

Supporting Information

Cobalt(III)-salen Decorated Stereoregular Optical Helical Polyisocyanides Enable Highly Effective Cooperative Asymmetric Catalysis toward Kinetic Resolution of Epoxides

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SI1 Instruments and Materials

SI1.1 Instruments and Measurement conditions

Structural characterization measurements. The NMR spectra were recorded on a Bruker 400 or 600 MHz spectrometer. The chemical shifts (δ) in ^1H NMR were reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of NMR solvent CDCl_3 (7.26 ppm). Coupling constants (J) are expressed in hertz. ^{13}C NMR spectra were recorded at 101 MHz or 151 MHz, and the chemical shifts (δ) were reported in ppm relative to CDCl_3 (77.10 ppm). HRMS analyses were performed on a Thermo Scientific Vanquish Q Exactive Plus system or a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

Circular dichroism (CD). CD spectra were obtained in a 0.1 cm quartz cell using a JASCO J1500 spectropolarimeter. All the samples, including polymers and small molecules, were dissolved in specific organic solvents, and measured at 25 °C. The salen units in all samples were fixed as 1.5×10^{-4} mol/L and measured in the range of 270 to 500 nm for **M1**, **P1** and **P1-Co-N₃**, and in the range of 250 to 500 nm for **S1** and **S1-Co-N₃**.

Size exclusion chromatograms (SEC). Molecular weights and molecular weight distributions were determined by a Waters 1515 pump and a Waters 2414 differential refractive index detector (set at 40 °C) with THF as a flow phase.

High Performance Liquid Chromatography (HPLC). HPLC were measured by JASCO Co. Ltd., with JASCO UV-4070 and CD-4095 detectors, and a JASCO Pu-418 pump, with *n*-hexane/*i*-PrOH as the flow phase.

High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM). HAADF-STEM observations were collected on a JEM-2100F high resolution transmission electron microscope at an acceleration voltage of 200.0 kV. The samples were prepared by casting the THF solutions of polymer **P1-Co-N₃** on copper mesh grids and drying in air under ambient temperature.

High Resolution Cold Field Emission Scanning Electron Microscopy (HR-FESEM). HR-FESEM observations were collected on a Hitachi Regulus 8230 electron microscope. The

samples were prepared by casting the THF solutions of polymer **P1–Co–N₃** on silicon substrate and drying in air under ambient temperature.

Atomic force microscope (AFM). AFM observations were performed on a Cypher S microscope (Oxford Instruments, Asylum Research). The samples were prepared by casting the THF solutions (0.01 mg/mL) of polymer **P1–Co–N₃** on silicon substrate and drying in air under ambient temperature.

Aberration-Corrected High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (AC-HAADF-STEM). AC-HAADF-STEM observations were collected on a FEI Titan Cubed Themis G2 300 double spherical aberration correction transmission electron microscope at an acceleration voltage of 200.0 kV. The samples were prepared by casting the THF solutions of polymer **P1–Co–N₃** on ultra-thin carbon films and drying in air under ambient temperature.

X-ray Photoelectron Spectroscopy (XPS). XPS characterization was performed on a Thermo ESCALAB250XI spectrometer using Al K_{α} radiation (1486.6 eV) operated at 20 kV. Spectra were calibrated by adjusting the binding energy of C1s to 284.6 eV. XPS spectra were analysed using XPS Peak 4.1 software. The Gaussian-Lorentzian mix function was 30% (Gaussian-to-Lorentzian ratio) with Shirley background subtraction.

Dynamic Light Scattering (DLS). DLS measurements were carried on a Nano-ZS90 Zetasizer of Malvern (UK) instrument, and all data were averaged over three-time measurements. The sample solutions were filtrated through filter membrane before measurement.

FT-IR spectra Measurements. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using pure sample and attenuated total refraction (ATR) method at 25 °C.

Elemental analysis. Elemental analysis was carried on vario EL cube Elemental Analyzer (C, H, N) and Vario MICRO CUBE Elemental Analyzer (O) using pure sample.

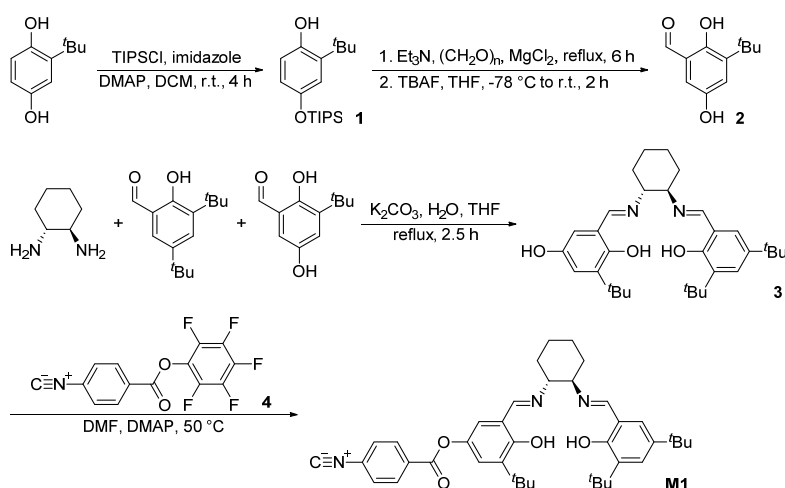
Computational simulation. Both molecular mechanics (MM) structure optimization and molecular dynamics (MD) simulations were calculated using the Forcite module of the Materials Studio software (version 2019), and Compass force field were used during all simulations. The geometric parameters of the main chain were fixed during the following Forcite geometry optimization. The polymer models of **P1₅–Co** and **P1₃₂–Co** were constructed using the Polymer

Builder module in the MS Modeling software with the suitable side-chain conformations. Atom-based methods were applied for modeling and calculation of van der Waals and electrostatic potential energy. The convergence thresholds for geometry optimization calculations of all the models were set as 1.0×10^{-5} kcal·mol⁻¹ for energy, 1.0×10^{-5} Å for maximum displacement, and 0.001 kcal·mol⁻¹·Å⁻¹ for maximum force. Then, we did dynamics simulations, canonical ensemble (NVT) was used, and the temperature was set to 298.15 K with the Nose temperature control method. The total simulation time was 200 ps with the step of 1 fs.

SI1.2 Materials

All solvents were purchased from Sinopharm. Co. Ltd. and were purified by the standard procedures before use. All chemicals were obtained from Aladdin, Sinopharm and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. THF and MeO'Bu were freshly distilled from sodium and using benzophenone as an indicator. Other solvents were dried over anhydrous CaH₂ and distilled before use.

SI2 Synthesis and Characterization of Intermediates, Monomers, and Polymer-supported Catalysts.

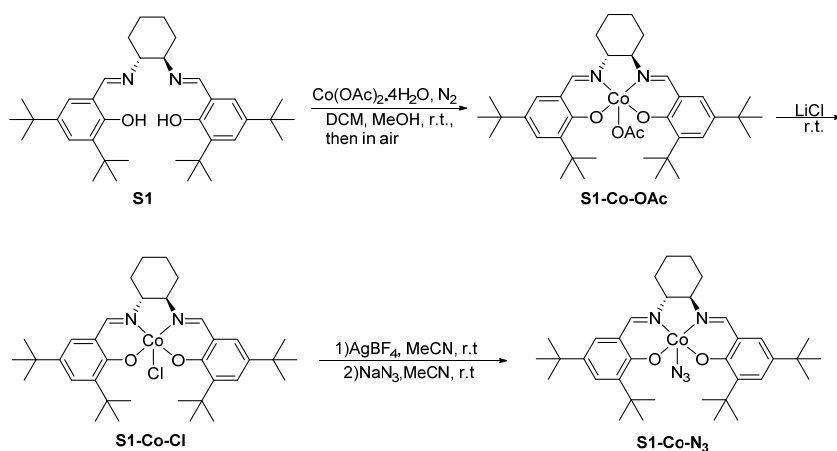


Synthesis of 1.[1] To a solution of *t*-butylhydroquinone (19.92 g, 120 mmol), DMAP (1.76 g, 14.4 mmol), and imidazole (10.21 g, 150 mmol) in anhydrous CH₂Cl₂ (120 mL) was added *i*-Pr₃SiCl (26.3 mL, 123 mmol). The solution was stirred at ambient temperature for 4 h, then quenched with sat. NH₄Cl aqueous solution. The separated organic phase was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by rapid column chromatography (SiO₂, petroleum ether/ethyl acetate, 9:1) to afford the pure product **1** as a yellow oil (35.19 g, 91%). ¹H NMR (600 MHz, CDCl₃): δ 6.81 (d, *J* = 2.9 Hz, 1H), 6.57 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.9 Hz, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 4.41 (s, 1H), 1.37 (s, 9H), 1.25–1.18 (m, 3H), 1.10 (d, *J* = 7.4 Hz, 18H).

Synthesis of 2.[1] Compound **1** (35.12 g, 109 mmol) was dissolved in anhydrous MeCN (500 mL). Then Et₃N (53.3 mL, 382.2 mmol), paraformaldehyde (19.66 g, 655.2 mmol), and anhydrous MgCl₂ (14.52 g, 152.9 mmol) were added under an N₂ atmosphere. The mixture was heated to reflux for 6 h, then cooled to ambient temperature and quenched with 1 M HCl aqueous solution (250 mL). The solution was filtered through Celite, rinsing with Et₂O (50 mL × 3), and the layers were separated. The aqueous layer was extracted with Et₂O (20 mL × 3), and the combined organic phase was washed with brine (200 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was dissolved in degassed THF (350 mL) and cooled to –78 °C. A

1.0 M aqueous solution of TBAF (124.5 mL, 124.5 mmol) was added slowly. After the completion of addition, the solution was warmed to ambient temperature for 2 h, then it was diluted with water and ethyl acetate and the layers were separated. The organic layer was washed with brine (200 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was redissolved in CH₂Cl₂ and cooled to 0 °C. The suspension was filtered, and the generated yellow solid was washed with cold CH₂Cl₂. Removing the solvent under vacuum to afford the pure product **2** as a yellow solid (10.48 g, 49% total yield from **1**). ¹H NMR (600 MHz, CDCl₃): δ 11.38 (s, 1H), 9.79 (s, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 6.83 (d, *J* = 3.1 Hz, 1H), 4.69 (s, 1H), 1.40 (s, 9H).

Synthesis of 3.[2] To a solution of K₂CO₃ (7.50 g, 54.6 mmol) and (1*R*,2*R*)-1,2-diaminocyclohexane (11.28 g, 49.5 mmol) in H₂O (300 mL) was added THF (120 mL) and the solution was heated to reflux for 2 h. 3-*tert*-butyl-2,5-dihydroxybenzaldehyde (4.80 g, 24.66 mmol) and 3,5-di-*tert*-butyl-salicylaldehyde (17.31 g, 73.98 mmol) in THF (60 mL) were added dropwise over 30 min. After cooling to ambient temperature, the solution was poured into Et₂O (600 mL) and the aqueous phase was washed with Et₂O (100 mL × 2). The combined organic phase was washed with brine (150 mL), dried over anhydrous Na₂SO₄, filtrated, and concentrated. The residue was purified by rapid column chromatography (SiO₂, petroleum ether/ethyl acetate, 9:1), concentrated and freeze-dried from CH₂Cl₂/benzene to afford **3** as a yellow solid (3.59 g, 77%). ¹H NMR (600 MHz, CDCl₃): δ 8.28 (s, 1H), 8.18 (s, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 3.35–3.27 (m, 1H), 1.95 (d, *J* = 13.8 Hz, 2H), 1.87 (d, *J* = 8.5 Hz, 2H), 1.78–1.68 (m, 2H), 1.50–1.43 (m, 2H), 1.41 (s, 9H), 1.38 (s, 9H), 1.23 (s, 9H).



Synthesis of S1–Co–N₃. [3] Small molecular control S1–Co–N₃ was synthesized according to the literature method. The complex was afforded as a brown solid with yield of 84%. HRMS (ESI-FT): Calcd. For [M + H]⁺, C₃₆H₅₃CoN₅O₂⁺: 646.3529. Found: 646.3531.

Table S1. Polymerization results of salen-decorated isocyanides M1 with I1 as the initiator.

Entry	Solvent	[M] ₀ /[cat] ₀	M _n (kDa) ^a	M _w /M _n ^a	Yield (%) ^b
1	CHCl ₃	100	71.4	1.51	62
2	THF	100	143.3	1.23	84
3	THF	25	35.7	1.29	68
4	THF	50	70.9	1.27	74
5	THF	150	199.6	1.25	90
6	THF	200	289.7	1.10	92

^aThe M_n and M_w/M_n values were determined by SEC with reference to polystyrene standards. ^bIsolated yields.

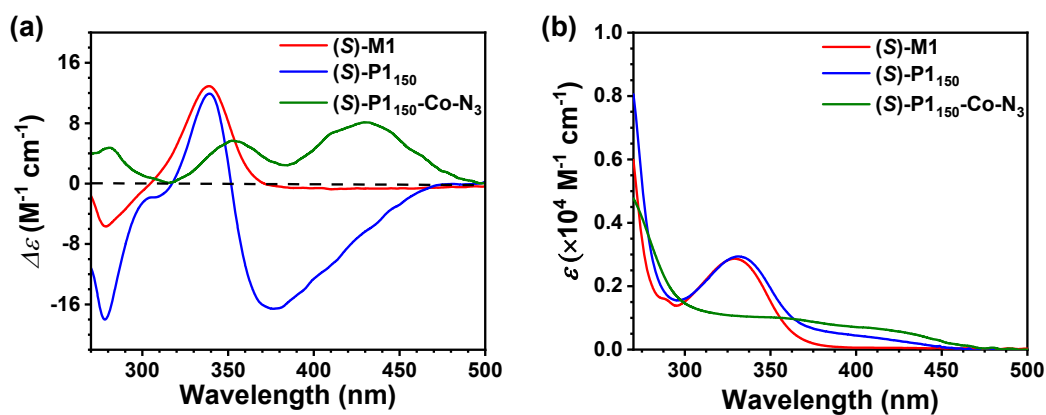


Figure S1. CD (a) and UV-vis spectra (b) of (S)-M1, (S)-P1₁₅₀, and (S)-P1₁₅₀-Co-N₃ measured in THF at 25 °C ($c = 1.5 \times 10^{-4}$ M according to amount of salen units).

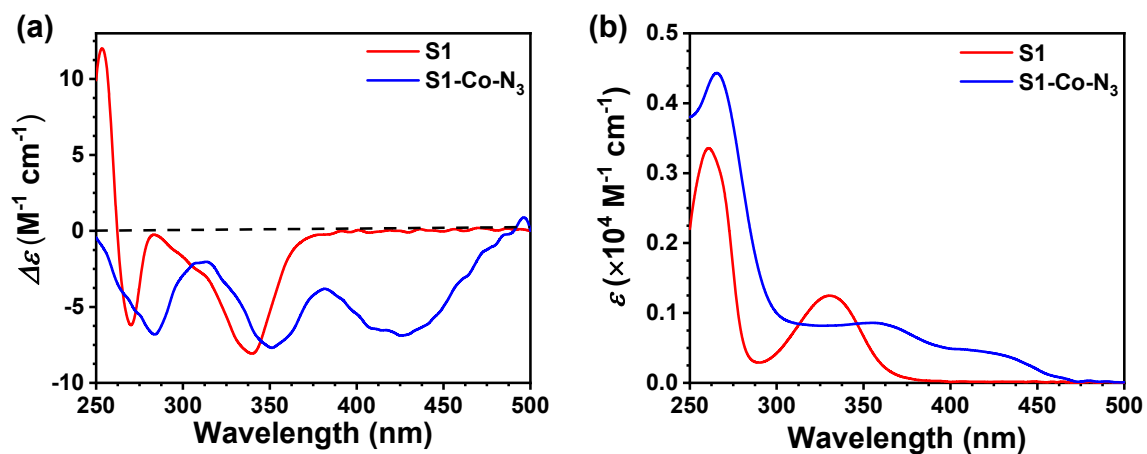


Figure S2. CD (a) and UV-vis spectra (b) of S1 and S1-Co-N₃ measured in THF at 25 °C ($c = 1.5 \times 10^{-4}$ M).

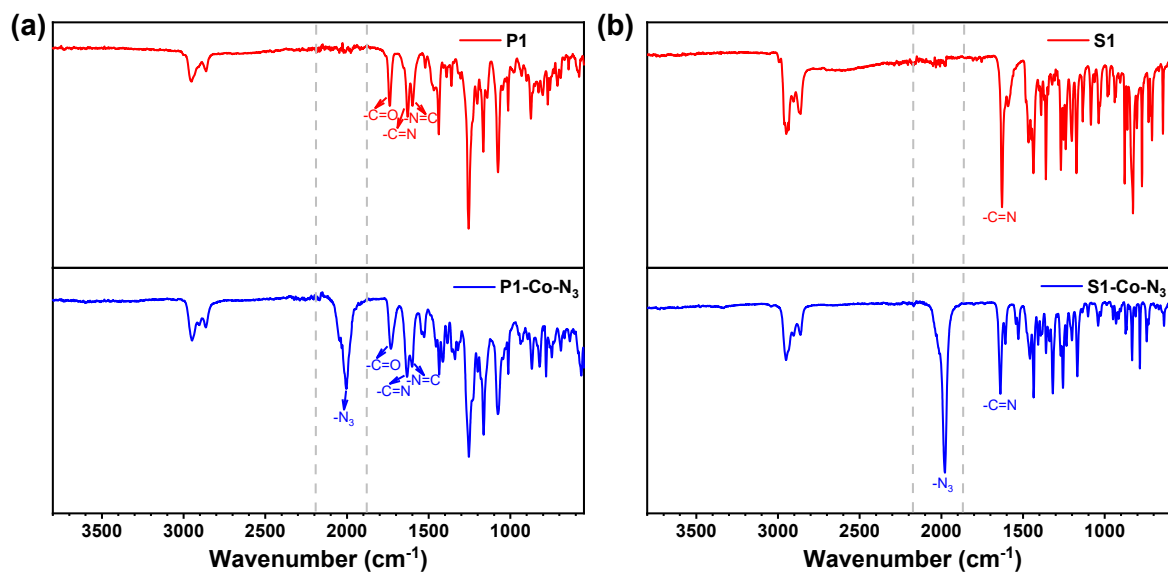


Figure S3. FT-IR spectra of (a) P1 and P1-Co-N₃; and (b) S1 (4) and S1-Co-N₃.

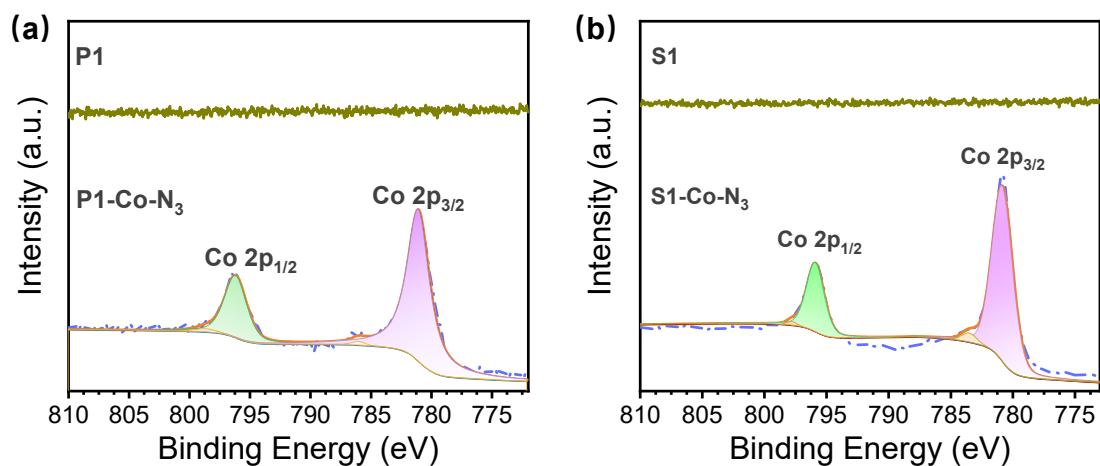


Figure S4. XPS Co 2p spectra of (a) pristine P1, P1-Co-N₃, and (b) pristine S1, S1-Co-N₃, respectively.

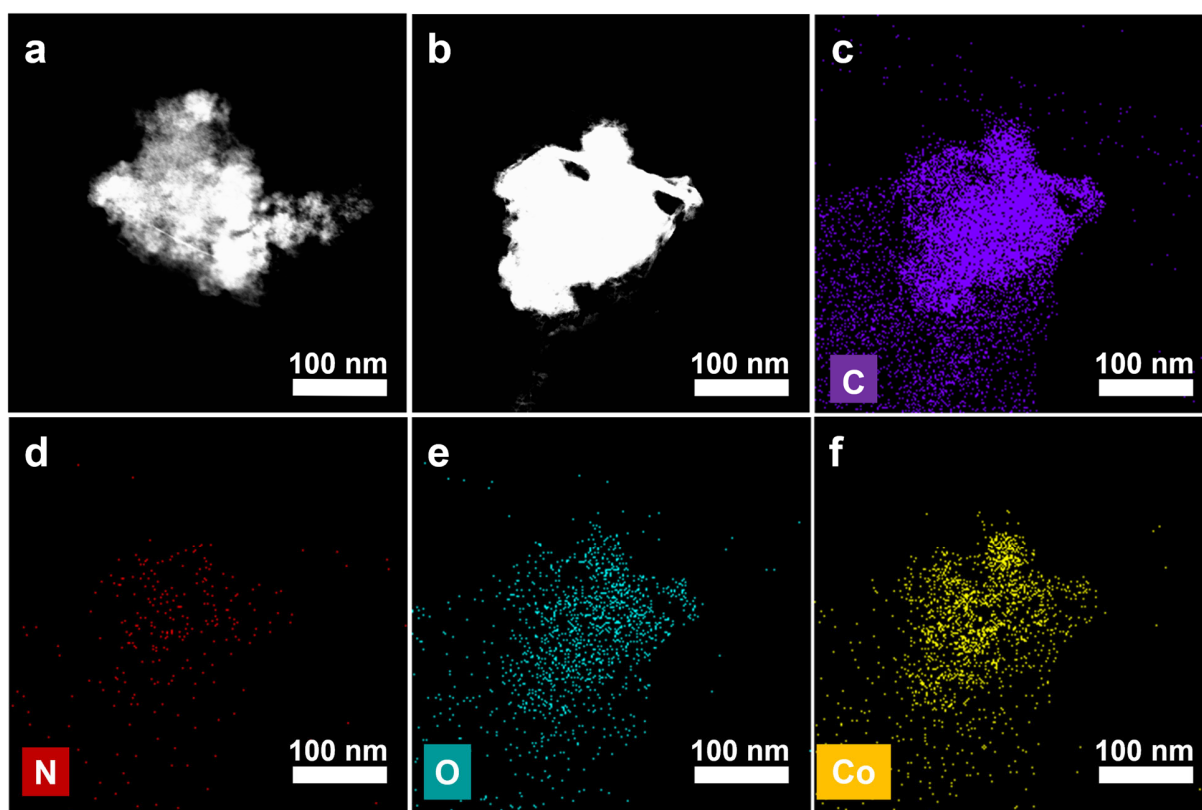


Figure S5. HAADF-STEM images of P1-Co-N₃ in THF (0.01 mg mL⁻¹) on copper mesh grids (a-b), and corresponding EDS mappings of merged elements, C (c), N (d), O (e), Co (f), respectively.

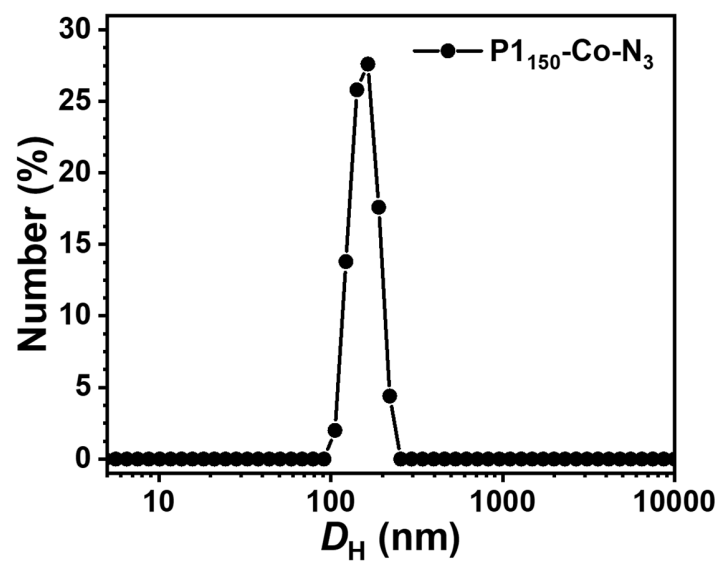


Figure S6. DLS curves of $P1_{150}\text{-Co-N}_3$ (0.05 mg/mL in THF).

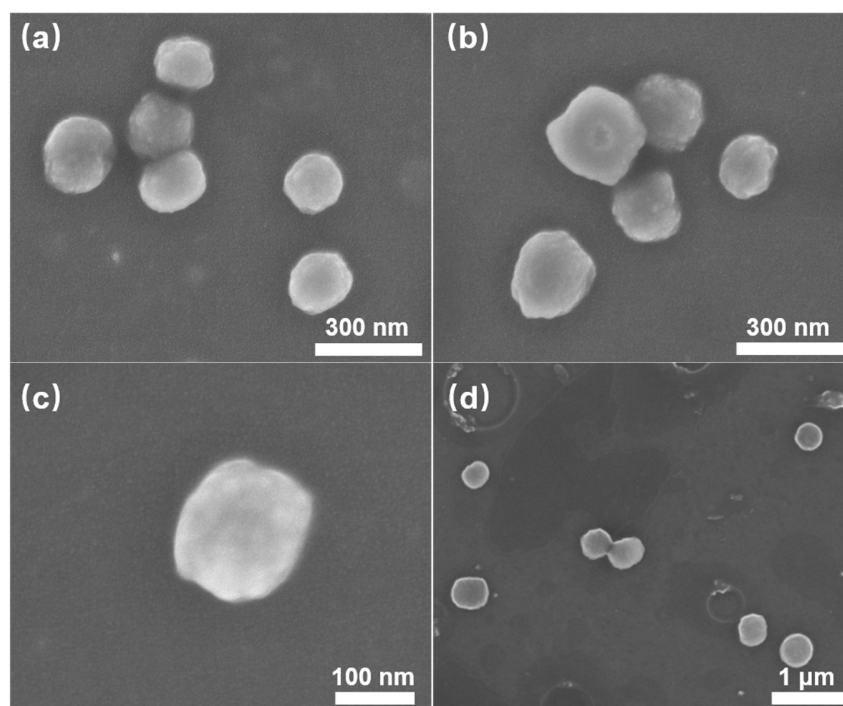


Figure S7. HR-FESEM images of $P1\text{-Co-N}_3$ in THF (0.02 mg/mL) on silicon substrate.

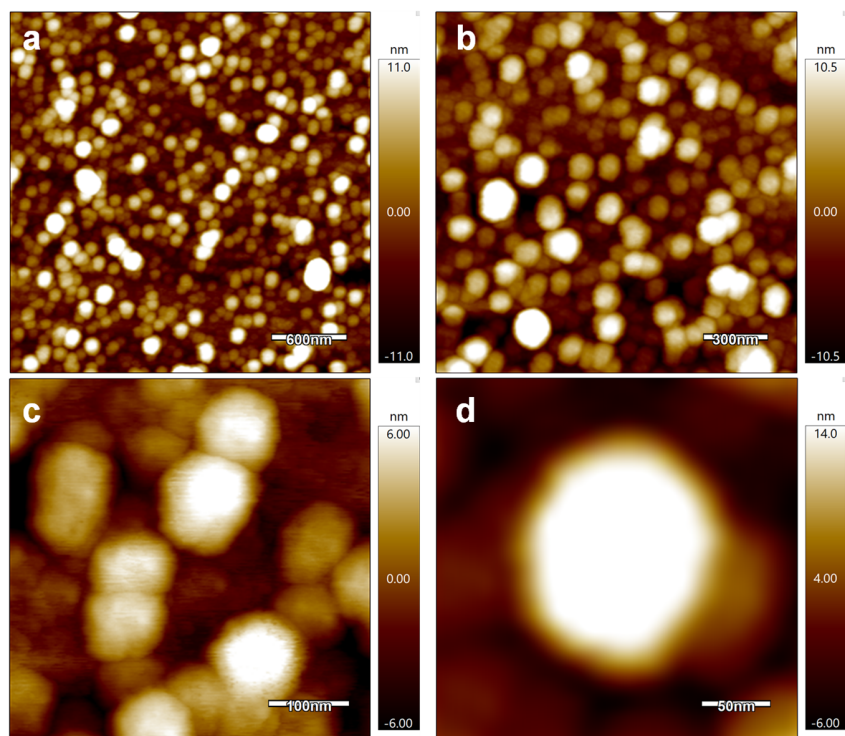


Figure S8. AFM images of **P1-Co-N₃** in THF (0.01 mg/mL) on silicon substrate.

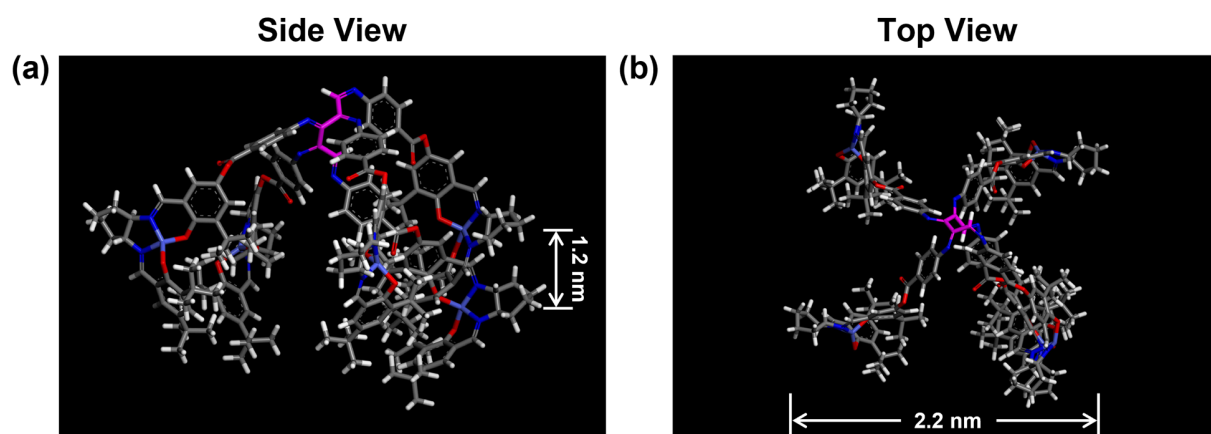


Figure S9. The side (a) and top (b) views of computational-simulated optimal helical conformation for **P1₅-Co**. Molecular modelling and molecular mechanics calculations were performed on Materials Studio software (version 2019, Accelrys Software Inc.) implemented with the COMPASS force field.

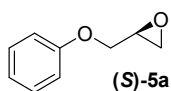
SI3 The Details of Catalytic Studies on Kinetic Resolution of Epoxides

SI3.1 The Studies on Kinetic Resolution of Epoxides

The racemic epoxide substrates **5a**, **5f**, **5g**, **5h**, **5i** were purchased from Aladdin and Sigma-Aldrich Co. Ltd. and were used as received without further purification otherwise denoted. The other racemic epoxide substrates **5b**,^[4] **5c**,^[5] **5d**,^[6] **5e**,^[7] and **5j**^[8] were synthesized according to the literature methods.

The racemic **6a** was synthesized from the reaction of epoxide **5a** and TMSN₃ catalyzed by Er(OTf)₃ according to the literature method.^[9]

The ten racemic azide alcohols **7a-j** were synthesized from the reactions of relative epoxides and sodium azide in the presence of ammonium chloride at 80 °C for 2–10 h according to the literature method.^[10]



(S)-5a.[11] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 19:1; 67 mg, isolated yield: 45%. The *ee* value 99% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 8.167 min (minor), 13.208 min (major). ¹H NMR (400 MHz, CDCl₃): δ 7.30 (dd, *J*₁ = 8.7 Hz, *J*₂ = 7.3 Hz, 2H), 7.02–6.90 (m, 3H), 4.22 (dd, *J*₁ = 11.0 Hz, *J*₂ = 3.2 Hz, 1H), 3.97 (dd, *J*₁ = 11.0 Hz, *J*₂ = 5.6 Hz, 1H), 3.43–3.30 (m, 1H), 2.99–2.86 (m, 1H), 2.77 (dd, *J*₁ = 5.0 Hz, *J*₂ = 2.7 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₉H₁₁O₂⁺: 151.0754; Found: 151.0756.

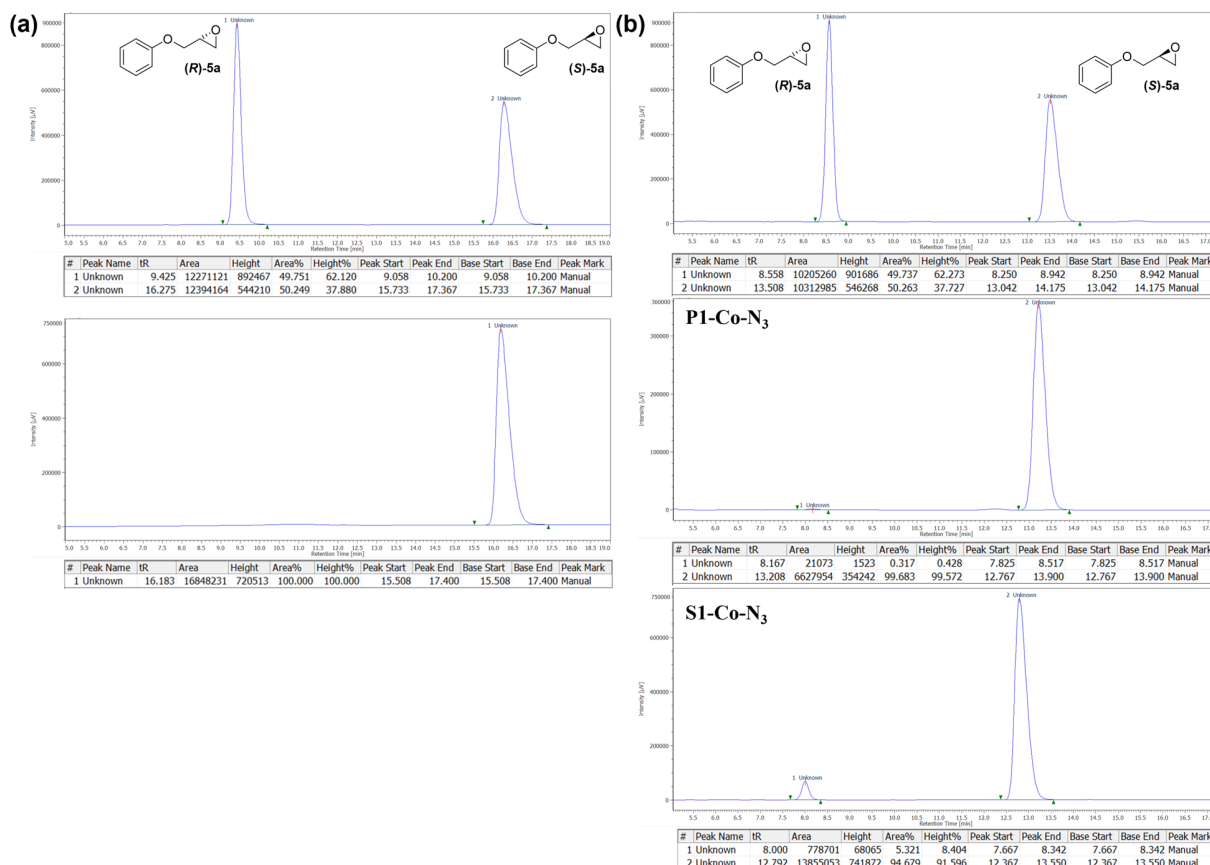
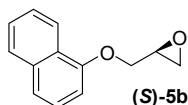


Figure S10. (a) The merged HPLC curves of (±)-5a and the purchased enantiopure (S)-5a, respectively. So, the absolute configuration of the compounds corresponding to each peak in this series epoxide substrates was determined;^[12] (b) The merged HPLC curves of (±)-5a and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-5b.[13] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 19:1; 96 mg, 48% isolated yield. The *ee* 96% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 11.808 min (minor), 14.250 min (major). ¹H NMR (600 MHz, CDCl₃): δ 8.34–8.29 (m, 1H), 7.81 (dd, *J*₁ = 6.5 Hz, *J*₂ = 2.9 Hz, 1H), 7.53–7.48 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.41–7.34 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.41 (dd, *J*₁ = 10.9 Hz, *J*₂ = 3.1 Hz, 1H), 4.15 (dd, *J*₁ = 10.9 Hz, *J*₂ = 5.6 Hz, 1H), 3.51 (ddt, *J*₁ = 5.7 Hz, *J*₂ = 4.1 Hz, *J*₃ = 2.9 Hz, 1H), 2.98 (dd, *J*₁ = 4.9 Hz, *J*₂ = 4.1 Hz, 1H), 2.86 (dd, *J*₁ = 4.9 Hz, *J*₂ = 2.7 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₃H₁₃O₂⁺: 201.0910; Found: 201.0909.

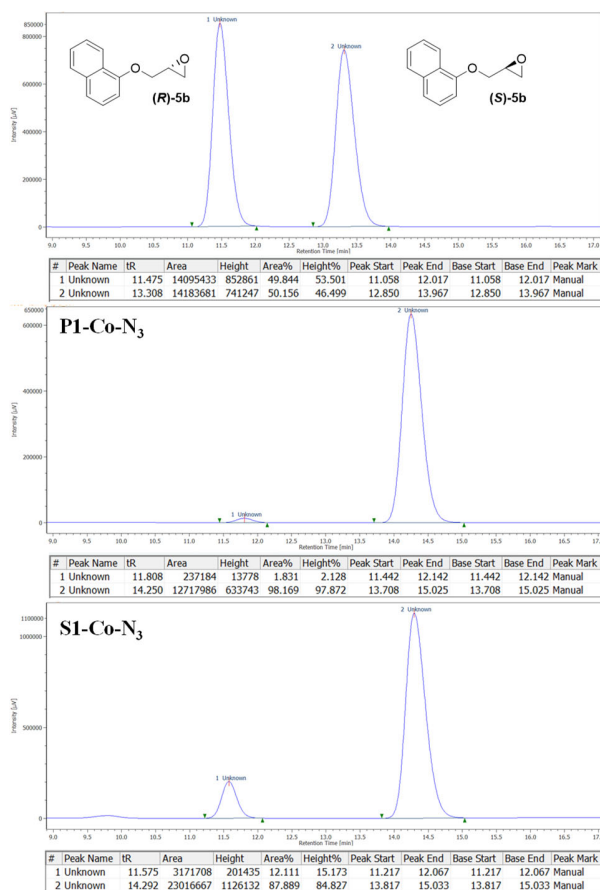
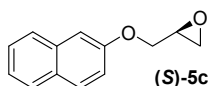


Figure S11. The merged HPLC curves of (±)-**5b** and the resolved ones by **P1-Co-N₃** and **S1-Co-N₃**, respectively.



(S)-5c.[5] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 19:1; 102 mg, 51% isolated yield. The *ee* 86% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 10.525 min (minor), 11.217 min (major). ¹H NMR (600 MHz, CDCl₃): δ 7.82–7.73 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.22 (dd, *J*₁ = 8.9 Hz, *J*₂ = 2.6 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 4.34 (dd, *J*₁ = 10.9 Hz, *J*₂ = 3.1 Hz, 1H), 4.06 (dd, *J*₁ = 10.9 Hz, *J*₂ = 5.7 Hz, 1H), 3.43 (d, *J* = 3.4 Hz, 1H), 2.94 (t, *J* = 4.6 Hz, 1H), 2.81 (dd, *J*₁ = 5.0 Hz, *J*₂ = 2.6 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₃H₁₃O₂⁺: 201.0910; Found: 209.0908.

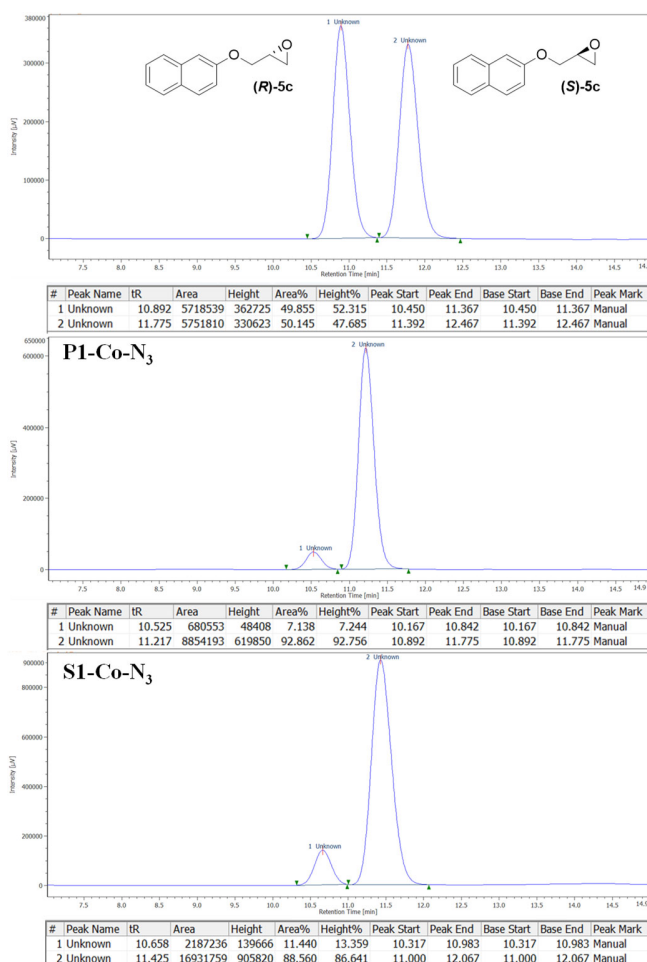
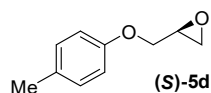


Figure S12. The merged HPLC curves of (±)-5c and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-5d.[11] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 10:1; 73 mg, 45% isolated yield. The *ee* 99% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 7.717 min (minor), 9.533 min (major). ¹H NMR (400 MHz, CDCl₃): δ 7.10 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.19 (dd, *J*₁ = 11.0 Hz, *J*₂ = 3.2 Hz, 1H), 3.93 (dd, *J*₁ = 11.0 Hz, *J*₂ = 5.6 Hz, 1H), 3.35 (dq, *J*₁ = 5.8 Hz, *J*₂ = 2.9 Hz, 1H), 2.90 (t, *J* = 4.5 Hz, 1H), 2.76 (dd, *J*₁ = 4.9 Hz, *J*₂ = 2.6 Hz, 1H), 2.30 (s, 3H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₃O₂⁺: 165.0910; Found: 165.0917.

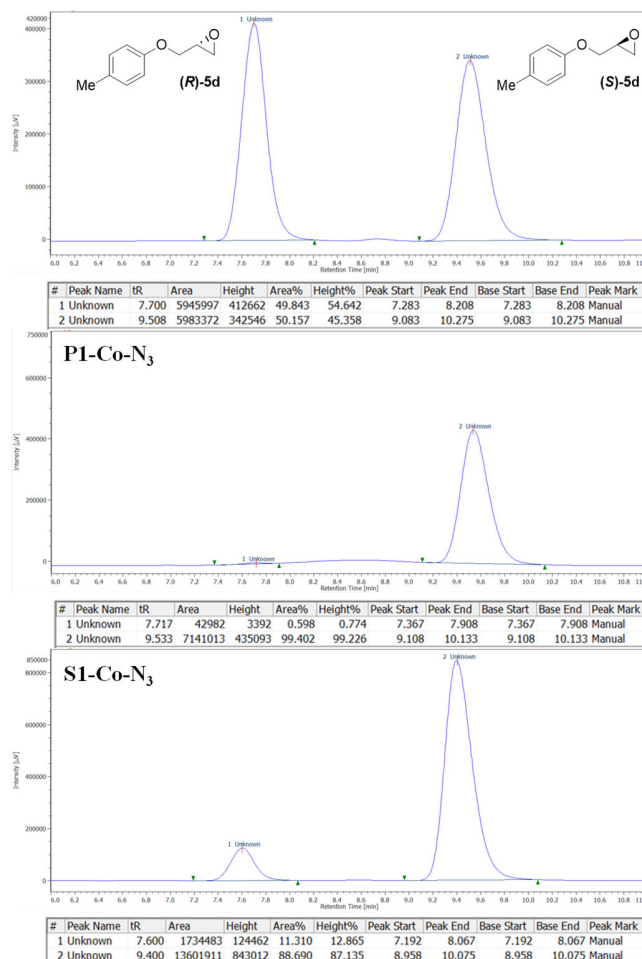
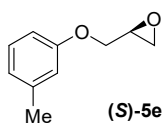


Figure S13. The merged HPLC curves of (±)-5d and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-5e.[13] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 10:1; 113 mg, 69% isolated yield. The *ee* 61% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 9.117 min (minor), 17.725 min (major). ¹H NMR (400 MHz, CDCl₃): δ 7.18 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.78–6.71 (m, 2H), 4.20 (dd, *J*₁ = 11.0 Hz, *J*₂ = 3.2 Hz, 1H), 3.95 (dd, *J*₁ = 11.0 Hz, *J*₂ = 5.6 Hz, 1H), 3.36 (dq, *J*₁ = 5.6 Hz, *J*₂ = 3.1 Hz, 1H), 2.91 (t, *J* = 4.6 Hz, 1H), 2.76 (dd, *J*₁ = 4.9 Hz, *J*₂ = 2.7 Hz, 1H), 2.34 (s, 3H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₃O₂⁺: 165.0910; Found: 165.0914.

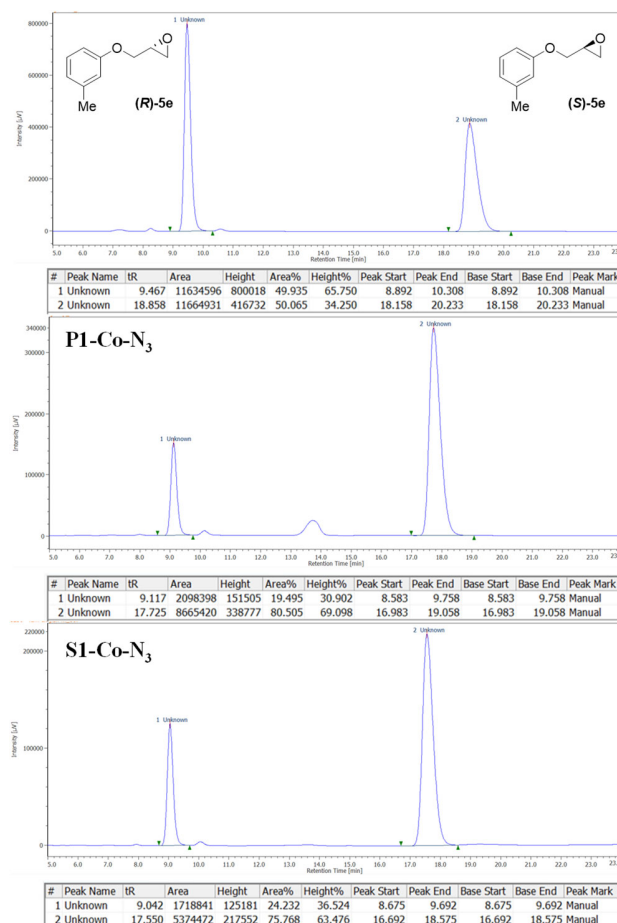
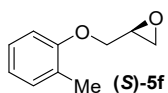


Figure S14. The merged HPLC curves of (±)-5e and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-5f.[13] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 10:1; 92 mg, 56% isolated yield. The *ee* 63% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 6.758 min (minor), 9.142 min (major). ¹H NMR (400 MHz, CDCl₃): δ 7.19–7.12 (m, 2H), 6.90 (t, *J* = 6.8 Hz, 1H), 6.82 (d, *J* = 9.5 Hz, 1H), 4.24 (dd, *J*₁ = 11.1 Hz, *J*₂ = 3.1 Hz, 1H), 3.99 (dd, *J*₁ = 11.1 Hz, *J*₂ = 5.4 Hz, 1H), 3.43–3.34 (m, 1H), 2.95–2.88 (m, 1H), 2.80 (dd, *J*₁ = 5.0 Hz, *J*₂ = 2.7 Hz, 1H), 2.27 (s, 3H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₃O₂⁺: 165.0910; Found: 165.0919.

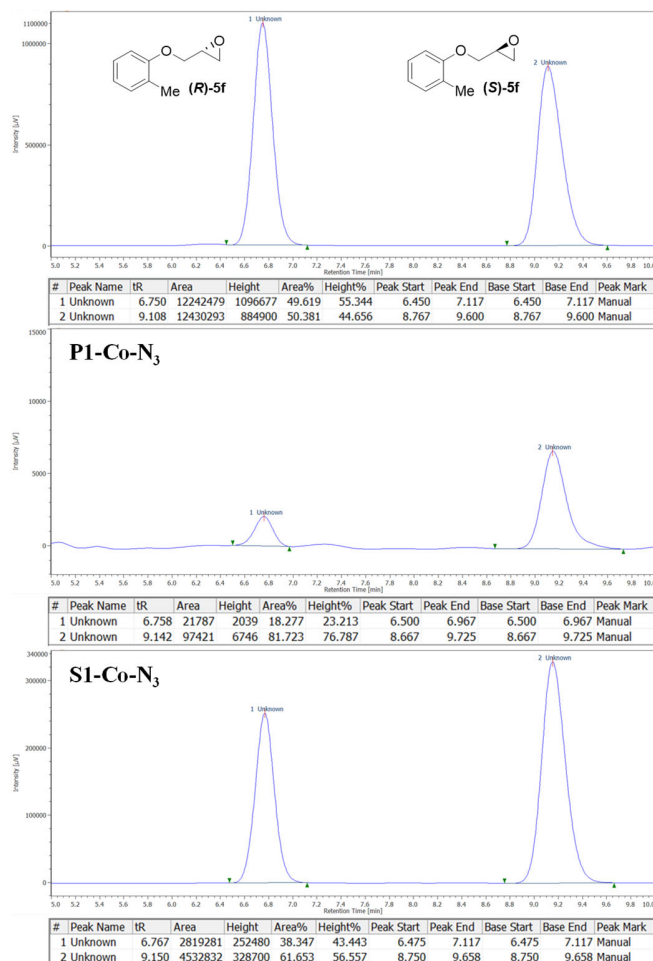
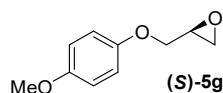


Figure S15. The merged HPLC curves of (±)-5f and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-5g.[11] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 6:1; 88 mg, 49% isolated yield. The *ee* 92% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 215 nm; retention time: 10.225 min (minor), 14.192 min (major). ¹H NMR (400 MHz, CDCl₃): δ 6.90–6.79 (m, 4H), 4.17 (dd, *J*₁ = 11.1 Hz, *J*₂ = 3.2 Hz, 1H), 3.91 (dd, *J*₁ = 11.0 Hz, *J*₂ = 5.6 Hz, 1H), 3.76 (s, 3H), 3.33 (td, *J*₁ = 5.7 Hz, *J*₂ = 4.2 Hz, 1H), 2.92–2.86 (m, 1H), 2.74 (dd, *J*₁ = 5.0 Hz, *J*₂ = 2.7 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₃O₃⁺: 181.0859; Found: 181.0862.

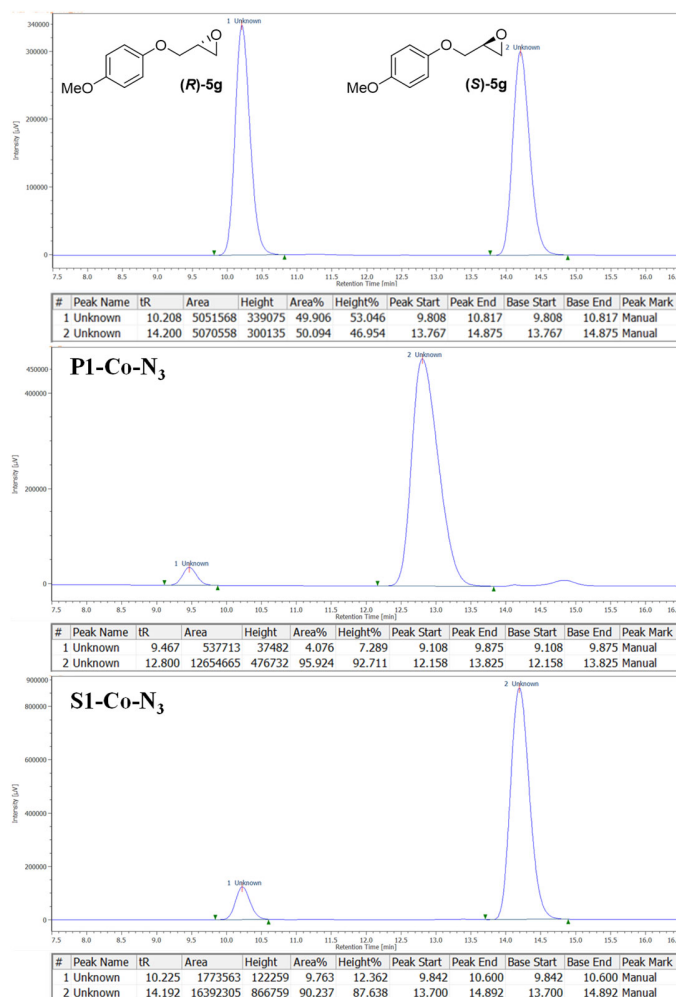
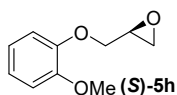


Figure S16. The merged HPLC curves of (±)-5g and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-5h.^[13] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 6:1; 94 mg, 52% isolated yield. The *ee* 89% on HPLC (Chiralcel OD-H column): 70/30 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 215 nm; retention time: 13.600 min (minor), 28.208 min (major). ¹H NMR (400 MHz, CDCl₃): δ 6.99–6.84 (m, 4H), 4.23 (dd, *J*₁ = 11.4 Hz, *J*₂ = 3.5 Hz, 1H), 4.02 (dd, *J*₁ = 11.4 Hz, *J*₂ = 5.6 Hz, 1H), 3.85 (s, 3H), 3.42–3.33 (m, 1H), 2.91–2.84 (m, 1H), 2.72 (dd, *J*₁ = 5.0 Hz, *J*₂ = 2.6 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₃O₃⁺: 181.0859; Found: 181.0866.

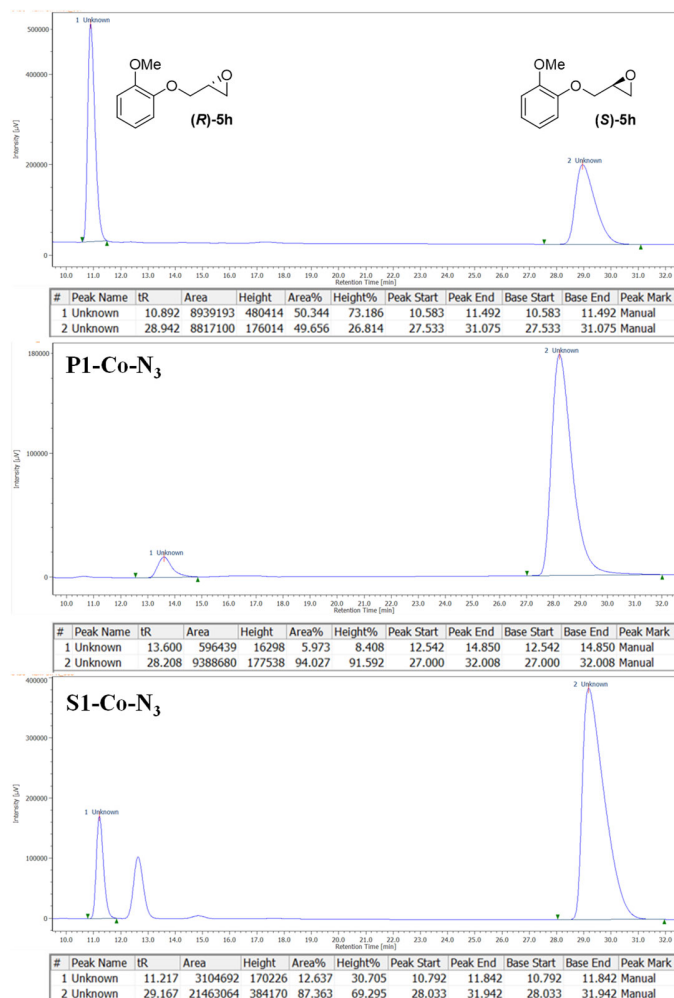
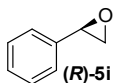


Figure S17. The merged HPLC curves of (±)-5h and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-5i.[14] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 8:1; 67 mg, isolated yield: 56%. The *ee* value 79% on HPLC (Chiralcel AS-H column): 99/1 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 7.408 min (major), 7.942 min (minor). ¹H NMR (400 MHz, CDCl₃): δ 7.38–7.26 (m, 5H), 3.89–3.84 (m, 1H), 3.15 (dd, *J*₁ = 5.6 Hz, *J*₂ = 4.1 Hz, 1H), 2.81 (dd, *J*₁ = 5.5 Hz, *J*₂ = 2.6 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₈H₉O⁺: 121.0575; Found: 121.0577.

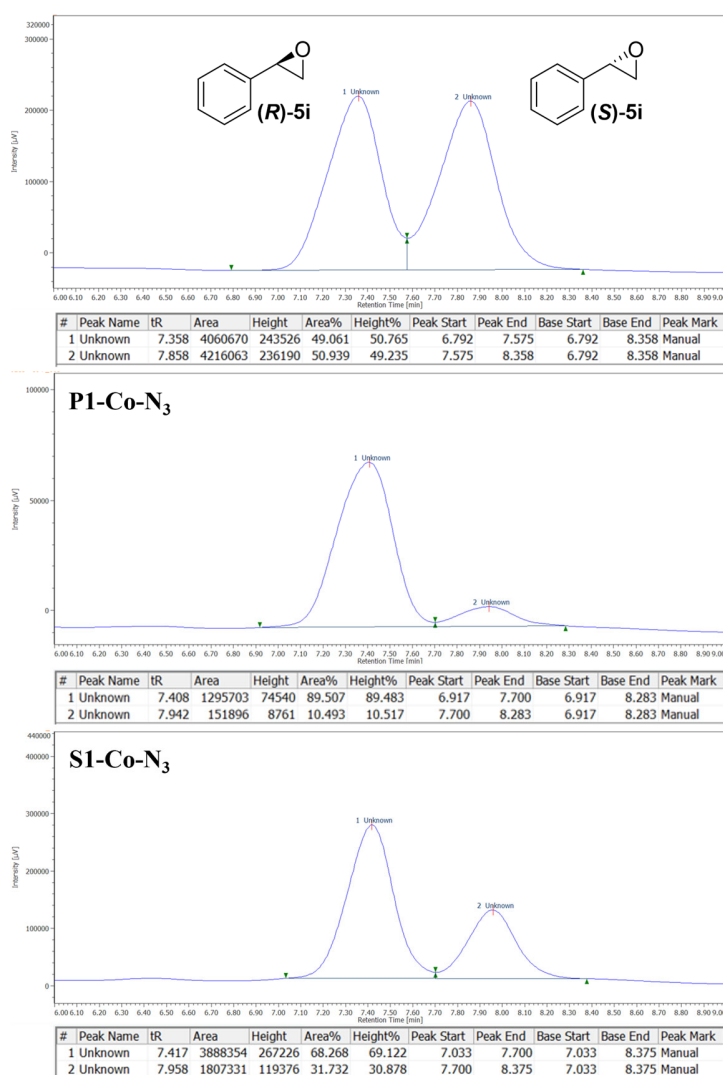
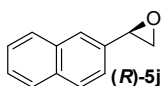


Figure S18. The merged HPLC curves of (±)-5i and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-5j.^[14] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 8:1; 103 mg, isolated yield: 61%. The *ee* value 56% on HPLC (Chiralcel OZ-H column): 99/1 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 7.808 min (major), 8.933 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.86–7.78 (m, 4H), 7.53–7.44 (m, 2H), 7.33 (dd, *J*₁ = 8.5 Hz, *J*₂ = 1.8 Hz, 1H), 4.04 (dd, *J*₁ = 4.1 Hz, *J*₂ = 2.5 Hz, 1H), 3.23 (dd, *J*₁ = 5.4 Hz, *J*₂ = 4.1 Hz, 1H), 2.91 (dd, *J*₁ = 5.4 Hz, *J*₂ = 2.6 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₂H₁₁O⁺: 171.0732; Found: 171.0738.

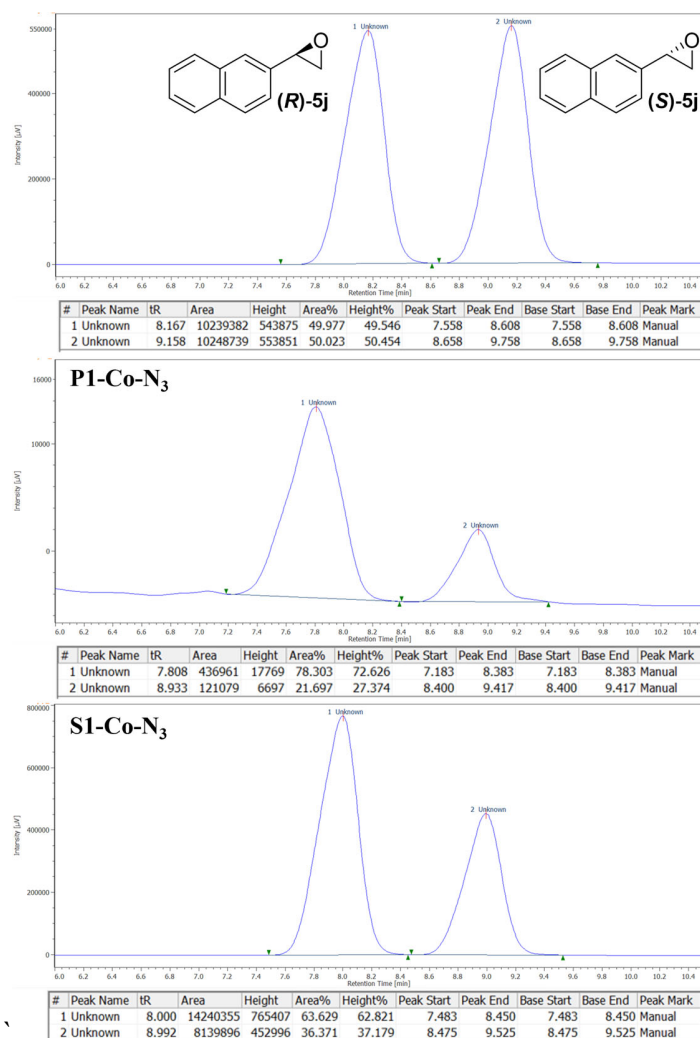
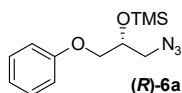


Figure S19. The merged HPLC curves of (±)-5i and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-6a.[15] Colorless oil, purification conditions: SiO₂, petroleum ether/ethyl acetate, 97:3; 97 mg, 47% isolated yield. The *ee* 99% on HPLC (Chiralcel OD-H column): 95/5 *n*-hexane/*i*-PrOH; flow rate 0.8 mL/min; detection wavelength: 220 nm; retention time: 5.375 min (minor), 6.450 min (major). ¹H NMR (600 MHz, CDCl₃): δ 7.29 (dd, *J*₁ = 8.7 Hz, *J*₂ = 7.4 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.89 (dd, *J*₁ = 8.8 Hz, *J*₂ = 1.0 Hz, 2H), 4.18 (qd, *J*₁ = 6.0 Hz, *J*₂ = 3.8 Hz, 1H), 3.93 (d, *J* = 5.9 Hz, 2H), 3.42 (dd, *J*₁ = 12.6 Hz, *J*₂ = 3.8 Hz, 1H), 3.36 (dd, *J*₁ = 12.6 Hz, *J*₂ = 6.1 Hz, 1H), 0.21 (s, 9H). HRMS (ESI-FT): Calcd. For [M – H][–], C₁₂H₁₈N₃O₂Si[–]: 264.1162. Found: 264.1151.

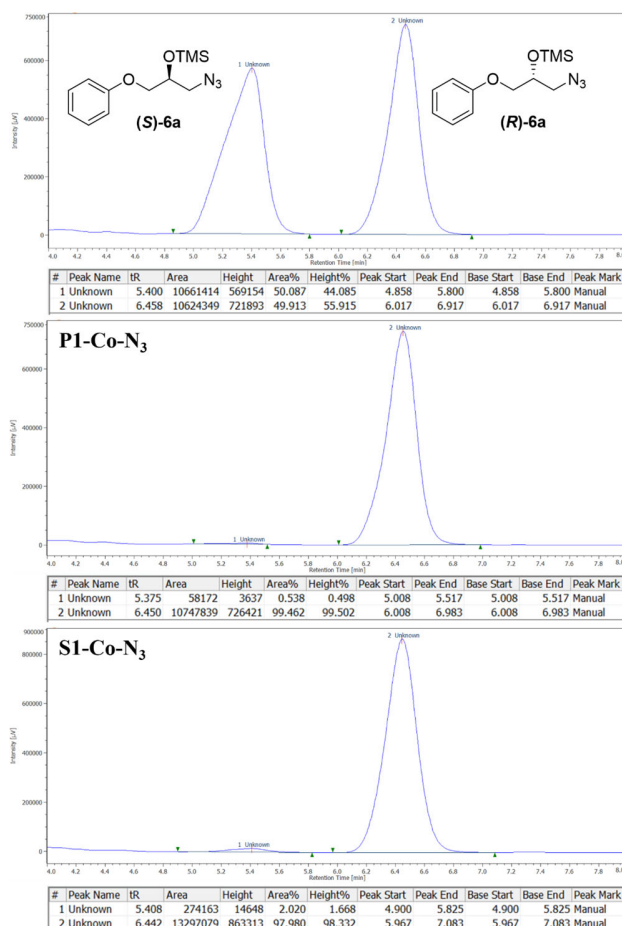
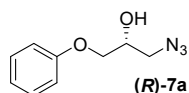


Figure S20. The merged HPLC curves of (±)-6a and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7a.[16] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 9:1; 63 mg, 42% isolated yield. The *ee* 99% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 12.875 min (major), 26.508 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.34–7.27 (m, 2H), 6.99 (td, *J*₁ = 7.4 Hz, *J*₂ = 1.1 Hz, 1H), 6.95–6.89 (m, 2H), 4.17 (dt, *J*₁ = 9.7 Hz, *J*₂ = 4.9 Hz, 1H), 4.06–3.98 (m, 2H), 3.53 (qd, *J*₁ = 13.1 Hz, *J*₂ = 5.4 Hz, 2H), 2.50 (d, *J* = 4.1 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₉H₁₂N₃O₂⁺: 193.0924; Found: 193.0926.

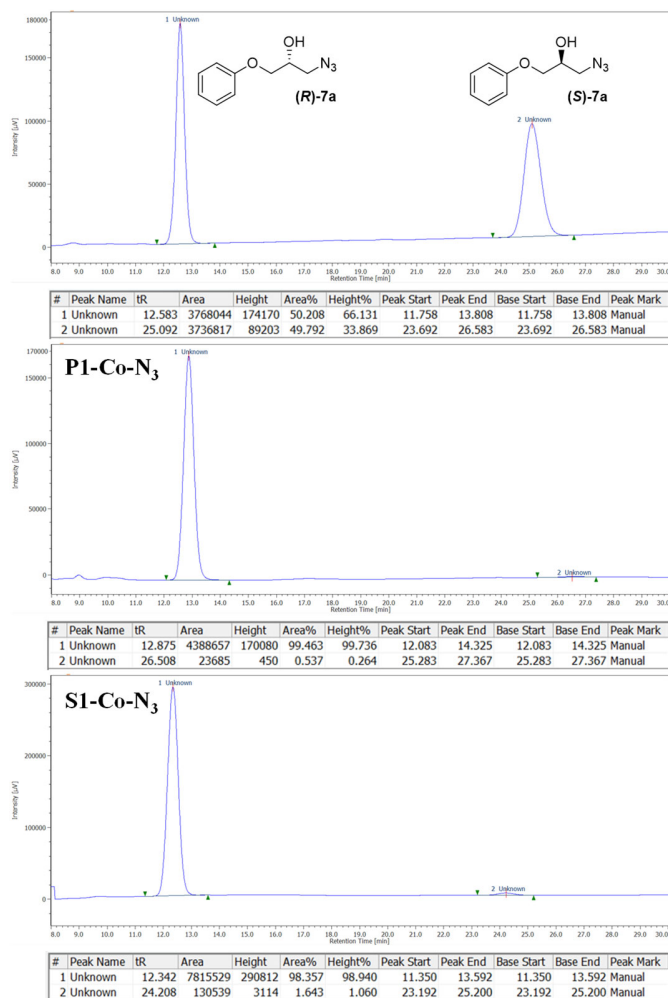
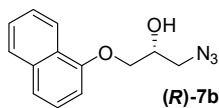


Figure S21. The merged HPLC curves of (±)-7a and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7b.[16] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 9:1; 105 mg, 43% isolated yield. The *ee* 97% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 31.125 min (major), 33.525 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 8.21 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.3 Hz, 1H), 7.82 (dd, *J*₁ = 7.0 Hz, *J*₂ = 2.5 Hz, 1H), 7.54–7.45 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.34 (dq, *J*₁ = 10.6, *J*₂ = 5.3 Hz, 1H), 4.25–4.17 (m, 2H), 3.70–3.59 (m, 2H), 2.53 (d, *J* = 5.3 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₃H₁₄N₃O₂⁺: 244.1081; Found: 244.1078.

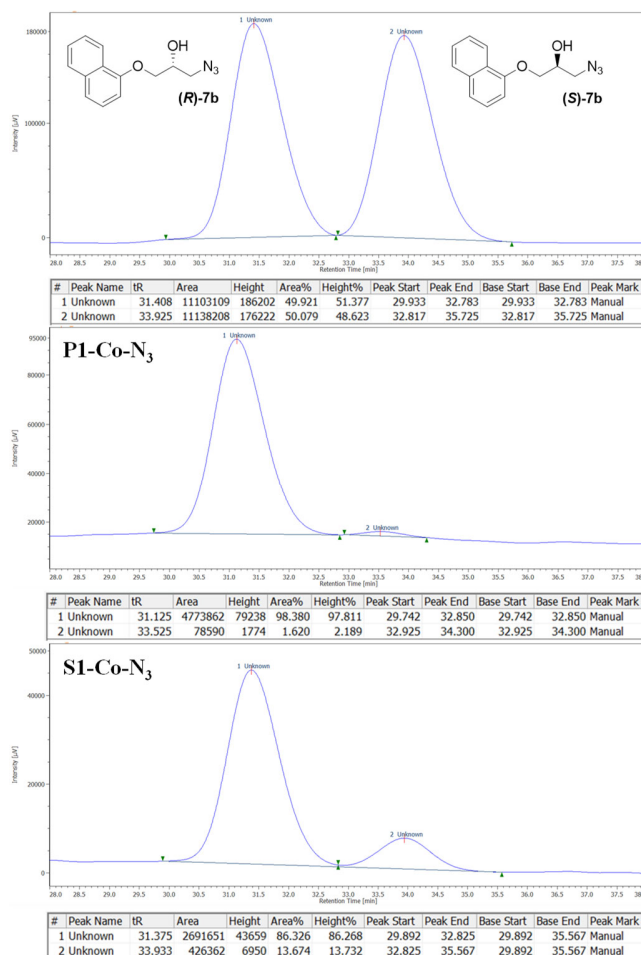
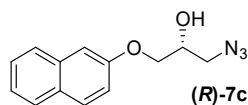


Figure S22. The merged HPLC curves of (±)-7b and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7c.[17] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 9:1; 102 mg, 42% isolated yield. The *ee* 94% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm; retention time: 20.367 min (major), 25.408 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.80–7.71 (m, 3H), 7.49–7.42 (m, 1H), 7.40–7.33 (m, 1H), 7.19–7.14 (m, 2H), 4.24 (dq, *J*₁ = 9.7 Hz, *J*₂ = 5.0 Hz, 1H), 4.18–4.11 (m, 2H), 3.58 (qd, *J*₁ = 12.7 Hz, *J*₂ = 5.3 Hz, 2H), 2.53 (d, *J* = 4.7 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₃H₁₄N₃O₂⁺: 244.1081; Found: 244.1080.

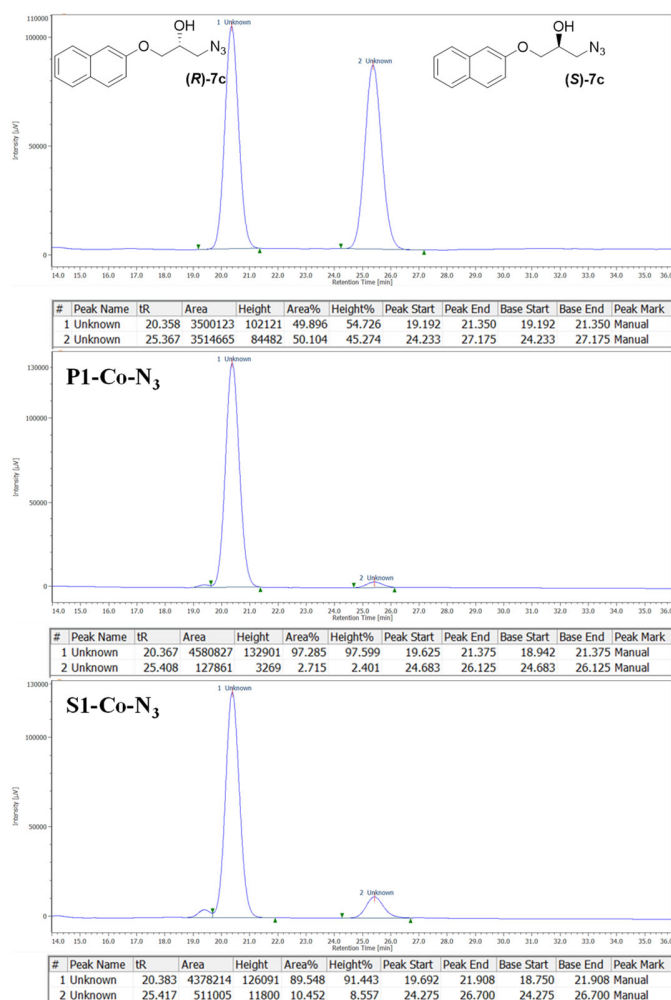
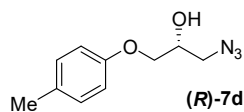


Figure S23. The merged HPLC curves of (±)-7c and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7d.[18] Colorless oil, purification conditions: SiO₂, petroleum ether/ethyl acetate, 8:1; 72 mg, 44% isolated yield. The *ee* 97% on HPLC (Chiralcel OD-H column): 80/20 *n*-hexane/*i*-PrOH; flow rate 0.8 mL/min; detection wavelength: 220 nm; retention time: 17.117 min (major), 18.958 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.10 (d, *J* = 8.3 Hz, 2H), 6.88–6.76 (m, 2H), 4.18–4.13 (m, 1H), 4.02–3.95 (m, 2H), 3.52 (qd, *J*₁ = 12.6 Hz, *J*₂ = 5.4 Hz, 2H), 2.58 (d, *J* = 4.5 Hz, 1H), 2.30 (s, 3H). MS (ESI): Calcd. For [M + H]⁺, C₁₀H₁₄N₃O₂⁺: 208.11; Found: 208.11.

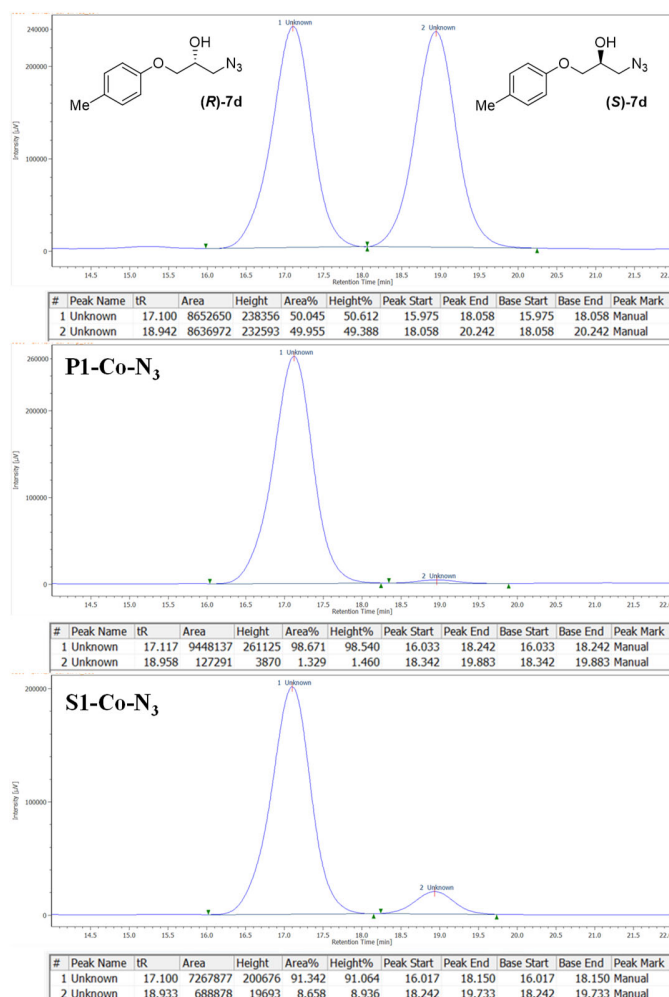
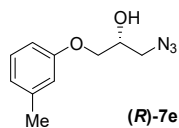


Figure S24. The merged HPLC curves of (±)-7d and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7e.[18] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 8:1; 69 mg, 42% isolated yield. The *ee* 97% on HPLC (Chiralcel OD-H column): 80/20 *n*-hexane/*i*-PrOH; flow rate 0.8 mL/min; detection wavelength: 220 nm; retention time: 13.617 min (major), 15.192 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.19 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.76–6.70 (m, 2H), 4.17 (h, *J* = 5.2 Hz, 1H), 4.04–3.98 (m, 2H), 3.52 (qd, *J*₁ = 12.7 Hz, *J*₂ = 5.4 Hz, 2H), 2.60 (d, *J* = 5.0 Hz, 1H), 2.34 (s, 3H). MS (ESI): Calcd. For [M + H]⁺, C₁₀H₁₄N₃O₂⁺: 208.11; Found: 208.11.

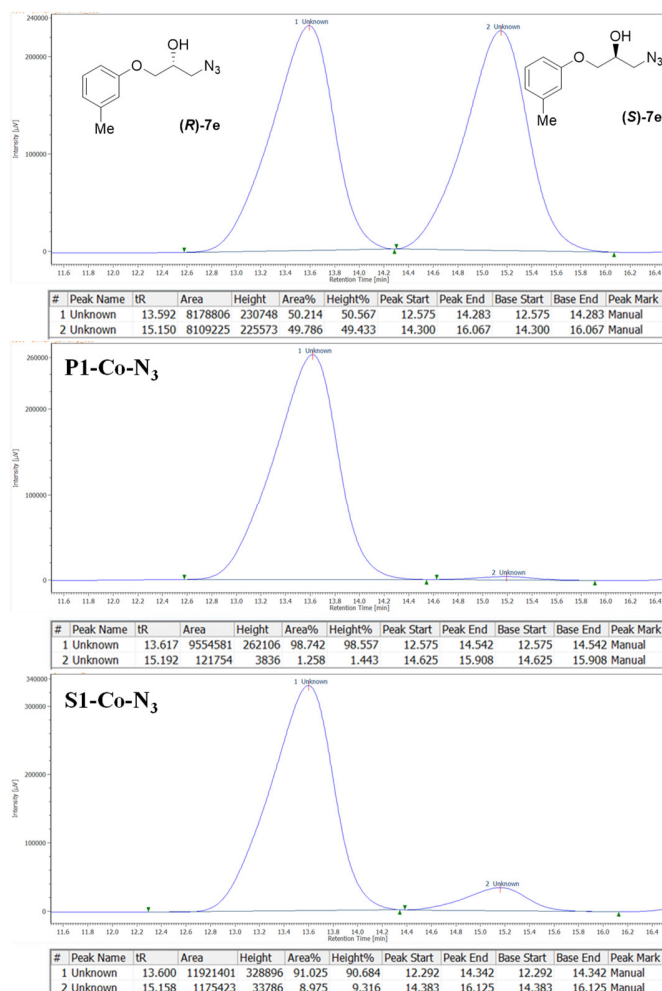
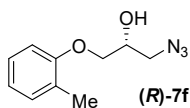


Figure S25. The merged HPLC curves of (±)-7e and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7f.[18] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 8:1; 66 mg, 32% isolated yield. The *ee* 96% on HPLC (Chiralcel OD-H column): 80/20 *n*-hexane/*i*-PrOH; flow rate 0.8 mL/min; detection wavelength: 220 nm; retention time: 6.592 min (major), 7.342 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.20 – 7.15 (m, 2H), 6.92 (dd, *J*₁ = 8.1 Hz, *J*₂ = 6.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.20 (h, *J* = 5.1 Hz, 1H), 4.03 (d, *J* = 4.2 Hz, 2H), 3.55 (qd, *J*₁ = 12.6 Hz, *J*₂ = 6.0 Hz, 2H), 2.64 (d, *J* = 5.1 Hz, 1H), 2.25 (s, 3H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₄N₃O₂⁺: 208.1081; Found: 208.1084.

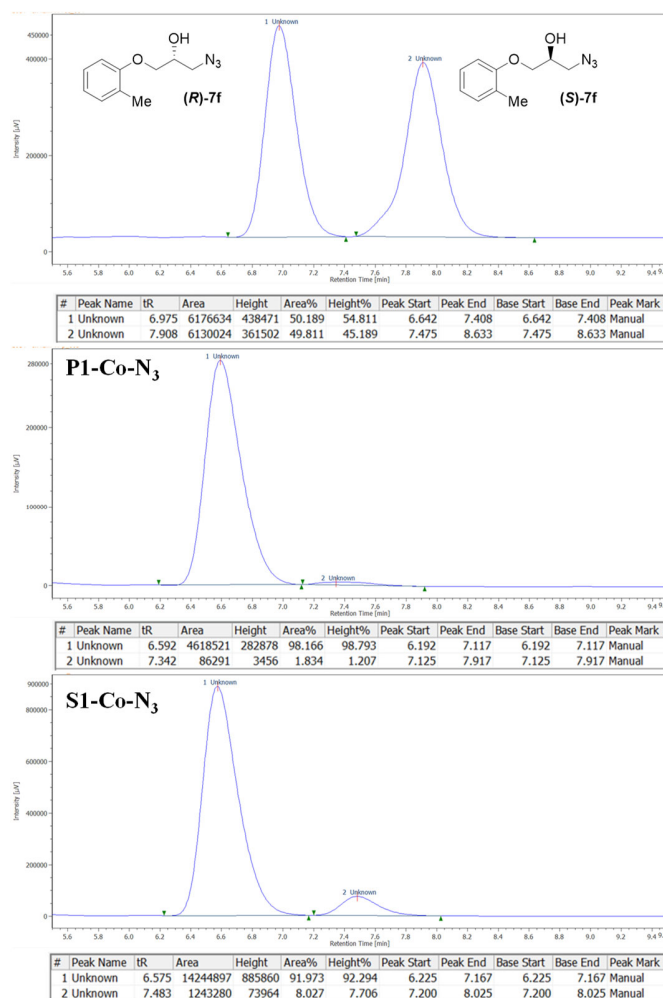
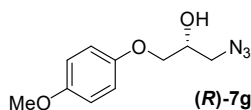


Figure S26. The merged HPLC curves of (±)-7f and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7g.[19] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 4:1; 82 mg, 37% isolated yield. The *ee* 97% on HPLC (Chiralcel OD-H column): 85/15 *n*-hexane/*i*-PrOH; flow rate 0.5 mL/min; detection wavelength: 220 nm; retention time: 21.125 min (major), 35.008 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 6.87–6.81 (m, 4H), 4.14 (h, *J* = 5.1 Hz, 1H), 4.00–3.92 (m, 2H), 3.77 (s, 3H), 3.50 (qd, *J*₁ = 12.6 Hz, *J*₂ = 5.4 Hz, 2H), 2.64 (d, *J* = 5.1 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₄N₃O₃⁺: 224.1030; Found: 224.1031.

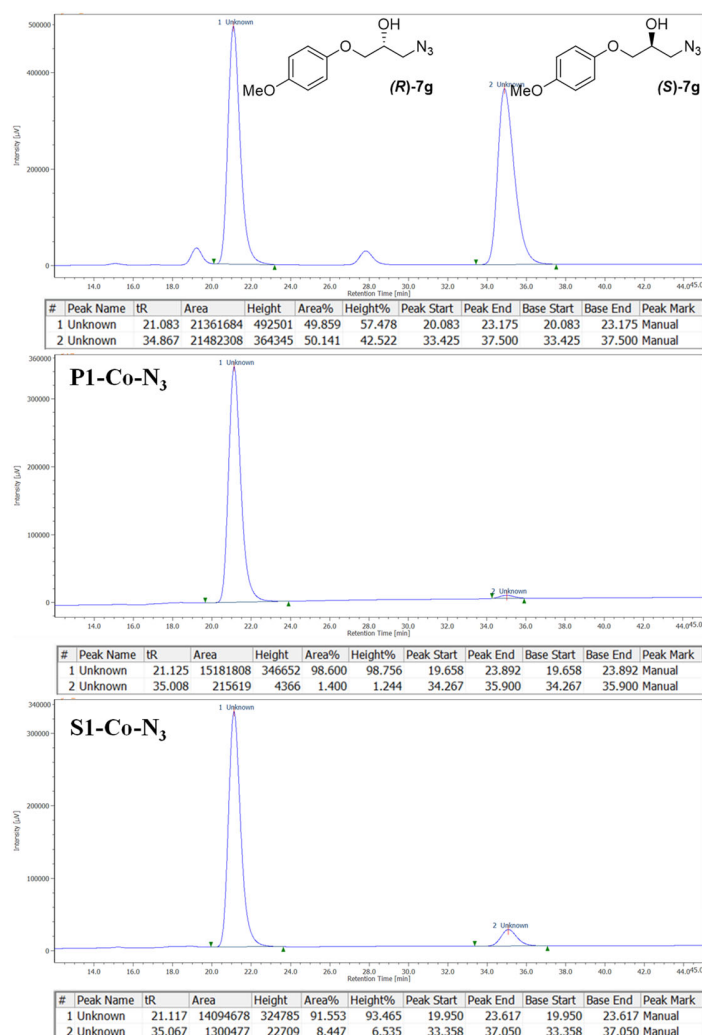
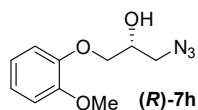


Figure S27. The merged HPLC curves of (±)-7g and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(R)-7h.[20] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 4:1; 77 mg, 35% isolated yield. The *ee* 90% on HPLC (Chiralcel OD-H column): 85/15 *n*-hexane/*i*-PrOH; flow rate 0.5 mL/min; detection wavelength: 220 nm; retention time: 21.817 min (major), 49.533 min (minor). ¹H NMR (600 MHz, CDCl₃): δ 7.03–6.94 (m, 2H), 6.93–6.88 (m, 2H), 4.16 (d, *J* = 6.0 Hz, 1H), 4.10–4.00 (m, 2H), 3.87 (d, *J* = 1.9 Hz, 3H), 3.55–3.44 (m, 2H), 3.21 (d, *J* = 4.8 Hz, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₀H₁₄N₃O₃⁺: 224.1030; Found: 224.1032.

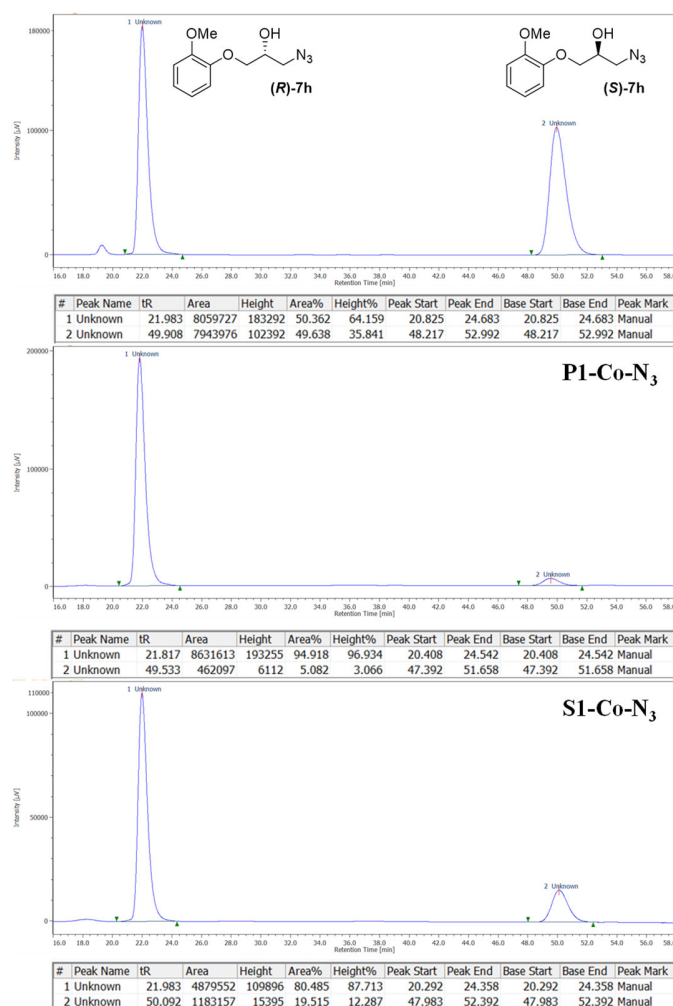
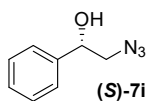


Figure S28. The merged HPLC curves of (±)-7h and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-7i.[21] Colorless oil; purification conditions: SiO₂, petroleum ether/ethyl acetate, 10:1; 63 mg, 39% isolated yield. The *ee* 99% on HPLC (Chiralcel OD-H column): 95/5 *n*-hexane/*i*-PrOH; flow rate 0.5 mL/min; detection wavelength: 210 nm; retention time: 33.108 min (minor), 35.908 min (major). ¹H NMR (600 MHz, CDCl₃): δ 7.38 (d, *J* = 4.3 Hz, 4H), 7.33 (q, *J* = 4.5 Hz, 1H), 4.89 (dd, *J*₁ = 8.3 Hz, *J*₂ = 3.8 Hz, 1H), 3.53–3.42 (m, 2H), 2.35 (s, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₈H₁₀N₃O⁺: 164.0818; Found: 164.0820.

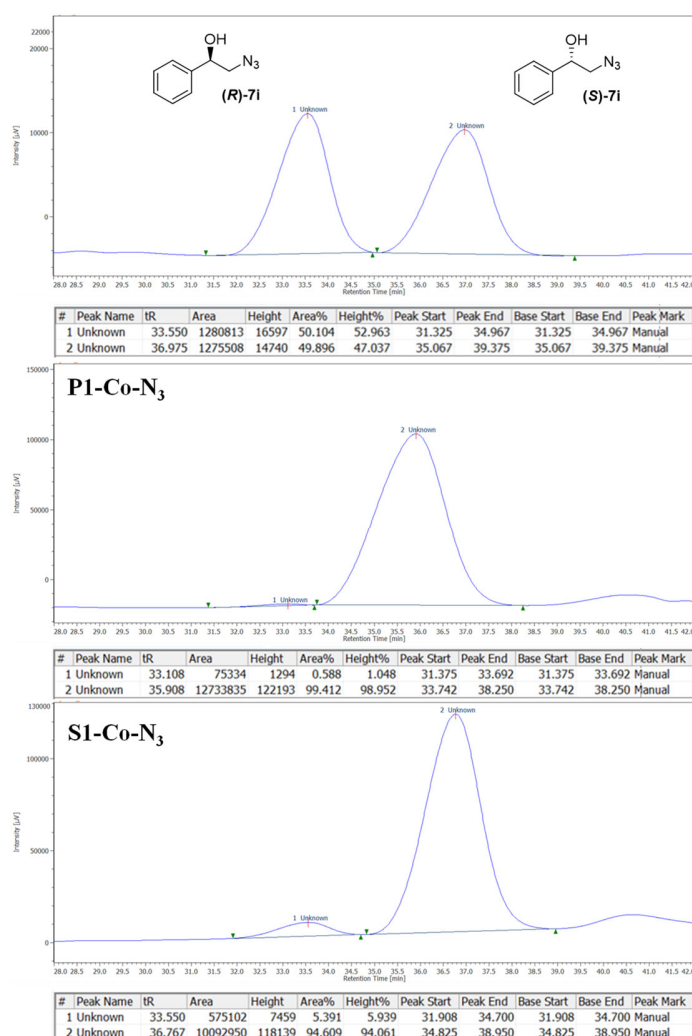
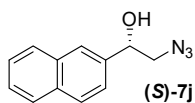


Figure S29. The merged HPLC curves of (±)-7i and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.



(S)-7j.[22] White solid; purification conditions: SiO₂, petroleum ether/ethyl acetate, 10:1; 78 mg, 37% isolated yield. The *ee* 96% on HPLC (Chiralcel OD-H column): 90/10 *n*-hexane/*i*-PrOH; flow rate 0.5 mL/min; detection wavelength: 220 nm; retention time: 20.817 min (minor), 24.908 min (major). ¹H NMR (600 MHz, CDCl₃): δ 7.93–7.80 (m, 4H), 7.56–7.44 (m, 3H), 5.06 (dt, *J*₁ = 7.3 Hz, *J*₂ = 3.3 Hz, 1H), 3.64–3.49 (m, 2H), 2.46 (s, 1H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₃H₁₄N₃O₂⁺: 214.0975; Found: 214.0977.

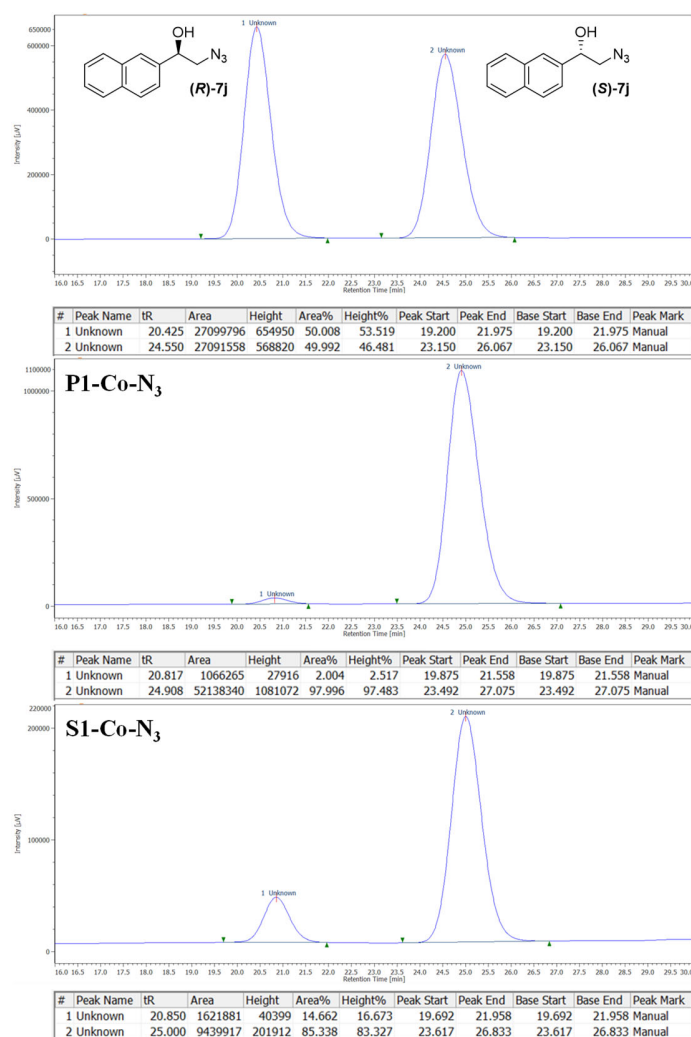


Figure S30. The merged HPLC curves of (±)-7j and the resolved ones by P1-Co-N₃ and S1-Co-N₃, respectively.

SI3.2 The Evaluation of Catalytic Activity and Recycle Ability

Recycle Experiment

In a 10 mL Schlenk flask, (\pm)-**5a** (150 mg, 1.0 mmol) and **P1-Co-N₃** (4.4 mg, 0.006 mmol, 0.6 mol %) were dissolved in dry MeO'Bu (0.4 mL, 2.5 M) under an N₂ atmosphere. The solution was stirred at 0 °C for 0.5 h. After TMSN₃ (66 μ L, 0.5 mmol, 0.5 eq) was added, the resulting solution was further stirred at 0 °C for 12 h. Then the reaction solution was concentrated, precipitated with *n*-hexane (2 mL). Polymer-supported catalyst **P1-Co-N₃** was separated by centrifugation and washed with small amount of methanol for three times and subjected to the next catalytic cycle. The combined supernatant was concentrated, and the residue was purified by rapid column chromatography (SiO₂, petroleum ether/ethyl acetate, 19:1) to determine the isolated yields and the *ee* values of (**S**)-**5a** and (**R**)-**6a**. In our treatment, the catalytic processes were consecutively repeated for 8 times.

Table S2. Recycle Experiment Results of **5a** to **6a**^a.

Recycle time	Yield of (S)- 5a (%) ^b	<i>ee</i> of (S)- 5a ^c	Yield of (R)- 6a (%) ^b	<i>ee</i> of (R)- 6a ^c
1	50	99	47	>99
2	51	99	45	99
3	52	99	44	99
4	52	99	44	99
5	53	99	42	98
6	53	99	42	98
7	54	98	40	98
8	54	98	40	98

^a Reaction conditions: [(\pm)-**5a**] = 2.50 M, [TMSN₃] = 1.25 M. ^b Isolated yield according to 50% theoretical yield. ^c The *ee*% value was determined by chiral HPLC column.

Experiments on the relationship between *M_n*-*ee* and *M_n*-yield

In five 10 mL Schlenk flask, (\pm)-**5a** (150 mg, 1.0 mmol), **P1-Co-N₃** with different *M_n*s (*M_n* = 35.7, 70.9, 143.3, 199.6, and 289.7 kDa, 4.4 mg, 0.006 mmol, 0.6 mol %) were dissolved in dry MeO'Bu (0.4 mL, 2.5 M) under an N₂ atmosphere. The solution was stirred at 0 °C for 0.5 h and subsequently TMSN₃ (66 μ L, 0.5 mmol, 0.5 eq) was added, then it was further stirred at 0 °C for 12 h. Next, the reaction solution was concentrated. The residue was subjected to rapid column chromatography to afford pure (**S**)-**5a** and (**R**)-**6a**.

Table S3. *M_n*-*ee* and *M_n*-yield Relationship Experiment Results of **5a** to **6a**^a.

Entry	M_n (kDa)	Yield of (R)- 5a (%) ^b	$ee_{(S)-5a}$ ^c	Yield of (S)- 6a (%) ^b	$ee_{(R)-6a}$ ^c
1	35.7	60	26	36	33
2	70.9	57	46	40	51
3	143.3	54	75	44	78
4	199.6	52	99	47	99.5
5	289.7	52	98	46	99

^aReaction conditions: [(±)-**5a**] = 2.50 M, [TMSN₃] = 1.25 M. ^bThe isolated yield was determined according to the theoretical yield of one enantiomer. ^cThe ee values were determined by chiral HPLC column.

Catalyst Loading Experiment

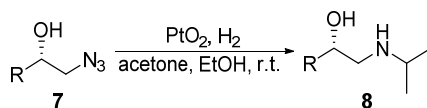
In five 10 mL Schlenk flasks, to dry MeO^tBu (0.4 mL, 2.5 M) were added (*rac*)-**5a** (150 mg, 1.0 mmol) and **P1-Co-N₃**/**S1-Co-N₃** with different catalyst loadings (0.1, 0.3, 0.6, 0.8, and 1.0 mol %) under an N₂ atmosphere. The solution was stirred at 0 °C for 0.5 h and TMSN₃ (66 μL, 0.5 mmol, 0.5 eq) was added, then it was further stirred at 0 °C for 12 h. Next, the reaction solution was concentrated, and the residue was subjected to rapid column chromatography (SiO₂, petroleum ether/ethyl acetate, 19:1) to afford pure (**S**)-**5a** and (**R**)-**6a**.

Table S4. Summary of Catalyst Loading Experiment of **5a** to **6a**^a.

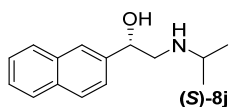
Entry	Cat. loading (mol %)	TON by P1-Co-N₃ ^b	TON by S1-Co-N₃ ^b	$ee_{(S)-6a}$ by P1-Co-N₃ ^c	$ee_{(S)-6a}$ by S1-Co-N₃ ^c
1	0.1	260	50	60	51
2	0.3	280	62	78	68
3	0.6	305	76	99.5	91
4	0.8	304	82	99.5	93
5	1.0	304	85	99.5	94

^aReaction conditions: [(*rac*)-**5a**] = 2.50 M, [TMSN₃] = 1.25 M. ^bThe TON values were calculated according to TMSN₃. ^cThe ee values were determined by chiral HPLC column.

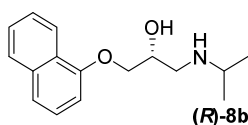
SI3.3 The Application to Pharmaceutical Synthesis.



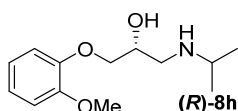
General Procedure for the synthesis of β -amino alcohol derivatives.[23] To a solution of **7** (8.0 mmol) and acetone (12.0 mmol) in ethanol (100 mL) was added PtO₂ powder (0.88 g, 4.0 mmol). The mixture was stirred vigorously, and H₂ was continuously purged in *via* a balloon at ambient temperature for 20 h. Subsequently the solid was filtered off through celite and washed with small amount of ethanol for three times. Finally, the combined filtrate was concentrated in vacuo to give the product.



(S)-8j ((S)-pronethalol).[23] White solid, 1.20 g, 71% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.93–7.78 (m, 4H), 7.50–7.45 (m, 3H), 4.91 (dd, $J_1 = 8.8$ Hz, $J_2 = 3.7$ Hz, 1H), 3.07 (dd, $J_1 = 12.1$ Hz, $J_2 = 3.7$ Hz, 1H), 2.93 (h, $J = 6.2$ Hz, 1H), 2.79 (dd, $J_1 = 12.1$ Hz, $J_2 = 8.8$ Hz, 1H), 2.62 (s, 1H), 1.28 (d, $J = 23.4$ Hz, 1H), 1.13 (dd, $J_1 = 6.3$ Hz, $J_2 = 3.5$ Hz, 6H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₅H₂₀NO⁺: 230.1539. Found: 230.1540.



(R)-8b ((R)-propranolol).[24] White solid, 1.32 g, 68% isolated yield. ¹H NMR (600 MHz, CDCl₃): δ 8.31–8.22 (m, 1H), 7.81 (dd, $J_1 = 5.9$ Hz, $J_2 = 2.2$ Hz, 1H), 7.59–7.42 (m, 3H), 7.37 (t, $J = 7.9$ Hz, 1H), 6.82 (d, $J = 8.6$ Hz, 1H), 4.26–4.08 (m, 3H), 3.11–2.72 (m, 5H), 1.12 (d, $J = 6.3$ Hz, 6H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₆H₂₂NO₂⁺: 260.1648. Found: 260.1651.



(R)-8h.[25] White solid, 1.22 g, 74% isolated yield. ¹H NMR (600 MHz, CDCl₃): δ 7.08–6.79 (m, 4H), 4.19–3.92 (m, 3H), 3.85 (s, 3H), 3.01–2.77 (m, 3H), 1.12 (d, $J = 6.3$ Hz, 6H). HRMS (ESI-FT): Calcd. For [M + H]⁺, C₁₃H₂₂NO₃⁺: 240.1597. Found: 240.1596.

SI4 NMR Spectra of Organic Compounds and Polymers.

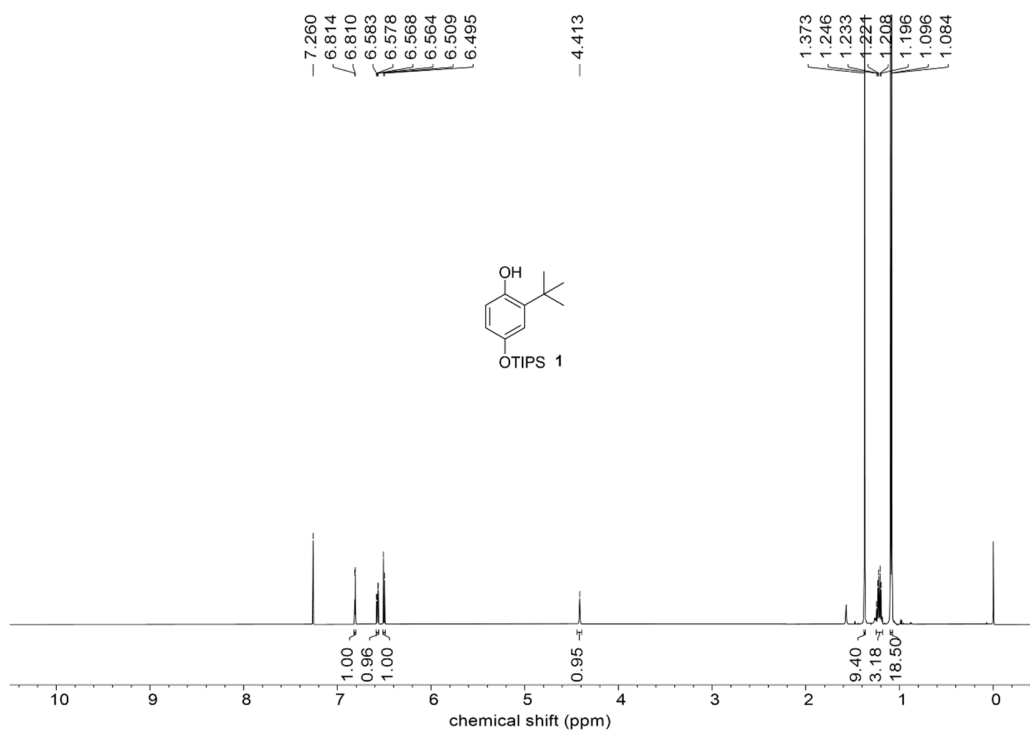


Figure S31. ¹H NMR spectrum of **1** measured in CDCl₃ at 25 °C (600 MHz).

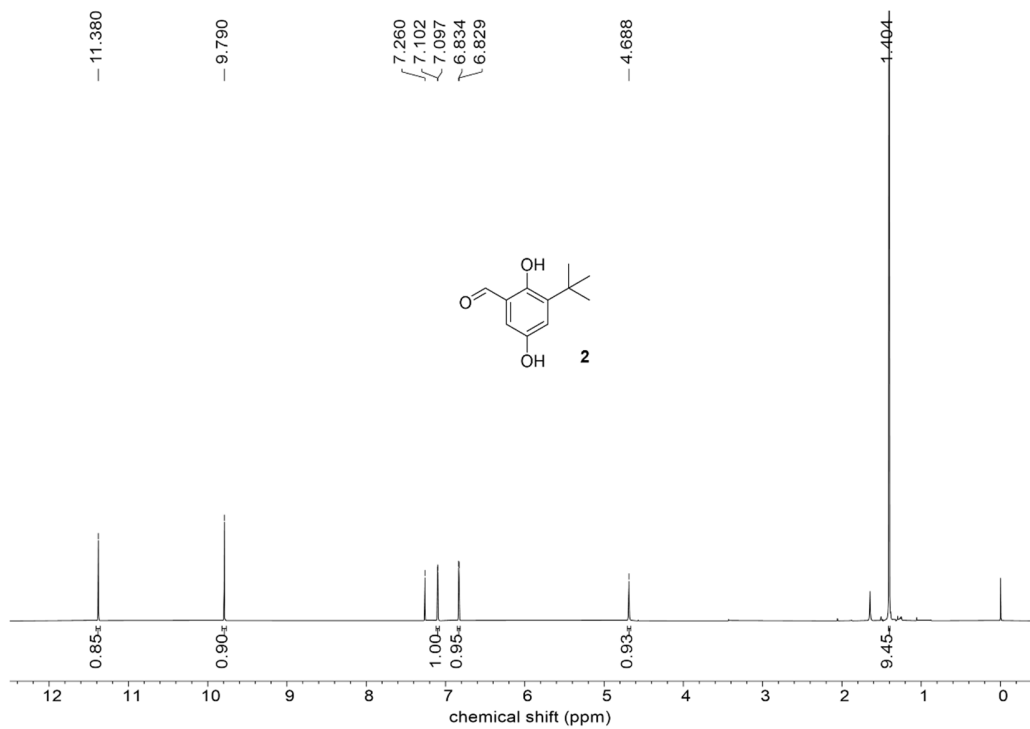


Figure S32. ¹H NMR spectrum of **2** measured in CDCl₃ at 25 °C (600 MHz).

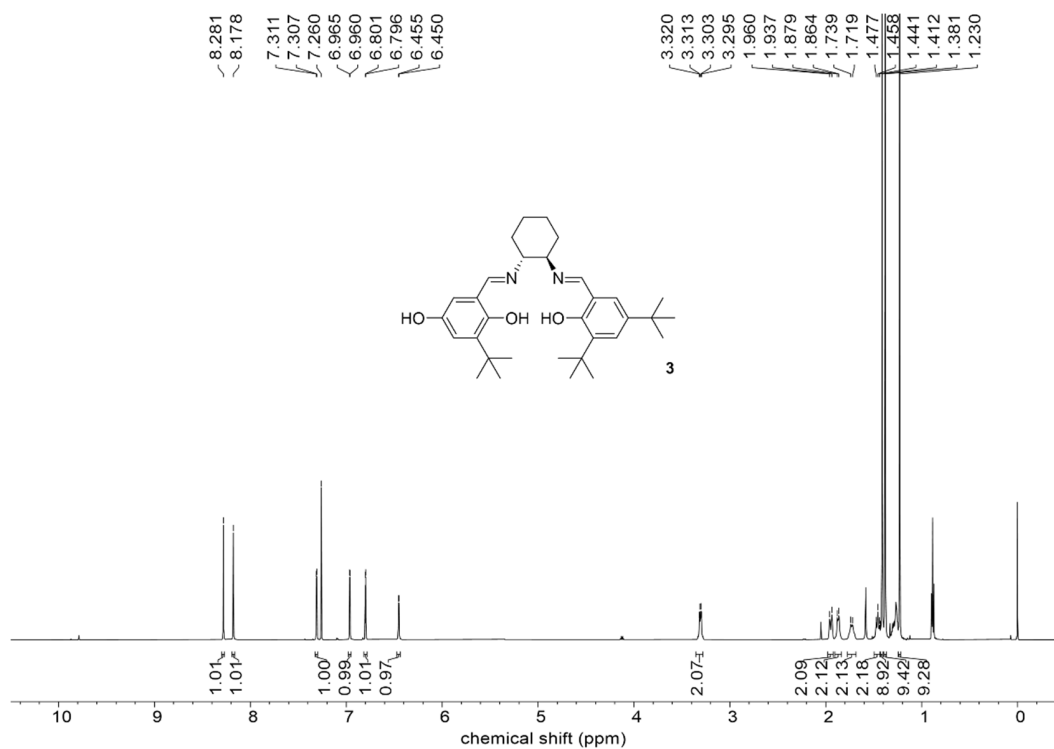


Figure S33. ^1H NMR spectrum of **3** measured in CDCl_3 at 25 °C (600 MHz).

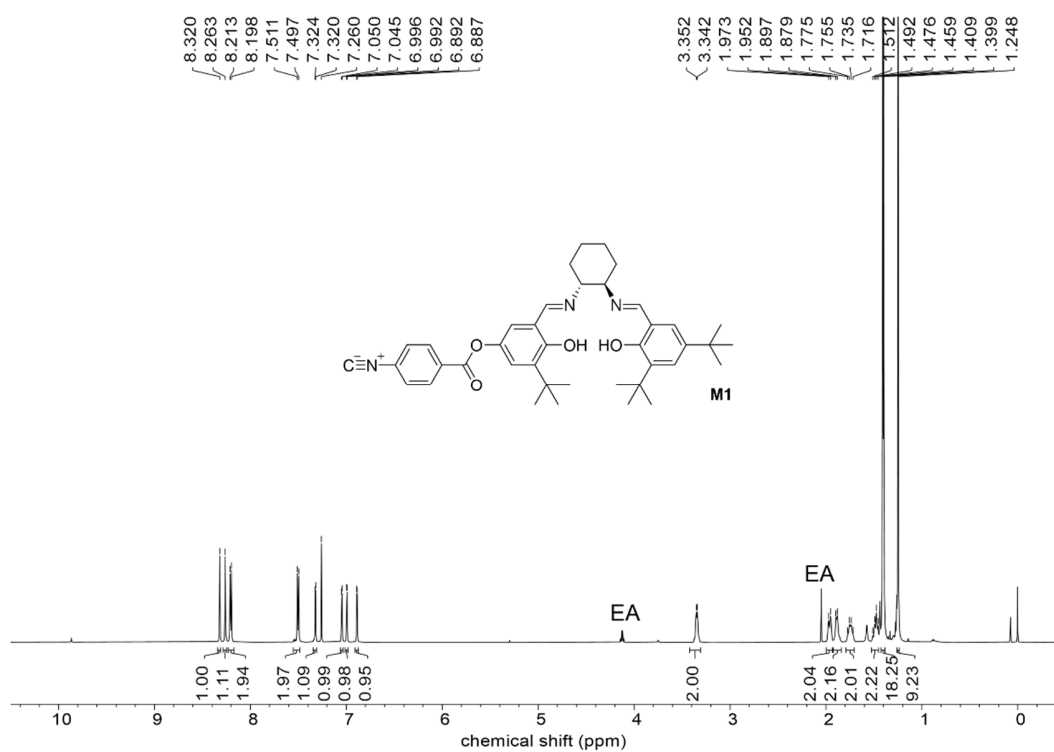


Figure S34. ^1H NMR spectrum of **M1** measured in CDCl_3 at 25 °C (600 MHz).

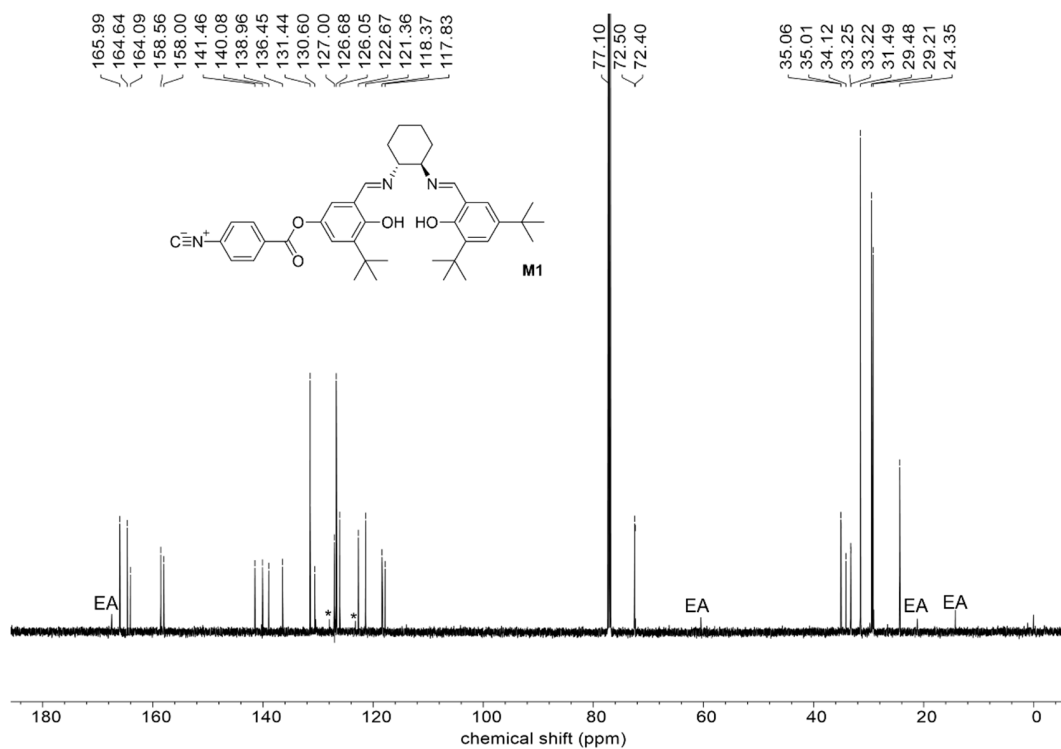


Figure S35. ¹³C NMR spectrum of **M1** measured in CDCl₃ at 25 °C (151 MHz).

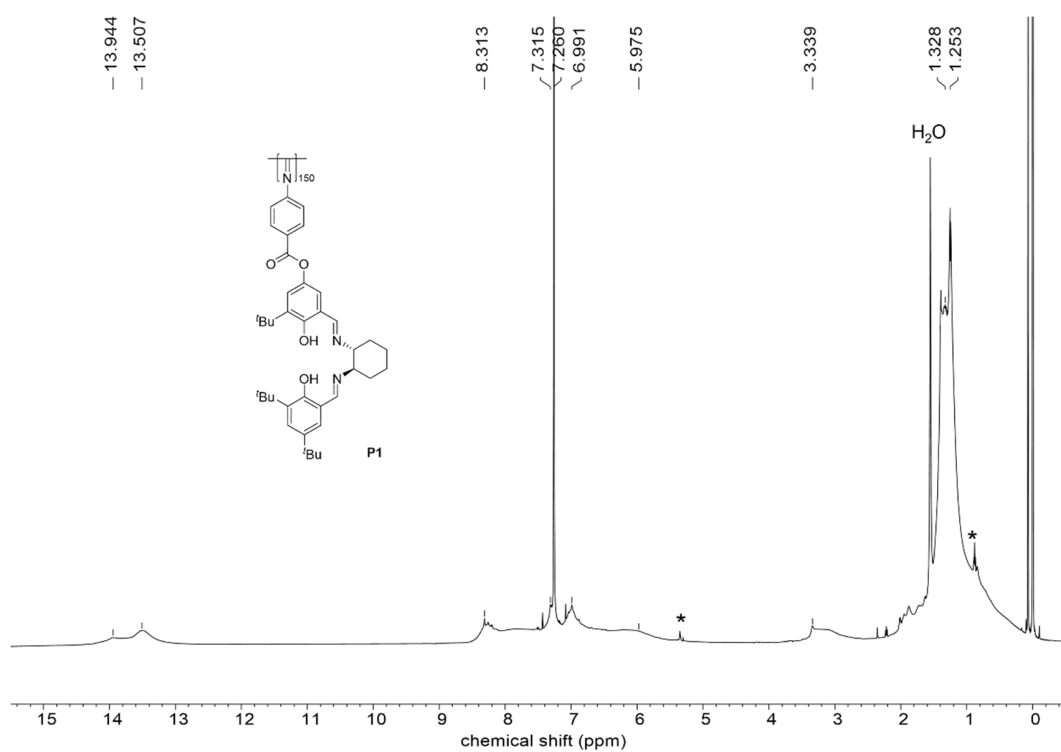


Figure S36. ¹H NMR spectrum of **P1** measured in CDCl₃ at 25 °C (600 MHz).

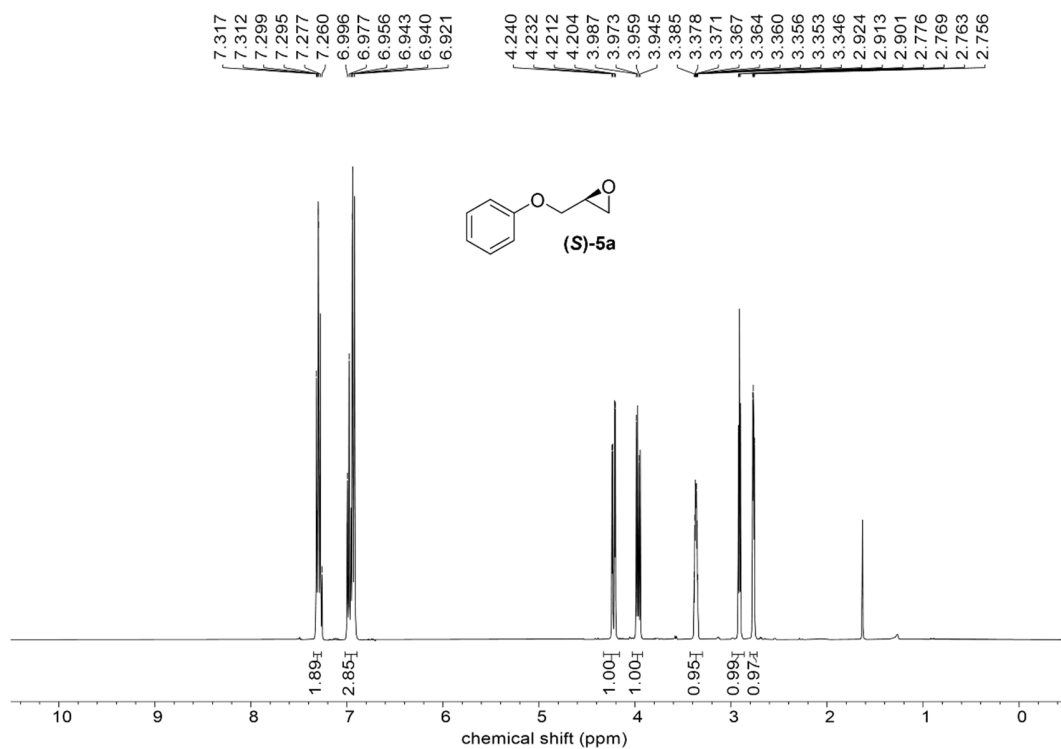


Figure S37. ^1H NMR spectrum of (S)-5a measured in CDCl_3 at 25 °C (400 MHz).

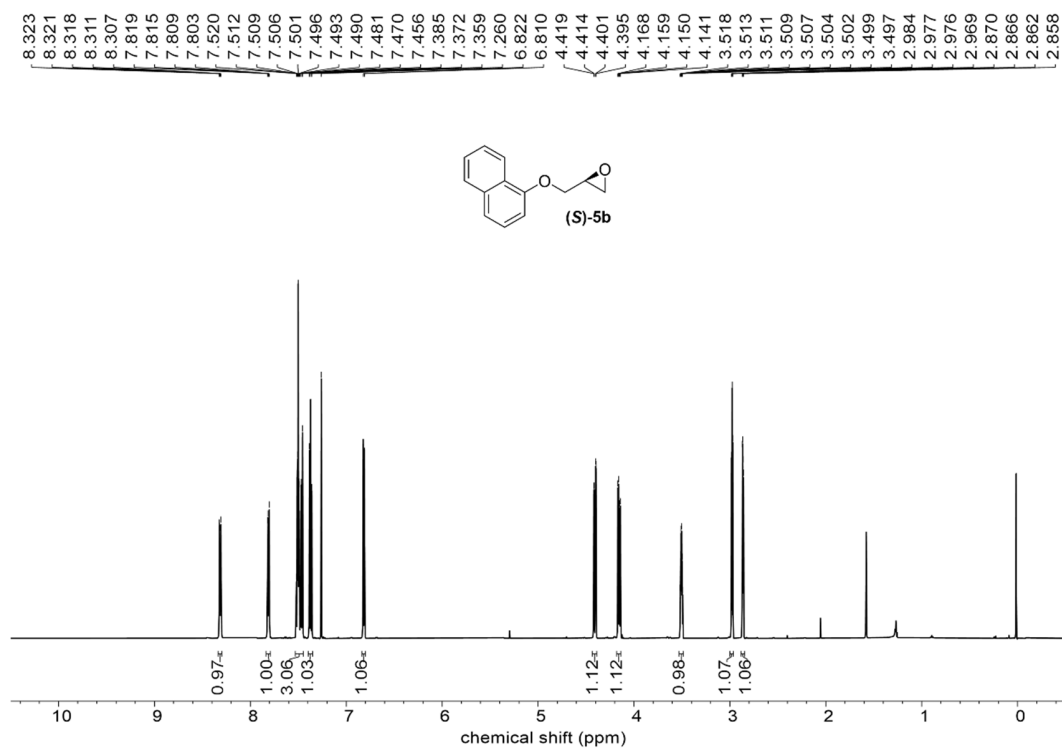


Figure S38. ^1H NMR spectrum of (S)-5b measured in CDCl_3 at 25 °C (600 MHz).

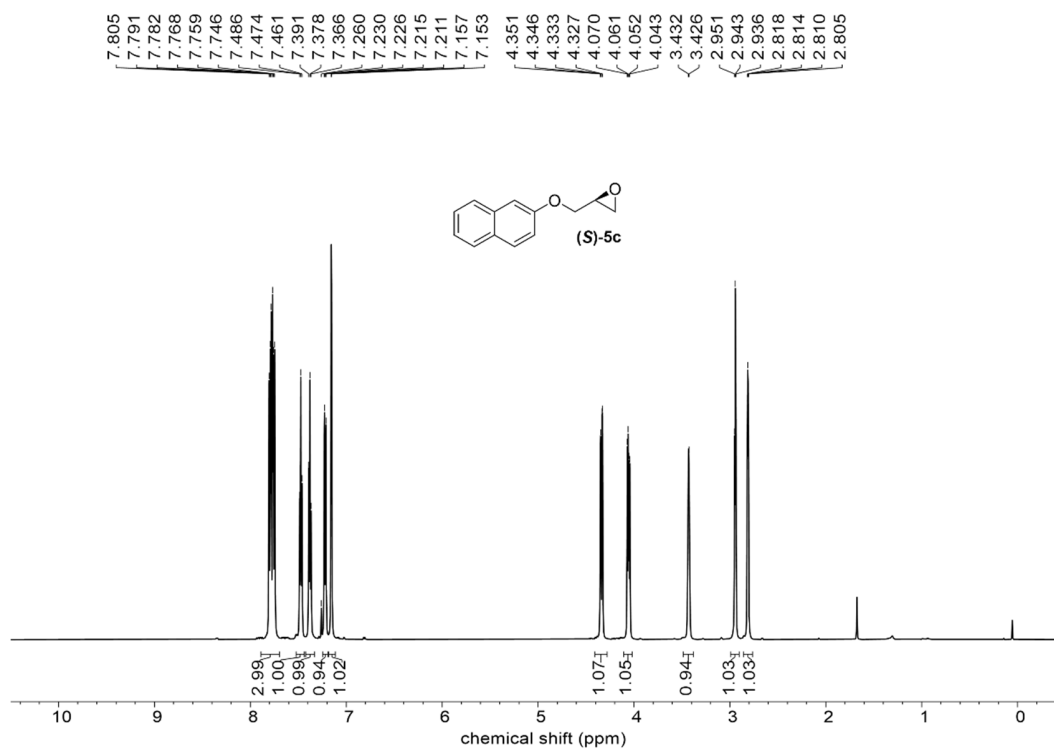


Figure S39. ^1H NMR spectrum of (S)-5c measured in CDCl_3 at 25 °C (600 MHz).

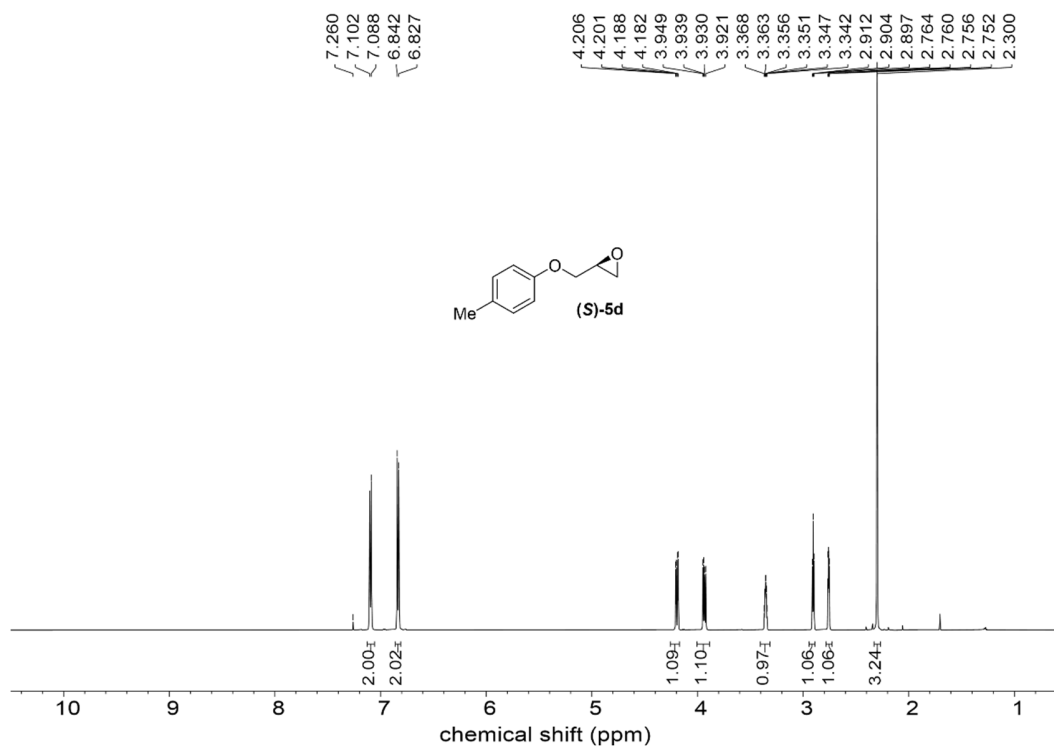


Figure S40. ^1H NMR spectrum of (S)-5d measured in CDCl_3 at 25 °C (600 MHz).

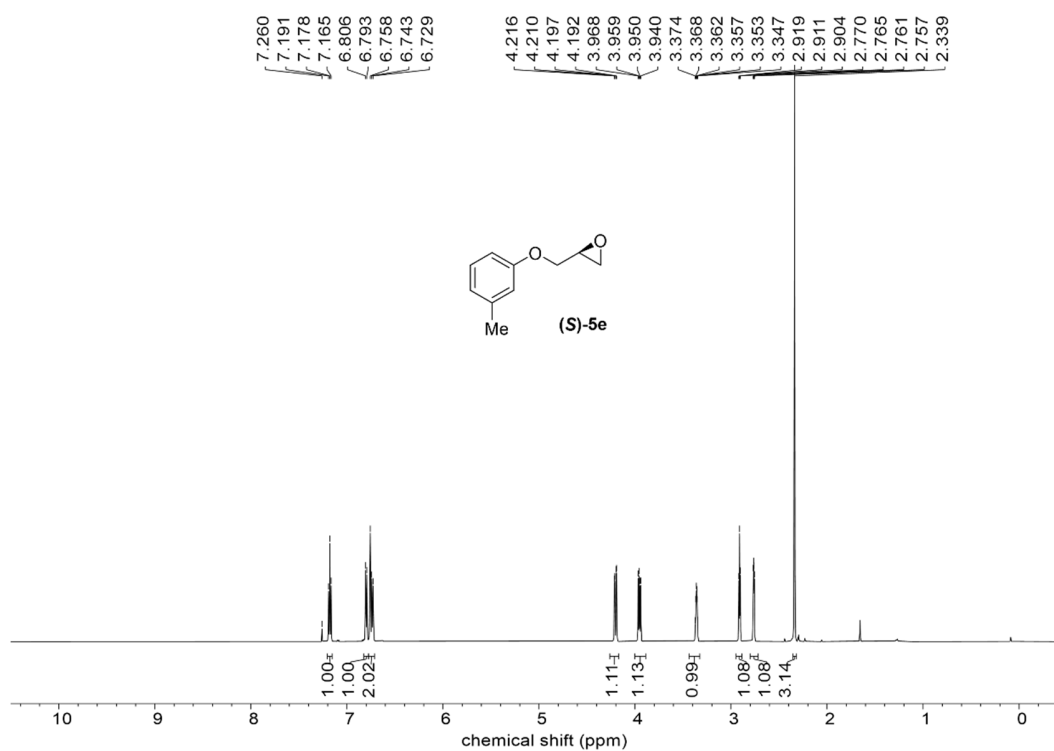


Figure S41. ^1H NMR spectrum of (S)-5e measured in CDCl_3 at 25 °C (600 MHz).

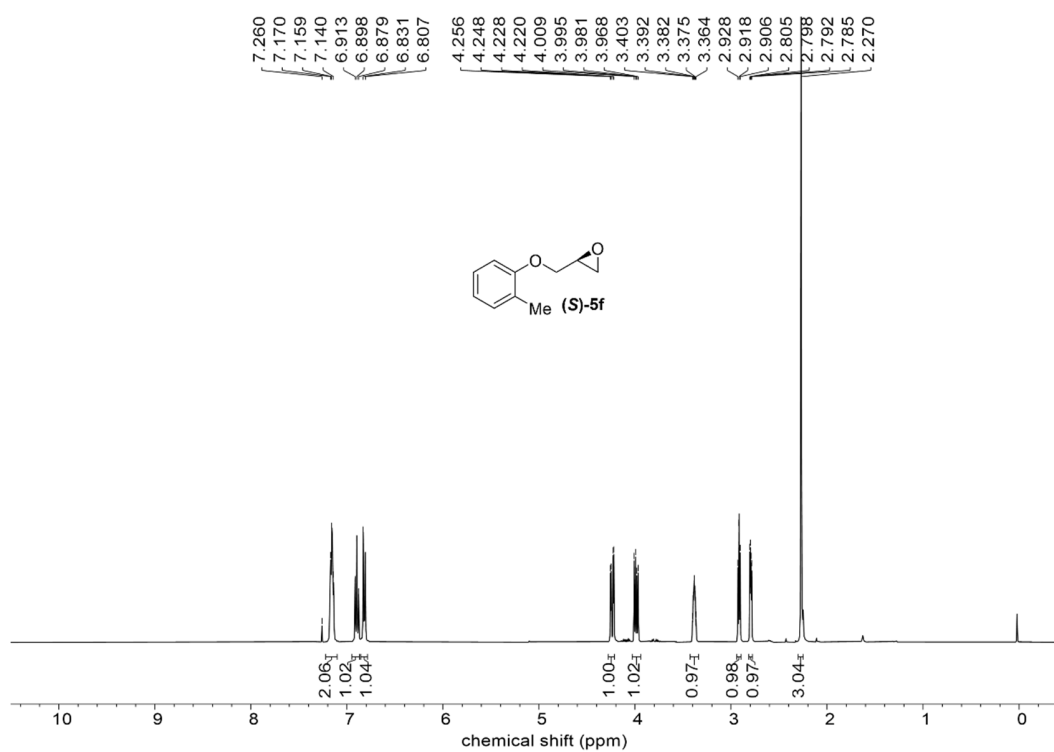


Figure S42. ^1H NMR spectrum of (S)-5f measured in CDCl_3 at 25 °C (400 MHz).

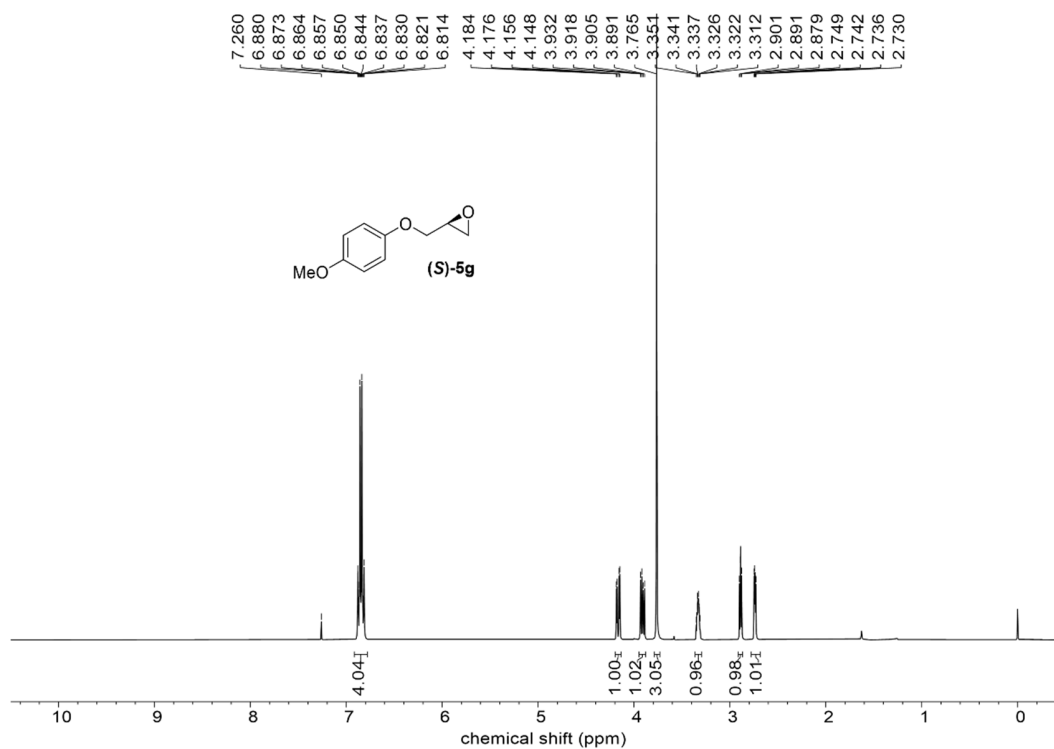


Figure S43. ^1H NMR spectrum of (S)-5g measured in CDCl_3 at 25 °C (400 MHz).

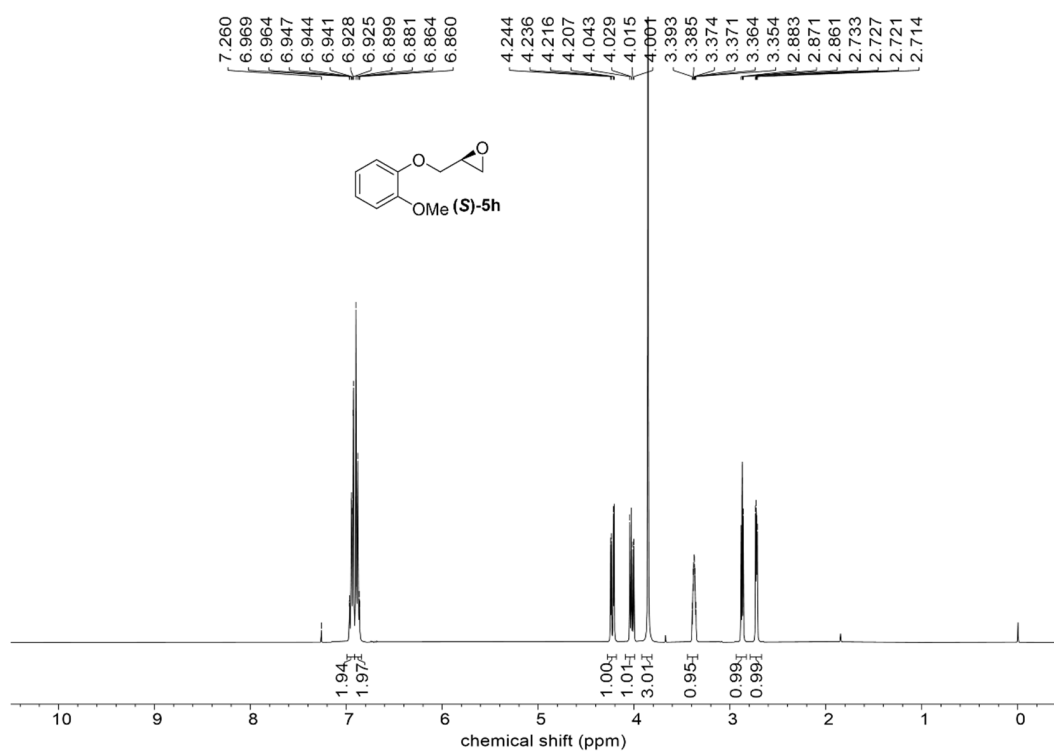


Figure S44. ^1H NMR spectrum of (S)-5h measured in CDCl_3 at 25 °C (400 MHz).

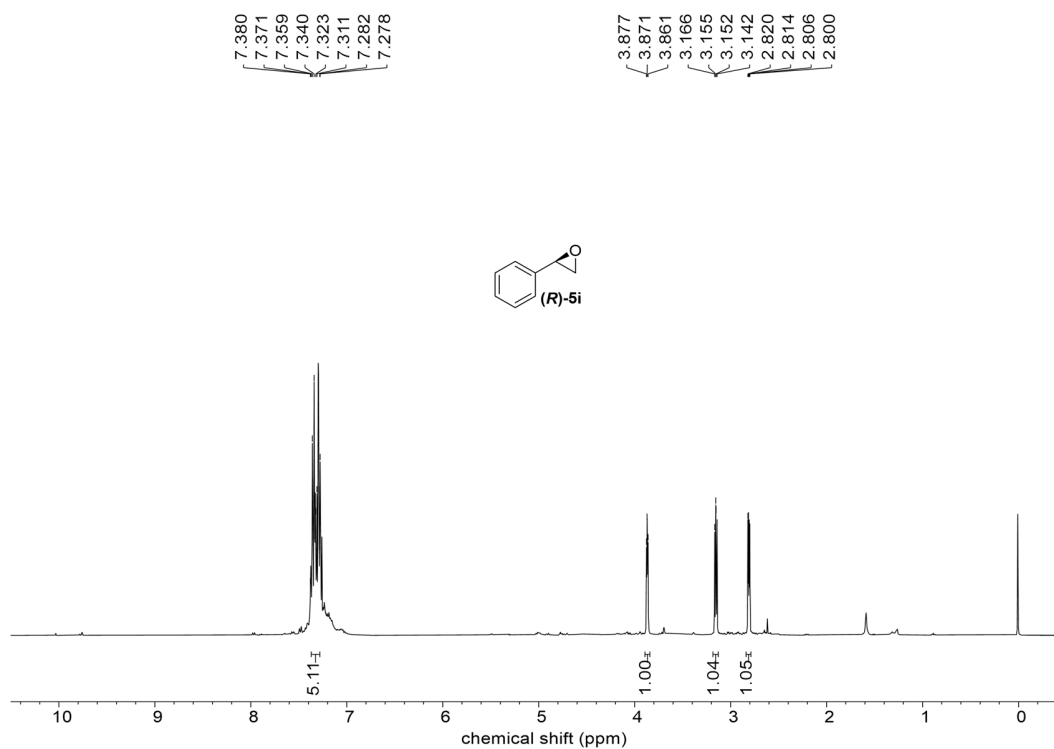


Figure S45. ¹H NMR spectrum of (*S*)-5i measured in CDCl₃ at 25 °C (400 MHz).

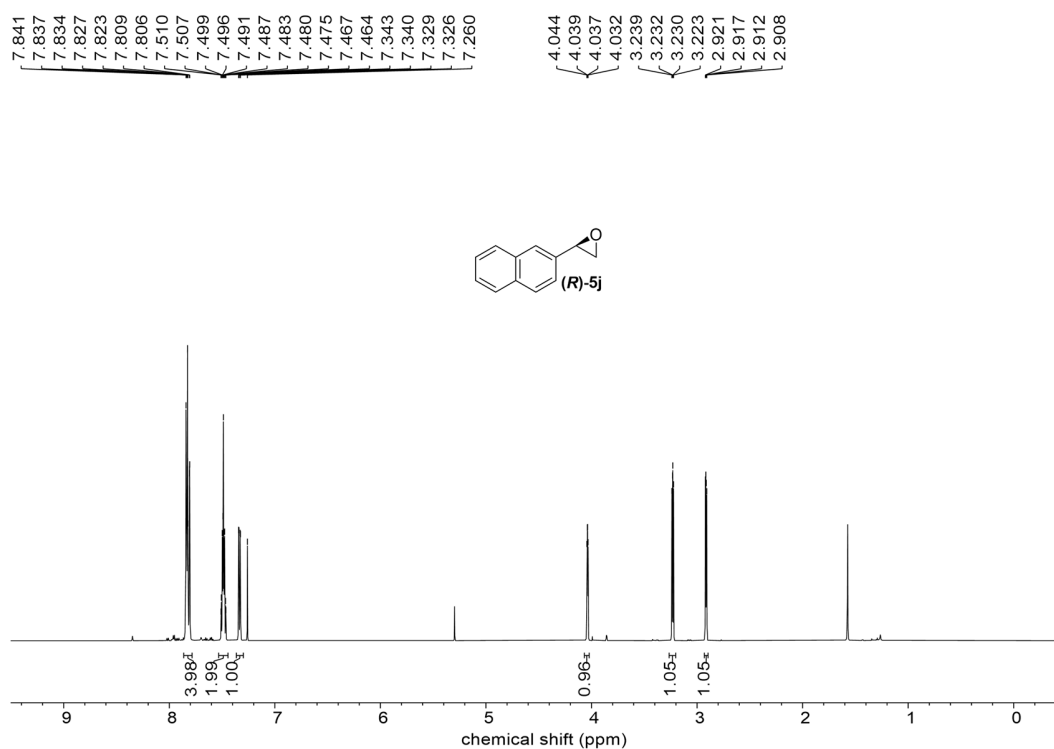


Figure S46. ¹H NMR spectrum of (*S*)-5j measured in CDCl₃ at 25 °C (400 MHz).

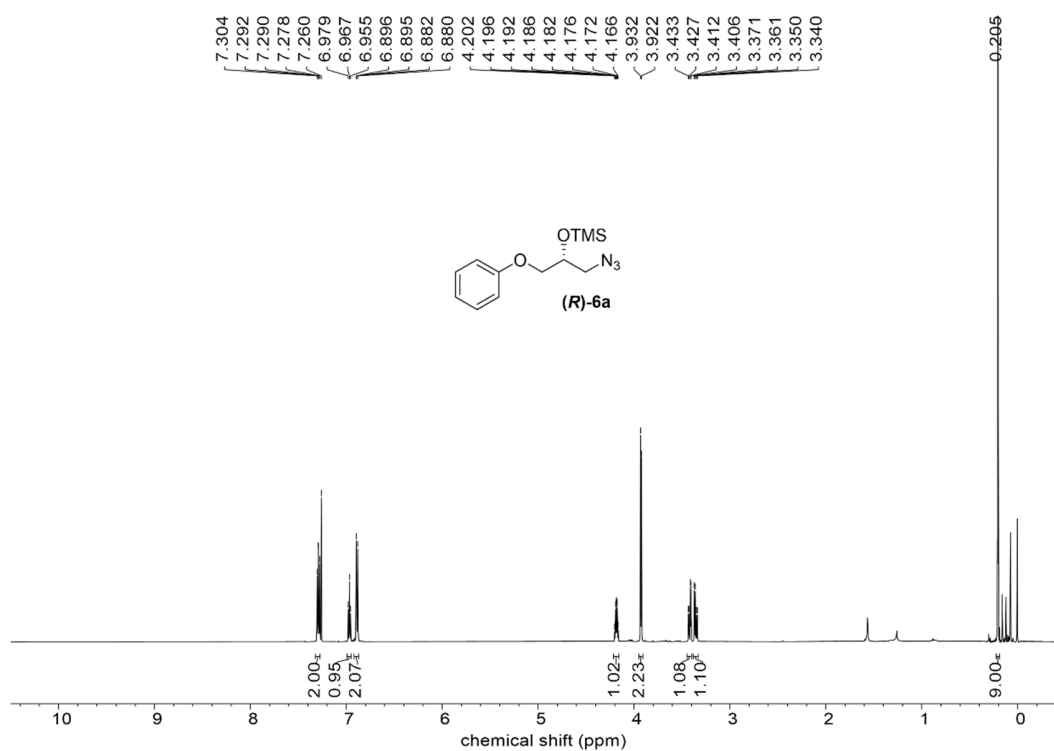


Figure S47. ^1H NMR spectrum of **(S)-6a** measured in CDCl_3 at 25°C (600 MHz).

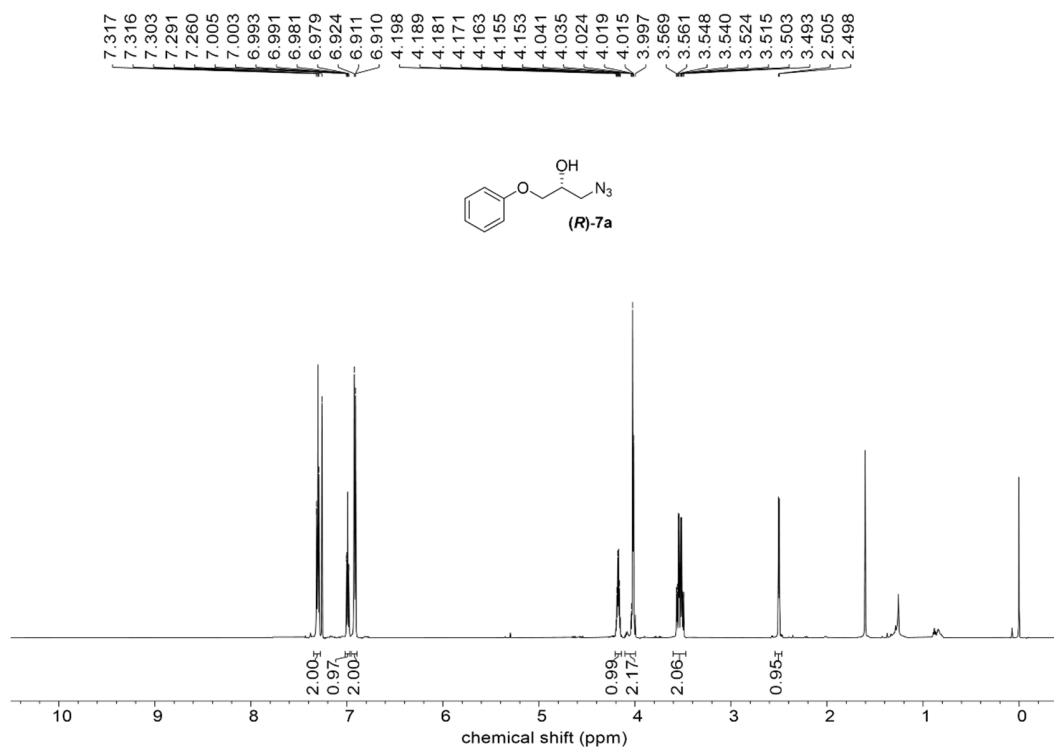


Figure S48. ^1H NMR spectrum of **(R)-7a** measured in CDCl_3 at 25°C (600 MHz).

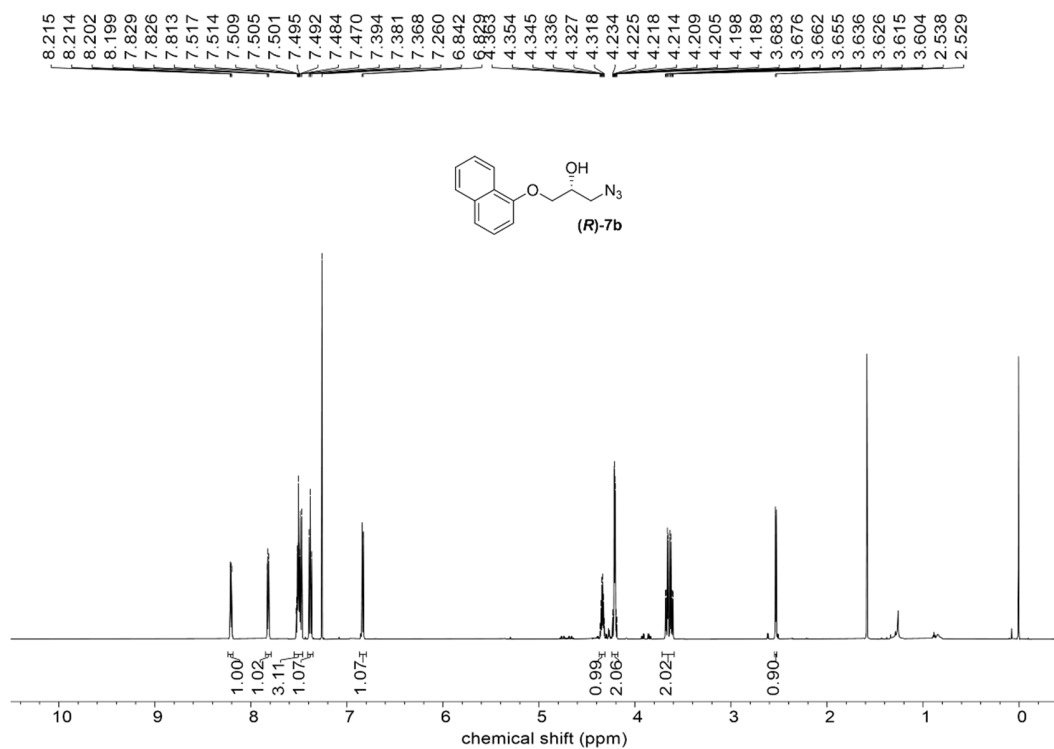


Figure S49. ^1H NMR spectrum of (*R*)-7b measured in CDCl_3 at 25 °C (600 MHz).

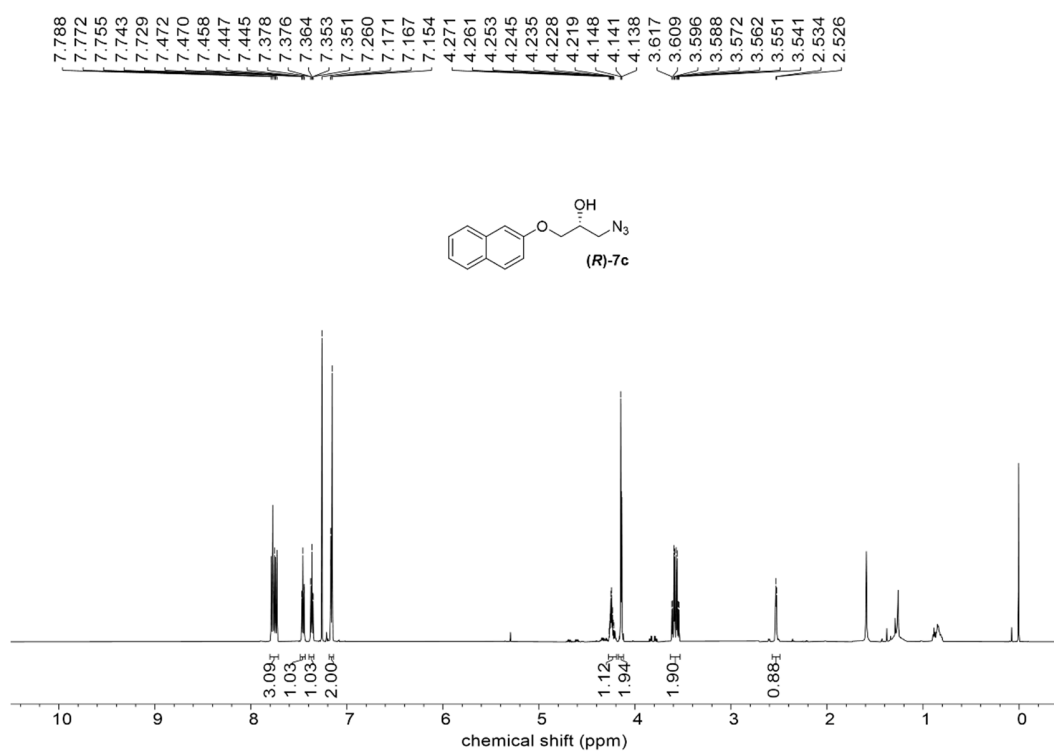


Figure S50. ^1H NMR spectrum of (*R*)-7c measured in CDCl_3 at 25 °C (600 MHz).

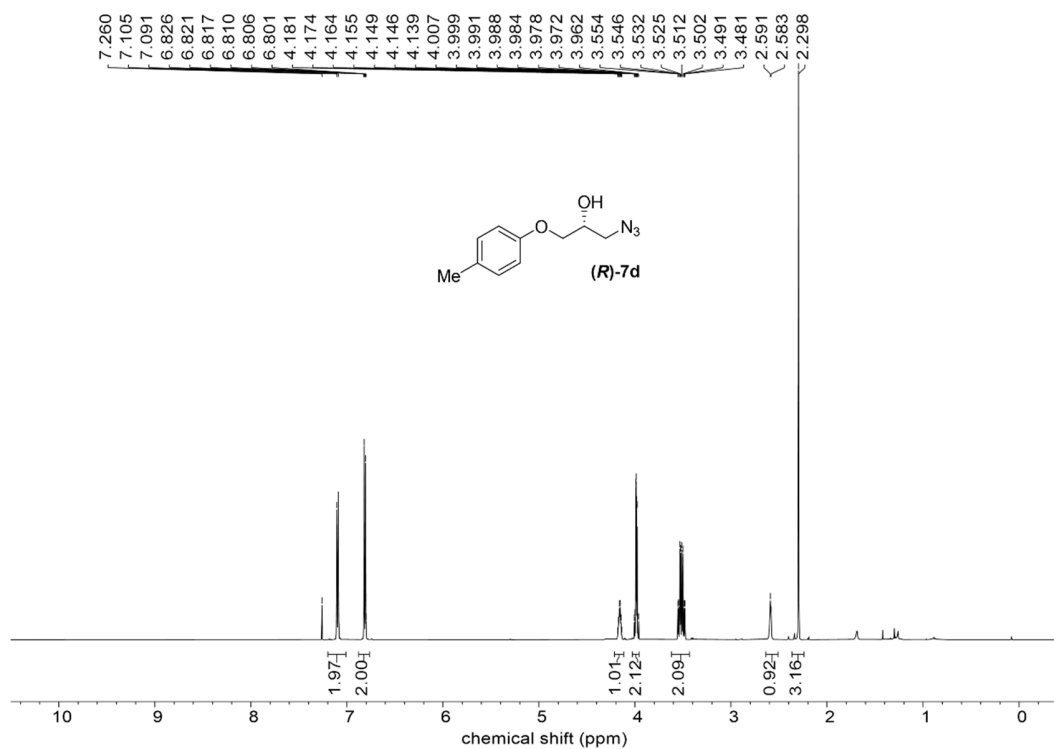


Figure S51. ^1H NMR spectrum of **(R)-7d** measured in CDCl_3 at 25°C (600 MHz).

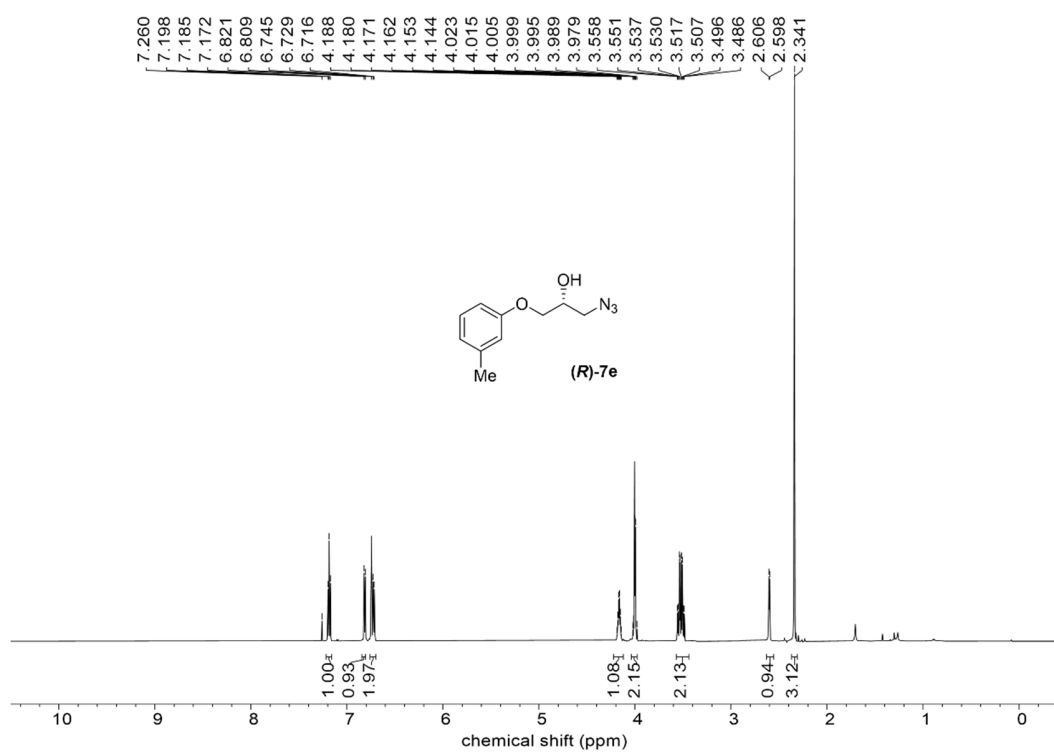


Figure S52. ^1H NMR spectrum of **(R)-7e** measured in CDCl_3 at 25°C (600 MHz).

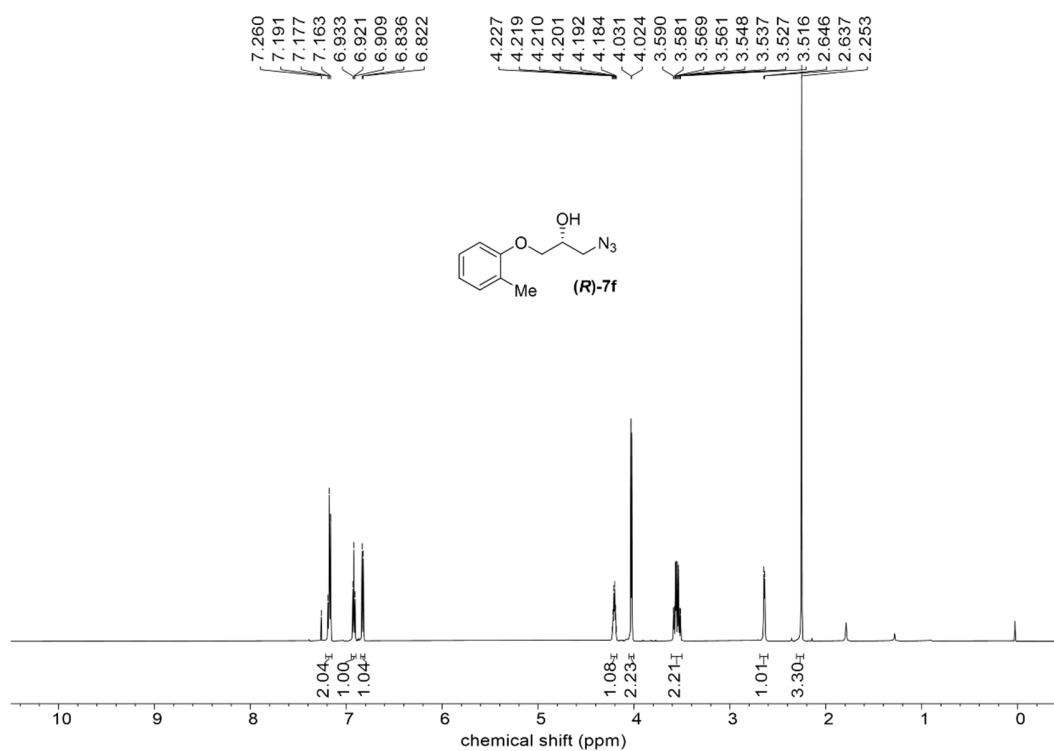


Figure S53. ¹H NMR spectrum of **(R)-7f** measured in CDCl₃ at 25 °C (600 MHz).

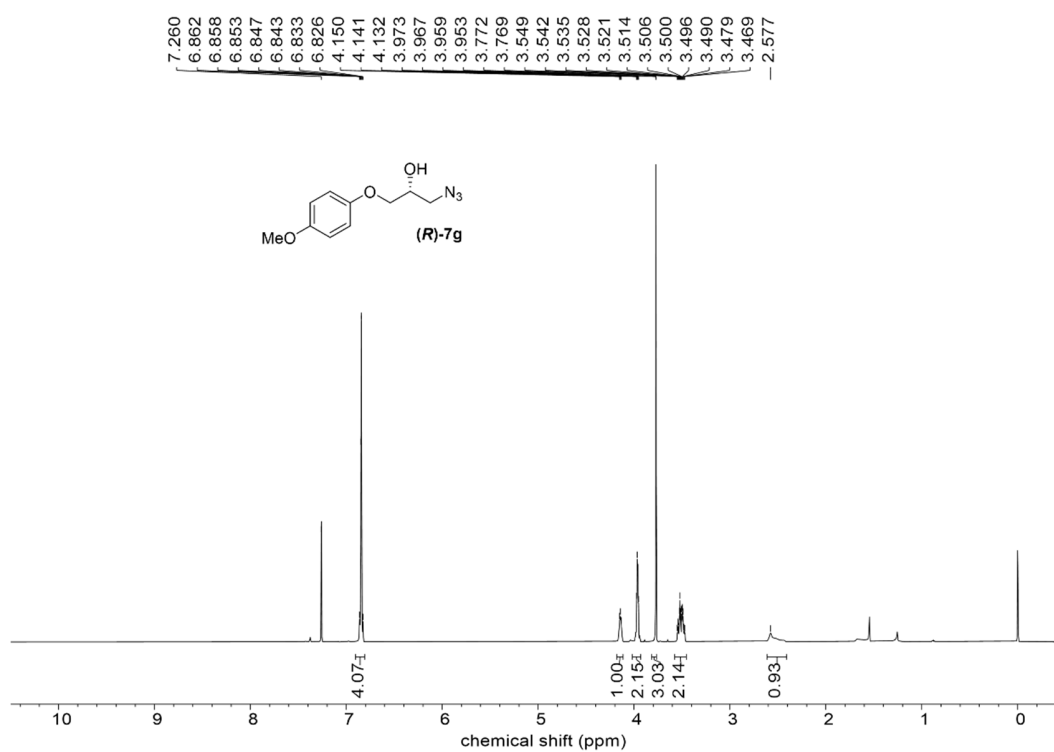


Figure S54. ¹H NMR spectrum of **(R)-7g** measured in CDCl₃ at 25 °C (600 MHz).

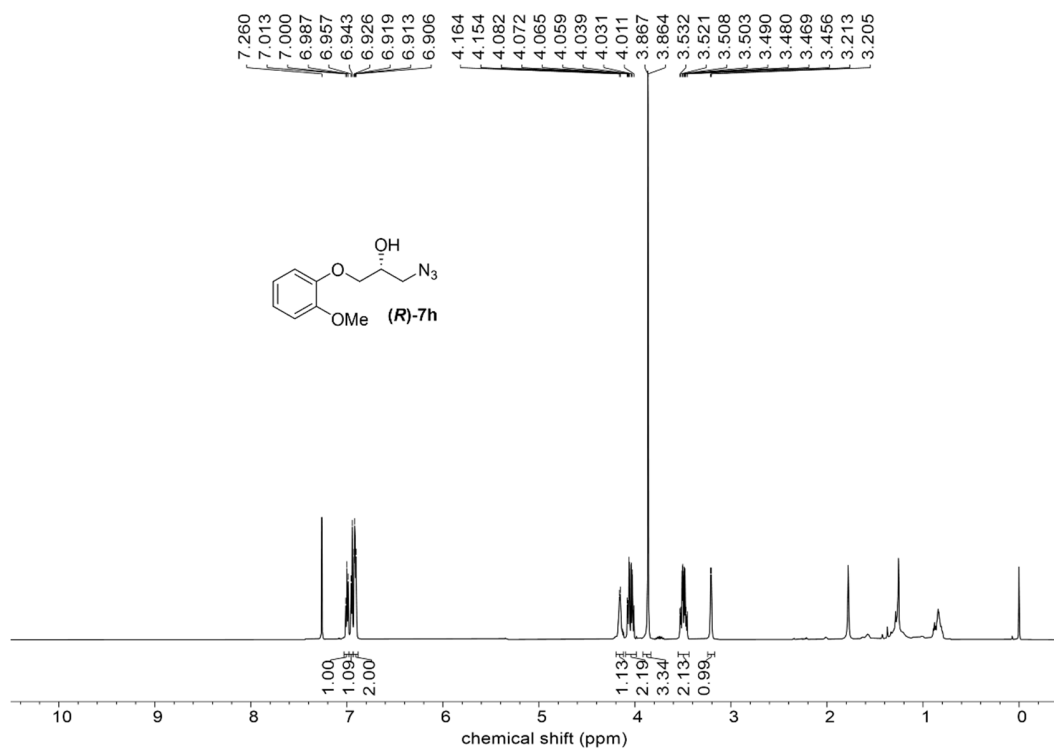


Figure S55. ^1H NMR spectrum of **(R)-7h** measured in CDCl_3 at 25 °C (600 MHz).

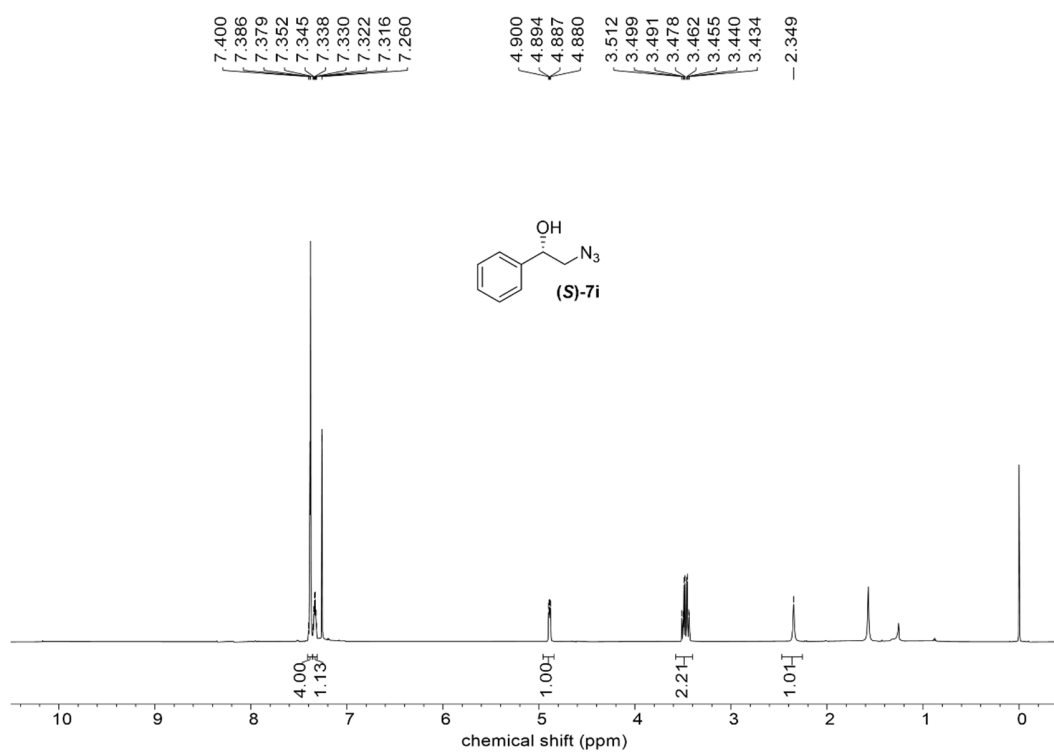


Figure S56. ^1H NMR spectrum of **(S)-7i** measured in CDCl_3 at 25 °C (600 MHz).

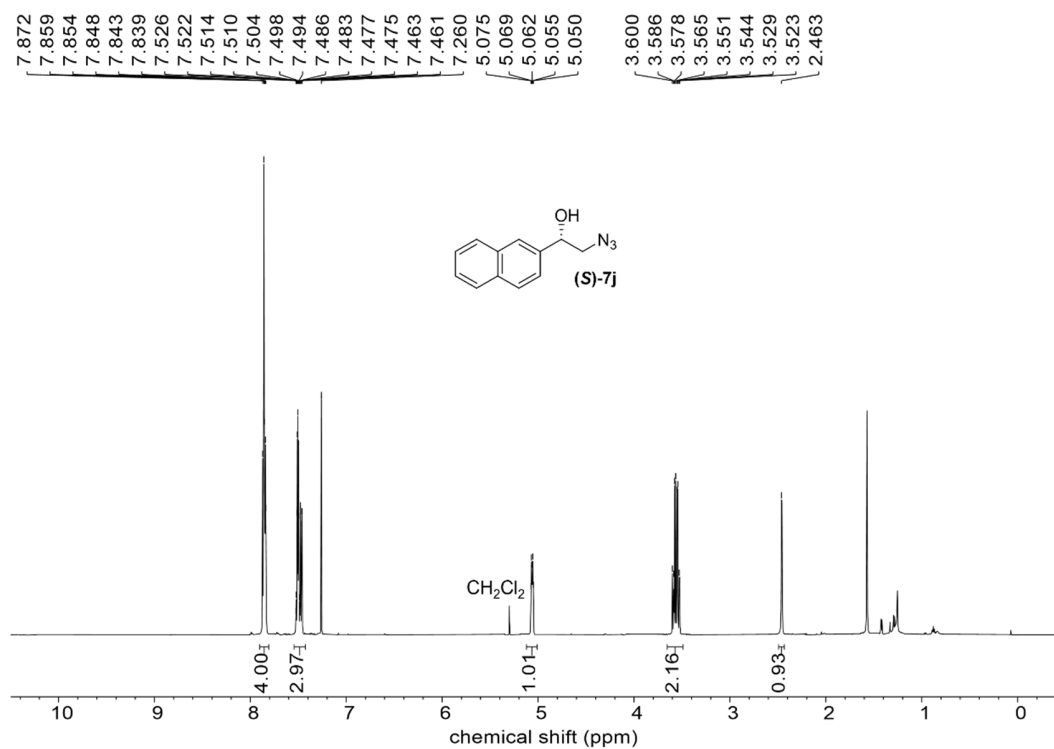


Figure S57. ¹H NMR spectrum of (S)-7j measured in CDCl₃ at 25 °C (600 MHz).

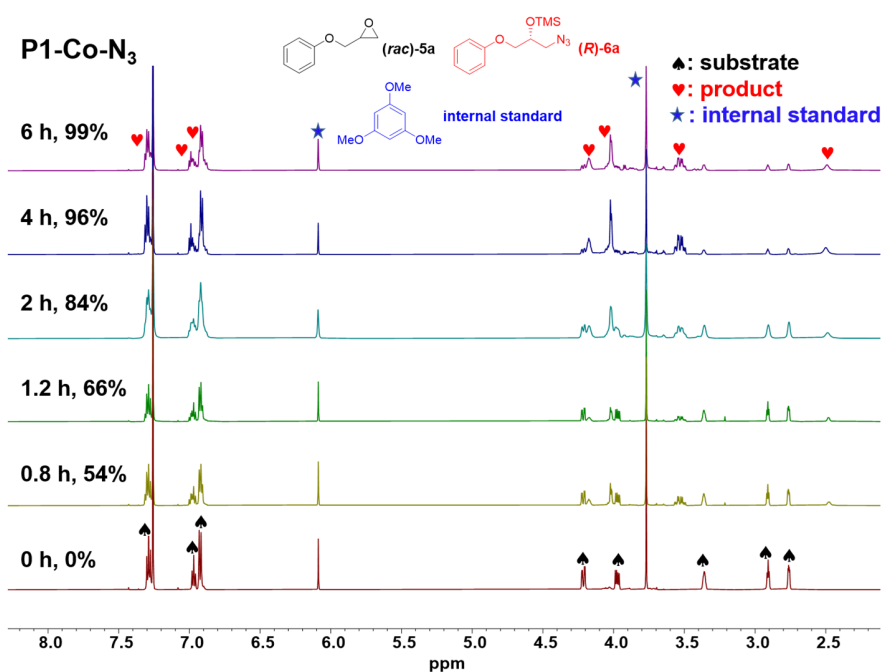


Figure S58. Stacked ¹H NMR spectra of kinetic resolution from (±)-5a to (R)-6a using P1-Co-N₃ as the catalyst under different reaction stages. Measured conditions: CDCl₃, 25 °C, and 600 MHz NMR.

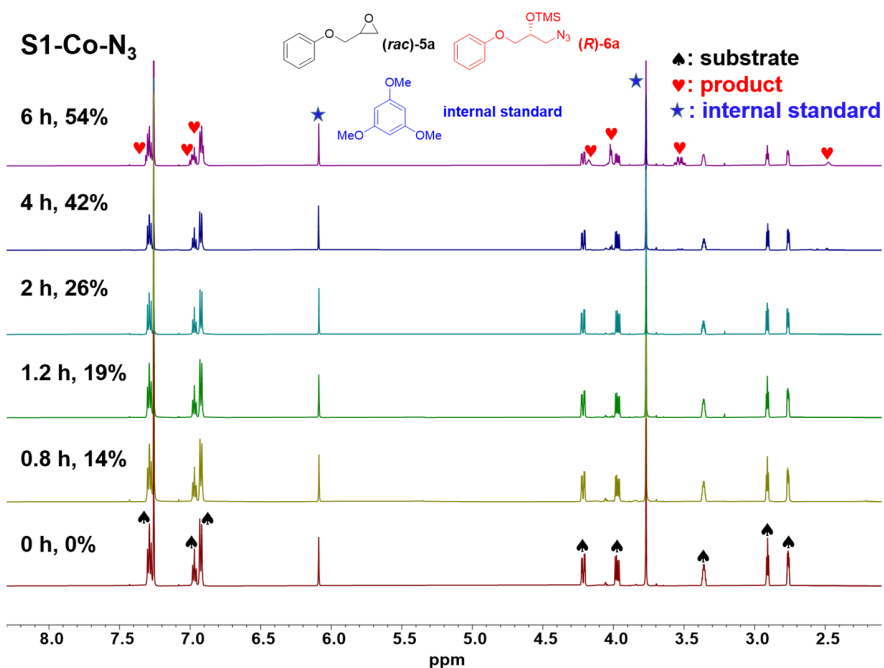


Figure S59. Stacked ¹H NMR spectra of reaction from (±)-5a to (S)-6a using S1-Co-N₃ as the catalyst under different reaction stages. Measured conditions: CDCl₃, 25 °C, and 600 MHz NMR.

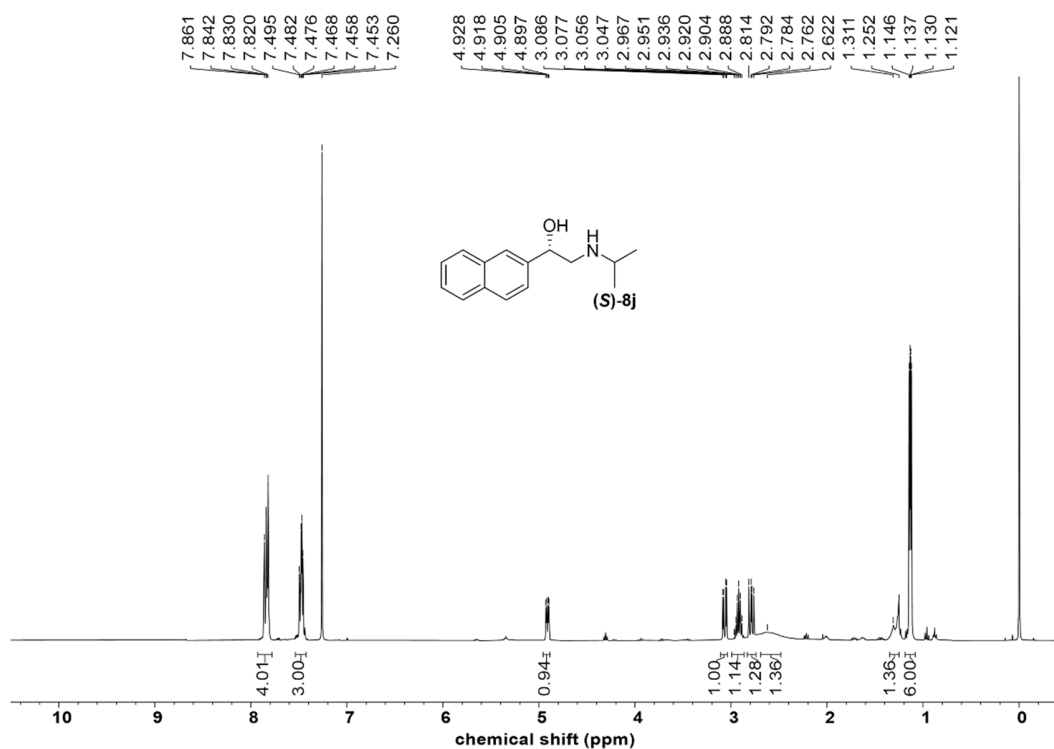


Figure S60. ¹H NMR spectrum of (S)-8j measured in CDCl₃ at 25 °C (600 MHz).

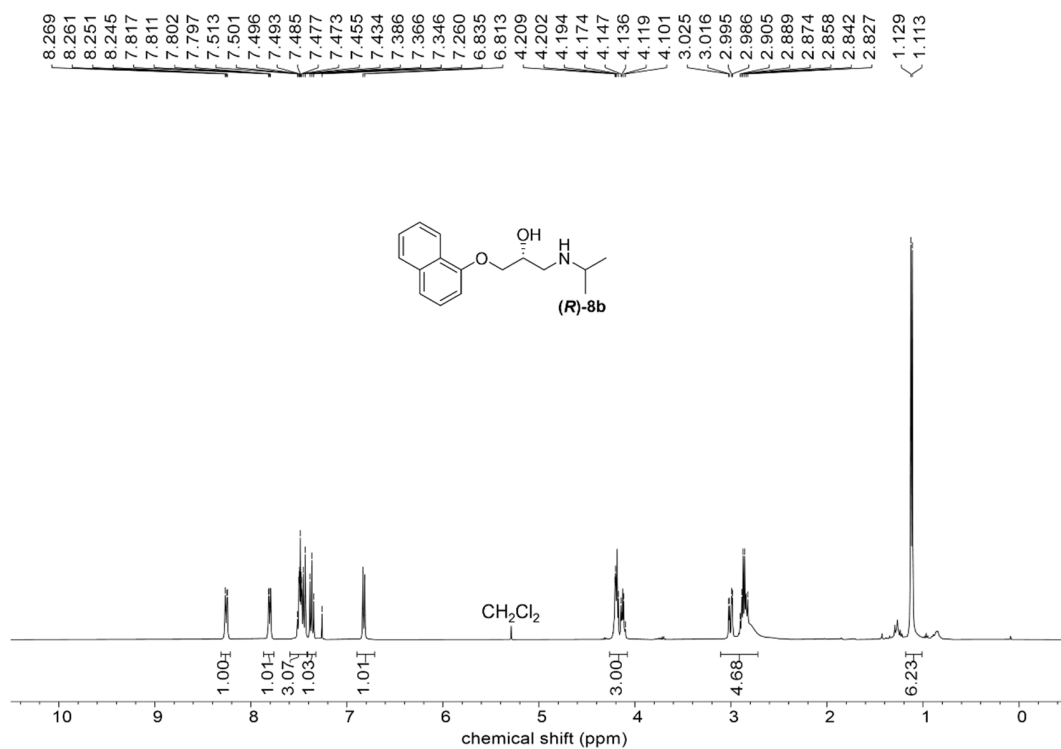


Figure S61. ¹H NMR spectrum of **(R)-8b** measured in CDCl₃ at 25 °C (400 MHz).

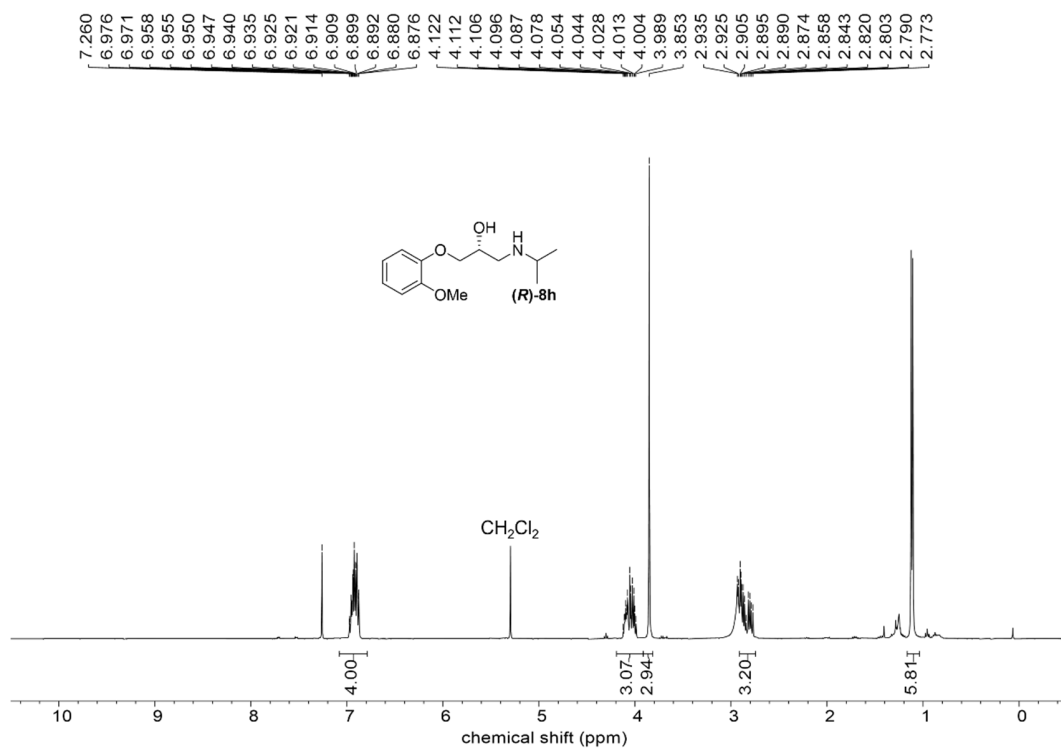


Figure S62. ¹H NMR spectrum of **(R)-8h** measured in CDCl₃ at 25 °C (400 MHz).

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