Supporting Information

Binuclear Chromium-Salan Complex Catalyzed Alternating Copolymerization of Epoxides and Cyclic Anhydrides

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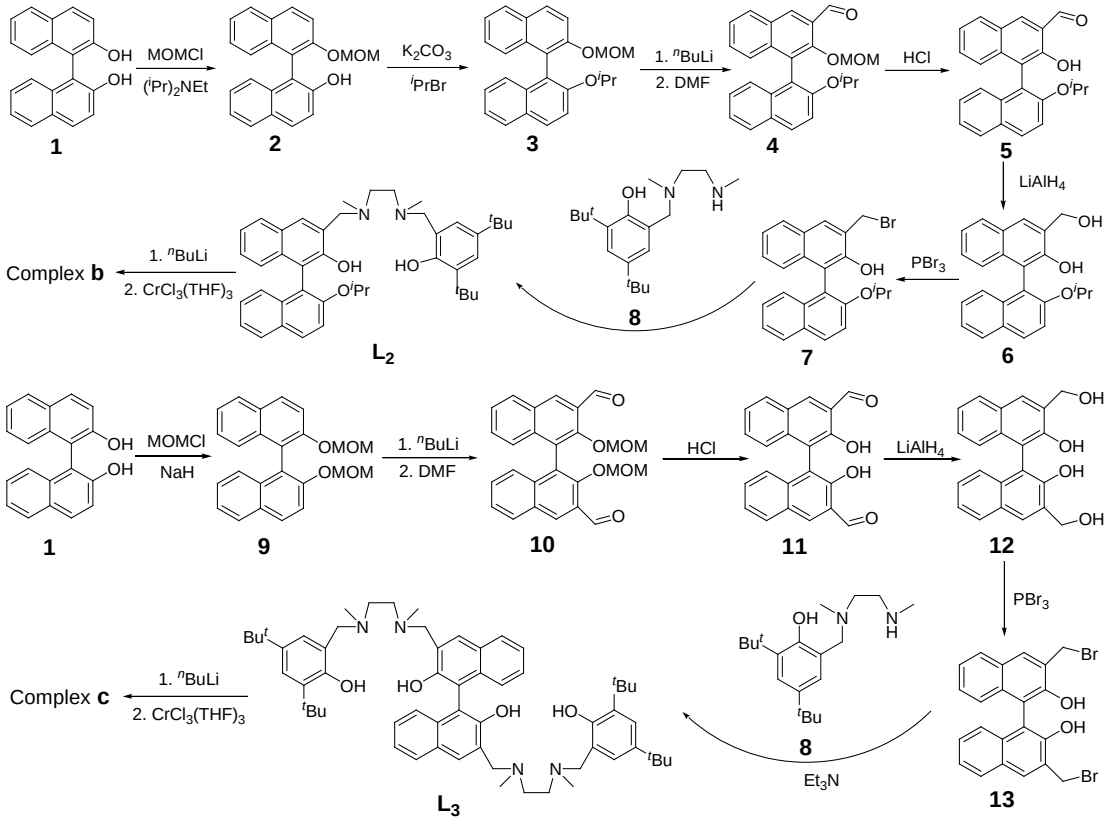
1. Synthesis of compounds 6-8, 12 and 13



Scheme S1. Synthetic routes of complexes **b** and **c**

Synthesis of compound **6.** To a stirred solution of compound **5** (5 g) dissolved in the dried THF of 40 mL was added dropwise a solution of 0.14 g $LiAlH_4$ in 5 mL dried

THF. The reaction mixture was stirred at the room temperature. After 3 h, methanol was added slowly. When the resulting solution was adjusted to 7 of pH using HCl (1 mol/L), water was added into the solution. The resultant mixture was extracted by ethyl acetate three times. The combined organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by chromatography (silica gel, dichloromethane/methanol = 20/1) to obtain the compound **6** as a white solid (3.4 g, 68%). ^{1}H NMR (400 MHz, C_3D_6O, 25 ^{o}C): δ 4.96 (d, *J* = 4.0 Hz 2H, C*H*$_2$), 6.97 (d, *J* = 8.0 Hz, 1H, BINOL), 7.16 (t, *J* = 4.0 Hz, 1H, BINOL), 7.27 (t, *J* = 4.0 Hz, 1H, BINOL), 7.87 (d, *J* = 8.0 Hz, 1H, BINOL), 7.99 (s, 1H, BINOL). ^{13}C NMR (100 MHz, C_3D_6O, 25 ^{o}C): δ 61.1 (*C*H$_2$), 113.3 (*C*), 122.9 (*C*H), 124.3 (*C*H), 125.7 (*C*H), 126.4 (*C*H), 127.8 (*C*H), 128.9 (*C*), 130.8 (*C*), 133.6 (*C*), 152.2 (*C*). HRMS: calcd for $[C_{22}H_{17}O_4]^-$ $([M-H])^-$: 357.1491; Found: 357.4107.

Synthesis of Compound **7.** To a solution of compound **6** (3.44 g, 9.6 mmol) in $CHCl_3$ (50 mL) was added PBr_3 (0.35 mL, 3.65 mmol). The white solid dissolved slowly when the mixture was stirred at room temperature for 2 h. The reaction mixture was then treated with cold water (30 mL) with vigorous stirring for 2 min. The organic layer was separated and the aqueous residue was extracted with $CHCl_3$ (2 × 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated and dried in vacuum to give the desired product as a pale yellow solid. The compound **7** was used in the following reactions without further purification. Yield: 4.23 g (97%).

Synthesis of Compound **8.** To a stirred solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1.20 g, 5.12 mmol) in methanol (40 mL) was added dropwise a solution of *N*,*N′*-dimethylethylendiamine (0.56 g, 6.4 mmol) in methanol (10 mL). The solution was stirred for 2 h, and $NaBH_4$ (0.4 g, 10.6 mmol) was added in small portions. After continuous stirring of 1 h, another portion of $NaBH_4$ (0.4 g, 10.6 mmol) was added and the reaction mixture was stirred over night at room temperature. Then the solvent was removed under vacuum. Water and HCl (5 mol/L) were added into the mixture till the pH = 2. Then the water phase was washed by ethyl acetate three times. After that $NaHCO_3$ was added into the water phase till the pH=7. The water phase was extracted by ethyl acetate and the extract was dried over anhydrous Na_2SO_4. The organic solvent was removed under vacuum to give the desired product **8** as a purple solid.(1.14 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 1.27 (s, 9H, C(C*H*$_3$)$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$), 2.33 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 2.59 (t, *J* = 4 Hz, 2H, C*H*$_2$), 2.75 (t, J = 8 Hz, 2H, C*H*$_2$), 3.68 (s, 2H, C*H*$_2$), 6.81 (d, *J* = 4 Hz, 1H, Ar), 7.20 (d, *J* = 4 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ 29.6 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 36.5 (*C*H$_3$), 42.1 (*C*H$_3$), 49.1 (*C*H$_2$), 56.5 (*C*H$_2$), 60.4 (*C*H$_2$), 117.9 (*C*), 123.7 (*C*), 124.1 (*C*), 128.7 (*C*H), 128.8 (*C*H), 156.7 (*C*). HRMS: calcd for $[C_{19}H_{35}N_2O]^+$ $([M+H])^+$: 307.2671; Found: 307.5436.

Synthesis of compound **12.** To a stirred solution of compound **11** (5 g) in the dried THF (50 mL) was added into 0.28 g $LiAlH_4$ in 5 mL dried THF. The reaction mixture was stirred at room temperature. After 3 h, MeOH was added slowly and HCl (1

mol/L) was also added till the pH of the solution is 7. Then water was added into the solution and the resulting mixture was extracted by ethyl acetate three times. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under vacuum. The resulting residue was purified by chromatography (silica gel, dichloromethane/methanol = 10/1) to obtain the compound **12** as a white solid (3 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 0.91 (d, J = 6.0, 3H, C*H*$_3$), 1.77 (d, J = 6.0, 3H, C*H*$_3$), 4.55 (m, 1H, C*H*), 5.03 (s, 2H, C*H*$_2$), 7.15 (m, 2H, BINOL), 7.26 (t, *J* = 8.4 Hz, 1H, BINOL), 7.35 (m, 3H, BINOL), 7.45 (d, *J* = 8.4 Hz, 1H, BINOL), 7.87 (d, *J* = 8.4 Hz, 1H, BINOL), 7.98 (d, *J* = 8.4 Hz, 1H, BINOL), 8.01 (d, *J* = 8.0 Hz, 1H, BINOL), 8.30 (s, 1H, BINOL). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ 25.8 (*C*H(*C*), 133.6 (*C*), 134.8 (*C*), 152.2 (*C*), 154.7 (*C*). HRMS: calcd for $[C_{22}H_{17}O_4]^-$ ([M-H])$^-$: 345.1127; Found: 345.3541.$_3$), 60.8 (*C*H$_3$), 73.4 (*C*H), 115.3 (*C*), 115.7(*C*), 122.9 (*C*H), 123.5 (*C*H), 124.3 (*C*H), 124.9 (*C*H), 125.7 (*C*H), 126.0 (*C*H), 126.4 (*C*H), 127.3 (*C*H), 127.8 (*C*H), 128.4(*C*H), 128.9 (*C*), 130.5(*C*), 130.8 (*C*), 131.3

Synthesis of Compound **13.** To a solution of compound **12** (3 g, 8.6 mmol) in $CHCl_3$ (80 mL) was added PBr_3 (0.55 mL, 3.65 mmol). The white solid dissolved slowly when the mixture was stirred at room temperature for 4 h. The reaction mixture was then treated with cold water (30 mL) with vigorous stirring for 2 min. The organic layer was separated and the aqueous residue was extracted with $CHCl_3$ (2 × 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated and dried in vacuum to give the desired product as a pale yellow solid.

The compound **13** was used in the following reactions without further purification.

Yield: 3.6 g (90%).

2. MALDI-ToF-MS spectrum of MA/ClPO copolymer

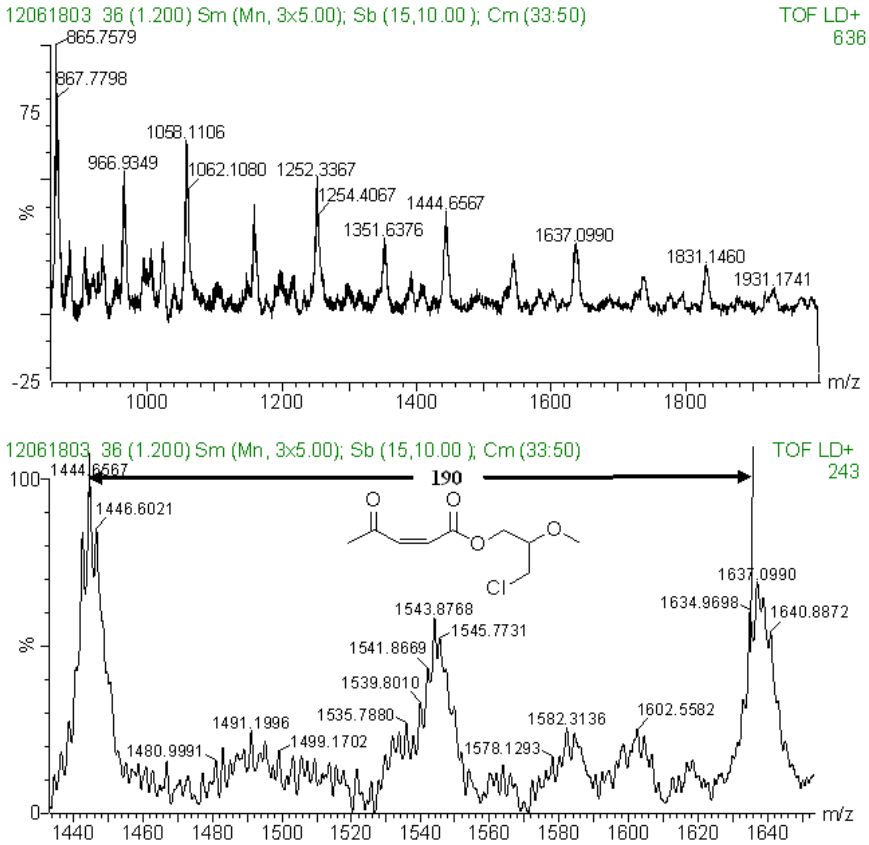


Figure S1. MALDI-ToF-MS spectrum of MA/ClPO copolymer

3. ^{1}H and ^{13}C NMR spectra of various polyesters

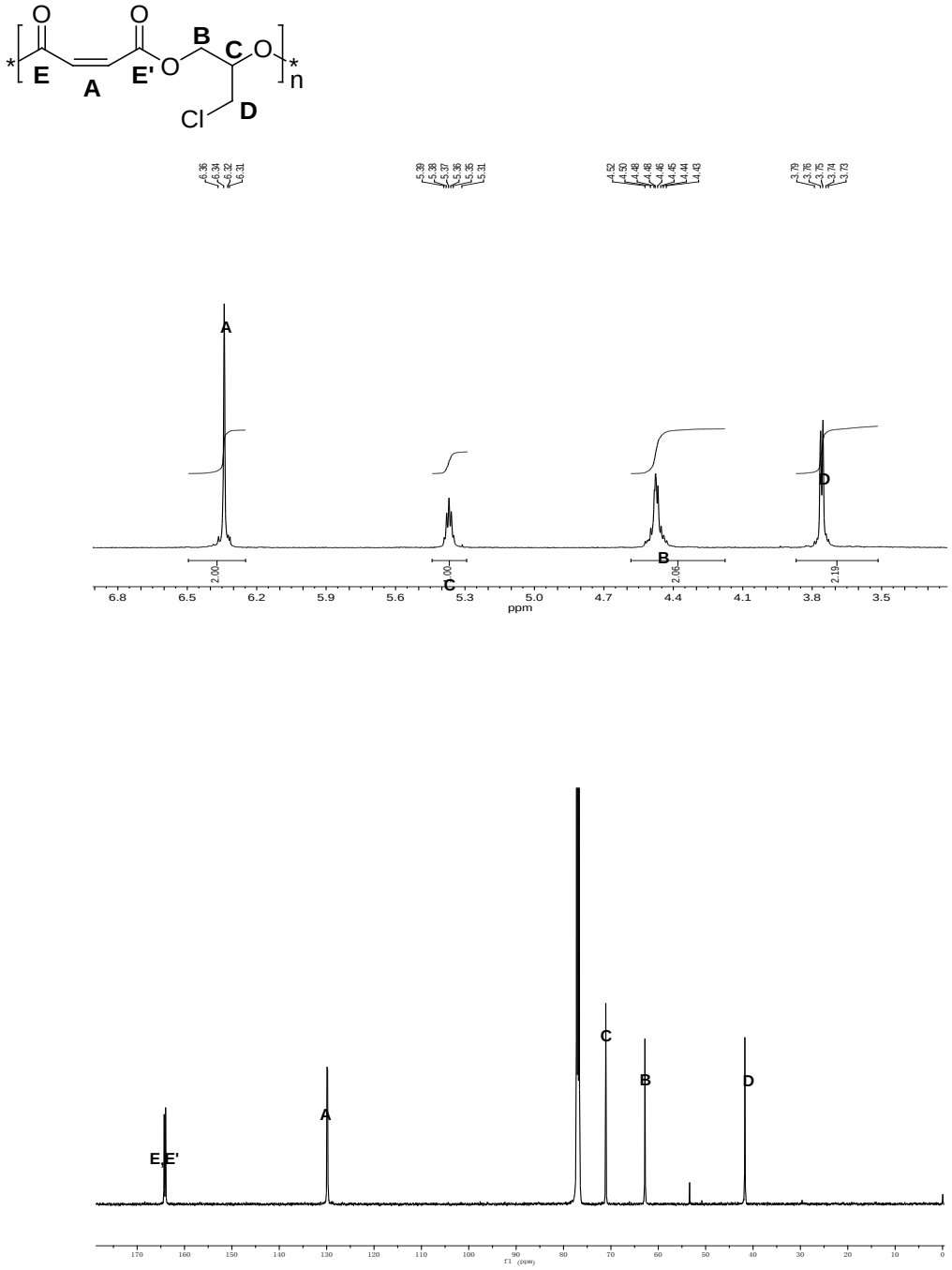


Figure S2. ^{1}H and ^{13}C NMR spectra of MA/ClPO copolymer in $CDCl_3$

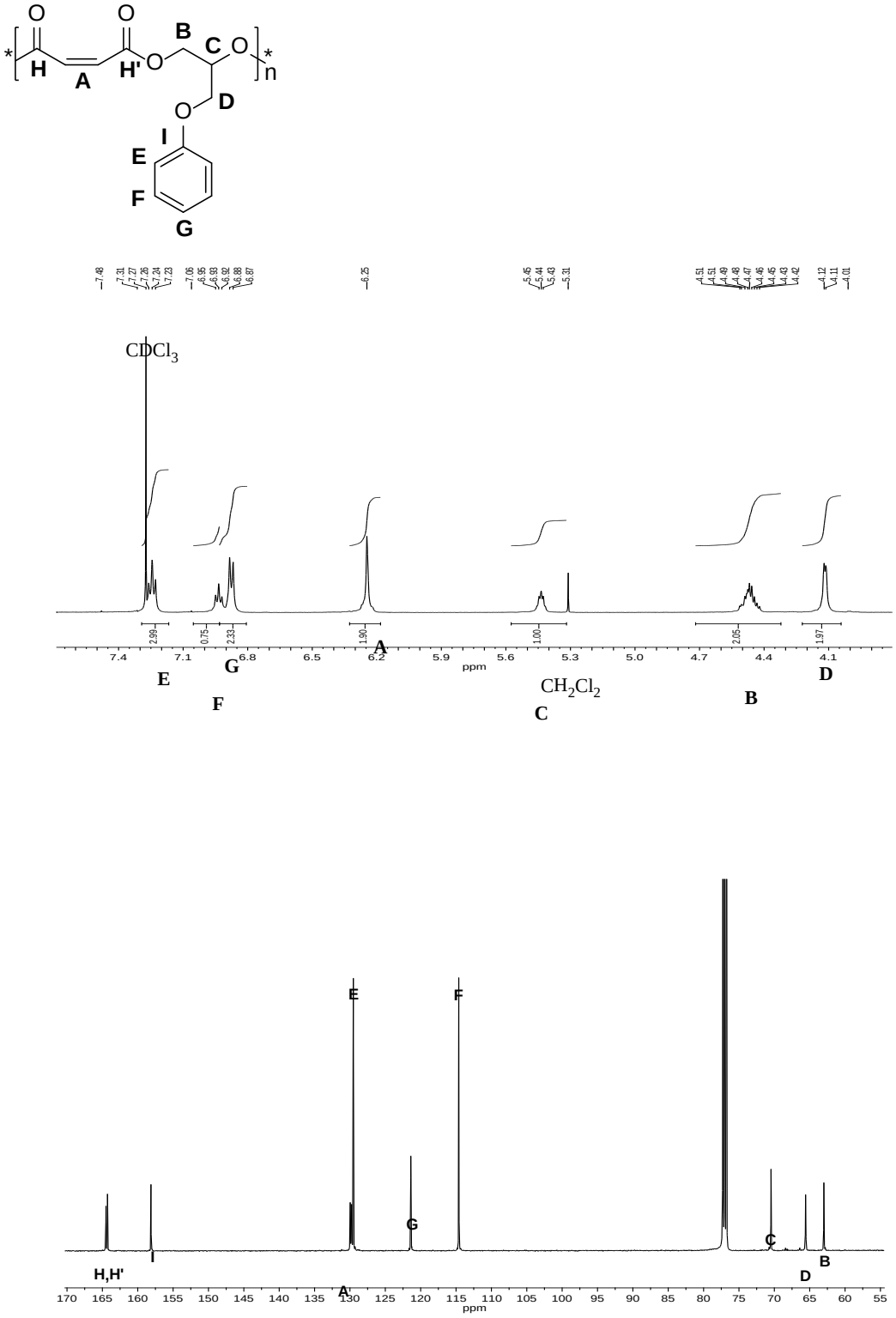


Figure S3. ^{1}H and ^{13}C NMR spectra of MA/GO copolymer in $CDCl_3$

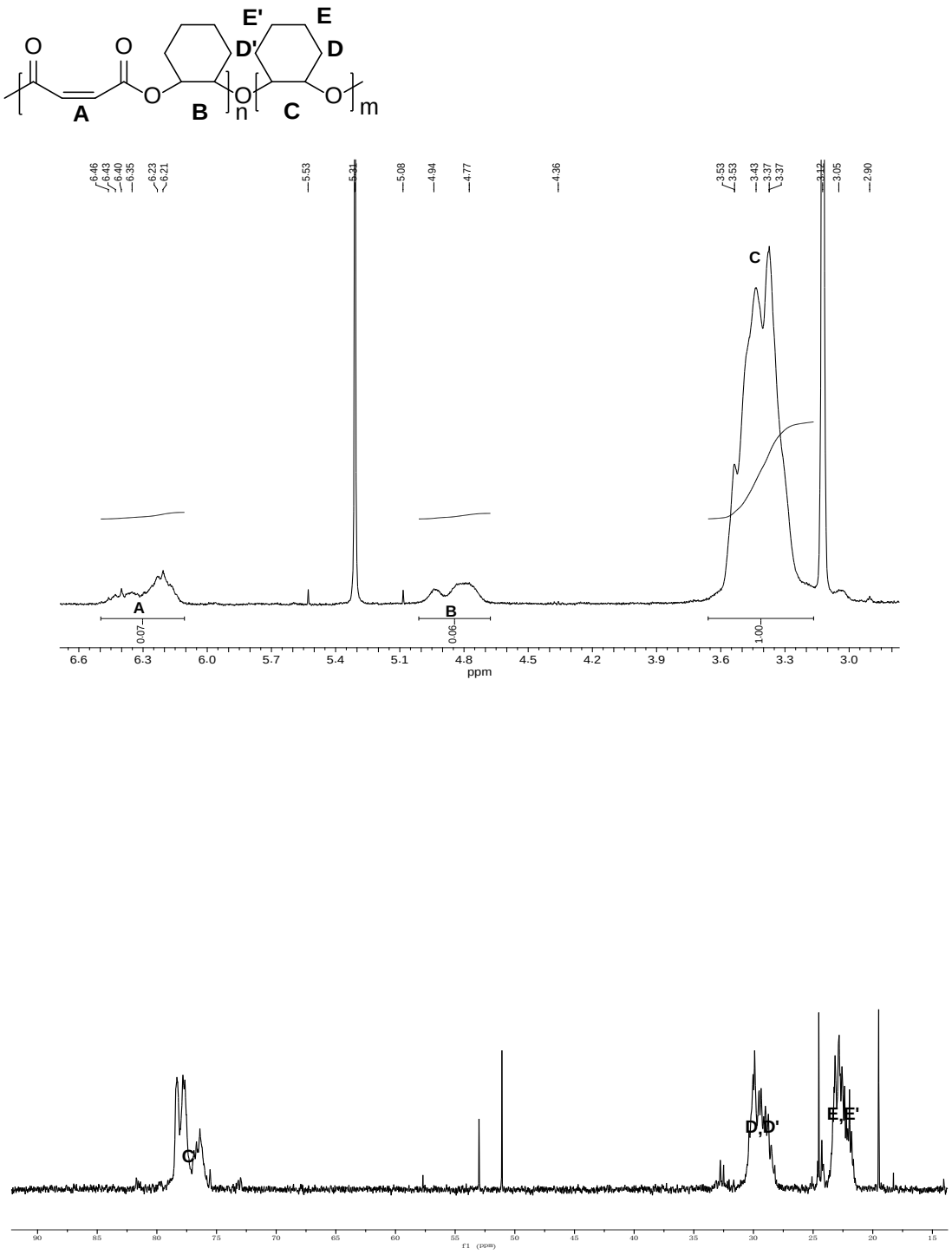


Figure S4. ^{1}H and ^{13}C NMR spectra of MA/CHO copolymer in $CDCl_3$

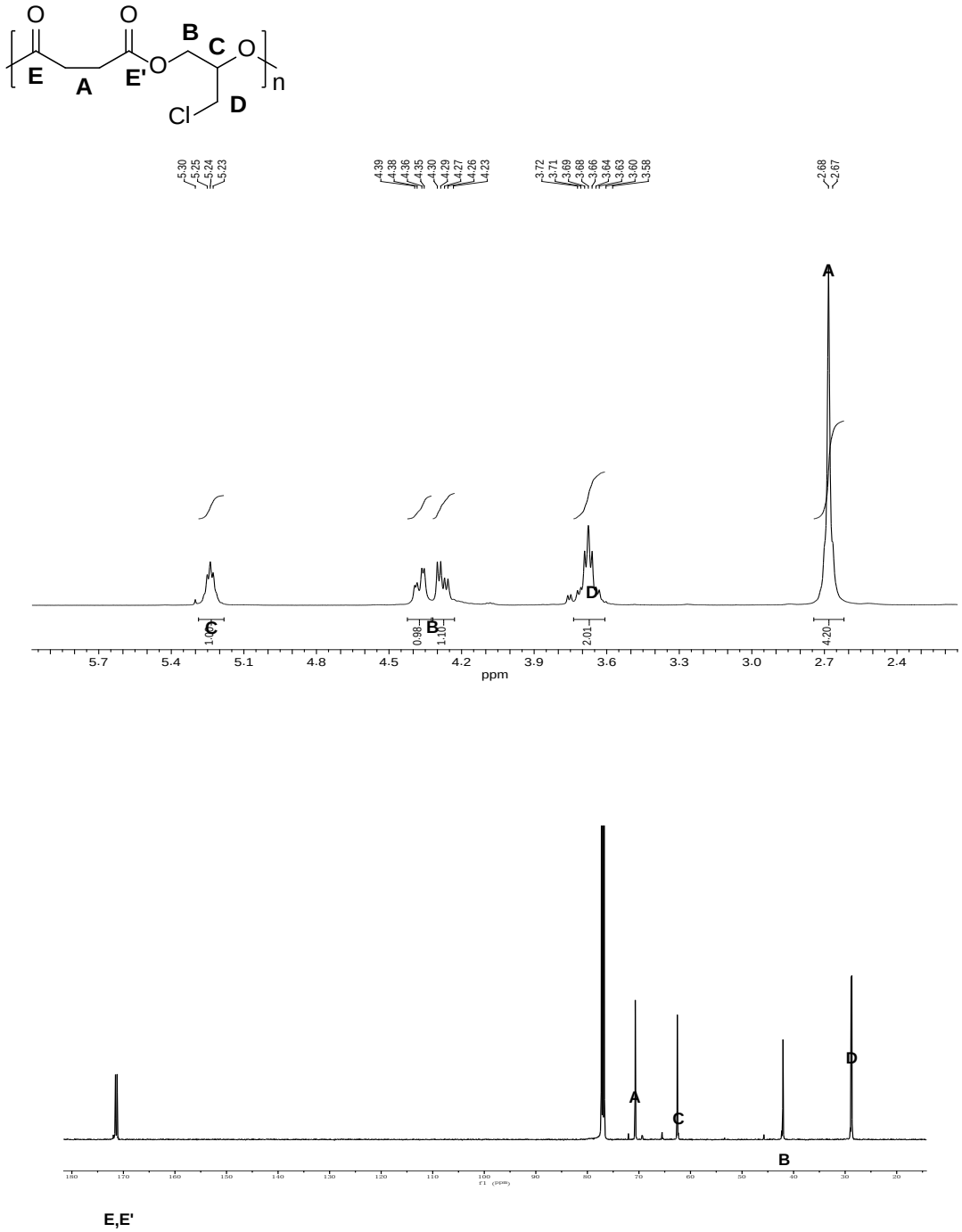


Figure S5. ^{1}H and ^{13}C NMR spectra of SA/ClPO copolymer in $CDCl_3$

4. ^{1}H-NMR spectra of ligands L2 and L3

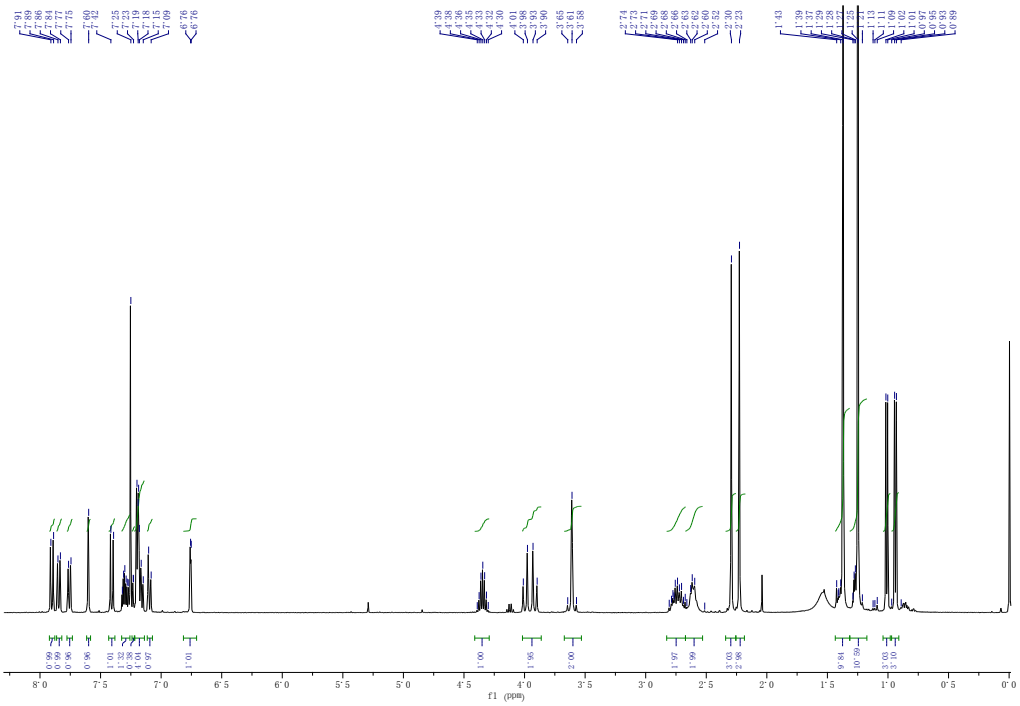


Figure S6. ^{1}H NMR spectrum of Ligand L2 in $CDCl_3$

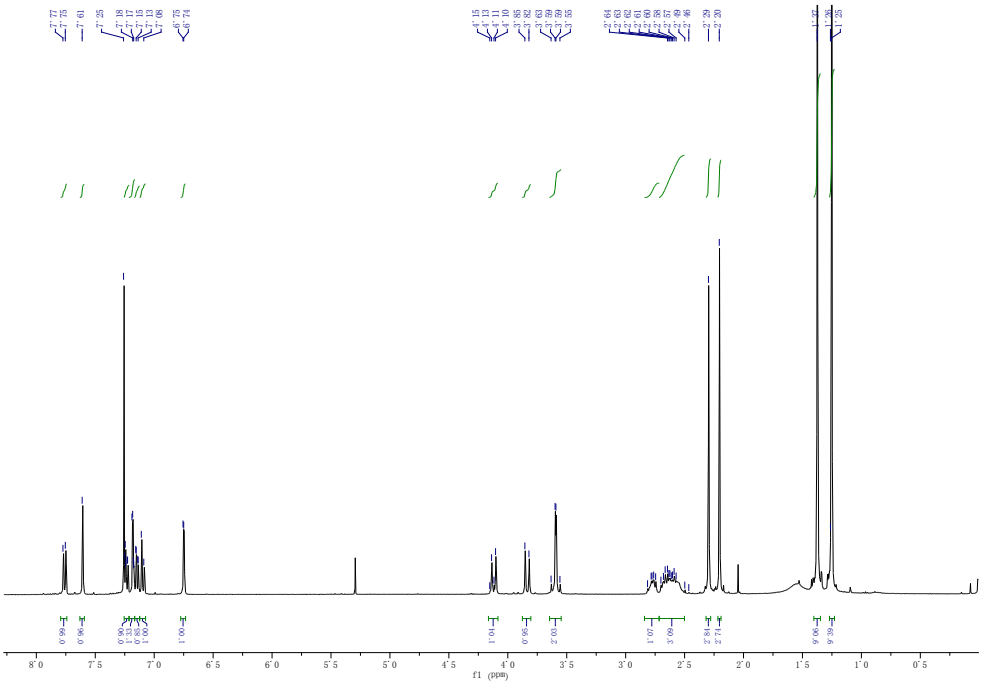


Figure S7. ^{1}H NMR spectrum of Ligand L3 in $CDCl_3$

5. Chiral HPLC analysis

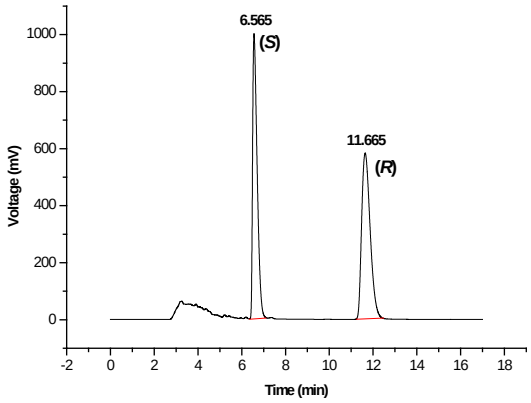


Figure S8. HPLC spectrum of (*rac*)-3-Phenoxy-1,2-propanediol resulted from the hydrolysis of the MA/(*rac*)-GO copolymer (Column: CHIRALCEL OD-H; n-Hexane/2-Propanol = 90/10; t_{R1} = 6.565 min; t_{R2} = 11.665 min).

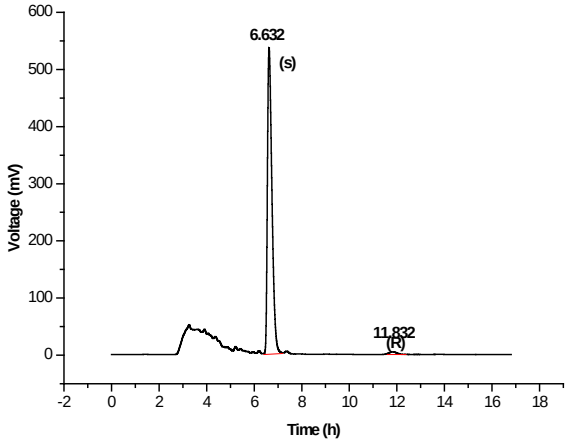


Figure S9. HPLC spectrum of (*S*)-3-Phenoxy-1,2-propanediol obtained from the hydrolysis of the MA/(*S*)-GO copolymer (Column: CHIRALCEL OD-H; n-Hexane/2-Propanol = 90/10; t_{R1} = 6.632 min; t_{R2} = 11.832 min).

6. Kinetic study of the catalysts a and c

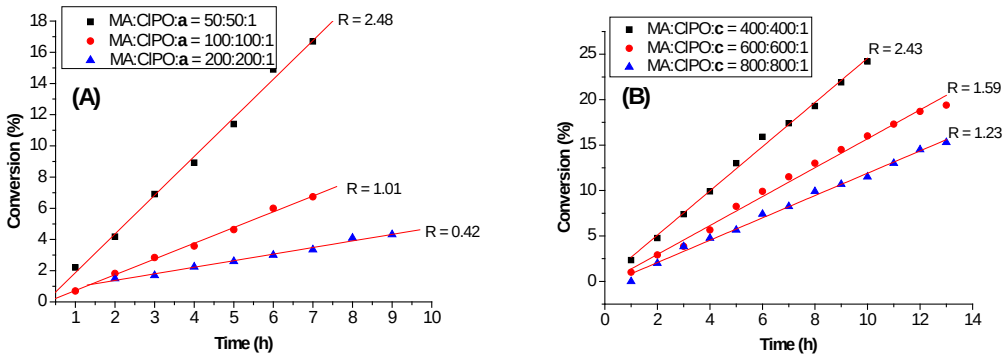


Figure S10. Determination of the copolymerization rate (*R*) as a change of the conversion with time at various catalyst loadings: (**A**) catalyst **a** and (**B**) catalyst **c**.