

Supporting Information

Catalytic enantioselective [3+2] and [4+2]-annulation of cyclic *N*-sulfonyl ketimines with γ - or δ -hydroxy- α,β -unsaturated ketones

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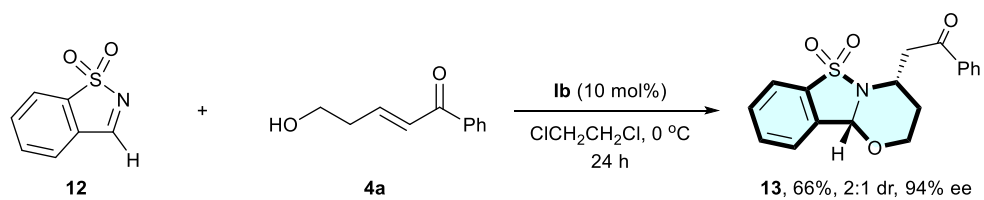
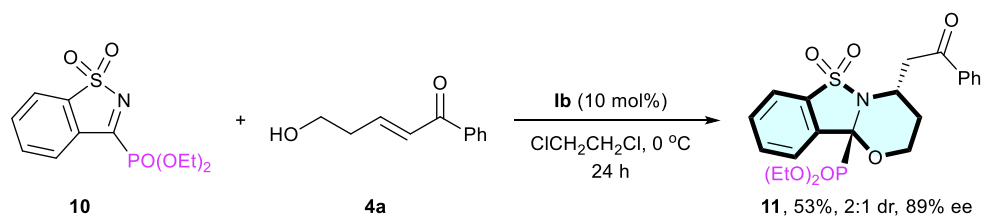
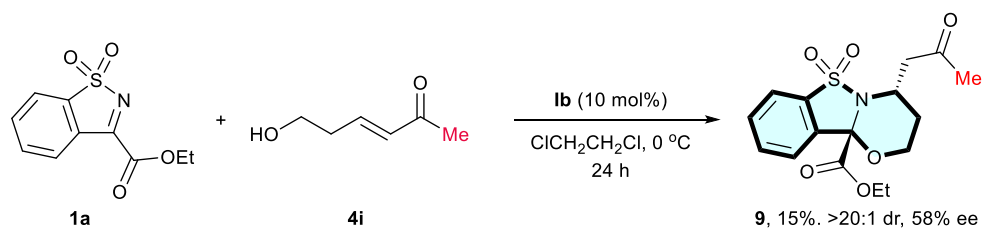
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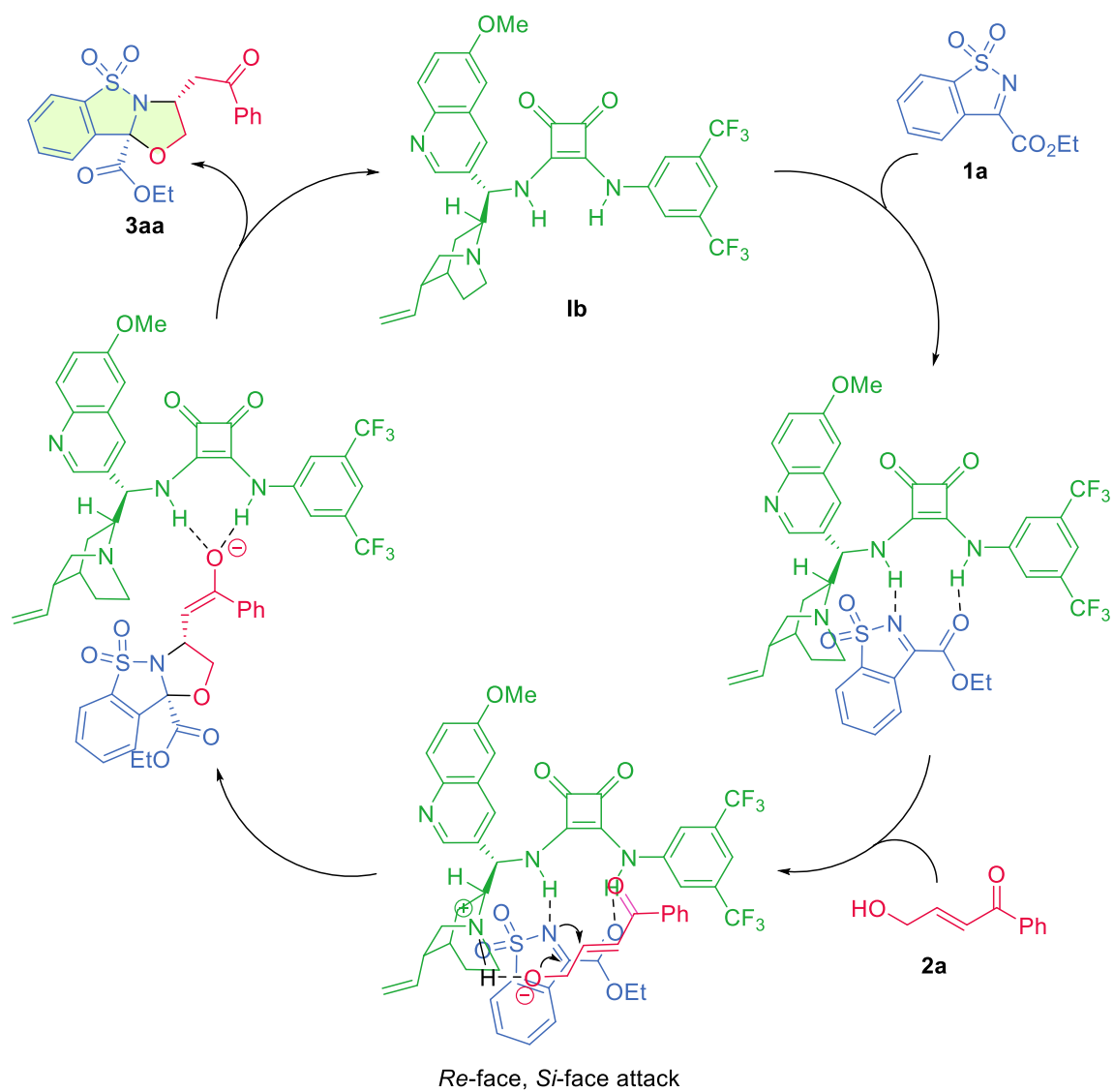
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1. General information. Organic solvents were distilled prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Developed chromatograms were visualized by fluorescence quenching and with anisaldehyde stain. ^1H , ^{13}C and ^{19}F NMR spectra were recorded (400 MHz for ^1H , 101 MHz for ^{13}C and 400 MHz for ^{19}F), and were internally referenced to residual protic solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on an FT IR spectrometer and are reported in wave numbers. Optical rotations were taken on a digital polarimeter. High-resolution mass spectra (HRMS) were measured on a double focusing mass spectrometer with EI-magnetic sector. The crystal structure was determined by single-crystal diffractometer (a Bruker D8 Venture PHOTON III M14 diffractometer) at the Western Seoul Center of Korea Basic Science Institute. Enantiomeric excesses were determined using an HPLC instrument with Chiralpak columns as noted. γ - or δ -Hydroxy- α,β -unsaturated ketones,¹ cyclic *N*-sulfonyl ketamine,² and organocatalysts³ were prepared according to literature.

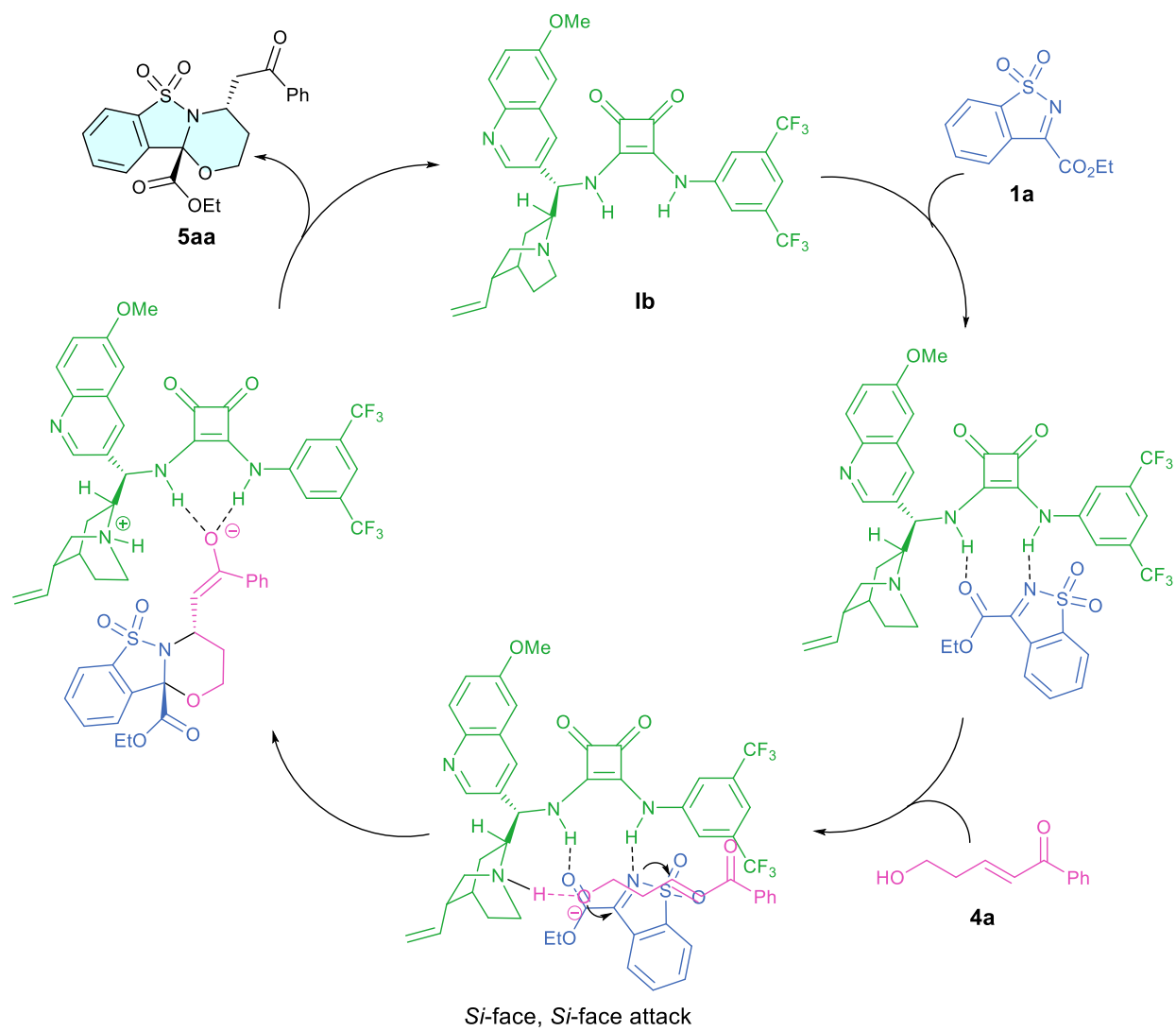
2. Control experiment



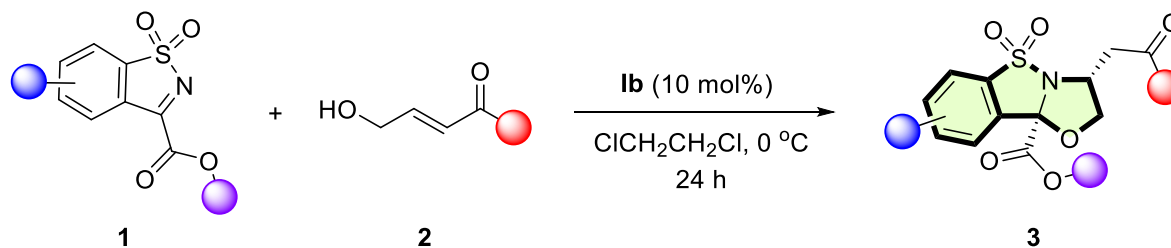
3. Proposed mechanism for asymmetric [3+2]-annulation



4. Proposed mechanism for asymmetric [4+2]-annulation

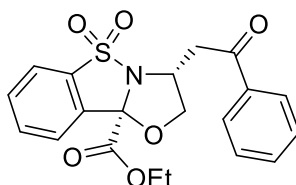


5. General procedure I for asymmetric [3+2]-annulation of γ -hydroxy- α,β -unsaturated ketones with cyclic *N*-sulfonyl ketimines.



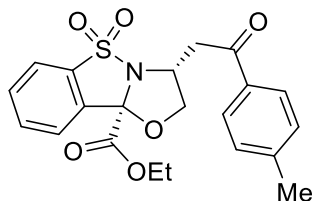
A solution of cyclic *N*-sulfonyl ketimine **1** (0.15 mmol, 1.5 equiv) and catalyst **Ib** (0.01 mmol, 0.1 equiv) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1.0 mL, 0.1 M) was stirred for 10 min at 0 °C and then added γ -hydroxy- α,β -unsaturated ketone **2** (0.10 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 24 h. Then, the resulting mixture was concentrated in vacuo and was purified by flash column chromatography with EtOAc/ CH_2Cl_2 /hexanes as eluent to afford desired product **3**. The enantiomeric excess was determined using HPLC analysis.

Ethyl (3*R*,9*bR*)-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3aa)



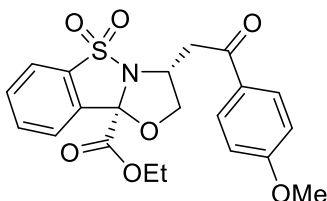
Synthesized by the general procedure I; 40 mg, yield 98%, 14:1 dr, $[\alpha]_D^{26} = -71.5$ ($c = 0.98$, CHCl_3); 96% ee; White solid; m.p. 133-135 °C; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.02–7.95 (m, 2H), 7.83–7.77 (m, 1H), 7.75–7.65 (m, 3H), 7.63–7.57 (m, 1H), 7.49 (tt, $J = 6.5, 1.3$ Hz, 2H), 4.84 (td, $J = 10.3, 6.1$ Hz, 1H), 4.55 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.17 (dd, $J = 9.0, 5.9$ Hz, 1H), 3.80 (dd, $J = 18.1, 4.4$ Hz, 1H), 3.43 (dd, $J = 18.1, 9.7$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.1, 167.5, 136.0, 135.9, 134.2, 133.8, 133.6, 132.0, 128.7, 128.0, 125.2, 121.4, 97.3, 74.4, 63.0, 56.6, 43.2, 13.9; IR (neat) 2950, 2916, 2864, 1737, 1676, 1597, 1450, 1361, 1257, 1170 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{19}\text{NO}_6\text{S}$: 401.0933 Found: 401.0946; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 52.8$ min and *minor*-isomer $t_r = 65.9$ min.

Ethyl (3*R*,9*bR*)-3-(2-oxo-2-(*p*-tolyl)ethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ab)



Synthesized by the general procedure I; 35 mg, yield 84%, 16:1 dr, $[\alpha]_D^{25} = -79.4$ ($c = 0.92$, CHCl_3); 97% ee; Yellow solid; m.p. 142-143 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, $J = 8.3$ Hz, 2H), 7.82–7.77 (m, 1H), 7.74–7.63 (m, 3H), 7.30–7.25 (m, 2H), 4.82 (dtd, $J = 10.3$, 6.1, 4.3 Hz, 1H), 4.56 (dd, $J = 8.9$, 6.4 Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.16 (dd, $J = 8.9$, 6.0 Hz, 1H), 3.77 (dd, $J = 18.0$, 4.3 Hz, 1H), 3.40 (dd, $J = 18.0$, 9.8 Hz, 1H), 2.42 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 196.7, 167.5, 144.6, 135.9, 134.3, 133.82, 133.6, 131.9, 129.4, 128.2, 125.2, 121.4, 97.3, 74.5, 62.9, 56.7, 43.1, 21.7, 13.9; IR (neat) 2940, 2909, 2845, 1751, 1671, 1473, 1419, 1325, 1254, 1175 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₁H₂₁NO₆S: 415.1090 Found: 415.1089; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 44.8$ min and *minor*-isomer $t_r = 54.3$ min.

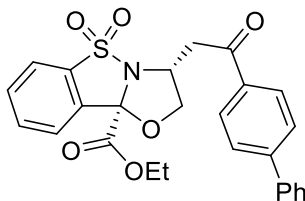
Ethyl (3*R*,9*bR*)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ac)



Synthesized by the general procedure I; 38 mg, yield 92%, 10:1 dr, $[\alpha]_D^{26} = -82.9$ ($c = 0.98$, CHCl_3); 97% ee; Yellow solid; m.p. 170-172 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, $J = 8.9$ Hz, 2H), 7.82–7.77 (m, 1H), 7.74–7.65 (m, 3H), 6.98–6.92 (m, 2H), 4.81 (dtd, $J = 10.3$, 6.2, 4.3 Hz, 1H), 4.56 (dd, $J = 8.9$, 6.4 Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.17 (dd, $J = 9.0$, 6.0 Hz, 1H), 3.88 (s, 3H), 3.75 (dd, $J = 17.8$, 4.3 Hz, 1H), 3.37 (dd, $J = 17.8$, 9.9 Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.5, 167.5, 163.9, 135.9, 134.3, 133.8, 131.9, 130.4, 129.2, 125.2, 121.4, 113.8, 97.3, 74.6, 62.9, 56.8, 55.5, 42.9, 13.9; IR (neat) 2940, 2926, 2845, 1758, 1678, 1602, 1576,

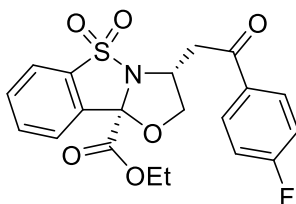
1423, 1326, 1259 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{21}\text{NO}_7\text{S}$: 431.1039 Found: 431.1039; Chiralpak IC column and IC guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 37.5$ min and *major*-isomer $t_r = 80.4$ min.

Ethyl (3*R*,9*bR*)-3-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ad)



Synthesized by the general procedure I; 41 mg, yield 85%, 11:1 dr, $[\alpha]_D^{25} = -70.8$ ($c = 1.02$, CHCl_3); 97% ee; Yellow solid; m.p. 133-135 $^\circ\text{C}$; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.5$ Hz, 2H), 7.75–7.70 (m, 1H), 7.67–7.58 (m, 5H), 7.56 (d, $J = 6.9$ Hz, 2H), 7.40 (t, $J = 7.3$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 1H), 4.78 (dt, $J = 10.5, 5.2$ Hz, 1H), 4.49 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 4.11 (dd, $J = 8.9, 5.9$ Hz, 1H), 3.76 (dd, $J = 18.0, 4.3$ Hz, 1H), 3.38 (dd, $J = 18.0, 9.7$ Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.7, 167.5146.3 139.6, 135.9, 134.7 134.2, 133.8, 132.0, 128.9, 128.6, 128.3, 127.3, 127.2, 125.2, 121.4, 97.3, 74.5, 63.0, 56.7, 43.2, 13.9; IR (neat) 3070, 2984, 2907, 1746, 1684, 1572, 1422, 1324, 1239, 1176 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{23}\text{NO}_6\text{S}$: 477.1246 Found: 477.1246; Chiralpak IC column and IC guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 30.5$ min and *major*-isomer $t_r = 76.8$ min.

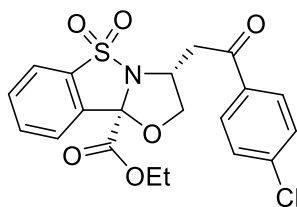
Ethyl (3*R*,9*bR*)-3-(2-(4-fluorophenyl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ae)



Synthesized by the general procedure I; 36 mg, yield 86%, 12:1 dr, $[\alpha]_D^{26} = -65.4$ ($c = 1.01$, CHCl_3); 97% ee; Yellow solid; m.p. 132-134 $^\circ\text{C}$; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.04–7.98 (m, 2H), 7.82–7.77 (m, 1H), 7.75–7.65 (m, 3H), 7.20–7.11 (m, 2H), 4.87–4.78 (m,

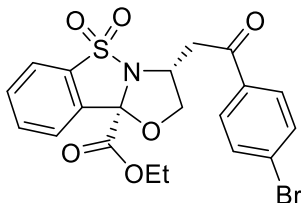
1H), 4.53 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.17 (dd, $J = 9.0, 5.8$ Hz, 1H), 3.77 (dd, $J = 18.1, 4.5$ Hz, 1H), 3.40 (dd, $J = 18.0, 9.5$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 167.4, 166.0 (d, $J^1 = 256.1$ Hz), 135.9, 134.2, 133.8, 132.5 (d, $J^4 = 2.8$ Hz), 132.0, 130.7 (d, $J^3 = 9.4$ Hz), 125.2, 121.4, 115.9 (d, $J^2 = 21.9$ Hz), 97.3, 74.3, 63.0, 56.6, 43.1, 13.9; ^{19}F NMR (376 MHz, CDCl_3) δ -104.03; IR (neat) 2925, 2874, 2851, 1739, 1686, 1594, 1504, 1447, 1324, 1211 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{20}\text{H}_{18}\text{FNO}_6\text{S}$: 419.0839 Found: 419.0859; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 52.1$ min and *minor*-isomer $t_r = 64.1$ min.

Ethyl (3*R*,9*bR*)-3-(2-(4-chlorophenyl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3af)



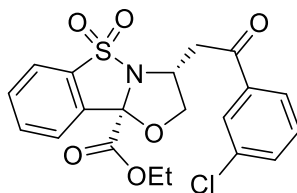
Synthesized by the general procedure I; 35 mg, yield 80%, 12:1 dr, $[\alpha]_D^{25} = -65.0$ ($c = 0.96$, CHCl_3); 97% ee; White solid; m.p. 140-141 $^\circ\text{C}$; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.83–7.76 (m, 1H), 7.76–7.63 (m, 3H), 7.46 (d, $J = 8.5$ Hz, 2H), 4.82 (dq, $J = 10.4, 5.9$ Hz, 1H), 4.52 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.16 (dd, $J = 8.9, 5.8$ Hz, 1H), 3.76 (dd, $J = 18.1, 4.6$ Hz, 1H), 3.39 (dd, $J = 18.1, 9.5$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.9, 167.4, 140.2, 135.9, 134.4, 134.2, 133.9, 132.0, 129.5, 129.1, 125.2, 121.4, 97.4, 74.3, 63.0, 56.5, 43.1, 13.9; IR (neat) 3014, 2983, 2907, 1747, 1684, 1572, 1473, 1423, 1324, 1245 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{20}\text{H}_{18}\text{ClNO}_6\text{S}$: 435.0543 Found: 435.0570; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 38.8$ min and *major*-isomer $t_r = 47.1$ min.

Ethyl (3*R*,9*bR*)-3-(2-(4-bromophenyl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ag)



Synthesized by the general procedure I; 39 mg, yield 81%, 12:1 dr, $[\alpha]_D^{24} = -67.7$ ($c = 0.61$, CHCl_3); 97% ee; Yellow solid; m.p. 153-154 °C; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.86–7.81 (m, 2H), 7.81–7.77 (m, 1H), 7.73–7.65 (m, 3H), 7.65–7.60 (m, 2H), 4.82 (dtd, $J = 9.5, 6.0, 4.5$ Hz, 1H), 4.52 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.16 (dd, $J = 8.9, 5.8$ Hz, 1H), 3.75 (dd, $J = 18.1, 4.6$ Hz, 1H), 3.39 (dd, $J = 18.1, 9.4$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.1, 167.4, 135.9, 134.7, 134.1, 133.8, 132.03, 131.97, 129.5, 128.9, 125.2, 121.3, 97.3, 74.3, 63.0, 56.5, 43.1, 13.9; IR (neat) 2951, 2892, 2851, 1746, 1682, 1583, 1448, 1399, 1317, 1260 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{18}\text{BrNO}_6\text{S}$: 479.0038 Found: 479.0015; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 42.3$ min and *major*-isomer $t_r = 53.3$ min.

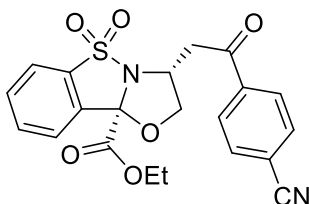
Ethyl (3R,9bR)-3-(2-(3-chlorophenyl)-2-oxoethyl)-2,3-dihydro-9bH-benzo[4,5]isothiazolo[3,2-b]oxazole-9b-carboxylate 5,5-dioxide (3ah)



Synthesized by the general procedure I; 37 mg, yield 85%, 12:1 dr, $[\alpha]_D^{26} = -59.3$ ($c = 0.89$, CHCl_3); 97% ee; Yellow gum; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.95 (t, $J = 1.9$ Hz, 1H), 7.85 (ddd, $J = 7.8, 1.7, 1.1$ Hz, 1H), 7.82–7.77 (m, 1H), 7.75–7.66 (m, 3H), 7.57 (ddd, $J = 8.0, 2.1, 1.0$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 4.88–4.79 (m, 1H), 4.52 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.16 (dd, $J = 8.9, 5.8$ Hz, 1H), 3.77 (dd, $J = 18.2, 4.6$ Hz, 1H), 3.40 (dd, $J = 18.2, 9.4$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.8, 167.4, 137.5, 135.9, 135.1, 134.2, 133.9, 133.6, 131.0, 130.1, 128.2, 126.2, 125.2, 121.4, 97.4, 74.2, 63.0, 56.4, 43.2, 13.9; IR (neat) 2985, 2928, 2892, 1746, 1684, 1571, 1423, 1325, 1237, 1115 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{18}\text{ClNO}_6\text{S}$: 435.0543

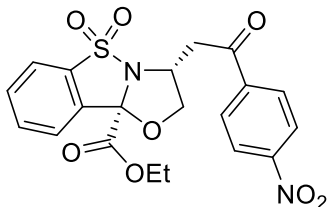
Found: 435.0531; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 53.1$ min and *minor*-isomer $t_r = 64.6$ min.

Ethyl (3*R*,9*bR*)-3-(2-(4-cyanophenyl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ai)



Synthesized by the general procedure I; 35 mg, yield 83%, >20:1 dr, $[\alpha]_D^{25} = -57.1$ ($c = 0.87$, CHCl_3); 94% ee; White solid; m.p. 178-180 °C; R_f 0.4 (EtOAc:CH₂Cl₂:Hexane=3:10:7); ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, $J = 8.5$ Hz, 2H), 7.81 (dd, $J = 9.0, 2.4$ Hz, 3H), 7.76–7.64 (m, 3H), 4.85 (dq, $J = 10.5, 5.4$ Hz, 1H), 4.49 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.17 (dd, $J = 9.0, 5.6$ Hz, 1H), 3.81 (dd, $J = 18.3, 4.9$ Hz, 1H), 3.43 (dd, $J = 18.2, 9.0$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.9 167.3, 138.8, 135.8, 134.0, 133.9, 132.6 132.0, 128.5 125.2, 121.3, 117.7, 116.8, 97.4, 74.0, 63.0, 56.3 43.3 13.9; IR (neat) 3071, 2984, 2909, 2361, 1747, 1684, 1571, 1472, 1422, 1324, 1235 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₁H₁₈N₂O₆S: 426.0886 Found: 426.0856; Chiralpak IA column and IA guard column (40% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 33.4$ min and *major*-isomer $t_r = 51.5$ min.

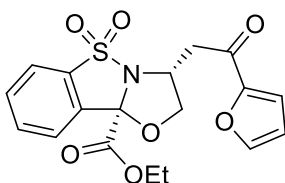
Ethyl (3*R*,9*bR*)-3-(2-(4-nitrophenyl)-2-oxoethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3aj)



Synthesized by the general procedure I; 34 mg, yield 77%, >20:1 dr, $[\alpha]_D^{25} = -55.4$ ($c = 1.00$, CHCl_3); 92% ee; White solid; m.p. 146-148 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=3:10:7); ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, $J = 8.9$ Hz, 2H), 8.07 (d, $J = 8.8$ Hz, 2H), 7.72 (dd, $J = 6.1, 1.5$ Hz, 1H), 7.69–7.56 (m, 3H), 4.84–4.73 (m, 1H), 4.42 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 4.10 (dd, $J = 9.0,$

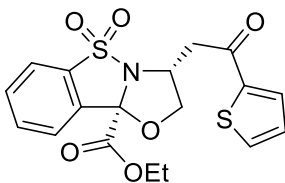
5.6 Hz, 1H), 3.77 (dd, $J = 18.3, 5.0$ Hz, 1H), 3.39 (dd, $J = 18.3, 8.9$ Hz, 1H), 1.17 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ ^{13}C NMR (100 MHz, CDCl_3) δ 195.7, 167.3, 150.6, 140.3, 135.8, 134.0, 133.9, 132.0, 129.2, 125.6, 123.9, 121.4, 97.4, 74.0, 63.1, 56.3, 43.5, 13.9; IR (neat) 3071, 2983, 2906, 1745, 1686, 1572, 1531, 1422, 1322, 1240 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_8\text{S}$: 446.0784 Found: 446.0764; Chiralpak IA column and IA guard column (50% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 32.2$ min and *major*-isomer $t_r = 38.4$ min.

Ethyl (3*R*,9*bR*)-3-(2-(furan-2-yl)-2-oxoethyl)-5-methylene-2,3-dihydro-5 λ^4 -benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*(5*H*)-carboxylate 5-oxide (3ak)



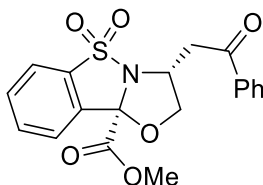
Synthesized by the general procedure I; 32 mg, yield 94%, >20:1 dr, $[\alpha]_D^{25} = -66.7$ ($c = 1.29$, CHCl_3); 92% ee; Yellow solid; m.p. 153-155 $^{\circ}\text{C}$; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:10:4); ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.76 (m, 1H), 7.75–7.65 (m, 3H), 7.62 (dd, $J = 1.8, 0.8$ Hz, 1H), 7.29–7.25 (m, 1H), 6.57 (dd, $J = 3.6, 1.7$ Hz, 1H), 4.78 (dtd, $J = 9.5, 6.0, 4.6$ Hz, 1H), 4.47 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.28 (qd, $J = 7.1, 1.4$ Hz, 2H), 4.19 (dd, $J = 9.0, 5.8$ Hz, 1H), 3.63 (dd, $J = 17.7, 4.6$ Hz, 1H), 3.29 (dd, $J = 17.7, 9.6$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ ^{13}C NMR (100 MHz, CDCl_3) δ 185.8, 167.4, 152.0, 146.8, 135.8, 134.1, 133.8, 132.0, 125.2, 121.3, 117.8, 112.4, 97.3, 74.2, 63.0, 56.2, 42.6, 13.8; IR (neat) 2985, 2939, 2892, 1745, 1684, 1571, 1471, 1422, 1322, 1240 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{17}\text{NO}_7\text{S}$: 498.0919 Found: 391.0701; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 36.8$ min and *minor*-isomer $t_r = 46.3$ min.

Ethyl (3*R*,9*bR*)-5-methylene-3-(2-oxo-2-(thiophen-2-yl)ethyl)-2,3-dihydro-5 λ^4 -benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*(5*H*)-carboxylate 5-oxide (3al)



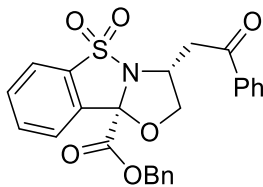
Synthesized by the general procedure I; 35 mg, yield 86%, >20:1 dr, $[\alpha]_D^{26} = -57.1$ ($c = 1.07$, CHCl_3); 95% ee; Yellow solid; m.p. 129-131 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.68 (m, 2H), 7.69–7.56 (m, 4H), 7.09 (dd, $J = 4.9, 3.8$ Hz, 1H), 4.72 (dtd, $J = 10.4, 6.1, 4.4$ Hz, 1H), 4.43 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 4.13 (dd, $J = 9.0, 5.9$ Hz, 1H), 3.65 (dd, $J = 17.5, 4.4$ Hz, 1H), 3.30 (dd, $J = 17.5, 9.8$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 189.8, 167.4, 143.2, 135.8, 134.4, 134.2, 133.9, 132.7, 132.0, 128.3, 125.2, 121.3, 97.3, 74.3, 63.0, 56.5, 43.5, 13.9; IR (neat) 2984, 2939, 2908, 1744, 1685, 1572, 1472, 1219, 1323, 1239 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₁₈H₁₇NO₆S₂: 407.0497 Found: 407.0490; Chiralpak IC column and IC guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 46.2$ min and *major*-isomer $t_r = 60.2$ min.

Methyl (3*R*,9*bR*)-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3*ba*)



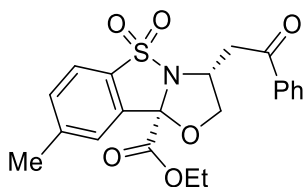
Synthesized by the general procedure I; 36 mg, yield 94%, >20:1 dr, $[\alpha]_D^{26} = -85.7$ ($c = 0.98$, CHCl_3); 95% ee; White solid; m.p. 137-139 °C; R_f 0.4 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.82–7.78 (m, 1H), 7.75–7.64 (m, 3H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 2H), 4.83 (dtd, $J = 10.4, 6.1, 4.4$ Hz, 1H), 4.57 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.17 (dd, $J = 9.0, 6.0$ Hz, 1H), 3.87–3.74 (m, 4H), 3.43 (dd, $J = 18.1, 9.7$ Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.0, 168.0, 135.9, 135.8, 134.1, 133.9, 133.7, 132.0, 128.7, 128.0, 125.2, 121.4, 97.2, 74.4, 56.7, 53.7, 43.1; IR (neat) 3070, 2983, 2902, 1748, 1682, 1595, 1450, 1326, 1266, 1215 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₁₉H₁₇NO₆S: 387.0777 Found: 387.0794; Chiralpak IC column and IC guard column (7% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 67.1$ min and *major*-isomer $t_r = 128.8$ min.

Benzyl (3*R*,9*bR*)-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3*ca*)



Synthesized by the general procedure I; 45 mg, yield 97%, 14:1 dr, $[\alpha]_D^{26} = -34.1$ ($c = 0.99$, CHCl_3); 94% ee; White solid; m.p. 112-114 °C; R_f 0.4 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ^1H NMR (400 MHz, CDCl₃) δ 7.86–7.77 (m, 3H), 7.68 (dd, $J = 5.7, 3.2$ Hz, 2H), 7.64–7.54 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.31 (s, 5H), 5.24 (d, $J = 2.4$ Hz, 2H), 4.85 (td, $J = 9.9, 6.0$ Hz, 1H), 4.52 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.11 (dd, $J = 9.0, 5.7$ Hz, 1H), 3.63 (dd, $J = 18.3, 4.3$ Hz, 1H), 3.27 (dd, $J = 18.3, 9.8$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) δ 197.0, 167.3, 135.8, 134.6, 133.9, 133.8, 133.6, 132.0, 128.63 (two peaks overlapping), 128.58, 128.5, 128.1, 128.0, 125.2, 121.4, 97.3, 74.6, 68.3, 56.3, 43.2; IR (neat) 3070, 2984, 2902, 1749, 1682, 1594, 1474, 1325, 1215, 1176 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₅H₂₁NO₆S: 463.1090 Found: 463.1081; Chiralpak IC column and IC guard column (7% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 56.4$ min and *major*-isomer $t_r = 104.8$ min.

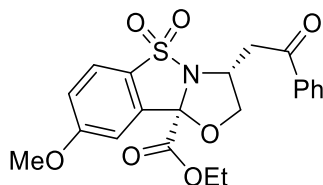
Ethyl (3R,9bR)-8-methyl-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9bH-benzo[4,5]isothiazolo[3,2-b]oxazole-9b-carboxylate 5,5-dioxide (3da)



Synthesized by the general procedure I; 37 mg, yield 90%, 11:1 dr, $[\alpha]_D^{26} = -65.3$ ($c = 1.01$, CHCl_3); 97% ee; White solid; m.p. 144-146 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ^1H NMR (400 MHz, CDCl₃) δ 7.97 (d, $J = 7.8$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 3H), 7.44 (s, 1H), 4.82 (td, $J = 10.2, 6.1$ Hz, 1H), 4.55 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.29 (qq, $J = 7.5, 3.6$ Hz, 2H), 4.15 (dd, $J = 8.9, 5.9$ Hz, 1H), 3.79 (dd, $J = 18.1, 4.3$ Hz, 1H), 3.41 (dd, $J = 18.1, 9.8$ Hz, 1H), 2.49 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) δ 197.1, 167.6, 145.2, 136.0, 134.5, 133.6, 133.2, 132.9, 128.7, 128.0, 125.2, 121.1, 97.2, 74.4, 62.9, 56.6, 43.2, 21.8, 13.9; IR (neat) 2985, 2927, 2901, 1747, 1653, 1574, 1473, 1419, 1326, 1247 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₁H₂₁NO₆S: 415.1090 Found: 415.1119; Chiralpak OJ-H column and OJ-H guard column (20%

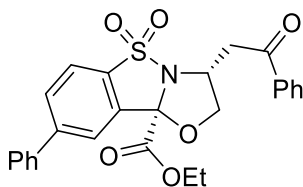
EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 49.4$ min and *minor*-isomer $t_r = 53.1$ min.

Ethyl (3*R*,9*bR*)-8-methoxy-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ea)



Synthesized by the general procedure I; 41 mg, yield 95%, 11:1 dr, $[\alpha]_D^{25} = -43.5$ ($c = 1.01$, CHCl_3); 96% ee; Yellow solid; m.p. 132-134 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.93 (m, 2H), 7.69 (d, $J = 8.7$ Hz, 1H), 7.64–7.57 (m, 1H), 7.49 (dd, $J = 8.2$, 7.1 Hz, 2H), 7.17 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.06 (d, $J = 2.3$ Hz, 1H), 4.83 (dtd, $J = 10.1$, 6.1, 4.2 Hz, 1H), 4.56 (dd, $J = 8.9$, 6.4 Hz, 1H), 4.29 (qq, $J = 7.0$, 3.6 Hz, 2H), 4.15 (dd, $J = 8.9$, 5.9 Hz, 1H), 3.89 (s, 3H), 3.79 (dd, $J = 18.1$, 4.2 Hz, 1H), 3.41 (dd, $J = 18.1$, 9.9 Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.1, 167.5, 164.0, 136.8, 136.0, 133.6, 128.7, 128.0, 127.8, 122.8, 119.3, 108.3, 96.8, 74.3, 62.9, 56.6, 56.0, 43.1, 13.9; IR (neat) 3071, 2984, 2908, 1746, 1685, 1572, 1422, 1324, 1241, 1115 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₁H₂₁NO₇S: 431.1039 Found: 431.1013; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 58.6$ min and *minor*-isomer $t_r = 72.7$ min.

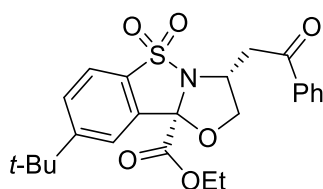
Ethyl (3*R*,9*bR*)-3-(2-oxo-2-phenylethyl)-8-phenyl-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3fa)



Synthesized by the general procedure I; 41 mg, yield 90%, 10:1 dr, $[\alpha]_D^{26} = -41.6$ ($c = 1.00$, CHCl_3); 96% ee; White solid; m.p. 180-182 °C; R_f 0.4 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.94 (m, 2H), 7.92–7.80 (m, 3H), 7.60 (d, $J = 7.2$ Hz, 3H), 7.55–7.41 (m, 5H), 4.87 (td, $J = 10.3$, 6.1 Hz, 1H), 4.59 (dd, $J = 8.9$, 6.4 Hz, 1H), 4.30 (qq, $J = 7.1$, 3.7 Hz, 2H), 4.19 (dd, $J = 9.0$,

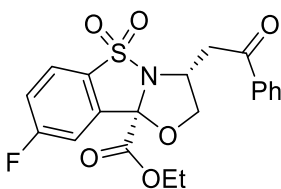
5.9 Hz, 1H), 3.82 (dd, $J = 18.1, 4.3$ Hz, 1H), 3.44 (dd, $J = 18.1, 9.7$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.1, 167.5, 147.4, 138.6, 136.0, 135.1, 134.4, 133.7, 131.0, 129.2, 128.9, 128.7, 128.0, 127.4, 123.5, 121.7, 97.3, 74.5, 63.0, 56.7, 43.2, 14.0; IR (neat) 2986, 2928, 2901, 1746, 1684, 1576, 1507, 1395, 1321, 1251, 1178 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{26}\text{H}_{23}\text{NO}_6\text{S}$: 477.1246 Found: 477.1235; Chiralpak IA column and IA guard column (30% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 26.2$ min and *minor*-isomer $t_r = 61.9$ min.

Ethyl (3*R*,9*bR*)-8-(*tert*-butyl)-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ga)



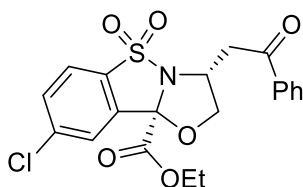
Synthesized by the general procedure I; 41 mg, yield 90%, 13:1 dr, $[\alpha]_D^{26} = -49.2$ ($c = 0.97$, CHCl_3); 96% ee; White solid; m.p. 146-148 $^{\circ}\text{C}$; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 7.0$ Hz, 2H), 7.72 (s, 2H), 7.65 (s, 1H), 7.63–7.57 (m, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 4.83 (td, $J = 10.4, 6.3$ Hz, 1H), 4.61 (dd, $J = 8.9, 6.4$ Hz, 1H), 4.30 (qd, $J = 7.1, 3.0$ Hz, 2H), 4.16 (dd, $J = 8.9, 6.1$ Hz, 1H), 3.81 (dd, $J = 18.1, 4.2$ Hz, 1H), 3.43 (dd, $J = 18.1, 9.8$ Hz, 1H), 1.36 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.1, 167.6, 158.4, 136.0, 134.2, 133.6, 133.0, 129.6, 128.7, 128.0, 121.7, 121.0, 97.4, 74.6, 62.8, 56.4, 43.3, 35.6, 31.0, 13.9; IR (neat) 2972, 2926, 2901, 1746, 1683, 1574, 1472, 1418, 1324, 1258 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{24}\text{H}_{27}\text{NO}_6\text{S}$: 457.1559 Found: 457.1546; Chiralpak IC column and IC guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 18.2$ min and *major*-isomer $t_r = 50.0$ min.

Ethyl (3*R*,9*bR*)-8-fluoro-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ha)



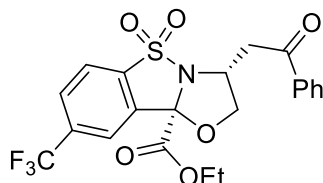
Synthesized by the general procedure I; 37 mg, yield 88%, 10:1 dr, $[\alpha]_D^{25} = -64.3$ ($c = 0.99$, CHCl_3); 94% ee; Pale yellow gum; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.01–7.95 (m, 2H), 7.79 (dd, $J = 8.6, 4.5$ Hz, 1H), 7.64–7.58 (m, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.43–7.32 (m, 2H), 4.90–4.80 (m, 1H), 4.54 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 4.18 (dd, $J = 9.0, 5.8$ Hz, 1H), 3.79 (dd, $J = 18.1, 4.5$ Hz, 1H), 3.43 (dd, $J = 18.2, 9.6$ Hz, 1H), 1.28 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.0, 166.9 (d, $J^1 = 256.4$ Hz), 164.3, 137.4 (d, $J^3 = 9.2$ Hz), 135.9, 133.7, 132.0 (d, $J^4 = 2.7$ Hz), 128.7, 128.0, 123.7 (d, $J^3 = 10.0$ Hz), 120.0 (d, $J^2 = 24.6$ Hz), 112.6 (d, $J^2 = 24.6$ Hz), 96.5 (d, $J^4 = 2.1$ Hz), 74.4, 63.2, 56.9, 43.1, 13.9; ^{19}F NMR (376 MHz, CDCl_3) δ -102.4; IR (neat) 3070, 2984, 2907, 1746, 1683, 1595, 1449, 1326, 1267, 1175 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{20}\text{H}_{18}\text{FNO}_6\text{S}$: 419.0839 Found: 419.0838; Chiralpak OJ-H column and OJ-H guard column (10% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 39.6$ min and *major*-isomer $t_r = 54.5$ min.

Ethyl (3R,9bR)-8-chloro-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9bH-benzo[4,5]isothiazolo[3,2-b]oxazole-9b-carboxylate 5,5-dioxide (3ia)



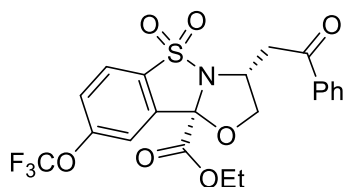
Synthesized by the general procedure I; 39 mg, yield 90%, 17:1 dr, $[\alpha]_D^{25} = -47.6$ ($c = 1.11$, CHCl_3); 92% ee; White solid; m.p. 127–129 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.01–7.94 (m, 2H), 7.72 (d, $J = 8.9$ Hz, 1H), 7.69–7.57 (m, 3H), 7.49 (t, $J = 7.6$ Hz, 2H), 4.88–4.79 (m, 1H), 4.52 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.29 (qt, $J = 7.0, 3.5$ Hz, 2H), 4.18 (dd, $J = 8.9, 5.7$ Hz, 1H), 3.79 (dd, $J = 18.2, 4.5$ Hz, 1H), 3.43 (dd, $J = 18.1, 9.5$ Hz, 1H), 1.28 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.0, 167.0, 140.3, 136.3, 135.9, 134.4, 133.7, 132.4, 128.7, 128.0, 125.6, 122.6, 96.6, 74.4, 63.2, 56.9, 43.0, 13.9; IR (neat) 2985, 2016, 2852, 1749, 1683, 1572, 1473, 1418, 1327, 1212 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{20}\text{H}_{18}\text{ClINO}_6\text{S}$: 435.0543 Found: 435.0528; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 41.1$ min and *minor*-isomer $t_r = 51.1$ min.

Ethyl (3*R*,9*bR*)-3-(2-oxo-2-phenylethyl)-8-(trifluoromethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ja)



Synthesized by the general procedure I; 42 mg, yield 89%, 14:1 dr, $[\alpha]_{\text{D}}^{25} = -47.2$ ($c = 1.04$, CHCl_3); 91% ee; White solid; m.p. 139-141 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.91 (m, 5H), 7.65–7.58 (m, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 4.91–4.81 (m, 1H), 4.54 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.31 (qd, $J = 7.1, 1.8$ Hz, 2H), 4.21 (dd, $J = 9.0, 5.7$ Hz, 1H), 3.82 (dd, $J = 18.1, 4.6$ Hz, 1H), 3.46 (dd, $J = 18.1, 9.5$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 196.9, 166.8, 139.2, 135.92, 135.90 (q, $J^2 = 33.4$ Hz), 135.4, 133.8, 129.2 (q, $J^3 = 3.4$ Hz), 128.8, 128.0, 123.0 (q, $J^3 = 3.8$ Hz), 122.8 (q, $J^1 = 273.5$ Hz), 122.3, 96.9, 74.6, 63.3, 57.0, 43.1, 13.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (neat) 2993, 2941, 2902, 1759, 1684, 1571, 1473, 1330, 1215, 1170 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₁H₁₈F₃NO₆S: 469.0807 Found: 469.0793; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 21.3$ min and *minor*-isomer $t_r = 28.4$ min.

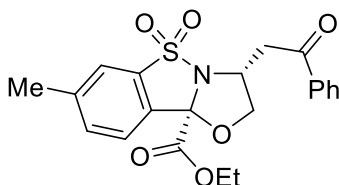
Ethyl (3*R*,9*bR*)-3-(2-oxo-2-phenylethyl)-8-(trifluoromethoxy)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ka)



Synthesized by the general procedure I; 45 mg, yield 93%, 14:1 dr, $[\alpha]_{\text{D}}^{25} = -47.9$ ($c = 1.09$, CHCl_3); 92% ee; Yellow solid; m.p. 128-130 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.94 (m, 2H), 7.84 (d, $J = 9.1$ Hz, 1H), 7.63–7.58 (m, 1H), 7.57–7.44 (m, 4H), 4.91–4.81 (m, 1H), 4.56 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 4.19 (dd, $J = 9.0, 5.8$ Hz, 1H), 3.81 (dd, $J = 18.1, 4.6$ Hz, 1H), 3.45 (dd, $J = 18.1, 9.5$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.0, 166.8, 152.9 (q, $J^2 = 1.8$ Hz), 137.0, 135.9, 134.1, 133.7, 128.7, 128.0, 124.5, 123.4, 121.1 (q, $J^1 = 260.3$ Hz), 117.4, 96.6, 74.6, 63.2, 56.9, 43.1, 13.8; ¹⁹F NMR (376 MHz,

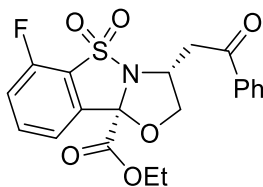
CDCl_3) δ -57.8; IR (neat) 2992, 2928, 2891, 1750, 1684, 1571, 1473, 1334, 1260, 1173 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{18}\text{F}_3\text{NO}_7\text{S}$: 485.0756 Found: 485.0736; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 16.7 min and *minor*-isomer t_r = 24.0 min.

Ethyl (3*R*,9*bR*)-7-methyl-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3la)



Synthesized by the general procedure I; 37 mg, yield 90%, 12:1 dr, $[\alpha]_D^{28}$ = -68.0 (c = 1.02, CHCl_3); 99% ee; Yellow solid; m.p. 139-142 $^\circ\text{C}$; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.56 – 7.46 (m, 4H), 4.83 (td, J = 10.2, 6.1 Hz, 1H), 4.54 (dd, J = 9.0, 6.4 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.15 (dd, J = 9.0, 5.8 Hz, 1H), 3.79 (dd, J = 18.1, 4.4 Hz, 1H), 3.42 (dd, J = 18.1, 9.7 Hz, 1H), 2.49 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.1, 167.6, 143.0, 136.0, 136.0, 134.9, 133.6, 131.4, 128.7, 128.0, 124.8, 121.2, 97.2, 74.4, 62.9, 56.5, 43.2, 21.4, 13.9; IR (neat) 2981, 2925, 2881, 1746, 1696, 1571, 1449, 1320, 1270, 1214, 1160 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{21}\text{NO}_6\text{S}$: 415.1090 Found: 415.1064; Chiralpak OJ-H column and OJ-H guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 72.0 min and *minor*-isomer t_r = 82.0 min.

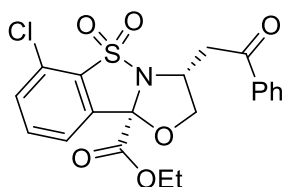
Ethyl (3*R*,9*bR*)-6-fluoro-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9*bH*-benzo[4,5]isothiazolo[3,2-*b*]oxazole-9*b*-carboxylate 5,5-dioxide (3ma)



Synthesized by the general procedure I; 35 mg, yield 84%, >20:1 dr, $[\alpha]_D^{25}$ = -63.1 (c = 0.97, CHCl_3); 90% ee; White solid; m.p. 132-134 $^\circ\text{C}$; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 7.0 Hz, 2H), 7.71 (td, J = 8.0, 4.7 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.54–7.41

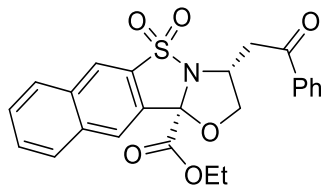
(m, 3H), 7.34 (t, $J = 8.2$ Hz, 1H), 4.86 (td, $J = 10.2, 6.1$ Hz, 1H), 4.56 (dd, $J = 9.0, 6.3$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 4.19 (dd, $J = 9.0, 5.8$ Hz, 1H), 3.79 (dd, $J = 18.1, 4.3$ Hz, 1H), 3.42 (dd, $J = 18.1, 9.8$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 167.0, 155.6 (d, $J^1 = 260.5$ Hz), 137.3, 136.4 (d, $J^3 = 6.8$ Hz), 135.9, 133.7, 128.7, 128.0, 124.1 (d, $J^2 = 23.3$ Hz), 120.8 (d, $J^3 = 4.2$ Hz), 118.7 (d, $J^2 = 18.4$ Hz), 96.9, 74.5, 63.2, 57.0, 43.1, 13.9; ^{19}F NMR (376 MHz, CDCl_3) δ -113.8; IR (neat) 2945, 2915, 2876, 1733, 1675, 1597, 1473, 1333, 1274, 1177 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{18}\text{FNO}_6\text{S}$: 419.0839 Found: 419.0862; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 39.8$ min and *minor*-isomer $t_r = 49.5$ min.

Ethyl (3R,9bR)-6-chloro-3-(2-oxo-2-phenylethyl)-2,3-dihydro-9bH-benzo[4,5]isothiazolo[3,2-b]oxazole-9b-carboxylate 5,5-dioxide (3na)



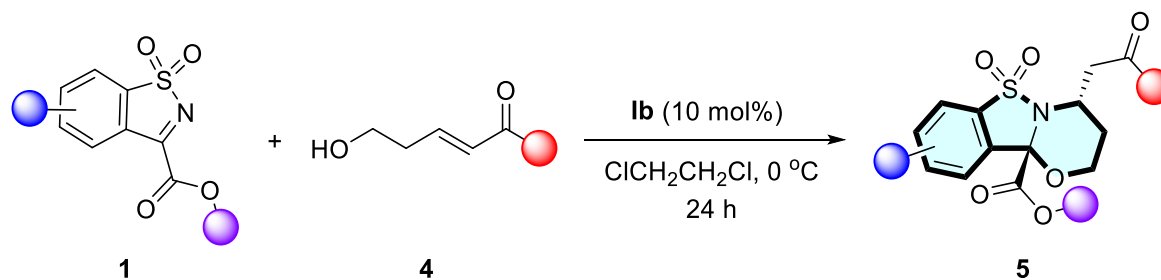
Synthesized by the general procedure I; 38 mg, yield 87%, >20:1 dr, $[\alpha]_D^{25} = -71.5$ ($c = 0.96$, CHCl_3); 91% ee; White solid; m.p. 132-134 $^{\circ}\text{C}$; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.1$ Hz, 2H), 7.67–7.59 (m, 3H), 7.55 (dd, $J = 7.1, 1.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 4.86 (td, $J = 10.1, 6.1$ Hz, 1H), 4.54 (dd, $J = 9.0, 6.3$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.18 (dd, $J = 9.0, 5.8$ Hz, 1H), 3.80 (dd, $J = 18.1, 4.3$ Hz, 1H), 3.43 (dd, $J = 18.1, 9.8$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.0, 167.1, 137.0, 135.9, 135.0, 134.0, 133.7, 132.6, 128.8 (two peaks overlapping), 128.0, 123.4, 96.1, 74.4, 63.2, 57.1, 43.1, 13.9; IR (neat) 2985, 2940, 2901, 1749, 1683, 1574, 1473, 1419, 1327, 1213, 1125 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{18}\text{ClNO}_6\text{S}$: 435.0543 Found: 435.0558; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 34.5$ min and *minor*-isomer $t_r = 44.0$ min.

Ethyl (3R,11bR)-3-(2-oxo-2-phenylethyl)-2,3-dihydro-11bH-naphtho[2',3':4,5]isothiazolo[3,2-b]oxazole-11b-carboxylate 5,5-dioxide (3oa)

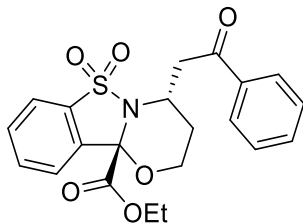


Synthesized by the general procedure I; 42 mg, yield 94%, 20:1 dr, $[\alpha]_D^{25} = -49.7$ ($c = 1.01$, CHCl_3); 97% ee; Yellow solid; m.p. 180-182 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:1:4); ¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 8.16 (s, 1H), 8.05–7.95 (m, 4H), 7.72–7.64 (m, 2H), 7.63–7.58 (m, 1H), 7.49 (t, $J = 7.7$ Hz, 2H), 4.90 (td, $J = 10.5, 6.1$ Hz, 1H), 4.60 (dd, $J = 9.0, 6.4$ Hz, 1H), 4.36–4.25 (m, 2H), 4.18 (dd, $J = 9.0, 6.0$ Hz, 1H), 3.84 (dd, $J = 18.1, 4.4$ Hz, 1H), 3.45 (dd, $J = 18.1, 9.7$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.1, 167.8, 136.0, 135.3, 134.0, 133.6, 133.2, 129.8, 129.3, 129.2, 128.9, 128.7, 128.6, 128.0, 125.2, 122.2, 97.3, 74.4, 63.0, 56.7, 43.3, 13.9; IR (neat) 2994, 2950, 2903, 1749, 1682, 1540, 1454, 1333, 1172, 1127 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₄H₂₁NO₆S: 451.1090 Found: 451.1118; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 64.2$ min and *minor*-isomer $t_r = 108.1$ min.

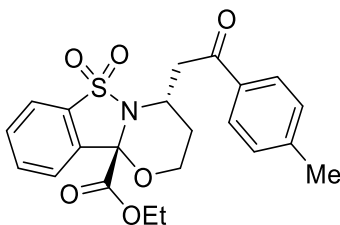
6. General procedure II for asymmetric [4+2]-annulation of δ -hydroxy- α,β -unsaturated ketones with cyclic *N*-sulfonyl ketimines.



A solution of cyclic *N*-sulfonyl ketimine **1** (0.15 mmol, 1.5 equiv) and catalyst **Ib** (0.01 mmol, 0.1 equiv) in ClCH₂CH₂Cl (1.0 mL, 0.1 M) was stirred for 10 min at 0 °C and then added δ -hydroxy- α,β -unsaturated ketone **4** (0.10 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 24 h. Then, the resulting mixture was concentrated in vacuo and was purified by flash column chromatography with EtOAc/CH₂Cl₂/hexanes as eluent to afford desired product **5**. The enantiomeric excess was determined using HPLC analysis.

Ethyl (4*S*,10*bS*)-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5aa)

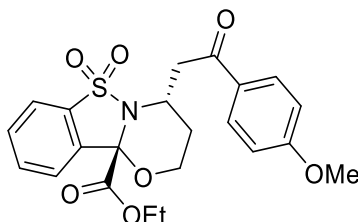
Synthesized by the general procedure II; 34 mg, yield 83%, >20:1 dr, $[\alpha]_D^{26} = 39.8$ ($c = 0.92$, CHCl_3); 99% ee; White solid; m.p. 149–151 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.12–8.02 (m, 2H), 7.85–7.78 (m, 1H), 7.71–7.57 (m, 4H), 7.51 (dd, $J = 8.3, 6.9$ Hz, 2H), 4.47–4.31 (m, 3H), 4.30–4.13 (m, 3H), 3.86 (dd, $J = 17.8, 9.8$ Hz, 1H), 2.23–2.08 (m, 1H), 1.77 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.8, 166.6, 136.3, 135.4, 133.6, 133.6, 133.6, 131.6, 128.7, 128.2, 124.1, 121.2, 89.4, 65.5, 63.2, 50.9, 39.2, 28.3, 14.1; IR (neat) 2957, 2898, 1747, 1684, 1597, 1449, 1373, 1242, 1162, 1053 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₁H₂₁NO₆S: 415.1090 Found: 415.1111; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 25.6$ min and *minor*-isomer $t_r = 66.4$ min.

Ethyl (4*S*,10*bS*)-4-(2-oxo-2-(*p*-tolyl)ethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5ab)

Synthesized by the general procedure II; 37 mg, yield 87%, >20:1 dr, $[\alpha]_D^{26} = 23.6$ ($c = 1.01$, CHCl_3); >99% ee; White solid; m.p. 132–134 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, $J = 8.3$ Hz, 2H), 7.84–7.77 (m, 1H), 7.72–7.60 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.47–4.30 (m, 3H), 4.26–4.11 (m, 3H), 3.84 (dd, $J = 17.7, 9.9$ Hz, 1H), 2.43 (s, 3H), 2.22–2.07 (m, 1H), 1.77 (dq, $J = 13.5, 2.4$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.4, 166.6, 144.5, 135.4, 133.9, 133.6, 133.6, 131.6, 129.4, 128.3, 124.1, 121.2, 89.4, 65.5, 63.2, 51.0, 39.1, 28.3, 21.7, 14.1; IR (neat) 2973, 2926, 1742, 1686, 1607, 1520, 1455, 1384, 1302, 1234, 1172, 1099 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₂H₂₃NO₆S: 429.1246 Found: 429.1235; Chiralpak IA column

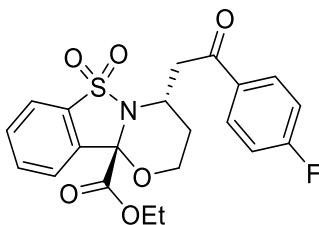
and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 26.1 min and *minor*-isomer t_r = 63.7 min.

Ethyl (4*S*,10*bS*)-4-(2-(4-methoxyphenyl)-2-oxoethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5ac)



Synthesized by the general procedure II; 44 mg, yield 99%, >20:1 dr, $[\alpha]_D^{26}$ = 18.6 (c = 1.00, CHCl₃); >99% ee; White solid; m.p. 146-148 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:4); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.9 Hz, 2H), 7.85–7.77 (m, 1H), 7.74–7.55 (m, 3H), 6.97 (d, J = 8.9 Hz, 2H), 4.47–4.30 (m, 3H), 4.18 (dt, J = 15.5, 3.6 Hz, 3H), 3.89 (s, 3H), 3.82 (dd, J = 17.5, 10.0 Hz, 1H), 2.22–2.07 (m, 1H), 1.77 (dq, J = 13.3, 2.3 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ¹³C NMR (100 MHz, CDCl₃) δ 194.2, 166.6, 163.8, 135.4, 133.64, 133.55, 131.6, 130.5, 129.5, 124.0, 121.2, 113.8, 89.4, 65.5, 63.2, 55.5, 51.1, 38.8, 28.3, 14.1; IR (neat) 2974, 2881, 1747, 1687, 1599, 1573, 1472, 1429, 1300, 1202, 1173 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₂H₂₃NO₇S: 445.1195 Found: 445.1203; Chiralpak IA column and IA guard column (30% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 26.8 min and *minor*-isomer t_r = 44.7 min.

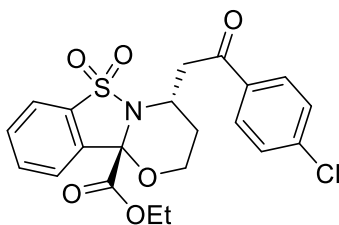
Ethyl (4*S*,10*bS*)-4-(2-(4-fluorophenyl)-2-oxoethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5ad)



Synthesized by the general procedure II; 39 mg, yield 91%, >20:1 dr, $[\alpha]_D^{26}$ = 24.9 (c = 0.90, CHCl₃); >99% ee; White solid; m.p. 150-152 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.14–8.04 (m, 2H), 7.86–7.77 (m, 1H), 7.72–7.61 (m, 3H), 7.23–7.11 (m, 2H), 4.47–4.31 (m, 3H), 4.28–4.13 (m, 3H), 3.78 (dd, J = 17.8, 9.6 Hz, 1H), 2.25–2.09 (m, 1H), 1.76 (dq, J = 13.2, 2.3 Hz,

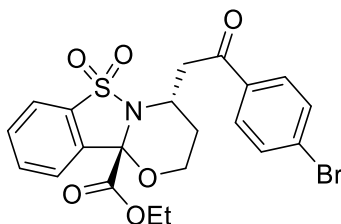
1H), 1.34 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.1, 166.9 (d, $J^1 = 255.3$ Hz), 164.7, 135.3, 133.63, 133.60, 132.8 (d, $J^4 = 3.1$ Hz), 131.7, 130.9 (d, $J^3 = 9.5$ Hz), 124.1, 121.2, 115.8 (d, $J^2 = 22.0$ Hz), 89.4, 65.5, 63.2, 50.8, 39.2, 28.3, 14.1; ^{19}F NMR (376 MHz, CDCl_3) δ -104.2; IR (neat) 2987, 2918, 1747, 1691, 1593, 1498, 1457, 1303, 1224, 1162, 1049 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{20}\text{FNO}_6\text{S}$: 433.0995 Found: 433.0992; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 25.7$ min and *minor*-isomer $t_r = 56.7$ min.

Ethyl (4S,10bS)-4-(2-(4-chlorophenyl)-2-oxoethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ae)



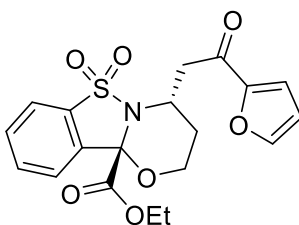
Synthesized by the general procedure II; 35 mg, yield 78%, >20:1 dr, $[\alpha]_{\text{D}}^{26} = 19.4$ ($c = 0.94$, CHCl_3); >99% ee; White solid; m.p. 144-146 $^{\circ}\text{C}$; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:10:9); ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.95 (m, 2H), 7.84–7.77 (m, 1H), 7.72–7.61 (m, 3H), 7.54–7.42 (m, 2H), 4.47–4.31 (m, 3H), 4.29–4.12 (m, 3H), 3.75 (dd, $J = 17.9, 9.4$ Hz, 1H), 2.25–2.10 (m, 1H), 1.75 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.5, 166.5, 140.1, 135.3, 134.7, 133.64, 133.58, 131.7, 129.6, 129.0, 124.1, 121.2, 89.4, 65.5, 63.2, 50.7, 39.2, 28.2, 14.1; IR (neat) 2909, 2891, 1744, 1685, 1589, 1507, 1400, 1361, 1317, 1225, 1134 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{20}\text{ClNO}_6\text{S}$: 449.0700 Found: 449.0705; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 29.1$ min and *minor*-isomer $t_r = 58.9$ min.

Ethyl (4S,10bS)-4-(2-(4-bromophenyl)-2-oxoethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxid (5af)



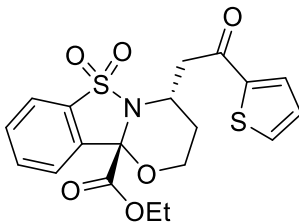
Synthesized by the general procedure II; 46 mg, yield 93%, >20:1 dr, $[\alpha]_D^{26} = 13.6$ ($c = 1.01$, CHCl_3); 99% ee; White solid; m.p. 76-79 °C; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:10:9); ^1H NMR (400 MHz, CDCl_3) δ 7.97–7.87 (m, 2H), 7.84–7.77 (m, 1H), 7.73–7.57 (m, 5H), 4.47–4.30 (m, 3H), 4.28–4.11 (m, 3H), 3.74 (dd, $J = 17.9, 9.4$ Hz, 1H), 2.25–2.07 (m, 1H), 1.74 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.7, 166.5, 135.3, 135.1, 133.63, 133.58, 132.0, 131.7, 129.7, 128.8, 124.1, 121.2, 89.4, 65.5, 63.2, 50.6, 39.2, 28.2, 14.1; IR (neat) 2991, 2896, 1743, 1686, 1589, 1543, 1488, 1432, 1391, 1235, 1138 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{20}\text{BrNO}_6\text{S}$: 493.0195 Found: 493.0181; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 56.7$ min and *major*-isomer $t_r = 69.1$ min.

Ethyl (4S,10bS)-4-(2-(furan-2-yl)-2-oxoethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ag)



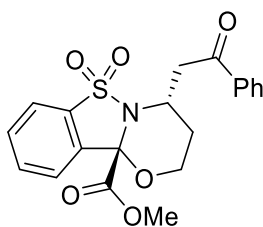
Synthesized by the general procedure II; 34 mg, yield 84%, >20:1 dr, $[\alpha]_D^{26} = 30.8$ ($c = 1.22$, CHCl_3); 99% ee; White solid; m.p. 166-168 °C; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:4:3); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (ddd, $J = 5.4, 2.4, 0.8$ Hz, 1H), 7.73–7.58 (m, 4H), 7.34 (dd, $J = 3.6, 0.8$ Hz, 1H), 6.58 (dd, $J = 3.6, 1.7$ Hz, 1H), 4.44–4.29 (m, 3H), 4.24–4.05 (m, 3H), 3.70 (dd, $J = 17.5, 9.7$ Hz, 1H), 2.27–2.09 (m, 1H), 1.70 (dq, $J = 13.3, 2.4$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 184.5, 166.5, 152.1, 147.0, 135.4, 133.58, 133.56, 131.6, 124.1, 121.2, 118.1, 112.4, 89.4, 65.4, 63.2, 50.3, 39.0, 28.2, 14.1; IR (neat) 2956, 2897, 1745, 1681, 1368, 1470, 1342, 1297, 1175, 1047 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{19}\text{NO}_7\text{S}$: 405.0882 Found: 405.0865; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 28.0$ min and *minor*-isomer $t_r = 52.9$ min.

Ethyl (4S,10bS)-4-(2-oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ah)



Synthesized by the general procedure II; 42 mg, yield 99%, >20:1 dr, $[\alpha]_D^{26} = 30.6$ ($c = 1.00$, CHCl_3); >99% ee; White solid; m.p. 163-165 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:4); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, $J = 3.8, 1.1$ Hz, 1H), 7.85–7.77 (m, 1H), 7.74–7.59 (m, 4H), 7.18 (dd, $J = 5.0, 3.8$ Hz, 1H), 4.46–4.30 (m, 3H), 4.25–4.10 (m, 3H), 3.79 (dd, $J = 17.2, 9.8$ Hz, 1H), 2.27–2.10 (m, 1H), 1.74 (dq, $J = 13.3, 2.4$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 188.6, 166.5, 143.6, 135.3, 134.4, 133.60, 133.57, 132.8, 131.6, 128.3, 124.1, 121.2, 89.4, 65.4, 63.2, 50.7, 39.8, 28.2, 14.1; IR (neat) 2965, 2898, 1746, 1664, 1518, 1416, 1297, 1230, 1132, 1051 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₁₉H₁₉NO₆S₂: 421.0654 Found: 421.0648; Chiralpak OJ-H column and OJ-H guard column (30% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 33.2$ min and *minor*-isomer $t_r = 52.0$ min.

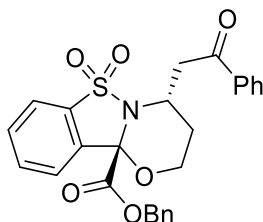
Methyl (4S,10bS)-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ba)



Synthesized by the general procedure II; 31 mg, yield 78%, >20:1 dr, $[\alpha]_D^{26} = 36.1$ ($c = 1.00$, CHCl_3); 99% ee; White solid; m.p. 142-144 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=3:20:17); ¹H NMR (400 MHz, CDCl₃) δ 8.13–7.97 (m, 2H), 7.86–7.77 (m, 1H), 7.73–7.57 (m, 4H), 7.51 (t, $J = 7.7$ Hz, 2H), 4.41 (ddt, $J = 12.5, 9.8, 3.2$ Hz, 1H), 4.30–4.12 (m, 3H), 3.89 (s, 4H), 2.24–2.08 (m, 1H), 1.78 (dq, $J = 13.3, 2.4$ Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.8, 167.3, 136.3, 135.3, 133.7, 133.6, 133.5, 131.7, 128.7, 128.2, 124.1, 121.2, 89.4, 65.6, 53.9, 51.0, 39.2, 28.3; IR (neat) 2955, 2853, 1746, 1684, 1597, 1449, 1373, 1241, 1176, 1029 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₀H₁₉NO₆S: 401.0933 Found:

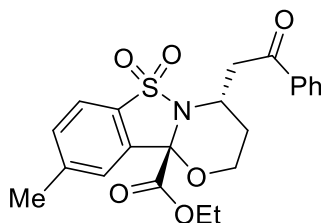
401.0916; Chiralpak IB column and IB guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 26.2 min and *minor*-isomer t_r = 31.7 min.

Benzyl (4*S*,10*bS*)-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5*ca*)



Synthesized by the general procedure II; 40 mg, yield 84%, >20:1 dr, $[\alpha]_D^{26}$ = 29.6 (c = 1.00, CHCl₃); >99% ee; White solid; m.p. 188-190 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.12–7.98 (m, 2H), 7.80 (dd, J = 7.5, 1.2 Hz, 1H), 7.66–7.55 (m, 3H), 7.54–7.45 (m, 3H), 7.32 (s, 5H), 5.40–5.24 (m, 2H), 4.40 (tt, J = 9.9, 3.1 Hz, 1H), 4.28–4.07 (m, 3H), 3.86 (dd, J = 17.7, 10.0 Hz, 1H), 2.13 (dtd, J = 13.2, 11.7, 5.7 Hz, 1H), 1.75 (dq, J = 13.3, 2.4 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.7, 166.5, 136.3, 135.3, 134.6, 133.6, 133.5, 133.4, 131.6, 128.7, 128.63, 128.60, 128.4, 128.2, 124.1, 121.2, 89.4, 68.5, 65.5, 51.0, 39.2, 28.3; IR (neat) 2956, 2854, 1746, 1684, 1597, 1449, 1303, 1242, 1134, 1053, cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₆H₂₃NO₆S: 477.1246 Found: 477.1224; Chiralpak IB column and IB guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 18.7 min and *minor*-isomer t_r = 22.5 min.

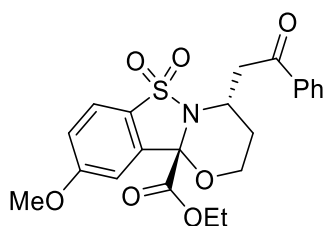
Ethyl (4*S*,10*bS*)-9-methyl-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5*da*)



Synthesized by the general procedure II; 36 mg, yield 85%, >20:1 dr, $[\alpha]_D^{26}$ = 24.3 (c = 1.00, CHCl₃); >99% ee; White solid; m.p. 161-163 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, J = 8.4, 1.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.64–7.57 (m, 1H), 7.54–7.41 (m, 4H), 4.47–4.30 (m, 3H), 4.28–4.11 (m, 3H), 3.85 (dd, J = 17.8, 9.9 Hz, 1H), 2.46 (s, 3H), 2.23–2.08

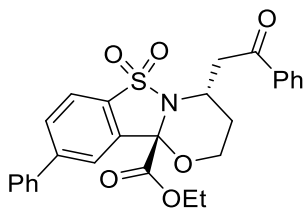
(m, 1H), 1.75 (dq, $J = 13.2, 2.3$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.8, 166.7, 144.9, 136.3, 133.8, 133.6, 132.6, 132.4, 128.7, 128.2, 124.2, 121.0, 89.3, 65.5, 63.2, 50.8, 39.2, 28.3, 21.8, 14.1; IR (neat) 2972, 2866, 1746, 1682, 1580, 1471, 1449, 1386, 1291, 1177, 1106 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{22}\text{H}_{23}\text{NO}_6\text{S}$: 429.1246 Found: 429.1265; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 33.5$ min and *minor*-isomer $t_r = 53.1$ min.

Ethyl (4*S*,10*bS*)-9-methoxy-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5ea)



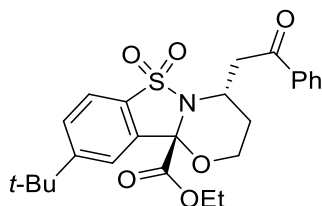
Synthesized by the general procedure II; 35 mg, yield 79%, >20:1 dr, $[\alpha]_D^{26} = 17.2$ ($c = 0.98$, CHCl_3); >99% ee; White solid; m.p. 63-65 °C; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:10:4); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.71 (d, $J = 8.6$ Hz, 1H), 7.64–7.57 (m, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.14 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.06 (d, $J = 2.2$ Hz, 1H), 4.46–4.29 (m, 3H), 4.28–4.11 (m, 3H), 3.89–3.80 (m, 4H), 2.24–2.10 (m, 1H), 1.76 (dq, $J = 13.3, 2.4$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.9, 166.7, 163.8, 136.3, 135.9, 133.6, 128.7, 128.2, 127.2, 122.7, 118.6, 107.9, 89.0, 65.5, 63.2, 56.0, 50.9, 39.2, 28.3, 14.1; IR (neat) 2970, 2899, 1746, 1684, 1597, 1449, 1301, 1241, 1176, 1134, 1053 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{22}\text{H}_{23}\text{NO}_7\text{S}$: 445.1195 Found: 445.1208; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 41.5$ min and *minor*-isomer $t_r = 75.3$ min.

Ethyl (4*S*,10*bS*)-4-(2-oxo-2-phenylethyl)-9-phenyl--3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5fa)



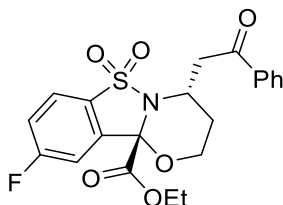
Synthesized by the general procedure II; 41 mg, yield 83%, >20:1 dr, $[\alpha]_D^{26} = -14.2$ ($c = 0.99$, CHCl_3); >99% ee; White solid; m.p. 181–183 °C; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:5:9); ^1H NMR (400 MHz, CDCl_3) δ 8.13–8.01 (m, 2H), 7.91–7.78 (m, 3H), 7.64–7.55 (m, 3H), 7.54–7.40 (m, 5H), 4.49–4.38 (m, 2H), 4.38–4.16 (m, 4H), 3.87 (dd, $J = 17.8, 9.8$ Hz, 1H), 2.26–2.10 (m, 1H), 1.79 (dq, $J = 13.2, 2.3$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.8, 166.6, 147.2, 138.7, 136.3, 134.4, 133.9, 133.6, 130.6, 129.1, 128.8, 128.7, 128.2, 127.4, 122.5, 121.6, 89.4, 65.5, 63.2, 50.9, 39.2, 28.3, 14.2; IR (neat) 2970, 2891, 1741, 1681, 1596, 1446, 1411, 1301, 1245, 1198, 1060 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{27}\text{H}_{25}\text{NO}_6\text{S}$: 491.1403 Found: 491.1406; Chiralpak OJ-H column and OJ-H guard column (40% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 34.4$ min and *minor*-isomer $t_r = 52.8$ min.

Ethyl (4S,10bS)-9-(tert-butyl)-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ga)



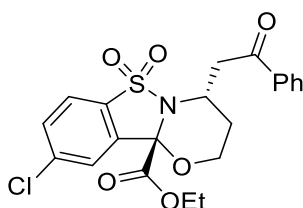
Synthesized by the general procedure II; 40 mg, yield 84%, >20:1 dr, $[\alpha]_D^{26} = 14.8$ ($c = 0.99$, CHCl_3); 99% ee; White solid; m.p. 70–72 °C; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=3:10:9); ^1H NMR (400 MHz, CDCl_3) δ 8.13–8.00 (m, 2H), 7.77–7.65 (m, 2H), 7.65–7.56 (m, 2H), 7.54–7.46 (m, 2H), 4.48–4.31 (m, 3H), 4.30–4.12 (m, 3H), 3.87 (dd, $J = 17.8, 10.0$ Hz, 1H), 2.24–2.08 (m, 1H), 1.77 (dq, $J = 13.2, 2.3$ Hz, 1H), 1.33 (d, $J = 3.3$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.9, 166.7, 158.1, 136.4, 133.61, 133.57, 132.5, 129.1, 128.7, 128.2, 120.8, 120.7, 89.5, 65.6, 63.0, 50.9, 39.2, 35.6, 31.0, 28.3, 14.1; IR (neat) 2958, 2904, 1746, 1684, 1616, 1507, 1449, 1363, 1298, 1226, 1149 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{25}\text{H}_{29}\text{NO}_6\text{S}$: 471.1716 Found: 471.1736; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 12.7$ min and *minor*-isomer $t_r = 22.8$ min.

Ethyl (4S,10bS)-9-fluoro-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ha)



Synthesized by the general procedure II; 33 mg, yield 76%, >20:1 dr, $[\alpha]_D^{26} = 25.8$ ($c = 0.82$, CHCl_3); >99% ee; White solid; m.p. 183–185 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.11–8.00 (m, 2H), 7.85–7.77 (m, 1H), 7.65–7.57 (m, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.41–7.29 (m, 2H), 4.49–4.33 (m, 3H), 4.27–4.11 (m, 3H), 3.83 (dd, $J = 17.8, 9.8$ Hz, 1H), 2.23–2.07 (m, 1H), 1.78 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 166.4 (d, $J^1 = 257.0$ Hz), 164.2, 136.5 (d, $J^3 = 8.9$ Hz), 136.3, 133.6, 131.3 (d, $J^4 = 4.5$ Hz), 128.7, 128.2, 123.6 (d, $J^3 = 9.5$ Hz), 119.5 (d, $J^2 = 24.6$ Hz), 111.8 (d, $J^2 = 25.4$ Hz), 88.7 (d, $J^5 = 2.1$ Hz), 65.8, 63.5, 51.0, 39.2, 28.2, 14.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -102.3; IR (neat) 2970, 2853, 1746, 1684, 1597, 1449, 1302, 1242, 1162, 1053, 1029 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{21}\text{H}_{20}\text{FNO}_6\text{S}$: 433.0995 Found: 433.1023; Chiralpak OJ-H column and OJ-H guard column (30% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 28.5$ min and *minor*-isomer $t_r = 56.4$ min.

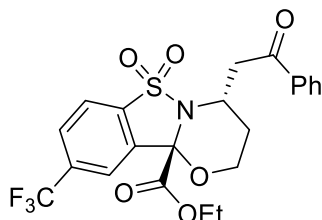
Ethyl (4S,10bS)-9-chloro-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5ia)



Synthesized by the general procedure II; 35 mg, yield 79%, >20:1 dr, $[\alpha]_D^{26} = 15.2$ ($c = 0.80$, CHCl_3); >99% ee; White solid; m.p. 162–164 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.10–7.99 (m, 2H), 7.74 (dd, $J = 8.1, 0.8$ Hz, 1H), 7.68–7.57 (m, 3H), 7.50 (t, $J = 7.6$ Hz, 2H), 4.48–4.32 (m, 3H), 4.26–4.11 (m, 3H), 3.82 (dd, $J = 17.8, 9.8$ Hz, 1H), 2.22–2.07 (m, 1H), 1.77 (dq, $J = 13.3, 2.3$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.6, 166.1, 140.2, 136.3, 135.4, 133.8, 133.6, 132.1, 128.7, 128.2, 124.6, 122.5, 88.8, 65.6, 63.5, 51.0, 39.2, 28.2, 14.1; IR (neat) 2982, 2901, 2862, 1749, 1693, 1586, 1449, 1416, 1371, 1237, 1175 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{21}\text{H}_{20}\text{ClNO}_6\text{S}$: 449.0700 Found: 449.0670; Chiralpak OJ-H column and OJ-H guard

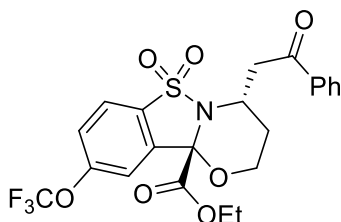
column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 29.4 min and *minor*-isomer t_r = 54.9 min.

Ethyl (4*S*,10*bS*)-4-(2-oxo-2-phenylethyl)-9-(trifluoromethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5ja)



Synthesized by the general procedure II; 42 mg, yield 87%, >20:1 dr, $[\alpha]_D^{26}$ = 15.5 (c = 0.95, CHCl₃); >99% ee; White solid; m.p. 132-134 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.09–8.03 (m, 2H), 7.94 (s, 3H), 7.65–7.59 (m, 1H), 7.56–7.46 (m, 2H), 4.53–4.34 (m, 3H), 4.29–4.14 (m, 3H), 3.83 (dd, J = 17.7, 9.8 Hz, 1H), 2.22–2.09 (m, 1H), 1.81 (dq, J = 13.4, 2.4 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.5, 166.0, 138.6, 136.2, 135.7 (q, J^2 = 33.6 Hz), 134.6, 133.7, 128.9 (q, J^3 = 3.5 Hz), 128.7, 128.2, 122.1, 89.0, 122.7 (q, J^1 = 273.4 Hz) 121.8 (q, J^3 = 3.8 Hz), 65.6, 63.6, 51.0, 39.2, 28.3, 14.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (neat) 2971, 2875, 1746, 1683, 1596, 1449, 1296, 1242, 1175, 1134, 1029 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₂H₂₀F₃NO₆S: 483.0963 Found: 483.0947; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 15.8 min and *minor*-isomer t_r = 25.4 min.

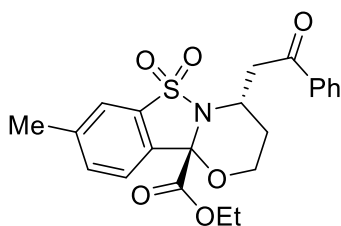
Ethyl (4*S*,10*bS*)-4-(2-oxo-2-phenylethyl)-9-(trifluoromethoxy)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5ka)



Synthesized by the general procedure II; 44 mg, yield 89%, >20:1 dr, $[\alpha]_D^{26}$ = 16.8 (c = 1.00, CHCl₃); >99% ee; White solid; m.p. 123-126 °C; R_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.10–7.99 (m, 2H), 7.86 (dd, J = 7.9, 1.0 Hz, 1H), 7.65–7.59 (m, 1H), 7.56–7.42 (m, 4H),

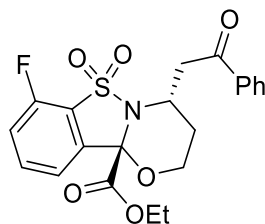
4.51–4.33 (m, 3H), 4.27–4.12 (m, 3H), 3.83 (dd, $J = 17.8, 9.8$ Hz, 1H), 2.22–2.08 (m, 1H), 1.79 (dq, $J = 13.3, 2.3$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.6, 166.0, 152.7 (q, $J^2 = 1.9$ Hz), 136.3, 136.1, 133.7, 133.5, 128.7, 128.2, 124.1, 123.3, 116.5, 120.1 (d, $J = 260.3$ Hz), 88.8, 65.6, 63.5, 51.0, 39.1, 28.2, 14.0; ^{19}F NMR (376 MHz, CDCl_3) δ -57.8; IR (neat) 2972, 2866, 1746, 1682, 1596, 1449, 1292, 1242, 1134 1018 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{22}\text{H}_{20}\text{F}_3\text{NO}_7\text{S}$: 499.0913 Found: 499.0898; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 14.9$ min and *minor*-isomer $t_r = 23.5$ min.

Ethyl (4*S*,10*bS*)-8-methyl-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5*la*)



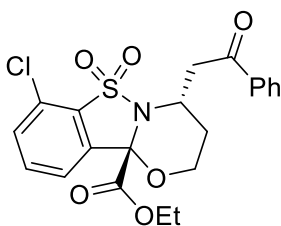
Synthesized by the general procedure II; 36 mg, yield 84%, >20:1 dr, $[\alpha]_D^{26} = 37.8$ ($c = 0.96$, CHCl_3); >99% ee; White solid; m.p. 164–166 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ^1H NMR (400 MHz, CDCl_3) δ 8.16–7.96 (m, 2H), 7.67–7.57 (m, 2H), 7.57–7.40 (m, 4H), 4.46–4.30 (m, 3H), 4.28–4.10 (m, 3H), 3.86 (dd, $J = 17.8, 9.9$ Hz, 1H), 2.47 (s, 3H), 2.21–2.07 (m, 1H), 1.76 (dq, $J = 13.3, 2.5$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.8, 166.7, 142.6, 136.3, 135.4, 134.5, 133.6, 130.9, 128.7, 128.2, 123.8, 121.1, 89.3, 65.4, 63.1, 50.9, 39.2, 28.3, 21.5, 14.1; IR (neat) 2890, 2802, 1742, 1693, 1558, 1507, 1456, 1299, 1221, 1163 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+ \text{C}_{22}\text{H}_{23}\text{NO}_6\text{S}$: 429.1246 Found: 429.1219; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 42.8$ min and *minor*-isomer $t_r = 51.6$ min.

Ethyl (4*S*,10*bS*)-7-fluoro-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (5*ma*)



Synthesized by the general procedure II; 38 mg, yield 87%, 12:1 dr, $[\alpha]_D^{26} = 18.0$ ($c = 1.06$, CHCl_3); >99% ee; White solid; m.p. 156-158 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.12–7.97 (m, 2H), 7.70–7.58 (m, 2H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.43 (d, $J = 7.1$ Hz, 1H), 7.31 (t, $J = 8.3$ Hz, 1H), 4.46–4.31 (m, 3H), 4.28–4.14 (m, 3H), 3.85 (dd, $J = 17.8, 9.9$ Hz, 1H), 2.25–2.06 (m, 1H), 1.79 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 166.2, 155.7 (d, $J^1 = 260.1$ Hz), 136.3, 136.0, 135.9, 133.7, 128.7, 128.2, 123.0 (d, $J^2 = 17.9$ Hz), 119.8 (d, $J^3 = 4.7$ Hz), 118.8 (d, $J^2 = 17.9$ Hz), 89.1, 65.6, 63.4, 51.0, 39.2, 28.3, 14.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -114.5; IR (neat) 2890, 2833, 1743, 1684, 1594, 1541, 1473, 1373, 1279, 1242, 1176 cm⁻¹; HRMS (EI) m/z calcd for $[M]^+$ C₂₁H₂₀FO₆S: 433.0995 Found: 433.0971; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 35.8$ min and *minor*-isomer $t_r = 50.9$ min.

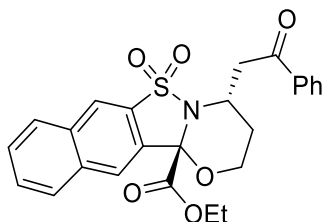
Ethyl (4S,10bS)-7-chloro-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2H,10bH-benzo[4,5]isothiazolo[3,2-b][1,3]oxazine-10b-carboxylate 6,6-dioxide (5na)



Synthesized by the general procedure II; 40 mg, yield 89%, 13:1 dr, $[\alpha]_D^{26} = 41.9$ ($c = 0.82$, CHCl_3); 99% ee; White solid; m.p. 174-176 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.10–8.00 (m, 2H), 7.64–7.56 (m, 3H), 7.56–7.43 (m, 3H), 4.47–4.32 (m, 3H), 4.30–4.16 (m, 3H), 3.87 (dd, $J = 17.9, 9.9$ Hz, 1H), 2.21–2.08 (m, 1H), 1.80 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.6, 166.3, 136.25, 136.18, 134.6, 133.7, 132.9, 132., 128.8, 128.7, 128.2, 122.3, 88.4, 65.5, 63.4, 51.0, 39.2, 28.4, 14.1; IR (neat) 2910, 2847, 1738, 1687, 1558, 1507, 1455, 1389, 1306, 1243, 1112 cm⁻¹; HRMS (EI) m/z calcd for $[M]^+$ C₂₁H₂₀ClNO₆S:

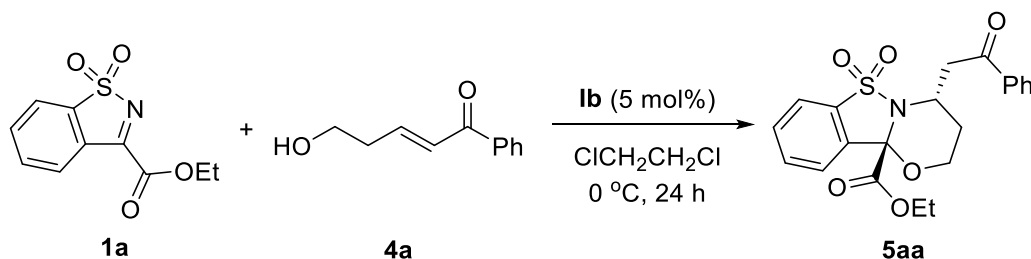
449.0700 Found: 449.0670; Chiralpak IA column and IA guard column (15% IPA:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 21.7$ min and *major*-isomer $t_r = 28.4$ min.

Ethyl (4*S*,12*bS*)-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,12*bH*-naphtho[2',3':4,5]isothiazolo[3,2-*b*][1,3]oxazine-12*b*-carboxylate 6,6-dioxide (5*oa*)



Synthesized by the general procedure II; 40 mg, yield 86%, >20:1 dr, $[\alpha]_D^{26} = -13.0$ ($c = 0.96$, CHCl_3); >99% ee; White solid; m.p. 208-210 °C; R_f 0.2 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 8.15–8.05 (m, 3H), 8.05–7.99 (m, 1H), 7.99–7.92 (m, 1H), 7.71–7.59 (m, 3H), 7.51 (t, $J = 7.6$ Hz, 2H), 4.52–4.41 (m, 2H), 4.38–4.17 (m, 4H), 3.89 (dd, $J = 17.7, 9.9$ Hz, 1H), 2.24 (qd, $J = 11.9, 5.4$ Hz, 1H), 1.78 (dq, $J = 13.4, 2.4$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.9, 166.8, 136.4, 135.1, 133.7, 133.6, 132.5, 129.3, 129.2, 129.1, 129.0, 128.7, 128.6, 128.2, 124.3, 122.1, 89.7, 65.6, 63.2, 51.2, 39.4, 28.2, 14.1; IR (neat) 2892, 2834, 1742, 1681, 1558, 1498, 1420, 1362, 1296, 1149, 1069 cm⁻¹; HRMS (EI) m/z calcd for $[\text{M}]^+$ C₂₅H₂₃NO₆S: 465.1246 Found: 465.1220; Chiralpak OJ-H column and OJ-H guard column (30% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 42.2$ min and *minor*-isomer $t_r = 58.1$ min.

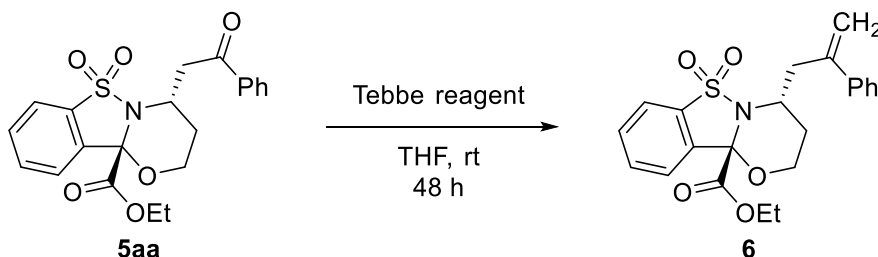
7. Procedure for the gram-scale synthesis of 5*aa*



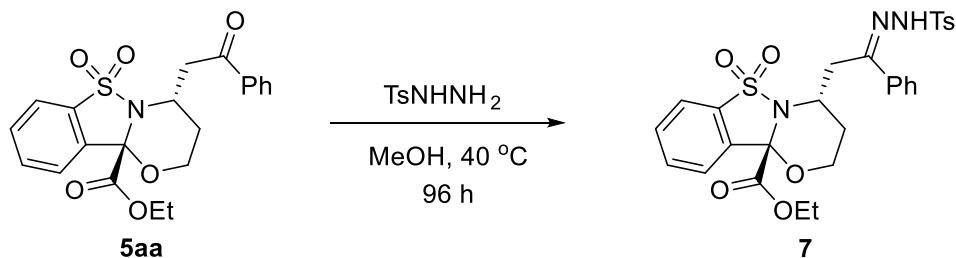
A solution of cyclic *N*-sulfonyl ketimine **1a** (1.08 g, 4.5 mmol, 1.5 equiv) and catalyst **Ib** (95 mg, 0.15 mmol, 0.05 equiv) in ClCH₂CH₂Cl (30 mL, 0.1 M) was stirred for 10 min at 0 °C and then added δ -hydroxy- α,β -unsaturated ketone **4a** (529 mg, 3.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 24 h. Then, the resulting mixture was concentrated in vacuo and was purified by flash

column chromatography with 20% to 30% EtOAc/hexanes as eluent to afford desired product **5aa** (1.08 g, 87% yield, >20:1 dr, >99% ee) as a white solid.

8. Synthetic transformation



Ethyl (4*R*,10*bS*)-4-(2-phenylallyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (6**);** To a solution of 1,3-oxazinane **5aa** (42 mg, 0.10 mmol) in THF (1.5 mL) was added dropwise Tebbe reagent (0.5 M solution in toluene, 0.60 mL, 0.30 mmol) at 0 °C. The reaction mixture was stirred for 48 hour at room temperature. Then, the resulting mixture was quenched with sat. NaHCO₃ solution and extracted with Et₂O. The combined organic layers were washed with brine, dried (anhydrous Na₂SO₄), and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **6**; 30 mg, yield 74%, [α]_D²³ = 140.5 (*c* = 1.03, CHCl₃); >99% ee; Yellow solid; m.p. 148-150 °C; *R*_f 0.3 (EtOAc:CH₂Cl₂:Hexane=1:10:9); ¹H NMR (400 MHz, CDCl₃) δ 7.85–7.80 (m, 1H), 7.68–7.58 (m, 3H), 7.52–7.45 (m, 2H), 7.38–7.33 (m, 2H), 7.32–7.27 (m, 1H), 5.47 (s, 1H), 5.31 (s, 1H), 4.27 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.18–4.08 (m, 2H), 3.86 (dtd, *J* = 24.5, 13.0, 2.6 Hz, 2H), 3.70–3.63 (m, 1H), 3.26 (dd, *J* = 13.8, 10.8 Hz, 1H), 2.09 (qd, *J* = 12.4, 4.9 Hz, 1H), 1.52 (dq, *J* = 13.8, 2.6 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7, 143.4, 139.4, 135.8, 133.4, 131.6, 128.6, 127.9, 126.1, 124.1, 121.2, 116.2, 89.3, 65.7, 62.9, 53.8, 36.9, 27.4, 14.0; IR (neat) 2973, 2924, 2874, 1737, 1598, 1493, 1452, 1377, 1303, 1256, 1237, 1164, 1092 cm⁻¹; HRMS (EI) *m/z* calcd for [M]⁺ C₂₂H₂₃NO₅S: 413.1297 Found: 413.1304; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer *t*_r = 32.8 min and *major*-isomer *t*_r = 58.1 min.



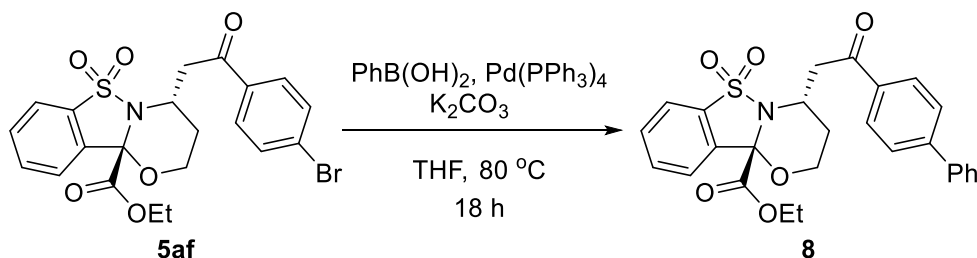
Ethyl (4*S*,10*bS*)-4-((*E*)-2-phenyl-2-(2-tosylhydrazineylidene)ethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (7);

To a solution of *p*-toluenesulfonyl hydrazide (38 mg, 0.20 mmol) and molecular sieve 4 Å (10 mg) in MeOH (1.0 mL) was added 1,3-oxazinane **5aa** (42 mg, 0.10 mmol) at room temperature. The reaction mixture was stirred at 40 °C in an oil bath until 1,3-oxazinane **5aa** was completely consumed, as determined by TLC. Then, the resulting mixture was filtered through the plug of celite. The filtrate was concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **7**; 53 mg, yield 91%, 2:1 dr.

Major isomer; 33 mg, yield 57%, $[\alpha]_{\text{D}}^{22} = 33.5$ ($c = 0.65$, CHCl₃); >99% ee; White solid; m.p. 100-102 °C; R_f 0.3 (Acetone:Hexane=3:7); ¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.91 (d, $J = 7.9$ Hz, 2H), 7.87–7.82 (m, 1H), 7.75–7.61 (m, 5H), 7.41–7.33 (m, 3H), 7.31–7.26 (m, 2H), 4.29–4.14 (m, 2H), 4.11–4.02 (m, 1H), 3.93 (t, $J = 11.1$ Hz, 1H), 3.85–3.70 (m, 2H), 3.55 (dd, $J = 14.5, 10.1$ Hz, 1H), 2.39 (s, 3H), 2.21 (qd, $J = 12.5, 4.8$ Hz, 1H), 1.34 (d, $J = 15.9$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.2, 150.8, 144.1, 135.7, 135.2, 135.1, 133.8, 133.2, 131.8, 129.9, 129.5, 128.6, 128.2, 126.4, 124.2, 121.4, 89.4, 65.2, 63.4, 51.9, 28.4, 28.1, 21.6, 14.0; IR (neat) 2923, 2845, 2802, 1744, 1698, 1595, 1444, 1395, 1299, 1235, 1164, 1133, 1053 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₈H₂₉N₃O₇S₂: 583.1447 Found: 583.1455; Chiralpak IC column and IC guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 47.8$ min and *major*-isomer $t_r = 72.1$ min.

Minor isomer; 16 mg, yield 28%, $[\alpha]_{\text{D}}^{24} = 46.2$ ($c = 1.03$, CHCl₃); >99% ee; White solid; m.p. 92-94 °C; R_f 0.2 (Acetone:Hexane=3:7); ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.72 (m, 3H), 7.70–7.60 (m, 3H), 7.56 (s, 1H), 7.53–7.43 (m, 3H), 7.26–7.16 (m, 4H), 4.35 (qd, $J = 7.1, 5.4$ Hz, 2H), 4.14 (dddd, $J = 16.8, 6.9, 4.6, 2.3$ Hz, 2H), 4.01 (td, $J = 12.2, 2.6$ Hz, 1H), 3.70 (dd, $J = 16.8, 4.0$ Hz, 1H), 3.25 (dd, $J = 16.8, 10.1$ Hz, 1H), 2.40 (s, 3H), 2.06 (qd, $J = 12.4, 5.0$ Hz, 1H), 1.54 (dq, $J = 13.3, 2.4$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.5, 152.6, 144.1, 135.5, 135.3, 133.60, 133.57, 132.1, 131.6, 130.3, 129.8, 129.5, 127.9, 126.8, 124.1, 121.1, 89.3, 65.5, 63.1, 51.7, 38.6, 27.6, 21.6, 14.1; IR (neat) 3234, 3202,

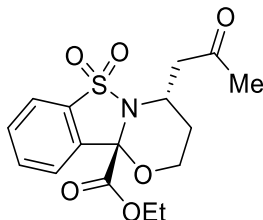
3187, 1743, 1597, 1493, 1445, 1385, 1341, 1302, 1235, 1163, 1092 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_7\text{S}_2$: 583.1447 Found: 583.1443; Chiralpak IC column and IC guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254 \text{ nm}$); *major*-isomer $t_r = 36.5 \text{ min}$ and *minor*-isomer $t_r = 61.2 \text{ min}$.



Ethyl (4*S*,10*bS*)-4-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (8); To a solution of 1,3-oxazinane **5af** (49 mg, 0.10 mmol), phenylboronic acid (37 mg, 0.30 mmol), and $\text{Ph}(\text{PPh}_3)_4$ (12 mg, 0.010 mmol) in THF (1.0 mL) was added K_2CO_3 (42 mg, 0.20 mmol) at room temperature. The reaction mixture was stirred at 80 °C in an oil bath until 1,3-oxazinane **5af** was completely consumed, as determined by TLC. Then, the resulting mixture was filtered through the plug of celite. The filtrate quenched with water and extracted with EtOAc. The combined organic layers were washed with brine, dried (anhydrous Na_2SO_4), and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexane/ CH_2Cl_2 as eluent to afford desired product **8**; 28 mg, yield 57%, >20:1 dr, $[\alpha]_D^{25} = 12.5$ ($c = 1.10$, CHCl_3); 99% ee; White solid; m.p. 148–150 °C; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=1:10:9); ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.5 \text{ Hz}$, 2H), 7.85–7.80 (m, 1H), 7.72 (d, $J = 8.5 \text{ Hz}$, 2H), 7.70–7.61 (m, 5H), 7.52–7.45 (m, 2H), 7.45–7.38 (m, 1H), 4.51–4.39 (m, 2H), 4.35 (qd, $J = 7.1, 3.5 \text{ Hz}$, 1H), 4.29 (dd, $J = 17.7, 3.8 \text{ Hz}$, 1H), 4.26–4.13 (m, 2H), 3.87 (dd, $J = 17.7, 9.7 \text{ Hz}$, 1H), 2.26–2.11 (m, 1H), 1.79 (dq, $J = 13.3, 2.3 \text{ Hz}$, 1H), 1.34 (t, $J = 7.1 \text{ Hz}$, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.3, 166.6, 146.2, 139.7, 135.6, 135.0, 133.63, 133.61, 131.6, 128.9, 128.8, 128.3, 127.3, 127.3, 124.1, 121.2, 89.4, 65.5, 63.2, 50.9, 39.3, 28.3, 14.1; IR (neat) 3024, 2093, 2924, 1742, 1682, 1603, 1454, 1385, 1302, 1237, 1195, 1161, 1054 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{27}\text{H}_{25}\text{NO}_6\text{S}$: 491.1403 Found: 491.1396; Chiralpak OD-H column and OD-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254 \text{ nm}$); *minor*-isomer $t_r = 17.6 \text{ min}$ and *major*-isomer $t_r = 26.9 \text{ min}$.

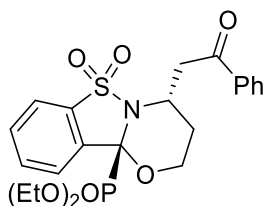
9. Control experiment

Ethyl (4*S*,10*bS*)-4-(2-oxopropyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazine-10*b*-carboxylate 6,6-dioxide (9)



Synthesized by the general procedure II; 5 mg, yield 15%, >20:1 dr, $[\alpha]_D^{26} = 16.8$ ($c = 0.21$, CHCl_3); 58% ee; Colorless gum; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=3:10:7); ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.76 (m, 1H), 7.73–7.57 (m, 3H), 4.43–4.28 (m, 2H), 4.26–4.07 (m, 3H), 3.75 (dd, $J = 18.2, 4.9$ Hz, 1H), 3.19 (dd, $J = 18.2, 8.8$ Hz, 1H), 2.29 (s, 3H), 2.10 (dtd, $J = 13.3, 12.1, 5.2$ Hz, 1H), 1.62 (dq, $J = 13.3, 2.5$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 204.2, 166.5, 135.3, 133.60, 133.58, 131.6, 124.1, 121.2, 89.3, 65.5, 63.2, 50.2, 43.9, 30.6, 28.0, 14.1; IR (neat) 2959, 2875, 1745, 1697, 1598, 1451, 1389, 1298, 1260, 1177, 1055 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_6\text{S}$: 353.0933 Found: 353.0941; Chiralpak OD-H column and OD-H guard column (7% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 19.9$ min and *minor*-isomer $t_r = 24.0$ min.

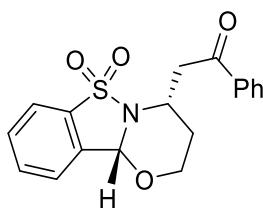
Diethyl ((4*S*,10*bS*)-6,6-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazin-10*b*-yl)phosphonate (11)



Synthesized by the general procedure I; 26 mg, yield 53%, 2:1 dr, $[\alpha]_D^{26} = 11.5$ ($c = 0.60$, CHCl_3); 89% ee; White solid; m.p. 132–134 $^{\circ}\text{C}$; R_f 0.2 (EtOAc: CH_2Cl_2 :Hexane=3:25:10); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.00 (m, 2H), 7.92 (d, $J = 7.7$ Hz, 1H), 7.78 (d, $J = 7.7$ Hz, 1H), 7.74–7.63 (m, 2H), 7.62–7.56 (m, 1H), 7.53–7.45 (m, 2H), 5.37 (dddd, $J = 12.1, 8.8, 5.2, 3.7$ Hz, 1H), 4.63 (dddd, $J = 11.7, 9.5, 4.3, 2.5$ Hz, 1H), 4.36–4.18 (m, 5H), 3.94 (dt, $J = 11.4, 4.6$ Hz, 1H), 3.73 (dd, $J = 17.8, 8.8$ Hz, 1H), 2.18 (dddd, $J = 13.2, 11.7, 9.6, 5.3$ Hz, 1H), 2.00 – 1.90 (m, 1H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.4$

Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.5, 136.7, 134.9 (d, $J = 3.8$ Hz), 133.9 (d, $J = 2.8$ Hz), 133.5, 133.3, 131.4, 128.6, 128.1, 126.3, 120.6, 88.6 (d, $J = 205.2$ Hz), 65.0 (d, $J = 6.5$ Hz), 64.1 (d, $J = 2.7$ Hz), 63.8 (d, $J = 6.8$ Hz), 49.4, 39.8, 28.7, 16.4 (d, $J = 5.6$ Hz), 16.3 (d, $J = 5.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 12.15; IR (neat) 2957, 2904, 1747, 1684, 1597, 1449, 1303, 1241, 1162, 1134, 1029 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{26}\text{NO}_7\text{PS}$: 479.1168 Found: 479.1138; Chiralpak OJ-H column and OJ-H guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 16.2$ min and *major*-isomer $t_r = 32.0$ min.

2-((4*S*,10*bR*)-6,6-dioxido-3,4-dihydro-2*H*,10*bH*-benzo[4,5]isothiazolo[3,2-*b*][1,3]oxazin-4-yl)-1-phenylethan-1-one (13)



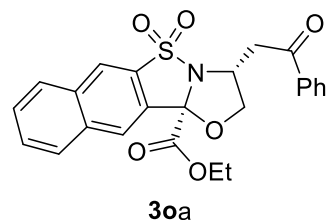
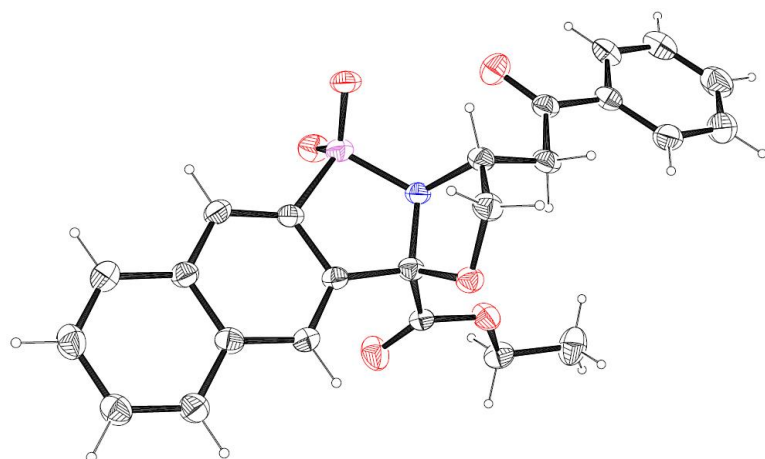
Synthesized by the general procedure II; 22 mg, yield 66%, 2:1 dr, $[\alpha]_D^{22} = 5.6$ ($c = 0.61$, CHCl_3); 94% ee; White solid; m.p. 187-189 $^\circ\text{C}$; R_f 0.3 (EtOAc: CH_2Cl_2 :Hexane=1:30:9); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.01 (m, 2H), 7.81–7.75 (m, 1H), 7.68–7.55 (m, 4H), 7.53–7.47 (m, 2H), 5.65 (s, 1H), 4.45 (tdd, $J = 9.0, 4.6, 2.3$ Hz, 1H), 4.31 (ddd, $J = 11.6, 4.6, 1.7$ Hz, 1H), 4.22 (dd, $J = 17.8, 4.7$ Hz, 1H), 4.07 (td, $J = 12.0, 2.3$ Hz, 1H), 3.69 (dd, $J = 17.8, 9.0$ Hz, 1H), 2.12 (dtd, $J = 13.4, 12.1, 4.6$ Hz, 1H), 1.79 (dd, $J = 13.3, 2.3$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.2, 136.7, 136.5, 134.1, 133.7, 133.3, 131.0, 128.8, 128.3, 125.0, 121.1, 86.4, 68.1, 52.9, 39.8, 29.3; IR (neat) 2925, 2854, 2352, 1727, 1676, 1449, 1361, 1260, 1166, 1137, 1092, 1054, 1029 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{17}\text{NO}_4\text{S}$: 343.0878 Found: 343.0892; Chiralpak IA column and IA guard column (50% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 19.8$ min and *major*-isomer $t_r = 26.8$ min.

1. (a) Huang, S.-H.; Shih, Y.-W.; Huang, W.-T.; Li, D.-H.; Yang, T.-F. *RSC Adv.* **2016**, *6*, 91870–91874.
(b) Liu, Y.; Ao, J.; Paladhi, S.; Song, C. E.; Yan, H. *J. Am. Chem. Soc.* **2016**, *138*, 16486–16492.
2. Yan, W.; Wang, D.; Feng, J.; Li, P.; Zhao, D.; Wang, R. *Org. Lett.* **2012**, *14*, 2512–2515.
3. (a) Malerich, J. P.; Hagihara, K.; Rawal, V. H. *J. Am. Chem. Soc.* **2008**, *130*, 14416–14417. (b) Yang, W.; Du, D. M. *Org. Lett.* **2010**, *12*, 5450–5453. (c) Zhu, Y.; Malerich, J. P.; Rawal, V. H. *Angew. Chem. Int. Ed.* **2010**, *49*, 153–156.

10. X-ray crystallography data of compound 30a and 5aa

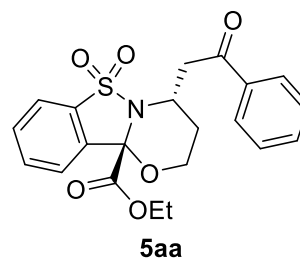
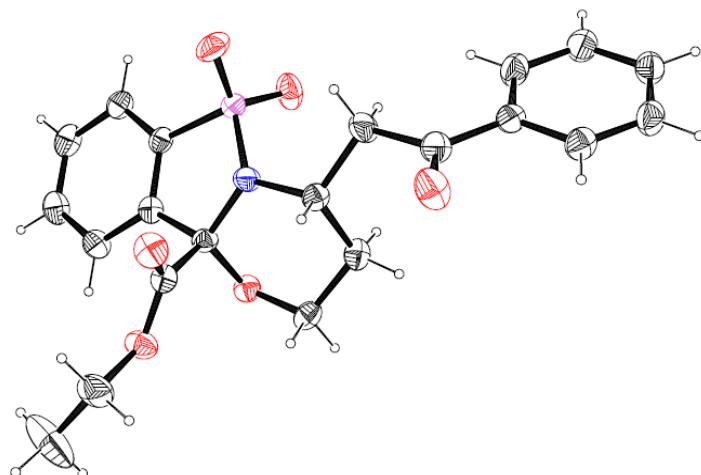
Sample preparation: The single crystal **30a** and **5aa** were obtained by slow diffusion of *n*-hexane in to a solution of **30a** or **5aa** in EtOAc at room temperature.

Crystal measurement: A crystal of **30a** and **5aa** were picked up with paratone oil and mounted on a Bruker D8 Venture PHOTON III M14 diffractometer equipped with a graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation source and a nitrogen cold stream (223 K). Data collection and integration were performed with SMART APEX3 (Bruker, 2016) and SAINT (Bruker, 2016). The absorption correction was performed by a multi-scan method implemented in SADABS. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added to their geometrically ideal positions. Thermal ellipsoids are drawn at 30% probability level.



Identification code	KGU_24_03_a	
Empirical formula	C ₂₄ H ₂₁ N O ₆ S	
Formula weight	451.48	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 9.792(2) Å	$\alpha = 90^\circ$.
	b = 10.139(3) Å	$\beta = 90^\circ$.

	$c = 21.399(6) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2124.5(9) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.412 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	944	
Crystal size	$0.253 \times 0.152 \times 0.122 \text{ mm}^3$	
Theta range for data collection	1.903 to 28.282° .	
Index ranges	$-13 \leq h \leq 10$, $-13 \leq k \leq 13$, $-28 \leq l \leq 28$	
Reflections collected	41951	
Independent reflections	5282 [$R(\text{int}) = 0.0960$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6646	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5282 / 0 / 290	
Goodness-of-fit on F^2	1.052	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0484$, $wR2 = 0.0844$	
R indices (all data)	$R1 = 0.1003$, $wR2 = 0.0988$	
Absolute structure parameter	0.03(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.179 and $-0.308 \text{ e.\AA}^{-3}$	

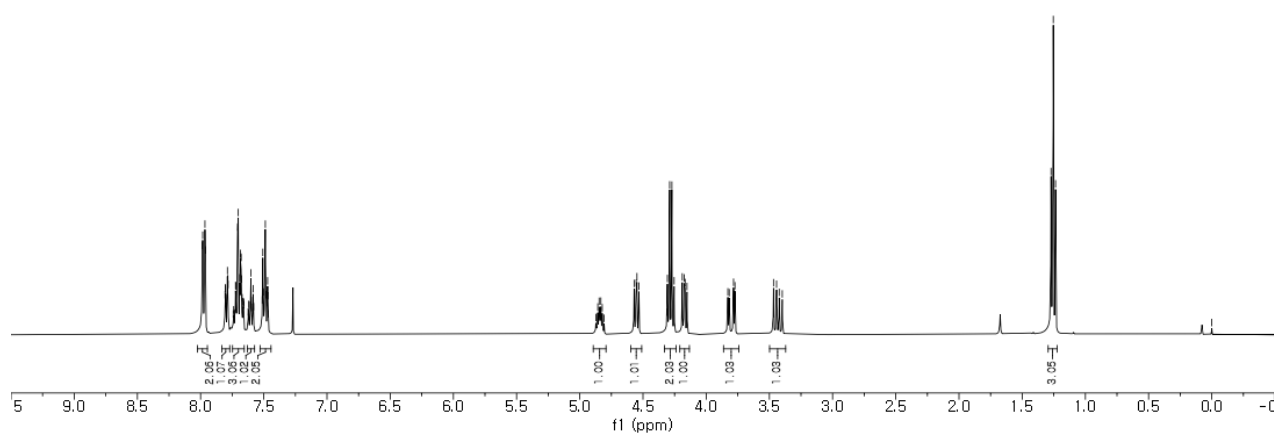
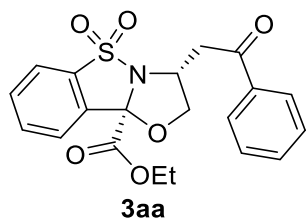
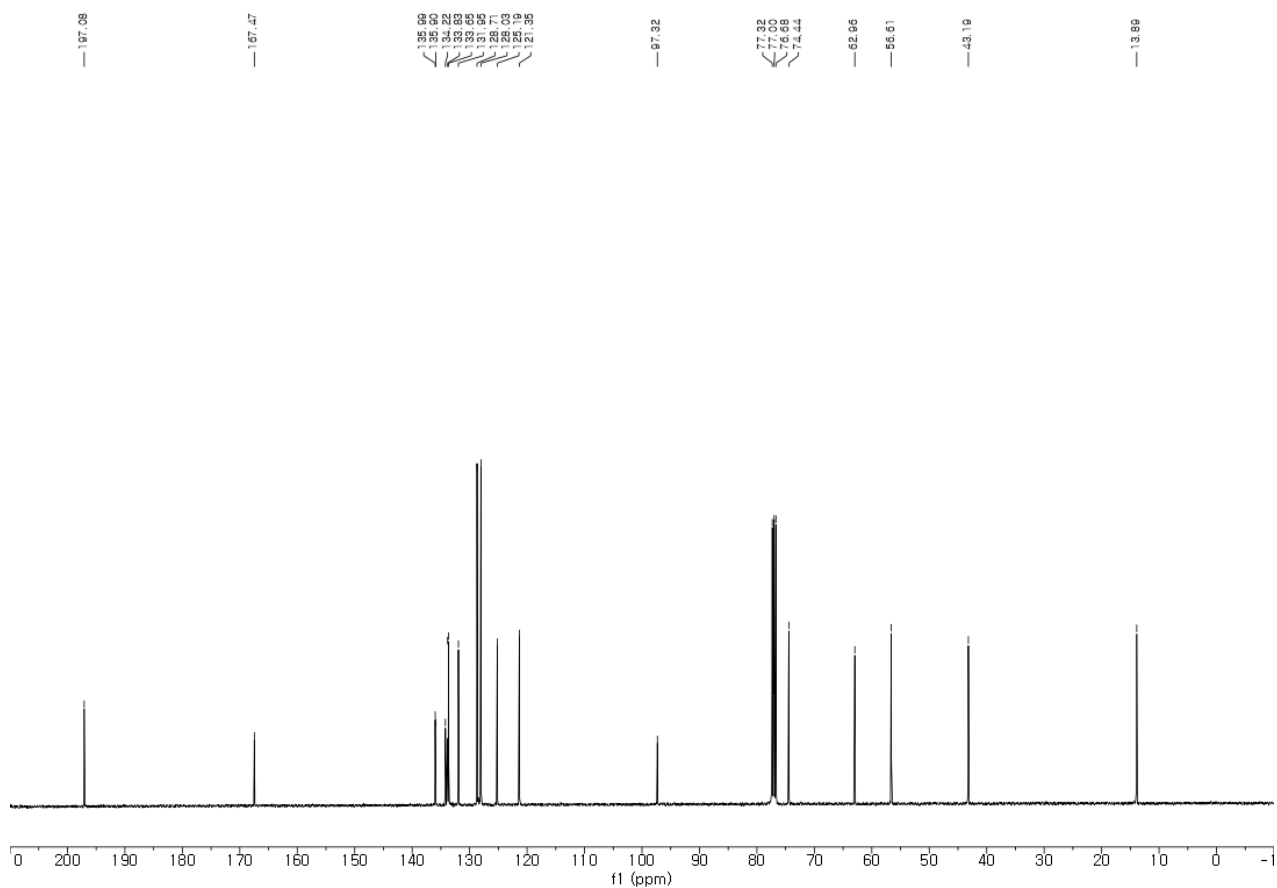


Identification code	KGU_24_06_a	
Empirical formula	C ₂₁ H ₂₁ N O ₆ S	
Formula weight	415.45	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4 ₁ 2 ₁ 2	
Unit cell dimensions	a = 8.4145(3) Å	α = 90°.
	b = 8.4145(3) Å	β = 90°.
	c = 56.119(4) Å	γ = 90°.
Volume	3973.5(4) Å ³	
Z	8	
Density (calculated)	1.389 Mg/m ³	
Absorption coefficient	0.202 mm ⁻¹	
F(000)	1744	
Crystal size	0.220 x 0.135 x 0.054 mm ³	
Theta range for data collection	2.448 to 28.275°.	
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 11, -74 ≤ l ≤ 74	
Reflections collected	98435	
Independent reflections	4926 [R(int) = 0.1444]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6765	
Refinement method	Full-matrix least-squares on F ²	

Data / restraints / parameters	4926 / 0 / 263
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0470$, $wR_2 = 0.0918$
R indices (all data)	$R_1 = 0.1172$, $wR_2 = 0.1172$
Absolute structure parameter	-0.03(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.204 and -0.270 e.Å ⁻³

^1H NMR (400 MHz) in CDCl_3 

8

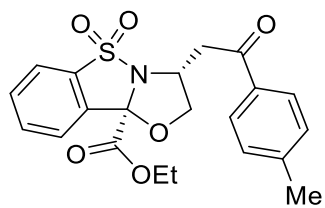
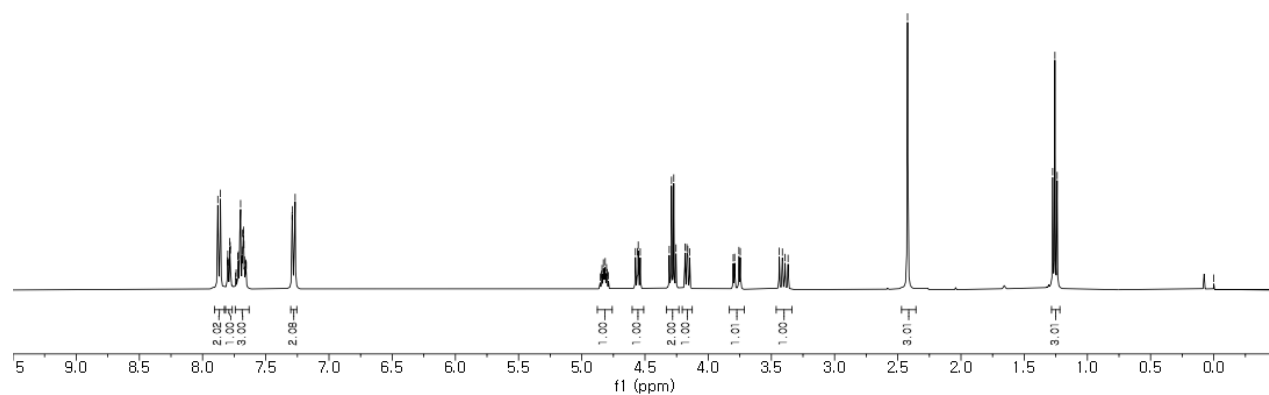
 **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3 

2.00

2.00

0.00

**3ab** **^{13}C NMR (100 MHz) in CDCl_3**

166.70

167.49

144.56

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97.31

77.32, 77.00, 76.68, 76.36, 76.04, 75.72, 75.40, 75.08, 74.76, 74.44, 74.12, 73.80, 73.48, 73.16, 72.84, 72.52, 72.20, 71.88, 71.56, 71.24, 70.92, 70.60, 70.28, 69.96, 69.64, 69.32, 69.00, 68.68, 68.36, 68.04, 67.72, 67.40, 67.08, 66.76, 66.44, 66.12, 65.80, 65.48, 65.16, 64.84, 64.52, 64.20, 63.88, 63.56, 63.24, 62.92, 62.60, 62.28, 61.96, 61.64, 61.32, 61.00, 60.68, 60.36, 60.04, 59.72, 59.40, 59.08, 58.76, 58.44, 58.12, 57.80, 57.48, 57.16, 56.84, 56.52, 56.20, 55.88, 55.56, 55.24, 54.92, 54.60, 54.28, 53.96, 53.64, 53.32, 53.00, 52.68, 52.36, 52.04, 51.72, 51.40, 51.08, 50.76, 50.44, 50.12, 49.80, 49.48, 49.16, 48.84, 48.52, 48.20, 47.88, 47.56, 47.24, 46.92, 46.60, 46.28, 45.96, 45.64, 45.32, 45.00, 44.68, 44.36, 44.04, 43.72, 43.40, 43.08, 42.76, 42.44, 42.12, 41.80, 41.48, 41.16, 40.84, 40.52, 40.20, 39.88, 39.56, 39.24, 38.92, 38.60, 38.28, 37.96, 37.64, 37.32, 37.00, 36.68, 36.36, 36.04, 35.72, 35.40, 35.08, 34.76, 34.44, 34.12, 33.80, 33.48, 33.16, 32.84, 32.52, 32.20, 31.88, 31.56, 31.24, 30.92, 30.60, 30.28, 29.96, 29.64, 29.32, 29.00, 28.68, 28.36, 28.04, 27.72, 27.40, 27.08, 26.76, 26.44, 26.12, 25.80, 25.48, 25.16, 24.84, 24.52, 24.20, 23.88, 23.56, 23.24, 22.92, 22.60, 22.28, 21.96, 21.64, 21.32, 21.00, 20.68, 20.36, 20.04, 19.72, 19.40, 19.08, 18.76, 18.44, 18.12, 17.80, 17.48, 17.16, 16.84, 16.52, 16.20, 15.88, 15.56, 15.24, 14.92, 14.60, 14.28, 13.96, 13.64, 13.32, 13.00, 12.68, 12.36, 12.04, 11.72, 11.40, 11.08, 10.76, 10.44, 10.12, 9.80, 9.48, 9.16, 8.84, 8.52, 8.20, 7.88, 7.56, 7.24, 6.92, 6.60, 6.28, 5.96, 5.64, 5.32, 5.00, 4.68, 4.36, 4.04, 3.72, 3.40, 3.08, 2.76, 2.44, 2.12, 1.80, 1.48, 1.16, 0.84, 0.52, 0.20, 0.00

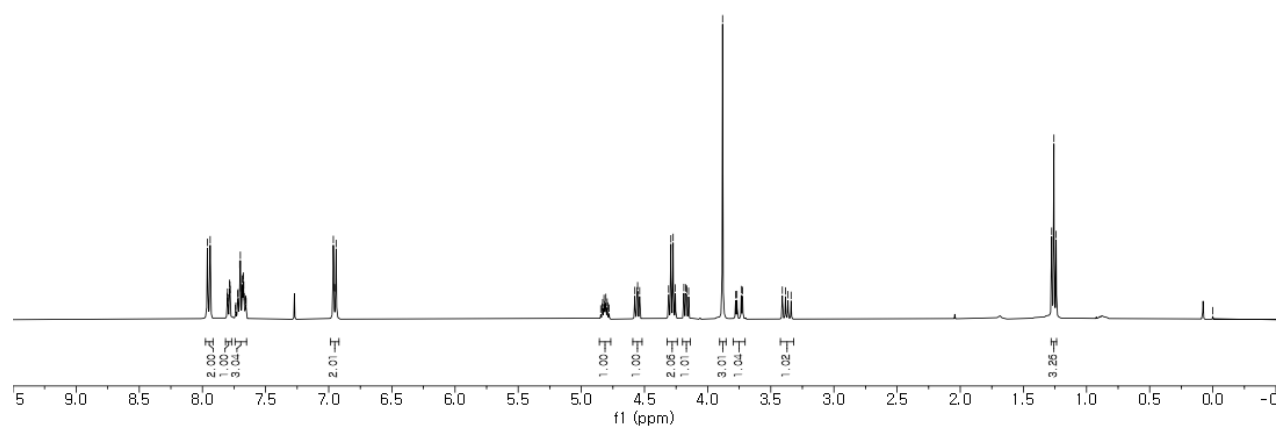
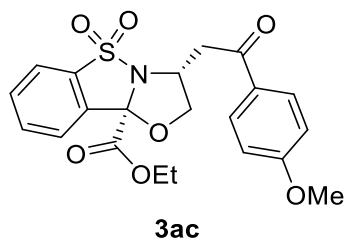
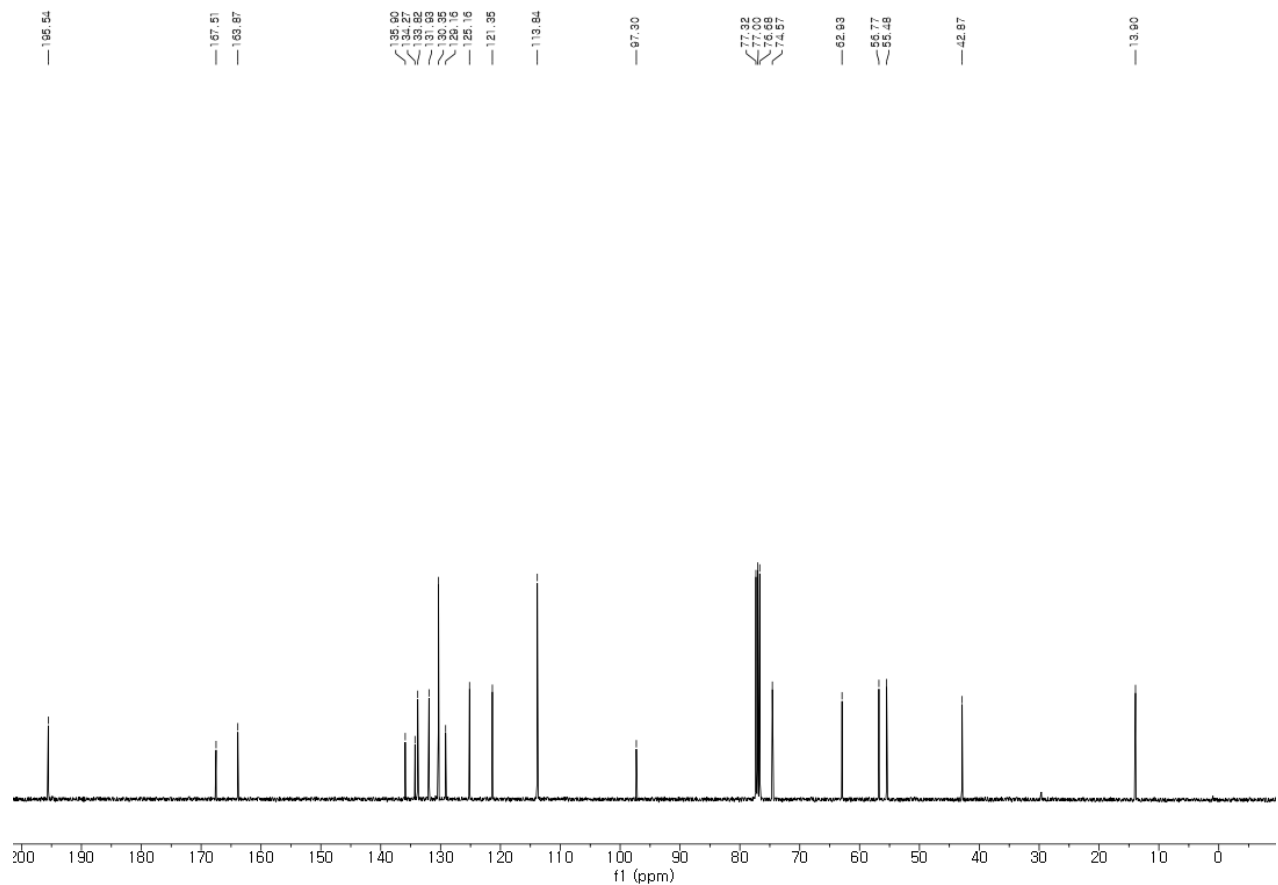
65.64

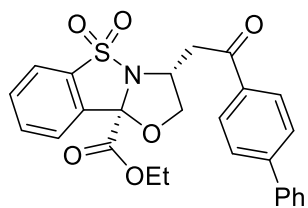
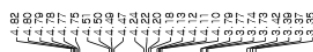
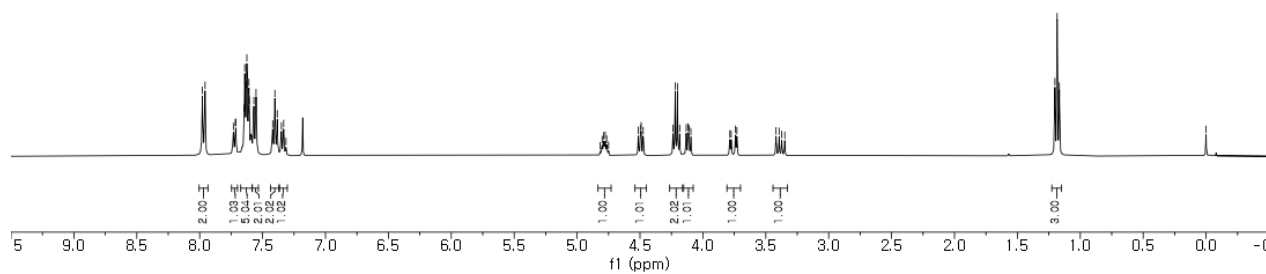
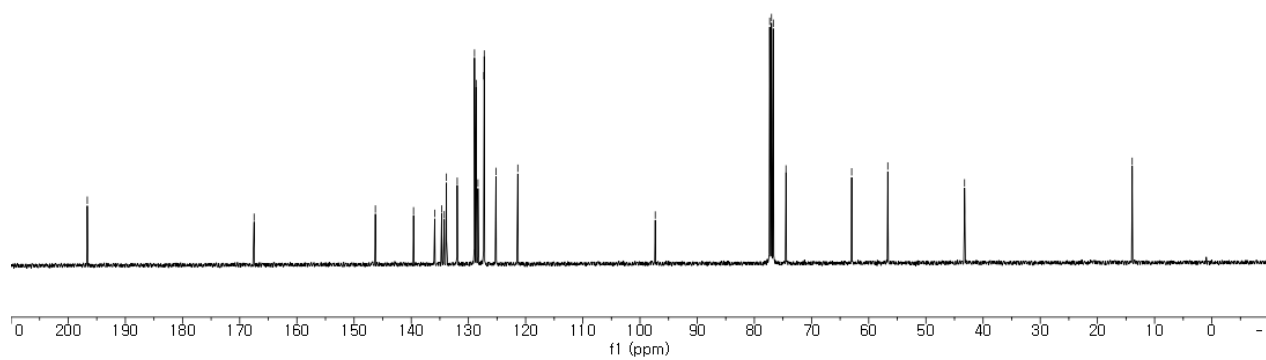
56.59

43.12

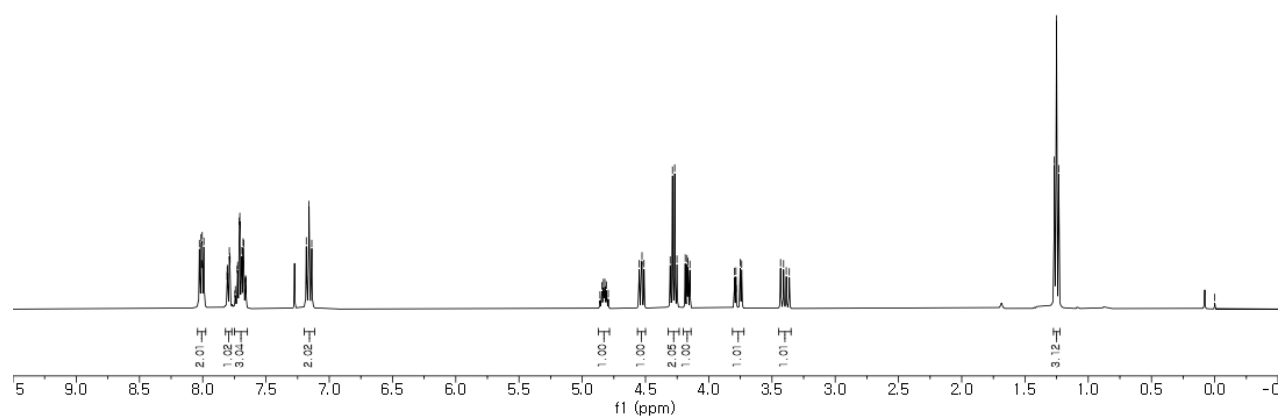
21.66

13.91

¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

^1H NMR (400 MHz) in CDCl_3 **3ad** **^{13}C NMR (100 MHz) in CDCl_3** 

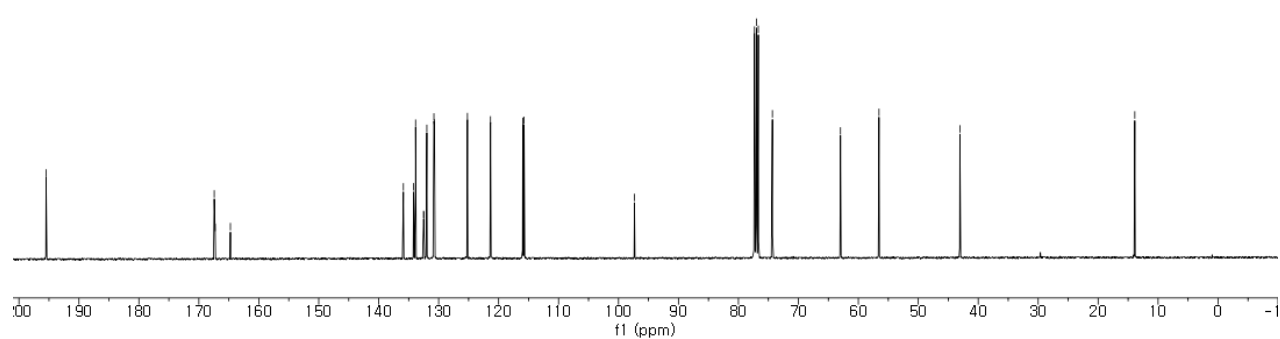
9.03
8.01
8.01
8.01
8.00
7.99
7.81
7.80
7.79
7.79
7.78
7.73
7.72
7.71
7.71
7.71
7.69
7.69
7.68
7.68
7.68
7.18
7.16
7.14
7.14

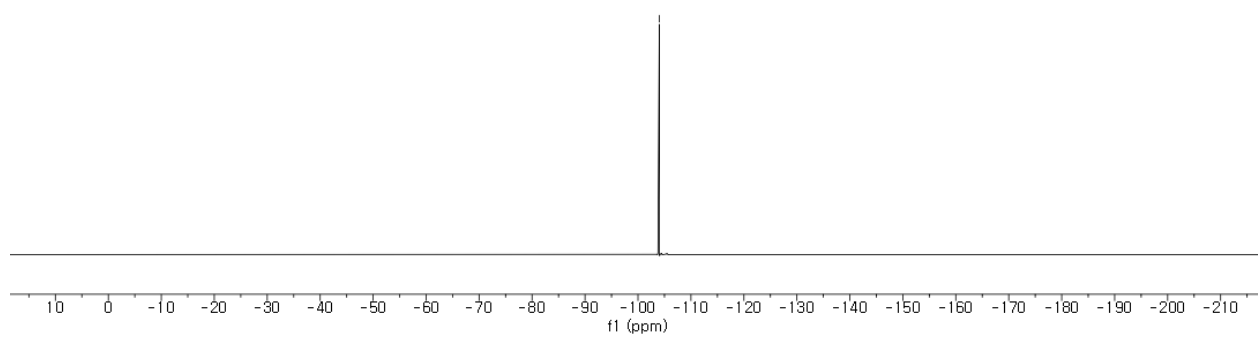
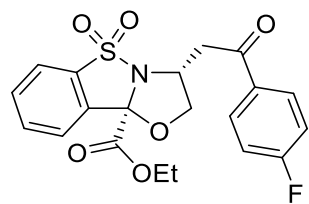


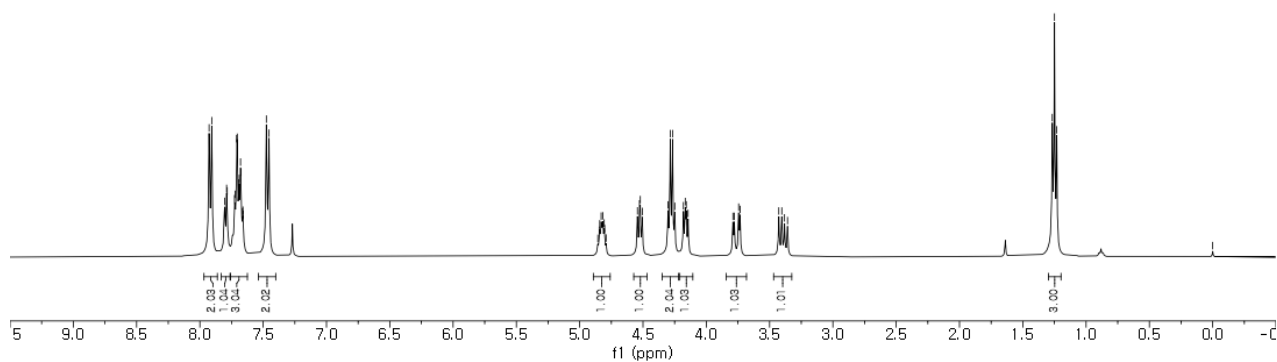
— 105.49 — 67.43
 67.29
 64.74

35.89
34.19
33.35
32.11
32.49
31.87
30.79
29.55

— 121.95 — 15.87
 15.75



^{19}F NMR (376 MHz) in CDCl_3 

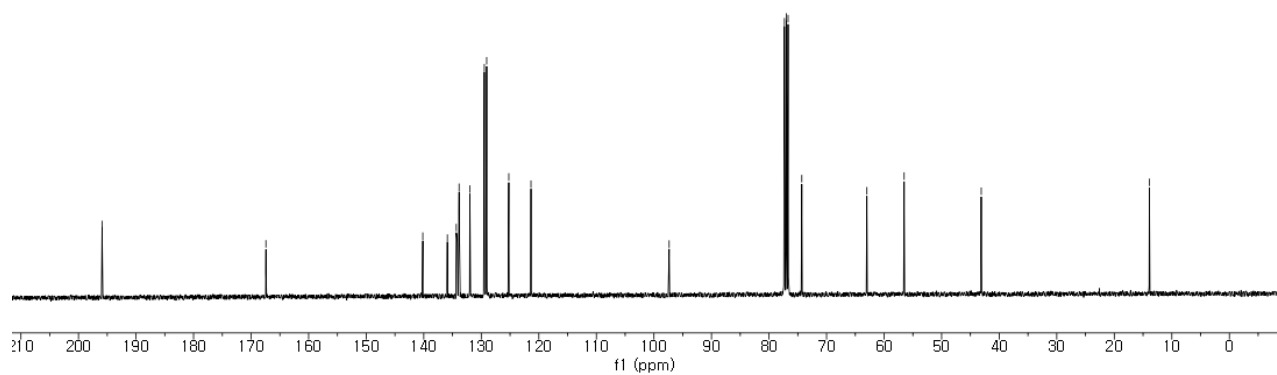


— 195.90

— 167.43

— 140.16

135.89
134.35
134.18
133.85
131.08
129.47
129.06
125.22
121.37

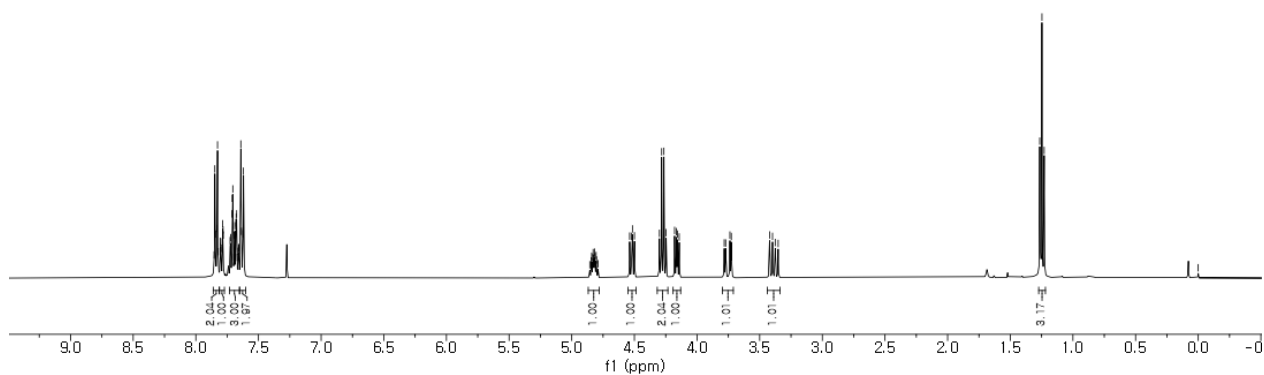
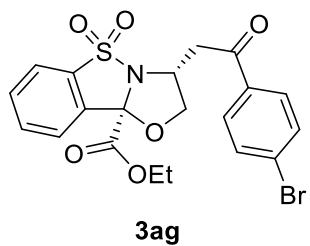


7.85
7.85
7.84
7.83
7.83
7.82
7.81
7.80
7.80
7.80
7.79
7.78
7.78
7.73
7.72
7.71
7.71
7.70
7.69
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.62
7.62

4.85
4.84
4.84
4.83
4.83
4.83
4.82
4.82
4.81
4.81
4.80
4.79
4.54
4.52
4.50
4.30
4.28
4.25
4.25
4.18
4.16
4.16
4.14
3.78
3.77
3.74
3.73
3.42
3.40
3.38
3.35

1.25
1.25
1.23

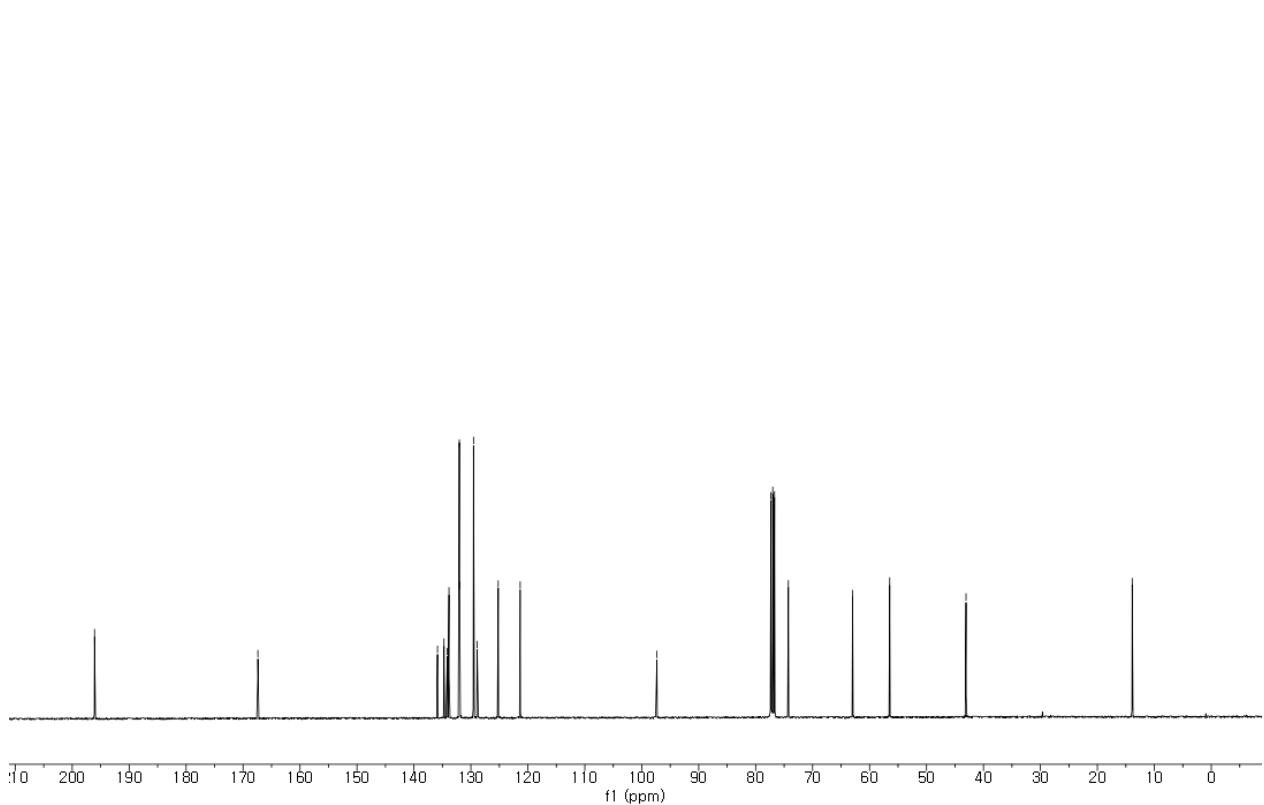
—0.00

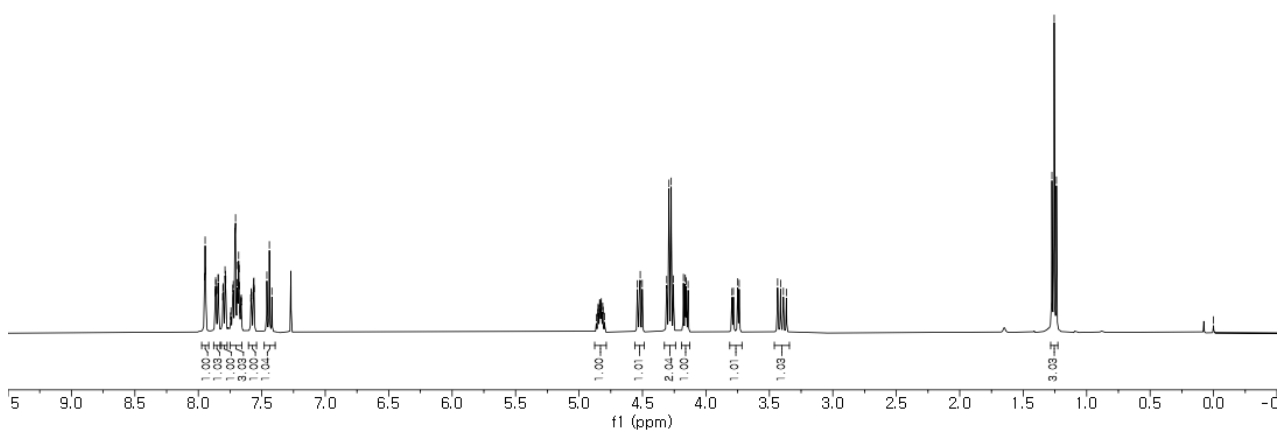
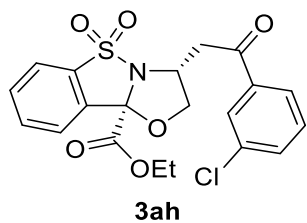


— 195.08

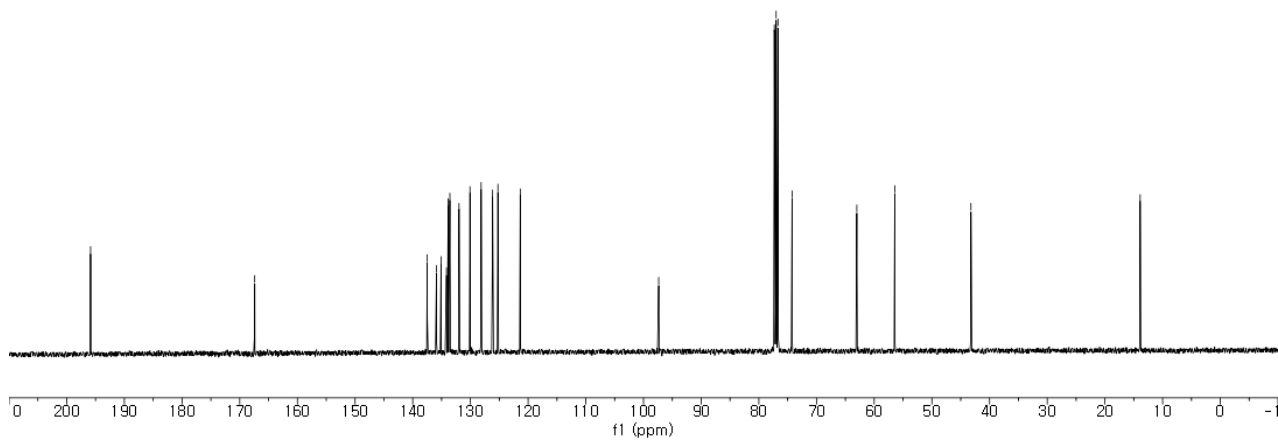
— 167.40

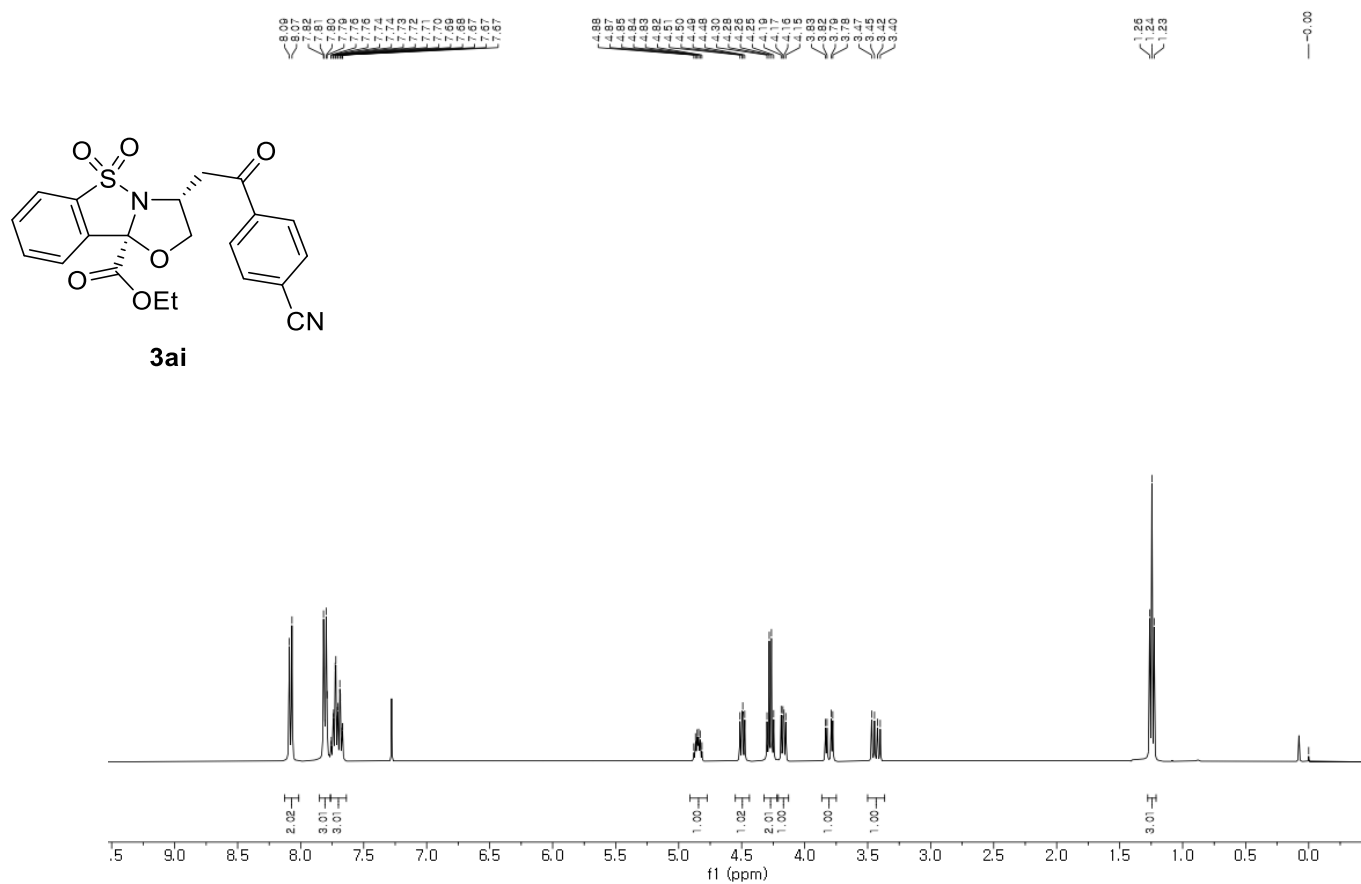
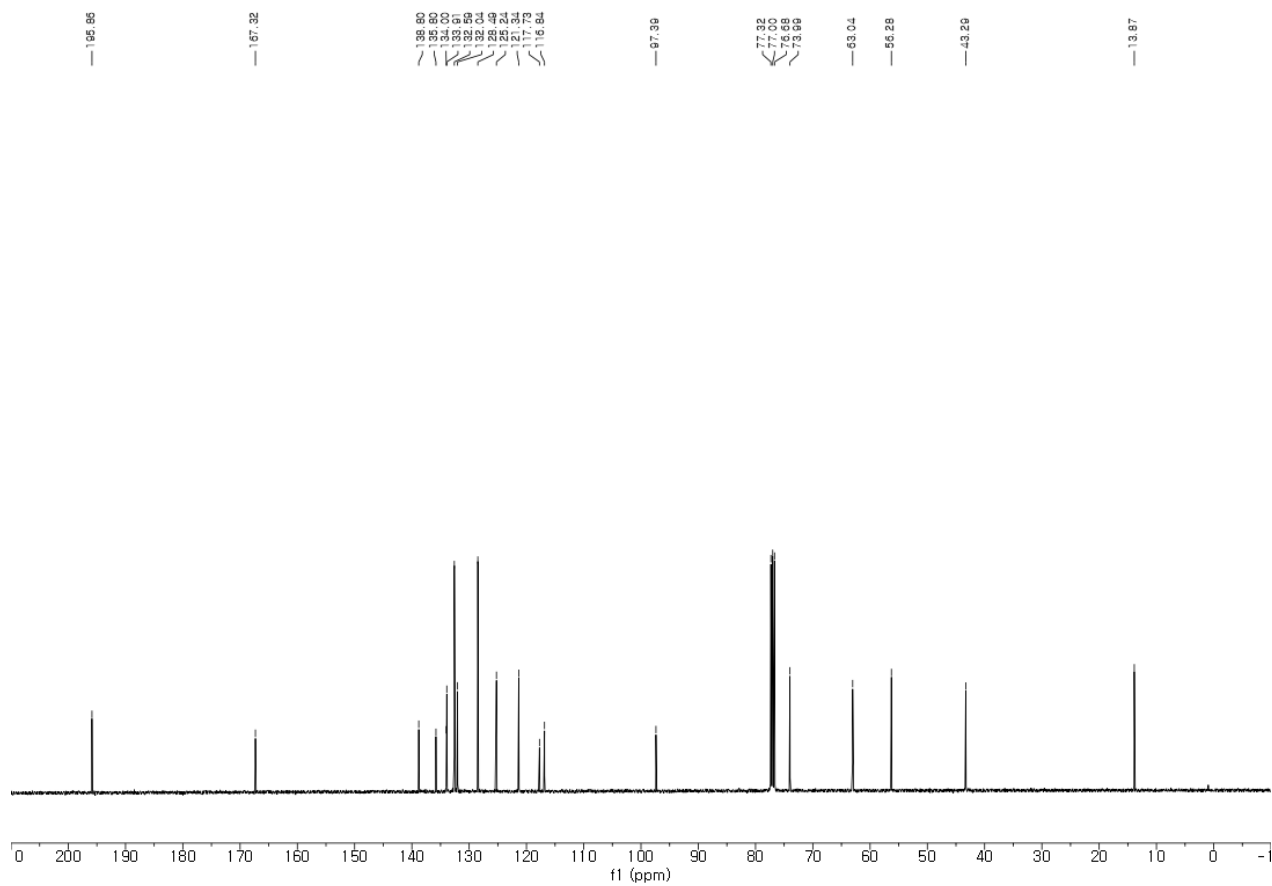
135.86
134.72
134.14
133.85
132.03
131.97
128.54
128.60
126.20
121.34

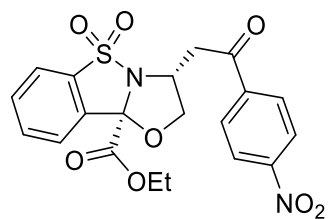
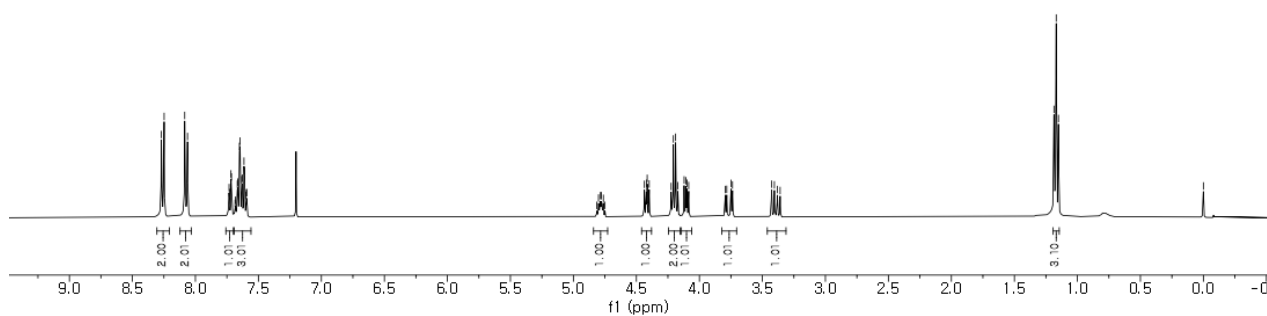


[illegible]

17.49
15.88
15.10
14.15
13.45
13.95
13.57
13.08
13.08
12.15
12.15
12.23
12.35



^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

¹H NMR (400 MHz) in CDCl₃**3aj****¹³C NMR (100 MHz) in CDCl₃**

196.69

167.33

150.55

140.27

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

138.51

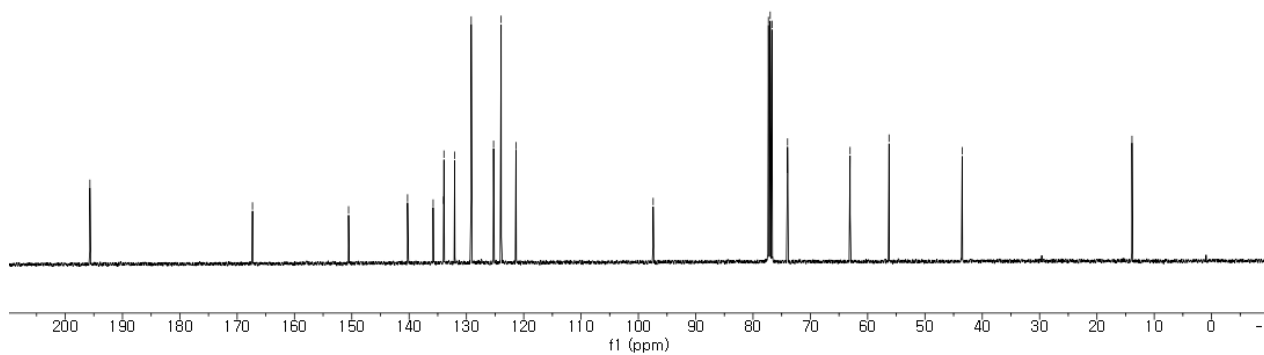
138.51

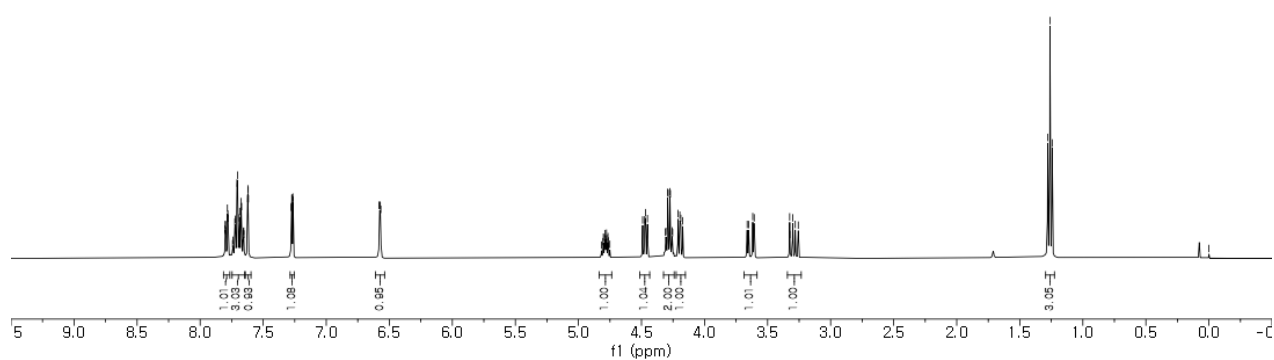
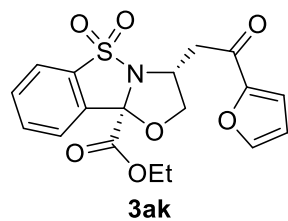
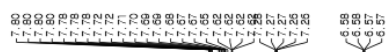
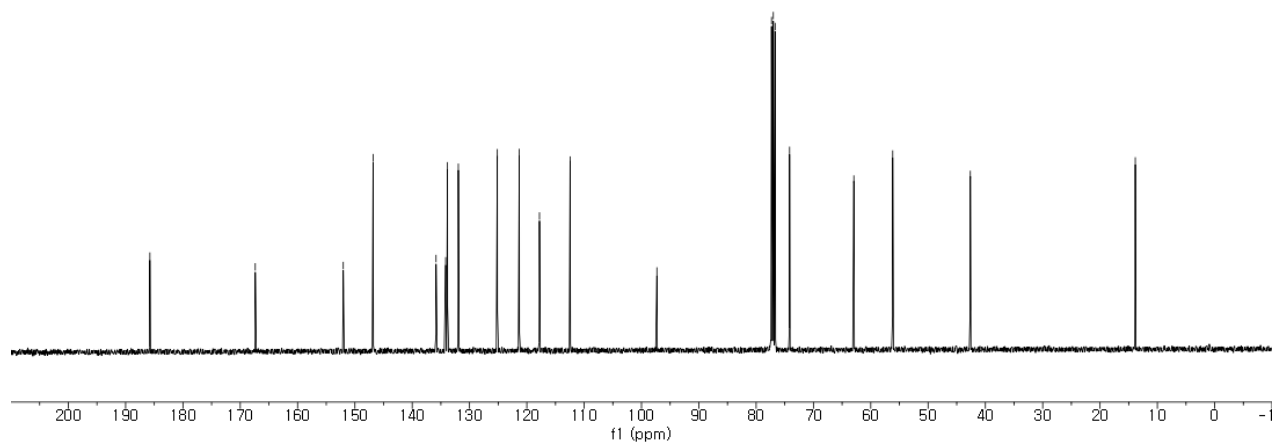
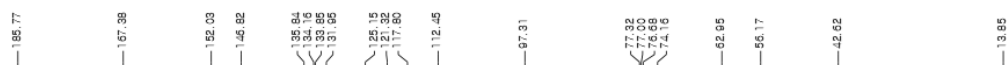
138.51

138.51

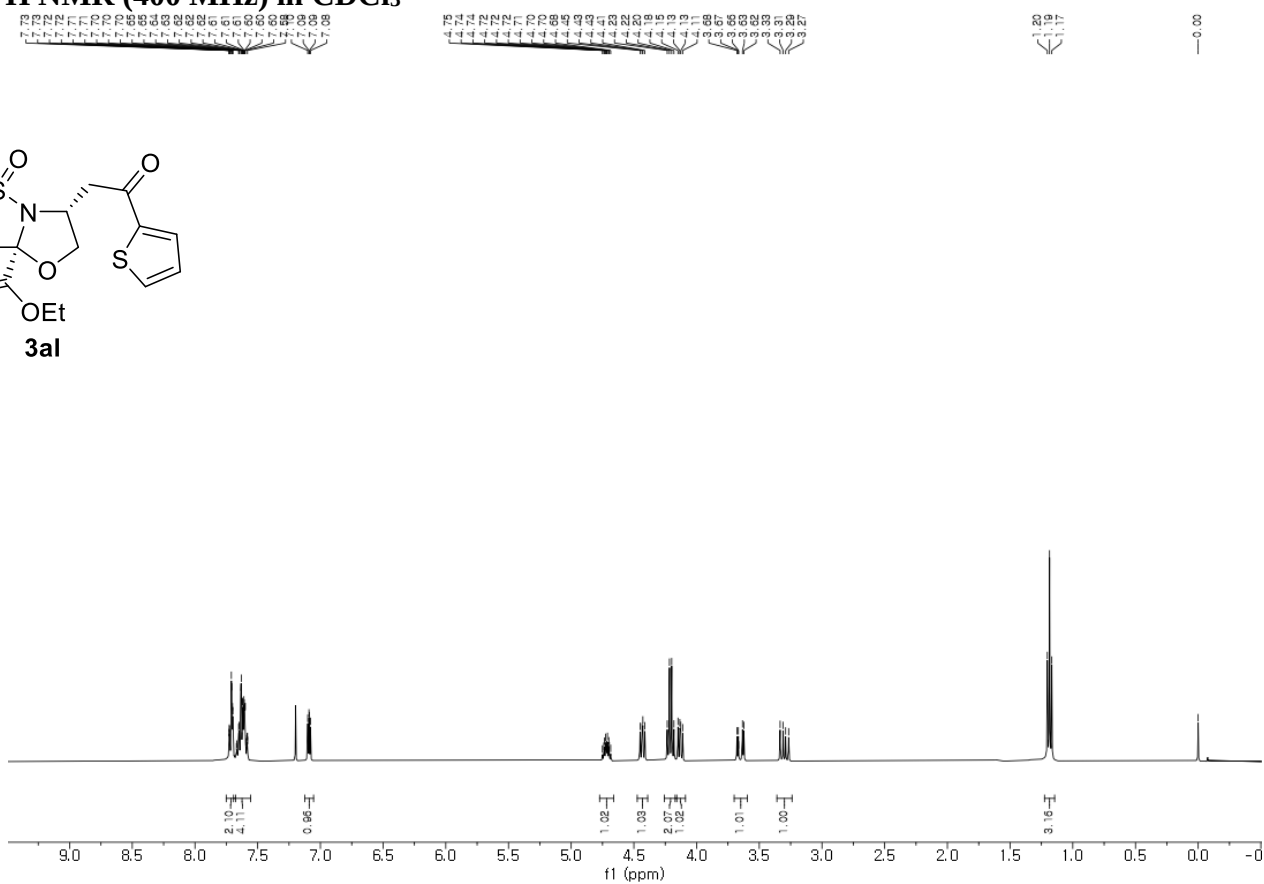
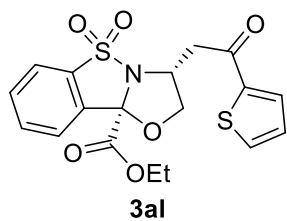
138.51

138.51



^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

7.73
7.73
7.72
7.72
7.71
7.71
7.70
7.70
7.70
7.65
7.65
7.64
7.63
7.62
7.62
7.61
7.61
7.61
7.60
7.60
7.59
7.09
7.08

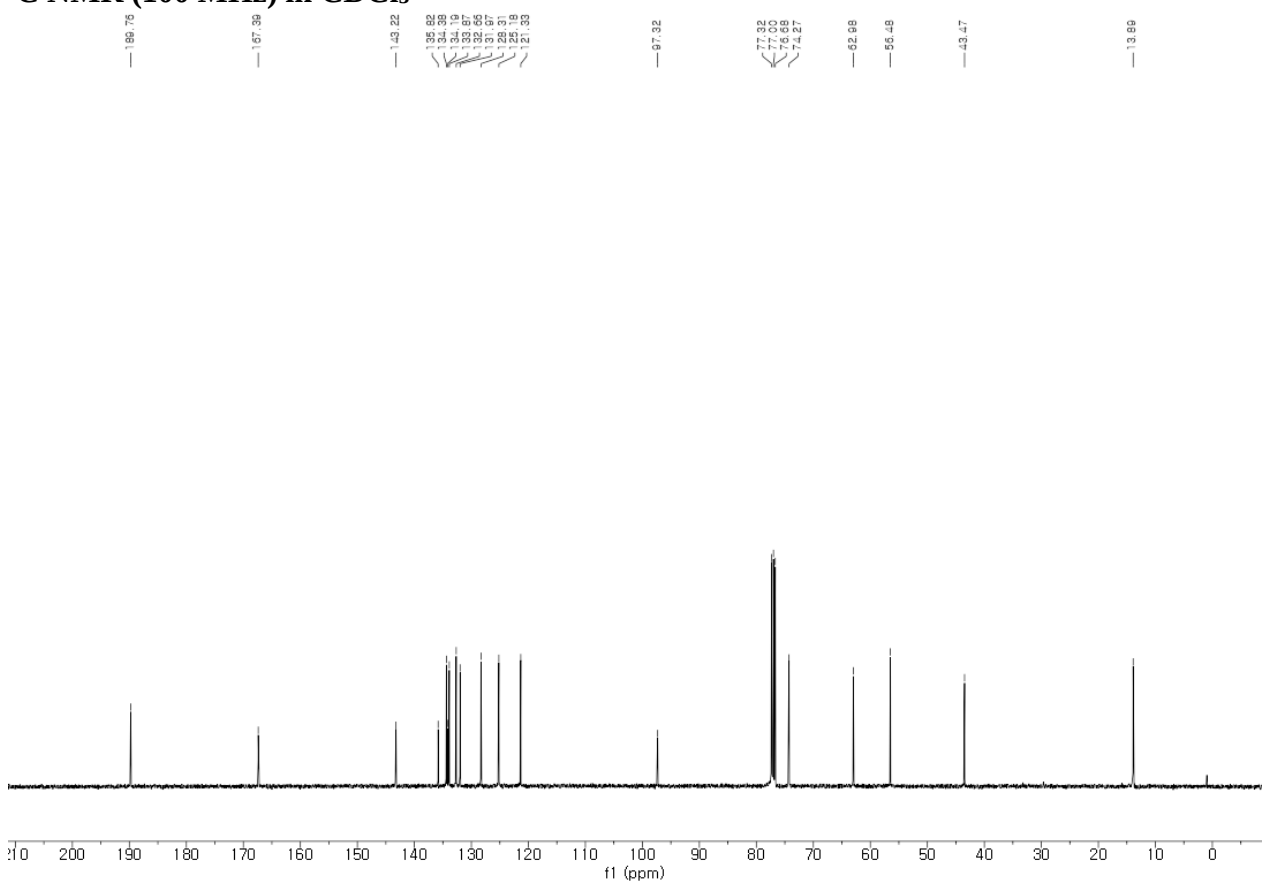


— 156.76

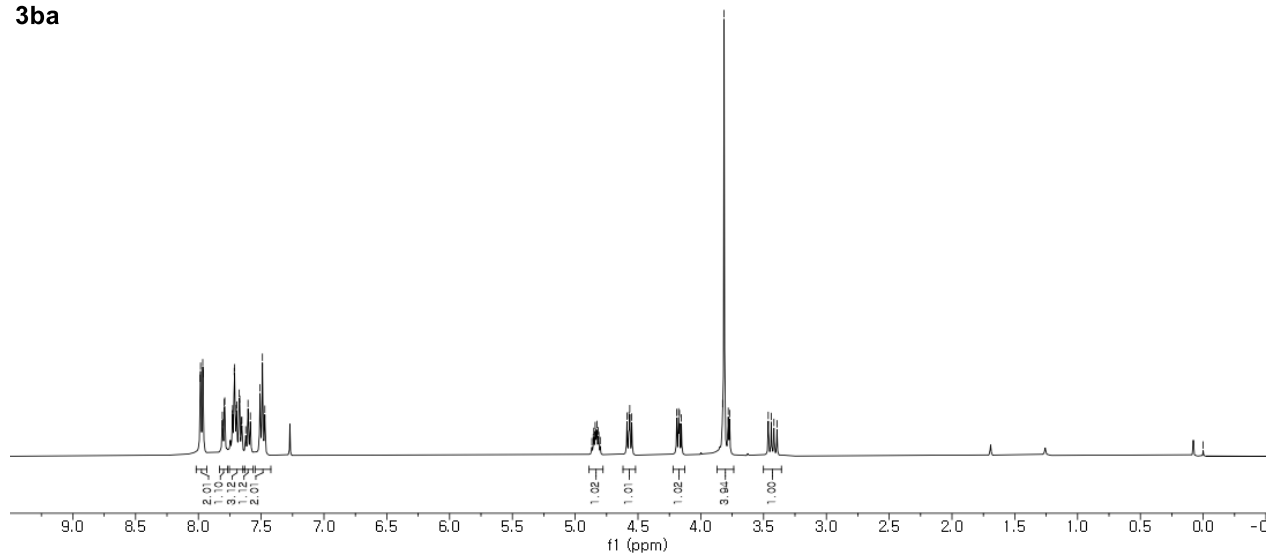
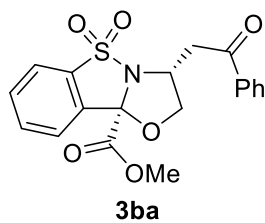
— 167.39

— 173.22

155.82
134.38
134.19
135.87
132.65
131.97
129.31
125.18
121.33



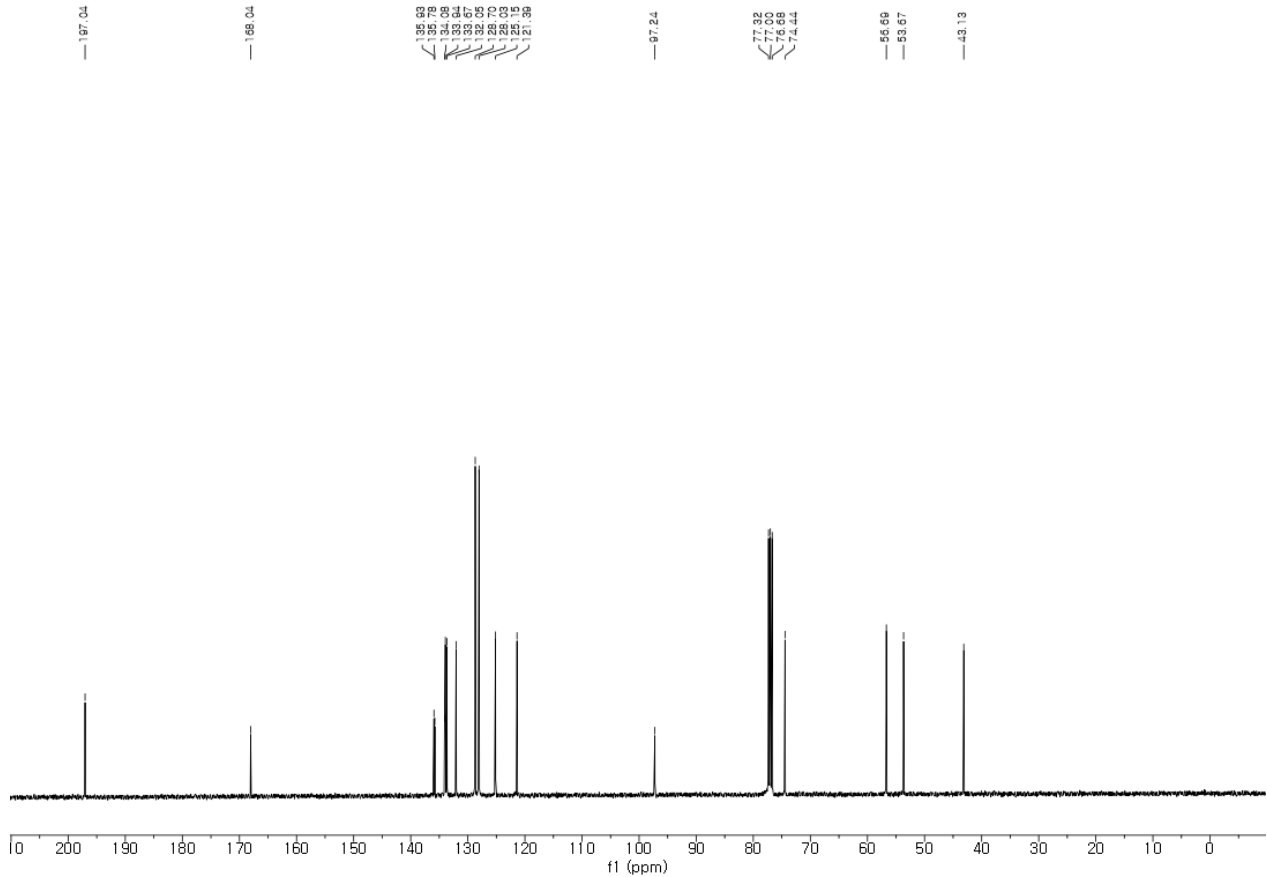
7.09
7.08
7.97
7.95
7.81
7.81
7.79
7.79
7.73
7.73
7.71
7.71
7.70
7.69
7.67
7.67
7.65
7.65
7.65
7.62
7.60
7.59
7.51
7.49
7.47

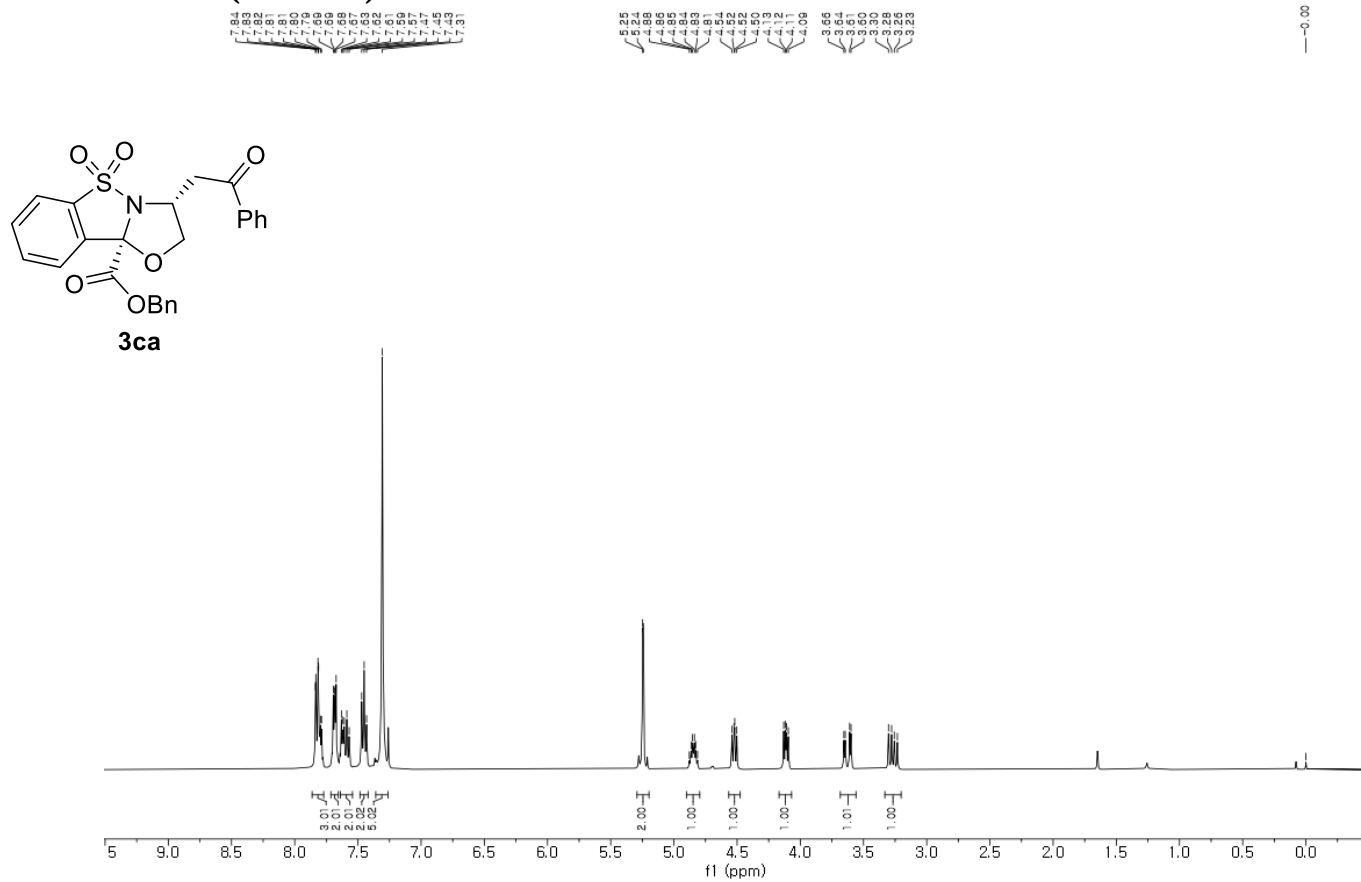
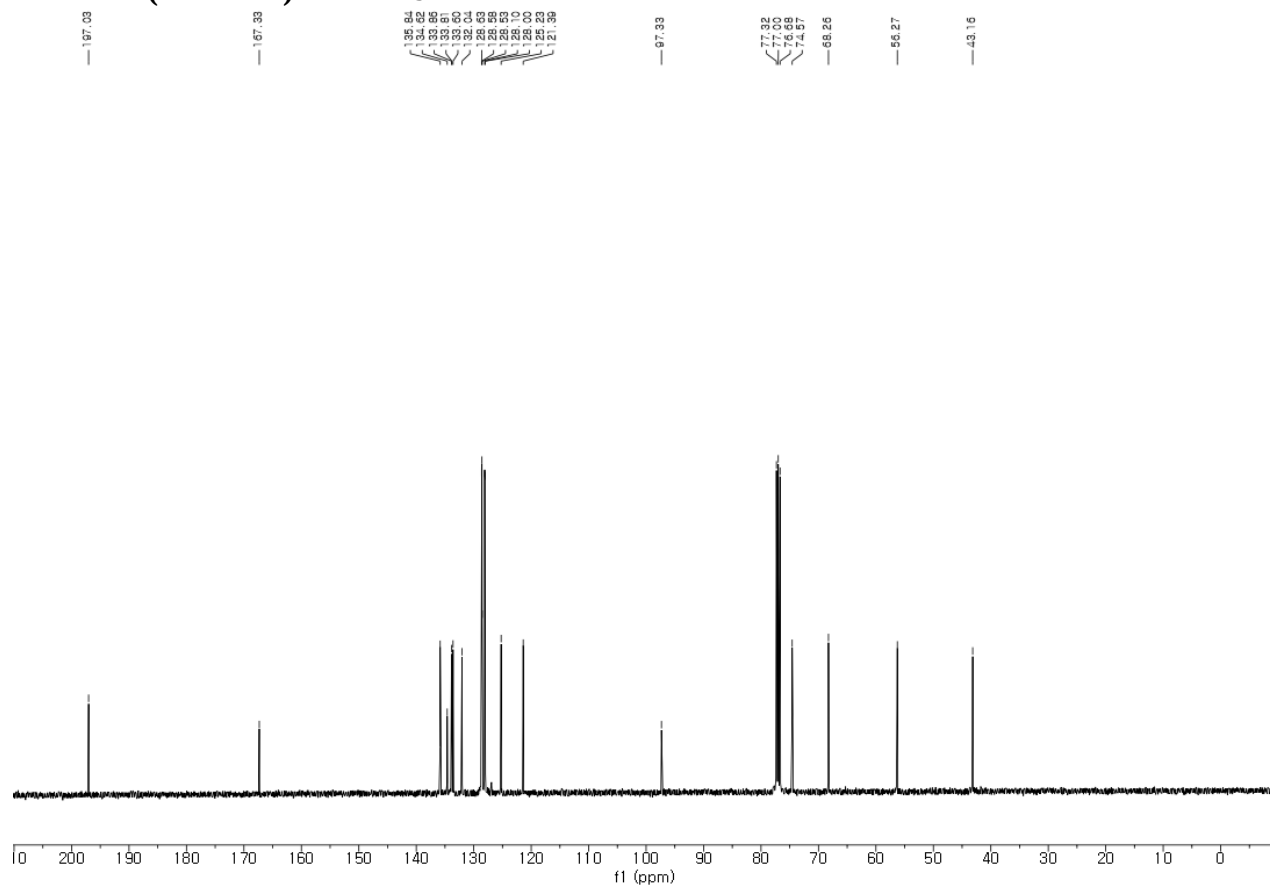


— 167.04

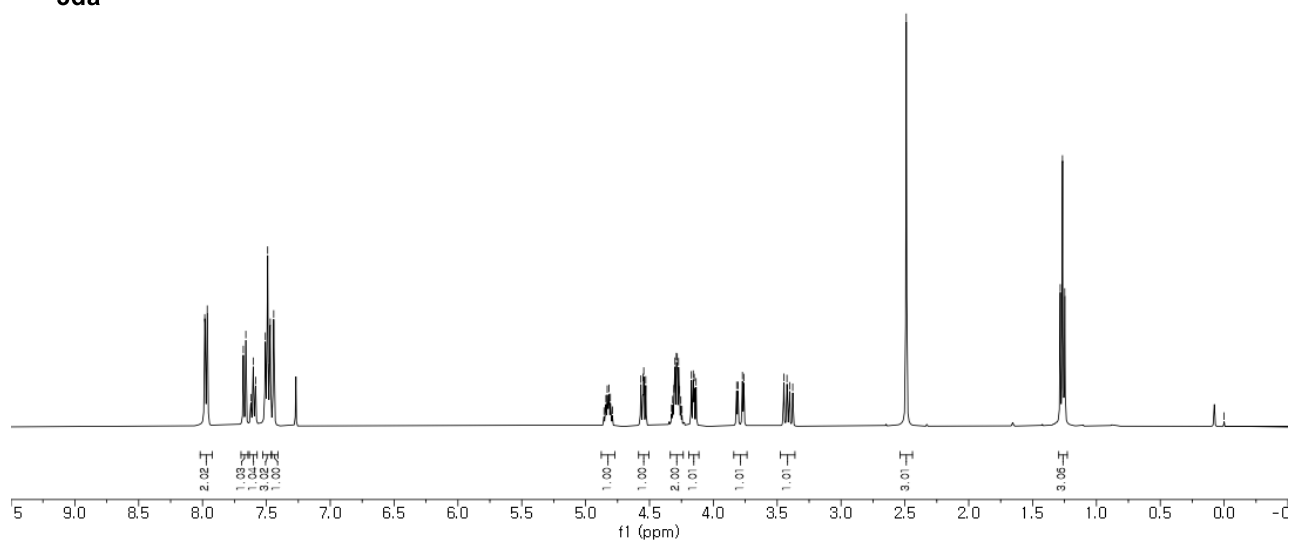
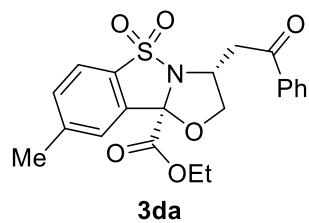
— 166.04

155.93
155.78
134.08
133.94
133.67
125.05
125.70
125.03
123.15
121.39

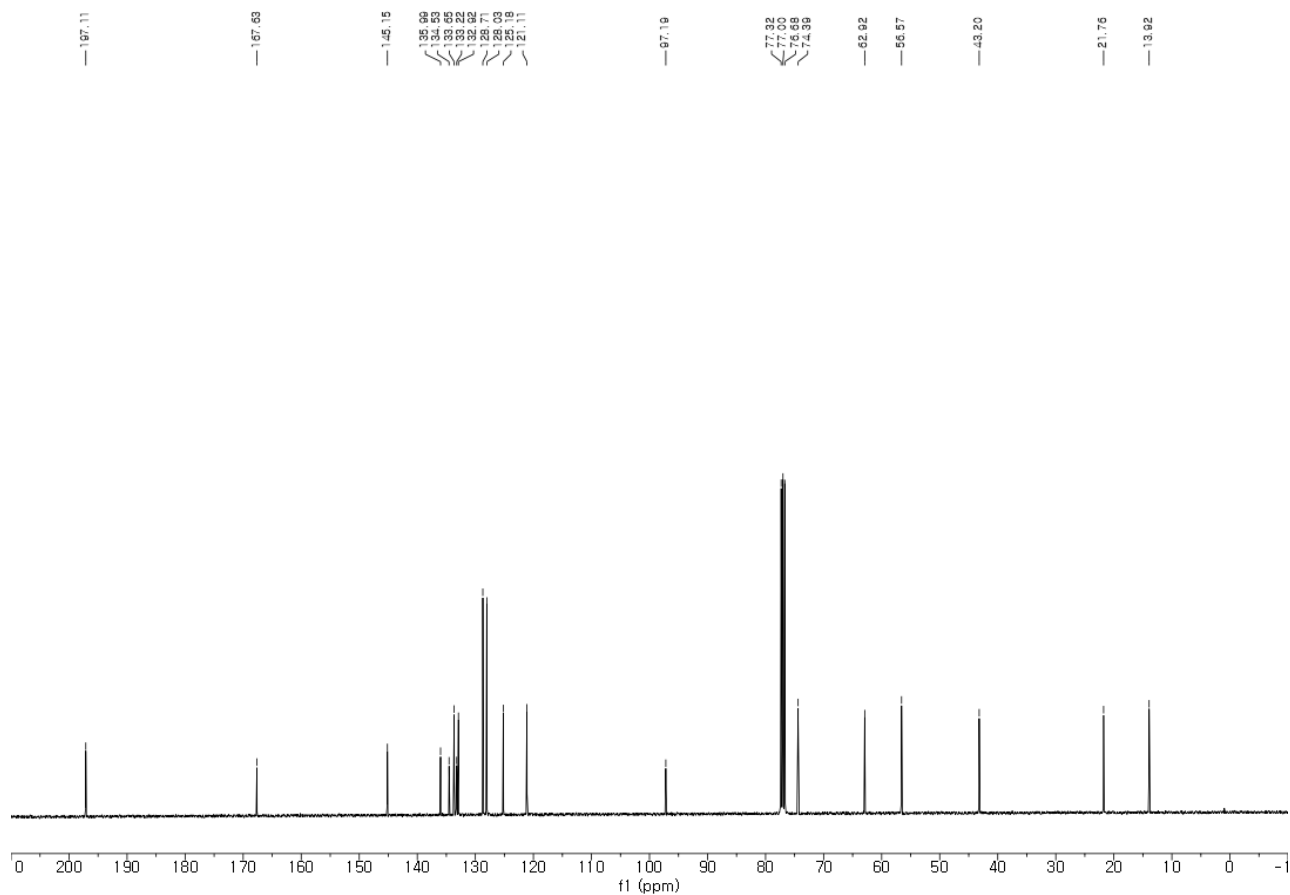


^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

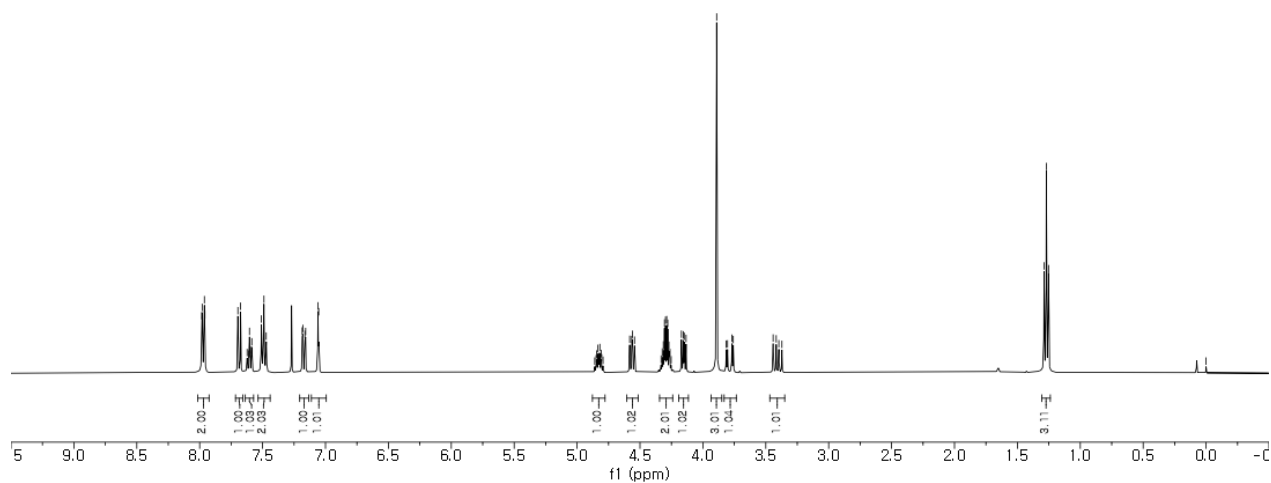
7.98
7.95
7.68
7.55
7.62
7.60
7.58
7.51
7.49
7.47
7.44



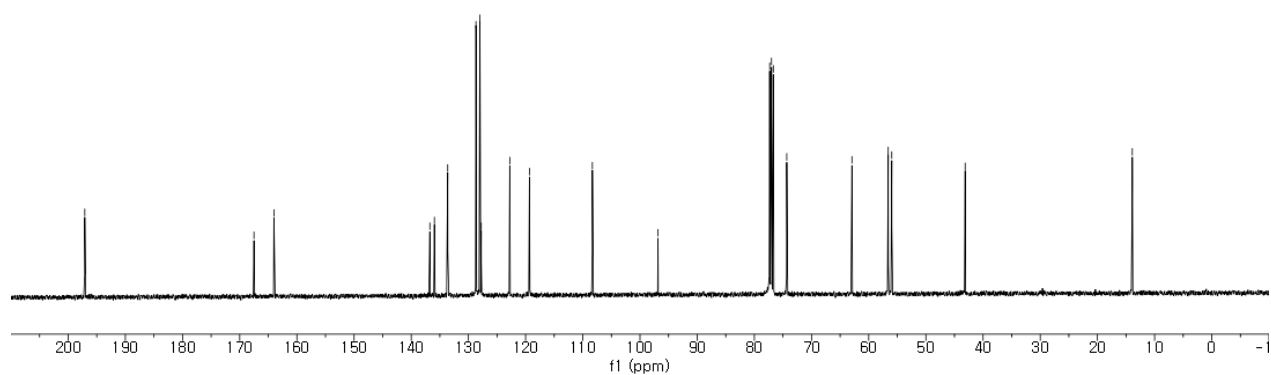
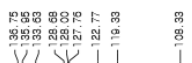
—107.11

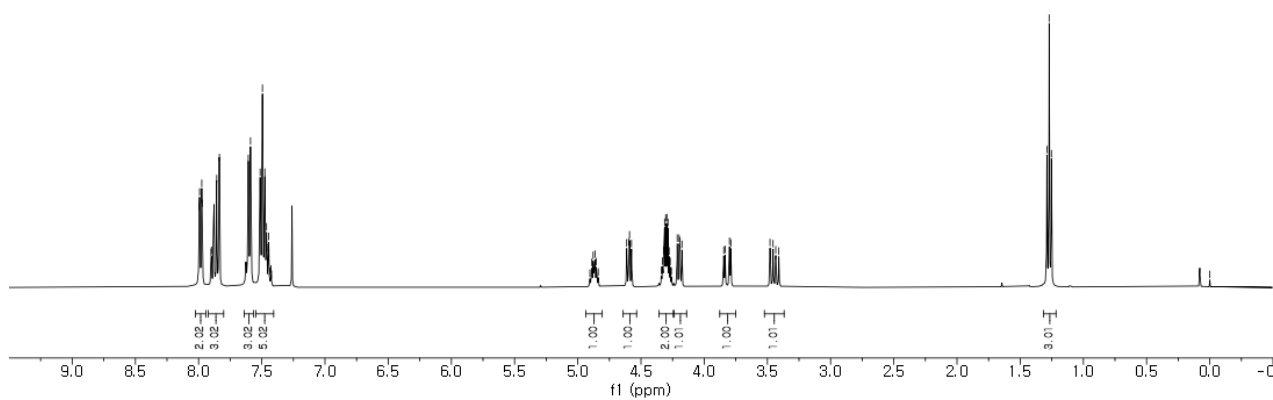
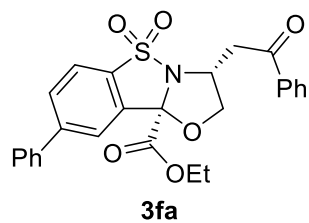


7.98
7.98
7.96
7.96
7.70
7.67
7.62
7.61
7.60
7.60
7.59
7.59
7.58
7.51
7.49
7.49
7.47
7.19
7.18
7.16
7.16
7.06
7.05



—	197.09
—	167.50
—	164.01



^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3**

197.06

167.53

147.38

138.62, 138.09, 133.67, 131.03, 130.10, 128.73, 128.04, 127.72, 127.12

97.26

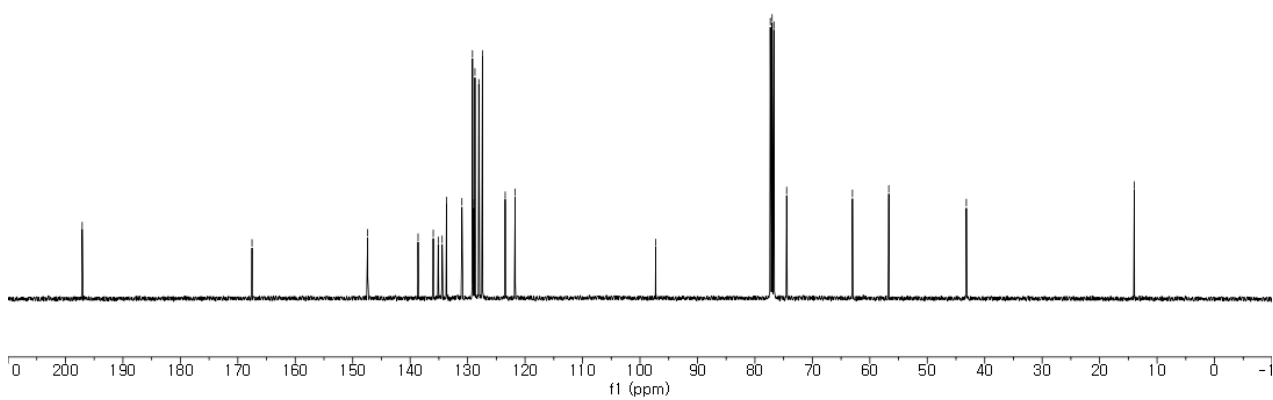
77.32, 77.00, 76.68, 76.47

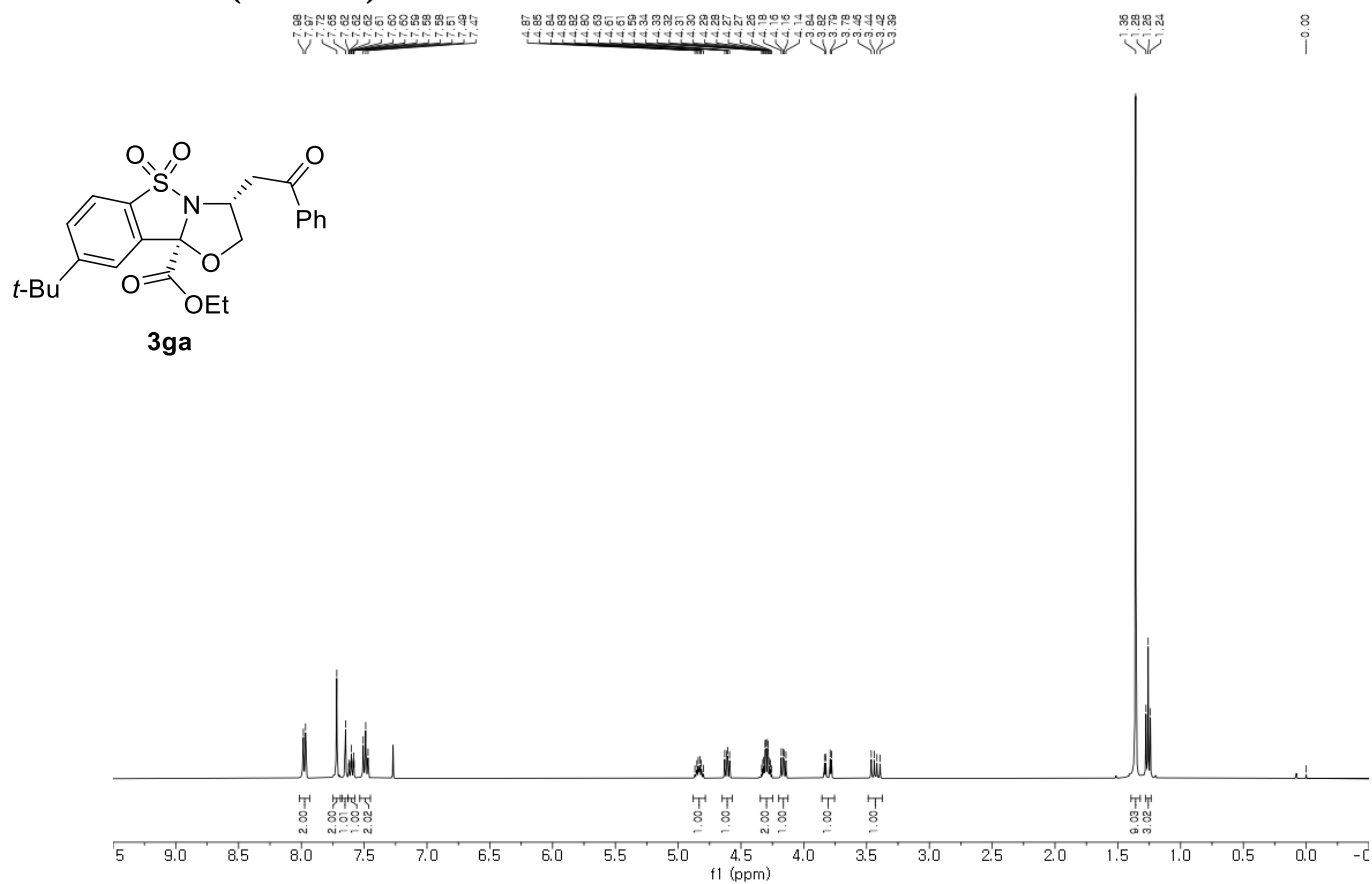
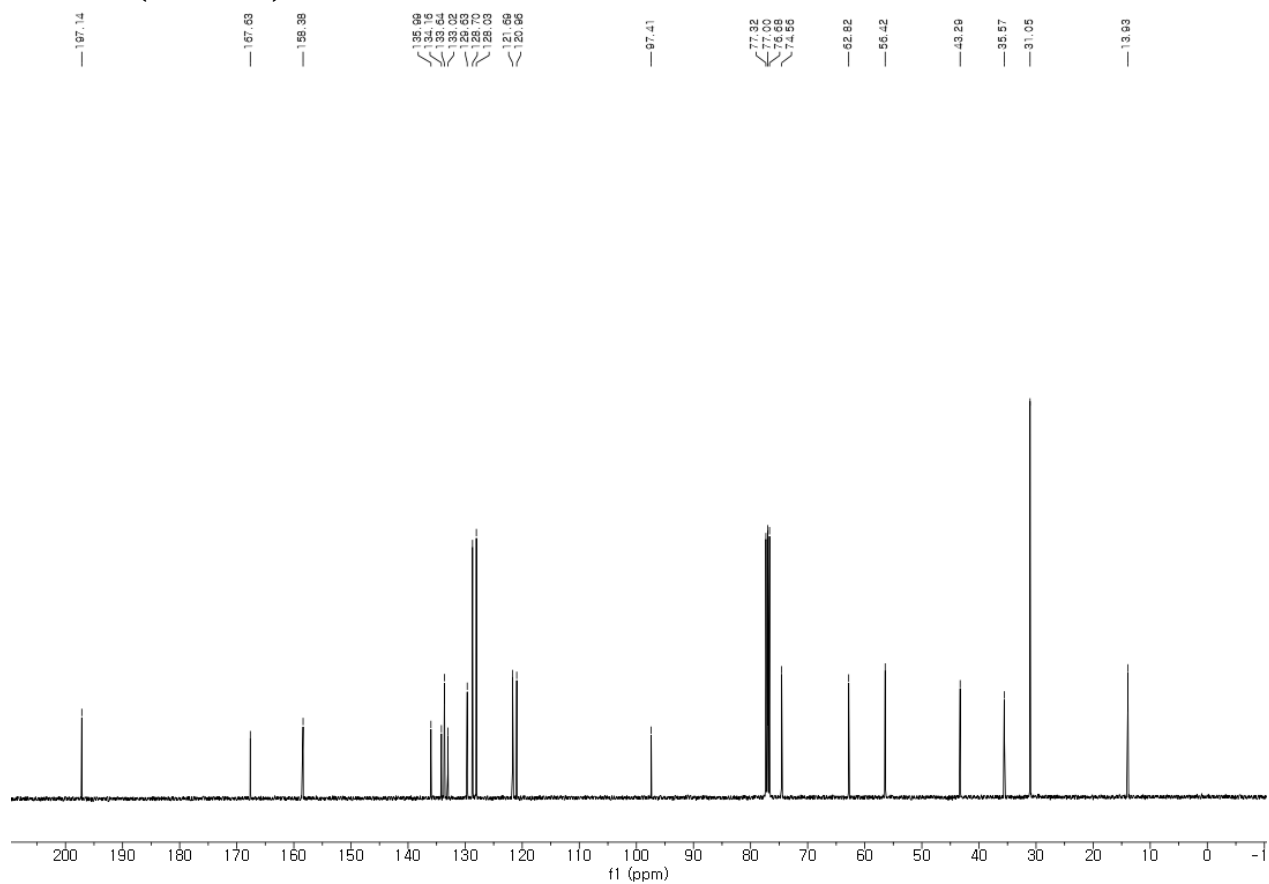
68.02

56.70

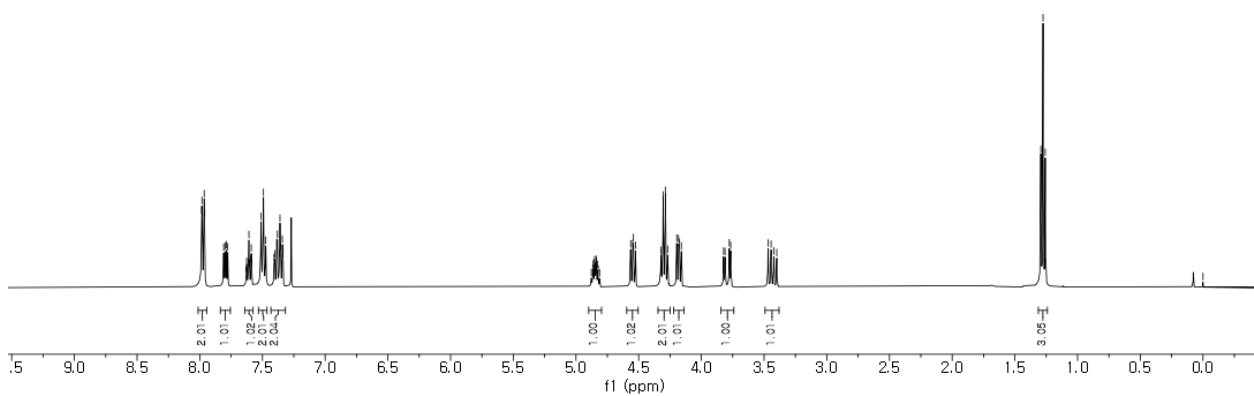
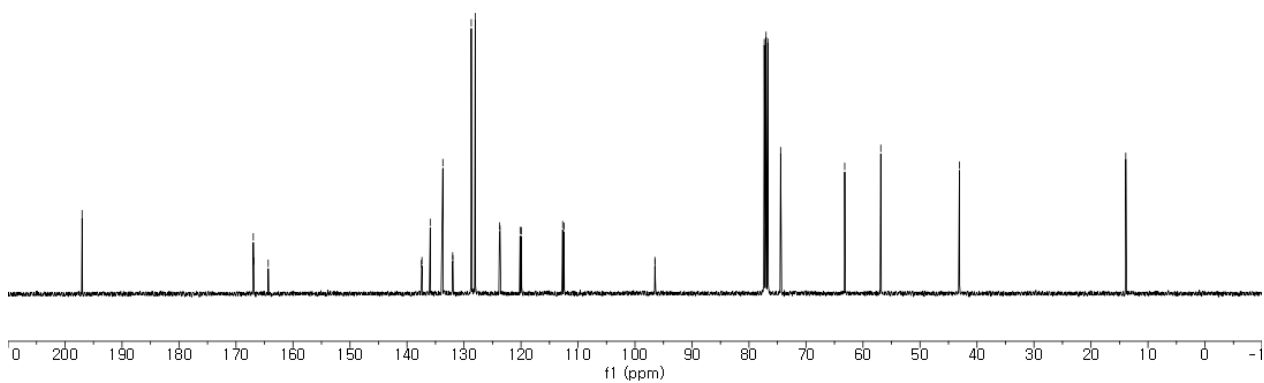
48.20

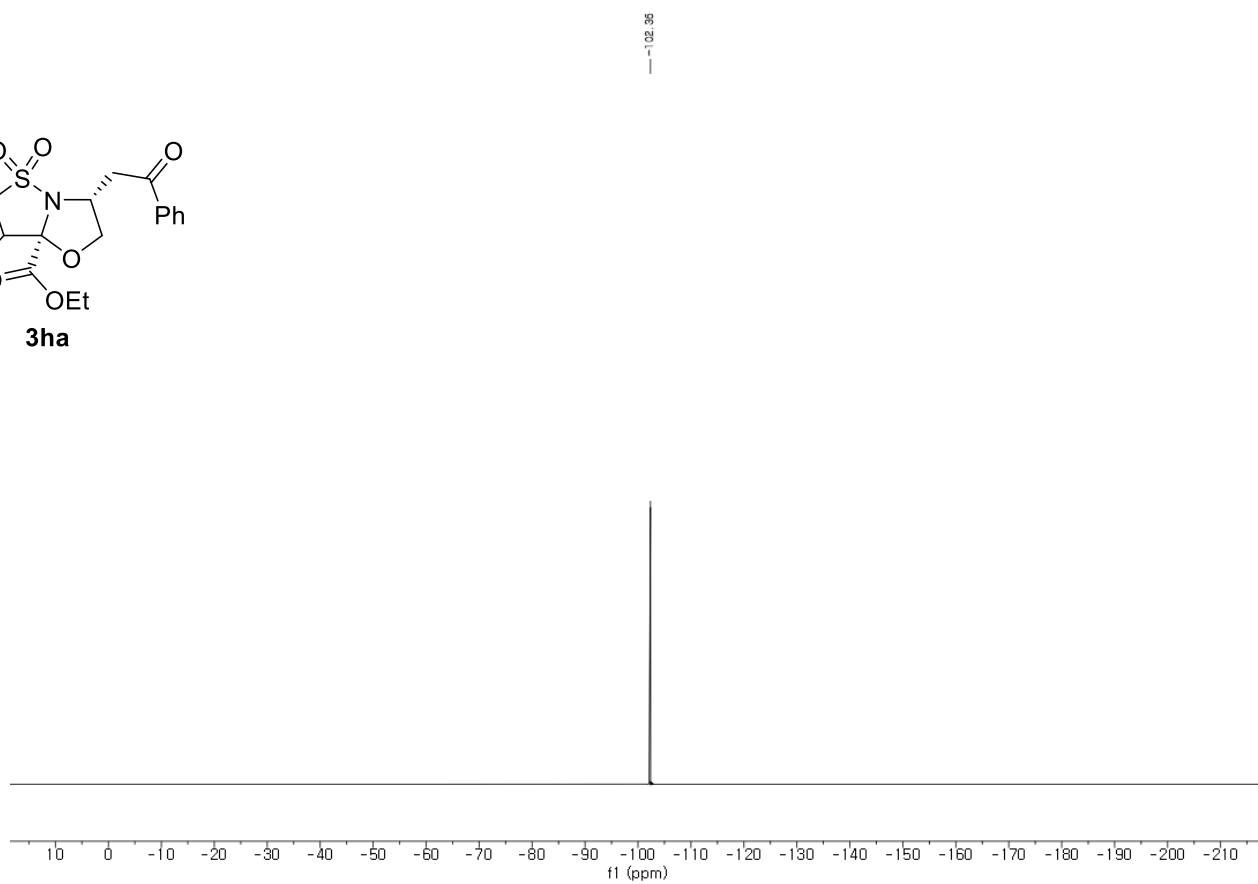
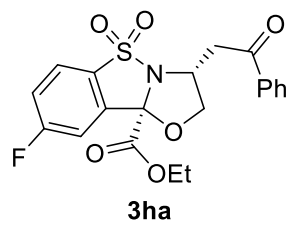
18.97

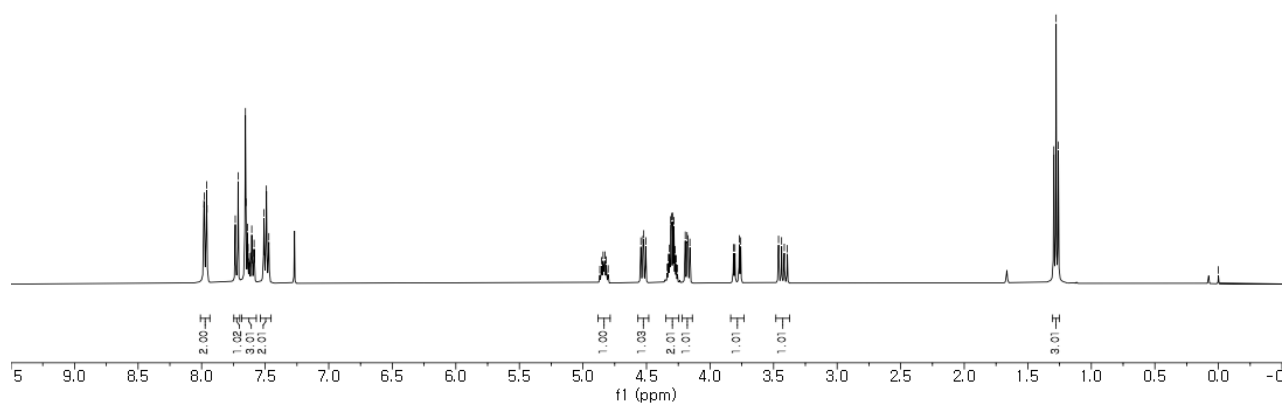
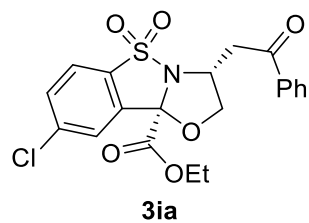
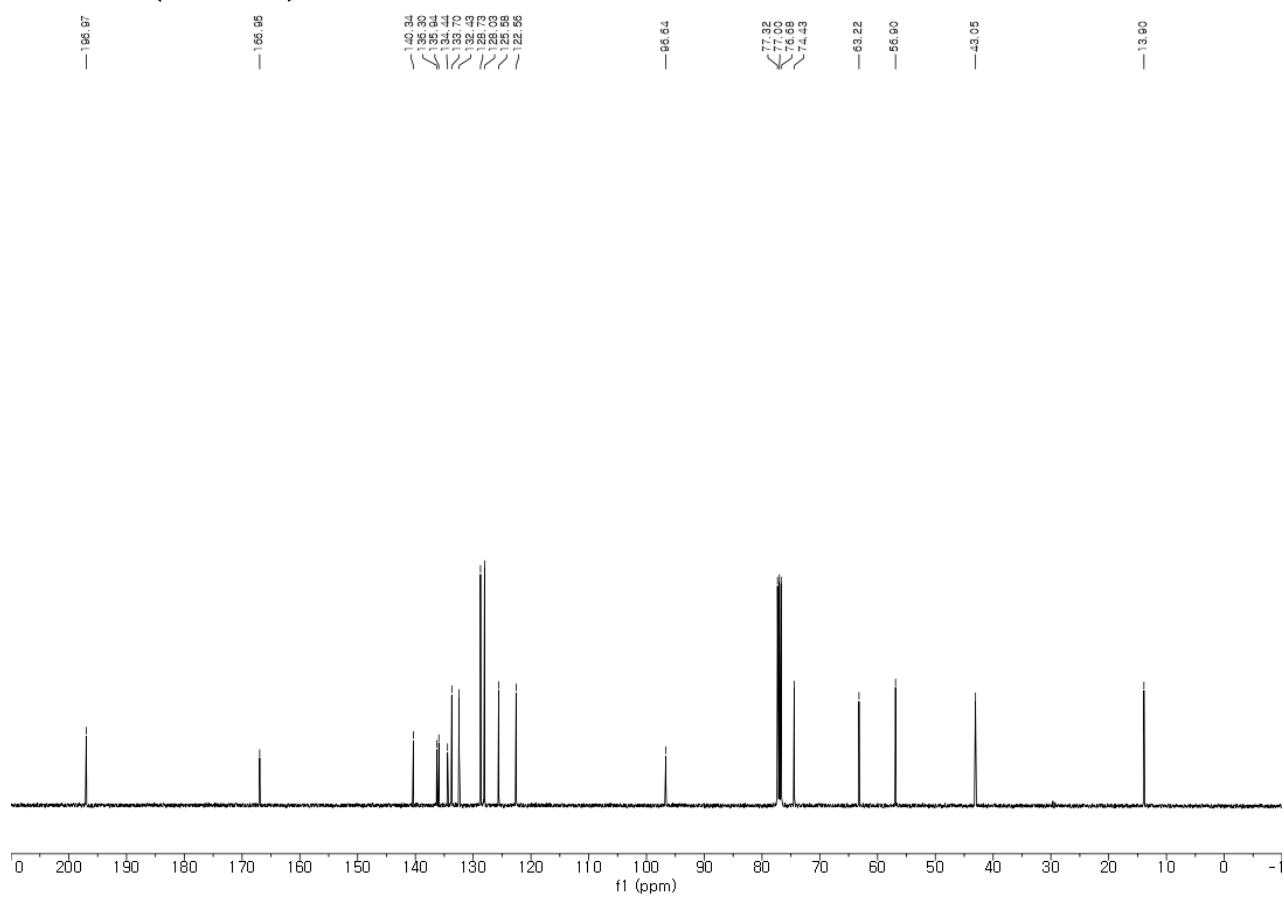


^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

3ha

[illegible]

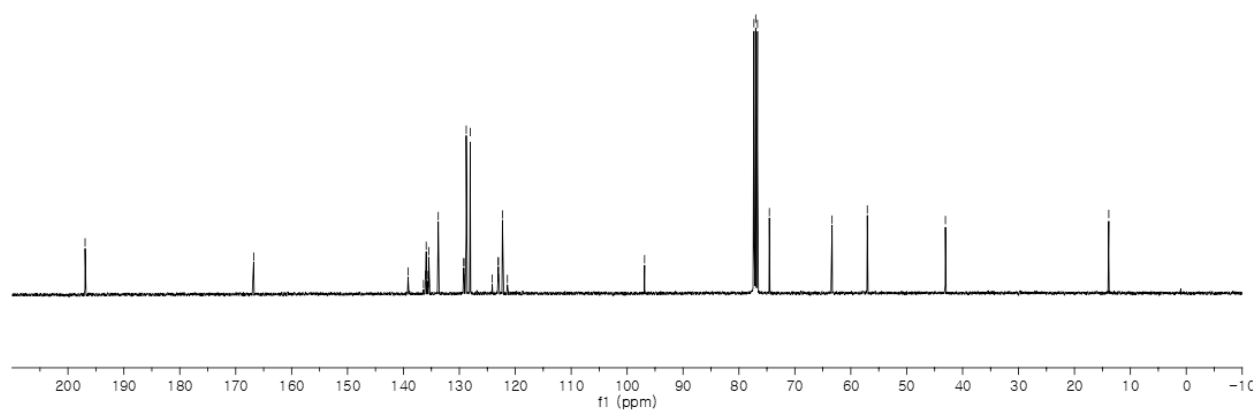
^{19}F NMR (376 MHz) in CDCl_3 

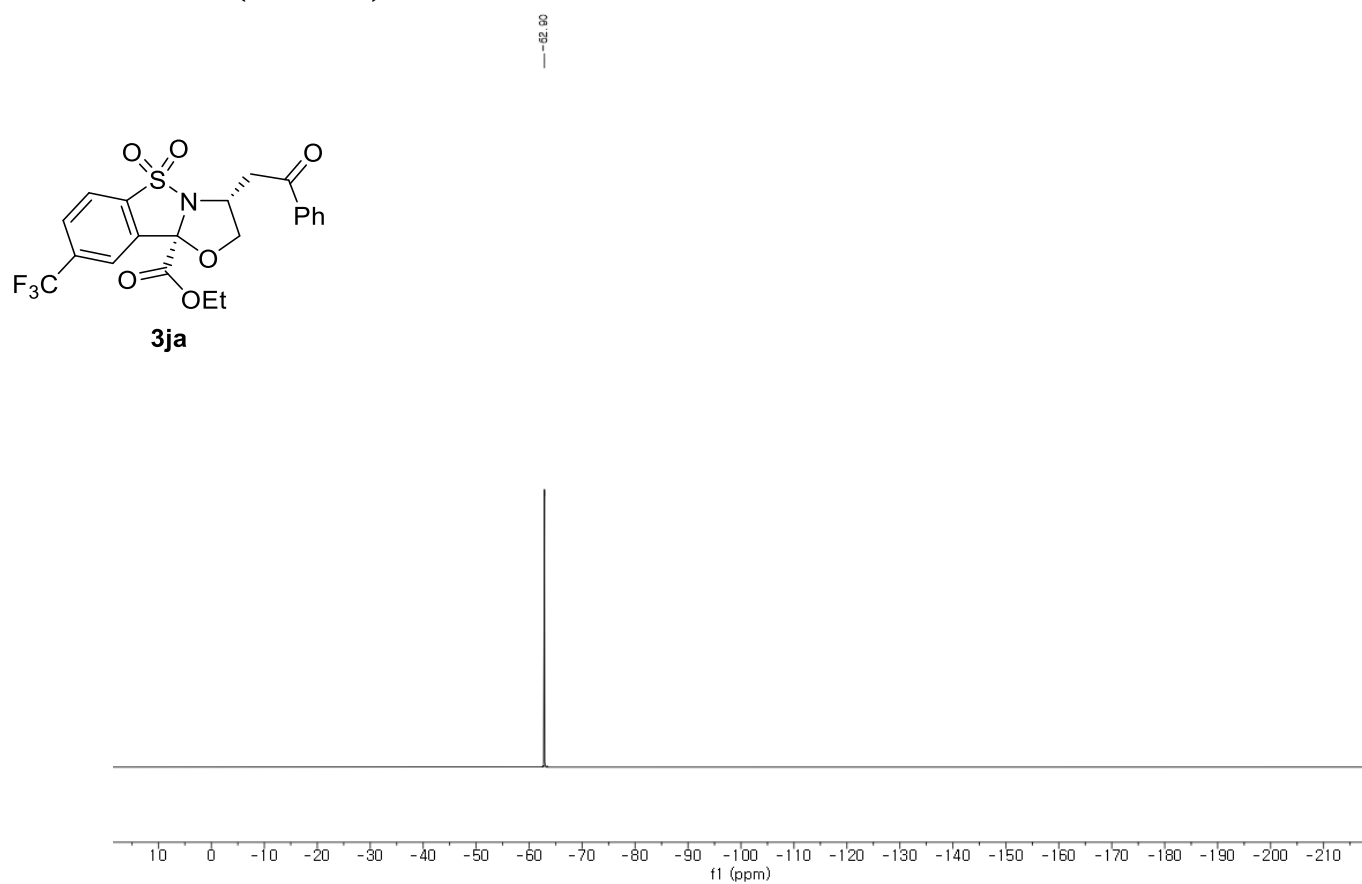
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

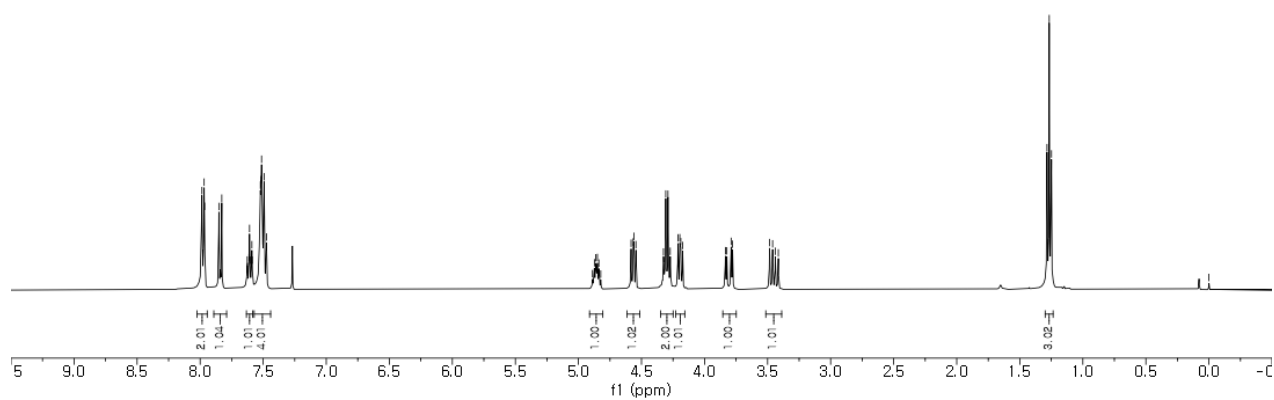
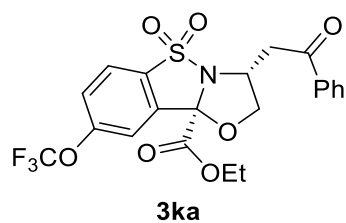
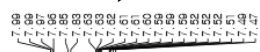
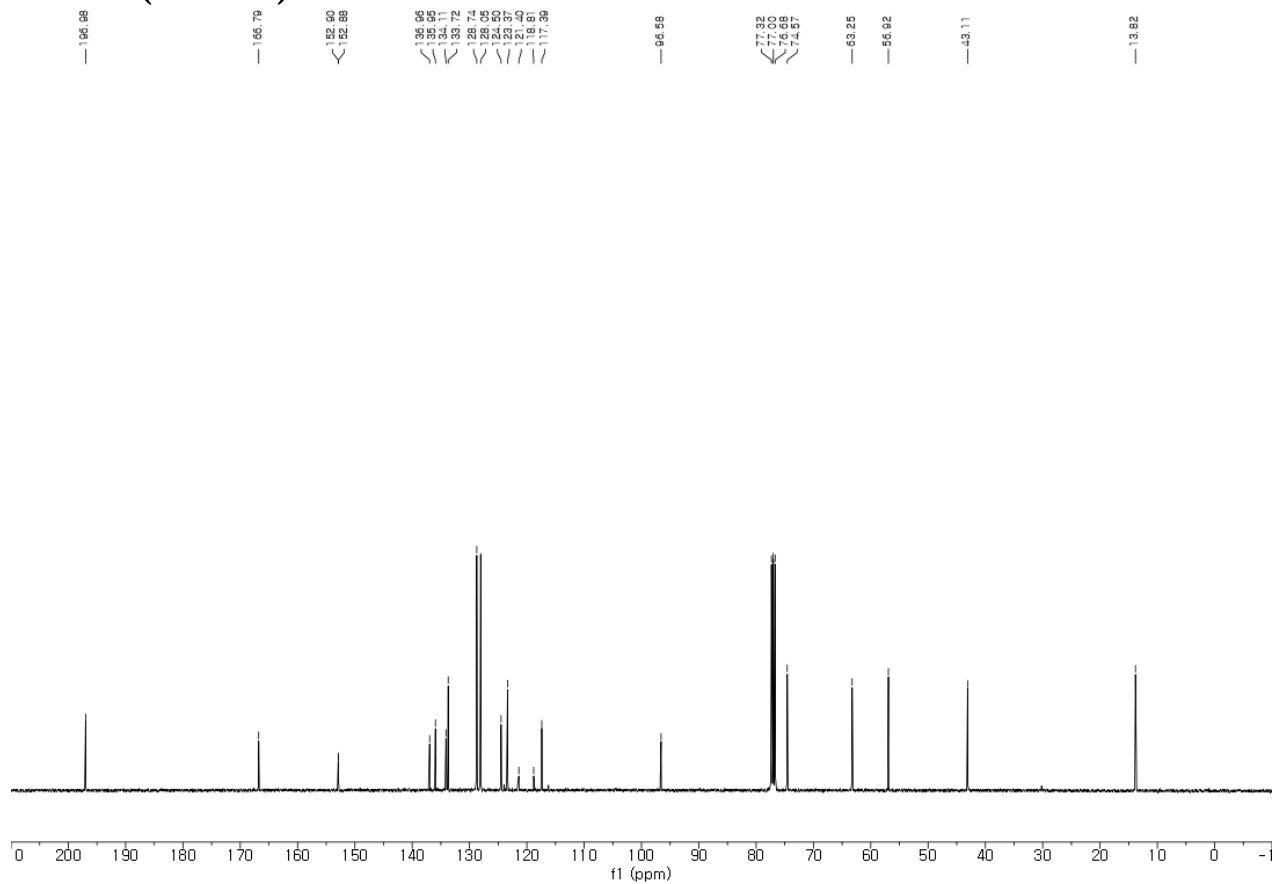
7.997
7.997
7.997
7.995
7.994
7.964
7.953
7.953
7.962
7.962
7.961
7.960
7.960
7.959
7.952
7.950
7.949

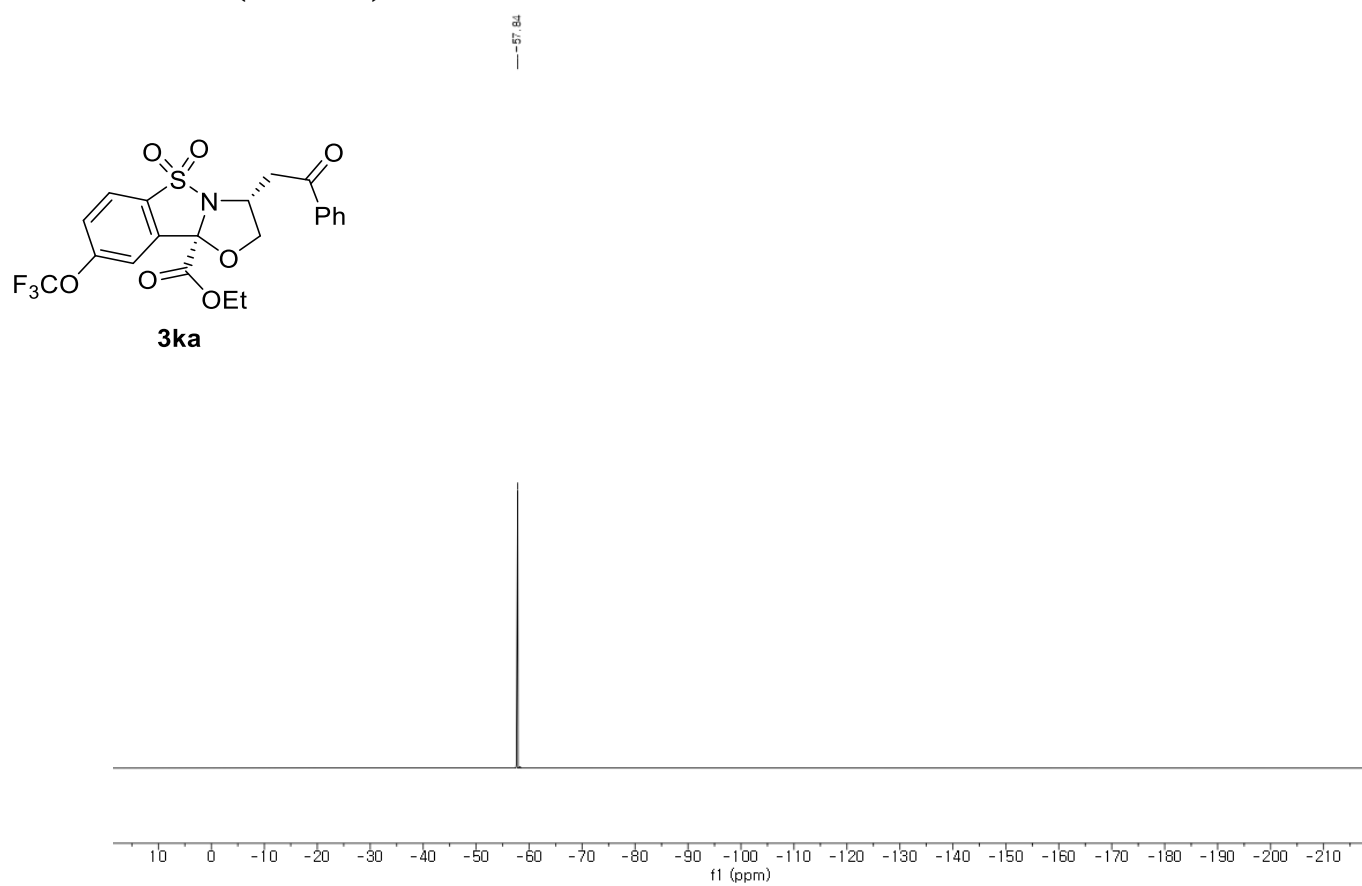


—166.93

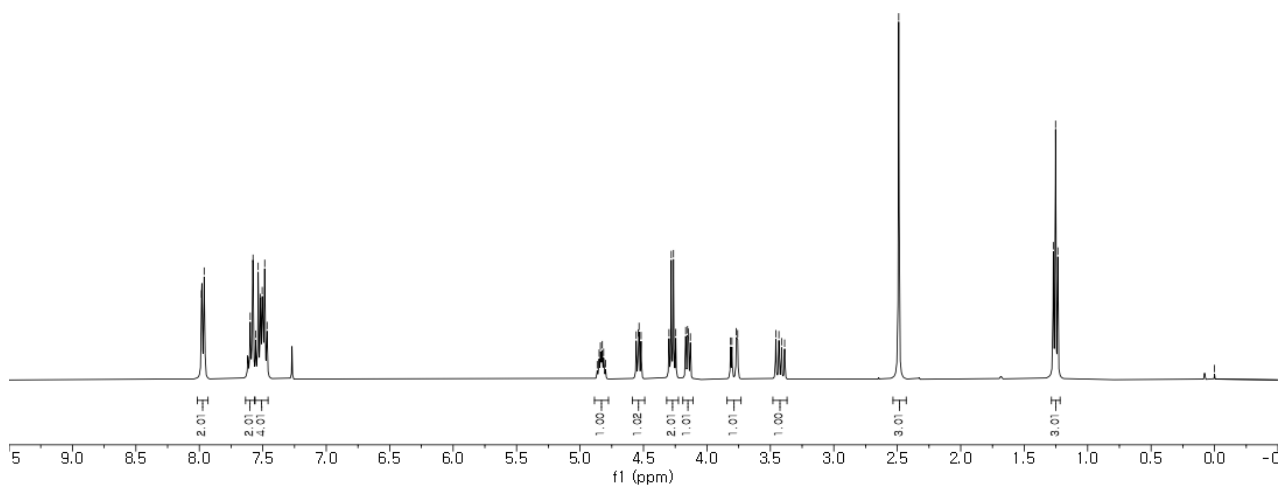
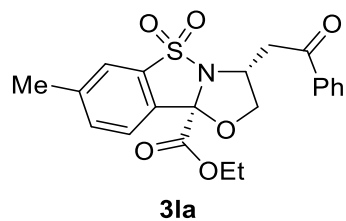


^{19}F NMR (376 MHz) in CDCl_3 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^{19}F NMR (376 MHz) in CDCl_3 

7.98
7.96
7.62
7.60
7.58
7.56
7.54
7.52
7.50
7.48
7.47

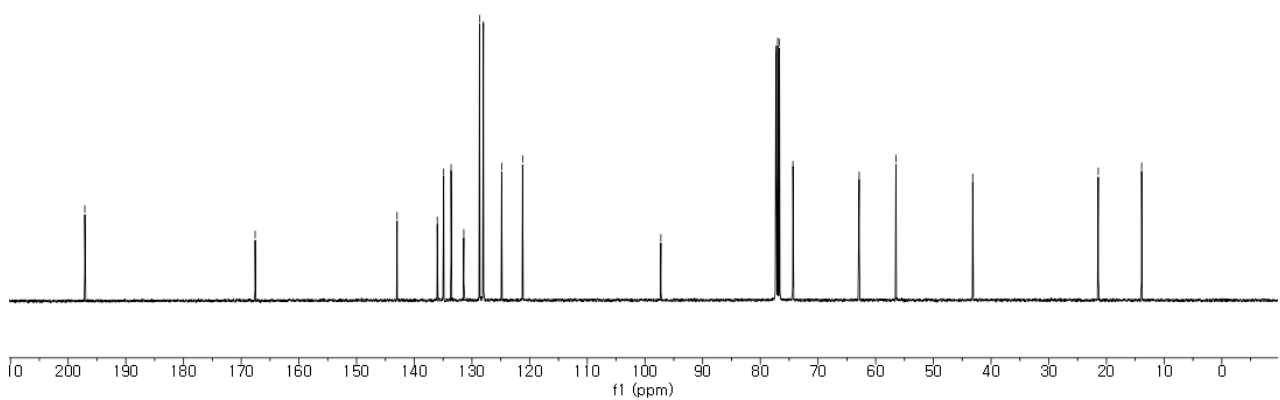


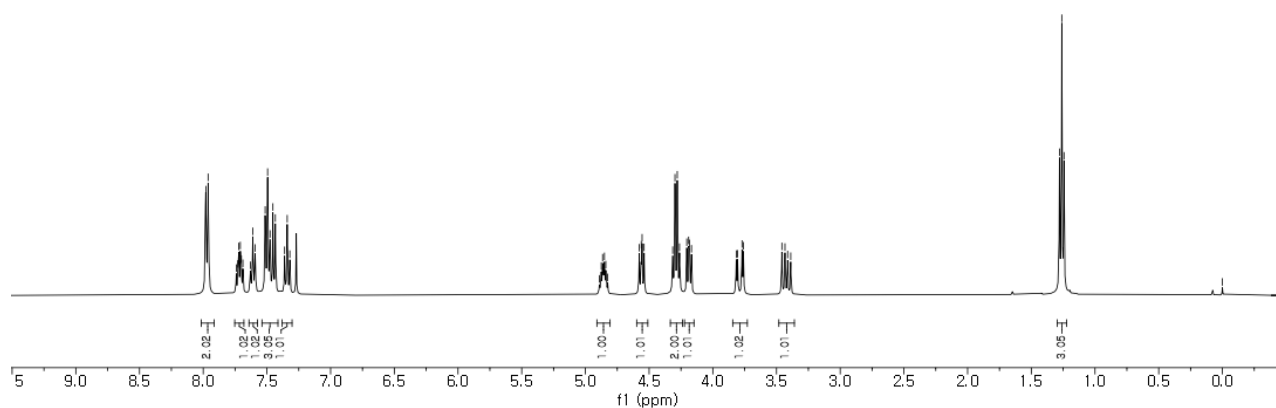
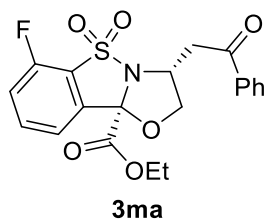
—167.11

—167.59

—142.97

136.01
135.98
134.90
133.61
131.43
128.56
128.02
124.95
121.22



^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3**

196.06

196.02

196.00

194.47

137.95

137.93

137.91

137.89

137.87

137.85

137.83

137.81

137.79

137.77

137.75

137.73

137.71

137.69

137.67

137.65

137.63

137.61

137.59

137.57

137.55

137.53

137.51

137.49

137.47

137.45

137.43

137.41

137.39

137.37

137.35

137.33

137.31

137.29

137.27

137.25

137.23

137.21

137.19

137.17

137.15

137.13

137.11

137.09

137.07

137.05

137.03

137.01

136.99

136.97

136.95

136.93

136.91

136.89

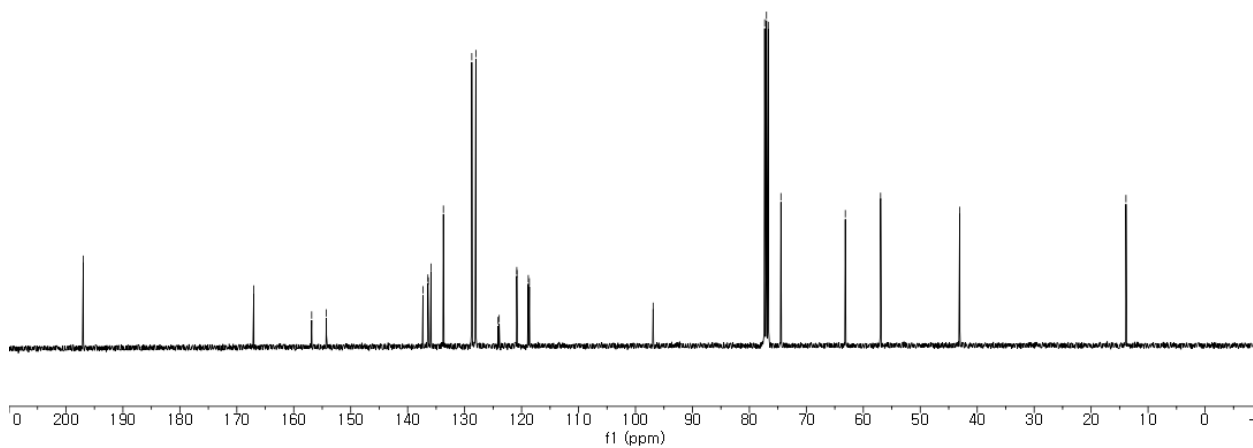
136.87

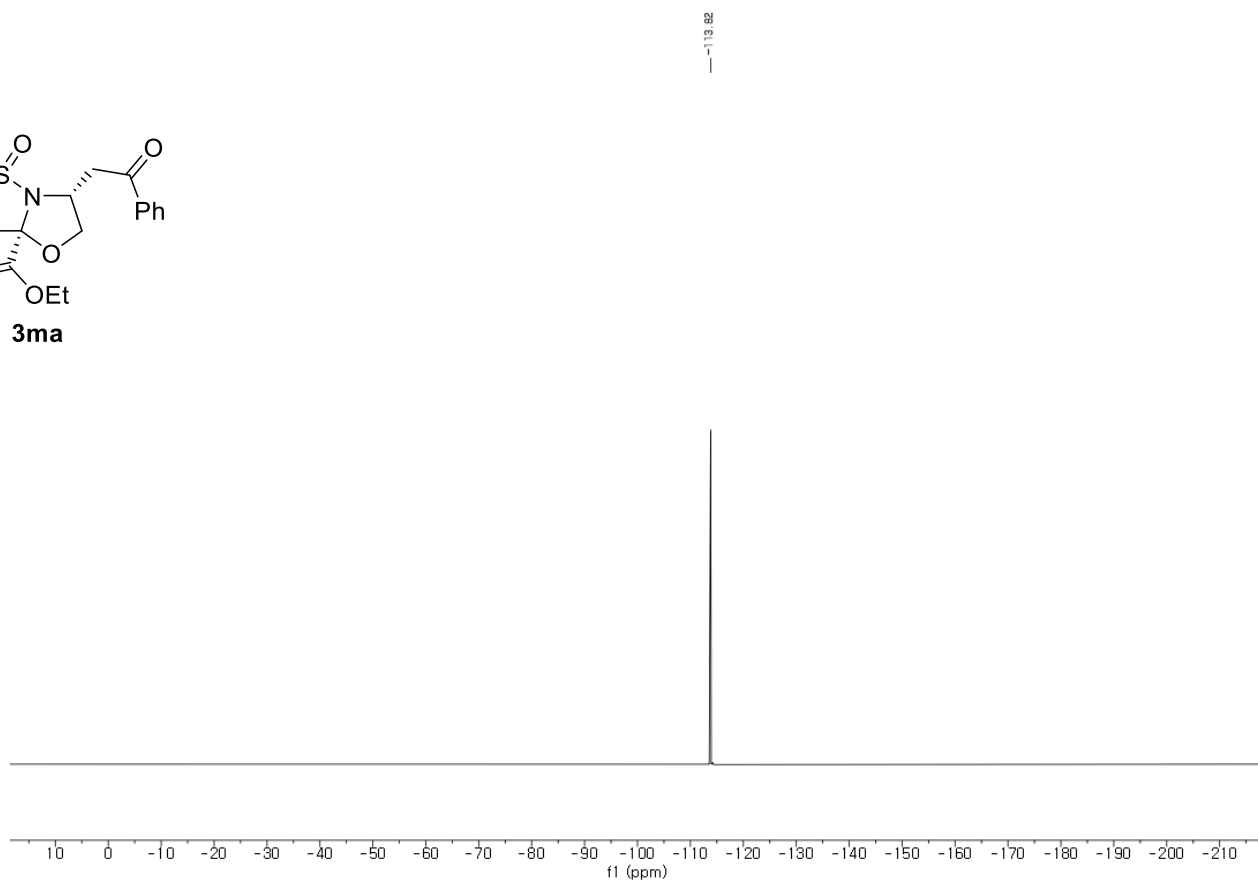
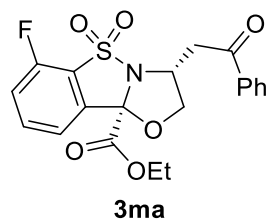
136.85

136.83

136.81

136.79

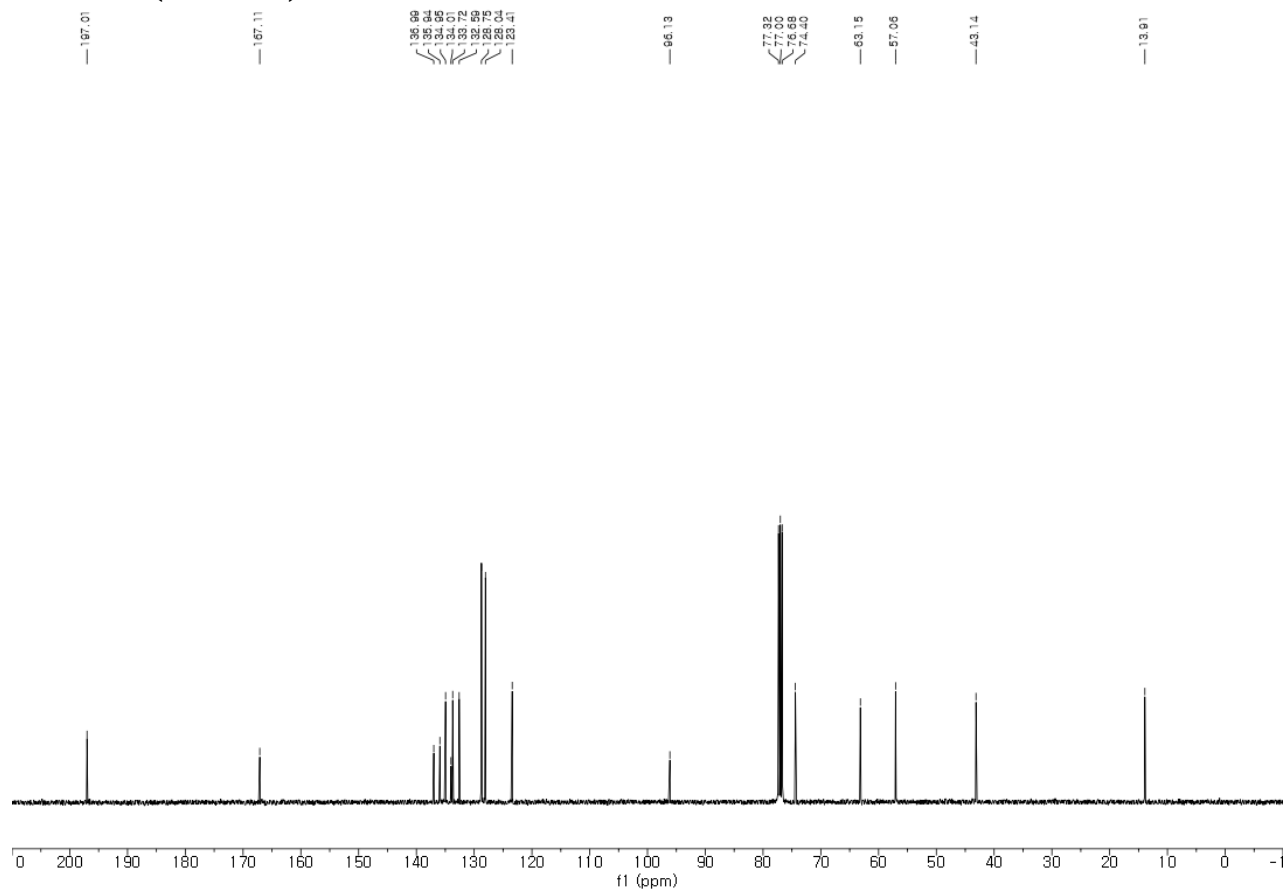


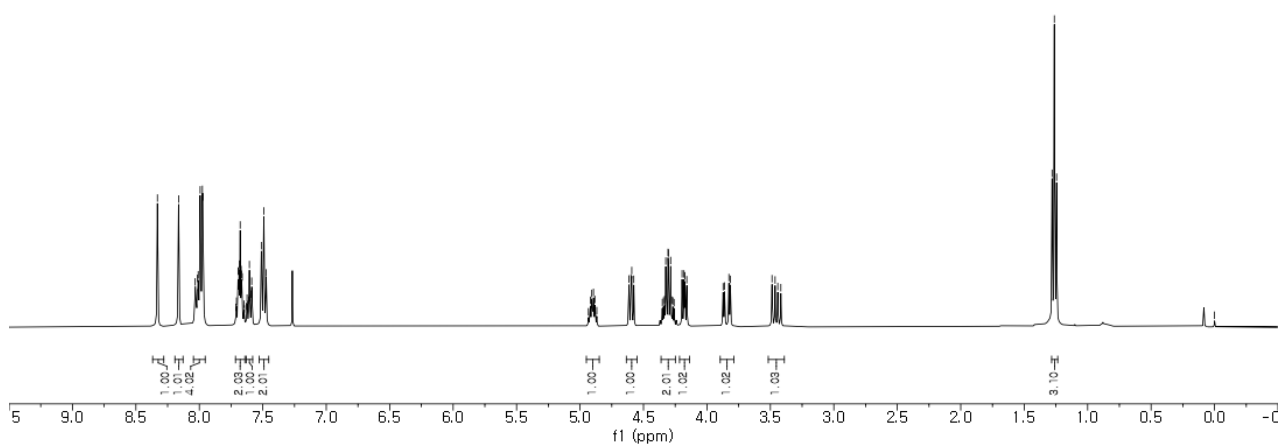
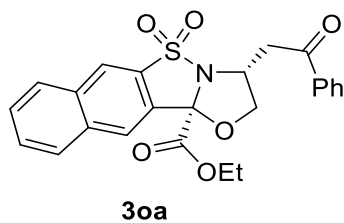
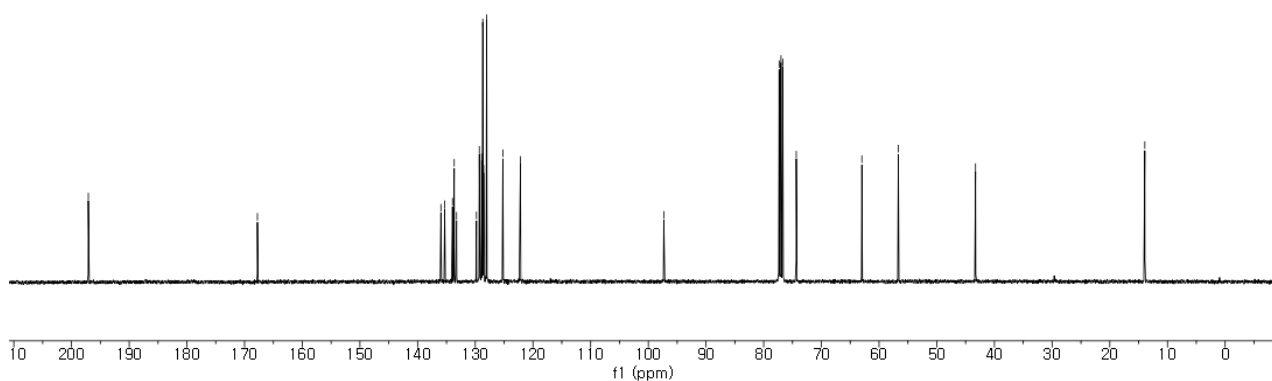
^{19}F NMR (376 MHz) in CDCl_3 

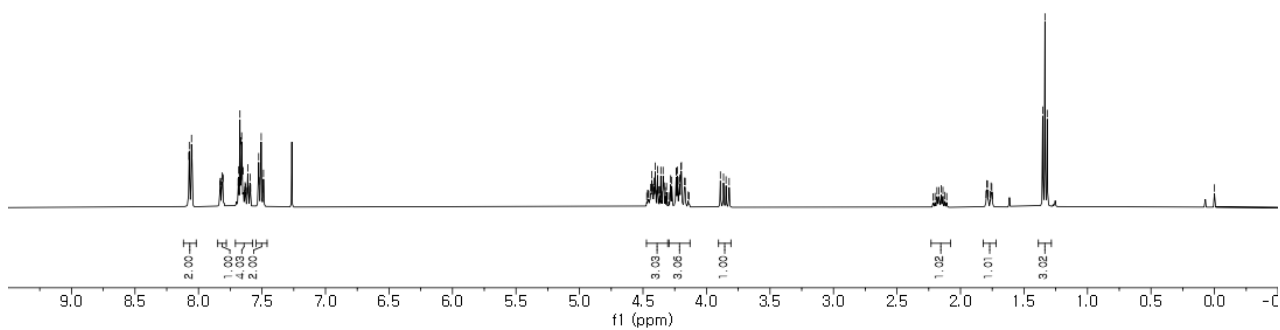
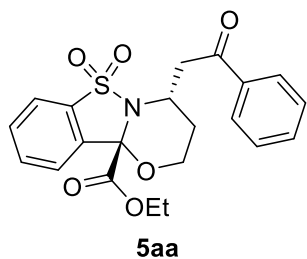
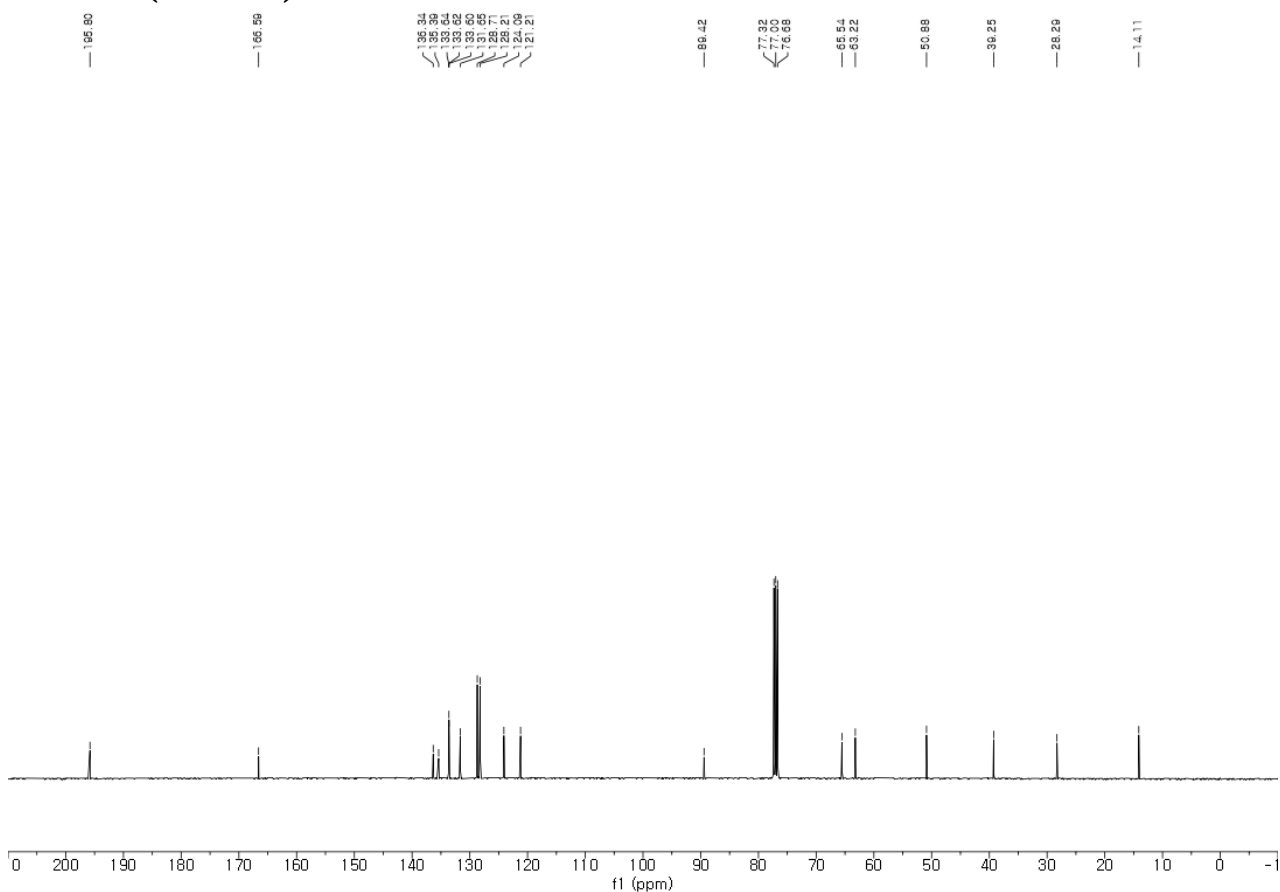
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7.49

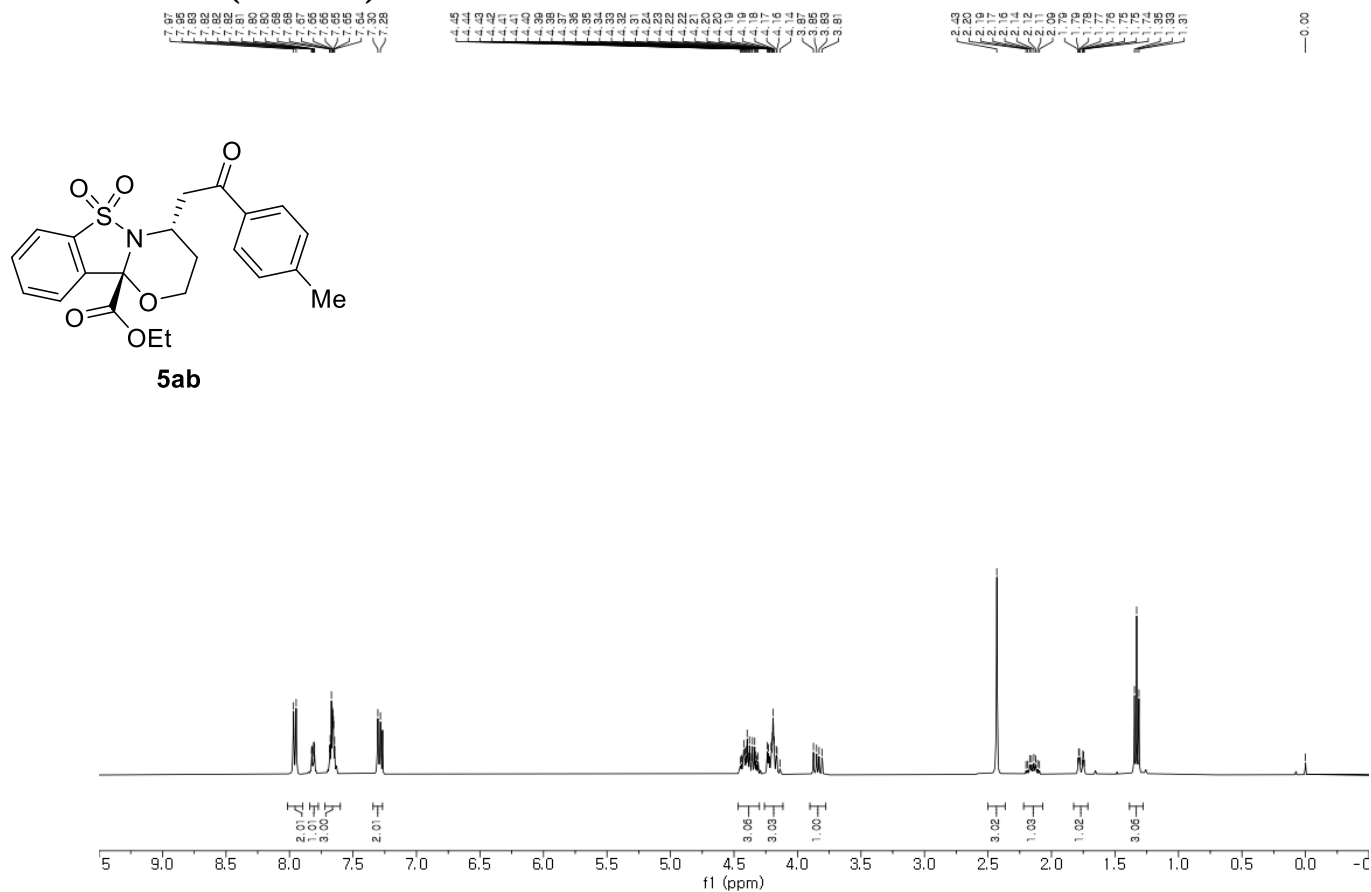
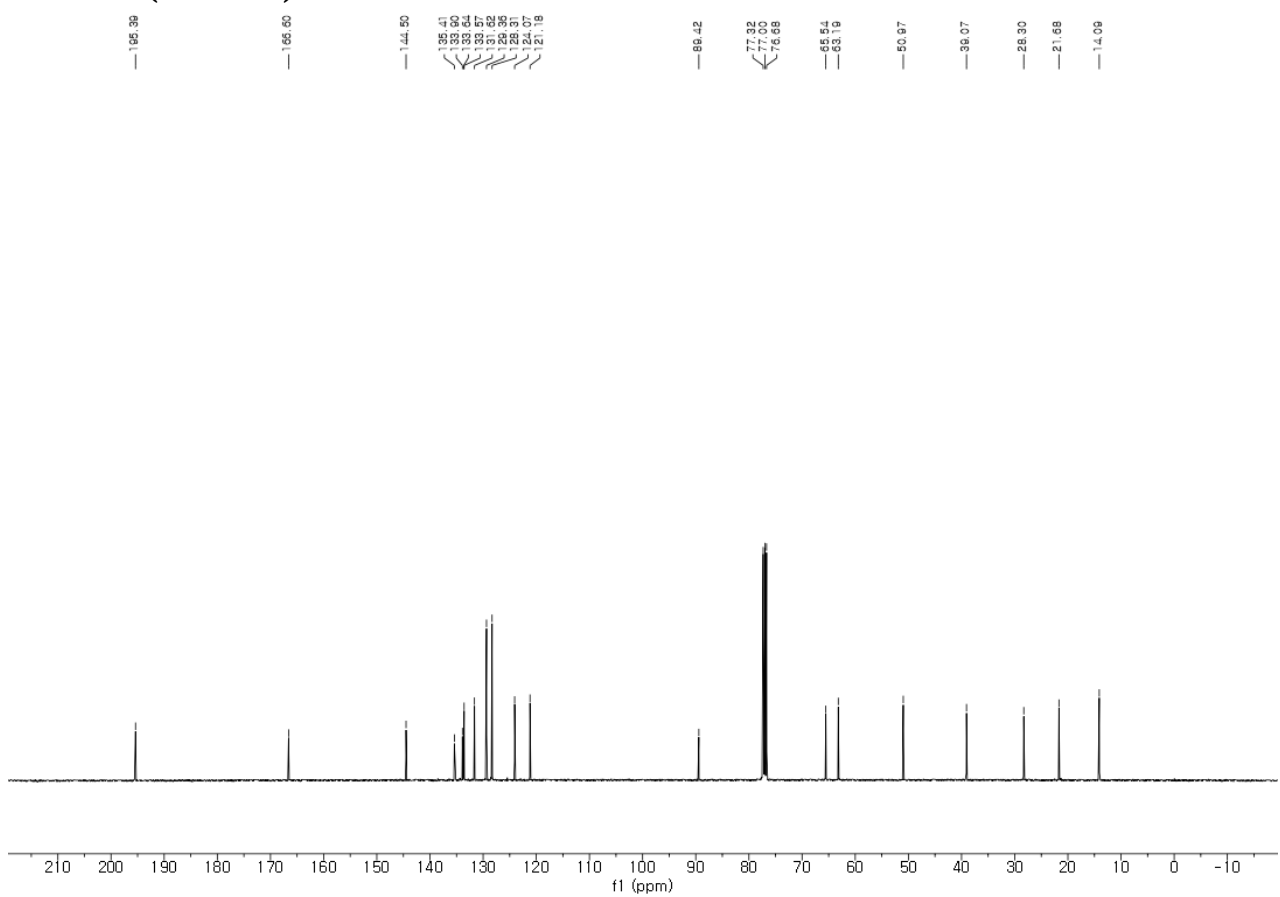


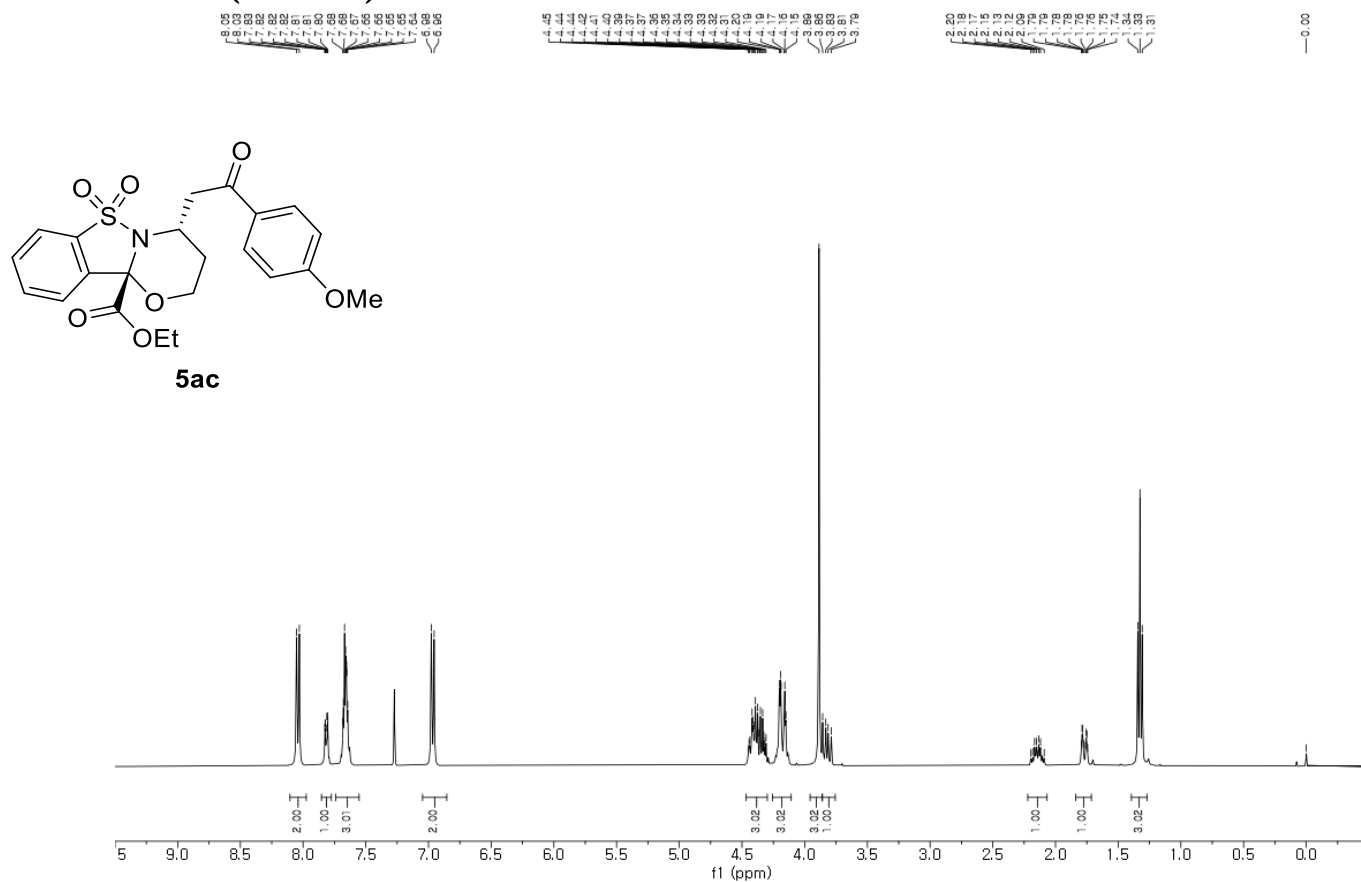
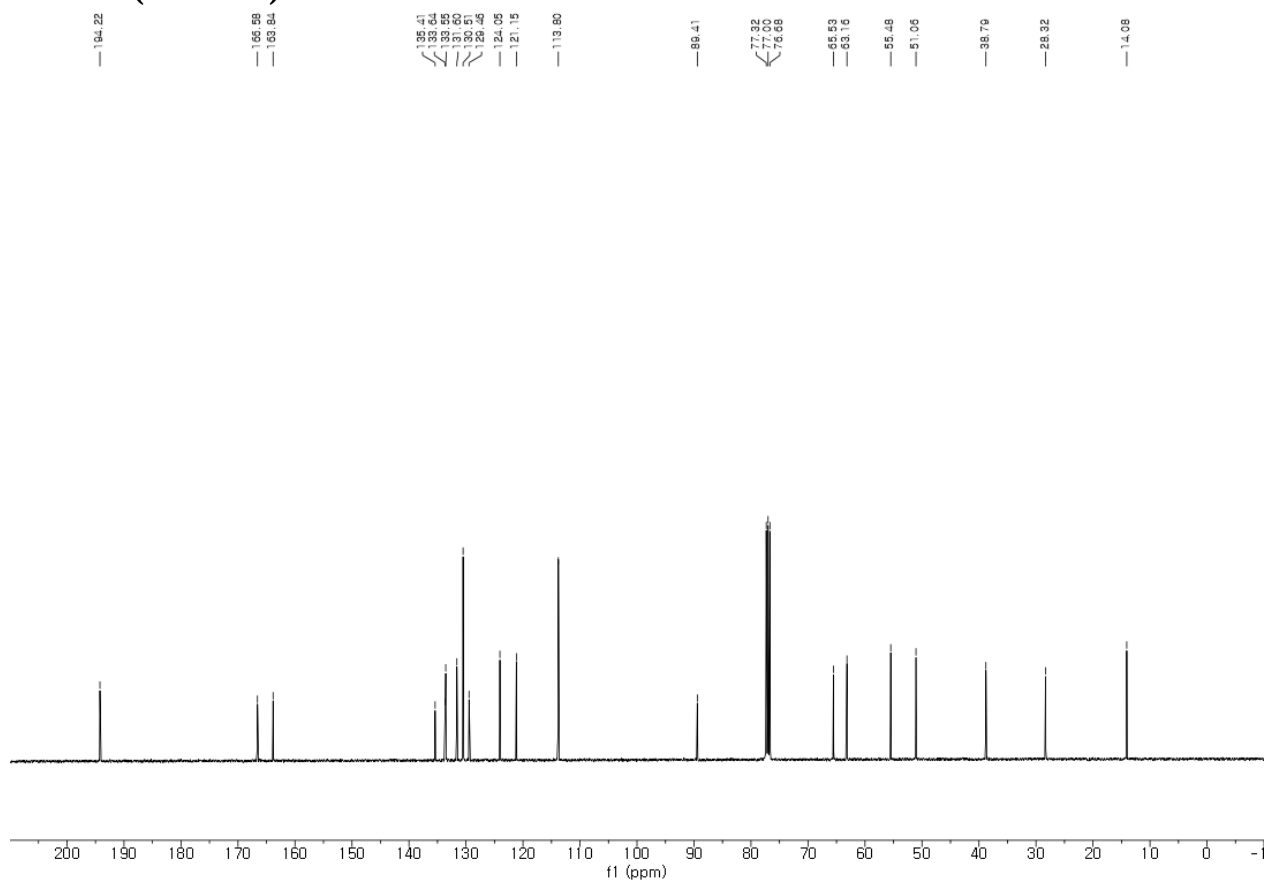
135.99
135.94
134.95
134.01
133.72
132.59
128.75
128.04
123.41

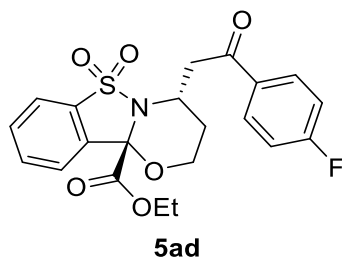
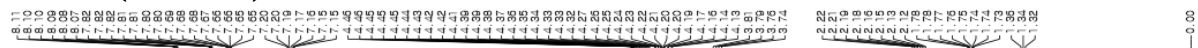
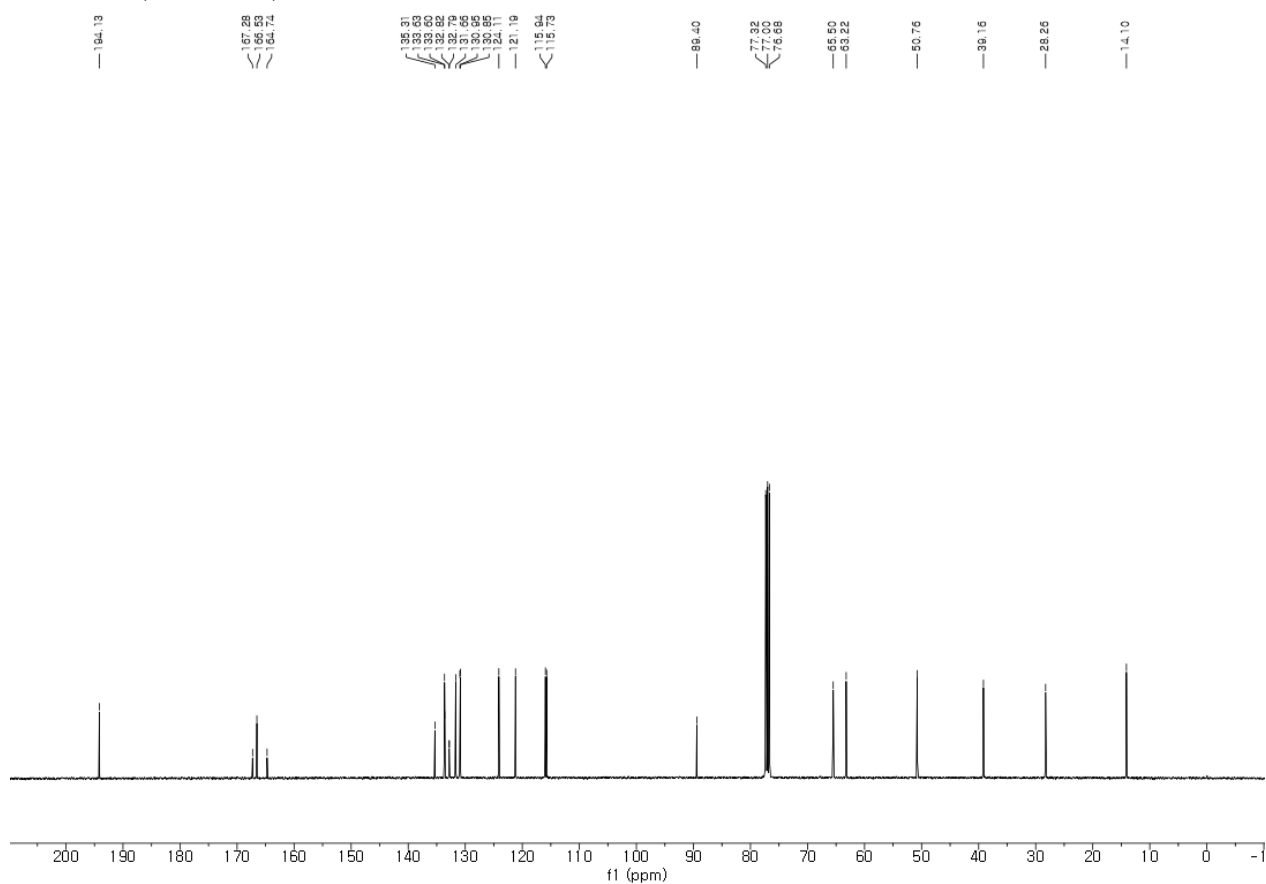


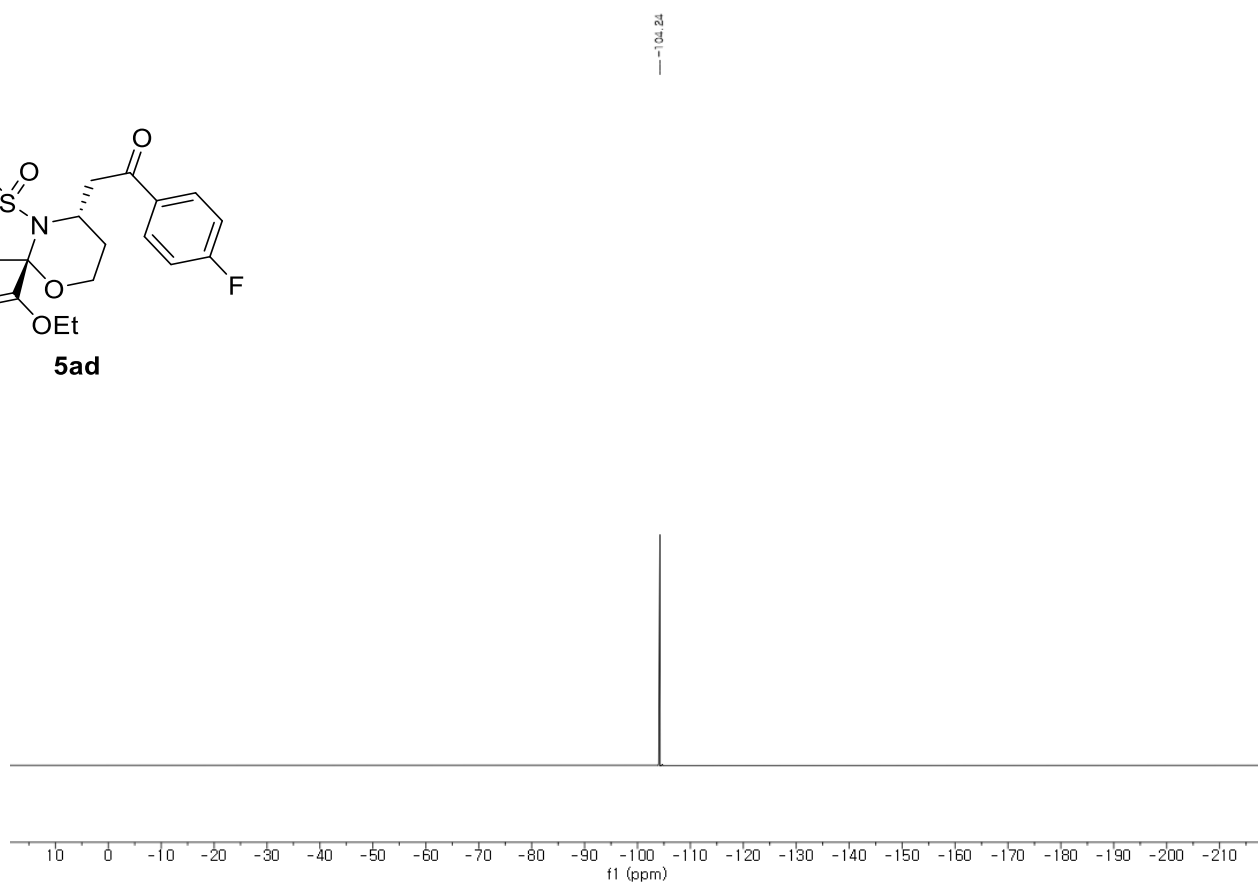
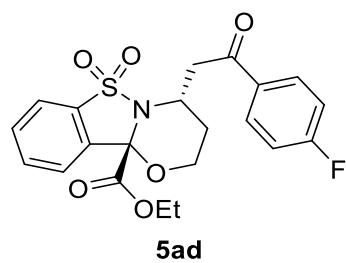
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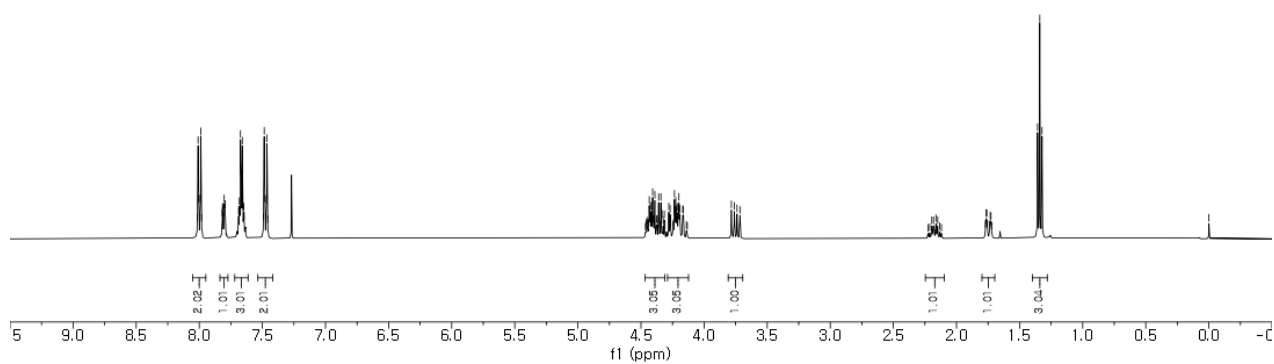
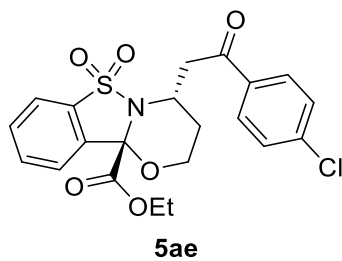
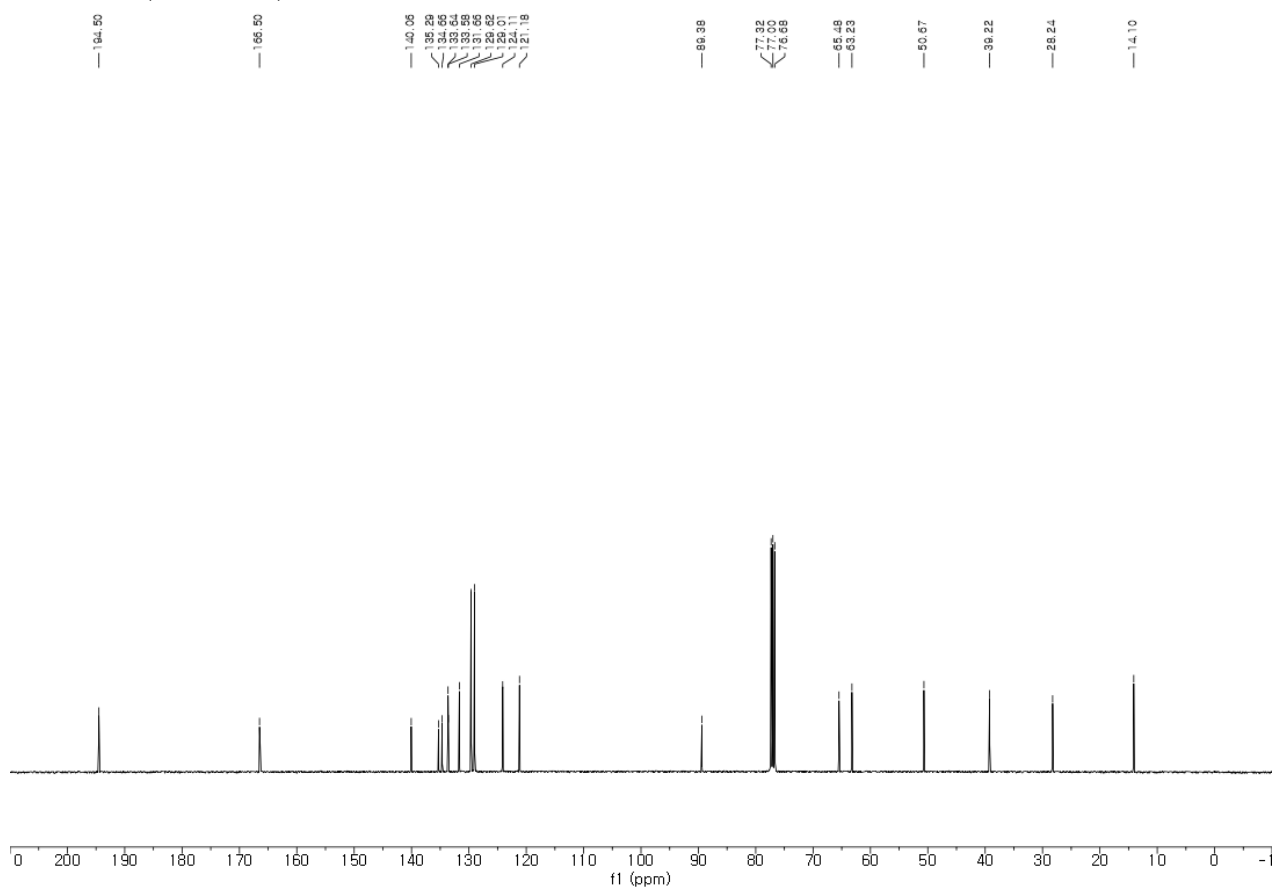
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

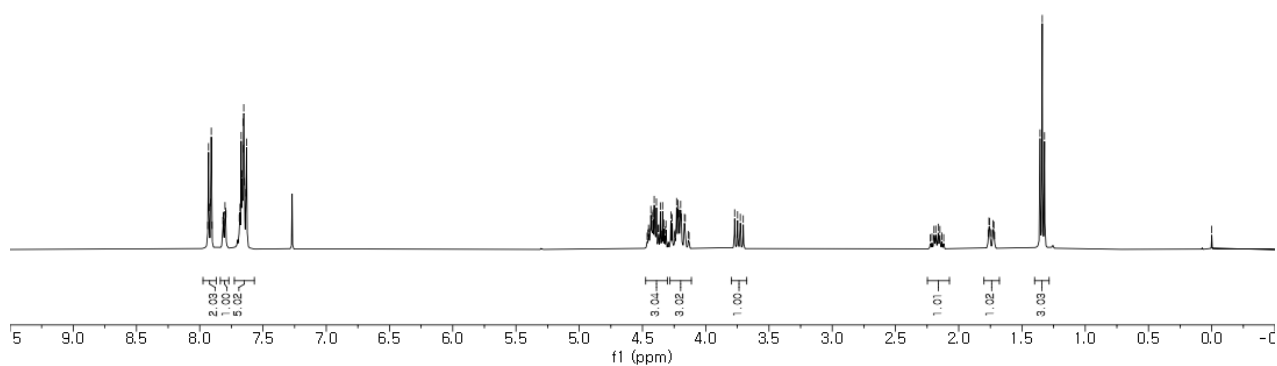
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

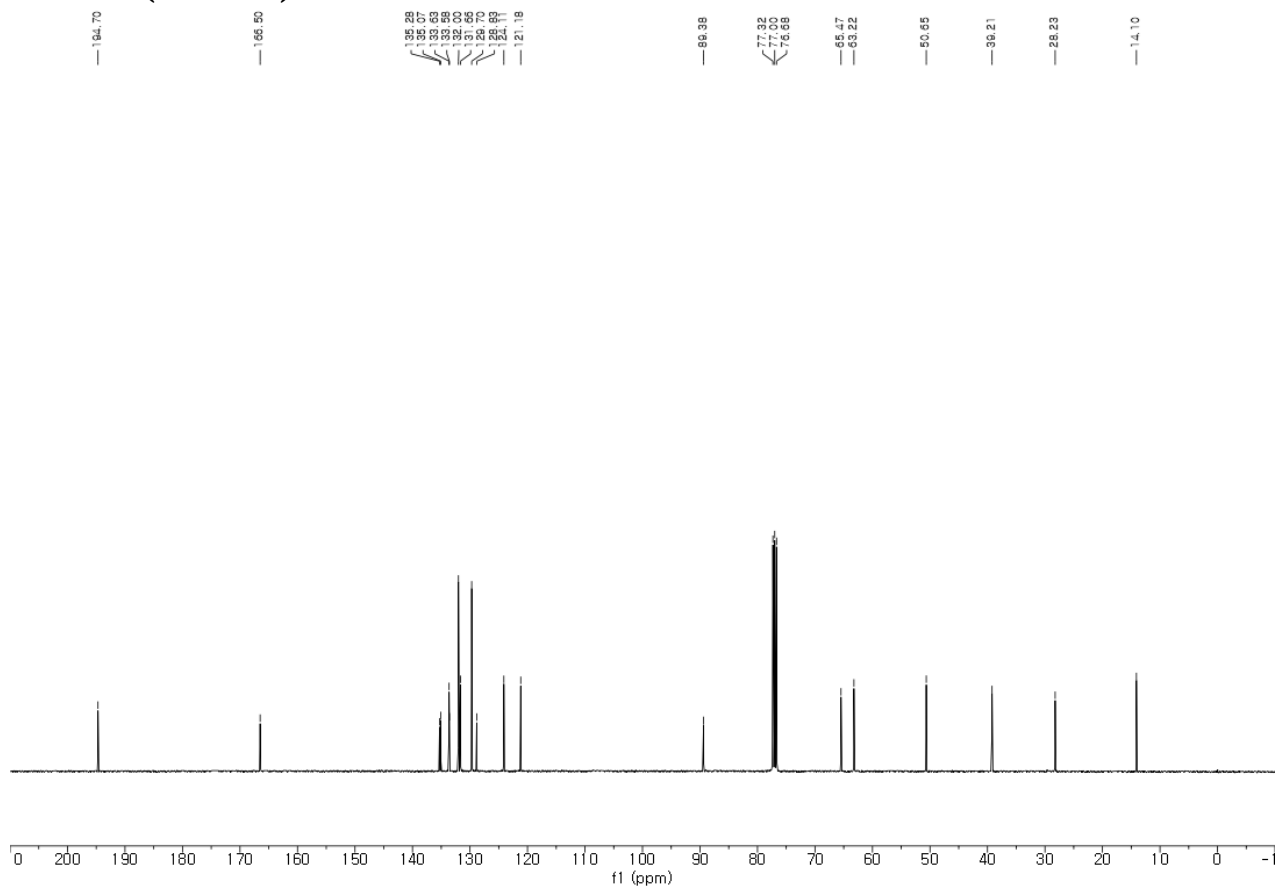
^{19}F NMR (376 MHz) in CDCl_3 

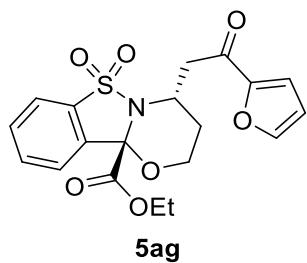
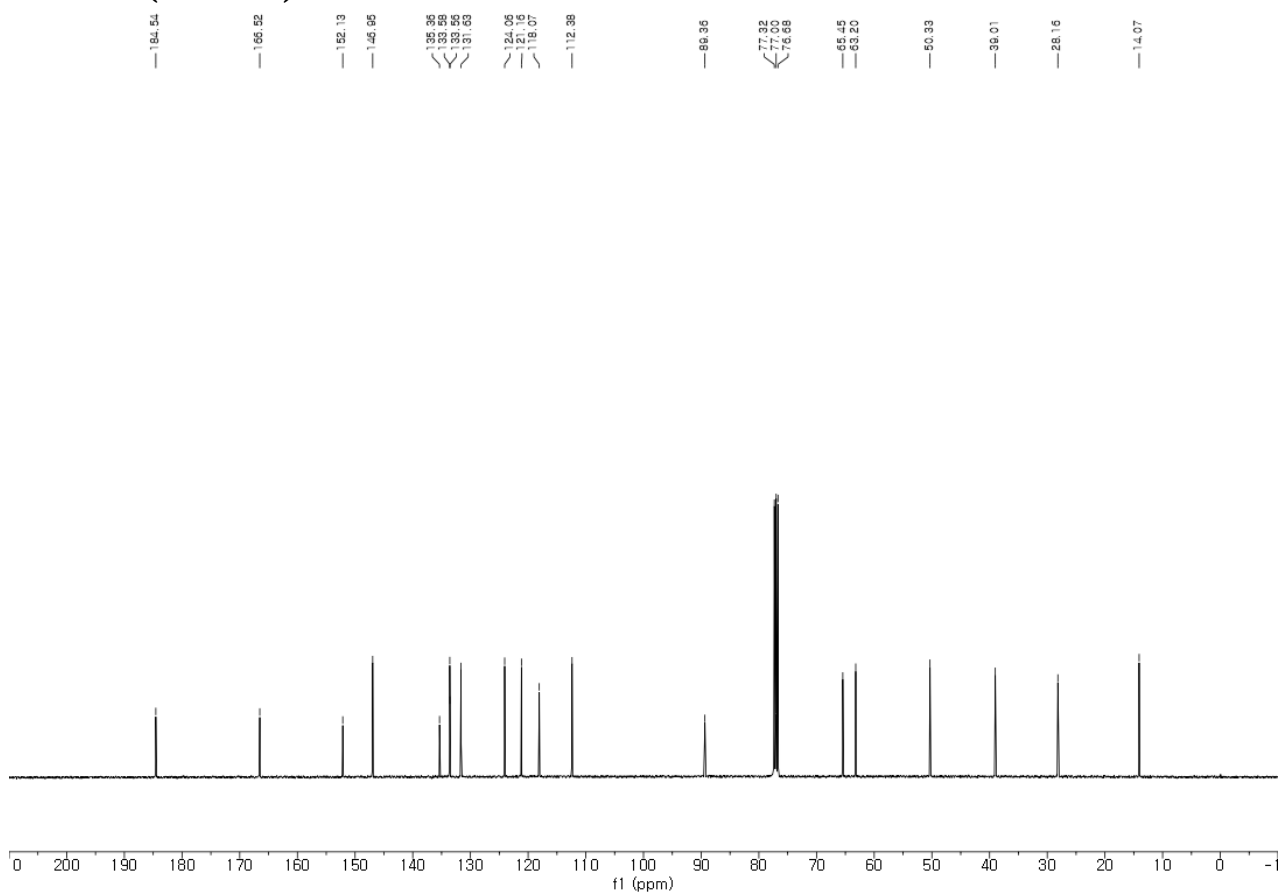
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

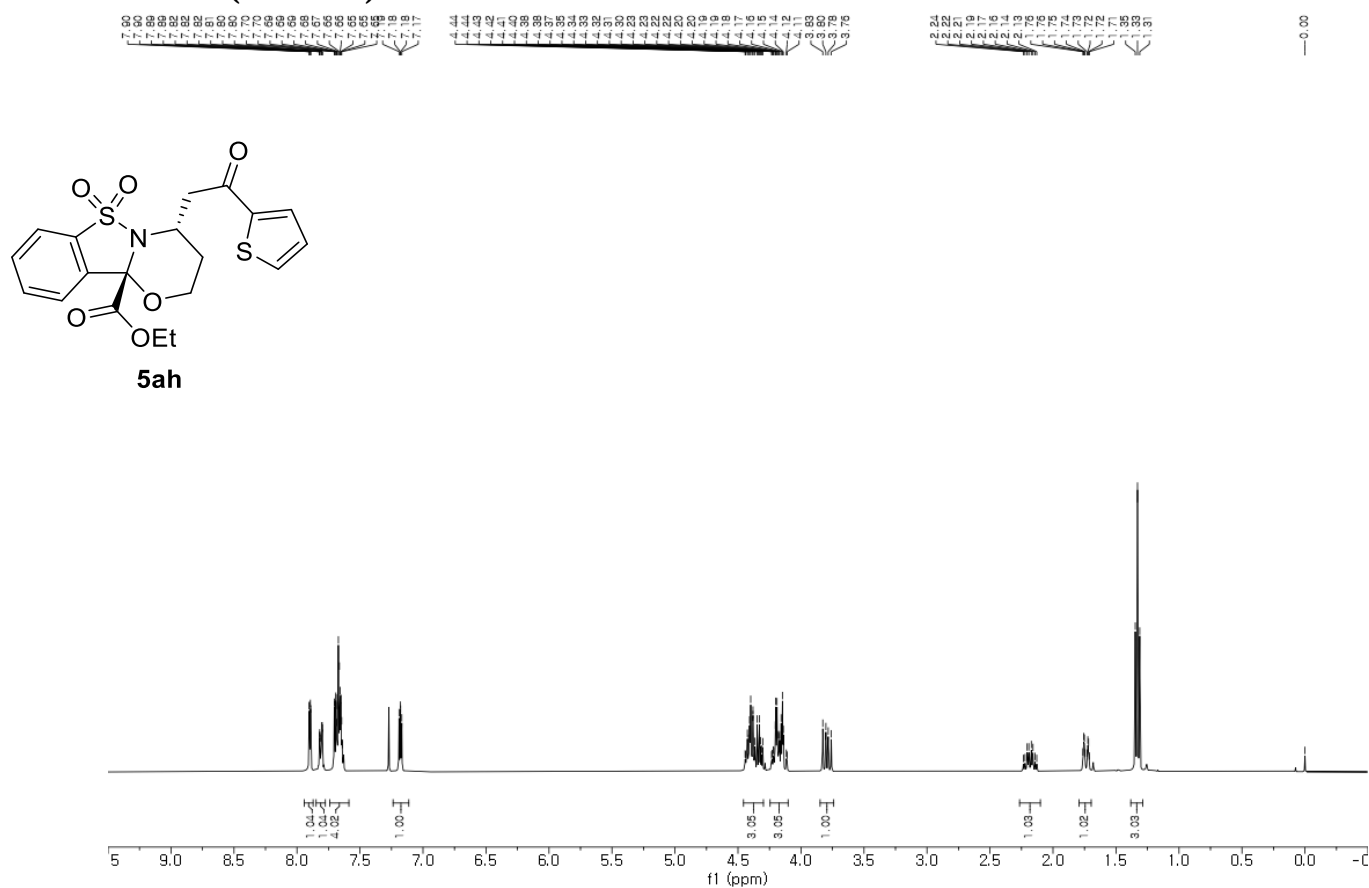
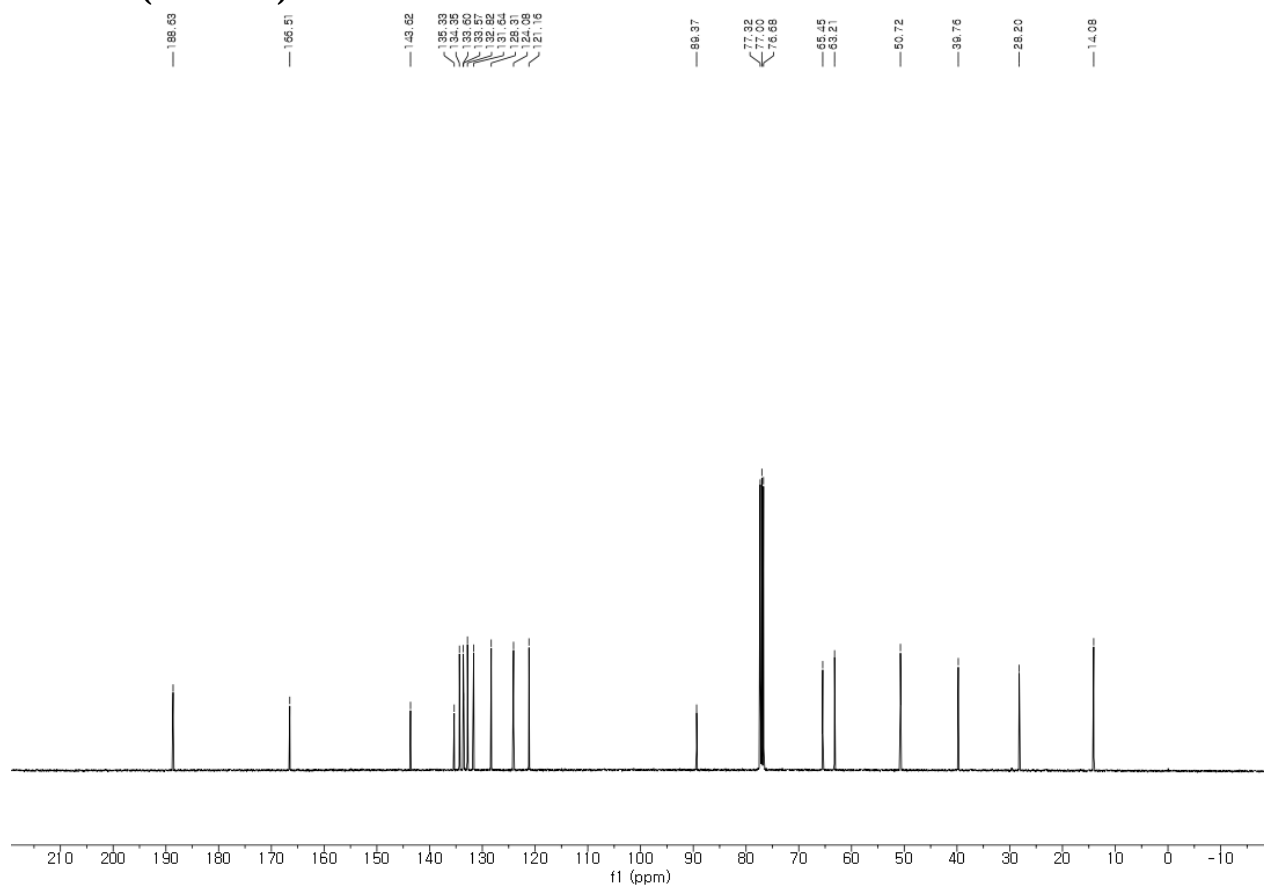
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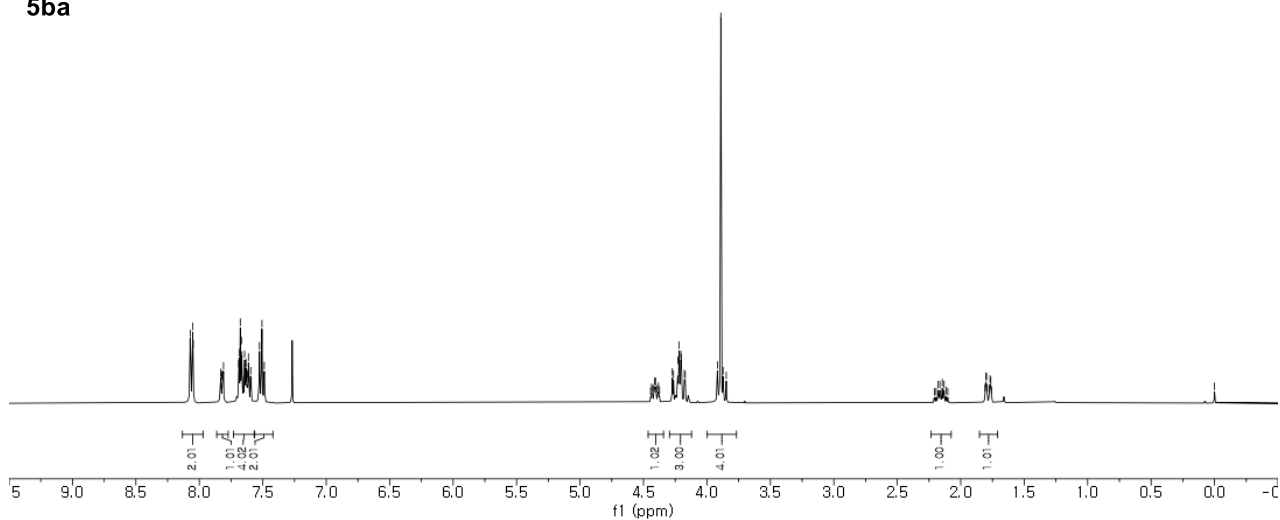
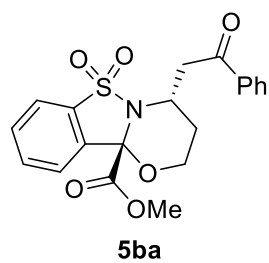
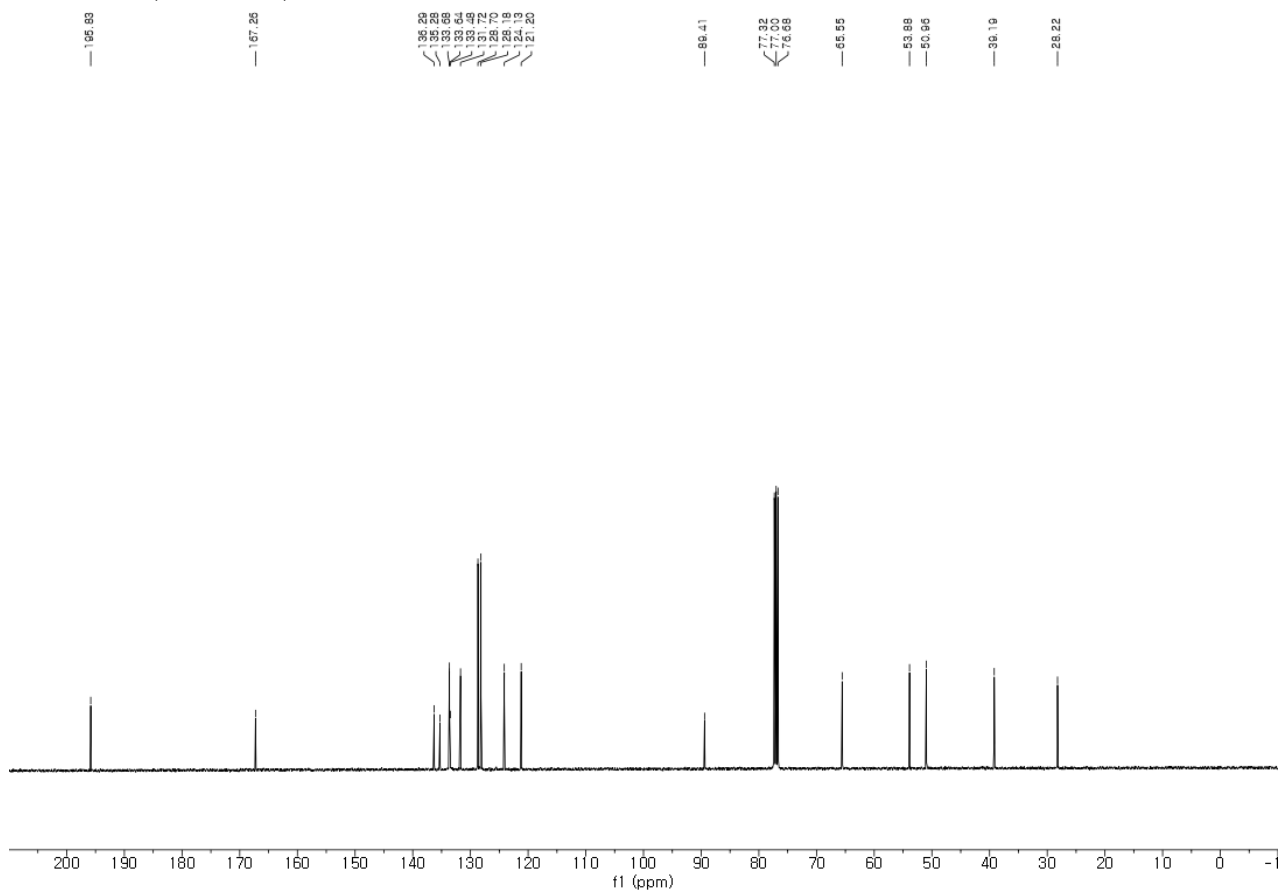


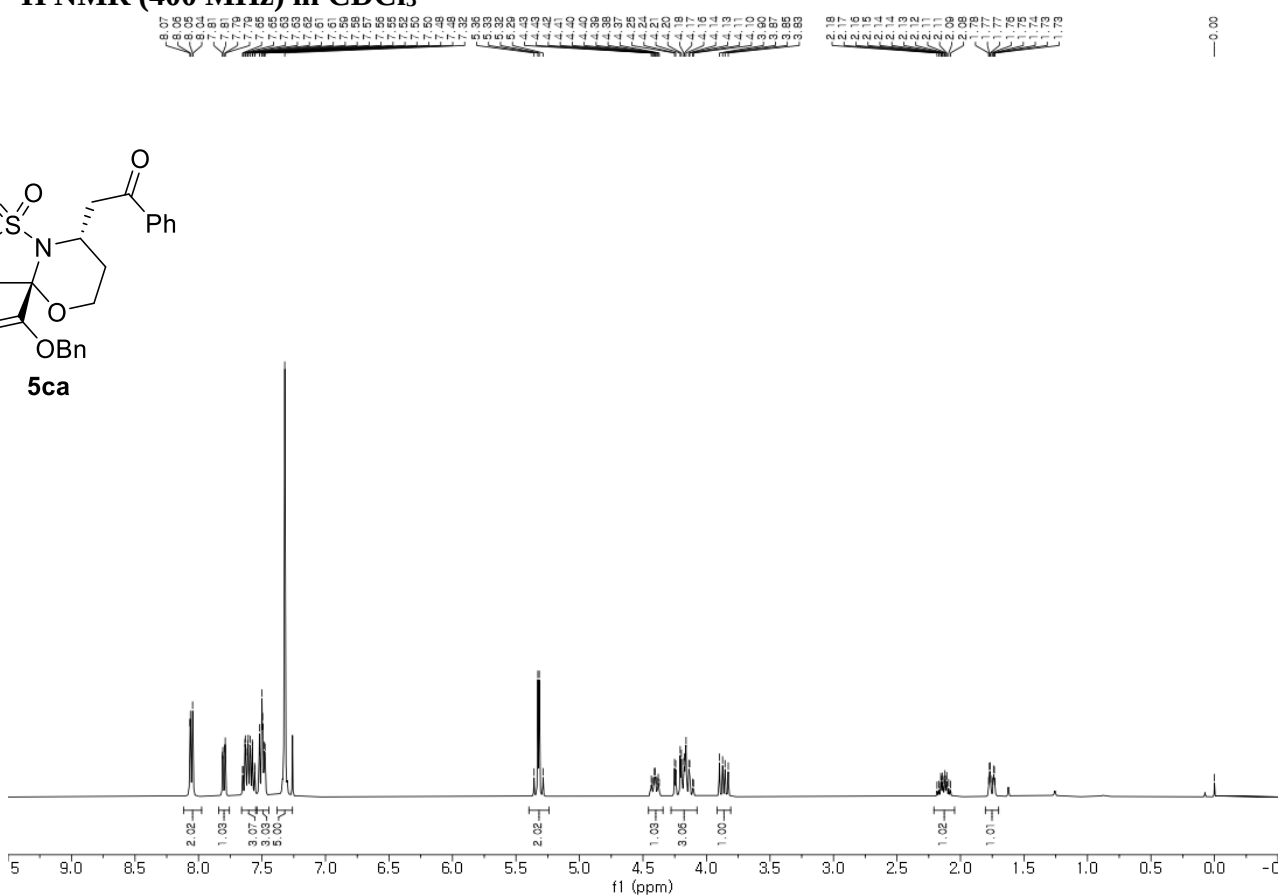
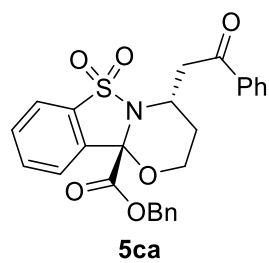
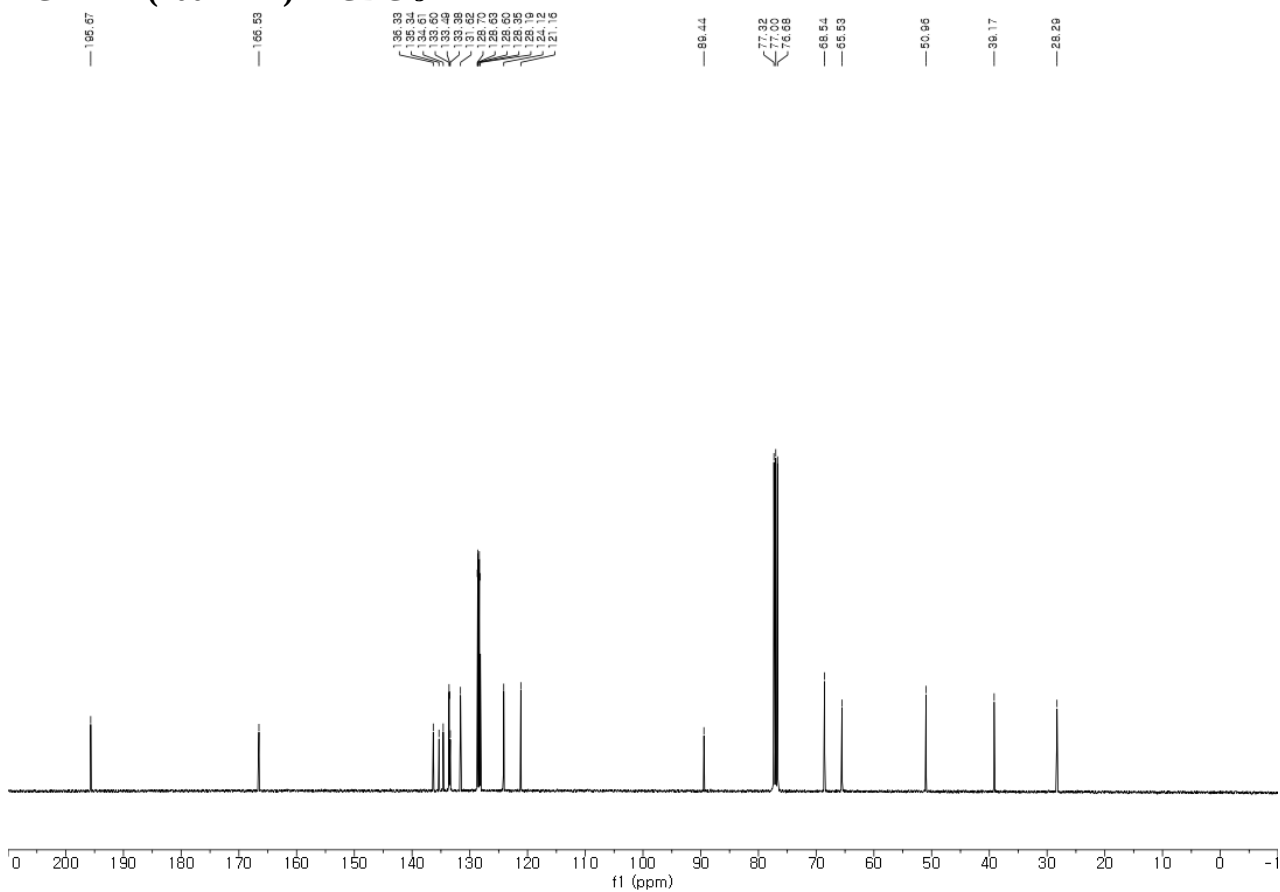
—184.70

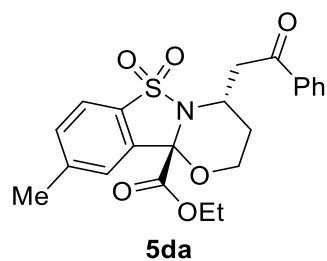
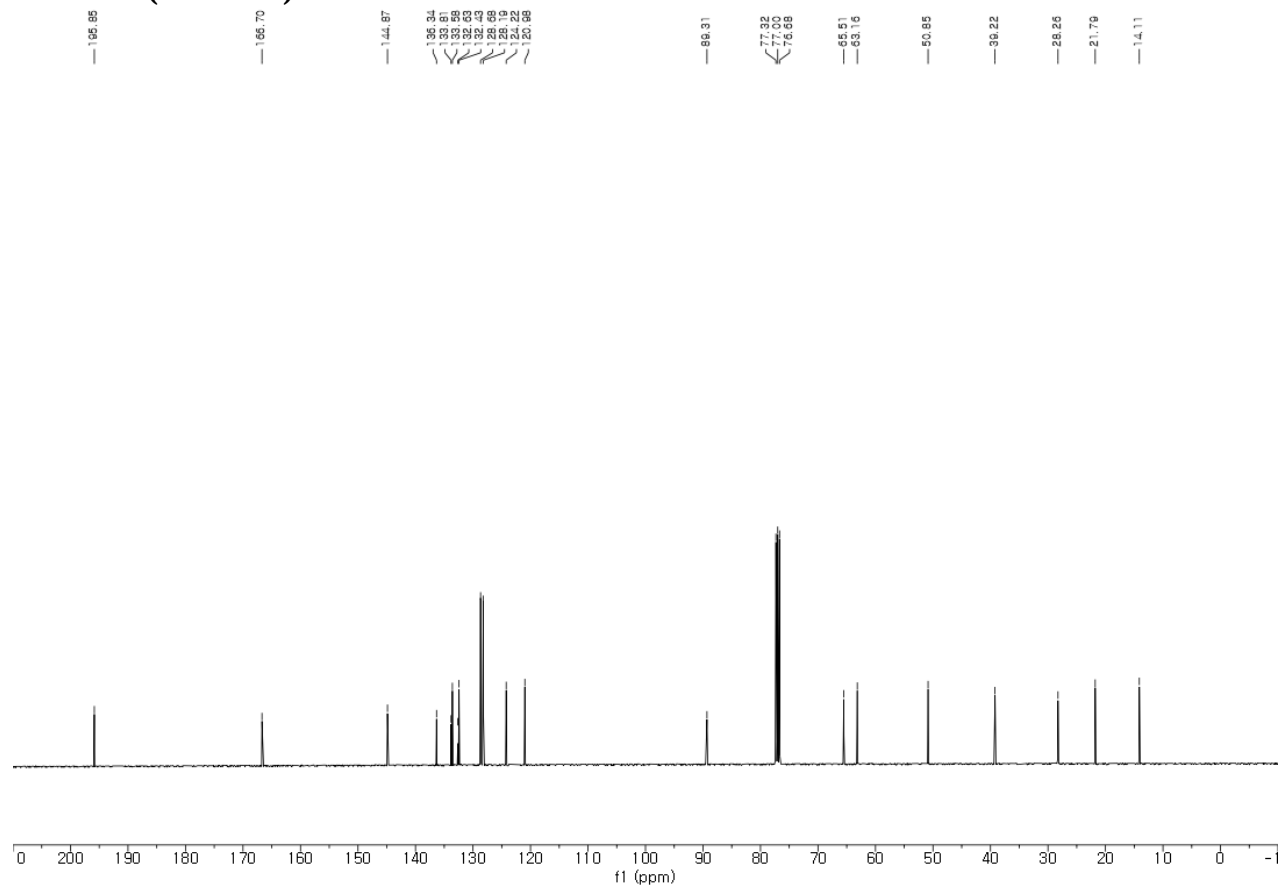


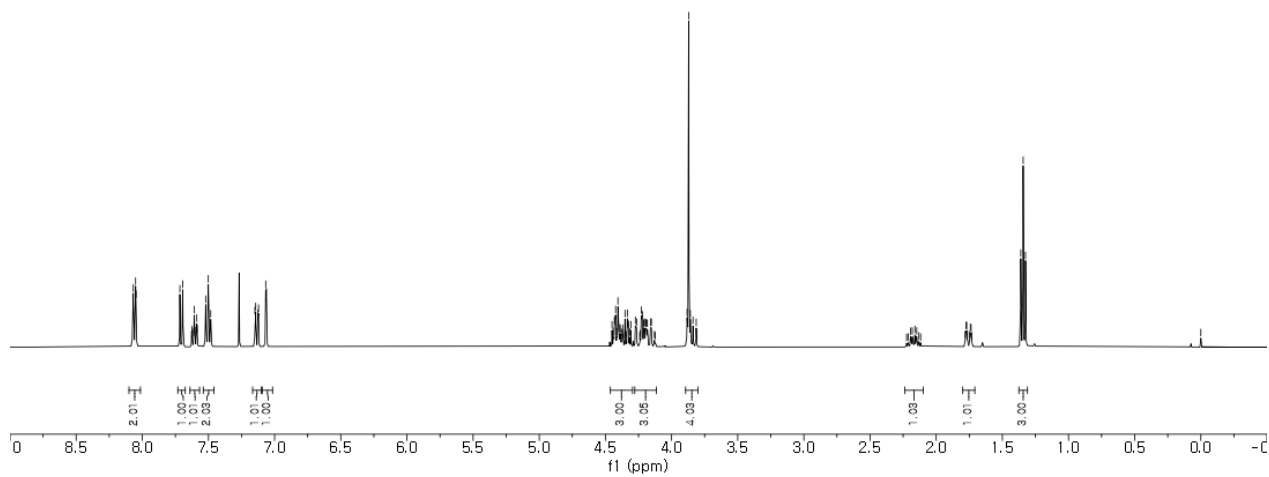
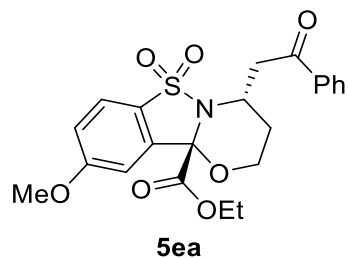
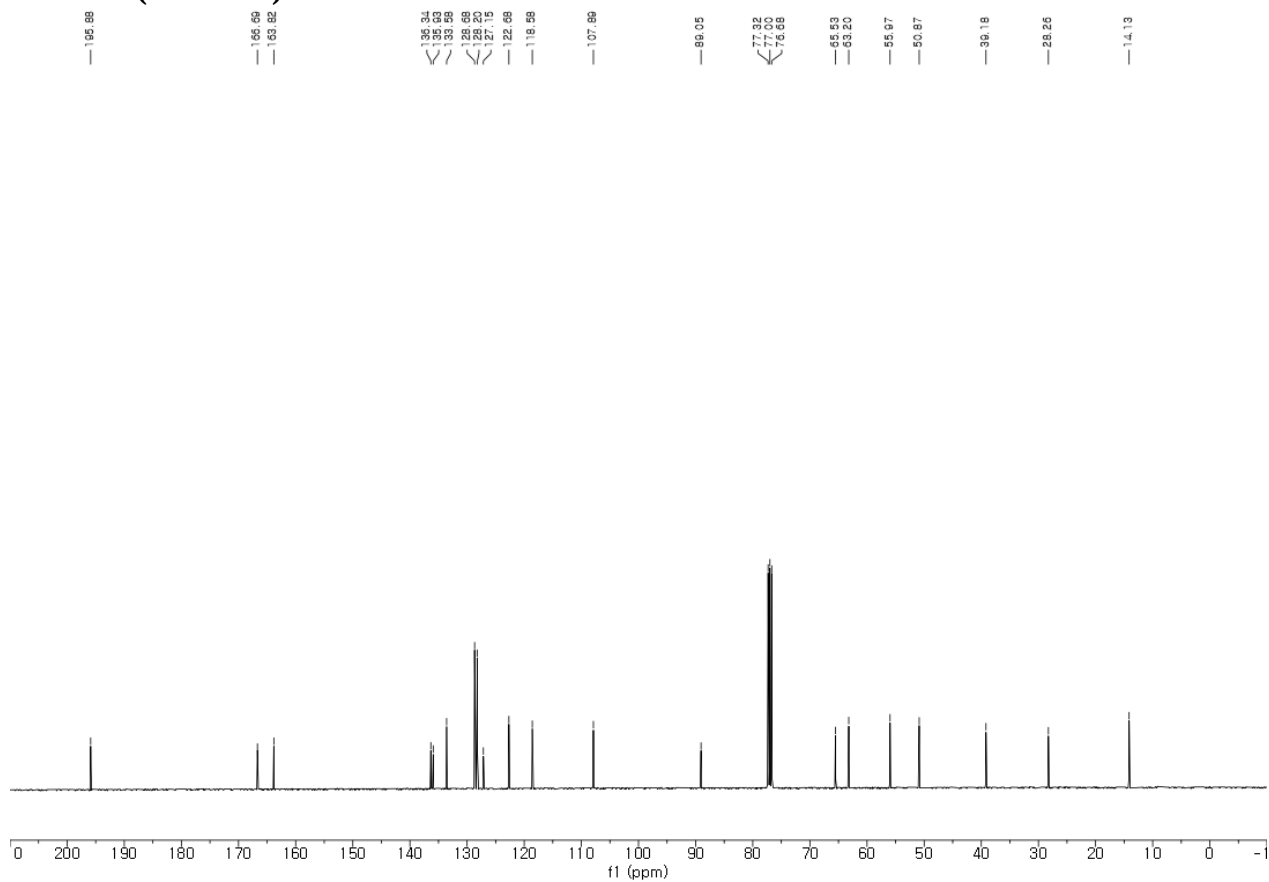
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

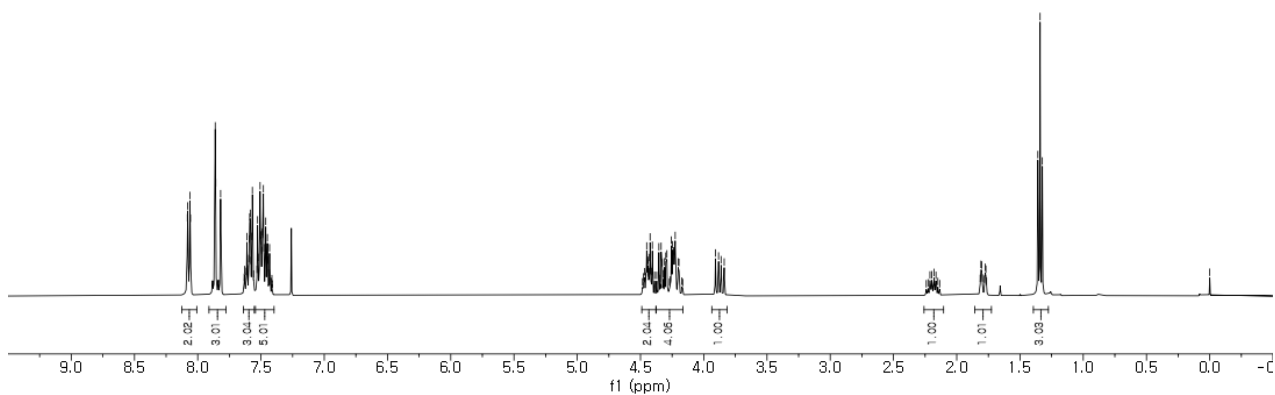
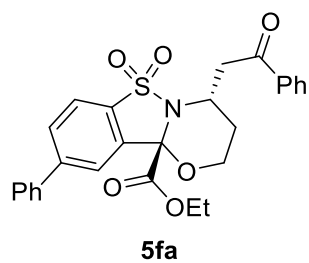
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

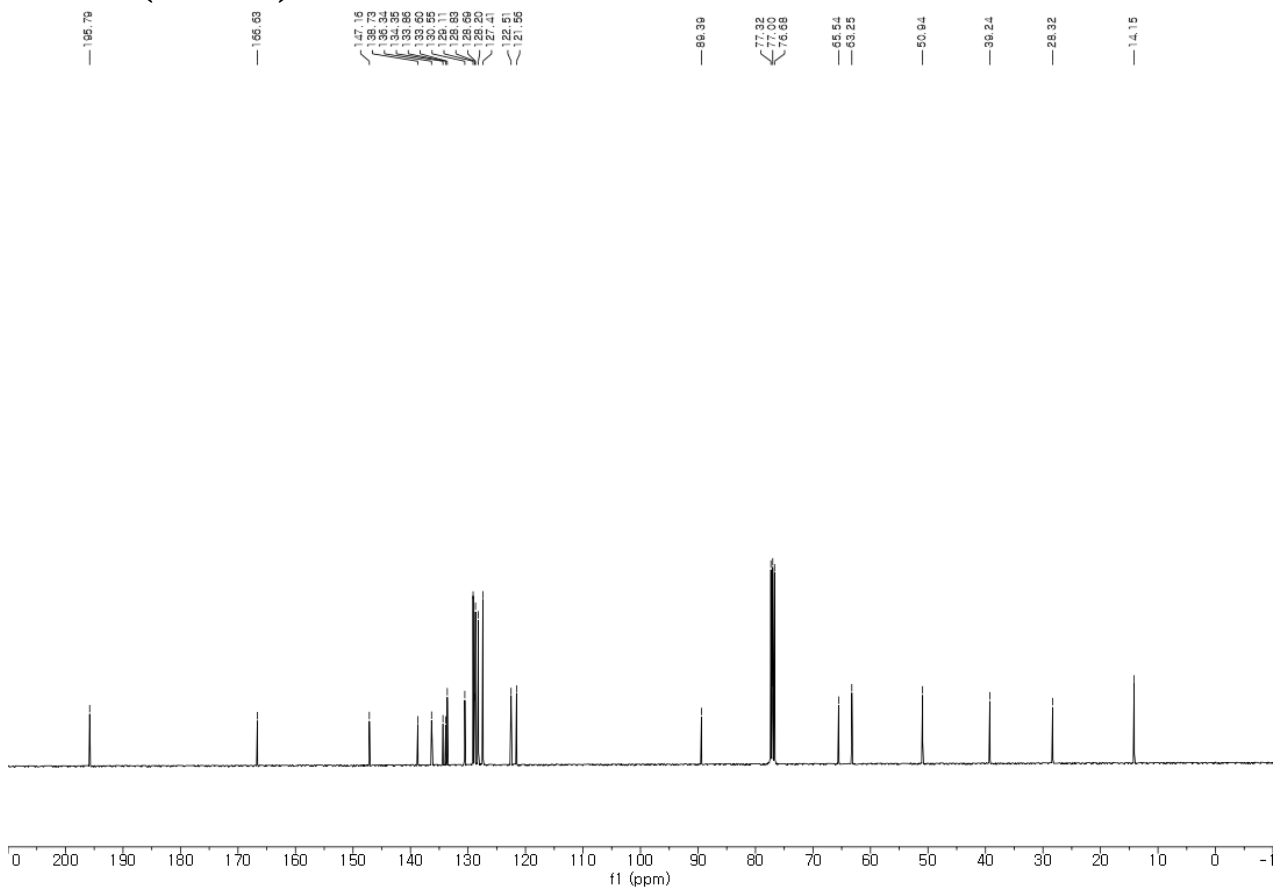
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

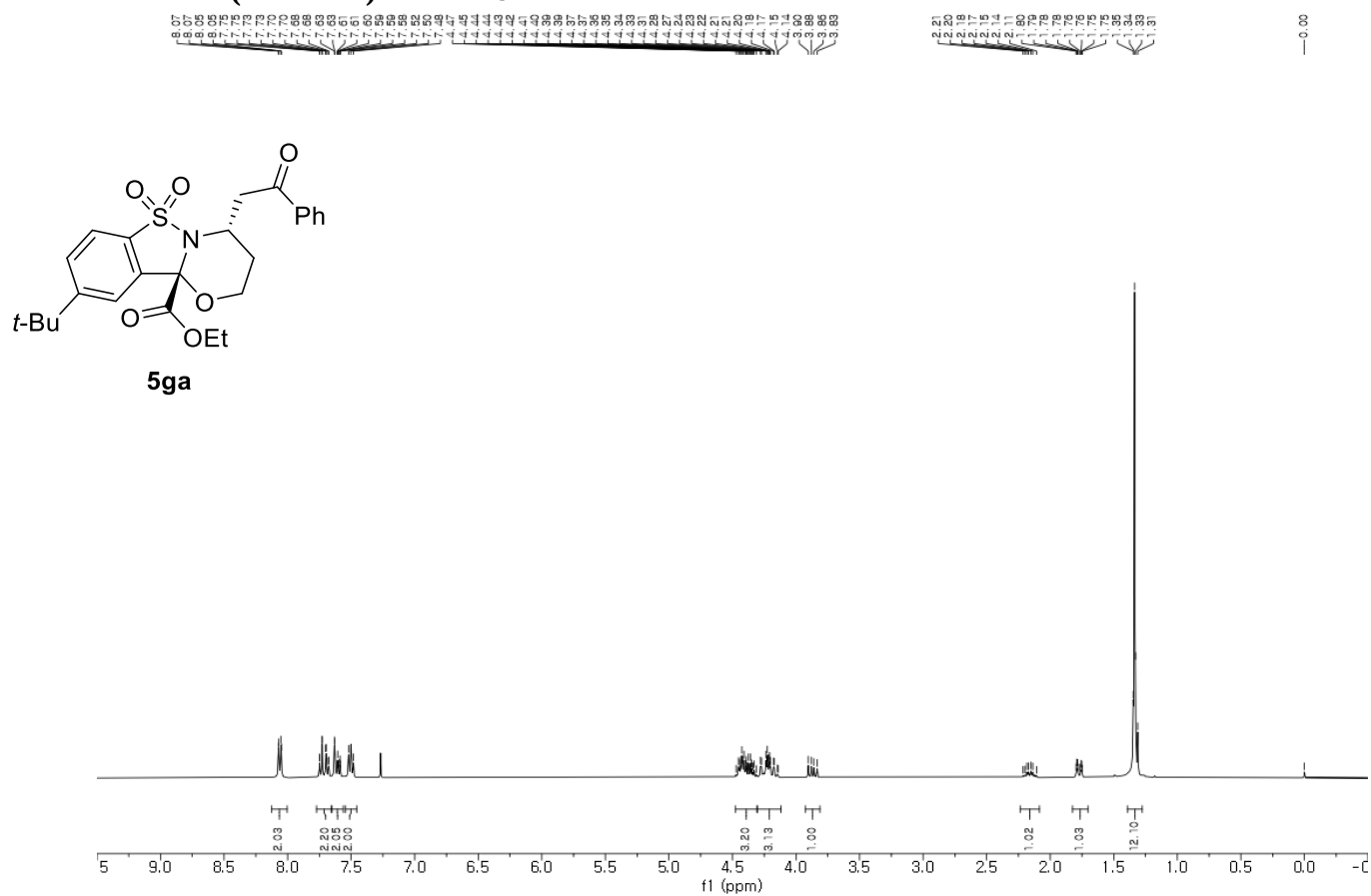
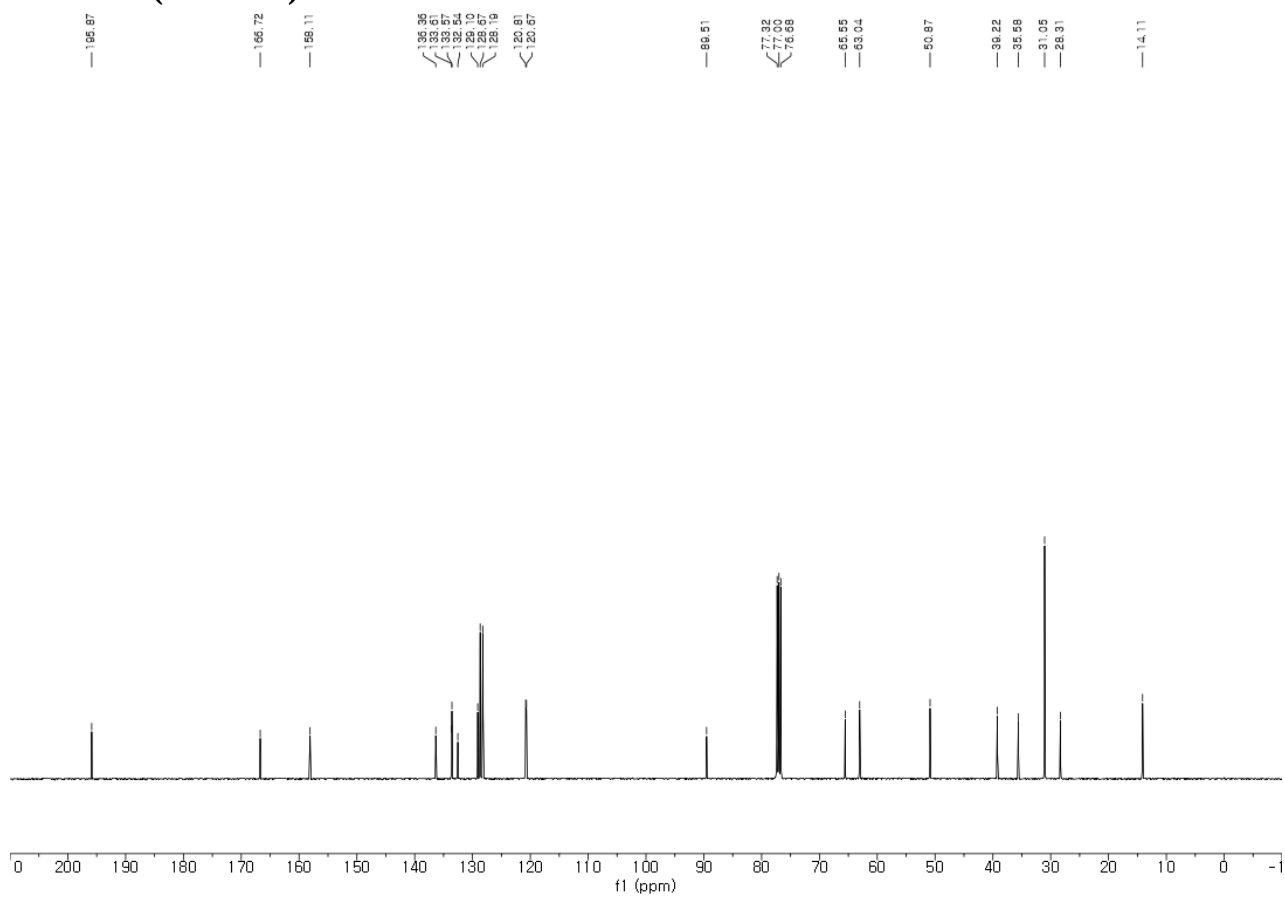
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

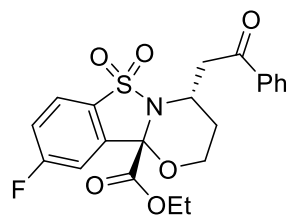
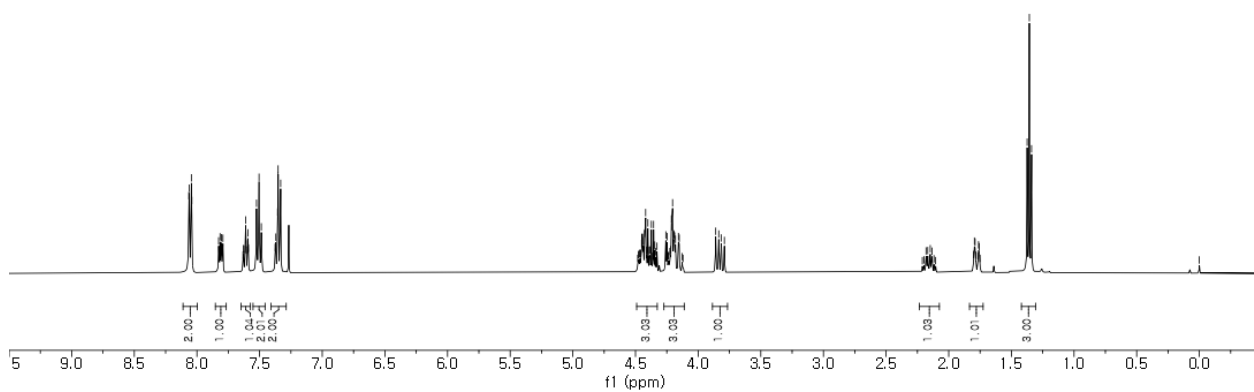
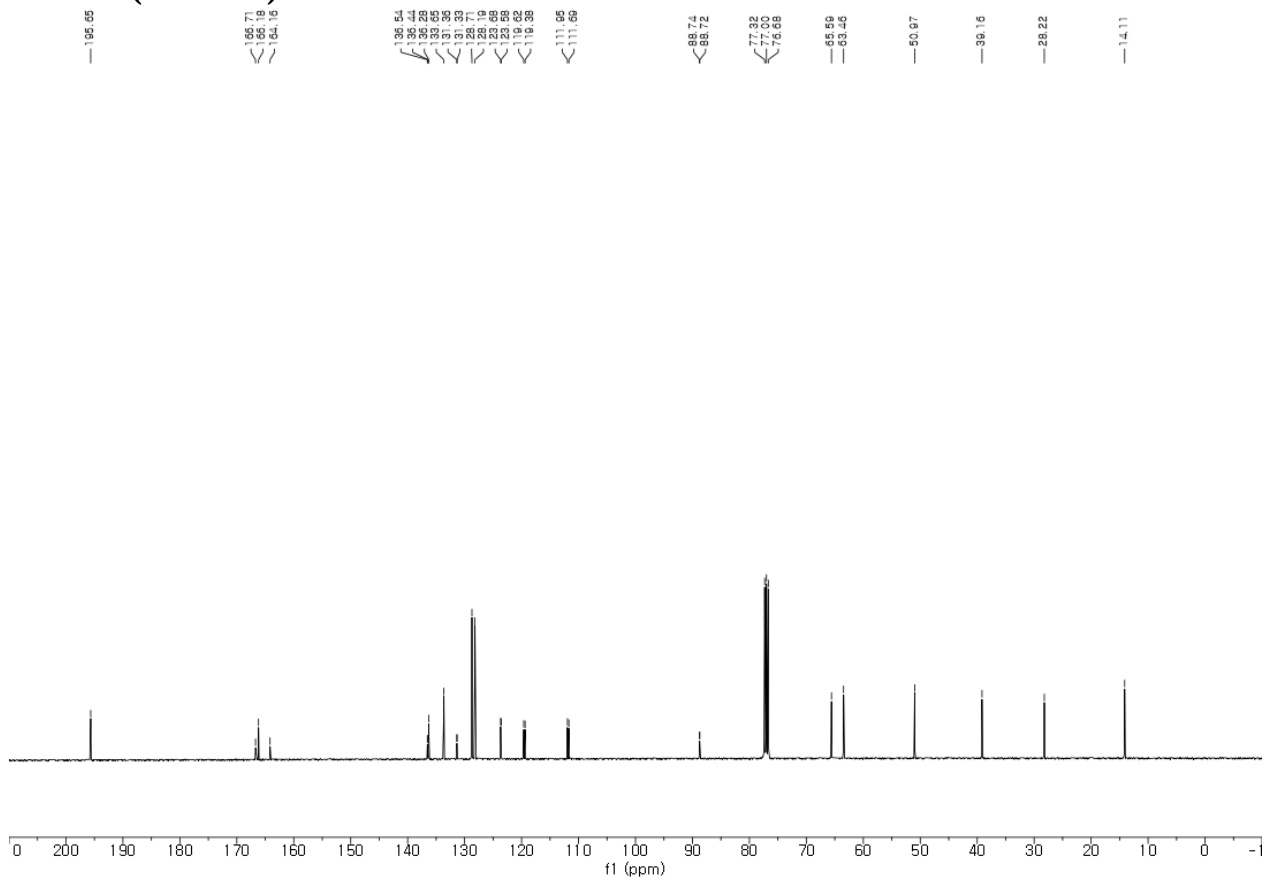
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

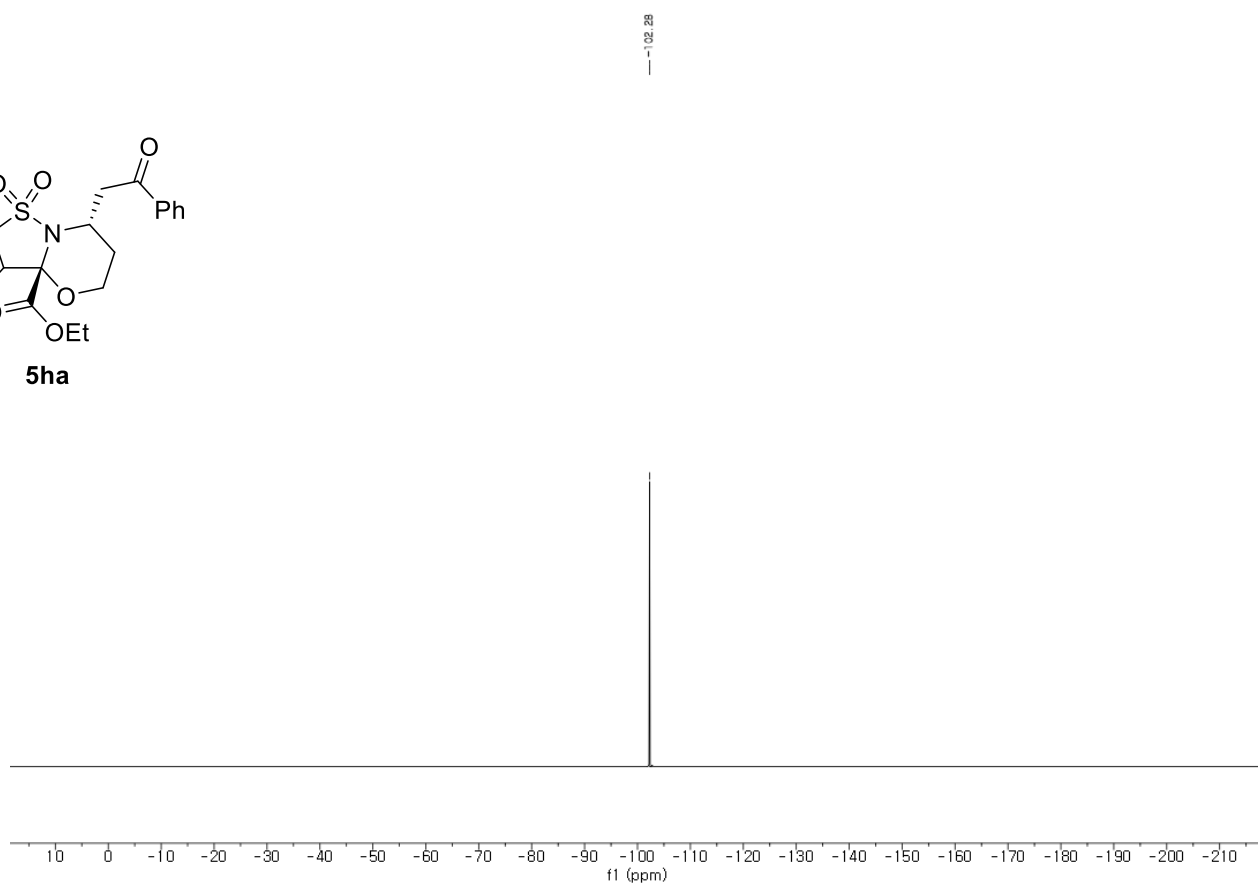
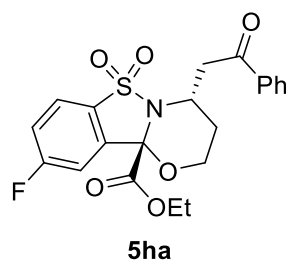


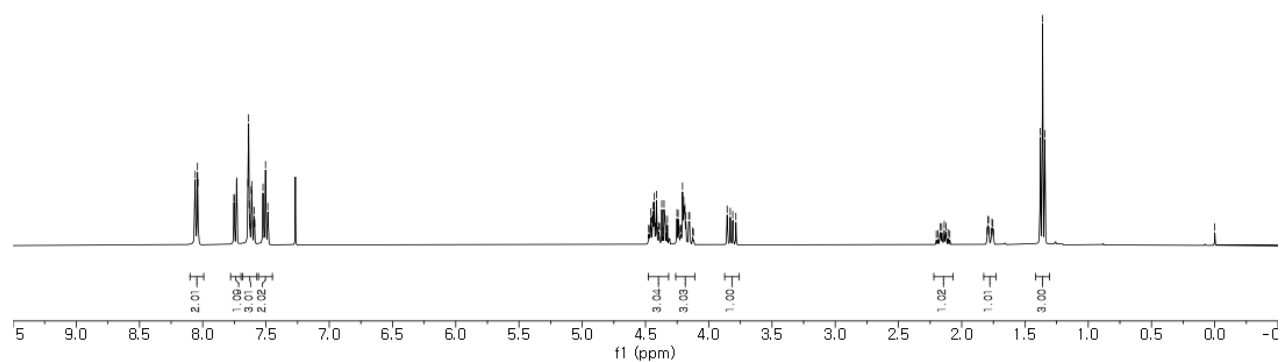
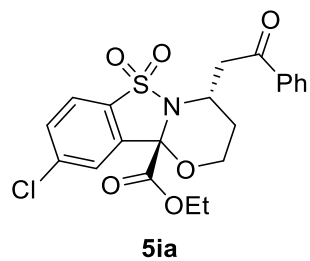
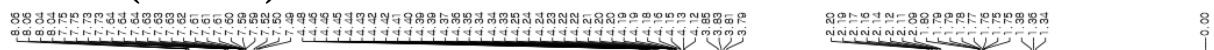
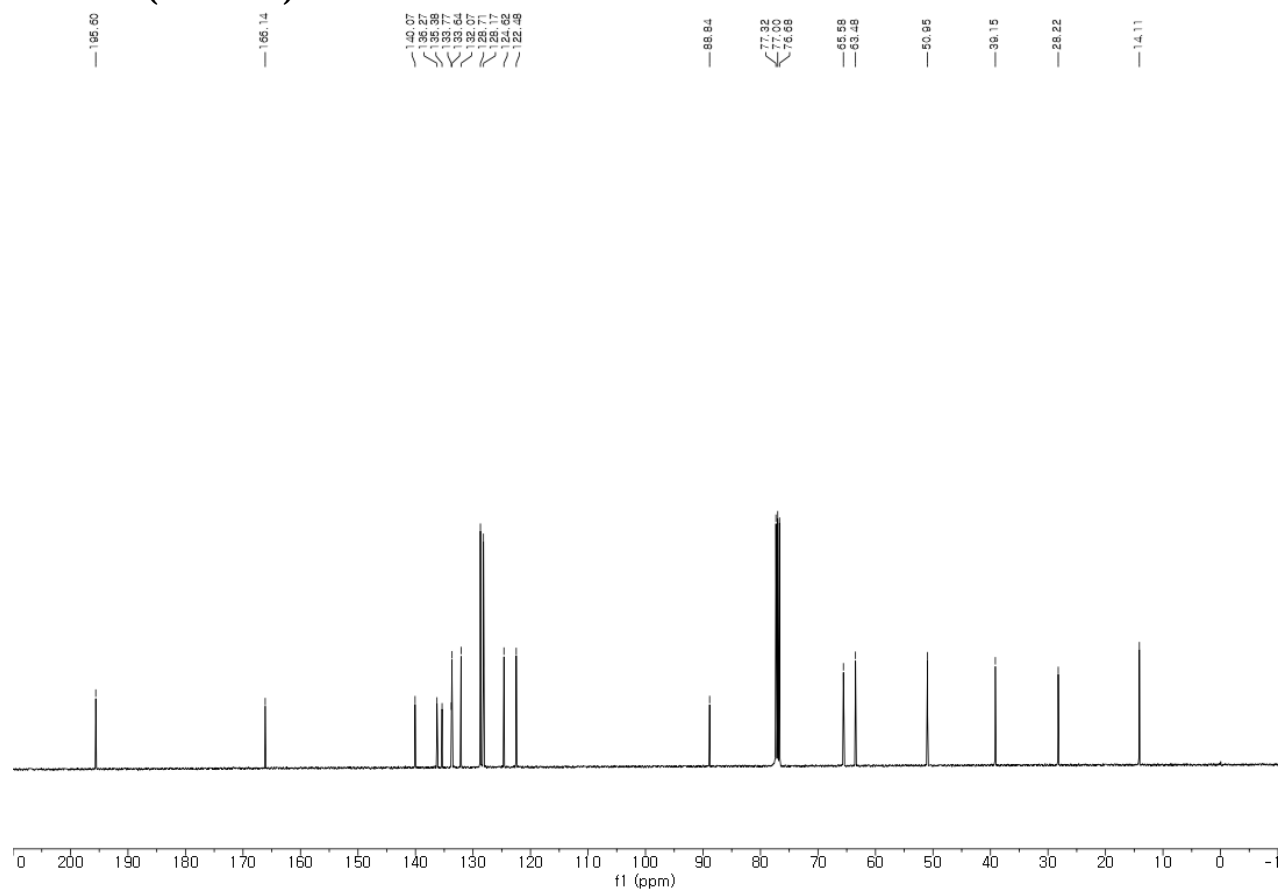
^{13}C NMR (100 MHz) in CDCl_3



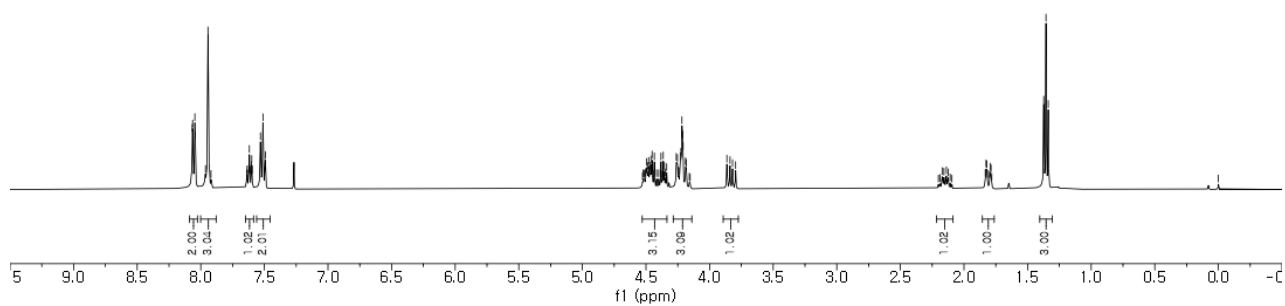
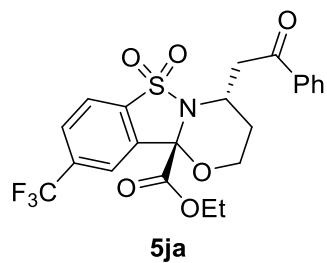
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3 **5ha** **^{13}C NMR (100 MHz) in CDCl_3** 

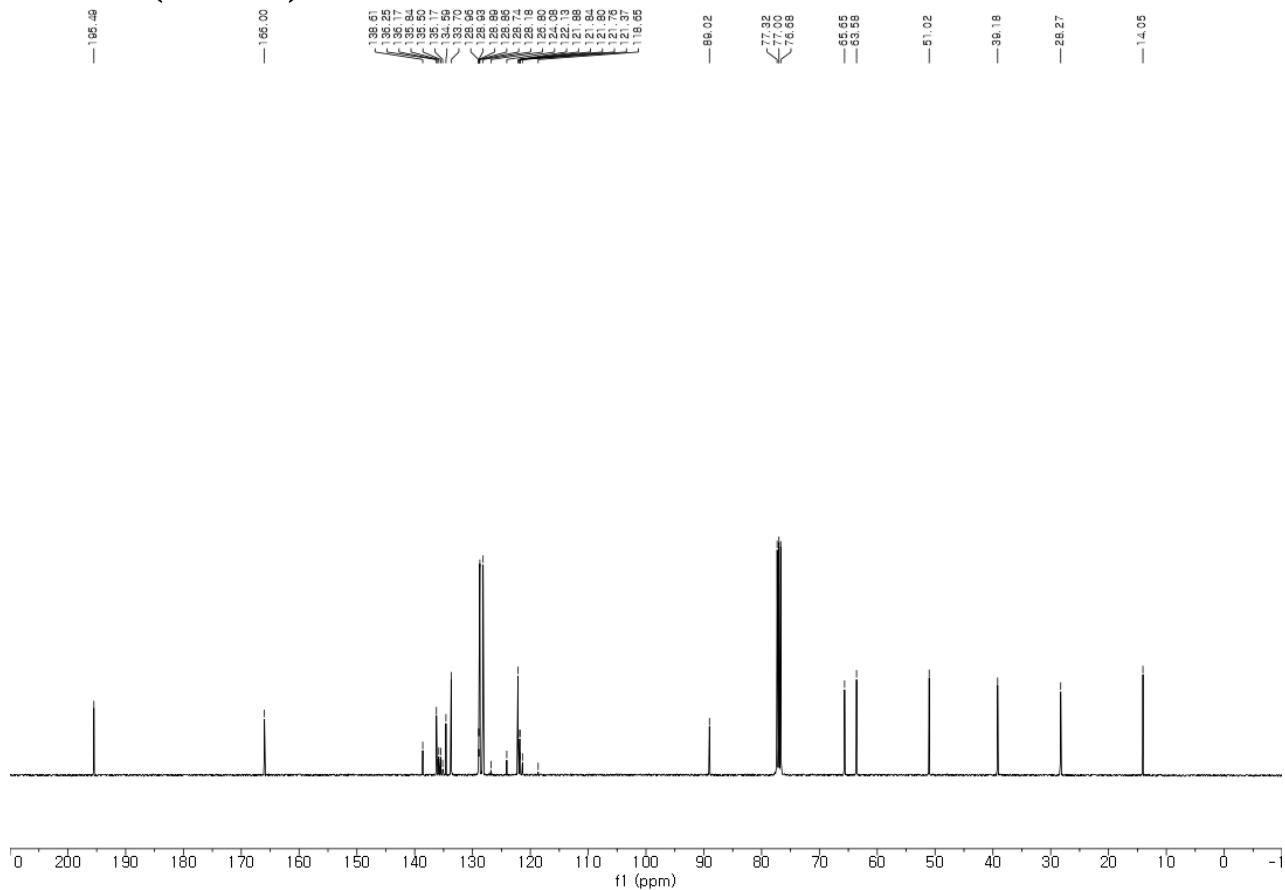
^{19}F NMR (376 MHz) in CDCl_3 

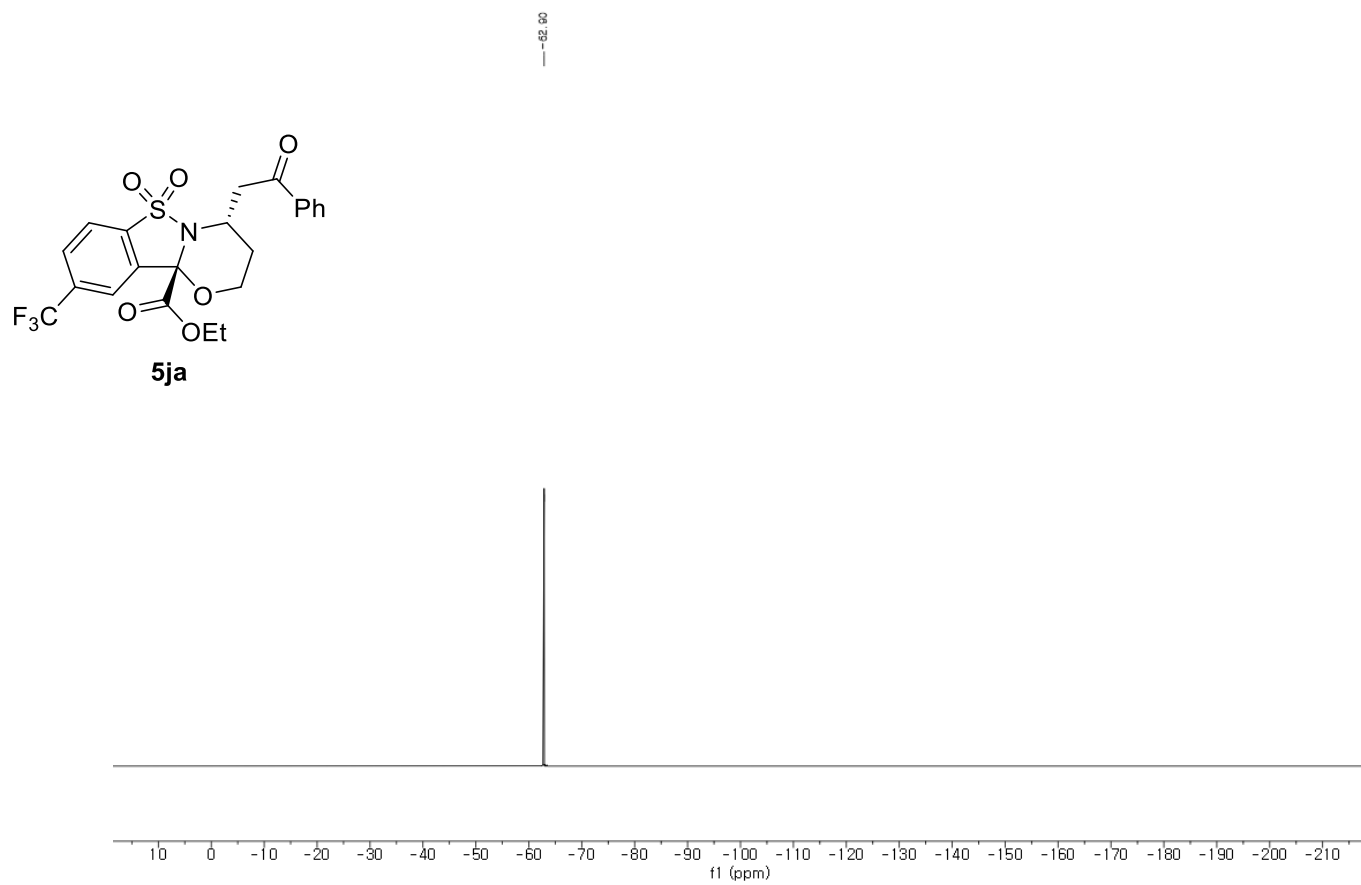
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

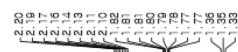
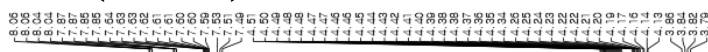
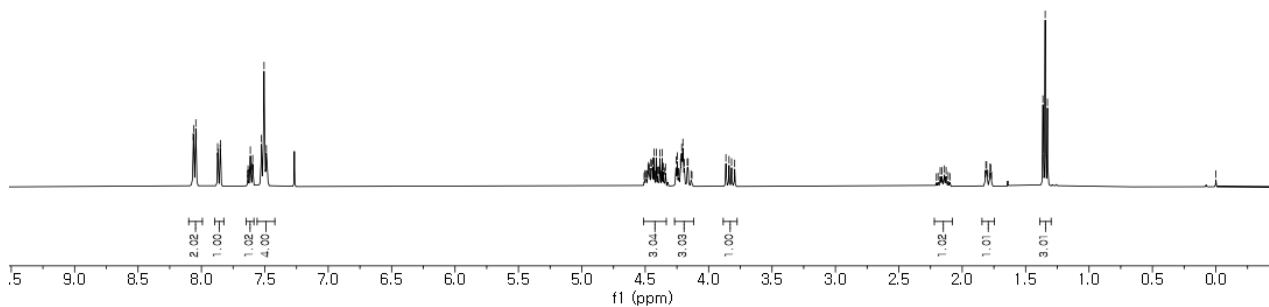
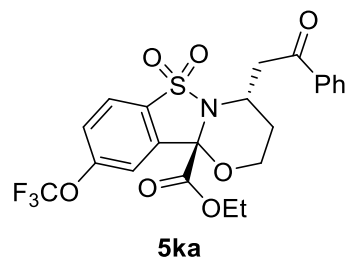
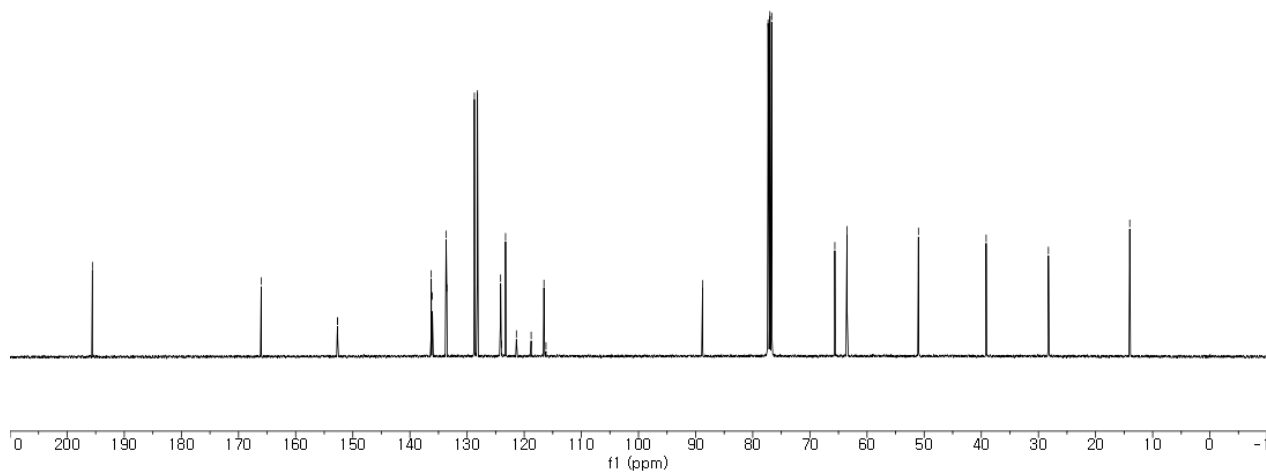
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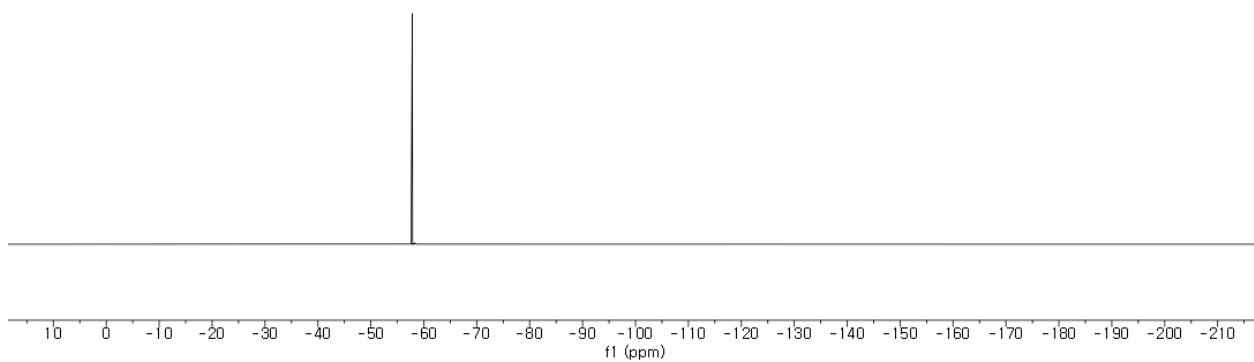
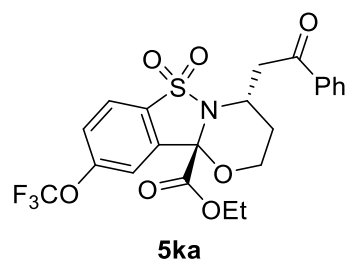


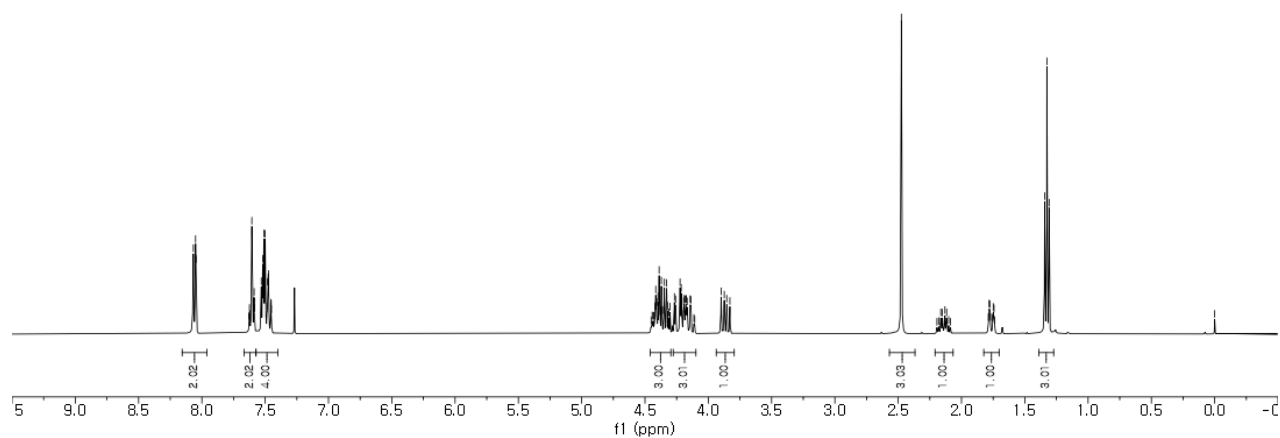
195.49 — 165.00



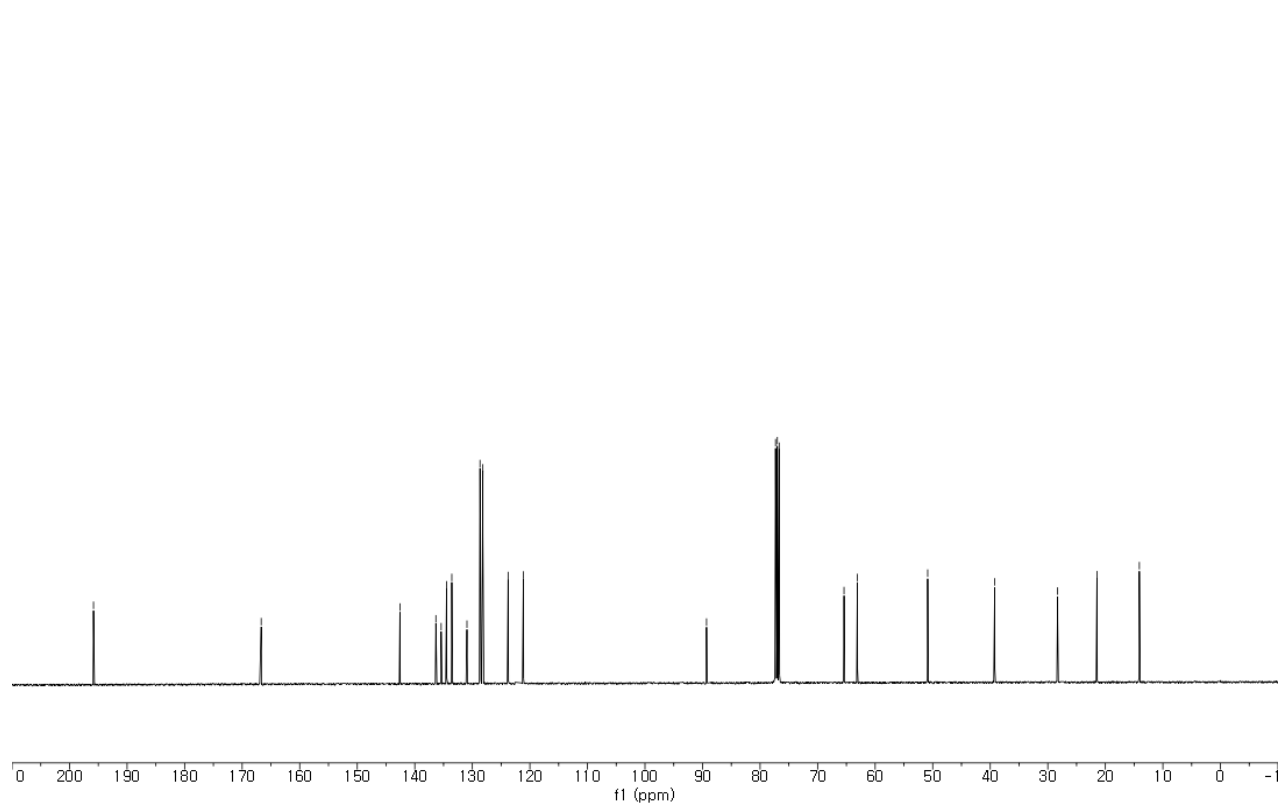
^{19}F NMR (376 MHz) in CDCl_3 

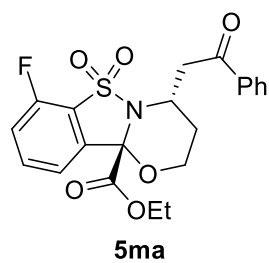
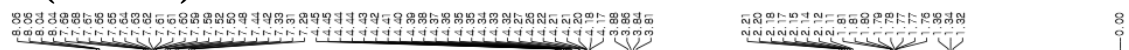
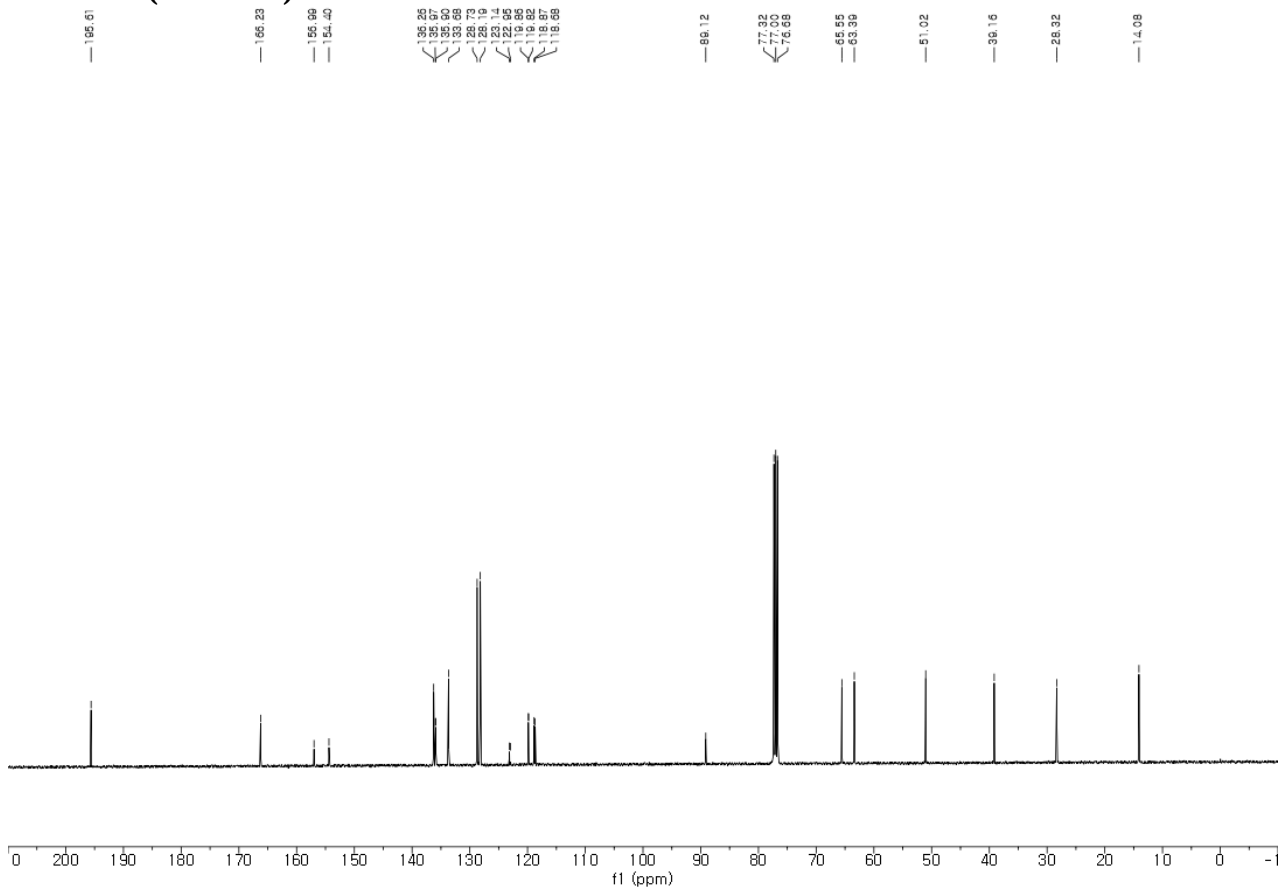
¹H NMR (400 MHz) in CDCl₃8
0**¹³C NMR (100 MHz) in CDCl₃**

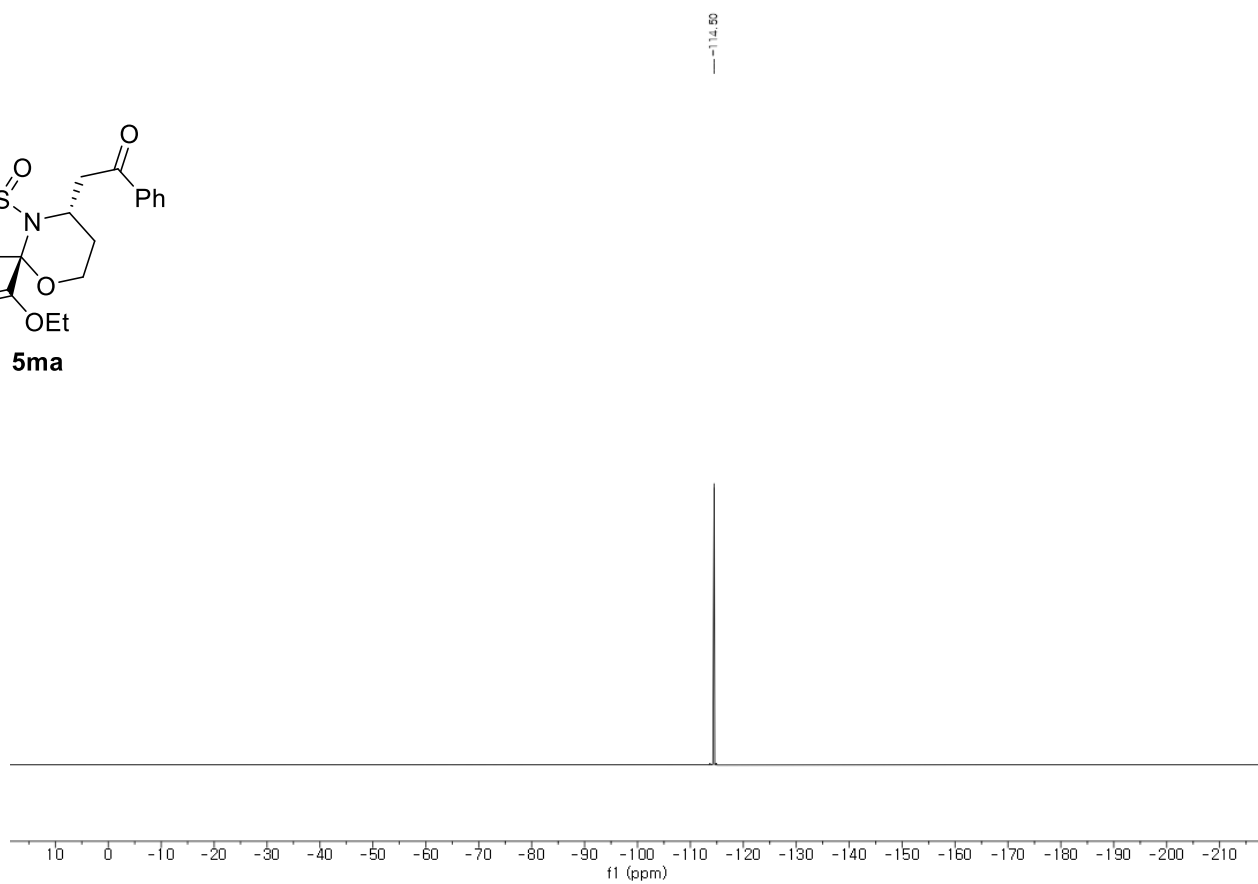
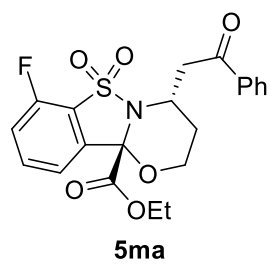
^{19}F NMR (376 MHz) in CDCl_3 83
5
1

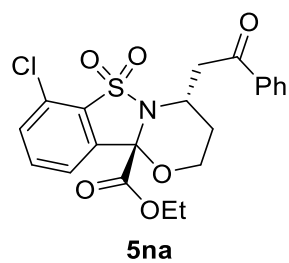
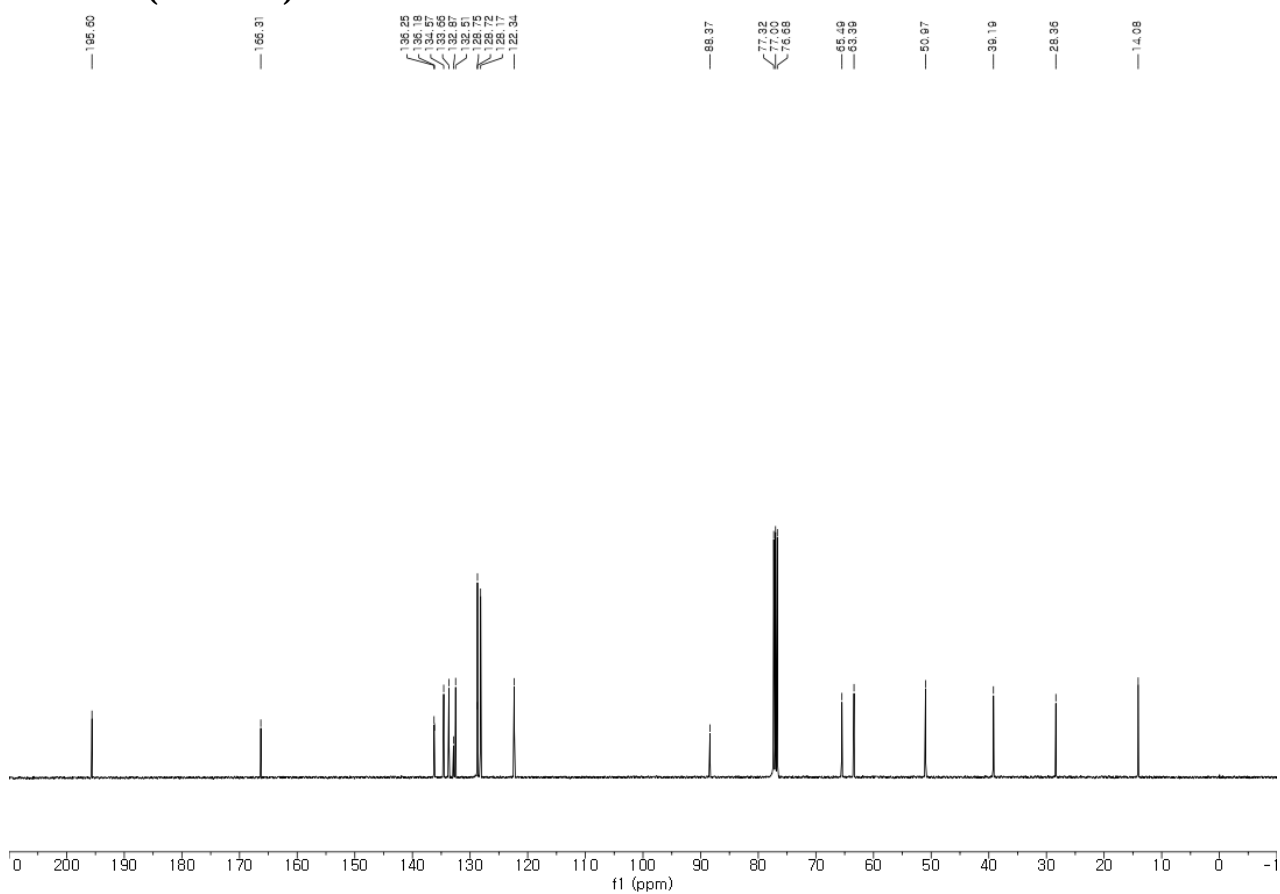


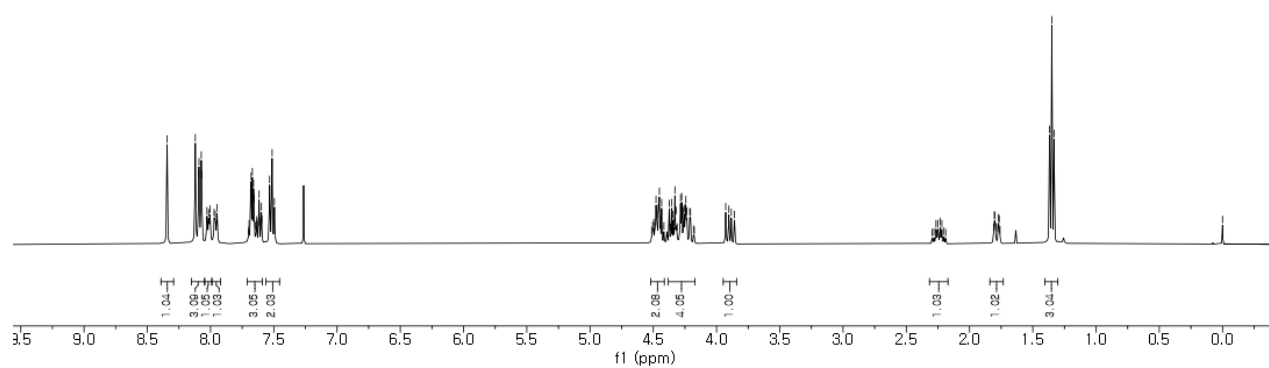
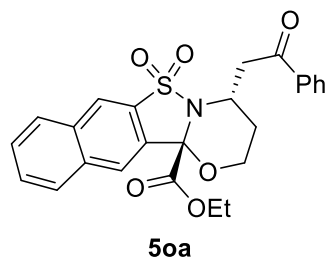
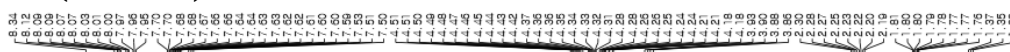
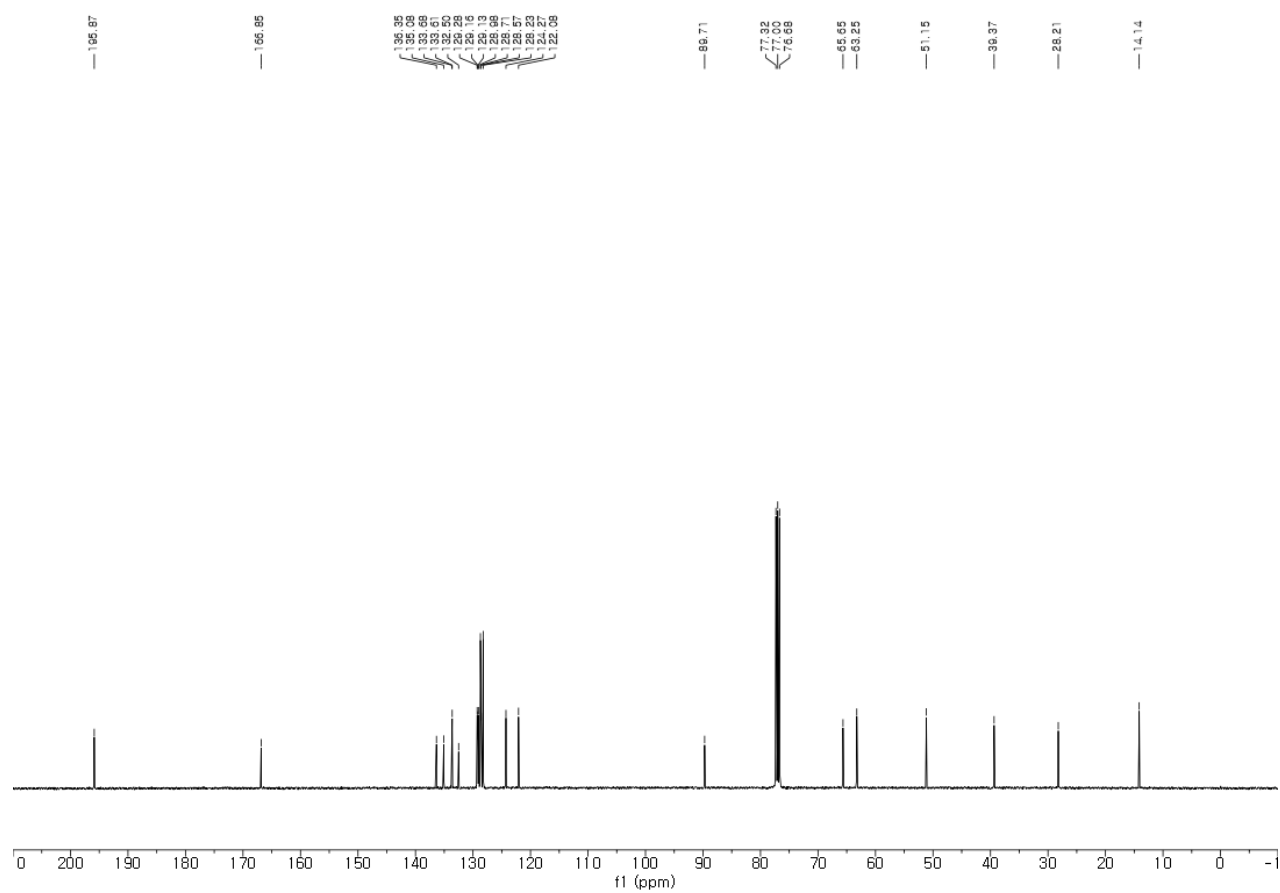
— 155.83

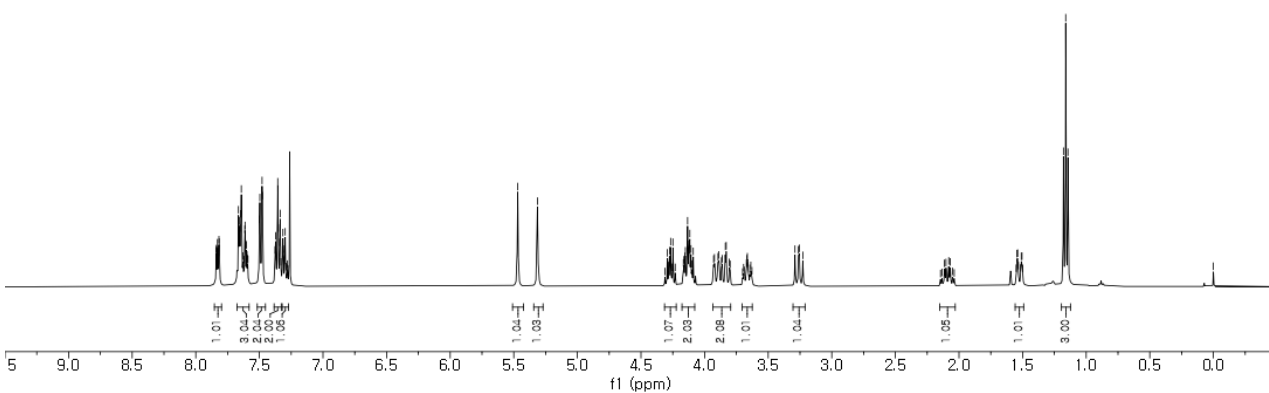
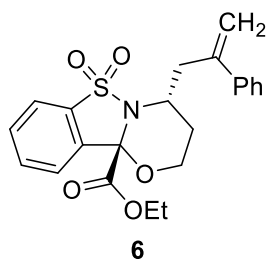
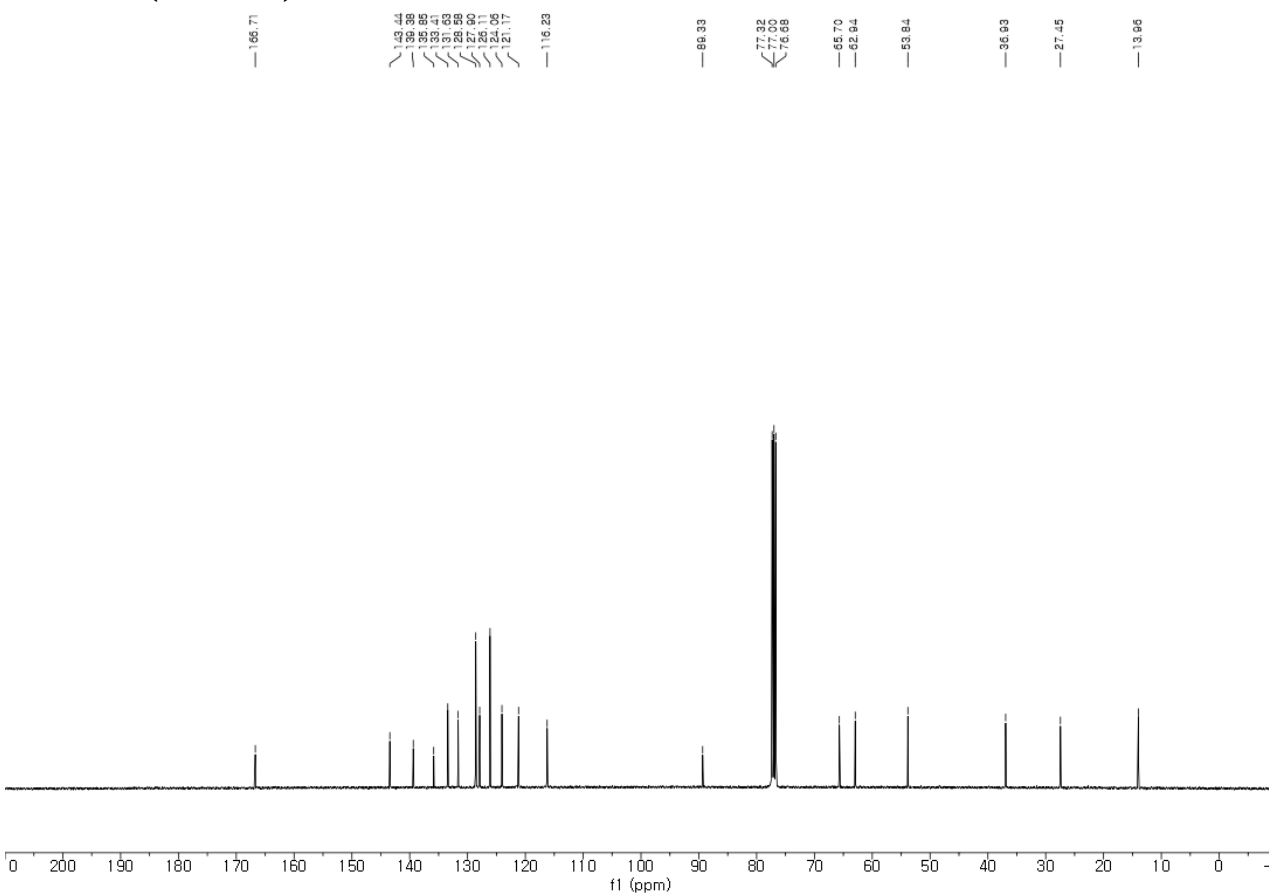


¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

^{19}F NMR (376 MHz) in CDCl_3 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

8.3920
7.790
7.786
7.785
7.784
7.784
7.773
7.772
7.771
7.769
7.768
7.767
7.765
7.764
7.764
7.763
7.762
7.738
7.737
7.736
7.729
7.727
7.726



—166.23

—150.84

—144.08

135.70
135.17
135.06
133.80
133.24
131.83
129.50
128.60
128.22
126.41
124.24
121.35

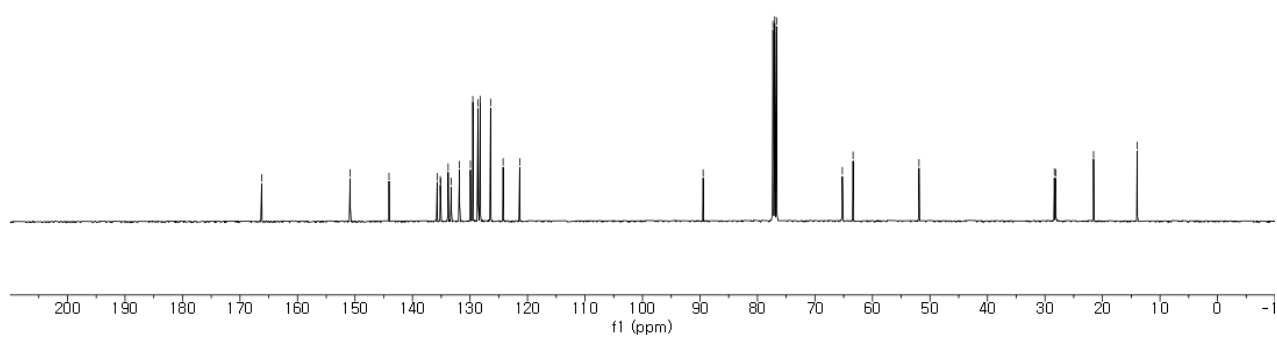
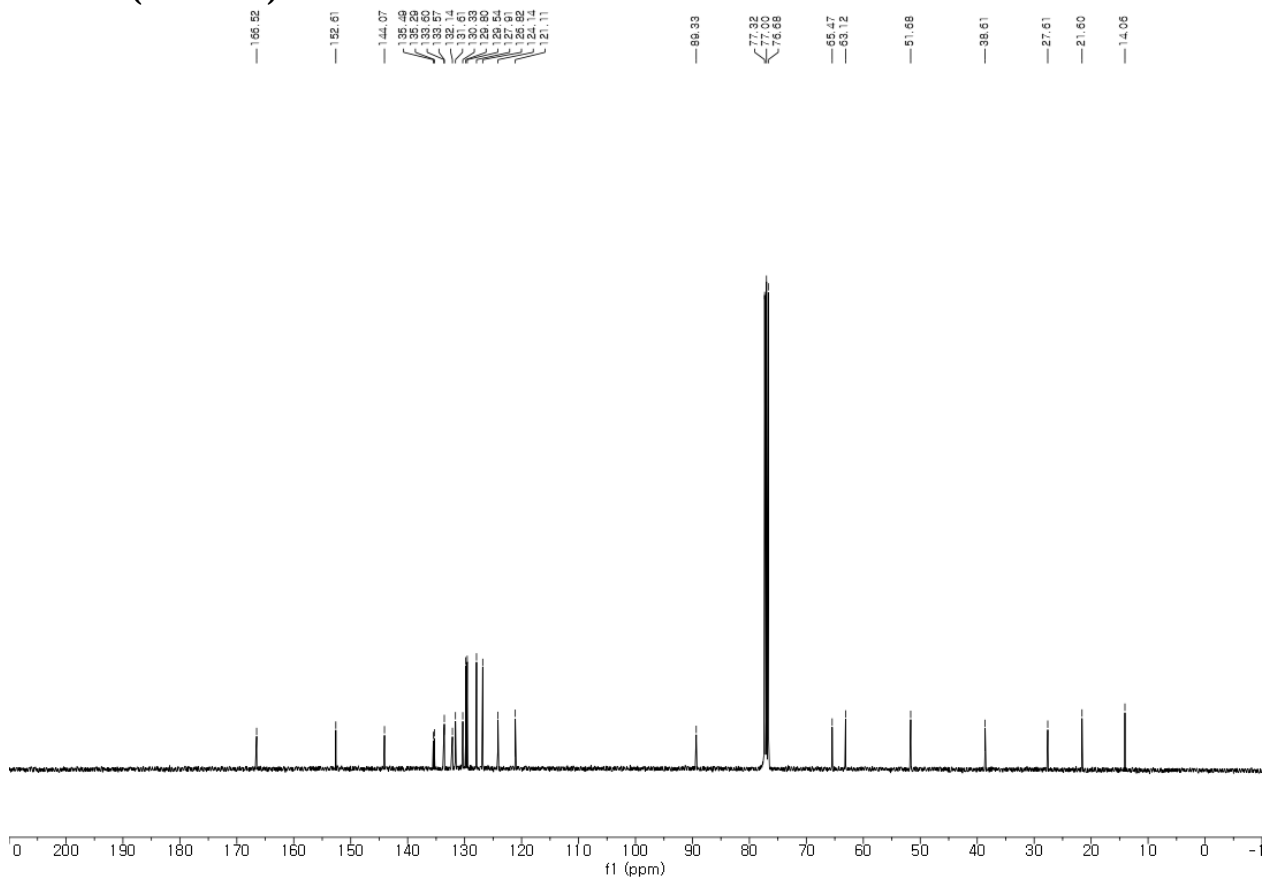
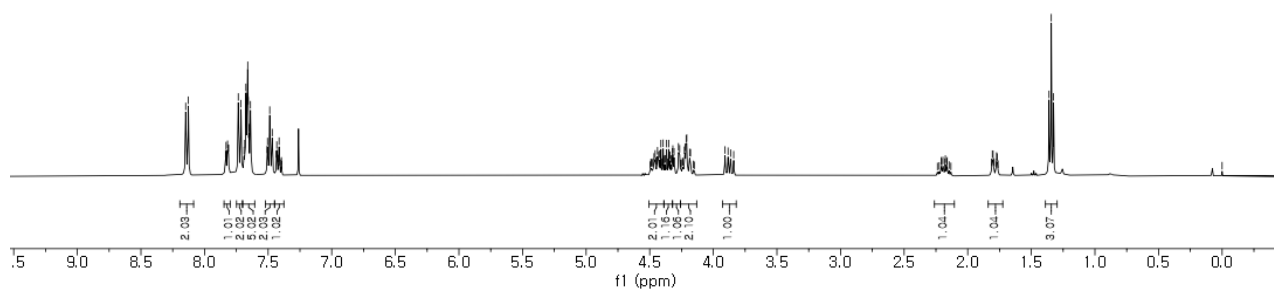
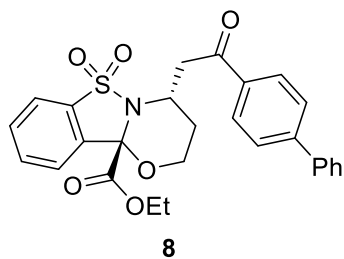


Figure 1

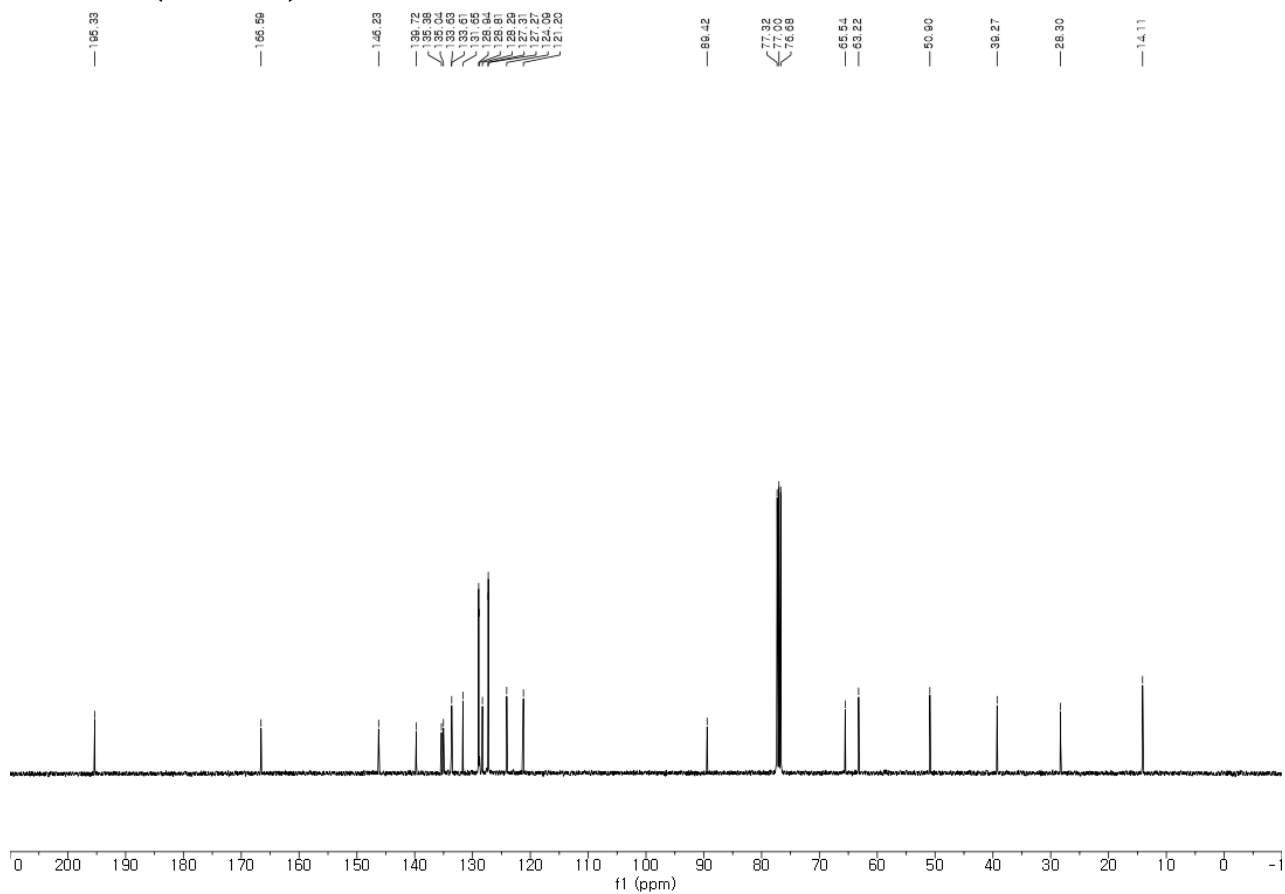
Figure 2

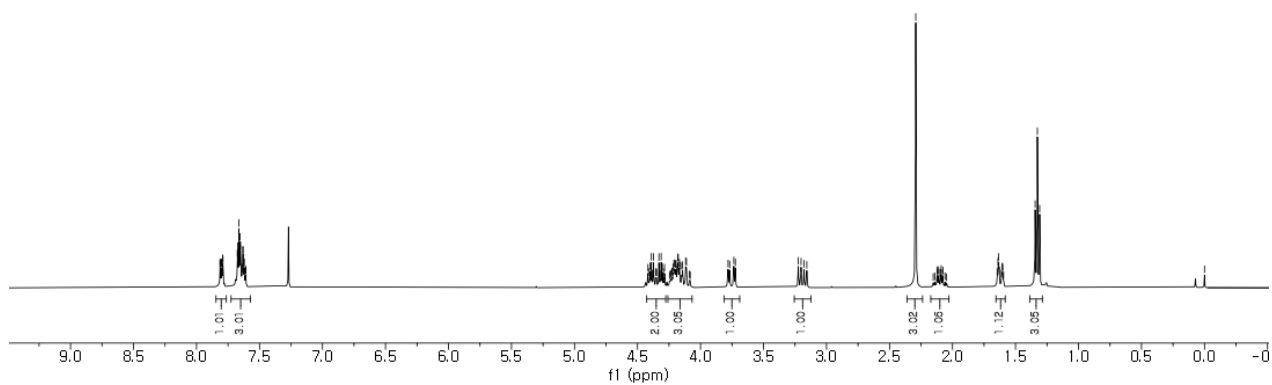
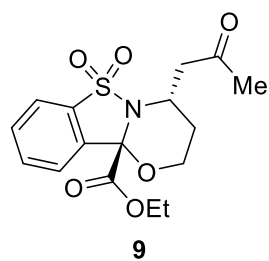
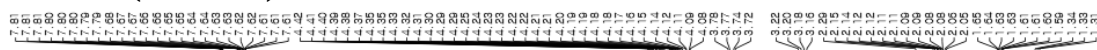
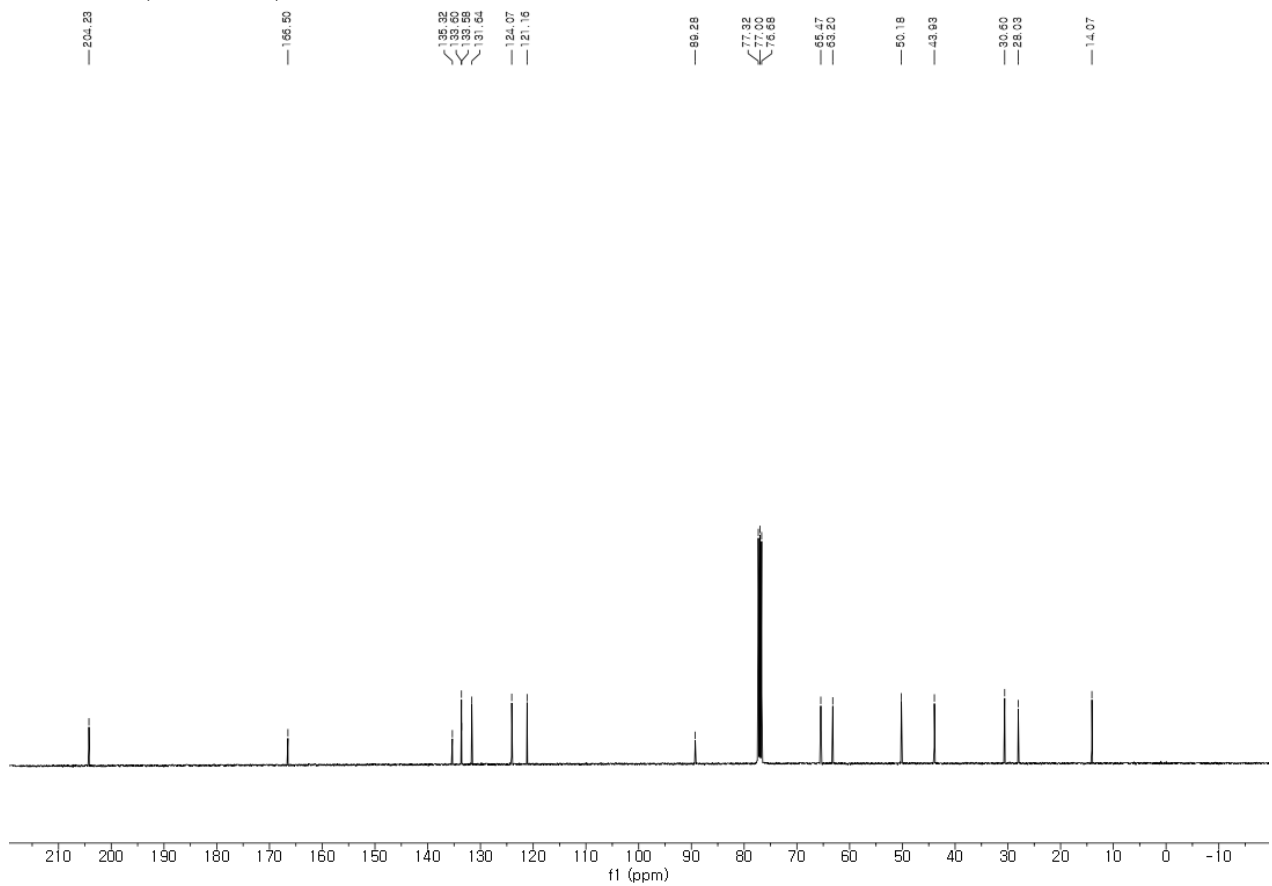
7 (minor)

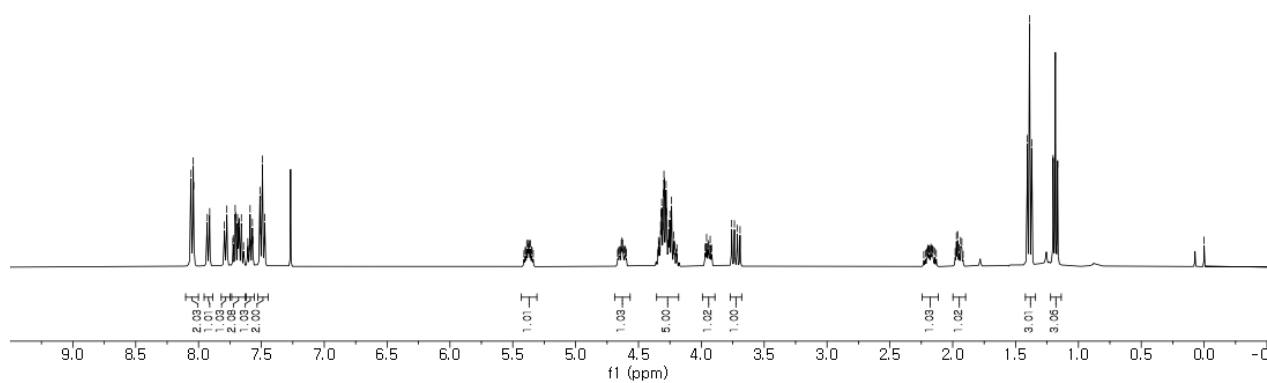
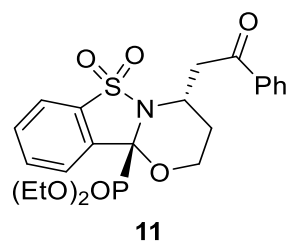
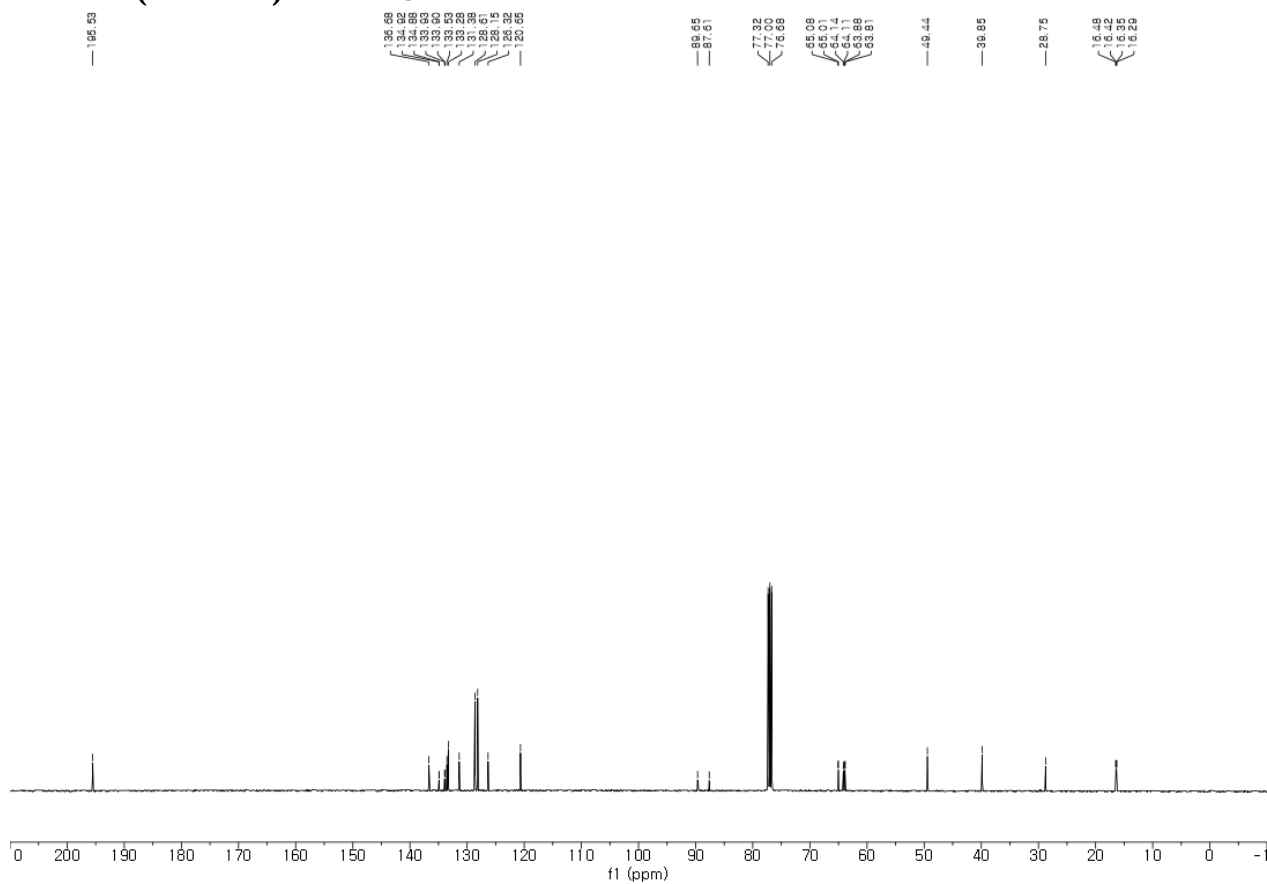


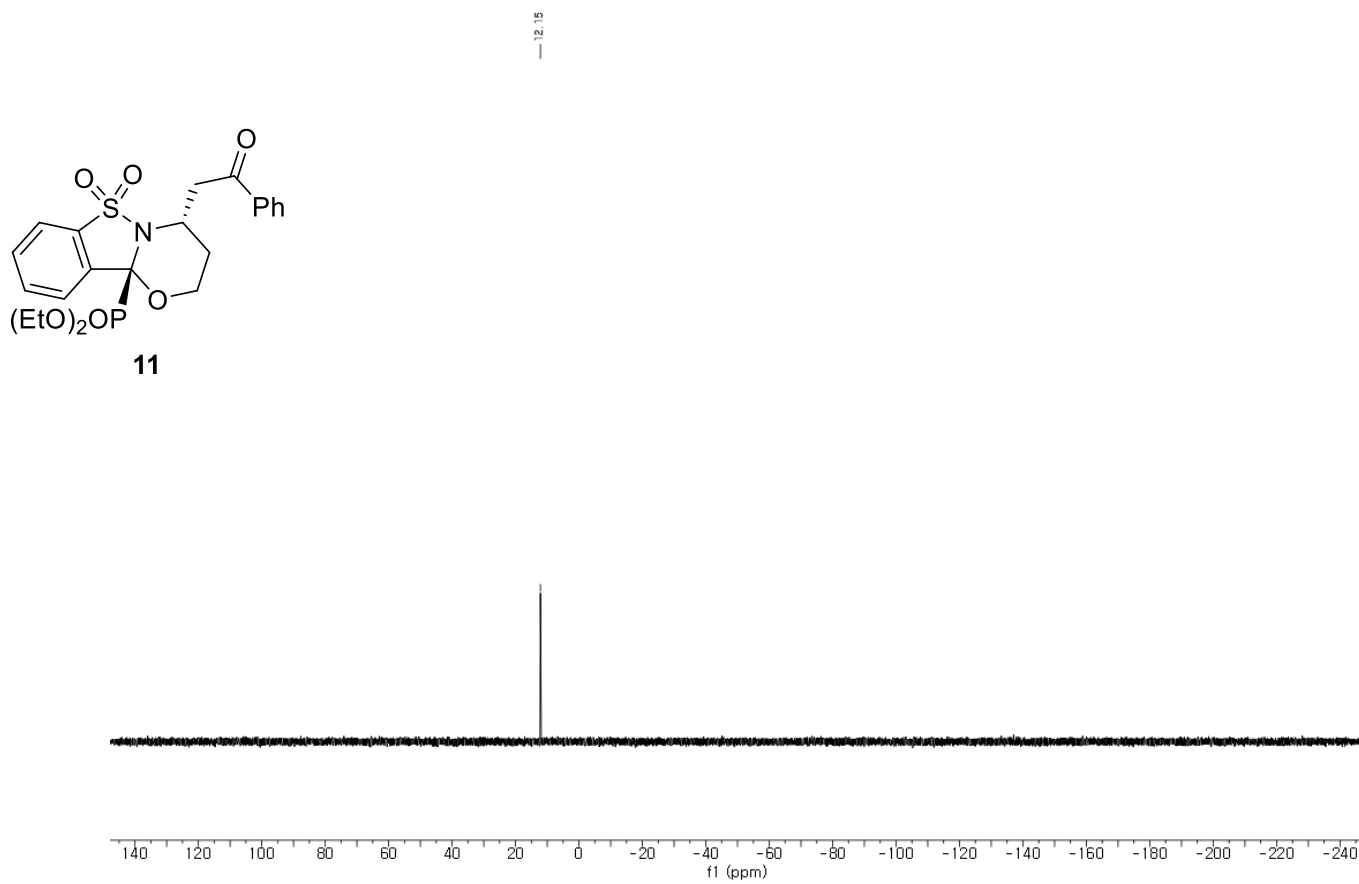
[illegible]

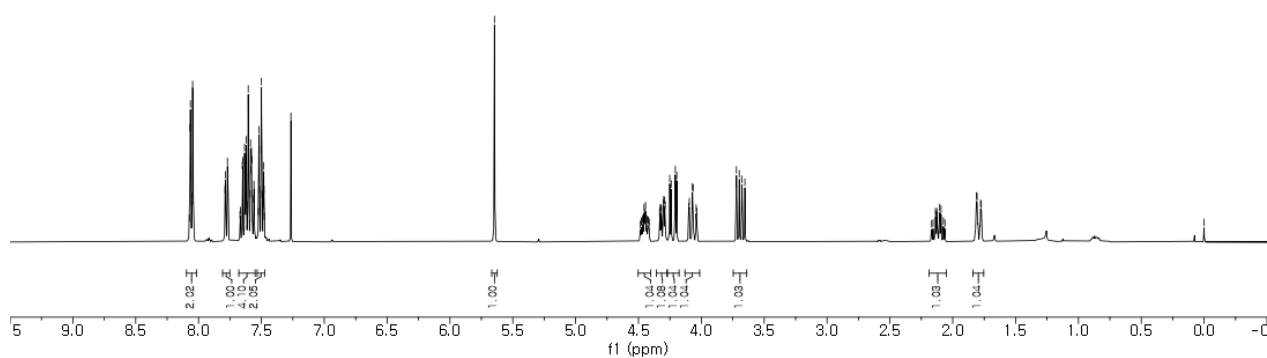
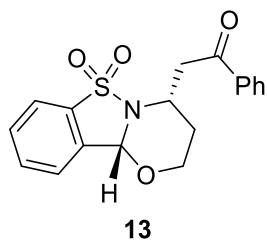
^{13}C NMR (100 MHz) in CDCl_3



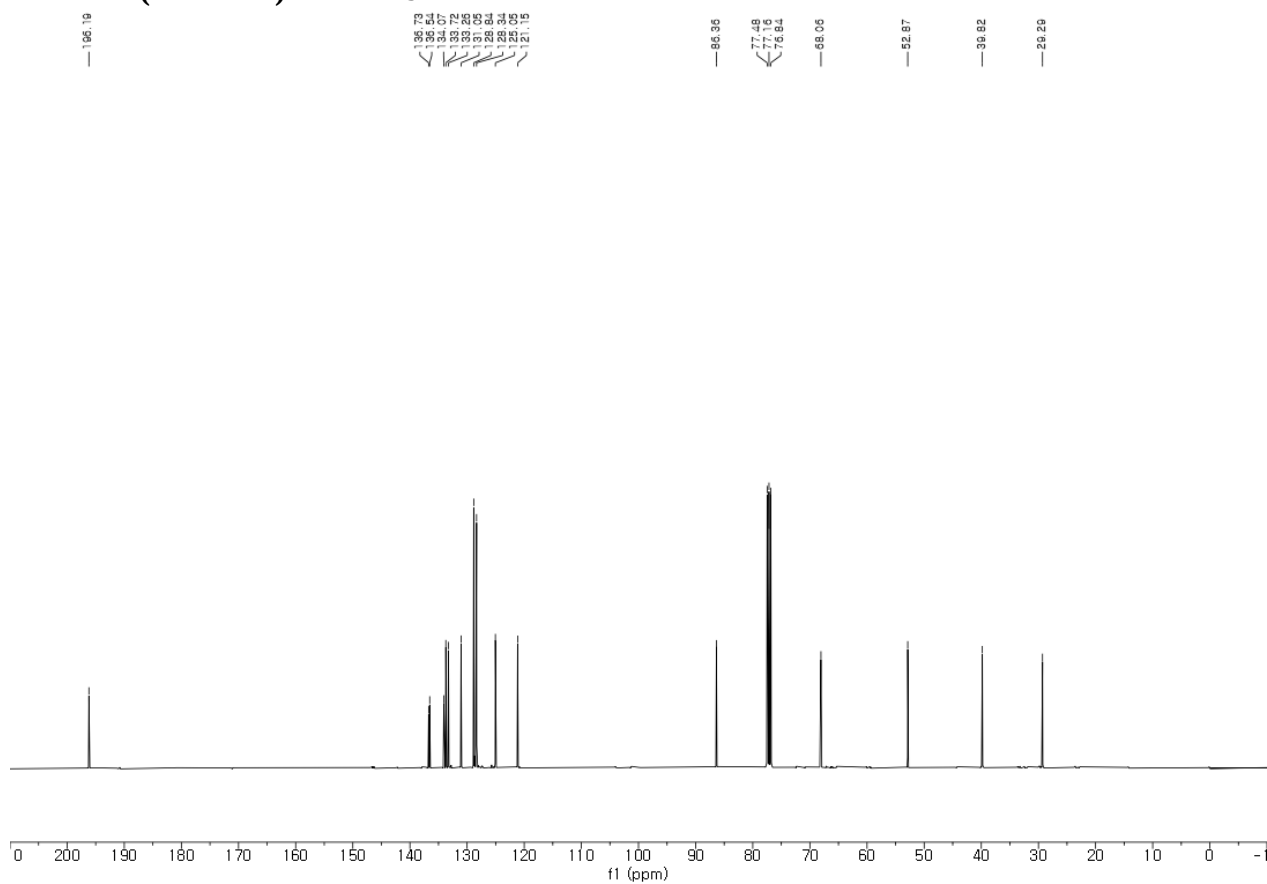
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

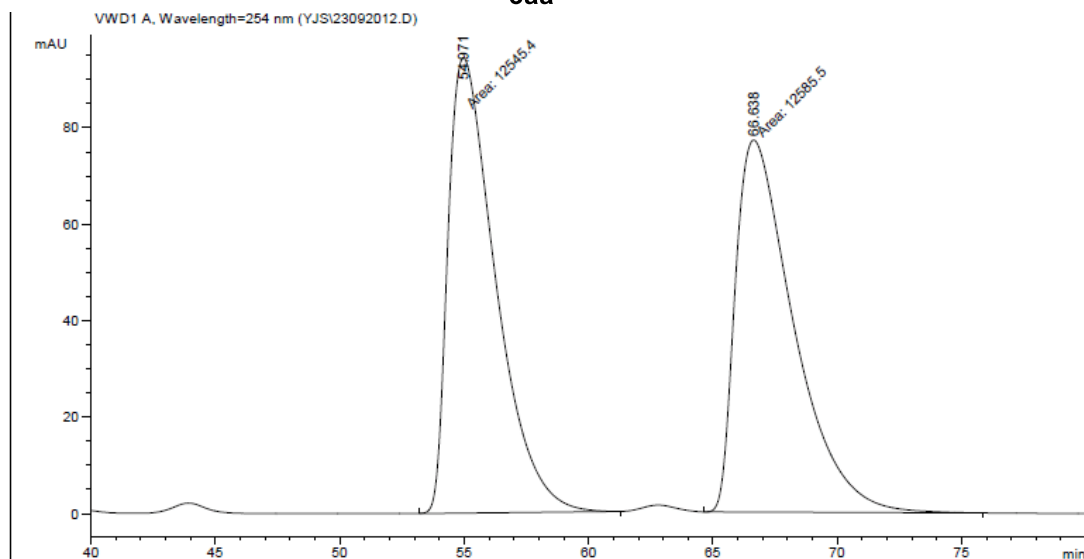
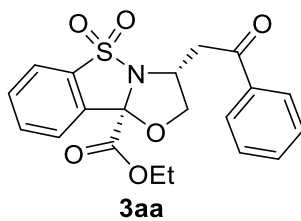
^{31}P NMR (162 MHz) in CDCl_3 



^{13}C NMR (100 MHz) in CDCl_3

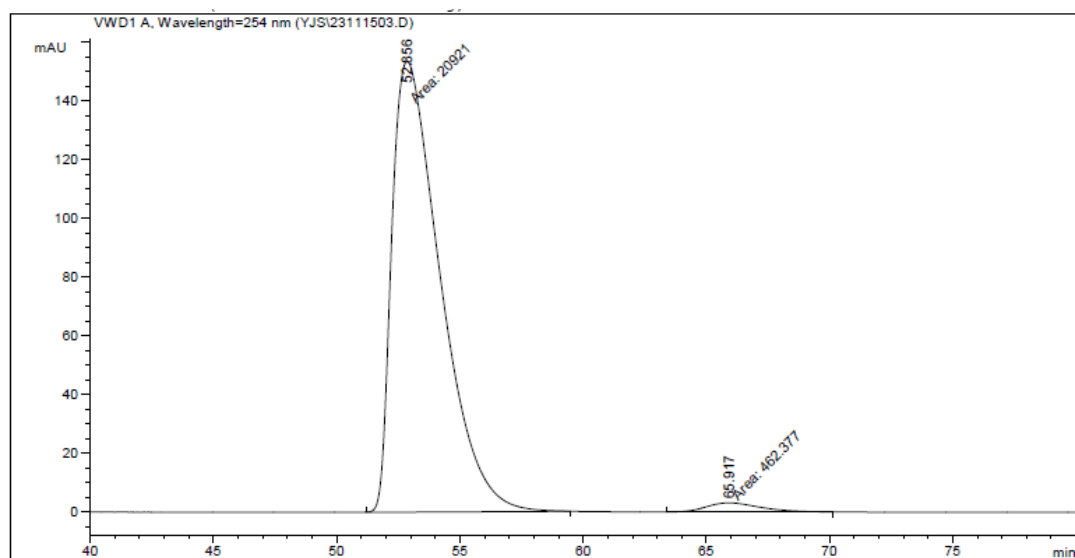


HPLC chromatogram



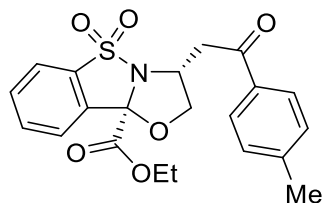
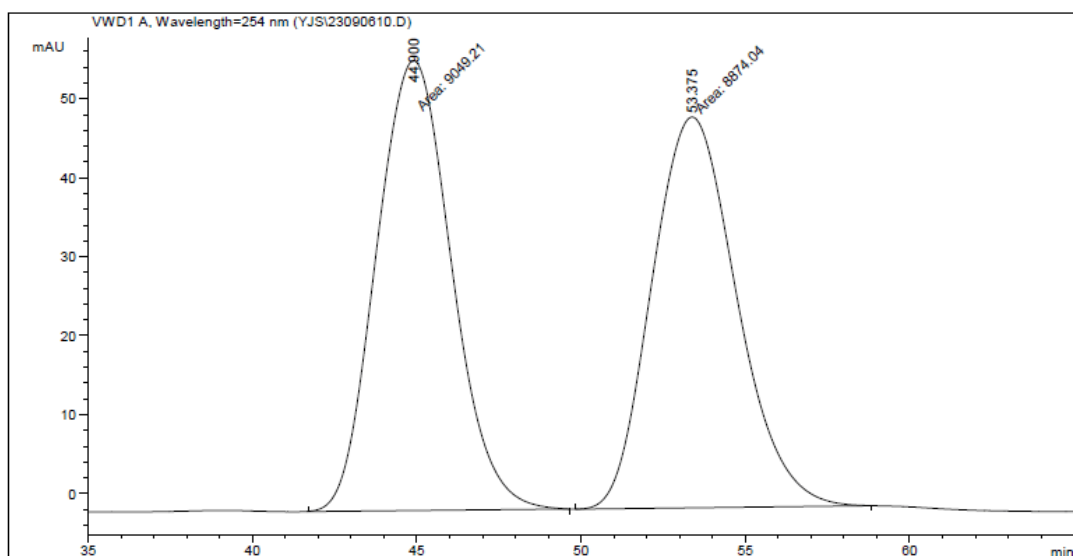
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	54.971	MM	2.2139	1.25454e4	94.44248	94.44248	49.9203
2	66.638	MM	2.7182	1.25855e4	77.16689	77.16689	50.0797
Totals :				2.51308e4	171.60937		



Area Percent Report

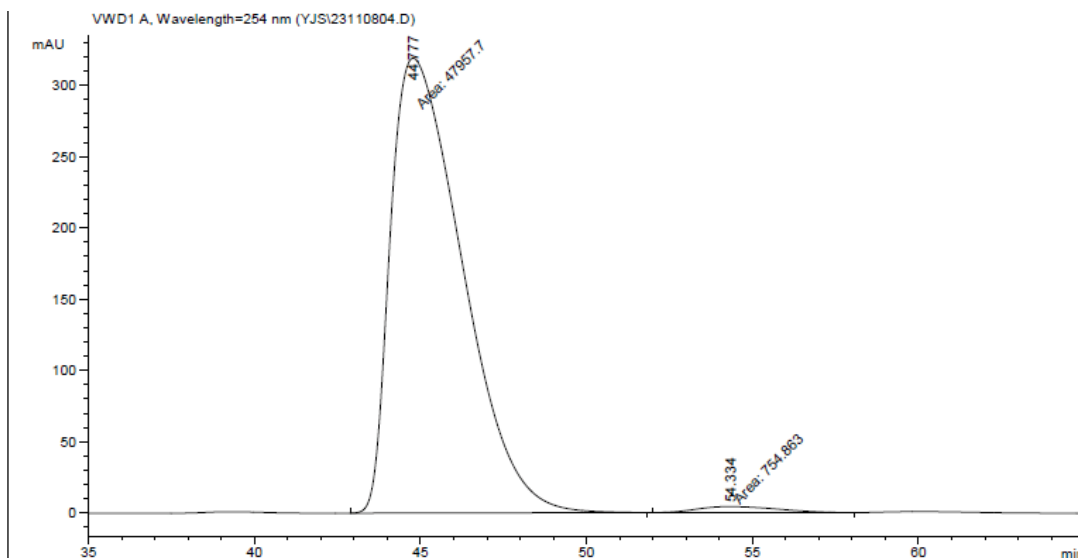
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	52.856	MM	2.2718	2.09210e4	153.48010	153.48010	97.8377
2	65.917	MM	2.4966	462.37704	3.08670	3.08670	2.1623

**3ab**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.900	MM	2.6460	9049.20801	56.99987	50.4887
2	53.375	MM	2.9872	8874.04004	49.51224	49.5113

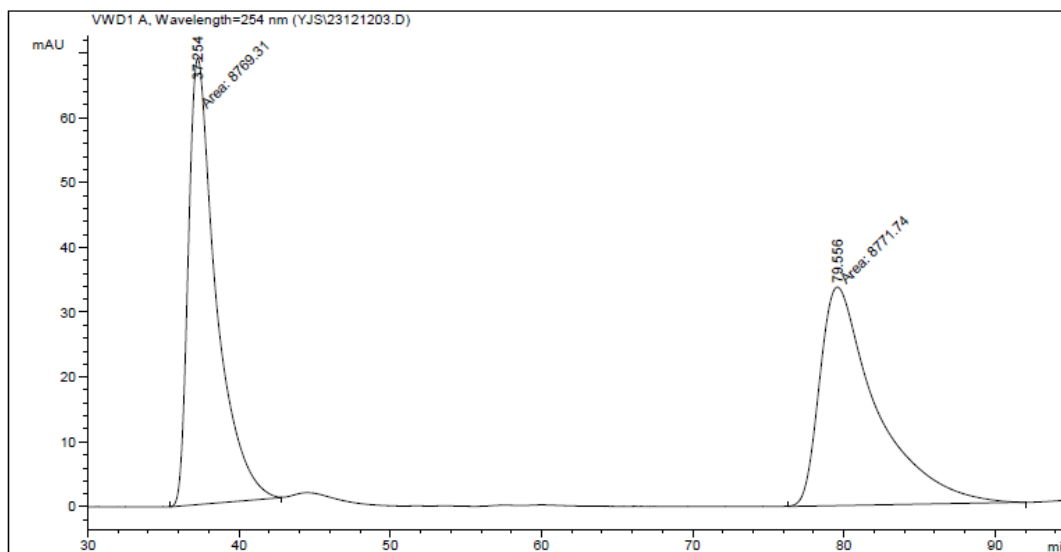
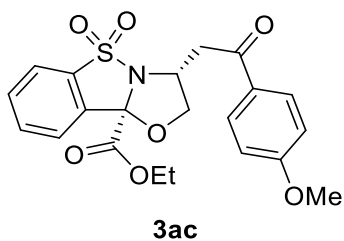
Totals : 1.79232e4 106.51211



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.777	MM	2.5050	4.79577e4	319.08612	98.4504
2	54.334	MM	2.8831	754.86316	4.36377	1.5496

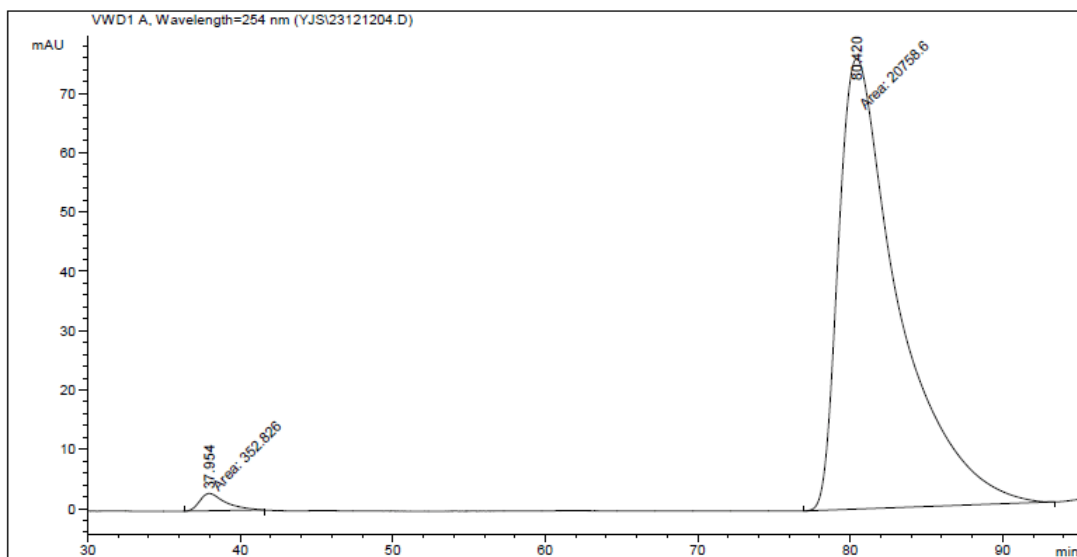
Totals : 4.87126e4 323.44989



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.254	MM	2.1233	8769.30957	68.83312	49.9931
2	79.556	MM	4.3374	8771.73730	33.70578	50.0069

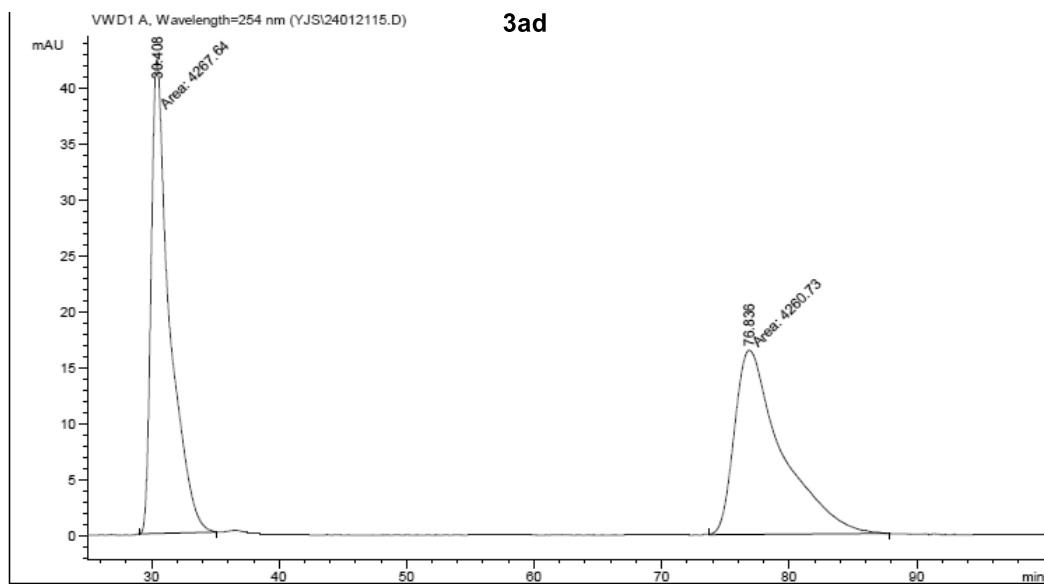
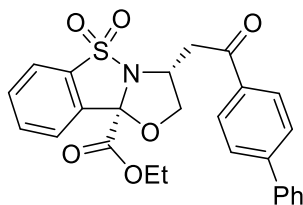
Totals : 1.75410e4 102.53890



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.954	MM	1.9881	352.82587	2.95775	1.6713
2	80.420	MM	4.5539	2.07586e4	75.97385	98.3287

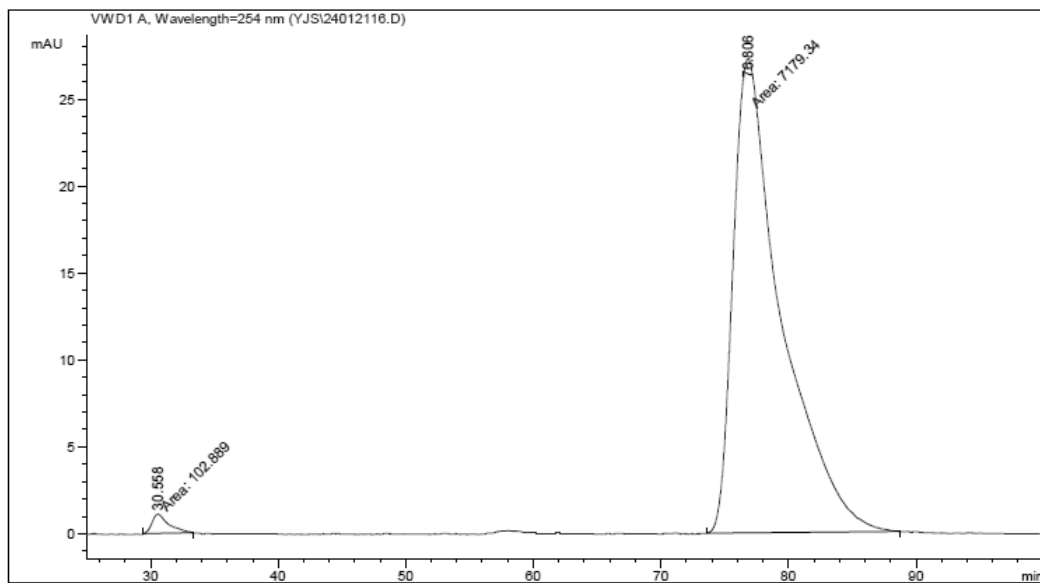
Totals : 2.11115e4 78.93160



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	30.408	MM	1.6781	4267.64063		42.38490	50.0405
2	76.836	MM	4.3126	4260.72705		16.46601	49.9595

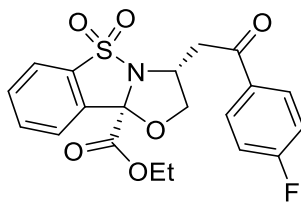
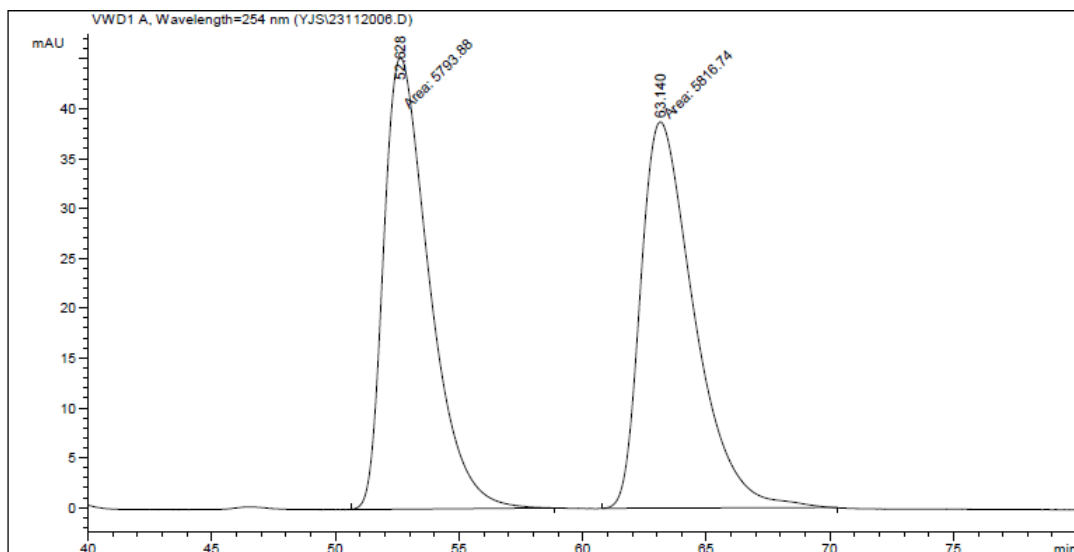
Totals : 8528.36768 58.85092



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	30.558	MM	1.5326	102.88939		1.11887	1.4129
2	76.806	MM	4.3839	7179.34424		27.29442	98.5871

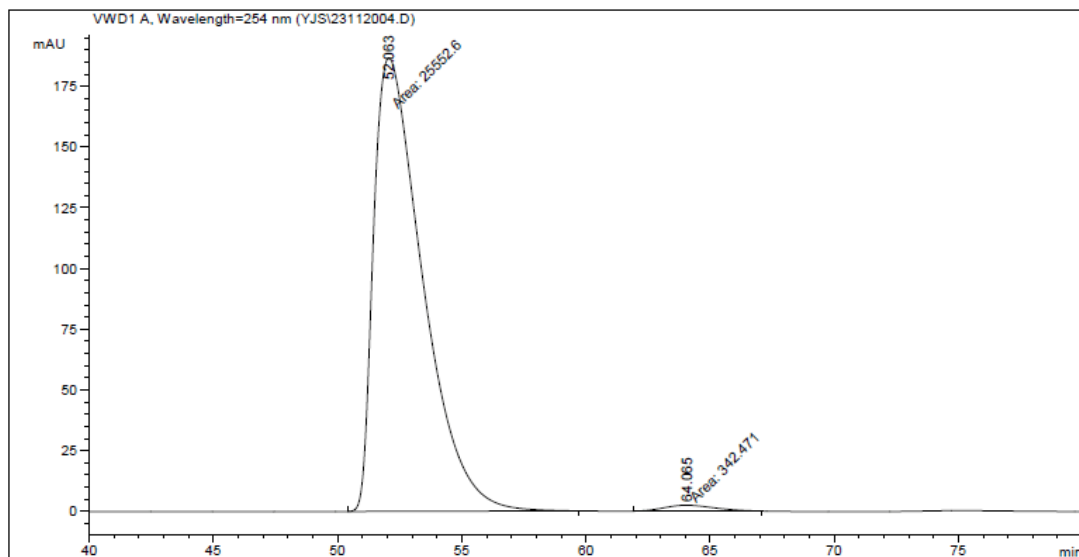
Totals : 7282.23363 28.41329

**3ae**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	52.628	MM	2.1333	5793.88428	45.26604	49.9016
2	63.140	MM	2.5025	5816.74023	38.73976	50.0984

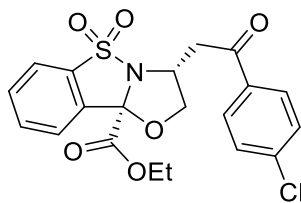
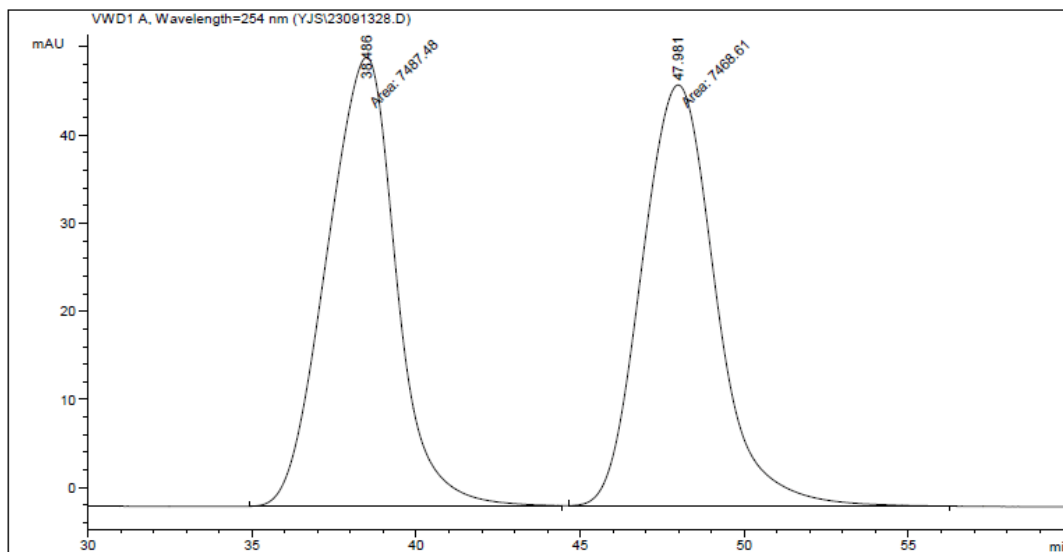
Totals : 1.16106e4 84.00581



Area Percent Report

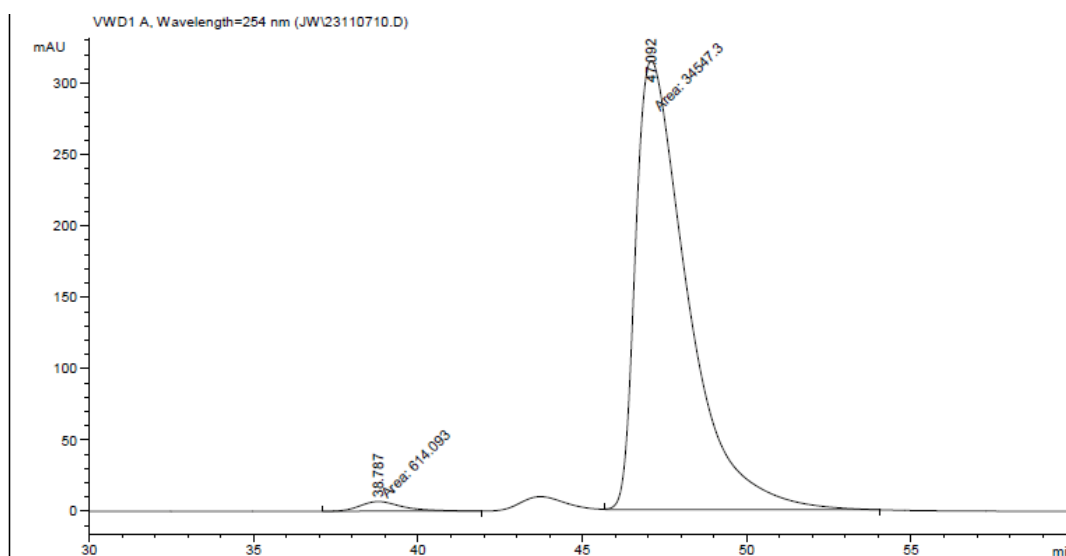
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	52.063	MM	2.2809	2.55526e4	186.71410	98.6775
2	64.065	MM	2.3391	342.47061	2.44016	1.3225

Totals : 2.58950e4 189.15426

**3af**

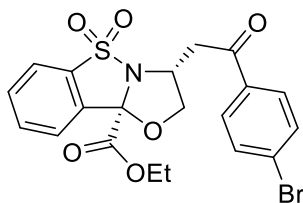
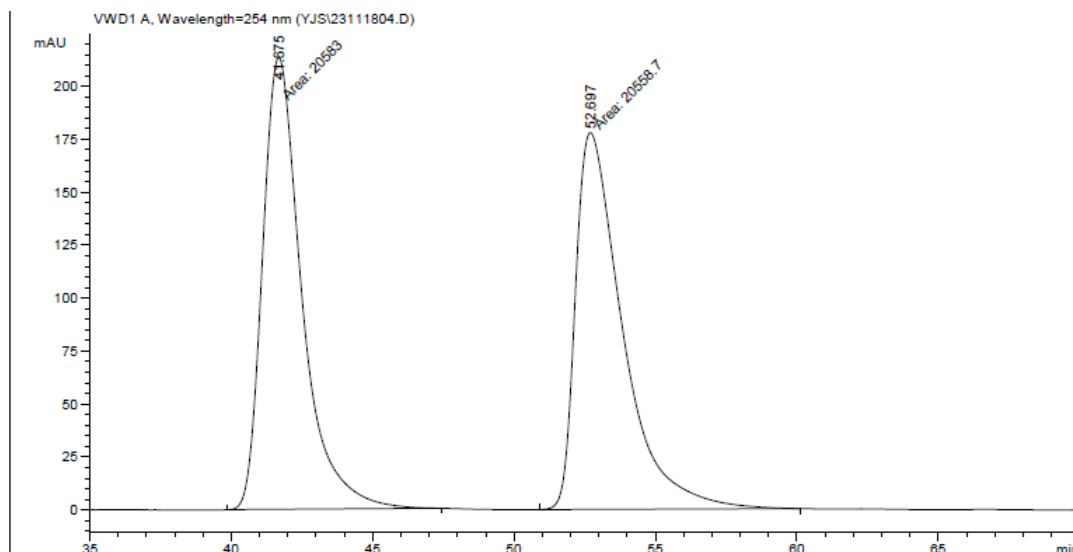
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	38.486	MM	2.4506	7487.48437	50.92266	50.0631
2	47.981	MM	2.6063	7468.61475	49.76084	49.9369
Totals :				1.49561e4	98.68350	



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Area Percent Report
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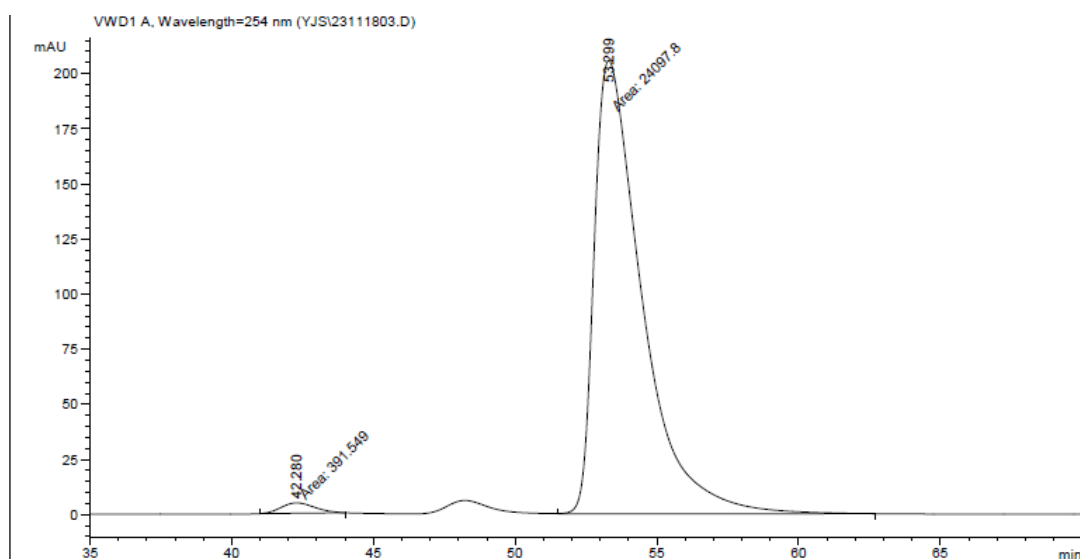
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	38.787	MM	1.5053	614.09296	6.79905	1.7465
2	47.092	MM	1.8293	3.45473e4	314.75281	98.2535
Totals :				3.51614e4	321.55186	

**3ag**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	41.675	MM	1.6079	2.05830e4		213.35580	50.0296
2	52.697	MM	1.9256	2.05587e4		177.94009	49.9704

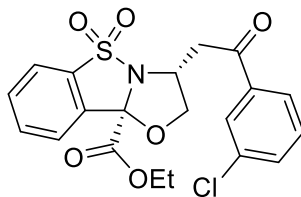
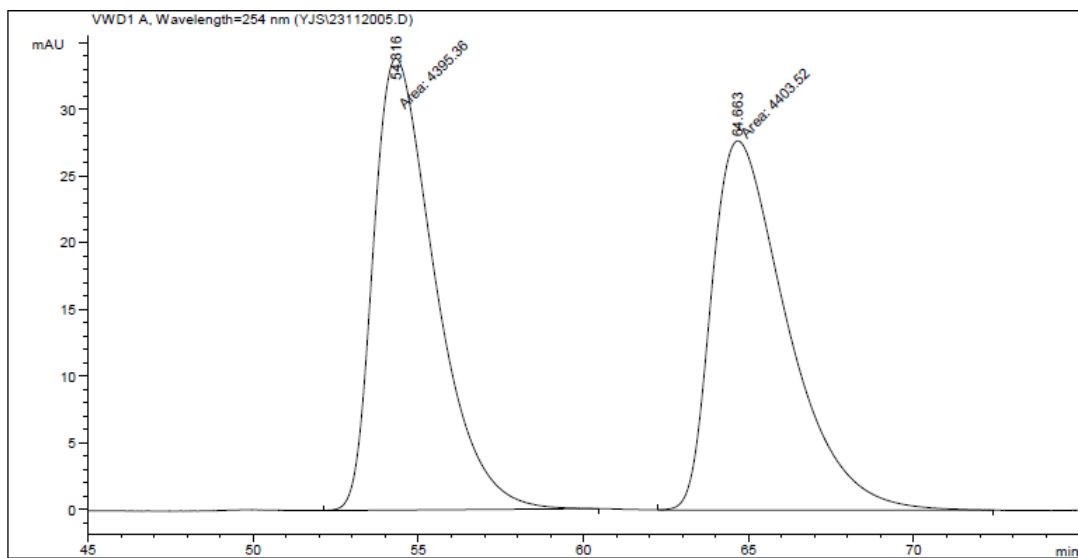
Totals : 4.11417e4 391.29590



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	42.280	MM	1.3769	391.54889		4.73942	1.5989
2	53.299	MM	1.9537	2.40978e4		205.57700	98.4011

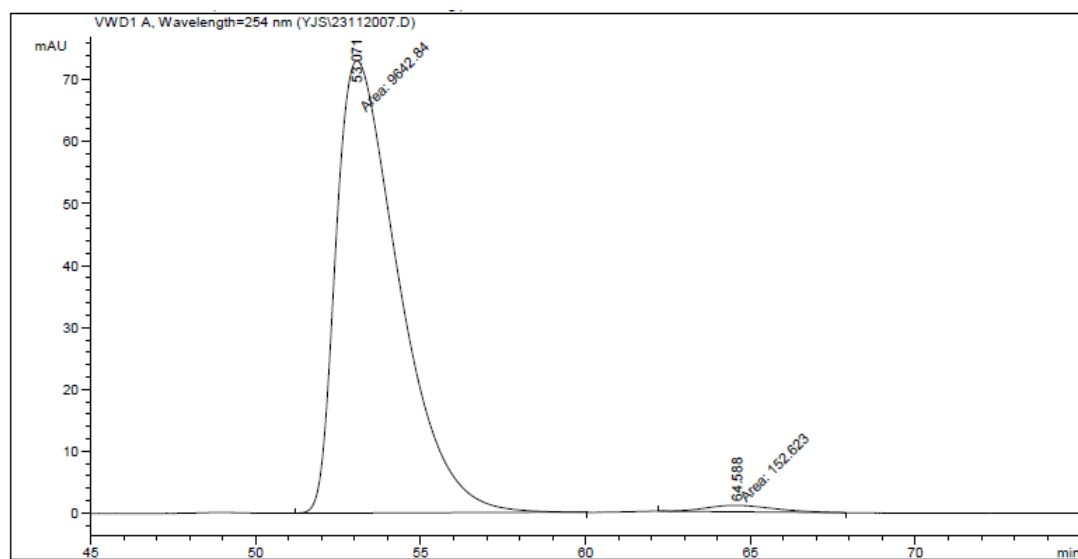
Totals : 2.44893e4 210.31642

**3ah**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	54.316	MM	2.1619	4395.35840		33.88573	49.9536
2	64.663	MM	2.6506	4403.52441		27.68893	50.0464

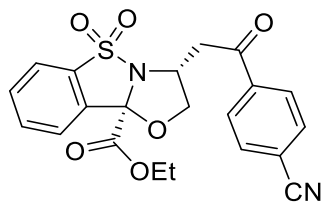
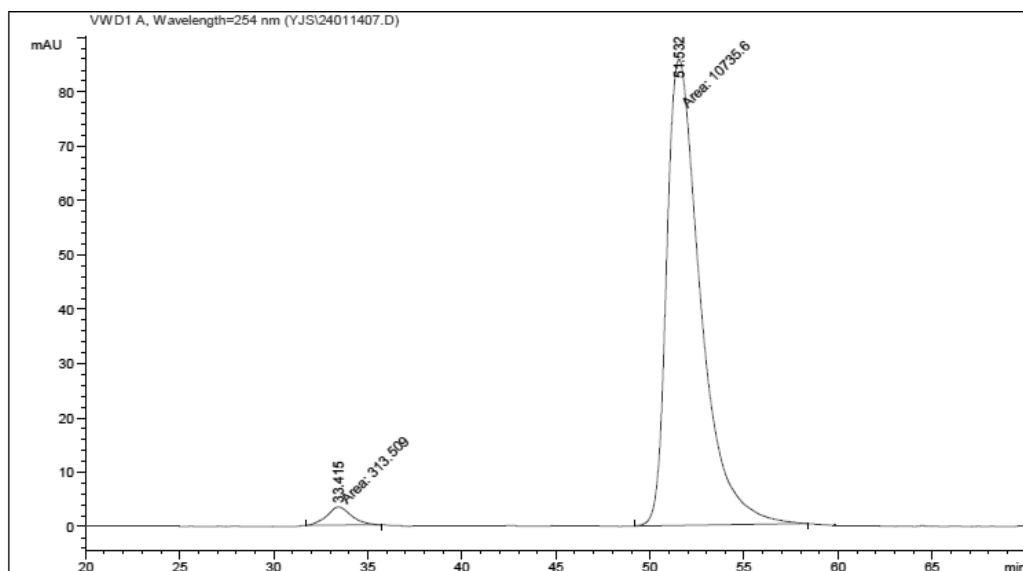
Totals : 8798.88281 61.57465



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	53.071	MM	2.1993	9642.83594		73.07610	98.4419
2	64.588	MM	2.3937	152.62308		1.06269	1.5581

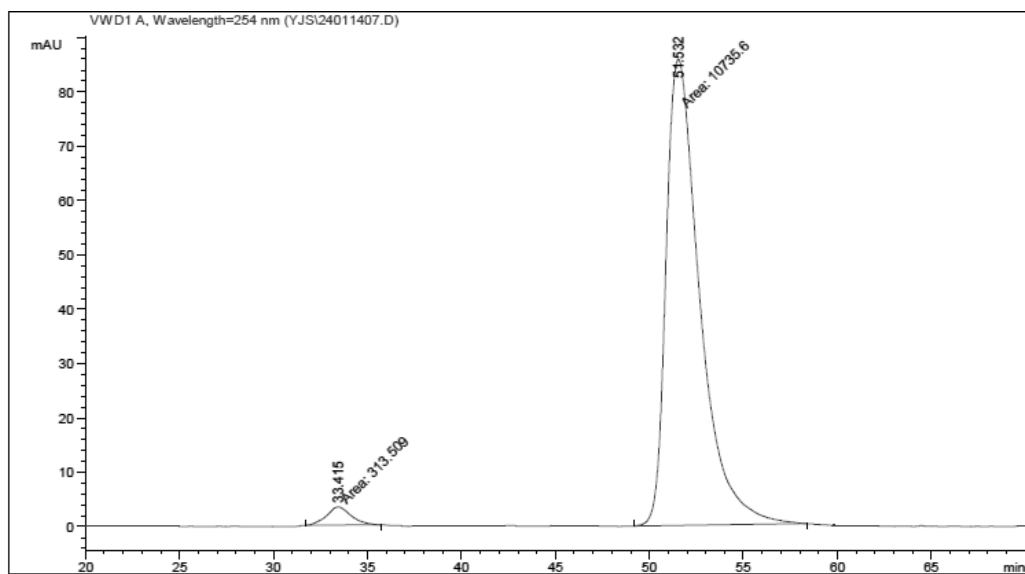
Totals : 9795.45901 74.13879

**3ai**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	33.415	MM	1.5421	313.50909		3.38840	2.8374
2	51.532	MM	2.0856	1.07356e4		85.79202	97.1626

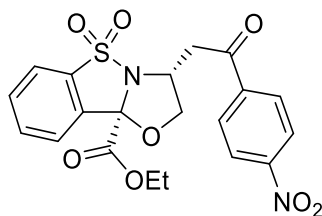
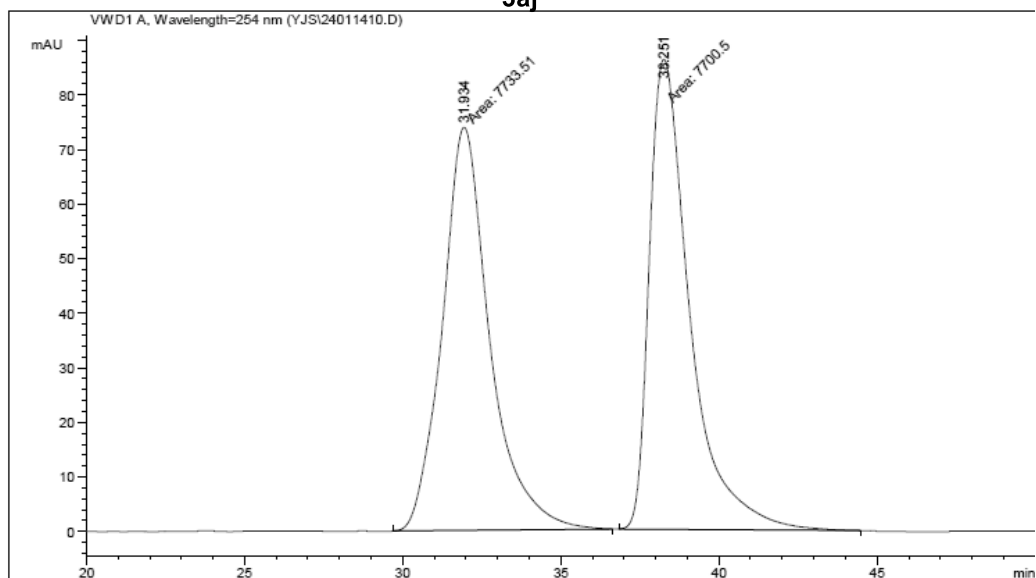
Totals : 1.10491e4 89.18041



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	33.415	MM	1.5421	313.50909		3.38840	2.8374
2	51.532	MM	2.0856	1.07356e4		85.79202	97.1626

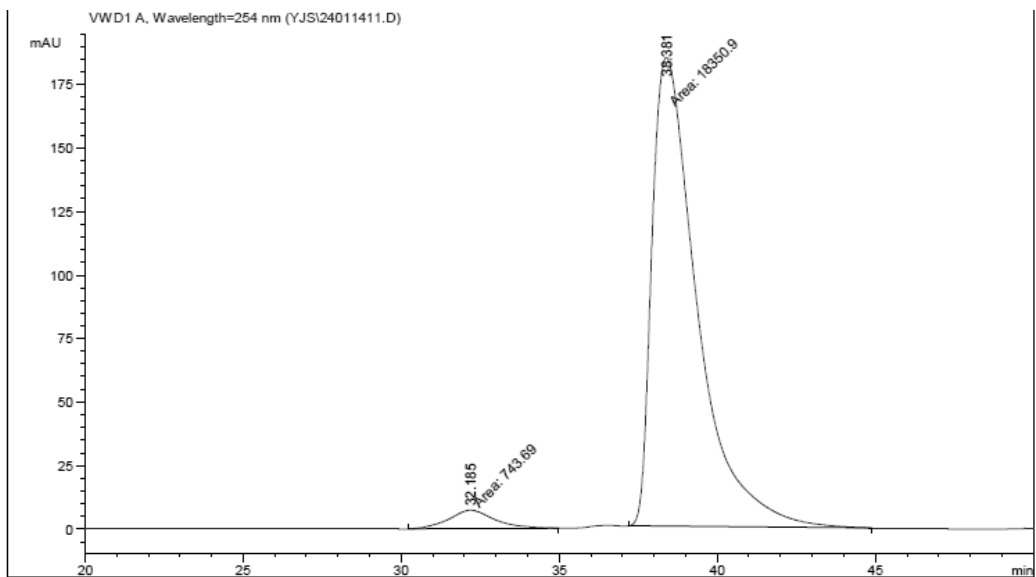
Totals : 1.10491e4 89.18041

**3aj**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	31.934	MM	1.7451	7733.51367	50.1069	73.85845
2	38.251	MM	1.4895	7700.50488	49.8931	86.16288

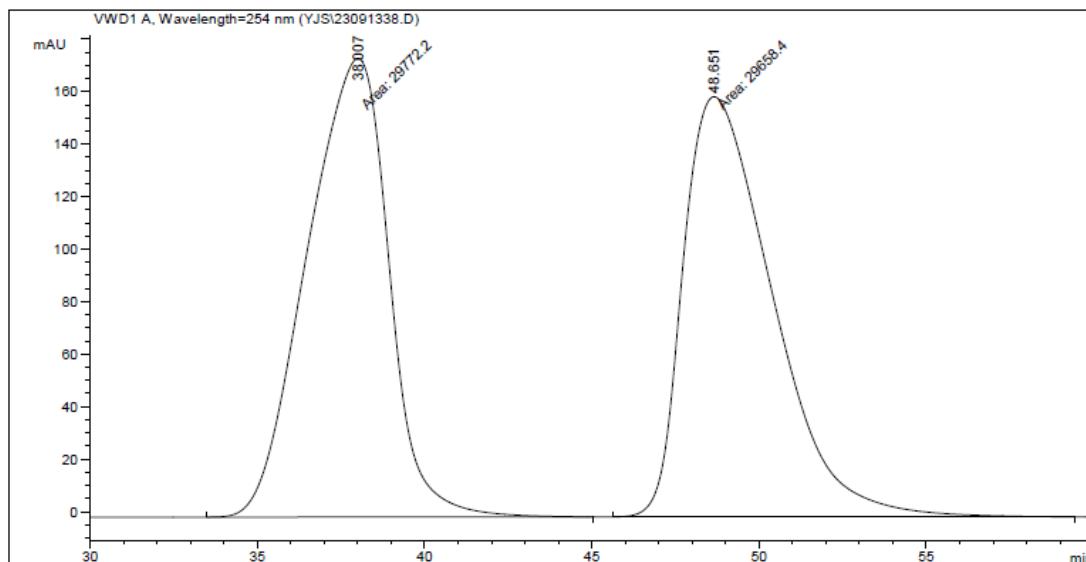
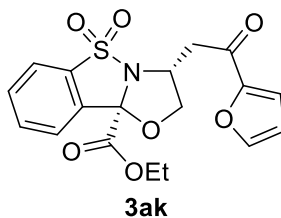
Totals : 1.54340e4 160.02133



Area Percent Report

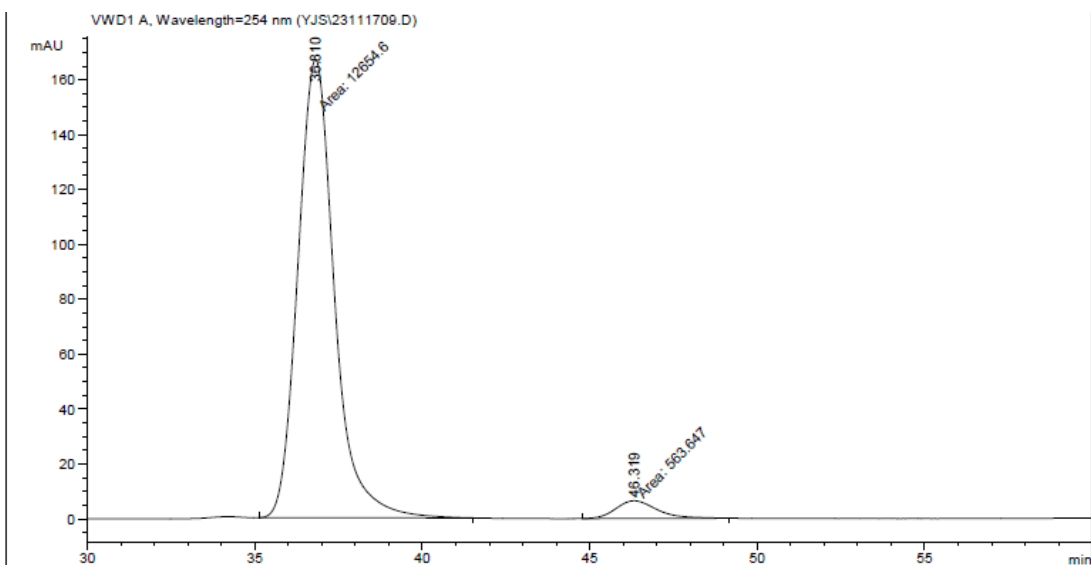
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	32.185	MM	1.6989	743.68994	3.8948	7.29582
2	38.381	MM	1.6569	1.83509e4	96.1052	184.59230

Totals : 1.90946e4 191.88812



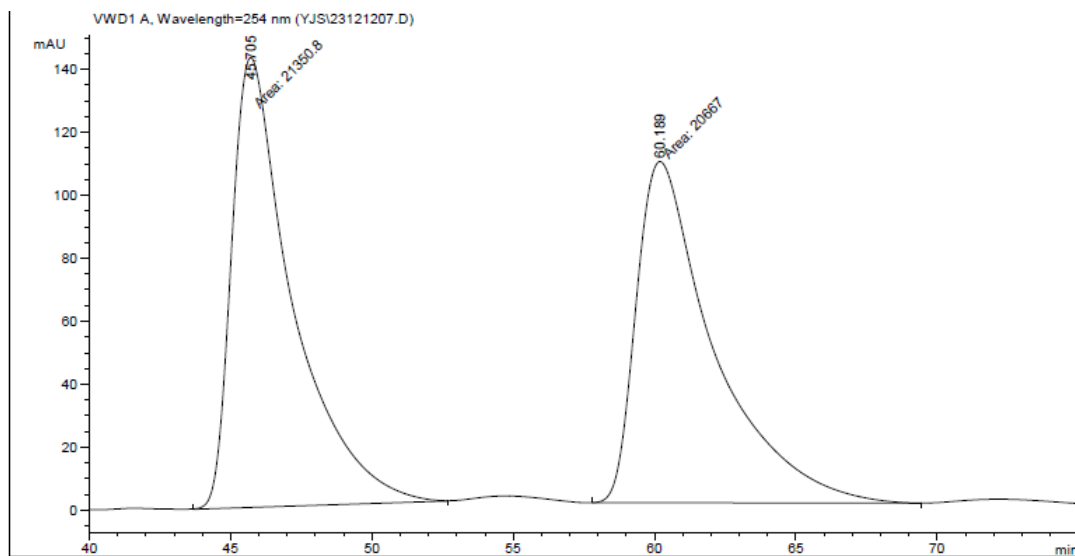
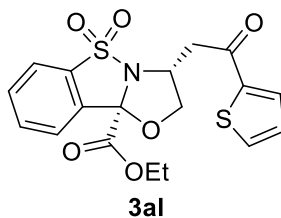
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	38.007	MM	2.8370	2.97722e4	174.90184	50.0958
2	48.651	MM	3.0863	2.96584e4	160.16086	49.9042
Totals :				5.94306e4	335.06270	



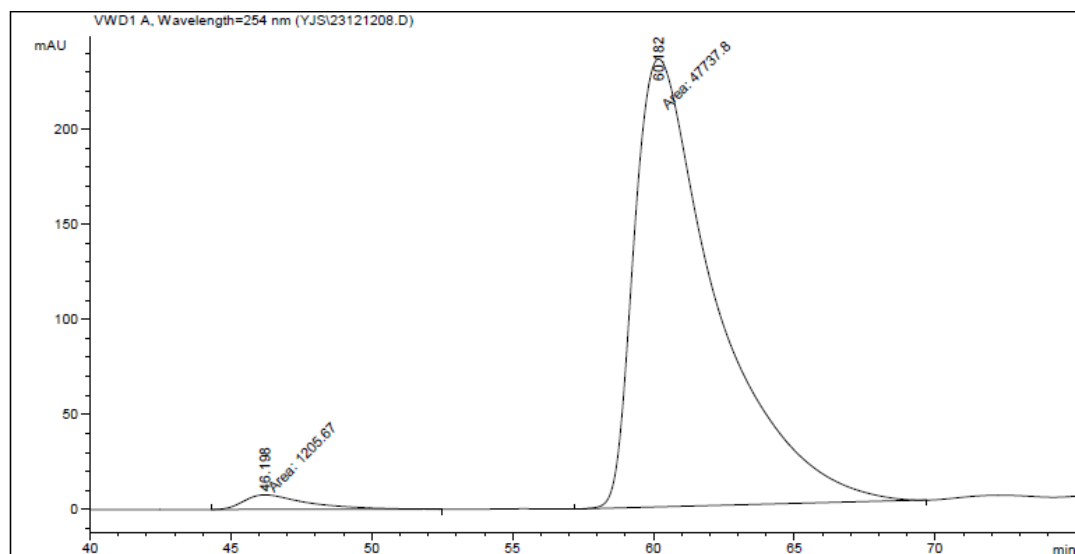
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	36.810	MM	1.2627	1.26546e4	167.02542	95.7358
2	46.319	MM	1.4420	563.64746	6.51460	4.2642
Totals :				1.32182e4	173.54002	



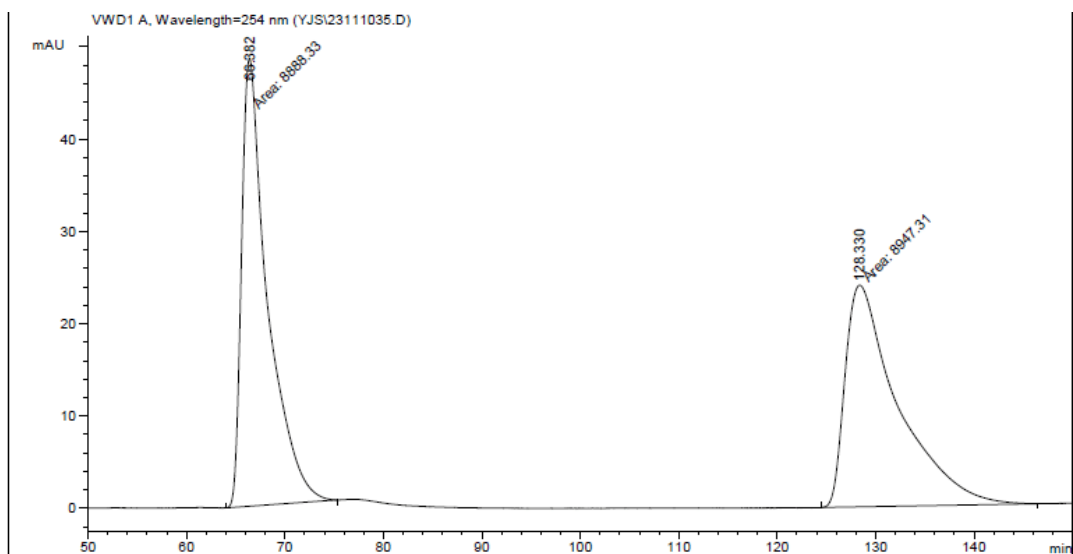
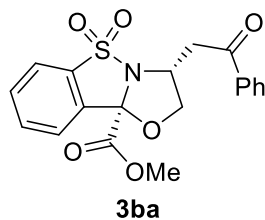
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.705	MM	2.4909	2.13508e4	142.86078	50.8137
2	60.189	MM	3.1776	2.06670e4	108.39913	49.1863
Totals :				4.20178e4	251.25991	

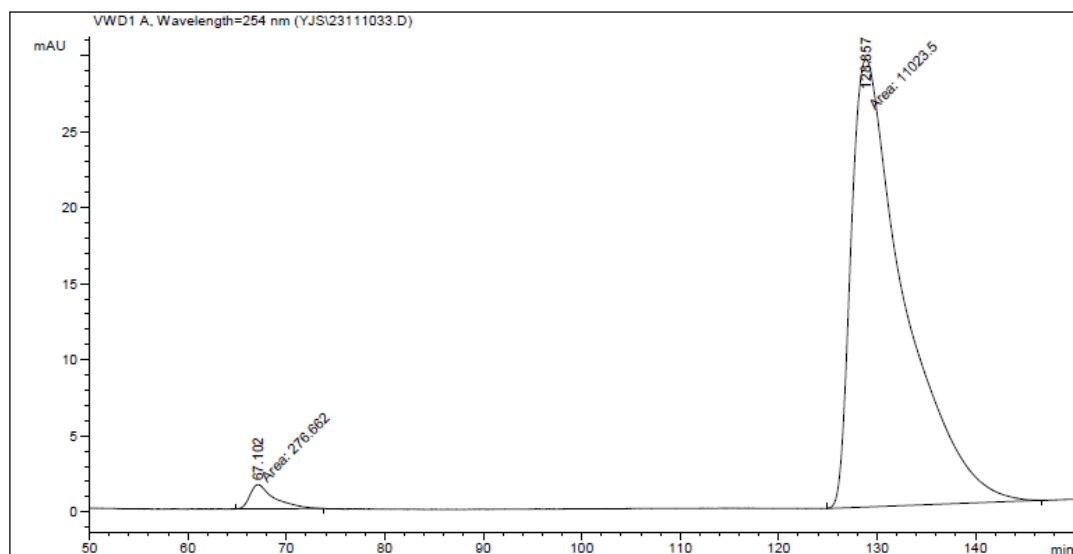


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Area Percent Report
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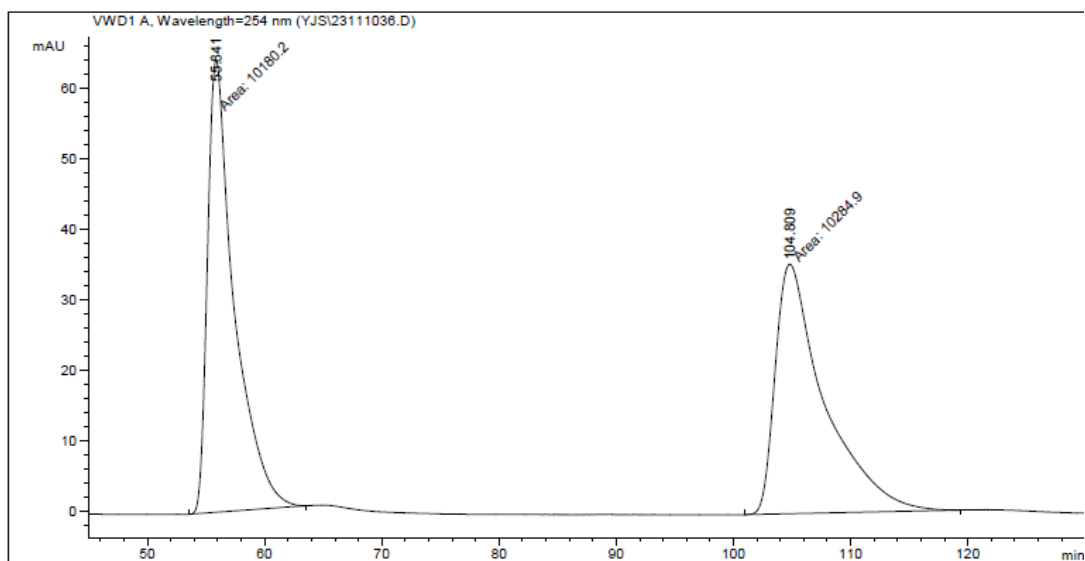
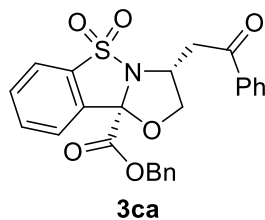
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	46.198	MM	2.6084	1205.66663	7.70381	2.4634
2	60.182	MM	3.3766	4.77378e4	235.63216	97.5366
Totals :				4.89435e4	243.33597	



Area Percent Report						
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	66.382	MM	3.0544	8888.33105	48.49949	49.8347
2	128.330	MM	6.2082	8947.30957	24.02021	50.1653
Totals :				1.78356e4	72.51970	

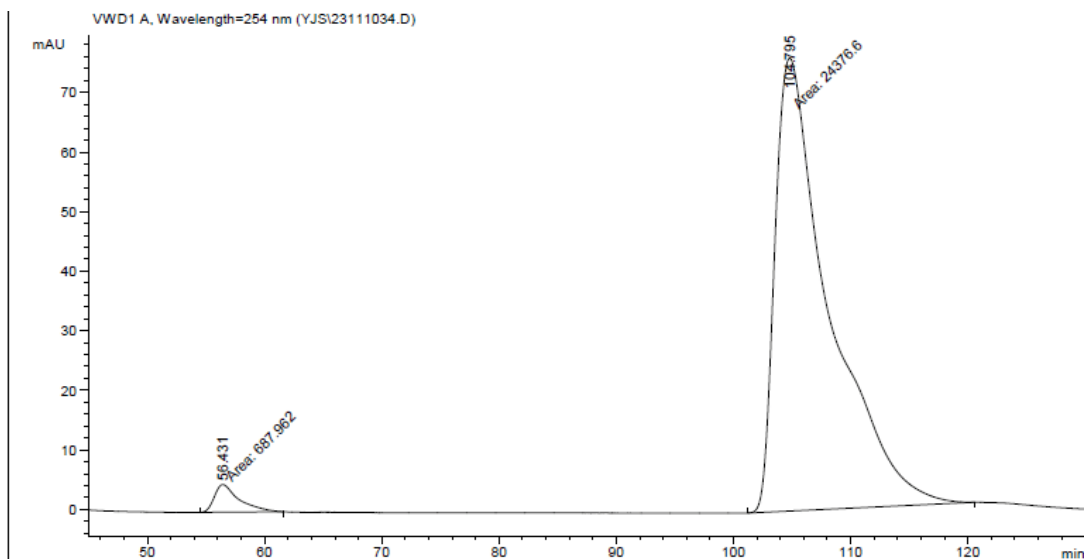


Area Percent Report						
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	67.102	MM	2.8922	276.66168	1.59427	2.4483
2	128.857	MM	6.2436	1.10235e4	29.42617	97.5517
Totals :				1.13001e4	31.02045	



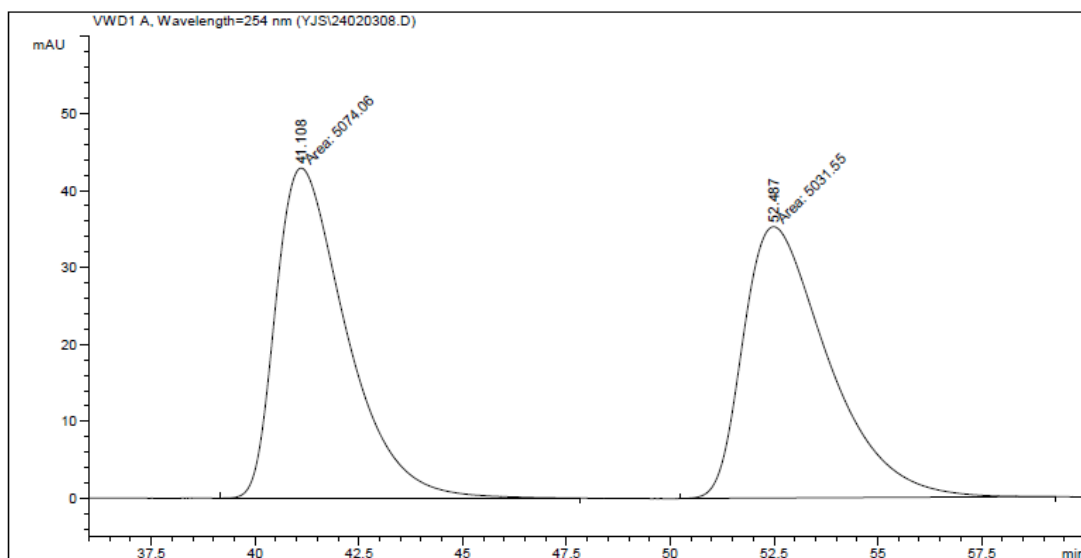
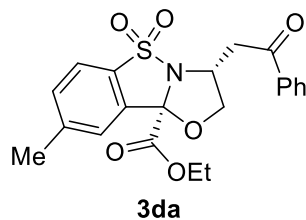
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	55.841	MM	2.6405	1.01802e4	49.7444	64.25721
2	104.809	MM	4.8352	1.02849e4	50.2556	35.45117
Totals :				2.04651e4	99.70838	



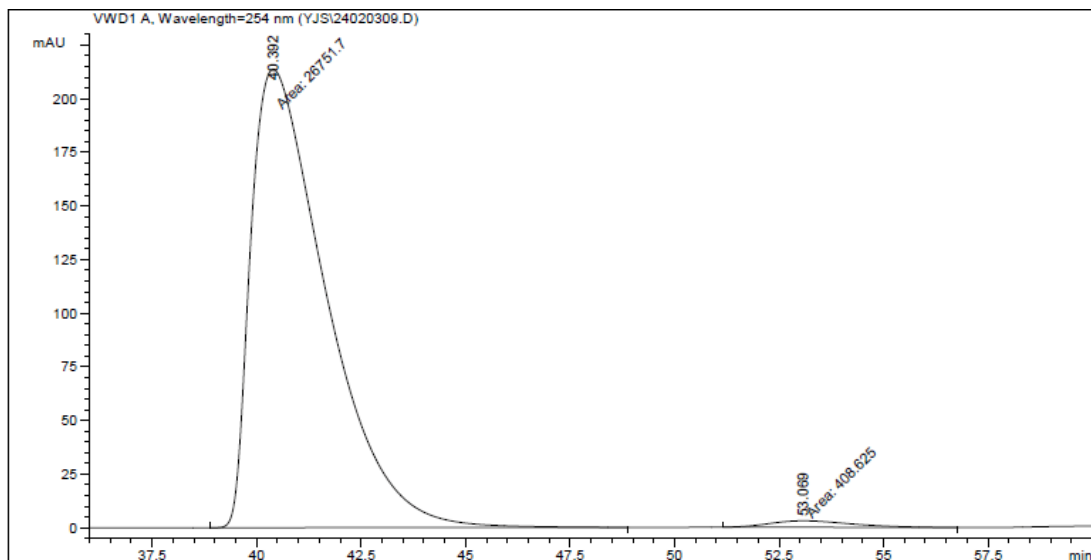
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	56.431	MM	2.4583	687.96246	2.7448	4.66414
2	104.795	MM	5.3405	2.43766e4	97.2552	76.07428
Totals :				2.50645e4	80.73842	



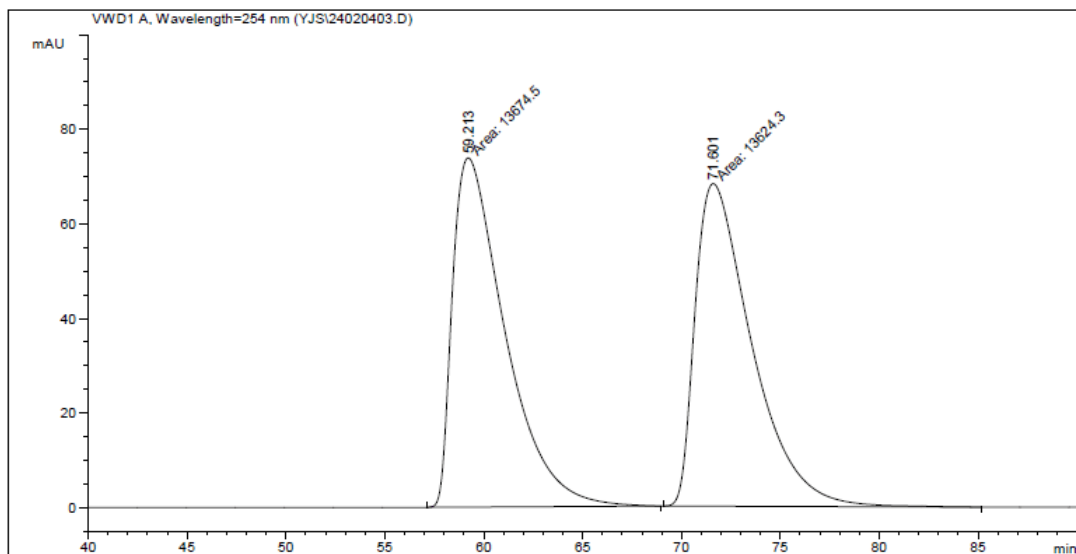
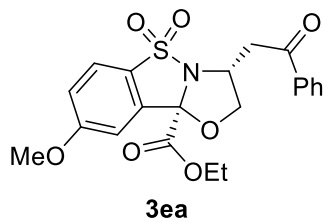
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.108	MM	1.9710	5074.05713	42.90505	50.2103
2	52.487	MM	2.3776	5031.55225	35.27067	49.7897
Totals :				1.01056e4	78.17572	



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Area Percent Report
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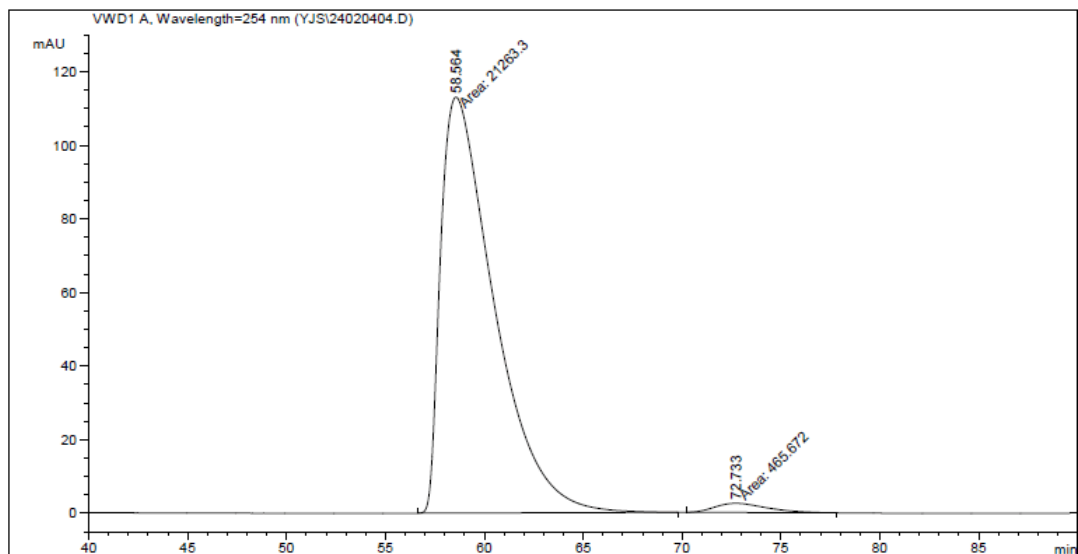
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.392	MM	2.0852	2.67517e4	213.82088	98.4955
2	53.069	MM	2.2588	408.62451	3.01503	1.5045
Totals :				2.71604e4	216.83591	



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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	59.213	MM	3.0819	1.36745e4	73.95036	50.0920
2	71.601	MM	3.3248	1.36243e4	68.29609	49.9080

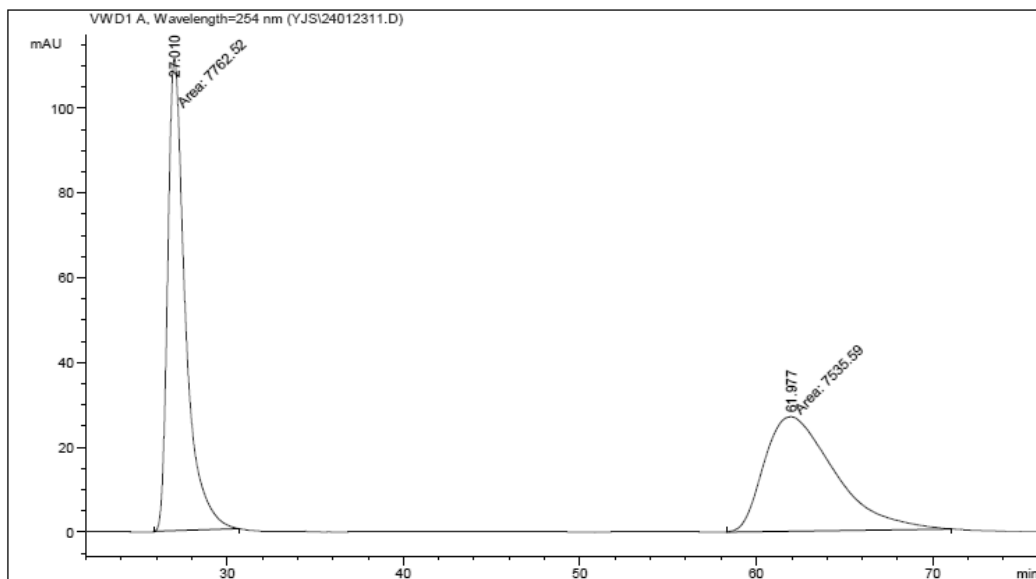
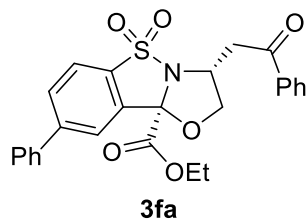
Totals : 2.72987e4 142.24644



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 Area Percent Report
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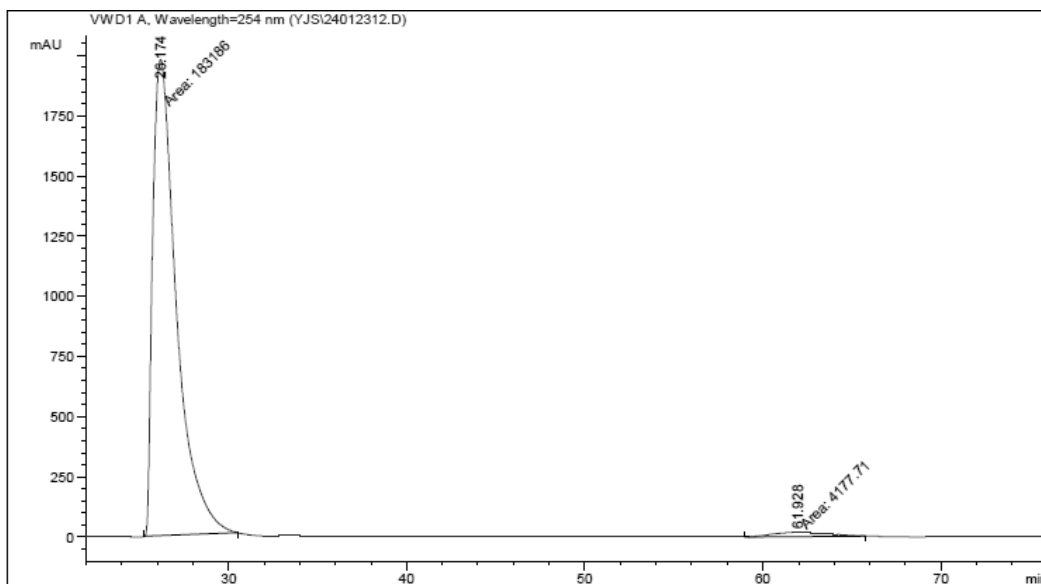
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	58.564	MM	3.1345	2.12633e4	113.06108	97.8569
2	72.733	MM	3.0685	465.67245	2.52933	2.1431

Totals : 2.17290e4 115.59041



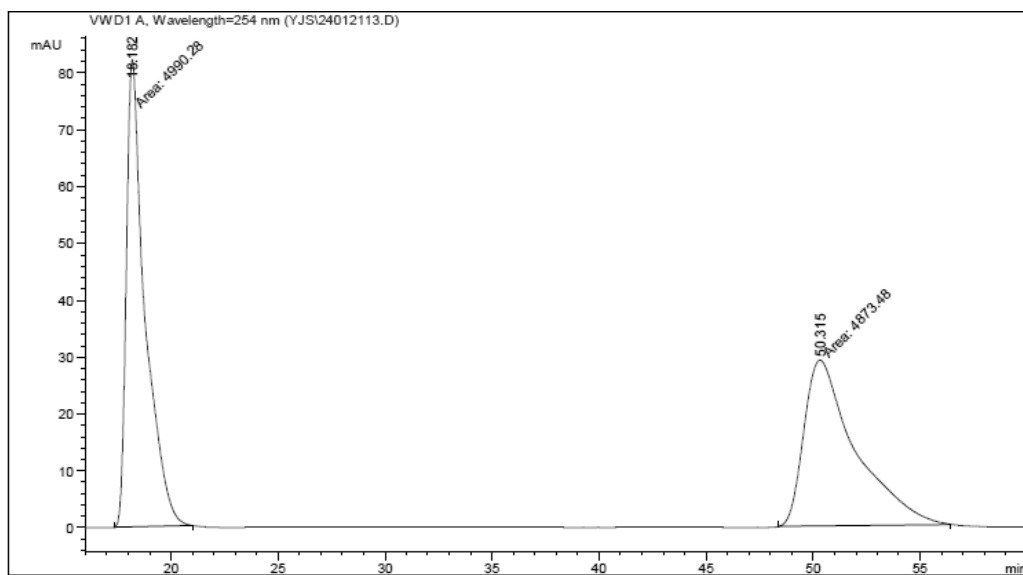
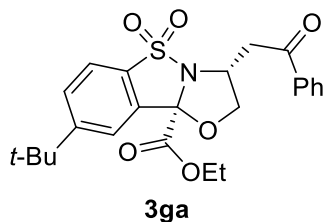
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.010	MM	1.1600	7762.52344	111.53474	50.7417
2	61.977	MM	4.6426	7535.59277	27.05228	49.2583
Totals :				1.52981e4	138.58702	



Area Percent Report

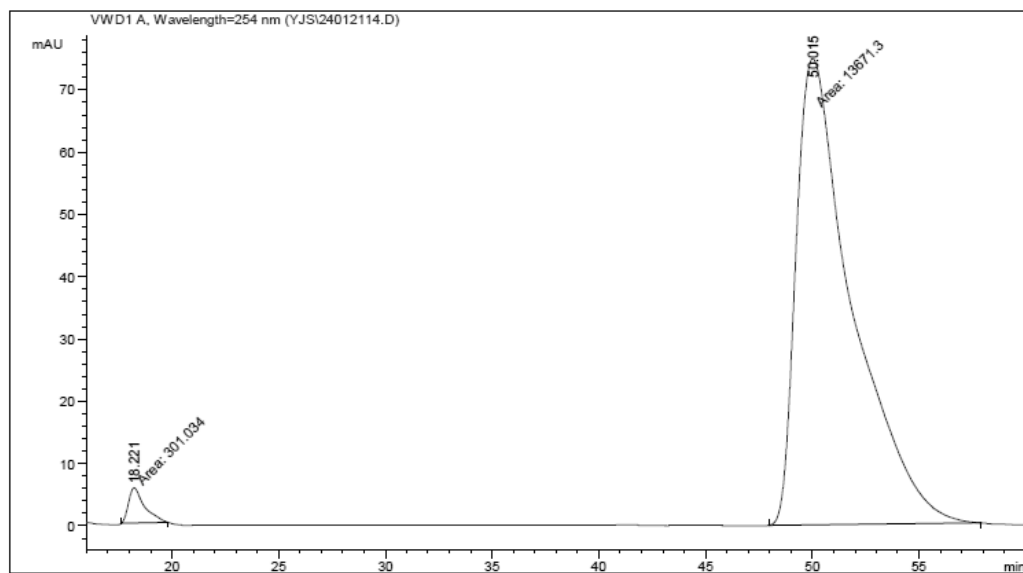
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.174	MM	1.5427	1.83186e5	1979.08765	97.7703
2	61.928	MM	2.7149	4177.71387	18.02417	2.2297
Totals :				1.87364e5	1997.11181	



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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	18.182	MM	1.0114	4990.28223	82.23005	50.5921	50.5921
2	50.315	MM	2.7816	4873.47998	29.20090	49.4079	49.4079

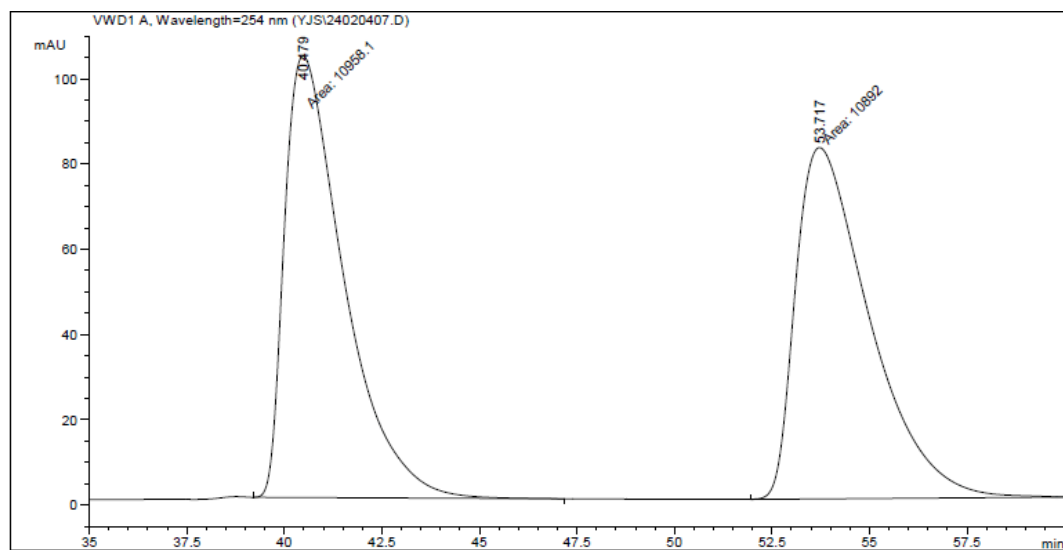
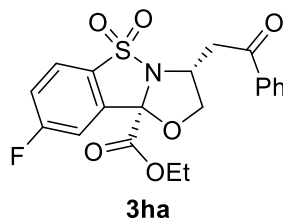
Totals : 9863.76221 111.43095



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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	18.221	MM	0.8817	301.03372	5.69030	2.1545	2.1545
2	50.015	MM	3.0429	1.36713e4	74.88007	97.8455	97.8455

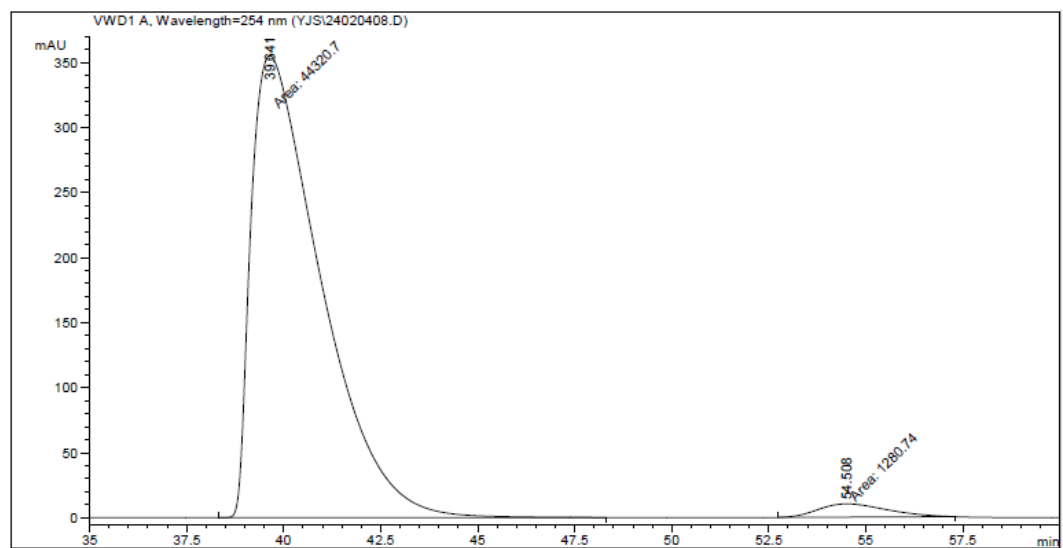
Totals : 1.39723e4 80.57037



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.479	MM	1.7609	1.09581e4	103.71749	50.1513
2	53.717	MM	2.2016	1.08920e4	82.45395	49.8487

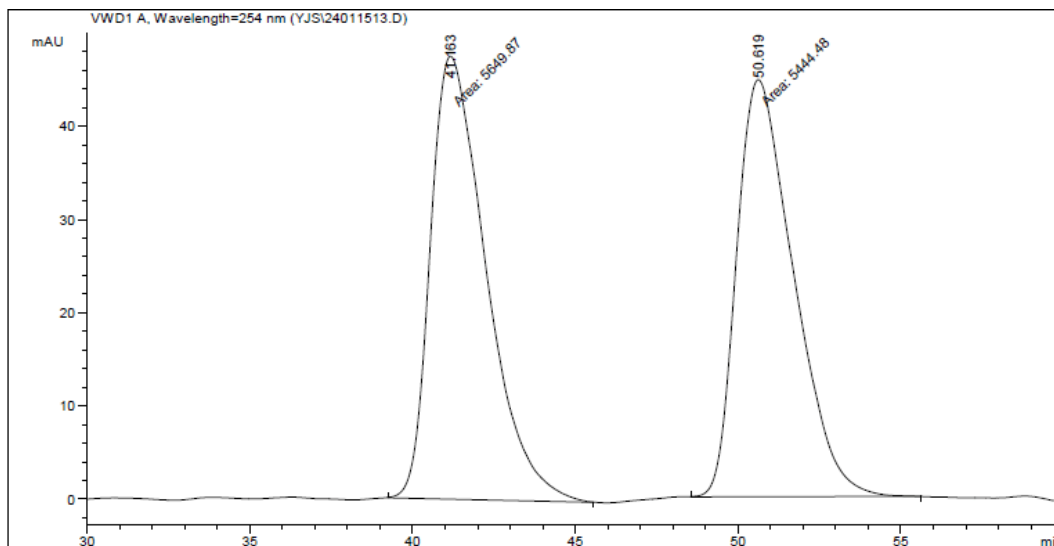
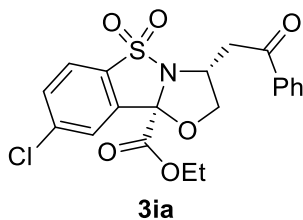
Totals : 2.18500e4 186.17144



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.641	MM	2.0793	4.43207e4	355.24704	97.1914
2	54.508	MM	2.0652	1280.74402	10.33570	2.8086

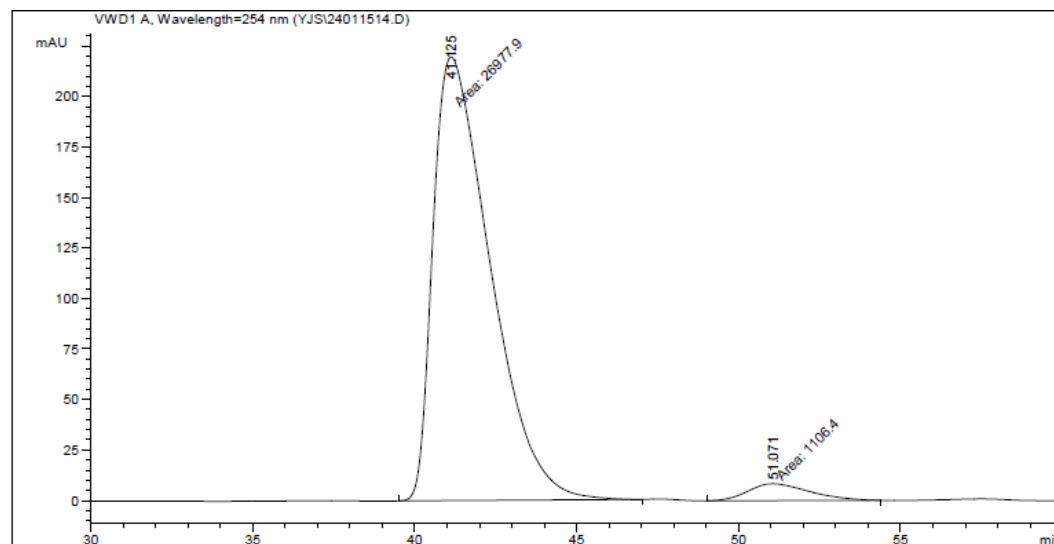
Totals : 4.56014e4 365.58274



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	41.163	MM	1.9806	5649.87354	47.54253	50.9257
2	50.619	MM	2.0268	5444.48242	44.77027	49.0743

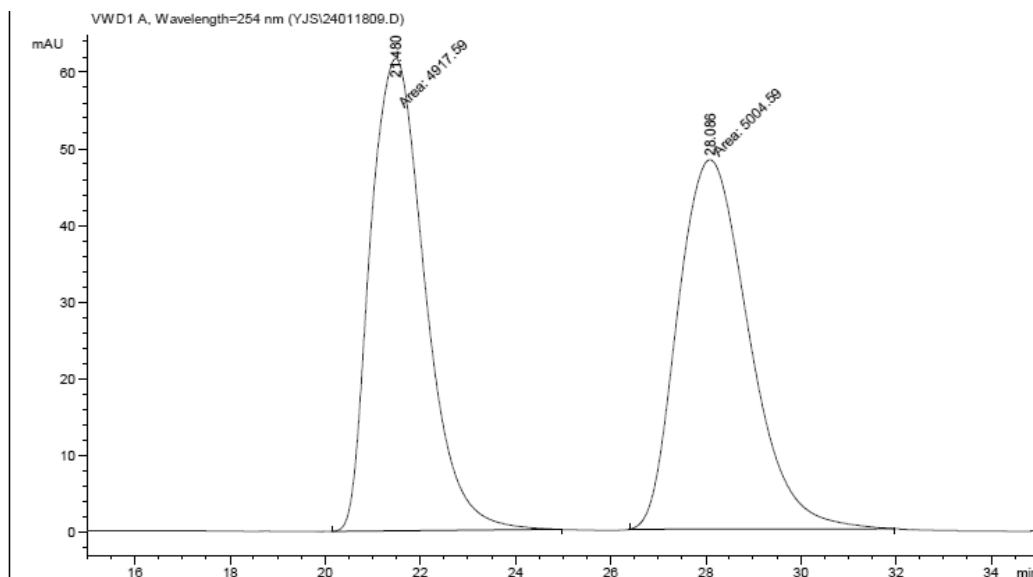
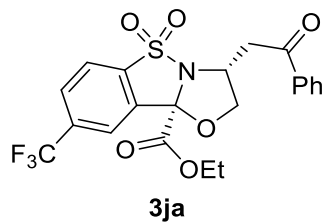
Totals : 1.10944e4 92.31280



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	41.125	MM	2.0460	2.69779e4	219.76683	96.0604
2	51.071	MM	2.1906	1106.40491	8.41775	3.9396

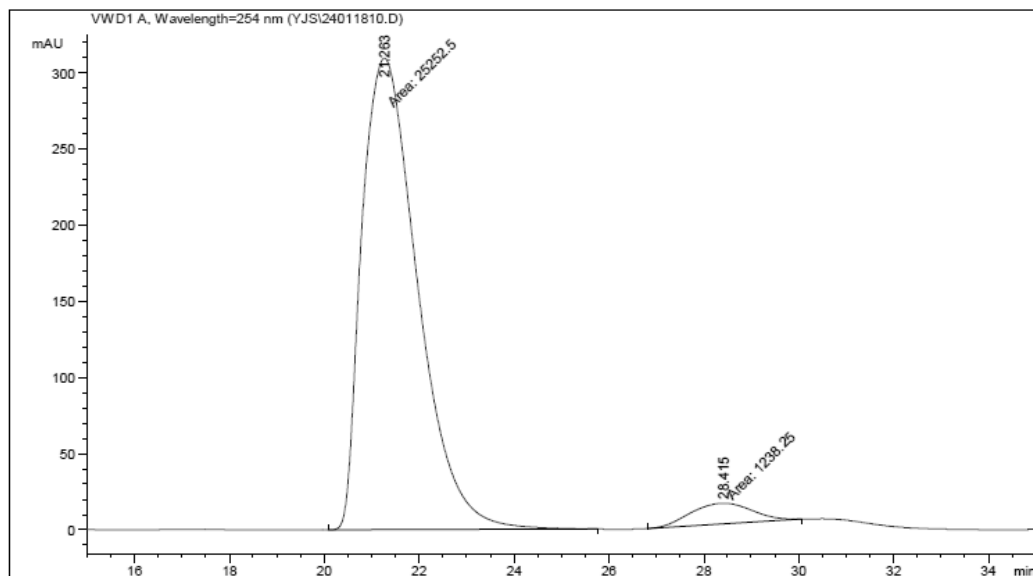
Totals : 2.80843e4 228.18458



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	21.480	MM	1.3297	4917.59131	61.63726	49.5616
2	28.086	MM	1.7304	5004.59082	48.20208	50.4384

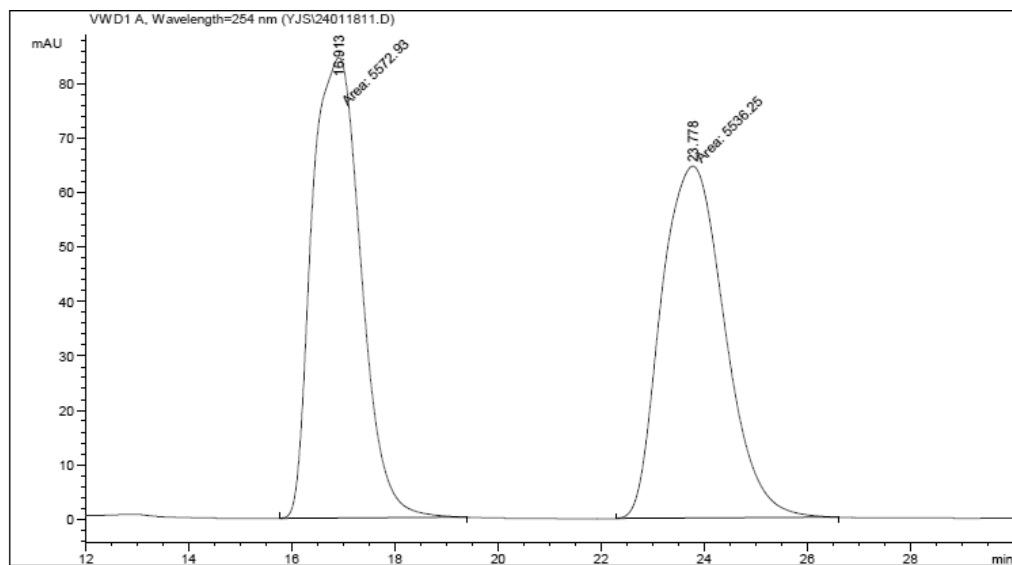
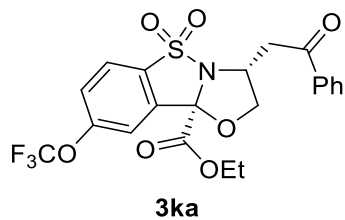
Totals : 9922.18213 109.83934



Area Percent Report

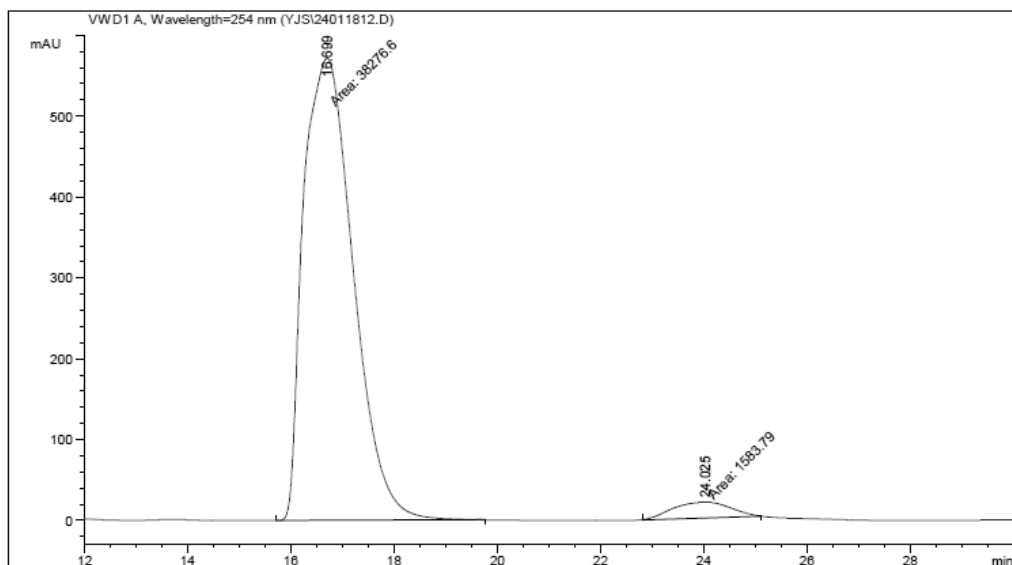
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	21.263	MM	1.3589	2.52525e4	309.70761	95.3257
2	28.415	MM	1.5179	1238.24792	13.59621	4.6743

Totals : 2.64907e4 323.30382



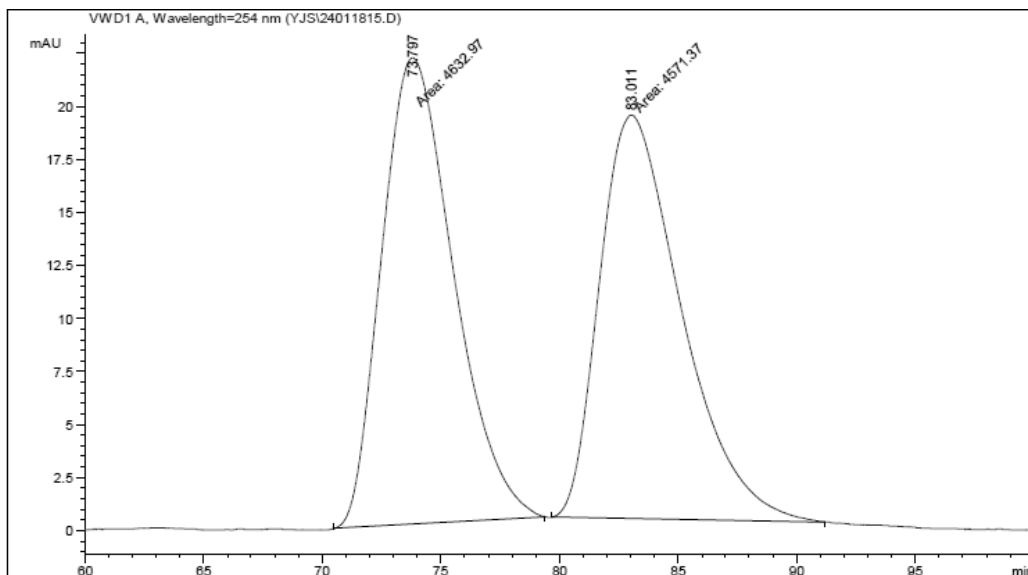
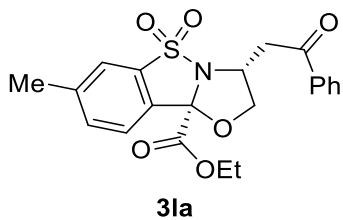
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	16.913	MM	1.0977	5572.93018	84.61305	50.1651
2	23.778	MM	1.4269	5536.25293	64.66332	49.8349
Totals :				1.11092e4	149.27637	



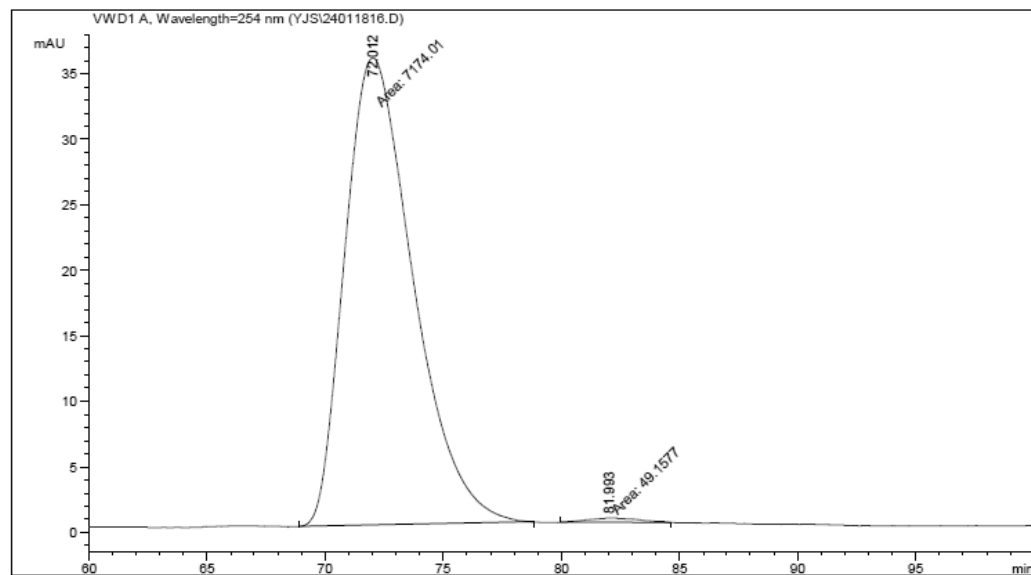
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	16.699	MM	1.1155	3.82766e4	571.88263	96.0266
2	24.025	MM	1.3126	1583.79407	20.10987	3.9734
Totals :				3.98604e4	591.99250	



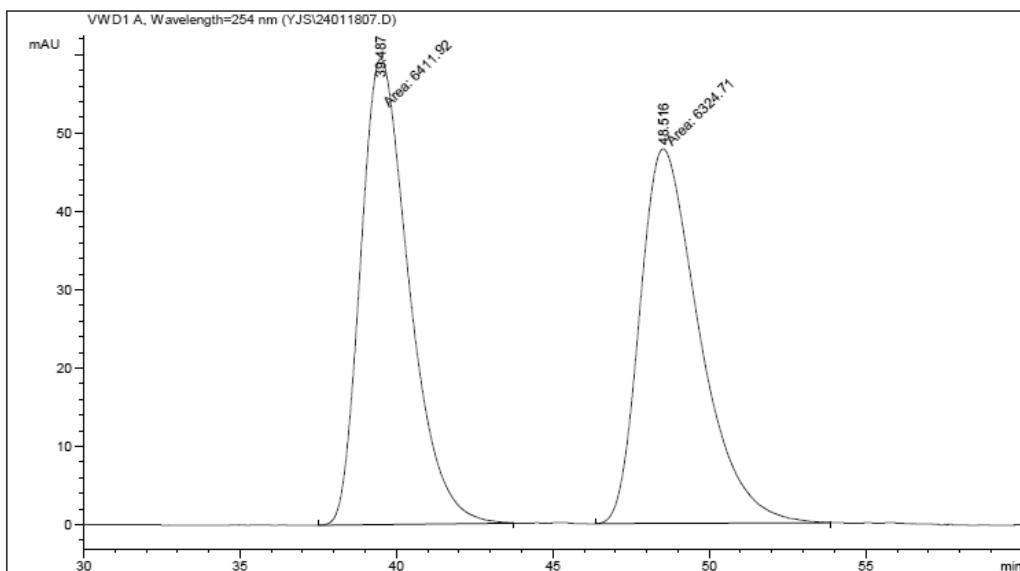
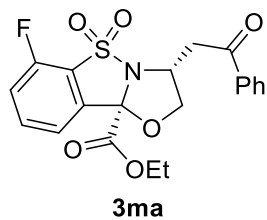
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	73.797	MM	3.5115	4632.96729	21.98962	50.3346
2	83.011	MM	4.0020	4571.36865	19.03792	49.6654
Totals :				9204.33594	41.02754	



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Area Percent Report
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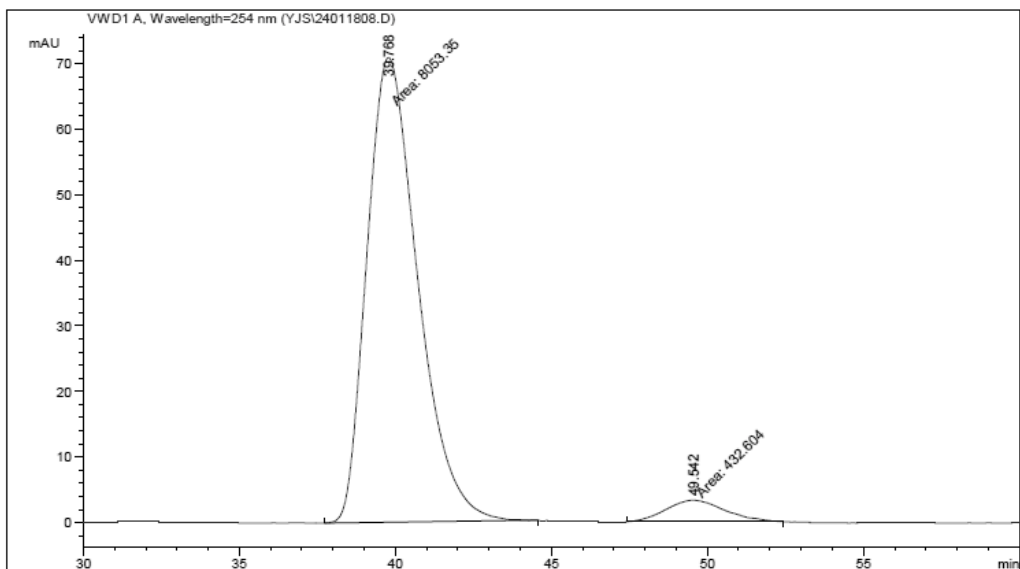
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	72.012	MM	3.3524	7174.01172	35.66621	99.3194
2	81.993	MM	2.5140	49.15774	3.25896e-1	0.6806
Totals :				7223.16946	35.99211	



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	39.487	MM	1.7950	6411.91748	59.53635	50.3424
2	48.516	MM	2.2033	6324.70703	47.84243	49.6576

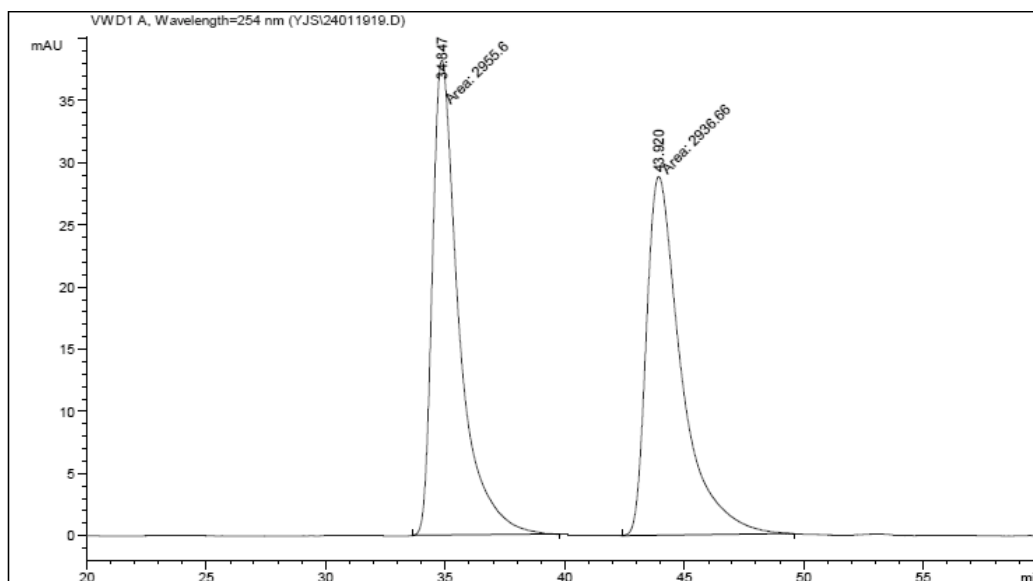
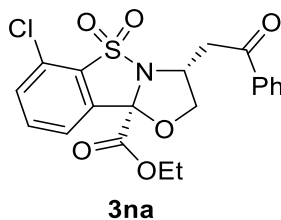
Totals : 1.27366e4 107.37878



Area Percent Report

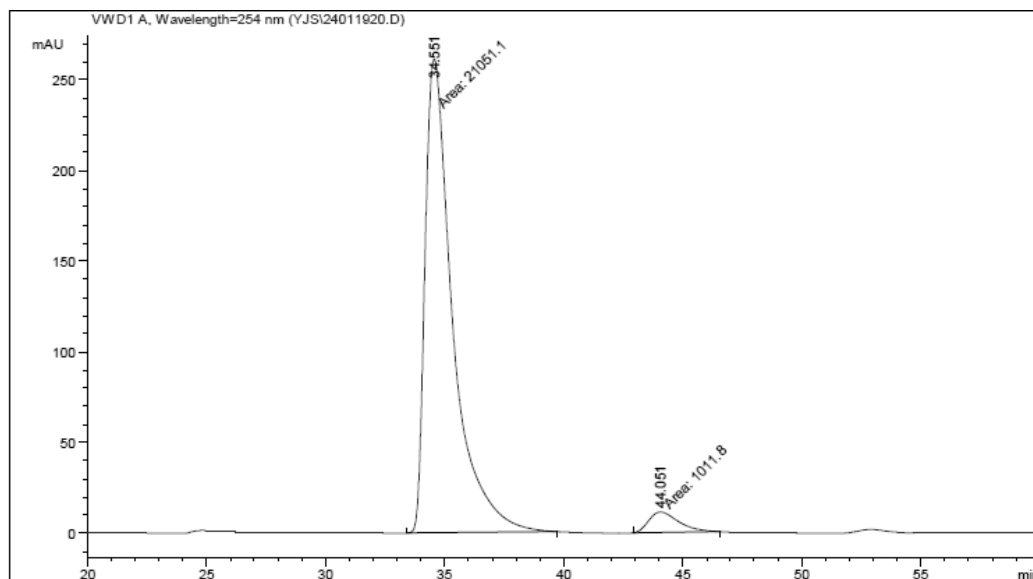
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	39.768	MM	1.8911	8053.34961	70.97485	94.9021
2	49.542	MM	2.1823	432.60382	3.30395	5.0979

Totals : 8485.95343 74.27880



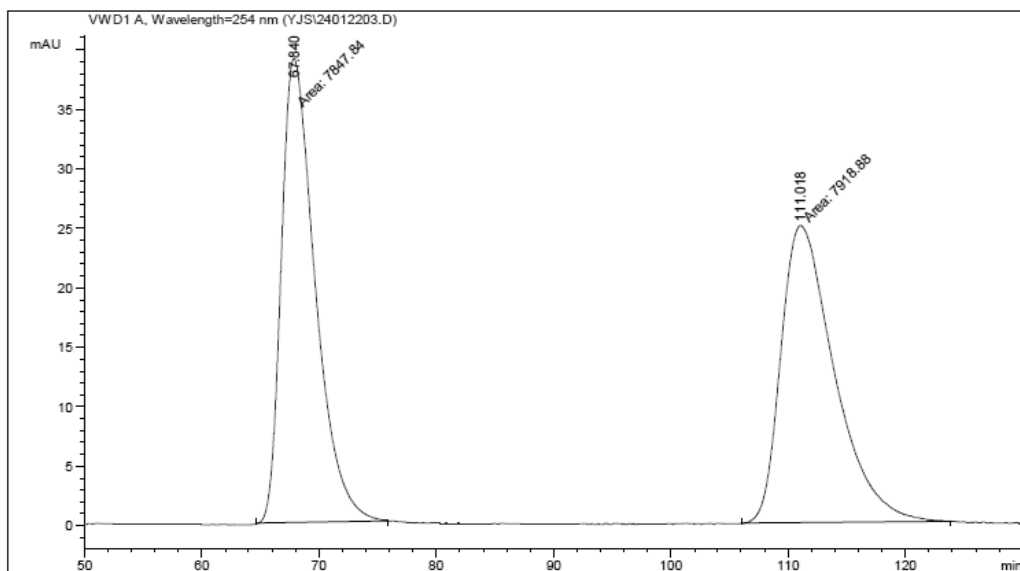
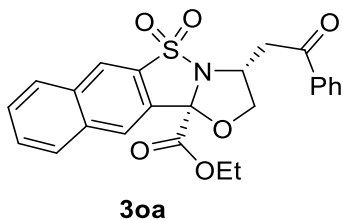
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.847	MM	1.2892	2955.60278	38.20910	50.1607
2	43.920	MM	1.6950	2936.66479	28.87659	49.8393
Totals :				5892.26758	67.08569	



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Area Percent Report
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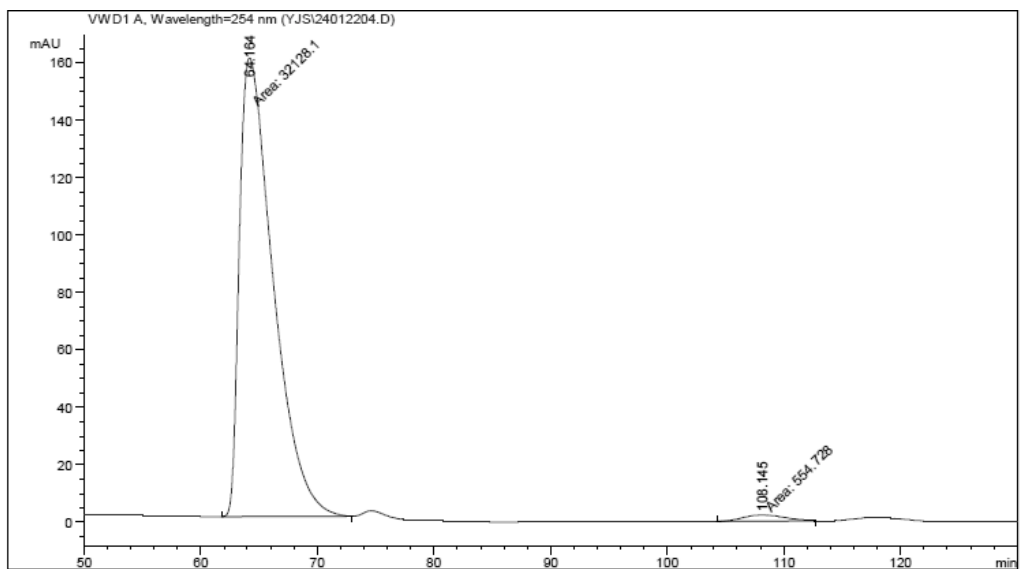
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.551	MM	1.3427	2.10511e4	261.30438	95.4140
2	44.051	MM	1.4823	1011.80121	11.37684	4.5860
Totals :				2.20629e4	272.68122	



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	67.840	MM	3.3530	7847.84131	49.7747	39.00858	49.7747
2	111.018	MM	5.2768	7918.88037	50.2253	25.01141	50.2253

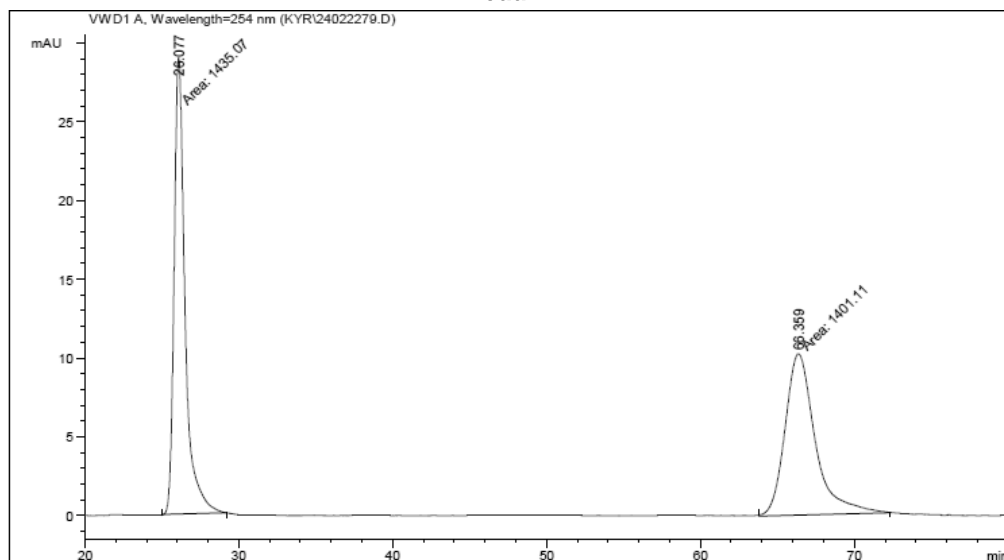
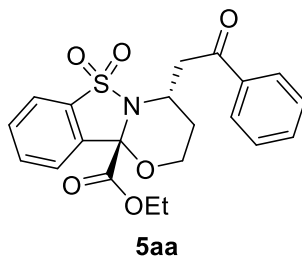
Totals : 1.57667e4 64.01999



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Area Percent Report
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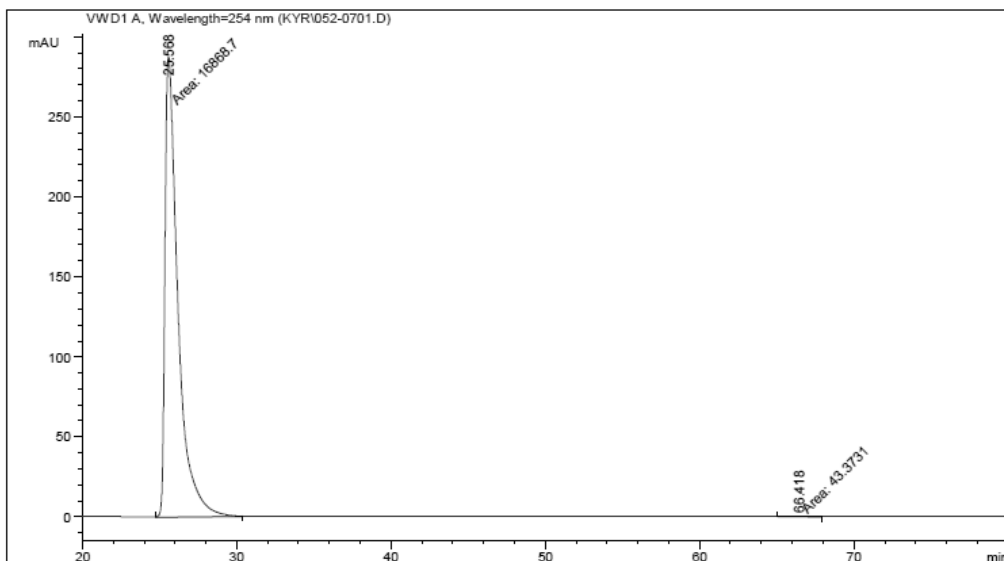
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	64.164	MM	3.3503	3.21281e4	98.3027	159.82529	98.3027
2	108.145	MM	4.2355	554.72772	1.6973	2.18286	1.6973

Totals : 3.26829e4 162.00814



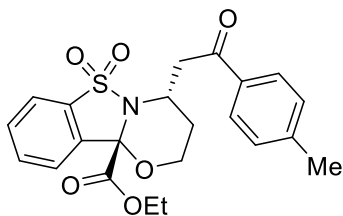
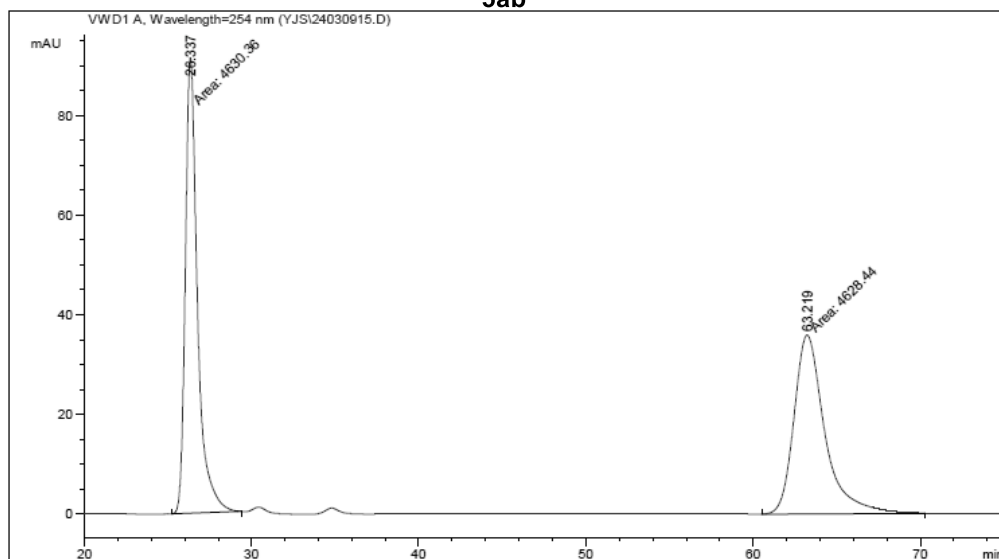
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	26.077	MM	0.8242	1435.06665	50.5987	29.01784	50.5987
2	66.359	MM	2.2803	1401.10547	49.4013	10.24048	49.4013
Totals :				2836.17212	39.25832		



Area Percent Report

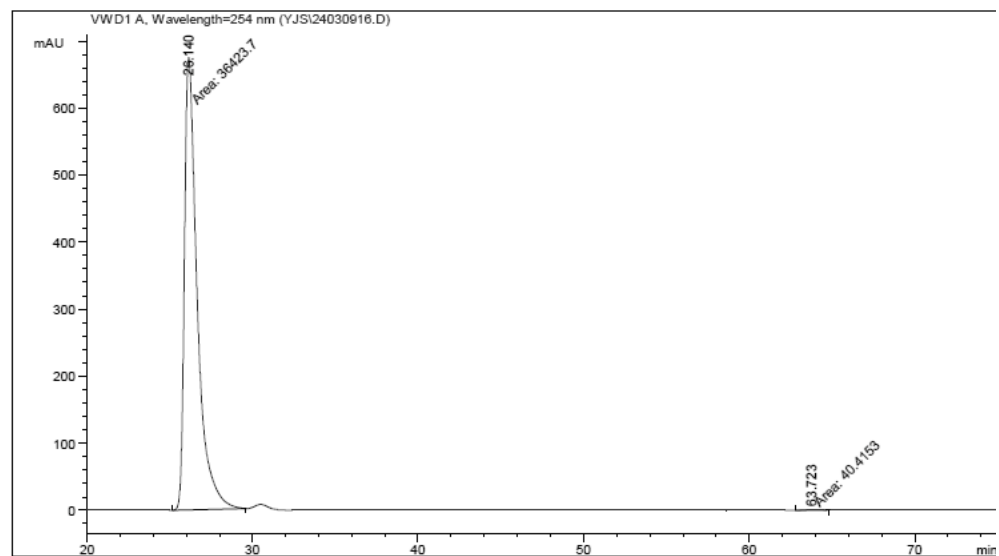
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	25.568	MM	0.9766	1.68687e4	99.7435	287.86905	99.7435
2	66.418	MM	1.7038	43.37315	0.2565	4.24270e-1	0.2565
Totals :				1.69121e4	288.29332		

**5ab**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	26.337	MM	0.8434	4630.36084		91.50466	50.0104
2	63.219	MM	2.1471	4628.43604		35.92761	49.9896

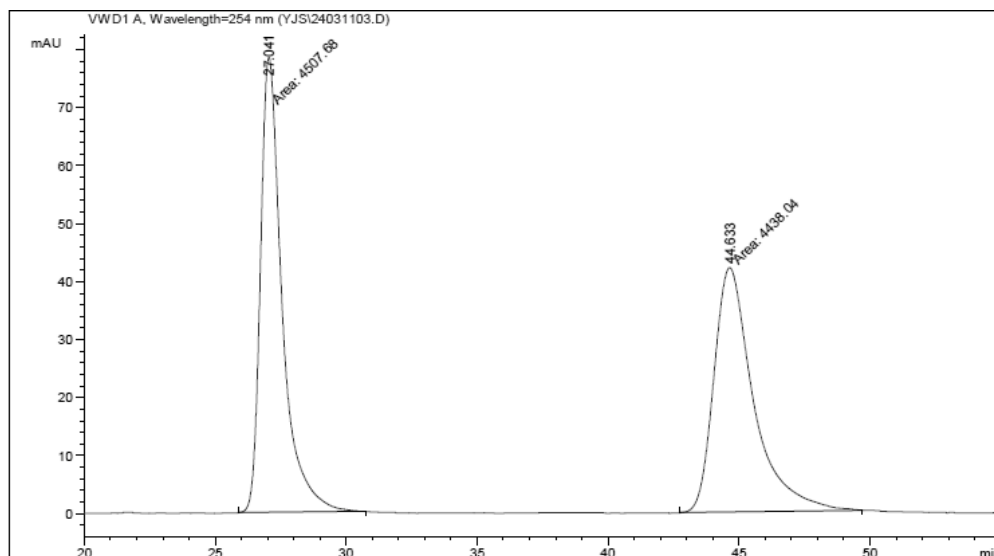
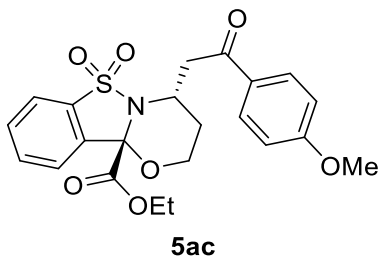
Totals : 9258.79688 127.43227



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	26.140	MM	0.8984	3.64237e4		675.69019	99.8892
2	63.723	MM	0.8724	40.41528		5.47247e-1	0.1108

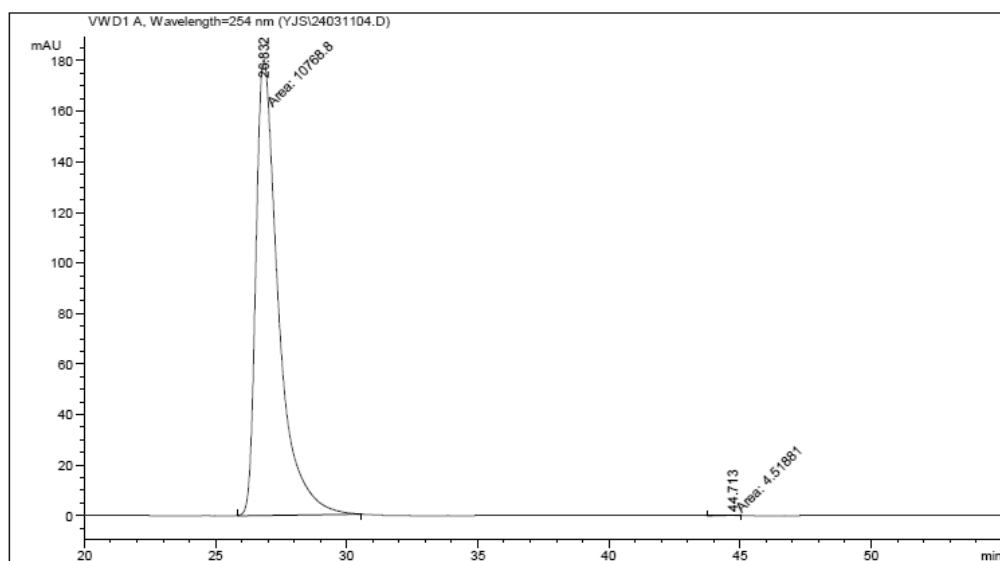
Totals : 3.64641e4 676.23743



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.041	MM	0.9569	4507.68262	78.51146	50.3892
2	44.633	MM	1.7550	4438.04199	42.14626	49.6108

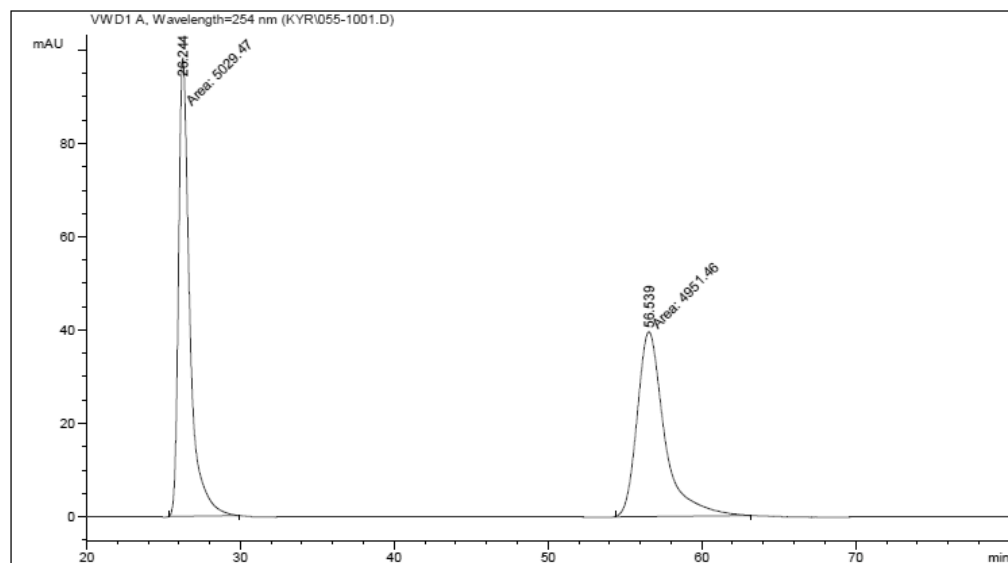
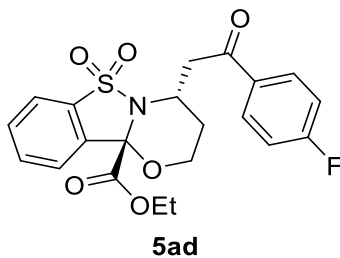
Totals : 8945.72461 120.65771



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Area Percent Report
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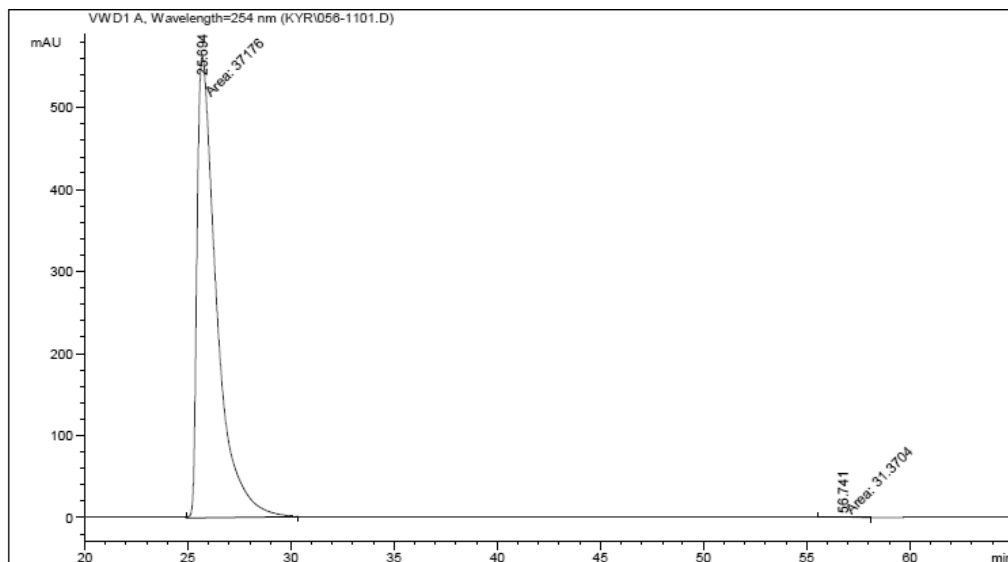
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.832	MM	0.9953	1.07688e4	180.32288	99.9581
2	44.713	MM	1.8151	4.51881	4.14933e-2	0.0419

Totals : 1.07733e4 180.36437



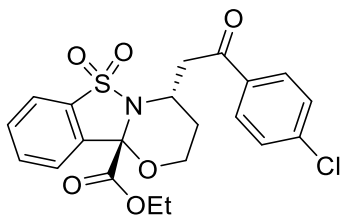
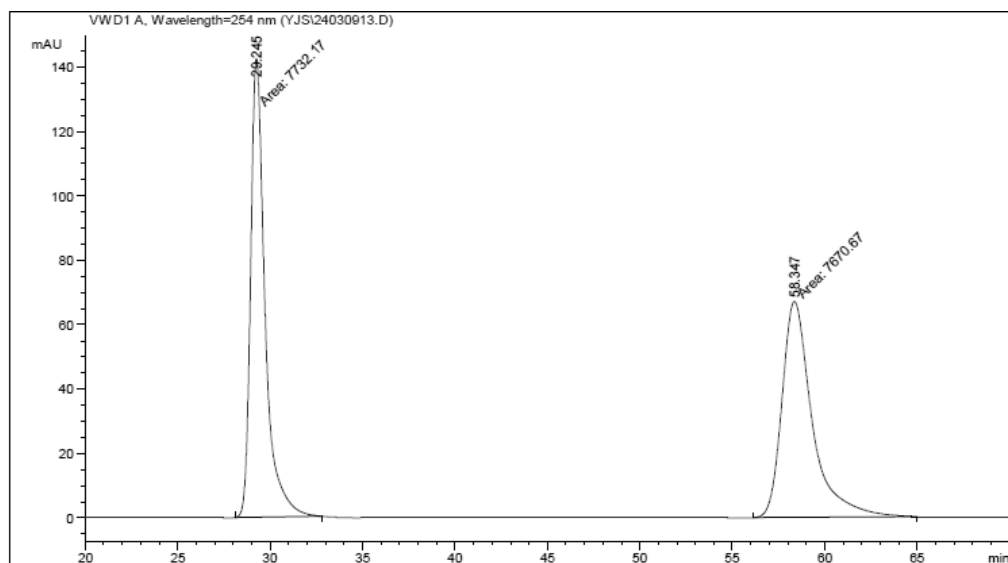
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	26.244	MM	0.8519	5029.47266	98.39513	50.3908	
2	56.539	MM	2.0802	4951.46045	39.67060	49.6092	
Totals :				9980.93311	138.06573		



Area Percent Report

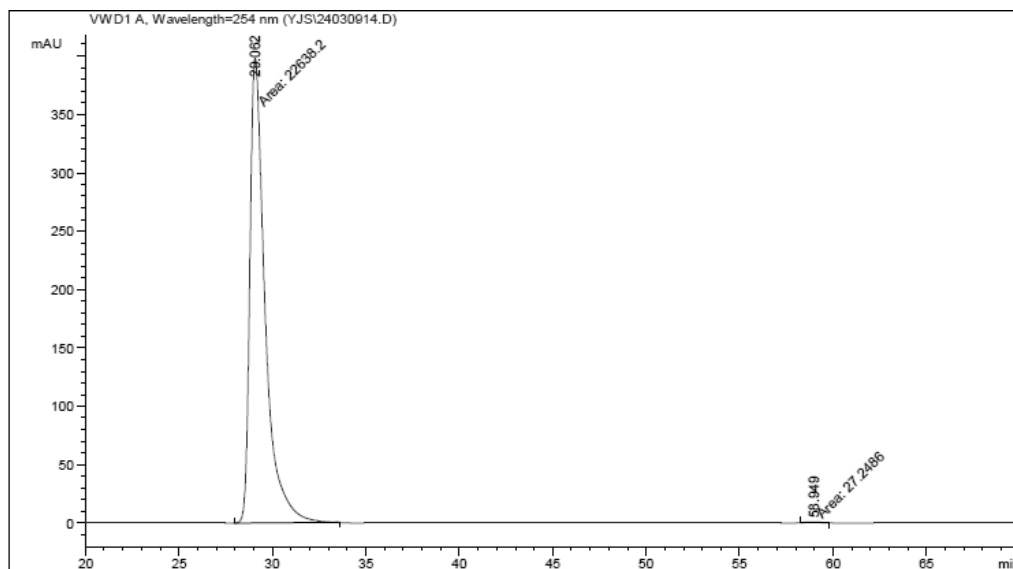
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	25.694	MM	1.1014	3.71760e4	562.57941	99.9157	
2	56.741	MM	1.0252	31.37039	5.09964e-1	0.0843	
Totals :				3.72074e4	563.08937		

**5ae**

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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	29.245	MM	0.9045	7732.17139	142.47307	50.1996	
2	58.347	MM	1.9047	7670.67236	67.12000	49.8004	

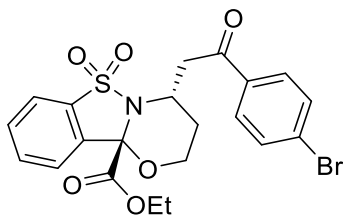
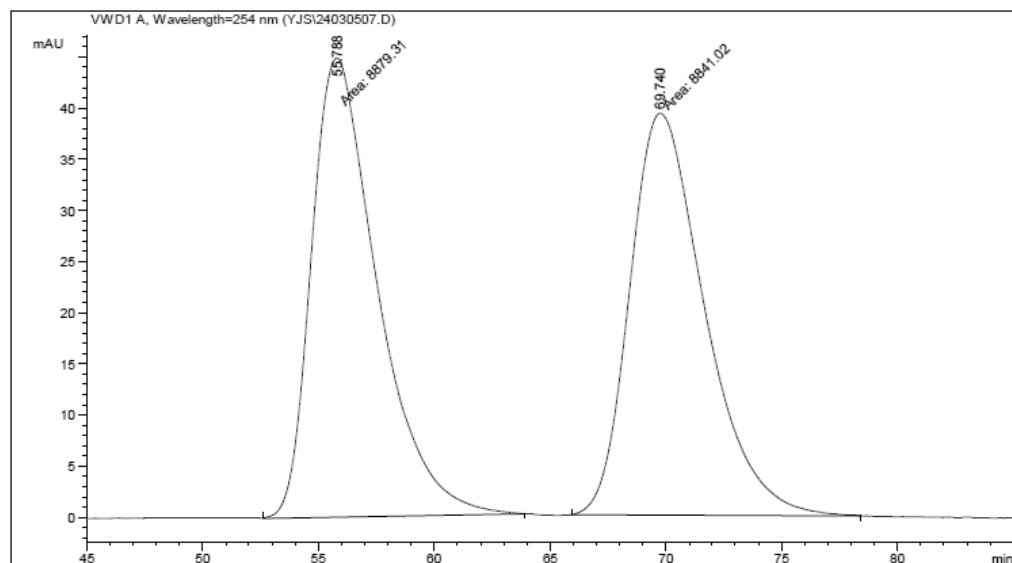
Totals : 1.54028e4 209.59307



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 Area Percent Report
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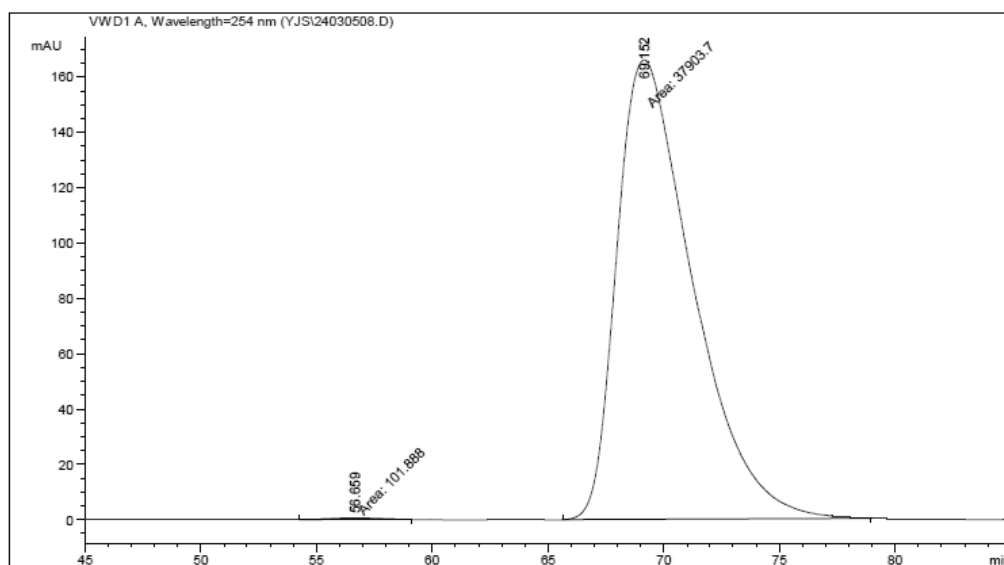
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	29.062	MM	0.9472	2.26382e4	398.34402	99.8798	
2	58.949	MM	1.0020	27.24857	4.53228e-1	0.1202	

Totals : 2.26654e4 398.79725

**5af**=====
Area Percent Report
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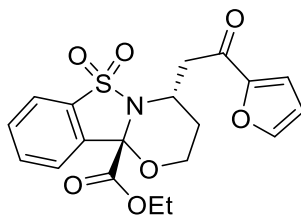
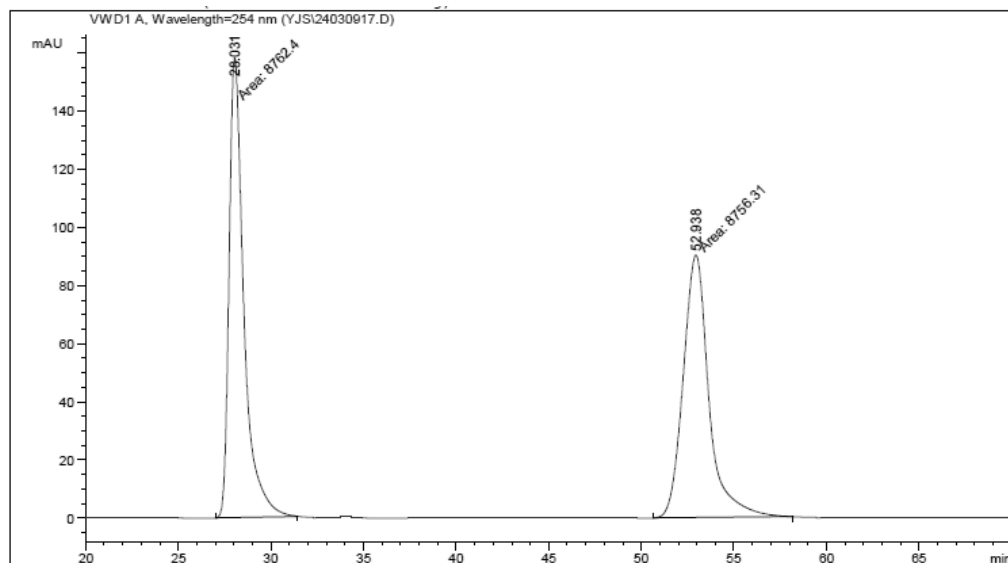
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	55.788	MM	3.2957	8879.31055		44.90297	50.1080
2	69.740	MM	3.7497	8841.02344		39.29702	49.8920

Totals : 1.77203e4 84.19999

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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	56.659	MM	2.6159	101.88846		6.49151e-1	0.2681
2	69.152	MM	3.8044	37903.7e4		166.05357	99.7319

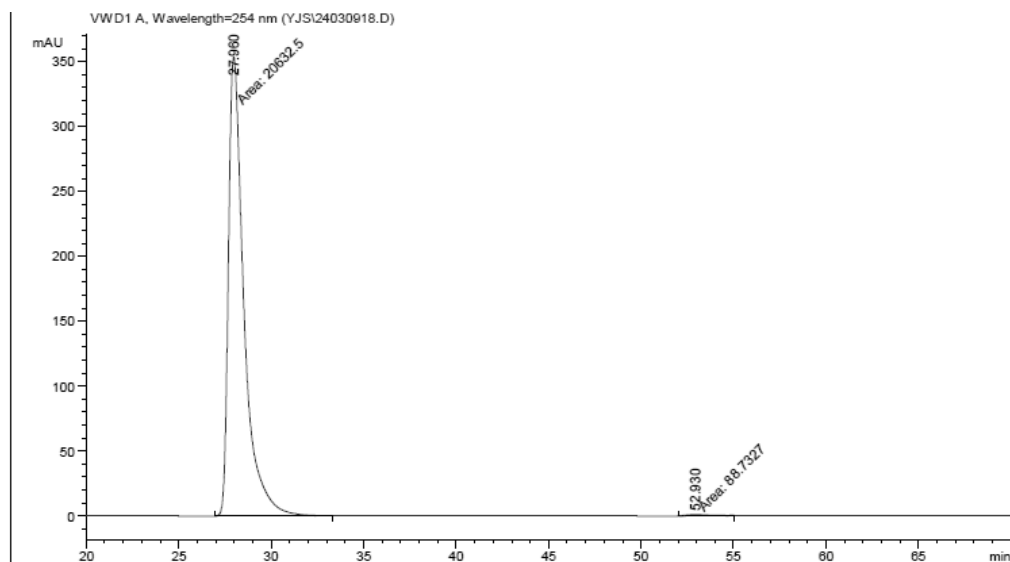
Totals : 3.80056e4 166.70272

**5ag**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	28.031	MM	0.9228	8762.40039	50.0174	158.26346	50.0174
2	52.938	MM	1.6147	8756.30664	49.9826	90.38179	49.9826

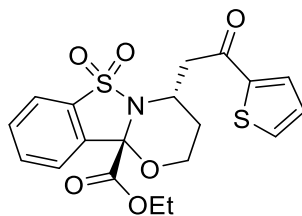
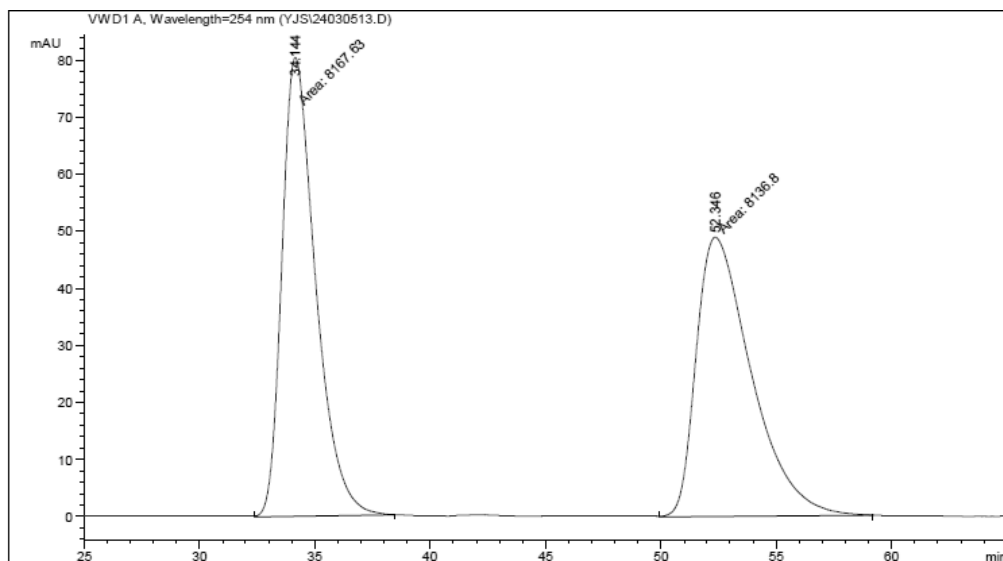
Totals : 1.75187e4 248.64525



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	27.960	MM	0.9722	2.06325e4	99.5718	353.70554	99.5718
2	52.930	MM	1.3779	88.73273	0.4282	1.07331	0.4282

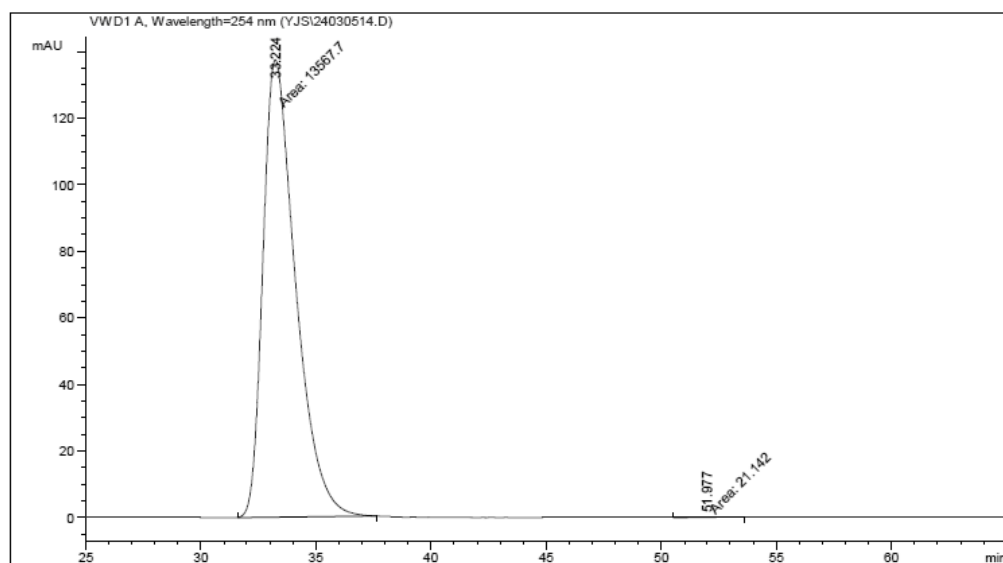
Totals : 2.07212e4 354.77885

**5ah**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	34.144	MM	1.6923	8167.62646		80.44122	50.0945
2	52.346	MM	2.7698	8136.79541		48.96076	49.9055

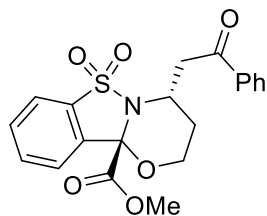
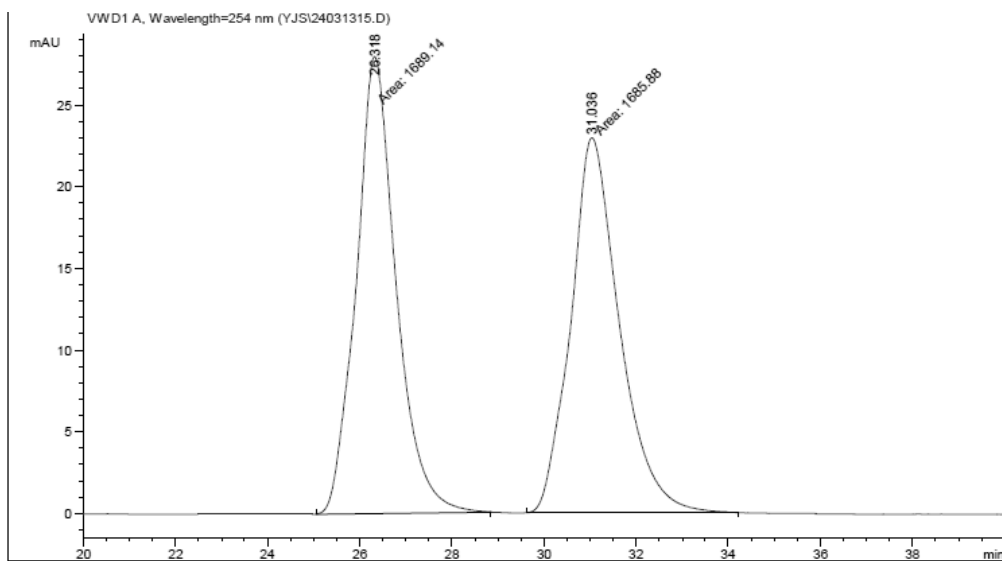
Totals : 1.63044e4 129.40197



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	33.224	MM	1.6439	1.35677e4		137.55606	99.8444
2	51.977	MM	1.7933	21.14202		1.96486e-1	0.1556

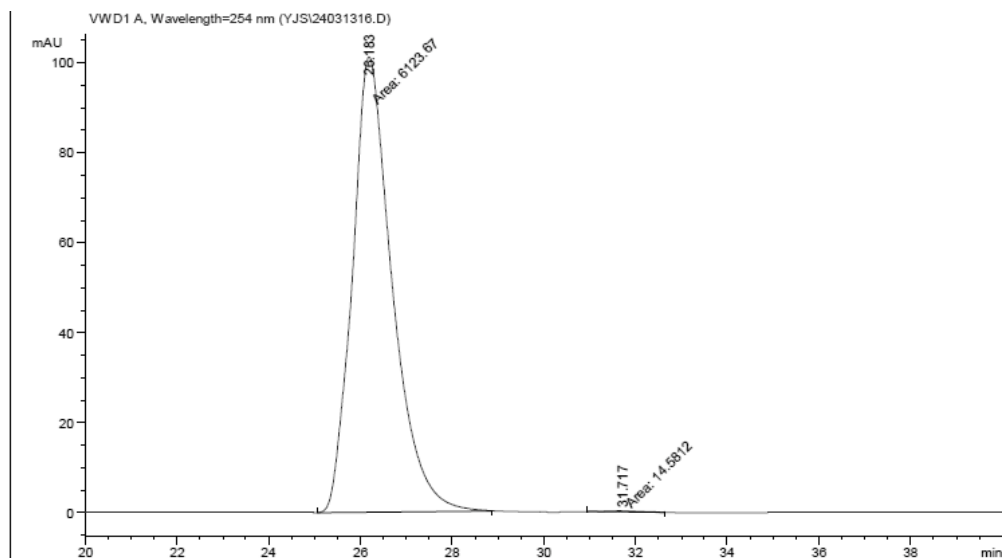
Totals : 1.35889e4 137.75255

**5ba**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	26.318	MM	1.0059	1689.13953		27.98795	50.0483
2	31.036	MM	1.2245	1685.87927		22.94571	49.9517

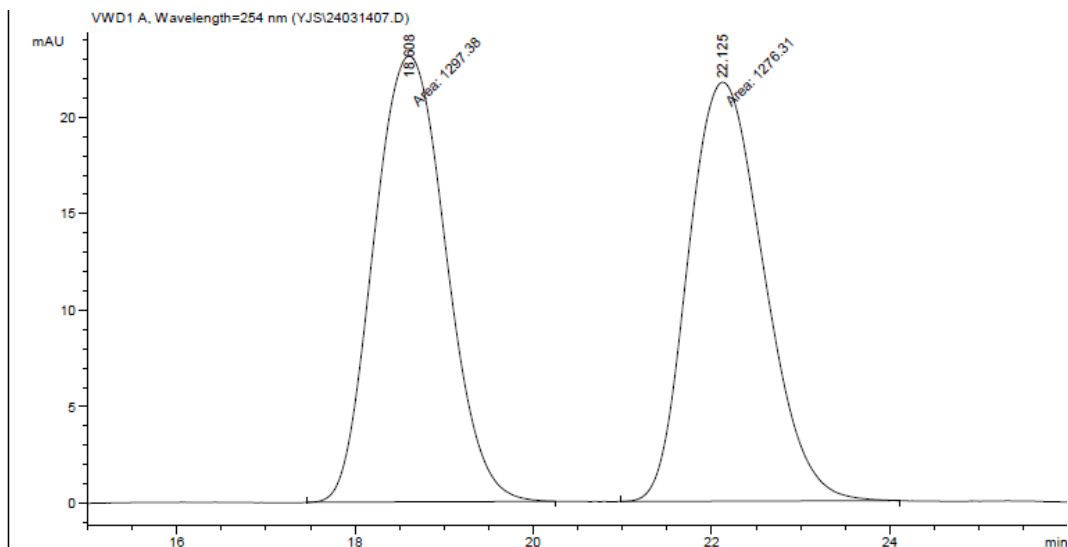
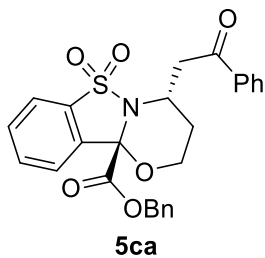
Totals : 3375.01880 50.93365



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	26.183	MM	1.0079	6123.66699		101.26205	99.7625
2	31.717	MM	0.8958	14.58122		2.71277e-1	0.2375

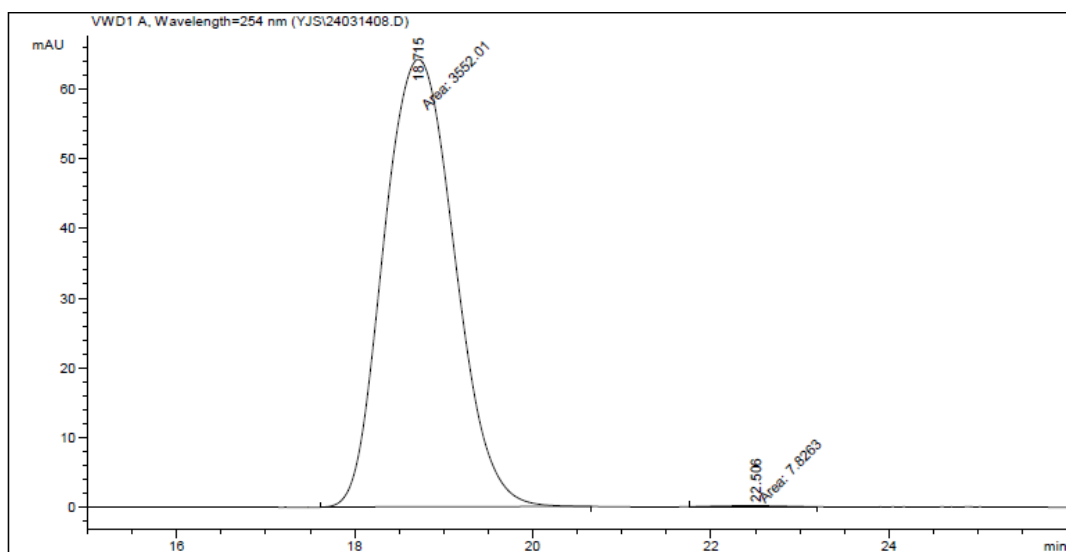
Totals : 6138.24821 101.53332



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	18.608	MM	0.9359	1297.37866	23.10303	50.4093
2	22.125	MM	0.9800	1276.31238	21.70555	49.5907

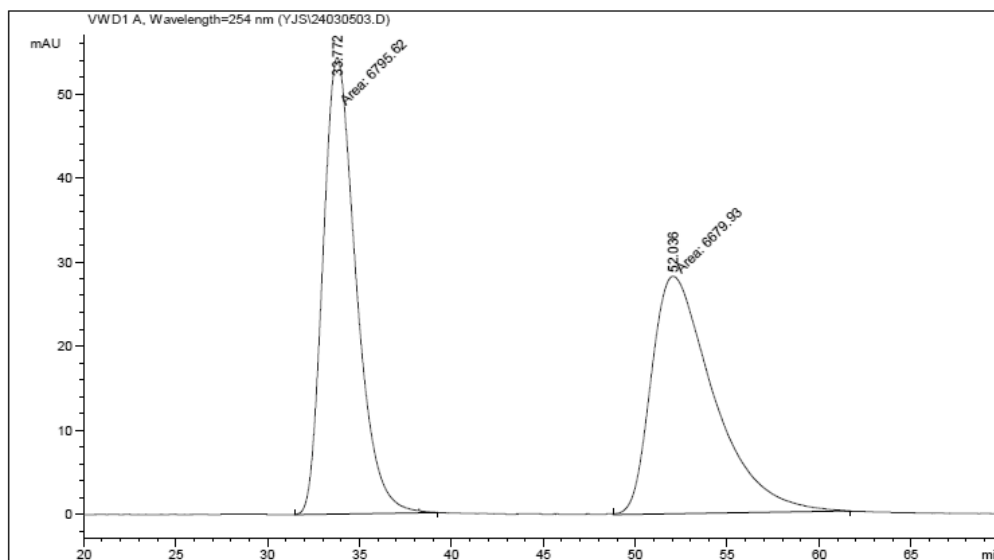
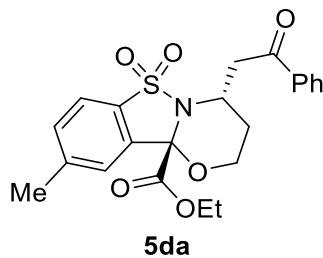
Totals : 2573.69104 44.80858



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	18.715	MM	0.9215	3552.00952	64.24580	99.7801
2	22.506	MM	0.8502	7.82630	1.53417e-1	0.2199

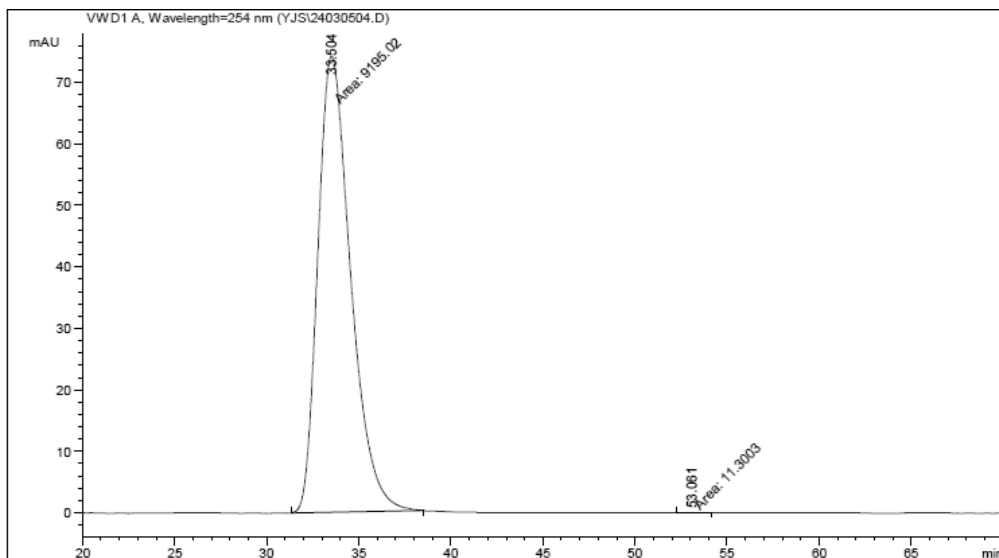
Totals : 3559.83582 64.39922



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.772	MM	2.0859	6795.62207	54.29781	50.4293
2	52.036	MM	3.9385	6679.93115	28.26743	49.5707

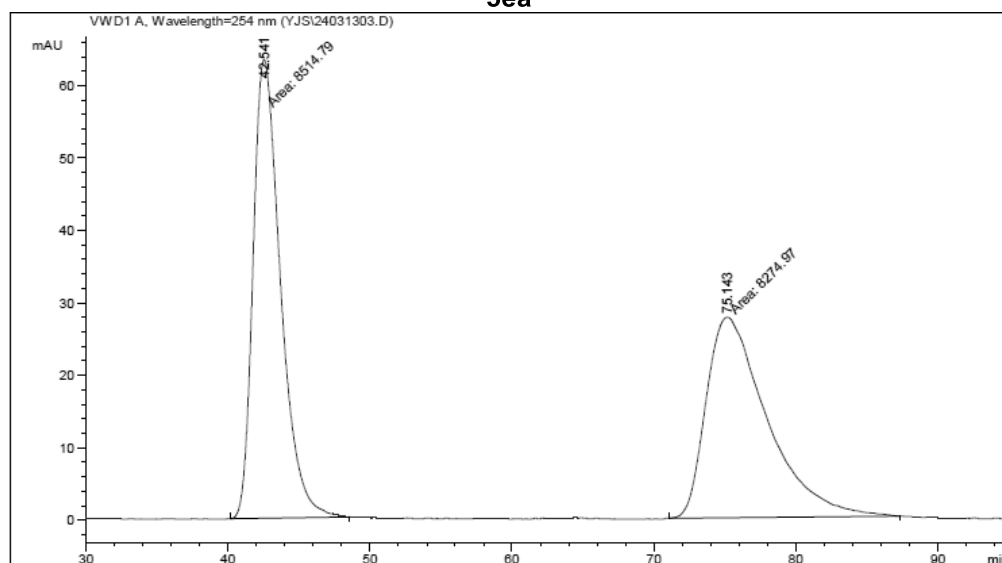
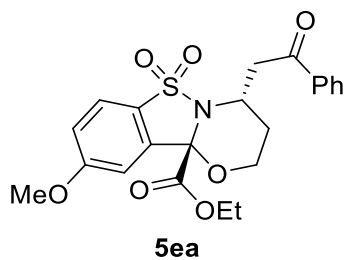
Totals : 1.34756e4 82.56524



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Area Percent Report
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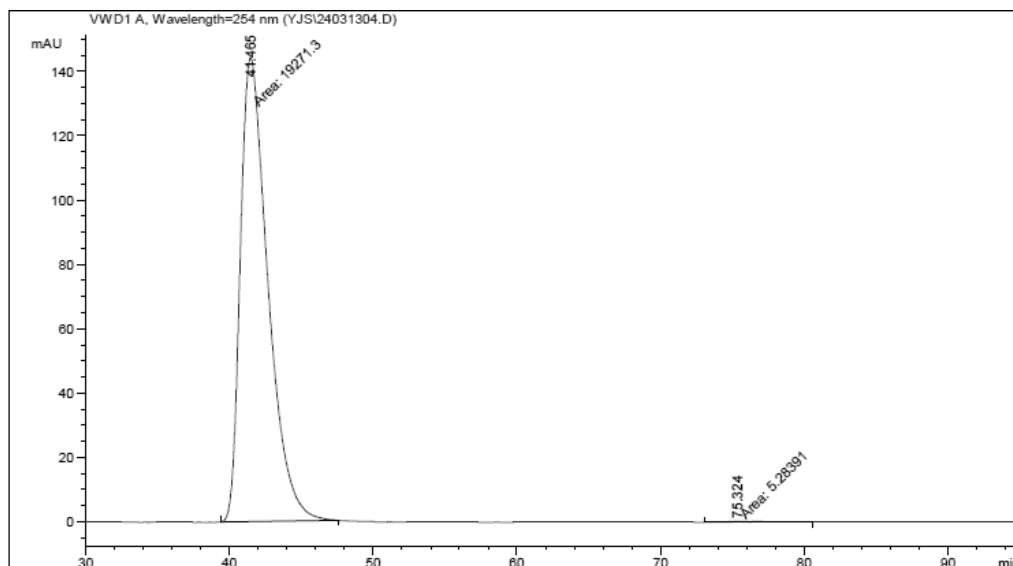
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.504	MM	2.0672	9195.02246	74.13548	99.8773
2	53.061	MM	1.5341	11.30028	1.22765e-1	0.1227

Totals : 9206.32274 74.25825



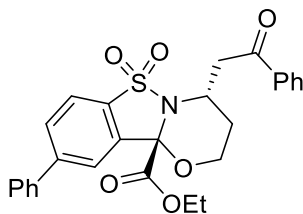
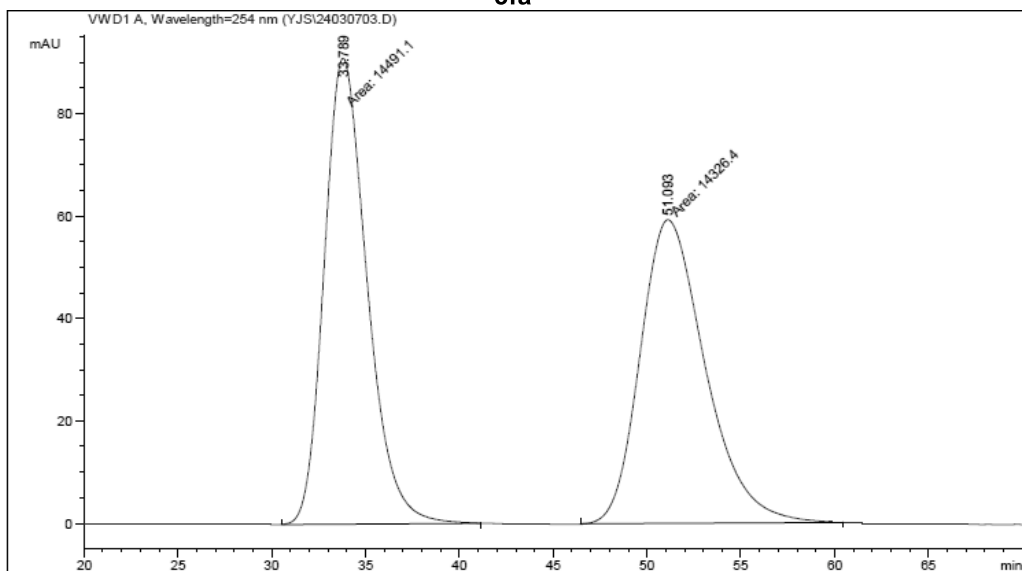
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	42.541	MM	2.2394	8514.78809	63.36987	50.7142	
2	75.143	MM	4.9787	8274.97070	27.70111	49.2858	
Totals :				1.67898e4	91.07098		



Area Percent Report

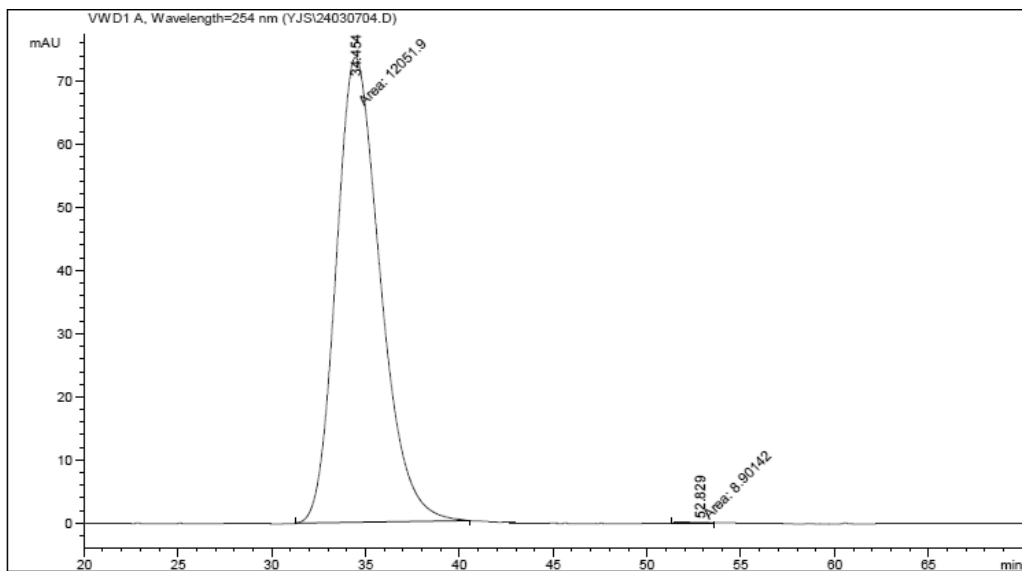
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	41.465	MM	2.2286	1.92713e4	144.12285	99.9726	
2	75.324	MM	1.3814	5.28391	6.37526e-2	0.0274	
Totals :				1.92766e4	144.18660		

**5fa**

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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	33.789	MM	2.6522	1.44911e4	50.2857	91.06343	50.2857
2	51.093	MM	4.0226	1.43264e4	49.7143	59.35849	49.7143

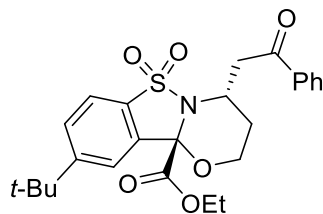
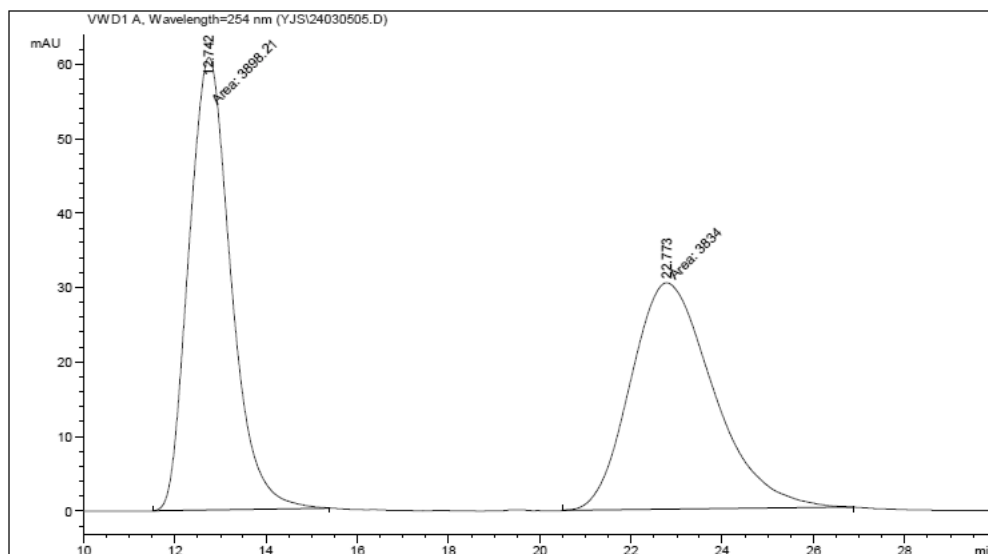
Totals : 2.88175e4 150.42192



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	34.454	MM	2.7278	1.20519e4	99.9262	73.63513	99.9262
2	52.829	MM	1.3495	8.90142	0.0738	1.09937e-1	0.0738

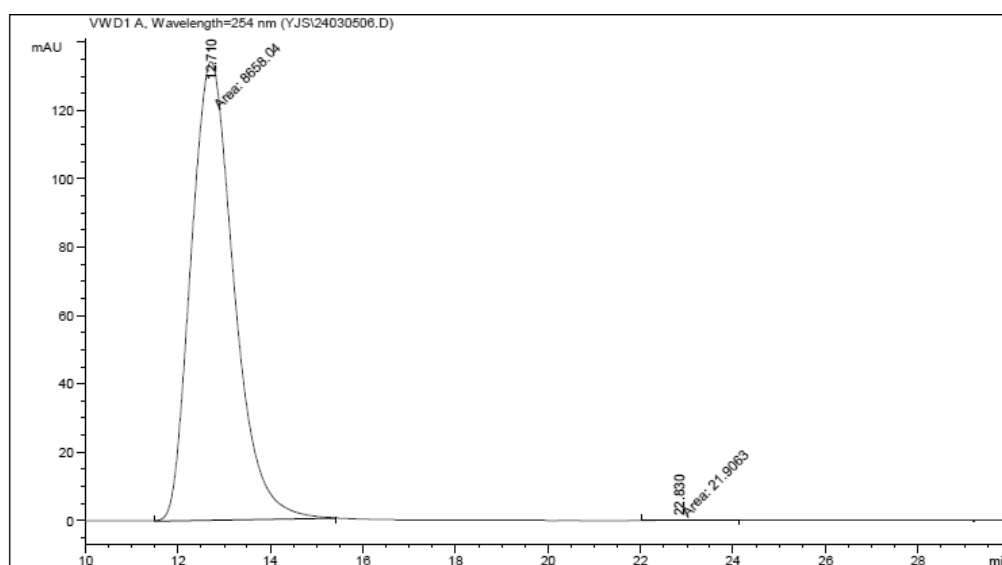
Totals : 1.20608e4 73.74507

**5ga**

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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	12.742	MM	1.0692	3898.21436		60.76381	50.4152
2	22.773	MM	2.1029	3834.00293		30.38699	49.5848

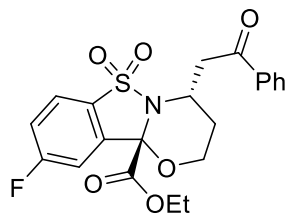
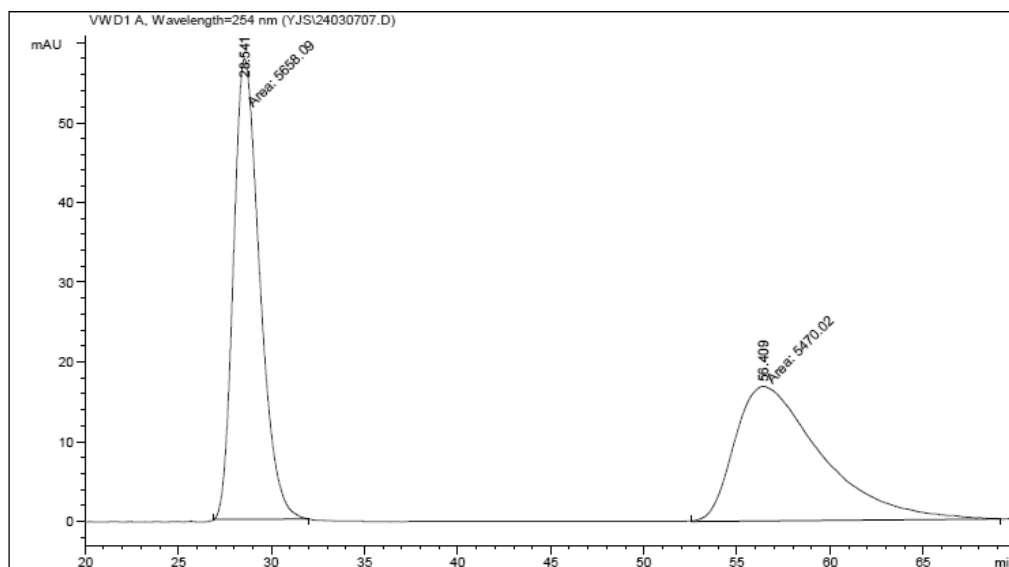
Totals : 7732.21729 91.15081



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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	12.710	MM	1.0747	8658.03906		134.26691	99.7476
2	22.830	MM	1.3739	21.90628		2.65750e-1	0.2524

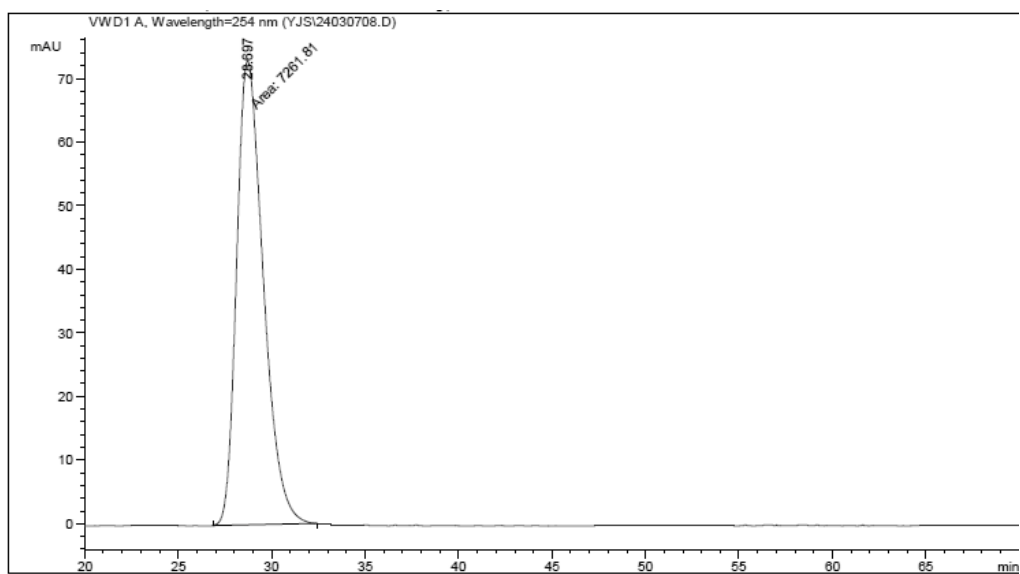
Totals : 8679.94534 134.53266

**5ha**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	28.541	MM	1.6333	5658.09229		57.73697	50.8450
2	56.409	MM	5.4038	5470.02490		16.87080	49.1550

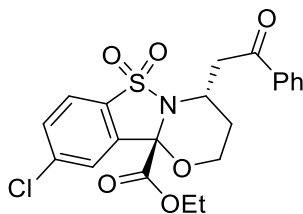
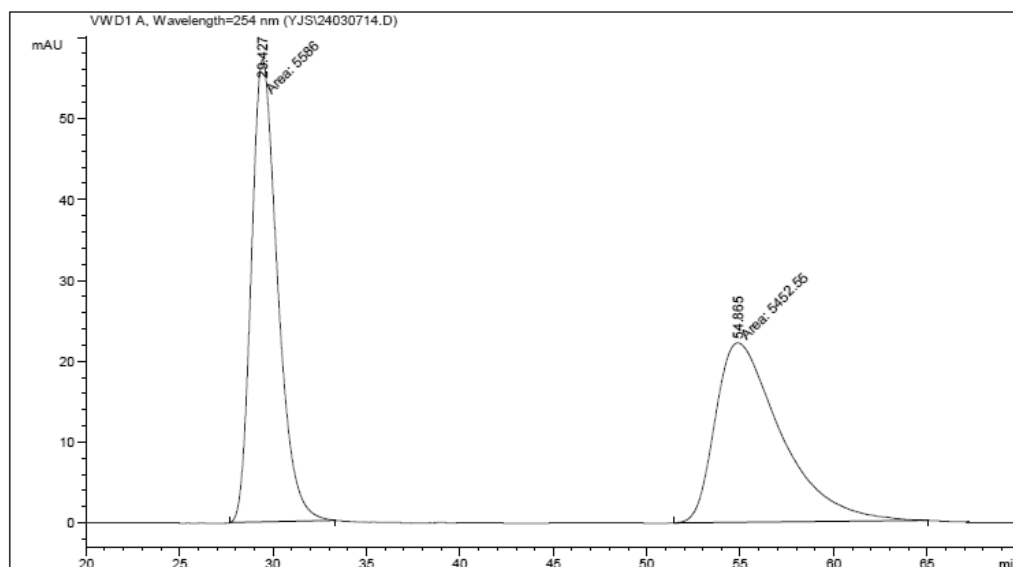
Totals : 1.11281e4 74.60777



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	28.697	MM	1.6574	7261.81104		73.02557	100.0000

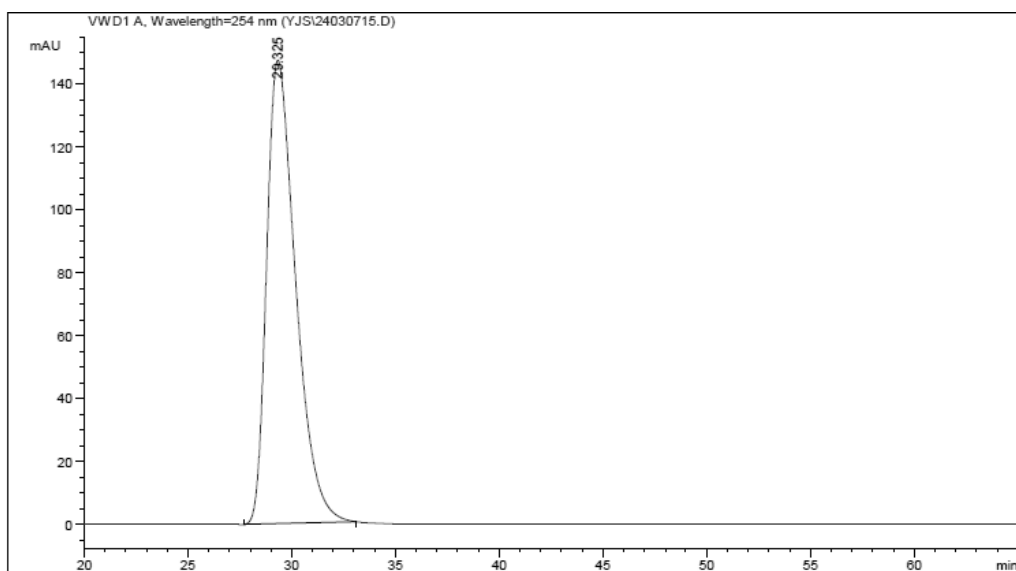
Totals : 7261.81104 73.02557

**5ia**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	29.427	MM	1.6278	5586.00098	57.19431	50.6045	
2	54.865	MM	4.0890	5452.55127	22.22460	49.3955	

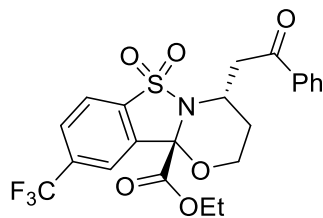
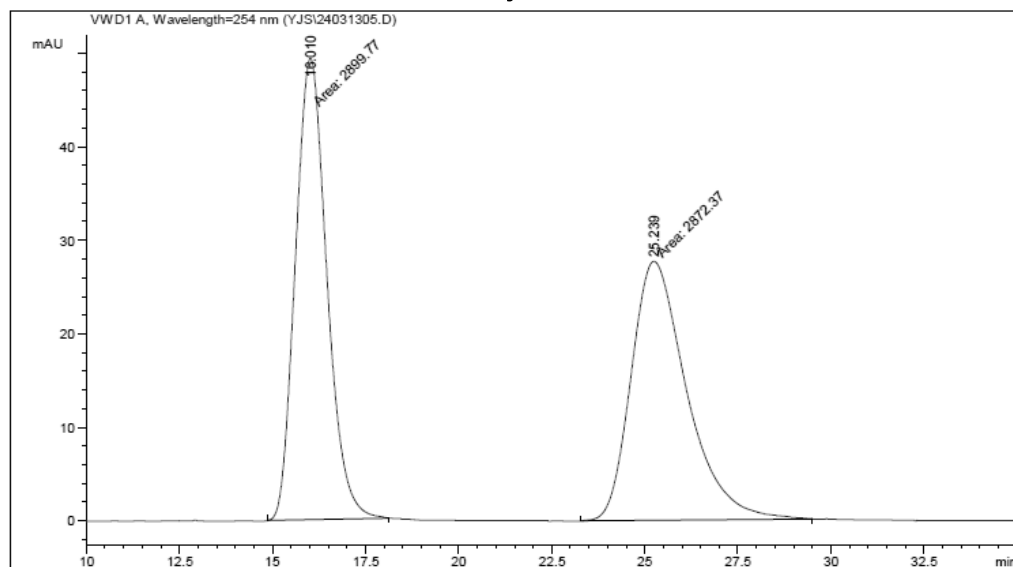
Totals : 1.10386e4 79.41891



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	29.325	BB	1.4698	1.43180e4	147.37784	100.0000	

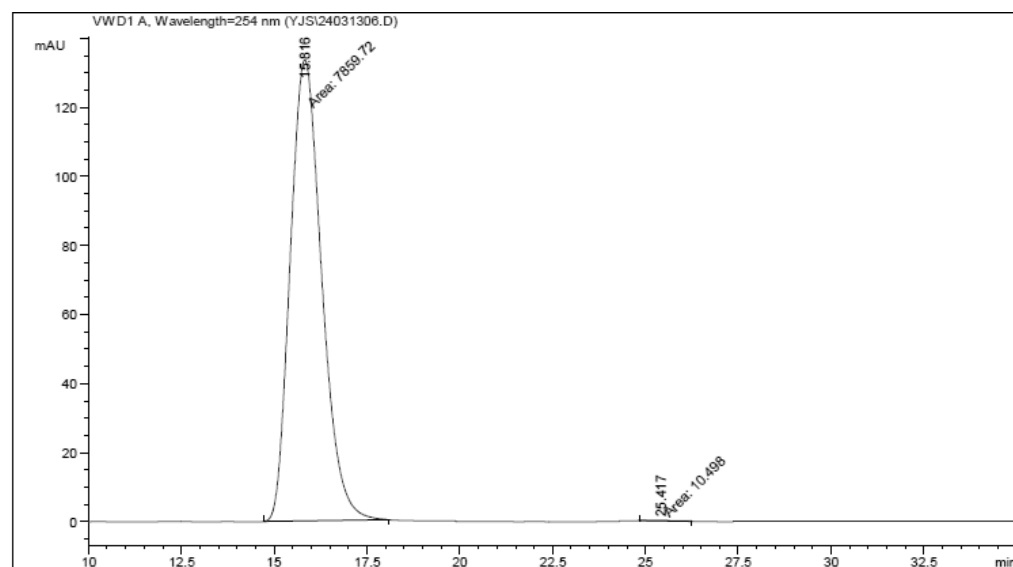
Totals : 1.43180e4 147.37784

**5ja**

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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	16.010	MM	0.9794	2899.77490	49.34570	50.2373	
2	25.239	MM	1.7289	2872.37451	27.68925	49.7627	

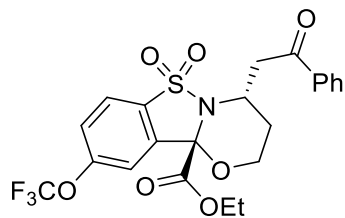
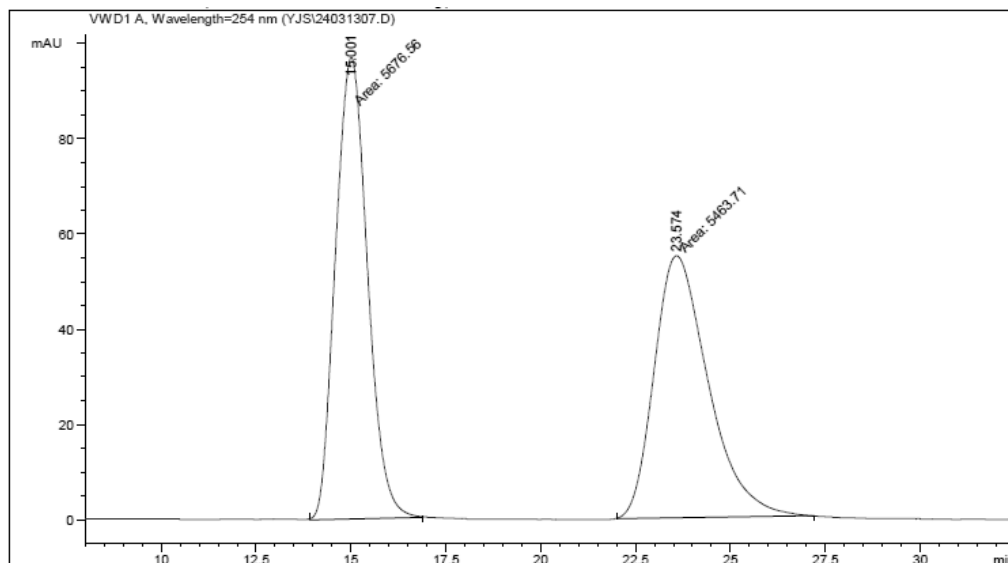
Totals : 5772.14941 77.03495



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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	15.816	MM	0.9810	7859.72168	133.53566	99.8666	
2	25.417	MM	1.0500	10.49804	1.66632e-1	0.1334	

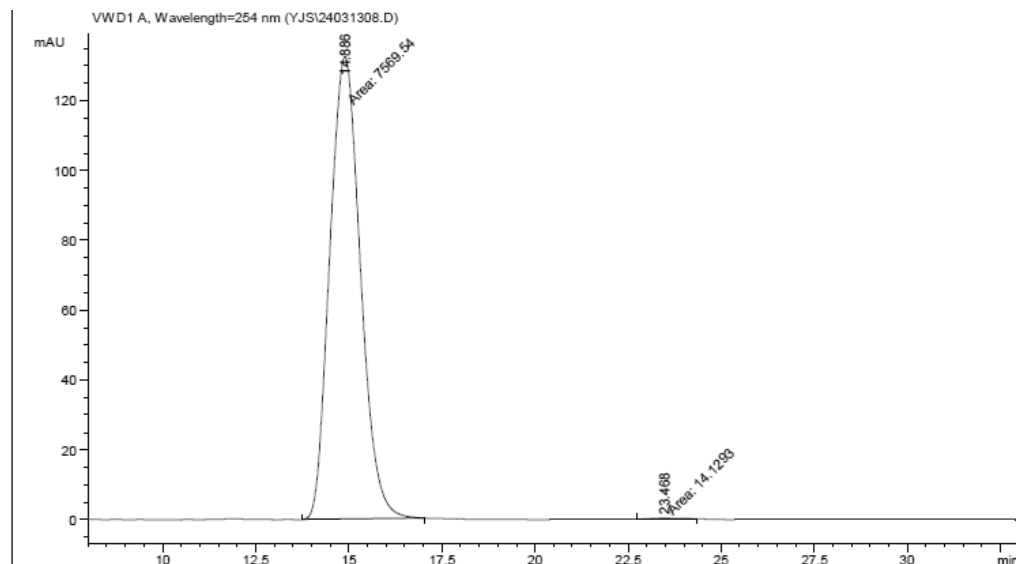
Totals : 7870.21972 133.70229

**5ka**

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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	15.001	MM	0.9758	5676.55811	96.95181	50.9553	
2	23.574	MM	1.6543	5463.70605	55.04451	49.0447	

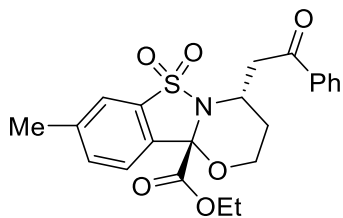
Totals : 1.11403e4 151.99633



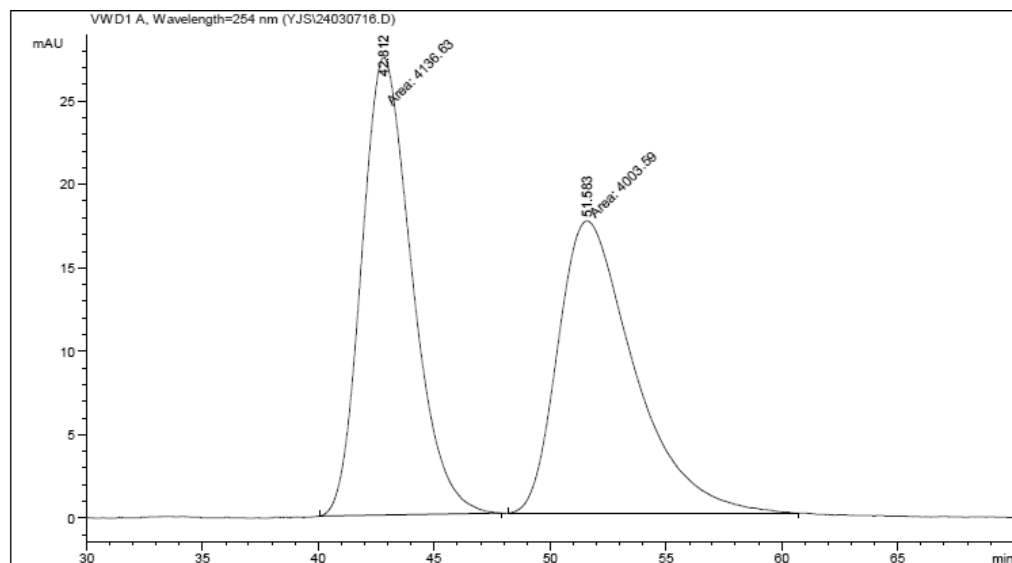
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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	14.886	MM	0.9521	7569.53516	132.50885	99.8137	
2	23.468	MM	0.9372	14.12932	2.51260e-1	0.1863	

Totals : 7583.66448 132.76011

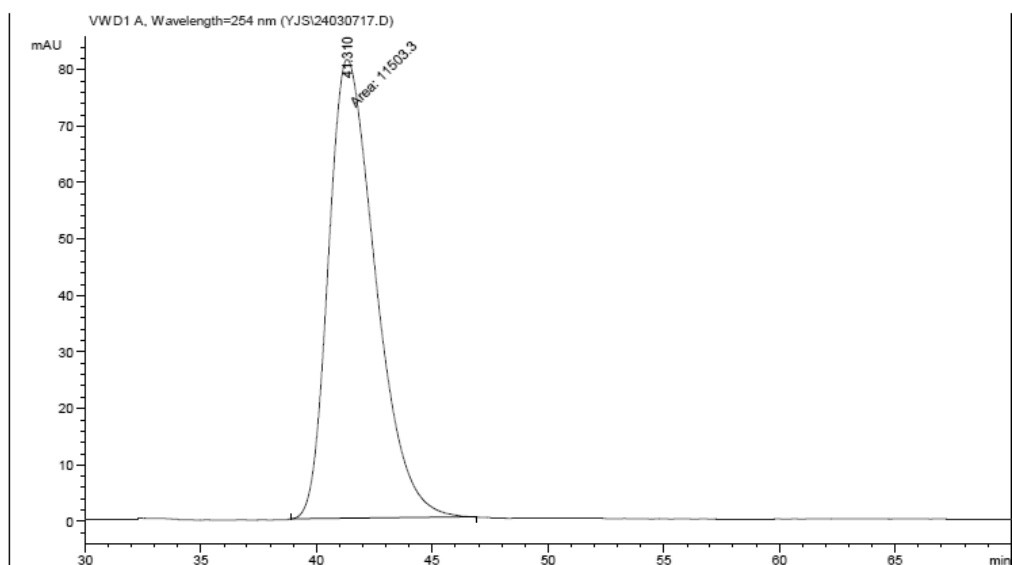


5la



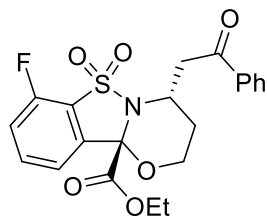
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	42.812	MM	2.5144	4136.62939	27.41990	50.8172	
2	51.583	MM	3.8117	4003.59155	17.50572	49.1828	
Totals :				8140.22095	44.92561		

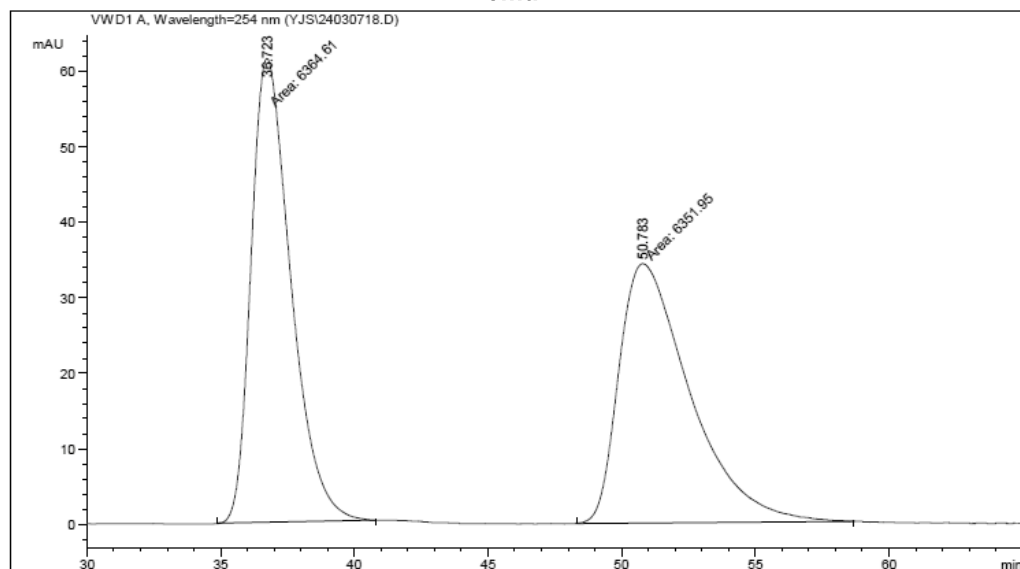


Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	41.310	MM	2.3578	1.15033e4	81.31471	100.0000	
Totals :				1.15033e4	81.31471		



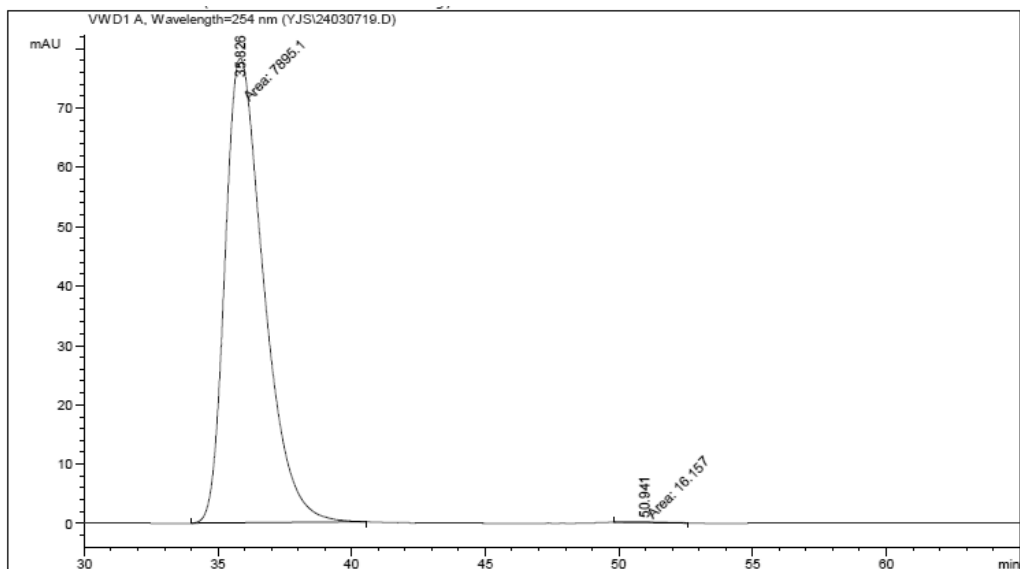
5ma



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	36.723	MM	1.7265	6364.60547	61.44190	50.0497
2	50.783	MM	3.0817	6351.95410	34.35361	49.9503

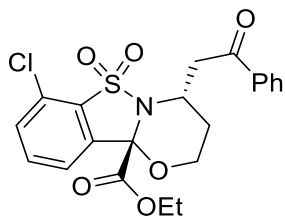
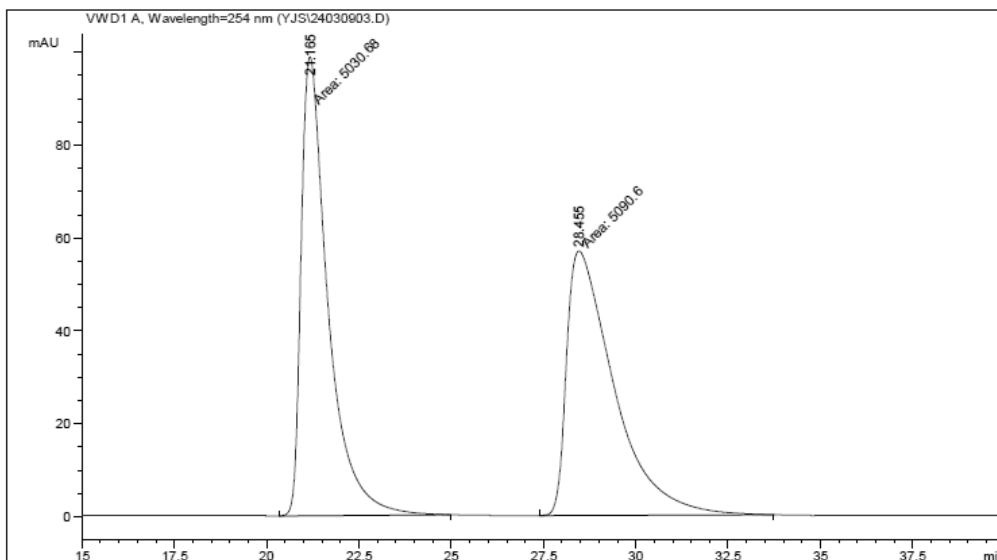
Totals : 1.27166e4 95.79551



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	35.826	MM	1.6805	7895.09766	78.30009	99.7958
2	50.941	MM	1.8129	16.15705	1.48539e-1	0.2042

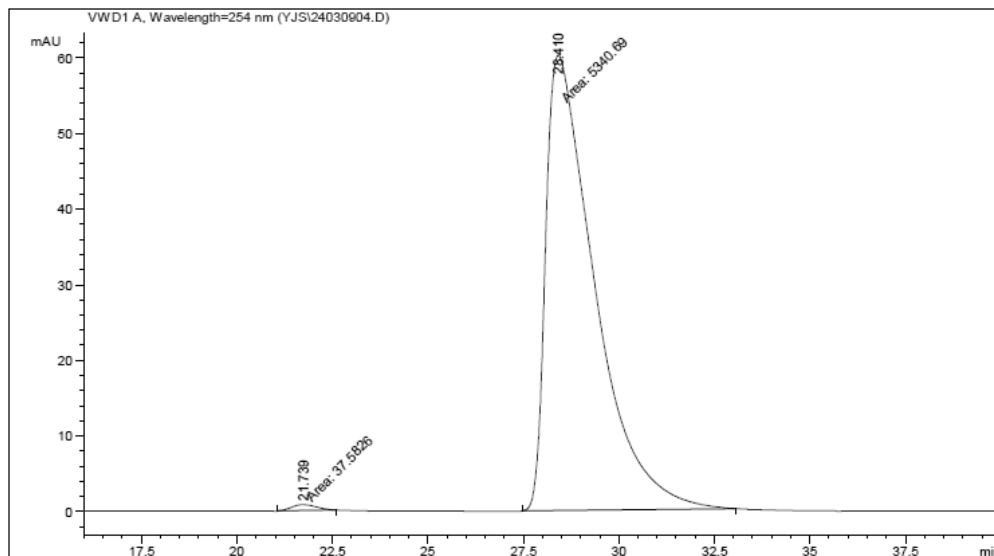
Totals : 7911.25470 78.44863

**5na**

Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	21.165	MM	0.8473	5030.68115		98.95753	49.7040
2	28.455	MM	1.4883	5090.60059		57.00760	50.2960

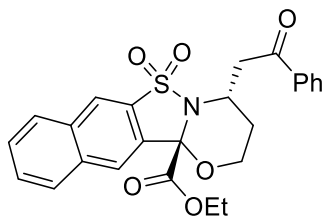
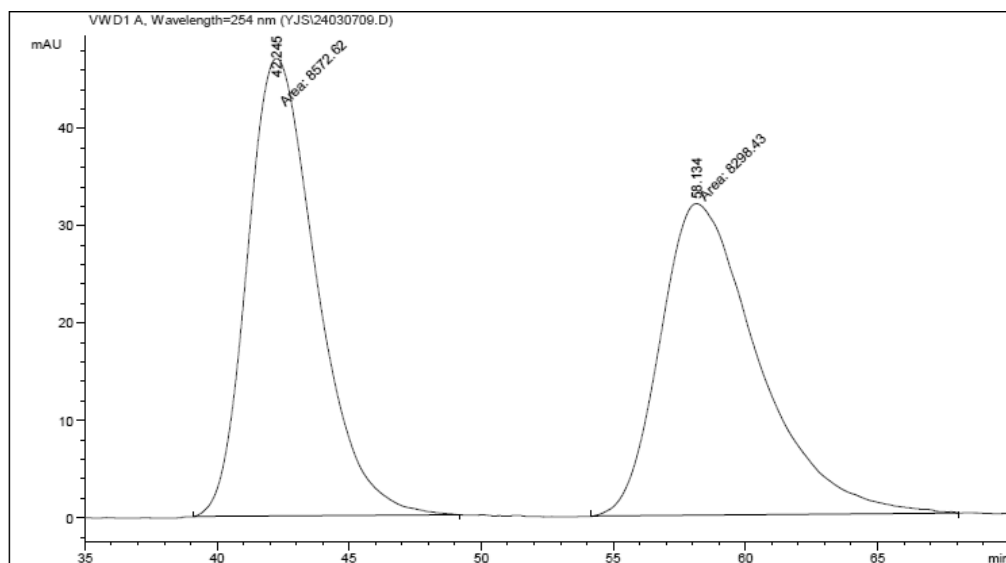
Totals : 1.01213e4 155.96512



Area Percent Report

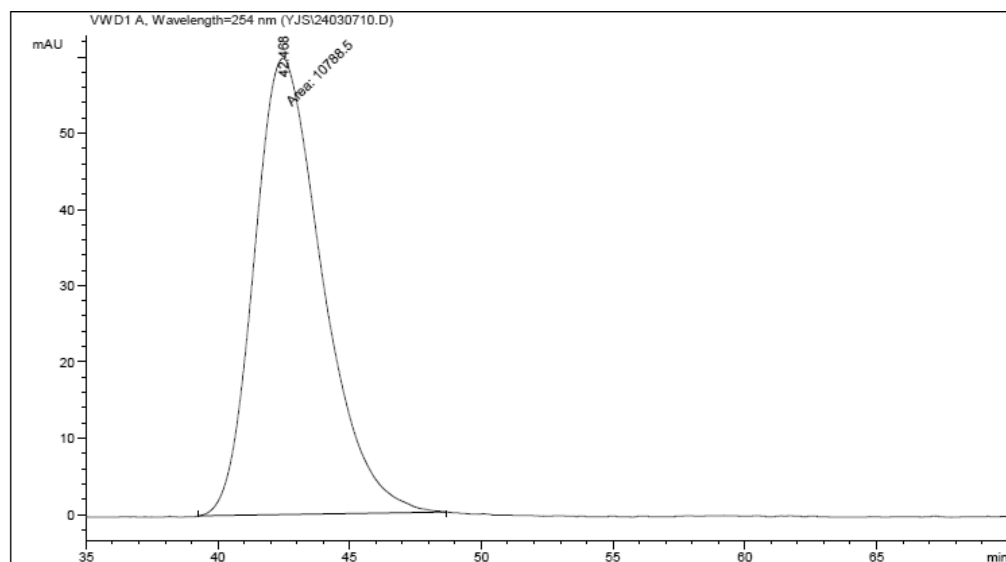
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	21.739	MM	0.7699	37.58263	8.13627e-1	0.6988	
2	28.410	MM	1.4799	5340.68896	60.14654	99.3012	

Totals : 5378.27159 60.96016

**50a**=====
Area Percent Report
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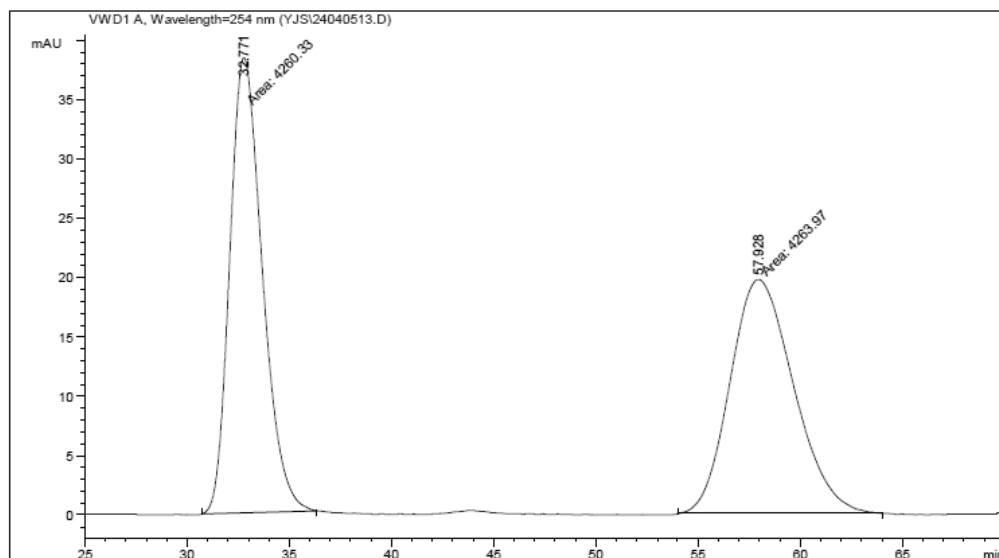
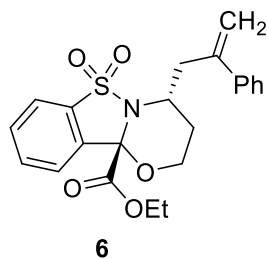
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	42.245	MM	3.0395	8572.62305		47.00602	50.8126
2	58.134	MM	4.3182	8298.43359		32.02880	49.1874

Totals : 1.68711e4 79.03482

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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	42.468	MM	3.0048	1.07885e4		59.83943	100.0000

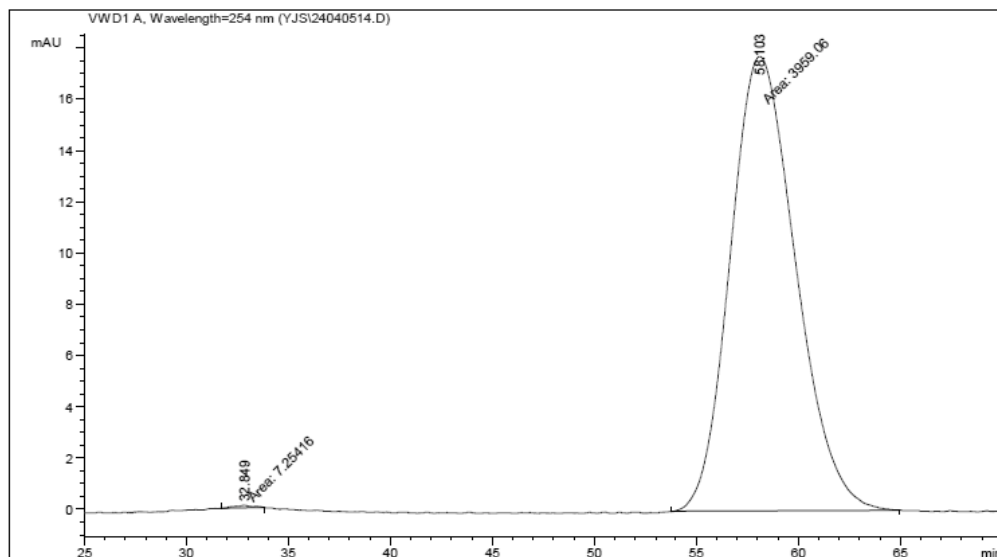
Totals : 1.07885e4 59.83943



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.771	MM	1.8495	4260.33252	38.39244	49.9787
2	57.928	MM	3.6019	4263.96582	19.73010	50.0213

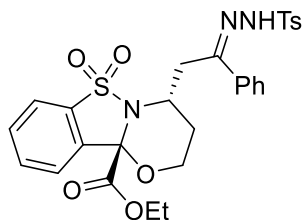
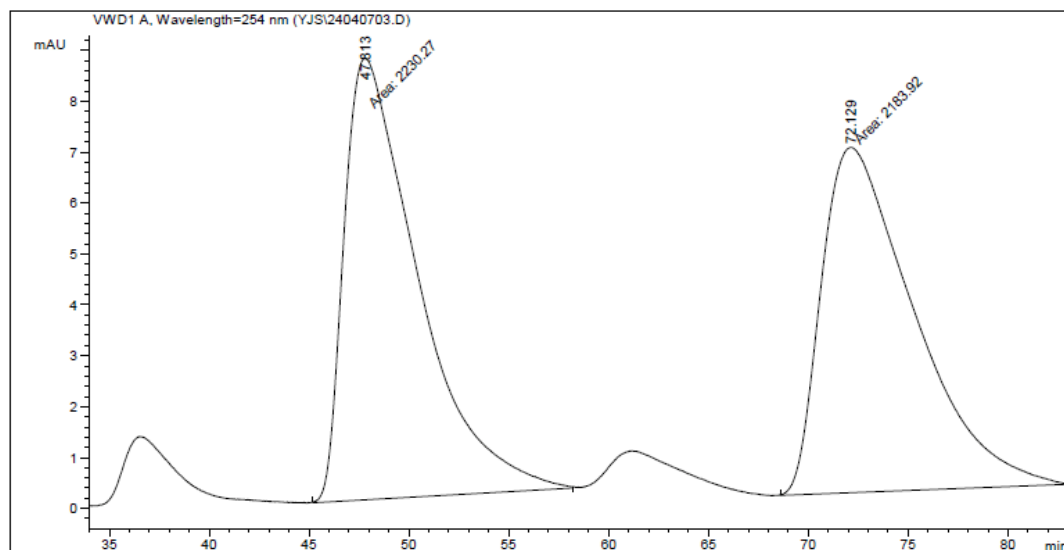
Totals : 8524.29834 58.12254



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Area Percent Report
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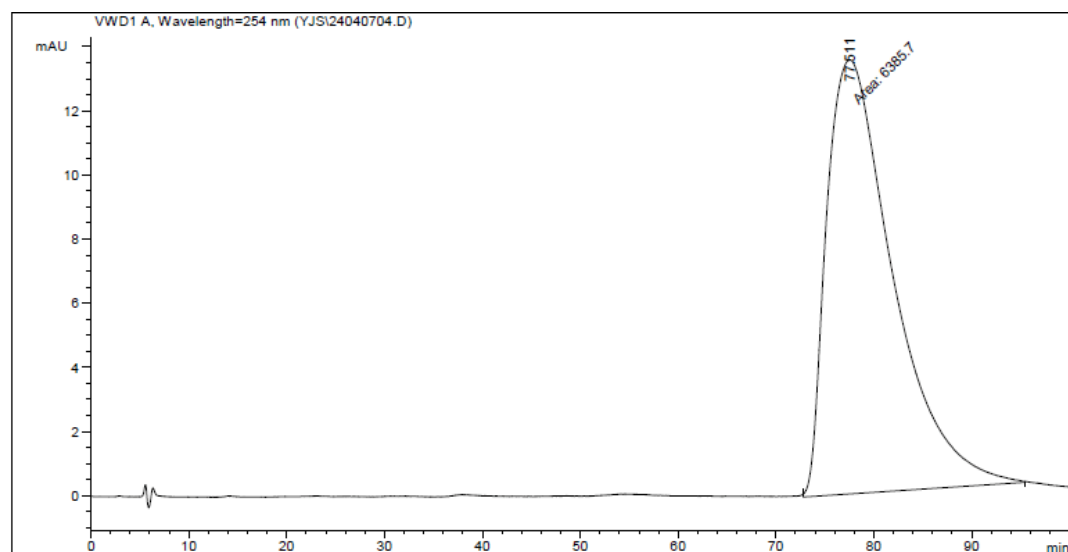
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.849	MM	1.1749	7.25416	1.02902e-1	0.1829
2	58.103	MM	3.7211	3959.05542	17.73268	99.8171

Totals : 3966.30958 17.83558

**7 (major)**

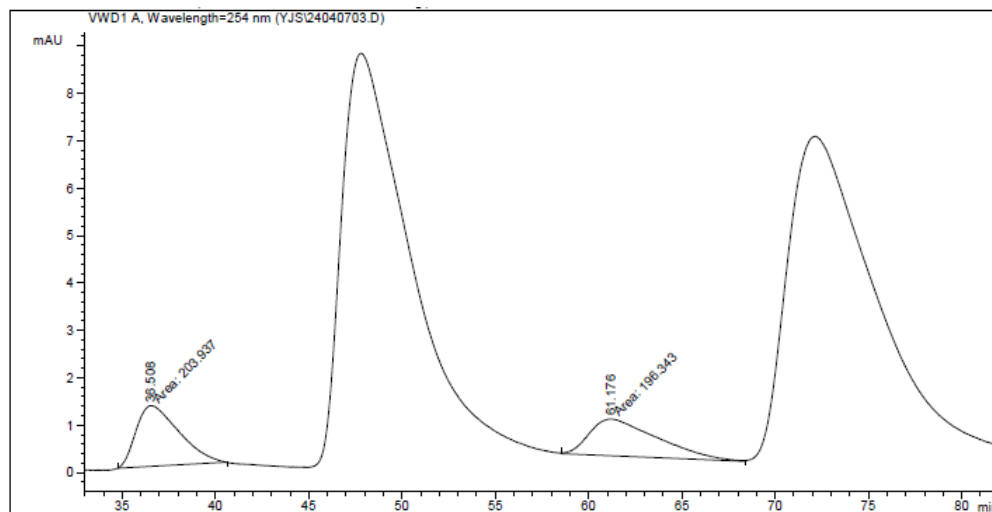
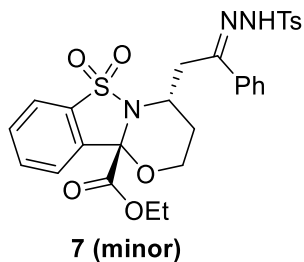
Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	47.813	MM	4.2833	2230.27100		8.67817	50.5250
2	72.129	MM	5.3655	2183.92065		6.78386	49.4750
Totals :				4414.19165		15.46203	



Area Percent Report

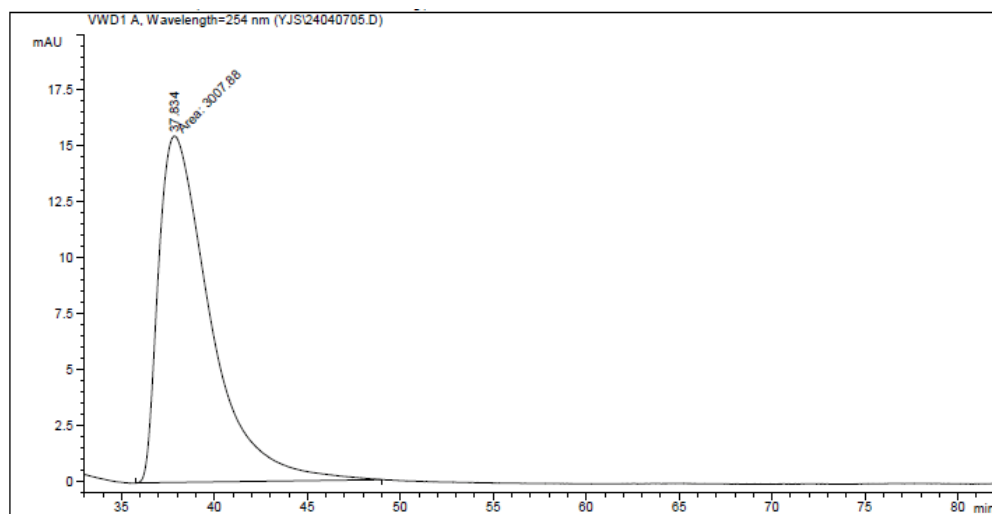
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	77.511	MM	7.8622	6385.70361		13.53672	100.0000
Totals :				6385.70361		13.53672	



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.508	MM	2.6549	203.93655	1.28025	50.9485
2	61.176	MM	4.2179	196.34338	7.75830e-1	49.0515

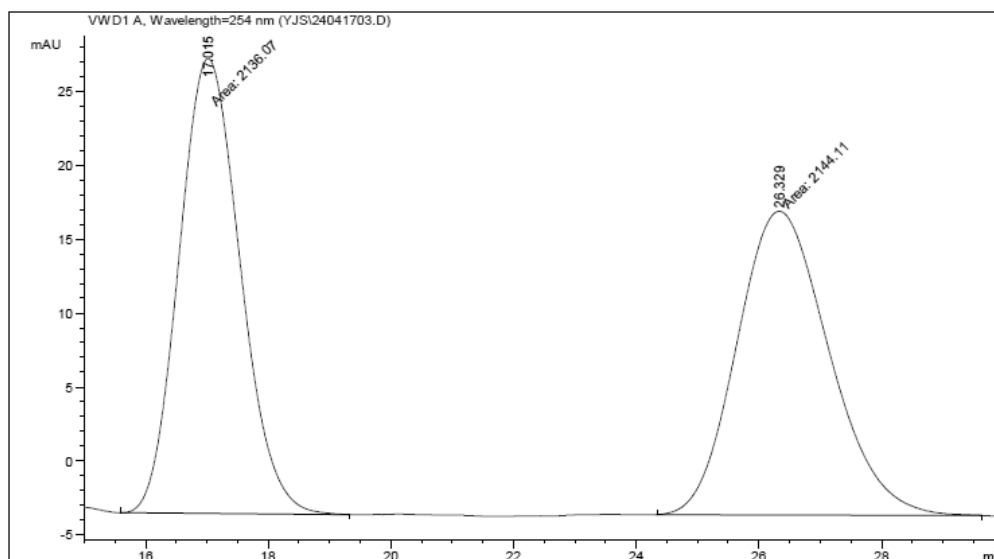
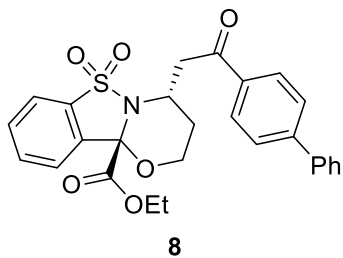
Totals : 400.27994 2.05608



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.834	MM	3.2347	3007.87720	15.49807	100.0000

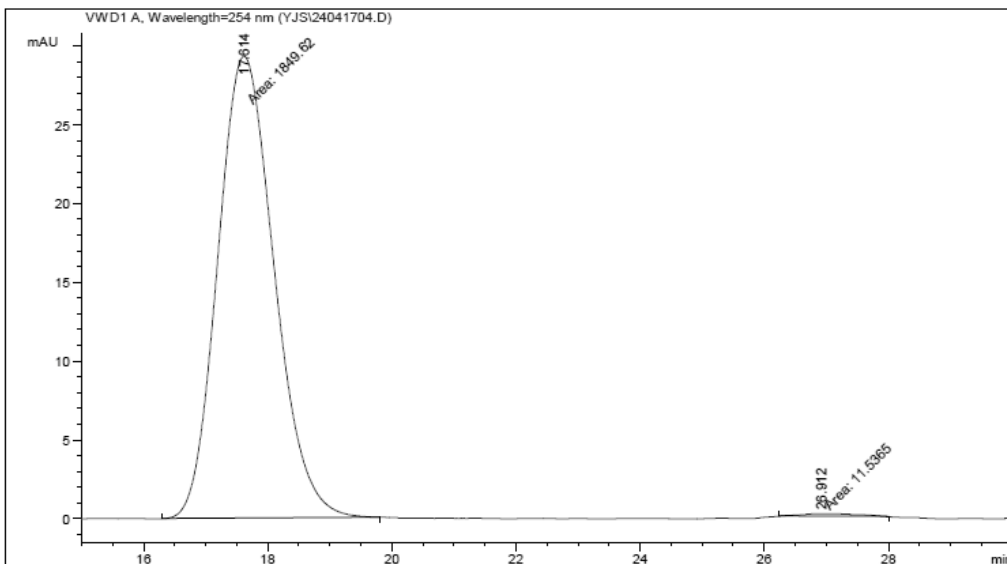
Totals : 3007.87720 15.49807



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	17.015	MM	1.1564	2136.07495	30.78555	49.9061
2	26.329	MM	1.7381	2144.11328	20.56036	50.0939

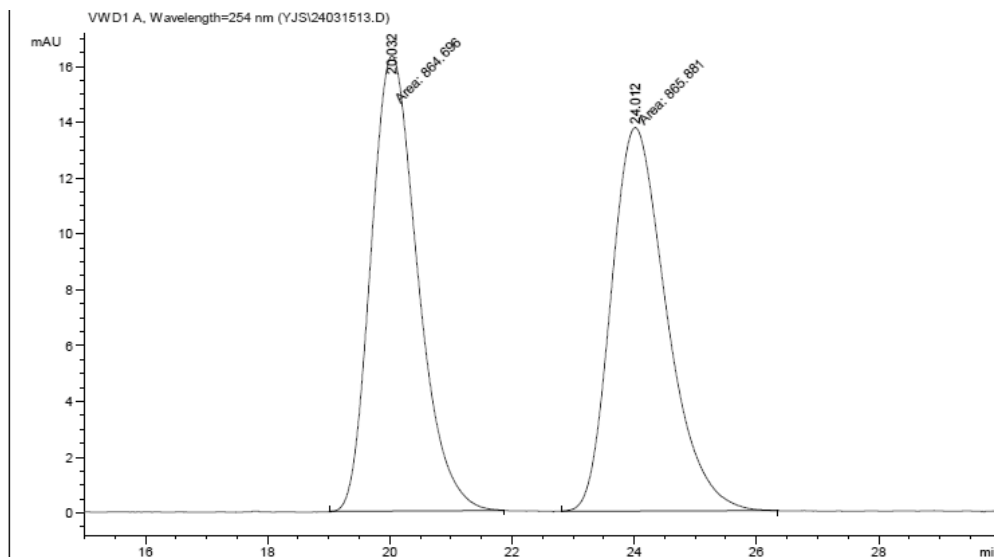
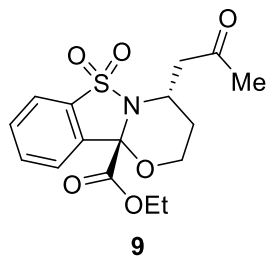
Totals : 4280.18823 51.34591



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	17.614	MM	1.0514	1849.61865	29.32053	99.3801
2	26.912	MM	1.0696	11.53654	1.79770e-1	0.6199

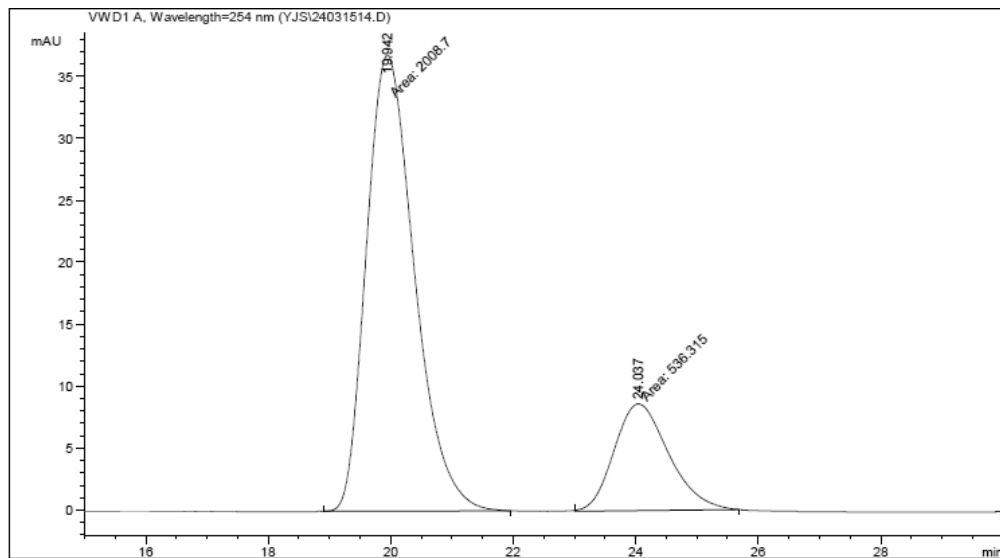
Totals : 1861.15519 29.50030



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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	20.032	MM	0.8833	864.69629	16.31497	49.9658	
2	24.012	MM	1.0501	865.88086	13.74317	50.0342	

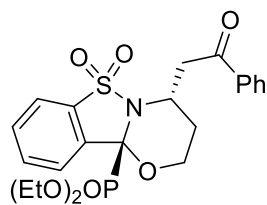
Totals : 1730.57715 30.05814



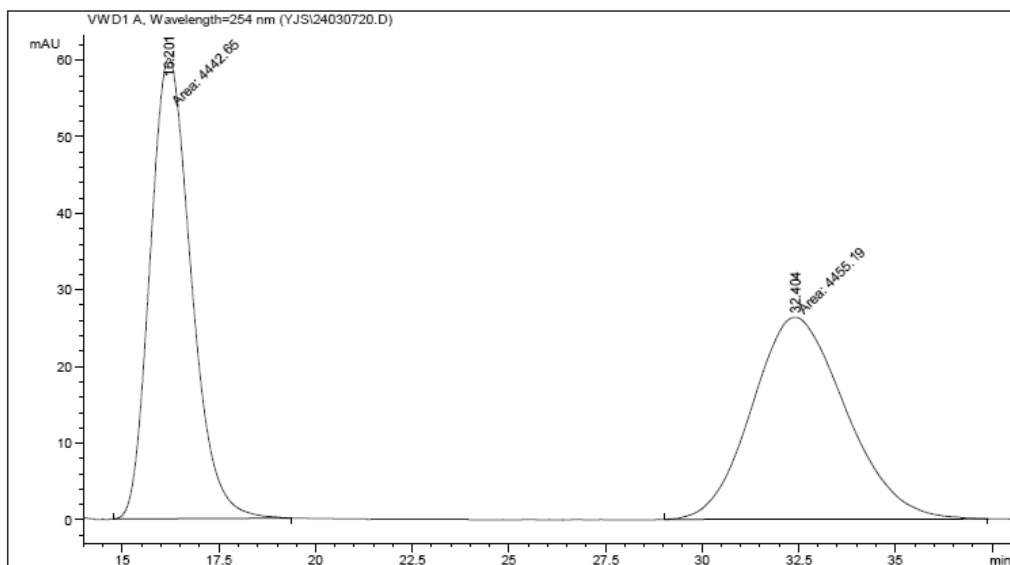
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Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	19.942	MM	0.9101	2008.69849		36.78579	78.9268
2	24.037	MM	1.0357	536.31464		8.63055	21.0732

Totals : 2545.01312 45.41634



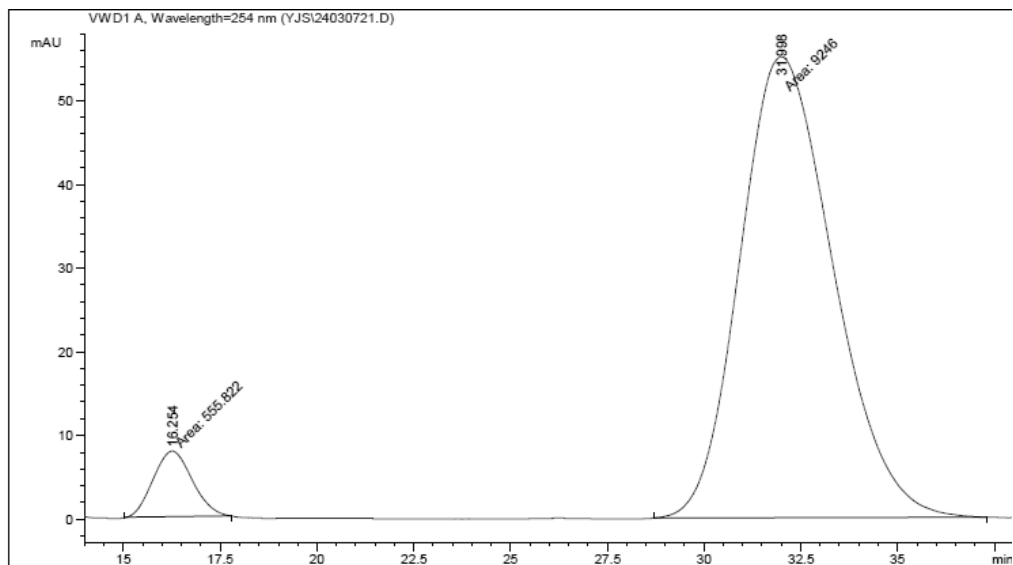
11



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	16.201	MM	1.2313	4442.64648	60.13655	49.9295
2	32.404	MM	2.8174	4455.19385	26.35565	50.0705

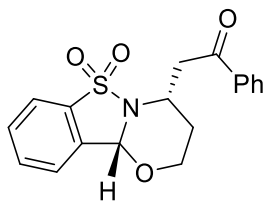
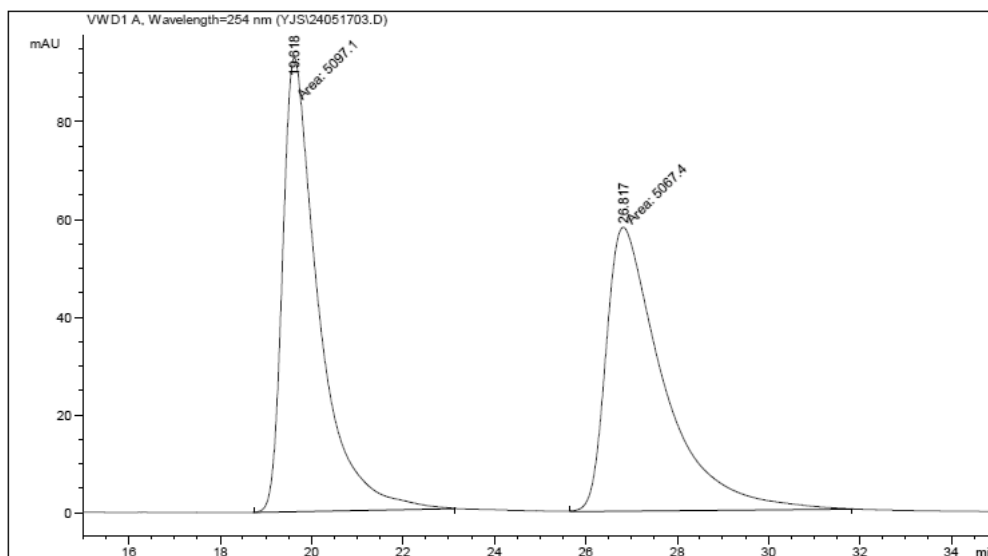
Totals : 8897.84033 86.49220



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	16.254	MM	1.1763	555.82202	7.87550	5.6706
2	31.998	MM	2.7966	9245.99512	55.10250	94.3294

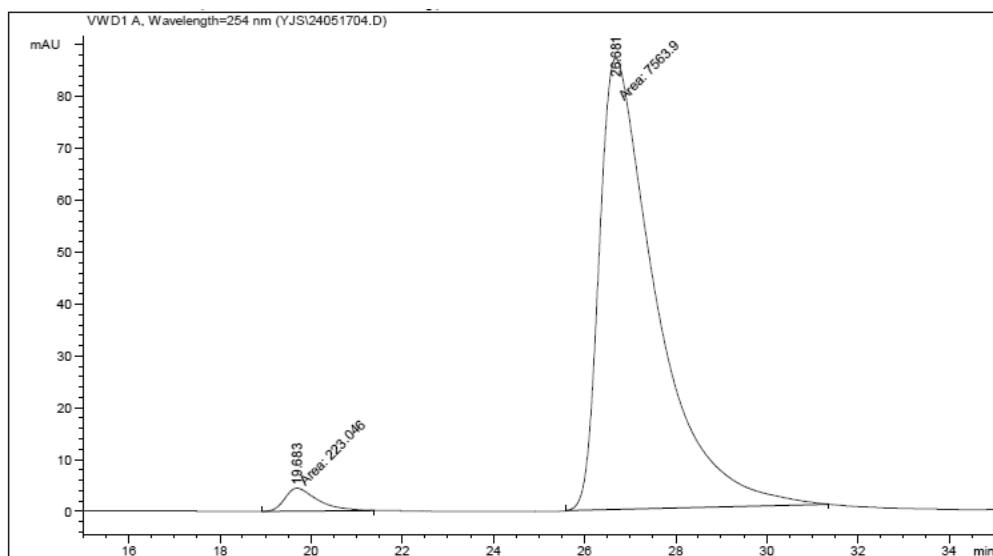
Totals : 9801.81714 62.97799

**13**

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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	19.618	MM	0.9138	5097.10010	92.96667	50.1461
2	26.817	MM	1.4532	5067.40039	58.11724	49.8539

Totals : 1.01645e4 151.08391



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 Area Percent Report
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Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	19.683	MM	0.8359	223.04604	4.44715	2.8644
2	26.681	MM	1.4488	7563.90381	87.01071	97.1356

Totals : 7786.94984 91.45786