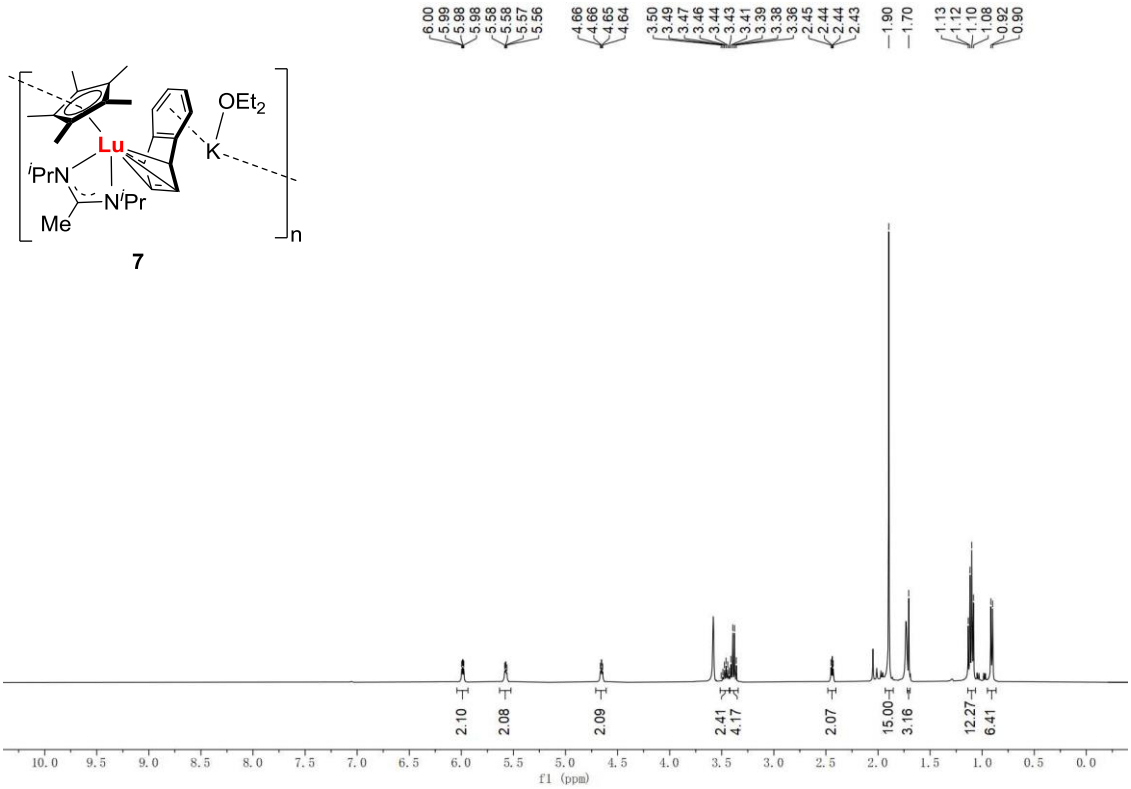


Figure S6. ^{1}H NMR spectrum of **7** (25 °C, 400 MHz, d^{8}-THF).

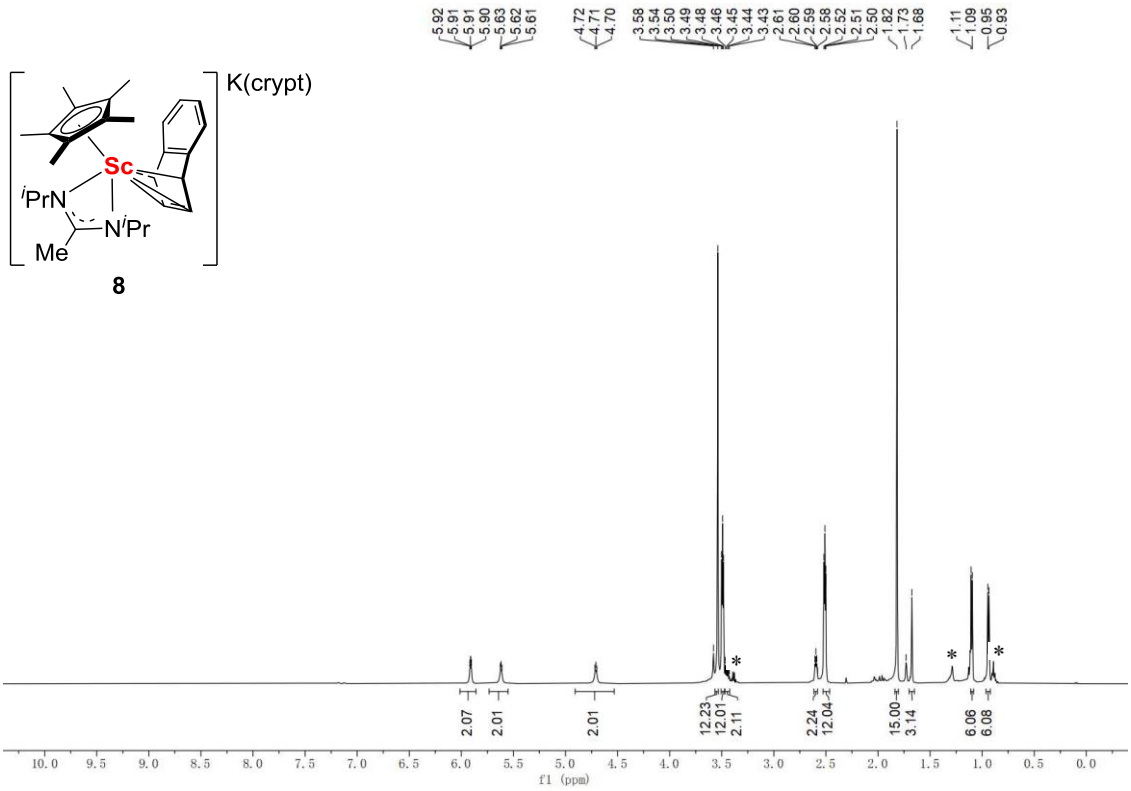


Figure S7. ^{1}H NMR spectrum of **8** (25 °C, 500 MHz, d^{8}-THF, "*" represents the residual Et_2O and hexane).

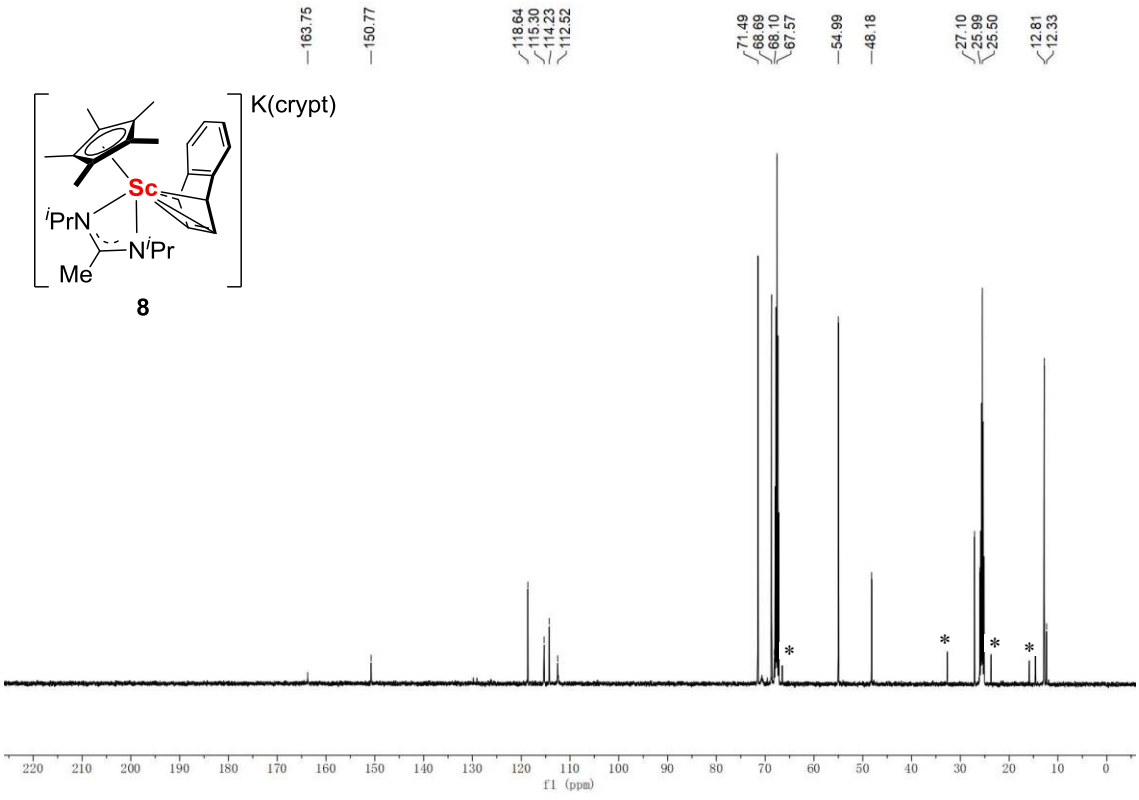


Figure S8. ^{13}C NMR spectrum of **8** (25 °C, 126 MHz, d^8-THF, "*" represents the residual Et_2O and hexane).

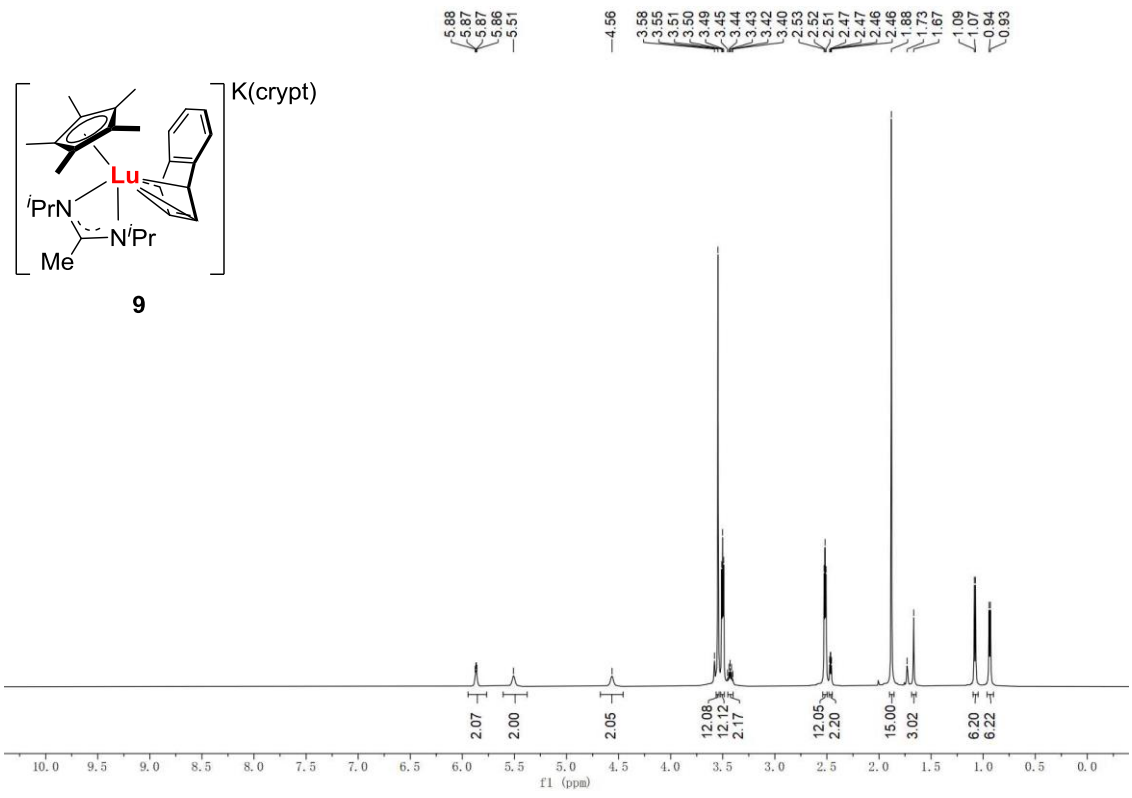


Figure S9. ^{1}H NMR spectrum of **9** (25 °C, 500 MHz, d^8-THF).

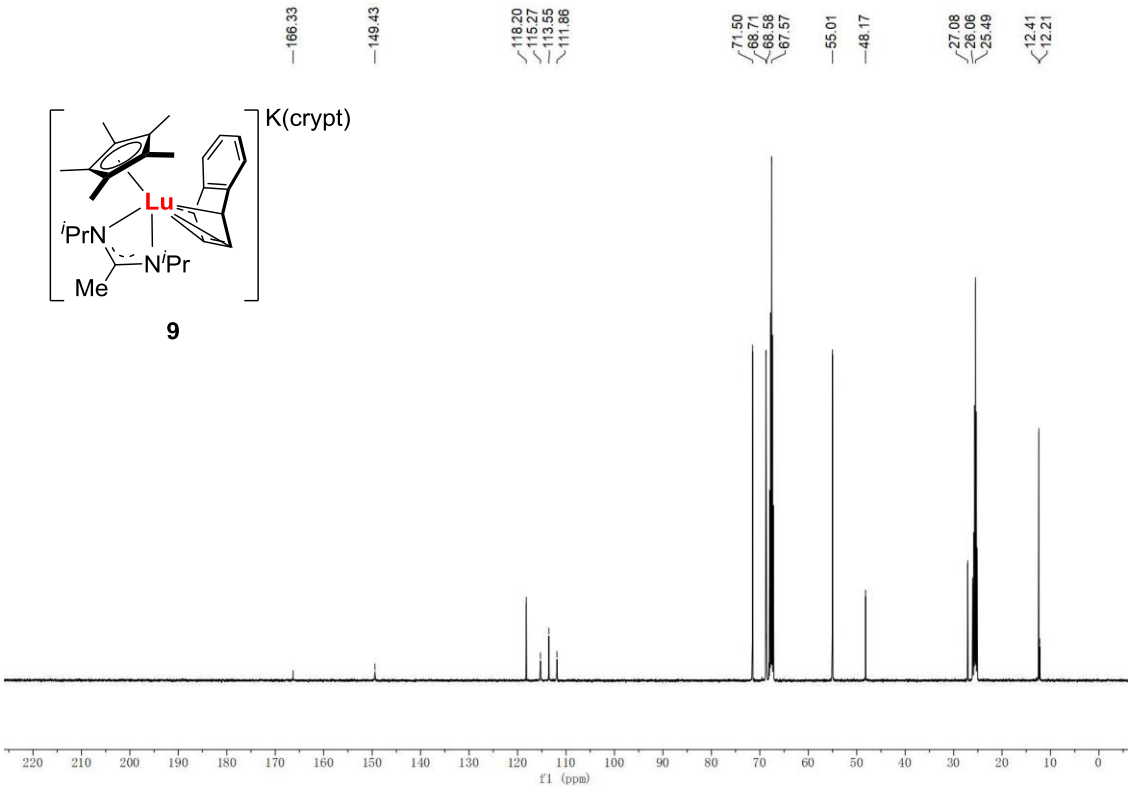


Figure S10. ^{13}C NMR spectrum of **9** (25 °C, 126 MHz, d^8-THF).

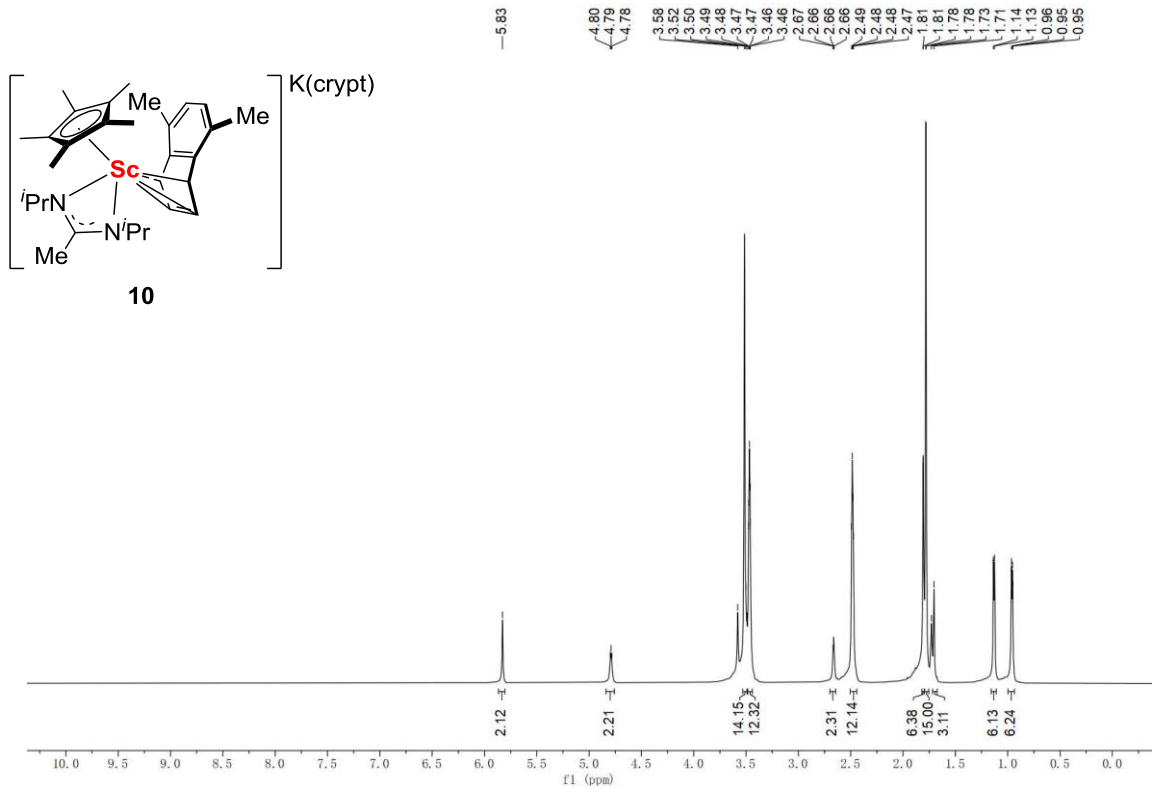


Figure S11. ^{1}H NMR spectrum of **10** (25 °C, 600 MHz, d^8-THF).

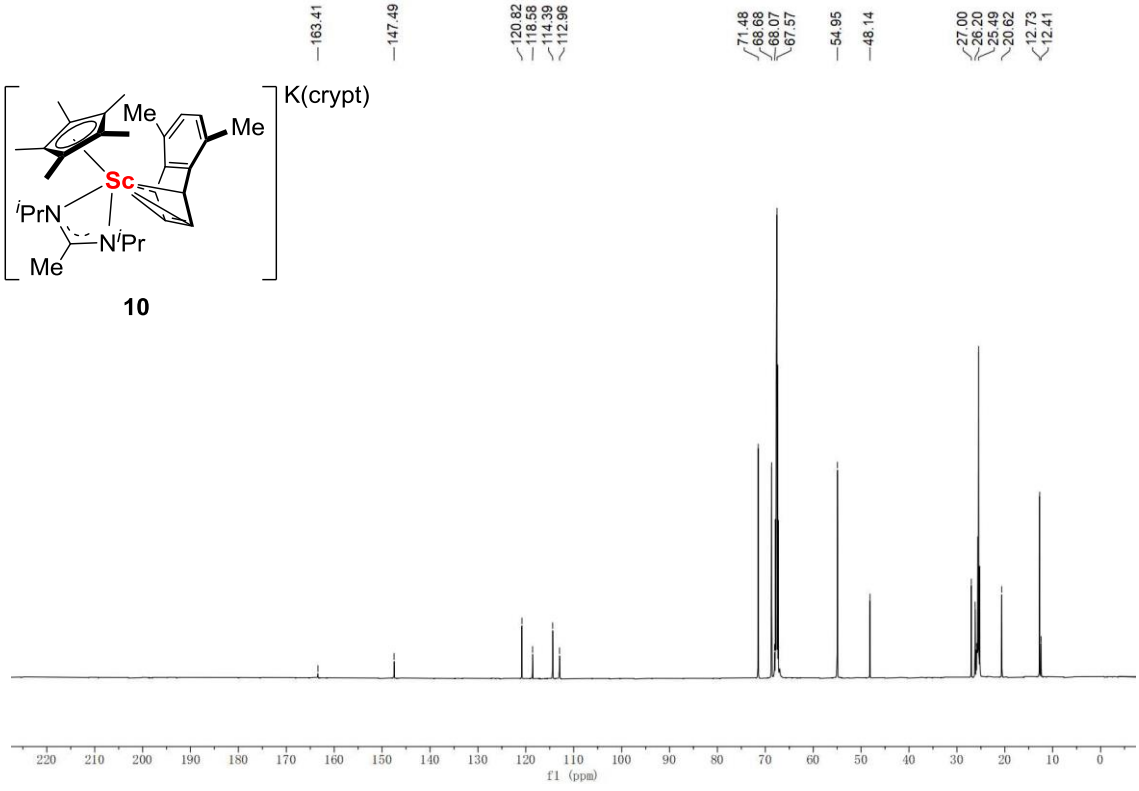


Figure S12. ^{13}C NMR spectrum of **10** (25 °C, 151 MHz, d^8-THF).

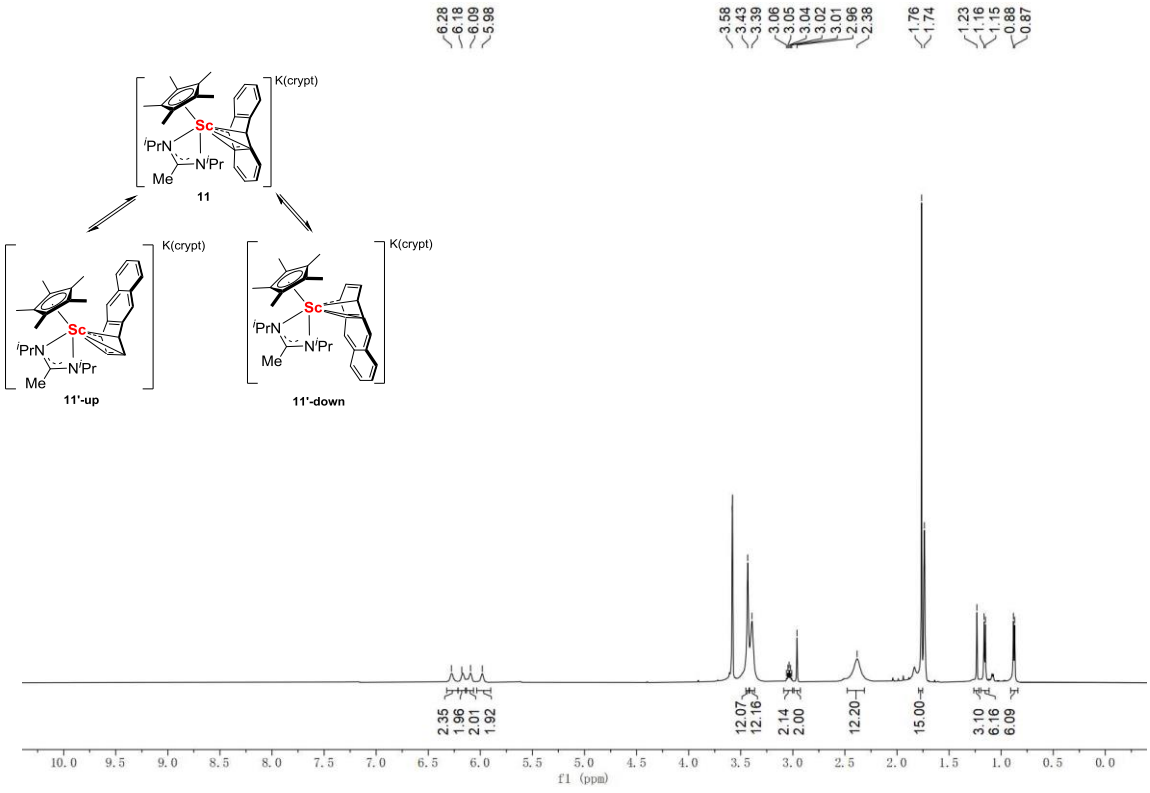


Figure S13. ^{1}H NMR spectrum of **11** (-40°C, 500 MHz, d^8-THF).

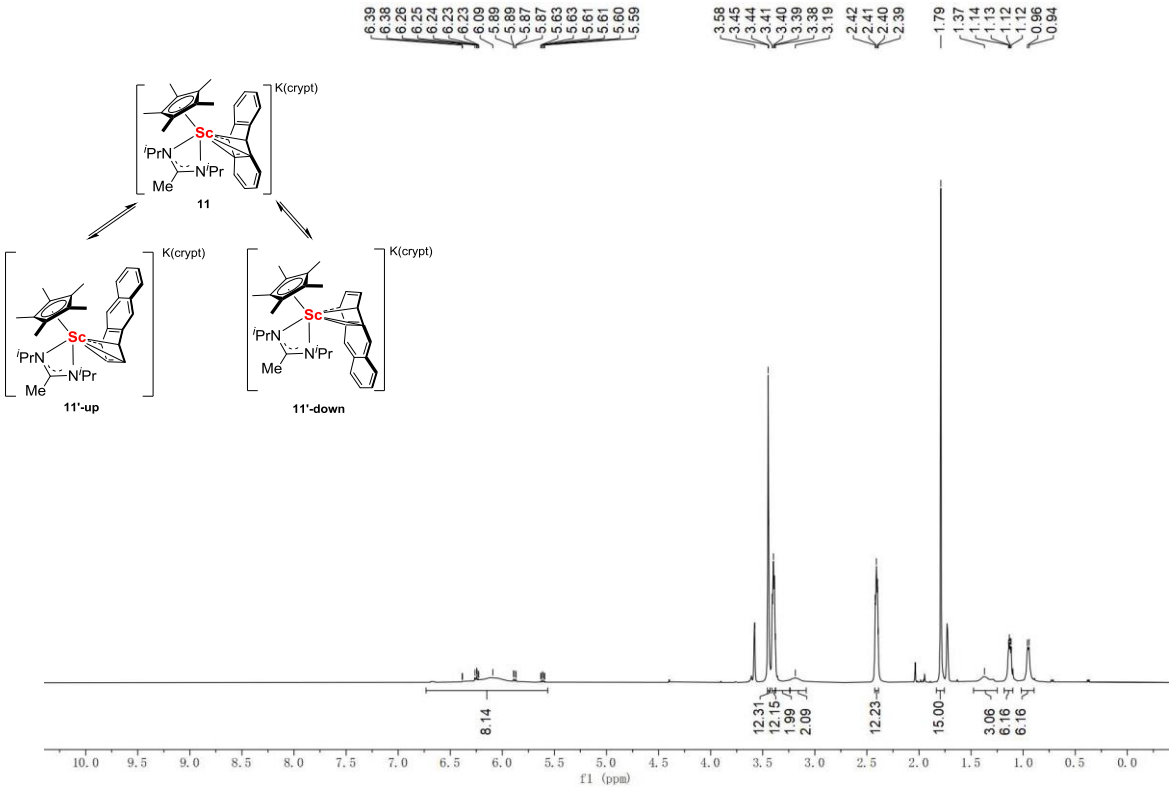


Figure S14. ^{1}H NMR spectrum of **11** (25 °C, 400 MHz, d^{8}-THF).

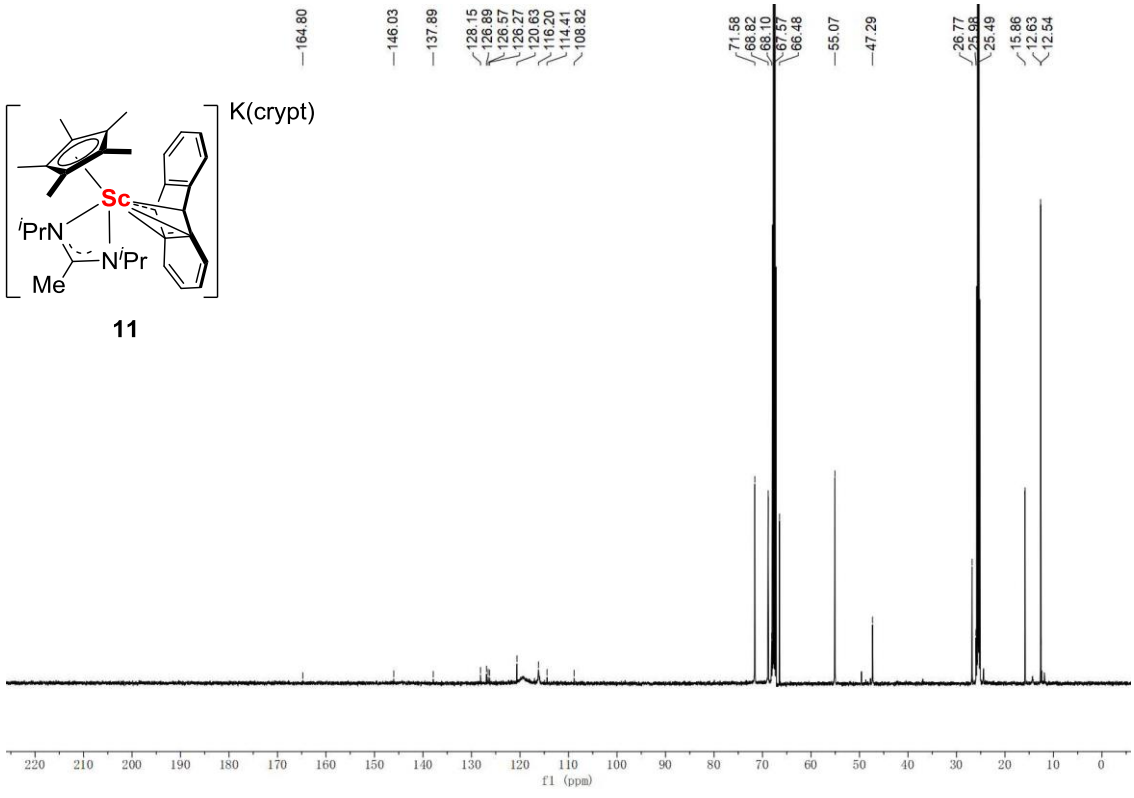


Figure S15. ^{13}C NMR spectrum of **11** (25 °C, 126 MHz, d^{8}-THF).

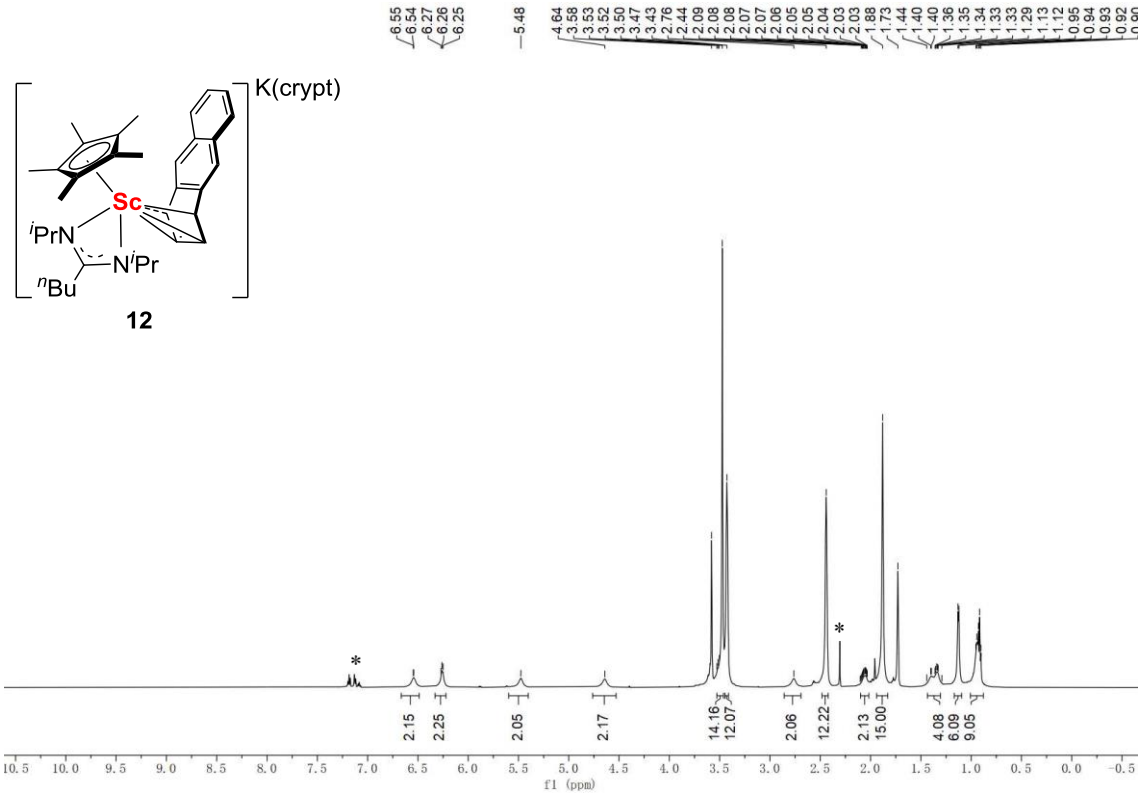


Figure S16. ^{1}H NMR spectrum of **12** (25 °C, 600 MHz, d^{8}-THF, "*" represents the residual toluene).

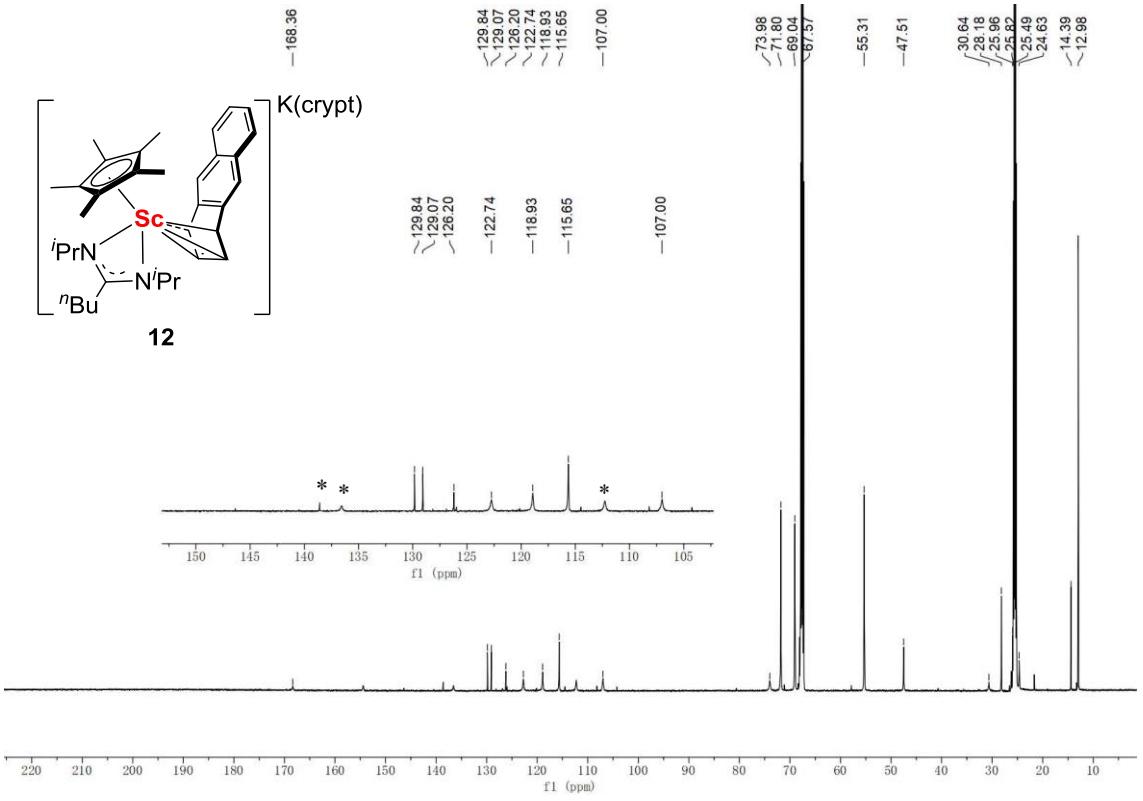


Figure S17. ^{13}C NMR spectrum of **12** (25 °C, 151 MHz, d^{8}-THF, "*" represents the isomers of **12**).

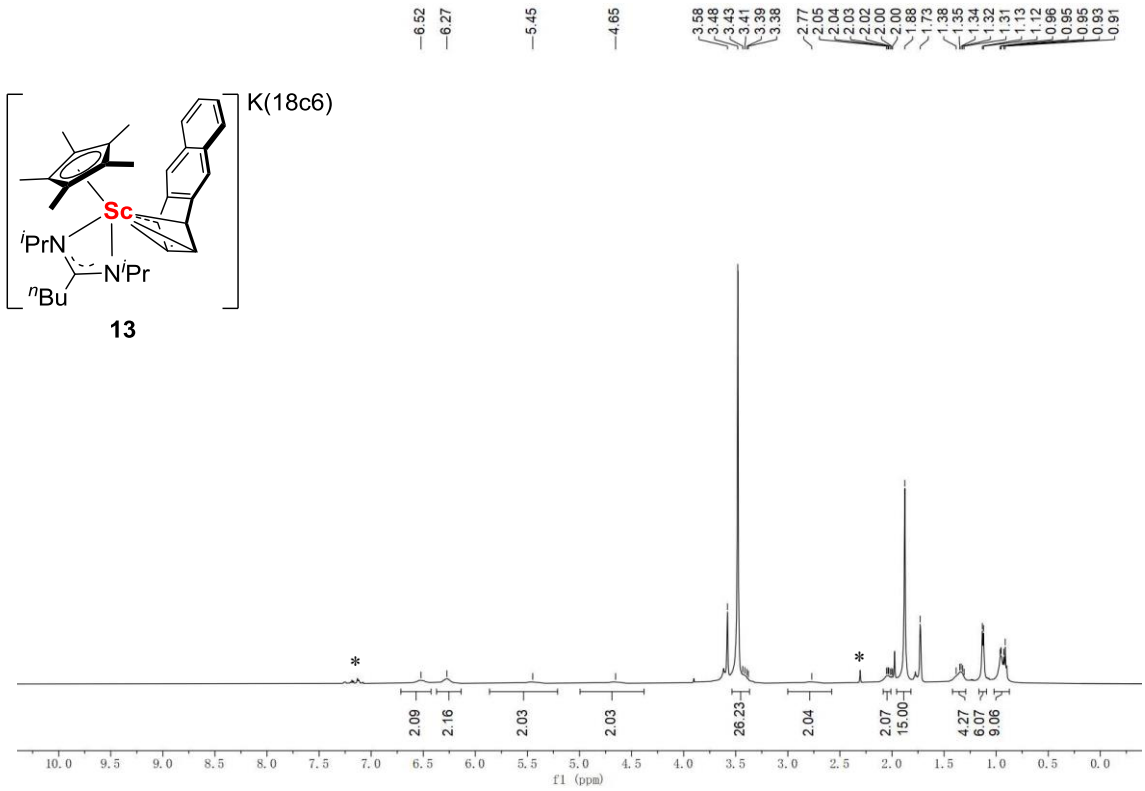


Figure S18. ^{1}H NMR spectrum of **13** (25 °C, 500 MHz, d^{8}-THF, "*" represents the residual toluene).

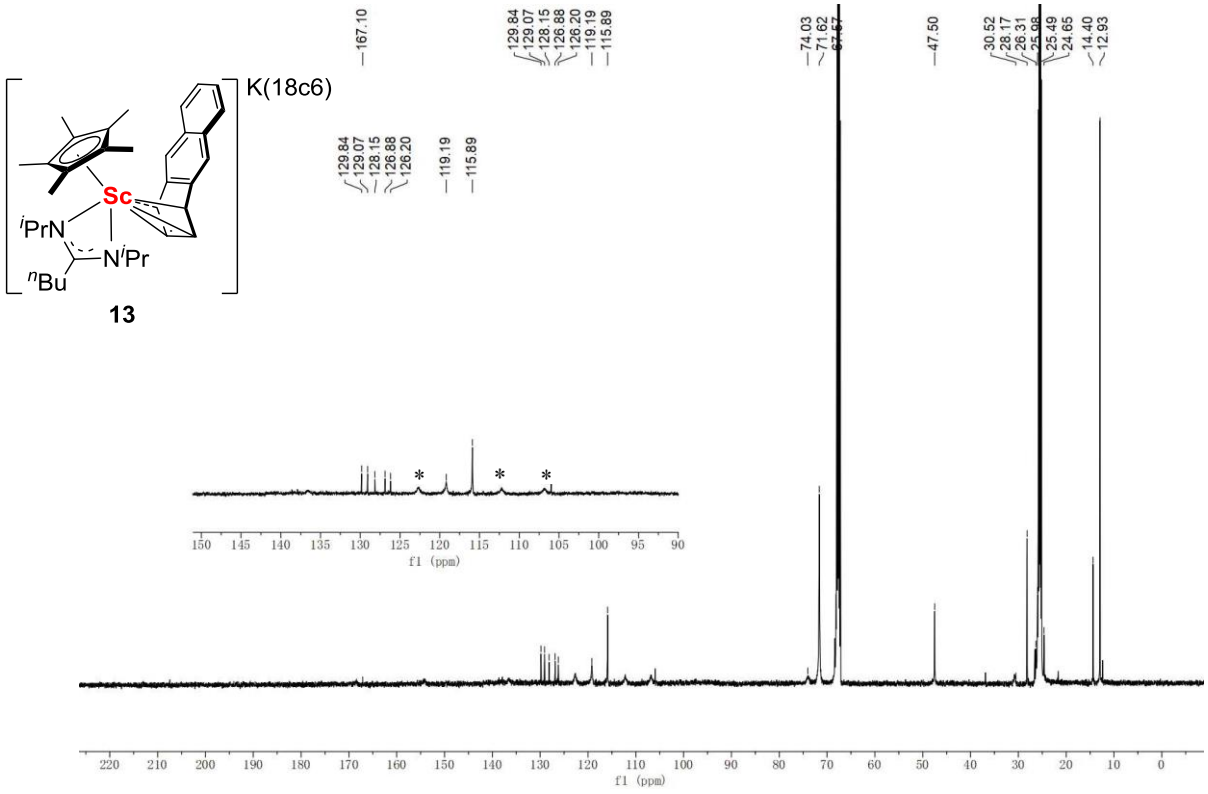


Figure S19. ^{13}C NMR spectrum of **13** (25 °C, 126 MHz, d^{8}-THF, "*" represents the isomers

of **13**).

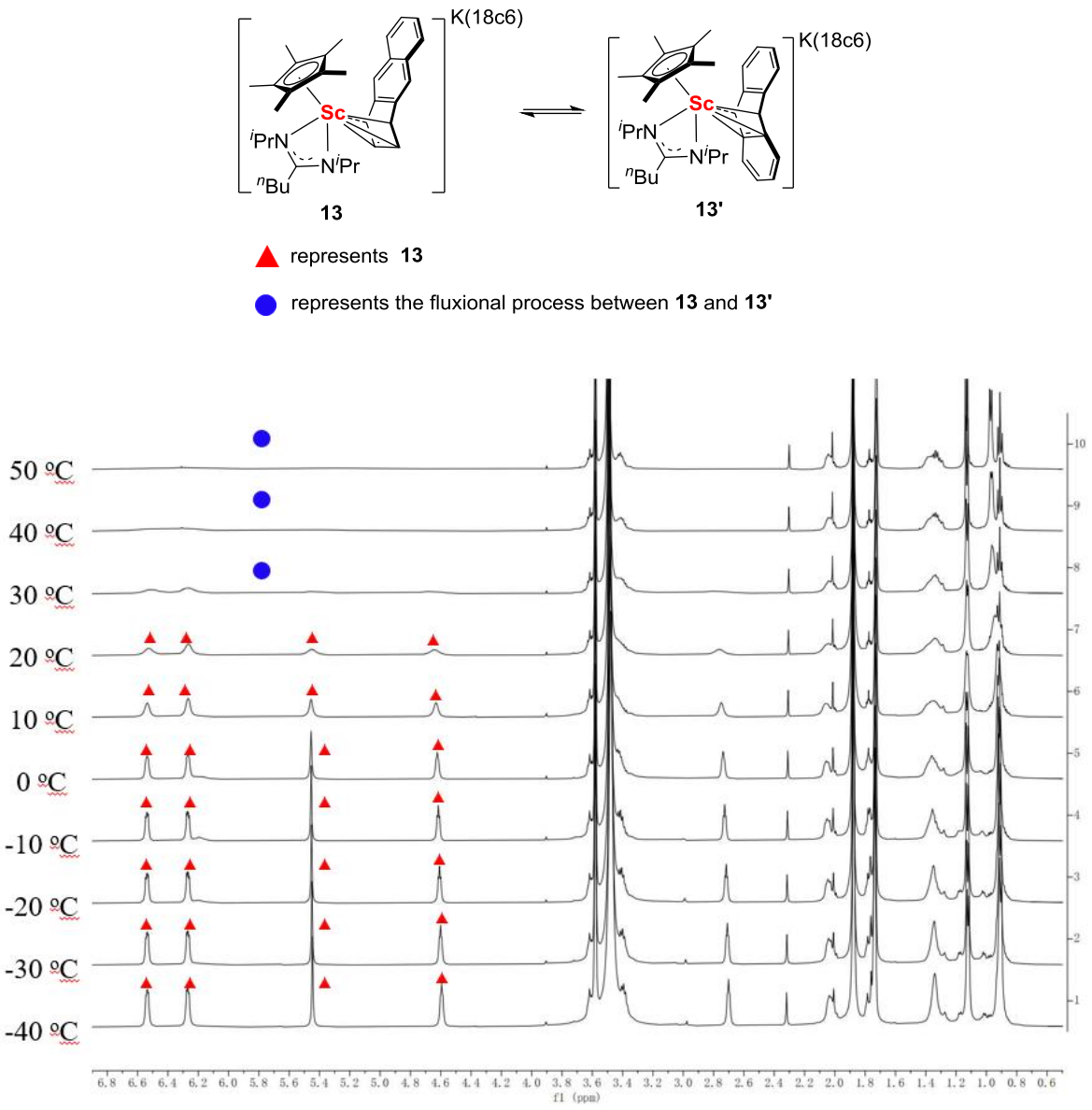


Figure S20. Variable temperature ^{1}H NMR spectrum of **13** (500 MHz, d^{8}-THF).

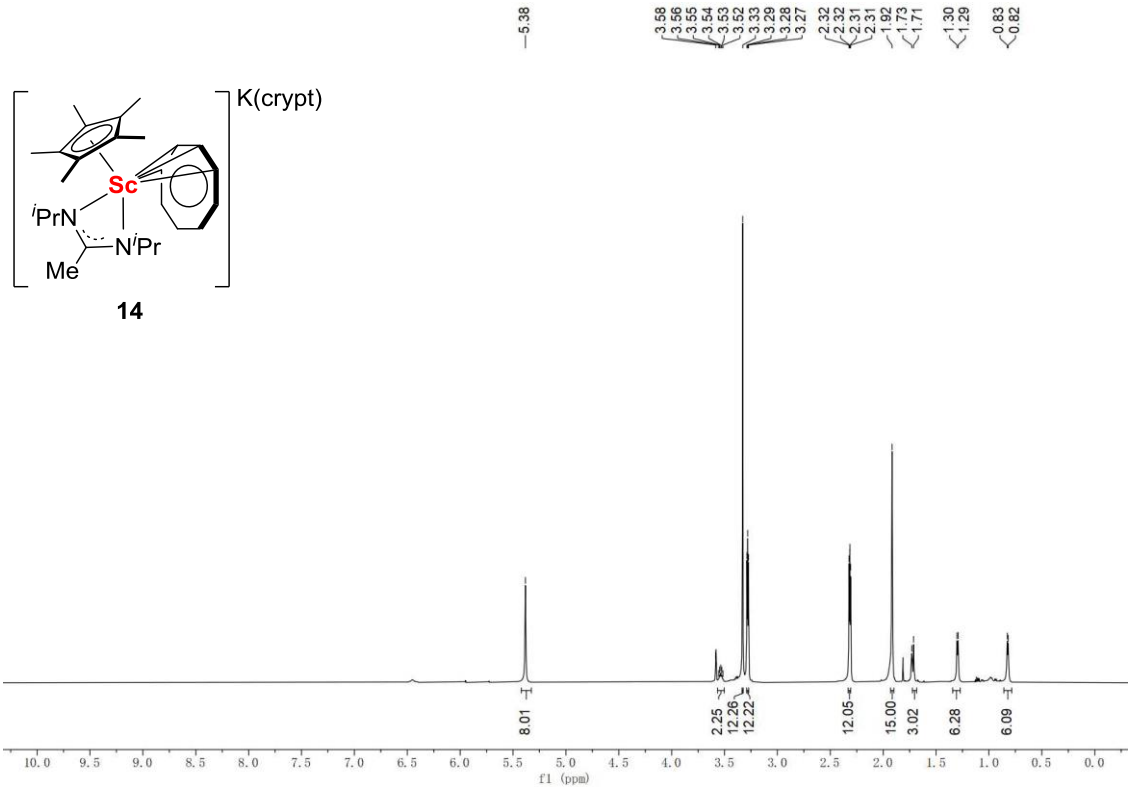


Figure S21. ^{1}H NMR spectrum of **14** (25 °C, 600 MHz, d^{8}-THF).

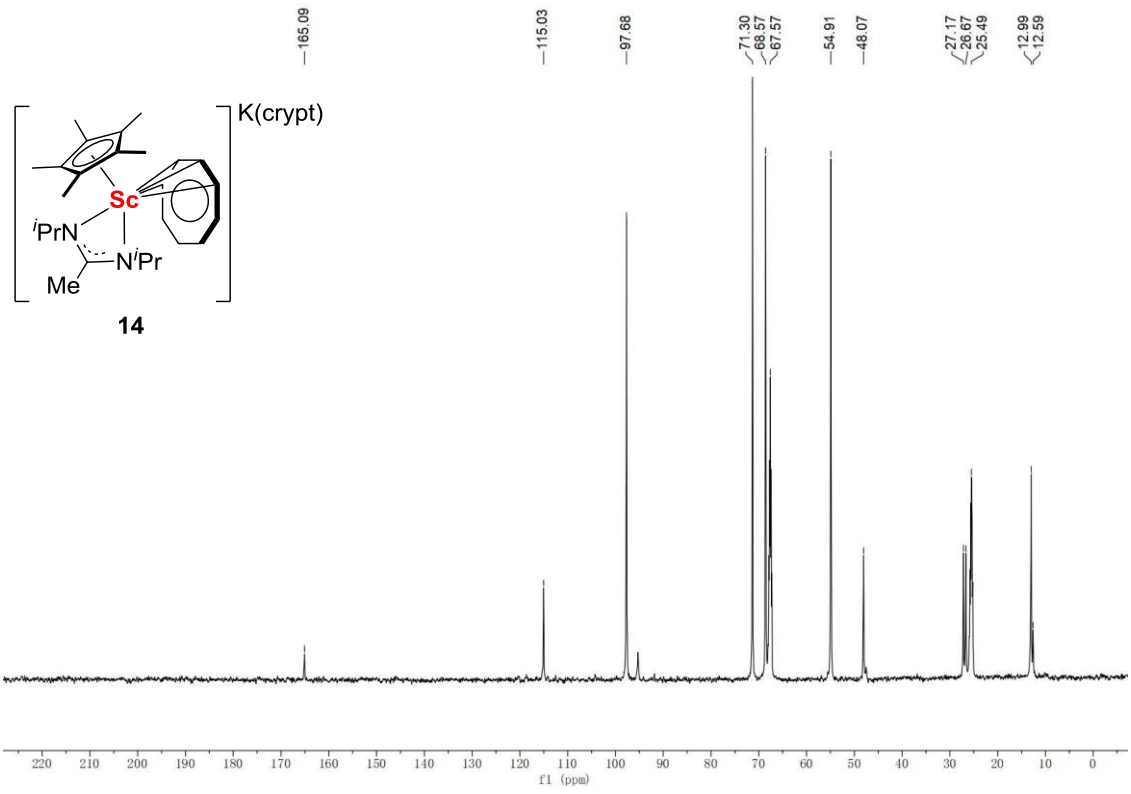


Figure S22. ^{13}C NMR spectrum of **14** (25 °C, 151 MHz, d^{8}-THF).

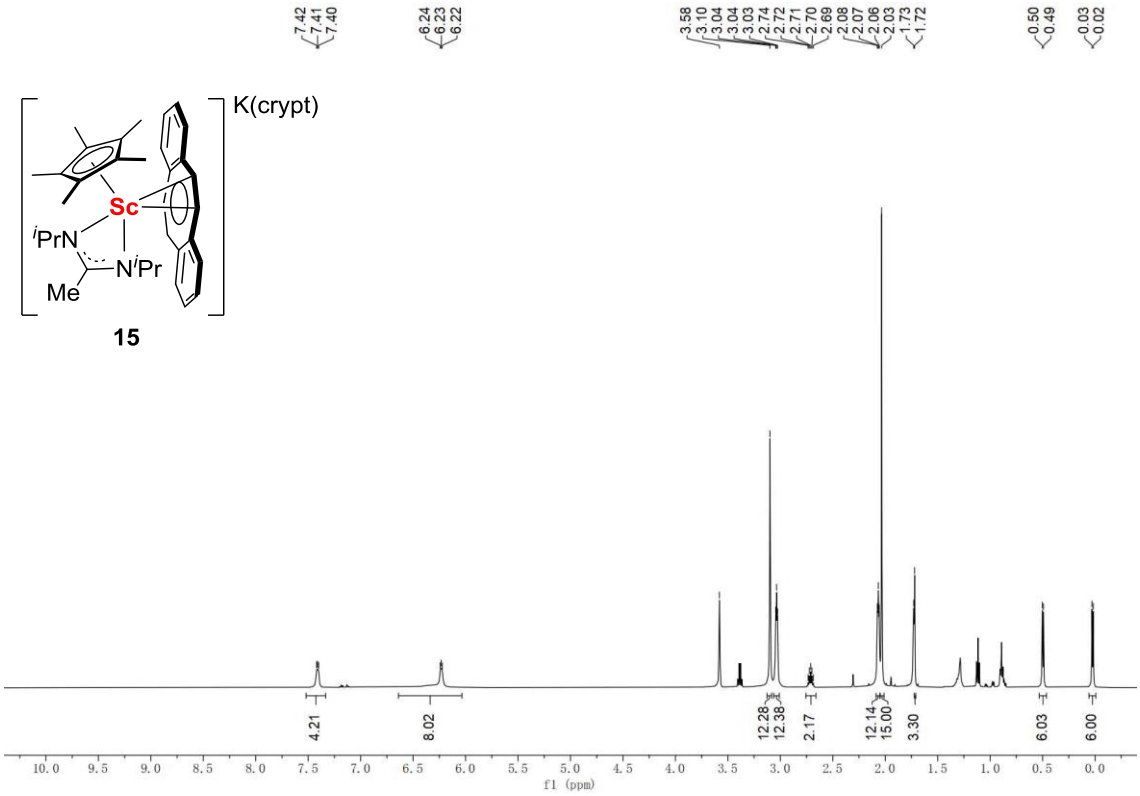


Figure S23. ^{1}H NMR spectrum of **15** (25 °C, 500 MHz, d^{8}-THF).

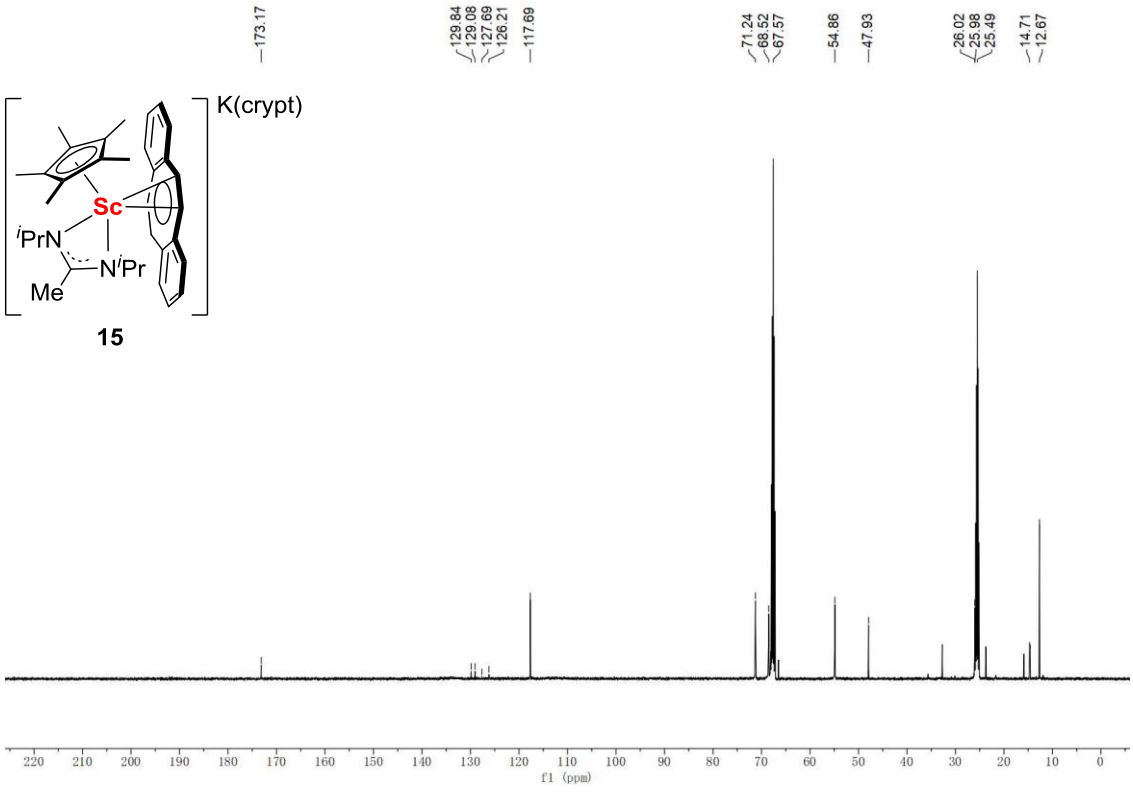


Figure S24. ^{13}C NMR spectrum of **15** (25 °C, 126 MHz, d^{8}-THF).

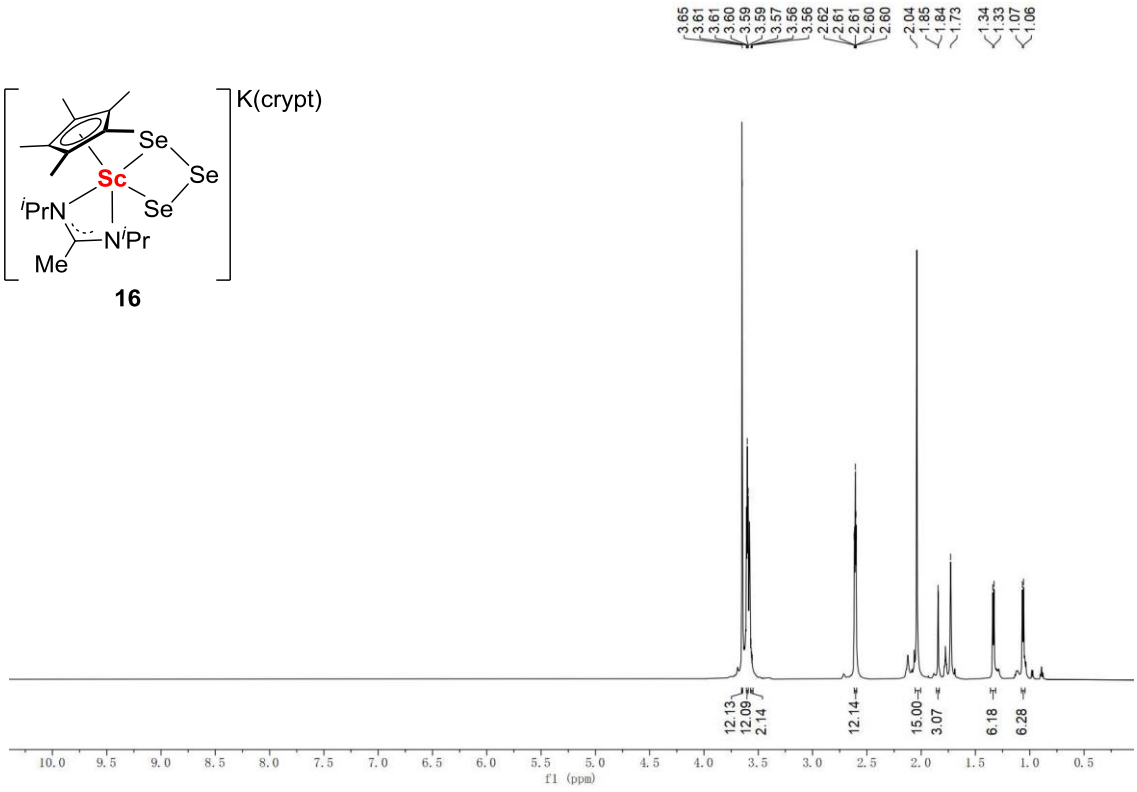


Figure S25. ^{1}H NMR spectrum of **16** (25 °C, 600 MHz, d^{8}-THF).

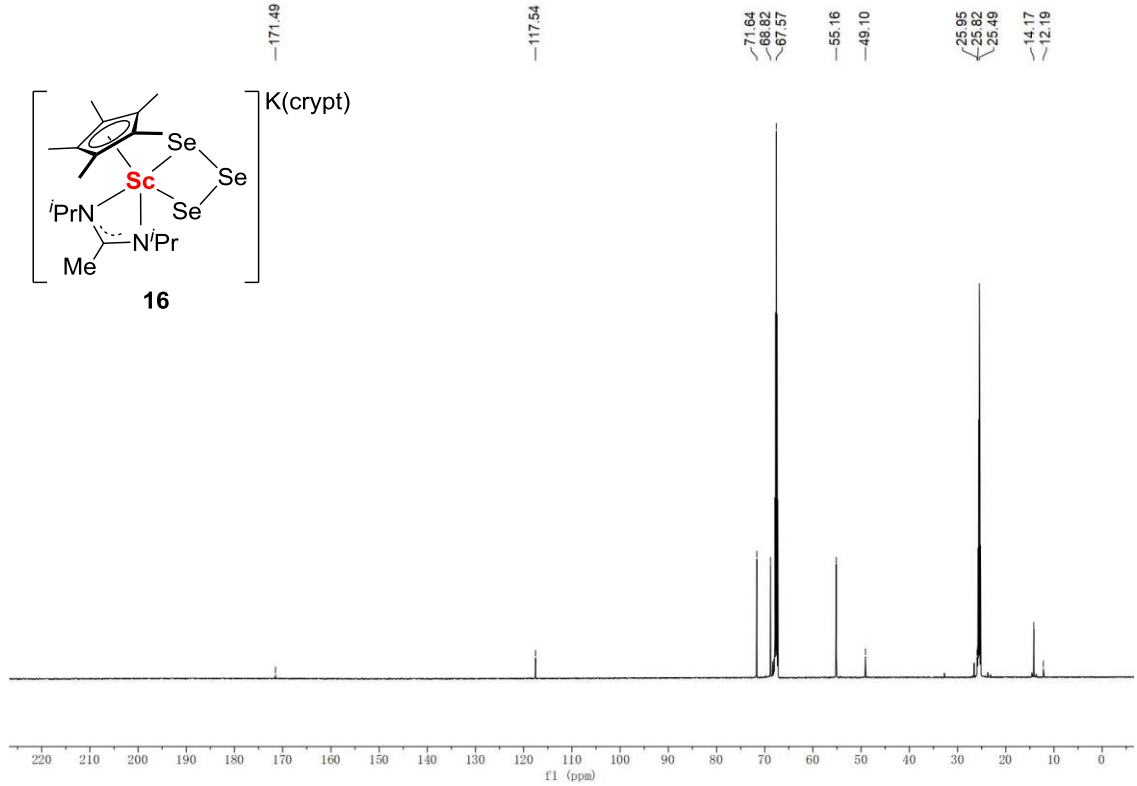


Figure S26. ^{13}C NMR spectrum of **16** (25 °C, 151 MHz, d^{8}-THF).

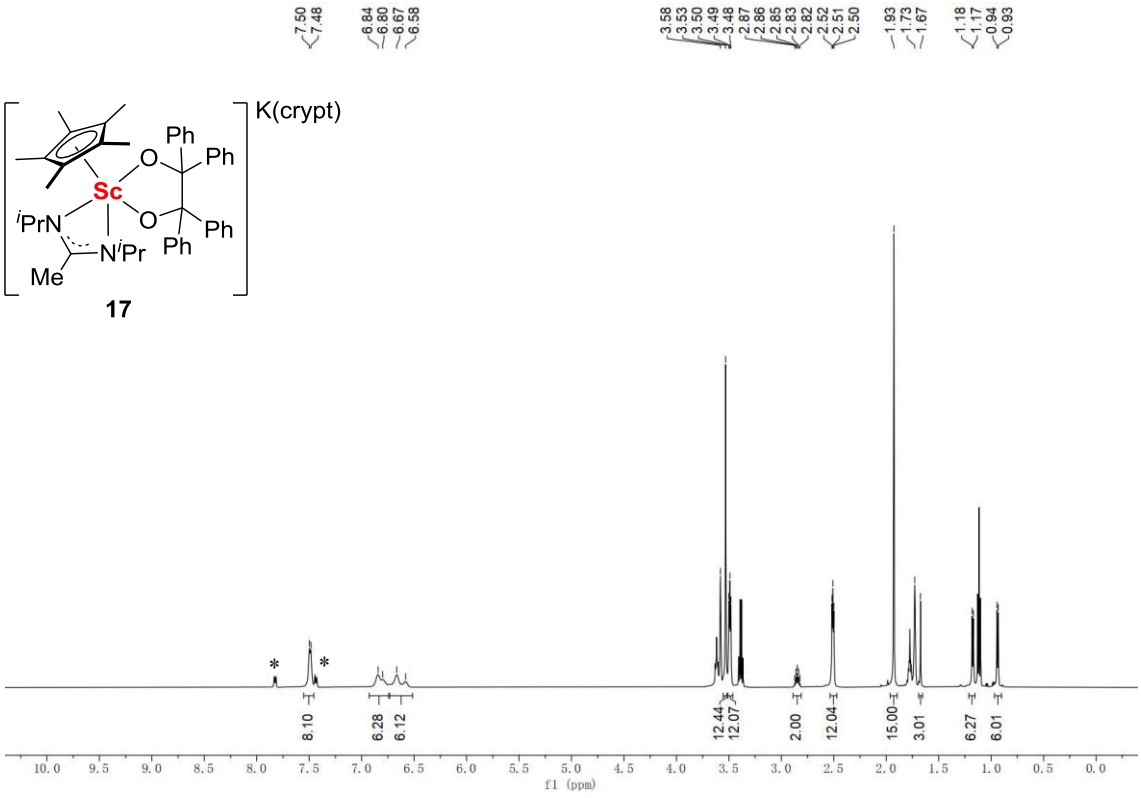


Figure S27. ^{1}H NMR spectrum of **17** (25 °C, 500 MHz, d^{8}-THF, "*" represents the residual naphthalene).

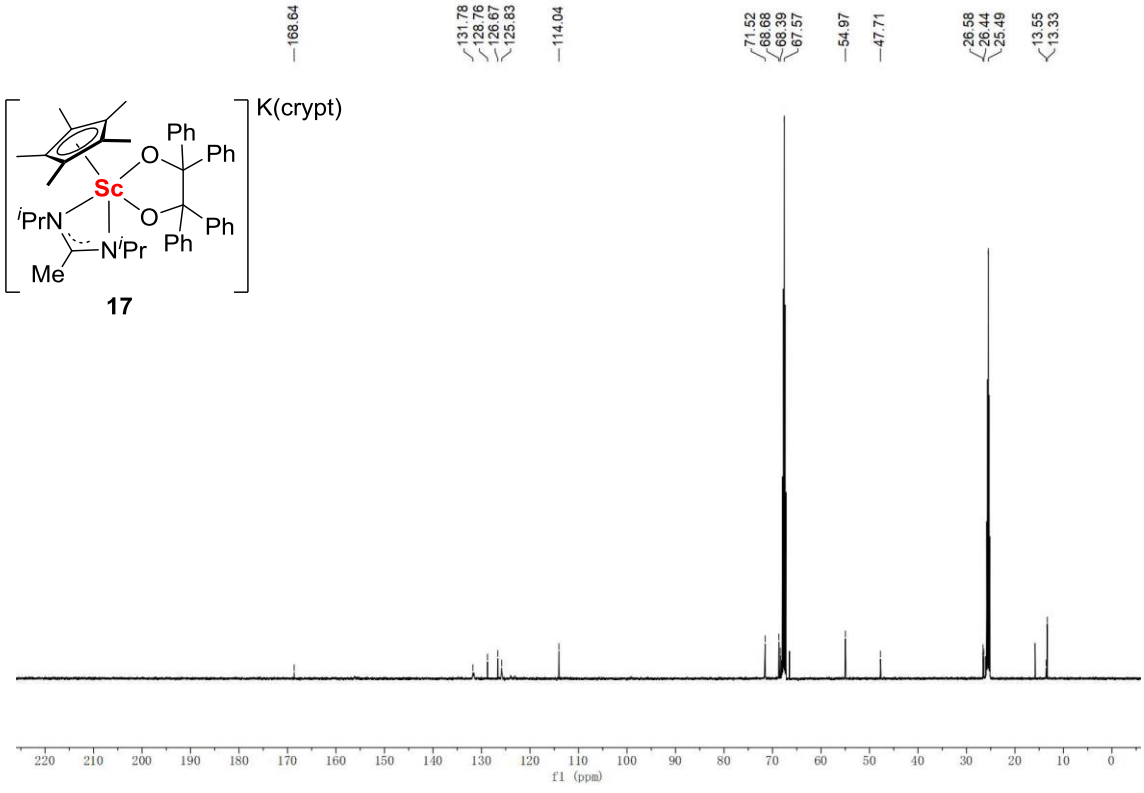


Figure S28. ^{13}C NMR spectrum of **17** (25 °C, 126 MHz, d^{8}-THF).

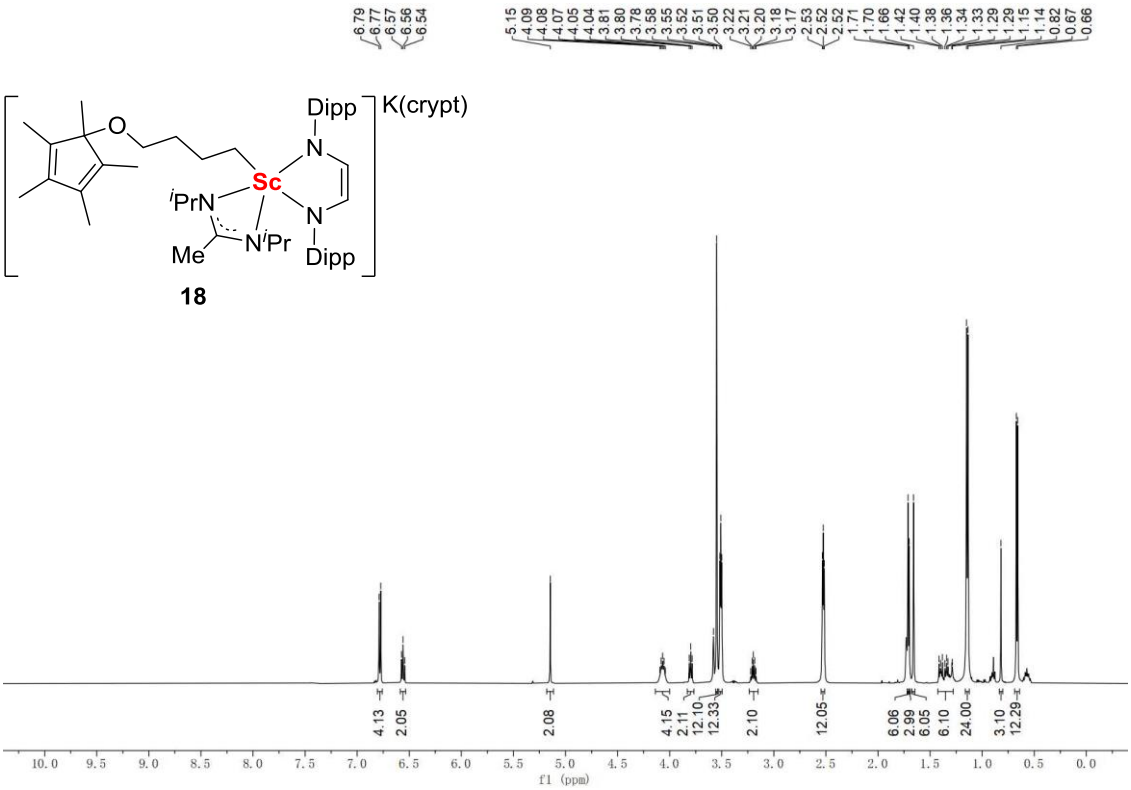


Figure S29. ^{1}H NMR spectrum of **18** (25 °C, 500 MHz, d^{8}-THF).

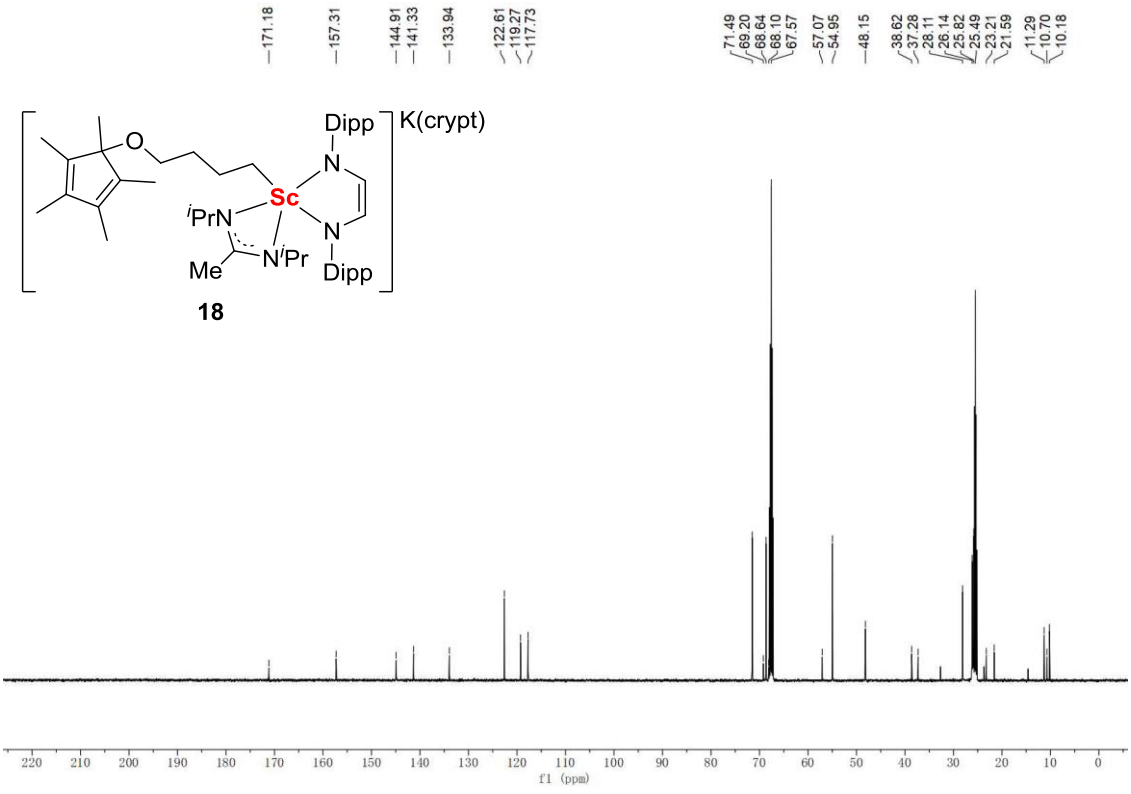


Figure S30. ^{13}C NMR spectrum of **18** (25 °C, 126 MHz, d^{8}-THF).

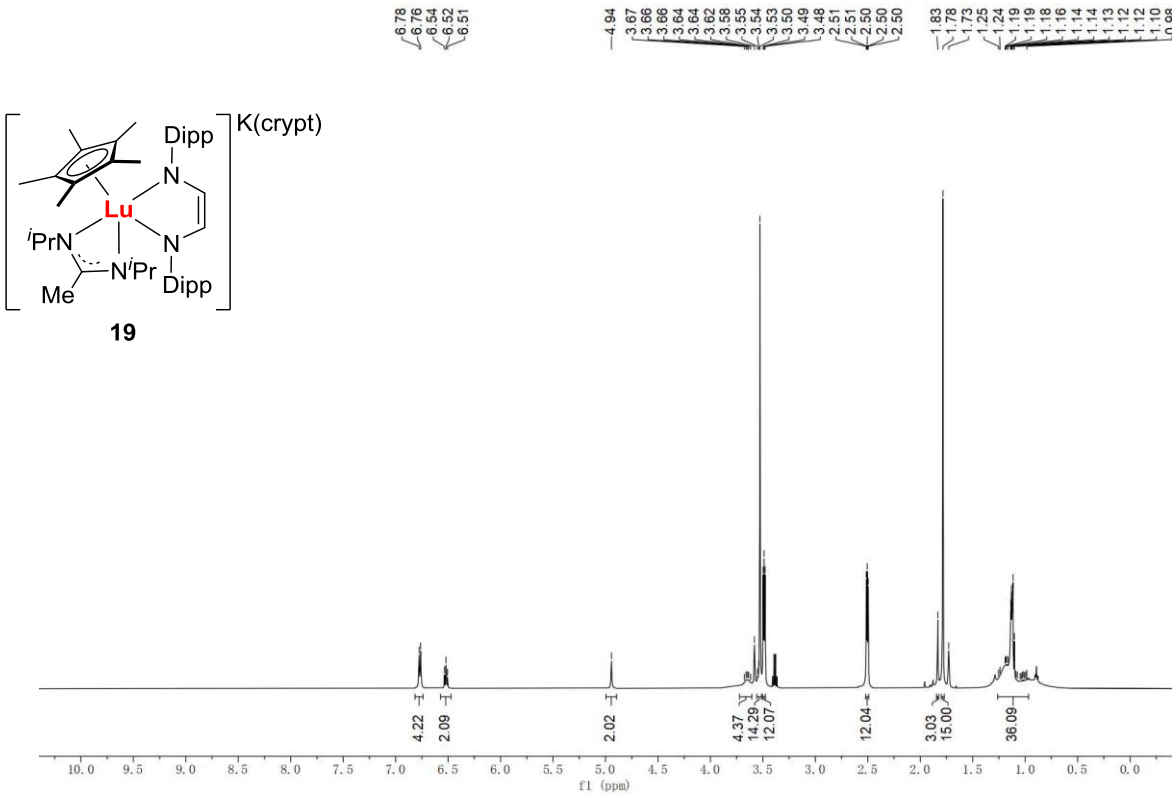


Figure S31. ^{1}H NMR spectrum of **19** (25 °C, 500 MHz, d^{8}-THF).

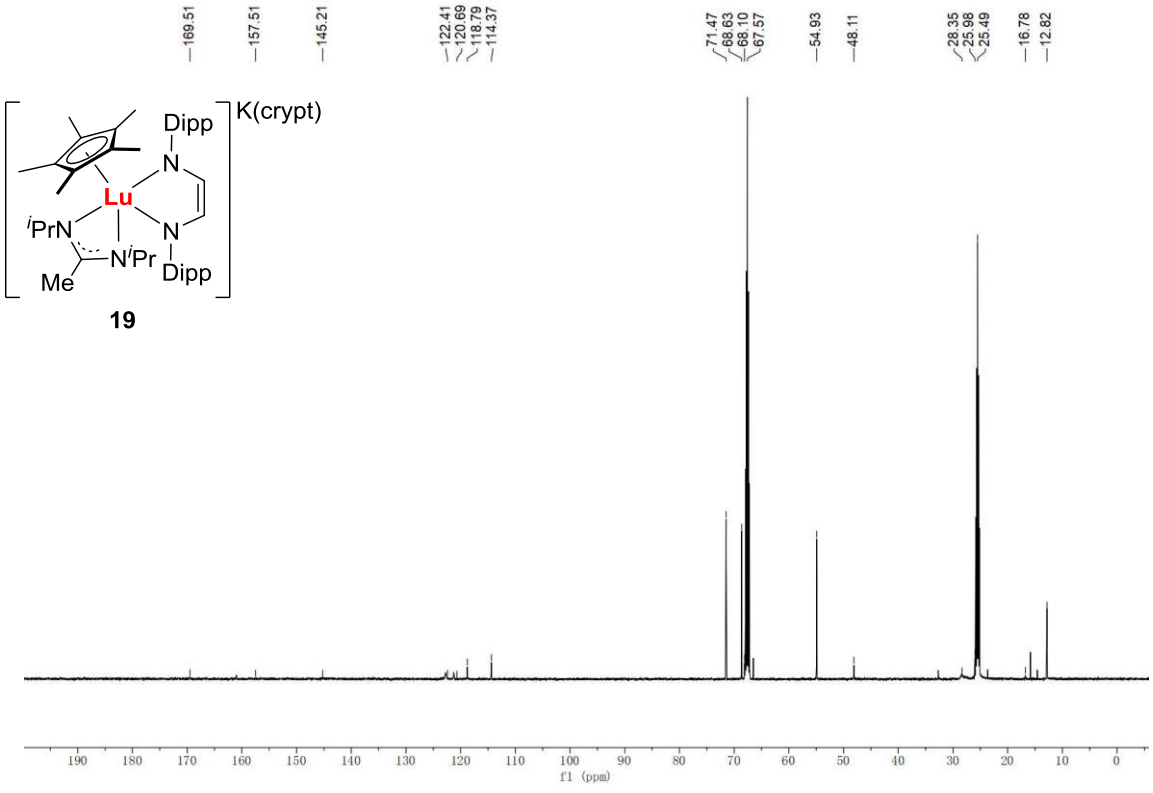


Figure S32. ^{13}C NMR spectrum of **19** (25 °C, 126 MHz, d^{8}-THF).

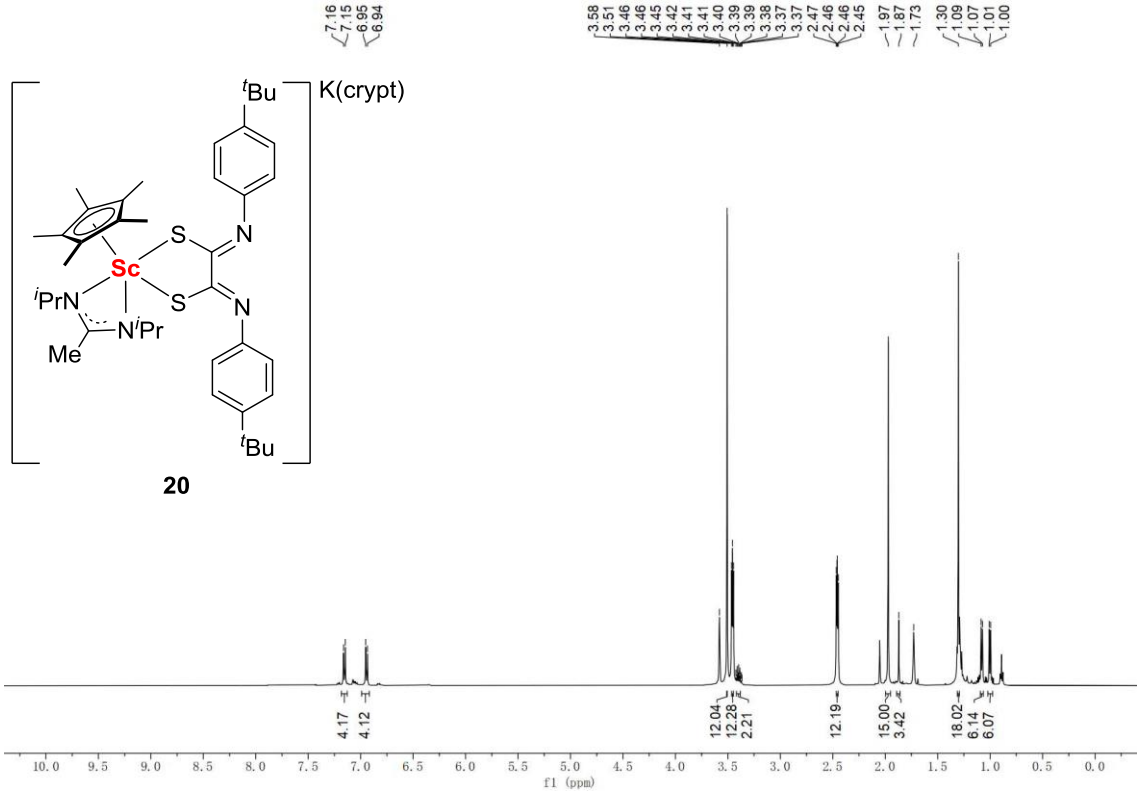


Figure S33. ^{1}H NMR spectrum of **20** (25 °C, 500 MHz, d^{8}-THF).

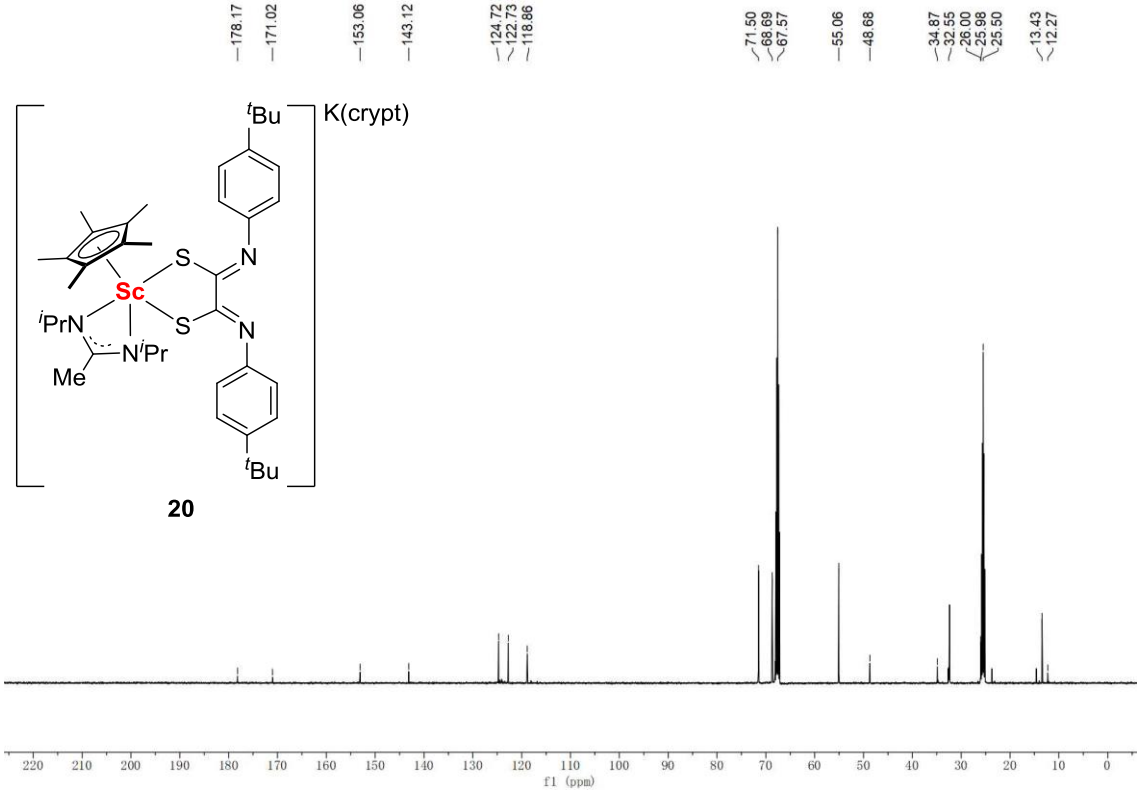


Figure S34. ^{13}C NMR spectrum of **20** (25 °C, 126 MHz, d^{8}-THF).

3) X-ray Crystallographic Studies

The single crystals of **5·0.5Et$_2$O**, **7**, **8·0.5THF**, **9·1.5THF**, **10·0.5THF**, **11**, **13·THF**, **14**, **15·Et$_2$O**, **16**, **17·2THF**, **18** and **19** suitable for X-ray analysis were obtained as described in the experimental details. In addition, even though the quality of the crystals of compound **20** was not satisfactory for determining the precise bond parameters, its data was also included here. Data collections were performed on a XtaLAB PRO 007HF(Mo): Kappa single diffractometer at 180 or 120 K. Using Olex2,[3] the structures were solved with Superflip[4] structure solution program using Charge Flipping or ShelXS-97[5] structure solution program using Direct Methods and refined with the ShelXL[6] refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication numbers: CCDC 2156576 (**5·0.5Et$_2$O**), CCDC 2155848 (**7**), CCDC 2210604 (**8·0.5THF**), CCDC 2210605 (**9·1.5THF**), CCDC 2210606 (**10·0.5THF**), CCDC 2210607 (**11**), CCDC 2210609 (**13·THF**), CCDC 2210610 (**14**), CCDC 2210611 (**15·Et$_2$O**), CCDC 2210617 (**16**), CCDC 2210618 (**17·2THF**), CCDC 2210619 (**18**), CCDC 2210620 (**19**), CCDC 2219302 (**20**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

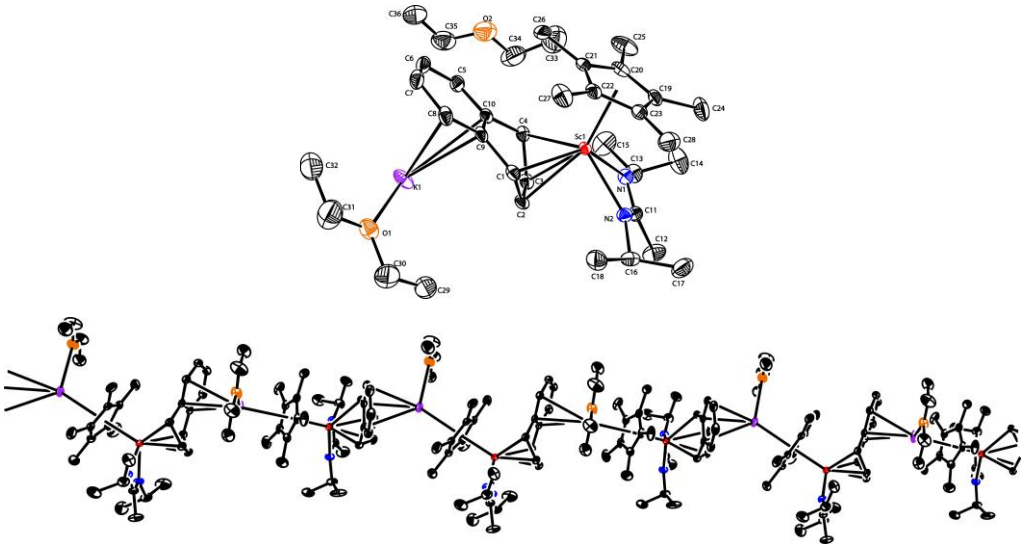
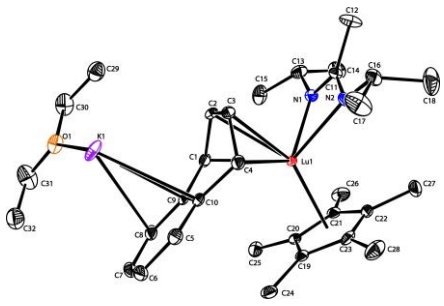


Figure S35. ORTEP drawing of repeating unit (top) and one dimensional molecular structure (bottom) of **5·0.5Et$_2$O** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S1 Crystal data and structure refinement for 5·0.5Et$_2$O.

Identification code	**5·0.5Et$_2$O**
Empirical formula	$C_{68}H_{110}K_2N_4O_3Sc_2$
Formula weight	1199.71
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6050(5)
b/Å	17.5505(7)
c/Å	15.2757(5)
α/°	90
β/°	100.663(4)
γ/°	90
Volume/Å^3	3584.5(2)
Z	2
ρ_{calc}g/cm^3	1.112
μ/mm^{-1}	0.349
F(000)	1300.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.01 to 54.968
Index ranges	-17 ≤ h ≤ 17, -22 ≤ k ≤ 22, -19 ≤ l ≤ 19
Reflections collected	38035
Independent reflections	8155 [R_{int} = 0.0293, R_{sigma} = 0.0258]
Data/restraints/parameters	8155/49/393
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.1016
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1065
Largest diff. peak/hole / e Å^{-3}	0.47/-0.29



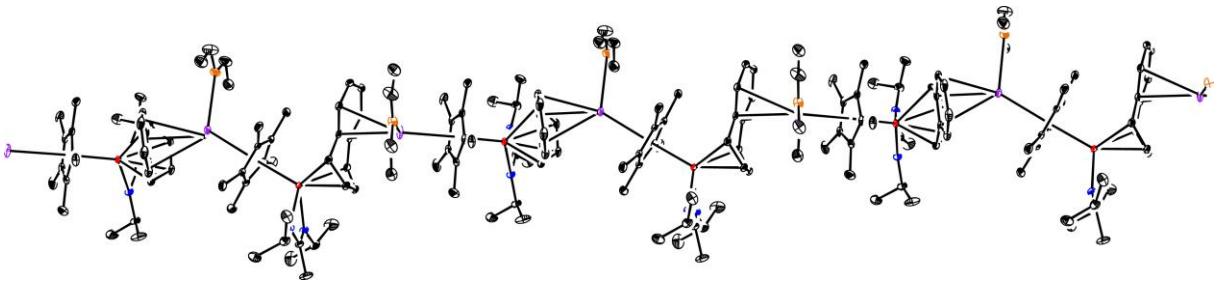


Figure S36. ORTEP drawing of repeating unit (top) and one dimensional molecular structure (bottom) of **7** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S2 Crystal data and structure refinement for 7.

Identification code	**7**
Empirical formula	$C_{32}H_{50}KLuN_2O$
Formula weight	692.81
Temperature/K	120.00(11)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6874(2)
b/Å	17.4996(3)
c/Å	15.2388(3)
α/°	90
β/°	100.245(2)
γ/°	90
Volume/Å^3	3591.86(11)
Z	4
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	2.887
F(000)	1416.0
Crystal size/mm^3	0.1 × 0.1 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.39 to 54.966
Index ranges	$-17 \le h \le 17$, $-22 \le k \le 22$, $-19 \le l \le 19$
Reflections collected	84148
Independent reflections	8221 [R_{int} = 0.0433, R_{sigma} = 0.0208]
Data/restraints/parameters	8221/0/361
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0209, wR_2 = 0.0501
Final R indexes [all data]	R_1 = 0.0250, wR_2 = 0.0513
Largest diff. peak/hole / e Å^{-3}	0.76/-0.39

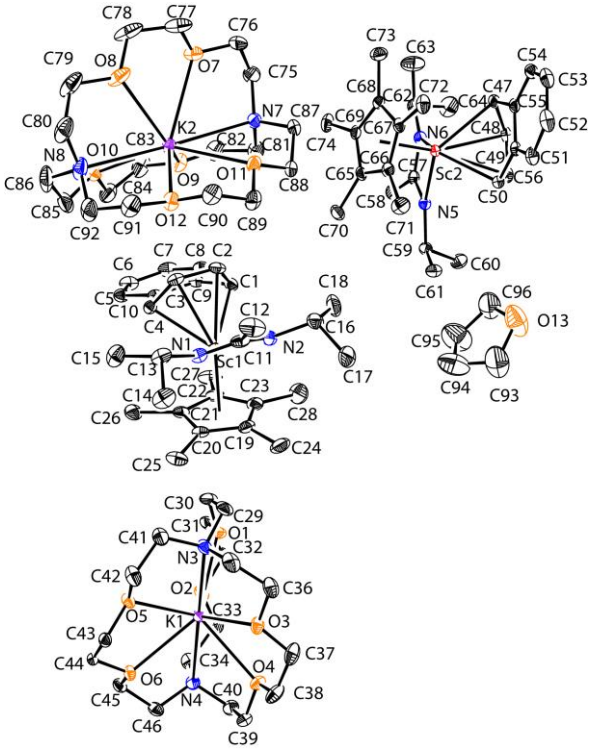


Figure S37. ORTEP drawing of **8·0.5THF** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for 8·0.5THF.

Identification code	**8·0.5THF**
Empirical formula	$C_{96}H_{160}K_2N_8O_{13}Sc_2$
Formula weight	1802.43
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.7946(3)
b/Å	18.3153(4)
c/Å	20.4944(4)
α/°	85.122(2)
β/°	85.020(2)
γ/°	88.474(2)
Volume/Å^3	5138.76(19)
Z	2
ρ_{calc}g/cm^3	1.165
μ/mm^{-1}	0.273
F(000)	1952.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.216 to 50.052
Index ranges	$-11 \le h \le 16$, $-21 \le k \le 21$, $-24 \le l \le 24$

Reflections collected	61520
Independent reflections	18137 [R_{int} = 0.0262, R_{sigma} = 0.0300]
Data/restraints/parameters	18137/0/1118
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.1000
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1048
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.39

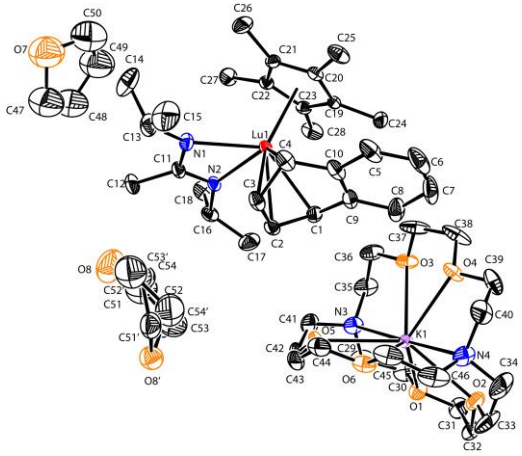


Figure S38. ORTEP drawing of **9·1.5THF,** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 4 Crystal data and structure refinement for 9·1.5THF.

Identification code	**9·1.5THF**
Empirical formula	$C_{104}H_{176}K_2Lu_2N_8O_{15}$
Formula weight	2206.66
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	30.2986(6)
b/Å	10.8607(2)
c/Å	33.5531(6)
α/°	90
β/°	96.797(2)
γ/°	90
Volume/$Å^3$	10963.5(4)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	1.928
F(000)	4624.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.124 to 54.97

Index ranges	-39 ≤ h ≤ 39, -14 ≤ k ≤ 13, -43 ≤ l ≤ 43
Reflections collected	41569
Independent reflections	12528 [R_{int} = 0.0238, R_{sigma} = 0.0257]
Data/restraints/parameters	12528/240/669
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0267, wR_2 = 0.0644
Final R indexes [all data]	R_1 = 0.0329, wR_2 = 0.0666
Largest diff. peak/hole / e $Å^{-3}$	0.73/-0.52

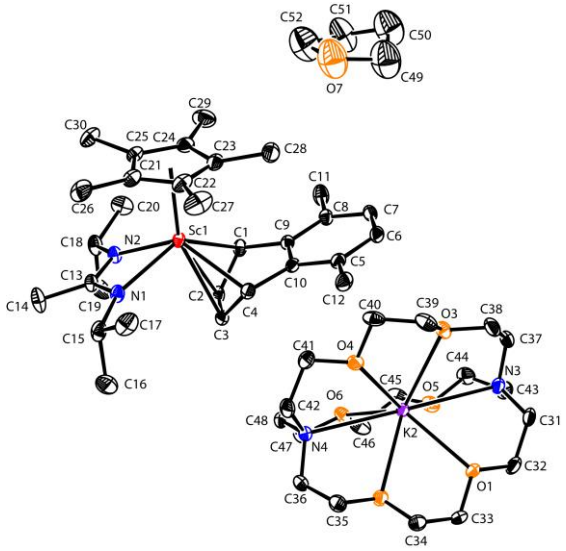


Figure S39. ORTEP drawing of **10·0.5THF,** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 5 Crystal data and structure refinement for 10·0.5THF.

Identification code	**10·0.5THF**
Empirical formula	$C_{100}H_{168}K_2N_8O_{13}Sc_2$
Formula weight	1858.53
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	P2/c
a/Å	13.6453(5)
b/Å	9.4122(3)
c/Å	40.3625(9)
α/°	90
β/°	93.140(3)
γ/°	90
Volume/$Å^3$	5176.1(3)

Z	2
ρ_{calc}g/cm^3	1.192
μ/mm^{-1}	0.273
F(000)	2016.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.042 to 54.97
Index ranges	-17 ≤ h ≤ 16, -12 ≤ k ≤ 9, -52 ≤ l ≤ 52
Reflections collected	31684
Independent reflections	11518 [R_{int} = 0.0337, R_{sigma} = 0.0379]
Data/restraints/parameters	11518/99/598
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.1190
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.64/-0.37

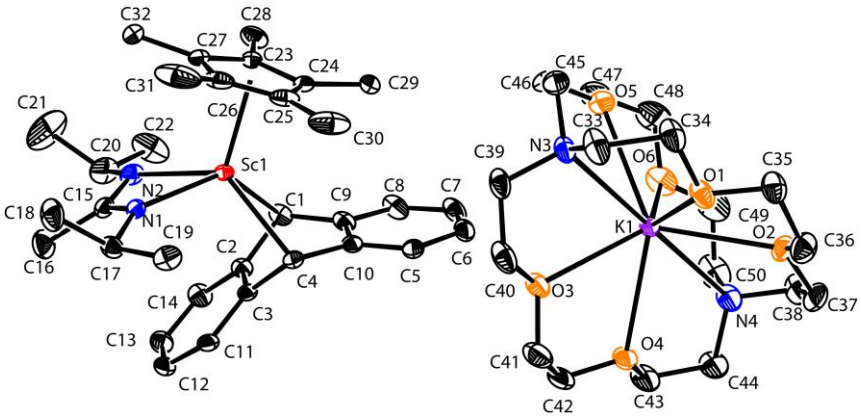


Figure S40. ORTEP drawing of **11** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 6 Crystal data and structure refinement for 11.

Identification code	**11**
Empirical formula	$C_{50}H_{78}KN_4O_6Sc$
Formula weight	915.22
Temperature/K	180.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.4070(2)
b/Å	15.5999(3)
c/Å	17.6211(3)
α/°	91.7330(10)
β/°	95.252(2)
γ/°	94.0910(10)
Volume/Å^3	2566.69(9)
Z	2

ρ_{calc}g/cm^3	1.184
μ/mm^{-1}	0.273
F(000)	988.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.744 to 54.966
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	47258
Independent reflections	11731 [R_{int} = 0.0263, R_{sigma} = 0.0243]
Data/restraints/parameters	11731/1/569
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0392, wR_2 = 0.1038
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.1083
Largest diff. peak/hole / e Å^{-3}	0.38/-0.33

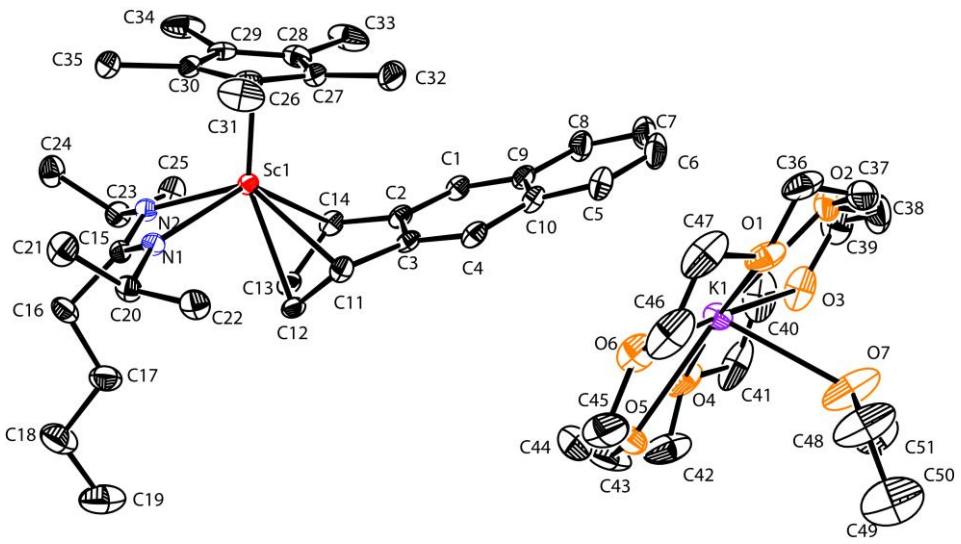


Figure S41. ORTEP drawing of **13·THF** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 7 Crystal data and structure refinement for 13·THF.

Identification code	**13·THF**
Empirical formula	$C_{51}H_{80}KN_2O_7Sc$
Formula weight	917.23
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.7124(5)
b/Å	13.9668(6)

c/Å	18.9725(6)
α/°	85.128(3)
β/°	88.404(4)
γ/°	86.159(4)
Volume/Å^3	2557.95(19)
Z	2
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.275
F(000)	992.0
Crystal size/mm^3	0.13 × 0.09 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.322 to 54.966
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	40027
Independent reflections	11028 [R_{int} = 0.0511, R_{sigma} = 0.0393]
Data/restraints/parameters	11028/23/569
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0820, wR_2 = 0.1894
Final R indexes [all data]	R_1 = 0.1113, wR_2 = 0.2152
Largest diff. peak/hole / e Å^{-3}	0.84/-0.47

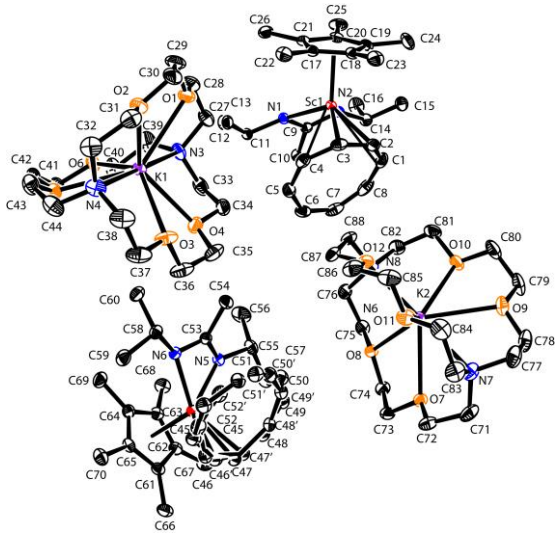


Figure S42. ORTEP drawing of **14** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 8 Crystal data and structure refinement for 14.

Identification code	**14**
Empirical formula	$C_{44}H_{76}KN_4O_6Sc$
Formula weight	841.14
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	16.0903(3)
b/Å	17.1168(4)

c/Å	17.4633(3)
α/°	100.677(2)
β/°	96.7050(10)
γ/°	93.635(2)
Volume/Å^3	4676.20(16)
Z	4
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	0.294
F(000)	1824.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.81 to 50.048
Index ranges	-19 ≤ h ≤ 18, -20 ≤ k ≤ 20, -20 ≤ l ≤ 20
Reflections collected	87215
Independent reflections	16502 [R_{int} = 0.0262, R_{sigma} = 0.0199]
Data/restraints/parameters	16502/246/1102
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0853
Final R indexes [all data]	R_1 = 0.0384, wR_2 = 0.0887
Largest diff. peak/hole / e Å^{-3}	0.48/-0.39

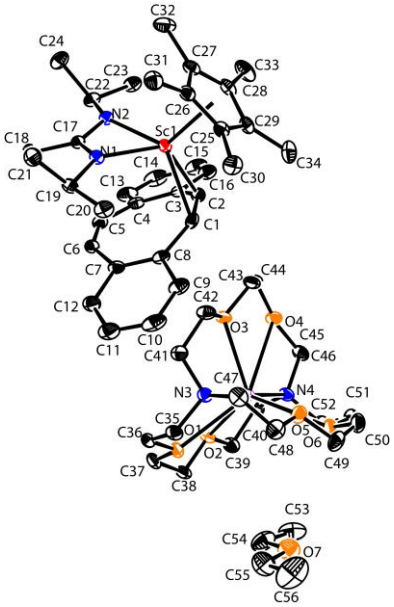


Figure S43. ORTEP drawing of **15·Et$_2$O** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 9 Crystal data and structure refinement for 15·Et$_2$O.

Identification code	**15·Et$_2$O**
Empirical formula	$C_{56}H_{90}KN_4O_7Sc$
Formula weight	1015.37
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.5935(5)
b/Å	14.3739(10)
c/Å	16.6262(10)
α/°	79.018(5)
β/°	75.788(4)
γ/°	85.957(4)
Volume/Å^3	2863.2(3)
Z	2
ρ_{calc}g/cm^3	1.178
μ/mm^{-1}	0.253
F(000)	1100.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.194 to 52.044
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 17, -20 ≤ l ≤ 20
Reflections collected	36620
Independent reflections	11266 [R_{int} = 0.0388, R_{sigma} = 0.0409]
Data/restraints/parameters	11266/0/634
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.1655
Final R indexes [all data]	R_1 = 0.0795, wR_2 = 0.1740
Largest diff. peak/hole / e Å^{-3}	0.94/-0.37

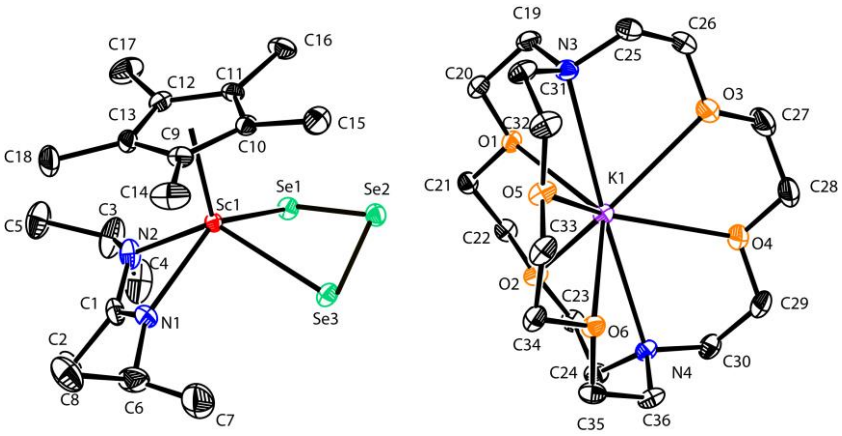


Figure S44. ORTEP drawing of **16** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 10 Crystal data and structure refinement for 16.

Identification code	**16**
Empirical formula	$C_{36}H_{68}KN_4O_6ScSe_3$
Formula weight	973.88
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.2246(3)
b/Å	13.9675(5)
c/Å	18.4487(5)
α/°	68.089(3)
β/°	87.193(3)
γ/°	86.058(3)
Volume/Å^3	2437.82(14)
Z	2
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	2.516
F(000)	1004.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.598 to 54.968
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23
Reflections collected	49833
Independent reflections	11123 [R_{int} = 0.0825, R_{sigma} = 0.0610]
Data/restraints/parameters	11123/0/470
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.1130
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1175
Largest diff. peak/hole / e Å^{-3}	1.24/-0.97

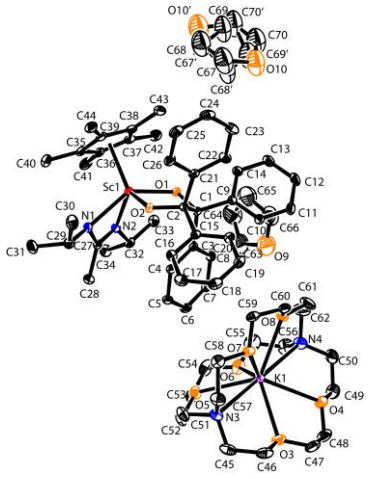


Figure S45. ORTEP drawing of **17·2THF** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 11 Crystal data and structure refinement for 17·2THF.

Identification code	**17·2THF**
Empirical formula	$C_{70}H_{104}KN_4O_{10}Sc$
Formula weight	1245.63
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.6359(4)
b/Å	17.6165(5)
c/Å	33.6917(10)
α/°	90
β/°	91.369(3)
γ/°	90
Volume/Å^3	6904.3(4)
Z	4
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	0.225
F(000)	2688.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.196 to 54.97
Index ranges	-15 ≤ h ≤ 15, -22 ≤ k ≤ 20, -42 ≤ l ≤ 43
Reflections collected	52686
Independent reflections	15630 [R_{int} = 0.0381, R_{sigma} = 0.0458]
Data/restraints/parameters	15630/343/831
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0541, wR_2 = 0.1433
Final R indexes [all data]	R_1 = 0.0750, wR_2 = 0.1549
Largest diff. peak/hole / e Å^{-3}	0.76/-0.52

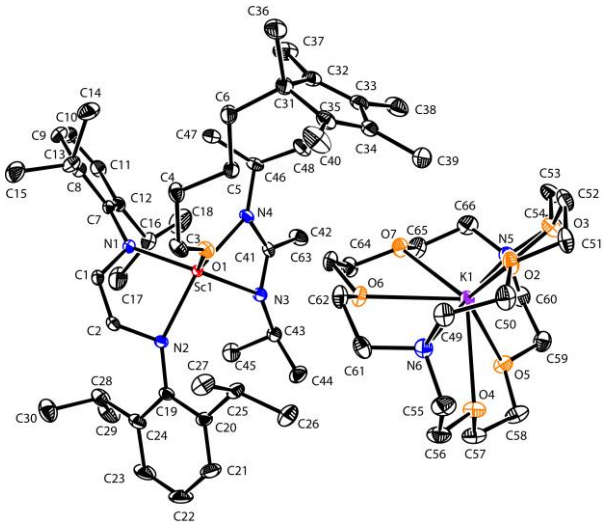


Figure S46. ORTEP drawing of **18** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 12 Crystal data and structure refinement for 18.

Identification code	**18**
Empirical formula	$C_{66}H_{112}KN_6O_7Sc$
Formula weight	1185.67
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.8502(2)
b/Å	15.8688(3)
c/Å	19.0795(3)
α/°	66.0290(17)
β/°	68.9222(16)
γ/°	68.3630(17)
Volume/Å^3	3451.33(12)
Z	2
ρ_{calc}g/cm^3	1.141
μ/mm^{-1}	0.219
F(000)	1292.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.822 to 50.054
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	61151
Independent reflections	12157 [R_{int} = 0.0289, R_{sigma} = 0.0217]
Data/restraints/parameters	12157/0/756
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0808
Final R indexes [all data]	R_1 = 0.0361, wR_2 = 0.0835
Largest diff. peak/hole / e Å^{-3}	0.20/-0.28

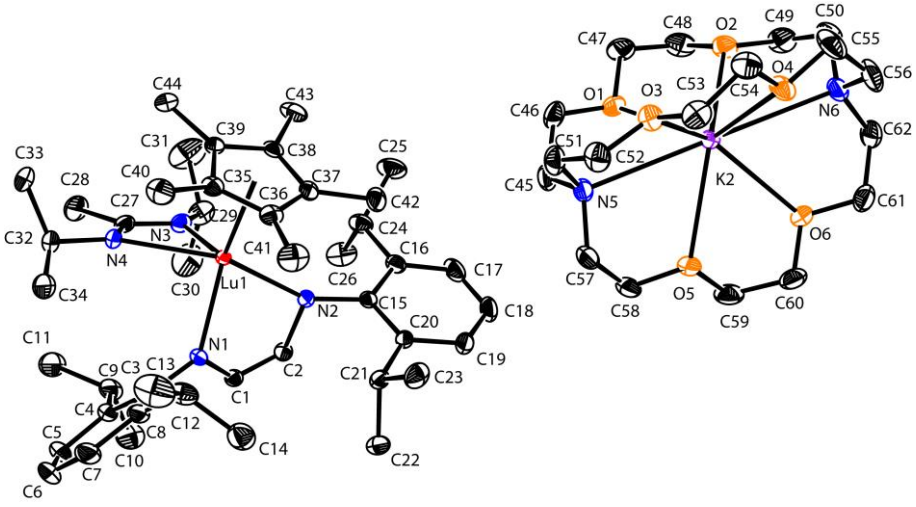


Figure S47. ORTEP drawing of **19** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 13 Crystal data and structure refinement for 19.

Identification code	**19**
Empirical formula	$C_{62}H_{104}KLuN_6O_6$
Formula weight	1243.58
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.4795(4)
b/Å	18.4821(4)
c/Å	23.1071(6)
α/°	90
β/°	106.350(2)
γ/°	90
Volume/Å^3	7163.0(3)
Z	4
ρ_{calc}g/cm^3	1.153
μ/mm^{-1}	1.482
F(000)	2624.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.858 to 54.966
Index ranges	$-22 \le h \le 20$, $-24 \le k \le 23$, $-29 \le l \le 30$
Reflections collected	78347
Independent reflections	16327 [R_{int}= 0.0319, R_{sigma} = 0.0271]
Data/restraints/parameters	16327/0/711
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0225, wR_2 = 0.0563
Final R indexes [all data]	R_1 = 0.0289, wR_2 = 0.0581
Largest diff. peak/hole / e Å^{-3}	0.42/-0.30

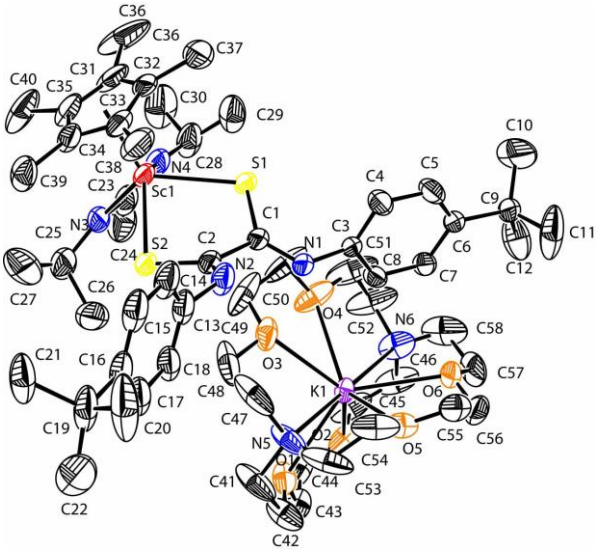


Figure S48. ORTEP drawing of **20** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 14 Crystal data and structure refinement for 20.

Identification code	**20**
Empirical formula	$C_{58}H_{94}KN_6O_6S_2Sc$
Formula weight	1119.57
Temperature/K	151(40)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.7649(6)
b/Å	25.5216(13)
c/Å	24.0285(16)
α/°	90
β/°	100.632(6)
γ/°	90
Volume/Å^3	6488.2(7)
Z	4
ρ_{calc}g/cm^3	1.146
μ/mm^{-1}	0.291
F(000)	2416.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.168 to 50.054
Index ranges	-12 ≤ h ≤ 12, -28 ≤ k ≤ 30, -28 ≤ l ≤ 23
Reflections collected	40548
Independent reflections	11420 [R_{int} = 0.0634, R_{sigma} = 0.0605]
Data/restraints/parameters	11420/0/683
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.1079, wR_2 = 0.2866
Final R indexes [all data]	R_1 = 0.1530, wR_2 = 0.3225
Largest diff. peak/hole / e Å^{-3}	0.88/-0.65

4) The Cyclic Voltammetry of 8 and 9

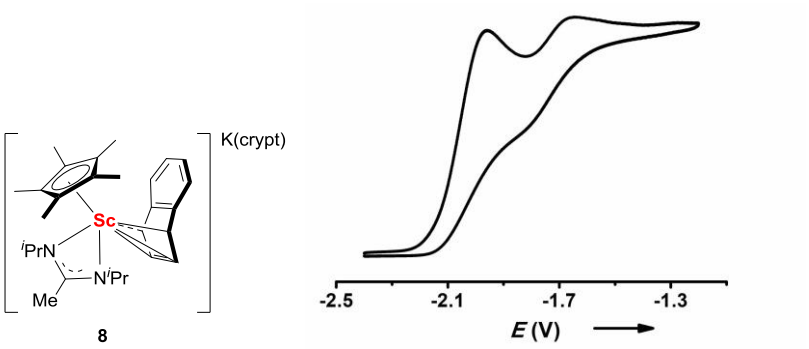


Figure S49. The cyclic voltammogram of compound **8** (0.002 M) in THF at room temperature containing 0.2 M $^{n}Bu_4NPF_6$ as the supporting electrolyte, measured at 100 mV/s. The cyclic voltammogram showed two oxidation peaks at -1.96 V and -1.64 V.

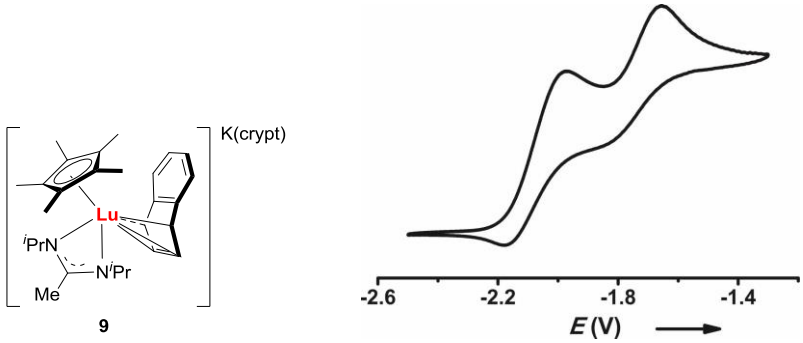


Figure S50. The cyclic voltammogram of compound **9** (0.002 M) in THF at room temperature containing 0.2 M $^{n}Bu_4NPF_6$ as the supporting electrolyte, measured at 100 mV/s. The cyclic voltammogram showed two oxidation peaks at -1.97 V and -1.65 V.

5) References

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