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Supporting Information

Dinuclear Zinc Catalysis of a Kinetic Resolution Strategy of Distinguishing One Pair of Diastereoisomers From Multiple Stereoisomers

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General Information

All the dry solvents were treated prior to use according to the standard methods. Unless otherwise noted, all reactions sensitive to air or moisture were carried out under nitrogen using standard Schlenk and vacuum line techniques. Diethylzinc (1.0 mol/L in hexane) was purchased from Aldrich and used as received. **Cat1**[1], **Cat2**[2], and substrates **1**[3] were synthesized according to the literature. Other reagents were obtained from commercial sources and used as received without further purification.

Melting points were determined using YRT-3 melting point apparatus and are uncorrected. Optical rotations were measured with Perkin Elmer, model 341 Polarimeter at 20 ^{o}C in THF. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX 400 NMR instrument (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR and ^{13}C NMR. NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex), coupling constant in Hertz (Hz), integration. FT-IR spectra were recorded on a Perkin Elmer Spectrum Two L600 and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained using an Agilent LC-MSAD-Trap-XCT instrument using electrospray ionization time-of-flight (ESI-TOF). High performance liquid chromatography (HPLC) was performed on instrument consisted of JASCO model PU-1580 intelligent HPLC pump and JASCO model UV-1575 intelligent UV-vis detector (254 nm) using Daicel Chiralpak IA, IC， ID, IE or IF (4.6 mm × 250 mm) columns.

S1. Trost, B. M.; Ito, H. *J. Am. Chem. Soc.* **2000**, *122*, 12003–12004.

S2. Hua, Y.-Z.; Han, X.-W.; Yang, X.-C.; Song, X.-X.; Wang, M.-C.; Chang, J.-B. *J. Org. Chem.* **2014**, *79*, 11690–11699.

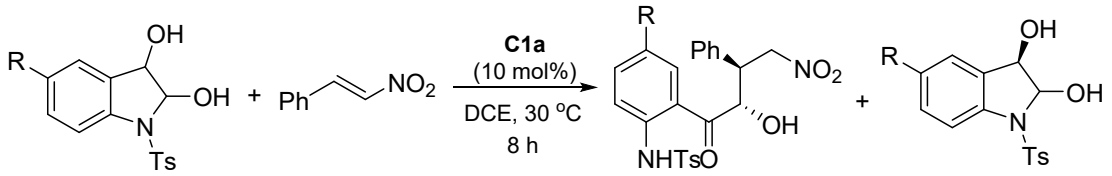
S3. Xing, S.-N.; Hua, Y.-Z.; Yang, X.-C.; Du, S.-S.; Jia, S.-K.; Mei, G.-J.; Wang, M.-C. *Org. Lett.* **2022**, *24*, 3909.

General Procedure for optimization of the reaction conditions

Under the nitrogen atmosphere, a solution of diethylzinc (20 μL, 1.0 M in hexane, 0.02 mmol) was added dropwise to a solution of **C** (0.01 mmol) and additives in solvent (2 mL). After the mixture was stirred for 30 min at room temperature. 1-tosylindoline-2,3-diol **1a** and (E)-(2-nitrovinyl)benzene **2a** (0.2 mmol, 29.83 mg) were added. The reaction mixture was stirred for corresponding time at the same temperature. The reaction was quenched with NH_4Cl solution (4 mL), and the organic layer was extracted with CH2Cl2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na2SO4.

The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography (DCM/acetone = 50/1) to afford the desired product 3aa and 1a'.

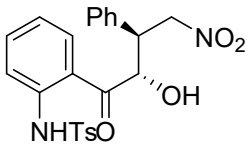
General Procedure for enantioenriched 3 and 1a'



1 **2a** **3aa-3ga** **1'**

In a flame-dried Schlenk tube, a solution of diethylzinc (40 uL, 1.0 mol/L in hexane, 0.04 mmol) was added to a solution of the chiral ligand (*S,S*)-**La** (0.02 mmol 14.1 mg) in dry DCE (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Thus, the preparation of **C1a** was finished. Then, **1a** (0.5 mmol, 152.6 mg) and **2a** (0.2 mmol, 29.83 mg) were added. The reaction mixture was stirred for 8 h at 30 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum DCM/acetone = 50/1 to afford the desired product **3** and **1'**.

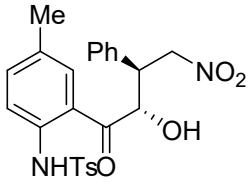
***N*-(2-(2-hydroxy-4-nitro-3-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide (3aa):**



3aa

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (80 mg, 88% yield, 3:1 dr); $[\alpha]_D^{20}$ = 50.8 (c = 1.0, DCM, 92% ee); **m.p.** = 116.5–118.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 7.83–7.75 (m, 3H), 7.52–7.47 (m, 1H), 7.46–7.41 (m, 1H), 7.29–7.26 (m, 2H), 7.26–7.24 (m, 2H), 7.22–7.18 (m, 2H), 5.27 (d, *J* = 3.6 Hz, 1H), 4.66–4.54 (m, 2H), 3.89 (s, 1H), 3.77–3.71 (m, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5, 144.6, 140.9, 137.2, 136.3, 136.2, 130.6, 129.9, 129.2, 128.5, 127.9, 127.4, 122.6, 119.3, 118.6, 75.3, 74.8, 48.1, 21.6.; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{23}H_{22}N_2O_6S]^+$: 477.1091, found: 477.1089; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 38.752 min and t_{minor} = 27.727 min.

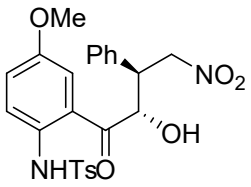
***N*-(2-(2-hydroxy-4-nitro-3-phenylbutanoyl)-4-methylphenyl)-4-methylbenzenesulfonamide (3ba):**



3ba

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (75 mg, 80% yield, 5:1 dr); $[\alpha]_D^{20}$ = 27.4 (c = 1.0, DCM, 85% ee); **m.p.** = 107.2–109.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.31–7.26 (m, 3H), 7.25 (t, *J* = 3.3 Hz, 4H), 7.14–7.10 (m, 3H), 5.21 (s, 1H), 4.60 (d, *J* = 7.4 Hz, 2H), 3.84 (d, *J* = 6.4 Hz, 1H), 3.66 (d, *J* = 4.5 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5, 144.4, 138.4, 137.2, 137.1, 136.4, 132.4, 130.9, 129.8, 129.2, 128.4, 127.9, 127.4, 119.8, 118.9, 75.3, 74.9, 48.4, 21.5, 20.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{24}N_2O_6S]^+$: 491.1247, found: 491.1244; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 36.05 min and t_{minor} = 24.68 min.

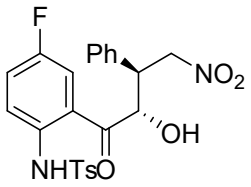
***N*-(2-(2-hydroxy-4-nitro-3-phenylbutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ca):**



3ca

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (87 mg, 90% yield, 10:1 dr); $[\alpha]_D^{20}$ = 48.3 (c = 1.0, DCM, 99% ee); **m.p.** = 92.5–93.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.79–7.67 (m, 3H), 7.24 (t, *J* = 5.3 Hz, 5H), 7.19–7.13 (m, 2H), 7.11–7.06 (m, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 5.18 (s, 1H), 4.59 (dd, *J* = 13.8, 8.6 Hz, 1H), 4.47 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.81 (s, 1H), 3.67 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.3, 155.0, 144.5, 137.1, 136.3, 133.7, 129.8, 129.3, 128.4, 127.9, 127.3, 122.4, 122.3, 120.6, 114.8, 75.2, 75.1, 55.9, 48.0, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{24}N_2O_7S]^+$: 507.1196, found: 507.1196; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 25.07 min and t_{minor} = 23.21 min.

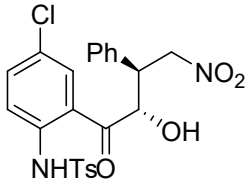
***N*-(4-fluoro-2-(2-hydroxy-4-nitro-3-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide (3da):**



3da

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (78 mg, 83% yield, 10:1 dr); $[\alpha]_D^{20}$ = 10.9 (c = 1.0, DCM, 99% ee); **m.p.** = 89.8–91.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm: δ 10.47 (s, 1H), 7.81–7.73 (m, 3H), 7.28 (s, 1H), 7.26–7.22 (m, 3H), 7.22–7.18 (m, 1H), 7.14–7.09 (m, 2H), 7.03–6.98 (m, 1H), 5.12 (d, *J* = 4.7 Hz, 1H), 4.74–4.66 (m, 1H), 4.63–4.55 (m, 1H), 3.71–3.64 (m, 1H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 157.3 (d, *J* = 245.7 Hz), 144.8, 136.9, 136.6, 136.1, 129.9, 129.4, 128.7, 127.8, 127.4, 123.6, 123.4, 121.8 (d, *J* = 7.4 Hz), 120.2, 120.1, 116.6 (d, *J* = 23.9 Hz), 75.2, 75.1, 48.2, 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.77; **HRMS** (ESI): m/z $[M + H]^+$ calcd for $[C_{23}H_{21}FN_2O_6S]^+$: 473.1177, found: 473.1171; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 26.59 min and t_{minor} = 21.20 min.

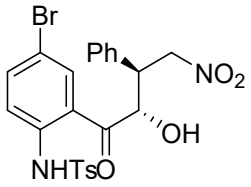
***N*-(4-chloro-2-(2-hydroxy-4-nitro-3-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide (3ea):**



3ea

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (81 mg, 83% yield, 5:1 dr); $[\alpha]_D^{20}$ = 12.5 (c = 1.0, DCM, 99% ee); **m.p.** = 94.2–95.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.42–7.38 (m, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.26–7.22 (m, 4H), 7.13–7.08 (m, 2H), 5.14 (s, 1H), 4.79 (dd, *J* = 14.0, 7.0 Hz, 1H), 4.59 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.74 (d, *J* = 5.4 Hz, 1H), 3.71–3.63 (m, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 144.8, 139.2, 136.6, 136.0, 135.8, 130.3, 130.0, 129.4, 128.7, 127.9, 127.7, 127.5, 120.6, 119.9, 75.2, 75.0, 48.4, 21.6. **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{23}H_{21}ClN_2O_6S]^+$: 511.0701, found: 511.0701; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 31.13 min and t_{minor} = 23.56 min.

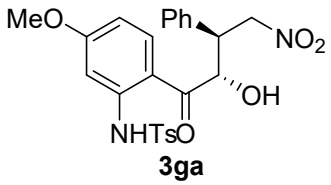
***N*-(4-bromo-2-(2-hydroxy-4-nitro-3-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide (3fa):**



3fa

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (83 mg, 78% yield, 8:1 dr); $[\alpha]_D^{20}$ = 12.0 (c = 1.0, DCM, 99% ee); **m.p.** = 88.7–89.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.26–7.22 (m, 3H), 7.13–7.08 (m, 2H), 5.14 (s, 1H), 4.82 (dd, *J* = 14.0, 7.0 Hz, 1H), 4.59 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.77 (s, 1H), 3.67 (dd, *J* = 12.4, 7.3 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 144.8, 139.6, 138.6, 136.6, 136.0, 133.3, 130.0, 129.4, 128.7, 127.7, 127.5, 120.7, 120.3, 115.0, 75.2, 75.0, 48.5, 21.6; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{23}H_{21}BrN_2O_6S]^+$: 555.0202, found: 555.0207; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 36.06 min and t_{minor} = 29.94 min.

***N*-(2-((2S,3S)-2-hydroxy-4-nitro-3-phenylbutanoyl)-5-methoxyphenyl)-4-methylbenzenesulfonamide (3ga):**

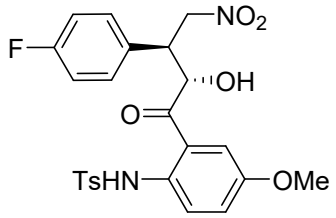


3ga

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (83 mg, 86% yield, 8:1 dr); $[\alpha]_D^{20}$ = 24.0 (c = 1.0, DCM, 96% ee); **m.p.** = 108.5–109.9 °C; **^{1}H NMR** (400 MHz,

DMSO) δ 11.63 (s, 1H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.30–7.26 (m, 2H), 7.20 (d, *J* = 6.4 Hz, 3H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.68–6.63 (m, 1H), 6.34 (d, *J* = 7.3 Hz, 1H), 5.27 (s, 1H), 5.10 (dd, *J* = 13.3, 5.2 Hz, 1H), 5.01–4.92 (m, 1H), 3.76 (s, 3H), 2.53–2.49 (m, 2H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.4, 169.4, 149.6, 147.5, 142.1, 140.5, 140.0, 135.3, 133.7, 133.6, 132.7, 132.2, 118.9, 113.6, 107.5, 82.9, 77.9, 61.0, 52.4, 26.2; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{24}H_{24}N_2O_7S]^+$: 507.1196, found: 507.1194; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.986 min and t_{minor} = 15.614 min.

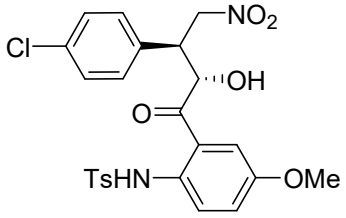
***N*-(2-(3-(4-fluorophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cb):**



3cb

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (88 mg, 88% yield, 8:1 dr); $[\alpha]_D^{20}$ = 10.4 (c = 1.0, DCM, 94% ee); **m.p.** = 83.2–84.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.79–7.69 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.17–7.09 (m, 3H), 6.95 (t, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 2.8 Hz, 1H), 5.14 (t, *J* = 4.5 Hz, 1H), 4.55 (dd, *J* = 13.7, 9.1 Hz, 1H), 4.37 (dd, *J* = 13.8, 5.9 Hz, 1H), 3.72 (s, 3H), 3.68 (dd, *J* = 8.5, 4.7 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.0, 162.6 (d, *J* = 248.1 Hz), 155.1, 144.5, 136.4, 133.6, 132.9, 132.9, 129.8, 129.6 (d, *J* = 8.2 Hz), 127.3, 122.7, 121.9, 120.6, 116.2 (d, *J* = 21.6 Hz), 115.1, 75.2, 75.1, 55.6, 47.3, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.06; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{24}H_{23}FN_2O_7S]^+$: 525.1102, found: 525.1111; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 31.76 min and t_{minor} = 26.73 min.

***N*-(2-(3-(4-chlorophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cc):**

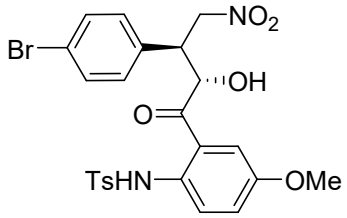


3cc

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (97 mg, 93% yield, 6:1 dr); $[\alpha]_D^{20}$ = 41.7 (c = 1.0, DCM, 93% ee); **m.p.** = 90.2–92.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.26–7.20 (m, 4H), 7.14–7.10 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 2.9 Hz, 1H), 5.14–5.10 (m, 1H), 4.56 (dd, *J* = 13.8, 9.1 Hz, 1H), 4.37 (dd, *J* = 13.8, 5.9 Hz, 1H), 3.78 (d, *J* = 6.1 Hz, 1H), 3.72 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.8, 155.1, 144.6, 136.4, 135.5, 134.5, 133.6, 129.8, 129.4, 129.2, 127.3, 122.7, 121.8, 120.6, 115.2, 75.0, 74.9, 55.7, 47.5, 21.5; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for

$[C_{24}H_{23}ClN_2O_7S]^+$: 541.0806, found: 541.0801; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 31.33 min and t_{minor} = 26.18 min.

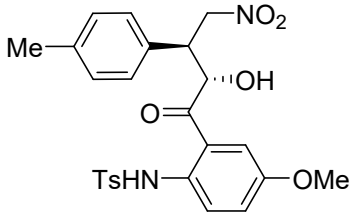
***N*-(2-(3-(4-bromophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cd):**



3cd

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (105 mg, 93% yield, 10:1 dr); $[\alpha]_D^{20}$ = 72.7 (c = 1.0, DCM, 99% ee); **m.p.** = 98.2–99.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.85–7.66 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.13–7.08 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 2.9 Hz, 1H), 5.13 (s, 1H), 4.57 (dd, *J* = 13.8, 9.2 Hz, 1H), 4.41 (dd, *J* = 13.8, 5.8 Hz, 1H), 3.86 (s, 1H), 3.72 (s, 3H), 3.65–3.59 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 155.1, 144.6, 136.3, 136.0, 133.4, 132.3, 129.8, 129.6, 127.3, 122.6, 122.6, 121.8, 120.8, 115.3, 75.0, 74.8, 55.7, 47.5, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{23}BrN_2O_7S]^+$: 585.0301, found: 585.0313; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 33.21 min and t_{minor} = 27.32 min.

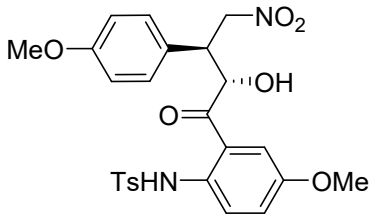
***N*-(2-(2-hydroxy-4-nitro-3-(p-tolyl)butanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ce):**



3ce

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (89 mg, 90% yield, 10:1 dr); $[\alpha]_D^{20}$ = 56.4 (c = 1.0, DCM, 99% ee); **m.p.** = 94.6–95.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.77–7.67 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.10–6.98 (m, 5H), 6.81 (d, *J* = 2.9 Hz, 1H), 5.15 (s, 1H), 4.57 (dd, *J* = 13.7, 8.7 Hz, 1H), 4.46 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.81 (s, 1H), 3.66 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 155.0, 144.5, 138.3, 136.3, 134.0, 133.6, 129.9, 129.8, 127.7, 127.3, 122.4, 122.2, 120.7, 114.8, 75.4, 75.3, 55.6, 47.7, 21.5, 21.0; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{26}N_2O_7S]^+$: 521.1353, found: 521.1349; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 49.59 min and t_{minor} = 37.89 min.

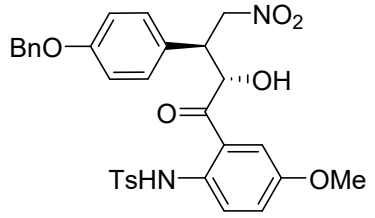
***N*-(2-(2-hydroxy-3-(4-methoxyphenyl)-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cf):**



3cf

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (98 mg, 95% yield, 6:1 dr); $[\alpha]_D^{20}$ = 54.0 (c = 1.0, DCM, 95% ee); **m.p.** = 113.6–115.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.78–7.69 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.11–7.03 (m, 3H), 6.82 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.13 (s, 1H), 4.55 (dd, *J* = 13.6, 8.9 Hz, 1H), 4.42 (dd, *J* = 13.6, 6.1 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.62 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 159.6, 155.0, 144.5, 136.4, 133.6, 129.8, 129.0, 128.9, 127.3, 122.4, 122.1, 120.6, 115.0, 114.6, 75.5, 75.3, 55.6, 55.3, 47.4, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{26}N_2O_8S]^+$: 537.1302, found: 537.1302; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 46.05 min and t_{minor} = 39.01 min.

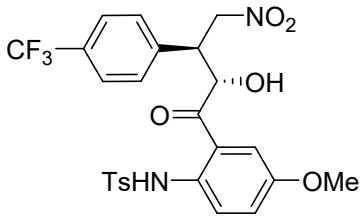
***N*-(2-(3-(4-(benzyloxy)phenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cg):**



3cg

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (106 mg, 90% yield, 8:1 dr); $[\alpha]_D^{20}$ = 36.0 (c = 1.0, DCM, 93% ee); **m.p.** = 108.5–110.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.77–7.68 (m, 3H), 7.42–7.32 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.10–7.01 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 3H), 5.14 (s, 1H), 4.99 (s, 2H), 4.55 (dd, *J* = 13.7, 8.9 Hz, 1H), 4.42 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.79 (d, *J* = 6.3 Hz, 1H), 3.66 (s, 3H), 3.62 (dd, *J* = 4.3, 3.1 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 158.8, 155.0, 144.5, 136.7, 136.3, 133.6, 129.8, 129.1, 129.0, 128.7, 128.1, 127.5, 127.3, 122.4, 122.2, 120.7, 115.5, 114.9, 75.5, 75.3, 70.0, 55.6, 47.4, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{31}H_{30}N_2O_8S]^+$: 613.1615, found: 613.1615; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 55.210 min and t_{minor} = 43.414 min.

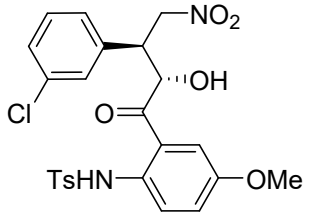
***N*-(2-(2-hydroxy-4-nitro-3-(4-(trifluoromethyl)phenyl)butanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ch):**



3ch

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (92 mg, 83% yield, 6:1 dr); $[\alpha]_D^{20}$ = 83.7 (c = 1.0, DCM, 90% ee); **m.p.** = 68.2–69.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.80–7.70 (m, 3H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 2H), 7.24 (s, 1H), 7.13–7.08 (m, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 5.15 (s, 1H), 4.62 (dd, *J* = 14.0, 9.2 Hz, 1H), 4.42 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.84 (d, *J* = 5.9 Hz, 1H), 3.71 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.6, 155.1, 144.6, 141.0, 136.4, 133.5, 129.8, 128.4, 127.3, 126.2, 126.1, 122.8, 121.7, 120.7, 115.3, 74.8, 74.6, 55.6, 47.8, 21.5; **^{19}F NMR** (376 MHz, CDCl3) δ -62.87; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{23}F_3N_2O_7S]^+$: 575.1070, found: 575.1074; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 24.15 min and t_{minor} = 21.58 min.

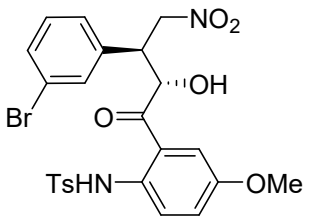
***N*-(2-(3-(3-chlorophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamid*e* (3ci):**



3ci

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (88 mg, 85% yield, 4:1 dr); $[\alpha]_D^{20}$ = 36.4 (c = 1.0, DCM, 96% ee); **m.p.** = 79.5–81.3 °C; **^{1}H NMR** (400 MHz, DMSO) δ 10.23 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.44 (s, 1H), 7.34–7.22 (m, 5H), 7.18 (s, 1H), 7.07–6.96 (m, 2H), 6.20 (s, 1H), 5.34 (s, 1H), 5.08–4.89 (m, 2H), 3.85 (s, 1H), 3.73 (s, 3H), 2.51 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 202.6, 156.4, 144.1, 140.6, 136.2, 133.5, 130.7, 130.2, 129.5, 128.6, 128., 127.8, 127.4, 124.3, 120.3, 115.8, 77.1, 74.6, 56.0, 46.7, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{23}ClN_2O_7S]^+$: 541.0806, found: 541.0817; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.26 min and t_{minor} = 19.47 min.

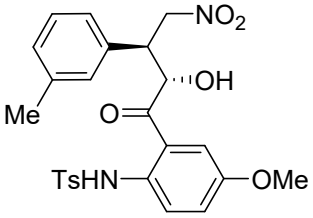
***N*-(2-(3-(3-bromophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cj):**



3cj

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (99 mg, 88% yield, 4:1 dr); $[\alpha]_D^{20}$ = 37.6 (c = 1.0, DCM, 85% ee); **m.p.** = 113.7–115.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.32 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.17–7.10 (m, 3H), 6.82 (d, *J* = 2.8 Hz, 1H), 5.15 (s, 1H), 4.55 (dd, *J* = 14.0, 8.8 Hz, 1H), 4.40 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.83 (s, 1H), 3.72 (s, 3H), 3.63 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.7, 155.1, 144.5, 139.5, 136.3, 133.6, 131.7, 131.0, 130.8, 129.8, 127.3, 126.6, 123.2, 122.8, 122.4, 120.6, 114.6, 74.9, 55.6, 47.5, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{23}BrN_2O_7S]^+$:585.0301, found: 585.0300; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 15.07 min and t_{minor} = 12.87 min.

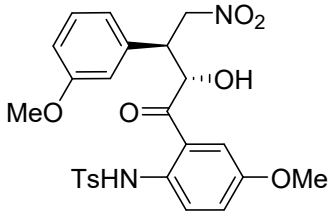
***N*-(2-(2-hydroxy-4-nitro-3-(m-tolyl)butanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ck):**



3ck

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (95 mg, 95% yield, 7:1 dr); $[\alpha]_D^{20}$ = 49.0 (c = 1.0, DCM, 90% ee); **m.p.** = 128.8–129.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.79–7.70 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.11–7.03 (m, 2H), 6.95 (s, 2H), 6.81 (d, *J* = 2.8 Hz, 1H), 5.16 (s, 1H), 4.57 (dd, *J* = 13.8, 8.5 Hz, 1H), 4.48 (dd, *J* = 13.8, 6.4 Hz, 1H), 3.79 (d, *J* = 6.1 Hz, 1H), 3.66 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.3, 154.9, 144.4, 139.0, 137.1, 136.3, 133.7, 129.8, 129.2, 129.1, 128.6, 127.3, 124.8, 122.3, 120.5, 114.7, 75.2, 75.2, 55.5, 47.9, 21.5, 21.4; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{26}N_2O_7S]^+$: 521.1353, found: 521.1348; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 12.51 min and t_{minor} = 11.03 min.

***N*-(2-(2-hydroxy-3-(3-methoxyphenyl)-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cl):**

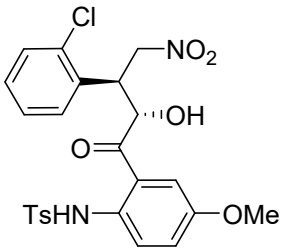


3cl

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (88 mg, 86% yield, 3:1 dr); $[\alpha]_D^{20}$ = 44.4 (c = 1.0, DCM, 98% ee); **m.p.** = 119.1–120.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.75–7.68 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 8.2 Hz, 1H), 7.11–7.05 (m, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.78 (s, 2H), 6.71 (d, *J* = 7.5 Hz, 1H), 5.19 (s, 1H), 4.58 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.49 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.85 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 160.1, 155.0, 144.5, 138.7, 136.2, 133.6, 130.3, 129.8, 127.3,

122.4, 122.3, 120.6, 120.1, 114.7, 113.8, 113.6, 75.2, 75.1, 55.6, 55.3, 47.9, 21.5; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{25}H_{26}N_2O_8S$]$^+$: 537.1302, found: 537.1302; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 56.56 min and t_{minor} = 47.95 min.

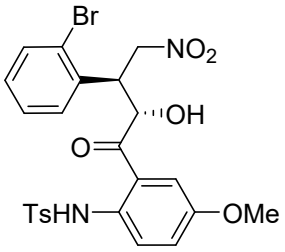
***N*-(2-(3-(2-chlorophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cm):**



3cm

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (93 mg, 90% yield, 5:1 dr); $[\alpha]_D^{20}$ = 49.3 (c = 1.0, DCM, 98% ee); **m.p.** = 98.2–99.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.62 (t, *J* = 16.3 Hz, 2H), 7.35 (s, 1H), 7.29 (d, *J* = 9.2 Hz, 1H), 7.19 (s, 1H), 7.16 (s, 2H), 7.14 (s, 1H), 7.11–7.04 (m, 2H), 5.17 (s, 1H), 4.50 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.34 (s, 1H), 4.14 (dd, *J* = 13.5, 5.6 Hz, 1H), 3.81 (s, 1H), 3.67 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 155.1, 144.5, 136.3, 134.4, 133.7, 133.5, 130.1, 129.8, 129.6, 127.7, 127.3, 122.7, 122.3, 120.4, 115.0, 73.4, 55.7, 43.6, 21.5; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{24}H_{23}ClN_2O_7S$]$^+$: 541.0806, found:541.0809; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 49.03 min and t_{minor} = 41.04 min.

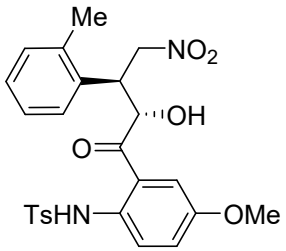
***N*-(2-(3-(2-bromophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cn):**



3cn

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (98 mg, 87% yield, 3:1 dr); $[\alpha]_D^{20}$ = 48.3 (c = 1.0, DCM, 94% ee); **m.p.** = 95.2–93.0 °C; **^{1}H NMR** (400 MHz, DMSO) δ 10.11 (s, 1H), 7.55 (t, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.22 (s, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 6.11 (s, 1H), 5.34 (s, 1H), 5.03–4.92 (m, 2H), 4.38 (dd, *J* = 14.2, 6.5 Hz, 1H), 3.73 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 202.9, 156.4, 144.1, 137.1, 136.2, 133.3, 130.1, 130.0, 129.8, 128.3, 127.4, 124.9, 124.6, 120.1, 115.6, 76.6, 74.6, 56.0, 45.3, 21.4; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{24}H_{23}BrN_2O_7S$]$^+$: 585.0301, found: 585.0304; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 30.96 min and t_{minor} = 23.51 min.

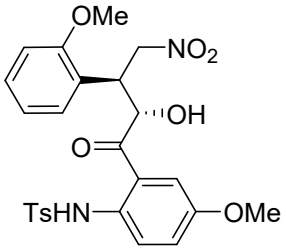
***N*-(2-(2-hydroxy-4-nitro-3-(o-tolyl)butanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3co):**



3co

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (83 mg, 83% yield, 10:1 dr); $[\alpha]_D^{20}$ = 22.7 (c = 1.0, DCM, 99% ee); **m.p.** = 89.9–91.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.71 (t, *J* = 9.1 Hz, 3H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.08–7.03 (m, 2H), 6.77 (d, *J* = 2.9 Hz, 1H), 5.17 (s, 1H), 4.62 (dd, *J* = 13.9, 7.1 Hz, 1H), 4.48 (dd, *J* = 13.9, 7.7 Hz, 1H), 4.05 (dd, *J* = 12.3, 7.4 Hz, 1H), 3.79 (s, 1H), 3.59 (s, 3H), 2.35 (s, 3H), 2.08 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5, 154.7, 144.3, 136.3, 136.1, 135.4, 133.8, 131.1, 129.8, 128.2, 127.3, 127.2, 127.1, 122.1, 121.8, 120.4, 115.1, 75.4, 74.7, 55.5, 42.7, 21.5, 19.4; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{26}N_2O_7S]^+$: 521.1353, found: 521.1350; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 33.82 min and t_{minor} = 27.24 min.

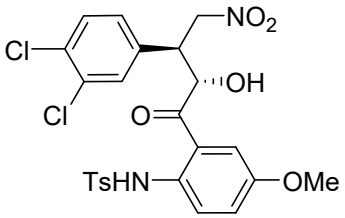
***N*-(2-(2-hydroxy-3-(2-methoxyphenyl)-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cp):**



3cp

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (90 mg, 88% yield, 10:1 dr); $[\alpha]_D^{20}$ = 29.6 (c = 1.0, DCM, 94% ee); **m.p.** = 95.3–96.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.71 (t, *J* = 8.9 Hz, 3H), 7.28 (d, *J* = 2.8 Hz, 1H), 7.24–7.18 (m, 3H), 7.08–7.04 (m, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.84–6.77 (m, 2H), 5.24 (s, 1H), 4.73 (dd, *J* = 13.8, 8.7 Hz, 1H), 4.38 (d, *J* = 6.1 Hz, 1H), 4.16 (s, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.66 (d, *J* = 6.4 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.1, 156.5, 154.8, 144.4, 136.5 133.3, 129.8, 129.3, 128.6, 127.3, 124.4, 121.8, 121.1, 121.0, 120.6, 117.4, 110.9, 73.7, 73.3, 55.7, 55.4, 42.9, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{26}N_2O_8S]^+$:537.1302, found: 537.1306; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 14.19 min and t_{minor} = 13.02 min.

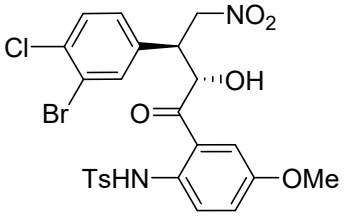
***N*-(2-(3-(3,4-dichlorophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cq):**



3cq

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a orange solid (92 mg, 83% yield, 5:1 dr); $[\alpha]_D^{20}$ = 49.7 (c = 1.0, DCM, 93% ee); **m.p.** = 84.9–86.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.26–7.19 (m, 3H), 7.16–7.10 (m, 1H), 7.03–6.99 (m, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 5.12 (s, 1H), 4.55 (dd, *J* = 13.9, 9.3 Hz, 1H), 4.36 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.86 (s, 1H), 3.74 (s, 3H), 3.63–3.55 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 155.2, 144.6, 137.3, 136.3, 133.4, 133.3, 132.9, 131.2, 130.0, 129.9, 127.3, 127.2, 123.0, 121.8, 120.8, 115.1, 74.8, 74.7, 55.7, 47.1, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{22}Cl_2N_2O_7S]^+$: 575.0417, found: 575.0420; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 28.162 min and t_{minor} = 25.732 min.

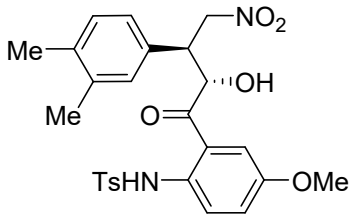
***N*-(2-(3-(3-bromo-4-chlorophenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cr):**



3cr

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (99 mg, 83% yield, 7:1 dr); $[\alpha]_D^{20}$ = 5.8 (c = 1.0, DCM, 80% ee); **m.p.** = 78.4–80.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.23 (s, 2H), 7.15–7.10 (m, 1H), 7.08–7.04 (m, 1H), 6.77 (d, *J* = 2.8 Hz, 1H), 5.11 (s, 1H), 4.54 (dd, *J* = 13.9, 9.2 Hz, 1H), 4.36 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.83 (d, *J* = 5.9 Hz, 1H), 3.74 (s, 3H), 3.60 – 3.54 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.4, 155.2, 144.6, 137.4, 136.3, 133.4, 133.2, 131.0, 129.8, 127.9, 127.3, 123.0, 121.9, 120.7, 115.0, 74.8, 74.7, 55.7, 47.0, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{22}BrClN_2O_7S]^+$: 618.9912, found: 618.9909; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 24.404 min and t_{minor} = 23.146 min.

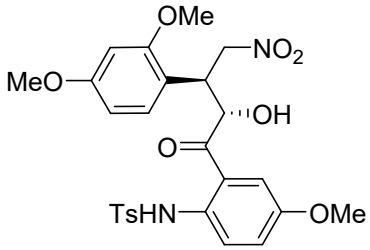
***N*-(2-(3-(3,4-dimethylphenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cs):**



3cs

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (82 mg, 80% yield, 7:1 dr); $[\alpha]_D^{20}$ = 25.9 (c = 1.0, DCM, 90% ee); **m.p.** = 105.5–106.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.78–7.70 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10–7.06 (m, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.90–6.84 (m, 2H), 6.79 (d, *J* = 2.9 Hz, 1H), 5.16–5.10 (m, 1H), 4.56 (dd, *J* = 13.8, 8.6 Hz, 1H), 4.45 (dd, *J* = 13.8, 6.4 Hz, 1H), 3.75 (d, *J* = 6.2 Hz, 1H), 3.66 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 154.9, 144.4, 137.6, 137.0, 136.4, 134.5, 133.7, 130.4, 129.8, 129.0, 127.3, 125.1, 122.3, 122.27, 120.5, 114.7, 75.4, 75.3, 55.5, 47.7, 21.5, 19.7, 19.4; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{26}H_{28}N_2O_7S]^+$: 535.1509, found: 535.1516; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 12.65 min and t_{minor} = 11.63 min.

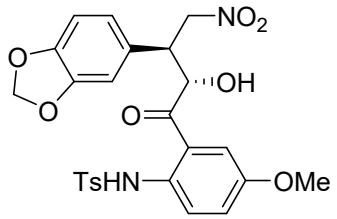
***N*-(2-(3-(2,4-dimethoxyphenyl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ct):**



3ct

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a deep yellow solid (93 mg, 85% yield, 5:1 dr); $[\alpha]_D^{20}$ = 46.8 (c = 1.0, DCM, 99% ee); **m.p.** = 76.9–78.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.75–7.68 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 3H), 7.08–7.03 (m, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 2.3 Hz, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 5.20 (s, 1H), 4.71 (dd, *J* = 13.6, 8.9 Hz, 1H), 4.35 (dd, *J* = 13.6, 6.0 Hz, 1H), 4.04 (s, 1H), 3.85 (s, 3H), 3.74 (d, *J* = 0.7 Hz, 6H), 3.60 (d, *J* = 6.5 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.3, 160.7, 157.6, 154.8, 144.3, 136.5, 133.2, 129.7, 129.3, 127.3, 121.7, 121.1, 120.4, 117.5, 116.5, 104.6, 99.0, 74.0, 73.5, 55.7, 55.4, 42.9, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{26}H_{28}N_2O_9S]^+$: 567.1408, found: 567.1419; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 59.23 min.

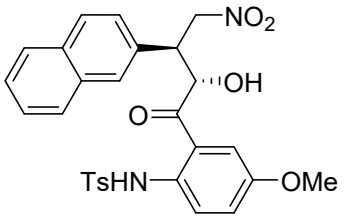
***N*-(2-(3-(benzo[d][1,3]dioxol-5-yl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cu):**



3cu

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (95 mg, 90% yield, 6:1 dr); $[\alpha]_D^{20}$ = 33.6 (c = 1.0, DCM, 91% ee); **m.p.** = 95.4–96.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.13–7.08 (m, 1H), 6.85 (d, *J* = 2.8 Hz, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.52–6.48 (m, 1H), 5.92 (s, 2H), 5.13 (d, *J* = 1.3 Hz, 1H), 4.53 (dd, *J* = 13.6, 9.0 Hz, 1H), 4.39 (dd, *J* = 13.7, 6.0 Hz, 1H), 3.79 (s, 1H), 3.71 (s, 3H), 3.60–3.54 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.2, 155.0, 148.3, 147.7, 144.5, 136.3, 133.6, 130.6, 129.8, 127.3, 122.5, 122.2, 121.5, 120.7, 114.9, 108.7, 107.9, 101.4, 75.5, 75.3, 55.6, 47.8, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{24}N_2O_9S]^+$: 551.1095, found: 551.1092; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 51.47 min and t_{minor} = 43.07 min.

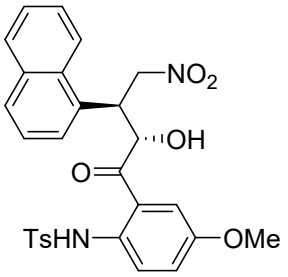
***N*-(2-(2-hydroxy-3-(naphthalen-2-yl)-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cv):**



3cv

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale orange solid (99 mg, 93% yield, 8:1 dr); $[\alpha]_D^{20}$ = 74.5 (c = 1.0, DCM, 92% ee); **m.p.** = 110.2–111.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.78–7.68 (m, 6H), 7.54 (s, 1H), 7.50–7.45 (m, 2H), 7.32–7.27 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.01–6.95 (m, 1H), 6.78 (d, *J* = 2.7 Hz, 1H), 5.25 (s, 1H), 4.70 (dd, *J* = 13.8, 8.7 Hz, 1H), 4.58 (dd, *J* = 13.9, 6.2 Hz, 1H), 3.89 (s, 1H), 3.85–3.79 (m, 1H), 3.50 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.2, 154.9, 144.5, 136.3, 134.5, 133.5, 133.3, 133.0, 129.8, 129.3, 127.8, 127.7, 127.4, 127.3, 126.7, 126.6, 125.1, 122.4, 122.1, 120.7, 114.9, 75., 75.2, 55.4, 48.1, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{26}N_2O_7S]^+$: 557.1353, found: 557.1356; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 47.440 min and t_{minor} = 39.195 min.

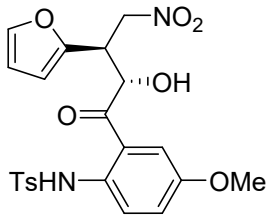
***N*-(2-(2-hydroxy-3-(naphthalen-1-yl)-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cw):**



3cw

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a pale yellow solid (102 mg, 96% yield, 10:1 dr); $[\alpha]_D^{20}$ = 8.0 (c = 1.0, DCM, 89% ee); **m.p.** = 102.7–103.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.92–7.74 (m, 6H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.51 (s, 3H), 7.29–7.24 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.83 (s, 1H), 5.34 (s, 1H), 4.80 (s, 1H), 4.65 (s, 2H), 4.01 (s, 1H), 3.39 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.2, 154.8, 144.3, 136.3, 130.8, 129.8, 129.4, 127.4, 127.2, 126.2, 125.6, 122.8, 121.8, 114.1, 77.3, 74.8, 55.2, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{26}N_2O_7S]^+$: 557.1353, found: 557.1351; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 34.87 min and t_{minor} = 16.90 min.

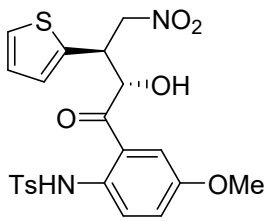
***N*-(2-(3-(furan-2-yl)-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cx):**



3cx

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (79 mg, 83% yield, 2:1 dr); $[\alpha]_D^{20}$ = 22.3 (c = 1.0, DCM, 92% ee); **m.p.** = 86.9–87.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.76–7.68 (m, 3H), 7.26–7.17 (m, 3H), 7.09–7.05 (m, 1H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 5.85 (d, *J* = 3.3 Hz, 1H), 5.28 (s, 1H), 4.70 (dd, *J* = 13.8, 8.8 Hz, 1H), 4.58 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.83–3.77 (m, 1H), 3.75 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.2, 155.1, 148.7, 144.4, 142.7, 136.4, 133.3, 129.8, 127.3, 122.3, 122.3, 121.0, 114.7, 110.7, 108.6, 73.6, 72.5, 55.6, 42.7, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{22}H_{22}N_2O_8S]^+$: 497.0989, found: 495.0987; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 35.56 min and t_{minor} = 26.75 min.

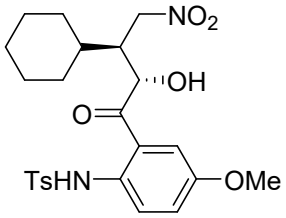
***N*-(2-(2-hydroxy-4-nitro-3-(thiophen-2-yl)butanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cy):**



3cy

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (78 mg, 80% yield, 6:1 dr); $[\alpha]_D^{20}$ = 15.9 (c = 1.0, DCM, 93% ee); **m.p.** = 92.9–93.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.23–7.17 (m, 3H), 7.16–7.10 (m, 1H), 6.98 (d, *J* = 2.9 Hz, 1H), 6.89–6.82 (m, 2H), 5.23 (s, 1H), 4.56 (dd, *J* = 13.8, 8.7 Hz, 1H), 4.35 (dd, *J* = 13.8, 5.7 Hz, 1H), 4.07 (dd, *J* = 8.1, 4.5 Hz, 1H), 3.75 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.7, 155.2, 144.5, 138.5, 136.3, 133.7, 129.8, 127.3, 126.7, 125.9, 122.7, 120.6, 114.4, 75.5, 75.0, 55.7, 43.5, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{22}H_{22}N_2O_7S_2]^+$: 513.0760, found: 513.0757; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 42.390 min and t_{minor} = 32.131 min.

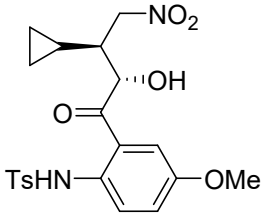
***N*-(2-(3-cyclohexyl-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cz):**



3cz

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (68 mg, 70% yield, 5:1 dr); $[\alpha]_D^{20}$ = 18.9 (c = 1.0, DCM, 94% ee); **m.p.** = 81.5–82.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.16–7.11 (m, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 5.22 (s, 1H), 4.24 (dd, *J* = 14.3, 6.5 Hz, 1H), 4.01 (dd, *J* = 14.3, 5.5 Hz, 1H), 3.80 (s, 3H), 3.63 (d, *J* = 5.0 Hz, 1H), 2.52 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H), 1.93 (d, *J* = 9.5 Hz, 1H), 1.80 (d, *J* = 9.4 Hz, 3H), 1.71 (d, *J* = 11.6 Hz, 1H), 1.28–1.13 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.6, 154.8, 144.3, 136.2, 134.1, 129.7, 127.3, 122.1, 119.7, 114.7, 72.7, 72.0, 55.7, 46.6, 40.2, 30.9, 30.1, 26.4, 26.1, 21.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{30}N_2O_7S]^+$: 513.1666, found: 513.1670; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 35.34 min and t_{minor} = 33.23 min.

***N*-(2-(3-cyclopropyl-2-hydroxy-4-nitrobutanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cza):**

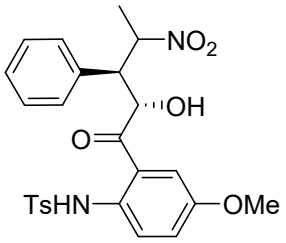


3cza

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (65 mg, 73% yield, 6:1 dr); $[\alpha]_D^{20}$ = 8.2 (c = 1.0, DCM, 98% ee); **m.p.** = 76.4–77.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.81 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.17–7.10 (m, 2H), 5.26 (s, 1H), 4.37 (dd, *J* = 12.9, 7.3 Hz, 1H), 3.98 (dd, *J* = 12.9, 5.5 Hz, 1H), 3.80 (s, 3H), 3.53 (d, *J* = 6.2 Hz, 1H), 2.33 (s, 3H), 1.06–0.97 (m, 1H), 0.64–0.55 (m, 1H), 0.50–0.41 (m, 1H), 0.19

(dd, *J* = 9.7, 4.8 Hz, 1H), 0.15–0.08 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.0, 155.0, 144.4, 136.4, 133.8, 129.7, 127.2, 122.3, 122.0, 120.6, 114.9, 74.9, 74.0, 55.7, 48.2, 21.5, 12.6, 5.0, 4.1; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{24}N_2O_7S]^+$: 471.1196, found: 471.1198; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 49.943 min and t_{minor} = 37.109 min.

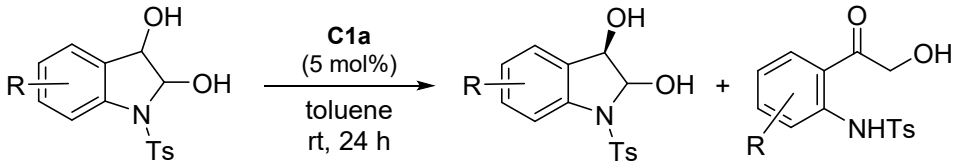
***N*-(2-((2S,3S)-2-hydroxy-4-nitro-3-phenylpentanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3czb):**



3czb

Obtained after purification by column chromatography (DCM/acetone = 60/1) as a yellow solid (87 mg, 88% yield, 6:1 dr); $[\alpha]_D^{20}$ = 6.2 (c = 1.0, DCM, 52% ee); **m.p.** = 96.3–97.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 3H), 7.26–7.20 (m, 4H), 7.08–7.04 (m, 1H), 6.76 (d, *J* = 2.9 Hz, 1H), 5.16 (dd, *J* = 5.7, 3.3 Hz, 1H), 5.08 (dd, *J* = 10.0, 6.9 Hz, 1H), 3.91 (d, *J* = 5.7 Hz, 1H), 3.62 (s, 3H), 3.55 (dd, *J* = 10.0, 3.2 Hz, 1H), 2.35 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 154.5, 144.0, 138.1, 136.3, 134.0, 129.7, 129.5, 128.5, 128.4, 127.7, 122.1, 121.2, 119.7, 114.5, 82.2, 76.1, 55.5, 52.9, 21.6, 19.4; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{26}N_2O_7S]^+$: 521.1353, found: 521.1350; **HPLC**: Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 35.064 min and t_{minor} = 27.734 min.

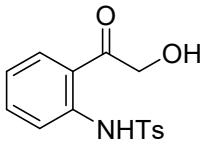
General Procedure for 4



1a-1f **1'** **4**

In a flame-dried Schlenk tube, a solution of diethylzinc (40 uL, 1.0 mol/L in hexane, 0.04 mmol) was added to a solution of the chiral ligand (*S,S*)-**La** (0.02 mmol 14.1 mg) in dry toluene (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Thus, the preparation of **C2a** was finished. Then, **1a** (0.2 mmol, 61.2 mg) were added. The reaction mixture was stirred for 24 h at room temperature. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum DCM/acetone = 50/1 to afford the desired product **4** and **1'**.

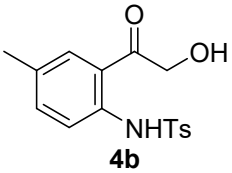
***N*-(2-(2-hydroxyacetyl)phenyl)-4-methylbenzenesulfonamide (4a):**



4a

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (29 mg, 48% yield); **m.p.** = 112.4–113.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 3H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.78 (s, 2H), 3.38 (s, 1H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.2, 144.2, 140.3, 136.3, 135.9, 129.8, 129.4, 127.3, 122.9, 119.3, 119.0, 65.4, 21.6; **HRMS** (ESI): m/z [M - H]$^-$ calcd for $[C_{15}H_{15}NO_4S]^-$: 304.0649, found: 304.0647.

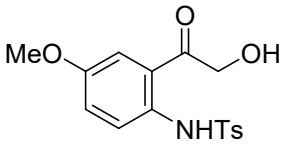
***N*-(2-(2-hydroxyacetyl)-4-methylphenyl)-4-methylbenzenesulfonamide (4b):**



4b

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (29 mg, 45% yield); **m.p.** = 98.3–99.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 1H), 7.22 (d, *J* = 20.3 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.66 (s, 2H), 3.32 (s, 1H), 2.29 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.2, 144.1, 137.7, 136.8, 136.3, 132.9, 130.2, 129.7, 129.5, 127.3, 119.8, 119.3, 65.4, 21.6, 20.7; **HRMS** (ESI): m/z [M - H]$^-$ calcd for $[C_{16}H_{17}NO_4S]^-$: 318.0805, found: 318.0810;

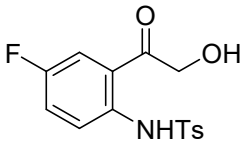
***N*-(2-(2-hydroxyacetyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (4c):**



4c

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (31 mg, 46% yield); **m.p.** = 103.4–105.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.66 (d, *J* = 9.1 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.19 (s, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 9.1 Hz, 1H), 6.93 (s, 1H), 4.54 (s, 2H), 3.72 (s, 3H), 3.20 (s, 1H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.0, 155.6, 144.0, 136.0, 132.7, 130.2, 129.6, 127.4, 127.2, 123.2, 121.6, 121.1, 114.0, 65.4, 55.8, 21.6; **HRMS** (ESI): m/z [M - H]$^-$ calcd for $[C_{16}H_{17}NO_5S]^-$: 334.0754, found: 334.0756;

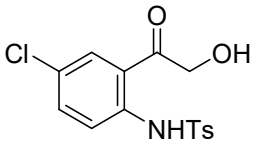
***N*-(4-fluoro-2-(2-hydroxyacetyl)phenyl)-4-methylbenzenesulfonamide (4d):**



4d

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (30 mg, 47% yield); **m.p.** = 112.5–113.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.81– 7.76 (m, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 4.7 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 3H), 4.68 (s, 2H), 3.25 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 157.7 (d, *J* = 245.7 Hz), 144.4, 136.3, 135.9, 129.8, 127.25, 123.4, 123.1, 122.4 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 23.3 Hz), 65.5, 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.31; **HRMS** (ESI): m/z [M - H]$^-$ calcd for $[C_{15}H_{14}FNO_4S]^-$: 322.0555, found: 322.0546;

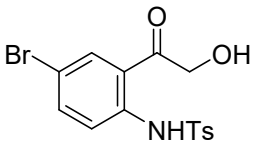
***N*-(4-chloro-2-(2-hydroxyacetyl)phenyl)-4-methylbenzenesulfonamide (4e):**



4e

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (33 mg, 48% yield); **m.p.** = 105.4–106.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.75–7.70 (m, 3H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.50–7.45 (m, 1H), 7.24 (s, 1H), 4.75 (s, 2H), 3.28 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 144.5, 138.7, 136.0, 135.8, 129.9, 129.0, 128.4, 127.3, 121.0, 120.1, 65.5, 21.6; **HRMS** (ESI): m/z [M - H]$^-$ calcd for $[C_{15}H_{14}ClNO_4S]^-$: 338.0259, found: 338.0257;

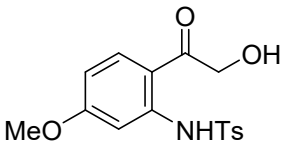
***N*-(4-bromo-2-(2-hydroxyacetyl)phenyl)-4-methylbenzenesulfonamide (4f):**



4f

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a yellow solid (33 mg, 43% yield); **m.p.** = 75.4–76.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.67–7.63 (m, 3H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.42–7.38 (m, 1H), 7.18 (d, *J* = 8.9 Hz, 2H), 4.67 (s, 2H), 3.24 (s, 1H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 144.6, 138.7, 135.8, 130.3, 129.9, 129.0, 127.3, 121.0, 120.1, 65.5, 21.6; **HRMS** (ESI): m/z $[M - H]^-$ calcd for $[C_{15}H_{14}BrNO_4S]^-$: 381.9754, found: 381.9752;

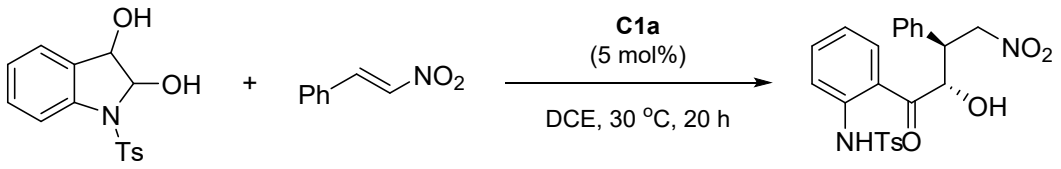
***N*-(2-(2-hydroxyacetyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (4g):**



4g

Obtained after purification by column chromatography (DCM/acetone = 50/1) as a white solid (33 mg, 43% yield); **m.p.** = 95.6–96.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.41 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 6.58–6.54 (m, 1H), 4.73 (d, *J* = 4.5 Hz, 2H), 3.84 (s, 3H), 3.48 (t, *J* = 4.6 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 165.3, 144.3, 143.1, 136.3, 131.5, 129.8, 127.3, 112.1, 109.7, 102.8, 64.8, 55.7, 21.6; **HRMS** (ESI): m/z $[M - H]^-$ calcd for $[C_{16}H_{17}NO_5S]^-$: 334.0754, found: 334.0753;

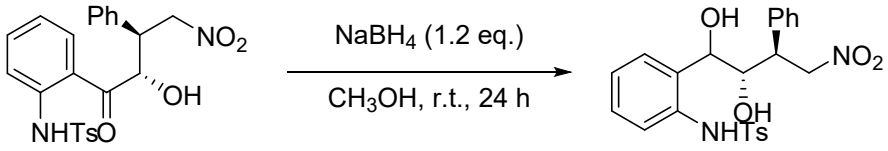
Gram-Scale Reaction



1a (2.5 mmol) **2a** (1 mmol) **3aa**

In a flame-dried Schlenk tube, a solution of diethylzinc (0.2 mL, 1.0 mol/L in hexane, 0.2 mmol) was added to a solution of the chiral ligand (*S,S*)-**La** (0.1 mmol 64 mg) in dry DCE (10 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Thus, the preparation of **C1a** was finished. Then, **1a** (2.5 mmol, 762 mg) and **2a** (1.0 mmol, 149 mg) were added. The reaction mixture was stirred for 20 h at 30 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum DCM/acetone = 50/1 to afford the desired product **3** in 75 yield (341mg, 92% ee).

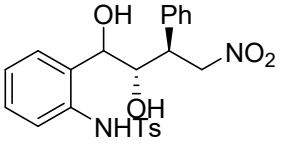
Derivatization of Product



3aa (92% ee) **5**: 82% yield, 89% ee

The mixture of **3aa** (45.4 mg, 0.1 mmol, 1.0 eq) and $NaBH_4$ (4.3 mg, 0.12 mmol, 1.2 eq) were add to the CH_3OH (3 mL) at 0 °C. Then, the resulting reaction mixture was stirred at room temperature for 24 h. Upon completion as shown by TLC, saturated aqueous NH_4Cl (3 mL) was then added to quench the reaction. The organic layer was extracted with DCM (3 x 5 mL), then washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified via column chromatography (petroleum ether/ethyl acetate = 1/1) on silica gel to afford pure product **5** as a white solid in 82% yield.

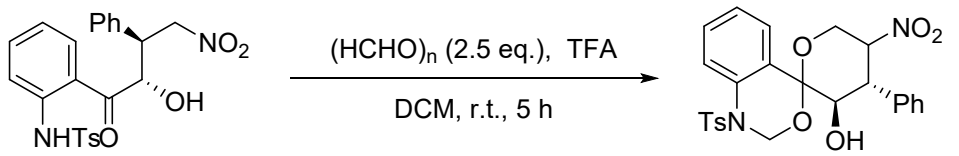
***N*-(2-((2S,3S)-1,2-dihydroxy-4-nitro-3-phenylbutyl)phenyl)-4-methylbenzenesulfonamide (5):**



5

White solid in 82% isolated yield (37.4 mg); $[\alpha]_D^{20}$ = -21.3 (c = 1.0, DCM, 89% ee); **m.p.** = 50.2–51.4 °C; **^{1}H NMR** (400 MHz, DMSO) δ 9.48 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.35–7.29 (m, 4H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.24–7.20 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.15–7.08 (m, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.03 (s, 1H), 5.93 (s, 1H), 5.06 (dd, *J* = 13.3, 4.5 Hz, 1H), 4.88 (dd, *J* = 13.3, 10.9 Hz, 1H), 4.55 (d, *J* = 6.3 Hz, 1H), 3.90–3.82 (m, 1H), 3.60 (dd, *J* = 10.6, 4.7 Hz, 1H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 143.8, 139.4, 137.5, 135.9, 134.4, 130.2, 129.3, 128.9, 128.8, 128.2, 127.6, 127.4, 124.6, 121.4,

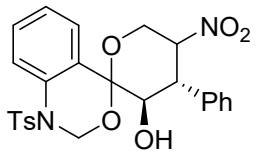
77.6, 76.8, 72.2, 46.3, 21.5; **HRMS** (ESI): m/z [M - H]$^-$ calcd for $[C_{23}H_{24}N_2O_6S]^+$: 455.1282 found: 455.1283; **HPLC**: Daicel Chiralpak IF, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 14.93 min and t_{minor} = 12.03 min.



3aa (92% ee) **6**: 76% yield, 90% ee

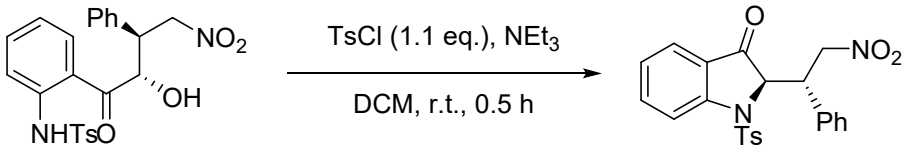
The mixture of **3aa** (45.4 mg, 0.1 mmol, 1.0 eq), (HCHO)n (25.2 mg ,0.25 mmol, 2.5 eq) and TFA (25.5 mg ,0.25mmol, 2.5 eq) were add to the DCM (2 mL) . Then, the resulting reaction mixture was stirred at room temperature for 24 h. Upon completion as shown by TLC, the solvent was evaporated and the mixture was directly purified by column chromatography on silica gel eluting with petroleum PE/EA = 4/1 to afford product 6 as a white solid in 76% yield.

(3'R,4'S)-5'-nitro-4'-phenyl-1-tosyl-1,2,3',4',5',6'-hexahydrospiro[benzo[d][1,3]oxazine-4,2'-pyran]-3'-ol (6):



6

yellow solid in 76% isolated yield (36.5 mg,); $[\alpha]_D^{20}$ = -42.7 (c = 1.0, DCM, 90% ee); **m.p.** = 45.2–46.4 °C; **^{1}H NMR** (400 MHz, DMSO) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 3H), 7.24 – 7.17 (m, 2H), 7.06 – 7.01 (m, 3H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.90 – 6.85 (m, 2H), 5.81 (d, *J* = 10.8 Hz, 1H), 5.22 (d, *J* = 14.3 Hz, 2H), 5.11 (dd, *J* = 13.4, 5.2 Hz, 1H), 4.99 – 4.88 (m, 2H), 4.44 (d, *J* = 6.3 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 145.0, 137.2, 136.9, 135.8, 130.7, 129.9, 128.8, 128.1, 128.0, 127.8, 127.6, 125.1, 123.7, 121.0, 101.7, 95.1, 85.5, 77.6, 72.3, 42.7, 21.5; **HRMS** (ESI): m/z [M + H]$^+$ calcd for $[C_{25}H_{24}N_2O_7S]^+$: 497.1382, found: 497.1390; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 12.13 min and t_{minor} = 13.90 min.

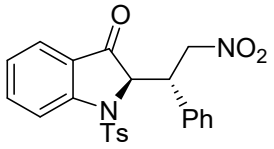


3aa (92% ee) **7**: 91% yield, 89% ee

The mixture of **3aa** (45.4mg, 0.1 mmol, 1.0 eq) and NEt_3 (0.5 mL) were add to the DCM (2 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Then, **TsCl** (42 mg, 0.11 mmol, 1.1 eq) were added. The reaction mixture was stirred for 0.5 h at room temperature. Upon completion as shown by TLC, saturated aqueous NH_4Cl (3 mL) was then added to quench the reaction. The organic layer was extracted with DCM (3 x 5 mL), then washed with brine, dried over Na_2SO_4 and concentrated

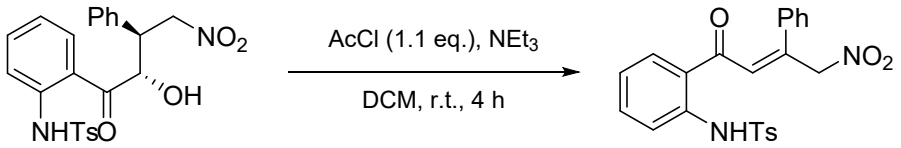
under reduced pressure. The crude reaction mixture was purified via column chromatography (petroleum ether/ethyl acetate = 1/1) on silica gel to afford pure product **7** as a yellow solid in 89% yield.

(R)-2-((S)-2-nitro-1-phenylethyl)-1-tosylindolin-3-one (7):



7

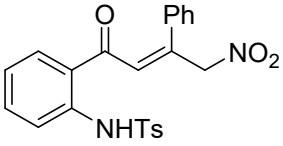
yellow solid in 91% isolated yield (39.7mg); $[\alpha]_D^{20}$ = -38.9 (c = 1.0, DCM, 89% ee); **m.p.** = 67.9–69.3°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.5 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.19 (s, 1H), 7.16–7.09 (m, 3H), 6.85–6.78 (m, 2H), 5.40–5.33 (m, 1H), 4.92 (d, *J* = 7.3 Hz, 1H), 3.48 (d, *J* = 6.0 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 147.3, 145.0, 139.3, 136.8, 135.3, 135.2, 131.0, 130.1, 129.8, 129.6, 128.4, 128.3, 128.6, 127.8, 127.6, 76.6, 53.7, 29.7, 21.7; **HRMS** (ESI): m/z $[M + H]^+$ calcd for $[C_{23}H_{20}N_2O_5S]^+$: 437.1166, found: 437.1170; **HPLC**: Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 26.49 min and t_{minor} = 34.79 min.



3aa (92% ee) **8**: 91% yield

The mixture of **3aa** (45.4 mg, 0.1 mmol, 1.0 eq) and NEt_3 (0.5 mL) were add to the DCM (2 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Then, **AcCl** (9 mg, 0.11 mmol, 1.1eq) were added. The reaction mixture was stirred for 4 h at room temperature. Upon completion as shown by TLC, saturated aqueous NH_4Cl (3 mL) was then added to quench the reaction. The organic layer was extracted with DCM (3 x 5 mL), then washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified via column chromatography (petroleum ether/ethyl acetate = 1/1) on silica gel to afford pure product **7** as a white solid in 91% yield.

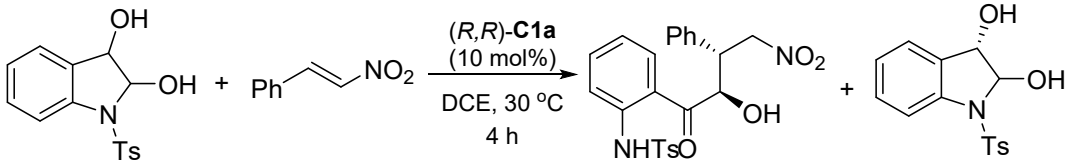
(E)-4-methyl-N-(2-(4-nitro-3-phenylbut-2-enoyl)phenyl)benzenesulfonamide (8):



8

White solid in 91% isolated yield (39.7 mg,); **m.p.** = 32.2–33.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.79–7.74 (m, 1H), 7.70 (d, *J* = 7.2 Hz, 3H), 7.54–7.48 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.90 (s, 1H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.6, 145.5, 144.0, 139.1, 136.3, 135.6, 134.5, 134.3, 131.7, 130.3, 129.5, 129.2, 128.8, 128.7, 128.6, 127.3, 125.4, 53.0, 21.5; **HRMS** (ESI): m/z $[M + H]^+$ calcd for $[C_{23}H_{20}N_2O_5S]^+$: 437.1166, found: 437.1168.

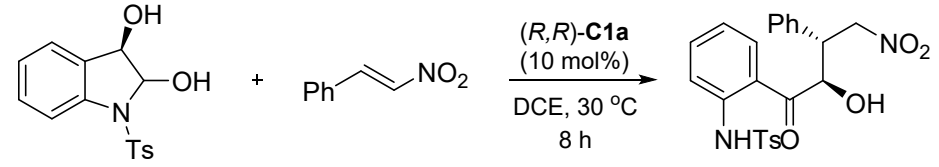
Control Experiment



1a **2a** *enti*-**3aa** 3*S*-**1a'**

90% yield, 3/1 dr, -92% ee 47% yield, -98% ee

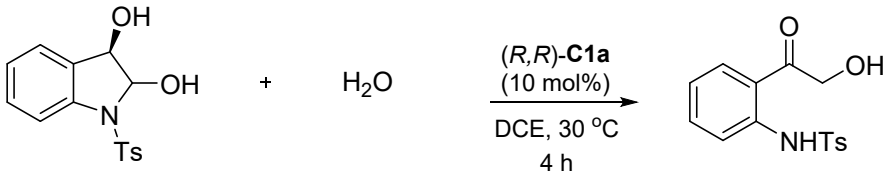
In a flame-dried Schlenk tube, a solution of diethylzinc (40 uL, 1.0 mol/L in hexane, 0.04 mmol) was added to a solution of the chiral ligand (*R,R*)-**La** (0.02 mmol 14.1 mg) in dry DCE (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Thus, the preparation of **C1a** was finished. Then, **1a** (0.5 mmol, 152.6 mg) and **2a** (0.2 mmol, 29.83 mg) were added. The reaction mixture was stirred for 4 h at 30 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum DCM/acetone = 50/1 to afford the desired product ***enti*-3aa** and **3*S*-1a'**.



3*R*-**1a'** (99% ee) **2a** *enti*-**3aa**

0.2 mmol 0.2 mmol 78% yield, 3/1 dr, 99% ee

In a flame-dried Schlenk tube, a solution of diethylzinc (40 uL, 1.0 mol/L in hexane, 0.04 mmol) was added to a solution of the chiral ligand (*R,R*)-**La** (0.02 mmol 14.1 mg) in dry DCE (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Thus, the preparation of **C1a** was finished. Then, **3*R*-1a'** (0.2 mmol, 61.5 mg) and **2a** (0.2 mmol, 29.83 mg) were added. The reaction mixture was stirred for 8 h at 30 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum DCM/acetone = 50/1 to afford the desired product ***enti*-3aa**.



3*R*-**1a'** (99% ee) 0.2 mmol **4a**: 93% yield

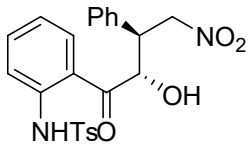
0.2 mmol

In a flame-dried Schlenk tube, a solution of diethylzinc (40 uL, 1.0 mol/L in hexane, 0.04 mmol) was added to a solution of the chiral ligand (*R,R*)-**La** (0.02 mmol 14.1 mg) in dry DCE (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Thus, the preparation of

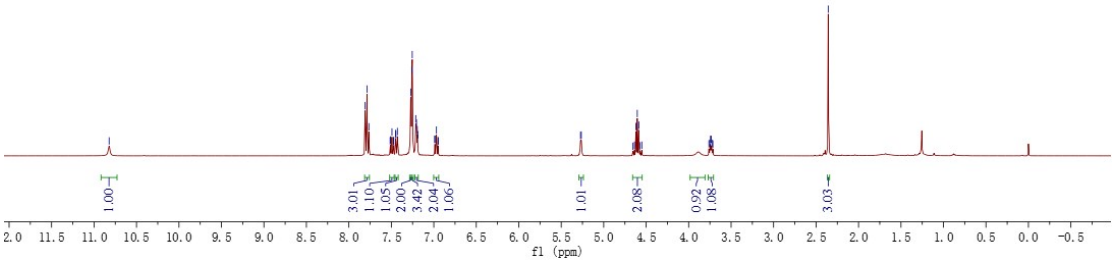
C1a was finished. Then, **3*R*-1a'** (0.2 mmol, 61.5 mg) and **H_2O** (0.2 mmol, 3.6 mg) were added. The reaction mixture was stirred for 4 h at 30 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum DCM/acetone = 50/1 to afford the desired product **4a**.

NMR Spectra of compounds 3, 4, 5, 6, 7 and 8

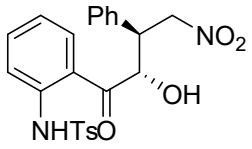
^{1}H NMR spectrum of compound **3aa** ($CDCl_3$, 400 MHz)



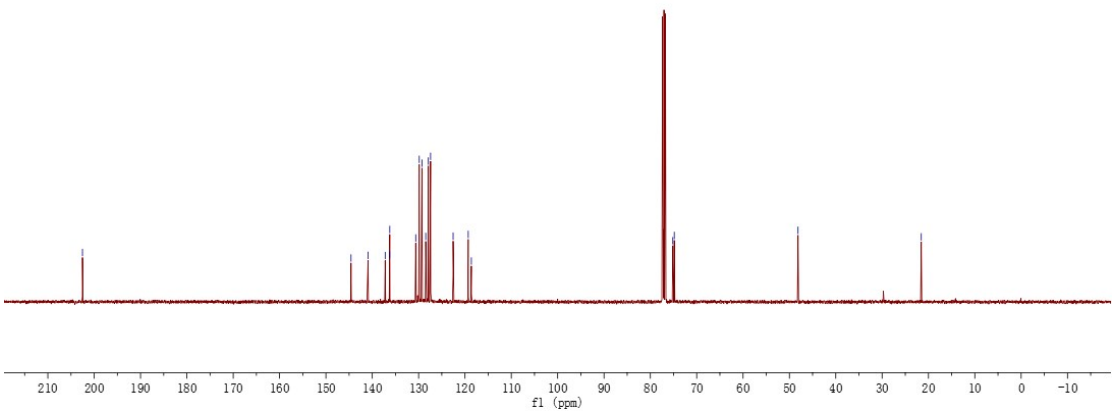
3aa



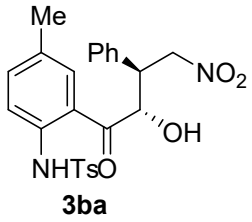
^{13}C NMR spectrum of compound **3aa** ($CDCl_3$, 400 MHz)



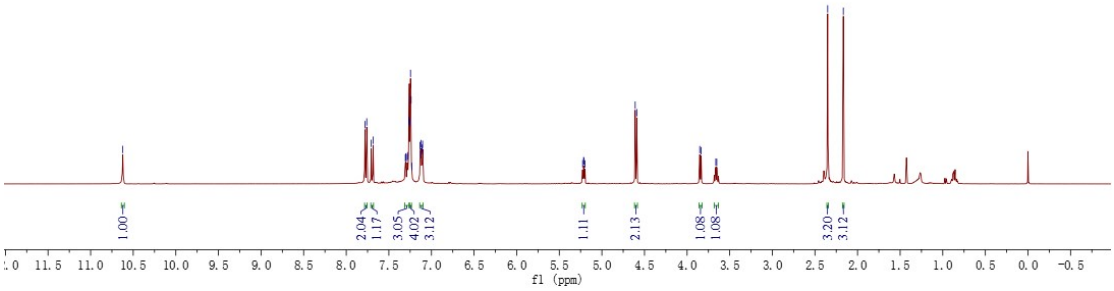
3aa



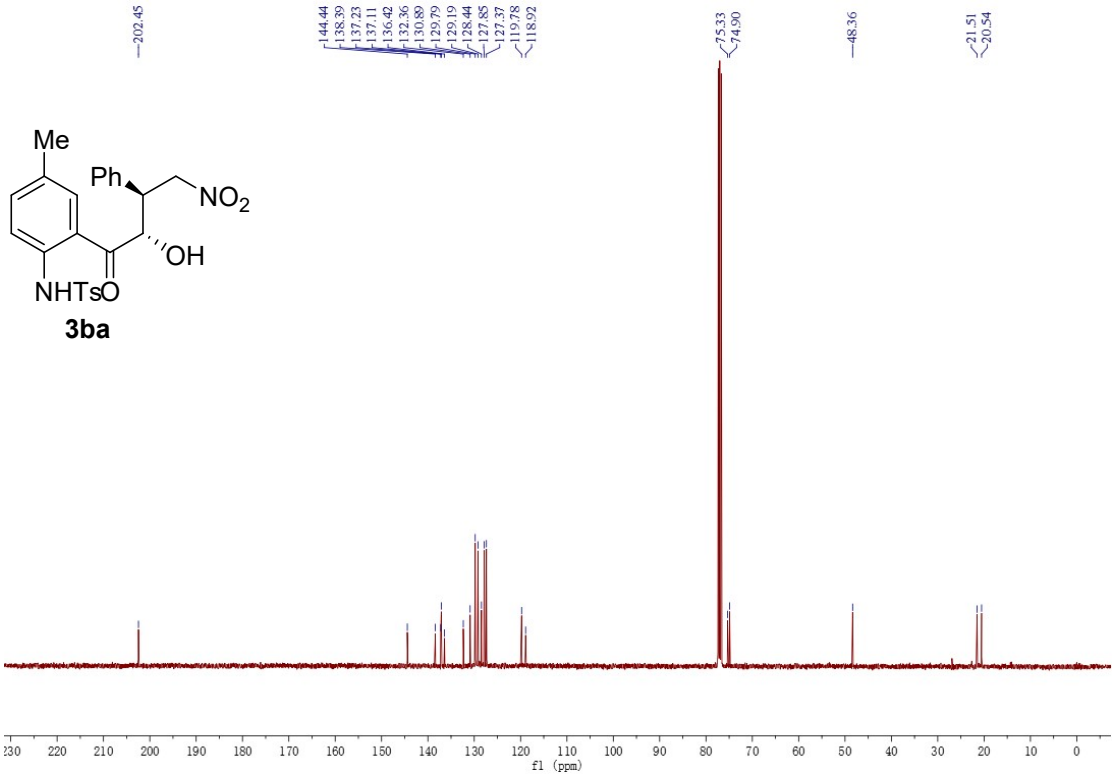
^{1}H NMR spectrum of compound **3ba** ($CDCl_3$, 400 MHz)



3ba

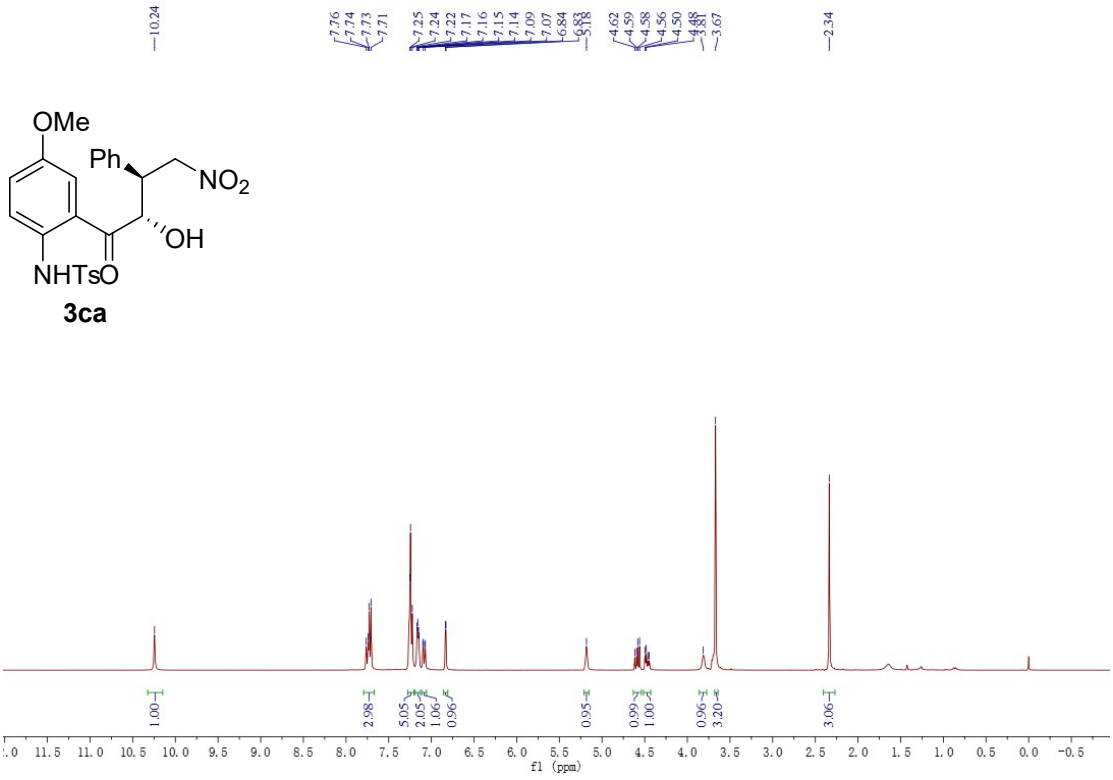


^{13}C NMR spectrum of compound **3ba** ($CDCl_3$, 400 MHz)

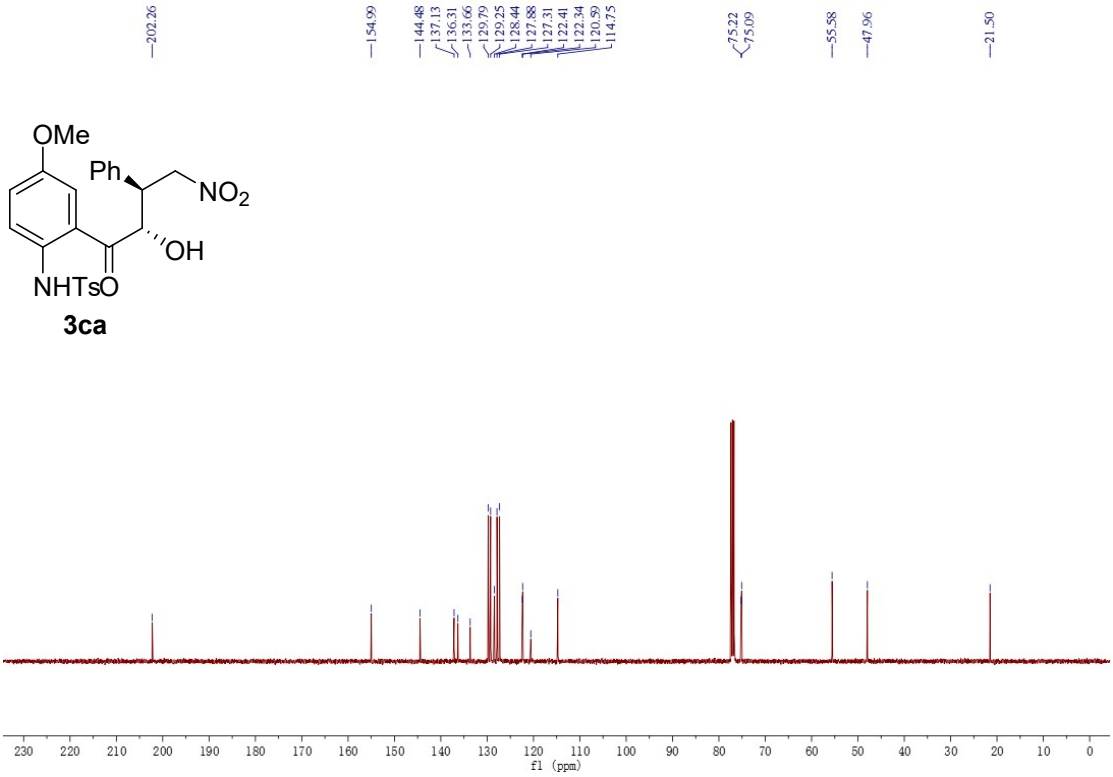


3ba

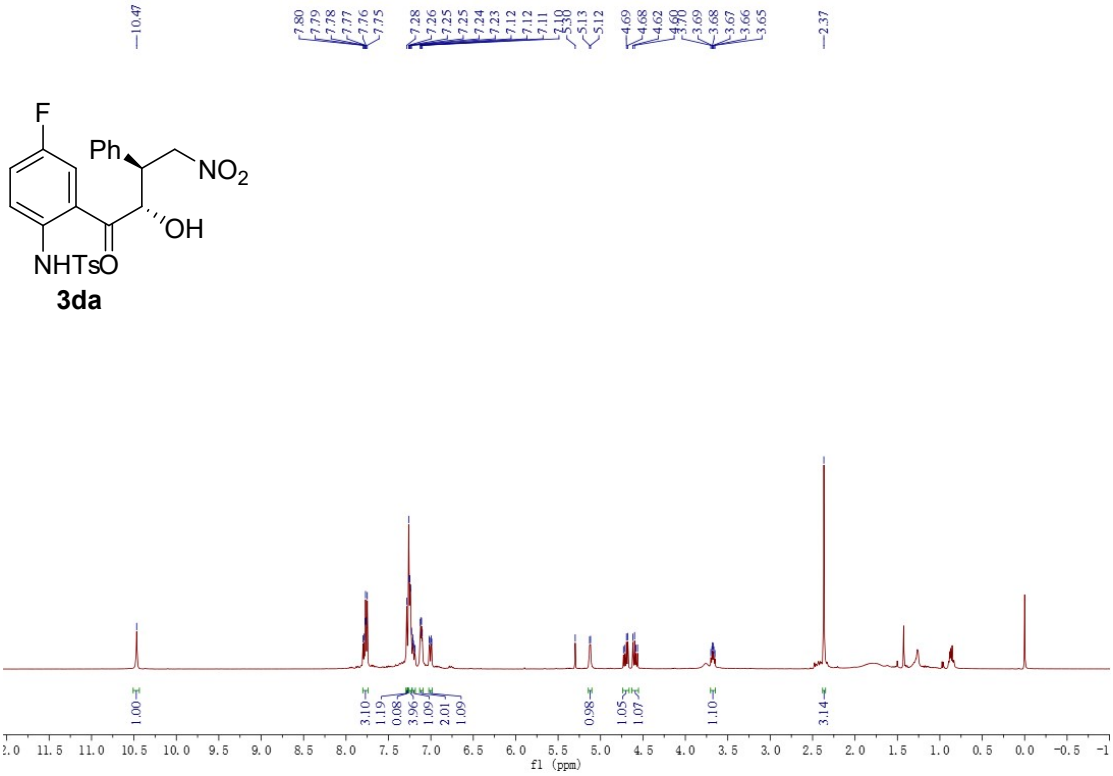
^{1}H NMR spectrum of compound **3ca** ($CDCl_3$, 400 MHz)



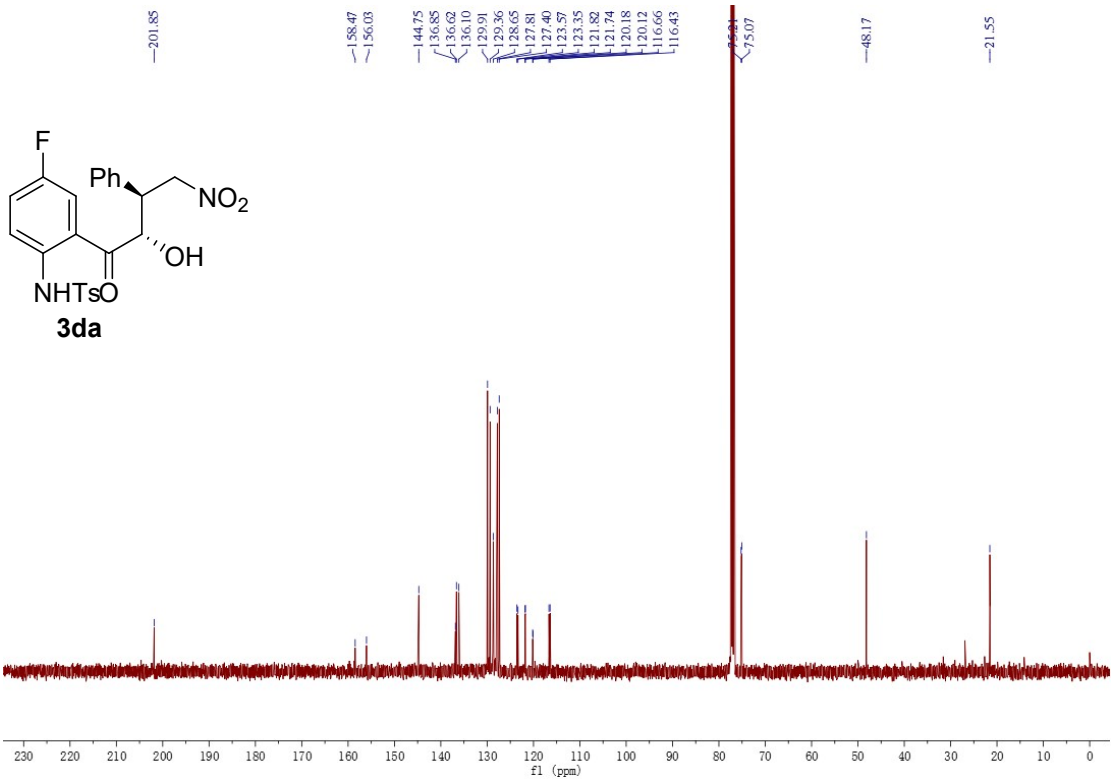
^{13}C NMR spectrum of compound **3ca** ($CDCl_3$, 400 MHz)



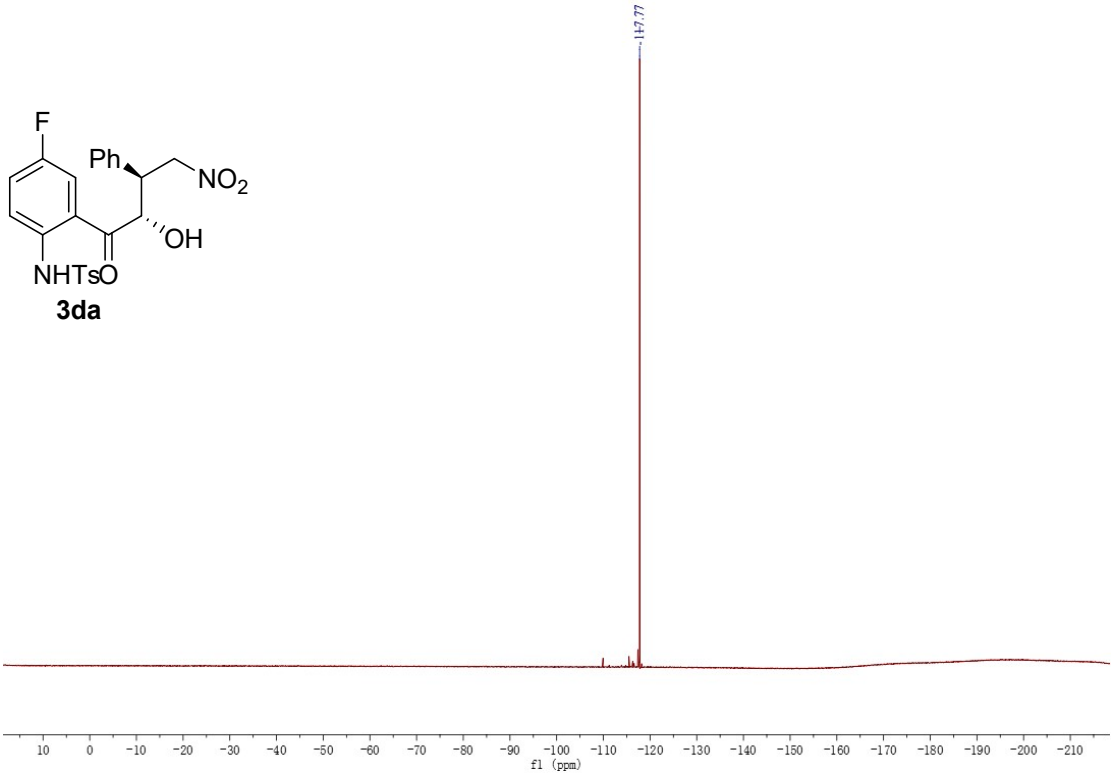
^{1}H NMR spectrum of compound **3da** ($CDCl_3$, 400 MHz)



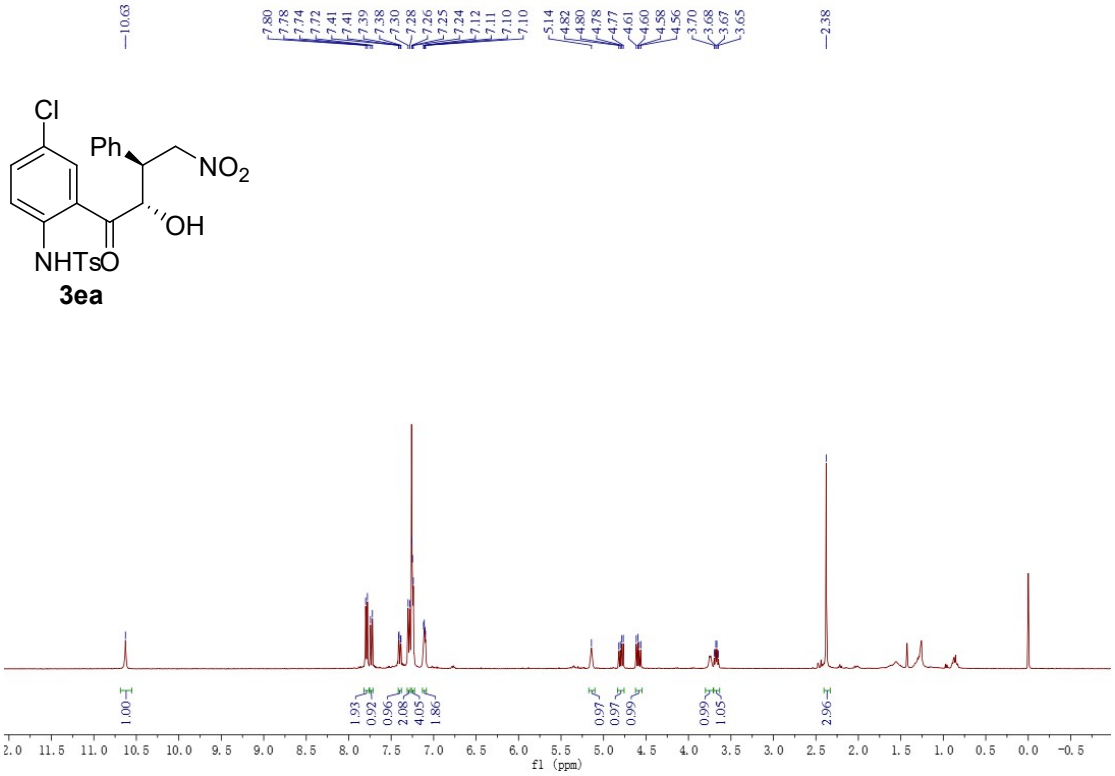
^{13}C NMR spectrum of compound **3da** ($CDCl_3$, 400 MHz)



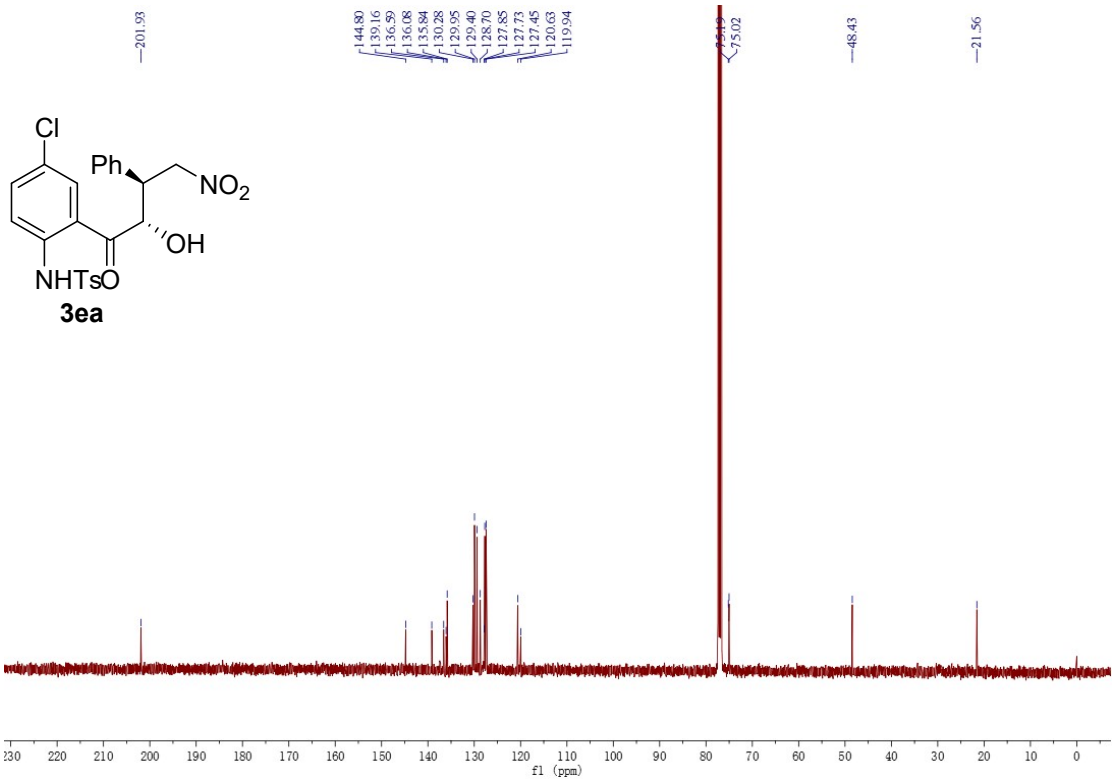
^{19}F NMR spectrum of compound **3da** ($CDCl_3$, 400 MHz)



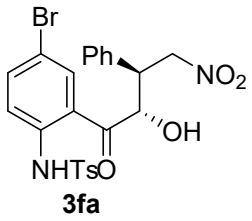
^{1}H NMR spectrum of compound **3ea** ($CDCl_3$, 400 MHz)



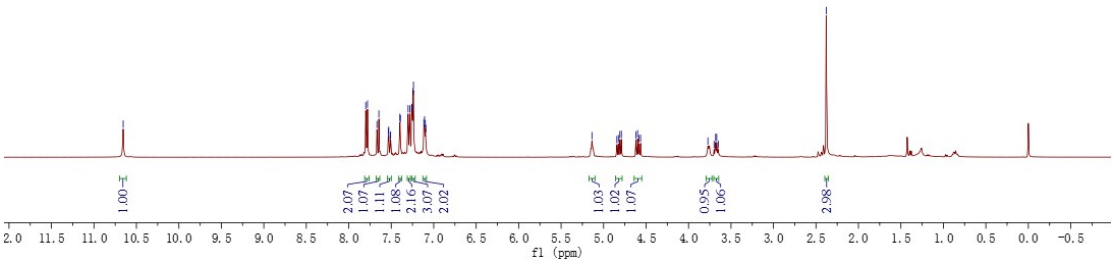
^{13}C NMR spectrum of compound **3ea** ($CDCl_3$, 400 MHz)



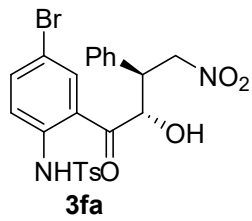
^{1}H NMR spectrum of compound **3fa** ($CDCl_3$, 400 MHz)



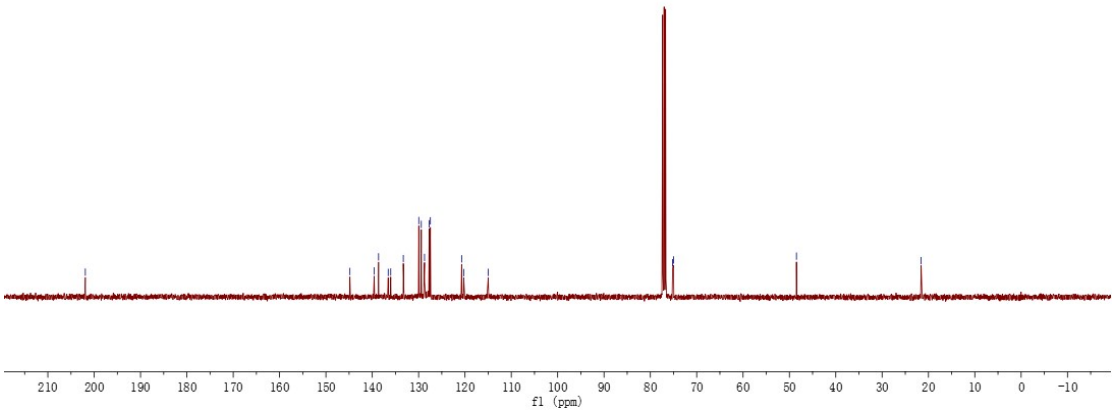
3fa



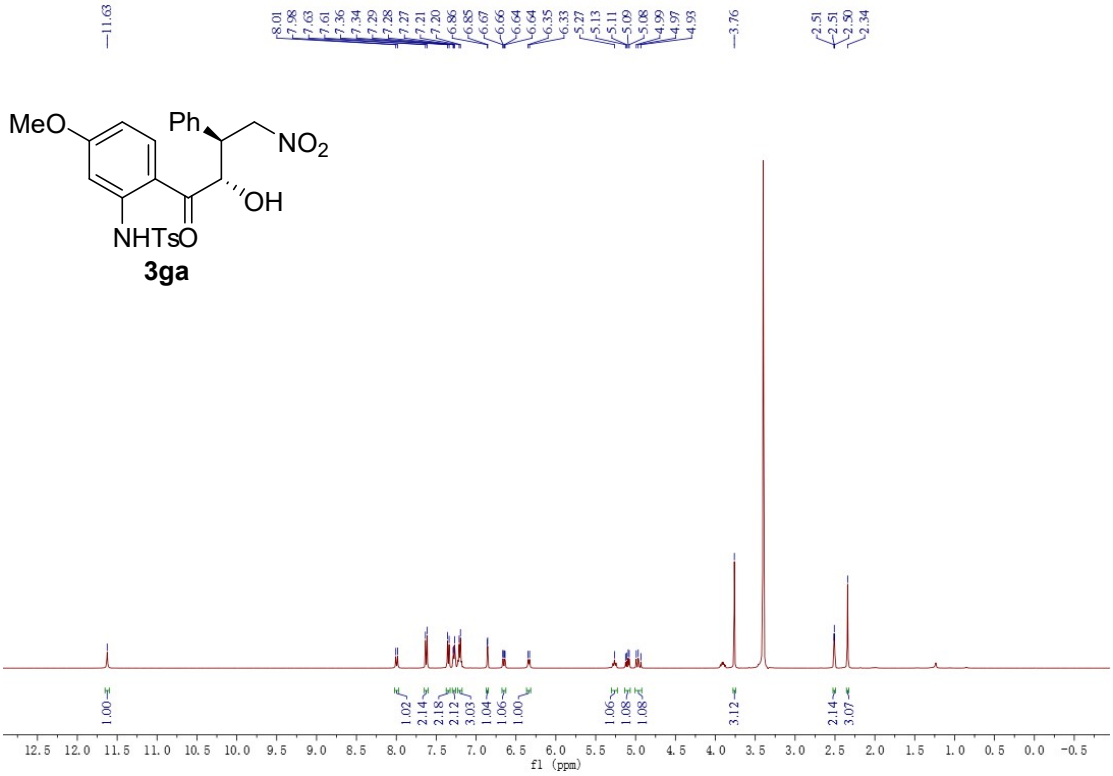
^{13}C NMR spectrum of compound **3fa** ($CDCl_3$, 400 MHz)



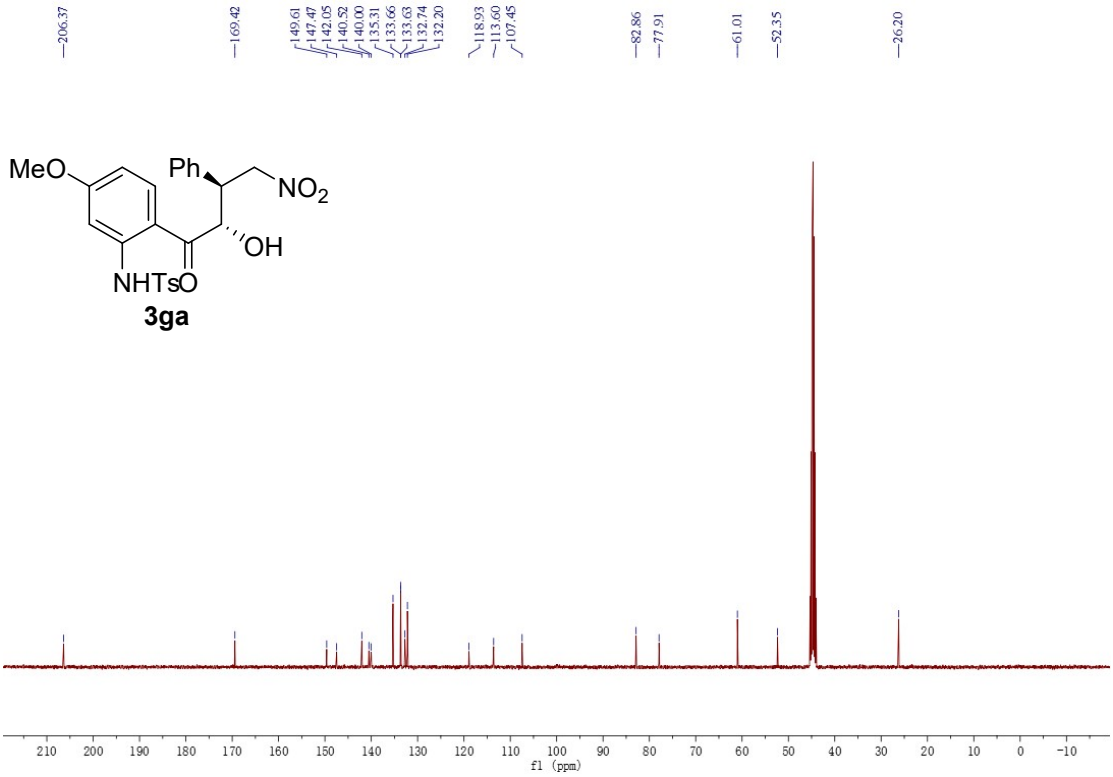
3fa



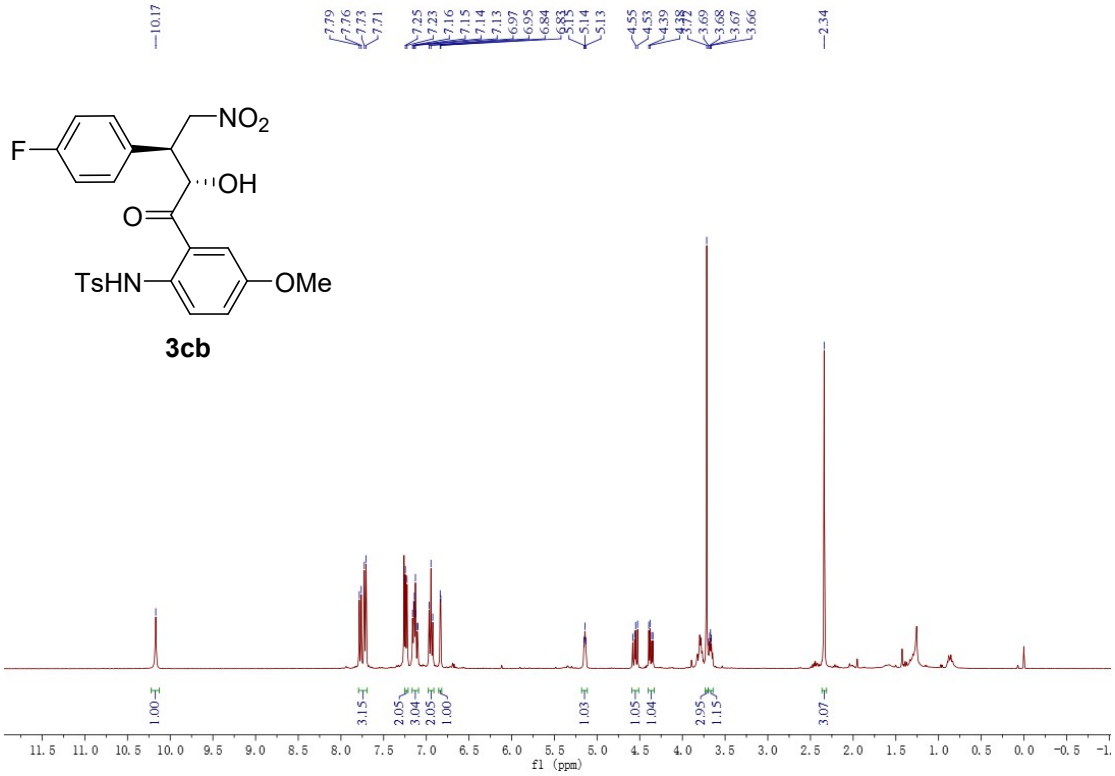
^{1}H NMR spectrum of compound **3ga** (DMSO, 400 MHz)



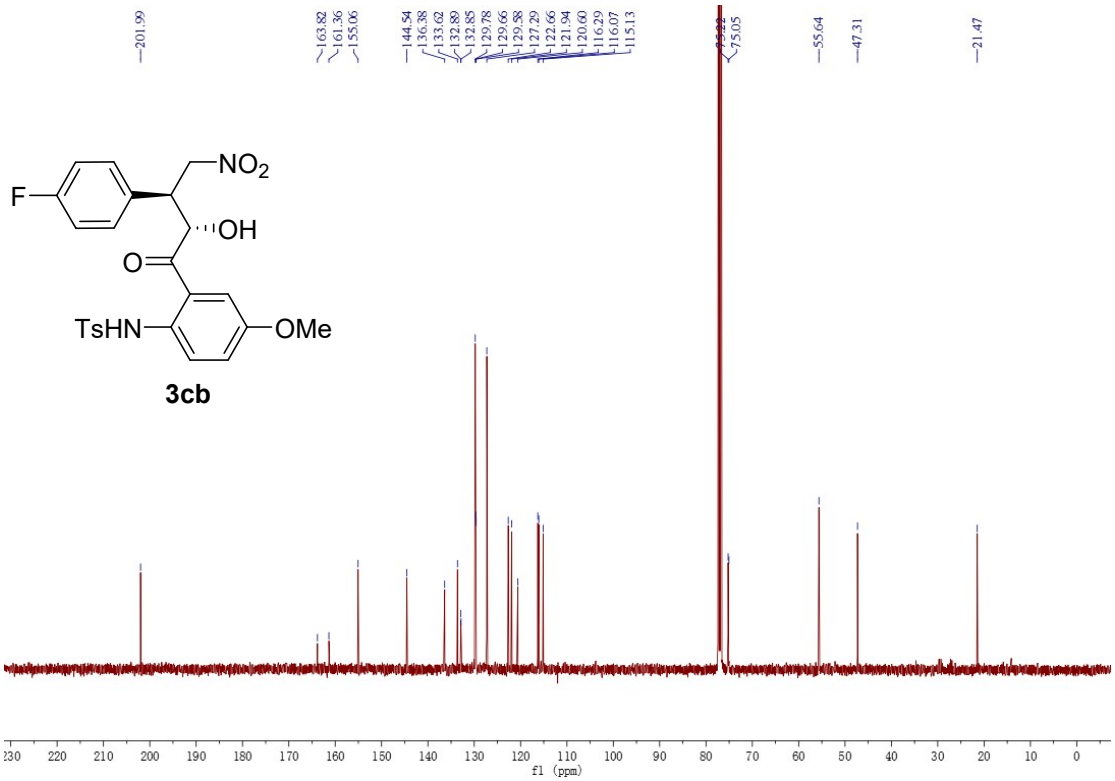
^{13}C NMR spectrum of compound **3ga** (DMSO, 400 MHz)



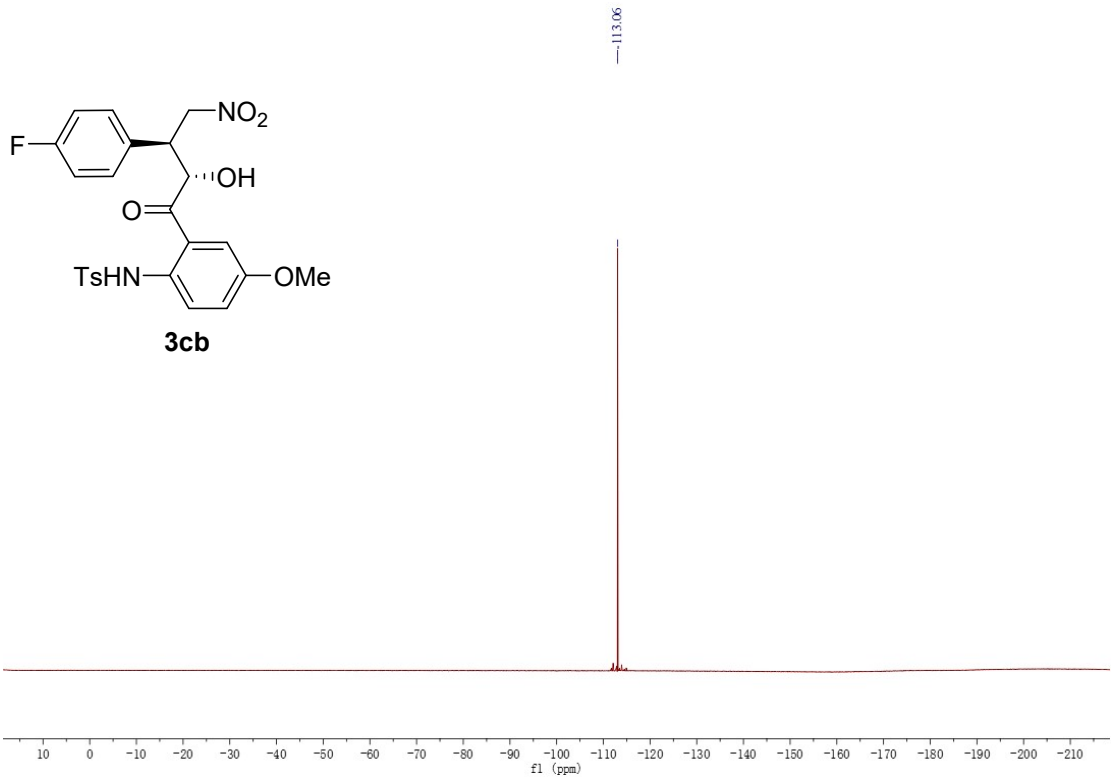
^{1}H NMR spectrum of compound **3cb** ($CDCl_3$, 400 MHz)



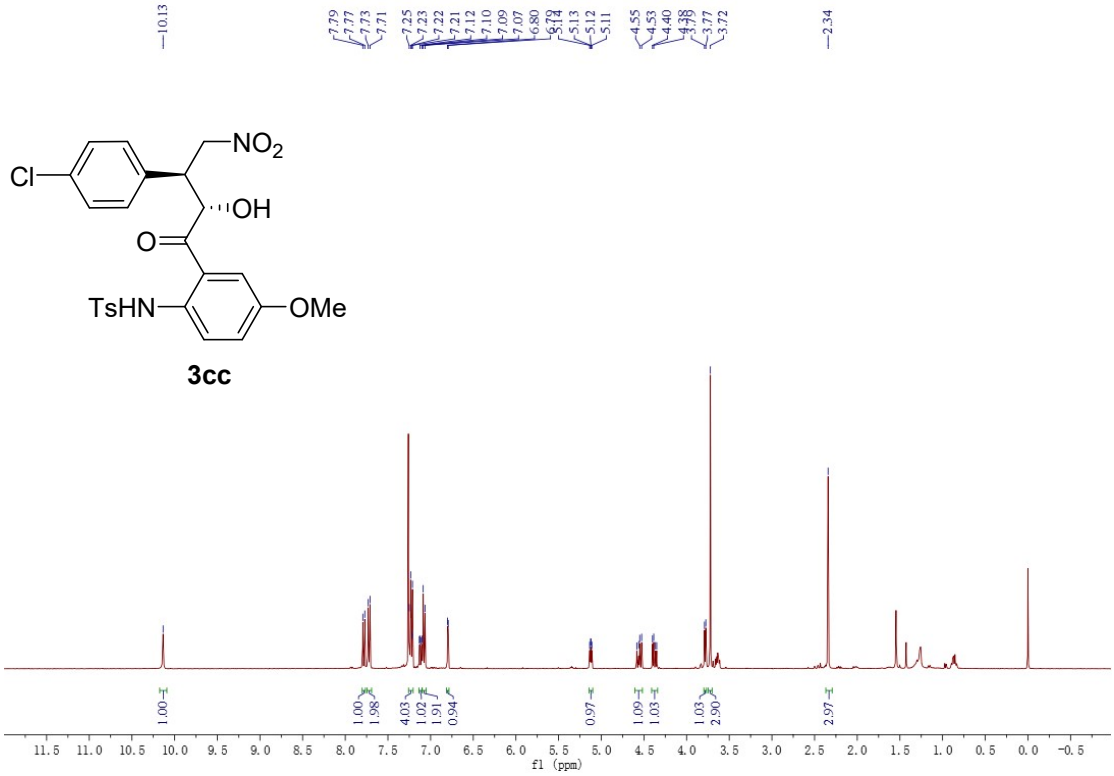
^{13}C NMR spectrum of compound **3cb** ($CDCl_3$, 400 MHz)



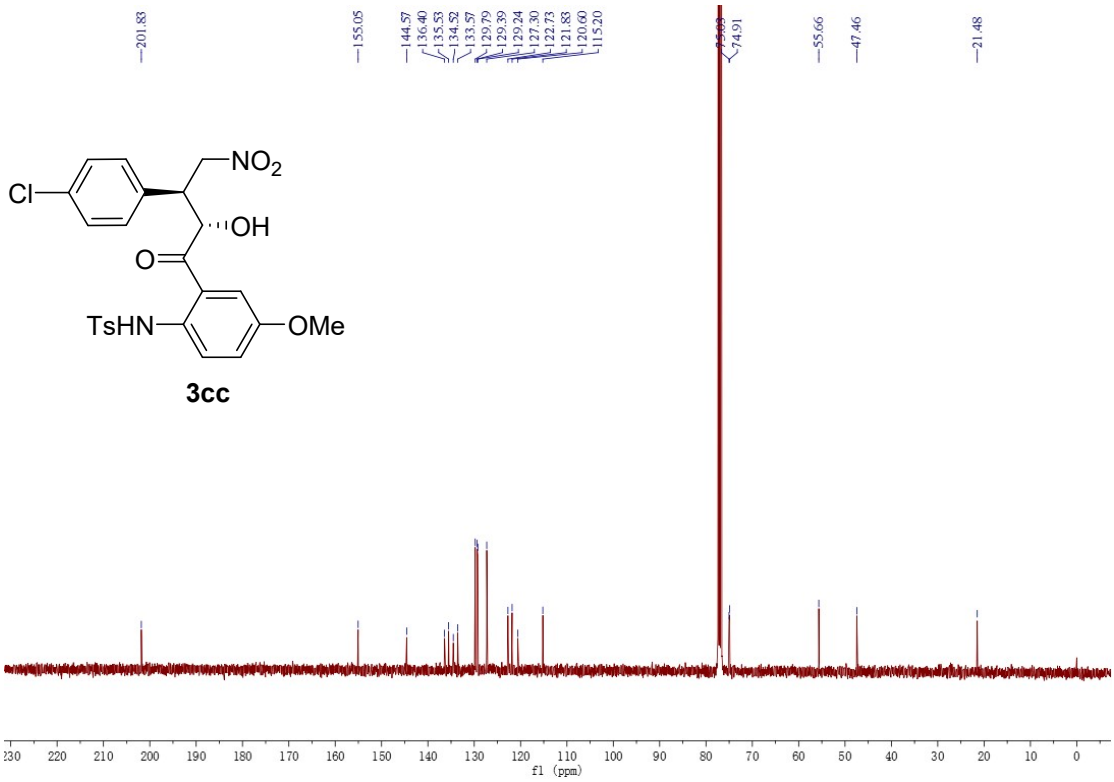
^{19}F NMR spectrum of compound **3cb** ($CDCl_3$, 400 MHz)



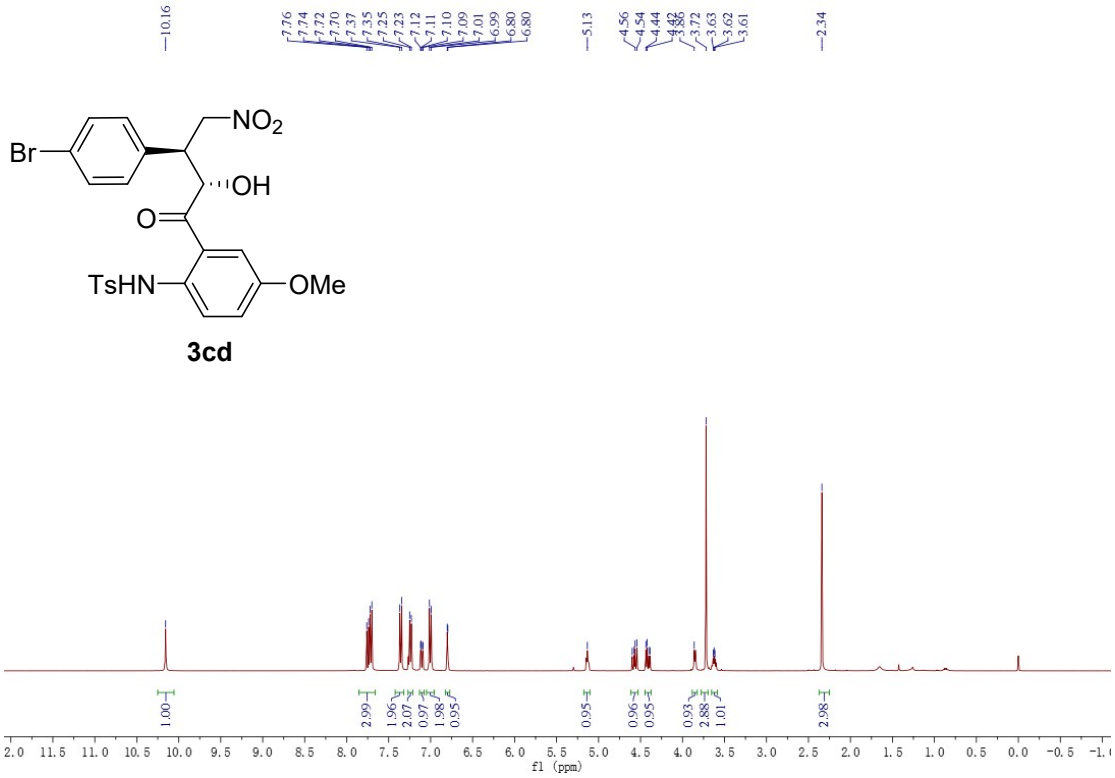
^{1}H NMR spectrum of compound **3cc** ($CDCl_3$, 400 MHz)



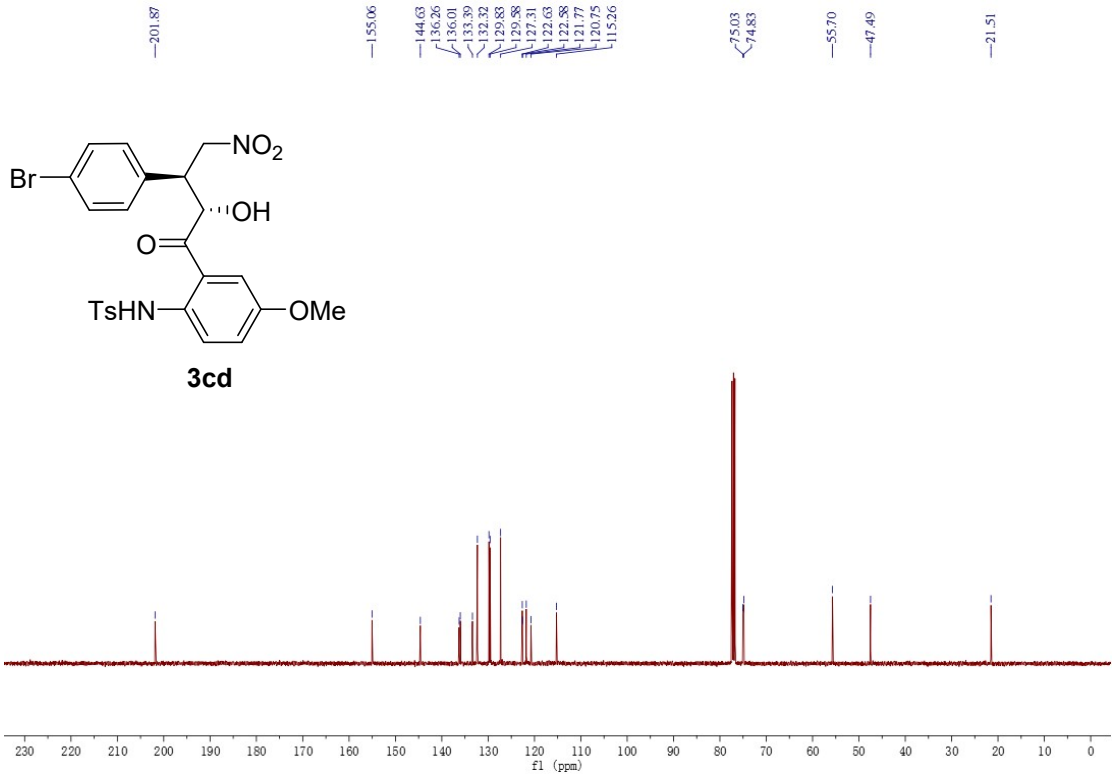
^{13}C NMR spectrum of compound **3cc** ($CDCl_3$, 400 MHz)



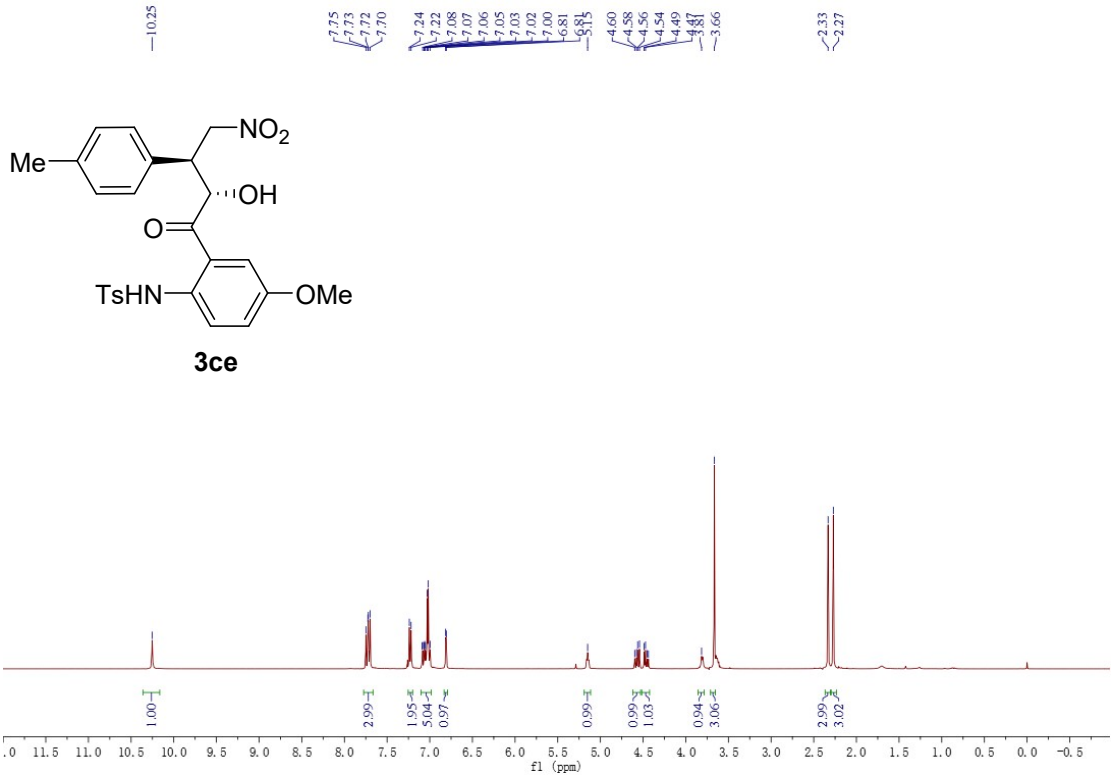
^{1}H NMR spectrum of compound **3cd** ($CDCl_3$, 400 MHz)



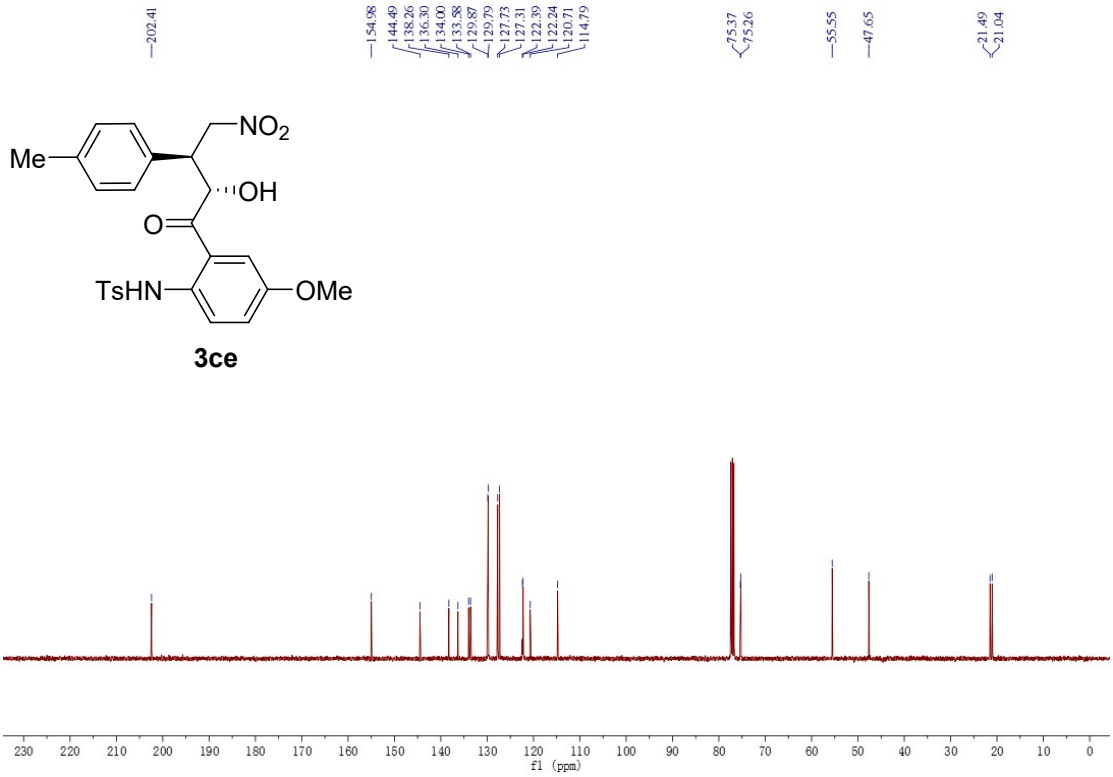
^{13}C NMR spectrum of compound **3cd** ($CDCl_3$, 400 MHz)



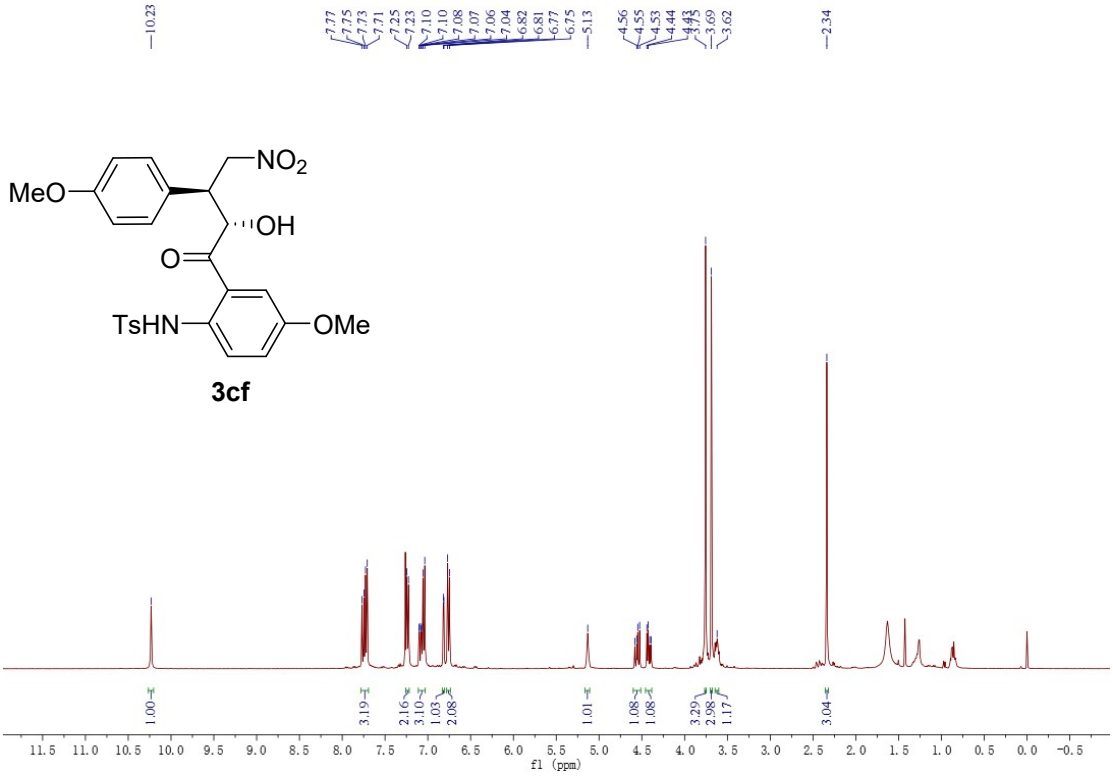
^{1}H NMR spectrum of compound **3ce** ($CDCl_3$, 400 MHz)



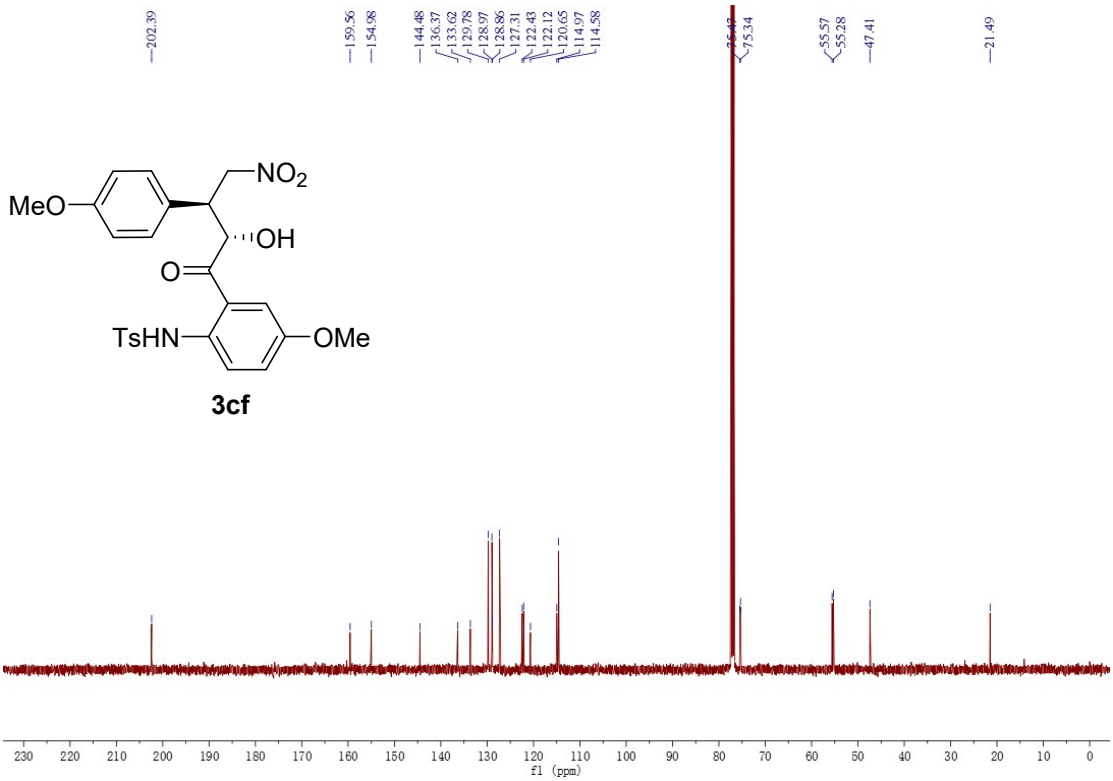
^{13}C NMR spectrum of compound **3ce** ($CDCl_3$, 400 MHz)



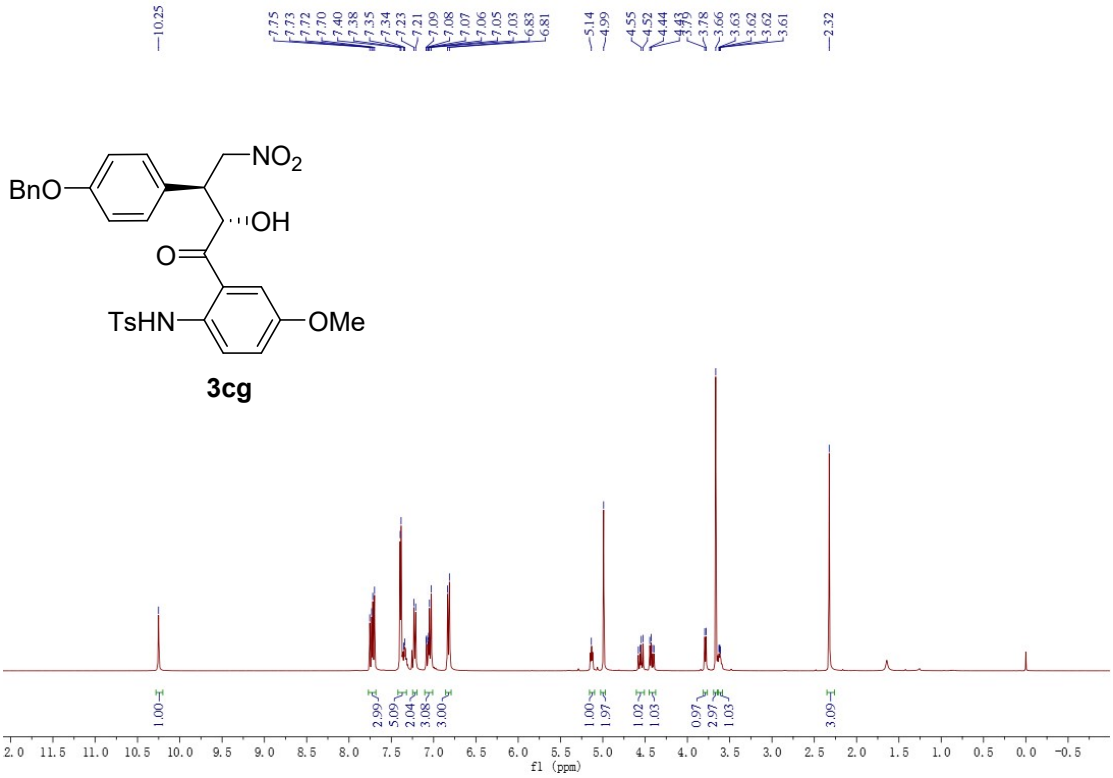
^{1}H NMR spectrum of compound **3cf** ($CDCl_3$, 400 MHz)



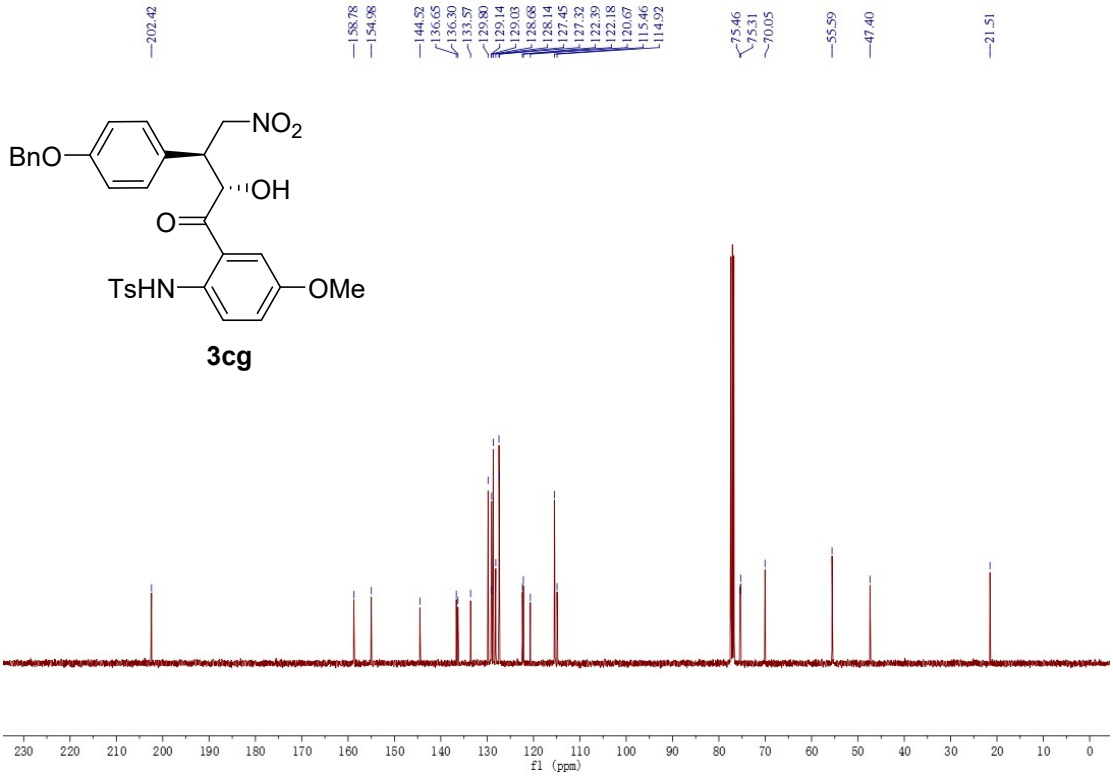
^{13}C NMR spectrum of compound **3cf** ($CDCl_3$, 400 MHz)



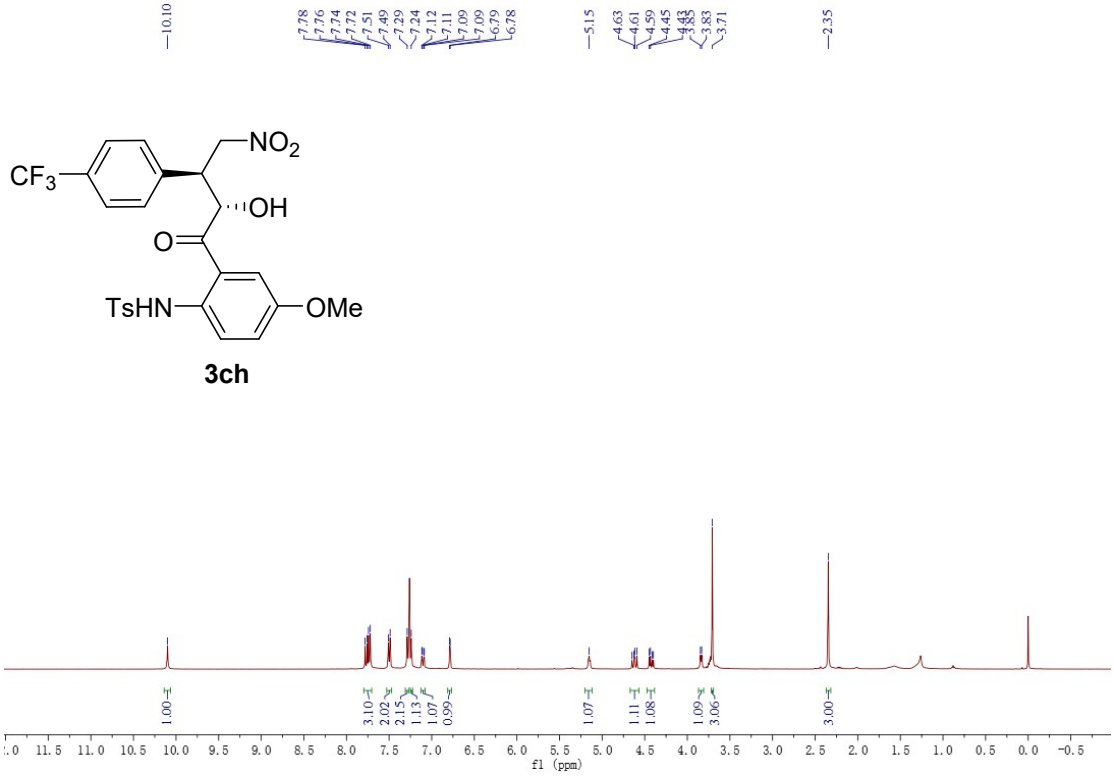
^{1}H NMR spectrum of compound **3cg** ($CDCl_3$, 400 MHz)



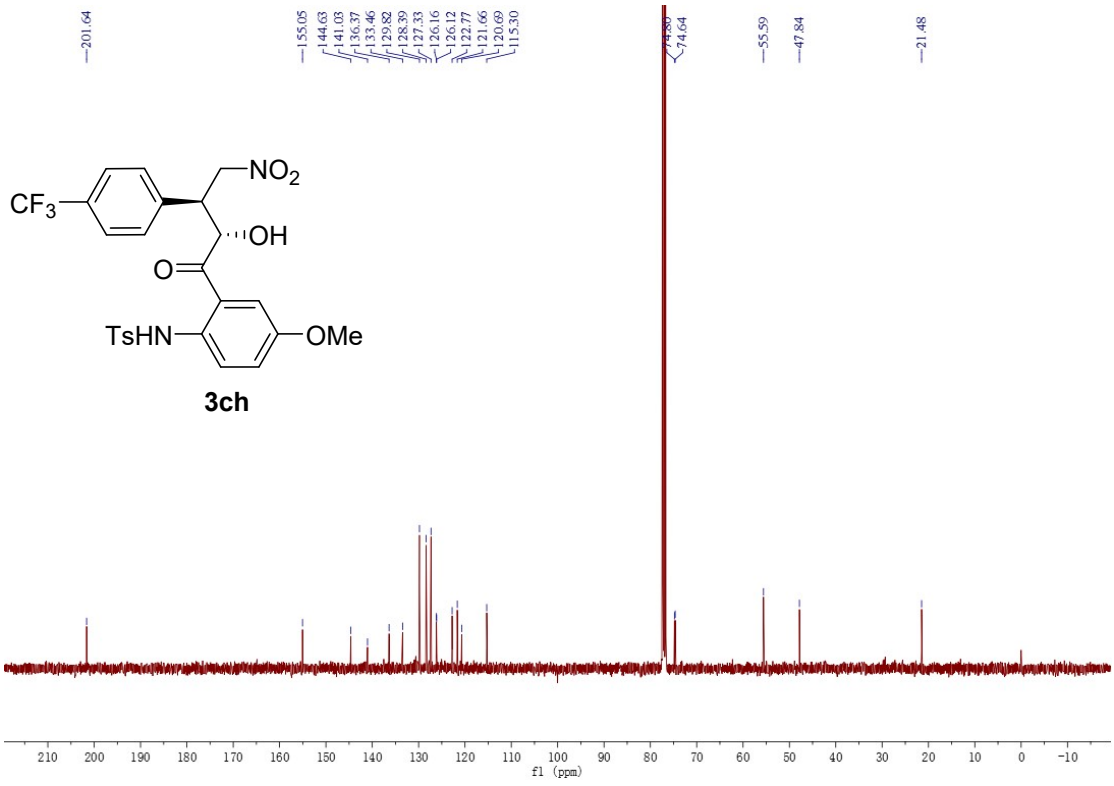
^{13}C NMR spectrum of compound **3cg** ($CDCl_3$, 400 MHz)



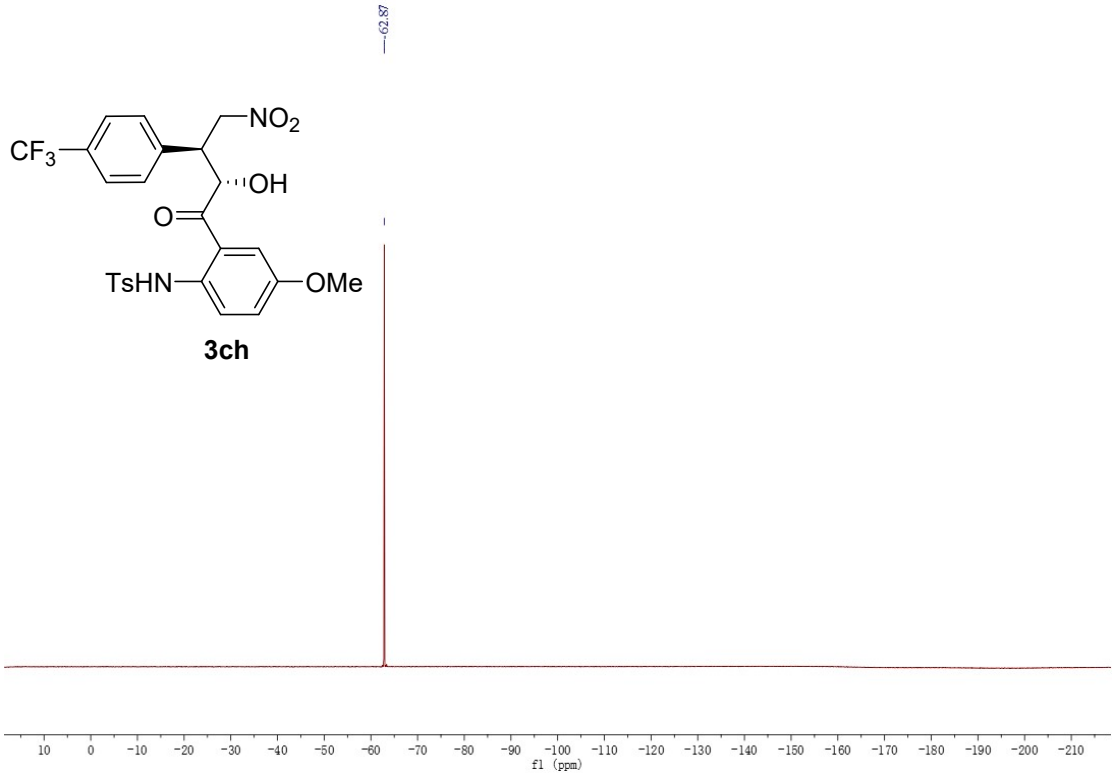
^{1}H NMR spectrum of compound **3ch** ($CDCl_3$, 400 MHz)



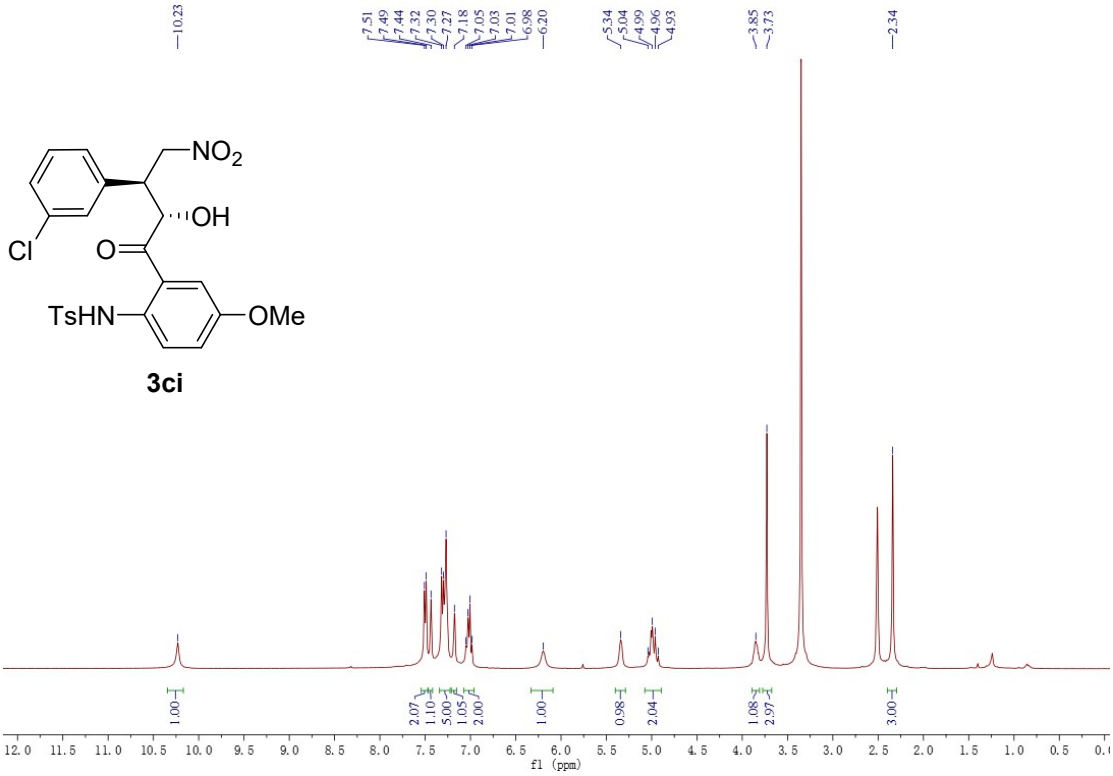
^{13}C NMR spectrum of compound **3ch** ($CDCl_3$, 400 MHz)



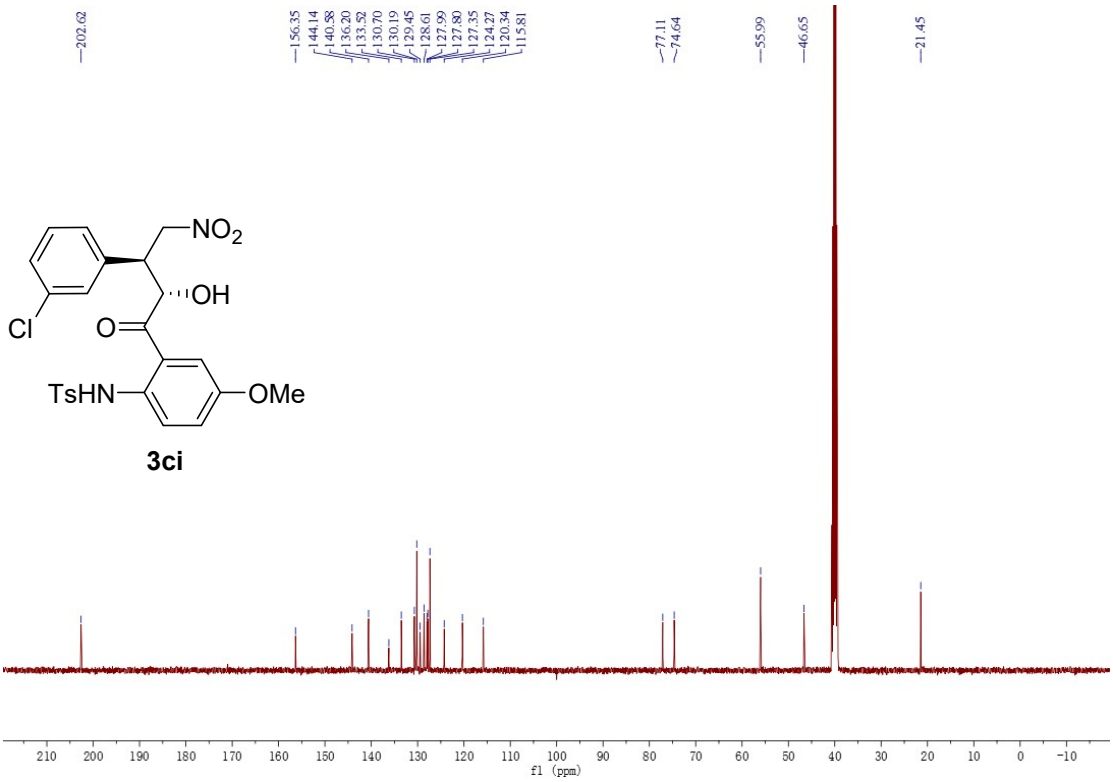
^{19}F NMR spectrum of compound **3ch** ($CDCl_3$, 400 MHz)



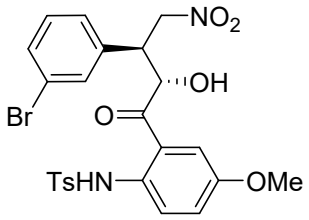
^{1}H NMR spectrum of compound **3ci** (DMSO, 400 MHz)



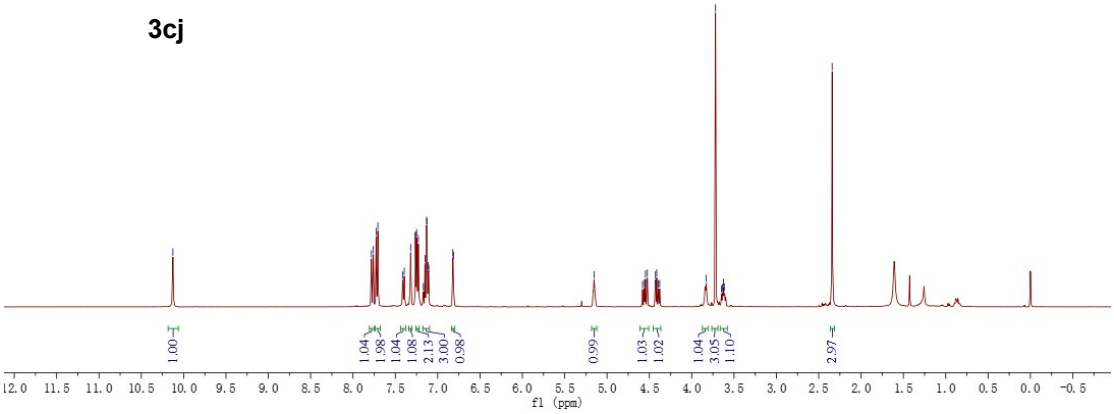
^{13}C NMR spectrum of compound **3ci** (DMSO, 400 MHz)



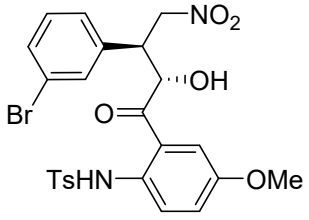
^{1}H NMR spectrum of compound **3cj** ($CDCl_3$, 400 MHz)



3cj

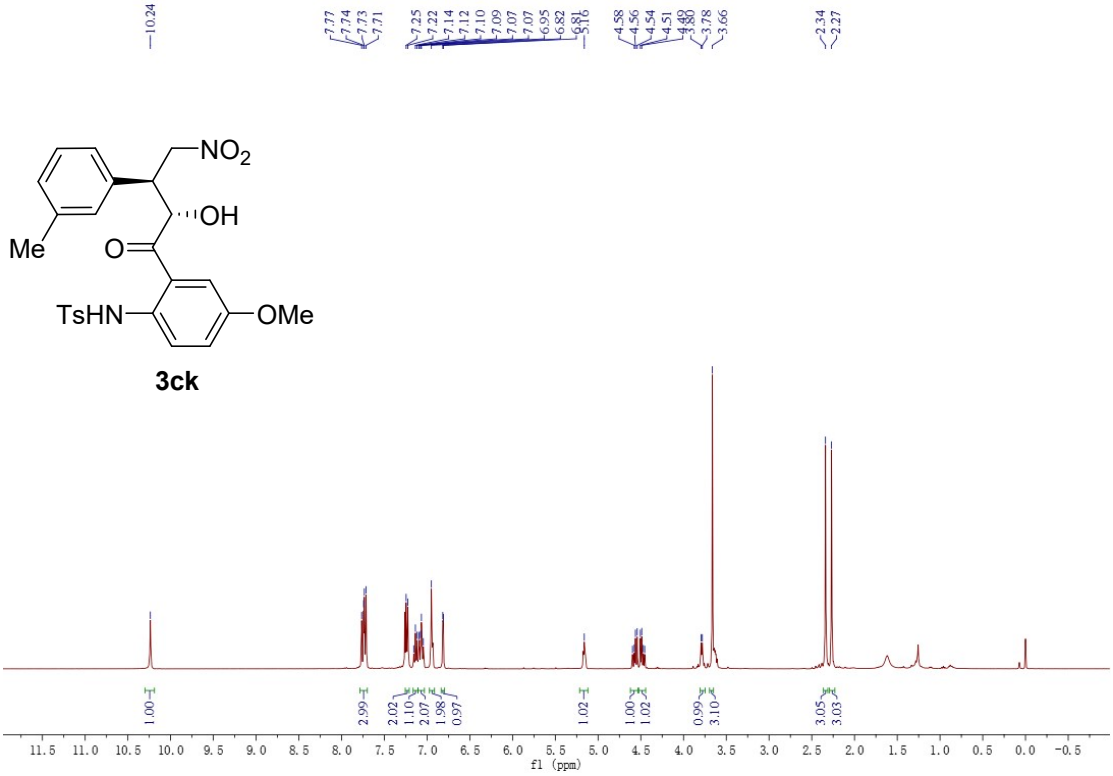


^{13}C NMR spectrum of compound **3cj** ($CDCl_3$, 400 MHz)

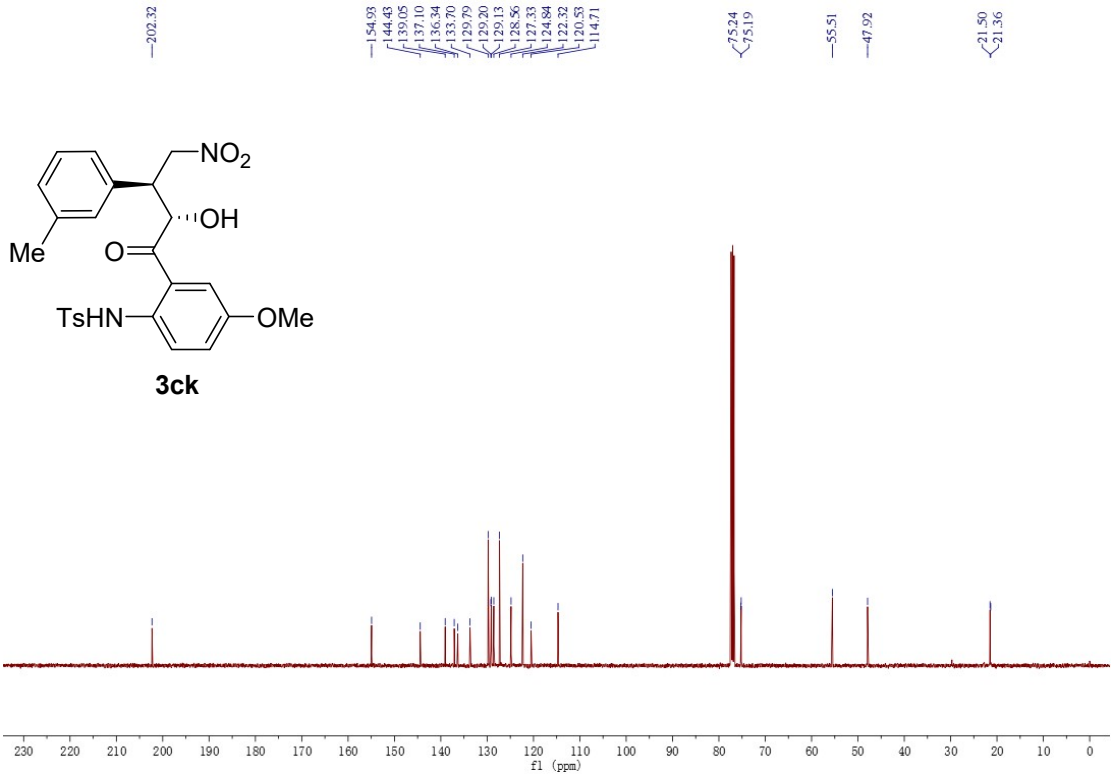


3cj

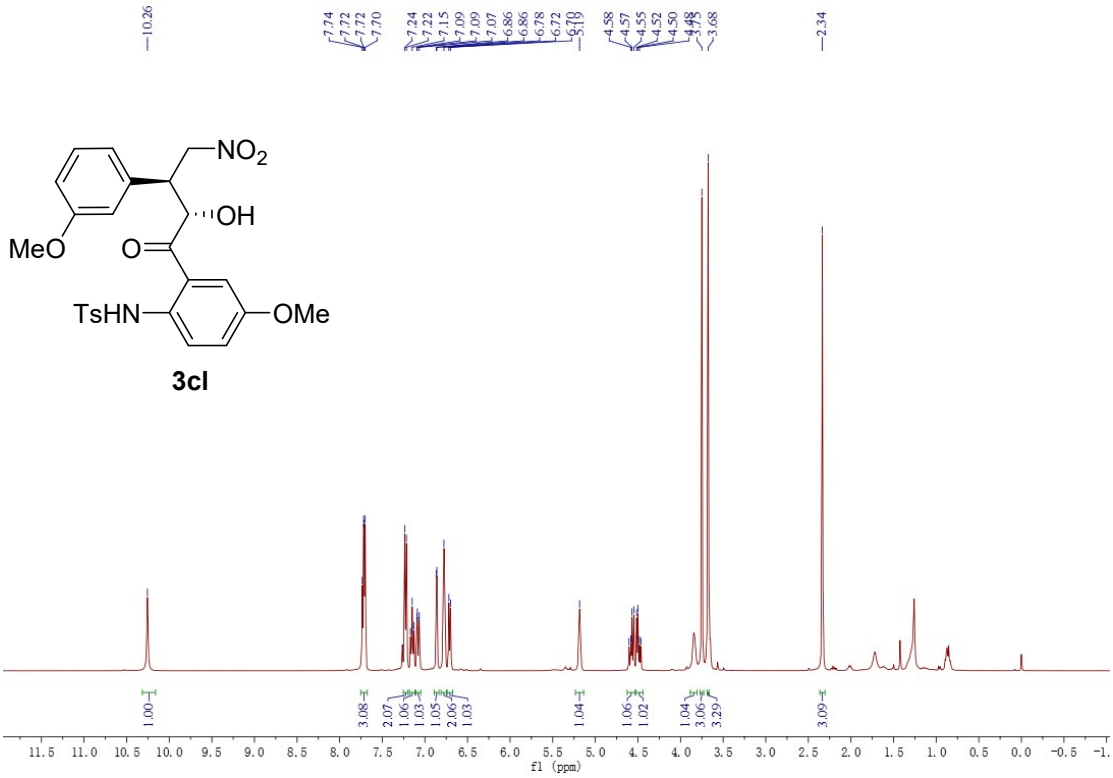
^{1}H NMR spectrum of compound **3ck** ($CDCl_3$, 400 MHz)



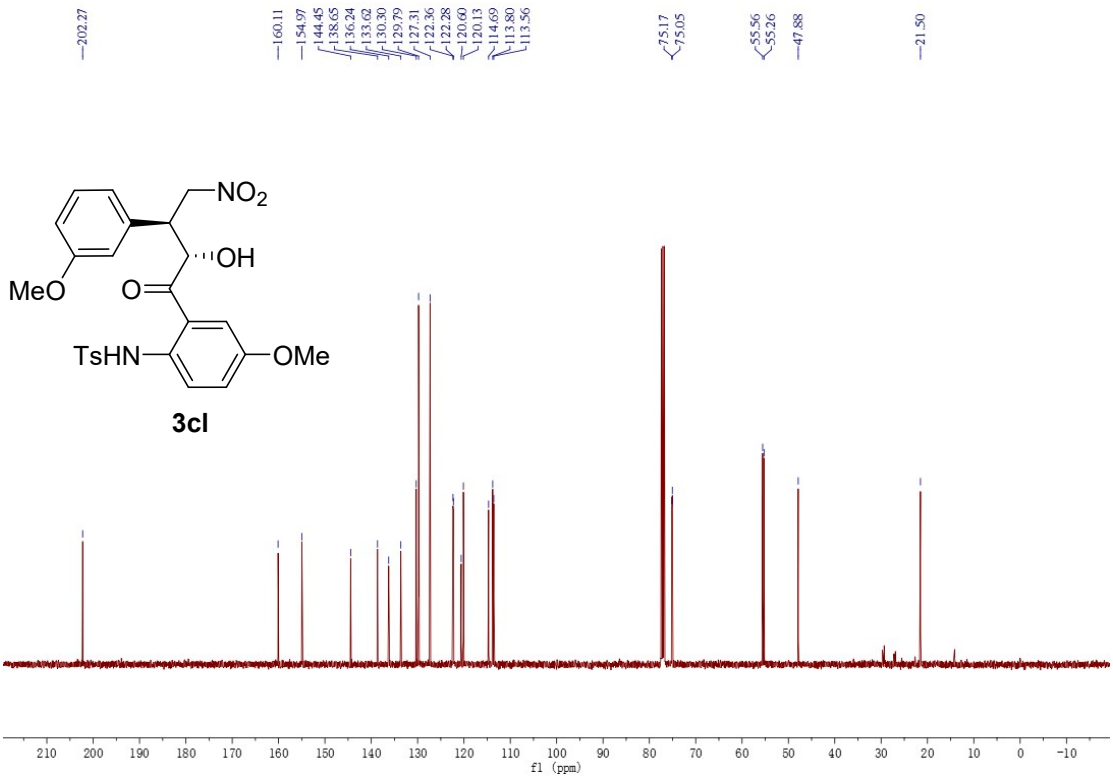
^{13}C NMR spectrum of compound **3ck** ($CDCl_3$, 400 MHz)



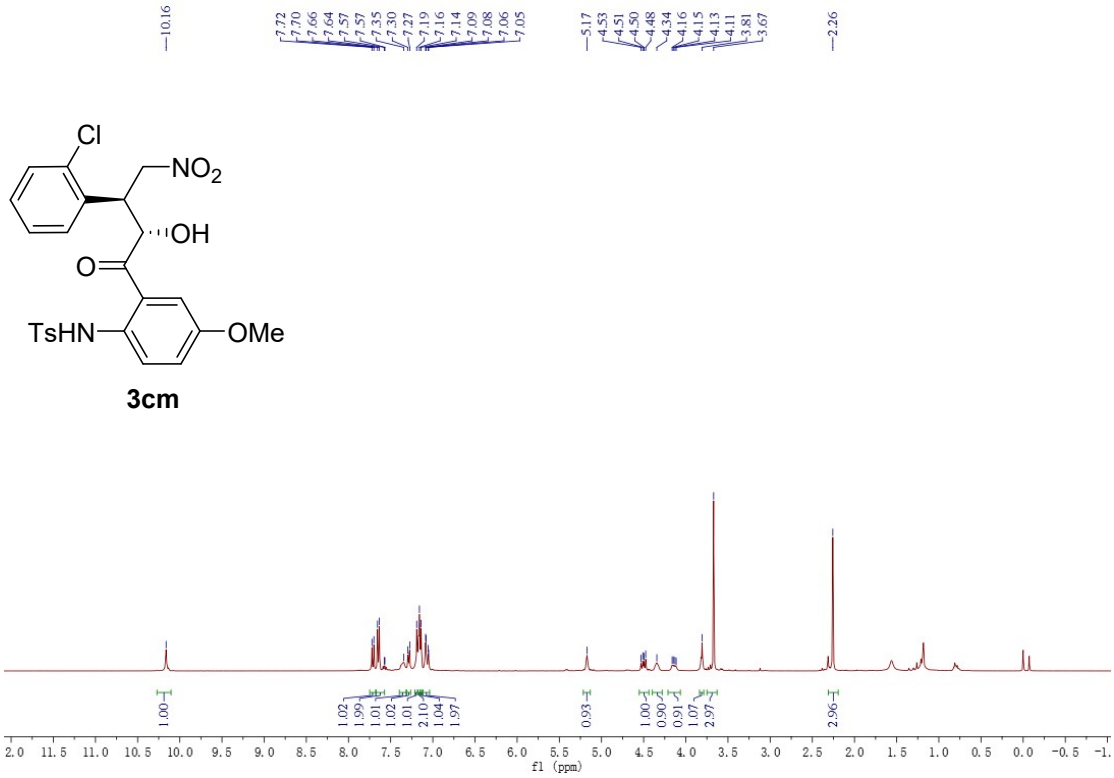
^{1}H NMR spectrum of compound **3cl** ($CDCl_3$, 400 MHz)



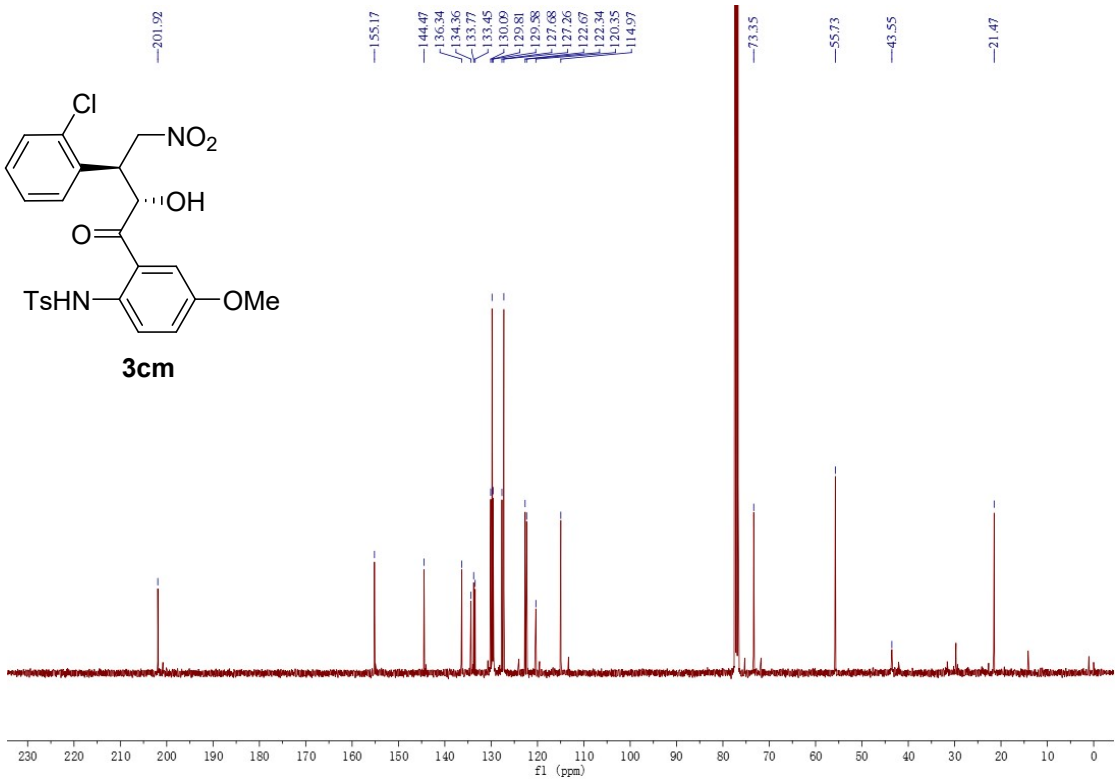
^{13}C NMR spectrum of compound **3cl** ($CDCl_3$, 400 MHz)



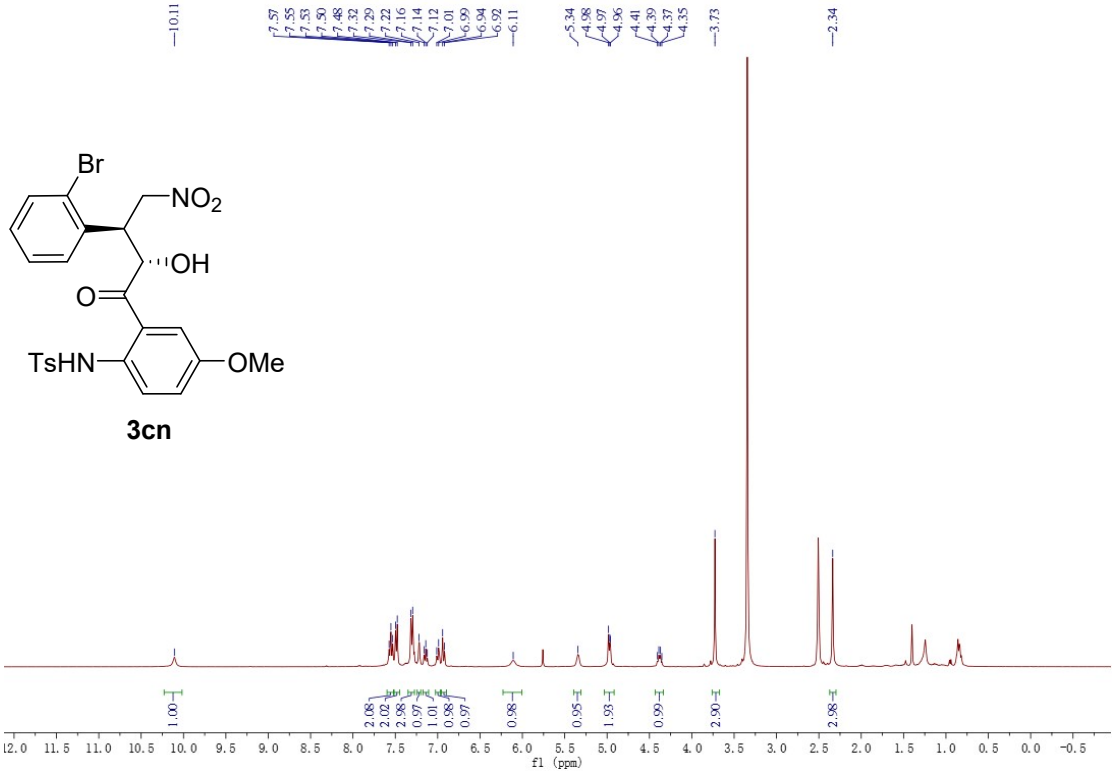
^{1}H NMR spectrum of compound **3cm** ($CDCl_3$, 400 MHz)



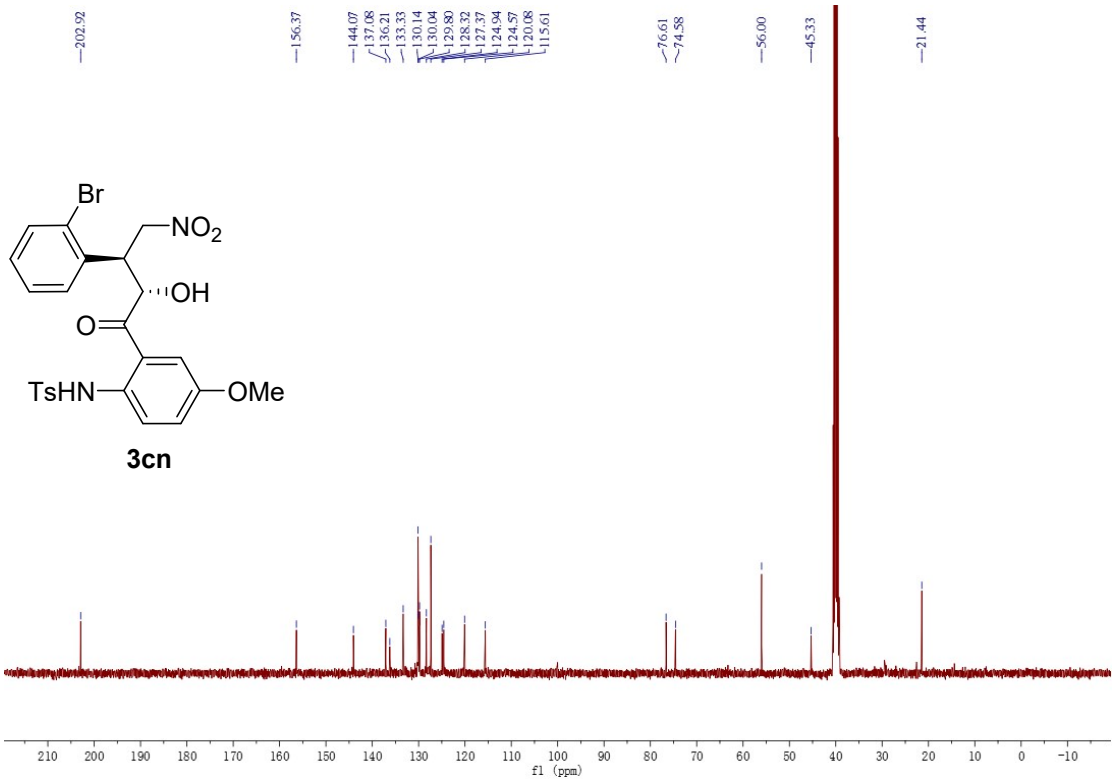
^{13}C NMR spectrum of compound **3cm** ($CDCl_3$, 400 MHz)



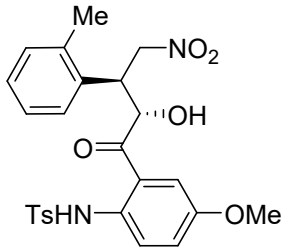
^{1}H NMR spectrum of compound **3cn** (DMSO, 400 MHz)



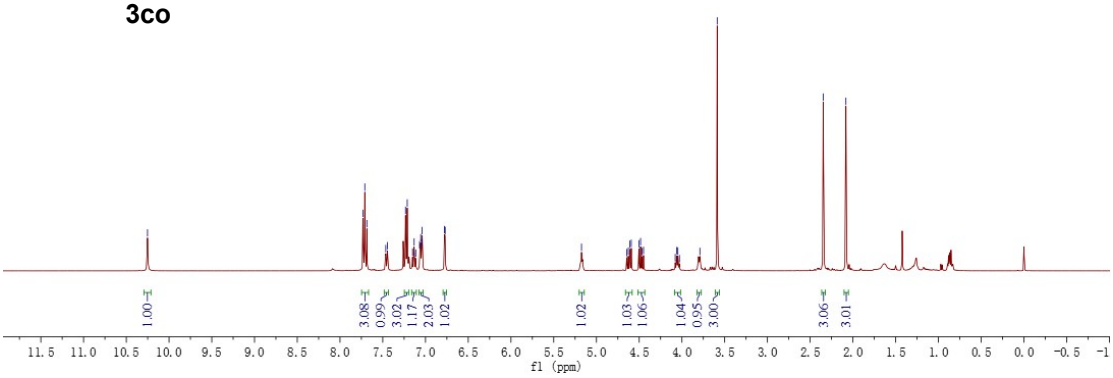
^{13}C NMR spectrum of compound **3cn** (DMSO, 400 MHz)



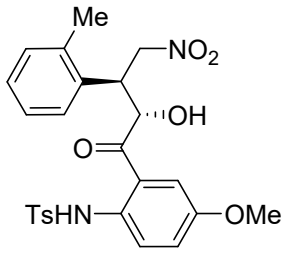
^{1}H NMR spectrum of compound **3co** ($CDCl_3$, 400 MHz)



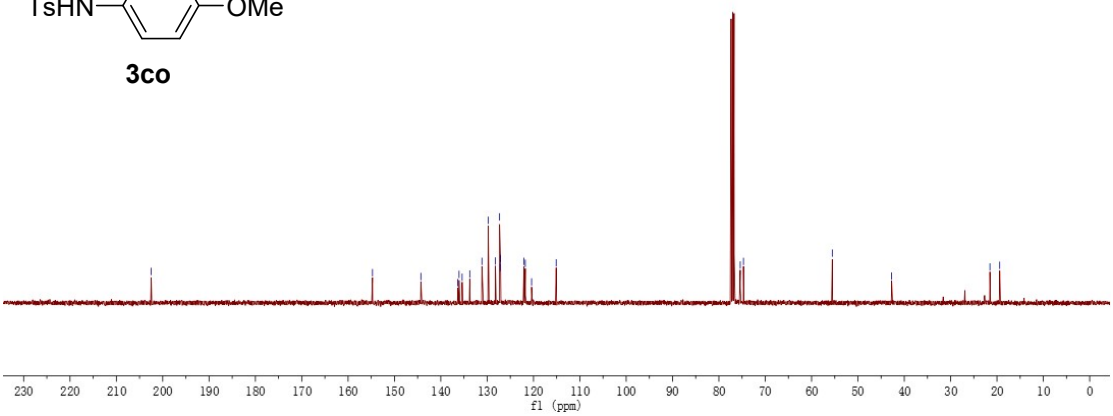
3co



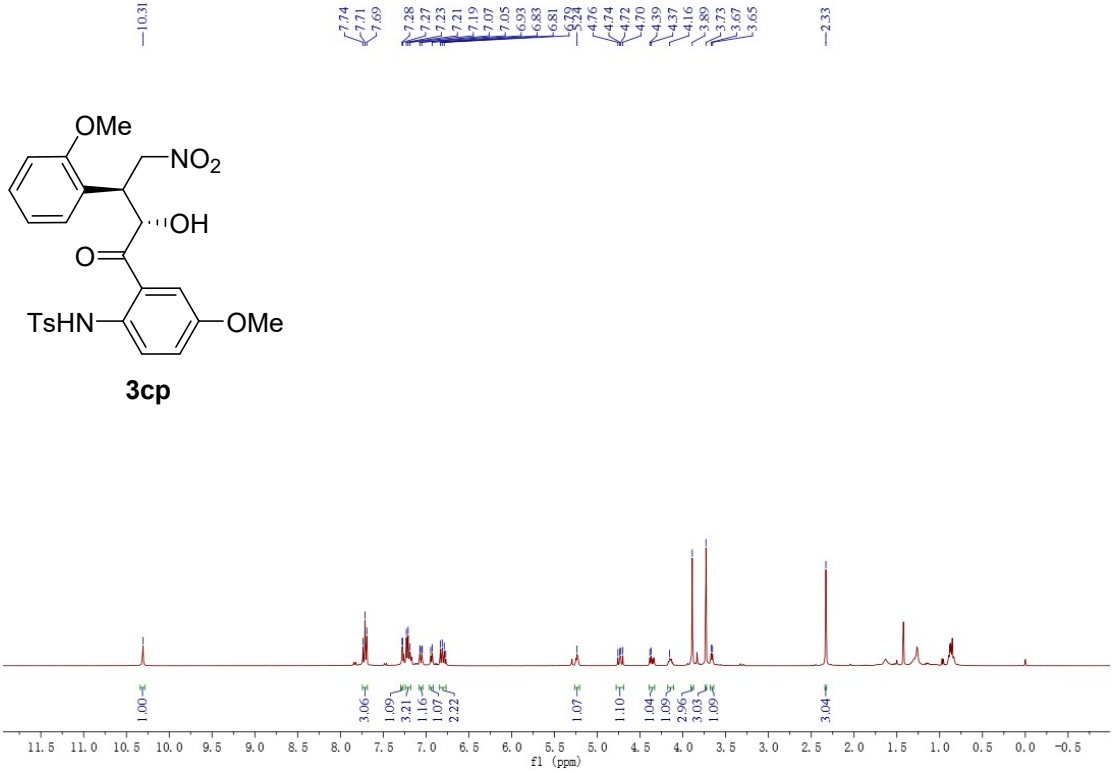
^{13}C NMR spectrum of compound **3co** ($CDCl_3$, 400 MHz)



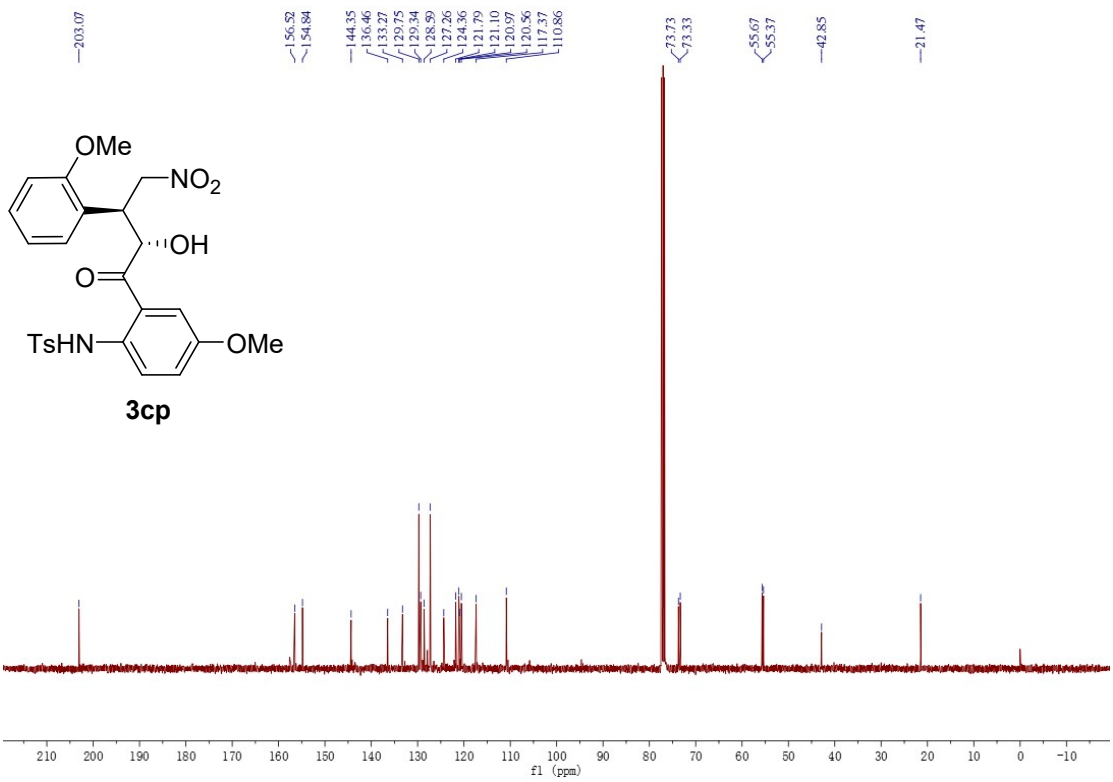
3co



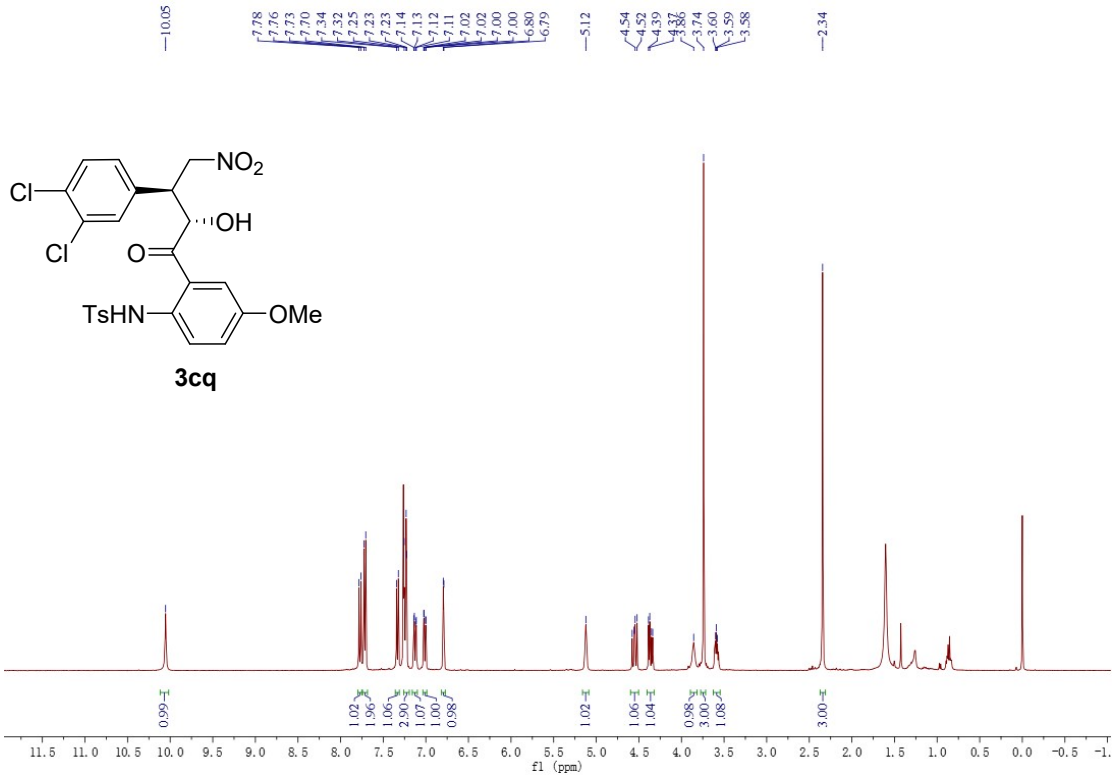
^{1}H NMR spectrum of compound **3cp** ($CDCl_3$, 400 MHz)



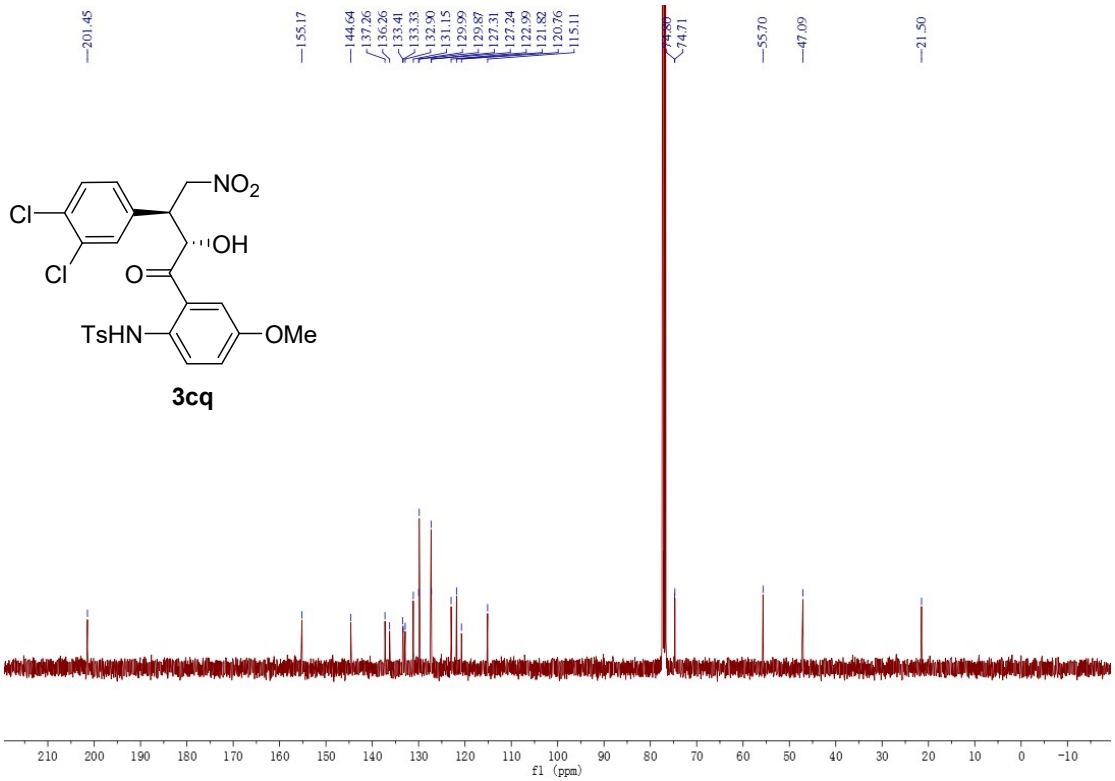
^{13}C NMR spectrum of compound **3cp** ($CDCl_3$, 400 MHz)



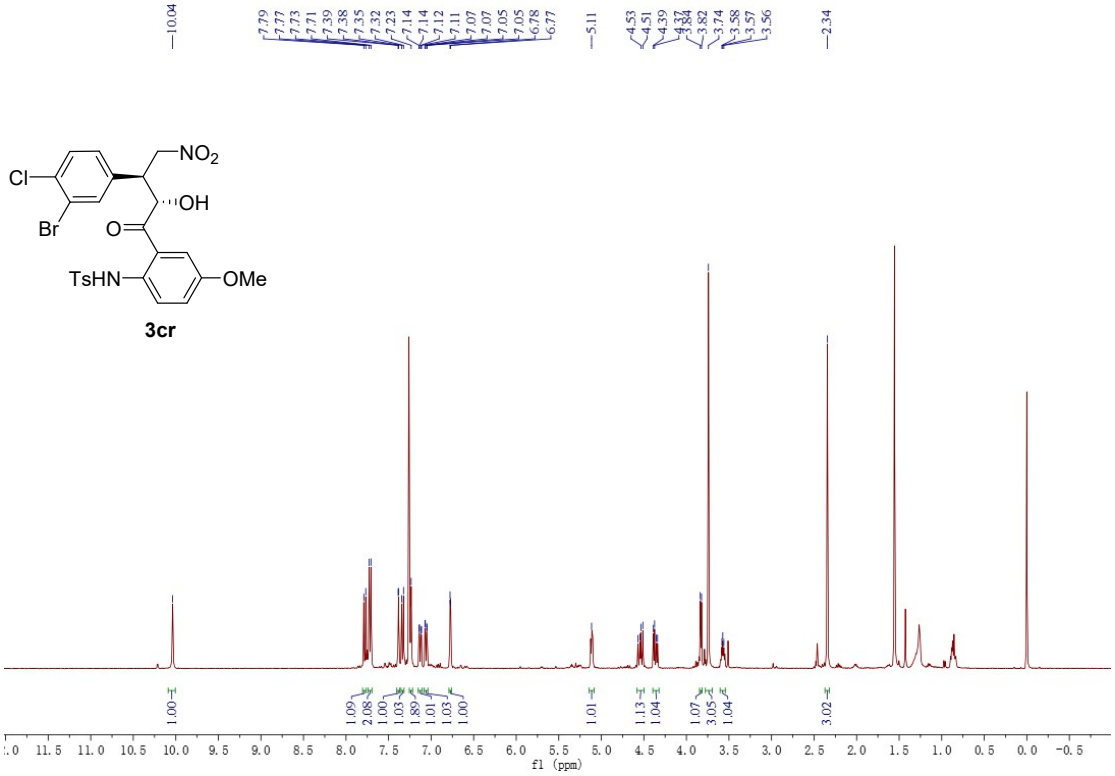
^{1}H NMR spectrum of compound **3cq** ($CDCl_3$, 400 MHz)



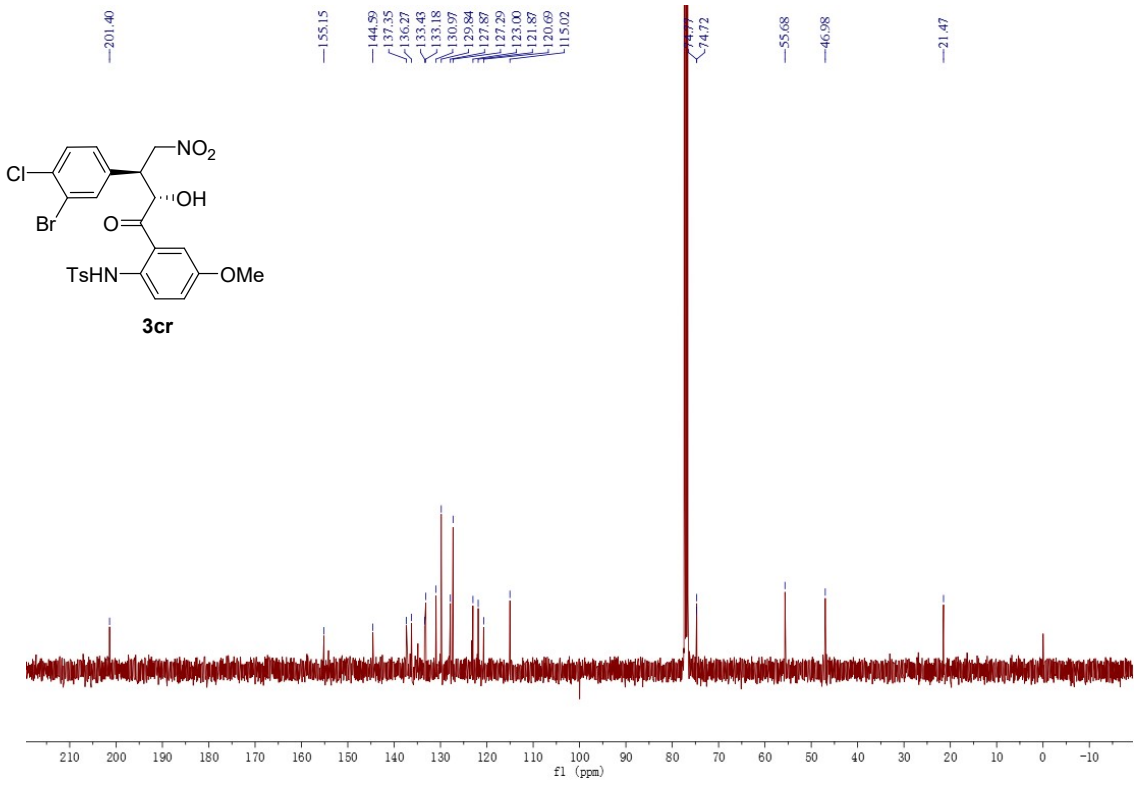
^{13}C NMR spectrum of compound **3cq** ($CDCl_3$, 400 MHz)



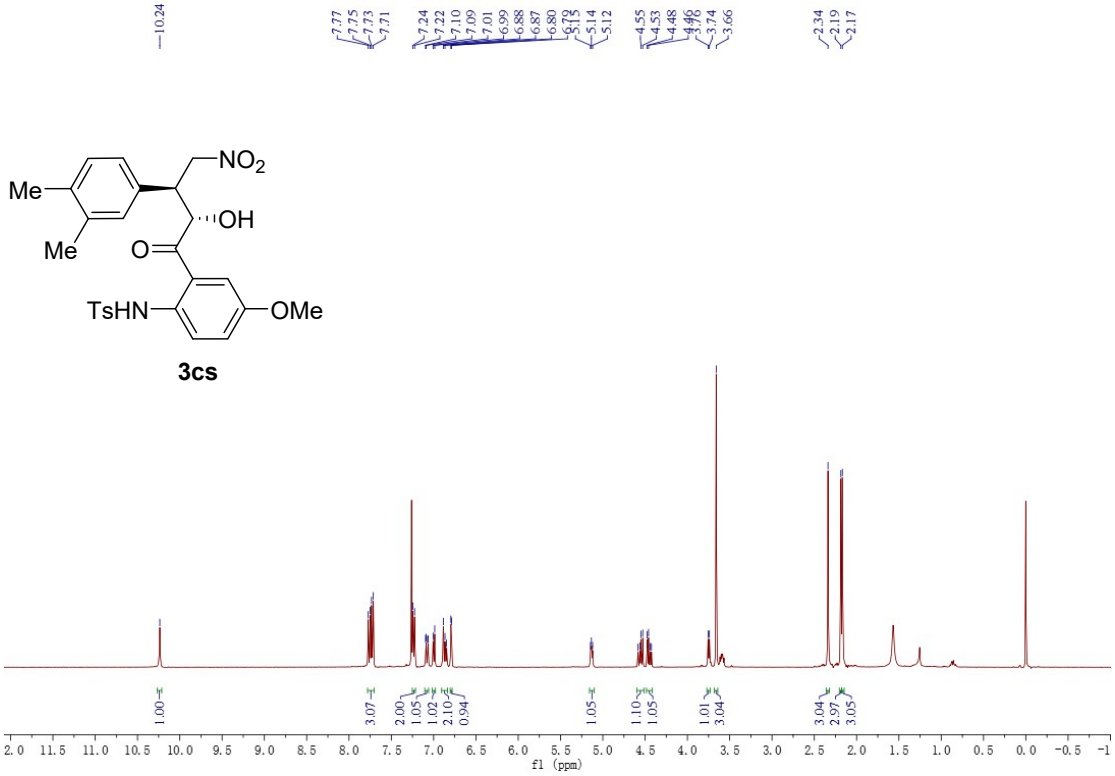
^{1}H NMR spectrum of compound **3cr** ($CDCl_3$, 400 MHz)



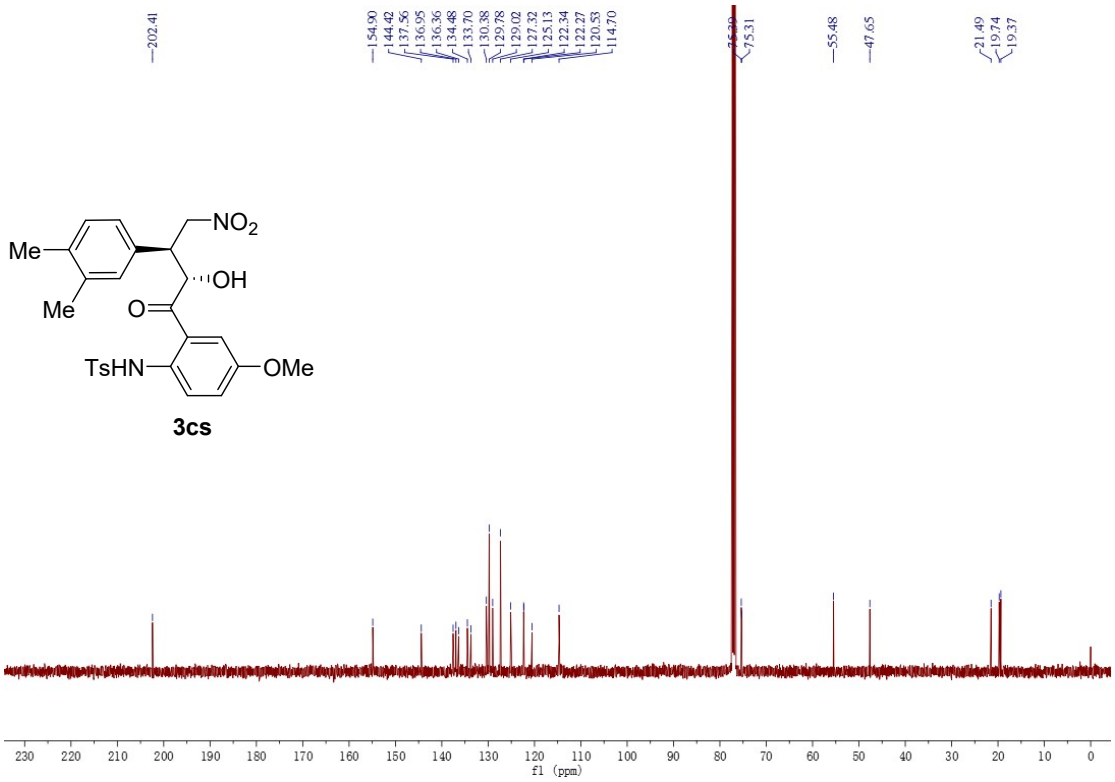
^{13}C NMR spectrum of compound **3cr** ($CDCl_3$, 400 MHz)



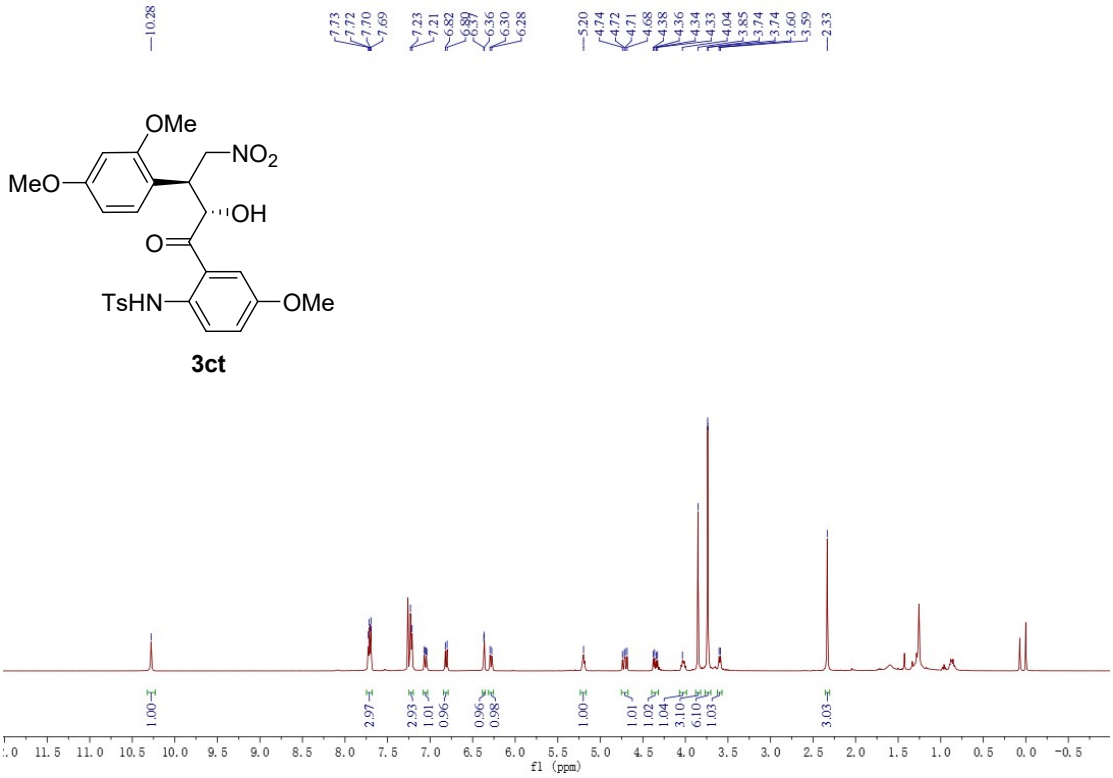
^{1}H NMR spectrum of compound **3cs** ($CDCl_3$, 400 MHz)



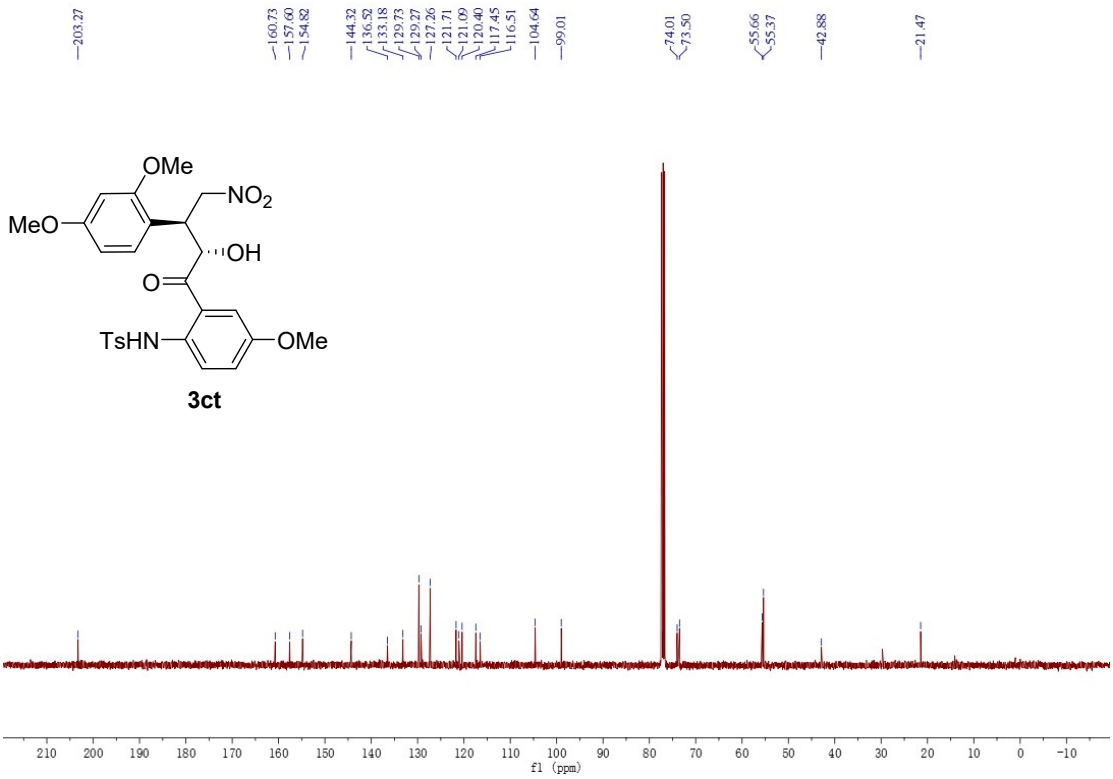
^{13}C NMR spectrum of compound **3cs** ($CDCl_3$, 400 MHz)



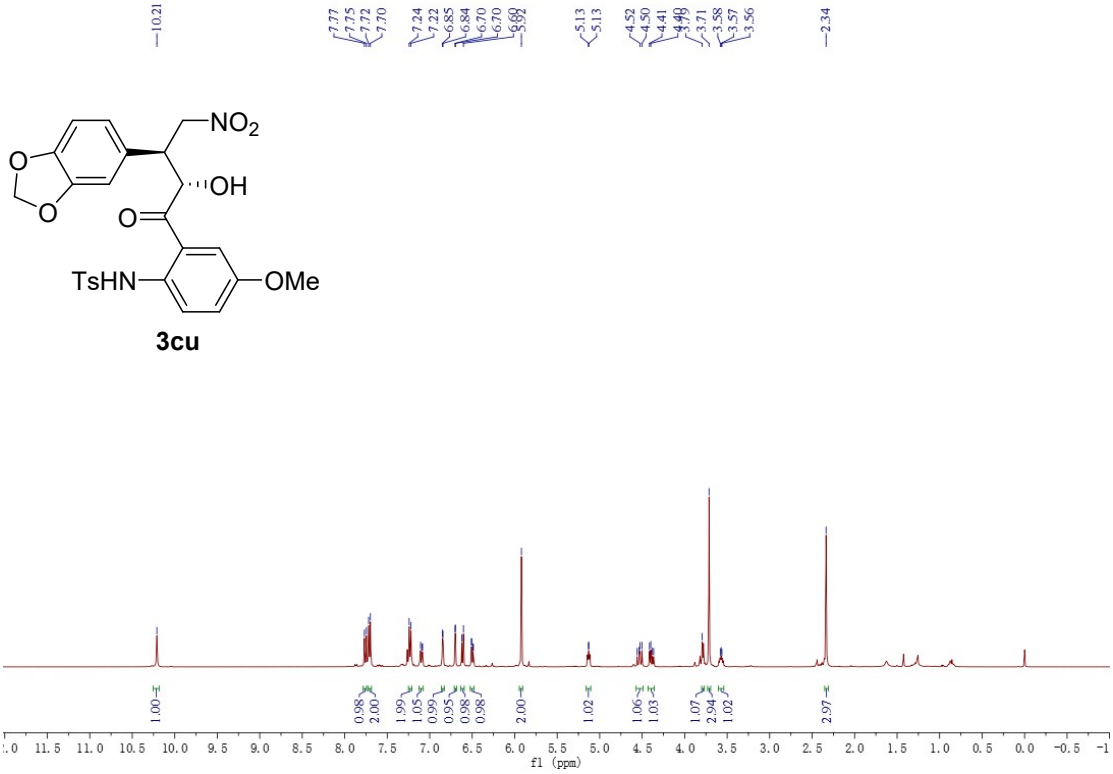
^{1}H NMR spectrum of compound **3ct** ($CDCl_3$, 400 MHz)



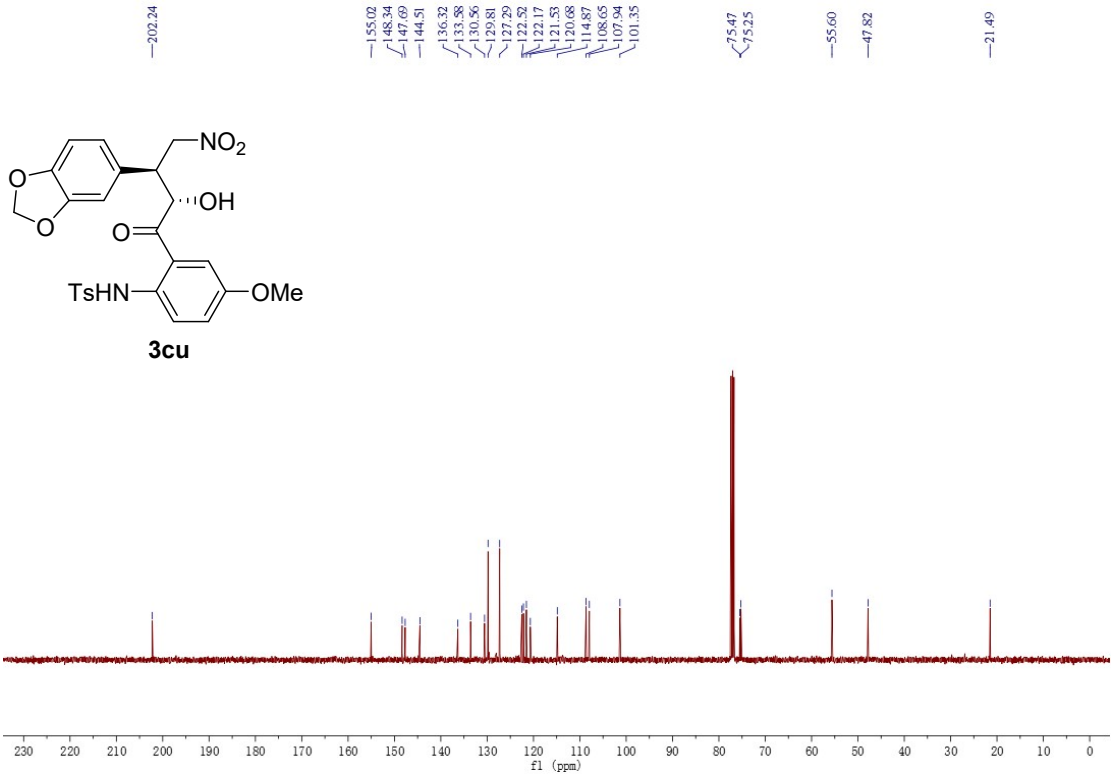
^{13}C NMR spectrum of compound **3ct** ($CDCl_3$, 400 MHz)



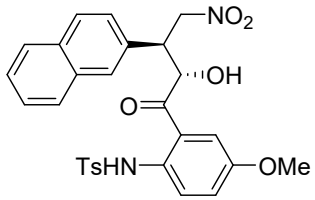
^{1}H NMR spectrum of compound **3cu** ($CDCl_3$, 400 MHz)



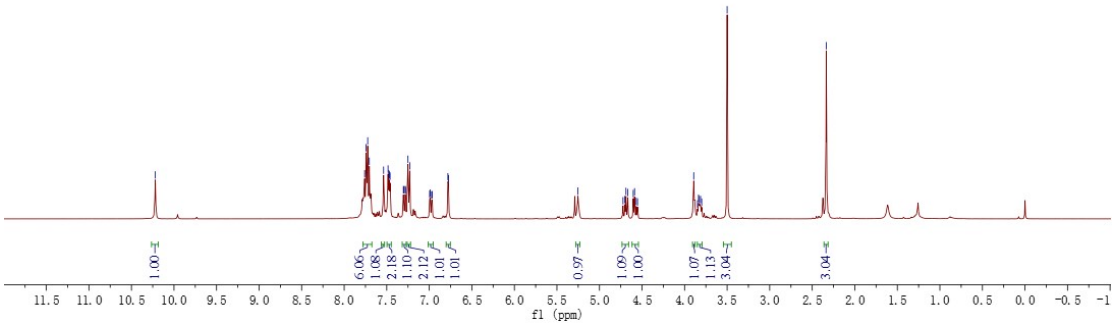
^{13}C NMR spectrum of compound **3cu** ($CDCl_3$, 400 MHz)



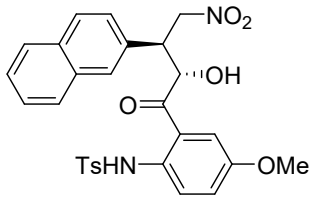
^{1}H NMR spectrum of compound **3cv** ($CDCl_3$, 400 MHz)



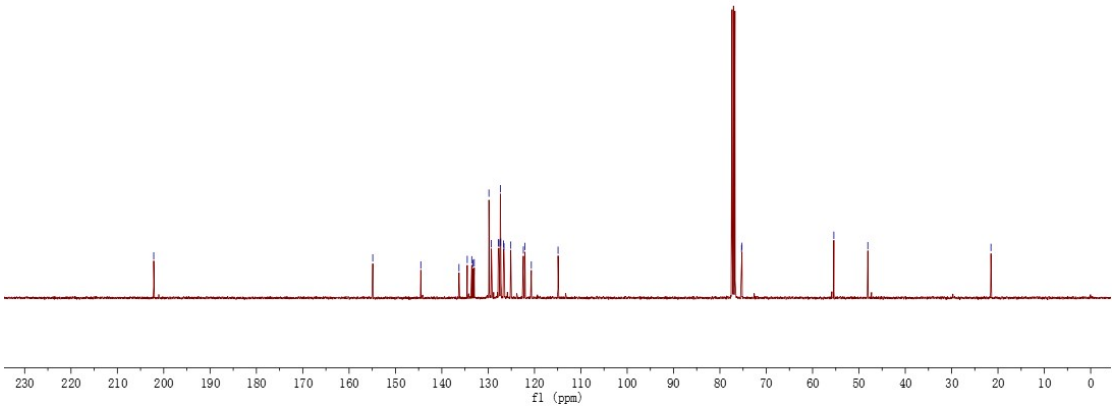
3cv



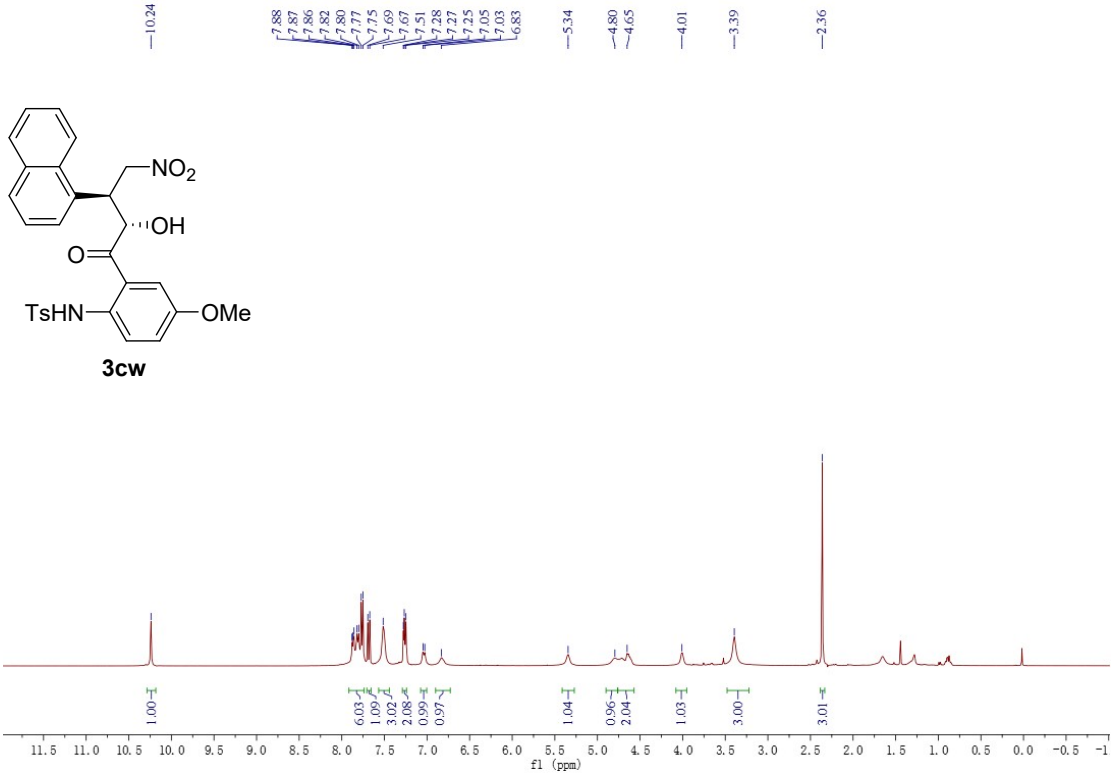
^{13}C NMR spectrum of compound **3cv** ($CDCl_3$, 400 MHz)



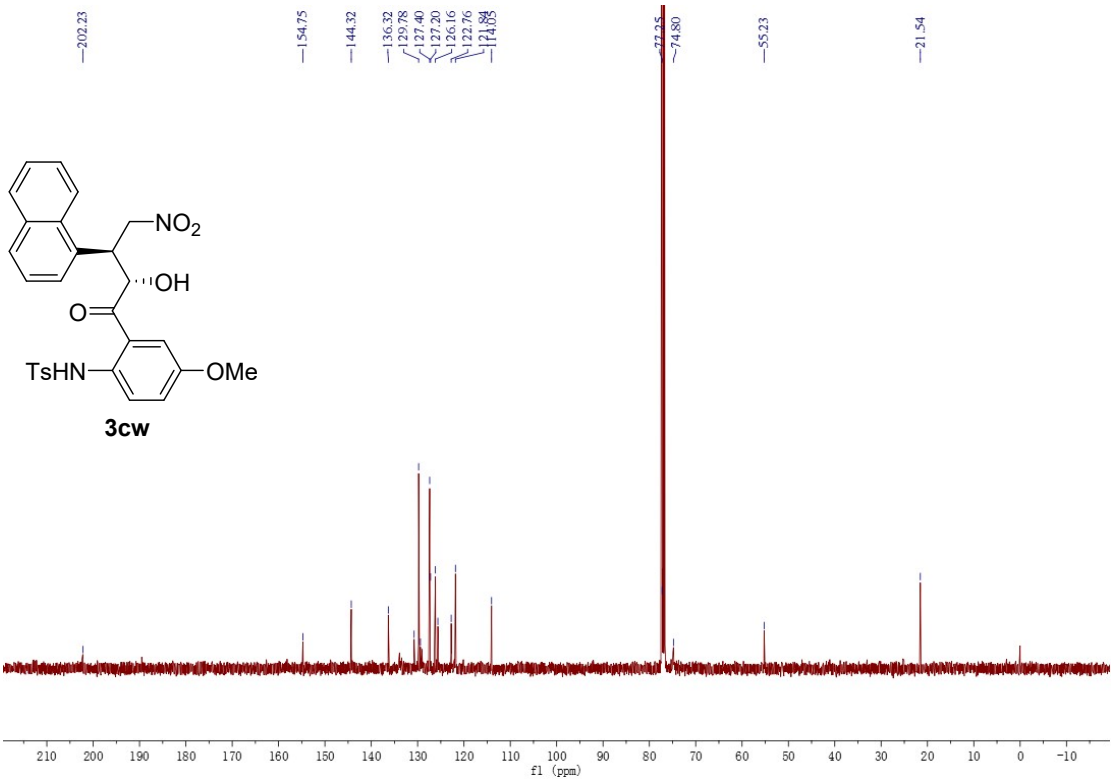
3cv



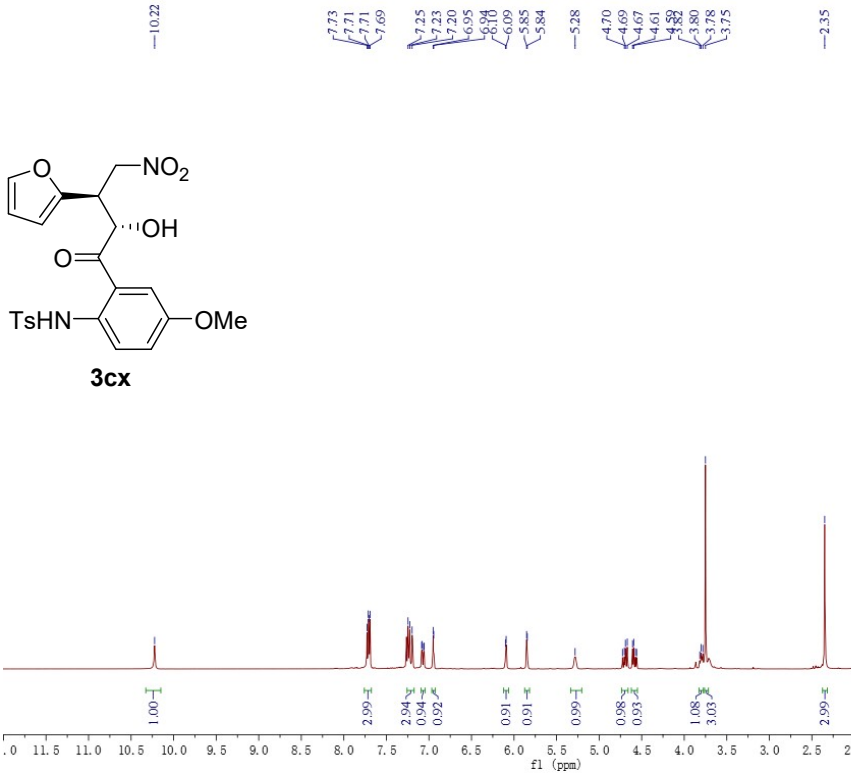
^{1}H NMR spectrum of compound **3cw** ($CDCl_3$, 400 MHz)



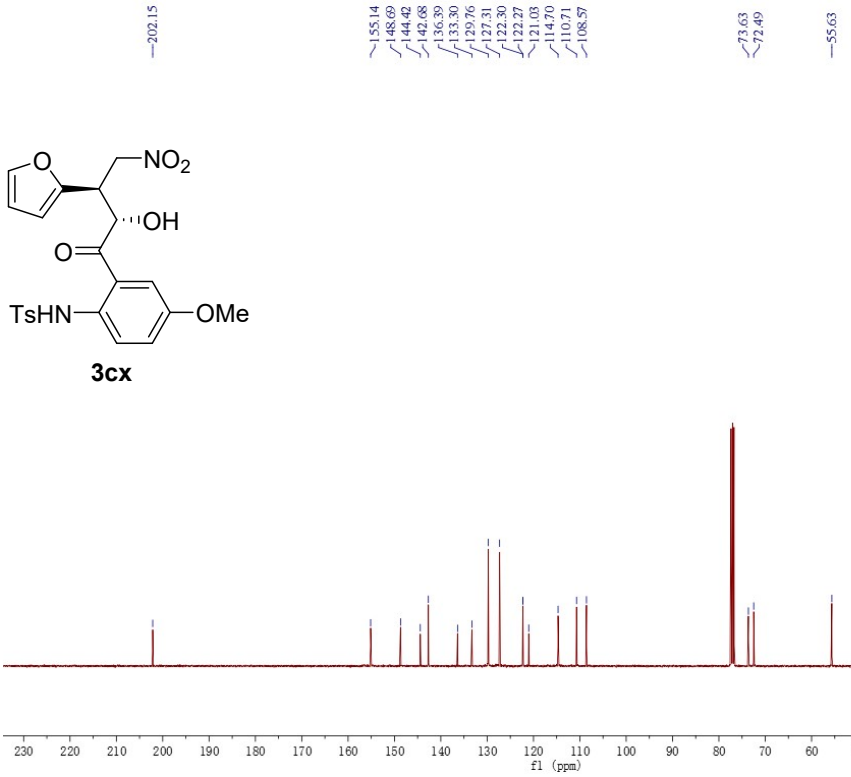
^{13}C NMR spectrum of compound **3cw** ($CDCl_3$, 400 MHz)



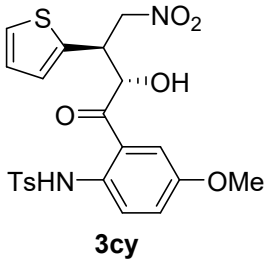
^{1}H NMR spectrum of compound **3cx** ($CDCl_3$, 400 MHz)



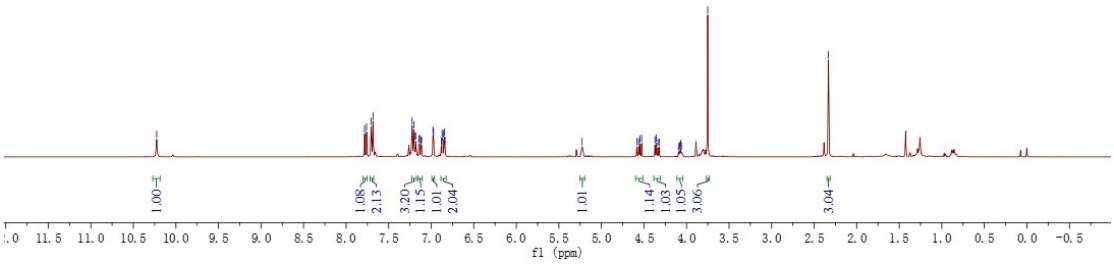
^{13}C NMR spectrum of compound **3cx** ($CDCl_3$, 400 MHz)



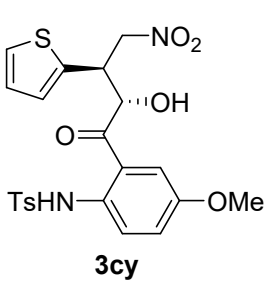
^{1}H NMR spectrum of compound **3cy** ($CDCl_3$, 400 MHz)



3cy

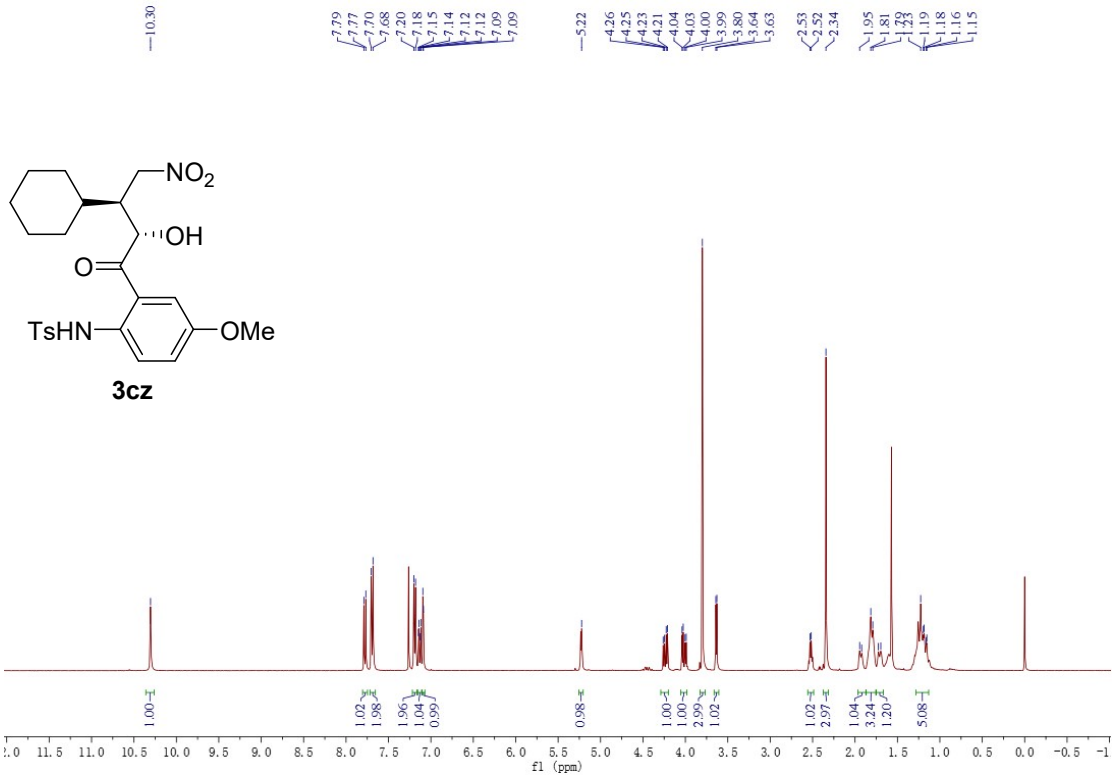


^{13}C NMR spectrum of compound **3cy** ($CDCl_3$, 400 MHz)

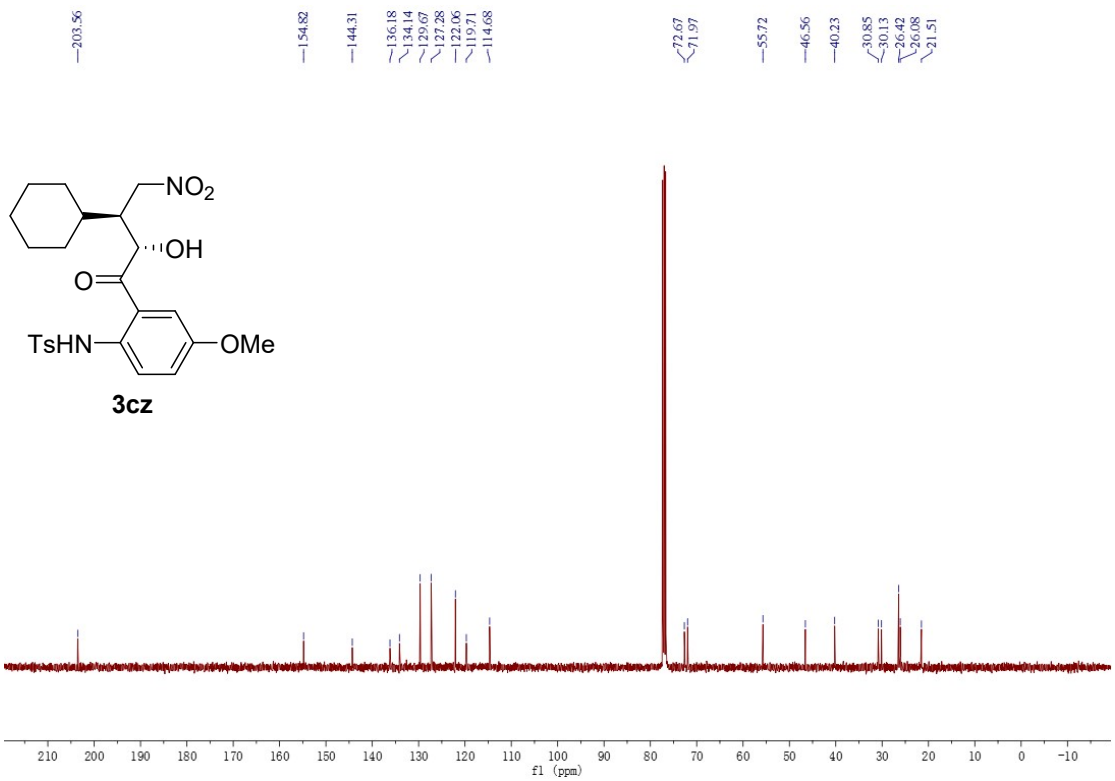


3cy

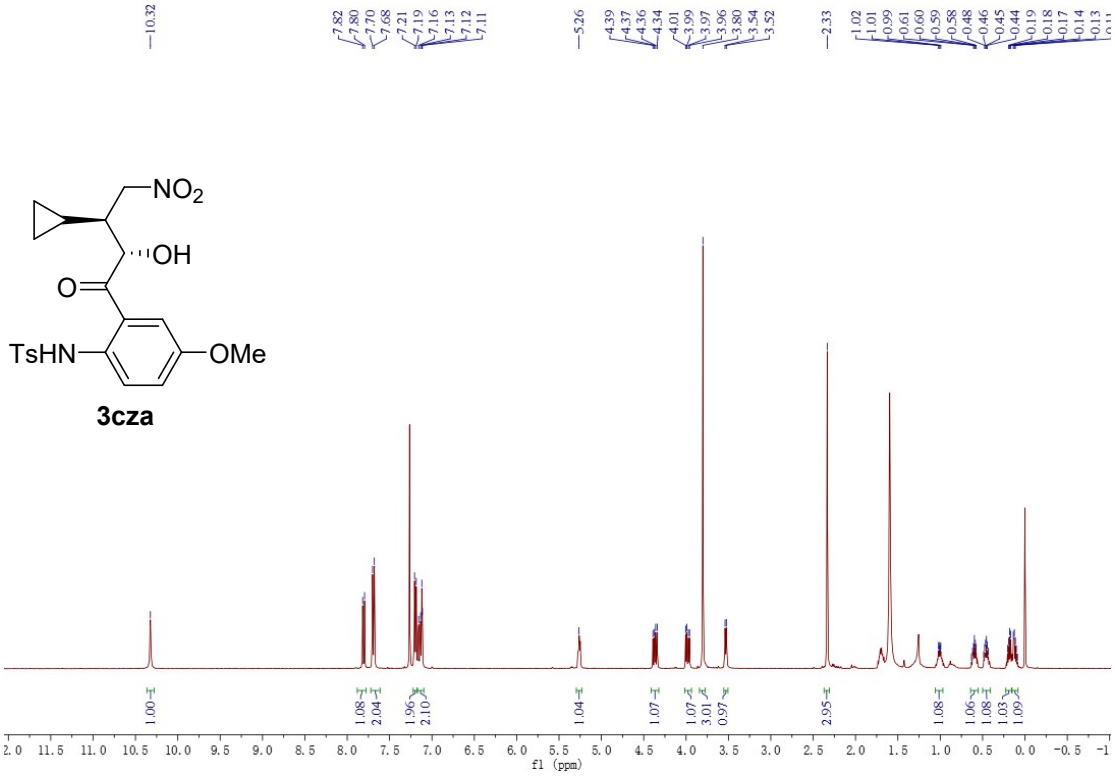
^{1}H NMR spectrum of compound **3cz** ($CDCl_3$, 400 MHz)



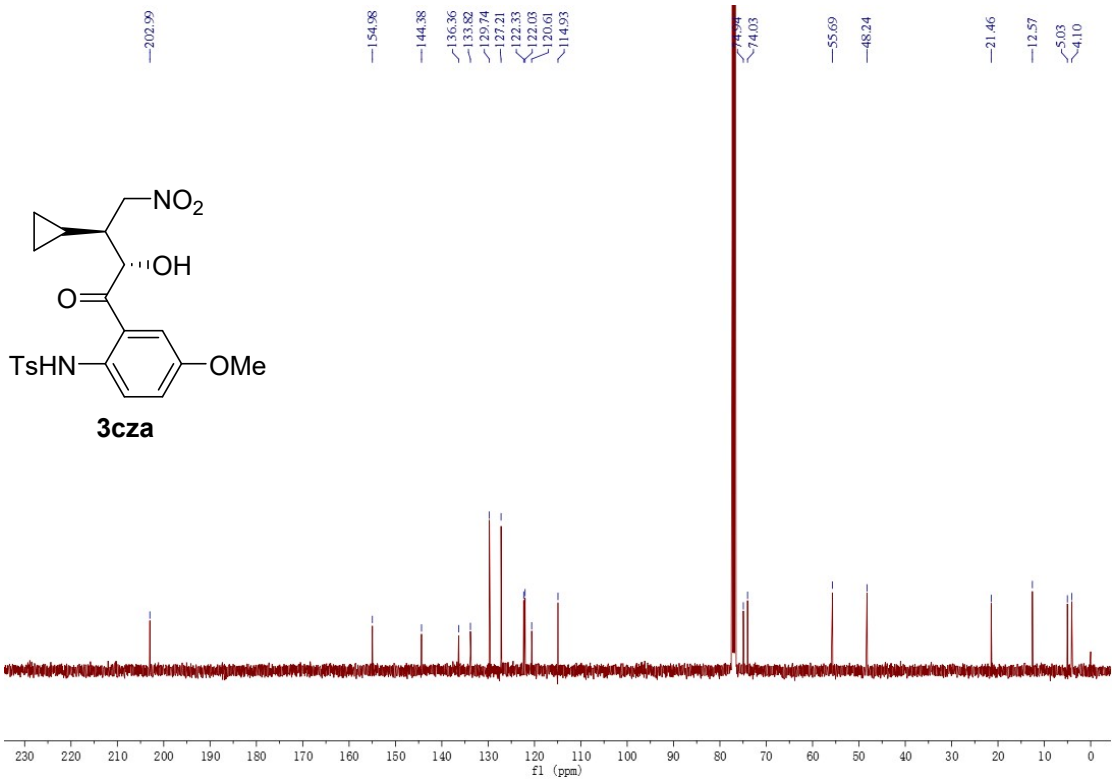
^{13}C NMR spectrum of compound **3cz** ($CDCl_3$, 400 MHz)



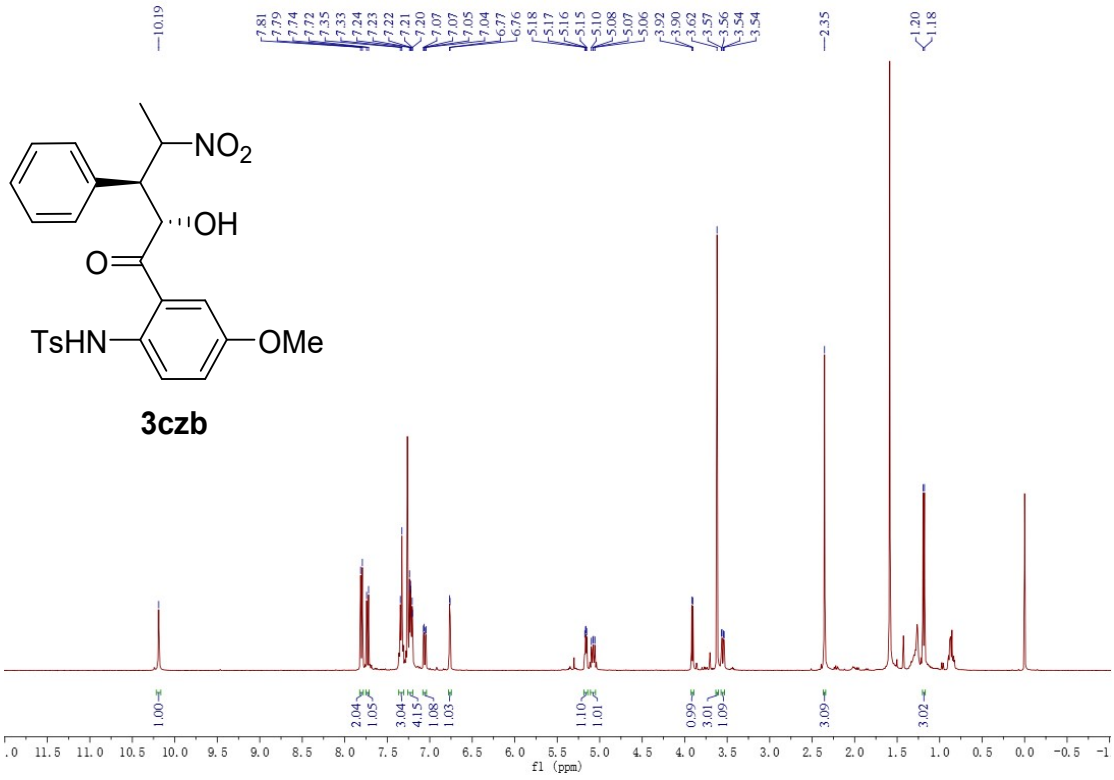
^{1}H NMR spectrum of compound **3cza** ($CDCl_3$, 400 MHz)



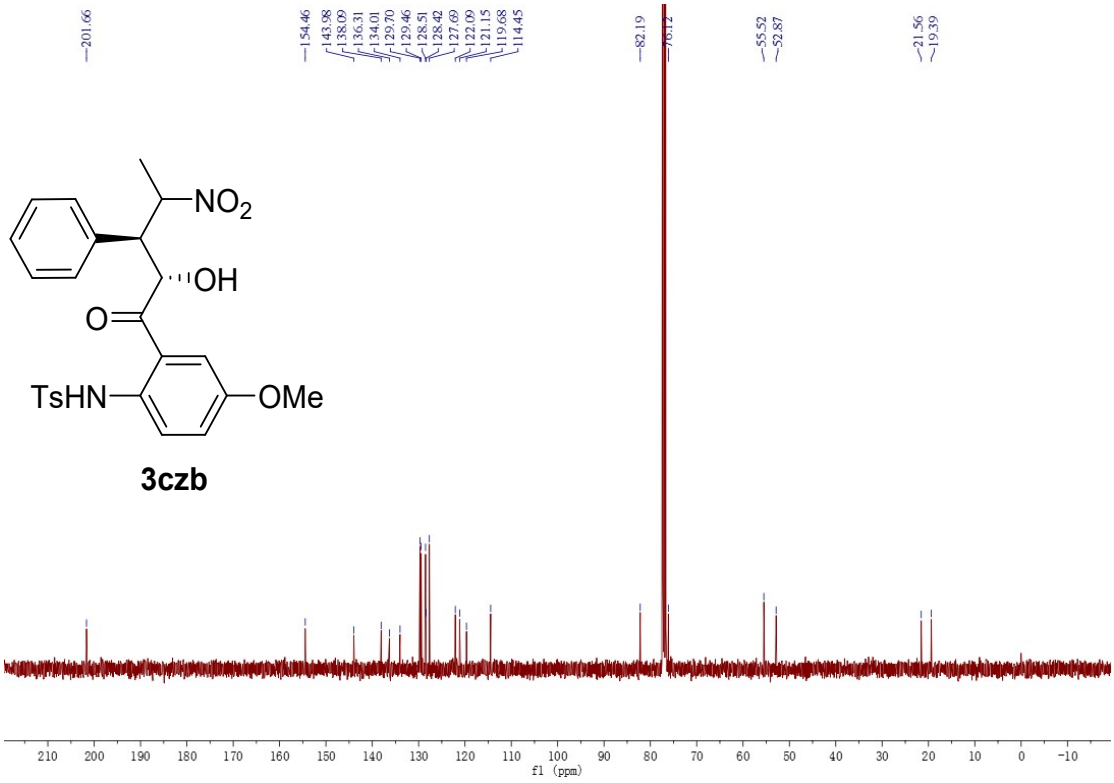
^{13}C NMR spectrum of compound **3cza** ($CDCl_3$, 400 MHz)



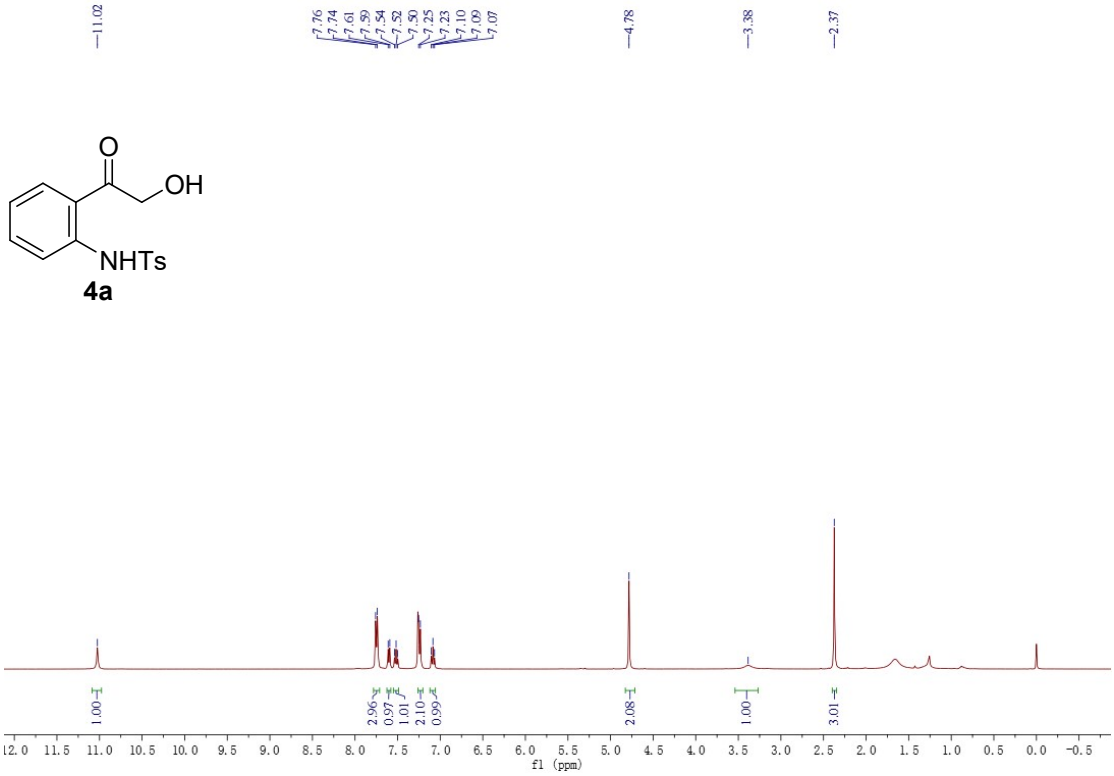
^{1}H NMR spectrum of compound **3czb** ($CDCl_3$, 400 MHz)



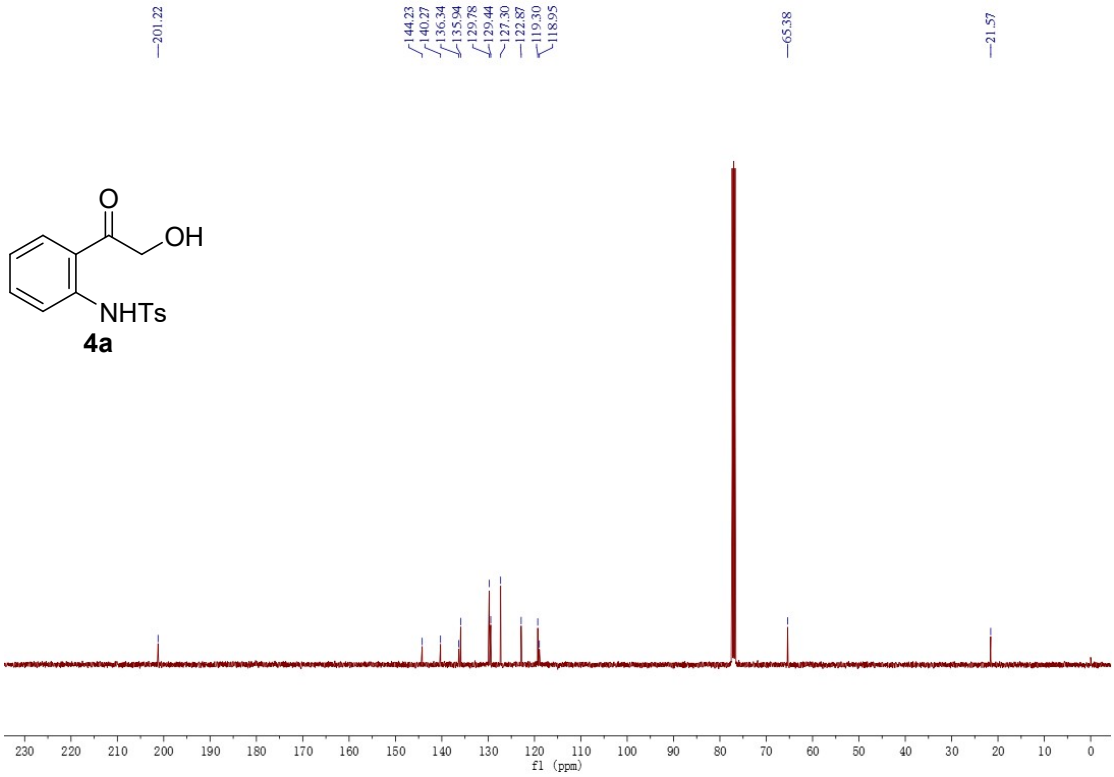
^{13}C NMR spectrum of compound **3czb** ($CDCl_3$, 400 MHz)



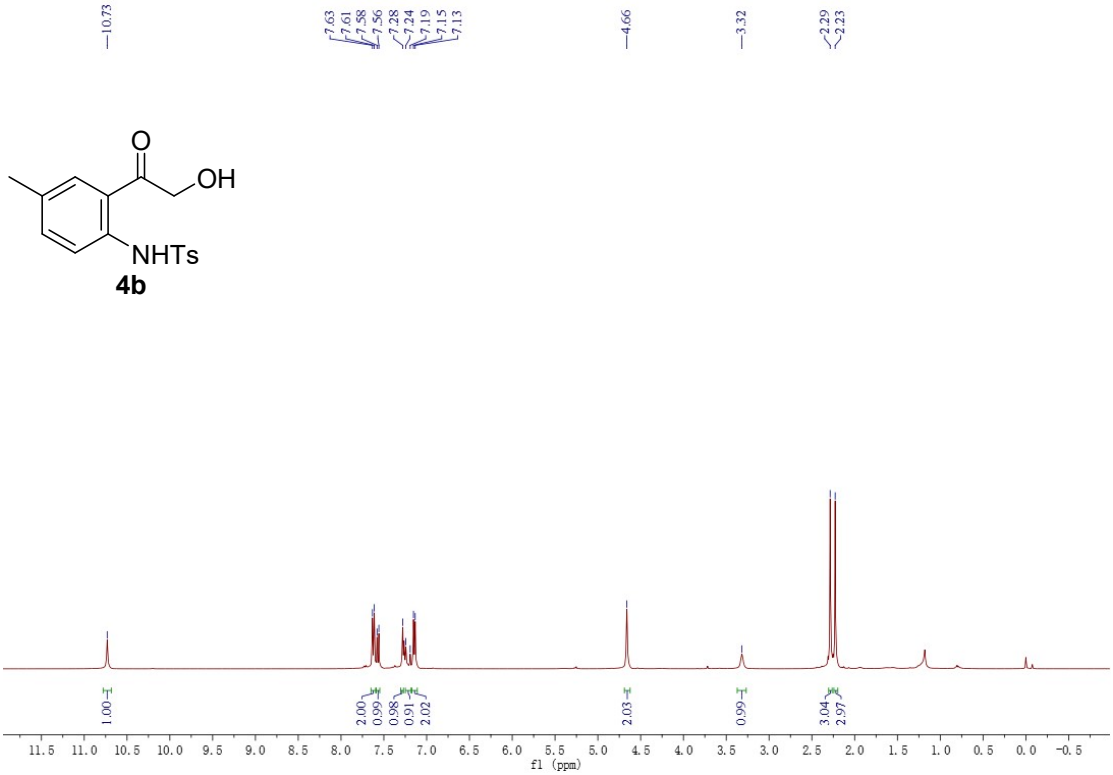
^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



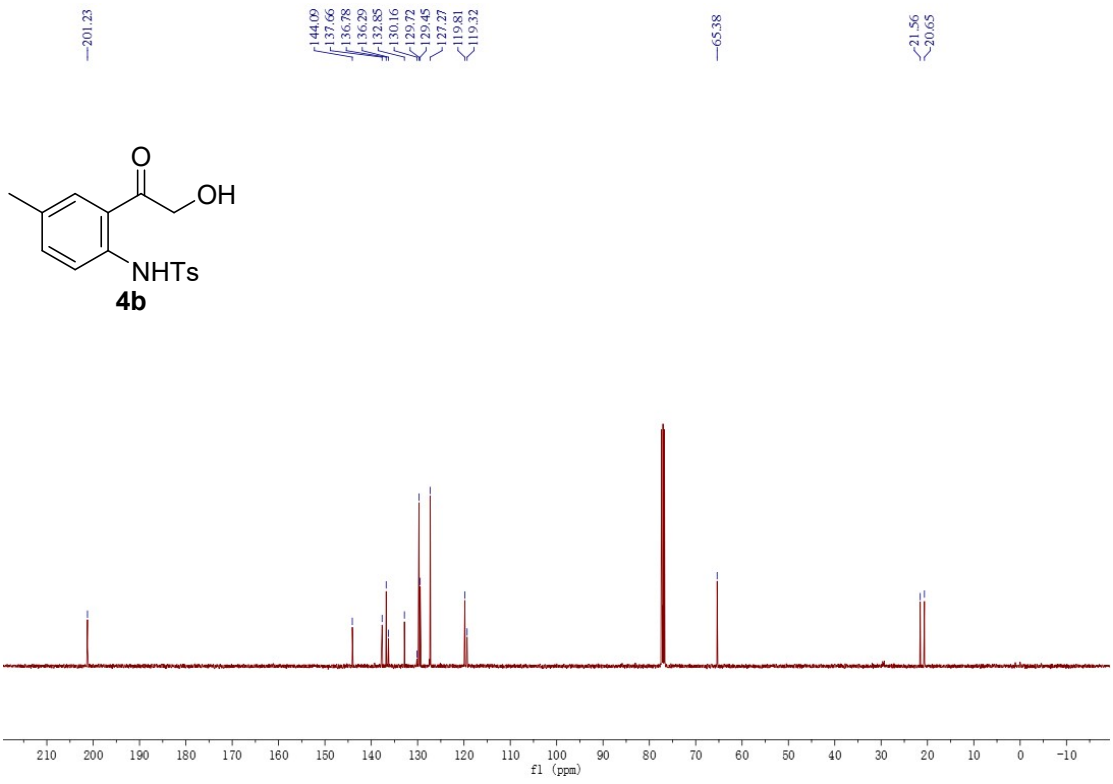
^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



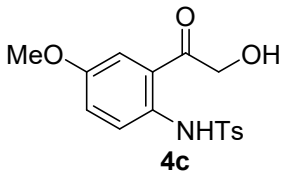
^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)



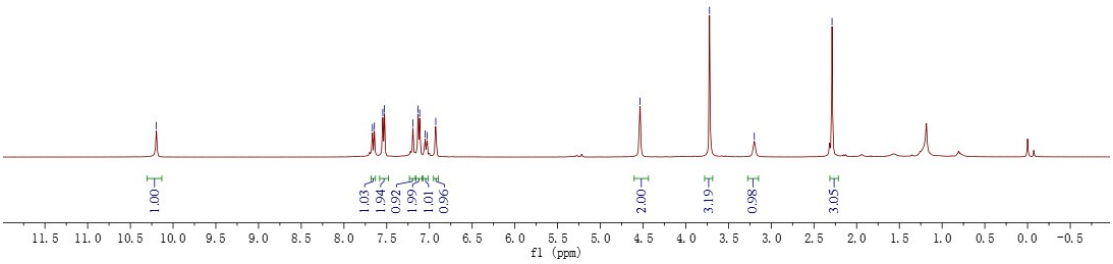
^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)



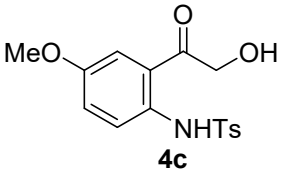
^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



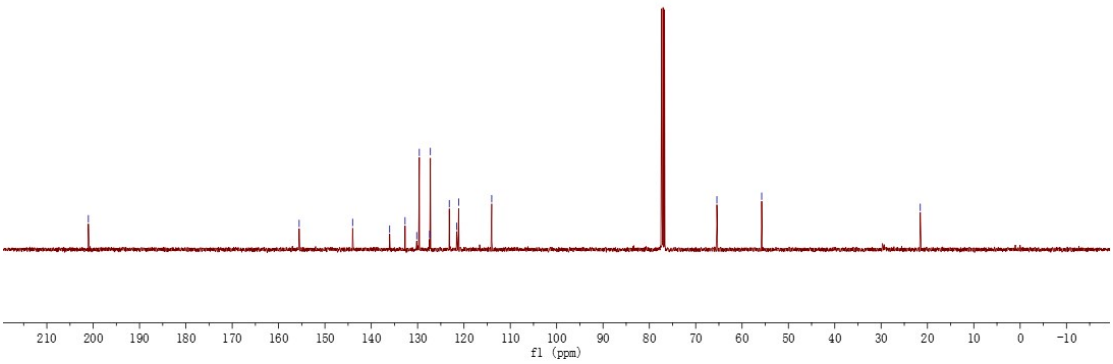
4c



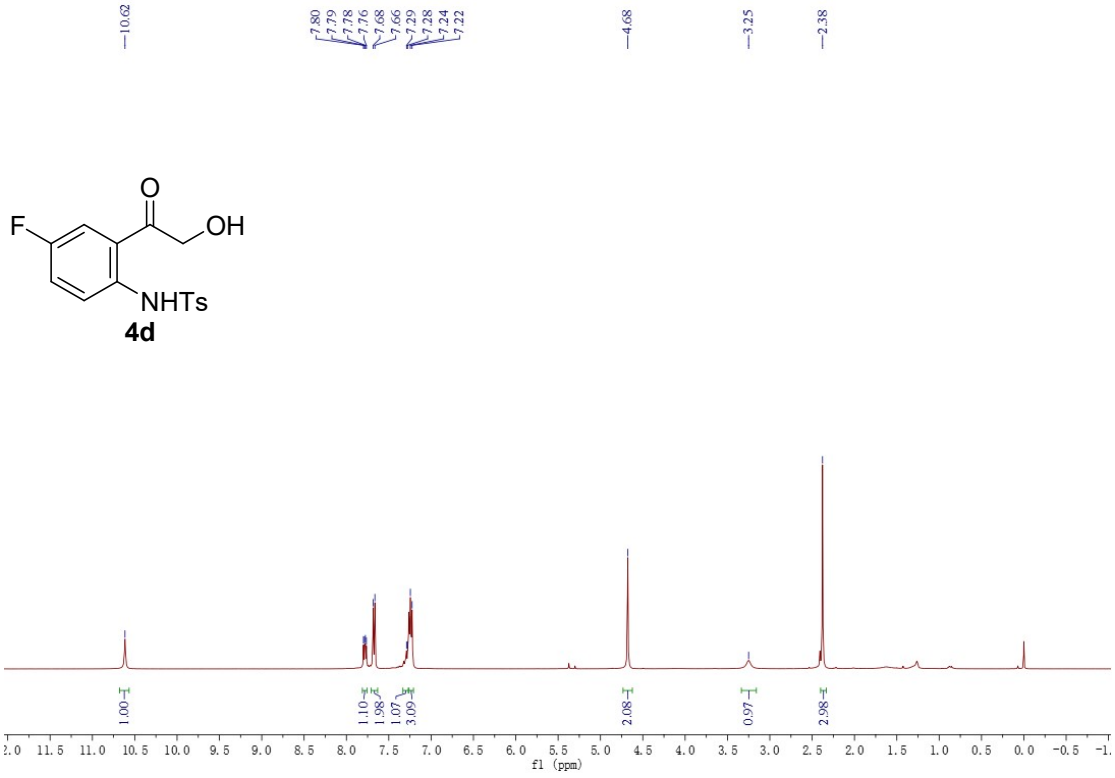
^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



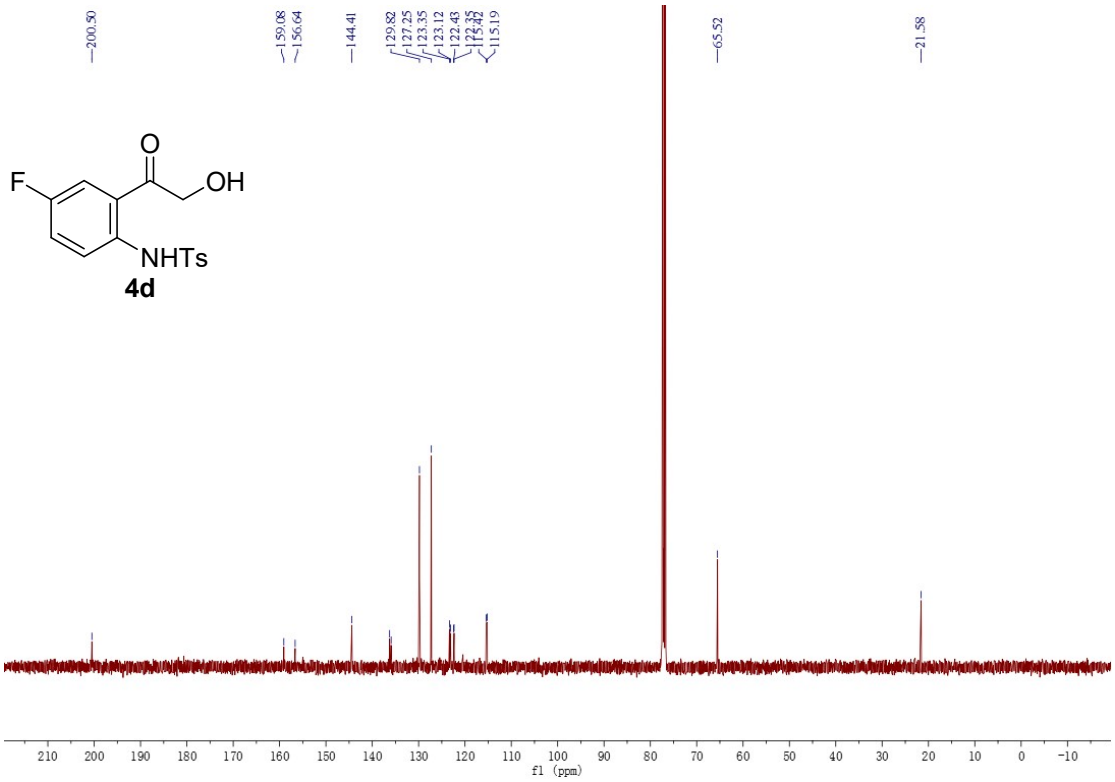
4c



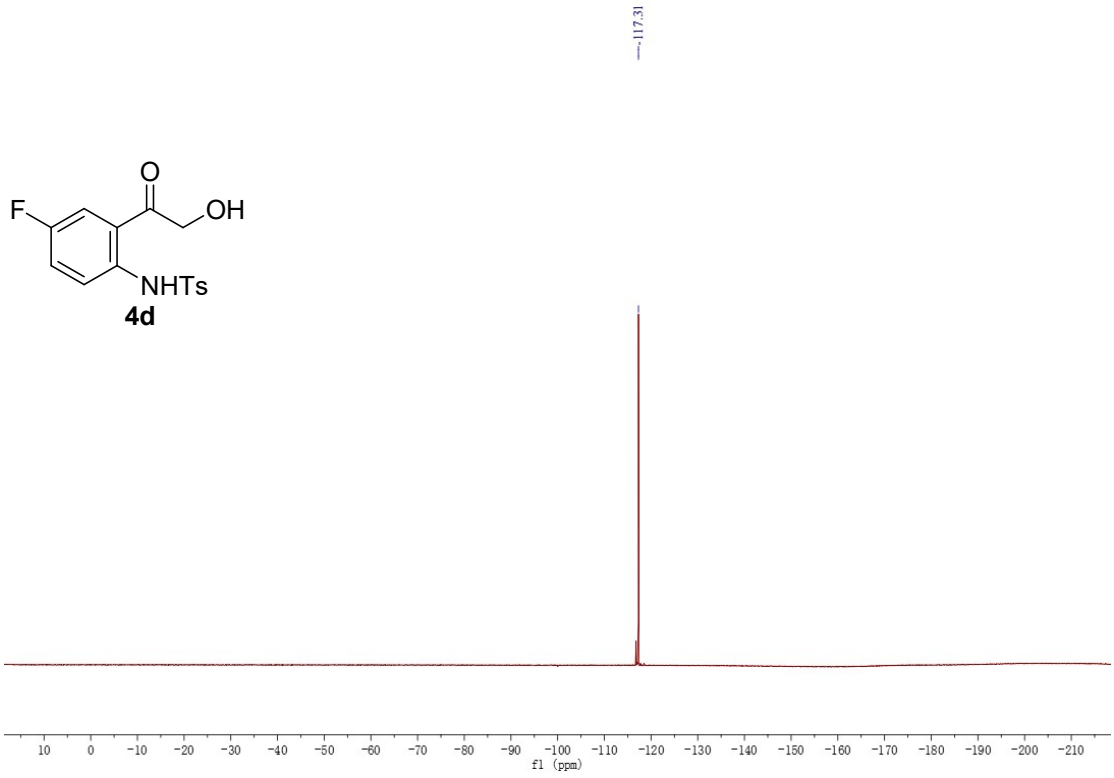
^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



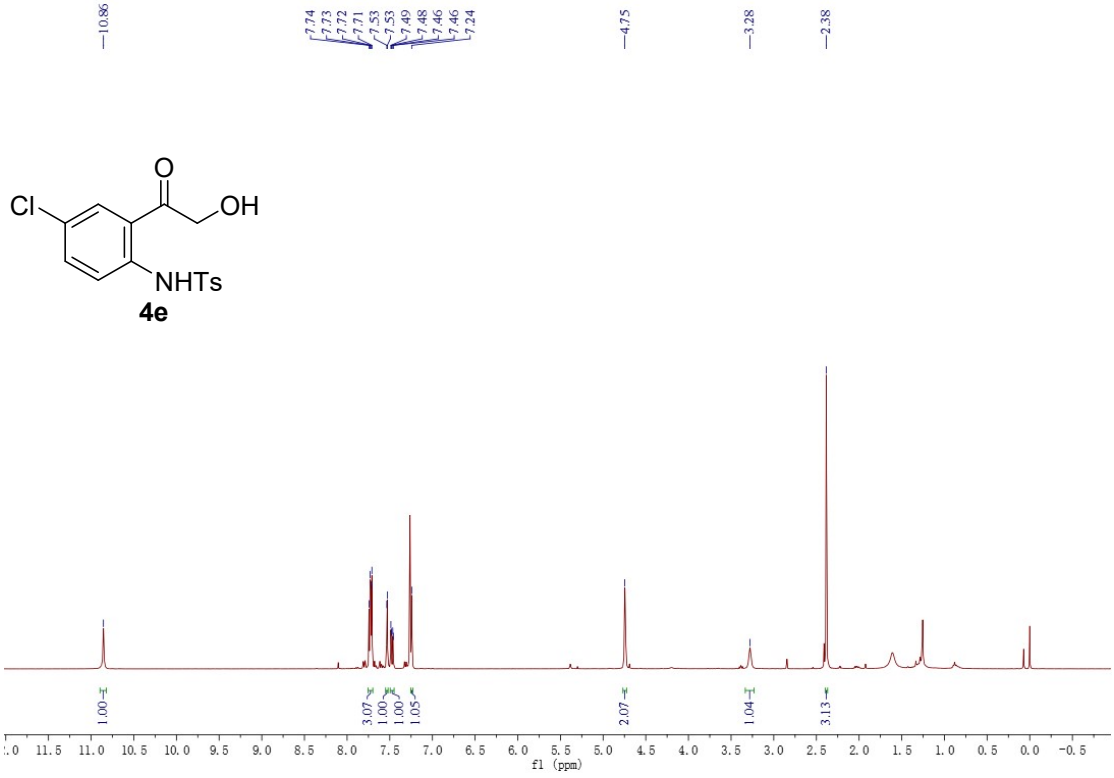
^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



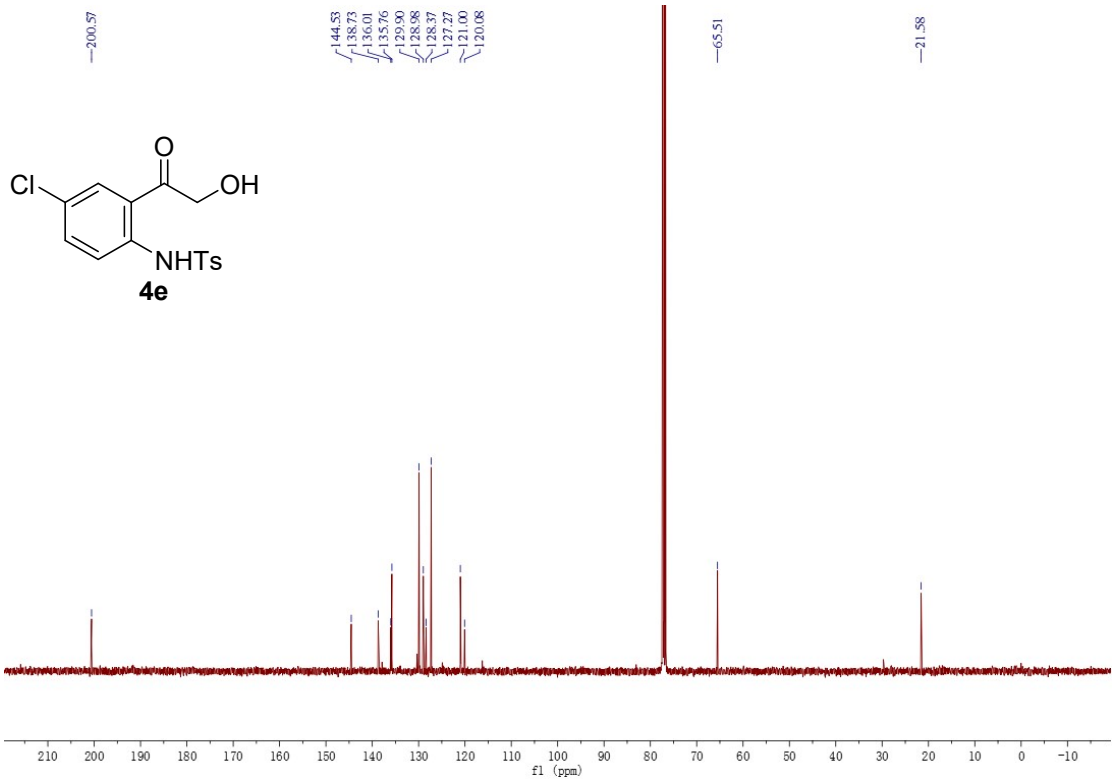
^{19}F NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



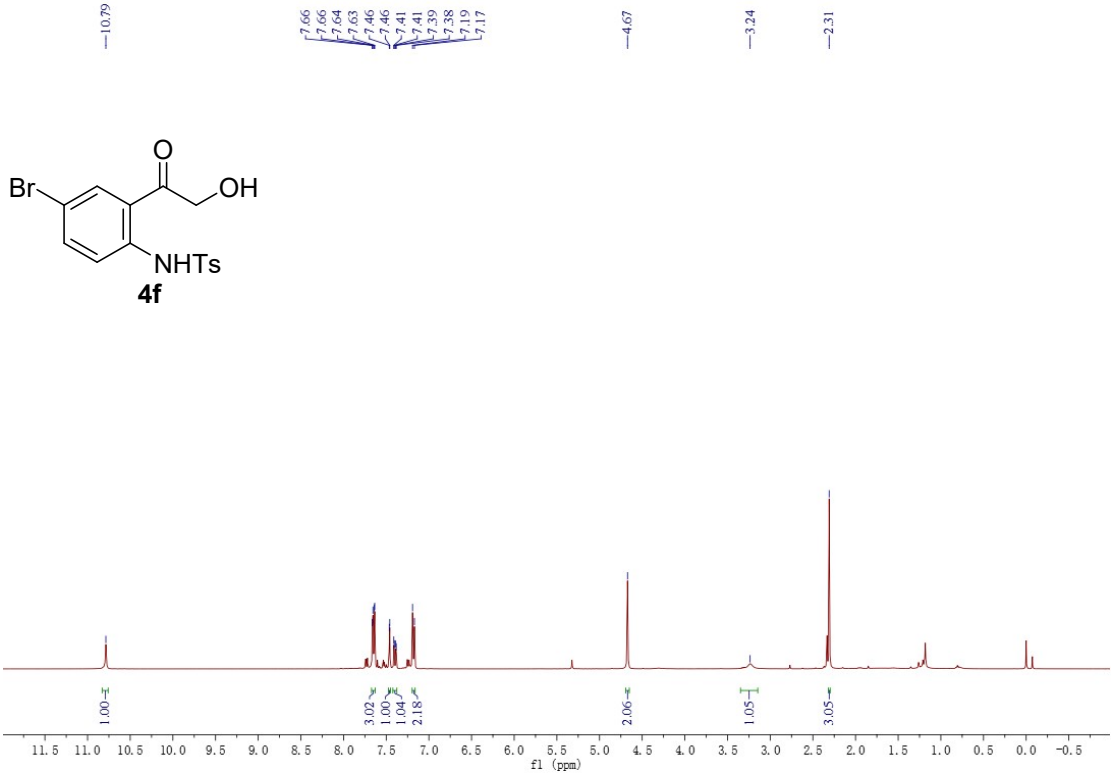
^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



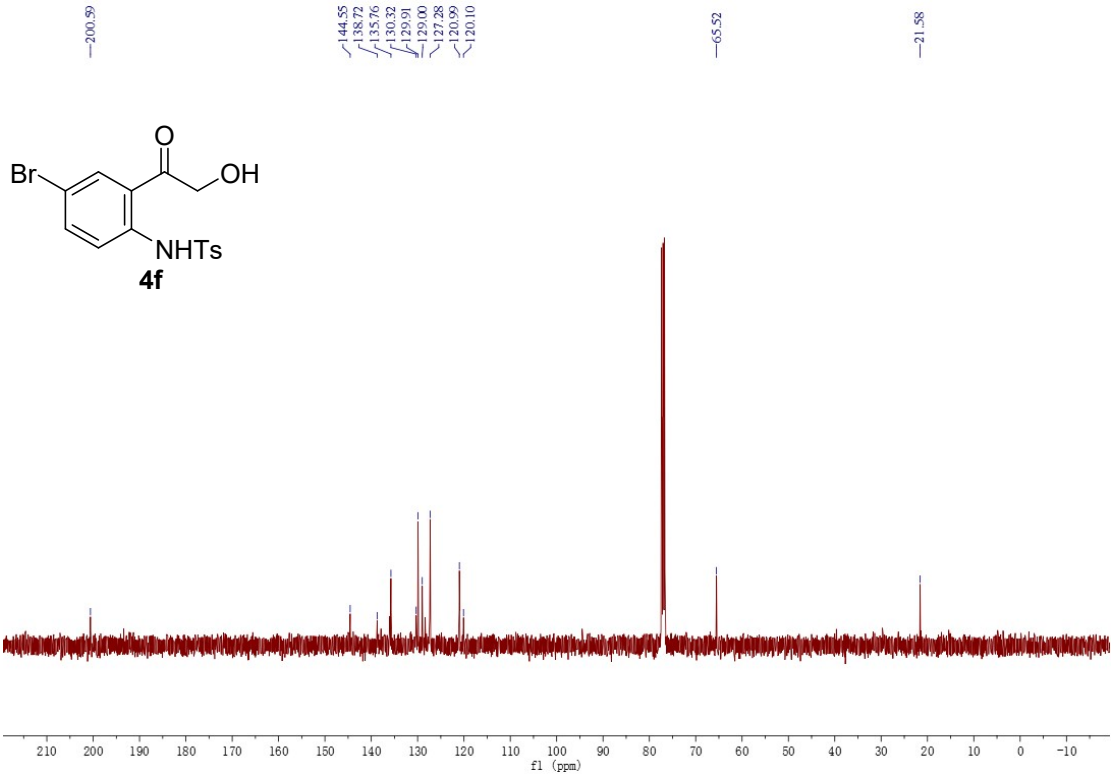
^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



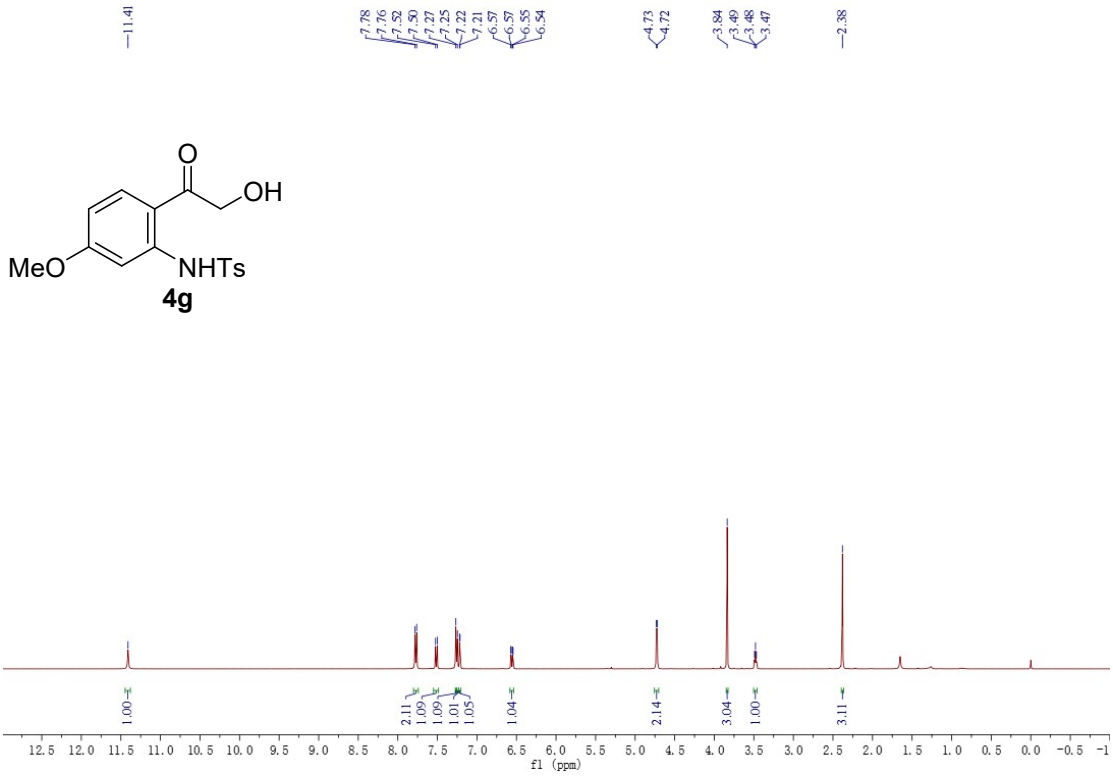
^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 400 MHz)



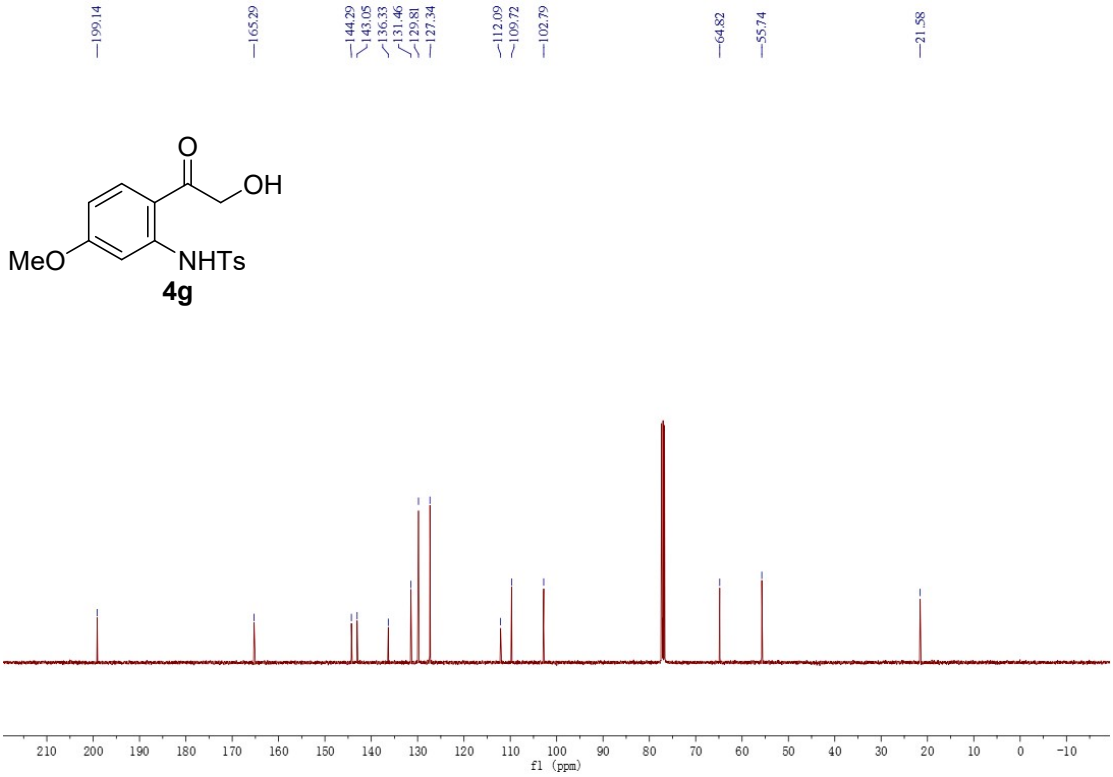
^{13}C NMR spectrum of compound **4f** ($CDCl_3$, 400 MHz)



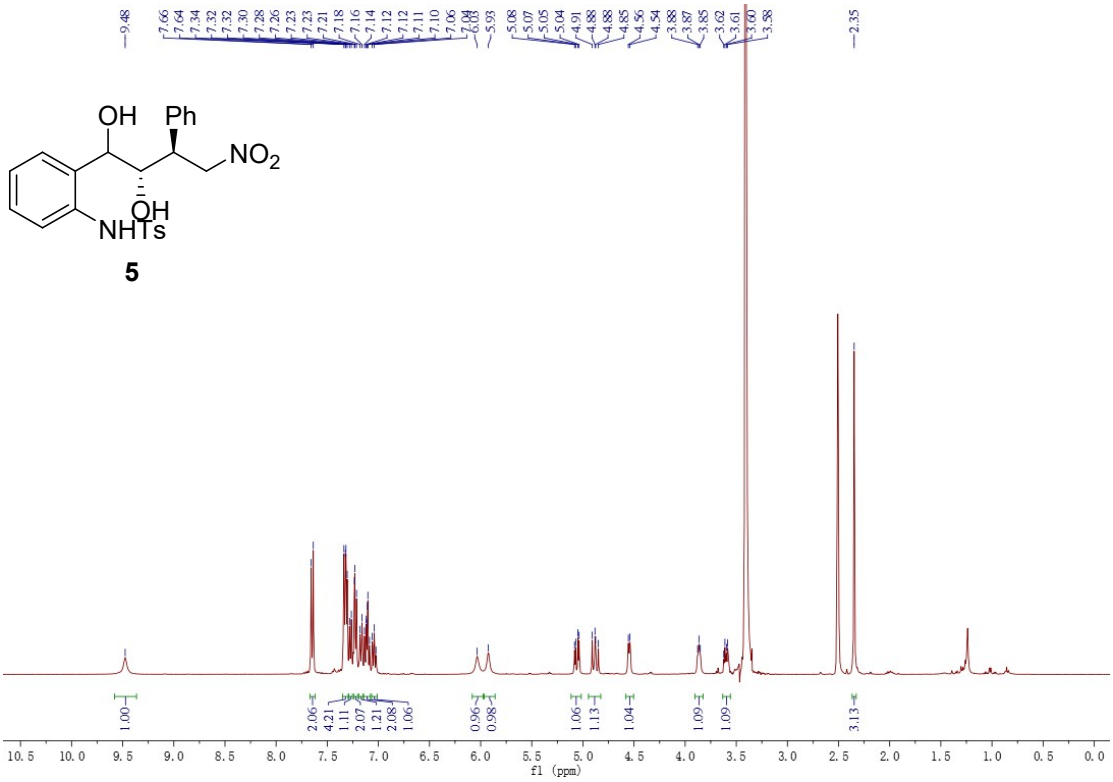
^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 400 MHz)



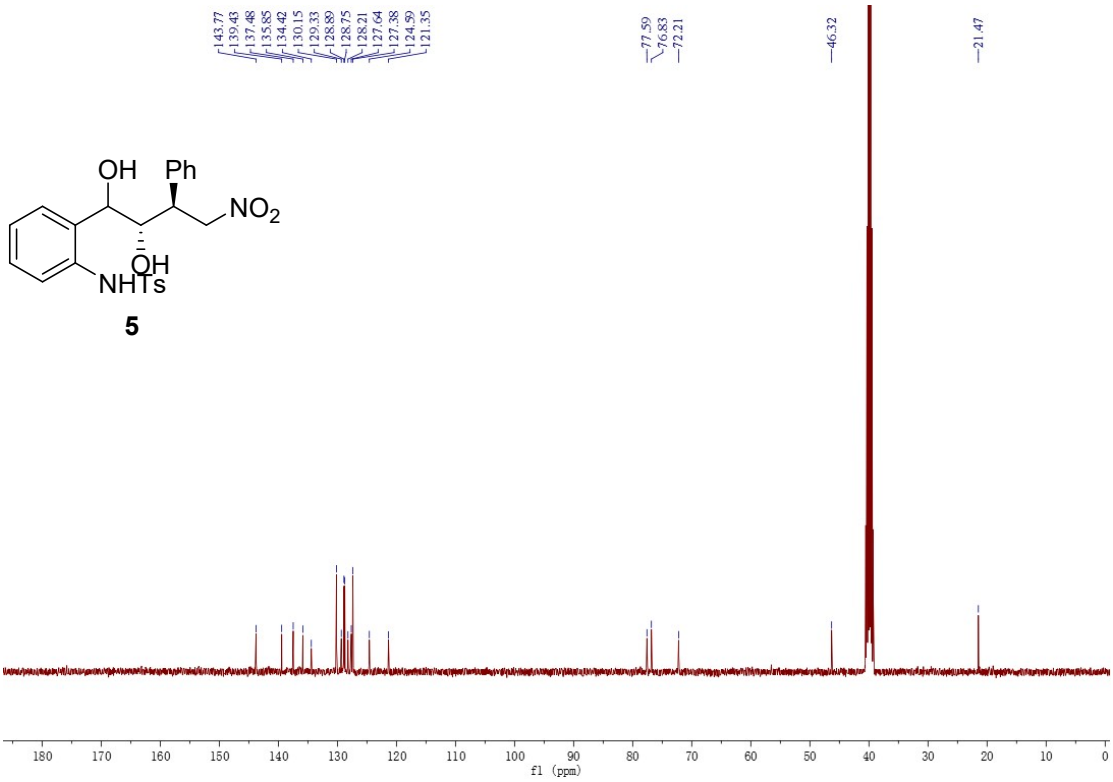
^{13}C NMR spectrum of compound **4g** ($CDCl_3$, 400 MHz)



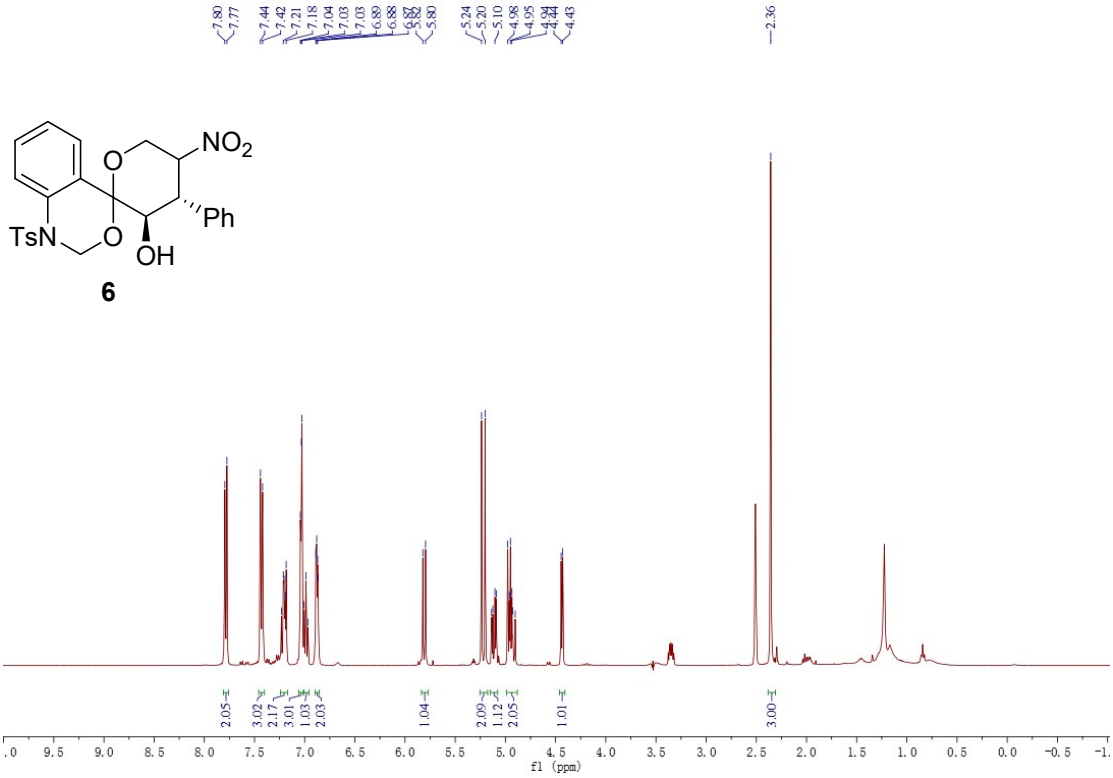
^{1}H NMR spectrum of compound **5** (DMSO, 400 MHz)



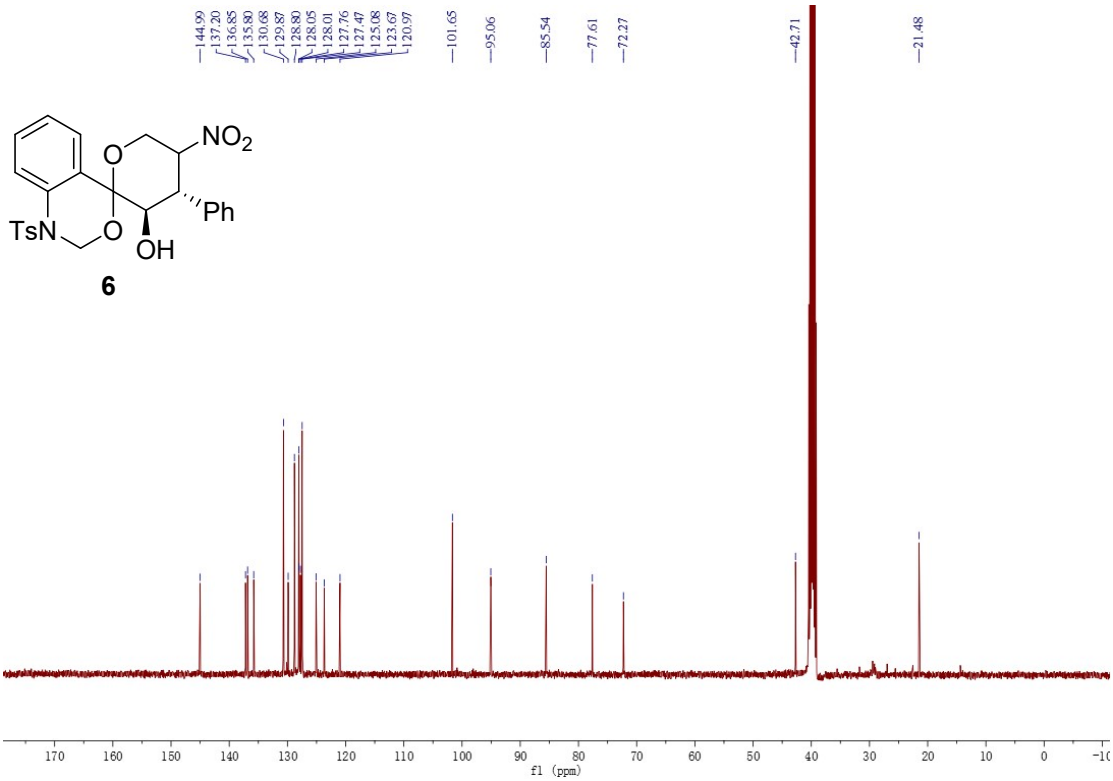
^{13}C NMR spectrum of compound **5** (DMSO, 400 MHz)



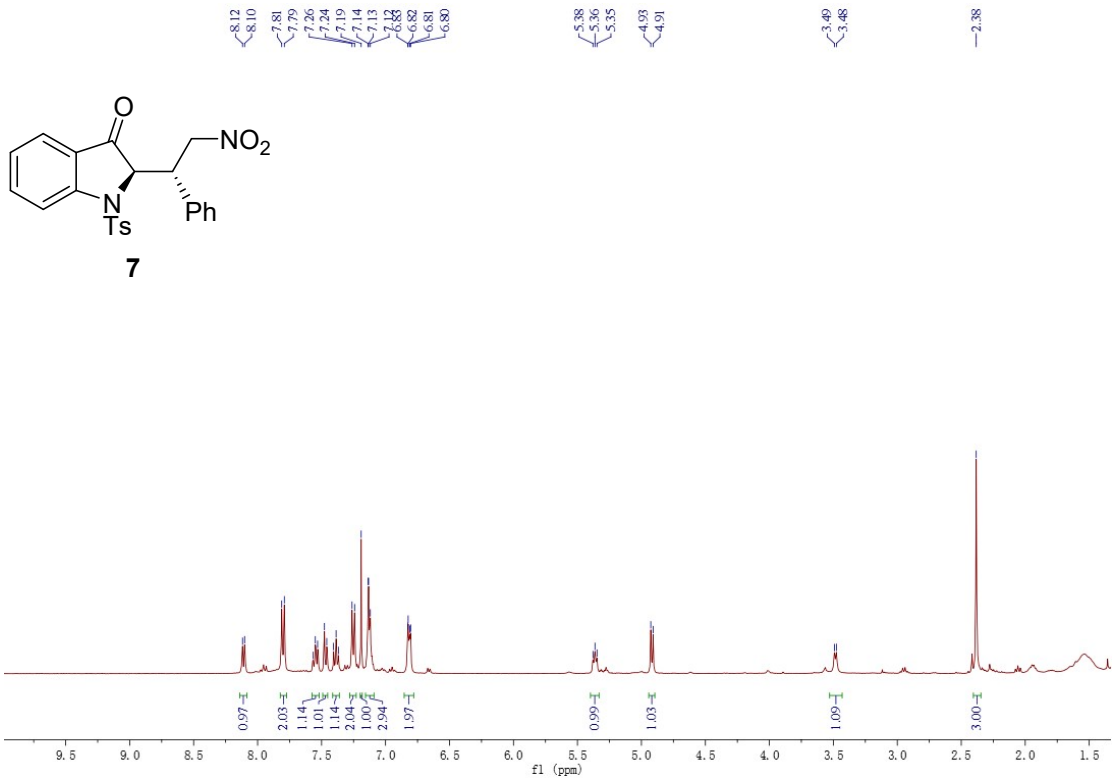
^{1}H NMR spectrum of compound **6** (DMSO, 400 MHz)



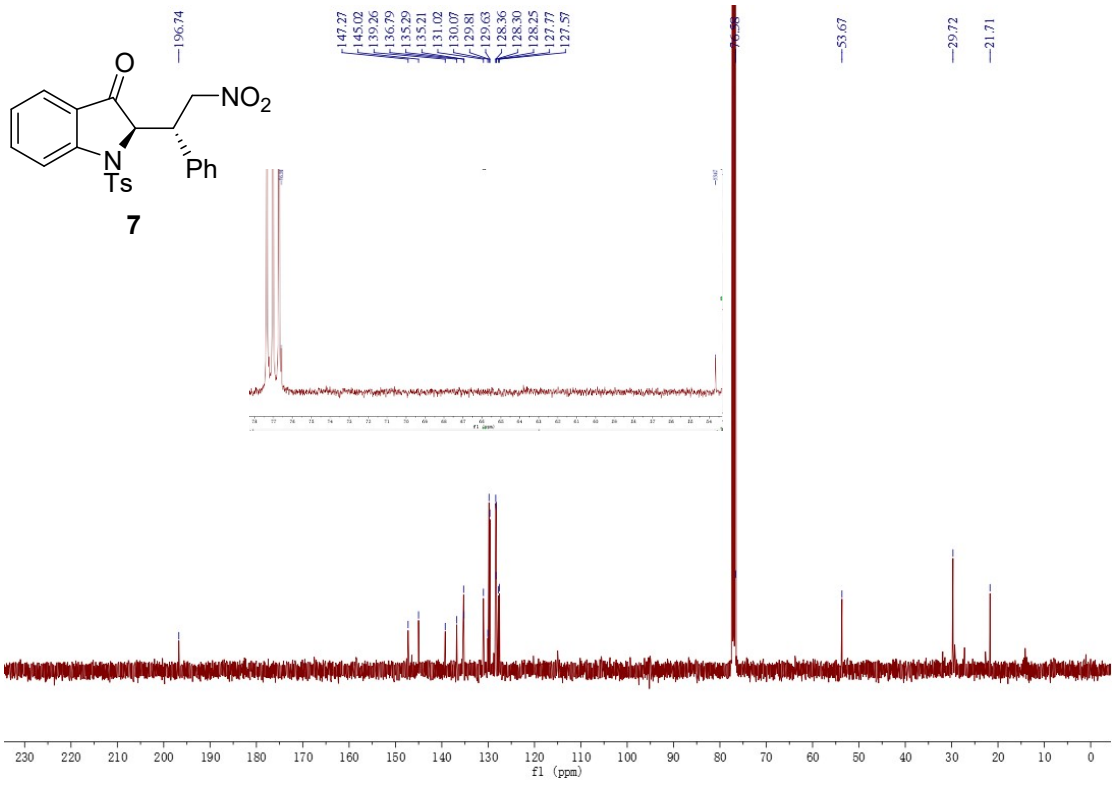
^{13}C NMR spectrum of compound **6** (DMSO, 400 MHz)



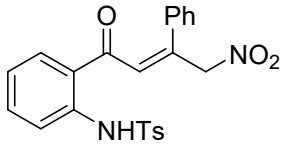
^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



^{1}H NMR spectrum of compound **8** ($CDCl_3$, 400 MHz)



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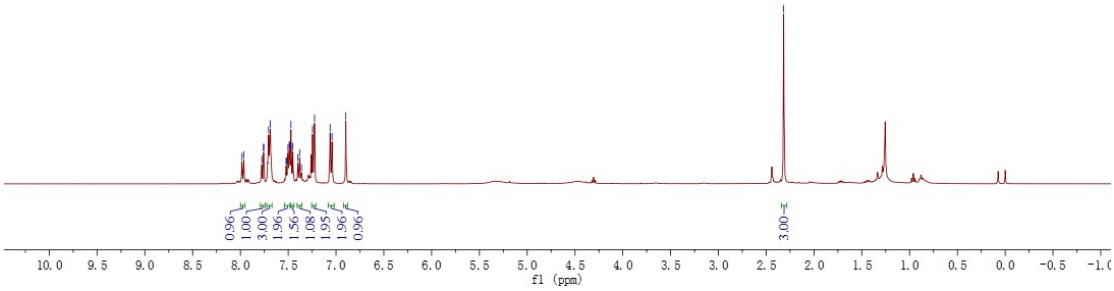
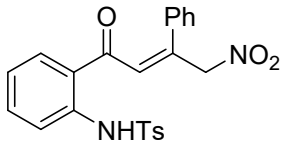
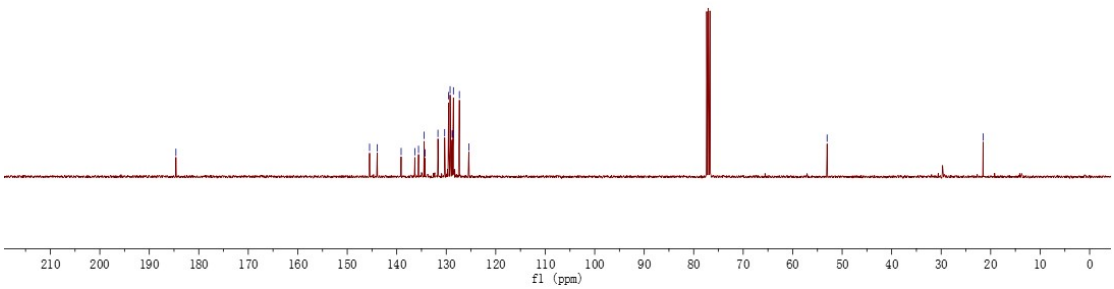


^{13}C NMR spectrum of compound **8** ($CDCl_3$, 400 MHz)



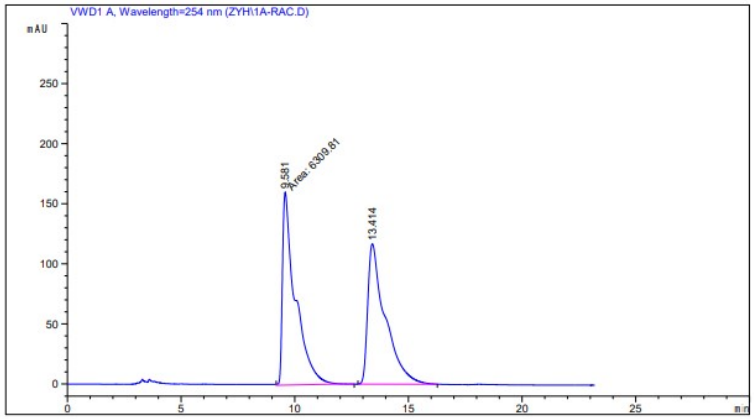
8



HPLC spectra of compounds

HPLC spectra of compound 1 and 3

rac-1a




```
================================================================================
                          Area Percent Report
================================================================================

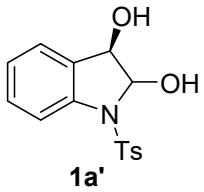
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

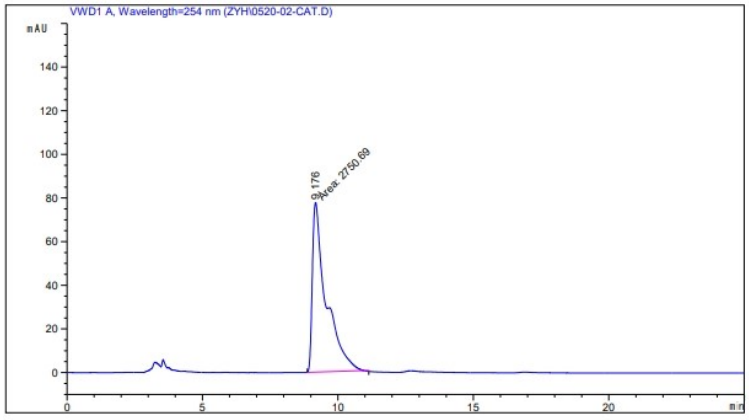
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1   9.581 MM    0.6554 6309.80908  160.45258  50.2902
   2  13.414 BB    0.7380 6236.98437  116.81078  49.7098

Totals :                 1.25468e4   277.26336
```

V



1a'



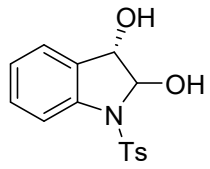

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

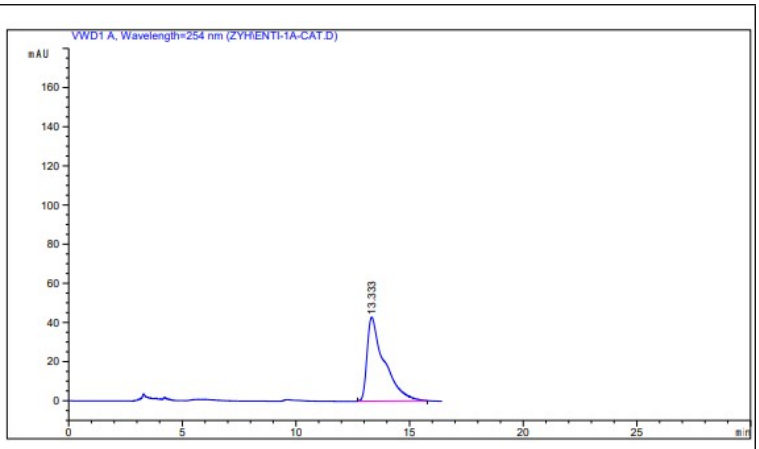

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1   9.176 MM    0.5896 2750.69385   77.75069 100.0000

Totals :                 2750.69385   77.75069
```



3*S*-**1a'**




```
================================================================================
                              Area Percent Report
================================================================================

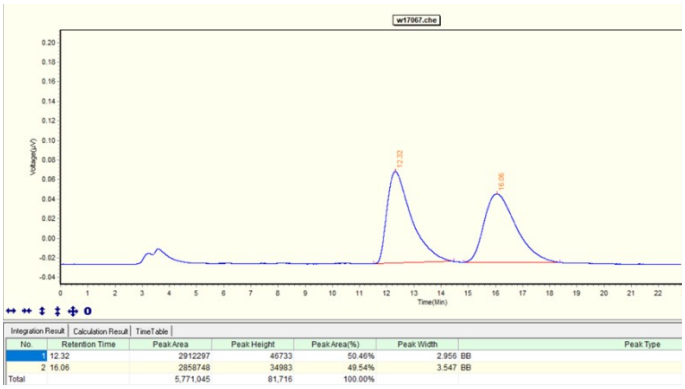
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

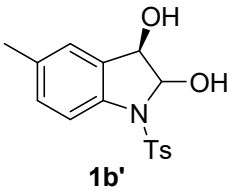

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  13.333 BB    0.7272 2249.02026   42.85896 100.0000

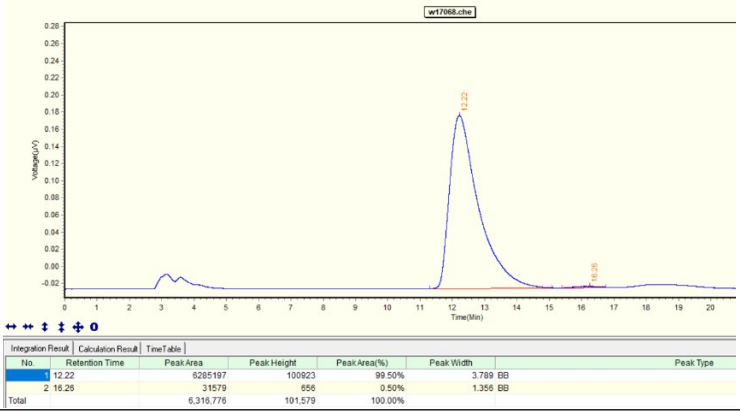
Totals :                  2249.02026   42.85896
```

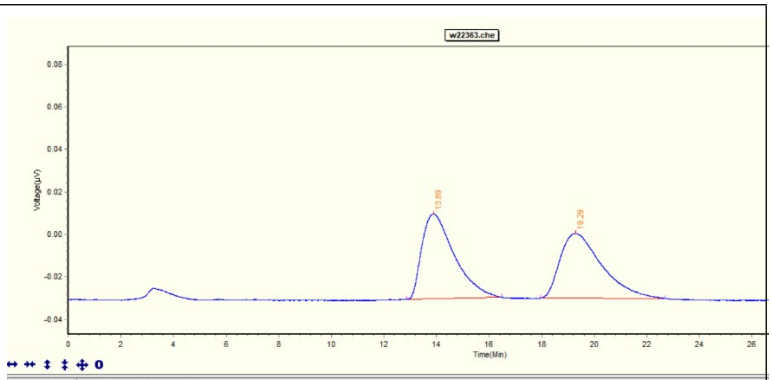
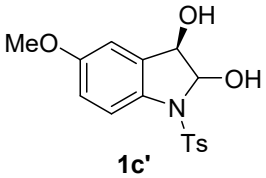
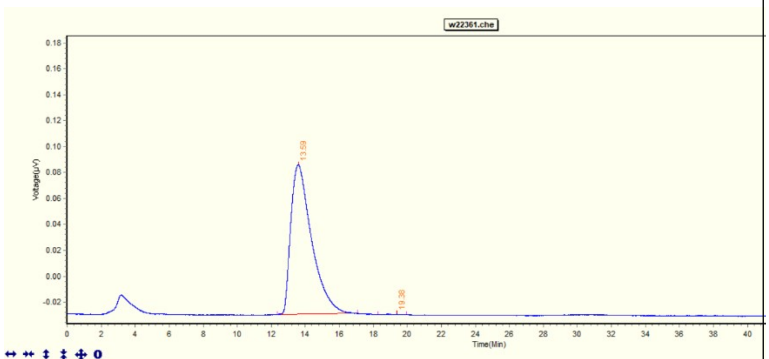
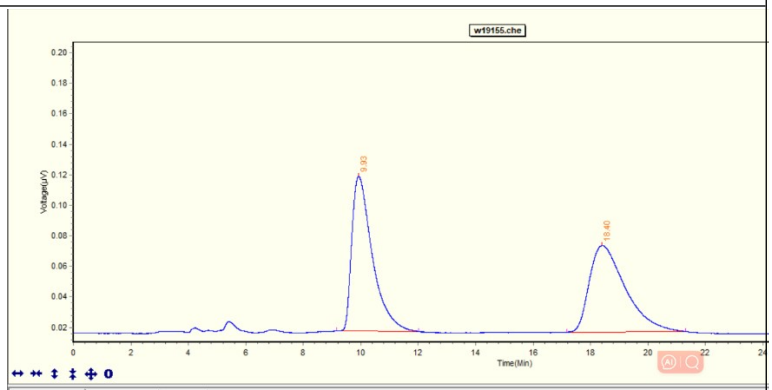
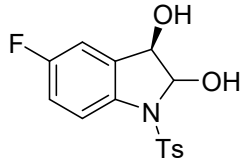
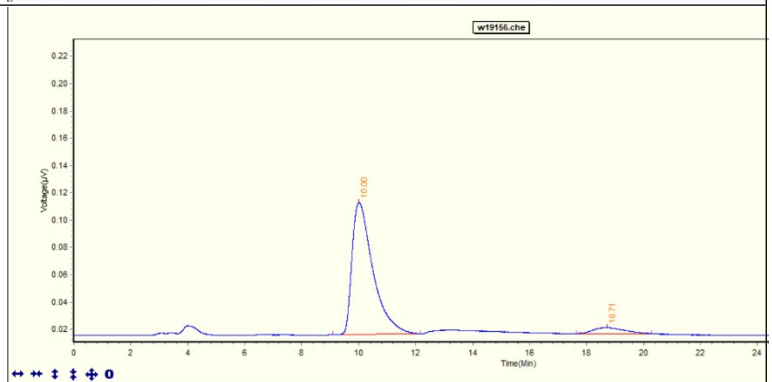
rac-1b



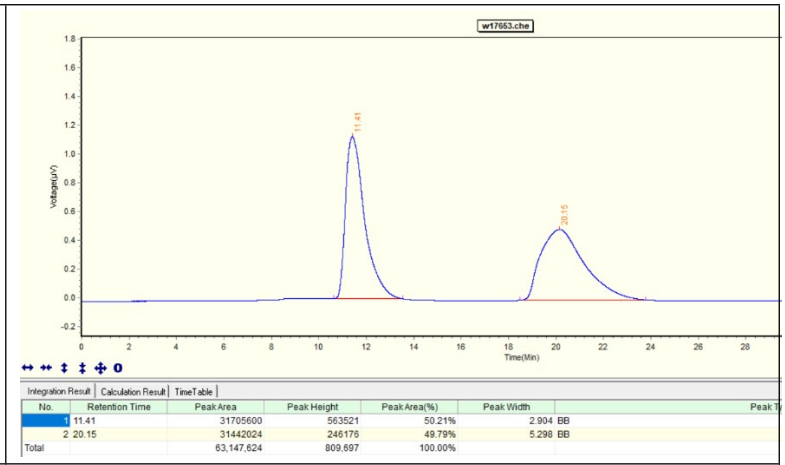


1b'



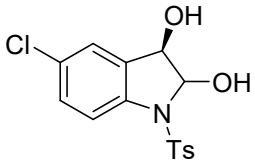
rac-1c	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 13.89 1706357 19962 50.55% 3.631 BB 2 19.29 1669545 15218 49.45% 4.738 BB Total 3,375,902 35,180 100.00%
 **1c'**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 13.59 4894241 57626 99.89% 4.719 BB 2 19.38 5161 188 0.11% 1.673 BB Total 4,899,402 57,814 100.00%
rac-1d	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak 1 9.93 2518075 50702 50.63% 2.858 BB 2 18.40 2455168 28320 49.37% 4.128 BB Total 4,973,243 79,022 100.00%
 **1d'**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak 1 10.00 2461784 48232 93.93% 3.066 BB 2 18.71 159197 2183 6.07% 2.636 BB Total 2,620,981 50,415 100.00%

rac-1e

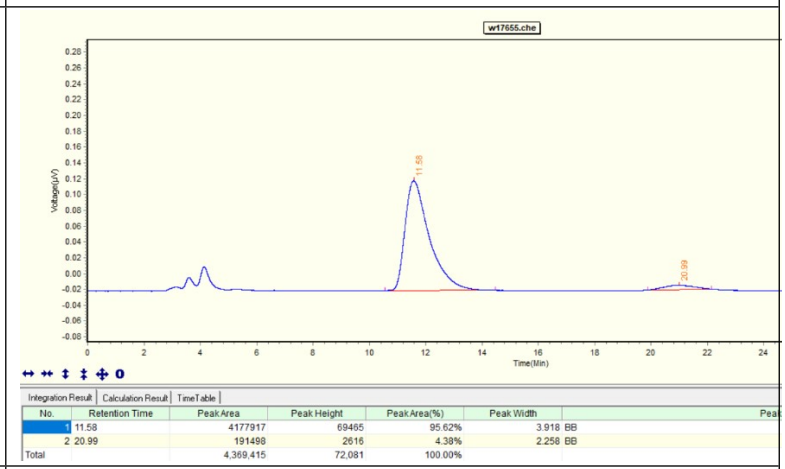


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Ty
1	11.41	31705600	563521	50.21%	2.904	BB
2	20.15	31442024	246176	49.79%	5.298	BB
Total		63,147,624	809,697	100.00%		



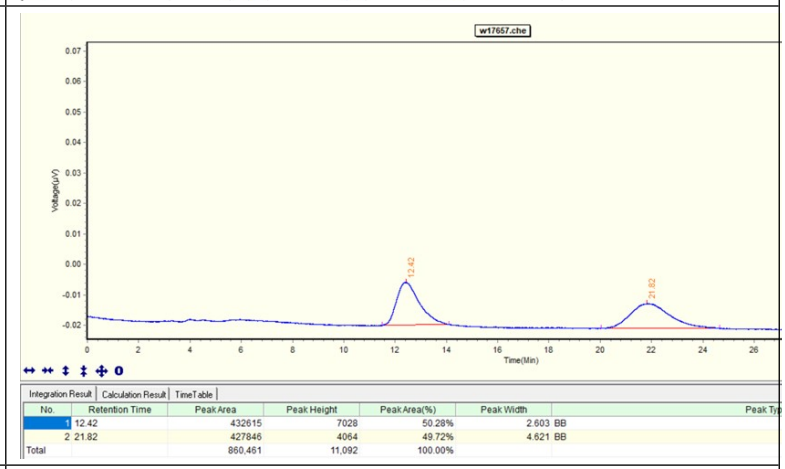
1e'



Integration Result | Calculation Result | TimeTable

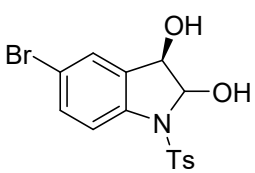
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak
1	11.58	4177917	69465	95.62%	3.918	BB
2	20.99	191498	2616	4.38%	2.258	BB
Total		4,369,415	72,081	100.00%		

rac-1f

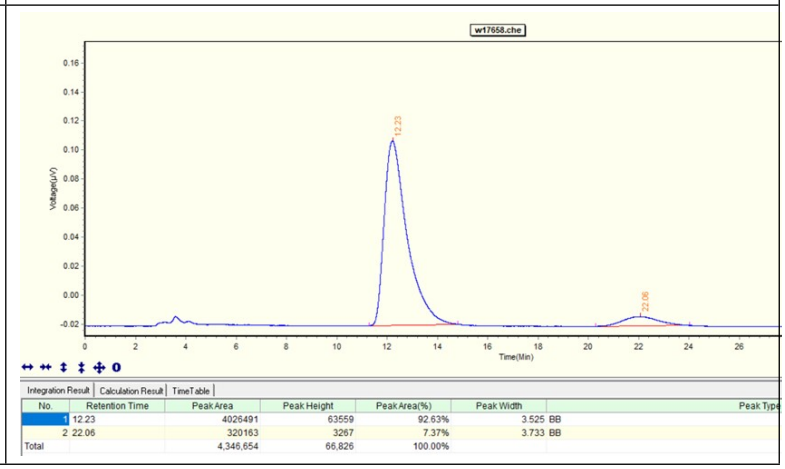


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Typ
1	12.42	432615	7028	50.28%	2.603	BB
2	21.82	427846	4064	49.72%	4.621	BB
Total		860,461	11,092	100.00%		



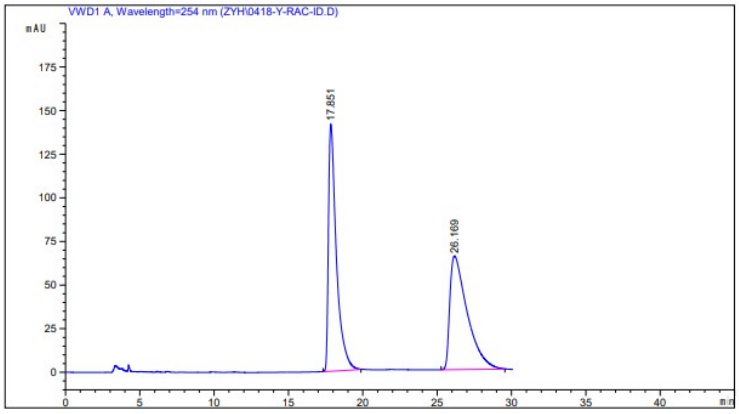
1f'



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.23	4026491	63559	92.63%	3.525	BB
2	22.06	320163	3267	7.37%	3.733	BB
Total		4,346,654	66,826	100.00%		

rac-1g



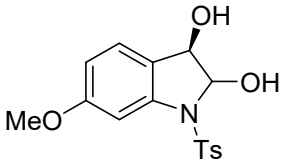

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

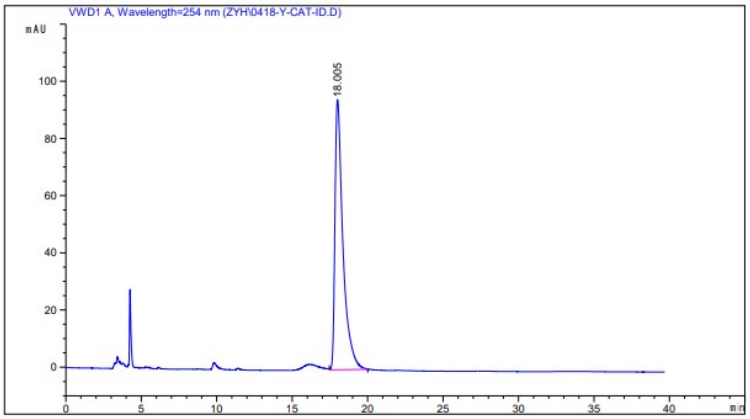

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  17.851 BB    0.5478 5269.28857  141.58293  49.8043
   2  26.169 BB    1.2017 5310.70801   65.13427  50.1957

Totals :                1.05800e4   206.71720
```



1g'




```
=====================================================================
                      Area Percent Report
=====================================================================

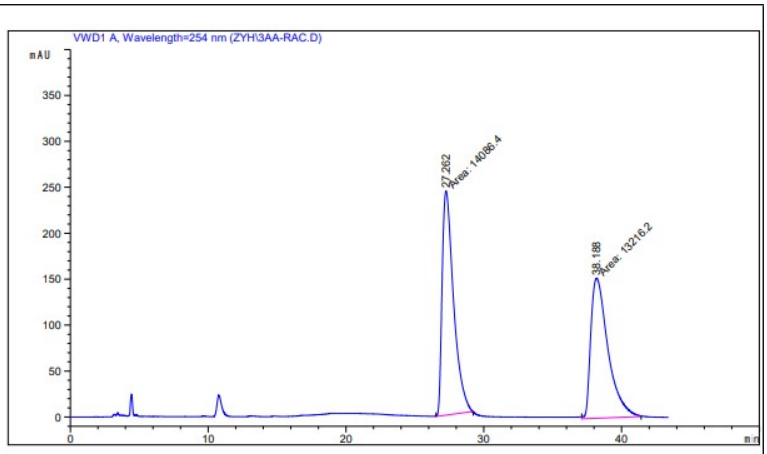
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  18.005 VB    0.5403 3477.87988   94.43565 100.0000

Totals :                3477.87988   94.43565
```

rac-3aa



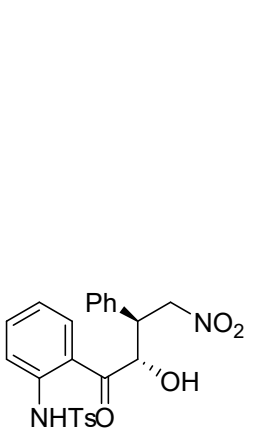

```
================================================================
                    Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

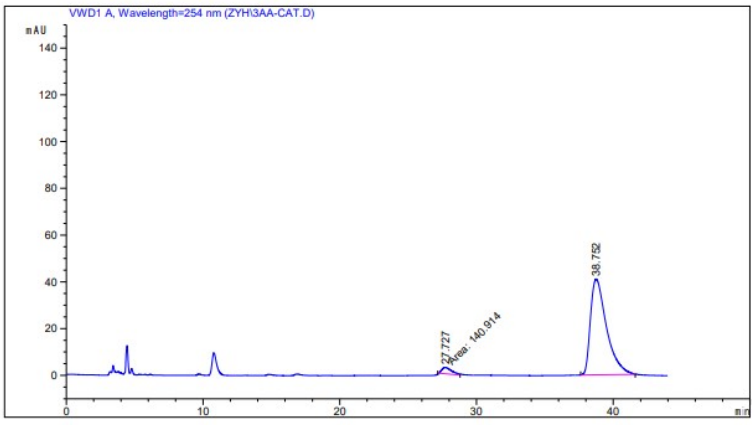

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.262 MM    0.9631 1.40864e4   243.75916  51.5936
   2  38.188 MM    1.4453 1.32162e4   152.40382  48.4064

Totals :                  2.73026e4   396.16298
```



3aa



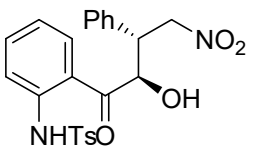

```
================================================================
                    Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

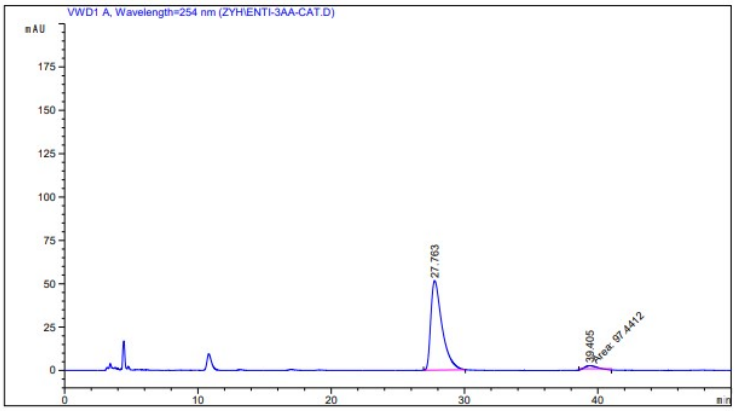

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.727 MM    0.8538  140.91402    2.75071   4.0435
   2  38.752 BB    1.2288 3344.06616   40.97520  95.9565

Totals :                  3484.98018   43.72592
```



enti-**3aa**




```
================================================================
                    Area Percent Report
================================================================

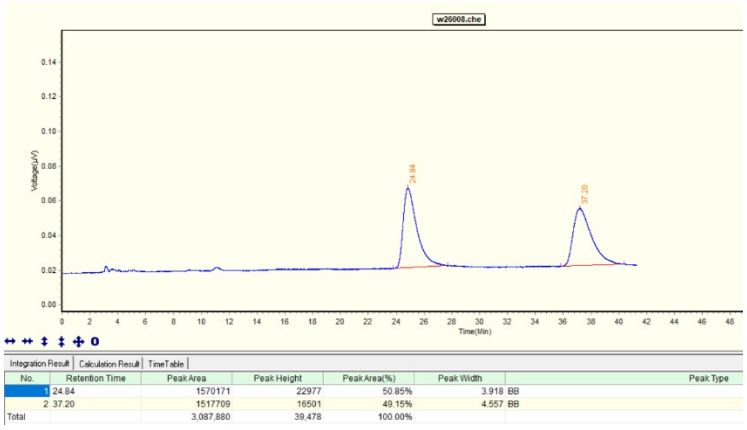
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

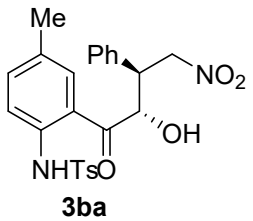
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.763 BB    0.8768 3027.93872   51.59699  96.8823
   2  39.405 MM    0.9001   97.44121    1.80431   3.1177

Totals :                  3125.37993   53.40130
```

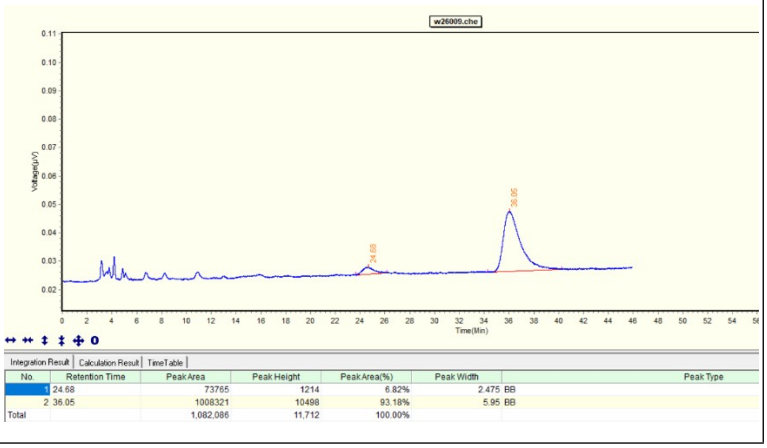
rac-3ba



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	24.84	1570171	22977	50.85%	3.918	BB
2	37.20	1517709	16501	49.15%	4.557	BB
Total		3,087,880	39,478	100.00%		

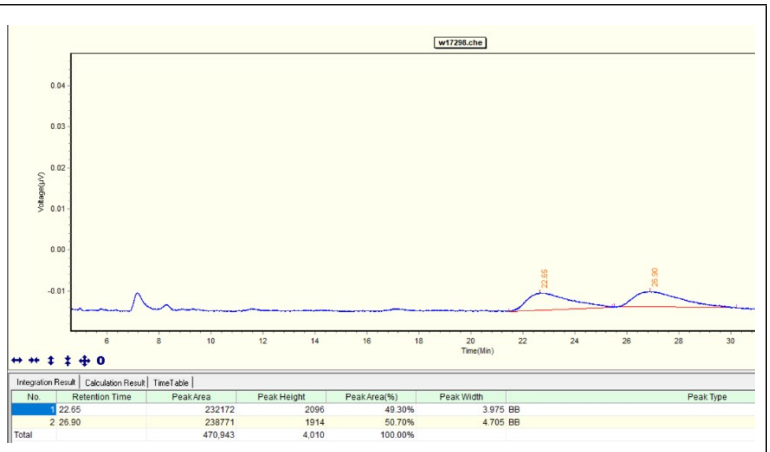


3ba

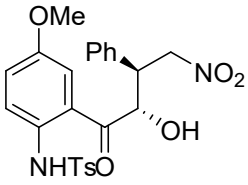


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	24.68	73765	1214	6.82%	2.475	BB
2	36.05	1008321	10498	93.18%	5.95	BB
Total		1,082,086	11,712	100.00%		

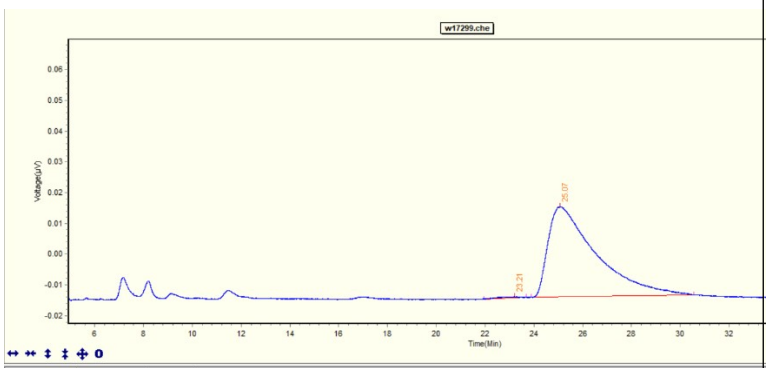
rac-3ca



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	22.65	232172	2096	49.30%	3.975	BB
2	26.90	238771	1914	50.70%	4.705	BB
Total		470,943	4,010	100.00%		

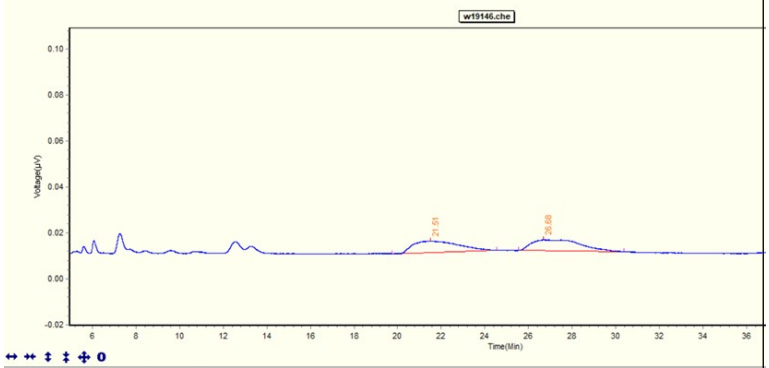


3ca

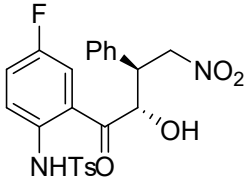


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.21	10716	174	0.54%	1.758	BB
2	25.07	1983660	14664	99.46%	6.673	BB
Total		1,994,376	14,838	100.00%		

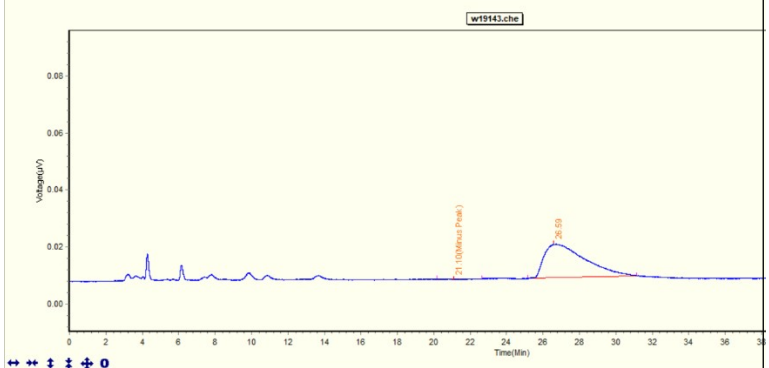
rac-3da



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	21.51	358728	2526	49.36%	4.798	BB
2	26.68	367961	2328	50.64%	4.832	BB
Total		726,689	4,854	100.00%		

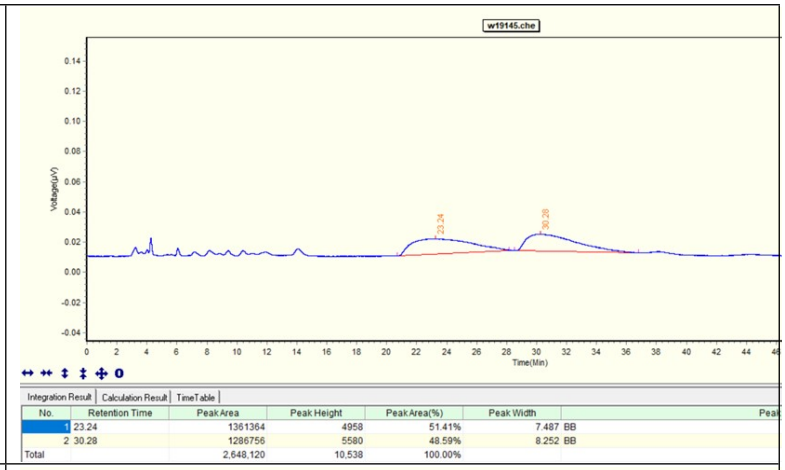


3da

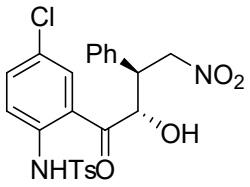


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak
1	21.10	2778	115	0.30%	2.469	BB
2	26.59	919911	5918	99.70%	5.984	BB
Total		922,689	6,033	100.00%		

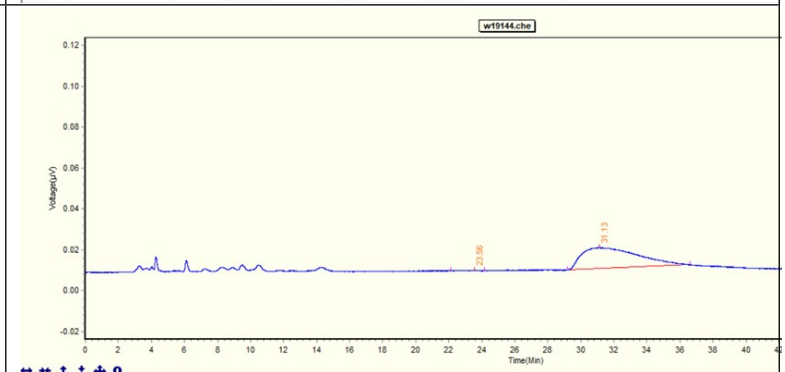
rac-3ea



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	23.24	1361364	4958	51.41%	7.487	BB
2	30.28	1286756	5580	48.59%	8.252	BB
Total		2,648,120	10,538	100.00%		

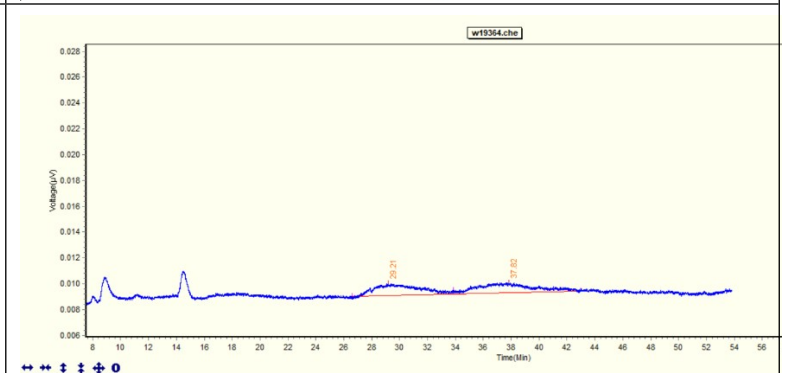


3ea

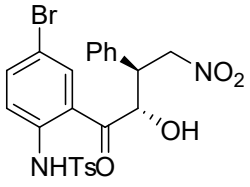


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	23.56	774	82	0.06%	2.033	BB
2	31.13	1197248	5075	99.94%	7.442	BB
Total		1,198,022	5,157	100.00%		

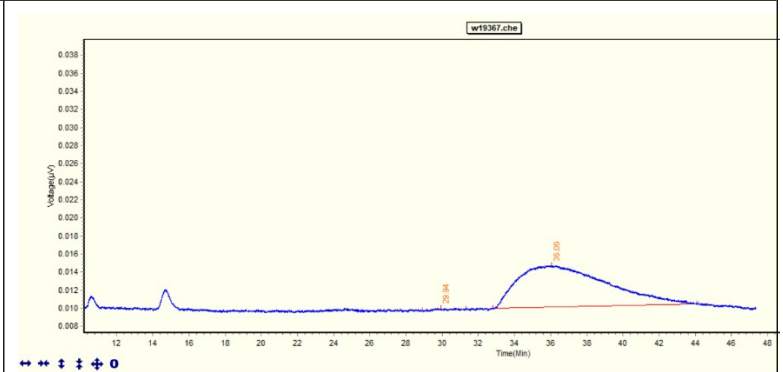
rac-3fa



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	29.21	91406	446	48.24%	7.308	BV
2	37.82	98091	385	51.76%	9.095	VB
Total		189,497	831	100.00%		

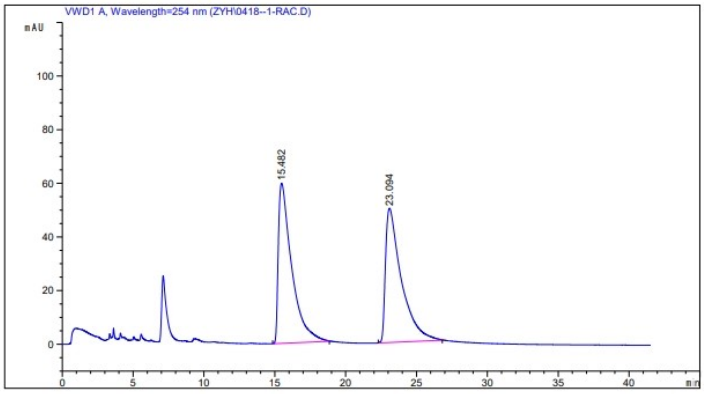


3fa



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	29.94	946	101	0.12%	2.456	BB
2	36.06	784988	2287	99.88%	11.299	BB
Total		785,934	2,388	100.00%		

rac-3ga



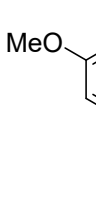

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

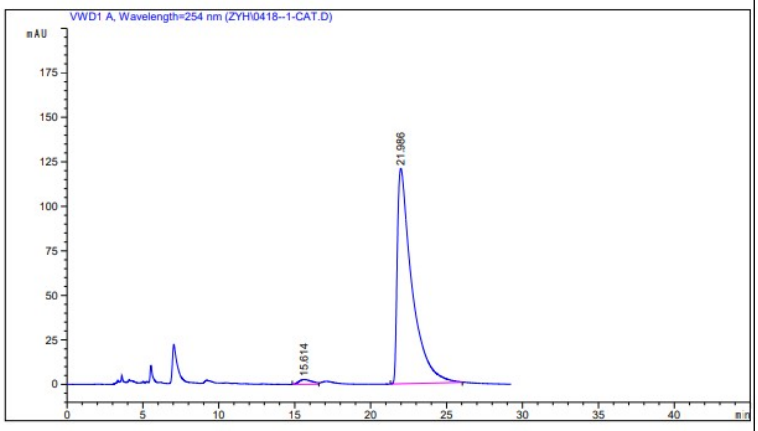

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  15.482 BB    0.9477 3933.90894   59.71409  50.2130
   2  23.094 BB    1.1104 3900.53296   50.03833  49.7870

Totals :                  7834.44189  109.75242
```



3ga



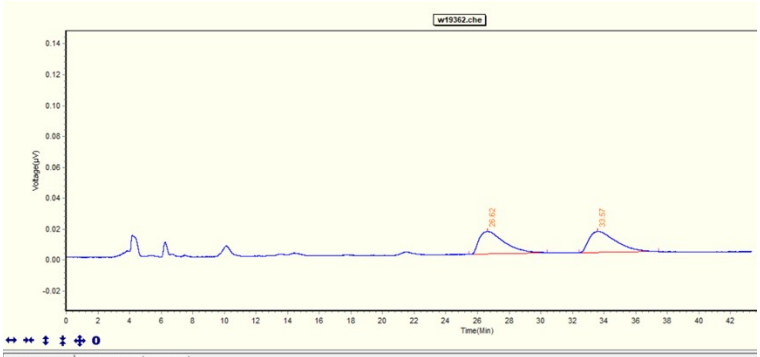
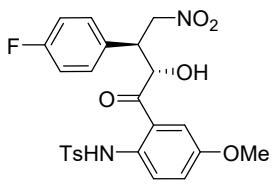
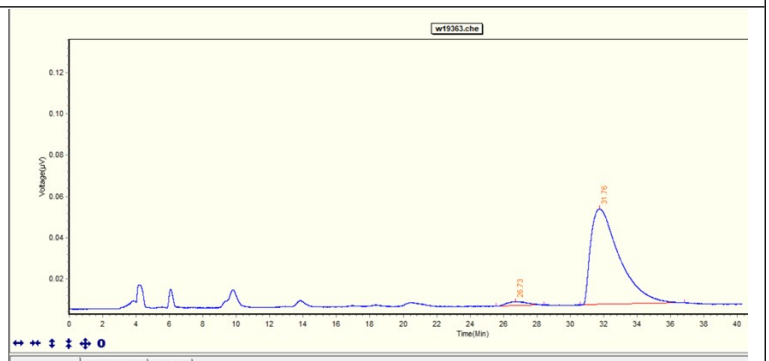
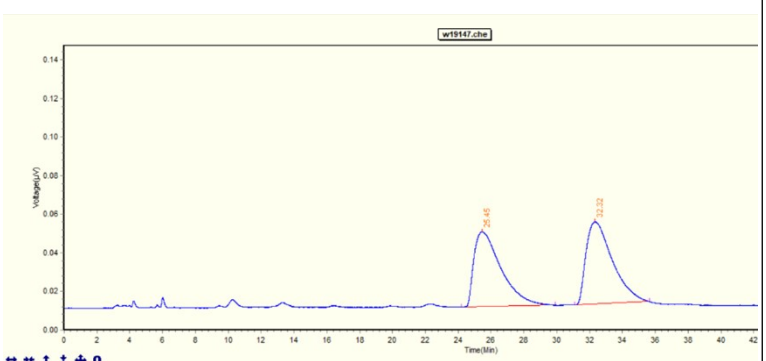
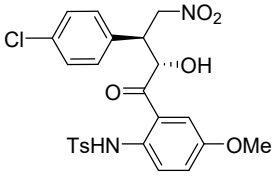
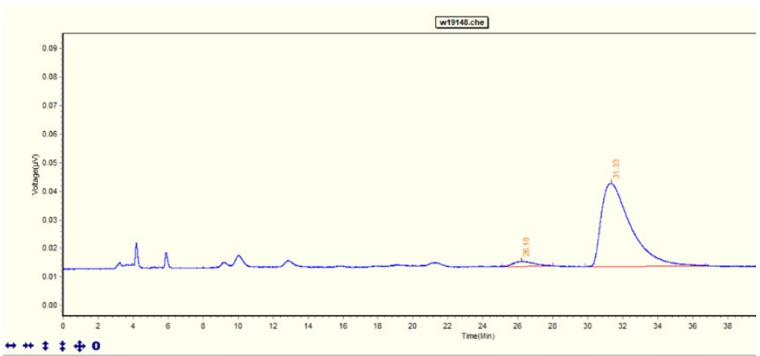

```
=====================================================================
                        Area Percent Report
=====================================================================

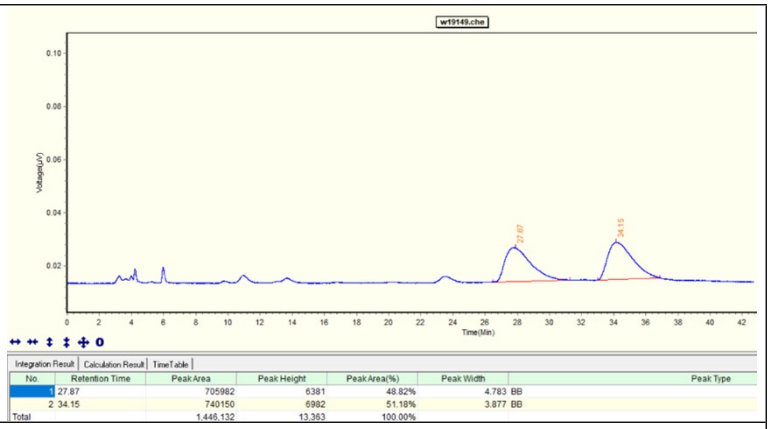
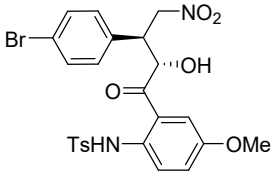
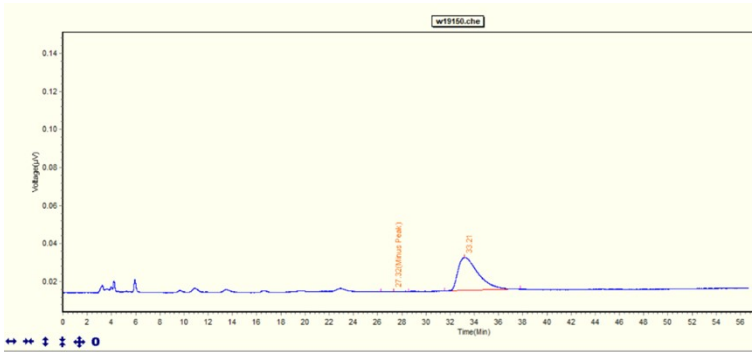
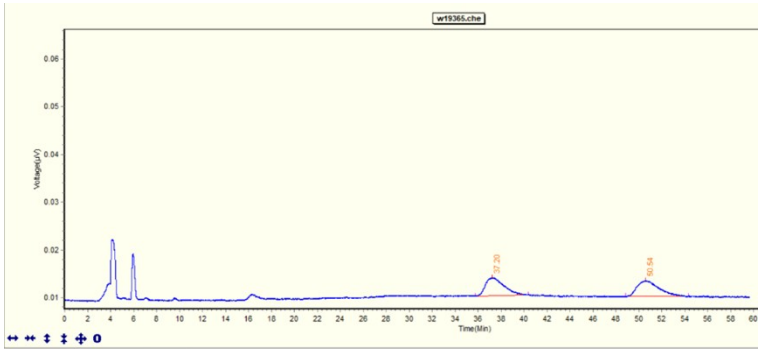
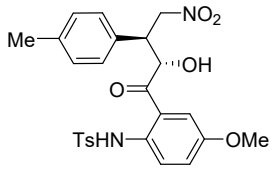
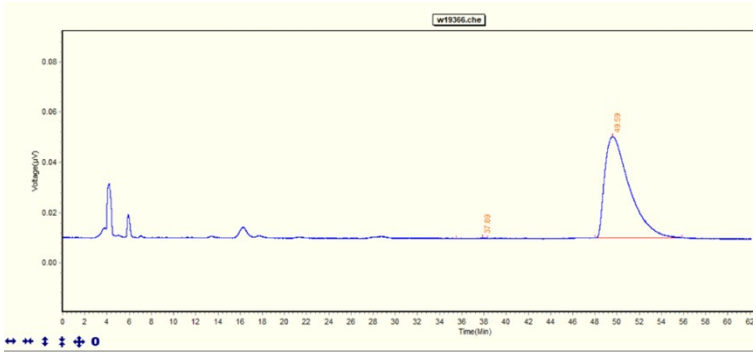
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

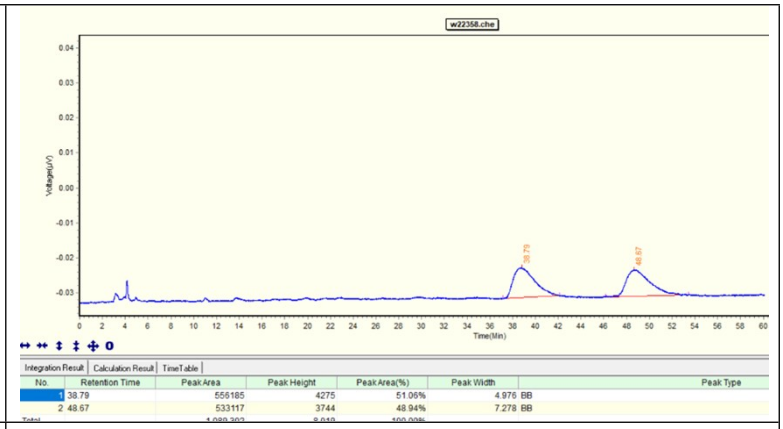
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  15.614 BV    0.8509  162.53969    2.68320   1.9654
   2  21.986 BB    0.9512 8107.35889  120.90555  98.0346

Totals :                  8269.89857  123.58875
```

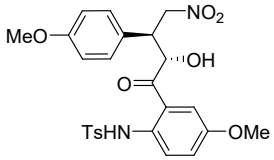
rac-3cb	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 26.62 809975 7278 50.30% 4.948 BB 2 33.57 800194 6797 49.70% 5.038 BB Total 1,610,169 14,075 100.00%
 **3cb**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 26.73 84517 1011 2.98% 2.872 BB 2 31.76 2754011 23146 97.02% 6.243 BB Total 2,838,528 24,157 100.00%
rac-3cc	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 25.45 2219607 19302 48.26% 5.73 BB 2 32.32 2379704 21271 51.74% 4.548 BB Total 4,599,311 40,573 100.00%
 **3cc**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 26.18 66406 858 3.76% 2.875 BB 2 31.33 1702053 14593 96.24% 6.901 BB Total 1,768,459 15,451 100.00%

rac-3cd	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 27.87 | 705982 | 6381 | 48.82% | 4.783 | BB 2 34.15 | 740150 | 6982 | 51.18% | 3.877 | BB Total | 1,446,132 | 13,363 | 100.00%
 **3cd**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 27.32 | 2171 | 100 | 0.21% | 2.235 | BB 2 33.21 | 1014773 | 8716 | 99.79% | 6.293 | BB Total | 1,016,944 | 8,816 | 100.00%
rac-3ce	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 37.20 | 206916 | 1878 | 50.08% | 4.638 | BB 2 50.54 | 206263 | 1611 | 49.92% | 5.441 | BB Total | 413,179 | 3,489 | 100.00%
 **3ce**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 37.89 | 670 | 123 | 0.02% | 2.833 | BB 2 49.59 | 3102031 | 20110 | 99.98% | 7.921 | BB Total | 3,102,701 | 20,233 | 100.00%

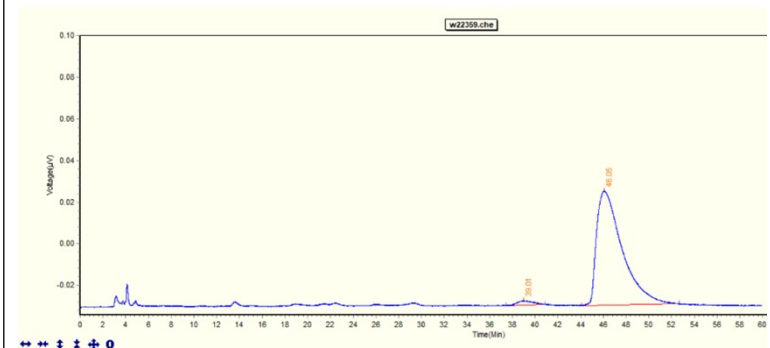
rac-3cf



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	38.79	556185	4275	51.06%	4.976	BB
2	48.67	533117	3744	48.94%	7.278	BB

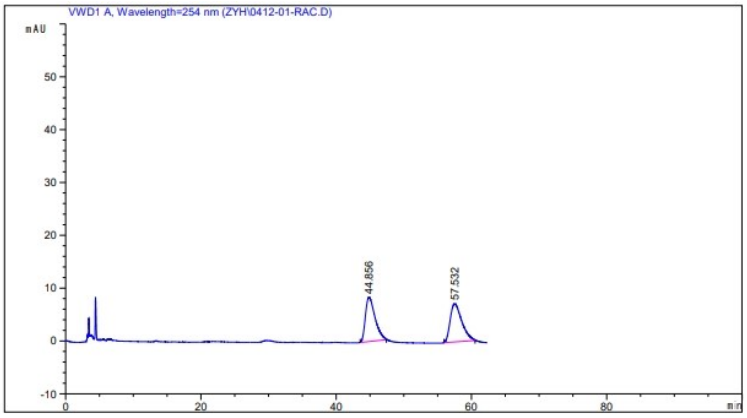


3cf



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	39.01	88585	942	2.03%	3.415	BB
2	46.05	4274138	27373	97.97%	8.568	BB
Total		4,362,723	28,315	100.00%		

rac-3cg

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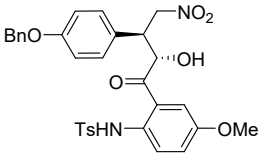
================================================================
                    Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

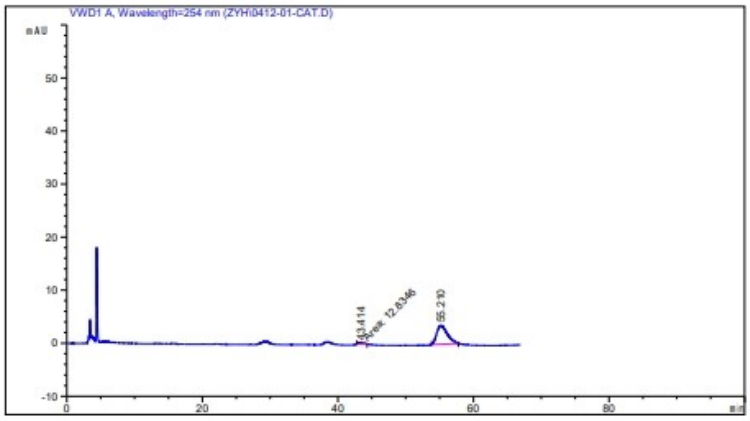

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  44.856 BB    1.3697  832.32837    8.41280  49.1536
   2  57.532 BB    1.4507  860.99445    7.24416  50.8464

Totals :                 1693.32281   15.65696
```



3cg




```
================================================================================
                          Area Percent Report
================================================================================

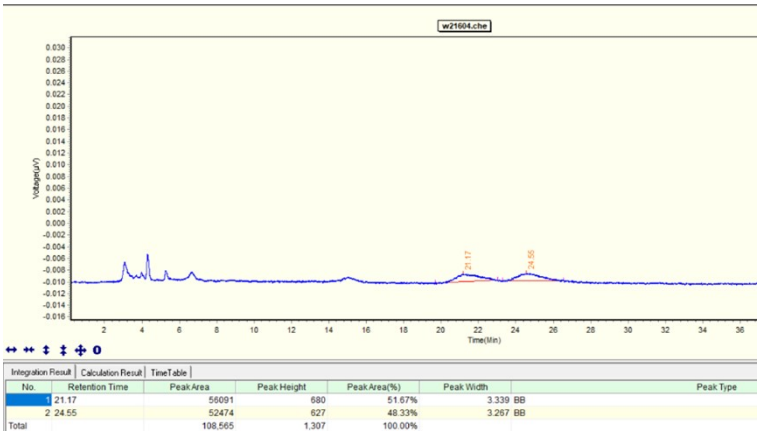
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

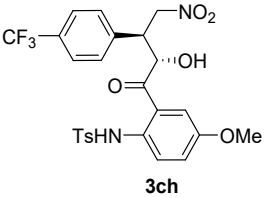
Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|---------|--------|
   1  43.414 MM    0.9151   12.83464 2.33765e-1   3.2524
   2  55.210 BB    1.2728  381.78671    3.52790  96.7476

Totals :                   394.62136    3.76166
```

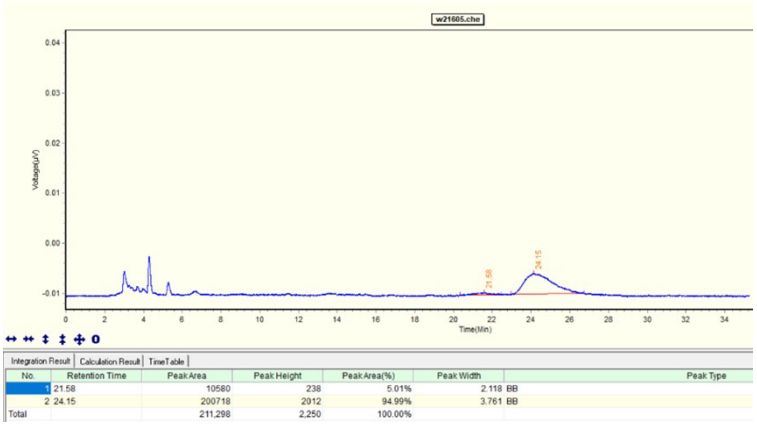
rac-3ch



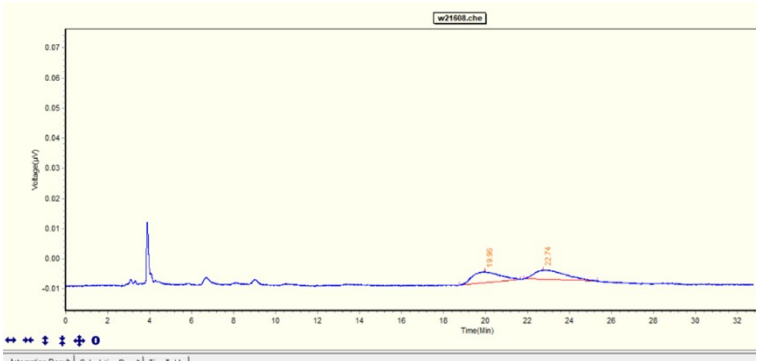
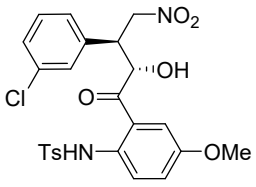
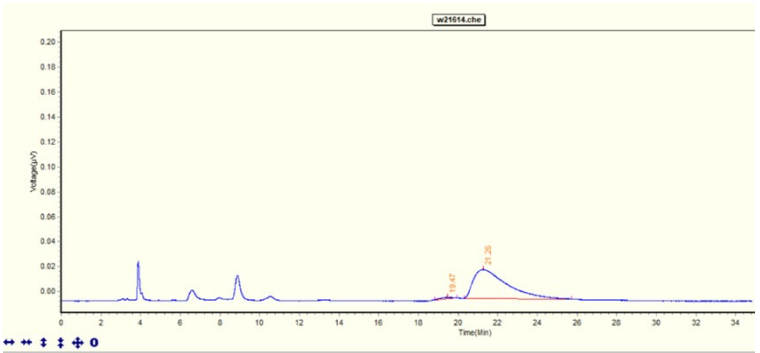
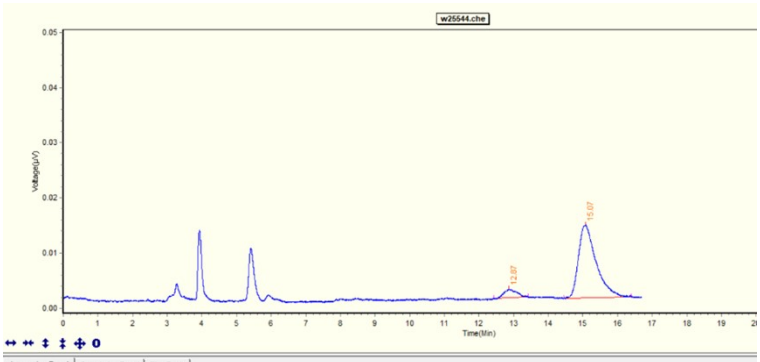
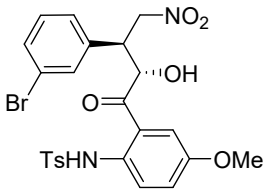
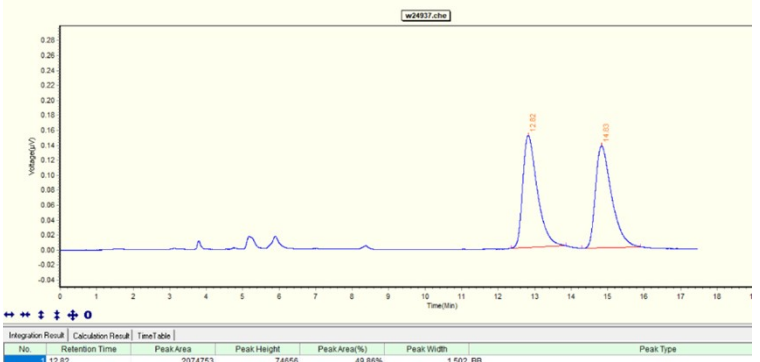
Integration Result	Calculation Result	TimeTable					
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width		Peak Type
1	21.17	56091	680	51.67%	3.339	BB	
2	24.55	52474	627	48.33%	3.267	BB	
Total		108,565	1,307	100.00%			

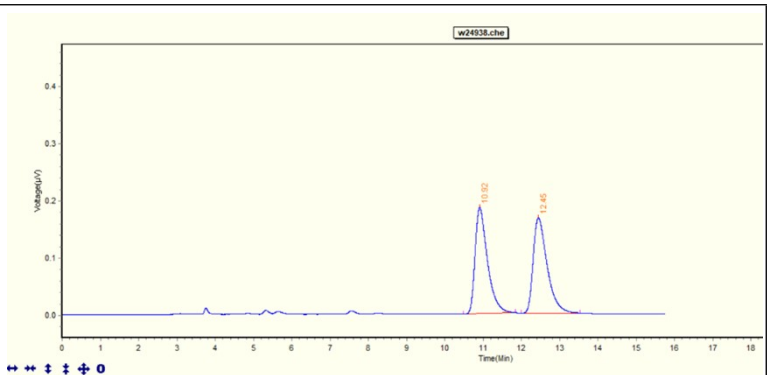
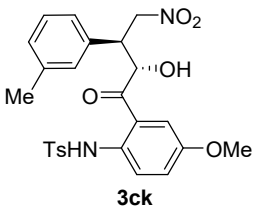
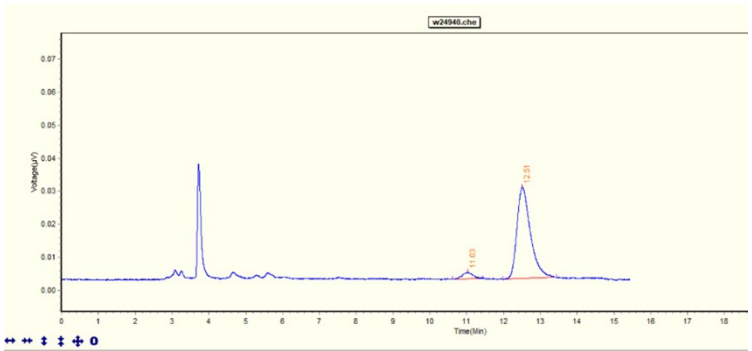
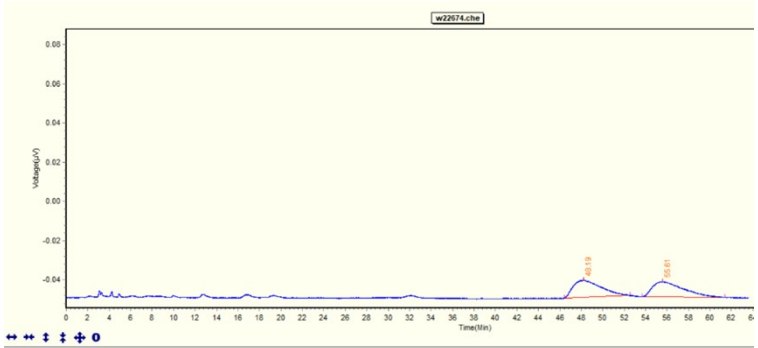
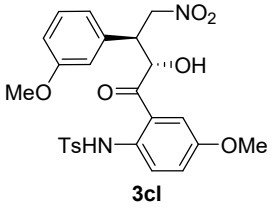
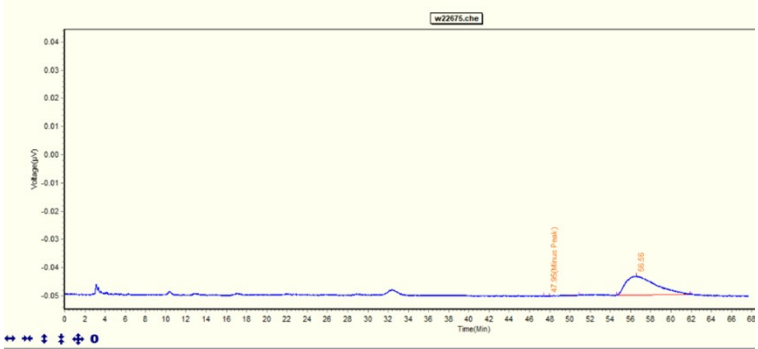


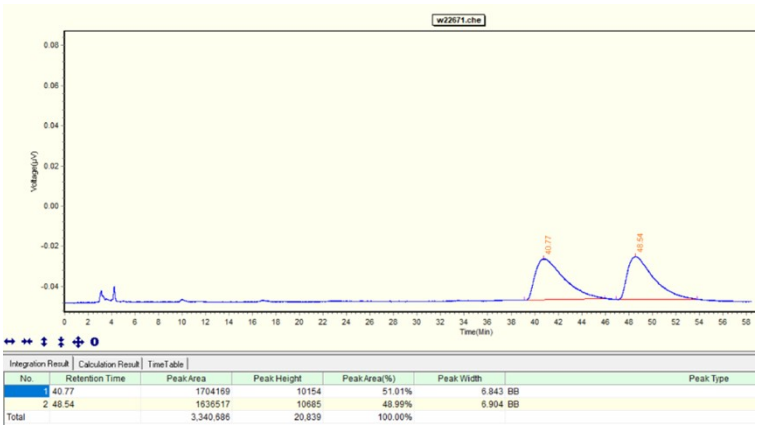
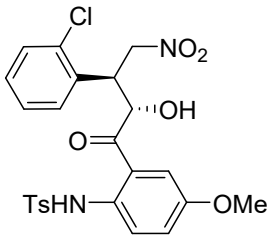
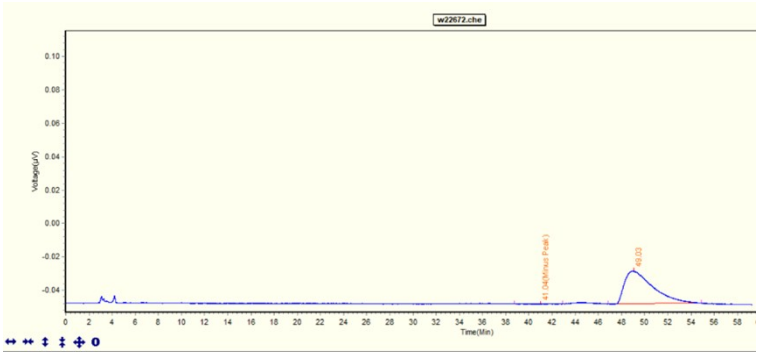
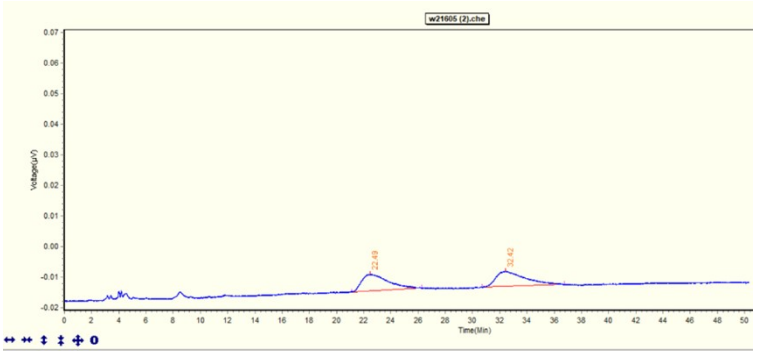
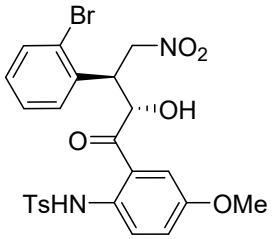
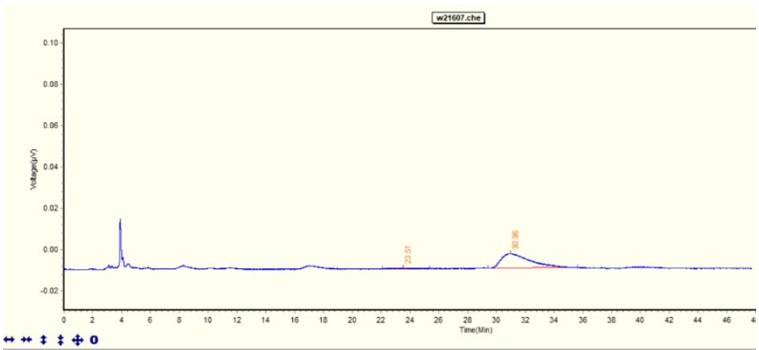
3ch

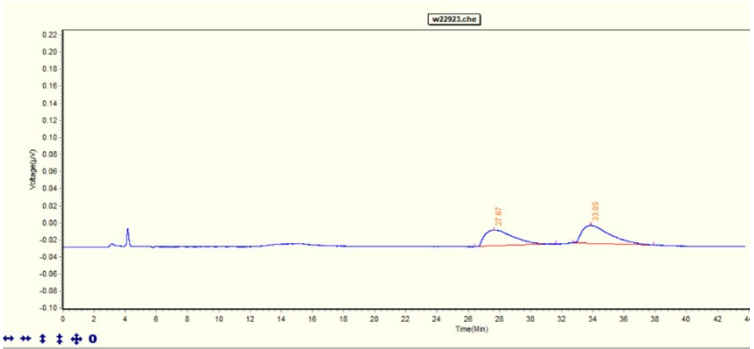
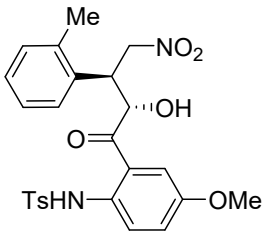
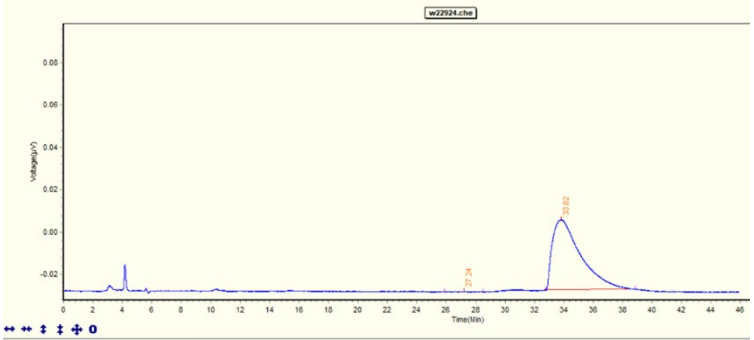
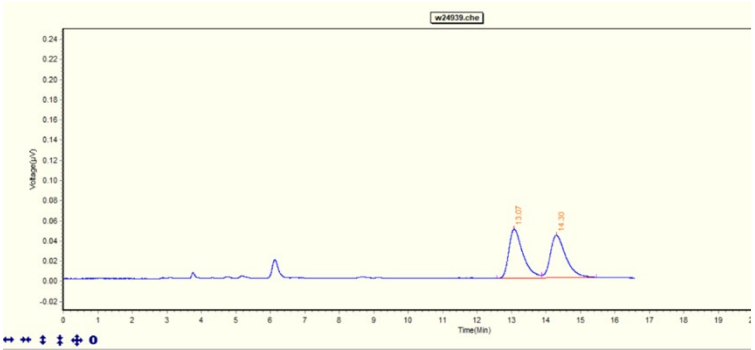
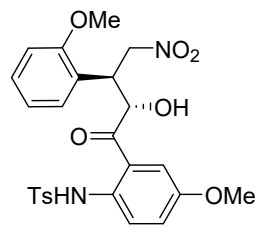
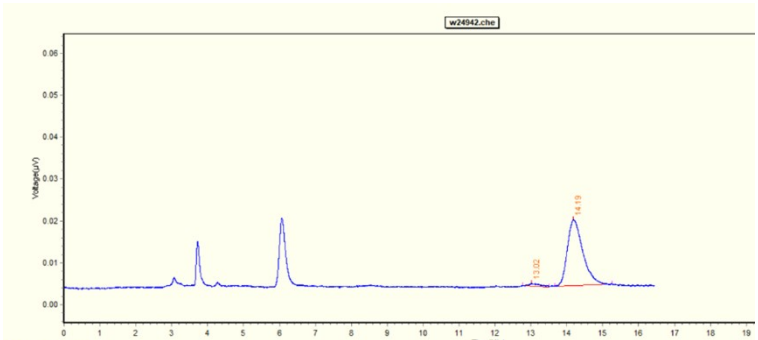


Integration Result	Calculation Result	TimeTable					
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width		Peak Type
1	21.58	10580	238	5.01%	2.118	BB	
2	24.15	200718	2912	94.99%	3.761	BB	
Total		211,298	2,250	100.00%			

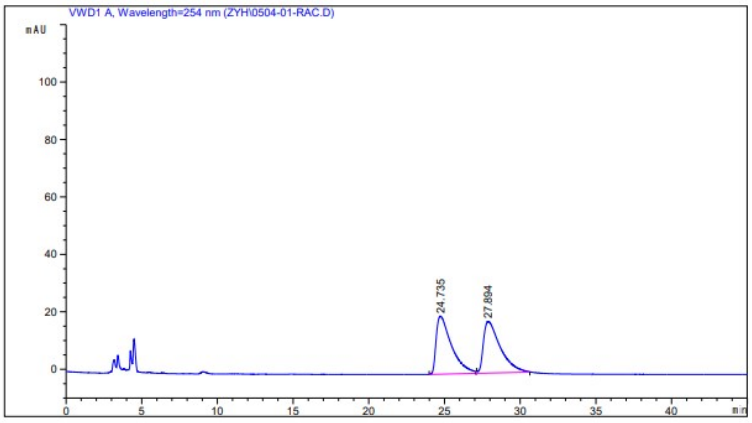
rac-3ci	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 19.96 156345 1814 49.24% 2.915 BB 2 22.74 161184 1561 50.76% 3.491 BB Total 317,529 3,375 100.00%
 **3ci**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 19.47 25382 610 1.84% 1.113 BB 2 21.26 1356379 11571 98.16% 5.425 BB Total 1,381,761 12,181 100.00%
rac-3cj	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 12.87 20167 792 7.97% 0.988 BB 2 15.07 233025 6599 92.03% 1.957 BB Total 253,192 7,391 100.00%
 **3cj**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 12.82 2074753 74656 49.86% 1.502 BB 2 14.83 2086105 68050 50.14% 1.611 BB Total 4,160,858 142,706 100.00%

rac-3ck	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 10.92 2080784 92648 49.72% 1.349 BB 2 12.45 2103945 83236 50.28% 1.528 BB Total 4,184,729 175,884 100.00%
 **3ck**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 11.03 18511 978 5.04% 0.833 BB 2 12.51 348694 13729 94.96% 1.458 BB Total 367,205 14,707 100.00%
rac-3cl	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 48.19 778815 4350 50.16% 6.124 BB 2 55.61 773707 3874 49.84% 7.705 BB Total 1,552,522 8,224 100.00%
 **3cl**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 47.95 6156 113 0.89% 3.501 BB 2 56.56 683361 3324 99.11% 7.282 BB Total 689,517 3,437 100.00%

rac-3cm	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 40.77 | 1704169 | 10154 | 51.01% | 6.843 | BB 2 | 48.54 | 1636517 | 10685 | 48.99% | 6.904 | BB Total | | 3,340,686 | 20,839 | 100.00% | |
 **3cm**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 41.04 | 11231 | 151 | 0.67% | 4.135 | BB 2 | 49.03 | 1671269 | 9821 | 99.33% | 8.043 | BB Total | | 1,682,500 | 9,972 | 100.00% | |
rac-3cn	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 22.49 | 361637 | 2713 | 49.62% | 5.162 | BB 2 | 32.42 | 367144 | 2459 | 50.38% | 6.048 | BB Total | | 728,781 | 5,172 | 100.00% | |
 **3cn**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 23.51 | 13108 | 182 | 2.65% | 3.261 | BB 2 | 30.96 | 482330 | 3455 | 97.35% | 6.226 | BB Total | | 495,438 | 3,637 | 100.00% | |

rac-3co	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 27.67 | 1195784 | 9391 | 47.82% | 5.213 | BB 2 33.85 | 1304837 | 10454 | 52.18% | 5.168 | BB Total | 2,500,621 | 19,845 | 100.00%
 **3co**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 27.24 | 2029 | 129 | 0.09% | 2.612 | BB 2 33.82 | 2218028 | 16564 | 99.91% | 6.08 | BB Total | 2,220,057 | 16,693 | 100.00%
rac-3cp	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 13.07 | 685521 | 24184 | 51.16% | 1.3 | BV 2 14.30 | 654340 | 21072 | 48.84% | 1.591 | VB Total | 1,339,861 | 45,256 | 100.00%
 **3cp**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 13.02 | 6949 | 329 | 2.86% | 0.751 | BB 2 14.19 | 236166 | 7870 | 97.14% | 1.587 | BB Total | 243,115 | 8,199 | 100.00%

rac-3cq

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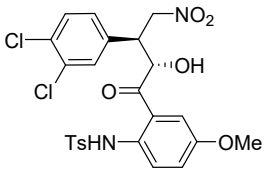
================================================================
                    Area Percent Report
================================================================

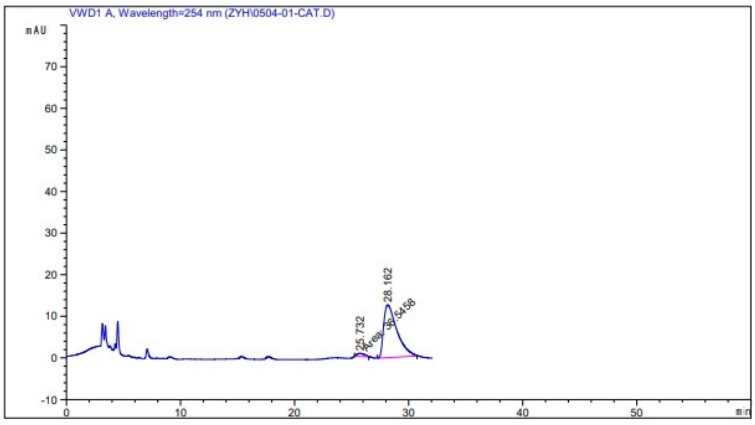
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  24.735 BB    1.0038 1420.40466   20.20076  50.4411
   2  27.894 BB    1.1290 1395.56433   17.99496  49.5589
```



3cq

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================================================================
                    Area Percent Report
================================================================

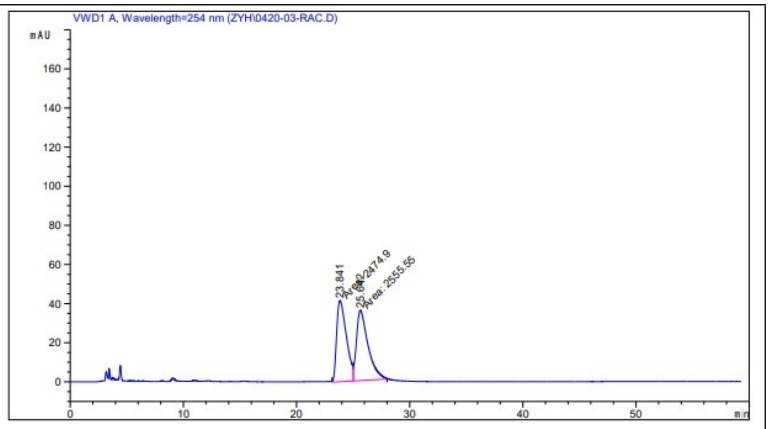
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  25.732 MM    0.7749   36.54585 7.85991e-1   3.4361
   2  28.162 BB    1.1199 1027.04968   12.67692  96.5639

Totals :                  1063.59553   13.46291
```

rac-3cr



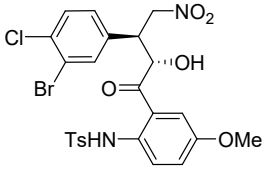

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

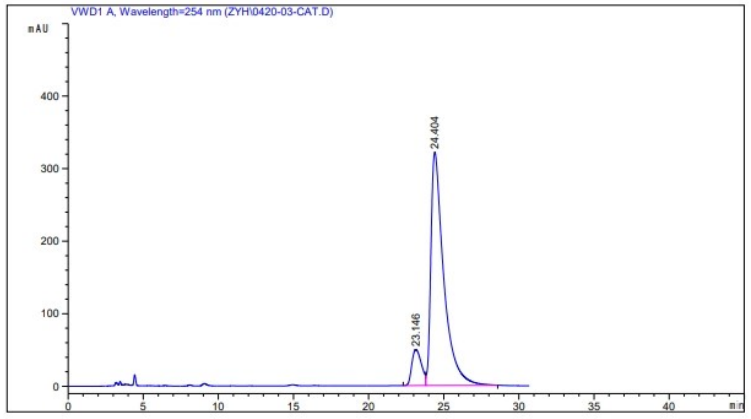

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|---------|---------|-------|
   1  23.841 MF    0.9953 2474.89868   41.44232  49.1984
   2  25.642 FM    1.1872 2555.55005   35.87693  50.8016

Totals :                  5030.44873   77.31925
```



3cr



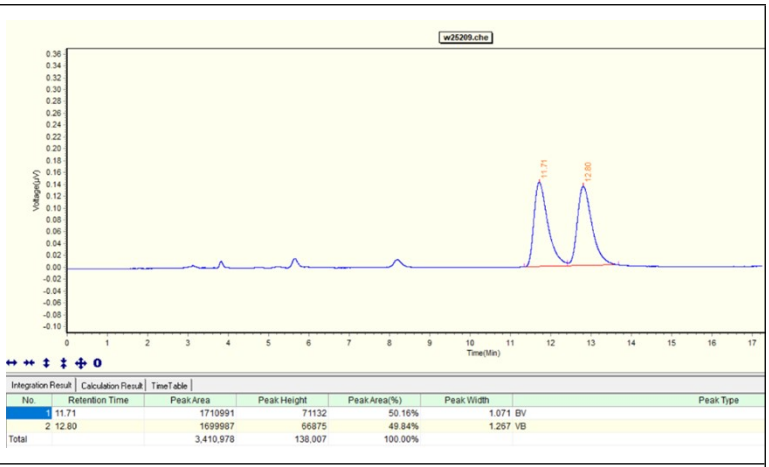
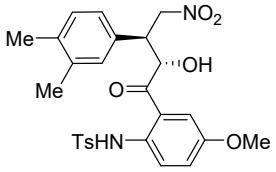
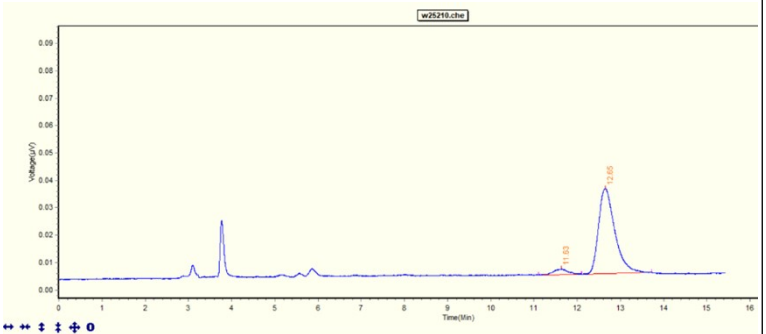
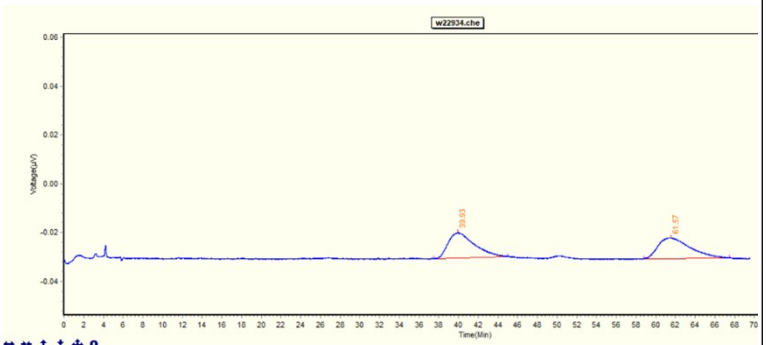
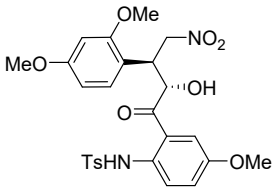
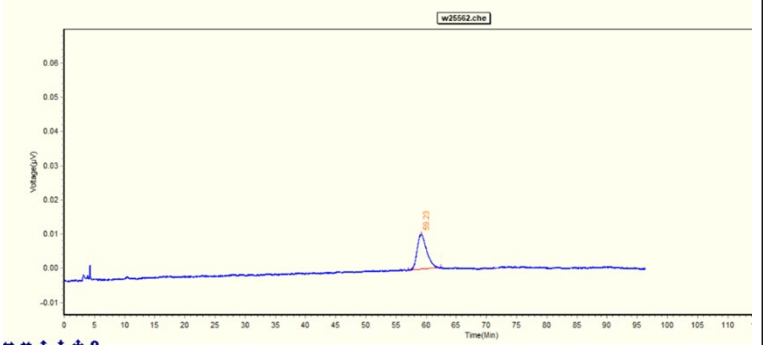

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

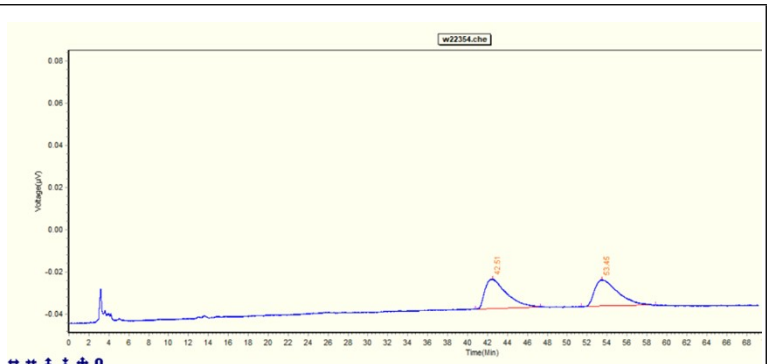

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|---------|---------|-------|
   1  23.146 BV    0.7065 2203.47827   49.56121  10.3552
   2  24.404 VB    0.8607 1.90755e4   321.69409  89.6448

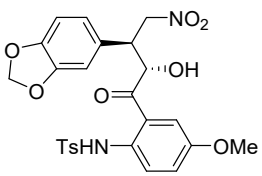
Totals :                  2.12789e4   371.25531
```

rac-3cs	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 11.71 | 1710991 | 71132 | 50.16% | 1.071 | BV 2 | 12.80 | 1699987 | 66875 | 49.84% | 1.267 | VB Total | | 3,410,978 | 138,007 | 100.00% | |
 **3cs**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 11.63 | 22894 | 996 | 5.35% | 0.993 | BB 2 | 12.65 | 404933 | 15464 | 94.65% | 1.618 | BB Total | | 427,827 | 16,460 | 100.00% | |
rac-3ct	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 39.93 | 950308 | 5183 | 50.28% | 7.494 | BB 2 | 61.57 | 939738 | 4218 | 49.72% | 8.647 | BB Total | | 1,890,046 | 9,401 | 100.00% | |
 **3ct**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 59.23 | 553886 | 5061 | 100.00% | 5.406 | BB Total | | 553,886 | 5,061 | 100.00% | |

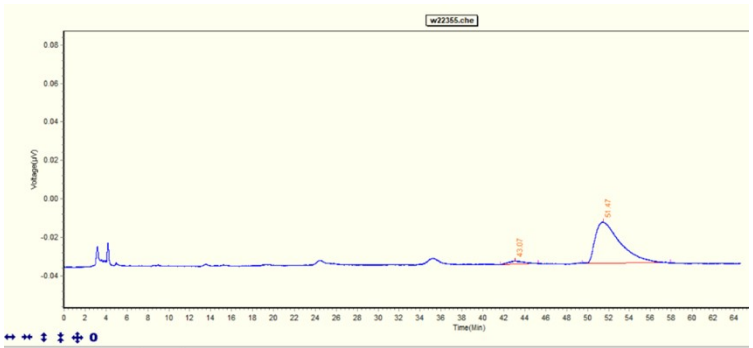
rac-3cu



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	42.51	1047569	6983	50.79%	6.524	BB
2	53.45	1014806	6197	49.21%	7.456	BB
Total		2,062,375	13,180	100.00%		

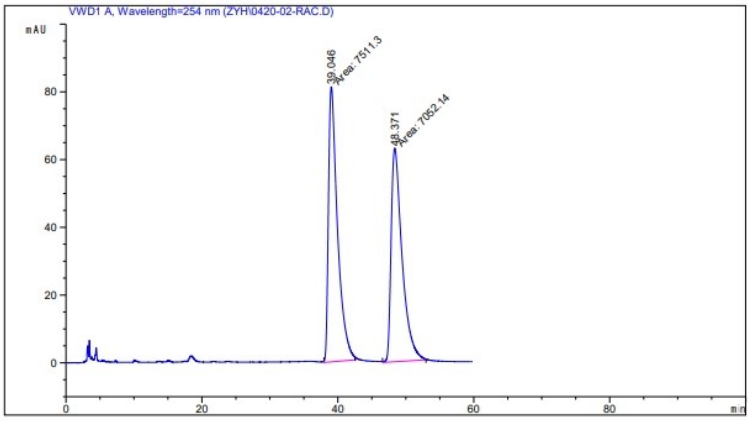


3cu



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	43.07	82636	829	4.48%	3.612	BB
2	51.47	1760896	10644	95.52%	8.427	BB
Total		1,843,532	11,473	100.00%		

rac-3cv

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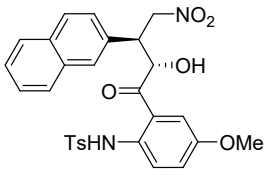
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

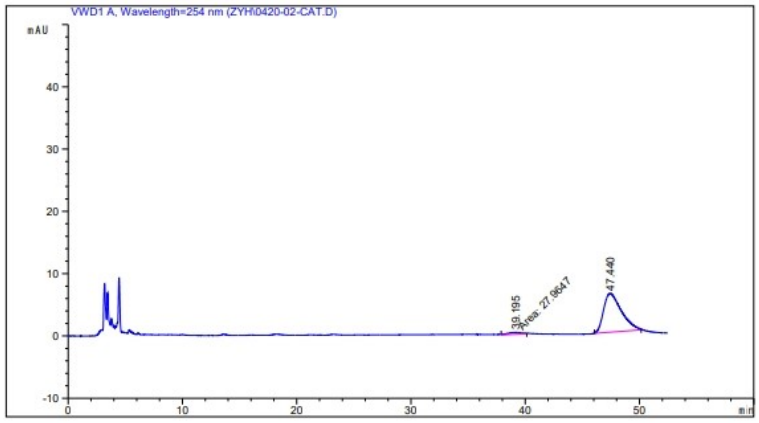

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  39.046 MM    1.5409 7511.29541   81.24149  51.5764
   2  48.371 MM    1.8658 7052.13916   62.99588  48.4236

Totals :                 1.45634e4   144.23737
```



3cv




```
================================================================
                    Area Percent Report
================================================================

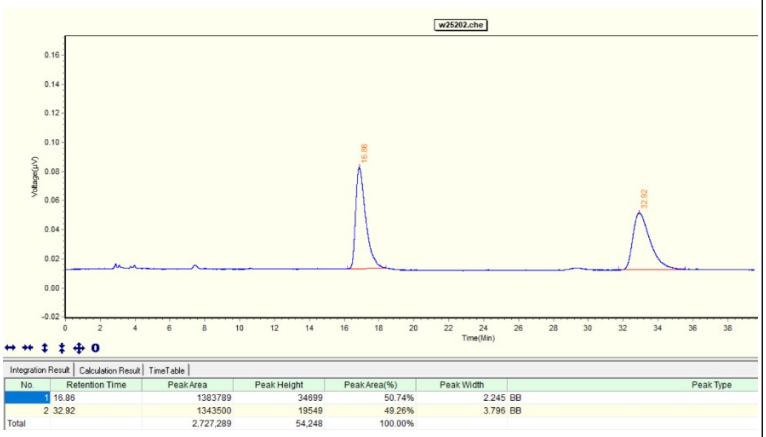
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

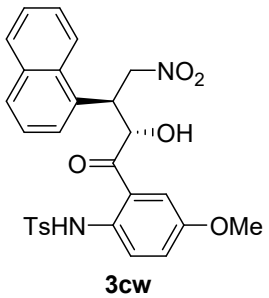
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  39.195 MM    1.5518   27.96471 3.00355e-1   3.9977
   2  47.440 BB    1.3587  671.55859    6.22703  96.0023

Totals :                   699.52331    6.52738
```

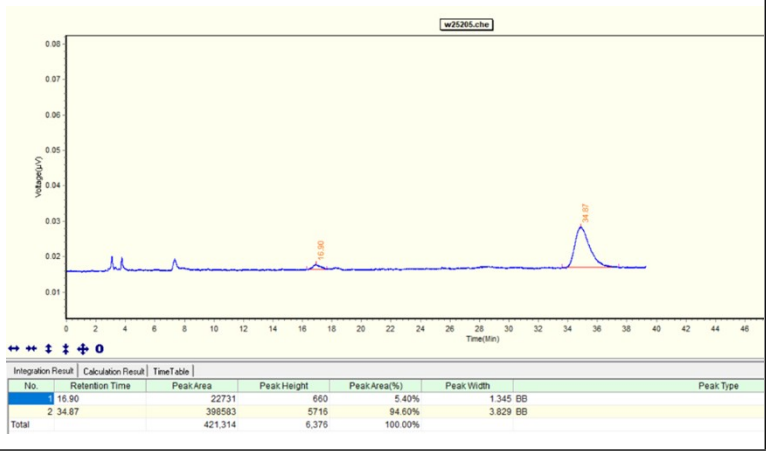
rac-3cw



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.86	1383789	34699	50.74%	2.245	BB
2	32.92	1343500	19549	49.26%	3.796	BB
Total		2,727,289	54,248	100.00%		

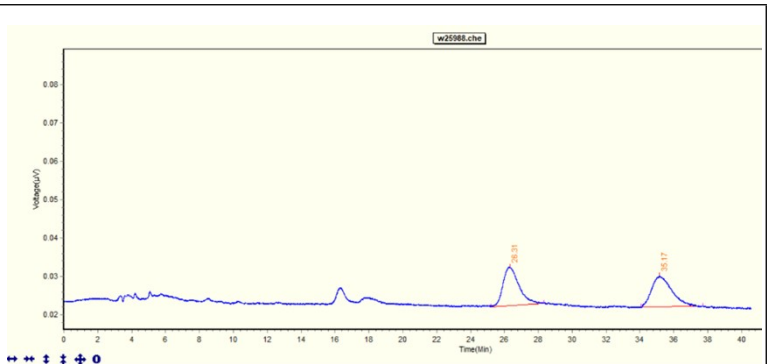


3cw

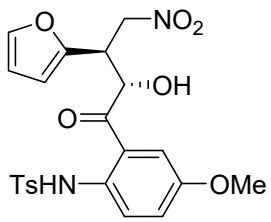


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.90	22731	660	5.40%	1.345	BB
2	34.87	398583	5716	94.60%	3.829	BB
Total		421,314	6,376	100.00%		

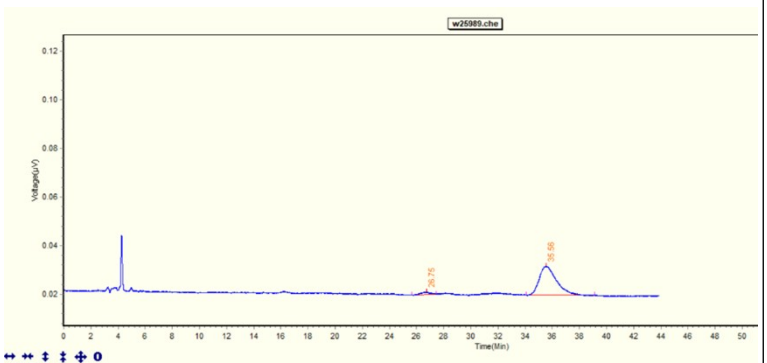
rac-3cx



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.31	325212	4980	49.35%	3.138	BB
2	35.17	333716	4035	50.65%	3.618	BB
Total		658,928	9,015	100.00%		

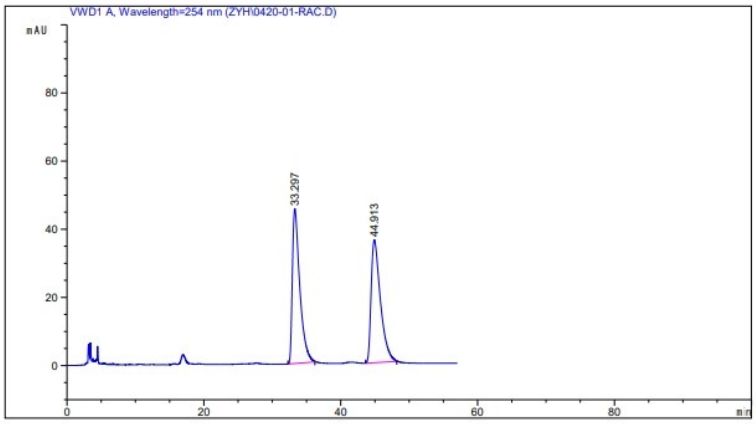


3cx



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.75	21514	521	3.95%	1.821	BB
2	35.56	522601	5962	96.05%	5.053	BB
Total		544,115	6,483	100.00%		

rac-3cy



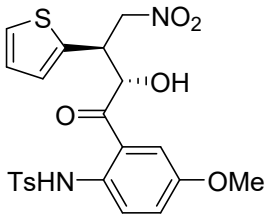

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

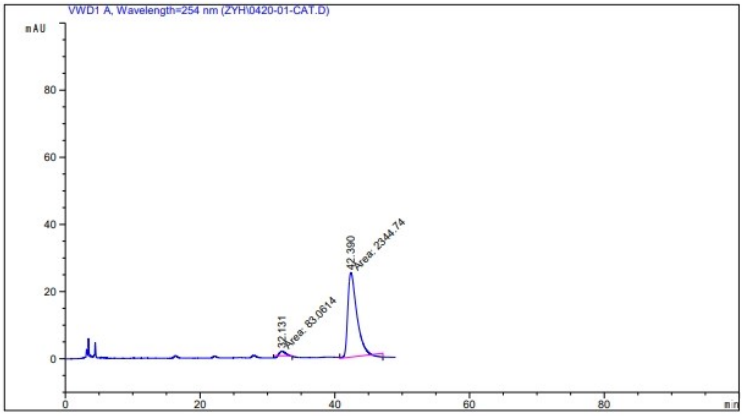

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  33.297 BB    1.1147 3427.12476   45.34668  50.2465
   2  44.913 BB    1.3962 3393.50146   35.92292  49.7535

Totals :                  6820.62622   81.26959
```



3cy




```
================================================================
                    Area Percent Report
================================================================

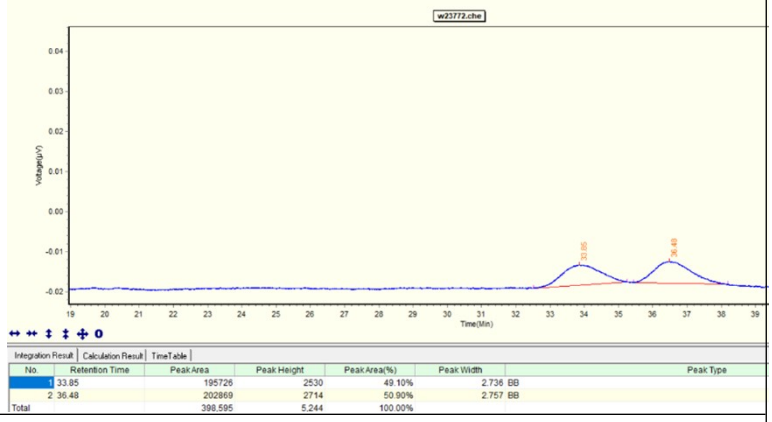
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

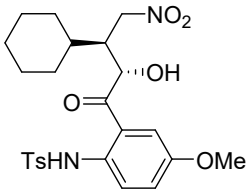
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  32.131 MM    1.0016   83.06136    1.38210   3.4213
   2  42.390 MM    1.5524 2344.73755   25.17379  96.5787

Totals :                  2427.79891   26.55589
```

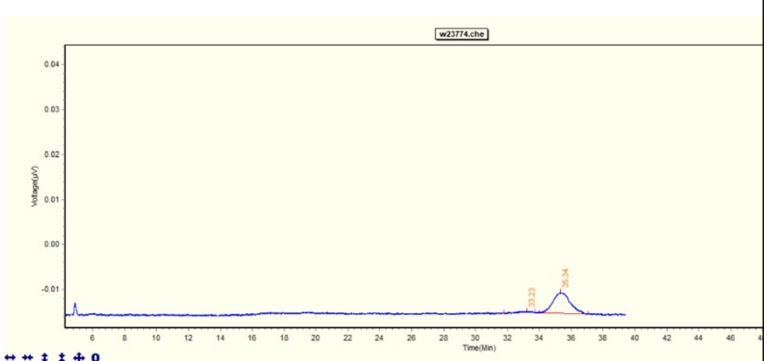
rac-3cz



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	33.85	195726	2530	49.10%	2.736	BB
2	36.48	202869	2714	50.90%	2.757	BB
Total		398.595	5.244	100.00%		

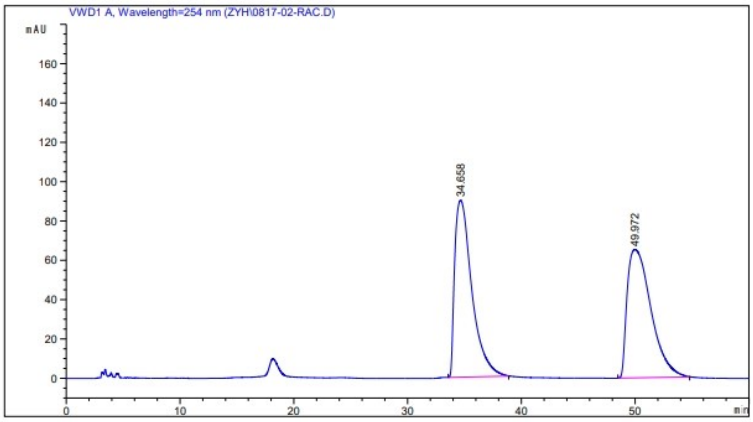


3cz



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	33.23	5471	140	3.08%	1.929	BB
2	35.34	172003	2304	96.92%	3.06	BB
Total		177,474	2,444	100.00%		

rac-3cza

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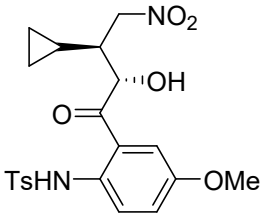
================================================================
                    Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

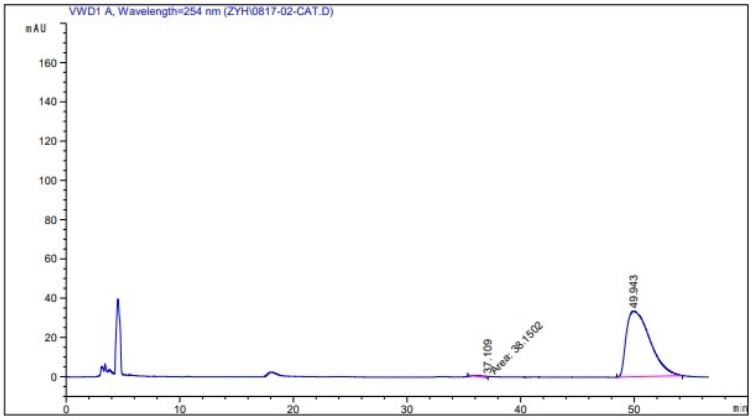

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  34.658 BB    1.6056 9423.04785   89.91567  49.7882
   2  49.972 BB    2.1013 9503.22168   65.29737  50.2118

Totals :                  1.89263e4   155.21304
```



3cza

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================================================================
                    Area Percent Report
================================================================

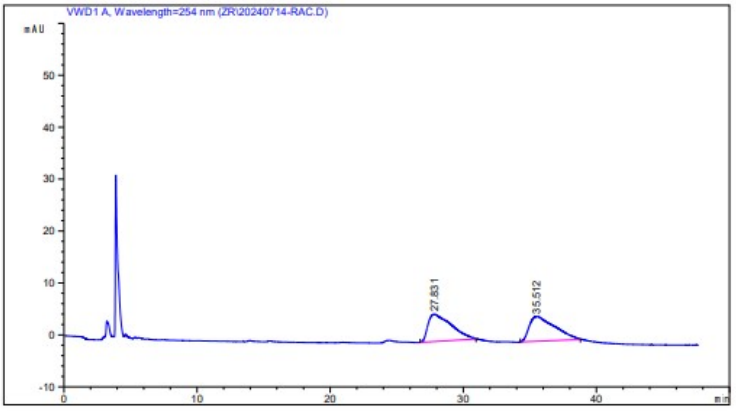
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  37.109 MM    0.8196   38.15019 7.75749e-1   0.7767
   2  49.943 BB    1.9495 4873.86279   33.43832  99.2233

Totals :                  4912.01299   34.21407
```

rac-3czb

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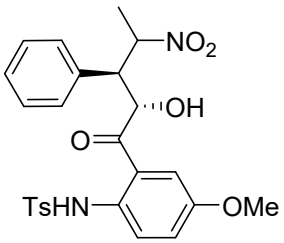
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

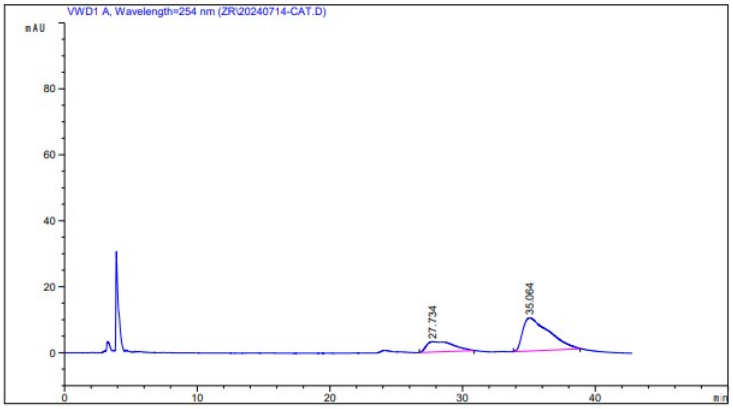

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.831 BB    1.4431  640.37787    5.26206  50.2619
   2  35.512 BB    1.5575  633.70526    4.77807  49.7381

Totals :               1274.08313   10.04012
```



3czb



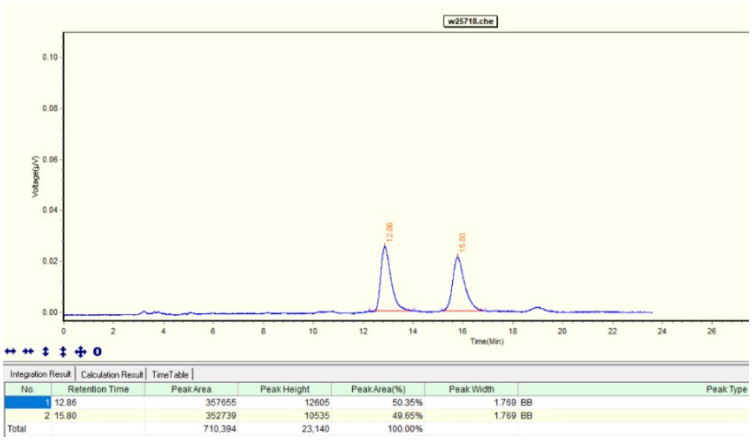
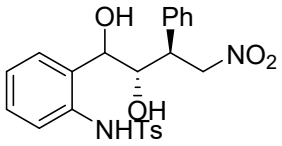
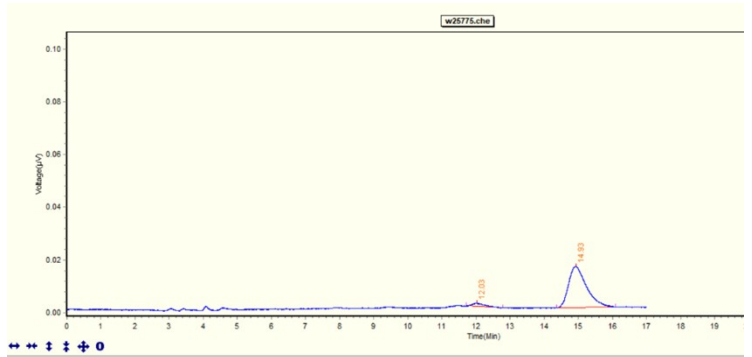
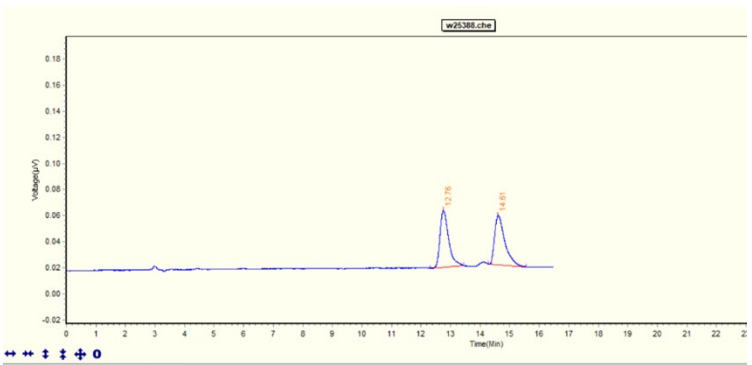
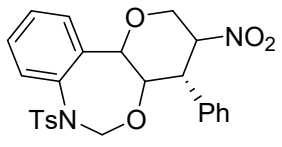
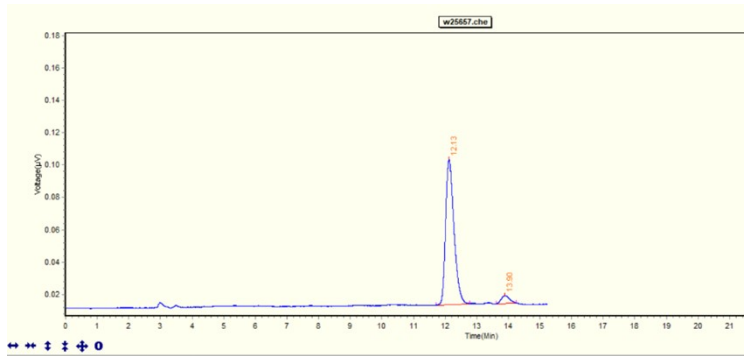

```
=====================================================================
                        Area Percent Report
=====================================================================

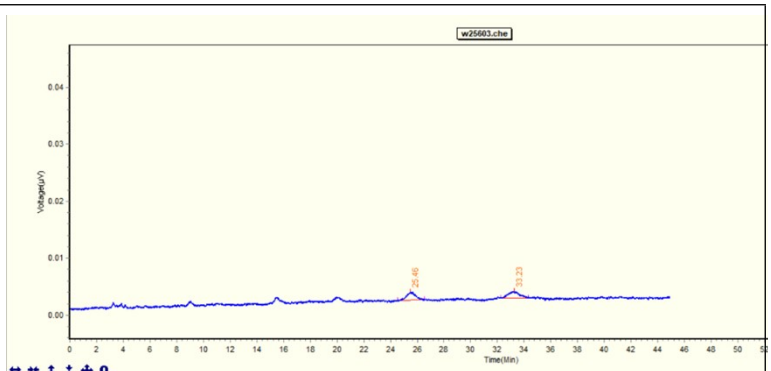
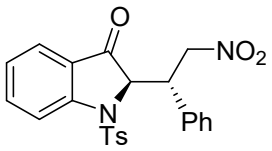
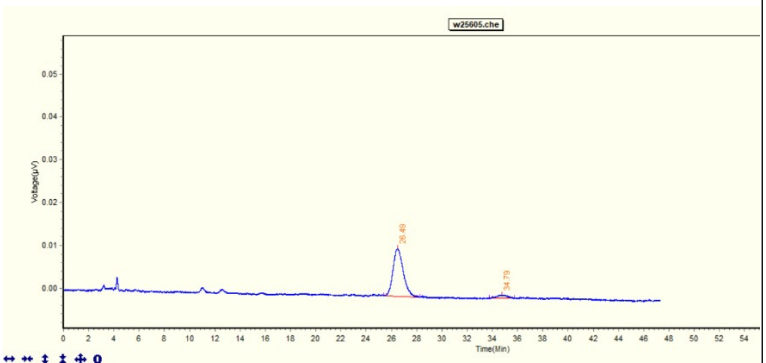
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.734 BB    1.6527  439.11621    3.13847  24.0743
   2  35.064 BB    1.6576 1384.88513   10.02905  75.9257
```

HPLC spectra of compound 5, 6 and 7

rac-5	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 12.86 | 357655 | 12605 | 50.35% | 1.769 | BB 2 | 15.80 | 352739 | 10535 | 49.65% | 1.769 | BB Total | | 710,394 | 23,140 | 100.00% | |
 **5**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 12.03 | 15656 | 591 | 5.29% | 1.077 | BB 2 | 14.93 | 280324 | 7732 | 94.71% | 1.729 | BB Total | | 295,980 | 8,323 | 100.00% | |
rac-6	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 12.76 | 435655 | 21667 | 49.02% | 1.13 | BB 2 | 14.61 | 453143 | 18925 | 50.98% | 1.278 | BB Total | | 888,798 | 40,592 | 100.00% | |
 **6**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 12.13 | 824889 | 44861 | 94.96% | 1.054 | BB 2 | 13.90 | 43810 | 2391 | 5.04% | 0.629 | BB Total | | 868,699 | 47,252 | 100.00% | |

rac-7	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 25.46 | 32845 | 710 | 50.68% | 2.049 | BB 2 | 33.23 | 31967 | 581 | 49.32% | 2.05 | BB Total | | 64,812 | 1,291 | 100.00% | |
 **7**	 Integration Result | Calculation Result | TimeTable No. | Retention Time | Peak Area | Peak Height | Peak Area(%) | Peak Width | Peak Type 1 | 26.49 | 316148 | 5604 | 94.54% | 2.907 | BB 2 | 34.79 | 18275 | 373 | 5.46% | 2.02 | BB Total | | 334,423 | 5,977 | 100.00% | |

Single-crystal X-ray diffraction

Single-crystal X-ray diffraction of 1c' (CCDC: 2348055)

X-ray analysis was carried out using the single crystal which was grown in DCM/Hexane.

The instrumentation used for the crystal measurement is Oxford Gemini E X-ray single-crystal diffractometer (ellipsoid contour at 30% probability level).

1c' X-ray of **1c'**
CCDC: 2348055

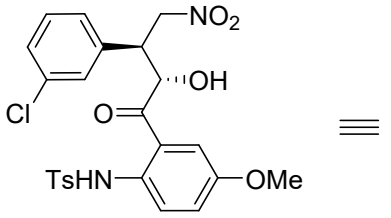
Table 1 Crystal data and structure refinement for 20230363_auto.

Identification code	20230363_auto
Empirical formula	$C_{16}H_{17}NO_5S$
Formula weight	335.36
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.1853(4)
b/Å	10.3385(4)
c/Å	18.6161(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1575.37(13)
Z	4
ρ_{calc}g/cm^3	1.414
μ/mm^{-1}	2.060
F(000)	704.0
Crystal size/mm^3	0.14 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.502 to 140.558
Index ranges	-9 ≤ h ≤ 6, -12 ≤ k ≤ 10, -22 ≤ l ≤ 21
Reflections collected	5663
Independent reflections	2937 [R_{int} = 0.0258, R_{sigma} = 0.0388]
Data/restraints/parameters	2937/2/215
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1068
Final R indexes [all data]	R_1 = 0.0464, wR_2 = 0.1125
Largest diff. peak/hole / e Å^{-3}	0.17/-0.20
Flack parameter	-0.008(17)

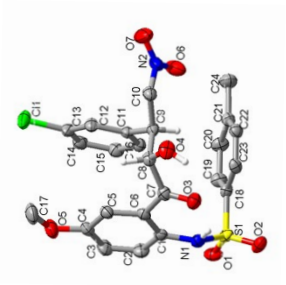
Single-crystal X-ray diffraction of 3ci (CCDC: 2348058)

X-ray analysis was carried out using the single crystal which was grown in DCM/Hexane.

The instrumentation used for the crystal measurement is Oxford Gemini E X-ray single-crystal diffractometer (ellipsoid contour at 30% probability level).



3ci



X-ray of **3ci**
CCDC:2348058

Table 1 Crystal data and structure refinement for 20230472_auto.

Identification code	20230472_auto
Empirical formula	$C_{24}H_{23}ClN_2O_7S$
Formula weight	518.95
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.80415(14)
b/Å	13.7157(2)
c/Å	22.4935(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2407.68(7)
Z	4
ρ_{calc}g/cm^3	1.432
μ/mm^{-1}	2.634
F(000)	1080.0
Crystal size/mm^3	0.16 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.55 to 140.722
Index ranges	-9 ≤ h ≤ 5, -14 ≤ k ≤ 16, -24 ≤ l ≤ 27
Reflections collected	8864
Independent reflections	4519 [R_{int} = 0.0316, R_{sigma} = 0.0489]
Data/restraints/parameters	4519/26/321
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1184
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.1272
Largest diff. peak/hole / e Å^{-3}	0.23/-0.29
Flack parameter	-0.063(17)