Supplementary Information

Catalytic asymmetric CO_2 utilization reaction for the enantioselective synthesis of chiral 2-oxazolidinones

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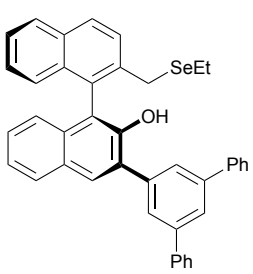
General Information

^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-ECZ 400R NMR instruments (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700N. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. Optical rotations were measured on a JASCO P-2100 polarimeter. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT and SPD-20A instruments using Daicel Chiralpak AD-3, IC-3, IE-3, and IF-3 columns (4.6 mm × 250 mm). All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm) or dyes. The products were purified by flash column chromatography on silica gel. Dehydrated solvents were purchased from Kanto Chemical.

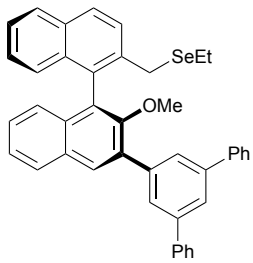
Experimental Section

1. Synthesis of catalysts

Chiral sulfide and selenide catalysts in Scheme 2 were prepared according to the literature method.[S1]



(*S*)-**2c**: $[\alpha]^{27}_{D}$ –165.4 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.01–7.91 (m, 5H), 7.83 (t, *J* = 1.6 Hz, 1H), 7.73–7.71 (m, 5H), 7.49–7.45 (m, 5H), 7.39–7.32 (m, 5H), 7.25 (td, *J* = 7.6, 1.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 5.20 (s, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.62 (d, *J* = 11.6 Hz, 1H), 2.43 (qd, *J* = 7.6, 1.2 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 141.8, 141.1, 139.1, 138.8, 133.14, 133.10, 132.9, 130.6, 130.4, 129.4, 129.2, 129.1, 128.8, 128.19, 128.15, 128.0, 127.5, 127.4, 127.3, 127.1, 126.7, 126.1, 125.8, 125.3, 124.6, 124.0, 118.1, 25.2, 18.5, 15.4; IR (neat) 3527, 904, 724, 698 cm^{-1}; HRMS (FAB) calcd for $C_{41}H_{32}OSe$: 620.1618 ($[M]^+$), found 620.1618.



(*S*)-**5**: $[\alpha]^{14}_{D}$ +7.8 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.00–7.84 (m, 6H), 7.80–7.72 (m, 5H), 7.49–7.35 (m, 8H), 7.30–7.22 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.78 (d, *J* = 12.4 Hz, 1H), 3.74 (d, *J* = 12.0 Hz, 1H), 3.11 (s, 3H), 2.43–2.30 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 141.7, 140.9, 139.6, 136.9, 134.7, 133.4, 133.1, 132.4, 131.9, 130.7, 128.7, 128.2, 127.9, 127.4, 127.2, 127.0, 126.4, 126.3, 126.1, 126.0, 125.3, 125.2, 125.0, 60.5, 25.7, 18.2, 15.4; IR (neat): 905, 727, 698 cm^{-1}; HRMS (FAB) calcd for $C_{42}H_{34}OSe$: 634.1775 ($[M]^+$), found 634.1773.

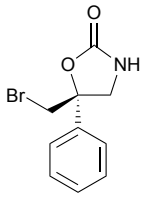
2. Synthesis of substrates

Allylamines **3** were prepared according to the literature method.[S2]

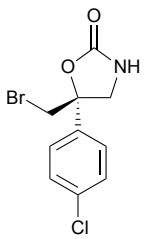
2-Methylallylamine **3h** was purchased from TCI.

3. General procedure for catalytic asymmetric synthesis of 2-oxazolidinone

A solution of allylamine substrate **3** (0.10 mmol) and catalyst (*S*)-**2c** (12.4 mg, 20 mol %, 0.020 mmol) in CH_2Cl_2 (2.0 mL) was cooled to –78 °C under CO_2 atmosphere (1 atm, using a balloon). After stirring for 10 min at –78 °C, 1,3-dibromo-5,5-dimethylhydantoin (DBH) (34.3 mg, 0.12 mmol) was added to the cooled reaction solution under CO_2 atmosphere (1 atm, using a balloon). The reaction mixture was stirred for 24 h at –78 °C under CO_2 atmosphere (1 atm, using a balloon). After 24 h, CO_2 balloon was removed and stirred for 5 min under open air. The reaction mixture was then placed under N_2 atmosphere (1 atm, using a balloon), and slowly quenched with saturated aqueous Na_2SO_3 (1.0 mL) at –78 °C. The resulting mixture was stirred for 10 min at –78 °C. The quenched reaction mixture was diluted with CH_2Cl_2 (2.0 mL) and warmed to 0 °C. The resulting solution was further stirred for 30 min at 0 °C. The organic materials were then extracted with CH_2Cl_2 for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **4**. The enantioselectivity of the product **4** was determined by HPLC analysis on a chiral stationary phase.

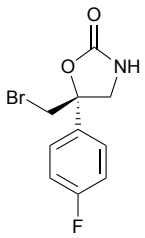


4a: $[\alpha]^{27}_D$ +33.3 (*c* = 0.91, $CHCl_3$, 89:11 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 29.7 min (major) and 40.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.35 (m, 5H), 5.23 (br s, 1H), 4.12 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.85 (dd, *J* = 8.6, 0.6 Hz, 1H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.69 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 140.0, 128.9, 124.7, 83.2, 50.5, 39.6; IR (neat): 3255, 3157, 2919, 2851, 1732, 1278, 1087, 1014, 965, 759, 720, 705, 681 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{10}BrNO_2$: 254.9895 ($[M]^+$), found 254.9893.

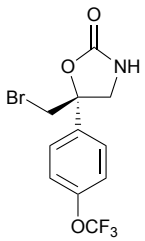


4b: $[\alpha]^{19}_D$ +24.2 (*c* = 0.95, $CHCl_3$, 92: 8 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 39.5 min (major) and 50.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.35 (dt, *J* = 8.4, 2.2 Hz, 2H), 5.31 (br s, 1H), 4.10 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.81 (dd, *J* = 8.8, 0.8 Hz, 1H),

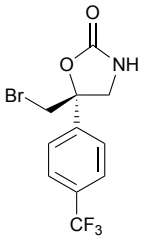
3.74 (d, J = 11.2 Hz, 1H), 3.65 (d, J = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 138.4, 135.0, 129.1, 126.3, 82.8, 50.3, 39.1; IR (neat): 3276, 1751, 1736, 1095, 913, 827, 743 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9BrClNO_2$: 288.9505 ([M]$^+$), found 288.9504.



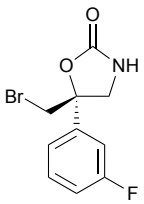
4c: [α]$^{19}_D$ +23.8 (c = 1.2, $CHCl_3$, 83:17 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 36.8 min (major) and 49.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 7.15–7.08 (m, 2H), 5.41 (br s, 1H), 4.11 (dd, J = 8.8, 0.8 Hz, 1H), 3.82 (d, J = 8.8 Hz, 1H), 3.74 (d, J = 11.2 Hz, 1H), 3.65 (d, J = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 248 Hz), 157.9, 135.7 (d, J = 2.9 Hz), 126.8 (d, J = 7.7 Hz), 115.9 (d, J = 22.0 Hz), 82.9, 50.4, 39.3; IR (neat): 3283, 2924, 1753, 1511, 1227, 838 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9BrFNO_2$: 272.9801 ([M]$^+$), found 272.9799.



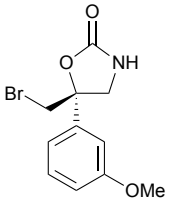
4d: [α]$^{19}_D$ +28.2 (c = 0.87, $CHCl_3$, 91: 9 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 55.4 min (minor) and 66.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dt, J = 8.8, 2.6 Hz, 2H), 7.30–7.25 (m, 2H), 5.29–5.17 (br m, 1H), 4.12 (dd, J = 8.8, 0.8 Hz, 1H), 3.83 (d, J = 8.4 Hz, 1H), 3.75 (d, J = 11.2 Hz, 1H), 3.67 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.4, 138.5, 126.5, 121.2, 120.3 (q, J = 257 Hz), 82.8, 50.4, 39.1; IR (neat): 3290, 1750, 1260, 1212, 1164 cm^{-1}; HRMS (EI) calcd for $C_{11}H_9BrF_3NO_3$: 338.9718 ([M]$^+$), found 338.9717.



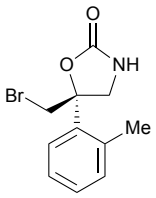
4e: [α]$^{23}_D$ +34.4 (c = 1.1, $CHCl_3$, 96: 4 er); HPLC analysis: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 30.3 min (minor) and 32.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.32 (br s, 1H), 4.14 (dd, J = 8.6, 1.0 Hz, 1H), 3.84 (dd, J = 8.6, 0.6 Hz, 1H), 3.76 (d, J = 11.2 Hz, 1H), 3.69 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 143.7, 131.2 (q, J = 32.6 Hz), 125.9 (q, J = 3.5 Hz), 125.4, 123.6 (q, J = 271 Hz), 82.8, 50.4, 38.8; IR (neat): 3289, 1764, 1328, 1169, 1126, 1115, 1070 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{10}BrF_3NO_2$: 323.9847 ([M+H]$^+$), found 323.9847.



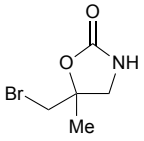
4f: $[\alpha]^{26}_{D}$ +31.1 (*c* = 1.1, $CHCl_3$, 86:14 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 28.5 min (major) and 34.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 1H), 7.19–7.14 (m, 2H), 7.11–7.06 (m, 1H), 5.30 (br s, 1H), 4.10 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.82 (d, *J* = 8.8 Hz, 1H), 3.75 (d, *J* = 11.2 Hz, 1H), 3.67 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246 Hz), 157.8, 142.4 (d, *J* = 6.7 Hz), 130.6 (d, *J* = 7.7 Hz), 120.4 (d, *J* = 2.9 Hz), 115.9 (d, *J* = 21.1 Hz), 112.4 (d, *J* = 23.9 Hz), 82.7, 50.4, 39.0; IR (neat): 3285, 1755, 1487, 1444, 1273, 1243, 967, 790, 702 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9BrFNO_2$: 272.9801 ($[M]^+$), found 272.9801.



4g: $[\alpha]^{26}_{D}$ +21.5 (*c* = 1.5, $CHCl_3$, 79:21 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 34.3 min (major) and 49.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.2 Hz, 1H), 6.98 (t, *J* = 2.0 Hz, 1H), 6.93–6.89 (m, 2H), 5.35 (br s, 1H), 4.09 (d, *J* = 8.0 Hz, 1H), 3.84 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.75 (d, *J* = 11.6 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 158.1, 141.6, 130.0, 116.8, 114.2, 110.6, 83.1, 55.4, 50.5, 39.6; IR (neat): 3295, 1753, 1488, 1291, 1247, 1035, 704 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}BrNO_3$: 285.0001 ($[M]^+$), found 285.0000.

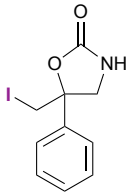


4h: $[\alpha]^{20}_{D}$ +39.2 (*c* = 1.1, $CHCl_3$, 81:19 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 35.7 min (major) and 41.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 1H), 7.31–7.20 (m, 3H), 5.43 (br s, 1H), 4.18 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.90 (d, *J* = 8.4 Hz, 1H), 3.82 (d, *J* = 12.0 Hz, 1H), 3.73 (d, *J* = 11.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 137.9, 133.0, 132.4, 128.9, 126.5, 125.9, 83.9, 50.2, 38.9, 20.7; IR (neat): 3278, 1754, 1280, 1013, 760, 729 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{13}BrNO_2$: 270.0130 ($[M+H]^+$), found 270.0130.



4i:[S3] $[\alpha]^{24}_{D}$ –2.5 (*c* = 0.75, $CHCl_3$, 60:40 er); HPLC analysis: Daicel Chiralpak IF-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 220 nm;

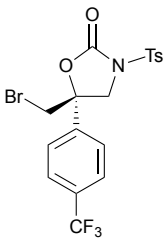
retention time: 33.0 min (major) and 38.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (br s, 1H), 3.70 (d, *J* = 8.8 Hz, 1H), 3.57 (d, *J* = 10.4 Hz, 1H), 3.46 (d, *J* = 10.4 Hz, 1H), 3.36 (d, *J* = 8.8 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 81.0, 49.8, 37.6, 24.5; IR (neat): 3291, 1740, 1375, 1365, 1228, 1217, 742 cm^{-1}; HRMS (EI) calcd for $C_5H_8BrNO_2$: 192.9738 ($[M]^+$), found 192.9738.



6: $[\alpha]^{18}_D$ +1.5 (*c* = 0.98, $CHCl_3$, 56:44 er); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 36.2 min (major) and 51.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.35 (m, 5H), 5.02 (br s, 1H), 4.01 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.90 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 3.62 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 140.1, 128.9, 128.8, 124.6, 82.8, 51.9, 14.8; IR (neat): 1734, 1364, 1217, 1205 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{10}INO_2$: 302.9756 ($[M]^+$), found 302.9756.

4. Transformations of product 4e

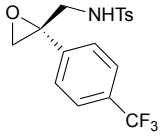
A solution of **4e** (32.4 mg, 0.10 mmol) in THF (0.60 mL)-DMF (0.40 mL) mixed solvent was cooled to 0 °C. To the cooled solution was added sodium hydride (60 wt.%) (8.0 mg, 0.20 mmol) and *p*-toluenesulfonyl chloride (24.8 mg, 0.13 mmol). The reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (5.0 mL). The organic materials were extracted with ethyl acetate for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 4:1–1:2 as eluent) to give product **8** (40.7 mg, 0.085 mmol).



8: $[\alpha]^{24}_D$ +34.7 (*c* = 0.81, $CHCl_3$, 93: 7 er); HPLC analysis: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 110.2 min (major) and 138.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.53 (d, *J* = 9.6 Hz, 1H), 4.25 (d, *J* = 9.6 Hz, 1H), 3.66 (d, *J* = 11.6 Hz, 1H), 3.62 (d, *J* = 11.6 Hz, 1H), 2.45

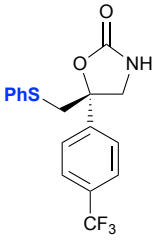
(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 146.1, 142.1, 133.7, 131.7 (q, J = 32.6 Hz), 129.9, 128.3, 126.2, 125.2, 123.5 (q, J = 271 Hz), 80.2, 53.7, 38.4, 21.7; IR (neat): 1778, 1372, 1326, 1161, 1125, 1116, 1092, 1069, 1035, 1012, 907, 811, 733 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{16}BrF_3NO_4S$: 477.9936 ($[M+H]^+$), found 477.9936.

To a solution of **8** (8.6 mg, 0.018 mmol) in methanol (0.50 mL) was added cesium carbonate (1.2 mg, 0.0036 mmol, 0.20 equiv). The reaction mixture was stirred for 24 h at room temperature. After 24 h, the reaction mixture was concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 50:1–3:1 as eluent) to give product **9** (5.3 mg, 0.014 mmol).



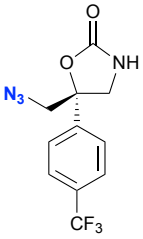
9: $[\alpha]^{24}_D$ +14.4 (c = 1.2, $CHCl_3$, 93: 7 er); HPLC analysis: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 87.0 min (minor) and 93.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dt, J = 8.4, 2.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.60–4.54 (br m, 1H), 3.56 (d, J = 6.0 Hz, 2H), 3.25 (d, J = 5.2 Hz, 1H), 2.75 (d, J = 4.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.0, 136.5, 130.5 (q, J = 32.6 Hz), 129.8, 126.9, 126.2, 125.5 (q, J = 3.5 Hz), 123.8 (q, J = 271 Hz), 58.3, 53.4, 45.7, 21.5; IR (neat): 3284, 1325, 1161, 1125, 1069, 842, 815 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{17}F_3NO_3S$: 372.0881 ($[M+H]^+$), found 372.0880.

To a solution of **4e** (32.4 mg, 0.10 mmol) in CH_3CN (2.0 mL) was added K_2CO_3 (41.5 mg, 0.30 mmol) and thiophenol (0.22 g, 2.0 mmol). The reaction mixture was warmed to 75 °C and stirred for 24 h. After 24 h, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (5.0 mL). The organic materials were extracted with ethyl acetate for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 4:1–1:2 as eluent) to give product **10** (29.0 mg, 0.082 mmol).



10: $[\alpha]^{24}_{D}$ +46.8 (*c* = 1.0, $CHCl_3$, 93: 7 er); HPLC analysis: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 60.5 min (minor) and 70.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.30–7.27 (m, 2H), 7.25–7.17 (m, 3H), 5.57–5.44 (br m, 1H), 4.04 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.76 (dd, *J* = 8.4, 0.4 Hz, 1H), 3.52 (d, *J* = 14.0 Hz, 1H), 3.47 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 145.1, 135.1, 130.7 (q, *J* = 32.6 Hz), 130.6, 129.1, 127.1, 125.6 (q, *J* = 3.8 Hz), 125.3, 123.7 (q, *J* = 271 Hz), 84.6, 50.6, 46.0; IR (neat): 3265, 1749, 1727, 1332, 1112, 1073, 836, 743, 691 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{14}F_3NO_2S$: 353.0697 ($[M]^+$), found 353.0697.

To a solution of **4e** (32.4 mg, 0.10 mmol) in DMF (2.0 mL) was added sodium azide (19.5 mg, 0.30 mmol). The reaction mixture was warmed to 100 °C and stirred for 24 h. After 24 h, the reaction mixture was cooled to room temperature and diluted with dichloromethane (30 mL). The resulting solution was poured into water (100 mL). The organic materials were extracted with ethyl acetate for three times (10 mL × 3). The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 4:1–1:2 as eluent) to give product **11** (26.6 mg, 0.093 mmol).



11: $[\alpha]^{25}_{D}$ +18.4 (*c* = 0.92, $CHCl_3$, 93: 7 er); HPLC analysis: Daicel Chiralpak IF-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm; retention time: 28.2 min (minor) and 33.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 5.59 (s, 1H), 4.03 (d, *J* = 8.8 Hz, 1H), 3.74–3.70 (m, 2H), 3.58 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 143.8, 131.1 (q, *J* = 32.6 Hz), 126.0 (q, *J* = 3.9 Hz), 125.1, 123.7 (q, *J* = 271 Hz), 83.9, 58.4, 49.4; IR (neat): 3299, 2960, 2924, 2853, 2106, 1752, 1325, 1262, 1167, 1118, 1085, 1069, 1015, 970, 842 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{10}F_3N_4O_2$: 287.0756 ($[M+H]^+$), found 287.0756.

5. X-ray diffraction analysis

Product **4b** was recrystallized from ethyl acetate-hexane. Product **4d** was recrystallized from dichloromethane-hexane. Data of X-ray diffraction were collected by a Rigaku XtaLAB diffractometer with Cu-Kα (Wavelength = 1.54184 Å) radiation at Kyusyu University. The absolute configurations were determined by reference to the Flack parameter.[S4]

The crystallographic data of **4b** were summarized in the following table.

Empirical formula	$C_{20}H_{18}Br_2Cl_2N_2O_4$
	$[C_{10}H_9BrClNO_2$ x 2]
Formula weight	581.08
	[290.54 x 2]
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.47910(10)
b/Å	14.1480(4)
c/Å	27.7407(8)
Volume/Å^3	2150.41(10)
Z	4
ρ_{calc}mg/mm^3	1.795
μ/mm^{-1}	7.338
F(000)	1152.0
Reflections collected	10628
Independent reflections	4281[R(int) = 0.0329]
Goodness-of-fit	1.036
Final R indexes [I >=2σ (I)]	R_1 = 0.0264, wR_2 = 0.0684
Final R indexes [all data]	R_1 = 0.0276, wR_2 = 0.0693
Flack parameter	–0.024(12)

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2244530). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

The crystallographic data of **4d** were summarized in the following table.

Empirical formula	$C_{11}H_9BrF_3NO_3$
Formula weight	340.10
Temperature/K	100(2)
Crystal system	monoclinic
Space group	*C*2
a/Å	12.3801(2)
b/Å	5.46613(14)
c/Å	18.0363(4)
Volume/Å^3	1218.01(4)
Z	4
ρ_{calc}mg/mm^3	1.855
μ/mm^{-1}	5.049
F(000)	672.0
Reflections collected	6540
Independent reflections	2195[R(int) = 0.0343]
Goodness-of-fit	1.047
Final R indexes [I >=2σ (I)]	R_1 = 0.0250, wR_2 = 0.0613
Final R indexes [all data]	R_1 = 0.0259, wR_2 = 0.0620
Flack parameter	–0.037(19)

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2244531). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

References

S1 (*a*) R. Nishiyori, J. R. J. Maynard and S. Shirakawa, *Asian J. Org. Chem.*, 2020, **9**, 192–196; (*b*) R. Nishiyori, M. Okada, J. R. J. Maynard and S. Shirakawa, *Asian J. Org. Chem.*, 2021, **10**, 1444–1448; (*c*) R. Nishiyori, K. Okuno, B. Chan and S. Shirakawa, *Chem. Pharm. Bull.*, 2022, **70**, 599–604.

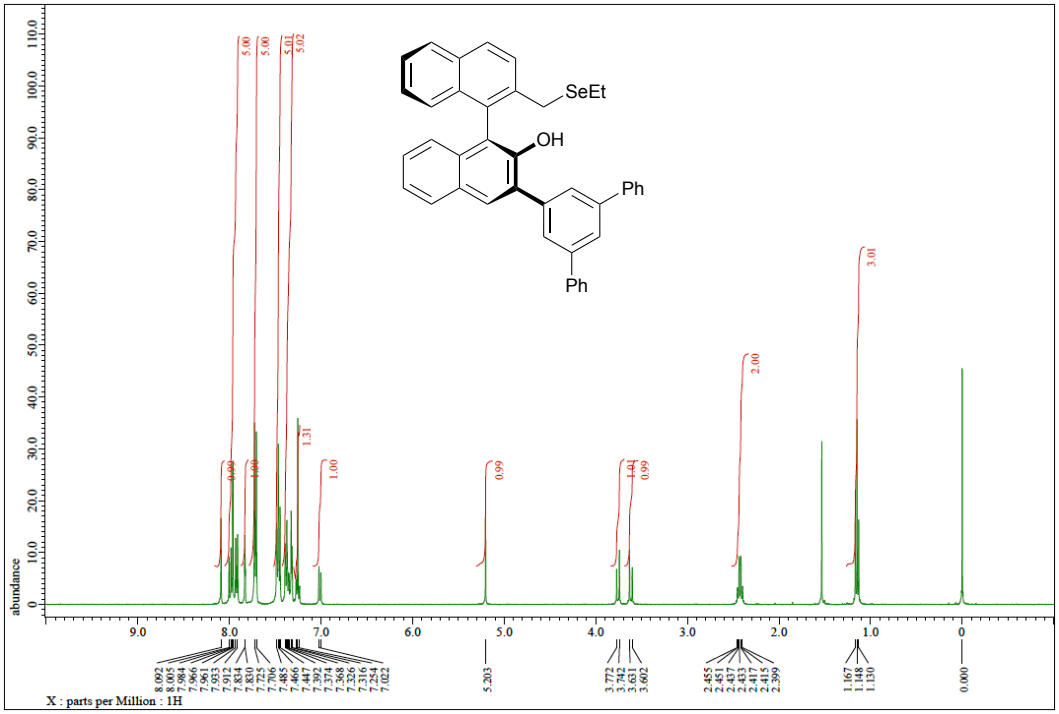
S2 (*a*) A. Garzan, A. Jaganathan, N. S. Marzijarani, R. Yousefi, D. C. Whitehead, J. E. Jackson and B. Borhan, *Chem.–Eur. J.*, 2013, **19**, 9015–9021; (*b*) Y. Kawato, A. Kubota, H. Ono, H. Egami and Y. Hamashima, *Org. Lett.*, 2015, **17**, 1244–1247; (*c*) K. Xu, S. Yang and Z. Ding, *Org. Chem. Front*, 2020, **7**, 69–72.

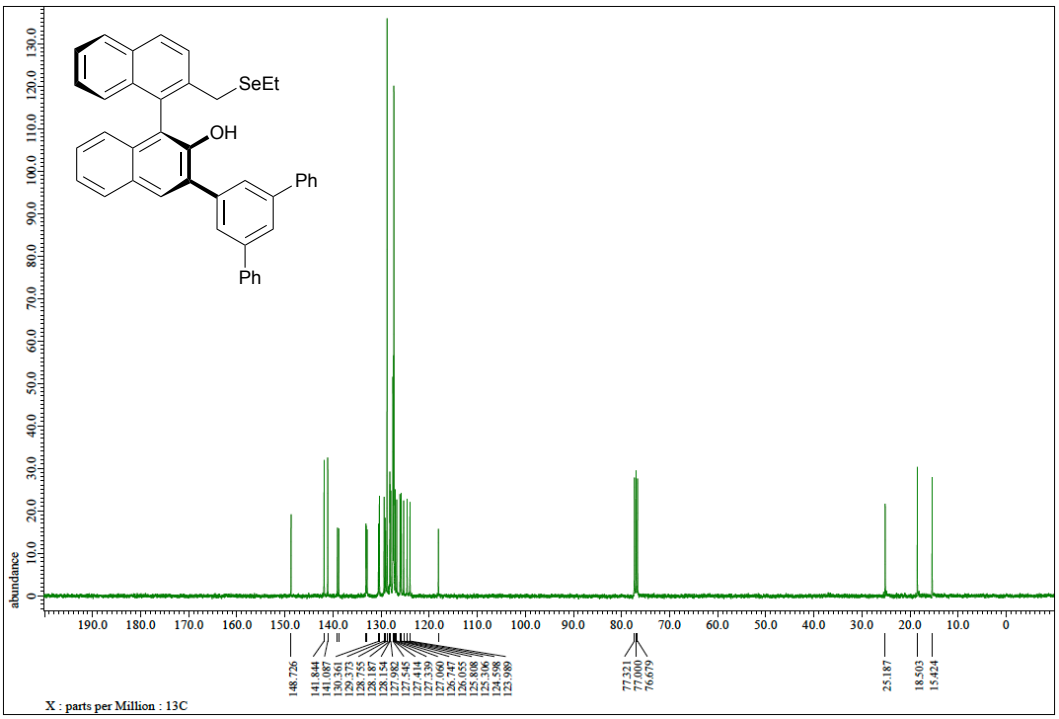
S3 (*a*) M. Majerić Elenkov, L. Tang, A. Meetsma, B. Hauer and D. B. Janssen, *Org. Lett.*, 2008, **10**, 2417–2420; (*b*) A. Mikleušević, Z. Hameršak, B. Salopek-Sondi, L. Tang, D. B. Janssen and M. Majerić Elenkov, *Adv. Synth. Catal.*, 2015, **357**, 1709–1714.

S4 H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876–881.

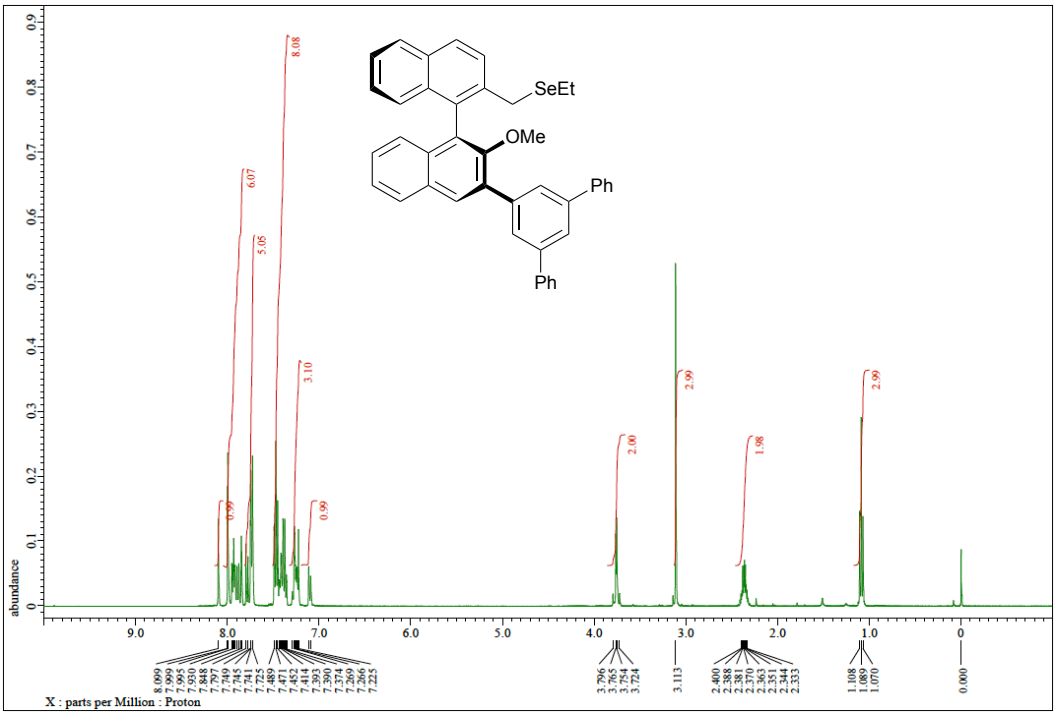
NMR Charts

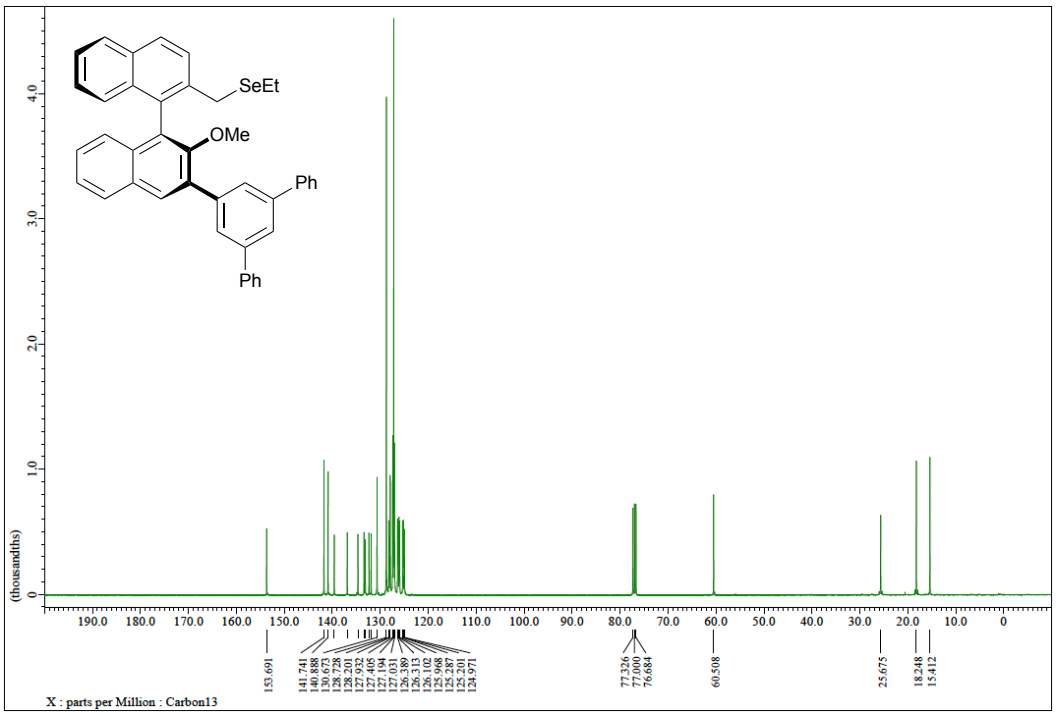
2c: ^{1}H and ^{13}C NMR



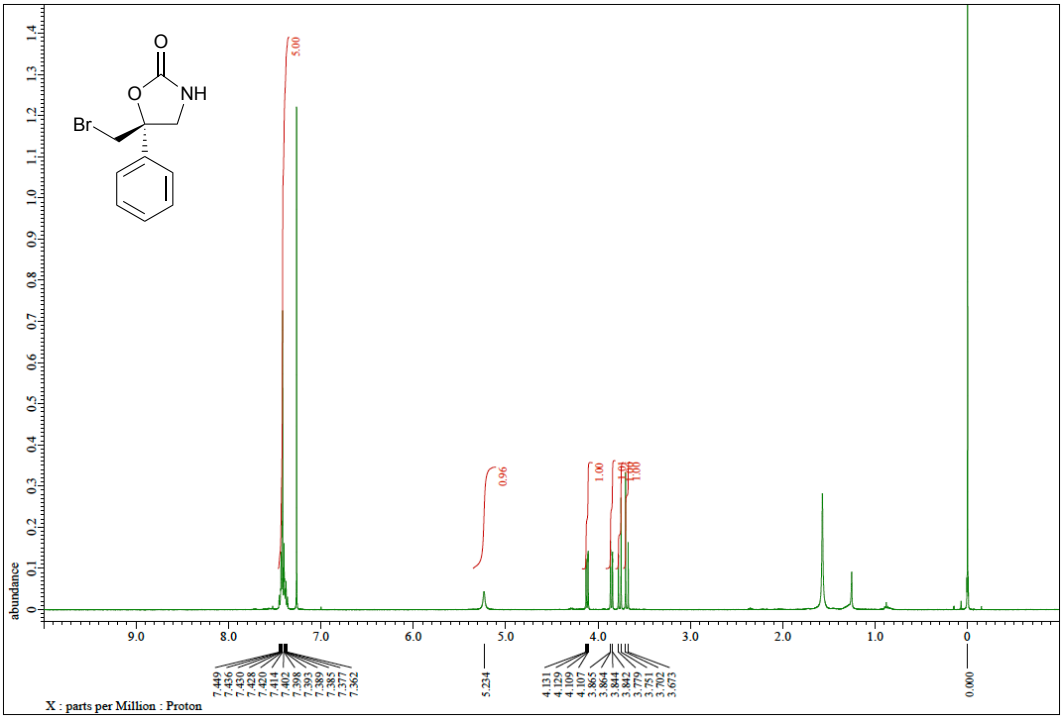


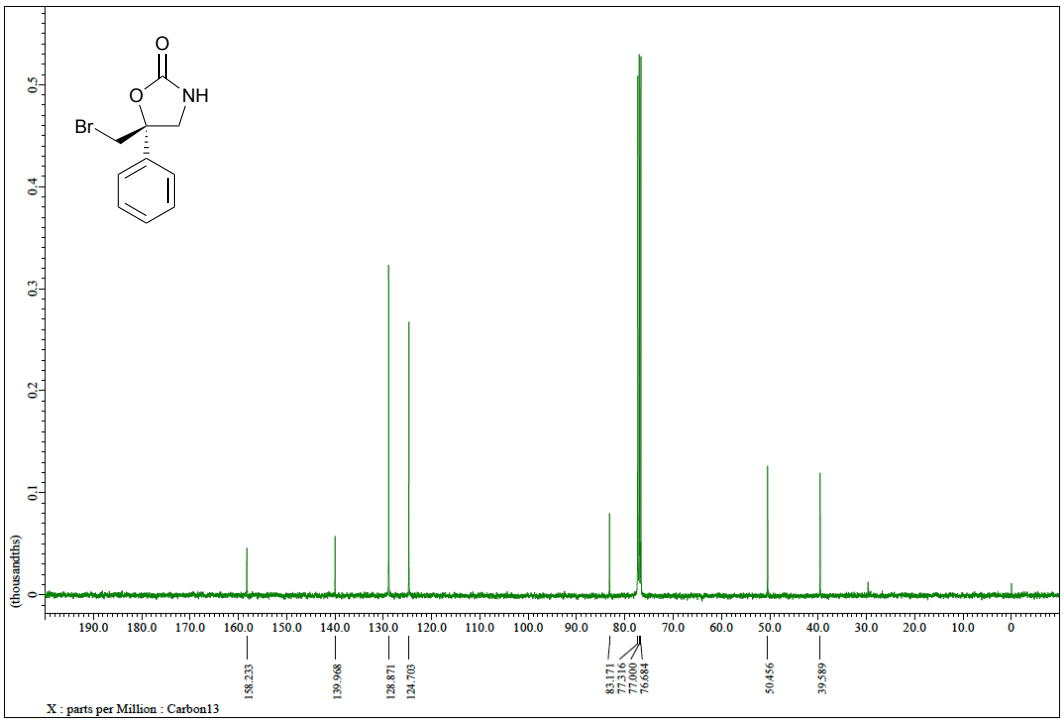
5: ^{1}H and ^{13}C NMR



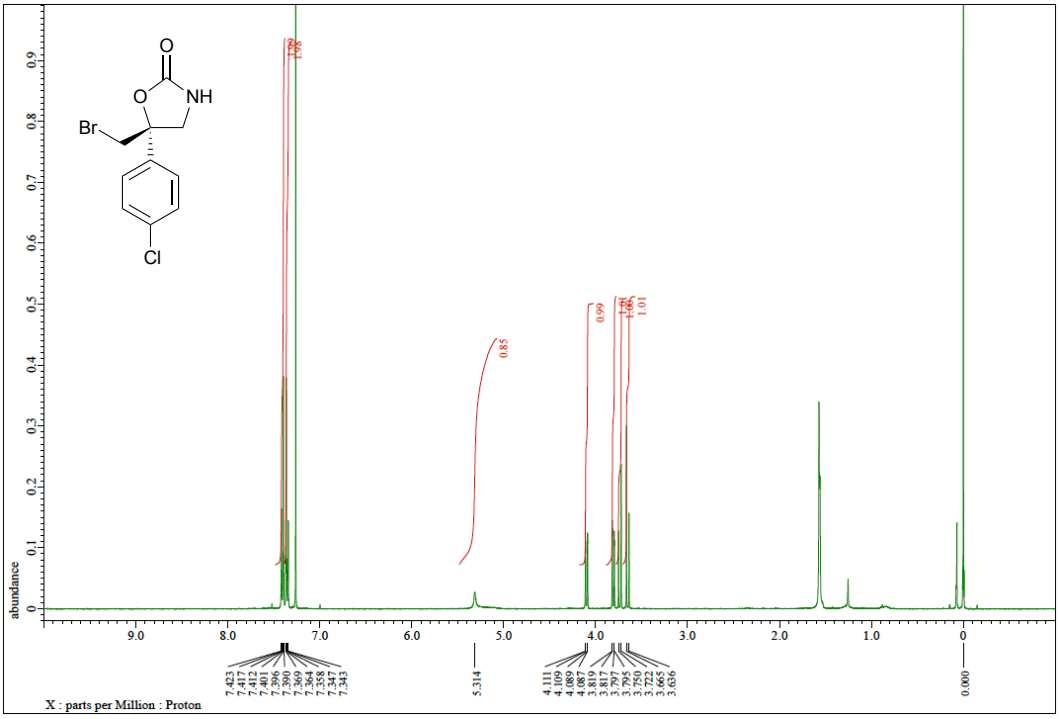


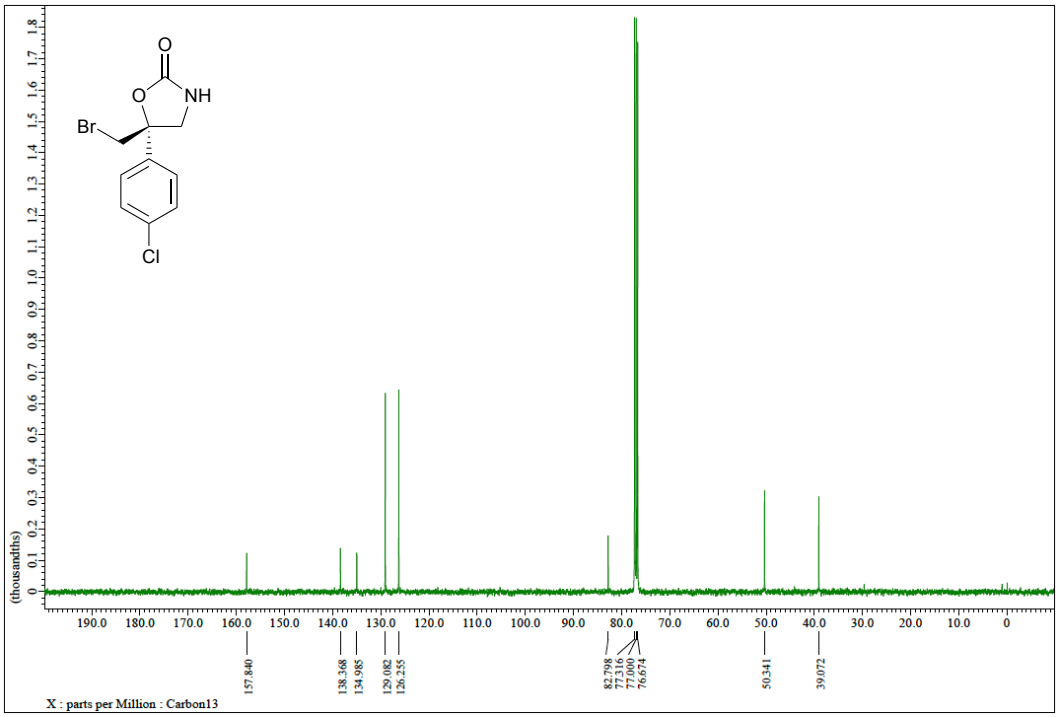
4a: ^{1}H and ^{13}C NMR



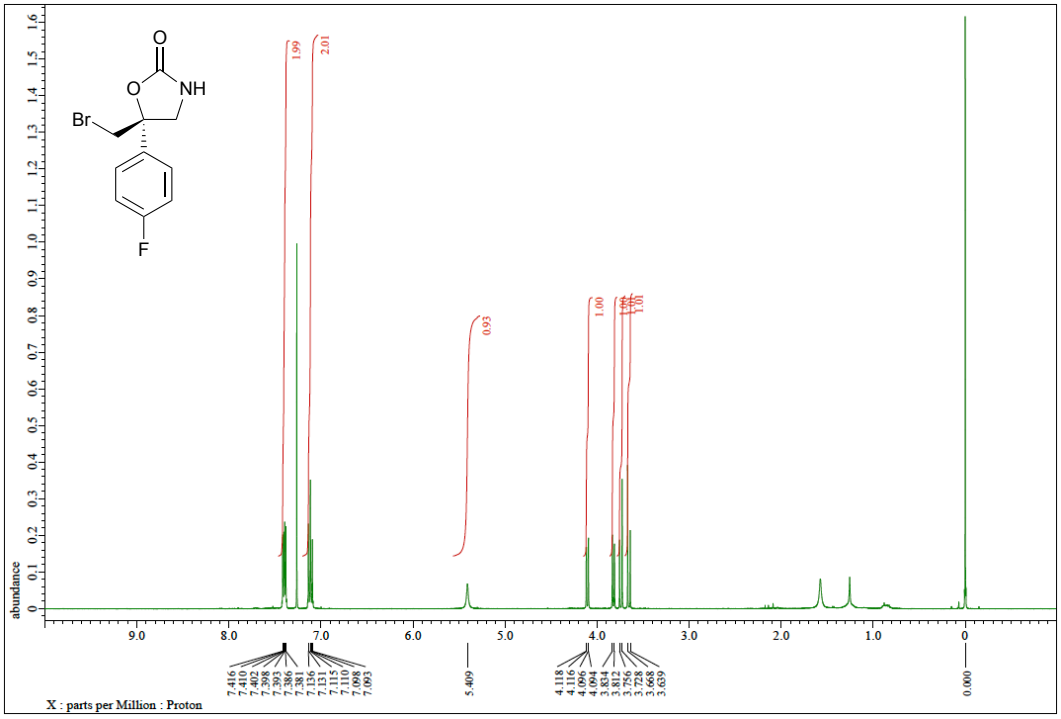


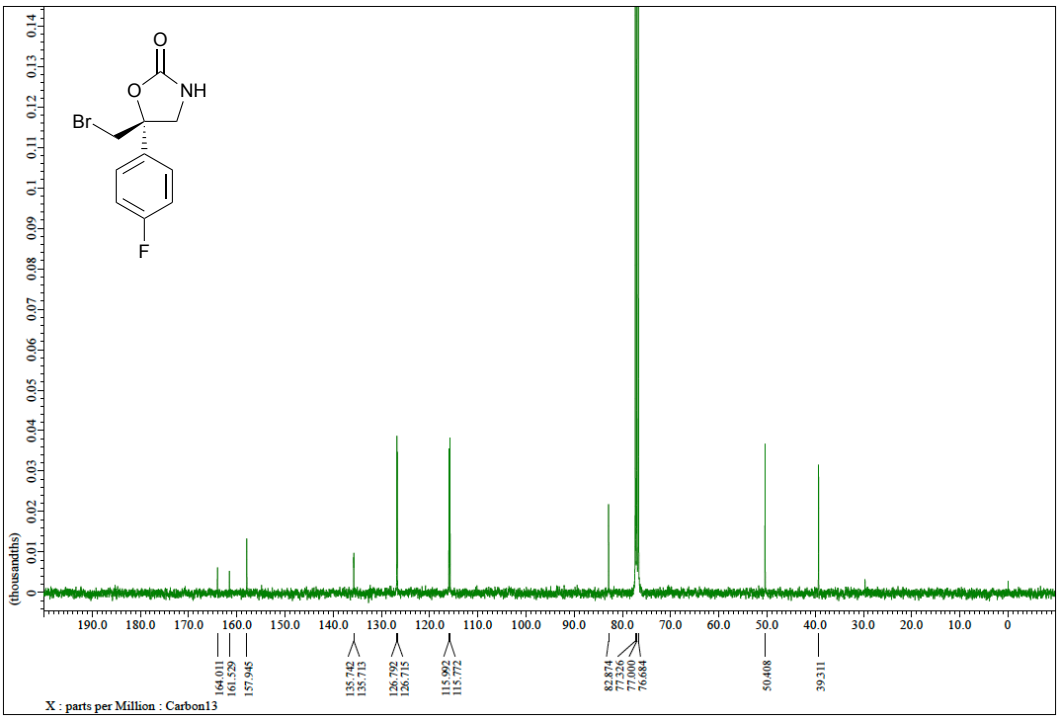
4b: ^{1}H and ^{13}C NMR



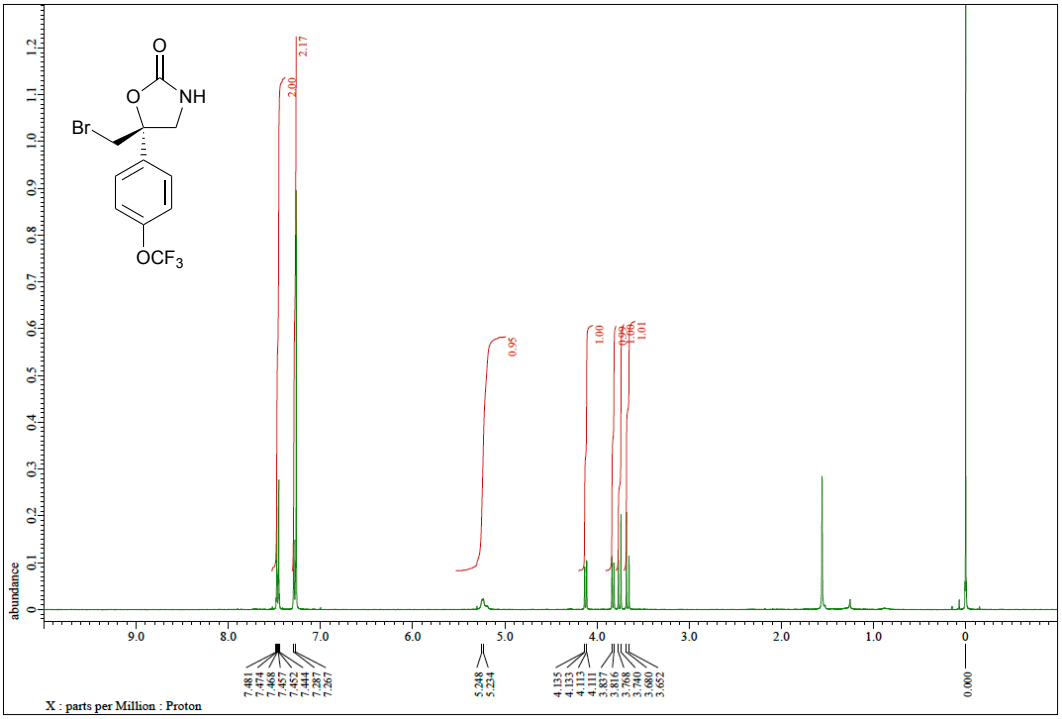


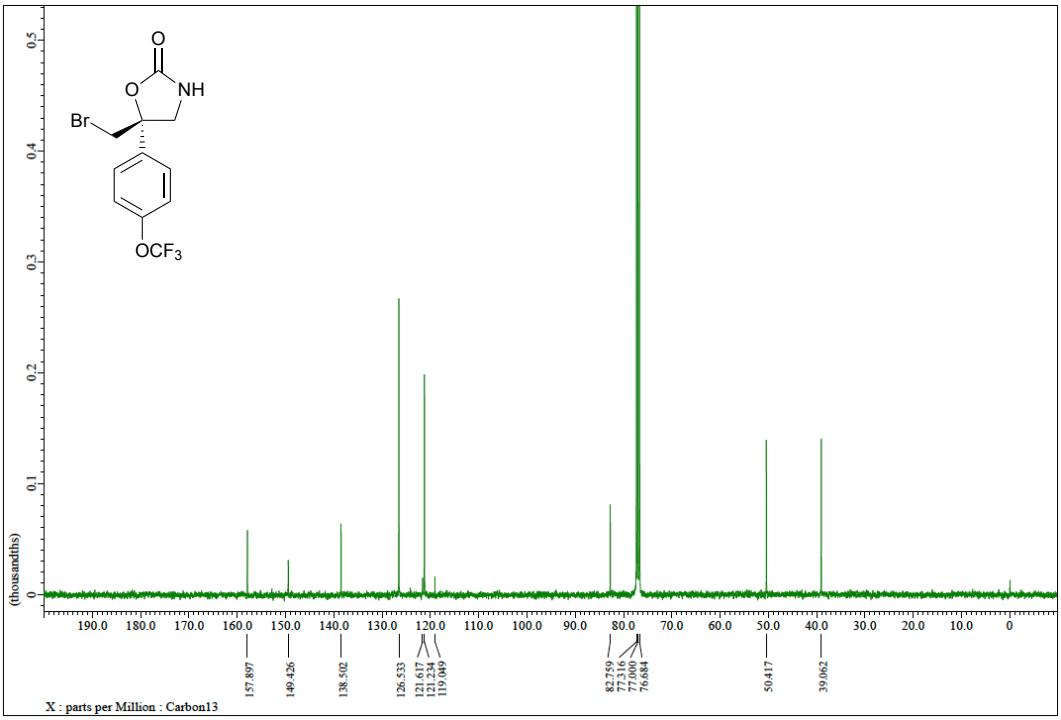
4c: ^{1}H and ^{13}C NMR



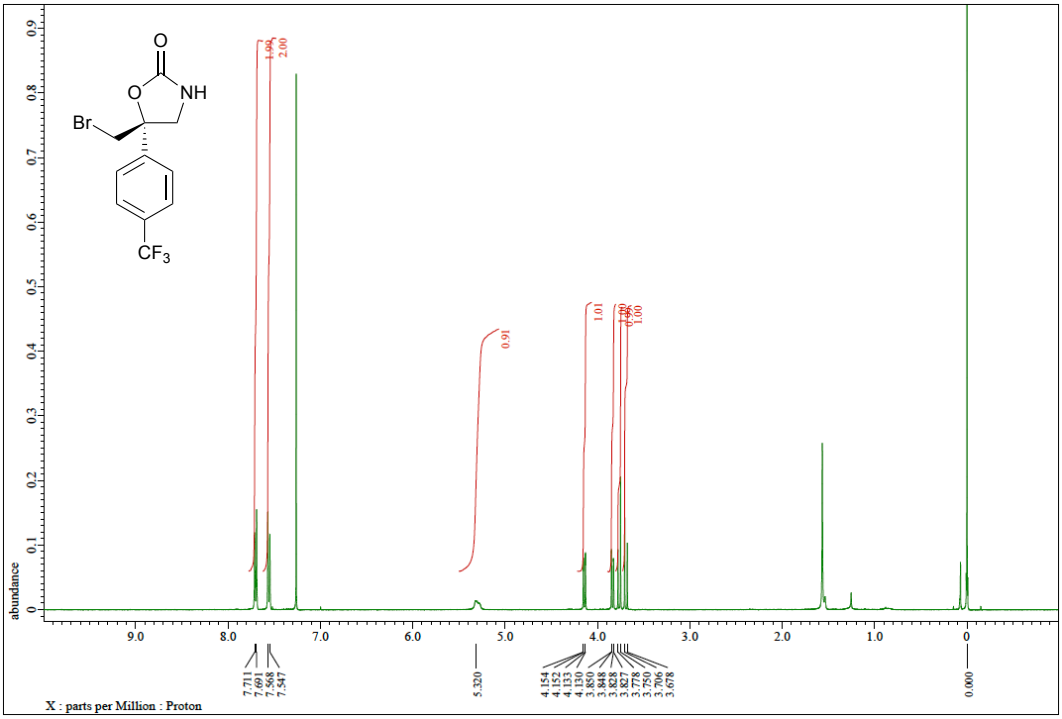


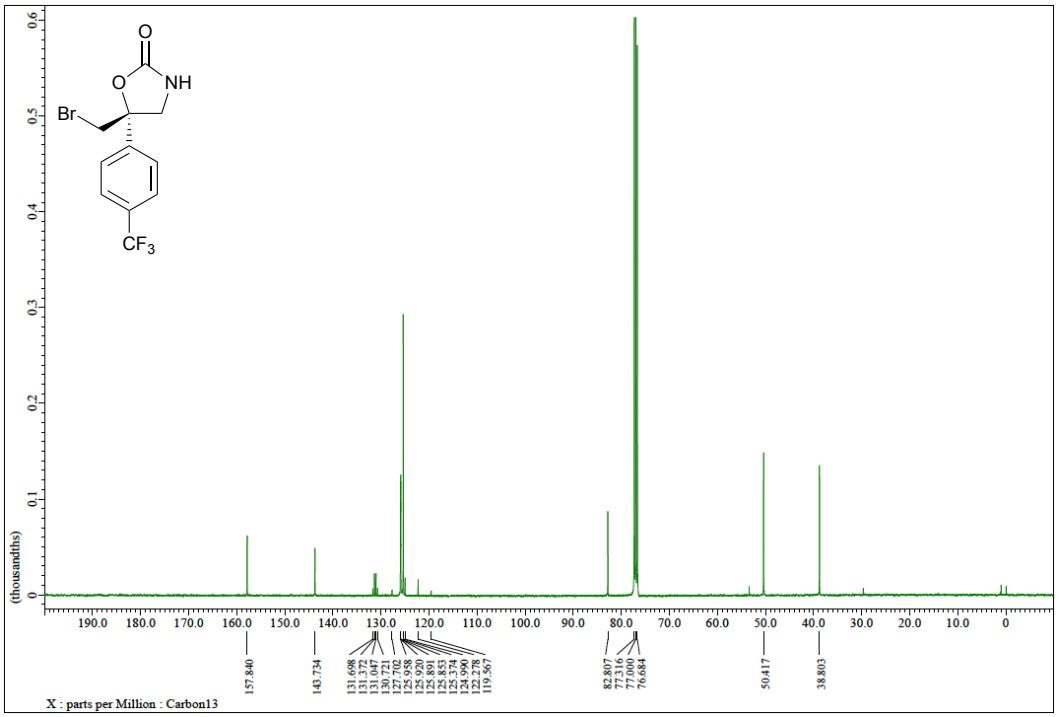
4d: ^{1}H and ^{13}C NMR



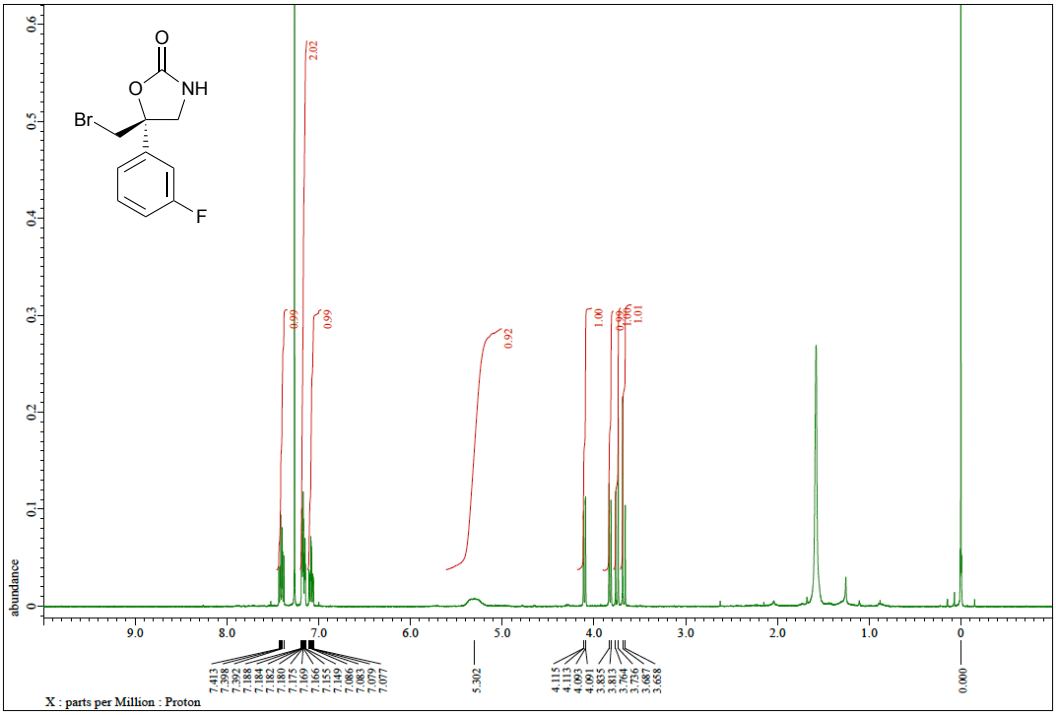


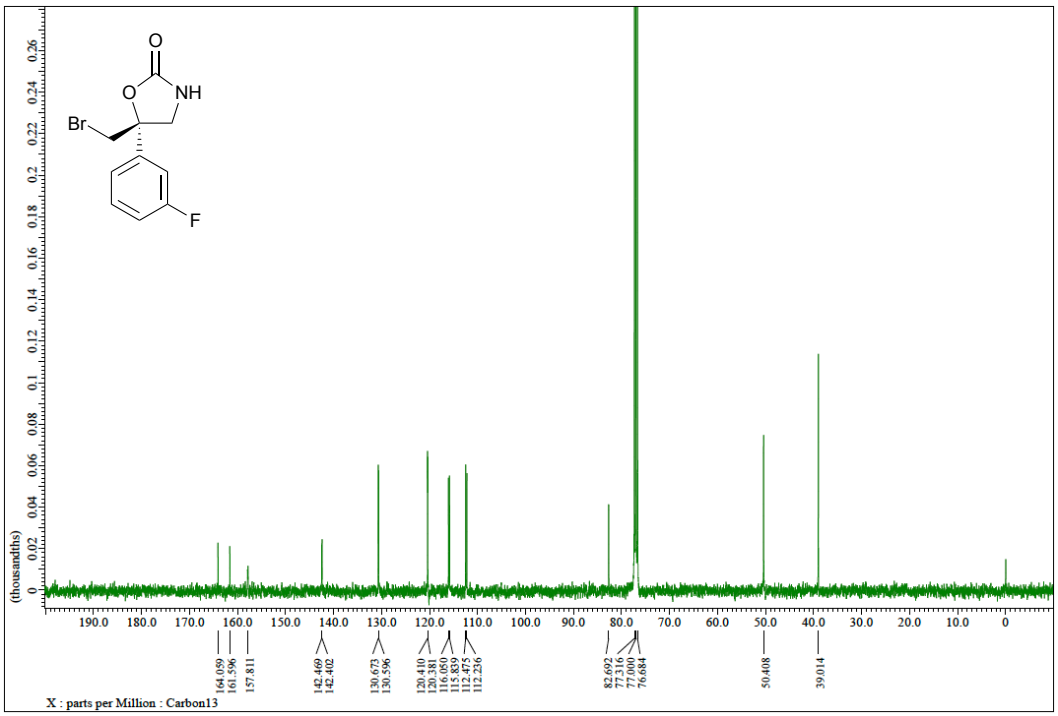
4e: ^{1}H and ^{13}C NMR



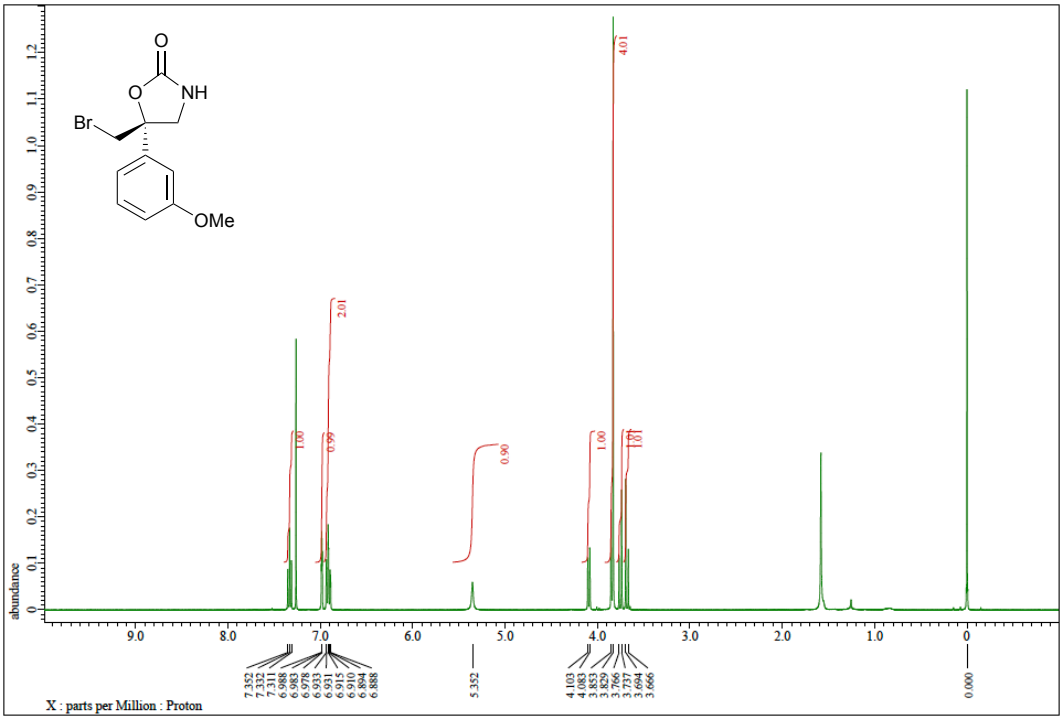


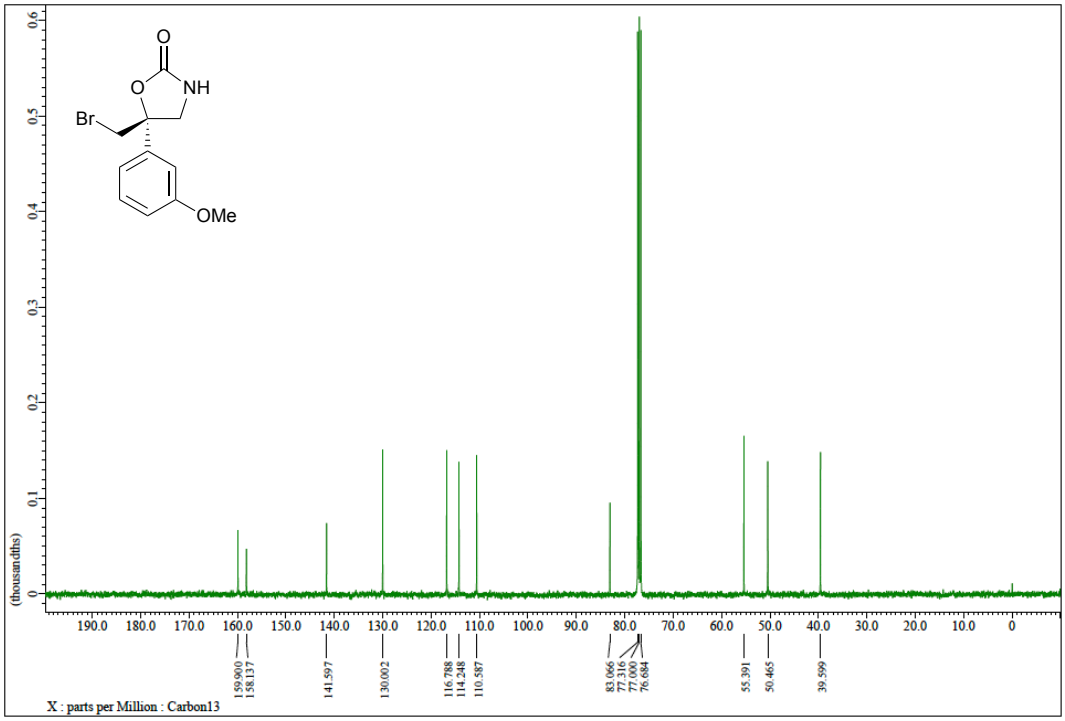
4f: ^{1}H and ^{13}C NMR



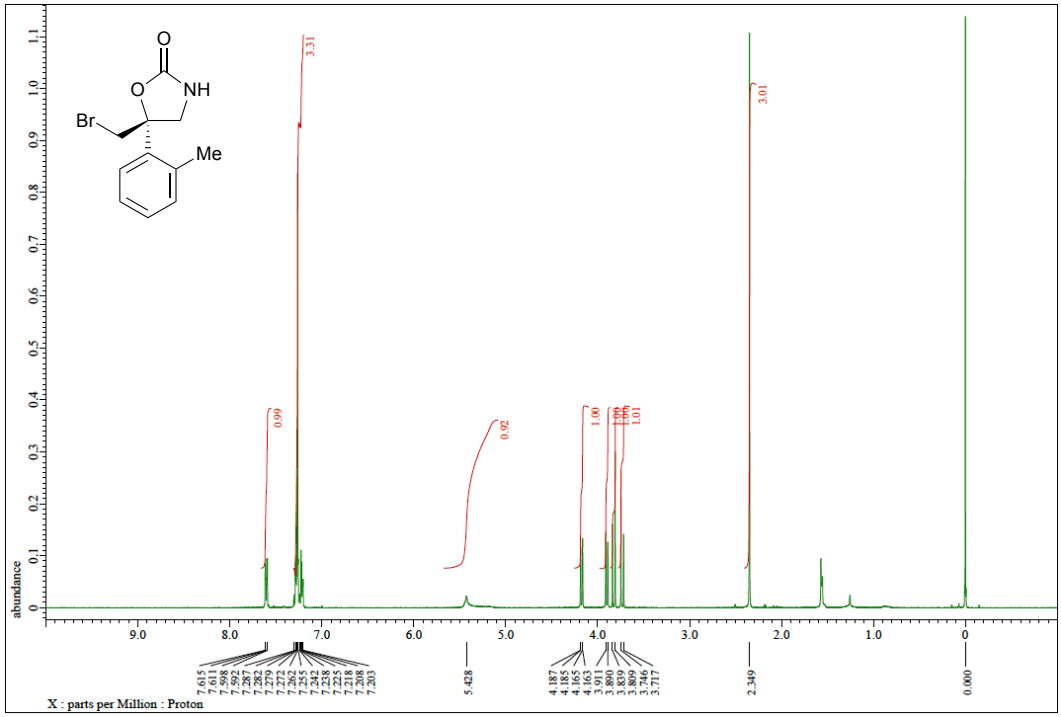


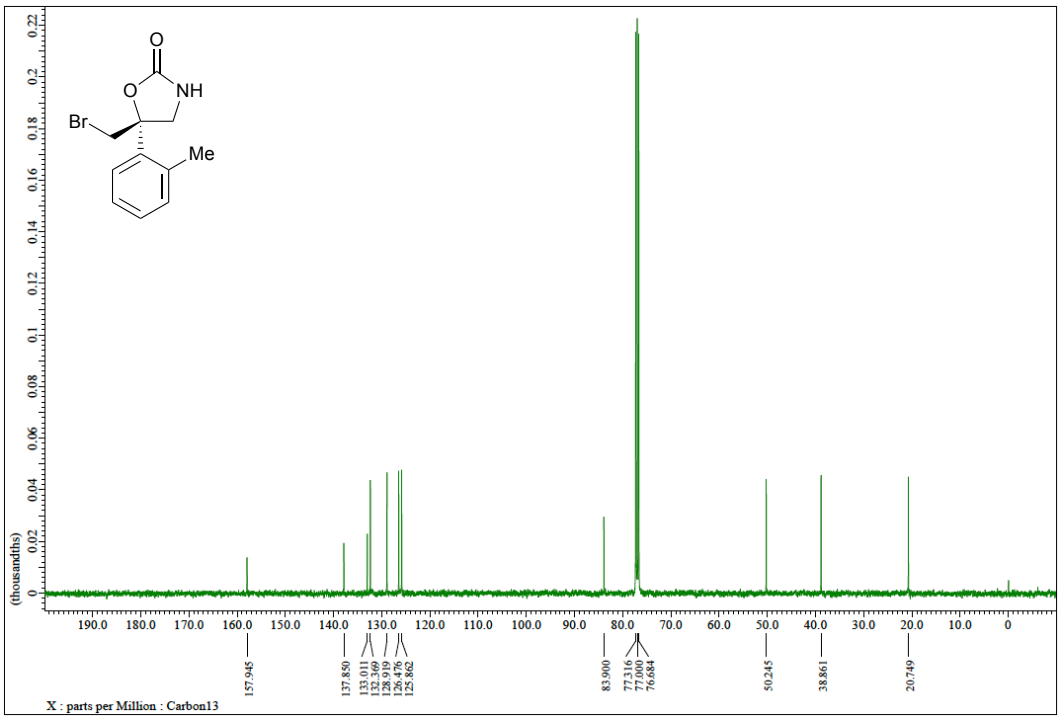
4g: ^{1}H and ^{13}C NMR



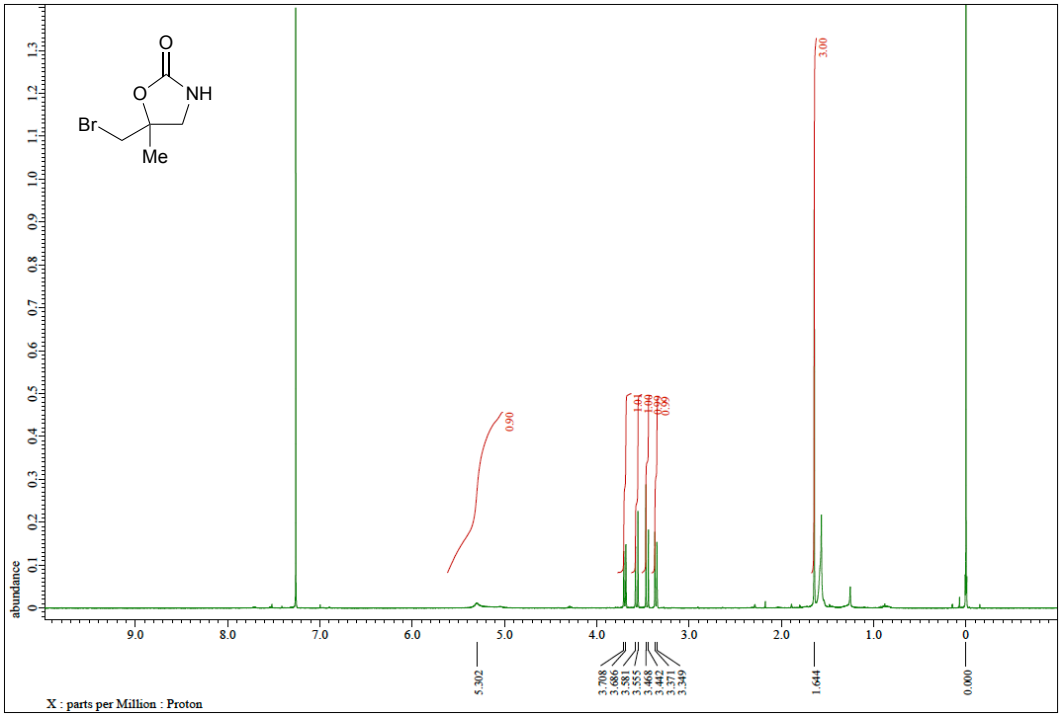


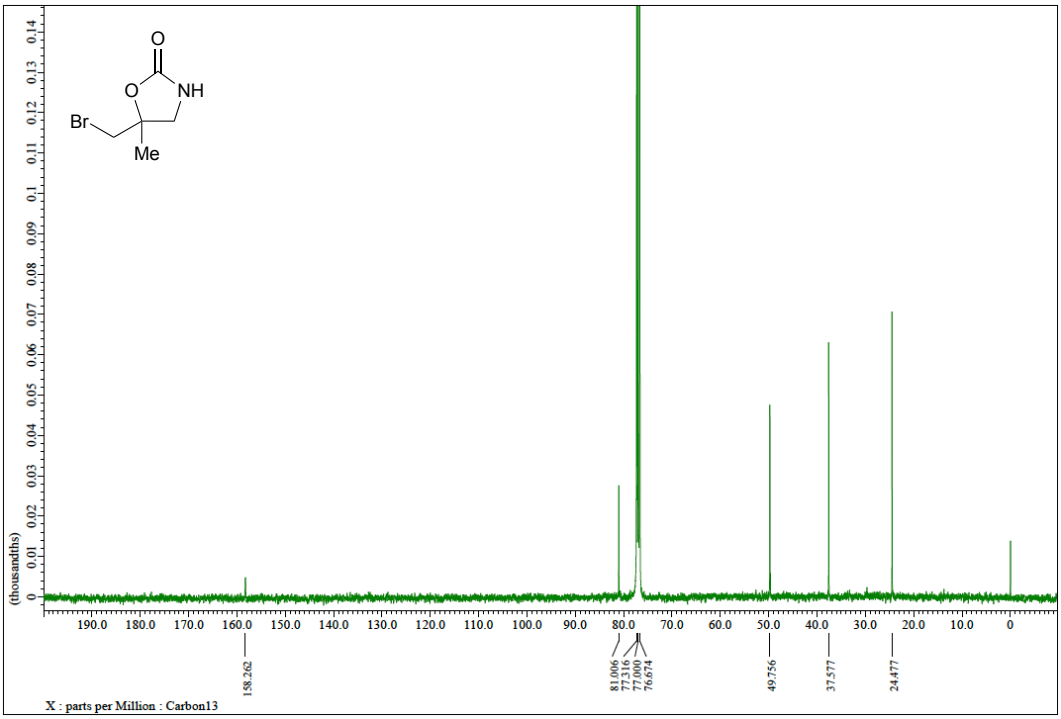
4h: ^{1}H and ^{13}C NMR



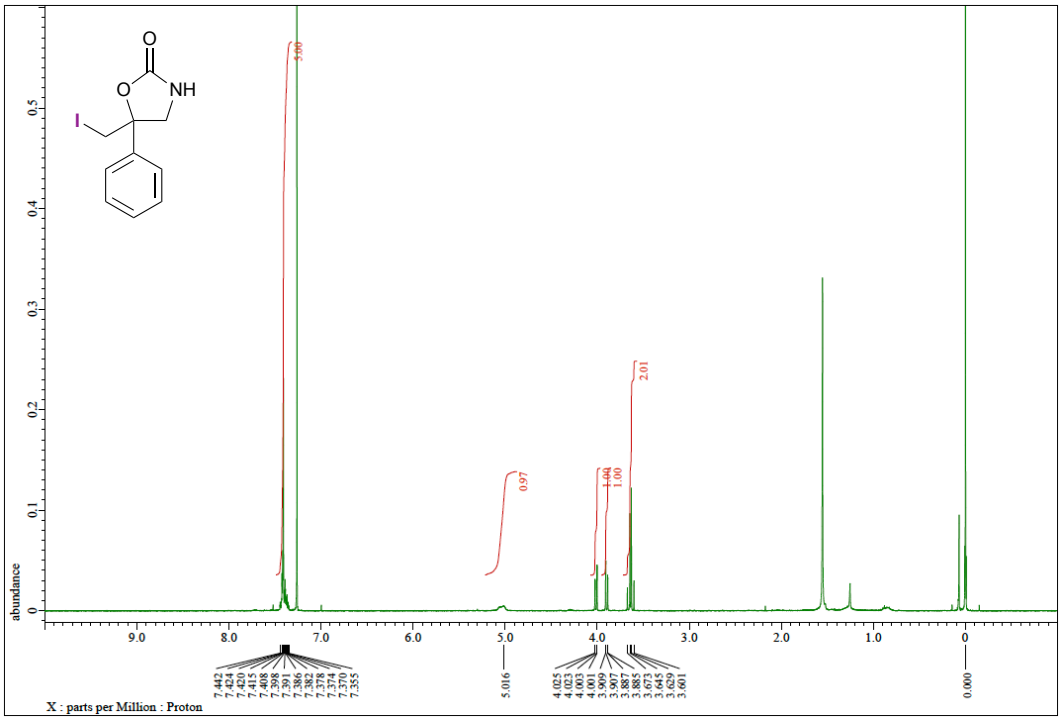


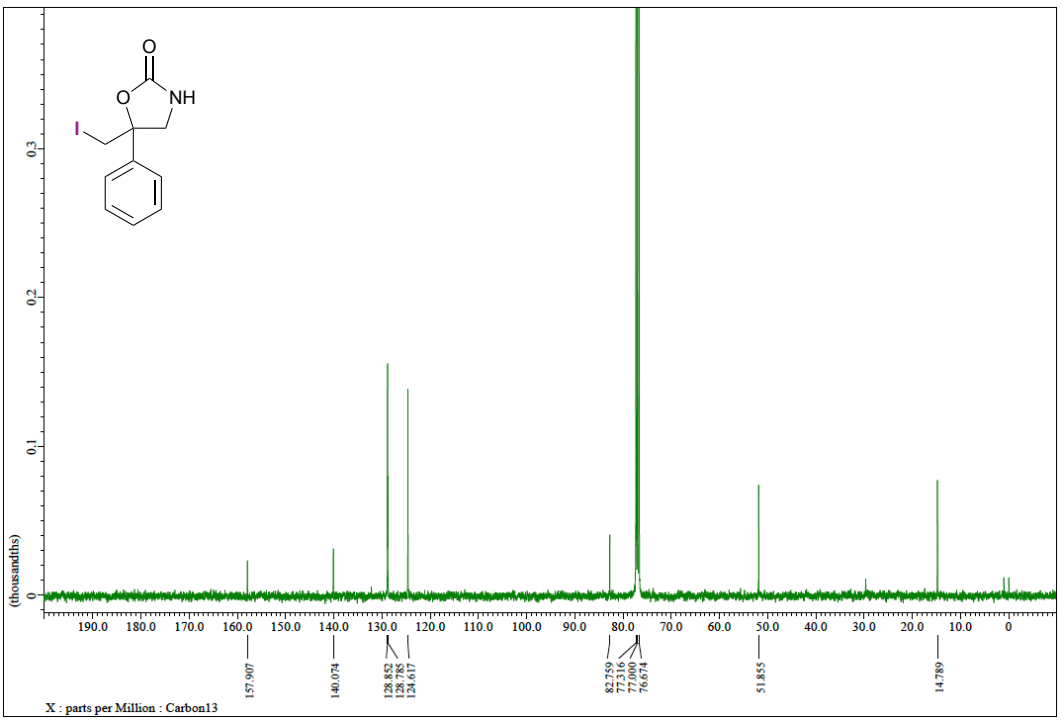
4i: ^{1}H and ^{13}C NMR



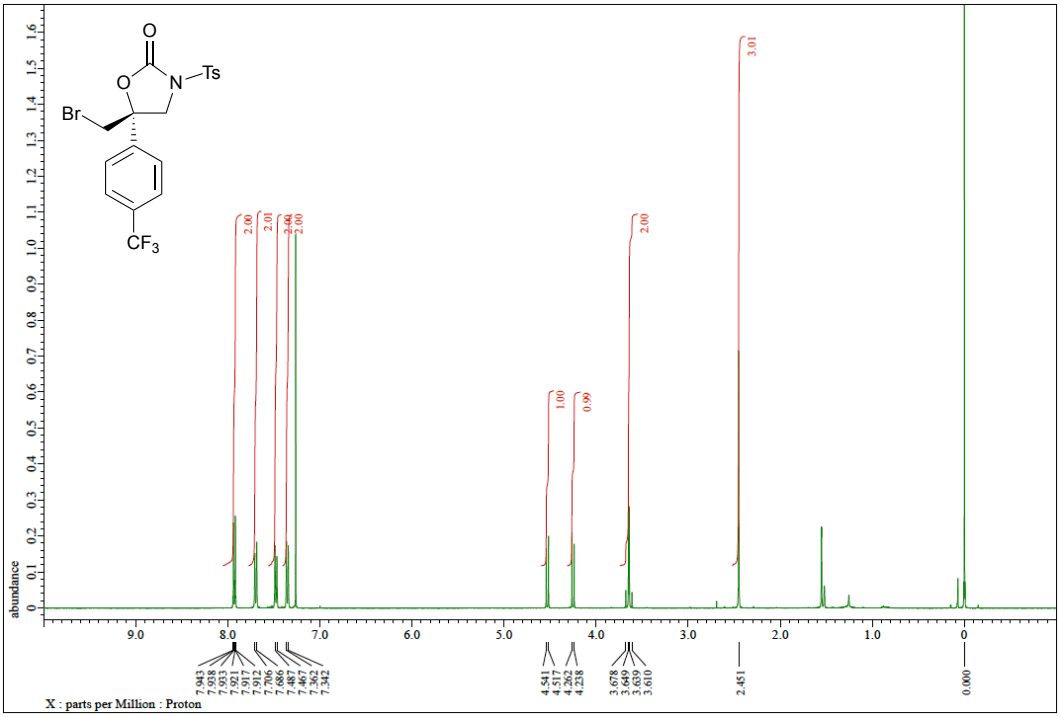


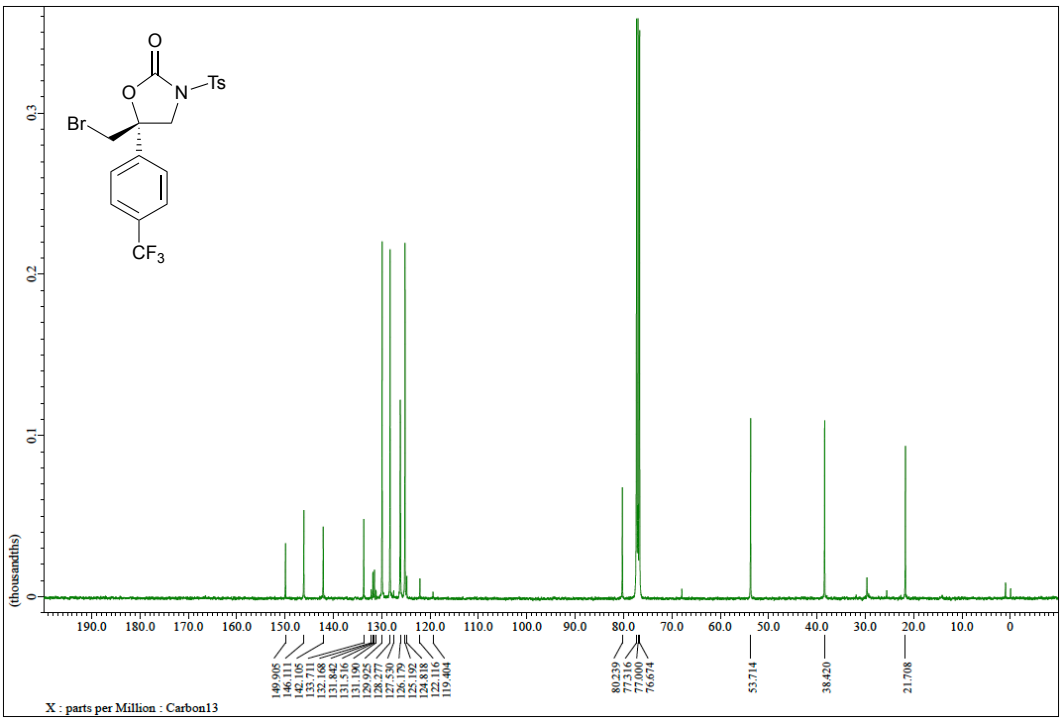
6: ^{1}H and ^{13}C NMR



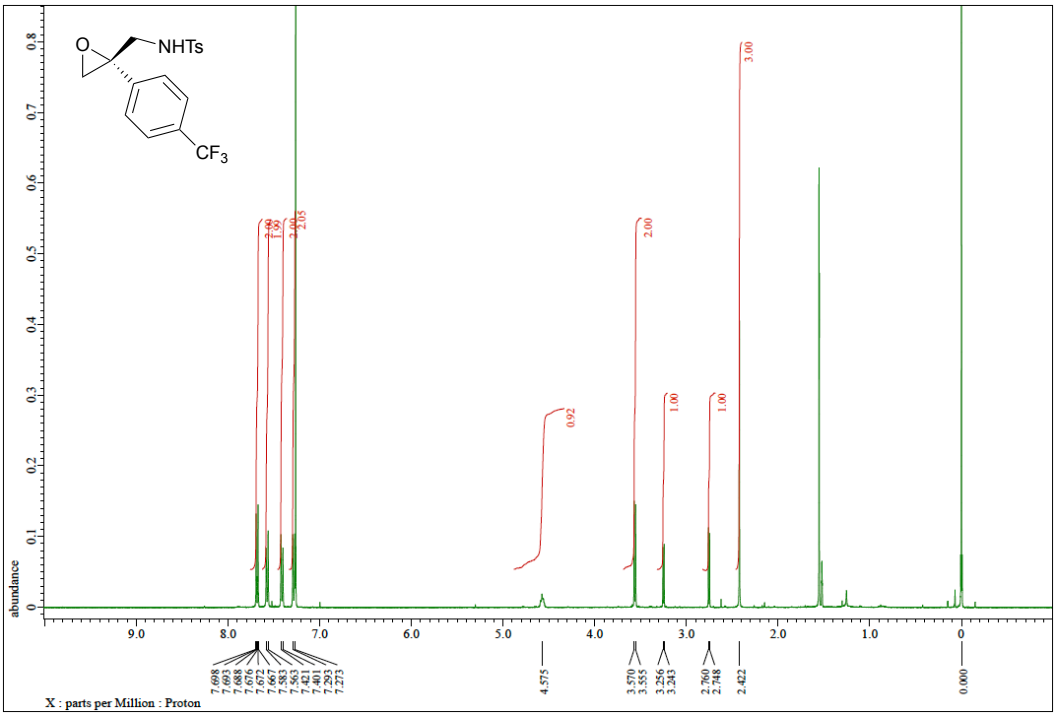


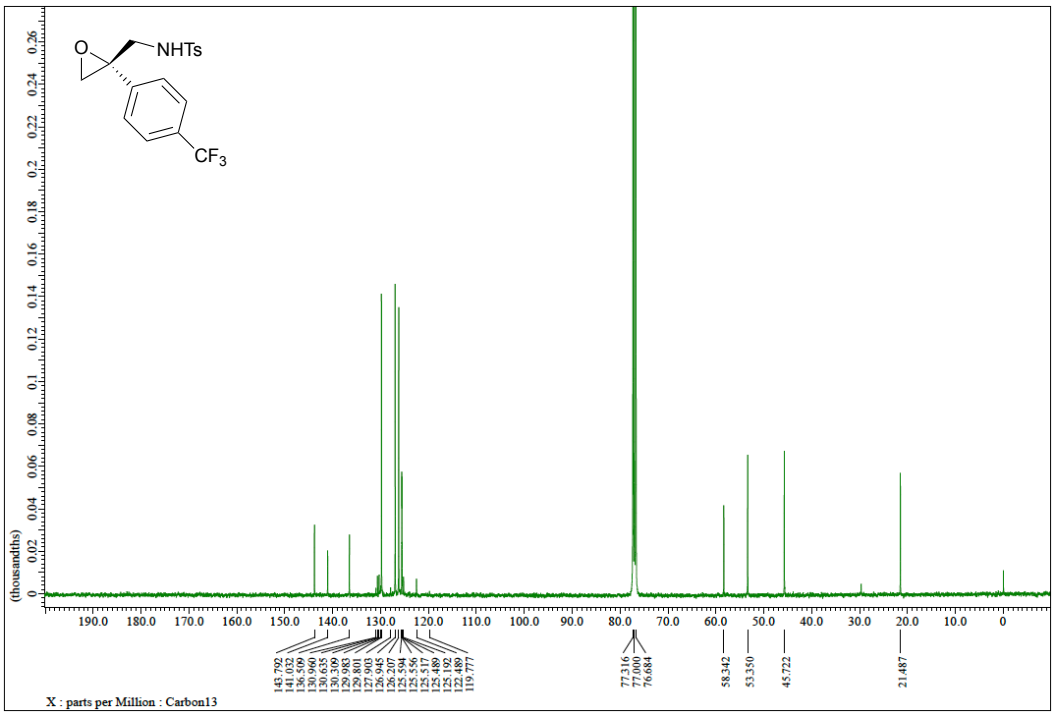
8: ^{1}H and ^{13}C NMR





9: ^{1}H and ^{13}C NMR





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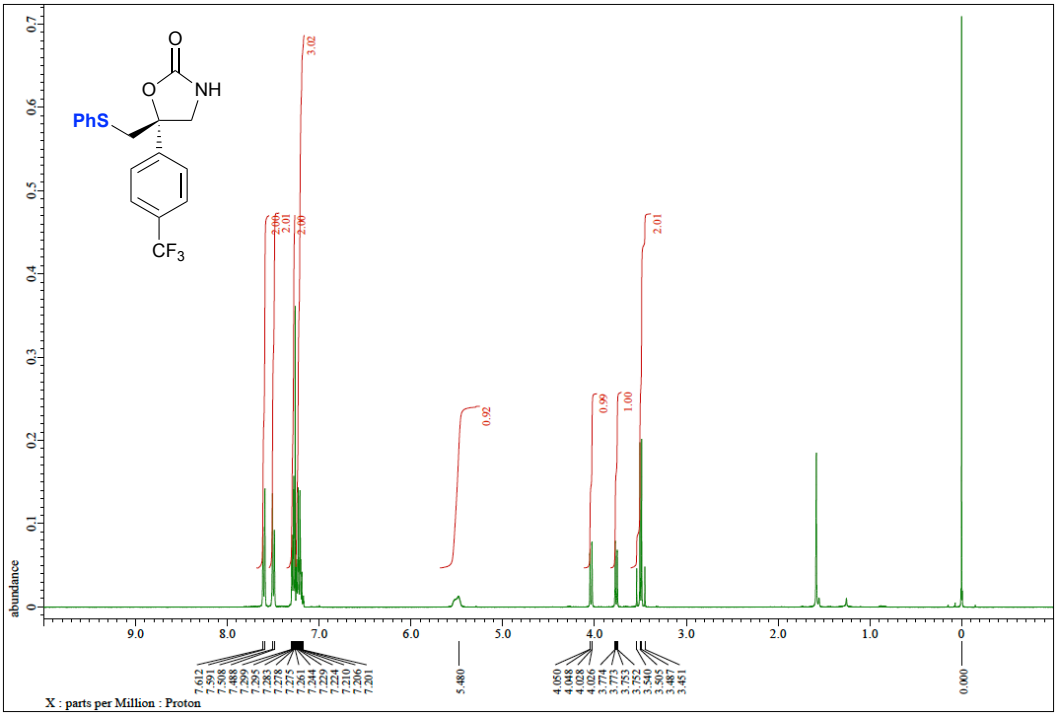
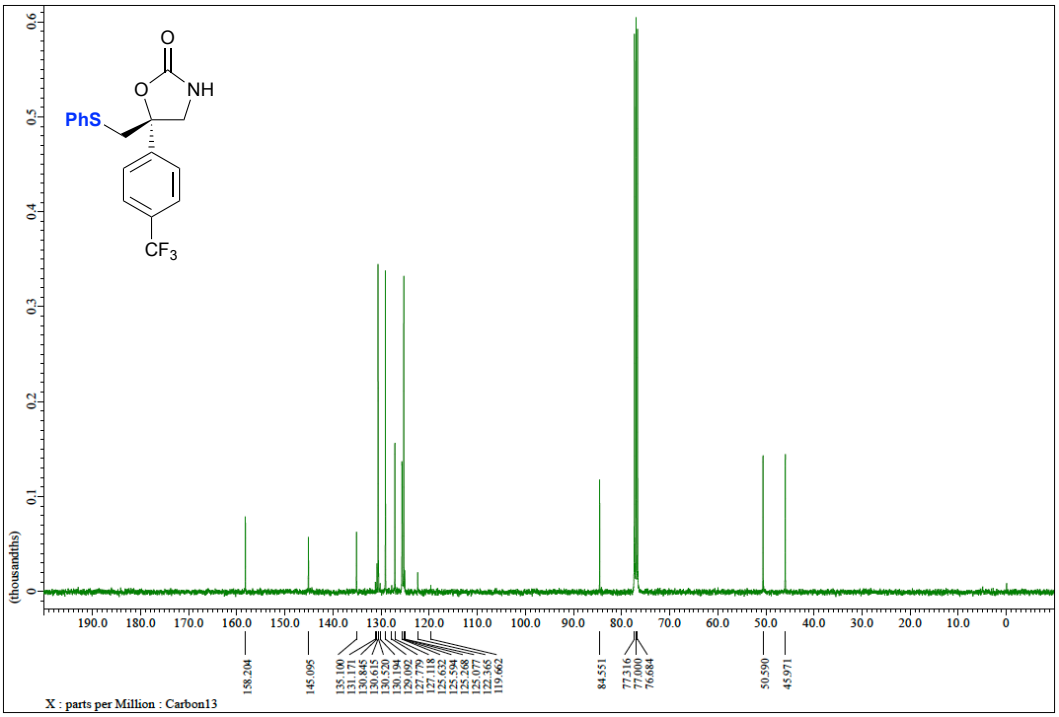
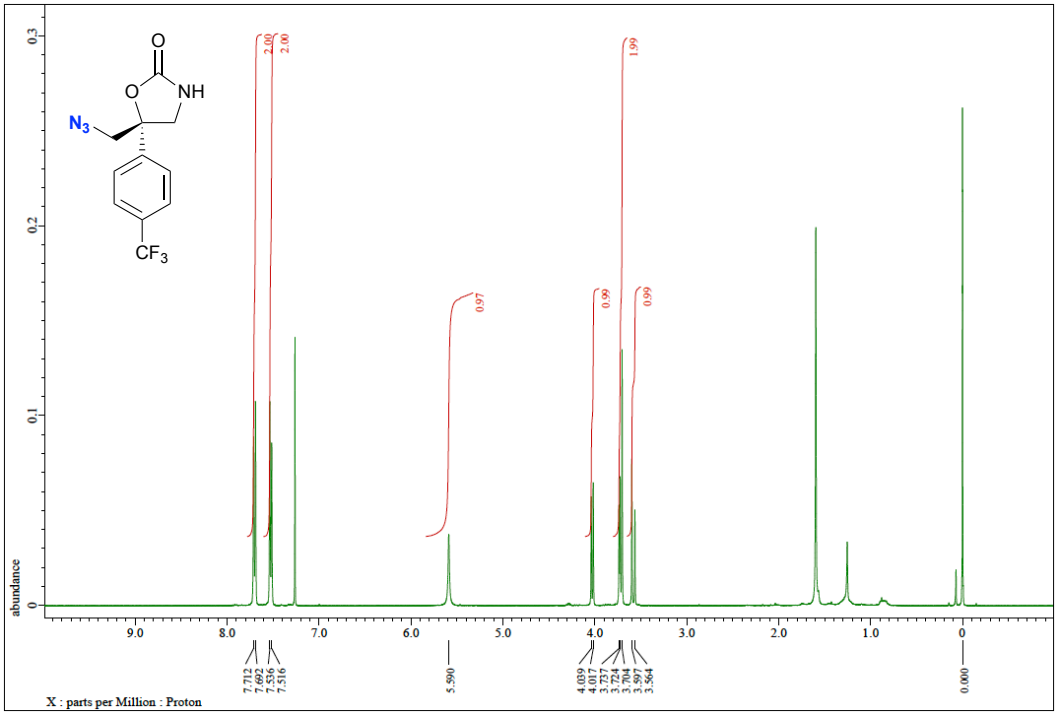
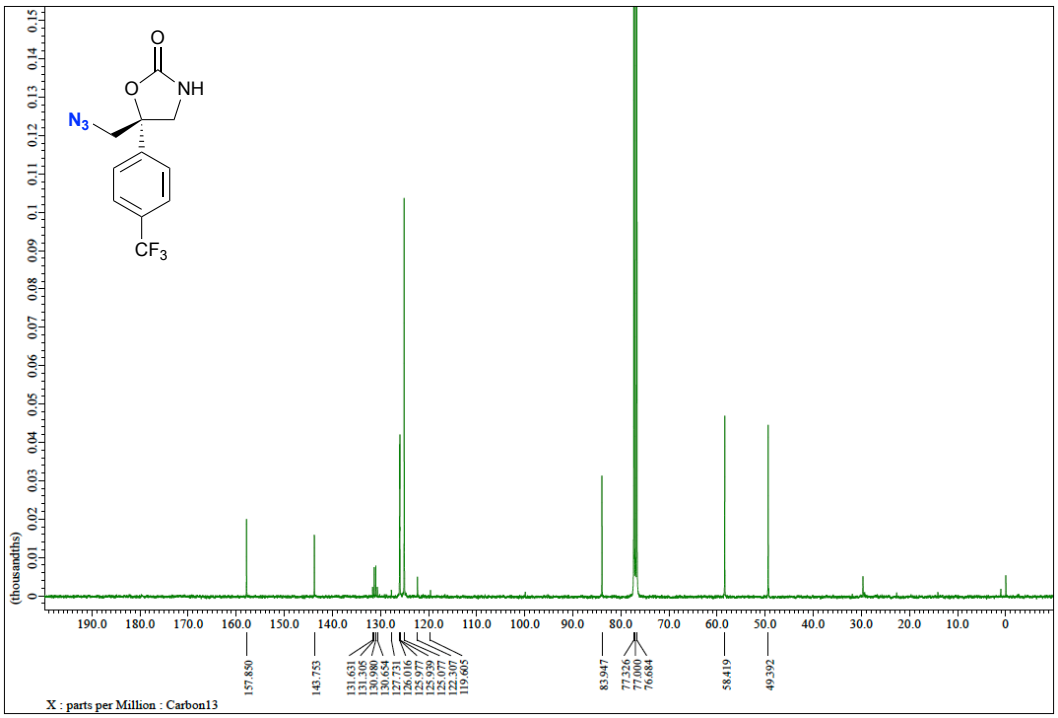




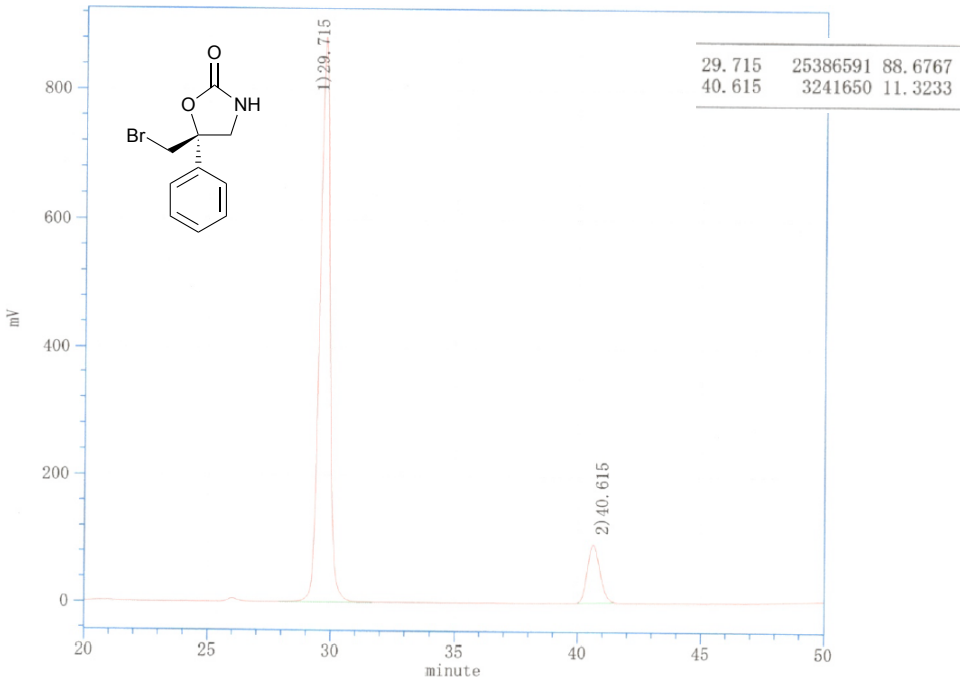
11: ^{1}H and ^{13}C NMR

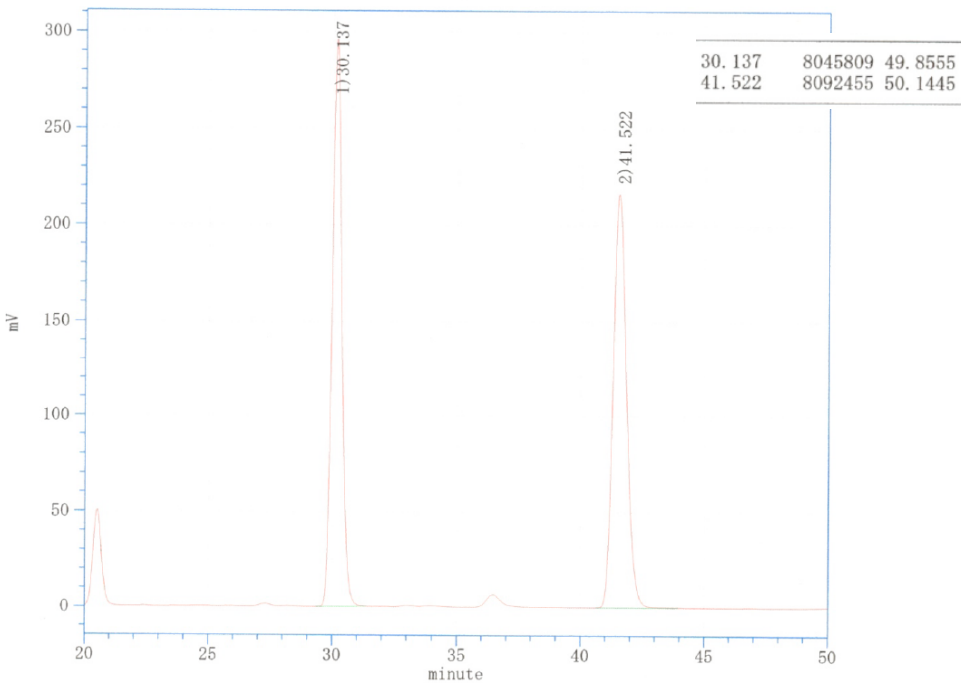




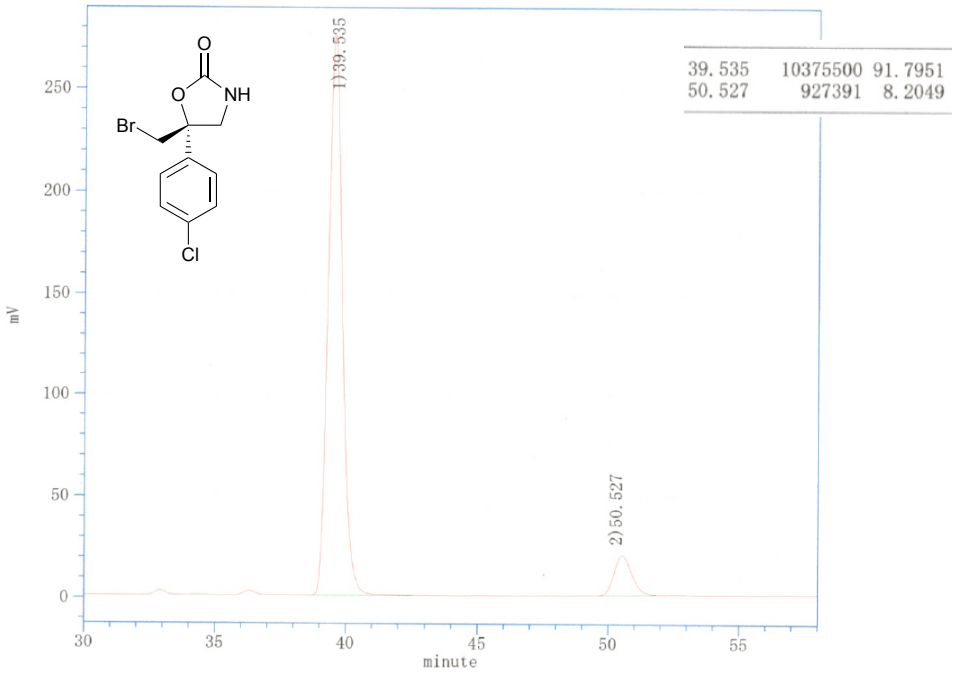
HPLC Charts

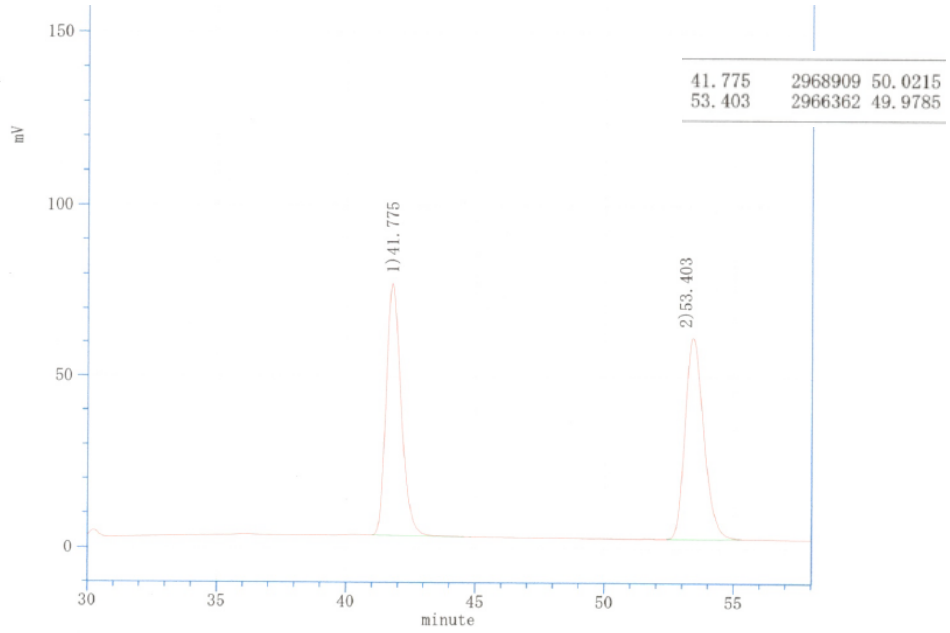
4a: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



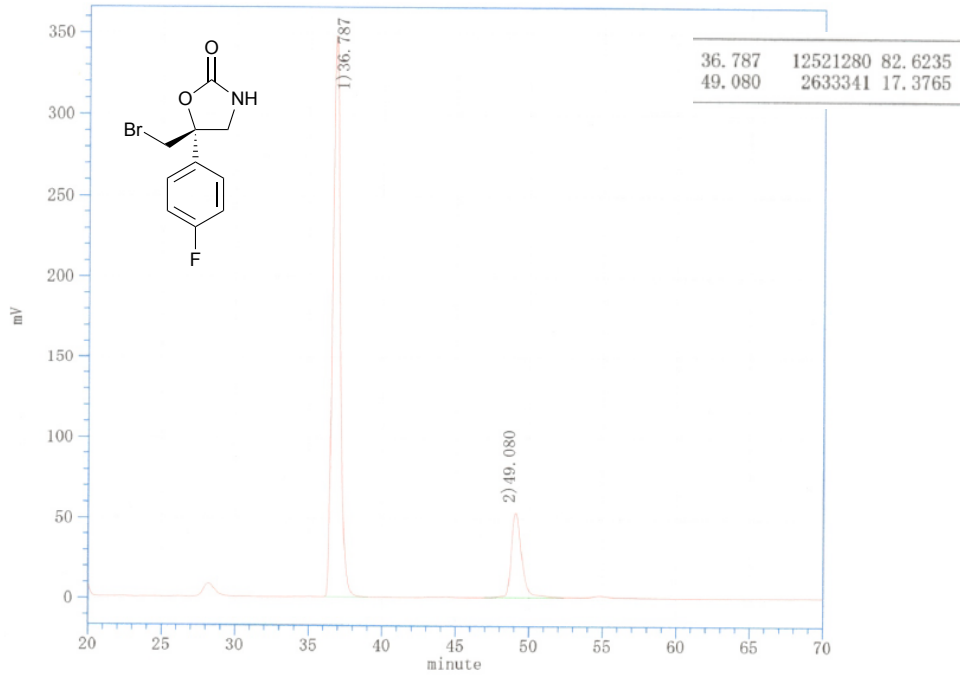


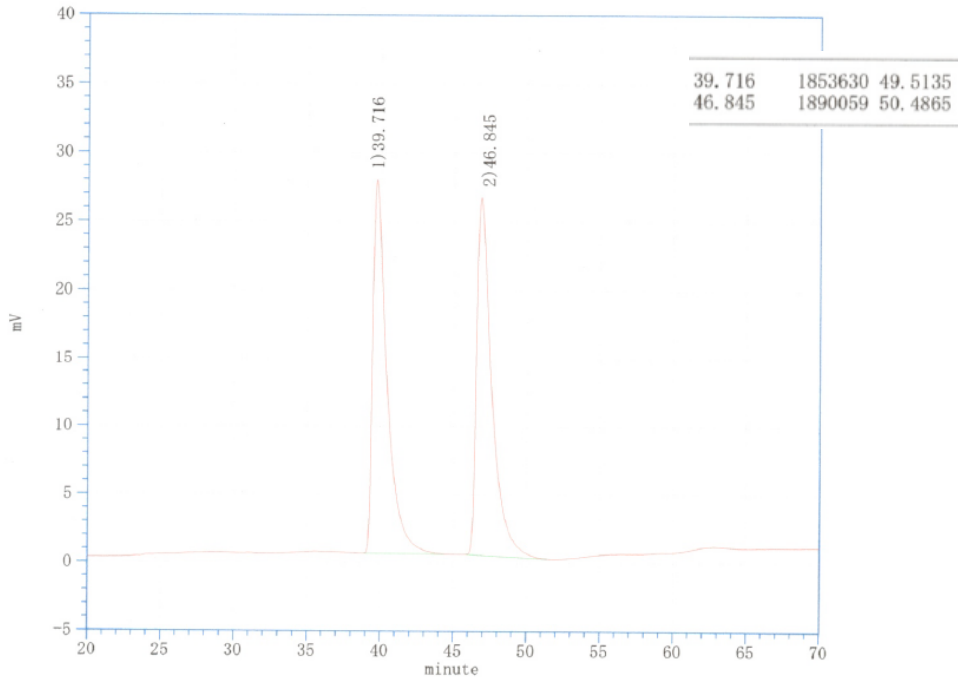
4b: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



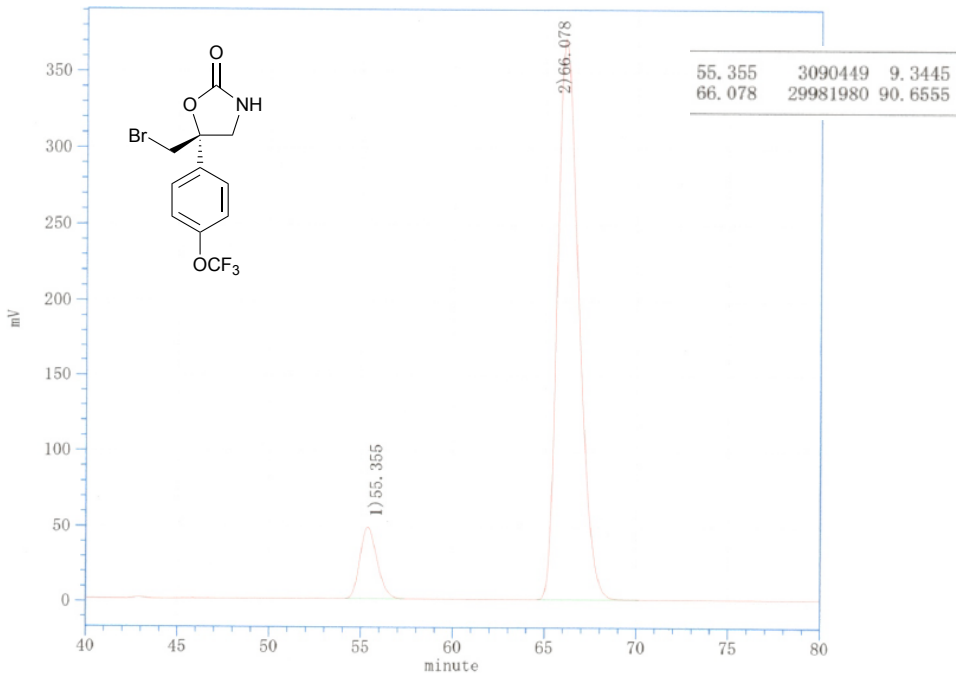


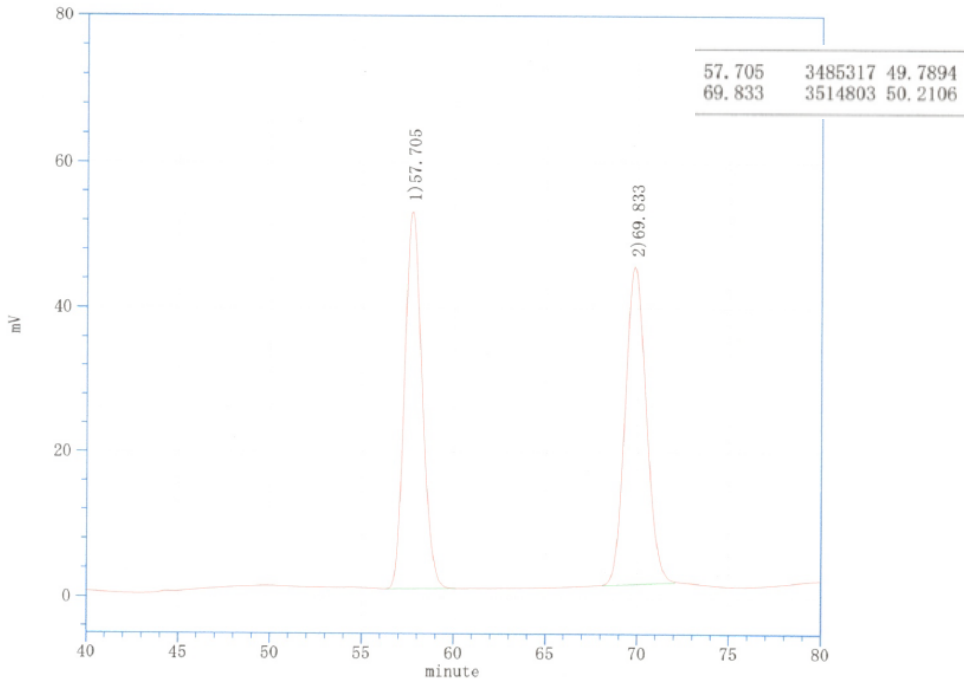
4c: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



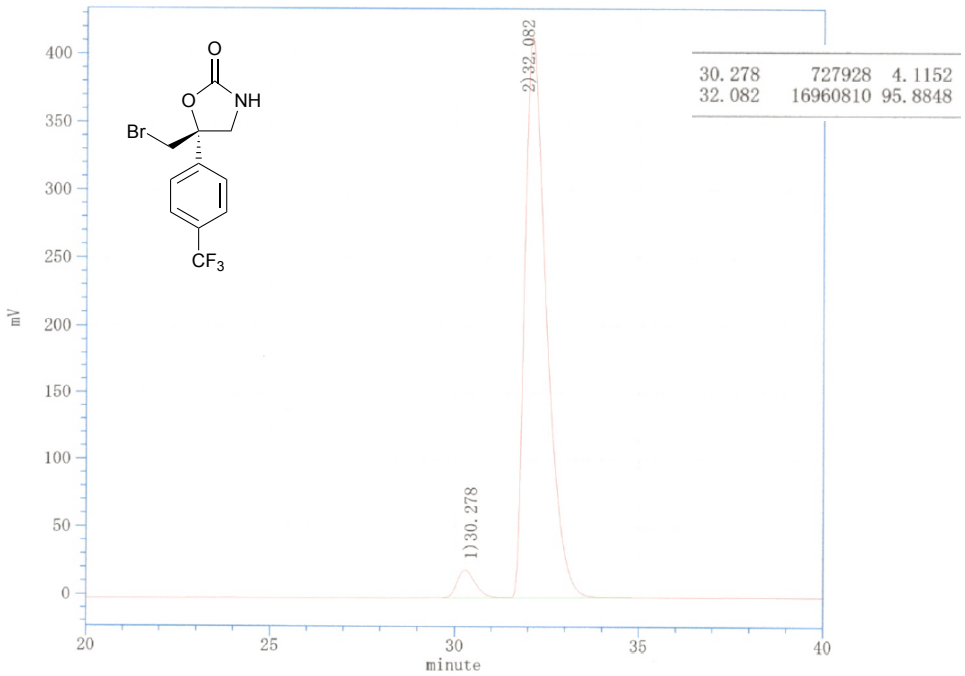


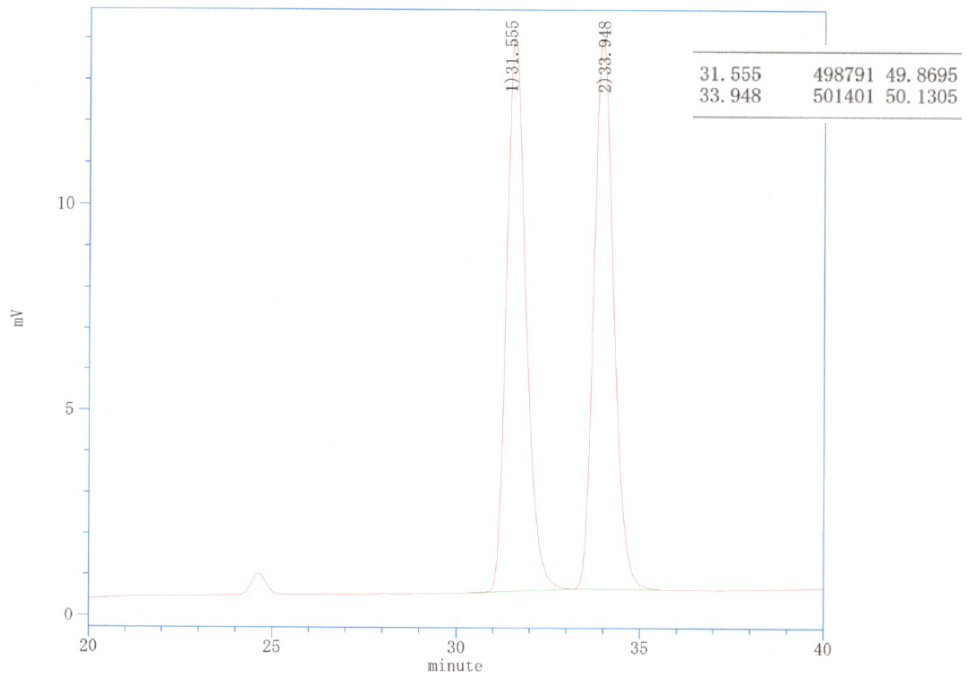
4d: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



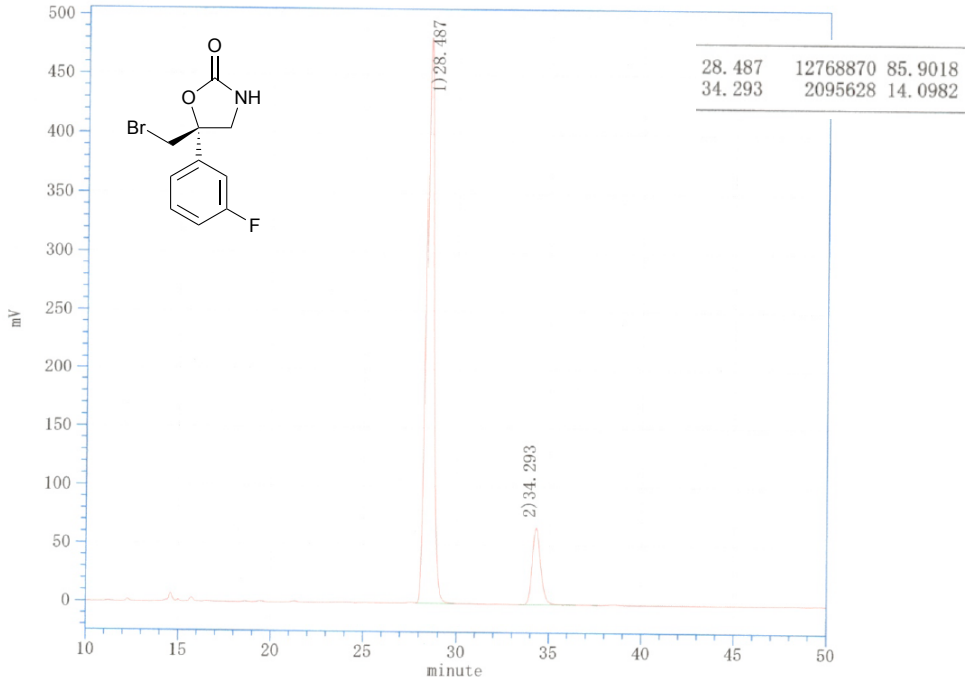


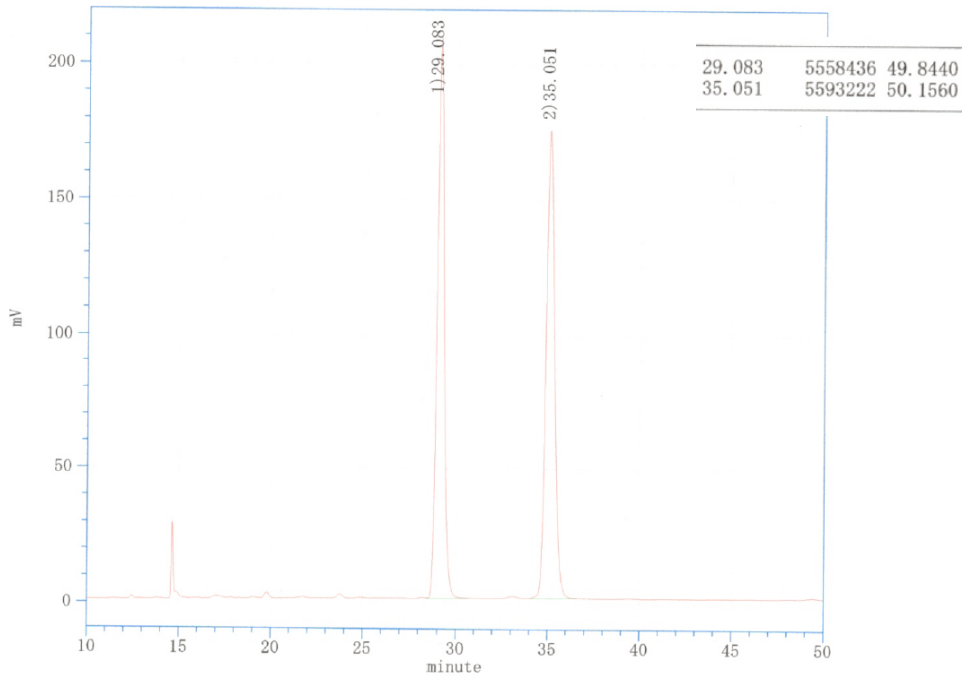
4e: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



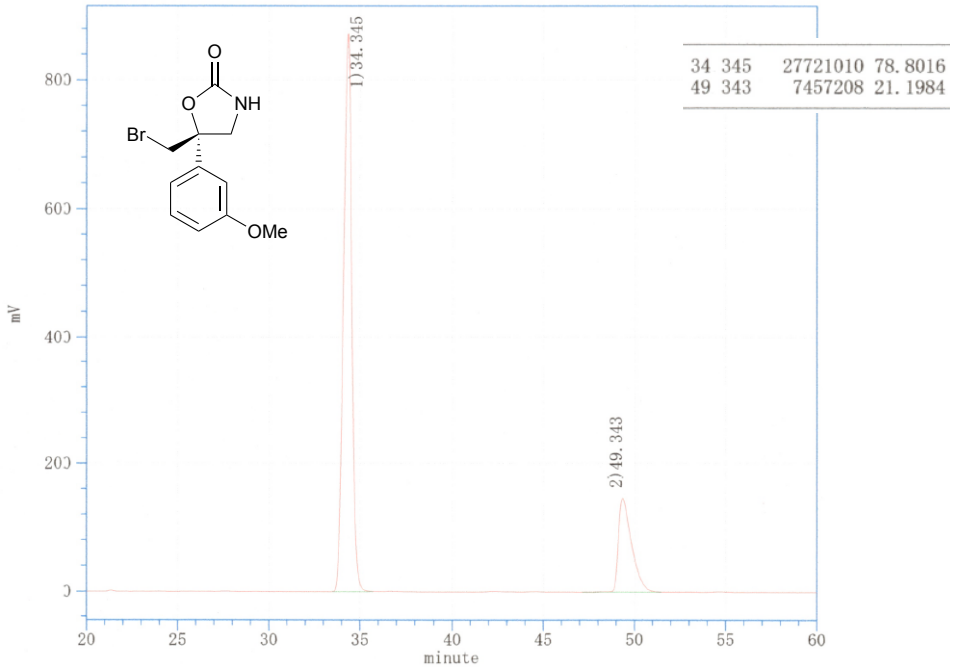


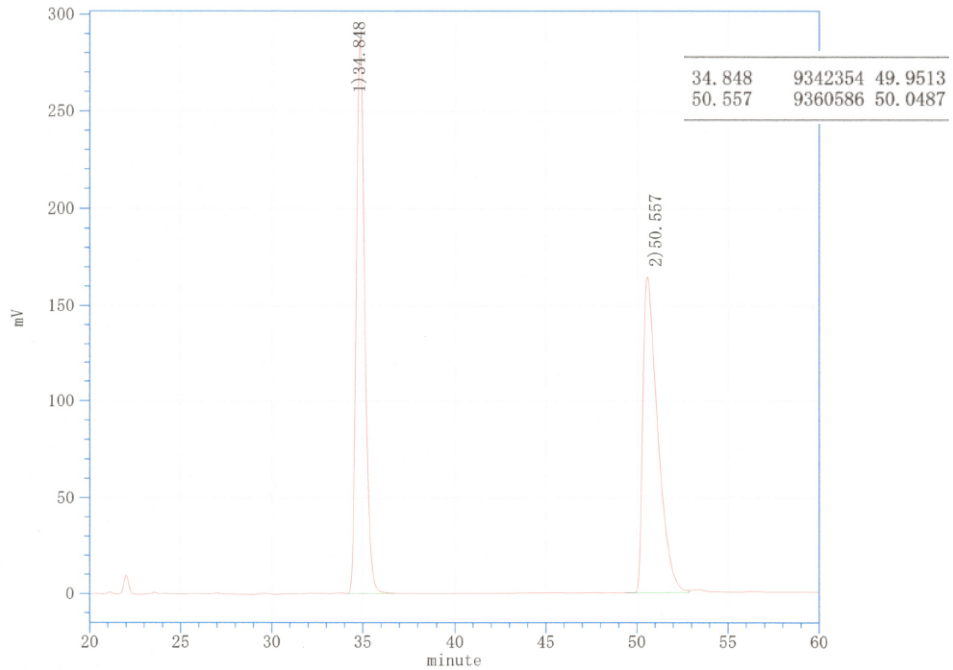
4f: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



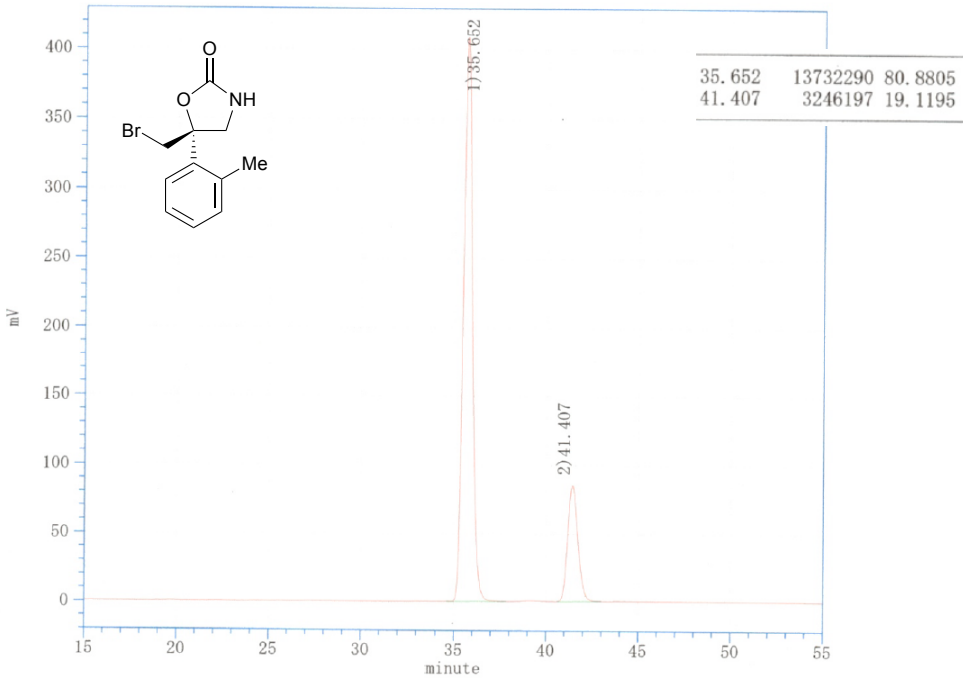


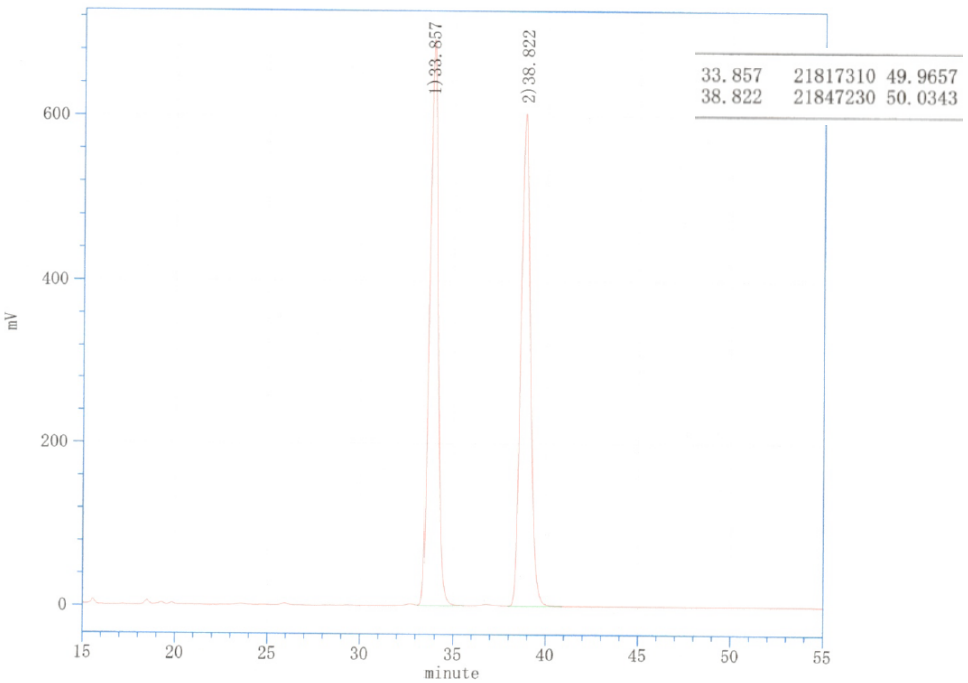
4g: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



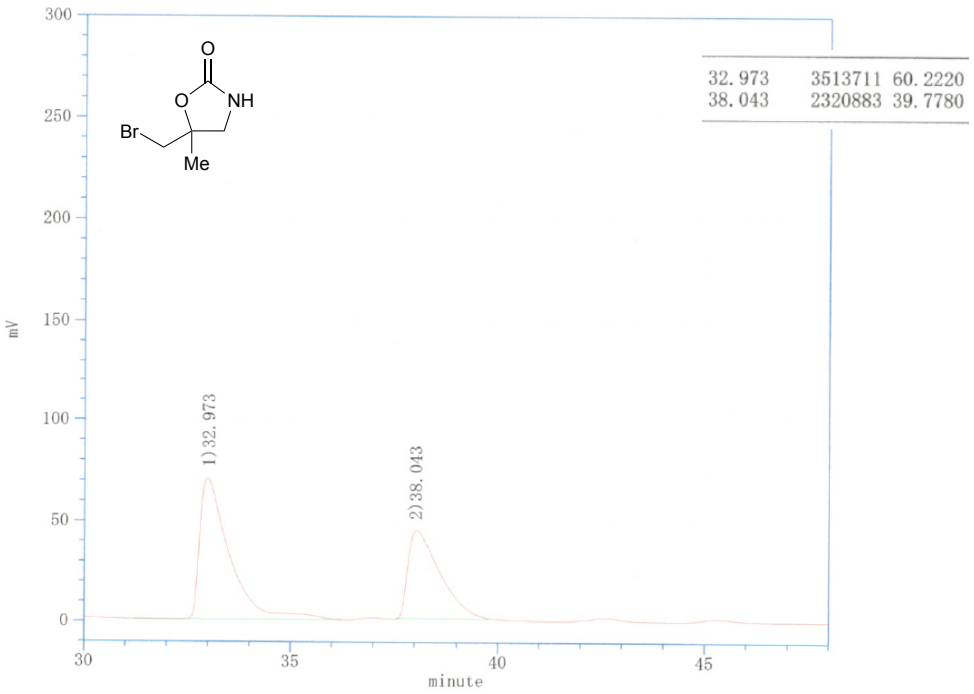


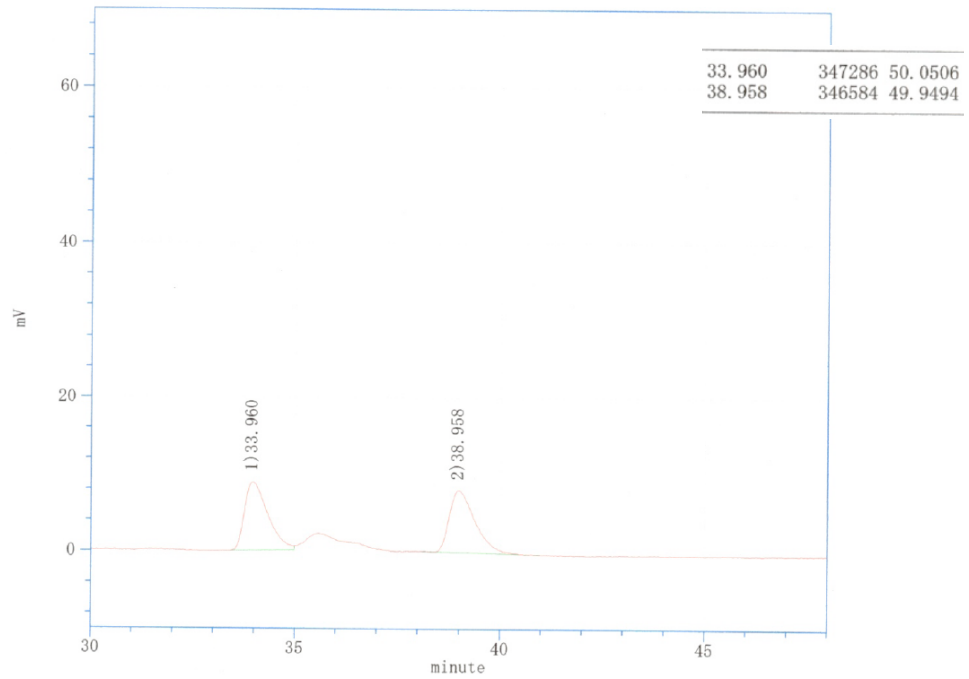
4h: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



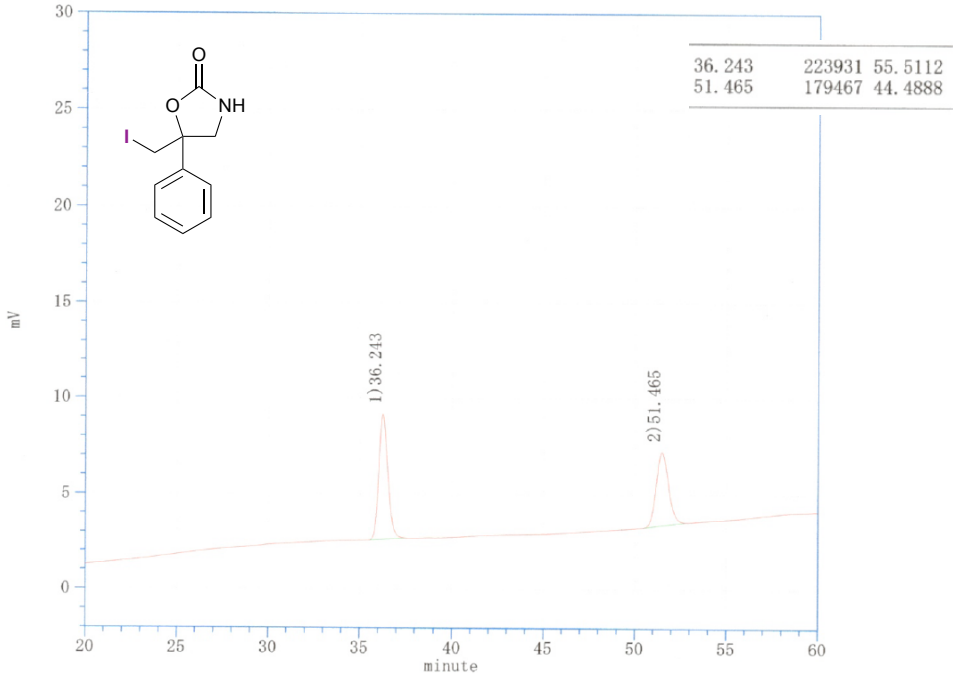


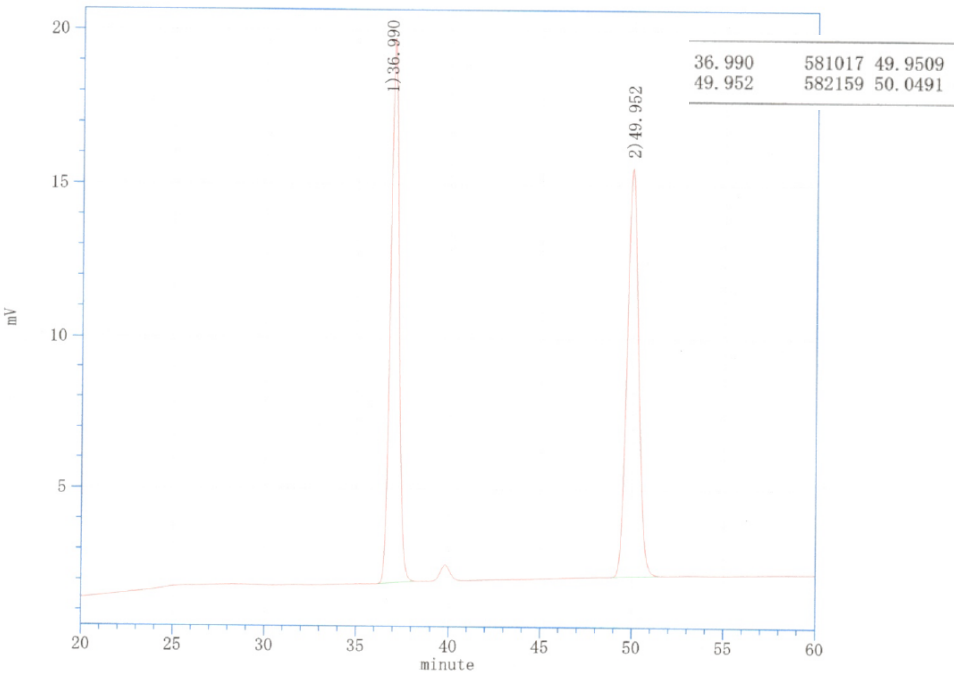
4i: Daicel Chiralpak IF-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 220 nm



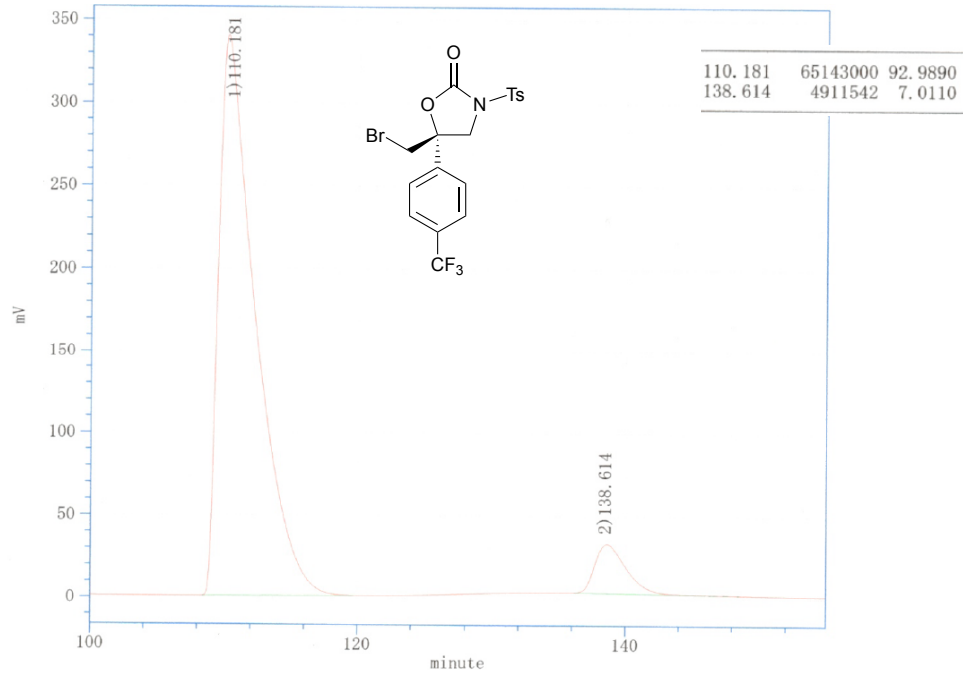


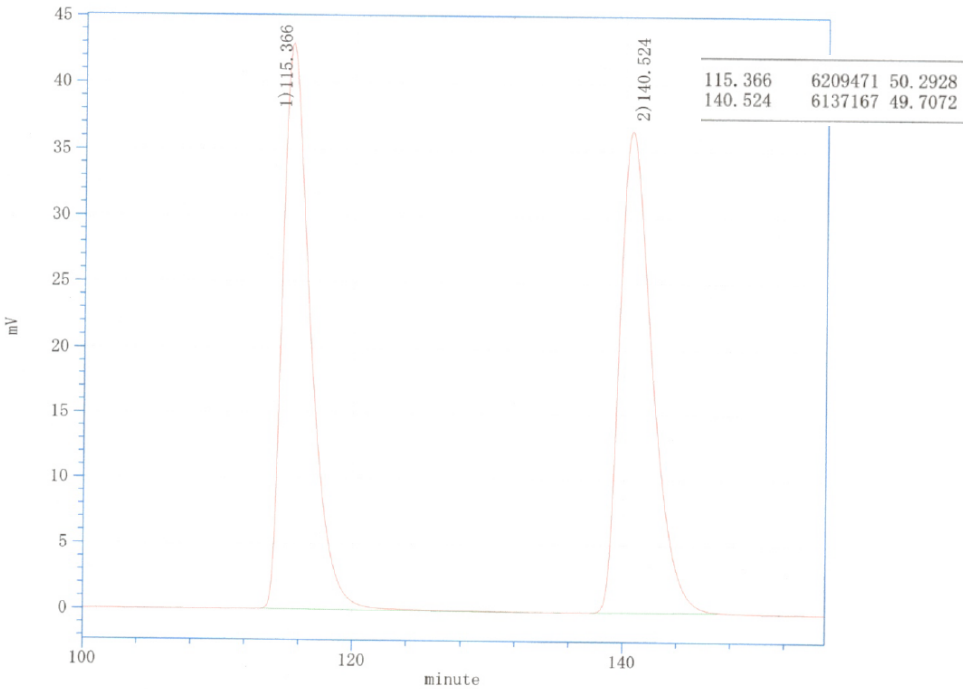
6: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



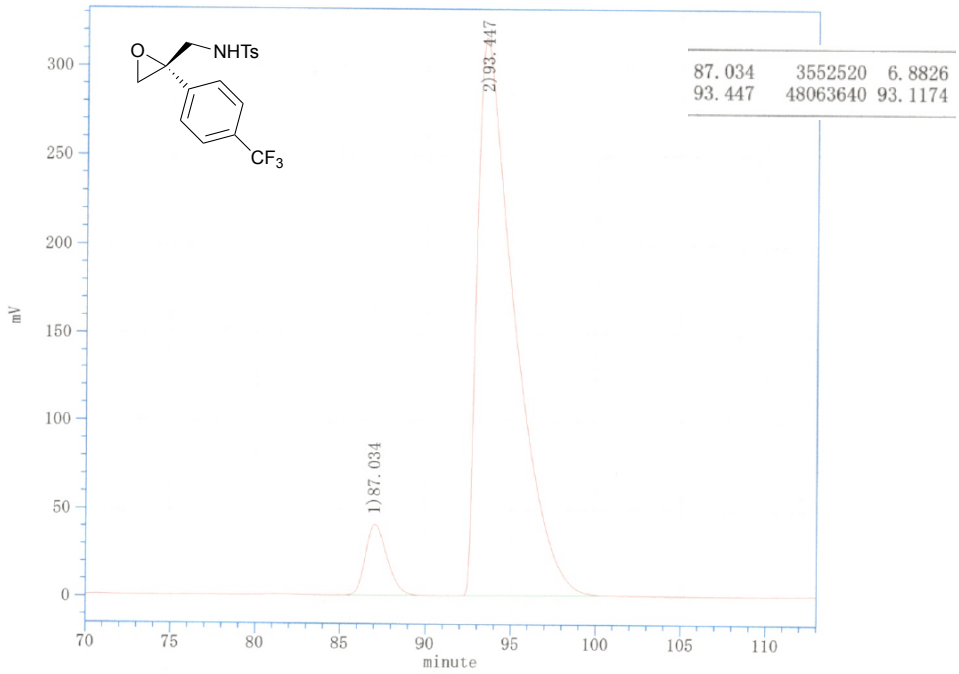


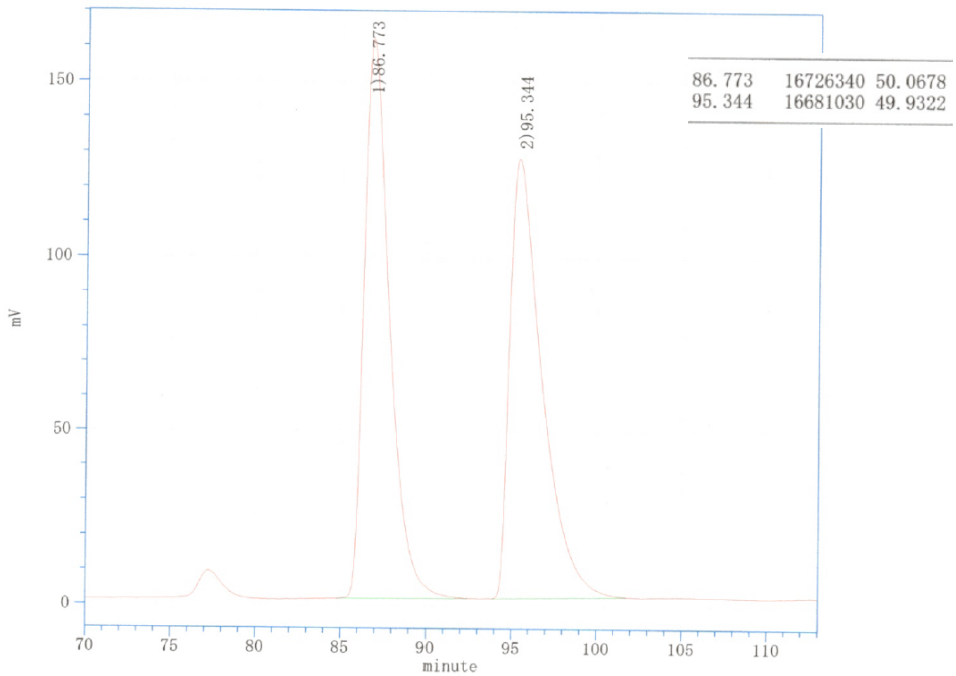
8: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm



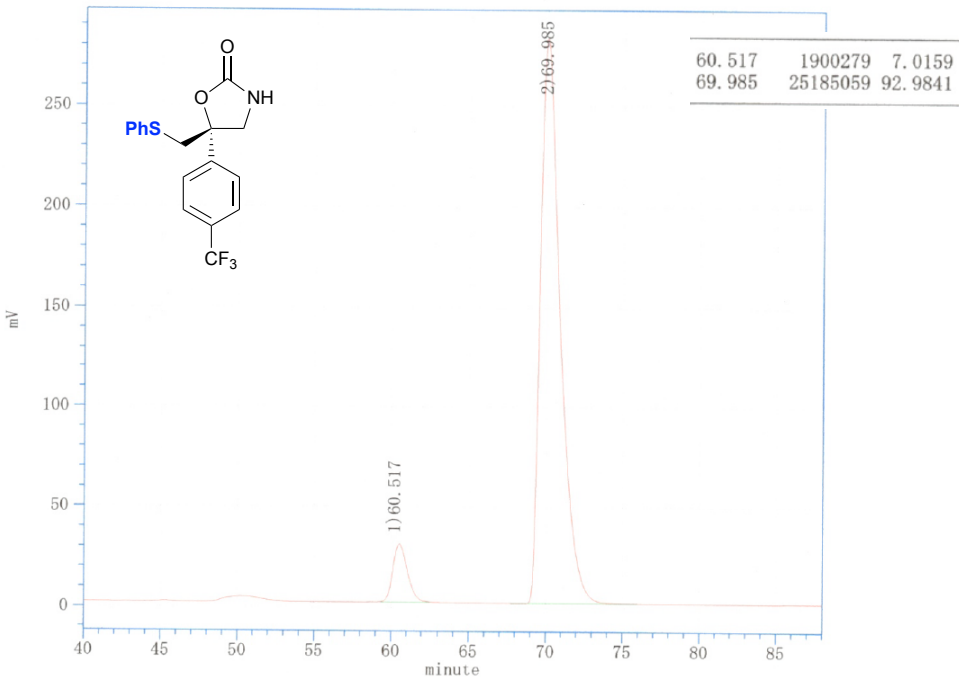


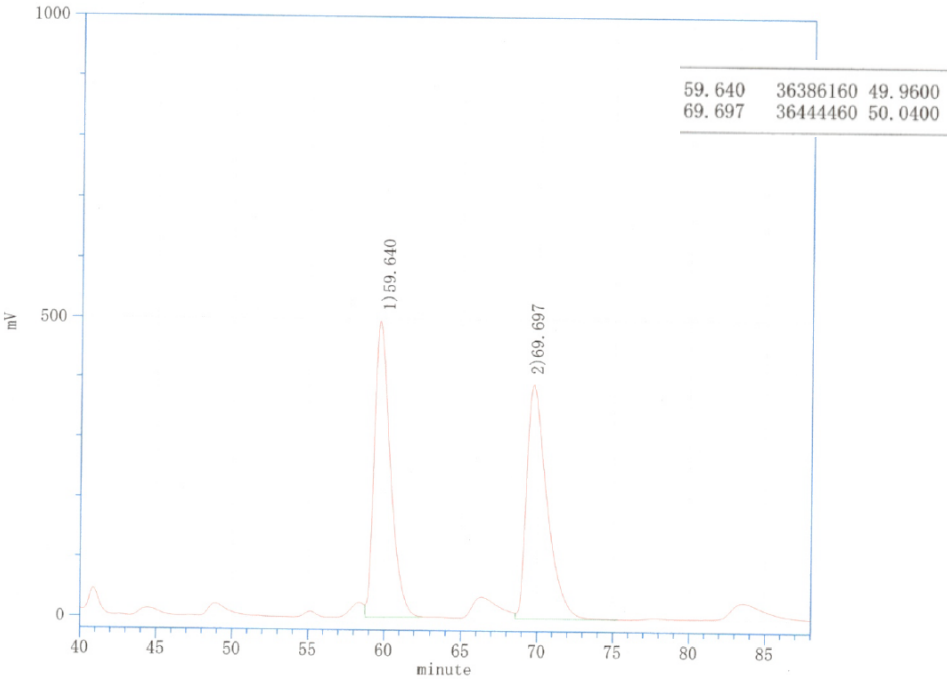
9: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm





10: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm





11: Daicel Chiralpak IF-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 214 nm