

Electronic Supporting Information

Achiral Benzoic Acid Appended Helical Polymers for Copper-catalyzed
Asymmetric Diels-Alder Reaction and Michael Addition with Excellent
Enantioselectivity and Recyclability

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1. Measurements

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 400 MHz spectrometer. Chemical shifts are expressed in delta (δ) in parts per million (ppm) from tetramethylsilane (TMS) downwards using residual proton solvent as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded at 25 °C on a FT-IR instrument (VERTEX 80V) using KBr pressure plates. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C). A series of three linear Styragel HR0.5, Styragel HR3 and Styragel HR4 were used. The number average molar mass (M_n) and its polydispersity (M_w/M_n) values were reported with reference to the polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. The CD were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1700 spectropolarimeter. The UV absorption spectra were recorded on PerkinElmer UV/vis double beam spectrophotometer in a 1.0 cm length quartz cell. High performance liquid chromatography (HPLC) with UV-vis detector was carried out on WUFENG LC-100 equipment using chiral column.

2. Materials

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The *trans*-bis(triethylphosphine)-((4-methoxyphenyl)ethynyl)palladium(II) chloride (alkyne-Pd(II) catalyst), *R*- and *S*-Weiphos, monomers **1**, **2**, and **3** were prepared according to the procedures reported by our group previously, and the structures were confirmed by ¹H NMR.¹⁻⁴ The substrates **4a-p** and **10a-l** for asymmetric reactions were prepared following the reported literatures and were confirmed by ¹H NMR analyses.^{5,6}

3. Typical polymerization procedure

Preparation of the Pd(II) catalysts. The Pd(II)/L^R and Pd(II)/L^S catalysts were prepared according to our previously reported procedure.¹⁻⁴ Taking Pd(II)/L^S as an example, under dry nitrogen atmosphere, a solution of alkyne-Pd(II) catalyst (10.0 mg, 0.020 mmol) in THF was first prepared and then treated with a solution of L^S (11.4 mg, 0.020 mmol) in THF (1 mL) at room temperature. The mixture was stirred at room temperature for 3 h to afford the desired Pd(II)/L^S catalyst. The resulting solution was directly used as catalyst for isocyanide polymerization without further isolation and purification. Pd(II)/L^R was prepared under the same way by using L^R instead of L^S ligand.

Synthesis of *S*-poly-**1**_ns: Taking *S*-poly-**1**₁₀₀ as an example, a 10 mL oven dried and nitrogen-filled flask was charged with monomer **1** (100 mg, 0.49 mmol), a THF solution of Pd(II)/L^S catalyst (0.245 mL, 0.02 M, 0.0049 mmol), dry THF (1.28 mL) and a stir bar. The feed ratio of monomer to catalyst was 100/1 ([**1**]₀/[Pd]₀ = 100). The resulting mixture was then stirred at 55 °C for 6 h. Then, the solution was cooled to room temperature and precipitated into methanol. The isolated precipitated solid was dissolved in a small amount of CHCl₃ (1.5 mL), and the solution was precipitated into acetone (10 mL). The precipitated solid was collected by centrifugation. After this procedure was repeated for three times, the desired *S*-poly-**1**₁₀₀ was obtained as an acetone-insoluble part (88 mg, 88% yield). SEC: $M_n = 22.3$ kDa, $M_w/M_n = 1.13$; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.14–6.44 (br, 2H, ArH), 6.44–4.48 (br, 2H, ArH), 1.84–0.97 (br, 9H, CH₃); FT-IR (KBr, cm⁻¹): 2968 (ν_{C-H}), 2920 (ν_{C-H}), 2850 (ν_{C-H}), 1711 (ν_{C=O}), 1610 (ν_{C=N}).

Synthesis of *S*-poly-**2**_ns: Taking *S*-poly-**2**₁₀₀ as an example, the *S*-poly-**1**₁₀₀ (80 mg) was dissolved in CH₂Cl₂ (1 mL) and cooled to 0 °C. To this solution, trifluoroacetic acid (45 μL, 0.6 mmol) was added. The mixture was warmed to 25 °C and stirred for 12 h. Then, the solution was precipitated into methanol, and the precipitated polymer was collected via centrifugation and dried under vacuum to afford *S*-poly-**2**₁₀₀ as a

yellow solid (56 mg, 86% yield). SEC: $M_n = 16.8$ kDa, $M_w/M_n = 1.17$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.38–7.12 (br, 2H, ArH), 6.78–5.52 (br, 2H, ArH); FT-IR (KBr, cm^{-1}): 3315–2871 ($\nu_{\text{O-H}}$), 2844 ($\nu_{\text{C-H}}$), 1687 ($\nu_{\text{OC=O}}$), 1592 ($\nu_{\text{C=N}}$).

Synthesis of *S*-poly-**3**_ms: Taking *S*-poly-**3**₃₀ as an example, a 10 mL oven dried and nitrogen-filled flask was charged with monomer **3** (100 mg, 0.45 mmol), a THF solution of Pd(II)/L^S catalyst (0.75 mL, 0.02 M, 0.015 mmol), dry THF (1.25 mL) and a stir bar. The feed ratio of monomer to catalyst was 30/1 ($[\mathbf{3}]_0/[\text{Pd}]_0 = 30$). The resulting mixture was then stirred at 55 °C for 6 h. The solution was then cooled to room temperature and precipitated into methanol. The isolated precipitated solid was dissolved in a small amount of CHCl_3 (1.5 mL), and the solution was precipitated into acetone (10 mL). The precipitated solid was collected by centrifugation. After this procedure was repeated for three times, *S*-poly-**3**₃₀ was obtained as an acetone-insoluble part (79 mg, 79% yield). SEC: $M_n = 6.3$ kDa, $M_w/M_n = 1.15$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.30–6.82 (br, 5H, ArH), 6.78–5.52 (br, 5H, ArH and NH); FT-IR (KBr, cm^{-1}): 3341 ($\nu_{\text{N-H}}$), 2944 ($\nu_{\text{C-H}}$), 1761 ($\nu_{\text{NHC=O}}$), 1637 ($\nu_{\text{OC=O}}$), 1588 ($\nu_{\text{C=N}}$).

Synthesis of *S*-poly(**3**_m-*b*-**1**_n)s: Taking *S*-poly(**3**₃₀-*b*-**1**₃₀) as an example, monomer **1** (54.8 mg, 0.27 mmol) and *S*-poly-**3**₃₀ (56.3 mg, 0.009 mmol) was mixed in THF (1.0 mL). The feed ratio of monomer to catalyst was 30/1 ($[\mathbf{1}]_0/[\text{S-poly-}\mathbf{3}_{30}]_0 = 30$). The mixture was stirred for 10 h at 55 °C, then cooled to 25 °C and precipitated in MeOH. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight (94 mg, 85% yield). SEC: $M_n = 12.5$ kDa, $M_w/M_n = 1.15$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.28–5.45 (br, 14H, ArH and NH), 1.84–0.97 (br, 9H, CH_3); FT-IR (KBr, cm^{-1}): 3341 ($\nu_{\text{N-H}}$), 2968 ($\nu_{\text{C-H}}$), 2920 ($\nu_{\text{C-H}}$), 2850 ($\nu_{\text{C-H}}$), 1761 ($\nu_{\text{NHC=O}}$), 1637 ($\nu_{\text{OC=O}}$), 1588 ($\nu_{\text{C=N}}$).

Synthesis of *S*-poly(**3**_m-*b*-**1**_n-*b*-**3**_m)s: Taking *S*-poly(**3**₃₀-*b*-**1**₃₀-*b*-**3**₃₀) as an example, monomer **3** (28.8 mg, 0.13 mmol) and *S*-poly(**3**₃₀-*b*-**1**₃₀) (55.1 mg, 0.0044 mmol) in THF (1.0 mL) was stirred for 10 h at 55 °C, then cooled to 25 °C and precipitated in

methanol. The feed ratio of monomer to catalyst was 30/1 ($[\mathbf{3}]_0/[\text{Pd(II)}]_0 = 30$). The isolated precipitated solid was dissolved in a small amount of CHCl_3 (1.5 mL), and the solution was precipitated into acetone (10 mL). The precipitated solid was collected by centrifugation. After this procedure was repeated for three times, *S*-poly($\mathbf{3}_{30}\text{-}b\text{-}\mathbf{1}_{30}\text{-}b\text{-}\mathbf{3}_{30}$) was obtained as an acetone-insoluble part (73 mg, 87% yield). SEC: $M_n = 19.7$ kDa, $M_w/M_n = 1.16$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.28–5.32 (br, 24H, ArH and NH), 1.86–0.97 (br, 9H, CH_3); FT-IR (KBr, cm^{-1}): 3339 ($\nu_{\text{N-H}}$), 2960 ($\nu_{\text{C-H}}$), 2917 ($\nu_{\text{C-H}}$), 2853 ($\nu_{\text{C-H}}$), 1758 ($\nu_{\text{NHC=O}}$), 1635 ($\nu_{\text{OC=O}}$), 1584 ($\nu_{\text{C=N}}$).

Synthesis of *S*-poly($\mathbf{3}_m\text{-}b\text{-}\mathbf{2}_n\text{-}b\text{-}\mathbf{3}_m$)s. Taking *S*-poly($\mathbf{3}_{30}\text{-}b\text{-}\mathbf{2}_{30}\text{-}b\text{-}\mathbf{3}_{30}$) as an example, the *S*-poly($\mathbf{3}_{30}\text{-}b\text{-}\mathbf{1}_{30}\text{-}b\text{-}\mathbf{3}_{30}$) (65 mg) was re-dissolved in CH_2Cl_2 (1 mL) and cooled to 0 °C. To this solution, trifluoroacetic acid (22 μL , 0.3 mmol) was added. The mixture was warmed to 25 °C and stirred for 12 h. Then, the solution was precipitated into methanol, and the precipitated polymer was collected and dried to afford *S*-poly($\mathbf{3}_{30}\text{-}b\text{-}\mathbf{2}_{30}\text{-}b\text{-}\mathbf{3}_{30}$) as a yellow solid (50 mg, 83% yield). SEC: $M_n = 18.4$ kDa, $M_w/M_n = 1.19$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.28–5.32 (br, 24H, ArH and NH); FT-IR (KBr, cm^{-1}): 3315–2871 ($\nu_{\text{O-H}}$), 3341 ($\nu_{\text{N-H}}$), 2944 ($\nu_{\text{C-H}}$), 1761 ($\nu_{\text{NHC=O}}$), 1637 ($\nu_{\text{OC=O}}$), 1588 ($\nu_{\text{C=N}}$).

R-poly- $\mathbf{3}_m$ was prepared followed the same procedure described above by using Pd(II)/ L^R as the catalyst. Taking *R*-poly- $\mathbf{3}_{30}$ as an example: (75 mg, 75% yield); SEC: $M_n = 6.2$ kDa, $M_w/M_n = 1.14$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.32–6.81 (br, 5H, ArH), 6.75–5.48 (br, 5H, ArH and NH); FT-IR (KBr, cm^{-1}): 3338 ($\nu_{\text{N-H}}$), 2947 ($\nu_{\text{C-H}}$), 1760 ($\nu_{\text{NHC=O}}$), 1635 ($\nu_{\text{OC=O}}$), 1590 ($\nu_{\text{C=N}}$).

R-poly($\mathbf{3}_m\text{-}b\text{-}\mathbf{1}_n$) was prepared followed the same procedure described above by using Pd(II)/ L^R as the catalyst. Taking *R*-poly($\mathbf{3}_{30}\text{-}b\text{-}\mathbf{1}_{30}$) as an example: (92 mg, 83% yield); SEC: $M_n = 12.1$ kDa, $M_w/M_n = 1.15$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C): δ 8.32–5.46 (br, 14H, ArH and NH), 1.88–0.95 (br, 9H, CH_3); FT-IR (KBr, cm^{-1}): 3345 ($\nu_{\text{N-H}}$), 2971 ($\nu_{\text{C-H}}$), 2918 ($\nu_{\text{C-H}}$), 2853 ($\nu_{\text{C-H}}$), 1762 ($\nu_{\text{NHC=O}}$), 1638 ($\nu_{\text{OC=O}}$), 1590 ($\nu_{\text{C=N}}$).

R-poly(**3_m-b-1_n-b-3_m**) was prepared followed the same procedure described above by using Pd(II)/L^R as the catalyst. Taking *R*-poly(**3₃₀-b-1₃₀-b-3₃₀**) as an example: (71 mg, 85% yield); SEC: $M_n = 20.1$ kDa, $M_w/M_n = 1.15$; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.27–5.30 (br, 24H, ArH and NH), 1.88–0.95 (br, 9H, CH₃); FT-IR (KBr, cm⁻¹): 3340 (ν_{N-H}), 2959 (ν_{C-H}), 2920 (ν_{C-H}), 2855 (ν_{C-H}), 1759 ($\nu_{NHC=O}$), 1637 ($\nu_{OC=O}$), 1587 ($\nu_{C=N}$).

R-poly(**3_m-b-2_n-b-3_m**) was prepared followed the same procedure described above by using Pd(II)/L^R as the catalyst. Taking *R*-poly(**3₃₀-b-2₃₀-b-3₃₀**) as an example, SEC: $M_n = 18.9$ kDa, $M_w/M_n = 1.17$; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.32–5.28 (br, ArH and NH), 1.86–0.96 (br, CH₃); FT-IR (KBr, cm⁻¹): 3374–2855 (ν_{O-H}), 3311 (ν_{N-H}), 2940 (ν_{C-H}), 1758 ($\nu_{NHC=O}$), 1630 ($\nu_{OC=O}$), 1568 ($\nu_{C=N}$).

The $\Delta\varepsilon_{364}(\max)$ and m was calculated by equation:

$$\Delta\varepsilon_{364}(n) = \Delta\varepsilon_{364}(\max) \frac{(n - 1 - 2m)}{n}$$

Where $\Delta\varepsilon_{364}(n)$ is the CD intensity at 364 nm ($\Delta\varepsilon_{364}$) of *S*-poly-**1_n**s and *S*-poly-**2_n**s at degree of polymerization n , $\Delta\varepsilon_{364}(\max)$ corresponds to the intrinsic CD intensity at 364 nm of an ideal infinitely long, perfectly one-handed helix, m represents the number of repeating units forming the loose-end domain at a single chain terminus. Fitting the experimental data of $\Delta\varepsilon_{364}(n)$ as a function of DP to the literature-reported loose-end domain model by nonlinear least-squares analysis would allow estimation of both $\Delta\varepsilon_{364}(\max)$ and m .⁷

4. Procedures for Diels–Alder reaction

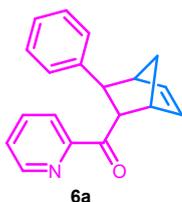
Compound **4a-p** was prepared according to the reported procedure and the structure was confirmed by ¹H NMR.⁵ The compound *S*-poly(**3₃₀-b-2₃₀-b-3₃₀**) (2 mol% relative to pendant carboxyl group) and CuCl₂ (134 μ L, 1 mg/mL, 0.001 mmol) was dissolved in THF/H₂O = 7/3 (v/v, 2.0 mL). After stirring for 12 h at 25 °C, **4a** (20.9 mg, 0.10 mmol) were added. The resultant mixture was stirred for about 1 h, followed by addition of **5** (13.2 mg, 0.20 mmol). The reaction mixture was vigorously stirred for

48 h at $-10\text{ }^{\circ}\text{C}$. After the reaction was accomplished as indicated by thin layer chromatography (TLC) analysis, methanol was added to precipitate the polymer, which was then isolated via centrifugation. While the solution was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography to afford the desired product.

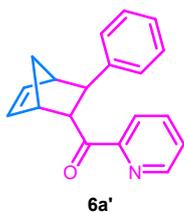
5. Procedures for Michael addition

The compound *S*-poly(**3**₃₀-*b*-**2**₃₀-*b*-**3**₃₀) (2 mol% relative to pendant carboxyl group) and $\text{Cu}(\text{OTf})_2$ (361 μL , 1 mg/mL, 0.001 mmol) was dissolved in CHCl_3 (2.0 mL). After stirring for 12 h at $25\text{ }^{\circ}\text{C}$, **9a** (12.1 mg, 0.10 mmol) were added. The resultant mixture was stirred for about 1 h, followed by addition of **10a** (29.8 mg, 0.20 mmol). The reaction mixture was vigorously stirred for 48 h at $-30\text{ }^{\circ}\text{C}$. After the reaction was accomplished as indicated by TLC analysis, methanol was added to precipitate the polymer, which was then isolated via centrifugation. The solution was evaporated to dryness under reduced pressure, and the residue was purified by silica gel column chromatography to afford the desired product.

6. Spectral data of asymmetric reaction products

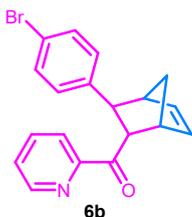


(**6a**): 87% yield. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (d, $J = 4.1$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.74 (t, $J = 7.9$ Hz, 1H), 7.37 (t, $J = 6.4$ Hz, 1H), 7.25–7.20 (m, 4H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.45–6.39 (m, 1H), 5.76 (d, $J = 4.8$ Hz, 1H), 4.49–4.43 (m, 1H), 3.47 (d, $J = 3.7$ Hz, 1H), 3.38 (d, $J = 6.7$ Hz, 1H), 3.02 (d, $J = 3.3$ Hz, 1H), 2.00 (d, $J = 8.4$ Hz, 1H), 1.54 (d, $J = 8.7$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, $T = 25\text{ }^{\circ}\text{C}$): $t_{\text{R}} = 8.6$ min (*exo*), $t_{\text{R}} = 9.6$ min (*exo*), $t_{\text{R}} = 10.4$ min (*endo*, major), $t_{\text{R}} = 13.2$ min (*endo*, minor), 90:10 *dr*, 98% *ee*.



6a'

(6a'): 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.60 (d, $J = 3.9$ Hz, 1H), 7.93 (d, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 8.0$ Hz, 1H), 7.37 (t, $J = 6.4$ Hz, 1H), 7.26–7.20 (m, 4H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.43–6.39 (m, 1H), 5.76 (d, $J = 4.8$ Hz, 1H), 4.50–4.42 (m, 1H), 3.47 (d, $J = 3.7$ Hz, 1H), 3.38 (d, $J = 6.7$ Hz, 1H), 3.02 (d, $J = 3.3$ Hz, 1H), 2.00 (d, $J = 8.4$ Hz, 1H), 1.54 (d, $J = 8.7$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 8.9$ min (*exo*), $t_{\text{R}} = 9.9$ min (*exo*), $t_{\text{R}} = 10.7$ min (*endo*, minor), $t_{\text{R}} = 13.4$ min (*endo*, major), 90:10 *dr*, –95% *ee*.



6b

(6b): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (d, $J = 4.8$ Hz, 1H), 8.00 (d, $J = 7.9$ Hz, 1H), 7.83 (t, $J = 6.9$ Hz, 1H), 7.50–7.43 (m, 1H), 7.39 (d, $J = 7.2$ Hz, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 6.51–6.45 (m, 1H), 5.83 (dd, $J = 5.7, 2.8$ Hz, 1H), 4.46 (t, $J = 4.8$ Hz, 1H), 3.55 (s, 1H), 3.39 (d, $J = 4.6$ Hz, 1H), 3.05 (s, 1H), 2.01 (d, $J = 8.6$ Hz, 1H), 1.62 (d, $J = 8.6$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 12.6$ min (*exo*), $t_{\text{R}} = 13.5$ min (*exo*), $t_{\text{R}} = 15.6$ min (*endo*, major), $t_{\text{R}} = 27.0$ min (*endo*, minor), 94:6 *dr*, 98% *ee*.



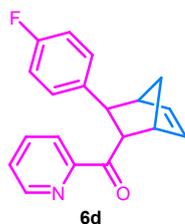
6b'

(6b'): 85% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (d, $J = 4.0$ Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 1H), 7.83 (t, $J = 6.9$ Hz, 1H), 7.51–7.43 (m, 1H), 7.38 (d, $J = 7.3$ Hz, 2H),

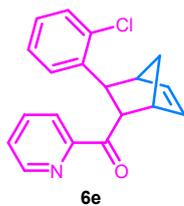
7.18 (d, $J = 8.8$ Hz, 2H), 6.52–6.45 (m, 1H), 5.82 (dd, $J = 5.7, 2.8$ Hz, 1H), 4.46 (t, $J = 4.8$ Hz, 1H), 3.55 (s, 1H), 3.39 (d, $J = 4.4$ Hz, 1H), 3.05 (s, 1H), 2.01 (d, $J = 8.4$ Hz, 1H), 1.61 (d, $J = 8.3$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 12.5$ min (*exo*), $t_R = 13.5$ min (*exo*), $t_R = 15.6$ min (*endo*, minor), $t_R = 26.8$ min (*endo*, major), 93:7 *dr*, –98% *ee*.



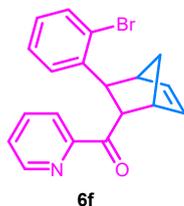
(**6c**): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.61 (d, $J = 4.8$ Hz, 1H), 7.93 (d, $J = 7.9$ Hz, 1H), 7.78–7.74 (m, 1H), 7.39 (t, $J = 4.8$ Hz, 1H), 7.19–7.12 (m, 4H), 6.41 (t, $J = 4.1$ Hz, 1H), 5.76 (d, $J = 3.7$ Hz, 1H), 4.38 (d, $J = 3.8$ Hz, 1H), 3.47 (d, $J = 3.8$ Hz, 1H), 3.34 (d, $J = 7.9$ Hz, 1H), 2.98 (d, $J = 4.2$ Hz, 1H), 1.94 (d, $J = 9.5$ Hz, 1H), 1.55 (d, $J = 8.5$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 8.5$ min (*exo*), $t_R = 8.9$ min (*exo*), $t_R = 9.9$ min (*endo*, major), $t_R = 12.0$ min (*endo*, minor), 90:10 *dr*, 98% *ee*.



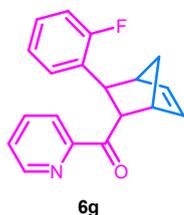
(**6d**): 85% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.61 (d, $J = 4.6$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.80–7.71 (m, 1H), 7.43–7.35 (m, 1H), 7.20 (t, $J = 4.0$ Hz, 2H), 6.88 (t, $J = 8.5$ Hz, 2H), 6.42–6.40 (m, 1H), 5.78–5.72 (m, 1H), 4.39 (t, $J = 4.6$ Hz, 1H), 3.48 (s, 1H), 3.35 (d, $J = 4.7$ Hz, 1H), 2.98 (d, $J = 4.2$ Hz, 1H), 1.96 (d, $J = 8.5$ Hz, 1H), 1.55 (d, $J = 7.5$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 8.6$ min (*exo*), $t_R = 8.7$ min (*exo*), $t_R = 10.1$ min (*endo*, major), $t_R = 12.2$ min (*endo*, minor), 87:13 *dr*, 97% *ee*.



(**6e**): 87% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.66 (d, $J = 4.5$ Hz, 1H), 8.03 (d, $J = 7.9$ Hz, 1H), 7.86–7.78 (m, 1H), 7.58–7.48 (m, 2H), 7.45 (s, 1H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.08–7.03 (m, 1H), 6.56–6.50 (m, 1H), 5.94–5.87 (m, 1H), 4.71–4.65 (m, 1H), 3.61 (s, 1H), 3.48 (d, $J = 3.7$ Hz, 1H), 3.06 (d, $J = 3.3$ Hz, 1H), 1.99 (d, $J = 7.9$ Hz, 1H), 1.60 (s, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, $T = 25$ °C): $t_{\text{R}} = 19.8$ min (*exo*), $t_{\text{R}} = 22.8$ min (*exo*), $t_{\text{R}} = 28.9$ min (*endo*, major), $t_{\text{R}} = 42.8$ min (*endo*, minor), 76:24 *dr*, 94% *ee*.

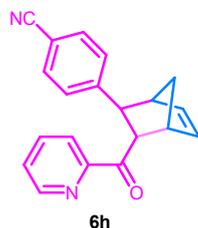


(**6f**): 85% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.66 (d, $J = 4.9$ Hz, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.87–7.78 (m, 1H), 7.54–7.41 (m, 2H), 7.32 (d, $J = 7.9$ Hz, 1H), 7.23 (s, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.55–6.48 (m, 1H), 5.90 (dd, $J = 5.5, 2.8$ Hz, 1H), 4.64–4.57 (m, 1H), 3.58 (d, $J = 7.5$ Hz, 1H), 3.45 (s, 1H), 3.13 (s, 1H), 1.99 (d, $J = 8.5$ Hz, 1H), 1.59 (d, $J = 8.5$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, $T = 25$ °C): $t_{\text{R}} = 8.9$ min (*exo*), $t_{\text{R}} = 10.2$ min (*exo*), $t_{\text{R}} = 12.9$ min (*endo*, major), $t_{\text{R}} = 14.8$ min (*endo*, minor), 74:26 *dr*, 93% *ee*.

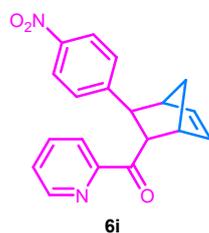


(**6g**): 89% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.66 (d, $J = 4.8$ Hz, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.83 (t, $J = 8.1$ Hz, 1H), 7.48–7.40 (m, 2H), 7.19–7.08 (m, 2H), 7.01–6.90 (m, 1H), 6.52–6.45 (m, 1H), 5.95–5.82 (m, 1H), 4.52 (t, $J = 4.2$ Hz, 1H), 3.53 (d, $J = 5.0$ Hz, 2H), 3.19 (s, 1H), 1.97 (d, $J = 8.5$ Hz, 1H), 1.62 (d, $J = 8.4$ Hz, 1H);

HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 8.6$ min (*exo*), $t_R = 9.7$ min (*exo*), $t_R = 11.9$ min (*endo*, major), $t_R = 14.5$ min (*endo*, minor), 70:30 *dr*, 93% *ee*.



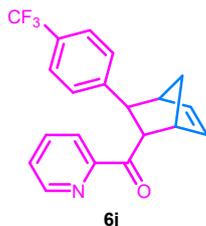
(**6h**): 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (d, $J = 4.5$ Hz, 1H), 8.01 (d, $J = 7.6$ Hz 1H), 7.91–7.78 (m, 1H), 7.63–7.54 (m, 2H), 7.48 (s, 1H), 7.40 (d, $J = 8.3$ Hz, 2H), 6.53–6.42 (m, 1H), 5.87–5.85 (m, 1H), 4.45 (d, $J = 3.9$ Hz, 1H), 3.58 (d, $J = 3.6$ Hz, 1H), 3.49 (d, $J = 4.8$ Hz, 1H), 3.10 (d, $J = 3.3$ Hz, 1H), 1.99 (d, $J = 8.6$ Hz, 1H), 1.65 (dd, $J = 8.6, 1.8$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 8.6$ min (*exo*), $t_R = 9.1$ min (*exo*), $t_R = 9.9$ min (*endo*, major), $t_R = 12.1$ min (*endo*, minor), 88:12 *dr*, 98% *ee*.



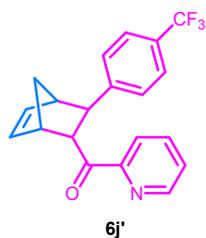
(**6i**): 82% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (s, 1H), 8.14 (s, 1H), 8.12–7.99 (m, 2H), 7.85 (s, 1H), 7.45 (d, $J = 7.5$ Hz, 3H), 6.52–6.46 (m, 1H), 5.90–5.84 (m, 1H), 4.47 (d, $J = 3.9$ Hz, 1H), 3.61 (s, 1H), 3.53 (s, 1H), 3.13 (s, 1H), 2.01 (d, $J = 4.8$ Hz, 1H), 1.67 (d, $J = 8.5$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 10.2$ min (*exo*), $t_R = 12.1$ min (*exo*), $t_R = 17.1$ min (*endo*, major), $t_R = 27.4$ min (*endo*, minor), 72:28 *dr*, 97% *ee*.



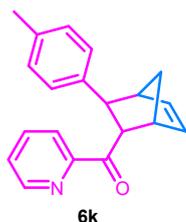
(**6i'**): 87% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.66 (s, 1H), 8.14 (s, 1H), 8.11–7.99 (m, 2H), 7.85 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 3H), 6.51–6.46 (m, 1H), 5.91–5.84 (m, 1H), 4.47 (d, *J* = 3.9 Hz, 1H), 3.61 (s, 1H), 3.53 (s, 1H), 3.13 (s, 1H), 2.01 (d, *J* = 4.7 Hz, 1H), 1.67 (d, *J* = 8.1 Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): *t*_R = 10.2 min (*exo*), *t*_R = 12.3 min (*exo*), *t*_R = 17.1 min (*endo*, minor), *t*_R = 27.9 min (*endo*, major), 61:39 *dr*, –96% *ee*.



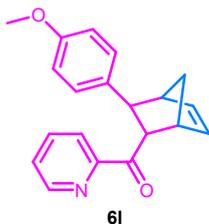
(**6j**): 78% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, *J* = 4.1 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 2H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.52–7.48 (m, 4H), 6.54–6.52 (m, 1H), 5.92 (d, *J* = 4.0 Hz, 1H), 4.52–4.50 (m, 1H), 3.64 (s, 1H), 3.57 (d, *J* = 4.8 Hz, 1H), 3.11 (s, 1H), 2.03 (d, *J* = 8.6 Hz, 1H), 1.72 (d, *J* = 8.6 Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 254 nm, 0.65 mL/min, T = 25 °C): *t*_R = 8.8 min (*exo*), *t*_R = 10.8 min (*exo*), *t*_R = 15.7 min (*endo*, major), *t*_R = 26.2 min (*endo*, minor), 73:27 *dr*, 98% *ee*.



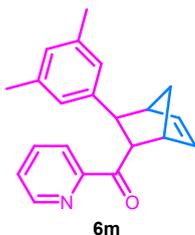
(**6j'**): 82% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, *J* = 3.9 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.51–7.49 (m, 4H), 6.54–6.51 (m, 1H), 5.92 (d, *J* = 4.0 Hz, 1H), 4.52–4.49 (m, 1H), 3.64 (s, 1H), 3.58 (d, *J* = 4.8 Hz, 1H), 3.11 (s, 1H), 2.03 (d, *J* = 8.4 Hz, 1H), 1.72 (d, *J* = 8.6 Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 254 nm, 0.65 mL/min, T = 25 °C): *t*_R = 8.8 min (*exo*), *t*_R = 10.8 min (*exo*), *t*_R = 15.7 min (*endo*, minor), *t*_R = 26.2 min (*endo*, major), 79:21 *dr*, –94% *ee*.



(6k): 82% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.60 (d, $J = 4.2$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.74 (t, $J = 8.6$ Hz, 1H), 7.41–7.34 (m, 1H), 7.14 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 7.9$ Hz, 2H), 6.45–6.38 (m, 1H), 5.78–5.71 (m, 1H), 4.45 (t, $J = 3.6$ Hz, 1H), 3.49–3.43 (m, 1H), 3.33 (d, $J = 3.1$ Hz, 1H), 3.00–2.95 (m, 1H), 2.23 (s, 3H), 1.99 (d, $J = 8.4$ Hz, 1H), 1.52 (d, $J = 7.6$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 7.8$ min (*exo*), $t_{\text{R}} = 8.5$ min (*endo*, major), $t_{\text{R}} = 9.3$ min (*exo*), $t_{\text{R}} = 16.3$ min (*endo*, minor), 90:10 *dr*, 91% *ee*.

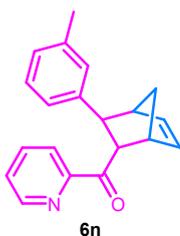


(6l): 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (s, 1H), 8.00 (d, $J = 8.6$ Hz, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.49–7.41 (m, 1H), 7.24 (d, $J = 7.4$ Hz, 2H), 6.82 (d, $J = 7.4$ Hz, 2H), 6.52–6.45 (m, 1H), 5.85–5.78 (m, 1H), 4.49 (d, $J = 4.6$ Hz, 1H), 3.77 (s, 3H), 3.53 (s, 1H), 3.42–3.36 (m, 1H), 3.05–3.00 (m, 1H), 2.06 (d, $J = 8.4$ Hz, 1H), 1.60 (d, $J = 7.5$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 11.3$ min (*exo*), $t_{\text{R}} = 12.2$ min (*exo*), $t_{\text{R}} = 14.6$ min (*endo*, major), $t_{\text{R}} = 21.2$ min (*endo*, minor), 95:5 *dr*, 97% *ee*.

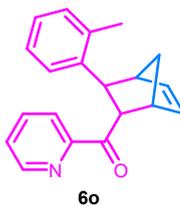


(6m): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.62 (d, $J = 4.6$ Hz, 1H), 7.94 (d, $J = 8.6$ Hz, 1H), 7.79–7.71 (m, 1H), 7.42–7.35 (m, 1H), 7.19 (s, 1H), 6.87 (d, $J = 2.3$

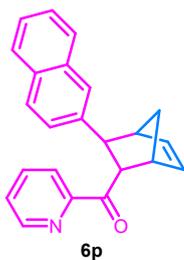
Hz, 2H), 6.41 (t, $J = 5.2$ Hz, 1H), 5.74 (d, $J = 5.2$ Hz, 1H), 4.46–4.39 (m, 1H), 3.50–3.45 (m, 1H), 3.31 (d, $J = 4.9$ Hz, 1H), 3.01 (s, 1H), 2.21 (s, 6H), 2.03 (d, $J = 8.4$ Hz, 1H), 1.52 (s, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 8.9$ min (*exo*), $t_R = 9.9$ min (*exo*), $t_R = 10.8$ min (*endo*, major), $t_R = 13.5$ min (*endo*, minor), 91:9 *dr*, 95% *ee*.



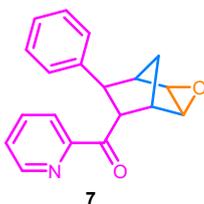
(**6n**): 77% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (d, $J = 4.5$ Hz, 1H), 8.01 (d, $J = 7.8$ Hz, 1H), 7.82 (t, $J = 7.7$ Hz, 1H), 7.47–7.44 (m, 1H), 7.16 (d, $J = 7.4$ Hz, 3H), 6.99 (s, 1H), 6.50–6.48 (m, 1H), 5.82–5.80 (m, 1H), 4.50 (d, $J = 3.5$ Hz, 1H), 3.54 (d, $J = 4.5$ Hz, 1H), 3.41 (d, $J = 4.4$ Hz, 1H), 3.06 (d, $J = 3.6$ Hz, 1H), 2.30 (s, 3H), 2.07 (d, $J = 8.7$ Hz, 1H), 1.59 (s, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 11.9$ min (*exo*), $t_R = 14.5$ min (*exo*), $t_R = 15.6$ min (*endo*, major), $t_R = 23.8$ min (*endo*, minor), 95:5 *dr*, 97% *ee*.



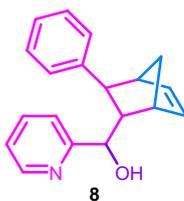
(**6o**): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.74 (d, $J = 39$ Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.89 (t, $J = 7.6$ Hz, 1H), 7.51 (s, 1H), 7.33 (s, 3H), 7.18 (s, 1H), 6.62–6.55 (m, 1H), 5.95–5.89 (m, 1H), 4.68 (t, $J = 4.3$ Hz, 1H), 3.56–3.48 (m, 2H), 3.09 (s, 1H), 2.28 (s, 3H), 2.18 (d, $J = 8.3$ Hz, 1H), 1.68 (d, $J = 8.8$ Hz, 1H), HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C): $t_R = 7.8$ min (*exo*), $t_R = 8.3$ min (*exo*), $t_R = 9.1$ min (*endo*, major), $t_R = 10.1$ min (*endo*, minor), 81:19 *dr*, 95% *ee*.



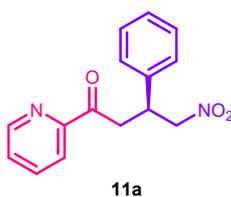
(6p): 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (d, $J = 4.5$ Hz, 1H), 8.04 (d, $J = 7.1$ Hz, 1H), 7.86–7.74 (m, 5H), 7.52–7.35 (m, 5H), 6.63–6.50 (m, 1H), 5.93–5.81 (m, 1H), 4.63 (t, $J = 5.4$ Hz, 1H), 3.60 (s, 1H), 3.24 (s, 1H), 2.17 (d, $J = 8.4$ Hz, 1H), 1.67 (d, $J = 8.5$ Hz, 1H); HPLC (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 8.1$ min (*exo*), $t_{\text{R}} = 9.1$ min (*exo*), $t_{\text{R}} = 9.9$ min (*endo*, major), $t_{\text{R}} = 20.6$ min (*endo*, minor), 88:12 *dr*, 94% *ee*.



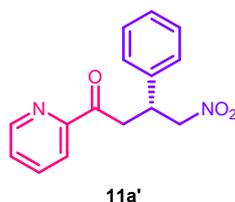
(7): 73% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.69 (d, $J = 4.6$ Hz, 1H), 8.10 (d, $J = 7.8$ Hz, 1H), 7.79 (s, 1H), 7.50–7.47 (m, 1H), 7.32–7.27 (m, 5H), 7.24–7.16 (m, 1H), 4.47 (t, $J = 3.8$ Hz, 1H), 3.70 (d, $J = 4.1$ Hz, 1H), 3.47 (d, $J = 3.7$ Hz, 1H), 3.28–3.24 (m, 1H), 3.02 (d, $J = 4.3$ Hz, 1H), 2.83 (s, 1H), 1.58 (s, 1H).



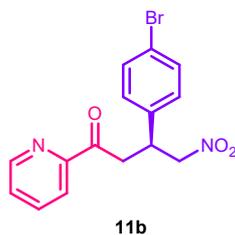
(8): 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.42 (d, $J = 4.6$ Hz, 1H), 7.46–7.43 (m, 1H), 7.14–6.97 (m, 5H), 6.89–6.86 (m, 2H), 6.46 (s, 1H), 6.37 (s, 1H), 4.31–4.26 (m, 1H), 3.45–3.42 (m, 1H), 3.23 (s, 1H), 2.78 (s, 1H), 2.58 (s, 1H), 2.39–2.35 (m, 1H), 1.77–1.74 (m, 1H), 1.55–1.51 (m, 1H).



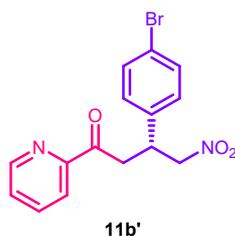
(11a): 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (s, 1 H), 7.99 (d, $J = 3.8$ Hz, 1H), 7.83 (s, 1 H), 7.39–7.34 (m, 2 H), 7.26 (s, 2H), 7.14 (d, $J = 7.4$ Hz, 2H), 4.73–4.63 (m, 1H), 4.62–4.54 (m, 1H), 4.26 (t, $J = 7.0$ Hz, 1H), 3.94 (d, $J = 12.2$ Hz, 1H), 3.68–3.57 (m, 1H); HPLC (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 25.9$ min (major), $t_{\text{R}} = 31.0$ min (minor), 98% *ee*.



(11a'): 84% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (s, 1 H), 7.98 (d, $J = 4.1$ Hz, 1H), 7.83 (s, 1 H), 7.38–7.34 (m, 2 H), 7.26 (s, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 4.74–4.63 (m, 1H), 4.62–4.55 (m, 1H), 4.26 (t, $J = 7.4$ Hz, 1H), 3.94 (d, $J = 12.2$ Hz, 1H), 3.67–3.58 (m, 1H); HPLC (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 25.9$ min (minor), $t_{\text{R}} = 31.0$ min (major), –96% *ee*.

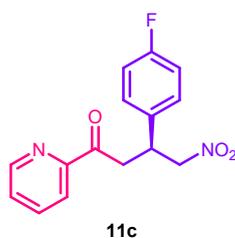


(11b): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.66 (d, $J = 4.7$ Hz, 1H), 8.03 (d, $J = 7.8$ Hz, 1H), 7.83 (t, $J = 7.1$ Hz, 1H), 7.58–7.45 (m, 3H), 7.24 (d, $J = 8.0$ Hz, 2H), 4.81 (dd, $J = 12.6, 6.5$ Hz, 1H), 4.69 (dd, $J = 12.6, 8.4$ Hz, 1H), 4.32–4.21 (m, 1H), 3.81 (dd, $J = 18.2, 7.3$ Hz, 1H), 3.63 (dd, $J = 18.2, 6.9$ Hz, 1H); HPLC (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): $t_{\text{R}} = 19.4$ min (major), $t_{\text{R}} = 21.7$ min (minor), 92% *ee*.

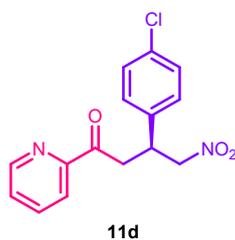


(11b'): 85% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (d, $J = 4.4$ Hz, 1H), 8.03 (d,

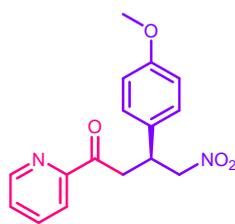
$J = 8.0$ Hz, 1H), 7.83 (t, $J = 7.1$ Hz, 1H), 7.58–7.46 (m, 3H), 7.24 (d, $J = 8.0$ Hz, 2H), 4.81 (dd, $J = 12.2, 6.8$ Hz, 1H), 4.69 (dd, $J = 12.6, 8.2$ Hz, 1H), 4.31–4.22 (m, 1H), 3.81 (dd, $J = 18.2, 7.8$ Hz, 1H), 3.63 (dd, $J = 18.2, 7.9$ Hz, 1H); HPLC (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): $t_R = 19.6$ min (minor), $t_R = 21.9$ min (major), –87% *ee*.



(11c): 85% yield. ^1H NMR (400 MHz, CDCl_3): δ 8.67 (d, $J = 4.3$ Hz, 1H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.84 (t, $J = 7.9$ Hz, 1H), 7.53–7.45 (m, 1H), 7.33–7.26 (m, 2H), 6.99 (t, $J = 8.2$ Hz, 2H), 4.84–4.73 (m, 1H), 4.72–4.57 (m, 1H), 4.34–4.16 (m, 1H), 3.78 (d, $J = 5.8$ Hz, 1H), 3.67–3.54 (m, 1H); HPLC (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): $t_R = 21.2$ min (major), $t_R = 23.6$ min (minor), 94% *ee*.

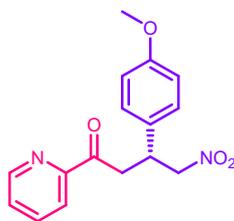


(11d): 82% yield. ^1H NMR (400 MHz, CDCl_3): δ 8.66 (d, $J = 4.4$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.87–7.80 (m, 1H), 7.48 (d, $J = 5.4$ Hz, 1H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.13–7.06 (m, 2H), 4.83–4.73 (m, 1H), 4.70–4.60 (m, 1H), 4.29–4.17 (m, 1H), 3.85–3.81 (m, 1H), 3.65–3.54 (m, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): $t_R = 23.1$ min (major), $t_R = 27.7$ min (minor), 95% *ee*.



11e

(11e): 85% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.69–8.63 (m, 1H), 7.99 (d, $J = 8.3$ Hz, 1H), 7.82 (t, $J = 7.7$ Hz, 1H), 7.52–7.45 (m, 1H), 7.26–7.19 (m, 3H), 6.84 (d, $J = 8.2$ Hz, 2H), 4.80–4.71 (m, 1H), 4.63 (dd, $J = 12.3, 8.3$ Hz, 1H), 4.26–4.14 (m, 1H), 3.77 (s, 3H), 3.59 (dd, $J = 18.1, 7.1$ Hz, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, $T = 25$ °C): $t_R = 20.2$ min (major), $t_R = 21.9$ min (minor), 95% *ee*.



11e'

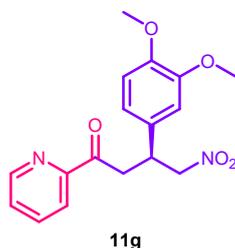
(11e'): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68–8.63 (m, 1H), 7.99 (d, $J = 8.1$ Hz, 1H), 7.82 (t, $J = 7.8$ Hz, 1H), 7.53–7.45 (m, 1H), 7.27–7.19 (m, 3H), 6.83 (d, $J = 8.2$ Hz, 2H), 4.81–4.71 (m, 1H), 4.63 (dd, $J = 12.1, 8.2$ Hz, 1H), 4.26–4.14 (m, 1H), 3.77 (s, 3H), 3.58 (dd, $J = 18.1, 7.1$ Hz, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, $T = 25$ °C): $t_R = 19.7$ min (minor), $t_R = 21.3$ min (major), –96% *ee*.



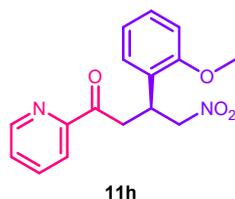
11f

(11f): 80% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.70 (d, $J = 5.5$ Hz, 1H), 8.01 (dd, $J = 8.1, 1.6$ Hz, 2H), 7.91–7.82 (m, 2H), 7.64–7.51 (m, 2H), 7.30 (s, 1H), 4.84 (dd, $J = 12.3, 6.8$ Hz, 1H), 4.72 (dd, $J = 12.3, 8.2$ Hz, 1H), 4.29–4.26 (m, 1H), 3.86 (dd, $J = 18.2, 7.1$ Hz, 1H), 3.65 (dd, $J = 18.1, 7.0$ Hz, 1H), 2.34 (s, 3H); HPLC (Daicel

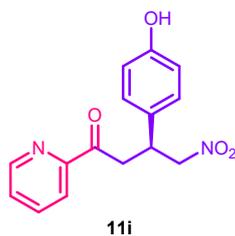
Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): t_R = 28.6 min (major), t_R = 30.5 min (minor), 92% *ee*.



(**11g**): 83% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.73–8.67 (m, 1H), 7.99 (d, J = 7.2 Hz, 1H), 7.83 (t, J = 7.7 Hz, 1H), 7.53–7.45 (m, 1H), 6.89–6.83 (m, 1H), 6.83–6.76 (m, 2H), 4.76 (dd, J = 12.3, 6.9 Hz, 1H), 4.66 (dd, J = 12.3, 8.2 Hz, 1H), 4.24–4.21 (m, 1H), 3.88–3.85 (m, 7H), 3.57 (dd, J = 18.0, 6.9 Hz, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): t_R = 39.3 min (major), t_R = 41.3 min (minor), 98% *ee*.



(**11h**): 82% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): 8.66 (d, J = 4.0 Hz, 1H), 7.87–7.73 (m, 2H), 7.49–7.41 (m, 1H), 7.18–7.14 (m, 1H), 6.94 (t, J = 7.4 Hz, 2H), 6.84–6.78 (m, 1H), 5.01–4.68 (m, 3H), 4.48 (dd, J = 12.4, 3.9 Hz, 1H), 4.02–4.00 (m, 1H), 3.89 (s, 3H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): t_R = 36.7 min (major), t_R = 56.3 min (minor), 97% *ee*.



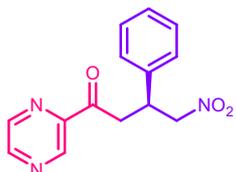
(**11i**): 81% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (d, J = 5.4 Hz, 1H), 8.00 (t, J = 6.6 Hz, 1H), 7.89–7.79 (m, 1H), 7.51–7.50 (m, 1H), 7.17–7.16 (m, 2H), 6.80–6.72 (m, 2H), 4.76 (m, 1H), 4.68–4.58 (m, 1H), 4.20–4.19 (m, 1H), 3.80–3.28 (m, 1H), 3.59–3.57 (m, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5

mL/min, 254 nm, T = 25 °C): t_R = 31.2 min (major), t_R = 45.8 min (minor), 97% *ee*.



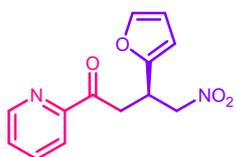
11j

(11j): 87% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (d, J = 5.4 Hz, 1 H), 8.41 (d, J = 4.0 Hz, 1H), 8.04–7.97 (m, 1H), 7.88–7.79 (m, 1H), 7.71–7.59 (m, 2H), 7.49 (dd, J = 8.3, 4.6 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 5.08 (dd, J = 13.6, 10.3 Hz, 1H), 5.02–4.92 (m, 1H), 4.78–4.67 (m, 1H), 3.89 (dd, J = 18.6, 6.5 Hz, 1H), 3.78 (dd, J = 18.6, 7.5 Hz, 1H), HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): t_R = 36.5 min (major), t_R = 40.0 min (minor), 97% *ee*.



11k

(11k): 82% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.17 (d, J = 3.5 Hz, 1H), 8.77 (d, J = 4.5 Hz, 1H), 8.63 (dd, J = 2.5, 1.5 Hz, 1H), 7.36–7.26 (m, 5H), 4.78 (dd, J = 12.5, 7.2 Hz, 1H), 4.69 (dd, J = 12.5, 7.7 Hz, 1H), 7.28–4.21 (m, 1H), 3.82 (dd, J = 18.2, 7.3 Hz, 1H), 3.60 (dd, J = 18.3, 6.8 Hz, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): t_R = 34.4 min (major), t_R = 36.1 min (minor), 98% *ee*.



11l

(11l): 84% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (d, J = 4.9 Hz, 1H), 8.04 (d, J = 7.5 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.54–7.47 (m, 1H), 7.34 (s, 1H), 6.28 (s, 1H), 6.20 (d, J = 3.6 Hz, 1H), 4.77 (d, J = 7.0 Hz, 2H), 4.36 (q, J = 7.3 Hz, 1H), 3.84 (dd, J = 18.3, 6.7 Hz, 1H), 3.64 (dd, J = 18.4, 7.2 Hz, 1H); HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C): t_R = 36.4 min (major), t_R

= 38.0 min (minor), 99% *ee*.

Table S1 Characterization data for helical polyisocyanides^a

Entry	Polymer	M_n^b (kDa)	M_w/M_n^b	Yield ^c (%)	$\Delta\epsilon_{364}^d$ (M ⁻¹ cm ⁻¹)
1	<i>S</i> -poly- 1 ₁₀	2.1	1.11	89	-0.47
2	<i>S</i> -poly- 1 ₂₀	4.4	1.13	86	-0.60
3	<i>S</i> -poly- 1 ₃₀	6.5	1.12	88	-0.74
4	<i>S</i> -poly- 1 ₄₀	8.8	1.12	84	-0.79
5	<i>S</i> -poly- 1 ₁₀₀	22.3	1.13	88	-0.89
6	<i>S</i> -poly- 1 ₂₀₀	43.5	1.14	87	-0.94
7	<i>R</i> -poly- 1 ₂₀₀	42.9	1.12	85	0.95
8	<i>S</i> -poly- 2 ₁₀	1.8	1.17	86	-0.73
9	<i>S</i> -poly- 2 ₂₀	3.3	1.17	84	-0.93
10	<i>S</i> -poly- 2 ₃₀	4.9	1.18	80	-1.14
11	<i>S</i> -poly- 2 ₄₀	6.5	1.16	85	-1.22
12	<i>S</i> -poly- 2 ₁₀₀	16.8	1.17	82	-1.45
13	<i>S</i> -poly- 2 ₂₀₀	33.5	1.17	89	-1.65
14	<i>R</i> -poly- 2 ₂₀₀	32.9	1.16	87	1.65
15	<i>S</i> -poly- 3 ₅₀	12.1	1.11	87	-6.25
16	<i>S</i> -poly(3 ₅₀ - <i>b</i> - 1 ₃₀)	16.8	1.16	84	-5.89
17	<i>S</i> -poly(3 ₁₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₁₀)	9.6	1.18	79	-3.38
18	<i>S</i> -poly(3 ₂₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₂₀)	14.9	1.19	83	-5.38
19	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	18.4	1.19	85	-7.02
20	<i>S</i> -poly(3 ₅₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₅₀)	31.5	1.19	80	-8.26
21	<i>S</i> -poly(3 ₇₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₇₀)	41.2	1.18	81	-8.33
22	<i>S</i> -poly(3 ₅₀ - <i>b</i> - 2 ₁₀ - <i>b</i> - 3 ₅₀)	28.6	1.19	84	-6.54
23	<i>S</i> -poly(3 ₅₀ - <i>b</i> - 2 ₂₀ - <i>b</i> - 3 ₅₀)	30.1	1.18	81	-5.37
24	<i>S</i> -poly(3 ₅₀ - <i>b</i> - 2 ₄₀ - <i>b</i> - 3 ₅₀)	34.7	1.18	77	-8.21
25	<i>R</i> -poly(3 ₅₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₅₀)	32.3	1.19	83	8.35

^aThe polymers were synthesized according to Fig. 1 using Pd(II)/L^S or Pd(II)/L^R catalysts. ^bThe M_n and M_w/M_n were determined by SEC with equivalent to polystyrene standards. ^cIsolated yields. ^dThe data were obtained from CD recorded in THF solution at 25 °C.

Table S2 Optimization of the reaction conditions^a

Entry	Ligand	Copper catalyst	solvent	T (°C)	yield ^b (%)	ee ^c (%)	dr ^c
1	<i>S</i> -poly- 2 ₄₀	CuCl ₂	THF	25	85	11	90:10
2	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	THF	25	79	14	90:10
3	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	CHCl ₃	25	83	11	89:11
4	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	AcOEt	25	82	11	92:8
5	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	MeCN	25	85	13	91:9
6	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	DMF	25	79	14	91:9
7	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	THF/H ₂ O (7/3)	25	85	16	90:10
8	<i>S</i> -poly- 2 ₂₀₀	Cu(NO ₃) ₂	THF/H ₂ O (7/3)	25	83	10	90:10
9	<i>S</i> -poly- 2 ₂₀₀	CuBr ₂	THF/H ₂ O (7/3)	25	84	14	92:8
10	<i>S</i> -poly- 2 ₂₀₀	Cu(OTf) ₂	THF/H ₂ O (7/3)	25	83	9	90:10
11	<i>S</i> -poly- 2 ₂₀₀	CuCl ₂	THF/H ₂ O (7/3)	-10	80	17	90:10
12	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF	25	85	47	90:10
13	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	AcOEt	25	78	41	88:12
14	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	MeCN	25	70	38	90:10
15	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	DMF	25	78	35	89:11
16	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	^{-d}	THF	25	^{-d}	^{-d}	^{-d}
17	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (1/1)	25	82	58	91:9
18	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	MeCN/H ₂ O (1/1)	25	80	43	90:10
19	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	DMF/H ₂ O (1/1)	25	86	36	89:11
20	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (1/2)	25	75	65	92:8
21	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (2/1)	25	86	63	91:9
22	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (4/1)	25	84	68	91:9
23	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (7/3)	25	85	71	90:10
24	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	Cu(NO ₃) ₂	THF/H ₂ O (7/3)	25	87	59	89:11
25	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuBr ₂	THF/H ₂ O (7/3)	25	83	67	92:8
26	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	Cu(OTf) ₂	THF/H ₂ O (7/3)	25	84	65	92:8
27	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (7/3)	25	87	53	91:9
28 ^e	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (7/3)	25	68	50	90:10
29 ^f	<i>S</i> -poly(3 ₃₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₃₀)	CuCl ₂	THF/H ₂ O (7/3)	25	75	52	90:10
30	<i>S</i> -poly(3 ₇₀ - <i>b</i> - 2 ₃₀ - <i>b</i> - 3 ₇₀)	CuCl ₂	THF/H ₂ O (7/3)	25	86	77	87:13
31	<i>S</i> -poly(3 ₅₀ - <i>b</i> - 2 ₄₀ - <i>b</i> - 3 ₅₀)	CuCl ₂	THF/H ₂ O (7/3)	0	86	72	91:9

^aAll reactions were performed with **4a** (0.1 mmol), polymer (2 mol% relative to pendant carboxyl group), copper salt (0.001 mmol), and **5** (0.2 mmol) in 2 mL of solvent. ^bIsolated yield. ^cee and dr were determined by HPLC. ^dIn the absence of copper salt, no product was formed. ^eReactions were performed with polymer (1 mol% relative to pendant carboxyl group). ^fReactions were performed with polymer (1.5 mol% relative to pendant carboxyl group).

Table S3 The *ee* dependence on substrate concentration^a

Entry	4a (eq. vs 5)	yield ^b (%)	<i>ee</i> ^c (%)	<i>dr</i> ^c
1	0.5	85	98	90:10
2	0.1	83	98	90:10
3	0.05	83	97	89:11
4	0.01	81	94	90:10
5	0.0025	85	90	91:9

^aAll reactions were performed with *S*-poly(**3**_{50-*b*}-**2**_{30-*b*}-**3**₅₀) (1 mol% relative to pendant carboxyl groups), **5** (0.2 mmol) and CuCl₂ (0.001 mmol), in 2 mL of a THF/H₂O (7:3) solvent mixture. ^bIsolated yield. ^c*ee* and *dr* were determined by HPLC.

Table S4 Optimization of polymer catalysts^a

Entry	Ligand	Copper catalyst	solvent	T(°C)	yield ^b (%)	<i>ee</i> ^c (%)
1	<i>R</i> -poly- 2 ₃₀	CuCl ₂	THF	25	75	11
2	<i>R</i> -poly(3 _{30-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₃₀)	CuCl ₂	THF	25	81	52
3	<i>R</i> -poly(3 _{30-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₃₀)	CuCl ₂	AcOEt	25	73	52
4	<i>R</i> -poly(3 _{30-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₃₀)	CuCl ₂	MeCN	25	85	50
5	<i>R</i> -poly(3 _{30-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₃₀)	CuCl ₂	DMF	25	79	48
6	<i>R</i> -poly(3 _{30-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₃₀)	Cu(NO ₃) ₂	CHCl ₃	25	84	57
7	<i>R</i> -poly(3 _{30-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₃₀)	CuBr ₂	CHCl ₃	25	76	61
8	<i>R</i> -poly(3 _{70-<i>b</i>} - 2 _{40-<i>b</i>} - 3 ₇₀)	Cu(OTf) ₂	CHCl ₃	25	80	70
9	<i>R</i> -poly(3 _{50-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₅₀)	Cu(OTf) ₂	CHCl ₃	-10	84	87
10	<i>R</i> -poly(3 _{50-<i>b</i>} - 2 _{30-<i>b</i>} - 3 ₅₀)	Cu(OTf) ₂	CHCl ₃	-20	79	92

^aAll reactions were carried out with **9a** (0.1 mmol), polymer (2 mol% relative to pendant carboxyl groups), copper salt (0.001 mmol mmol), and **10a** (0.2 mmol) in 2 mL of solvent. ^bIsolated yield. ^c*ee* and *dr* were determined by HPLC.

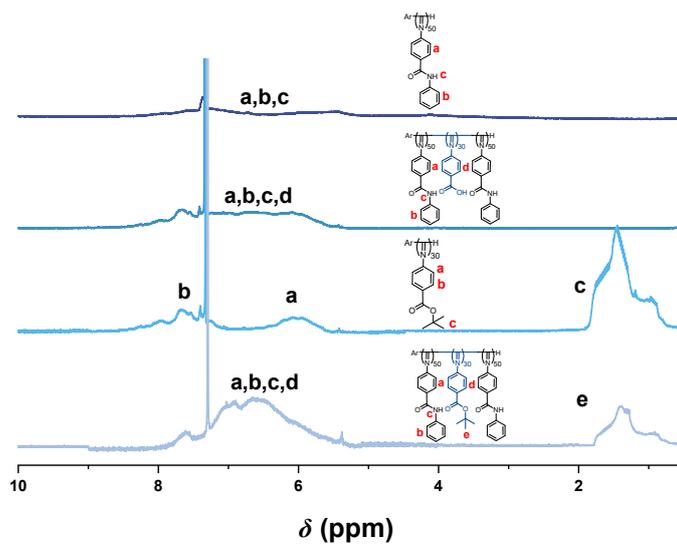


Fig. S1 ^1H NMR (400 MHz) spectra of *S*-poly- $\mathbf{3}_{50}$, *S*-poly($\mathbf{3}_{50}$ -*b*- $\mathbf{2}_{30}$ -*b*- $\mathbf{3}_{50}$), *S*-poly- $\mathbf{1}_{30}$ and *S*-poly($\mathbf{3}_{50}$ -*b*- $\mathbf{1}_{30}$ -*b*- $\mathbf{3}_{50}$) measured in CDCl_3 at 25 °C.

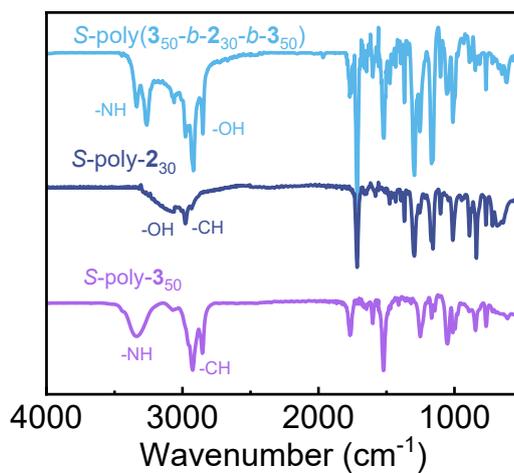


Fig. S2 FT-IR spectra of *S*-poly($\mathbf{3}_{50}$ -*b*- $\mathbf{2}_{30}$ -*b*- $\mathbf{3}_{50}$), *S*-poly- $\mathbf{2}_{30}$ and *S*-poly- $\mathbf{3}_{50}$ measured at 25 °C using KBr pellets.

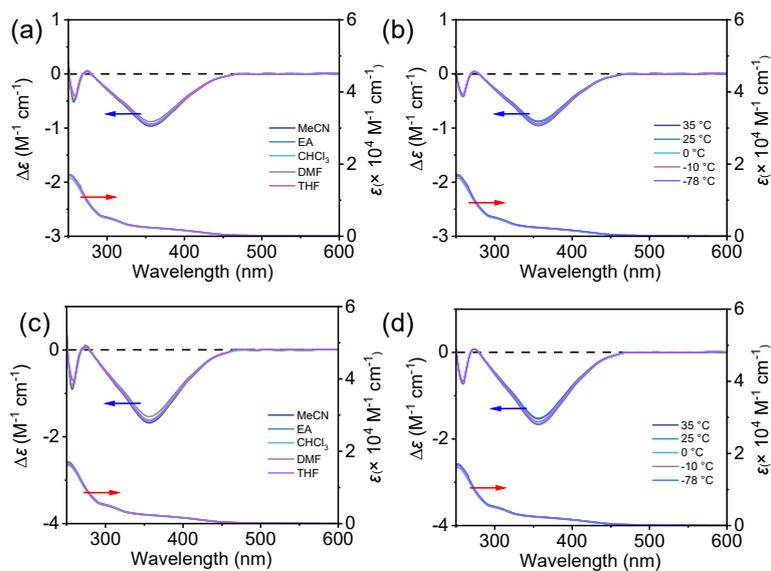


Fig. S3 CD and UV-vis spectra of *S*-poly-1₂₀₀ measured in different solvents at room temperature (a), and in THF at different temperatures (b) (*c* = 0.2 mg/mL). CD and UV-vis spectra of *S*-poly-2₂₀₀ measured in different solvents at room temperature (c), and in THF at different temperatures (d) (*c* = 0.2 mg/mL).

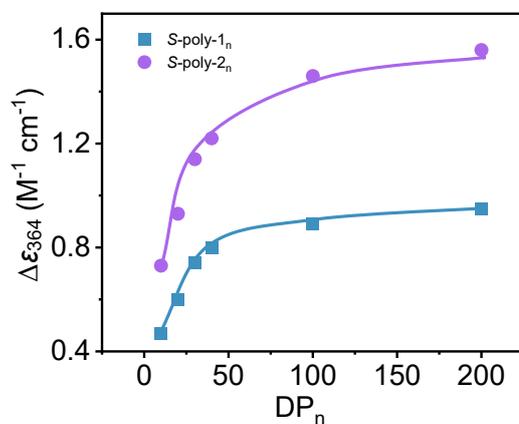


Fig. S4 Fitting curves of *S*-poly-1_n and *S*-poly-2_n based on the loose-end-domain model.

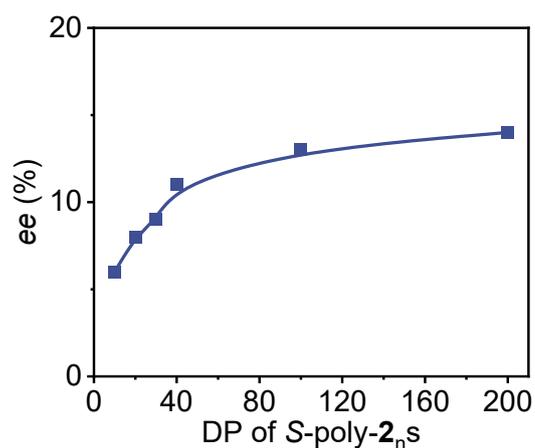


Fig. S5 Plot of the *ee* value of product **6a** as a function of the DP of *S*-poly-**2_nS**.

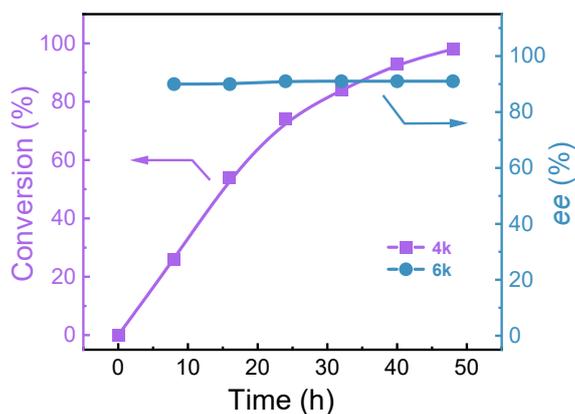


Fig. S6 Plots of conversion of **4k** and *ee* value of **6k** versus the reaction time.

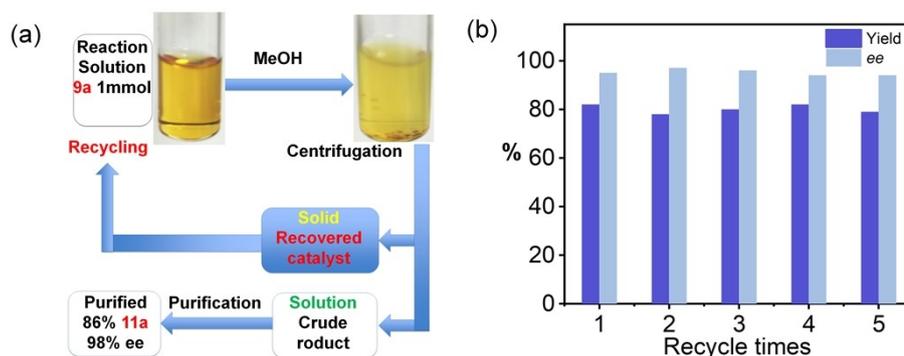


Fig. S7 (a) Process of the catalyst recovery and recycling. (b) Yields and *ee* values of products obtained by asymmetric Michael addition using the recovered *R*-poly(**3₅₀-b-2₃₀-b-3₅₀**): yield remained at ~80% (no obvious change), *ee* value slightly decreased from 97% to 94%.

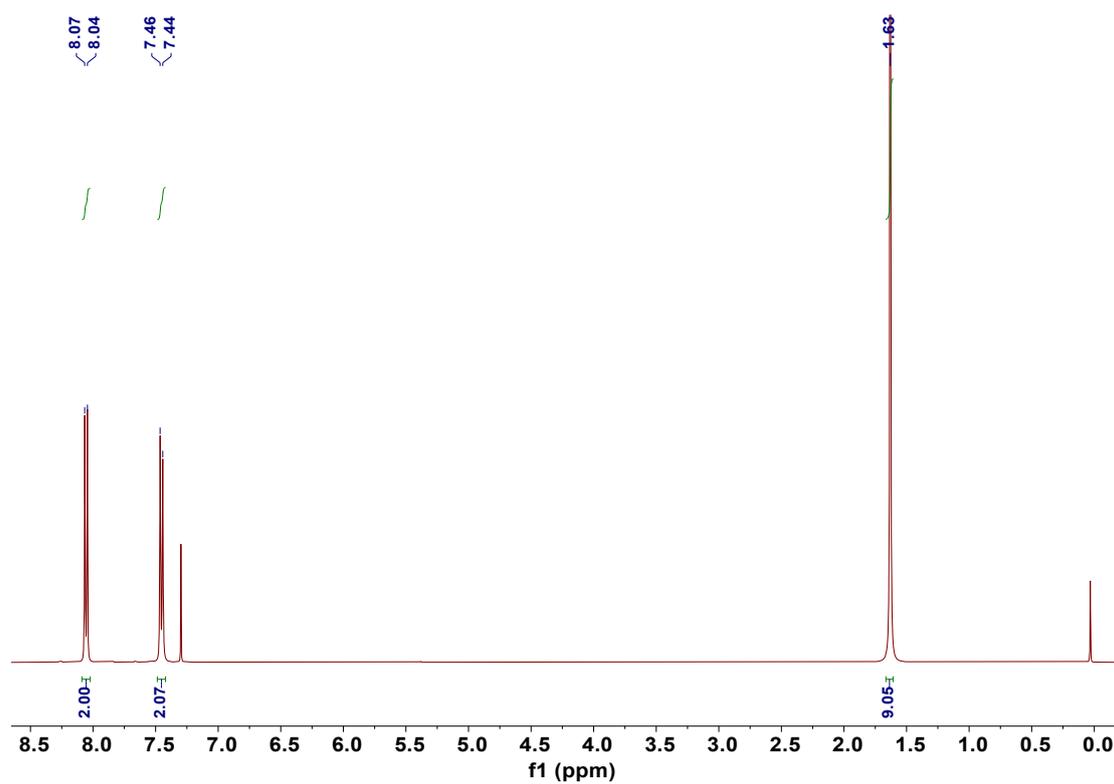


Fig. S8 ^1H NMR (400 MHz) spectrum of **1** measured in CDCl_3 at 25 $^\circ\text{C}$.

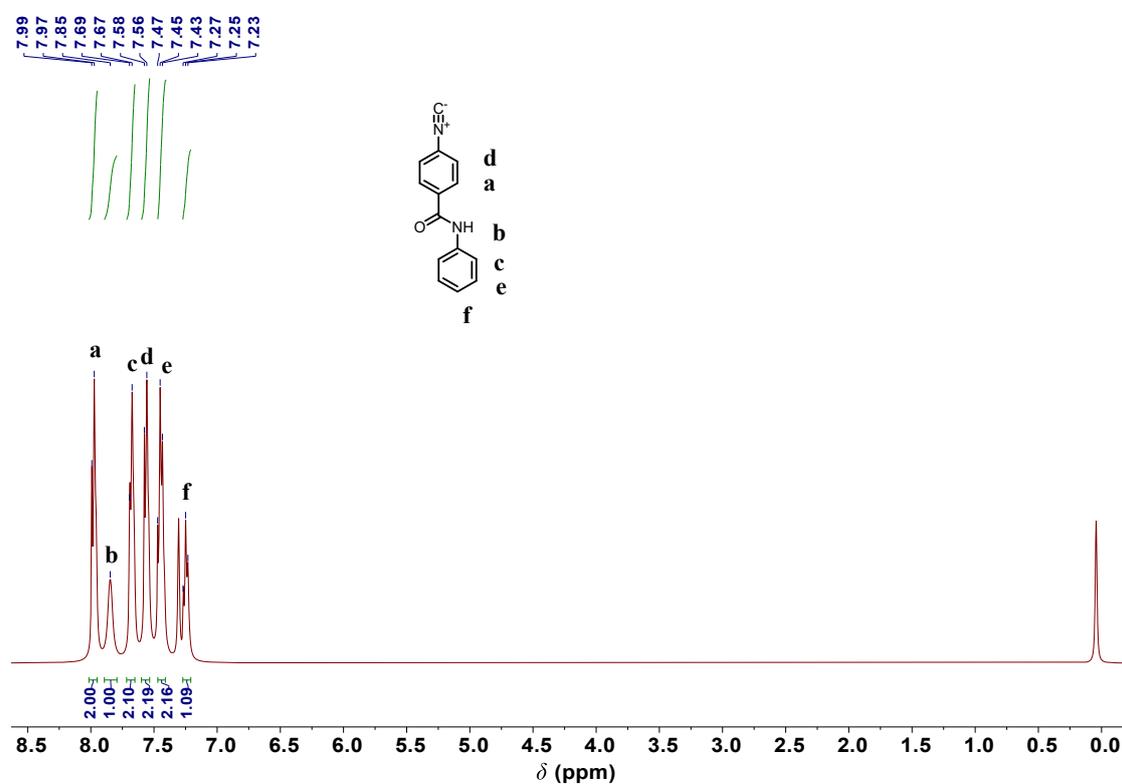


Fig. S9 ^1H NMR (400 MHz) spectrum of **3** measured in CDCl_3 at 25 $^\circ\text{C}$.

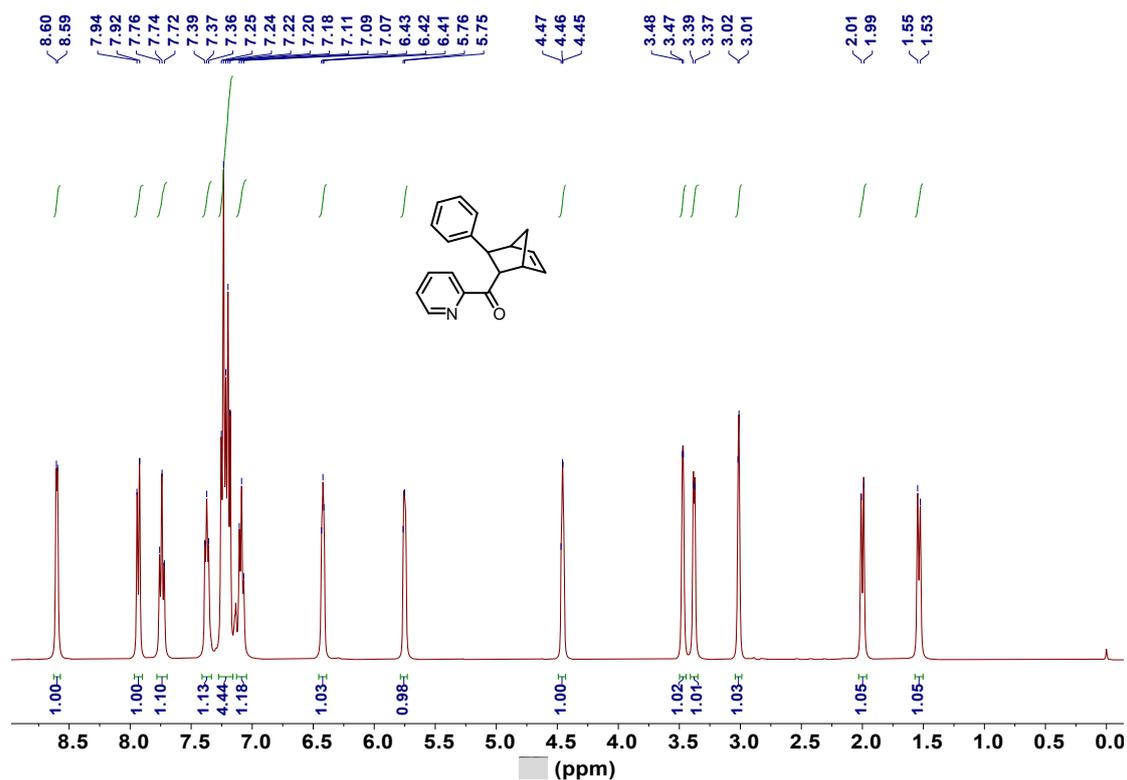


Fig. S10 ^1H NMR (400 MHz) spectrum of **6a** measured in CDCl_3 at 25 °C.

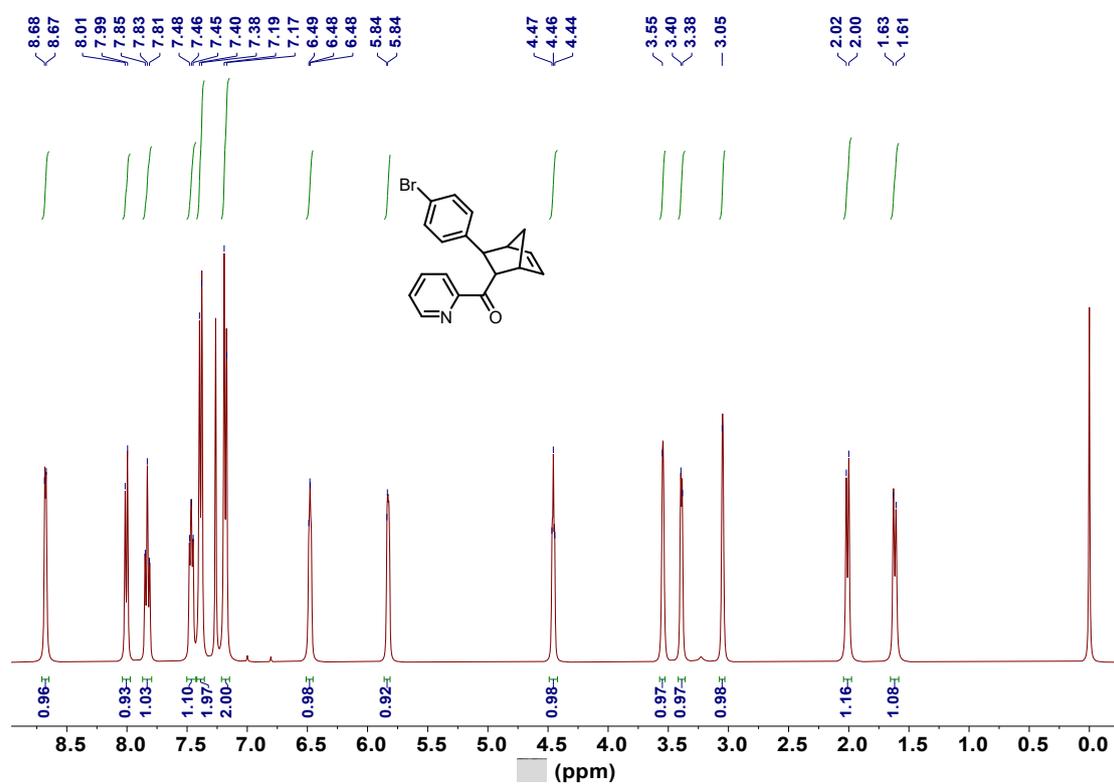


Fig. S11 ^1H NMR (400 MHz) spectrum of **6b** measured in CDCl_3 at 25 °C.

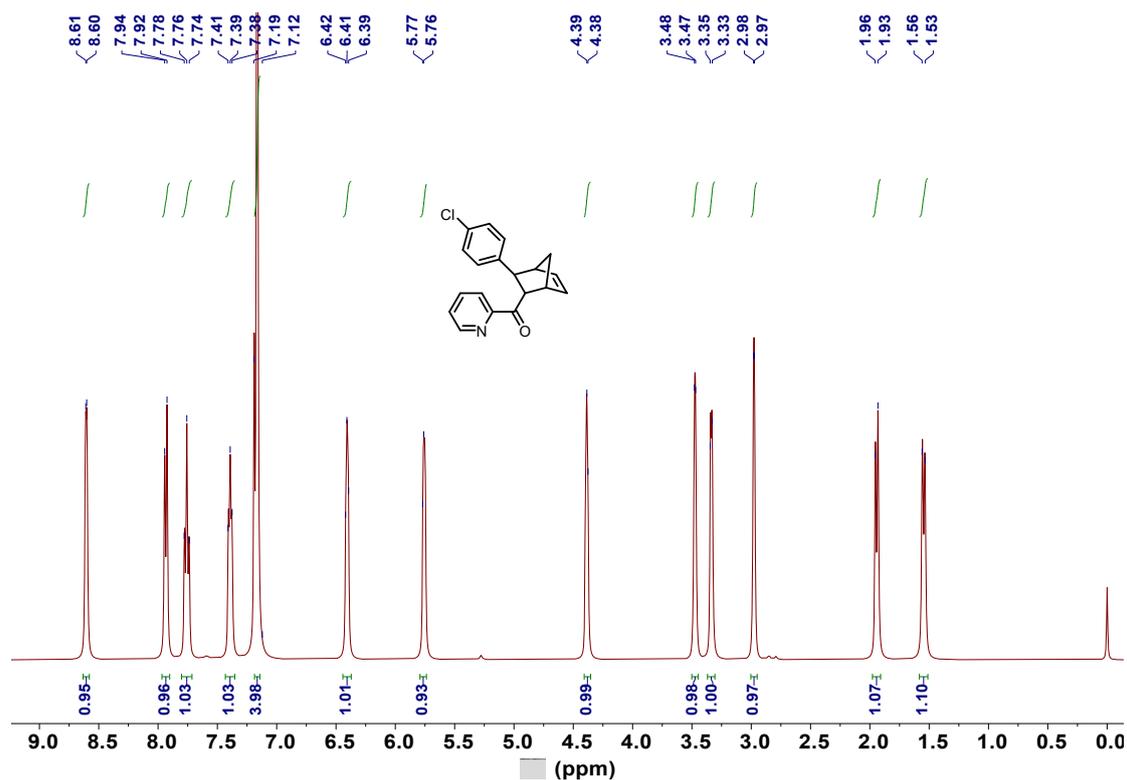


Fig. S12 ^1H NMR (400 MHz) spectrum of **6c** measured in CDCl_3 at 25 °C.

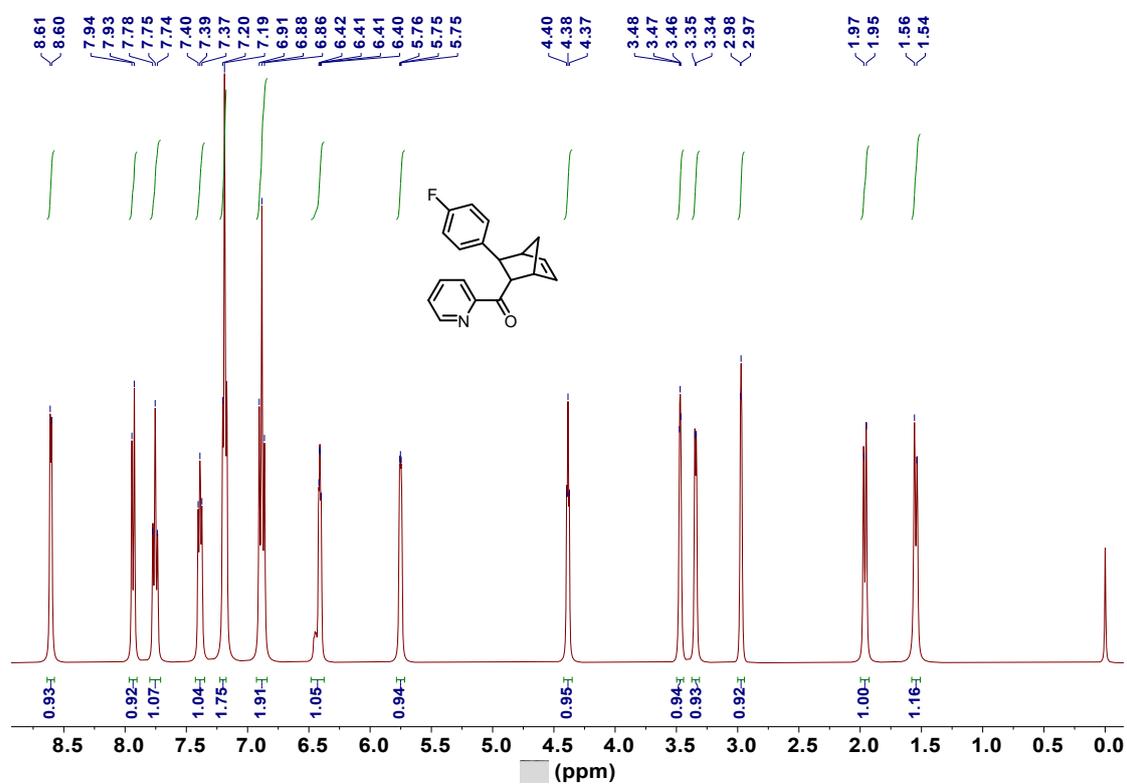


Fig. S13 ^1H NMR (400 MHz) spectrum of **6d** measured in CDCl_3 at 25 °C.

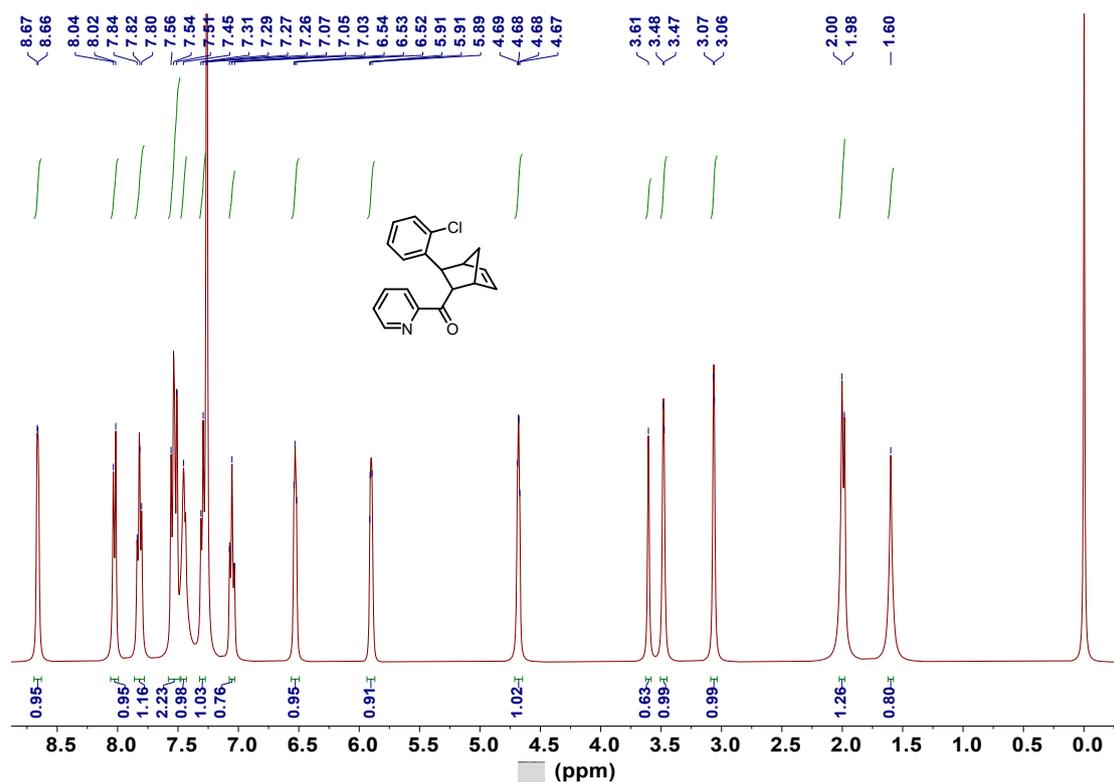


Fig. S14 ^1H NMR (400 MHz) spectrum of **6e** measured in CDCl_3 at 25 °C.

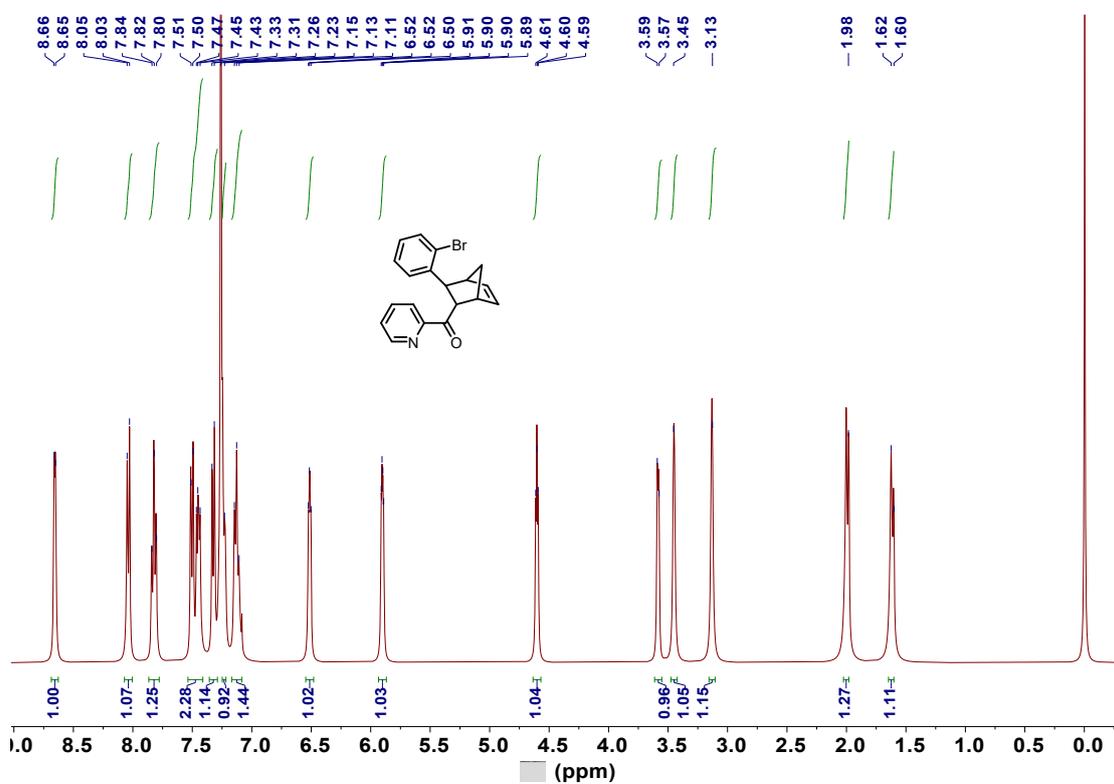


Fig. S15 ^1H NMR (400 MHz) spectrum of **6f** measured in CDCl_3 at 25 °C.

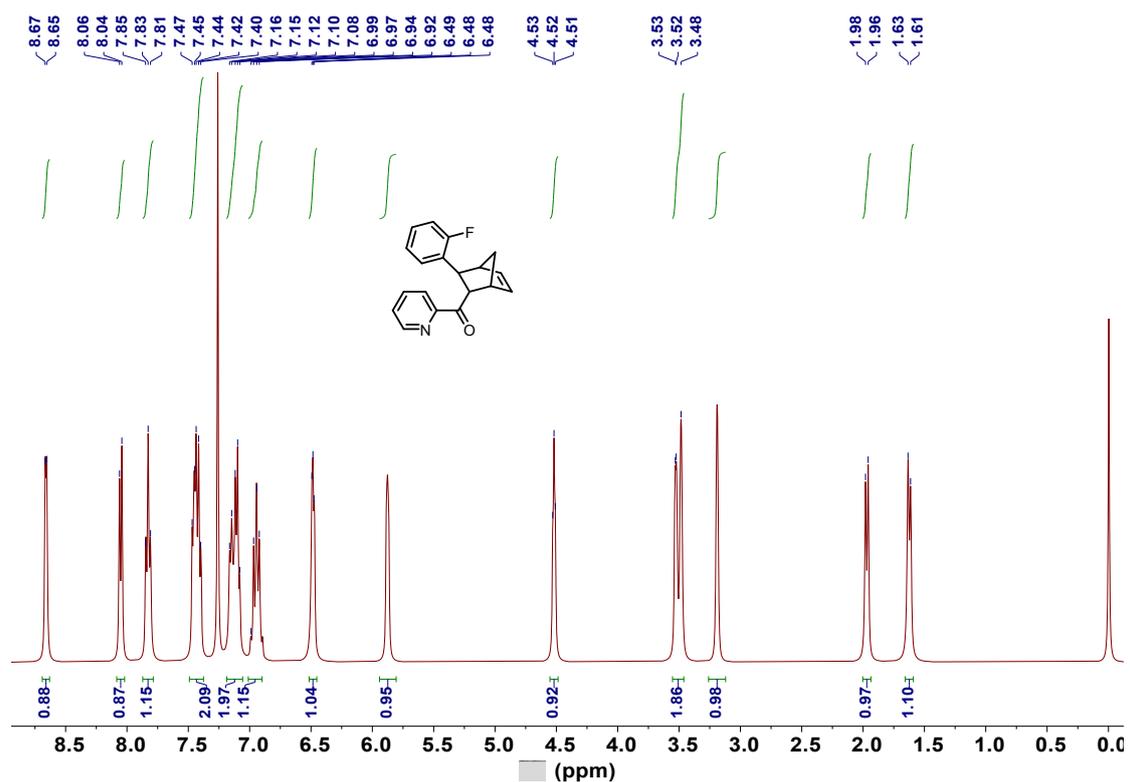


Fig. S16 ^1H NMR (400 MHz) spectrum of **6g** measured in CDCl_3 at 25 $^\circ\text{C}$.

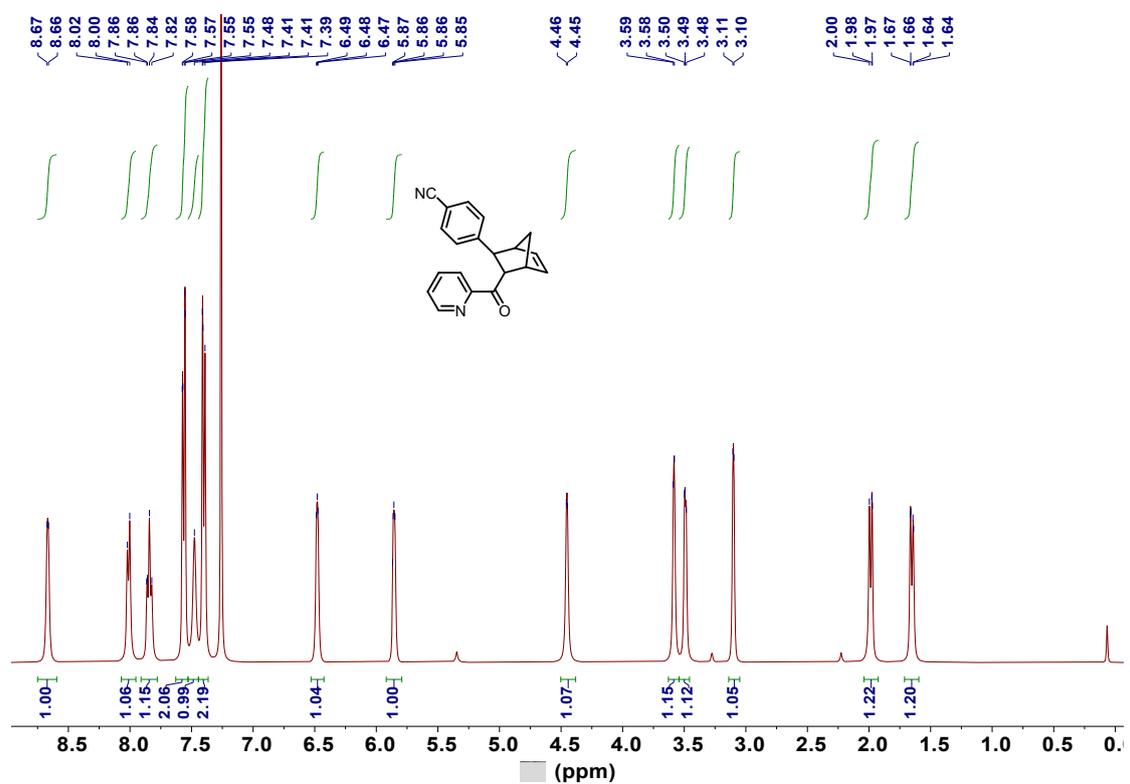


Fig. S17 ^1H NMR (400 MHz) spectrum of **6h** measured in CDCl_3 at 25 $^\circ\text{C}$.

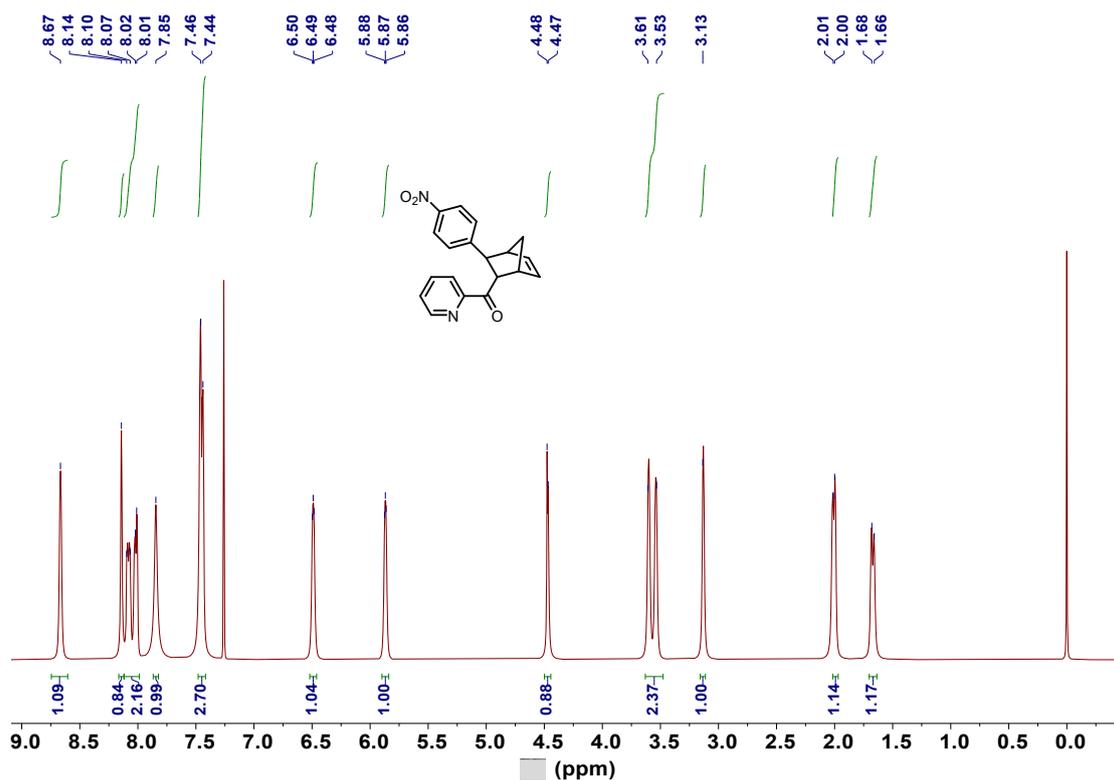


Fig. S18 ^1H NMR (400 MHz) spectrum of **6i** measured in CDCl_3 at 25 °C.

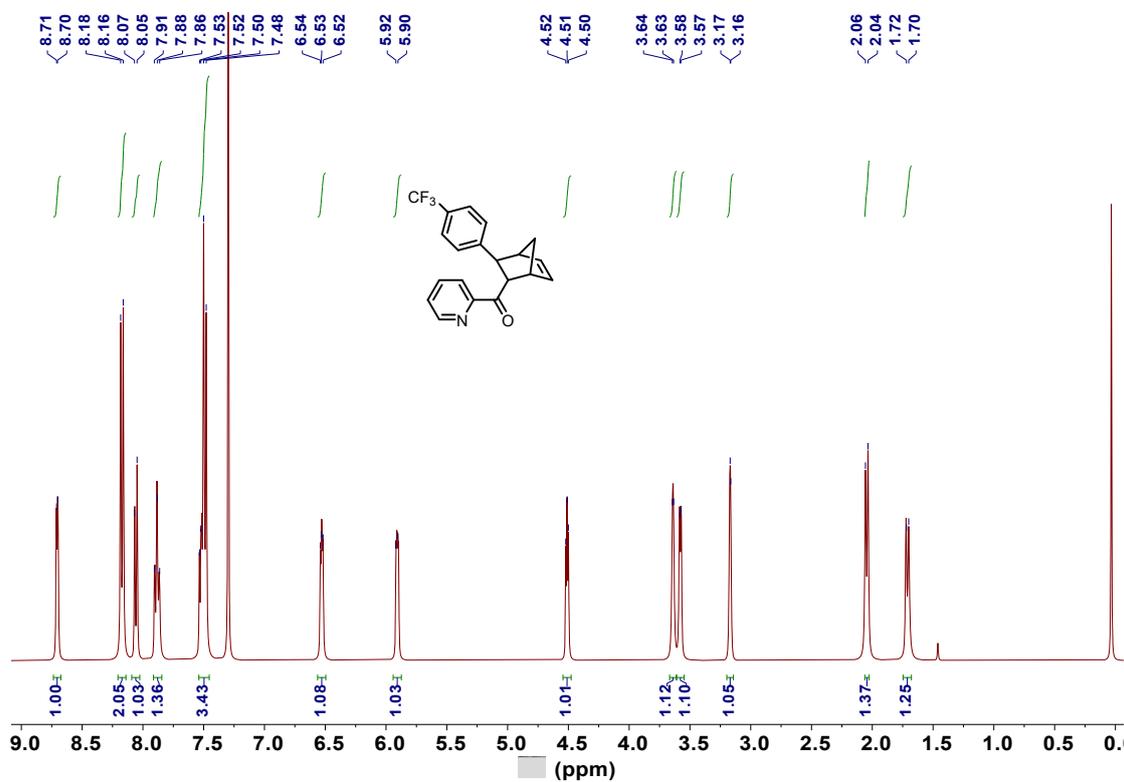


Fig. S19 ^1H NMR (400 MHz) spectrum of **6j** measured in CDCl_3 at 25 °C.

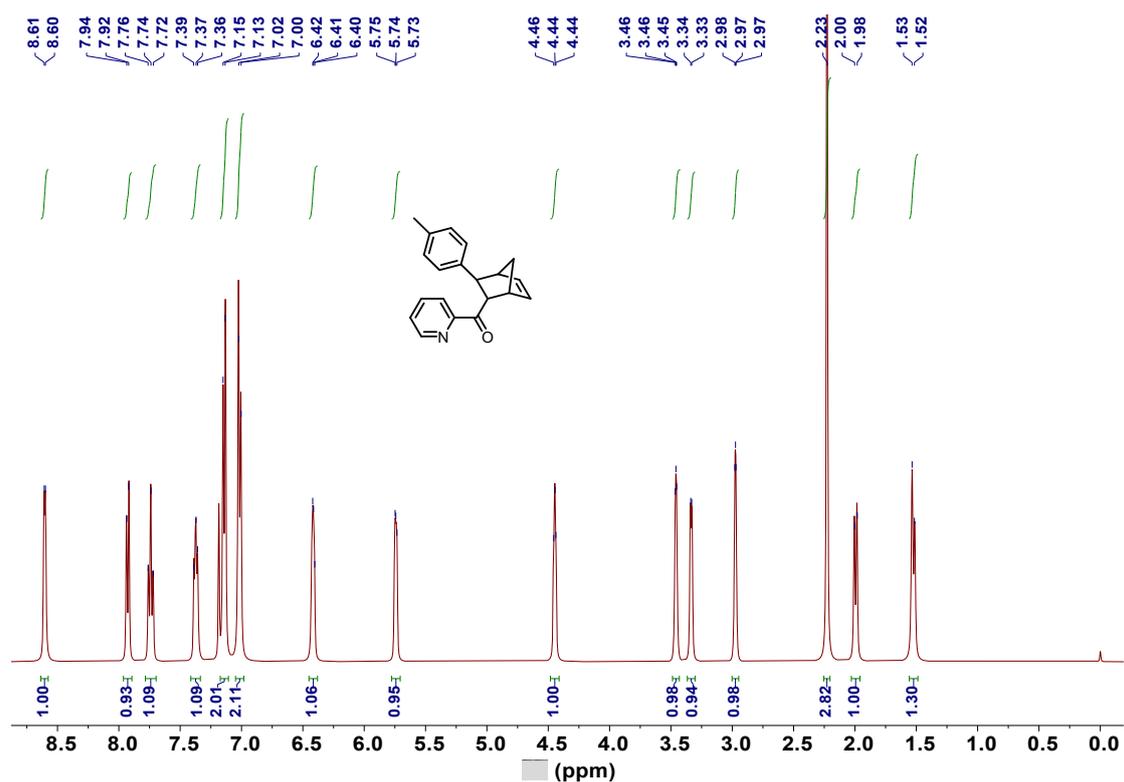


Fig. S20 ^1H NMR (400 MHz) spectrum of **6k** measured in CDCl_3 at 25 $^\circ\text{C}$.

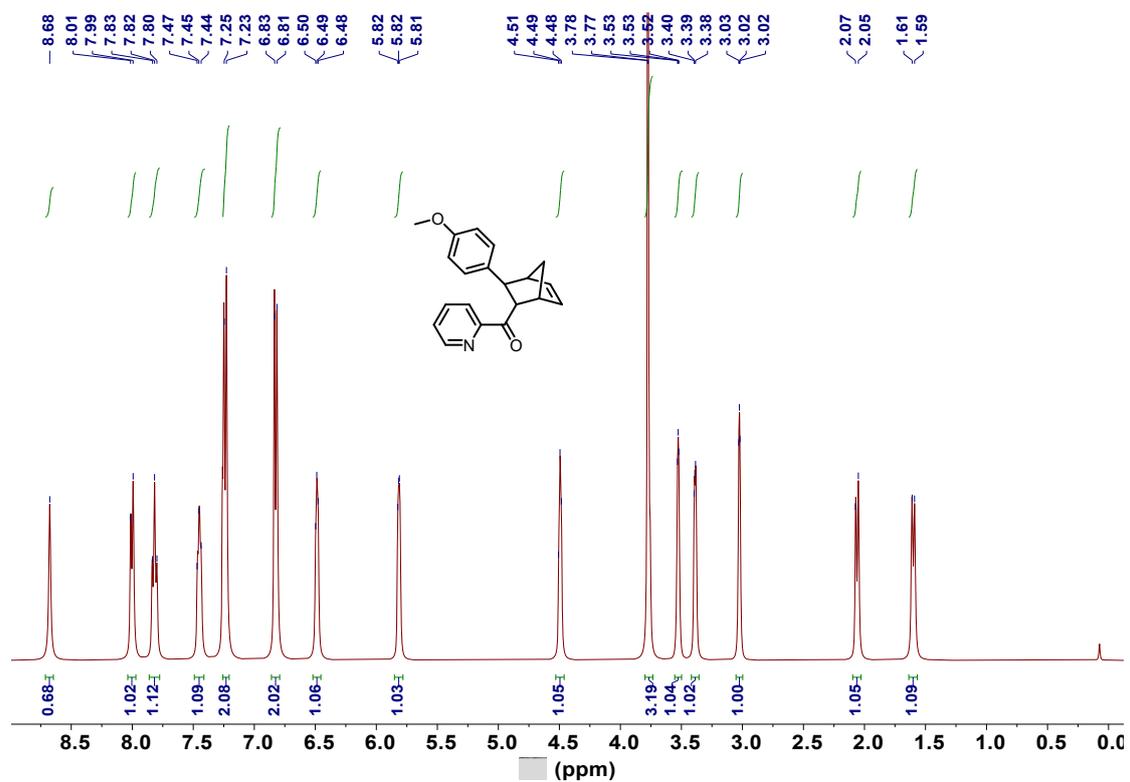


Fig. S21 ^1H NMR (400 MHz) spectrum of **6l** measured in CDCl_3 at 25 $^\circ\text{C}$.

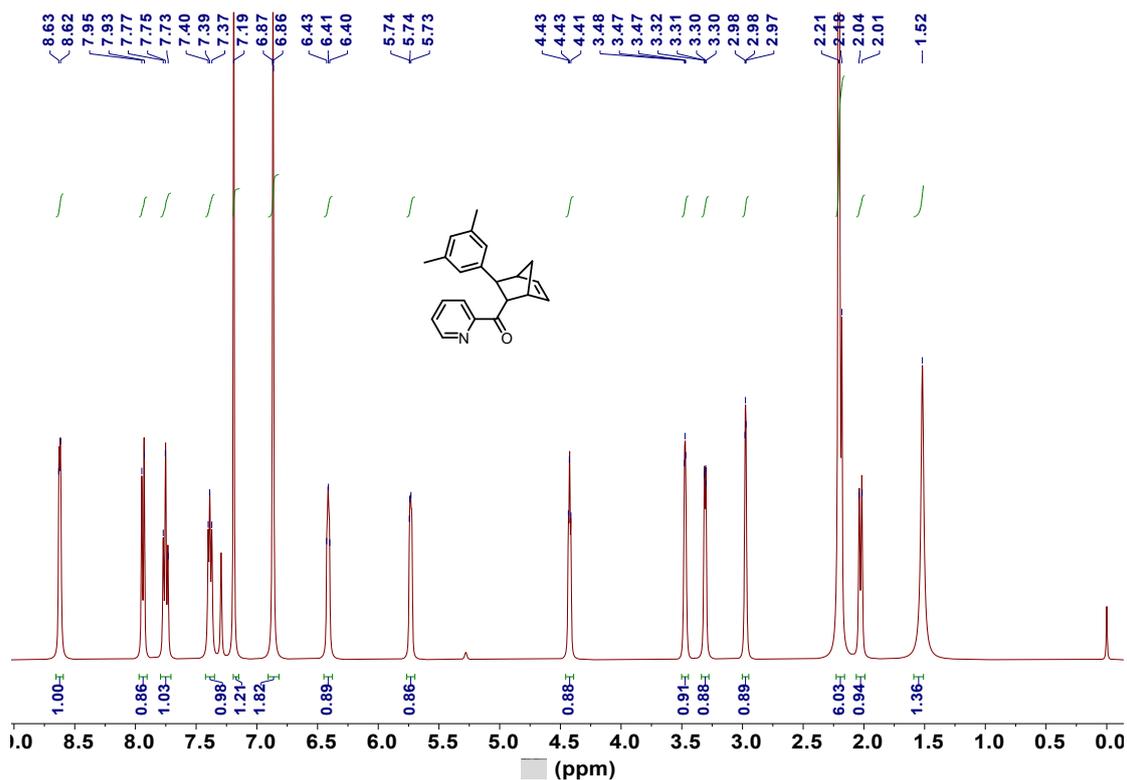


Fig. S22 ^1H NMR (400 MHz) spectrum of **6m** measured in CDCl_3 at 25 °C.

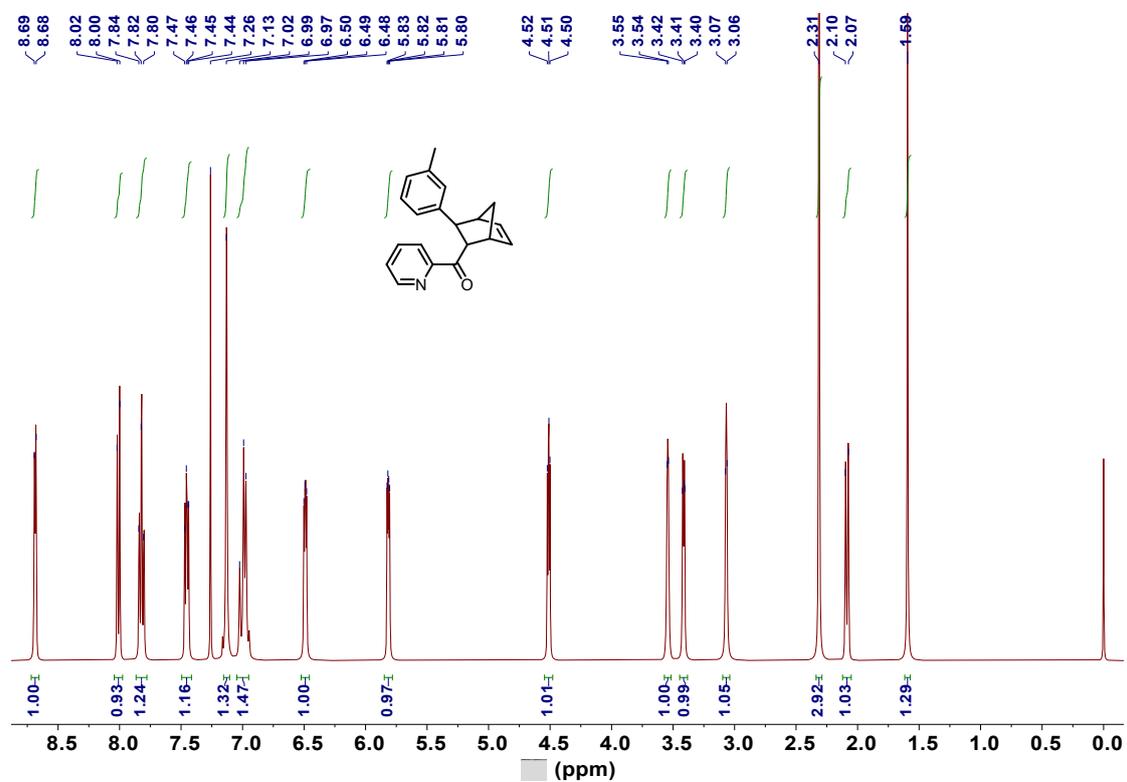


Fig. S23 ^1H NMR (400 MHz) spectrum of **6n** measured in CDCl_3 at 25 °C.

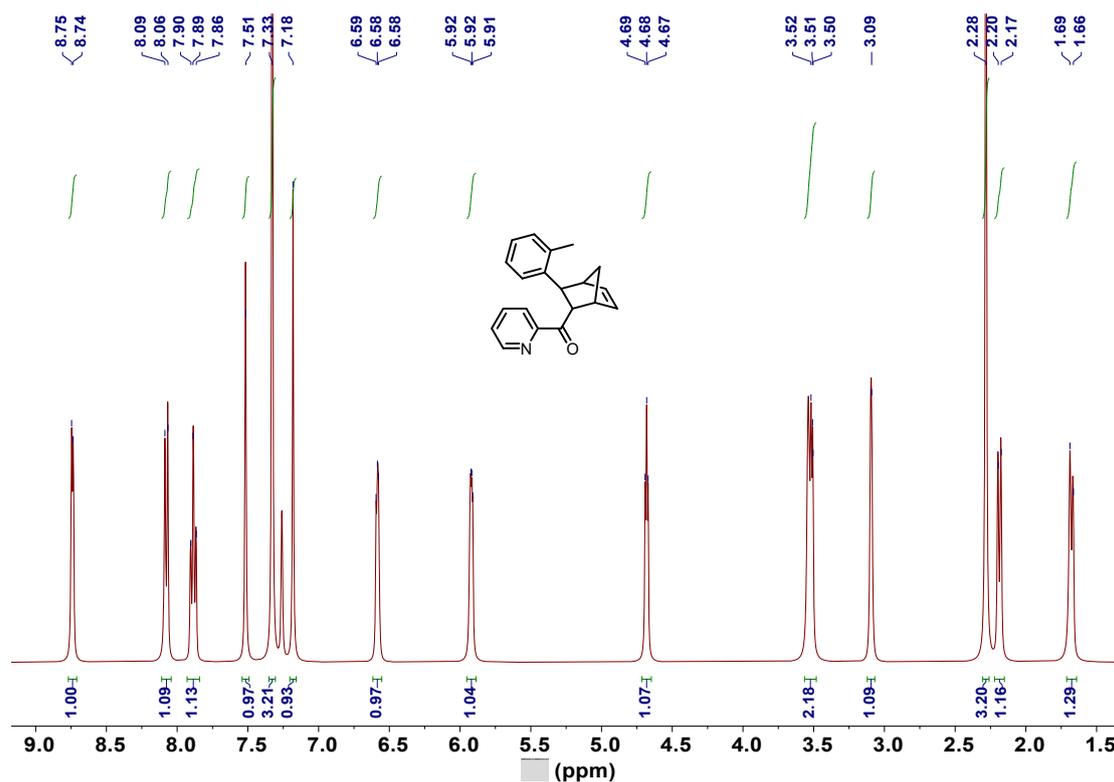


Fig. S24 ^1H NMR (400 MHz) spectrum of **6o** measured in CDCl_3 at 25 $^\circ\text{C}$.

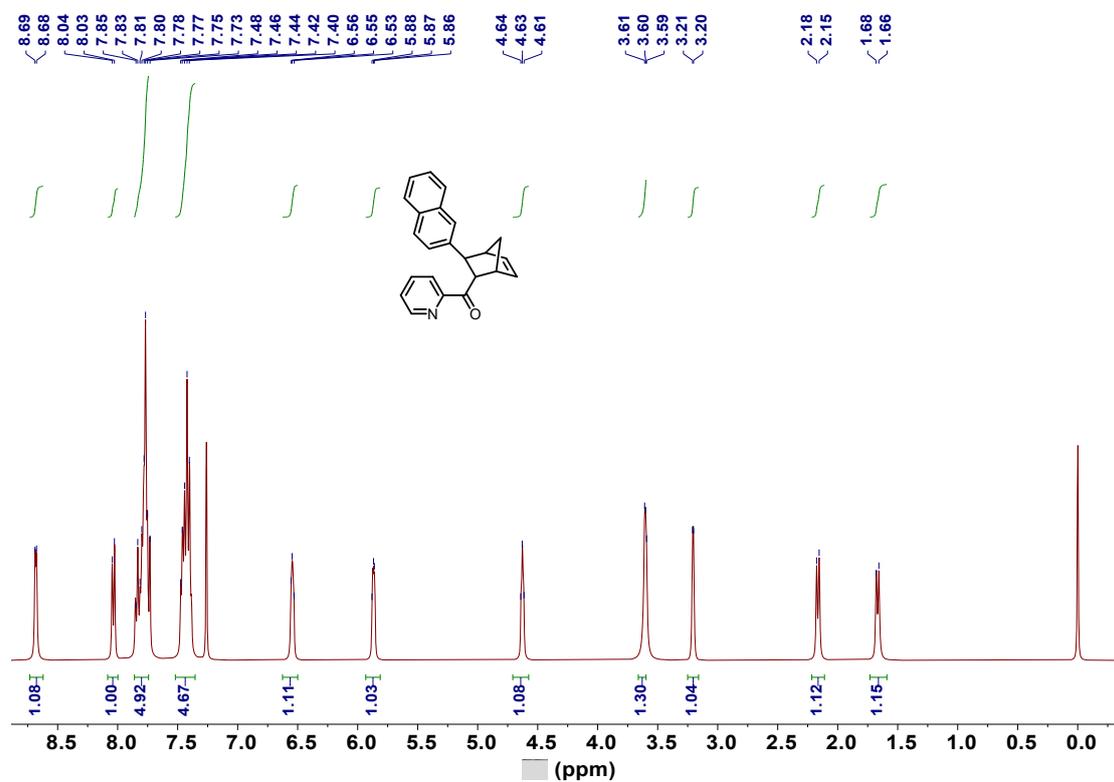


Fig. S25 ^1H NMR (400 MHz) spectrum of **6p** measured in CDCl_3 at 25 $^\circ\text{C}$.

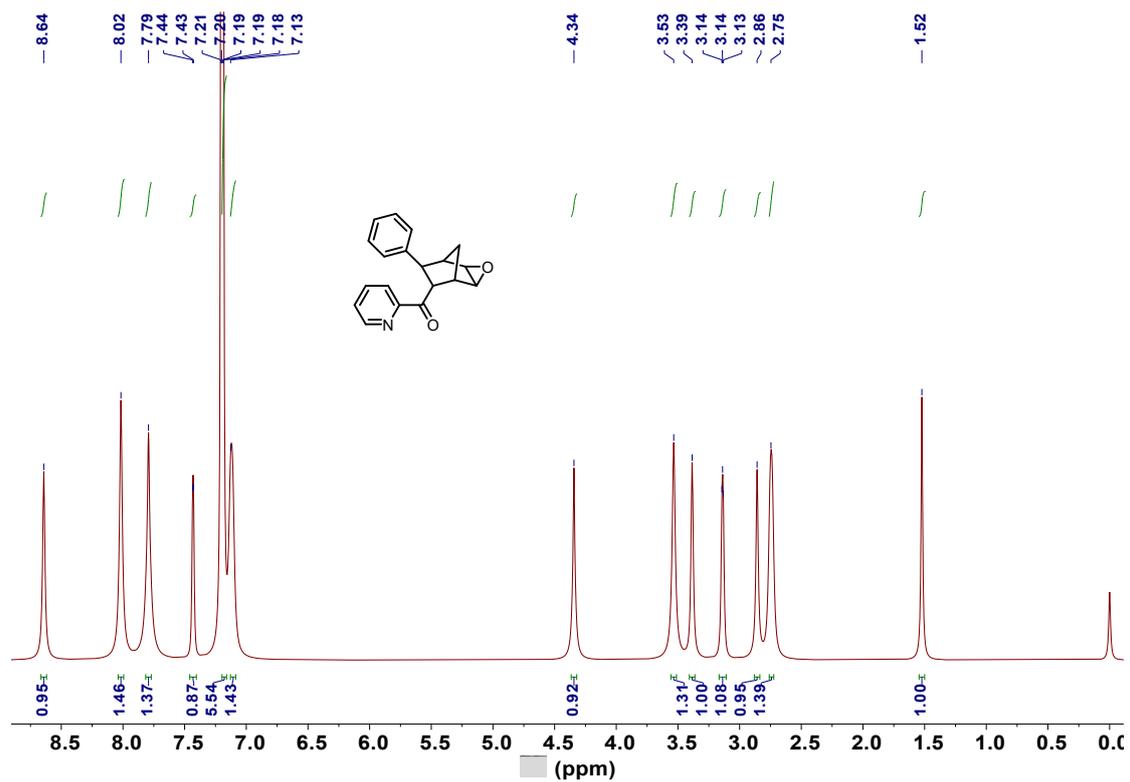


Fig. S26 ^1H NMR (400 MHz) spectrum of **7** measured in CDCl_3 at 25°C .

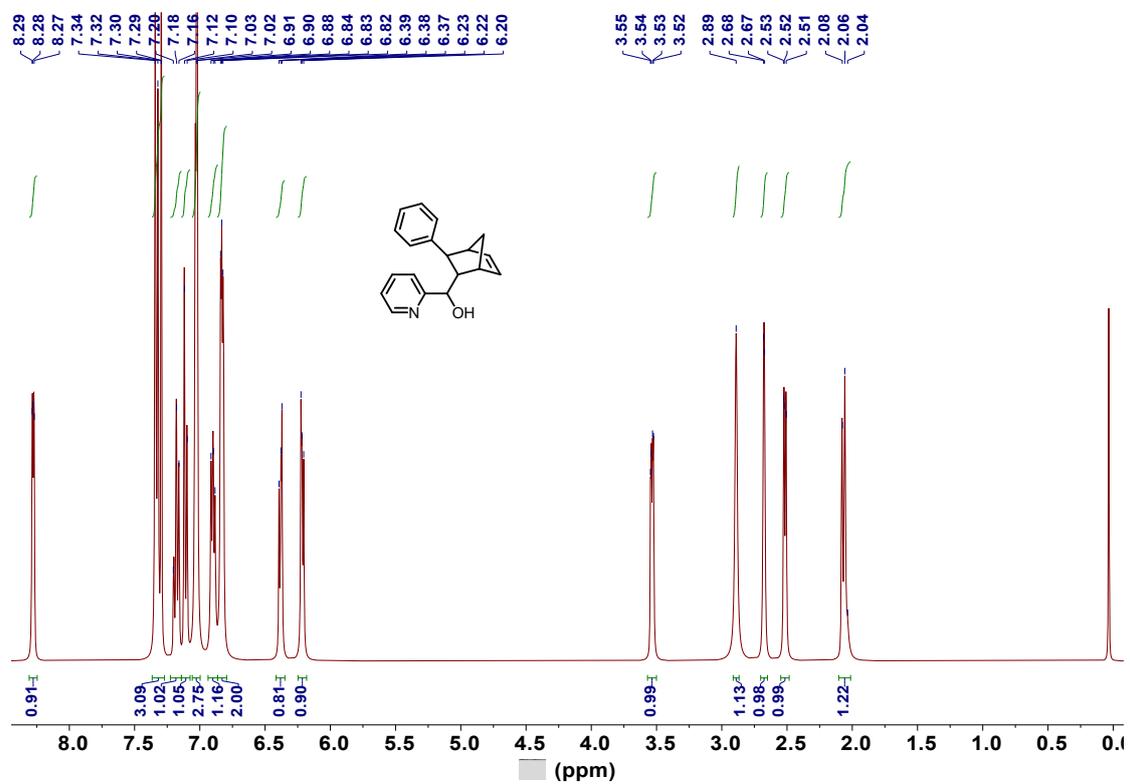


Fig. S27 ^1H NMR (400 MHz) spectrum of **8** measured in CDCl_3 at 25°C .

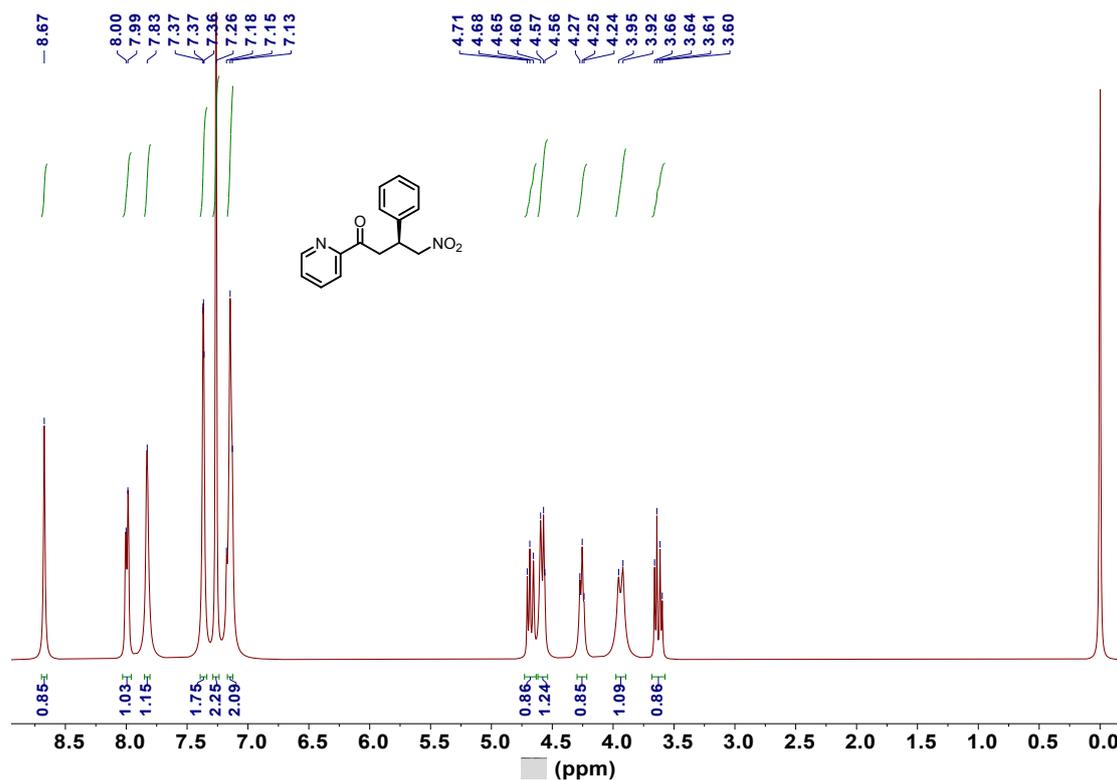


Fig. S28 ^1H NMR (400 MHz) spectrum of **11a** measured in CDCl_3 at 25°C .

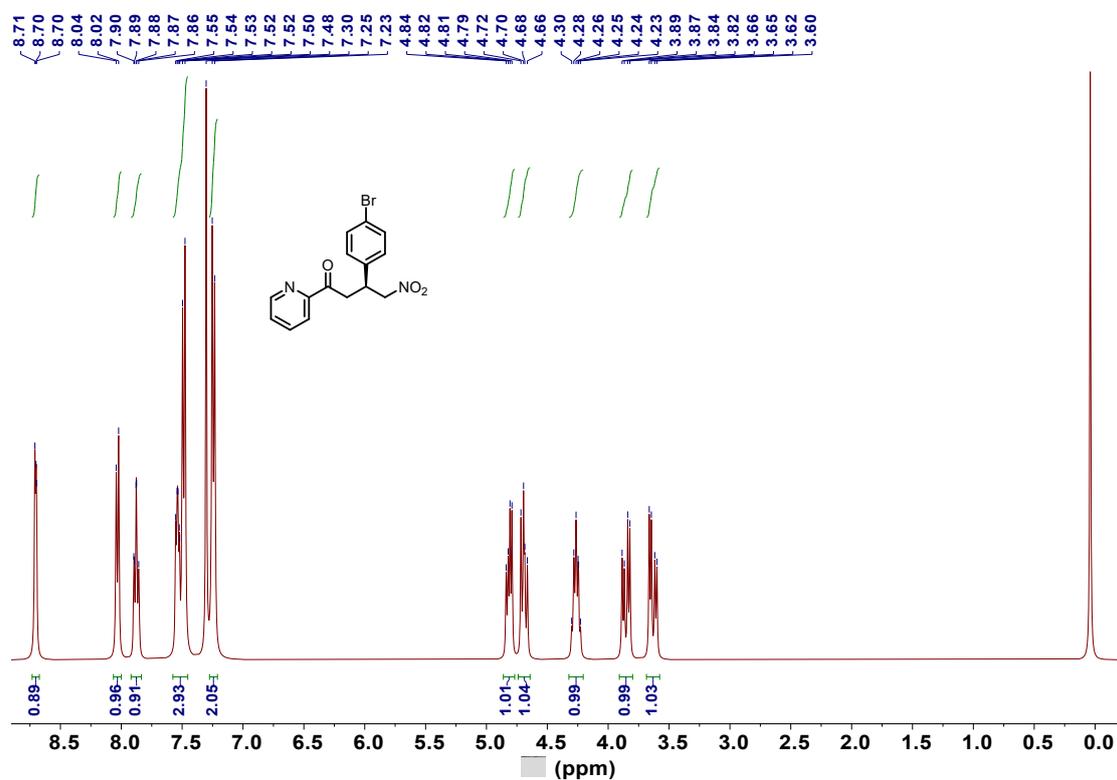


Fig. S29 ^1H NMR (400 MHz) spectrum of **11b** measured in CDCl_3 at 25°C .

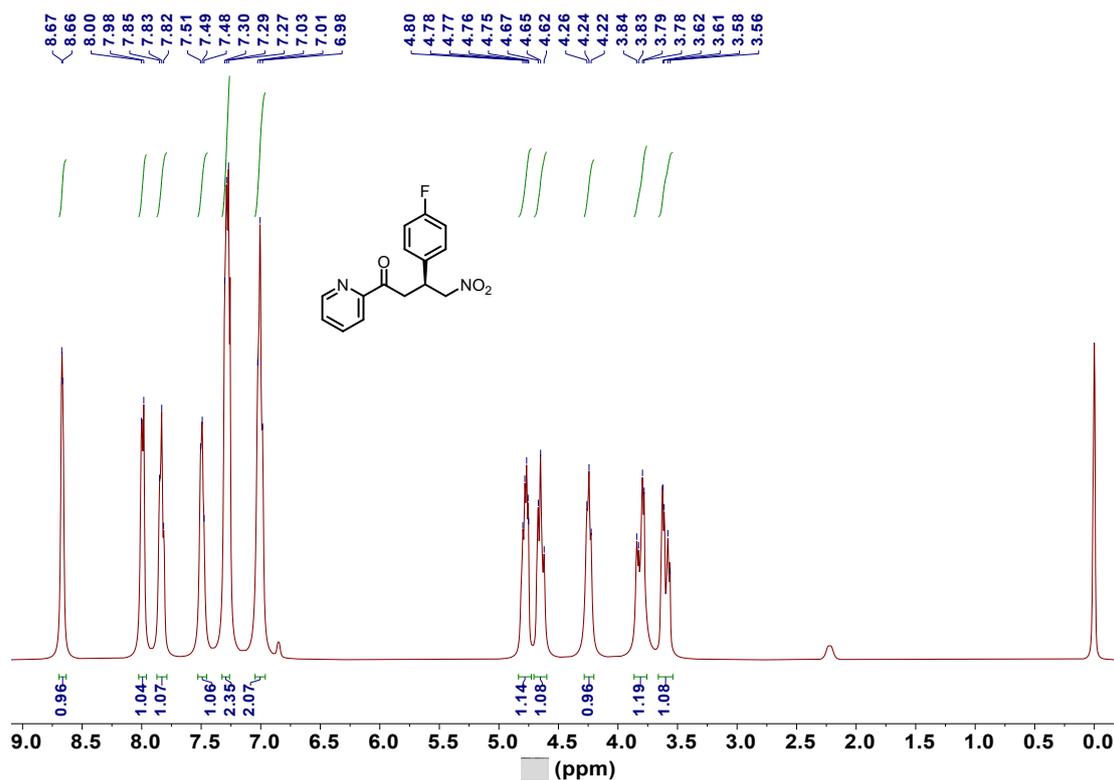


Fig. S30 ^1H NMR (400 MHz) spectrum of **11c** measured in CDCl_3 at 25°C .

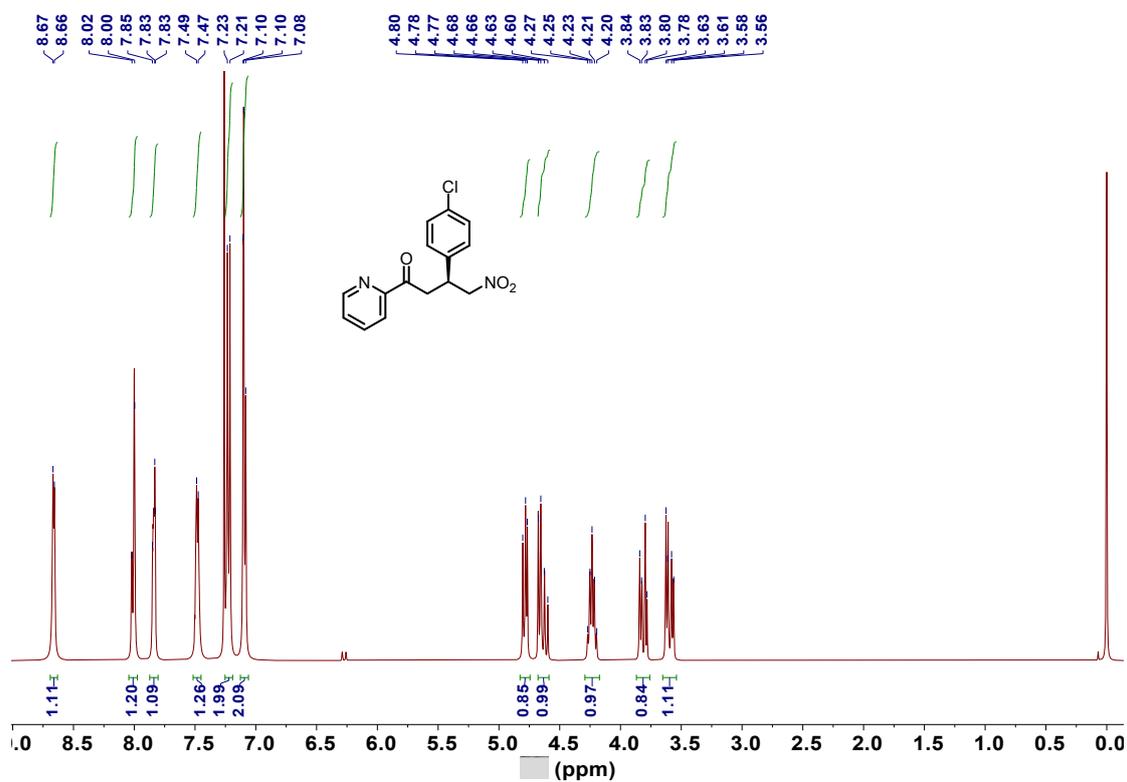


Fig. S31 ^1H NMR (400 MHz) spectrum of **11d** measured in CDCl_3 at 25°C .

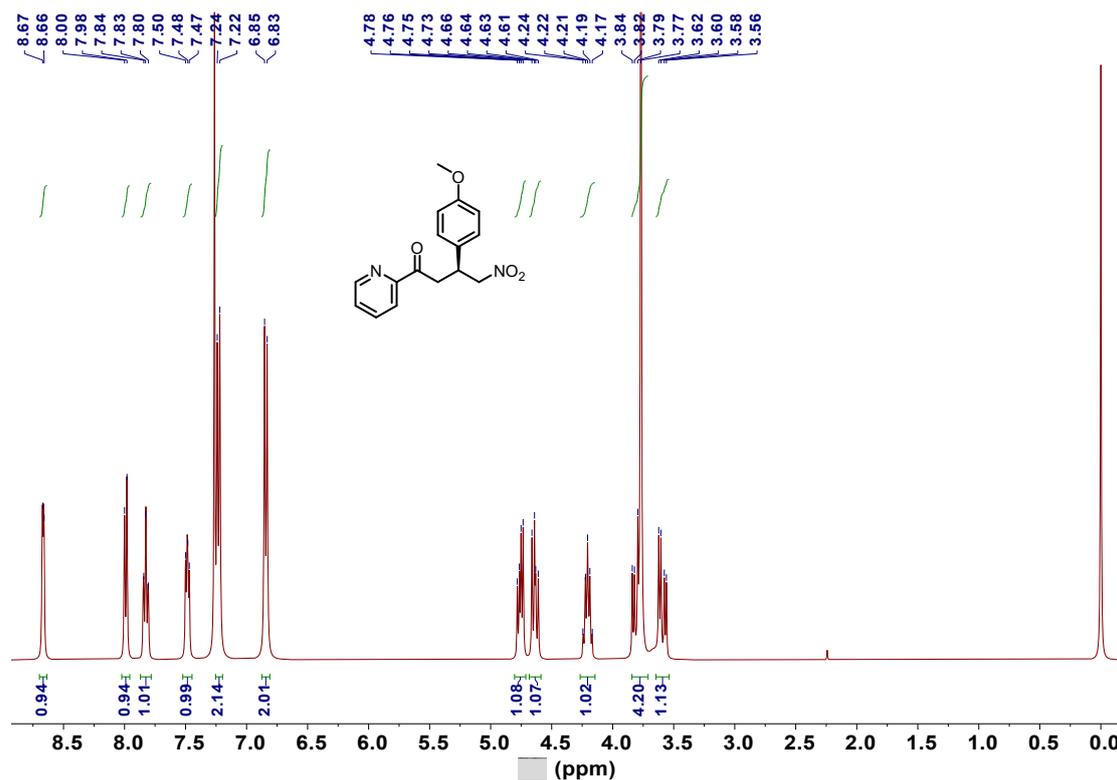


Fig. S32 ^1H NMR (400 MHz) spectrum of **11e** measured in CDCl_3 at 25 $^\circ\text{C}$.

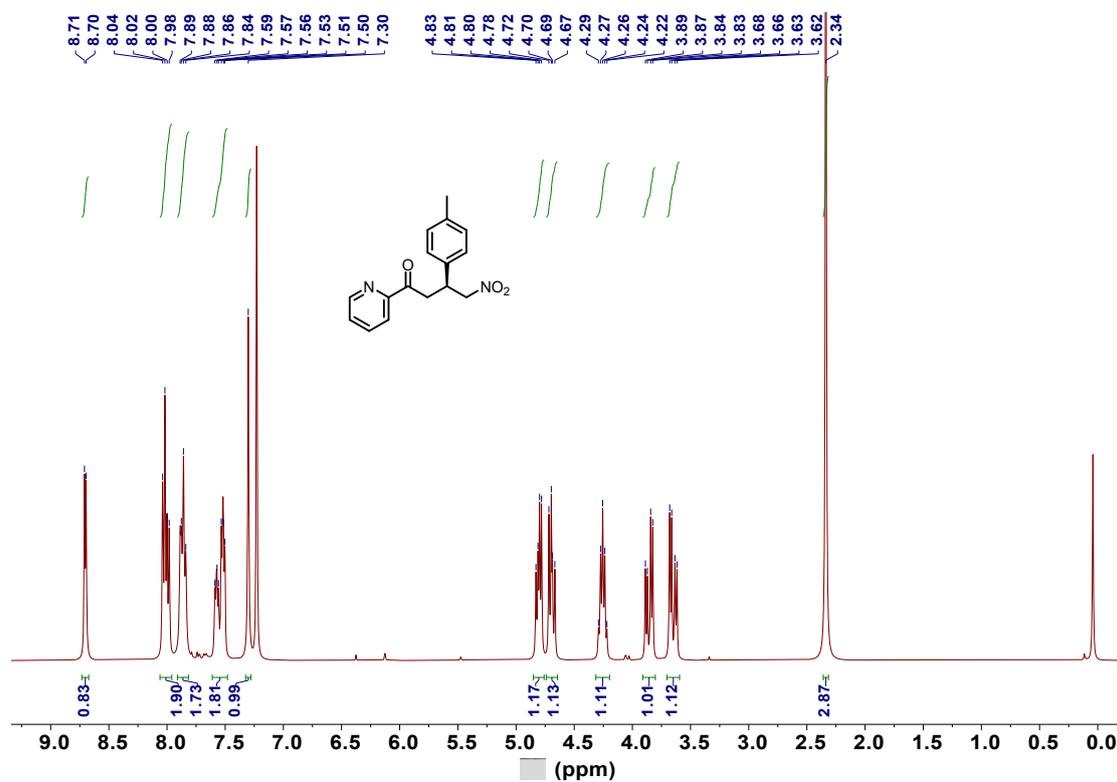
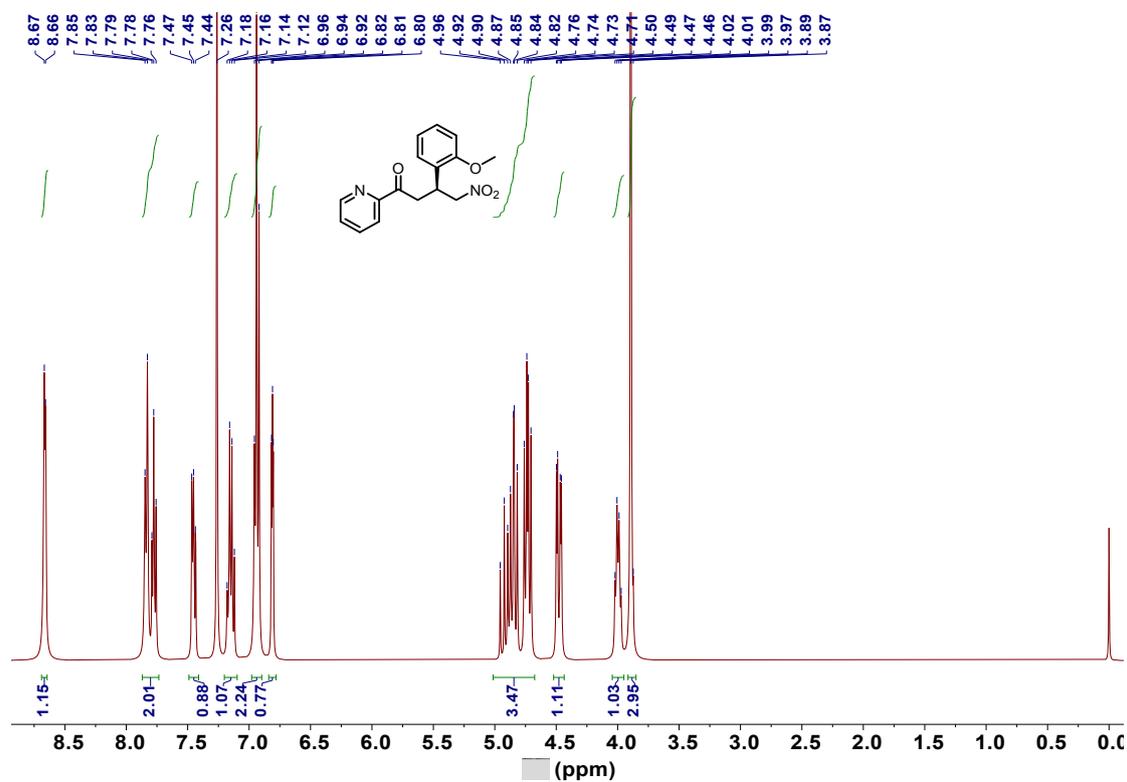
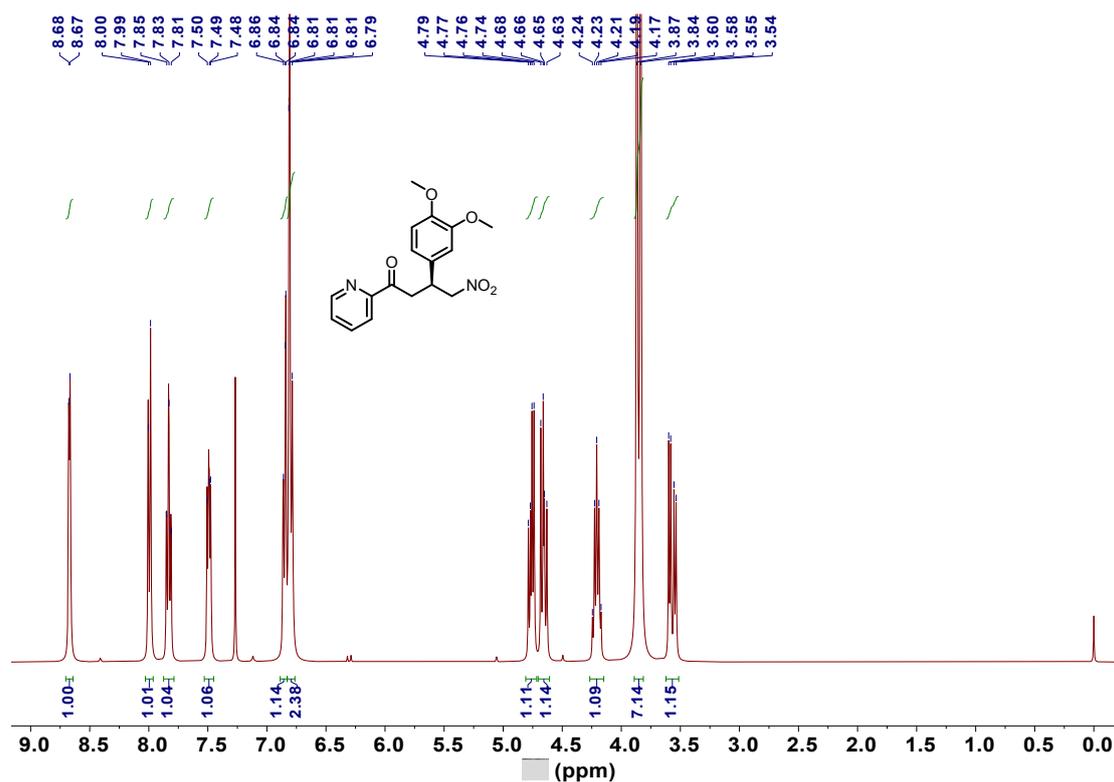


Fig. S33 ^1H NMR (400 MHz) spectrum of **11f** measured in CDCl_3 at 25 $^\circ\text{C}$.



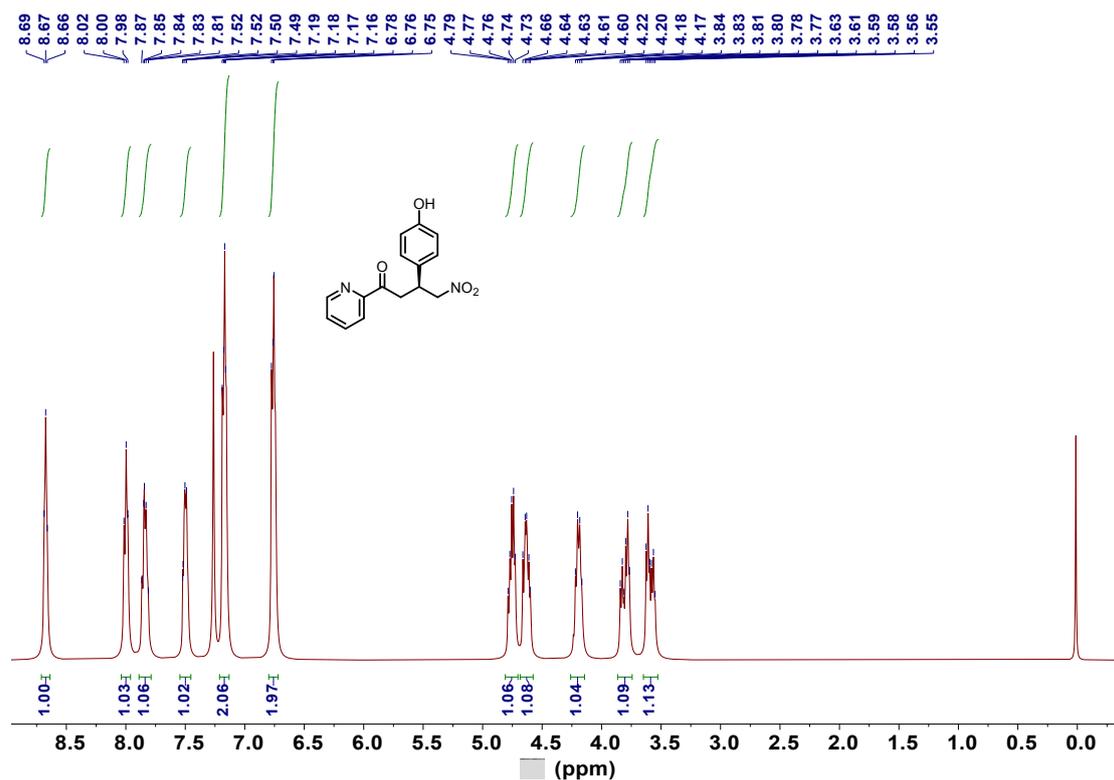


Fig. S36 ^1H NMR (400 MHz) spectrum of **11i** measured in CDCl_3 at 25 $^\circ\text{C}$.

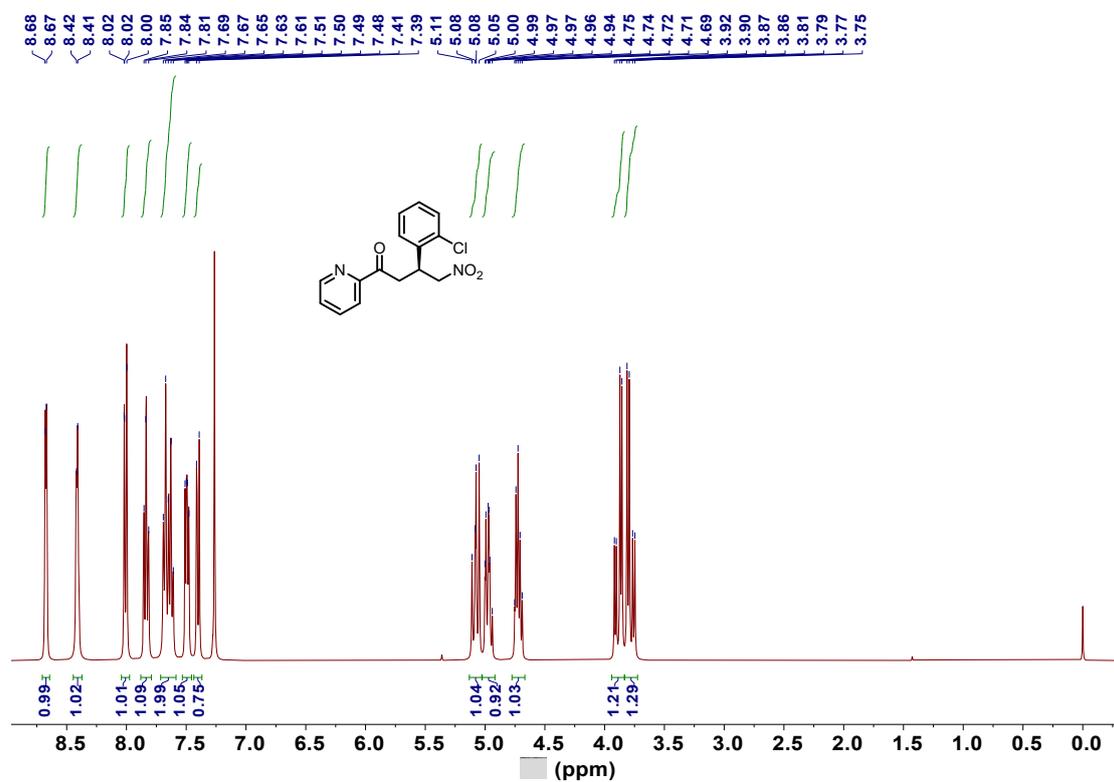


Fig. S37 ^1H NMR (400 MHz) spectrum of **11j** measured in CDCl_3 at 25 $^\circ\text{C}$.

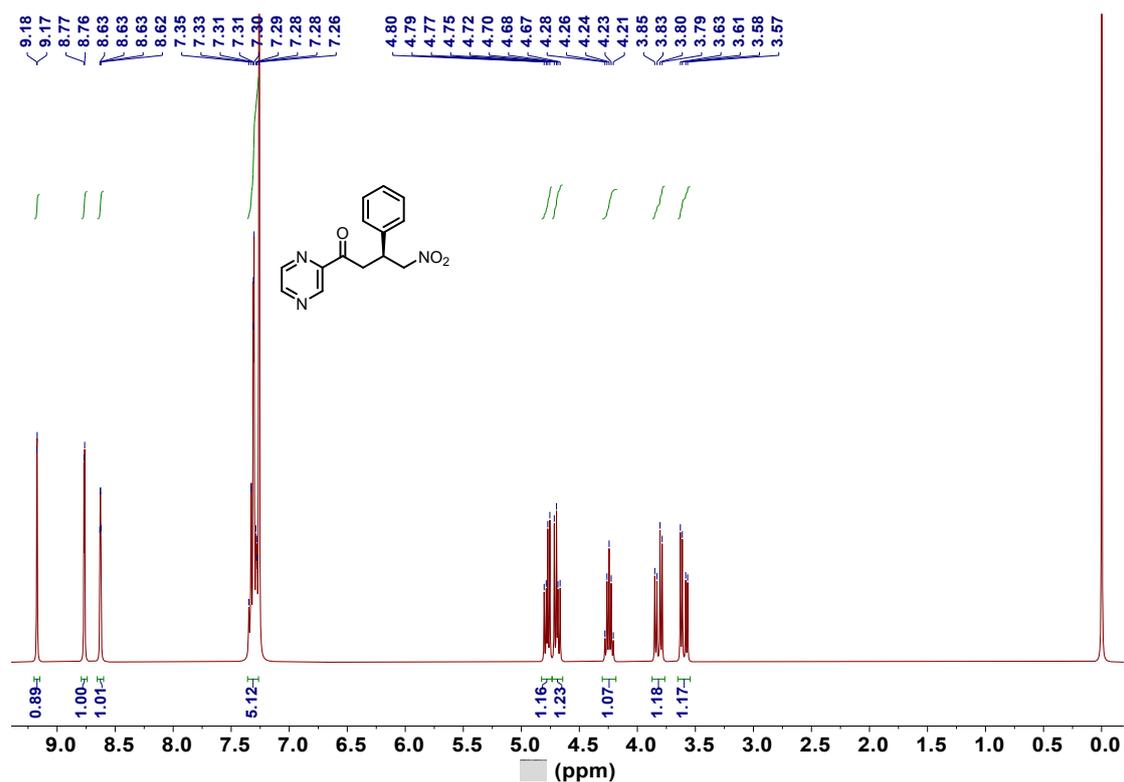


Fig. S38 ^1H NMR (400 MHz) spectrum of **11k** measured in CDCl_3 at 25 °C.

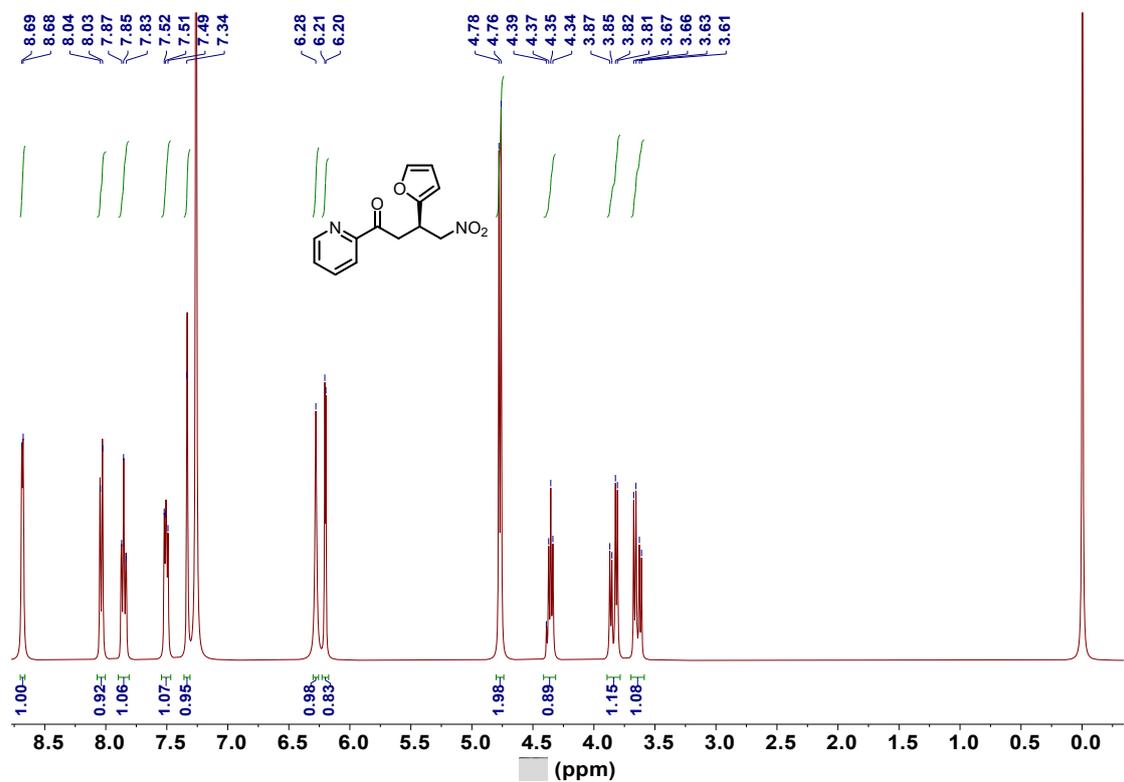
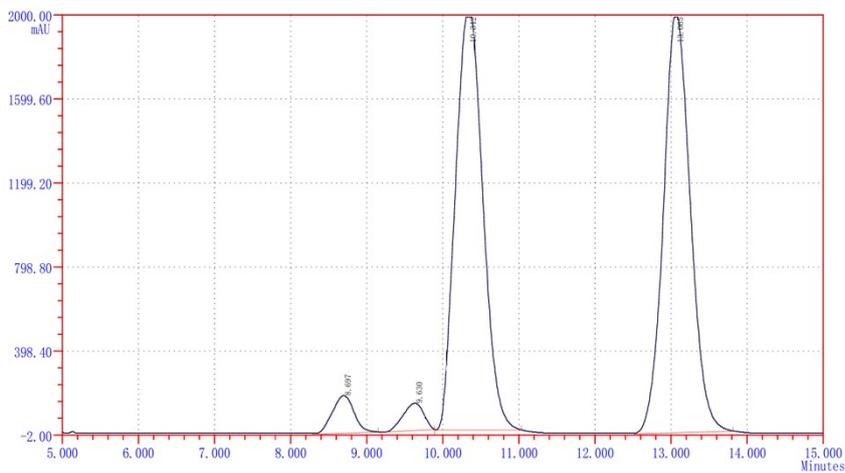
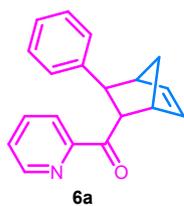


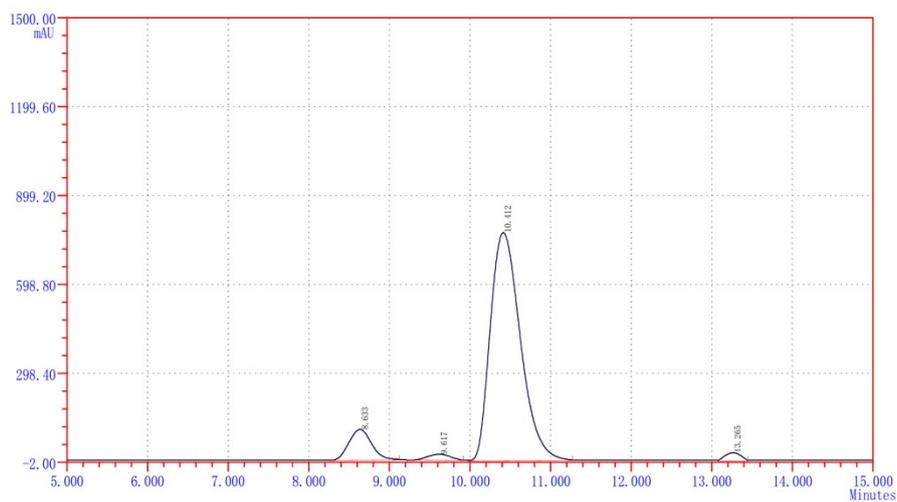
Fig. S39 ^1H NMR (400 MHz) spectrum of **11l** measured in CDCl_3 at 25 °C.

7. HPLC of the products



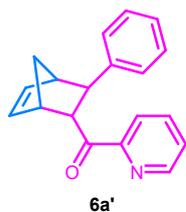
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.697	179.12	3575.584	4.1339
2	9.630	130.10	3058.189	3.0026
3	10.342	2020.10	50189.560	46.6221
4	13.065	2003.60	49239.076	46.2413

Fig. S40 HPLC curve of racemic **6a** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

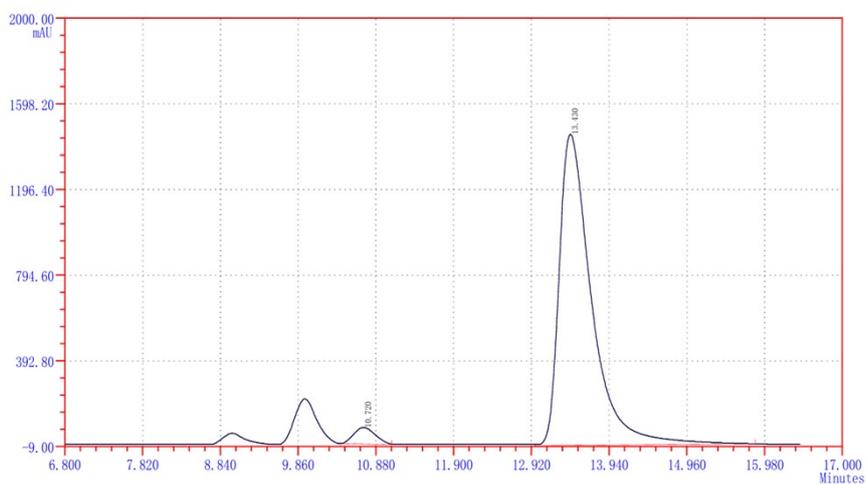


Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	8.633	104.63	2064.360	9.0259
2	9.616	20.77	414.533	1.8124
3	10.411	770.88	20148.038	88.0919
4	13.265	28.04	244.713	1.0699

Fig. S41 HPLC curve of **6a** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

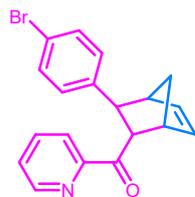


6a'

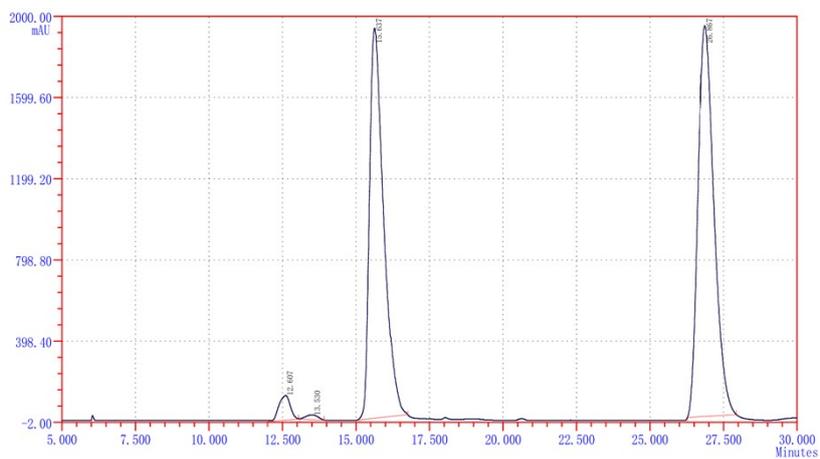


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.9917	50.1	909.284	1.829
2	9.9483	211.46	4242.163	8.5328
3	10.72	77.58	1225.523	2.4650
4	13.43	1458.65	43338.954	87.1732

Fig. S42 HPLC curve of 6a' catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

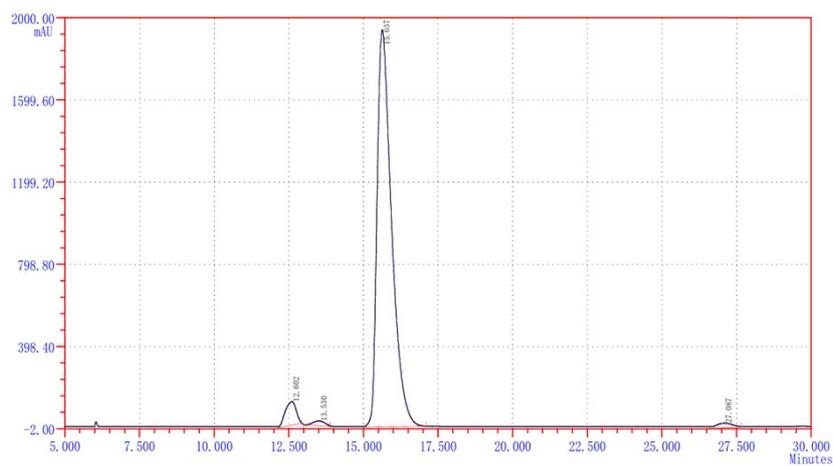


6b



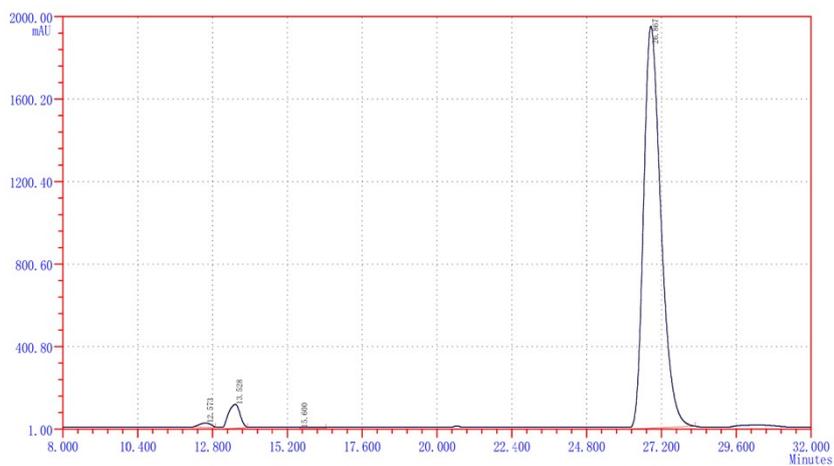
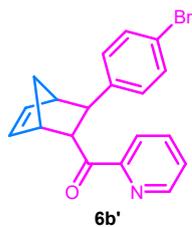
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	12.6067	120.49	3226.403	3.0166
2	13.5300	23.44	664.763	0.5868
3	15.6367	1923.71	64238.080	48.1621
4	26.8667	1926.60	72821.160	48.2345

Fig. S43 HPLC curve of racemic **6b** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



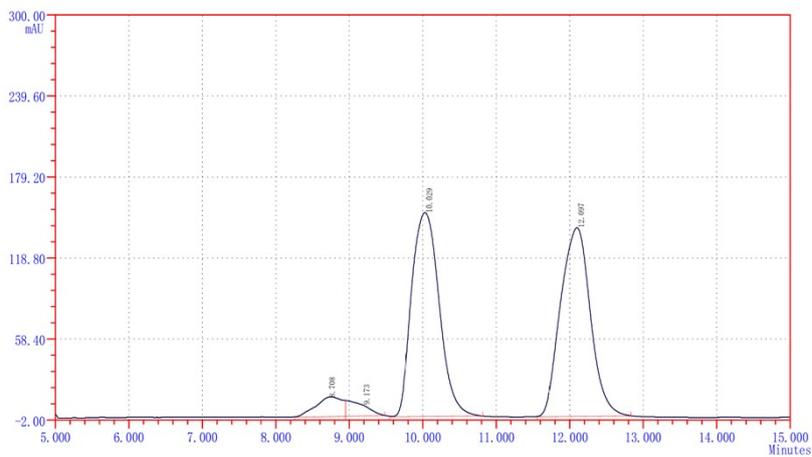
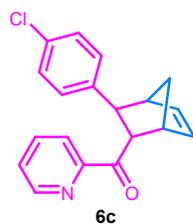
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	12.6017	114.77	2958.535	5.4827
2	13.53	19.72	652.295	1.1331
3	15.6367	1902.82	65176.55	92.3336
4	27.0867	21.99	810.371	1.0505

Fig. S44 HPLC curve of **6b** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



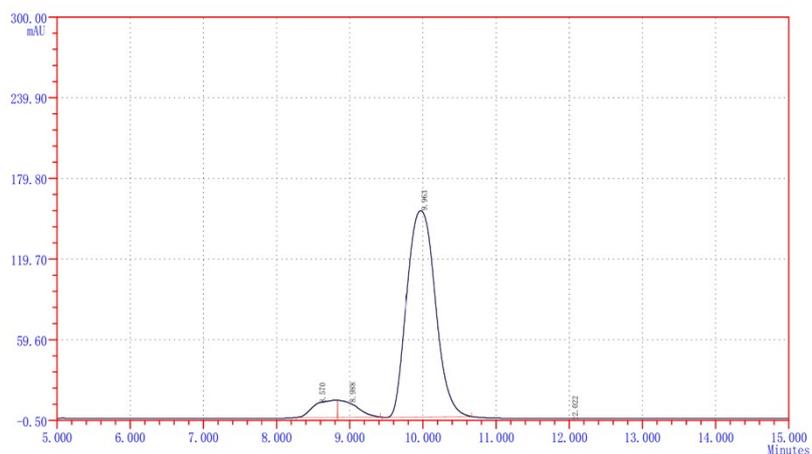
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	12.5733	20.73	538.825	0.994
2	13.5283	115.45	2958.514	5.5356
3	15.6	2	101.949	0.0959
4	26.8667	1947.42	75184.42	93.3746

Fig. S45 HPLC curve of **6b'** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



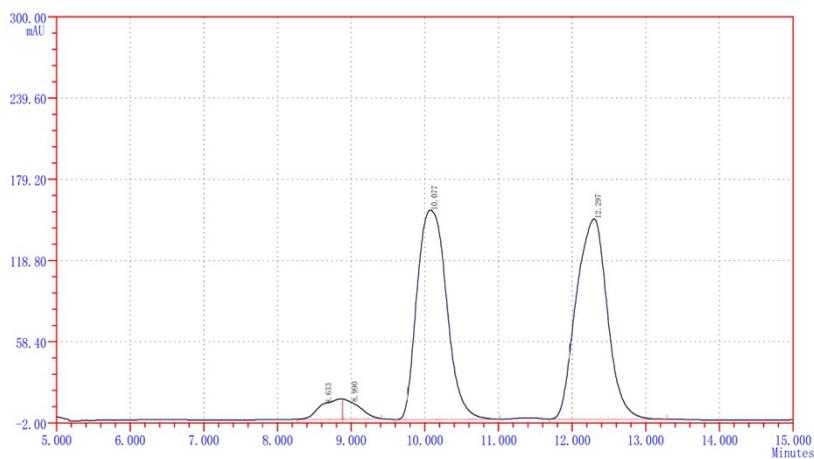
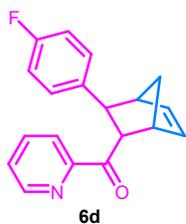
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.7084	14.71	368.117	4.3145
2	9.1735	11.73	207.433	2.4312
3	10.0286	151.98	3979.199	46.6384
4	12.097	140.65	3977.269	46.6158

Fig. S46 HPLC curve of racemic **6c** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



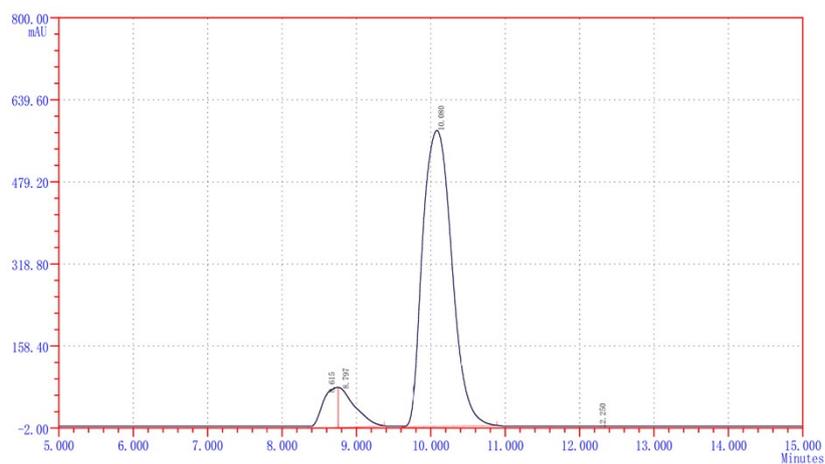
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.57	12.82	270.618	5.8614
2	8.9883	12.77	226.5	5.0689
3	9.9633	153.74	4163.956	88.8021
4	12.023	1.3	20.184	0.668

Fig. S47 HPLC curve of **6c** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



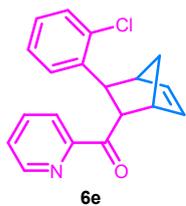
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.6333	15.2	297.641	4.5342
2	8.9901	15.1	235.838	4.5044
3	10.0768	155.83	4360.229	46.4845
4	12.2968	149.1	4377.755	44.4769

Fig. S48 HPLC curve of racemic **6d** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

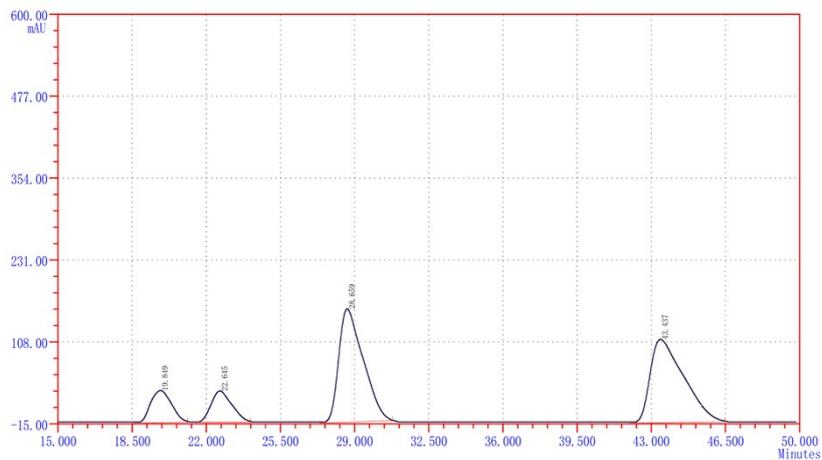


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.615	78.56	1089.583	6.7573
2	8.7967	78.46	1200.543	7.3436
3	10.08	578.34	15621.07	84.4536
4	12.25	7.43	237.884	1.2861

Fig. S49 HPLC curve of **6d** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

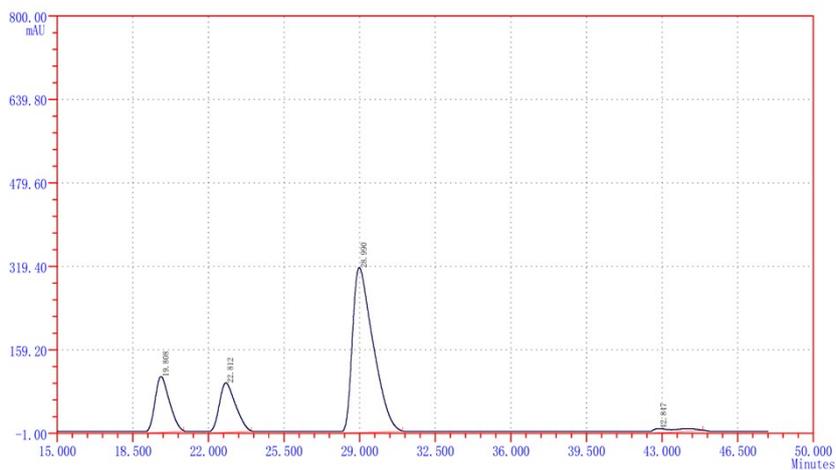


6e



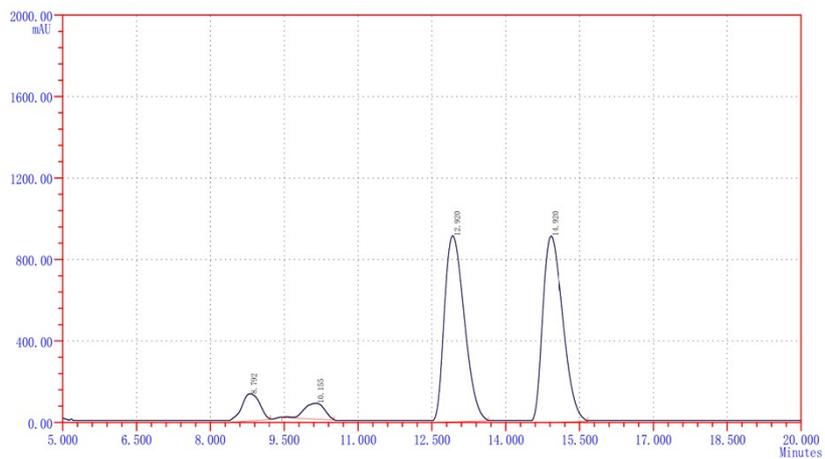
Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	19.8488	48.34	3313.306	12.3809
2	22.6453	47.22	3239.081	12.094
3	28.6586	170.05	13571.49	43.5534
4	43.437	124.83	13710.46	31.9716

Fig. S50 HPLC curve of racemic **6e** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).



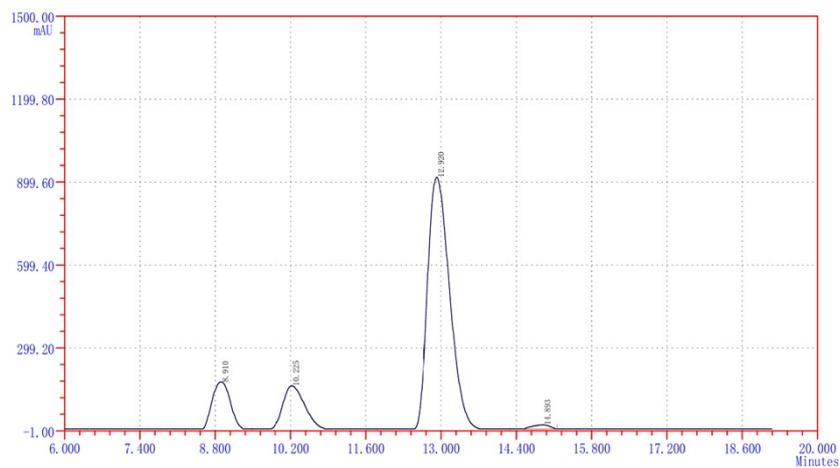
Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	19.8083	107.19	4972.862	20.3675
2	22.8117	94.62	4960.634	17.979
3	28.99	316.53	21052.71	60.1448
4	42.8467	7.94	717.385	1.5087

Fig. S51 HPLC curve of **6e** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).



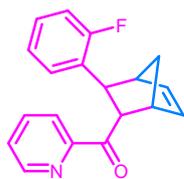
Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	8.7917	133.33	3426.664	6.5359
2	10.155	77.97	2266.906	3.8221
3	12.92	913.3	25778.59	44.7705
4	14.92	915.36	25940.57	44.8715

Fig. S52 HPLC curve of racemic **6f** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

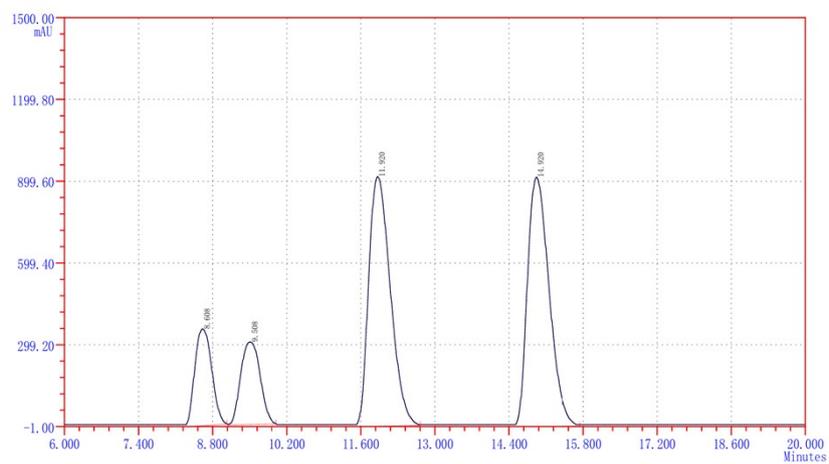


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.91	180.48	4508.438	14.0522
2	10.225	166.28	5250.914	12.9466
3	12.92	921.15	26202.56	70.5895
4	14.8933	16.44	871.056	2.412

Fig. S53 HPLC curve of **6f** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

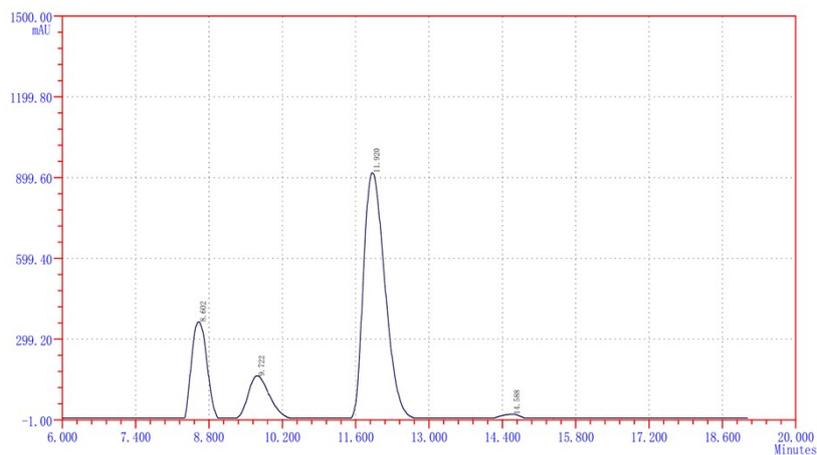


6g



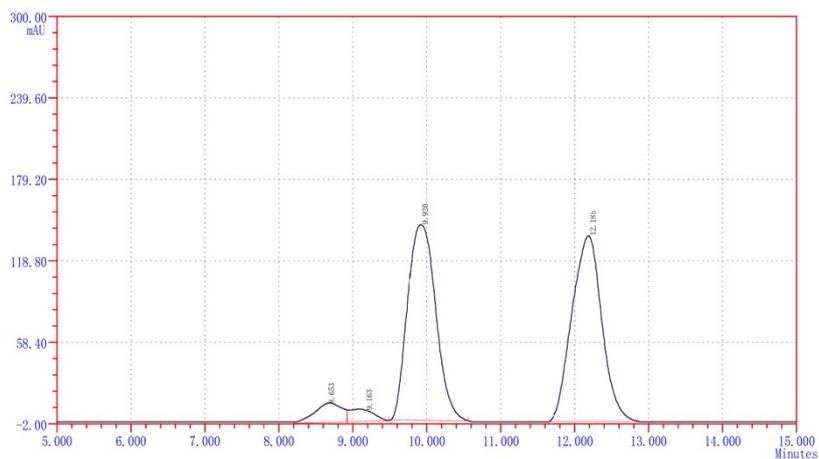
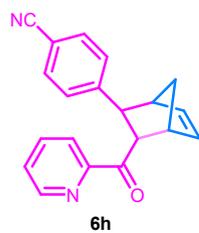
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.6083	355.83	7936.113	11.7003
2	9.5083	302.74	7746.193	11.4203
3	11.92	916.75	26101.81	38.482
4	14.92	915.73	26044.46	38.3975

Fig. S54 HPLC curve of racemic **6g** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



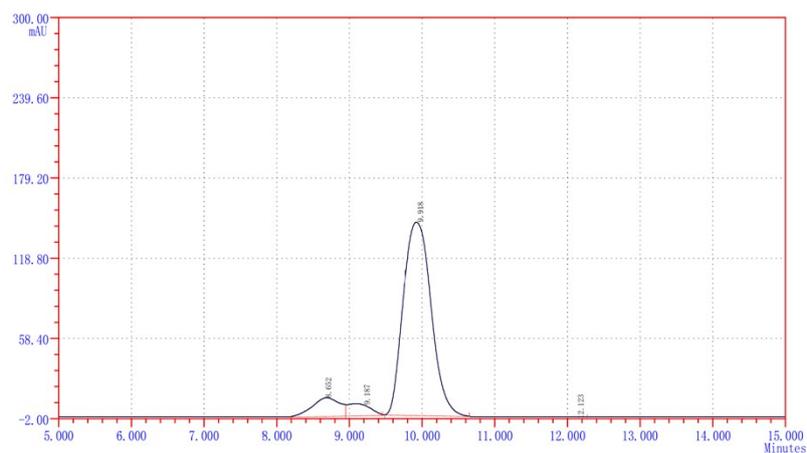
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.6017	384.09	8309.549	18.6961
2	9.7217	181.35	6693.043	15.0591
3	11.92	931.56	28295.45	64.0457
4	14.5883	28.94	1147.219	2.1991

Fig. S55 HPLC curve of **6g** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



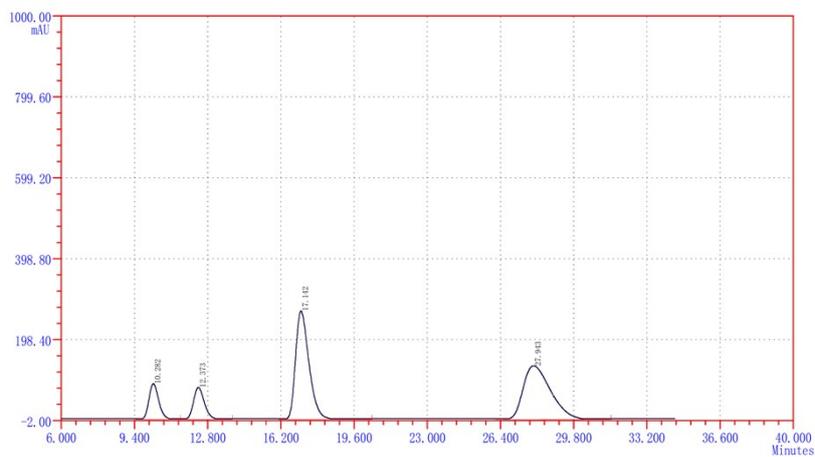
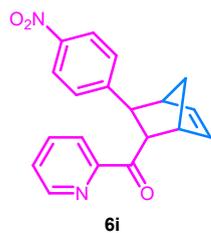
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.6533	14.22	362.383	4.6428
2	9.1633	9.25	213.872	3.0201
3	9.92	144.94	3843.304	47.3227
4	12.185	137.87	3889.787	45.0144

Fig. S56 HPLC curve of racemic **6h** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



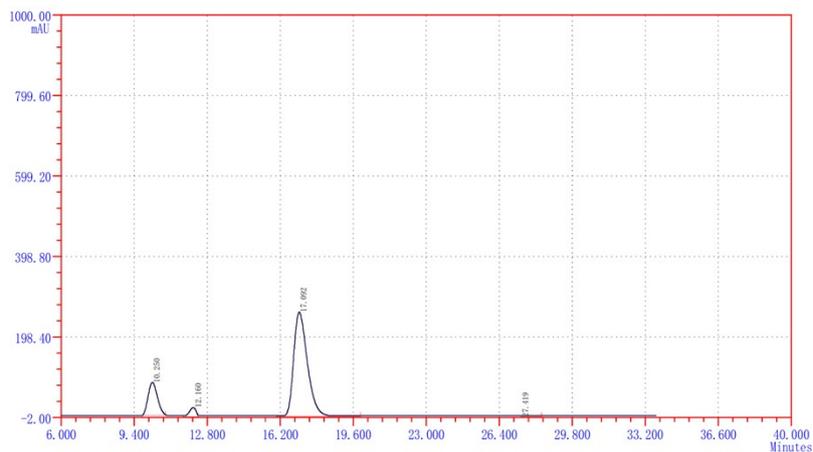
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.6517	14.11	374.971	8.3511
2	9.1867	9.18	198.26	4.4155
3	9.9183	145.57	3891.242	86.6631
4	12.123	1.36	25.608	0.5703

Fig. S57 HPLC curve of **6h** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



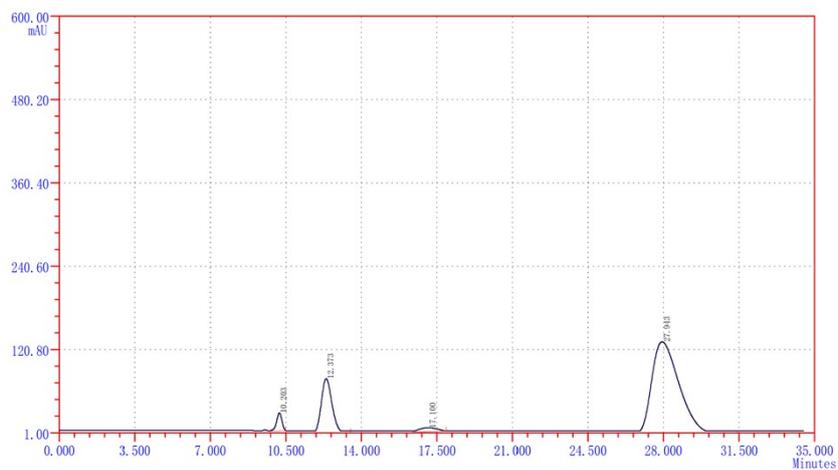
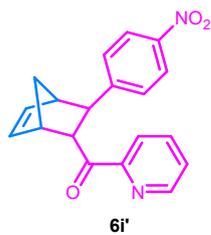
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	10.2817	88.82	2831.425	9.6924
2	12.3733	79.39	2800.726	9.5873
3	17.1417	268.69	11719.19	40.1166
4	27.9433	133.27	11861.46	40.6036

Fig. S58 HPLC curve of racemic **6i** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



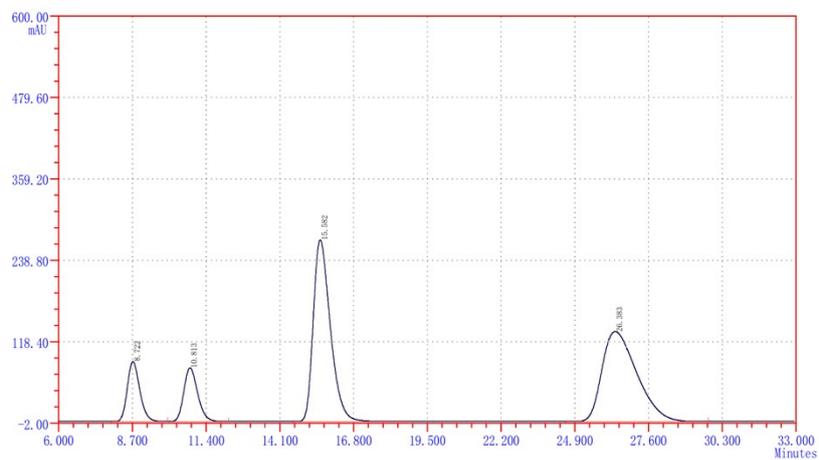
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	10.25	82.4	2479.546	22.5865
2	12.16	22.75	481.045	6.236
3	17.0917	259.67	11252.59	70.1099
4	27.4191	2.35	259.165	1.425

Fig. S59 HPLC curve of **6i** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



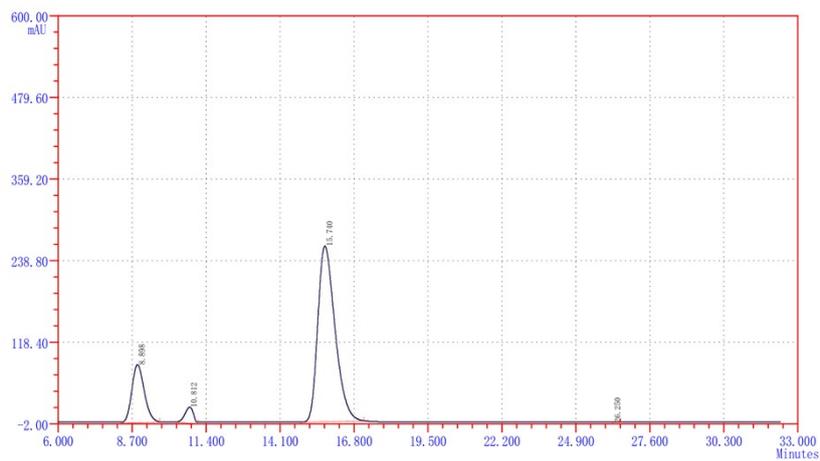
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	10.2033	25.84	454.976	10.6587
2	12.3733	77.55	2624.655	31.9886
3	17.1	5.79	280.646	1.3106
4	27.9433	133.25	11904.95	56.0420

Fig. S60 HPLC curve of **6i'** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.7217	88.82	2830.397	15.5786
2	10.8133	79.37	2795.763	13.9211
3	15.5817	268.7	11718.54	47.1288
4	26.3833	133.25	11853.69	23.3715

Fig. S61 HPLC curve of racemic **6j** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

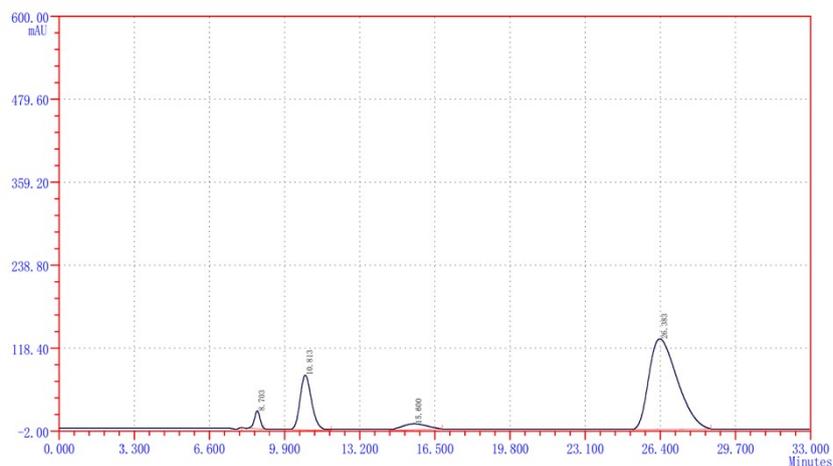


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.8983	85.72	2730.517	23.2493
2	10.8117	23.62	506.782	6.0063
3	15.74	259.36	11372.95	70.3445
4	26.25	2.31	6.785	0.4239

Fig. S62 HPLC curve of **6j** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).

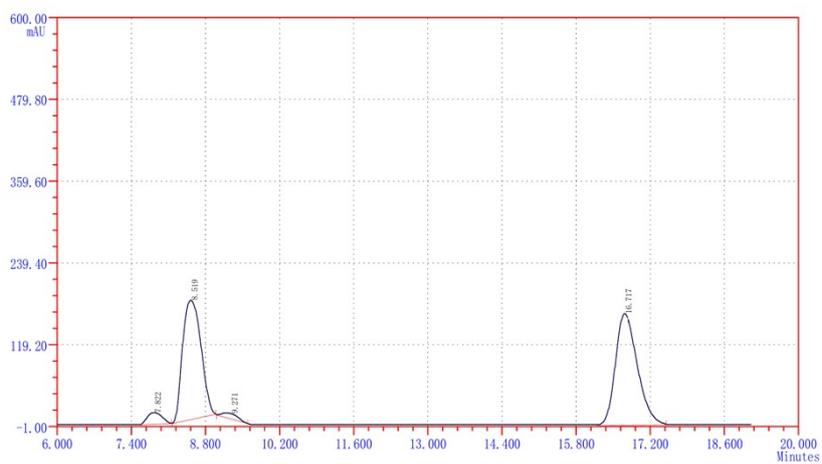
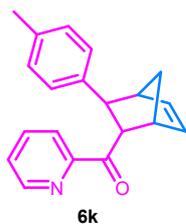


6j'



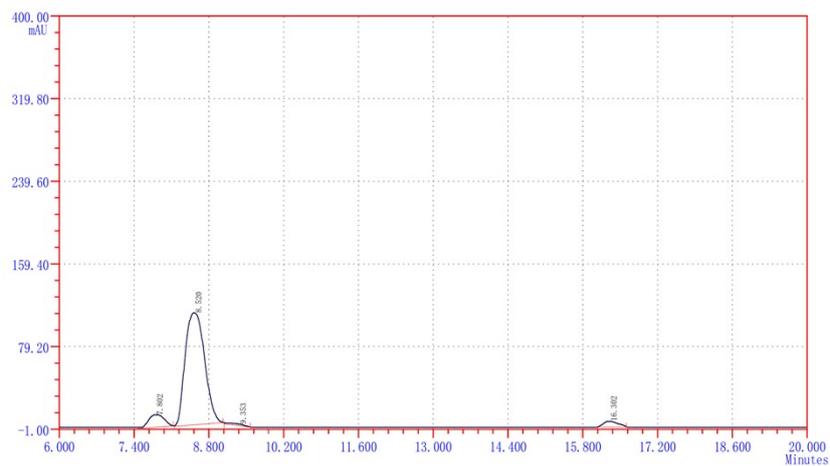
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.7033	25.95	449.523	2.9342
2	10.8133	79.52	2814.145	18.3689
3	15.6	8.51	429.978	2.1311
4	26.3833	131.46	11626.52	76.5659

Fig. S63 HPLC curve of 6j' catalyzed by *R*-poly(3₅₀-*b*-2₃₀-*b*-3₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



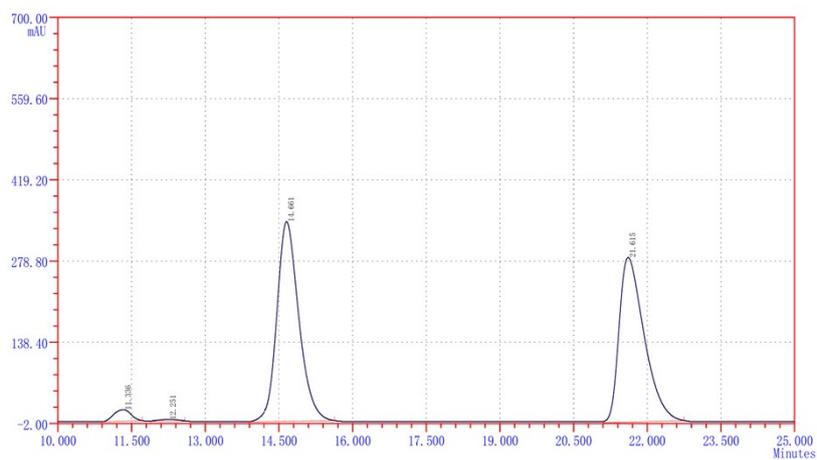
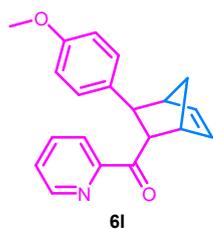
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	7.8222	17.39	342.893	4.7661
2	8.519	175.51	4242.182	48.1021
3	9.2707	7.74	159.051	2.1213
4	16.7171	164.23	4749.121	45.0106

Fig. S64 HPLC curve of racemic **6k** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



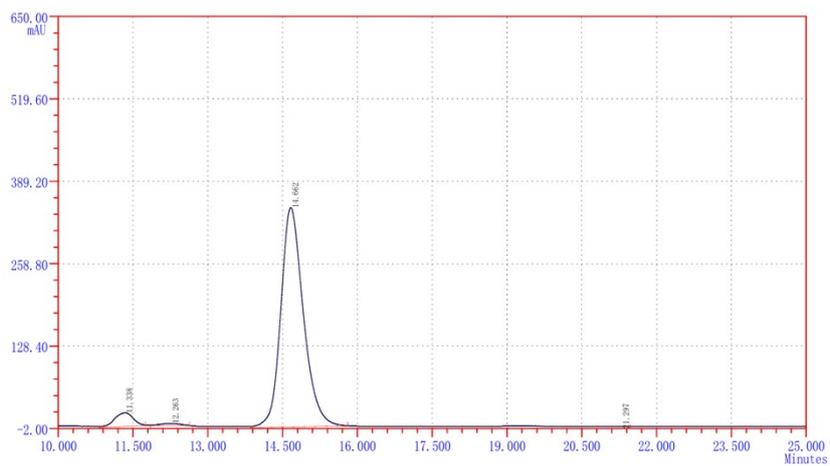
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	7.8017	12.16	243	9.4697
2	8.52	108.85	2751.622	84.7675
3	9.3533	1.66	35.004	1.2927
4	16.3017	5.74	109.289	4.4701

Fig. S65 HPLC curve of **6k** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



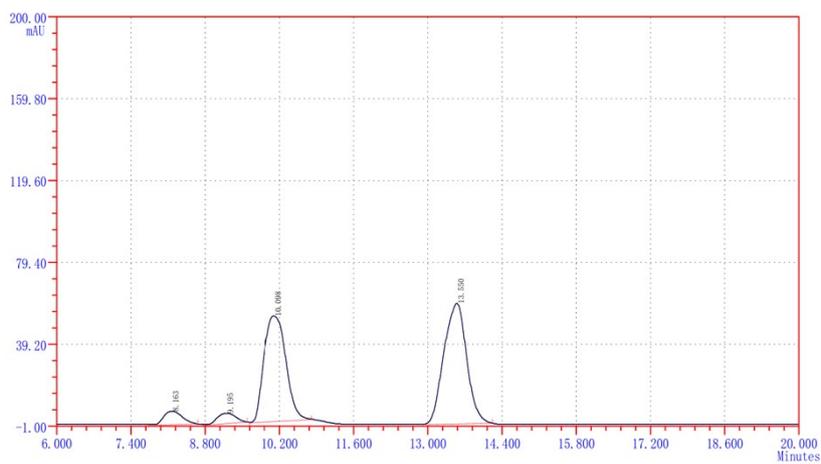
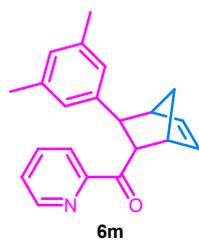
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	11.3362	20.15	496.565	2.3189
2	12.2514	3.45	99.558	0.4649
3	14.6614	345.37	10730.17	50.1078
4	21.6147	284.57	10087.89	47.1085

Fig. S66 HPLC curve of racemic **61** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).



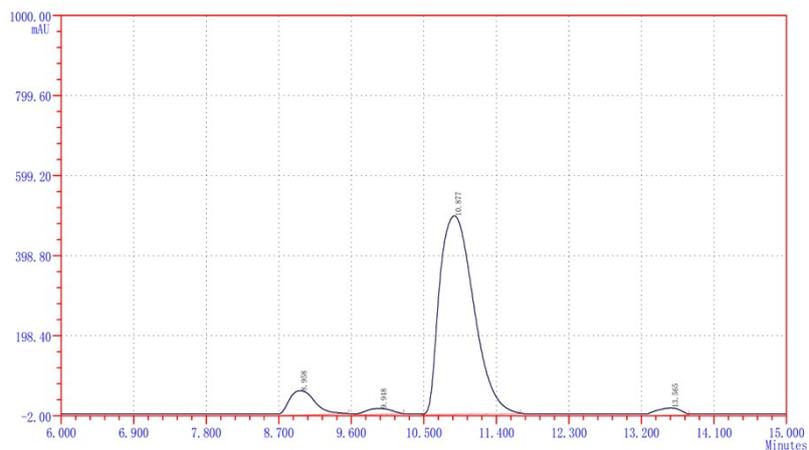
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	11.3383	21.46	571.063	4.5379
2	12.2633	3.46	96.294	0.704
3	14.6617	347.2	10941.59	94.2399
4	21.2967	2.3	67.201	0.44

Fig. S67 HPLC curve of **6I** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).



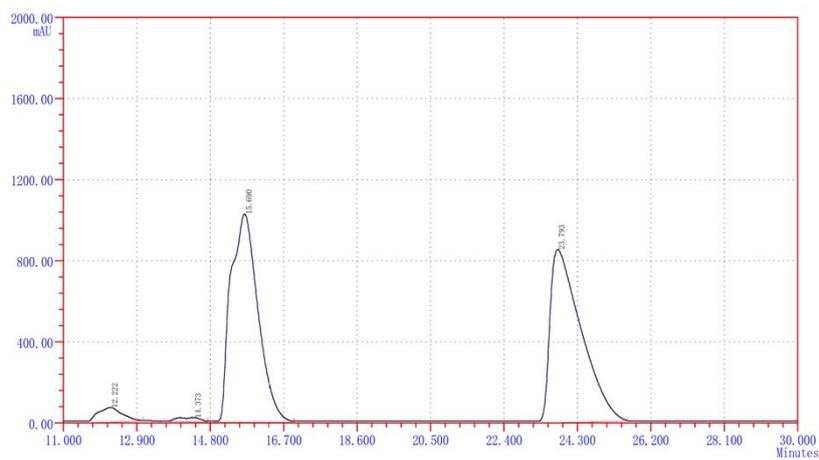
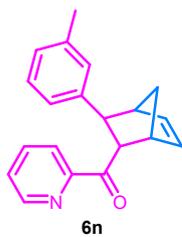
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.1633	6.62	163.088	5.394
2	9.195	5.09	123.985	4.1473
3	10.0983	51.79	1589.166	45.1983
4	13.55	59.23	1678.705	45.2604

Fig. S68 HPLC curve of racemic **6m** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



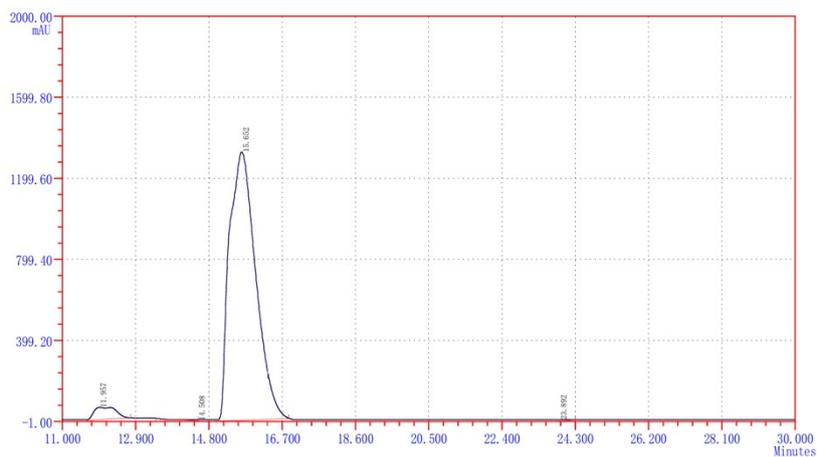
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.9583	60.17	1340.944	8.0545
2	9.9483	14.39	318.639	1.9139
3	10.8767	496.56	14602.08	87.7089
4	13.565	18.39	386.675	2.3226

Fig. S69 HPLC curve of **6m** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



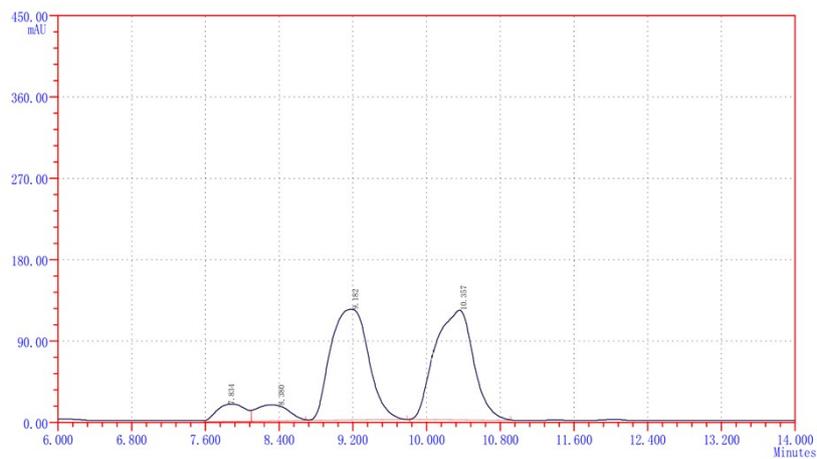
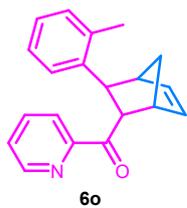
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	12.2216	71.42	3127.055	3.6174
2	14.3733	21.44	899.81	1.0859
3	15.69	1026.65	50264.22	51.9999
4	23.7931	854.82	47801.7	43.2967

Fig. S70 HPLC curve of racemic **6n** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).



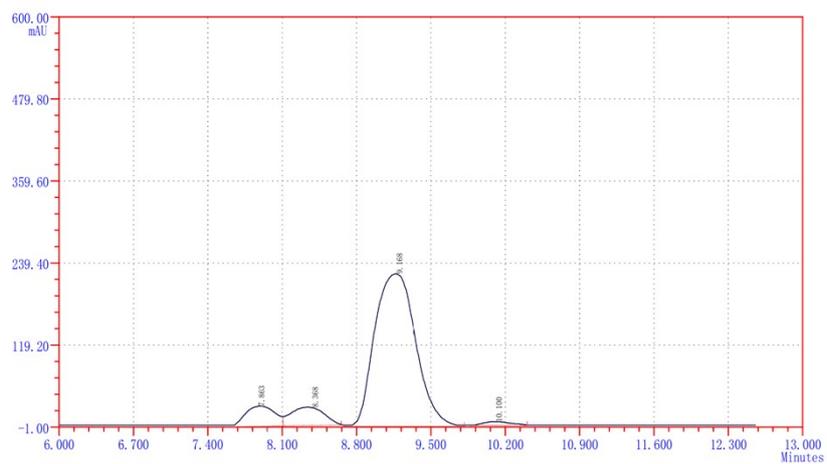
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	11.9567	61.1	2400.777	4.3861
2	14.5083	0.44	2.863	0.0316
3	15.6517	1324.4	62805.72	95.072
4	23.8917	7.11	185.326	0.5104

Fig. S71 HPLC curve of **6n** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).



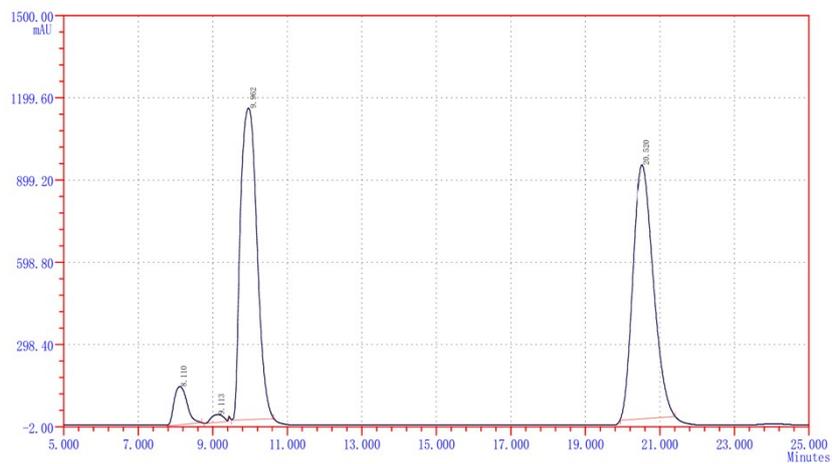
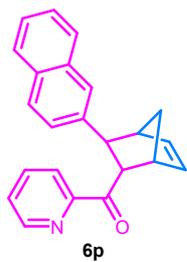
Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	7.8335	19.12	407.047	5.1678
2	8.3802	17.58	426.325	5.4126
3	9.182	122.58	3510.142	44.5643
4	10.3566	121.4	3533.066	44.8553

Fig. S72 HPLC curve of racemic **60** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



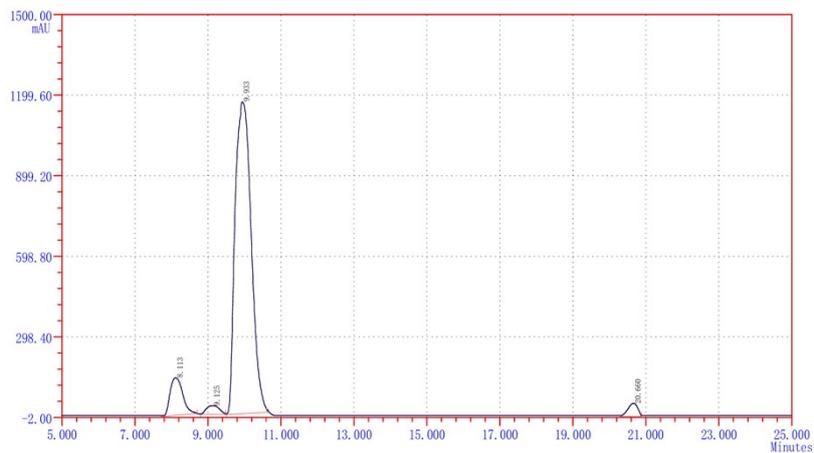
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	7.8633	29.67	575.794	10.381
2	8.3683	26.96	592.392	9.4328
3	9.1683	223.33	5986.417	78.1393
4	10.1	5.85	111.461	2.0468

Fig. S73 HPLC curve of **60** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, 0.65 mL/min, 254 nm, T = 25 °C).



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.110	139.60	3355.740	4.5358
2	9.113	28.40	627.420	0.8481
3	9.961	1136.94	34937.030	47.2222
4	20.520	927.32	35064.060	47.3939

Fig. S74 HPLC curve of racemic **6p** (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).

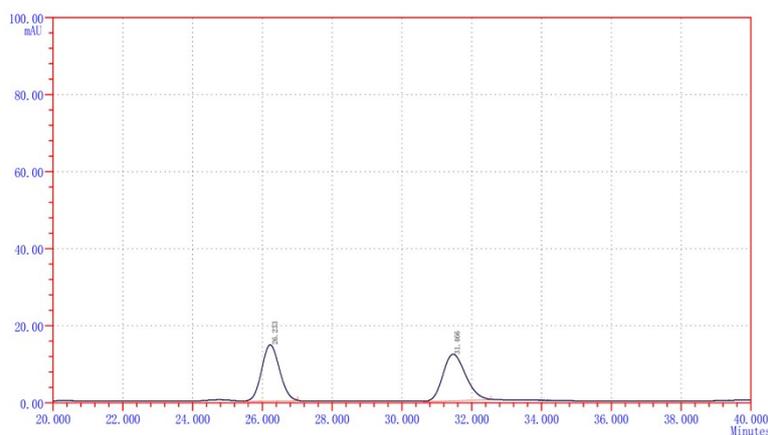


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	8.1133	140.2	3386.257	10.1392
2	9.125	31.79	763.186	2.299
3	9.9333	1163.07	35620.97	84.1128
4	20.66	47.69	876.041	3.4489

Fig. S75 HPLC curve of **6p** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, 0.65 mL/min, 254 nm, T = 25 °C).

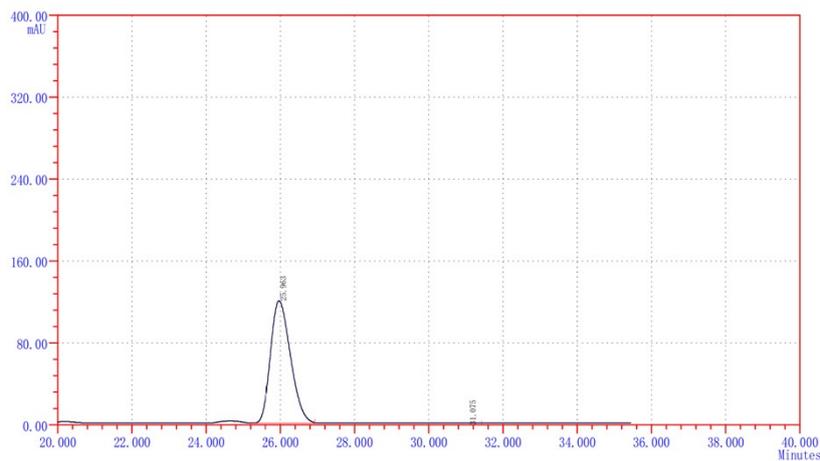


11a



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	26.2335	14.57	518.863	50.6102
2	31.4664	13.11	547.844	49.3898

Fig. S76 HPLC curve of racemic **11a** (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

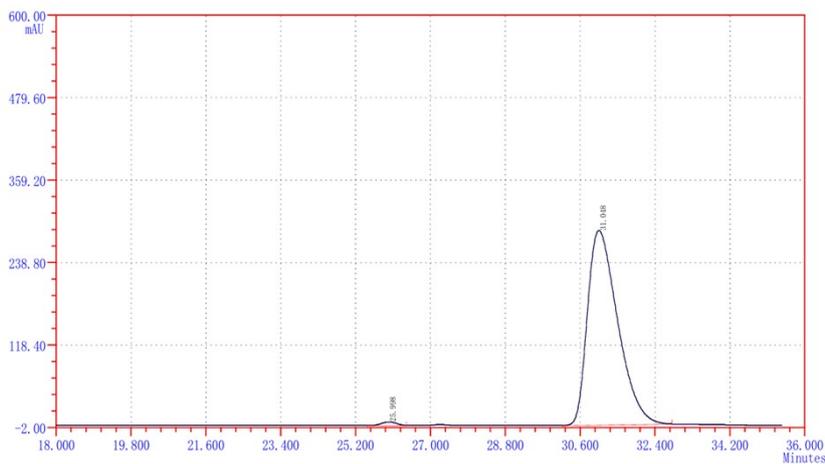


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	25.9633	119.71	4488.588	98.7869
2	31.075	1.47	44.417	1.2131

Fig. S77 HPLC curve of **11a** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.65 mL/min, 254 nm, T = 25 °C).

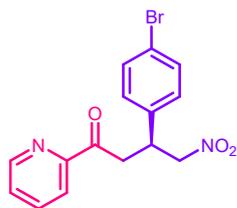


11a'

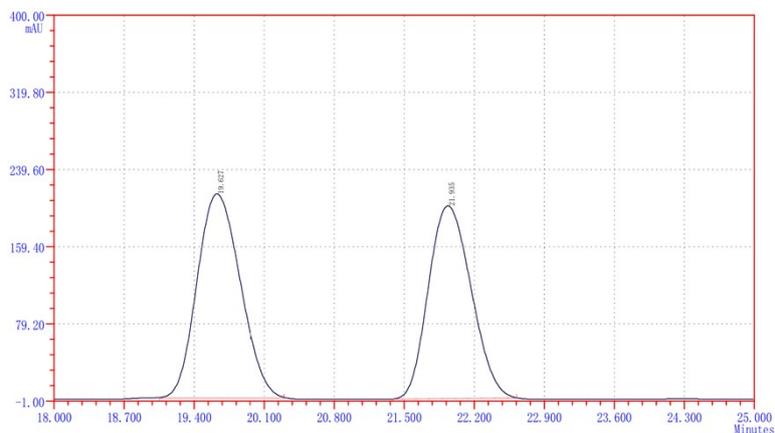


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	25.9983	5.93	166.254	2.0417
2	31.0483	284.52	14394.02	97.9583

Fig. S78 HPLC curve of **11a'** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

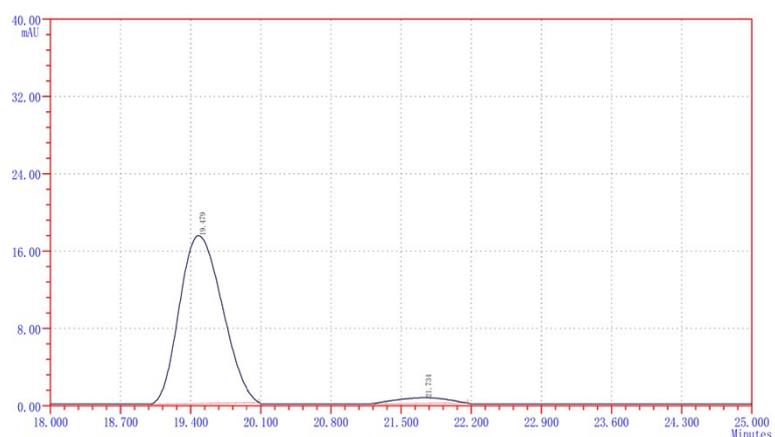


11b



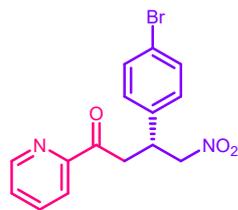
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	19.6267	211.88	6372.272	51.4197
2	21.935	200.18	5947.482	48.5803

Fig. S79 HPLC curve of racemic **11b** (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

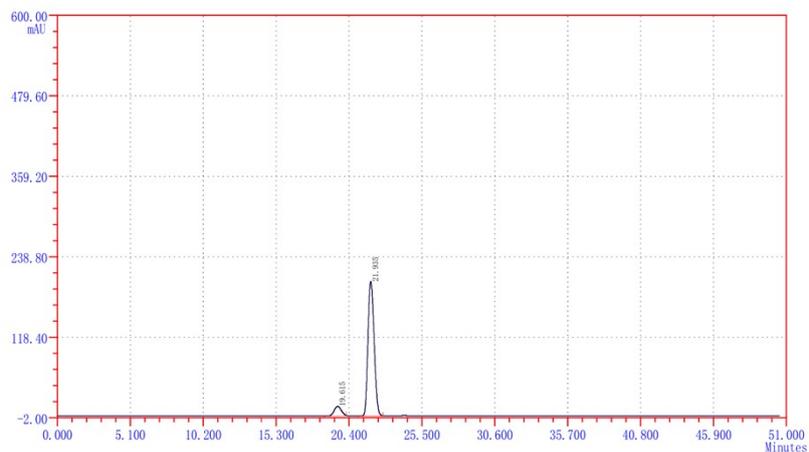


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	19.4791	17.36	514.997	96.0712
2	21.7343	0.59	21.061	3.9288

Fig. S80 HPLC curve of **11b** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

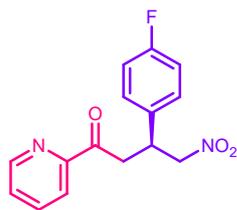


11b'

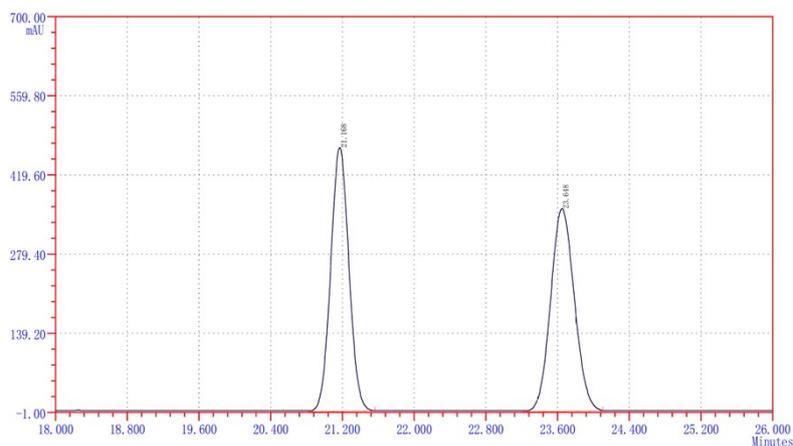


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	19.615	14.43	410.582	6.222
2	21.935	201.73	6188.292	93.778

Fig. S81 HPLC curve of **11b'** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

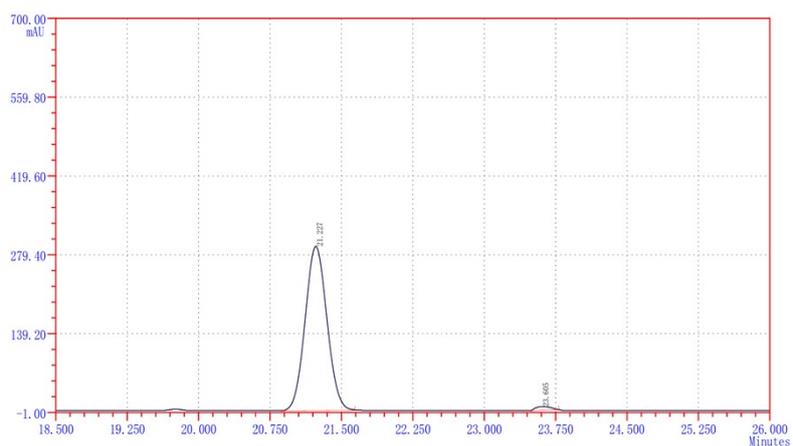


11c



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	21.1683	466.73	6611.417	49.9462
2	23.6483	359.11	6625.669	50.0538

Fig. S82 HPLC curve of racemic **11c** (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

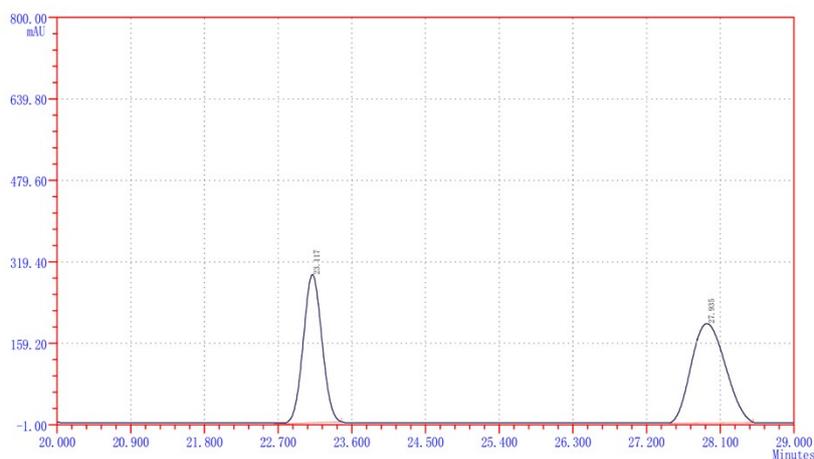


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	21.2267	292.5	4672.282	97.552
2	23.605	7.34	81.315	2.448

Fig. S83 HPLC curve of **11c** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

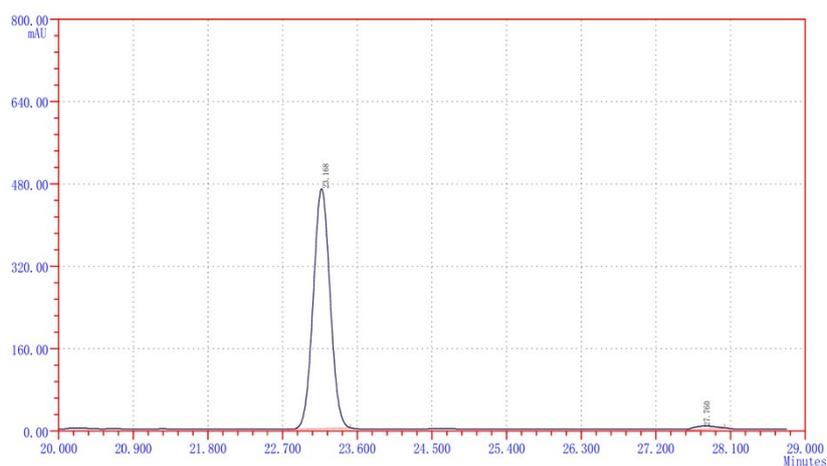


11d



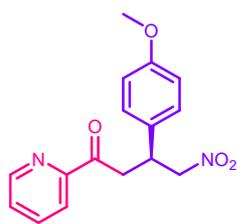
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	23.1167	291.55	4630.486	49.0246
2	27.935	195.58	5653.854	50.9754

Fig. S84 HPLC curve of racemic **11d** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

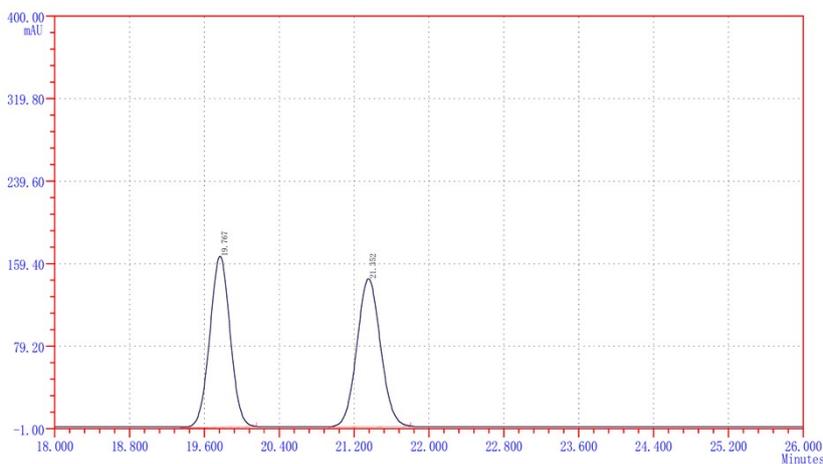


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	23.1683	466.46	6598.224	98.6778
2	27.76	6.25	116.123	1.3222

Fig. S85 HPLC curve of **11d** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

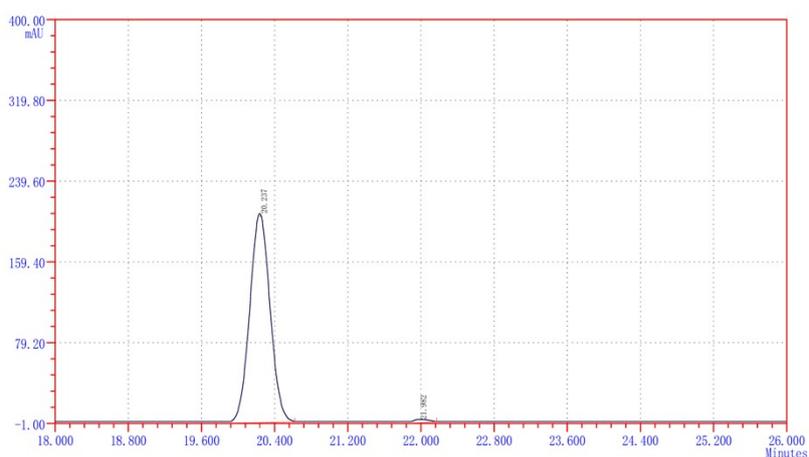


11e



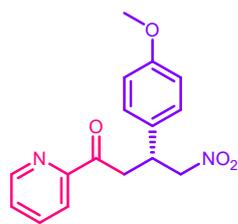
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	19.7667	166.08	2512.264	49.7007
2	21.3517	143.92	2542.518	50.2993

Fig. S86 HPLC curve of racemic **11e** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

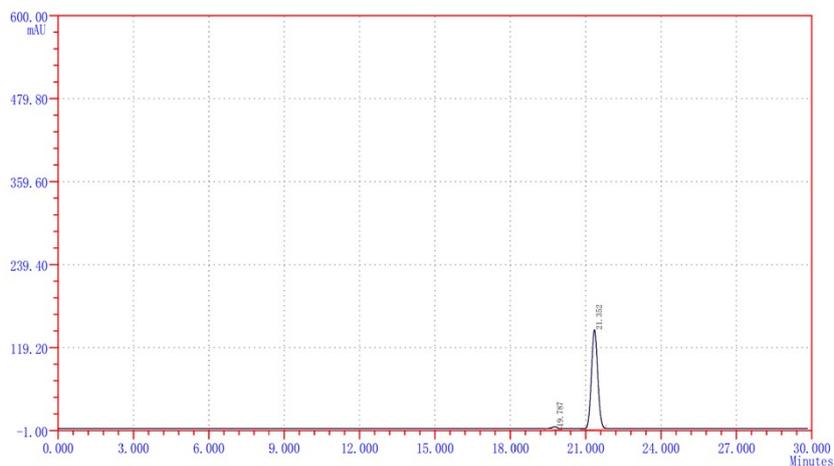


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	20.2367	207.51	3206.374	98.7596
2	21.9817	3.47	40.273	1.2404

Fig. S87 HPLC curve of **11e** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).



11e'

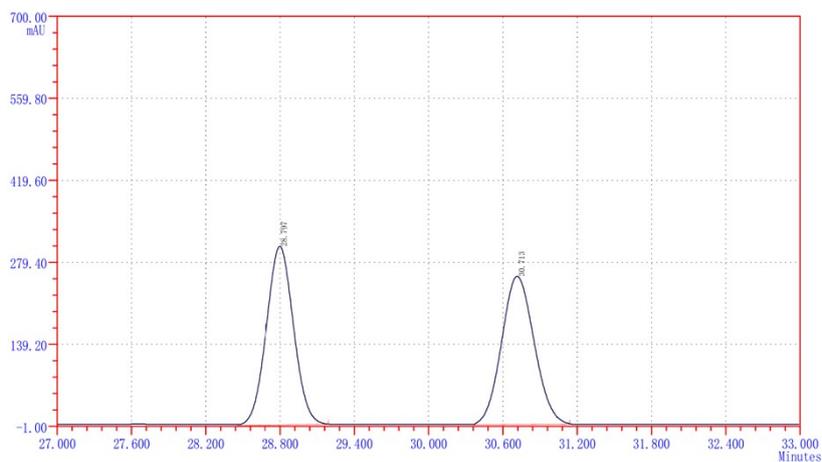


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	19.7867	3.53	64.769	2.475
2	21.3517	144.03	2552.203	97.525

Fig. S88 HPLC curve of **11e'** catalyzed by *S*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

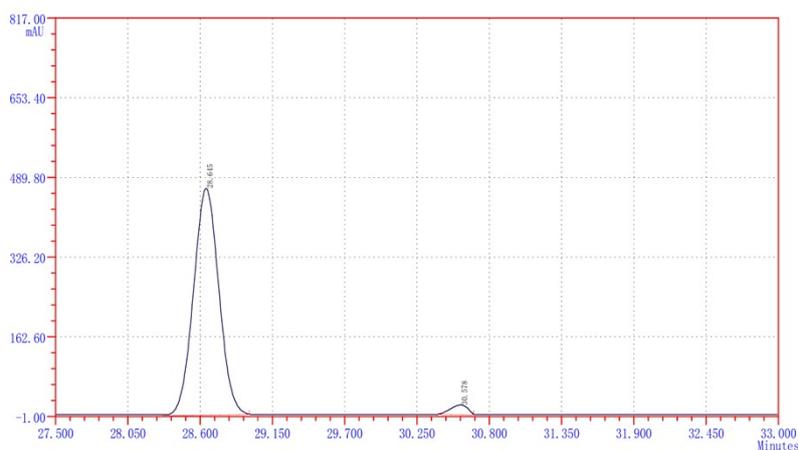


11f



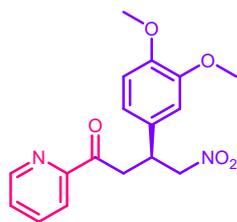
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	28.7967	305.52	4652.48	49.9941
2	30.7133	253.43	4653.584	50.0059

Fig. S89 HPLC curve of racemic **11f** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

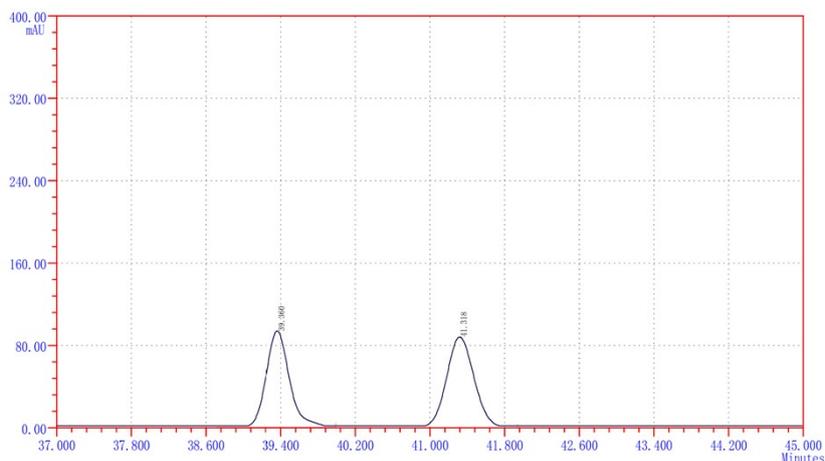


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	28.645	464.95	6244.438	96.8265
2	30.5783	20.25	187.227	3.1735

Fig. S90 HPLC curve of **11f** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

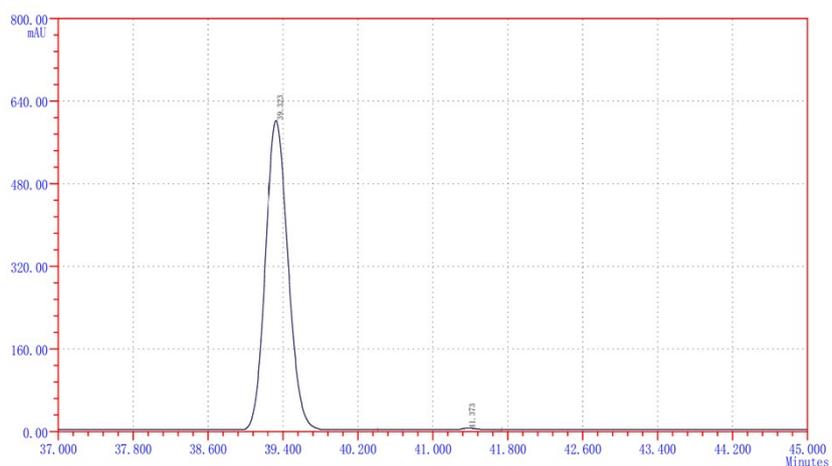


11g



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	39.36	93.5	1633.065	51.3877
2	41.3183	88.45	1841.38	48.6123

Fig. S91 HPLC curve of racemic **11g** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

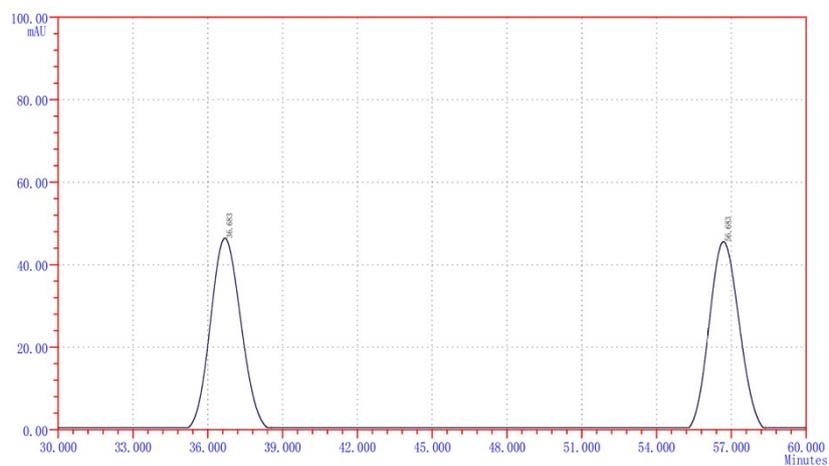


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	39.3233	602.44	10181.02	98.9228
2	41.3733	6.56	109.585	1.0772

Fig. S92 HPLC curve of **11g** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

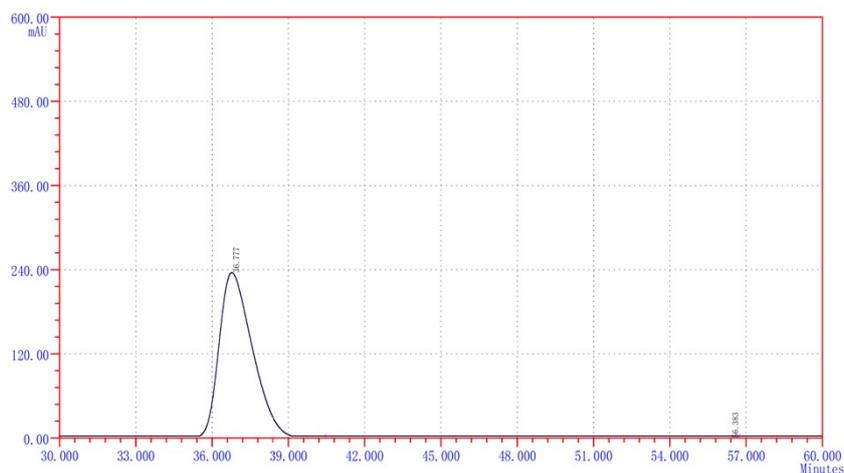


11h



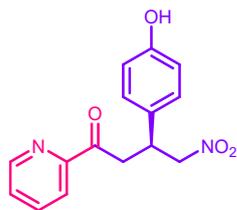
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	36.6833	46.91	4037.203	50.506
2	56.6833	45.97	3862.104	49.494

Fig. S93 HPLC curve of racemic **11h** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

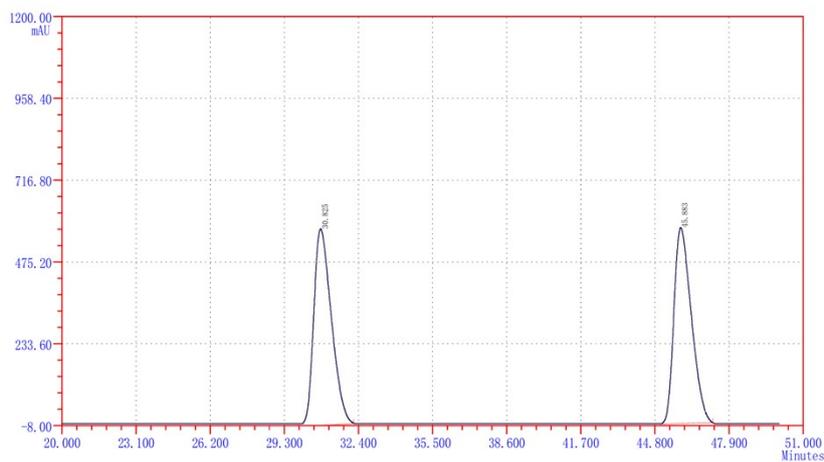


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	36.7767	235.93	21527.3	98.807
2	56.3833	2.53	211.948	1.193

Fig. S94 HPLC curve of **11h** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

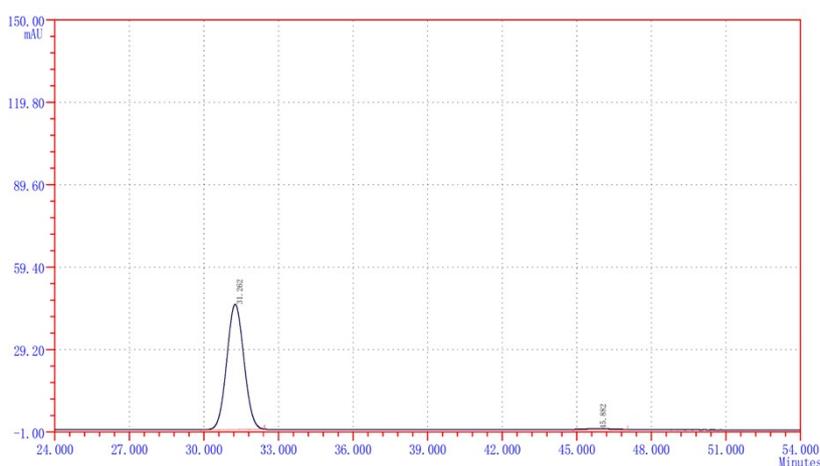


11i



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	30.825	580.27	29712.67	50.0686
2	45.8833	578.68	29344.99	49.9314

Fig. S95 HPLC curve of racemic **11i** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

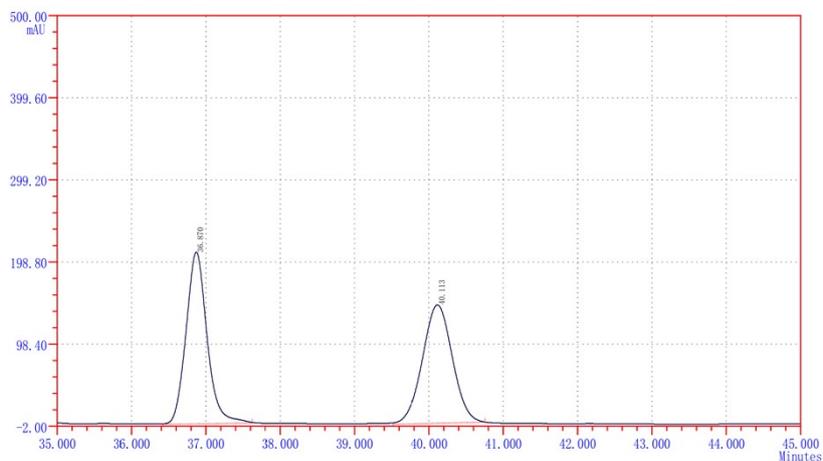


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	31.2618	45.94	2215.172	98.902
2	45.8816	0.51	52.182	1.098

Fig. S96 HPLC curve of **11i** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

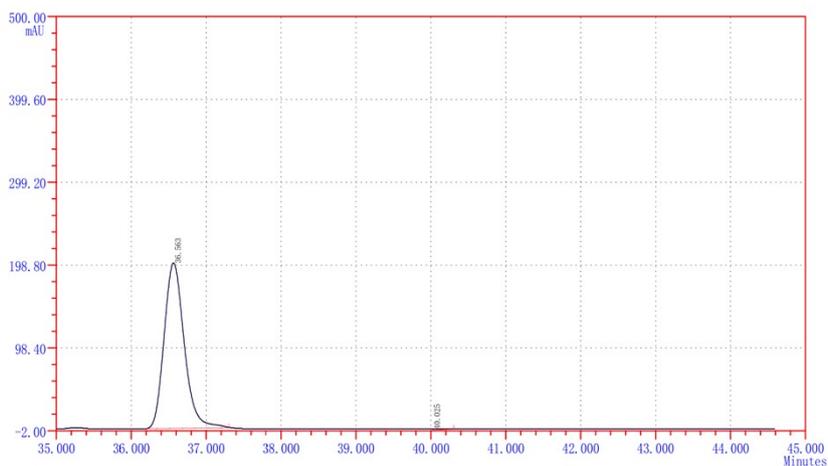


11j



Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	36.87	209.76	4119.868	59.1723
2	40.1133	144.73	4049.873	40.8277

Fig. S97 HPLC curve of racemic **11j** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

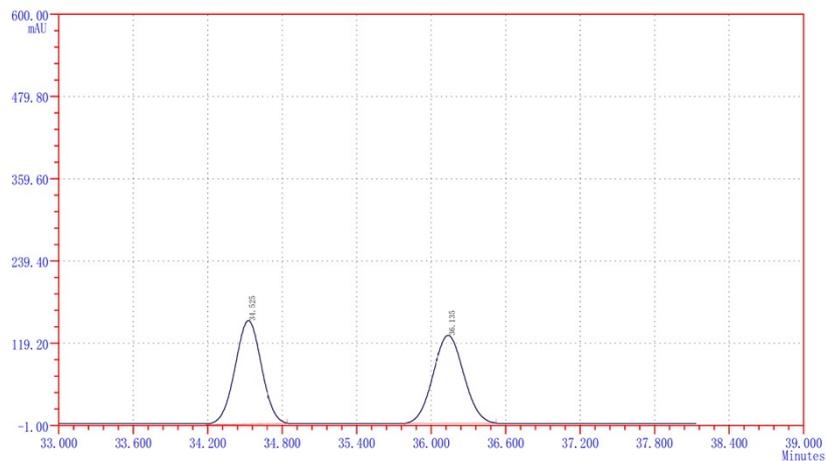


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	36.56	199.32	3621.448	98.732
2	40.0333	1.14	98.681	1.268

Fig. S98 HPLC curve of **11j** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

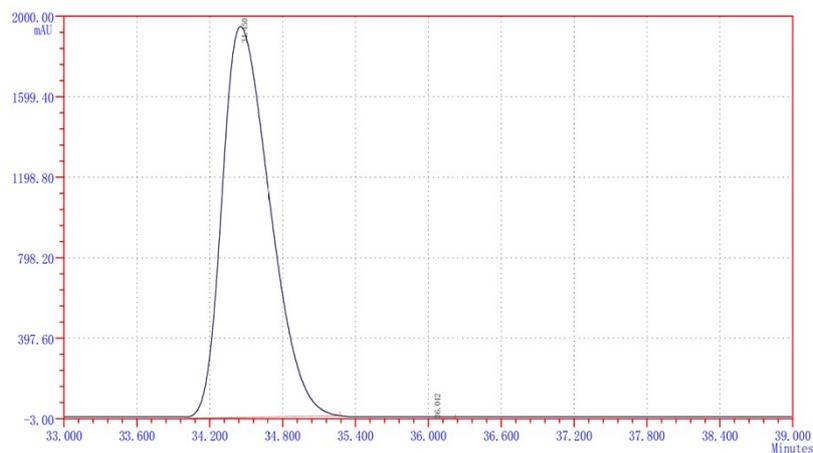


11k



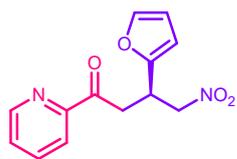
Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	34.525	150.95	2239.484	50.2766
2	36.135	128.66	2214.847	49.7234

Fig. S99 HPLC curve of racemic **11k** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

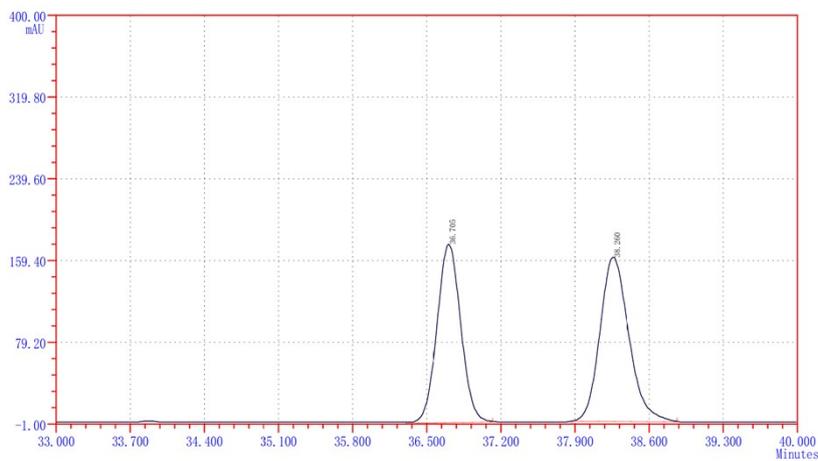


Peak	Ret.Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel.Area %
1	34.450	1944.71	53030.51	98.9763
2	36.0417	1.52	32.571	1.0237

Fig. S100 HPLC curve of **11k** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

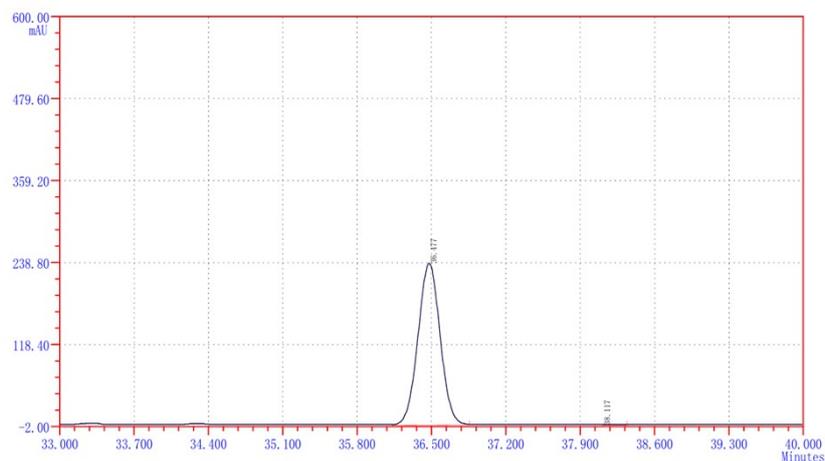


111



Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	36.705	174.9	2728.536	52.035
2	38.26	161.22	3065.275	47.965

Fig. S101 HPLC curve of racemic **111** (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).



Peak	Ret. Time min	Height mV($\times 10^3$)	Area mV*min($\times 10^3$)	Rel. Area %
1	36.4767	237.31	3440.175	98.773
2	38.1167	0.54	17.317	1.227

Fig. S102 HPLC curve of **111** catalyzed by *R*-poly(**3**₅₀-*b*-**2**₃₀-*b*-**3**₅₀) (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, 254 nm, T = 25 °C).

8. References

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