

## Supplementary Information for

### **Neutral Inverse-Sandwich Rare-Earth Metal Complexes of the Benzene Tetraanion**

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## S1. Materials and Methods

### S1.1. General Considerations

All experiments were performed under a dry argon atmosphere using standard Schlenk techniques or in a nitrogen filled Vigor glove box unless otherwise specified. Celite (purchased from Sigma-Aldrich) and 4 Å molecular sieves (purchased from Sinopharm) were dried under dynamic vacuum at 250 °C for at least 48 h prior to use. Solvents including hexanes, *n*-pentane, diethyl ether (Et<sub>2</sub>O) and toluene, were collected from a Vigor YJC-5 Solvent Purification System under argon, transferred to the glove box without exposure to air, and stored over activated molecular sieves. Tetrahydrofuran (THF) was freshly distilled over sodium benzophenone ketyl and stored over activated molecular sieves prior to use. Deuterated solvents, benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) and toluene-*d*<sub>8</sub> (C<sub>7</sub>D<sub>8</sub>) were obtained from Cambridge Isotope Laboratories, degassed three times using freeze-pump-thaw method and stored over activated molecular sieves for one week prior to use. Super dry benzene was purchased from J&K and stored over activated molecular sieves for one week prior to use. *para*-Xylene (*p*-xylene) was obtained from Energy Chemical, degassed three times using freeze-pump-thaw method and stored over activated molecular sieves for one week prior to use. (BDI)H (HC{C(Me)N[2,6-(3-pentyl-phenyl)]}<sub>2</sub>),<sup>1</sup> (BDI)K,<sup>2</sup> KC<sub>8</sub>,<sup>3</sup> YI<sub>3</sub>(THF)<sub>3.5</sub> and SmI<sub>3</sub>(THF)<sub>3.5</sub><sup>4</sup> were prepared according to literature procedures. All other reagents were purchased from commercial suppliers and used as received.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 400 MHz or 600 MHz spectrometers at room temperature. Variable temperature <sup>1</sup>H NMR was recorded on Bruker Avance 500 MHz spectrometers. Chemical shifts are referenced internally to the residual proteo-solvent signal, i.e., C<sub>6</sub>D<sub>5</sub>H at 7.16 ppm. CHN analyses were performed on a Vario EL elemental analyzer at the Analytical Instrumentation Center of Peking University. The single crystal X-ray diffraction data were collected at 180 K using a Rigaku Oxford diffractometer equipped with a CCD collector using Mo K $\alpha$  radiation, XtaLAB PRO 007HF(Mo). UV–Vis–NIR spectra were obtained on a SHIMADZU UV3600Plus in a 1 mm quartz cuvette at the Analytical Instrumentation Center of Peking University. Fourier transform infrared (FTIR) spectra in the range of 4000–400 cm<sup>-1</sup> were recorded on a Bruker Tensor 27 spectrometer using a KBr cell (for solution samples) at the Analytical Center of Peking University.

### S1.2. Synthetic Details

**Synthesis of (BDI)YI<sub>2</sub>(THF) (1-Y).** (BDI)K (200 mg, 0.35 mmol) was dissolved in 5 mL of Et<sub>2</sub>O and YI<sub>3</sub>(THF)<sub>3.5</sub> (305 mg, 0.42 mmol, 1.2 equiv) was dispersed in 2 mL of Et<sub>2</sub>O. Both mixtures were cooled at -78 °C for 15 min. The cold solution of (BDI)K was added to the suspension of YI<sub>3</sub>(THF)<sub>3.5</sub> dropwise with stirring. The mixture was warmed to room temperature and stirred for 5 h. The volatiles were removed under reduced pressure and the residue was extracted into hexanes (ca. 10 mL). Then the filtrate was concentrated to ca. 2 mL. After storing at -35 °C for 2 d, colorless crystals precipitated from the solution. The mother liquor was decanted and the crystals were washed with cold *n*-pentane and dried under reduced pressure to yield **1-Y** as a pale yellow solid (Yield: 148 mg, 45%). Single crystals of **1-Y** suitable for X-ray crystallography were grown from a hexanes solution at -35 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ , ppm: 7.14–7.04 (m, 6H, CH of aryl), 5.17 (s, 1H, CCHC), 3.61 (s, 4H,

$CH(CH_2CH_3)_2$ , 3.28 (s, 4H,  $OCH_2$ ), 2.01–1.80 (m, 8H,  $CH_2CH_3$ ), 1.77–1.57 (m, 14H,  $CH_2CH_3$  (8H) &  $CCH_3$  (6H)), 1.23–1.11 (m, 16H,  $OCH_2CH_2$  (4H) &  $CH_2CH_3$  (12H)), 0.90 (s, 12H,  $CH_2CH_3$ ).  $^{13}C\{H\}$  NMR (101 MHz,  $C_6D_6$ )  $\delta$ , ppm: 168.25 ( $C(CH_3)N$ ), 146.62, 139.46, 126.61, 125.13 ( $C$  of aryl), 96.60 ( $CCHC$ ), 71.92 ( $OCH_2$ ), 40.71 ( $CH(CH_2CH_3)_2$ ), 27.36 ( $CH_2CH_3$ ), 26.99 ( $OCH_2CH_2$ ), 25.71 ( $CCH_3$ ), 24.91 ( $CH_2CH_3$ ), 11.80 ( $CH_2CH_3$ ), 10.82 ( $CH_2CH_3$ ). Anal. (%): Calcd. for  $C_{44}H_{71}I_2N_2OY$ ,  $M_w = 986.78$ , as in the formula of  $(BDI)YI_2(THF) \cdot 0.5C_6H_{14}(\text{hexanes})$ : C, 53.56; H, 7.25; N, 2.84. Found: C, 53.77; H, 7.08; N, 2.81.

**Synthesis of  $(BDI)SmI_2(THF)$  (1-Sm).**  $(BDI)K$  (300 mg, 0.53 mmol) was dissolved in 12 mL of  $Et_2O$  and  $SmI_3(THF)_{3.5}$  (496 mg, 0.63 mmol, 1.2 equiv) was dispersed in 5 mL of  $Et_2O$ . Both were cooled at  $-78\text{ }^\circ\text{C}$  for 15 min. The cold solution of  $(BDI)K$  was added to the suspension of  $SmI_3(THF)_{3.5}$  dropwise with stirring. The mixture was warmed to room temperature and stirred overnight. The brown suspension was then filtered through Celite and washed with  $Et_2O$  (ca. 5 mL  $\times$  3). The volatiles were removed under reduced pressure and the residue was extracted into hexanes/ $Et_2O$  (ca. 15 mL, 1:1 v/v). A small amount of THF (100  $\mu\text{L}$ ) was added to facilitate the dissolution. Then the filtrate was concentrated to ca. 3 mL. After standing at room temperature for 1 h, orange crystals precipitated from the solution. The mother liquor was decanted and the crystals were dried under reduced pressure to yield **1-Sm** as an orange solid (Yield: 292 mg, 55%). Single crystals of **1-Sm** suitable for X-ray crystallography were grown from a  $Et_2O$  solution at room temperature.  $^1H$  NMR (400 MHz,  $C_6D_6$ )  $\delta$ , ppm: 7.86 (s, 1H,  $CCHC$ ), 7.04 (t,  $J = 7.7$  Hz, 2H, *para-CH* of aryl), 6.73 (d,  $J = 7.8$  Hz, 4H, *meta-CH* of aryl), 4.51 (s, 4H,  $OCH_2$ ), 2.68 (s, 6H,  $CCH_3$ ), 2.00 (s, 4H,  $OCH_2CH_2$ ), 1.88–1.11 (m, 16H,  $CH_2CH_3$ ), 0.84 (s, 12H,  $CH_2CH_3$ ), 0.65 (s, 4H,  $CH(CH_2CH_3)_2$ ), 0.42 (s, 12H,  $CH_2CH_3$ ). Anal. (%): Calcd. for  $C_{42}H_{67.5}I_2N_2O_{1.25}Sm$ ,  $M_w = 1024.68$ , as in the formula of  $(BDI)SmI_2(THF) \cdot 0.25C_4H_{10}O(Et_2O)$ : C, 49.23; H, 6.64; N, 2.73. Found: C, 49.41; H, 6.69; N, 2.78.

**Synthesis of  $[(BDI)Y]_2(\mu-\eta^6, \eta^6-C_6H_6)$  (2-Y).** **1-Y** (100 mg, 0.11 mmol) and  $KC_8$  (34 mg, 0.25 mmol, 2.4 equiv) were dispersed in 1 mL of  $C_6H_6$ . The mixture stirred vigorously at room temperature overnight. The volatiles of resulting black suspension were removed under reduced pressure. The residue was extracted into *n*-pentane (ca. 10 mL) and the volatiles were removed under reduced pressure. The black remaining solid was then extracted into  $Et_2O$  (ca. 8 mL) and the filtrate was concentrated to ca. 3 mL. After storing at  $-35\text{ }^\circ\text{C}$  for 10 d, black crystals precipitated from the solution. The mother liquor was decanted and the crystals were washed with cold *n*-pentane and dried under reduced pressure to yield **2-Y** as a black solid (Yield: 39 mg, 56%). Single crystals of **2-Y** suitable for X-ray crystallography were grown from a *n*-pentane solution at  $-35\text{ }^\circ\text{C}$ .  $^1H$  NMR (400 MHz,  $C_6D_6$ )  $\delta$ , ppm: 7.12–7.06 (m, 4H, *para-CH* of aryl), 6.99 (d,  $J = 7.6$  Hz, 8H, *meta-CH* of aryl), 4.92 (s, 2H,  $CCHC$ ), 3.03–2.95 (m, 8H,  $CH(CH_2CH_3)_2$ ), 2.37 (t,  $J_{Y-H} = 1.6$  Hz, 6H, *CH* of the bound benzene), 1.92–1.82 (m, 16H,  $CH_2CH_3$ ), 1.75 (s, 12H,  $CCH_3$ ), 1.71–1.58 (m, 16H,  $CH_2CH_3$ ), 1.08 (t,  $J = 7.3$  Hz, 24H,  $CH_2CH_3$ ), 0.80 (t,  $J = 7.4$  Hz, 24H,  $CH_2CH_3$ ).  $^{13}C\{H\}$  NMR (101 MHz,  $C_6D_6$ )  $\delta$ , ppm: 164.57 ( $C(CH_3)N$ ), 144.56, 140.58, 125.05, 123.96 ( $C$  of aryl), 96.01 ( $CCHC$ ), 65.74 (*CH* of the bound benzene,  $J_{Y-C} = 4.8$  Hz), 41.61 ( $CH(CH_2CH_3)_2$ ), 28.40 ( $CH_2CH_3$ ), 24.50 ( $CH_2CH_3$ ), 23.99 ( $CH(CH_2CH_3)_2$ ), 11.92 ( $CH_2CH_3$ ), 10.84 ( $CH_2CH_3$ ). Anal. (%): Calcd. For  $C_{80}H_{120}N_4Y_2$ ,  $M_w$

= 1315.68, as in the formula of [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>): C, 73.03; H, 9.19; N, 4.26. Found: C, 73.26; H, 9.42; N, 4.12.

**Synthesis of [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (2-Sm).** **1-Sm** (150 mg, 0.15 mmol) and KC<sub>8</sub> (48 mg, 0.36 mmol, 2.4 equiv) were dispersed in 1.5 mL of C<sub>6</sub>H<sub>6</sub>. The mixture stirred vigorously at room temperature for 4 h. The volatiles of resulting black suspension were removed under reduced pressure. The residue was extracted into Et<sub>2</sub>O (ca. 10 mL) and the filtrate was concentrated to ca. 5 mL. A small amount of THF (50 μL) was added to the solution. After storing at -35 °C overnight, black crystals precipitated from the solution. The mother liquor was decanted and the crystals were dried under reduced pressure to yield **2-Sm** as a black solid (Yield: 89 mg, 76%). Single crystals of **2-Sm** suitable for X-ray crystallography were grown from a *n*-pentane solution containing a few drops of THF at -35 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ, ppm: 21.73 (s, 6H, CH of the bound benzene), 10.68 (s, 2H, CCHC), 6.68 (t, *J* = 7.8 Hz, 4H, *para*-CH of aryl), 6.31 (d, *J* = 8.0 Hz, 8H, *meta*-CH of aryl), 5.39 (s, 12H, CCH<sub>3</sub>), 2.10–1.95 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.45–1.31 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.00 (t, *J* = 7.4 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), -0.22 (s, 8H, CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), -1.82 (t, *J* = 7.1 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), -2.67 to -2.82 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), -5.40 to -5.64 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>). The peaks of coordinating THF molecules are not observed probably due to the loss of THF molecules under reduced pressure during drying process. Anal. (%): Calcd. For C<sub>86</sub>H<sub>126</sub>N<sub>4</sub>Sm<sub>2</sub>, M<sub>w</sub> = 1516.70, as in the formula of [(BDI)Sm]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)·C<sub>6</sub>H<sub>6</sub>(benzene): C, 68.10; H, 8.37; N, 3.69. Found: C, 67.91; H, 8.70; N, 3.88.

**Synthesis of [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (3-Y).** **1-Y** (150 mg, 0.16 mmol) and KC<sub>8</sub> (52 mg, 0.38 mmol, 2.4 equiv) were dispersed in 2 mL of *p*-xylene. The mixture was stirred vigorously at room temperature for 3 d. The volatiles of resulting black suspension were removed under reduced pressure. The residue was extracted into *n*-pentane (ca. 20 mL) and the filtrate was concentrated to ca. 5 mL. After storing at -35 °C for 7 d, black crystals precipitated from the solution. The mother liquor was decanted and the crystals were washed with cold *n*-pentane and dried under reduced pressure to yield **3-Y** as a black solid (Yield: 41 mg, 38%). Single crystals of **3-Y** suitable for X-ray crystallography were grown from a *n*-pentane solution at -35 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ, ppm: 7.05 (s, 12H, CH of aryl), 4.93 (s, 2H, CCHC), 3.03–2.92 (m, 8H, CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 2.71 (t, *J*<sub>Y-H</sub> = 1.7 Hz, 4H, CH of the bound xylene), 2.00–1.77 (m, 16H, CH<sub>2</sub>CH<sub>3</sub>), 1.74–1.57 (m, 28H, CCH<sub>3</sub> (12H) & CH<sub>2</sub>CH<sub>3</sub> (16H)), 1.14 (t, *J* = 7.3 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), 0.82–0.76 (m, 30H, CH<sub>2</sub>CH<sub>3</sub> (24H) & CH<sub>3</sub> of the bound xylene (6H)). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ, ppm: 165.48 (C(CH<sub>3</sub>)N), 146.23, 140.46, 125.49, 123.84 (C of aryl), 96.40 (CCHC), 73.01 (CMe of the bound xylene, *J*<sub>Y-C</sub> = 6.8 Hz), 71.14 (CH of the bound xylene, *J*<sub>Y-C</sub> = 4.0 Hz), 41.93 (CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 28.27 (CH<sub>2</sub>CH<sub>3</sub>), 24.75 (CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 23.77 (CH<sub>2</sub>CH<sub>3</sub>), 19.05 (CH<sub>3</sub> of the bound xylene), 12.63 (CH<sub>2</sub>CH<sub>3</sub>), 10.53 (CH<sub>2</sub>CH<sub>3</sub>). Anal. (%): Calcd. For C<sub>82</sub>H<sub>124</sub>N<sub>4</sub>Y<sub>2</sub>, M<sub>w</sub> = 1343.73, as in the formula of [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>): C, 73.30; H, 9.30; N, 4.17. Found: C, 73.08; H, 9.26; N, 4.12.

**Synthesis of [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (3-Sm).** **1-Sm** (100 mg, 0.10 mmol) and KC<sub>8</sub> (32 mg, 0.24 mmol, 2.4 equiv) were dispersed in 1 mL of *p*-xylene. The mixture stirred vigorously at room temperature for 2 d. The volatiles of resulting black suspension were removed under reduced pressure. The residue was extracted into *n*-pentane (ca. 5 mL) and the filtrate was concentrated to ca. 3 mL. A small amount of THF (50 μL) was added to the solution.

After storing at  $-35\text{ }^{\circ}\text{C}$  overnight, black crystals precipitated from the solution. The mother liquor was decanted and the crystals were washed with cold *n*-pentane and dried under reduced pressure to yield **3-Sm** as a black solid (Yield: 55 mg, 69%). Single crystals of **3-Sm** suitable for X-ray crystallography were grown from a *n*-pentane solution containing a few drops of THF at  $-35\text{ }^{\circ}\text{C}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{C}_7\text{D}_8$ ) immediately  $\delta$ , ppm: 26.43 (s, 4H, *CH* of the bound *p*-xylene), 8.80 (s, 2H, *CCHC*), 6.36 (t,  $J = 7.7\text{ Hz}$ , 4H, *para-CH* of aryl), 6.19 (d,  $J = 7.7\text{ Hz}$ , 8H, *meta-CH* of aryl), 5.17 (s, 12H, *CCH}\_3*), 2.28–2.15 (m, 8H, *CH}\_2\text{CH}\_3*), 1.50–1.35 (m, 8H, *CH}\_2\text{CH}\_3*), 0.98 (t,  $J = 7.4\text{ Hz}$ , 24H, *CH}\_2\text{CH}\_3*), 0.53 (s, 8H, *CH(CH}\_2\text{CH}\_3)\_2*), 0.20 (t,  $J = 6.9\text{ Hz}$ , 24H, *CH}\_2\text{CH}\_3*),  $-0.54$  to  $-0.72$  (m, 8H, *CH}\_2\text{CH}\_3*),  $-1.64$  to  $-1.82$  (m, 8H, *CH}\_2\text{CH}\_3*),  $-7.95$  (s, 6H, *CH}\_3* of the bound *p*-xylene). The peaks of coordinating THF molecules are not observed probably due to the loss of THF molecules under reduced pressure during drying process. Anal. (%): Calcd. for  $\text{C}_{82}\text{H}_{124}\text{N}_4\text{Sm}_2$ ,  $M_w = 1466.64$ , as in the formula of  $[(\text{BDI})\text{Sm}]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$ : C, 67.15; H, 8.52; N, 3.82. Found: C, 67.11; H, 8.73; N, 3.67.

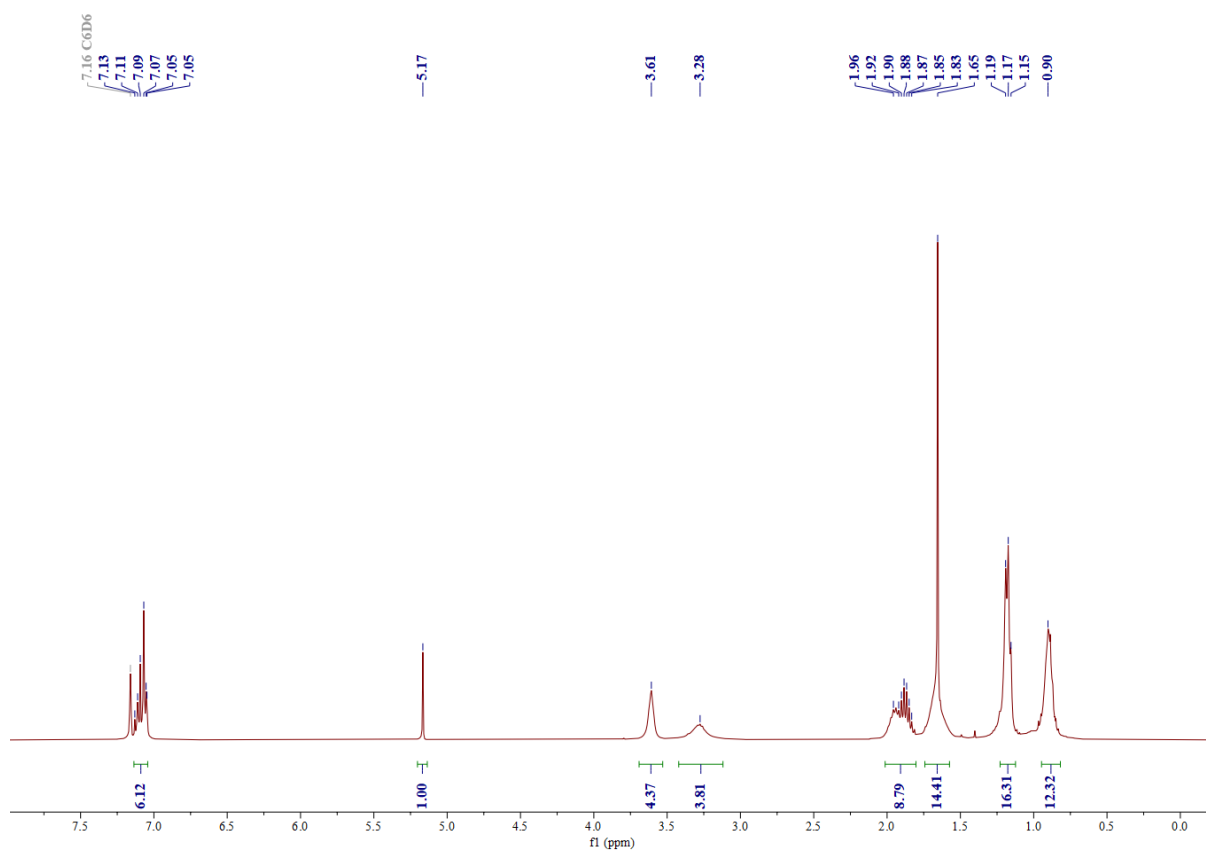
**Arene exchange reaction of 3-Sm.** **3-Sm** (6 mg, 0.004 mmol) was dissolved in  $\text{C}_6\text{D}_6$  (ca. 0.6 mL) and the black solution was transferred to a J. Young tube. The arene exchange reaction was monitored by  $^1\text{H NMR}$  spectroscopy at room temperature over the course of 24 h. There was significant exchange after 5 min (Figure S9). The reaction reached completion and **3-Sm** was fully converted to  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_6\text{D}_6)$  after 24 h (Figure S10).

**Synthesis of (BDI)Sm( $\eta^8$ -COT) (4-Sm).** **2-Sm** (80 mg, 0.05 mmol) and cyclooctatetraene (COT) (13 mg, 0.13 mmol, 2.5 equiv) were dissolved in 6 mL and 2 mL of  $\text{Et}_2\text{O}$ , respectively. Both solutions were cooled at  $-78\text{ }^{\circ}\text{C}$  for 15 min. The cold solution of **2-Sm** was added to the solution of COT dropwise with stirring. The mixture was warmed to room temperature and stirred for 30 min. The volatiles of resulting brown solution were removed under reduced pressure. The residue was extracted into *n*-pentane (ca. 8 mL) and the filtrate was concentrated to ca. 3 mL. A small amount of THF (30  $\mu\text{L}$ ) was added to the solution. After standing at room temperature for 1 h, light purple solid precipitated from the solution. The mother liquor was decanted and the solid was dried under reduced pressure to yield **4-Sm** as a light purple solid (Yield: 82 mg, 95%). Single crystals of **4-Sm** suitable for X-ray crystallography were grown from a  $\text{Et}_2\text{O}$  solution at  $-35\text{ }^{\circ}\text{C}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ , ppm: 8.20 (s, 8H, *CH* of COT), 7.99 (t,  $J = 7.8\text{ Hz}$ , 2H, *para-CH* of aryl), 7.77 (s, 1H, *CCHC*), 7.49 (d,  $J = 7.8\text{ Hz}$ , 4H, *meta-CH* of aryl), 3.58 (s, 10H, *CCH}\_3* & *OCH}\_2* of free THF), 1.72–1.59 (m, 4H, *CH}\_2\text{CH}\_3*), 1.45–1.37 (m, 4H, *OCH}\_2\text{CH}\_2* of free THF), 1.00–0.89 (m, 4H, *CH}\_2\text{CH}\_3*), 0.70 (t,  $J = 7.4\text{ Hz}$ , 12H, *CH}\_2\text{CH}\_3*),  $-1.46$  (t,  $J = 7.2\text{ Hz}$ , 12H, *CH}\_2\text{CH}\_3*),  $-1.78$  to  $-1.92$  (m, 4H, *CH}\_2\text{CH}\_3*),  $-1.99$  to  $-2.11$  (m, 4H, *CH}\_2\text{CH}\_3*),  $-2.21$  (s, 4H, *CH(CH}\_2\text{CH}\_3)\_2*). Anal. (%): Calcd. For  $\text{C}_{51.5}\text{H}_{79}\text{N}_2\text{OSm}$ ,  $M_w = 878.54$ , as in the formula of  $(\text{BDI})\text{Sm}(\eta^8\text{-COT})\cdot\text{THF}\cdot 0.5\text{C}_5\text{H}_{12}(\textit{n}\text{-pentane})$ : C, 69.30; H, 8.92; N, 3.14. Found: C, 69.22; H, 8.89; N, 3.34.

**Synthesis of (BDI)Sm( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>) (5-Sm).** **2-Sm** (25 mg, 0.016 mmol) and 1,4-diphenylbutadiyne (8 mg, 0.038 mmol, 2.4 equiv) were each dissolved in 1 mL of  $\text{Et}_2\text{O}$ . Both solutions were cooled at  $-78\text{ }^{\circ}\text{C}$  for 15 min. The cold solution of **2-Sm** was added to the solution of 1,4-diphenylbutadiyne dropwise with stirring. The mixture was warmed to room temperature and stirred for 1 h. The volatiles of resulting red brown solution were removed under reduced pressure. The residue was extracted into *n*-pentane (ca. 3 mL) and the filtrate was concentrated to ca. 1 mL. After storing at  $-78\text{ }^{\circ}\text{C}$  for 1 h, red crystals precipitated from the

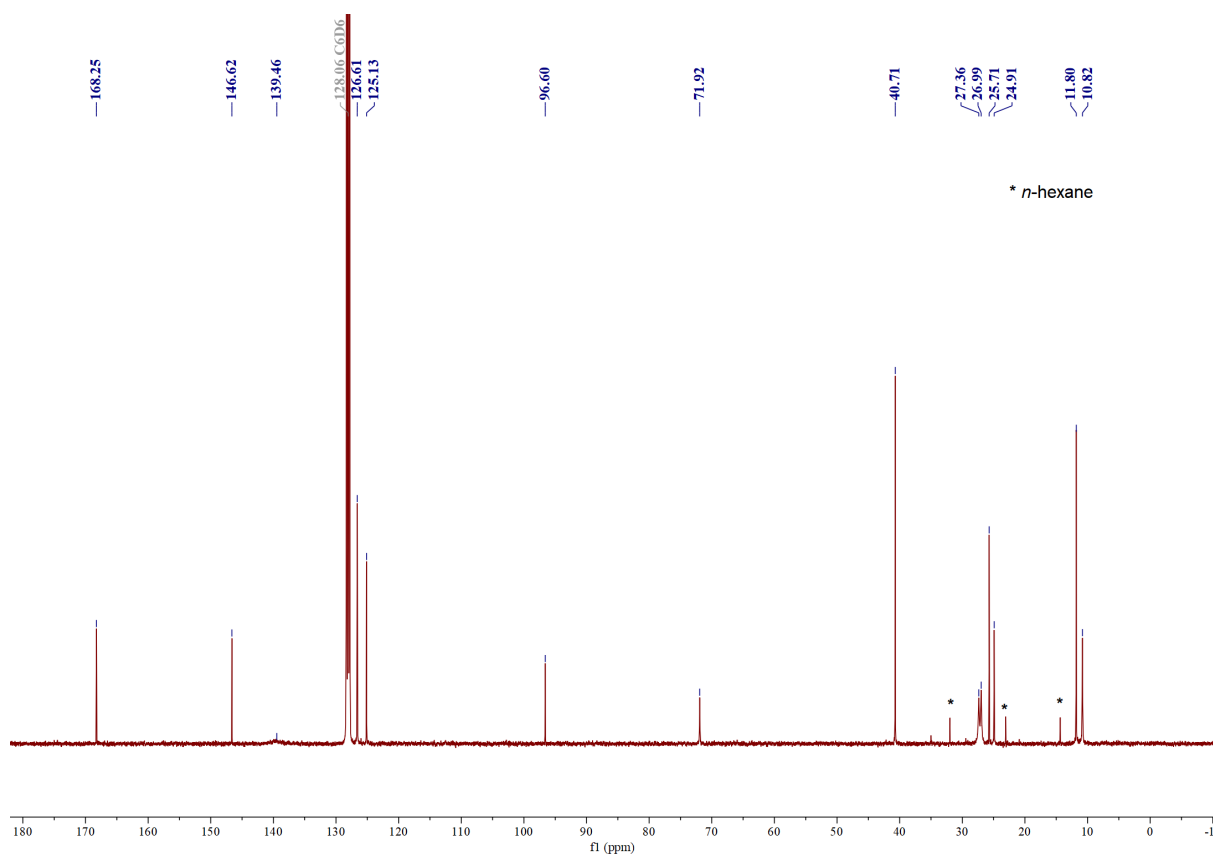
solution. The mother liquor was decanted and the crystals were washed with cold *n*-pentane. The remaining solid was dried under reduced pressure to yield **5-Sm** as a dark red solid (Yield: 21 mg, 75%). Single crystals of **5-Sm** suitable for X-ray crystallography were grown from a *n*-pentane solution at  $-35\text{ }^{\circ}\text{C}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ , ppm: 15.23 (s, 1H, CCHC), 13.39 (d,  $J = 7.4\text{ Hz}$ , 4H), 8.42 (t,  $J = 7.0\text{ Hz}$ , 4H, *meta*-CH of  $\text{C}_4\text{Ph}_2$ ), 8.22 (t,  $J = 7.2\text{ Hz}$ , 2H), 5.15 (t,  $J = 7.6\text{ Hz}$ , 2H), 4.10 (s, 4H), 2.18 (s, 6H, CCH<sub>3</sub>), 0.25 (s, 12H, CH<sub>2</sub>CH<sub>3</sub>),  $-0.26$  to  $-1.07$  (m, 20H, CH<sub>2</sub>CH<sub>3</sub> (12H) & CH<sub>2</sub>CH<sub>3</sub> (8H)),  $-2.69$  (s, 4H),  $-3.99$  (s, 4H),  $-12.01$  (br s, 4H). The signals cannot be completely assigned due to the signal broadening and similar signal splitting in aryl groups of the ligand backbone and the [ $\text{C}_4\text{Ph}_2$ ] unit. Anal. (%): Calcd. For  $\text{C}_{53}\text{H}_{67}\text{N}_2\text{Sm}$ ,  $M_w = 882.49$ , as in the formula of (BDI)Sm( $\eta^4$ - $\text{C}_4\text{Ph}_2$ ): C, 72.13; H, 7.65; N, 3.17. Found: C, 72.27; H, 7.66; N, 3.00.

## S2. NMR Spectra

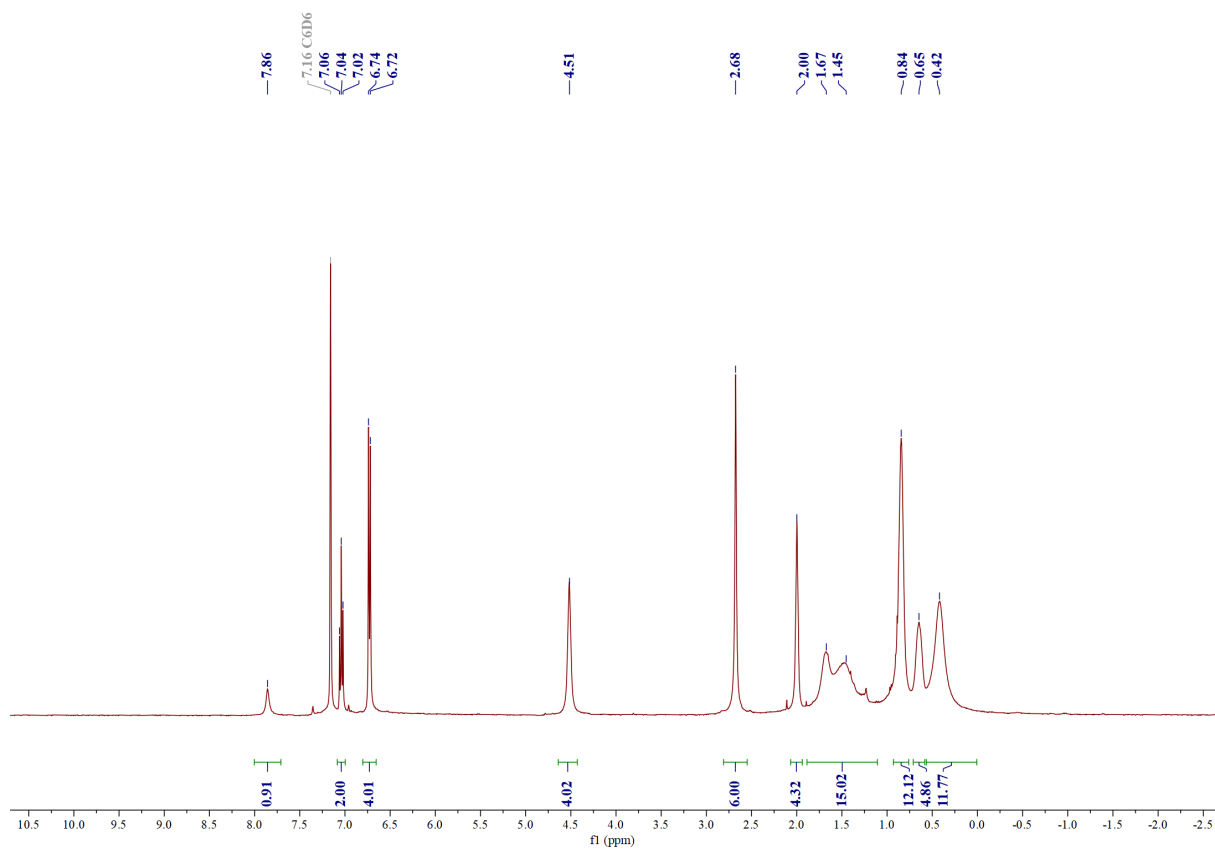


**Fig. S1.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) spectrum of (BDI)YI<sub>2</sub>(THF) (**1-Y**),  $\delta$ , ppm: 7.14–7.04 (m, 6H, CH of aryl), 5.17 (s, 1H, CCHC), 3.61 (s, 4H, CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.28 (s, 4H, OCH<sub>2</sub>), 2.01–1.80 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.77–1.57 (m, 14H, CH<sub>2</sub>CH<sub>3</sub> (8H) & CCH<sub>3</sub> (6H)), 1.23–1.11 (m, 16H, OCH<sub>2</sub>CH<sub>2</sub> (4H) & CH<sub>2</sub>CH<sub>3</sub> (12H)), 0.90 (s, 12H, CH<sub>2</sub>CH<sub>3</sub>).

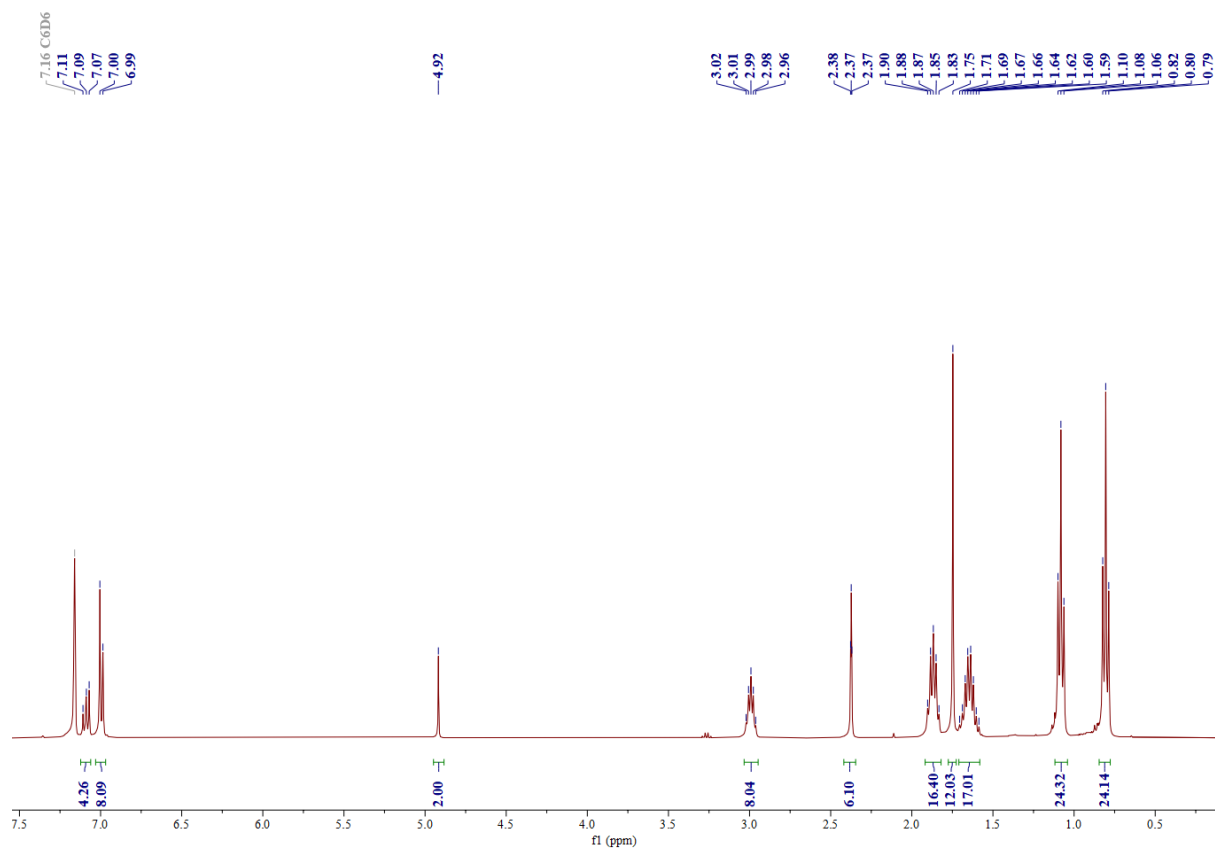




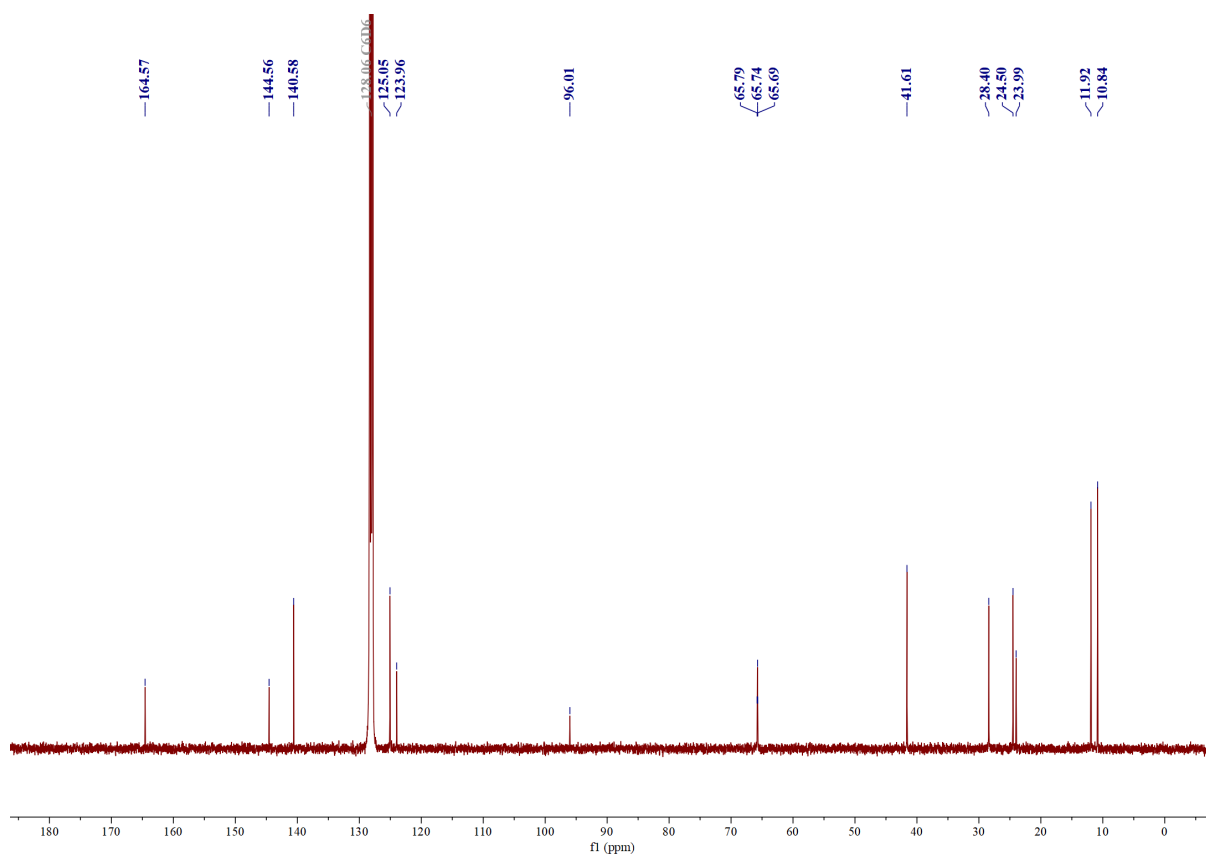
**Fig. S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) spectrum of (BDI)YI<sub>2</sub>(THF) (**1-Y**),  $\delta$ , ppm: 168.25 (C(CH<sub>3</sub>)N), 146.62, 139.46, 126.61, 125.13 (C of aryl), 96.60 (CCHC), 71.92 (OCH<sub>2</sub>), 40.71 (CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 27.36 (CH<sub>2</sub>CH<sub>3</sub>), 26.99 (OCH<sub>2</sub>CH<sub>2</sub>), 25.71 (CCH<sub>3</sub>), 24.91 (CH<sub>2</sub>CH<sub>3</sub>), 11.80 (CH<sub>2</sub>CH<sub>3</sub>), 10.82 (CH<sub>2</sub>CH<sub>3</sub>).



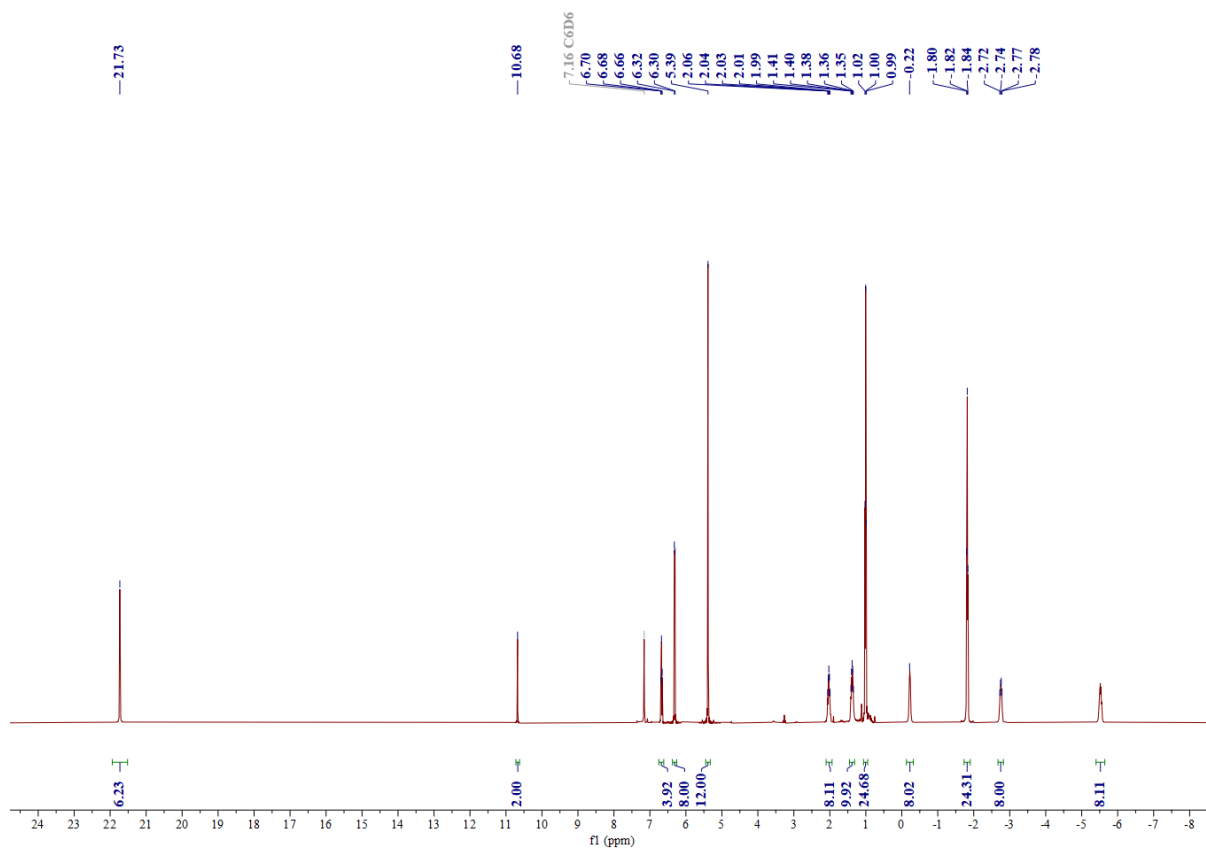
**Fig. S3.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298K) spectrum of  $(\text{BDI})\text{SmI}_2(\text{THF})$  (**1-Sm**),  $\delta$ , ppm: 7.86 (s, 1H, *CCHC*), 7.04 (t,  $J = 7.7$  Hz, 2H, *para-CH* of aryl), 6.73 (d,  $J = 7.8$  Hz, 4H, *meta-CH* of aryl), 4.51 (s, 4H,  $\text{OCH}_2$ ), 2.68 (s, 6H,  $\text{CCH}_3$ ), 2.00 (s, 4H,  $\text{OCH}_2\text{CH}_2$ ), 1.88–1.11 (m, 16H,  $\text{CH}_2\text{CH}_3$ ), 0.84 (s, 12H,  $\text{CH}_2\text{CH}_3$ ), 0.65 (s, 4H,  $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 0.42 (s, 12H,  $\text{CH}_2\text{CH}_3$ ).



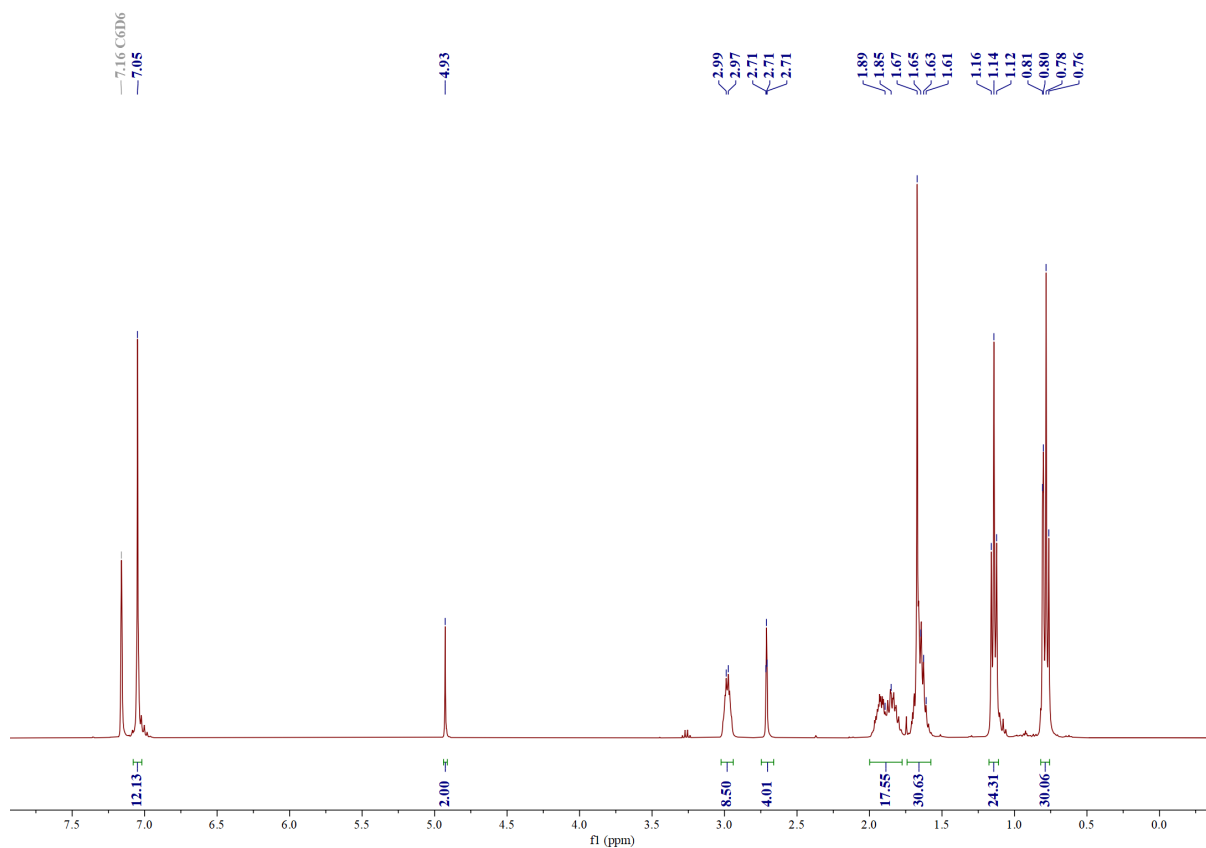
**Fig. S4.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298K) spectrum of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_6\text{H}_6)$  (**2-Y**),  $\delta$ , ppm: 7.12–7.06 (m, 4H, *para-CH* of aryl), 6.99 (d,  $J = 7.6$  Hz, 8H, *meta-CH* of aryl), 4.92 (s, 2H, CCHC), 3.03–2.95 (m, 8H,  $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 2.37 (t,  $J_{\text{Y-H}} = 1.6$  Hz, 6H, *CH* of the bound benzene), 1.92–1.82 (m, 16H,  $\text{CH}_2\text{CH}_3$ ), 1.75 (s, 12H, CCH<sub>3</sub>), 1.71–1.58 (m, 16H,  $\text{CH}_2\text{CH}_3$ ), 1.08 (t,  $J = 7.3$  Hz, 24H,  $\text{CH}_2\text{CH}_3$ ), 0.80 (t,  $J = 7.4$  Hz, 24H,  $\text{CH}_2\text{CH}_3$ ).



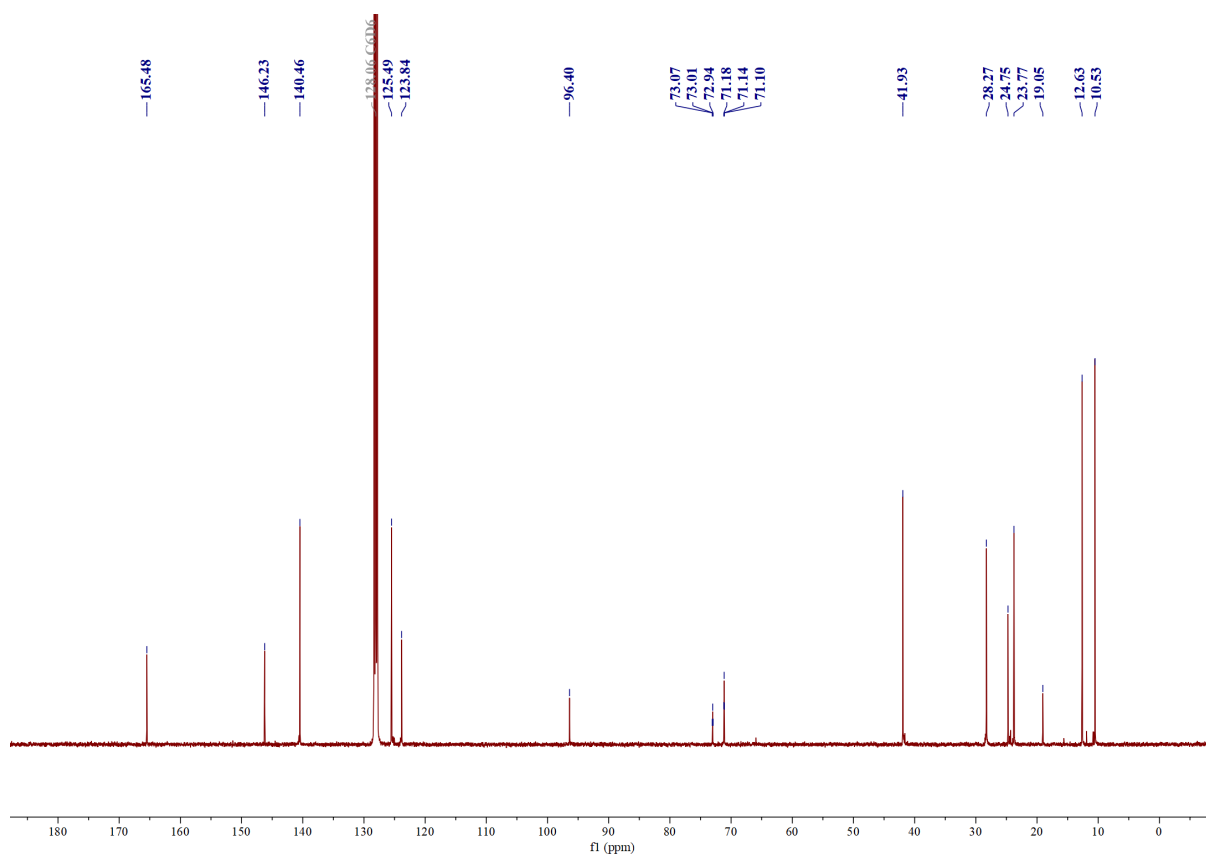
**Fig. S5.**  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ , 298K) spectrum of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6,\eta^6\text{-C}_6\text{H}_6)$  (**2-Y**),  $\delta$ , ppm: 164.57 ( $\text{C}(\text{CH}_3)\text{N}$ ), 144.56, 140.58, 125.05, 123.96 ( $\text{C}$  of aryl), 96.01 ( $\text{CCHC}$ ), 65.74 ( $\text{CH}$  of the bound benzene,  $J_{\text{Y-C}} = 4.8$  Hz), 41.61 ( $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 28.40 ( $\text{CH}_2\text{CH}_3$ ), 24.50 ( $\text{CH}_2\text{CH}_3$ ), 23.99 ( $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 11.92 ( $\text{CH}_2\text{CH}_3$ ), 10.84 ( $\text{CH}_2\text{CH}_3$ ).



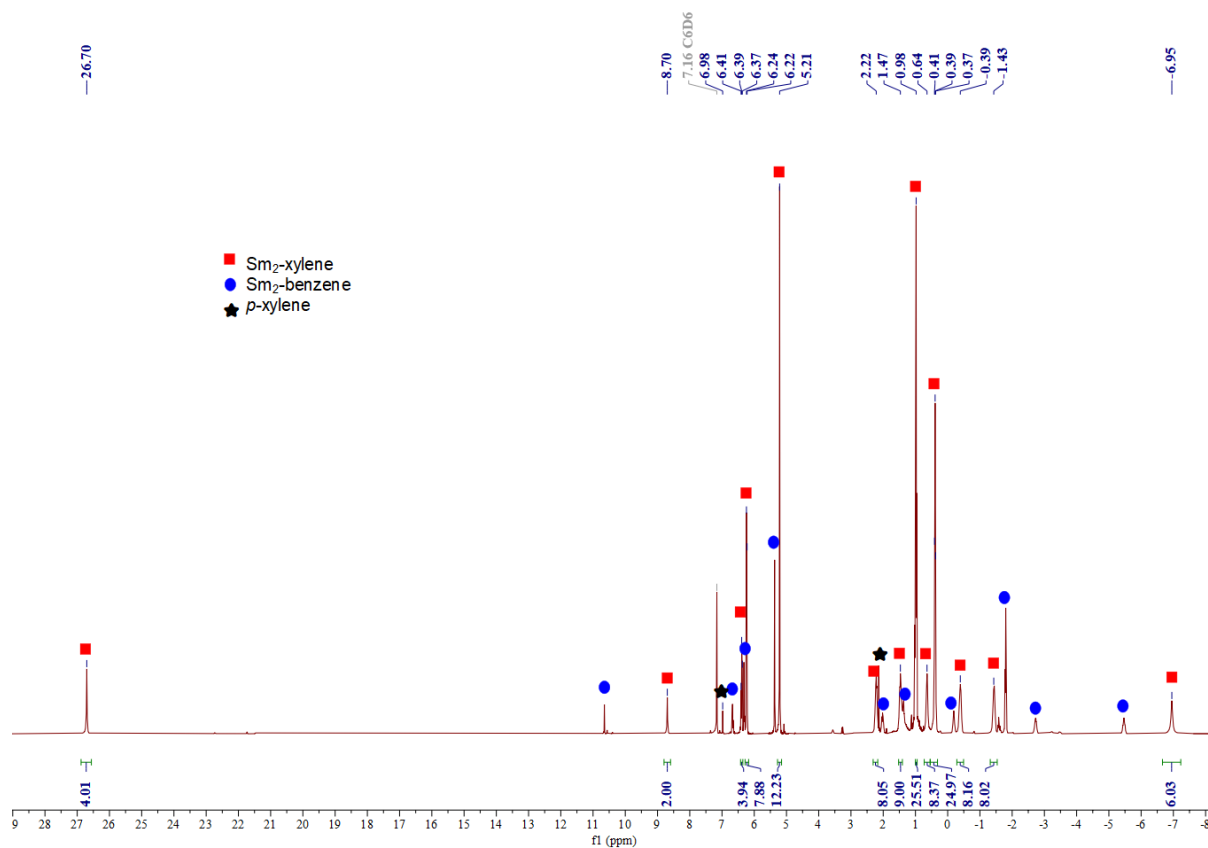
**Fig. S6.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) spectrum of [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (**2-Sm**), δ, ppm: 21.73 (s, 6H, CH of the bound benzene), 10.68 (s, 2H, CCHC), 6.68 (t, *J* = 7.8 Hz, 4H, *para*-CH of aryl), 6.31 (d, *J* = 8.0 Hz, 8H, *meta*-CH of aryl), 5.39 (s, 12H, CCH<sub>3</sub>), 2.10–1.95 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.45–1.31 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.00 (t, *J* = 7.4 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), –0.22 (s, 8H, CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), –1.82 (t, *J* = 7.1 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), –2.67 to –2.82 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), –5.40 to –5.64 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>). The peaks of coordinating THF molecules are not observed probably due to the loss of THF molecules under reduced pressure during drying process.



**Fig. S7.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) spectrum of [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (**3-Y**), δ, ppm: 7.05 (s, 12H, CH of aryl), 4.93 (s, 2H, CCHC), 3.03–2.92 (m, 8H, CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 2.71 (t, *J*<sub>Y-H</sub> = 1.7 Hz, 4H, CH of the bound *p*-xylene), 2.00–1.77 (m, 16H, CH<sub>2</sub>CH<sub>3</sub>), 1.74–1.57 (m, 28H, CCH<sub>3</sub> (12H) & CH<sub>2</sub>CH<sub>3</sub> (16H)), 1.14 (t, *J* = 7.3 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), 0.82–0.76 (m, 30H, CH<sub>2</sub>CH<sub>3</sub> (24H) & CH<sub>3</sub> of the bound *p*-xylene (6H)).

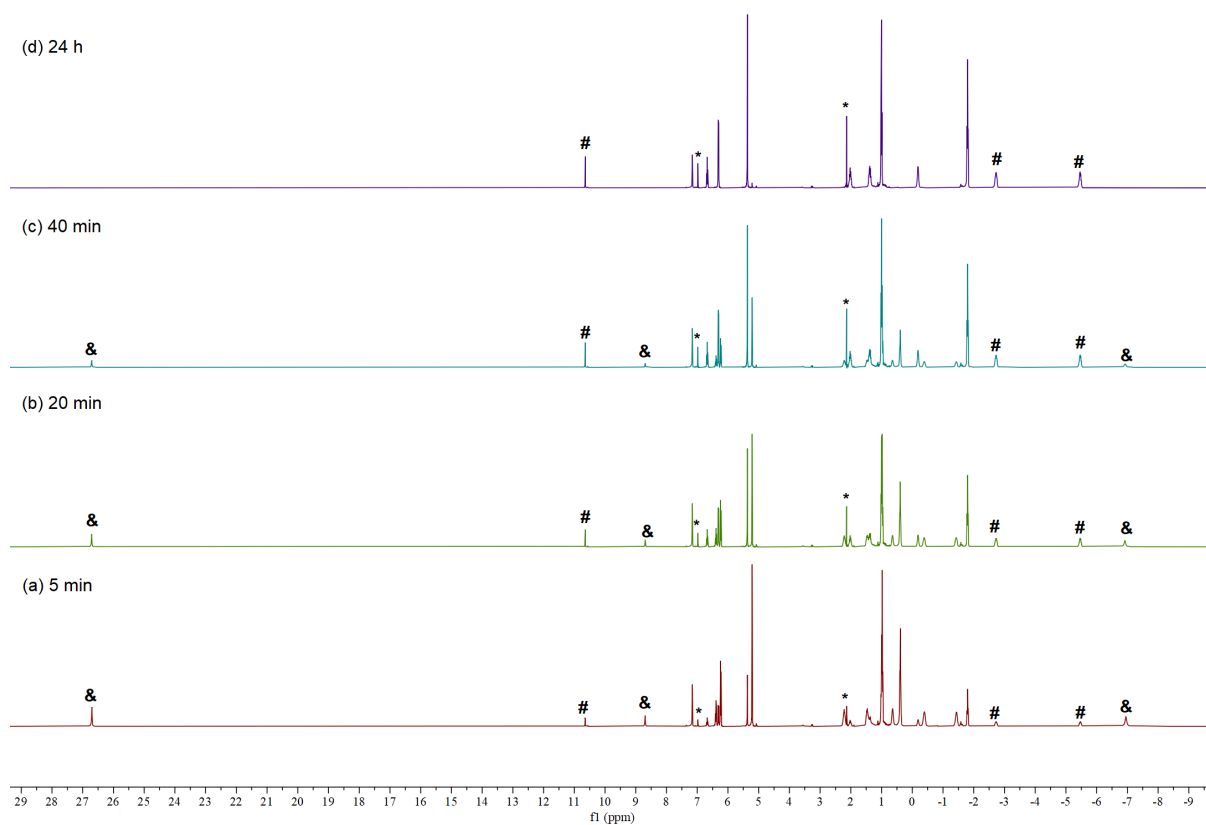


**Fig. S8.**  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ , 298K) spectrum of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$  (**3-Y**),  $\delta$ , ppm: 165.48 ( $\text{C}(\text{CH}_3)\text{N}$ ), 146.23, 140.46, 125.49, 123.84 ( $\text{C}$  of aryl), 96.40 ( $\text{CCHC}$ ), 73.01 ( $\text{CMe}$  of the bound xylene,  $J_{\text{Y-C}} = 6.8$  Hz), 71.14 ( $\text{CH}$  of the bound *p*-xylene,  $J_{\text{Y-C}} = 4.0$  Hz), 41.93 ( $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 28.27 ( $\text{CH}_2\text{CH}_3$ ), 24.75 ( $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 23.77 ( $\text{CH}_2\text{CH}_3$ ), 19.05 ( $\text{CH}_3$  of the bound *p*-xylene), 12.63 ( $\text{CH}_2\text{CH}_3$ ), 10.53 ( $\text{CH}_2\text{CH}_3$ ).

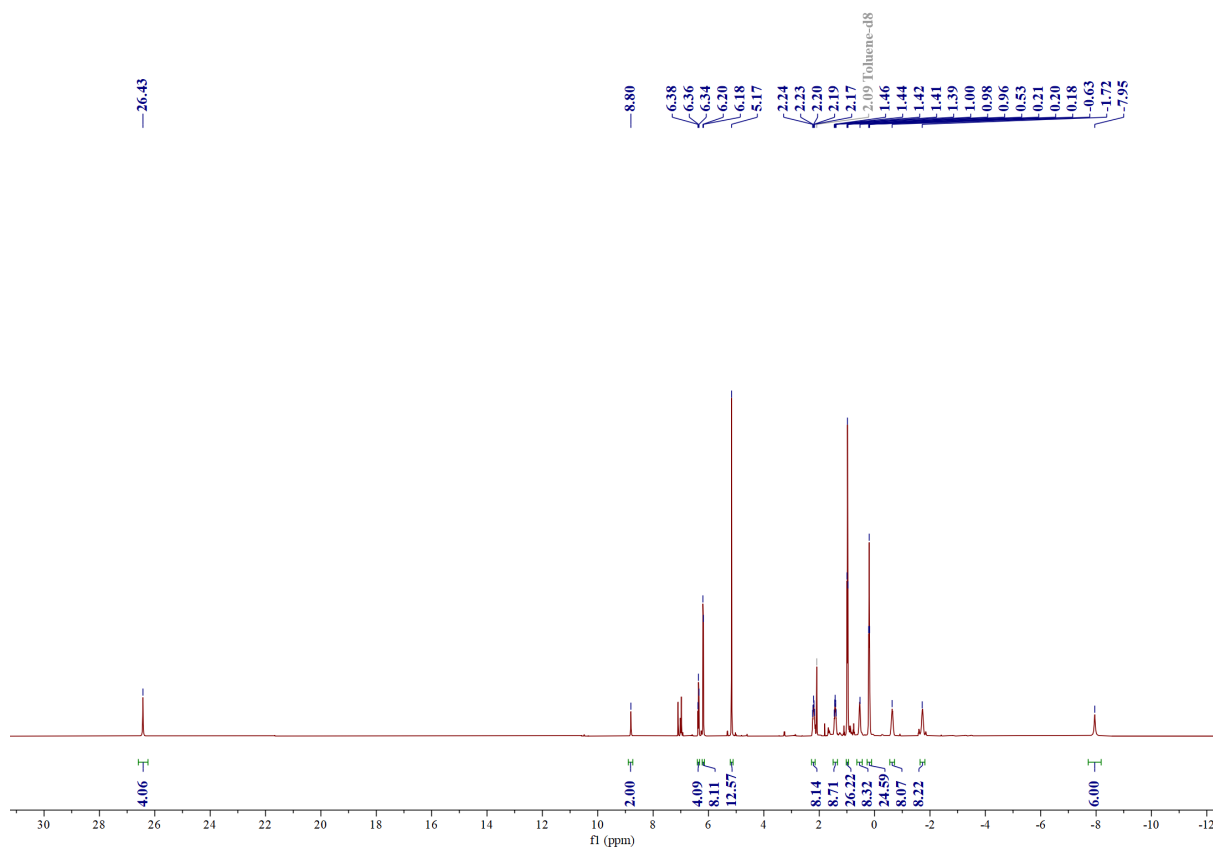


**Fig. S9.**  $^1\text{H}$  NMR (400 MHz, 298K) spectrum of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$  (**3-Sm**) in  $\text{C}_6\text{D}_6$  (5 min after dissolution). 26.70 (s, 4H,  $\text{CH}$  of the bound  $p$ -xylene), 8.70 (s, 2H,  $\text{CCHC}$ ), 6.39 (t,  $J = 7.8$  Hz, 4H,  $\text{para-CH}$  of aryl), 6.23 (d,  $J = 7.8$  Hz, 8H,  $\text{meta-CH}$  of aryl), 5.21 (s, 12H,  $\text{CCH}_3$ ), 2.31–2.15 (m, 8H,  $\text{CH}_2\text{CH}_3$ ), 1.54–1.40 (m, 8H,  $\text{CH}_2\text{CH}_3$ ), 0.98 (t,  $J = 7.3$  Hz, 24H,  $\text{CH}_2\text{CH}_3$ ), 0.64 (s, 8H,  $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 0.39 (t,  $J = 6.7$  Hz, 24H,  $\text{CH}_2\text{CH}_3$ ),  $-0.30$  to  $-0.47$  (m, 8H,  $\text{CH}_2\text{CH}_3$ ),  $-1.32$  to  $-1.53$  (m, 8H,  $\text{CH}_2\text{CH}_3$ ),  $-6.95$  (s, 6H,  $\text{CH}_3$  of the bound  $p$ -xylene).



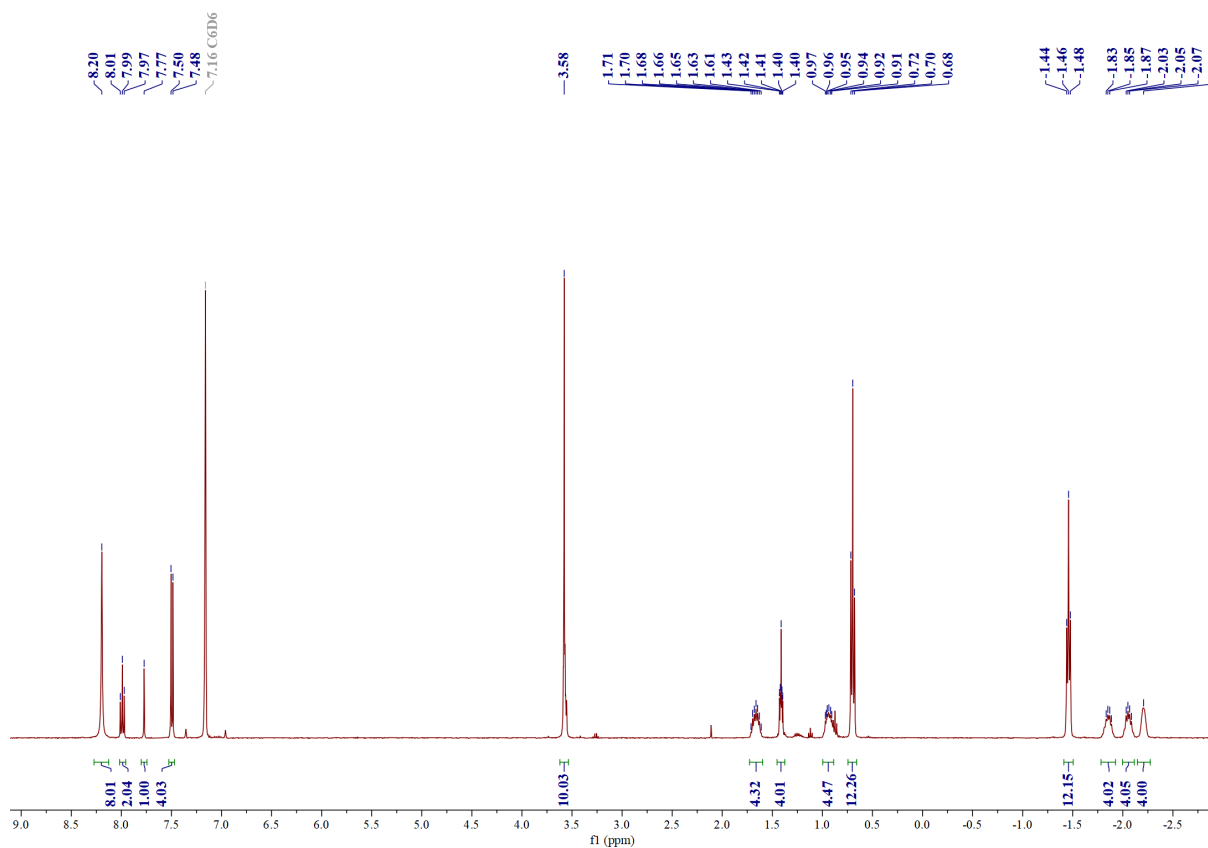


**Fig. S10.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) spectra for monitoring the arene exchange reaction of **3-Sm** (characteristic peaks labelled with “&”) in C<sub>6</sub>D<sub>6</sub> at 25 °C. #: the characteristic peaks of [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>D<sub>6</sub>); \*: the peaks of free *p*-xylene. From bottom to top: (a) 5 min; (b) 20 min; (c) 40 min; (d) 24 h (full conversion).

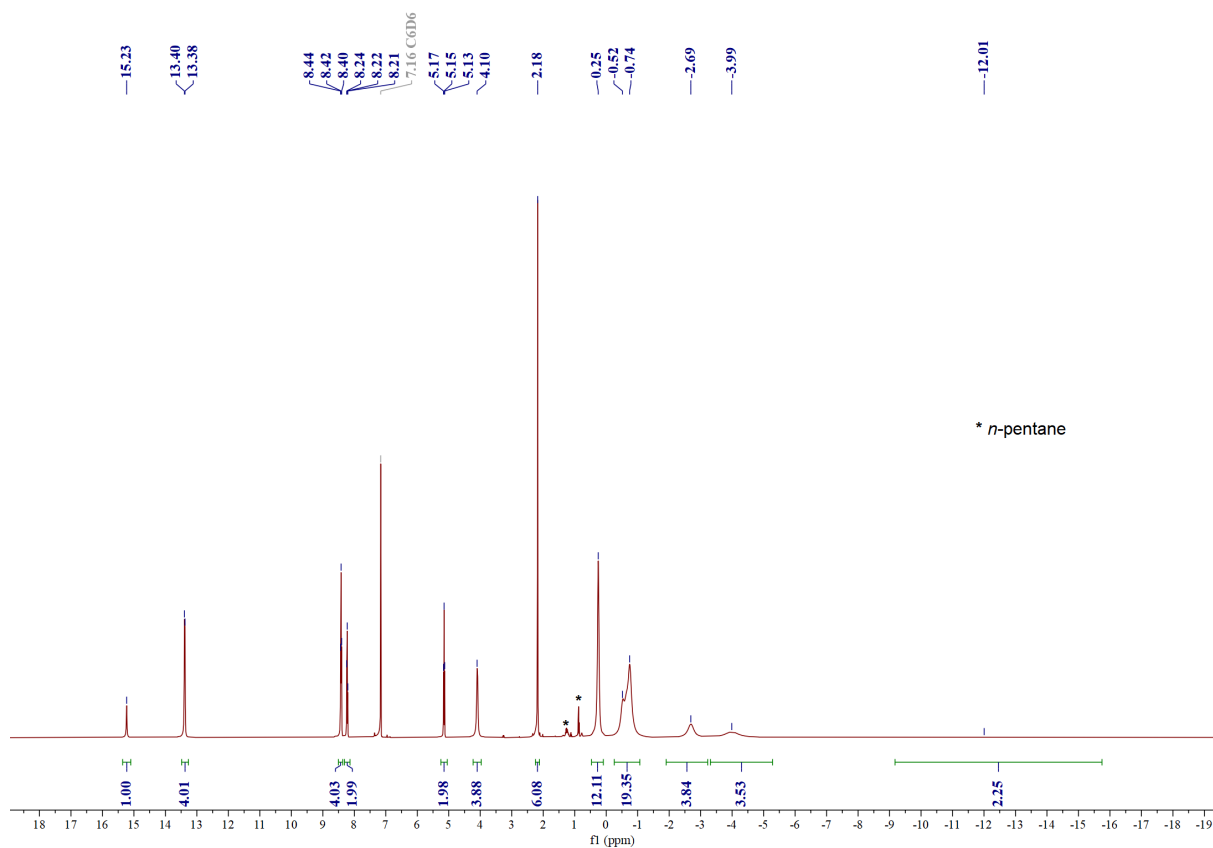


**Fig. S11.**  $^1\text{H}$  NMR (400 MHz, 298K) spectrum of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$  (**3-Sm**) in  $\text{C}_7\text{D}_8$  (10 min after dissolution). 26.43 (s, 4H,  $\text{CH}$  of the bound  $p$ -xylene), 8.80 (s, 2H,  $\text{CCHC}$ ), 6.36 (t,  $J = 7.7$  Hz, 4H,  $\text{para-CH}$  of aryl), 6.19 (d,  $J = 7.7$  Hz, 8H,  $\text{meta-CH}$  of aryl), 5.17 (s, 12H,  $\text{CCH}_3$ ), 2.28–2.15 (m, 8H,  $\text{CH}_2\text{CH}_3$ ), 1.50–1.35 (m, 8H,  $\text{CH}_2\text{CH}_3$ ), 0.98 (t,  $J = 7.4$  Hz, 24H,  $\text{CH}_2\text{CH}_3$ ), 0.53 (s, 8H,  $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 0.20 (t,  $J = 6.9$  Hz, 24H,  $\text{CH}_2\text{CH}_3$ ),  $-0.54$  to  $-0.72$  (m, 8H,  $\text{CH}_2\text{CH}_3$ ),  $-1.64$  to  $-1.82$  (m, 8H,  $\text{CH}_2\text{CH}_3$ ),  $-7.95$  (s, 6H,  $\text{CH}_3$  of the bound  $p$ -xylene). The peaks of coordinating THF molecules are not observed probably due to the loss of THF molecules under reduced pressure during drying process.

Note: The arene exchange reaction of **3-Sm** in  $\text{C}_7\text{D}_8$  was slower than that in  $\text{C}_6\text{D}_6$ . Only a small amount of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_7\text{D}_8)$  was observed after 50 min at room temperature.



**Fig. S12.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298K) spectrum of  $(\text{BDI})\text{Sm}(\eta^8\text{-COT})$  (**4-Sm**),  $\delta$ , ppm: 8.20 (s, 8H, *CH* of COT), 7.99 (t,  $J = 7.8$  Hz, 2H, *para-CH* of aryl), 7.77 (s, 1H, CCHC), 7.49 (d,  $J = 7.8$  Hz, 4H, *meta-CH* of aryl), 3.58 (s, 10H,  $\text{CCH}_3$  &  $\text{OCH}_2$  of free THF), 1.72–1.59 (m, 4H,  $\text{CH}_2\text{CH}_3$ ), 1.45–1.37 (m, 4H,  $\text{OCH}_2\text{CH}_2$  of free THF), 1.00–0.89 (m, 4H,  $\text{CH}_2\text{CH}_3$ ), 0.70 (t,  $J = 7.4$  Hz, 12H,  $\text{CH}_2\text{CH}_3$ ), -1.46 (t,  $J = 7.2$  Hz, 12H,  $\text{CH}_2\text{CH}_3$ ), -1.78 to -1.92 (m, 4H,  $\text{CH}_2\text{CH}_3$ ), -1.99 to -2.11 (m, 4H,  $\text{CH}_2\text{CH}_3$ ), -2.21 (s, 4H,  $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ).



**Fig. S13.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298K) spectrum of  $(\text{BDI})\text{Sm}(\eta^4\text{-C}_4\text{Ph}_2)$  (**5-Sm**),  $\delta$ , ppm: 15.23 (s, 1H, CCHC), 13.39 (d,  $J = 7.4$  Hz, 4H), 8.42 (t,  $J = 7.0$  Hz, 4H, *meta*-CH of  $\text{C}_4\text{Ph}_2$ ), 8.22 (t,  $J = 7.2$  Hz, 2H), 5.15 (t,  $J = 7.6$  Hz, 2H), 4.10 (s, 4H), 2.18 (s, 6H, CCH<sub>3</sub>), 0.25 (s, 12H, CH<sub>2</sub>CH<sub>3</sub>), -0.26 to -1.07 (m, 20H, CH<sub>2</sub>CH<sub>3</sub> (12H) & CH<sub>2</sub>CH<sub>3</sub> (8H)), -2.69 (s, 4H), -3.99 (s, 4H), -12.01 (br s, 4H). The signals cannot be assigned completely because of the signal broadening and similar signal splitting in aryl groups of ligand backbone and  $\text{C}_4\text{Ph}_4$ .

## S3. X-ray Crystallography

### S3.1. General

All structures were solved by the intrinsic phasing method with SHELXT<sup>5</sup> and refined by full-matrix least-squares procedures utilizing SHELXL<sup>6, 7</sup> within Olex2 crystallographic software package.<sup>8</sup> The PLATON<sup>9</sup> routine SQUEEZE<sup>10</sup> was used in the refinement of some structures.

### S3.2. CCDC Deposition

All crystal structures reported in this work have been deposited to the Cambridge Crystallographic Data Center (CCDC) with the following deposition numbers:

CCDC-2345765: (BDI)YI<sub>2</sub>(THF) (**1-Y**)

CCDC-2345766: (BDI)SmI<sub>2</sub>(THF) (**1-Sm**)

CCDC-2345769: [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (**2-Y**)

CCDC-2345764: [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (**2-Sm**)

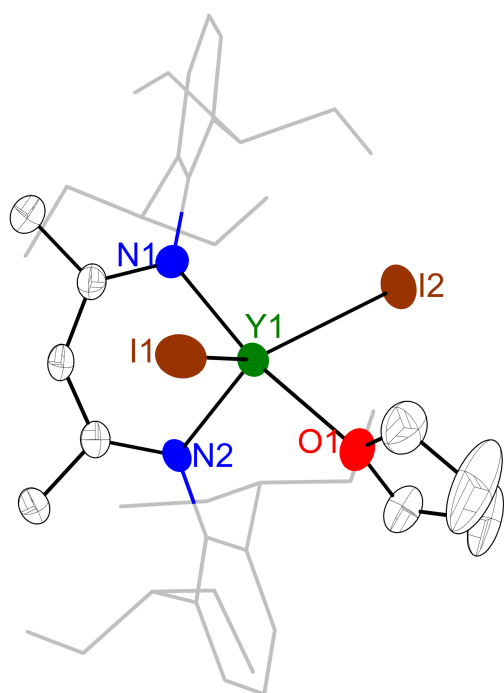
CCDC-2345768: [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (**3-Y**)

CCDC-2345762: [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (**3-Sm**)

CCDC-2345767: (BDI)Sm(η<sup>8</sup>-COT) (**4-Sm**)

CCDC-2345763: (BDI)Sm(η<sup>4</sup>-C<sub>4</sub>Ph<sub>2</sub>) (**5-Sm**)

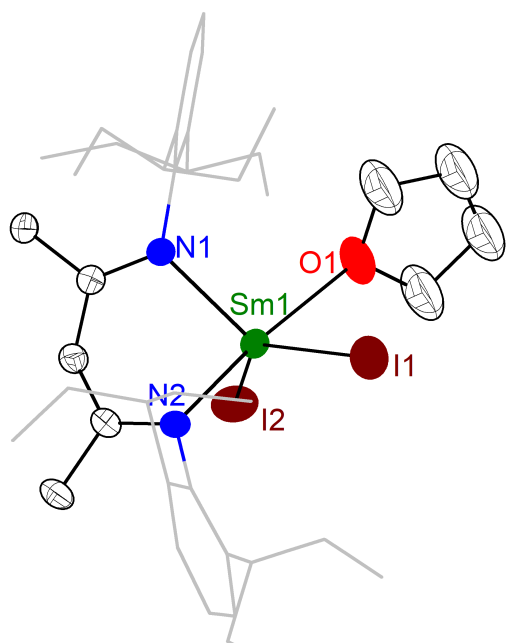
**(BDI)YI<sub>2</sub>(THF) (1-Y)**



**Fig. S14.** Representation of (BDI)YI<sub>2</sub>(THF) (**1-Y**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and disordered counterpart (THF) were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances (Å) and angles (°): Y1–N1 2.2760(48), Y1–N2 2.2681(48), Y1–I1 2.9239(7), Y1–I2 2.9469(6), Y1–O1 2.3725(40), N1–Y1–N2 87.736(170), I1–Y1–I2 136.217(21).

Single crystals suitable for X-ray crystallography were grown from a hexanes solution at –35 °C. A total of 24757 reflections ( $-17 \leq h \leq 16$ ,  $-30 \leq k \leq 26$ ,  $-21 \leq l \leq 13$ ) were collected at  $T = 180.00$  K with  $2\theta_{\max} = 58.984^\circ$ , of which 10611 were unique. The residual peak and hole electron density were 1.72 and  $-1.22$  eÅ<sup>-3</sup>. The least-squares refinement converged normally with residuals of  $R_1 = 0.0662$  and GOF = 1.077. Crystal and refinement data for **1-Y**: formula C<sub>41</sub>H<sub>65</sub>I<sub>2</sub>N<sub>2</sub>OY, space group  $P2_1/n$ ,  $a = 12.5793(4)$  Å,  $b = 21.9106(6)$  Å,  $c = 15.8022(4)$  Å,  $\beta = 99.436(3)^\circ$ ,  $V = 4296.5(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 2.825$  mm<sup>-1</sup>,  $F(000) = 1912.0$ ,  $R_1 = 0.1008$  and  $wR_2 = 0.1970$  (based on all data).

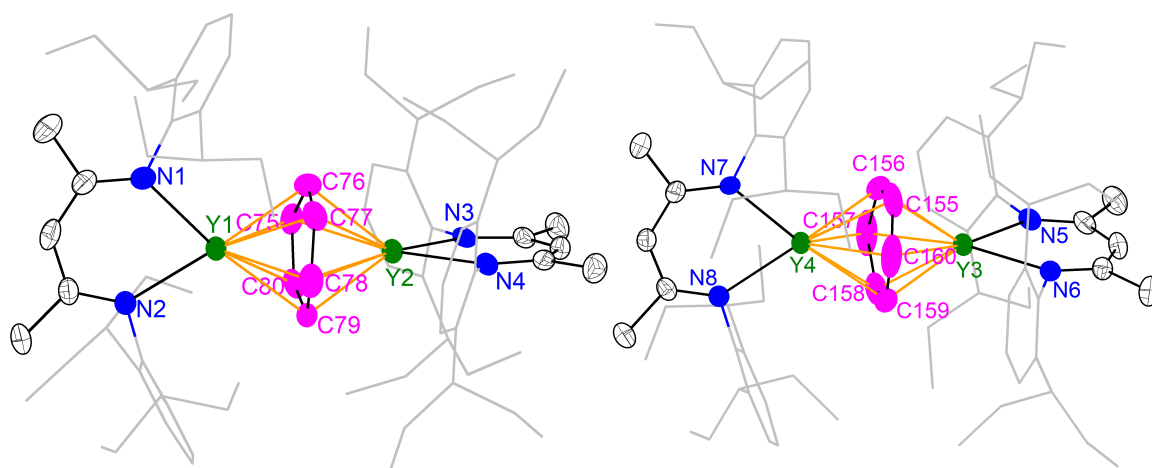
**(BDI)SmI<sub>2</sub>(THF) (1-Sm)**



**Fig. S15.** Representation of (BDI)SmI<sub>2</sub>(THF) (**1-Sm**) with thermal ellipsoids set at 50% probability. Hydrogen atoms were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances (Å) and angles (°): Sm1–N1 2.3088(27), Sm1–N2 2.3133(35), Sm1–I1 3.0166(5), Sm1–I2 2.9896(5), Sm1–O1 2.4409(37), N1–Sm1–N2 86.557(109), I1–Sm1–I2 137.905(14).

Single crystals suitable for X-ray crystallography were grown from a Et<sub>2</sub>O solution at room temperature. A total of 32901 reflections ( $-16 \leq h \leq 17$ ,  $-29 \leq k \leq 30$ ,  $-21 \leq l \leq 22$ ) were collected at  $T = 180.00$  K with  $2\theta_{\max} = 59.032^\circ$ , of which 10887 were unique. The residual peak and hole electron density were 1.60 and  $-1.53$  eÅ<sup>-3</sup>. The least-squares refinement converged normally with residuals of  $R_1 = 0.0387$  and GOF = 1.061. Crystal and refinement data for **1-Sm**: formula C<sub>41</sub>H<sub>65</sub>I<sub>2</sub>N<sub>2</sub>OSm, space group  $P2_1/n$ ,  $a = 12.5729(3)$  Å,  $b = 21.8852(4)$  Å,  $c = 15.9583(3)$  Å,  $\beta = 99.806(2)^\circ$ ,  $V = 4326.94(16)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 2.814$  mm<sup>-1</sup>,  $F(000) = 2004.0$ ,  $R_1 = 0.0480$  and  $wR_2 = 0.1038$  (based on all data).

**[(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (2-Y)**

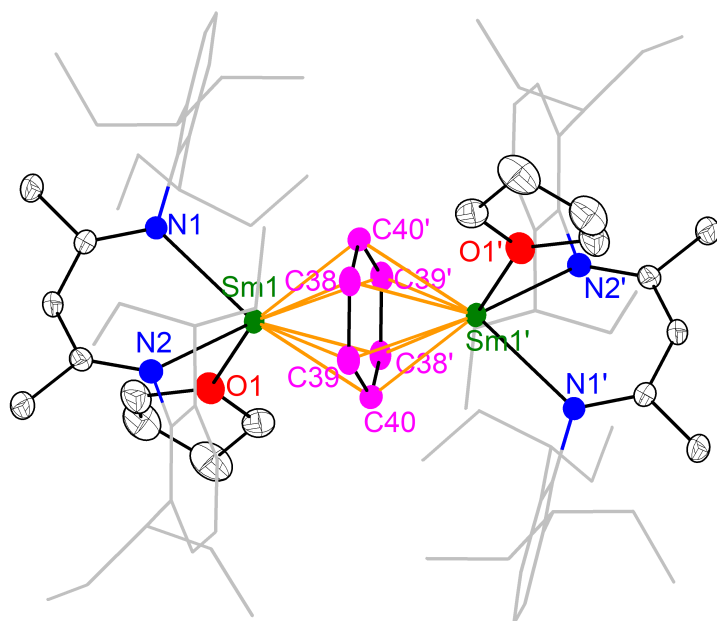


**Fig. S16.** Representation of [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (**2-Y**) with thermal ellipsoids set at 50% probability. Hydrogen atoms were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Both crystallographically independent molecules in an unsymmetric unit were shown. Selected distances (Å) and angles (°): For independent molecule 1: Y1–N1 2.3848(32), Y1–N2 2.3547(49), Y2–N3 2.3913(40), Y2–N4 2.3748(40), Y1–Y2 3.9984(8), Y1–C75 2.4106(54), Y1–C76 2.5190(65), Y1–C77 2.4780(59), Y1–C78 2.4196(49), Y1–C79 2.5339(40), Y1–C80 2.4673(44), Y2–C75 2.5195(48), Y2–C76 2.4138(43), Y2–C77 2.4643(44), Y2–C78 2.5268(56), Y2–C79 2.4106(61), Y2–C80 2.4645(59), Y1–R<sub>cent</sub> 2.0022(6), Y2–R<sub>cent</sub> 1.9962(6), C75–C76 1.4635(77), C76–C77 1.4364(79), C77–C78 1.4493(72), C78–C79 1.4647(73), C79–C80 1.4524(78), C80–C75 1.4440(69), N1–Y1–N2 76.330(151), N3–Y2–N4 75.207(143), Y1–R<sub>cent</sub>–Y2 179.585(25). Torsion angles: C77–C78/C79–C80 –13.1(8), C75–C76/C78–C79 10.8(5). For independent molecule 2: Y3–N5 2.3715(33), Y3–N6 2.3859(43), Y4–N7 2.3909(33), Y4–N8 2.3681(33), Y3–Y4 3.9997(6), Y3–C155 2.4020(48), Y3–C156 2.4537(57), Y3–C157 2.5247(59), Y3–C158 2.4027(47), Y3–C159 2.4543(47), Y3–C160 2.5221(43), Y4–C155 2.4987(47), Y4–C156 2.4481(60), Y4–C157 2.3928(44), Y4–C158 2.5108(48), Y4–C159 2.4769(57), Y4–C160 2.4161(57), Y3–R<sub>cent</sub> 2.0017(4), Y4–R<sub>cent</sub> 1.9982(4), C155–C156 1.4247(117), C156–C157 1.4467(94), C157–C158 1.4480(95), C158–C159 1.4057(104), C159–C160 1.4312(92), C160–C155 1.4415(94), N5–Y3–N6 74.948(135), N7–Y4–N8 75.688(129), Y3–R<sub>cent</sub>–Y4 178.907(21). Torsion angles: C156–C157/C158–C159 12.7(9), C157–C158/C160–C155 –10.9(5).

Single crystals suitable for X-ray crystallography were grown from a *n*-pentane solution at –35 °C. A total of 189297 reflections ( $-38 \leq h \leq 40$ ,  $-30 \leq k \leq 27$ ,  $-34 \leq l \leq 35$ ) were collected at  $T = 179.99(10)$  K with  $2\theta_{\max} = 59.1^\circ$ , of which 38188 were unique. The residual peak and hole electron density were 1.99 and  $-1.23$  eÅ<sup>-3</sup>. The least-squares refinement converged normally with residuals of  $R_1 = 0.0833$  and  $\text{GOF} = 1.033$ . Crystal and refinement data for **2-Y**: formula C<sub>80</sub>H<sub>120</sub>N<sub>4</sub>Y<sub>2</sub>, space group  $P2_1/c$ ,  $a = 28.8724(5)$  Å,  $b = 21.9655(2)$  Å,  $c = 25.9782(4)$  Å,  $\beta = 116.683(2)^\circ$ ,  $V = 14720.7(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $\mu = 1.613$  mm<sup>-1</sup>,  $F(000) = 5648.0$ ,  $R_1 = 0.1634$  and  $wR_2 = 0.1870$  (based on all data).



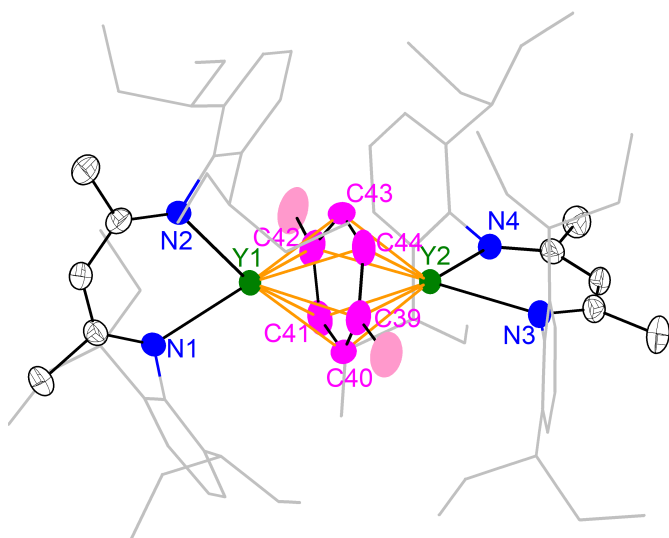
**[(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (2-Sm)**



**Fig. S17.** Representation of [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>) (**2-Sm**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and disordered counterpart (THF) were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances (Å) and angles (°): Sm1–N1 2.5099(15), Sm1–N2 2.5096(18), Sm1–Sm1' 4.1906(4), Sm1–C38 2.5590(15), Sm1–C39 2.4927(13), Sm1–C40 2.6025(17), Sm1–C38' 2.5335(19), Sm1–C39' 2.5979(22), Sm1–C40' 2.6025(17), Sm1–R<sub>cent</sub> 2.0953(3), C38–C39 1.4533(34), C39–C40 1.4501(27), C40–C38' 1.4547(28), N1–Sm1–N2 76.436(47), Sm1–R<sub>cent</sub>–Sm1' 180.000(11). Torsion angles: C40'–C38/C39–C40 12.8(3), C38–C39/C38'–C39' 0(2).

Single crystals suitable for X-ray crystallography were grown from a *n*-pentane solution containing a few drops of THF at –35 °C. A total of 27011 reflections ( $-10 \leq h \leq 17$ ,  $-18 \leq k \leq 16$ ,  $-21 \leq l \leq 20$ ) were collected at  $T = 179.99(10)$  K with  $2\theta_{\max} = 59.192^\circ$ , of which 10250 were unique. The residual peak and hole electron density were 0.64 and  $-0.43$  eÅ<sup>-3</sup>. The least-squares refinement converged normally with residuals of  $R_1 = 0.0219$  and  $\text{GOF} = 1.055$ . Crystal and refinement data for **2-Sm**: formula C<sub>88</sub>H<sub>136</sub>N<sub>4</sub>O<sub>2</sub>Sm<sub>2</sub>, space group *P*-1,  $a = 12.8287(2)$  Å,  $b = 13.2492(2)$  Å,  $c = 15.2084(2)$  Å,  $\alpha = 110.2990(10)^\circ$ ,  $\beta = 94.3910(10)^\circ$ ,  $\gamma = 118.829(2)^\circ$ ,  $V = 2028.26(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu = 1.481$  mm<sup>-1</sup>,  $F(000) = 832.0$ ,  $R_1 = 0.0246$  and  $wR_2 = 0.0558$  (based on all data).

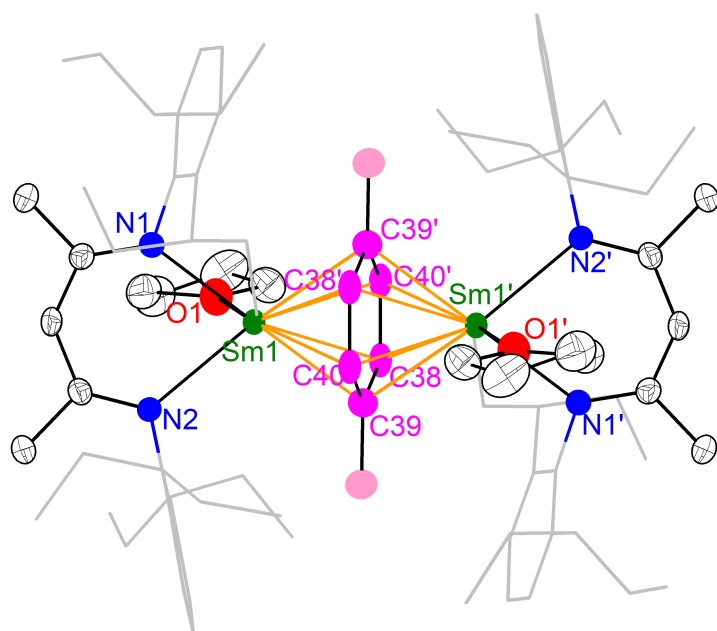
**[(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (3-Y)**



**Fig. S18.** Representation of [(BDI)Y]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (**3-Y**) with thermal ellipsoids set at 50% probability. Hydrogen atoms were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances (Å) and angles (°): Y1–N1 2.3776(25), Y1–N2 2.3919(26), Y2–N3 2.4083(28), Y2–N4 2.4137(25), Y1–Y2 4.0210(7), Y1–C39 2.4128(34), Y1–C40 2.5141(36), Y1–C41 2.4984(33), Y1–C42 2.3934(33), Y1–C43 2.5003(38), Y1–C44 2.5007(40), Y2–C39 2.5950(32), Y2–C40 2.4361(37), Y2–C41 2.4410(39), Y2–C42 2.5696(36), Y2–C43 2.4318(37), Y2–C44 2.4537(34), Y1–R<sub>cent</sub> 1.9993(5), Y2–R<sub>cent</sub> 2.0220(5), C39–C40 1.4388(52), C40–C41 1.4584(53), C41–C42 1.4662(55), C42–C43 1.4619(55), C43–C44 1.4451(62), C44–C39 1.4572(56), N1–Y1–N2 77.009(86), N3–Y2–N4 76.222(88), Y1–R<sub>cent</sub>–Y2 178.704(18). Torsion angles: C44–C39/C40–C41 –14.2(6), C42–C43/C39–C40 12.4(3).

Single crystals suitable for X-ray crystallography were grown from a *n*-pentane solution at –35 °C. A total of 44814 reflections ( $-30 \leq h \leq 21$ ,  $-15 \leq k \leq 18$ ,  $-32 \leq l \leq 35$ ) were collected at  $T = 180.00$  K with  $2\theta_{\max} = 59.032^\circ$ , of which 18550 were unique. The residual peak and hole electron density were 1.43 and  $-0.88$  eÅ<sup>-3</sup>. The least-squares refinement converged normally with residuals of  $R_1 = 0.0565$  and  $\text{GOF} = 1.047$ . Crystal and refinement data for **3-Y**: formula C<sub>82</sub>H<sub>124</sub>N<sub>4</sub>Y<sub>2</sub>, space group  $P2_1/c$ ,  $a = 22.0209(6)$  Å,  $b = 13.3172(3)$  Å,  $c = 25.7853(6)$  Å,  $\beta = 96.038(3)^\circ$ ,  $V = 7519.8(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 1.580$  mm<sup>-1</sup>,  $F(000) = 2888.0$ ,  $R_1 = 0.0895$  and  $wR_2 = 0.1649$  (based on all data).

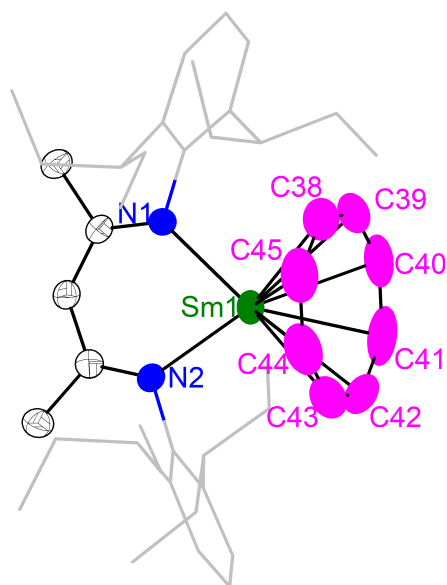
**[(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (**3-Sm**)**



**Fig. S19.** Representation of [(BDI)Sm(THF)]<sub>2</sub>(μ-η<sup>6</sup>,η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (**3-Sm**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and disordered counterpart (THF) were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances (Å) and angles (°): Sm1–N1 2.5242(17), Sm1–N2 2.5406(18), Sm1–Sm1' 4.2182(5), Sm1–C38 2.5799(20), Sm1–C39 2.5440(23), Sm1–C40 2.5770(31), Sm1–C38' 2.5262(31), Sm1–C39' 2.5978(26), Sm1–C40' 2.5945(22), Sm1–R<sub>cent</sub> 2.1091(3), C38–C39 1.4499(42), C39–C40 1.4825(43), C40–C38' 1.4752(27), N1–Sm1–N2 75.915(65), Sm1–R<sub>cent</sub>–Sm1' 180.000. Torsion angles: C40–C38'/C39'–C40' 5.1(4), C38–C39/C38'–C39' 0(3).

Single crystals suitable for X-ray crystallography were grown from a *n*-pentane solution containing a few drops of THF at –35 °C. A total of 26322 reflections ( $-17 \leq h \leq 16$ ,  $-18 \leq k \leq 14$ ,  $-21 \leq l \leq 20$ ) were collected at  $T = 179.99(10)$  K with  $2\theta_{\max} = 58.7^\circ$ , of which 10253 were unique. The residual peak and hole electron density were 1.06 and  $-0.75 \text{ e}\text{\AA}^{-3}$ . The least-squares refinement converged normally with residuals of  $R_1 = 0.0304$  and  $\text{GOF} = 1.082$ . Crystal and refinement data for **3-Sm**: formula C<sub>90</sub>H<sub>140</sub>N<sub>4</sub>O<sub>2</sub>Sm<sub>2</sub>, space group *P*–1,  $a = 12.7862(7)$  Å,  $b = 13.2072(6)$  Å,  $c = 15.4523(6)$  Å,  $\alpha = 64.913(4)^\circ$ ,  $\beta = 70.485(4)^\circ$ ,  $\gamma = 61.214(5)^\circ$ ,  $V = 2043.3(2)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu = 1.471 \text{ mm}^{-1}$ ,  $F(000) = 848.0$ ,  $R_1 = 0.0381$  and  $wR_2 = 0.0775$  (based on all data).

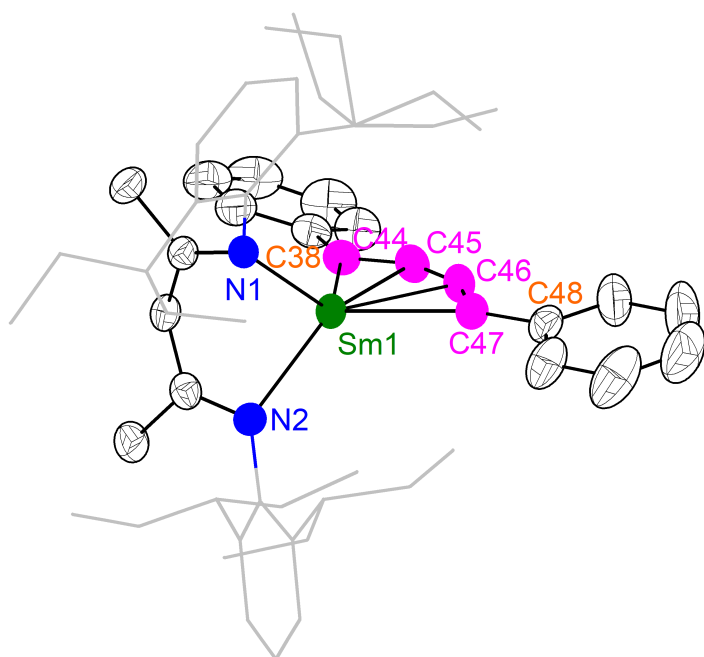
**(BDI)Sm( $\eta^8$ -COT) (4-Sm)**



**Fig. S20.** Representation of (BDI)Sm( $\eta^8$ -COT) (**4-Sm**) with thermal ellipsoids set at 50% probability. Hydrogen atoms were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Sm1–N1 2.4606(20), Sm1–N2 2.4280(17), Sm1–C38 2.6342(39), Sm1–C39 2.6366(38), Sm1–C40 2.6239(33), Sm1–C41 2.6207(37), Sm1–C42 2.6332(40), Sm1–C43 2.6274(34), Sm1–C44 2.6257(31), Sm1–C45 2.6271(36), Sm1–R<sub>cent</sub> 1.8948(3), C38–C39 1.3780(52), C39–C40 1.392(7), C40–C41 1.4121(69), C41–C42 1.4289(61), C42–C43 1.4201(65), C43–C44 1.3538(71), C44–C45 1.3862(61), C45–C38 1.3847(51), N1–Sm1–N2 73.408(59).

Single crystals suitable for X-ray crystallography were grown from a Et<sub>2</sub>O solution at  $-35^\circ\text{C}$ . A total of 32606 reflections ( $-19 \leq h \leq 19$ ,  $-20 \leq k \leq 24$ ,  $-21 \leq l \leq 21$ ) were collected at  $T = 180.00\text{ K}$  with  $2\theta_{\text{max}} = 58.992^\circ$ , of which 10231 were unique. The residual peak and hole electron density were 0.89 and  $-0.72\text{ e}\text{\AA}^{-3}$ . The least-squares refinement converged normally with residuals of  $R_1 = 0.0321$  and  $\text{GOF} = 1.055$ . Crystal and refinement data for **4-Sm**: formula C<sub>45</sub>H<sub>65</sub>N<sub>2</sub>Sm, space group  $P2_1/n$ ,  $a = 14.4271(4)\text{ \AA}$ ,  $b = 17.8919(4)\text{ \AA}$ ,  $c = 16.0725(4)\text{ \AA}$ ,  $\beta = 102.800(3)^\circ$ ,  $V = 4045.67(18)\text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 1.483\text{ mm}^{-1}$ ,  $F(000) = 1644.0$ ,  $R_1 = 0.0437$  and  $wR_2 = 0.0838$  (based on all data).

**(BDI)Sm( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>) (5-Sm)**



**Fig. S21.** Representation of (BDI)Sm( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>) (**5-Sm**) with thermal ellipsoids set at 50% probability. Hydrogen atoms were omitted for clarity. Sections of aryl substituents were shown as wireframe for clarity. Selected distances (Å) and angles (°): Sm1–N1 2.3875(22), Sm1–N2 2.3780(23), Sm1–C44 2.4487(26), Sm1–C45 2.4459(26), Sm1–C46 2.4467(27), Sm1–C47 2.4914(30), C44–C45 1.3195(41), C45–C46 1.3097(40), C46–C47 1.3063(41), C38–C44 1.4670(41), C47–C48 1.4761(40), N1–Sm1–N2 84.043(72), C44–C45–C46 148.978(304), C47–C46–C45 150.998(298), C44–Sm1–C47 92.994(103).

Single crystals suitable for X-ray crystallography were grown from a *n*-pentane solution at –35 °C. A total of 31410 reflections ( $-14 \leq h \leq 15$ ,  $-15 \leq k \leq 15$ ,  $-24 \leq l \leq 25$ ) were collected at  $T = 180.00$  K with  $2\theta_{\max} = 61.432^\circ$ , of which 12197 were unique. The residual peak and hole electron density were 1.39 and  $-1.32$  eÅ<sup>-3</sup>. The least-squares refinement converged normally with residuals of  $R_1 = 0.0412$  and  $\text{GOF} = 1.125$ . Crystal and refinement data for **5-Sm**: formula C<sub>53</sub>H<sub>67</sub>N<sub>2</sub>Sm, space group *P*-1,  $a = 10.8737(4)$  Å,  $b = 11.7593(5)$  Å,  $c = 18.5401(8)$  Å,  $\alpha = 98.600(4)^\circ$ ,  $\beta = 93.568(3)^\circ$ ,  $\gamma = 92.844(3)^\circ$ ,  $V = 2335.30(17)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 1.292$  mm<sup>-1</sup>,  $F(000) = 922.0$ ,  $R_1 = 0.0486$  and  $wR_2 = 0.1071$  (based on all data).

**Table. S1.** Selected distances (Å) and angles (°) of **2-Y** and **3-Y**.

|                         | <b>2-Y<sup>a</sup></b> | <b>2-Y<sup>b</sup></b> |                      | <b>3-Y</b> |
|-------------------------|------------------------|------------------------|----------------------|------------|
| Y1(3)–N1(5)             | 2.3848(32)             | 2.3715(33)             | Y1–N1                | 2.3776(25) |
| Y1(3)–N2(6)             | 2.3547(49)             | 2.3859(43)             | Y1–N2                | 2.3919(26) |
| Y2(4)–N3(7)             | 2.3913(40)             | 2.3909(33)             | Y2–N3                | 2.4083(28) |
| Y2(4)–N4(8)             | 2.3748(40)             | 2.3681(33)             | Y2–N4                | 2.4137(25) |
| Y1(3)–Y2(4)             | 3.9984(8)              | 3.9997(6)              | Y1–Y2                | 4.0210(7)  |
| Y1(3)–C75(155)          | 2.4106(54)             | 2.4020(48)             | Y1–C39               | 2.4128(34) |
| Y1(3)–C76(156)          | 2.5190(65)             | 2.4537(57)             | Y1–C40               | 2.5141(36) |
| Y1(3)–C77(157)          | 2.4780(59)             | 2.5247(59)             | Y1–C41               | 2.4984(33) |
| Y1(3)–C78(158)          | 2.4196(49)             | 2.4027(47)             | Y1–C42               | 2.3934(33) |
| Y1(3)–C79(159)          | 2.5339(40)             | 2.4543(47)             | Y1–C43               | 2.5003(38) |
| Y1(3)–C80(160)          | 2.4673(44)             | 2.5221(43)             | Y1–C44               | 2.5007(40) |
| Y2(4)–C75(155)          | 2.5195(48)             | 2.4987(47)             | Y2–C39               | 2.5950(32) |
| Y2(4)–C76(156)          | 2.4138(43)             | 2.4481(60)             | Y2–C40               | 2.4361(37) |
| Y2(4)–C77(157)          | 2.4643(44)             | 2.3928(44)             | Y2–C41               | 2.4410(39) |
| Y2(4)–C78(158)          | 2.5268(56)             | 2.5108(48)             | Y2–C42               | 2.5696(36) |
| Y2(4)–C79(159)          | 2.4106(61)             | 2.4769(57)             | Y2–C43               | 2.4318(37) |
| Y2(4)–C80(160)          | 2.4645(59)             | 2.4161(57)             | Y2–C44               | 2.4537(34) |
| Y1(3)–R <sub>cent</sub> | 2.0022(6)              | 2.0017(4)              | Y1–R <sub>cent</sub> | 1.9993(5)  |
| Y2(4)–R <sub>cent</sub> | 1.9962(6)              | 1.9982(4)              | Y2–R <sub>cent</sub> | 2.0220(5)  |
| C75(155)–C76(156)       | 1.4635(77)             | 1.4247(117)            | C39–C40              | 1.4388(52) |
| C76(156)–C77(157)       | 1.4364(79)             | 1.4467(94)             | C40–C41              | 1.4584(53) |
| C77(157)–C78(158)       | 1.4493(72)             | 1.4480(95)             | C41–C42              | 1.4662(55) |
| C78(158)–C79(159)       | 1.4647(73)             | 1.4057(104)            | C42–C43              | 1.4619(55) |

|                                |                                                                   |                                                                   |                          |                                                                   |
|--------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------|-------------------------------------------------------------------|
| C79(159)–C80(160)              | 1.4524(78)                                                        | 1.4312(92)                                                        | C43–C44                  | 1.4451(62)                                                        |
| C80(160)–C75(155)              | 1.4440(69)                                                        | 1.4415(94)                                                        | C44–C39                  | 1.4572(56)                                                        |
| N1(5)–Y1(3)–N2(6)              | 76.330(151)                                                       | 74.948(135)                                                       | N1–Y1–N2                 | 77.009(86)                                                        |
| N3(7)–Y2(4)–N4(8)              | 75.207(143)                                                       | 75.688(129)                                                       | N3–Y2–N4                 | 76.222(88)                                                        |
| Y1(3)–R <sub>cent</sub> –Y2(4) | 179.585(25)                                                       | 178.907(21)                                                       | Y1–R <sub>cent</sub> –Y2 | 178.704(18)                                                       |
| Torsion angles                 | C77–C78/<br>C79–C80<br>–13.1(8)<br>C75–C76/<br>C78–C79<br>10.8(5) | C44–C39/<br>C40–C41<br>–14.2(6)<br>C42–C43/<br>C39–C40<br>12.4(3) | Torsion angles           | C44–C39/<br>C40–C41<br>–14.2(6)<br>C42–C43/<br>C39–C40<br>12.4(3) |

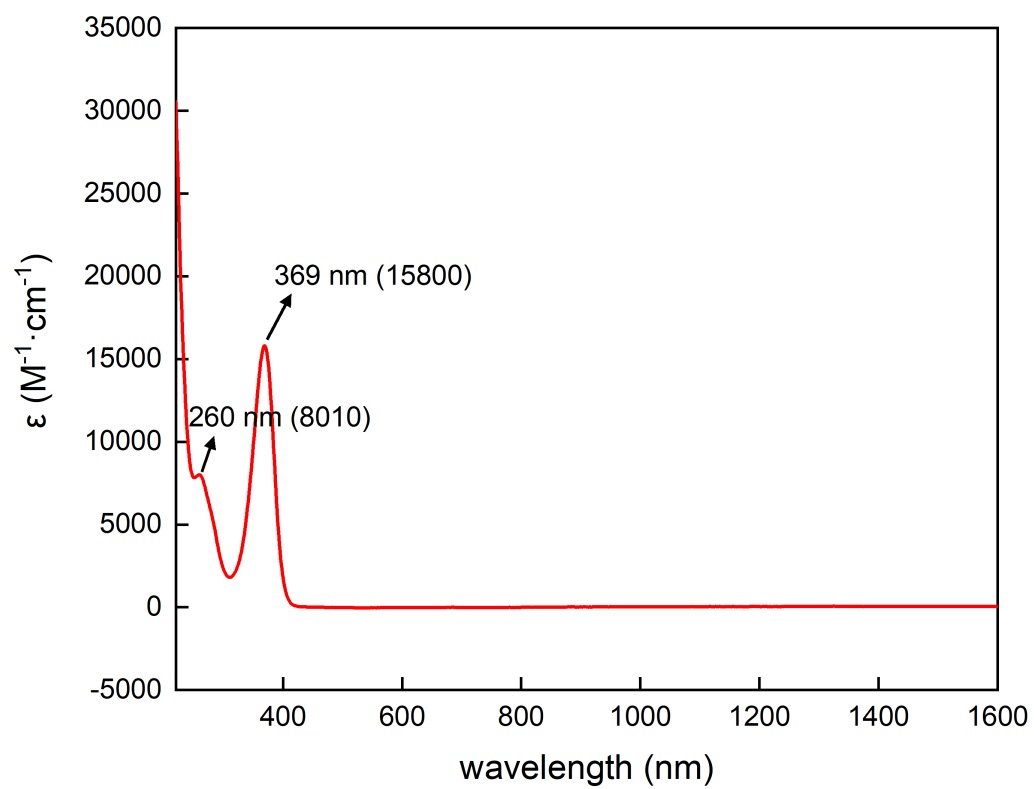
<sup>a</sup> independent molecule 1; <sup>b</sup> independent molecule 2.

**Table. S2.** Selected distances (Å) and angles (°) of **2-Sm** and **3-Sm**.

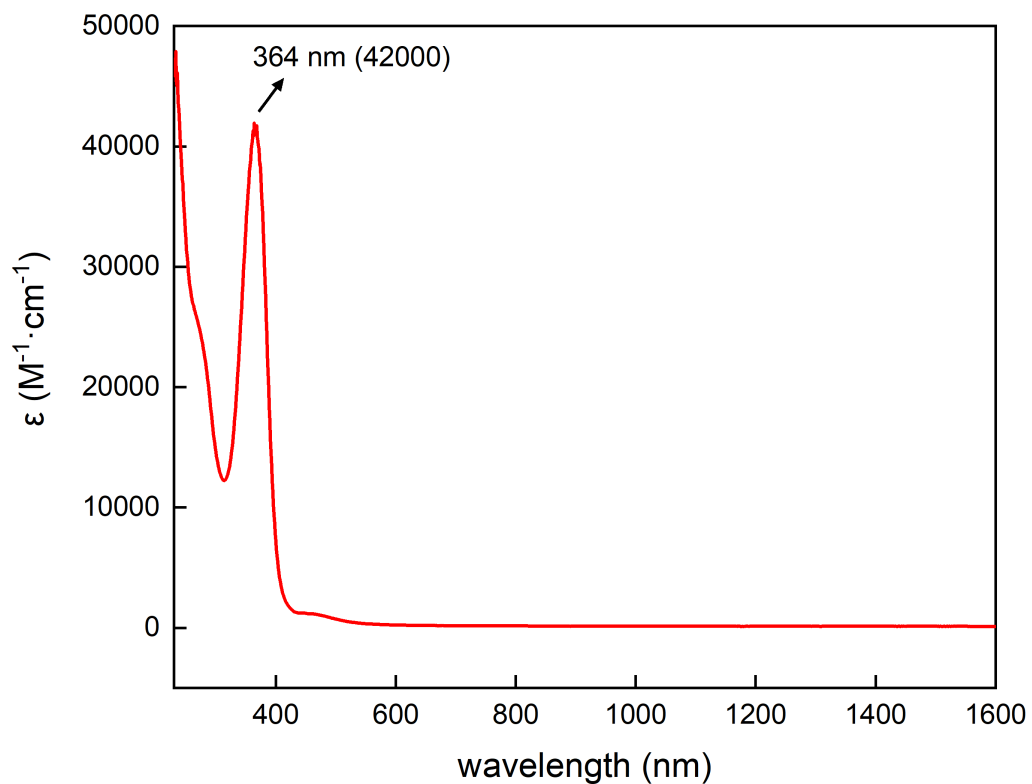
|                             | <b>2-Sm</b>                                              |                             | <b>3-Sm</b>                                               |
|-----------------------------|----------------------------------------------------------|-----------------------------|-----------------------------------------------------------|
| Sm1–N1                      | 2.5099(15)                                               | Sm1–N1                      | 2.5242(17)                                                |
| Sm1–N2                      | 2.5096(18)                                               | Sm1–N2                      | 2.5406(18)                                                |
| Sm1–Sm1'                    | 4.1906(4)                                                | Sm1–Sm1'                    | 4.2182(5)                                                 |
| Sm1–C38                     | 2.5590(15)                                               | Sm1–C38                     | 2.5799(20)                                                |
| Sm1–C39                     | 2.4927(13)                                               | Sm1–C39                     | 2.5440(23)                                                |
| Sm1–C40                     | 2.6025(17)                                               | Sm1–C40                     | 2.5770(31)                                                |
| Sm1–C38'                    | 2.5335(19)                                               | Sm1–C38'                    | 2.5262(31)                                                |
| Sm1–C39'                    | 2.5979(22)                                               | Sm1–C39'                    | 2.5978(26)                                                |
| Sm1–C40'                    | 2.6025(17)                                               | Sm1–C40'                    | 2.5945(22)                                                |
| Sm1–R <sub>cent</sub>       | 2.0953(3)                                                | Sm1–R <sub>cent</sub>       | 2.1091(3)                                                 |
| C38–C39                     | 1.4533(34)                                               | C38–C39                     | 1.4499(42)                                                |
| C39–C40                     | 1.4501(27)                                               | C39–C40                     | 1.4825(43)                                                |
| C40–C38'                    | 1.4547(28)                                               | C40–C38'                    | 1.4752(27)                                                |
| N1–Sm1–N2                   | 76.436(47)                                               | N1–Sm1–N2                   | 75.915(65)                                                |
| Sm1–R <sub>cent</sub> –Sm1' | 180.000(11)                                              | Sm1–R <sub>cent</sub> –Sm1' | 180.000                                                   |
| Torsion angles              | C40'–C38/C39–C40<br>12.8(3)<br>C38–C39/C38'–C39'<br>0(2) | Torsion angles              | C40–C38'/C39'–C40'<br>5.1(4)<br>C38–C39/C38'–C39'<br>0(3) |



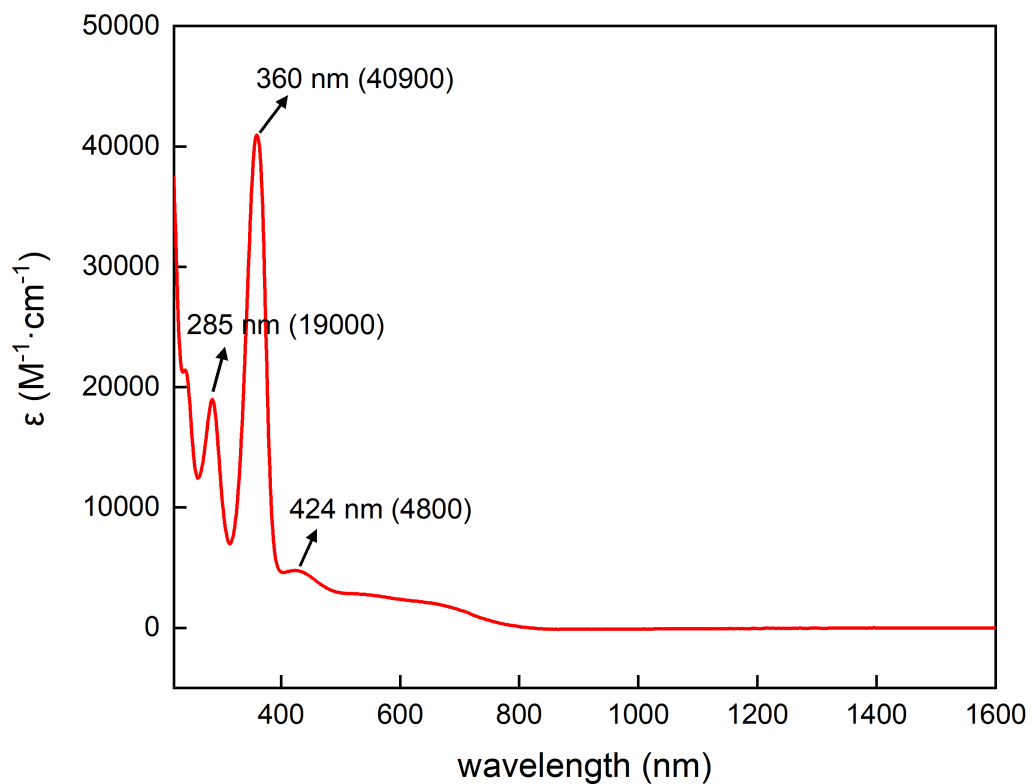
## S4. UV–Vis–NIR Spectra



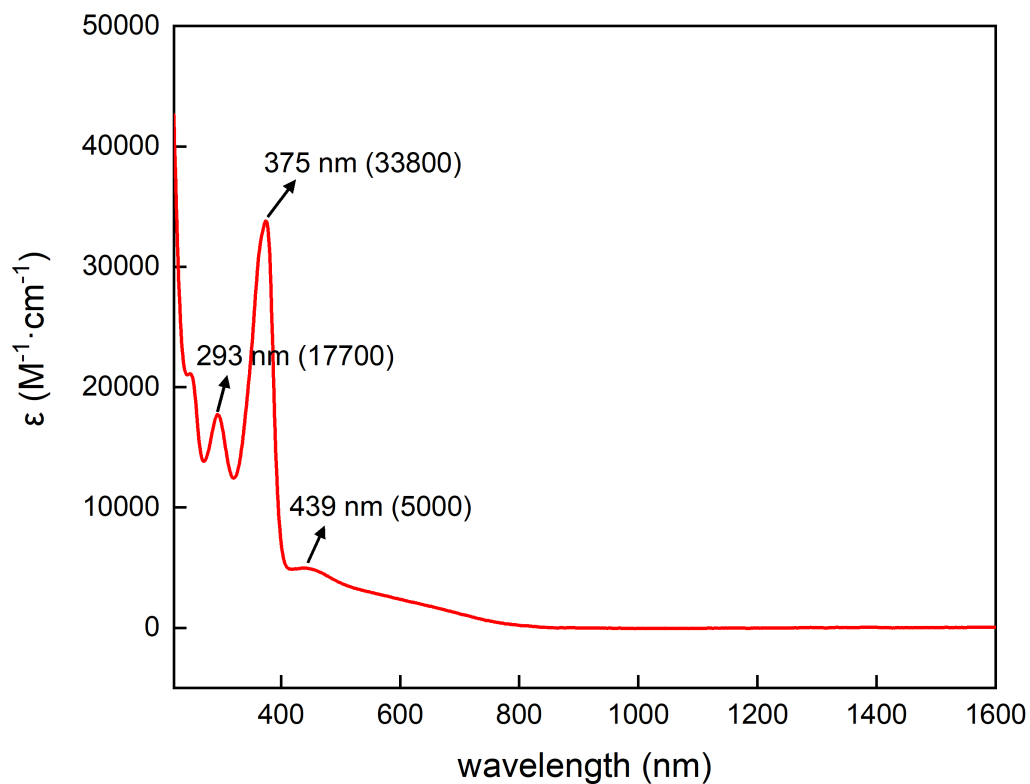
**Fig. S22.** UV–Vis–NIR spectrum (220–1600 nm) of (BDI)YI<sub>2</sub>(THF) (**1-Y**) (298 K, 1.0 mM in Et<sub>2</sub>O).  $\lambda_{\text{max}}$  / nm ( $\epsilon$  / M<sup>-1</sup>·cm<sup>-1</sup>): 260 (8010), 369 (15800).



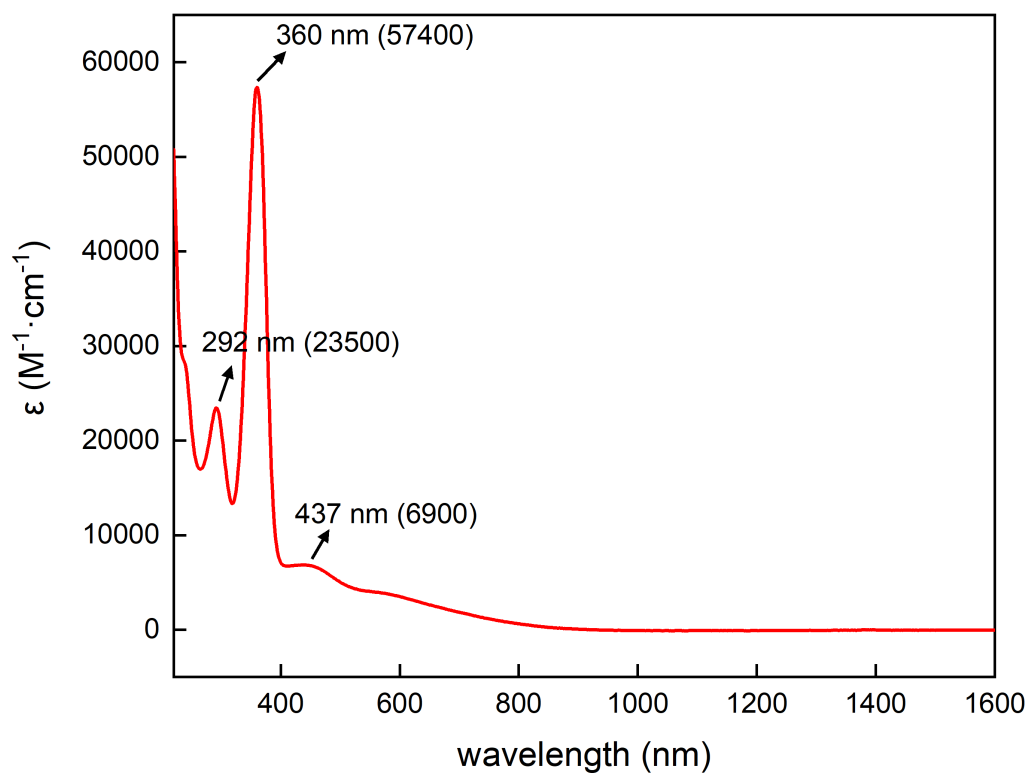
**Fig. S23.** UV-Vis-NIR spectrum (230–1600 nm) of (BDI)SmI<sub>2</sub>(THF) (**1-Sm**) (298 K, 1.0 mM in Et<sub>2</sub>O).  $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{M}^{-1}\cdot\text{cm}^{-1}$ ): 364 (42000), 437–487 (1230–900).



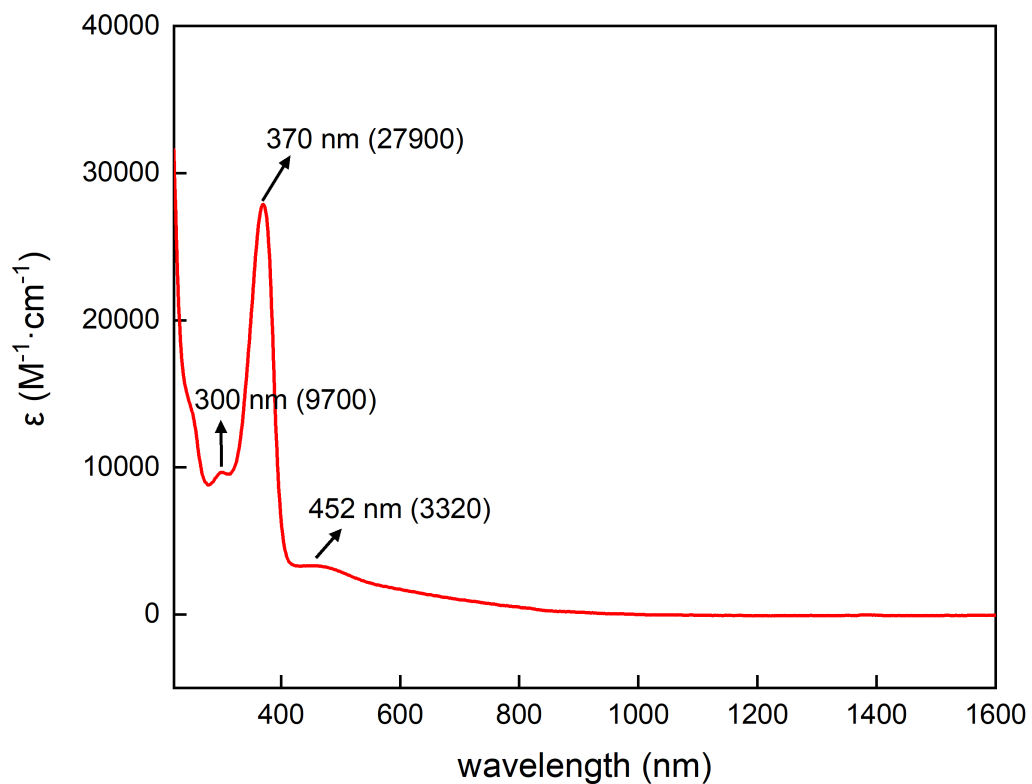
**Fig. S24.** UV–Vis–NIR spectrum (220–1600 nm) of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_6\text{H}_6)$  (**2-Y**) (298 K, 0.5 mM in *n*-pentane).  $\lambda_{\text{max}} / \text{nm}$  ( $\epsilon / \text{M}^{-1}\cdot\text{cm}^{-1}$ ): 285 (19000), 360 (40900), 424 (4800), 500–726 (2920–1000).



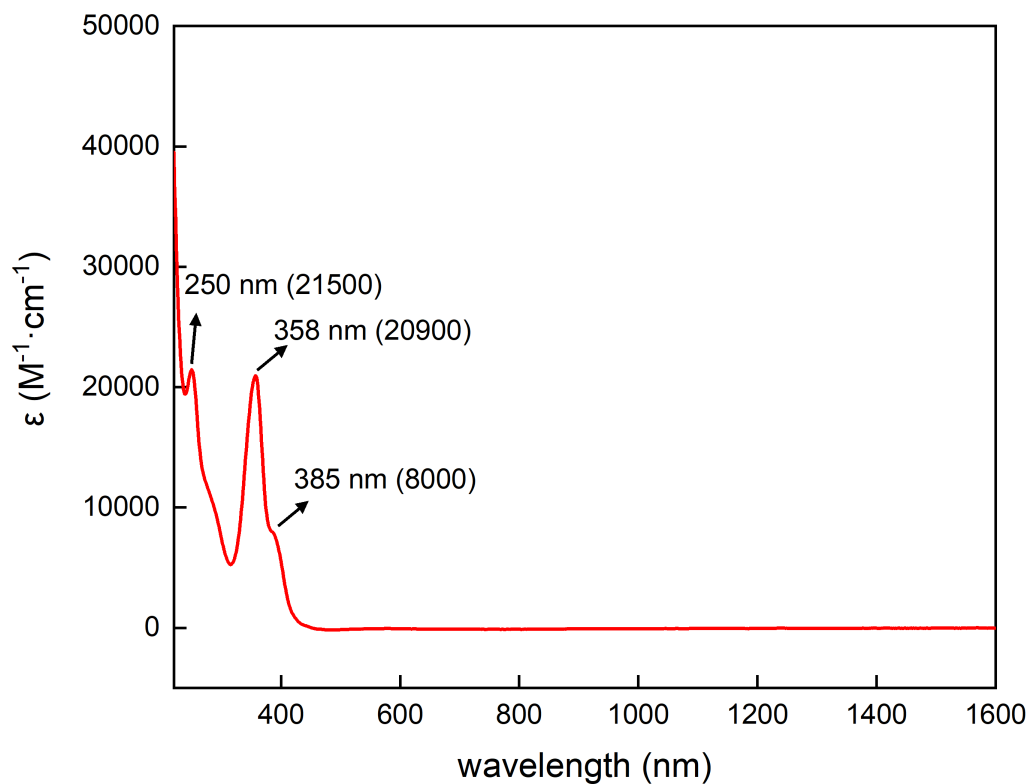
**Fig. S25.** UV–Vis–NIR spectrum (220–1600 nm) of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_6\text{H}_6)$  (**2-Sm**) (298 K, 0.5 mM in *n*-pentane).  $\lambda_{\text{max}} / \text{nm}$  ( $\epsilon / \text{M}^{-1}\cdot\text{cm}^{-1}$ ): 293 (17700), 375 (33800), 439 (5000), 523–651 (3300–1800).



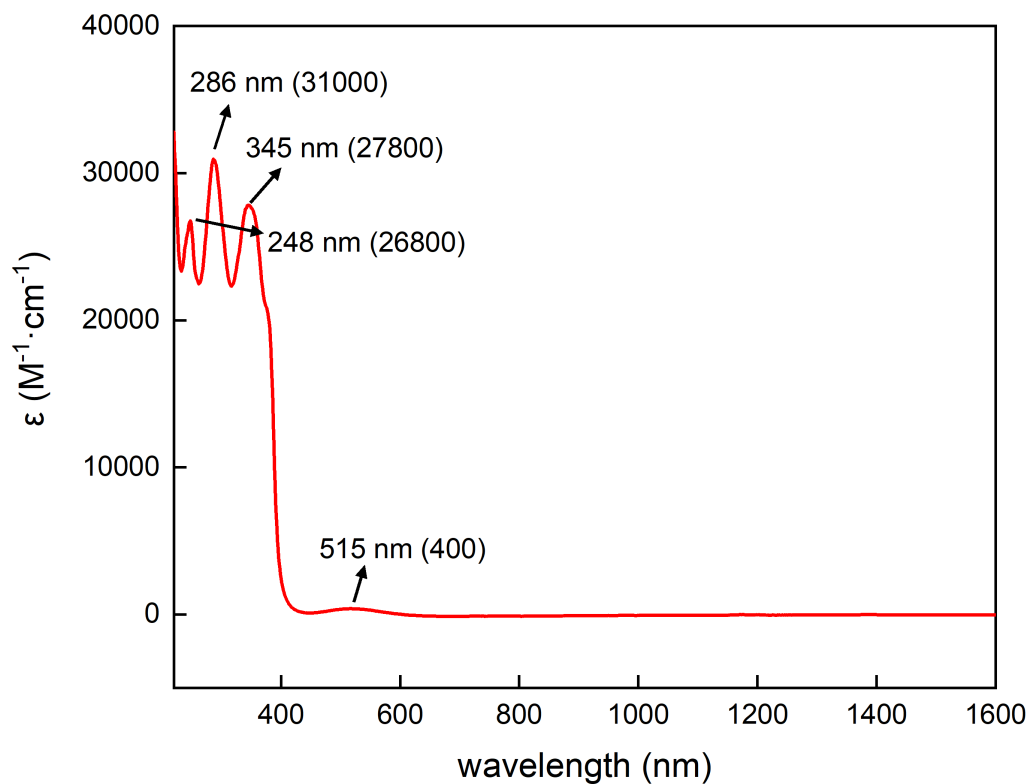
**Fig. S26.** UV–Vis–NIR spectrum (220–1600 nm) of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6,\eta^6\text{-C}_8\text{H}_{10})$  (**3-Y**) (298 K, 0.5 mM in *n*-pentane).  $\lambda_{\text{max}} / \text{nm}$  ( $\epsilon / \text{M}^{-1}\cdot\text{cm}^{-1}$ ): 292 (23500), 360 (57400), 437 (6900), 543–690 (4100–2000).



**Fig. S27.** UV-Vis-NIR spectrum (220–1600 nm) of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$  (**3-Sm**) (298 K, 0.5 mM in *n*-pentane).  $\lambda_{\text{max}} / \text{nm}$  ( $\epsilon / \text{M}^{-1}\cdot\text{cm}^{-1}$ ): 300 (9700), 370 (27900), 452 (3320), 545–705 (2180–1000).



**Fig. S28.** UV-Vis-NIR spectrum (220–1600 nm) of (BDI)Sm(η<sup>8</sup>-COT) (**4-Sm**) (298 K, 1.0 mM in *n*-pentane).  $\lambda_{\text{max}} / \text{nm}$  ( $\epsilon / \text{M}^{-1} \cdot \text{cm}^{-1}$ ): 250 (21500), 358 (20900), 385 (8000).

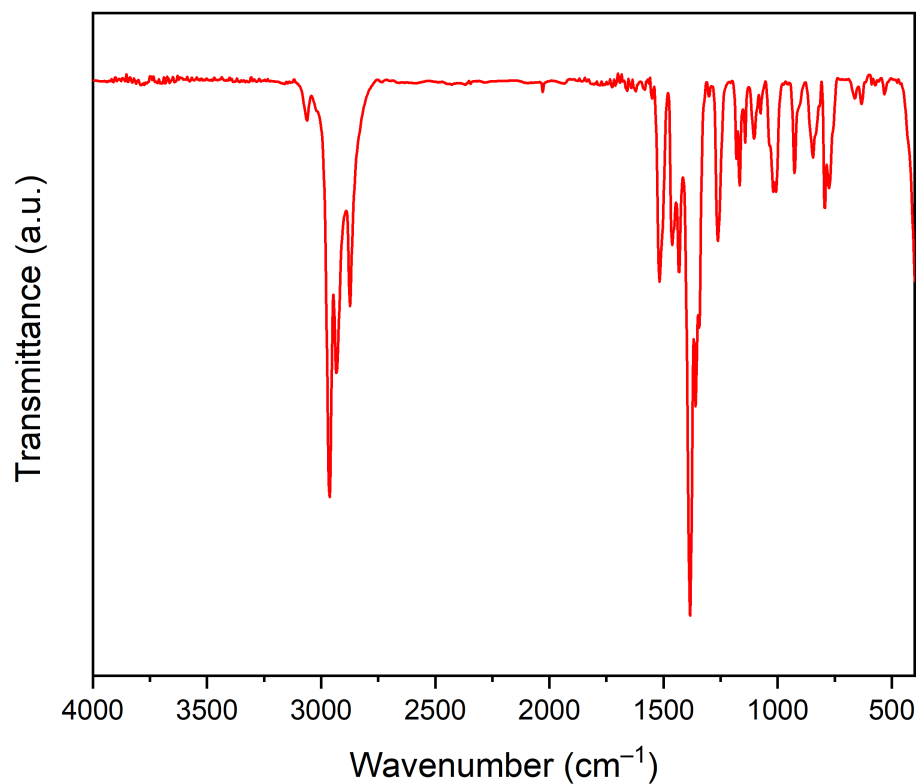


**Fig. S29.** UV–Vis–NIR spectrum (220–1600 nm) of (BDI)Sm( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>) (**5-Sm**) (298 K, 1.0 mM in *n*-pentane).  $\lambda_{\text{max}}$  / nm ( $\epsilon$  / M<sup>-1</sup>·cm<sup>-1</sup>): 248 (26800), 286 (31000), 345 (27800), 515 (400).

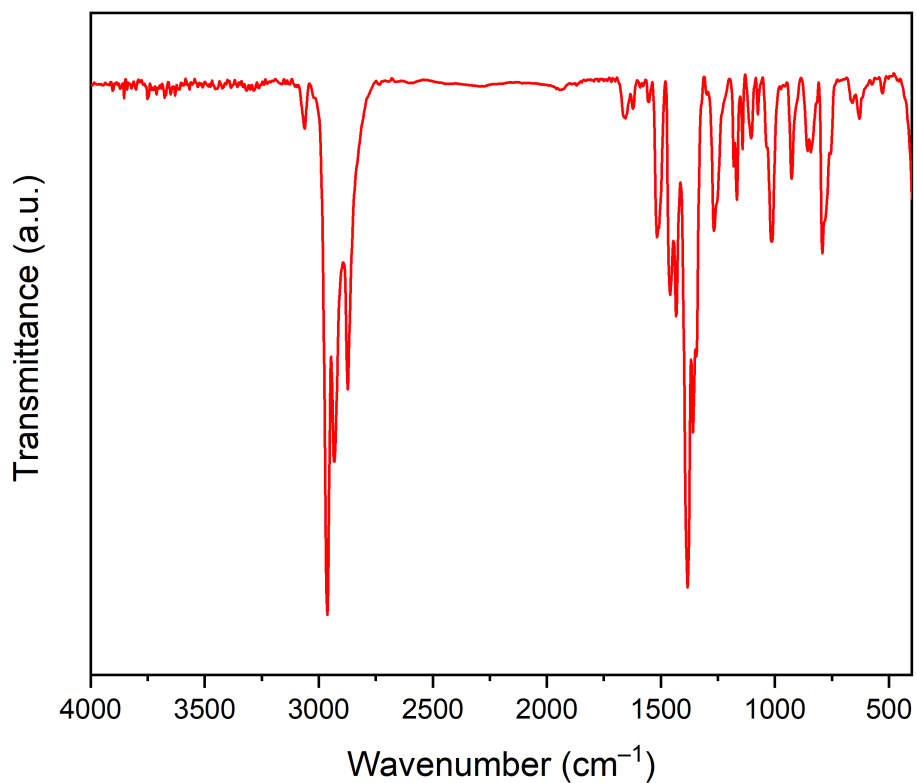


## S5. IR Spectra

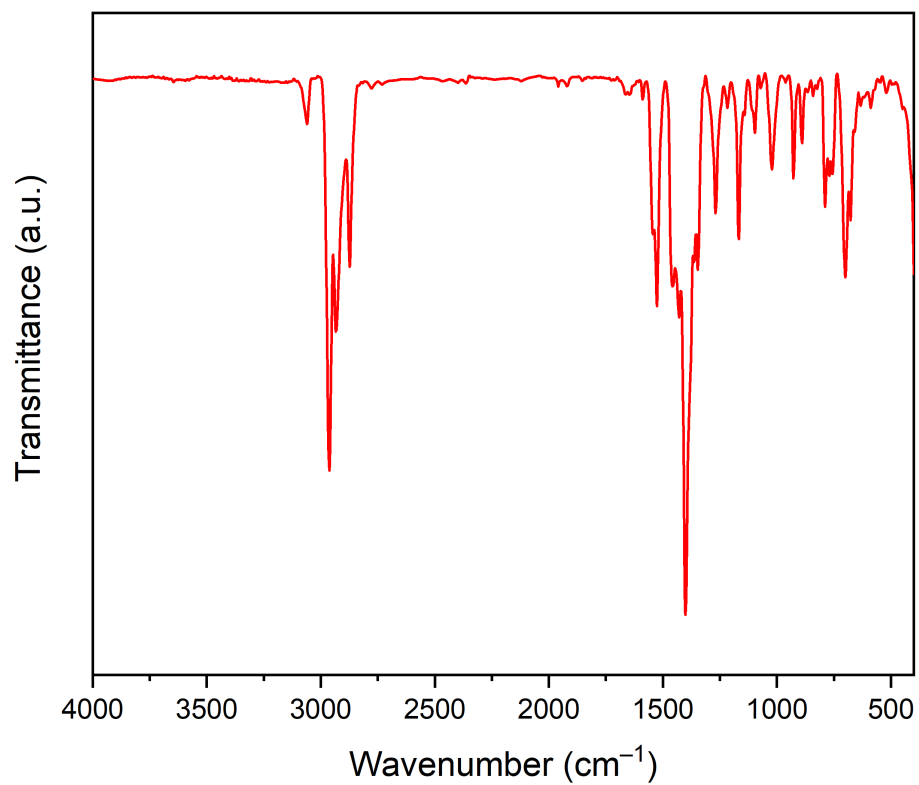
All IR spectra were recorded in the range of 4000–400  $\text{cm}^{-1}$ .



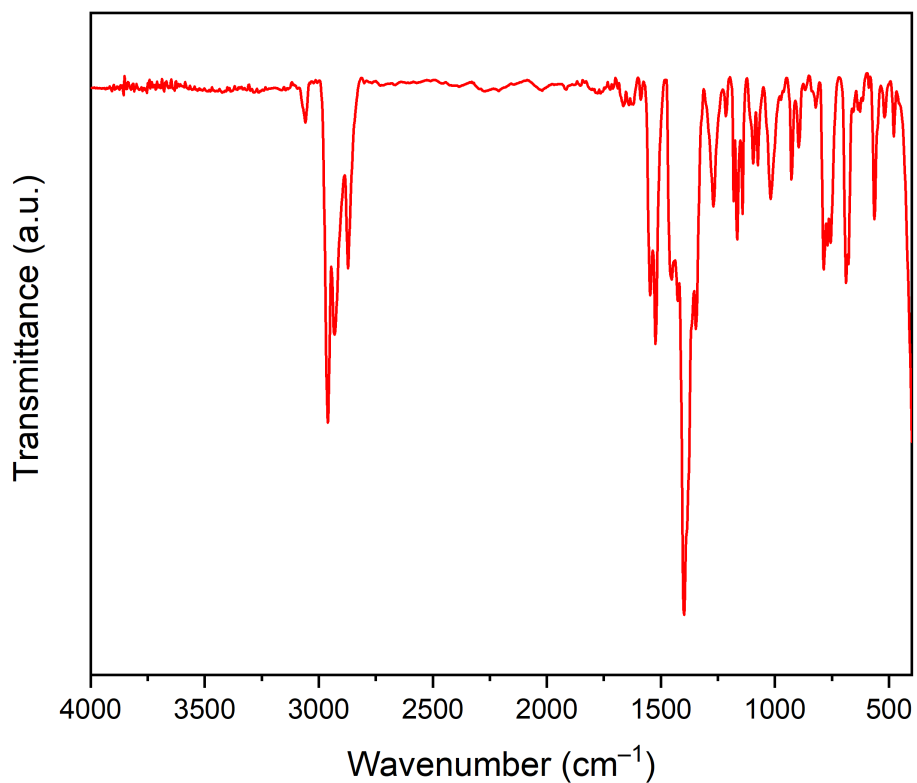
**Fig. S30.** IR spectrum of (BDI)YI<sub>2</sub>(THF) (**1-Y**) in KBr,  $\tilde{\nu}$  /  $\text{cm}^{-1}$ : 774 (w), 794 (w), 845 (w), 926 (w), 1019 (m), 1103 (w), 1142 (w), 1167 (w), 1180 (w), 1262 (m), 1359 (m), 1384 (s), 1432 (m), 1462 (m), 1518 (m), 2874 (m), 2933 (m), 2963 (s).



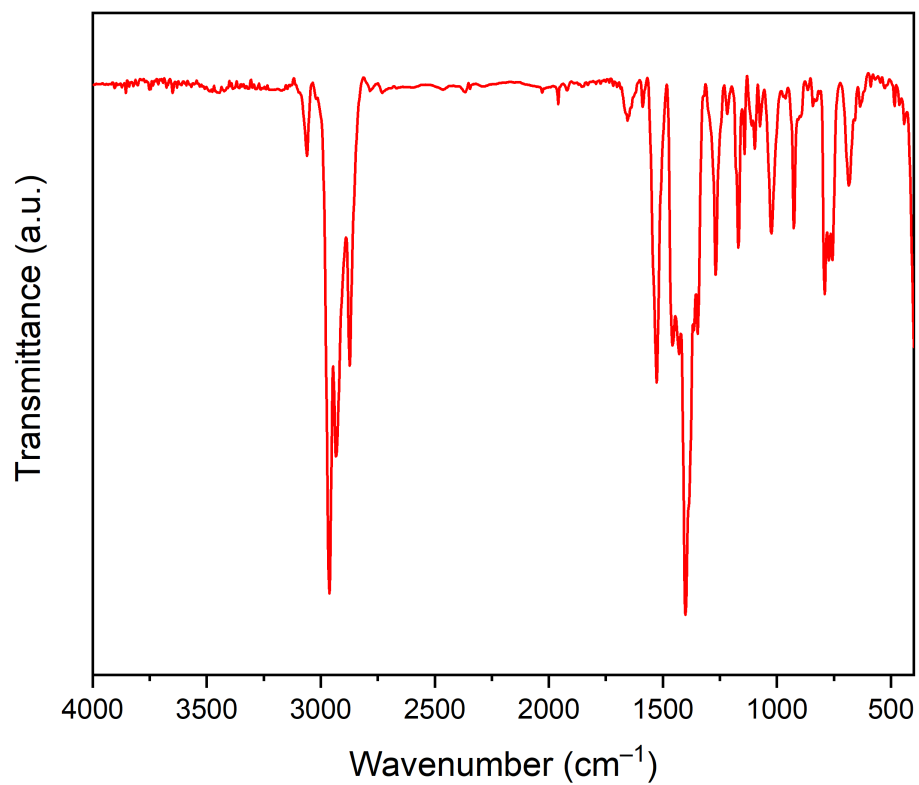
**Fig. S31.** IR spectrum of (BDI)SmI<sub>2</sub>(THF) (**1-Sm**) in KBr,  $\tilde{\nu}$  / cm<sup>-1</sup>: 629 (w), 792 (m), 842 (w), 857 (w), 926 (w), 1014 (m), 1075 (w), 1104 (w), 1142 (w), 1167 (w), 1180 (w), 1267 (m), 1359 (m), 1383 (s), 1433 (m), 1459 (m), 1517 (m), 1533 (w), 1622 (w), 1655 (w), 2873 (m), 2932 (m), 2963 (s), 3062 (w).



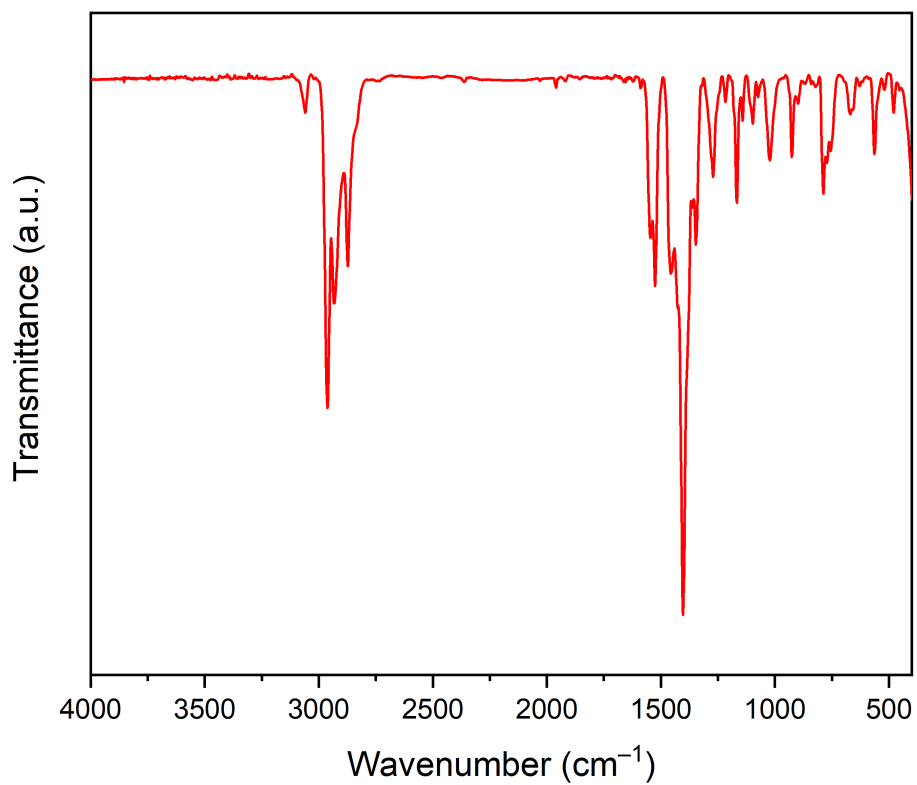
**Fig. S32.** IR spectrum of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6,\eta^6\text{-C}_6\text{H}_6)$  (**2-Y**) in KBr,  $\tilde{\nu} / \text{cm}^{-1}$ : 677 (w), 700 (m), 789 (w), 890 (w), 927 (w), 1022 (m), 1097 (w), 1167 (m), 1268 (m), 1347 (w), 1401 (s), 1429 (w), 1526 (m), 2873 (m), 2933 (m), 2963 (s), 3060 (w).



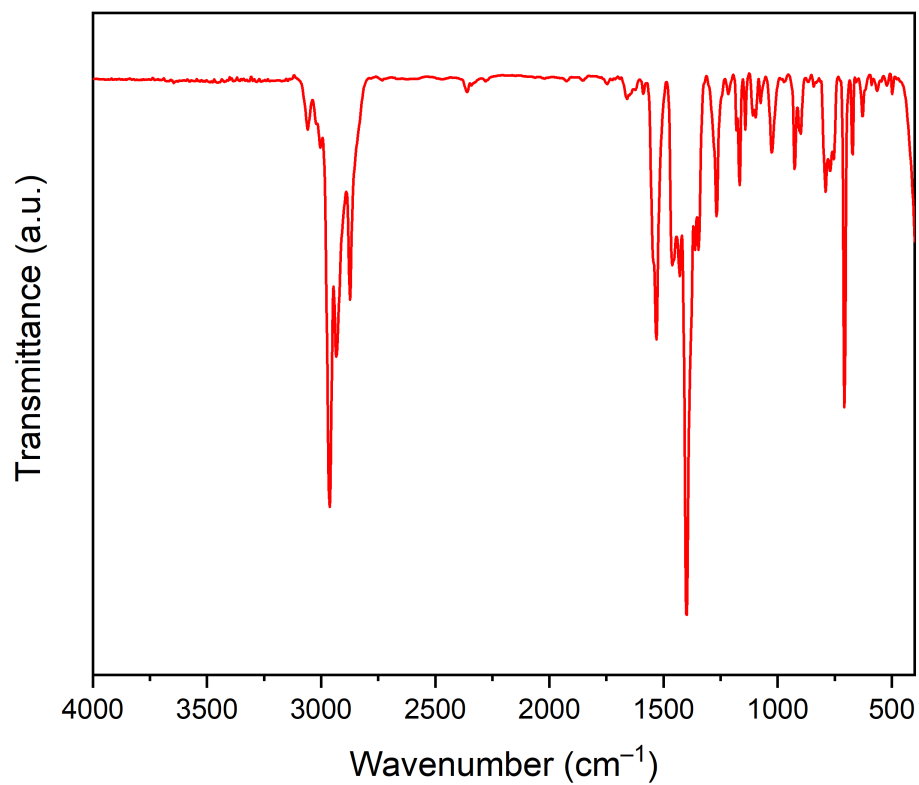
**Fig. S33.** IR spectrum of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_6\text{H}_6)$  (**2-Sm**) in KBr,  $\tilde{\nu} / \text{cm}^{-1}$ : 478 (w), 563 (w), 688 (m), 755 (w), 770 (w), 786 (m), 895 (w), 927 (w), 1018 (m), 1075 (w), 1095 (w), 1142 (w), 1166 (m), 1180 (w), 1269 (m), 1346 (m), 1398 (s), 1453 (m), 1523 (m), 1546 (m), 2872 (m), 2931 (m), 2960 (s), 3059 (w).



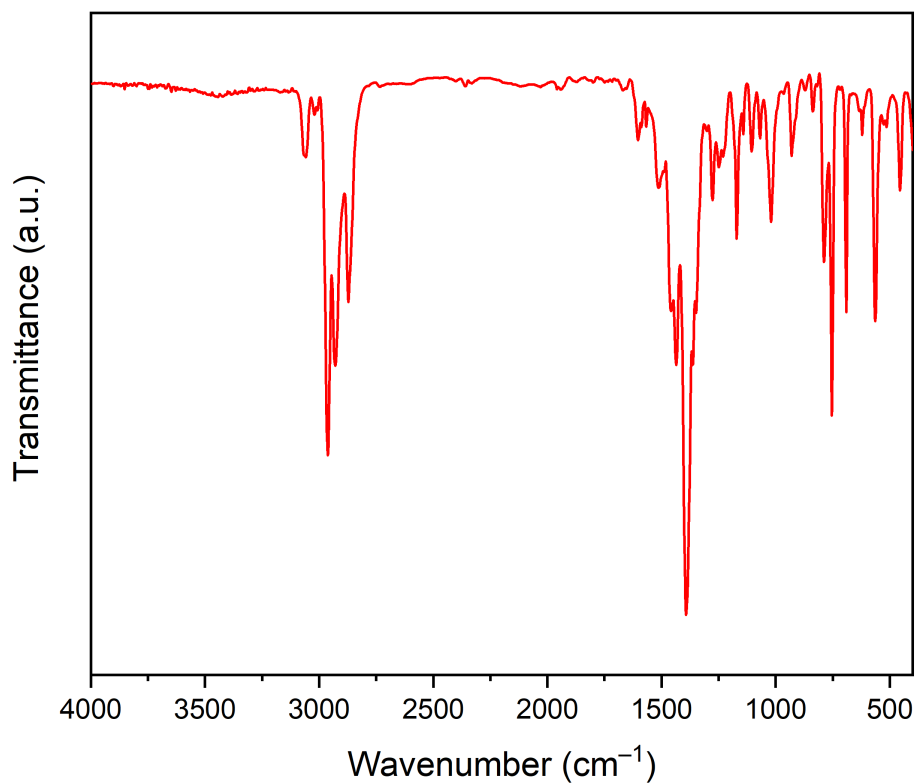
**Fig. S34.** IR spectrum of  $[(\text{BDI})\text{Y}]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$  (**3-Y**) in KBr,  $\tilde{\nu} / \text{cm}^{-1}$ : 684 (w), 757 (m), 772 (w), 791 (m), 925 (m), 1024 (m), 1097 (w), 1142 (w), 1169 (m), 1268 (m), 1347 (m), 1401 (s), 1429 (w), 1457 (m), 1527 (m), 2873 (m), 2933 (m), 2962 (s), 3060 (w).



**Fig. S35.** IR spectrum of  $[(\text{BDI})\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^6, \eta^6\text{-C}_8\text{H}_{10})$  (**3-Sm**) in KBr,  $\tilde{\nu} / \text{cm}^{-1}$ : 479 (w), 563 (788), 670 (w), 788 (m), 925 (w), 1022 (m), 1097 (w), 1141 (w), 1167 (w), 1217 (w), 1271 (m), 1346 (w), 1403 (s), 1456 (m), 1525 (m), 2873 (m), 2933 (m), 2962 (s), 3059 (w).



**Fig. S36.** IR spectrum of (BDI)Sm( $\eta^8$ -COT) (**4-Sm**) in KBr,  $\tilde{\nu}$  /  $\text{cm}^{-1}$ : 628 (w), 672 (w), 707 (m), 790 (m), 899 (w), 925 (w), 1026 (w), 1096 (w), 1142 (w), 1167 (w), 1267 (m), 1346 (w), 1362 (w), 1399 (s), 1429 (w), 1462 (w), 1531 (m), 2873 (m), 2933 (m), 2963 (s), 3029 (w).



**Fig. S37.** IR spectrum of (BDI)Sm( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>) (**5-Sm**) in KBr,  $\tilde{\nu}$  / cm<sup>-1</sup>: 455 (w), 564 (m), 620 (w), 690 (m), 753 (m), 788 (w), 930 (w), 1020 (w), 1069 (w), 1105 (w), 1142 (w), 1170 (w), 1249 (w), 1276 (w), 1392 (s), 1435 (m), 1513 (w), 1603 (w), 2872 (m), 2930 (m), 2962 (s), 3058 (w).



## S6. Density Functional Theory (DFT) Calculations

### S6.1. Computational Details

DFT calculations were performed on the simplified models of neutral inverse-sandwich rare-earth metal complexes **2-M** and **3-M** (M = Y and Sm) by replacing 3-pentyl by methyl. All DFT calculations were performed ORCA v. 5.0.1,<sup>11</sup> with geometry optimization starting from the single crystal structures. The hybrid functional PBE0<sup>12</sup> with dispersion correction (“D3BJ”),<sup>13, 14</sup> was used and scalar relativistic effect was taken into account with the zeroth order regular approximation (ZORA).<sup>15</sup> For metals, segmented all-electron relativistically contracted (SARC) basis sets were chosen.<sup>16, 17</sup> For the bound arenes and other atoms directly bound to metals (N and O), adapted versions of the valence triple-zeta basis sets with polarization functions, def2-TZVP, were applied and for the other light atoms, the valence double-zeta basis sets with polarization functions, def2-SVP, were selected.<sup>18</sup> Single-point energy calculations were then performed with all atoms at triple-zeta level, except for **3-Sm** due to convergence problem (the single-point calculations of **3-Sm** was done with the same level of theory as geometry optimization). The natural bond orbital (NBO) analysis was carried out with NBO 6.0.<sup>19</sup> Representations of the molecular orbitals were rendered by VMD v. 1.9.3,<sup>20</sup> combined with the wave function analysis program Multiwfn.<sup>21</sup>

## S6.2. Comparison between Experimental and Calculated Structures

**Table. S3.** Key structural parameters of **2-Y**.

| Selected distances [Å] and torsion angles [°] | Exp.     | Calc. | Diff.  |
|-----------------------------------------------|----------|-------|--------|
| Y1–N1                                         | 2.385(5) | 2.332 | –0.053 |
| Y1–N2                                         | 2.355(5) | 2.367 | 0.012  |
| Y2–N3                                         | 2.391(4) | 2.340 | –0.051 |
| Y3–N4                                         | 2.375(4) | 2.366 | –0.009 |
| Y1–C1                                         | 2.411(5) | 2.392 | –0.019 |
| Y1–C2                                         | 2.519(6) | 2.524 | 0.005  |
| Y1–C3                                         | 2.478(6) | 2.450 | –0.028 |
| Y1–C4                                         | 2.420(5) | 2.377 | –0.043 |
| Y1–C5                                         | 2.534(4) | 2.514 | –0.020 |
| Y1–C6                                         | 2.467(4) | 2.443 | –0.024 |
| Y2–C1                                         | 2.520(5) | 2.521 | 0.001  |
| Y2–C2                                         | 2.414(4) | 2.394 | –0.020 |
| Y2–C3                                         | 2.464(4) | 2.450 | –0.014 |
| Y2–C4                                         | 2.527(6) | 2.513 | –0.014 |
| Y2–C5                                         | 2.411(6) | 2.367 | –0.044 |
| Y2–C6                                         | 2.465(6) | 2.443 | –0.022 |
| Y1–C <sub>cent</sub>                          | 1.996(1) | 1.966 | –0.030 |
| Y2–C <sub>cent</sub>                          | 2.002(1) | 1.964 | –0.038 |
| C1–C2                                         | 1.464(8) | 1.464 | 0      |
| C2–C3                                         | 1.436(8) | 1.467 | 0.031  |
| C3–C4                                         | 1.449(7) | 1.465 | 0.016  |
| C4–C5                                         | 1.465(7) | 1.465 | 0      |
| C5–C6                                         | 1.452(8) | 1.467 | 0.015  |
| C1–C6                                         | 1.444(7) | 1.466 | 0.022  |
| Avg. C–C (the bound ring)                     | 1.452(8) | 1.466 | 0.014  |
| C3–C4/C5–C6                                   | –13.1(8) | –15.9 | –2.8   |
| C1–C2/C4–C5                                   | 10.8(5)  | 14.0  | 3.2    |

**Table. S4.** Key structural parameters of **3-Y**.

| Selected distances [Å] and torsion angles [°] | Exp.     | Calc. | Diff.  |
|-----------------------------------------------|----------|-------|--------|
| Y1–N1                                         | 2.378(2) | 2.351 | –0.027 |
| Y1–N2                                         | 2.392(3) | 2.360 | –0.032 |
| Y2–N3                                         | 2.408(3) | 2.392 | –0.016 |
| Y3–N4                                         | 2.414(3) | 2.388 | –0.026 |
| Y1–C1                                         | 2.413(3) | 2.382 | –0.031 |
| Y1–C2                                         | 2.514(4) | 2.523 | 0.009  |
| Y1–C3                                         | 2.498(3) | 2.453 | –0.045 |
| Y1–C4                                         | 2.393(3) | 2.373 | –0.020 |
| Y1–C5                                         | 2.500(4) | 2.526 | 0.026  |
| Y1–C6                                         | 2.501(4) | 2.463 | –0.038 |
| Y2–C1                                         | 2.595(3) | 2.572 | –0.023 |
| Y2–C2                                         | 2.436(4) | 2.398 | –0.038 |
| Y2–C3                                         | 2.441(4) | 2.450 | 0.009  |
| Y2–C4                                         | 2.570(4) | 2.568 | –0.002 |
| Y2–C5                                         | 2.432(4) | 2.394 | –0.038 |
| Y2–C6                                         | 2.454(3) | 2.451 | –0.003 |
| Y1–C <sub>cent</sub>                          | 1.999(1) | 1.971 | –0.028 |
| Y2–C <sub>cent</sub>                          | 2.022(1) | 1.995 | –0.027 |
| C1–C2                                         | 1.439(5) | 1.466 | 0.027  |
| C2–C3                                         | 1.458(5) | 1.471 | 0.013  |
| C3–C4                                         | 1.466(5) | 1.465 | –0.001 |
| C4–C5                                         | 1.462(6) | 1.467 | 0.005  |
| C5–C6                                         | 1.445(6) | 1.470 | 0.025  |
| C1–C6                                         | 1.457(6) | 1.463 | 0.006  |
| Avg. C–C (the bound ring)                     | 1.455(6) | 1.467 | 0.012  |
| C1–C7                                         | 1.519(5) | 1.500 | –0.019 |
| C4–C8                                         | 1.513(5) | 1.500 | –0.013 |
| C6–C1/C2–C3                                   | –14.2(6) | –17.5 | –3.3   |
| C1–C2/C4–C5                                   | 12.4(3)  | 15.6  | 3.2    |

**Table. S5.** Key structural parameters of **2-Sm**.

| Selected distances [Å] and<br>torsion angles [°] | Exp.     | 2-Sm ( <sup>11</sup> A) |        | 2-Sm ( <sup>13</sup> A) |        |
|--------------------------------------------------|----------|-------------------------|--------|-------------------------|--------|
|                                                  |          | Calc.                   | Diff.  | Calc.                   | Diff.  |
| Sm1–N1                                           | 2.510(2) | 2.486                   | –0.024 | 2.541                   | 0.031  |
| Sm1–N2                                           | 2.510(2) | 2.471                   | –0.039 | 2.467                   | –0.043 |
| Sm2–N3                                           | 2.510(2) | 2.521                   | 0.011  | 2.528                   | 0.018  |
| Sm3–N4                                           | 2.510(2) | 2.455                   | –0.055 | 2.458                   | –0.052 |
| Sm1–C1                                           | 2.559(2) | 2.544                   | –0.015 | 2.658                   | 0.099  |
| Sm1–C2                                           | 2.493(1) | 2.470                   | –0.023 | 2.664                   | 0.171  |
| Sm1–C3                                           | 2.603(2) | 2.564                   | –0.039 | 2.688                   | 0.085  |
| Sm1–C4                                           | 2.534(2) | 2.519                   | –0.015 | 2.714                   | 0.180  |
| Sm1–C5                                           | 2.598(2) | 2.582                   | –0.016 | 2.711                   | 0.113  |
| Sm1–C6                                           | 2.502(2) | 2.494                   | –0.008 | 2.680                   | 0.178  |
| Sm2–C1                                           | 2.534(2) | 2.513                   | –0.021 | 2.728                   | 0.194  |
| Sm2–C2                                           | 2.598(2) | 2.581                   | –0.017 | 2.740                   | 0.142  |
| Sm2–C3                                           | 2.502(2) | 2.484                   | –0.018 | 2.691                   | 0.189  |
| Sm2–C4                                           | 2.559(2) | 2.543                   | –0.016 | 2.659                   | 0.100  |
| Sm2–C5                                           | 2.493(1) | 2.494                   | 0.001  | 2.651                   | 0.158  |
| Sm2–C6                                           | 2.603(2) | 2.572                   | –0.031 | 2.671                   | 0.068  |
| Sm1–C <sub>cent</sub>                            | 2.095(1) | 2.069                   | –0.026 | 2.269                   | 0.174  |
| Sm2–C <sub>cent</sub>                            | 2.095(1) | 2.071                   | –0.024 | 2.274                   | 0.179  |
| Sm1–O                                            | 2.576(1) | 2.560                   | –0.016 | 2.590                   | 0.014  |
| Sm2–O                                            | 2.576(1) | 2.563                   | –0.013 | 2.582                   | 0.006  |
| C1–C2                                            | 1.453(3) | 1.465                   | 0.012  | 1.491                   | 0.038  |
| C2–C3                                            | 1.450(3) | 1.454                   | 0.004  | 1.408                   | –0.042 |
| C3–C4                                            | 1.455(3) | 1.451                   | –0.004 | 1.414                   | –0.041 |
| C4–C5                                            | 1.453(3) | 1.464                   | 0.011  | 1.491                   | 0.038  |
| C5–C6                                            | 1.450(3) | 1.454                   | 0.004  | 1.409                   | –0.041 |
| C1–C6                                            | 1.455(3) | 1.453                   | –0.002 | 1.412                   | –0.043 |
| Avg. C–C (the bound ring)                        | 1.453(3) | 1.457                   | 0.004  | 1.437                   | –0.016 |
| C3–C4/C5–C6                                      | –12.8(3) | –12.1                   | 0.7    | –0.6                    | 12.2   |

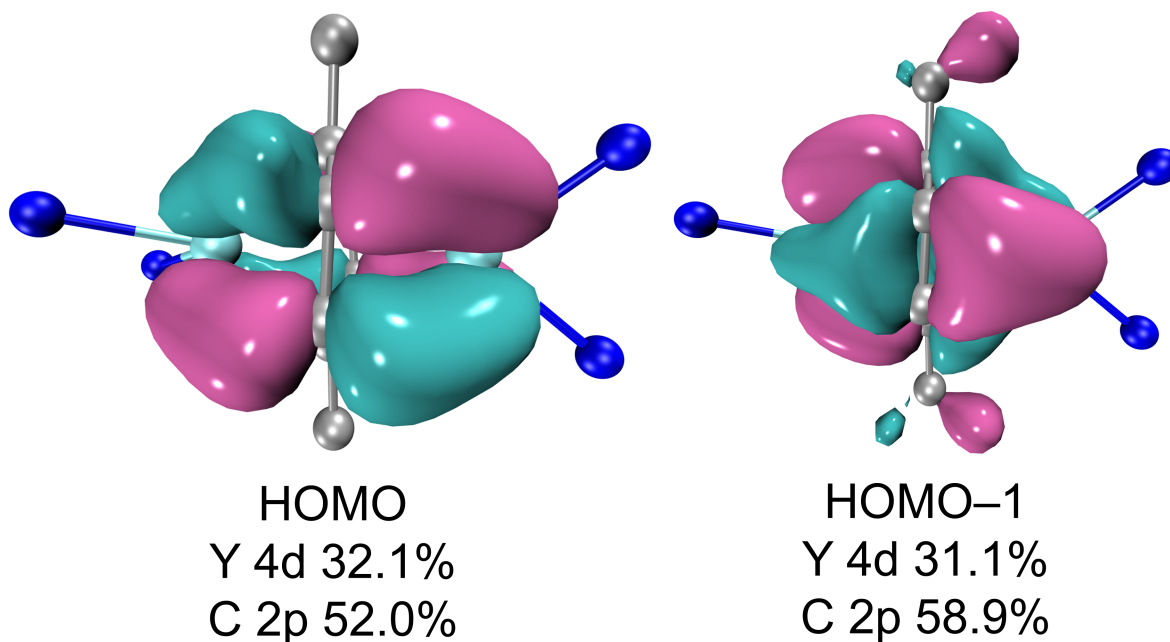
|             |      |      |      |     |     |
|-------------|------|------|------|-----|-----|
| C1-C2/C4-C5 | 0(2) | -0.8 | -0.8 | 0.6 | 0.6 |
|-------------|------|------|------|-----|-----|

**Table. S6.** Key structural parameters of **3-Sm**.

| Selected distances [Å] and torsion angles [°] | Exp.     | 3-Sm ( <sup>11</sup> A) |        | 3-Sm ( <sup>13</sup> A) |        |
|-----------------------------------------------|----------|-------------------------|--------|-------------------------|--------|
|                                               |          | Calc.                   | Diff.  | Calc.                   | Diff.  |
| Sm1–N1                                        | 2.524(2) | 2.489                   | –0.035 | 2.505                   | –0.019 |
| Sm1–N2                                        | 2.541(2) | 2.508                   | –0.033 | 2.518                   | –0.023 |
| Sm2–N3                                        | 2.524(2) | 2.515                   | –0.009 | 2.504                   | –0.020 |
| Sm3–N4                                        | 2.541(2) | 2.481                   | –0.060 | 2.518                   | –0.023 |
| Sm1–C1                                        | 2.526(3) | 2.557                   | 0.031  | 2.676                   | 0.150  |
| Sm1–C2                                        | 2.598(3) | 2.553                   | –0.045 | 2.730                   | 0.132  |
| Sm1–C3                                        | 2.594(2) | 2.534                   | –0.060 | 2.765                   | 0.171  |
| Sm1–C4                                        | 2.580(2) | 2.540                   | –0.040 | 2.770                   | 0.190  |
| Sm1–C5                                        | 2.544(2) | 2.567                   | 0.023  | 2.727                   | 0.183  |
| Sm1–C6                                        | 2.577(3) | 2.519                   | –0.058 | 2.680                   | 0.103  |
| Sm2–C1                                        | 2.580(2) | 2.527                   | –0.053 | 2.769                   | 0.189  |
| Sm2–C2                                        | 2.544(2) | 2.526                   | –0.018 | 2.727                   | 0.183  |
| Sm2–C3                                        | 2.577(3) | 2.519                   | –0.058 | 2.681                   | 0.104  |
| Sm2–C4                                        | 2.526(3) | 2.541                   | 0.015  | 2.678                   | 0.152  |
| Sm2–C5                                        | 2.598(3) | 2.571                   | –0.027 | 2.732                   | 0.134  |
| Sm2–C6                                        | 2.594(2) | 2.602                   | 0.008  | 2.765                   | 0.171  |
| Sm1–C <sub>cent</sub>                         | 2.109(1) | 2.089                   | –0.020 | 2.316                   | 0.207  |
| Sm2–C <sub>cent</sub>                         | 2.109(1) | 2.093                   | –0.016 | 2.317                   | 0.208  |
| Sm1–O                                         | 2.585(3) | 2.576                   | –0.009 | 2.571                   | –0.014 |
| Sm2–O                                         | 2.585(3) | 2.589                   | 0.004  | 2.573                   | –0.012 |
| C1–C2                                         | 1.450(4) | 1.449                   | –0.001 | 1.405                   | –0.045 |
| C2–C3                                         | 1.483(4) | 1.450                   | –0.033 | 1.413                   | –0.070 |
| C3–C4                                         | 1.475(3) | 1.465                   | –0.010 | 1.489                   | 0.014  |
| C4–C5                                         | 1.450(4) | 1.439                   | –0.011 | 1.405                   | –0.045 |
| C5–C6                                         | 1.483(4) | 1.455                   | –0.028 | 1.413                   | –0.070 |
| C1–C6                                         | 1.475(3) | 1.462                   | –0.013 | 1.489                   | 0.014  |
| Avg. C–C (the bound ring)                     | 1.469(4) | 1.453                   | –0.016 | 1.436                   | –0.033 |
| C1–C7                                         | 1.513(3) | 1.499                   | –0.014 | 1.495                   | –0.018 |

|             |          |       |        |       |        |
|-------------|----------|-------|--------|-------|--------|
| C4-C8       | 1.513(3) | 1.497 | -0.016 | 1.495 | -0.018 |
| C3-C4/C5-C6 | 5.1(4)   | -2.5  | -7.6   | 0.7   | -4.4   |
| C1-C2/C4-C5 | 0(3)     | 2.3   | 2.3    | 0     | 0      |

### S6.3. Representations of Molecular Orbitals (MOs)

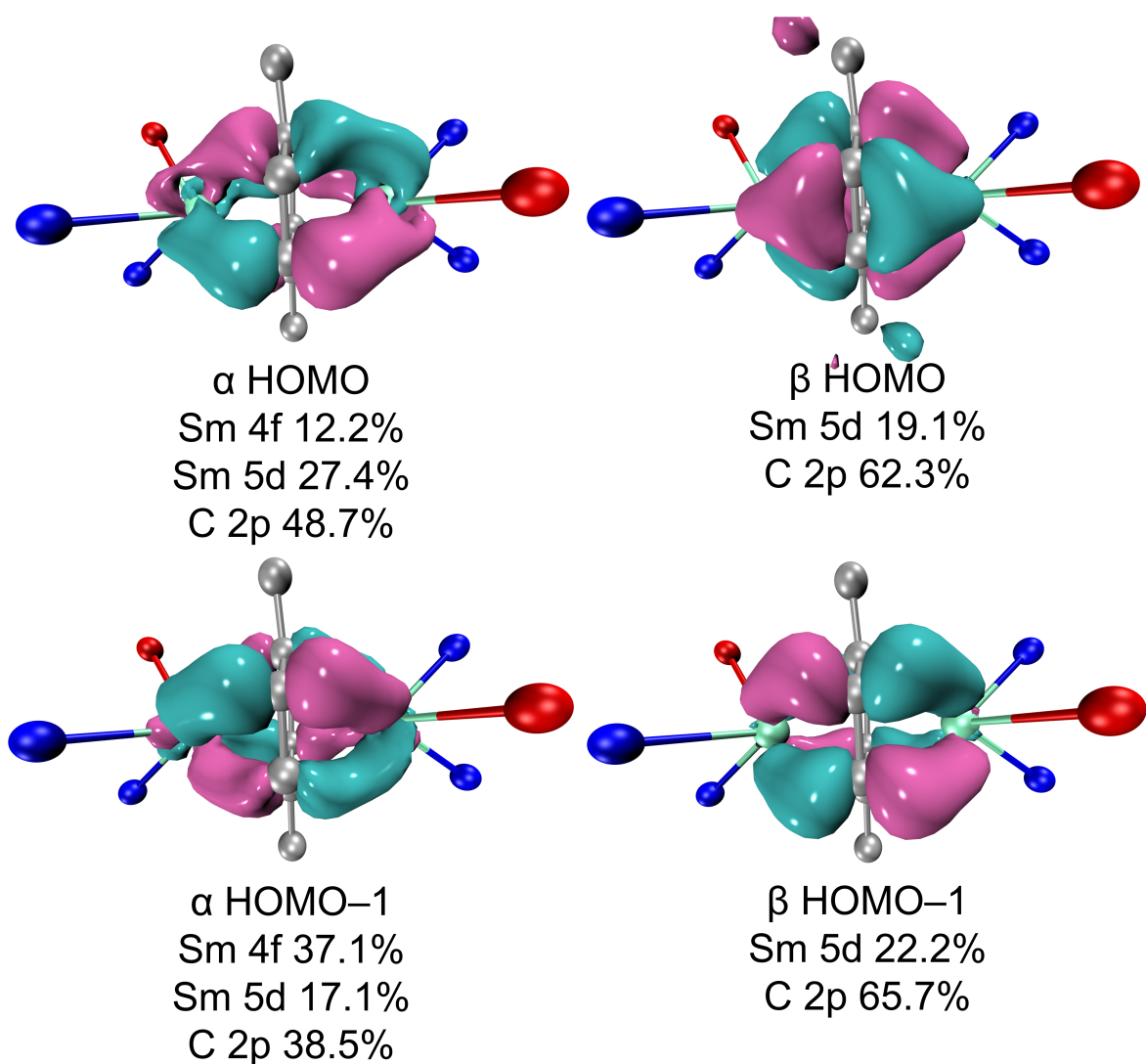


**Fig. S38.** Kohn-Sham orbitals (isovalue 0.04) with composition analysis for the frontier orbitals of **3-Y**. Only the metal, the atoms directly bound to the metal, and all carbon atoms of the bound arene are shown for clarity. Nitrogen in blue, oxygen in red, metal in cyan, and carbon in grey.

**Table. S7.** Energy levels of frontier orbitals of **2-Y** and **3-Y**.

| $E$ (eV) | <b>2-Y</b> | <b>3-Y</b> |
|----------|------------|------------|
| HOMO     | -3.55      | -3.36      |
| HOMO-1   | -3.59      | -3.65      |





**Fig. S39.** Kohn-Sham orbitals (isovalue 0.04) with composition analysis for the frontier orbitals of **3-Sm** ( $^{11}\text{A}$ ). Only the metal, the atoms directly bound to the metal, and all carbon atoms of the bound arene are shown for clarity. Nitrogen in blue, oxygen in red, metal in cyan, and carbon in grey.

**Table. S8.** Energy levels of frontier orbitals of **2-Sm** ( $^{11}\text{A}$ ) and **3-Sm** ( $^{11}\text{A}$ ).

| $E$ (eV) | <b>2-Sm</b> ( $^{11}\text{A}$ ) |         | <b>3-Sm</b> ( $^{11}\text{A}$ ) |         |
|----------|---------------------------------|---------|---------------------------------|---------|
|          | $\alpha$                        | $\beta$ | $\alpha$                        | $\beta$ |
| HOMO     | -2.93                           | -2.84   | -2.68                           | -2.51   |
| HOMO-1   | -3.09                           | -2.96   | -2.93                           | -2.83   |

#### S6.4. Population analysis

**Table. S9.** Natural population analysis for 2-Y.

| Atom | No. | Natural Charge | Core     | Valence | Rydberg | Total    |
|------|-----|----------------|----------|---------|---------|----------|
| Y    | 1   | 1.56479        | 35.9734  | 1.36435 | 0.09746 | 37.43521 |
| Y    | 2   | 1.56772        | 35.97335 | 1.36226 | 0.09668 | 37.43228 |
| N    | 3   | -0.67235       | 1.9992   | 5.65049 | 0.02266 | 7.67235  |
| N    | 4   | -0.67165       | 1.9992   | 5.64973 | 0.02273 | 7.67165  |
| N    | 5   | -0.67439       | 1.9992   | 5.6527  | 0.02249 | 7.67439  |
| N    | 6   | -0.67158       | 1.99921  | 5.64977 | 0.0226  | 7.67158  |
| C    | 7   | -0.67266       | 1.99944  | 4.66232 | 0.0109  | 6.67266  |
| H    | 8   | 0.23027        | 0        | 0.76808 | 0.00165 | 0.76973  |
| H    | 9   | 0.22339        | 0        | 0.77531 | 0.00129 | 0.77661  |
| H    | 10  | 0.23019        | 0        | 0.76829 | 0.00152 | 0.76981  |
| C    | 11  | 0.31452        | 1.99916  | 3.66651 | 0.01981 | 5.68548  |
| C    | 12  | -0.432         | 1.99909  | 4.41534 | 0.01756 | 6.432    |
| H    | 13  | 0.21057        | 0        | 0.78742 | 0.002   | 0.78943  |
| C    | 14  | 0.31474        | 1.99916  | 3.66625 | 0.01986 | 5.68526  |
| C    | 15  | -0.67229       | 1.99944  | 4.66185 | 0.01099 | 6.67229  |
| H    | 16  | 0.22998        | 0        | 0.76837 | 0.00165 | 0.77002  |
| H    | 17  | 0.22355        | 0        | 0.77518 | 0.00126 | 0.77645  |
| H    | 18  | 0.22972        | 0        | 0.76873 | 0.00155 | 0.77028  |
| C    | 19  | 0.12025        | 1.99879  | 3.85851 | 0.02245 | 5.87975  |
| C    | 20  | -0.02888       | 1.99907  | 4.01193 | 0.01788 | 6.02888  |
| C    | 21  | -0.21584       | 1.99914  | 4.20011 | 0.01659 | 6.21584  |
| H    | 22  | 0.21192        | 0        | 0.7865  | 0.00159 | 0.78808  |
| C    | 23  | -0.21813       | 1.99923  | 4.20163 | 0.01727 | 6.21813  |
| H    | 24  | 0.21578        | 0        | 0.78284 | 0.00137 | 0.78422  |
| C    | 25  | -0.21472       | 1.99915  | 4.19921 | 0.01636 | 6.21472  |
| H    | 26  | 0.21225        | 0        | 0.78608 | 0.00167 | 0.78775  |
| C    | 27  | -0.02442       | 1.99906  | 4.00776 | 0.0176  | 6.02442  |

|   |    |          |         |         |         |         |
|---|----|----------|---------|---------|---------|---------|
| C | 28 | -0.62747 | 1.99944 | 4.61762 | 0.01042 | 6.62747 |
| H | 29 | 0.2274   | 0       | 0.77095 | 0.00165 | 0.7726  |
| C | 30 | -0.63295 | 1.99944 | 4.62286 | 0.01065 | 6.63295 |
| H | 31 | 0.23385  | 0       | 0.7644  | 0.00175 | 0.76615 |
| C | 32 | 0.1193   | 1.99878 | 3.85959 | 0.02233 | 5.8807  |
| C | 33 | -0.02773 | 1.99907 | 4.01074 | 0.01792 | 6.02773 |
| C | 34 | -0.21575 | 1.99914 | 4.19995 | 0.01666 | 6.21575 |
| H | 35 | 0.21211  | 0       | 0.78631 | 0.00159 | 0.78789 |
| C | 36 | -0.21809 | 1.99922 | 4.2016  | 0.01727 | 6.21809 |
| H | 37 | 0.216    | 0       | 0.78262 | 0.00138 | 0.784   |
| C | 38 | -0.21481 | 1.99914 | 4.19916 | 0.01651 | 6.21481 |
| H | 39 | 0.21228  | 0       | 0.78605 | 0.00167 | 0.78772 |
| C | 40 | -0.02501 | 1.99906 | 4.0083  | 0.01765 | 6.02501 |
| C | 41 | -0.62757 | 1.99944 | 4.61774 | 0.01039 | 6.62757 |
| H | 42 | 0.22849  | 0       | 0.76989 | 0.00162 | 0.77151 |
| C | 43 | -0.63055 | 1.99944 | 4.62049 | 0.01062 | 6.63055 |
| H | 44 | 0.22181  | 0       | 0.77635 | 0.00184 | 0.77819 |
| C | 45 | -0.67187 | 1.99944 | 4.66137 | 0.01106 | 6.67187 |
| H | 46 | 0.22971  | 0       | 0.76867 | 0.00163 | 0.77029 |
| H | 47 | 0.22357  | 0       | 0.77517 | 0.00126 | 0.77643 |
| H | 48 | 0.22975  | 0       | 0.7687  | 0.00155 | 0.77025 |
| C | 49 | 0.31378  | 1.99915 | 3.66714 | 0.01993 | 5.68622 |
| C | 50 | -0.43242 | 1.99909 | 4.41571 | 0.01762 | 6.43242 |
| H | 51 | 0.21034  | 0       | 0.78765 | 0.00201 | 0.78966 |
| C | 52 | 0.31366  | 1.99916 | 3.66731 | 0.01988 | 5.68634 |
| C | 53 | -0.67211 | 1.99944 | 4.66182 | 0.01085 | 6.67211 |
| H | 54 | 0.23044  | 0       | 0.76795 | 0.00161 | 0.76956 |
| H | 55 | 0.22322  | 0       | 0.7755  | 0.00128 | 0.77678 |
| H | 56 | 0.22955  | 0       | 0.7689  | 0.00155 | 0.77045 |
| C | 57 | 0.11852  | 1.99878 | 3.86048 | 0.02222 | 5.88148 |
| C | 58 | -0.02877 | 1.99907 | 4.01191 | 0.0178  | 6.02877 |

|   |    |          |         |         |         |         |
|---|----|----------|---------|---------|---------|---------|
| C | 59 | -0.21524 | 1.99914 | 4.19955 | 0.01654 | 6.21524 |
| H | 60 | 0.21212  | 0       | 0.78628 | 0.0016  | 0.78788 |
| C | 61 | -0.21772 | 1.99923 | 4.20119 | 0.0173  | 6.21772 |
| H | 62 | 0.21596  | 0       | 0.78265 | 0.00139 | 0.78404 |
| C | 63 | -0.21469 | 1.99914 | 4.19896 | 0.01658 | 6.21469 |
| H | 64 | 0.21227  | 0       | 0.78611 | 0.00162 | 0.78773 |
| C | 65 | -0.02323 | 1.99907 | 4.00648 | 0.01769 | 6.02323 |
| C | 66 | -0.62678 | 1.99944 | 4.61688 | 0.01046 | 6.62678 |
| H | 67 | 0.22665  | 0       | 0.77171 | 0.00163 | 0.77335 |
| C | 68 | -0.63057 | 1.99944 | 4.62054 | 0.0106  | 6.63057 |
| H | 69 | 0.22105  | 0       | 0.77713 | 0.00183 | 0.77895 |
| C | 70 | 0.12341  | 1.9988  | 3.85541 | 0.02239 | 5.87659 |
| C | 71 | -0.02867 | 1.99907 | 4.01182 | 0.01778 | 6.02867 |
| C | 72 | -0.21622 | 1.99915 | 4.20052 | 0.01656 | 6.21622 |
| H | 73 | 0.21179  | 0       | 0.78663 | 0.00159 | 0.78821 |
| C | 74 | -0.21952 | 1.99923 | 4.20295 | 0.01734 | 6.21952 |
| H | 75 | 0.21569  | 0       | 0.78293 | 0.00138 | 0.78431 |
| C | 76 | -0.21428 | 1.99914 | 4.19877 | 0.01637 | 6.21428 |
| H | 77 | 0.21206  | 0       | 0.78628 | 0.00166 | 0.78794 |
| C | 78 | -0.02592 | 1.99906 | 4.00922 | 0.01764 | 6.02592 |
| C | 79 | -0.62728 | 1.99943 | 4.61761 | 0.01024 | 6.62728 |
| H | 80 | 0.22844  | 0       | 0.76991 | 0.00165 | 0.77156 |
| C | 81 | -0.63215 | 1.99944 | 4.62208 | 0.01063 | 6.63215 |
| H | 82 | 0.22232  | 0       | 0.77588 | 0.0018  | 0.77768 |
| H | 83 | 0.22388  | 0       | 0.77432 | 0.0018  | 0.77612 |
| H | 84 | 0.21987  | 0       | 0.77882 | 0.00131 | 0.78013 |
| H | 85 | 0.21877  | 0       | 0.77989 | 0.00134 | 0.78123 |
| H | 86 | 0.22179  | 0       | 0.77638 | 0.00182 | 0.77821 |
| H | 87 | 0.2231   | 0       | 0.7751  | 0.0018  | 0.7769  |
| H | 88 | 0.21943  | 0       | 0.77925 | 0.00131 | 0.78057 |
| H | 89 | 0.23165  | 0       | 0.76662 | 0.00172 | 0.76835 |

|         |     |          |           |           |         |           |
|---------|-----|----------|-----------|-----------|---------|-----------|
| H       | 90  | 0.21904  | 0         | 0.77962   | 0.00134 | 0.78096   |
| H       | 91  | 0.2238   | 0         | 0.7744    | 0.00181 | 0.7762    |
| H       | 92  | 0.22     | 0         | 0.77869   | 0.00132 | 0.78      |
| H       | 93  | 0.2187   | 0         | 0.78      | 0.0013  | 0.7813    |
| H       | 94  | 0.23309  | 0         | 0.76517   | 0.00174 | 0.76691   |
| H       | 95  | 0.22192  | 0         | 0.77624   | 0.00184 | 0.77808   |
| H       | 96  | 0.21841  | 0         | 0.7803    | 0.00129 | 0.78159   |
| H       | 97  | 0.21929  | 0         | 0.77938   | 0.00133 | 0.78071   |
| H       | 98  | 0.23208  | 0         | 0.76618   | 0.00174 | 0.76792   |
| C       | 99  | -0.57775 | 1.99883   | 4.55246   | 0.02646 | 6.57775   |
| H       | 100 | 0.26438  | 0         | 0.73403   | 0.00159 | 0.73562   |
| C       | 101 | -0.58027 | 1.99877   | 4.55328   | 0.02821 | 6.58027   |
| H       | 102 | 0.27112  | 0         | 0.72699   | 0.00189 | 0.72888   |
| C       | 103 | -0.58369 | 1.99878   | 4.55704   | 0.02787 | 6.58369   |
| H       | 104 | 0.2717   | 0         | 0.72635   | 0.00194 | 0.7283    |
| C       | 105 | -0.58502 | 1.99882   | 4.55955   | 0.02665 | 6.58502   |
| H       | 106 | 0.26545  | 0         | 0.73295   | 0.00159 | 0.73455   |
| C       | 107 | -0.58256 | 1.99878   | 4.55547   | 0.02831 | 6.58256   |
| H       | 108 | 0.27138  | 0         | 0.72671   | 0.0019  | 0.72862   |
| C       | 109 | -0.57877 | 1.99879   | 4.55203   | 0.02796 | 6.57877   |
| H       | 110 | 0.27032  | 0         | 0.72777   | 0.00191 | 0.72968   |
| *Total* |     | 0.00000  | 175.90213 | 272.88291 | 1.21496 | 450.00000 |

Average charge on yttrium: 1.57

Total charge of the bound benzene (C+H)/(C): -1.87/-3.49

Average charge on nitrogen donors of the BDI ligand: -0.67

**Table. S10.** Natural population analysis for **3-Y**.

| Atom | No. | Natural Charge | Core     | Valence | Rydberg | Total    |
|------|-----|----------------|----------|---------|---------|----------|
| Y    | 1   | 1.65854        | 35.96993 | 1.24543 | 0.1261  | 37.34146 |
| Y    | 2   | 1.7125         | 35.9727  | 1.21659 | 0.0982  | 37.2875  |
| N    | 3   | -0.68441       | 1.99921  | 5.66225 | 0.02295 | 7.68441  |
| N    | 4   | -0.68076       | 1.99921  | 5.65836 | 0.02319 | 7.68076  |
| N    | 5   | -0.69831       | 1.99927  | 5.67612 | 0.02292 | 7.69831  |
| N    | 6   | -0.69964       | 1.99927  | 5.67746 | 0.02291 | 7.69964  |
| C    | 7   | -0.67097       | 1.99944  | 4.66068 | 0.01085 | 6.67097  |
| H    | 8   | 0.22922        | 0        | 0.76926 | 0.00152 | 0.77078  |
| H    | 9   | 0.22371        | 0        | 0.77502 | 0.00128 | 0.77629  |
| H    | 10  | 0.2288         | 0        | 0.76954 | 0.00166 | 0.7712   |
| C    | 11  | 0.31213        | 1.99914  | 3.66841 | 0.02032 | 5.68787  |
| C    | 12  | -0.42917       | 1.99909  | 4.4123  | 0.01778 | 6.42917  |
| H    | 13  | 0.21084        | 0        | 0.78709 | 0.00207 | 0.78916  |
| C    | 14  | 0.31244        | 1.99914  | 3.66809 | 0.02033 | 5.68756  |
| C    | 15  | -0.67082       | 1.99944  | 4.6606  | 0.01077 | 6.67082  |
| H    | 16  | 0.22912        | 0        | 0.76935 | 0.00152 | 0.77088  |
| H    | 17  | 0.22347        | 0        | 0.77525 | 0.00127 | 0.77653  |
| H    | 18  | 0.2289         | 0        | 0.7694  | 0.0017  | 0.7711   |
| C    | 19  | 0.11551        | 1.99876  | 3.86287 | 0.02286 | 5.88449  |
| C    | 20  | -0.02716       | 1.99906  | 4.01007 | 0.01803 | 6.02716  |
| C    | 21  | -0.21644       | 1.99914  | 4.20042 | 0.01688 | 6.21644  |
| H    | 22  | 0.21414        | 0        | 0.78417 | 0.00169 | 0.78586  |
| C    | 23  | -0.21781       | 1.99923  | 4.20125 | 0.01733 | 6.21781  |
| H    | 24  | 0.21691        | 0        | 0.78171 | 0.00138 | 0.78309  |
| C    | 25  | -0.21427       | 1.99914  | 4.19851 | 0.01661 | 6.21427  |
| H    | 26  | 0.2131         | 0        | 0.7853  | 0.0016  | 0.7869   |
| C    | 27  | -0.02895       | 1.99907  | 4.0117  | 0.01818 | 6.02895  |
| C    | 28  | -0.62632       | 1.99944  | 4.61566 | 0.01122 | 6.62632  |

|   |    |          |         |         |         |         |
|---|----|----------|---------|---------|---------|---------|
| H | 29 | 0.22703  | 0       | 0.77109 | 0.00189 | 0.77297 |
| C | 30 | -0.62465 | 1.99944 | 4.61468 | 0.01053 | 6.62465 |
| H | 31 | 0.22645  | 0       | 0.77191 | 0.00164 | 0.77355 |
| C | 32 | 0.11995  | 1.99877 | 3.85834 | 0.02294 | 5.88005 |
| C | 33 | -0.02712 | 1.99905 | 4.01004 | 0.01802 | 6.02712 |
| C | 34 | -0.21696 | 1.99914 | 4.20108 | 0.01674 | 6.21696 |
| H | 35 | 0.214    | 0       | 0.7843  | 0.0017  | 0.786   |
| C | 36 | -0.21932 | 1.99922 | 4.20276 | 0.01733 | 6.21932 |
| H | 37 | 0.21678  | 0       | 0.78184 | 0.00138 | 0.78322 |
| C | 38 | -0.21551 | 1.99914 | 4.19966 | 0.01671 | 6.21551 |
| H | 39 | 0.21295  | 0       | 0.78545 | 0.0016  | 0.78705 |
| C | 40 | -0.02989 | 1.99907 | 4.01268 | 0.01815 | 6.02989 |
| C | 41 | -0.62812 | 1.99944 | 4.61746 | 0.01122 | 6.62812 |
| H | 42 | 0.22818  | 0       | 0.76992 | 0.0019  | 0.77182 |
| C | 43 | -0.6211  | 1.99944 | 4.61127 | 0.01038 | 6.6211  |
| H | 44 | 0.22421  | 0       | 0.7741  | 0.00169 | 0.77579 |
| C | 45 | -0.67431 | 1.99944 | 4.66362 | 0.01125 | 6.67431 |
| H | 46 | 0.23192  | 0       | 0.76644 | 0.00164 | 0.76808 |
| H | 47 | 0.22256  | 0       | 0.77618 | 0.00126 | 0.77744 |
| H | 48 | 0.23215  | 0       | 0.76615 | 0.0017  | 0.76785 |
| C | 49 | 0.30957  | 1.99914 | 3.67085 | 0.02044 | 5.69043 |
| C | 50 | -0.43407 | 1.99908 | 4.41674 | 0.01824 | 6.43407 |
| H | 51 | 0.20978  | 0       | 0.78797 | 0.00225 | 0.79022 |
| C | 52 | 0.30985  | 1.99914 | 3.67066 | 0.02036 | 5.69015 |
| C | 53 | -0.67414 | 1.99944 | 4.66367 | 0.01103 | 6.67414 |
| H | 54 | 0.23179  | 0       | 0.76657 | 0.00163 | 0.76821 |
| H | 55 | 0.22248  | 0       | 0.77621 | 0.0013  | 0.77752 |
| H | 56 | 0.23226  | 0       | 0.76605 | 0.00169 | 0.76774 |
| C | 57 | 0.12972  | 1.99881 | 3.84853 | 0.02294 | 5.87028 |
| C | 58 | -0.03049 | 1.99904 | 4.01326 | 0.01819 | 6.03049 |
| C | 59 | -0.21513 | 1.99913 | 4.19881 | 0.01719 | 6.21513 |

|   |    |          |         |         |         |         |
|---|----|----------|---------|---------|---------|---------|
| H | 60 | 0.2128   | 0       | 0.78559 | 0.00161 | 0.7872  |
| C | 61 | -0.21789 | 1.99922 | 4.2011  | 0.01757 | 6.21789 |
| H | 62 | 0.2168   | 0       | 0.78179 | 0.00141 | 0.7832  |
| C | 63 | -0.21739 | 1.99913 | 4.20094 | 0.01732 | 6.21739 |
| H | 64 | 0.21323  | 0       | 0.78521 | 0.00156 | 0.78677 |
| C | 65 | -0.03579 | 1.99904 | 4.01841 | 0.01834 | 6.03579 |
| C | 66 | -0.63398 | 1.99944 | 4.62308 | 0.01146 | 6.63398 |
| H | 67 | 0.22314  | 0       | 0.77502 | 0.00183 | 0.77686 |
| C | 68 | -0.63026 | 1.99944 | 4.62001 | 0.01081 | 6.63026 |
| H | 69 | 0.22904  | 0       | 0.76931 | 0.00165 | 0.77096 |
| C | 70 | 0.13037  | 1.99881 | 3.8478  | 0.02303 | 5.86963 |
| C | 71 | -0.02924 | 1.99904 | 4.01225 | 0.01794 | 6.02924 |
| C | 72 | -0.21435 | 1.99913 | 4.19837 | 0.01685 | 6.21435 |
| H | 73 | 0.21257  | 0       | 0.78579 | 0.00164 | 0.78743 |
| C | 74 | -0.21818 | 1.99922 | 4.20155 | 0.01741 | 6.21818 |
| H | 75 | 0.21662  | 0       | 0.78198 | 0.0014  | 0.78338 |
| C | 76 | -0.21782 | 1.99914 | 4.20164 | 0.01704 | 6.21782 |
| H | 77 | 0.21326  | 0       | 0.78516 | 0.00158 | 0.78674 |
| C | 78 | -0.03654 | 1.99904 | 4.01931 | 0.01819 | 6.03654 |
| C | 79 | -0.63386 | 1.99944 | 4.62322 | 0.0112  | 6.63386 |
| H | 80 | 0.22286  | 0       | 0.77528 | 0.00186 | 0.77714 |
| C | 81 | -0.63019 | 1.99944 | 4.62008 | 0.01067 | 6.63019 |
| H | 82 | 0.22867  | 0       | 0.76969 | 0.00164 | 0.77133 |
| H | 83 | 0.22187  | 0       | 0.77619 | 0.00194 | 0.77813 |
| H | 84 | 0.22138  | 0       | 0.77717 | 0.00145 | 0.77862 |
| H | 85 | 0.22063  | 0       | 0.77804 | 0.00133 | 0.77937 |
| H | 86 | 0.22455  | 0       | 0.7737  | 0.00176 | 0.77545 |
| H | 87 | 0.22097  | 0       | 0.77707 | 0.00196 | 0.77903 |
| H | 88 | 0.22133  | 0       | 0.77718 | 0.00148 | 0.77867 |
| H | 89 | 0.22009  | 0       | 0.77859 | 0.00131 | 0.77991 |
| H | 90 | 0.22354  | 0       | 0.77466 | 0.0018  | 0.77646 |



|         |     |          |           |           |         |           |
|---------|-----|----------|-----------|-----------|---------|-----------|
| H       | 91  | 0.21772  | 0         | 0.78094   | 0.00134 | 0.78228   |
| H       | 92  | 0.23487  | 0         | 0.76327   | 0.00187 | 0.76513   |
| H       | 93  | 0.2183   | 0         | 0.78037   | 0.00132 | 0.7817    |
| H       | 94  | 0.22404  | 0         | 0.77412   | 0.00184 | 0.77596   |
| H       | 95  | 0.21759  | 0         | 0.78105   | 0.00136 | 0.78241   |
| H       | 96  | 0.23533  | 0         | 0.76284   | 0.00184 | 0.76467   |
| H       | 97  | 0.21831  | 0         | 0.78036   | 0.00133 | 0.78169   |
| H       | 98  | 0.22389  | 0         | 0.77423   | 0.00188 | 0.77611   |
| C       | 99  | -0.59855 | 1.99942   | 4.58631   | 0.01282 | 6.59855   |
| H       | 100 | 0.20562  | 0         | 0.7925    | 0.00187 | 0.79438   |
| H       | 101 | 0.22314  | 0         | 0.77398   | 0.00288 | 0.77686   |
| H       | 102 | 0.21608  | 0         | 0.78177   | 0.00215 | 0.78392   |
| C       | 103 | -0.39567 | 1.99876   | 4.36515   | 0.03175 | 6.39567   |
| C       | 104 | -0.59955 | 1.99883   | 4.57193   | 0.02879 | 6.59955   |
| C       | 105 | -0.60228 | 1.99889   | 4.57698   | 0.02641 | 6.60228   |
| C       | 106 | -0.39955 | 1.99876   | 4.36918   | 0.03161 | 6.39955   |
| C       | 107 | -0.59791 | 1.99883   | 4.57013   | 0.02895 | 6.59791   |
| C       | 108 | -0.59617 | 1.99889   | 4.5707    | 0.02658 | 6.59617   |
| C       | 109 | -0.59858 | 1.99942   | 4.58619   | 0.01296 | 6.59858   |
| H       | 110 | 0.2042   | 0         | 0.79375   | 0.00205 | 0.7958    |
| H       | 111 | 0.22343  | 0         | 0.77381   | 0.00277 | 0.77657   |
| H       | 112 | 0.21776  | 0         | 0.78011   | 0.00213 | 0.78224   |
| H       | 113 | 0.26538  | 0         | 0.733     | 0.00162 | 0.73462   |
| H       | 114 | 0.27234  | 0         | 0.72558   | 0.00208 | 0.72766   |
| H       | 115 | 0.26563  | 0         | 0.73275   | 0.00161 | 0.73437   |
| H       | 116 | 0.27126  | 0         | 0.72671   | 0.00203 | 0.72874   |
| *Total* |     | 0.00000  | 179.89694 | 284.79409 | 1.30896 | 466.00000 |

Average charge on yttrium: 1.69

Total charge of the bound *p*-xylene excluding two methyl groups (C+H)/(C): -2.02/-3.19

Average charge on nitrogen donors of the BDI ligand: -0.69

**Table. S11.** Natural population analysis for **2-Sm (<sup>11</sup>A)**.

| Atom | No. | Natural Charge | Core     | Valence | Rydberg | Total    | Natural Spin Density |
|------|-----|----------------|----------|---------|---------|----------|----------------------|
| Sm   | 1   | 1.21576        | 53.95759 | 6.3465  | 0.48015 | 60.78424 | 5.13626              |
| O    | 2   | -0.53232       | 1.99963  | 6.50743 | 0.02527 | 8.53232  | 0.00414              |
| N    | 3   | -0.65186       | 1.99903  | 5.62202 | 0.03081 | 7.65186  | 0.00141              |
| N    | 4   | -0.6449        | 1.99902  | 5.61437 | 0.03151 | 7.6449   | -0.00356             |
| C    | 5   | -0.67324       | 1.99944  | 4.66277 | 0.01103 | 6.67324  | -0.00051             |
| H    | 6   | 0.23164        | 0        | 0.76668 | 0.00168 | 0.76836  | 0.00016              |
| H    | 7   | 0.2218         | 0        | 0.77695 | 0.00125 | 0.7782   | -0.00007             |
| H    | 8   | 0.22517        | 0        | 0.77322 | 0.00161 | 0.77483  | 0.00019              |
| C    | 9   | 0.31818        | 1.99907  | 3.66196 | 0.02079 | 5.68182  | 0.0042               |
| C    | 10  | -0.44746       | 1.99907  | 4.42977 | 0.01863 | 6.44746  | -0.00302             |
| H    | 11  | 0.20851        | 0        | 0.78959 | 0.0019  | 0.79149  | 0.00023              |
| C    | 12  | 0.32074        | 1.99906  | 3.65972 | 0.02048 | 5.67926  | 0.00526              |
| C    | 13  | -0.673         | 1.99943  | 4.66249 | 0.01108 | 6.673    | -0.00068             |
| H    | 14  | 0.22621        | 0        | 0.77216 | 0.00163 | 0.77379  | 0.00017              |
| H    | 15  | 0.22115        | 0        | 0.77755 | 0.00129 | 0.77885  | -0.00011             |
| H    | 16  | 0.23363        | 0        | 0.76489 | 0.00148 | 0.76637  | 0.00019              |
| C    | 17  | 0.13974        | 1.99869  | 3.83568 | 0.02589 | 5.86026  | 0.00567              |
| C    | 18  | -0.03405       | 1.99905  | 4.01599 | 0.01901 | 6.03405  | -0.00039             |
| C    | 19  | -0.20805       | 1.99914  | 4.19268 | 0.01623 | 6.20805  | 0.00062              |
| H    | 20  | 0.2098         | 0        | 0.78856 | 0.00164 | 0.7902   | -0.00001             |
| C    | 21  | -0.22233       | 1.99922  | 4.20619 | 0.01692 | 6.22233  | -0.00112             |
| H    | 22  | 0.21403        | 0        | 0.78459 | 0.00138 | 0.78597  | 0.00004              |
| C    | 23  | -0.21368       | 1.99913  | 4.1979  | 0.01664 | 6.21368  | 0.00054              |
| H    | 24  | 0.20878        | 0        | 0.78964 | 0.00158 | 0.79122  | -0.00002             |
| C    | 25  | -0.02752       | 1.99907  | 4.00866 | 0.01979 | 6.02752  | -0.00011             |
| C    | 26  | -0.61817       | 1.99944  | 4.60745 | 0.01127 | 6.61817  | 0.00049              |
| H    | 27  | 0.21774        | 0        | 0.78027 | 0.00199 | 0.78226  | 0                    |

|    |    |          |          |         |         |          |          |
|----|----|----------|----------|---------|---------|----------|----------|
| C  | 28 | -0.6206  | 1.99943  | 4.61082 | 0.01035 | 6.6206   | 0.00037  |
| H  | 29 | 0.23197  | 0        | 0.76576 | 0.00227 | 0.76803  | 0.0019   |
| C  | 30 | 0.13419  | 1.9987   | 3.84085 | 0.02626 | 5.86581  | 0.00503  |
| C  | 31 | -0.02399 | 1.99906  | 4.00502 | 0.0199  | 6.02399  | 0.00172  |
| C  | 32 | -0.21602 | 1.99913  | 4.20037 | 0.01652 | 6.21602  | -0.00079 |
| H  | 33 | 0.2078   | 0        | 0.79063 | 0.00156 | 0.7922   | 0.00002  |
| C  | 34 | -0.21695 | 1.99922  | 4.20073 | 0.017   | 6.21695  | 0.00135  |
| H  | 35 | 0.21158  | 0        | 0.78693 | 0.00149 | 0.78842  | -0.00004 |
| C  | 36 | -0.20453 | 1.99914  | 4.18952 | 0.01586 | 6.20453  | -0.00098 |
| H  | 37 | 0.20858  | 0        | 0.78965 | 0.00177 | 0.79142  | 0.00004  |
| C  | 38 | -0.03356 | 1.99905  | 4.01591 | 0.0186  | 6.03356  | 0.00176  |
| C  | 39 | -0.6237  | 1.99943  | 4.61337 | 0.0109  | 6.6237   | 0.00005  |
| H  | 40 | 0.23103  | 0        | 0.76669 | 0.00228 | 0.76897  | 0.00163  |
| C  | 41 | -0.61907 | 1.99944  | 4.6088  | 0.01083 | 6.61907  | 0.00058  |
| H  | 42 | 0.21662  | 0        | 0.7814  | 0.00199 | 0.78338  | 0.00016  |
| C  | 43 | -0.07093 | 1.99926  | 4.05529 | 0.01637 | 6.07093  | 0.00139  |
| H  | 44 | 0.22724  | 0        | 0.77045 | 0.00231 | 0.77276  | 0.00028  |
| H  | 45 | 0.18161  | 0        | 0.81623 | 0.00216 | 0.81839  | 0.0002   |
| C  | 46 | -0.43231 | 1.99946  | 4.42215 | 0.0107  | 6.43231  | -0.0001  |
| H  | 47 | 0.22634  | 0        | 0.77223 | 0.00142 | 0.77366  | -0.00009 |
| H  | 48 | 0.21288  | 0        | 0.78556 | 0.00156 | 0.78712  | 0.00001  |
| C  | 49 | -0.43515 | 1.99946  | 4.42557 | 0.01011 | 6.43515  | 0.00013  |
| H  | 50 | 0.22627  | 0        | 0.77231 | 0.00142 | 0.77373  | -0.00002 |
| H  | 51 | 0.20943  | 0        | 0.78894 | 0.00163 | 0.79057  | -0.00003 |
| C  | 52 | -0.07005 | 1.99931  | 4.05295 | 0.01779 | 6.07005  | 0.00187  |
| H  | 53 | 0.20087  | 0        | 0.79718 | 0.00195 | 0.79913  | 0.00016  |
| H  | 54 | 0.19316  | 0        | 0.80472 | 0.00212 | 0.80684  | 0.00024  |
| Sm | 55 | 1.21694  | 53.95728 | 6.36056 | 0.46522 | 60.78306 | 5.16754  |
| O  | 56 | -0.53572 | 1.99964  | 6.51225 | 0.02383 | 8.53572  | 0.00626  |
| N  | 57 | -0.64431 | 1.99906  | 5.61255 | 0.03271 | 7.64431  | 0.00039  |
| N  | 58 | -0.64939 | 1.99901  | 5.62012 | 0.03025 | 7.64939  | -0.00247 |

|   |    |          |         |         |         |         |          |
|---|----|----------|---------|---------|---------|---------|----------|
| C | 59 | -0.67473 | 1.99944 | 4.66422 | 0.01108 | 6.67473 | -0.00072 |
| H | 60 | 0.23284  | 0       | 0.76549 | 0.00168 | 0.76716 | 0.00026  |
| H | 61 | 0.22045  | 0       | 0.77824 | 0.00131 | 0.77955 | -0.00013 |
| H | 62 | 0.22634  | 0       | 0.77209 | 0.00157 | 0.77366 | 0.00027  |
| C | 63 | 0.31664  | 1.99908 | 3.66348 | 0.0208  | 5.68336 | 0.00634  |
| C | 64 | -0.44919 | 1.99906 | 4.43139 | 0.01874 | 6.44919 | -0.00266 |
| H | 65 | 0.20823  | 0       | 0.78986 | 0.00191 | 0.79177 | 0.00022  |
| C | 66 | 0.31856  | 1.99905 | 3.66172 | 0.02067 | 5.68144 | 0.00712  |
| C | 67 | -0.67114 | 1.99943 | 4.6608  | 0.0109  | 6.67114 | -0.00082 |
| H | 68 | 0.22408  | 0       | 0.77428 | 0.00165 | 0.77592 | 0.00027  |
| H | 69 | 0.22188  | 0       | 0.77687 | 0.00125 | 0.77812 | -0.0001  |
| H | 70 | 0.23234  | 0       | 0.76616 | 0.0015  | 0.76766 | 0.0003   |
| C | 71 | 0.1538   | 1.99875 | 3.82148 | 0.02598 | 5.8462  | 0.00329  |
| C | 72 | -0.03915 | 1.99905 | 4.02076 | 0.01934 | 6.03915 | 0.00271  |
| C | 73 | -0.20493 | 1.99914 | 4.18969 | 0.01611 | 6.20493 | -0.00097 |
| H | 74 | 0.20882  | 0       | 0.78942 | 0.00176 | 0.79118 | 0.00003  |
| C | 75 | -0.22373 | 1.99921 | 4.20757 | 0.01695 | 6.22373 | 0.00215  |
| H | 76 | 0.21203  | 0       | 0.78644 | 0.00153 | 0.78797 | -0.00007 |
| C | 77 | -0.21668 | 1.99914 | 4.20101 | 0.01654 | 6.21668 | -0.00081 |
| H | 78 | 0.20788  | 0       | 0.79049 | 0.00163 | 0.79212 | 0.00002  |
| C | 79 | -0.03232 | 1.99905 | 4.01413 | 0.01915 | 6.03232 | 0.00178  |
| C | 80 | -0.61915 | 1.99944 | 4.60831 | 0.0114  | 6.61915 | 0.00057  |
| H | 81 | 0.2153   | 0       | 0.78266 | 0.00204 | 0.7847  | 0.00015  |
| C | 82 | -0.62336 | 1.99943 | 4.61346 | 0.01046 | 6.62336 | -0.00027 |
| H | 83 | 0.23141  | 0       | 0.76673 | 0.00186 | 0.76859 | 0.00088  |
| C | 84 | 0.12499  | 1.99866 | 3.84861 | 0.02774 | 5.87501 | 0.00634  |
| C | 85 | -0.02366 | 1.99907 | 4.00393 | 0.02066 | 6.02366 | 0.00158  |
| C | 86 | -0.21322 | 1.99913 | 4.19749 | 0.01659 | 6.21322 | 0.00002  |
| H | 87 | 0.20899  | 0       | 0.78947 | 0.00153 | 0.79101 | 0        |
| C | 88 | -0.21772 | 1.99922 | 4.20152 | 0.01699 | 6.21772 | 0.00011  |
| H | 89 | 0.21325  | 0       | 0.78538 | 0.00137 | 0.78675 | 0        |

|   |     |          |         |         |         |         |          |
|---|-----|----------|---------|---------|---------|---------|----------|
| C | 90  | -0.20642 | 1.99914 | 4.19121 | 0.01607 | 6.20642 | 0.0002   |
| H | 91  | 0.20941  | 0       | 0.78896 | 0.00164 | 0.79059 | 0.00001  |
| C | 92  | -0.03509 | 1.99906 | 4.01617 | 0.01986 | 6.03509 | 0.00147  |
| C | 93  | -0.61972 | 1.99943 | 4.60949 | 0.0108  | 6.61972 | 0.0003   |
| H | 94  | 0.2309   | 0       | 0.76682 | 0.00228 | 0.7691  | 0.00219  |
| C | 95  | -0.61956 | 1.99944 | 4.60942 | 0.01069 | 6.61956 | 0.00072  |
| H | 96  | 0.21775  | 0       | 0.78027 | 0.00198 | 0.78225 | 0.00012  |
| C | 97  | -0.07212 | 1.99926 | 4.05638 | 0.01647 | 6.07212 | 0.00112  |
| H | 98  | 0.2278   | 0       | 0.76992 | 0.00228 | 0.7722  | 0.00031  |
| H | 99  | 0.18212  | 0       | 0.81569 | 0.00219 | 0.81788 | 0.00006  |
| C | 100 | -0.43339 | 1.99946 | 4.42331 | 0.01062 | 6.43339 | 0.00005  |
| H | 101 | 0.2265   | 0       | 0.77206 | 0.00144 | 0.7735  | -0.00005 |
| H | 102 | 0.21362  | 0       | 0.78481 | 0.00157 | 0.78638 | 0.00001  |
| C | 103 | -0.43509 | 1.99946 | 4.42537 | 0.01026 | 6.43509 | 0.00012  |
| H | 104 | 0.22643  | 0       | 0.77218 | 0.00139 | 0.77357 | -0.00009 |
| H | 105 | 0.20893  | 0       | 0.78942 | 0.00164 | 0.79107 | -0.00003 |
| C | 106 | -0.06871 | 1.99931 | 4.05203 | 0.01737 | 6.06871 | 0.00146  |
| H | 107 | 0.20213  | 0       | 0.79599 | 0.00188 | 0.79787 | 0.00006  |
| H | 108 | 0.19199  | 0       | 0.80589 | 0.00211 | 0.80801 | 0.00014  |
| H | 109 | 0.21919  | 0       | 0.77935 | 0.00146 | 0.78081 | 0.00009  |
| H | 110 | 0.22482  | 0       | 0.7725  | 0.00268 | 0.77518 | 0.00256  |
| H | 111 | 0.21958  | 0       | 0.77851 | 0.00191 | 0.78042 | -0.00014 |
| H | 112 | 0.21494  | 0       | 0.78375 | 0.00131 | 0.78506 | 0.00002  |
| H | 113 | 0.21612  | 0       | 0.78257 | 0.00131 | 0.78388 | 0.00007  |
| H | 114 | 0.22551  | 0       | 0.77269 | 0.0018  | 0.77449 | 0.00005  |
| H | 115 | 0.22804  | 0       | 0.76927 | 0.00269 | 0.77196 | 0.00227  |
| H | 116 | 0.21789  | 0       | 0.78073 | 0.00139 | 0.78211 | 0.00009  |
| H | 117 | 0.21776  | 0       | 0.78081 | 0.00143 | 0.78224 | 0.00008  |
| H | 118 | 0.22535  | 0       | 0.77187 | 0.00278 | 0.77465 | 0.00308  |
| H | 119 | 0.21956  | 0       | 0.77849 | 0.00195 | 0.78044 | 0.00005  |
| H | 120 | 0.21375  | 0       | 0.78491 | 0.00134 | 0.78625 | 0.00006  |

|         |     |          |           |           |         |         |          |
|---------|-----|----------|-----------|-----------|---------|---------|----------|
| H       | 121 | 0.21641  | 0         | 0.78231   | 0.00128 | 0.78359 | 0.00011  |
| H       | 122 | 0.22623  | 0         | 0.77201   | 0.00176 | 0.77377 | 0.00005  |
| H       | 123 | 0.22901  | 0         | 0.76855   | 0.00244 | 0.77099 | 0.00175  |
| H       | 124 | 0.2181   | 0         | 0.78057   | 0.00133 | 0.7819  | 0.00005  |
| C       | 125 | -0.5386  | 1.99824   | 4.50304   | 0.03732 | 6.5386  | -0.06323 |
| H       | 126 | 0.25973  | 0         | 0.73846   | 0.00181 | 0.74027 | 0.0033   |
| C       | 127 | -0.53991 | 1.99824   | 4.50254   | 0.03913 | 6.53991 | -0.05277 |
| H       | 128 | 0.2719   | 0         | 0.72616   | 0.00194 | 0.7281  | 0.00328  |
| C       | 129 | -0.51719 | 1.99822   | 4.48267   | 0.0363  | 6.51719 | -0.073   |
| H       | 130 | 0.28342  | 0         | 0.7146    | 0.00198 | 0.71658 | 0.00382  |
| C       | 131 | -0.53274 | 1.99827   | 4.49557   | 0.0389  | 6.53274 | -0.07569 |
| H       | 132 | 0.25822  | 0         | 0.73979   | 0.00199 | 0.74178 | 0.00435  |
| C       | 133 | -0.52758 | 1.99826   | 4.49117   | 0.03815 | 6.52758 | -0.06413 |
| H       | 134 | 0.27025  | 0         | 0.72783   | 0.00192 | 0.72975 | 0.00359  |
| C       | 135 | -0.52189 | 1.99826   | 4.48499   | 0.03863 | 6.52189 | -0.07828 |
| H       | 136 | 0.27924  | 0         | 0.71883   | 0.00194 | 0.72076 | 0.00398  |
| *Total* |     | 0        | 231.85957 | 341.84428 | 2.29615 | 576     | 10       |

Average spin density on samarium: 5.15

Average charge on samarium: 1.22

Total charge of the bound benzene (C+H)/(C): -1.56/-3.18

Average charge on nitrogen donors of the BDI ligand: -0.65

Average charge on oxygen of THF: -0.53

**Table. S12.** Natural population analysis for **3-Sm (<sup>11</sup>A)**.

| Atom | No. | Natural Charge | Core     | Valence | Rydberg | Total    | Natural Spin Density |
|------|-----|----------------|----------|---------|---------|----------|----------------------|
| Sm   | 1   | 1.44316        | 53.95481 | 6.10745 | 0.49458 | 60.55684 | 5.09428              |
| O    | 2   | -0.64288       | 1.99964  | 6.6146  | 0.02864 | 8.64288  | 0.00644              |
| N    | 3   | -0.74173       | 1.99906  | 5.7088  | 0.03387 | 7.74173  | 0.00403              |
| N    | 4   | -0.74019       | 1.99906  | 5.70406 | 0.03706 | 7.74019  | 0.00607              |
| C    | 5   | -0.7165        | 1.99913  | 4.70685 | 0.01052 | 6.7165   | -0.00059             |
| H    | 6   | 0.24615        | 0        | 0.75214 | 0.00171 | 0.75385  | 0.00054              |
| H    | 7   | 0.24213        | 0        | 0.75663 | 0.00124 | 0.75787  | -0.00006             |
| H    | 8   | 0.25445        | 0        | 0.74404 | 0.0015  | 0.74555  | 0.00053              |
| C    | 9   | 0.32208        | 1.99854  | 3.65973 | 0.01965 | 5.67792  | 0.01233              |
| C    | 10  | -0.45096       | 1.99869  | 4.43443 | 0.01783 | 6.45096  | -0.00641             |
| H    | 11  | 0.23193        | 0        | 0.76647 | 0.00161 | 0.76807  | 0.00027              |
| C    | 12  | 0.31863        | 1.99855  | 3.66327 | 0.01955 | 5.68137  | 0.01182              |
| C    | 13  | -0.71746       | 1.99913  | 4.70777 | 0.01057 | 6.71746  | -0.0006              |
| H    | 14  | 0.25396        | 0        | 0.74445 | 0.00159 | 0.74604  | 0.00055              |
| H    | 15  | 0.24189        | 0        | 0.75686 | 0.00125 | 0.75811  | -0.00006             |
| H    | 16  | 0.24718        | 0        | 0.7512  | 0.00161 | 0.75282  | 0.0005               |
| C    | 17  | 0.15229        | 1.99833  | 3.82622 | 0.02316 | 5.84771  | 0.00375              |
| C    | 18  | -0.04581       | 1.99869  | 4.02896 | 0.01816 | 6.04581  | 0.00166              |
| C    | 19  | -0.22884       | 1.9988   | 4.213   | 0.01704 | 6.22884  | -0.00002             |
| H    | 20  | 0.23613        | 0        | 0.76211 | 0.00176 | 0.76387  | 0                    |
| C    | 21  | -0.23939       | 1.99887  | 4.22286 | 0.01766 | 6.23939  | 0.00013              |
| H    | 22  | 0.23849        | 0        | 0.75992 | 0.0016  | 0.76151  | 0                    |
| C    | 23  | -0.23334       | 1.99881  | 4.2177  | 0.01683 | 6.23334  | -0.00012             |
| H    | 24  | 0.23604        | 0        | 0.76224 | 0.00172 | 0.76396  | 0                    |
| C    | 25  | -0.0559        | 1.99868  | 4.03885 | 0.01836 | 6.0559   | 0.00153              |
| C    | 26  | -0.66047       | 1.99917  | 4.64853 | 0.01277 | 6.66047  | -0.00052             |
| H    | 27  | 0.23499        | 0        | 0.76133 | 0.00368 | 0.76501  | 0.00241              |

|    |    |          |          |         |         |          |          |
|----|----|----------|----------|---------|---------|----------|----------|
| C  | 28 | -0.66611 | 1.99916  | 4.65466 | 0.01228 | 6.66611  | 0.00061  |
| H  | 29 | 0.23871  | 0        | 0.75962 | 0.00168 | 0.76129  | 0.00008  |
| C  | 30 | 0.1651   | 1.99836  | 3.81394 | 0.02261 | 5.8349   | 0.00256  |
| C  | 31 | -0.05047 | 1.99868  | 4.03412 | 0.01767 | 6.05047  | 0.00157  |
| C  | 32 | -0.23182 | 1.99881  | 4.21613 | 0.01687 | 6.23182  | -0.00021 |
| H  | 33 | 0.23459  | 0        | 0.76367 | 0.00174 | 0.76541  | -0.00001 |
| C  | 34 | -0.24697 | 1.99887  | 4.23067 | 0.01743 | 6.24697  | -0.00009 |
| H  | 35 | 0.2368   | 0        | 0.76159 | 0.00161 | 0.7632   | 0.00001  |
| C  | 36 | -0.23818 | 1.99881  | 4.22211 | 0.01727 | 6.23818  | -0.00016 |
| H  | 37 | 0.23392  | 0        | 0.76433 | 0.00175 | 0.76608  | 0        |
| C  | 38 | -0.04467 | 1.9987   | 4.02825 | 0.01772 | 6.04467  | 0.00123  |
| C  | 39 | -0.66918 | 1.99916  | 4.65711 | 0.01291 | 6.66918  | 0.0008   |
| H  | 40 | 0.23914  | 0        | 0.7591  | 0.00176 | 0.76086  | 0.00003  |
| C  | 41 | -0.66478 | 1.99917  | 4.65291 | 0.01269 | 6.66478  | 0.00036  |
| H  | 42 | 0.2405   | 0        | 0.75608 | 0.00342 | 0.7595   | 0.00156  |
| C  | 43 | -0.06643 | 1.99884  | 4.0495  | 0.0181  | 6.06643  | 0.00094  |
| H  | 44 | 0.23389  | 0        | 0.76311 | 0.003   | 0.76611  | 0.00014  |
| H  | 45 | 0.21015  | 0        | 0.78653 | 0.00332 | 0.78985  | 0.00018  |
| C  | 46 | -0.49217 | 1.99906  | 4.47851 | 0.0146  | 6.49217  | 0.00004  |
| H  | 47 | 0.25217  | 0        | 0.74614 | 0.00169 | 0.74783  | -0.00014 |
| H  | 48 | 0.23761  | 0        | 0.75984 | 0.00255 | 0.76239  | 0.00001  |
| C  | 49 | -0.4933  | 1.99906  | 4.47969 | 0.01455 | 6.4933   | 0.00007  |
| H  | 50 | 0.25175  | 0        | 0.74659 | 0.00167 | 0.74825  | -0.00001 |
| H  | 51 | 0.2378   | 0        | 0.75978 | 0.00242 | 0.7622   | 0.00001  |
| C  | 52 | -0.06692 | 1.99889  | 4.04983 | 0.01819 | 6.06692  | 0.00108  |
| H  | 53 | 0.23145  | 0        | 0.76522 | 0.00333 | 0.76855  | 0.00047  |
| H  | 54 | 0.21344  | 0        | 0.78317 | 0.0034  | 0.78656  | 0.00016  |
| Sm | 55 | 1.32043  | 53.95364 | 6.1752  | 0.55072 | 60.67957 | 5.20124  |
| O  | 56 | -0.63342 | 1.99963  | 6.60898 | 0.02481 | 8.63342  | 0.00731  |
| N  | 57 | -0.7106  | 1.99902  | 5.66931 | 0.04227 | 7.7106   | -0.00418 |
| N  | 58 | -0.7437  | 1.99901  | 5.70686 | 0.03783 | 7.7437   | 0.00362  |



|   |    |          |         |         |         |         |          |
|---|----|----------|---------|---------|---------|---------|----------|
| C | 59 | -0.71634 | 1.99913 | 4.70687 | 0.01033 | 6.71634 | -0.00077 |
| H | 60 | 0.24671  | 0       | 0.7517  | 0.00159 | 0.75329 | 0.00014  |
| H | 61 | 0.24282  | 0       | 0.75587 | 0.00132 | 0.75718 | -0.00011 |
| H | 62 | 0.25342  | 0       | 0.74508 | 0.0015  | 0.74658 | 0.00028  |
| C | 63 | 0.33379  | 1.99856 | 3.64753 | 0.02013 | 5.66621 | 0.00723  |
| C | 64 | -0.46036 | 1.9987  | 4.4437  | 0.01795 | 6.46036 | -0.00057 |
| H | 65 | 0.23429  | 0       | 0.76416 | 0.00156 | 0.76571 | 0.00016  |
| C | 66 | 0.31886  | 1.99854 | 3.66264 | 0.01996 | 5.68114 | 0.00355  |
| C | 67 | -0.71388 | 1.99912 | 4.70425 | 0.01051 | 6.71388 | -0.00057 |
| H | 68 | 0.25251  | 0       | 0.74596 | 0.00153 | 0.74749 | 0.00013  |
| H | 69 | 0.24156  | 0       | 0.75718 | 0.00126 | 0.75844 | -0.00005 |
| H | 70 | 0.24766  | 0       | 0.75084 | 0.0015  | 0.75234 | 0.00012  |
| C | 71 | 0.17102  | 1.99834 | 3.80714 | 0.02349 | 5.82898 | 0.00389  |
| C | 72 | -0.03971 | 1.99869 | 4.02338 | 0.01764 | 6.03971 | 0.00234  |
| C | 73 | -0.23995 | 1.99882 | 4.22388 | 0.01725 | 6.23995 | -0.00069 |
| H | 74 | 0.23303  | 0       | 0.76519 | 0.00178 | 0.76697 | 0.00001  |
| C | 75 | -0.2525  | 1.99888 | 4.23576 | 0.01786 | 6.2525  | 0.0012   |
| H | 76 | 0.23453  | 0       | 0.76378 | 0.00169 | 0.76547 | -0.00004 |
| C | 77 | -0.23389 | 1.99881 | 4.21862 | 0.01646 | 6.23389 | -0.00008 |
| H | 78 | 0.23482  | 0       | 0.76347 | 0.00171 | 0.76518 | 0        |
| C | 79 | -0.0485  | 1.99867 | 4.03139 | 0.01844 | 6.0485  | 0.00143  |
| C | 80 | -0.66787 | 1.99916 | 4.65654 | 0.01216 | 6.66787 | 0.00043  |
| H | 81 | 0.24232  | 0       | 0.75454 | 0.00314 | 0.75768 | 0.0014   |
| C | 82 | -0.66639 | 1.99917 | 4.6542  | 0.01303 | 6.66639 | 0.00068  |
| H | 83 | 0.2407   | 0       | 0.75771 | 0.00159 | 0.7593  | 0.00007  |
| C | 84 | 0.16113  | 1.99831 | 3.81813 | 0.02243 | 5.83887 | 0.00436  |
| C | 85 | -0.05755 | 1.99861 | 4.03939 | 0.01955 | 6.05755 | 0.00149  |
| C | 86 | -0.23015 | 1.9988  | 4.21411 | 0.01724 | 6.23015 | 0.0007   |
| H | 87 | 0.23424  | 0       | 0.76411 | 0.00165 | 0.76576 | -0.00002 |
| C | 88 | -0.24249 | 1.99887 | 4.22609 | 0.01753 | 6.24249 | 0.00024  |
| H | 89 | 0.23747  | 0       | 0.76094 | 0.00159 | 0.76253 | -0.00001 |

|   |     |          |         |         |         |         |          |
|---|-----|----------|---------|---------|---------|---------|----------|
| C | 90  | -0.23004 | 1.99882 | 4.21424 | 0.01699 | 6.23004 | 0.00014  |
| H | 91  | 0.23566  | 0       | 0.76257 | 0.00177 | 0.76434 | -0.00002 |
| C | 92  | -0.04597 | 1.99869 | 4.03016 | 0.01712 | 6.04597 | 0.00052  |
| C | 93  | -0.65834 | 1.99909 | 4.64467 | 0.01457 | 6.65834 | -0.00078 |
| H | 94  | 0.24392  | 0       | 0.75439 | 0.00169 | 0.75608 | 0.00021  |
| C | 95  | -0.67503 | 1.99916 | 4.66455 | 0.01132 | 6.67503 | 0.00005  |
| H | 96  | 0.2467   | 0       | 0.75096 | 0.00234 | 0.7533  | 0.00035  |
| C | 97  | -0.07169 | 1.99881 | 4.05455 | 0.01833 | 6.07169 | 0.00119  |
| H | 98  | 0.24192  | 0       | 0.75484 | 0.00324 | 0.75808 | 0.00002  |
| H | 99  | 0.20684  | 0       | 0.79004 | 0.00312 | 0.79316 | 0.00019  |
| C | 100 | -0.48878 | 1.99906 | 4.47507 | 0.01465 | 6.48878 | 0.00006  |
| H | 101 | 0.25371  | 0       | 0.7446  | 0.00169 | 0.74629 | -0.00003 |
| H | 102 | 0.23794  | 0       | 0.75985 | 0.00221 | 0.76206 | 0.00003  |
| C | 103 | -0.49516 | 1.99906 | 4.48167 | 0.01443 | 6.49516 | 0.00012  |
| H | 104 | 0.25398  | 0       | 0.74448 | 0.00154 | 0.74602 | -0.00001 |
| H | 105 | 0.23958  | 0       | 0.75793 | 0.00249 | 0.76042 | 0        |
| C | 106 | -0.07283 | 1.99889 | 4.05537 | 0.01857 | 6.07283 | 0.00205  |
| H | 107 | 0.22931  | 0       | 0.76785 | 0.00284 | 0.77069 | 0.00001  |
| H | 108 | 0.21024  | 0       | 0.7862  | 0.00356 | 0.78976 | 0.00029  |
| H | 109 | 0.24688  | 0       | 0.75133 | 0.0018  | 0.75312 | 0.00005  |
| H | 110 | 0.24004  | 0       | 0.75865 | 0.00131 | 0.75996 | 0.00008  |
| H | 111 | 0.23957  | 0       | 0.75902 | 0.00141 | 0.76043 | 0.00002  |
| H | 112 | 0.24158  | 0       | 0.75539 | 0.00303 | 0.75842 | 0.00146  |
| H | 113 | 0.23942  | 0       | 0.75914 | 0.00145 | 0.76058 | 0.00002  |
| H | 114 | 0.24058  | 0       | 0.75589 | 0.00353 | 0.75942 | 0.00183  |
| H | 115 | 0.24695  | 0       | 0.75132 | 0.00174 | 0.75305 | 0.00002  |
| H | 116 | 0.23774  | 0       | 0.7609  | 0.00136 | 0.76226 | 0.00005  |
| H | 117 | 0.24389  | 0       | 0.75439 | 0.00172 | 0.75611 | 0.00014  |
| H | 118 | 0.23803  | 0       | 0.76061 | 0.00136 | 0.76197 | 0.00004  |
| H | 119 | 0.24105  | 0       | 0.75747 | 0.00148 | 0.75895 | 0.00002  |
| H | 120 | 0.23943  | 0       | 0.75745 | 0.00312 | 0.76057 | 0.00087  |

|         |     |          |           |           |         |         |          |
|---------|-----|----------|-----------|-----------|---------|---------|----------|
| H       | 121 | 0.24739  | 0         | 0.75122   | 0.00139 | 0.75261 | -0.00017 |
| H       | 122 | 0.22809  | 0         | 0.76605   | 0.00586 | 0.77191 | 0.00358  |
| H       | 123 | 0.24071  | 0         | 0.75722   | 0.00207 | 0.75929 | 0.00005  |
| H       | 124 | 0.24025  | 0         | 0.75827   | 0.00148 | 0.75975 | -0.00005 |
| C       | 125 | -0.54578 | 1.99827   | 4.50125   | 0.04625 | 6.54578 | -0.08266 |
| H       | 126 | 0.26783  | 0         | 0.72915   | 0.00302 | 0.73217 | 0.00376  |
| C       | 127 | -0.33276 | 1.99813   | 4.28626   | 0.04837 | 6.33276 | -0.12074 |
| C       | 128 | -0.60165 | 1.99824   | 4.55203   | 0.05138 | 6.60165 | -0.00459 |
| H       | 129 | 0.26586  | 0         | 0.73023   | 0.00391 | 0.73414 | 0.00237  |
| C       | 130 | -0.57457 | 1.99941   | 4.56026   | 0.0149  | 6.57457 | 0.00938  |
| H       | 131 | 0.22145  | 0         | 0.77392   | 0.00463 | 0.77855 | -0.00862 |
| H       | 132 | 0.23068  | 0         | 0.76697   | 0.00235 | 0.76932 | -0.00167 |
| H       | 133 | 0.21096  | 0         | 0.78703   | 0.00201 | 0.78904 | -0.00333 |
| C       | 134 | -0.54178 | 1.99827   | 4.49737   | 0.04614 | 6.54178 | -0.05727 |
| H       | 135 | 0.27249  | 0         | 0.7236    | 0.00391 | 0.72751 | 0.00297  |
| C       | 136 | -0.31204 | 1.99822   | 4.25891   | 0.0549  | 6.31204 | -0.12926 |
| C       | 137 | -0.58373 | 1.99832   | 4.53602   | 0.04939 | 6.58373 | -0.00318 |
| H       | 138 | 0.2638   | 0         | 0.73291   | 0.00329 | 0.7362  | 0.00193  |
| C       | 139 | -0.57566 | 1.9994    | 4.56031   | 0.01595 | 6.57566 | 0.01165  |
| H       | 140 | 0.21797  | 0         | 0.77991   | 0.00212 | 0.78203 | -0.00479 |
| H       | 141 | 0.23157  | 0         | 0.76589   | 0.00254 | 0.76843 | -0.00184 |
| H       | 142 | 0.19577  | 0         | 0.80073   | 0.0035  | 0.80423 | -0.01121 |
| *Total* |     | 0        | 235.83384 | 353.58819 | 2.57797 | 592     | 10       |

Average spin density on samarium: 5.15

Average charge on samarium: 1.38

Total charge of the bound *p*-xylene excluding two methyl groups (C+H)/(C): -1.69/-2.92

Average charge on nitrogen donors of the BDI ligand: -0.73

Average charge on oxygen of THF: -0.64

**Table. S13.** Calculated natural charges for **2-M** and **3-M** (M = Y and Sm).

| Cpd.                         | avg. M | Total (C+H)/(C) of the bound ring (excluding Me) | avg. N | avg. O | avg. Spin density of M |
|------------------------------|--------|--------------------------------------------------|--------|--------|------------------------|
| <b>2-Y</b>                   | 1.57   | -1.87/-3.49                                      | -0.67  | /      | /                      |
| <b>3-Y</b>                   | 1.69   | -2.02/-3.19                                      | -0.69  | /      | /                      |
| <b>2-Sm (<sup>11</sup>A)</b> | 1.22   | -1.56/-3.18                                      | -0.65  | -0.53  | 5.15                   |
| <b>3-Sm (<sup>11</sup>A)</b> | 1.38   | -1.69/-2.92                                      | -0.73  | -0.64  | 5.15                   |

**Table. S14.** Wiberg bond index for **2-M** and **3-M** (M = Y and Sm).

| Complexes                    | Avg. M–N | Avg. M–O | Avg. M–C | Avg. C–C for<br>the bound arene |
|------------------------------|----------|----------|----------|---------------------------------|
| <b>2-Y</b>                   | 0.23     | /        | 0.25     | 1.12                            |
| <b>3-Y</b>                   | 0.20     | /        | 0.22     | 1.12                            |
| <b>2-Sm (<sup>11</sup>A)</b> | 0.22     | 0.16     | 0.27     | 1.12                            |
| <b>3-Sm (<sup>11</sup>A)</b> | 0.19     | 0.14     | 0.24     | 1.11                            |

## S7. References

1. T. X. Gentner, B. Rösch, G. Ballmann, J. Langer, H. Elsen and S. Harder, *Angew. Chem. Int. Ed.*, 2019, **58**, 607-611.
2. B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eyselien, L. Zhao, C. Ding, G. Frenking and S. Harder, *Science*, 2021, **371**, 1125-1128.
3. D. E. Bergbreiter and J. M. Killough, *J. Am. Chem. Soc.*, 1978, **100**, 2126-2134.
4. K. Izod, S. T. Liddle and W. Clegg, *Inorg. Chem.*, 2004, **43**, 214-218.
5. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3-8.
6. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
7. G. Sheldrick, *Acta Crystallogr. Sect. C-Struct. Chem.*, 2015, **71**, 3-8.
8. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
9. A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
10. A. Spek, *Acta Crystallogr. Sect. C-Struct. Chem.*, 2015, **71**, 9-18.
11. F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73-78.
12. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
13. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
14. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
15. E. v. Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597-4610.
16. D. A. Pantazis and F. Neese, *J. Chem. Theory Comput.*, 2009, **5**, 2229-2238.
17. J. D. Rolfes, F. Neese and D. A. Pantazis, *J. Comput. Chem.*, 2020, **41**, 1842-1849.
18. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
19. E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429-1437.
20. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33-38.
21. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.