

## Electronic Supplementary Information

### Coplanar binuclear group 4 post-metallocene complexes supported by chelating $\mu$ -( $\sigma$ -aryl) ligands: characterisation and olefin polymerisation catalysis

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Experimental details and characterisation data for  $H_2L^{1-3}$  ligands and complexes **2**, **3**, **5**, **6** and **M1**; selected NMR spectra and data; polymerisation results.

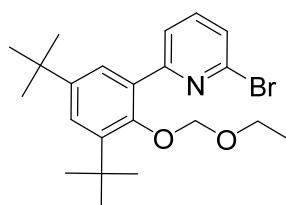
#### Experimental section

**General methods.** All reactions were performed using standard Schlenk techniques under an argon atmosphere or in a Braun dry-box under a nitrogen atmosphere. All solvents were appropriately dried and distilled then degassed prior to use.  $^1H$ ,  $^{13}C$  (referenced to residual solvent peaks) and  $^{19}F$  (external trifluoroacetic acid reference) NMR spectra were recorded at 298 K on a Bruker Avance 600 (or 400/300) FT-NMR spectrometer (ppm). Peak assignments were based on combinations of DEPT-135, and 2-D  $^1H$ - $^1H$ ,  $^{13}C$ - $^1H$  and NOE (plus [ $^1H$ , $^{19}F$ ]-COSY for **4–6**) correlation NMR experiments. The  $^1H$  NMR spectra of precursors, ligands and complexes are provided below. Elemental analyses were performed on a Vario EL elemental analyzer (Elementar Analysensysteme GmbH).

For polymer analysis, gel permeation chromatographs were obtained on a PL-GPC 220 instrument (at 1.0 mL/min versus polystyrene standards; 2  $\times$  PLgel Olexis (300 x 7.5 mm) Mixed B columns) at 150 °C in 1,2,4-trichlorobenzene. The polymer melting point was determined using a PerkinElmer STA6000 simultaneous thermal analyser under a nitrogen

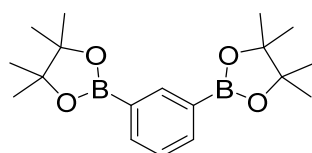
atmosphere: 1) polymer samples were first equilibrated at 30 °C, then heated to 170 °C at a rate of 10 °C/min, 2) this temperature was maintained for 5 min, then samples were cooled to 30 °C at a rate of 10 °C/min, 3) this temperature was maintained for 5 min, then samples were reheated to 170 °C at a rate of 10 °C/min, 4) the melting temperature ( $T_m$ ) was determined from the second heating scan. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer; polymer samples (4 mg) were pressed under 3.5 MPa into a transparent thin film, which was clipped using two KBr crystal plates for analysis.<sup>1</sup> Molecular structures were optimized using DFT calculations (M06L level,<sup>2</sup> using the Gaussian 16 program package<sup>3</sup>) with the LanL2DZ basis set<sup>4</sup> for transition metals and the 6-311G(d,p) basis set for non-metal atoms. The synthesis of H<sub>2</sub>L<sup>4</sup> and **I-1** were described previously.<sup>5,6</sup>

### Synthesis of I-2



Toluene (50 mL) was added to a mixture of **I-1** (5.00 g, 12.8 mmol), 2,6-dibromopyridine (3.34 g, 14.1 mmol), tetrakis(triphenylphosphine)palladium(0) (0.740 g, 0.640 mmol) and potassium phosphate tribasic (5.50 g, 25.6 mmol) at 20 °C under a nitrogen atmosphere. The mixture was stirred at 20 °C for 25 minutes and at 100 °C for 7 days. Upon cooling, the mixture was filtered through a thin layer of celite. The product was obtained as a white solid after purification by silica gel flash chromatography using *n*-hexane: ethyl acetate (40:1) as eluent. Yield: 4.00 g, 74%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.67 (d,  $J = 7.6$ , 1H), 7.55 (t,  $J = 7.7$  Hz, 1H), 7.49–7.39 (m, 3H), 4.61 (s, 2H), 3.53 (q,  $J = 7.1$  Hz, 2H), 1.46 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu), 1.11 (t,  $J = 7.1$  Hz, 3H).

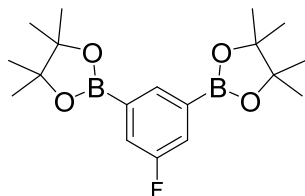
### Synthesis of I-3



Bis(pinacolato)diboron (12.9 g, 50.9 mmol), 1,3-dibromobenzene (5.00 g, 21.2 mmol), potassium acetate (12.5 g, 127.2 mmol), Pd(dppf)Cl<sub>2</sub> (1.55 g, 2.12 mmol) and dimethylformamide (50 mL) were combined in a 250 mL Schlenk flask and heated at 100 °C under a nitrogen atmosphere for three days. After extraction with ethyl acetate (40 mL), the

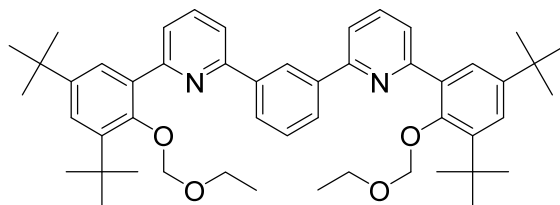
combined organic layers were dried over anhydrous magnesium sulphate. Evaporation of all volatiles by vacuum, and purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (50:1) as eluent, gave a white solid. Yield: 5.89 g, 84%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.28 (s, 1H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 1.34 (s, 24H).

### Synthesis of I-4



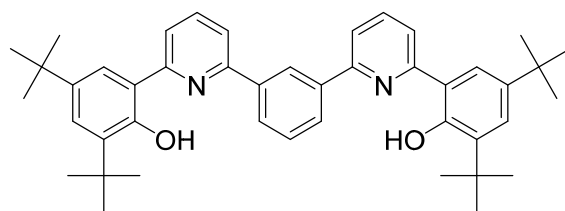
The procedure for the synthesis of **I-3** was adopted using bis(pinacolato)diboron (13.2 g, 51.9 mmol), 1,3-dibromo-5-fluorobenzene (6.00 g, 23.6 mmol), potassium acetate (14.0 g, 142.7 mmol), Pd(dppf)Cl<sub>2</sub> (1.73 g, 2.36 mmol) and toluene (100 mL). Yield: 6.41 g, 78%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 8.71 (d, *J* = 1.0 Hz, 1H), 7.95 (dd, *J* = 9.0, 1.0 Hz, 2H), 1.05 (s, 24H). <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>): δ -114.88.

### Synthesis of I-5



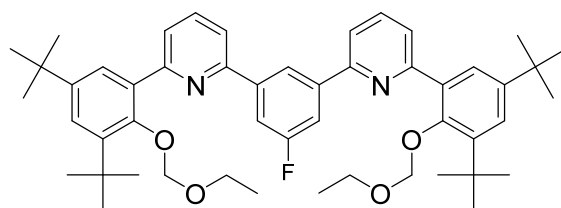
**I-2** (1.00g, 2.38 mmol), **I-3** (0.356 g, 1.08 mmol), potassium carbonate (0.896 g, 6.48 mmol), Pd(dppf)Cl<sub>2</sub> (0.0395 g, 0.0540 mmol), dioxane (10 mL) and H<sub>2</sub>O (2 mL) were combined in a 100 mL Schlenk flask and heated at 100 °C for 4 days under a nitrogen atmosphere. The resultant mixture was extracted with dichloromethane (50 mL) and the combined organic layers were dried over anhydrous magnesium sulphate. Evaporation of all volatiles by vacuum, and purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (20:1) as eluent, gave a pale yellow solid. Yield: 0.670 g, 82%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.37–8.01 (m, 1H), 7.86 (m, 1H), 7.76–7.67 (m, 2H), 7.66 (s, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.45–7.40 (m, 4H), 7.39 (d, *J* = 2.5 Hz, 2H), 4.61 (s, 4H), 3.53 (q, *J* = 7.0 Hz, 4H), 1.46 (s, 18H, *t*-Bu), 1.33 (s, 18H, *t*-Bu), 1.12 (t, *J* = 7.1 Hz, 6H).

## Synthesis of H<sub>4</sub>L<sup>1</sup>



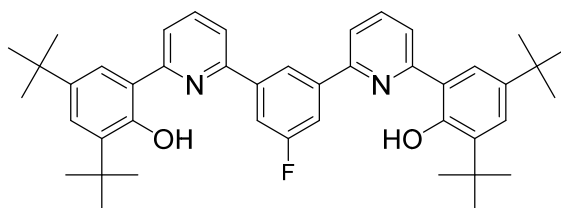
**I-5** (0.650 g, 0.885 mmol), concentrated hydrochloric acid (4 mL) and methanol (20 mL) were added into a 100 mL round-bottom flask and stirred at 60 °C for 12 hours. The resultant mixture was extracted with dichloromethane (50 mL) and washed with brine. The combined organic layers were dried over anhydrous magnesium sulphate. The product was obtained as a pale yellow solid after purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (20:1) as eluent. Yield: 0.499 g, 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 14.83 (s, 2H), 8.55 (s, 1H), 8.12 (d, *J* = 1.7 Hz, 1H), 8.10 (d, *J* = 1.7 Hz, 1H), 8.00–7.89 (m, 4H), 7.80–7.71 (m, 5H), 7.45 (d, *J* = 2.3 Hz, 2H), 1.53 (s, 18H, *t*-Bu), 1.39 (s, 18H, *t*-Bu).

## Synthesis of I-6



The procedure for the synthesis of **I-5** was adopted using **I-2** (1.50 g, 3.57 mmol), **I-4** (0.580 g, 1.67 mmol), potassium carbonate (1.38 g, 9.96 mmol), Pd(dppf)Cl<sub>2</sub> (0.0611 g, 0.0835 mmol), dioxane (10 mL) and H<sub>2</sub>O (2 mL). Yield: 1.03 g, 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.63 (t, *J* = 1.5 Hz, 1H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.96 (d, *J* = 1.5 Hz, 1H), 7.86–7.80 (m, 4H), 7.74–7.766 (m, 2H), 7.61 (d, *J* = 2.6 Hz, 2H), 7.49 (d, *J* = 2.6 Hz, 2H), 4.67 (s, 4H), 3.58 (q, *J* = 7.1 Hz, 4H), 1.53 (s, 18H, *t*-Bu), 1.39 (s, 18H, *t*-Bu), 1.12 (t, *J* = 7.0 Hz, 6H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -112.95.

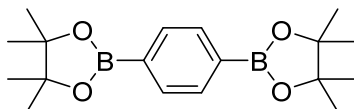
## Synthesis of H<sub>4</sub>L<sup>2</sup>



The procedure for the synthesis of H<sub>4</sub>L<sup>1</sup> was adopted using **I-6** (0.910 g, 1.17 mmol), concentrated hydrochloric acid (4 mL) and methanol (20 mL). Yield: 0.702 g, 90%. <sup>1</sup>H NMR

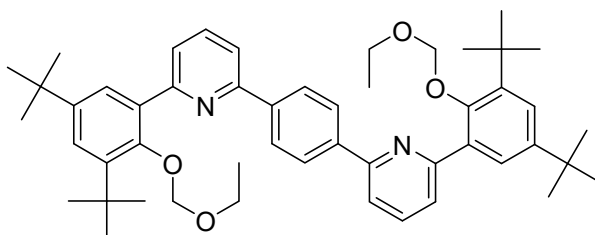
(400 MHz, CDCl<sub>3</sub>):  $\delta$  14.54 (s, 2H), 8.34 (t,  $J = 1.6$  Hz, 1H), 7.99–7.92 (m, 4H), 7.79 (d,  $J = 1.5$  Hz, 1H), 7.77 (d,  $J = 1.6$  Hz, 1H), 7.75 (d,  $J = 2.4$  Hz, 1H), 7.73 (d,  $J = 2.4$  Hz, 1H), 7.71 (d,  $J = 2.4$  Hz, 2H), 7.45 (d,  $J = 2.4$  Hz, 2H), 1.53 (s, 18H, *t*-Bu), 1.39 (s, 18H, *t*-Bu). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -110.70.

### Synthesis of I-7



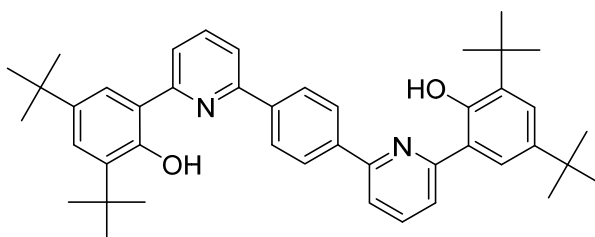
The procedure for the synthesis of **I-3** was adopted using bis(pinacolato)diboron (5.15 g, 20.3 mmol), 1,4-dibromobenzene (2.00 g, 8.48 mmol), potassium acetate (7.03 g, 50.9 mmol), Pd(dppf)Cl<sub>2</sub> (0.620 g, 0.848 mmol) and toluene (70 mL). Yield: 2.10 g, 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.80 (s, 4H), 1.35 (s, 24H).

### Synthesis of I-8



The procedure for the synthesis of **I-5** was adopted using **I-2** (1.00g, 2.38 mmol), **I-7** (0.356 g, 1.08 mmol), potassium carbonate (0.896 g, 6.48 mmol), Pd(dppf)Cl<sub>2</sub> (0.0395 g, 0.0540 mmol), dioxane (10 mL) and H<sub>2</sub>O (2 mL). Yield: 0.703 g, 86%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.26 (s, 4H), 7.84–7.75 (m, 4H), 7.69 (m, 2H), 7.59 (d,  $J = 2.5$  Hz, 2H), 7.45 (d,  $J = 2.6$  Hz, 2H), 4.66 (s, 4H), 3.56 (q,  $J = 7.1$  Hz, 4H), 1.50 (s, 18H), 1.37 (s, 18H), 1.11 (t,  $J = 7.1$  Hz, 6H).

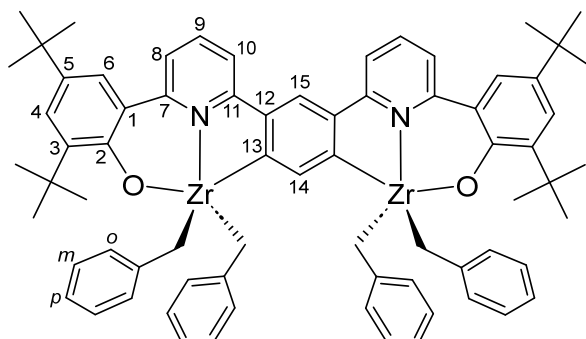
### Synthesis of H<sub>4</sub>L<sup>3</sup>



The procedure for the synthesis of H<sub>4</sub>L<sup>1</sup> was adopted using **I-8** (0.863 g, 1.14 mmol), concentrated hydrochloric acid (4 mL) and methanol (20 mL). Yield: 0.621 g, 85%. <sup>1</sup>H NMR

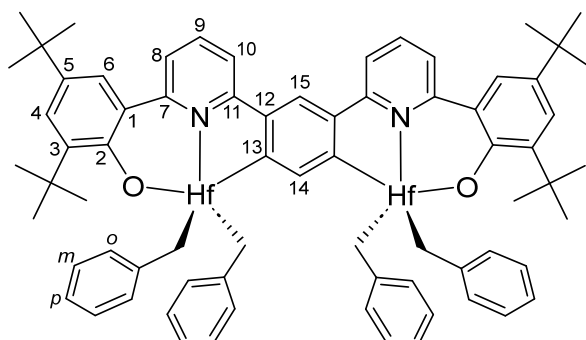
(300 MHz, CDCl<sub>3</sub>):  $\delta$  14.69 (s, 2H), 8.14 (s, 4H), 7.98–7.89 (m, 4H), 7.72 (d,  $J = 2.3$  Hz, 3H), 7.70 (d,  $J = 2.5$  Hz, 1H), 7.44 (d,  $J = 2.4$  Hz, 2H), 1.53 (s, 18H), 1.39 (s, 18H).

### Synthesis of complex 2



The procedure for the synthesis of complex 1 was adopted using H<sub>4</sub>L<sup>1</sup> (0.090 g, 0.140 mmol) and Zr(CH<sub>2</sub>Ph)<sub>4</sub> (0.132 g, 0.291 mmol). The resultant orange precipitate was collected and dried under vacuum. Yield: 0.096 g, 58%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub> with 3 drops of d<sub>8</sub>-THF):  $\delta$  9.72 (s, 1H, H<sup>14</sup>), 7.78 (s, 1H, H<sup>15</sup>), 7.70 (d,  $J = 2.0$  Hz, 2H, H<sup>4</sup>), 7.56 (d,  $J = 1.9$  Hz, 2H, H<sup>6</sup>), 7.43 (d,  $J = 7.8$  Hz, 2H, H<sup>8</sup>), 7.33 (d,  $J = 7.8$  Hz, 2H, H<sup>10</sup>), 7.19 (t,  $J = 7.8$  Hz, 2H, H<sup>9</sup>), 7.10 (d,  $J = 7.6$  Hz, 8H, *o*-Ph), 6.95 (t,  $J = 7.5$  Hz, 8H, *m*-Ph), 6.67 (t,  $J = 7.2$  Hz, 4H, *p*-Ph), 3.28 (d,  $J = 10.4$  Hz, 4H, CH<sub>2</sub>), 3.14 (d,  $J = 10.4$  Hz, 4H, CH<sub>2</sub>), 1.75 (s, 18H, 3-*t*-Bu), 1.39 (s, 18H, 5-*t*-Bu). <sup>13</sup>C NMR (151 MHz, C<sub>6</sub>D<sub>6</sub> with 3 drops of d<sub>8</sub>-THF):  $\delta$  193.42 (C<sup>13</sup>), 163.67 (C<sup>11</sup>), 158.28 (C<sup>7</sup>), 155.92 (C<sup>2</sup>), 145.73 (*ipso*-Ph), 143.46 (C<sup>12</sup>), 141.59 (C<sup>5</sup>), 141.36 (C<sup>14</sup>), 138.49 (C<sup>9</sup>), 137.69 (C<sup>3</sup>), 128.14 (*m*-Ph), 127.95 (*o*-Ph), 126.21 (C<sup>1</sup>), 125.87 (C<sup>4</sup>), 124.95 (C<sup>6</sup>), 121.80 (C<sup>8</sup>), 120.59 (*p*-Ph), 117.08 (C<sup>15</sup>), 115.70 (C<sup>10</sup>), 71.52 (<sup>1</sup>J<sub>C,H</sub> = 122.0 Hz, CH<sub>2</sub>), 35.45 (5-CMe<sub>3</sub>), 34.25 (3-CMe<sub>3</sub>), 31.48 (3-CMe<sub>3</sub>), 30.19 (5-CMe<sub>3</sub>). Anal. Calcd for C<sub>72</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>Zr<sub>2</sub> (1183.9): C, 73.05; H, 6.47; N, 2.37. Found: C, 73.35; H, 6.42; N, 2.30.

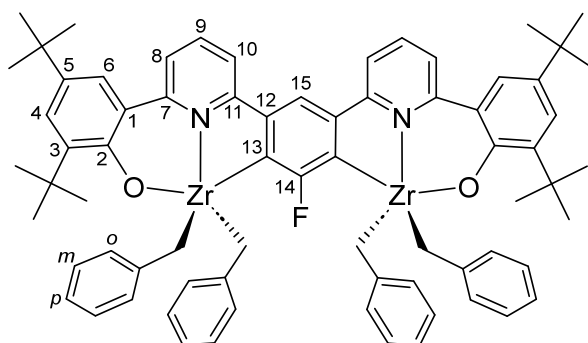
### Synthesis of complex 3



The procedure for the synthesis of complex 1 was adopted using H<sub>4</sub>L<sup>1</sup> (0.090 g, 0.140 mmol) and Hf(CH<sub>2</sub>Ph)<sub>4</sub> (0.158 g, 0.291 mmol). The resultant pale orange precipitate was collected

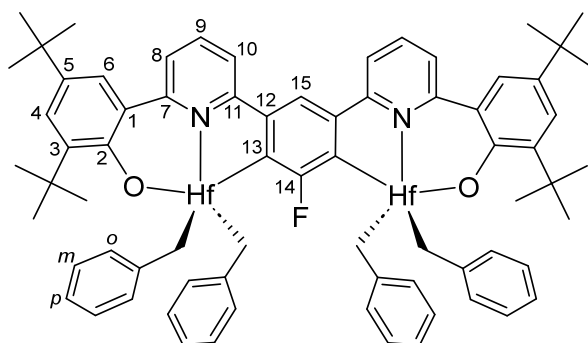
and dried under vacuum. Yield: 0.131 g, 69%.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  9.43 (s, 1H,  $\text{H}^{14}$ ), 7.73 (d,  $J = 2.3$  Hz, 2H,  $\text{H}^4$ ), 7.61 (s, 1H,  $\text{H}^{15}$ ), 7.44 (d,  $J = 2.2$  Hz, 2H,  $\text{H}^6$ ), 7.28 (d,  $J = 7.8$  Hz, 2H,  $\text{H}^8$ ), 7.10 (d,  $J = 7.8$  Hz, 2H,  $\text{H}^{10}$ ), 7.06 (d,  $J = 7.5$  Hz, 8H, *o*-Ph), 6.96 (t,  $J = 7.8$  Hz, 2H,  $\text{H}^9$ ), 6.83 (t,  $J = 7.6$  Hz, 8H, *m*-Ph), 6.59 (t,  $J = 7.3$  Hz, 4H, *p*-Ph), 2.96 (s, 8H,  $\text{CH}_2$ ), 1.79 (s, 18H, 3-*t*-Bu), 1.40 (s, 18H, 5-*t*-Bu).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  203.02 ( $\text{C}^{13}$ ), 164.14 ( $\text{C}^{11}$ ), 158.47 ( $\text{C}^7$ ), 155.91 ( $\text{C}^2$ ), 144.82 ( $\text{C}^{14}$ ), 144.45 ( $\text{C}^{12}$ ), 141.27 ( $\text{C}^5$ ), 139.11 ( $\text{C}^9$ ), 137.77 (*ipso*-Ph), 137.67 ( $\text{C}^3$ ), 129.60 (*o*-Ph), 128.65 (*m*-Ph), 126.61 ( $\text{C}^4$ ), 125.81 ( $\text{C}^1$ ), 124.61 ( $\text{C}^6$ ), 123.03 (*p*-Ph), 122.44 ( $\text{C}^8$ ), 117.17 ( $\text{C}^{15}$ ), 115.71 ( $\text{C}^{10}$ ), 77.59 ( $^1J_{\text{C,H}} = 127.4$  Hz,  $\text{CH}_2$ ), 35.37 (5- $\text{CMe}_3$ ), 34.23 (3- $\text{CMe}_3$ ), 31.51 (3- $\text{CMe}_3$ ), 30.29 (5- $\text{CMe}_3$ ). Anal. Calcd for  $\text{C}_{72}\text{H}_{76}\text{Hf}_2\text{N}_2\text{O}_2$  (1358.4): C, 63.66; H, 5.64; N, 2.06. Found: C, 63.43; H, 5.53; N, 1.88.

### Synthesis of complex 5



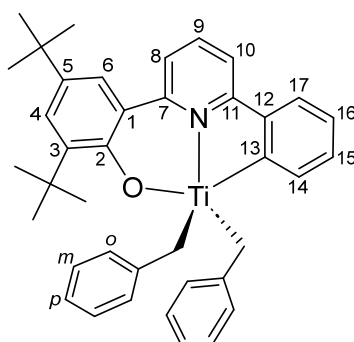
A mixture of *n*-pentane (10 mL) and THF (0.5 mL) was slowly added to  $\text{H}_4\text{L}^2$  (0.110 g, 0.167 mmol) and  $\text{Zr}(\text{CH}_2\text{Ph})_4$  (0.153 g, 0.337 mmol) at  $-78$  °C under an argon atmosphere. The reaction was stirred at  $-78$  °C for an hour and at 20 °C for 12 hours. The resultant dark orange precipitate was collected and dried under vacuum. Yield: 0.104 g, 52%.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$  with 10 drops of  $\text{d}_8$ -THF):  $\delta$  7.70 (d,  $J = 2.4$  Hz, 2H,  $\text{H}^4$ ), 7.46 (d,  $J = 2.4$  Hz, 2H,  $\text{H}^6$ ), 7.41 (d,  $J = 3.6$  Hz, 1H,  $\text{H}^{15}$ ), 7.27 (d,  $J = 8.1$  Hz, 3H,  $\text{H}^8$ ), 7.21–7.13 (m, 10H, *o*-Ph and  $\text{H}^{10}$ ), 7.01 (t,  $J = 7.8$  Hz, 2H,  $\text{H}^9$ ), 6.89 (t,  $J = 7.7$  Hz, 8H, *m*-Ph), 6.63 (t,  $J = 7.1$  Hz, 4H, *p*-Ph), 3.32 (d,  $J = 10.0$  Hz, 4H,  $\text{CH}_2$ ), 3.14 (d,  $J = 10.0$  Hz, 4H,  $\text{CH}_2$ ), 1.71 (s, 18H, 3-*t*-Bu), 1.40 (s, 18H, 5-*t*-Bu).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$  with 10 drops of  $\text{d}_8$ -THF):  $\delta$  172.94 (d,  $^2J_{\text{C,F}} = 77.0$  Hz,  $\text{C}^{13}$ ), 171.73 (d,  $^1J_{\text{C,F}} = 213.4$  Hz,  $\text{C}^{14}$ ), 163.25 ( $\text{C}^{11}$ ), 158.60 ( $\text{C}^7$ ), 155.21 ( $\text{C}^2$ ), 145.86 (d,  $^3J_{\text{C,F}} = 20.7$  Hz,  $\text{C}^{12}$ ), 141.62 ( $\text{C}^5$ ), 140.27 (*ipso*-Ph), 138.68 ( $\text{C}^9$ ), 137.06 ( $\text{C}^3$ ), 129.02 (*m*-Ph), 128.80 (*o*-Ph), 126.48 ( $\text{C}^1$ ), 126.36 ( $\text{C}^4$ ), 124.95 ( $\text{C}^6$ ), 122.76 ( $\text{C}^8$ ), 122.34 (*p*-Ph), 116.24 ( $\text{C}^{10}$ ), 114.64 ( $\text{C}^{15}$ ), 70.47 ( $^1J_{\text{C,H}} = 121.8$  Hz,  $\text{CH}_2$ ), 35.39 (3- $\text{CMe}_3$ ), 34.25 (5- $\text{CMe}_3$ ), 31.49 (5- $\text{CMe}_3$ ), 30.29 (3- $\text{CMe}_3$ ).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$  with 10 drops of  $\text{d}_8$ -THF):  $\delta$   $-63.76$ . Anal. Calcd for  $\text{C}_{72}\text{H}_{75}\text{FN}_2\text{O}_2\text{Zr}_2$  (1201.9): C, 71.96; H, 6.29; N, 2.33. Found: C, 72.13; H, 6.02; N, 2.18.

## Synthesis of complex 6



The procedure for the synthesis of complex **1** was adopted using  $\text{H}_4\text{L}^2$  (0.113 g, 0.208 mmol) and  $\text{Hf}(\text{CH}_2\text{Ph})_4$  (0.187 g, 0.344 mmol). The resultant orange precipitate was collected and dried under vacuum. Yield: 0.166 g, 70%.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$  with 3 drops of  $\text{d}_8$ -THF):  $\delta$  7.77–7.75 (m, 3H,  $\text{H}^4$  and  $\text{H}^{15}$ ), 7.53 (d,  $J = 2.4$  Hz, 2H,  $\text{H}^6$ ), 7.40 (d,  $J = 7.9$  Hz, 2H,  $\text{H}^8$ ), 7.25 (d,  $J = 7.3$  Hz, 2H,  $\text{H}^{10}$ ), 7.16–7.12 (m, 10H,  $\text{H}^9$  and *o*-Ph), 6.97 (t,  $J = 7.5$  Hz, 8H, *m*-Ph), 6.62 (t,  $J = 7.1$  Hz, 4H, *p*-Ph), 3.11 (d,  $J = 11.6$  Hz, 4H,  $\text{CH}_2$ ), 2.94 (d,  $J = 11.6$  Hz, 4H,  $\text{CH}_2$ ), 1.85 (s, 18H, 3-*t*-Bu), 1.41 (s, 18H, 5-*t*-Bu).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$  with 3 drops of  $\text{d}_8$ -THF):  $\delta$  180.40 (d,  $^2J_{\text{C,F}} = 75.5$  Hz,  $\text{C}^{13}$ ), 174.04 (d,  $^1J_{\text{C,F}} = 217.4$  Hz,  $\text{C}^{14}$ ), 163.16 ( $\text{C}^{11}$ ), 158.70 ( $\text{C}^7$ ), 155.81 ( $\text{C}^2$ ), 148.42 (d,  $^3J_{\text{C,F}} = 21.1$  Hz,  $\text{C}^{12}$ ), 148.20 (*ipso*-Ph), 141.85 ( $\text{C}^5$ ), 138.88 ( $\text{C}^9$ ), 138.39 ( $\text{C}^3$ ), 127.35 (*m*-Ph), 126.82 (*o*-Ph), 126.54 ( $\text{C}^4$ ), 125.51 ( $\text{C}^1$ ), 124.79 ( $\text{C}^6$ ), 122.07 ( $\text{C}^8$ ), 120.05 (*p*-Ph), 116.57 ( $\text{C}^{10}$ ), 116.33 ( $\text{C}^{15}$ ), 80.33 ( $^1J_{\text{C,H}} = 117.6$  Hz,  $\text{CH}_2$ ), 35.53 (3- $\text{CMe}_3$ ), 34.20 (5- $\text{CMe}_3$ ), 31.58 (5- $\text{CMe}_3$ ), 30.32 (3- $\text{CMe}_3$ ).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$  with 3 drops of  $\text{d}_8$ -THF):  $\delta$  -59.01. Anal. Calcd for  $\text{C}_{72}\text{H}_{75}\text{FHf}_2\text{N}_2\text{O}_2$  (1376.4): C, 62.83; H, 5.49; N, 2.04. Found: C, 62.70; H, 5.26; N, 1.98.

## Synthesis of complex M1

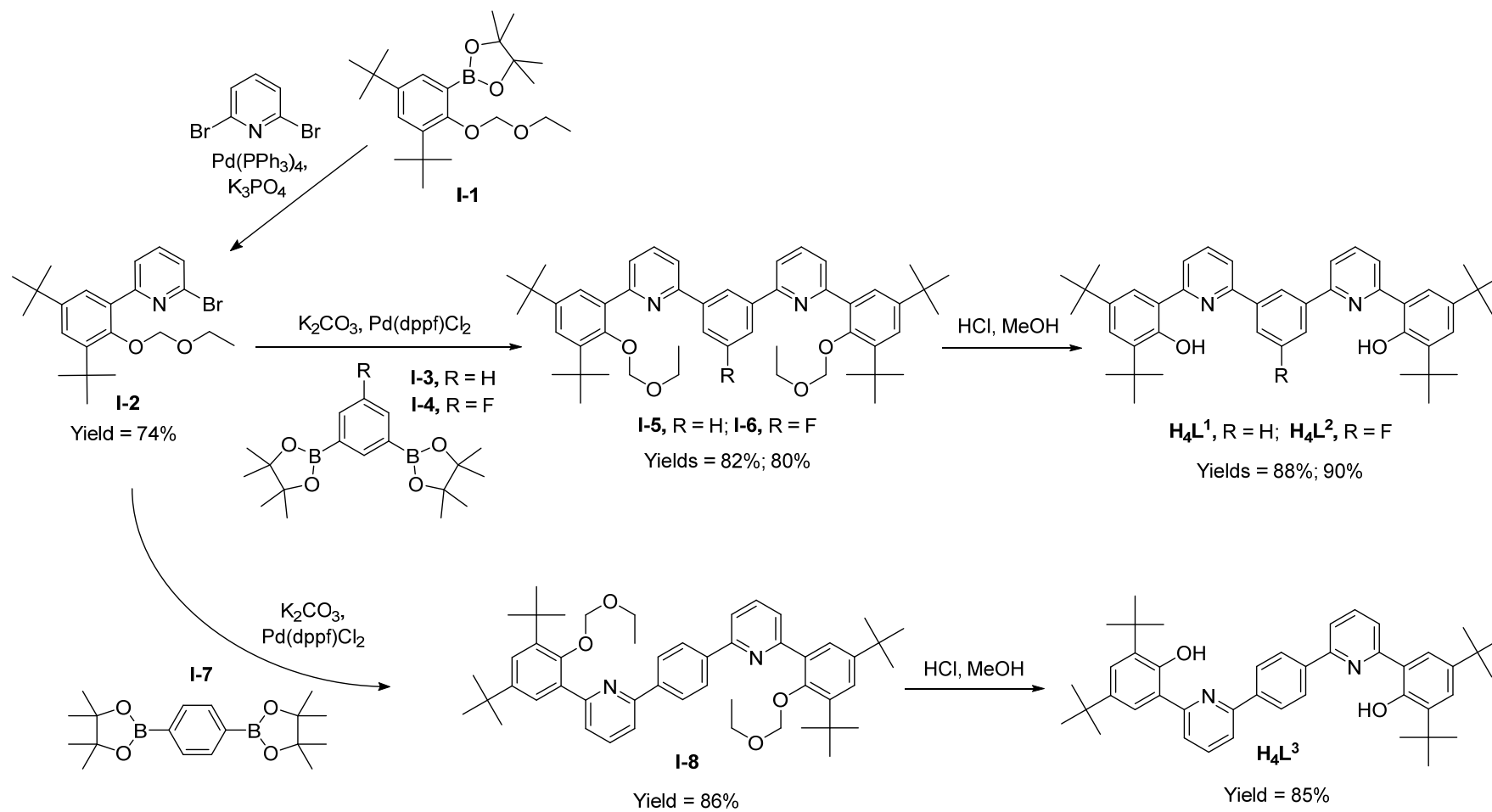


A solution of  $\text{H}_2\text{L}^4$  (0.100 g, 0.278 mmol) in *n*-pentane (8 mL) was added dropwise to  $\text{Ti}(\text{CH}_2\text{Ph})_4$  (0.119 g, 0.289 mmol) in *n*-pentane (5 mL) at  $-20$  °C under an argon atmosphere. The reaction was stirred at  $-20$  °C for one hour and at  $20$  °C for 12 hours, after which half of the volume of solvent was removed by vacuum. The product was obtained as a dark red solid,



from the filtrate of the mixture, after storage at  $-20\text{ }^{\circ}\text{C}$  for 12 hours. Yield: 0.110 g, 67%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.53 (d,  $J = 6.8\text{ Hz}$ , 1H,  $\text{H}^{14}$ ), 7.70 (d,  $J = 2.4\text{ Hz}$ , 1H,  $\text{H}^4$ ), 7.42 (d,  $J = 2.4\text{ Hz}$ , 1H,  $\text{H}^6$ ), 7.31 (td,  $J = 6.8\text{ Hz}$ , 1.2 Hz, 1H,  $\text{H}^{15}$ ), 7.21–7.10 (m, 3H,  $\text{H}^8$ ,  $\text{H}^{16}$  and  $\text{H}^{17}$ ), 6.78 (d,  $J = 7.2\text{ Hz}$ , 4H, *o*-Ph), 6.75–6.69 (m, 2H,  $\text{H}^9$  and  $\text{H}^{10}$ ), 6.59 (t,  $J = 7.8\text{ Hz}$ , 4H, *m*-Ph), 6.42 (t,  $J = 7.4\text{ Hz}$ , 2H, *p*-Ph), 4.20 (d,  $J = 8.3\text{ Hz}$ , 2H,  $\text{CH}_2$ ), 3.96 (d,  $J = 8.3\text{ Hz}$ , 2H,  $\text{CH}_2$ ), 1.84 (s, 9H, 3-*t*-Bu), 1.36 (s, 9H, 5-*t*-Bu).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  200.82 ( $\text{C}^{13}$ ), 139.17 ( $\text{C}^9$ ), 135.25 ( $\text{C}^{14}$ ), 131.22 (*o*-Ph), 129.13 ( $\text{C}^{15}$ ), 128.31 ( $\text{C}^{16}$ ), 127.80 (*m*-Ph), 126.70 ( $\text{C}^4$ ), 124.29 ( $\text{C}^6$ ), 123.50 (*p*-Ph), 122.27 ( $\text{C}^{17}$ ), 121.92 ( $\text{C}^8$ ), 114.93 ( $\text{C}^{10}$ ), 93.20 ( $^1J_{\text{C,H}} = 134.3\text{ Hz}$ ,  $\text{CH}_2$ ), 35.73 (3- $\text{CMe}_3$ ), 34.58 (5- $\text{CMe}_3$ ), 31.74 (5- $\text{CMe}_3$ ), 30.87 (3- $\text{CMe}_3$ );  $4^{\circ}$  carbons: 164.07, 157.44, 157.10, 142.02, 141.73, 137.41, 136.85, 127.04. Anal. Calcd for  $\text{C}_{39}\text{H}_{41}\text{NOTi}$  (587.6): C, 79.71; H, 7.03; N, 2.38. Found: C, 79.32; H, 7.13; N, 2.22.

**Polymerisation procedures.** Schlenk-line ethylene polymerisation tests were carried out under atmospheric pressure in toluene in a 100 mL glass reactor containing a magnetic stir bar, which was equilibrated at the required temperature. The reactor was maintained under 1 atmosphere of continuous ethylene supply for the duration of the experiment. Polymerisation was initiated by adding a toluene solution of the cocatalyst ( $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^i\text{Bu}_3\text{Al}$ ) with stirring. After the prescribed reaction time, 10% HCl in methanol (40 mL) was added to terminate the polymerisation, the ethylene gas feed was stopped, and the resultant mixture was allowed to stir at  $80\text{ }^{\circ}\text{C}$  for 1 hour. The polymer was collected by filtration, washed with methanol (20 mL), and dried under vacuum at  $80\text{ }^{\circ}\text{C}$  for 12 hours to a constant weight. The same procedure was adopted for ethylene/1-octene copolymerisation tests, except the 1-octene substrate was combined with the toluene solution of the cocatalyst before polymerisation. Errors for catalytic activities are estimated to be  $\pm 10\%$ , based on previous polymerisation tests using the same experimental procedure.



**Scheme S1.** Synthesis of H<sub>4</sub>L<sup>1-3</sup>.

**Table S1.** Selected NMR parameters (600 MHz, 298 K) for complexes **1–7** and **M1**

Complex, M	$CH_2$ (ppm)	$C_{\text{methylene}}$ (ppm)	$^2J_{\text{H,H}}$ (Hz)	$^1J_{\text{C,H}}$ (Hz)	$C^{13}$ (ppm)	$H^{14}$ (ppm)
<b>1</b> , Ti <sub>2</sub> <sup>a</sup>	4.15, 4.58	93.64	8.8	134.5	203.8	10.14
<b>2</b> , Zr <sub>2</sub> <sup>b</sup>	3.14, 3.28	71.52	10.4	122.0	193.4	9.72
<b>3</b> , Hf <sub>2</sub> <sup>a</sup>	2.96	77.59	–	127.4	203.0	9.43
<b>4</b> , Ti <sub>2</sub> <sup>b</sup>	4.36, 4.90	96.72	8.7	131.9	183.5	–
<b>5</b> , Zr <sub>2</sub> <sup>b</sup>	3.14, 3.32	70.47	10.0	121.8	172.9	–
<b>6</b> , Hf <sub>2</sub> <sup>b</sup>	2.93, 3.10	80.33	11.6	117.6	180.4	–
<b>7</b> , Ti <sub>2</sub> <sup>b</sup>	3.65, 4.06	94.05	9.1	128.5	205.4	8.82
<b>M1</b> , Ti <sup>a</sup>	3.96, 4.20	93.20	8.3	134.3	200.8	8.53

<sup>a</sup> C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> C<sub>6</sub>D<sub>6</sub> with d<sub>8</sub>-THF.

Figure S1. Full (bottom) and expanded (top)  $^1\text{H}$  NMR spectra of complex **1** (600 MHz,  $\text{C}_6\text{D}_6$ , 298 K).

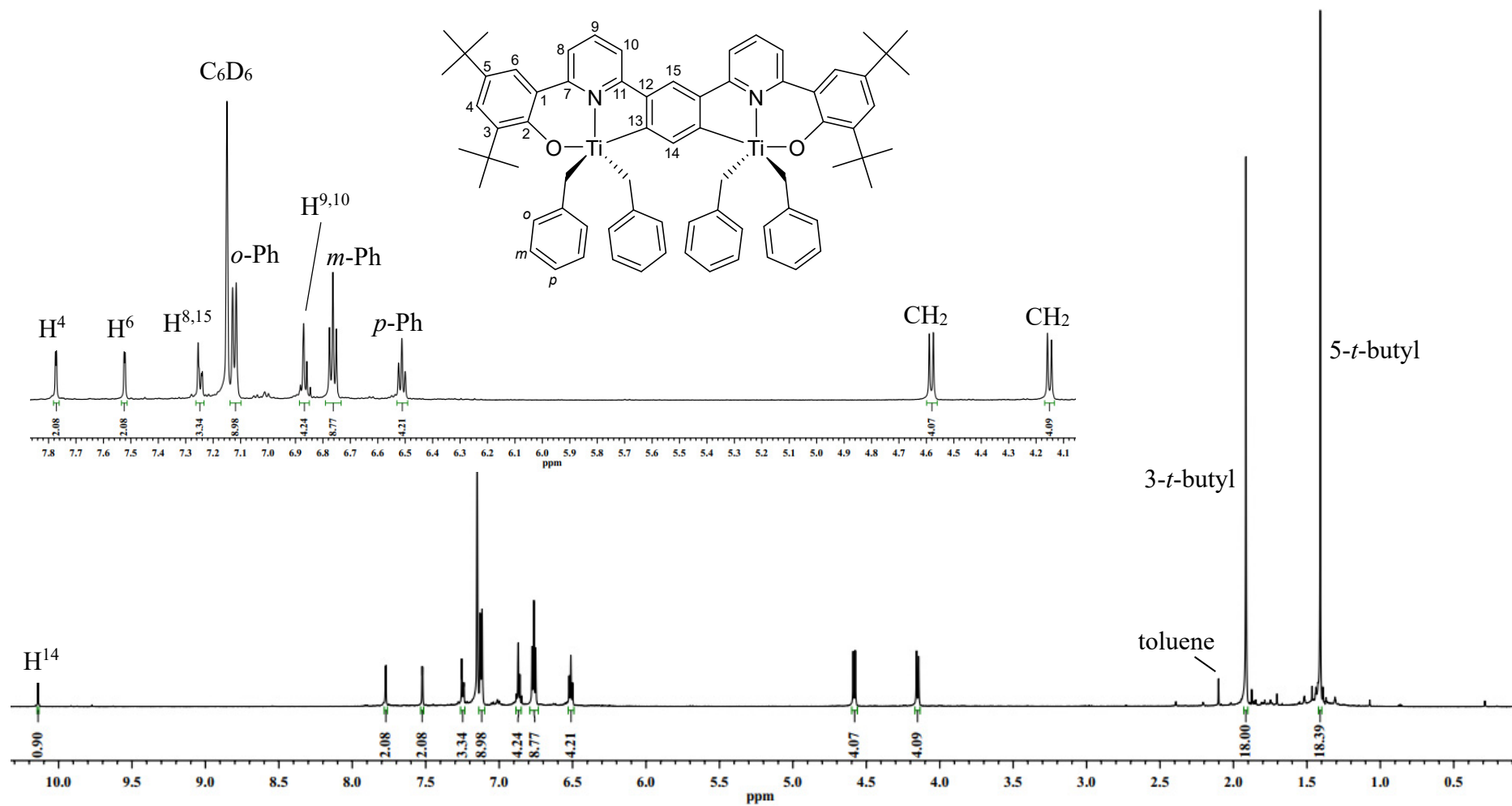
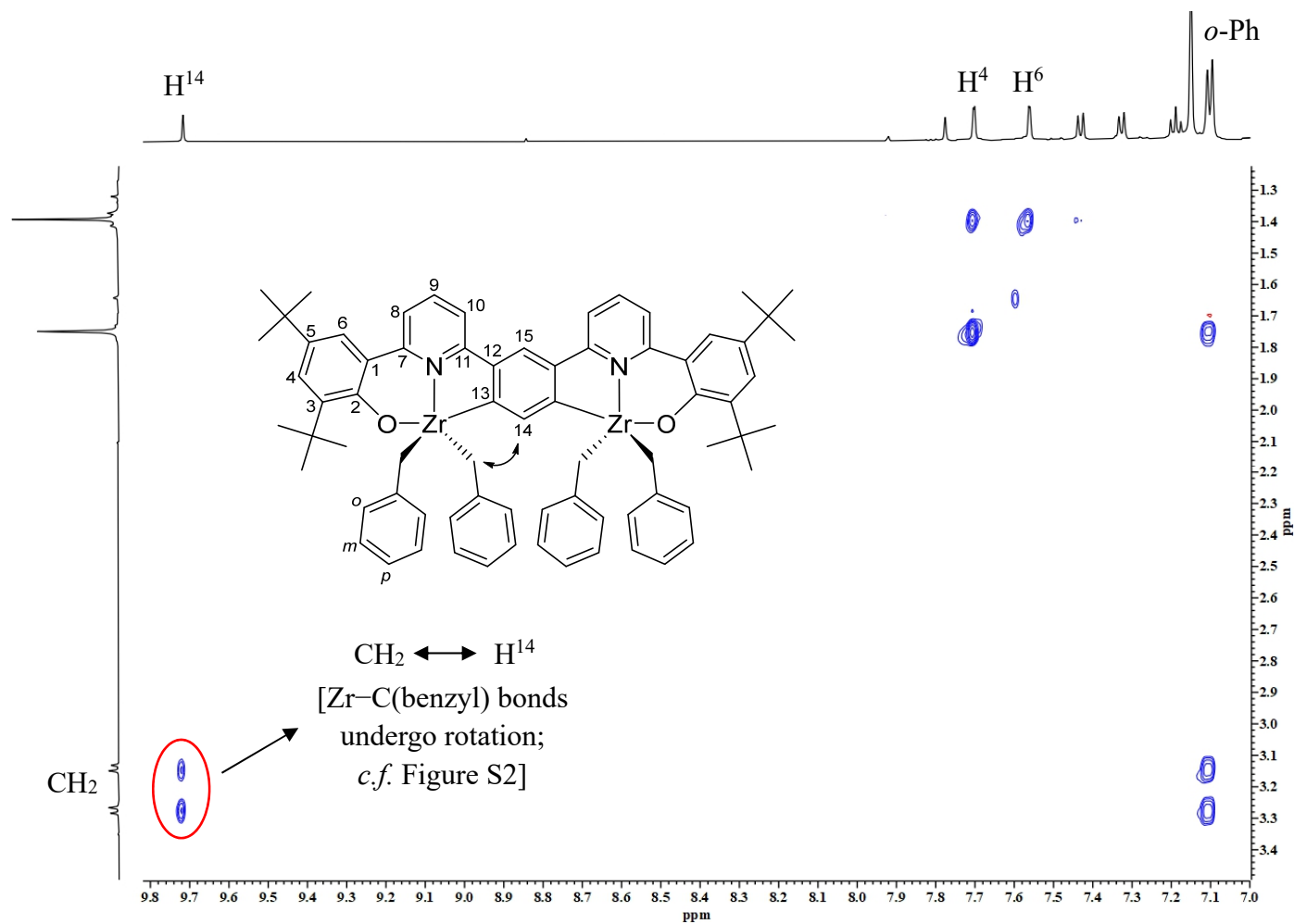
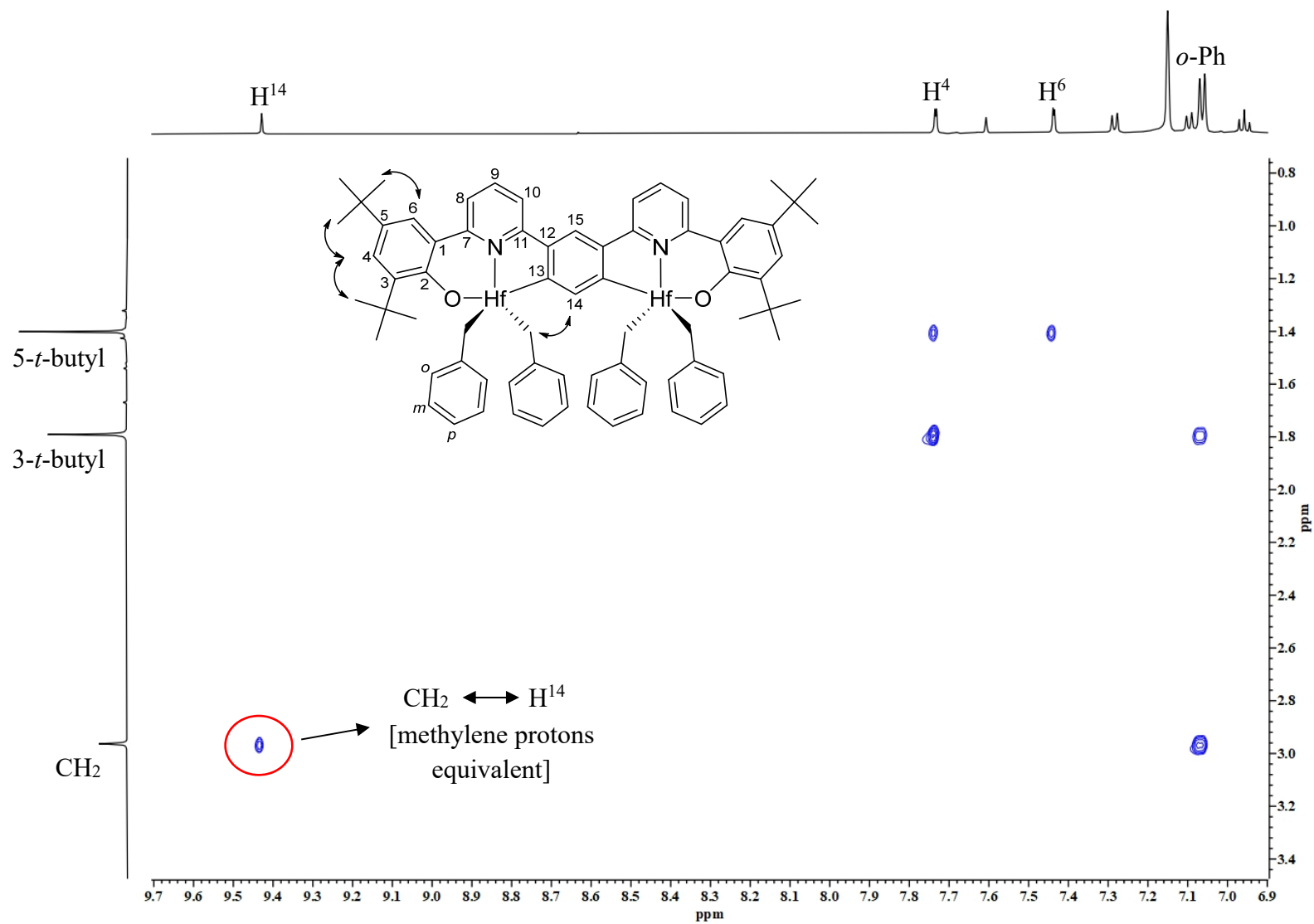




Figure S3. Expanded  $[\text{}^1\text{H}, \text{}^1\text{H}]$ -ROESY spectrum of complex **2** (600 MHz,  $\text{C}_6\text{D}_6$  with  $\text{d}_8$ -THF, 298 K).



**Figure S4.** Expanded  $[\text{}^1\text{H}, \text{}^1\text{H}]$ -ROESY spectrum of complex **3** (600 MHz,  $\text{C}_6\text{D}_6$ , 298 K).



**Figure S5.** Expanded  $[\text{H}, \text{H}]$ -ROESY spectra of complex **7** (600 MHz,  $\text{C}_6\text{D}_6$  with  $\text{d}_8$ -THF, 298 K).

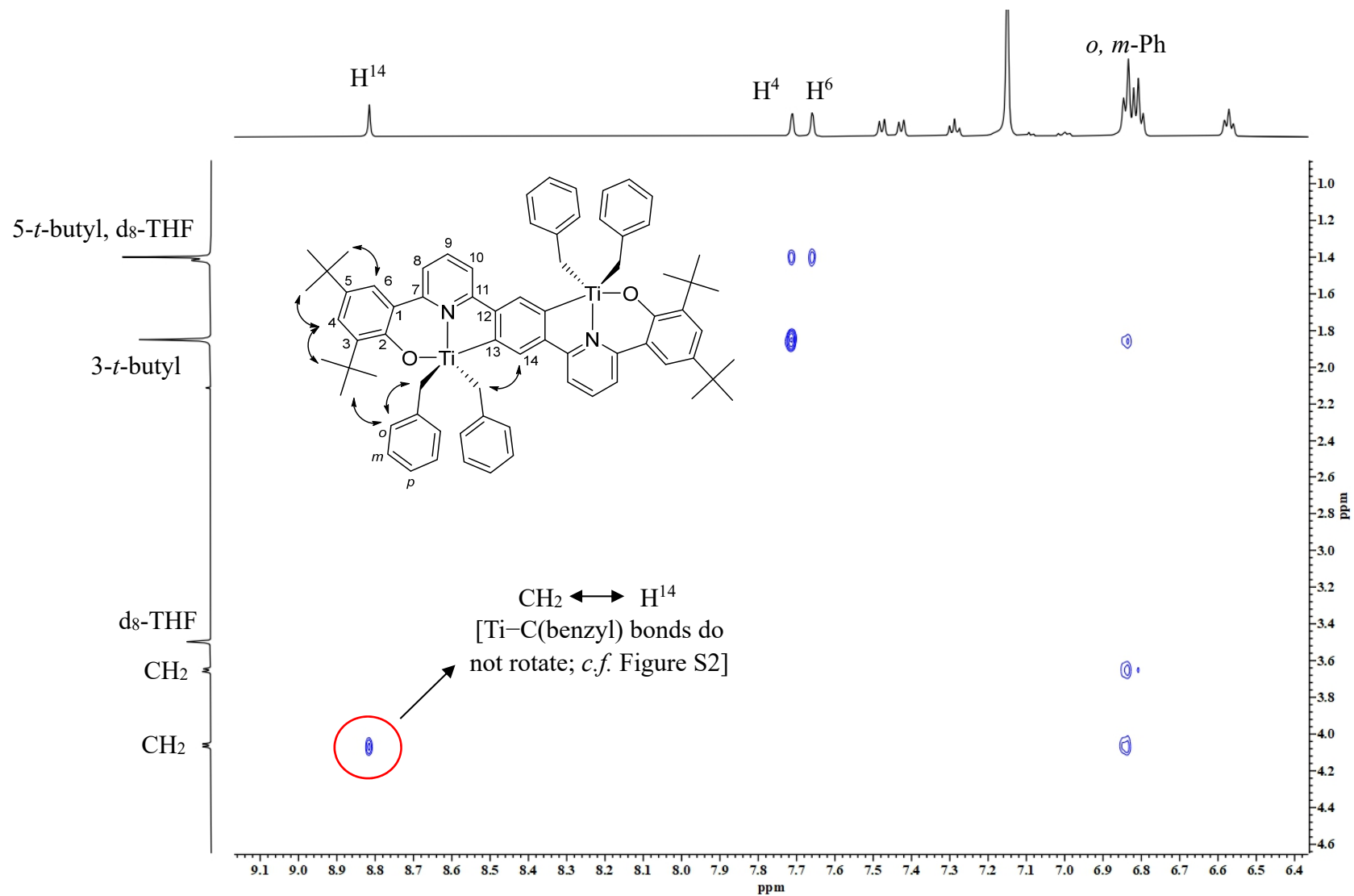
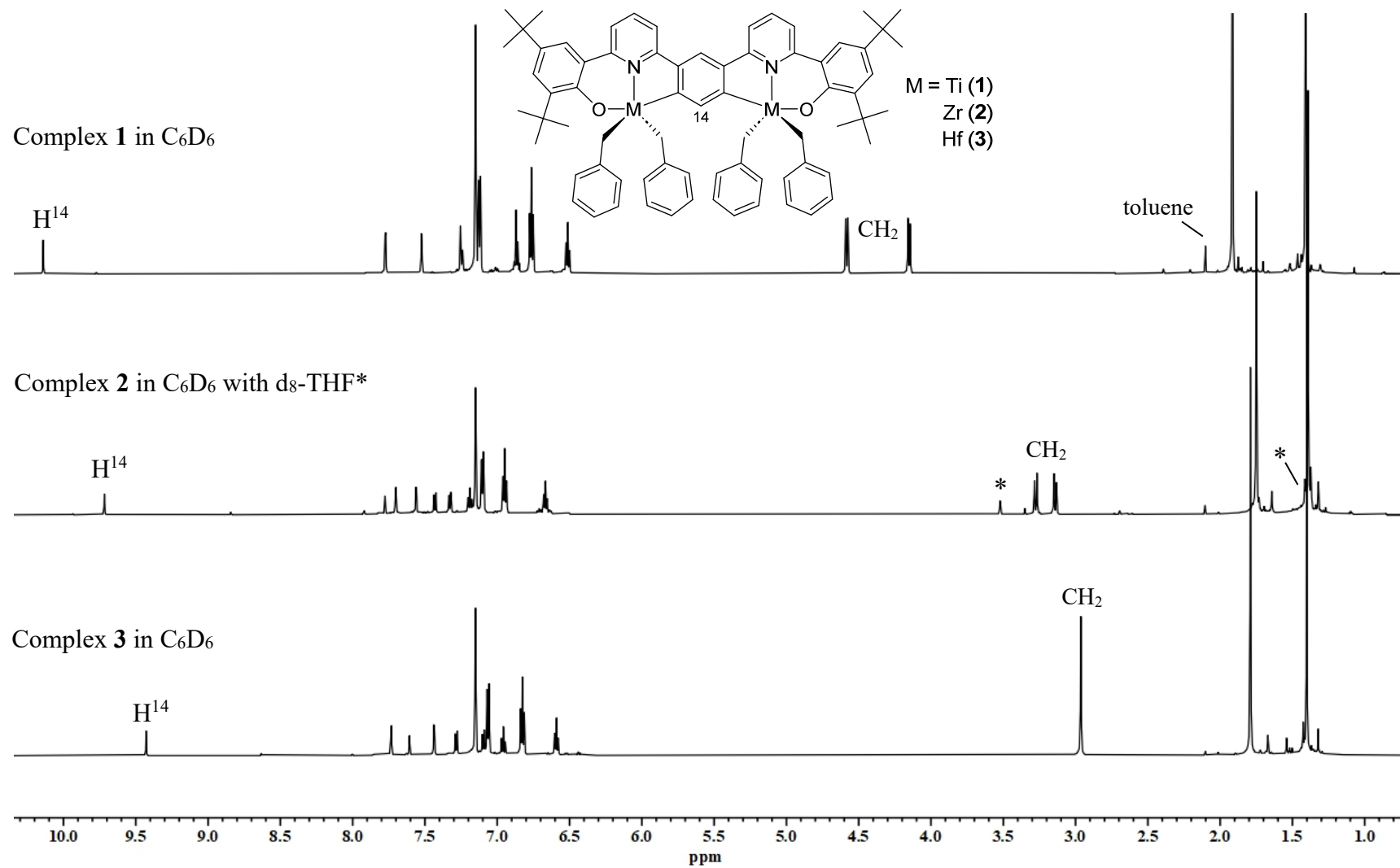
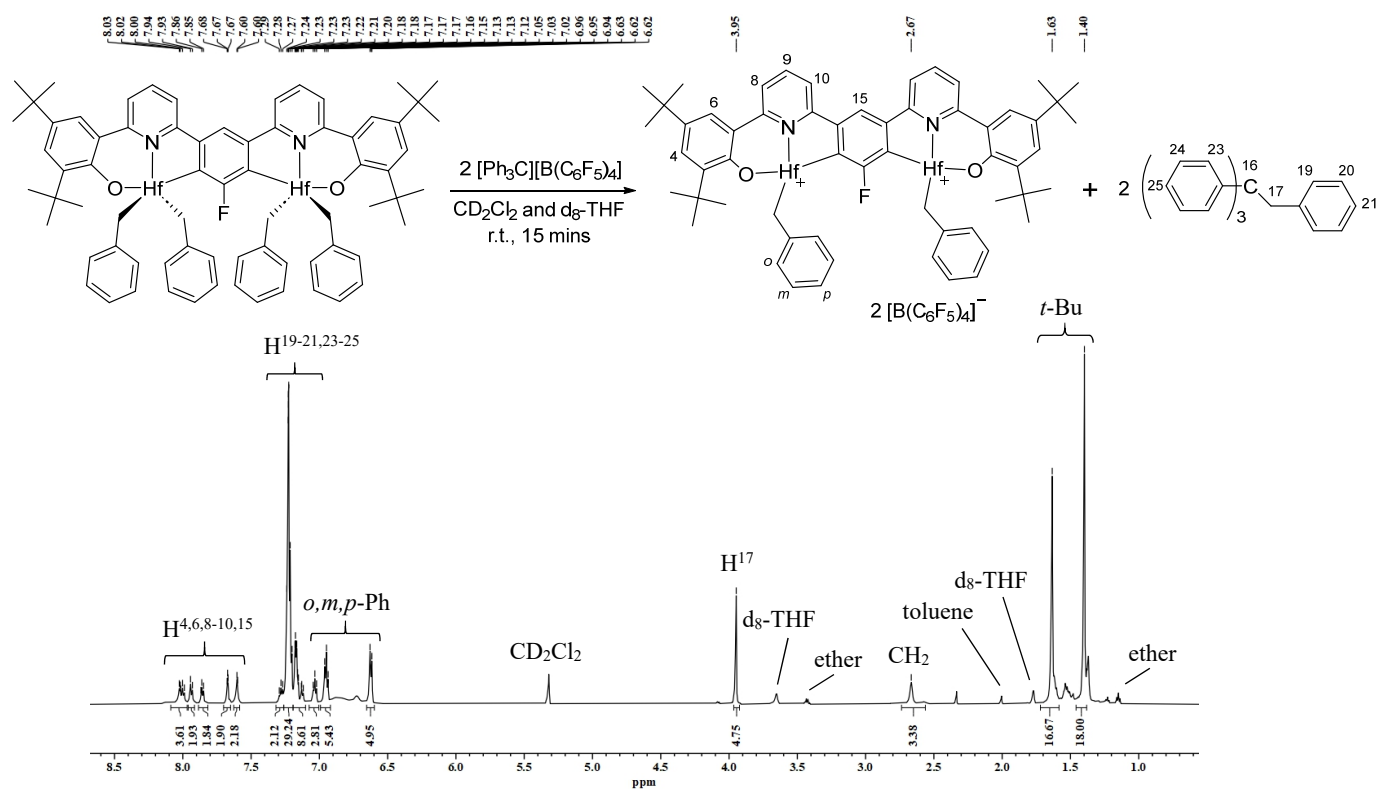




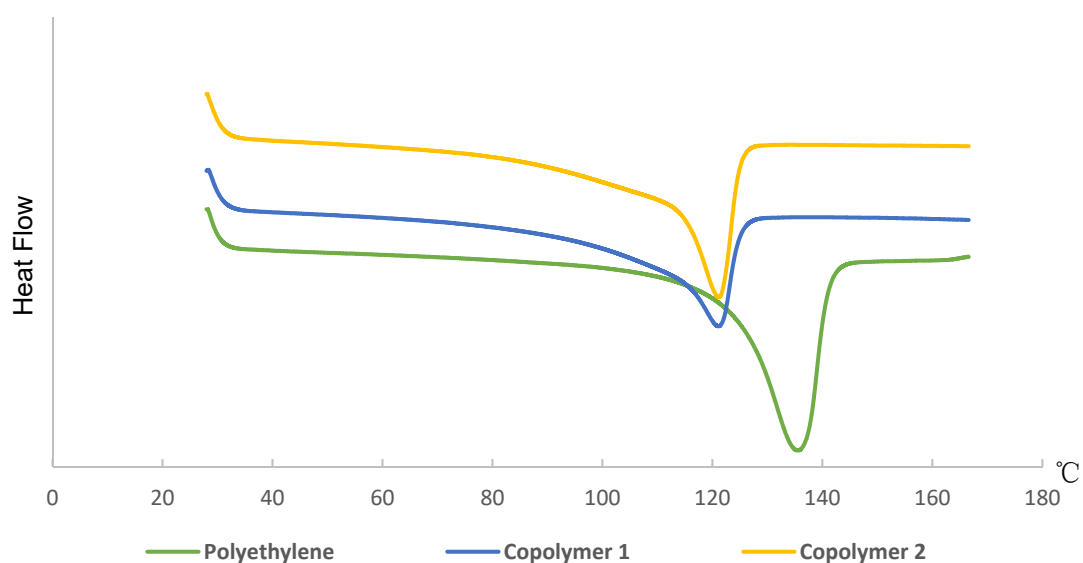
Figure S6.  $^1\text{H}$  NMR spectra of complexes 1–3 (600 MHz, 298 K).



**Figure S7.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CD}_2\text{Cl}_2$  with 3 drops of  $\text{d}_8\text{-THF}$ , 298 K) for dication derived from reaction of complex **6** with 2 equiv. of trityl borate.

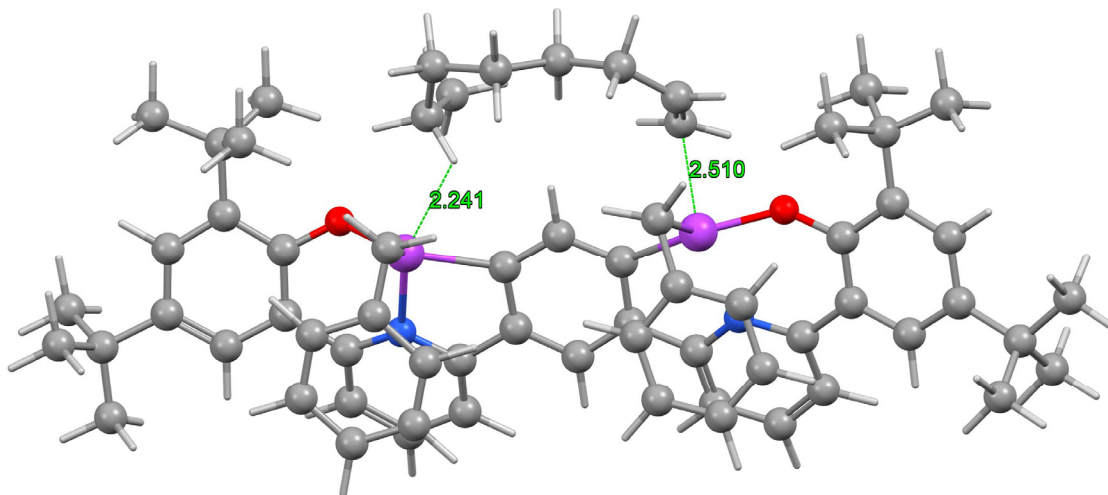


**Figure S8.** DSC profiles for **Polyethylene** (Table 1, entry 1) and **Copolymer 1** (Table S2, entry 1), both produced by catalyst **1**, and **Copolymer 2** (Table S2, entry 2) produced by catalyst **4**.

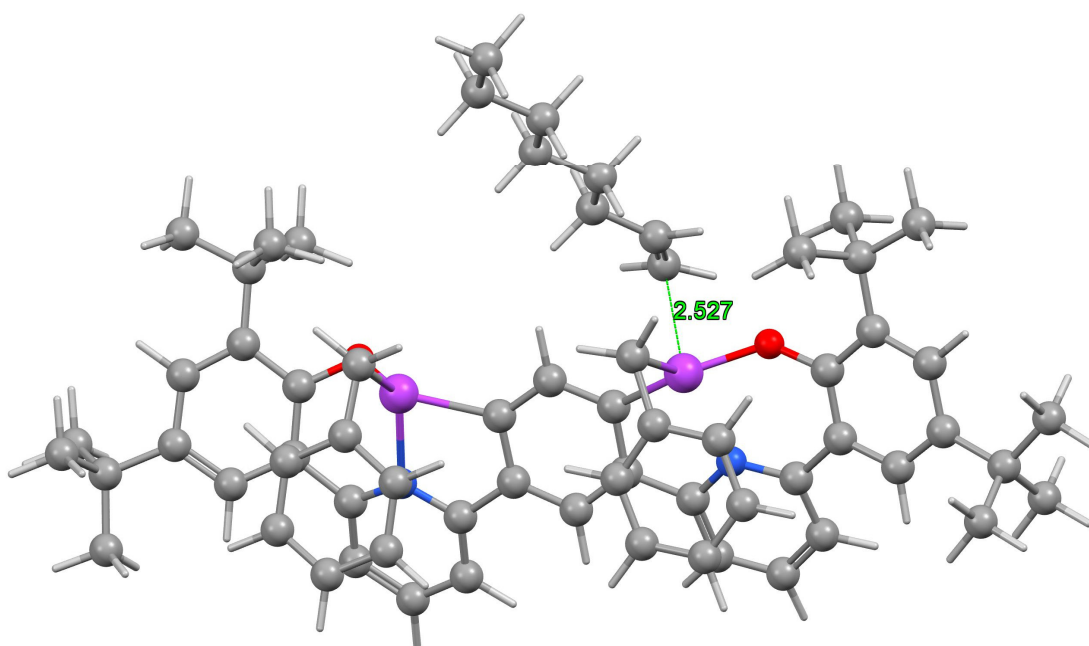


**Figure S9.** Energy-minimised calculated (Gaussian) structures for  $\pi$ (octene)-complex of  $1^{2+}$  (generated by abstraction of one benzyl group from each Ti).

Agostic structure:  $\text{Ti}\cdots\text{Ti} = 6.200 \text{ \AA}$ ;  $\text{Ti}-\text{C}(\pi) = 2.510 \text{ \AA}$ ;  
 $\text{Ti}\cdots\text{H}(\text{agostic}) = 2.241 \text{ \AA}$  [effective charge for "agostic" Ti = +1.19].

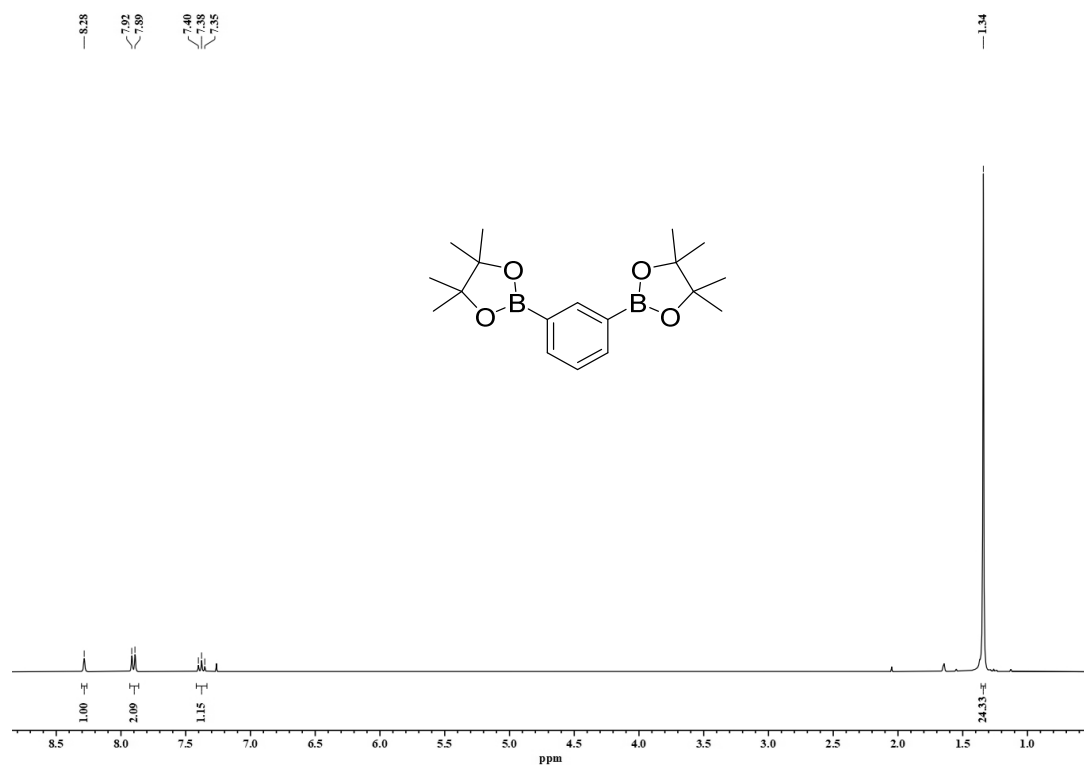


Non-agostic structure (less stable by 7.20 kcal/mol):  $\text{Ti}\cdots\text{Ti} = 6.230 \text{ \AA}$ ;  $\text{Ti}-\text{C}(\pi) = 2.527 \text{ \AA}$ ;  
[effective charge for "non-agostic" Ti = +1.26].





**Figure S10.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz, 298 K) of I-2.



**Figure S11.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz, 298 K) of I-3.

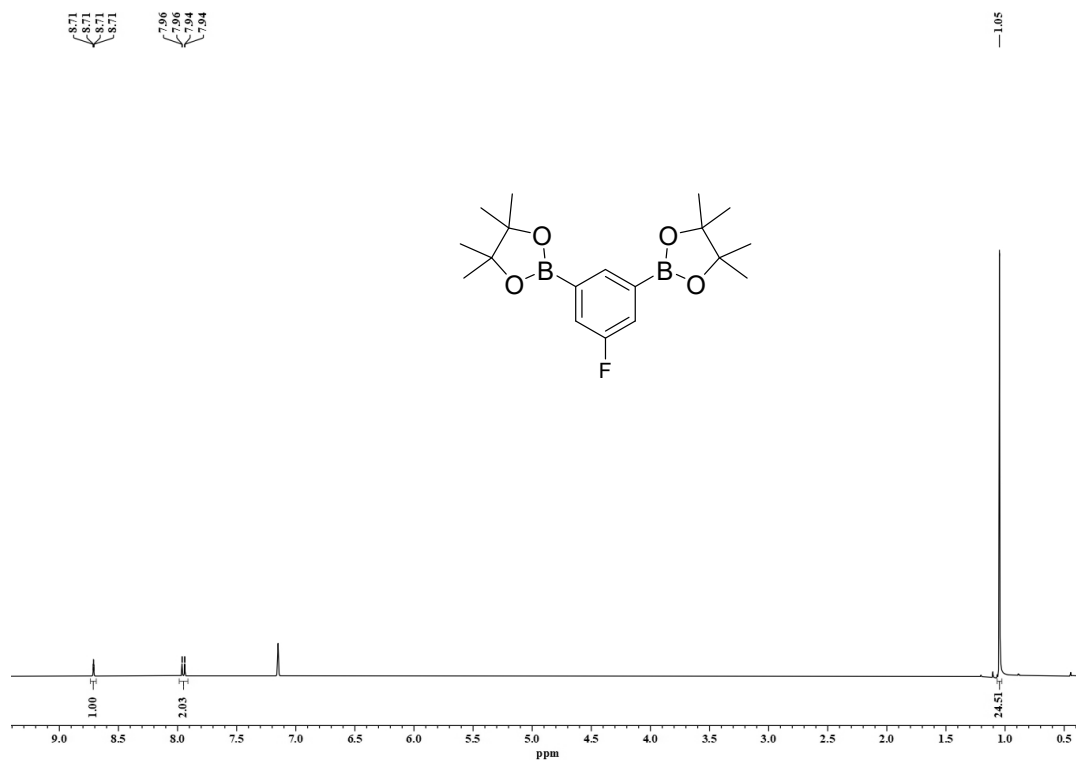
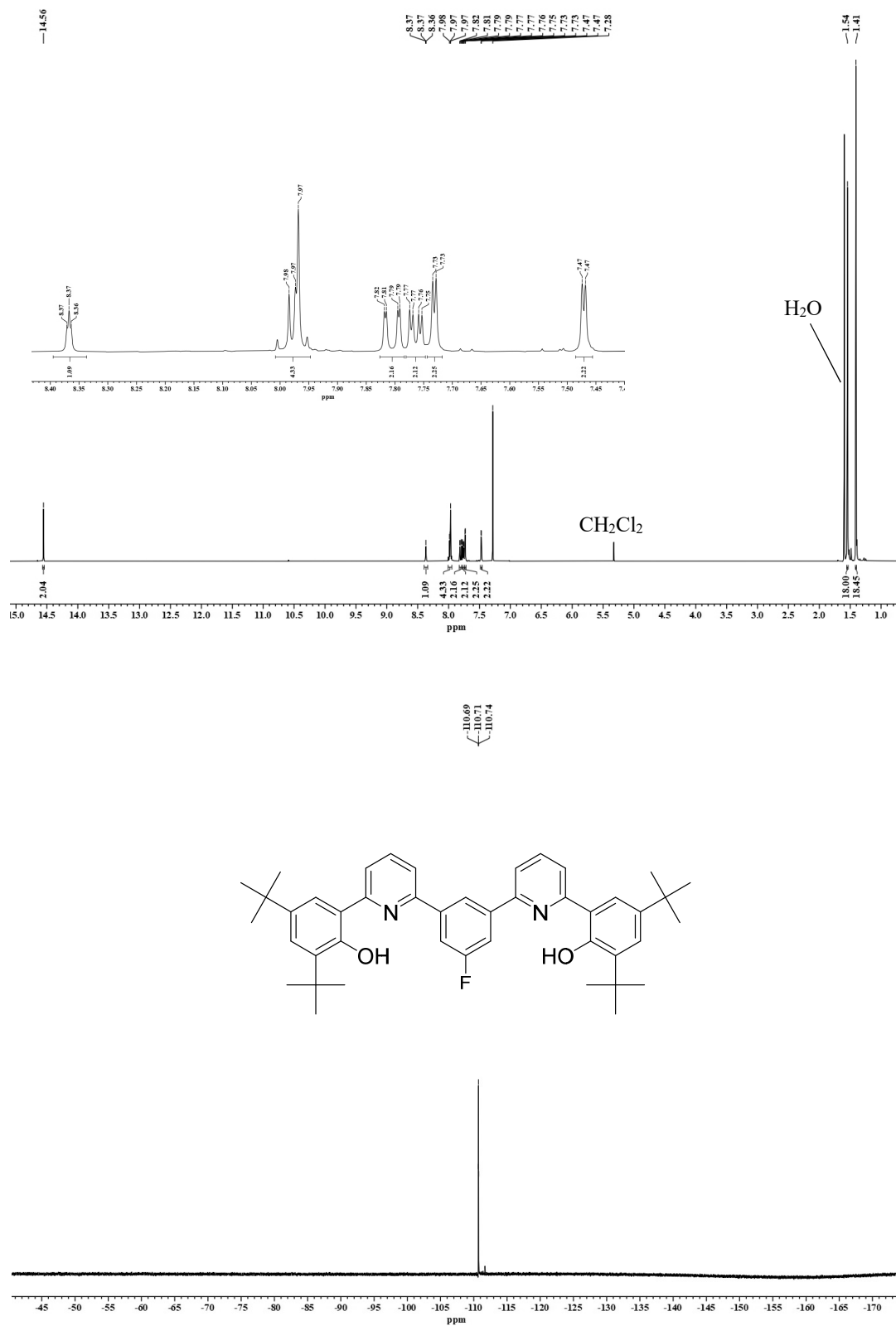


Figure S12. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 298 K) of I-4.



Figure S13. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz, 298 K) of I-5.





**Figure S16.** <sup>1</sup>H (top; 400 MHz) and <sup>19</sup>F (bottom; 376 MHz) NMR spectra (CDCl<sub>3</sub>, 298 K) of **H<sub>4</sub>L<sup>2</sup>**.

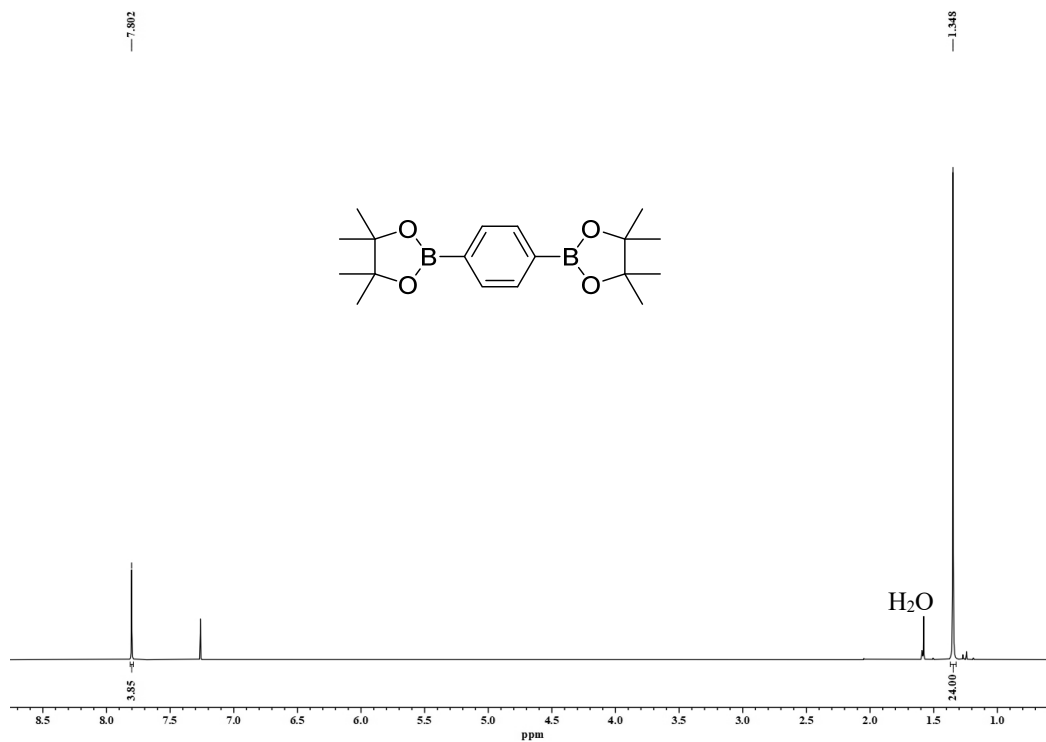


Figure S17. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of I-7.

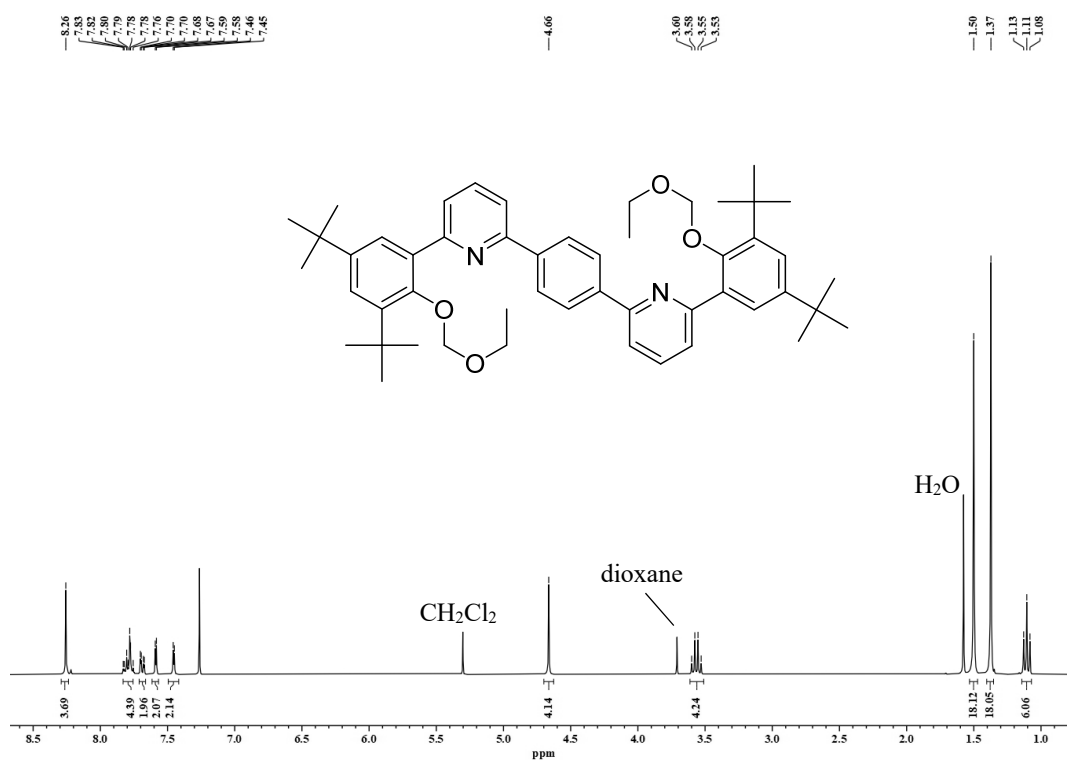


Figure S18. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz, 298 K) of I-8.



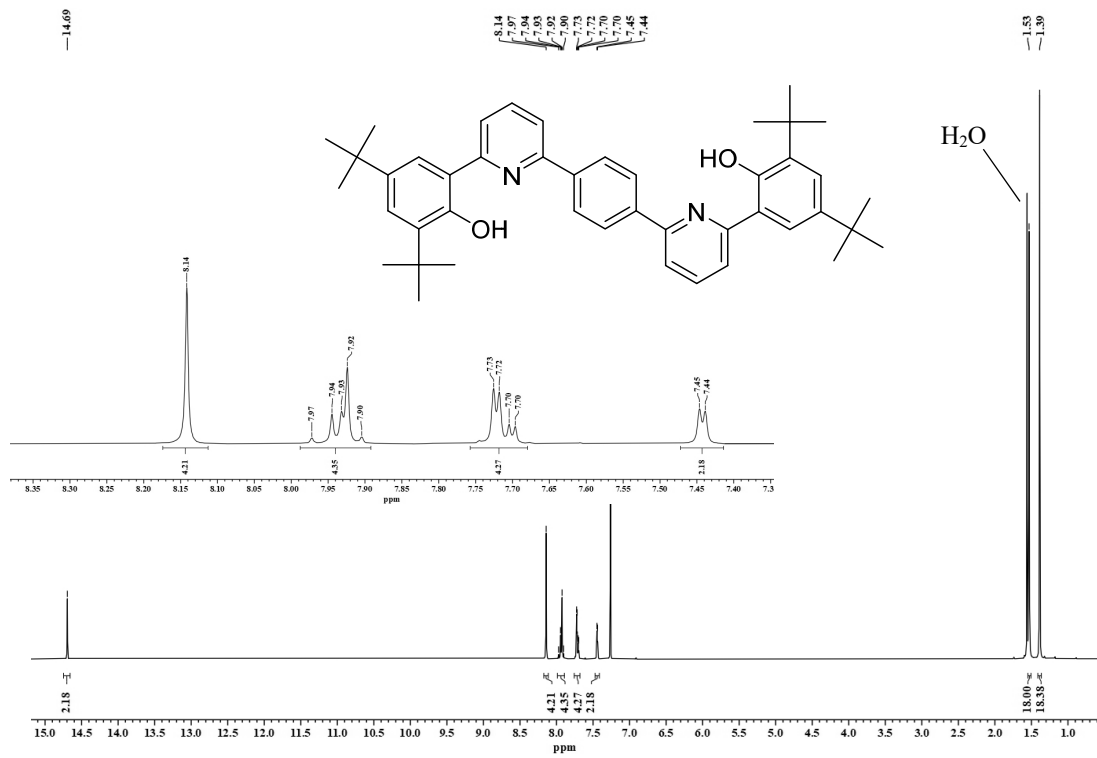
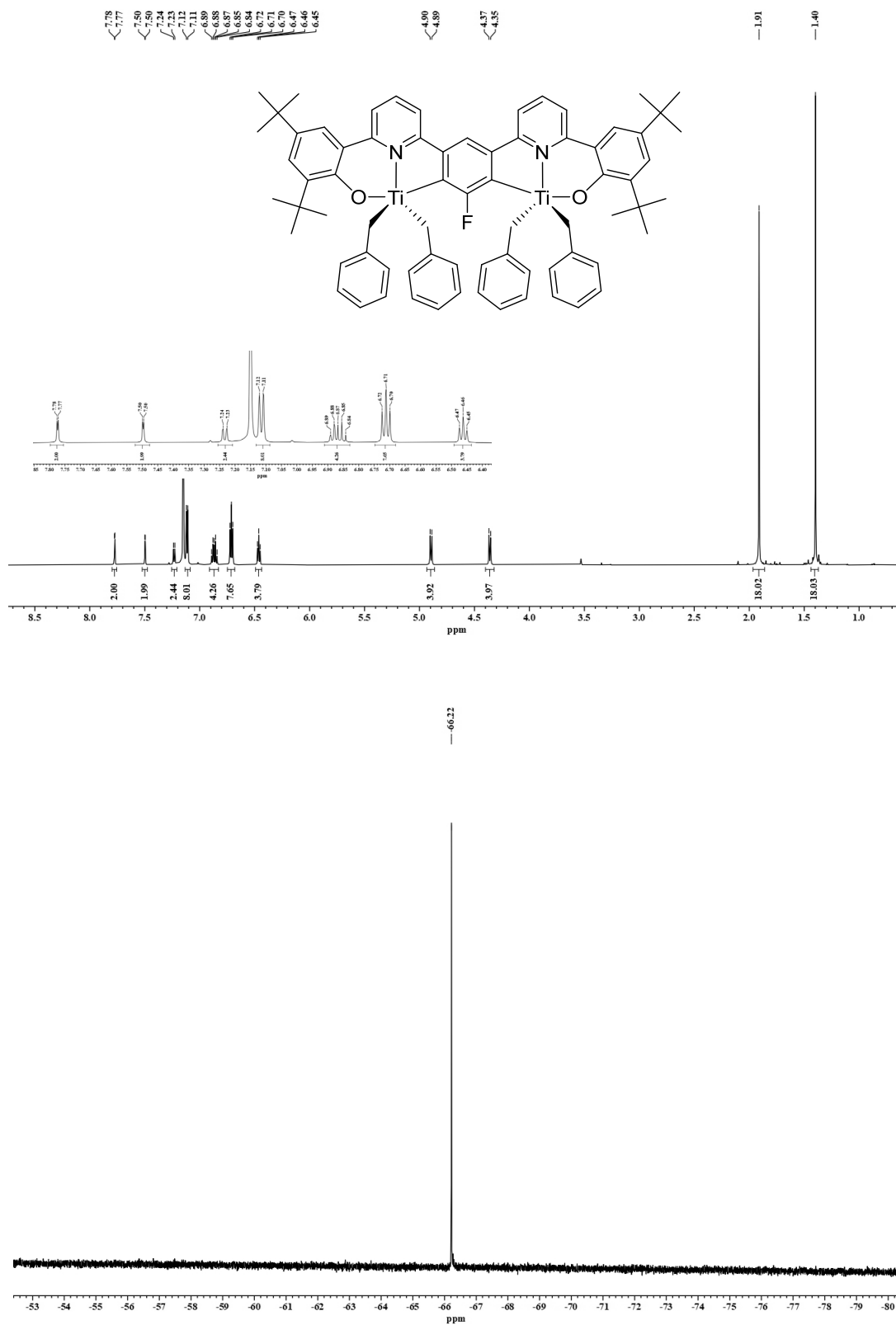
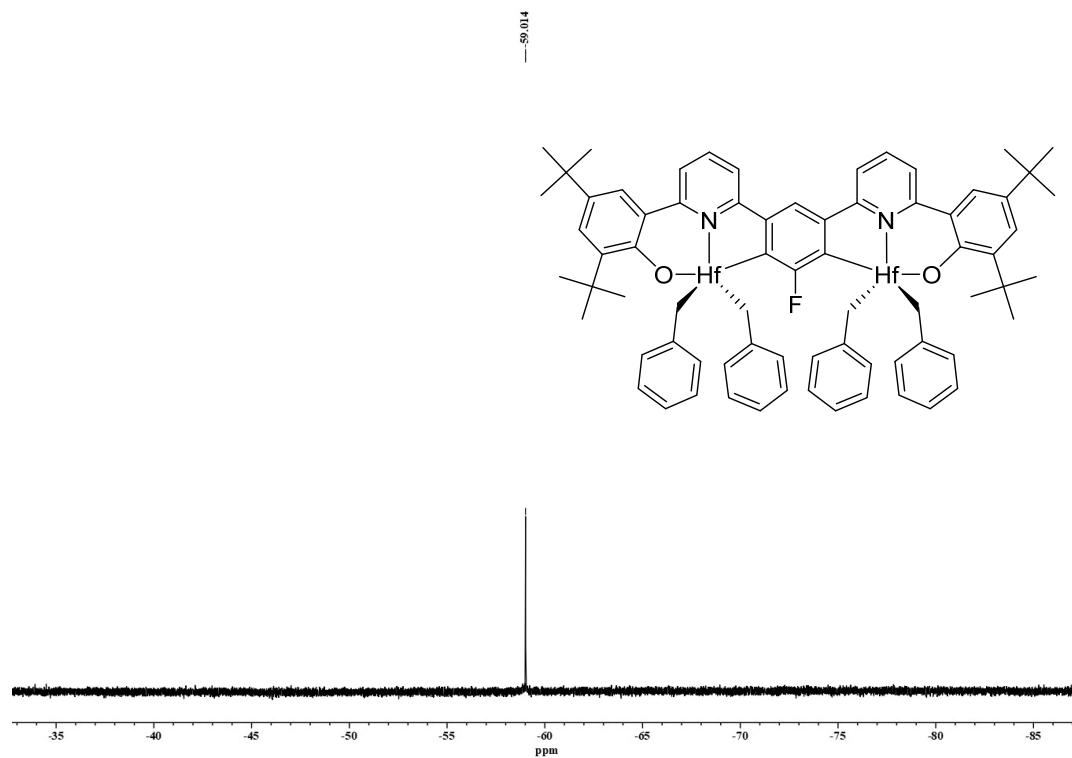
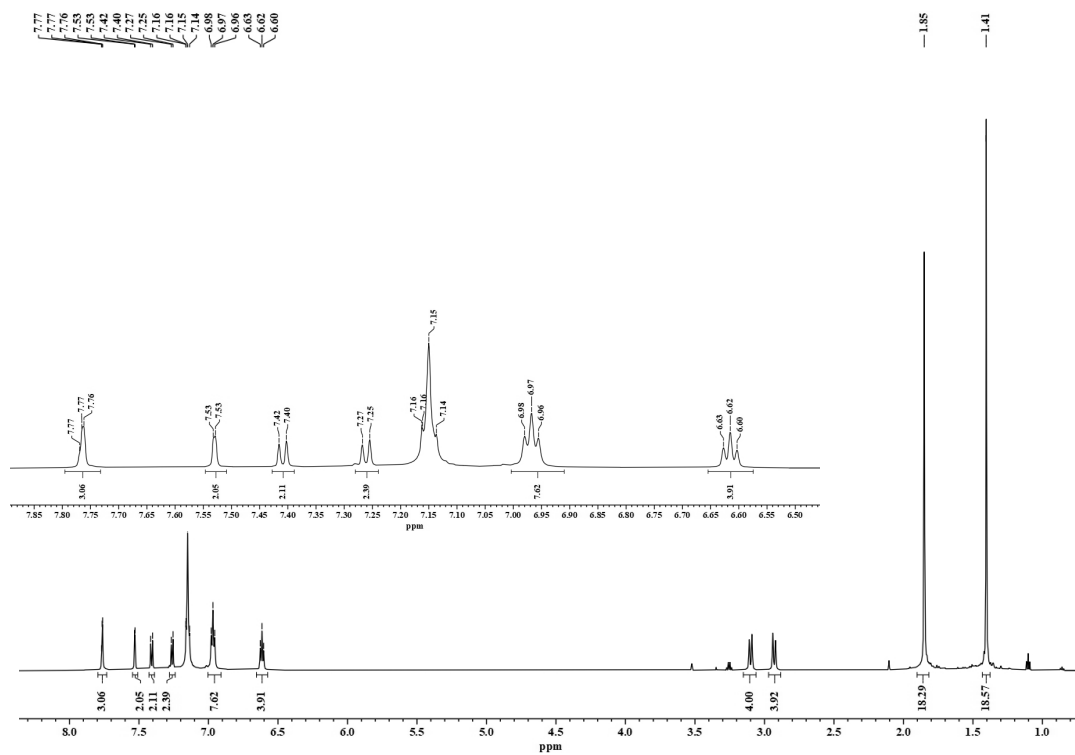


Figure S19.  $^1H$  NMR spectrum (CDCl<sub>3</sub>, 300 MHz, 298 K) of  $H_4L^3$ .



**Figure S20.** <sup>1</sup>H (top; 600 MHz) and <sup>19</sup>F (bottom; 565 MHz) NMR spectra (C<sub>6</sub>D<sub>6</sub> with d<sub>8</sub>-THF, 298 K) of complex 4.





**Figure S22.**  $^1\text{H}$  (top; 600 MHz) and  $^{19}\text{F}$  (bottom; 565 MHz) NMR spectra ( $\text{C}_6\text{D}_6$  with  $d_8$ -THF, 298 K) of complex **6**.

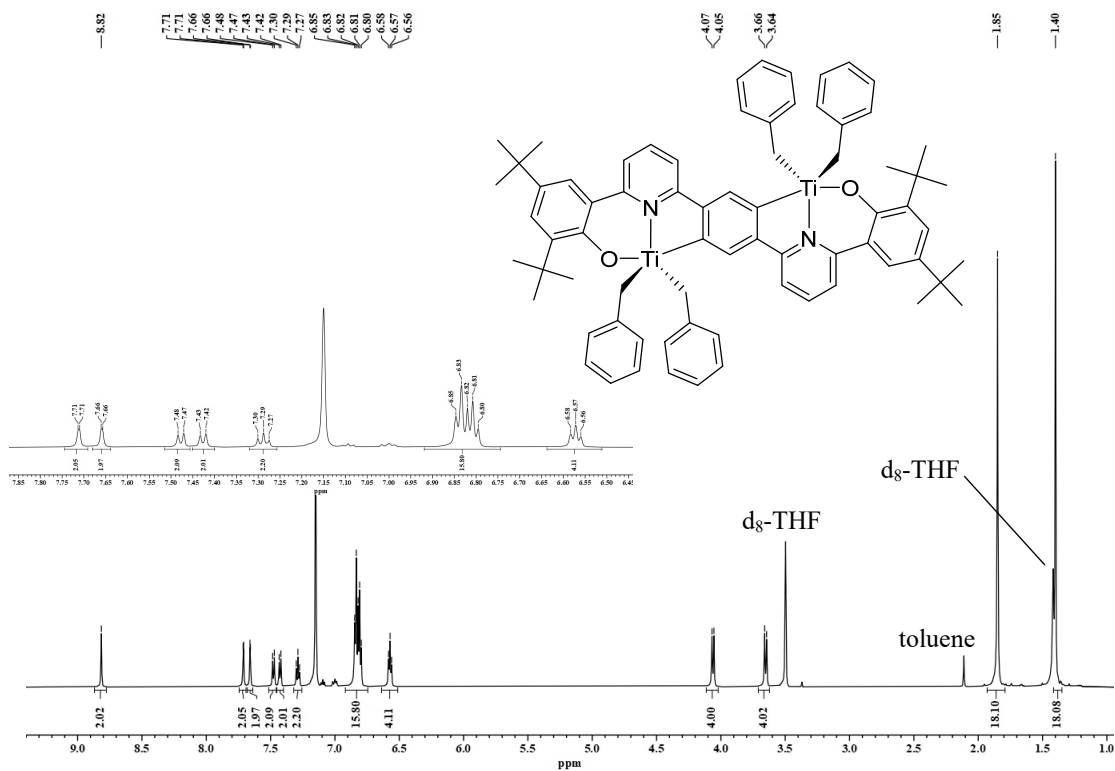


Figure S23. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub> with d<sub>8</sub>-THF, 600 MHz, 298 K) of complex 7.

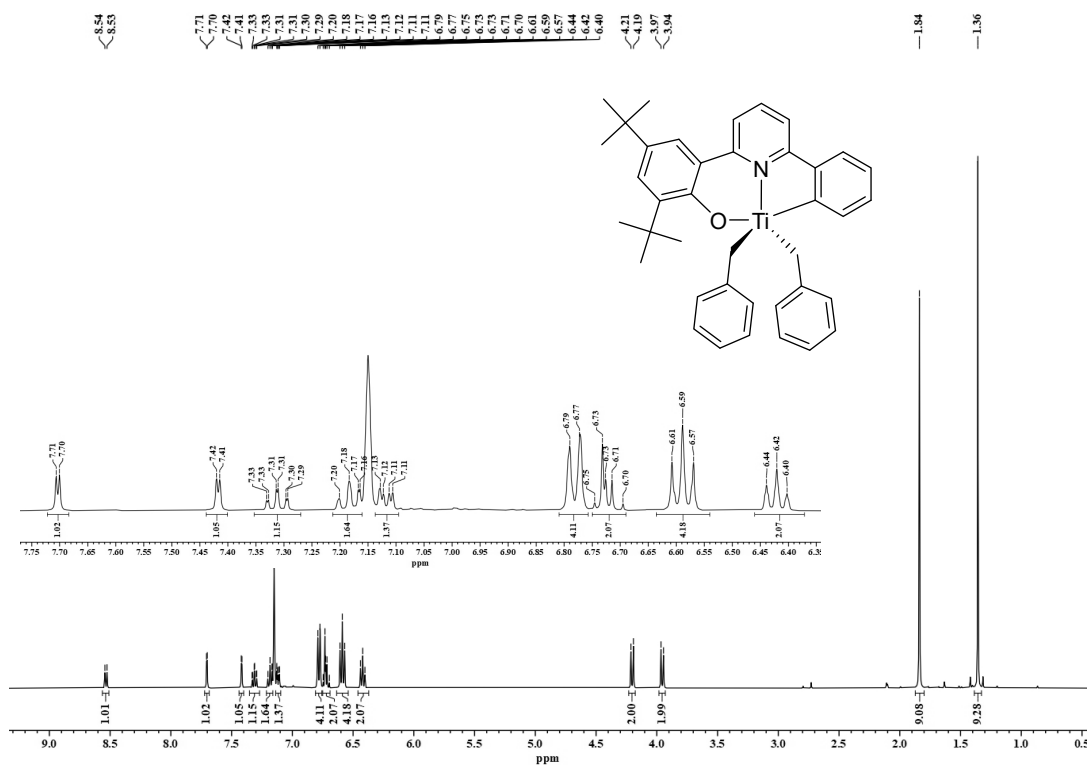


Figure S24. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 298 K) of complex M1.

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