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Manuscript Title:

Selective C−C Coupling of Two Nitriles Affording Rare-Earth Diazametallacyclopentadienes: Synthesis, Cooperative Reactivity and Mechanistic Studies

Authors:

Miaomiao Zhu,‡ Zhengqi Chai,‡ Tianyu Li, Junnian Wei, Ze-Jie Lv,* and Wen-Xiong Zhang*

Affiliations:

Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Rare Earth Materials Chemistry and Applications & Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

‡ Authors contributed equally to this work.

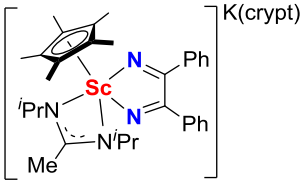
Contents:

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{^{1}H} NMR spectra were recorded on a Bruker Avance 400 MHz, 500 MHz or 600 MHz spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were reported with reference to solvent resonances of d^8-THF at 1.73 and 25.37 ppm, $(CD_3)_2CO$ (TMS) at 2.05 and 29.84 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.

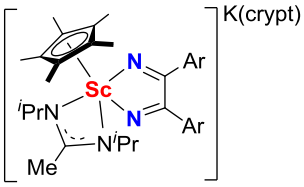
Compounds **1**[1] and *N*,*N*′-diphenylcarbodiimide[2] were prepared following the literature procedures.



2a-Sc

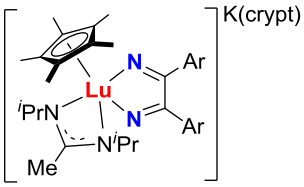
Synthesis of 2a-Sc: In the glovebox, PhCN (44.9 μL, 0.44 mmol) was added to a pre-cooled (-35 °C) THF (5 mL) solution of **1-Sc** (97.7 mg, 0.2 mmol) and the reaction mixture gradually turned to pink. The solution was stirred at room temperature for 1 h. [2.2.2]cryptand (75.3 mg, 0.2 mmol) was added to the reaction mixture and the mixture was stirred at room temperature for 1 h. After that, the solvents were removed under reduced pressure to afford deep red solid. The solid was washed with Et_2O (1 mL × 3) thrice and dried under vacuum affording deep red powder. This red powder was pure enough for NMR experiment without further purification. Yield: 70% (132.1 mg, 0.14 mmol). ^{1}H NMR (500 MHz, d^8-THF) δ 1.16 (d, J = 6.3 Hz, 6H, $(CH_3)_2$CH), 1.24 (d, J = 6.3 Hz, 6H, $(CH_3)_2$CH), 1.80 (s, 3H, CCH_3), 2.00 (s, 15H, C_5Me_5), 2.48-2.50 (m, 12H, N$CH_2$$CH_2$O), 3.33-3.37 (m, 2H, $(CH_3)_2CH$), 3.47-3.49 (m, 12H, NCH$_2$$CH_2$O), 3.52 (s, 12H, O$CH_2$$CH_2$O), 6.77-6.80 (m, 2H, Ph), 6.83-6.86 (m, 4H, Ph), 7.12-7.14 (m, 4H, Ph). ^{13}C{^{1}H} NMR (126 MHz, d^8-THF) δ 10.91 (CCH_3), 12.77 (C_5Me_5), 25.86 ((CH_3)$_2$CH), 26.63 ((CH_3)$_2$CH), 48.62 ((CH_3)$_2$CH), 54.82

(NCH$_2$CH$_2$O), 68.50 (NCH$_2$*C*H$_2$O), 71.35 (O*C*H$_2$*C*H$_2$O), 114.74 (*C*$_5$Me$_5$), 124.44 (Ph), 126. 49 (Ph), 128.86 (Ph), 148.46 (Ph), 163.20 (Ph*C*N), 171.04 (N*C*N). After recrystallization by slowly diffusion of hexane into the THF solution of **2a-Sc** for 3 days, the single crystals suitable for X-ray analysis could be obtained. Anal. Calcd for C$_{50}$H$_{78}$KN$_6$O$_6$Sc of **2a-Sc**: C, 63.67; H, 8.34; N, 8.91. Found: C 63.92; H 8.68; N 8.24.



Ar = 4-biphenyl
2b-Sc

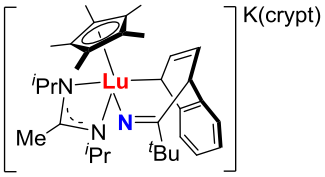
Synthesis of 2b-Sc: This complex was prepared from the reaction of **1-Sc** (97.7 mg, 0.2 mmol) and 4-phenylbenzonitrile (78.9 mg, 0.44 mmol) in THF by an analogous procedure as the synthesis of **2a-Sc**. The solid was washed with Et$_2$O (1 mL ×3) thrice and dried under vacuum affording deep purple powder. This deep purple powder was pure enough for NMR experiment without further purification. Yield: 127.1 mg, 58%. ^{1}H NMR (500 MHz, d^8-THF) δ 1.19-1.21 (m, 6H, (*CH*$_3$)$_2$CH), 1.27 (d, J = 6.2 Hz, 6H, (*CH*$_3$)$_2$CH), 1.82 (s, 3H, C*CH*$_3$), 2.02 (s, 15H, C$_5$*Me*$_5$), 2.45-2.46 (m, 12H, N*CH*$_2$CH$_2$O), 3.35-3.38 (m, 2H, (CH$_3$)$_2$*CH*), 3.42-3.45 (m, 12H, NCH$_2$*CH*$_2$O), 3.48 (s, 12H, O*CH*$_2$*CH*$_2$O), 7.13-7.17 (m, 2H, biphenyl), 7.22-7.23 (m, 4H, biphenyl), 7.28-7.31 (m, 8H, biphenyl), 7.54-7.56 (m, 4H, biphenyl). ^{13}C{^{1}H} NMR (126 MHz, d^8-THF) δ 10.93 (C*C*H$_3$), 12.78 (C$_5$*Me*$_5$), 25.86 ((*C*H$_3$)$_2$CH), 26.65 ((*C*H$_3$)$_2$CH), 48.65 ((CH$_3$)$_2$*C*H), 54.78 (N*C*H$_2$CH$_2$O), 68.48 (NCH$_2$*C*H$_2$O), 71.34 (O*C*H$_2$*C*H$_2$O), 114.87 (*C*$_5$Me$_5$), 125.35 (biphenyl), 126.71 (biphenyl), 127.37 (biphenyl), 129.15 (biphenyl), 129.42 (biphenyl), 137.13 (biphenyl), 143.32 (biphenyl), 147.19 (biphenyl), 162.69 (Ar*C*N), 171.13 (N*C*N). After recrystallization by slowly diffusion of hexane into the THF solution of **2b-Sc** for 3 days, the single crystals of **2b-Sc ·THF** suitable for X-ray analysis could be obtained. Anal. Calcd for C$_{66}$H$_{94}$KN$_6$O$_7$Sc of **2b-Sc ·THF**: C, 67.90; H, 8.12; N, 7.20. Found: C 67.64; H 7.82; N 7.34.



Ar = 4-biphenyl
2b-Lu

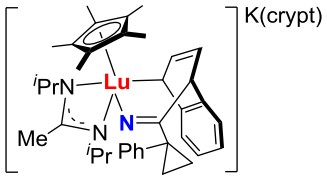
Synthesis of 2b-Lu: This complex was prepared from the reaction of **1-Lu** (123.7 mg, 0.2 mmol) and 4-phenylbenzonitrile (78.9 mg, 0.44 mmol) in THF by an analogous procedure as the synthesis of **2a-Sc**. The solid was washed with Et$_2$O (1 mL ×3) thrice and dried under vacuum affording deep purple powder. This deep purple powder was pure enough for NMR experiment without further purification. Yield: 122.5 mg, 50%. ^{1}H NMR (500 MHz, d^8-THF) δ 1.21 (br, 12H, (*CH*$_3$)$_2$CH), 1.80 (s, 3H, C*CH*$_3$), 2.03 (s, 15H, C$_5$*Me*$_5$), 2.41-2.43 (m, 12H, N*CH*$_2$CH$_2$O), 3.37-3.41 (m, 14H, (CH$_3$)$_2$*CH*), NCH$_2$*CH*$_2$O), 3.45 (s, 12H, O*CH*$_2$*CH*$_2$O), 7.14-7.17 (m, 2H, biphenyl), 7.23-7.24 (m, 4H,

biphenyl), 7.28-7.31 (m, 4H, biphenyl), 7.34-7.36 (m, 4H, biphenyl), 7.54-7.55 (m, 4H, biphenyl). $^{13}C\{^{1}H\}$ NMR (126 MHz, d^8-THF) δ 11.32 (CCH_3), 12.22 (C_5Me_5), 25.86 ((CH_3)$_2$$CH$), 26.83 (($CH_3$)$_2$$CH$), 48.28 (($CH_3$)$_2$$CH$), 54.95 (N$CH_2CH_2$O), 68.71 (N$CH_2CH_2$O), 71.66 (O$CH_2CH_2$O), 113.59 ($C_5Me_5$), 125.35 (biphenyl), 126.74 (biphenyl), 127.37 (biphenyl), 129.16 (biphenyl), 129.46 (biphenyl), 137.10 (biphenyl), 143.28 (biphenyl), 148.56 (biphenyl), 164.06 (ArCN), 170.98 (NCN). After recrystallization by slowly diffusion of hexane into the THF solution of **2b-Lu**·**THF** for 3 days, the single crystals suitable for X-ray analysis could be obtained. Anal. Calcd for $C_{66}H_{94}KLuN_6O_7$ of **2b-Lu**·**THF**: C, 61.09; H, 7.30; N, 6.48. Found: C 61.05; H 7.50; N 6.53.



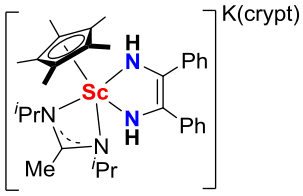
3a-Lu

Synthesis of 3a-Lu: In the glovebox, ^{t}BuCN (26.5 μL, 0.24 mmol) was added to a THF solution of **1-Lu** (123.7 mg, 0.2 mmol) at −35 ^{o}C. Then this solution was warmed to room temperature and stirred for 1 h. The reaction mixture gradually turned to yellow. After that, [2.2.2]cryptand (75.3 mg, 0.2 mmol) was added to the reaction mixture and the mixture was stirred at room temperature for 1 h. Then the volatiles were removed under reduced pressure to afford yellow solid. The solid was washed with Et_2O (1 mL ×3) thrice and dissolved in 3 mL THF. Slowly diffracting of hexane into this THF solution for 3 days afforded the yellow single crystals of **3a-Lu**. Yield: 133.7 mg, 62%. ^{1}H NMR (600 MHz, d^8-THF) δ -0.12 (d, J = 6.1 Hz, 3H, (CH_3)$_2$CH), 1.10-1.12 (m, 6H, (CH_3)$_2$CH), 1.16 (s, 9H, (CH_3)$_3$C), 1.45 (d, J = 6.5 Hz, 3H, (CH_3)$_2$CH), 1.50 (s, 3H, CCH_3), 2.03 (s, 15H, C_5Me_5), 2.49-2.52 (m, 12H, NCH_2CH$_2$O), 2.58-2.59 (1H, naph), 2.94-2.99 (m, 1H, (CH$_3$)$_2$$CH$), 3.48-3.50 (m, 12H, NCH$_2$$CH_2$O), 3.54 (s, 12H, O$CH_2CH_2$O), 3.61-3.65 (m, 1H, (CH$_3$)$_2$$CH$), 4.22-4.25 (m, 1H, naph), 4.49-4.51 (m, 1H, naph), 5.87-5.91 (m, 1H, naph), 6.17-6.24 (m, 1H, naph), 6.28-6.34 (m, 2H, naph), 6.40-6.42 (m, 1H, naph). $^{13}C\{^{1}H\}$ NMR (151 MHz, d^8-THF) δ 10.68 (CCH_3), 12.80 (C_5Me_5), 25.97 ((CH_3)$_2$CH), 27.76 ((CH_3)$_2$CH), 29.36 ((CH_3)$_3$C), 41.69 ((CH_3)$_3$$C$), 48.36 (($CH_3$)$_2$$CH$), 48.50 (($CH_3$)$_2$$CH$), 50.02 (Lu-N=C-$CH$), 54.81 (N$CH_2CH_2$O), 66.28 (Lu-$CH$), 68.52 (NCH$_2$$CH_2$O), 71.34 (O$CH_2$$CH_2$O), 105.03 (naph), 113.13 (C_5Me$_5$), 117.1 (naph), 122.35 (naph), 122.50 (naph), 126.68 (naph), 130.93 (naph), 132.74 (naph), 145.08 (naph), 170.22 (NCN), 174.92 (Lu-NC). Anal. Calcd for $C_{51}H_{85}KLuN_5O_6$ of **3a-Lu**: C, 56.81; H, 7.95; N, 6.49. Found: C 56.97; H 8.22; N 6.32.



3b-Lu

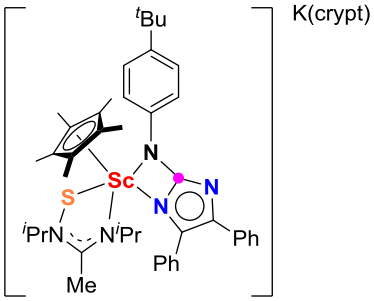
Synthesis of 3b-Lu: This complex was prepared from the reaction of **1-Lu** (123.7 mg, 0.2 mmol) and 1-phenylcyclopropanecarbonitrile (34.4 μL, 0.24 mmol) in THF by an analogous procedure as the synthesis of **3a-Lu**. The single crystals of **3b-Lu** suitable for X-ray analysis could be acquired by slowly diffusion of hexane into the THF solution for 3 days. Yield: 129.8 mg, 57%. ^{1}H NMR (400 MHz, d^{8}-THF) δ 1.00 (d, J = 6.1 Hz, 3H, (CH_3)$_2$CH), 1.15-1.16 (m, 6H, (CH_3)$_2$CH), 1.31 (d, J = 6.4 Hz, 3H, (CH_3)$_2$CH), 1.69-1.72 (m, 2H, CH_2), 1.80 (s, 3H, CCH_3), 1.85 (s, 15H, C$_5Me_5$), 1.93-1.98 (m, 2H, CH_2), 2.45-2.48 (m, 12H, NCH_2CH$_2$O), 2.72 (d, J = 6.0 Hz, 1H, Ar), 3.43-3.46 (m, 12H, NCH$_2CH_2$O), 3.49 (s, 12H, OCH_2CH_2O), 3.53-3.58 (m, 1H, (CH$_3$)$_2CH$), 3.62-3.67 (m, 1H, (CH$_3$)$_2CH$), 4.12-4.14 (m, 1H, Ar), 4.33-4.37 (m, 1H, Ar), 5.86-5.89 (m, 1H, Ar), 6.20-6.26 (m, 1H, Ar), 6.50-6.54 (m, 2H, Ar), 6.65-6.68 (m, 1H, Ar), 6.97-7.03 (m, 1H, Ar), 7.14-7.18 (m, 2H, Ar), 7.43-7.45 (m, 2H, Ar). ^{13}C{^{1}H} NMR (151 MHz, d^{8}-THF) δ 11.67 (CCH_3), 12.50 (C$_5Me_5$), 13.27 (CH_2), 14.11 (CH_2), 25.99 ((CH_3)$_2$CH), 27.30 ((CH_3)$_2$CH), 27.72 ((CH_3)$_2$CH), 35.74 (C-CN), 48.11 ((CH$_3$)$_2C$H), 48.21 ((CH$_3$)$_2C$H), 52.74 (Sc-N=C-CH), 54.80 (NCH_2CH$_2$O), 66.76 (Sc-CH), 68.50 (NCH$_2CH_2$O), 71.31 (OCH_2CH_2O), 104.67 (Ar), 109.93 (Ar), 113.17 (C_5Me$_5$), 116.55 (Ar), 121.85 (Ar), 123.05 (Ar), 124.85 (Ar), 127.01 (Ar), 128.29 (Ar), 130.49 (Ar), 132.81 (Ar), 147.61 (Ar), 150.02 (Ar), 169.92 (NCN), 170.51 (Lu-NC). Anal. Calcd for C$_{56}$H$_{85}$KLuN$_5$O$_6$ of **3b-Lu**: C, 59.08; H, 7.53; N, 6.15. Found: C 59.13; H 7.58; N 6.28.



4-Sc

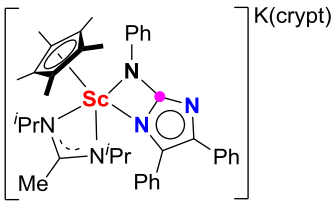
Synthesis of 4-Sc from 1,4-cyclohexadiene: In the glovebox, 1,4-cyclohexadiene (18.9 μL, 0.2 mmol) was added to a THF solution of **2a-Sc** (188.7 mg, 0.2 mmol). Then this solution was warmed to room temperature and stirred at room temperature for 1 day. After that, the volatiles were removed under reduced pressure to afford blue solid. The solid was washed with Et$_2$O (1 mL × 3) thrice and dried under vacuum affording blue powder. This blue powder was pure enough for NMR experiment without further purification. Yield: 141.8 mg, 75%. After recrystallization by slowly diffusion of hexane into the THF solution of **4-Sc** for 3 days, the single crystals of **4-Sc·0.5THF** suitable for X-ray analysis could be obtained. ^{1}H NMR (500 MHz, d^{8}-THF) δ 1.15 (d, J = 6.3 Hz, 6H, (CH_3)$_2$CH), 1.19 (d, J = 6.3 Hz, 6H, (CH_3)$_2$CH), 1.76-1.79 (m, 2H, β-CH_2 for THF), 1.80 (s, 3H, CCH_3), 1.94 (s, 15H, C$_5Me_5$), 2.45-2.47 (m, 12H, NCH_2CH$_2$O), 3.43-3.45 (m, 12H, NCH$_2CH_2$O), 3.45-3.48 (m, 14H, (CH$_3$)$_2CH$, OCH_2CH_2O), 3.60-3.63 (m, 2H, α-CH_2 for THF), 3.91 (br, 2H, NH), 6.43-6.46 (m,

2H, Ph), 6.71-6.74 (m, 4H, Ph), 7.05-7.08 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR (126 MHz, d^8-THF) δ 11.43 (CCH_3), 12.85 (C_5Me_5), 25.86 (β-*C* for THF), 26.44 ((CH_3)$_2$CH), 27.01 ((CH_3)$_2$CH), 48.31 ((CH_3)$_2$*C*H), 54.78 (N*C*H$_2$CH$_2$O), 68.27 (α-*C* for THF), 68.45 (NCH$_2$*C*H$_2$O), 71.33 (O*C*H$_2$*C*H$_2$O), 113.54 (C_5Me$_5$), 119.86 (Ph), 127.24 (Ph), 128.32 (Ph), 131.17 (Ph*C*), 147.12 (Ph), 167.14 (N*C*N). Anal. Calcd for $C_{52}H_{84}KN_6O_{6.5}Sc$ of **4-Sc·0.5THF**: C, 63.64; H, 8.63; N, 8.56. Found: C 63.63; H 8.85; N 8.66.



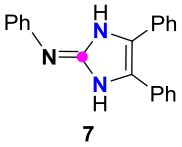
5-Sc

Synthesis 5-Sc: In the glovebox, 4-*tert*-butylphenyl isothiocyanate (38.5 mg, 0.2 mmol) was added to a THF solution of **2a-Sc** (188.7 mg, 0.2 mmol) at −35ºC and the reaction mixture gradually turned to yellow. Then this solution was warmed to room temperature and stirred for 1 h. After that, the volatiles were removed under reduced pressure to afford yellow solid. The solid was washed with Et_2O (1 mL ×3) thrice. This yellow powder was pure enough for NMR experiment without further purification. Yield: 145.4 mg, 64%. ^{1}H NMR (500 MHz, d^8-THF) δ 0.31 (br, 3H, (CH_3)$_2$CH), 1.14 (d, J = 6.5 Hz, 6H, (CH_3)$_2$CH), 1.27 (s, 9H, (CH_3)$_3$C), 1.38 (d, J = 6.3 Hz, 3H, (CH_3)$_2$CH), 1.95 (s, 15H, C_5Me_5), 2.01 (s, 3H, CCH_3), 2.30-2.32 (m, 12H, NCH_2CH$_2$O), 3.28-3.30 (m, 12H, NCH$_2$$CH_2$O), 3.36 (s, 12H, O$CH_2$$CH_2$O), 3.80-3.87 (m, 1H, (CH$_3$)$_2$*CH*), 4.05-4.11 (m, 1H, (CH$_3$)$_2$*CH*), 6.69-6.72 (m, 1H, Ar), 6.91-6.95 (m, 4H, Ar), 7.01-7.04 (m, 1H, Ar), 7.15-7.18 (t, J = 7.5 Hz, 2H, Ar), 7.50-7.62 (m, 4H, Ar), 7.66-7.68 (m, 2H, Ar). $^{13}C\{^{1}H\}$ NMR (126 MHz, d^8-THF) δ 12.73 (C_5Me_5), 18.37 (CCH_3), 21.39 ((CH_3)$_2$CH), 23.04 ((CH_3)$_2$CH), 23.68 ((CH_3)$_2$CH), 24.64 ((CH_3)$_2$CH), 32.72 ((CH_3)$_3$C), 34.33 ((CH_3)$_3$*C*), 46.16 ((CH_3)$_2$*C*H), 51.89 ((CH_3)$_2$*C*H), 54.72 (N*C*H$_2$CH$_2$O), 68.55 (NCH$_2$*C*H$_2$O), 71.26 (O*C*H$_2$*C*H$_2$O), 118.16 (C_5Me$_5$), 119.30 (Ar), 122.28 (Ar), 124.10 (Ar), 124.68 (Ar), 127.37 (Ar), 127.46 (Ar), 127.77 (Ar), 130.49 (Ar), 131.07 (Ar), 133.31 (Ar), 133.41 (Ar), 141.25 (Ar), 141.64 (Ph*C*), 150.70 (Ph*C*), 160.37 (ArN*C*N), 165.04 (^{i}PrN*C*N^{i}Pr). After recrystallization by slowly diffusion of hexane into the THF solution of **5-Sc** for 3 days, the single crystals of **5-Sc·THF** suitable for X-ray analysis could be obtained. Anal. Calcd for $C_{65}H_{99}KN_7O_7SSc$ of **5-Sc·THF**: C, 64.70; H, 8.27; N, 8.13. Found: C, 64.61; H, 8.38; N, 8.42.



6-Sc

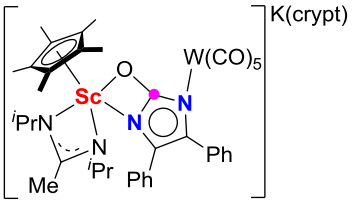
Synthesis of 6-Sc: In the glovebox, PhNC (22 μL, 0.2 mmol) was added to a THF solution of **2a-Sc** (188.7 mg, 0.2 mmol) at −35 °C and the reaction mixture gradually turned to brown. Then this solution was warmed to room temperature and stirred for 1 h. After that, the volatiles were removed under reduced pressure to afford brown solid. The solid was collected and washed with Et_2O (1 mL × 3) thrice. This brown powder was pure enough for NMR experiment without further purification. Yield: 150.7 mg, 72%. ^{1}H NMR (500 MHz, d^8-THF) δ 0.57 (d, J = 6.5 Hz, 3H, $(CH_3)_2CH$), 0.78 (d, J = 7.5 Hz, 3H, $(CH_3)_2CH$), 0.89 (d, J = 6.6 Hz, 3H, $(CH_3)_2CH$), 1.12-1.14 (m, 3H, $(CH_3)_2CH$), 1.80 (s, 3H, CCH_3), 2.04 (s, 15H, C_5Me_5), 2.37-2.38 (m, 12H, NCH_2CH_2O), 3.23 (br, 1H, $(CH_3)_2CH$), 3.35-3.37 (m, 12H, NCH_2CH_2O), 3.41 (s, 12H, OCH_2CH_2O), 3.81 (br, 1H, $(CH_3)_2CH$), 6.15 (t, J = 7.0 Hz, 1H, Ph), 6.71 (t, J = 7.2 Hz, 1H, Ph), 6.85-6.88 (m, 2H, Ph), 6.92-6.98 (m, 3H, Ph), 7.12 (t, J = 7.5 Hz, 2H, Ph), 7.64 (t, J = 8.5 Hz, 4H, Ph), 7.77-7.78 (m, 2H, Ar). ^{13}C{^{1}H} NMR (126 MHz, d^8-THF) δ 12.44 (C_5Me_5), 16.59 (CCH_3), 25.46 ($(CH_3)_2CH$), 25.62 ($(CH_3)_2CH$), 25.86 ($(CH_3)_2CH$), 47.82 ($(CH_3)_2CH$), 47.38 ($(CH_3)_2CH$), 54.74 (NCH_2CH_2O), 68.48 (NCH_2CH_2O), 71.29 (OCH_2CH_2O), 112.00 (Ph), 113.66 (Ph), 117.61 (C_5Me_5), 119.66 (Ph), 122.28 (Ph), 124.37 (Ph), 127.49 (Ph), 127.65 (Ph), 127.68 (Ph), 130.64 (Ph), 133.48 (Ph), 134.07 (Ph), 141.63 (Ph), 141.71 (PhC), 152.63 (PhC), 161.34 (PhNCN), 172.07 (NCN). The single crystals of **6-Sc** suitable for X-ray analysis could be acquired by slowly diffusion of hexane into the THF solution for 3 days. Anal. Calcd for $C_{57}H_{81}KN_7O_6Sc$ of **6-Sc**: C, 65.55; H, 7.82; N, 9.39. Found: C, 65.12; H, 8.04; N, 9.38.



7

Synthesis of 7: Under an argon atmosphere, a THF solution **6-Sc** (104.6 mg, 0.1 mmol) was treated with $NEt_3 \cdot HCl$ (55.1 mg, 0.4 mmol). The reaction mixture was stirred for 1 day at room temperature. After that, the volatiles were removed under reduced pressure to afford yellow solid. Then the crude products were washed with hexane thrice to afford yellowish solid. The solid was extracted by ethyl acetate (5 mL). The extracts were combined and dried over $MgSO_4$ and the solvent was removed under vacuum affording yellowish oil. After that, the oil was dissolved in ethyl acetate (1 mL), evaporated onto silica and purified by column chromatography (ethyl acetate: hexane = 1:5) to yield a colorless oil. **7** is unstable at room temperature and will gradually decompose resulting in low yield. Yield: 7.8 mg, 25%. ^{1}H NMR (600 MHz, d^6- Acetone) δ 6.84-6.88 (m, 1H, Ph), 7.22-7.28 (m, 4H, Ph), 7.30-7.33 (m, 4H, Ph), 7.55-7.56 (m, 4H, Ph), 7.66-7.68 (m, 2H, Ph), 8.06 (br, 2H, NH). ^{13}C{^{1}H} NMR (126 MHz, d^6-Acetone) δ 117.01 (Ph), 120.72 (Ph),

127.41 (Ph), 128.33 (Ph), 129.15, (Ph), 129.64 (Ph), 130.18 (Ph), 143.13 (Ph), 146.34 (Ph*C*=NH), 172.44 (PhN=*C*). HRMS (m/z): $[M+H]^+$ calcd. for $C_{21}H_{18}N_3$, 312.1497; found, 312.1495.

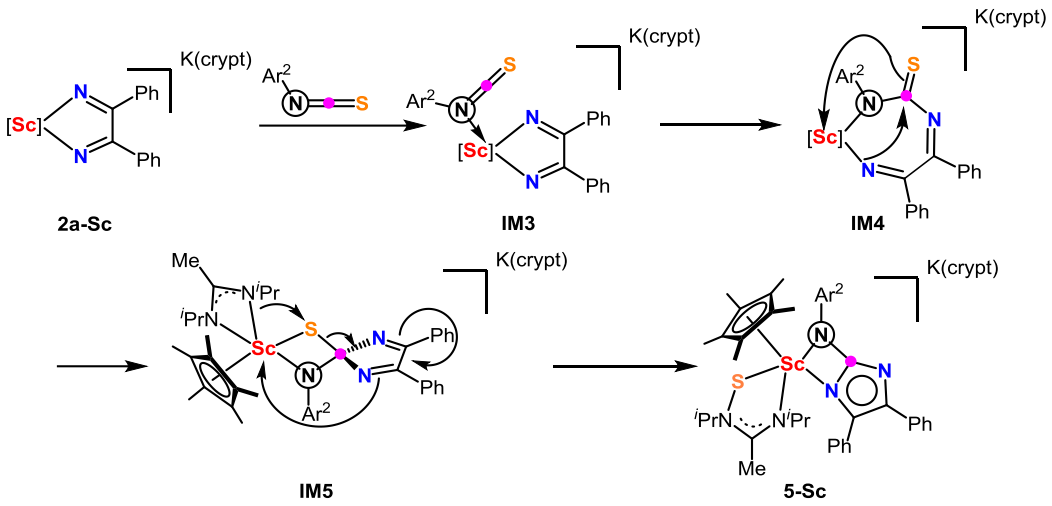


8-Sc

Synthesis of 8-Sc: In the glovebox, $W(CO)_6$ (70.4 mg, 0.2 mmol) was added to a THF solution of **2a-Sc** (188.7 mg, 0.2 mmol) at −35 °C and the reaction mixture gradually turned to yellow. Then this solution was warmed to room temperature and stirred for 1 h. After that, the volatiles were removed under reduced pressure to afford yellow solid. The solid was collected and washed with Et_2O (1 mL × 3) thrice. This yellow powder was pure enough for NMR experiment without further purification. Yield: 176.1 mg, 68%. ^{1}H NMR (500 MHz, d^8-THF) δ 0.97-1.12 (m, 6H, $(CH_3)_2$CH), 1.19 (d, J = 6.5 Hz, 6H, $(CH_3)_2$CH), 1.89 (s, 3H, CCH_3), 1.96 (s, 15H, C_5Me_5), 2.53-2.55 (m, 12H, NCH_2CH_2O), 3.44-3.49 (m, 2H, $(CH_3)_2CH$), 3.51-3.53 (m, 12H, NCH$_2CH_2$O), 3.57 (s, 12H, OCH_2CH_2O), 6.75-6.78 (m, 1H, Ph), 6.89-6.92 (m, 2H, Ph), 7.13-7.16 (m, 1H, Ph), 7.17-7.21 (m, 4H, Ph), 7.30-7.32 (m, 2H, Ph). ^{13}C{^{1}H} NMR (126 MHz, d^8-THF) δ 12.29 (C_5Me_5), 12.66 (CCH_3), 25.86 ((CH_3)$_2$CH), 25.99 ((CH_3)$_2$CH), 48.44 ((CH_3)$_2$CH), 54.84 (NCH_2CH_2O), 68.52 (NCH$_2CH_2$O), 71.37 (OCH_2CH_2O), 118.28 (C_5Me$_5$), 123.50 (Ph), 126.67 (Ph), 127.42 (Ph), 128.05 (Ph), 128.17 (Ph), 129.92 (Ph), 133.37 (Ph), 135.03 (Ph), 138.48 (O*C*N), 141.03 (Ph*C*), 168.72 (Ph*C*), 172.07 (N*C*N), 200.83 (*C*O), 205.10 (*C*O). The single crystals of **8-Sc·THF** suitable for X-ray analysis could be acquired by slowly diffusion of hexane into the THF solution for 3 days. Anal. Calcd for $C_{60}H_{86}KN_6O_{13}ScW$ of **8-Sc·THF**: C, 52.71; H, 6.34; N, 6.15. Found: C, 52.22; H, 6.20; N, 6.51.

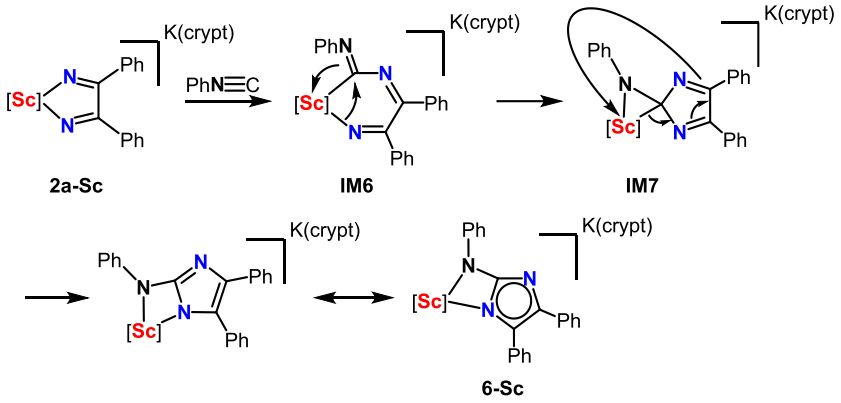
2) Possible Mechanisms for the Formation of 5-Sc and 6-Sc.

The formation of **5-Sc** is proposed to proceed as described in **Scheme S1**, where initially the insertion of C=N bond into the Sc−N bond occurs, giving **IM4**. Then, **IM4** undergoes intramolecular nucleophilic attack giving the spiro complex **IM5**. The nitrogen of the amidinate then nucleophilically attacks the sulfur atom giving the final product **5-Sc**.



Scheme S1. The proposed mechanism for the formation of **5-Sc**.

The formation of **6-Sc** includes three possible steps (Scheme S2): the initial 1,1-insertion of PhNC into Sc−N bond affording **IM6**; the subsequently nucleophilic attack of the Sc−N bond on the C=N double bond providing a strained spiro metallacycle **IM7**, followed by intramolecular rearrangement giving **6-Sc**.



Scheme S2. The proposed mechanism for the formation of **6-Sc**

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

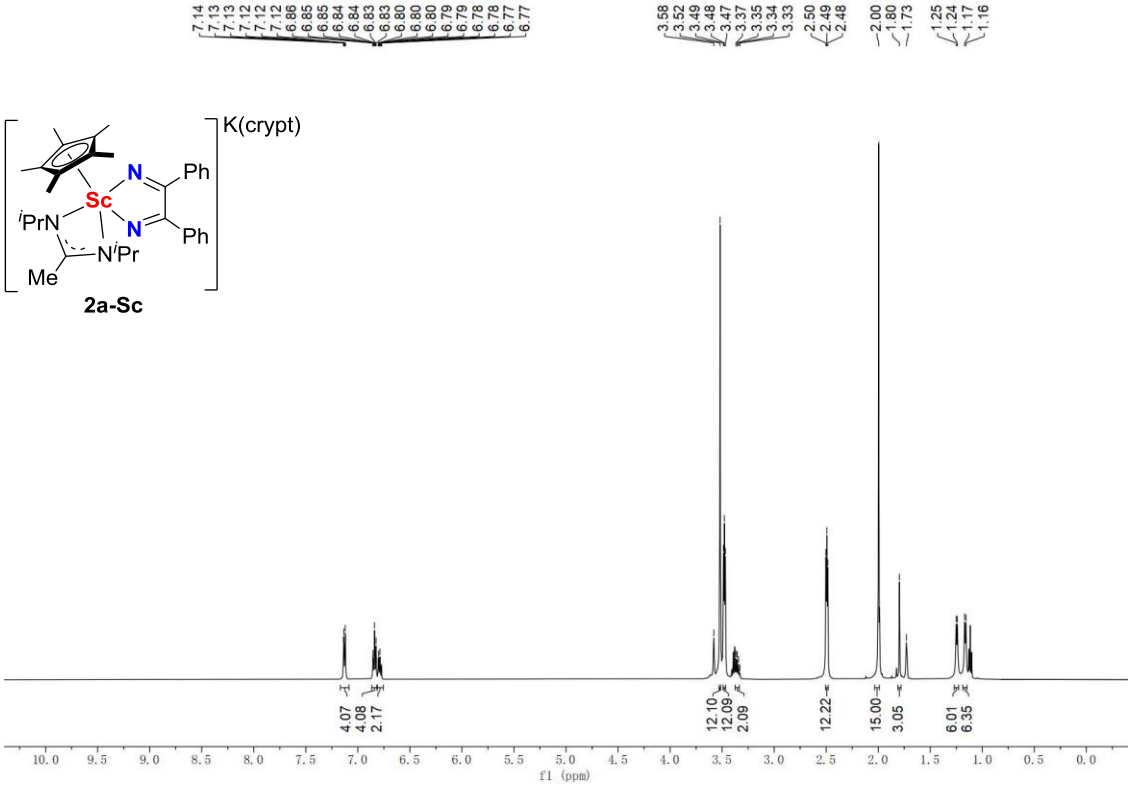


Figure S1. ^{1}H NMR spectrum of **2a-Sc** (25 ℃, 500 MHz, d^{8}-THF).

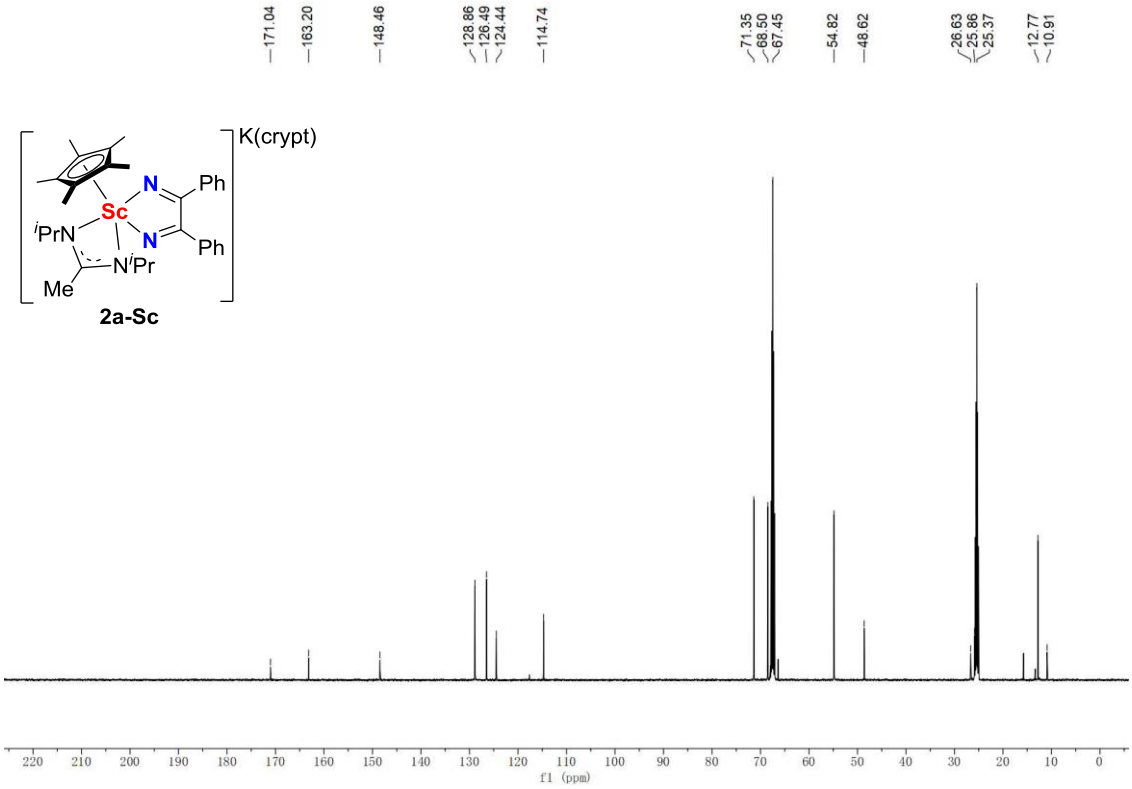


Figure S2. ^{13}C{^{1}H} NMR spectrum of **2a-Sc** (25 ℃, 126 MHz, d^{8}-THF).

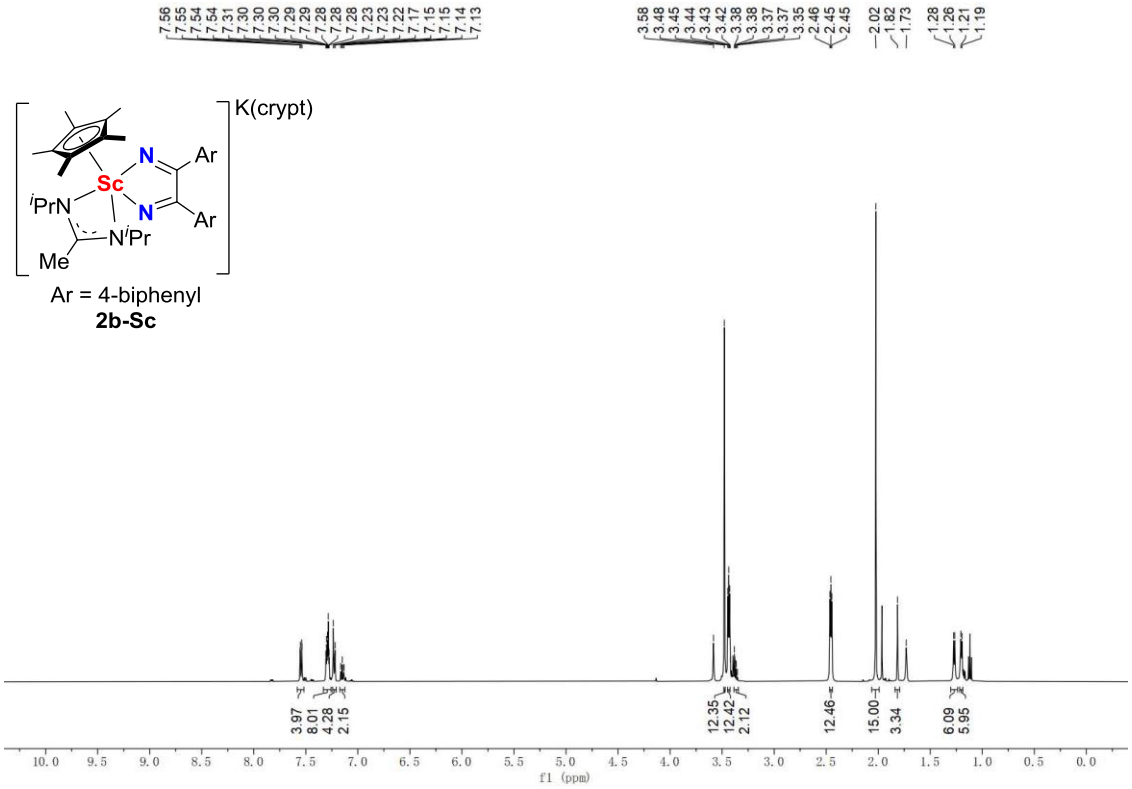


Figure S3. ^{1}H NMR spectrum of **2b-Sc** (25 ℃, 500 MHz, d^{8}-THF).

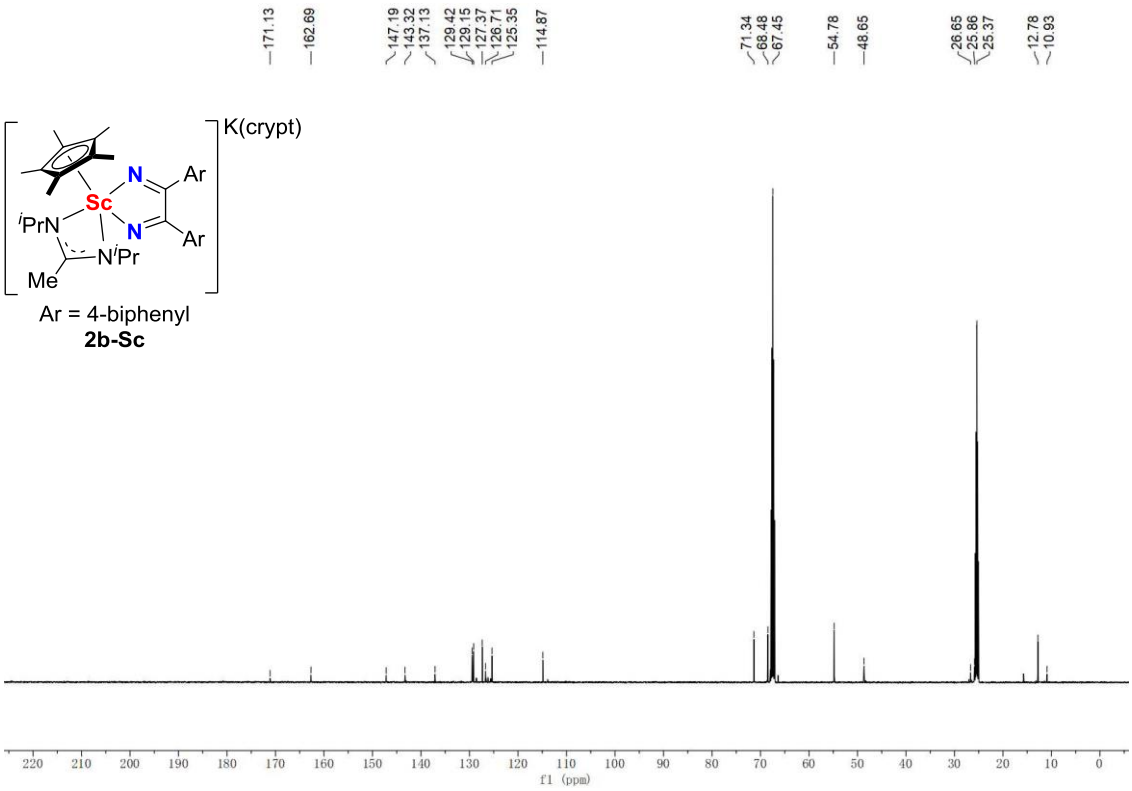


Figure S4. ^{13}C{^{1}H} NMR spectrum of **2b-Sc** (25 ℃, 126 MHz, d^{8}-THF).

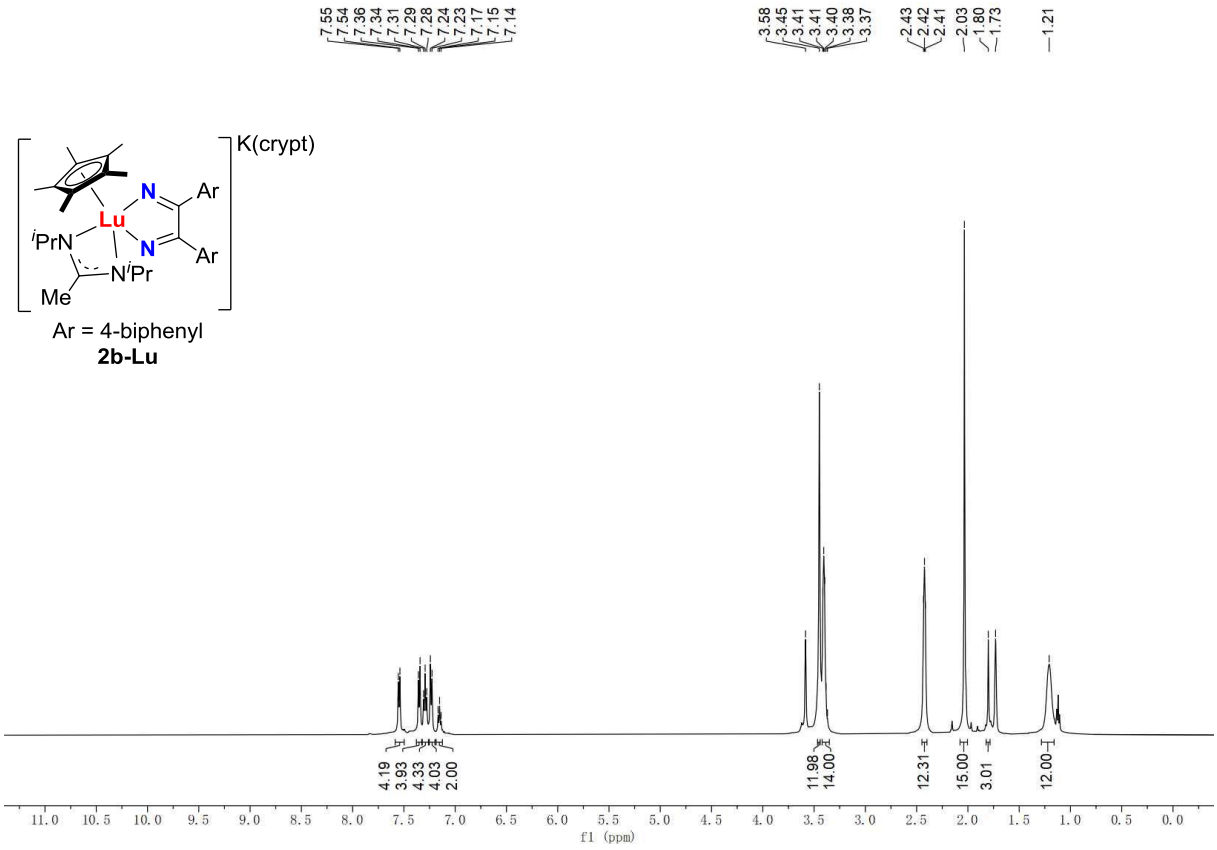


Figure S5. ^{1}H NMR spectrum of **2b-Lu** (25 ℃, 500 MHz, d^{8}-THF).

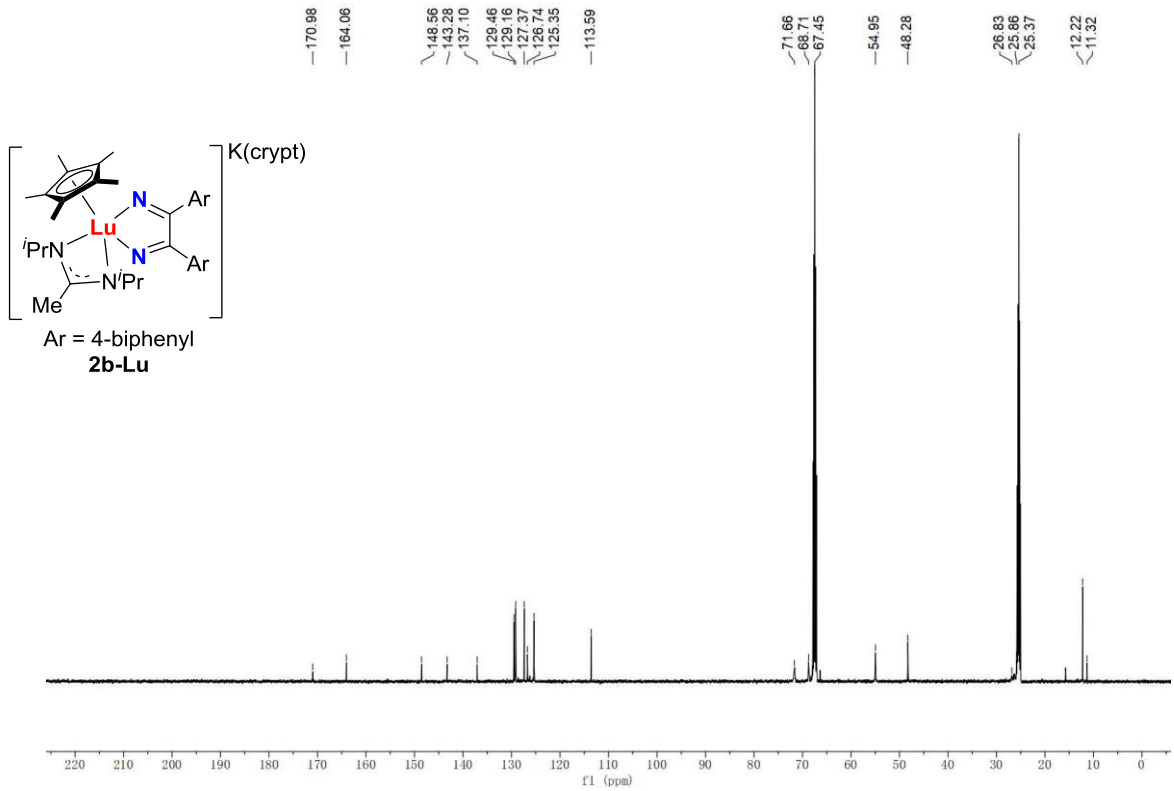


Figure S6. ^{13}C{^{1}H} NMR spectrum of **2b-Lu** (25 ℃, 126 MHz, d^{8}-THF).

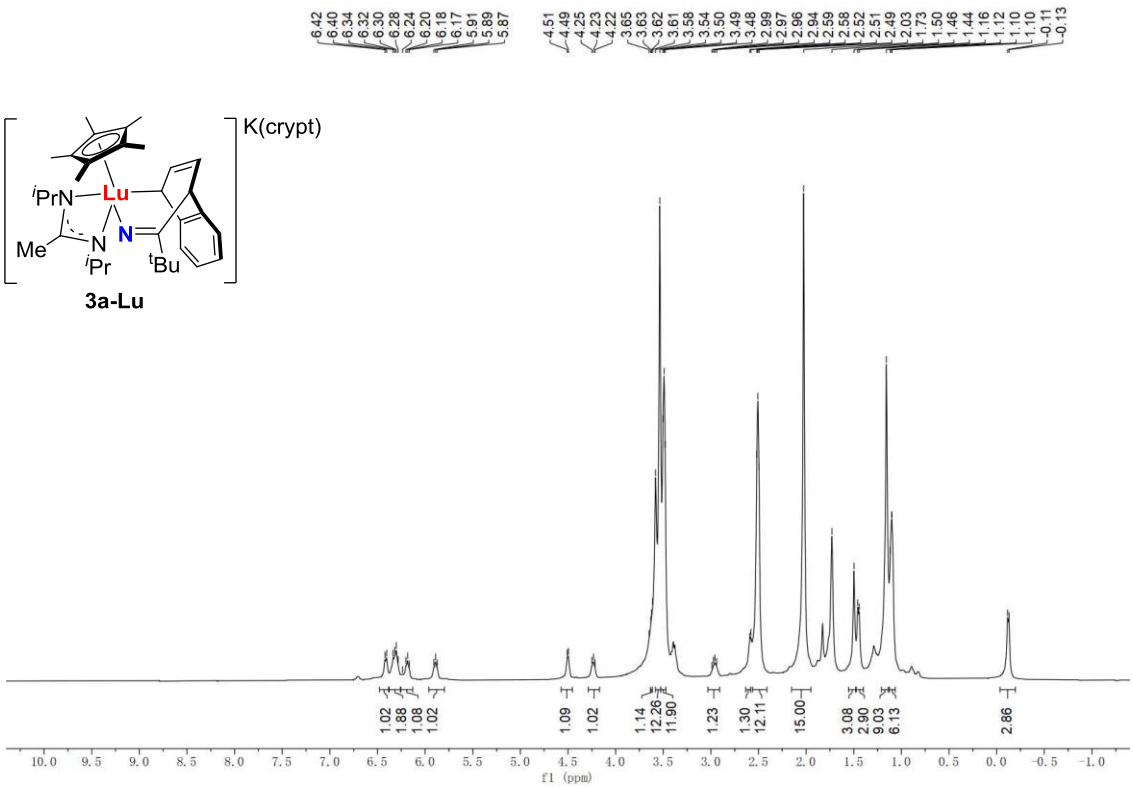


Figure S7. ^{1}H NMR spectrum of **3a-Lu** (25 ℃, 600 MHz, d^{8}-THF).

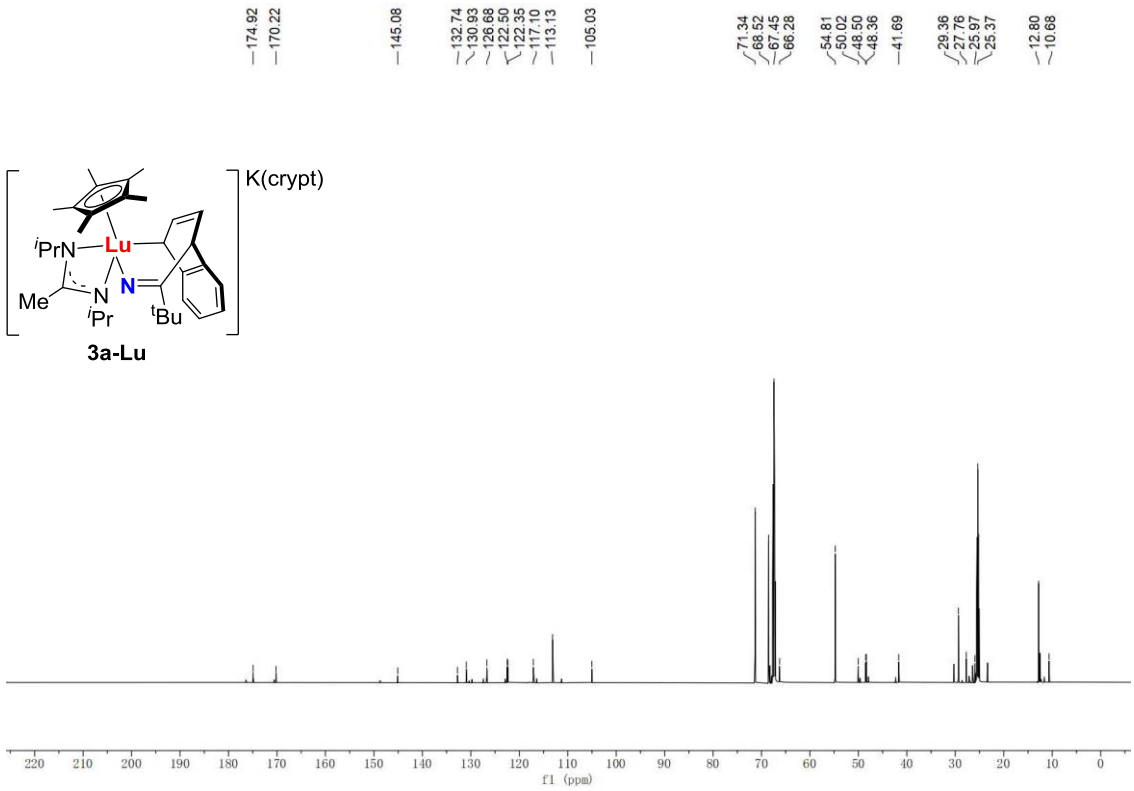


Figure S8. ^{13}C{^{1}H} NMR spectrum of **3a-Lu** (25 ℃, 151 MHz, d^{8}-THF).

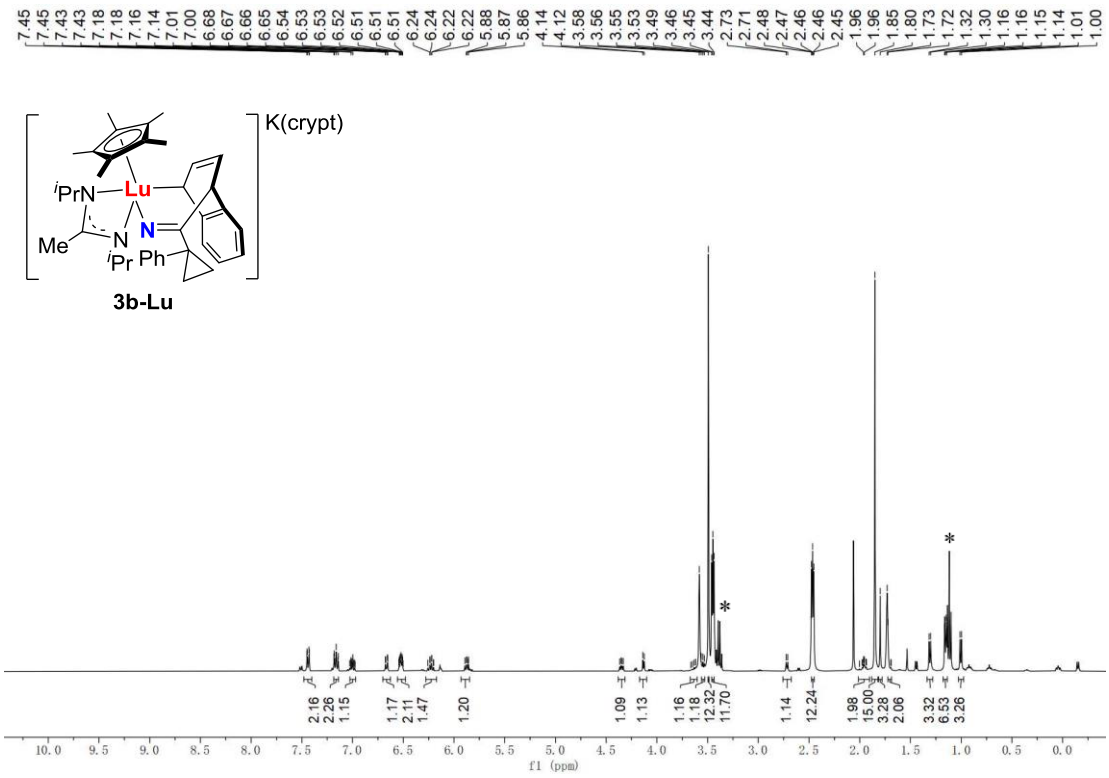


Figure S9. ^{1}H NMR spectrum of **3b-Lu** (25 ℃, 400 MHz, d^{8}-THF, "*" represents the residual Et_2O).

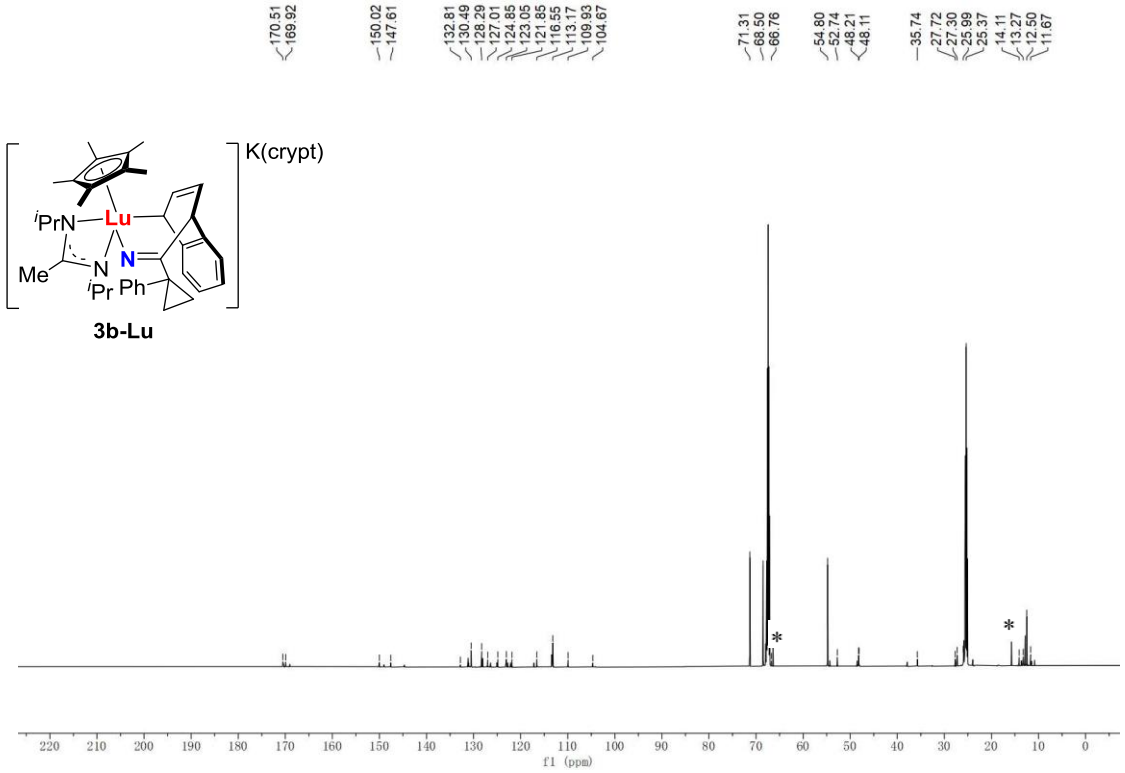


Figure S10. ^{13}C{^{1}H} NMR spectrum of **3b-Lu** (25 ℃, 151 MHz, d^{8}-THF, "*" represents the residual Et_2O).

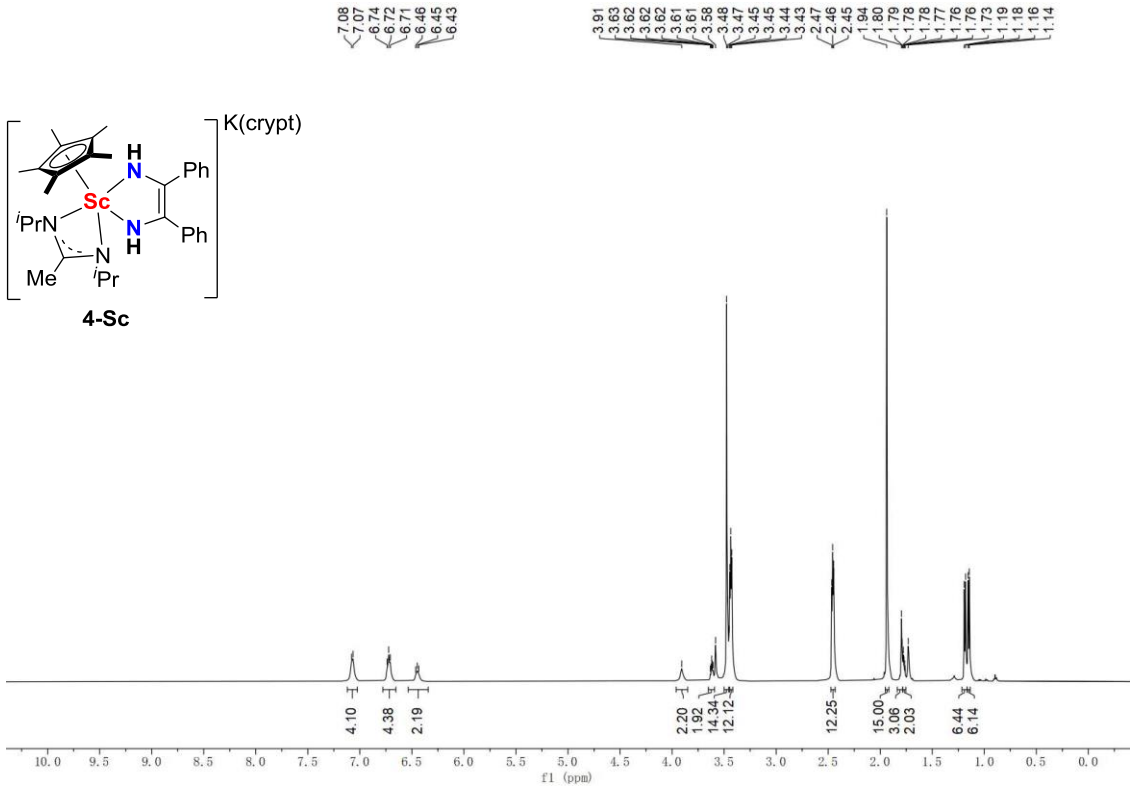


Figure S11. ^{1}H NMR spectrum of **4-Sc·0.5THF** (25 ℃, 500 MHz, d^{8}-THF).

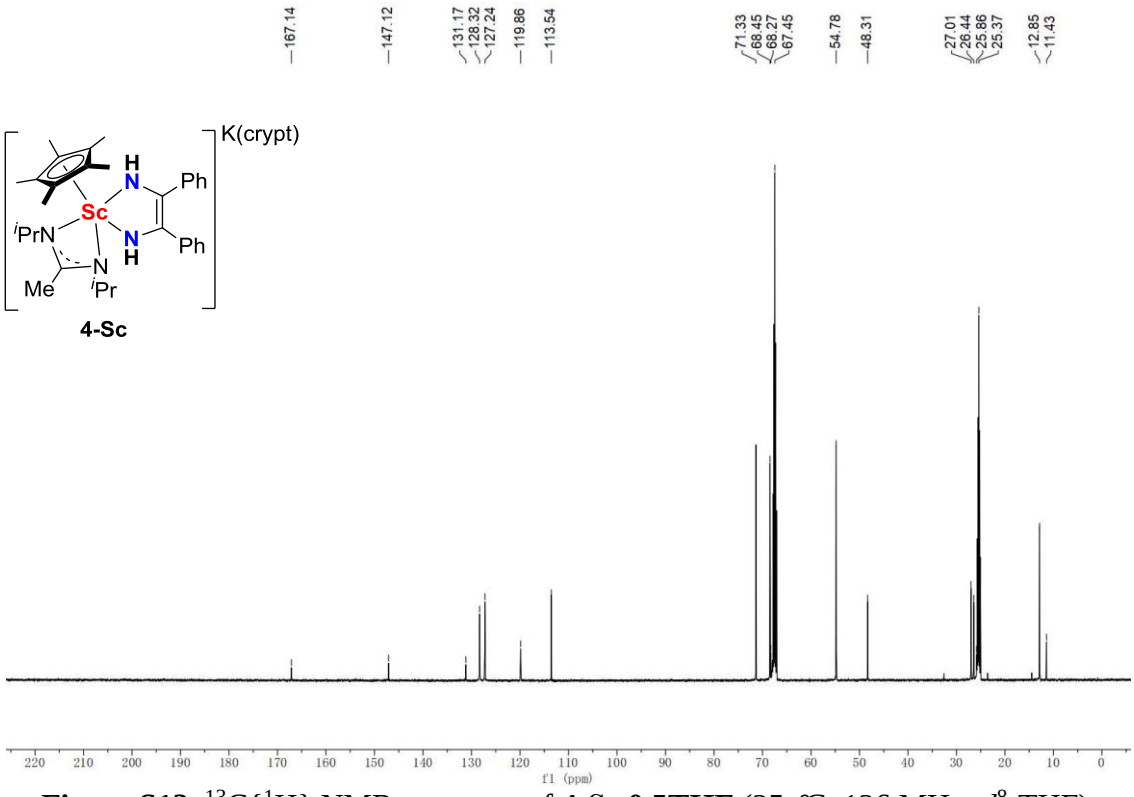


Figure S12. ^{13}C{^{1}H} NMR spectrum of **4-Sc·0.5THF** (25 ℃, 126 MHz, d^{8}-THF).

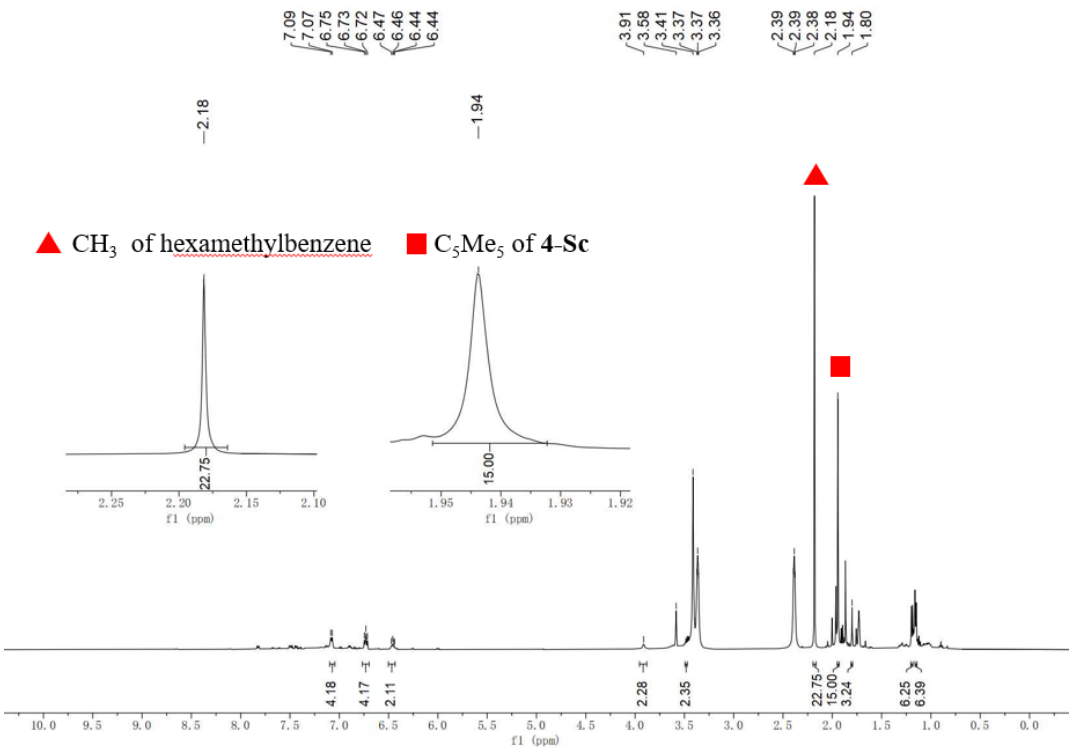


Figure S13. *In situ* ^{1}H NMR of the reaction of **2a-Sc** and H_2/N_2 (25 ℃, 500 MHz, d^8-THF).

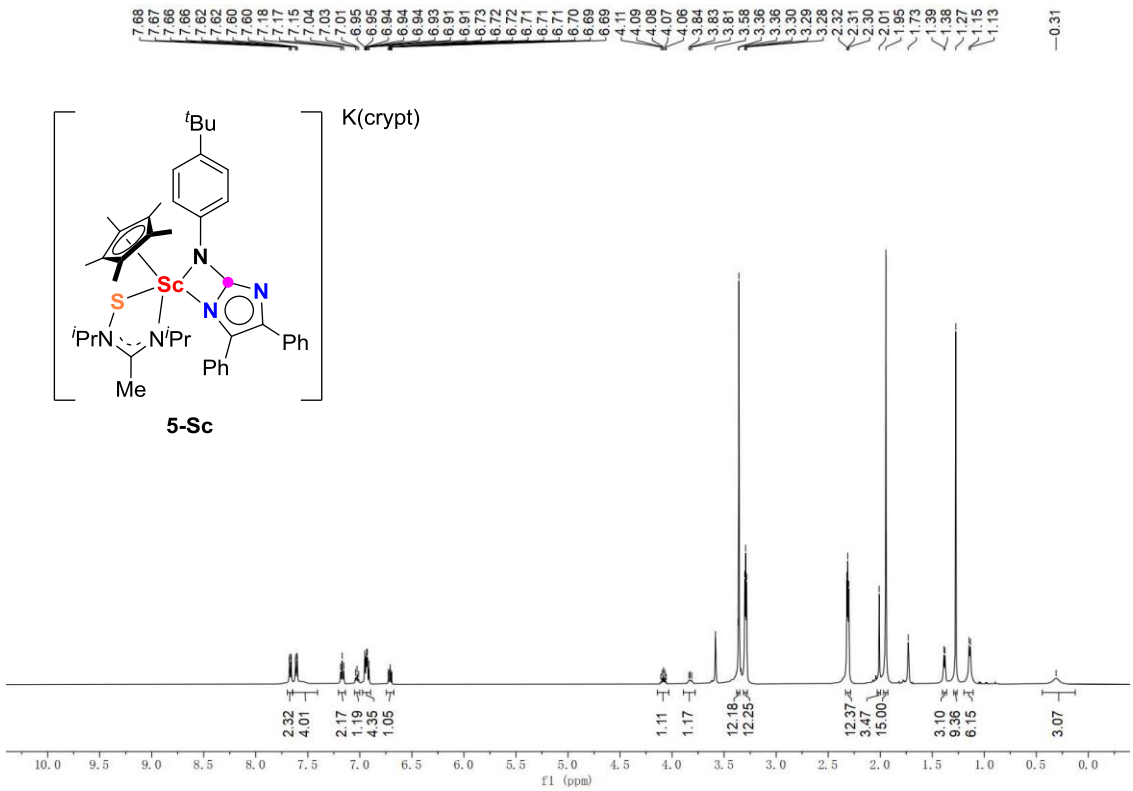


Figure S14. ^{1}H NMR spectrum of **5-Sc** (25 ℃, 500 MHz, d^8-THF).

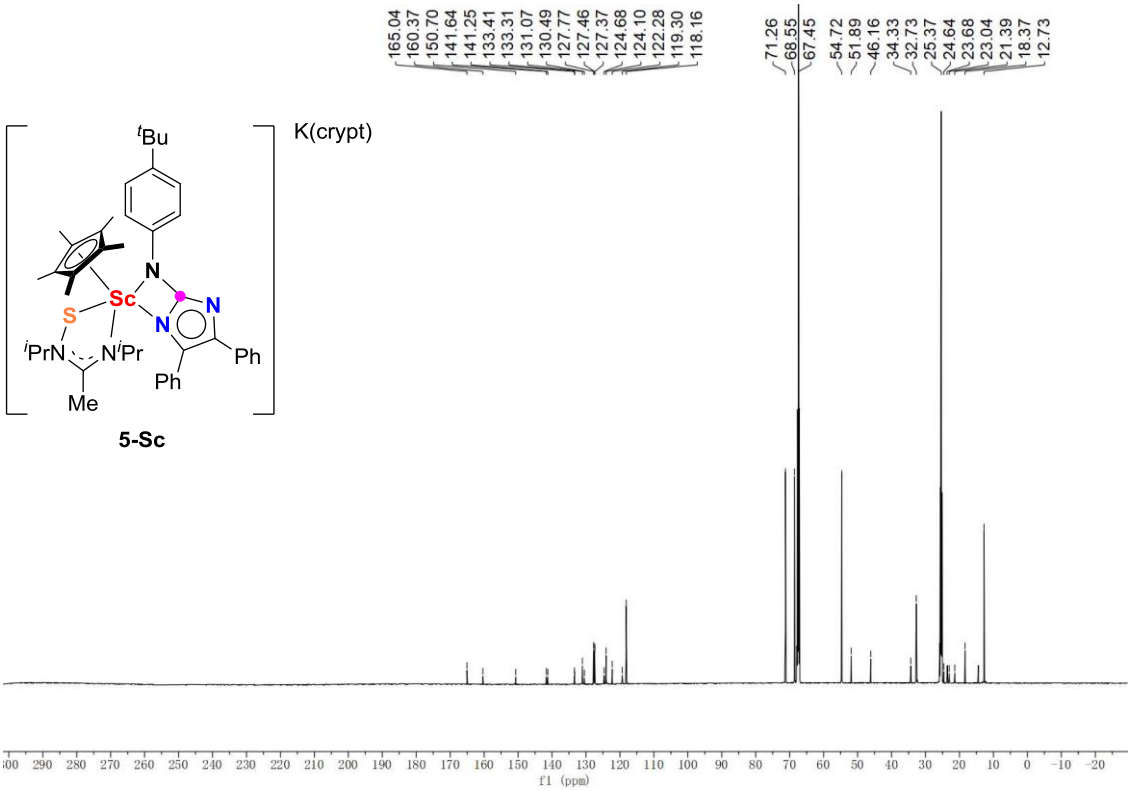


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **5-Sc** (25 ℃, 151 MHz, d^8-THF).

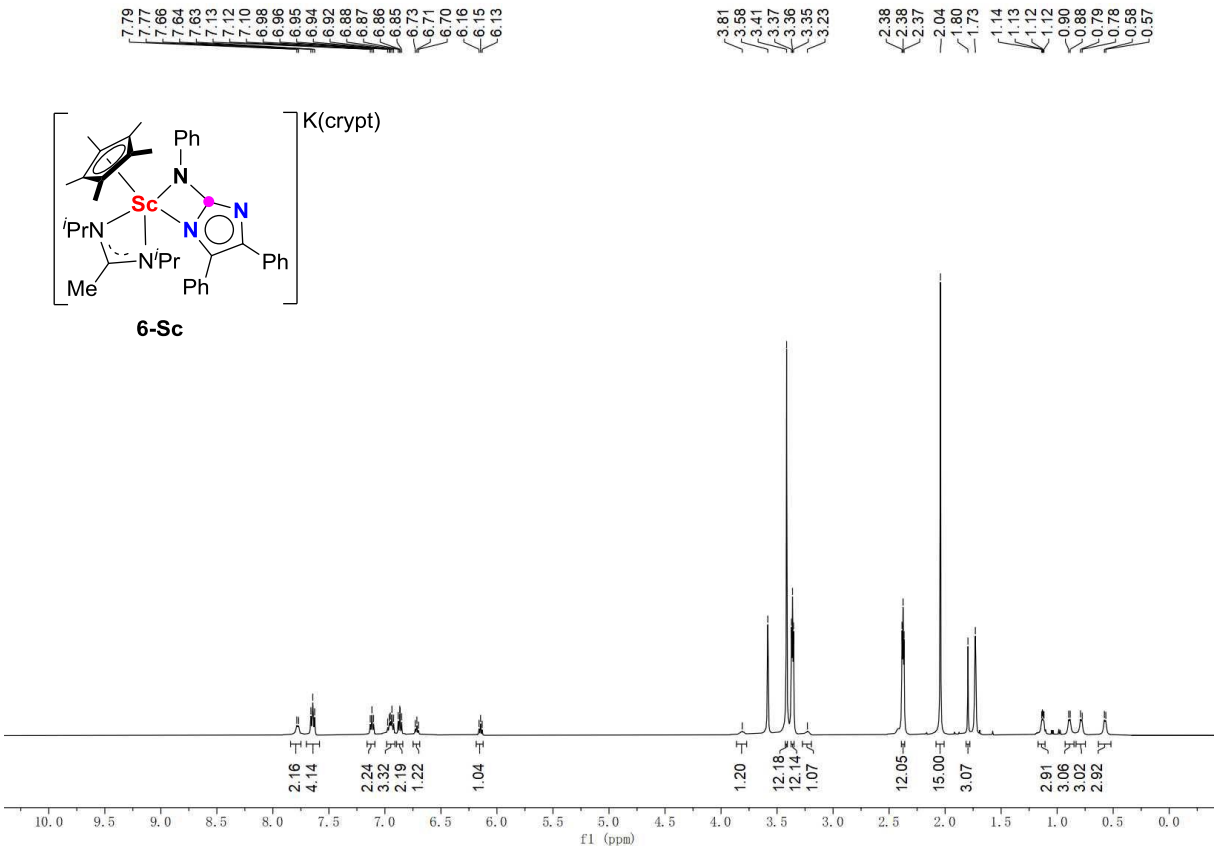


Figure S16. ^{1}H NMR spectrum of **6-Sc** (25 ℃, 500 MHz, d^8-THF).

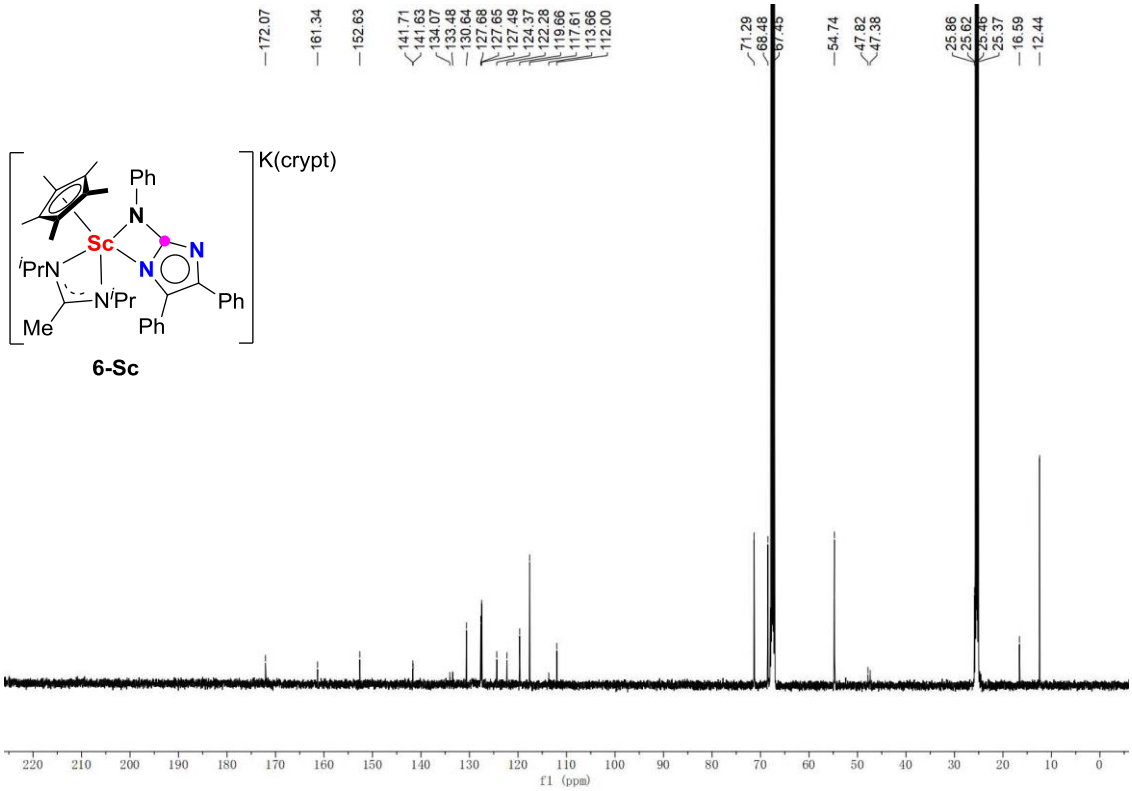


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **6-Sc** (25 ℃, 126 MHz, d^8-THF).

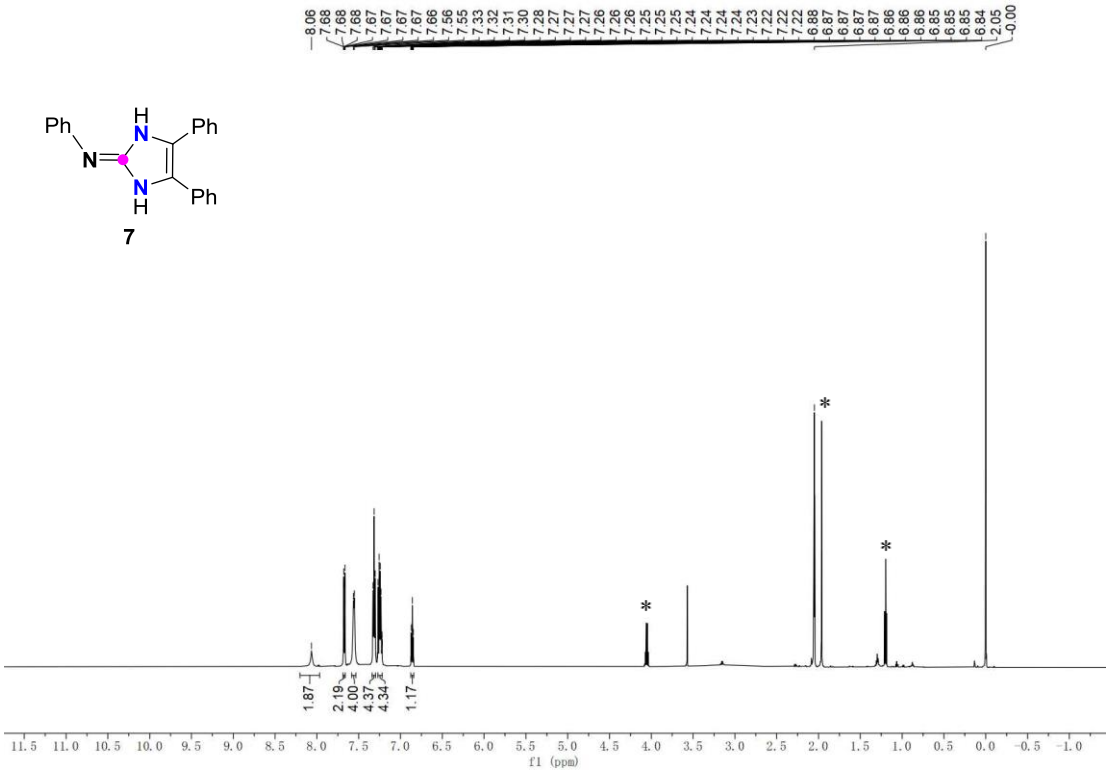


Figure S18. ^{1}H NMR spectrum of **7** (25 ℃, 600 MHz, d^6- Acetone, "*" represents the residual ethyl acetate).

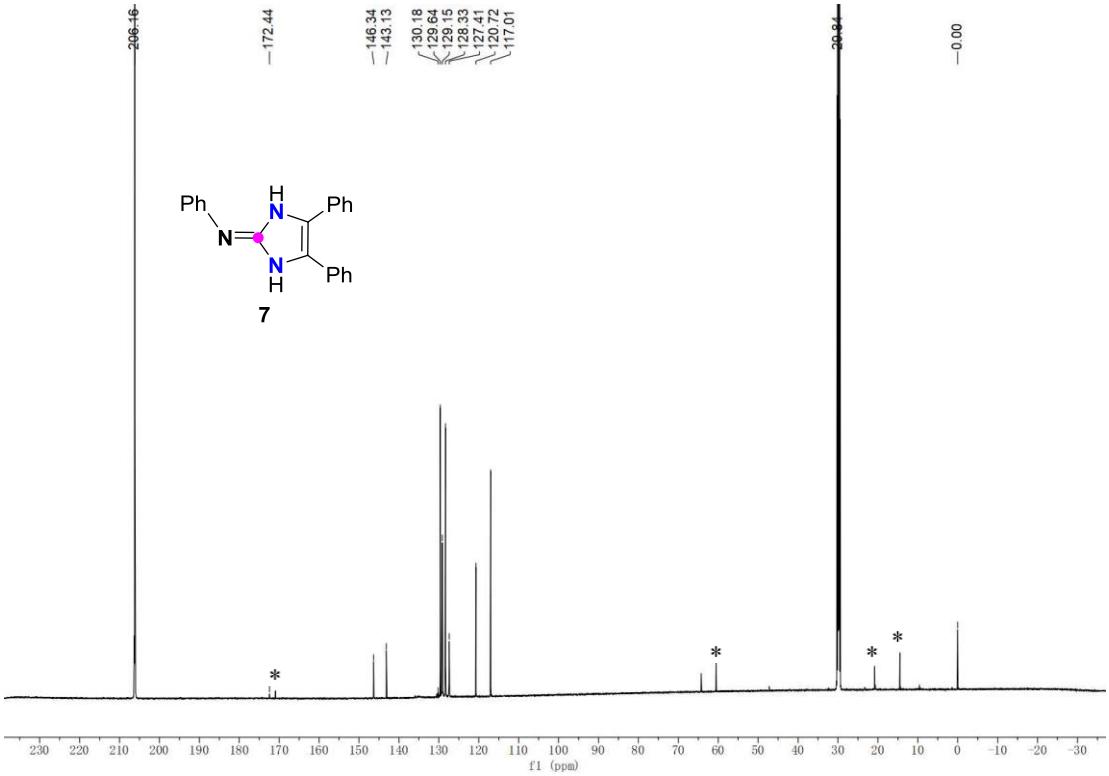


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **7** (25 ℃, 126 MHz, d^6- Acetone, "*" represents the residual ethyl acetate).

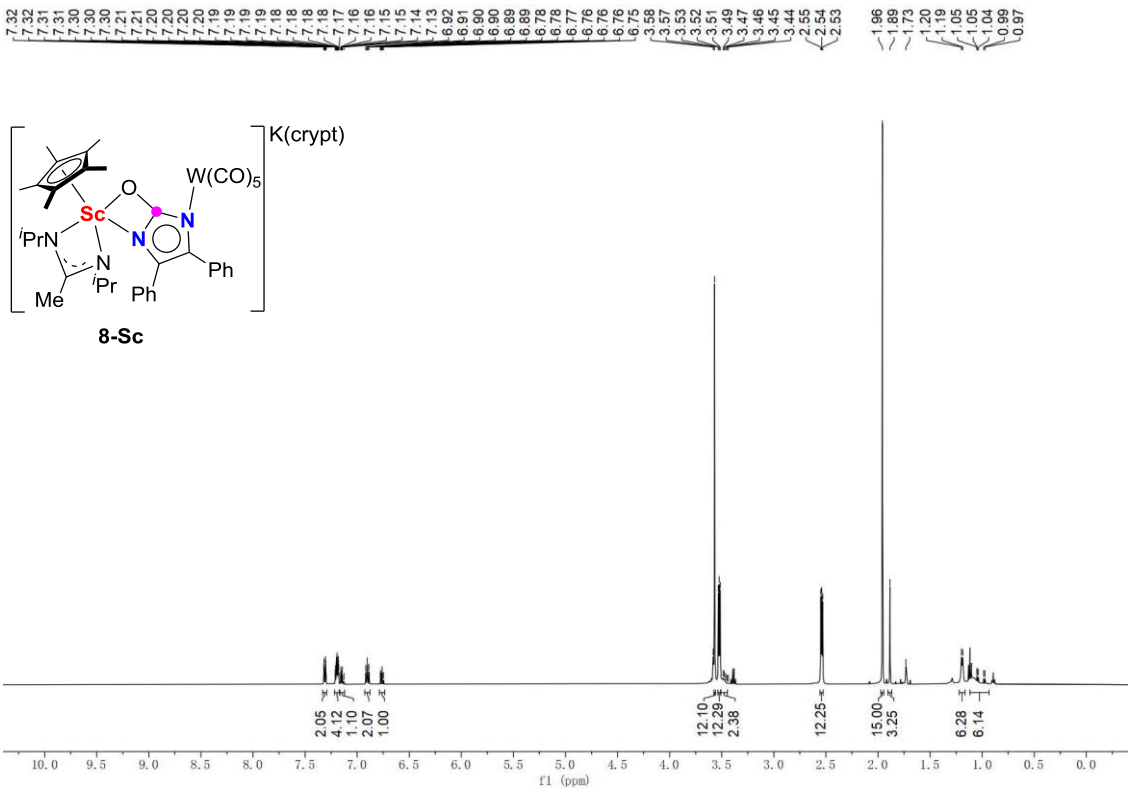


Figure S20. ^{1}H NMR spectrum of **8-Sc** (25 ℃, 500 MHz, d^8-THF).

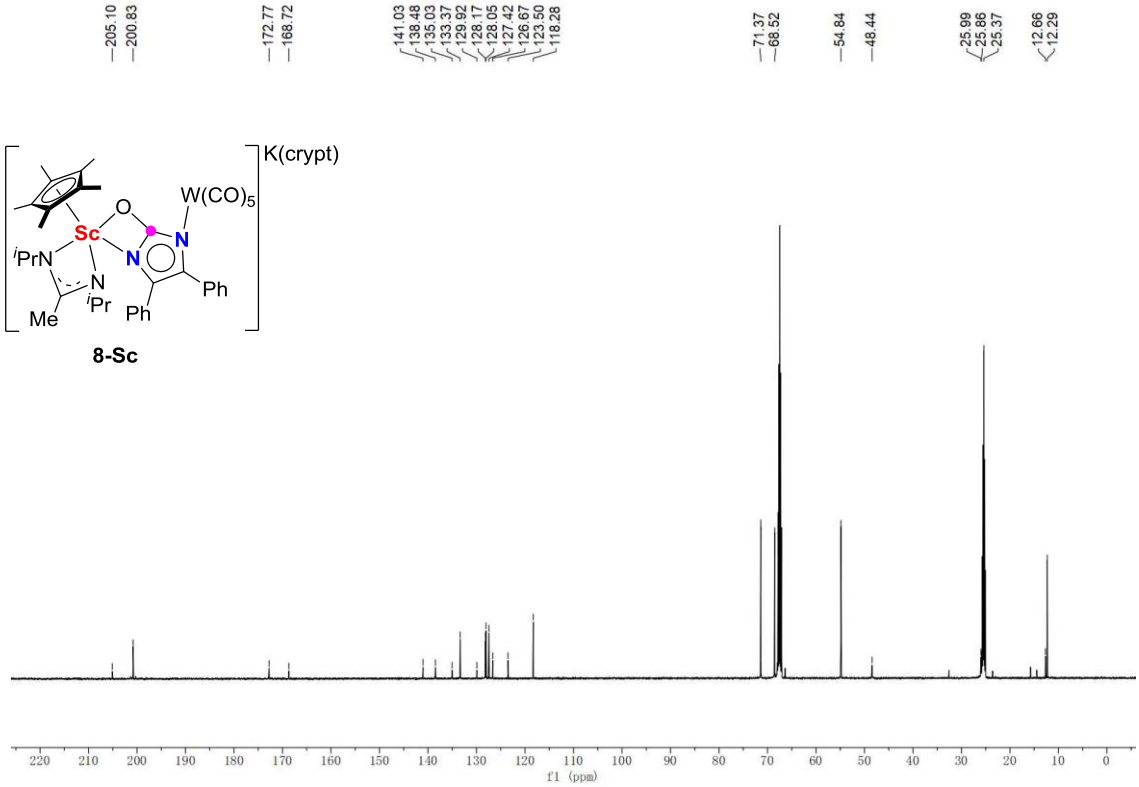


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **8-Sc** (25 ℃, 126 MHz, d^8-THF).

4) X-ray Crystallographic Studies

The single crystals of **2a-Sc**, **2b-Sc·THF, 2b-Lu·THF, 3a-Lu, 3b-Lu, 4-Sc·0.5THF, 5-Sc·THF, 6-Sc** and **8-Sc·THF** suitable for X-ray analysis were obtained as described in the experimental details. 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 2163492 (**2a-Sc**), CCDC 2163496 (**2b-Sc·THF**), CCDC 2163498 (**2b-Lu·THF**), CCDC 2163501 (**3a-Lu**), CCDC 2163502 (**3b-Lu**), CCDC 2163503 (**4-Sc·0.5THF**), CCDC 2163508 (**5-Sc·THF**), CCDC 2163510 (**6-Sc**), CCDC 2163511 (**8-Sc·THF**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

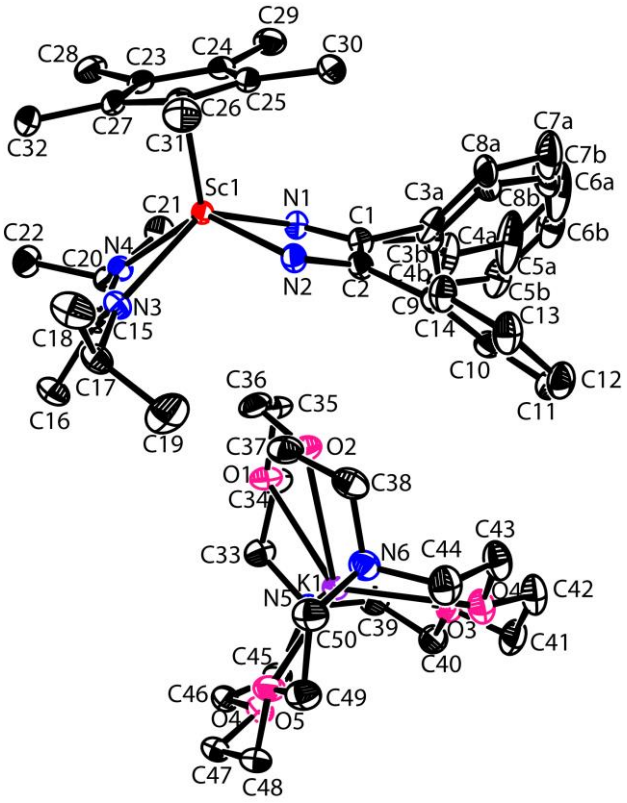


Figure S22. ORTEP drawing of **2a-Sc** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for 2a-Sc.

Identification code	**2a-Sc**
Empirical formula	$C_{50}H_{78}KN_6O_6Sc$
Formula weight	943.24
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.1547(3)
b/Å	17.8841(4)
c/Å	20.0564(4)
α/°	90
β/°	90.467(2)
γ/°	90
Volume/Å^3	5794.3(2)
Z	4
ρ_{calc}g/cm^3	1.081
μ/mm^{-1}	0.245
F(000)	2032.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/ °	3.968 to 54.968
Index ranges	-20 ≤ h ≤ 20, -21 ≤ k ≤ 23, -25 ≤ l ≤ 26

Reflections collected	66442
Independent reflections	13242 [R_{int} = 0.0259, R_{sigma} = 0.0224]
Data/restraints/parameters	13242/18/658
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0970
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1016
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.21

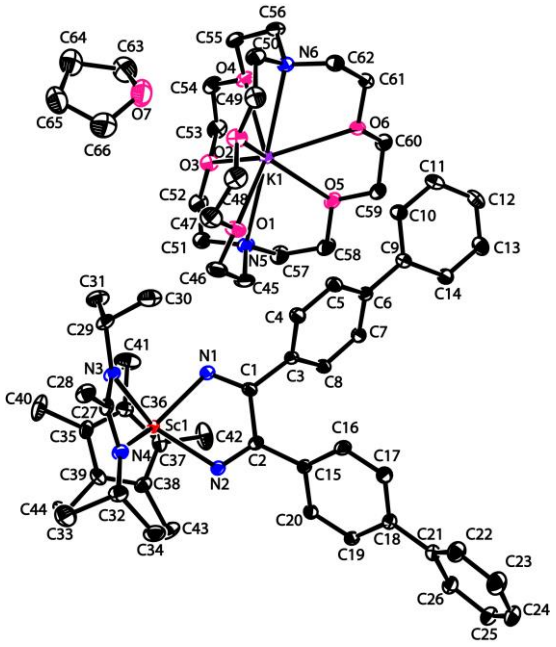


Figure S23. ORTEP drawing of **2b-Sc·THF**, with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for 2b-Sc·THF.

Identification code	**2b-Sc·THF**
Empirical formula	$C_{66}H_{94}KN_6O_7Sc$
Formula weight	1167.53
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3366(4)
b/Å	17.1251(5)
c/Å	18.0626(5)
α/°	88.915(2)
β/°	75.361(3)
γ/°	71.712(3)
Volume/$Å^3$	3214.51(18)
Z	2
ρ_{calc}g/cm^3	1.206

μ/mm^{-1}	0.235
F(000)	1256.0
Crystal size/mm^3	0.02 × 0.01 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/ °	4.672 to 54.97
Index ranges	-14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -23 ≤ l ≤ 23
Reflections collected	45235
Independent reflections	14628 [R_{int} = 0.0440, R_{sigma} = 0.0467]
Data/restraints/parameters	14628/0/740
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1348
Final R indexes [all data]	R_1 = 0.0710, wR_2 = 0.1453
Largest diff. peak/hole / e Å^{-3}	0.46/-0.28

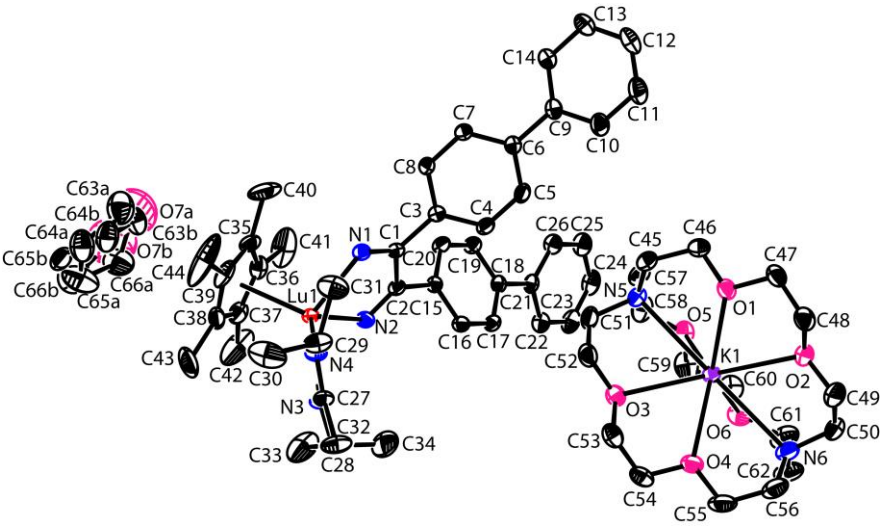


Figure S24. ORTEP drawing of **2b-Lu·THF** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for 2b-Lu·THF.

Identification code	**2b-Lu·THF**
Empirical formula	$C_{66}H_{94}KLuN_6O_7$
Formula weight	1297.54
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3091(3)
b/Å	16.7804(3)
c/Å	18.9103(4)
α/°	82.925(2)
β/°	75.666(2)
γ/°	70.712(2)

Volume/Å^3	3278.39(14)
Z	2
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	1.624
F(000)	1356.0
Crystal size/mm^3	0.2 ×0.1 ×0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.17 to 52.044
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	66539
Independent reflections	12846 [R_{int} = 0.0314, R_{sigma} = 0.0222]
Data/restraints/parameters	12846/81/786
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0265, wR_2 = 0.0670
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0684
Largest diff. peak/hole / e Å^{-3}	1.04/-0.46

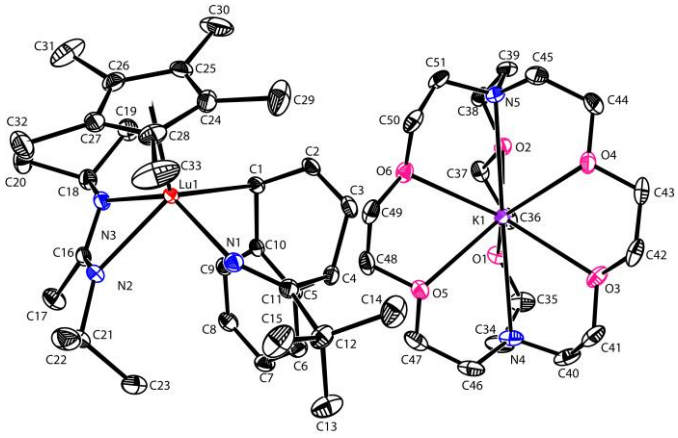


Figure S25. ORTEP drawing of **3a-Lu** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for 3a-Lu.

Identification code	**3a-Lu**
Empirical formula	$C_{51}H_{85}KLuN_5O_6$
Formula weight	1078.30
Temperature/K	180.01(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.4894(4)
b/Å	16.0831(3)
c/Å	31.2872(5)
α/°	90

β/°	97.900(2)
γ/°	90
Volume/Å^3	11209.2(3)
Z	8
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	1.883
F(000)	4512.0
Crystal size/mm^3	0.2 ×0.2 ×0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.2 to 54.968
Index ranges	-29 ≤ h ≤ 29, -20 ≤ k ≤ 19, -40 ≤ l ≤ 40
Reflections collected	91968
Independent reflections	12830 [R_{int} = 0.0310, R_{sigma} = 0.0203]
Data/restraints/parameters	12830/0/590
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0214, wR_2 = 0.0512
Final R indexes [all data]	R_1 = 0.0243, wR_2 = 0.0520
Largest diff. peak/hole / e Å^{-3}	0.81/-1.12

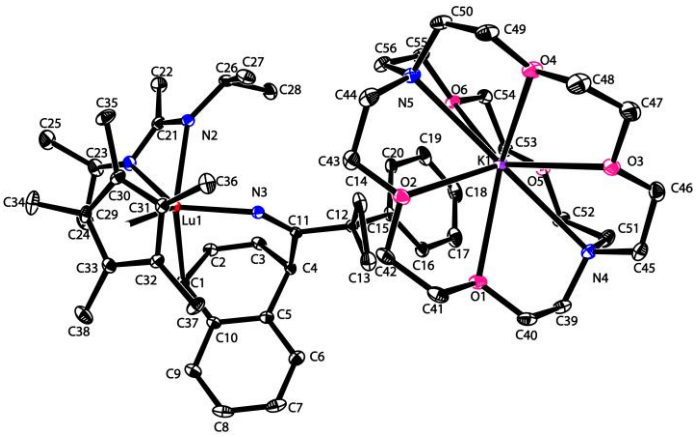


Figure S26. ORTEP drawing of **3b-Lu** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S5. Crystal data and structure refinement for 3b-Lu.

Identification code	**3b-Lu**
Empirical formula	$C_{56}H_{85}KLuN_5O_6$
Formula weight	1138.35
Temperature/K	120.02(12)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.0174(2)
b/Å	30.4304(5)

c/Å	15.4433(3)
α/°	90
β/°	90.3280(10)
γ/°	90
Volume/Å^3	5647.43(17)
Z	4
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	1.873
F(000)	2376.0
Crystal size/mm^3	0.2 ×0.1 ×0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.32 to 54.968
Index ranges	-15 ⩽ h ⩽ 15, -39 ⩽ k ⩽ 39, -20 ⩽ l ⩽ 19
Reflections collected	101197
Independent reflections	12944 [R_{int} = 0.0311, R_{sigma} = 0.0191]
Data/restraints/parameters	12944/0/632
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0186, wR_2 = 0.0404
Final R indexes [all data]	R_1 = 0.0216, wR_2 = 0.0411
Largest diff. peak/hole / e Å^{-3}	0.43/-0.54

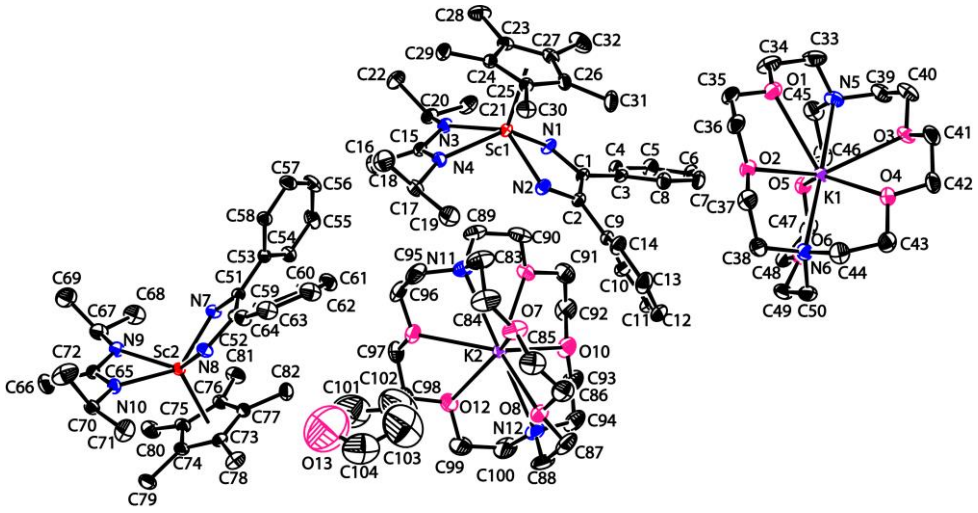


Figure S27. ORTEP drawing of **4-Sc·0.5THF** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for 4-Sc·0.5THF

Identification code	**4-Sc·0.5THF**
Empirical formula	$C_{104}H_{168}K_2N_{12}O_{13}Sc_2$
Formula weight	1962.61
Temperature/K	179.99(10)
Crystal system	triclinic

Space group	P-1
a/Å	10.0236(2)
b/Å	20.0100(3)
c/Å	28.1102(5)
α/°	89.1040(10)
β/°	81.5760(10)
γ/°	86.1240(10)
Volume/Å^3	5564.45(17)
Z	2
ρ_{calc}g/cm^3	1.171
μ/mm^{-1}	0.258
F(000)	2120.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.164 to 54.968
Index ranges	-13 ≤ h ≤ 12, -25 ≤ k ≤ 25, -35 ≤ l ≤ 36
Reflections collected	92797
Independent reflections	25412 [R_{int} = 0.0456, R_{sigma} = 0.0454]
Data/restraints/parameters	25412/2710/1258
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.1104
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1173
Largest diff. peak/hole / e Å^{-3}	0.32/-0.29

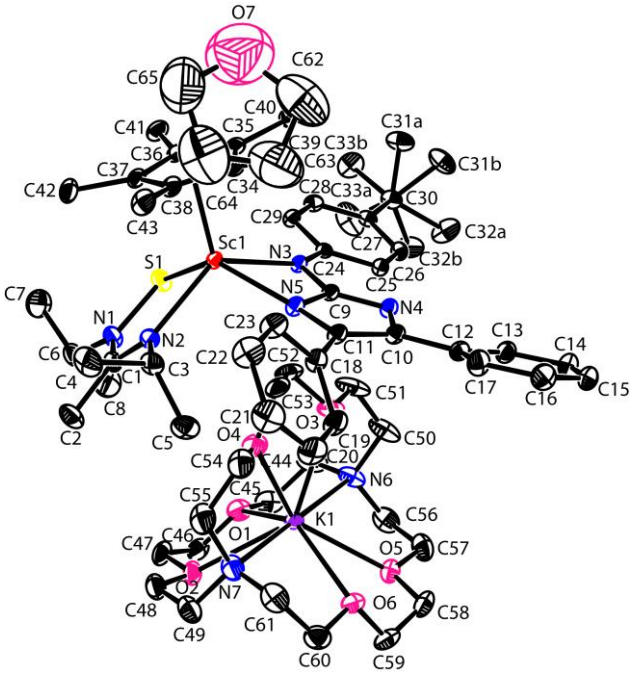


Figure S28. ORTEP drawing of **5-Sc·THF** with 30% thermal ellipsoids. H atoms are omitted

for clarity.

Table S7. Crystal data and structure refinement for 5-Sc·THF.

Identification code	**5-Sc·THF**
Empirical formula	$C_{65}H_{99}KN_7O_7SSc$
Formula weight	1206.63
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.7515(3)
b/Å	16.1744(5)
c/Å	17.9918(4)
α/°	85.841(2)
β/°	86.772(2)
γ/°	74.600(2)
Volume/Å^3	3565.47(16)
Z	2
ρ_{calc}g/cm^3	1.124
μ/mm^{-1}	0.242
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/°	4.142 to 54.964
Index ranges	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -23 ≤ l ≤ 21
Reflections collected	66866
Independent reflections	16330 [R_{int} = 0.0302, R_{sigma} = 0.0289]
Data/restraints/parameters	16330/96/783
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0551, wR_2 = 0.1286
Largest diff. peak/hole / e Å^{-3}	0.41/-0.43

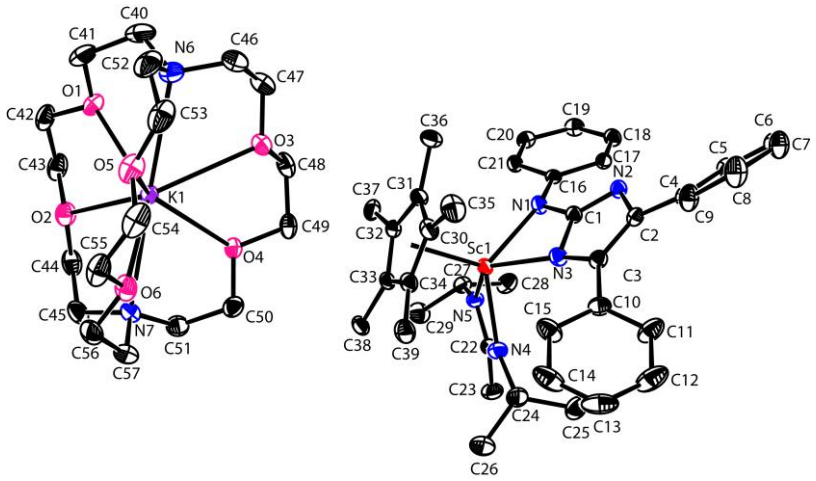


Figure S29. ORTEP drawing of **6-Sc** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S8. Crystal data and structure refinement for 6-Sc.

Identification code	**6-Sc**
Empirical formula	$C_{57}H_{81}KN_7O_6Sc$
Formula weight	1044.34
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.0310(4)
b/Å	16.3699(5)
c/Å	20.8212(6)
α/°	90
β/°	91.375(2)
γ/°	90
Volume/Å^3	5803.2(3)
Z	4
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	0.251
F(000)	2240.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/ °	3.996 to 54.97
Index ranges	-22 ≤ h ≤ 22, -17 ≤ k ≤ 21, -27 ≤ l ≤ 24
Reflections collected	66471
Independent reflections	13246 [R_{int} = 0.0273, R_{sigma} = 0.0225]
Data/restraints/parameters	13246/0/670
Goodness-of-fit on F^2	1.034

Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0511, wR_2 = 0.1162
Largest diff. peak/hole / e Å^{-3}	0.66/-0.29

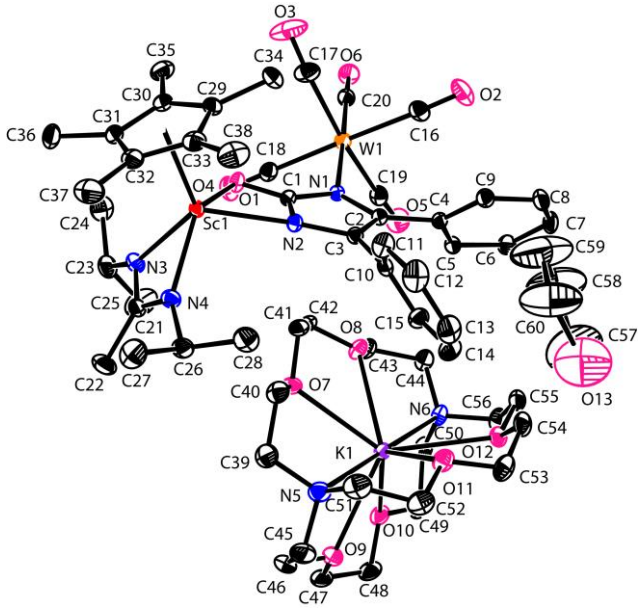


Figure S30. ORTEP drawing of **8-Sc·THF** with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table S9. Crystal data and structure refinement for 8-Sc·THF.

Identification code	**8-Sc·THF**
Empirical formula	$C_{60}H_{86}KN_6O_{13}ScW$
Formula weight	1367.25
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.1928(2)
b/Å	13.2264(3)
c/Å	24.7839(6)
α/°	99.878(2)
β/°	97.836(2)
γ/°	95.700(2)
Volume/Å^3	3235.07(13)
Z	2
ρ_{calc}g/cm^3	1.404
μ/mm^{-1}	2.009
F(000)	1412.0
Crystal size/mm^3	0.2 ×0.1 ×0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.82 to 54.968

Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -29 ≤ l ≤ 32
Reflections collected	62494
Independent reflections	14679 [R_{int} = 0.0313, R_{sigma} = 0.0288]
Data/restraints/parameters	14679/70/749
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0264, wR_2 = 0.0625
Final R indexes [all data]	R_1 = 0.0313, wR_2 = 0.0640
Largest diff. peak/hole / e $Å^{-3}$	0.88/-0.69

5) Details of DFT Calculations

All calculations were carried out with GAUSSIAN 16 program package.[7] The structures were optimized at BP86-D3 level[8,9] using the Def2SVP basis set[10] in gas phase. The effect of solvent was examined by performing single-point self-consistent reaction field (SCRF) calculations based on the solvation model density (SMD)[11] for gas-phase optimized structures. THF was used as solvent, and solvation free energies (ΔG_{sol}) were calculated at BP86-D3/LANL2TZ+ (for Sc)/6-311+G(d,p) (for other elements) level,[12,13] by adding the solvation energies to the computed gas phase relative free energies (ΔG_{gas}). Harmonic frequency calculations were performed at the same level for every structure to confirm it as a local minimum and to derive the thermochemical corrections for enthalpies and free energies. The intrinsic reaction coordinate (IRC) analysis was carried out throughout the pathways to confirm that all stationary points are smoothly connected to each other. All enthalpies and the Gibbs free energies in the text were given in Hartree. All distances were given in Å.

1-Sc

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.628867
Thermal correction to Gibbs Free Energy = 0.529042
Sum of electronic and thermal Enthalpies = -1960.051761
Sum of electronic and thermal Free Energies = -1960.151586
298 K, in THF
Sum of electronic and thermal Free Energies = -1247.180466

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	21	0	-0.072055	-0.013752	-0.080209
2	7	0	-1.939499	1.208650	-0.662372
3	7	0	-2.026511	-1.045567	-0.767501

4	6	0	1.438566	-1.325516	-1.420810
5	1	0	1.427146	-2.429474	-1.407435
6	6	0	2.751671	-0.681311	-1.224223
7	6	0	0.524696	-0.642824	-2.337582
8	1	0	-0.176749	-1.195463	-2.984263
9	6	0	0.513470	0.747152	-2.301109
10	1	0	-0.196399	1.321674	-2.918551
11	6	0	1.043880	-1.050091	1.959945
12	6	0	2.748898	0.759043	-1.218216
13	6	0	-0.366033	-1.205544	2.150197
14	6	0	3.968684	-1.361301	-1.005553
15	1	0	3.970609	-2.465566	-1.012361
16	6	0	1.336598	0.352726	1.996378
17	6	0	-2.618641	0.123567	-1.058490
18	6	0	1.424627	1.395115	-1.354916
19	1	0	1.405334	2.497415	-1.303599
20	6	0	-0.950595	0.093531	2.293445
21	6	0	5.169227	0.748121	-0.764308
22	1	0	6.097794	1.309185	-0.561266
23	6	0	3.966213	1.445626	-1.035797
24	1	0	3.960048	2.550080	-1.044942
25	6	0	5.168873	-0.653788	-0.741315
26	1	0	6.097269	-1.209102	-0.522436
27	6	0	0.104380	1.059032	2.197202
28	6	0	-2.452641	2.550249	-0.877791
29	1	0	-3.049265	2.602274	-1.825137
30	6	0	-2.564704	-2.315960	-1.229118
31	1	0	-2.920581	-2.233321	-2.290884
32	6	0	2.046748	-2.165378	1.858778
33	1	0	1.625307	-3.041304	1.322312
34	1	0	2.381291	-2.516795	2.863309
35	1	0	2.945234	-1.847695	1.293282
36	6	0	-1.103036	-2.498576	2.347259
37	1	0	-2.111833	-2.461071	1.890849
38	1	0	-1.239748	-2.728934	3.430703
39	1	0	-0.563466	-3.359023	1.901152
40	6	0	-2.415359	0.334649	2.537084
41	1	0	-2.639173	1.410226	2.673610
42	1	0	-2.769199	-0.198540	3.449177
43	1	0	-3.031422	-0.026341	1.683644
44	6	0	2.705712	0.971232	1.996630
45	1	0	3.453217	0.327114	1.494111
46	1	0	3.059811	1.158658	3.038214
47	1	0	2.721641	1.939756	1.458021
48	6	0	-3.776158	-2.784351	-0.387537
49	1	0	-3.461902	-2.984651	0.657416
50	1	0	-4.220244	-3.717635	-0.799914
51	1	0	-4.570399	-2.010707	-0.351214
52	6	0	-1.297846	3.552037	-1.033146
53	1	0	-0.615596	3.482972	-0.163262

54	1	0	-1.679391	4.593197	-1.107217
55	1	0	-0.698954	3.330941	-1.937483
56	6	0	-0.004648	2.547454	2.382258
57	1	0	0.681496	3.090718	1.698895
58	1	0	0.259405	2.857922	3.420858
59	1	0	-1.030486	2.915407	2.179920
60	6	0	-3.399071	2.993068	0.261765
61	1	0	-4.209925	2.253073	0.422496
62	1	0	-3.862778	3.981008	0.045127
63	1	0	-2.835652	3.076199	1.213482
64	6	0	-3.927603	0.236944	-1.837539
65	1	0	-3.817689	0.959982	-2.672607
66	1	0	-4.745925	0.614847	-1.189335
67	1	0	-4.249871	-0.729002	-2.266931
68	6	0	-1.464962	-3.389979	-1.224866
69	1	0	-0.661618	-3.138372	-1.942317
70	1	0	-1.878471	-4.386196	-1.491870
71	1	0	-0.999315	-3.455821	-0.221803

PhCN
298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.103599
Thermal correction to Gibbs Free Energy = 0.065982
Sum of electronic and thermal Enthalpies = -324.155885
Sum of electronic and thermal Free Energies = -324.193502
298 K, in THF
Sum of electronic and thermal Free Energies = -324.522432

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.055752	-0.000004	-0.000013
2	7	0	-3.230621	0.000003	-0.000046
3	6	0	-0.617919	-0.000000	-0.000003
4	6	0	0.091644	-1.226677	0.000003
5	6	0	0.091644	1.226677	0.000003
6	6	0	1.493886	-1.219203	0.000016
7	1	0	-0.465913	-2.175221	-0.000001
8	6	0	1.493885	1.219204	0.000016
9	1	0	-0.465913	2.175222	-0.000001
10	6	0	2.196217	0.000000	0.000022
11	1	0	2.043481	-2.173342	0.000021
12	1	0	2.043481	2.173343	0.000021
13	1	0	3.297573	0.000000	0.000031

ad1

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.734505
Thermal correction to Gibbs Free Energy = 0.616887
Sum of electronic and thermal Enthalpies = -2284.240225
Sum of electronic and thermal Free Energies = -2284.357843
298 K, in THF
Sum of electronic and thermal Free Energies = -1571.698772

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.269749	-1.688557	0.191671
2	6	0	-5.691815	-0.524390	0.747513
3	6	0	-4.307581	-0.340206	0.781953
4	6	0	-3.432234	-1.341026	0.223048
5	6	0	-4.027837	-2.532191	-0.328286
6	6	0	-5.412279	-2.688050	-0.337411
7	6	0	-2.045494	-1.140714	0.194379
8	7	0	-0.857920	-1.054640	0.340168
9	6	0	-2.318231	0.135772	-2.133166
10	6	0	-1.085995	-0.391264	-2.558789
11	6	0	0.121522	0.261856	-2.265698
12	6	0	0.139302	1.526488	-1.565141
13	6	0	-1.139510	2.182415	-1.315071
14	6	0	-2.374586	1.457014	-1.549560
15	6	0	-3.611488	2.079662	-1.226432
16	6	0	-3.663842	3.394166	-0.725686
17	6	0	-2.472389	4.129326	-0.583795
18	6	0	-1.236234	3.534088	-0.894182
19	21	0	0.997475	-0.015938	0.177712
20	6	0	2.469761	1.074171	1.911457
21	6	0	1.395135	1.989615	1.672993
22	6	0	0.183657	1.363227	2.128455
23	6	0	0.522486	0.074260	2.660481
24	6	0	1.933437	-0.110360	2.512395
25	6	0	1.568079	3.408809	1.203301
26	6	0	3.935481	1.355632	1.757672
27	6	0	-1.208232	1.939114	2.102861
28	6	0	2.761755	-1.278202	2.975738
29	6	0	-0.434798	-0.859513	3.348825
30	7	0	1.932133	-2.009549	-0.254386
31	6	0	1.501329	-3.400707	-0.290117
32	6	0	0.915667	-3.803293	1.072808
33	7	0	3.045204	-0.203385	-1.021582
34	6	0	4.028249	0.463324	-1.867481
35	6	0	3.659751	1.941787	-2.055448
36	6	0	2.901721	-1.537902	-1.048849
37	6	0	3.733191	-2.472155	-1.926993

38	6	0	0.467722	-3.637569	-1.414259
39	6	0	5.476198	0.340219	-1.333261
40	1	0	1.023823	2.177582	-1.643515
41	1	0	1.069556	-0.156715	-2.641682
42	1	0	-1.057967	-1.366969	-3.070979
43	1	0	-0.308563	4.119752	-0.800041
44	1	0	-3.262459	-0.373805	-2.376081
45	1	0	-4.635957	3.851567	-0.476687
46	1	0	-4.540217	1.512179	-1.396329
47	1	0	-2.502992	5.175347	-0.234100
48	1	0	2.375734	-4.073009	-0.483445
49	1	0	4.027640	0.010720	-2.894548
50	1	0	2.001319	3.474827	0.181457
51	1	0	2.246260	3.976691	1.880020
52	1	0	0.598937	3.941590	1.175339
53	1	0	4.482497	0.454187	1.416972
54	1	0	4.389024	1.678824	2.724782
55	1	0	4.127633	2.160931	1.020772
56	1	0	2.130251	-2.064263	3.435037
57	1	0	3.515913	-0.969629	3.735407
58	1	0	3.307755	-1.747302	2.128470
59	1	0	-1.203685	3.022537	1.878109
60	1	0	-1.725166	1.787940	3.074886
61	1	0	-1.839072	1.475036	1.314311
62	1	0	5.596200	0.912162	-0.392292
63	1	0	6.207695	0.734651	-2.072887
64	1	0	5.741502	-0.715182	-1.117978
65	1	0	-0.420323	-2.999415	-1.237317
66	1	0	0.149281	-4.702240	-1.458055
67	1	0	0.879495	-3.357197	-2.406522
68	1	0	-1.459843	-0.767976	2.939186
69	1	0	-0.486413	-0.648015	4.442361
70	1	0	-0.134276	-1.919458	3.226635
71	1	0	1.678850	-3.710567	1.870474
72	1	0	0.546475	-4.850969	1.055857
73	1	0	0.071620	-3.129393	1.323210
74	1	0	3.075113	-3.117552	-2.542789
75	1	0	4.349756	-3.144390	-1.293883
76	1	0	4.410569	-1.928843	-2.610090
77	1	0	2.705354	2.047030	-2.607156
78	1	0	4.449487	2.482061	-2.619308
79	1	0	3.534313	2.432778	-1.068449
80	1	0	-3.871600	0.568673	1.218900
81	1	0	-3.371308	-3.307833	-0.752821
82	1	0	-6.340726	0.261390	1.170552
83	1	0	-5.844248	-3.608821	-0.765927
84	1	0	-7.363021	-1.820276	0.173231

TS1

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.733616
Thermal correction to Gibbs Free Energy = 0.617635
Sum of electronic and thermal Enthalpies = -2284.240666
Sum of electronic and thermal Free Energies = -2284.356646
298 K, in THF
Sum of electronic and thermal Free Energies = -1571.697807

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.250850	-1.717283	0.289470
2	6	0	-5.681206	-0.539451	0.818445
3	6	0	-4.300221	-0.315562	0.771110
4	6	0	-3.434170	-1.283298	0.163058
5	6	0	-4.019358	-2.478511	-0.368202
6	6	0	-5.398566	-2.684440	-0.297167
7	6	0	-2.050437	-1.006969	-0.006529
8	7	0	-0.882788	-0.992898	0.308486
9	6	0	-2.252751	0.108118	-2.090703
10	6	0	-1.015852	-0.363396	-2.610359
11	6	0	0.176028	0.302562	-2.327077
12	6	0	0.197636	1.532163	-1.559398
13	6	0	-1.088229	2.187800	-1.323330
14	6	0	-2.318609	1.461266	-1.560669
15	6	0	-3.558107	2.092303	-1.277017
16	6	0	-3.619195	3.412952	-0.794492
17	6	0	-2.428365	4.146009	-0.636393
18	6	0	-1.189750	3.543591	-0.918558
19	21	0	0.993616	-0.011795	0.184150
20	6	0	2.463818	1.061411	1.932338
21	6	0	1.406425	1.993685	1.683498
22	6	0	0.180804	1.387463	2.127376
23	6	0	0.493062	0.093781	2.663000
24	6	0	1.902093	-0.114324	2.528685
25	6	0	1.604920	3.406935	1.205861
26	6	0	3.935517	1.317255	1.789726
27	6	0	-1.202211	1.982943	2.093280
28	6	0	2.707461	-1.296546	2.996621
29	6	0	-0.494010	-0.823223	3.331521
30	7	0	1.880037	-2.028123	-0.233936
31	6	0	1.412342	-3.407446	-0.268128
32	6	0	0.791373	-3.779006	1.088096
33	7	0	3.043767	-0.250957	-0.993795
34	6	0	4.048613	0.391174	-1.832278
35	6	0	3.722164	1.879978	-2.017169
36	6	0	2.862488	-1.580843	-1.026364
37	6	0	3.670620	-2.535093	-1.904609

38	6	0	0.390351	-3.628367	-1.406212
39	6	0	5.488442	0.226103	-1.287733
40	1	0	1.073308	2.195408	-1.646111
41	1	0	1.125404	-0.093674	-2.724636
42	1	0	-0.986280	-1.318555	-3.159570
43	1	0	-0.262488	4.129027	-0.817156
44	1	0	-3.195753	-0.371178	-2.396675
45	1	0	-4.595241	3.875201	-0.571266
46	1	0	-4.485385	1.523875	-1.454475
47	1	0	-2.461965	5.195834	-0.298572
48	1	0	2.272473	-4.103852	-0.440848
49	1	0	4.042728	-0.057827	-2.861094
50	1	0	2.042126	3.458750	0.184884
51	1	0	2.290363	3.967892	1.881039
52	1	0	0.644801	3.955715	1.171505
53	1	0	4.468750	0.406458	1.451938
54	1	0	4.388340	1.631656	2.760134
55	1	0	4.147762	2.119320	1.054687
56	1	0	2.060399	-2.068692	3.458036
57	1	0	3.466715	-1.000070	3.755996
58	1	0	3.244739	-1.779587	2.151583
59	1	0	-1.183512	3.062725	1.852397
60	1	0	-1.720433	1.852488	3.067889
61	1	0	-1.838356	1.513093	1.312478
62	1	0	5.613494	0.785361	-0.339655
63	1	0	6.236549	0.609291	-2.016645
64	1	0	5.724868	-0.837862	-1.080915
65	1	0	-0.484521	-2.968101	-1.246220
66	1	0	0.048081	-4.685830	-1.445699
67	1	0	0.821648	-3.365969	-2.394944
68	1	0	-1.490677	-0.765283	2.851631
69	1	0	-0.616982	-0.565274	4.409476
70	1	0	-0.173070	-1.882620	3.274763
71	1	0	1.542639	-3.698808	1.898488
72	1	0	0.392991	-4.816050	1.075509
73	1	0	-0.037099	-3.076870	1.313779
74	1	0	2.997292	-3.167051	-2.517557
75	1	0	4.272831	-3.219378	-1.270495
76	1	0	4.359007	-2.008182	-2.589718
77	1	0	2.773927	2.013898	-2.573123
78	1	0	4.529809	2.399792	-2.574944
79	1	0	3.604873	2.370893	-1.029232
80	1	0	-3.865155	0.601874	1.191941
81	1	0	-3.362787	-3.228815	-0.836944
82	1	0	-6.328518	0.220782	1.287772
83	1	0	-5.825360	-3.617374	-0.703588
84	1	0	-7.339018	-1.883286	0.333557

IM1

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.736112
Thermal correction to Gibbs Free Energy = 0.620946
Sum of electronic and thermal Enthalpies = -2284.259940
Sum of electronic and thermal Free Energies = -2284.375106
298 K, in THF
Sum of electronic and thermal Free Energies = -1571.715199

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.921105	-2.278408	0.395018
2	6	0	-5.940528	-1.098252	-0.367242
3	6	0	-4.738307	-0.448636	-0.702630
4	6	0	-3.488533	-0.947738	-0.265175
5	6	0	-3.490278	-2.135626	0.507499
6	6	0	-4.683278	-2.797231	0.825968
7	6	0	-2.161169	-0.283375	-0.564671
8	7	0	-1.121904	-0.532823	0.121702
9	6	0	-2.097050	0.718153	-1.787806
10	6	0	-0.905850	0.366150	-2.654371
11	6	0	0.325310	0.888600	-2.361990
12	6	0	0.524328	1.860327	-1.290172
13	6	0	-0.661385	2.651833	-0.961026
14	6	0	-1.970306	2.140863	-1.249577
15	6	0	-3.103800	2.931567	-0.989021
16	6	0	-2.998890	4.222591	-0.438653
17	6	0	-1.716576	4.745205	-0.179120
18	6	0	-0.576207	3.978820	-0.453519
19	21	0	0.901203	-0.038055	0.193483
20	6	0	2.516759	0.522527	2.065073
21	6	0	1.610040	1.625192	1.977870
22	6	0	0.305157	1.147539	2.342063
23	6	0	0.422548	-0.240561	2.686337
24	6	0	1.784078	-0.632963	2.495773
25	6	0	2.013901	3.047213	1.698879
26	6	0	4.009673	0.572417	1.918120
27	6	0	-0.980815	1.926007	2.415722
28	6	0	2.408028	-1.976375	2.761929
29	6	0	-0.713462	-1.075490	3.206450
30	7	0	1.399030	-2.107771	-0.503477
31	6	0	0.691172	-3.368601	-0.676202
32	6	0	0.051437	-3.762453	0.664427
33	7	0	2.873989	-0.494812	-1.067412
34	6	0	3.991897	0.045071	-1.828313
35	6	0	3.990239	1.580178	-1.779575
36	6	0	2.429981	-1.742114	-1.278373
37	6	0	3.012100	-2.694733	-2.321970

38	6	0	-0.385707	-3.281099	-1.780502
39	6	0	5.357238	-0.498138	-1.340867
40	1	0	1.470105	2.426970	-1.299437
41	1	0	1.205364	0.553355	-2.938186
42	1	0	-1.036007	-0.382672	-3.451753
43	1	0	0.423334	4.412699	-0.291699
44	1	0	-3.032018	0.632320	-2.381180
45	1	0	-3.904336	4.814401	-0.226588
46	1	0	-4.103384	2.522632	-1.217054
47	1	0	-1.604748	5.765142	0.227301
48	1	0	1.408278	-4.180973	-0.960934
49	1	0	3.904505	-0.232445	-2.913267
50	1	0	2.538207	3.158720	0.724878
51	1	0	2.702598	3.433124	2.485178
52	1	0	1.131819	3.714172	1.670690
53	1	0	4.394127	-0.346519	1.431920
54	1	0	4.515858	0.664510	2.908856
55	1	0	4.338190	1.434449	1.303160
56	1	0	1.665974	-2.694988	3.163735
57	1	0	3.237111	-1.903292	3.502288
58	1	0	2.824148	-2.420072	1.831111
59	1	0	-0.873494	2.949438	2.008182
60	1	0	-1.351399	2.004786	3.463658
61	1	0	-1.777093	1.433187	1.818164
62	1	0	5.567103	-0.143852	-0.311727
63	1	0	6.184977	-0.156914	-2.001642
64	1	0	5.368672	-1.607333	-1.321099
65	1	0	-1.140929	-2.522826	-1.497877
66	1	0	-0.892741	-4.259482	-1.930525
67	1	0	0.051090	-2.960886	-2.749259
68	1	0	-1.581071	-1.011431	2.518084
69	1	0	-1.039834	-0.730469	4.214479
70	1	0	-0.434874	-2.145381	3.290766
71	1	0	0.825731	-3.971476	1.428332
72	1	0	-0.599396	-4.656649	0.560491
73	1	0	-0.556997	-2.904866	1.018160
74	1	0	2.208878	-3.109130	-2.963054
75	1	0	3.506907	-3.553780	-1.821373
76	1	0	3.755241	-2.206201	-2.978431
77	1	0	3.103934	1.997251	-2.294991
78	1	0	4.901004	1.994777	-2.261880
79	1	0	3.959087	1.927633	-0.726645
80	1	0	-4.779411	0.472847	-1.301254
81	1	0	-2.516496	-2.520070	0.845024
82	1	0	-6.901278	-0.675722	-0.706600
83	1	0	-4.651186	-3.726827	1.418911
84	1	0	-6.862453	-2.791904	0.652152

TS2

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.733233
Thermal correction to Gibbs Free Energy = 0.617443
Sum of electronic and thermal Enthalpies = -2284.218752
Sum of electronic and thermal Free Energies = -2284.334543
298 K, in THF
Sum of electronic and thermal Free Energies = -1571.675502

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.663975	-1.703210	0.287974
2	6	0	-4.999015	-0.656969	0.953626
3	6	0	-3.614290	-0.482256	0.818516
4	6	0	-2.853647	-1.379017	0.021862
5	6	0	-3.534594	-2.432908	-0.659421
6	6	0	-4.917088	-2.587059	-0.526592
7	6	0	-1.432322	-1.226454	-0.177603
8	7	0	-0.395981	-1.863880	-0.332440
9	6	0	-2.412315	0.472266	-2.543464
10	6	0	-1.055945	0.341854	-2.877593
11	6	0	-0.061892	0.910381	-2.063527
12	6	0	-0.473621	1.523902	-0.825551
13	6	0	-1.838061	1.994686	-0.680077
14	6	0	-2.841664	1.405603	-1.534465
15	6	0	-4.199624	1.768519	-1.333952
16	6	0	-4.570071	2.718851	-0.365243
17	6	0	-3.583417	3.337475	0.424488
18	6	0	-2.228951	2.982860	0.256249
19	21	0	0.920686	-0.224292	0.196315
20	6	0	2.441991	-0.171168	2.214651
21	6	0	1.480439	0.879427	2.381987
22	6	0	0.191046	0.277993	2.582572
23	6	0	0.356615	-1.143479	2.529481
24	6	0	1.739370	-1.415338	2.285607
25	6	0	1.747529	2.353002	2.513078
26	6	0	3.934251	-0.060627	2.077091
27	6	0	-1.053855	1.030876	2.965436
28	6	0	2.383092	-2.771169	2.244255
29	6	0	-0.700241	-2.187086	2.761647
30	7	0	2.487549	-1.268218	-1.039830
31	6	0	2.499491	-2.461052	-1.882463
32	6	0	2.170491	-3.720833	-1.068680
33	7	0	2.767523	0.961990	-0.748375
34	6	0	3.404506	2.234769	-1.081150
35	6	0	2.415547	3.409050	-0.997244
36	6	0	3.158886	-0.157385	-1.381286
37	6	0	4.242126	-0.150696	-2.459329

38	6	0	1.512731	-2.294587	-3.058157
39	6	0	4.651685	2.525232	-0.216093
40	1	0	0.284839	2.073044	-0.231528
41	1	0	0.995463	0.891167	-2.360980
42	1	0	-0.764626	-0.233513	-3.772003
43	1	0	-1.449971	3.477939	0.860530
44	1	0	-3.184754	-0.030698	-3.148552
45	1	0	-5.634161	2.971483	-0.223259
46	1	0	-4.971266	1.280988	-1.952851
47	1	0	-3.864090	4.093121	1.177134
48	1	0	3.518873	-2.618821	-2.320015
49	1	0	3.754469	2.219637	-2.143434
50	1	0	2.710897	2.640940	2.049537
51	1	0	1.784116	2.669557	3.582057
52	1	0	0.951668	2.960454	2.031151
53	1	0	4.284627	-0.464999	1.102515
54	1	0	4.451781	-0.633156	2.880107
55	1	0	4.277143	0.988620	2.141129
56	1	0	1.678380	-3.547724	1.886749
57	1	0	2.740140	-3.083662	3.254080
58	1	0	3.257862	-2.776801	1.563603
59	1	0	-1.443522	1.673678	2.148392
60	1	0	-0.866766	1.696010	3.839265
61	1	0	-1.870639	0.337329	3.246108
62	1	0	4.360567	2.695123	0.840707
63	1	0	5.186798	3.432554	-0.573672
64	1	0	5.360534	1.671927	-0.227984
65	1	0	0.493590	-2.130427	-2.652705
66	1	0	1.508153	-3.188362	-3.720528
67	1	0	1.777559	-1.407532	-3.672075
68	1	0	-1.721424	-1.767727	2.665163
69	1	0	-0.609884	-2.640828	3.775115
70	1	0	-0.626651	-3.002563	2.012222
71	1	0	2.944317	-3.906878	-0.298152
72	1	0	2.122337	-4.610480	-1.733125
73	1	0	1.190724	-3.591463	-0.567071
74	1	0	3.844728	0.261452	-3.411813
75	1	0	4.609965	-1.172425	-2.668152
76	1	0	5.109666	0.470584	-2.163517
77	1	0	1.562039	3.263803	-1.687944
78	1	0	2.922501	4.362260	-1.260543
79	1	0	2.009682	3.513702	0.028364
80	1	0	-3.110060	0.366926	1.296770
81	1	0	-2.945311	-3.119469	-1.287618
82	1	0	-5.569123	0.061888	1.564382
83	1	0	-5.424801	-3.416496	-1.048655
84	1	0	-6.755658	-1.821982	0.383227

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naphthalene

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.151449
Thermal correction to Gibbs Free Energy = 0.112163
Sum of electronic and thermal Enthalpies = -385.471870
Sum of electronic and thermal Free Energies = -385.511156
298 K, in THF
Sum of electronic and thermal Free Energies = -385.888375

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000001	-2.450989	0.712318
2	6	0	0.000001	-1.251763	1.412643
3	6	0	-0.000000	0.000000	0.723219
4	6	0	-0.000000	0.000000	-0.723219
5	6	0	0.000001	-1.251763	-1.412643
6	6	0	0.000001	-2.450989	-0.712318
7	1	0	-0.000000	1.249249	2.515094
8	1	0	0.000001	-3.408535	1.257018
9	1	0	0.000001	-1.249250	2.515094
10	6	0	-0.000000	1.251763	1.412643
11	6	0	-0.000000	1.251763	-1.412643
12	1	0	0.000001	-1.249250	-2.515094
13	1	0	0.000001	-3.408535	-1.257018
14	6	0	-0.000001	2.450989	-0.712319
15	6	0	-0.000001	2.450989	0.712319
16	1	0	-0.000000	1.249249	-2.515094
17	1	0	-0.000001	3.408536	-1.257017
18	1	0	-0.000001	3.408536	1.257017

IM2
298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.581820
Thermal correction to Gibbs Free Energy = 0.477903
Sum of electronic and thermal Enthalpies = -1898.744901
Sum of electronic and thermal Free Energies = -1898.848819
298 K, in THF
Sum of electronic and thermal Free Energies = -1185.832760

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.728034	-1.422170	-0.191712
2	6	0	-2.156028	-1.646007	1.106951
3	6	0	-0.971264	-2.439894	0.939100

4	6	0	-0.813857	-2.701934	-0.461378
5	6	0	-1.897681	-2.081696	-1.160140
6	6	0	0.306458	-3.468005	-1.109446
7	6	0	-0.064682	-2.960452	2.024308
8	6	0	-2.743904	-1.123886	2.390335
9	21	0	-0.553406	-0.204460	-0.162737
10	6	0	-2.049075	-2.081679	-2.659185
11	6	0	-3.986849	-0.631510	-0.434492
12	7	0	0.808730	-0.216268	-1.728454
13	6	0	1.533051	-0.302929	-0.668452
14	7	0	-1.458517	1.814867	-0.622241
15	6	0	-1.612688	2.577152	-1.851825
16	6	0	-2.573837	1.812778	-2.776521
17	6	0	-0.907036	2.318634	0.494483
18	6	0	-0.587910	3.799596	0.671501
19	7	0	-0.590389	1.405275	1.424167
20	6	0	0.115264	1.736300	2.650181
21	6	0	-0.871725	2.071998	3.789893
22	6	0	-0.259728	2.810335	-2.561645
23	6	0	1.013442	0.549238	3.034256
24	1	0	-2.075987	3.578070	-1.639821
25	1	0	-0.853458	4.148820	1.689112
26	1	0	-1.125918	4.425956	-0.065487
27	1	0	0.501124	3.970078	0.534285
28	1	0	0.428109	3.405948	-1.925847
29	1	0	-0.393501	3.351622	-3.524823
30	1	0	0.228439	1.827742	-2.745489
31	1	0	0.786143	2.623236	2.510159
32	1	0	-3.870444	0.425825	-0.108142
33	1	0	-4.856814	-1.059509	0.115062
34	1	0	-4.251197	-0.608771	-1.511299
35	1	0	-2.154249	0.807793	-2.991510
36	1	0	-2.721846	2.345981	-3.740072
37	1	0	-3.560087	1.671359	-2.290439
38	1	0	0.386265	-0.345499	3.231694
39	1	0	1.616183	0.766876	3.942569
40	1	0	1.685431	0.294066	2.188207
41	1	0	-1.528509	2.925777	3.518375
42	1	0	-0.337920	2.329820	4.731578
43	1	0	-1.527281	1.197371	3.984566
44	1	0	-2.047471	-1.258759	3.243580
45	1	0	-3.698847	-1.635482	2.656714
46	1	0	-2.955272	-0.035132	2.319939
47	1	0	0.654320	-2.952283	-2.028905
48	1	0	0.004699	-4.505931	-1.386308
49	1	0	1.186146	-3.539194	-0.437445
50	1	0	-0.133931	-4.068227	2.130303
51	1	0	-0.315559	-2.521895	3.011864
52	1	0	0.998938	-2.712350	1.820316
53	1	0	-2.112378	-3.114603	-3.070271

54	1	0	-1.176874	-1.586151	-3.142213
55	1	0	-2.963439	-1.541009	-2.979445
56	6	0	3.010050	-0.264238	-0.582461
57	6	0	3.764584	0.634644	-1.382805
58	6	0	3.706765	-1.054194	0.365283
59	6	0	5.153645	0.754341	-1.220665
60	1	0	3.219730	1.232527	-2.133268
61	6	0	5.100698	-0.964742	0.501712
62	1	0	3.117749	-1.739367	0.999860
63	6	0	5.833608	-0.047075	-0.281167
64	1	0	5.721256	1.471382	-1.840615
65	1	0	5.624335	-1.604274	1.233409
66	1	0	6.925271	0.047073	-0.153693

2a-Sc

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.688750
Thermal correction to Gibbs Free Energy = 0.572879
Sum of electronic and thermal Enthalpies = -2222.970620
Sum of electronic and thermal Free Energies = -2223.086492
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.376130

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.326600	-0.665515	1.749050
2	7	0	2.449199	1.459541	1.005782
3	6	0	-1.464836	0.796349	-0.162559
4	6	0	-1.515350	-0.729878	0.175129
5	6	0	2.147398	-1.701640	2.754896
6	1	0	2.980804	-1.671623	3.506973
7	6	0	0.808477	-1.529862	3.507804
8	1	0	0.759652	-0.554580	4.035235
9	1	0	0.656030	-2.335756	4.259472
10	1	0	-0.015407	-1.564750	2.763241
11	6	0	2.182222	-3.073864	2.063569
12	1	0	1.371221	-3.109845	1.306362
13	1	0	2.028264	-3.896524	2.794606
14	1	0	3.150417	-3.233624	1.549433
15	6	0	2.569620	0.620325	2.046491
16	6	0	2.941443	1.101314	3.444011
17	1	0	3.732406	1.876702	3.388259
18	1	0	3.301711	0.270086	4.079910
19	1	0	2.066437	1.564110	3.945372
20	6	0	2.396768	2.906600	1.162907
21	1	0	3.164554	3.251839	1.904481

22	6	0	1.003968	3.366621	1.651522
23	1	0	0.246245	3.036128	0.906071
24	1	0	0.957394	4.472027	1.767942
25	1	0	0.745083	2.907590	2.628794
26	6	0	2.719893	3.568140	-0.186002
27	1	0	3.744751	3.312049	-0.520584
28	1	0	2.632560	4.674084	-0.123698
29	1	0	2.003717	3.199655	-0.949149
30	6	0	2.964675	-0.038841	-2.042875
31	6	0	1.706948	0.292250	-2.636265
32	6	0	0.853172	-0.856585	-2.524182
33	6	0	1.596659	-1.912001	-1.897511
34	6	0	2.895305	-1.400951	-1.581493
35	6	0	4.195640	0.818643	-1.927643
36	1	0	4.046428	1.812320	-2.395332
37	1	0	5.072722	0.341974	-2.422966
38	1	0	4.465594	0.994765	-0.863417
39	6	0	1.299018	1.601389	-3.258661
40	1	0	0.470984	2.065079	-2.678068
41	1	0	0.949453	1.464232	-4.306527
42	1	0	2.140161	2.324241	-3.278757
43	6	0	-0.561189	-0.948579	-3.025621
44	1	0	-1.098274	0.011180	-2.877675
45	1	0	-1.131885	-1.725122	-2.477581
46	1	0	-0.608313	-1.197672	-4.111870
47	6	0	1.062348	-3.293232	-1.626318
48	1	0	0.156259	-3.232523	-0.983358
49	1	0	1.804913	-3.918672	-1.090167
50	1	0	0.792528	-3.821727	-2.568232
51	6	0	4.046676	-2.123139	-0.934761
52	1	0	4.329707	-1.651027	0.031658
53	1	0	4.950149	-2.119705	-1.587052
54	1	0	3.794434	-3.181381	-0.721562
55	7	0	-0.397915	-1.325331	0.376991
56	7	0	-0.325153	1.291008	-0.484178
57	21	0	1.290351	-0.089111	-0.169671
58	6	0	-2.811680	-1.504557	0.158021
59	6	0	-3.843088	-1.220185	-0.767364
60	6	0	-2.972724	-2.611323	1.023657
61	6	0	-5.000329	-2.016922	-0.822942
62	1	0	-3.728056	-0.368490	-1.456087
63	6	0	-4.138034	-3.391323	0.988642
64	1	0	-2.142048	-2.844556	1.709514
65	6	0	-5.159199	-3.098969	0.061348
66	1	0	-5.786774	-1.788130	-1.561760
67	1	0	-4.252626	-4.240954	1.683286
68	1	0	-6.072021	-3.716783	0.025609
69	6	0	-2.679280	1.682541	-0.016037
70	6	0	-3.659611	1.469504	0.981626
71	6	0	-2.811266	2.815174	-0.853185

72	6	0	-4.736028	2.360887	1.136286
73	1	0	-3.572142	0.596339	1.647027
74	6	0	-3.897689	3.691873	-0.717715
75	1	0	-2.020619	2.985655	-1.601938
76	6	0	-4.866882	3.470180	0.281753
77	1	0	-5.482232	2.184252	1.929202
78	1	0	-3.990804	4.560821	-1.391322
79	1	0	-5.718146	4.162098	0.395067

TS3'
298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.686846
Thermal correction to Gibbs Free Energy = 0.571505
Sum of electronic and thermal Enthalpies = -2222.907867
Sum of electronic and thermal Free Energies = -2223.023208
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.316743

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.259367	-2.073672	-1.315233
2	6	0	0.964067	-2.693956	-1.290402
3	6	0	0.112408	-1.976095	-2.187771
4	6	0	0.863492	-0.882826	-2.724364
5	6	0	2.203774	-0.966997	-2.222258
6	6	0	1.673130	-0.636138	2.316738
7	6	0	2.028575	-0.541764	3.801889
8	6	0	0.648273	-3.954929	-0.537182
9	6	0	-1.245498	-2.370820	-2.695749
10	6	0	0.323495	0.135058	-3.691006
11	6	0	3.335612	-0.099054	-2.694485
12	6	0	3.453628	-2.588853	-0.556760
13	7	0	2.410955	-0.097369	1.342283
14	6	0	3.566657	0.736506	1.637097
15	6	0	3.149360	2.163940	2.059854
16	7	0	0.570944	-1.274311	1.890608
17	6	0	-0.416277	-1.753271	2.851002
18	6	0	-1.440620	-0.652195	3.207661
19	6	0	4.508205	0.807908	0.428681
20	6	0	-1.116703	-3.007330	2.314444
21	6	0	0.372142	2.029213	-0.695665
22	7	0	1.517227	1.620569	-0.809725
23	6	0	-0.357130	3.292482	-0.533213
24	6	0	-1.604832	3.566366	-1.149808
25	6	0	-2.249241	4.793528	-0.916763
26	6	0	-1.669979	5.763142	-0.078817

27	6	0	-0.427203	5.499768	0.530708
28	6	0	0.222408	4.277174	0.306325
29	1	0	-2.046340	2.793225	-1.789434
30	1	0	-3.218911	4.995180	-1.401692
31	1	0	-2.181900	6.723796	0.097234
32	1	0	0.038816	6.252494	1.187937
33	1	0	1.186248	4.059031	0.790577
34	1	0	0.082870	-2.051283	3.806996
35	1	0	-0.927897	0.254974	3.591528
36	1	0	-2.161242	-0.998188	3.981505
37	1	0	-2.011999	-0.358231	2.306080
38	1	0	-1.497123	-2.797974	1.298584
39	1	0	-1.971990	-3.305887	2.957512
40	1	0	-0.409268	-3.858120	2.246016
41	1	0	3.036613	-0.118723	3.964955
42	1	0	1.994522	-1.545525	4.273462
43	1	0	1.297609	0.095187	4.341909
44	1	0	4.159097	0.295543	2.481751
45	1	0	2.627559	2.641836	1.206127
46	1	0	4.030045	2.786130	2.335208
47	1	0	2.452816	2.144092	2.924041
48	1	0	4.835111	-0.205579	0.126331
49	1	0	5.409073	1.415447	0.664031
50	1	0	3.973727	1.268921	-0.422656
51	1	0	3.152010	0.968398	-2.445265
52	1	0	3.457906	-0.173815	-3.798841
53	1	0	4.298916	-0.389379	-2.231686
54	1	0	-0.631152	0.563123	-3.312179
55	1	0	0.118867	-0.300710	-4.697311
56	1	0	1.029443	0.979195	-3.822807
57	1	0	-1.983422	-1.544658	-2.625574
58	1	0	-1.660849	-3.238023	-2.145988
59	1	0	-1.186725	-2.663343	-3.770201
60	1	0	1.099991	-4.853674	-1.020865
61	1	0	-0.443900	-4.129880	-0.464158
62	1	0	1.037598	-3.901192	0.500011
63	1	0	4.395300	-2.141726	-0.935945
64	1	0	3.549074	-3.693689	-0.651260
65	1	0	3.387995	-2.340508	0.525139
66	21	0	0.673488	-0.384828	-0.255518
67	7	0	-1.310085	0.822184	-0.816729
68	6	0	-1.563342	-0.293229	-0.262738
69	6	0	-2.982085	-0.716517	-0.075440
70	6	0	-3.944897	0.271862	0.262354
71	6	0	-3.411134	-2.062629	-0.133325
72	6	0	-5.274722	-0.077206	0.543197
73	1	0	-3.608899	1.321197	0.301403
74	6	0	-4.746288	-2.411269	0.122833
75	1	0	-2.677720	-2.841402	-0.384299
76	6	0	-5.686470	-1.421930	0.471859

77	1	0	-6.001429	0.707151	0.816921
78	1	0	-5.055721	-3.468114	0.058867
79	1	0	-6.730285	-1.699013	0.694864

2a'-Sc

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.689534
Thermal correction to Gibbs Free Energy = 0.575105
Sum of electronic and thermal Enthalpies = -2222.947787
Sum of electronic and thermal Free Energies = -2223.062215
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.353206

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.973594	-2.299176	2.086151
2	6	0	1.909113	-1.210750	2.205928
3	6	0	1.177611	-0.038148	2.577447
4	6	0	-0.209927	-0.393069	2.657717
5	6	0	-0.330419	-1.795764	2.391452
6	6	0	1.521208	-1.964444	-1.928984
7	6	0	1.915974	-2.487219	-3.308859
8	6	0	3.397992	-1.363771	2.064053
9	6	0	1.731343	1.284019	3.031970
10	6	0	-1.327486	0.536025	3.042152
11	6	0	-1.624063	-2.558920	2.466198
12	6	0	1.360569	-3.713771	1.741224
13	7	0	0.443812	-2.411894	-1.269227
14	6	0	-0.580493	-3.239754	-1.893467
15	6	0	-1.459787	-2.407340	-2.852696
16	7	0	2.231788	-1.019074	-1.288854
17	6	0	3.330363	-0.348350	-1.975203
18	6	0	2.827496	0.880282	-2.764804
19	6	0	-1.452183	-3.877067	-0.803574
20	6	0	4.449315	0.033478	-0.993203
21	6	0	-2.085139	0.641222	-0.182571
22	7	0	-1.623583	-0.550678	-0.051613
23	6	0	-3.564158	0.914025	-0.322914
24	6	0	-4.086106	2.226600	-0.393222
25	6	0	-5.470750	2.442759	-0.514167
26	6	0	-6.357783	1.352452	-0.571766
27	6	0	-5.846457	0.039840	-0.504991
28	6	0	-4.466530	-0.173989	-0.379980
29	1	0	-3.370678	3.060912	-0.346446
30	1	0	-5.862282	3.473317	-0.564198
31	1	0	-7.443593	1.522264	-0.667482

32	1	0	-6.534805	-0.821406	-0.550052
33	1	0	-4.032256	-1.185773	-0.321256
34	1	0	3.803661	-1.039022	-2.716607
35	1	0	2.054934	0.581730	-3.503827
36	1	0	3.655532	1.384223	-3.310592
37	1	0	2.361110	1.614757	-2.079924
38	1	0	4.060104	0.683639	-0.185865
39	1	0	5.263463	0.583488	-1.512239
40	1	0	4.881001	-0.869386	-0.516529
41	1	0	1.307162	-3.360590	-3.605668
42	1	0	2.983637	-2.788332	-3.320052
43	1	0	1.789963	-1.700229	-4.080646
44	1	0	-0.106912	-4.071400	-2.478984
45	1	0	-1.930833	-1.587837	-2.268925
46	1	0	-2.257212	-3.027310	-3.318797
47	1	0	-0.854695	-1.954375	-3.666172
48	1	0	-0.832577	-4.468680	-0.100214
49	1	0	-2.224133	-4.542234	-1.246568
50	1	0	-1.950657	-3.064106	-0.238402
51	1	0	-2.375738	-2.104134	1.785872
52	1	0	-2.038766	-2.545379	3.499337
53	1	0	-1.497718	-3.618085	2.168025
54	1	0	-1.251201	1.500838	2.498681
55	1	0	-1.327224	0.759883	4.134552
56	1	0	-2.313378	0.104251	2.781484
57	1	0	1.146934	2.137673	2.633336
58	1	0	2.784382	1.433150	2.719440
59	1	0	1.706787	1.356478	4.144598
60	1	0	3.841944	-1.915690	2.926033
61	1	0	3.909333	-0.382293	2.001391
62	1	0	3.653893	-1.924499	1.140929
63	1	0	0.506826	-4.408668	1.875078
64	1	0	2.192413	-4.077837	2.385457
65	1	0	1.687507	-3.802653	0.681927
66	21	0	0.452032	-0.728261	0.214620
67	7	0	-1.276039	1.837529	-0.203200
68	6	0	0.015517	1.601653	-0.104901
69	6	0	0.863994	2.831465	-0.166940
70	6	0	0.368736	4.096091	-0.580868
71	6	0	2.236025	2.742913	0.162023
72	6	0	1.212523	5.212695	-0.659661
73	1	0	-0.701248	4.155108	-0.837898
74	6	0	3.087039	3.857263	0.095631
75	1	0	2.617480	1.756692	0.465686
76	6	0	2.577807	5.101347	-0.319607
77	1	0	0.810010	6.185592	-0.991858
78	1	0	4.152843	3.752183	0.359276
79	1	0	3.240837	5.980443	-0.386079

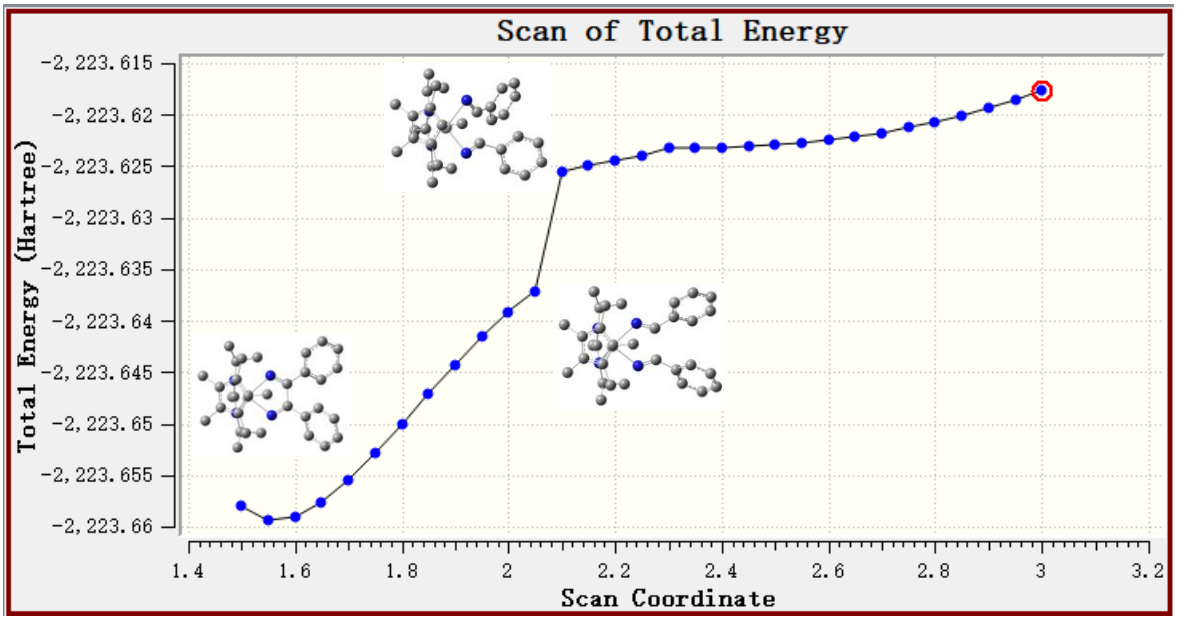

Figure S31. The energy profile of the scanning for the formation of **2a-Sc**.

After many attempts, it was found that a transition state **TS3-B3LYP** for the formation of **2a-Sc-B3LYP** from **IM2-B3LYP** could be found at B3LYP-D3 level[14] using the 6-31G(d,p) basis set in gas phase. The effect of solvent was examined by performing single-point self-consistent reaction field (SCRF) calculations based on the solvation model density (SMD)[11] for gas-phase optimized structures. THF was used as solvent, and solvation free energies (ΔG_{sol}) were calculated at B3LYP-D3/LANL2TZ+ (for Sc)/6-311+G(d,p) (for other elements) level,[12,13] At this calculation level, the formation of **2a-Sc-B3LYP** is also both kinetically and thermodynamically favored over the formation of **2a'-Sc-B3LYP**.

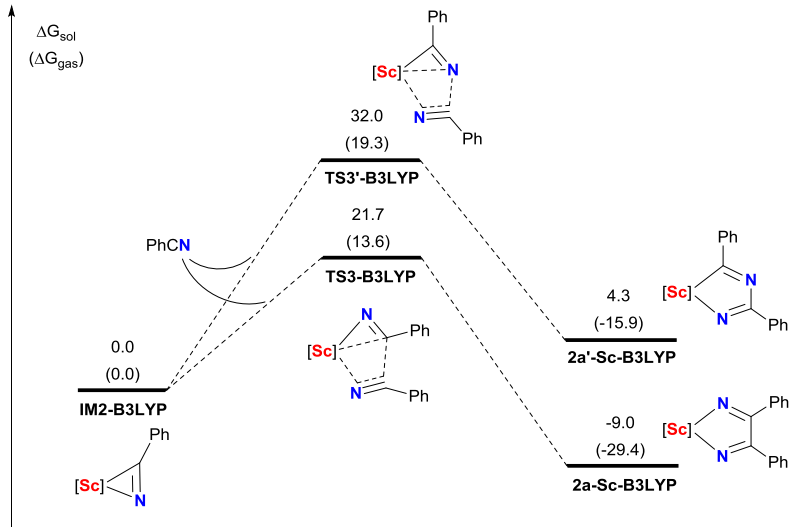

Figure S32. DFT-calculated energy profiles of the transformation of **IM2-B3LYP**.

IM2-B3LYP
298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.601305
Thermal correction to Gibbs Free Energy = 0.498502
Sum of electronic and thermal Enthalpies = -1899.575206
Sum of electronic and thermal Free Energies = -1899.678009
298 K, in THF
Sum of electronic and thermal Free Energies = -1185.797366

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.504902	-1.735926	-0.077680
2	6	0	-1.963028	-1.738879	1.238929
3	6	0	-0.693851	-2.387629	1.194409
4	6	0	-0.456410	-2.785744	-0.151397
5	6	0	-1.569967	-2.383173	-0.937291
6	6	0	0.759331	-3.488467	-0.684515
7	6	0	0.206511	-2.677008	2.364504
8	6	0	-2.665130	-1.187629	2.447932
9	21	0	-0.454272	-0.230356	-0.155731
10	6	0	-1.678226	-2.598395	-2.422524
11	6	0	-3.843448	-1.153854	-0.442915
12	7	0	1.005459	-0.242630	-1.610512
13	6	0	1.643038	-0.140023	-0.502269
14	7	0	-1.633623	1.557290	-0.924083
15	6	0	-1.831832	2.141805	-2.241408
16	6	0	-2.499343	1.089466	-3.134142
17	6	0	-1.292101	2.279473	0.146012
18	6	0	-1.298611	3.803059	0.160619
19	7	0	-0.886720	1.564562	1.195302
20	6	0	-0.402211	2.184395	2.415481
21	6	0	-1.549711	2.423454	3.415366
22	6	0	-0.503475	2.601290	-2.872838
23	6	0	0.670232	1.278677	3.032284
24	1	0	-2.514425	3.010070	-2.188561
25	1	0	-1.729707	4.184360	1.089458
26	1	0	-1.863899	4.213511	-0.676764
27	1	0	-0.272425	4.180546	0.093552
28	1	0	-0.037834	3.395955	-2.280616
29	1	0	-0.657816	2.983191	-3.890772
30	1	0	0.189863	1.754539	-2.899677
31	1	0	0.075527	3.158830	2.213101
32	1	0	-3.873800	-0.072099	-0.264176
33	1	0	-4.655589	-1.611667	0.139149
34	1	0	-4.071830	-1.311475	-1.501007
35	1	0	-1.841878	0.219499	-3.226283
36	1	0	-2.692586	1.486688	-4.137838

37	1	0	-3.445045	0.756348	-2.697599
38	1	0	0.230969	0.310381	3.295718
39	1	0	1.097227	1.725058	3.938833
40	1	0	1.463613	1.088682	2.304637
41	1	0	-2.327017	3.062947	2.983316
42	1	0	-1.186764	2.898488	4.336173
43	1	0	-2.015488	1.468095	3.676281
44	1	0	-1.974470	-1.044877	3.284821
45	1	0	-3.469106	-1.852099	2.799952
46	1	0	-3.113978	-0.212179	2.232405
47	1	0	1.092750	-3.026977	-1.619414
48	1	0	0.569618	-4.555114	-0.876897
49	1	0	1.596901	-3.421592	0.015936
50	1	0	0.060286	-3.694340	2.758299
51	1	0	0.026928	-1.984743	3.193200
52	1	0	1.261231	-2.579653	2.088664
53	1	0	-1.726103	-3.666136	-2.678744
54	1	0	-0.808746	-2.176006	-2.940852
55	1	0	-2.572140	-2.122359	-2.836073
56	6	0	3.126351	-0.021544	-0.398868
57	6	0	3.907968	0.455912	-1.465799
58	6	0	3.775699	-0.356466	0.798914
59	6	0	5.287557	0.599645	-1.335635
60	1	0	3.394898	0.698653	-2.393032
61	6	0	5.160469	-0.235952	0.928062
62	1	0	3.166330	-0.714597	1.626165
63	6	0	5.922442	0.250944	-0.137478
64	1	0	5.877628	0.979125	-2.168590
65	1	0	5.646716	-0.512518	1.861693
66	1	0	6.999932	0.361798	-0.035566

PhCN-B3LYP

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.106360
Thermal correction to Gibbs Free Energy = 0.069024
Sum of electronic and thermal Enthalpies = -324.400594
Sum of electronic and thermal Free Energies = -324.437931
298 K, in THF
Sum of electronic and thermal Free Energies = -324.527452

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.044109	-0.000168	0.000269
2	7	0	-3.207350	0.000089	-0.000510
3	6	0	-0.609729	-0.000080	0.000138

4	6	0	0.091179	-1.217769	0.000088
5	6	0	0.091032	1.217696	0.000085
6	6	0	1.483576	-1.210883	0.000013
7	1	0	-0.459053	-2.152597	0.000125
8	6	0	1.483428	1.210981	0.000010
9	1	0	-0.459316	2.152455	0.000120
10	6	0	2.180130	0.000090	-0.000029
11	1	0	2.025572	-2.151320	-0.000014
12	1	0	2.025313	2.151482	-0.000020
13	1	0	3.265888	0.000156	-0.000092

TS3-B3LYP
298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.708593
Thermal correction to Gibbs Free Energy = 0.594644
Sum of electronic and thermal Enthalpies = -2223.980534
Sum of electronic and thermal Free Energies = -2224.094483
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.290236

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.364764	-0.955308	-1.121732
2	6	0	-2.353487	-1.566166	-1.907781
3	6	0	-1.657767	-2.491151	-1.073959
4	6	0	-2.263999	-2.473780	0.216932
5	6	0	-3.299744	-1.502747	0.190581
6	6	0	-1.856697	2.183936	0.829504
7	6	0	-2.112499	3.589364	1.364298
8	6	0	-2.049653	-1.343055	-3.361663
9	6	0	-0.540067	-3.379242	-1.546831
10	6	0	-2.015163	-3.448020	1.334603
11	6	0	-4.258196	-1.160507	1.294909
12	6	0	-4.408533	0.035671	-1.552619
13	6	0	1.003979	0.402578	-0.700521
14	6	0	2.356435	1.024266	-0.722842
15	6	0	2.714372	1.942386	0.276005
16	6	0	3.981944	2.524649	0.297003
17	6	0	4.930558	2.170289	-0.667024
18	6	0	4.588775	1.249801	-1.663511
19	6	0	3.310788	0.695675	-1.699581
20	7	0	-1.622995	1.152394	1.637488
21	6	0	-1.463808	1.329287	3.070399
22	6	0	0.015851	1.586888	3.418849
23	7	0	-1.853227	1.889433	-0.472136

24	6	0	-1.748826	2.919780	-1.499360
25	6	0	-0.379789	3.630003	-1.466755
26	6	0	-1.991884	0.099210	3.819589
27	6	0	-1.958820	2.287118	-2.878999
28	6	0	1.326546	-1.620691	1.513484
29	7	0	0.307367	-1.720535	2.077714
30	6	0	2.652625	-1.686537	0.977189
31	6	0	2.928549	-2.525867	-0.115462
32	6	0	4.225885	-2.606590	-0.609203
33	6	0	5.251370	-1.854154	-0.029259
34	6	0	4.974004	-1.012513	1.049939
35	6	0	3.682258	-0.925431	1.557235
36	1	0	2.121063	-3.079566	-0.578723
37	1	0	4.434580	-3.247553	-1.460829
38	1	0	6.258643	-1.905581	-0.432359
39	1	0	5.759391	-0.399037	1.479424
40	1	0	3.452018	-0.253810	2.375941
41	1	0	-2.534636	3.685824	-1.363635
42	1	0	-0.185013	4.088369	-0.491971
43	1	0	-0.327458	4.418274	-2.229290
44	1	0	0.411752	2.902336	-1.656890
45	1	0	-1.218936	1.496183	-3.029640
46	1	0	-1.842741	3.039970	-3.668354
47	1	0	-2.955868	1.851495	-2.962898
48	1	0	-2.920190	3.568824	2.102470
49	1	0	-2.393135	4.282444	0.571890
50	1	0	-1.222414	3.983355	1.865584
51	1	0	-2.040269	2.196483	3.432952
52	1	0	0.622723	0.744871	3.076795
53	1	0	0.159770	1.714653	4.500034
54	1	0	0.380173	2.488144	2.913956
55	1	0	-3.064333	-0.020667	3.646636
56	1	0	-1.823159	0.197314	4.899679
57	1	0	-1.483358	-0.799242	3.464220
58	1	0	-4.005810	-1.684494	2.220536
59	1	0	-5.292681	-1.431533	1.034864
60	1	0	-4.245895	-0.086321	1.514196
61	1	0	-1.007596	-3.868980	1.294621
62	1	0	-2.726180	-4.286894	1.288779
63	1	0	-2.116755	-2.979207	2.316991
64	1	0	0.216411	-2.796296	-2.085366
65	1	0	-0.893418	-4.166486	-2.229834
66	1	0	-0.048417	-3.883398	-0.707583
67	1	0	-2.188194	-2.262884	-3.948210
68	1	0	-1.014321	-1.007309	-3.489171
69	1	0	-2.698832	-0.576173	-3.793875
70	1	0	-4.243293	1.017377	-1.093420
71	1	0	-5.413462	-0.303413	-1.264821
72	1	0	-4.410789	0.171974	-2.637874
73	1	0	3.021550	-0.006935	-2.475982

74	1	0	1.974840	2.178735	1.037472
75	1	0	5.325773	0.966062	-2.412965
76	1	0	4.237009	3.245575	1.071335
77	1	0	5.927482	2.604854	-0.641242
78	7	0	0.345505	0.052794	-1.730720
79	21	0	-1.025907	-0.196704	-0.171446

TS3'-B3LYP

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.708907
Thermal correction to Gibbs Free Energy = 0.592944
Sum of electronic and thermal Enthalpies = -2223.967186
Sum of electronic and thermal Free Energies = -2224.083150
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.273888

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.408356	-2.642842	1.808323
2	6	0	1.437301	-1.697327	2.099755
3	6	0	0.836936	-0.576409	2.731006
4	6	0	-0.557073	-0.818321	2.818893
5	6	0	-0.821399	-2.111697	2.283737
6	6	0	0.324650	-2.105836	-2.123816
7	6	0	0.406515	-2.683115	-3.539120
8	6	0	2.906971	-1.968606	1.967550
9	6	0	1.521428	0.622797	3.324445
10	6	0	-1.553075	0.108910	3.456315
11	6	0	-2.145732	-2.811790	2.362845
12	6	0	0.628595	-3.974549	1.144459
13	7	0	-0.815086	-2.128605	-1.433581
14	6	0	-2.032375	-2.645134	-2.044748
15	6	0	-2.819671	-1.528527	-2.760472
16	7	0	1.354560	-1.558741	-1.483962
17	6	0	2.589293	-1.274038	-2.206644
18	6	0	2.453537	-0.016192	-3.087463
19	6	0	-2.914923	-3.338053	-1.002668
20	6	0	3.764866	-1.128087	-1.241587
21	6	0	-2.173519	0.769026	0.184809
22	7	0	-2.370191	-0.401430	0.352104
23	6	0	-2.861485	2.039713	-0.016498
24	6	0	-2.436500	3.240129	0.573312
25	6	0	-3.168180	4.409309	0.367547
26	6	0	-4.313782	4.400882	-0.431321
27	6	0	-4.737557	3.207735	-1.022043

28	6	0	-4.017864	2.032673	-0.813945
29	1	0	-1.533515	3.235672	1.166376
30	1	0	-2.836237	5.335142	0.830038
31	1	0	-4.874487	5.318341	-0.592042
32	1	0	-5.630623	3.190675	-1.641434
33	1	0	-4.342271	1.099125	-1.262229
34	1	0	2.851788	-2.114503	-2.872186
35	1	0	1.630990	-0.128286	-3.802161
36	1	0	3.374472	0.179546	-3.652474
37	1	0	2.241361	0.855725	-2.465741
38	1	0	3.555594	-0.350658	-0.508732
39	1	0	4.678770	-0.855898	-1.783635
40	1	0	3.945329	-2.064451	-0.708740
41	1	0	0.173177	-3.752890	-3.519309
42	1	0	1.389900	-2.563107	-3.988806
43	1	0	-0.325438	-2.204304	-4.195680
44	1	0	-1.793404	-3.407774	-2.802718
45	1	0	-3.127630	-0.776835	-2.031207
46	1	0	-3.714265	-1.924133	-3.259794
47	1	0	-2.198229	-1.030652	-3.512599
48	1	0	-2.367776	-4.158554	-0.528761
49	1	0	-3.818249	-3.749900	-1.471493
50	1	0	-3.206968	-2.627739	-0.229870
51	1	0	-2.957201	-2.176141	1.996160
52	1	0	-2.380657	-3.088066	3.401074
53	1	0	-2.153878	-3.730581	1.772826
54	1	0	-1.353861	1.151904	3.183101
55	1	0	-1.529138	0.051878	4.555349
56	1	0	-2.571496	-0.120544	3.132824
57	1	0	1.244198	1.552925	2.815548
58	1	0	2.609750	0.532413	3.271796
59	1	0	1.256443	0.739025	4.384463
60	1	0	3.316513	-2.405619	2.891501
61	1	0	3.485653	-1.067106	1.751040
62	1	0	3.103796	-2.677554	1.160642
63	1	0	-0.315288	-4.406013	0.802369
64	1	0	1.108304	-4.703330	1.814640
65	1	0	1.265071	-3.860112	0.260009
66	21	0	-0.097676	-0.672996	0.258583
67	7	0	-0.148307	1.683368	0.039404
68	6	0	1.017270	1.200812	0.076356
69	6	0	2.190166	2.113011	-0.084509
70	6	0	2.124454	3.194178	-0.982676
71	6	0	3.385289	1.913255	0.620593
72	6	0	3.221038	4.031457	-1.179529
73	1	0	1.192213	3.356160	-1.515684
74	6	0	4.476141	2.765067	0.445332
75	1	0	3.447804	1.081649	1.312208
76	6	0	4.403722	3.823433	-0.463392
77	1	0	3.154262	4.853113	-1.889852

78	1	0	5.389043	2.595153	1.011741
79	1	0	5.260176	4.475886	-0.615657

2a-Sc-B3LYP

298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.710898
Thermal correction to Gibbs Free Energy = 0.595734
Sum of electronic and thermal Enthalpies = -2224.036093
Sum of electronic and thermal Free Energies = -2224.151257
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.339238

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.263276	-0.628669	1.782753
2	7	0	2.330985	1.489941	1.060915
3	6	0	-1.490118	0.766997	-0.222891
4	6	0	-1.527978	-0.755554	0.124603
5	6	0	2.105695	-1.669660	2.787132
6	1	0	2.934300	-1.641225	3.518342
7	6	0	0.776396	-1.515397	3.552337
8	1	0	0.731166	-0.561157	4.087491
9	1	0	0.641587	-2.321776	4.284810
10	1	0	-0.046069	-1.545214	2.831212
11	6	0	2.144241	-3.033743	2.088971
12	1	0	1.333952	-3.081935	1.355514
13	1	0	2.016880	-3.847126	2.813660
14	1	0	3.095132	-3.175854	1.569432
15	6	0	2.473707	0.652486	2.089775
16	6	0	2.844305	1.130660	3.486169
17	1	0	3.625088	1.894155	3.429345
18	1	0	3.202945	0.310558	4.109605
19	1	0	1.980907	1.583391	3.982616
20	6	0	2.263156	2.934287	1.229678
21	1	0	3.038732	3.284621	1.934025
22	6	0	0.884717	3.375424	1.762170
23	1	0	0.116077	3.059891	1.049621
24	1	0	0.839244	4.465021	1.887846
25	1	0	0.662831	2.914682	2.730453
26	6	0	2.525142	3.600862	-0.125306
27	1	0	3.516305	3.338603	-0.503953
28	1	0	2.457215	4.692484	-0.045333
29	1	0	1.775703	3.255417	-0.843358
30	6	0	3.064810	0.003323	-1.976499
31	6	0	1.837538	0.302115	-2.625486

32	6	0	1.015939	-0.861009	-2.560632
33	6	0	1.748344	-1.889367	-1.900435
34	6	0	3.008724	-1.350257	-1.524976
35	6	0	4.268726	0.888508	-1.813281
36	1	0	4.119550	1.861394	-2.289084
37	1	0	5.161714	0.434180	-2.265537
38	1	0	4.490580	1.072874	-0.755581
39	6	0	1.435765	1.597158	-3.275769
40	1	0	0.505336	1.976379	-2.839427
41	1	0	1.280773	1.474829	-4.356647
42	1	0	2.198975	2.368680	-3.138260
43	6	0	-0.370163	-0.987142	-3.125381
44	1	0	-0.912680	-0.040947	-3.036426
45	1	0	-0.946830	-1.741685	-2.583025
46	1	0	-0.362879	-1.270969	-4.188196
47	6	0	1.241022	-3.284298	-1.658055
48	1	0	0.287059	-3.257277	-1.120343
49	1	0	1.940552	-3.863255	-1.047963
50	1	0	1.093153	-3.829371	-2.600353
51	6	0	4.148378	-2.048498	-0.836333
52	1	0	4.372241	-1.590819	0.134570
53	1	0	5.065075	-2.007976	-1.441534
54	1	0	3.922344	-3.102965	-0.656363
55	7	0	-0.417451	-1.343625	0.324393
56	7	0	-0.366373	1.273838	-0.541120
57	21	0	1.260108	-0.080375	-0.175555
58	6	0	-2.820651	-1.534181	0.127361
59	6	0	-3.850658	-1.277149	-0.790828
60	6	0	-2.974889	-2.611048	1.014664
61	6	0	-4.999222	-2.070272	-0.819834
62	1	0	-3.747640	-0.451374	-1.487679
63	6	0	-4.128921	-3.390864	1.002568
64	1	0	-2.157578	-2.824837	1.696895
65	6	0	-5.148528	-3.124801	0.082349
66	1	0	-5.780480	-1.860629	-1.546755
67	1	0	-4.234418	-4.213129	1.707028
68	1	0	-6.047511	-3.736366	0.067328
69	6	0	-2.714977	1.639035	-0.090809
70	6	0	-3.674650	1.443177	0.914722
71	6	0	-2.868073	2.740079	-0.948394
72	6	0	-4.752359	2.319145	1.057613
73	1	0	-3.574789	0.598589	1.589137
74	6	0	-3.953296	3.603783	-0.821765
75	1	0	-2.102516	2.902711	-1.701006
76	6	0	-4.902401	3.398218	0.185124
77	1	0	-5.478644	2.154566	1.850204
78	1	0	-4.059408	4.443883	-1.504731
79	1	0	-5.747629	4.074371	0.289138

2a'-Sc-B3LYP
298 K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.711333
Thermal correction to Gibbs Free Energy = 0.596819
Sum of electronic and thermal Enthalpies = -2224.014710
Sum of electronic and thermal Free Energies = -2224.129224
298 K, in THF
Sum of electronic and thermal Free Energies = -1510.318018

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.951741	-2.976565	-1.364170
2	6	0	-2.060919	-2.126796	-1.638007
3	6	0	-1.605439	-1.052789	-2.449273
4	6	0	-0.205157	-1.228817	-2.659817
5	6	0	0.190821	-2.433785	-2.009842
6	6	0	-1.471337	-1.197874	2.264141
7	6	0	-1.872802	-1.335072	3.726878
8	6	0	-3.471797	-2.426785	-1.217494
9	6	0	-2.482653	-0.025998	-3.109138
10	6	0	0.714307	-0.347272	-3.457762
11	6	0	1.578732	-3.007783	-2.047497
12	6	0	-1.057631	-4.257355	-0.585251
13	7	0	-0.391543	-1.815834	1.777434
14	6	0	0.638695	-2.378828	2.641576
15	6	0	1.554977	-1.275835	3.208480
16	7	0	-2.147491	-0.476879	1.369673
17	6	0	-3.293004	0.338713	1.750600
18	6	0	-2.860641	1.619288	2.490321
19	6	0	1.475982	-3.384558	1.843698
20	6	0	-4.108583	0.702705	0.506804
21	6	0	2.126759	0.610004	-0.143897
22	7	0	1.654712	-0.570813	-0.102949
23	6	0	3.606926	0.885559	-0.068585
24	6	0	4.130665	2.185626	-0.144611
25	6	0	5.508653	2.402951	-0.074192
26	6	0	6.386028	1.327894	0.077895
27	6	0	5.872711	0.028462	0.158063
28	6	0	4.499532	-0.187766	0.084296
29	1	0	3.434372	3.008465	-0.256678
30	1	0	5.898276	3.416906	-0.136640
31	1	0	7.458885	1.498184	0.134400
32	1	0	6.548332	-0.815797	0.278276
33	1	0	4.074582	-1.185205	0.144116
34	1	0	-3.966721	-0.228286	2.417284
35	1	0	-2.294325	1.381249	3.396293
36	1	0	-3.730564	2.222200	2.780314

37	1	0	-2.221868	2.225157	1.843474
38	1	0	-3.484900	1.257122	-0.197361
39	1	0	-4.961198	1.337571	0.774876
40	1	0	-4.484351	-0.193221	0.009991
41	1	0	-1.805269	-2.382027	4.035702
42	1	0	-2.887449	-0.983671	3.912129
43	1	0	-1.192872	-0.762928	4.365157
44	1	0	0.182304	-2.917096	3.490431
45	1	0	2.058358	-0.772865	2.378721
46	1	0	2.310887	-1.697389	3.883370
47	1	0	0.982638	-0.526571	3.765727
48	1	0	0.859190	-4.216853	1.495809
49	1	0	2.287962	-3.788185	2.460745
50	1	0	1.906141	-2.875468	0.976392
51	1	0	2.304374	-2.272953	-1.685345
52	1	0	1.859082	-3.308648	-3.066330
53	1	0	1.663893	-3.889767	-1.405983
54	1	0	0.306631	0.661119	-3.571233
55	1	0	0.901646	-0.747971	-4.464875
56	1	0	1.680149	-0.246959	-2.953165
57	1	0	-1.902444	0.833835	-3.454450
58	1	0	-3.262671	0.345774	-2.436744
59	1	0	-2.991141	-0.443638	-3.990629
60	1	0	-3.787614	-3.419404	-1.568622
61	1	0	-4.175723	-1.698210	-1.629047
62	1	0	-3.580205	-2.414393	-0.126643
63	1	0	-0.106377	-4.794982	-0.565203
64	1	0	-1.807040	-4.929378	-1.026764
65	1	0	-1.350764	-4.068727	0.453770
66	21	0	-0.437845	-0.747348	-0.182062
67	7	0	1.337515	1.820831	-0.234335
68	6	0	0.056798	1.605491	-0.355497
69	6	0	-0.740484	2.866508	-0.332147
70	6	0	-0.418538	3.912334	0.556024
71	6	0	-1.865445	3.034303	-1.154398
72	6	0	-1.200906	5.063030	0.629080
73	1	0	0.458938	3.791324	1.183376
74	6	0	-2.636746	4.196223	-1.103358
75	1	0	-2.126910	2.240456	-1.842829
76	6	0	-2.315495	5.213633	-0.202605
77	1	0	-0.941808	5.849647	1.335005
78	1	0	-3.497861	4.301291	-1.759645
79	1	0	-2.927778	6.110370	-0.144509

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