## **Supporting Information for**

## Redox-controlled syndio-specific polymerization of styrene catalyzed

## by ferrocenyl functionalized half-sandwich scandium complexes

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Figure S1. <sup>1</sup>H NMR spectrum of  $[Fc(1-C_9H_6)]Sc(CH_2C_6H_4NMe_2-o)_2$  (1). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.17 (s, 4H, CH<sub>2</sub>NMe<sub>2</sub>), 2.09 (s, 6H, CH<sub>2</sub>NMe<sub>2</sub>), 2.22 (s, 6H, CH<sub>2</sub>NMe<sub>2</sub>), 3.87 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.17 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.68 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.76 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 5.58 (s, 1H, Ind-CH), 6.53 (s, 1H, Ind-CH), 6.69 (d, J = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.83 (t, 2H, J = 7.0 Hz, C<sub>6</sub>H<sub>4</sub>), 7.02-7.08 (m, 6H, C<sub>6</sub>H<sub>4</sub>), 7.46 (d, 1H, J = 7.5 Hz, Ind-C<sub>6</sub>H<sub>4</sub>), 7.84 (d, J = 9.0 Hz, 1H, Ind-C<sub>6</sub>H<sub>4</sub>).



Figure S2. <sup>13</sup>C NMR spectrum of  $[Fc(1-C_9H_6)]Sc(CH_2C_6H_4NMe_2-o)_2$  (1) <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  44.2 (*C*H<sub>2</sub>), 46.9 (N*Me*<sub>2</sub>), 66.0, 67.1, 67.4, 68.0 (Fc-C<sub>5</sub>H<sub>4</sub>), 69.8 (Fc-C<sub>5</sub>H<sub>5</sub>), 84.1 (Ind-*C*), 101.9 (Ind-*C*), 117.3, 121.3, 121.5, 122.2, 122.7, 124.7, 127.2, 130.5 (Ind-*C* and Aryl-*C*), 143.8, 146.0 (Aryl-*C*).



Figure S3. FT-IR spectrum (KBr) of  $[Fc(1-C_9H_6)]Sc(CH_2C_6H_4NMe_2-o)_2$  (1)



o)(THF)<sub>2</sub>} {[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]} (**2-THF**<sub>2</sub>)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>/THF- $d_8$ , 25 °C):  $\delta$  1.50 (m, 8H, THF), 2.19 (br s, 6H, CH<sub>2</sub>NMe<sub>2</sub>), 2.46 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 3.52 (m, 8H, THF), 3.92 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.22 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.26 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.56 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.74 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 6.13 (s, 1H, Ind-CH), 6.64 (d, 1H, J = 8.0 Hz, Ind-CH), 6.79 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 6.89 (t, 1H, J = 7.5 Hz, Ind-CH), 7.05 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.11 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.48 (d, 1H, J = 7.5 Hz, Ind-C<sub>6</sub>H<sub>4</sub>), 8.03 (s, 1H, Ind-C<sub>6</sub>H<sub>4</sub>).



Figure S5. <sup>13</sup>C NMR spectrum of { $[Fc(1-C_9H_6)]Sc(CH_2C_6H_4NMe_2-o)(THF)_2$ } { $[B(C_6F_5)_4]$ } (**2-THF<sub>2</sub>**)

<sup>13</sup>C NMR (125 MHz, THF- $d_8/C_6D_6$ , 25 °C):  $\delta$  24.3 (THF- $\alpha$ -*C*), 25.4 (N*Me*<sub>2</sub>), 39.7 (*C*H<sub>2</sub>), 66.1, 66.8 (THF- $\beta$ -*C*), 67.5, 67.7 (Fc- $C_5H_4$ ), 69.3 (Fc- $C_5H_5$ ), 81.9 (Ind-*C*), 112.5, 117.4, 118.3, 119.0, 122.5, 123.4, 123.6, 123.7, 124.2, 128.6, 131.1 (Ind-*C* and Aryl-*C*), 135.6, 137.5, 139.4, 147.6, 149.5 ( $C_6F_5$ ).

Cyclic voltammograms of **1** (Figure S6), Ferrocene (Figure S7), AgBF<sub>4</sub> (Figure S8a), and cobaltacene (Cp<sub>2</sub>Co; see Figure S8b) were measured on 0.01 mmol complex in 5 mL chlorobenzene solution of 0.2 M tetrabutylammonium hexafluorophosphate ( $^{n}Bu_{4}NPF_{6}$ ) as supporting electrolyte. Platinum working and counter electrodes were employed, along with an Ag/AgNO<sub>3</sub> reference electrode and a scan rate of 0.03 V·s<sup>-1</sup>. All potentials were referenced to the ferrocene-ferrocenium couple (Fc/Fc<sup>+</sup>).

Compound	$E_p^A(V)^b$	$E_p^{C}(V)$	$E_{1/2}(V)$	$\Delta E(V)^{c}$	$i_p^A / i_p^C$
1	0.10	-0.04	+0.03	0.14	1.00
<b>2-THF</b> <sub>2</sub>	0.09	-0.05	+0.02	0.14	1.00
<b>2-THF</b> <sup>2</sup> ox	0.08	-0.05	+0.02	0.13	0.99
AgBF <sub>4</sub>	0.80	0.46	+0.63	0.34	-
Cp <sub>2</sub> Co	-1.27	-1.38	-1.32	0.11	0.98

<sup>*a*</sup> Measured by CVs at 0.03V s<sup>-1</sup> in chlorobenzene with tetrabutylammonium hexafluorophosphate as supporting electrolyte. <sup>*b*</sup> All potentials are referenced to the ferrocene-ferrocenium couple (Fc/Fc<sup>+</sup>). <sup>*c*</sup>  $\Delta E$  is the peak separation of oxidation and reduction peaks.



Figure S6. Cyclic voltammogram of complex 1 measured at 0.03 V·s<sup>-1</sup>.



Figure S7. Cyclic voltammogram of Ferrocene



Figure S8. Cyclic voltammograms of (a) AgBF<sub>4</sub> irreversibly oxidized at  $E_{1/2} = +0.63$  V, and (b) Cp<sub>2</sub>Co indicating a reversible one-electron oxidation at  $E_{1/2} = -1.32$  V.

As for the sweeping direction, all CV curves were swept from negative to positive potential for several cycles with optimized scanning parameters (marked by arrows in figures), and all exhibited data was the third cycle. Although the reduction of 2-THF<sub>2</sub><sup>ox</sup> cannot be proved by the CV curve in Scheme 3, the first cycle of its CV before optimization exhibited a very weak oxidation peak (the supporting figure below), indicating that Fe(II) in 2-THF<sub>2</sub><sup>ox</sup>.



Figure S9. First cycle of CV of  $2\text{-THF}_2^{\text{ox}}$  with a very weak oxidation peak



Figure S10. <sup>13</sup>C NMR spectrum for polymer sample in 1,1,2,2–tetrachloroethane– $d_2$  (Table 1, run



Figure S11. DSC curve for polymer sample (Table 1, run 4)



Figure S12. DSC curve for polymer sample (Table 1, run 5)



Figure S13. DSC curve for polymer sample (Table 1, run 6)



Figure S14. DSC curve for polymer sample (Table 1, run 7)



Figure S15. DSC curve for polymer sample (Table 1, run 8)



Figure S16. DSC curve for polymer sample (Table 1, run 10)



Figure S17. DSC curve for polymer sample (Table 1, run 11)



Figure S18. <sup>13</sup>C NMR spectrum for polymer sample in 1,1,2,2-tetrachloroethane-d<sub>2</sub> (Table 1, run

10)



Figure S19. GPC trace for polymer sample (Table 1, run 4)



Figure S20. GPC trace for polymer sample (Table 1, run 5)



Figure S21. GPC trace for polymer sample (Table 1, run 6)



Figure S22. GPC trace for polymer sample (Table 1, run 7)



Figure S23. GPC trace for polymer sample (Table 1, run 8)



Figure S24. GPC trace for polymer sample (Table 1, run 10)



Figure S25. GPC trace for representative polymer (Table 1, run 11)



Figure S26. Overlay of GPC traces of the sPS samples produced by the redox-controlled styrene polymerization catalyzed by  $1/[Ph_3C][B(C_6F_5)_4]$  at the different time points. (A) at 6 minutes,  $M_n = 2548$  g/mol, PDI = 2.01; (B) at 12 minutes,  $M_n = 6168$  g/mol, PDI = 1.93; (C) at 21 minutes,  $M_n = 6174$  g/mol, PDI = 1.96; (D) at 24 minutes,  $M_n = 7753$  g/mol, PDI = 2.02; (E) at 30 minutes,  $M_n = 10286$  g/mol, PDI = 2.11.