Supporting Information for

One-pot synthesis of chiral β-hydroxysulfones from alkynes via aerobic oxysulfonylation and asymmetric reduction in MeOH/H_2O

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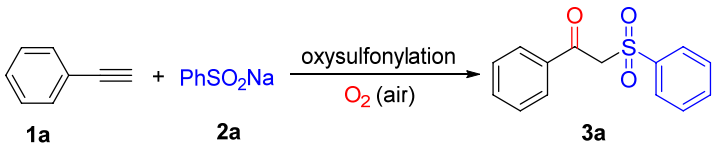
1. General information

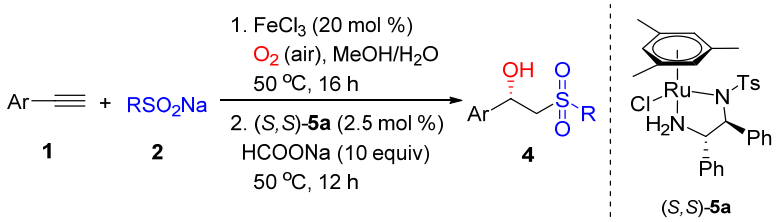
Unless otherwise noted, all reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification. Column chromatography was performed with silica gel (200-300 mesh). NMR spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometers. $CDCl_3$ was the solvent used for the NMR analysis, with tetramethylsilane as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^1H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. Optical rotation was measured on a MCP-500. Melting point were determined using X-4 made by Peking Taike Apparatus Co. Ltd. HPLC analysis was conducted on a Waters 2489 Series instrument with chiral column OJ-H, AD-H, AS-H and OD-H. HRMS spectra were acquired using an Agilent 6210 ESI/TOF mass spectrometer.

2. Screening the optimal conditions for the aerobic oxysulfonylation of phenylacetylene



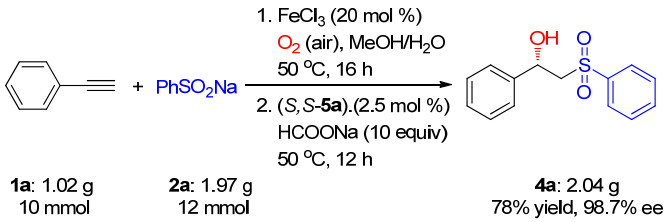
Phenylacetylene **1a** (0.2 mmol, 21 mg), sodium benzenesulfinate **2a** (0.3 mmol, 49 mg), and $FeCl_3$ (0.04 mmol, 6.5 mg) were put into a 10 mL of glass tube, then 4 mL of MeOH/H_2O (v/v = 3/1) was added. The mixture was stirred at 50℃ for 16 h under air atmosphere. After the reaction was complete, 5.0 mL of H_2O was added, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by silica gel column chromatography to give the product **3a** (48 mg, 93% yield). White solid, mp. 93-95℃. **^1H NMR** (400 MHz, $CDCl_3$): δ = 7.99-7.93 (m, 4H), 7.73-7.64 (m, 2H), 7.62-7.57 (m, 2H), 7.54-7.50 (m, 2H), 4.79 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 188.0, 138.7, 135.7, 134.4, 134.3, 129.3, 129.2, 128.9, 128.6, 63.5.

3. General procedure for the one-pot synthesis of chiral *β*-hydroxysulfones



The corresponding alkyne **1** (0.2 mmol), sodium sulfinate **2** (0.3 mmol), and $FeCl_3$ (0.04 mmol, 6.5 mg) were put into a 10 mL of glass tube, then 4 mL of MeOH/H_2O (v/v = 3/1) was added. The mixture was stirred at 50℃ for 16 h under air atmosphere. After the aerobic oxysulfonylation of alkyne **1** was complete monitored by TLC, (*S,S*)-**5a** (0.005 mmol, 3.2 mg) and HCOONa (2 mmol, 136 mg) were added, and then degassed 3 time, the mixture was stirred at 50℃ for 12 h under nitrogen atmosphere. After the reaction was complete, 5.0 mL of H_2O was added, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding chiral *β*-hydroxysulfone **4**.

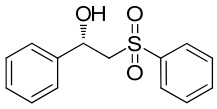
4. Gram-scale one-pot synthesis of chiral *β*-hydroxysulfone 4a



Phenylacetylene **1a** (10 mmol, 1.02 g), sodium benzenesulfinate **2a** (12 mmol, 1.97 g), and $FeCl_3$ (2 mmol, 324 mg) were put into a 50 mL of glass tube, then 20 mL of MeOH/H_2O (v/v = 3/1) was added. After the aerobic oxysulfonylation of alkyne **1a** was complete monitored by TLC, (*S,S*)-**5a** (0.2 mmol, 131 mg) and HCOONa (50 mmol, 3.4 g) were added, and then degassed 3 time, the mixture was stirred at 50℃ for 12 h under nitrogen atmosphere. After the reaction was complete, 5.0 mL of H_2O was added, the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by silica gel column chromatography to give chiral *β*-hydroxysulfone **4a** (2.04 g, 78% yield, 98.7% ee).

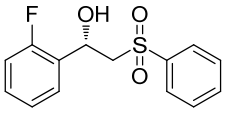
5. Analytical data of the products

(*S*)-1-phenyl-2-(phenylsulfonyl)ethanol (**4a**, CAS: 224634-51-9, known compound[1])



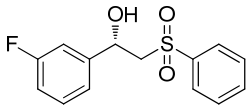
Colourless oil; 82% yield (42.1 mg), 99.6% ee. Purified by flash column chromatography (PE: EA = 4:1). ($[\alpha]^{20}_{D}$ -49.03 (*c* 0.04, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.03-8.00 (m, 2H), 7.77-7.72 (m, 1H), 7.67-7.63 (m, 2H), 7.39-7.32 (m, 5H), 5.35 (d, J = 10.0 Hz, 1H), 3.71 (d, J = 2.4 Hz, 1H), 3.55 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.39 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.6, 139.4, 134.1, 129.5, 128.8, 128.4, 128.0, 125.6, 68.5, 64.0. **HPLC** (Chiralcel AD-H column, n-hexane/*i*-PrOH = 90:10 (v/v), 1.0 mL/min, 215 nm, 25℃), t_1 = 28.872 min (major), t_2 = 34.006 min (minor).

(*S*)-1-(2-Fluorophenyl)-2-(phenylsulfonyl)ethanol (**4b**, CAS: 1572476-84-6, known compound[1])



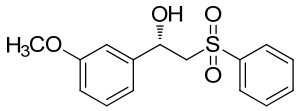
Yellow oil; 79% yield (44.2 mg), 99.8% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.66-7.58 (m, 3H), 7.30-7.27 (m, 1H), 7.20 (t , J = 7.6 Hz, 1H), 7.01-6.96 (m, 1H), 5.49 (br,1H), 3.87 (d, J = 2.8 Hz 1H), 3.54-3.52 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.0 (d, $^1J_{C\text{-}F}$ = 244.6 Hz), 138.8, 134.2, 129.8 (d, $^3J_{C\text{-}F}$ = 8.2Hz), 129.5, 128.0, 127.3, 127.2, 124.7 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 115.3, (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 63.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 62.2 (d, $J_{C\text{-}F}$ = 1.3 Hz). **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 29.031 min (major), t_2 = 41.486 min (minor).

(*S*)-1-(3-Fluorophenyl)-2-(phenylsulfonyl)ethanol (**4c**,CAS: 1572476-86-8, known compound[1])



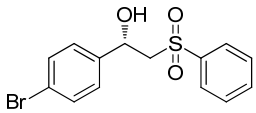
Yellow oil; 74% yield (41.4 mg), 97.1% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 7.2 Hz, 2H), 7.75 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 2H), 7.35-7.30 (m, 1H), 7.09 (d, J = 6.8 Hz, 2H), 7.02-6.99 (m, 1H), 5.33 (d, J = 10.0 Hz, 1H), 3.84 (d, J = 2.0 Hz, 1H), 3.51 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.37 (d, J = 14.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 163.0 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 143.2 (d, $^3J_{C\text{-}F}$ = 6.9 Hz), 139.0, 134.3, 130.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 129.6, 128.0, 121.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 115.3 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 112.9 (d,$^2J_{C\text{-}F}$ = 22.5 Hz), 67.9 (d, $J_{C\text{-}F}$ = 1.8 Hz), 63.8. **HPLC** (Chiralcel OD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 23.297 min (minor), t_2 = 25.981 min (major).

(*S*)-1-(3-methoxyphenyl)-2-(phenylsulfonyl)ethanol (**4d**,CAS:2244130-72-9, known compound[2])



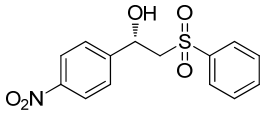
Yellow solid, mp. 74-75 ℃; 71% yield (39.3 mg), 97.5% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.02-8.00 (m, 2H), 7.74-7.72 (m, 1H), 7.64 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 6.92-6.84 (m, 3H), 5.30 (d, J = 10.0 Hz, 1H), 3.82 (s, 3H), 3.70 (d, J = 2.4 Hz, 1H), 3.57-3.51 (m, 1H), 3.39 (dd, J_1 = 14.4 Hz, J_2 =1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.9, 142.1, 139.2, 134.2, 129.9, 129.5, 128.0, 117.8, 113.9, 111.1, 68.4, 64.0, 55.3. **HPLC** (Chiralcel OJ-H, n-hexane/*i*-PrOH = 85/15, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 30.646 min (major), t_2 = 40.201 min (minor).

(*S*)-1-(4-bromophenyl)-2-(phenylsulfonyl)ethanol (**4e**, CAS: 1572476-81-3, known compound[1])



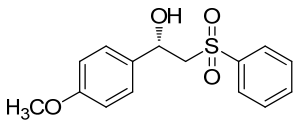
Yellowish oil; 72% yield (49.1 mg), 97.8% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 8.00-7.98 (m, 2H), 7.77-7.63 (m, 3H), 7.50-7.48 (m, 2H), 7.24 (d, J = 8.8 Hz, 2H), 5.30 (d, J = 10.0 Hz, 1H), 3.80 (d, J = 2.0 Hz, 1H), 3.50 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.37 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 139.6, 139.0, 134.3, 131.9, 129.6, 128.0, 127.4, 122.3, 67.9, 63.8. **HPLC** (Chiralcel OJ-H, n-hexane/*i*-PrOH = 80/20, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 35.052 min (major), t_2 = 50.457 min (minor).

(*S*)-1-(4-nitrophenyl)-2-(phenylsulfonyl)ethanol (**4f**, CAS: 1634620-32-8, known compound[3])



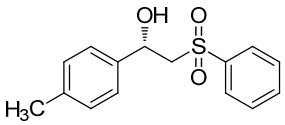
Yellow solid, mp. 63-64 ℃; 77% yield (47.3 mg), 99.0% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.24-8.22 (m, 2H), 8.02-8.00 (m, 2H), 7.77 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.48 (d, J = 8.0 Hz, 1H), 4.05 (s, 1H), 3.50 (dd, J_1 = 14.4 Hz, J_2 = 10 Hz, 1H), 3.39 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 147.6, 138.8, 134.5, 129.7, 128.0, 126.6, 124.0, 67.6, 63.6. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 85/15, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 48.457 min (major), t_2 = 68.203 min (minor).

(*S*)-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanol (**4g**, CAS:502188-71-8, known compound[4])



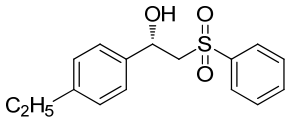
Yellow oil; 69% yield (40.3 mg), 99.3% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.2 Hz, 2H), 7.75 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.27 (d, J = 8.4 Hz, 1H), 3.82 (s, 3H), 3.64 (s, 1H), 3.55 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.36 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.6, 139.3, 134.1, 132.8, 129.5, 128.0, 127.0, 114.1, 68.1, 63.9, 55.3. **HPLC** (Chiralcel OJ-H, n-hexane/*i*-PrOH = 80/20, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 46.799 min (major), t_2 = 72.356 min (minor).

(*S*)-2-(phenylsulfonyl)-1-(*p*-tolyl)ethanol (**4h**, CAS: 502188-72-9, known compound[1])



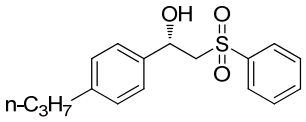
Yellow solid, mp. 67-68 ℃. 79% yield (43.6 mg), 99.6% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.4 Hz, 2H), 7.73 (t, J = 7.6 Hz 1H), 7.64 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 5.29 (d, J = 10.0 Hz, 1H), 3.64 (s, 1H), 3.52 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.39 (d, J = 14.4 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 139.2, 138.2, 137.7, 134.1, 129.5, 129.4, 128.0, 125.6, 68.4, 64.0, 21.1. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 35.443 min (major), t_2 = 39.281 min (minor).

(*S*)-1-(4-ethylphenyl)-2-(phenylsulfonyl)ethanol (**4i**, unknown compound)



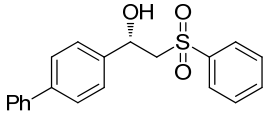
Yellow oil; 74% yield (50.8 mg), 99.5% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 6.8 Hz, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.31 (d, J = 10.4 Hz, 1H), 3.63 (s, 1H), 3.56 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.38 (dd, J_1 = 14.4 Hz, J_2 = 1.6 Hz, 1H), 2.65 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 144.6, 139.2, 137.9, 134.1, 129.5, 128.3, 128.0, 125.7, 68.4, 63.9, 28.6, 15.6. **HRMS** (ESI) calcd for $C_{16}H_{18}O_3NaS$ ($[M+Na]^+$): 313.0869, Found: 313.0870. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 25.266 min (minor), t_2 = 28.599 min (major).

(*S*)-2-(phenylsulfonyl)-1-(4-propylphenyl)ethanol (**4j**, unknown compound)



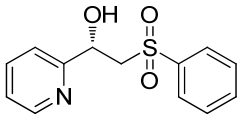
Yellow solid; mp. 54-55 ℃, 72% yield (43.7 mg), 99.4% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 6.8 Hz, 2H), 7.74 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.30 (d, J = 10.4 Hz, 1H), 3.63 (d, J = 2.0 Hz, 1H), 3.54 (dd, J_1 = 14.4, J_2 = 10.0 Hz, 1H), 3.39 (dd, J_1 = 14.4, J_2 = 1.6 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 1.67-1.63(m, 2H), 0.95(t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 143.1,139.3，137.9, 134.1, 129.5, 128.9, 128.0, 125.6, 68.4, 64.0, 37.7, 24.5, 13.8. **HRMS** (ESI) calcd for $C_{17}H_{20}O_3NaS$ ($[M+Na]^+$): 327.1025, Found: 327.1028. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 39.111 min (minor), t_2 = 43.609 min (major).

(*S*)-1-([1,1'-biphenyl]-4-yl)-2-(phenylsulfonyl)ethanol (**4k**, unknown compound)



Yellow solid, mp. 86-87 ℃, 71% yield (52.8 mg), 99.9% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.04-8.01 (m, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 8.0 Hz, 2H), 7.60 (m, 4H), 7.49 (m, 2H), 7.43 (m, 3H), 5.39 (d, J = 10.0 Hz, 1H), 3.74 (d, J = 2.0 Hz, 1H), 3.60 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.44 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.4, 140.5, 139.6, 139.2, 134.2, 129.5, 128.8, 128.0, 127.5, 127.1, 126.1, 68.3, 63.9. **HRMS** (ESI) calcd for $C_{20}H_{18}O_3NaS$ ($[M+Na]^+$): 361.0869, Found: 361.0870. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 51.863 min (major), t_2 = 57.968 min (minor).

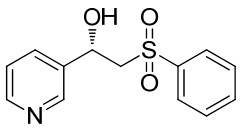
(*S*)-2-(phenylsulfonyl)-1-(pyridin-2-yl)ethanol (**4l**, unknown compound)



Yellow oil; 57% yield (30.1 mg), 99.5% ee. Purified by flash column chromatography (PE: EA = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.8 Hz, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.69-7.56 (m, 4H), 7.19 (d, J = 7.6 Hz, 1H), 7.13 (m, 1H), 3.68-3.64 (m, 2H), 3.28-3.24 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.1, 149.4, 139.1, 136.7, 133.7, 129.3, 128.1, 123.3, 122.0, 55.2, 30.8. **HRMS** (ESI) calcd for $C_{13}H_{14}O_3NS$ ($[M+H]^+$): 264.0689, Found: 264.0690. **HPLC** (Chiralcel OD-H,

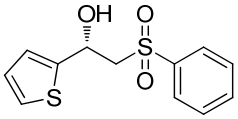
n-hexane/*i*-PrOH = 80/20, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 22.283 min (major), t_2 = 25.515 min (minor).

(*S*)-2-(phenylsulfonyl)-1-(pyridin-3-yl)ethanol (**4m**, unknown compound)



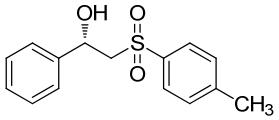
Yellow oil; 47% yield (24.6 mg), 95.1% ee. Purified by flash column chromatography (PE: EA = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.03 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.78-7.75 (m, 2H), 7.67 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 6.0 Hz, 2H), 5.40 (d, J = 11.6 Hz, 1H), 3.59 (s, 1H), 3.54 (dd, J_1 = 14.4 Hz, J_2 = 4.4 Hz, 1H), 3.40 (dd, J_1 = 14.0 Hz, J_2 = 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.7, 147.5, 138.9, 134.4, 133.6, 129.7, 128.0, 123.7, 66.5, 63.6. **HRMS** (ESI) calcd for $C_{13}H_{14}O_3NS$ ($[M+H]^+$): 264.0689, Found: 264.0691. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 26.283 min (major), t_2 = 34.820 min (minor).

(*S*)-2-(phenylsulfonyl)-1-(thiophen-2-yl)ethanol (**4n**, CAS:1572476-92-6, known compound[1])



Yellow oil; 56% yield (29.6 mg), 99.6% ee. Purified by flash column chromatography (PE: EA = 6:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.8 Hz, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 3.6 Hz, 1H), 6.98 (d, J = 3.6 Hz, 2H), 5.61 (d, J = 9.6 Hz, 1H), 3.81 (s, 1H), 3.66 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.52 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 144.1, 139.1, 134.2, 129.5, 128.0, 126.8, 125.6, 124.2, 65.0, 63.8. **HRMS** (ESI) calcd for $C_{12}H_{12}NaO_3S_2$ ($[M+Na]^+$): 291.0120, Found: 291.0119. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 85/15, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 40.665 min (major), t_2 = 51.234 min (minor).

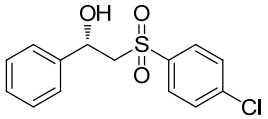
(*S*)-1-phenyl-2-tosylethanol (**4o**, CAS: 71899-75-7, known compound[3])



Yellow solid, mp. 52-53 ℃, 72% yield (39.7 mg), 95.7% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.39-7.31 (m, 5H), 5.30 (d, J = 10.0 Hz, 1H), 3.80 (s, 1H), 3.42 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.36 (dd, J_1 = 14.4 Hz, J_2 = 1.6 Hz, 1H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 145.3, 140.7, 136.1, 130.1, 128.8, 128.3, 128.0, 125.7, 68.5, 64.0, 21.7. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0

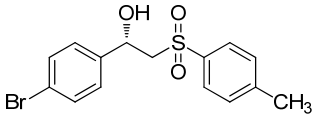
mL/min, 25 ℃), t_1 = 28.455 min (major), t_2 = 46.323 min (minor).

(*S*)-2-((4-chlorophenyl)sulfonyl)-1-phenylethanol (**4p**, unknown compound)



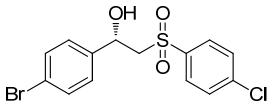
Yellow oil; 77% yield (45.6 mg), 99.5% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.38-7.33 (m, 5H), 5.35 (d, J = 9.6 Hz, 1H), 3.60-3.37 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.0, 140.5, 137.8, 129.8, 129.6, 128.9, 128.5, 125.7, 68.6, 64.1. **HRMS** (ESI) calcd for $C_{14}H_{13}O_3ClNaS$ ($[M+Na]^+$): 319.0166, Found: 319.0164. **HPLC** (Chiralcel OD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 27.056 min (major), t_2 = 33.930 min (minor).

(*S*)-1-(4-bromophenyl)-2-tosylethanol (**4q**, unknown compound)



Yellow oil; 69% yield (48.9 mg), 99.2% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.27 (d, J = 10.0 Hz, 1H), 3.86 (d, J = 2.0 Hz, 1H), 3.48 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.32 (dd, J_1 = 14.4 Hz, J_2 = 1.6 Hz, 1H), 2.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 145.5, 139.7, 136.0, 131.9, 130.2, 128.0, 127.4, 122.2, 67.9, 63.8, 21.7. **HRMS** (ESI) calcd for $C_{15}H_{15}BrO_3NaS$ ($[M+Na]^+$): 376.9817, Found: 376.9819. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 34.273 min (major), t_2 = 50.817 min (minor).

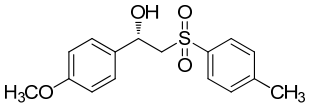
(*S*)-1-(4-bromophenyl)-2-((4-chlorophenyl)sulfonyl)ethanol (**4r**, unknown compound)



Yellow oil; 71% yield (53.1 mg), 99.5% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 5.31 (d, J = 9.6 Hz, 1H), 3.61 (s, 1H), 3.51 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.34 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.1, 139.5, 137.6, 132.0, 129.9, 129.5, 127.4, 122.4, 68.0, 63.9. **HRMS** (ESI) calcd for $C_{14}H_{12}O_3BrClNaS$ ($[M+Na]^+$): 396.9271, Found: 396.9273. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, detector: 215 nm, flow rate:

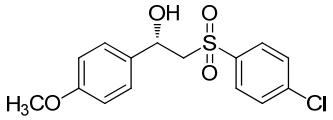
1.0 mL/min, 25 ℃), t_1 = 28.571 min (major), t_2 = 48.253 min (minor).

(*S)*-1-(4-methoxyphenyl)-2-tosylethanol (**4s**, CAS: 398139-23-6, known compound[3])



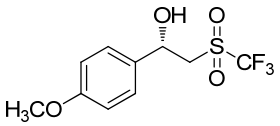
Yellow oil; 67% yield (41.1 mg), 99.3% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.24 (d, J = 8.4 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 1H), 3.52 (dd, J_1 = 14.4 Hz, J_2 = 10.4 Hz, 1H), 3.33 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.6, 145.2, 136.2, 132.9, 130.1, 128.0, 127.0, 114.1, 68.1, 64.0, 55.3, 21.7. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 50.476 min (major), t_2 = 60.133 min (minor).

(*S*)-2-((4-chlorophenyl)sulfonyl)-1-(4-methoxyphenyl)ethanol (**4t**, unknown compound)



Yellow oil; 64% yield (41.7 mg), 97.1% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.27 (d, J = 10.0 Hz, 1H), 3.82 (s, 3H), 3.60 (dd, J_1 = 14.4 Hz, J_2 = 10.0 Hz, 1H), 3.38 (dd, J_1 = 14.4 Hz, J_2 = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.7, 140.8, 137.9, 132.7, 129.7, 129.6, 127.0,114.2, 68.3, 64.0, 55.3. **HRMS** (ESI) calcd for $C_{15}H_{15}O_4ClNaS$ ($[M+Na]^+$): 349.0272, Found: 349.0273. **HPLC** (Chiralcel AD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 41.336 min (major), t_2 = 57.460 min (minor).

(*S*)-1-(4-methoxyphenyl)-2-((trifluoromethyl)sulfonyl)ethanol (**4u**, unknown compound)



Colourless oil; 17% yield (10.1 mg), 71.2% ee. Purified by flash column chromatography (PE: EA = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.91 (q, J = 6.4 Hz, 1H), 3.85 (s, 3H), 1.78 (brs, 1H), 1.53 (d, J = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.0, 138.0, 126.7, 113.9, 77.24, 70.0, 55.3, 25.0. **HRMS** (ESI) calcd for $C_{10}H_{11}F_3NaO_4S$ ($[M+Na]^+$): 307.0222, Found: 307.0221. **HPLC** (Chiralcel OD-H, n-hexane/*i*-PrOH = 90/10, 215 nm, 1.0 mL/min, 25 ℃), t_1 = 7.592 min (major), t_2 = 8.100 min (minor).

Reference:

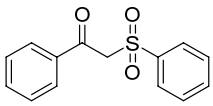
[1] Huang, X. F.; Zhang, S. Y.; Geng, Z. C.; Liu, P.; Li, H. Y.; Wang, X. W. *Adv. Synth. Catal*, **2013**, *355*, 2860.

[2] Enders, D.; Grossmann, A.; Huang, H.; Raabe, G. *Eur. J. Org. Chem*. **2011**, 4298.

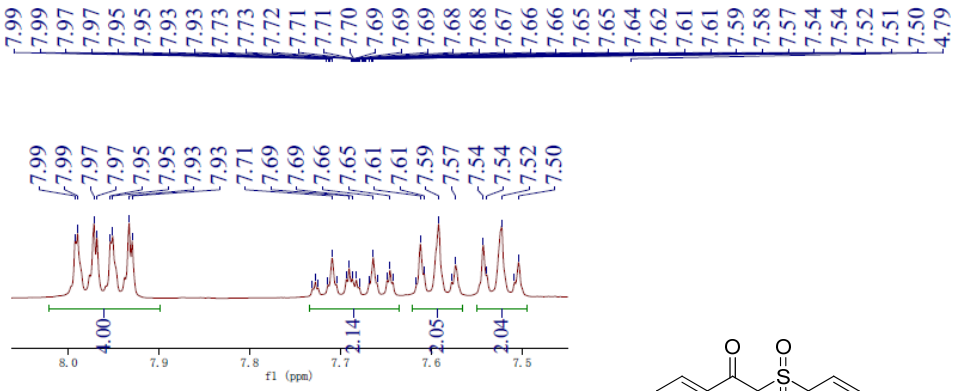
[3] Zhang, D. C.; Cheng, T. Y.; Zhao, Q. K.; Xu, J. Y.; Liu, G. H. *Org. Lett*. **2014**, *16*, 5764.

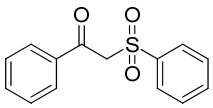
[4] Zhao, G.; Hu, J. B.; Qian, Z. S.; Yin, W. X. *Tetrahedron Asymmetry*, **2002**, *12*, 2095.

6. NMR spectra of the products



3a





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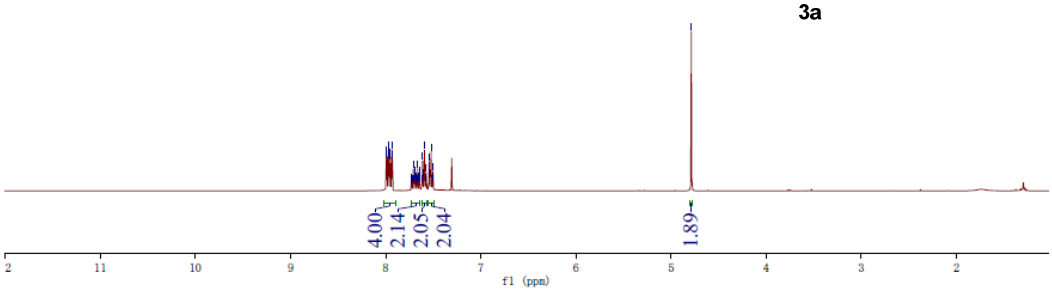

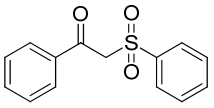

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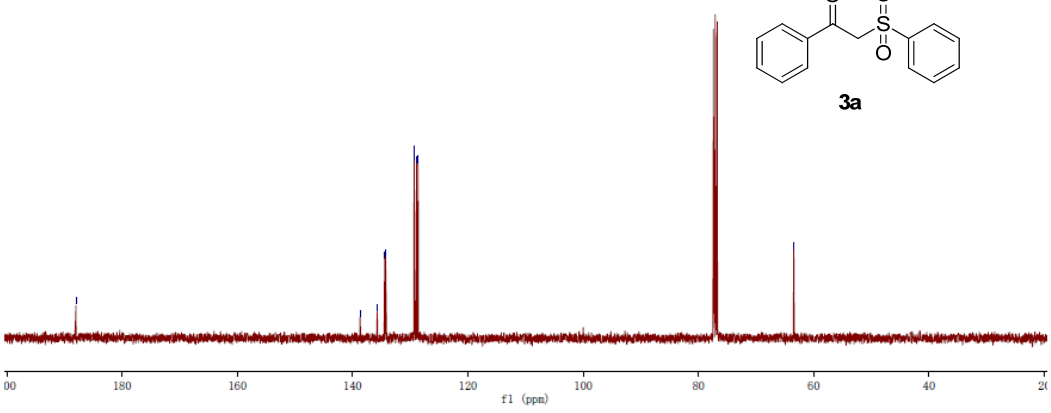

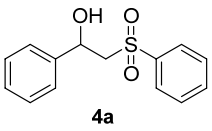
OH
O
S
O

4a


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8.003
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7.758
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7.727
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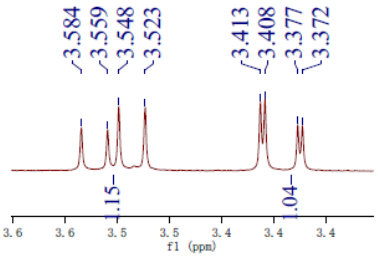
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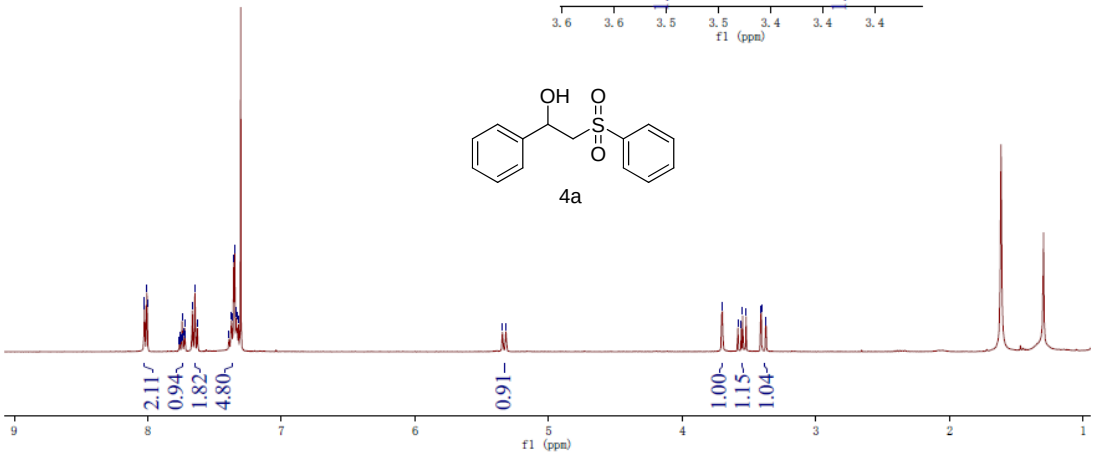
3.5
3.4
3.4
3.4
f1 (ppm)

OH
O
S
O

4a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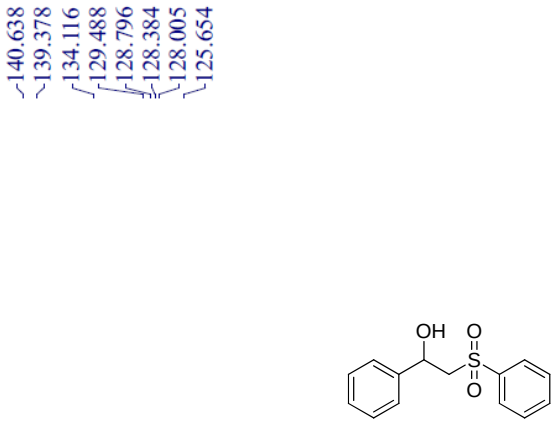
1.04
9
8
7
6
5
4
3
2
1
f1 (ppm)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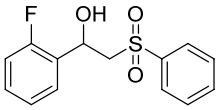
130
120
110
100
90
80
70
60
f1 (ppm)

OH
O
S
O

4a


F
OH
O
S
O

4b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8.000
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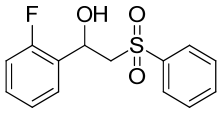
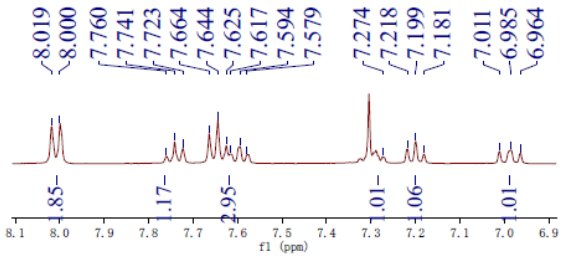

F
OH
O
S
O

4b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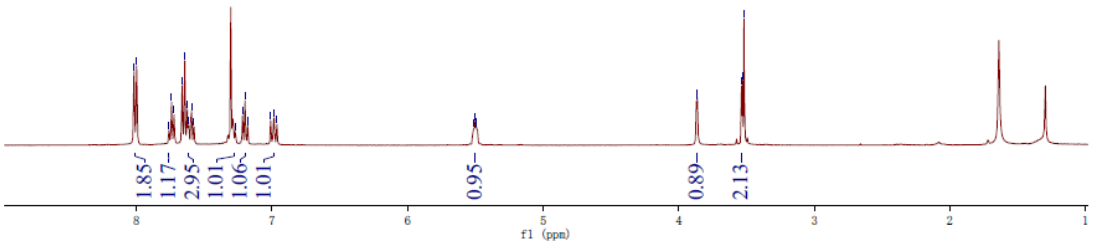
6.9
f1 (ppm)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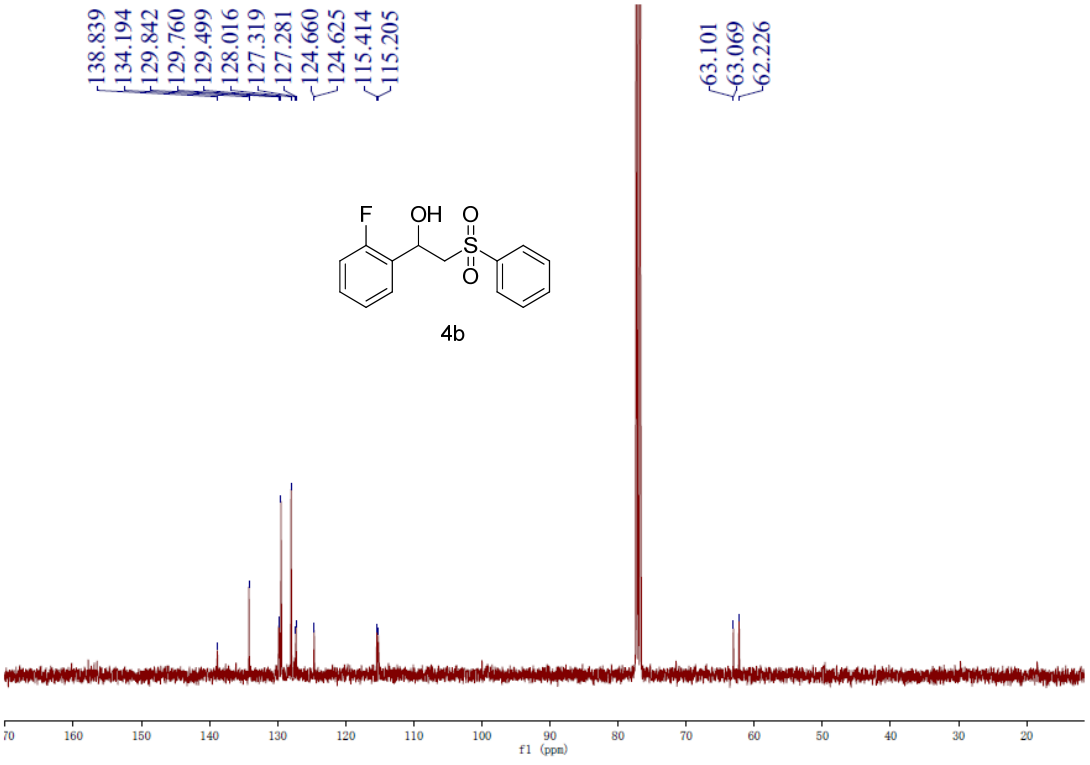
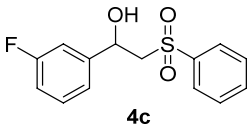
2
1
f1 (ppm)

F
OH
O
S
O

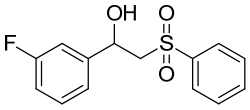
4b


138.839
134.194
129.842
129.760
129.499
128.016
127.319
127.281
124.660
124.625
115.414
115.205
63.101
63.069
62.226
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

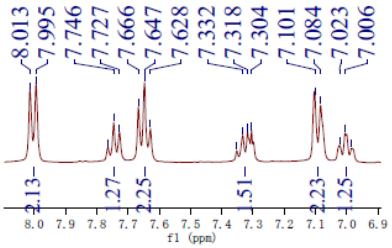


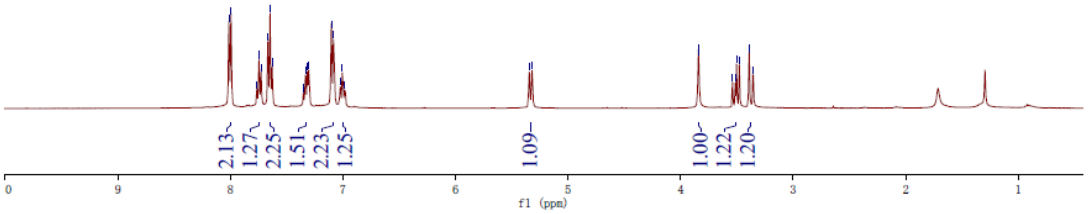
4c

8.013
7.995
7.764
7.746
7.727
7.666
7.647
7.628
7.352
7.332
7.318
7.304
7.101
7.084
7.023
7.006
6.985
5.345
5.320
3.843
3.838
3.539
3.514
3.503
3.478
3.394
3.390
3.359
3.354

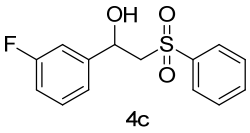


4c

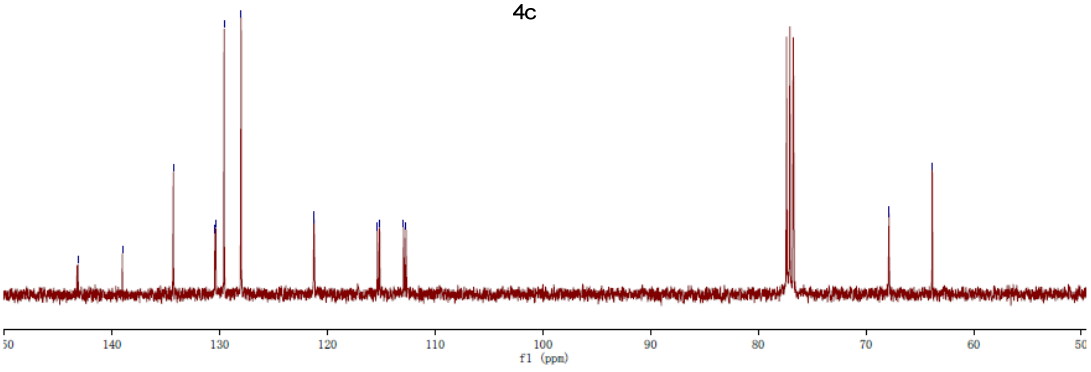


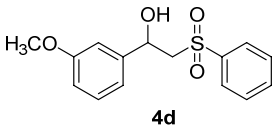


143.155
139.029
134.293
130.433
130.353
129.577
128.002
121.244
121.214
115.358
115.148
112.917
112.692
67.872
67.854
63.842

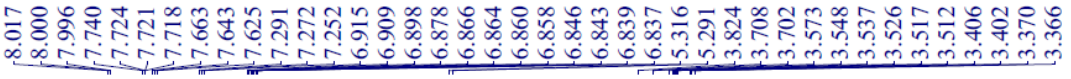


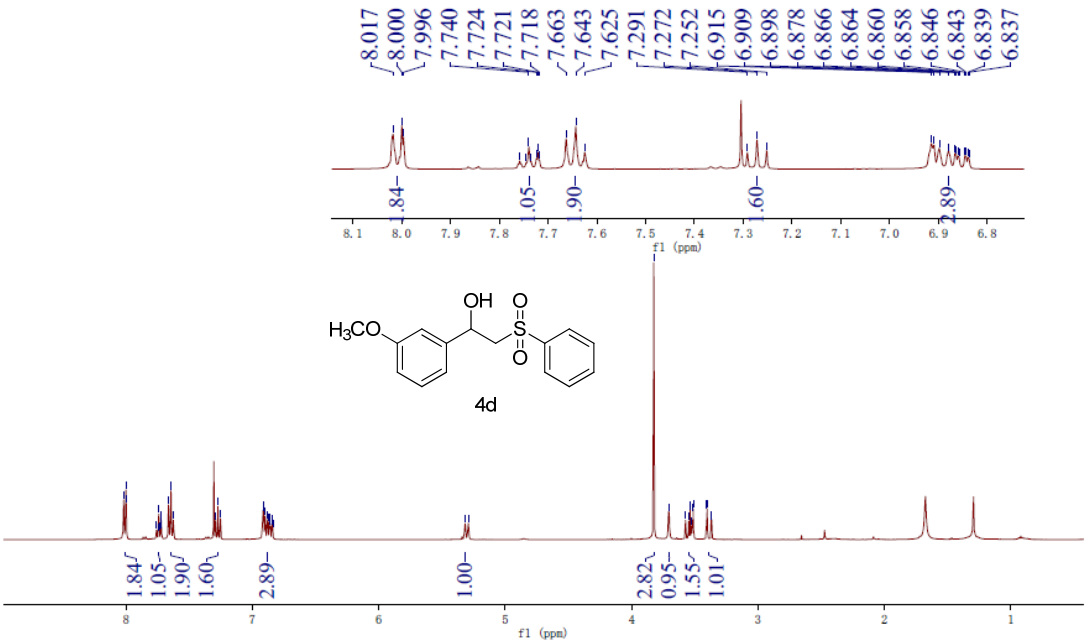
4c

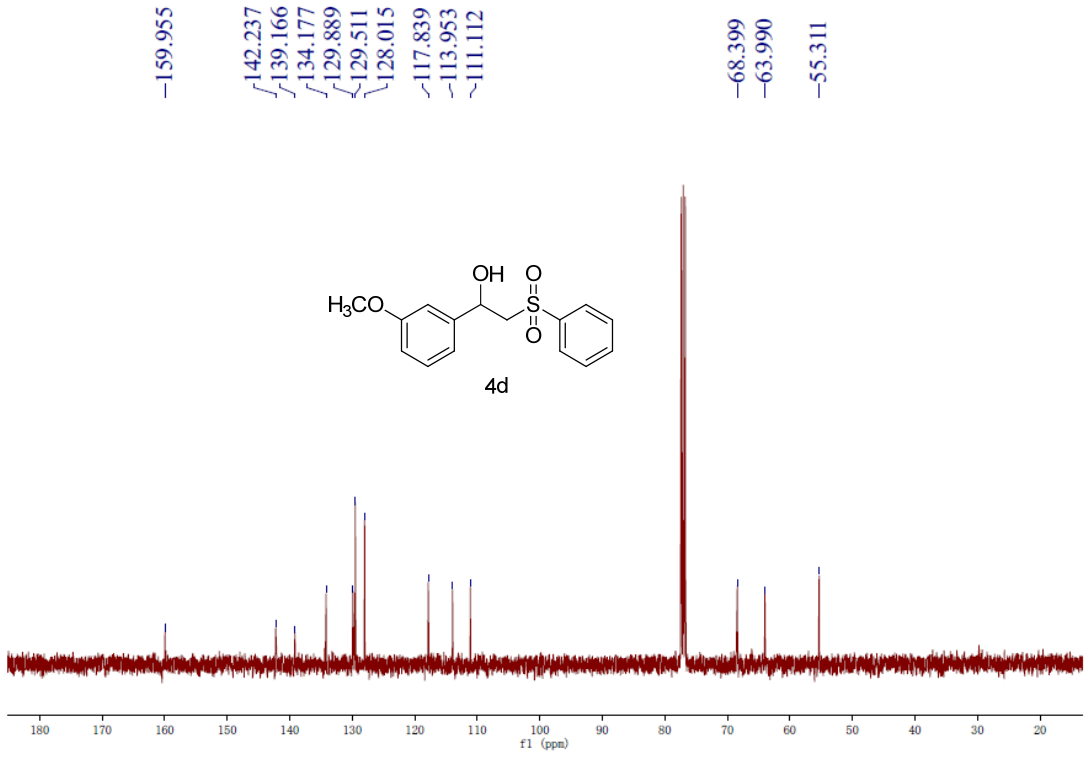


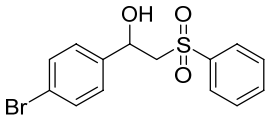

OH
O
H3CO
S
O

4d

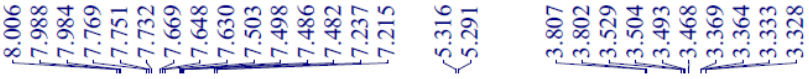

8.017
8.000
7.996
7.740
7.724
7.721
7.718
7.663
7.643
7.625
7.291
7.272
7.252
6.915
6.909
6.898
6.878
6.866
6.864
6.860
6.858
6.846
6.843
6.839
6.837
5.316
5.291
3.824
3.708
3.702
3.573
3.548
3.537
3.526
3.517
3.512
3.406
3.402
3.370
3.366

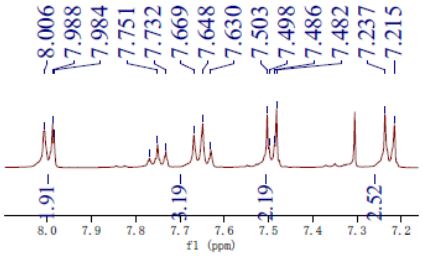

8.017
8.000
7.996
7.740
7.724
7.721
7.718
7.663
7.643
7.625
7.291
7.272
7.252
6.915
6.909
6.898
6.878
6.866
6.864
6.860
6.858
6.846
6.843
6.839
6.837
1.84
1.05
1.90
1.60
2.89
1.00
2.82
0.95
1.55
1.01
f1 (ppm)
OH
O
H3CO
S
O
4d

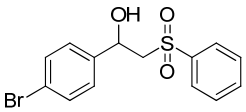

159.955
142.237
139.166
134.177
129.889
129.511
128.015
117.839
113.953
111.112
68.399
63.990
55.311
f1 (ppm)
OH
O
H3CO
S
O
4d


OH
O
S
O
Br

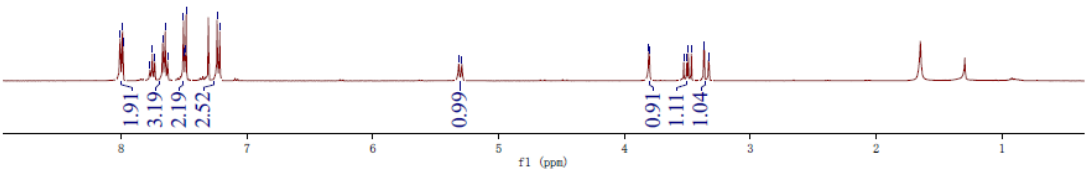
4e


8.006
7.988
7.984
7.769
7.751
7.732
7.669
7.648
7.630
7.503
7.498
7.486
7.482
7.237
7.215
5.316
5.291
3.807
3.802
3.529
3.504
3.493
3.468
3.369
3.364
3.333
3.328


8.006
7.988
7.984
7.751
7.732
7.669
7.648
7.630
7.503
7.498
7.486
7.482
7.237
7.215
1.91
3.19
2.19
2.52
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)


OH
O
S
O
Br

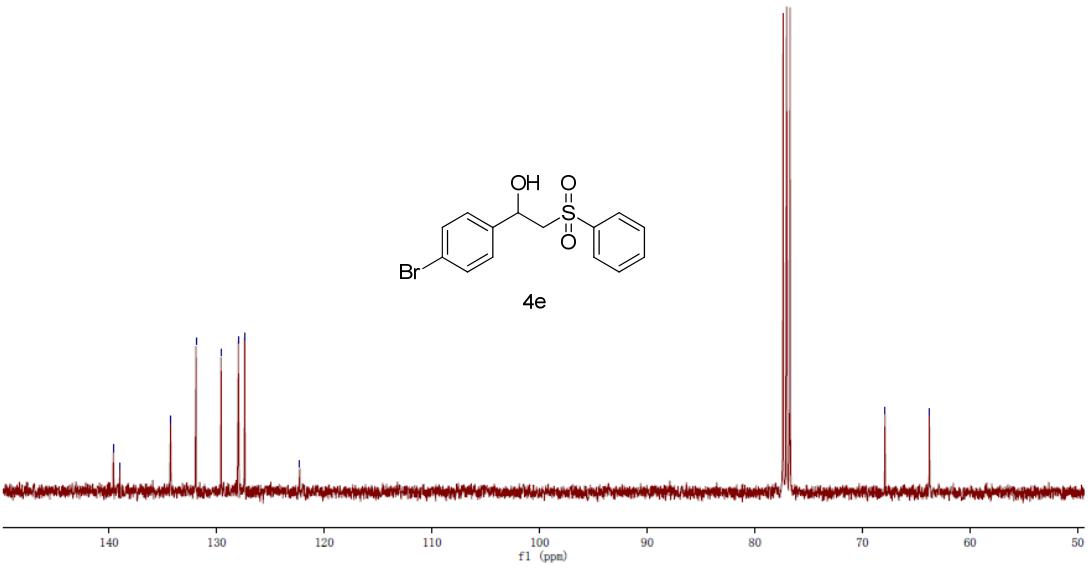
4e

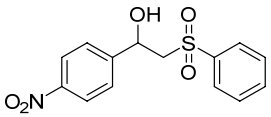

1.91
3.19
2.19
2.52
0.99
0.91
1.11
1.04
8
7
6
5
4
3
2
1
f1 (ppm)


139.61
139.01
134.29
131.92
129.59
127.99
127.40
122.28
67.90
63.78

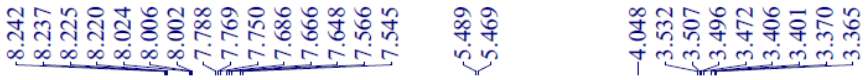
OH
O
S
O
Br

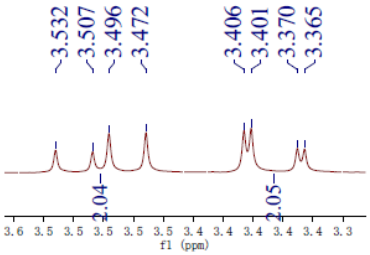
4e

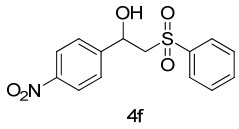

140
130
120
110
100
90
80
70
60
50
f1 (ppm)


OH
O
S
O
O_2N

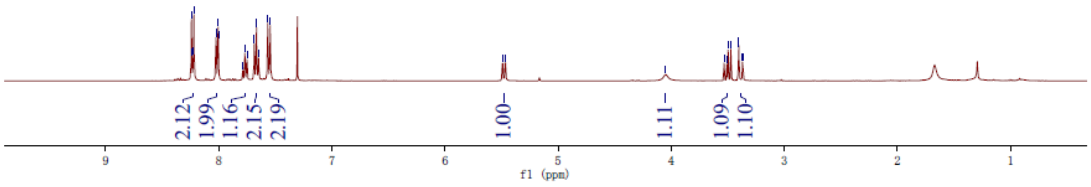
4f

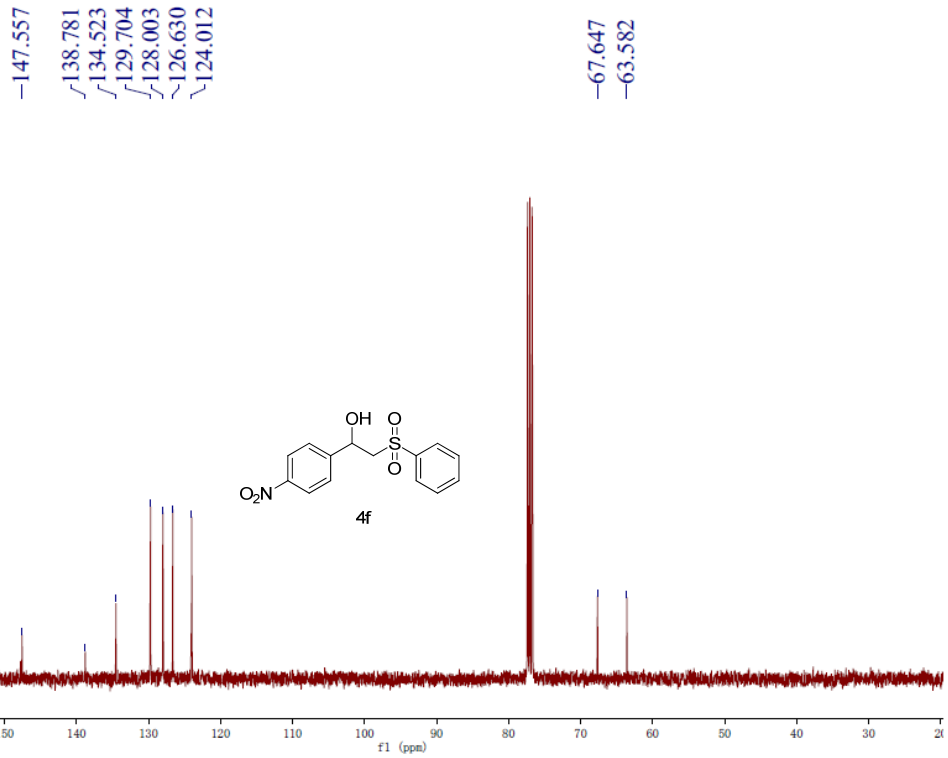

8.242
8.237
8.225
8.220
8.024
8.006
8.002
7.788
7.769
7.750
7.686
7.666
7.648
7.566
7.545
5.489
5.469
4.048
3.532
3.507
3.496
3.472
3.406
3.401
3.370
3.365

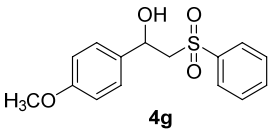

3.532
3.507
3.496
3.472
3.406
3.401
3.370
3.365
2.04
2.05
3.6 3.5 3.5 3.5 3.5 3.5 3.4 3.4 3.4 3.4 3.4 3.3
f1 (ppm)


OH
O
S
O
O_2N

4f

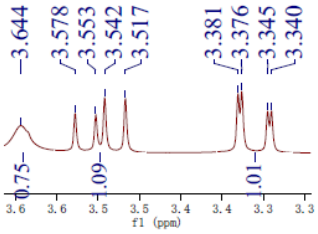

2.12
1.99
1.16
2.15
2.19
1.00
1.11
1.09
1.10
9 8 7 6 5 4 3 2 1
f1 (ppm)


147.557
138.781
134.523
129.704
128.003
126.630
124.012
67.647
63.582
OH
O
S
O
O_2N
4f
160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)

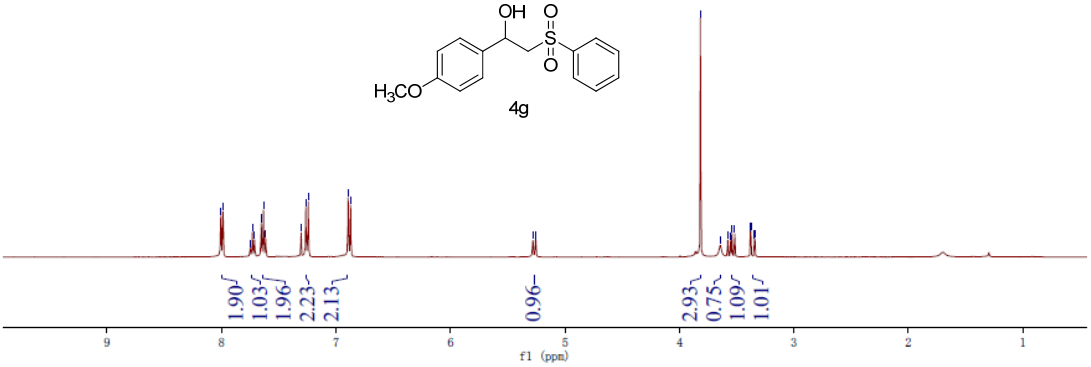


4g

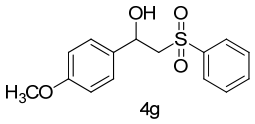
8.006
7.988
7.749
7.730
7.712
7.653
7.633
7.614
7.304
7.264
7.242
6.894
6.872
5.280
5.258
3.817
3.644
3.578
3.553
3.542
3.517
3.381
3.376
3.345
3.340



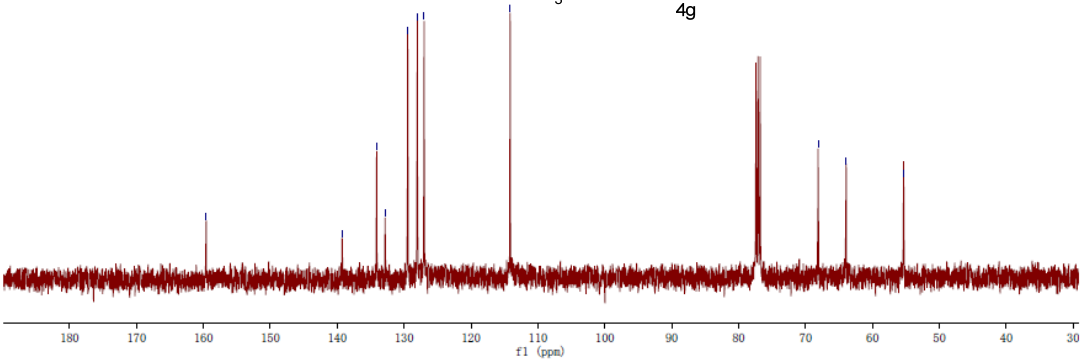
4g

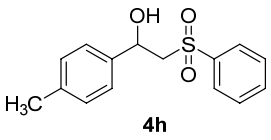


159.589
139.261
134.104
132.848
129.472
128.010
127.014
114.149
68.125
63.927
55.351



4g

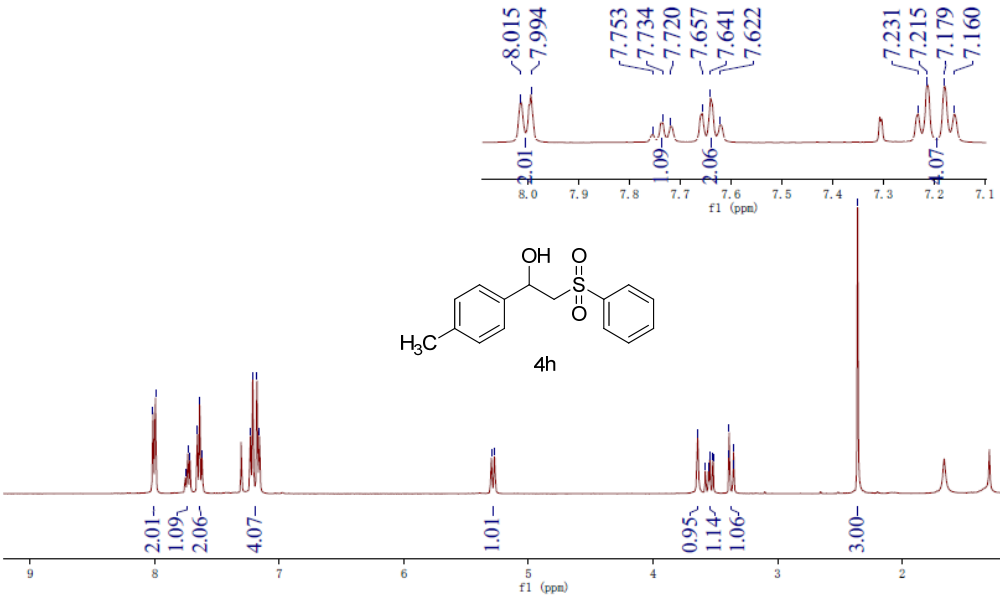




4h

8.015
7.994
7.753
7.734
7.720
7.657
7.641
7.622
7.231
7.215
7.179
7.160

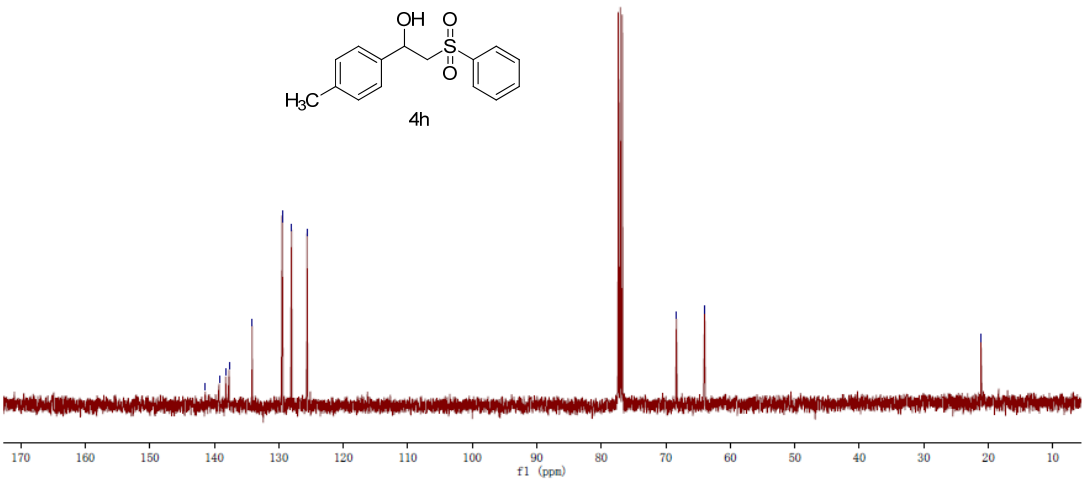
5.298
5.273
3.641
3.581
3.556
3.552
3.545
3.542
3.520
3.516
3.393
3.389
3.357
3.353
2.358

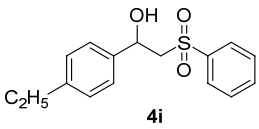


141.407
139.240
138.233
137.699
134.114
129.483
129.450
128.018
125.613

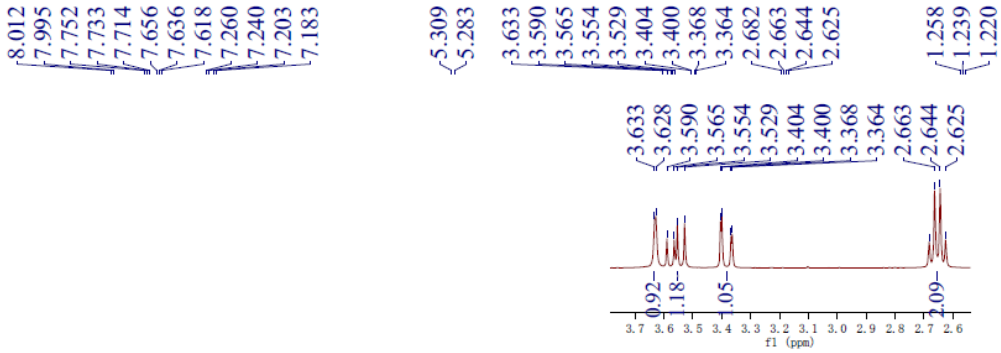
68.352
63.974

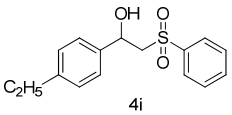
21.143



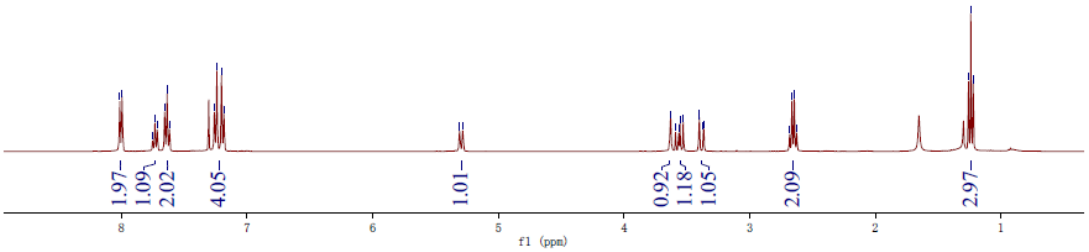

OH
O
S
O
C_2H_5

4i

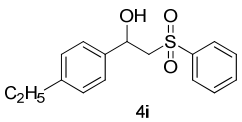

8.012
7.995
7.752
7.733
7.714
7.656
7.636
7.618
7.260
7.240
7.203
7.183
5.309
5.283
3.633
3.590
3.565
3.554
3.529
3.404
3.400
3.368
3.364
2.682
2.663
2.644
2.625
1.258
1.239
1.220
3.633
3.628
3.590
3.565
3.554
3.529
3.404
3.400
3.368
3.364
2.663
2.644
2.625
0.92
1.18
1.05
2.09
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6
f1 (ppm)


OH
O
S
O
C_2H_5

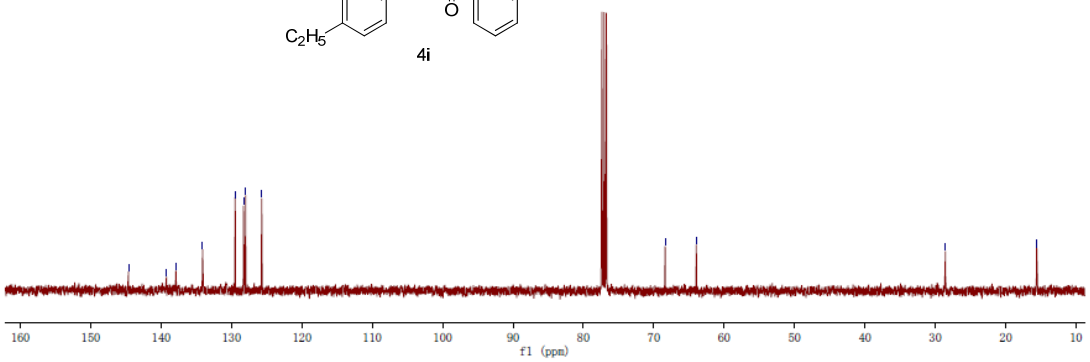
4i

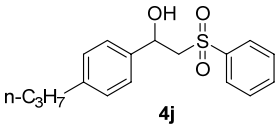

1.97
1.09
2.02
4.05
1.01
0.92
1.18
1.05
2.09
2.97
8
7
6
5
4
3
2
1
f1 (ppm)


144.632
139.251
137.898
134.107
129.476
128.292
128.012
125.705
68.378
63.950
28.560
15.594


OH
O
S
O
C_2H_5

4i


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



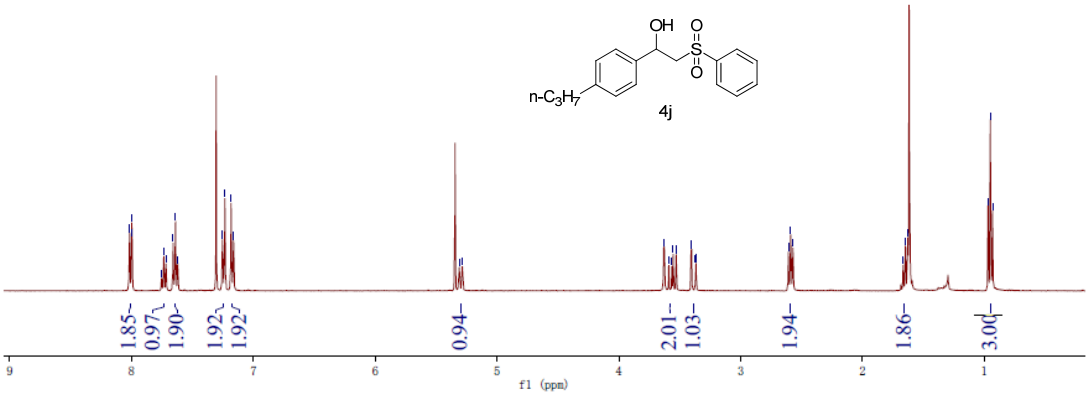
4j

8.016
7.999
7.995
7.754
7.735
7.717
7.659
7.639
7.621
7.254
7.234
7.182
7.162

5.310
5.284
3.631
3.626
3.590
3.565
3.554
3.529
3.406
3.402
3.370
3.366

2.608
2.589
2.569

1.666
1.647
1.628
0.968
0.950
0.931



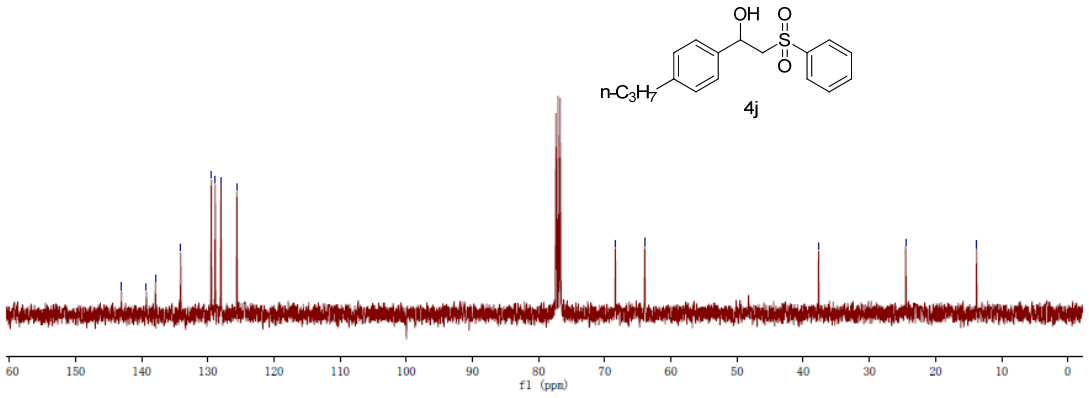
143.057
139.280
137.926
134.093
129.467
128.877
128.012
125.610

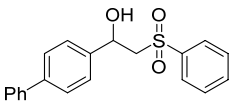
68.386
63.958

37.683

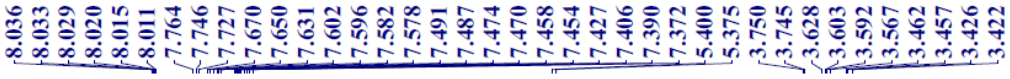
24.514

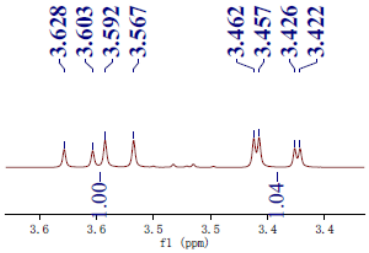
13.781

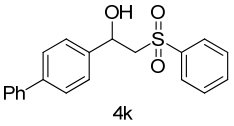



OH
O
S
O
Ph

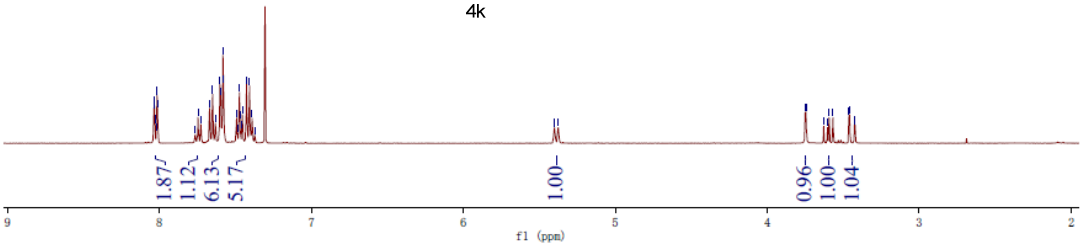
4k


8.036
8.033
8.029
8.020
8.015
8.011
7.764
7.746
7.727
7.670
7.650
7.631
7.602
7.596
7.582
7.578
7.491
7.487
7.474
7.470
7.458
7.454
7.427
7.406
7.390
7.372
5.400
5.375
3.750
3.745
3.628
3.603
3.592
3.567
3.462
3.457
3.426
3.422


3.628
3.603
3.592
3.567
3.462
3.457
3.426
3.422
1.00
1.04
3.6
3.6
3.5
3.5
3.4
3.4
f1 (ppm)

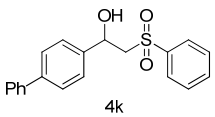

OH
O
S
O
Ph

4k

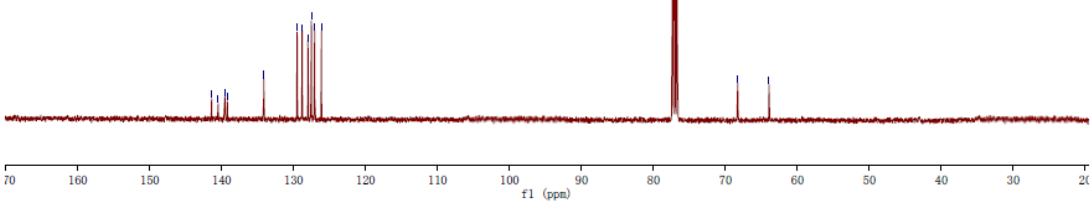

1.87
1.12
6.13
5.17
1.00
0.96
1.00
1.04
9
8
7
6
5
4
3
2
f1 (ppm)

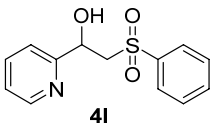

141.406
140.497
139.560
139.222
134.163
129.522
128.830
128.021
127.536
127.094
126.139


68.291
63.946


OH
O
S
O
Ph

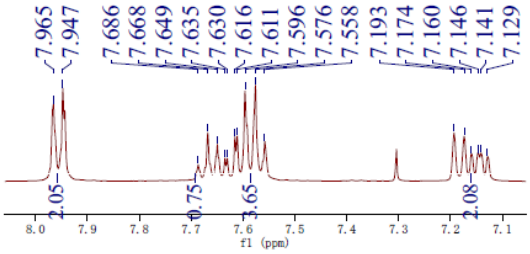
4k

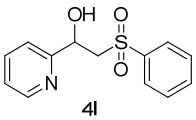

70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


OH
O
S
O
N

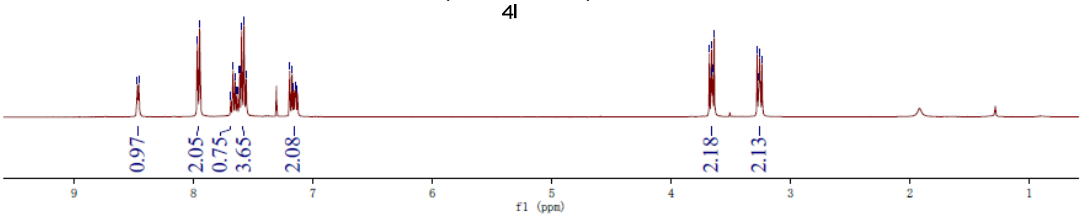
4l


8.469
8.457
7.965
7.947
7.686
7.668
7.649
7.635
7.630
7.616
7.611
7.596
7.576
7.558
7.193
7.174
7.160
7.146
7.141
7.129
3.679
3.665
3.659
3.652
3.639
3.279
3.266
3.258
3.239

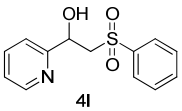

7.965
7.947
7.686
7.668
7.649
7.635
7.630
7.616
7.611
7.596
7.576
7.558
7.193
7.174
7.160
7.146
7.141
7.129
2.05
0.75
3.65
2.08
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)


OH
O
S
O
N

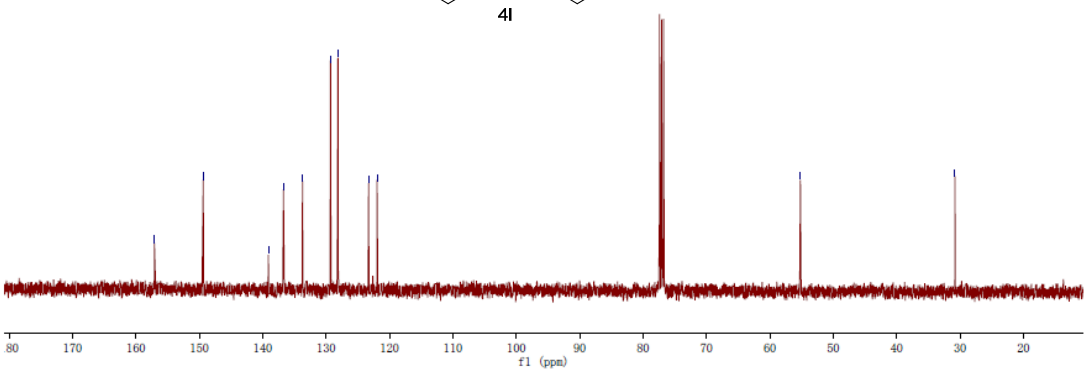
4l

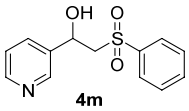

0.97
2.05
0.75
3.65
2.08
2.18
2.13
9
8
7
6
5
4
3
2
1
f1 (ppm)


157.081
149.385
139.091
136.729
133.723
129.295
128.126
123.292
121.953
55.171
30.788


OH
O
S
O
N

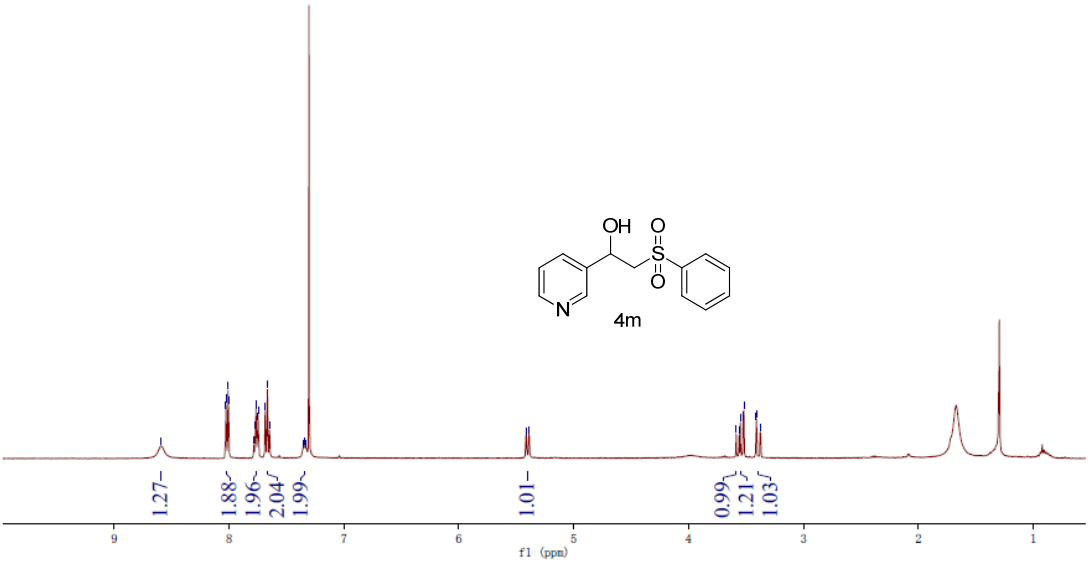
4l

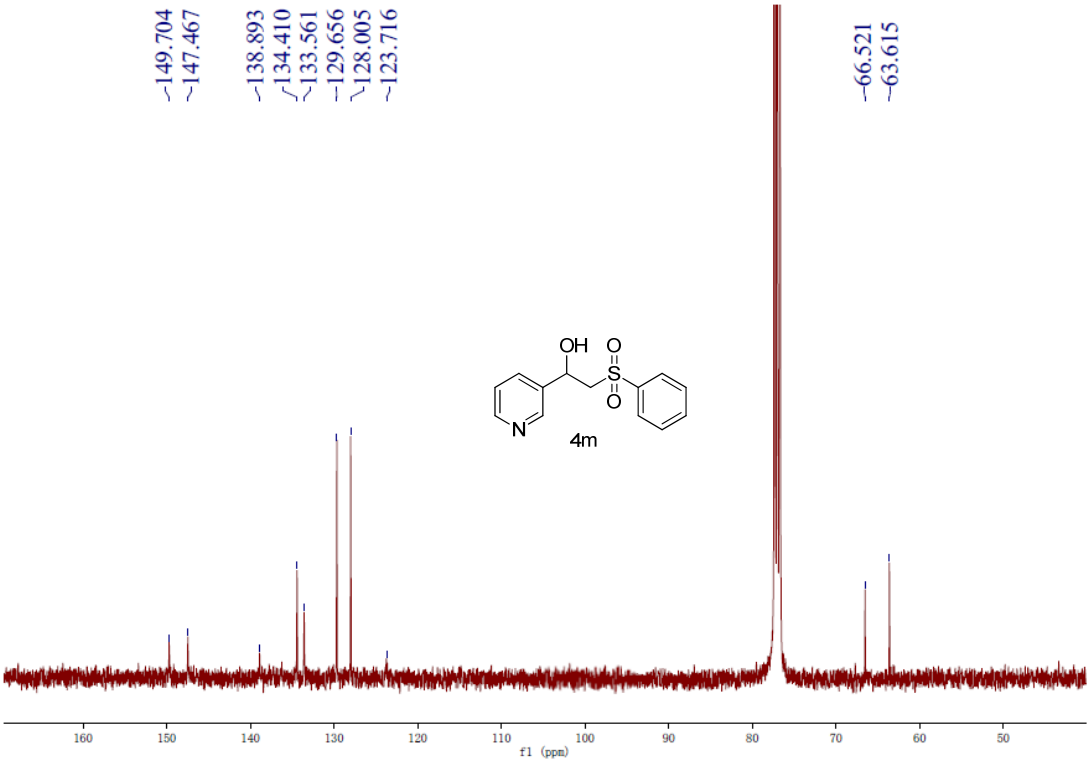

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

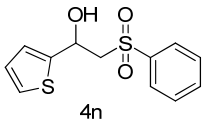

OH
O
S
O
N

4m


8.591
8.030
8.027
8.009
8.006
7.784
7.771
7.766
7.751
7.747
7.687
7.667
7.648
7.357
7.342
7.327
5.416
5.387
3.585
3.560
3.549
3.524
3.518
3.413
3.409
3.378
3.373

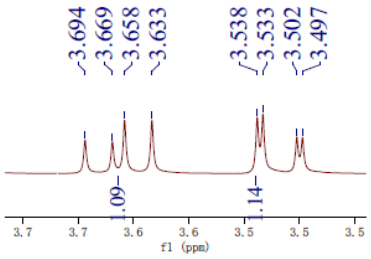

OH
O
S
O
N
4m
1.27
1.88
1.96
2.04
1.99
1.01
0.99
1.21
1.03
f1 (ppm)

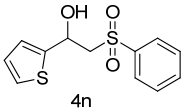

149.704
147.467
138.893
134.410
133.561
129.656
128.005
123.716
66.521
63.615
OH
O
S
O
N
4m
f1 (ppm)


OH
O
S
O
S

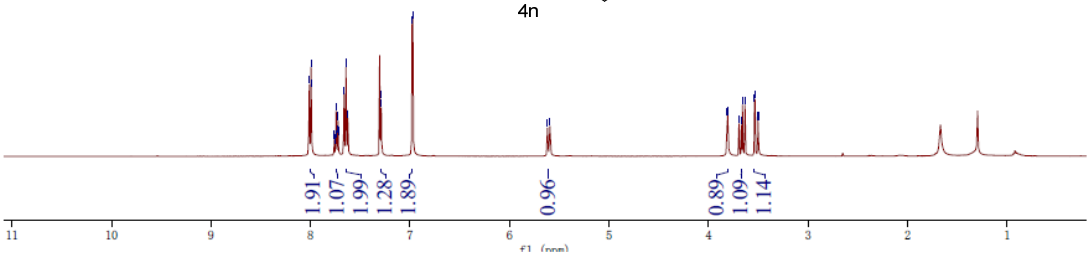
4n


8.012
7.994
7.990
7.760
7.757
7.747
7.742
7.737
7.726
7.723
7.720
7.663
7.643
7.625
7.296
7.288
6.980
6.971
5.618
5.594
3.812
3.806
3.694
3.669
3.658
3.633
3.538
3.533
3.502
3.497

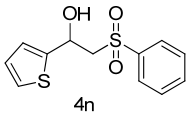

3.694
3.669
3.658
3.633
3.538
3.533
3.502
3.497
1.09
1.14
3.7
3.7
3.6
3.6
3.5
3.5
3.5
f1 (ppm)


OH
O
S
O
S

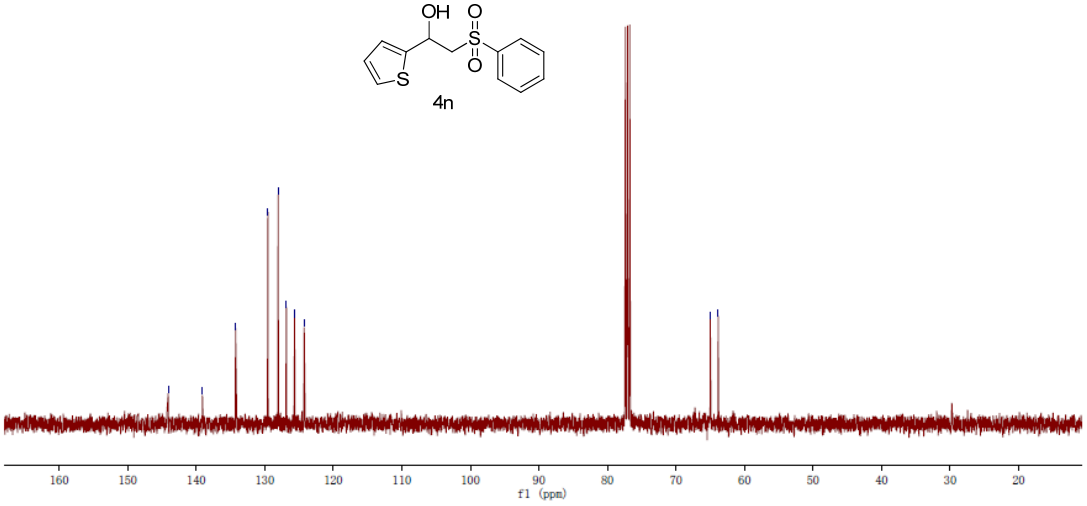
4n

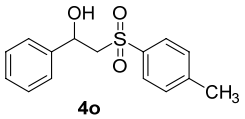

1.91
1.07
1.99
1.28
1.89
0.96
0.89
1.09
1.14
11
10
9
8
7
6
5
4
3
2
1


144.084
139.094
134.254
129.543
128.053
126.846
125.638
124.245
64.987
63.829

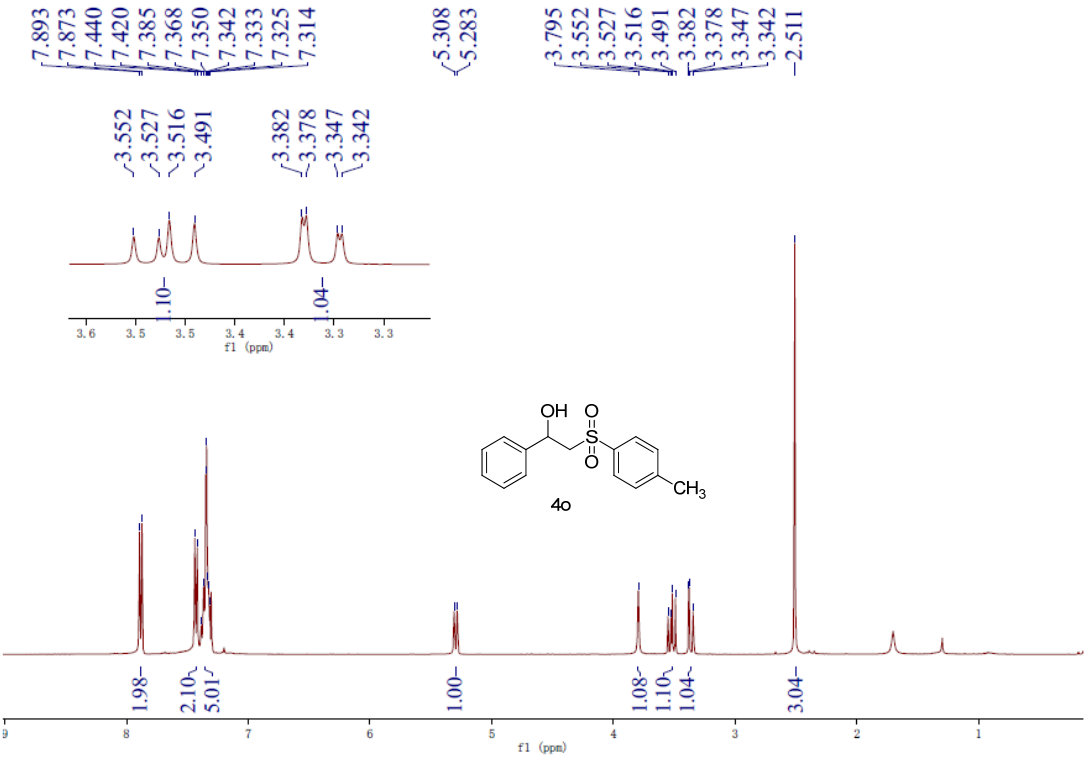

OH
O
S
O
S

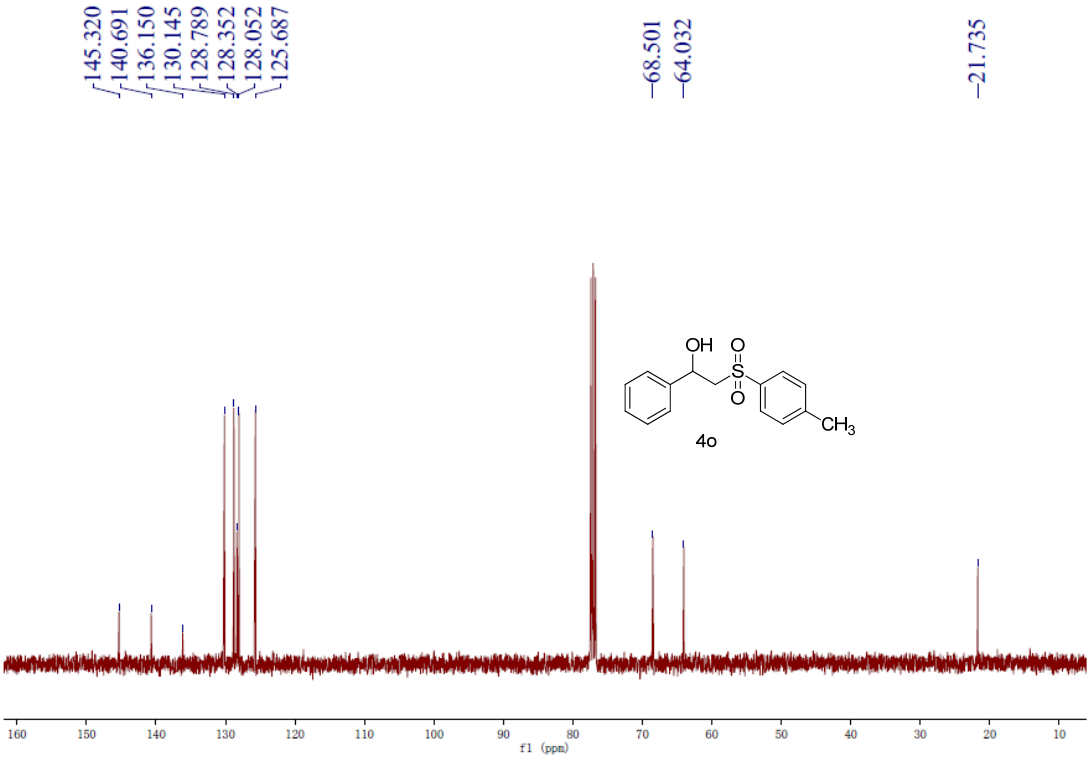
4n

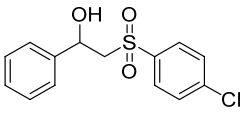

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


OH
O
S
O
CH3

4o

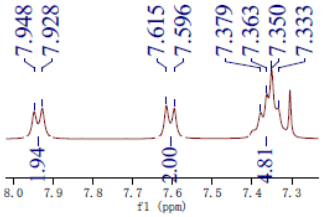

7.893
7.873
7.440
7.420
7.385
7.368
7.350
7.342
7.333
7.325
7.314
5.308
5.283
3.795
3.552
3.527
3.516
3.491
3.382
3.378
3.347
3.342
2.511
1.10
1.04
f1 (ppm)
OH
O
S
O
CH3
4o
1.98
2.10
5.01
1.00
1.08
1.10
1.04
3.04
f1 (ppm)

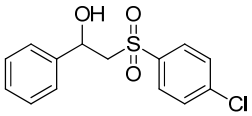

145.320
140.691
136.150
130.145
128.789
128.352
128.052
125.687
68.501
64.032
21.735
OH
O
S
O
CH3
4o
f1 (ppm)


OH
O
S
O
Cl

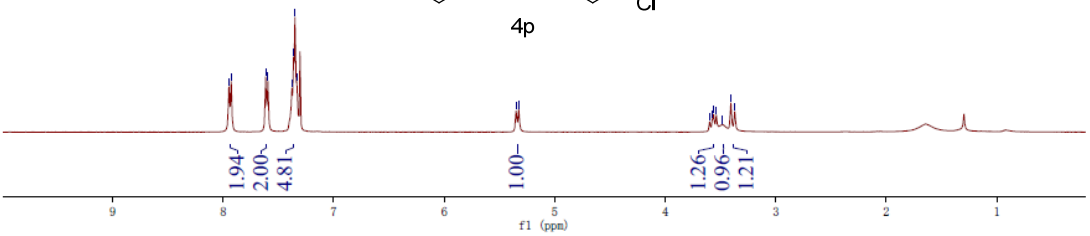
4p


7.948
7.928
7.615
7.596
7.379
7.363
7.350
7.333
5.349
5.325
3.598
3.573
3.562
3.537
3.479
3.406
3.370


7.948
7.928
7.615
7.596
7.379
7.363
7.350
7.333
1.94
2.00
4.81
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)


OH
O
S
O
Cl

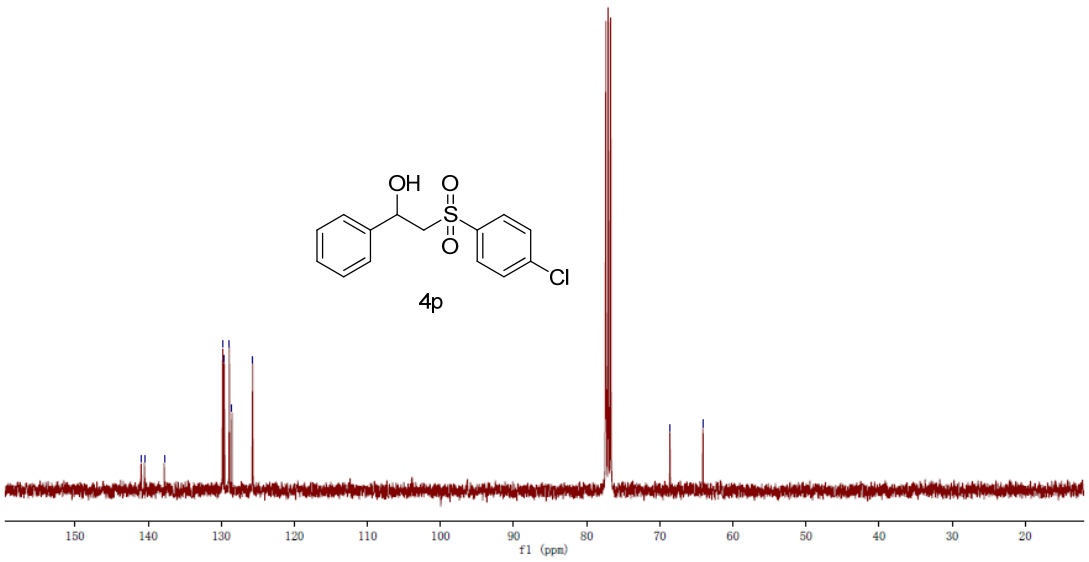
4p

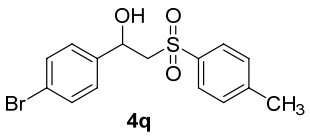

1.94
2.00
4.81
1.00
1.26
0.96
1.21
9
8
7
6
5
4
3
2
1
f1 (ppm)


140.956
140.510
137.803
129.803
129.598
128.892
128.538
125.691
68.630
64.089

OH
O
S
O
Cl

4p


150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



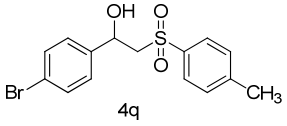
4q

7.878
7.857
7.500
7.479
7.445
7.425
7.231
7.210

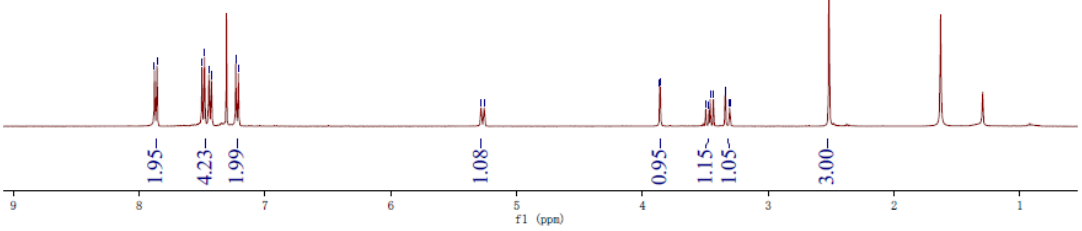
5.282
5.257

3.862
3.857
3.496
3.471
3.460
3.435
3.343
3.339
3.307
3.303

2.517



4q

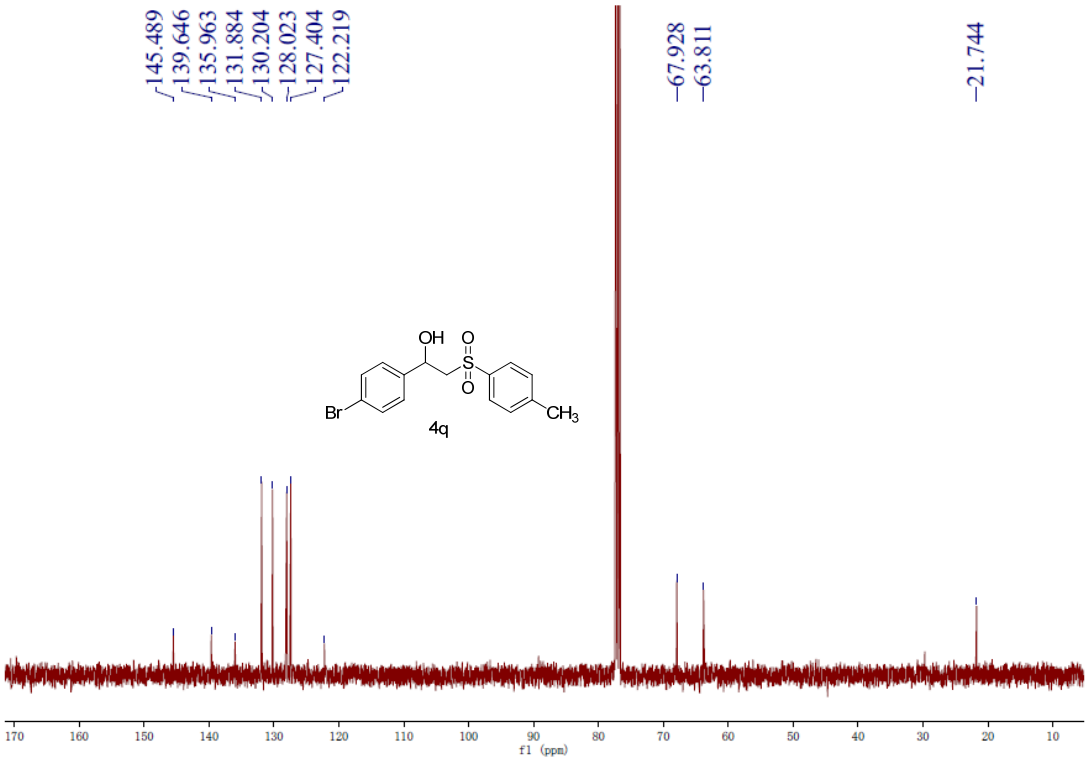


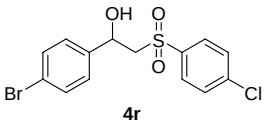
145.489
139.646
135.963
131.884
130.204
128.023
127.404
122.219

67.928
63.811

21.744

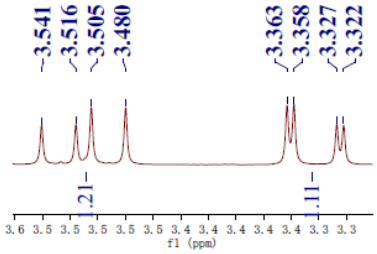
4q

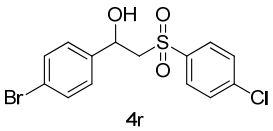



OH
O
S
O
Br
Cl

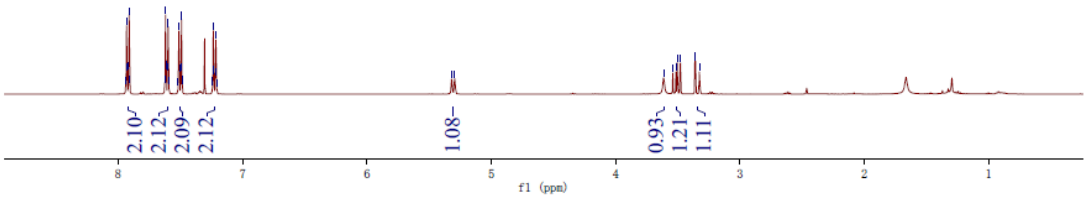
4r

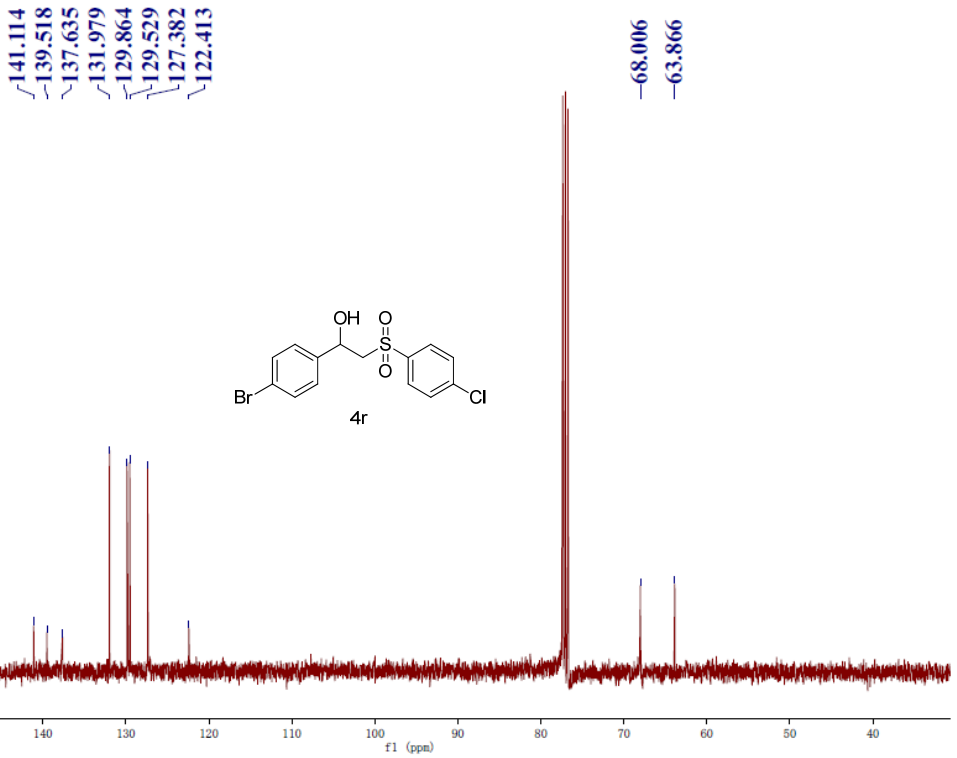

7.939
7.933
7.928
7.916
7.911
7.905
7.626
7.620
7.615
7.603
7.598
7.592
7.517
7.511
7.506
7.495
7.490
7.483
7.242
7.235
7.230
7.219
7.214
7.207
5.317
5.293
3.614
3.541
3.516
3.505
3.480
3.363
3.358
3.327
3.322

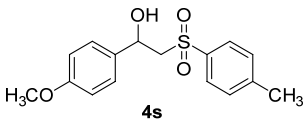

3.541
3.516
3.505
3.480
3.363
3.358
3.327
3.322
1.21
1.11
3.6 3.5 3.5 3.5 3.5 3.5 3.4 3.4 3.4 3.4 3.4 3.3 3.3
f1 (ppm)


OH
O
S
O
Br
Cl

4r

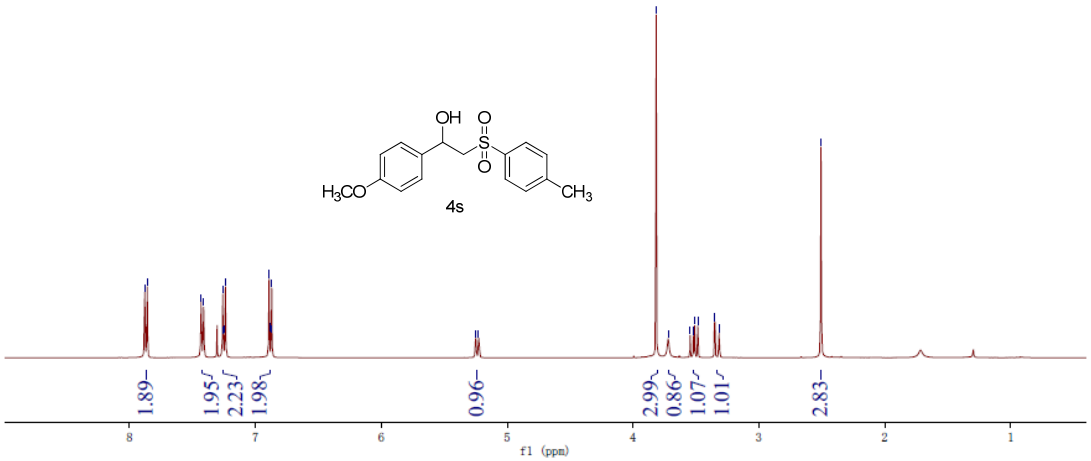

2.10
2.12
2.09
2.12
1.08
0.93
1.21
1.11
8
7
6
5
4
3
2
1
f1 (ppm)


141.114
139.518
137.635
131.979
129.864
129.529
127.382
122.413
68.006
63.866
OH
O
S
O
Br
Cl
4r
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

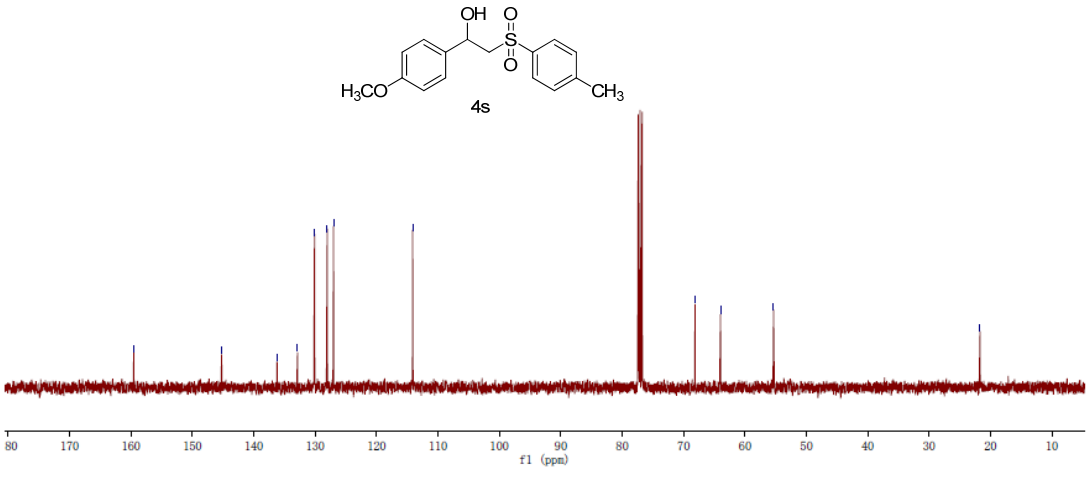


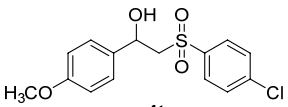
4s

7.880
7.859
7.431
7.411
7.260
7.255
7.244
7.238
6.892
6.887
6.875
6.870
5.247
5.226
3.816
3.720
3.546
3.520
3.510
3.485
3.353
3.348
3.317
3.312
2.506



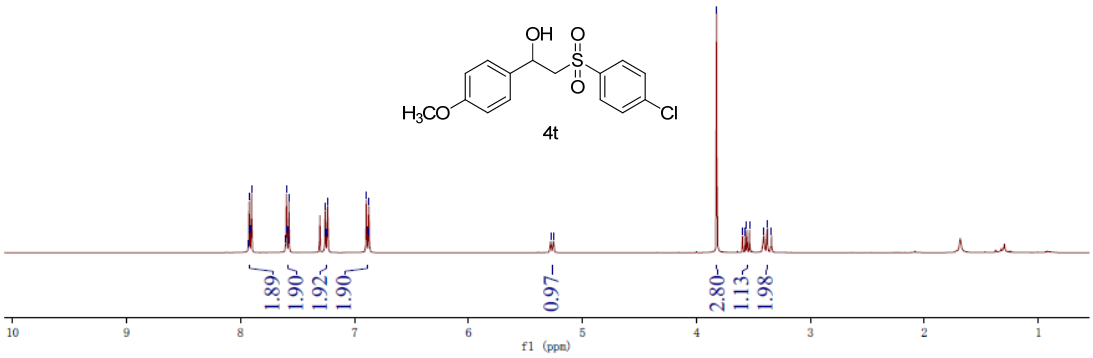
159.564
145.248
136.212
132.875
130.111
128.043
127.007
114.123
68.136
63.987
55.340
21.725





4t

7.933
7.925
7.921
7.909
7.904
7.604
7.598
7.593
7.582
7.577
7.570
7.258
7.253
7.242
7.237
6.896
6.891
6.879
6.874
5.280
5.255
3.823
3.595
3.570
3.559
3.534
3.409
3.382
3.377
3.346
3.341



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132.690
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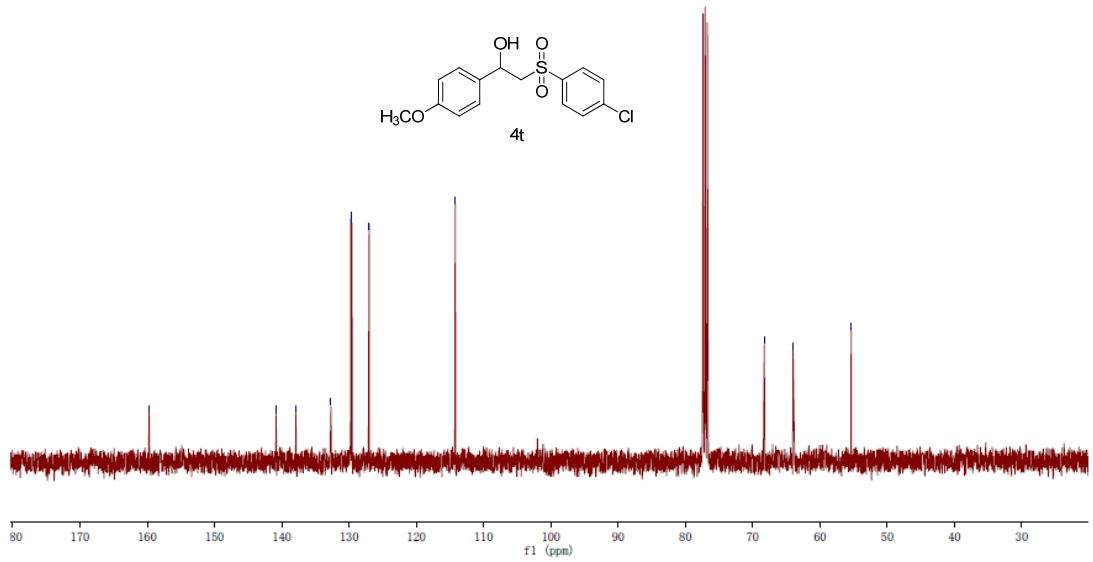
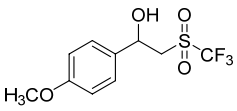
129.569
127.015
114.212
68.271
64.003
55.352





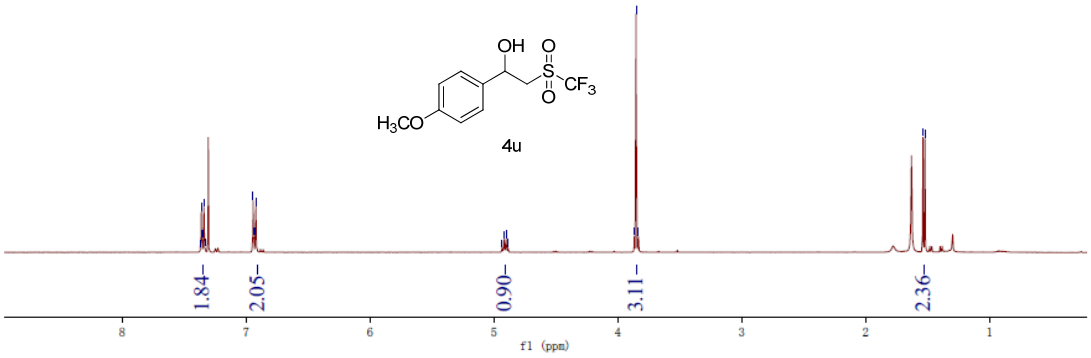
4u

7.369
7.362
7.356
7.345
7.340
7.332
6.943
6.937
6.926
6.921

4.933
4.917
4.901
4.885

3.866
3.852
3.832

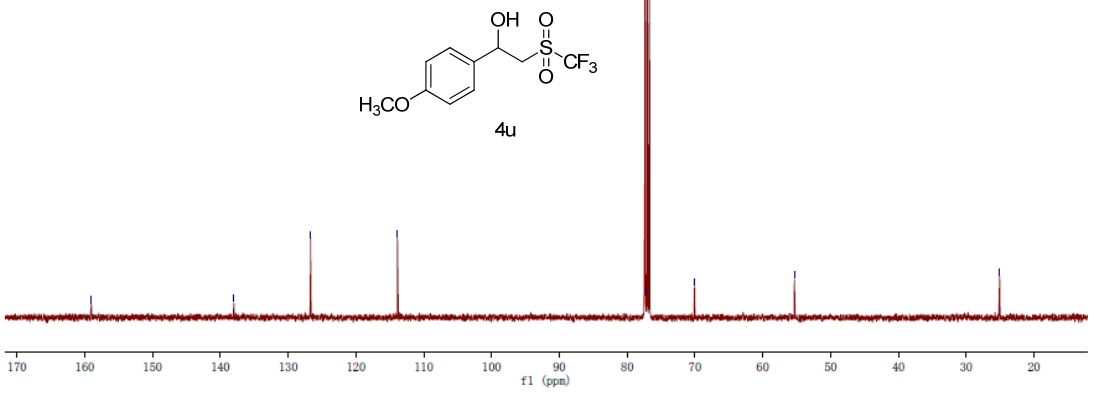
1.536
1.520



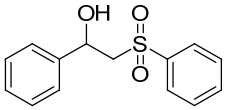
159.017
137.990
126.686
113.873

77.241
70.043
55.330

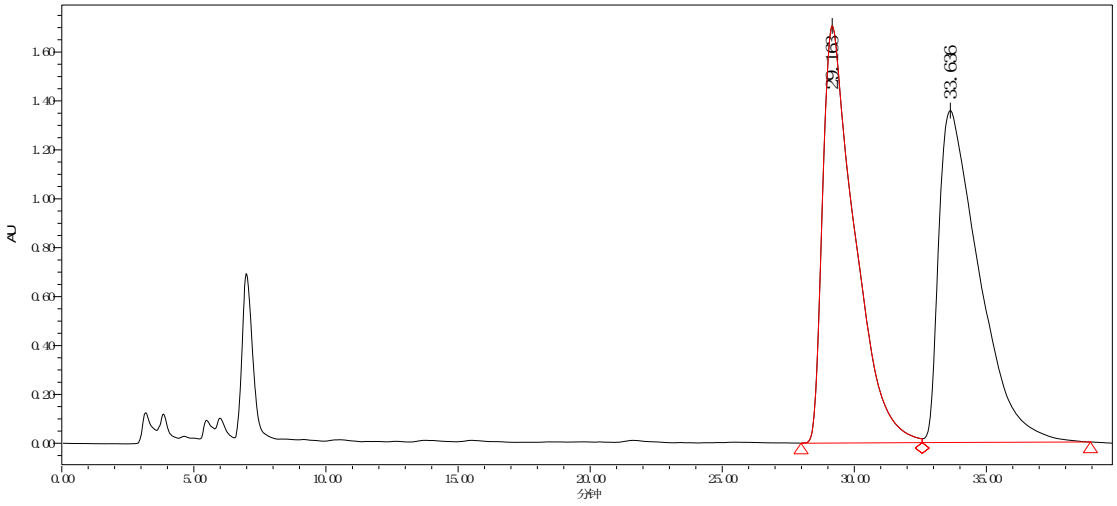
25.049



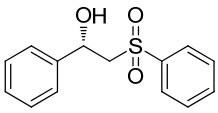
7. HPLC spectra of the products



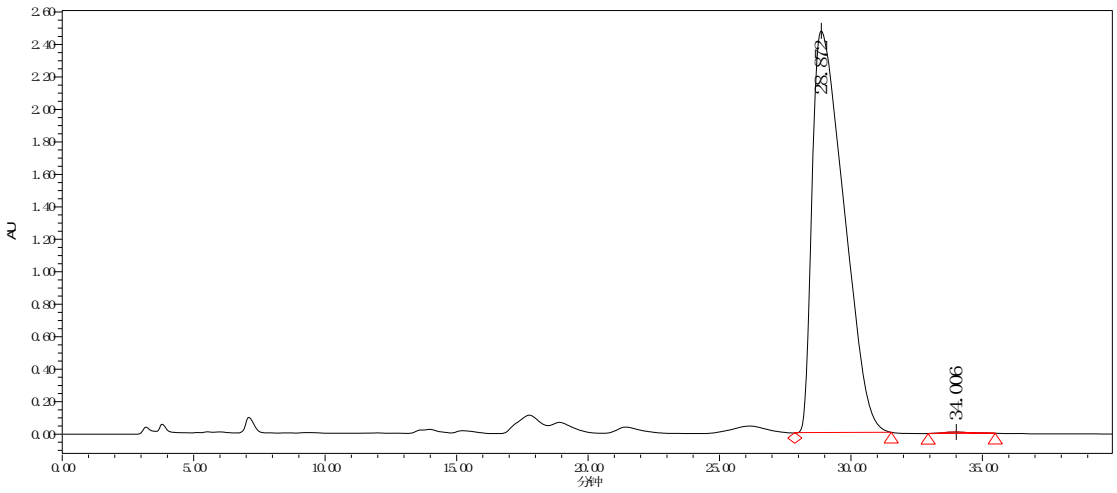
Racemate-**4a**



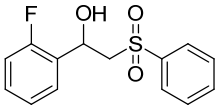
Peak	Ret Time [min]	% Area	ee value (%)
1	29.163	50.13	0
2	33.636	49.87	



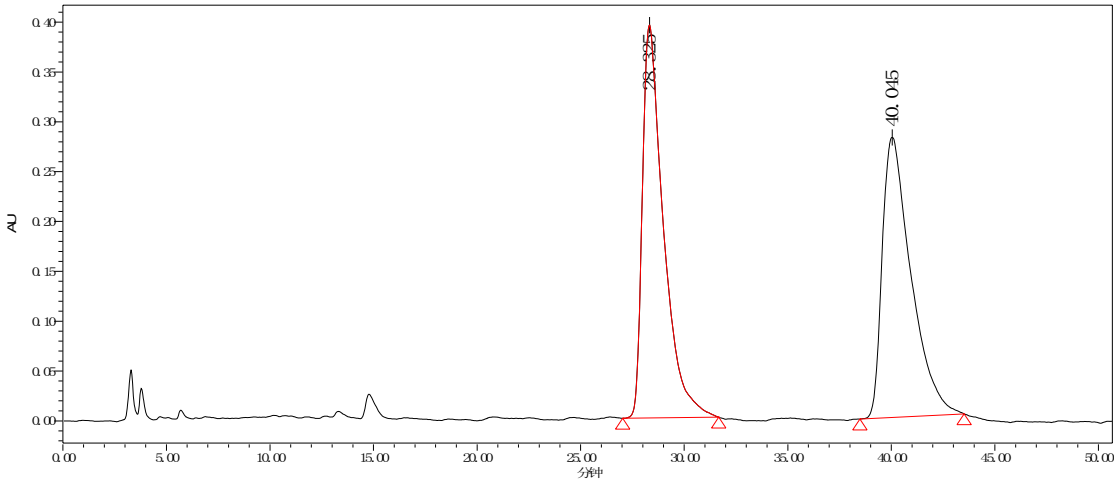
(*S*)-**4a**



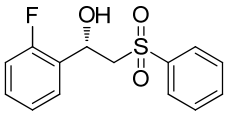
Peak	Ret Time [min]	% Area	ee value(%)
1	28.872	99.81	99.6
2	34.006	0.19	



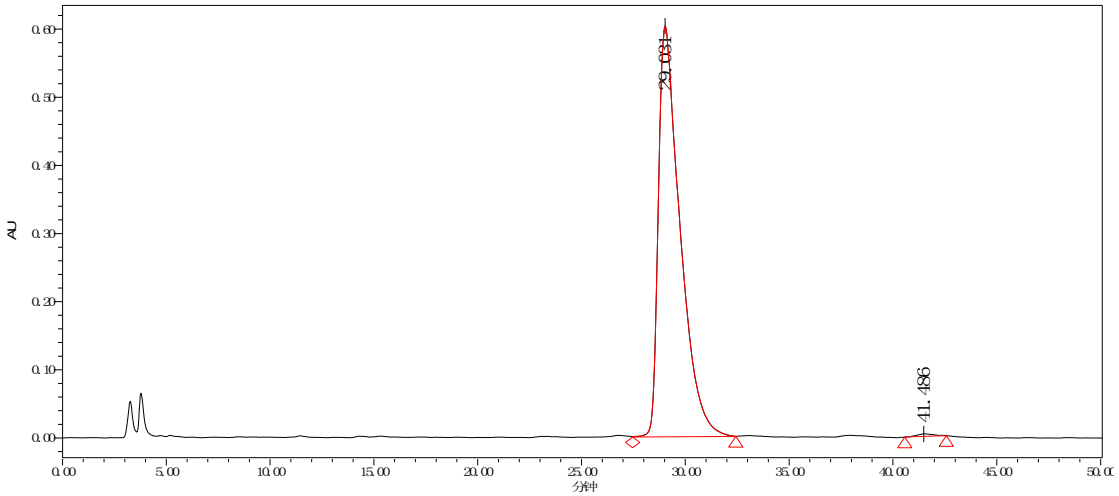
Racemate-**4b**



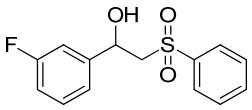
Peak	Ret Time [min]	% Area	ee value(%)
1	28.325	50.23	0
2	40.045	49.77	



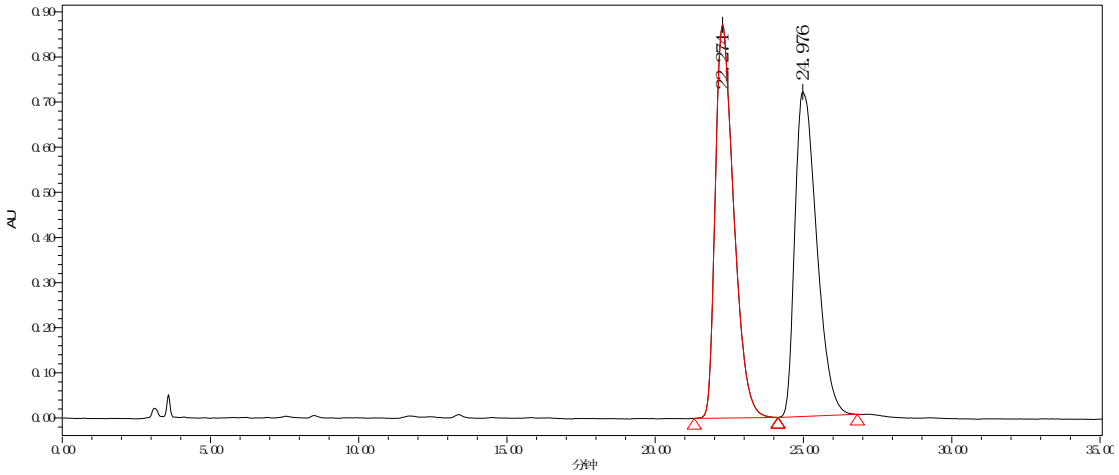
(*S*)-**4b**



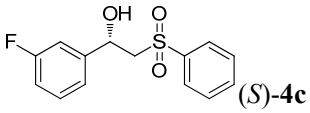
Peak	Ret Time [min]	% Area	ee value(%)
1	29.031	99.90	99.8
2	41.486	0.10	



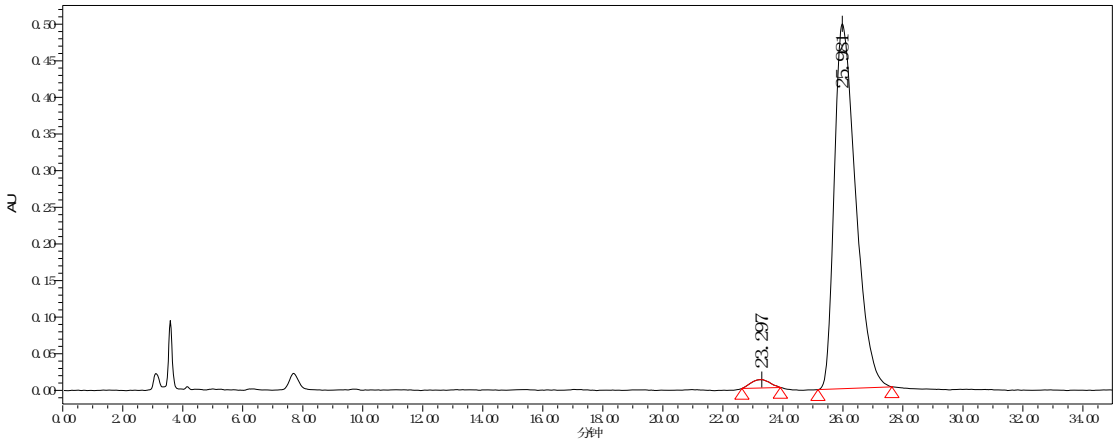
Racemate-**4c**



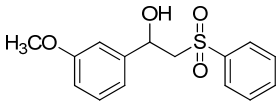
Peak	Ret Time [min]	% Area	ee value(%)
1	22.274	50.36	0
2	24.976	49.64	



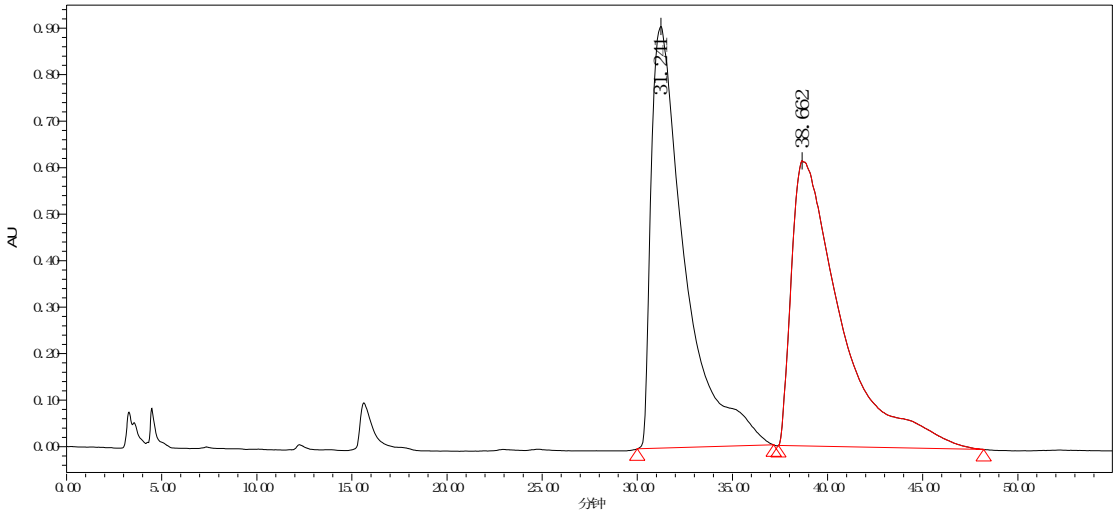
(*S*)-**4c**



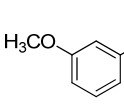
Peak	Ret Time [min]	% Area	ee value(%)
1	23.297	1.47	97.1
2	25.981	98.53	



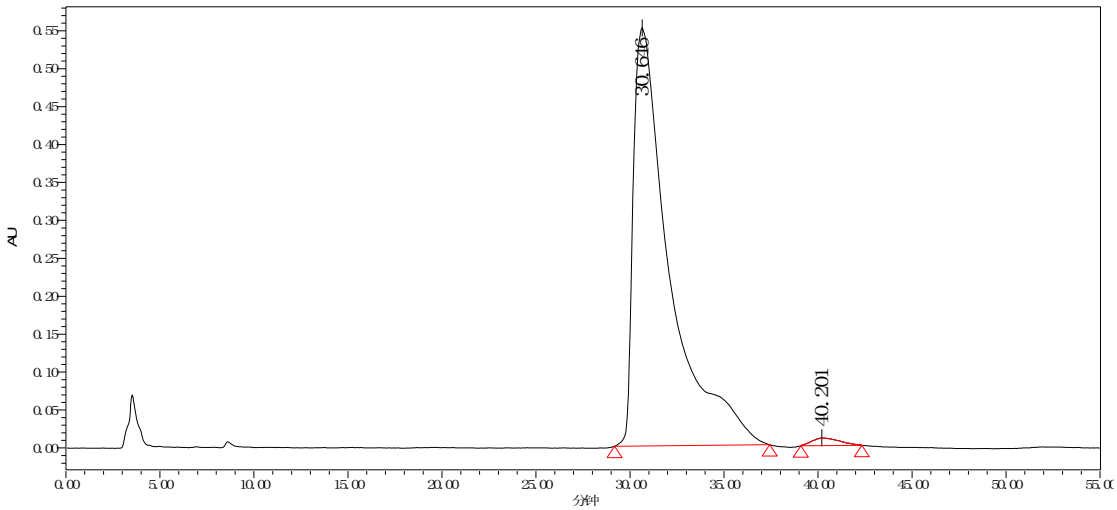
Racemate-**4d**



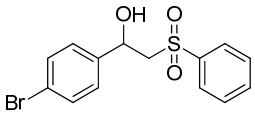
Peak	Ret Time [min]	% Area	ee value(%)
1	31.241	50.67	0
2	38.662	49.33	



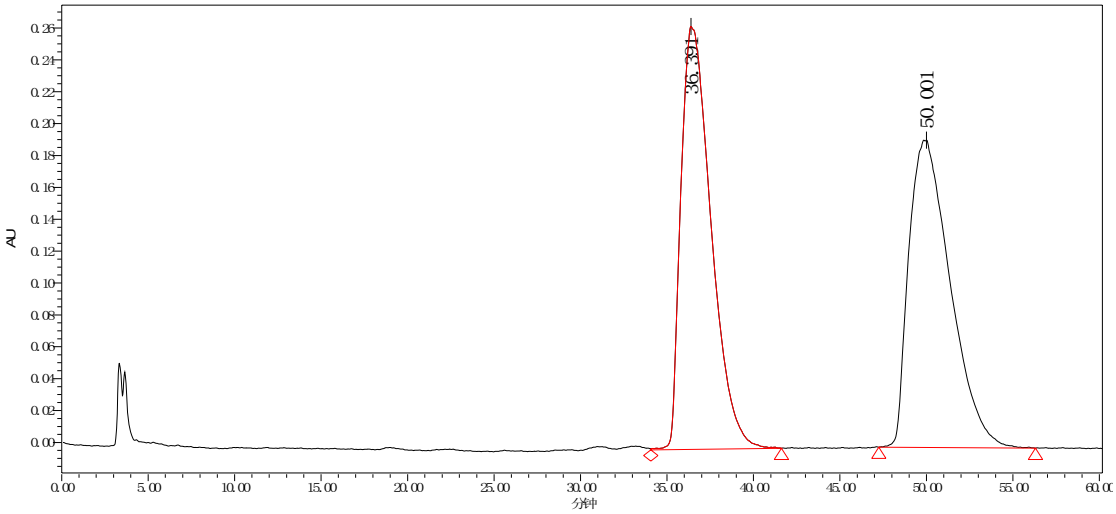
(*S*)-**4d**



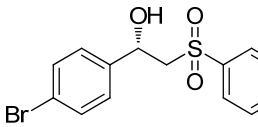
Peak	Ret Time [min]	% Area	ee value(%)
1	30.646	98.74	97.5
2	40.201	1.26	



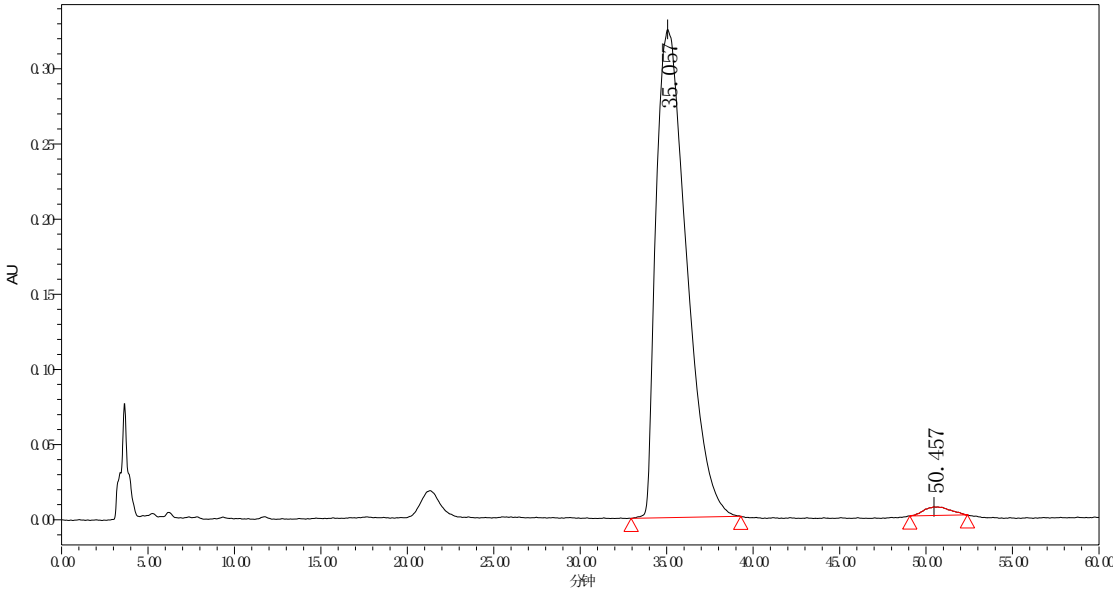
Racemate-**4e**



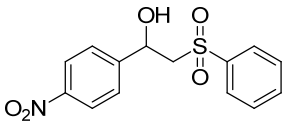
Peak	Ret Time [min]	% Area	ee value(%)
1	36.391	50.06	0
2	50.001	49.94	



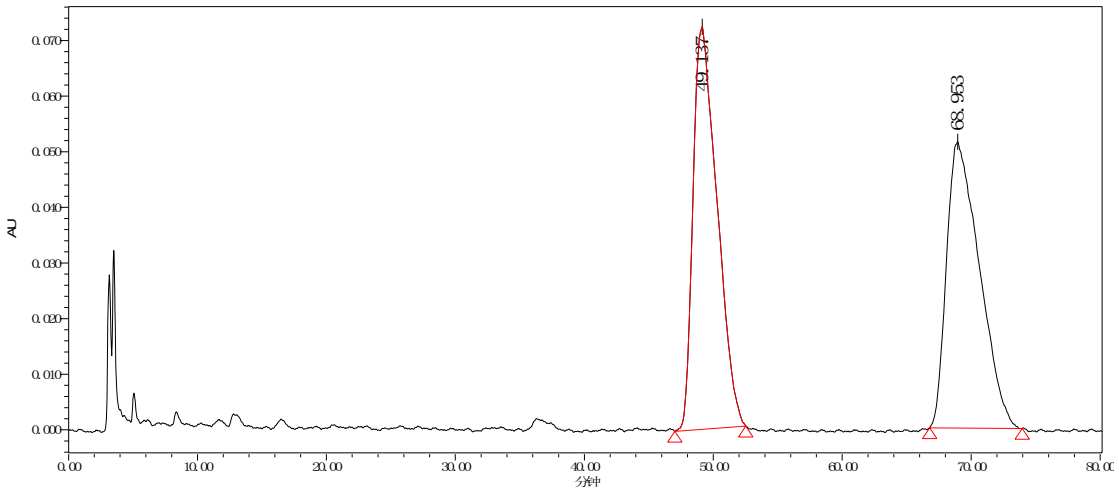
(*S*)-**4e**



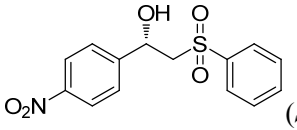
Peak	Ret Time [min]	% Area	ee value(%)
1	35.057	98.92	97.8
2	50.457	1.08	



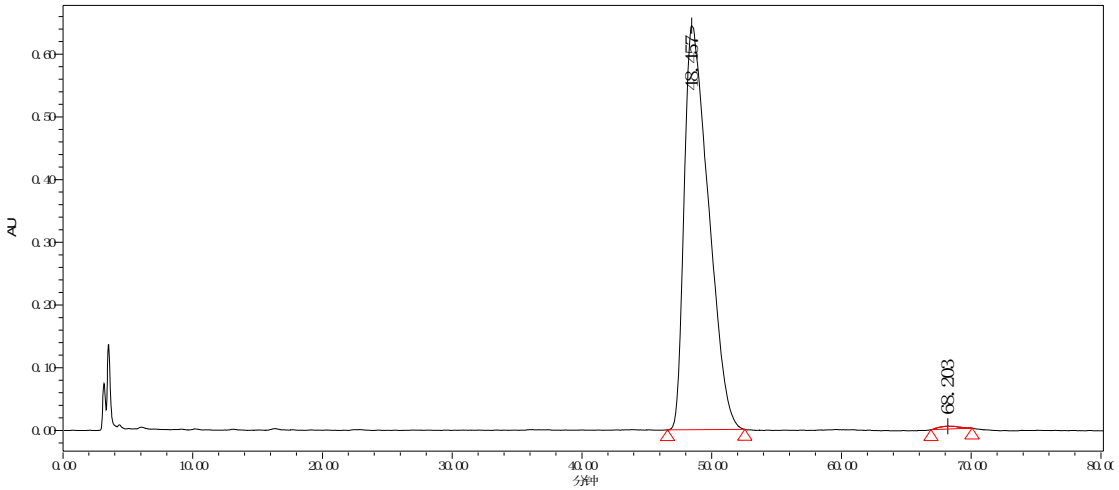
Racemate-**4f**



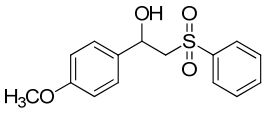
Peak	Ret Time [min]	% Area	ee value(%)
1	49.137	50.44	0
2	68.953	49.56	



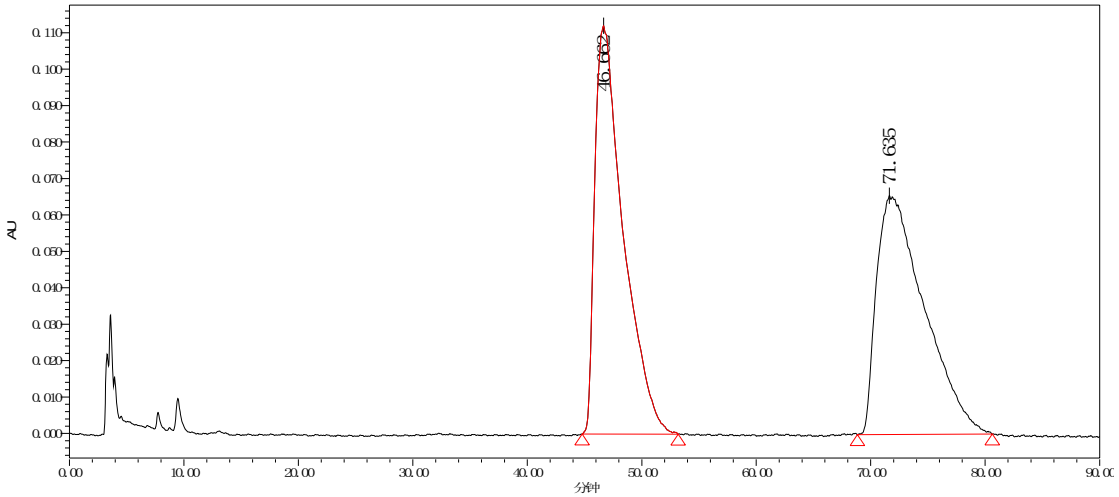
(*S*)-**4f**



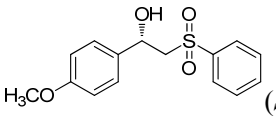
Peak	Ret Time [min]	% Area	ee value(%)
1	48.457	99.52	99.0
2	68.203	0.48	



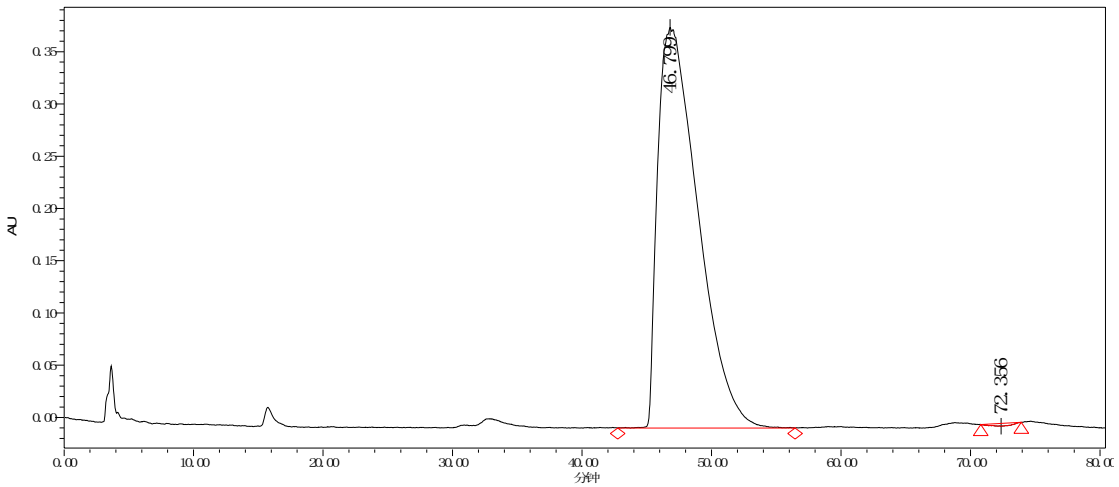
Racemate-**4g**



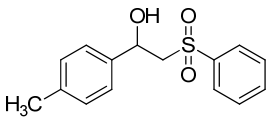
Peak	Ret Time [min]	% Area	ee value(%)
1	46.662	50.22	0
2	71.635	49.78	



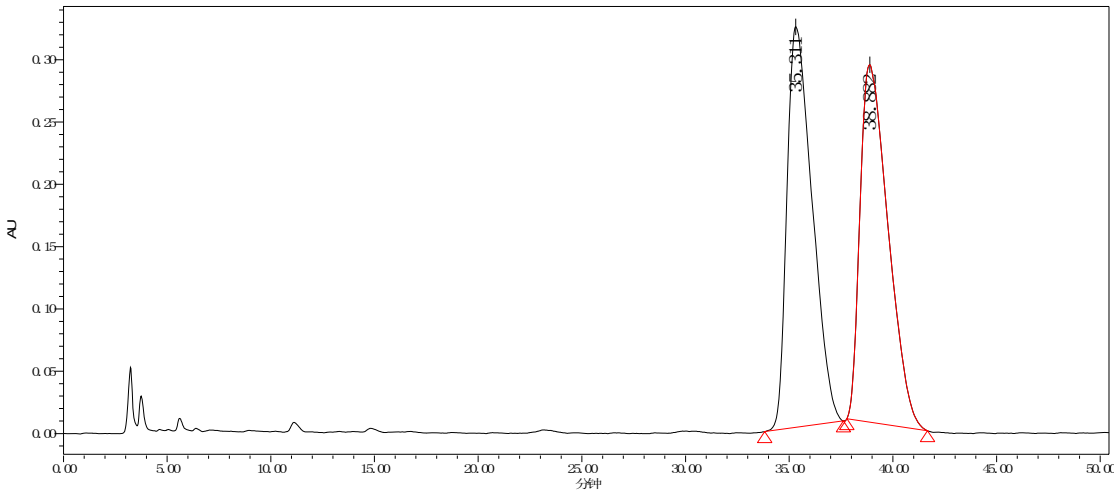
(*S*)-**4g**



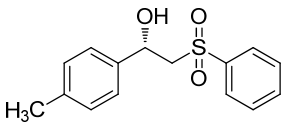
Peak	Ret Time [min]	% Area	ee value(%)
1	46.799	99.68	99.3
2	72.356	0.32	



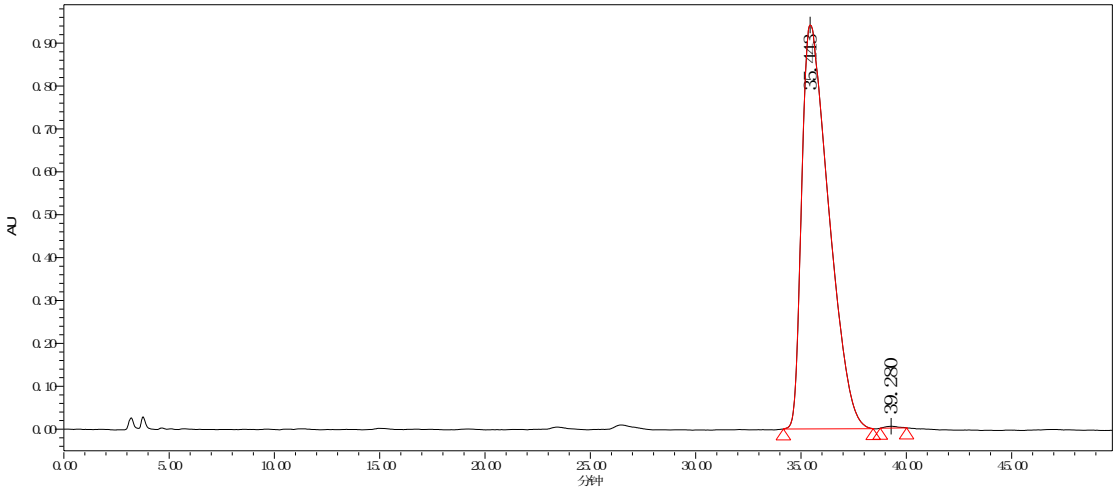
Racemate-**4h**



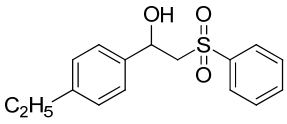
Peak	Ret Time [min]	% Area	ee value(%)
1	35.311	50.02	0
2	38.882	49.98	



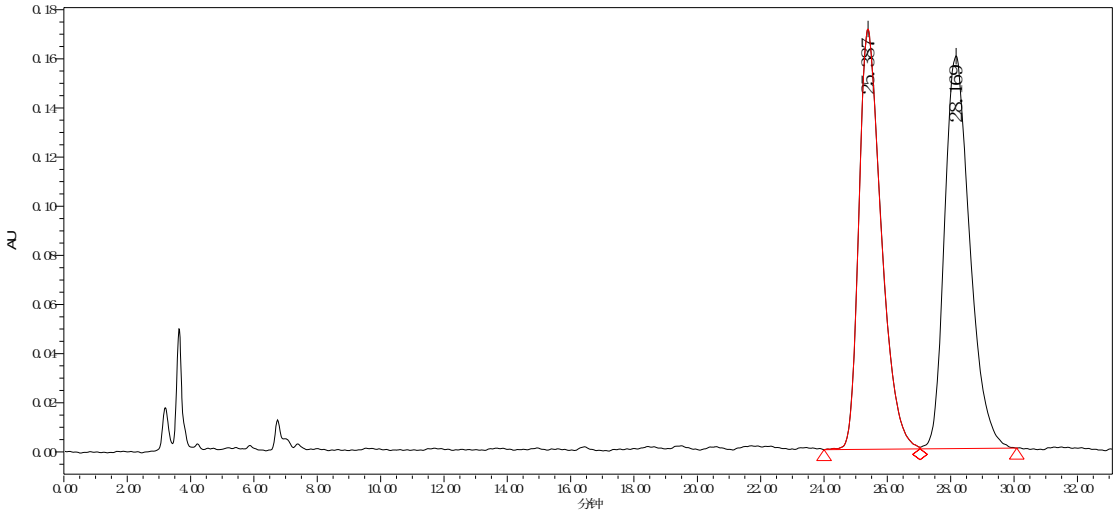
(*S*)-**4h**



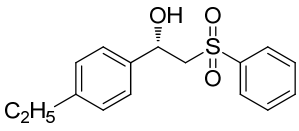
Peak	Ret Time [min]	% Area	ee value(%)
1	35.443	99.81	99.6
2	39.281	0.19	



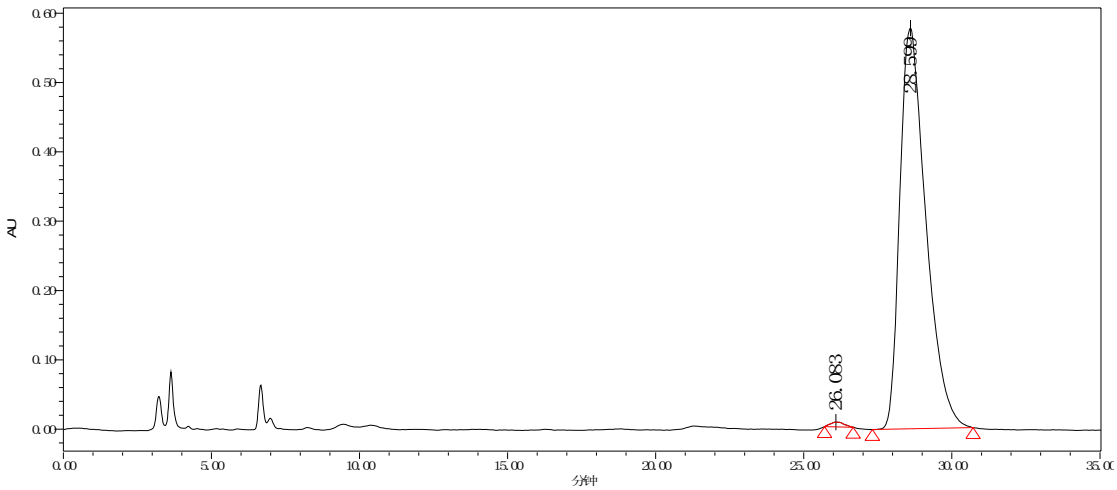
Racemate-**4i**



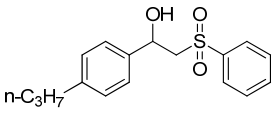
Peak	Ret Time [min]	% Area	ee value(%)
1	25.387	49.59	0
2	28.169	50.41	



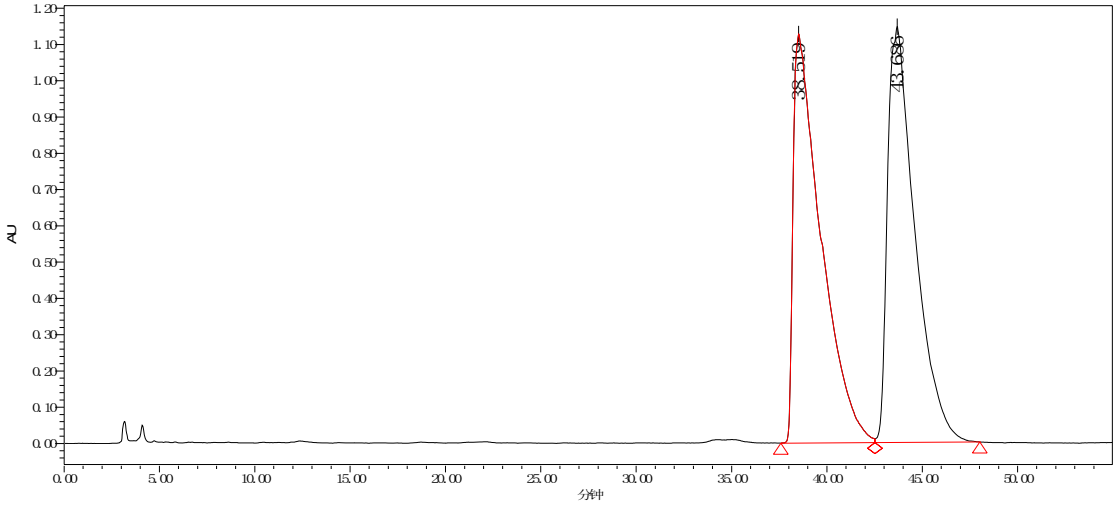
(*S*)-**4i**



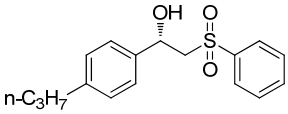
Peak	Ret Time [min]	% Area	ee value(%)
1	25.266	0.21	99.5
2	28.599	99.79	



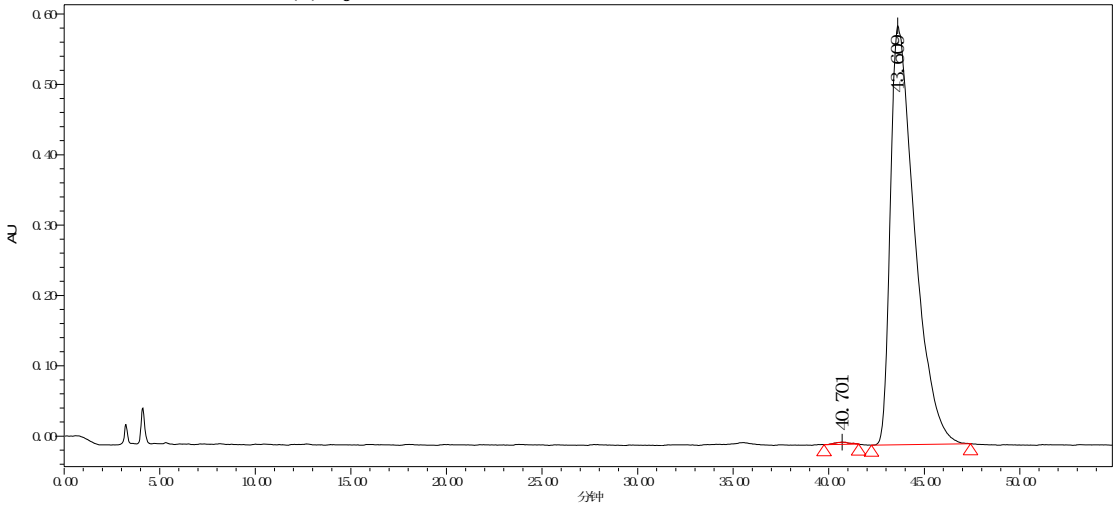
Racemate-**4j**



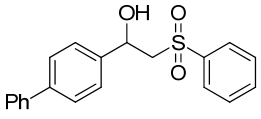
Peak	Ret Time [min]	% Area	ee value(%)
1	38.519	49.84	0
2	43.686	50.16	



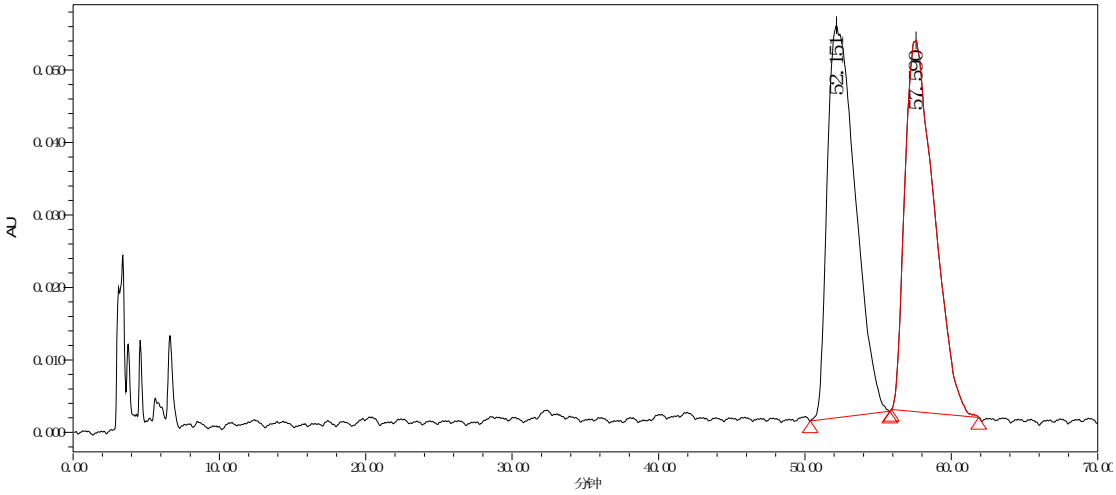
(*S*)-**4j**



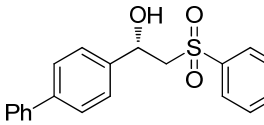
Peak	Ret Time [min]	% Area	ee value(%)
1	39.111	0.29	99.4
2	43.609	99.71	



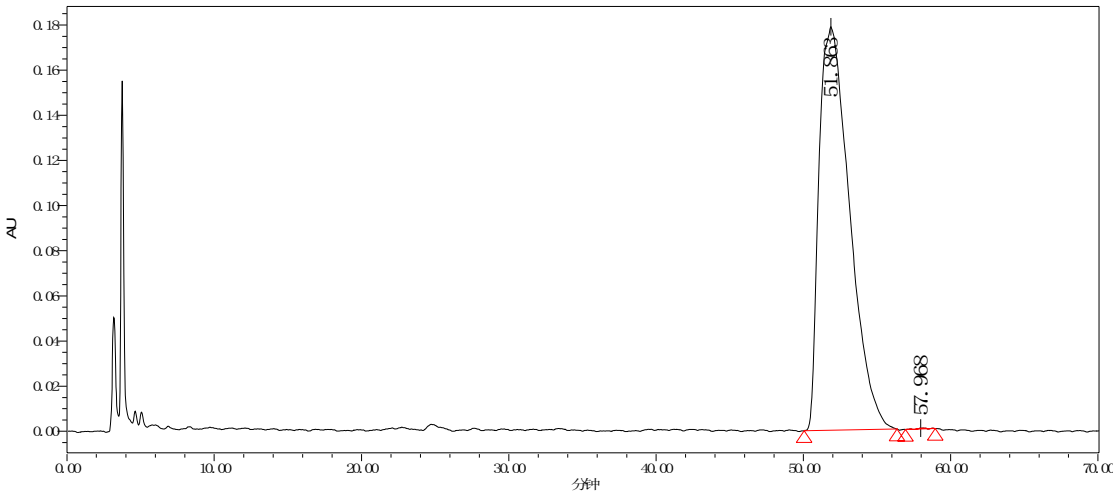
Racemate-**4k**



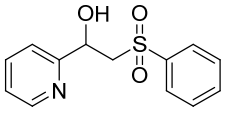
Peak	Ret Time [min]	% Area	ee value(%)
1	52.151	50.42	0
2	57.590	49.58	



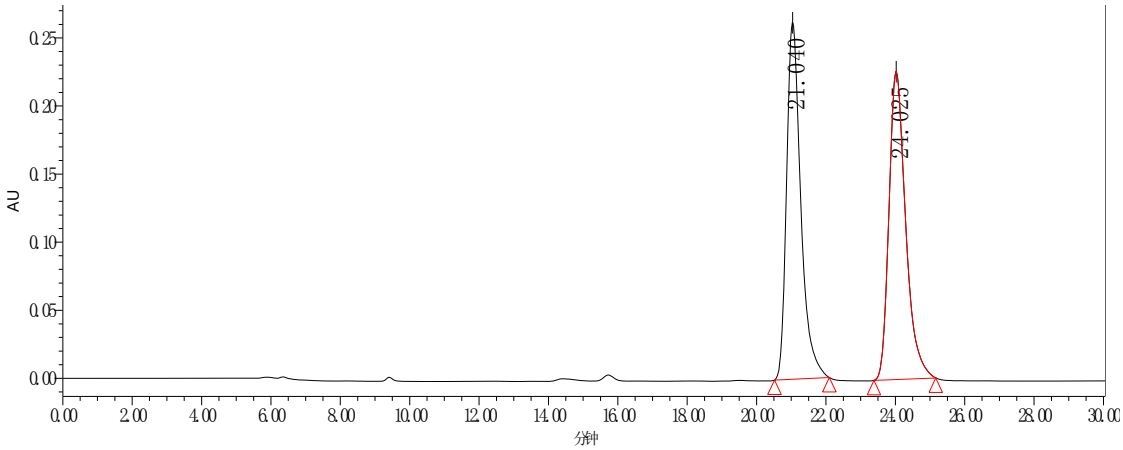
(*S*)-**4k**



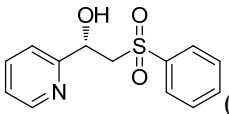
Peak	Ret Time [min]	% Area	ee value(%)
1	51.863	99.95	99.9
2	57.968	0.05	



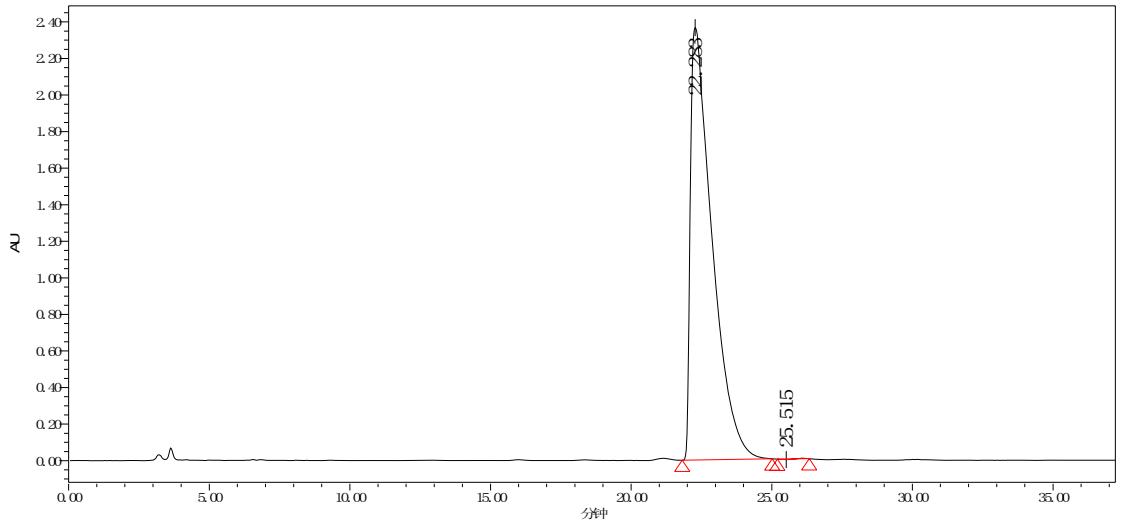
Racemate-**4l**



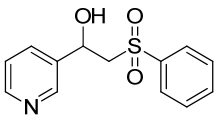
Peak	Ret Time [min]	% Area	ee value(%)
1	21.040	49.54	0
2	24.025	50.46	



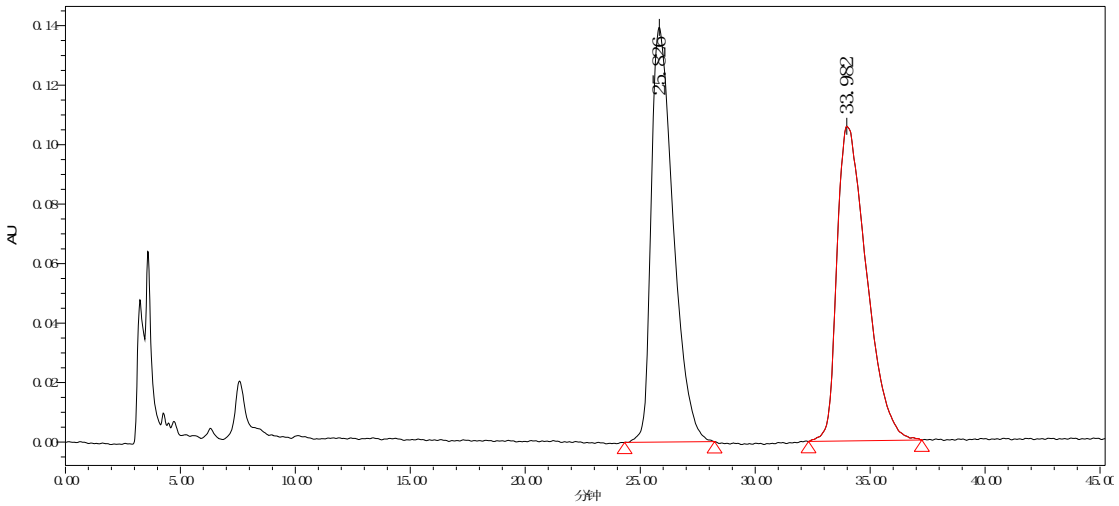
(*S*)-**4l**



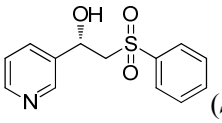
Peak	Ret Time [min]	% Area	ee value(%)
1	22.283	99.79	99.5
2	25.515	0.21	



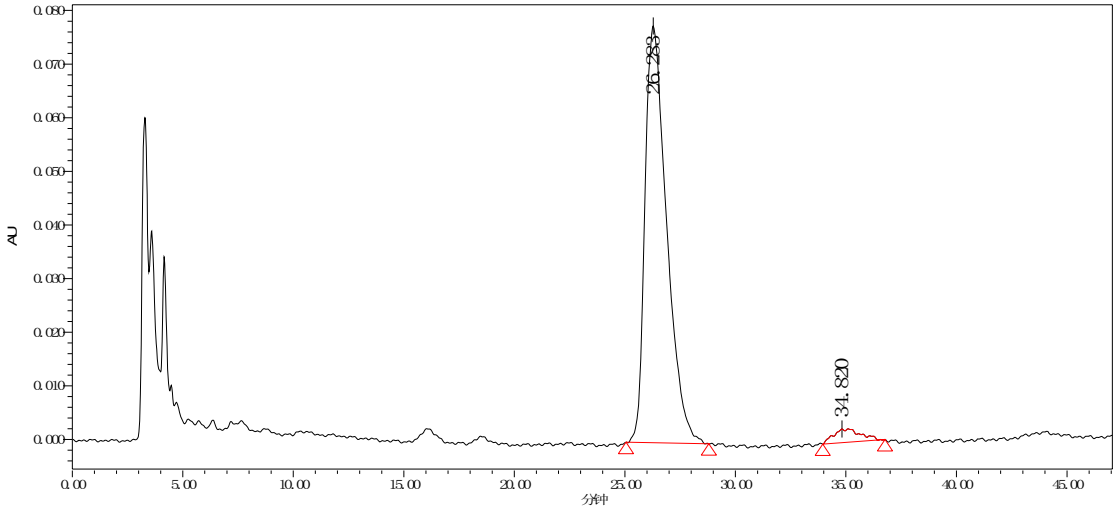
Racemate-**4m**



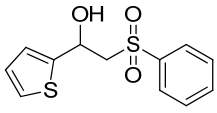
Peak	Ret Time [min]	% Area	ee value(%)
1	25.826	50.19	0
2	33.982	49.81	



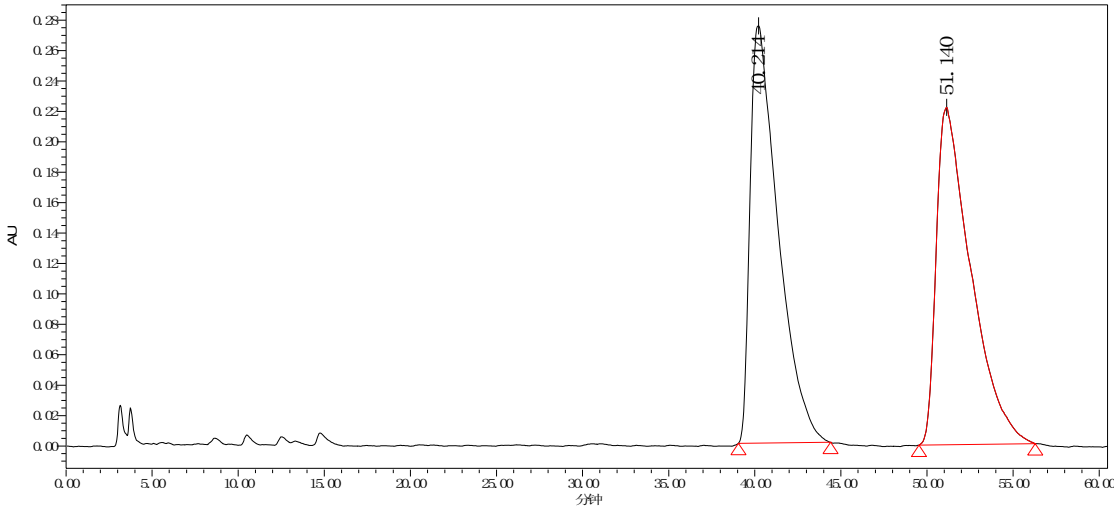
(*S*)-**4m**



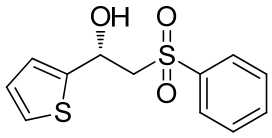
Peak	Ret Time [min]	% Area	ee value(%)
1	26.283	97.51	95.1
2	34.820	2.49	



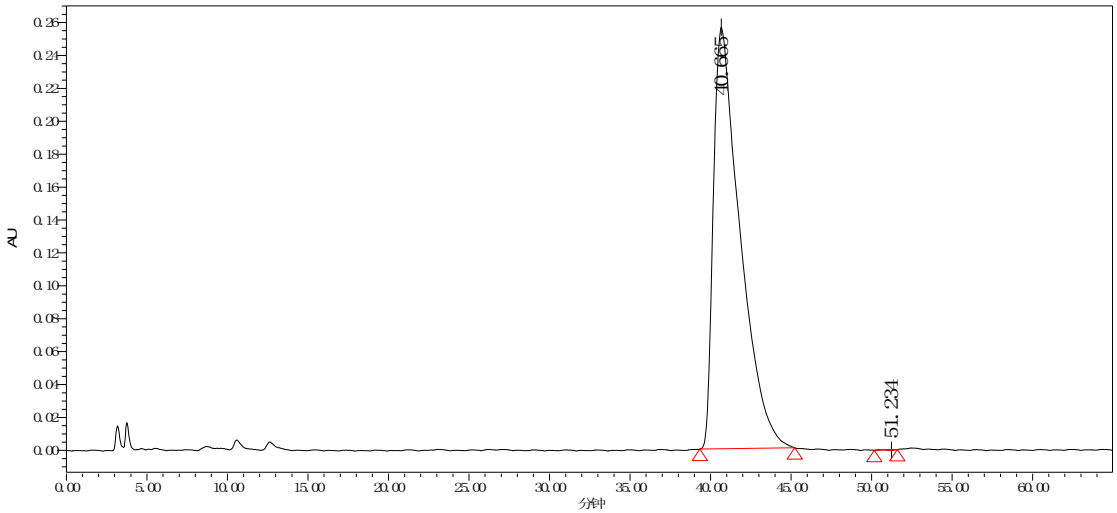
Racemate-**4n**



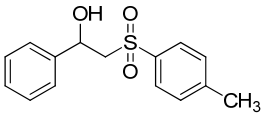
Peak	Ret Time [min]	% Area	ee value(%)
1	40.214	50.12	0
2	51.140	49.88	



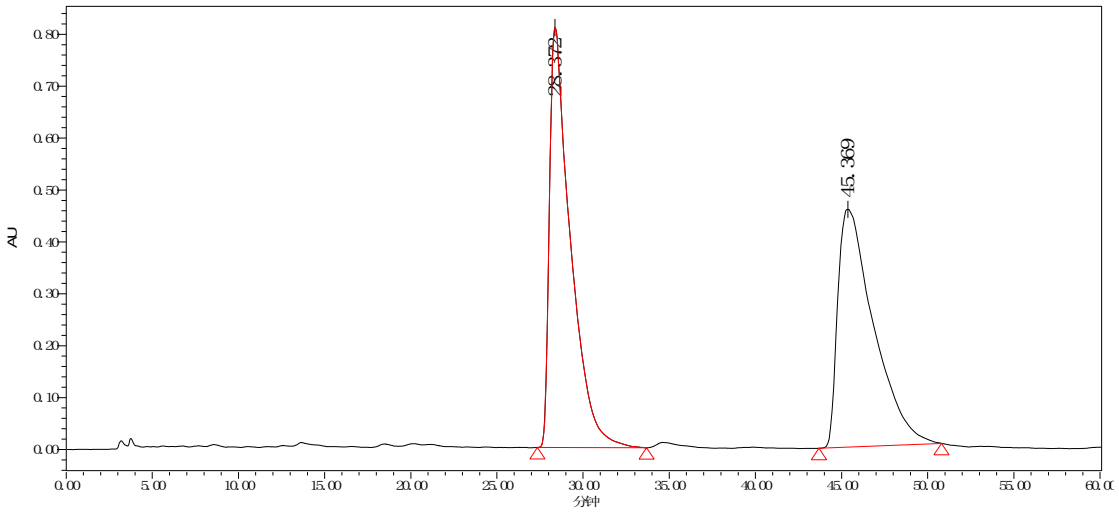
(*S*)-**4n**



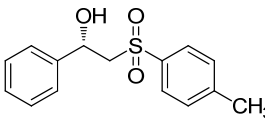
Peak	Ret Time [min]	% Area	ee value(%)
1	40.665	99.82	99.6
2	51.234	0.18	



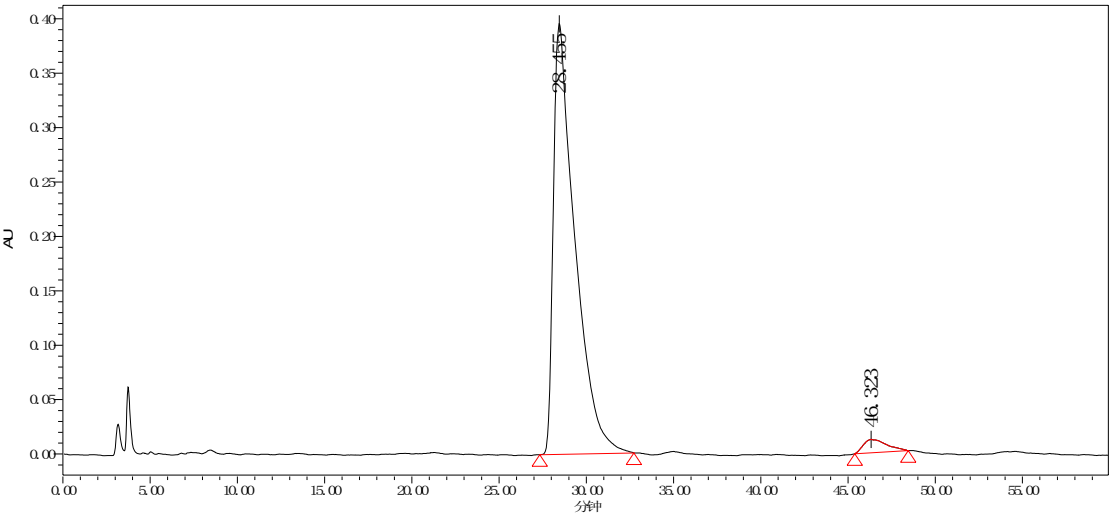
Racemate-**4o**



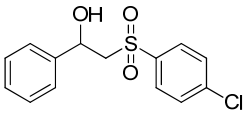
Peak	Ret Time [min]	% Area	ee value(%)
1	28.372	50.52	0
2	45.369	49.48	



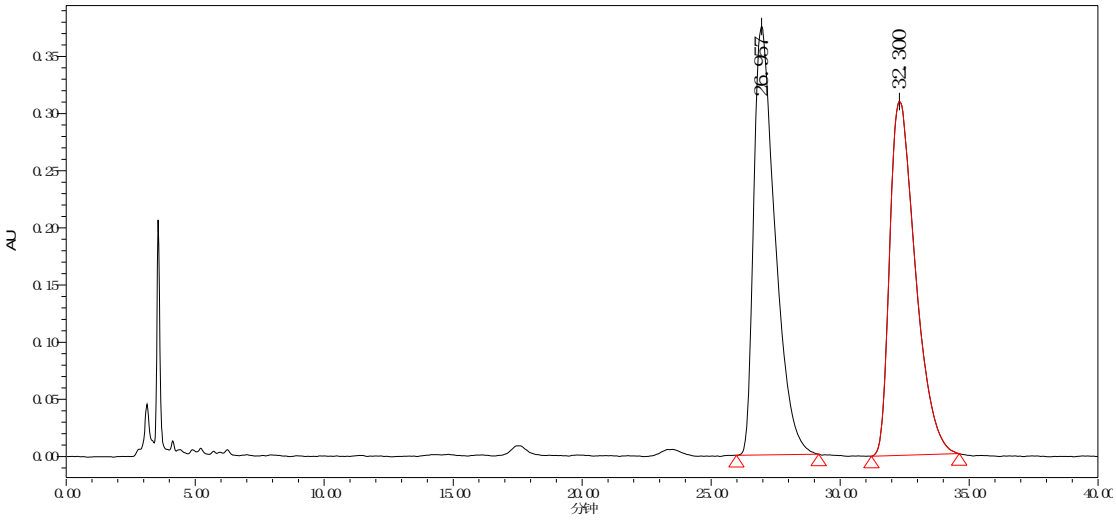
(*S*)-**4o**



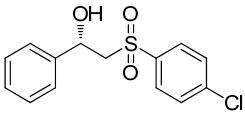
Peak	Ret Time [min]	% Area	ee value(%)
1	28.455	97.89	95.7
2	46.323	2.11	



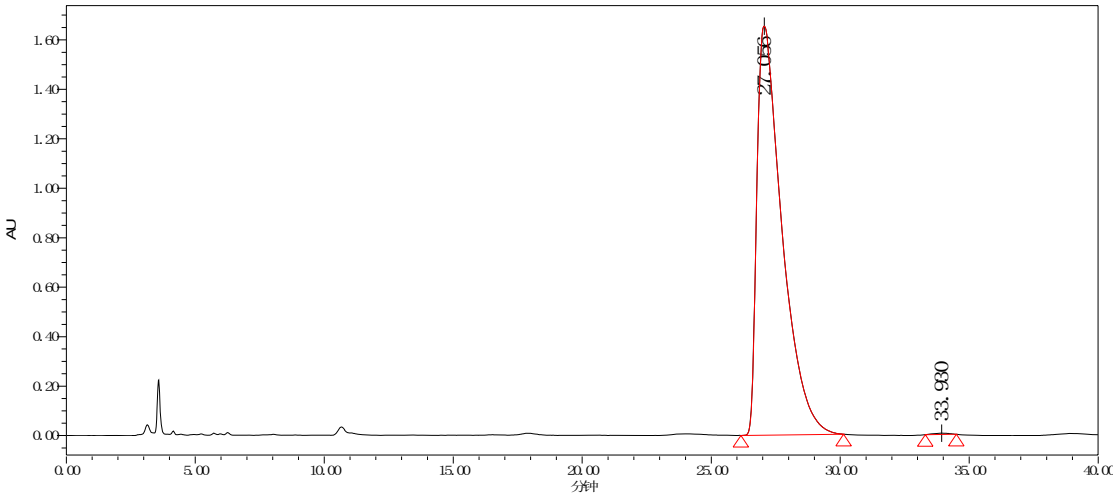
Racemate-**4p**



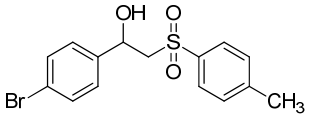
Peak	Ret Time [min]	% Area	ee value(%)
1	26.957	50.19	0
2	32.300	49.81	



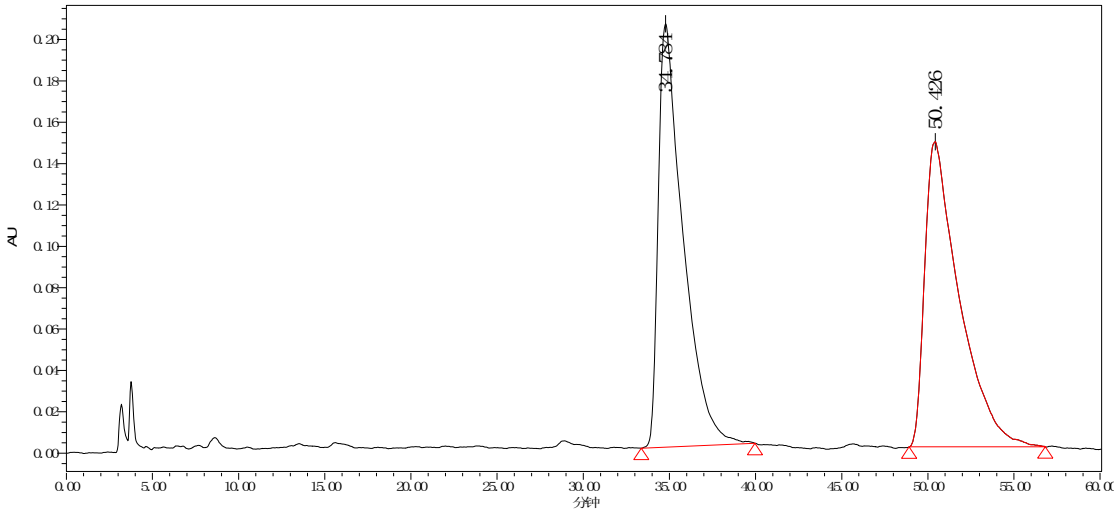
(*S*)-**4p**



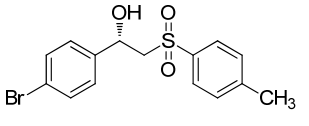
Peak	Ret Time [min]	% Area	ee value(%)
1	27.056	99.78	99.5
2	33.930	0.22	



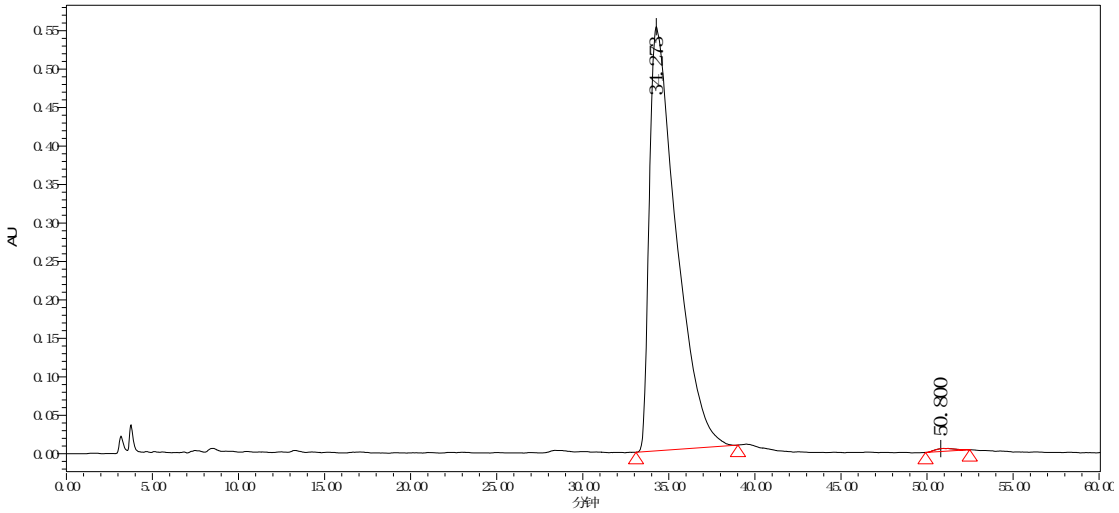
Racemate-**4q**



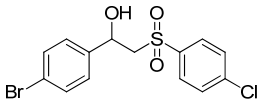
Peak	Ret Time [min]	% Area	ee value(%)
1	34.784	49.45	0
2	50.426	50.55	



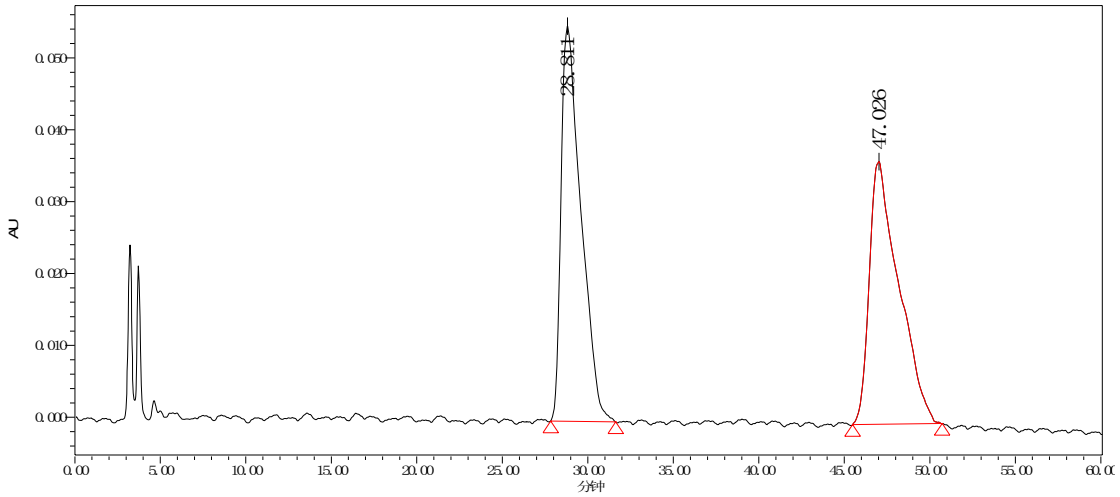
(*S*)-**4q**



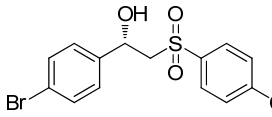
Peak	Ret Time [min]	% Area	ee value(%)
1	34.273	99.60	99.2
2	50.817	0.40	



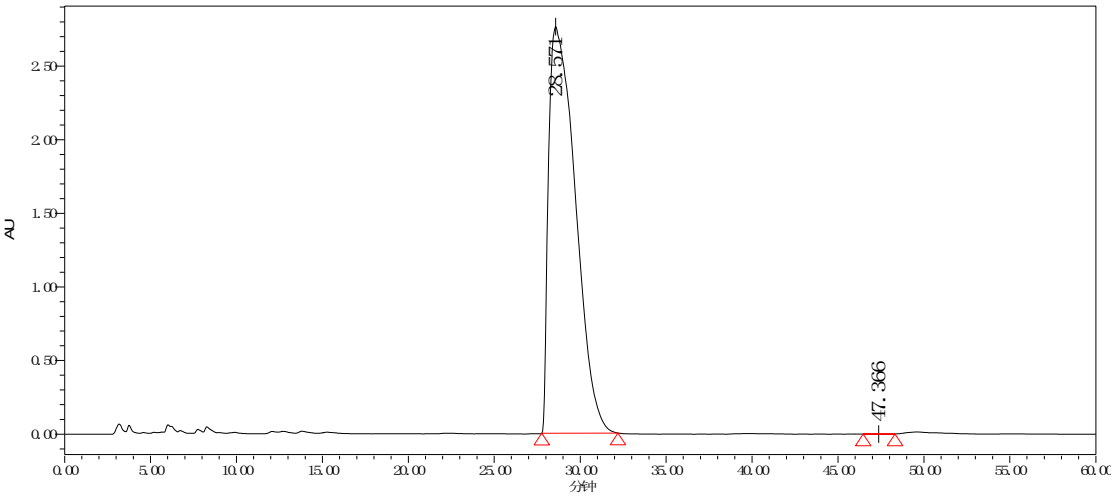
Racemate-**4r**



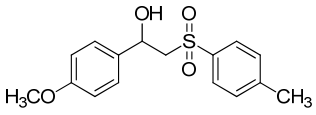
Peak	Ret Time [min]	% Area	ee value(%)
1	28.811	50.17	0
2	47.026	49.83	



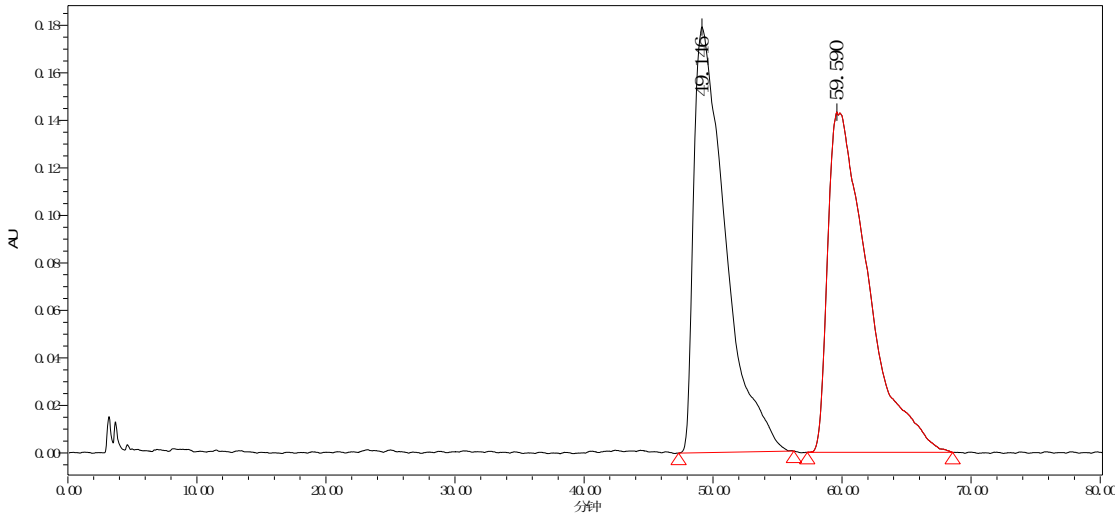
(*S*)-**4r**



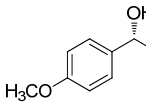
Peak	Ret Time [min]	% Area	ee value(%)
1	28.571	99.77	99.5
2	48.253	0.23	



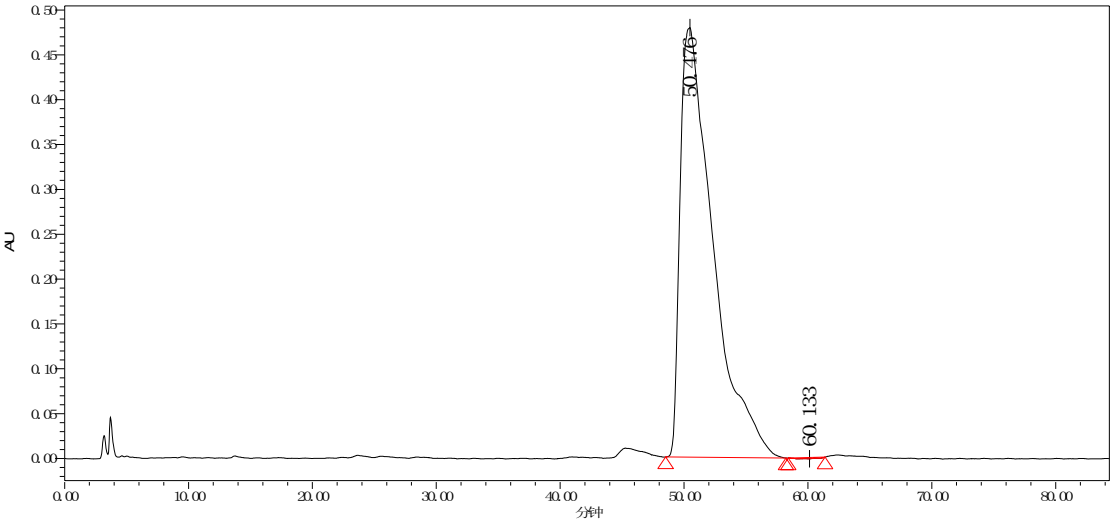
Racemate-**4s**



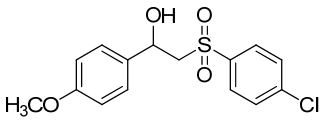
Peak	Ret Time [min]	% Area	ee value(%)
1	49.146	49.75	0
2	59.590	50.25	



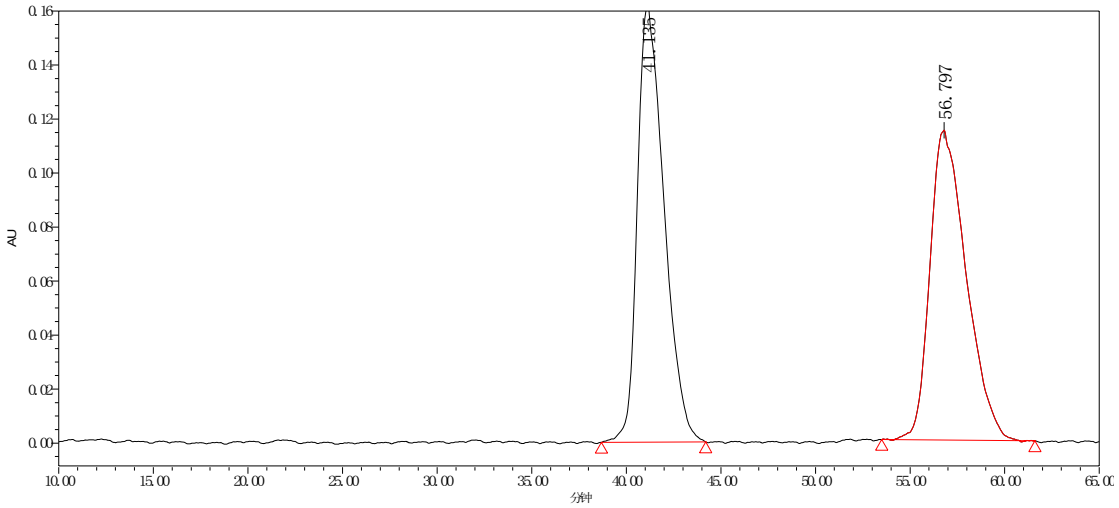
(*S*)-**4s**



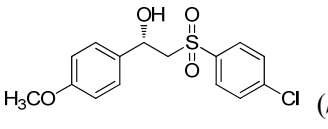
Peak	Ret Time [min]	% Area	ee value(%)
1	50.476	99.65	99.3
2	60.133	0.35	



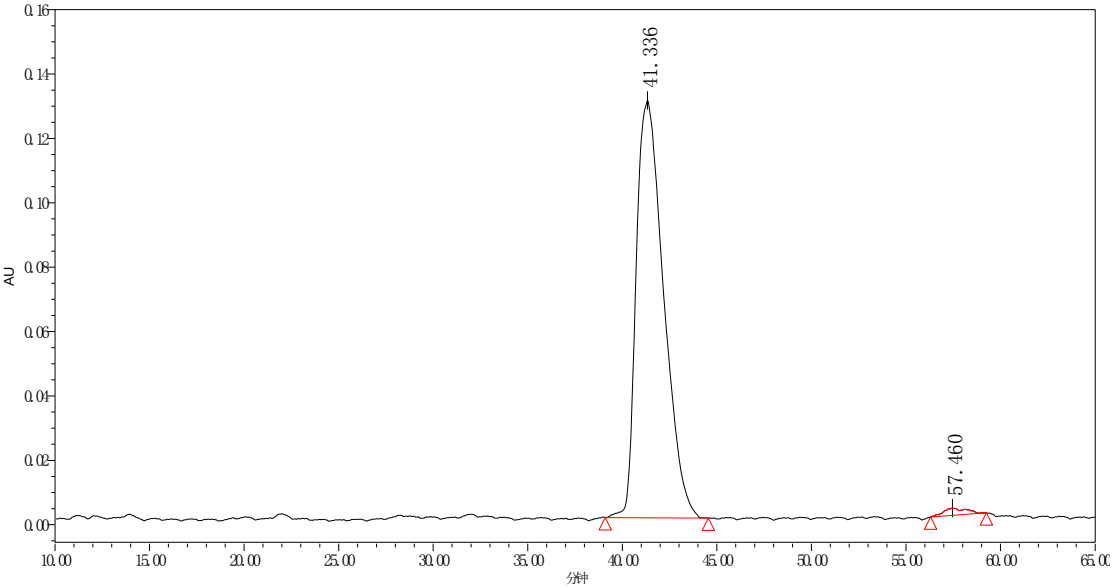
Racemate-**4t**



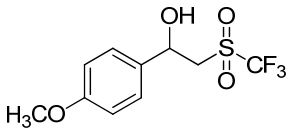
Peak	Ret Time [min]	% Area	ee value(%)
1	41.135	50.86	0
2	56.797	49.14	



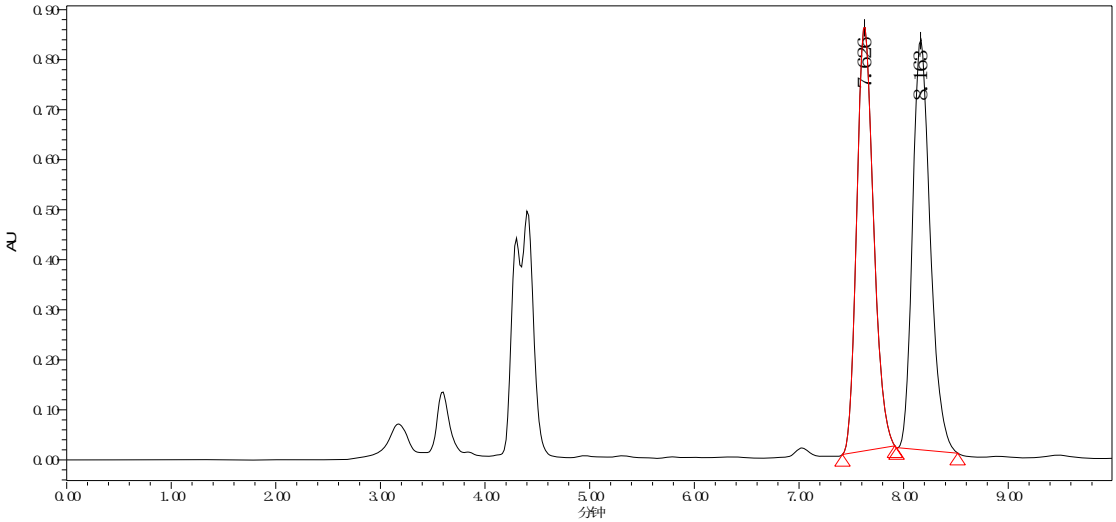
(*S*)-**4t**



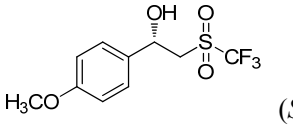
Peak	Ret Time [min]	% Area	ee value(%)
1	41.336	98.59	97.1
2	57.460	1.41	



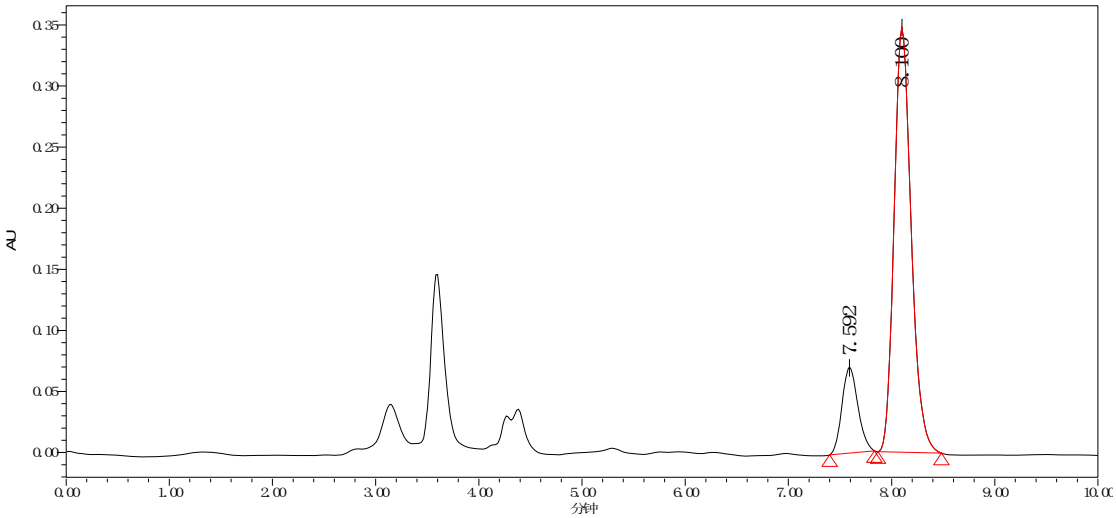
Racemate-**4u**



Peak	Ret Time [min]	% Area	ee value(%)
1	7.626	50.04	0
2	8.163	49.96	



(*S*)-**4u**



Peak	Ret Time [min]	% Area	ee value(%)
1	7.592	12.14	71.2
2	8.100	83.36	