

Supporting Information

Chiral SalenCo(III) Complexes with Bulky Substituents as Catalysts for Stereoselective Alternating Copolymerization of Racemic Propylene Oxide with Carbon Dioxide and Succinic Anhydride

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1. Synthesis and characterizations of phenols with bulky substituents 1a-d
4-*tert*-butyl-2-substitutedphenols **1a**, **1b**, **1c** and **1d** were prepared according to the literature procedures.

4-*tert*-Butyl-2-(2,3-dimethylbut-2-yl)phenol (**1a**)

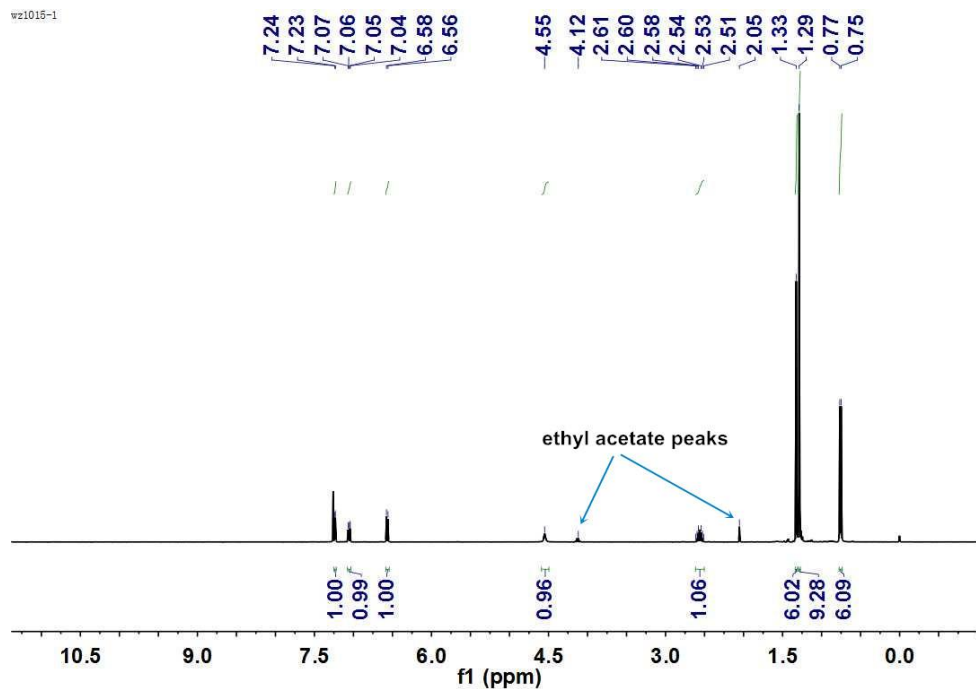


Figure S1. ¹H NMR (400 MHz, CDCl₃, 298K) spectrum of **1a**.

4-*tert*-Butyl-2-(2-phenylpropan-2-yl)phenol (**1b**)

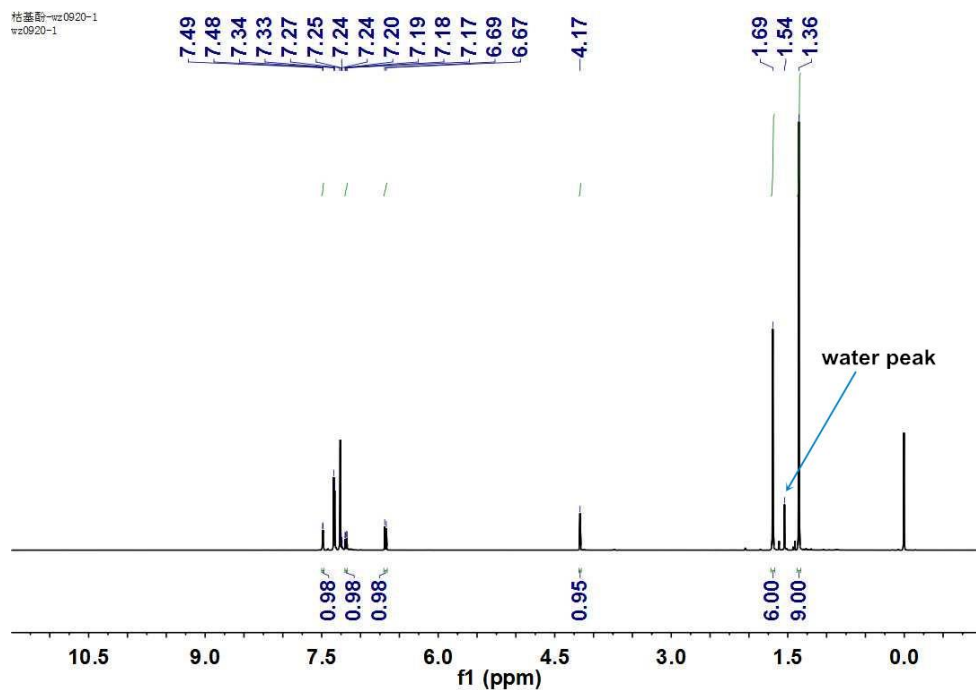


Figure S2. ¹H NMR (400 MHz, CDCl₃, 298K) spectrum of **1b**.

4-*tert*-butyl-2-(1,1-diphenylethyl)phenol (**1c**)

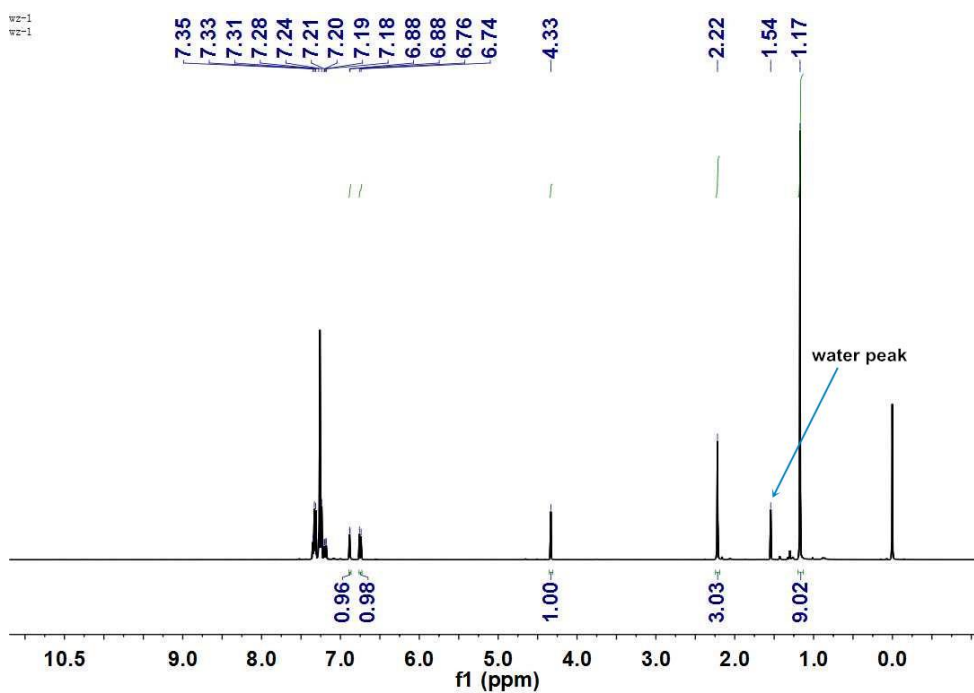


Figure S3. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of **1c**.

4-*tert*-butyl-2-(trityl)phenol (**1d**)

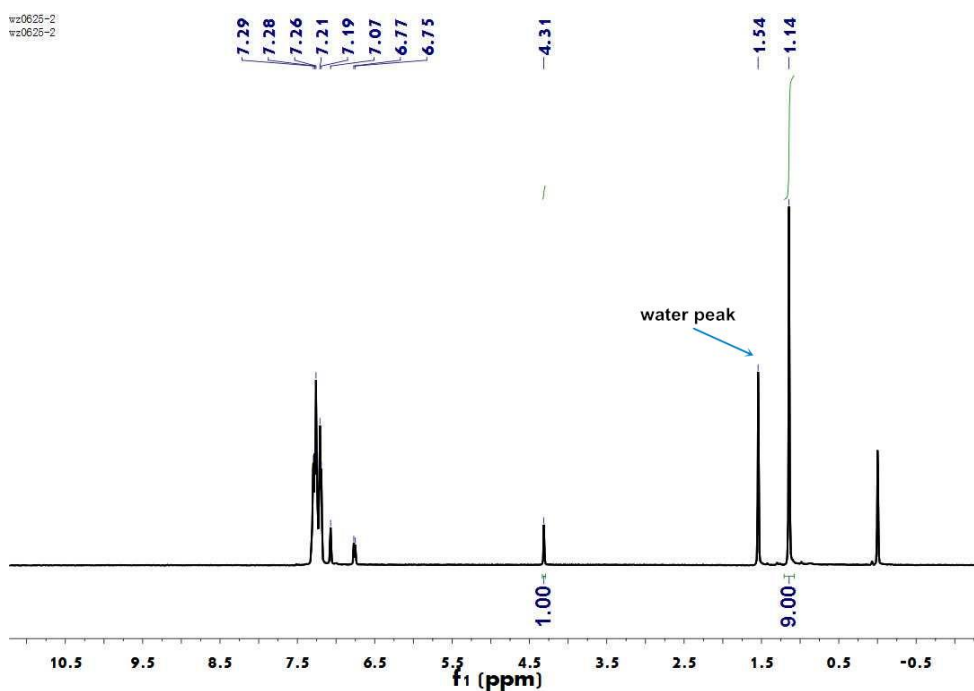


Figure S4. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of **1d**.

2. Synthesis and characterizations of salicylaldehydes 2a-d

The corresponding salicylaldehydes were prepared according to the literature procedures.⁴

5-*tert*-butyl-3-(2,3-dimethylbutan-2-yl)-2-hydroxybenzaldehyde (**2a**)

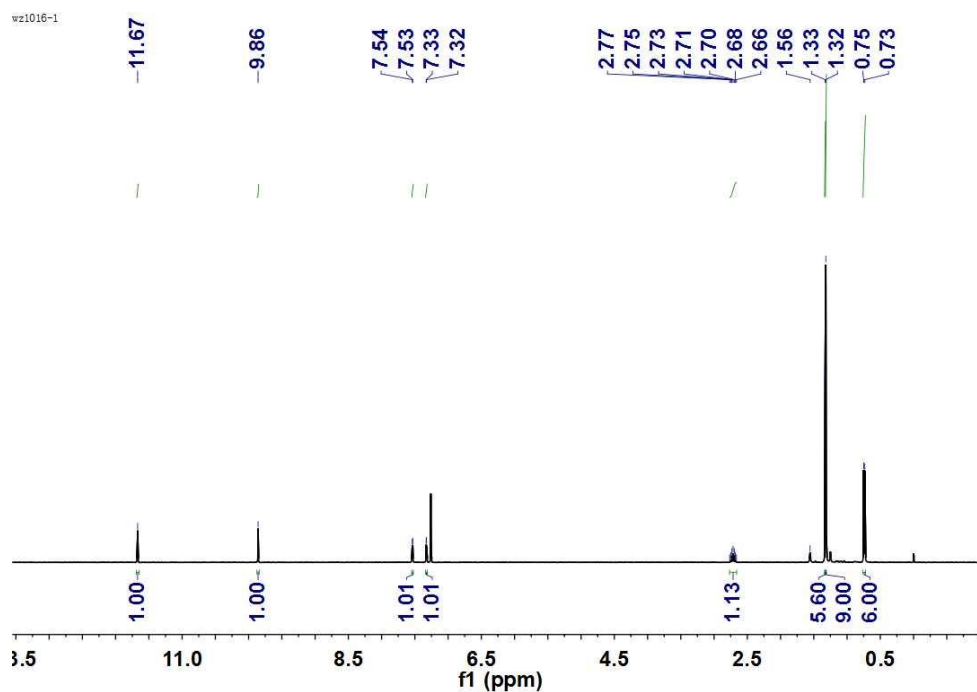


Figure S5. ¹H NMR (400 MHz, CDCl₃, 298K) spectrum of **2a**.

5-*tert*-butyl-2-hydroxy-3-(2-phenylpropan-2-yl)benzaldehyde (**2b**)

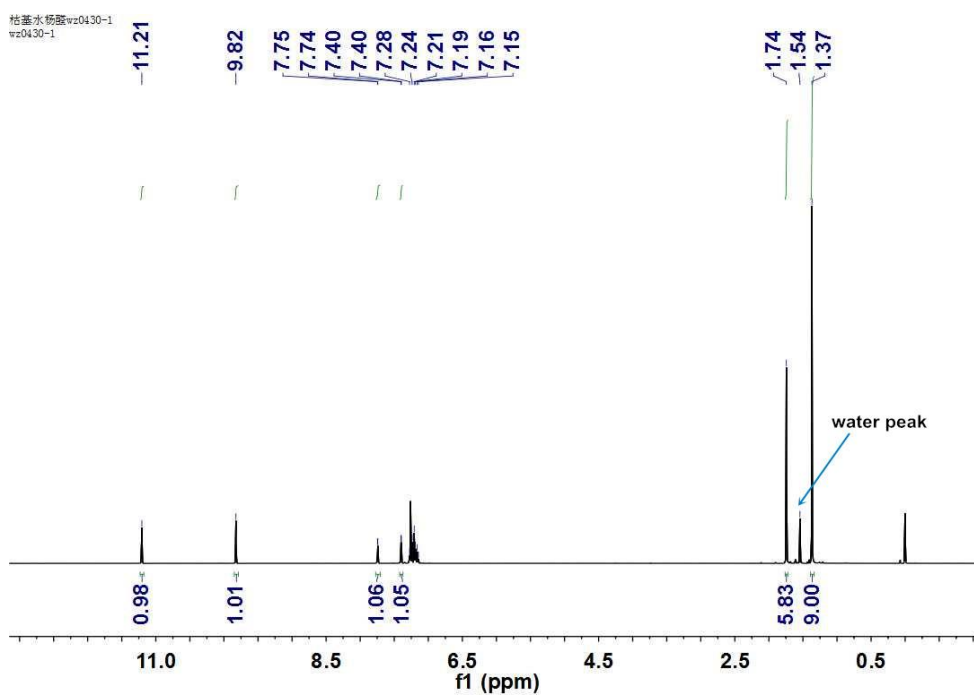


Figure S6. ¹H NMR (400 MHz, CDCl₃, 298K) spectrum of **2b**.

5-*tert*-butyl-3-(1,1-diphenylethyl)-2-hydroxybenzaldehyde (**2c**)

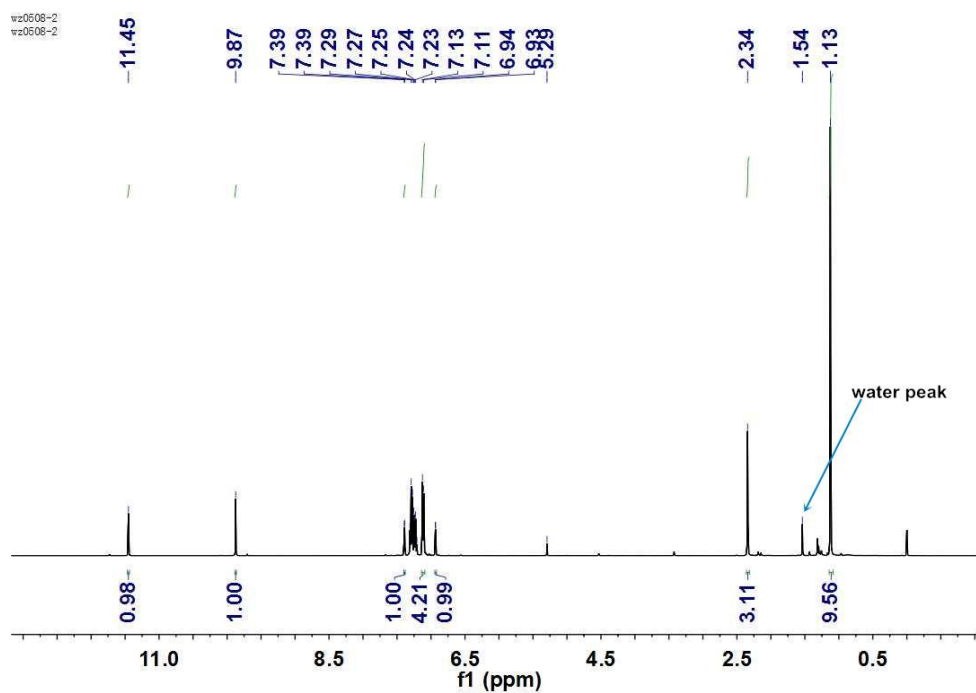


Figure S7. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of **2c**.

5-*tert*-butyl-3-(trityl)-2-hydroxybenzaldehyde (**2d**)

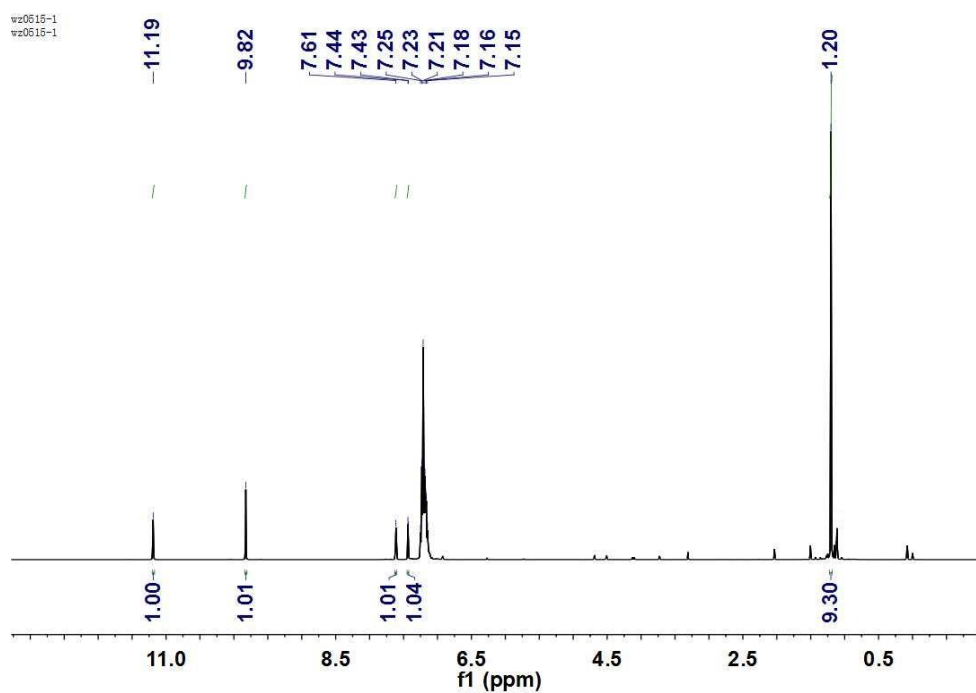


Figure S8. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of **2d**.

3. ^1H NMR spectra of salen ligands 3a-d

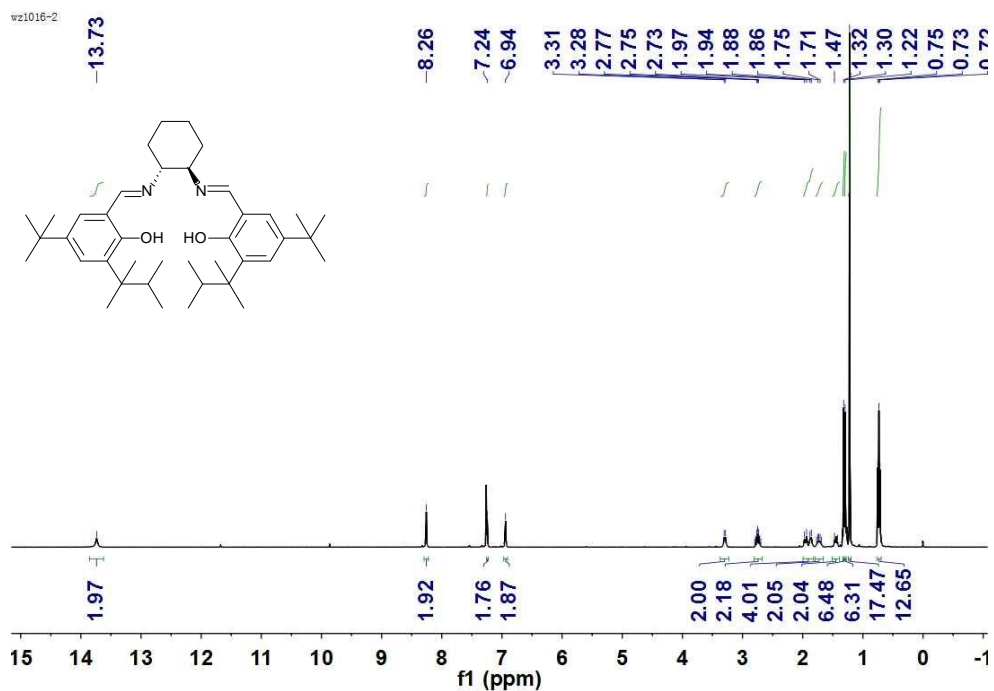


Figure S9. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of **3a**.

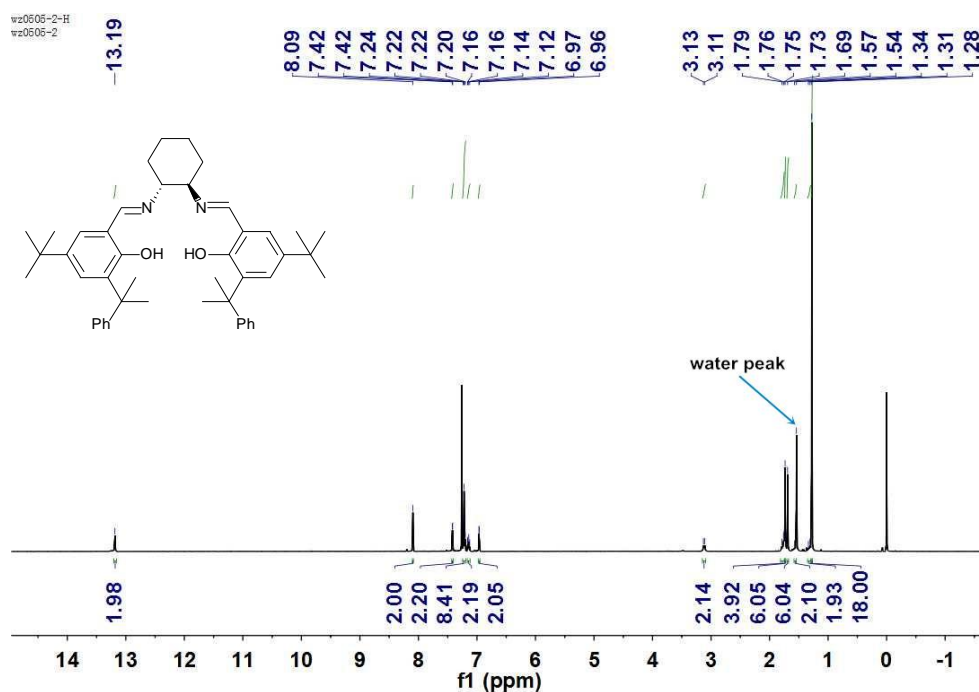
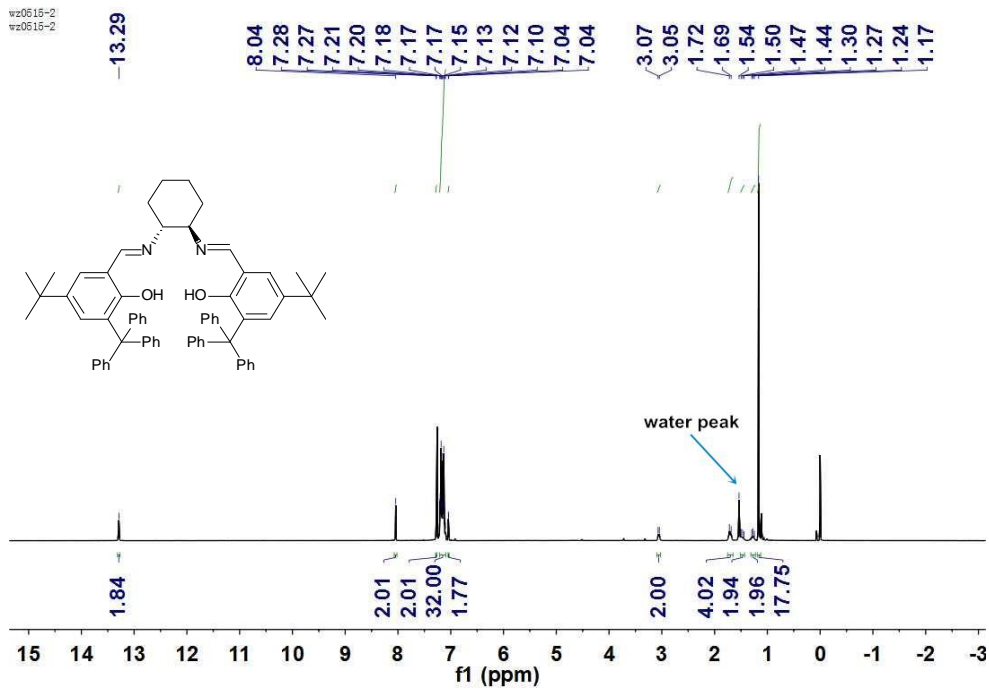
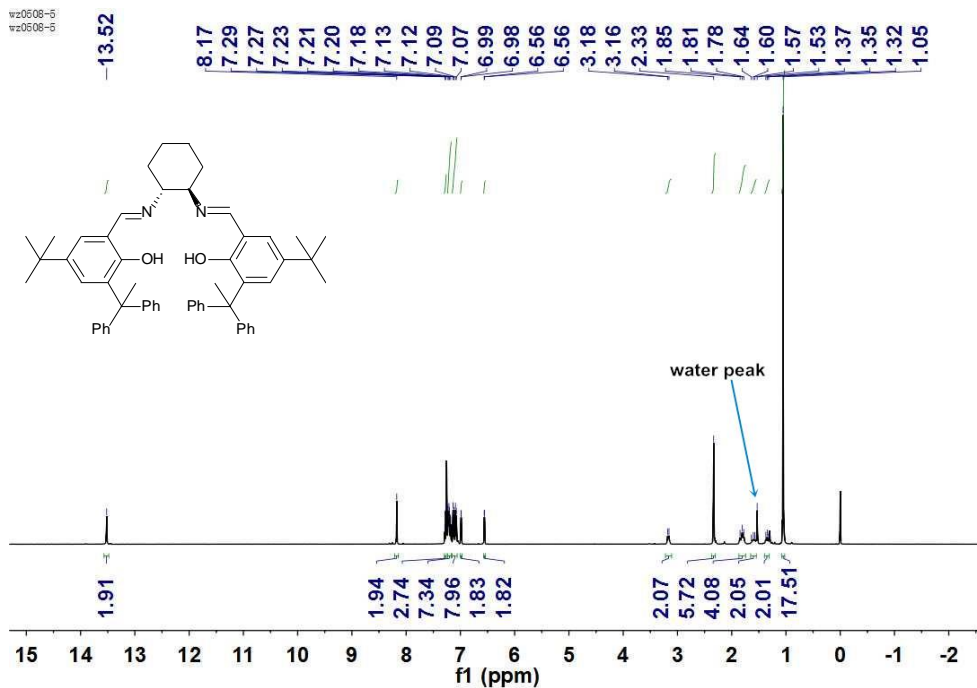
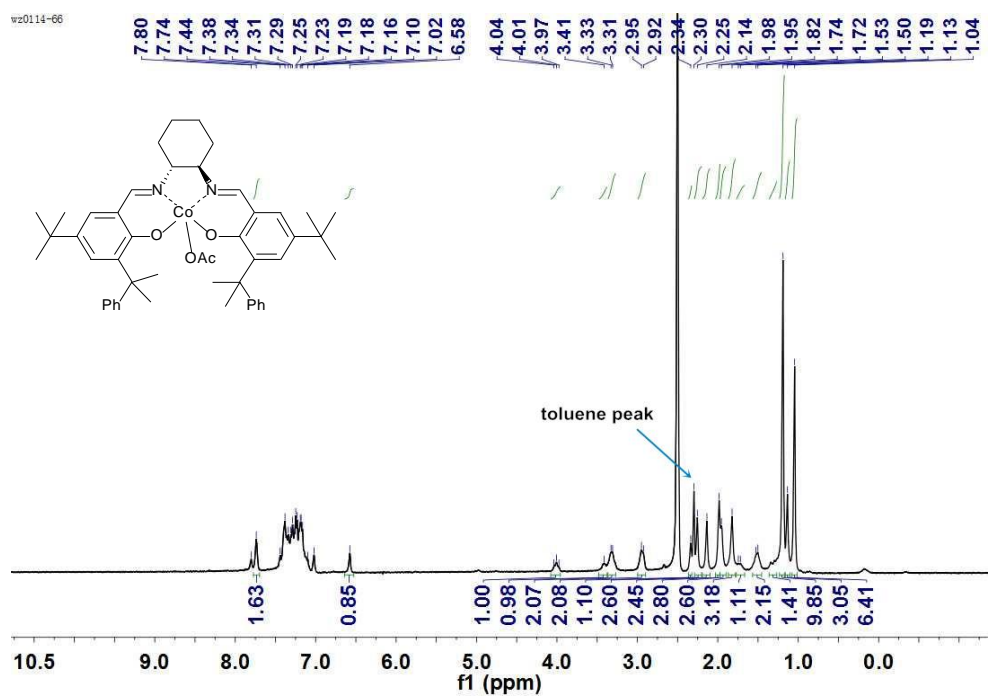
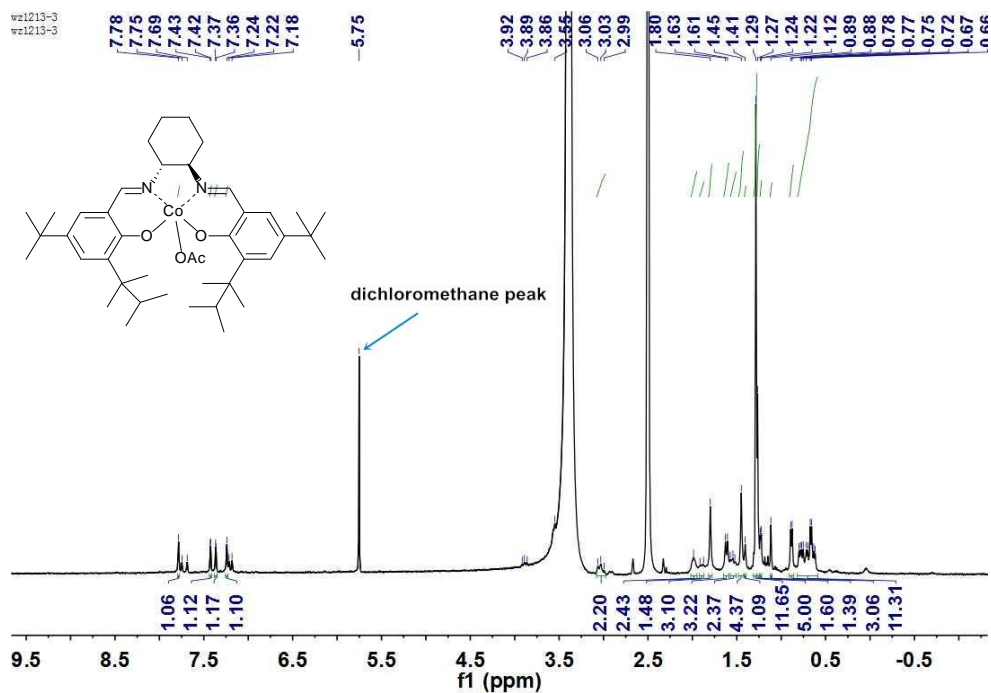


Figure S10. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of **3b**.



4. ^1H NMR and HRMS spectra of salenCo(III)

salenCoOAc (**4a**, **4b**, **4c**)



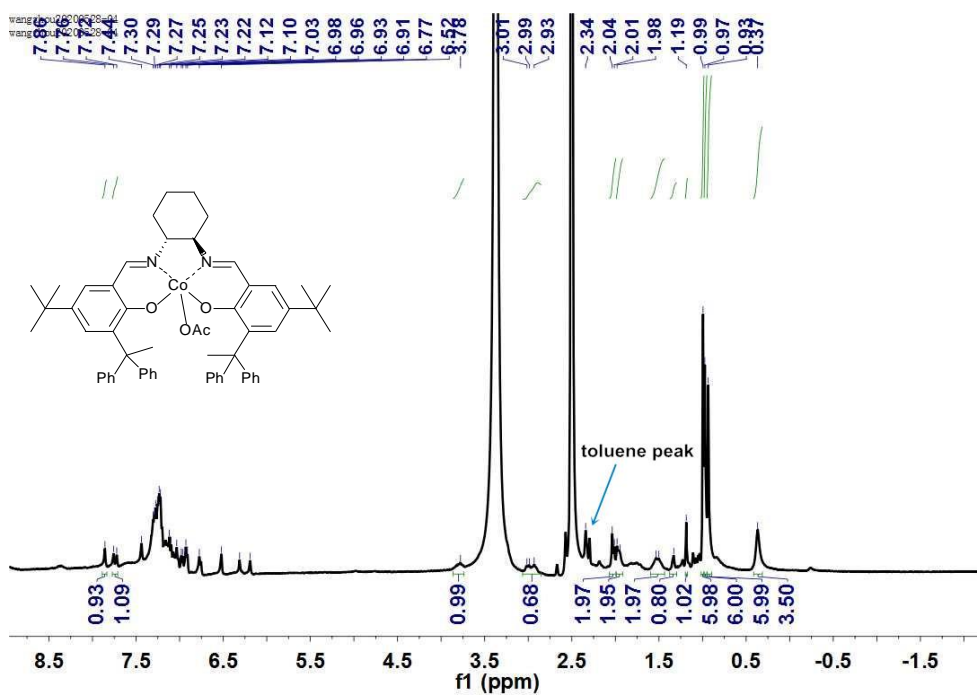


Figure S15. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 298K) spectrum of **4c**.

salenCoDNP (**5a**, **5b**, **5c**)

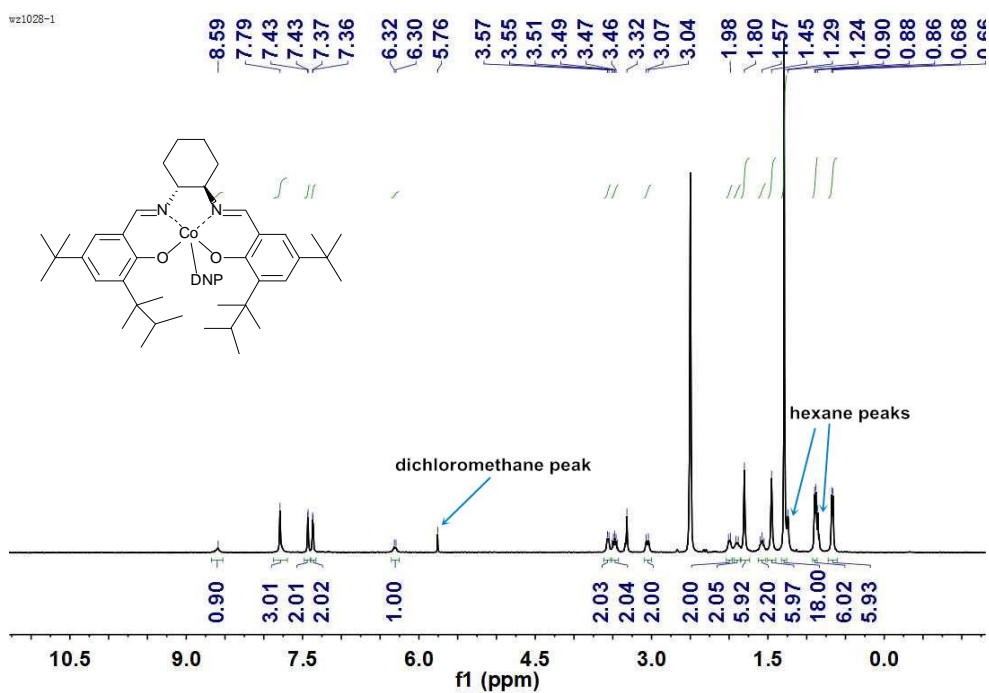
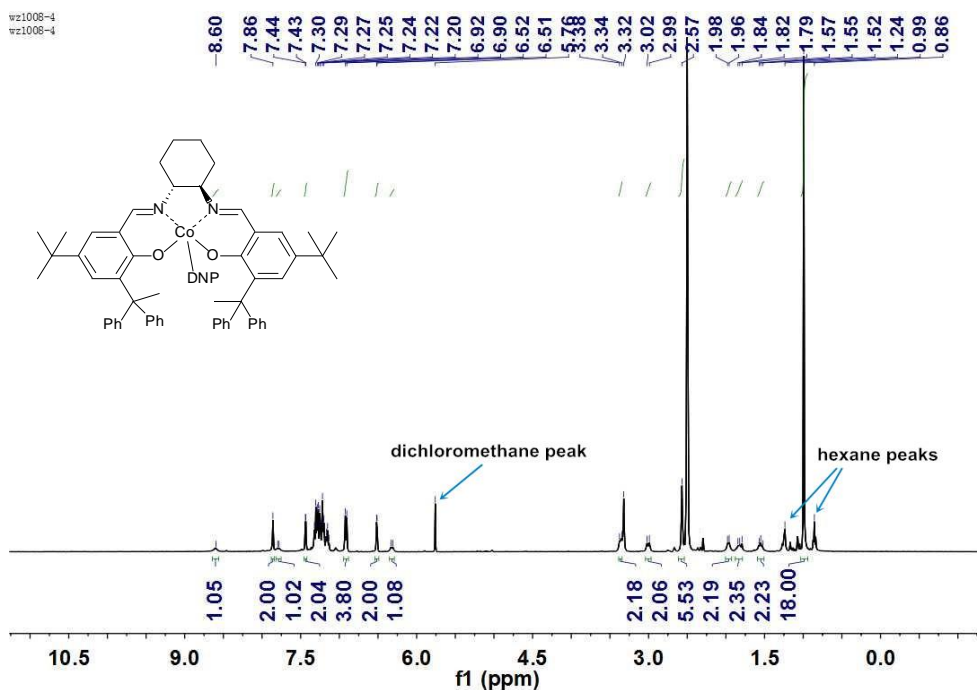
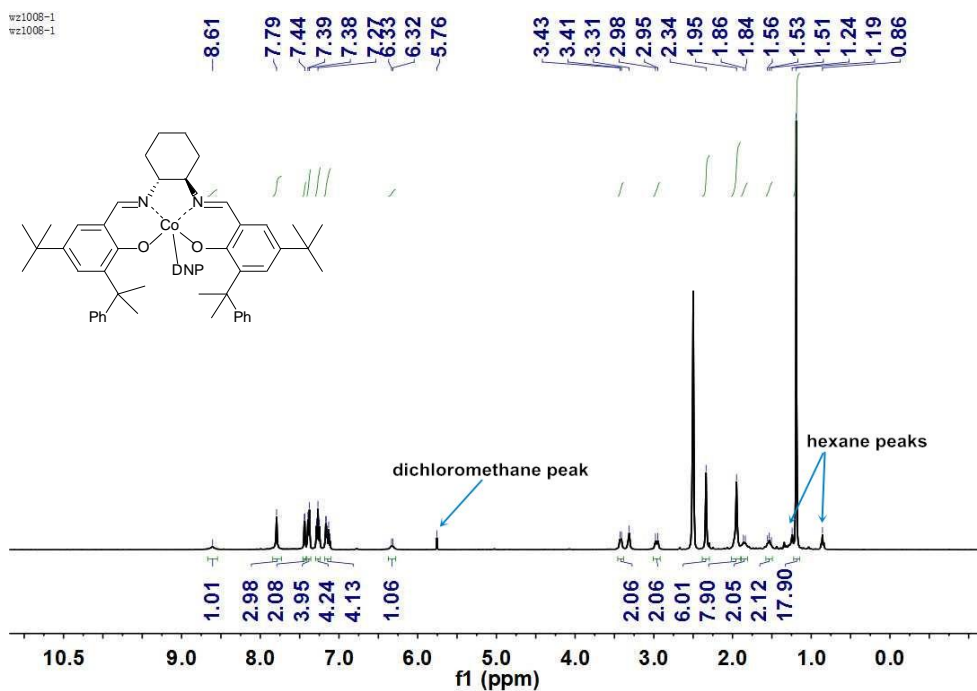


Figure S16. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 298K) spectrum of **5a**.



salenCoBr (**6a**, **6b**, **6c**)

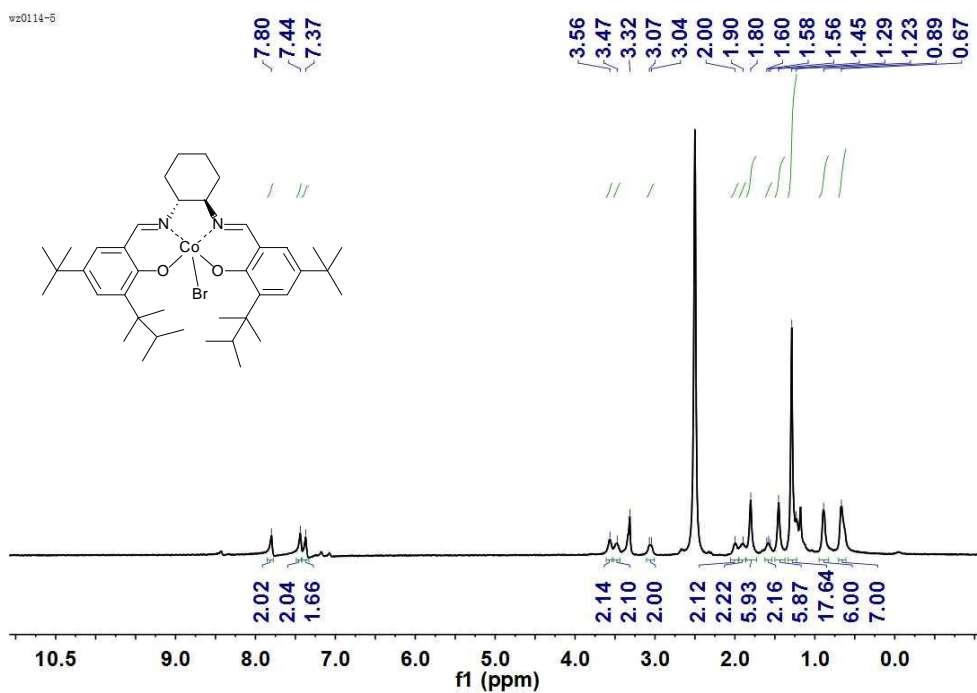


Figure S19. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 298K) spectrum of **6a**.

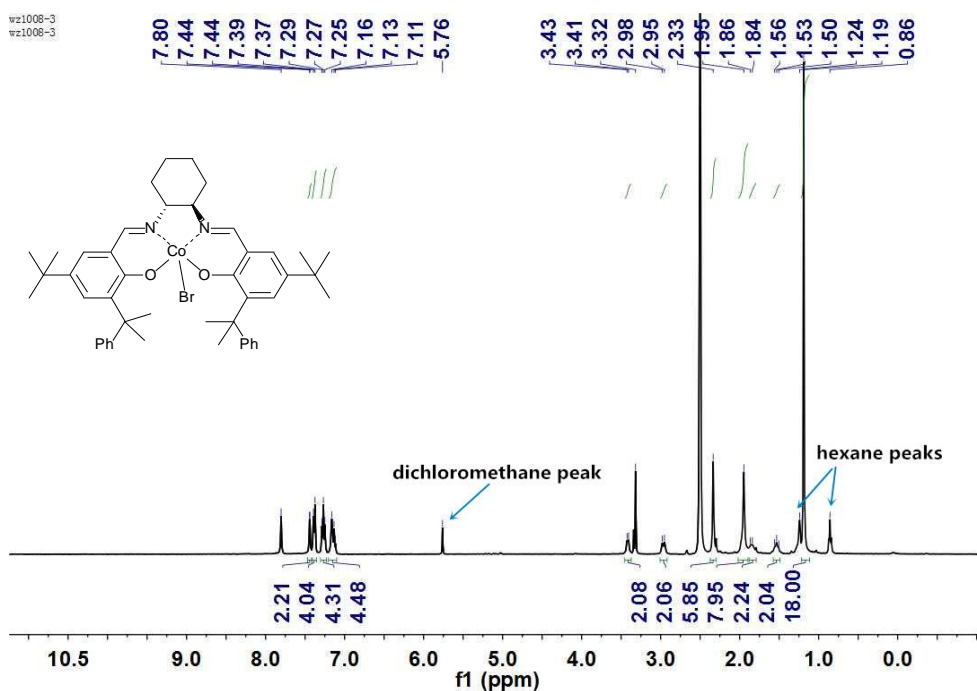


Figure S20. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 298K) spectrum of **6b**.

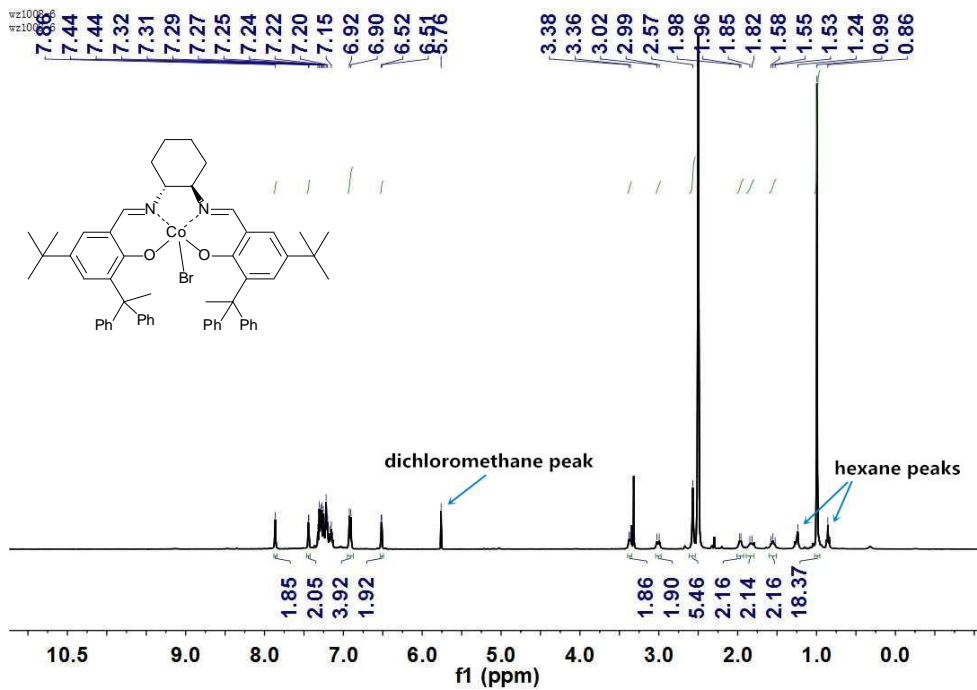


Figure S21. ¹H NMR (400 MHz, DMSO-*d*₆, 298K) spectrum of **6c**.

salenCoDNP (**5a**, **5b**, **5c**)

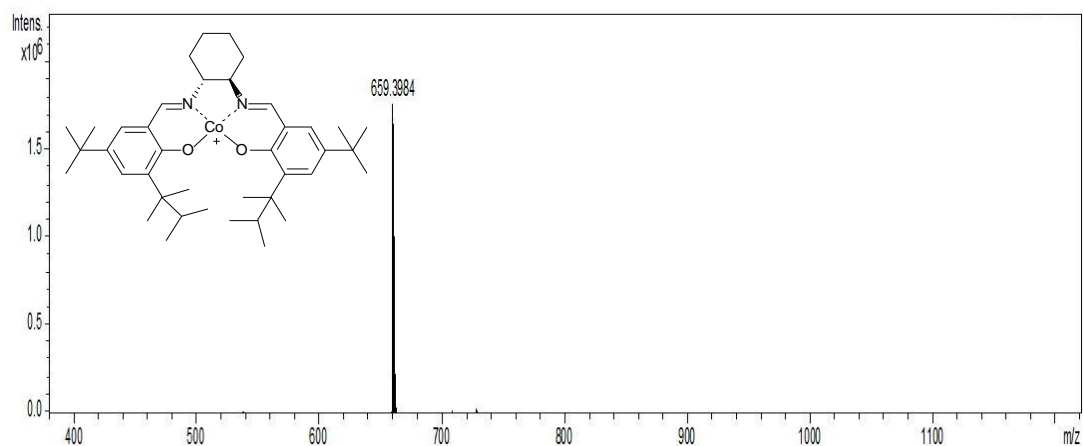


Figure S22. HRMS spectrum of **5a**.

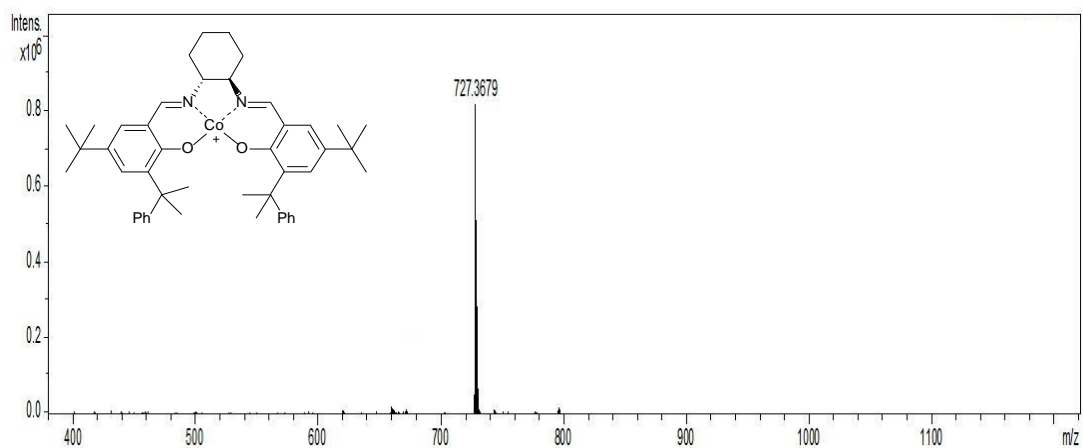


Figure S23. HRMS spectrum of **5b**.

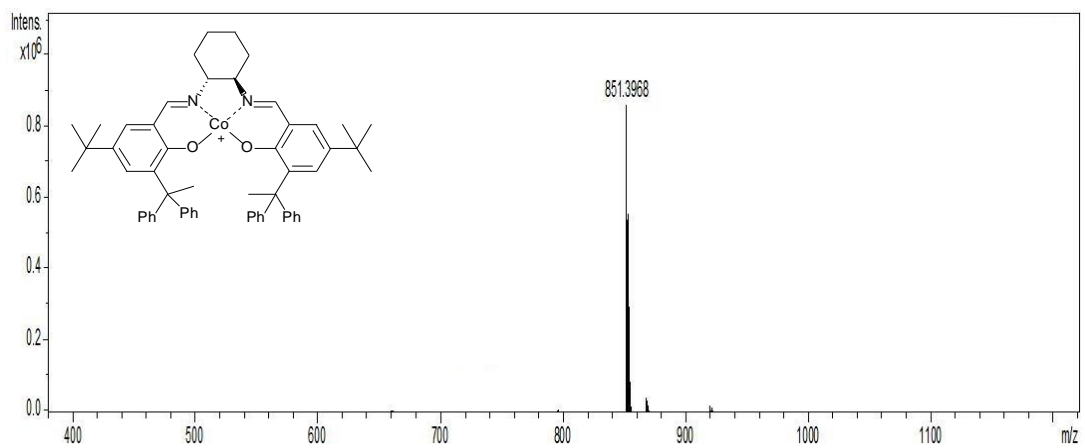


Figure S24. HRMS spectrum of **5c**.

5. ^{13}C NMR spectra of the PPCs and PPS

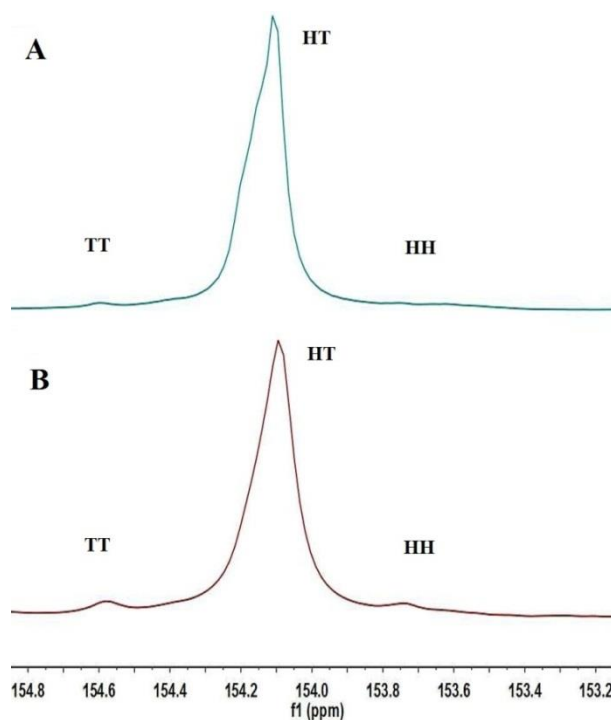


Figure S25. Carbonyl region of the ^{13}C NMR (100 MHz, CDCl_3 , 298K) spectra of PPC generated with the use of **5c**/PPNDNP at 0 °C (A) and PPC generated with the use of **5c**/DMAP at 25 °C (B).

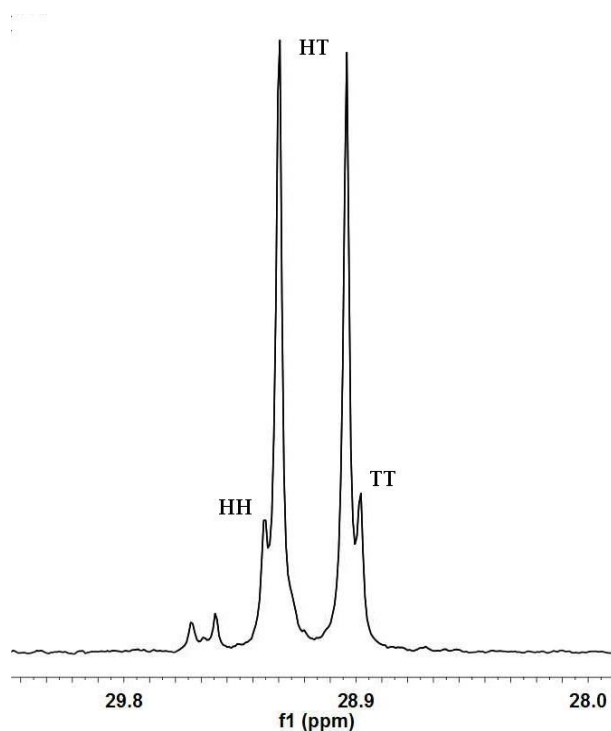


Figure S26. Methylene region of the ^{13}C NMR (100 MHz, CDCl_3 , 298K) spectrum of PPS generated with the use of **5c**/PPNDNP at 30 °C.

6. Chiral GC chromatograms

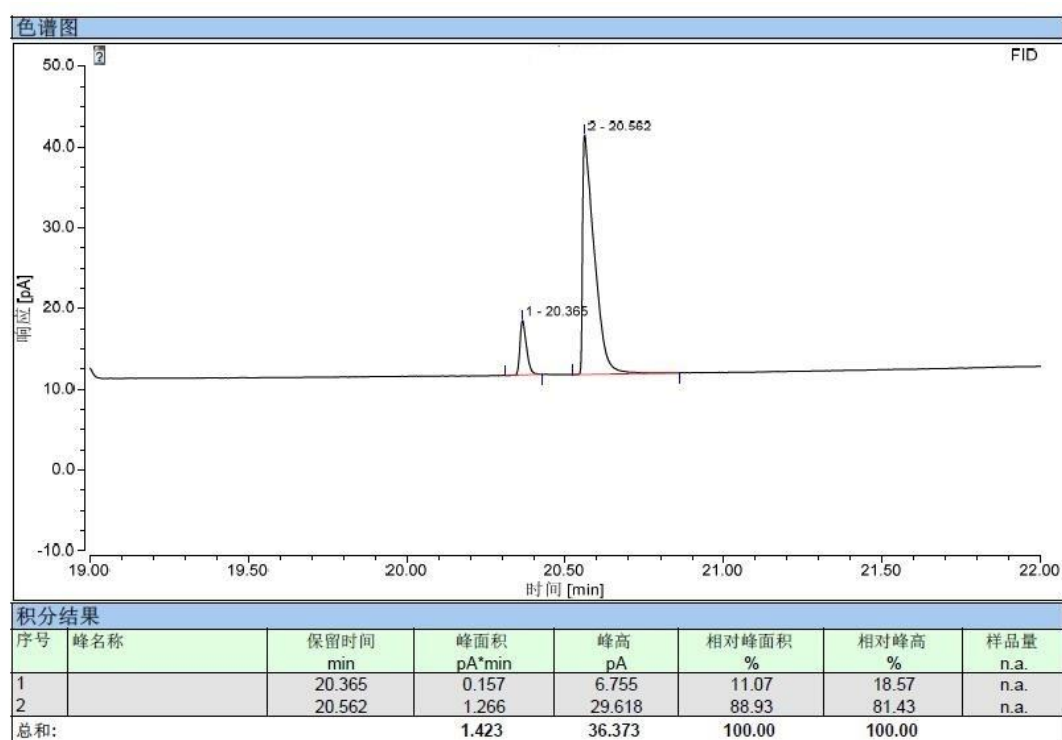
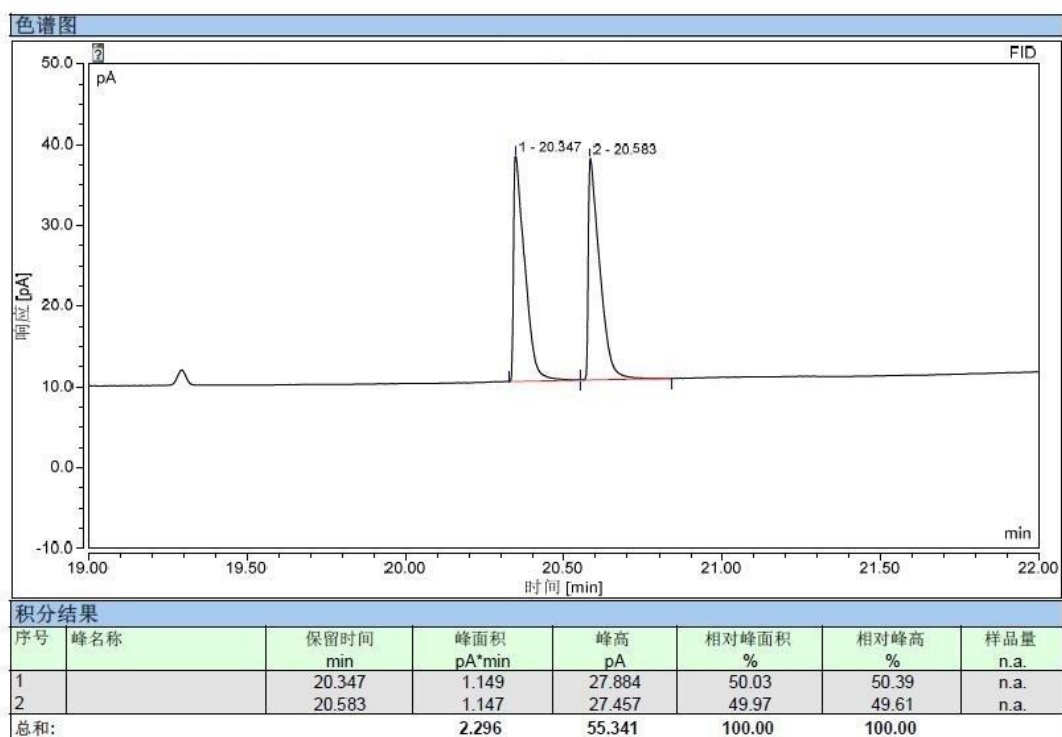


Figure S27. Chiral GC chromatogram of PC after degradation of PPC.

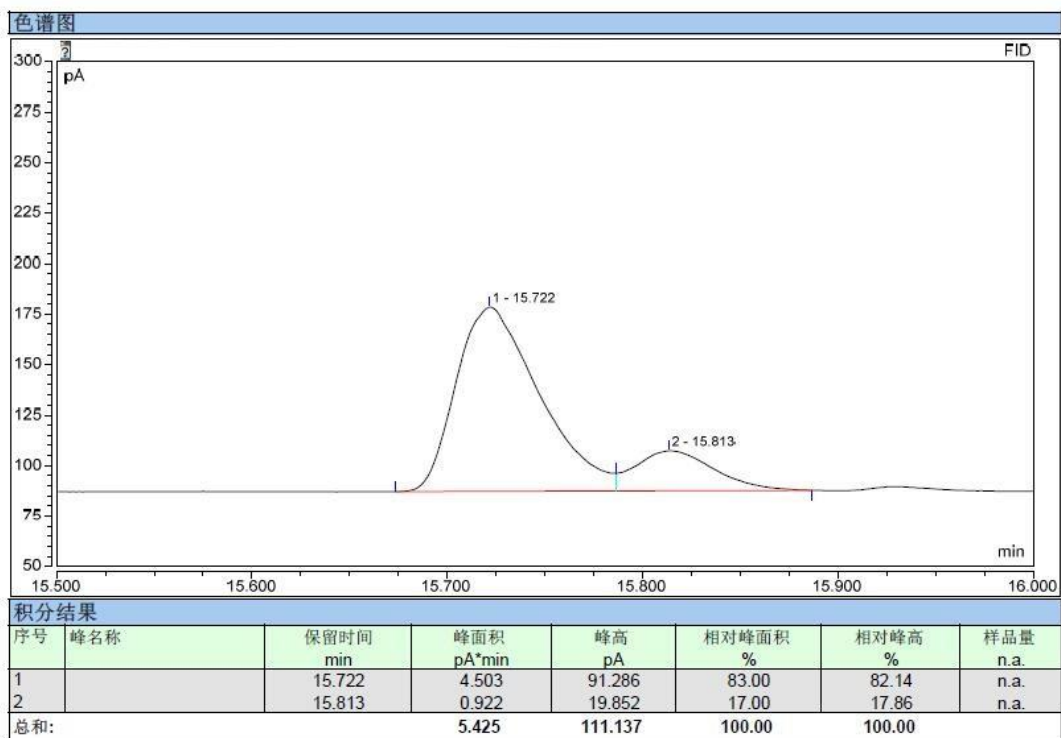
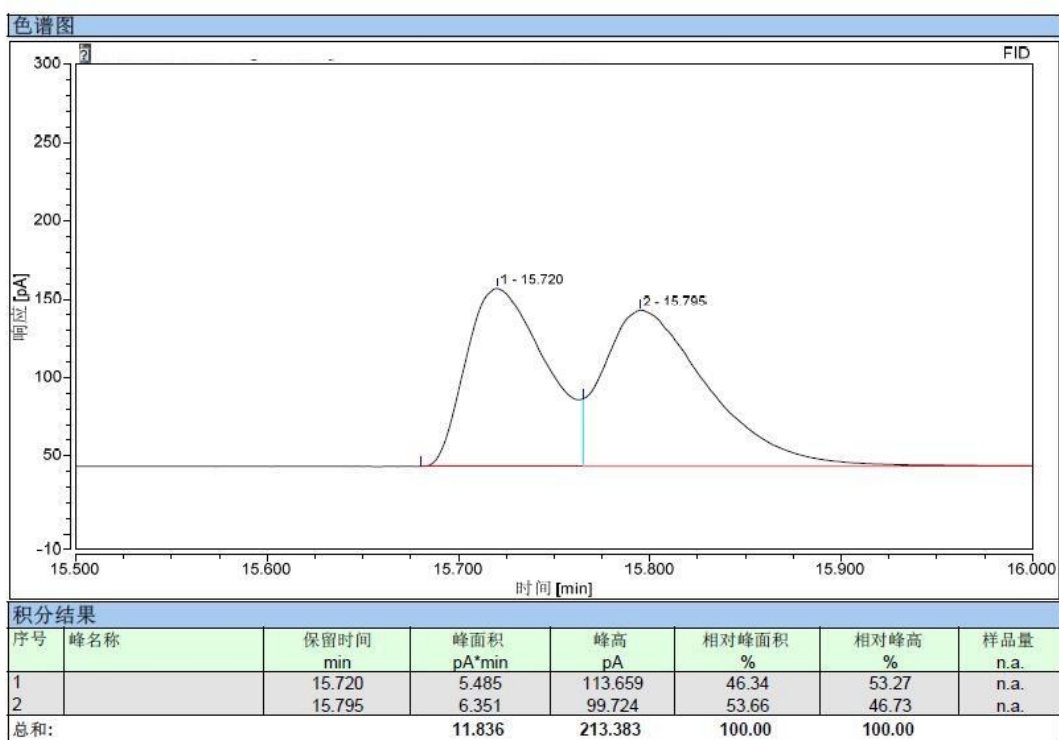


Figure S28. Chiral GC chromatogram of propanediol diacetate from propanediol after degradation of PPS.

7. Kinetic study for the copolymerization of PO and SA with 5c/PPNDNP catalyst system

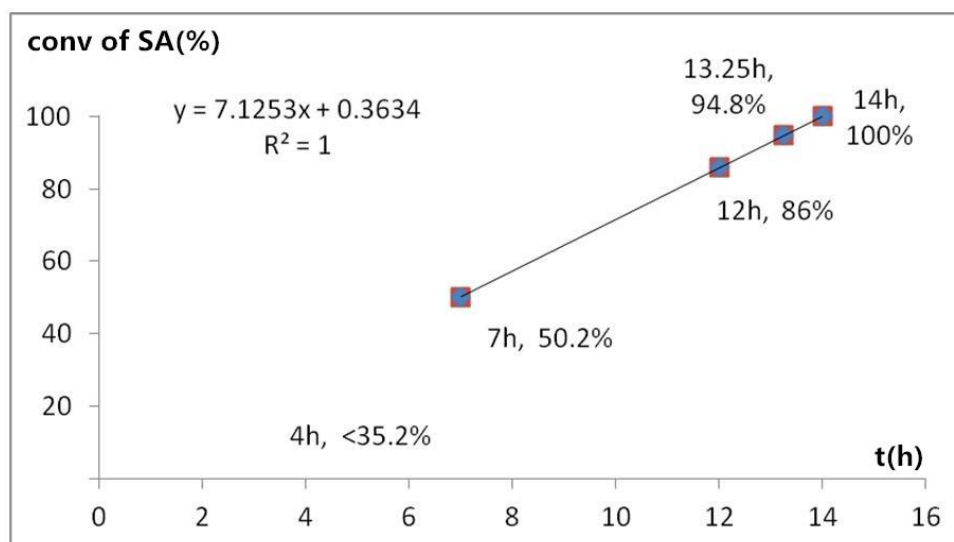


Figure S29. Plots of conversion of SA versus time, with the use of 5c/PPNDNP. (Determined by ^1H NMR spectroscopy. For reaction after 4h, unreacted SA was not fully dissolved in CDCl_3)

8. NMR spectra of the block polymers

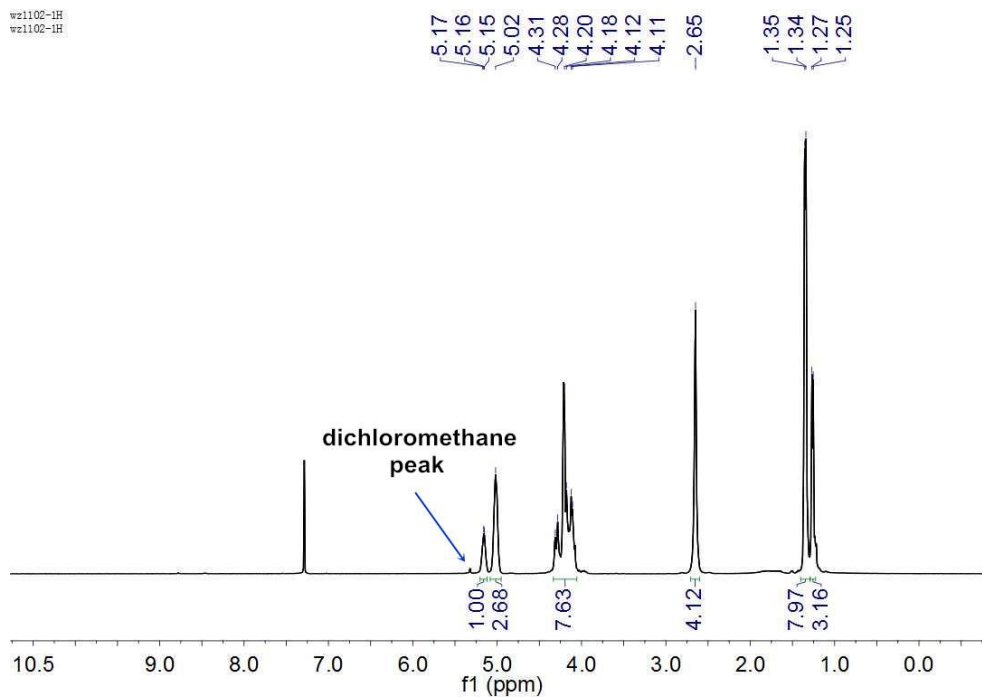


Figure S30. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of block polymer obtained by one-step procedure.

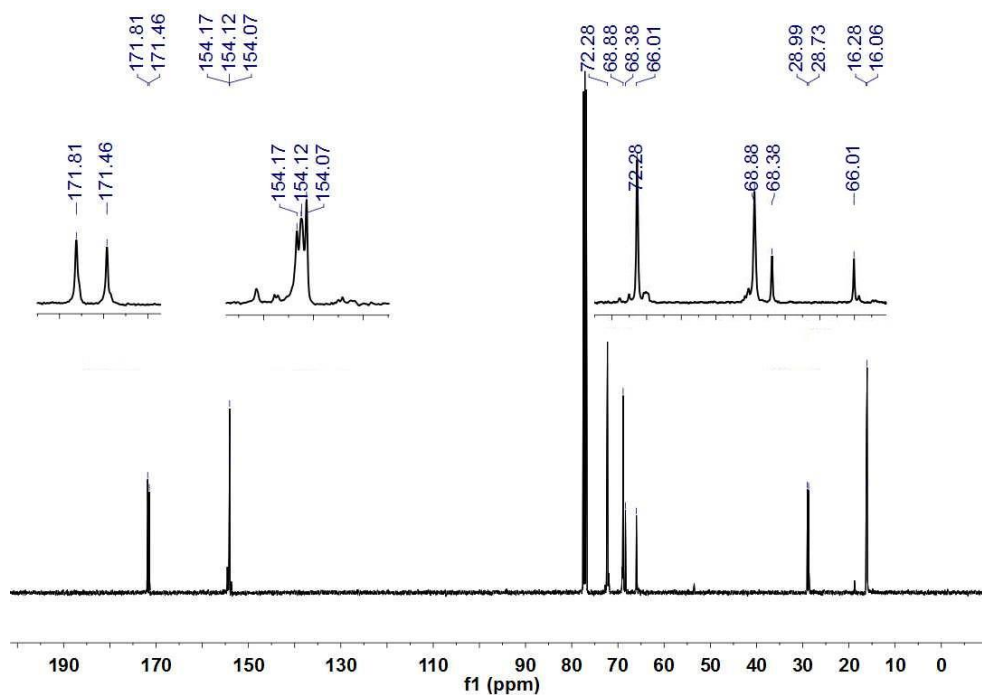


Figure S31. ^{13}C NMR (100 MHz, CDCl_3 , 298K) spectrum of block polymer obtained by one-step procedure.

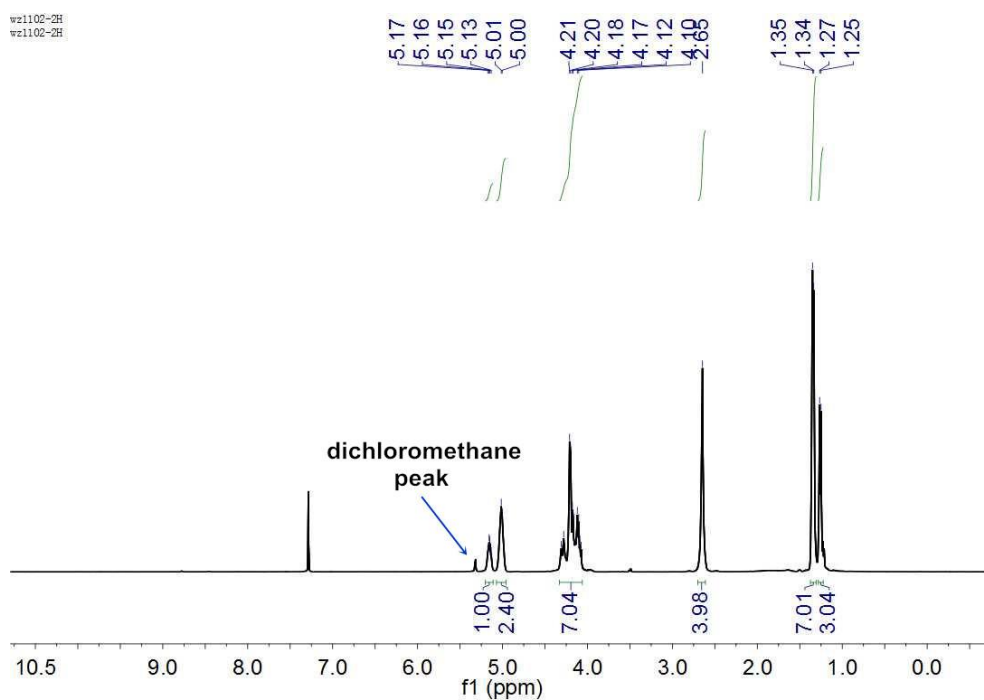


Figure S32. ^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of block polymer obtained by two-step procedure.

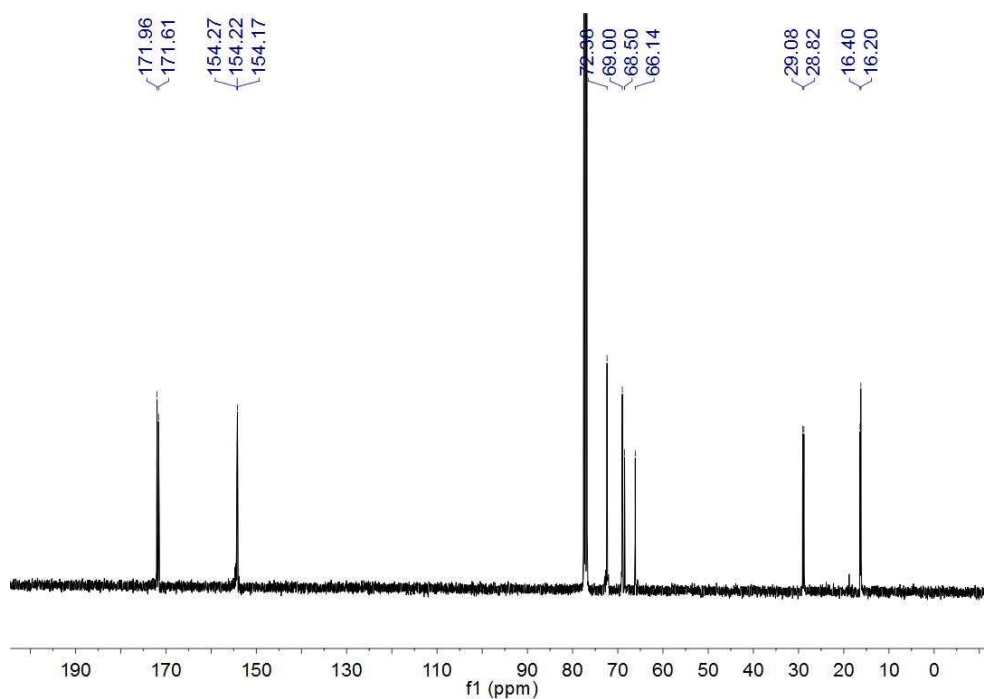
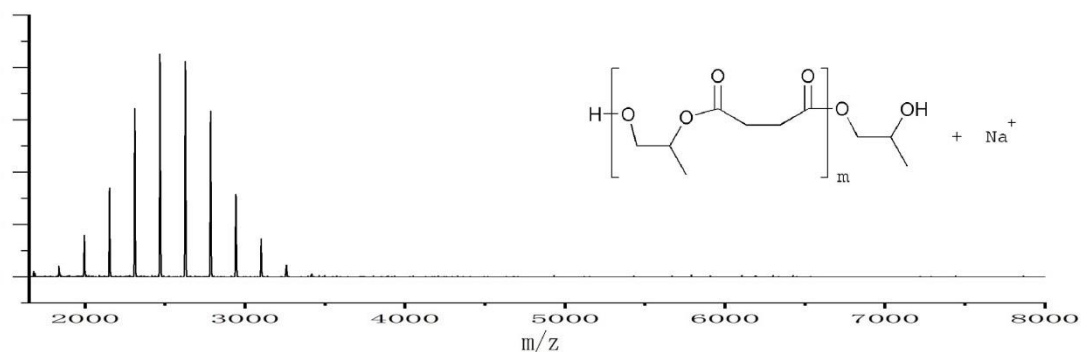


Figure S33. ^{13}C NMR (100 MHz, CDCl_3 , 298K) spectrum of block polymer obtained by two-step procedure.

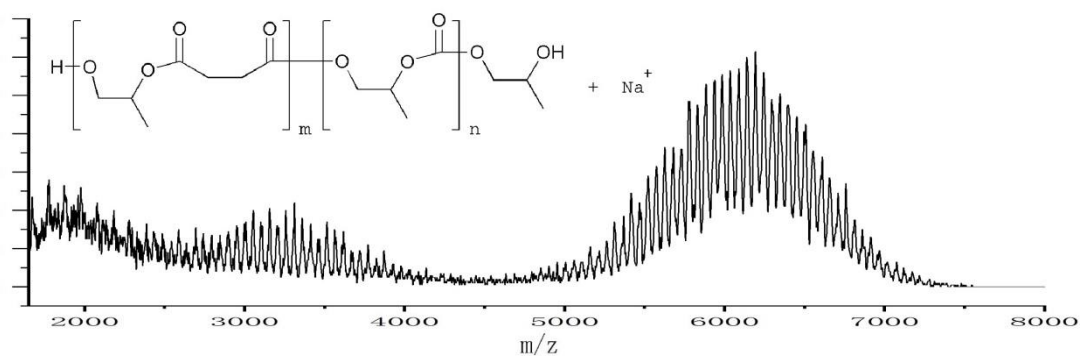
9. Peaks found in MALDI-TOF-MS spectra and related polymer chains

Table S1. Peaks found in MALDI-TOF-MS spectrum of PPS and related polymer chains.



peak	structure	peak	structure	peak	structure	peak	structure
1679.4	m=10	2153.4	m=13	2627.4	m=16	3101.1	m=19
1836.7	m=11	2311.7	m=14	2784.8	m=17	3261.1	m=20
1996.2	m=12	2469.2	m=15	2943.5	m=18		

Table S2. Peaks found in MALDI-TOF-MS spectrum of block polymer obtained by two-step procedure and related polymer chains.



peak	structure	peak	structure	peak	structure
1671.1	m=8, n=3	3256.9	m=9, n=17	5726.8	m=13, n=35
1771.3	m=8, n=4	3303.8	m=8, n=19	5774.0	m=12, n=37
1873.2	m=8, n=5	3312.3	m=10, n=16	5781.5	m=14, n=34
1976.3	m=8, n=6	3359.2	m=9, n=18	5829.4	m=13, n=36
2078.5	m=8, n=7	3414.7	m=10, n=17	5883.2	m=14, n=35
2182.6	m=8, n=8	3460.9	m=9, n=19	5938.7	m=15, n=34
2272.8	m=6, n=12	3469.2	m=11, n=16	5984.8	m=14, n=36
2280.7	m=8, n=9	3507.4	m=8, n=21	6036.0	Unknown

2297.2	Unknown	3515.8	m=10, n=18	6088.8	m=14, n=37
2385.9	m=8, n=10	3562.3	m=9, n=20	6140.4	m=15, n=36
2430.8	m=7, n=12	3571.1	m=11, n=17	6191.2	m=14, n=38
2438.7	m=9, n=9	3609.1	m=8, n=22	6244.7	m=15, n=37
2486.0	m=8, n=11	3618.0	m=10, n=19	6294.0	m=14, n=39
2494.6	m=10, n=8	3665.6	m=9, n=21	6302.8	m=16, n=36
2543.0	m=9, n=10	3675.6	m=11, n=18	6346.9	m=15, n=38
2587.9	m=8, n=12	3720.2	m=10, n=20	6393.2	m=14, n=40
2597.9	m=10, n=9	3772.6	Unknown	6450.0	m=15, n=39
2635.0	m=7, n=14	3823.4	m=10, n=21	6496.1	m=14, n=41
2696.0	m=10, n=10	3869.6	m=9, n=23	6506.6	m=16, n=38
2735.7	m=7, n=15	3925.4	m=10, n=22	6552.4	m=15, n=40
2742.8	m=9, n=12	3980.0	m=11, n=21	6609.9	m=16, n=39
2791.7	m=8, n=14	4136.9	m=12, n=21	6654.6	m=15, n=41
2846.5	m=9, n=13	5159.5	m=12, n=31	6698.9	m=14, n=43
2893.6	m=8, n=15	5216.3	m=13, n=30	6710.0	m=16, n=40
2905.2	m=10, n=12	5261.8	m=12, n=32	6758.1	m=15, n=42
2951.8	m=9, n=14	5309.7	m=11, n=34	6801.8	m=14, n=44
2997.1	m=8, n=16	5371.4	m=14, n=30	6811.4	m=16, n=41
3006.6	m=10, n=13	5418.1	m=13, n=32	6859.9	m=15, n=43
3053.7	m=9, n=15	5467.2	m=12, n=34	6913.6	m=16, n=42
3100.4	m=8, n=17	5521.1	m=13, n=33	6958.3	m=15, n=44
3110.4	m=10, n=14	5575.7	m=14, n=32	6968.6	m=17, n=41
3155.1	m=9, n=16	5626.0	m=13, n=34	7015.0	m=16, n=43
3201.6	m=8, n=18	5670.5	m=12, n=36	7073.4	m=17, n=42
3212.4	m=10, n=15	5679.8	m=14, n=33	7118.1	m=16, n=44

10. Low molecular weight region of MALDI-TOF-MS spectra of the polymers

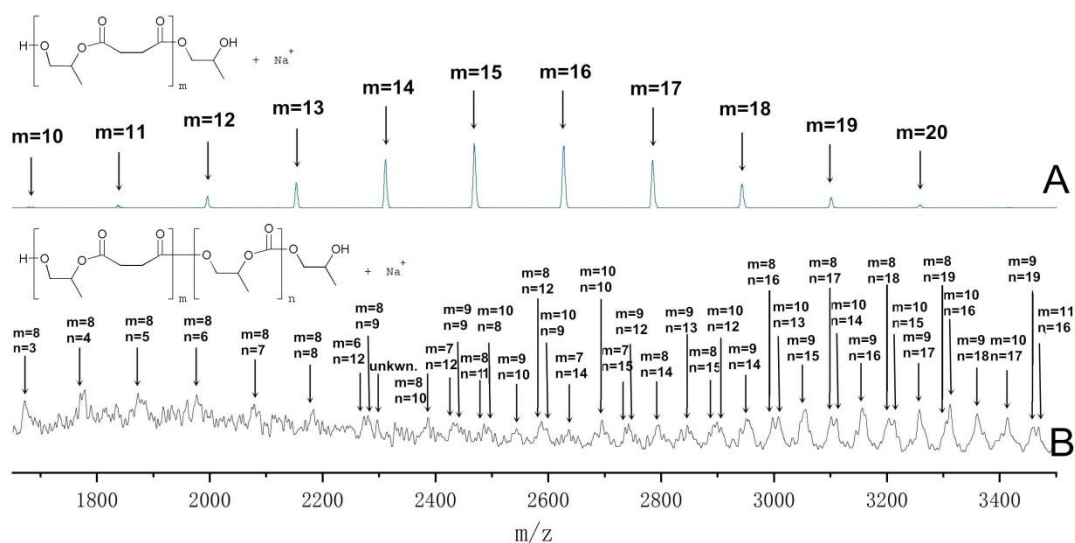


Figure S34. Low molecular weight region of MALDI-TOF-MS spectra of the PPS (A) and block polymer obtained by the two-step procedure (B).

Reference:

1. R. Kowalczyk, P. Kwiatkowski, J. Skarzewski and J. Jurczak, *J. Org. Chem.*, 2009, **74**, 753-756.
2. V. Busico, R. Cipullo, R. Pellecchia, S. Ronca, G. Roviello and G., Talarico, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15321-15326.
3. C. Zeng, D. Yuan, B. Zhao and Y. Yao, *Org. Lett.*, 2015, **17**, 2242-2245.
4. (a) N. U. Hofslkken and L. Skattebl, *Acta. Chem. Scand.*, 1999, **53**, 258-262; (b) T. V. Hansen and L. Skattebøl, *Tetrahedron Lett.*, 2005, **46**, 3829-3830.