Systematic Studies of Early Actinide Complexes:

Thorium(IV) Fluoroketimides

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Electronic Supporting Information:

Supporting Information: Experimental

General Synthetic Procedures. Unless otherwise noted, reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres Model HE-553-2 inert atmosphere (N_2 or He) drybox with a MO-40-2 Dri-Train, or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained in C_6D_6 using a Bruker Avance 300 MHz spectrometer at ambient temperature. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent impurities and ^{19}F NMR resonances were referenced to $CFCl_3$ at δ 0.00 ppm. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility, using either VG ProSpec (EI) or VG70-SE (FAB) mass spectrometers. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried in vacuo at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich), hexanes (Aldrich), diethyl ether (Aldrich), and tetrahydrofuran (Aldrich) were passed through a column of activated alumina (A2, 12 × 32, Purifry) under nitrogen and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 (Cambridge Isotope Laboratories), 2-fluorobenzonitrile (Aldrich), 3-fluorobenzonitrile (Aldrich), 2,6-difluorobenzonitrile (Aldrich), and pentafluorobenzonitrile (Aldrich) were purified by storage over activated 4 Å molecular sieves under N_2 prior to use. $(C_5Me_5)_2Th(CH_3)_2$

was prepared according to literature procedures.[1] *Caution*: Natural thorium (isotope ^{232}Th) is a weak α-emitter with a half-life 1.41 x 10^{10} years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

(1) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650-6667.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(3\text{-}F\text{-}C_6H_4)]_2$ (4). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (1.00 g, 1.88 mmol) and toluene (50 mL). To the clear, colorless solution 3-fluorobenzonitrile (0.485 g, 4.00 mmol) was added dropwise with stirring. Excess 3-fluorobenzonitrile was rinsed into the reaction using the toluene mixture. The reaction mixture turned bright orange over 30 seconds and was stirred at room temperature for 14 h. The volatiles were then removed under reduced pressure and the oily orange residue dissolved in pentane (50 mL) and filtered hot through a Celite-padded coarse frit. The filtrate was left to evaporate to dryness for 1 week and analytically pure orange solid collected (0.64 g, 0.83 mmol, 44%). ^{1}H NMR: δ 7.61 (d, *J* = 9.6 Hz, 2H, *o*-Ar-*H*), 7.46 (d, *J* = 7.2 Hz, 2H, *o*-Ar-*H*), 7.02 (m, 2H, *p*-Ar-*H*), 6.88 (t, ^3J = 6.9 Hz, 2H, *m*-Ar-H), 2.34 (s, 6H, -C*H*$_3$), 1.95 (s, 30H, $C_5(CH_3)_5$). ^{13}C{^{1}H} NMR: δ 167.99 (s, -N=*C*), 163.93 (d, $^1J_{CF}$ = 245.3 Hz, *m*-Ar-*C*-F), 144.21 (d, $^3J_{CF}$ = 5.3 Hz, N=C(CH$_3$)-*C*), 130.15 (d, J_{CF} = 7.5 Hz, Ar-*C*), 123.16 (s, $C_5(CH_3)_5$), 122.99 (s, Ar-*C*), 116.53 (d, J_{CF} = 21.9 Hz, Ar-*C*), 114.05 (d, J_{CF} = 21.9 Hz, Ar-*C*), 30.49 (s, -*C*H$_3$), 11.50 (s, $C_5(CH_3)_5$). ^{13}C{^{1}H}DEPT NMR: δ 129.56 (d, J_{CF} = 7.5 Hz, Ar-*C*), 122.41 (d, J_{CF} = 2.3 Hz, Ar-*C*), 115.98 (d, J_{CF} = 21.1 Hz, Ar-*C*), 113.45 (d, J_{CF} = 21.9 Hz, Ar-*C*), 29.90 (s, -*C*H$_3$), 10.91 (s, $C_5(CH_3)_5$). ^{19}F NMR: δ -50.85 (m, *m*-Ar-*F*). MS (EI, 70 eV): *m/z*

774.8 (M^+). Anal. Calcd for $C_{36}H_{44}N_2F_2Th$ (mol wt 774.79): C, 55.81; H, 5.72; N, 3.62. Found: C, 56.20; H, 5.81; N, 3.42.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (5). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (0.23 g, 0.62 mmol) and toluene (40 mL). To the clear, colorless solution 4-fluorobenzonitrile (0.16 g, 1.4 mmol) was added dropwise with stirring. Excess 4-fluorobenzonitrile was rinsed into the reaction with additional toluene (3 x 2 mL). The reaction mixture immediately turned bright yellow and was stirred at room temperature for 1 h. The volatiles were then removed under reduced pressure and the resulting yellow solid residue dissolved in pentane (~50 mL) and filtered through a Celite-padded coarse frit. The filtrate was collected and the volatiles were removed under reduced pressure to give crude **5** as a yellow solid. Analytically pure samples of **5** were obtained by recrystallization from pentane at -35 °C (0.23 g, 0.30 mmol, 48 %). ^{1}H NMR: δ 7.64 (dd, J_1 = 8.7 Hz, J_2 = 5.3 Hz, 4H, meta Ar-*H*), 6.87 (t, $^3J_{HH}$ = 8.6 Hz, 4H, ortho Ar-*H*), 2.31 (s, 6H, -C*H*$_3$), 1.97 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.89 (s, -N=*C*), 164.46 (d, $^1J_{CF}$ = 248.3 Hz, Ar-*C*-F), 138.21 (d, $^4J_{CF}$ = 3.0 Hz, N=C(CH$_3$)-*C*), 129.42 (d, $^3J_{CF}$ = 8.3 Hz, *o*-Ar-*C*), 122.99 (s, $C_5(CH_3)_5$), 115.28 (d, $^2J_{CF}$ = 21.1 Hz, *m*-Ar-*C*), 30.46 (s, -*C*H$_3$), 11.53 (s, $C_5(CH_3)_5$). ^{19}F NMR (C_6D_6,): δ -50.04 (*m,p*-Ar-F). MS (EI, 70 eV): *m/z* 774.7 (M^+). Anal. Calcd for $C_{36}H_{44}N_2F_2Th$ (mol wt 774.79): C, 55.81; H, 5.72; N, 3.62. Found: C, 55.82; H, 5.82; N, 3.55.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(2\text{-}F\text{-}C_6H_4)]_2$ (6). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (0.51 g, 0.95 mmol) and toluene (50 mL). To the clear, colorless solution was dropwise added a 5 mL toluene solution of 2-fluorobenzonitrile (0.22 g, 1.92 mmol) with stirring. The reaction mixture instantly turned a bright yellow

color and was stirred at room temperature for 16 h. The resultant reaction mixture was filtered through a Celite-padded coarse frit and the volatiles were removed under reduced pressure. The resulting yellow solid was triturated with pentane (2 × 10 mL) and dried to give analytically pure **6** (0.60 g, 0.77 mmol, 81%). Crystals suitable for X-ray diffraction were obtained from a saturated pentane solution of **6** at -35 °C. ^{1}H NMR: δ 7.64 (t, J = 7.8 Hz, 2H, Ar-*H*), 6.85 (m, 6H, Ar-*H*), 2.50 (d, $^{5}J_{HF}$ =4.5 Hz, 6H, CH_3), 1.98 (s, 30H, $C_5(CH_3)_5$). ^{13}C{^{1}H} NMR: δ 167.56 (d, $^{3}J_{CF}$ = 3.0 Hz, -N=*C*), 161.59 (d, $^{1}J_{CF}$ = 246.80 Hz, *o*-Ar-*C*-F), 132.32 (d, $^{2}J_{CF}$ = 16.6 Hz, N=C(CH_3)-*C*), 130.81 (d, J_{CF} = 4.5 Hz, Ar-*C*), 130.56 (d, J_{CF} = 7.5 Hz, Ar-*C*), 124.37 (d, J_{CF} = 3.0 Hz, Ar-*C*), 123.15 (s, $C_5(CH_3)_5$), 116.52 (d, J_{CF} = 24.2 Hz, Ar-*C*), 34.60 (d, $^{4}J_{CF}$ = 5.3 Hz, -*C*H_3), 11.44 (s, $C_5(CH_3)_5$). ^{13}C{^{1}H}DEPT NMR: δ 130.80 (d, J_{CF} = 4.5 Hz, Ar-*C*), 130.56 (d, J_{CF} = 7.5 Hz, Ar-*C*), 124.37 (d, J_{CF} = 3.0 Hz, Ar-*C*), 116.56 (d, J_{CF} = 24.2 Hz, Ar-*C*), 34.60 (s, -*C*H_3), 11.44 (s, $C_5(CH_3)_5$). ^{19}F NMR: δ -50.44 (m, *o*-Ar-*F*). MS (EI, 70 eV): *m/z* 774 (M^+). Anal. Calcd for $C_{36}H_{44}N_2F_2Th$ (mol wt 774.79): C, 55.81; H, 5.72; N, 3.62. Found: C, 55.47; H, 5.40; N, 3.38.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(3,5\text{-}F_2\text{-}C_6H_3)]_2$ (7). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (1.03 g, 1.94 mmol) and toluene (50 mL). To the clear, colorless solution 3,5-difluorobenzonitrile (0.55 g, 3.95 mmol) was added with stirring. The reaction mixture instantly turned a dark orange color and was stirred at room temperature for 3 h. The volatiles were then removed under reduced pressure and the resultant oil dissolved in ~75 mL pentane and filtered through a Celite-padded coarse frit. The filtrate was collected and allowed to evaporate affording **7** as a crystalline orange solid containing X-ray quality crystals (1.1 g, 1.36 mmol, 70%). ^{1}H NMR: δ 7.27 (m, 4H,

o-Ar-*H*), 6.56 (tt, $^{3}J_{HF}$ = 8.2 Hz, $^{4}J_{HH}$ = 2.4 Hz, 2H, *p*-Ar-*H*), 2.22 (s, 6H, CH_3), 1.91 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^{1}H\}$ NMR: δ 166.73 (s, -N=*C*), 163.86 (dd, $^{1}J_{CF}$ = 248.4 Hz, $^{3}J_{CF}$ = 12.1 Hz, *m*-Ar-C), 145.05 (t, $^{3}J_{CF}$ = 6.8 Hz, N=C(CH_3)-*C*), 123.43 (s, $C_5(CH_3)_5$), 110.04 (dd, $^{2}J_{CF}$ = 17.3 Hz, $^{4}J_{CF}$ = 7.6 Hz, *o*-Ar-*C*), 104.89 (t, $^{2}J_{CF}$ = 26.0 Hz, *p*-Ar-*C*), 30.19 (s, -*C*H_3), 11.43 (s, $C_5(CH_3)_5$). $^{13}C\{^{1}H\}$DEPT NMR: δ 109.99 (dd, $^{2}J_{CF}$ = 17.3 Hz, $^{4}J_{CF}$ = 7.6 Hz, *o*-Ar-*C*), 104.88 (t, $^{2}J_{CF}$ = 25.7 Hz, *p*-Ar-*C*), 30.18 (s, -*C*H_3), 11.42 (s, $C_5(CH_3)_5$). ^{19}F NMR: δ -47.56 (t, $^{2}J_{HF}$ = 8.0 Hz, *m*-Ar-*F*). MS (EI, 70 eV): *m/z* 810 (M^+). Multiple elemental analyses for **7** were consistently low in carbon, though the NMR data, crystal structure, and sum of data for **4-11** support the assigned formula.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(3,4,5\text{-}F_3\text{-}C_6H_2)]_2$ (8). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (0.25 g, 0.47 mmol) and toluene (20 mL). To the clear, colorless solution 3,4,5-trifluorobenzonitrile (0.15 g, 0.96 mmol) was added with stirring. The reaction mixture instantly turned a bright yellow color and was stirred at room temperature for 15 h and became a bright orange solution. The volatiles were then removed under reduced pressure to give an orange solid. This solid was dissolved a 40 mL mixture of hexanes and 5 drops toluene and filtered through a Celite-padded coarse frit. The filtrate was collected and cooled to -30 °C to afford **8** as an orange crystalline solid. The analytically pure crystals were isolated by decanting the yellow supernatant, washed with cold hexanes (3 × 5 mL) and dried under reduced pressure (0.19 g, 0.22 mmol, 48%). ^{1}H NMR: δ 7.21 (m, 4H, Ar-*H*), 2.13 (s, 6H, -CH_3), 1.90 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^{1}H\}$ NMR: δ 165.56 (s, -N=*C*), 151.72 (ddd, $^{1}J_{CF}$ = 249.6 Hz, $^{2}J_{CF}$ = 10.6 Hz, $^{3}J_{CF}$ = 3.0 Hz, *m*-Ar-*C*-F), 141.59 (dt, $^{1}J_{CF}$ = 253.6 Hz, $^{2}J_{CF}$ = 15.84 Hz, *p*-Ar-*C*-F), 137.21 (m, N=C(CH_3)-*C*), 123.48 (s, $C_5(CH_3)_5$), 111.10 (dd, $^{2}J_{CF}$ = 14.5 Hz, $^{3}J_{CF}$ = 5.5

Hz, *o*-Ar-*C*), 29.75 (s, -*C*H_3), 11.42 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$DEPT NMR: δ 111.10 (dd, $^2J_{CF}$ = 14.5 Hz, $^3J_{CF}$ = 5.5 Hz, *o*-Ar-*C*), 29.75 (s, -*C*H_3), 11.42 (s, $C_5(CH_3)_5$). ^{19}F NMR: δ -72.06 (m, *m*-Ar-*F*), -97.34 (tt, $^3J_{FF}$ = 22.6 Hz, $^4J_{HF}$ = 8.5 Hz, *p*-Ar-*F*). MS (EI, 70 eV): *m/z* 847 (M^+). Anal. Calcd for $C_{36}H_{40}N_2F_6Th$ (mol wt 846.76): C, 51.06; H, 4.76; N, 3.31. Found: C, 51.22; H, 4.86; N, 3.38.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(2,6\text{-}F_2\text{-}C_6H_3)]_2$ (9). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (1.00 g, 1.88 mmol) and toluene (40 mL). To the clear, colorless solution was dropwise added a 5 mL toluene solution of 2,6-difluorobenzonitrile (0.54 g, 3.87 mmol) with stirring. The reaction mixture instantly turned a bright yellow color and was stirred at room temperature for 15 h and the volatiles removed under reduced pressure. The solid was then dissolved in a 4:1 v/v mixture of hexanes/toluene, filtered thorough a Celite-padded coarse frit. The filtrate was collected and the volatiles were removed under reduced pressure to give **9** as an analytically pure yellow solid (1.05 g, 1.29 mmol, 69%). ^1H NMR: δ 6.55 (m, 2H, *p*-Ar-*H*), 6.49 (m, 4H, *m*-Ar-*H*), 2.21 (s, 6H, CH_3), 2.07 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR: δ 161.79 (s, -N=*C*), 160.26 (dd, $^1J_{CF}$ = 246.8 Hz, $^3J_{CF}$ = 9.4 Hz, *o*-Ar-*C*-F), 128.25 (m, *p*-Ar-*C*), 125.09 (t, $^2J_{CF}$ = 23.2 Hz, N=C(CH_3)-*C*), 123.69 (s, $C_5(CH_3)_5$), 111.88 (dd, $^2J_{CF}$ = 18.7 Hz, $^4J_{CF}$ = 8.3 Hz, *m*-Ar-*C*), 35.24 (s, -*C*H_3), 11.25 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$DEPT NMR: δ 128.25 (t, $^3J_{CF}$ = 10.1 Hz, *p*-Ar-*C*), 111.88 (dd, $^2J_{CF}$ = 18.7 Hz, $^4J_{CF}$ = 8.3 Hz, *m*-Ar-*C*), 35.24 (s, -*C*H_3), 11.25 (s, $C_5(CH_3)_5$). ^{19}F NMR: δ -51.66 (t, $^1J_{HF}$ = 5.6 Hz, *o*-Ar-*F*). MS (EI, 70 eV): *m/z* 810 (M^+). Anal. Calcd for $C_{36}H_{42}N_2F_4Th$ (mol wt 810.77): C, 53.33; H, 5.22; N, 3.46. Found: C, 53.59; H, 5.25; N, 3.27.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(2,4,6\text{-}F_3\text{-}C_6H_2)]_2$ (10). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (0.25 g, 0.47 mmol) and toluene (40 mL). To the clear, colorless solution 2,4,6-trifluorobenzonitrile (0.15 g, 0.93 mmol) was added with stirring. The reaction mixture instantly turned a bright yellow color and was stirred at room temperature for 15 h. The volatiles were then removed under reduced pressure and the resultant solid dissolved in 40 mL of a 5:1 v/v mixture of hexanes/toluene and filtered through a Celite padded coarse frit. The yellow filtrate was collected and cooled to and cooled to -30 °C to afford **10** as an orange crystalline solid. The analytically pure crystals were isolated by decanting the yellow supernatant, washed with cold hexanes (3 × 5 mL) and dried under reduced pressure (0.21 g, 0.25 mmol, 53%). ^{1}H NMR: δ 6.19 (t, J_{HF} = 8.1 Hz, 4H, Ar-*H*), 2.14 (s, 6H, -CH_3), 2.03 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR: δ 161.62 (dt, $^1J_{CF}$ = 247.5 Hz, ^3J = 15.1 Hz, *p*-Ar-*C*-F), 160.69 (s, -N=*C*), 160.27 (ddd, $^1J_{CF}$ = 246.8 Hz, $^3J_{CF}$ = 12.5 Hz, $^3J_{CF}$ = 15.0 Hz, *o*-Ar-*C*-F), 123.74 (s, $C_5(CH_3)_5$), 121.53 (td, $^2J_{CF}$ = 23.4 Hz, $^4J_{CF}$ = 4.5 Hz, N=C(CH$_3$)-*C*), 100.54 (ddd, $^2J_{CF}$ = 29.8 Hz, $^2J_{CF}$ = 25.6 Hz, $^4J_{CF}$ = 2.8 Hz, *m*-Ar-*C*), 35.14 (s, -*C*H$_3$), 11.20 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$DEPT NMR: δ 99.92 (ddd, $^2J_{CF}$ = 29.8 Hz, $^2J_{CF}$ = 25.6 Hz, $^4J_{CF}$ = 2.8 Hz, *m*-Ar-*C*), 34.54 (s, -*C*H$_3$), 10.61 (s, $C_5(CH_3)_5$). ^{19}F NMR: δ -48.17 (m, 2F, *p*-Ar-*F*), -48.99 (t, $^3J_{HF}$ = 8.5 Hz, *o*-Ar-*F*). MS (EI, 70 eV): *m/z* 846 (M^+). Anal. Calcd for $C_{36}H_{40}N_2F_6Th$ (mol wt 846.76): C, 51.06; H, 4.76; N, 3.31. Found: C, 51.19; H, 4.71; N, 3.26.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(C_6F_5)]_2$ (11). A 125 mL flask was charged with $(C_5Me_5)_2Th(CH_3)_2$ (0.454 g, 0.85 mmol) and toluene (60 mL). To the clear, colorless solution was dropwise added pentafluorobenzonitrile (0.377 g, 0.25 mL, 1.96 mmol) with stirring. The reaction mixture instantly turned yellow in color, was stirred at

room temperature for 15 h, and then filtered through a Celite-padded coarse frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **11** as an analytically pure orange solid (0.747 g, 0.813 mmol, 95 %). ^{1}H NMR: δ 2.08 (s, 6H, C*H*$_3$), 1.94 (s, 15H, C$_5$(C*H*$_3$)$_5$). ^{13}C{^{1}H} NMR: δ 157.92 (s, -N=*C*), 143.73 (dm, J_{CF} = 244.5 Hz, *o/m*-Ar-*C*-F), 140.82 (dm, J_{CF} = 252.1 Hz, *p*-Ar-*C*-F), 137.98 (dm, J_{CF} = 252.8 Hz, *o/m*-Ar-*C*-F), 124.14 (s, *C*$_5$(CH$_3$)$_5$), 121.40 (t, $^{2}J_{CF}$ = 11.32 Hz, N=C(CH$_3$)-*C*), 34.99, (s, -*C*H$_3$), 11.15 (s, C$_5$(*C*H$_3$)$_5$). ^{19}F NMR: δ -82.18 (dd, $^{3}J_{FF}$ = 25.4 Hz, $^{4}J_{FF}$ = 8.5 Hz, *o*-Ar-*F*), -95.06 (*t*, $^{3}J_{FF}$ = 22.6, *p*-Ar-*F*), -99.87 (m, *m*-Ar-*F*). MS (EI, 70 eV): *m/z* 918 (M^{+}). Anal. Calcd for $C_{36}H_{36}N_2F_{10}Th$ (mol wt 918.72): C, 47.06; H, 3.95; N, 3.05. Found: C, 46.96; H, 4.23; N, 2.65.

Table S1. Calculated Singlet Transition Orbitals for $(C_5Me_5)_2Th[-N=C(CH_3)(C_6F_5)]_2$ (**11**), $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (**5**), and $(C_5Me_5)_2Th[-N=C(Ph)_2]_2$ (**1**).

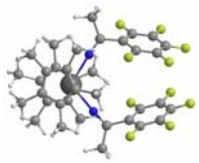
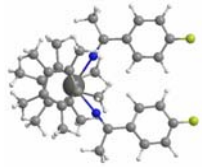
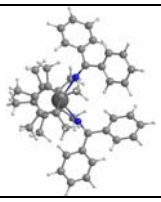
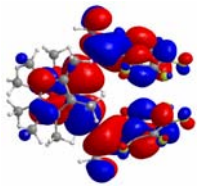
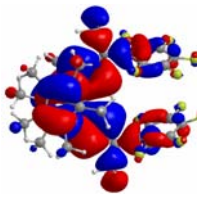
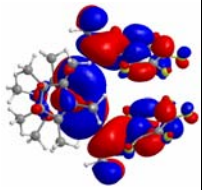
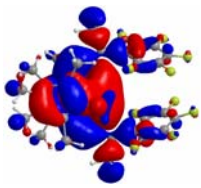
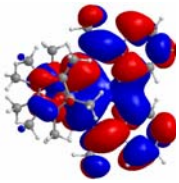
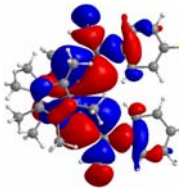
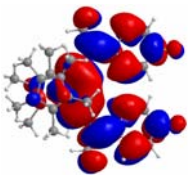
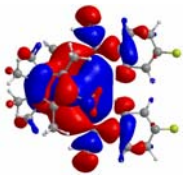
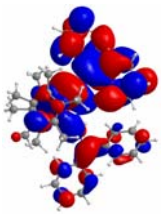
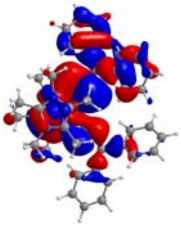
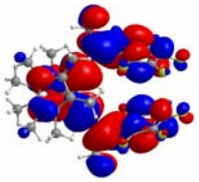
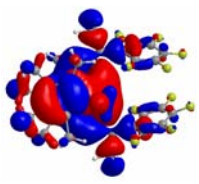
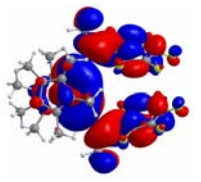
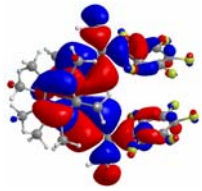
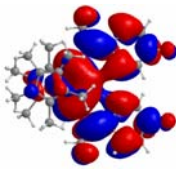
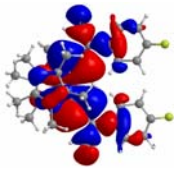
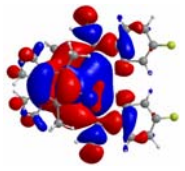
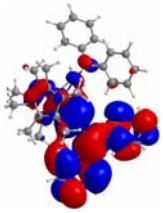
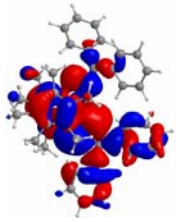
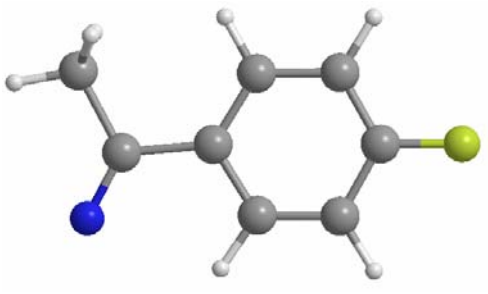
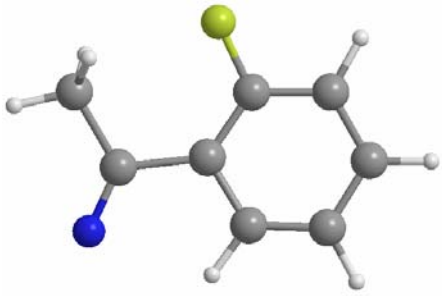
		(11)		**(5)**		**(1)**
						
S1	P ↑ H	3.03 eV   77 %	409 nm   22 %	2.69 eV   84 %	461 nm   16 %	2.56 eV  
S2	P ↑ H	3.05eV   54 %	406 nm   46 %	2.76 eV   67 %	450 nm   33 %	2.61 eV  

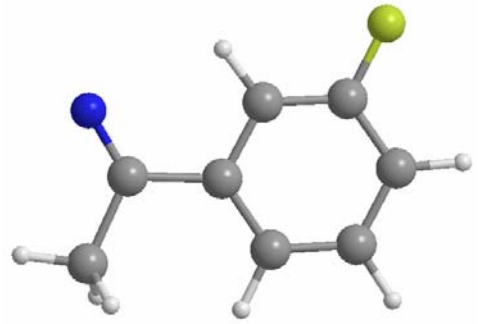
Table S2. Calculated Geometries of Ketimide Ligand Anions.



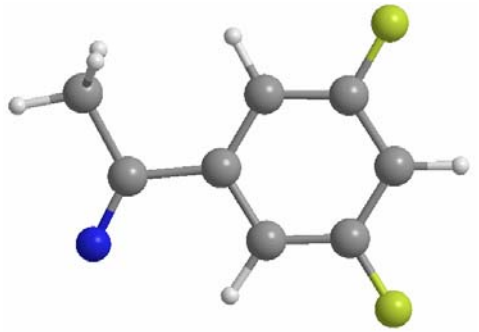
$[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]^-$



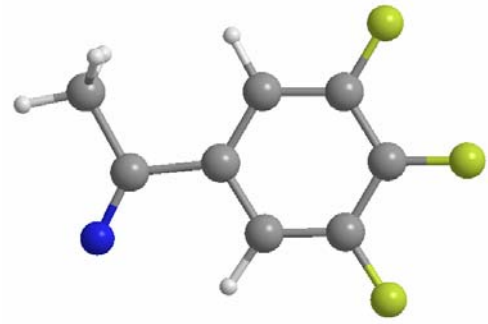
$[-N=C(CH_3)(2\text{-}F\text{-}C_6H_4)]^-$



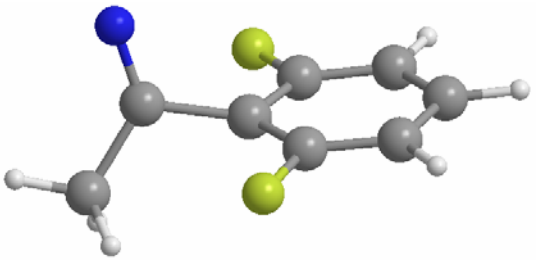
$[-N=C(CH_3)(3\text{-}F\text{-}C_6H_4)]^-$



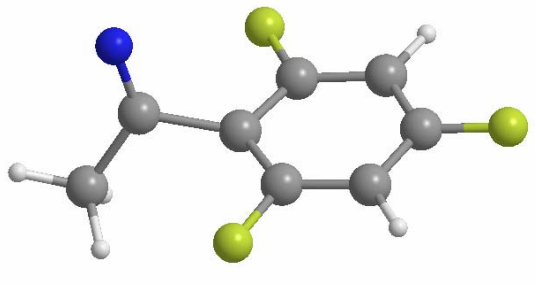
$[-N=C(CH_3)(3,5\text{-}F_2\text{-}C_6H_3)]^-$



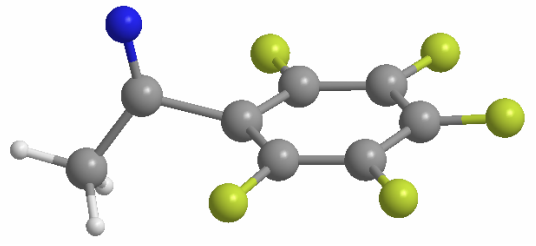
$[-N=C(CH_3)(3,4,5\text{-}F_3\text{-}C_6H_2)]^-$



$[-N=C(CH_3)(2,6\text{-}F_2\text{-}C_6H_3)]^-$



$[-N=C(CH_3)(2,4,6\text{-}F_3\text{-}C_6H_2)]^-$



$[-N=C(CH_3)(C_6F_5)]^-$

Table S3. Calculated Nitrogen and Carbon Charges, Bond Distances and Bond Orders for Ketimide Ligand Anions.

Ligand	C NBO Charge	N NBO Charge	R(N=C)	Bond Order N=C	R(C-C)	Bond Order C-C
$[-N=C(CH_3)(Ph)_2]^-$	0.0758	-0.646	1.258	2.100	1.536	0.897
$[-N=C(CH_3)(3\text{-}F\text{-}C_6H_4)]^-$	0.0861	-0.692	1.254	2.210	1.543	0.93
$[-N=C(CH_3)(3,5\text{-}F_2\text{-}C_6H_3)]^-$	0.0854	-0.683	1.254	2.204	1.543	0.93
$[-N=C(CH_3)(3,4,5\text{-}F_3\text{-}C_6H_2)]^-$	0.0890	-0.681	1.253	2.213	1.547	0.92
$[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]^-$	0.0893	-0.701	1.254	2.214	1.544	0.93
$[-N=C(CH_3)(2\text{-}F\text{-}C_6H_4)]^-$	0.0990	-0.696	1.249	2.236	1.579	0.87
$[-N=C(CH_3)(2,6\text{-}F_2\text{-}C_6H_3)]^-$	0.1152	-0.615	1.239	2.284	1.581	0.724
$[-N=C(CH_3)(2,4,6\text{-}F_3\text{-}C_6H_2)]^-$	0.1153	-0.616	1.236	2.300	1.594	0.705
$[-N=C(CH_3)(C_6F_5)]^-$	0.1267	-0.580	1.230	2.320	1.623	0.653

Table S4. Calculated Coordinates for Optimized Ketimide Ligands and Corresponding Thorium Bis(ketimide) Complexes.

$(C_5Me_5)_2Th[-N=C(Ph)_2]_2$ **(1)**

```
0 1
 Th                -0.00676100   -0.93750300    0.19637500
 N                 -1.89611100    0.29790600    0.11726300
 N                  1.77467400    0.42099200   -0.13597700
 C                  0.83875800   -2.22704500    2.52892200
 C                 -0.59482100   -2.25627200    2.57795900
 C                 -1.02458100   -0.92061000    2.82698500
 C                  0.11127900   -0.09612400    2.89516300
 C                  1.24969200   -0.88870200    2.73078200
 C                  1.75191500   -3.43155900    2.43689700
 H                  1.16015400   -4.32041800    2.27518900
 H                  2.30881400   -3.53223000    3.35674900
 H                  2.43802800   -3.30105900    1.61311300
 C                 -1.46728100   -3.45515700    2.51691100
 H                 -2.50206600   -3.15041300    2.56936600
 H                 -1.24151100   -4.10737800    3.34759500
 H                 -1.29321700   -3.98020700    1.58932000
 C                 -2.44973100   -0.52471000    3.14208400
 H                 -3.09818000   -1.37810700    3.00931400
 H                 -2.75827000    0.26871300    2.47749100
 H                 -2.51053100   -0.18201800    4.16446700
 C                  0.12991400    1.40188300    3.15607000
 H                 -0.88382700    1.76827800    3.22303300
 H                  0.64071200    1.90197000    2.34650300
 H                  0.64610900    1.59929800    4.08395500
 C                  2.65726800   -0.42428500    2.96215400
 H                  3.34032100   -1.24068100    2.77957300
 H                  2.76231600   -0.08851400    3.98324300
 H                  2.88250500    0.39068700    2.29022500
 C                 -1.13024300   -2.61469500   -1.77009300
 C                  0.04512900   -3.30316300   -1.41302600
 C                  1.14352500   -2.56397300   -1.88408200
 C                  0.63957000   -1.40066200   -2.53104600
 C                 -0.76801600   -1.44749900   -2.44515000
 C                 -2.54101200   -3.15741700   -1.51586700
 H                 -2.47585100   -4.09095200   -0.97673200
 H                 -3.03938000   -3.32096100   -2.45994400
 H                 -3.10182100   -2.44276700   -0.93177000
 C                  0.12555400   -4.69299100   -0.81790300
 H                 -0.86396800   -5.02213600   -0.53699300
 H                  0.76025800   -4.67434800    0.05571200
 H                  0.53774000   -5.37389600   -1.54788200
 C                  2.57551500   -3.01900000   -1.87625200
 H                  3.20032000   -2.24880300   -2.30381900
 H                  2.66907500   -3.92333400   -2.45919800
 H                  2.88639400   -3.21191800   -0.86011300
 C                  1.48203600   -0.41004800   -3.30445100
 H                  2.52728400   -0.65094800   -3.17866600
 H                  1.29542500    0.58731800   -2.93453500
 H                  1.22477800   -0.45940200   -4.35220300
 C                 -1.70496900   -0.45158400   -3.08895100
```

H	-2.72641600	-0.72096600	-2.86427700
H	-1.55784500	-0.45847900	-4.15886100
H	-1.50016800	0.53639700	-2.70378900
C	-2.88502800	1.06750900	-0.00808600
C	-4.20774800	0.57234600	-0.55183000
C	-4.93728400	1.29852900	-1.49471200
H	-4.60044900	2.28416100	-1.78014500
C	-6.06987400	0.78633600	-2.06387500
H	-6.60456600	1.36349500	-2.80373400
C	-6.53657500	-0.46103800	-1.70222000
H	-7.43479000	-0.86292000	-2.14730500
C	-5.83475300	-1.18365600	-0.76260200
H	-6.18810100	-2.16045600	-0.46695400
C	-4.69781800	-0.67881200	-0.20120900
H	-4.16670800	-1.26624200	0.53312600
C	-2.80123700	2.53010400	0.35499000
C	-3.90755800	3.24299700	0.80113200
H	-4.87450600	2.76522700	0.85723200
C	-3.76096500	4.59635000	1.18112400
H	-4.61923900	5.15146500	1.52985400
C	-2.54791300	5.20376900	1.11066300
H	-2.44966600	6.23875300	1.40316100
C	-1.43314000	4.50541900	0.66585600
H	-0.47289200	4.99652500	0.60982800
C	-1.55679100	3.17847900	0.29477000
H	-0.68723800	2.63538700	-0.04483000
C	2.76869200	1.19342500	-0.31837900
C	4.18834200	0.67102700	-0.42380500
C	4.45392100	-0.65399400	-0.08821800
H	3.66005800	-1.27689400	0.29672100
C	5.72268400	-1.18082700	-0.24243800
H	5.91171900	-2.21005000	0.02470700
C	6.73879500	-0.40968900	-0.73002600
H	7.72758600	-0.82560900	-0.85533700
C	6.48804600	0.91181100	-1.06227800
H	7.28813200	1.52928400	-1.44305500
C	5.22440300	1.44574000	-0.91071000
H	5.04359600	2.47725300	-1.17469900
C	2.59822000	2.69080200	-0.49554000
C	3.22948600	3.59634300	0.30731000
H	3.86954800	3.24241500	1.10195200
C	3.06725400	4.95329200	0.12523100
H	3.56498700	5.64855200	0.78498600
C	2.26818000	5.42688200	-0.90083700
H	2.15079700	6.48809800	-1.06344800
C	1.63163600	4.52433400	-1.70290000
H	0.99980600	4.87668000	-2.50480000
C	1.78572100	3.15866400	-1.50141300
H	1.26414400	2.45996100	-2.13872800

$(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (**5**)

0 1

Th	1.18736200	-0.00003000	0.00000600
F	-6.39308700	-2.91135500	0.48267900

C	-2.94230800	-1.81438100	0.35717100
C	3.17912500	0.18156000	-2.06834400
C	2.07202000	-0.46695100	-2.69515400
C	-0.25619800	-4.07222500	-1.26749200
H	0.82285800	-3.94330200	-1.36063200
H	-0.66677700	-4.28885400	-2.26260600
H	-0.46122000	-4.94694800	-0.63735200
C	-3.15700300	-3.91311500	-0.80759400
C	1.48192500	1.73045700	-2.30481100
C	-4.52296300	-3.93919000	-0.52601400
N	-0.15475800	-1.77698500	-0.43638300
C	-4.30159100	-1.82492200	0.65281200
C	-5.07417000	-2.89227800	0.20247200
C	2.81105300	1.54161200	-1.82448300
C	-0.28822800	0.25959900	-3.54462300
H	-0.18495500	0.41564100	-4.62845900
H	-1.06658600	0.94668700	-3.19639700
H	-0.66283100	-0.75888600	-3.39857600
C	-0.86645100	-2.80367300	-0.67457100
C	0.77044100	3.05290000	-2.41436900
H	1.05020500	3.73584900	-1.60626000
H	-0.31732000	2.93987200	-2.38196200
H	1.01857900	3.55210500	-3.36258800
C	3.71588700	2.63037300	-1.30530700
H	4.21705400	3.16101200	-2.12825800
H	4.50560600	2.23801700	-0.65557300
H	3.16357800	3.38517600	-0.73357000
C	4.55757800	-0.41090800	-1.91545200
H	4.52842900	-1.47745600	-1.66389600
H	5.14329800	0.09511700	-1.14164400
H	5.12758500	-0.32455000	-2.85228000
C	-2.34171000	-2.85167500	-0.37745500
C	1.02081700	0.48635900	-2.83144600
C	2.08823100	-1.85728300	-3.27388100
H	1.07911500	-2.26627100	-3.37349800
H	2.66684300	-2.55745100	-2.66032100
H	2.54310000	-1.86178300	-4.27571900
F	-6.39292800	2.91160500	-0.48265300
C	-2.94235200	1.81406900	-0.35649900
C	3.17858900	-0.18197800	2.06883500
C	2.07147100	0.46678600	2.69536400
C	-0.25581700	4.07247200	1.26685300
H	0.82319400	3.94336000	1.36025000
H	-0.66657900	4.28942000	2.26182200
H	-0.46051900	4.94708600	0.63645600
C	-3.15650300	3.91394000	0.80631800
C	1.48100400	-1.73051000	2.30493600
C	-4.52248600	3.94003000	0.52484600
N	-0.15458300	1.77711100	0.43608300
C	-4.30166600	1.82459400	-0.65198700
C	-5.07398200	2.89253500	-0.20258100
C	2.81028500	-1.54195700	1.82491900
C	-0.28911200	-0.25925200	3.54432600
H	-0.18612200	-0.41535300	4.62818000
H	-1.06755600	-0.94614400	3.19590400
H	-0.66343700	0.75932700	3.39822600
C	-0.86618600	2.80390500	0.67409200

C	0.76921100	-3.05280000	2.41434600
H	1.04902400	-3.73582200	1.60631400
H	-0.31851700	-2.93954300	2.38167000
H	1.01701200	-3.55204100	3.36263300
C	3.71500600	-2.63092100	1.30596800
H	4.21585300	-3.16167000	2.12904300
H	4.50497100	-2.23874000	0.65642800
H	3.16267000	-3.38560300	0.73409700
C	4.55720800	0.41018800	1.91627200
H	4.52835200	1.47673900	1.66469700
H	5.14300700	-0.09597300	1.14261200
H	5.12696600	0.32371500	2.85324000
C	-2.34146500	2.85194100	0.37707500
C	1.02004000	-0.48630200	2.83143900
C	2.08783700	1.85713300	3.27405100
H	1.07878500	2.26634300	3.37340500
H	2.66675300	2.55715700	2.66061200
H	2.54246000	1.86156700	4.27600100
H	-2.31854200	-0.99394700	0.69477300
H	-4.76687900	-1.02554400	1.22024900
H	-5.15784800	-4.75322400	-0.86032100
H	-2.73273800	-4.73359800	-1.37603300
H	-4.76717900	1.02475300	-1.21858500
H	-2.31878900	0.99317900	-0.69336400
H	-2.73202000	4.73487300	1.37394400
H	-5.15717100	4.75451100	0.85844500

$(C_5Me_5)_2Th[-N=C(CH_3)(C_6F_5)]_2$ (**11**)

0 1

Th	-4.01671400	-0.00017200	4.74157000
F	-3.08771400	-1.99017200	-2.85543000
F	-2.09371400	-3.95717200	1.29157000
F	-5.94671400	-1.27617200	0.78957000
F	-5.33371400	-0.90417200	-1.80543000
F	-1.44971400	-3.50317200	-1.28243000
C	-4.83071400	-1.84817200	0.30057000
C	-2.15571400	-0.78417200	6.64757000
C	-1.91971400	-1.63617200	5.53457000
C	-4.76271400	-4.16917200	3.03457000
H	-4.79571400	-4.21717200	4.01257000
H	-4.10771400	-4.81517200	2.69657000
H	-5.64771400	-4.37817200	2.66757000
C	-2.92271400	-3.18717200	0.55257000
C	-1.24671400	0.46582800	4.96557000
C	-2.57671400	-2.98017200	-0.77143000
N	-4.29371400	-1.78917200	3.37557000
C	-4.52571400	-1.64717200	-1.02743000
C	-3.39371400	-2.20617200	-1.56043000
C	-1.73471400	0.51982800	6.27657000
C	-0.86971400	-1.36817200	3.17257000
H	0.10328600	-1.25717200	3.11957000
H	-1.29671400	-0.85317200	2.45757000
H	-1.09571400	-2.31617200	3.07357000
C	-4.36171400	-2.78217200	2.61457000

C	-0.58871400	1.61282800	4.24057000
H	-1.00471400	2.45582800	4.51657000
H	-0.69971400	1.49482800	3.27357000
H	0.36628600	1.63282800	4.45957000
C	-1.73871400	1.74482800	7.15457000
H	-0.81771400	2.05382800	7.28757000
H	-2.13671400	1.52282800	8.02257000
H	-2.26271400	2.45282800	6.72557000
C	-2.67871400	-1.23617200	7.99857000
H	-3.43671400	-1.84317200	7.86957000
H	-2.96871400	-0.45517200	8.51457000
H	-1.96671400	-1.70217200	8.48457000
C	-4.03471400	-2.62517200	1.13057000
C	-1.35771400	-0.87417200	4.50757000
C	-2.16071400	-3.13317200	5.53057000
H	-2.12871400	-3.46617200	4.60957000
H	-3.04071400	-3.32317200	5.91757000
H	-1.46671400	-3.57617200	6.06257000
F	-4.94571400	1.98982800	-2.85543000
F	-5.93871400	3.95682800	1.29157000
F	-2.08571400	1.27582800	0.78957000
F	-2.69871400	0.90482800	-1.80543000
F	-6.58271400	3.50382800	-1.28243000
C	-3.20271400	1.84782800	0.30057000
C	-5.87671400	0.78482800	6.64757000
C	-6.11271400	1.63582800	5.53457000
C	-3.26971400	4.16882800	3.03457000
H	-3.23771400	4.21782800	4.01257000
H	-3.92471400	4.81482800	2.69657000
H	-2.38571400	4.37782800	2.66757000
C	-5.10971400	3.18682800	0.55257000
C	-6.78571400	-0.46517200	4.96557000
C	-5.45571400	2.98082800	-0.77143000
N	-3.73871400	1.78982800	3.37557000
C	-3.50671400	1.64682800	-1.02743000
C	-4.63971400	2.20682800	-1.56043000
C	-6.29871400	-0.52017200	6.27657000
C	-7.16371400	1.36782800	3.17257000
H	-8.13571400	1.25682800	3.11957000
H	-6.73571400	0.85282800	2.45757000
H	-6.93671400	2.31582800	3.07357000
C	-3.67171400	2.78282800	2.61457000
C	-7.44371400	-1.61317200	4.24057000
H	-7.02771400	-2.45617200	4.51657000
H	-7.33271400	-1.49517200	3.27357000
H	-8.39871400	-1.63317200	4.45957000
C	-6.29471400	-1.74417200	7.15457000
H	-7.21471400	-2.05417200	7.28757000
H	-5.89571400	-1.52317200	8.02257000
H	-5.76971400	-2.45217200	6.72557000
C	-5.35471400	1.23682800	7.99857000
H	-4.59571400	1.84282800	7.86957000
H	-5.06371400	0.45582800	8.51457000
H	-6.06571400	1.70282800	8.48457000
C	-3.99771400	2.62482800	1.13057000
C	-6.67471400	0.87382800	4.50757000
C	-5.87171400	3.13282800	5.53057000

H	-5.90371400	3.46682800	4.60957000
H	-4.99171400	3.32282800	5.91757000
H	-6.56571400	3.57682800	6.06257000

[-N=C(CH_3)(Ph)]$^-$

-1 1

N	-0.00007600	2.41637500	0.00043100
C	0.00006200	1.15840500	0.00009500
C	-1.30552200	0.34950600	-0.00169600
C	-1.48716700	-0.89395600	0.62973000
H	-0.63049600	-1.39297700	1.07759700
C	-2.74923100	-1.49476700	0.71037800
H	-2.86119100	-2.45008100	1.22395600
C	-3.86188900	-0.87850500	0.13830600
H	-4.84311900	-1.34805700	0.19209900
C	-3.69810800	0.36111200	-0.49800100
H	-4.55909700	0.85498500	-0.94917300
C	-2.44622900	0.96503200	-0.54810300
H	-2.29307900	1.95528800	-0.97285300
C	1.30565300	0.34951400	0.00177800
C	1.48701800	-0.89433700	-0.62896400
H	0.63017900	-1.39368700	-1.07613100
C	2.74895300	-1.49522200	-0.70998000
H	2.86061400	-2.45071100	-1.22327800
C	3.86182400	-0.87858900	-0.13877900
H	4.84311600	-1.34801300	-0.19281500
C	3.69828500	0.36125600	0.49715000
H	4.55944300	0.85517600	0.94791200
C	2.44648300	0.96522200	0.54763000
H	2.29337100	1.95542200	0.97240500

[-N=C(CH_3)(2-F-C_6H_4)]$^-$

-1 1

F	-0.21350100	2.11547800	-0.00280300
C	0.46797200	0.92061300	-0.00122500
C	-2.65277300	0.68735800	0.00515800
H	-3.69736400	0.35782100	0.00698200
H	-2.48283300	1.33062200	-0.87319600
H	-2.47809000	1.32593700	0.88599000
C	0.59913200	-1.43240600	0.00115400
C	1.98835100	-1.37149300	0.00191900
N	-2.20604200	-1.76086000	-0.00524400
C	1.85930100	1.03128600	-0.00075000
C	2.63416800	-0.12761600	0.00100900
C	-1.77447500	-0.58872900	-0.00081100
C	-0.22312200	-0.29244700	-0.00007200
H	2.57771800	-2.28871900	0.00308200
H	2.31003600	2.02213800	-0.00165300
H	3.72121100	-0.05779600	0.00135700
H	0.02179800	-2.36268500	0.00107900

[-N=C(CH_3)(3-F-C_6H_4)]$^-$

```
-1 1
 F                  2.79275200   -1.36864700    0.00052700
 C                  0.46759700   -0.87722900    0.00000200
 C                 -3.11436900    0.58098700    0.00117400
 H                 -4.08143400    0.06899700    0.00174500
 H                 -3.07195100    1.24340500   -0.88225000
 H                 -3.07038700    1.24292900    0.88487600
 C                 -0.24107900    1.42303400   -0.00062300
 C                  1.09537100    1.83825300   -0.00043500
 N                 -2.23925600   -1.75805200   -0.00099700
 C                  1.77682800   -0.44689000    0.00025400
 C                  2.13171000    0.90316200    0.00005100
 C                 -2.01291200   -0.52419600   -0.00018400
 C                 -0.58381000    0.05665500   -0.00036400
 H                  0.15853600   -1.92389500   -0.00021700
 H                 -1.02617000    2.17471400   -0.00119200
 H                  3.17893400    1.19348200    0.00040100
 H                  1.33647800    2.90190900   -0.00036700
```

[-N=C(CH_3)(4-F-C_6H_4)]$^-$

```
-1 1
 F                 -3.48094200   -0.09501200    0.00049600
 C                 -0.08801700    1.23580900   -0.00000600
 C                  3.00520500   -1.09389700    0.00086600
 H                  4.07202400   -0.85028800    0.00071100
 H                  2.79195400   -1.72318900   -0.88246300
 H                  2.79196200   -1.72234000    0.88480900
 C                  0.01147000   -1.16090300   -0.00071300
 C                 -1.38987900   -1.22725100   -0.00049900
 N                  2.76636800    1.39246700   -0.00048400
 C                 -1.47741600    1.19798700    0.00020800
 C                 -2.11085000   -0.04403300    0.00005800
 C                  2.22748200    0.26002200   -0.00000600
 C                  0.69588600    0.06721000   -0.00031000
 H                  0.57306700   -2.09197900   -0.00141500
 H                 -1.92021100   -2.17757700   -0.00057800
 H                  0.49343500    2.15998400   -0.00002300
 H                 -2.08161300    2.10356100    0.00029100
```

[-N=C(CH_3)(3,5-F_2-C_6H_3)]$^-$

```
-1 1
 F                  2.20314100   -2.24055500    0.00036700
 F                  1.85716700    2.46658700   -0.00048600
 C                  0.04679400   -1.24293900    0.00009600
 C                 -3.10975800    0.99161200    0.00088700
 H                 -4.16793300    0.71395800    0.00076300
 H                 -2.91694500    1.62620400   -0.88244800
 H                 -2.91667400    1.62508500    0.88496100
```

C	-0.13202900	1.16463200	-0.00002100
C	1.25607500	1.23667500	-0.00010000
N	-2.78491000	-1.48588100	-0.00112200
C	1.41832300	-1.11916400	0.00019100
C	2.07448100	0.11514900	0.00011500
C	-2.28973700	-0.33358900	-0.00022400
C	-0.76523800	-0.09370200	0.00004100
H	-0.49278100	-2.19092200	-0.00017200
H	-0.70337200	2.08700500	-0.00019100
H	3.15584400	0.19349900	0.00010900

[-N=C(CH_3)(3,4,5-F_3-C_6H_2)]$^-$

-1 1

F	3.09123400	0.11174500	0.00033700
F	1.83815100	-2.30473800	0.00070300
F	1.62481200	2.40438500	-0.00081300
C	-0.30562300	-1.24936900	0.00002600
C	-3.40829600	1.05078200	0.00168700
H	-4.47240000	0.79749800	0.00187700
H	-3.20168000	1.68087300	-0.88150400
H	-3.20065800	1.67882600	0.88609100
C	-0.41960900	1.16198300	-0.00019900
C	0.97011300	1.20857100	-0.00037700
N	-3.12904500	-1.43249100	-0.00191100
C	1.06920000	-1.17939200	0.00025100
C	1.73502600	0.04947900	-0.00001600
C	-2.61694700	-0.28921900	-0.00026600
C	-1.08404200	-0.07845600	-0.00020200
H	-0.88211500	-2.17797600	-0.00031700
H	-0.96655200	2.09942200	-0.00023900

[-N=C(CH_3)(2,6-F_2-C_6H_3)]$^-$

-1 1

F	0.29739500	2.33247100	-0.01597900
F	-0.06155700	-2.38843300	-0.24351400
C	-0.61578500	-1.14914100	-0.11025500
C	2.68965300	0.20641100	-0.88601800
H	3.73741500	0.13245500	-0.56859300
H	2.48896900	1.23277800	-1.23255900
H	2.52989900	-0.45899600	-1.75119800
C	-0.44437800	1.17897800	0.01001000
C	-1.82648800	1.32086800	0.06702100
N	2.07055900	-0.51104300	1.44600200
C	-2.00279900	-1.08298200	-0.07253900
C	-2.62067700	0.17083200	0.03201800
C	1.77755500	-0.16846400	0.29245600
C	0.23868700	-0.04127700	-0.04774000
H	-2.26142600	2.31640500	0.11963000
H	-2.58150200	-2.00096400	-0.14144300
H	-3.70442200	0.24793200	0.07786800

[-N=C(CH_3)(2,4,6-F_3-C_6H_2)]$^-$

```
-1 1
 F                  3.59419000   -0.10457200    0.06115000
 F                 -0.56919400   -2.33117800   -0.01938700
 F                 -0.38902900    2.39657800   -0.26485500
 C                  0.20526900    1.18018500   -0.12984900
 C                 -3.05305700   -0.33000100   -0.85565600
 H                 -4.10180400   -0.29456400   -0.53556100
 H                 -2.80740100   -1.35532500   -1.17476200
 H                 -2.92720100    0.31716800   -1.73996300
 C                  0.12186200   -1.14961200    0.00225800
 C                  1.51149300   -1.24810500    0.05655500
 N                 -2.45339900    0.48973300    1.44816300
 C                  1.59682300    1.17450500   -0.10078200
 C                  2.22955200   -0.06107000    0.00895800
 C                 -2.15535300    0.12047200    0.30641200
 C                 -0.60498800    0.04230000   -0.05747000
 H                  2.01085000   -2.20990600    0.11593200
 H                  2.16604200    2.09499100   -0.17751700
```

[-N=C(CH_3)(C_6F_5)]$^-$

```
-1 1
 F                 -3.24598200    0.07949400    0.13263400
 F                  0.90108600    2.34372000   -0.15716900
 F                  0.75715300   -2.41551300   -0.21122600
 F                 -1.95150600   -2.32483200   -0.09780600
 F                 -1.81202800    2.41420200    0.00831000
 C                  0.16190400   -1.19775200   -0.09046200
 C                  3.41824000    0.13626400   -0.85848700
 H                  4.46729600    0.12514200   -0.53886500
 H                  3.19749800    1.10104200   -1.34087000
 H                  3.26550500   -0.64539000   -1.61956100
 C                  0.22962800    1.15948500   -0.05561000
 C                 -1.15676500    1.22466200    0.00506500
 N                  2.76113800   -0.26110100    1.54106600
 C                 -1.22535800   -1.17880500   -0.03921900
 C                 -1.89521000    0.04374900    0.01968000
 C                  2.51115100   -0.08504800    0.34988000
 C                  0.94028300   -0.04034300   -0.05765600
```

Figure S1. Comparison of the electronic absorption and emission spectral properties of (A) $Cp_2Zr[-N=C(Ph)_2]_2$ (**12**) and (B) $Cp^*_2Th[-N=C(Ph)_2]_2$ (**1**). Room temperature absorption and 77 K emission data were obtained in THF. 77 K absorption data were obtained in 2-Me-THF. Molar absorptivity scale applies only to the room temperature absorption data.

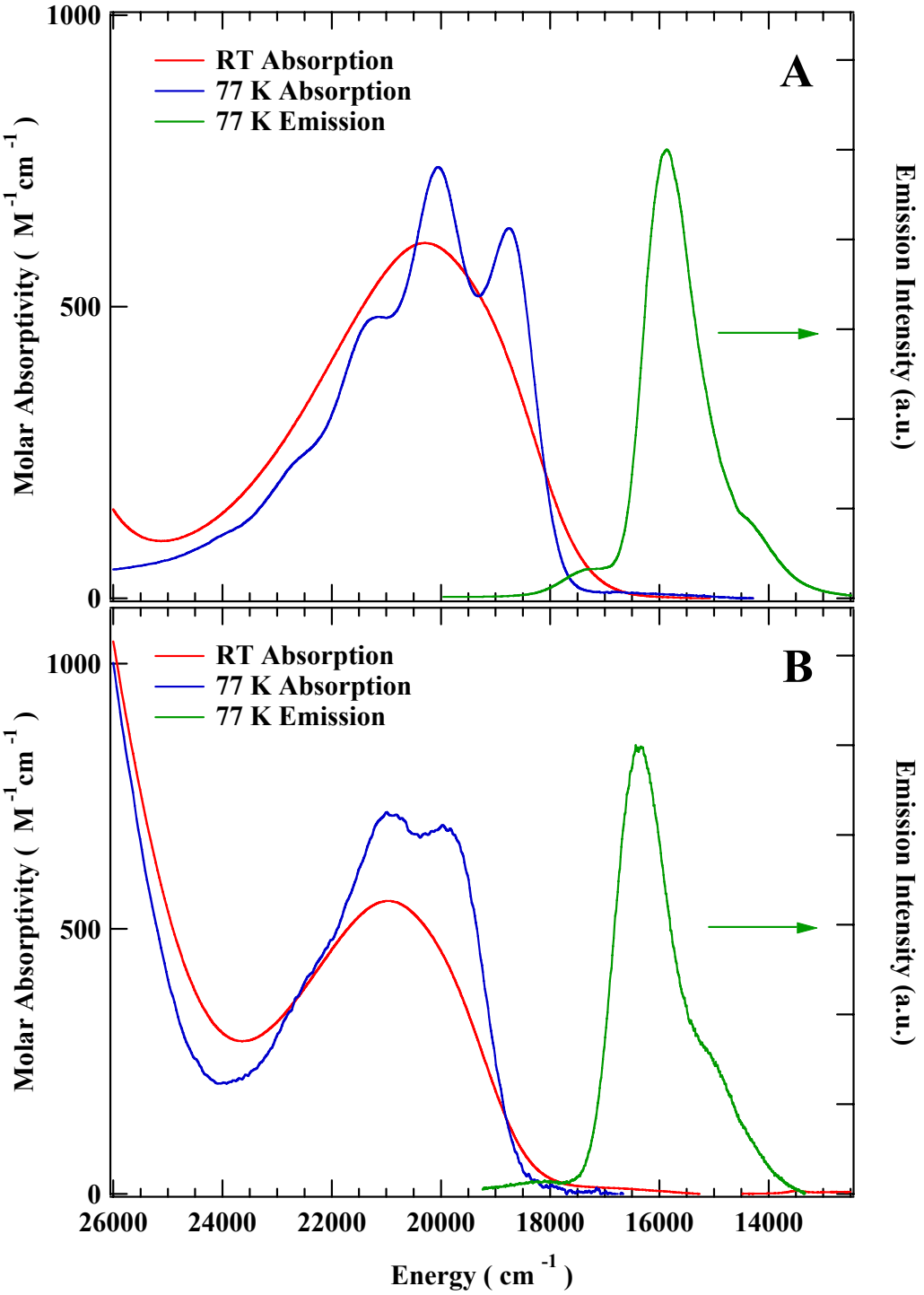
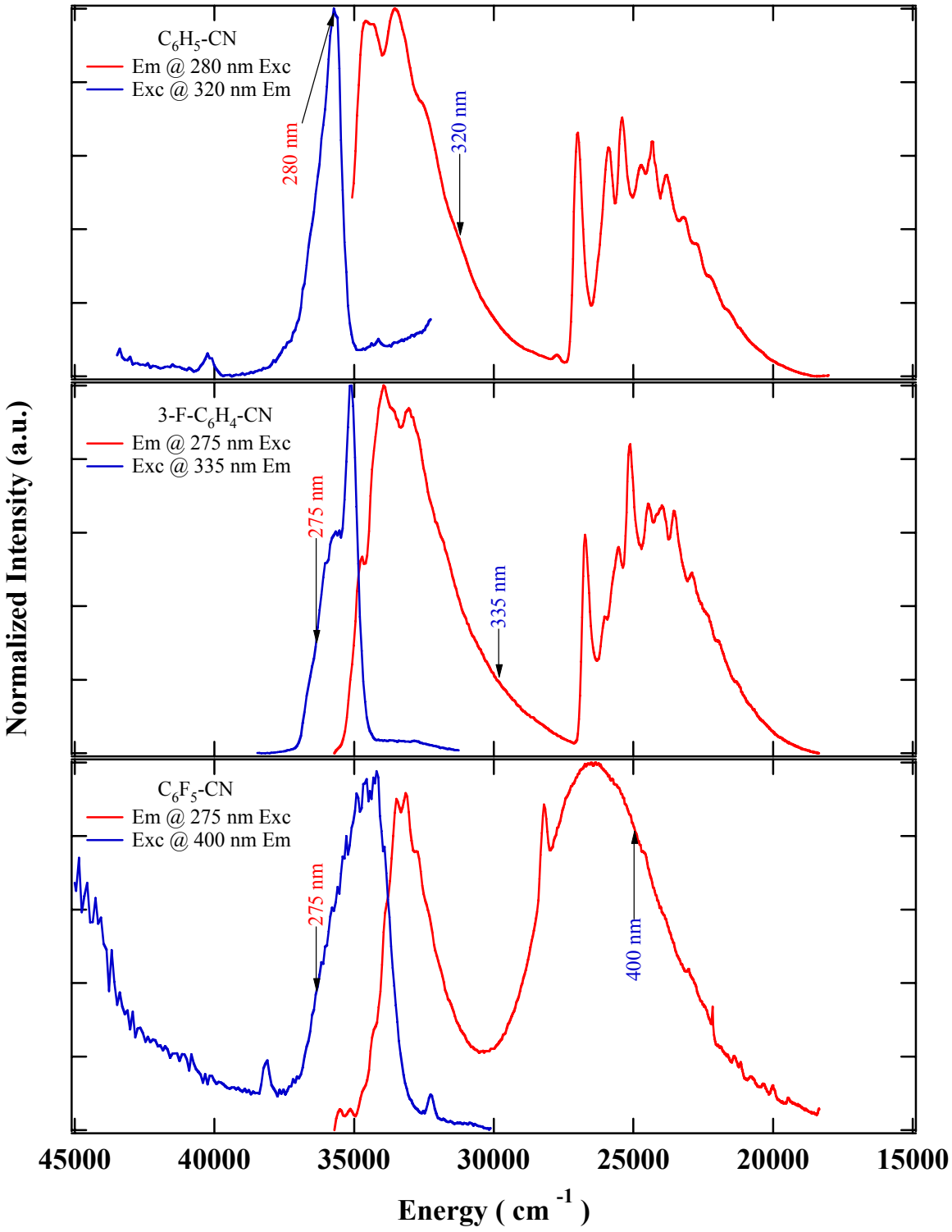


Figure S2. 77 K emission spectral data for ~10 mM solutions of PhC≡N (top), 3-F-$C_6H_4C{\equiv}N$ (middle), and $C_6F_5C{\equiv}N$ (bottom) obtained with continuous wave excitation. Emission excitation spectra are shown in blue and emission spectra in red. Excitation wavelengths for emission spectra are indicated in red, emission wavelengths for excitation spectra are indicated in blue.



Crystallographic Experimental Details for **5–11.**

Crystals of **5**, **8**, **9**, and **11** were mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. The data were collected on a Bruker D8 APEX II charge-coupled-device (CCD) diffractometer, with KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with graphite monochromatized MoKα X-ray source (λ= 0.71073 Å), with MonoCap X-ray source optics. A hemisphere of data was collected using ω scans, with 5-second frame exposures and 0.3º frame widths. Data collection and initial indexing and cell refinement were handled using APEX II[1] software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+[2] software. The data were corrected for absorption using the SADABS[3] program. Decay of reflection intensity was monitored *via* analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. The Cp* ligands of **9** were disordered, and were refined as rigid bodies in two one-half occupancy positions. All hydrogen atom positions were idealized, and rode on the atom they were attached to. Hydrogen atom positions were not included on disordered atoms. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL[5].

Crystals of **6**, **7**, and **10** were mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. The crystal was placed on a Bruker P4 diffractometer with 1k CCD, and cooled to 203 K using a Bruker LT-2 liquid nitrogen vapor low temperature device. The instrument was equipped with a sealed, graphite monochromatized MoKα X-ray source (λ= 0.71073 Å). A hemisphere of data was collected using φ scans, with 30 second frame exposures and 0.3º frame widths. Data collection and initial indexing and cell refinement were handled using SMART[6] software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT[7] software. The data were corrected for absorption using the SADABS[8] program. Decay of reflection intensity was monitored *via* analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom they were attached to. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL[5]. Additional details of data collection and structure refinement are listed in Table 1.

(1) APEX II 1.08, **2004**, Bruker AXS, Inc., Madison, Wisconsin 53719.
(2) SAINT+ 7.06, **2003**, Bruker AXS, Inc., Madison, Wisconsin 53719.
(3) SADABS 2.03, **2001**, George Sheldrick, University of Göttingen, Germany.
(5) SHELXTL 6.14, **2000**, Bruker AXS, Inc., Madison, Wisconsin 53719.
(6) SMART-NT 4, **1996**, Bruker AXS, Inc., Madison, Wisconsin 53719.
(7) SAINT-NT 5.050, **1998**, Bruker AXS, Inc., Madison, Wisconsin 53719.
(8) SADABS 1.0, **1996**, George Sheldrick, University of Göttingen, Germany.
(9) SHELXTL Version 6.10, **2001**, Bruker AXS, Inc., Madison, Wisconsin 53719.

Figure S3. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (**5**) with ellipsoids projected at the 30% probability level.

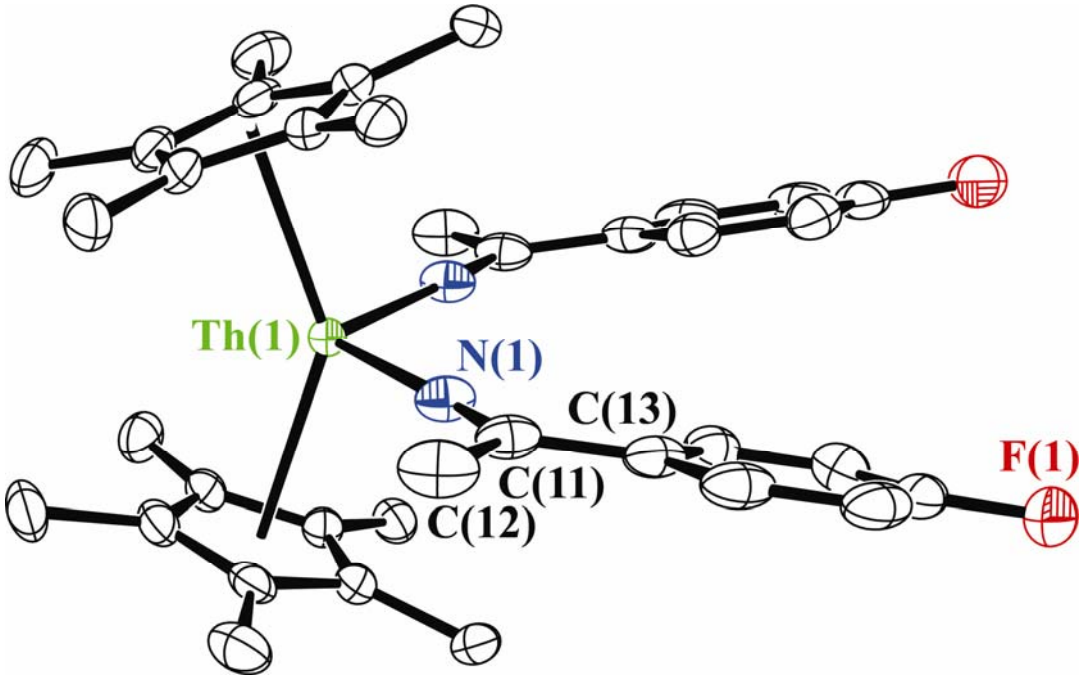


Table S5. Crystal Data and Structure Refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (**5**).

Empirical formula	$C_{36}\ H_{44}\ F_2\ N_2\ Th$	
Formula weight	774.77	
Temperature	141 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 12.9201(6) Å	α= 90°
	b = 14.0054(7) Å	β= 98.677(1)°
	c = 18.2113(9) Å	γ = 90°
Volume	3257.6(3) $Å^3$	
Z	4	
Density (calculated)	1.580 Mg/m^3	
Absorption coefficient	4.615 mm^{-1}	
F(000)	1528	
Crystal size	0.24 x 0.16 x 0.14 mm^3	
θ range for data collection	2.16 to 28.85°	
Index ranges	$-17 \le h \le 17, -18 \le k \le 18, -23 \le l \le 23$	
Reflections collected	17967	
Independent reflections	4014 [R(int) = 0.0222]	
Completeness to θ = 25.00°	100.0 %	
Max. and min. transmission	0.5643 and 0.4038	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4014 / 0 / 186	
Goodness-of-fit on F^2	1.564	
Final R indices [I>2σ(I)]	R1 = 0.0204, wR2 = 0.0574	
R indices (all data)	R1 = 0.0220, wR2 = 0.0578	
Largest diff. peak and hole	1.500 and -0.455 $e.Å^{-3}$	

Table S6. Bond distances [Å] and angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (**5**).

Th(1)-N(1)#1	2.250(2)	N(1)#1-Th(1)-N(1)	108.83(13)
Th(1)-N(1)	2.250(2)	N(1)#1-Th(1)-C(2)	92.71(8)
Th(1)-C(2)	2.805(2)	N(1)-Th(1)-C(2)	124.18(8)
Th(1)-C(2)#1	2.805(2)	N(1)#1-Th(1)-C(2)#1	124.18(8)
Th(1)-C(3)	2.808(3)	N(1)-Th(1)-C(2)#1	92.71(8)
Th(1)-C(3)#1	2.808(3)	C(2)-Th(1)-C(2)#1	116.87(11)
Th(1)-C(4)	2.820(3)	N(1)#1-Th(1)-C(3)	121.60(8)
Th(1)-C(4)#1	2.820(3)	N(1)-Th(1)-C(3)	104.90(9)
Th(1)-C(1)	2.820(3)	C(2)-Th(1)-C(3)	29.38(8)
Th(1)-C(1)#1	2.820(3)	C(2)#1-Th(1)-C(3)	99.71(8)
Th(1)-C(5)#1	2.822(3)	N(1)#1-Th(1)-C(3)#1	104.90(9)
Th(1)-C(5)	2.822(3)	N(1)-Th(1)-C(3)#1	121.60(8)
F(1)-C(16)	1.364(4)	C(2)-Th(1)-C(3)#1	99.71(8)
N(1)-C(11)	1.259(4)	C(2)#1-Th(1)-C(3)#1	29.38(8)
C(1)-C(5)	1.417(4)	C(3)-Th(1)-C(3)#1	95.68(11)
C(1)-C(2)	1.413(4)	N(1)#1-Th(1)-C(4)	122.73(8)
C(1)-C(6)	1.509(4)	N(1)-Th(1)-C(4)	77.83(8)
C(2)-C(3)	1.423(4)	C(2)-Th(1)-C(4)	48.16(8)
C(2)-C(7)	1.506(4)	C(2)#1-Th(1)-C(4)	111.73(8)
C(3)-C(4)	1.415(4)	C(3)-Th(1)-C(4)	29.12(8)
C(3)-C(8)	1.508(4)	C(3)#1-Th(1)-C(4)	119.53(8)
C(4)-C(5)	1.427(4)	N(1)#1-Th(1)-C(4)#1	77.83(8)
C(4)-C(9)	1.502(4)	N(1)-Th(1)-C(4)#1	122.73(8)
C(5)-C(10)	1.510(4)	C(2)-Th(1)-C(4)#1	111.73(8)
C(11)-C(13)	1.506(5)	C(2)#1-Th(1)-C(4)#1	48.16(8)
C(11)-C(12)	1.523(4)	C(3)-Th(1)-C(4)#1	119.53(8)
C(13)-C(14)	1.396(4)	C(3)#1-Th(1)-C(4)#1	29.12(8)
C(13)-C(18)	1.404(4)	C(4)-Th(1)-C(4)#1	147.05(12)
C(14)-C(15)	1.384(4)	N(1)#1-Th(1)-C(1)	77.02(8)
C(15)-C(16)	1.377(5)	N(1)-Th(1)-C(1)	106.20(8)
C(16)-C(17)	1.368(6)	C(2)-Th(1)-C(1)	29.10(7)
C(17)-C(18)	1.386(5)	C(2)#1-Th(1)-C(1)	145.57(7)
		C(3)-Th(1)-C(1)	48.15(7)
		C(3)#1-Th(1)-C(1)	127.18(8)

C(4)-Th(1)-C(1)	48.07(8)	C(2)-C(1)-C(6)	126.1(3)
C(4)#1-Th(1)-C(1)	129.92(8)	C(5)-C(1)-Th(1)	75.55(16)
N(1)#1-Th(1)-C(1)#1	106.20(8)	C(2)-C(1)-Th(1)	74.85(15)
N(1)-Th(1)-C(1)#1	77.02(8)	C(6)-C(1)-Th(1)	120.26(18)
C(2)-Th(1)-C(1)#1	145.57(7)	C(1)-C(2)-C(3)	108.1(2)
C(2)#1-Th(1)-C(1)#1	29.10(7)	C(1)-C(2)-C(7)	125.3(3)
C(3)-Th(1)-C(1)#1	127.18(8)	C(3)-C(2)-C(7)	126.4(3)
C(3)#1-Th(1)-C(1)#1	48.15(7)	C(1)-C(2)-Th(1)	76.06(15)
C(4)-Th(1)-C(1)#1	129.92(8)	C(3)-C(2)-Th(1)	75.42(14)
C(4)#1-Th(1)-C(1)#1	48.07(8)	C(7)-C(2)-Th(1)	118.28(18)
C(1)-Th(1)-C(1)#1	174.64(10)	C(4)-C(3)-C(2)	107.9(2)
N(1)#1-Th(1)-C(5)#1	78.61(8)	C(4)-C(3)-C(8)	124.7(3)
N(1)-Th(1)-C(5)#1	94.40(8)	C(2)-C(3)-C(8)	127.1(3)
C(2)-Th(1)-C(5)#1	140.94(8)	C(4)-C(3)-Th(1)	75.92(15)
C(2)#1-Th(1)-C(5)#1	48.10(8)	C(2)-C(3)-Th(1)	75.20(14)
C(3)-Th(1)-C(5)#1	143.70(8)	C(8)-C(3)-Th(1)	119.76(18)
C(3)#1-Th(1)-C(5)#1	48.20(8)	C(3)-C(4)-C(5)	108.0(2)
C(4)-Th(1)-C(5)#1	158.59(8)	C(3)-C(4)-C(9)	125.7(3)
C(4)#1-Th(1)-C(5)#1	29.29(8)	C(5)-C(4)-C(9)	126.1(3)
C(1)-Th(1)-C(5)#1	152.08(8)	C(3)-C(4)-Th(1)	74.96(15)
C(1)#1-Th(1)-C(5)#1	29.09(8)	C(5)-C(4)-Th(1)	75.46(15)
N(1)#1-Th(1)-C(5)	94.40(8)	C(9)-C(4)-Th(1)	120.07(18)
N(1)-Th(1)-C(5)	78.61(8)	C(1)-C(5)-C(4)	107.8(2)
C(2)-Th(1)-C(5)	48.10(8)	C(1)-C(5)-C(10)	125.9(2)
C(2)#1-Th(1)-C(5)	140.94(8)	C(4)-C(5)-C(10)	126.2(3)
C(3)-Th(1)-C(5)	48.20(8)	C(1)-C(5)-Th(1)	75.37(16)
C(3)#1-Th(1)-C(5)	143.70(8)	C(4)-C(5)-Th(1)	75.25(15)
C(4)-Th(1)-C(5)	29.29(8)	C(10)-C(5)-Th(1)	118.62(17)
C(4)#1-Th(1)-C(5)	158.59(8)	N(1)-C(11)-C(13)	122.5(3)
C(1)-Th(1)-C(5)	29.09(8)	N(1)-C(11)-C(12)	121.2(3)
C(1)#1-Th(1)-C(5)	152.08(8)	C(13)-C(11)-C(12)	116.3(2)
C(5)#1-Th(1)-C(5)	168.09(11)	C(14)-C(13)-C(18)	118.1(3)
C(11)-N(1)-Th(1)	175.5(2)	C(14)-C(13)-C(11)	119.1(2)
C(5)-C(1)-C(2)	108.3(2)	C(18)-C(13)-C(11)	122.8(3)
C(5)-C(1)-C(6)	125.4(2)	C(15)-C(14)-C(13)	121.3(3)

C(16)-C(15)-C(14)	118.2(3)	C(17)-C(16)-C(15)	123.1(3)
F(1)-C(16)-C(17)	118.7(3)	C(16)-C(17)-C(18)	118.2(3)
F(1)-C(16)-C(15)	118.2(3)	C(17)-C(18)-C(13)	121.1(3)

Figure S4. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(2\text{-}F\text{-}C_6H_4)]_2$ (**6**) with ellipsoids projected at the 30% probability level.

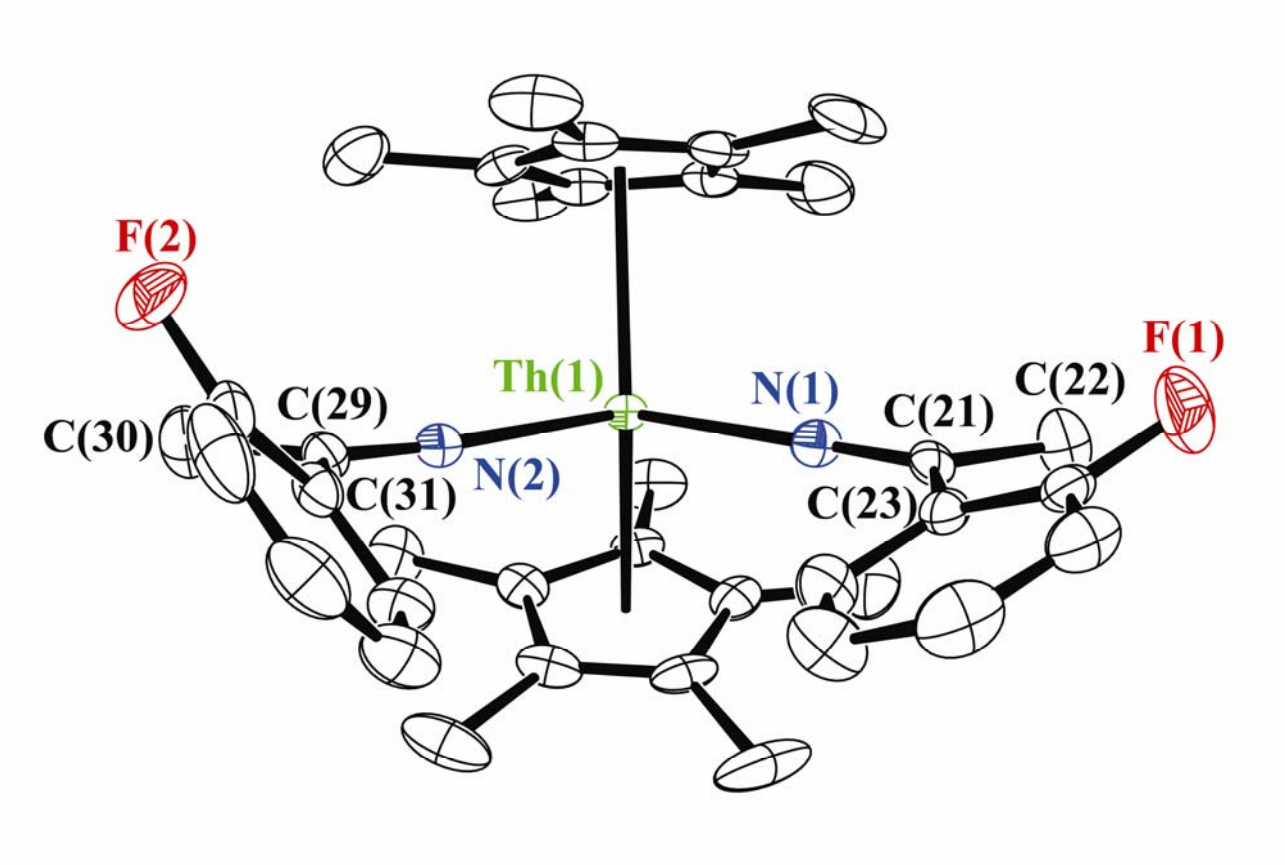


Table S7. Crystal data and structure refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(2\text{-}F\text{-}C_6H_4)]_2$ (**6**).

Empirical formula	$C_{36}\ H_{44}\ F_2\ N_2\ Th$	
Formula weight	774.77	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P\ 2_1\ 2_1\ 2_1$	
Unit cell dimensions	a = 10.180(5) Å	α= 90°
	b = 17.880(8) Å	β= 90°
	c = 18.364(8) Å	γ = 90°
Volume	3343(3) $Å^3$	
Z	4	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	4.498 mm^{-1}	
F(000)	1528	
Crystal size	0.20 x 0.16 x 0.16 mm^3	
θ range for data collection	1.59 to 28.33°	
Index ranges	$-13 \le h \le 13, -9 \le k \le 21, -24 \le l \le 24$	
Reflections collected	17515	
Independent reflections	7206 [R(int) = 0.0379]	
Completeness to θ = 25.00°	97.4 %	
Max. and min. transmission	0.5331 and 0.4666	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7206 / 0 / 370	
Goodness-of-fit on F^2	0.990	
Final R indices [I>2σ(I)]	R1 = 0.0359, wR2 = 0.0757	
R indices (all data)	R1 = 0.0471, wR2 = 0.0794	
Absolute structure parameter	0.014(11)	
Largest diff. peak and hole	2.271 and -1.650 e.$Å^{-3}$	

Table S8. Bond distances [Å] and angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(2\text{-}F\text{-}C_6H_4)]_2$ (**6**).

Th(1)-N(1)	2.260(5)	C(14)-C(19)	1.512(10)
Th(1)-N(2)	2.269(5)	C(15)-C(20)	1.489(10)
Th(1)-C(2)	2.782(6)	C(21)-C(23)	1.511(10)
Th(1)-C(1)	2.791(7)	C(21)-C(22)	1.513(9)
Th(1)-C(11)	2.796(6)	C(23)-C(28)	1.361(10)
Th(1)-C(3)	2.798(7)	C(23)-C(24)	1.386(11)
Th(1)-C(15)	2.806(7)	C(24)-C(25)	1.372(12)
Th(1)-C(5)	2.813(8)	C(25)-C(26)	1.390(12)
Th(1)-C(14)	2.818(7)	C(26)-C(27)	1.354(12)
Th(1)-C(4)	2.819(8)	C(27)-C(28)	1.389(12)
Th(1)-C(12)	2.824(7)	C(29)-C(30)	1.505(10)
Th(1)-C(13)	2.827(8)	C(29)-C(31)	1.523(11)
F(1)-C(28)	1.353(10)	C(31)-C(36)	1.374(11)
F(2)-C(36)	1.357(12)	C(31)-C(32)	1.386(11)
N(1)-C(21)	1.265(8)	C(32)-C(33)	1.373(12)
N(2)-C(29)	1.248(8)	C(33)-C(34)	1.356(14)
C(1)-C(2)	1.401(9)	C(34)-C(35)	1.339(16)
C(1)-C(5)	1.414(11)	C(35)-C(36)	1.403(15)
C(1)-C(10)	1.509(10)		
C(2)-C(3)	1.417(9)	N(1)-Th(1)-N(2)	108.65(19)
C(2)-C(6)	1.517(9)	N(1)-Th(1)-C(2)	111.16(19)
C(3)-C(4)	1.417(10)	N(2)-Th(1)-C(2)	116.9(2)
C(3)-C(7)	1.507(10)	N(1)-Th(1)-C(1)	82.7(2)
C(4)-C(5)	1.395(11)	N(2)-Th(1)-C(1)	124.2(2)
C(4)-C(8)	1.509(12)	C(2)-Th(1)-C(1)	29.12(19)
C(5)-C(9)	1.508(12)	N(1)-Th(1)-C(11)	122.2(2)
C(11)-C(12)	1.355(10)	N(2)-Th(1)-C(11)	105.8(2)
C(11)-C(15)	1.413(10)	C(2)-Th(1)-C(11)	91.9(2)
C(11)-C(16)	1.549(10)	C(1)-Th(1)-C(11)	113.2(2)
C(12)-C(13)	1.393(11)	N(1)-Th(1)-C(3)	125.7(2)
C(12)-C(17)	1.511(10)	N(2)-Th(1)-C(3)	87.5(2)
C(13)-C(14)	1.393(10)	C(2)-Th(1)-C(3)	29.43(19)
C(13)-C(18)	1.534(11)	C(1)-Th(1)-C(3)	48.1(2)

C(14)-C(15)	1.436(11)	C(11)-Th(1)-C(3)	100.5(2)
N(1)-Th(1)-C(15)	93.8(2)	C(7)-C(3)-Th(1)	116.4(5)
N(2)-Th(1)-C(15)	126.7(2)	C(5)-C(4)-C(3)	108.4(8)
C(2)-Th(1)-C(15)	97.1(2)	C(5)-C(4)-C(8)	126.8(10)
C(1)-Th(1)-C(15)	105.8(2)	C(3)-C(4)-C(8)	124.6(8)
C(11)-Th(1)-C(15)	29.2(2)	C(5)-C(4)-Th(1)	75.4(6)
C(3)-Th(1)-C(15)	117.7(2)	C(3)-C(4)-Th(1)	74.5(5)
N(1)-Th(1)-C(5)	78.1(2)	C(8)-C(4)-Th(1)	119.8(6)
N(2)-Th(1)-C(5)	97.8(2)	C(4)-C(5)-C(1)	108.0(8)
C(2)-Th(1)-C(5)	48.1(2)	C(4)-C(5)-C(9)	126.4(10)
C(1)-Th(1)-C(5)	29.2(2)	C(1)-C(5)-C(9)	125.2(9)
C(11)-Th(1)-C(5)	139.8(2)	C(4)-C(5)-Th(1)	75.9(5)
C(3)-Th(1)-C(5)	48.0(2)	C(1)-C(5)-Th(1)	74.5(4)
C(15)-Th(1)-C(5)	134.5(2)	C(9)-C(5)-Th(1)	121.7(6)
N(1)-Th(1)-C(14)	77.7(2)	C(12)-C(11)-C(15)	110.1(7)
N(2)-Th(1)-C(14)	108.8(2)	C(12)-C(11)-C(16)	125.5(7)
C(2)-Th(1)-C(14)	126.0(2)	C(15)-C(11)-C(16)	123.8(7)
C(1)-Th(1)-C(14)	126.9(2)	C(12)-C(11)-Th(1)	77.2(4)
C(11)-Th(1)-C(14)	47.6(2)	C(15)-C(11)-Th(1)	75.8(4)
C(3)-Th(1)-C(14)	146.5(2)	C(16)-C(11)-Th(1)	120.8(5)
C(15)-Th(1)-C(14)	29.6(2)	C(11)-C(12)-C(13)	108.4(7)
C(5)-Th(1)-C(14)	148.5(2)	C(11)-C(12)-C(17)	125.7(7)
N(1)-Th(1)-C(4)	103.1(2)	C(13)-C(12)-C(17)	125.6(7)
N(2)-Th(1)-C(4)	76.7(2)	C(11)-C(12)-Th(1)	74.9(4)
C(2)-Th(1)-C(4)	48.1(2)	C(13)-C(12)-Th(1)	75.8(4)
C(1)-Th(1)-C(4)	47.8(2)	C(17)-C(12)-Th(1)	119.6(5)
C(11)-Th(1)-C(4)	129.4(2)	C(14)-C(13)-C(12)	108.5(7)
C(3)-Th(1)-C(4)	29.2(2)	C(14)-C(13)-C(18)	126.2(8)
C(15)-Th(1)-C(4)	144.9(2)	C(12)-C(13)-C(18)	125.2(8)
C(5)-Th(1)-C(4)	28.7(2)	C(14)-C(13)-Th(1)	75.3(5)
C(14)-Th(1)-C(4)	174.0(2)	C(12)-C(13)-Th(1)	75.6(4)
N(1)-Th(1)-C(12)	122.5(2)	C(18)-C(13)-Th(1)	118.0(5)
N(2)-Th(1)-C(12)	80.4(2)	C(13)-C(14)-C(15)	107.6(6)
C(2)-Th(1)-C(12)	114.0(2)	C(13)-C(14)-C(19)	126.8(9)
C(1)-Th(1)-C(12)	139.6(2)	C(15)-C(14)-C(19)	125.4(8)
C(11)-Th(1)-C(12)	27.9(2)	C(13)-C(14)-Th(1)	76.1(5)

C(3)-Th(1)-C(12)	111.0(2)	C(15)-C(14)-Th(1)	74.8(4)
C(15)-Th(1)-C(12)	47.5(2)	C(19)-C(14)-Th(1)	119.1(5)
C(5)-Th(1)-C(12)	159.0(2)	C(11)-C(15)-C(14)	105.3(6)
C(14)-Th(1)-C(12)	47.3(2)	C(11)-C(15)-C(20)	129.0(8)
C(4)-Th(1)-C(12)	133.5(2)	C(14)-C(15)-C(20)	125.6(8)
N(1)-Th(1)-C(13)	94.8(2)	C(11)-C(15)-Th(1)	75.0(4)
N(2)-Th(1)-C(13)	81.8(2)	C(14)-C(15)-Th(1)	75.7(4)
C(2)-Th(1)-C(13)	138.6(2)	C(20)-C(15)-Th(1)	117.2(5)
C(1)-Th(1)-C(13)	153.4(2)	N(1)-C(21)-C(23)	121.1(6)
C(11)-Th(1)-C(13)	46.7(2)	N(1)-C(21)-C(22)	121.8(7)
C(3)-Th(1)-C(13)	139.3(2)	C(23)-C(21)-C(22)	117.2(6)
C(15)-Th(1)-C(13)	47.8(2)	C(28)-C(23)-C(24)	116.3(8)
C(5)-Th(1)-C(13)	172.4(2)	C(28)-C(23)-C(21)	124.6(7)
C(14)-Th(1)-C(13)	28.6(2)	C(24)-C(23)-C(21)	119.2(6)
C(4)-Th(1)-C(13)	155.5(2)	C(25)-C(24)-C(23)	122.2(8)
C(12)-Th(1)-C(13)	28.5(2)	C(24)-C(25)-C(26)	119.5(9)
C(21)-N(1)-Th(1)	176.6(5)	C(27)-C(26)-C(25)	119.7(10)
C(29)-N(2)-Th(1)	174.7(5)	C(26)-C(27)-C(28)	119.3(8)
C(2)-C(1)-C(5)	108.2(6)	F(1)-C(28)-C(23)	121.3(8)
C(2)-C(1)-C(10)	124.6(8)	F(1)-C(28)-C(27)	115.6(7)
C(5)-C(1)-C(10)	127.0(8)	C(23)-C(28)-C(27)	123.1(8)
C(2)-C(1)-Th(1)	75.1(4)	N(2)-C(29)-C(30)	125.3(8)
C(5)-C(1)-Th(1)	76.2(4)	N(2)-C(29)-C(31)	119.9(7)
C(10)-C(1)-Th(1)	119.1(5)	C(30)-C(29)-C(31)	114.8(6)
C(1)-C(2)-C(3)	108.0(6)	C(36)-C(31)-C(32)	114.6(8)
C(1)-C(2)-C(6)	125.2(7)	C(36)-C(31)-C(29)	125.9(8)
C(3)-C(2)-C(6)	126.0(6)	C(32)-C(31)-C(29)	119.4(7)
C(1)-C(2)-Th(1)	75.8(4)	C(33)-C(32)-C(31)	123.1(8)
C(3)-C(2)-Th(1)	75.9(4)	C(34)-C(33)-C(32)	118.9(10)
C(6)-C(2)-Th(1)	122.8(4)	C(35)-C(34)-C(33)	122.2(12)
C(4)-C(3)-C(2)	107.4(6)	C(34)-C(35)-C(36)	117.4(10)
C(4)-C(3)-C(7)	125.6(7)	F(2)-C(36)-C(31)	117.3(9)
C(2)-C(3)-C(7)	127.0(7)	F(2)-C(36)-C(35)	118.8(9)
C(4)-C(3)-Th(1)	76.3(5)	C(31)-C(36)-C(35)	123.8(10)
C(2)-C(3)-Th(1)	74.7(4)		

Figure S5. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(3,5-F_2C_6H_3)]_2$ (**7**) with ellipsoids projected at the 30% probability level.

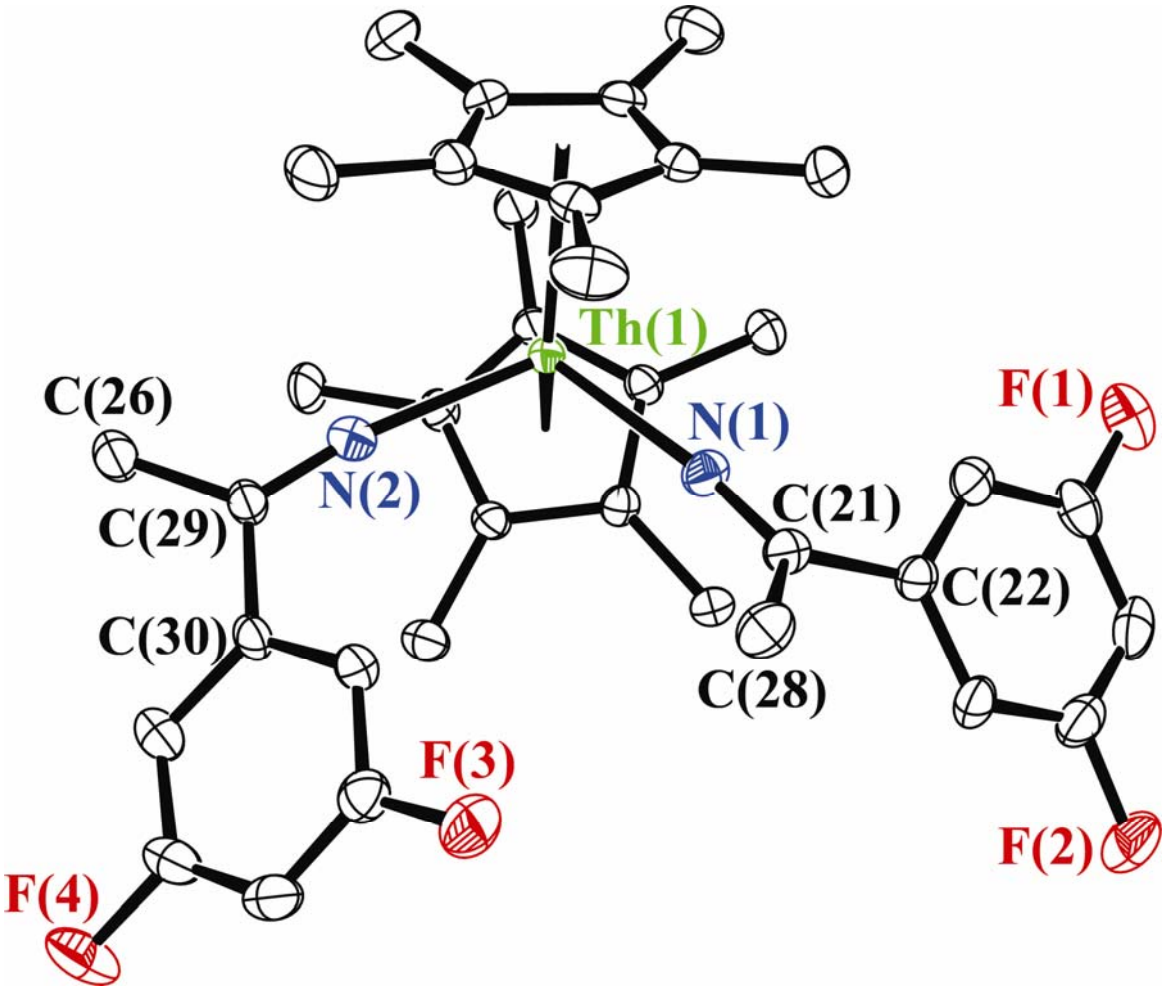


Table S9. Crystal data and structure refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(3,5-F_2C_6H_3)]_2$ (**7**).

Empirical formula	$C_{36}\ H_{42}\ F_4\ N_2\ Th$	
Formula weight	810.76	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 15.568(2) Å	α= 90°
	b = 11.3893(17) Å	β= 90.668(3)°
	c = 18.841(3) Å	γ = 90°
Volume	3340.3(9) $Å^3$	
Z	4	
Density (calculated)	1.612 Mg/m^3	
Absorption coefficient	4.513 mm^{-1}	
F(000)	1592	
Crystal size	0.22 x 0.12 x 0.04 mm^3	
θ range for data collection	1.31 to 28.26°	
Index ranges	$-20 \le h \le 20$, $-15 \le k \le 15$, $-24 \le l \le 24$	
Reflections collected	32910	
Independent reflections	7690 [R(int) = 0.0820]	
Completeness to θ = 25.00°	100.0 %	
Max. and min. transmission	0.8401 and 0.4368	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7690 / 0 / 400	
Goodness-of-fit on F^2	0.981	
Final R indices [I>2σ(I)]	R1 = 0.0413, wR2 = 0.0742	
R indices (all data)	R1 = 0.0806, wR2 = 0.0860	
Largest diff. peak and hole	1.941 and -1.166 $e.Å^{-3}$	

Table S10. Bond distances [Å] and angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(3,5\text{-}F_2C_6H_3)]_2$ (**7**).

Th(1)-N(2)	2.263(5)	C(12)-C(17)	1.509(8)
Th(1)-N(1)	2.286(5)	C(13)-C(14)	1.424(8)
Th(1)-C(12)	2.771(5)	C(13)-C(18)	1.505(7)
Th(1)-C(1)	2.781(6)	C(14)-C(19)	1.507(8)
Th(1)-C(13)	2.795(5)	C(22)-C(27)	1.386(8)
Th(1)-C(2)	2.803(6)	C(22)-C(23)	1.393(8)
Th(1)-C(5)	2.811(5)	C(22)-C(21)	1.515(8)
Th(1)-C(11)	2.816(5)	C(27)-C(26)	1.384(9)
Th(1)-C(3)	2.823(5)	C(26)-C(25)	1.381(10)
Th(1)-C(14)	2.828(5)	C(25)-C(24)	1.358(10)
Th(1)-C(4)	2.831(5)	C(24)-C(23)	1.371(9)
Th(1)-C(15)	2.839(5)	C(21)-C(28)	1.519(8)
F(1)-C(26)	1.346(8)	C(29)-C(30)	1.502(8)
F(2)-C(24)	1.362(8)	C(29)-C(36)	1.503(8)
F(3)-C(32)	1.362(7)	C(30)-C(31)	1.390(8)
F(4)-C(34)	1.355(7)	C(30)-C(35)	1.394(8)
N(1)-C(21)	1.245(7)	C(32)-C(31)	1.356(8)
N(2)-C(29)	1.268(7)	C(32)-C(33)	1.360(9)
C(1)-C(5)	1.407(8)	C(33)-C(34)	1.361(9)
C(1)-C(2)	1.410(8)	C(34)-C(35)	1.378(9)
C(1)-C(6)	1.505(9)		
C(2)-C(3)	1.406(9)	N(2)-Th(1)-N(1)	107.37(17)
C(2)-C(7)	1.511(8)	N(2)-Th(1)-C(12)	123.65(16)
C(3)-C(4)	1.395(8)	N(1)-Th(1)-C(12)	96.09(17)
C(3)-C(8)	1.510(8)	N(2)-Th(1)-C(1)	95.56(17)
C(4)-C(5)	1.412(8)	N(1)-Th(1)-C(1)	123.09(17)
C(4)-C(9)	1.504(8)	C(12)-Th(1)-C(1)	113.25(17)
C(5)-C(10)	1.506(8)	N(2)-Th(1)-C(13)	104.19(17)
C(15)-C(14)	1.407(8)	N(1)-Th(1)-C(13)	81.63(16)
C(15)-C(11)	1.422(8)	C(12)-Th(1)-C(13)	29.50(16)
C(15)-C(20)	1.513(8)	C(1)-Th(1)-C(13)	141.97(17)
C(11)-C(12)	1.417(8)	N(2)-Th(1)-C(2)	77.66(17)
C(11)-C(16)	1.496(8)	N(1)-Th(1)-C(2)	106.79(18)
C(12)-C(13)	1.417(8)	C(12)-Th(1)-C(2)	142.46(18)

C(1)-Th(1)-C(2)	29.25(17)	C(1)-Th(1)-C(4)	47.81(17)
C(13)-Th(1)-C(2)	170.59(17)	C(13)-Th(1)-C(4)	133.45(17)
N(2)-Th(1)-C(5)	123.54(16)	C(2)-Th(1)-C(4)	47.59(17)
N(1)-Th(1)-C(5)	102.43(17)	C(5)-Th(1)-C(4)	28.98(16)
C(12)-Th(1)-C(5)	98.82(16)	C(11)-Th(1)-C(4)	119.32(17)
C(1)-Th(1)-C(5)	29.13(16)	C(3)-Th(1)-C(4)	28.56(16)
C(13)-Th(1)-C(5)	127.04(16)	C(14)-Th(1)-C(4)	161.66(17)
C(2)-Th(1)-C(5)	47.94(16)	N(2)-Th(1)-C(15)	78.23(16)
N(2)-Th(1)-C(11)	105.73(17)	N(1)-Th(1)-C(15)	127.71(16)
N(1)-Th(1)-C(11)	125.28(16)	C(12)-Th(1)-C(15)	47.95(16)
C(12)-Th(1)-C(11)	29.36(16)	C(1)-Th(1)-C(15)	107.37(17)
C(1)-Th(1)-C(11)	95.16(17)	C(13)-Th(1)-C(15)	47.90(16)
C(13)-Th(1)-C(11)	48.49(16)	C(2)-Th(1)-C(15)	124.75(18)
C(2)-Th(1)-C(11)	122.10(18)	C(5)-Th(1)-C(15)	117.50(17)
C(5)-Th(1)-C(11)	93.83(17)	C(11)-Th(1)-C(15)	29.12(16)
N(2)-Th(1)-C(3)	93.10(17)	C(3)-Th(1)-C(15)	153.35(17)
N(1)-Th(1)-C(3)	78.89(17)	C(14)-Th(1)-C(15)	28.76(15)
C(12)-Th(1)-C(3)	142.22(17)	C(4)-Th(1)-C(15)	145.92(16)
C(1)-Th(1)-C(3)	47.84(18)	C(21)-N(1)-Th(1)	172.8(4)
C(13)-Th(1)-C(3)	157.08(18)	C(29)-N(2)-Th(1)	170.8(4)
C(2)-Th(1)-C(3)	28.95(18)	C(5)-C(1)-C(2)	108.1(6)
C(5)-Th(1)-C(3)	47.58(17)	C(5)-C(1)-C(6)	126.4(6)
C(11)-Th(1)-C(3)	140.50(17)	C(2)-C(1)-C(6)	125.2(6)
N(2)-Th(1)-C(14)	77.03(16)	C(5)-C(1)-Th(1)	76.6(3)
N(1)-Th(1)-C(14)	100.10(16)	C(2)-C(1)-Th(1)	76.2(3)
C(12)-Th(1)-C(14)	48.31(16)	C(6)-C(1)-Th(1)	118.6(4)
C(1)-Th(1)-C(14)	136.07(17)	C(3)-C(2)-C(1)	107.6(5)
C(13)-Th(1)-C(14)	29.33(16)	C(3)-C(2)-C(7)	125.9(6)
C(2)-Th(1)-C(14)	147.44(17)	C(1)-C(2)-C(7)	126.2(6)
C(5)-Th(1)-C(14)	141.94(16)	C(3)-C(2)-Th(1)	76.3(3)
C(11)-Th(1)-C(14)	48.16(16)	C(1)-C(2)-Th(1)	74.5(3)
C(3)-Th(1)-C(14)	169.37(17)	C(7)-C(2)-Th(1)	120.1(4)
N(2)-Th(1)-C(4)	121.29(16)	C(4)-C(3)-C(2)	108.5(5)
N(1)-Th(1)-C(4)	76.24(17)	C(4)-C(3)-C(8)	126.0(6)
C(12)-Th(1)-C(4)	113.70(16)	C(2)-C(3)-C(8)	125.3(6)
C(4)-C(3)-Th(1)	76.0(3)	C(14)-C(13)-C(18)	125.2(5)

C(2)-C(3)-Th(1)	74.7(3)	C(12)-C(13)-Th(1)	74.3(3)
C(8)-C(3)-Th(1)	119.3(4)	C(14)-C(13)-Th(1)	76.6(3)
C(3)-C(4)-C(5)	108.2(5)	C(18)-C(13)-Th(1)	119.3(3)
C(3)-C(4)-C(9)	125.9(6)	C(15)-C(14)-C(13)	107.8(5)
C(5)-C(4)-C(9)	125.5(6)	C(15)-C(14)-C(19)	127.0(5)
C(3)-C(4)-Th(1)	75.4(3)	C(13)-C(14)-C(19)	125.0(5)
C(5)-C(4)-Th(1)	74.7(3)	C(15)-C(14)-Th(1)	76.1(3)
C(9)-C(4)-Th(1)	121.7(4)	C(13)-C(14)-Th(1)	74.1(3)
C(1)-C(5)-C(4)	107.6(5)	C(19)-C(14)-Th(1)	120.1(4)
C(1)-C(5)-C(10)	126.2(6)	C(27)-C(22)-C(23)	118.4(6)
C(4)-C(5)-C(10)	125.7(6)	C(27)-C(22)-C(21)	119.9(5)
C(1)-C(5)-Th(1)	74.3(3)	C(23)-C(22)-C(21)	121.5(5)
C(4)-C(5)-Th(1)	76.3(3)	C(26)-C(27)-C(22)	119.9(6)
C(10)-C(5)-Th(1)	121.6(4)	F(1)-C(26)-C(25)	118.9(6)
C(14)-C(15)-C(11)	109.0(5)	F(1)-C(26)-C(27)	118.8(7)
C(14)-C(15)-C(20)	125.7(5)	C(25)-C(26)-C(27)	122.3(7)
C(11)-C(15)-C(20)	125.2(5)	C(24)-C(25)-C(26)	116.0(6)
C(14)-C(15)-Th(1)	75.2(3)	C(25)-C(24)-F(2)	117.5(7)
C(11)-C(15)-Th(1)	74.6(3)	C(25)-C(24)-C(23)	124.4(7)
C(20)-C(15)-Th(1)	120.4(4)	F(2)-C(24)-C(23)	118.1(7)
C(12)-C(11)-C(15)	106.9(5)	C(24)-C(23)-C(22)	118.9(6)
C(12)-C(11)-C(16)	127.0(5)	N(1)-C(21)-C(22)	121.4(5)
C(15)-C(11)-C(16)	125.6(5)	N(1)-C(21)-C(28)	123.4(6)
C(12)-C(11)-Th(1)	73.6(3)	C(22)-C(21)-C(28)	115.2(5)
C(15)-C(11)-Th(1)	76.3(3)	N(2)-C(29)-C(30)	119.5(5)
C(16)-C(11)-Th(1)	122.3(4)	N(2)-C(29)-C(36)	123.8(5)
C(11)-C(12)-C(13)	108.8(5)	C(30)-C(29)-C(36)	116.8(5)
C(11)-C(12)-C(17)	125.1(5)	C(31)-C(30)-C(35)	118.8(5)
C(13)-C(12)-C(17)	125.9(5)	C(31)-C(30)-C(29)	119.3(5)
C(11)-C(12)-Th(1)	77.1(3)	C(35)-C(30)-C(29)	122.0(5)
C(13)-C(12)-Th(1)	76.2(3)	C(31)-C(32)-F(3)	118.0(6)
C(17)-C(12)-Th(1)	117.1(4)	C(31)-C(32)-C(33)	123.9(7)
C(12)-C(13)-C(14)	107.5(5)	F(3)-C(32)-C(33)	118.0(6)
C(12)-C(13)-C(18)	127.1(5)	C(32)-C(33)-C(34)	116.2(6)
F(4)-C(34)-C(33)	118.6(6)		
F(4)-C(34)-C(35)	117.9(6)		

C(33)-C(34)-C(35)	123.5(6)
C(34)-C(35)-C(30)	118.4(6)
C(32)-C(31)-C(30)	119.2(6)

Figure S6. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(3,4,5\text{-}F_3C_6H_2)]_2$ (**8**) with ellipsoids projected at the 30% probability level.

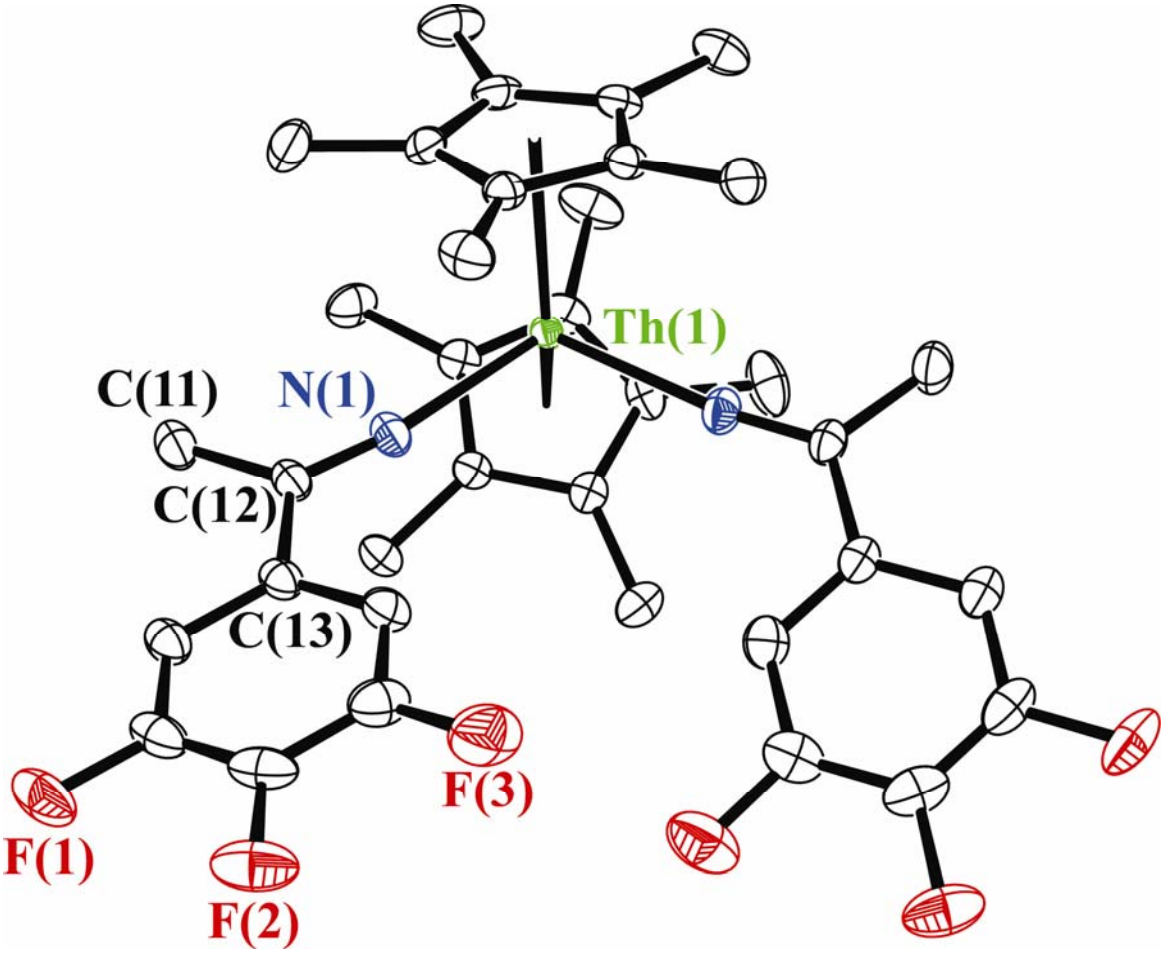


Table S11. Crystal data and structure refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(3,4,5\text{-}F_3C_6H_2)]_2$ (**8**).

Empirical formula	$C_{36}\ H_{40}\ F_6\ N_2\ Th$	
Formula weight	846.74	
Temperature	141(1) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 13.087(3) Å	α= 90°
	b = 13.927(3) Å	β= 99.272(3)°
	c = 18.783(5) Å	γ = 90°
Volume	3378.7(14) $Å^3$	
Z	4	
Density (calculated)	1.665 Mg/m^3	
Absorption coefficient	4.474 mm^{-1}	
F(000)	1656	
Crystal size	0.12 x 0.08 x 0.06 mm^3	
θ range for data collection	2.15 to 25.34°	
Index ranges	$-15 \le h \le 15, -16 \le k \le 16, -22 \le l \le 22$	
Reflections collected	19037	
Independent reflections	3100 [R(int) = 0.0252]	
Completeness to θ = 25.00°	100.0 %	
Max. and min. transmission	0.7751 and 0.6158	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3100 / 0 / 210	
Goodness-of-fit on F^2	1.185	
Final R indices [I>2σ(I)]	R1 = 0.0145, wR2 = 0.0362	
R indices (all data)	R1 = 0.0172, wR2 = 0.0372	
Largest diff. peak and hole	0.352 and -0.308 $e.Å^{-3}$	

Table S12. Bond distances [Å] and angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(3,4,5\text{-}F_3C_6H_2)]_2$ (**8**).

Th(1)-N(1)	2.2727(19)
Th(1)-N(1)#1	2.273(2)
Th(1)-C(2)#1	2.794(2)
Th(1)-C(2)	2.794(2)
Th(1)-C(1)#1	2.804(2)
Th(1)-C(1)	2.804(2)
Th(1)-C(3)#1	2.805(2)
Th(1)-C(3)	2.805(2)
Th(1)-C(5)#1	2.810(2)
Th(1)-C(5)	2.810(2)
Th(1)-C(4)#1	2.821(3)
Th(1)-C(4)	2.821(3)
N(1)-C(11)	1.256(3)
F(1)-C(15)	1.352(3)
F(2)-C(16)	1.354(4)
F(3)-C(17)	1.346(4)
C(1)-C(2)	1.413(4)
C(1)-C(5)	1.417(4)
C(1)-C(6)	1.499(4)
C(2)-C(3)	1.419(4)
C(2)-C(7)	1.512(4)
C(3)-C(4)	1.407(3)
C(3)-C(8)	1.507(4)
C(4)-C(5)	1.417(4)
C(4)-C(9)	1.504(3)
C(5)-C(10)	1.501(3)
C(11)-C(12)	1.507(4)
C(11)-C(13)	1.518(3)
C(13)-C(18)	1.387(4)
C(13)-C(14)	1.399(3)
C(14)-C(15)	1.370(4)
C(15)-C(16)	1.355(5)
C(16)-C(17)	1.379(4)
C(17)-C(18)	1.369(4)
C(1)#1-Th(1)-C(5)#1	29.23(8)
N(1)-Th(1)-N(1)#1	109.72(11)
N(1)-Th(1)-C(2)#1	120.48(8)
N(1)#1-Th(1)-C(2)#1	106.39(8)
N(1)-Th(1)-C(2)	106.39(8)
N(1)#1-Th(1)-C(2)	120.48(8)
C(2)#1-Th(1)-C(2)	93.40(11)
N(1)-Th(1)-C(1)#1	122.81(8)
N(1)#1-Th(1)-C(1)#1	79.13(8)
C(2)#1-Th(1)-C(1)#1	29.25(8)
C(2)-Th(1)-C(1)#1	116.85(9)
N(1)-Th(1)-C(1)	79.13(8)
N(1)#1-Th(1)-C(1)	122.81(8)
C(2)#1-Th(1)-C(1)	116.85(9)
C(2)-Th(1)-C(1)	29.25(8)
C(1)#1-Th(1)-C(1)	144.26(13)
N(1)-Th(1)-C(3)#1	91.45(8)
N(1)#1-Th(1)-C(3)#1	125.29(7)
C(2)#1-Th(1)-C(3)#1	29.35(7)
C(2)-Th(1)-C(3)#1	98.81(8)
C(1)#1-Th(1)-C(3)#1	48.15(7)
C(1)-Th(1)-C(3)#1	110.22(8)
N(1)-Th(1)-C(3)	125.29(7)
N(1)#1-Th(1)-C(3)	91.45(8)
C(2)#1-Th(1)-C(3)	98.81(8)
C(2)-Th(1)-C(3)	29.35(7)
C(1)#1-Th(1)-C(3)	110.22(8)
C(1)-Th(1)-C(3)	48.15(7)
C(3)#1-Th(1)-C(3)	116.82(11)
N(1)-Th(1)-C(5)#1	94.87(7)
N(1)#1-Th(1)-C(5)#1	79.30(7)
C(2)#1-Th(1)-C(5)#1	48.33(8)
C(2)-Th(1)-C(5)#1	141.70(8)
C(2)-C(1)-C(5)	108.3(2)

C(1)-Th(1)-C(5)#1	157.87(8)	C(2)-C(1)-C(6)	125.5(3)
C(3)#1-Th(1)-C(5)#1	48.20(7)	C(5)-C(1)-C(6)	125.9(3)
C(3)-Th(1)-C(5)#1	139.30(7)	C(2)-C(1)-Th(1)	74.99(14)
N(1)-Th(1)-C(5)	79.30(7)	C(5)-C(1)-Th(1)	75.61(13)
N(1)#1-Th(1)-C(5)	94.87(8)	C(6)-C(1)-Th(1)	119.46(17)
C(2)#1-Th(1)-C(5)	141.70(8)	C(1)-C(2)-C(3)	107.8(2)
C(2)-Th(1)-C(5)	48.33(8)	C(1)-C(2)-C(7)	125.2(3)
C(1)#1-Th(1)-C(5)	157.87(8)	C(3)-C(2)-C(7)	126.5(3)
C(1)-Th(1)-C(5)	29.23(8)	C(1)-C(2)-Th(1)	75.77(14)
C(3)#1-Th(1)-C(5)	139.30(7)	C(3)-C(2)-Th(1)	75.75(14)
C(3)-Th(1)-C(5)	48.20(7)	C(7)-C(2)-Th(1)	121.25(18)
C(5)#1-Th(1)-C(5)	169.97(10)	C(4)-C(3)-C(2)	107.9(2)
N(1)-Th(1)-C(4)#1	76.76(7)	C(4)-C(3)-C(8)	125.8(2)
N(1)#1-Th(1)-C(4)#1	106.80(7)	C(2)-C(3)-C(8)	126.2(3)
C(2)#1-Th(1)-C(4)#1	48.01(7)	C(4)-C(3)-Th(1)	76.12(14)
C(2)-Th(1)-C(4)#1	126.69(7)	C(2)-C(3)-Th(1)	74.90(14)
C(1)#1-Th(1)-C(4)#1	47.89(7)	C(8)-C(3)-Th(1)	118.43(17)
C(1)-Th(1)-C(4)#1	129.69(7)	C(3)-C(4)-C(5)	108.6(2)
C(3)#1-Th(1)-C(4)#1	28.97(7)	C(3)-C(4)-C(9)	126.3(2)
C(3)-Th(1)-C(4)#1	145.12(7)	C(5)-C(4)-C(9)	124.9(2)
C(5)#1-Th(1)-C(4)#1	29.14(7)	C(3)-C(4)-Th(1)	74.91(14)
C(5)-Th(1)-C(4)#1	151.95(7)	C(5)-C(4)-Th(1)	75.01(14)
N(1)-Th(1)-C(4)	106.80(7)	C(9)-C(4)-Th(1)	121.07(16)
N(1)#1-Th(1)-C(4)	76.76(7)	C(1)-C(5)-C(4)	107.4(2)
C(2)#1-Th(1)-C(4)	126.69(7)	C(1)-C(5)-C(10)	127.3(2)
C(2)-Th(1)-C(4)	48.01(7)	C(4)-C(5)-C(10)	125.2(2)
C(1)#1-Th(1)-C(4)	129.69(7)	C(1)-C(5)-Th(1)	75.16(14)
C(1)-Th(1)-C(4)	47.89(7)	C(4)-C(5)-Th(1)	75.85(14)
C(3)#1-Th(1)-C(4)	145.12(7)	C(10)-C(5)-Th(1)	118.08(16)
C(3)-Th(1)-C(4)	28.97(7)	N(1)-C(11)-C(12)	122.6(2)
C(5)#1-Th(1)-C(4)	151.95(7)	N(1)-C(11)-C(13)	121.5(2)
C(5)-Th(1)-C(4)	29.14(7)	C(12)-C(11)-C(13)	115.9(2)
C(4)#1-Th(1)-C(4)	174.03(9)	C(18)-C(13)-C(14)	118.7(3)
C(11)-N(1)-Th(1)	170.5(2)	C(18)-C(13)-C(11)	119.4(2)
C(17)-C(18)-C(13)	119.8(3)		
C(14)-C(13)-C(11)	121.9(2)		

C(15)-C(14)-C(13)	119.7(3)
F(1)-C(15)-C(16)	118.5(3)
F(1)-C(15)-C(14)	120.0(3)
C(16)-C(15)-C(14)	121.6(3)
F(2)-C(16)-C(15)	121.1(3)
F(2)-C(16)-C(17)	119.9(3)
C(15)-C(16)-C(17)	119.0(3)
F(3)-C(17)-C(18)	120.8(3)
F(3)-C(17)-C(16)	117.9(3)
C(18)-C(17)-C(16)	121.2(3)

Figure S7. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(2,6\text{-}F_2C_6H_2)]_2$ (**9**) with ellipsoids projected at the 30% probability level.

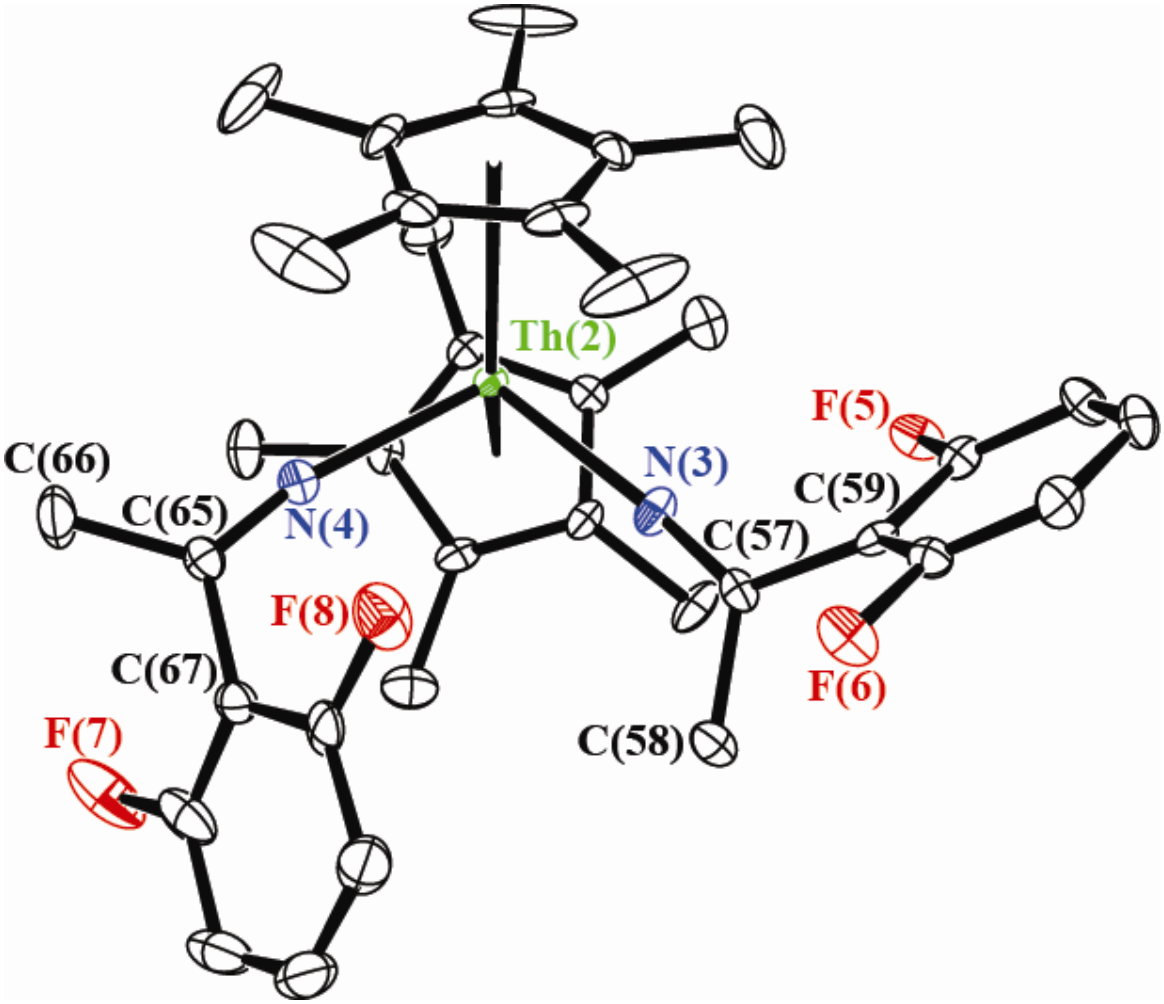


Table S13. Crystal data and structure refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(2,6\text{-}F_2C_6H_2)]_2$ (**9**).

Empirical formula	$C_{36}\ H_{42}\ F_4\ N_2\ Th$	
Formula weight	810.76	
Temperature	141(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 10.7290(5) Å	α= 108.7590(10)°.
	b = 17.7108(8) Å	β= 90.1920(10)°.
	c = 19.3565(9) Å	γ = 102.9020(10)°.
Volume	3383.5(3) $Å^3$	
Z	4	
Density (calculated)	1.592 Mg/m^3	
Absorption coefficient	4.455 mm^{-1}	
F(000)	1592	
Crystal size	0.10 x 0.08 x 0.04 mm^3	
θ range for data collection	1.11 to 29.02°.	
Index ranges	$-13 \le h \le 14, -23 \le k \le 24, -26 \le l \le 24$	
Reflections collected	33978	
Independent reflections	15894 [R(int) = 0.0437]	
Completeness to θ = 25.00°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8419 and 0.6643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15894 / 6 / 645	
Goodness-of-fit on F^2	1.157	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1002	
R indices (all data)	R1 = 0.0710, wR2 = 0.1092	
Largest diff. peak and hole	1.571 and -1.694 $e.Å^{-3}$	

Table S14. Table of Bond Distances and Angles for $(C_5Me_5)_2Th[-N=C(CH_3)(2,6\text{-}F_2C_6H_2)]_2$ (**9**).

Th(1)-N(1)	2.255(5)
Th(1)-N(2)	2.261(5)
Th(1)-C(15')	2.702(6)
Th(1)-C(4)	2.760(5)
Th(1)-C(14')	2.762(6)
Th(1)-C(11')	2.761(7)
Th(1)-C(3)	2.768(5)
Th(1)-C(5)	2.790(5)
Th(1)-C(2)	2.802(5)
Th(1)-C(1)	2.815(5)
Th(1)-C(1')	2.831(6)
Th(1)-C(5')	2.837(6)
Th(2)-N(4)	2.255(5)
Th(2)-N(3)	2.263(5)
Th(2)-C(39)	2.787(6)
Th(2)-C(48)	2.800(6)
Th(2)-C(49)	2.802(6)
Th(2)-C(41)	2.802(6)
Th(2)-C(37)	2.807(5)
Th(2)-C(40)	2.809(6)
Th(2)-C(38)	2.812(6)
Th(2)-C(50)	2.820(6)
Th(2)-C(47)	2.824(6)
Th(2)-C(51)	2.833(6)
F(1)-C(24)	1.363(8)
F(2)-C(28)	1.334(9)
F(3)-C(32)	1.335(8)
F(4)-C(36)	1.352(9)
F(5)-C(60)	1.365(7)
F(6)-C(64)	1.365(7)
F(7)-C(68)	1.386(10)
F(8)-C(72)	1.349(9)
N(1)-C(21)	1.272(8)
N(2)-C(29)	1.280(8)
N(3)-C(57)	1.262(8)
N(4)-C(65)	1.273(8)
C(1)-C(5')	1.237(7)
C(1)-C(2)	1.4200
C(1)-C(5)	1.4200
C(1)-C(6')	1.440(7)
C(1)-C(6)	1.5095
C(2)-C(2')	0.614(7)
C(2)-C(1')	1.043(8)
C(2)-C(3)	1.4200
C(2)-C(7)	1.5095
C(2)-C(7')	1.595(7)
C(3)-C(3')	0.633(7)
C(3)-C(2')	0.854(7)
C(3)-C(4)	1.4200
C(3)-C(8)	1.5095
C(4)-C(3')	0.973(7)
C(4)-C(5)	1.4200
C(4)-C(9)	1.5095
C(4)-C(5')	1.608(7)
C(5)-C(4')	1.203(7)
C(5)-C(10)	1.5095
C(5)-C(1')	1.566(7)
C(5)-C(10')	1.597(7)
C(6)-C(6')	0.905(10)
C(7)-C(7')	1.149(9)
C(8)-C(8')	1.168(9)
C(8)-C(3')	1.655(7)
C(9)-C(9')	0.962(10)
C(9)-C(4')	1.445(7)
C(10)-C(10')	0.768(10)
C(10)-C(5')	1.535(7)
C(11)-C(12')	0.756(8)

C(11)-C(11')	0.694(8)	C(5')-C(10')	1.5095
C(11)-C(12)	1.4200	C(11')-C(12')	1.4200
C(11)-C(15)	1.4200	C(11')-C(15')	1.4200
C(11)-C(16)	1.5095	C(11')-C(16')	1.5095
C(12)-C(12')	1.010(8)	C(12')-C(13')	1.4200
C(12)-C(13)	1.4200	C(12')-C(17')	1.5095
C(12)-C(17)	1.5095	C(13')-C(14')	1.4200
C(12)-C(14')	1.598(8)	C(13')-C(18')	1.5095
C(13)-C(13')	1.150(8)	C(14')-C(15')	1.4200
C(13)-C(14)	1.4200	C(14')-C(19')	1.5095
C(13)-C(18)	1.5095	C(15')-C(20')	1.5095
C(13)-C(19')	1.508(8)	C(21)-C(22)	1.498(10)
C(14)-C(15')	0.772(8)	C(21)-C(23)	1.513(9)
C(14)-C(14')	0.983(8)	C(23)-C(28)	1.372(10)
C(14)-C(15)	1.4200	C(23)-C(24)	1.371(9)
C(14)-C(19)	1.5095	C(24)-C(25)	1.350(10)
C(14)-C(20')	1.636(8)	C(25)-C(26)	1.377(13)
C(15)-C(15')	0.668(9)	C(26)-C(27)	1.402(14)
C(15)-C(11')	0.912(8)	C(27)-C(28)	1.367(12)
C(15)-C(20)	1.5095	C(29)-C(30)	1.506(9)
C(16)-C(17')	1.503(11)	C(29)-C(31)	1.507(8)
C(16)-C(12')	1.615(9)	C(31)-C(36)	1.359(9)
C(17)-C(18')	1.173(11)	C(31)-C(32)	1.365(9)
C(17)-C(13')	1.521(8)	C(32)-C(33)	1.394(10)
C(18)-C(19')	1.192(11)	C(33)-C(34)	1.349(11)
C(19)-C(20')	1.521(11)	C(34)-C(35)	1.358(11)
C(20)-C(16')	1.687(11)	C(35)-C(36)	1.378(10)
C(1')-C(2')	1.4200	C(37)-C(41)	1.404(9)
C(1')-C(5')	1.4200	C(37)-C(38)	1.411(8)
C(1')-C(6')	1.5095	C(37)-C(42)	1.517(9)
C(2')-C(3')	1.4200	C(38)-C(39)	1.397(8)
C(2')-C(7')	1.5095	C(38)-C(43)	1.508(8)
C(3')-C(4')	1.4200	C(39)-C(40)	1.418(8)
C(3')-C(8')	1.5095	C(39)-C(44)	1.510(9)
C(4')-C(5')	1.4200	C(40)-C(41)	1.432(9)
C(4')-C(9')	1.5095	C(40)-C(45)	1.513(9)

C(41)-C(46)	1.515(8)	N(2)-Th(1)-C(14')	78.25(19)
C(47)-C(48)	1.394(10)	C(15')-Th(1)-C(14')	30.10(7)
C(47)-C(51)	1.408(9)	C(4)-Th(1)-C(14')	163.51(19)
C(47)-C(52)	1.504(10)	N(1)-Th(1)-C(11')	83.04(19)
C(48)-C(49)	1.403(10)	N(2)-Th(1)-C(11')	123.40(19)
C(48)-C(53)	1.511(11)	C(15')-Th(1)-C(11')	30.11(7)
C(49)-C(50)	1.398(10)	C(4)-Th(1)-C(11')	141.85(18)
C(49)-C(54)	1.505(10)	C(14')-Th(1)-C(11')	49.16(9)
C(50)-C(51)	1.401(10)	N(1)-Th(1)-C(3)	77.01(16)
C(50)-C(55)	1.496(10)	N(2)-Th(1)-C(3)	123.89(17)
C(51)-C(56)	1.510(10)	C(15')-Th(1)-C(3)	141.85(19)
C(57)-C(59)	1.507(8)	C(4)-Th(1)-C(3)	29.77(5)
C(57)-C(58)	1.524(9)	C(14')-Th(1)-C(3)	151.74(17)
C(59)-C(64)	1.380(8)	C(11')-Th(1)-C(3)	112.70(18)
C(59)-C(60)	1.400(8)	N(1)-Th(1)-C(5)	109.33(17)
C(60)-C(61)	1.369(8)	N(2)-Th(1)-C(5)	79.48(17)
C(61)-C(62)	1.390(9)	C(15')-Th(1)-C(5)	163.93(18)
C(62)-C(63)	1.387(9)	C(4)-Th(1)-C(5)	29.64(5)
C(63)-C(64)	1.371(8)	C(14')-Th(1)-C(5)	133.88(18)
C(65)-C(66)	1.506(9)	C(11')-Th(1)-C(5)	150.54(17)
C(65)-C(67)	1.516(9)	C(3)-Th(1)-C(5)	48.84(7)
C(67)-C(72)	1.371(10)	N(1)-Th(1)-C(2)	103.48(17)
C(67)-C(68)	1.374(10)	N(2)-Th(1)-C(2)	125.96(17)
C(68)-C(69)	1.396(12)	C(15')-Th(1)-C(2)	131.69(16)
C(69)-C(70)	1.406(14)	C(4)-Th(1)-C(2)	48.79(7)
C(70)-C(71)	1.335(13)	C(14')-Th(1)-C(2)	124.72(17)
C(71)-C(72)	1.395(10)	C(11')-Th(1)-C(2)	103.32(17)
		C(3)-Th(1)-C(2)	29.5
N(1)-Th(1)-N(2)	107.35(19)	C(5)-Th(1)-C(2)	48.52(7)
N(1)-Th(1)-C(15')	86.55(19)	N(1)-Th(1)-C(1)	124.85(16)
N(2)-Th(1)-C(15')	93.7(2)	N(2)-Th(1)-C(1)	97.69(17)
N(1)-Th(1)-C(4)	80.50(17)	C(15')-Th(1)-C(1)	140.59(16)
N(2)-Th(1)-C(4)	94.40(17)	C(4)-Th(1)-C(1)	48.66(8)
C(15')-Th(1)-C(4)	166.29(19)	C(14')-Th(1)-C(1)	117.14(17)
N(1)-Th(1)-C(14')	115.7(2)	C(11')-Th(1)-C(1)	121.87(18)
C(3)-Th(1)-C(1)	48.59(7)	N(3)-Th(2)-C(41)	119.05(18)

C(5)-Th(1)-C(1)	29.35(5)	C(39)-Th(2)-C(41)	48.21(18)
C(2)-Th(1)-C(1)	29.3	C(48)-Th(2)-C(41)	159.4(2)
N(1)-Th(1)-C(1')	118.50(17)	C(49)-Th(2)-C(41)	135.0(2)
N(2)-Th(1)-C(1')	105.12(18)	N(4)-Th(2)-C(37)	78.89(19)
C(15')-Th(1)-C(1')	140.91(16)	N(3)-Th(2)-C(37)	90.43(18)
C(4)-Th(1)-C(1')	46.12(13)	C(39)-Th(2)-C(37)	47.97(18)
C(14')-Th(1)-C(1')	121.20(17)	C(48)-Th(2)-C(37)	171.5(2)
C(11')-Th(1)-C(1')	118.21(18)	C(49)-Th(2)-C(37)	156.7(2)
C(3)-Th(1)-C(1')	41.60(14)	C(41)-Th(2)-C(37)	28.99(18)
C(5)-Th(1)-C(1')	32.34(15)	N(4)-Th(2)-C(40)	104.37(18)
C(2)-Th(1)-C(1')	21.34(15)	N(3)-Th(2)-C(40)	121.63(18)
C(1)-Th(1)-C(1')	8.07(15)	C(39)-Th(2)-C(40)	29.35(17)
N(1)-Th(1)-C(5')	113.51(17)	C(48)-Th(2)-C(40)	137.6(2)
N(2)-Th(1)-C(5')	80.35(17)	C(49)-Th(2)-C(40)	130.3(2)
C(15')-Th(1)-C(5')	159.93(18)	C(41)-Th(2)-C(40)	29.58(18)
C(4)-Th(1)-C(5')	33.35(15)	C(37)-Th(2)-C(40)	48.33(18)
C(14')-Th(1)-C(5')	130.17(18)	N(4)-Th(2)-C(38)	106.71(18)
C(11')-Th(1)-C(5')	147.03(18)	N(3)-Th(2)-C(38)	75.39(18)
C(3)-Th(1)-C(5')	50.05(14)	C(39)-Th(2)-C(38)	28.89(18)
C(5)-Th(1)-C(5')	4.64(15)	C(48)-Th(2)-C(38)	146.0(2)
C(2)-Th(1)-C(5')	46.59(14)	C(49)-Th(2)-C(38)	173.46(19)
C(1)-Th(1)-C(5')	25.29(15)	C(41)-Th(2)-C(38)	47.90(17)
C(1')-Th(1)-C(5')	29.02(6)	C(37)-Th(2)-C(38)	29.09(17)
N(4)-Th(2)-N(3)	104.8(2)	C(40)-Th(2)-C(38)	48.13(17)
N(4)-Th(2)-C(39)	123.96(18)	N(4)-Th(2)-C(50)	88.1(2)
N(3)-Th(2)-C(39)	93.48(19)	N(3)-Th(2)-C(50)	128.69(19)
N(4)-Th(2)-C(48)	102.7(2)	C(39)-Th(2)-C(50)	120.1(2)
N(3)-Th(2)-C(48)	81.10(19)	C(48)-Th(2)-C(50)	47.6(2)
C(39)-Th(2)-C(48)	132.6(2)	C(49)-Th(2)-C(50)	28.8(2)
N(4)-Th(2)-C(49)	79.79(19)	C(41)-Th(2)-C(50)	112.20(19)
N(3)-Th(2)-C(49)	104.0(2)	C(37)-Th(2)-C(50)	140.86(19)
C(39)-Th(2)-C(49)	145.98(19)	C(40)-Th(2)-C(50)	101.6(2)
C(48)-Th(2)-C(49)	29.0(2)	C(38)-Th(2)-C(50)	148.3(2)
N(4)-Th(2)-C(41)	77.21(19)	N(4)-Th(2)-C(47)	127.24(18)
N(3)-Th(2)-C(47)	89.3(2)	C(2)-C(1)-Th(1)	74.84(16)
C(39)-Th(2)-C(47)	104.97(19)	C(5)-C(1)-Th(1)	74.33(16)

C(48)-Th(2)-C(47)	28.7(2)	C(6')-C(1)-Th(1)	117.1(5)
C(49)-Th(2)-C(47)	47.46(19)	C(6)-C(1)-Th(1)	116.89(15)
C(41)-Th(2)-C(47)	138.4(2)	C(2')-C(2)-C(1')	115.4(9)
C(37)-Th(2)-C(47)	152.9(2)	C(2')-C(2)-C(1)	118.3(6)
C(40)-Th(2)-C(47)	110.5(2)	C(1')-C(2)-C(1)	6.0(5)
C(38)-Th(2)-C(47)	126.05(19)	C(2')-C(2)-C(3)	17.3(7)
C(50)-Th(2)-C(47)	47.46(19)	C(1')-C(2)-C(3)	106.7(4)
N(4)-Th(2)-C(51)	116.7(2)	C(1)-C(2)-C(3)	108.0
N(3)-Th(2)-C(51)	118.0(2)	C(2')-C(2)-C(7)	114.2(6)
C(39)-Th(2)-C(51)	98.65(19)	C(1')-C(2)-C(7)	127.0(4)
C(48)-Th(2)-C(51)	47.4(2)	C(1)-C(2)-C(7)	126.0
C(49)-Th(2)-C(51)	47.4(2)	C(3)-C(2)-C(7)	126.0
C(41)-Th(2)-C(51)	113.8(2)	C(2')-C(2)-C(7')	70.9(7)
C(37)-Th(2)-C(51)	139.31(19)	C(1')-C(2)-C(7')	163.1(8)
C(40)-Th(2)-C(51)	91.02(19)	C(1)-C(2)-C(7')	166.4(4)
C(38)-Th(2)-C(51)	127.0(2)	C(3)-C(2)-C(7')	83.3(3)
C(50)-Th(2)-C(51)	28.7(2)	C(7)-C(2)-C(7')	43.3(3)
C(47)-Th(2)-C(51)	28.83(19)	C(2')-C(2)-Th(1)	90.4(8)
C(21)-N(1)-Th(1)	171.4(5)	C(1')-C(2)-Th(1)	80.9(5)
C(29)-N(2)-Th(1)	177.1(5)	C(1)-C(2)-Th(1)	75.87(16)
C(57)-N(3)-Th(2)	171.9(5)	C(3)-C(2)-Th(1)	73.91(16)
C(65)-N(4)-Th(2)	167.3(5)	C(7)-C(2)-Th(1)	116.32(16)
C(5')-C(1)-C(2)	114.0(3)	C(7')-C(2)-Th(1)	115.4(4)
C(5')-C(1)-C(5)	6.3(3)	C(3')-C(3)-C(2')	145.1(11)
C(2)-C(1)-C(5)	108.0	C(3')-C(3)-C(2)	141.4(6)
C(5')-C(1)-C(6')	154.2(7)	C(2')-C(3)-C(2)	12.4(5)
C(2)-C(1)-C(6')	90.7(4)	C(3')-C(3)-C(4)	35.2(6)
C(5)-C(1)-C(6')	160.5(4)	C(2')-C(3)-C(4)	115.5(5)
C(5')-C(1)-C(6)	120.0(3)	C(2)-C(3)-C(4)	108.0
C(2)-C(1)-C(6)	126.0	C(3')-C(3)-C(8)	91.7(6)
C(5)-C(1)-C(6)	126.0	C(2')-C(3)-C(8)	117.7(5)
C(6')-C(1)-C(6)	35.6(4)	C(2)-C(3)-C(8)	126.0
C(5')-C(1)-Th(1)	78.4(4)	C(4)-C(3)-C(8)	126.0
C(3')-C(3)-Th(1)	96.1(8)	C(4')-C(5)-Th(1)	82.1(4)
C(2')-C(3)-Th(1)	88.3(5)	C(4)-C(5)-Th(1)	74.03(16)
C(2)-C(3)-Th(1)	76.56(16)	C(1)-C(5)-Th(1)	76.32(16)

C(4)-C(3)-Th(1)	74.82(17)	C(10)-C(5)-Th(1)	115.79(15)
C(8)-C(3)-Th(1)	114.87(16)	C(1')-C(5)-Th(1)	75.3(3)
C(3')-C(4)-C(3)	22.0(4)	C(10')-C(5)-Th(1)	112.7(5)
C(3')-C(4)-C(5)	129.1(4)	C(6')-C(6)-C(1)	68.0(4)
C(3)-C(4)-C(5)	108.0	C(7')-C(7)-C(2)	72.3(3)
C(3')-C(4)-C(9)	104.6(4)	C(8')-C(8)-C(3)	84.3(4)
C(3)-C(4)-C(9)	126.0	C(8')-C(8)-C(3')	61.8(4)
C(5)-C(4)-C(9)	126.0	C(3)-C(8)-C(3')	22.5(2)
C(3')-C(4)-C(5')	123.9(5)	C(9')-C(9)-C(4')	74.7(5)
C(3)-C(4)-C(5')	103.0(3)	C(9')-C(9)-C(4)	92.0(4)
C(5)-C(4)-C(5')	5.2(3)	C(4')-C(9)-C(4)	17.4(3)
C(9)-C(4)-C(5')	131.0(3)	C(10')-C(10)-C(5)	82.1(5)
C(3')-C(4)-Th(1)	88.6(5)	C(10')-C(10)-C(5')	73.6(5)
C(3)-C(4)-Th(1)	75.42(16)	C(5)-C(10)-C(5')	8.7(3)
C(5)-C(4)-Th(1)	76.32(16)	C(11')-C(11)-C(12')	156.6(13)
C(9)-C(4)-Th(1)	114.54(15)	C(11')-C(11)-C(12)	135.9(7)
C(5')-C(4)-Th(1)	76.0(3)	C(12')-C(11)-C(12)	43.1(6)
C(4')-C(5)-C(4)	17.4(3)	C(11')-C(11)-C(15)	32.3(7)
C(4')-C(5)-C(1)	125.3(3)	C(12')-C(11)-C(15)	148.7(6)
C(4)-C(5)-C(1)	108.0	C(12)-C(11)-C(15)	108.0
C(4')-C(5)-C(10)	108.6(3)	C(11')-C(11)-C(16)	96.2(7)
C(4)-C(5)-C(10)	126.0	C(12')-C(11)-C(16)	83.9(6)
C(1)-C(5)-C(10)	126.0	C(12)-C(11)-C(16)	126.0
C(4')-C(5)-C(1')	111.5(5)	C(15)-C(11)-C(16)	126.0
C(4)-C(5)-C(1')	94.3(3)	C(11')-C(11)-Th(1)	75.6(7)
C(1)-C(5)-C(1')	14.3(3)	C(12')-C(11)-Th(1)	82.8(7)
C(10)-C(5)-C(1')	139.6(3)	C(12)-C(11)-Th(1)	76.09(16)
C(4')-C(5)-C(10')	137.1(5)	C(15)-C(11)-Th(1)	76.86(15)
C(4)-C(5)-C(10')	154.5(4)	C(16)-C(11)-Th(1)	113.45(15)
C(1)-C(5)-C(10')	97.5(4)	C(12')-C(12)-C(11)	30.7(4)
C(10)-C(5)-C(10')	28.5(4)	C(12')-C(12)-C(13)	137.4(4)
C(1')-C(5)-C(10')	111.2(4)	C(11)-C(12)-C(13)	108.0
C(12')-C(12)-C(17)	96.0(4)	C(13)-C(14)-C(19)	126.0
C(11)-C(12)-C(17)	126.0	C(15)-C(14)-C(19)	126.0
C(13)-C(12)-C(17)	126.0	C(15')-C(14)-C(20')	66.8(6)
C(12')-C(12)-C(14')	121.9(6)	C(14')-C(14)-C(20')	170.4(8)

C(11)-C(12)-C(14')	92.6(3)	C(13)-C(14)-C(20')	174.1(4)
C(13)-C(12)-C(14')	15.5(3)	C(15)-C(14)-C(20')	68.5(4)
C(17)-C(12)-C(14')	141.3(3)	C(19)-C(14)-C(20')	57.7(4)
C(12')-C(12)-Th(1)	79.5(5)	C(15')-C(14)-Th(1)	66.7(6)
C(11)-C(12)-Th(1)	75.12(16)	C(14')-C(14)-Th(1)	71.5(5)
C(13)-C(12)-Th(1)	77.23(15)	C(13)-C(14)-Th(1)	75.42(16)
C(17)-C(12)-Th(1)	113.98(15)	C(15)-C(14)-Th(1)	74.60(15)
C(14')-C(12)-Th(1)	70.1(3)	C(19)-C(14)-Th(1)	116.10(15)
C(13')-C(13)-C(14)	122.2(4)	C(20')-C(14)-Th(1)	98.9(4)
C(13')-C(13)-C(12)	14.7(4)	C(15')-C(15)-C(11')	127.3(10)
C(14)-C(13)-C(12)	108.0	C(15')-C(15)-C(11)	109.1(6)
C(13')-C(13)-C(18)	111.7(4)	C(11')-C(15)-C(11)	24.0(5)
C(14)-C(13)-C(18)	126.0	C(15')-C(15)-C(14)	10.5(7)
C(12)-C(13)-C(18)	126.0	C(11')-C(15)-C(14)	129.1(5)
C(13')-C(13)-C(19')	157.9(7)	C(11)-C(15)-C(14)	108.0
C(14)-C(13)-C(19')	79.5(4)	C(15')-C(15)-C(20)	123.9(6)
C(12)-C(13)-C(19')	172.5(4)	C(11')-C(15)-C(20)	103.9(5)
C(18)-C(13)-C(19')	46.5(4)	C(11)-C(15)-C(20)	126.0
C(13')-C(13)-Th(1)	76.3(4)	C(14)-C(15)-C(20)	126.0
C(14)-C(13)-Th(1)	76.30(15)	C(15')-C(15)-Th(1)	67.9(7)
C(12)-C(13)-Th(1)	74.25(15)	C(11')-C(15)-Th(1)	73.3(5)
C(18)-C(13)-Th(1)	115.62(15)	C(11)-C(15)-Th(1)	74.46(15)
C(19')-C(13)-Th(1)	107.9(5)	C(14)-C(15)-Th(1)	77.03(15)
C(15')-C(14)-C(14')	107.3(8)	C(20)-C(15)-Th(1)	114.77(15)
C(15')-C(14)-C(13)	109.0(5)	C(17')-C(16)-C(11)	85.4(3)
C(14')-C(14)-C(13)	4.0(5)	C(17')-C(16)-C(12')	57.8(4)
C(15')-C(14)-C(15)	9.1(7)	C(11)-C(16)-C(12')	27.7(3)
C(14')-C(14)-C(15)	107.0(4)	C(18')-C(17)-C(12)	82.6(4)
C(13)-C(14)-C(15)	108.0	C(18')-C(17)-C(13')	66.7(4)
C(15')-C(14)-C(19)	124.3(5)	C(12)-C(17)-C(13')	16.1(3)
C(14')-C(14)-C(19)	126.9(4)	C(19')-C(18)-C(13)	66.7(4)
C(14)-C(19)-C(20')	65.3(3)	C(3)-C(3')-C(4')	124.2(6)
C(15)-C(20)-C(16')	75.6(3)	C(4)-C(3')-C(4')	3.2(5)
C(2)-C(1')-C(2')	23.0(4)	C(2')-C(3')-C(4')	108.0
C(2)-C(1')-C(5')	129.1(4)	C(3)-C(3')-C(8')	108.7(6)
C(2')-C(1')-C(5')	108.0	C(4)-C(3')-C(8')	126.6(4)

C(2)-C(1')-C(6')	104.3(4)	C(2')-C(3')-C(8')	126.0
C(2')-C(1')-C(6')	126.0	C(4')-C(3')-C(8')	126.0
C(5')-C(1')-C(6')	126.0	C(3)-C(3')-C(8)	65.8(6)
C(2)-C(1')-C(5)	122.1(5)	C(4)-C(3')-C(8)	166.3(7)
C(2')-C(1')-C(5)	101.1(3)	C(2')-C(3')-C(8)	83.3(3)
C(5')-C(1')-C(5)	7.0(3)	C(4')-C(3')-C(8)	167.5(4)
C(6')-C(1')-C(5)	132.8(3)	C(8')-C(3')-C(8)	43.0(3)
C(2)-C(1')-Th(1)	77.7(5)	C(3)-C(3')-Th(1)	71.4(7)
C(2')-C(1')-Th(1)	77.22(18)	C(4)-C(3')-Th(1)	71.8(5)
C(5')-C(1')-Th(1)	75.72(18)	C(2')-C(3')-Th(1)	74.55(17)
C(6')-C(1')-Th(1)	113.45(17)	C(4')-C(3')-Th(1)	74.94(18)
C(5)-C(1')-Th(1)	72.4(3)	C(8')-C(3')-Th(1)	116.59(17)
C(2)-C(2')-C(3)	150.3(12)	C(8)-C(3')-Th(1)	103.7(4)
C(2)-C(2')-C(3')	145.1(7)	C(5)-C(4')-C(3')	111.3(3)
C(3)-C(2')-C(3')	14.8(5)	C(5)-C(4')-C(5')	3.7(4)
C(2)-C(2')-C(1')	41.6(7)	C(3')-C(4')-C(5')	108.0
C(3)-C(2')-C(1')	120.0(5)	C(5)-C(4')-C(9)	160.5(6)
C(3')-C(2')-C(1')	108.0	C(3')-C(4')-C(9)	88.1(4)
C(2)-C(2')-C(7')	86.5(7)	C(5')-C(4')-C(9)	163.9(4)
C(3)-C(2')-C(7')	113.4(5)	C(5)-C(4')-C(9')	122.6(3)
C(3')-C(2')-C(7')	126.0	C(3')-C(4')-C(9')	126.0
C(1')-C(2')-C(7')	126.0	C(5')-C(4')-C(9')	126.0
C(2)-C(2')-Th(1)	77.2(8)	C(9)-C(4')-C(9')	37.9(4)
C(3)-C(2')-Th(1)	74.4(5)	C(5)-C(4')-Th(1)	73.5(4)
C(3')-C(2')-Th(1)	76.99(17)	C(3')-C(4')-Th(1)	76.65(18)
C(1')-C(2')-Th(1)	73.96(18)	C(5')-C(4')-Th(1)	73.87(18)
C(7')-C(2')-Th(1)	115.24(17)	C(9)-C(4')-Th(1)	110.8(5)
C(3)-C(3')-C(4)	122.8(9)	C(9')-C(4')-Th(1)	115.65(16)
C(3)-C(3')-C(2')	20.1(7)	C(1)-C(5')-C(4')	122.6(3)
C(4)-C(3')-C(2')	107.3(4)	C(1)-C(5')-C(1')	15.3(3)
C(4')-C(5')-C(1')	108.0	C(12')-C(11')-C(15')	108.0
C(1)-C(5')-C(10')	111.2(3)	C(11)-C(11')-C(16')	125.4(6)
C(4')-C(5')-C(10')	126.0	C(15)-C(11')-C(16')	105.8(5)
C(1')-C(5')-C(10')	126.0	C(12')-C(11')-C(16')	126.0
C(1)-C(5')-C(10)	140.4(6)	C(15')-C(11')-C(16')	126.0
C(4')-C(5')-C(10)	96.8(4)	C(11)-C(11')-Th(1)	90.3(7)

C(1')-C(5')-C(10)	155.2(4)	C(15)-C(11')-Th(1)	88.2(6)
C(10')-C(5')-C(10)	29.2(4)	C(12')-C(11')-Th(1)	79.1(2)
C(1)-C(5')-C(4)	107.0(5)	C(15')-C(11')-Th(1)	72.6(2)
C(4')-C(5')-C(4)	15.6(2)	C(16')-C(11')-Th(1)	114.5(2)
C(1')-C(5')-C(4)	92.5(2)	C(11)-C(12')-C(12)	106.2(8)
C(10')-C(5')-C(4)	141.5(2)	C(11)-C(12')-C(13')	107.3(6)
C(10)-C(5')-C(4)	112.3(4)	C(12)-C(12')-C(13')	5.1(5)
C(1)-C(5')-Th(1)	76.4(4)	C(11)-C(12')-C(11')	11.2(6)
C(4')-C(5')-Th(1)	77.40(18)	C(12)-C(12')-C(11')	107.8(4)
C(1')-C(5')-Th(1)	75.26(18)	C(13')-C(12')-C(11')	108.0
C(10')-C(5')-Th(1)	113.70(17)	C(11)-C(12')-C(17')	125.5(6)
C(10)-C(5')-Th(1)	112.4(5)	C(12)-C(12')-C(17')	125.9(4)
C(4)-C(5')-Th(1)	70.7(3)	C(13')-C(12')-C(17')	126.0
C(6)-C(6')-C(1)	76.4(5)	C(11')-C(12')-C(17')	126.0
C(6)-C(6')-C(1')	91.5(5)	C(11)-C(12')-C(16)	68.3(6)
C(1)-C(6')-C(1')	15.3(3)	C(12)-C(12')-C(16)	167.5(9)
C(7)-C(7')-C(2')	87.0(4)	C(13')-C(12')-C(16)	172.3(5)
C(7)-C(7')-C(2)	64.4(4)	C(11')-C(12')-C(16)	69.1(4)
C(2')-C(7')-C(2)	22.6(2)	C(17')-C(12')-C(16)	57.4(4)
C(8)-C(8')-C(3')	75.1(3)	C(11)-C(12')-Th(1)	82.0(6)
C(9)-C(9')-C(4')	67.4(4)	C(12)-C(12')-Th(1)	80.2(5)
C(10)-C(10')-C(5')	77.2(5)	C(13')-C(12')-Th(1)	75.6(2)
C(10)-C(10')-C(5)	69.4(5)	C(11')-C(12')-Th(1)	71.7(2)
C(5')-C(10')-C(5)	8.0(3)	C(17')-C(12')-Th(1)	118.58(19)
C(11)-C(11')-C(15)	123.8(10)	C(16)-C(12')-Th(1)	109.4(4)
C(11)-C(11')-C(12')	12.2(7)	C(13)-C(13')-C(12')	123.6(4)
C(15)-C(11')-C(12')	127.4(5)	C(13)-C(13')-C(14')	15.9(4)
C(11)-C(11')-C(15')	107.3(6)	C(12')-C(13')-C(14')	108.0
C(15)-C(11')-C(15')	22.0(5)	C(13)-C(13')-C(18')	110.3(4)
C(12')-C(13')-C(18')	126.0	C(11')-C(15')-C(20')	126.0
C(14')-C(13')-C(18')	126.0	C(15)-C(15')-Th(1)	98.8(8)
C(13)-C(13')-C(17)	155.3(7)	C(14)-C(15')-Th(1)	98.0(7)
C(12')-C(13')-C(17)	80.5(4)	C(14')-C(15')-Th(1)	77.3(2)
C(14')-C(13')-C(17)	171.1(4)	C(11')-C(15')-Th(1)	77.3(2)
C(18')-C(13')-C(17)	45.5(4)	C(20')-C(15')-Th(1)	112.0(2)
C(13)-C(13')-Th(1)	80.6(4)	C(11')-C(16')-C(20)	74.6(3)

C(12')-C(13')-Th(1)	75.6(2)	C(16)-C(17')-C(12')	64.9(3)
C(14')-C(13')-Th(1)	71.7(2)	C(17)-C(18')-C(13')	67.8(4)
C(18')-C(13')-Th(1)	118.6(2)	C(18)-C(19')-C(14')	83.6(4)
C(17)-C(13')-Th(1)	113.8(5)	C(18)-C(19')-C(13)	66.8(4)
C(14)-C(14')-C(15')	31.3(5)	C(14')-C(19')-C(13)	16.9(3)
C(14)-C(14')-C(13')	138.6(5)	C(15')-C(20')-C(19)	85.0(3)
C(15')-C(14')-C(13')	108.0	C(15')-C(20')-C(14)	28.1(3)
C(14)-C(14')-C(19')	95.1(5)	C(19)-C(20')-C(14)	57.0(3)
C(15')-C(14')-C(19')	126.0	N(1)-C(21)-C(22)	125.1(7)
C(13')-C(14')-C(19')	126.0	N(1)-C(21)-C(23)	120.3(6)
C(14)-C(14')-C(12)	124.0(7)	C(22)-C(21)-C(23)	114.6(6)
C(15')-C(14')-C(12)	93.7(3)	C(28)-C(23)-C(24)	115.4(7)
C(13')-C(14')-C(12)	14.6(3)	C(28)-C(23)-C(21)	121.3(7)
C(19')-C(14')-C(12)	140.2(3)	C(24)-C(23)-C(21)	123.3(6)
C(14)-C(14')-Th(1)	88.8(5)	C(25)-C(24)-F(1)	118.0(7)
C(15')-C(14')-Th(1)	72.6(2)	C(25)-C(24)-C(23)	124.1(8)
C(13')-C(14')-Th(1)	79.1(2)	F(1)-C(24)-C(23)	117.9(6)
C(19')-C(14')-Th(1)	114.6(2)	C(24)-C(25)-C(26)	117.6(9)
C(12)-C(14')-Th(1)	77.0(3)	C(25)-C(26)-C(27)	122.5(8)
C(15)-C(15')-C(14)	160.5(14)	C(28)-C(27)-C(26)	114.9(9)
C(15)-C(15')-C(14')	134.8(6)	F(2)-C(28)-C(27)	113.8(8)
C(14)-C(15')-C(14')	41.4(6)	F(2)-C(28)-C(23)	120.7(7)
C(15)-C(15')-C(11')	30.7(7)	C(27)-C(28)-C(23)	125.5(9)
C(14)-C(15')-C(11')	148.3(6)	N(2)-C(29)-C(30)	124.5(6)
C(14')-C(15')-C(11')	108.0	N(2)-C(29)-C(31)	120.2(6)
C(15)-C(15')-C(20')	97.6(6)	C(30)-C(29)-C(31)	115.3(6)
C(14)-C(15')-C(20')	85.1(6)	C(36)-C(31)-C(32)	113.4(6)
C(14')-C(15')-C(20')	126.0	C(36)-C(31)-C(29)	122.3(6)
C(32)-C(31)-C(29)	124.3(6)	C(37)-C(41)-C(46)	126.7(6)
F(3)-C(32)-C(31)	117.2(6)	C(40)-C(41)-C(46)	124.7(6)
F(3)-C(32)-C(33)	117.7(7)	C(37)-C(41)-Th(2)	75.7(3)
C(31)-C(32)-C(33)	125.0(7)	C(40)-C(41)-Th(2)	75.5(3)
C(34)-C(33)-C(32)	117.5(7)	C(46)-C(41)-Th(2)	120.1(4)
C(33)-C(34)-C(35)	120.8(7)	C(48)-C(47)-C(51)	107.9(6)
C(34)-C(35)-C(36)	118.5(7)	C(48)-C(47)-C(52)	126.5(8)
F(4)-C(36)-C(31)	116.9(7)	C(51)-C(47)-C(52)	125.5(8)

F(4)-C(36)-C(35)	118.3(7)	C(48)-C(47)-Th(2)	74.7(4)
C(31)-C(36)-C(35)	124.7(7)	C(51)-C(47)-Th(2)	75.9(3)
C(41)-C(37)-C(38)	108.1(6)	C(52)-C(47)-Th(2)	115.1(4)
C(41)-C(37)-C(42)	126.1(6)	C(47)-C(48)-C(49)	108.1(7)
C(38)-C(37)-C(42)	125.7(6)	C(47)-C(48)-C(53)	127.5(8)
C(41)-C(37)-Th(2)	75.3(3)	C(49)-C(48)-C(53)	124.2(9)
C(38)-C(37)-Th(2)	75.6(3)	C(47)-C(48)-Th(2)	76.6(4)
C(42)-C(37)-Th(2)	118.2(4)	C(49)-C(48)-Th(2)	75.6(4)
C(39)-C(38)-C(37)	108.1(5)	C(53)-C(48)-Th(2)	117.1(4)
C(39)-C(38)-C(43)	126.3(6)	C(50)-C(49)-C(48)	108.1(6)
C(37)-C(38)-C(43)	125.3(6)	C(50)-C(49)-C(54)	124.9(8)
C(39)-C(38)-Th(2)	74.6(3)	C(48)-C(49)-C(54)	126.9(9)
C(37)-C(38)-Th(2)	75.3(3)	C(50)-C(49)-Th(2)	76.3(4)
C(43)-C(38)-Th(2)	120.7(4)	C(48)-C(49)-Th(2)	75.4(4)
C(38)-C(39)-C(40)	109.0(5)	C(54)-C(49)-Th(2)	118.2(4)
C(38)-C(39)-C(44)	125.1(6)	C(49)-C(50)-C(51)	107.9(6)
C(40)-C(39)-C(44)	125.7(6)	C(49)-C(50)-C(55)	126.9(8)
C(38)-C(39)-Th(2)	76.6(4)	C(51)-C(50)-C(55)	125.1(8)
C(40)-C(39)-Th(2)	76.2(4)	C(49)-C(50)-Th(2)	74.9(4)
C(44)-C(39)-Th(2)	117.7(4)	C(51)-C(50)-Th(2)	76.1(3)
C(39)-C(40)-C(41)	106.4(6)	C(55)-C(50)-Th(2)	117.7(4)
C(39)-C(40)-C(45)	128.1(6)	C(50)-C(51)-C(47)	107.9(6)
C(41)-C(40)-C(45)	124.8(6)	C(50)-C(51)-C(56)	126.5(8)
C(39)-C(40)-Th(2)	74.5(4)	C(47)-C(51)-C(56)	125.3(8)
C(41)-C(40)-Th(2)	75.0(4)	C(50)-C(51)-Th(2)	75.1(4)
C(45)-C(40)-Th(2)	123.2(4)	C(47)-C(51)-Th(2)	75.3(3)
C(37)-C(41)-C(40)	108.3(5)	C(56)-C(51)-Th(2)	120.8(4)
N(3)-C(57)-C(59)	120.7(6)	C(60)-C(61)-C(62)	118.6(6)
N(3)-C(57)-C(58)	123.4(6)	C(61)-C(62)-C(63)	120.0(6)
C(59)-C(57)-C(58)	115.9(6)	C(64)-C(63)-C(62)	117.9(6)
C(64)-C(59)-C(60)	113.4(6)	F(6)-C(64)-C(63)	116.7(6)
C(64)-C(59)-C(57)	123.1(6)	F(6)-C(64)-C(59)	117.6(5)
C(60)-C(59)-C(57)	123.4(6)	C(63)-C(64)-C(59)	125.7(6)
F(5)-C(60)-C(61)	118.1(6)	N(4)-C(65)-C(66)	123.0(7)
F(5)-C(60)-C(59)	117.5(5)	N(4)-C(65)-C(67)	120.2(6)
C(61)-C(60)-C(59)	124.4(6)	C(66)-C(65)-C(67)	116.8(6)

C(72)-C(67)-C(68)	114.2(7)
C(72)-C(67)-C(65)	122.0(6)
C(68)-C(67)-C(65)	123.8(7)
C(67)-C(68)-F(7)	116.4(8)
C(67)-C(68)-C(69)	125.0(9)
F(7)-C(68)-C(69)	118.6(8)
C(68)-C(69)-C(70)	116.6(8)
C(71)-C(70)-C(69)	120.6(9)
C(70)-C(71)-C(72)	119.5(10)
F(8)-C(72)-C(67)	118.4(7)
F(8)-C(72)-C(71)	117.7(8)
C(67)-C(72)-C(71)	123.9(8)

Figure S8. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(2,4,6\text{-}F_3\text{-}C_6H_2)]_2$ (**10**) with ellipsoids projected at the 30% probability level.

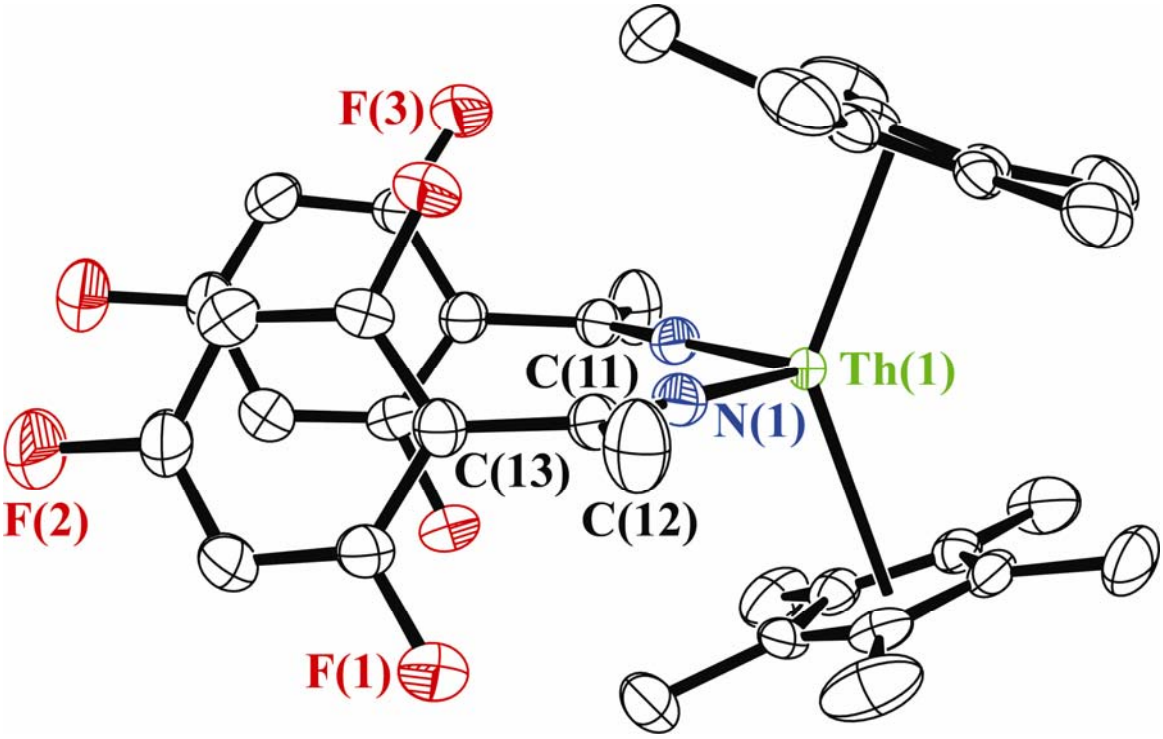


Table S15. Crystal data and structure refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(2,4,6\text{-}F_3\text{-}C_6H_2)]_2$ (**10**).

Empirical formula	$C_{36}\ H_{40}\ F_6\ N_2\ Th$	
Formula weight	846.74	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 14.566(2) Å	α= 90°
	b = 16.206(2) Å	β= 94.027(2)°
	c = 15.119(2) Å	γ = 90°
Volume	3560.1(8) $Å^3$	
Z	4	
Density (calculated)	1.580 Mg/m^3	
Absorption coefficient	4.246 mm^{-1}	
F(000)	1656	
Crystal size	0.20 x 0.20 x 0.08 mm^3	
θ range for data collection	1.88 to 28.28°	
Index ranges	$-18 \le h \le 14, -21 \le k \le 21, -19 \le l \le 19$	
Reflections collected	13525	
Independent reflections	4027 [R(int) = 0.0825]	
Completeness to θ = 25.00°	100.0 %	
Max. and min. transmission	0.7276 and 0.4839	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4027 / 0 / 204	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2σ(I)]	R1 = 0.0309, wR2 = 0.0746	
R indices (all data)	R1 = 0.0362, wR2 = 0.0790	
Largest diff. peak and hole	3.058 and -0.698 $e.Å^{-3}$	

Table S16. Bond distances [Å] and angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(2,4,6\text{-}F_3C_6H_2)]_2$ (**10**).

Th(1)-N(1)	2.263(3)
Th(1)-N(1)#1	2.263(3)
Th(1)-C(4)	2.786(4)
Th(1)-C(4)#1	2.786(4)
Th(1)-C(3)	2.811(4)
Th(1)-C(3)#1	2.811(4)
Th(1)-C(1)	2.806(5)
Th(1)-C(1)#1	2.806(5)
Th(1)-C(5)	2.817(4)
Th(1)-C(5)#1	2.817(4)
Th(1)-C(2)	2.828(4)
Th(1)-C(2)#1	2.828(4)
F(1)-C(14)	1.349(6)
F(2)-C(16)	1.360(7)
F(3)-C(18)	1.345(6)
N(1)-C(11)	1.253(5)
C(1)-C(5)	1.400(7)
C(1)-C(2)	1.406(7)
C(1)-C(6)	1.525(7)
C(2)-C(3)	1.405(7)
C(2)-C(7)	1.509(7)
C(3)-C(4)	1.400(6)
C(3)-C(8)	1.514(6)
C(4)-C(5)	1.389(6)
C(4)-C(9)	1.521(6)
C(5)-C(10)	1.515(7)
C(11)-C(13)	1.508(6)
C(11)-C(12)	1.508(7)
C(13)-C(18)	1.367(8)
C(13)-C(14)	1.378(7)
C(14)-C(15)	1.384(8)
C(15)-C(16)	1.356(9)
C(16)-C(17)	1.365(9)
C(17)-C(18)	1.378(8)
C(3)-Th(1)-C(5)	47.62(12)
N(1)-Th(1)-N(1)#1	108.2(2)
N(1)-Th(1)-C(4)	125.74(13)
N(1)#1-Th(1)-C(4)	96.26(13)
N(1)-Th(1)-C(4)#1	96.26(13)
N(1)#1-Th(1)-C(4)#1	125.74(13)
C(4)-Th(1)-C(4)#1	107.56(18)
N(1)-Th(1)-C(3)	103.18(14)
N(1)#1-Th(1)-C(3)	123.54(13)
C(4)-Th(1)-C(3)	28.97(12)
C(4)#1-Th(1)-C(3)	95.08(12)
N(1)-Th(1)-C(3)#1	123.54(13)
N(1)#1-Th(1)-C(3)#1	103.18(14)
C(4)-Th(1)-C(3)#1	95.08(12)
C(4)#1-Th(1)-C(3)#1	28.97(12)
C(3)-Th(1)-C(3)#1	96.57(19)
N(1)-Th(1)-C(1)	83.85(14)
N(1)#1-Th(1)-C(1)	90.65(15)
C(4)-Th(1)-C(1)	47.36(12)
C(4)#1-Th(1)-C(1)	140.70(14)
C(3)-Th(1)-C(1)	47.54(13)
C(3)#1-Th(1)-C(1)	141.60(13)
N(1)-Th(1)-C(1)#1	90.65(15)
N(1)#1-Th(1)-C(1)#1	83.85(14)
C(4)-Th(1)-C(1)#1	140.70(14)
C(4)#1-Th(1)-C(1)#1	47.36(12)
C(3)-Th(1)-C(1)#1	141.60(13)
C(3)#1-Th(1)-C(1)#1	47.54(13)
C(1)-Th(1)-C(1)#1	170.64(18)
N(1)-Th(1)-C(5)	112.15(14)
N(1)#1-Th(1)-C(5)	77.08(13)
C(4)-Th(1)-C(5)	28.70(13)
C(4)#1-Th(1)-C(5)	136.26(13)
C(5)-C(1)-C(2)	108.7(4)

C(3)#1-Th(1)-C(5)	119.99(13)	C(5)-C(1)-C(6)	124.6(5)
C(1)-Th(1)-C(5)	28.82(15)	C(2)-C(1)-C(6)	126.4(5)
C(1)#1-Th(1)-C(5)	153.83(16)	C(5)-C(1)-Th(1)	76.0(3)
N(1)-Th(1)-C(5)#1	77.08(13)	C(2)-C(1)-Th(1)	76.4(3)
N(1)#1-Th(1)-C(5)#1	112.15(14)	C(6)-C(1)-Th(1)	119.0(3)
C(4)-Th(1)-C(5)#1	136.26(13)	C(1)-C(2)-C(3)	107.3(4)
C(4)#1-Th(1)-C(5)#1	28.70(13)	C(1)-C(2)-C(7)	125.9(6)
C(3)-Th(1)-C(5)#1	119.99(13)	C(3)-C(2)-C(7)	126.7(6)
C(3)#1-Th(1)-C(5)#1	47.62(12)	C(1)-C(2)-Th(1)	74.7(2)
C(1)-Th(1)-C(5)#1	153.83(16)	C(3)-C(2)-Th(1)	74.9(2)
C(1)#1-Th(1)-C(5)#1	28.82(15)	C(7)-C(2)-Th(1)	120.2(3)
C(5)-Th(1)-C(5)#1	164.96(19)	C(2)-C(3)-C(4)	107.6(4)
N(1)-Th(1)-C(2)	78.44(13)	C(2)-C(3)-C(8)	124.8(5)
N(1)#1-Th(1)-C(2)	119.41(14)	C(4)-C(3)-C(8)	127.0(5)
C(4)-Th(1)-C(2)	47.56(12)	C(2)-C(3)-Th(1)	76.3(2)
C(4)#1-Th(1)-C(2)	112.46(13)	C(4)-C(3)-Th(1)	74.5(2)
C(3)-Th(1)-C(2)	28.86(14)	C(8)-C(3)-Th(1)	122.1(3)
C(3)#1-Th(1)-C(2)	123.09(15)	C(5)-C(4)-C(3)	109.1(4)
C(1)-Th(1)-C(2)	28.90(15)	C(5)-C(4)-C(9)	125.1(5)
C(1)#1-Th(1)-C(2)	156.33(14)	C(3)-C(4)-C(9)	125.4(5)
C(5)-Th(1)-C(2)	47.64(13)	C(5)-C(4)-Th(1)	76.9(2)
C(5)#1-Th(1)-C(2)	127.51(14)	C(3)-C(4)-Th(1)	76.5(2)
N(1)-Th(1)-C(2)#1	119.41(14)	C(9)-C(4)-Th(1)	118.5(3)
N(1)#1-Th(1)-C(2)#1	78.44(13)	C(4)-C(5)-C(1)	107.3(4)
C(4)-Th(1)-C(2)#1	112.46(13)	C(4)-C(5)-C(10)	126.0(5)
C(4)#1-Th(1)-C(2)#1	47.56(12)	C(1)-C(5)-C(10)	126.4(5)
C(3)-Th(1)-C(2)#1	123.09(15)	C(4)-C(5)-Th(1)	74.4(2)
C(3)#1-Th(1)-C(2)#1	28.86(14)	C(1)-C(5)-Th(1)	75.2(3)
C(1)-Th(1)-C(2)#1	156.33(14)	C(10)-C(5)-Th(1)	120.5(3)
C(1)#1-Th(1)-C(2)#1	28.90(15)	N(1)-C(11)-C(13)	120.8(4)
C(5)-Th(1)-C(2)#1	127.51(14)	N(1)-C(11)-C(12)	124.0(5)
C(5)#1-Th(1)-C(2)#1	47.64(13)	C(13)-C(11)-C(12)	115.2(4)
C(2)-Th(1)-C(2)#1	151.3(2)	C(18)-C(13)-C(14)	114.3(5)
C(11)-N(1)-Th(1)	174.7(4)	C(18)-C(13)-C(11)	123.3(5)
C(14)-C(13)-C(11)	122.4(5)		
F(1)-C(14)-C(15)	117.8(5)		

F(1)-C(14)-C(13)	117.4(5)
C(15)-C(14)-C(13)	124.8(5)
C(16)-C(15)-C(14)	116.3(5)
F(2)-C(16)-C(17)	118.3(6)
F(2)-C(16)-C(15)	118.6(6)
C(17)-C(16)-C(15)	123.1(5)
C(16)-C(17)-C(18)	117.0(6)
F(3)-C(18)-C(13)	118.2(5)
F(3)-C(18)-C(17)	117.4(5)
C(13)-C(18)-C(17)	124.4(5)

Figure S9. Thermal ellipsoid plot of $(C_5Me_5)_2Th[-N=C(CH_3)(C_6F_5)]_2$ (**11**) with ellipsoids projected at the 30% probability level.

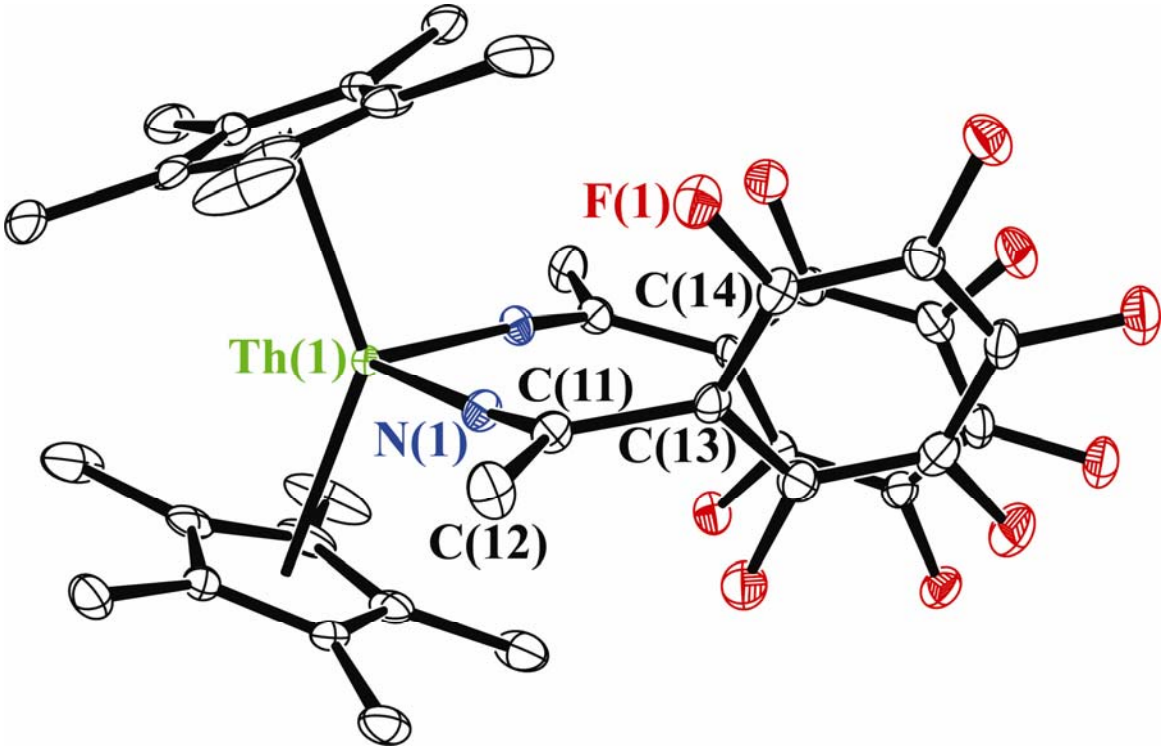


Table S17. Crystal data and structure refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(C_6F_5)]_2$ (**11**).

Empirical formula	$C_{36}\ H_{36}\ F_{10}\ N_2\ Th$	
Formula weight	918.71	
Temperature	141(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 16.066(3) Å	α= 90°
	b = 16.393(3) Å	β= 90°
	c = 26.997(5) Å	γ = 90°
Volume	7110(2) $Å^3$	
Z	8	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	4.275 mm^{-1}	
F(000)	3568	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
θ range for data collection	1.51 to 28.98°	
Index ranges	$-19 \le h \le 21$, $-21 \le k \le 22$, $-34 \le l \le 32$	
Reflections collected	53982	
Independent reflections	8877 [R(int) = 0.0559]	
Completeness to θ = 28.98°	94.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8147 and 0.4819	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8877 / 0 / 455	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2σ(I)]	R1 = 0.0249, wR2 = 0.0518	
R indices (all data)	R1 = 0.0583, wR2 = 0.0594	
Largest diff. peak and hole	1.271 and -0.853 $e.Å^{-3}$	

Table S18. Bond distances [Å] and angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(C_6F_5)]_2$ (**11**).

Th(1)-N(1)	2.268(3)	C(6)-C(1)	1.504(5)
Th(1)-N(1)#1	2.268(3)	C(11)-C(13)	1.528(4)
Th(1)-C(5)	2.775(3)	Th(2)-N(2)#2	2.273(3)
Th(1)-C(5)#1	2.775(3)	Th(2)-N(2)	2.273(3)
Th(1)-C(4)	2.777(3)	Th(2)-C(21)#2	2.781(3)
Th(1)-C(4)#1	2.777(3)	Th(2)-C(21)	2.781(3)
Th(1)-C(3)	2.799(3)	Th(2)-C(20)	2.790(3)
Th(1)-C(3)#1	2.799(3)	Th(2)-C(20)#2	2.790(3)
Th(1)-C(1)	2.808(3)	Th(2)-C(19)	2.804(3)
Th(1)-C(1)#1	2.808(3)	Th(2)-C(19)#2	2.804(3)
Th(1)-C(2)	2.817(3)	Th(2)-C(22)	2.814(3)
Th(1)-C(2)#1	2.817(3)	Th(2)-C(22)#2	2.814(3)
F(3)-C(16)	1.348(4)	Th(2)-C(23)	2.824(3)
F(5)-C(18)	1.352(3)	Th(2)-C(23)#2	2.824(3)
F(1)-C(14)	1.346(4)	F(6)-C(32)	1.352(3)
F(2)-C(15)	1.346(4)	F(8)-C(34)	1.344(4)
F(4)-C(17)	1.344(4)	F(10)-C(36)	1.359(3)
C(14)-C(15)	1.378(5)	F(7)-C(33)	1.340(3)
C(14)-C(13)	1.387(4)	F(9)-C(35)	1.342(4)
C(4)-C(3)	1.420(5)	C(32)-C(33)	1.381(4)
C(4)-C(5)	1.421(5)	C(32)-C(31)	1.387(4)
C(4)-C(9)	1.518(5)	C(36)-C(31)	1.372(4)
C(5)-C(1)	1.398(5)	C(36)-C(35)	1.375(4)
C(5)-C(10)	1.516(5)	C(21)-C(22)	1.412(4)
C(12)-C(11)	1.503(4)	C(21)-C(20)	1.424(5)
C(18)-C(13)	1.374(4)	C(21)-C(26)	1.516(4)
C(18)-C(17)	1.384(4)	N(2)-C(29)	1.251(4)
C(2)-C(3)	1.399(5)	C(27)-C(22)	1.502(5)
C(2)-C(1)	1.420(5)	C(28)-C(23)	1.517(4)
C(2)-C(7)	1.509(4)	C(19)-C(23)	1.416(4)
C(17)-C(16)	1.374(5)	C(19)-C(20)	1.428(4)
N(1)-C(11)	1.253(4)	C(19)-C(24)	1.495(5)
C(15)-C(16)	1.371(5)	C(33)-C(34)	1.373(5)
C(3)-C(8)	1.507(4)	C(25)-C(20)	1.504(4)

C(35)-C(34)	1.379(5)
C(30)-C(29)	1.513(5)
C(31)-C(29)	1.521(4)
C(22)-C(23)	1.413(5)

N(1)-Th(1)-N(1)#1	105.96(13)
N(1)-Th(1)-C(5)	78.43(10)
N(1)#1-Th(1)-C(5)	123.00(10)
N(1)-Th(1)-C(5)#1	123.00(10)
N(1)#1-Th(1)-C(5)#1	78.43(10)
C(5)-Th(1)-C(5)#1	146.79(18)
N(1)-Th(1)-C(4)	105.81(11)
N(1)#1-Th(1)-C(4)	123.65(10)
C(5)-Th(1)-C(4)	29.66(11)
C(5)#1-Th(1)-C(4)	118.47(13)
N(1)-Th(1)-C(4)#1	123.65(10)
N(1)#1-Th(1)-C(4)#1	105.81(11)
C(5)-Th(1)-C(4)#1	118.47(13)
C(5)#1-Th(1)-C(4)#1	29.66(11)
C(4)-Th(1)-C(4)#1	93.31(16)
N(1)-Th(1)-C(3)	125.21(9)
N(1)#1-Th(1)-C(3)	94.81(10)
C(5)-Th(1)-C(3)	48.46(10)
C(5)#1-Th(1)-C(3)	110.47(11)
C(4)-Th(1)-C(3)	29.51(10)
C(4)#1-Th(1)-C(3)	96.75(11)
N(1)-Th(1)-C(3)#1	94.81(10)
N(1)#1-Th(1)-C(3)#1	125.21(9)
C(5)-Th(1)-C(3)#1	110.47(11)
C(5)#1-Th(1)-C(3)#1	48.46(10)
C(4)-Th(1)-C(3)#1	96.75(11)
C(4)#1-Th(1)-C(3)#1	29.51(10)
C(3)-Th(1)-C(3)#1	113.49(14)
N(1)-Th(1)-C(1)	79.65(9)
N(1)#1-Th(1)-C(1)	94.54(10)
C(5)-Th(1)-C(1)	28.98(10)
C(5)#1-Th(1)-C(1)	157.29(10)
C(4)-Th(1)-C(1)	48.32(11)
C(4)#1-Th(1)-C(1)	141.22(11)
C(3)-Th(1)-C(1)	48.06(10)
C(3)#1-Th(1)-C(1)	139.45(10)
N(1)-Th(1)-C(1)#1	94.54(10)
N(1)#1-Th(1)-C(1)#1	79.65(9)
C(5)-Th(1)-C(1)#1	157.29(10)
C(5)#1-Th(1)-C(1)#1	28.98(10)
C(4)-Th(1)-C(1)#1	141.22(11)
C(4)#1-Th(1)-C(1)#1	48.32(11)
C(3)-Th(1)-C(1)#1	139.45(10)
C(3)#1-Th(1)-C(1)#1	48.06(10)
C(1)-Th(1)-C(1)#1	170.43(15)
N(1)-Th(1)-C(2)	107.38(9)
N(1)#1-Th(1)-C(2)	78.30(9)
C(5)-Th(1)-C(2)	48.09(10)
C(5)#1-Th(1)-C(2)	128.50(10)
C(4)-Th(1)-C(2)	48.18(10)
C(4)#1-Th(1)-C(2)	123.87(10)
C(3)-Th(1)-C(2)	28.85(9)
C(3)#1-Th(1)-C(2)	142.04(10)
C(1)-Th(1)-C(2)	29.24(9)
C(1)#1-Th(1)-C(2)	152.36(10)
N(1)-Th(1)-C(2)#1	78.30(9)
N(1)#1-Th(1)-C(2)#1	107.38(9)
C(5)-Th(1)-C(2)#1	128.50(10)
C(5)#1-Th(1)-C(2)#1	48.09(10)
C(4)-Th(1)-C(2)#1	123.87(10)
C(4)#1-Th(1)-C(2)#1	48.18(10)
C(3)-Th(1)-C(2)#1	142.04(10)
C(3)#1-Th(1)-C(2)#1	28.85(9)
C(1)-Th(1)-C(2)#1	152.36(10)
C(1)#1-Th(1)-C(2)#1	29.24(9)
C(2)-Th(1)-C(2)#1	170.86(14)

F(1)-C(14)-C(15)	118.1(3)	C(2)-C(3)-C(8)	125.3(3)
F(1)-C(14)-C(13)	119.8(3)	C(4)-C(3)-C(8)	126.4(3)
C(15)-C(14)-C(13)	122.1(3)	C(2)-C(3)-Th(1)	76.3(2)
C(3)-C(4)-C(5)	107.3(3)	C(4)-C(3)-Th(1)	74.37(19)
C(3)-C(4)-C(9)	127.5(4)	C(8)-C(3)-Th(1)	117.9(2)
C(5)-C(4)-C(9)	125.2(4)	N(1)-C(11)-C(12)	125.2(3)
C(3)-C(4)-Th(1)	76.12(19)	N(1)-C(11)-C(13)	119.8(3)
C(5)-C(4)-Th(1)	75.11(19)	C(12)-C(11)-C(13)	115.0(3)
C(9)-C(4)-Th(1)	117.7(2)	C(18)-C(13)-C(14)	116.2(3)
C(1)-C(5)-C(4)	108.4(3)	C(18)-C(13)-C(11)	122.6(3)
C(1)-C(5)-C(10)	126.9(4)	C(14)-C(13)-C(11)	121.1(3)
C(4)-C(5)-C(10)	124.6(4)	C(5)-C(1)-C(2)	108.0(3)
C(1)-C(5)-Th(1)	76.84(19)	C(5)-C(1)-C(6)	127.1(3)
C(4)-C(5)-Th(1)	75.23(19)	C(2)-C(1)-C(6)	124.8(4)
C(10)-C(5)-Th(1)	117.5(2)	C(5)-C(1)-Th(1)	74.2(2)
F(5)-C(18)-C(13)	120.0(3)	C(2)-C(1)-Th(1)	75.73(19)
F(5)-C(18)-C(17)	117.1(3)	C(6)-C(1)-Th(1)	118.9(2)
C(13)-C(18)-C(17)	122.9(3)	N(2)#2-Th(2)-N(2)	104.90(13)
C(3)-C(2)-C(1)	108.2(3)	N(2)#2-Th(2)-C(21)#2	94.78(10)
C(3)-C(2)-C(7)	124.9(3)	N(2)-Th(2)-C(21)#2	125.28(9)
C(1)-C(2)-C(7)	126.6(3)	N(2)#2-Th(2)-C(21)	125.28(9)
C(3)-C(2)-Th(1)	74.8(2)	N(2)-Th(2)-C(21)	94.78(10)
C(1)-C(2)-Th(1)	75.04(19)	C(21)#2-Th(2)-C(21)	114.34(13)
C(7)-C(2)-Th(1)	121.1(2)	N(2)#2-Th(2)-C(20)	106.48(10)
F(4)-C(17)-C(16)	120.0(3)	N(2)-Th(2)-C(20)	123.80(9)
F(4)-C(17)-C(18)	121.0(3)	C(21)#2-Th(2)-C(20)	97.01(10)
C(16)-C(17)-C(18)	119.0(3)	C(21)-Th(2)-C(20)	29.62(10)
C(11)-N(1)-Th(1)	176.0(2)	N(2)#2-Th(2)-C(20)#2	123.80(9)
F(2)-C(15)-C(16)	119.8(3)	N(2)-Th(2)-C(20)#2	106.48(10)
F(2)-C(15)-C(14)	120.3(3)	C(21)#2-Th(2)-C(20)#2	29.62(10)
C(16)-C(15)-C(14)	119.9(3)	C(21)-Th(2)-C(20)#2	97.01(10)
F(3)-C(16)-C(15)	119.7(3)	C(20)-Th(2)-C(20)#2	92.88(14)
F(3)-C(16)-C(17)	120.5(3)	N(2)#2-Th(2)-C(19)	78.87(9)
C(15)-C(16)-C(17)	119.8(3)	N(2)-Th(2)-C(19)	123.56(9)
C(2)-C(3)-C(4)	108.2(3)	C(21)#2-Th(2)-C(19)	110.01(10)
C(21)-Th(2)-C(19)	48.52(9)		

C(20)-Th(2)-C(19)	29.57(9)	C(22)-Th(2)-C(23)	29.03(10)
C(20)#2-Th(2)-C(19)	117.58(10)	C(22)#2-Th(2)-C(23)	152.26(10)
N(2)#2-Th(2)-C(19)#2	123.56(9)	N(2)#2-Th(2)-C(23)#2	94.97(9)
N(2)-Th(2)-C(19)#2	78.87(9)	N(2)-Th(2)-C(23)#2	79.38(9)
C(21)#2-Th(2)-C(19)#2	48.52(9)	C(21)#2-Th(2)-C(23)#2	47.97(9)
C(21)-Th(2)-C(19)#2	110.01(10)	C(21)-Th(2)-C(23)#2	139.15(10)
C(20)-Th(2)-C(19)#2	117.58(10)	C(20)-Th(2)-C(23)#2	140.89(9)
C(20)#2-Th(2)-C(19)#2	29.57(9)	C(20)#2-Th(2)-C(23)#2	48.28(9)
C(19)-Th(2)-C(19)#2	145.66(14)	C(19)-Th(2)-C(23)#2	157.03(10)
N(2)#2-Th(2)-C(22)	106.52(9)	C(19)#2-Th(2)-C(23)#2	29.14(9)
N(2)-Th(2)-C(22)	78.30(9)	C(22)-Th(2)-C(23)#2	152.26(10)
C(21)#2-Th(2)-C(22)	143.16(10)	C(22)#2-Th(2)-C(23)#2	29.03(10)
C(21)-Th(2)-C(22)	29.22(9)	C(23)-Th(2)-C(23)#2	170.81(13)
C(20)-Th(2)-C(22)	48.59(10)	F(6)-C(32)-C(33)	117.7(3)
C(20)#2-Th(2)-C(22)	124.71(10)	F(6)-C(32)-C(31)	119.4(3)
C(19)-Th(2)-C(22)	48.35(10)	C(33)-C(32)-C(31)	122.9(3)
C(19)#2-Th(2)-C(22)	128.70(10)	F(10)-C(36)-C(31)	119.4(3)
N(2)#2-Th(2)-C(22)#2	78.30(9)	F(10)-C(36)-C(35)	117.4(3)
N(2)-Th(2)-C(22)#2	106.52(9)	C(31)-C(36)-C(35)	123.2(3)
C(21)#2-Th(2)-C(22)#2	29.22(9)	C(22)-C(21)-C(20)	108.8(3)
C(21)-Th(2)-C(22)#2	143.16(10)	C(22)-C(21)-C(26)	124.5(3)
C(20)-Th(2)-C(22)#2	124.71(10)	C(20)-C(21)-C(26)	126.7(3)
C(20)#2-Th(2)-C(22)#2	48.59(10)	C(22)-C(21)-Th(2)	76.66(18)
C(19)-Th(2)-C(22)#2	128.70(10)	C(20)-C(21)-Th(2)	75.52(18)
C(19)#2-Th(2)-C(22)#2	48.35(10)	C(26)-C(21)-Th(2)	115.8(2)
C(22)-Th(2)-C(22)#2	172.34(13)	C(29)-N(2)-Th(2)	177.1(2)
N(2)#2-Th(2)-C(23)	79.38(9)	C(23)-C(19)-C(20)	107.7(3)
N(2)-Th(2)-C(23)	94.97(9)	C(23)-C(19)-C(24)	127.1(3)
C(21)#2-Th(2)-C(23)	139.15(10)	C(20)-C(19)-C(24)	125.1(3)
C(21)-Th(2)-C(23)	47.97(9)	C(23)-C(19)-Th(2)	76.18(18)
C(20)-Th(2)-C(23)	48.28(9)	C(20)-C(19)-Th(2)	74.64(17)
C(20)#2-Th(2)-C(23)	140.89(9)	C(24)-C(19)-Th(2)	118.7(2)
C(19)-Th(2)-C(23)	29.14(9)	F(7)-C(33)-C(34)	120.6(3)
C(19)#2-Th(2)-C(23)	157.03(10)	F(7)-C(33)-C(32)	120.5(3)
F(9)-C(35)-C(36)	121.3(3)	C(34)-C(33)-C(32)	118.9(3)
F(9)-C(35)-C(34)	119.5(3)		

C(36)-C(35)-C(34)	119.2(3)
F(8)-C(34)-C(33)	120.6(3)
F(8)-C(34)-C(35)	119.4(3)
C(33)-C(34)-C(35)	120.0(3)
C(21)-C(20)-C(19)	107.2(3)
C(21)-C(20)-C(25)	127.3(3)
C(19)-C(20)-C(25)	125.2(3)
C(21)-C(20)-Th(2)	74.86(17)
C(19)-C(20)-Th(2)	75.78(17)
C(25)-C(20)-Th(2)	119.7(2)
C(36)-C(31)-C(32)	115.8(3)
C(36)-C(31)-C(29)	122.9(3)
C(32)-C(31)-C(29)	121.3(3)
N(2)-C(29)-C(30)	124.9(3)
N(2)-C(29)-C(31)	120.4(3)
C(30)-C(29)-C(31)	114.7(3)
C(21)-C(22)-C(23)	107.5(3)
C(21)-C(22)-C(27)	125.9(3)
C(23)-C(22)-C(27)	126.4(3)
C(21)-C(22)-Th(2)	74.12(17)
C(23)-C(22)-Th(2)	75.87(18)
C(27)-C(22)-Th(2)	119.7(2)
C(22)-C(23)-C(19)	108.8(3)
C(22)-C(23)-C(28)	124.6(3)
C(19)-C(23)-C(28)	126.4(3)
C(22)-C(23)-Th(2)	75.09(18)
C(19)-C(23)-Th(2)	74.68(17)
C(28)-C(23)-Th(2)	120.5(2)

Complete Author Listing for the Gaussian Reference (ref 16).

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