## **Electronic Supplementary Information**

# Synthesis and spectroscopic characterization of group 4 post-metallocenes bearing (σ-aryl)-2-phenolate-6-pyridyl and -isoquinolinyl auxiliaries

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#### **Synthetic Methods**

The synthesis of I-1 and  $H_2L^2$  were described previously.<sup>1</sup>

#### Synthesis of I-8



A solution of 2,6-dibromopyridine (7.2 g, 30.5 mmol) in diethyl ether (120 mL) was added dropwise to n-butyllithium (20.0 mL, 32.0 mmol) in diethyl ether (30 mL) at -78 °C under a nitrogen atmosphere. The mixture was stirred for 1 hour, after which 1,1,2-trichlorotrifluoroethane (5.5 mL, 46.1 mmol) was added. The resultant mixture was stirred for 12 hours at room temperature, and dilute hydrochloric acid was then added. The product was extracted with diethyl ether, washed by brine and water and dried over magnesium sulphate. Evaporation of solvents gave a white solid. Yield: 5.0 g, 85 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.43 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H). ESI-MS (+ve, m/z): 193 [M<sup>+</sup>].

Synthesis of H<sub>2</sub>L<sup>1</sup>



A solution of 2-bromo-6-chloropyridine (**I-8**; 4.1 g, 22 mmol) in diethyl ether (60 ml) was added to n-butyllithium (9 mL, 23 mmol) in diethyl ether (40 ml) at -78 °C and stirred for 2 hours under a nitrogen atmosphere, after which trimethyltin chloride (4.5 g, 23 mmol) in THF (20 ml) was added. The resultant mixture was stirred at -78 °C for 2 hours and at room temperature for 24 hours, and all volatiles were removed under vacuum. **I-1** (7.0 g, 19 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.5 mmol) in toluene (100 ml) were then added under nitrogen, and the mixture was heated under reflux for 24 hours. The resultant mixture was allowed to cool to room temperature and dilute hydrochloric acid (0.1 M) was added. The product was extracted with diethyl ether, washed by a saturated sodium chloride solution, and finally dried over sodium sulphate. The solvent was removed by evaporation to give a white solid, which was purified by silica gel flash chromatography using n-hexane:ethyl acetate (50:1) as eluent to give a white solid. Yield: 3.4 g, 40 %. <sup>1</sup>H NMR (400



MHz, CDCl<sub>3</sub>):  $\delta$  1.33 (s, 9H, <sup>t</sup>Bu), 1.48 (s, 9H, <sup>t</sup>Bu), 5.21 (s, 1H, OH), 7.11 (d, J = 3.1 Hz, 1H), 7.29 (dd, J = 9.4, 1.2 Hz, 1H), 7.36 (d, J = 2.9 Hz, 1H), 7.53 (dt, J = 9.6, 1.7 Hz, 1H), 7.61 (t, J = 10.1 Hz, 1H), 7.68 (dd, J = 9.6, 1.2 Hz, 1H), 7.73 (t, J = 9.6 Hz, 1H), 8.06 (m, 2H). EI-MS (+ve, m/z): 393 [M<sup>+</sup>].

### Synthesis of I-9



n-Butyllithium (6.7 mL, 10.7 mmol) was added dropwise to 3,5-dibromotoluene (2.6 g, 10.2 mmol) in THF (85 mL) at -78 °C under a nitrogen atmosphere and stirred for 1 hour. Trimethyl borate (1.4 mL, 12.6 mmol) was then added, and the resultant mixture was allowed to stir for 12 hours at room temperature. After addition of dilute hydrochloric acid (0.1 M), the product was extracted with diethyl ether, washed by water and brine, and dried over magnesium sulphate. After removal of volatiles, the crude product was washed with cold pentane to give a white solid. Yield: 1.43 g, 65 %.

#### Synthesis of I-10



2-Iodo-4,6-di–tert-butylphenol (3.03 g, 9.12 mmol), **I-9** (1.96 g, 9.12 mmol), potassium carbonate (1.64 g, 11.87 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.105 g, 0.087 mmol) were placed in a 100 mL round-bottom flask under a nitrogen atmosphere. A mixture of toluene (45 ml) and ethanol (15 ml) was added. The resultant suspension was heated under reflux at 110 °C for 24 hours. The suspension was cooled to 0 °C and dilute hydrogen peroxide was added slowly until no more bubbling was observed. The product was extracted with diethyl ether, washed by brine and water, and dried over magnesium sulphate. Evaporation of volatiles gave a brown oil, which was purified by silica gel flash chromatography using pentane as eluent to give a colourless oily product. Yield: 1.33 g, 39 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.32 (s, 9H, <sup>1</sup>Bu), 1.44 (s, 9H, <sup>1</sup>Bu), 2.40 (s, 3H, Me), 5.19 (s, 1H, OH), 7.02 (d, *J* = 2.4 Hz, 1H), 7.19–7.21 (m, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.37–7.39 (m, 1H), 7.39–7.42 (m, 1H).

Synthesis of H<sub>2</sub>L<sup>3</sup>



The procedure for the synthesis of  $H_2L^1$  was adopted using **I-8** (1.3 g, 6.8 mmol) and **I-10** (2.3 g, 6.1 mmol), except a brown oily crude product was obtained, which was purified by silica gel flash chromatography using n-hexane:dichloromethane (20:1) as eluent to give a white solid. Yield: 0.55 g, 22 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.33 (s, 9H, <sup>t</sup>Bu), 1.45 (s, 9H, <sup>t</sup>Bu), 2.50 (s, 3H, Me), 5.27 (s, 1H, OH), 7.09 (d, *J* = 2.6 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.34–7.35 (m, 2H), 7.66 (d, *J* = 6.5 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.80 (s, 1H), 7.89 (s, 1H). ESI-MS (+ve, m/z): 409 [M<sup>+</sup>].

### Synthesis of I-11



The procedure for the synthesis of **I-8** was adopted, using **I-8** (5.0 g, 25.98 mmol) and iodine (6.5 g, 25.61 mmol) to give a pale brown solid. Yield: 5.0 g, 80 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.28–7.33 (m, 2H), 7.67 (dd, *J* = 6.5, 2.1 Hz, 1H).

Synthesis of I-12



A solution of 2-iodo-4,6-di–tert-butylphenol (4.9 g, 14.75 mmol) in THF (30 mL) was slowly added at 0 °C to a suspension of NaH (0.46 g, 19.17 mmol) in THF (5 mL) under a nitrogen atmosphere. The yellow suspension was then stirred at room temperature for an hour, after which chloromethylethylether (1.9 mL, 20.48 mmol) was added. After stirring at room temperature for 12 hours, ice water was added to the resultant suspension, and the product was extracted with diethyl ether, washed by brine and water, and dried over magnesium sulphate. After evaporation of volatiles, the product was purified by silica gel flash chromatography using n-hexane as eluent to give a yellow oil. Yield: 5.2 g, 90 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.28 (s, 9H, <sup>t</sup>Bu), 1.32 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>*CH*<sub>3</sub>), 1.42 (s, 9H, <sup>t</sup>Bu),

3.97 (q, *J* = 7.1 Hz, 2H, O*CH*<sub>2</sub>CH<sub>3</sub>), 5.22 (s, 2H, OCH<sub>2</sub>O), 7.34 (d, *J* = 2.4 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H).

Synthesis of I-13



A solution of n-butyllithium (3.7 mL, 5.92 mmol) was added dropwise to a suspension of 2,4dibromoanisole (1.5 g, 5.64 mmol) in pentane (45 mL) at -20 °C under a nitrogen atmosphere. The suspension was stirred at -10 °C for 30 minutes, after which trimethyltin chloride (1.18 g, 5.92 mmol) was added at -30 °C. The resultant white suspension was slowly warmed to room temperature and stirred for a further 12 hours. The desired product was afforded as a white solid by filtration and removal of volatiles. Yield: 1.64 g, 83 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.27 (s, 9H, SnMe<sub>3</sub>), 3.76 (S, 3H, OMe), 6.68–6.71 (m, 1H), 7.37–7.40 (m, 2H).





Tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.06 mmol), **I-11** (1.40 g, 5.85 mmol) and **I-13** (1.8 g, 5.15 mmol) were refluxed in toluene (30 mL) for 48 hours under a nitrogen atmosphere. The product was extracted with dichloromethane, washed by brine and water, and dried over magnesium sulphate. After evaporation of solvent, the product was purified by silica gel flash chromatography using n-hexane:ethyl acetate (100:1) as eluent to give a white solid. Yield: 0.3 g, 19 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.85 (s, 3H, OMe), 6.87 (d, *J* = 8.8 Hz, 1H), 7.25–7.28 (m, 1H), 7.47 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 2.3 Hz, 1H).

Synthesis of I-15



**I-14** (0.26 g, 0.87 mmol), bis(pinacolato)diboron (0.20 g, 0.79 mmol), potassium acetate (0.26 g, 2.65 mmol) and Pd(dppf)Cl<sub>2</sub> (0.004 g, 0.005 mmol) in DMSO (10 mL) were heated

at 120 °C for 12 hours. The product was extracted with toluene, washed by brine and water, and dried over magnesium sulphate. Removal of the solvent gave a pale brown solid. Yield: 0.19 g, 63 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.34 (s, 12H, C–Me), 3.87 (s, 3H, OMe), 6.98 (d, *J* = 8.1 Hz, 1H), 7.14–7.28 (m, 2H), 7.61–7.66 (m, 1H), 7.84 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.16 (d, *J* = 1.8 Hz, 1H).

Synthesis of I-16



**I-12** (0.28 g, 0.72 mmol), **I-15** (0.28 g, 0.81 mmol), potassium carbonate (0.55 g, 3.98 mmol) and Pd(dppf)Cl<sub>2</sub> (0.002 g, 0.002 mmol) in 1,4-dioxane (10 mL) and water (1 mL) were heated at 150 °C for 36 hours. The product was extracted with dichloromethane, washed by brine and water, and dried over magnesium sulphate. The crude product was purified by silica gel flash chromatography using n-hexane:ethyl acetate (50:1) as eluent to give a colourless oil, which slowly changed to a white solid. Yield: 0.2 g, 57 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.08 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>*CH*<sub>3</sub>), 1.33 (s, 9H, <sup>t</sup>Bu), 1.48 (s, 9H, <sup>t</sup>Bu), 3.53 (q, *J* = 7.1 Hz, 2H, O*CH*<sub>2</sub>CH<sub>3</sub>), 3.91 (s, 3H, OMe), 4.60 (s, 2H, OCH<sub>2</sub>O), 7.05 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 2.1 Hz, 1H).

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



**I-16** (0.78 g, 1.62 mmol) was heated in THF (10 mL) and HCl (5 mL) at 80 °C for 12 hours. The product was extracted with dichloromethane, washed by brine and water, and dried over magnesium sulphate. The crude product was purified by silica gel flash chromatography using n-hexane:ethyl acetate (50:1) as eluent to give a white solid. Yield: 0.40 g, 58 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.31 (s, 9H, <sup>t</sup>Bu), 1.44 (s, 9H, <sup>t</sup>Bu), 3.92 (s, 3H, OMe), 5.26 (s, 1H, OH), 7.07 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.25–7.28 (m, 1H), 7.31 (d, *J* =

2.1 Hz, 1H), 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 2.1 Hz, 1H). ESI-MS (+ve, m/z): 424.3 [M<sup>+</sup>].

Synthesis of I-17



α-Cyano-o-tolunitrile (6.0 g, 42.2 mmol) and HBr (33 % in acetic acid, 35 mL, 202.7 mmol) in dichloromethane (30 mL) and water (5 mL) were stirred at room temperature for 1 hour. The product was extracted by dichloromethane, washed by brine and saturated potassium carbonate solution and water, and dried over magnesium sulphate. Evaporation of the solvent gave a yellow-brown solid. Yield: 8.6 g, 91 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.49 (br s, 2H, NH<sub>2</sub>), 6.68 (s, 1H), 7.27–7.34 (m, 1H), 7.50–7.52 (m, 2H), 8.06 (dd, J = 8.4, 0.8 Hz, 1H).

Synthesis of I-2



The procedure for the synthesis of **I-12** was adopted using **I-1** (3.2 g, 8.9 mmol). Yield: 3.4 g, 91 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.12 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>*CH*<sub>3</sub>), 1.33 (s, 9H, <sup>t</sup>Bu), 1.47 (s, 9H, <sup>t</sup>Bu), 3.51 (q, *J* = 7.0 Hz, 2H, O*CH*<sub>2</sub>CH<sub>3</sub>), 4.54 (s, 2H, OCH<sub>2</sub>O), 7.10 (d, *J* = 2.8 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.45–7.49 (m, 2H), 7.72 (t, *J* = 1.7 Hz, 1H).





The procedure for the synthesis of **I-15** was adopted using **I-2** (0.9 g, 2.15 mmol), except the reaction mixture was heated at 80 °C for 12 hours. The product was obtained as a brown oil. Yield: 0.9 g, 90 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.07 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.32

(s, 12H, O–C–CH<sub>3</sub>), 1.36 (s, 9H, <sup>t</sup>Bu), 1.48 (s, 9H, <sup>t</sup>Bu), 3.43 (q, *J* = 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 4.47 (s, 2H, OCH<sub>2</sub>O), 7.13 (d, *J* = 2.3 Hz, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.63 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.77 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.96 (s, 1H).

Synthesis of I-4



**I-17** (8.6 g, 38.6 mmol) and HCl (60 ml) were stirred at 0 °C for 30 mins. Sodium nitrite (5.3 g, 76.8 mmol) was added slowly to the yellow-brown mixture, which was stirred at 0 °C for 15 mins, then at room temperature for a further 12 hours. The product was extracted by dichloromethane, washed by brine, saturated potassium carbonate solution and water, and dried over magnesium sulphate. The crude product was purified by silica gel flash chromatography using n-hexane:ethyl acetate (400:1) as eluent to give a white solid. Yield: 1.85 g, 20 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.66–7.73 (m, 2H), 7.77 (d, *J* = 3.2 Hz, 2H), 8.28 (dd, *J* = 8.4, 0.8 Hz, 1H).

Synthesis of I-6



The procedure for the synthesis of **I-16** was adopted using **I-3** (0.9 g, 1.9 mmol) and **I-4** (0.4 g, 1.6 mmol), except the reaction mixture was heated at 100 °C for 48 hours. The crude product was purified by silica gel flash chromatography using n-hexane as eluent to give a white solid. Yield: 0.55 g, 69 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.07 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.33 (s, 9H, <sup>t</sup>Bu), 1.47 (s, 9H, <sup>t</sup>Bu), 3.51 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 4.63 (s, 2H, OCH<sub>2</sub>O), 7.21 (d, *J* = 2.4 Hz, 1H), 7.38 (d, *J* = 2.7 Hz, 1H), 7.50–7.57 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.65–7.71 (m, 3H), 7.74 (d, *J* = 0.9 Hz, 1H), 7.82–7.87 (m, 2H), 8.15 (dd, *J* = 9.2, 0.9 Hz, 1H)

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Synthesis of H<sub>2</sub>L<sup>5</sup>



The procedure for the synthesis of  $H_2L^4$  was adopted using **I-6** (0.76 g, 1.51 mmol), except the crude product was purified by silica gel flash chromatography using n-hexane:ethyl acetate (100:1) as eluent to give a white solid. Yield: 0.27 g, 40 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.32 (s, 9H, <sup>t</sup>Bu), 1.45 (s, 9H, <sup>t</sup>Bu), 5.35 (s, 1H, OH), 7.14 (d, J = 2.5 Hz, 1H), 7.35 (d, J = 2.2 Hz, 1H), 7.53–7.59 (m, 1H), 7.61–7.77 (m, 5H), 7.80–7.86 (m, 2H), 8.14 (dd, J = 8.6, 1.0 Hz, 1H). ESI-MS (+ve, m/z): 444.1 [M<sup>+</sup>].

#### Synthesis of I-5



Tetrafluoroboric acid (60 mL) was cooled to 0 °C in a PETE cup. I-17 (2.5 g, 11.21 mmol) was added as a suspension in MeOH (70 mL), and the mixture was stirred for 30 mins at 0 °C. Sodium nitrite (2.55 g, 36.96 mmol) in water (20 mL) was added dropwise to the yellow suspension. The reaction mixture was allowed to stir for 1 hour at 0 °C, and a further hour at room temperature, then cooled again to 0 °C. A saturated sodium hydroxide solution was then slowly added until a change to basic pH was detected by pH paper. The product was extracted with dichloromethane, washed by brine and water, dried over magnesium sulphate, and finally purified by silica gel flash chromatography using n-hexane as eluent to give a white solid. Yield: 1.05 g, 42 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (m, 1H), 7.63 (m, 1H), 7.74 (m, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 8.28 (m, 1H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  –77.59.

## Synthesis of I-7



The procedure for the synthesis of I-6 was adopted using I-5 (0.8 g, 3.54 mmol), and purification by silica gel flash chromatography using n-hexane:ethyl acetate (50:1) as eluent

gave a white oil. Yield: 1.4 g, 81 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.07 (t, *J* = 7.2 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.33 (s, 9H, <sup>t</sup>Bu), 1.47 (s, 9H, <sup>t</sup>Bu), 3.50 (q, *J* = 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 4.63 (s, 2H, OCH<sub>2</sub>O), 7.21 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 2.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.67–7.72 (m, 3H), 7.86–7.89 (m, 2H), 8.20 (d, *J* = 8.9 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  –77.74.

Synthesis of H<sub>2</sub>L<sup>6</sup>



The procedures for the synthesis of  $H_2L^5$  were adopted using I-7 (1.4 g, 2.88 mmol). Yield: 0.90 g, 73 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.25 (s, 9H, <sup>t</sup>Bu), 1.33 (s, 9H, <sup>t</sup>Bu), 5.35 (s, 1H, OH), 7.15 (d, J = 2.4 Hz, 1H), 7.28 (d, J = 0.8 Hz, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.48–7.53 (m, 1H), 7.63–7.72 (m, 3H), 7.77 (dt, J = 7.2, 1.6 Hz, 1H), 7.83 (t, J = 1.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.19 (dd, J = 8.8, 0.8 Hz, 1H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  –77.74. ESI-MS (+ve, m/z): 428.5 [M<sup>+</sup>].



**Fig. S1** <sup>1</sup>H NMR spectrum for **8** (400 MHz,  $C_6D_6$ , 298 K).



Fig. S2 Methylene region in <sup>1</sup>H and <sup>1</sup>H{<sup>19</sup>F} (top left and right respectively), and [<sup>1</sup>H,<sup>19</sup>F]-HMQC (bottom) NMR spectra for 8 (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K).



**Fig. S3** (a) <sup>1</sup>H NMR spectrum (400 MHz,  $C_6D_6$ , 298 K) for **3**, and 1D [<sup>1</sup>H, <sup>19</sup>F]-HMBC NMR spectra showing signals arising b) from <sup>1</sup>H-<sup>19</sup>F scalar (*J*) and cross correlation (CR) interactions; c) exclusively from scalar coupling (*J*); d) exclusively from dipolar cross correlation (CR).



Fig. S4 Methylene region of  ${}^{1}$ H NMR spectra for 5 and 7 (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K).



**Fig. S5** Methylene region of <sup>1</sup>H NMR spectrum for methyl-substituted analogue (400 MHz,  $C_6D_6$ , 298 K; unpublished result).

Cpd	Catalyst	Vield (g)	Activity <sup>b</sup>	
	(µmol)	Tield (g)		
1	6.1	0.007	7	
2	6.8	0.001	1	
3	6.5	nil	_	
4	7.4	< 0.001	<1	
5	6.3	< 0.001	<1	
6	6.8	0.005	4	
7	6.4	0.023	22 <sup>c</sup>	
8	7.0	0.070	60 <sup>d</sup>	

Table S1	Ethylene	polymer	rization	results	using	MAO <sup><i>a</i></sup>
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<sup>*a*</sup> Conditions: 500 equiv. of MAO, 20 ml of toluene, 1 atm ethylene feed, 20 °C, 10 min reaction time. <sup>*b*</sup> Activity in g(polymer) (mmol catalyst)<sup>-1</sup> h<sup>-1</sup> (±10%). <sup>*c*</sup>  $M_n$  and  $M_w/M_n$  values of  $3.5 \times 10^5$  and 4.2 respectively, and  $T_m$  of 134 °C, were determined for resultant polymer. <sup>*d*</sup>  $M_n$  and  $M_w/M_n$  values of  $4.0 \times 10^5$  and 3.8 respectively, and  $T_m$  of 138 °C, were determined for resultant polymer.

## **ESI Reference**

 L.-C. So, C.-C. Liu, M. C. W. Chan, J. C. Y. Lo, K.-H. Sze and N. Zhu, *Chem. Eur. J.*, 2012, 18, 565.