Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Novel poly(2-oxazoline)s with pendant L-prolinamide moieties as efficient organocatalysts for direct asymmetric aldol reaction

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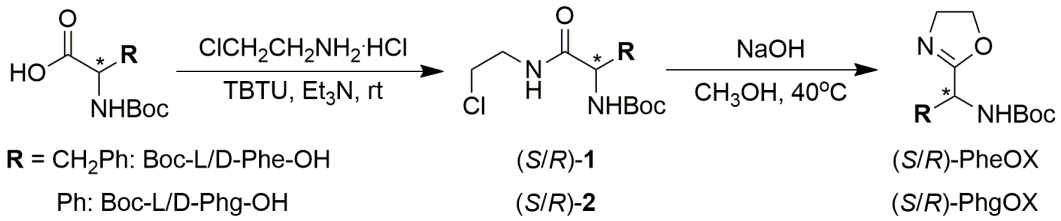
1. **Monomer synthesis**



2. **Spectroscopic data**

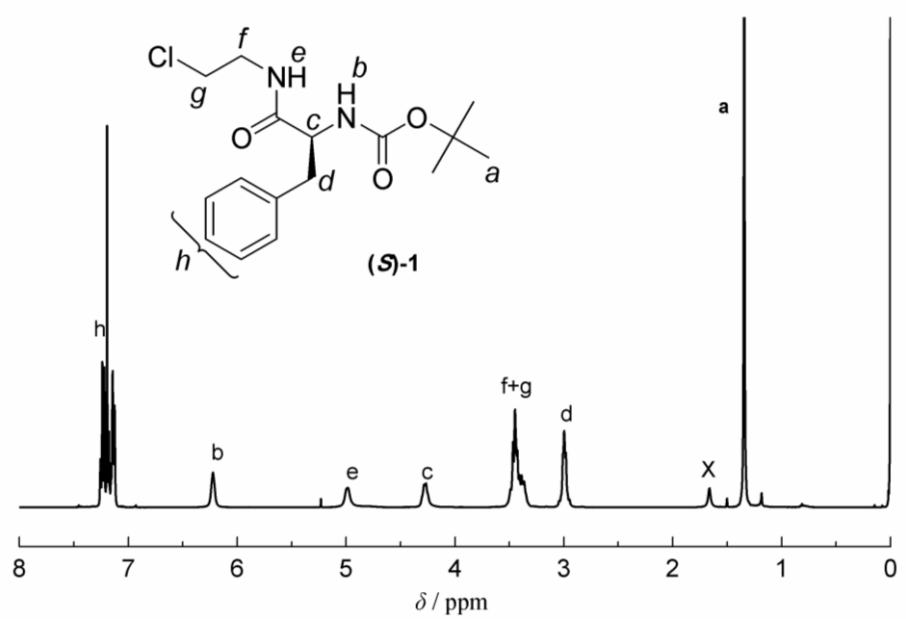


Figure S1. ^{1}H NMR of the intermediate product (*S*)-**1**

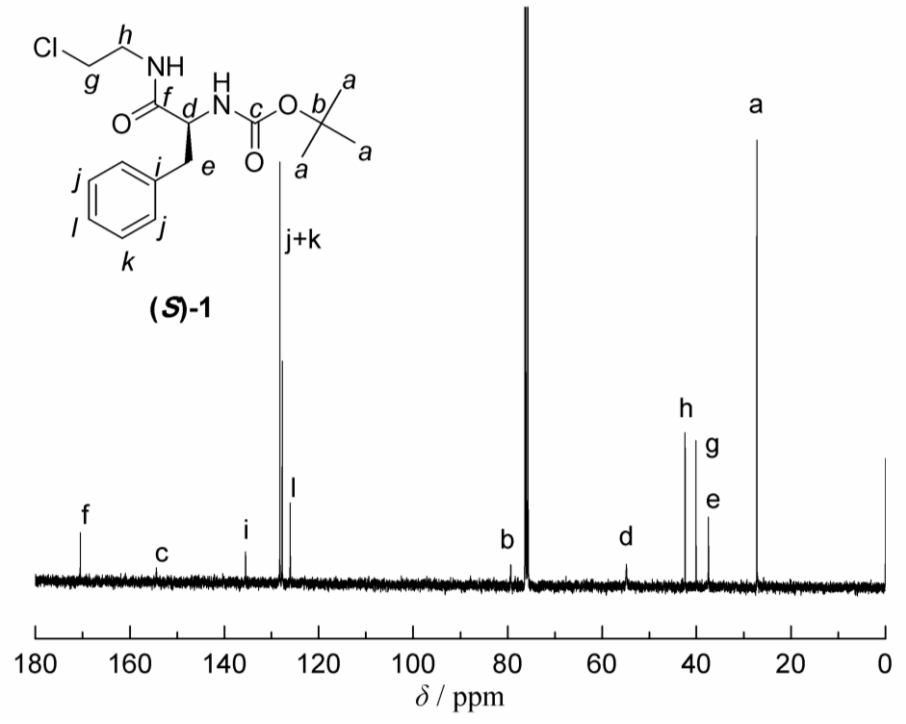


Figure S2. ^{13}C NMR spectrum of the intermediate product (*S*)-**1**

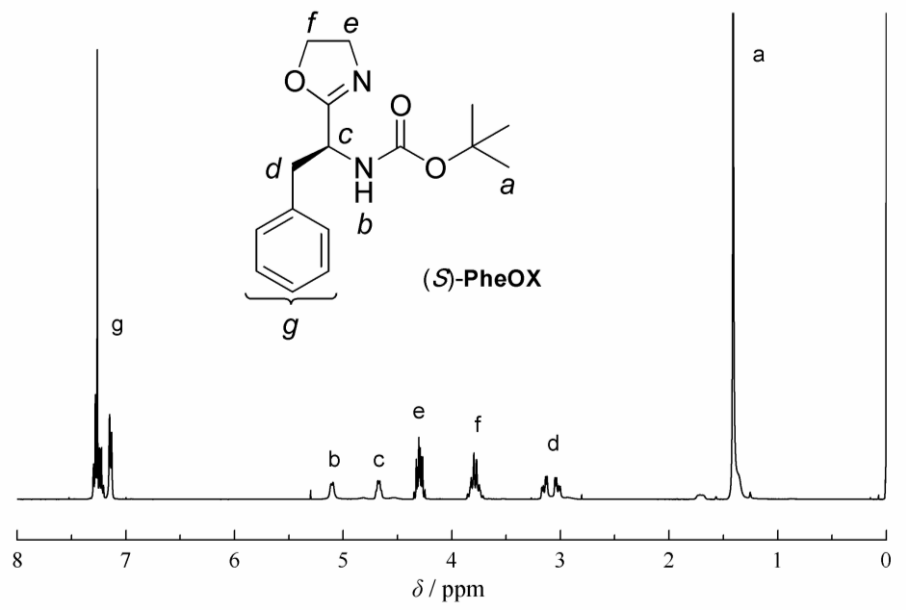


Figure S3. ^{1}H NMR spectrum of (*S*)-PheOX

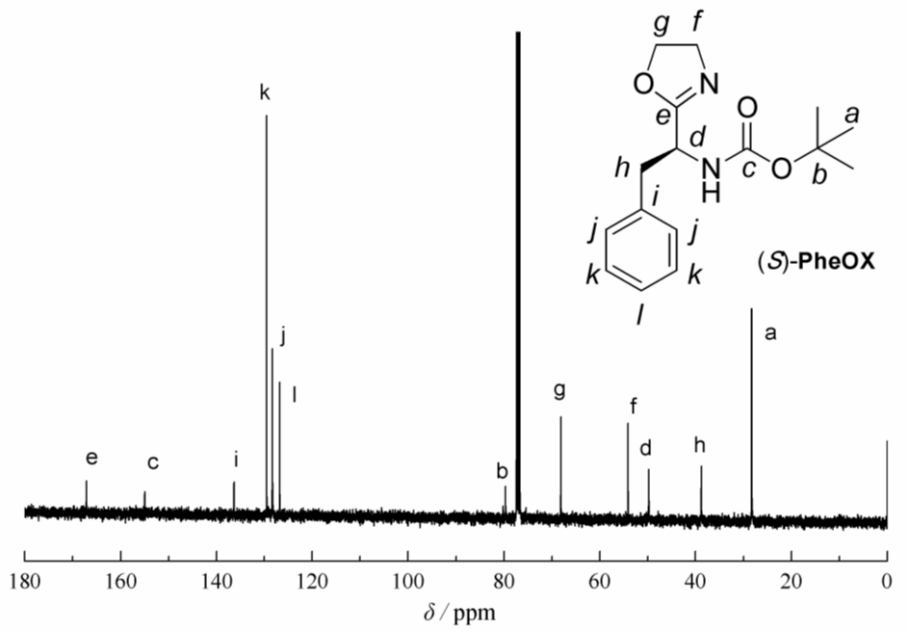


Figure S4. ^{13}C NMR spectrum of (*S*)-PheOX

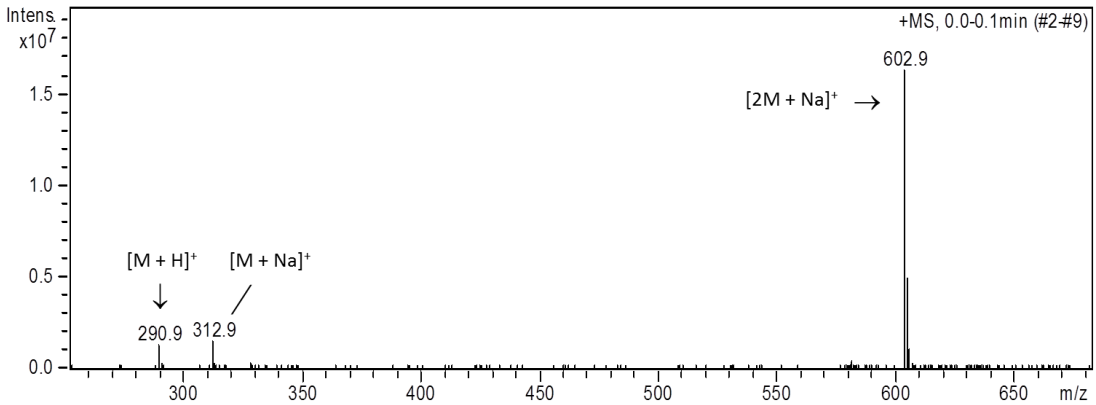


Figure S5. MS (ESI+) of (*S*)-PheOX

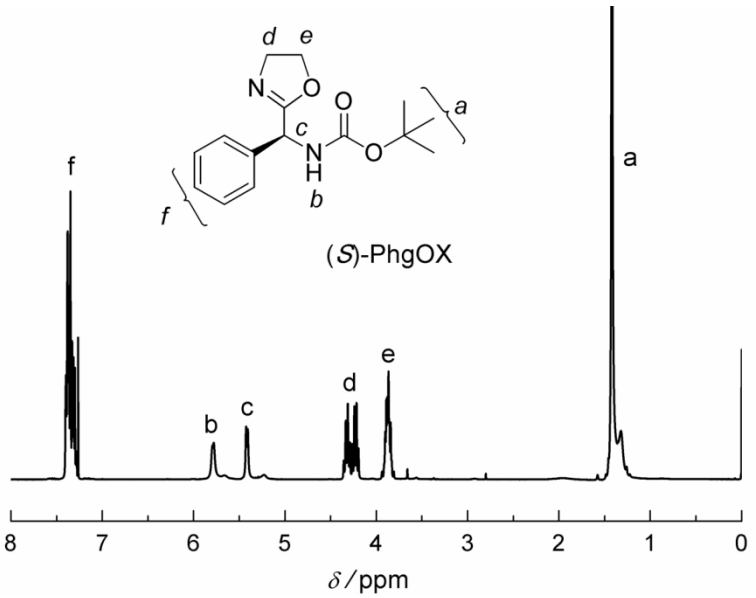


Figure S6. ^{1}H NMR spectrum of (*S*)-PhgOX

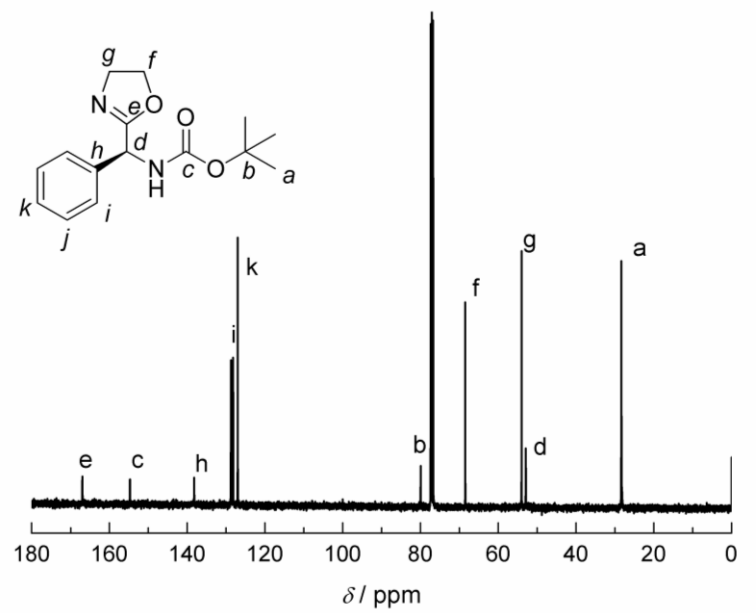


Figure S7. ^{13}C NMR spectrum of (*S*)-PhgOX

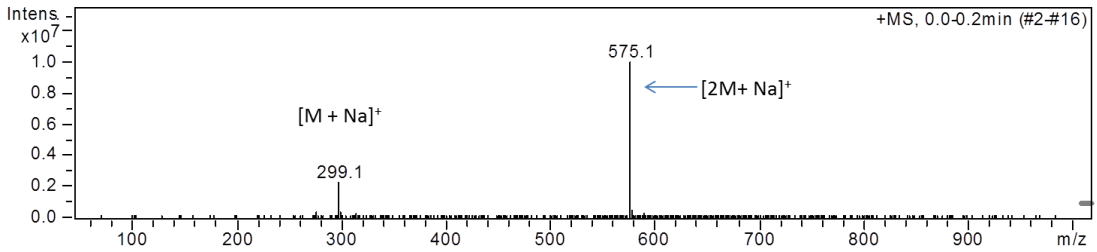


Figure S8. MS (ESI+) of (*S*)-PhgOX

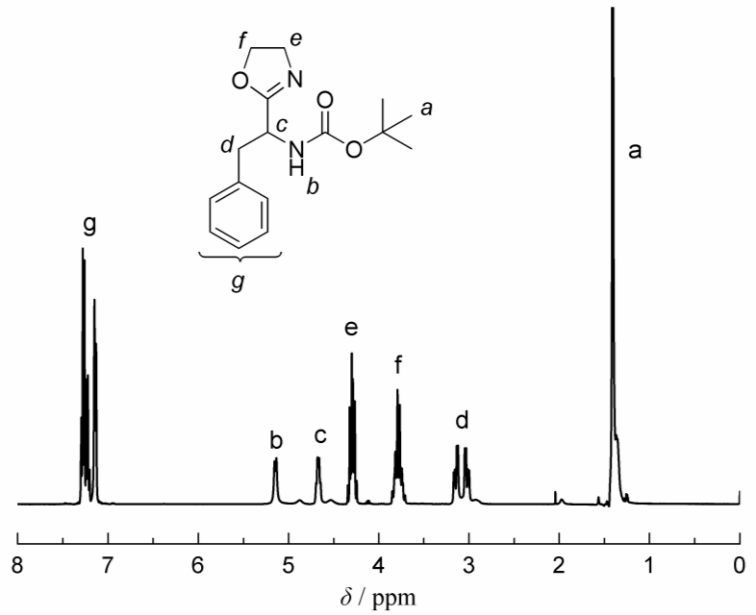


Figure S9. ^{1}H NMR spectrum of (*RS*)-PheOX

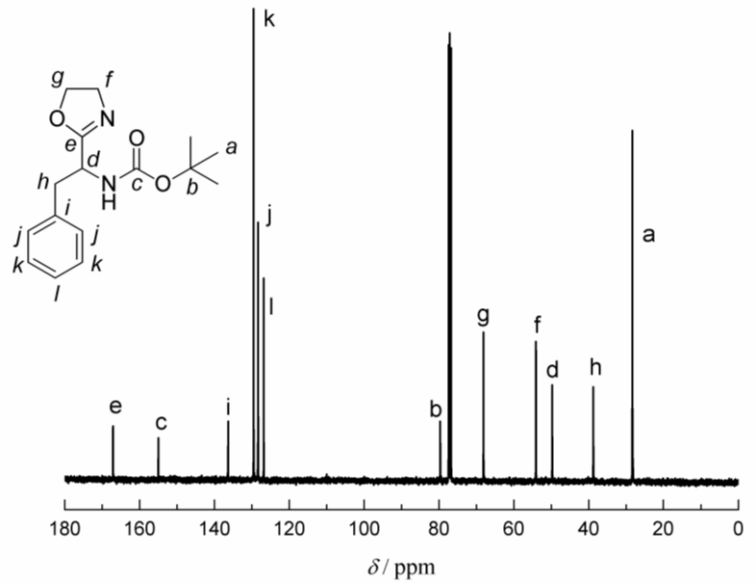


Figure S10. ^{13}C NMR spectrum of (*RS*)-PheOX

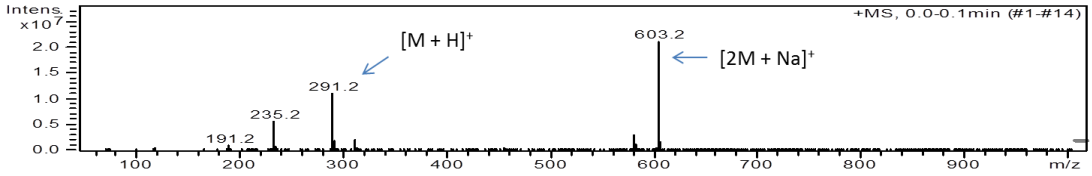


Figure 11. MS (ESI+) of (*RS*)-PheOX

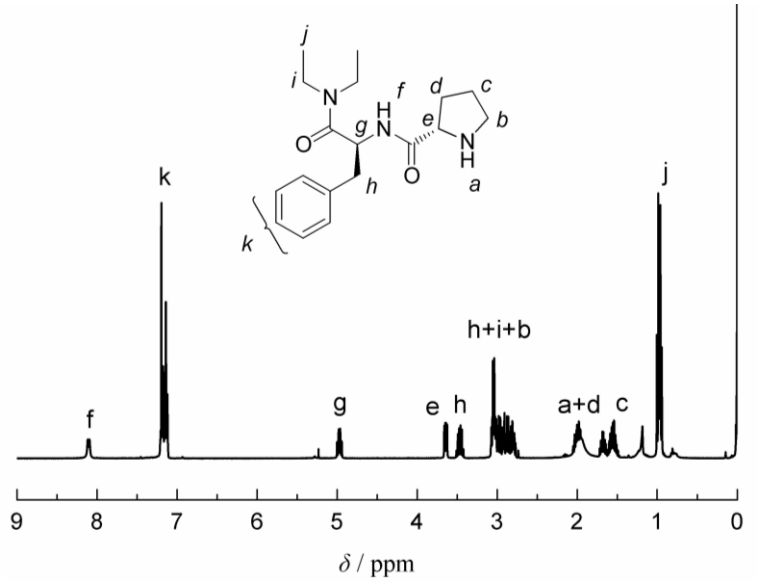


Figure S12. ^{1}H NMR spectrum of the model compound (*S*)-**M1**

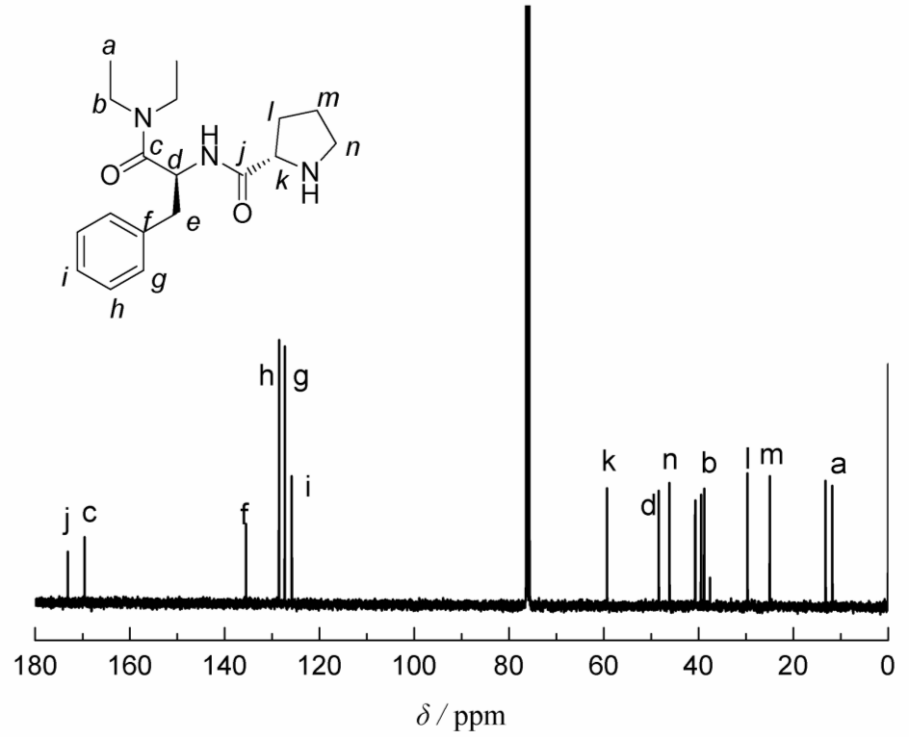


Figure S13. ^{13}C NMR spectrum of (*S*)-**M1**

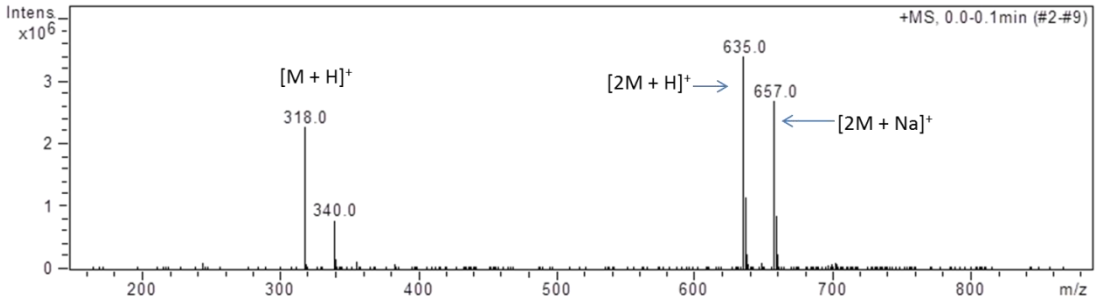


Figure S14. MS (ESI+) of (*S*)-**M1**

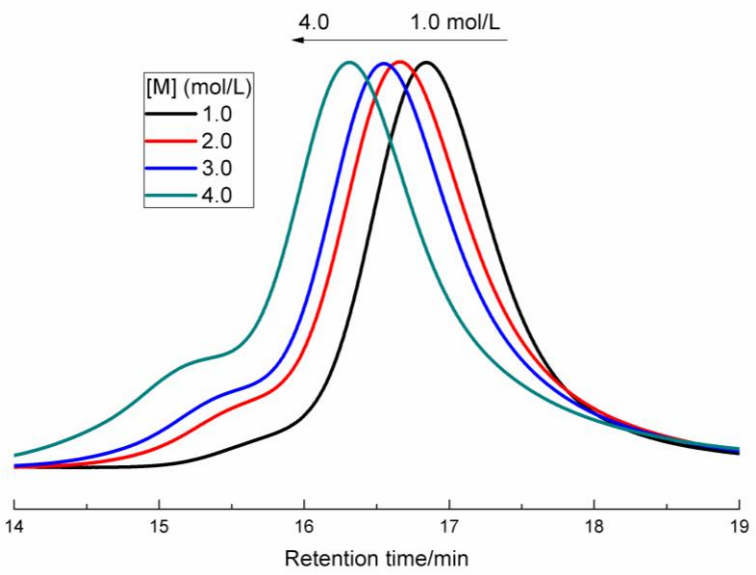


Figure S15. SEC traces of (*S*)-PPheOX$_{NHBoc}$ samples, PMMA standard, DMF with 50 mM LiBr as the eluent. Polymerization conditions: $[M]_0$ = 1~4.0 M, $[M]_0/[I]_0$ = 100, acetonitrile, using $Sc(OTf)_3$ as the initiator, 90°C, 2 h.

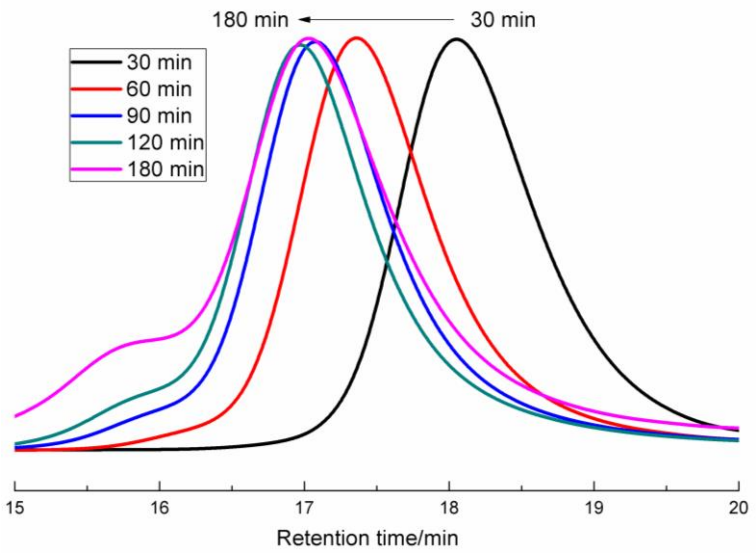


Figure S16. SEC traces of (*S*)-PPheOX$_{NHBoc}$ samples collected periodically from the polymerization kinetic experiments, PMMA standard, DMF with 50 mM LiBr as the eluent. Polymerization conditions: $[M]_0$ = 2 M, $[M]_0/[I]_0$ = 100, acetonitrile, using $Sc(OTf)_3$ as the initiator, reaction temperature: 90°C.

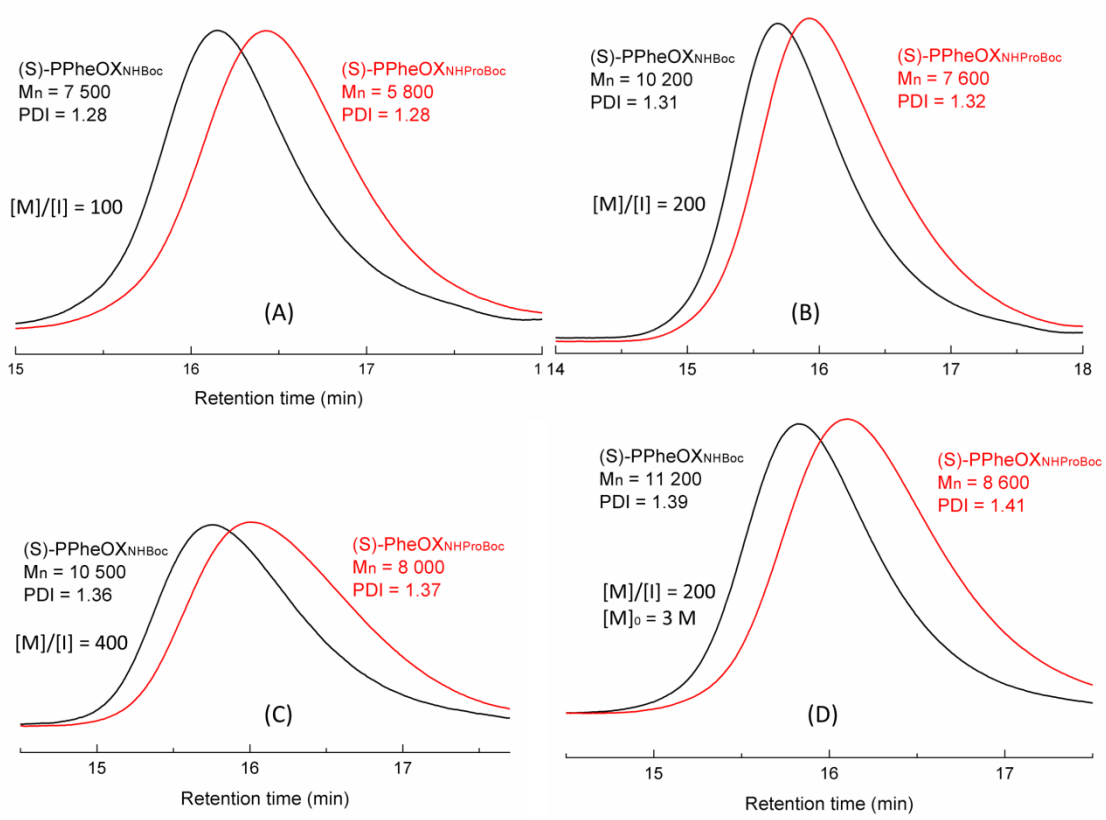


Figure S17. Comparison of SEC traces of (*S*)-PPheOX$_{NHBoc}$ and (*S*)-PPheOX$_{NHProBoc}$. (A), (B), C, and D correspond to Entries 2–5 in Table 1, respectively.

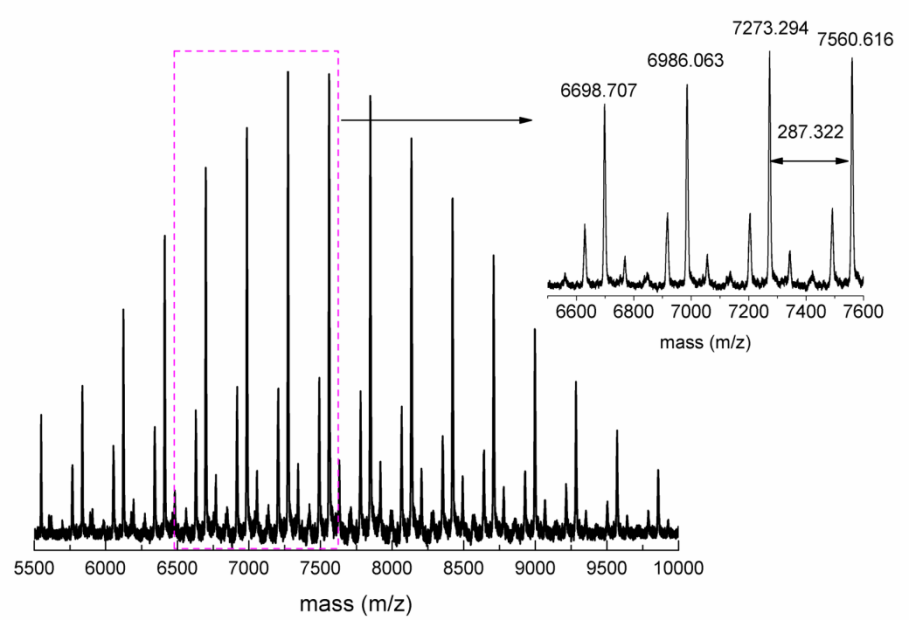
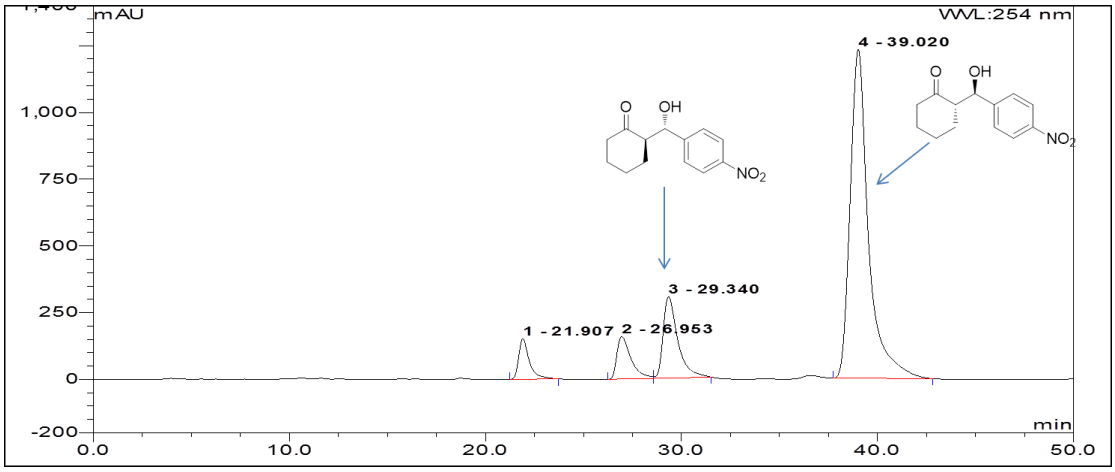
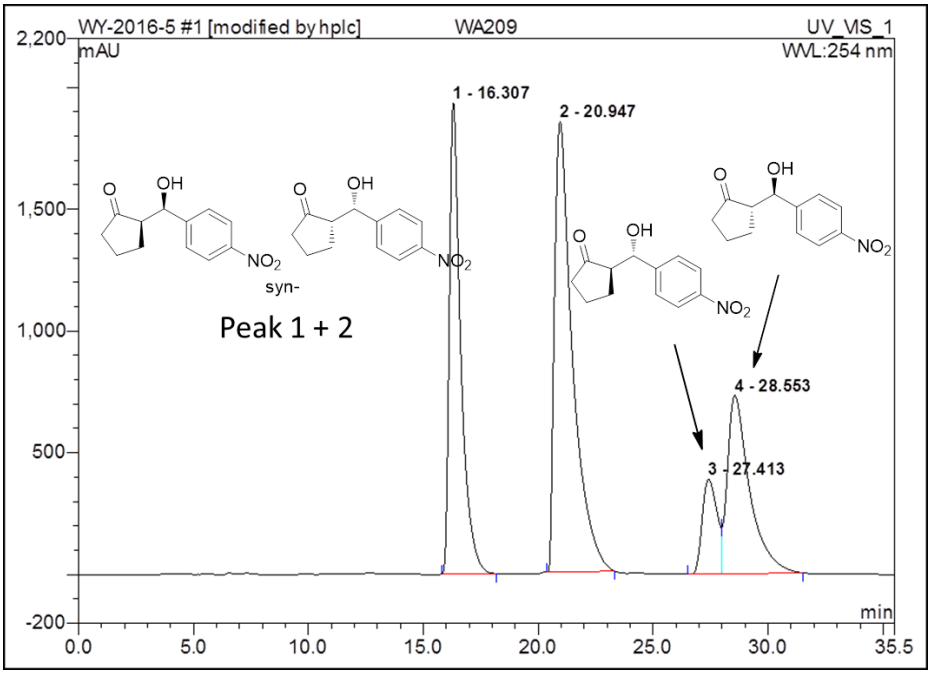


Figure S18. A representative Maldi Tof MS of (*S*)-PPheOX$_{NHPro}$.



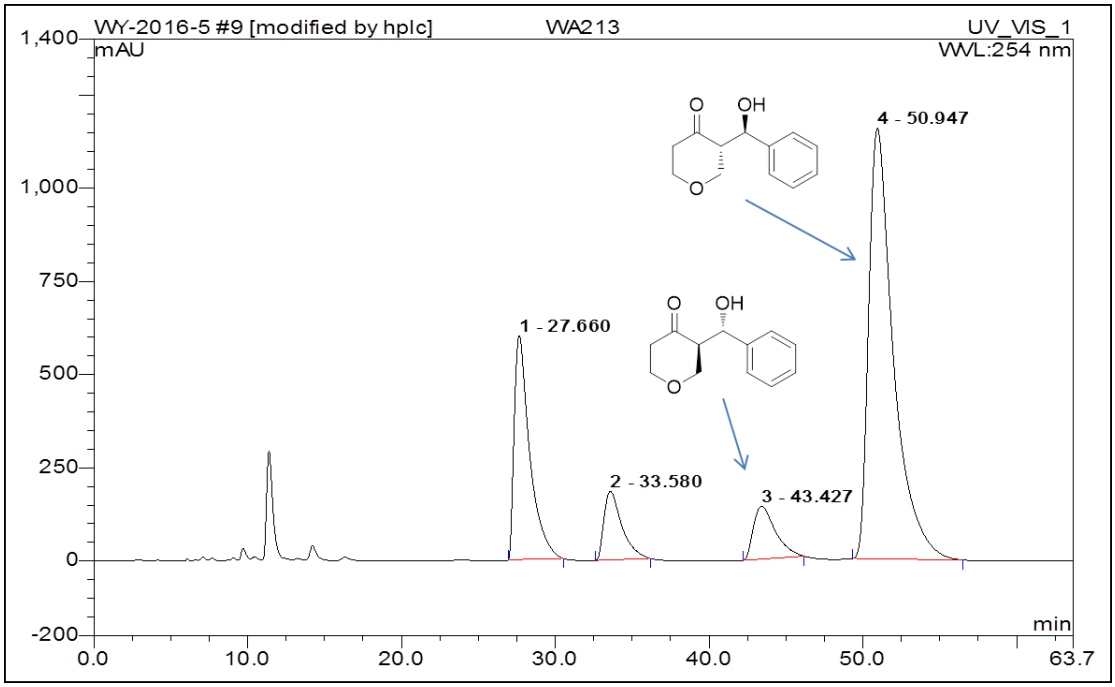
No.	Ret.Time/min	Peak Name	Height/ mAU	Area/ mAU*min	Rel.Area/%
1	21.91	1#	151.894	95.055	5.22
2	26.95	2#	159.086	132.068	7.25
3	29.34	3#	305.176	262.831	14.43
4	39.02	4#	1231.101	1331.268	73.10
Total:			1847.256	1821.222	100.00

Figure S19. Representative HPLC curve of aldol products of cyclohexanone with 4-nitrobenzaldehyde and the corresponding analysis data.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %
1	16.31	1#	1934.904	1110.879	28.44
2	20.95	2#	1849.659	1682.576	43.07
3	27.41	3#	389.444	289.231	7.40
4	28.55	4#	732.105	823.675	21.09
Total:			4906.111	3906.361	100.00

Figure S20. Representative HPLC curve of aldol products of cyclopentanone with 4-nitrobenzaldehyde and the corresponding analysis data.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %
1	27.66	1#	600.274	701.190	21.02
2	33.58	2#	184.272	247.817	7.43
3	43.43	3#	141.953	235.589	7.06
4	50.95	4#	1155.043	2151.849	64.50
Total:			2081.542	3336.446	100.00

Figure S21. Representative HPLC curve of aldol products of 4-pyranone with 4-nitrobenzaldehyde and the corresponding analysis data.

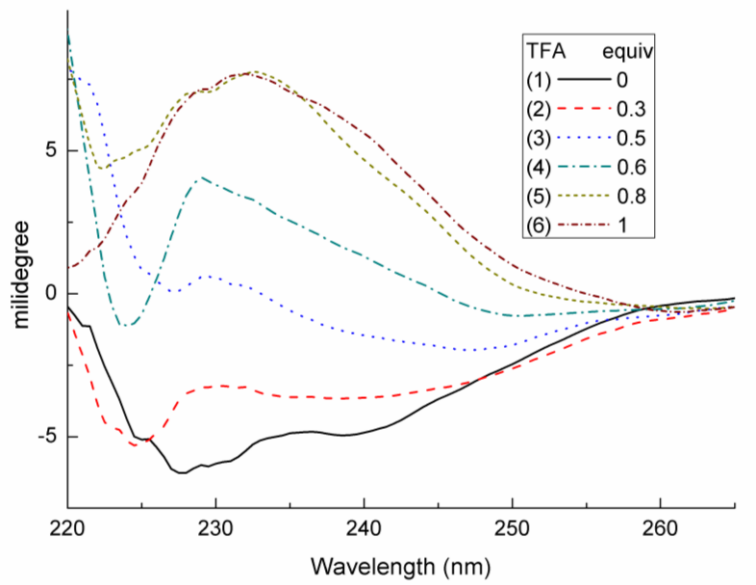


Figure S22. CD titration of (*RS*)-PPheOX$_{NHPro}$ (10^{-3} M) with TFA (0 ~ 1 equiv.) in CH_2Cl_2 containing ~1% water at 25°C.

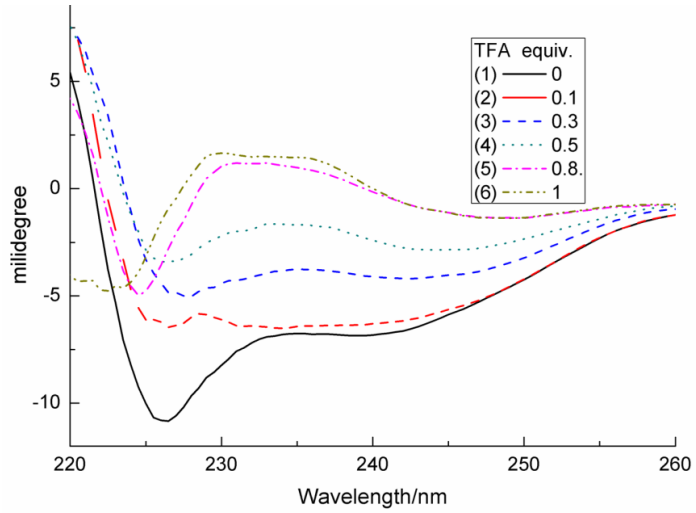


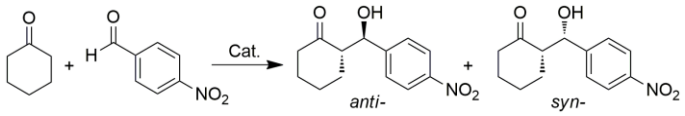
Figure 23. CD titration of (*S*)-**M1** with TFA (0 ~ 1 equiv.) in CH_2Cl_2 containing ~1% water at 25°C.

Table S1 Results on the cationic ring-opening polymerization of 2-oxazolines and the post-modification for the resulting polymers [a]

P**OX**$_{\mathbf{NHBoc}}$	M/I	Yield (%)[b]	M_n[c] (10^3)	PDI[c]	**POX**$_{\mathbf{NHPro}}$	E_{NHPro}[d]	$[\alpha]_D^{20}$ [e]
(*R*)-P1	100	90	6.7	1.13	(*R*)-PPheOX$_{NHPro}$	97	–30
	200	83	10.0	1.09		95	–30
(*RS*)-P1	100	92	7.6	1.09	(*RS*)-PPheOX$_{NHPro}$	95	–26
	200	75	10.1	1.1		95	–28
(*S*)-P2	100	87	5.7	1.16	(*S*)-PPhgOX$_{NHPro}$	97	–31
	200	75	9.2	1.11		98	–32
(*R*)-P2	100	90	5.9	1.15	(*R*)-PPhgOX$_{NHPro}$	96	–35
	200	71	8.3	1.12		98	–39

[a] Polymerization conditions: [M] = 2 mol/L, CH_3CN, 90°C, 3 h. [b] Isolated yield. [c] Determined by SEC measurements, PS calibration, THF as the eluent. [d] Amide coupling efficiency of repeating monomeric units was measured by ^{1}H NMR integration ($CDCl_3$). [e] *c* = 10 mg/mL, MeOH, 20°C. (*R*)-P1 = (*R*)-PPheOX$_{NHBoc}$, (*RS*)-P1 = (*RS*)-PPheOX$_{NHBoc}$, (*S*)-P2 = (*S*)-PPhgOX$_{NHBoc}$, (*R*)-P2 = (*R*)-PPhgOX$_{NHBoc}$. The corresponding monomers are (*R*)-PheOX, (*RS*)-PheOX, (*S*)-PhgOX, and (*R*)-PhgOX, respectively.

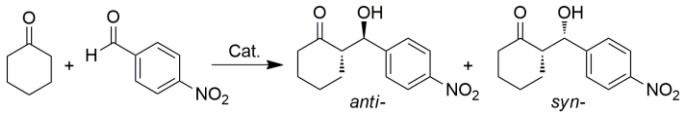
Table S2 Effect of solvent on the direct asymmetric aldol reaction of cyclohexanone with 4-nitrobenzaldehyde in the presence of polymeric catalyst (*S*)-PPheOX$_{NHPro}$[a]



Entry	Loading [b] [mol-%]	Solvent (total 1 mL)	Time [h]	Yield [c] [%]	anti:syn [d]	ee [e]
1	20	MeOH or DMSO or NMP	48	<5	–	–
2	20	H_2O	12	82	81:19	65
3	10	MeOH/H_2O (1:1)	36	85	72:28	45
4	20	MeOH/H_2O (1:1)	12	72	79:21	74
5	10	NMP/H_2O (1:1)	12	95	88:12	68
6	20	NMP/H_2O (1:1)	12	98	83:17	80
7	20	DMSO/H_2O (1:1)	24	82	81:19	60
8[f]	20	none	48	<5	–	–

[a] Reaction conditions: aldehyde (0.25 mmol), cyclohexanone (5 mmol, 0.516 mL), 10°C. [b] Catalyst 20 mol-% or 10 mol-% in the repeating units. [c] Isolated yield. [d] Determined by ^{1}H NMR spectroscopic analysis of the crude product. [e] Determined by HPLC using a chiral column; *ee* values are referred to the major isomer. [f] In this case, cyclohexanone served as solvent.

Table S3 Effect of the molar mass on the catalytic activity of (*S*)-PPheOX$_{NHPro}$ in the direct aldol reaction.



Entry	M_n	H_2O/TFA(μL)	Time (h)	Yield [b] (%)	anti/syn [c]	ee [d] (%)
1	4000	9:2	12	92	80/20	92
2	4000	9:2.6	24	70	80/20	93
3	6700	9:2	12	96	78/22	91
4	6700	9:2.6	24	66	71/29	93
5	9000	9:2	12	98	84/16	89

6	9000	9:2.6	24	68	77/23	92
7	10400	9:2	12	97	78/22	88
8	10400	9:2.6	24	64	83/17	89