Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Dinuclear iron(III) complexes bearing phenylene-bridged bis(amino triphenolate) 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], (1,2-bis-(3-tert-butyl-2-hydroxy-benzaldehyde)-benzene (**6**)[2], Bis(3,5-di-tert-butyl-2-hydroxybenzyl)amine (**9a**),[3] Bis(3,5-di-methyl-2-hydroxybenzyl)amine (**9b**)[4] (1,4-bis-(3-tert-butyl-2-hydroxy-benzaldehyde)-benzene (**13**),[1] and 5-phenyl-3-tert-butyl salicylaldehyde (**16**)[5] 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 $NaBH_4$ (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 Na_2SO_4 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%). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.40-7.29 (m, 4H), 6.85-6.76 (m, 4H), 4.81 (s, 4H), 1.23 (s, 18H). ^{13}C NMR (126 MHz, Acetone-d_6) 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 $[C_{28}H_{34}O_4-H]^-$: 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 CH_2Cl_2 (5 mL) was added thionyl chloride (0.64 g, 5.37 mmol) in CH_2Cl_2 (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.

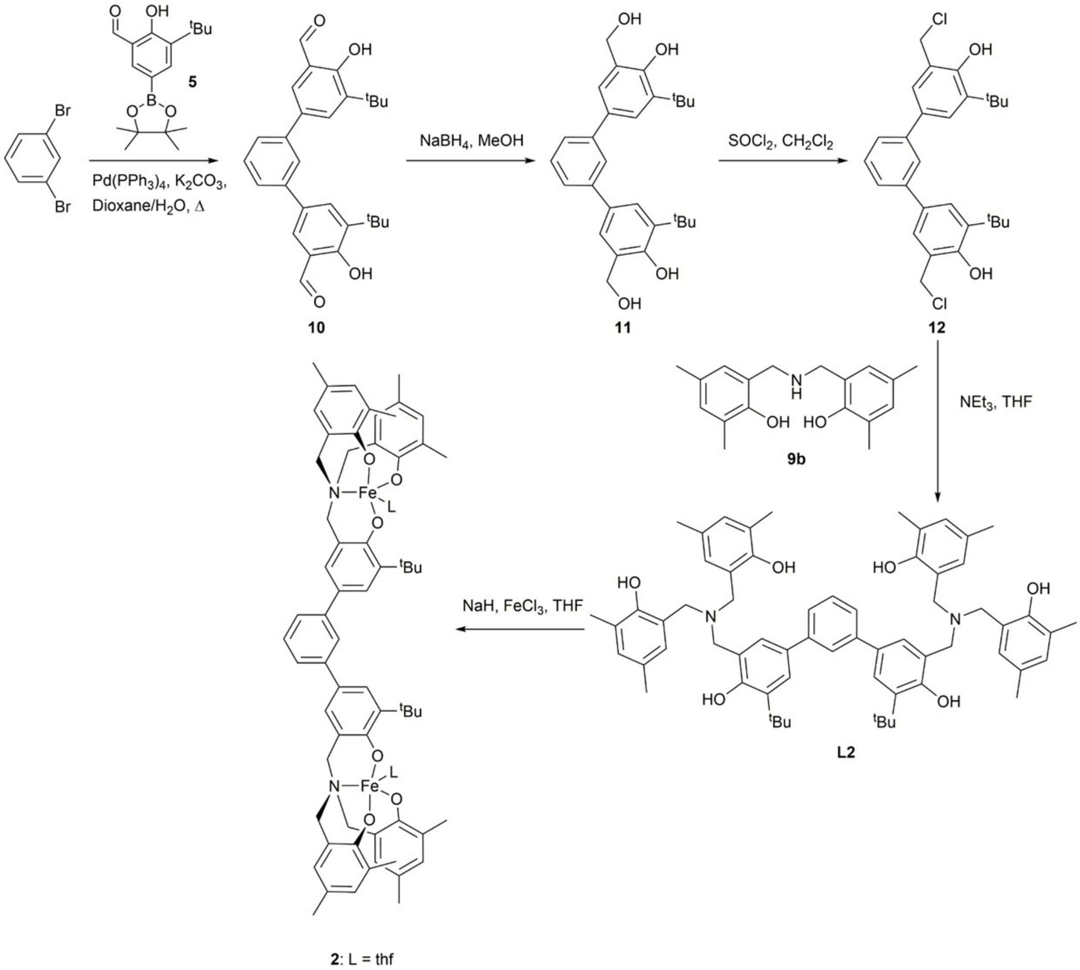
Synthesis of ligand L1a. A solution of **9a** (1.33 g, 2.94 mmol) and triethylamine (0.42 mL, 3.02 mmol) in THF (10 mL) was added dropwise to a stirred solution of **8**

(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_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_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, CDCl3) δ 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, CDCl3) δ 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 $[C_{88}H_{124}N_2O_6+2H]^{2+}$: 653.4803, found: 653.4809. $[M+H]^+$ Calcd. for $[C_{88}H_{124}N_2O_6+H]^+$: 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_2Cl_2 and washed with water. The organic phase was dried with anhydrous Na_2SO_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) δ 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) δ 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 $[C_{64}H_{76}N_2O_6+H]^+$: 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 $FeCl_3$ (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): $[M+NH_4-2THF]^+$ Calcd. for $[C_{88}H_{118}Fe_2N_2O_6+NH_4]^+$: 1428.8033, found: 1428.8010. Anal. Calcd for $C_{96}H_{134}Fe_2N_2O_8$: C 74.11; H 8.68; N 1.80; 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 $FeCl_3$ (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 $[C_{64}H_{70}Fe_2N_2O_6+H]^+$: 1075.4005, found: 1075.4054. Anal. Calcd for $C_{72}H_{86}Fe_2N_2O_8$: 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) λ_{max} in nm (log ε): 342 nm (4.22), 438 nm (4.04).



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

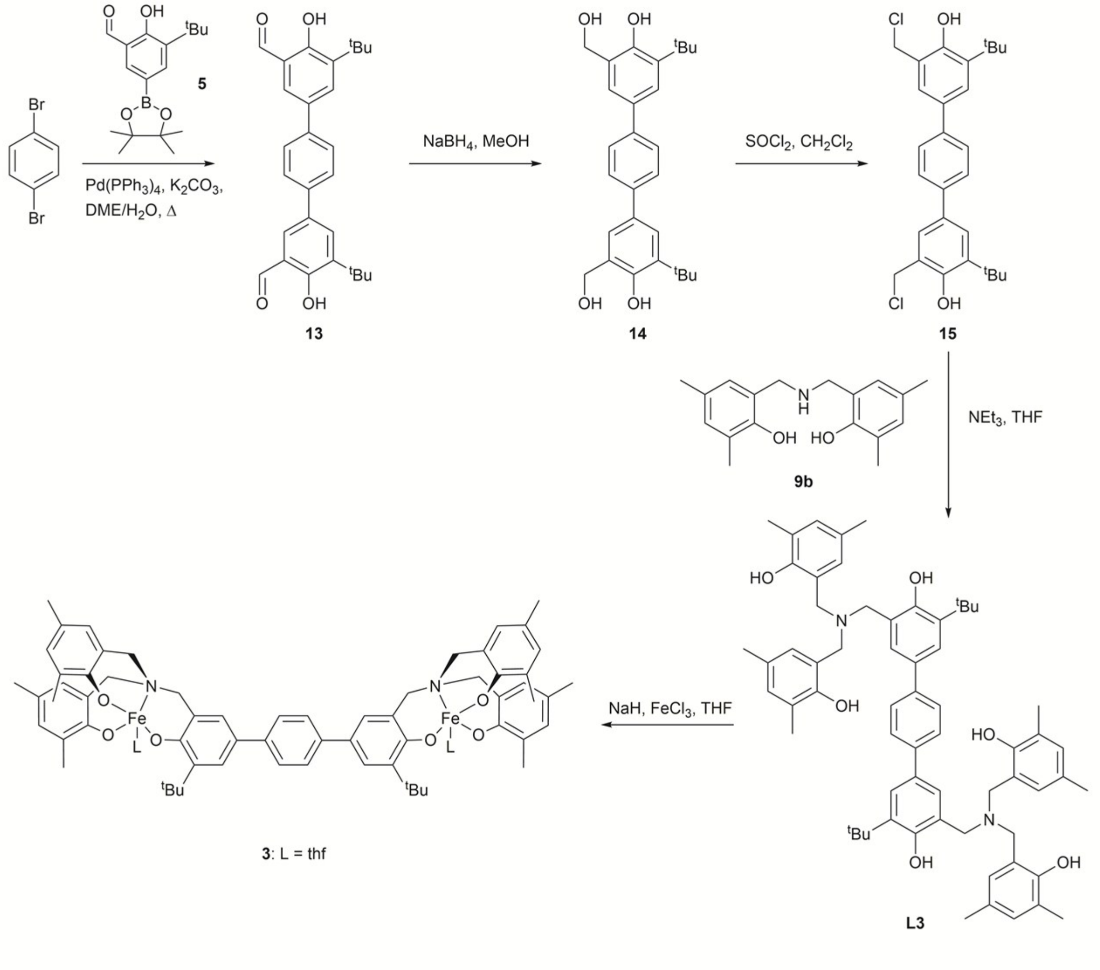
Synthesis of 1,3-bis-(3-tert-butyl-2-hydroxy-benzaldehyde)-benzene (10). It was synthesized as a similar procedure of **6** reported by previous literature.[2] To a suspension of tetrakis(triphenylphosphine)palladium(0) (0.33 g, 0.28 mmol), 1,3-dibromobenzene (0.66 g, 2.82 mmol) and K_2CO_3 (1.42 g, 9.40 mmol) in 1,4-dioxane (40 mL) and H_2O (7 mL) was added **5** (1.8 g, 5.91 mmol). The mixture was reflux for 20 h, and then cooled to room temperature, CH_2Cl_2 (25 mL) and H_2O (25 mL) was added to the solution and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (25 mL × 2). The extracts were combined and then dried over $MgSO_4$, 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, $CDCl_3$) δ 11.83 (s, 2H), 9.98 (s, 2H), 7.80 (d, J = 2.2 Hz, 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, $CDCl_3$) δ 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) δ 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) δ 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) δ 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) δ 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 $[C_{64}H_{76}N_2O_6+H]^+$: 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 $[C_{64}H_{70}Fe_2N_2O_6+H]^+$: 1075.4005, found: 1075.4053. Anal. Calcd for $C_{72}H_{86}Fe_2N_2O_8$: 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), 754 (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) λ_{max} in nm (log ε): 344 nm (4.10), 437 nm (3.96).



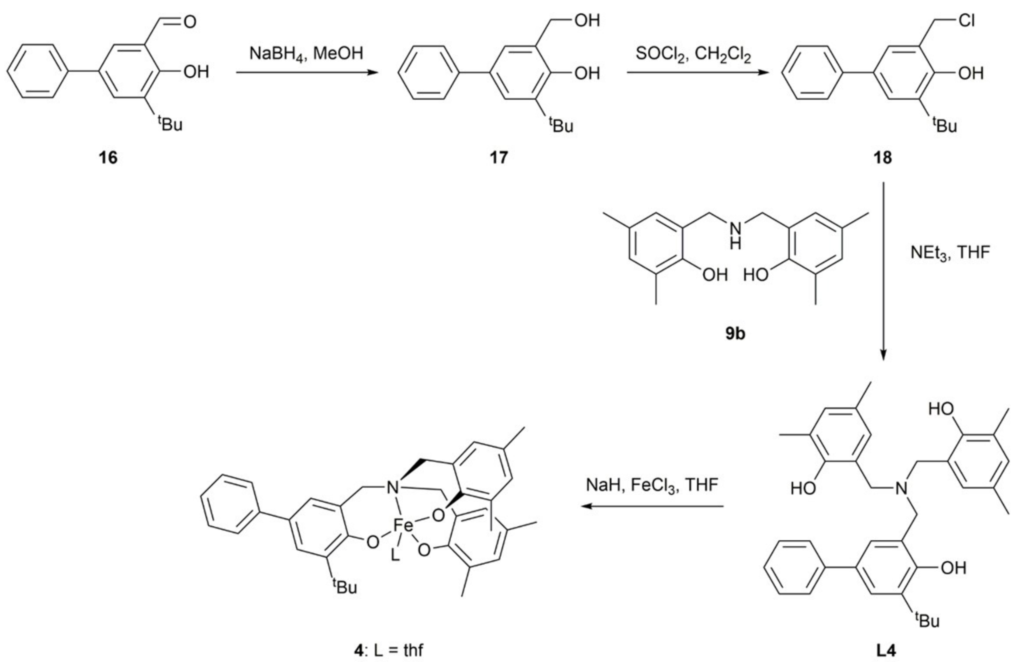
Scheme S2. Synthetic routes for dinuclear iron(III) complex **3**

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$_6$) δ 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$_6$) δ 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.

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 [$C_{64}H_{76}N_2O_6$+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 [$C_{64}H_{70}Fe_2N_2O_6$+2H]$^{2+}$: 538.2039, found: 538.2046. Anal. Calcd for $C_{72}H_{86}Fe_2N_2O_8$: 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), 2918 (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) λ_{max} in nm (log ε): 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$_3$) δ 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$_3$) δ 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$_8$) δ 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$_8$) δ 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 **L4** (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; N 2.16; 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 (m), 1295 (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) λ_{max} in nm (log ε): 345 nm (3.84), 438 nm (3.73).

2. ^{1}H and ^{13}C NMR spectra of Ligands 1-4

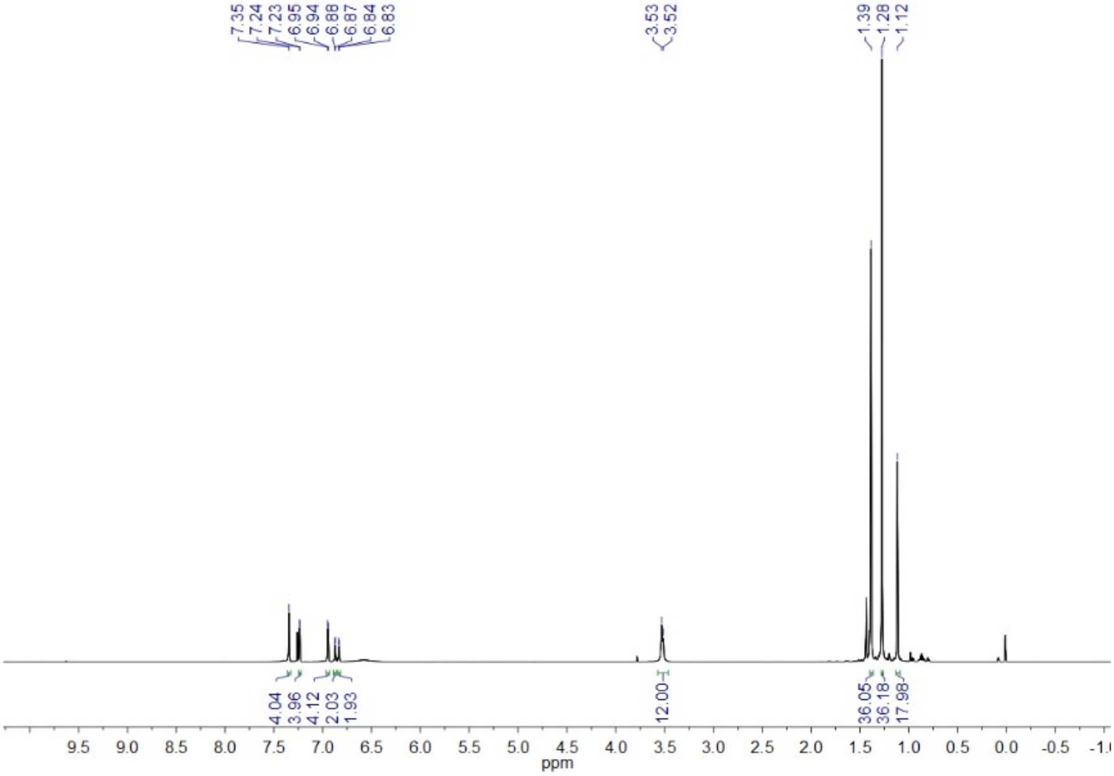


Figure S1. ^{1}H NMR spectrum of **L1a** in $CDCl_3$

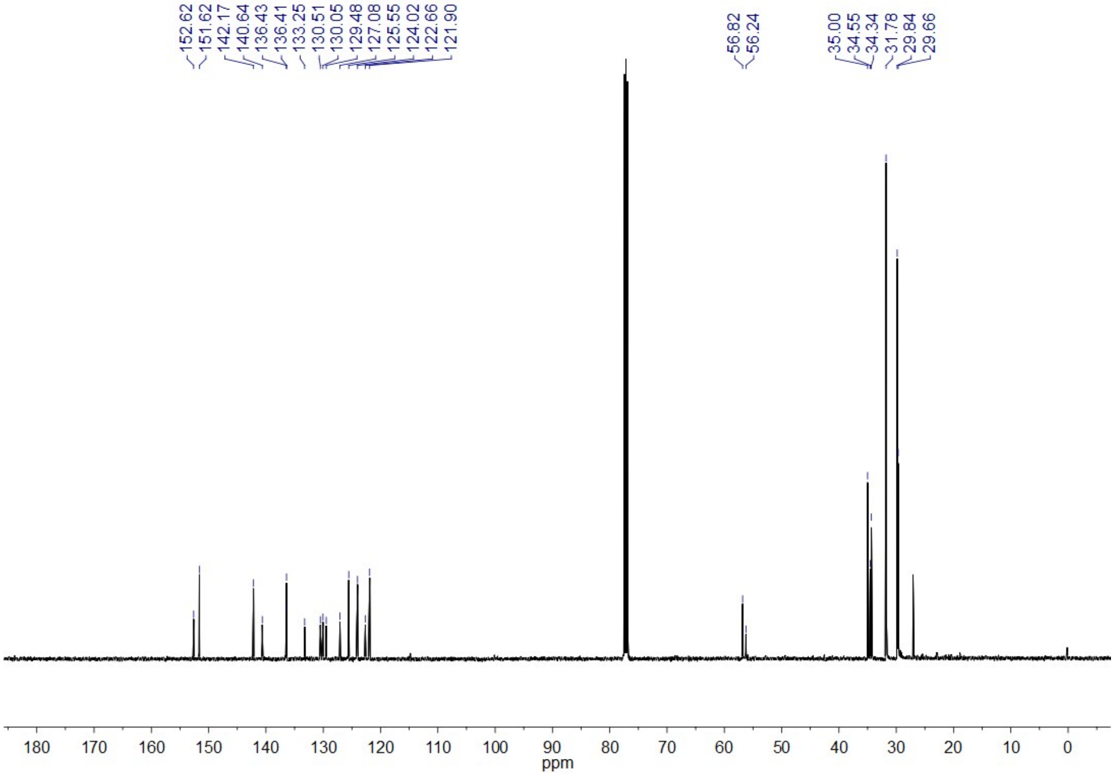


Figure S2. ^{13}C NMR spectrum of **L1a** in $CDCl_3$

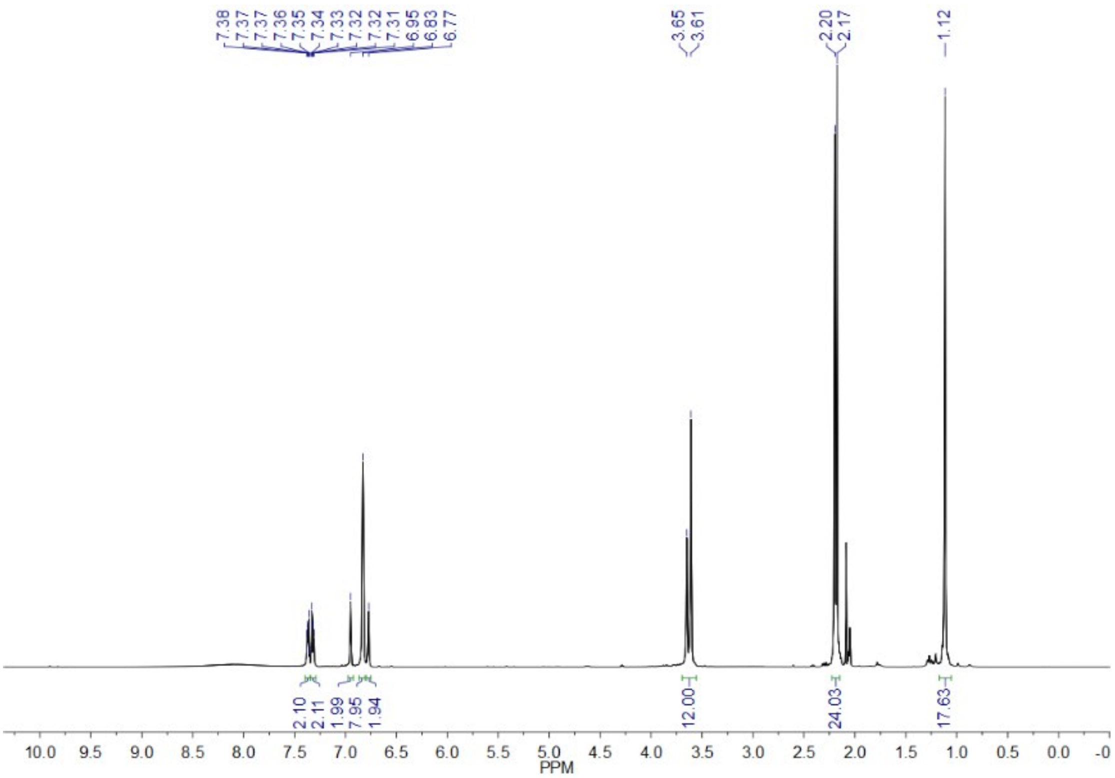


Figure S3. ^{1}H NMR spectrum of **L1b** in acetone-d_6

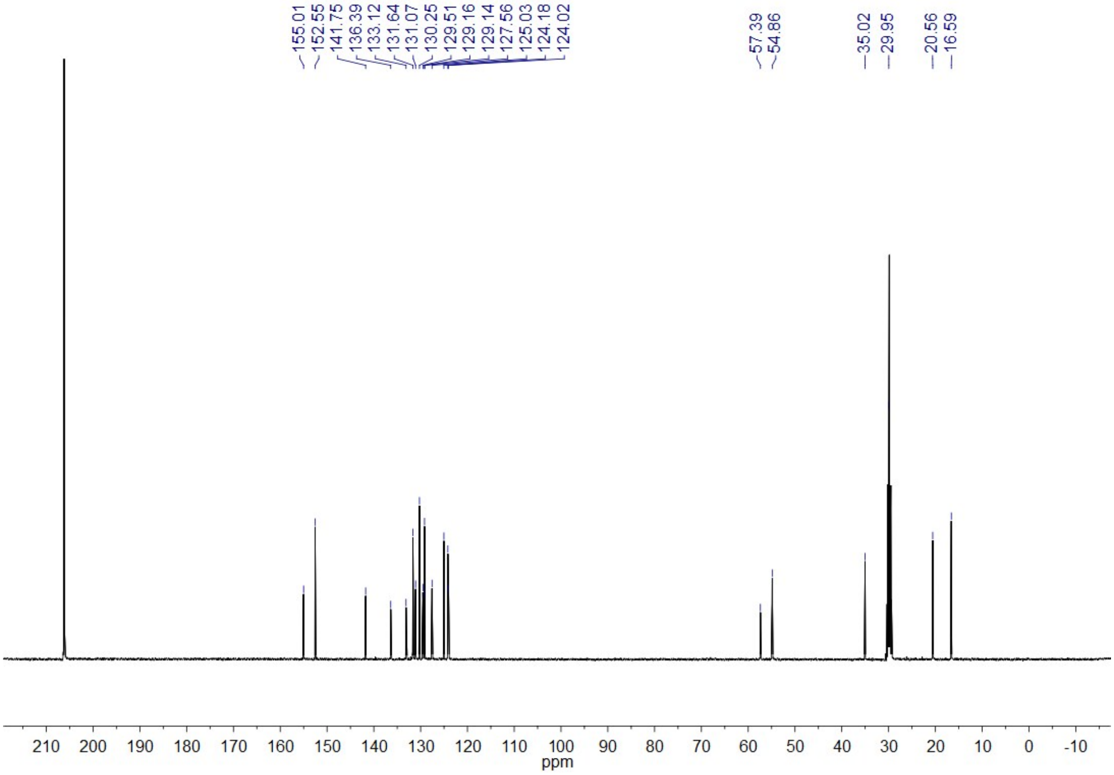


Figure S4. ^{13}C NMR spectrum of **L1b** in acetone-d_6

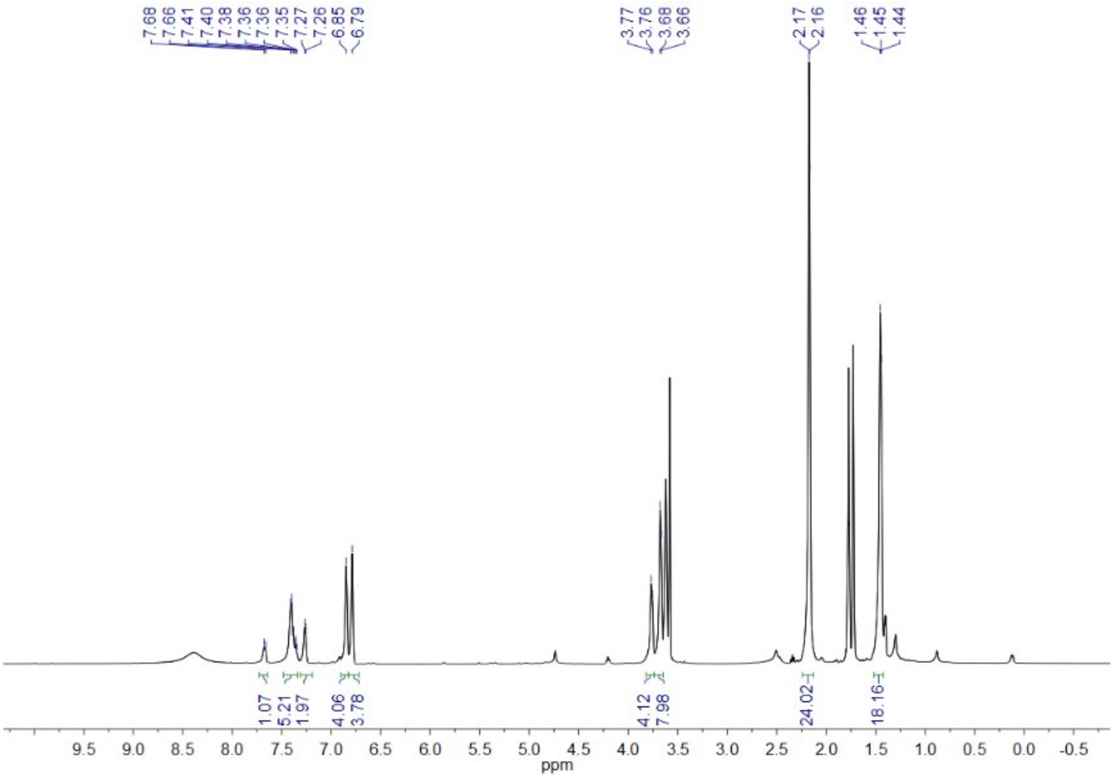


Figure S5. ^{1}H NMR spectrum of **L2** in THF-d_8

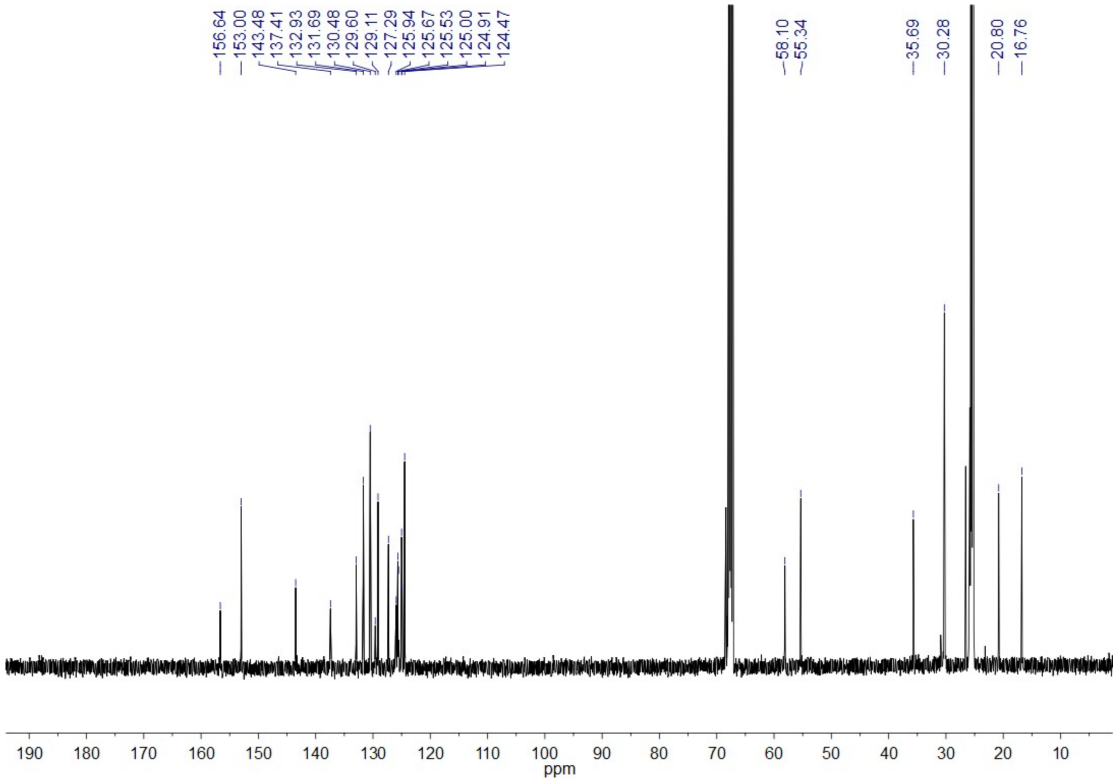


Figure S6. ^{13}C NMR spectrum of **L2** in THF-d_8

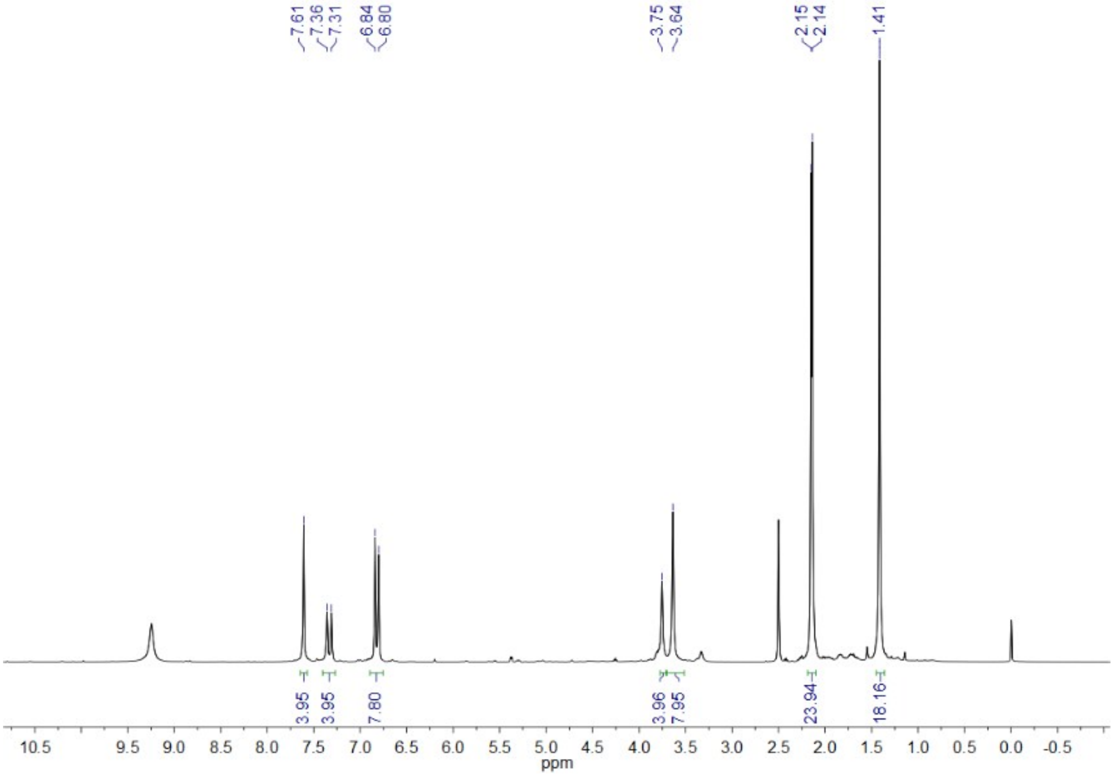


Figure S7. ^{1}H NMR spectrum of **L3** in DMSO-d_6

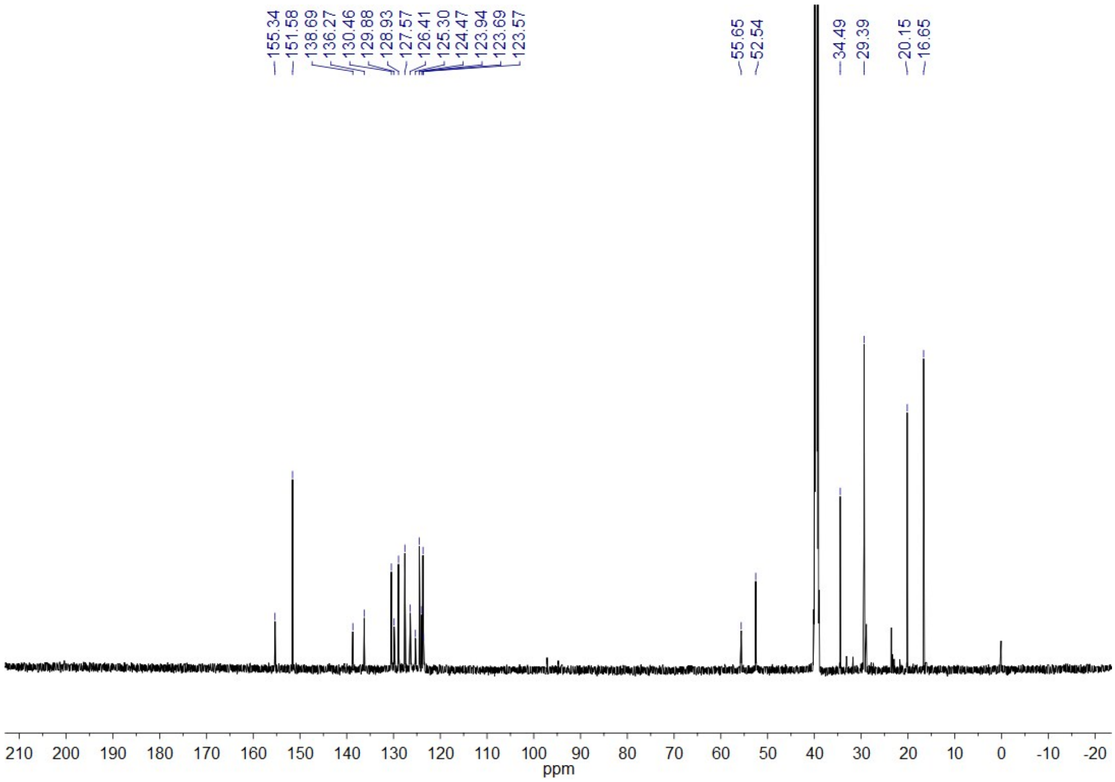


Figure S8. ^{13}C NMR spectrum of **L3** in DMSO-d_6

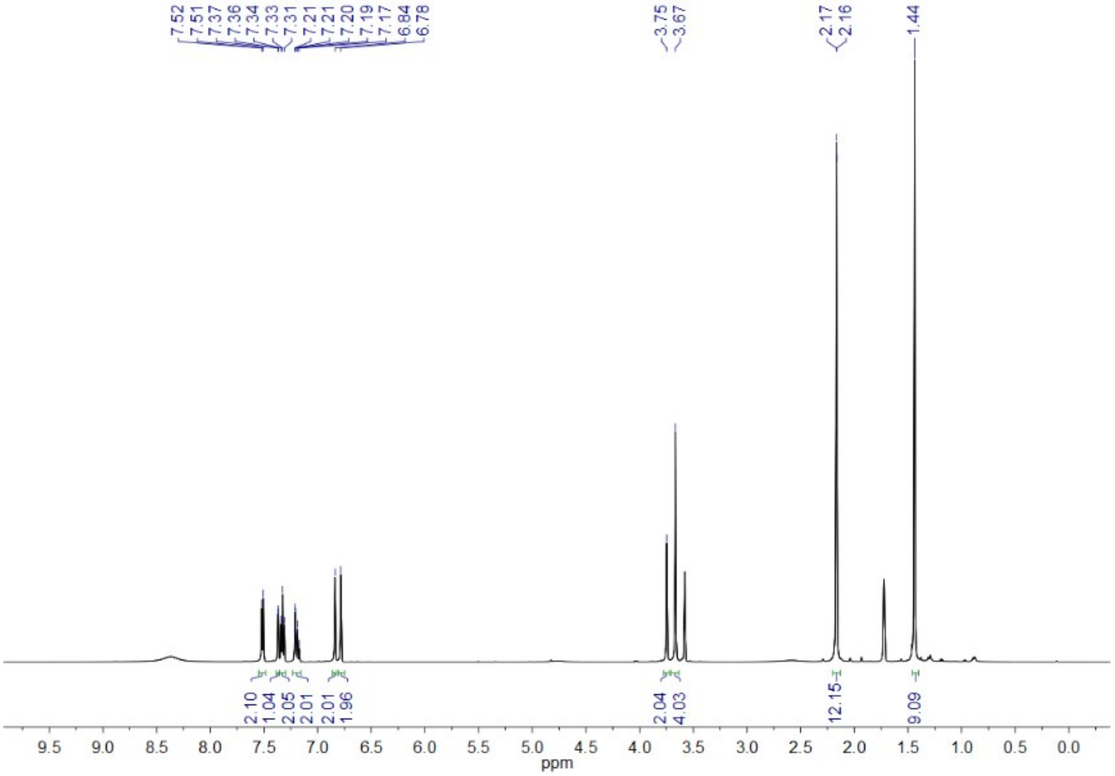


Figure S9. ^{1}H NMR spectrum of **L4** in THF-d_8

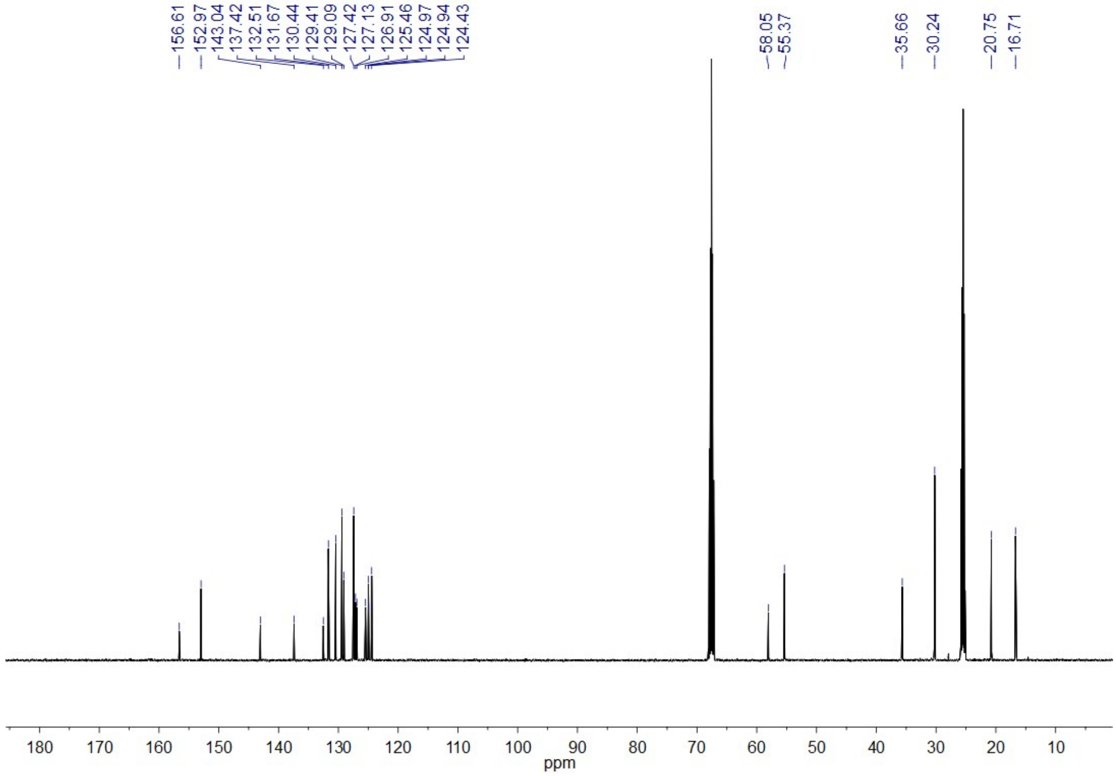


Figure S10. ^{13}C NMR spectrum of **L4** in THF-d_8

3 UV–vis spectra of iron(III) complexes

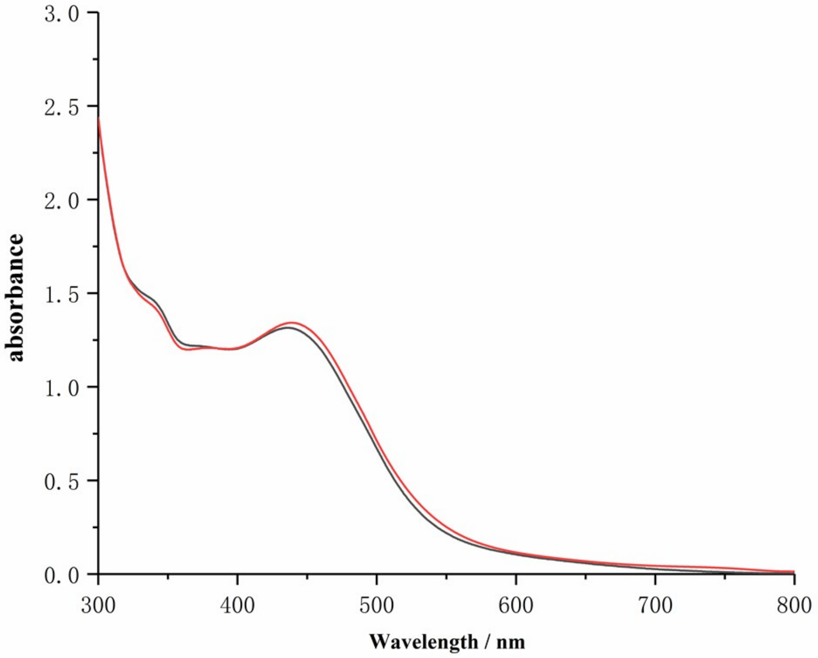


Figure S11. UV–vis spectra of complex **1a** in toluene (0.1 mM; black curve) and in presence of 500 equiv. of CHO (red curve).

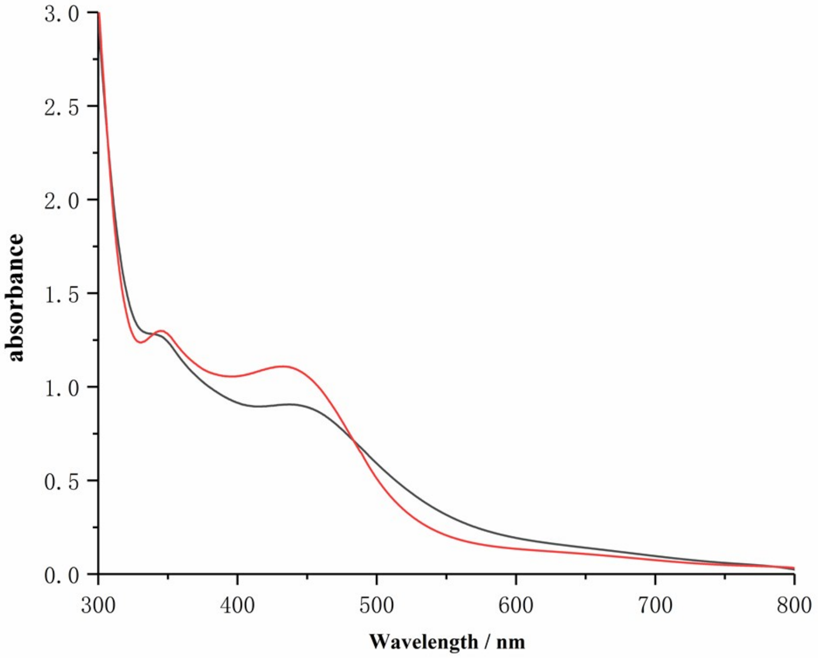


Figure S12. UV–vis spectra of complex **2** in toluene (0.1 mM; black curve) and in presence of 500 equiv. of CHO (red curve).

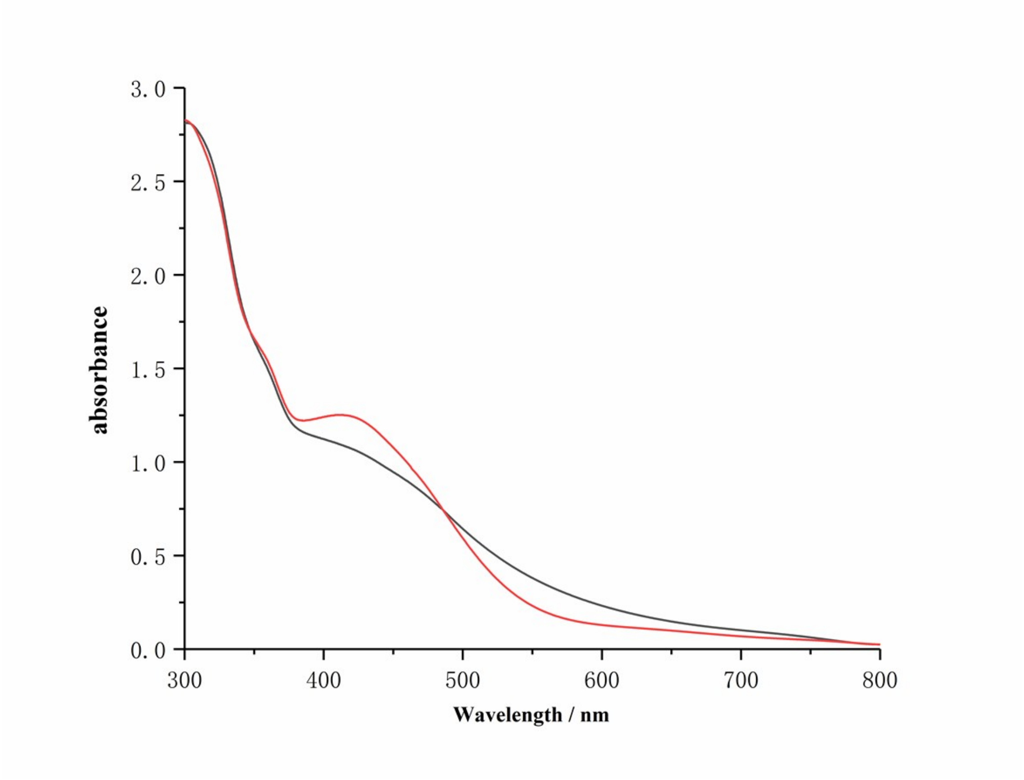


Figure S13. UV–vis spectra of complex **3** in toluene (0.1 mM; black curve) and in presence of 500 equiv. of CHO (red curve).

4 ^{1}H NMR spectrum and FT-IR spectra of the reaction mixture after catalytic test

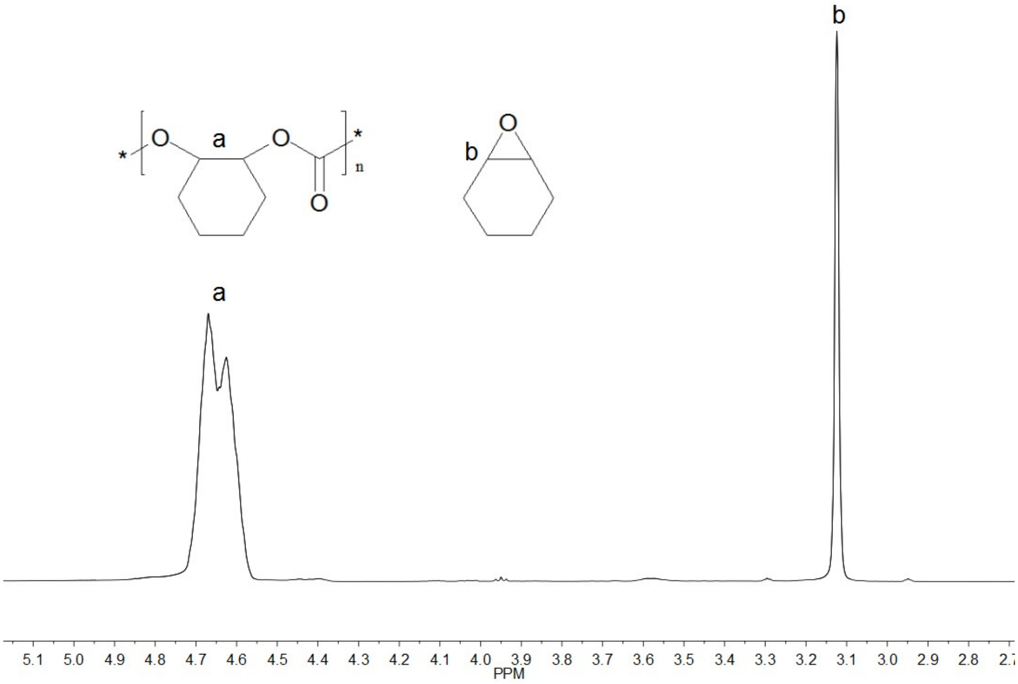


Figure S14. ^{1}H NMR spectrum of the crude reaction mixture of CHO/CO_2 copolymerization (Table 1, entry 2) in $CDCl_3$

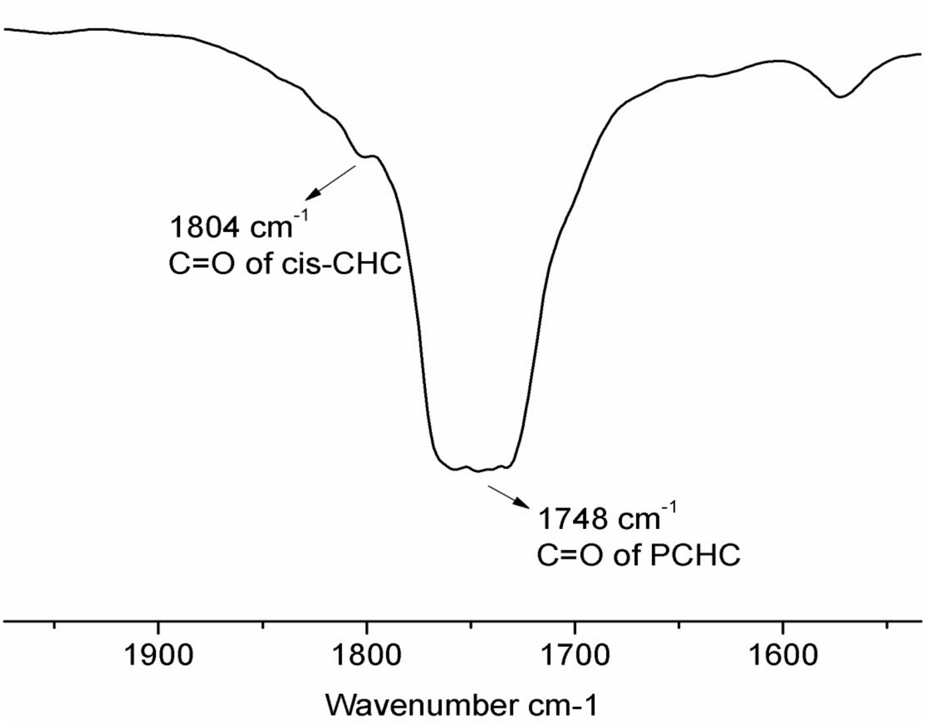


Figure S15. FT-IR spectrum of crude reaction mixture of CHO/CO_2 copolymerization (Table 2, entry 3)

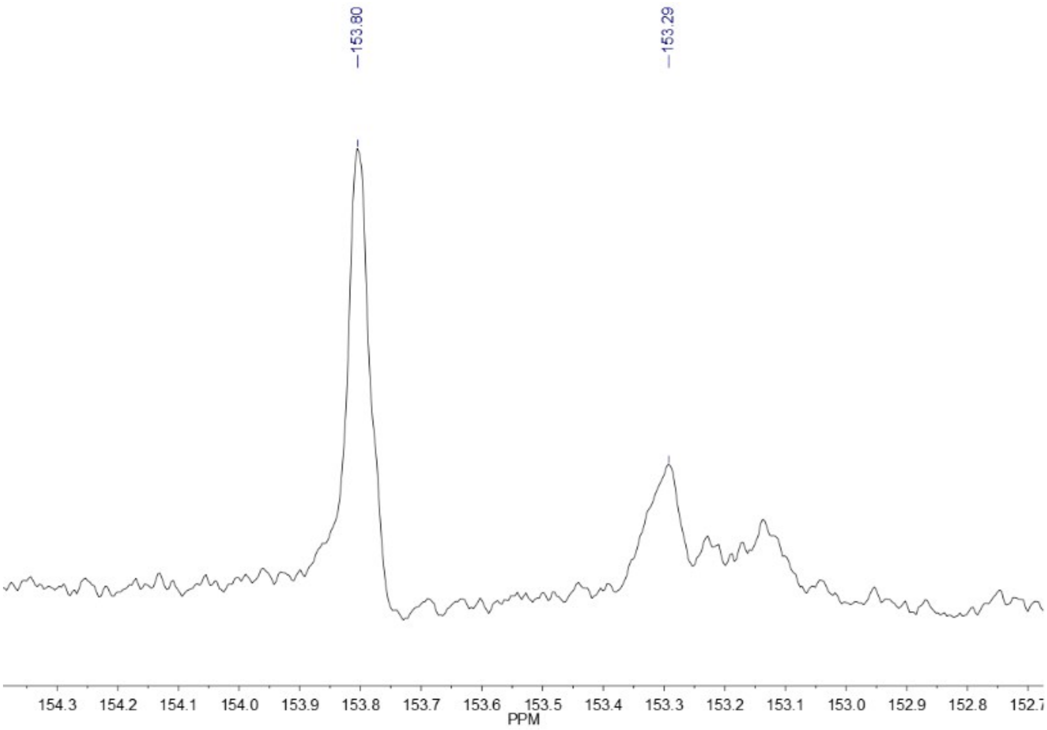


Figure S16. Carbonyl region of ^{13}C NMR spectrum of PCHC (Table 1, entry 2) in CDCl$_3$. According to literatures,[7, 8] this spectrum indicates the formation of atactic PCHC.

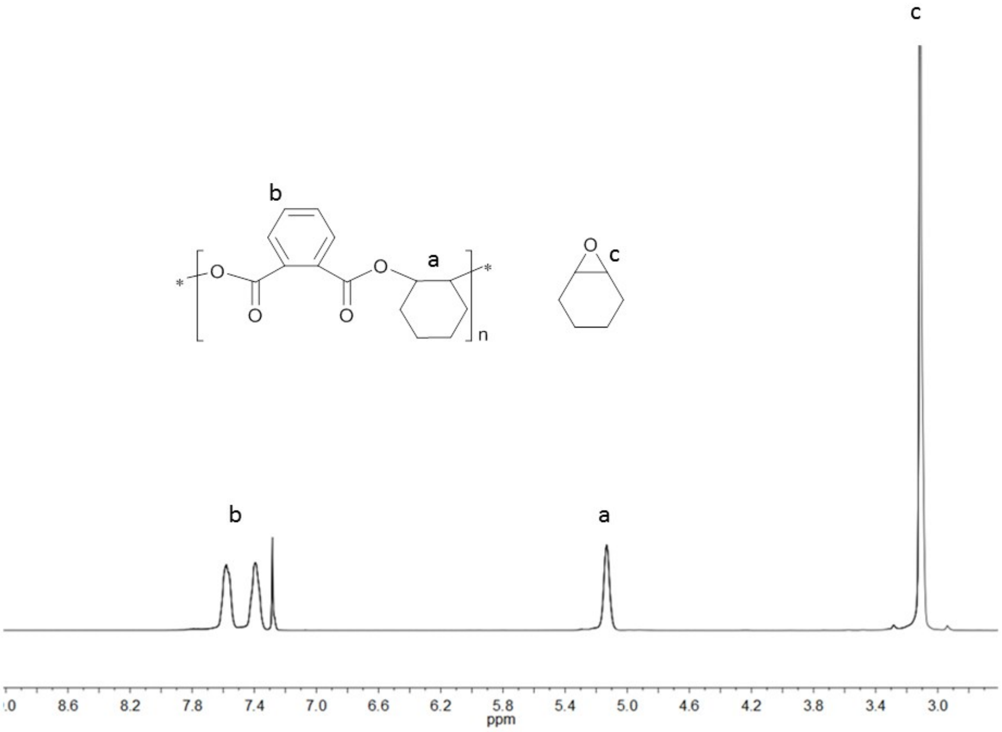


Figure S17. ^{1}H NMR spectrum of the crude reaction mixture of CHO/PA copolymerization in neat (Table 4, entry 1) in $CDCl_3$

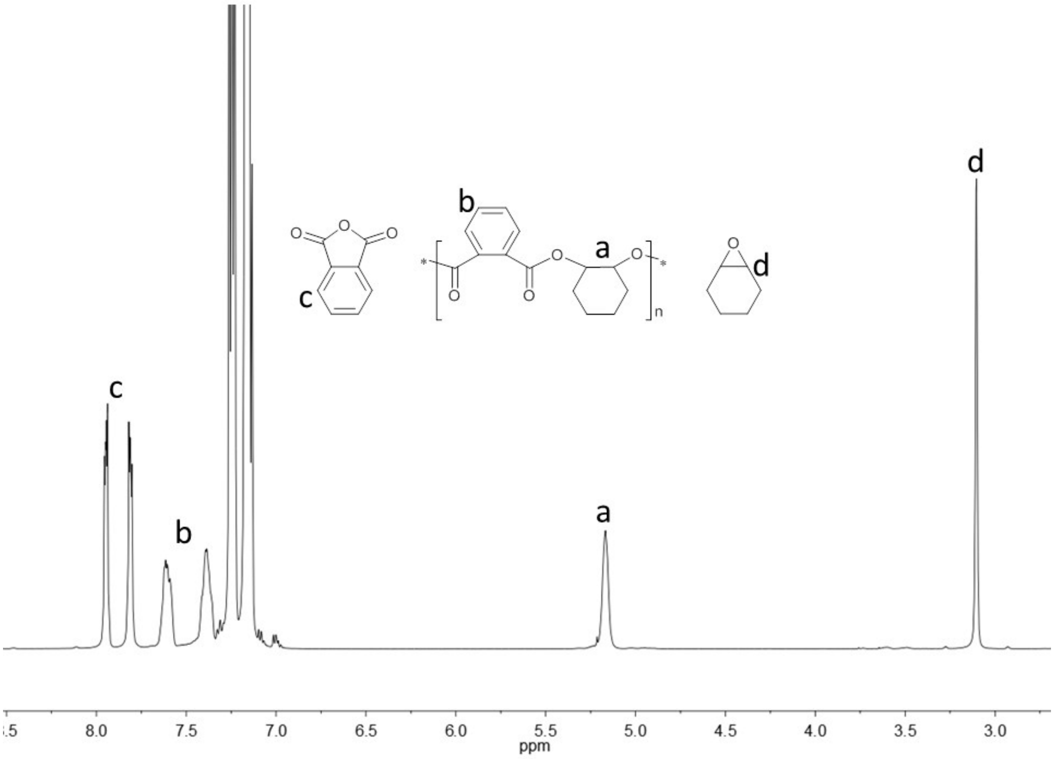


Figure S18. ^{1}H NMR spectrum of the crude reaction mixture of CHO/PA copolymerization in toluene (Table 3, entry 6) in $CDCl_3$

5 MALDI-TOF mass spectrum of copolymers

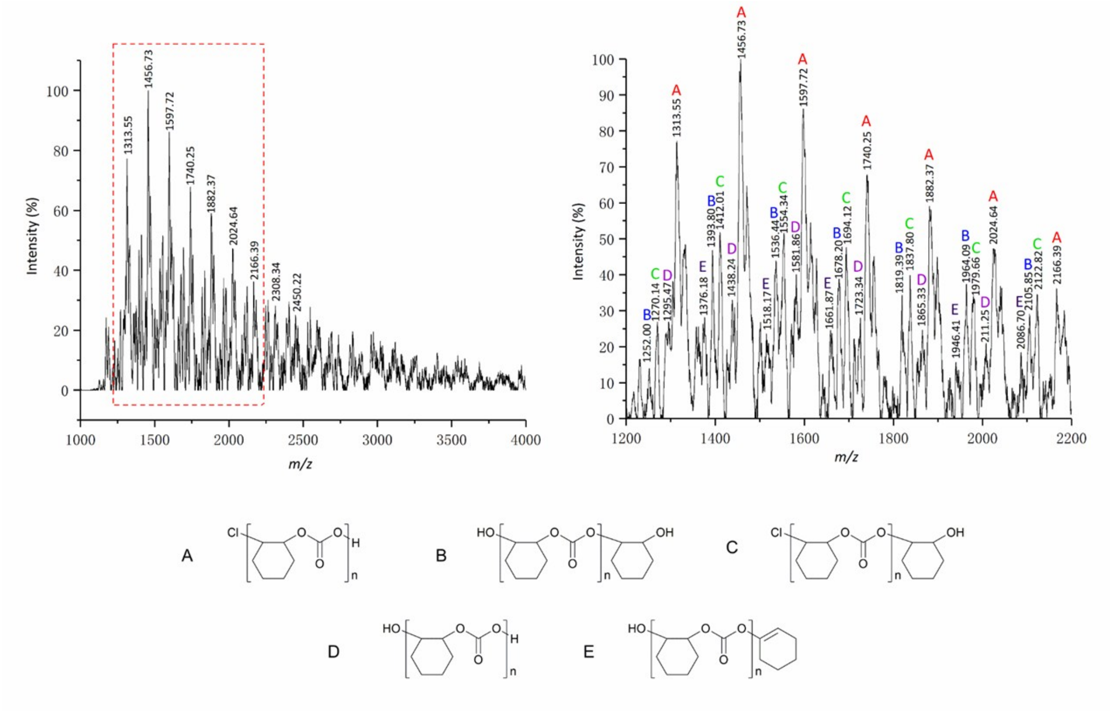


Figure S19. The MALDI-TOF mass spectra of PCHC produced by complex **1b**/PPNCl (Table 1, entry 2).

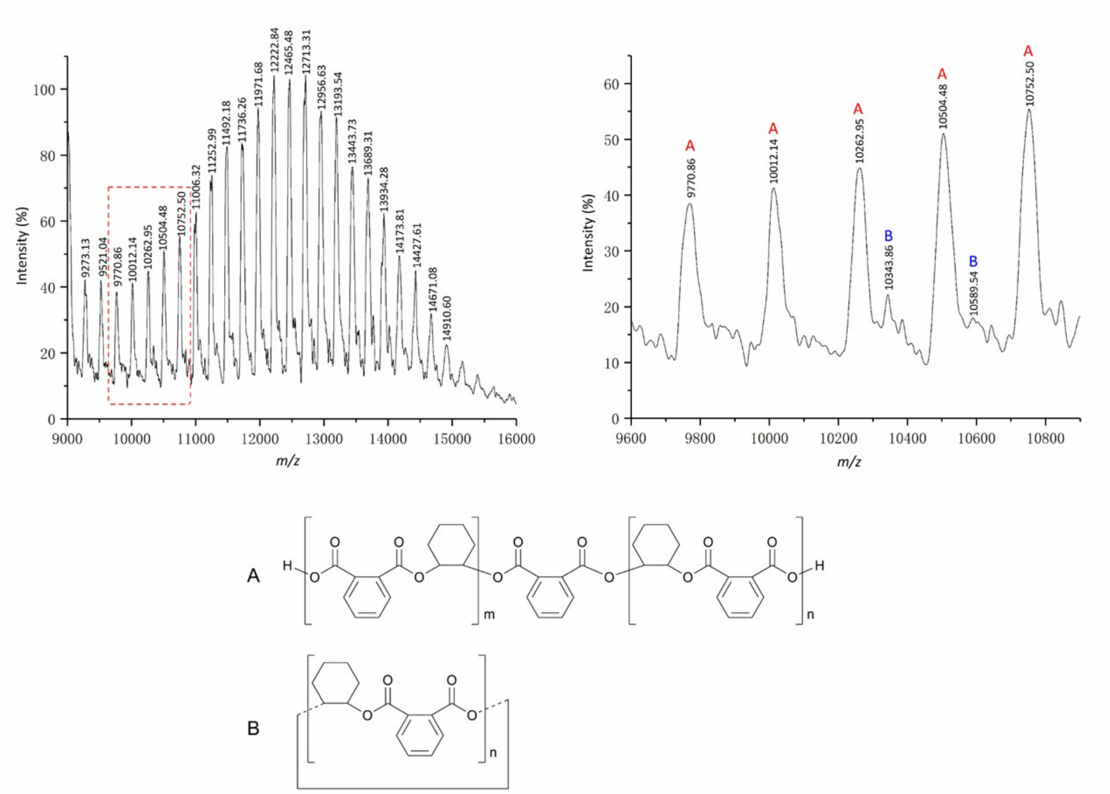
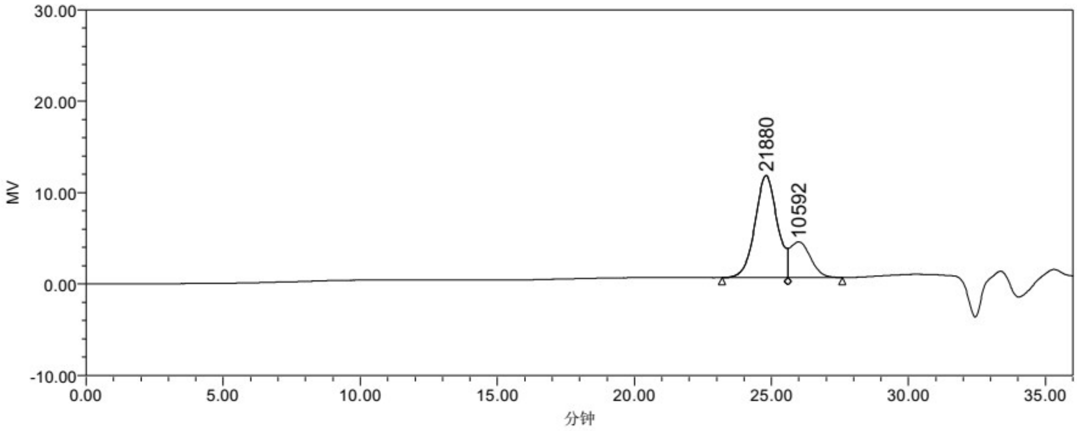


Figure S20. High molecular weight region of the MALDI-TOF mass spectra of polyester produced by complex **1b**/PPNCl (Table 4, entry 6).

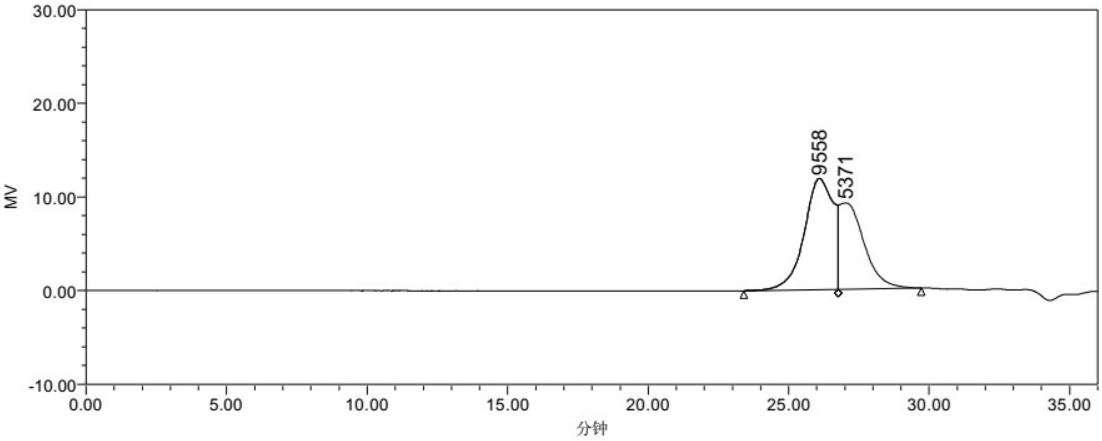
6 GPC and DSC data for copolymers



GPC结果

	Mn 数均分子量 (道尔顿)	Mw 重均分子量 (道尔顿)	MP 峰位分子量	Mz Z均分子量 (道尔顿)	Mz+1 Z+1均分子量 (道尔顿)	Mv 粘均分子量 (道尔顿)	Polydispersity 多分散性	K (dl/g)	alpha
1	21245	22401	21880	23675	25077	22223	1.054428	0.0001600	0.7060
2	9658	10072	10592	10446	10777	10015	1.042913	0.0001600	0.7060

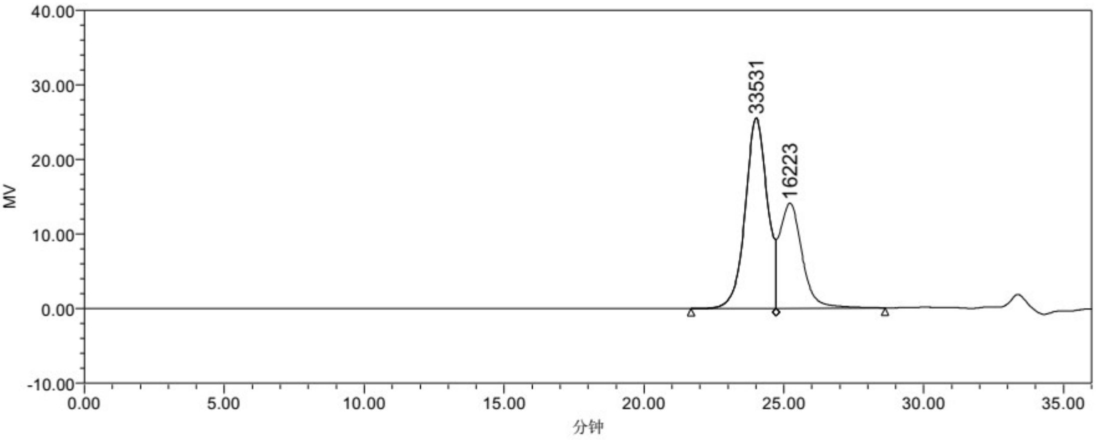
Figure S21. GPC chart of the product PCHC (Table 1, entry 2, M_n: 21245 and 9658, M_w/M_n = 1.05 and 1.04)



GPC结果

	Mn 数均分子量 (道尔顿)	Mw 重均分子量 (道尔顿)	MP 峰位分子量	Mz Z均分子量 (道尔顿)	Mz+1 Z+1均分子量 (道尔顿)	Mv 粘均分子量 (道尔顿)	Polydispersity 多分散性	K (dl/g)	alpha
1	9562	10416	9558	11606	13318	10268	1.089330	0.0001600	0.7060
2	4119	4494	5371	4782	5007	4447	1.091073	0.0001600	0.7060

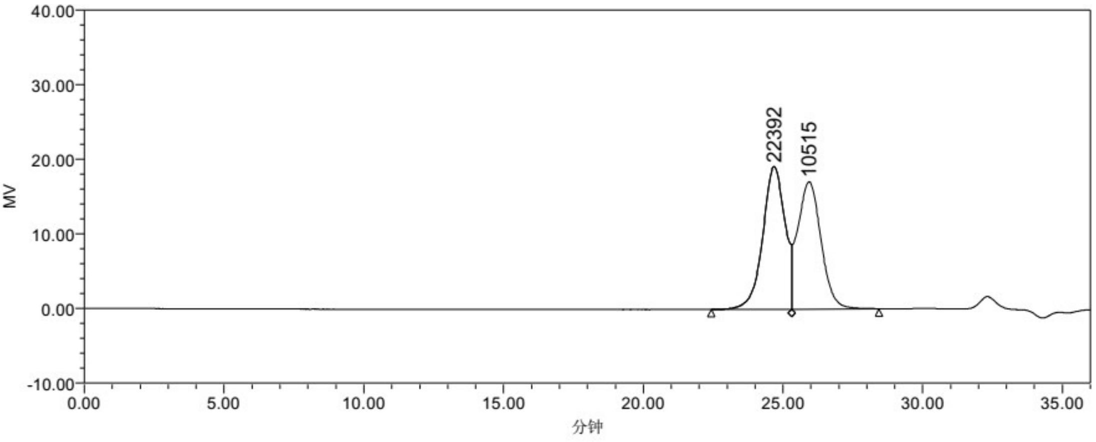
Figure S22. GPC chart of the product PCHC (Table 2, entry 6, M_n: 9562 and 4119, M_w/M_n = 1.09 and 1.09)



GPC结果

	Mn 数均分子量 (道尔顿)	Mw 重均分子量 (道尔顿)	MP 峰位分子量	Mz Z均分子量 (道尔顿)	Mz+1 Z+1均分子量 (道尔顿)	Mv 粘均分子量 (道尔顿)	Polydispersity 多分散性	K (dl/g)	alpha
1	32883	34629	33531	36707	39267	34349	1.053100	0.0001600	0.7060
2	14446	15604	16223	16419	17065	15471	1.080204	0.0001600	0.7060

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)



GPC结果

	Mn 数均分子量 (道尔顿)	Mw 重均分子量 (道尔顿)	MP 峰位分子量	Mz Z均分子量 (道尔顿)	Mz+1 Z+1均分子量 (道尔顿)	Mv 粘均分子量 (道尔顿)	Polydispersity 多分散性	K (dl/g)	alpha
1	22266	23464	22392	24948	26847	23268	1.053821	0.0001600	0.7060
2	9880	10474	10515	10999	11469	10394	1.060143	0.0001600	0.7060

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)

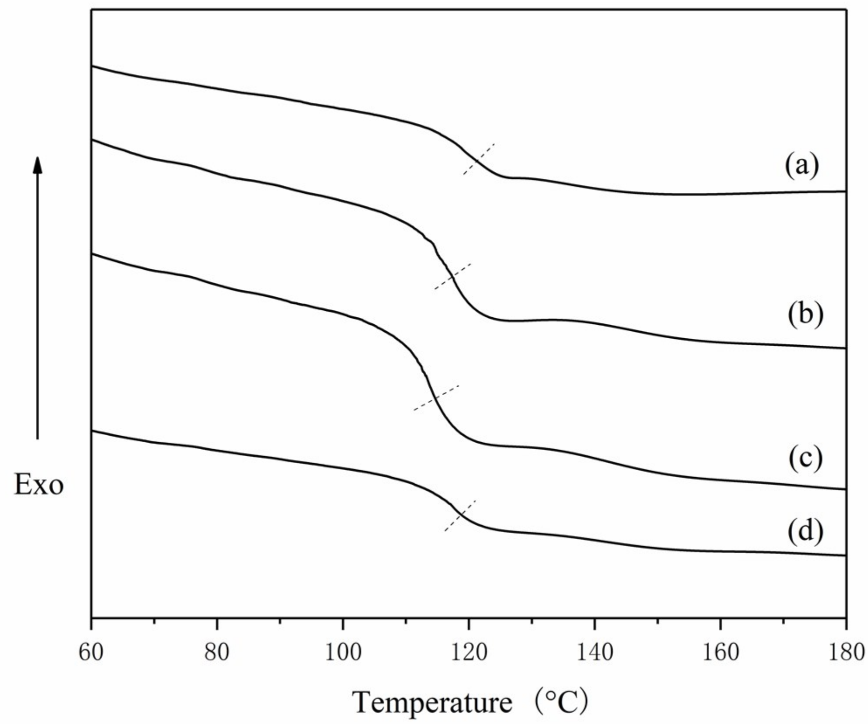


Figure S25. DSC plots of PCHC produced by iron(III) complexes/PPNCl: (a)Table 1, entry 2, T_g = 119 °C; (b)Table 1, entry 5, T_g = 117 °C; (c)Table 1, entry 8, T_g = 114 °C; (d)Table 1, entry 11, T_g = 114 °C.

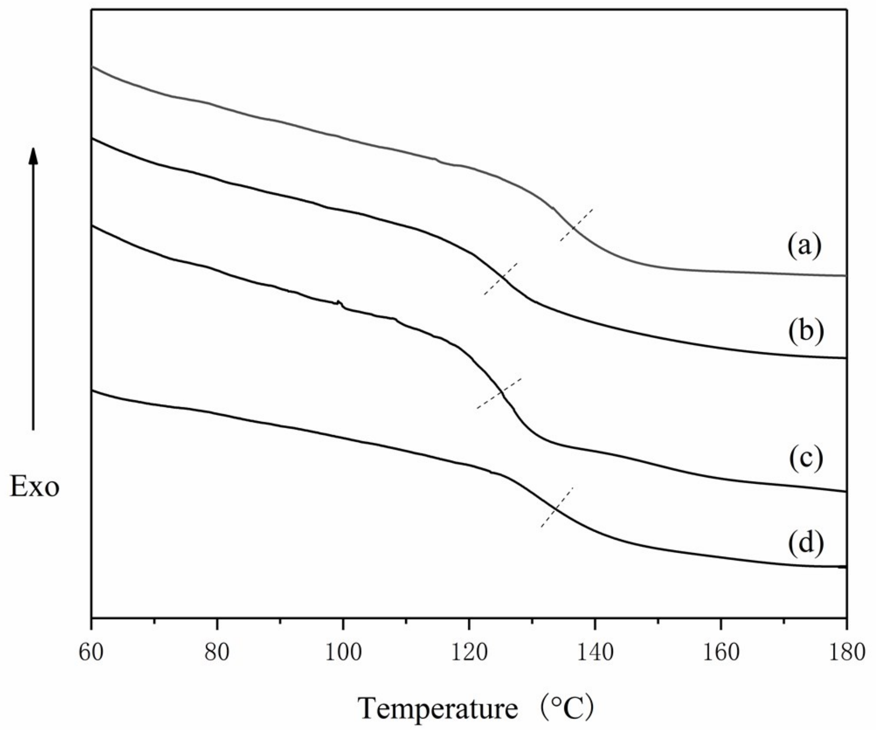


Figure S26. DSC plots of polyesters produced by iron(III) complexes/PPNCl: (a)Table 3, entry 2, $T_g = 136$ °C; (b)Table 3, entry 3, $T_g = 125$ °C; (c)Table 3, entry 4, $T_g = 125$ °C; (d)Table 3, entry 5, $T_g = 133$ °C.

7 References

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