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Supporting Information

for

Highly efficient organocatalysts for the asymmetric aldol reaction

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Experimental Section

General Information

The NMR spectra were recorded on 400 MHz spectrometer Varian Inova 400 e Bruker Avance 400. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard in spectra made in CDCl3. Coupling constants are reported in Hz. All enantiomeric excesses were obtained from HPLC using chiral stationary phase in a Shimadzu LC-20AT chromatograph. Optical rotations were obtained in a Jasco P-2000 polarimeter. Melting points were obtained in a Buchi Melting Point M-560 equipment. Infrared spectra were obtained in a Shimadzu IR Prestige-21 spectrometer. HRMS spectra were obtained in a Micromass Q-Tof micro mass spectrometer. All the column chromatography separations were done by using silica gel 230-400 Mesh. Solvents were purified by usual methods.[1] Other reagents were obtained from commercial source and used without further purification.

General procedure for the synthesis of phenacyl esters 3a-e

The amino acid (5 mmol) was added to a solution of triethylamine (0.8 mL, 5 mmol) in ethyl acetate (30 mL) at room temperature. Then the corresponding 2-bromoacetophenone (5 mmol) was introduced and the reaction mixture was stirred for 24 h. The reaction was treated with aqueous $NaHCO_3$ 5% solution (30 mL) and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The organic extracts were combined, washed with water (3 x 20 mL), dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was used without further purification.

3-(*tert*-butyl) 4-(2-oxo-2-phenylethyl) (*R*)-thiazolidine-3,4-dicarboxylate (3a)

The product was obtained as a white solid. Yield: 90 %. Mp 88-92 °C. $[\alpha]_D^{20}$= -59 (*c* 0.4, CH_2Cl_2). IR (KBr): 3392, 3007, 2981, 2936, 2890, 1760, 1706, 1388, 1367, 1174, 1137. ^{1}H NMR (400 MHz, $CDCl_3$, conformer mixture) δ: 7.90 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), [5.58 (d, *J* = 16.3 Hz), 5.47 (d, *J* = 16.4 Hz), 5.36 (d, *J* = 16.1 Hz) and 5.26 (d, *J* = 16.4 Hz), 2H], [5.05-4.93 (m) and 4.92-4.78 (m), 1H], 4.66 (d, *J* = 8.5 Hz, 1H), 4.57-4.45 (m, 1H), 3.55-3.35 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, conformer mixture) δ: 191.6, 191.2, 170.3, 170.2, 153.3, 153.1, 134.0, 133.9, 128.9, 127.7, 81.3, 66.5, 61.3, 49.1, 48.5, 34.7, 33.5, 28.3, 28.2.

3-(*tert*-butyl) 4-(2-(4-methoxyphenyl)-2-oxoethyl) (*R*)-thiazolidine-3,4-dicarboxylate (3b)

The product was obtained as a brown oil. Yield: 79 %. $[\alpha]_D^{20}$= -16 (*c* 0.5, CH_2Cl_2). IR (film): 3009, 2972, 2935, 2841, 1758, 1704, 1690, 1601, 1385, 1370, 1241, 1169. ^{1}H NMR (400 MHz, $CDCl_3$, conformer mixture) δ: 7.87 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), [5.53 (d, *J* = 16.2 Hz), 5.42 (d, *J* = 16.0 Hz), 5.30 (d, *J* = 15.9 Hz) and 5.21 (d, *J* = 16.6 Hz), 2H], [5.03-4.94 (m) and 4.89-4.80 (m), 1H], 4.65 (d, *J* = 8.7 Hz, 1H), 4.56-4.46 (m, 1H), 3.87 (s, 3H), 3.56-3.36 (m, 2H), 1.54-1.37 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, conformer mixture) δ: 190.0, 189.6, 170.4, 170.3, 164.1, 163.4, 153.3, 153.1, 131.1, 130.0, 126.9, 114.1, 113.8, 81.3, 66.4, 66.2, 61.3, 55.5, 49.1, 48.6, 34.8, 34.4, 28.3, 28.2.

4-(2-(4-bromophenyl)-2-oxoethyl) 3-(*tert*-butyl) (*R*)-thiazolidine-3,4-dicarboxylate (3c)

The product was obtained as a yellow oil. Yield: 90 %. $[\alpha]_D^{20}$= -24 (*c* 0.6, CH_2Cl_2). IR (film): 3382, 3087, 2975, 2936, 2882, 1755, 1706, 1679, 1587, 1168, 1071. ^{1}H NMR (400 MHz, $CDCl_3$, conformer mixture) δ: 7.69 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), [5.45 (d, *J* = 16.3 Hz), 5.35 (d, *J* = 16.2 Hz), 5.24 (d, *J* = 16.3 Hz) and 5.15 (d, *J* = 16.4 Hz), 2H], [4.92 (dd, *J* = 6.0; 3.9 Hz) and 4.84-4.74 (m), 1H], 4.58 (d, *J* = 8.7 Hz, 1H), 4.44 (d, *J* = 9.0 Hz, 1H), 3.45-3.28 (m, 2H), 1.48-1.32 (m, 9H). ^{13}C NMR (100

MHz, $CDCl_3$, conformer mixture) δ: 190.8, 190.4, 170.3, 170.1, 153.3, 153.1, 132.6, 132.3, 131.8, 131.6, 129.2, 81.4, 66.3, 61.3, 49.1, 48.5, 34.7, 33.5, 28.3, 28.2.

3-(*tert*-butyl) 4-(2-(4-nitrophenyl)-2-oxoethyl) (*R*)-thiazolidine-3,4-dicarboxylate (3d)

The product was obtained as a yellow wax. Yield: 96 %. $[\alpha]_D^{20}$= -46 (*c* 0.5, CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$, conformer mixture) δ: 8.36 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), [5.57 (d, *J* = 16.4 Hz), 5.48 (d, *J* = 16.5 Hz), 5.38 (d, *J* = 16.4 Hz) and 5.28 (d, *J* = 16.7 Hz), 2H], [5.04-4.96 (m) and 4.93-4.83 (m), 1H], 4.74-4.57 (m, 1H), 4.51 (dd, *J* = 15.1; 8.9 Hz, 1H), 3.50-3.39 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, conformer mixture) δ: 190.6, 190.2, 170.2, 170.1, 153.2, 153.0, 150.7, 138.8, 131.0, 129.0, 124.1, 123.5, 81.4, 66.6, 66.5, 61.3, 49.0, 48.5, 34.6, 33.4, 28.2.

1-(*tert*-butyl) 2-(2-oxo-2-phenylethyl) (*S*)-pyrrolidine-1,2-dicarboxylate (3e)

The product was obtained as a white solid. Yield: 85 %. Mp 78-81 °C. $[\alpha]_D^{20}$= -54 (*c* 1, CH_2Cl_2) [lit.[2] Mp 80-83 °C, $[\propto]_D^{20}$ = -67.8 (c 1, DMF)]. IR (KBr): 3394, 3025, 2976, 2936, 2893, 1758, 1707, 1597, 1450, 1398, 1370, 1171, 1119. ^{1}H NMR (400 MHz, $CDCl_3$, conformer mixture) δ: 7.93-7.87 (m, 2H), 7.65-7.57 (m, 1H), 7.46-7.54 (m, 2H), [5.57 (d, *J* = 16.4 Hz), 5.42 (d, *J* = 16.3 Hz), 5.34 (d, *J* = 16.3 Hz) and 5.22 (d, *J* = 16.4 Hz), 2H], 4.49 (dd, *J* = 8.5; 3.7 Hz) and 4.48-4.36 (m), 1H], 3.64-3.51 (m, 1H), 3.51-3.35 (m, 1H), 2.40-2.22 (m, 2H), 2.15-1.98 (m, 1H), 1.98-1.77 (m, 1H), 1.60-1.38 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, conformer mixture) δ: 192.2, 191.8, 172.6, 172.5, 154.5, 153.9, 134.2, 134.1, 134.0, 133.9, 128.9, 128.8, 127.7, 80.0, 79.9, 66.1, 65.9, 59.0, 58.7, 46.7, 46.4, 31.0, 30.1, 28.5, 28.4, 24.3, 23.6.

General procedure for the synthesis of compounds 5a-e

Ammonium acetate (1.54 g, 20 mmol) was added to a solution of the corresponding phenacyl ester (2 mmol) in toluene (20 mL). The mixture was refluxed with a Dean-Stark trap for 19 h. Then the reaction was cooled to room temperature and poured into water (20 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ solution (20 mL) and water (20 mL), dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was dissolved in ethyl acetate (2 mL) and a solution of

TFA (4 mL) in ethyl acetate (4 mL) was added. The mixture was stirred at room temperature and the reaction was monitored by TLC. After 1-2 h, the mixture was neutralized with K_2CO_3 and the aqueous layer was extracted with ethyl acetate (3 x 5 mL). The organic extracts were combined, washed with water, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The product was purified with flash column cromatography on silica gel using ethyl acetate.

(*R*)-4-(5-phenyl-1*H*-imidazol-2-yl)thiazolidine (5a)

The product was obtained as a yellow solid. Yield: 91 %. Mp 178-182 °C. $[\alpha]_D^{20}$= -19 (*c* 0.3, CH_2Cl_2). IR (KBr): 3042, 2979, 2945, 1684, 1441, 1208, 1140. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.3 (bs, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.48 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.40 (t, *J* = 6.4 Hz, 1H), 4.17 (s, 2H), 3.23 (dd, *J* = 9.8; 6.4 Hz, 1H), 3.16 (dd, *J* = 9.8; 6.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 147.1, 133.9, 128.5, 126.0, 124.2, 113.9, 61.9, 53.9, 37.4. HRMS calculated for $[C_{12}H_{13}N_3S+H]^+$: 232.0909, obtained: 232.0986.

(*R*)-4-(5-(4-methoxyphenyl)-1*H*-imidazol-2-yl)thiazolidine (5b)

The product was obtained as a brown solid. Yield: 83 %. Mp 166-169 °C. $[\alpha]_D^{20}$= -50 (*c* 0.3, CH_2Cl_2). IR (KBr): 3055, 2946, 2887, 1687, 1208, 1141. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65-7.40 (m, 2H), 7.08 (s, 1H), 6.93-6.65 (m, 2H), 4.32-4.05 (m, 1H), 3.90-3.55 (m, 5H), 3.50-2.95 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.9, 130.2, 126.6, 125.6, 114.2, 114.0, 55.2, 55.0. HRMS calculated for $[C_{13}H_{15}N_3OS+H]^+$: 262.1014, obtained: 262.1082.

(*R*)-4-(5-(4-bromophenyl)-1*H*-imidazol-2-yl)thiazolidine (5c)

The product was obtained as a yellow solid. Yield: 93 %. Mp 174-178 °C. $[\alpha]_D^{20}$= -34 (*c* 0.3, CH_2Cl_2). IR (film): 3261, 3035, 2981, 2943, 2893, 1687, 1476, 1435, 1208, 1140. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.18 (s, 1H), 4.45 (t, *J* = 6.8 Hz, 1H), 4.20 (s, 2H), 3.33 (dd, *J* = 10.3; 6.8 Hz, 1H), 3.28 (dd, *J* = 10.3; 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 147.4, 132.0, 131.8, 126.4, 120.9, 114.6, 61.4, 50.7, 37.4. HRMS calculated for $[C_{12}H_{12}BrN_3S+H]^+$: 310.0013, obtained: 309.9938.

(***R***)-4-(5-(4-nitrophenyl)-1***H***-imidazol-2-yl)thiazolidine (5d)

The product was obtained as a yellow solid. Yield: 95 %. Mp 185-190 °C. $[\alpha]_D^{20}$= -23 (*c* 0.2, CH_2Cl_2). IR (KBr): 3265, 3021, 2981, 2946, 2885, 1588, 1506, 1333, 1146, 1111. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.50 (s, 1H), 4.99-4.92 (m, 1H), 4.34-4.30 (m, 2H), 3.64 (dd, *J* = 11.2; 8.4 Hz, 1H), 3.47 (dd, *J* = 11.1; 6.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 148.5, 145.1, 141.6, 137.8, 124.6, 124.1, 116.8, 61.8, 53.9, 37.2. HRMS calculated for $[C_{12}H_{12}N_4O_2S+H]^+$: 277.0759, obtained: 277.0804.

(***S***)-5-phenyl-2-(pyrrolidin-2-yl)-1***H***-imidazole (5e)

The product was obtained as a brown oil. Yield: 81 %. $[\alpha]_D^{20}$= -38 (*c* 0.2, CH_2Cl_2). IR (film): 3036, 2948, 2913, 1655, 1450, 1402, 1290, 1186. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 4.54 (t, *J* = 6.7 Hz, 1H), 3.29-3.19 (m, 1H), 3.17-3.07 (m, 1H), 2.35-2.19 (m, 1H), 2.18-2.07 (m, 1H), 2.03-1.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 133.9, 130.9, 128.8, 128.2, 125.6, 55.2, 46.3, 30.9, 25.2. HRMS calculated for $[C_{13}H_{15}N_3+2H]^+$: 215.1422, obtained: 215.1365.

General procedure for organocatalytic asymmetric direct aldol reaction

A solution of organocatalyst **5d** (0.014 g, 0.05 mmol), benzoic acid (0.006 g, 0.05 mmol) and the corresponding ketone (5 mmol) was stirred at room temperature for 0.5 h. Then the system was cooled to 0 °C, the aldehyde (0.5 mmol) was added and the reaction mixture was stirred for 120 h. The solution was returned to room temperature, treated with saturated aqueous NH_4Cl solution (1 mL) and extracted with dichloromethane (3 x 2 mL). The organic extracts were combined, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The product was purified with flash column cromatography on silica gel using ethyl acetate and hexane (20:80).

(***S***)-2-((***R***)-hydroxy(phenyl)methyl)cyclohexan-1-one (8a)

The product was obtained in 81 % yield with >99 % *ee* and >19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel OD-H, hexane/2-propanol 90:10, 221 nm, flow rate 0.5 mL/min: $t_{R(maj)}$ = 17.9 min (*S,R*); $t_{R(min)}$ = 26.7 min (*R,S*). $[\propto]_D^{25}$= +18 (*c* 1, $CHCl_3$) [lit.[3] $[\propto]_D^{25}$ = +19 (c 1, $CHCl_3$)]. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37-7.23 (m, 5H), 4.79 (d, *J* = 8.8 Hz, 1H), 3.99 (bs, 1H), 2.63 (ddd, *J* = 12.8; 8.8; 5.5 Hz, 1H), 2.48 (ddd, *J* = 13.7, 4.5, 3.0 Hz, 1H), 2.42-2.30 (m, 1H), 2.08 (dtt, *J* = 11.8; 5.7; 3.1 Hz, 1H), 1.83-1.74 (m, 1H), 1.73-1.60 (m, 1H), 1.62-1.46 (m, 2H), 1.36-1.22 (m, 1H).

(*S*)-2-((*R*)-hydroxy(p-tolyl)methyl)cyclohexan-1-one (8b)

The product was obtained in 42 % yield with >99 % *ee* and >19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 90:10, 220 nm, flow rate 0.5 mL/min: $t_{R(maj)}$ = 23.1 min (*S,R*). $[\propto]_D^{25}$= +17 (*c* 0.2, $CHCl_3$) [lit.[4]$[\propto]_D^{24}$ = +12.9 (c 0.17, $CHCl_3$)]. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.15-6.90 (m, 4H), 4.68 (d, *J* = 8.7 Hz, 1H), 4.13 (bs, 1H), 2.58-1.85 (m, 4H), 1.73-1.35 (m, 5H).

(*S*)-2-((*R*)-(4-bromophenyl)(hydroxy)methyl)cyclohexan-1-one (8c)

The product was obtained in 99 % yield with 98 % *ee* and >19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 90:10, 220 nm, flow rate 1.0 mL/min: $t_{R(maj)}$ = 13.8 min (*S,R*); $t_{R(min)}$ = 11.7 min (*R,S*). $[\propto]_D^{25}$= +24 (*c* 1, $CHCl_3$) [lit.[4] $[\propto]_D^{24}$ = +22.6 (c 0.7, $CHCl_3$)]. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.74 (d, *J* =8.5 Hz, 1H), 2.65-2.15 (m, 3H), 2.13-1.90 (m, 1H), 1.83-1.35 (m, 4H), 1.32-1.10 (m, 1H).

4-((*R*)-hydroxy((*S*)-2-oxocyclohexyl)methyl)benzonitrile (8d)

The product was obtained in 92 % yield with 99 % *ee* and 8:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 80:20, 220 nm, flow rate 0.5 mL/min: $t_{R(maj)}$ = 24.2 min (*R,S*); $t_{R(min)}$ = 30.0 min (*R,S*). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.68-7.60 (m, 2H), 7.48-7.40 (m, 2H), 4.85 (d, *J* =8.4 Hz, 1H), 4.08 (bs, 1H), 2.58 (dddd, *J* = 13.0, 8.4, 5.5, 1.2 Hz, 1H), 2.53-2.44 (m, 1H), 2.36 (td, *J* = 13.6, 6.1, 1.2 Hz, 1H), 2.17-2.06 (m, 1H), 1.87-1.78 (m, 1H), 1.75-1.52 (m, 3H), 1.40-1.32 (m, 1H).

(*S*)-2-((*R*)-hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (8e)

The product was obtained in 98 % yield with >99 % *ee* and >19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 90:10, 254 nm, flow rate 1.0 mL/min: $t_{R(maj)}$ = 29.1 min (*S*,*R*); $t_{R(min)}$ = 21.8 min (*R*,*S*). $[\propto]_{D}^{25}$= +10 (*c* 1, $CHCl_3$) [lit.[4] $[\propto]_{D}^{25}$ = +12.8 (c 1.85, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 4.90 (d, *J* = 8.3 Hz, 1H), 3.13 (bs, 1H), 2.65-2.25 (m, 3H), 2.18-2.03 (m, 1H), 1.90-1.45 (m, 5H).

(*S*)-2-((*R*)-hydroxy(3-nitrophenyl)methyl)cyclohexan-1-one (8f)

The product was obtained in 93 % yield with >99 % *ee* and >19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 95:05, 254 nm, flow rate 0.8 mL/min: $t_{R(maj)}$ = 34.2 min (*S*,*R*); $t_{R(min)}$ = 45.2 min (*R*,*S*). $[\propto]_{D}^{25}$= +26 (*c* 1, $CHCl_3$) [lit.[4] $[\propto]_{D}^{25}$ = +32.5 (c 1.35, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.52-7.34 (m, 1H), 4.88 (d, *J* = 8.4 Hz, 1H), 4.45 (bs, 1H), 2.69-2.19 (m, 3H), 2.15-1.90 (m, 1H), 1.89-1.38 (m, 5H).

(*S*)-2-((*R*)-hydroxy(2-nitrophenyl)methyl)cyclohexan-1-one (8g)

The product was obtained in 99 % yield with 99 % *ee* and >19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 90:10, 254 nm, flow rate 1.0 mL/min: $t_{R(maj)}$ = 16.5 min (*S*,*R*); $t_{R(min)}$ = 18.0 min (*R*,*S*). $[\propto]_{D}^{25}$= +15 (*c* 1, $CHCl_3$) [lit.[4] $[\propto]_{D}^{24}$ = +19.8 (c 1.6, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 5.38 (d, *J* = 7.0 Hz, 1H), 2.69 (dt, *J* = 12.7; 6.4 Hz, 1H), 2.46-2.34 (m, 1H), 2.27 (td, *J* = 13.2; 6.1 Hz, 1H), 2.08-1.98 (m, 1H), 1.83-1.74 (m, 1H), 1.74-1.46 (m, 4H).

(*S*)-2-((*R*)-hydroxy(4-nitrophenyl)methyl)cyclopentan-1-one (8h)

The product was obtained in 81 % yield with 98 % *ee* and 3:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 90:10, 280 nm, flow rate 0.5 mL/min: $t_{R(maj)}$ = 55.5 min (*S*,*R*), $t_{R(min)}$ = 52.5 min (*R*,*S*). $[\propto]_{D}^{25}$= -25 (*c* 0.5, $CHCl_3$) [lit.[4] $[\propto]_{D}^{25}$ = -30.6 (c 0.56, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 4.85 (d, *J* = 9.8 Hz, 1H), 2.55-2.25 (m, 2H), 2.23-1.90 (m, 3H), 1.85-1.65 (m, 2H).

(*S*)-2-((*R*)-hydroxy(2-nitrophenyl)methyl)cyclopentan-1-one (8i)

The product was obtained in 99 % yield with 99 % *ee* and 3:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel OD-H, hexane/2-propanol 95:5, 254 nm, flow rate 1.0 mL/min: $t_{R(maj)}$ = 24.2 min (*S,R*), $t_{R(min)}$ = 26.3 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13-7.85 (m, 1H), 7.81 (td, *J* = 8.1; 1.3 Hz, 1H), 7.69-7.62 (m, 1H), 7.47-7.40 (m, 1H), 5.44 (d, *J* = 8.5 Hz, 1H), 4.49 (bs, 1H), 2.58-2.48 (m, 1H), 2.47-2.38 (m, 1H), 2.37-2.24 (m, 1H), 2.08-1.97 (m, 1H), 1.83-1.67 (m, 3H).

(*S*)-2-((*R*)-(4-bromophenyl)(hydroxy)methyl)cyclopentan-1-one (8j)

The product was obtained in 99 % yield with >99 % *ee* and 5:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AD-H, hexane/2-propanol 95:5, 220 nm, flow rate 1.0 mL/min: $t_{R(maj)}$ = 22.3 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.42 (m, 2H), 7.23-7.16 (m, 2H), 4.67 (d, *J* = 9.1 Hz, 1H), 2.47-2.29 (m, 2H), 218-2.12 (m, 1H), 2.00-1.90 (m, 2H), 1.80-1.62 (m, 2H).

Procedure for organocatalytic asymmetric Michael reaction

A solution of organocatalyst **5d** (0.014 g, 0.05 mmol), benzoic acid (0.006 g, 0.05 mmol) and the cyclohexanone (0.52 mL, 5 mmol) was stirred at room temperature for 0.5 h. β-nitrostyrene (0.075 g, 0.5 mmol) was then added and the reaction mixture was stirred for 72 h. The solution was treated with saturated aqueous NH_4Cl solution (1 mL) and extracted with dichloromethane (3 x 5 mL). The organic extracts were combined, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The product was purified with flash column cromatography on silica gel using ethyl acetate and hexane (20:80).

(R)-2-((S)-2-nitro-1-phenylethyl)cyclohexan-1-one (10)

The product was obtained in 35% yield with >99 % *ee* and 19:1 *dr*. The enantiomeric excess was determined by HPLC on Chiralcel AS-H, hexane/2-propanol 75:25, 254 nm, flow rate 1.0 mL/min: $t_{R(min)}$ = 8.23 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.23

(m, 3H), 7.19-7.06 (m, 2H), 4.95 (dd, *J* = 11.2 Hz; 4.5 Hz, 1H), 4.56 (dd, 2H), 3.68 (dt, *J* = 4.5 Hz; 9.9 Hz, 1H), 2.67 (ddd, *J* = 12.0 Hz; 8.6 Hz, 8.0 Hz; 2H), 2.45-2.20 (m, 2H), 1.78-1.41 (m, 4H), 1.20-1.05 (m, 1H).

References

1. Purification of Laboratory Chemicals; D. D. Perrin and W. L. Armarego, Eds., 4a ed.; Pergamon: New York, 1997.
2. S. Kokinaki, L. Leondiadis and F. Nikolas, *Org. Lett.* 2005, **7**, 1723.
3. M. R. Vishnumaya and V. K. Singh, *J. Org. Chem.* 2009, **74**, 4289.
4. Y. Wu, Y. Zhang, M. Yu, G. Zhao and S. Wang, *Org. Lett.* 2006, **8**, 4417.

NMR spectra of catalysts and synthetic intermediates

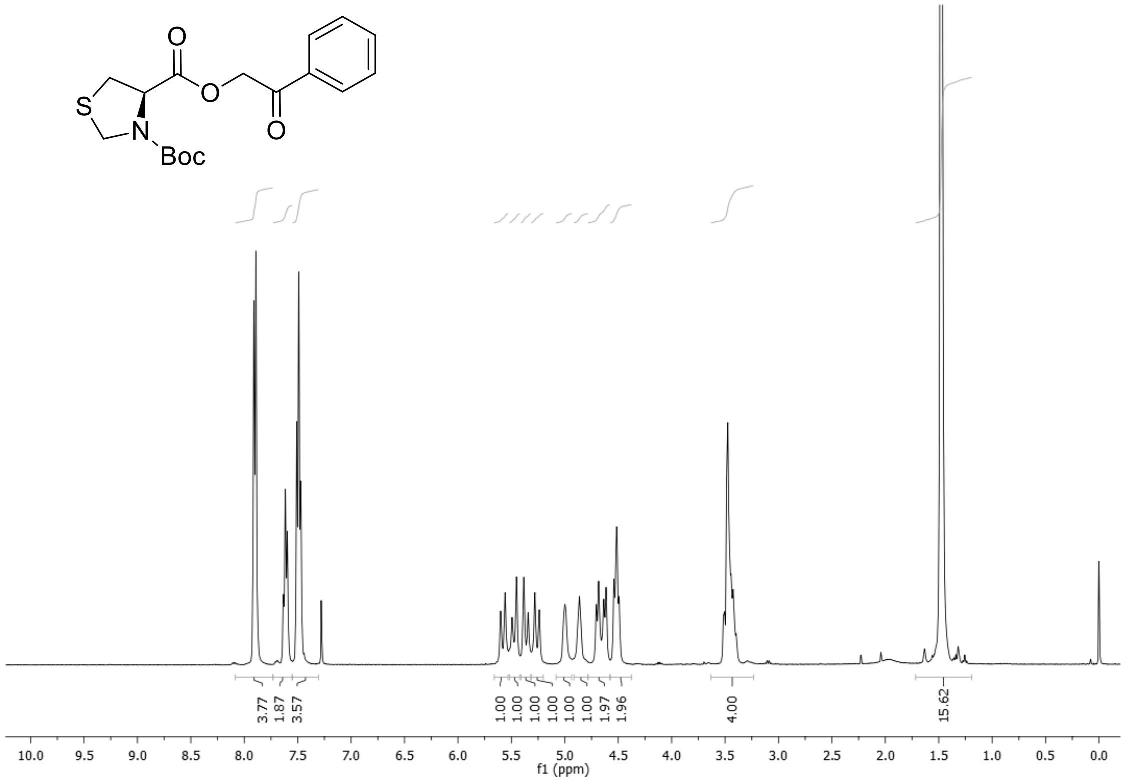


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**.

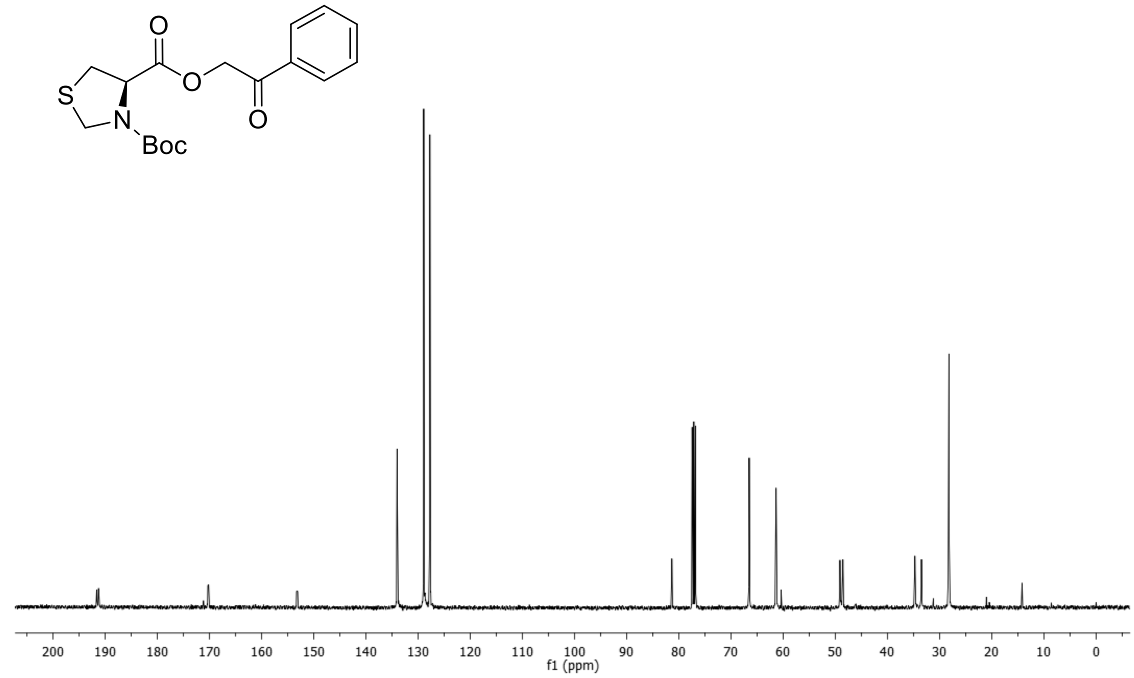


Figure S2. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **3a**.

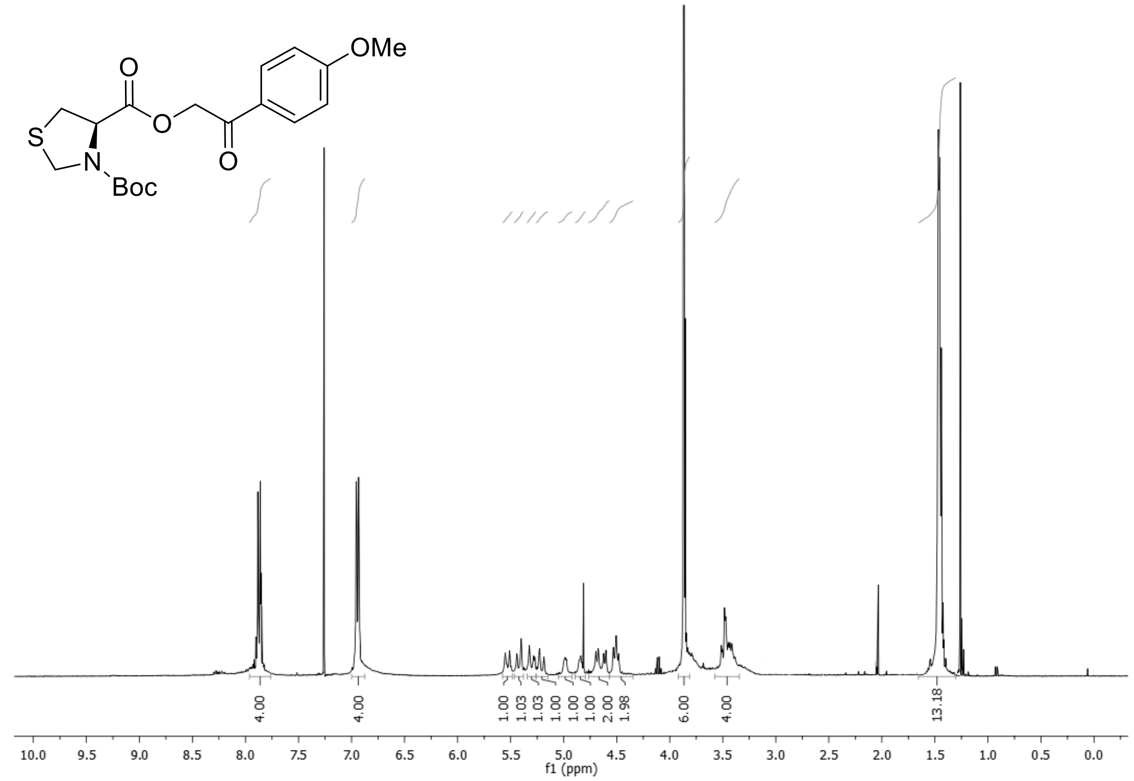


Figure S3. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **3b**.

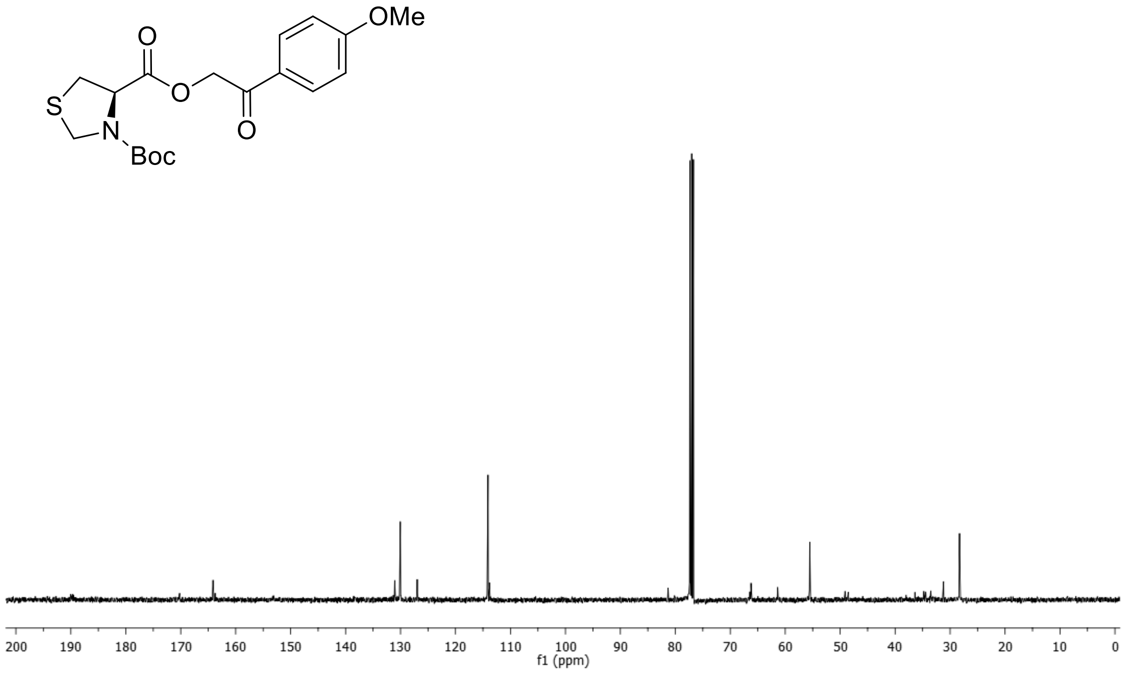


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b**.

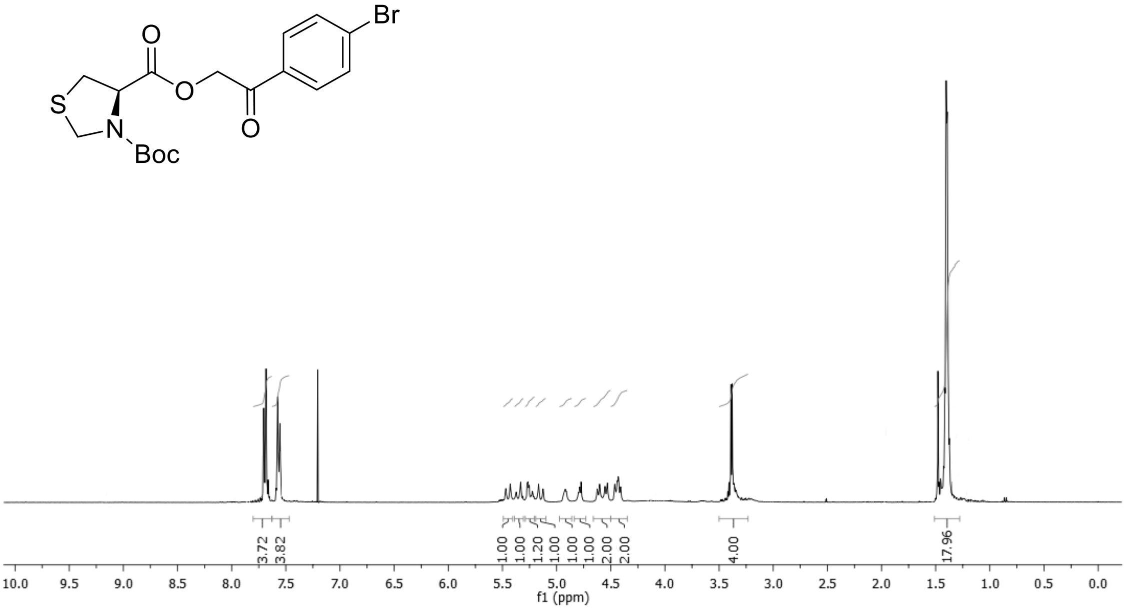


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**.

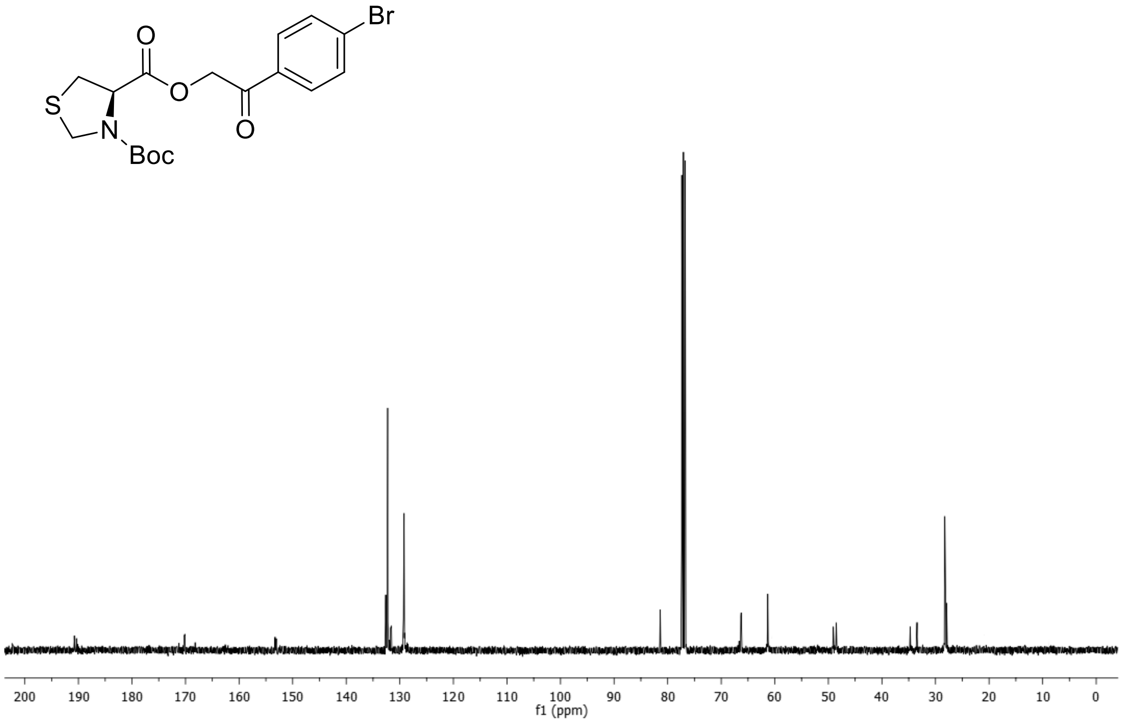


Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3c**.

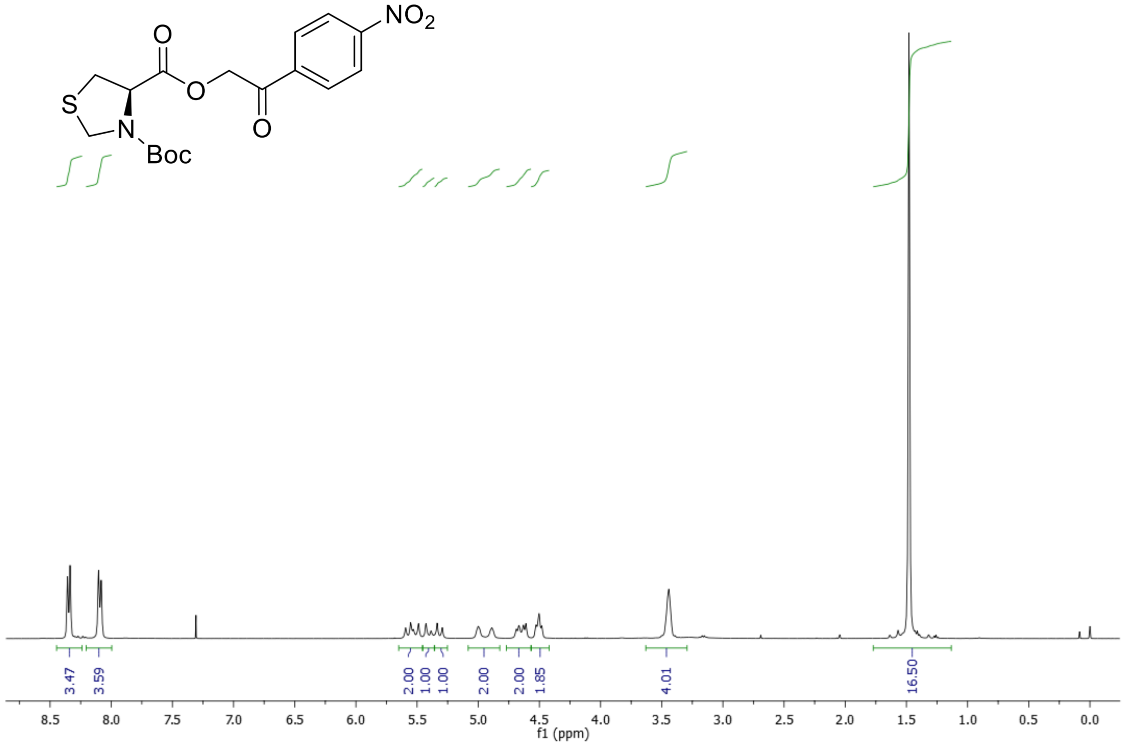


Figure S7. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **3d**.

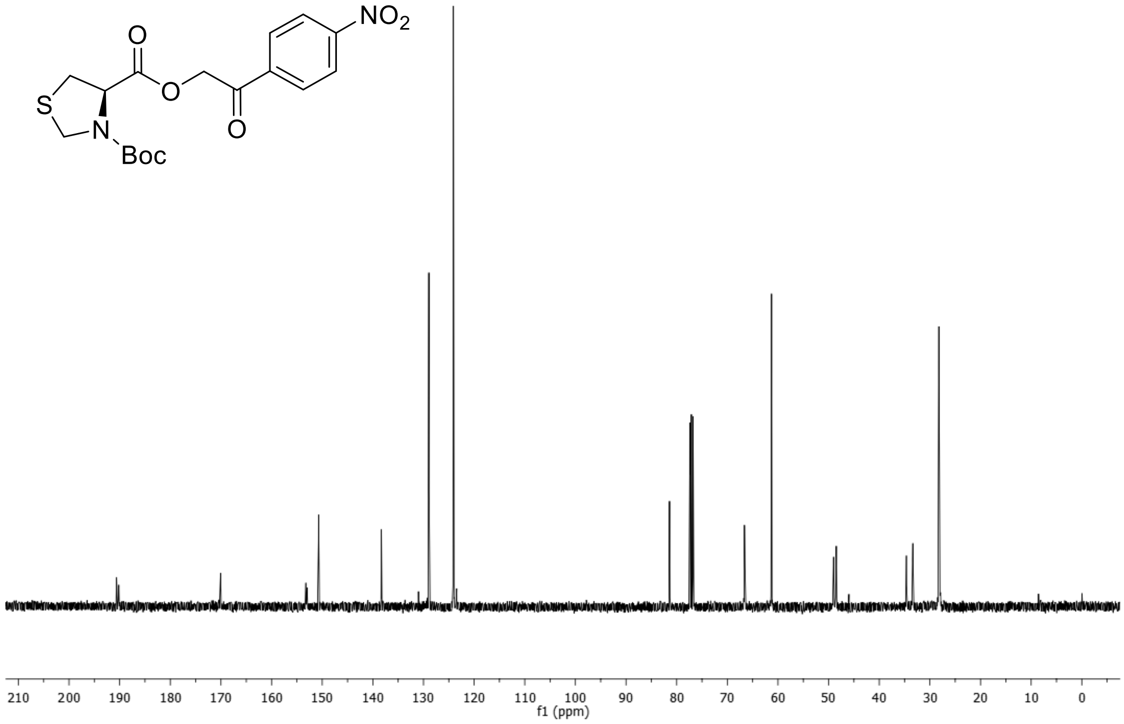


Figure S8. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **3d**.

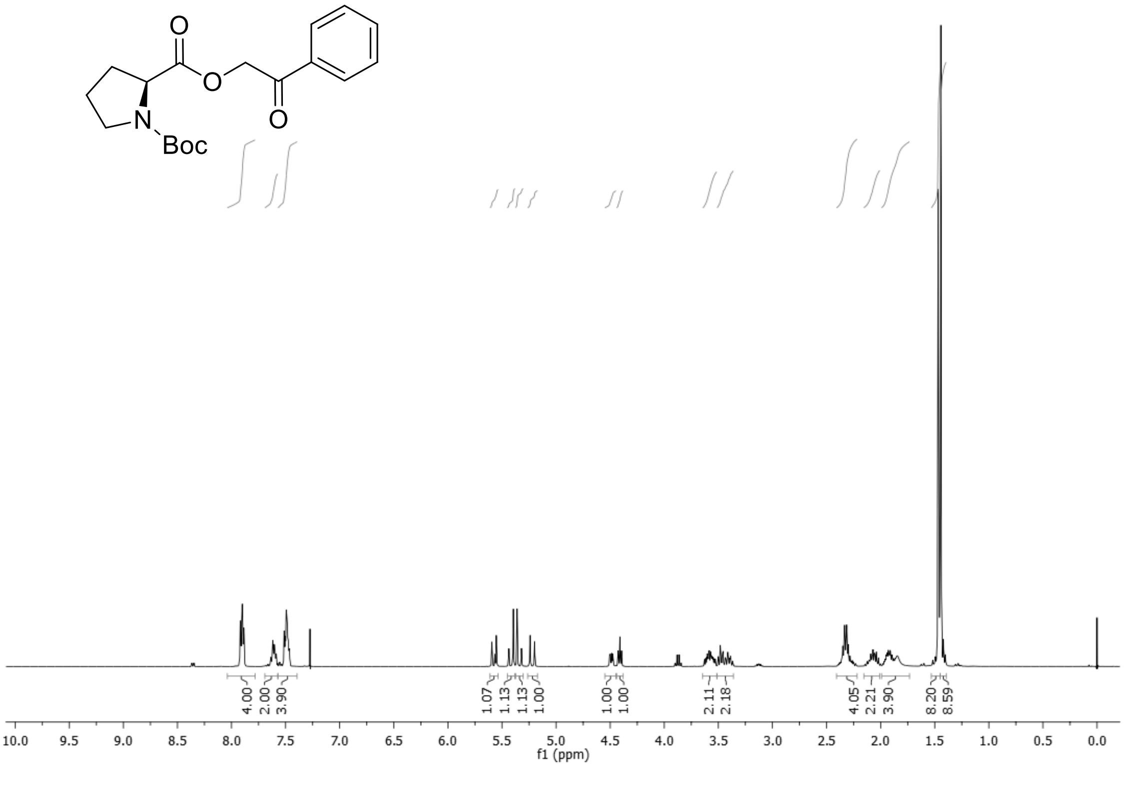


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e** precursor.

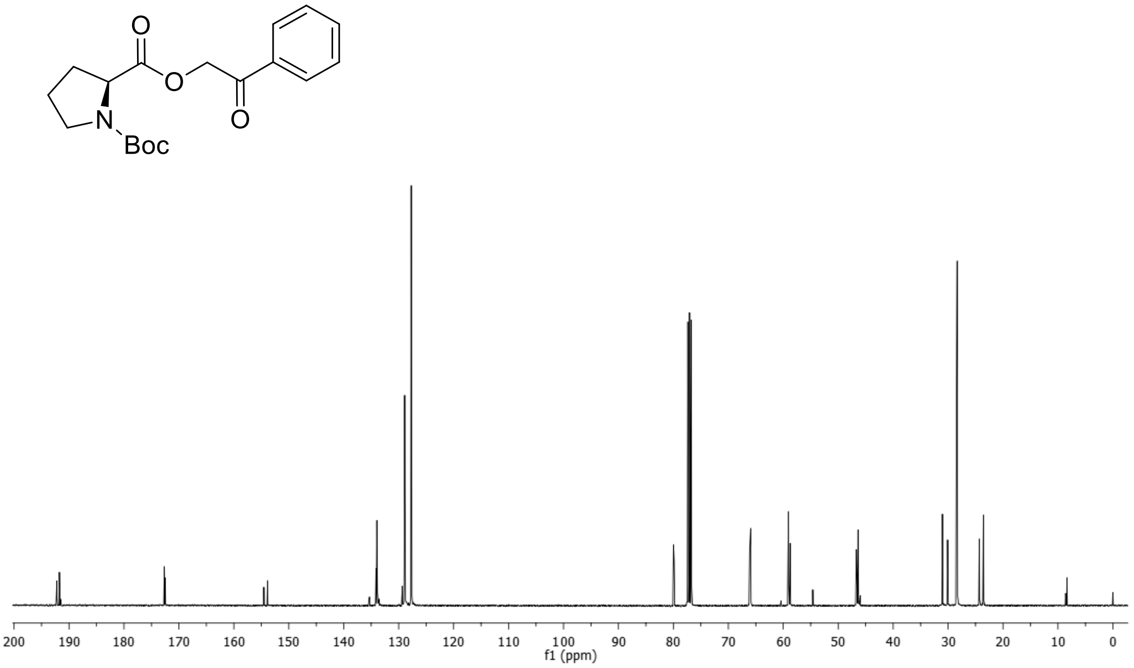


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5e** precursor.

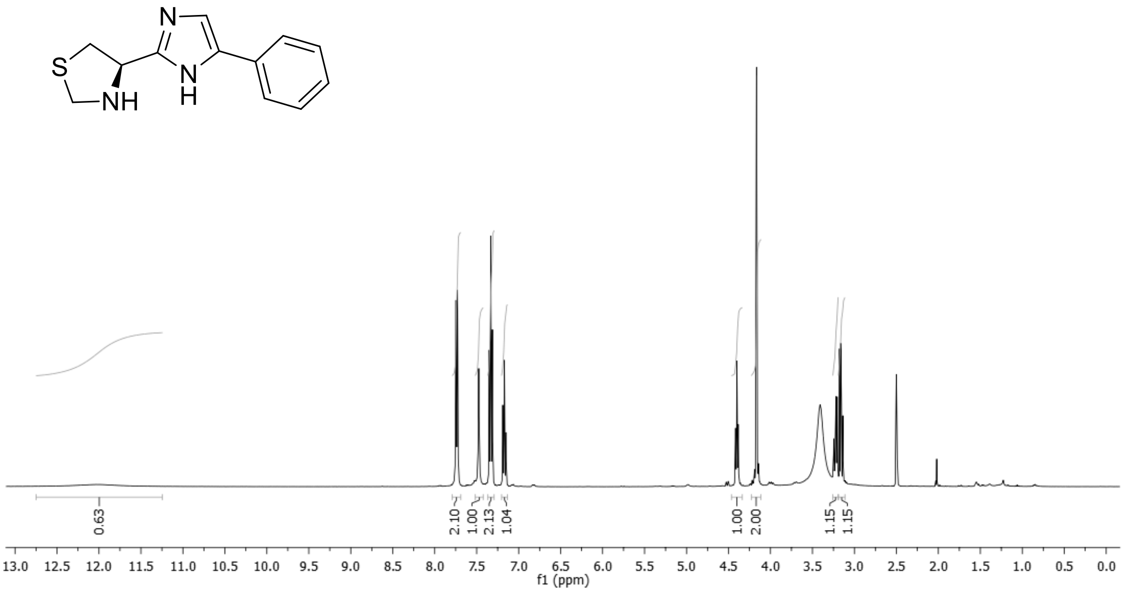


Figure S11. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **5a**.

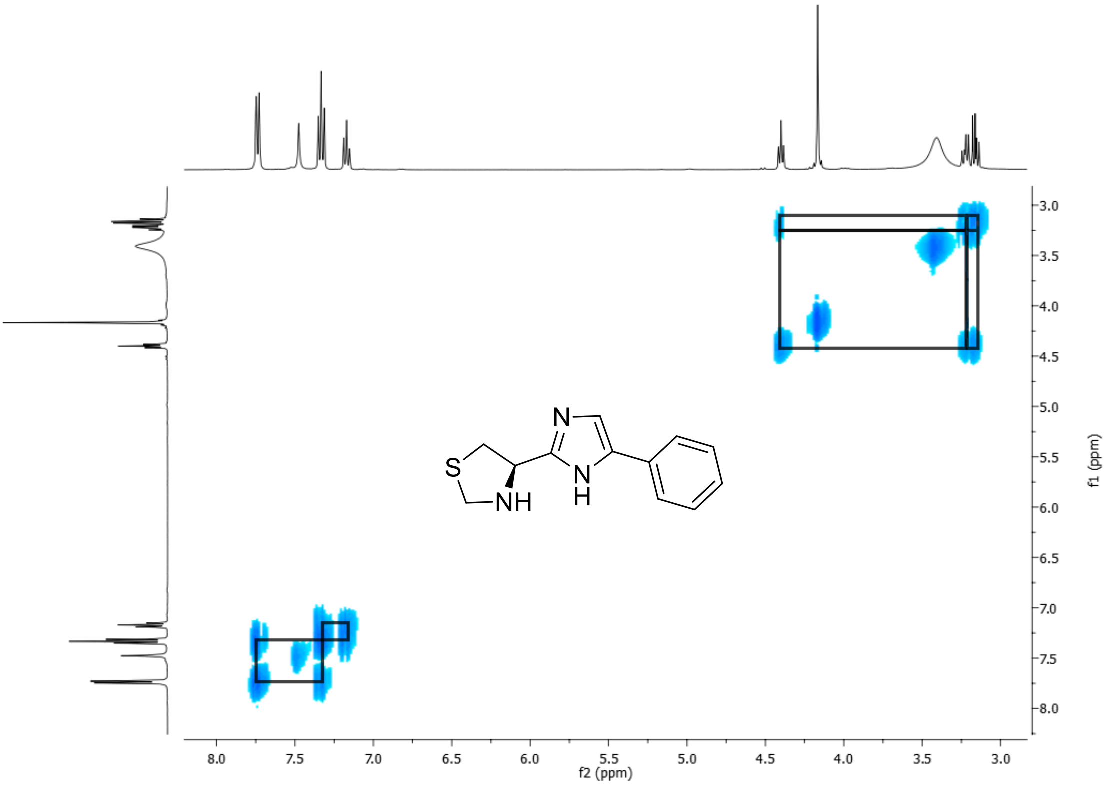


Figure S12. ^{1}H-^{1}H COSY (400 MHz, DMSO-d_6) spectrum of **5a**.

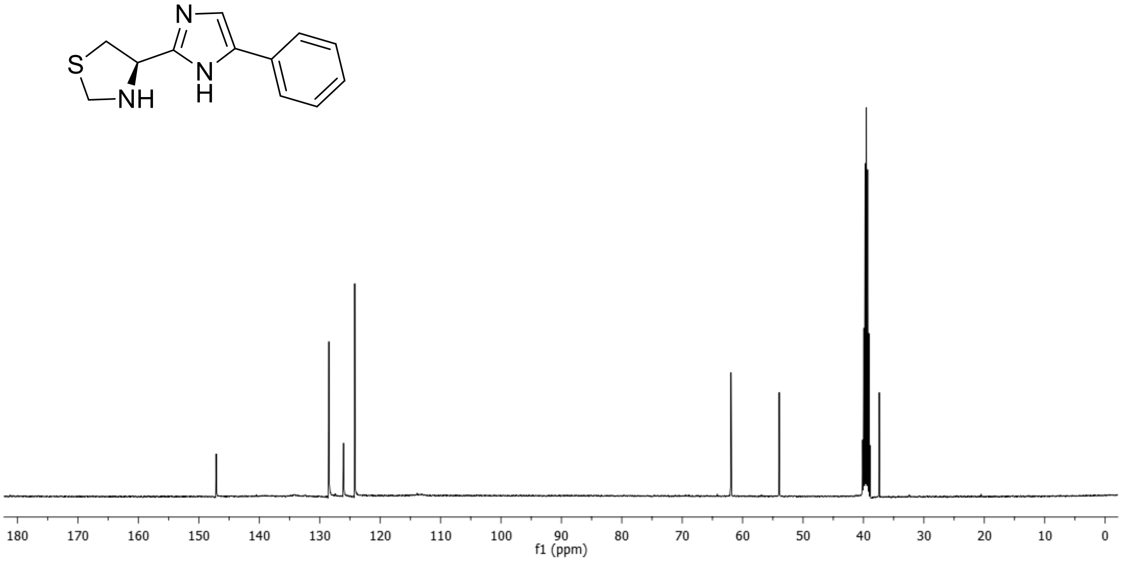


Figure S13. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **5a**.

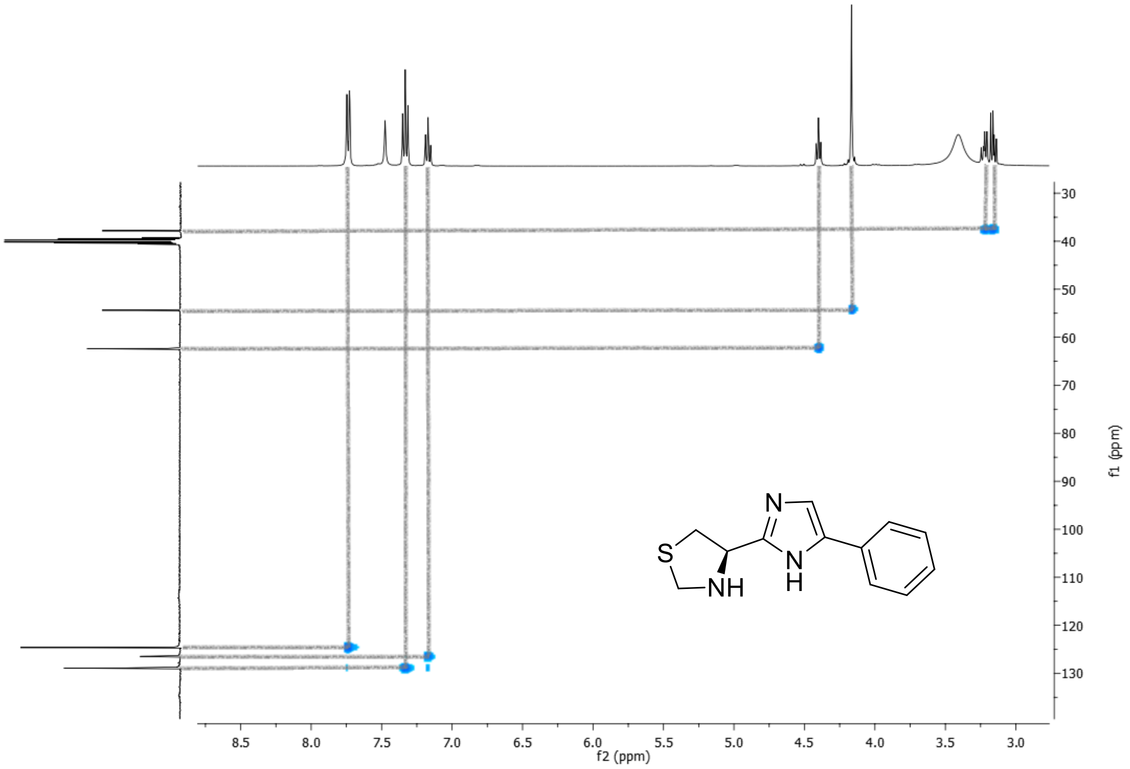


Figure S14. ^{1}H-^{13}C HSQC (400 MHz, DMSO-d$_6$) spectrum of **5a**.

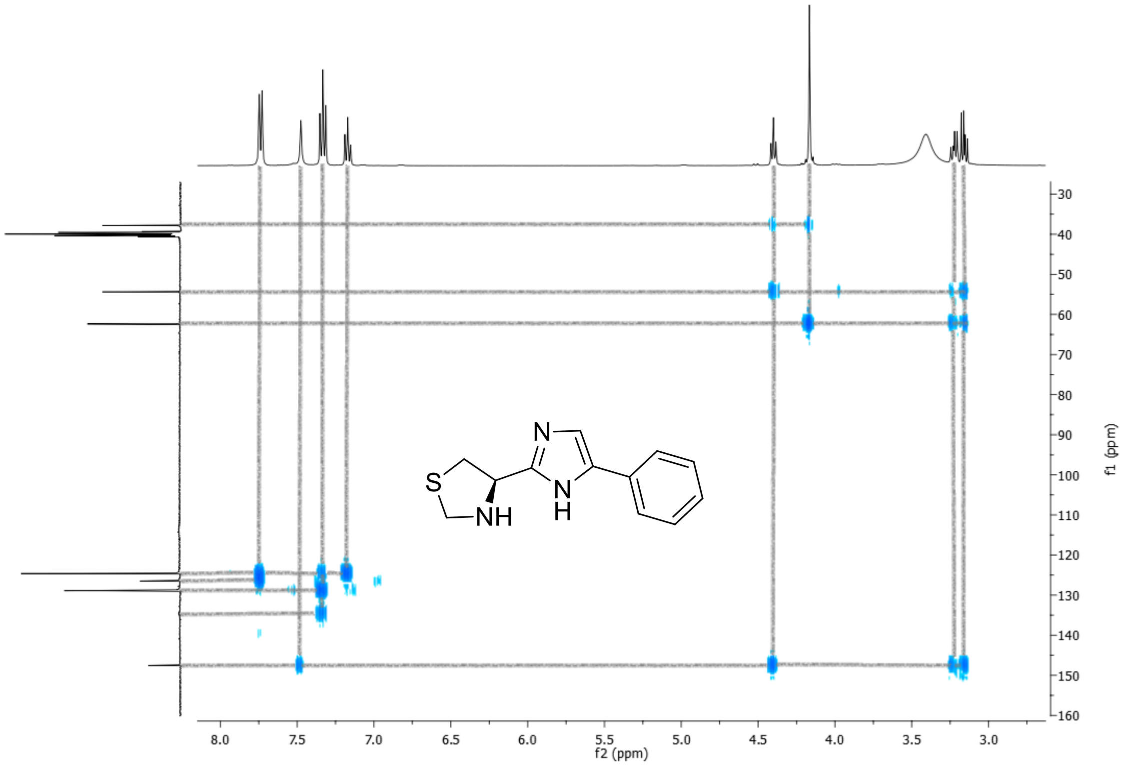


Figure S15. ^{1}H-^{13}C HMBC (400 MHz, DMSO-d$_6$) spectrum of **5a**.

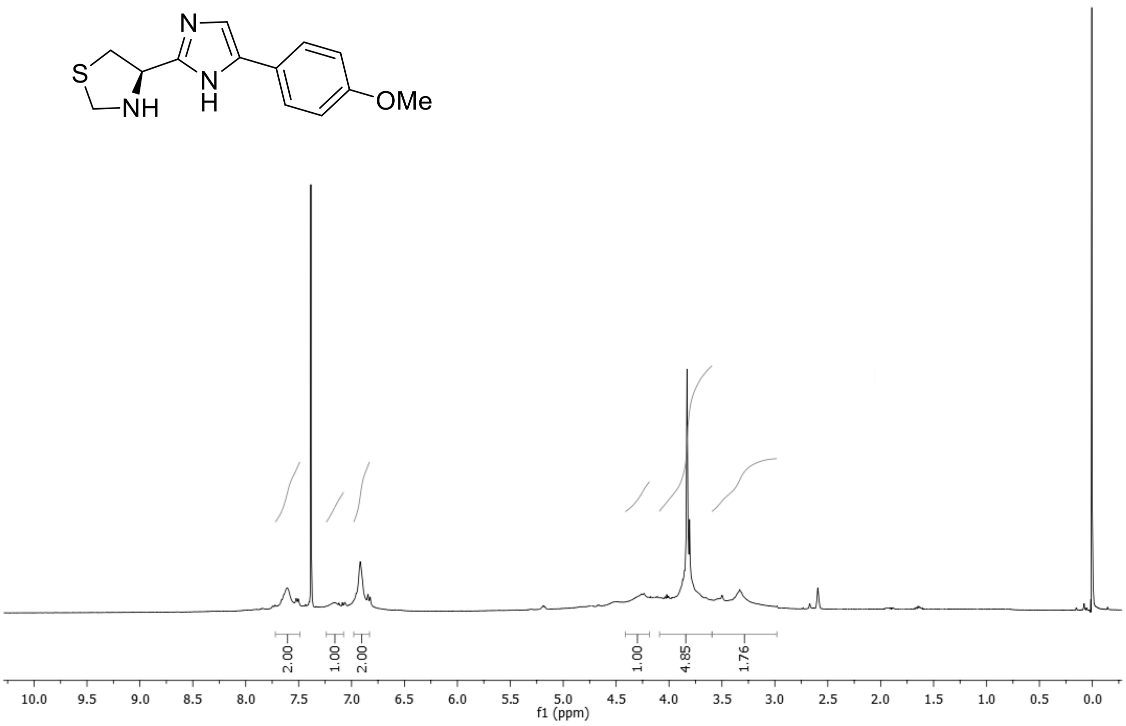


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of **5b**.

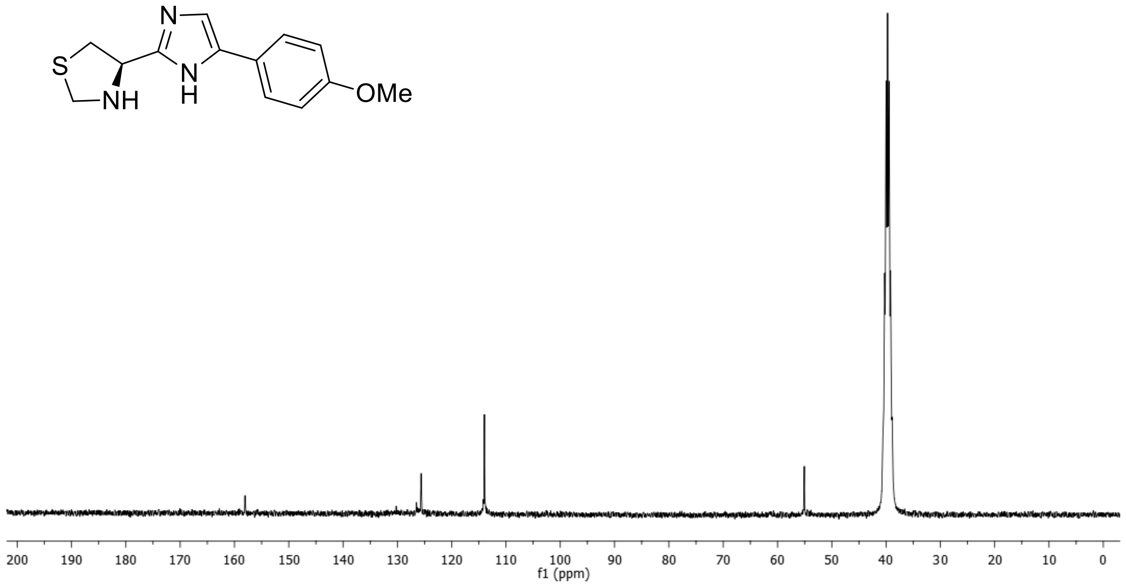


Figure S17. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **5b**.

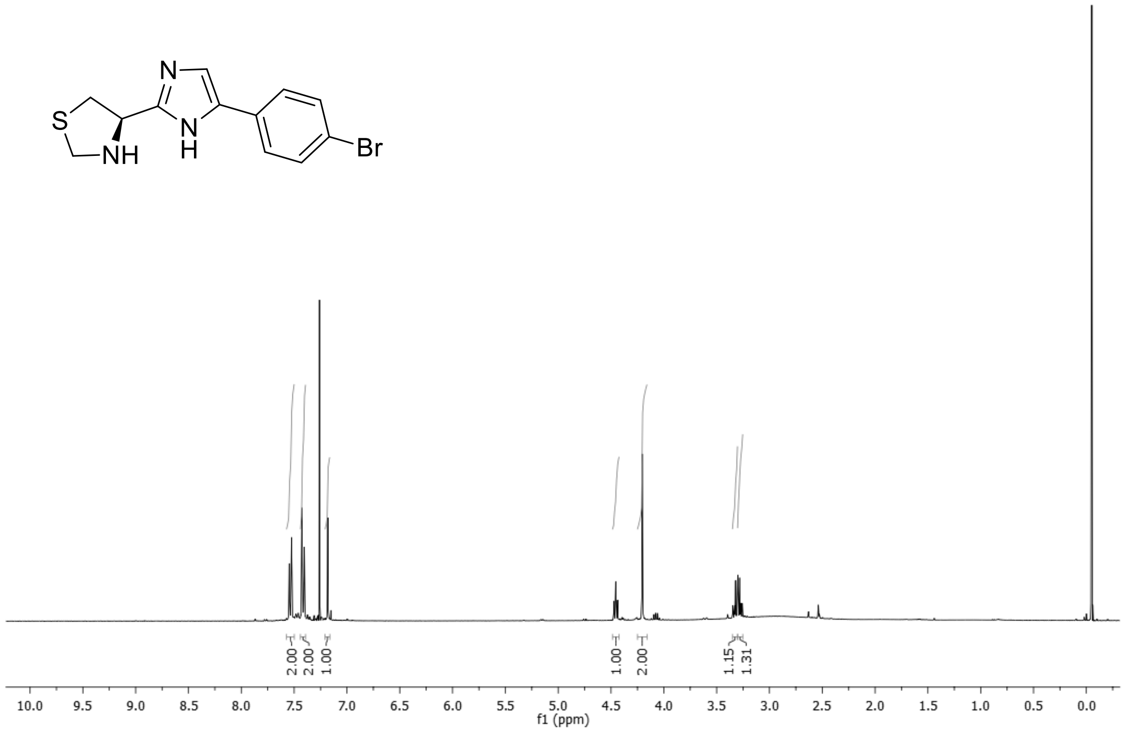


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5c**.

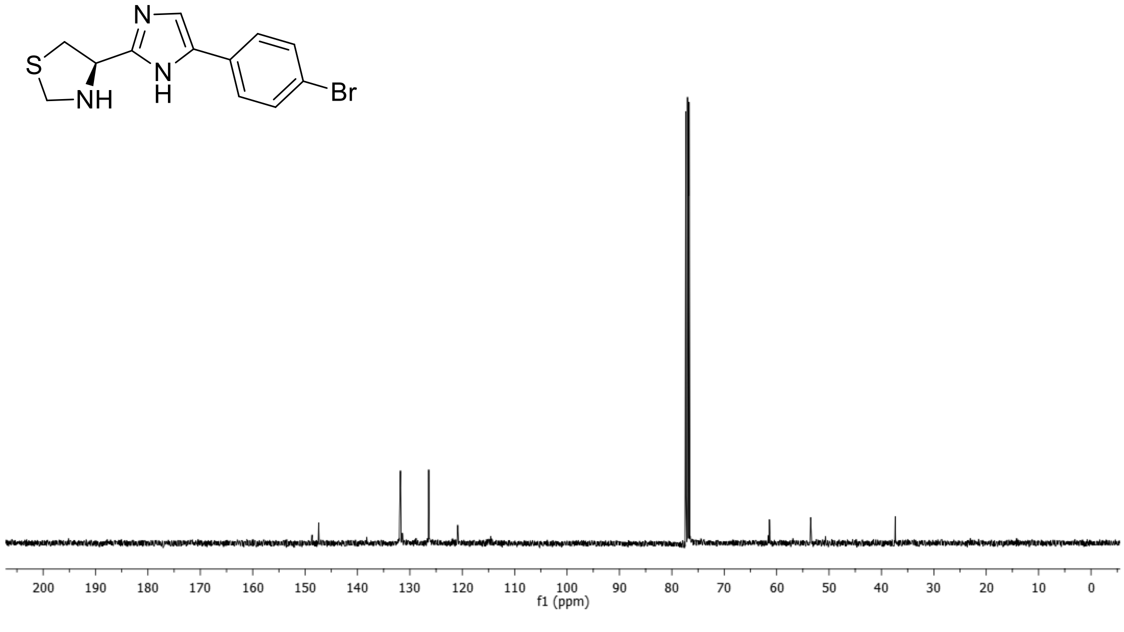


Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5c**.

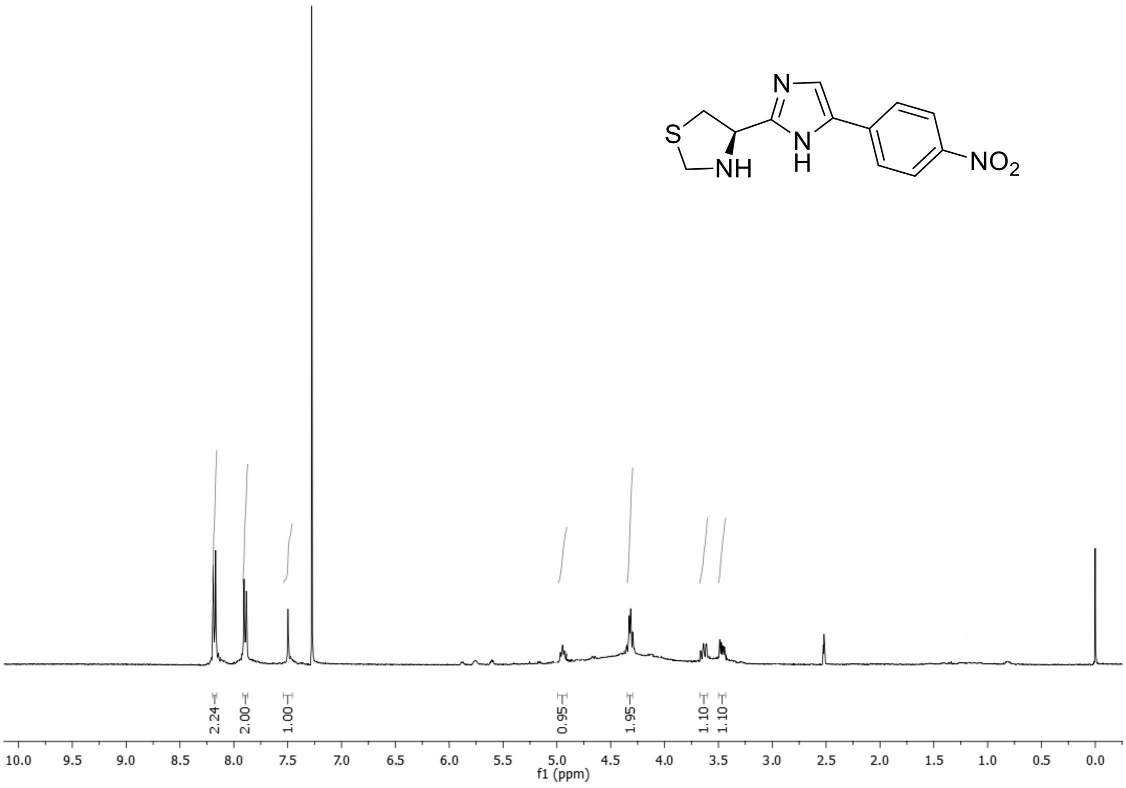


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of **5d**.

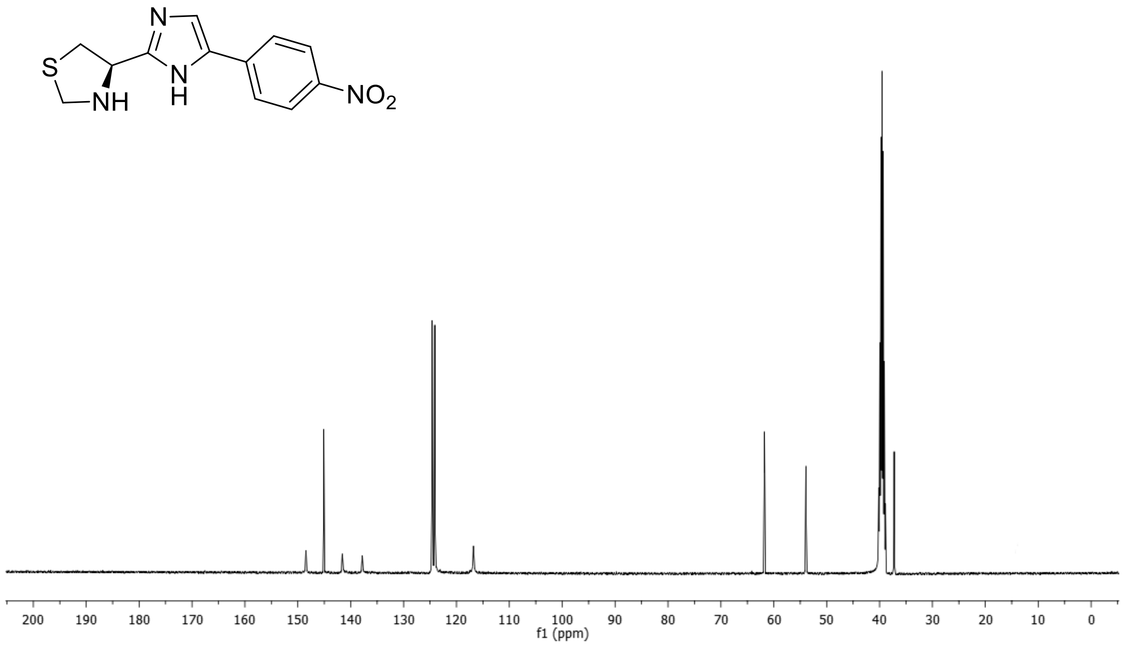


Figure S21. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **5d**.

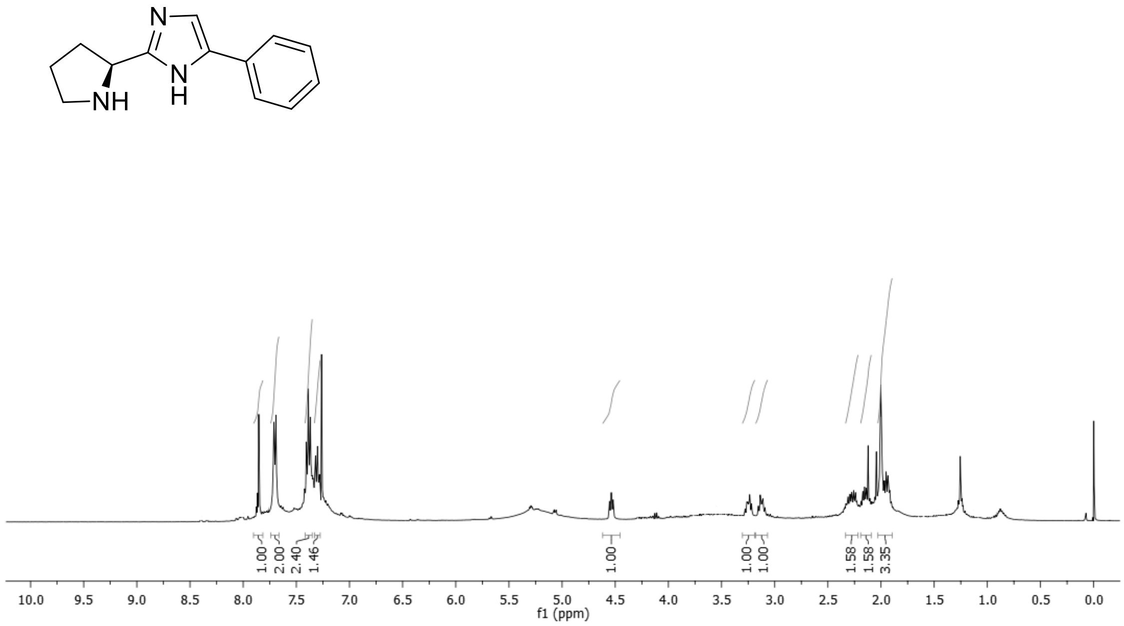


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of **5e**.

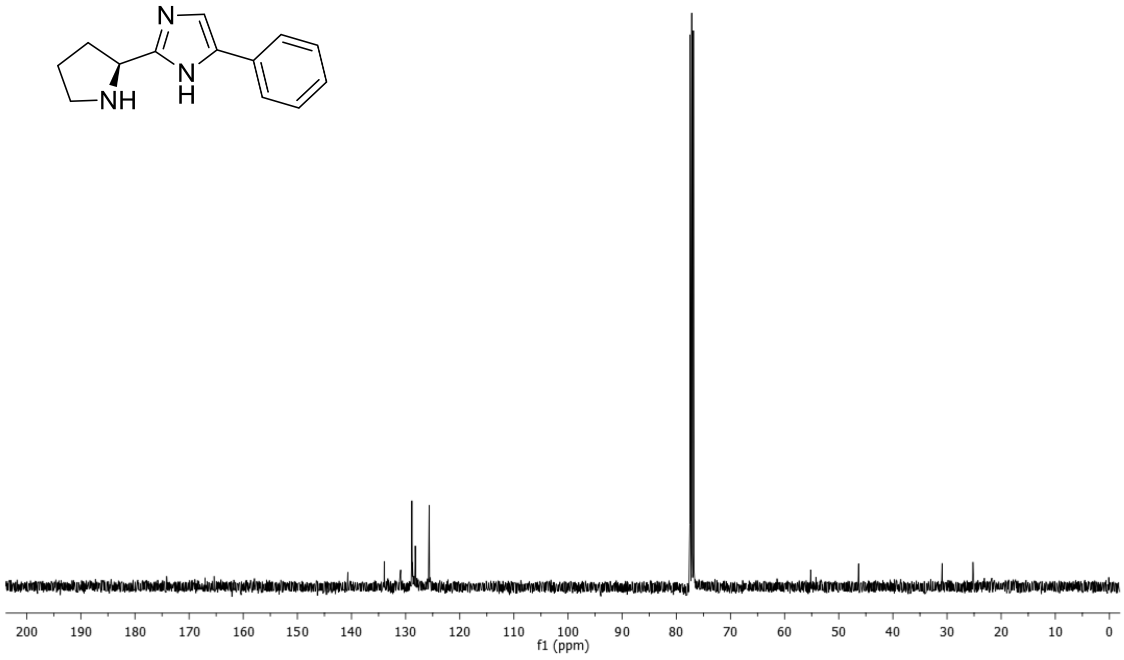


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5e**.

HPLC chromatograms and NMR spectra of products

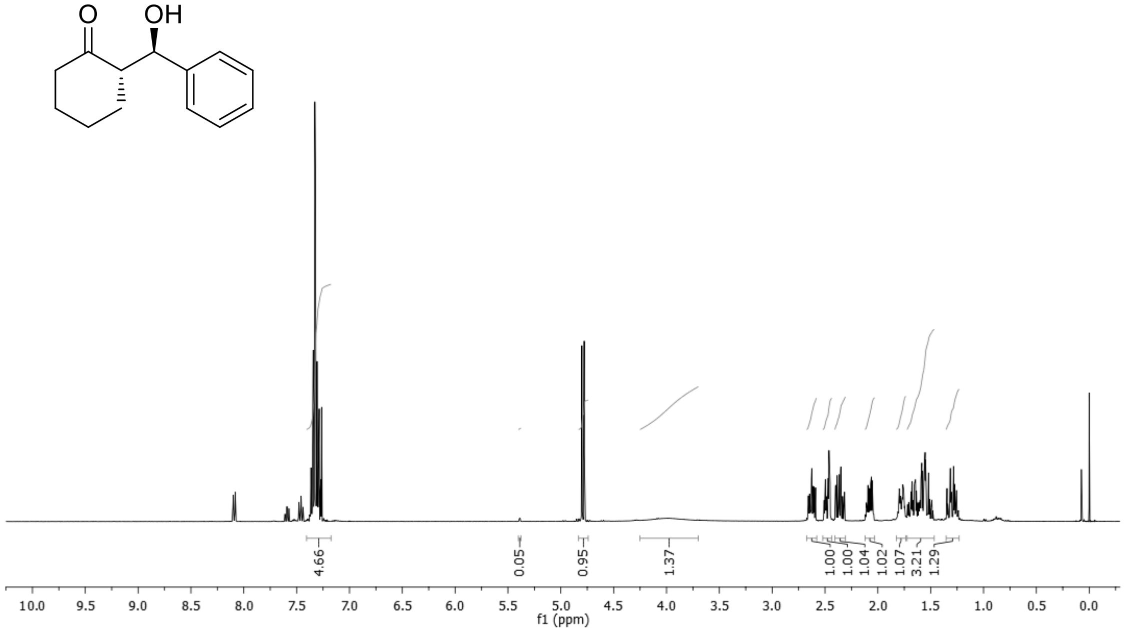
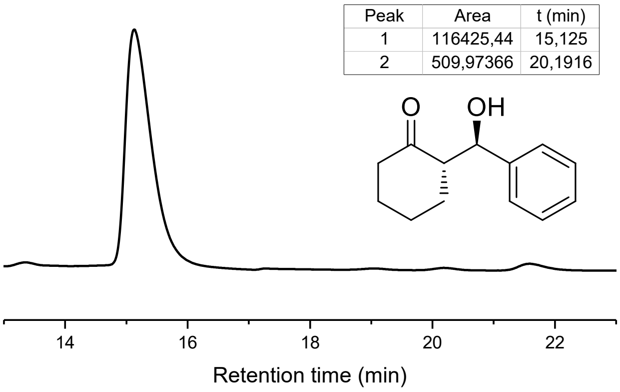
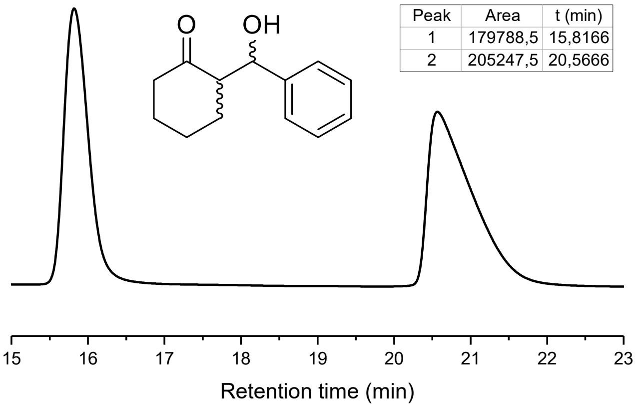


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8a**.



Peak	Area	t (min)
1	116425,44	15,125
2	509,97366	20,1916

Figure S25. HPLC chromatogram of **8a**.



Peak	Area	t (min)
1	179788,5	15,8166
2	205247,5	20,5666

Figure S26. HPLC chromatogram of racemic standard of **8a**.

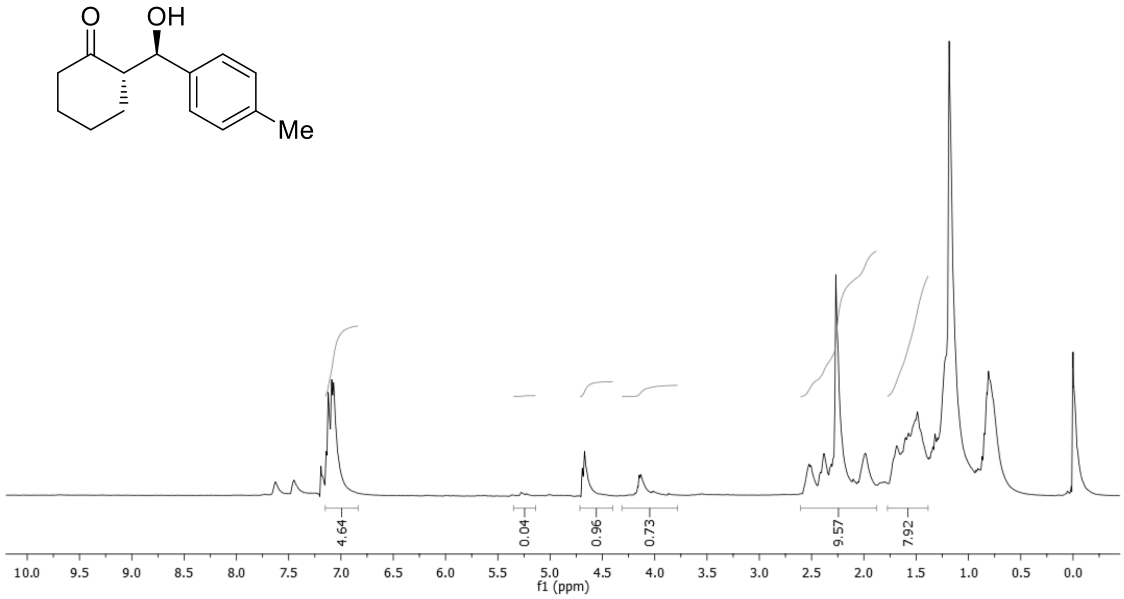
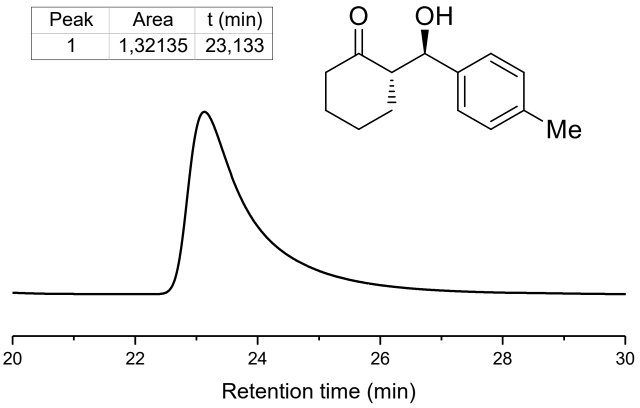
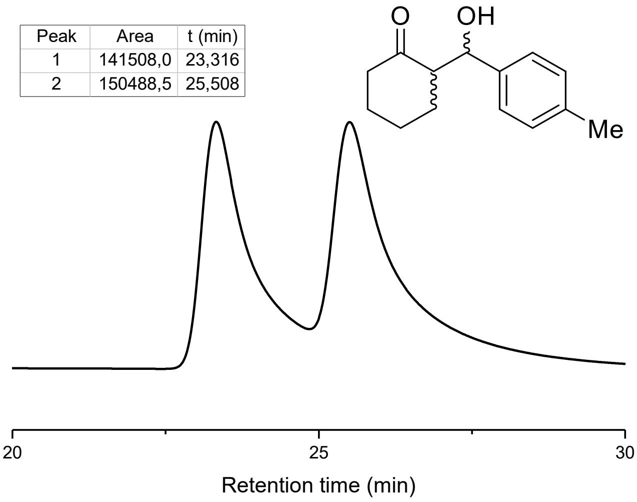


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8b**.



Peak	Area	t (min)
1	1,32135	23,133

Figure S28. HPLC chromatogram of **8b**.



Peak	Area	t (min)
1	141508,0	23,316
2	150488,5	25,508

Figure S29. HPLC chromatogram of racemic standard of **8b**.

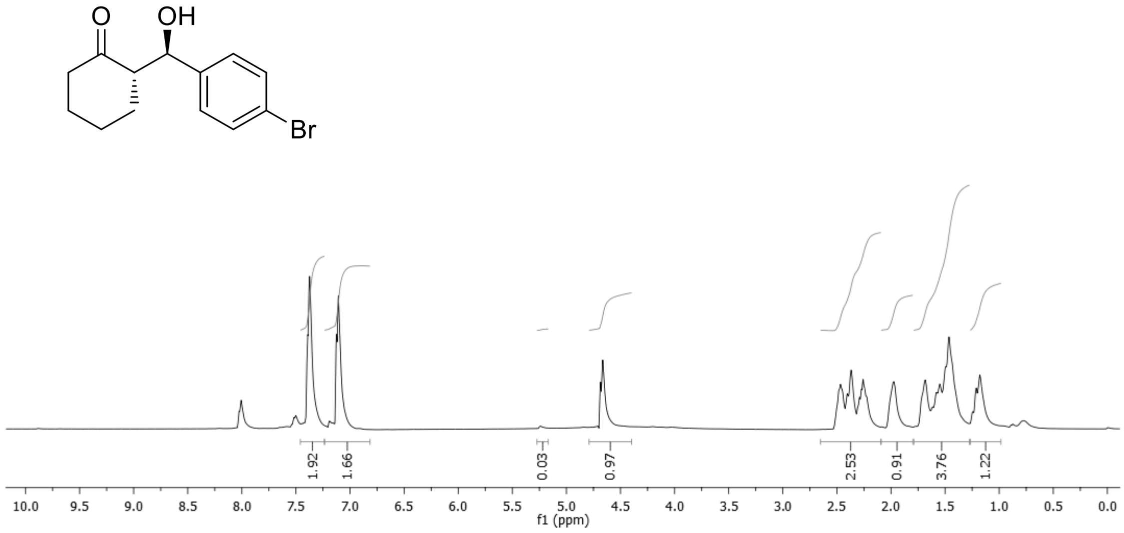
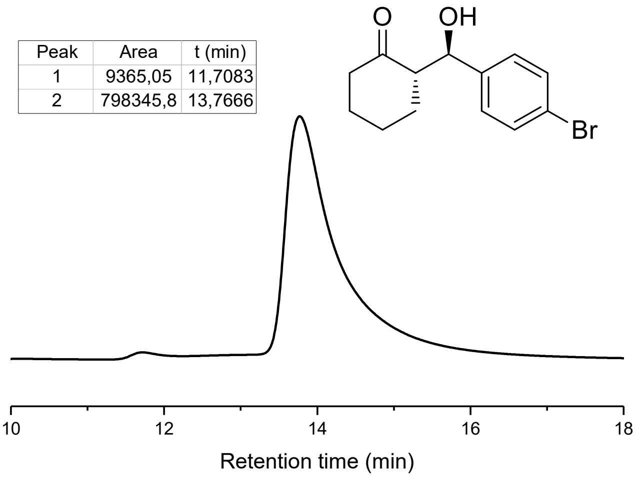
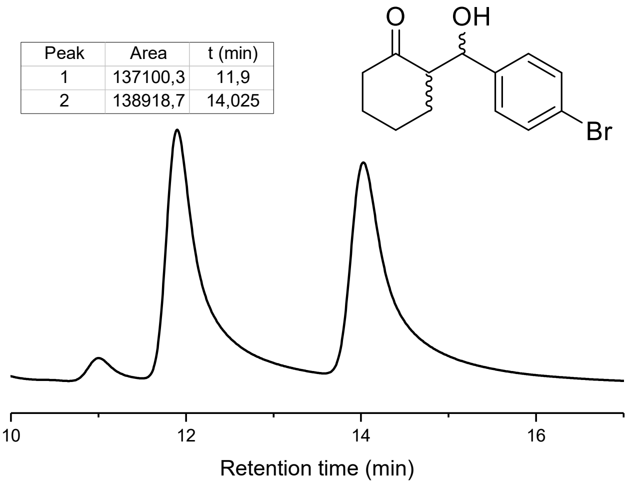


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8c**.



Peak	Area	t (min)
1	9365,05	11,7083
2	798345,8	13,7666

Figure S31. HPLC chromatogram of **8c**.



Peak	Area	t (min)
1	137100,3	11,9
2	138918,7	14,025

Figure S32. HPLC chromatogram of racemic standard of **8c**.

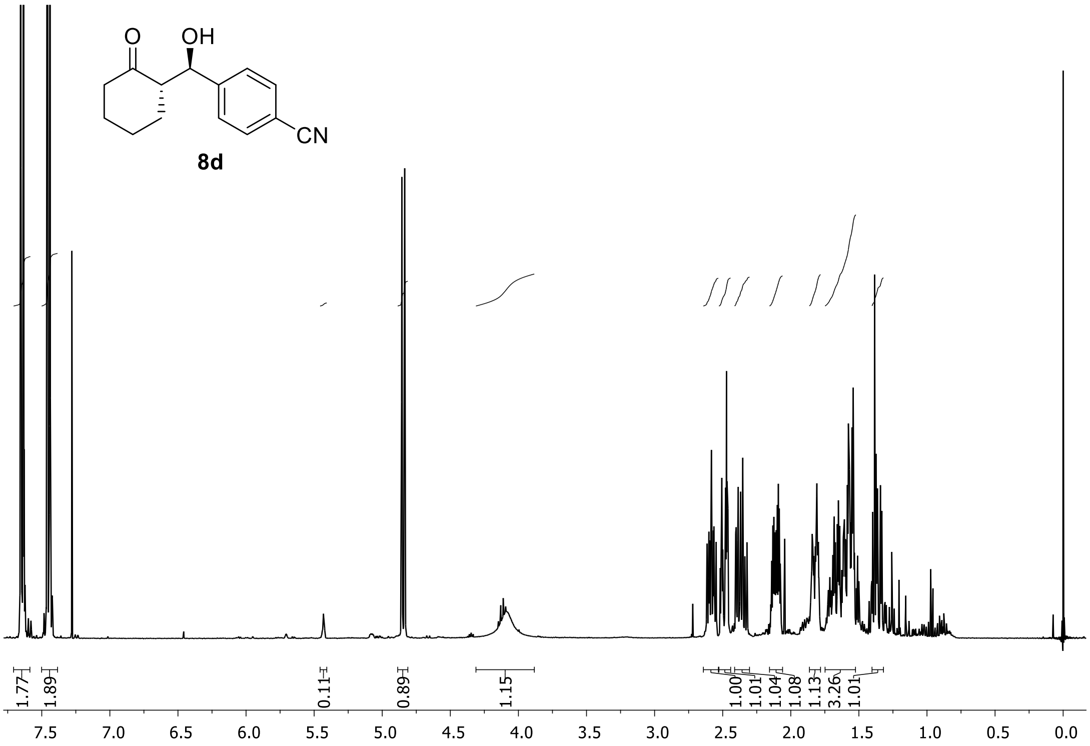
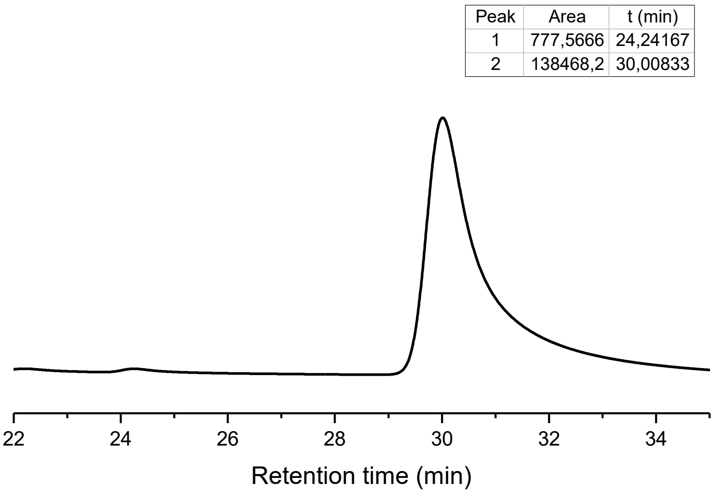


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8d**.



Peak	Area	t (min)
1	777,5666	24,24167
2	138468,2	30,00833

Figure S34. HPLC chromatogram of **8d**.

Peak	Area	t (min)
1	100515,4	24,025
2	109569,8	29,83333

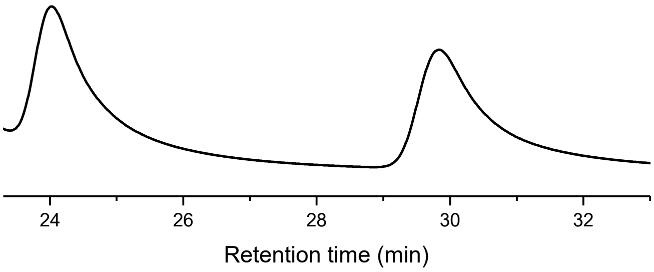


Figure S35. HPLC chromatogram of racemic standard of **8d**.

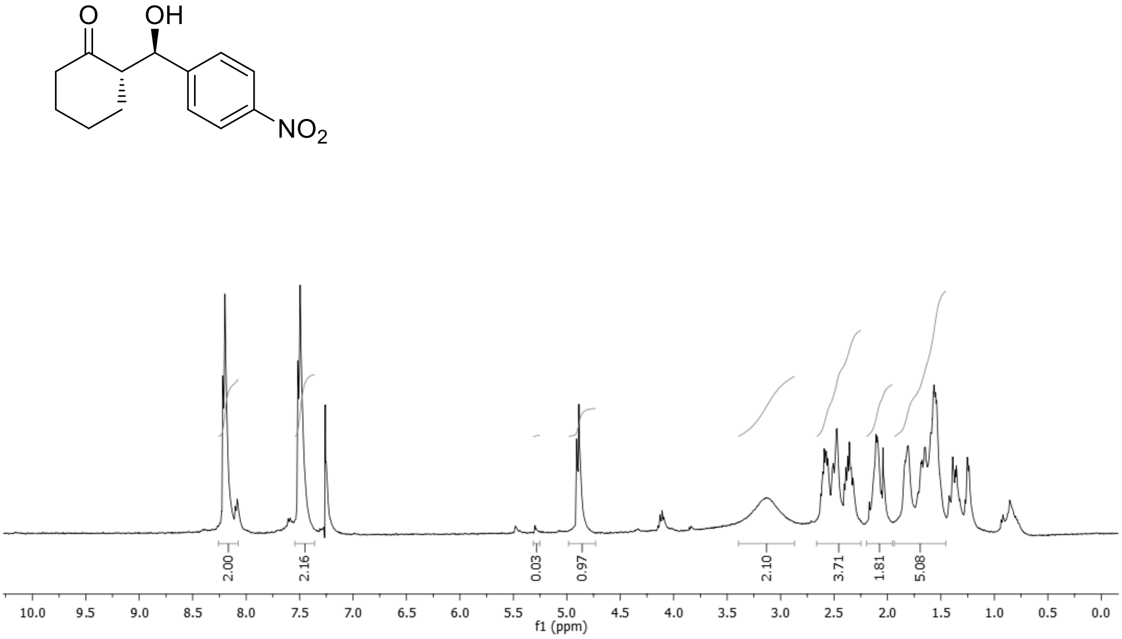
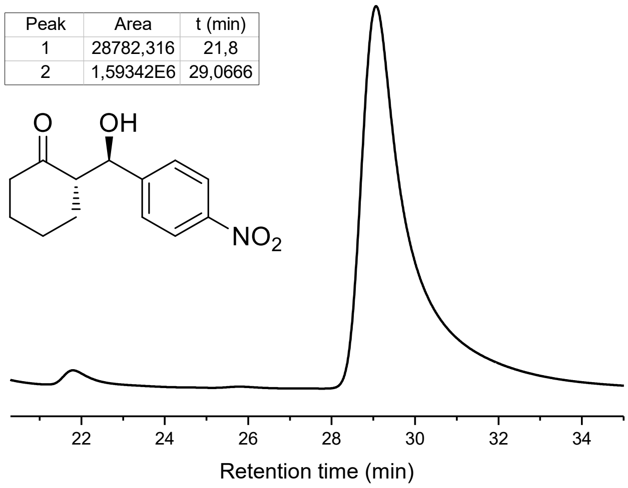
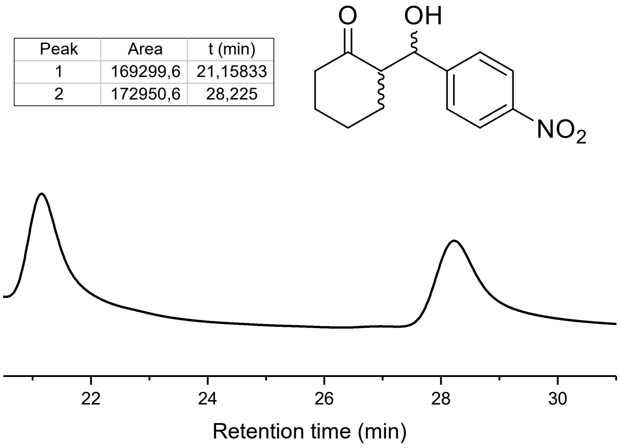


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8e**.



Peak	Area	t (min)
1	28782,316	21,8
2	1,59342E6	29,0666

Figure S37. HPLC chromatogram of **8e**.



Peak	Area	t (min)
1	169299,6	21,15833
2	172950,6	28,225

Figure S38. HPLC chromatogram of racemic standard of **8e**.

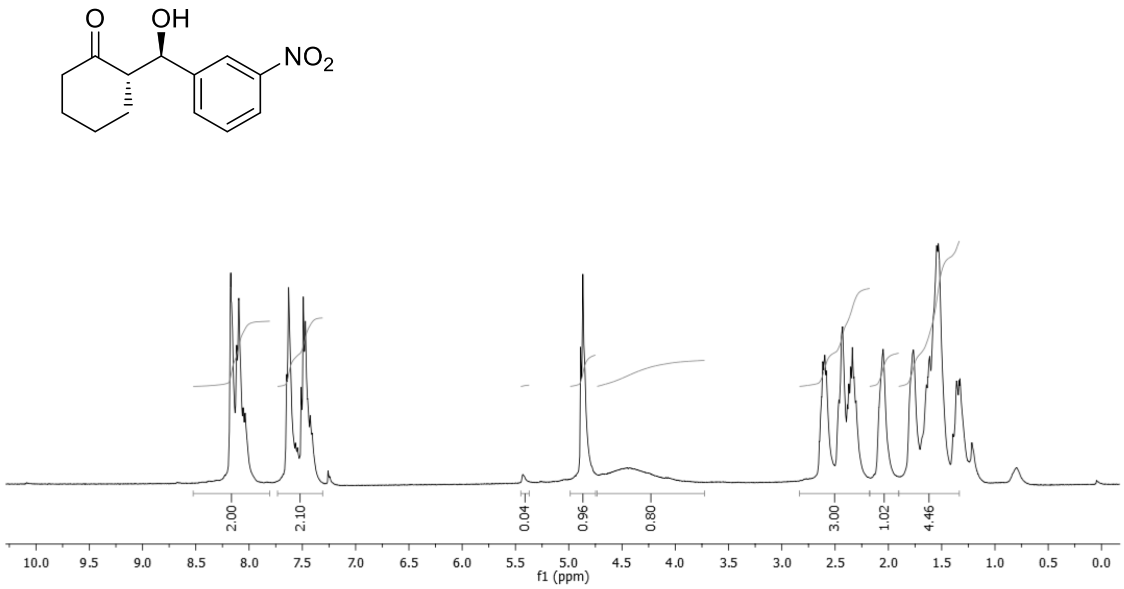
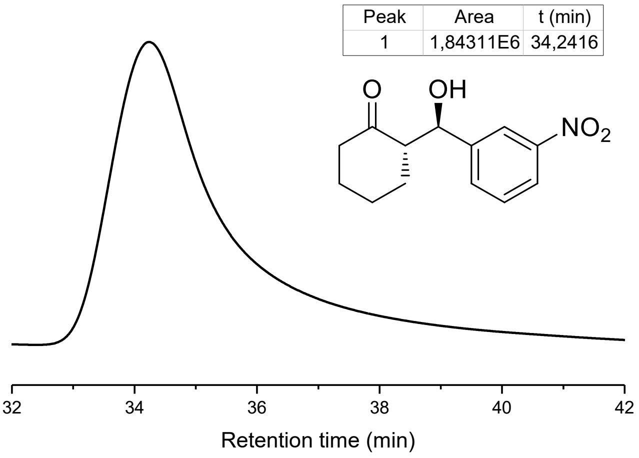
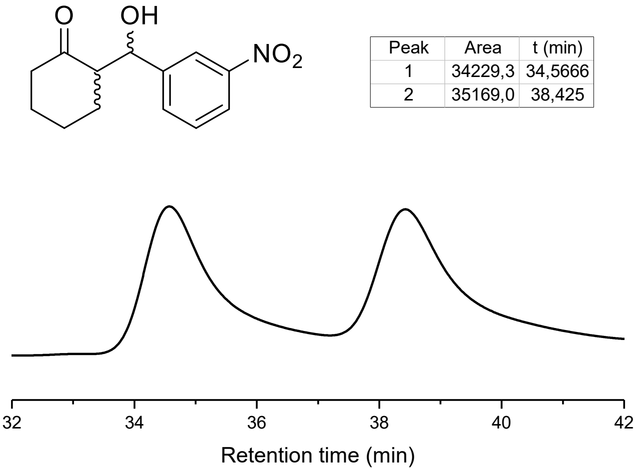


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8f**.



Peak	Area	t (min)
1	1,84311E6	34,2416

Figure S40. HPLC chromatogram of **8f**.



Peak	Area	t (min)
1	34229,3	34,5666
2	35169,0	38,425

Figure S41. HPLC chromatogram of racemic standard of **8f**.

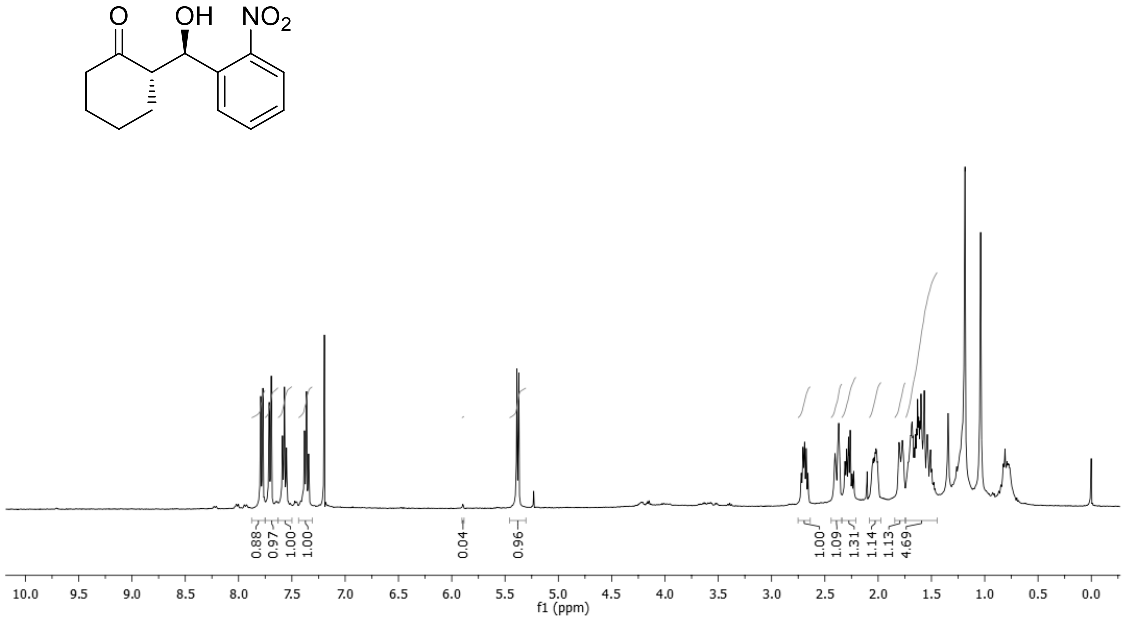
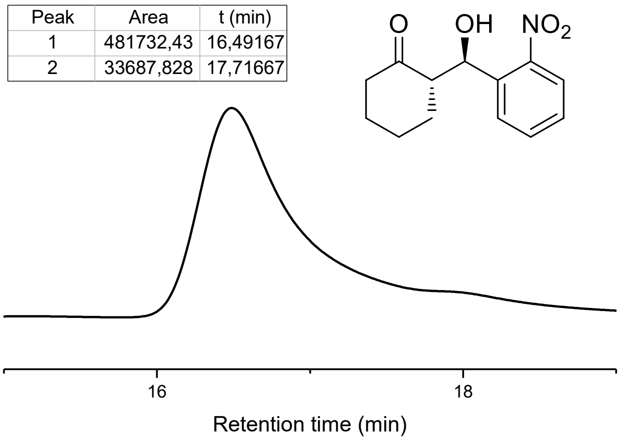
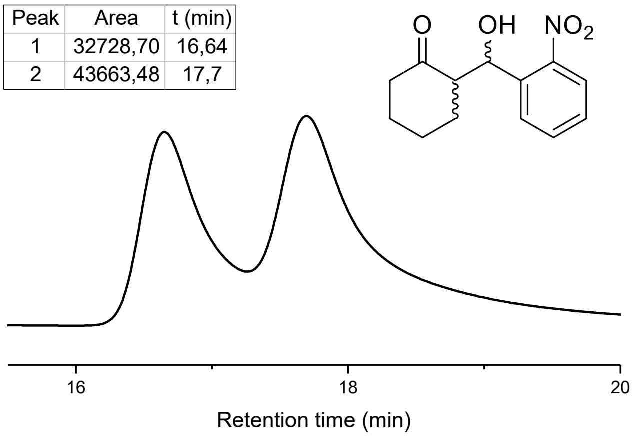


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8g**.



Peak	Area	t (min)
1	481732,43	16,49167
2	33687,828	17,71667

Figure S43. HPLC chromatogram of **8g**.



Peak	Area	t (min)
1	32728,70	16,64
2	43663,48	17,7

Figure S44. HPLC chromatogram of racemic standard of **8g**.

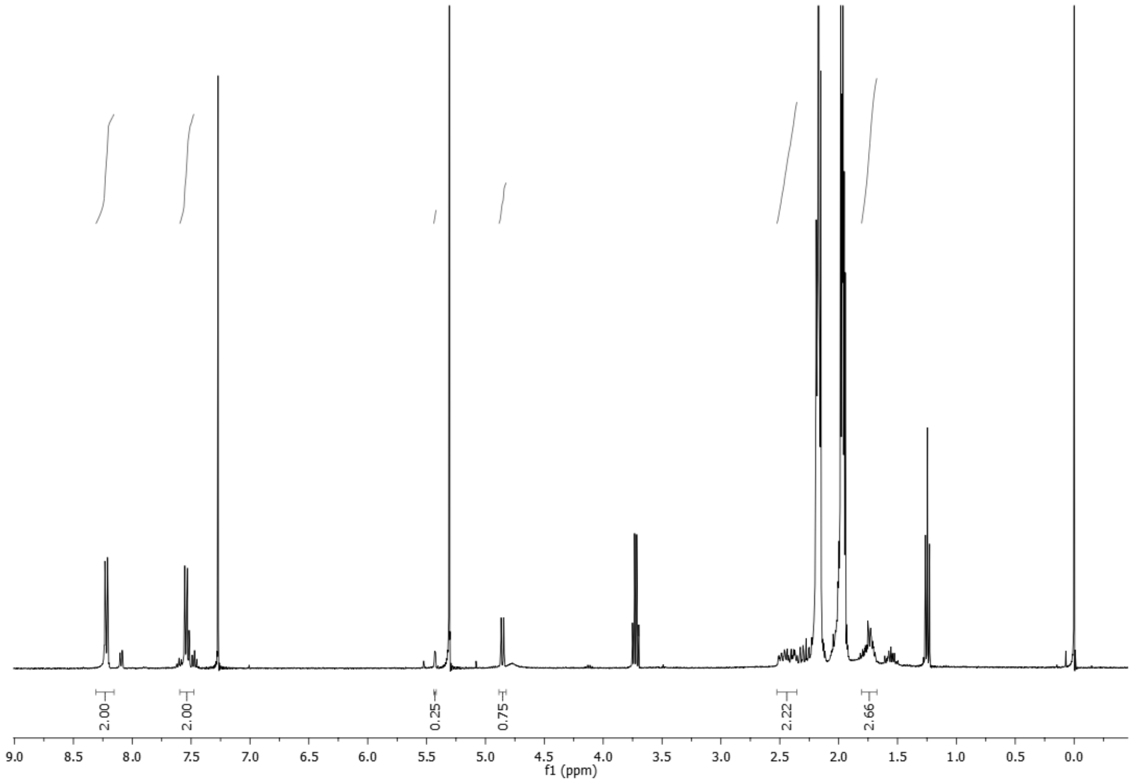
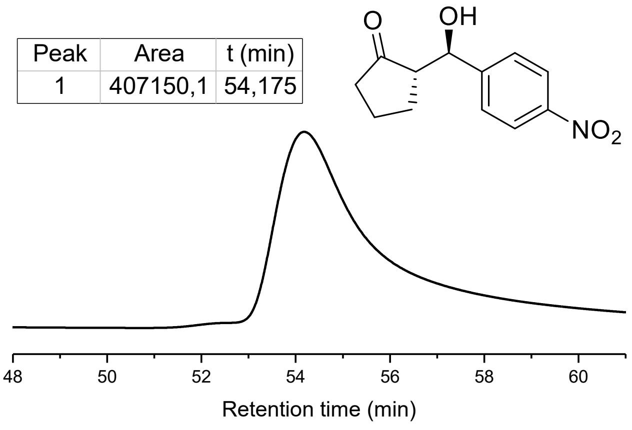
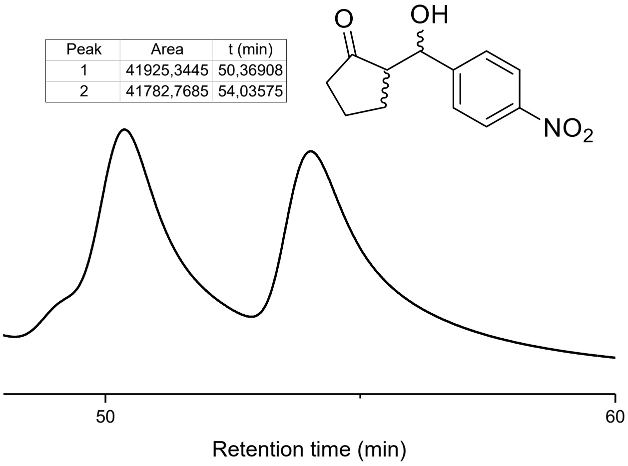


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8h**.



Peak	Area	t (min)
1	407150,1	54,175

Figure S46. HPLC chromatogram of **8h**.



Peak	Area	t (min)
1	41925,3445	50,36908
2	41782,7685	54,03575

Figure S47. HPLC chromatogram of racemic standard of **8h**.

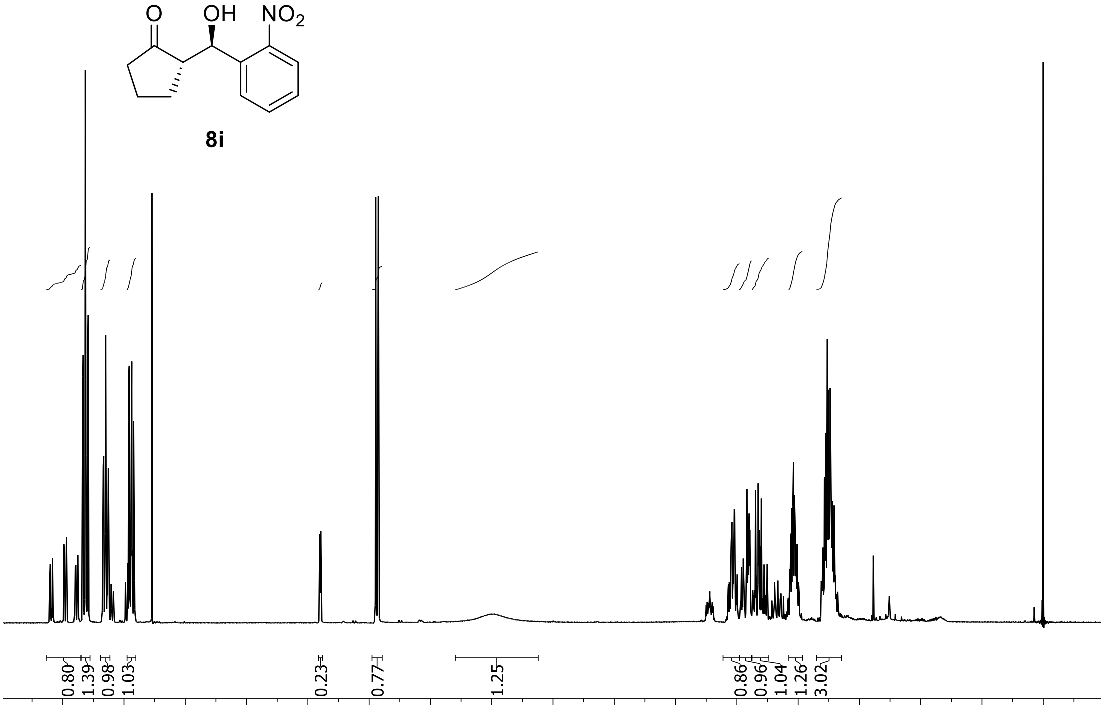
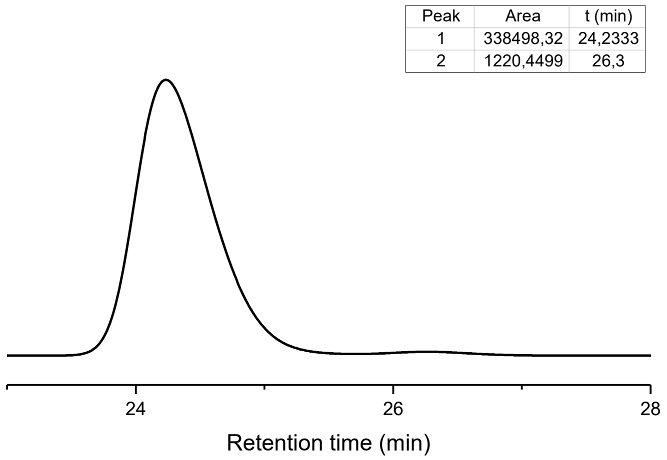
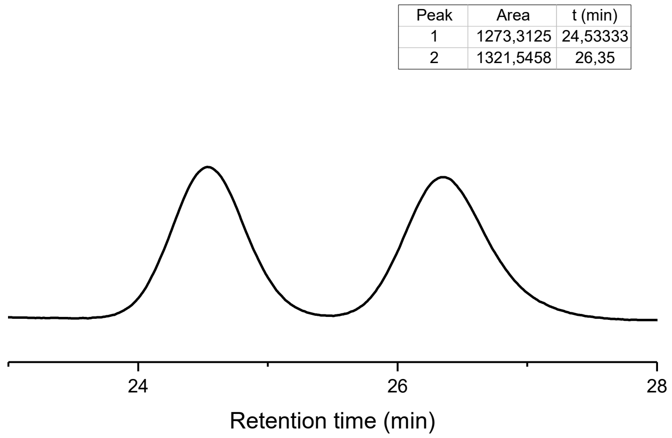


Figure S48. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **8i**.



Peak	Area	t (min)
1	338498,32	24,2333
2	1220,4499	26,3

Figure S49. HPLC chromatogram of **8i**.



Peak	Area	t (min)
1	1273,3125	24,53333
2	1321,5458	26,35

Figure S50. HPLC chromatogram of racemic standard of **8i**.

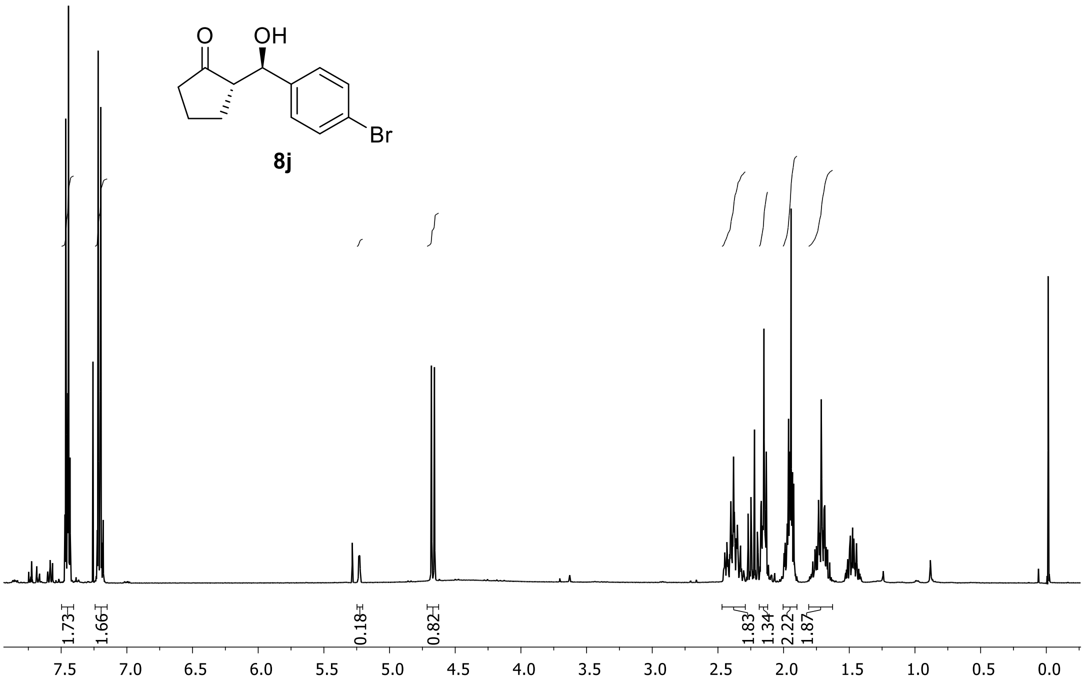
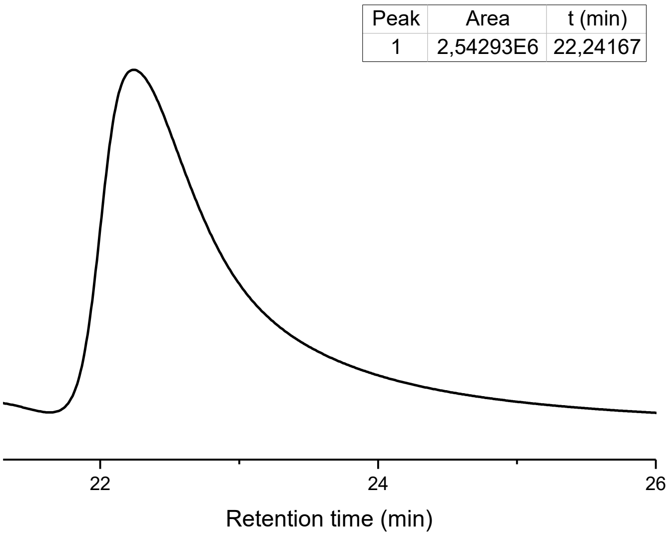
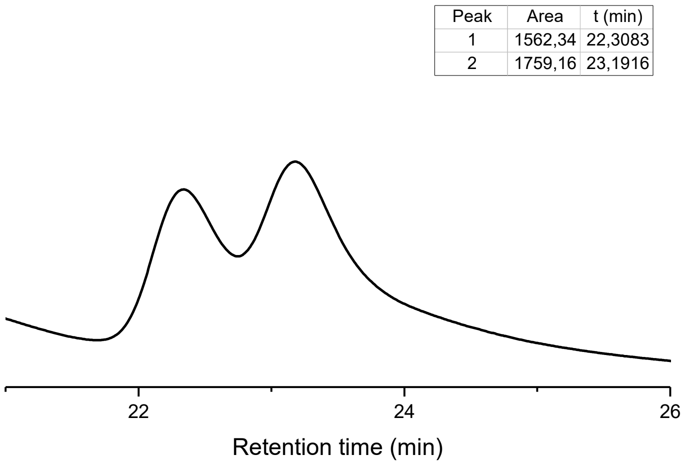


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8j**.



Peak	Area	t (min)
1	2,54293E6	22,24167

Figure S52. HPLC chromatogram of **8j**.



Peak	Area	t (min)
1	1562,34	22,3083
2	1759,16	23,1916

Figure S53. HPLC chromatogram of racemic standard of **8j**.

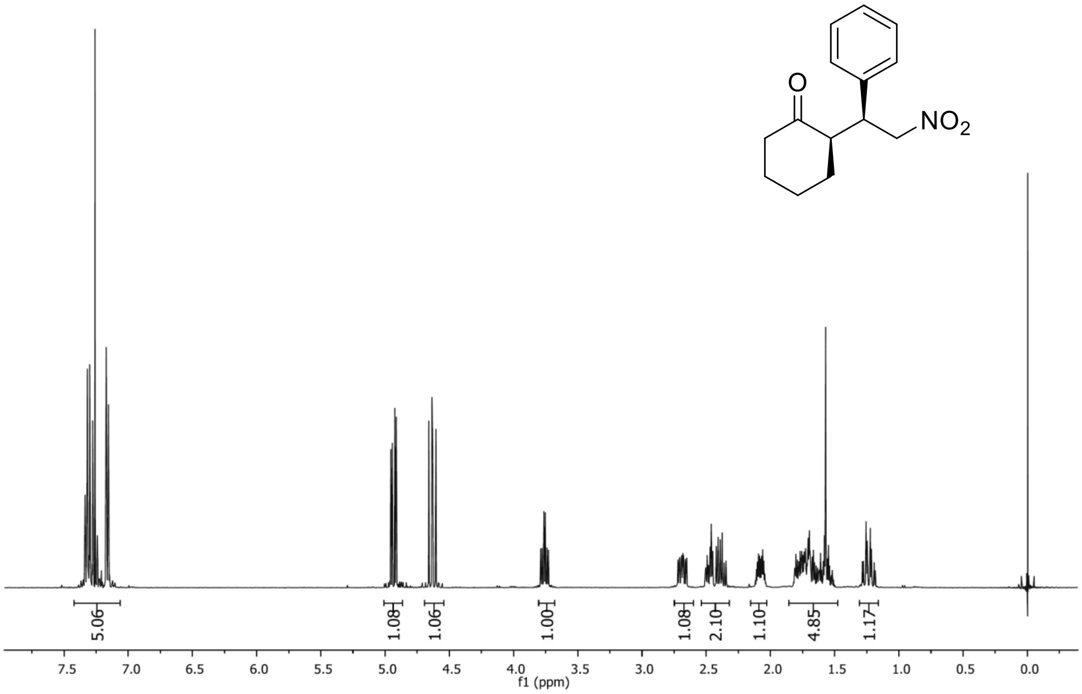
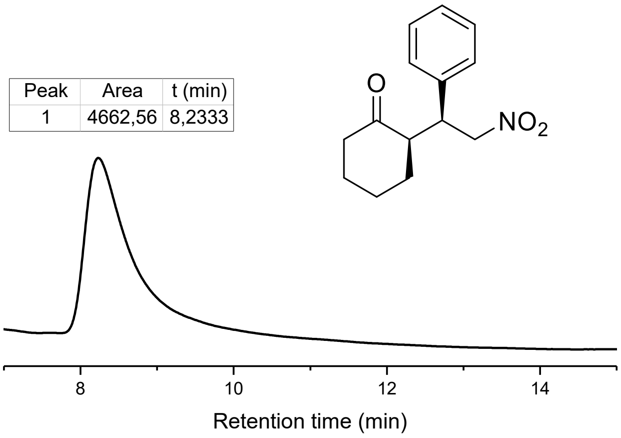
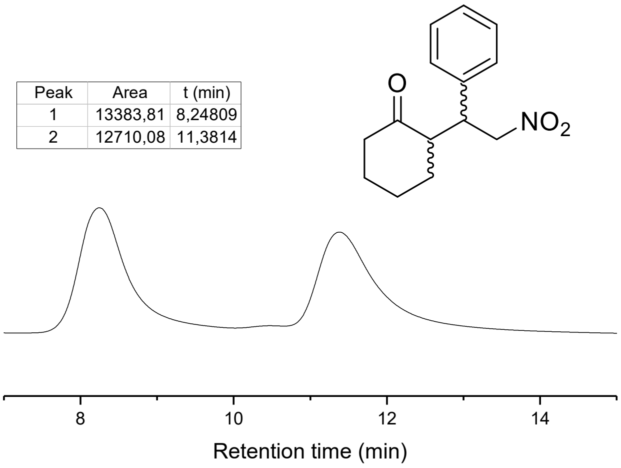


Figure S54. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **10**.



Peak	Area	t (min)
1	4662,56	8,2333

Figure S55. HPLC chromatogram of **10**.



Peak	Area	t (min)
1	13383,81	8,24809
2	12710,08	11,3814

Figure S56. HPLC chromatogram of racemic standard of **10**.