Supporting Information for

Dinuclear iron(III) complexes bearing phenylene-bridged bis(aminotriphenolate) ligands as catalysts for the copolymerization of cyclohexene oxide with carbon dioxide or phthalic anhydride

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1. Synthetic procedures of ligands and iron(III) complexes

Compounds 3-tert-butyl-2-hydroxy-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzaldehyde (5), (1,2-bis-(3-tert-butyl-2-hydroxy-benzaldehyde)-benzene (6), Bis(3,5-di-tert-butyl-2-hydroxybenzyl)amine (9a), Bis(3,5-di-methyl-2-hydroxybenzyl)amine (9b), (1,4-bis-(3-tert-butyl-2-hydroxy-benzaldehyde)-benzene (13), and 5-phenyl-3-tert-butyl salicylaldehyde (16) was synthesized following procedures described in literatures.

Synthesis of 1,2-bis-(3-tert-Butyl-2-hydroxybenzyl alcohol)-benzene (7). To a suspension of 6 (0.93 g, 2.16 mmol) in methanol (10 mL) was added NaBH₄ (0.21 g, 5.55 mmol) slowly. The reaction mixture was stirred for 2 h at room temperature. The volatiles were then removed under reduced pressure and the residue was mixed with water (10 mL). Addition of acetic acid to the mixture for neutralization gave a white precipitate, which was further extracted with ethyl acetate (3 × 10 mL). The extract were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane/methanol, 20/1) to afford 7 as a white solid (0.82 g, 88%). ¹H NMR (500 MHz, Acetone-d₆) δ 7.40-7.29 (m, 4H), 6.85-6.76 (m, 4H), 4.81 (s, 4H), 1.23 (s, 18H). ¹³C NMR (126 MHz, Acetone-d₆) δ 155.45 (s), 141.75 (s), 136.61 (s), 133.11 (s), 131.01 (s), 129.27 (s), 127.73 (s), 127.05 (s), 125.99 (s), 65.21 (s), 35.21 (s), 30.01 (s). HRMS (m/z): [M-H]- Calcd. for [C₂₈H₃₄O₄-H]: 433.2384, found: 433.2420.

Synthesis of 1,2-bis-(3-tert-butyl-2-(chloromethyl)phenol)-benzene (8). To a solution of 7 (0.93 g, 2.16 mmol) in CH₂Cl₂ (5 mL) was added thionyl chloride (0.64 g, 5.37 mmol) in CH₂Cl₂ (5 mL) dropwise under nitrogen atmosphere. After stirring the resulting solution at room temperature for 3 h, the solvent was removed by rotatory evaporation and the residue was kept under vacuum for 12 hours to remove residual thionyl chloride and hydrogen chloride. The compound 8 was used in the following reactions without further purification.

Synthesis of ligand L1a. A solution of 9a (1.33 g, 2.94 mmol) and triethylamine (0.42 mL, 3.02 mmol) in THF (10 mL) was added dropwise to a stirred solution of 8
(0.66 g, 1.40 mmol) in THF (10 mL) under nitrogen atmosphere. A white solid had formed and the reaction mixture was left to stir at room temperature for 12 h. The white solid was removed by filtration. The filtrate was evaporated to dryness and the residue was dissolved in CH$_2$Cl$_2$ and washed with water. The organic phase was dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 20/1) to yield **L1a** (0.97 g, 53%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 (s, 4H), 7.24 (d, $J = 2.3$ Hz, 4H), 6.95 (d, $J = 2.3$ Hz, 4H), 6.87 (d, $J = 2.0$ Hz, 2H), 6.83 (d, $J = 1.8$ Hz, 2H), 3.52 (d, $J = 6.9$ Hz, 12H), 1.39 (s, 36H), 1.28 (s, 36H), 1.12 (s, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.62 (s), 151.62 (s), 142.17 (s), 140.64 (s), 136.43 (s), 136.41 (s), 133.25 (s), 130.51 (s), 130.05 (s), 129.48 (s), 127.08 (s), 125.55 (s), 124.02 (s), 122.66 (s), 121.90 (s), 56.82 (s), 56.24 (s), 35.00 (s), 34.55 (s), 34.34 (s), 31.78 (s), 29.84 (s), 29.66 (s). HRMS (ESI m/z): [M+2H]$^{2+}$ Calcd. for [C$_{88}$H$_{124}$N$_2$O$_6$+2H]$^{2+}$: 653.4803, found: 653.4809. [M+H]$^+$ Calcd. for [C$_{88}$H$_{124}$N$_2$O$_6$+H]$^+$: 1305.9532, found: 1305.9582.

**Synthesis of ligand L1b.** A solution of 9b (0.84 g, 2.94 mmol) and triethylamine (0.42 mL, 3.02 mmol) in THF (10 mL) was added dropwise to a stirred solution of 8 (0.66 g, 1.40 mmol) in THF (10 mL) under nitrogen atmosphere. A white solid had formed and the reaction mixture was stirred for 8 h at room temperature, and the white solid was removed by filtration. The filtrate was evaporated to dryness and the residue was dissolved in CH$_2$Cl$_2$ and washed with water. The organic phase was dried with anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The obtained residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 5/1) to yield **L1b** (0.8 g, 78%). $^1$H NMR (500 MHz, Acetone-d$_6$) $\delta$ 7.37 (dt, $J = 7.2$, 3.6 Hz, 2H), 7.34-7.29 (m, 2H), 6.95 (s, 2H), 6.83 (s, 8H), 6.77 (s, 2H), 3.63 (d, $J = 20.3$ Hz, 12H), 2.19 (d, $J = 10.5$ Hz, 24H), 1.12 (s, 18H). $^{13}$C NMR (126 MHz, Acetone-d$_6$) $\delta$ 155.01 (s), 152.55 (s), 141.75 (s), 136.39 (s), 133.12 (s), 131.64 (s), 131.07 (s), 130.25 (s), 129.51 (s), 129.16 (s), 129.14 (s), 127.56 (s), 125.03 (s), 124.18 (s), 124.02 (s), 57.39 (s), 54.86 (s), 35.02 (s), 29.95 (s), 20.56 (s), 16.59 (s). HRMS (ESI m/z): [M+H]$^+$ Calcd. for [C$_{64}$H$_{76}$N$_2$O$_6$+H]$^+$: 969.5776, found: 969.5787.
Synthesis of complex 1a. NaH (34 mg, 1.42 mmol) was suspended in THF (4 mL) and a solution of L1a (346 mg, 0.23 mmol) dissolved in THF (4 mL) was slowly added under protective nitrogen atmosphere. The mixture was stirred at room temperature for 12 h and then a solution of FeCl₃ (75 mg, 0.46 mmol) in THF (4 mL) was added to it. The resulting mixture was stirred at 70 °C for a further 12 h and then filtered through celite. The solvent was removed under vacuum. The corresponding residue was purified by flash chromatography (silica gel, petroleum ether/dichloromethane, 1/1). The second band was collected and concentrated to give 1a as a black solid (132 mg, 37%). HRMS (ESI m/z): [M+NH₄-2THF]⁺ Calcd. for [C₈₈H₁₁₈Fe₂N₂O₆⁺NH₄]⁺: 1428.8033, found: 1428.8010. Anal. Calcd for C₉₆H₁₃₄Fe₂N₂O₈: C 74.11; H 8.68; Fe 7.18; found: C 72.78; H 8.88; N 1.71; Fe 6.74. FT-IR (KBr, cm⁻¹): 2954 (vs), 2904 (s), 2868 (s), 1765 (w), 1603 (m), 1467 (s), 1438 (vs), 1413 (m), 1389 (w), 1362 (m), 1303 (m), 1263 (vs), 1240 (s), 1203 (m), 1169 (m), 1132 (w), 1076 (w), 1031 (w), 977 (vw), 913 (w), 875 (s), 840 (s), 813 (m), 774 (m), 751 (s), 690 (vw), 660 (vw), 647 (vw), 625 (m), 608 (s), 575 (m), 559 (s), 498 (m), 487 (m), 453 (vw). UV–vis (toluene, 0.1 mM) λ_max in nm (log ε): 338 nm (4.17), 436 nm (4.12).

Synthesis of complex 1b. NaH (78 mg, 3.25 mmol) was suspended in THF (10 mL) and a solution of L1b (513 mg, 0.53 mmol) dissolved in THF (10 mL) was slowly added under nitrogen atmosphere. The mixture was stirred at room temperature for 12 h and then a solution of FeCl₃ (172 mg, 1.06 mmol) in THF (10 mL) was added to it. The resulting mixture was stirred at 70 °C for a further 8 h and then filtered through celite. The solvent was removed under vacuum. The corresponding residue was recrystallized from THF via liquid diffusion of hexane for 3 times to give 1b as a black solid (484 mg, 75%). HRMS (ESI m/z): [M+H-2THF]⁺ Calcd. for [C₆₄H₇₀Fe₂N₂O₆⁺H]⁺: 1075.4005, found: 1075.4054. Anal. Calcd for C₇₂H₈₆Fe₂N₂O₈: C 70.93; H 7.11; N 2.30; Fe 9.16; found: C 71.07; H 6.75; N 2.49; Fe 8.98. FT-IR (KBr, cm⁻¹): 2997 (m), 2953 (s), 2912 (s), 2864 (m), 1598 (m), 1473 (vs), 1437 (s), 1415 (w), 1385 (vw), 1375 (vw), 1359 (m), 1330 (vw), 1308 (m), 1294 (m), 1261 (vs), 1222 (m), 1161 (s), 1072 (m), 1033 (m), 986 (vw), 972 (vw), 959 (vw), 933 (w), 920 (vw), 890 (vw), 875 (m), 862 (s), 825
(s), 794 (m), 773 (w), 754 (w), 692 (w), 660 (w), 631 (m), 606 (s), 572 (w), 557 (m),
520 (vw), 507 (w), 488 (w), 459 (vw), 420 (w), 405 (w). UV–vis (toluene, 0.1 mM)
λmax in nm (log ε): 342 nm (4.22), 438 nm (4.04).

Scheme S1. Synthetic routes for dinuclear iron(III) complex 2

Synthesis of 1,3-bis-(3-tert-butyl-2-hydroxy-benzaldehyde)-benzene (10). It was
synthesized as a similar procedure of 6 reported by previous literature.2 To a suspension
of tetrakis(triphenylphosphine)palladium(0) (0.33 g, 0.28 mmol), 1,3-dibromobenzene
(0.66 g, 2.82 mmol) and K2CO3 (1.42 g, 9.40 mmol) in 1,4-dioxane (40 mL) and H2O
(7 mL) was added 5 (1.8 g, 5.91 mmol). The mixture was reflux for 20 h, and then
cooled to room temperature, CH2Cl2 (25 mL) and H2O (25 mL) was added to the
solution and the organic phase was separated. The aqueous phase was extracted with
CH2Cl2 (25 mL × 2). The extracts were combined and then dried over MgSO4,
concentrated under reduced pressure, the residue was purified by column chromatography (silica gel; petroleum ether / dichloromethane, 3/1) to afford 10 as a light green solid (0.85 g, 70%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 11.83 (s, 2H), 9.98 (s, 2H), 7.67 (s, 1H), 7.65 (d, $J = 2.2$ Hz, 2H), 7.53 (d, $J = 1.1$ Hz, 3H), 1.49 (s, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.17 (s), 160.79 (s), 141.01 (s), 138.93 (s), 133.23 (s), 132.30 (s), 130.16 (s), 129.51 (s), 125.68 (s), 125.25 (s), 120.75 (s), 35.07 (s), 29.24 (s). HRMS (m/z): [M-H]$^-$ Calcd. for [C$_{28}$H$_{30}$O$_4$-H]$^-$: 429.2071, found: 429.2101.

**Synthesis of 1,3-bis-(3-tert-Butyl-2-hydroxybenzyl alcohol)-benzene (11).** It was synthesized as a similar procedure of synthesis of 7. Yield: 90% $^1$H NMR (500 MHz, Acetone-d$_6$) $\delta$ 8.87 (s, 2H), 7.72 (s, 1H), 7.46 (ddd, $J = 14.9$, 8.5, 4.0 Hz, 5H), 7.27 (d, $J = 1.5$ Hz, 2H), 4.95 (s, 4H), 1.48 (s, 18H). $^{13}$C NMR (126 MHz, Acetone-d$_6$) $\delta$ 156.46 (s), 142.91 (s), 137.65 (s), 132.69 (s), 129.93 (s), 126.90 (s), 125.61 (s), 125.50 (s), 124.97 (s), 65.16 (s), 35.44 (s), 29.99 (s). HRMS (m/z): [M-H]$^-$ Calcd. for [C$_{28}$H$_{34}$O$_4$-H]$^-$: 433.2384, found: 433.2412.

**Synthesis of 1,3-bis-(3-tert-butyl-2-(chloromethyl)phenol)-benzene (12).** It was synthesized as a similar procedure of 8.

**Synthesis of ligand L2.** It was synthesized as a similar procedure of L1b. Yield: 75% $^1$H NMR (500 MHz, THF-d$_8$) $\delta$ 7.67 (d, $J = 7.6$ Hz, 1H), 7.48-7.34 (m, 5H), 7.26 (d, $J = 5.2$ Hz, 2H), 6.85 (s, 4H), 6.79 (s, 4H), 3.76 (d, $J = 6.1$ Hz, 4H), 3.67 (d, $J = 6.1$ Hz, 8H), 2.17 (d, $J = 4.3$ Hz, 24H), 1.52-1.42 (m, 18H). $^{13}$C NMR (126 MHz, THF-d$_8$) $\delta$ 156.64 (s), 153.00 (s), 143.48 (s), 137.41 (s), 132.93 (s), 131.69 (s), 130.48 (s), 129.60 (s), 129.11 (s), 127.29 (s), 125.94 (s), 125.67 (s), 125.53 (s), 125.00 (s), 124.91 (s), 124.47 (s), 58.10 (s), 55.34 (s), 35.69 (s), 30.28 (s), 20.80 (s), 16.76 (s). HRMS (ESI m/z): [M+H]$^+$ Calcd. for [C$_{64}$H$_{76}$N$_2$O$_6$+H]$^+$: 969.5776, found: 969.5795.

**Synthesis of complex 2.** It was synthesized as a similar procedure of 1b. Yield: 70% HRMS (ESI m/z): [M+H-2THF]$^+$ Calcd. for [C$_{64}$H$_{70}$Fe$_2$N$_2$O$_6$+H]$^+$: 1075.4005, found: 1075.4053. Anal. Calcd for C$_{72}$H$_{86}$Fe$_2$N$_2$O$_8$: C 70.93; H 7.11; N 2.30; Fe 9.16; found, C 71.25; H 6.98; N 2.42; Fe 8.99. FT-IR (KBr, cm$^{-1}$): 2997 (m), 2952 (s), 2921 (s), 2854
(m), 1651 (w), 1601 (m), 1474 (vs), 1436 (s), 1414 (m), 1384 (vw), 1357 (m), 1333 (vw), 1308 (m), 1292 (m), 1261 (vs), 1222 (m), 1160 (s), 1072 (m), 1032 (m), 986 (vw), 974 (vw), 958 (vw), 934 (vw), 920 (vw), 890 (vw), 877 (m), 858 (m), 824 (s), 794 (w), 774 (w), 694 (w), 659 (w), 629 (m), 604 (s), 572 (w), 556 (m), 520 (vw), 506 (w), 490 (w), 460 (vw), 419 (w), 405 (w). UV–vis (toluene, 0.1 mM) $\lambda_{\text{max}}$ in nm (log $\varepsilon$): 344 nm (4.10), 437 nm (3.96).

Scheme S2. Synthetic routes for dinuclear iron(III) complex 3

Synthesis of 1,4-bis-(3-tert-Butyl-2-hydroxybenzyl alcohol)-benzene (14). It was synthesized as a similar procedure of 7 Yield: 82%. $^1$H NMR (500 MHz, Acetone-$d_6$) $\delta$ 8.86 (s, 2H), 7.62 (s, 4H), 7.50 (d, J = 2.1 Hz, 2H), 7.26 (d, J = 2.0 Hz, 2H), 4.95 (s, 4H), 1.48 (s, 18H). $^{13}$C NMR (126 MHz, Acetone-$d_6$) $\delta$ 156.50 (s), 140.43 (s), 137.79 (s), 132.20 (s), 127.66 (s), 127.06 (s), 125.38 (s), 124.72 (s), 65.30 (s), 35.57 (s), 30.11 (s). HRMS ($m/z$): [M-H]$^-$ Calcd. for [C$_{28}$H$_{34}$O$_4$H]: 433.2384, found: 433.2410.

S7
Synthesis of 1,4-bis-(3-tert-butyl-2-(chloromethyl)phenol)-benzene (15). It was synthesized as a similar procedure of 8.

Synthesis of ligand L3. It was synthesized as a similar procedure of L1b. Yield: 66%.

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 7.61 (s, 4H), 7.33 (d, J = 23.5 Hz, 4H), 6.82 (d, J = 19.3 Hz, 8H), 3.75 (s, 4H), 3.64 (s, 8H), 2.14 (d, J = 6.0 Hz, 24H), 1.41 (s, 18H). $^{13}$C NMR (126 MHz, DMSO-d$_6$) δ 155.34 (s), 151.58 (s), 138.69 (s), 136.27 (s), 130.46 (s), 129.88 (s), 128.93 (s), 127.57 (s), 126.41 (s), 125.30 (s), 124.47 (s), 123.94 (s), 123.69 (s), 123.57 (s), 55.65 (s), 52.54 (s), 34.49 (s), 29.39 (s), 20.15 (s), 16.65 (s). HRMS (ESI m/z): [M+H]$^+$ Calcd. for [C$_{64}$H$_{76}$N$_2$O$_6$+H]$^+$: 969.5776, found: 969.5823.

Synthesis of complex 3. It was synthesized as a similar procedure of complex 1b. Yield: 75%. HRMS (ESI m/z): [M+2H-2THF]$^{2+}$ Calcd. for [C$_{64}$H$_{70}$Fe$_2$N$_2$O$_6$+2H]$^{2+}$: 538.2039, found: 538.2046. Anal. Calcd for C$_{72}$H$_{86}$Fe$_2$N$_2$O$_8$: C 70.93; H 7.11; N 2.30; Fe 9.16; found: C 71.10; H 6.88; N 2.51; Fe 8.86. FT-IR (KBr, cm$^{-1}$): 2997 (m), 2951 (s), 2854 (m), 1649 (w), 1605 (w), 1474 (s), 1437 (s), 1410 (w), 1386 (w), 1357 (w), 1309 (w), 1292 (vw), 1262 (vs), 1160 (s), 1072 (m), 1032 (m), 957 (w), 932 (w), 920 (w), 892 (w), 878 (w), 857 (m), 822 (s), 773 (vw), 756 (m), 683(vw), 629 (vw), 606 (s), 570 (w), 553 (m), 515 (m), 486 (vw), 463 (vw), 421 (w), 405 (vw). UV–vis (toluene, 0.1 mM) $\lambda_{\text{max}}$ in nm (log $\varepsilon$): 360 nm (4.17), 412 nm (4.04).
Scheme S3. Synthetic routes for mononuclear iron(III) complex 4

Synthesis of 5-phenyl-3-tert-butyl-2-hydroxybenzyl alcohol (17). It was synthesized as a similar procedure of 7. Yield: 95%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.81 (s, 1H), 7.49 (dd, $J = 17.1$, 4.8 Hz, 3H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 2.0$ Hz, 1H), 4.90 (d, $J = 5.2$ Hz, 2H), 2.18 (t, $J = 5.4$ Hz, 1H), 1.47 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.33 (s), 141.47 (s), 137.79 (s), 132.50 (s), 128.82 (s), 126.92 (s), 126.68 (s), 126.20 (s), 125.06 (s), 124.63 (s), 65.78 (s), 35.06 (s), 29.76 (s). HRMS (ESI m/z): [M-H]$^{-}$ Calcd. for [C$_{17}$H$_{20}$O$_2$-H]$^{-}$: 255.1391, found: 255.1383.

Synthesis of 5-phenyl 3-tert-butyl-2-(chloromethyl)phenol (18). It was synthesized as a similar procedure of 8.

Synthesis of ligand L4. It was synthesized as a similar procedure of L1b. Yield: 85% $^1$H NMR (500 MHz, THF-d$_8$) $\delta$ 7.51 (d, $J = 7.4$ Hz, 2H), 7.37 (d, $J = 2.0$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.23-7.15 (m, 2H), 6.84 (s, 2H), 6.78 (s, 2H), 3.75 (s, 2H), 3.67 (s, 4H), 2.17 (d, $J = 1.8$ Hz, 12H), 1.44 (s, 9H). $^{13}$C NMR (126 MHz, THF-d$_8$) $\delta$ 156.61 (s), 152.97 (s), 143.04 (s), 137.42 (s), 132.51 (s), 131.67 (s), 130.44 (s), 129.41 (s), 129.09 (s), 127.42 (s), 127.13 (s), 126.91 (s), 125.46 (s), 124.97 (s), 124.94 (s), 124.43 (s), 58.05 (s), 55.37 (s), 35.66 (s), 30.24 (s), 20.75 (s), 16.71 (s). HRMS (ESI m/z):
[M+H]$^+$ Calcd. for [C$_{35}$H$_{41}$NO$_3$+H]$^+$: 524.3159, found: 524.3165.

**Synthesis of complex 4.** It was synthesized following procedures described in literatures.$^6$ NaH (71 mg, 2.96 mmol) was suspended in THF (10 mL) and a solution of L$_4$ (513 mg, 0.98 mmol) dissolved in THF (10 mL) was slowly added under nitrogen atmosphere. The mixture was stirred at room temperature for 12 h and then a solution of FeCl$_3$ (159 mg, 0.98 mmol) in THF (10 mL) was added to it. The resulting mixture was stirred at room temperature for a further 8 h and then filtered through celite. The solvent was removed under vacuum to give 4 as a black solid (572 mg, 90%). HRMS (ESI m/z): [M+H-THF]$^+$ Calcd. for [C$_{35}$H$_{38}$FeNO$_3$+H]$^+$: 577.2274, found: 577.2280.

Anal. Calcd for C$_{39}$H$_{46}$FeNO$_4$: C 72.22; H 7.15; Fe 8.61; found: C 71.80; H 7.32; N 1.98; Fe 8.51. FT-IR (KBr, cm$^{-1}$): 2997 (m), 2948 (s), 2915 (s), 2854 (m), 1652 (vw), 1601 (m), 1474 (vs), 1437 (vs), 1407 (m), 1387 (w), 1363 (m), 1309 (w), 1259 (vs), 1231 (vw), 1160 (s), 1071 (s), 1029 (s), 898 (m), 877 (s), 859 (s), 818 (vs), 771 (s), 760 (s), 697 (s), 656 (vw), 624 (s), 604 (vs), 570 (m), 557 (s), 547 (s), 509 (s), 492 (m), 460 (vw), 420 (m), 403 (m). UV–vis (toluene, 0.2 mM) $\lambda_{\text{max}}$ in nm (log $\varepsilon$): 345 nm (3.84), 438 nm (3.73).
2. $^1$H and $^{13}$C NMR spectra of Ligands 1-4

**Figure S1.** $^1$H NMR spectrum of L1a in CDCl$_3$

**Figure S2.** $^{13}$C NMR spectrum of L1a in CDCl$_3$
Figure S3. $^1$H NMR spectrum of L1b in acetone-d$_6$.

Figure S4. $^{13}$C NMR spectrum of L1b in acetone-d$_6$. 
Figure S5. $^1$H NMR spectrum of L2 in THF-d$_8$

Figure S6. $^{13}$C NMR spectrum of L2 in THF-d$_8$
Figure S7. $^1$H NMR spectrum of L3 in DMSO-d$_6$

Figure S8. $^{13}$C NMR spectrum of L3 in DMSO-d$_6$
Figure S9. $^1$H NMR spectrum of L4 in THF-d$_8$

Figure S10. $^{13}$C NMR spectrum of L4 in THF-d$_8$
3 UV–vis spectra of iron(III) complexes

**Figure S11.** UV–vis spectra of complex 1a in toluene (0.1 mM; black curve) and in presence of 500 equiv. of CHO (red curve).

**Figure S12.** UV–vis spectra of complex 2 in toluene (0.1 mM; black curve) and in...
Figure S13. UV–vis spectra of complex 3 in toluene (0.1 mM; black curve) and in presence of 500 equiv. of CHO (red curve).
4. $^1$H NMR spectrum and FT-IR spectra of the reaction mixture after catalytic test

**Figure S14.** $^1$H NMR spectrum of the crude reaction mixture of CHO/CO$_2$ copolymerization (Table 1, entry 2) in CDCl$_3$

**Figure S15.** FT-IR spectrum of crude reaction mixture of CHO/CO$_2$ copolymerization (Table 2, entry 3)
Figure S16. Carbonyl region of $^{13}$C NMR spectrum of PCHC (Table 1, entry 2) in CDCl$_3$. According to literatures,$^7$, $^8$ this spectrum indicates the formation of atactic PCHC.

Figure S17. $^1$H NMR spectrum of the crude reaction mixture of CHO/PA
copolymerization in neat (Table 4, entry 1) in CDCl$_3$

Figure S18. $^1$H NMR spectrum of the crude reaction mixture of CHO/PA copolymerization in toluene (Table 3, entry 6) in CDCl$_3$
5  MALDI-TOF mass spectrum of copolymers

Figure S19. The MALDI-TOF mass spectra of PCHC produced by complex 1b/PPNCl (Table 1, entry 2).
Figure S20. High molecular weight region of the MALDI-TOF mass spectra of polyester produced by complex 1b/PPNC1 (Table 4, entry 6).
6 GPC and DSC data for copolymers

**Figure S21.** GPC chart of the product PCHC (Table 1, entry 2, $M_n$: 21245 and 9658, $M_w/M_n = 1.05$ and 1.04)

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</tbody>
</table>

**Figure S22.** GPC chart of the product PCHC (Table 2, entry 6, $M_n$: 9562 and 4119, $M_w/M_n = 1.09$ and 1.09)

<table>
<thead>
<tr>
<th></th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_P$</th>
<th>$M_z$</th>
<th>$M_{z+1}$</th>
<th>Polydispersity</th>
<th>$K$</th>
<th>alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9562</td>
<td>10416</td>
<td>9558</td>
<td>11606</td>
<td>13318</td>
<td>1.089330</td>
<td>0.0001600</td>
<td>0.7060</td>
</tr>
<tr>
<td>2</td>
<td>4119</td>
<td>4494</td>
<td>5371</td>
<td>4782</td>
<td>5007</td>
<td>1.091073</td>
<td>0.0001600</td>
<td>0.7060</td>
</tr>
</tbody>
</table>
**Figure S23.** GPC chart of the product PE (Table 3, entry 2, $M_n$: 32883 and 14446, $M_w/M_n = 1.05$ and 1.08)

**Figure S24.** GPC chart of the product PE (Table 4, entry 2, $M_n$: 22266 and 9880, $M_w/M_n = 1.05$ and 1.06)
**Figure S25.** DSC plots of PCHC produced by iron(III) complexes/PPNCl: (a) Table 1, entry 2, $T_g = 119 \, ^\circ\text{C}$; (b) Table 1, entry 5, $T_g = 117 \, ^\circ\text{C}$; (c) Table 1, entry 8, $T_g = 114 \, ^\circ\text{C}$; (d) Table 1, entry 11, $T_g = 114 \, ^\circ\text{C}$. 
Figure S26. DSC plots of polyesters produced by iron(III) complexes/PPNCl:
(a) Table 3, entry 2, $T_g = 136$ °C; (b) Table 3, entry 3, $T_g = 125$ °C; (c) Table 3, entry 4, $T_g = 125$ °C; (d) Table 3, entry 5, $T_g = 133$ °C.
7 References


