Ni(II)-Catalyzed Enantioselective Mukaiyama-Mannich Reaction Between Silyl Enol Ethers and Cyclic *N*-Sulfonyl α-Ketiminoesters

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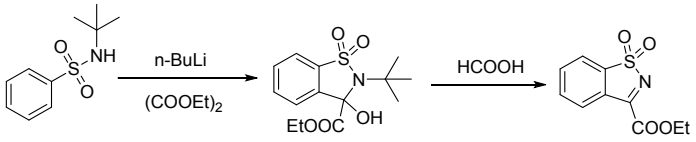
Contents

1. General Information:

All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (100–200 mesh). NMR spectra were recorded with a Bruker Avance DPX300 spectrometer with tetramethylsilane as the internal standard. Mass spectra were obtained on Bruker APEX II FT-ICRMS mass spectrometer. Optical rotations were measured on a Perkine-Elmer 341 LC polarimeter. The enantiomeric excesses were determined by HPLC analysis over a chiral column (Daicel Chiralcel OD-H or Chiralpak AD-H, eluted with hexane-isopropyl alcohol; monitored by UV detector).[1]

2. Preparation of N-sulfonyl cyclic ketimines *1*[2]



Under nitrogen atmosphere, a solution of aryl sulfonamide (10 mmol) in THF (40 mL) was cooled to –78 °C in an acetone-ice bath. The solution of *n*-Butyllithium in hexanes (25 mmol) was added dropwise over a 20 minute period. After stirred at -20 °C for 1 h, the yellow mixture was cooled further to -78 °C and diethyl oxalate (30 mmol) was added. The solution was allowed to stir for 1 h then warm slowly to room temperature, and stirred at ambient temperature for another 2 h. The reaction was quenched with 5% HCl (20 mL), water (100 mL) was added, and extracted with ethyl acetate (60 mL×3). The organic phase was washed with brine (100 ml), dried over sodium sulfate. The solvent was removed and the obtained crude product was further purified by flash chromatography (PE/EA = 10/1 – 5/1).

Under nitrogen atmosphere, the above product was dissolved in formic acid (10 mL), and subsequently stirred at room temperature. After 24 h the solution was concentrated and the residue was dissolved in CH_2Cl_2 (50 mL) and washed with $NaHCO_3$ saturated solution (50 mL×2) to remove traces of formic acid. Then the organic phase was washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. Purification by flash column chromatography (PE/EA = 5/1, v/v) gave the title products **1a-k** in high yield.

3. Preparation of enol silyl ethers

General procedure I [3a] (for **2a-2r, 2t, 2v, 2x**):

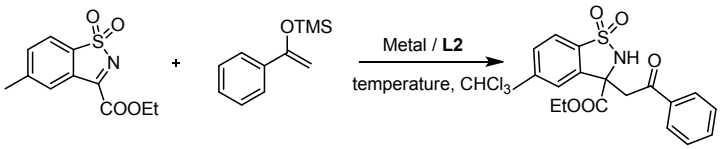
To a stirred solution of aromatic ketone (5 mmol) in THF (20 mL), LiHMDS (6 mmol, 1M in THF) was added dropwise over a period of 5 min at room temperature. After 20 min, the mixture was quenched with chlorotrimethylsilane (5.5 mmol). and was stirred for another 2h. The solvent was removed and the mixture was diluted with hexane. The resulting precipitate was filtered through the Celite (washing with pentane), and the filtrate was concentrated in vacuo to afford the crude enol silyl ether, which was stored at -20 °C, and the obtained product was distilled prior to use.

Other enol silyl ethers such as **2s, 2w, 2u, 2y** and **2z** were prepared according to the corresponding literatures[3b, 3c, 3d]

4. General procedure for the catalytic asymmetric Mukaiyama-Mannich reaction.

Under nitrogen atmosphere, ligand (**L2**) (0.0022mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.002mmol) were dissolved in $CHCl_3$ (1.0 mL), and stirred for 1 h at room temperature. Subsequently *N*-sulfonyl cyclic ketimines **1** (0.1 mmol) was added, and the resulting mixture was cooled to 0°C and stirred for 10 min before the silyl enol ether **2** (0.20 mmol) was added. The reaction mixture was stirred at 0 °C until the completion of the reaction (monitored by TLC). Then the mixture was directly subjected to flash column chromatography (Petroleum / Ethyl acetate, 10/1~3/1, V/V) to afford the corresponding product **3**.

Table ST1. Screening of Lewis acids[a]



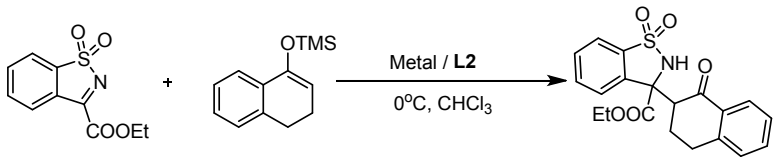
1b **2a** **3ba**

Entry	Metal	T (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	$Co(ClO_4)_2 \cdot 6H_2O$	0	12	96	97
2	$Zn(ClO_4)_2 \cdot 6H_2O$	0	12	89	94
3	$Cu(ClO_4)_2 \cdot 6H_2O$	0	48	54	57
4	$Mg(ClO_4)_2 \cdot 6H_2O$	0	36	90	93
5	$Mg(OTf)_2$	0	96	36	8
6	$Cu(OTf)_2$	0	48	40	20

7	$Ni(OTf)_2$	0	48	43	80
8	$Ni(acac)_2$	0	96	trace	-
9	$Ni(OAc)_2·4H_2O$	0	72	75	93
10	$Ni(ClO_4)_2·6H_2O$	25	12	98	86

[a] Reaction conditions: **1b** (0.1 mmol) and **2a** (0.2 mmol), 10 mol % metal salts and 11 mol % **L2** in 2.0 mL $CHCl_3$ at 0 °C [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] Not determined.

Table ST2 Optimization of reaction conditions for 1-tetralone derived enol silyl ether as the substrate[a]

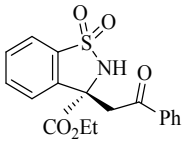


1a **2x** **3ax**

Entry	Metal	Time (h)	Yield (%)[b]	d.r.[c]	ee (%)[c]
1	$Ni(ClO_4)_2·6H_2O$	48	94	1.1:1	64, 66
2	$Cu(ClO_4)_2·6H_2O$	96	trace	-[d]	-
3	$Co(ClO_4)_2·6H_2O$	96	33	3.5:1	96, 98
4	$Mg(ClO_4)_2·6H_2O$	96	trace	-	-
5	$Zn(ClO_4)_2·6H_2O$	48	95	11.5:1	98
6	$Ni(OTf)_2$	96	trace	-	-
7	$Fe(OTf)_2$	96	trace	-	-
8	$Cu(OTf)_2$	96	35	-	-
9	$Zn(OTf)_2$	48	95	25:1	99

[a] Reaction conditions: **1a** (0.1 mmol) and **2x** (0.2 mmol), 10 mol % metal salts and 11 mol % **L2** in 2.0 mL $CHCl_3$ at 0 °C; [b] Isolated yields; [c] Determined by chiral HPLC analysis; [d] Not determined.

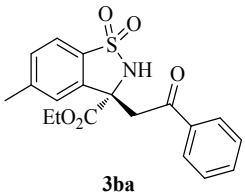
5. Characterization data for the Mukaiyama-Mannich products 3



3aa

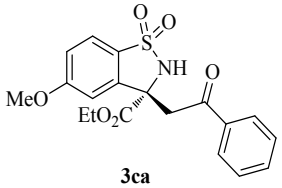
White solid, m.p. 59−60 °C, 99% yield. [α]20 D = –167.9 (c, 1.20, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 17.85 min, t (minor) = 24.75 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95–7.87 (m, 2H), 7.85–7.78 (m, 1H), 7.75 –7.53 (m, 4H), 7.50 –7.41 (m, 2H), 6.09 (s, 1H), 4.31 (qq, *J* = 10.8, 7.2 Hz, 2H), 4.08 (d, *J* = 17.8 Hz, 1H), 3.72 (d, *J* = 17.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.65, 169.27, 136.60, 135.28, 133.67, 133.33, 130.49, 128.47, 127.86, 123.92, 121.54, 65.16, 63.17, 48.81, 13.61. ESI-HRMS: Calcd for $C_{18}H_{17}NNaO_5S^+$ ([M+Na^+]): 382.0720; Found:

382.0723.



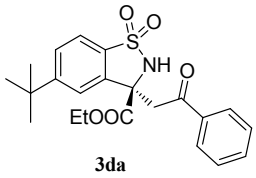
3ba

White solid, m.p. 60 – 62 °C, 99% yield; [α]20 D = –117.4 (c, 1.02, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 13.44 min, t (minor) = 21.91 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.73 – 7.67 (m, 1H), 7.65 – 7.56 (m, 1H), 7.52 – 7.40 (m, 4H), 6.04 (s, 1H), 4.42 – 4.22 (m, 2H), 4.09 (d, *J* = 17.8 Hz, 1H), 3.70 (d, *J* = 17.8 Hz, 1H), 2.50 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.73, 169.39, 144.51, 136.90, 135.34, 133.61, 132.57, 131.40, 128.44, 127.85, 124.05, 121.26, 76.28, 65.00, 63.07, 48.95, 21.53, 13.61. ESI-HRMS: Calcd for $C_{19}H_{20}NO_5S^+$ ([M+H$^+$]): 374.1057; Found: 374.1060.



3ca

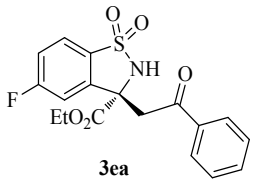
White solid, m.p. 152–153.5 °C, 99% yield; [α]20 D = –170.9 (c, 0.67, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 14.83 min, t (minor) = 22.17 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95–7.86 (m, 2H), 7.74 –7.66 (m, 1H), 7.63 –7.54 (m, 1H), 7.50–7.40 (m, 2H), 7.15 – 7.08 (m, 2H), 6.09 (s, 1H), 4.44–4.20 (m, 2H), 4.08 (d, *J* = 17.8 Hz, 1H), 3.91 (s, 3H), 3.72 (d, *J* = 17.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.65, 169.27, 163.62, 139.18, 135.29, 133.63, 128.44, 127.84, 127.19, 122.88, 116.94, 108.30, 64.85, 63.11, 55.73, 48.94, 13.65. ESI-HRMS: Calcd for $C_{19}H_{20}NO_6S^+$ ([M+H$^+$]): 390.1006; Found: 390.1007.



3da

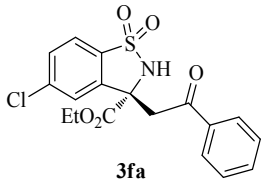
White solid, m.p. 150–151 °C, 98% yield. [α]20 D = –163.4 (c, 0.76, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 7.20 min, t (minor) = 12.30 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.77 – 7.71 (m, 1H), 7.70 – 7.63 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.41 (m, 2H), 6.08 (s, 1H), 4.47 – 4.18 (m, 2H), 4.08 (d, *J* = 17.8 Hz, 1H), 3.75 (d, *J* = 17.8 Hz, 1H), 1.38 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.72, 169.40, 157.82, 136.77, 135.35, 133.62, 132.52, 128.43, 128.14, 127.89, 121.04, 120.31, 65.19, 62.96, 48.89, 35.29, 30.86, 13.70. ESI-HRMS: Calcd for

$C_{22}H_{25}NNaO_5S^+$ ([M+Na^+]): 438.1346; Found: 438.1350.



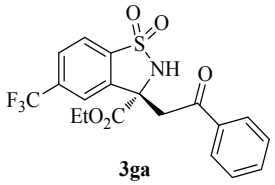
3ea

White solid, m.p. 63 –64 °C, 99% yield. [α]20 D = –124.1 (c, 0.80, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 10.85 min, t (minor) = 17.42 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.85 – 7.77 (m, 1H), 7.64 – 7.56 (m, 1H), 7.52 – 7.28 (m, 4H), 6.20 (s, 1H), 4.43 – 4.25 (m, 2H), 4.05 (d, *J* = 17.7 Hz, 1H), 3.75 (d, *J* = 17.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.30, 168.80, 165.28 (d, *J* = 256.0 Hz), 139.82 (d, *J* = 9.1 Hz), 135.15, 133.77, 131.40 (d, *J* = 2.7 Hz), 128.50, 127.87, 123.81 (d, *J* = 9.9 Hz), 118.48 (d, *J* = 24.0 Hz), 111.33 (d, *J* = 25.0 Hz), 64.74 (d, *J* = 2.1 Hz), 63.44, 48.69, 13.60. ESI-HRMS: Calcd for $C_{18}H_{16}FNNaO_5S^+$ ([M+Na^+]): 400.0625; Found: 400.0625.



3fa

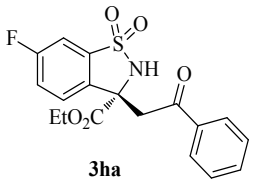
White solid, m.p. 65–66.5 °C,; [α]20 D = –161.4 (c, 0.66, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 10.82 min, t (minor) = 19.38 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H), 7.79 – 7.72 (m, 1H), 7.71 – 7.67 (m, 1H), 7.65 –7.55 (m, 2H), 7.51 – 7.42 (m, 2H), 6.19 (s, 1H), 4.34 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.07 (d, *J* = 17.7 Hz, 1H), 3.73 (d, *J* = 17.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.32, 168.77, 139.76, 138.66, 135.14, 133.87, 133.77, 130.98, 128.50, 127.88, 124.28, 122.74, 64.78, 63.46, 48.69, 13.61. ESI-HRMS: Calcd for $C_{18}H_{17}ClNO_5S^+$ ([M+H^+]): 394.0510; Found: 394.0514.



3ga

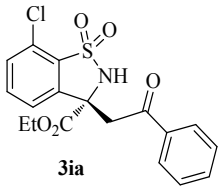
White solid, m.p. 58–59 °C, 97% yield. [α]20 D = –138.3 (c, 0.83, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 8.26 min, t (minor) = 18.11 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 5H), 7.65 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 6.29 (s, 1H), 4.48 – 4.24 (m, 2H), 4.13 (d, *J* = 17.7 Hz, 1H), 3.76 (d, *J* = 17.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.23, 168.63, 138.69, 137.73, 135.36 (q, *J* = 33.3 Hz), 135.07, 133.84, 128.51, 127.90,

127.79 (dd, *J* = 7.3, 3.8 Hz), 122.58 (d, *J* = 273.4 Hz), 122.48, 121.43 (q, *J* = 3.9 Hz), 65.07, 63.54, 48.59, 13.56. ESI- HRMS: Calcd for $C_{19}H_{16}F_3NNaO_5S^+$ ([M+Na$^+$]): 450.0593; Found: 450.0597.



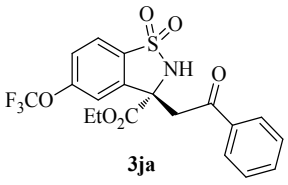
3ha

White solid, m.p. 92– 94 °C, 99% yield. [α]20 D = –161.1 (c, 1.24, CH_2Cl_2); 94% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 16.34 min, t (minor) = 21.53 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.89 (m, 2H), 7.73 – 7.57 (m, 3H), 7.54 – 7.34 (m, 3H), 6.33 (s, 1H), 4.50 (d, *J* = 17.8 Hz, 1H), 4.37 – 4.19 (m, 2H), 3.61 (d, *J* = 17.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.94, 168.32, 157.66 (d, *J* = 257.7 Hz), 137.79 (d, *J* = 2.6 Hz), 135.33, 133.73, 133.07 (d, *J* = 7.2 Hz), 128.49, 127.87, 122.68 (d, *J* = 16.8 Hz), 120.71 (d, *J* = 21.3 Hz), 117.72 (d, *J* = 4.3 Hz), 64.30, 64.25, 63.19, 45.36, 45.33, 13.43. ESI-HRMS: Calcd for $C_{18}H_{16}FNNaO_5S^+$ ([M+H$^+$]): 400.0625; Found: 400.0629.



3ia

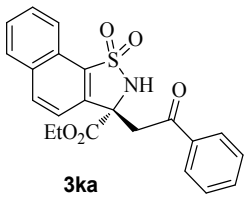
White solid, m.p. 66–68 °C, 97% yield. [α]20 D = –128 (c, 1.23, CH_2Cl_2); 97% ee, determined by HPLC analysis [Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (minor) = 22.10 min, t (major) = 26.94 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.68 – 7.52 (m, 4H), 7.49 – 7.42 (m, 2H), 6.20 (s, 1H), 4.33 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.05 (d, *J* = 17.7 Hz, 1H), 3.73 (d, *J* = 17.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.28, 168.83, 139.36, 135.17, 134.48, 133.75, 133.36, 131.25, 129.19, 128.50, 127.85, 122.25, 64.20, 63.43, 48.61, 13.61. ESI-HRMS: Calcd for $C_{18}H_{16}ClNNaO_5S^+$ ([M+H$^+$]): 416.0330; Found: 416.0334.



3ja

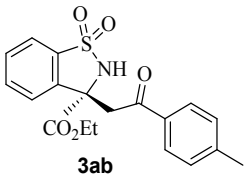
White solid, m.p. 50–52 °C, 98% yield. [α]20 D = –133.6 (c, 1.33, CH_2Cl_2); 96% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 8.04 min, t (minor) = 18.02 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.82 (m, 3H), 7.65 – 7.41 (m, 5H), 6.25 (s, 1H), 4.47 – 4.22 (m, 2H), 4.05 (d, *J* = 17.7 Hz, 1H), 3.78 (d, *J* = 17.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ

195.19, 168.64, 152.47 (q, J = 1.7 Hz), 139.42, 135.12, 133.79, 133.70, 128.50, 127.89, 123.47, 122.98, 119.83 (q, J = 260.2 Hz), 116.15, 64.81, 63.49, 48.56, 13.52. ESI-HRMS: Calcd for $C_{19}H_{17}F_3NO_6S^+$ ([M+H$^+$]): 444.0723; Found: 444.0725.



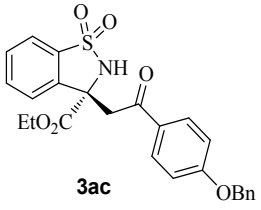
3ka

White solid, m.p. 92–95 ^{o}C, 99% yield. [α]20 D = –163.3 (c, 0.73, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 15.86 min, t (minor) = 24.68 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 – 8.38 (m, 1H), 8.17 – 8.10 (m, 1H), 8.02 – 7.95 (m, 1H), 7.94 – 7,86 (m, 2H), 7.77 – 7.62 (m, 3H), 7.61 – 7.53 (m, 1H), 7.48 – 7.39 (m, 2H), 6.28 (s, 1H), 4.43 – 4.25 (m, 2H), 4.21 (d, J = 17.7 Hz, 1H), 3.75 (d, J = 17.8 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.58, 169.26, 135.43, 135.29, 134.60, 133.67, 130.76, 129.12, 128.46, 128.36, 128.12, 127.85, 125.14, 122.86, 119.42, 65.21, 63.24, 48.57, 13.66. ESI-HRMS: Calcd for $C_{22}H_{19}NNaO_5S^+$ ([M+H$^+$]): 432.0876; Found: 432.0879.



3ab

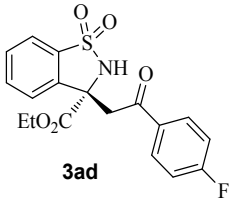
White solid, m.p. 58–61 ^{o}C, 99% yield. [α]20 D = (c, 1.26, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 16.90 min, t (minor) = 19.91 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 3H), 7.73 – 7.59 (m, 3H), 7.29 – 7.23 (m, 2H), 6.09 (s, 1H), 4.39 – 4.22 (m, 2H), 4.07 (d, J = 17.7 Hz, 1H), 3.70 (d, J = 17.7 Hz, 1H), 2.41 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.22, 169.33, 144.67, 136.65, 135.26, 133.29, 132.86, 130.43, 129.13, 127.98, 123.95, 121.50, 65.21, 63.10, 48.70, 21.37, 13.60. ESI-HRMS: Calcd for $C_{19}H_{19}NNaO_5S^+$ ([M+Na$^+$]): 396.0876; Found: 396.0874.



3ac

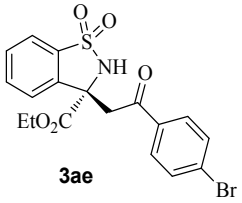
White solid, m.p. 68–70 ^{o}C, 98% yield. [α]20 D = –142.8 (c, 0.86, CH_2Cl_2); 95% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (minor) = 28.09 min, t (major) = 86.78 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.83 – 7.78 (m, 1H), 7.73 – 7.58 (m, 3H), 7.47 – 7.29 (m, 5H), 7.03 – 6.96 (m, 2H),

6.10 (s, 1H), 5.12 (s, 2H), 4.30 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.04 (d, *J* = 17.6 Hz, 1H), 3.66 (d, *J* = 17.6 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.02, 169.39, 162.99, 136.68, 135.65, 135.26, 133.27, 130.42, 130.24, 128.58, 128.38, 127.96, 127.13, 123.95, 121.50, 114.50, 69.89, 65.27, 63.08, 48.50, 29.35, 13.62. ESI-HRMS: Calcd for $C_{25}H_{23}NNaO_6S^+$ ([M+Na$^+$]): 488.1138; Found: 488.1144.



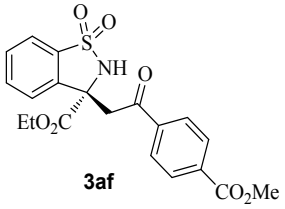
3ad

White solid, m.p. 62–64 °C, 96% yield. [α]20 D = –153.1 (c, 0.70, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 19.04 min, t (major) = 25.08 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.85 – 7.79 (m, 1H), 7.74 – 7.60 (m, 3H), 7.18 – 7.07 (m, 2H), 6.12 (s, 1H), 4.32 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.07 (d, *J* = 17.7 Hz, 1H), 3.69 (d, *J* = 17.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.09, 169.19, 165.87 (d, *J* = 256.4 Hz), 136.52, 135.23, 133.39, 131.79 (d, *J* = 3.1 Hz), 130.61 (d, *J* = 11.0 Hz), 130.55, 123.96, 121.48, 115.63 (d, *J* = 22.1 Hz), 65.13, 63.20, 48.61, 13.59. ESI-HRMS: Calcd for $C_{18}H_{17}FNO_5S^+$ ([M+H$^+$]): 378.0806; Found: 378.0809.



3ae

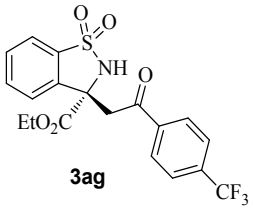
White solid, m.p. 65–68 °C, 94% yield. [α]20 D= –135.2 (c, 1.0, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 21.77 min, t (major) = 31.21 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.54 (m, 8H), 6.12 (s, 1H), 4.32 (qq, *J* = 10.8, 7.1 Hz, 2H), 4.06 (d, *J* = 17.8 Hz, 1H), 3.68 (d, *J* = 17.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.74, 169.15, 136.44, 135.18, 133.98, 133.44, 131.80, 130.58, 129.36, 128.99, 123.95, 121.51, 65.06, 63.27, 48.64, 13.63. ESI-HRMS: Calcd for $C_{18}H_{16}BrNNaO_5S^+$ ([M+Na$^+$]): 459.9825; Found: 459.9830.



3af

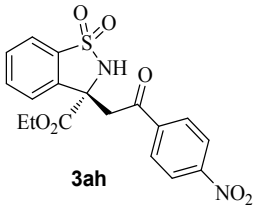
White solid, m.p. 66–68 °C, 95% yield. [α]20 D = –133.7 (c, 1.10, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (minor) = 16.73 min, t (major) = 38.84 min]; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 8.20 – 8.05 (m, 2H), 8.03 – 7.92 (m, 2H), 7.86 – 7.81 (m, 1H), 7.77 – 7.59 (m, 3H), 6.10 (s, 1H), 4.33 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.10 (d, *J* = 17.8 Hz, 1H), 3.95 (s, 3H), 3.75 (d, *J* = 17.9 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.22, 169.08, 165.62, 138.38, 136.47, 135.31, 134.33, 133.38, 130.57, 129.63, 127.79, 123.88, 121.57, 65.03, 63.28, 52.19, 49.02, 13.61. ESI-HRMS: Calcd for $C_{20}H_{19}NNaO_7S^+$ ([M+Na$^+$]): 440.0774; Found: 440.0779.



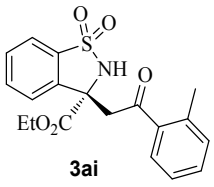
3ag

White solid, m.p. 60 –62 °C, 97% yield. [α]20 D = –126.7 (c, 1.34, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 17.22 min, t (major) = 26.03 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.86 – 7.81 (m, 1H), 7.78 – 7.60 (m, 5H), 6.10 (s, 1H), 4.34 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.09 (d, *J* = 17.8 Hz, 1H), 3.75 (d, *J* = 17.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.81, 169.00, 137.93, 136.46, 135.34, 134.84 (q, *J* = 32.7 Hz), 133.42, 130.61, 128.25, 125.54 (q, *J* = 3.6 Hz), 123.88, 123.07 (q, *J* = 272.9 Hz), 121.57, 65.01, 63.34, 48.86, 13.60. ESI-HRMS: Calcd for $C_{19}H_{16}F_3NNaO_5S^+$ ([M+Na$^+$]): 450.0593; Found: 450.0588.



3ah

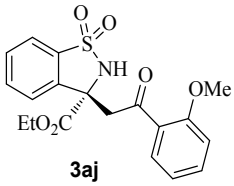
White solid, m.p. 73 –74 °C, 96% yield. [α]20 D = –133.2 (c, 0.88, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (minor) = 30.95 min, t (major) = 60.06 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 2H), 8.13 – 8.05 (m, 2H), 7.87 – 7.81 (m, 1H), 7.77 – 7.62 (m, 3H), 6.09 (s, 1H), 4.35 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.10 (d, *J* = 17.8 Hz, 1H), 3.78 (d, *J* = 17.8 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.33, 168.85, 150.45, 139.65, 136.37, 135.36, 133.48, 130.70, 128.99, 123.84, 123.67, 121.61, 64.95, 63.45, 48.98, 13.62. ESI-HRMS: Calcd for $C_{18}H_{16}N_2NaO_7S^+$ ([M+Na$^+$]): 427.0570; Found: 427.0572.



3ai

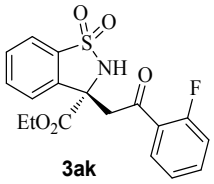
White solid, m.p. 50 – 52 °C, 98% yield. [α]20 D = –140.8 (c, 1.18 CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 13.98 min, t (minor) = 26.64 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.72 – 7.59

(m, 4H), 7.45 – 7.36 (m, 1H), 7.29 – 7.21 (m, 2H), 6.11 (s, 1H), 4.42 – 4.25 (m, 2H), 4.05 (d, *J* = 17.7 Hz, 1H), 3.65 (d, *J* = 17.7 Hz, 1H), 2.53 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.88, 169.36, 138.78, 136.68, 135.45, 135.32, 133.28, 131.97, 131.94, 130.42, 128.68, 125.52, 123.89, 121.52, 65.36, 63.13, 51.07, 21.18, 13.64. ESI-HRMS: Calcd for $C_{19}H_{19}NNaO_5S^+$ ([M+Na$^+$]): 396.0876; Found: 396.0879.



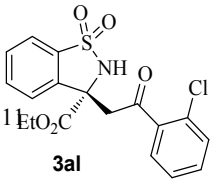
3aj

White solid, m.p. 132–133 °C, 96% yield. [α]20 D = –147.7 (c, 0.97, CH_2Cl_2); 96% ee, determined by HPLC analysis [Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (major) = 31.50 min, t (minor) = 40.03 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.76 (m, 2H), 7.74 – 7.58 (m, 3H), 7.55 – 7.47 (m, 1H), 7.05 – 6.93 (m, 2H), 6.09 (s, 1H), 4.29 (qt, *J* = 14.2, 5.3 Hz, 2H), 4.12 (t, *J* = 11.4 Hz, 1H), 3.86 (d, *J* = 6.6 Hz, 3H), 3.74 (d, *J* = 18.6 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.50, 169.63, 159.15, 136.86, 135.16, 134.69, 133.30, 130.50, 130.30, 125.42, 124.09, 121.38, 120.48, 111.42, 65.60, 62.91, 55.25, 54.12, 13.63. ESI-HRMS: Calcd for $C_{19}H_{19}NNaO_6S^+$ ([M+Na$^+$]): 412.0825; Found: 412.0830.



3ak

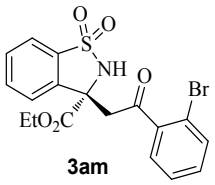
White solid, m.p. 92–93 °C, 97% yield. [α]20 D = –147.5 (c, 1.11, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 12.69 min, t (minor) = 15.30 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 1H), 7.86 – 7.80 (m, 1H), 7.76 – 7.50 (m, 4H), 7.31 – 7.23 (m, 1H), 7.19 – 7.09 (m, 1H), 6.06 (s, 1H), 4.32 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.14 (dd, *J* = 18.6, 3.7 Hz, 1H), 3.67 (dd, *J* = 18.6, 3.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.54 (d, *J* = 3.9 Hz), 169.29, 162.06 (d, *J* = 255.7 Hz), 136.41, 135.45 (d, *J* = 9.3 Hz), 135.18, 133.34, 130.46, 130.37 (d, *J* = 2.1 Hz), 124.41 (d, *J* = 3.3 Hz), 123.97, 123.64 (d, *J* = 12.4 Hz), 121.52, 116.46 (d, *J* = 23.6 Hz), 65.16 (d, *J* = 3.2 Hz), 63.14, 53.41 (d, *J* = 9.0 Hz), 13.60. ESI-HRMS: Calcd for $C_{18}H_{16}FNNaO_5S^+$ ([M+Na$^+$]): 400.0625; Found: 400.0629.



3al

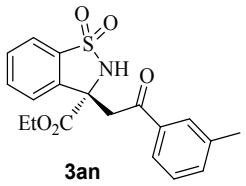
White solid, m.p. 50 – 53 °C,, 96% yield. [α]20 D = –125.1 (c, 1.09, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-

hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 15.80 min, t (minor) = 24.28 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.72 – 7.58 (m, 4H), 7.47 – 7.29 (m, 3H), 6.09 (s, 1H), 4.44 – 4.28 (m, 2H), 4.14 (d, *J* = 18.0 Hz, 1H), 3.69 (d, *J* = 18.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.80, 169.03, 136.68, 136.50, 135.29, 133.36, 132.51, 131.28, 130.56, 130.51, 129.51, 126.81, 123.91, 121.51, 65.29, 63.33, 52.44, 13.65. ESI-HRMS: Calcd for $C_{18}H_{16}ClNNaO_5S^+$ ([M+Na$^+$]): 416.0330; Found: 416.0334.



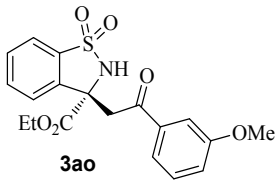
3am

White solid, m.p. 45−46 °C, 96% yield. [α]20 D = –71.2 (c, 0.83, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 12.91 min, t (minor) = 20.69 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.70 – 7.57 (m, 4H), 7.53 – 7.47 (m, 1H), 7.41 – 7.27 (m, 2H), 6.08 (s, 1H), 4.45 – 4.26 (m, 2H), 4.08 (d, *J* = 18.0 Hz, 1H), 3.65 (d, *J* = 18.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.75, 168.95, 139.01, 136.50, 135.31, 133.76, 133.36, 132.22, 130.52, 128.97, 127.29, 123.88, 121.51, 118.77, 77.15, 76.73, 76.31, 65.21, 63.39, 51.93, 13.70. ESI-HRMS: Calcd for $C_{18}H_{17}BrNO_5S^+$ ([M+H$^+$]): 438.0005; Found: 438.0009.



3an

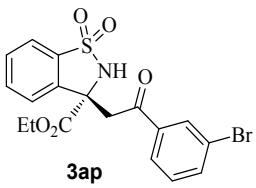
White solid, m.p. 57–58 °C, 98% yield. [α]20 D = –156.3 (c, 1.13, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 14.96 min, t (minor) = 26.69 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.77 – 7.58 (m, 5H), 7.44 – 7.30 (m, 2H), 6.11 (s, 1H), 4.31 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.09 (d, *J* = 17.8 Hz, 1H), 3.72 (d, *J* = 17.8 Hz, 1H), 2.38 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.82, 169.30, 138.33, 136.65, 135.31, 135.27, 134.43, 133.35, 130.47, 128.37, 128.34, 125.09, 123.99, 121.48, 65.19, 63.13, 48.86, 20.94, 13.62. ESI-HRMS: Calcd for $C_{19}H_{20}NO_5S^+$ ([M+H$^+$]): 374.1057; Found: 374.1058.



3ao

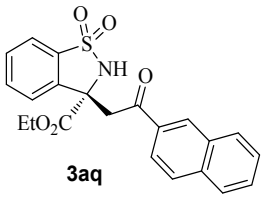
White solid, m.p. 53–54 °C, 96% yield. [α]20 D = –146.7 (c, 1.09, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 22.95 min, t (minor) = 69.05 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86

– 7.80 (m, 1H), 7.75 – 7.58 (m, 3H), 7.51 – 7.42 (m, 2H), 7.40 – 7.32 (m, 1H), 7.17 – 7.11 (m, 1H), 6.08 (s, 1H), 4.32 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.07 (d, *J* = 17.8 Hz, 1H), 3.84 (s, 3H), 3.71 (d, *J* = 17.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.50, 169.24, 159.63, 136.62, 135.31, 133.31, 130.48, 129.44, 123.92, 121.53, 120.52, 120.29, 111.94, 65.18, 63.17, 55.16, 48.89, 13.62. ESI-HRMS: Calcd for $C_{19}H_{20}NO_6S^+$ ([M+H$^+$]): 390.1006; Found: 390.1005.



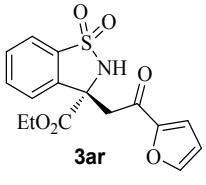
3ap

White solid, m.p. 58 – 60 °C, 98% yield. [α]20 D = –137.2 (c, 1.13, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 17.99 min, t (minor) = 30.46 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 1H), 7.89 – 7.79 (m, 2H), 7.76 – 7.60 (m, 4H), 7.39 – 7.31 (m, 1H), 6.07 (s, 1H), 4.33 (qq, *J* = 10.7, 7.1 Hz, 2H), 4.05 (d, *J* = 17.8 Hz, 1H), 3.69 (d, *J* = 17.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.36, 169.06, 136.97, 136.48, 135.32, 133.38, 130.90, 130.57, 130.07, 126.39, 123.89, 122.80, 121.57, 65.00, 63.29, 48.77, 13.62. ESI-HRMS: Calcd for $C_{18}H_{16}BrNNaO_5S^+$ ([M+Na$^+$]): 459.9825; Found: 459.9828.



3aq

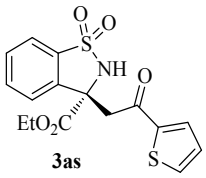
White solid, m.p. 73 –74 °C, 98% yield. [α]20 D = –134.4 (c, 1.17, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 23.68 min, t (major) = 26.01 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.03 – 7.49 (m, 10H), 6.15 (s, 1H), 4.44 – 4.25 (m, 2H), 4.22 (d, *J* = 17.7 Hz, 1H), 3.88 (d, *J* = 17.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.55, 169.32, 136.71, 135.60, 135.37, 133.33, 132.64, 132.04, 130.49, 130.00, 129.28, 128.64, 128.41, 127.51, 126.72, 124.00, 123.08, 121.56, 65.27, 63.19, 48.87, 13.64. ESI-HRMS: Calcd for $C_{22}H_{19}NNaO_5S^+$ ([M+Na$^+$]): 432.0876; Found: 432.0880.



3ar

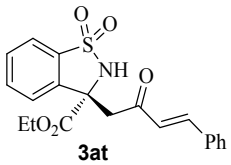
White solid, m.p. 56–58 °C, 98% yield. [α]20 D = –133.6 (c, 1.09, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (major) = 24.23 min, t (minor) = 36.80 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 –7.79 (m, 1H), 7.74–7.58 (m, 4H), 7.27 – 7.23

(m, 1H), 6.59 – 6.55 (m, 1H), 6.07 (s, 1H), 4.44–4.21 (m, 2H), 3.95 (d, *J* = 17.7 Hz, 1H), 3.60 (d, *J* = 17.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.31, 169.05, 151.37, 146.77, 136.53, 135.21, 133.32, 130.47, 123.94, 121.48, 117.93, 112.35, 64.87, 63.26, 48.15, 13.59. ESI-HRMS: Calcd for $C_{16}H_{15}NNaO_6S^+$ ([M+Na$^+$]): 372.0512; Found: 372.0516.



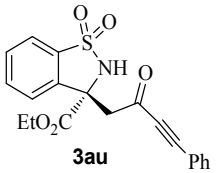
3as

White solid, m.p. 64–66 °C, 97% yield. [α]20 D = –154 (c, 1.14, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 20.85 min, t (major) = 23.03 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.76 – 7.57 (m, 5H), 7.15 – 7.10 (m, 1H), 6.09 (s, 1H), 4.42 – 4.22 (m, 2H), 4.04 (d, *J* = 17.4 Hz, 1H), 3.65 (d, *J* = 17.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.27, 169.04, 142.17, 136.47, 135.21, 134.57, 133.41, 132.76, 130.54, 128.10, 124.01, 121.45, 65.16, 63.27, 48.86, 13.61. ESI-HRMS: Calcd for $C_{16}H_{16}NO_5S_2^+$ ([M+H$^+$]): 366.0464; Found: 366.0466.



3at

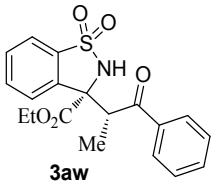
White solid, m.p. 64–65 °C, 93% yield. [α]20 D = –157 (c, 0.73, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 25.49 min, t (major) = 34.44 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.78 (m, 1H), 7.72–7.49 (m, 6H), 7.45 – 7.35 (m, 3H), 6.71 (d, *J* = 16.3 Hz, 1H), 6.08 (s, 1H), 4.31 (qq, *J* = 10.7, 7.1 Hz, 2H), 3.83 (d, *J* = 17.6 Hz, 1H), 3.42 (d, *J* = 17.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.37, 169.20, 144.34, 136.64, 135.23, 133.61, 133.29, 130.72, 130.42, 128.72, 128.16, 124.72, 123.92, 121.48, 65.13, 63.15, 50.09, 13.62. ESI-HRMS: Calcd for $C_{20}H_{20}NO_5S^+$ ([M+H$^+$]): 386.1057; Found: 386.1058.



3au

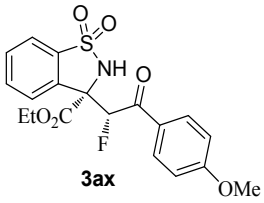
White solid, m.p. 49 – 51 °C, 96% yield. [α]20 D = –111.2 (c, 0.91, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 14.45 min, t (major) = 30.54 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.72 – 7.58 (m, 3H), 7.58 – 7.51 (m, 2H), 7.51 – 7.42 (m, 1H), 7.42 – 7.33 (m, 2H), 5.99 (s, 1H), 4.43 – 4.20 (m, 2H), 3.84 (d, *J* = 18.2 Hz, 1H), 3.40 (d, *J* = 18.2 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C

NMR (75 MHz, $CDCl_3$) δ 182.20, 168.68, 136.10, 135.21, 133.37, 132.84, 130.91, 130.57, 128.40, 123.83, 121.54, 118.92, 93.14, 86.60, 64.66, 63.42, 54.39, 13.61. ESI-HRMS: Calcd for $C_{20}H_{18}NO_5S^+$ ([M+H$^+$]): 384.0900; Found: 384.0900.



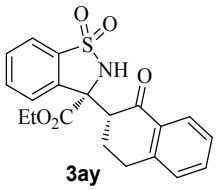
3aw

White solid, m.p. 47–49 °C, 98% yield. [α]20 D = –50.1 (c, 1.22, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 10.29 min, t (minor) = 13.34 min]; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.97–7.88 (m, 2H), 7.84–7.75 (m, 2H), 7.68–7.52 (m, 3H), 7.49 –7.40 (m, 2H), 6.15 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.27 (q, *J* = 7.5 Hz, 1H), 1.48 (d, *J* = 7.5 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.78, 168.81, 136.93, 135.43, 133.33, 132.35, 130.24, 128.49, 128.27, 126.08, 121.31, 68.62, 63.18, 49.94, 14.38, 13.72. ESI-HRMS: Calcd for $C_{19}H_{19}NNaO_5S^+$ ([M+Na$^+$]): 396.0876; Found: 396.0877.



3ax

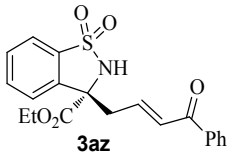
White solid, m.p. 52–53 °C, 97% yield. [α]20 D=–142.1 (c, 1.15, CH_2Cl_2); >20:1 dr, 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 13.18 min, t (minor) = 21.00 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.93 – 7.86 (m, 1H), 7.86 – 7.80 (m, 1H), 7.75 – 7.64 (m, 2H), 7.00 – 6.90 (m, 2H), 5.99 (s, 1H), 5.65 (d, *J* = 46.1 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ190.00 (d, *J* = 20.0 Hz), 167.45, 164.37, 135.71, 133.26, 133.01, 131.86, 131.81, 130.91, 126.91, 126.84, 121.25, 113.75, 92.08 (d, *J* = 201.3 Hz), 66.19 (d, *J* = 22.6 Hz), 63.48, 55.27, 13.62. ESI-HRMS: Calcd for $C_{19}H_{18}FNNaO_6S^+$ ([M+Na$^+$]): 430.0731; Found: 430.0735.



3ay

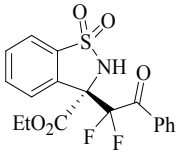
White solid, m.p. 85–86 °C, 95% yield. [α]20 D = –141.0 (c, 1.07, CH_2Cl_2); 98:2 dr, 99% ee, determined by HPLC analysis [Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.9 mL/min, 220 nm; t (minor) = 32.82 min, t (major) = 35.45 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 1H), 7.84–7.77 (m, 1H), 7.76–7.59 (m, 3H), 7.52 –7.44 (m, 1H), 7.35 – 7.27 (m, 1H), 7.24 – 7.17 (m, 1H), 5.85 (s,

1H), 4.44 –4.22 (m, 2H), 3.81 (dd, *J* = 13.9, 4.2 Hz, 1H), 3.07 – 2.84 (m, 2H), 2.29 – 2.08 (m, 1H), 1.56 – 1.42 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 196.25, 169.90, 143.61, 135.45, 135.22, 133.84, 133.54, 131.54, 130.52, 128.45, 127.23, 126.55, 123.87, 121.65, 69.16, 63.16, 55.95, 28.48, 23.08, 13.59. ESI-HRMS: Calcd for $C_{20}H_{19}NNaO_5S^+$ ([M+Na$^+$]): 408.0876; Found: 408.0881.



3az

White solid, m.p. 40–41 °C, 96% yield. [α]20 D = –65 (c, 1.08, CH_2Cl_2); 96% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 20.35 min, t (minor) = 23.37 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91–7.84 (m, 2H), 7.83–7.74 (m, 2H), 7.74 – 7.53 (m, 3H), 7.51–7.42 (m, 2H), 6.99 (d, *J* = 15.5 Hz, 1H), 6.92–6.79 (m, 1H), 5.86 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.23 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.98 (dd, *J* = 14.1, 6.9 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.98, 168.64, 139.74, 137.15, 136.89, 135.31, 133.38, 132.72, 130.83, 130.51, 128.36, 128.31, 124.42, 121.35, 67.85, 63.72, 42.89, 13.82. ESI-HRMS: Calcd for $C_{20}H_{19}NNaO_5S^+$ ([M+Na$^+$]): 408.0876; Found: 408.0881.

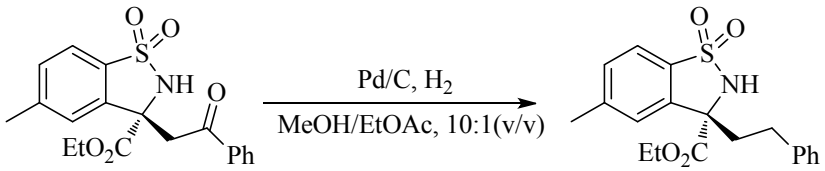


3ax'

Viscous oil, 21% yield. [α]20 D = –46 (c, 0.43, $CHCl_3$); 30% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 60:40, 1.0 mL/min, 230 nm; t (major) = 14.95 min, t (minor) = 25.56 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 2H), 8.00 – 7.94 (m, 1H), 7.91 – 7.85 (m, 1H), 7.81 – 7.65 (m, 3H), 7.56 – 7.48 (m, 2H), 6.01 (s, 1H), 4.47 – 4.36 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.48 (dd, *J* = 32.0, 28.9 Hz), 165.26 (dd, *J* = 7.2, 2.0 Hz), 136.32, 134.89, 133.26, 131.48, 130.88, 130.11 (d, *J* = 2.2 Hz), 130.06 (d, *J* = 2.5 Hz), 128.52, 126.72 (d, *J* = 5.6 Hz), 121.62, δ 115.10 (t, *J* = 269.8 Hz), 68.23 (dd, *J* = 26.0, 23.9 Hz), 64.08, 13.52. ESI-HRMS: Calcd for $C_{18}H_{14}F_2NO_5S^-$ ([M-H$^-$]): 394.0566; Found: 394.0569.

6. Transformations of product 3 to 4, 5 and 6

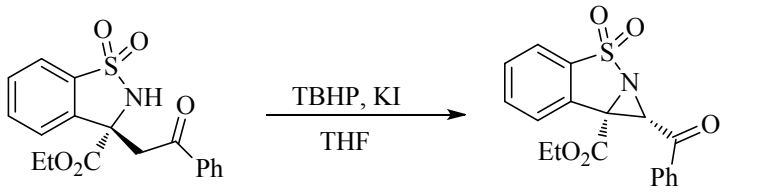
6.1 The preparation of *4*



3ba **4**

A solution of ***3ba*** (0.2 mmol) in MeOH (8.5 mL) and EtOAc(0.8 mL) was added to a mixture of Pd/C(10% on carbon, 35 mg) in MeOH (0.5 mL).The mixture was stirred under H_2 (1atm) for 24 hours. The reaction mixture was then filtered through Celite and the filtrate was concentrated under reduced pressure. The remained oil was purified through flash column chromatography (PE/EA = 5/1) to give product ***4ba*** as a viscous liquid. 78% yield. [α]20 D= –32.1 (c, 1.33, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 15.73 min, t (major) = 24.16 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.49 – 7.44 (m, 1H), 7.40 – 7.33 (m, 1H), 7.30 – 7.11 (m, 5H), 5.84 (s, 1H), 4.34 – 4.18 (m, 2H), 2.81 – 2.59 (m, 2H), 2.57 – 2.47 (m, 1H), 2.45 (s, 3H), 2.37–2.22 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.68, 144.33, 139.93, 138.13, 132.35, 131.11, 128.14, 128.11, 125.90, 124.70, 120.88, 68.48, 63.24, 41.67, 30.61, 21.53, 13.79. ESI-HRMS: Calcd for $C_{18}H_{19}NNaO_4S^+$ ([M+Na^+]): 368.0927; Found: 368.0926.

6.2 The preparation of 5 [8]



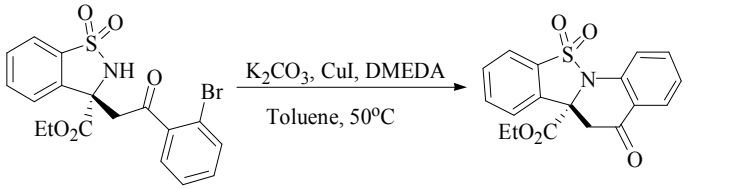
3aa **5** 95%yield,98%ee

To a suspension of product **3aa** (0.3mmol), KI (0.6 mmol) and THF (3 mL) was added TBHP (0.60 mmol, 5.5 mol/L in n-decane) in portions during 2 h. After completion of the reaction (monitored by TLC), the solvent was evaporated in vacuo. Purification of the residue by column chromatography (PE/EA = 10/1 − 5/1, V/V) afforded the desired aziridine product **5**.

95% yield. [α]20 D = +78.8 (c, 0.92, EtOAc); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 0.8 mL/min, 215 nm; t (major) = 11.39 min, t (minor) = 12.86 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 1H), 8.16 – 8.08 (m, 2H), 7.85 – 7.74 (m, 2H), 7.73 – 7.63 (m, 2H), 7.59 – 7.49 (m, 2H), 4.46 – 4.20 (m, 2H), 3.94 (s, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.36, 163.08, 134.34, 134.31, 133.73,

133.23, 132.87, 130.90, 128.82, 128.68, 126.90, 123.02, 77.12, 76.70, 76.28, 62.75, 59.60, 53.32, 13.43. ESI-HRMS: Calcd for $C_{18}H_{16}NO_5S^+$ ([M+H$^+$]): 358.0743; Found: 358.0744.

The preparation of 6



3am **6** 95%yield, 98 % ee

Under nitrogen atmosphere, to a solution of **3am** (88mg, 0.2mmol) in anhydrous toluene (3 mL) was added CuI (0.5 equiv), DMEDA (1.0 equiv), K_2CO_3 (2.5 equiv). After heating for 1 h at 50 °C, the heterogeneous mixture was cooled to room temperature and AcOEt (6 mL) was added, the mixture was then passed through a pad of Celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 3/1m V'V) to afford the product **6** in 95% yield.

White solid, m.p. 55 −56 °C, 95% yield. [α]20 D = –143.5 (c, 0.35, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (mnior) = 24.53 min, t (major) = 26.23 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.97 (m, 1H), 7.97 – 7.89 (m, 1H), 7.89 – 7.82 (m, 1H), 7.80 – 7.59 (m, 4H), 7.25 – 7.18 (m, 1H), 4.21 – 3.97 (m, 2H), 3.76 (d, *J* = 16.4 Hz, 1H), 2.97 (d, *J* = 13.3 Hz, 1H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.33, 167.91, 138.31, 135.76, 133.95, 133.64, 133.54, 130.82, 127.99, 123.99, 123.19, 121.74, 121.67, 118.01, 77.19, 76.76, 76.34, 68.62, 63.12, 45.86, 13.37. ESI-HRMS: Calcd for $C_{18}H_{15}NNaO_5S^+$ ([M+Na$^+$]): 380.0563; Found: 380.0566.

References.

1 Liu, R.-R.; Wang, D.-J.; Wu, L.; Xiang, B.; Zhang, G.-Q.; Gao, J.-R.; Jia, Y.-X. *ACS Catal.* **2015** , *5* , 6524.

2 (a) Wang, H.; Jiang T.; Xu, M.-H. *J. Am. Chem. Soc*. **2013**, *135*, 971; (b) Yan, Z., Wu, B., Gao, X., Chen, M. W., Zhou, Y. G. *Org. Lett*. **2016**, *18*, 692.

3 (a) Wiles, C., Watts, P., Haswell, S. J., Pombo-Villar, E. *Tetrahedron.* **2005**, *61*, 10757; (b) Tanis, S. P., Evans, B. R., Nieman, J. A., Parker, T. T., Taylor, W. D., Heasley, S. E., Hester, M.

R. *Tetrahedron: Asymmetry*. **2006** *17*, 2154. (c) Ferrié, L., Boulard, L., Pradaux, F., Bouzbouz, S., Reymond, S., Capdevielle, P., Cossy, J. *J. Org. Chem*. **2008**, *73*, 1864. (d) Hoffmann, R.V.; Kim, O. *J. Org. Chem*. **1991**, *36*, 1014.

4. He, Y., Zhang, X., Shen, N., Fan, X. *J. Fluorine Chem.* **2013**, *156*, 9.

5 Schuler, M., Silva, F., Bobbio, C., Tessier, A., Gouverneur, V. *Angew. Chem. Int. Ed.* **2008**, *47*, 7927-7930.

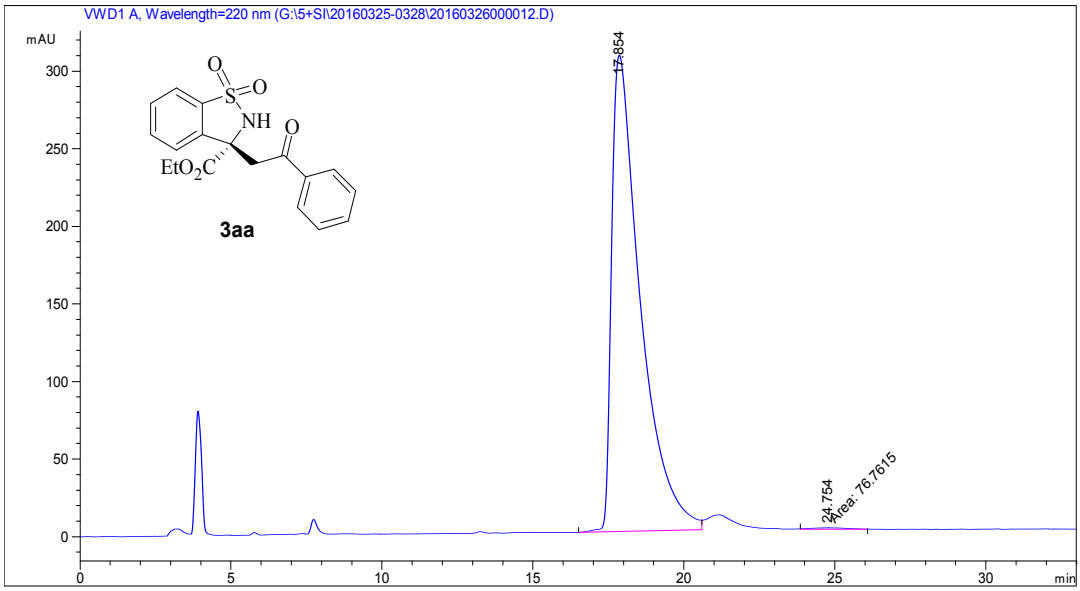
6. Qiao, B., Huang, Y. J., Nie, J., Ma, J. A. *Org. Lett*. **2015**, *17*, 4608.

7 Fu, J.P.;; Karur, S.; Madera, A. M.; Pecchi, S.; Sweeney, Z. K.; Tjandra, M.; Yifru, A. Patent Appl. WO 2014160649A1, **2014**.

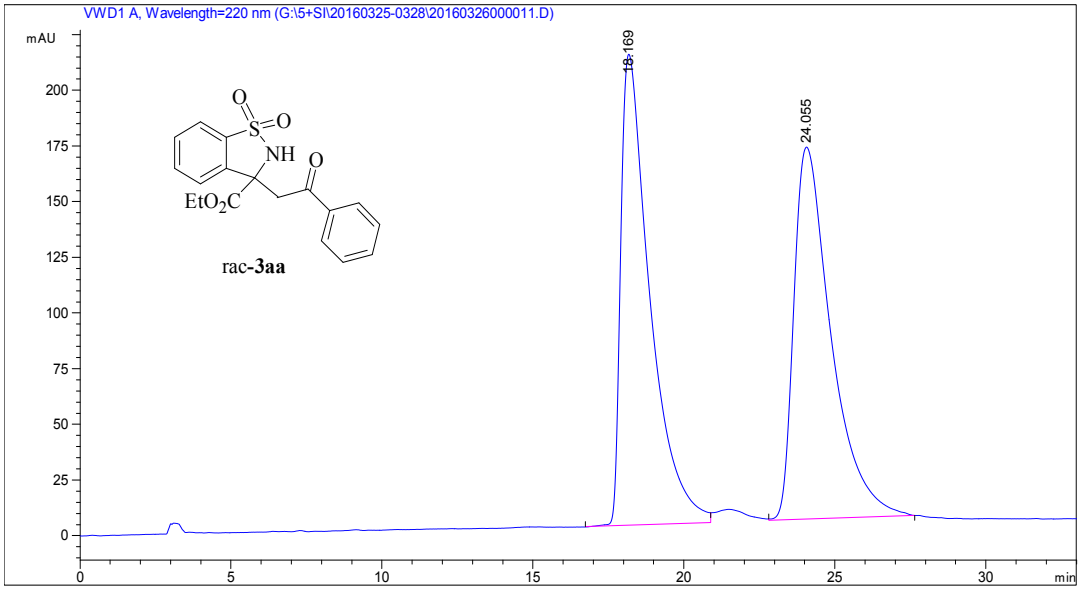
8. Lai, B. N., Qiu, J. F., Zhang, H. X., Nie, J., Ma, J. A. *Org. Lett*. **2016**, *18*, 520.

7. HPLC Chromatograms for All Products

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 17.85 min, t_R (minor) = 24.75 min; 99% ee.

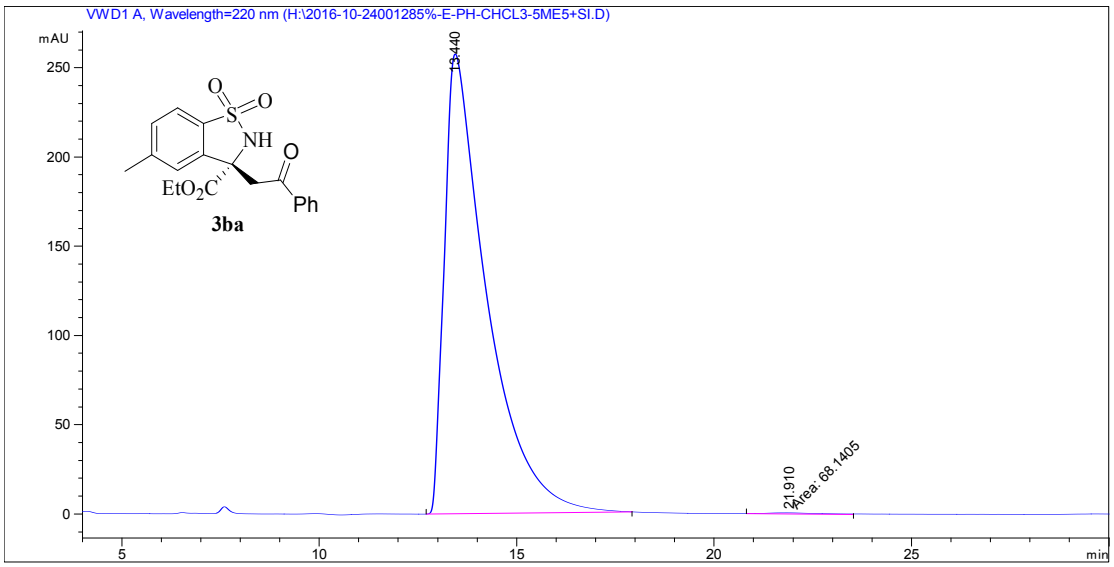


#	Time	Area	Height	Width	Area%	Symmetry
1	17.854	20333.3	307.1	0.9559	99.624	0.331
2	24.754	76.8	9.5E-1	1.3508	0.376	0.847

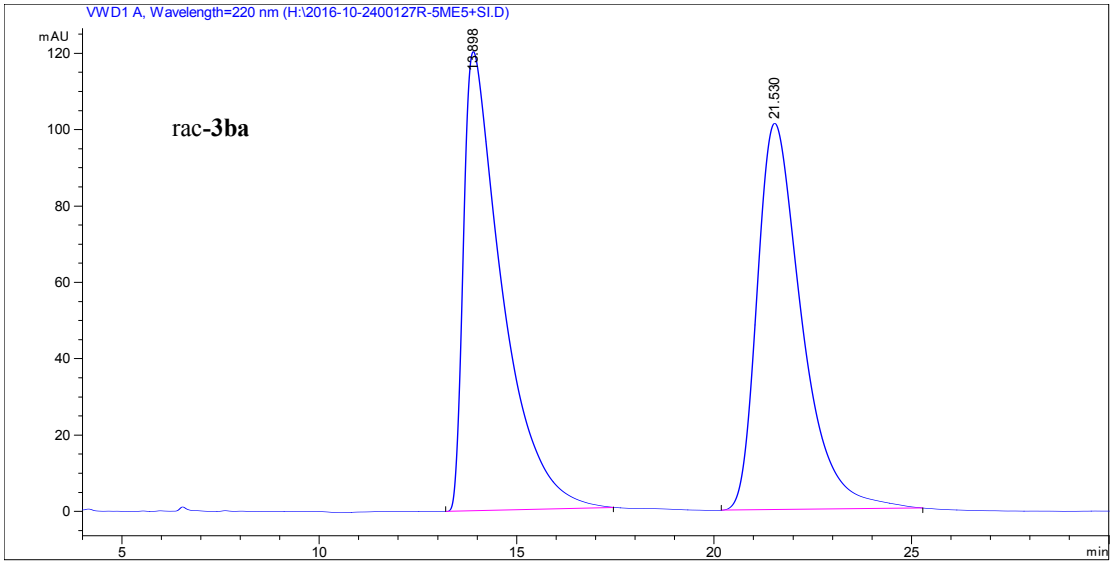


#	Time	Area	Height	Width	Area%	Symmetry
1	18.169	14190.9	211.6	0.9528	49.744	0.351
2	24.055	14337.2	167.1	1.2454	50.256	0.481

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 13.44 min, t_R (minor) = 21.91 min; 99% ee.

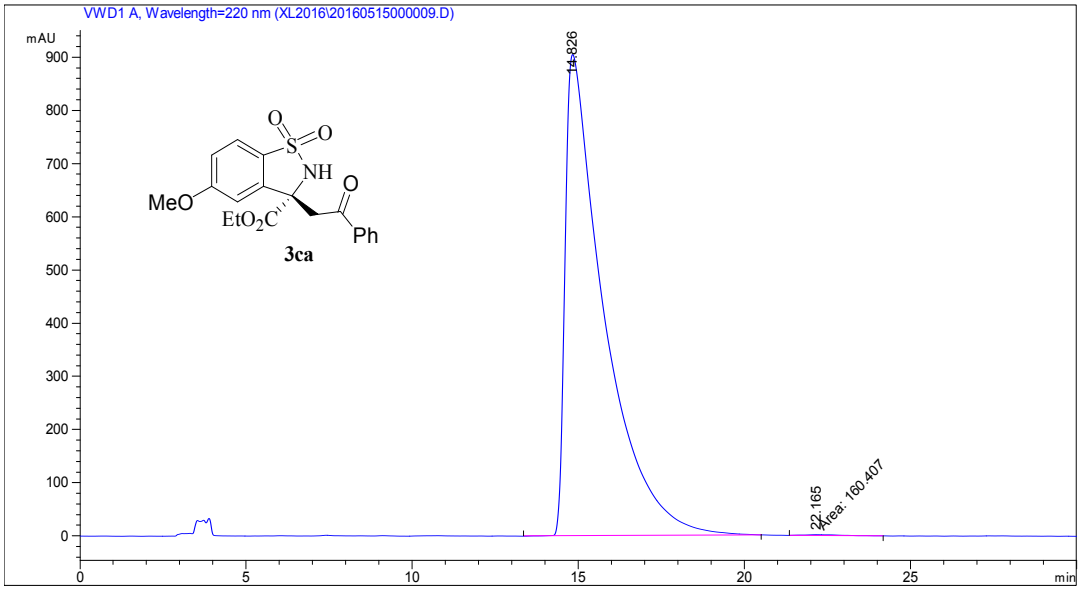


#	Time	Area	Height	Width	Area%	Symmetry
1	13.44	19219.6	257.7	1.0363	99.647	0.315
2	21.91	68.1	6.8E-1	1.6601	0.353	0.506

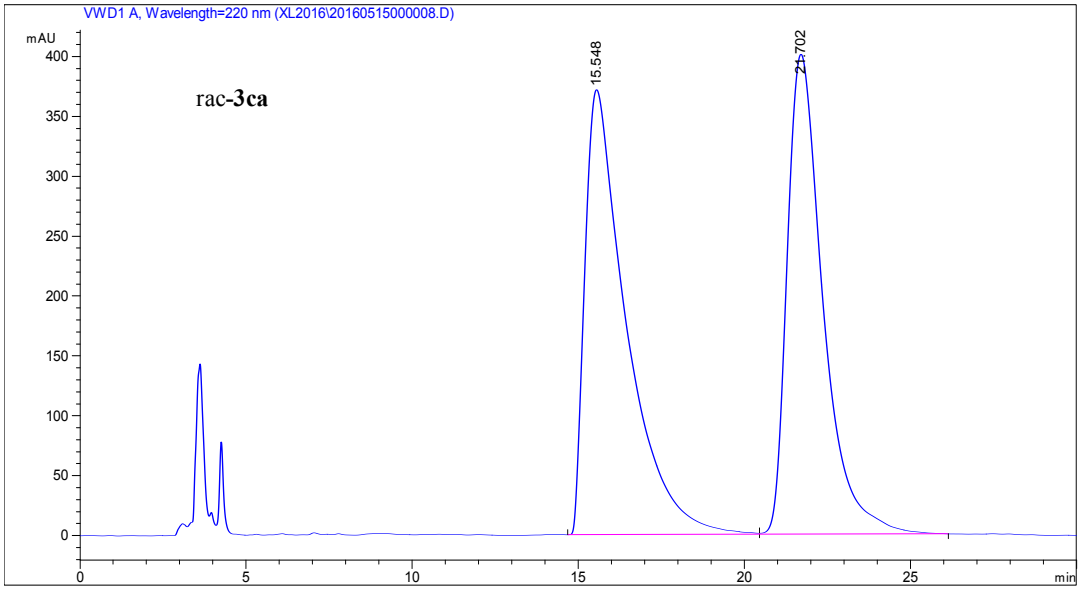


#	Time	Area	Height	Width	Area%	Symmetry
1	13.898	8208.2	120.3	0.98	50.768	0.31
2	21.53	7959.8	101.2	1.1943	49.232	0.6

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 14.83 min, t_R (minor) = 22.17 min; 99% ee.

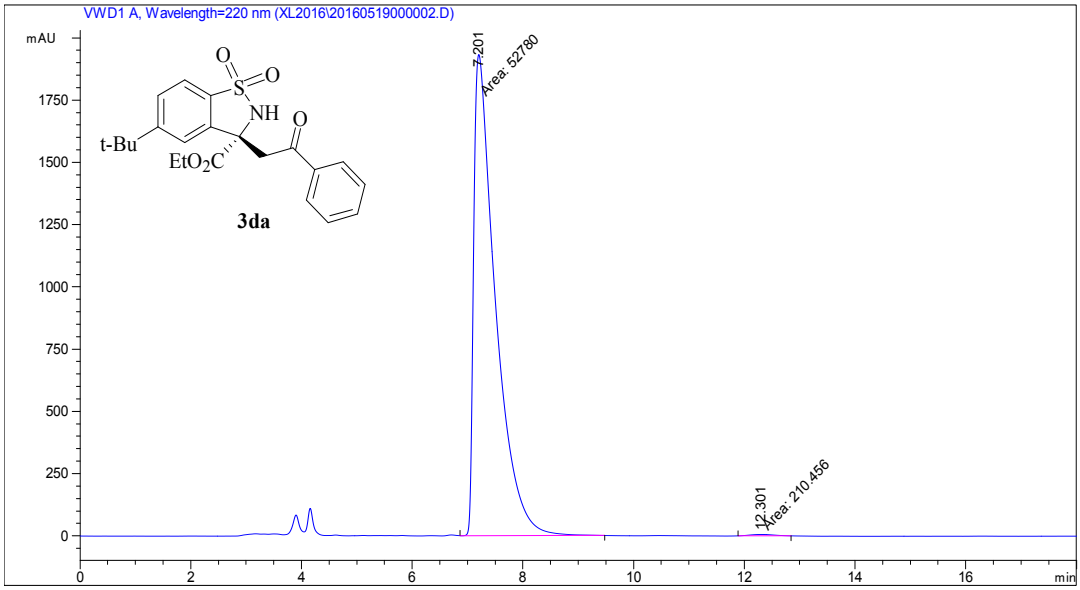


#	Time	Area	Height	Width	Area%	Symmetry
1	14.826	73485.6	905.1	1.1176	99.782	0.218
2	22.165	160.4	1.9	1.4436	0.218	0.5

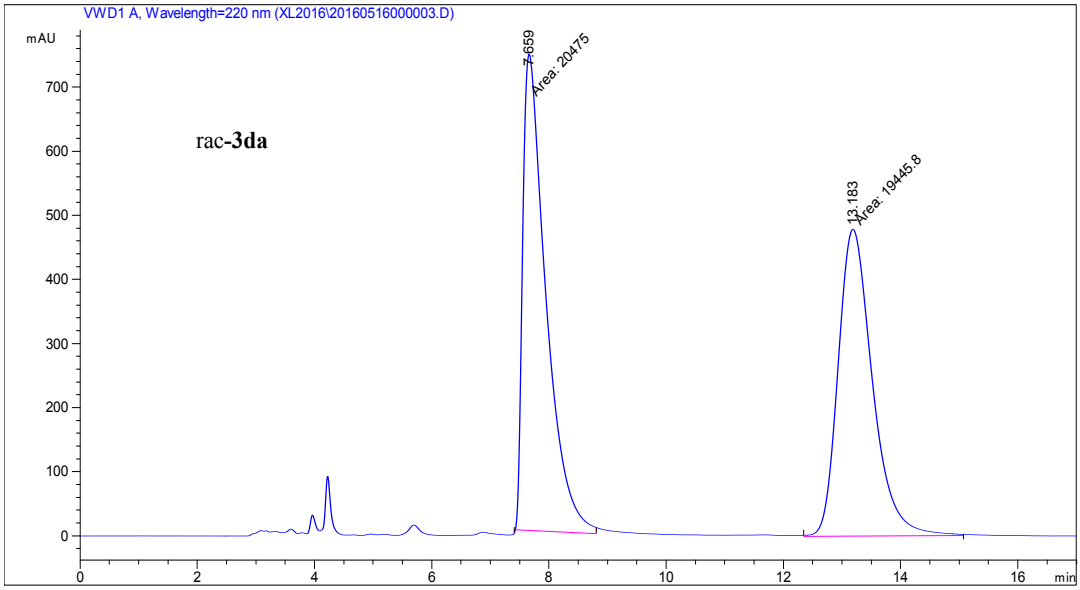


#	Time	Area	Height	Width	Area%	Symmetry
1	15.548	32253	371.8	1.2379	51.771	0.36
2	21.702	30046.8	400.9	1.1424	48.229	0.575

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 7.20 min, t_R (minor) = 12.30 min; 99% ee.

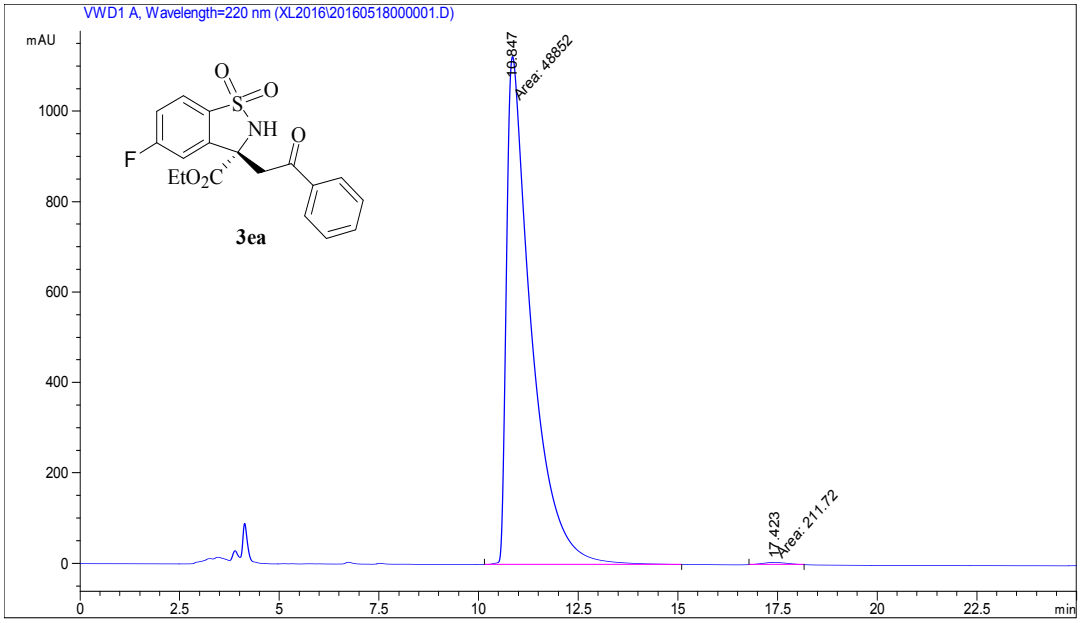


#	Time	Area	Height	Width	Area%	Symmetry
1	7.201	52780	1933.7	0.4549	99.603	0.295
2	12.301	210.5	6.3	0.5557	0.397	0.829

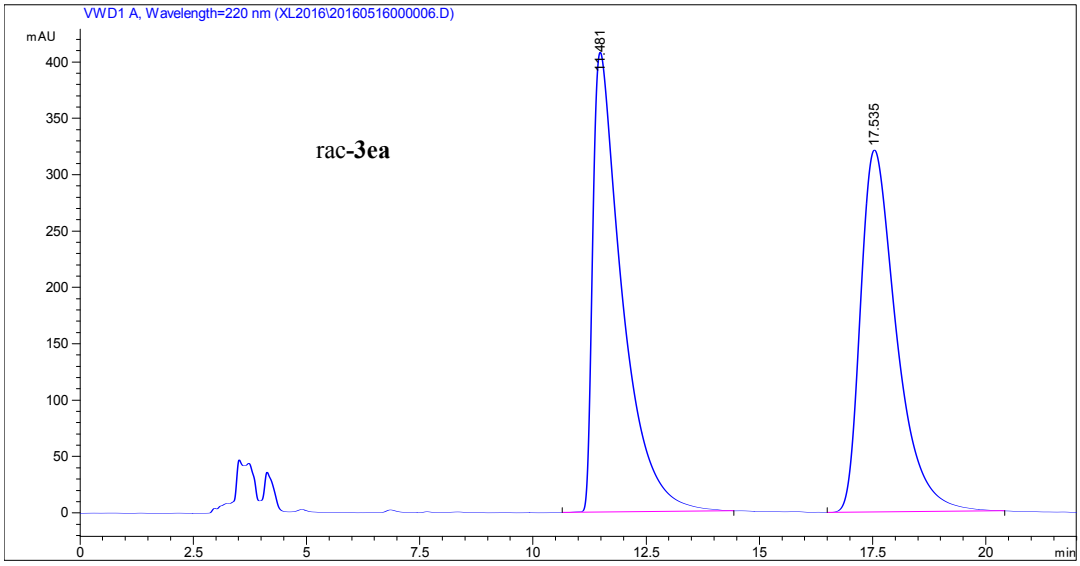


#	Time	Area	Height	Width	Area%	Symmetry
1	7.659	20475	743	0.4593	51.289	0.367
2	13.183	19445.8	478.8	0.6769	48.711	0.726

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 10.85 min, t_R (minor) = 17.42 min; 99% ee.

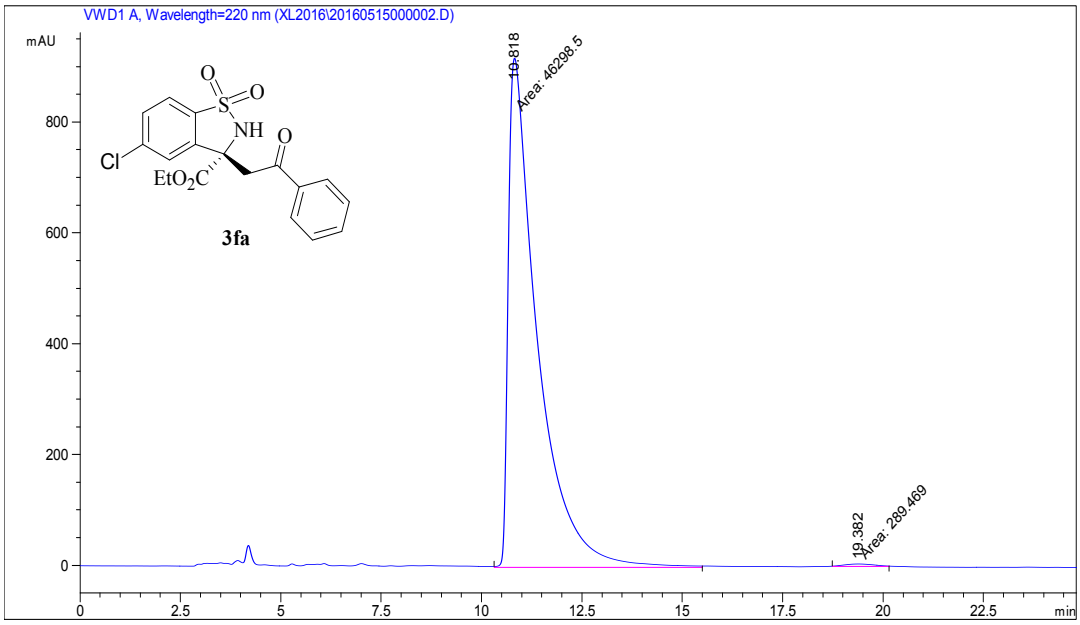


#	Time	Area	Height	Width	Area%	Symmetry
1	10.847	48852	1124.2	0.7242	99.568	0.307
2	17.423	211.7	4.8	0.7385	0.432	0.73

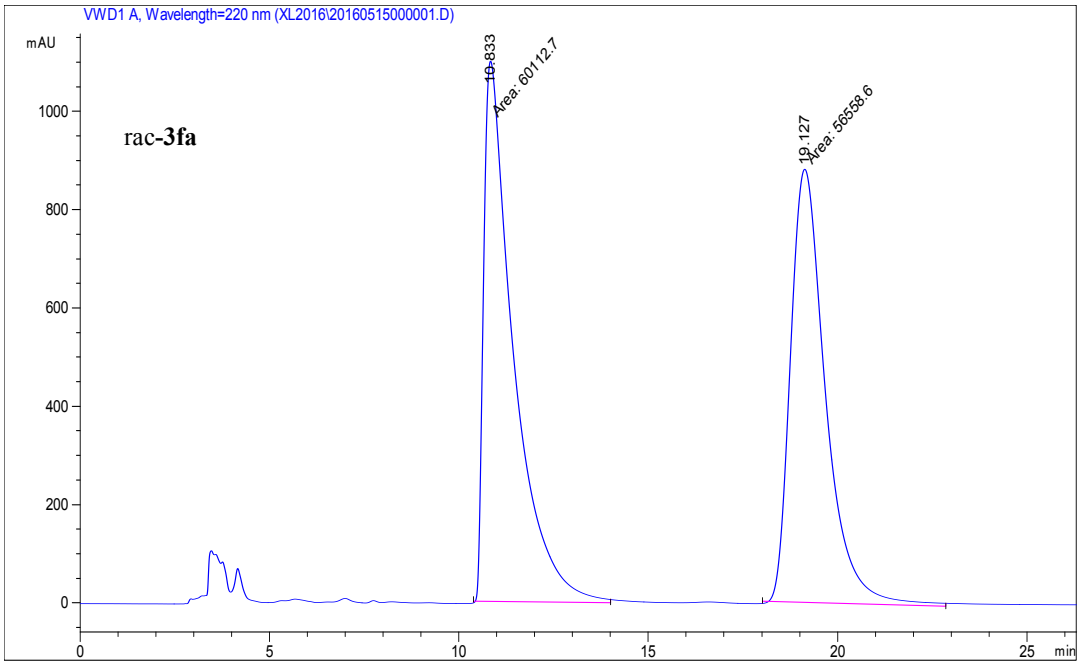


#	Time	Area	Height	Width	Area%	Symmetry
1	11.481	18344.4	408	0.6454	50.863	0.308
2	17.535	17722	321.2	0.8433	49.137	0.584

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 10.82 min, t_R (minor) = 19.38 min; 99% ee.

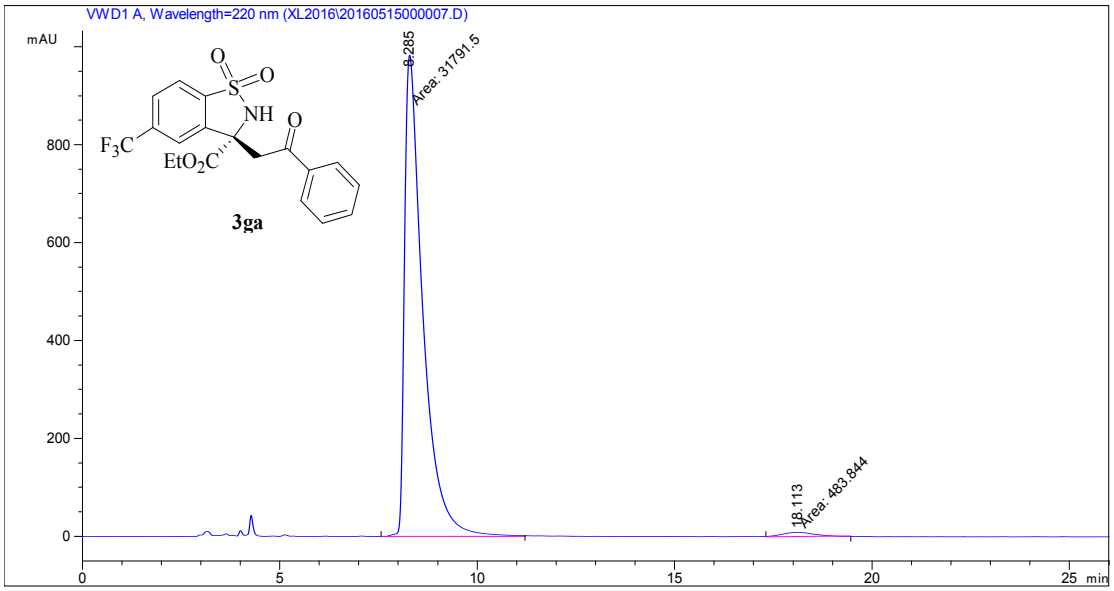


#	Time	Area	Height	Width	Area%	Symmetry
1	10.818	46298.5	919.2	0.8394	99.379	0.261
2	19.382	289.5	5.1	0.9453	0.621	0.871

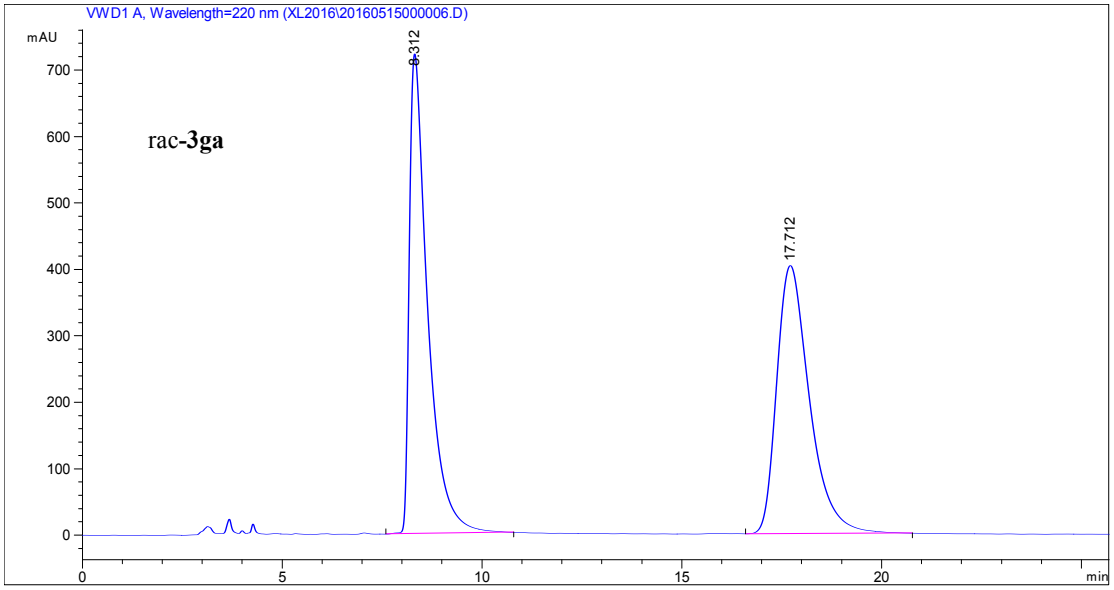


#	Time	Area	Height	Width	Area%	Symmetry
1	10.833	60112.7	1099.6	0.9111	51.523	0.29
2	19.127	56558.6	881.5	1.0693	48.477	0.649

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 8.26 min, t_R (minor) = 18.11 min; 97% ee.

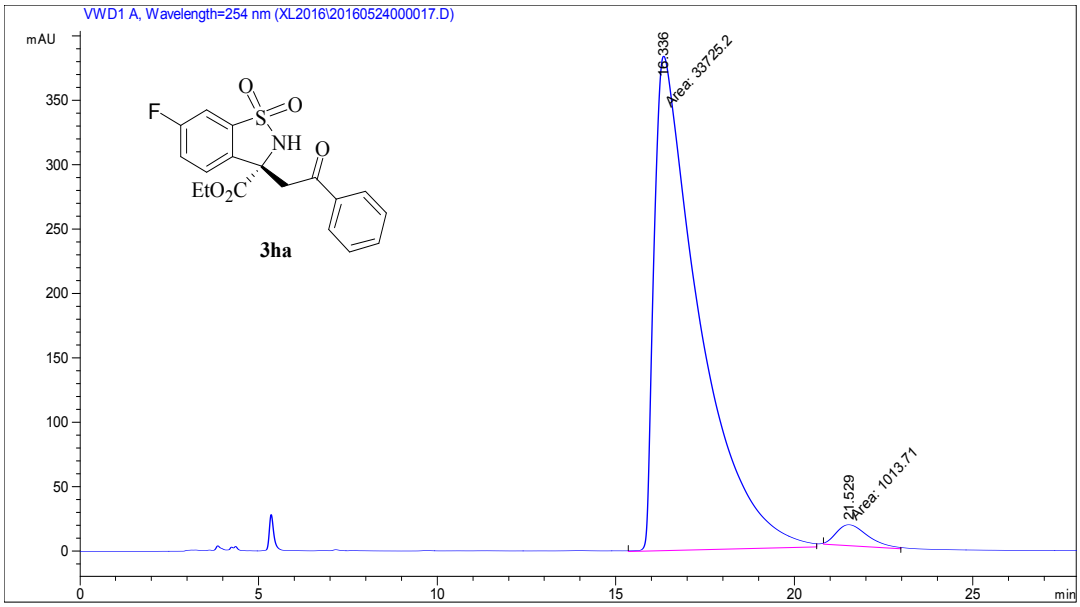


#	Time	Area	Height	Width	Area%	Symmetry
1	8.285	31791.5	983.4	0.5388	98.501	0.369
2	18.113	483.8	8.8	0.9178	1.499	1.016

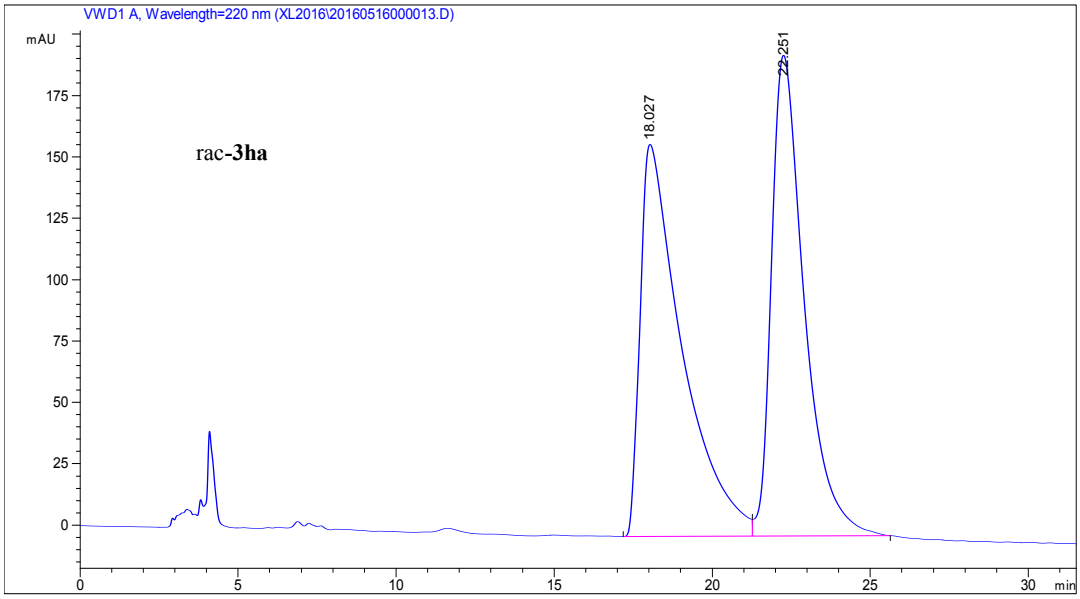


#	Time	Area	Height	Width	Area%	Symmetry
1	8.312	23086.3	722.1	0.4676	50.138	0.374
2	17.712	22958.9	403.5	0.8735	49.862	0.655

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 16.34 min, t_R (minor) = 21.53 min; 94% ee.

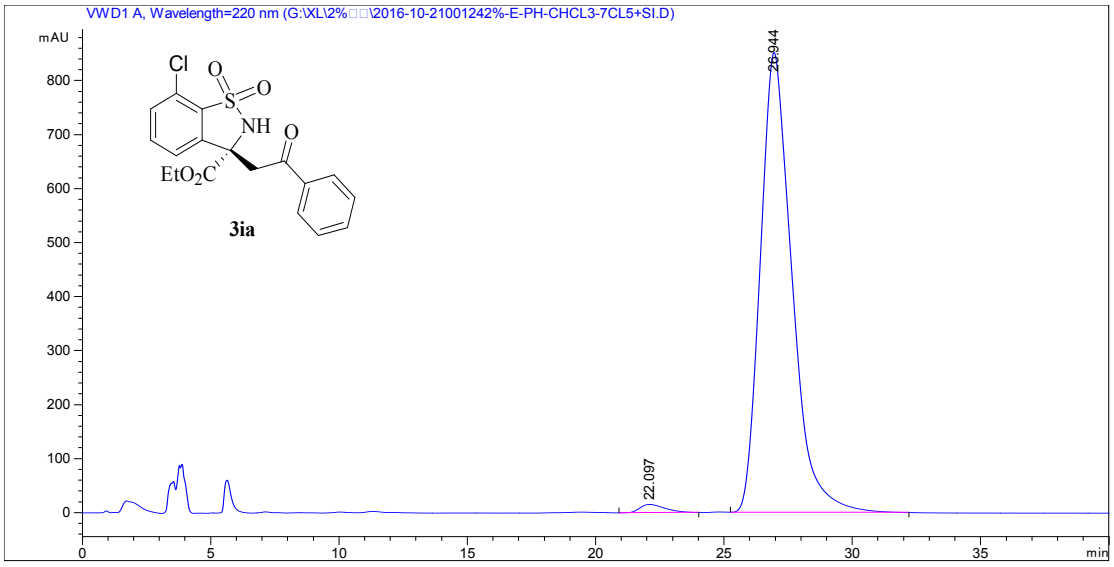


#	Time	Area	Height	Width	Area%	Symmetry
1	16.336	33725.2	384.3	1.4626	97.082	0.261
2	21.529	1013.7	16.4	1.0331	2.918	0.612

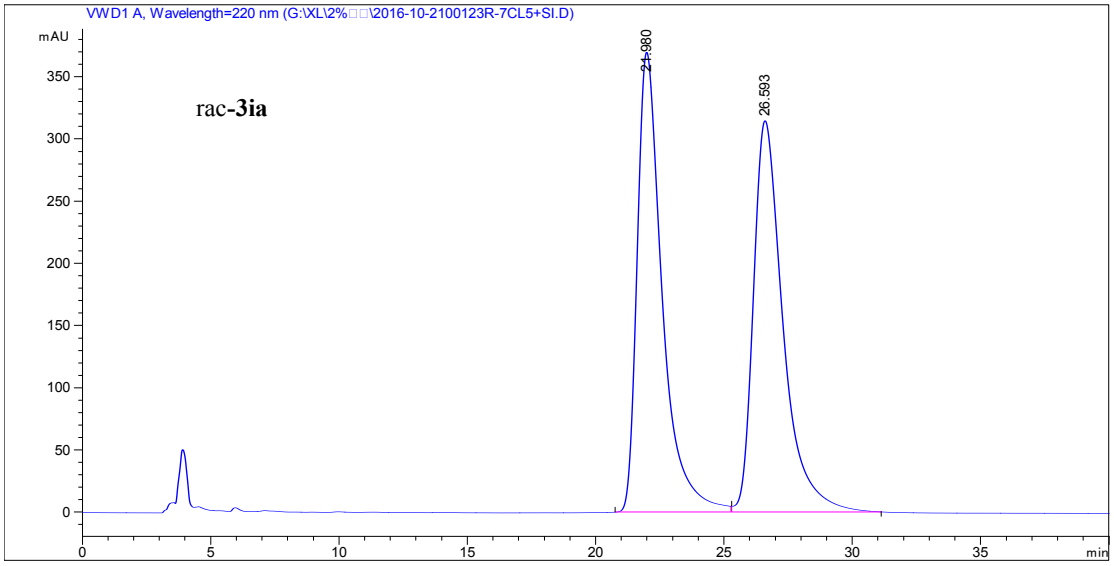


#	Time	Area	Height	Width	Area%	Symmetry
1	18.027	14665.4	159.7	1.2707	50.891	0.285
2	22.251	14151.9	195.9	1.089	49.109	0.54

Daicel Chiralpak AD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (minor) = 18.95 min, t_R (major) = 23.01 min; 97% ee.

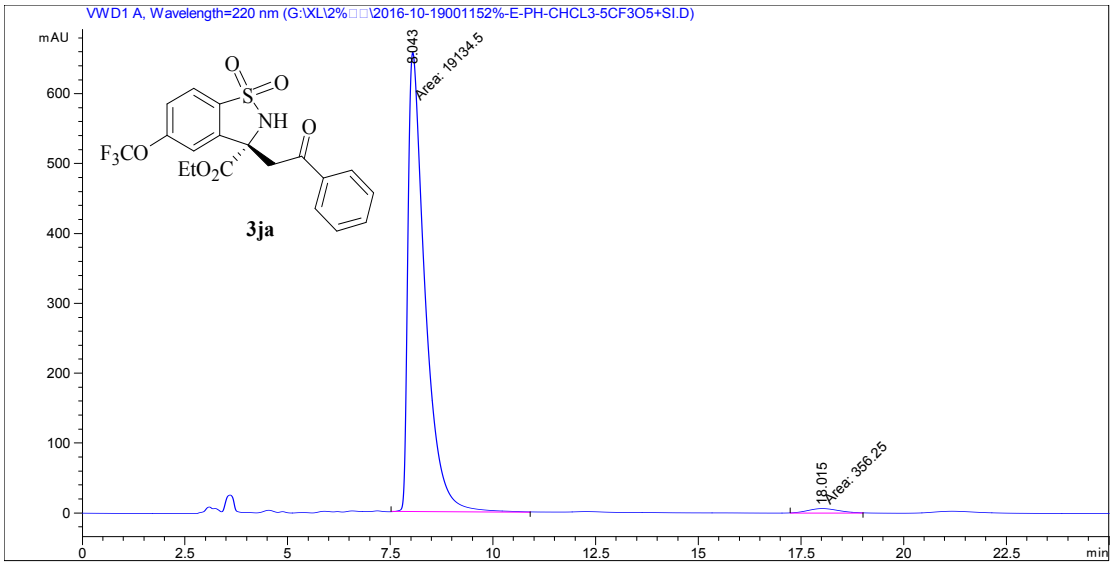


#	Time	Area	Height	Width	Area%	Symmetry
1	22.097	1058.9	15.4	1.0323	1.432	0.587
2	26.944	72874.1	851.9	1.285	98.568	0.712

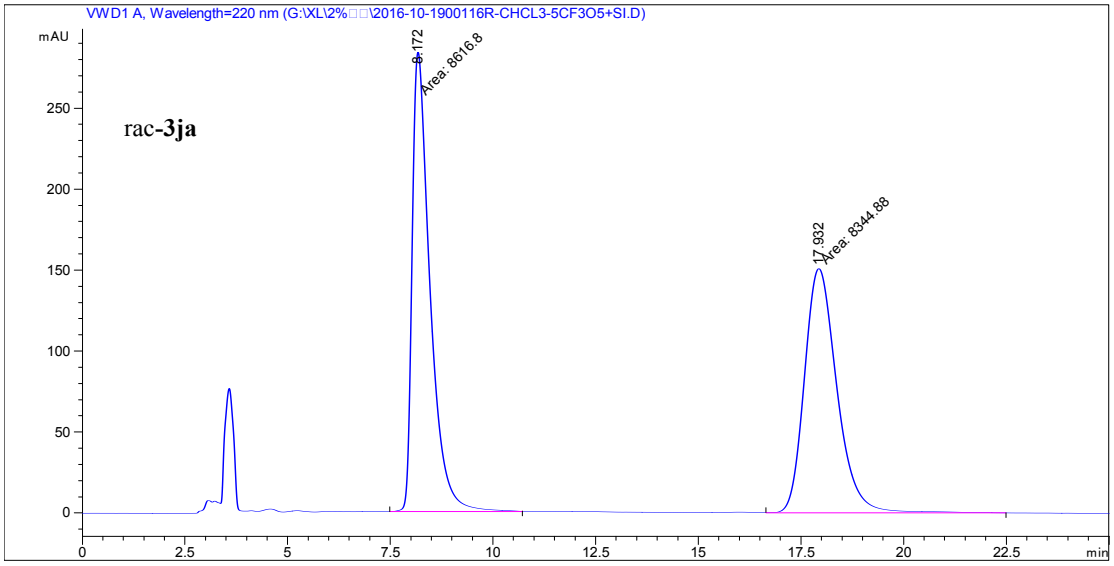


#	Time	Area	Height	Width	Area%	Symmetry
1	21.98	25093.1	369.8	1.0077	49.860	0.557
2	26.593	25233.6	314.6	1.2167	50.140	0.599

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 7.62 min, t_R (minor) = 15.36 min; 96% ee.

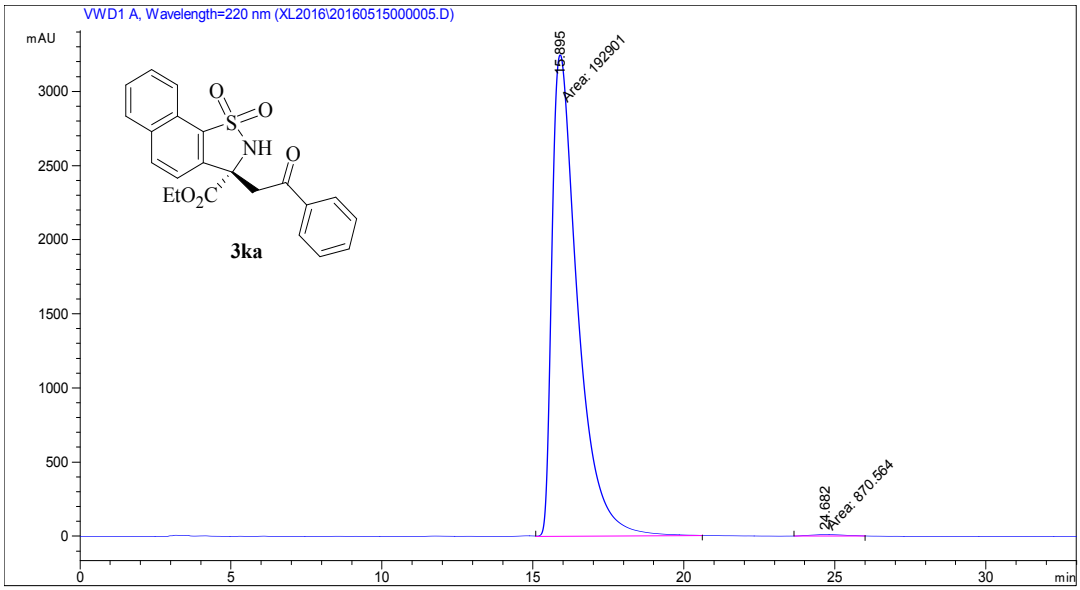


#	Time	Area	Height	Width	Area%	Symmetry
1	8.043	19134.5	657.6	0.485	98.172	0.376
2	18.015	356.3	6.6	0.8978	1.828	0.842

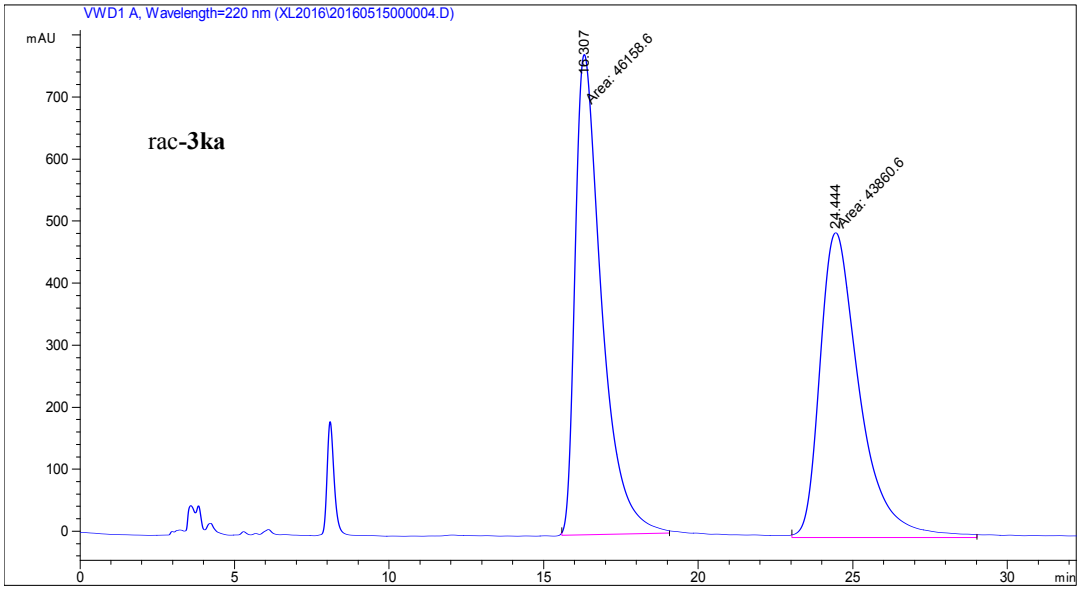


#	Time	Area	Height	Width	Area%	Symmetry
1	8.172	8616.8	283.8	0.506	50.802	0.472
2	17.932	8344.9	150.9	0.9215	49.198	0.754

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 15.86 min, t_R (minor) = 24.68 min; 99% ee.

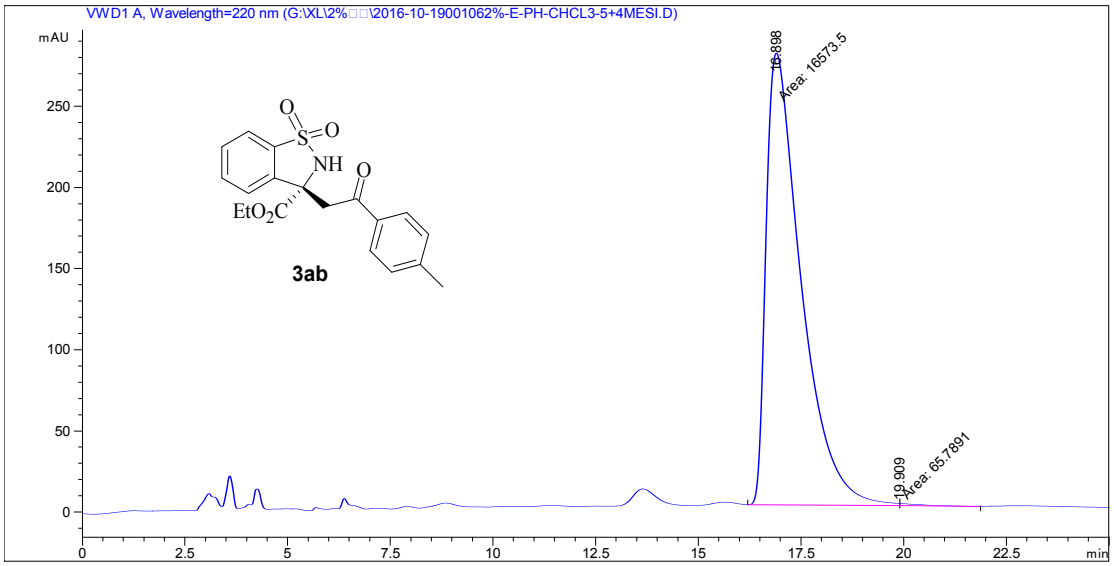


#	Time	Area	Height	Width	Area%	Symmetry
1	15.895	192901.2	3248.4	0.9897	99.551	0.444
2	24.682	870.6	10.9	1.3344	0.449	0.759

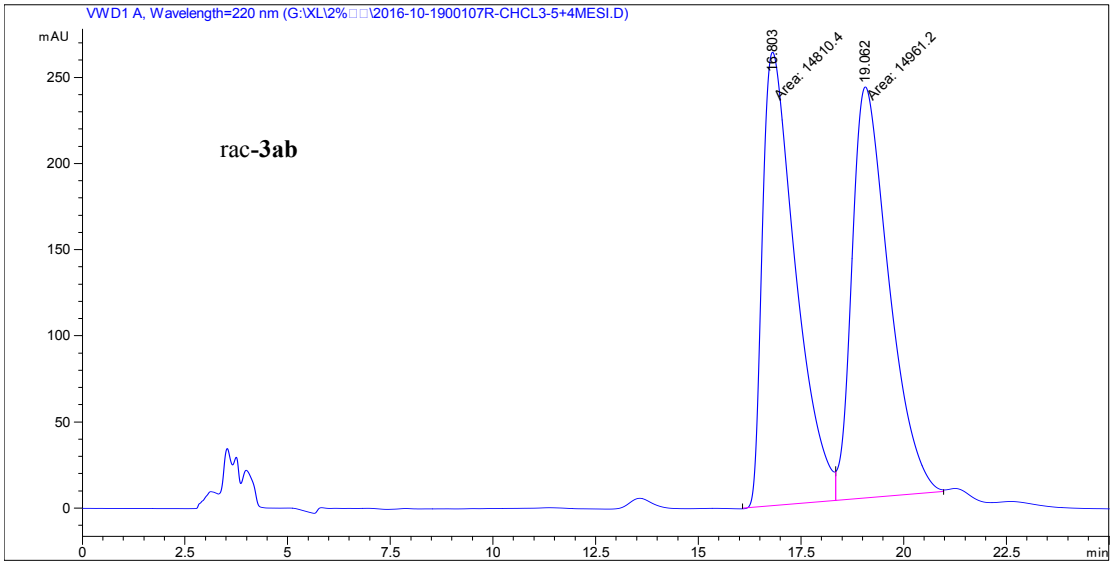


#	Time	Area	Height	Width	Area%	Symmetry
1	16.307	46158.6	774.8	0.9929	51.276	0.502
2	24.444	43860.6	491.4	1.4875	48.724	0.632

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 19.62 min, t_R (major) = 20.80 min; 99% ee.

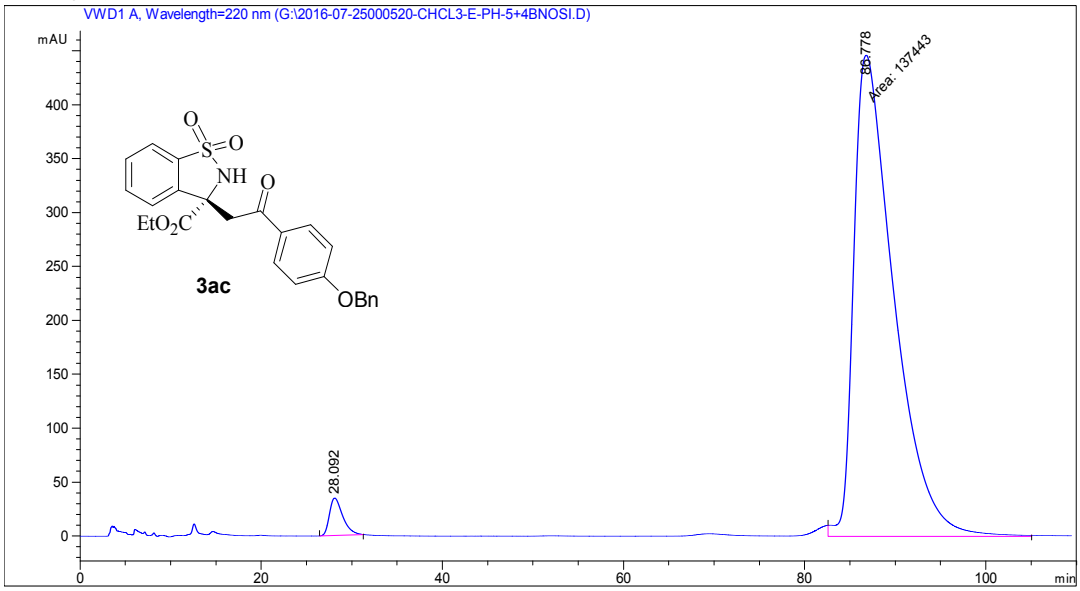


#	Time	Area	Height	Width	Area%	Symmetry
1	16.898	16573.5	278.5	0.992	99.605	0.396
2	19.909	65.8	1.5	0.7291	0.395	0

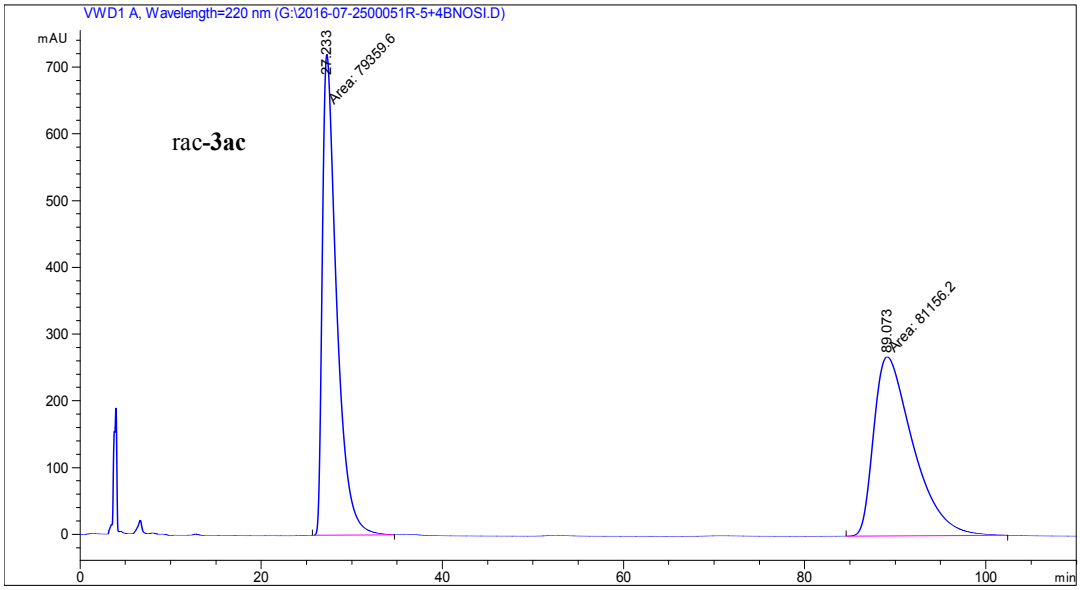


#	Time	Area	Height	Width	Area%	Symmetry
1	16.803	14810.4	263.4	0.9372	49.747	0
2	19.062	14961.2	238.7	1.0447	50.253	0.555

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (minor) = 28.09 min, t_R (major) = 86.78 min; 95% ee.

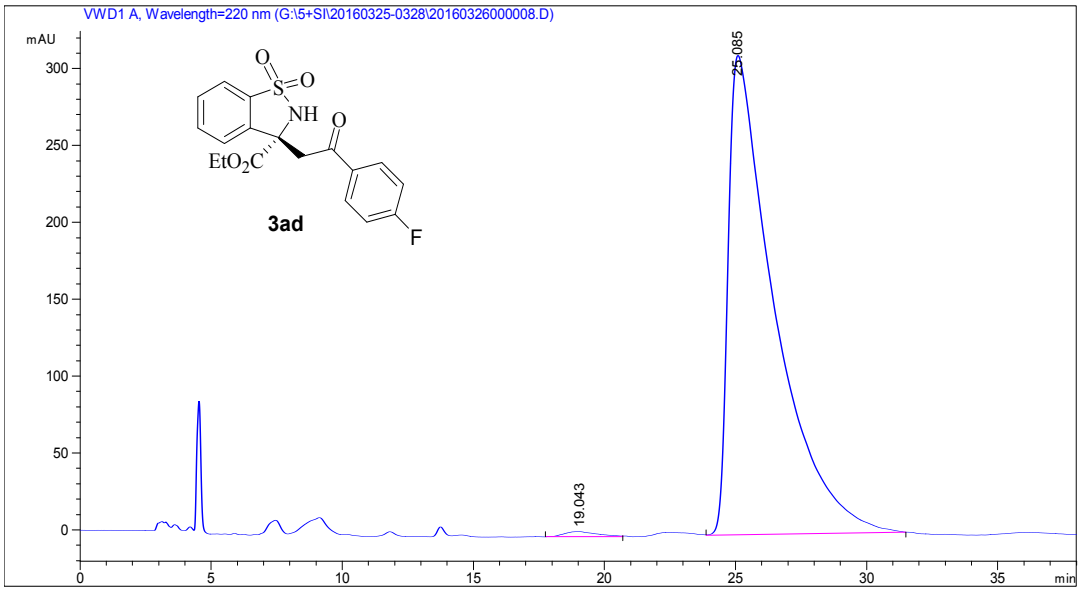


#	Time	Area	Height	Width	Area%	Symmetry
1	28.092	3548.7	34.8	1.5428	2.517	0.606
2	86.778	137443.2	446.5	5.1309	97.483	0.439

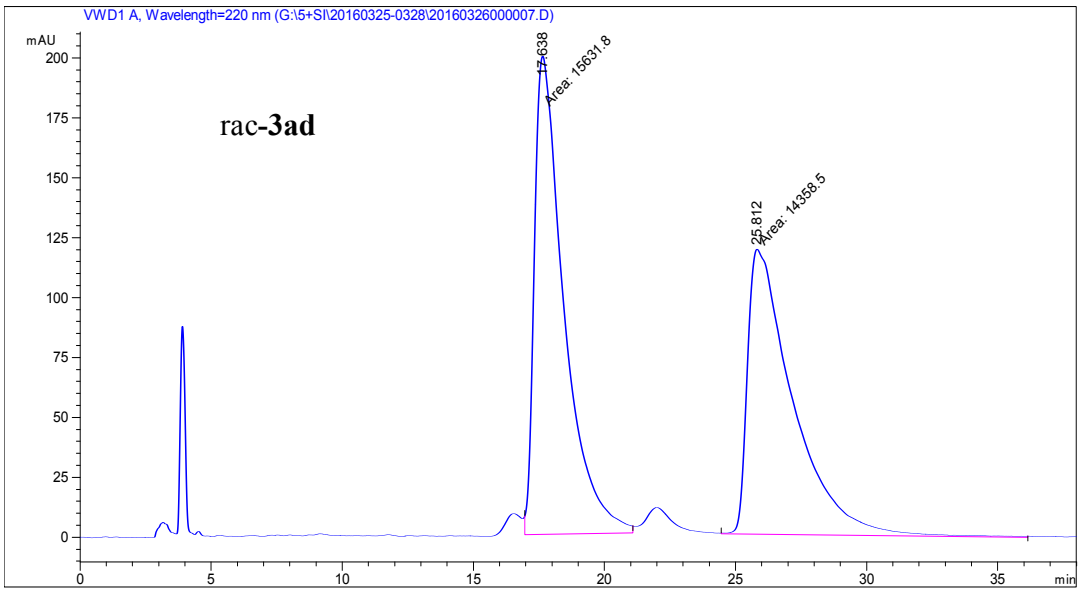


#	Time	Area	Height	Width	Area%	Symmetry
1	27.233	79359.6	720.6	1.8355	49.440	0.442
2	89.073	81156.2	268.7	5.0336	50.560	0.498

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 19.04 min, t_R (major) = 25.08 min; 98% ee.

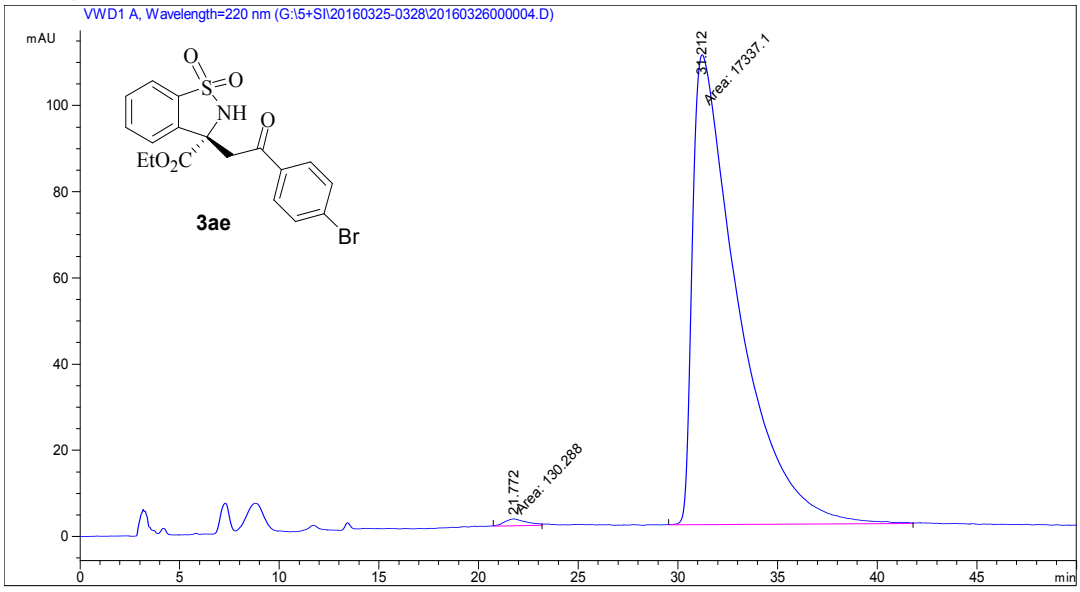


#	Time	Area	Height	Width	Area%	Symmetry
1	19.043	314.8	3.5	1.0687	0.818	0.82
2	25.085	38145.9	312	1.6188	99.182	0.25

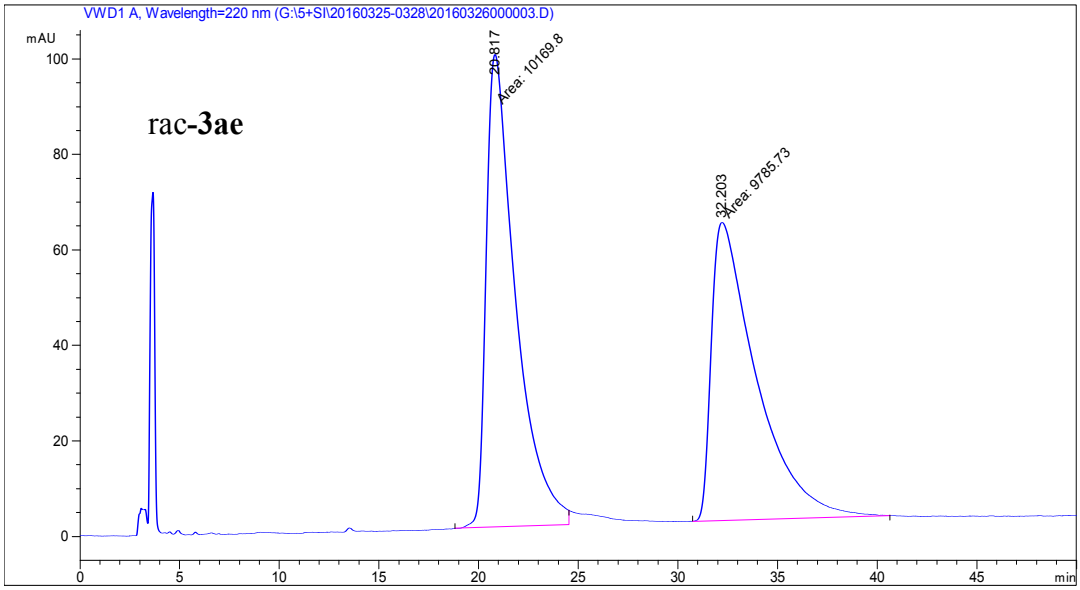


#	Time	Area	Height	Width	Area%	Symmetry
1	17.638	15631.8	199.6	1.3054	52.123	0.377
2	25.812	14358.5	118.9	2.012	47.877	0.26

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 21.77 min, t_R (major) = 31.21 min; 98%.

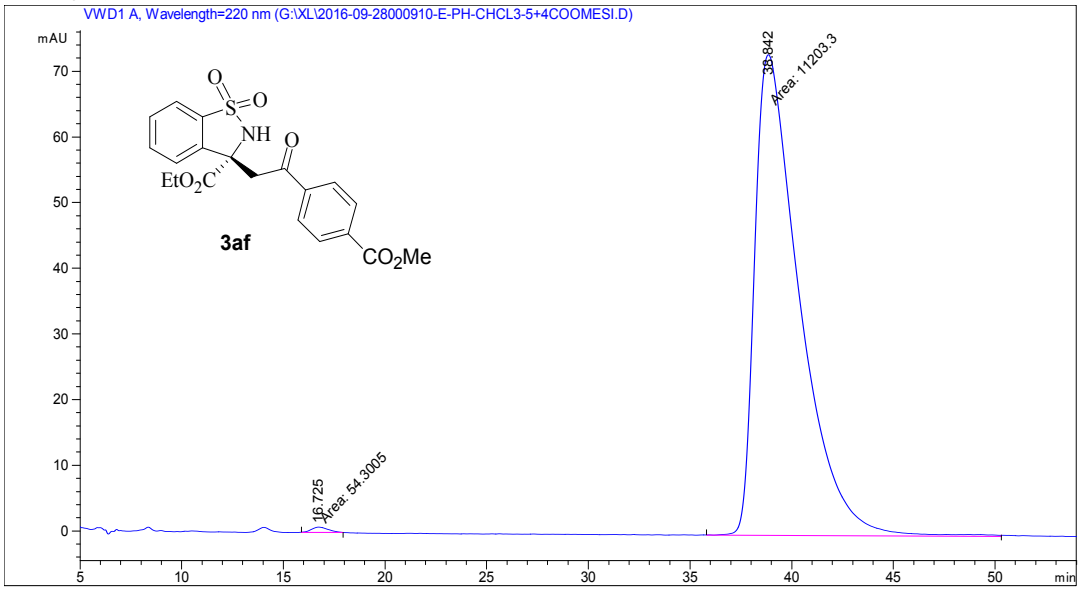


#	Time	Area	Height	Width	Area%	Symmetry
1	21.772	130.3	1.7	1.2896	0.746	0.777
2	31.212	17337.1	109	2.6502	99.254	0.262

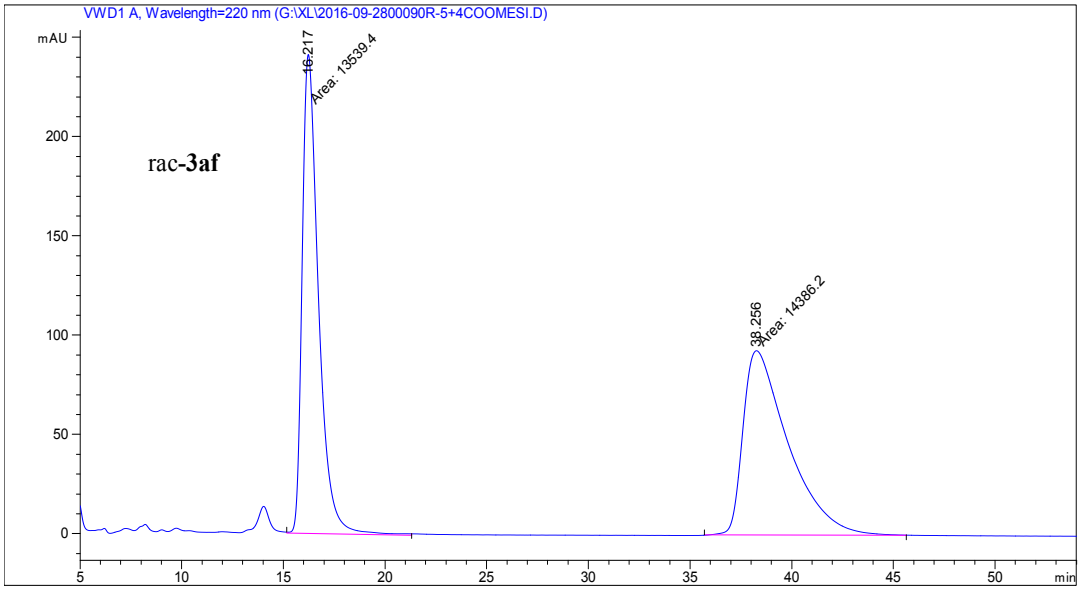


#	Time	Area	Height	Width	Area%	Symmetry
1	20.817	10169.8	99	1.7126	50.962	0.413
2	32.203	9785.7	62.5	2.6102	49.038	0.299

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (minor) = 16.73 min, t_R (major) = 38.84 min; 99% ee.

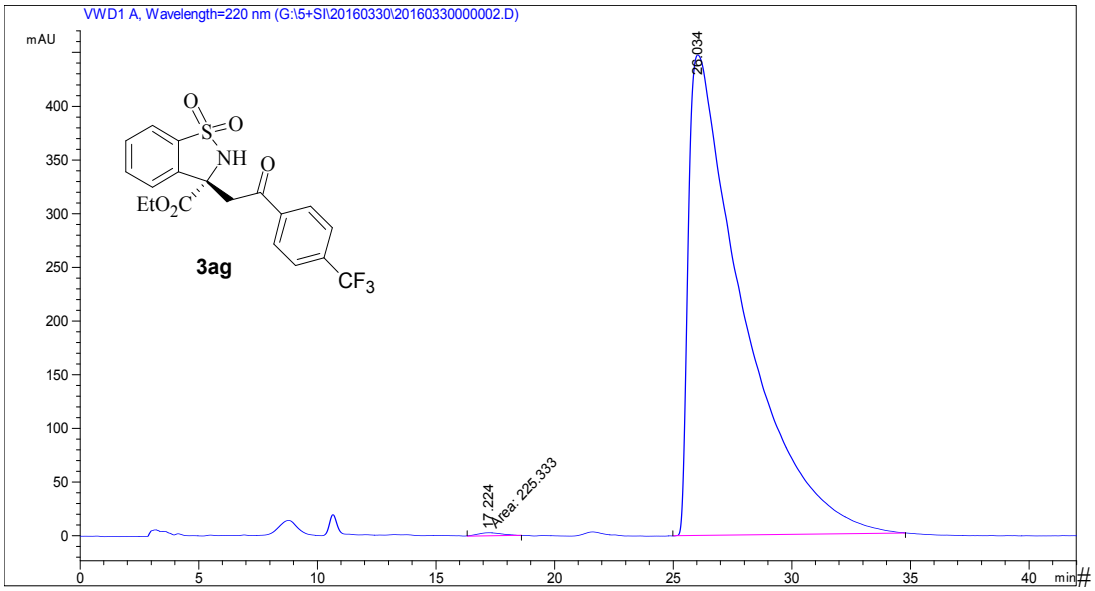


#	Time	Area	Height	Width	Area%	Symmetry
1	16.725	54.3	8.8E-1	1.031	0.482	0.736
2	38.842	11203.3	73.2	2.5503	99.518	0.423

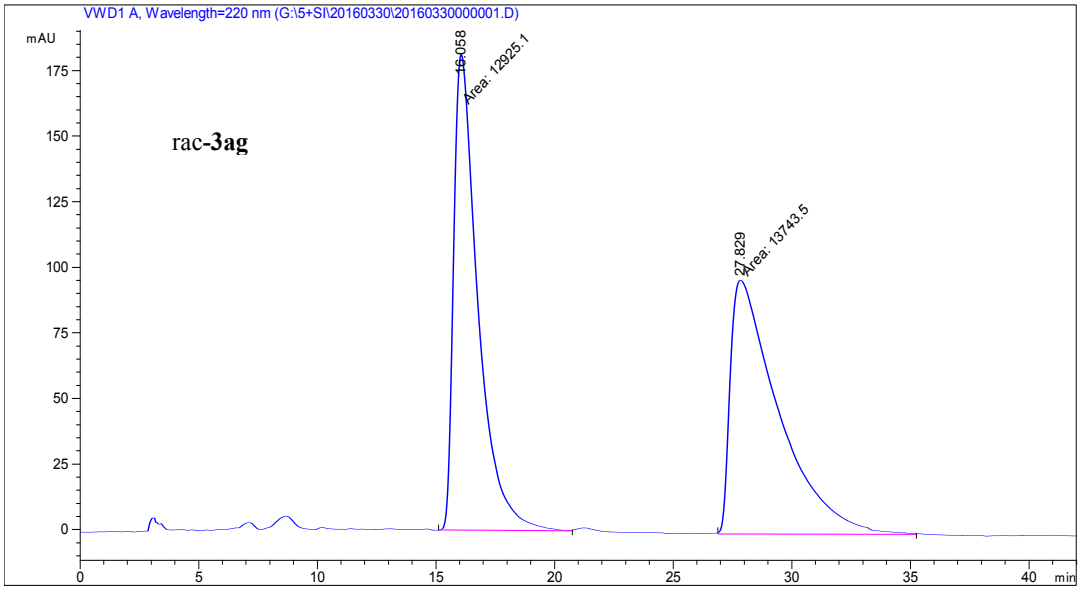


#	Time	Area	Height	Width	Area%	Symmetry
1	16.217	13539.4	241.4	0.9349	48.484	0.57
2	38.256	14386.2	92.9	2.5812	51.516	0.411

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 17.22 min, t_R (major) = 26.03 min; 99% ee.

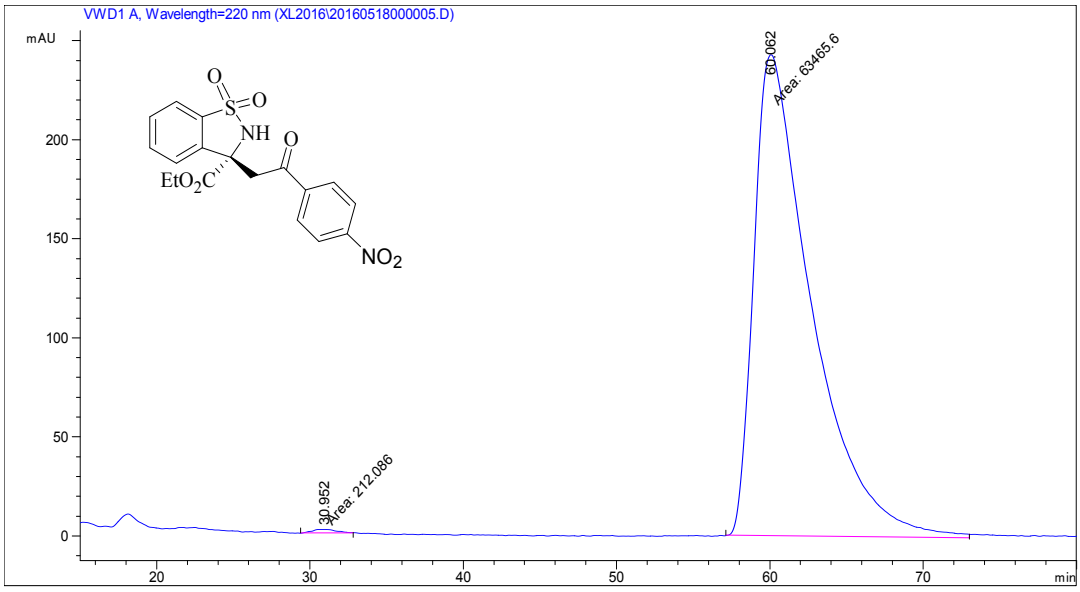


	Time	Area	Height	Width	Area%	Symmetry
1	17.224	225.3	3	1.2328	0.313	0.867
2	26.034	71848.7	447.6	2.1057	99.687	0.19

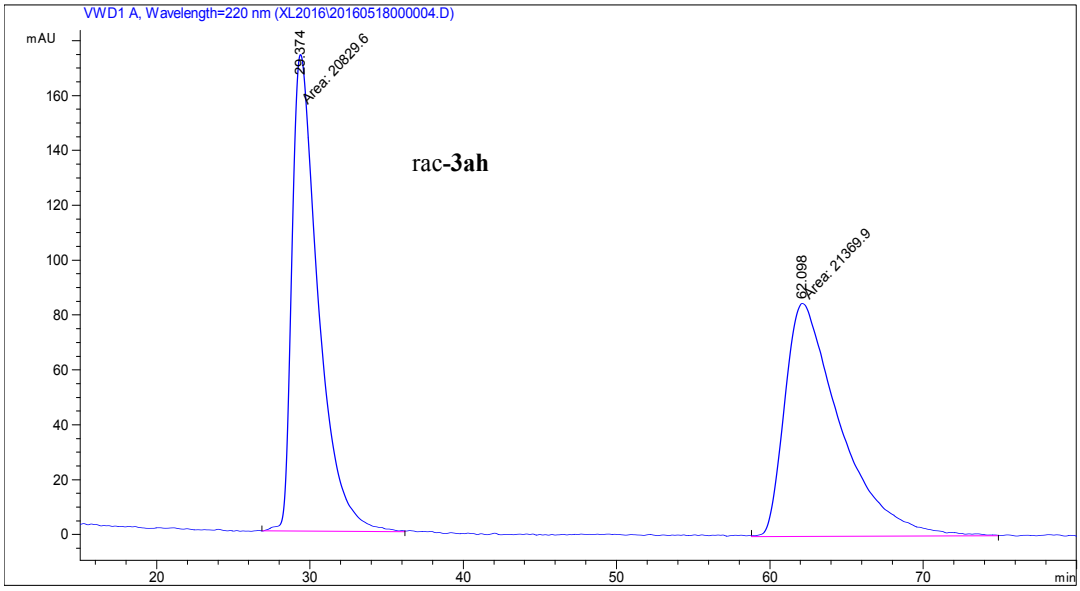


#	Time	Area	Height	Width	Area%	Symmetry
1	16.058	12925.1	181.4	1.1875	48.466	0.428
2	27.829	13743.5	96.8	2.3662	51.534	0.256

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (minor) = 30.95 min, t_R (major) = 60.06 min; 99% ee.

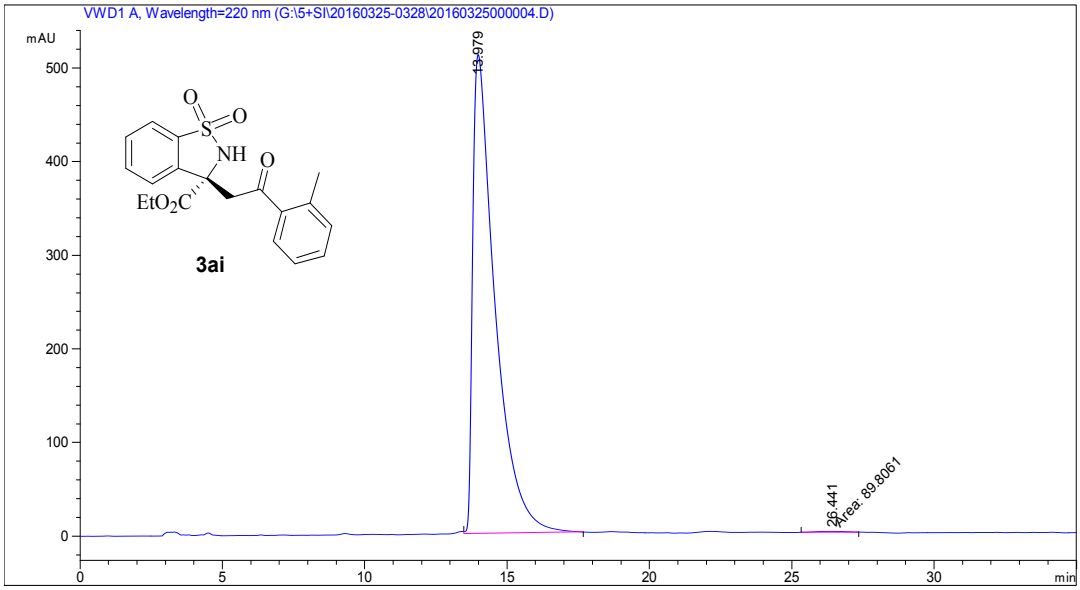


#	Time	Area	Height	Width	Area%	Symmetry
1	30.952	212.1	1.9	1.8912	0.333	1.027
2	60.062	63465.6	242.8	4.357	99.667	0.405

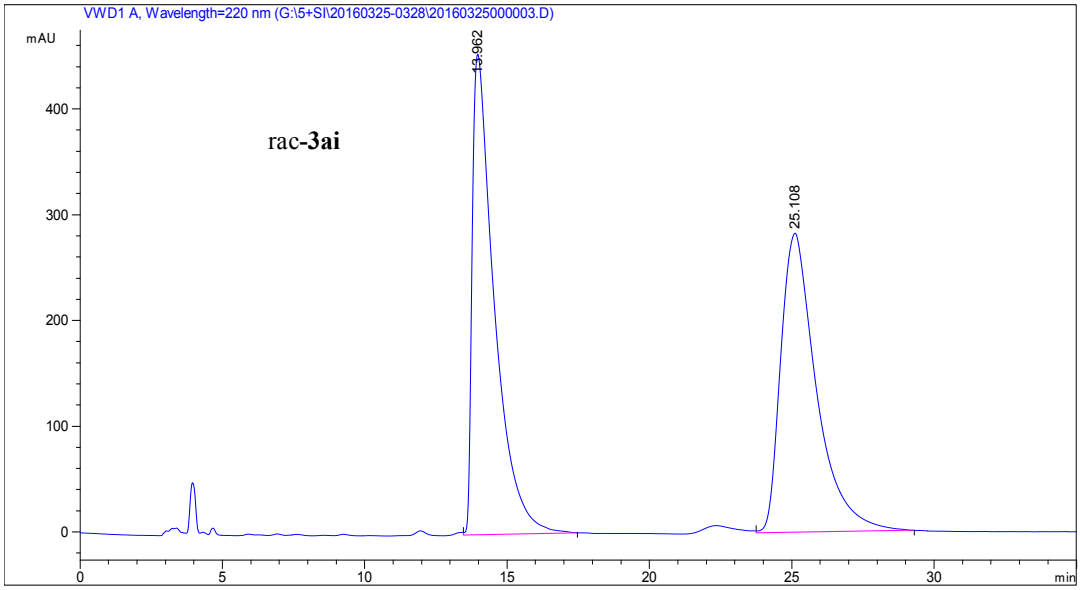


#	Time	Area	Height	Width	Area%	Symmetry
1	29.374	20829.6	173.7	1.9984	49.360	0.466
2	62.098	21369.9	85.1	4.1875	50.640	0.444

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 13.98 min, t_R (minor) = 26.44 min; 99% ee.

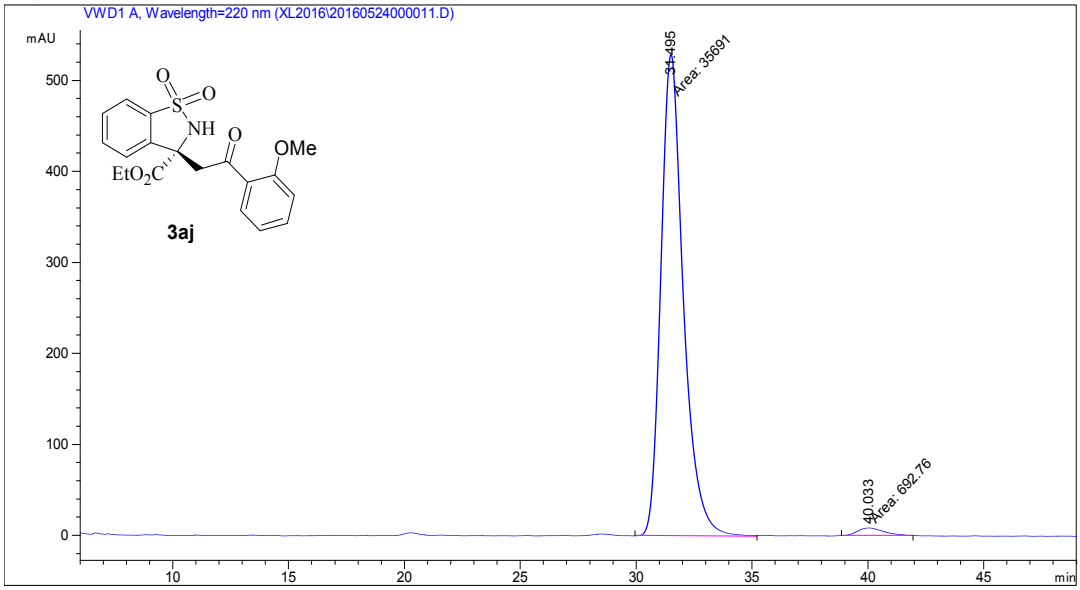


#	Time	Area	Height	Width	Area%	Symmetry
1	13.979	27900.8	511.9	0.7757	99.679	0.292
2	26.441	89.8	1.1	1.3116	0.321	1.129

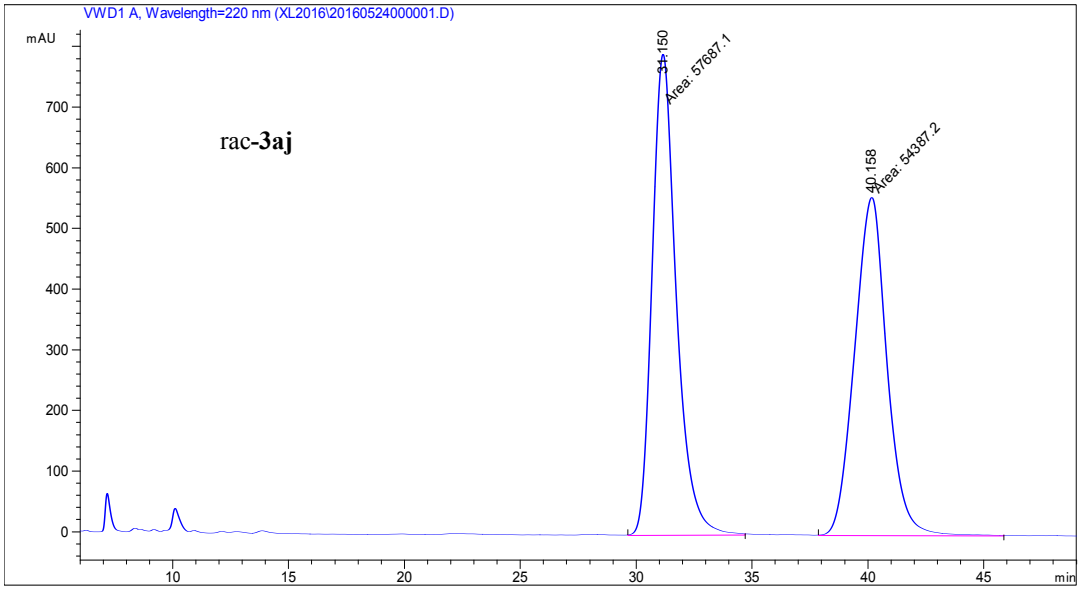


#	Time	Area	Height	Width	Area%	Symmetry
1	13.962	24622.2	454.7	0.7789	49.980	0.298
2	25.108	24642.4	282.9	1.2943	50.020	0.611

Daicel Chiralpak AD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (major) = 31.50 min, t_R (minor) = 40.03 min; 96% ee.

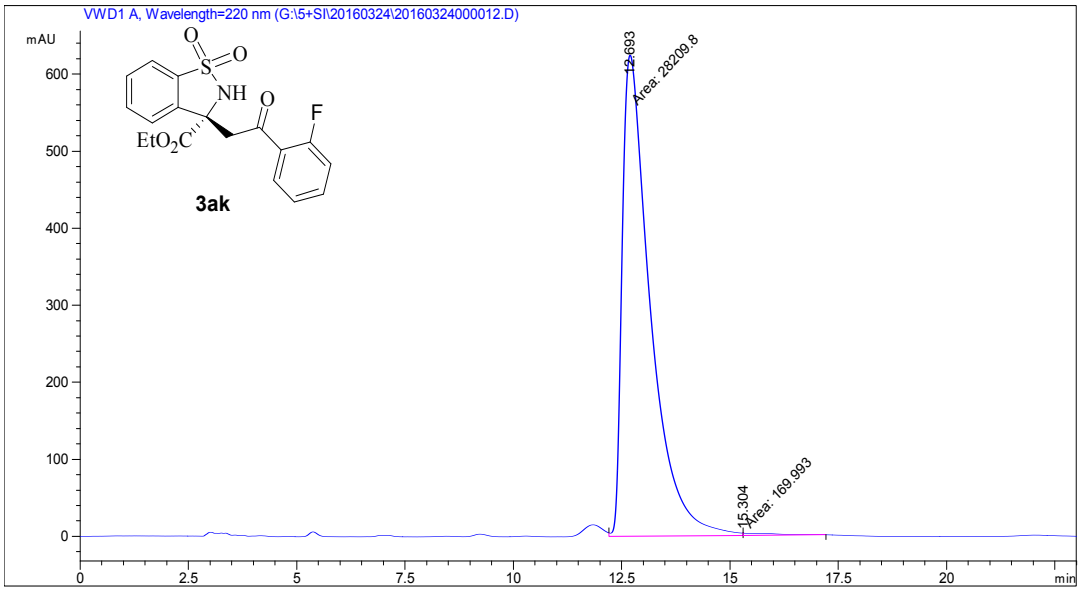


#	Time	Area	Height	Width	Area%	Symmetry
1	31.495	35691	529	1.1246	98.096	0.776
2	40.033	692.8	8.6	1.3488	1.904	0.726

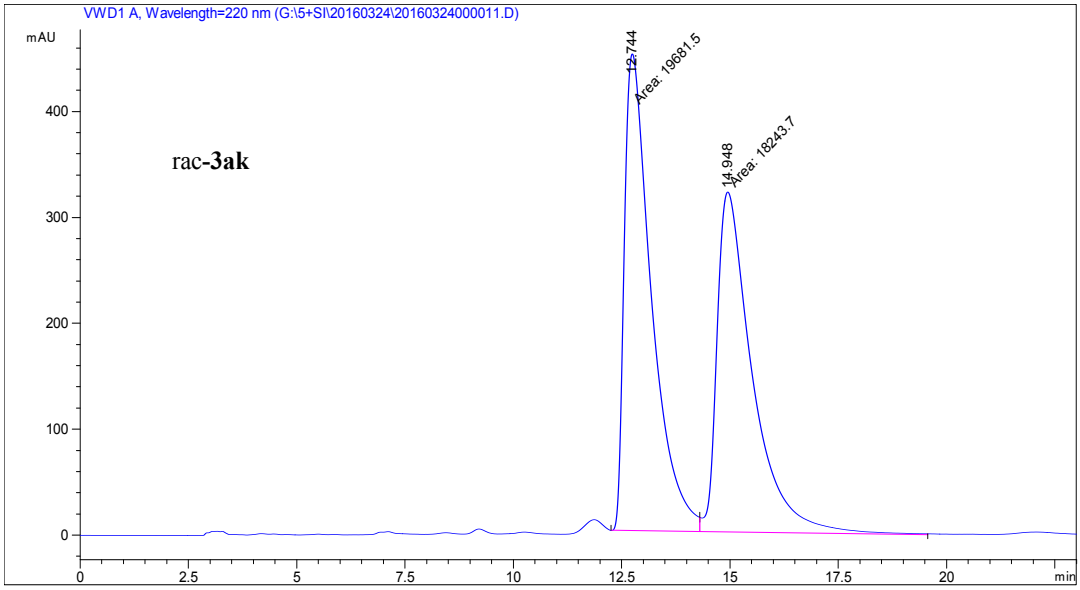


#	Time	Area	Height	Width	Area%	Symmetry
1	31.15	57687.1	793.4	1.2118	51.472	0.779
2	40.158	54387.2	557.8	1.6249	48.528	1.058

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 12.69 min, t_R (minor) = 15.30 min; 99% ee.

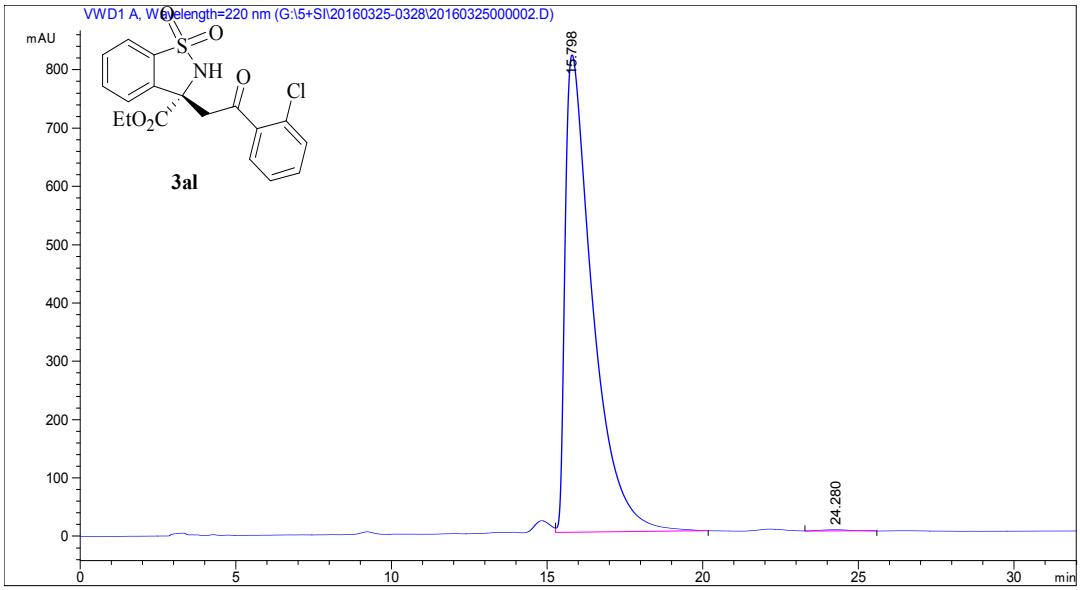


#	Time	Area	Height	Width	Area%	Symmetry
1	12.693	28209.8	624.8	0.7525	99.401	0.376
2	15.304	170	3.1	0.9207	0.599	0

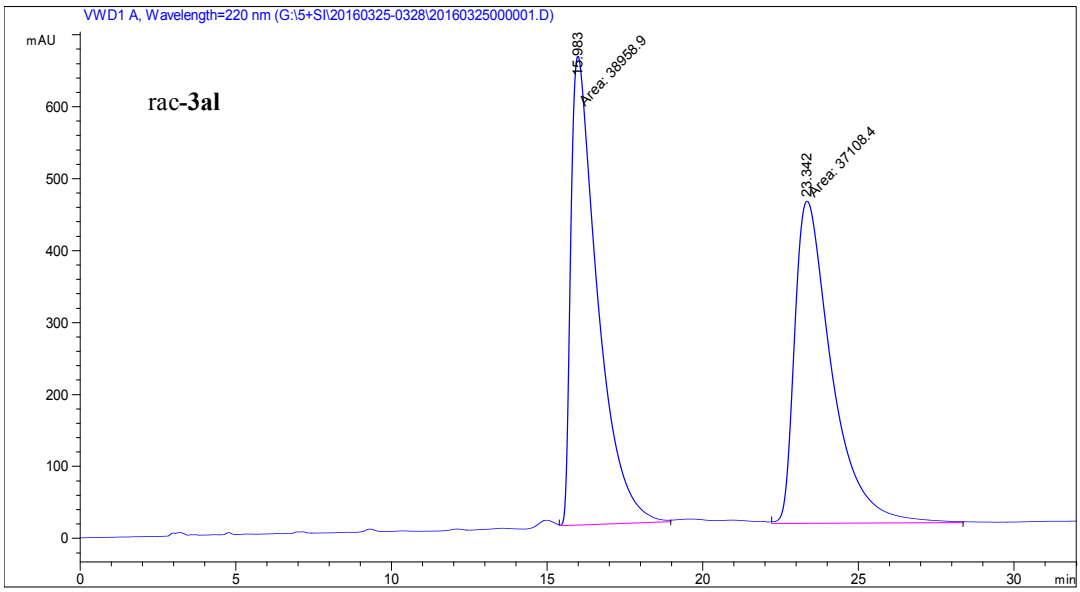


#	Time	Area	Height	Width	Area%	Symmetry
1	12.744	19681.5	450.2	0.7287	51.896	0.397
2	14.948	18243.7	321.1	0.9471	48.104	0.42

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 15.80 min, t_R (minor) = 24.28 min; 99% ee.

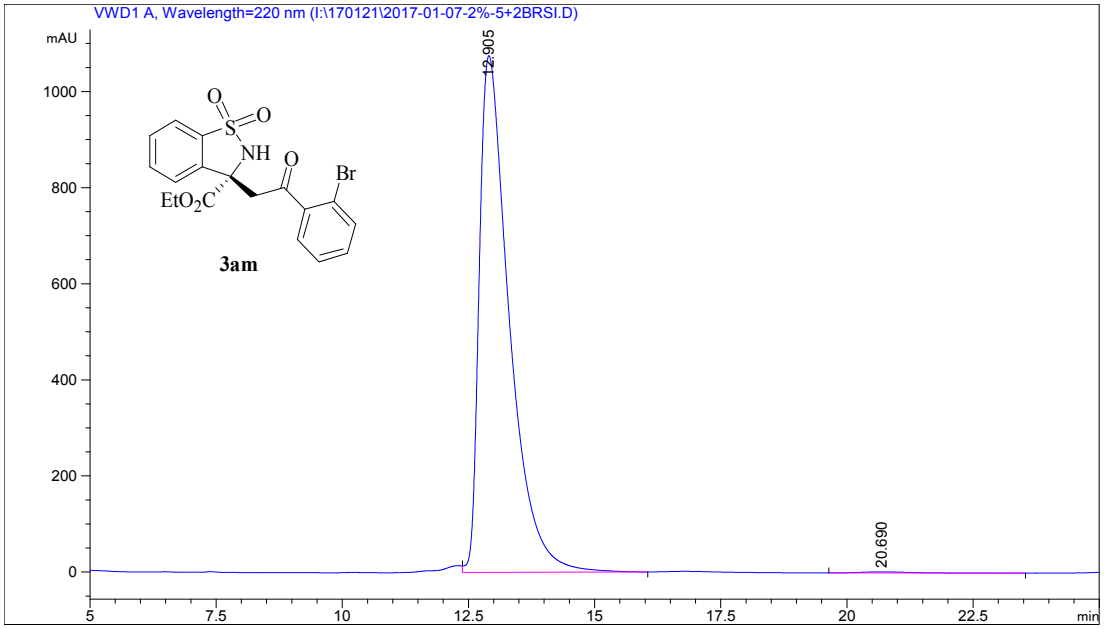


#	Time	Area	Height	Width	Area%	Symmetry
1	15.798	50280.4	819.4	0.8906	99.680	0.308
2	24.28	161.3	2.3	0.8352	0.320	1.104

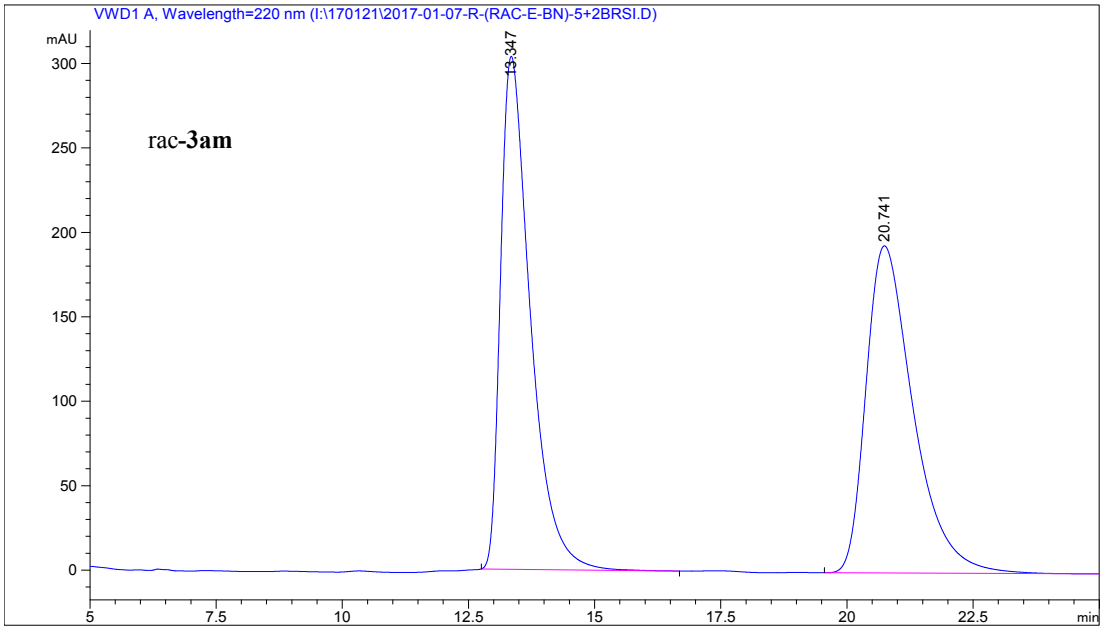


#	Time	Area	Height	Width	Area%	Symmetry
1	15.983	38958.9	652.1	0.9958	51.216	0.346
2	23.342	37108.4	448	1.3806	48.784	0.482

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 12.91 min, t_R (major) = 20.69 min; 99% ee.

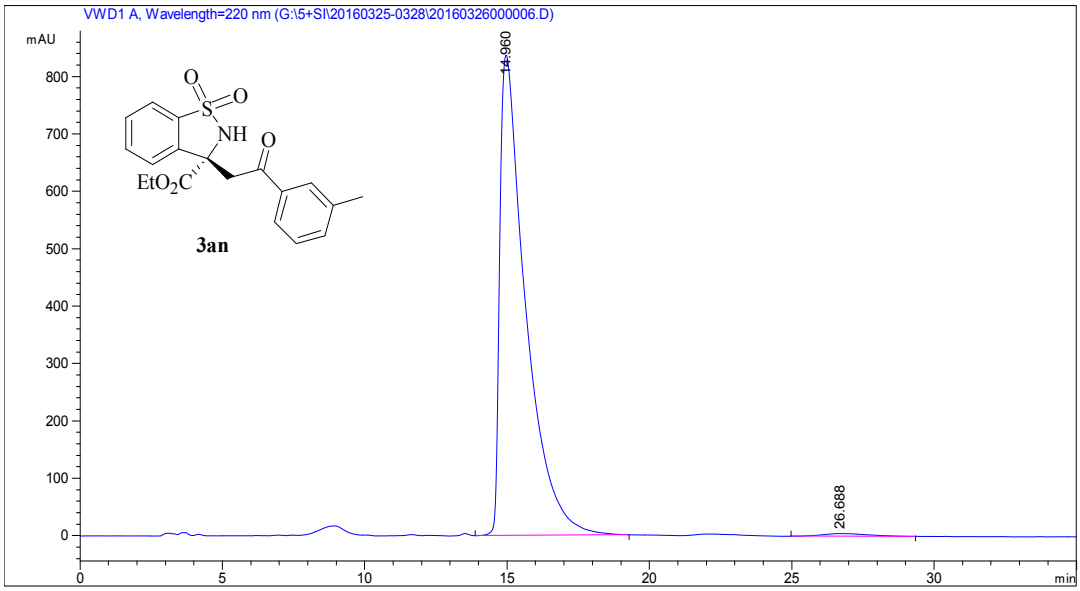


#	Time	Area	Height	Width	Area%	Symmetry
1	12.905	44398.8	1075.7	0.6165	99.662	0.431
2	20.69	150.4	2.3	0.8493	0.338	0.742

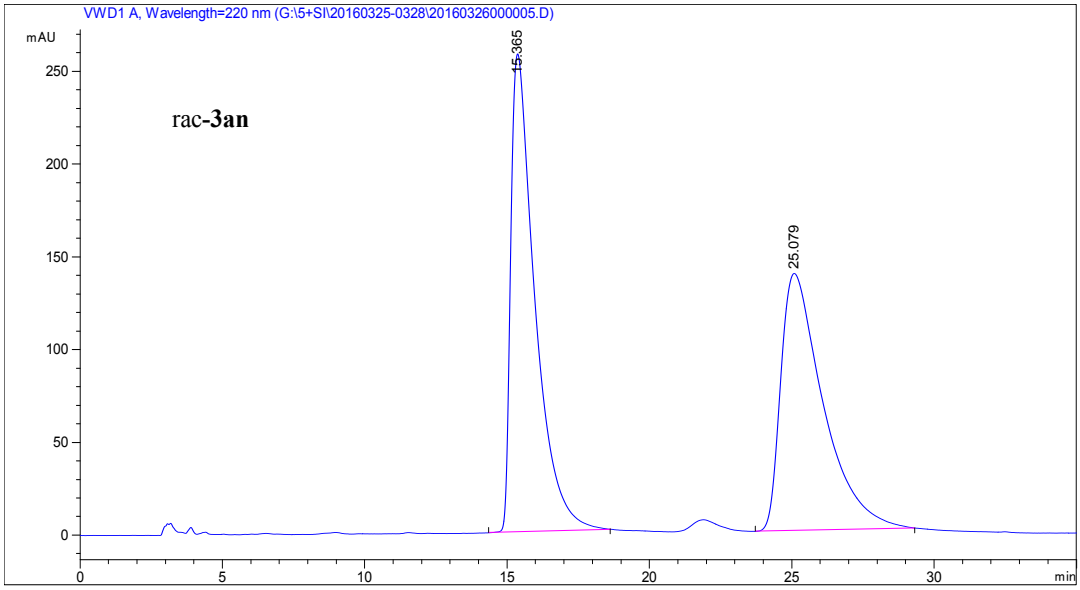


#	Time	Area	Height	Width	Area%	Symmetry
1	13.347	12482	303.7	0.5874	49.755	0.503
2	20.741	12604.9	193.8	0.9919	50.245	0.594

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 14.96 min, t_R (minor) = 26.69 min; 98% ee.

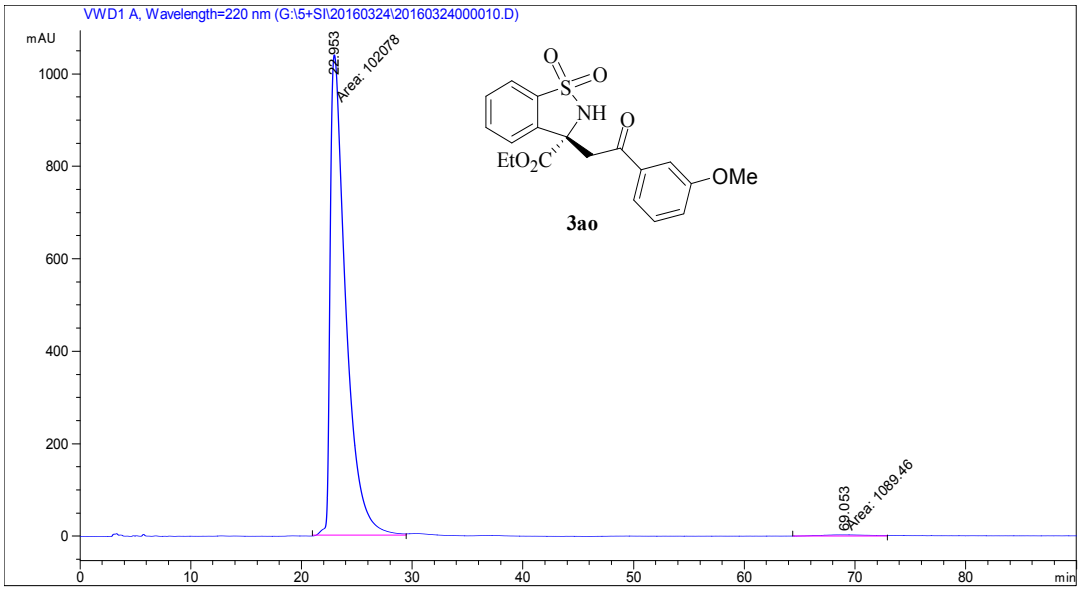


#	Time	Area	Height	Width	Area%	Symmetry
1	14.96	52905.9	837.2	0.9062	98.964	0.291
2	26.688	553.8	4.8	1.3484	1.036	0.628

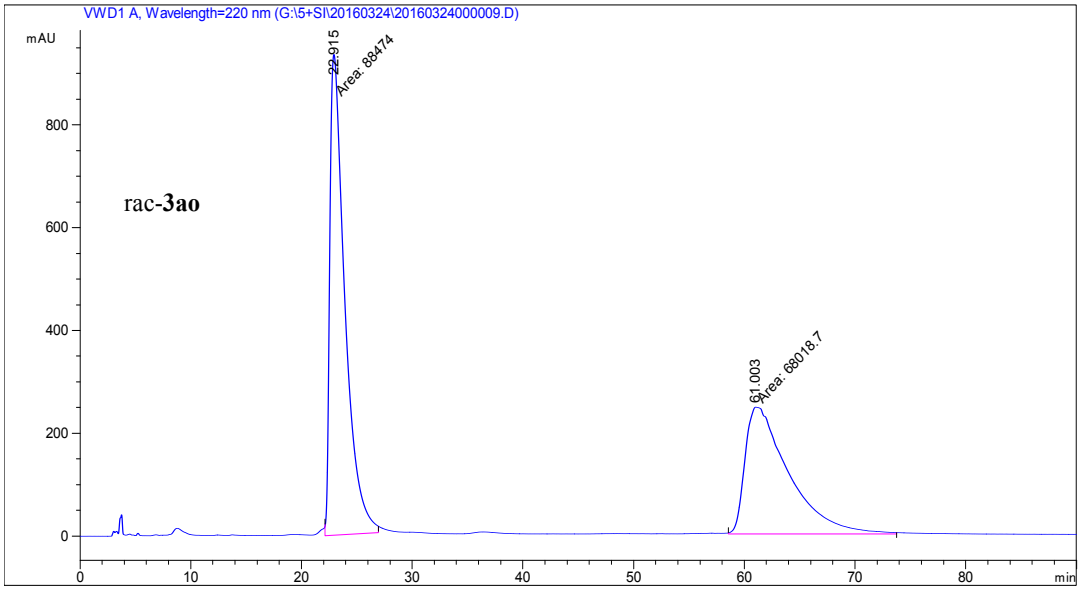


#	Time	Area	Height	Width	Area%	Symmetry
1	15.365	15185.5	257.7	0.8477	51.433	0.363
2	25.079	14339.3	138.6	1.4345	48.567	0.431

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 22.95 min, t_R (minor) = 69.05 min; 98% ee.

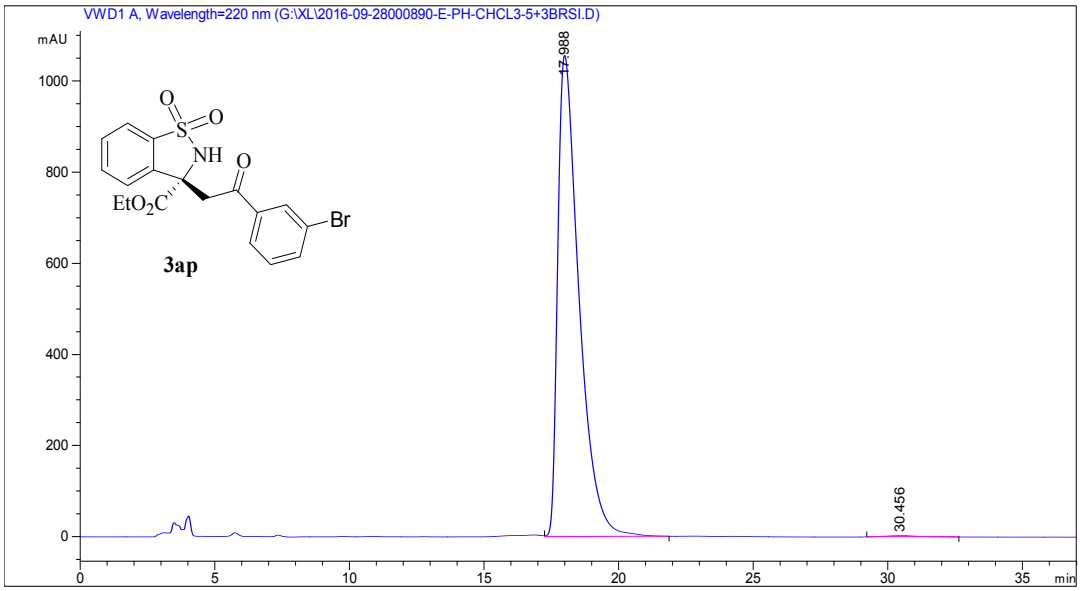


#	Time	Area	Height	Width	Area%	Symmetry
1	22.953	102077.6	1039.7	1.6363	98.944	0.348
2	69.053	1089.5	3.2	5.7164	1.056	0.827

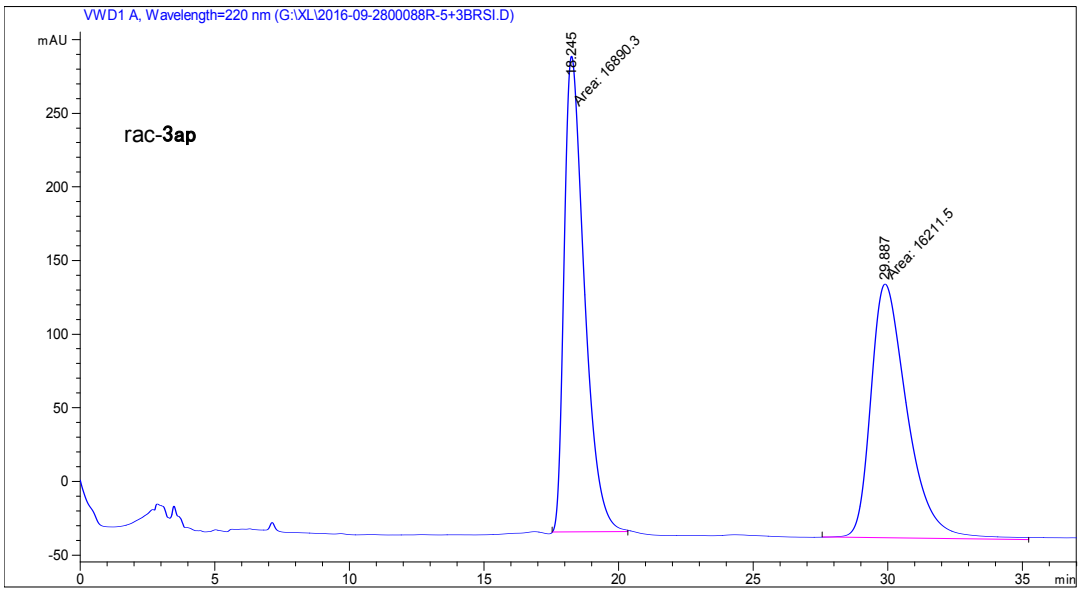


#	Time	Area	Height	Width	Area%	Symmetry
1	22.915	88474	935.4	1.5764	56.536	0.359
2	61.003	68018.7	247	4.5891	43.464	0.314

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 17.99 min, t_R (minor) = 30.46 min; 99% ee.

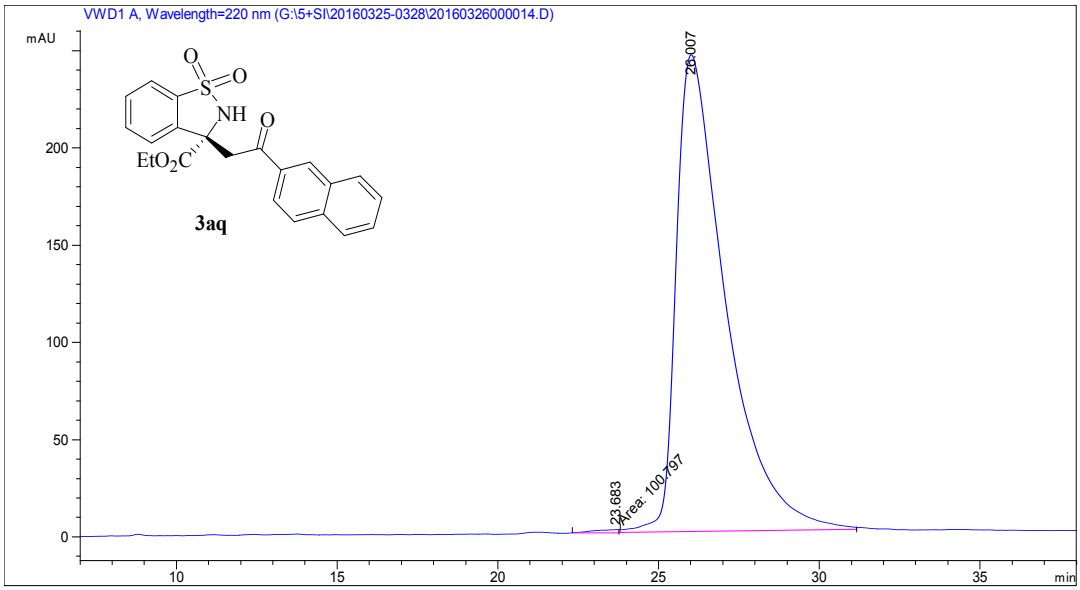


#	Time	Area	Height	Width	Area%	Symmetry
1	17.988	57941	1056.3	0.8169	99.596	0.439
2	30.456	235.3	2.7	1.1501	0.404	0.794

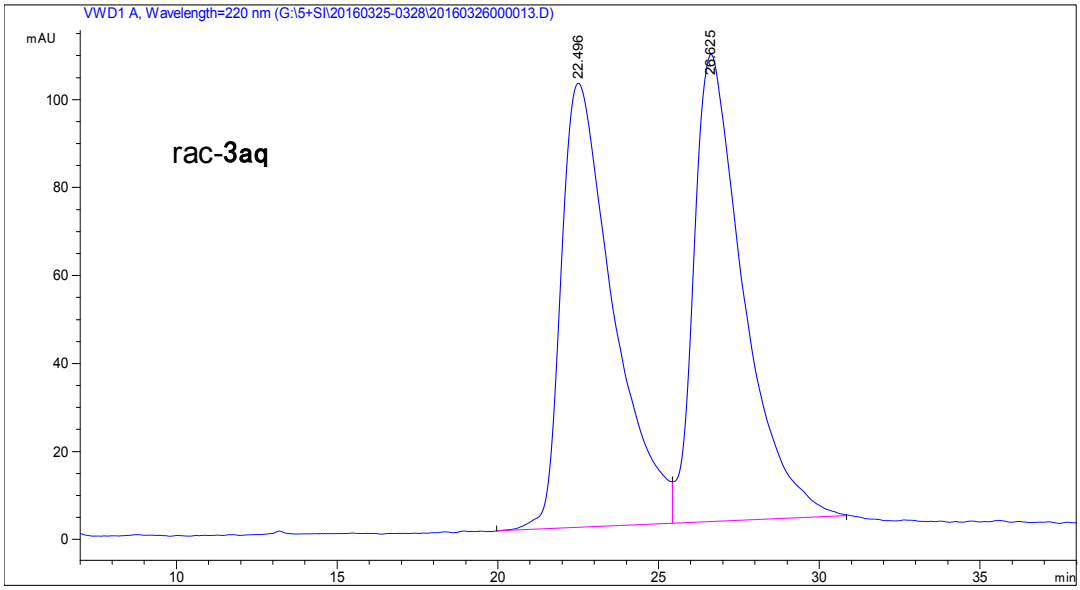


#	Time	Area	Height	Width	Area%	Symmetry
1	18.245	16890.3	323.2	0.871	51.025	0.553
2	29.887	16211.5	172.4	1.5673	48.975	0.615

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 23.68min, t_R (major) = 26.01 min; 99% ee.

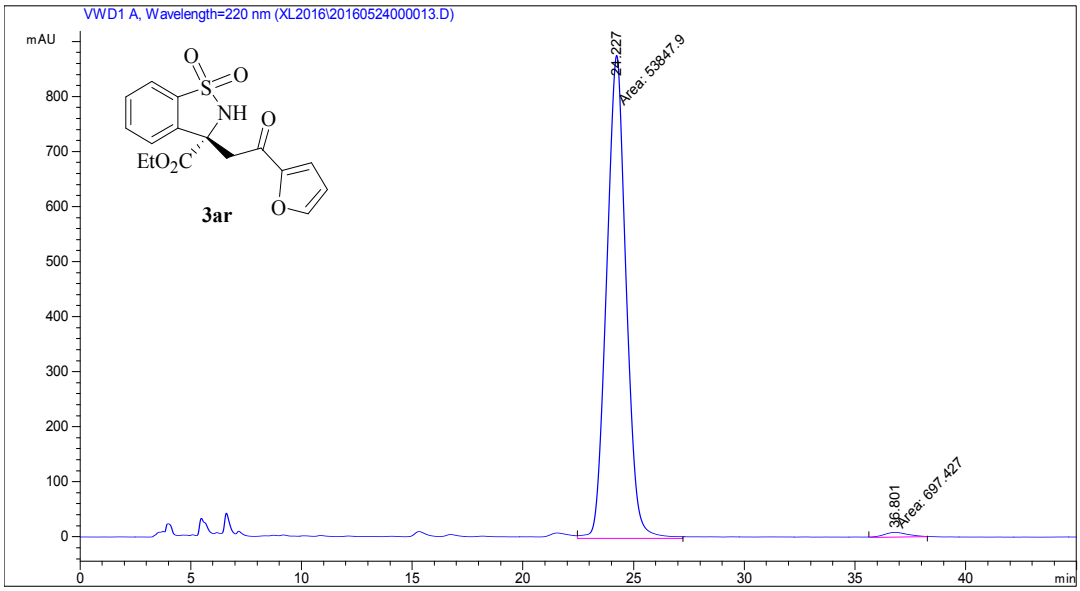


#	Time	Area	Height	Width	Area%	Symmetry
1	23.683	100.8	1.8	0.9157	0.382	8.889
2	26.007	26288.4	245.3	1.5432	99.618	0.408

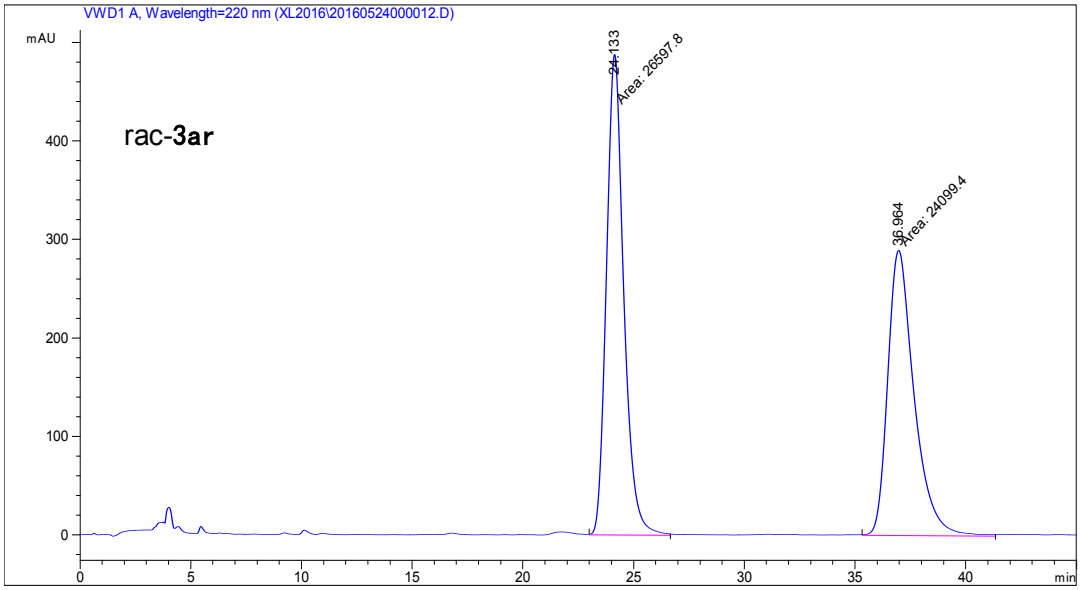


#	Time	Area	Height	Width	Area%	Symmetry
1	22.496	11355.3	101	1.5955	49.928	0.47
2	26.625	11387.9	106.2	1.4722	50.072	0.497

Daicel Chiralpak AD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (major) = 24.23 min, t_R (minor) = 36.80 min; 98% ee.

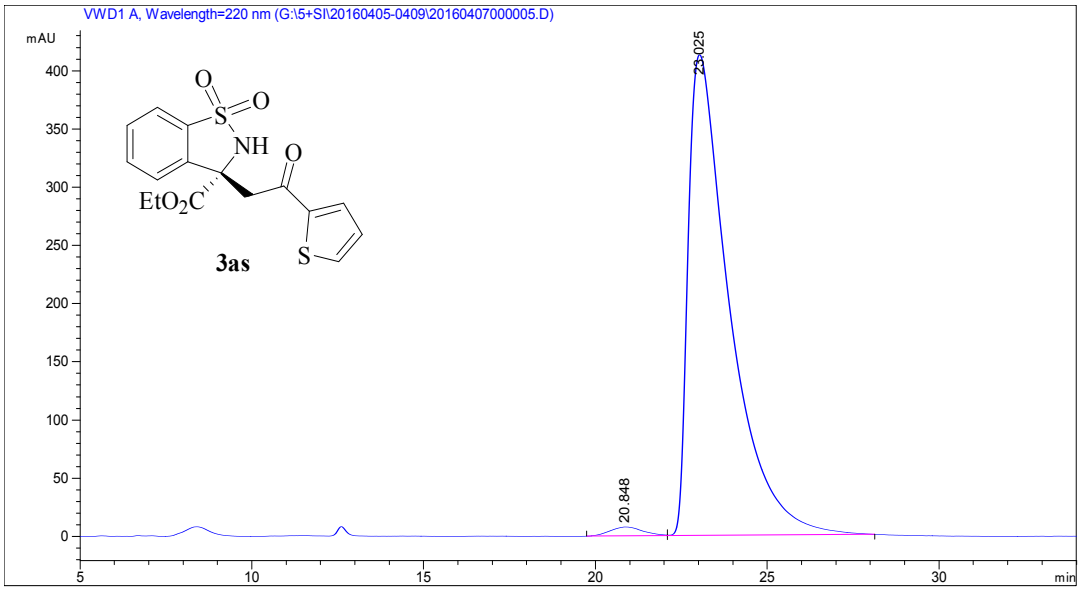


#	Time	Area	Height	Width	Area%	Symmetry
1	24.227	53847.9	878.2	1.0219	98.721	1.008
2	36.801	697.4	8.9	1.3074	1.279	0.9

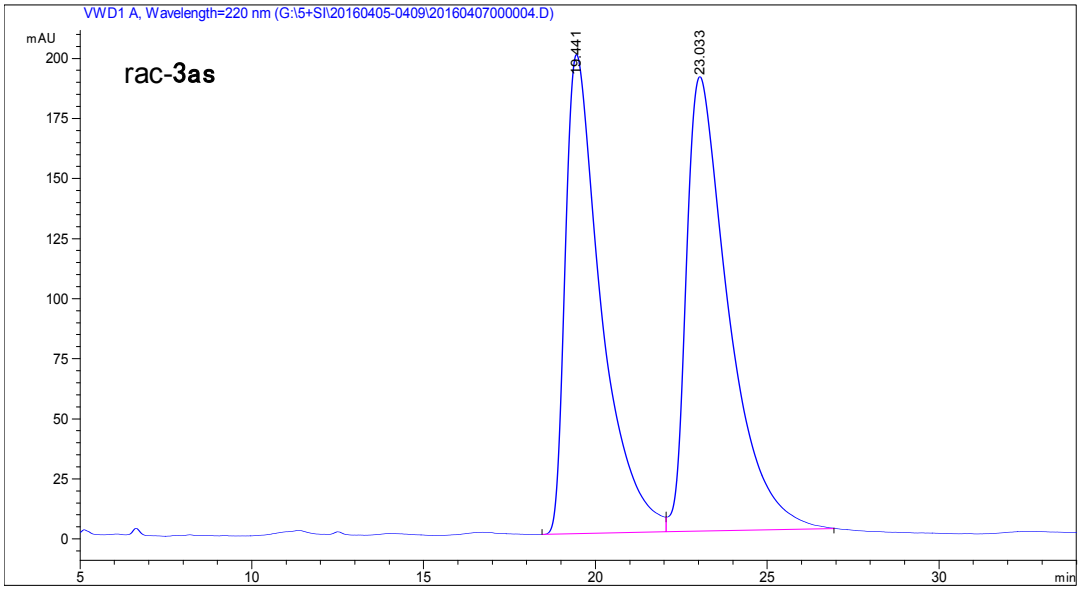


#	Time	Area	Height	Width	Area%	Symmetry
1	24.133	26597.8	488.4	0.9076	52.464	0.837
2	36.964	24099.4	290.1	1.3846	47.536	0.677

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 20.85min, t_R (major) = 23.03 min; 97% ee.

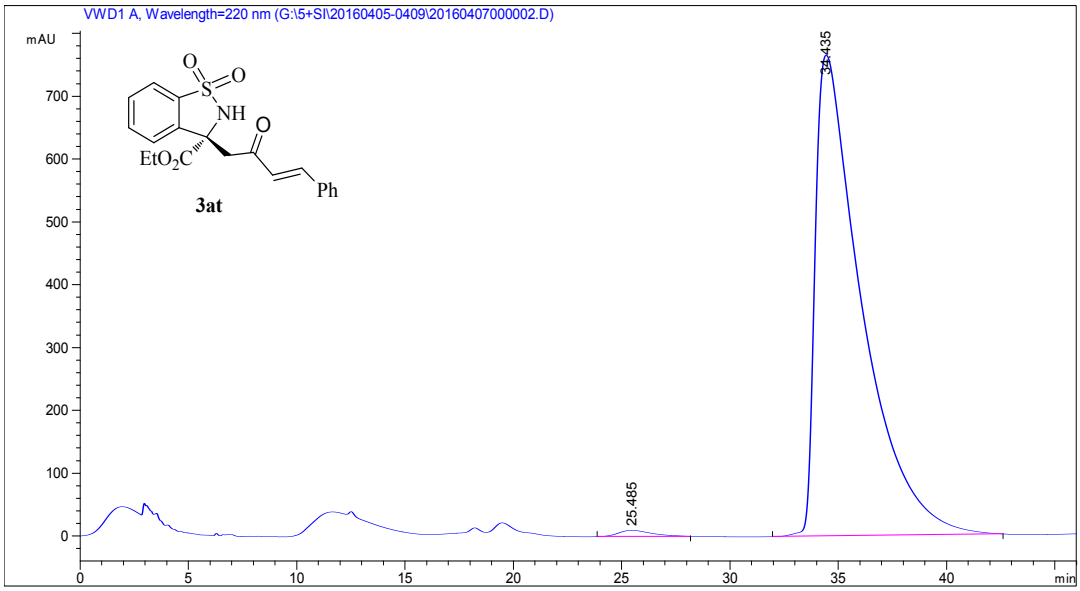


#	Time	Area	Height	Width	Area%	Symmetry
1	20.848	529.2	7.8	0.8119	1.508	0.794
2	23.025	34570.1	413.1	1.1788	98.492	0.348

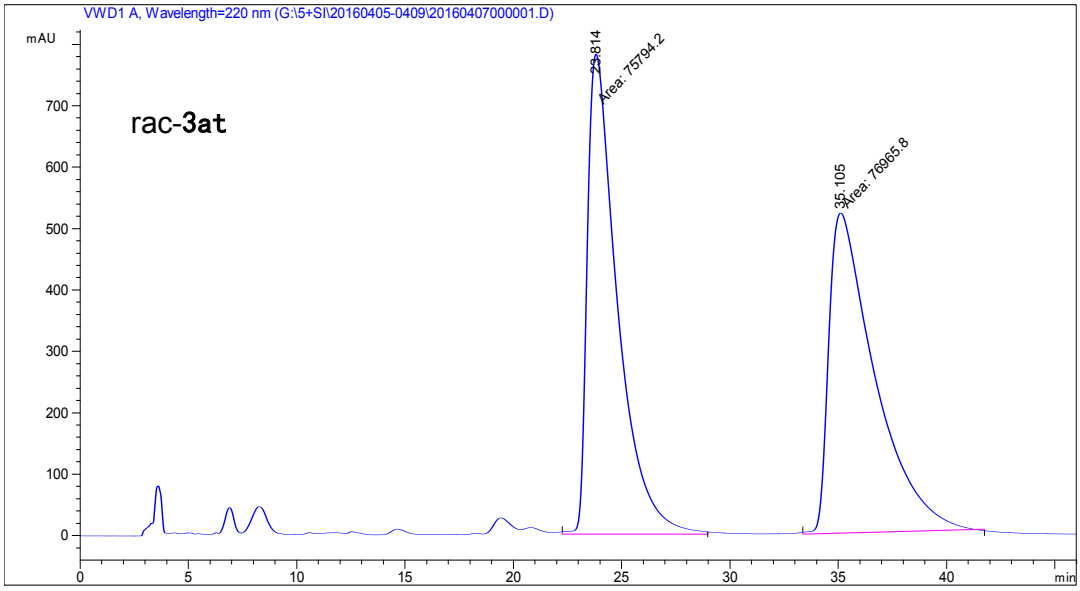


#	Time	Area	Height	Width	Area%	Symmetry
1	19.441	14454.4	199.5	1.0476	47.216	0.414
2	23.033	16159	189.3	1.2144	52.784	0.44

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 25.49 min, t_R (major) = 34.44 min; 98% ee.

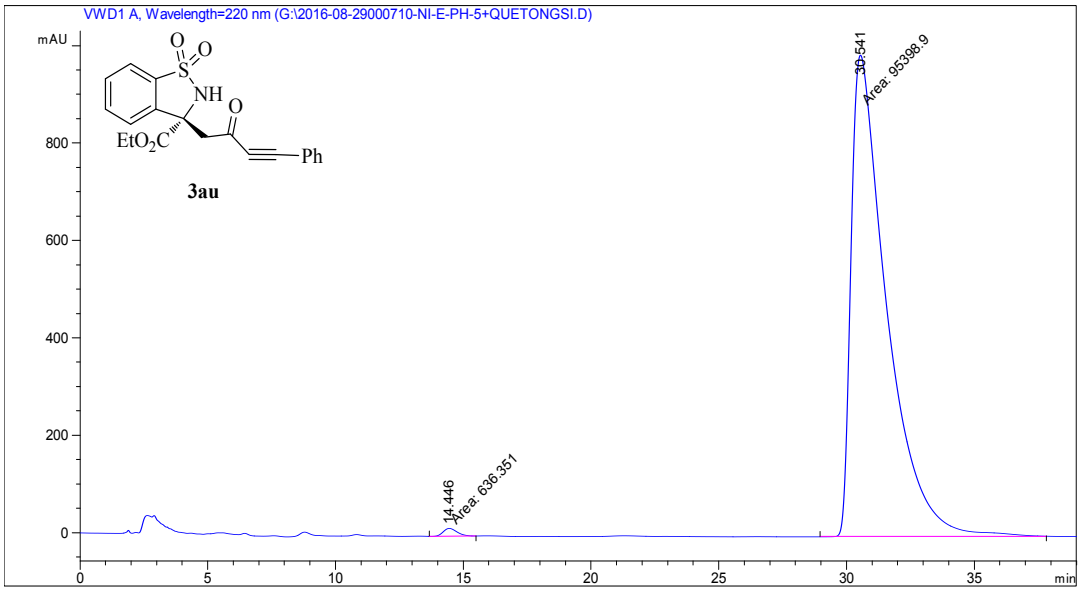


#	Time	Area	Height	Width	Area%	Symmetry
1	25.485	1089.5	10.1	1.275	0.946	0.697
2	34.435	114050.5	765.5	1.9771	99.054	0.282

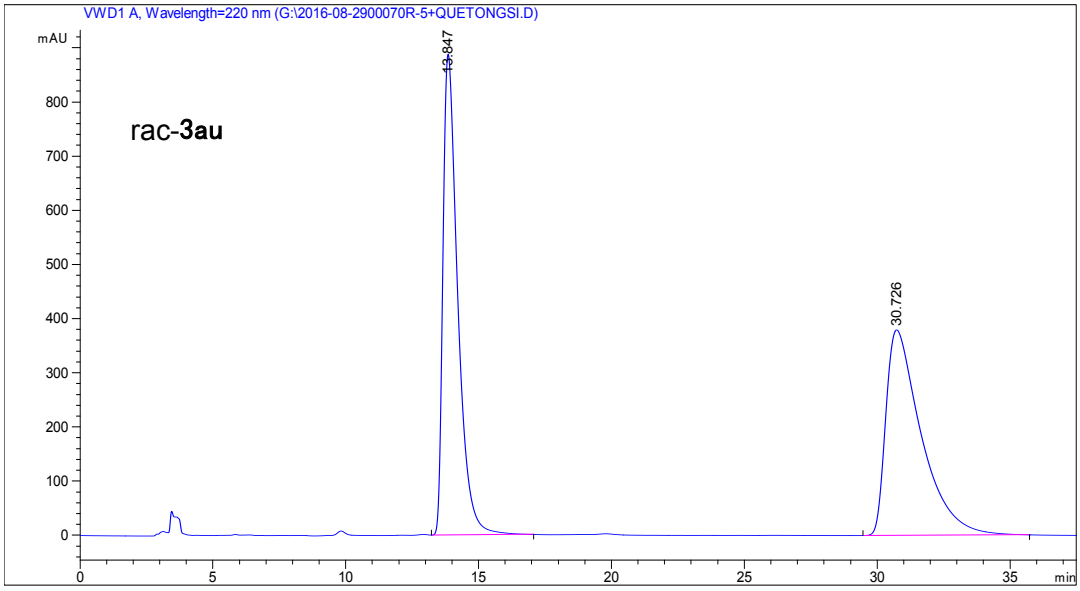


#	Time	Area	Height	Width	Area%	Symmetry
1	23.814	75794.2	781.6	1.6161	49.617	0.394
2	35.105	76965.8	521.5	2.4599	50.383	0.335

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 14.45 min, t_R (major) = 30.54min; 99% ee.

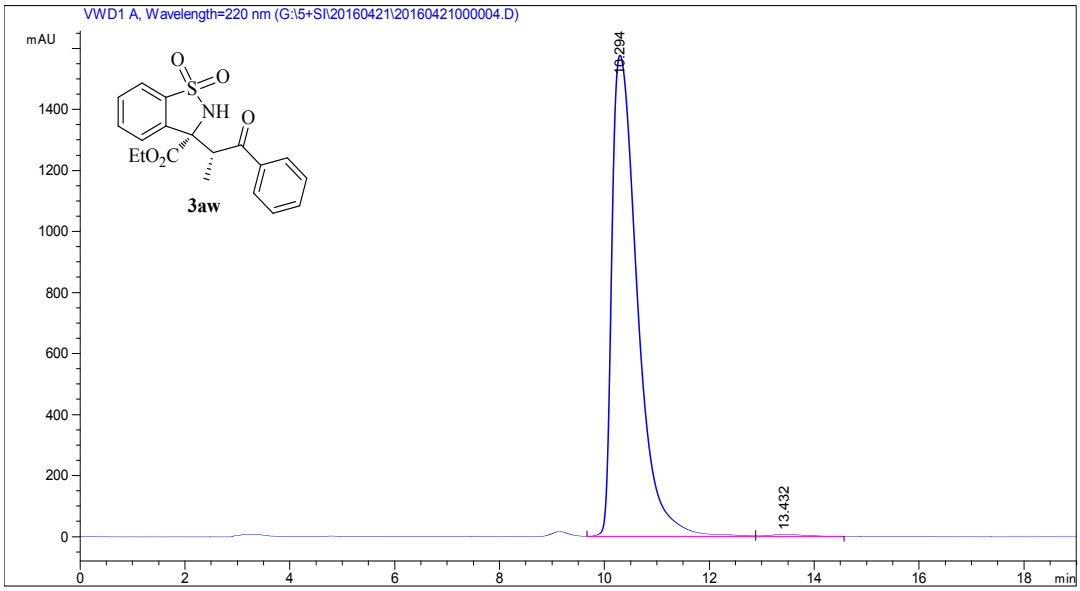


#	Time	Area	Height	Width	Area%	Symmetry
1	14.446	636.4	16.4	0.6482	0.663	0.779
2	30.541	95398.9	988.2	1.6089	99.337	0.344

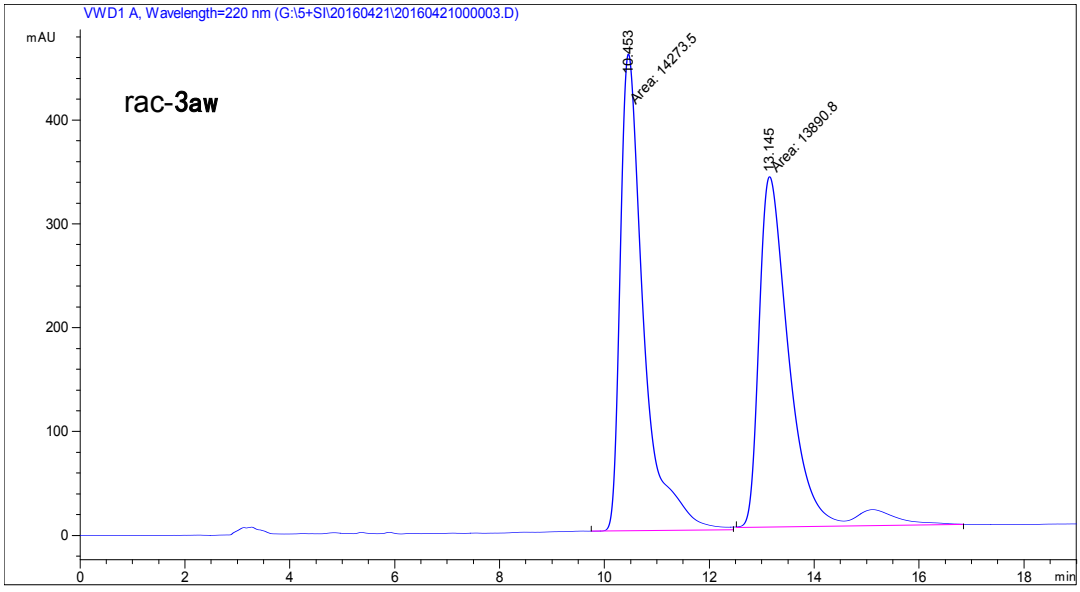


#	Time	Area	Height	Width	Area%	Symmetry
1	13.847	34450.8	887.9	0.5837	49.522	0.492
2	30.726	35115.5	379.4	1.3527	50.478	0.404

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 10.29 min, t_R (minor) = 13.43 min; 99% ee.

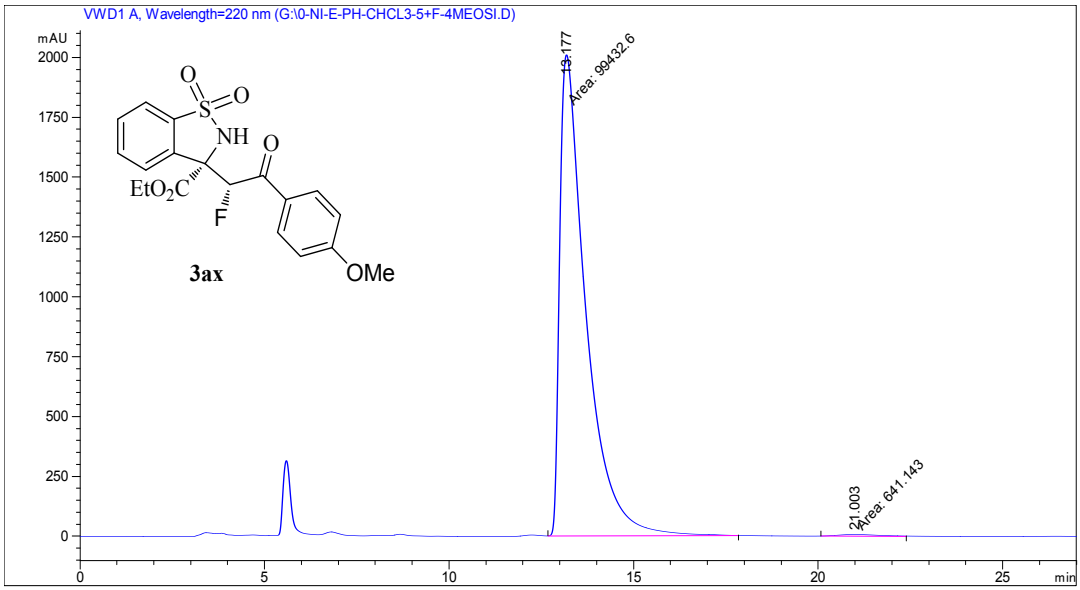


#	Time	Area	Height	Width	Area%	Symmetry
1	10.294	53298.6	1578.2	0.5192	99.228	0.434
2	13.432	414.6	7.9	0.6681	0.772	0.64

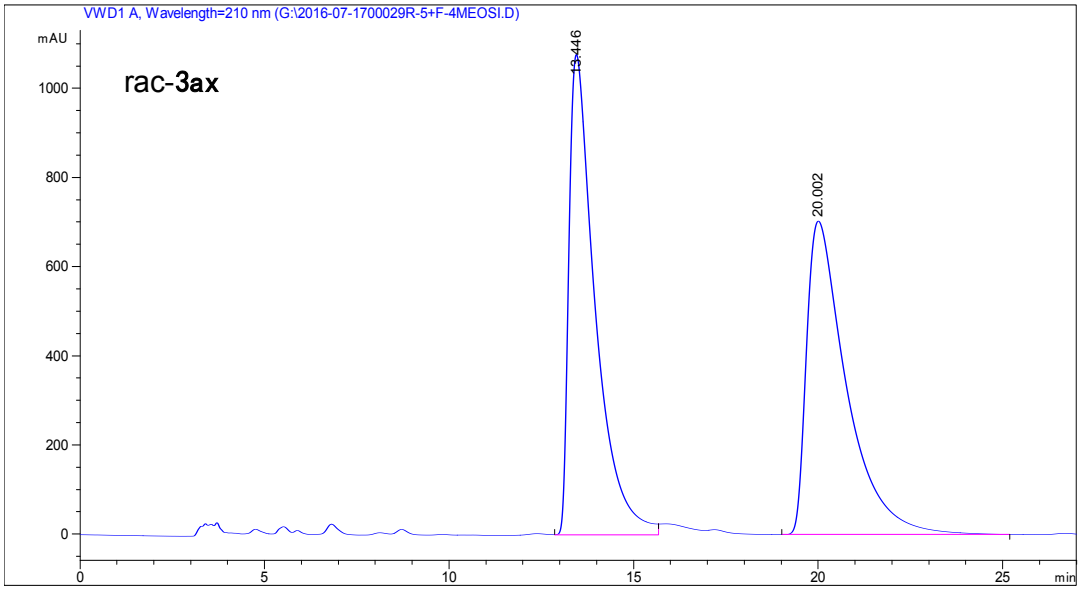


#	Time	Area	Height	Width	Area%	Symmetry
1	10.453	14273.5	459.5	0.5177	50.679	0.512
2	13.145	13890.8	337.5	0.686	49.321	0.486

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t_R (major) = 13.18 min, t_R (minor) = 21.00 min; 99% ee.



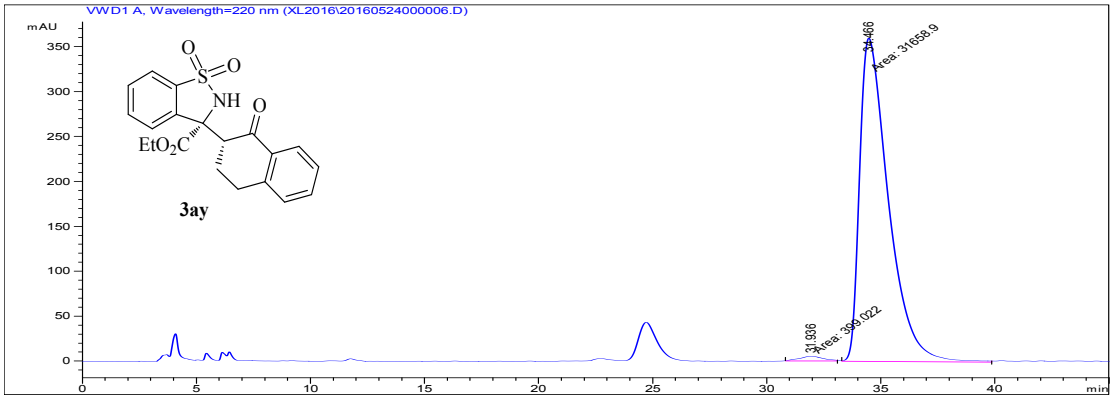
#	Time	Area	Height	Width	Area%	Symmetry
1	13.177	99432.6	2011.1	0.824	99.359	0.332
2	21.003	641.1	7.8	1.368	0.641	0.638



#	Time	Area	Height	Width	Area%	Symmetry
1	13.446	53427.5	1078.3	0.7261	50.287	0.359
2	20.002	52817	703.2	1.1052	49.713	0.382

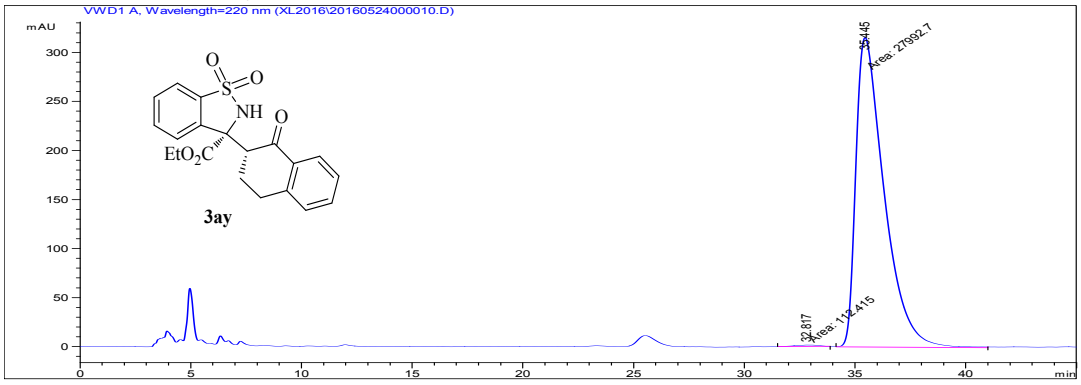
Daicel Chiralpak AD-H, n-hexane/i-PrOH = 70:30, 1.0 mL/min, 220 nm; t_R (minor) = 32.82 min, t_R (major) = 35.45 min; 99% ee.

$Zn(ClO_4)_2$–L2 as catalyst: 92:8, 97%ee

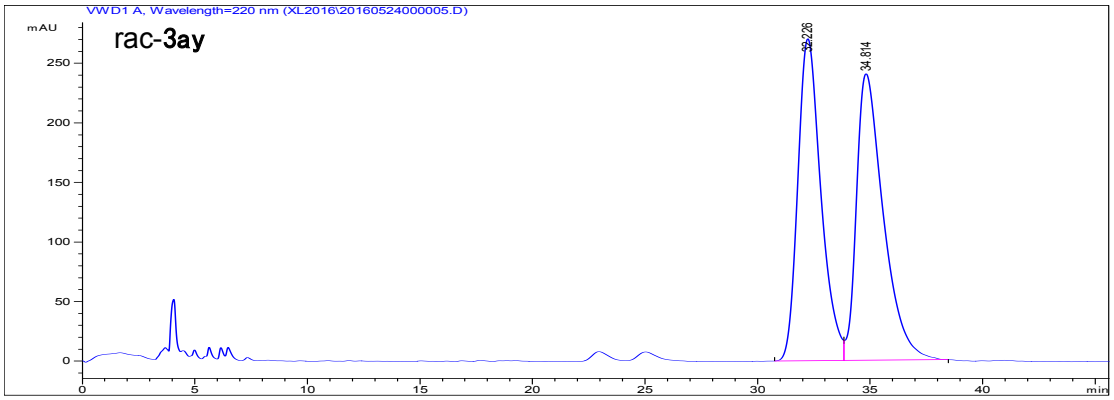


#	Time	Area	Height	Width	Area%	Symmetry
1	31.936	399	5.4	1.2394	1.245	0.958
2	34.466	31658.9	360.2	1.4647	98.755	0.454

$Zn(OTf)_2$–L2 as catalyst: dr 98:2; 99% ee

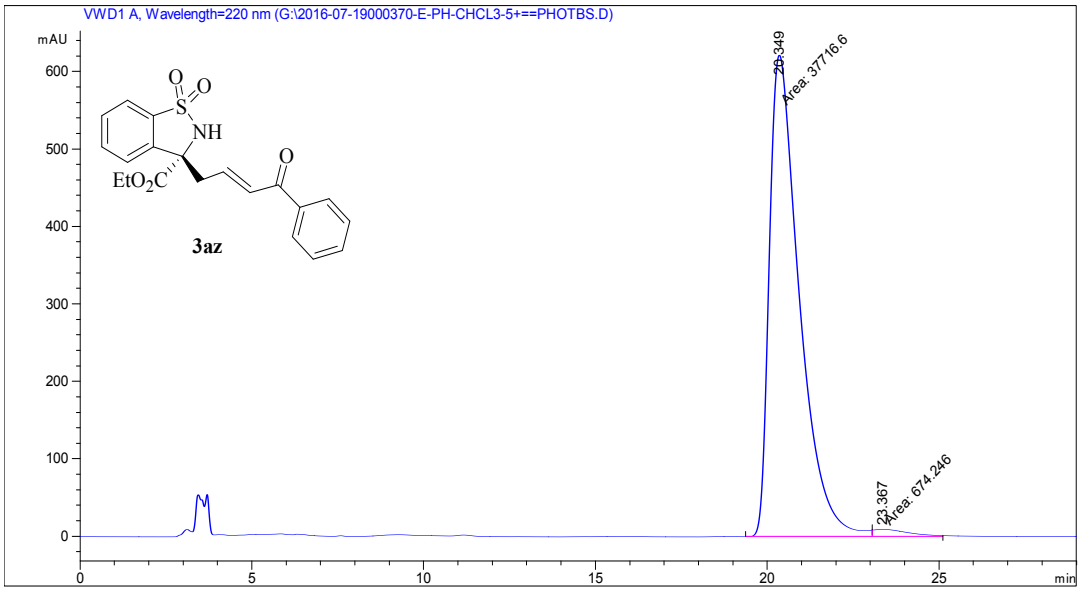


#	Time	Area	Height	Width	Area%	Symmetry
1	32.817	112.4	1.5	1.2558	0.400	1.121
2	35.445	27992.7	315.7	1.4778	99.600	0.466

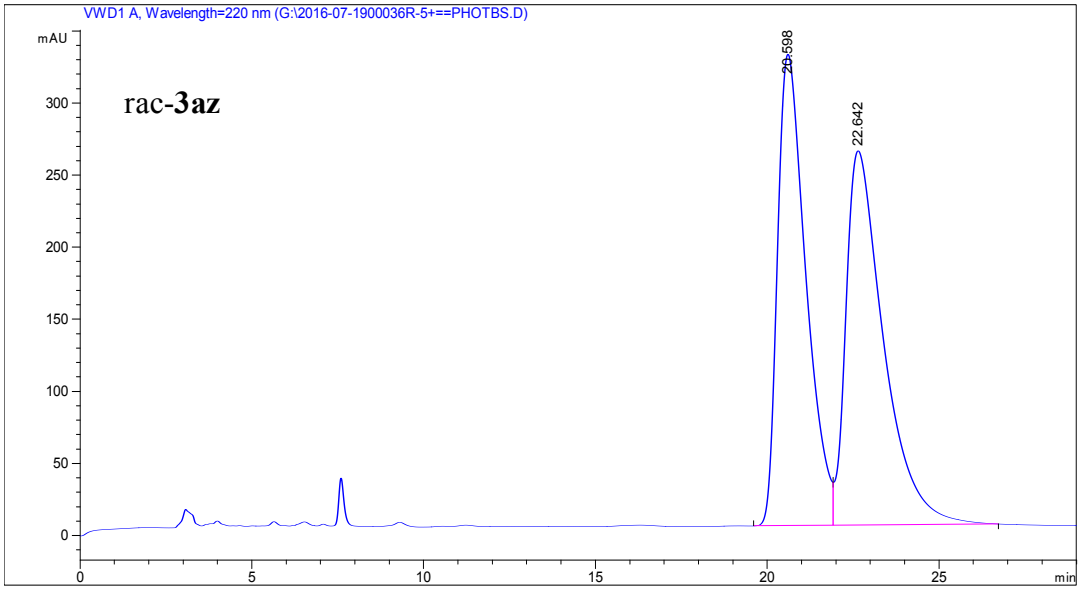


#	Time	Area	Height	Width	Area%	Symmetry
1	32.226	19376.5	270.3	1.0707	49.189	0.723
2	34.814	20015.6	240.6	1.2369	50.811	0.519

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (major) = 20.35 min, t_R (minor) = 23.37 min; 96% ee.

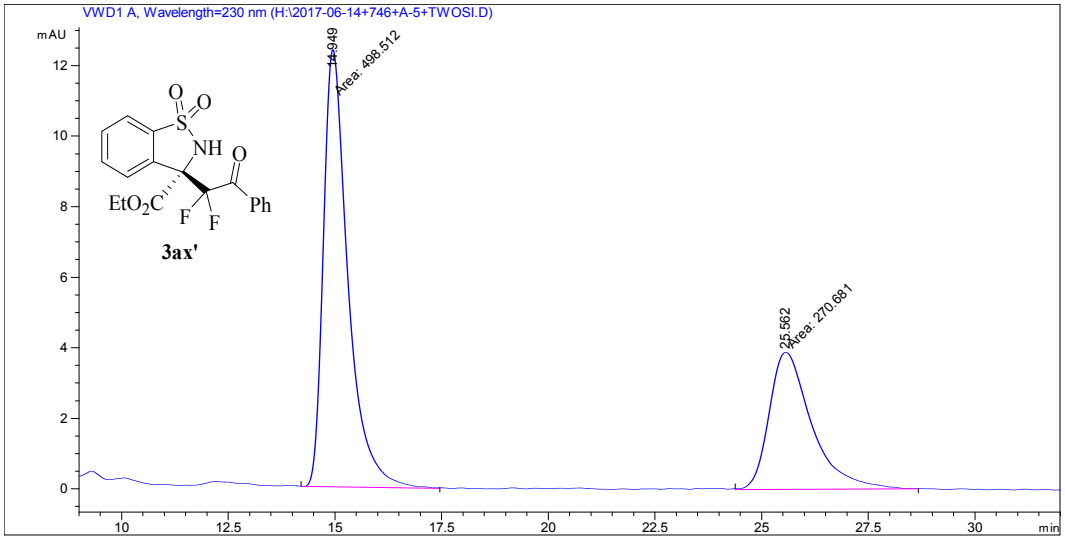


#	Time	Area	Height	Width	Area%	Symmetry
1	20.349	37716.6	621.6	1.0113	98.244	0
2	23.367	674.2	9.4	1.1992	1.756	0.324

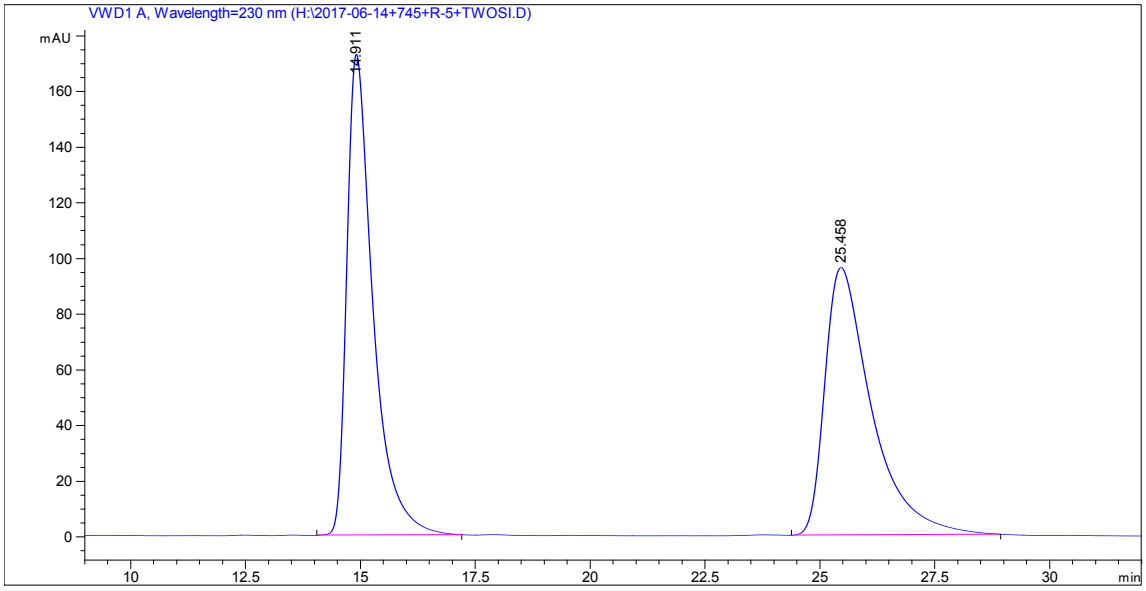


#	Time	Area	Height	Width	Area%	Symmetry
1	20.598	18863.8	27	0.8791	48.783	0.542
2	22.642	19805.1	259.7	1.1248	51.217	0.445

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm; t_R (major) = 14.95 min, t_R (minor) = 25.56 min; 30% ee.

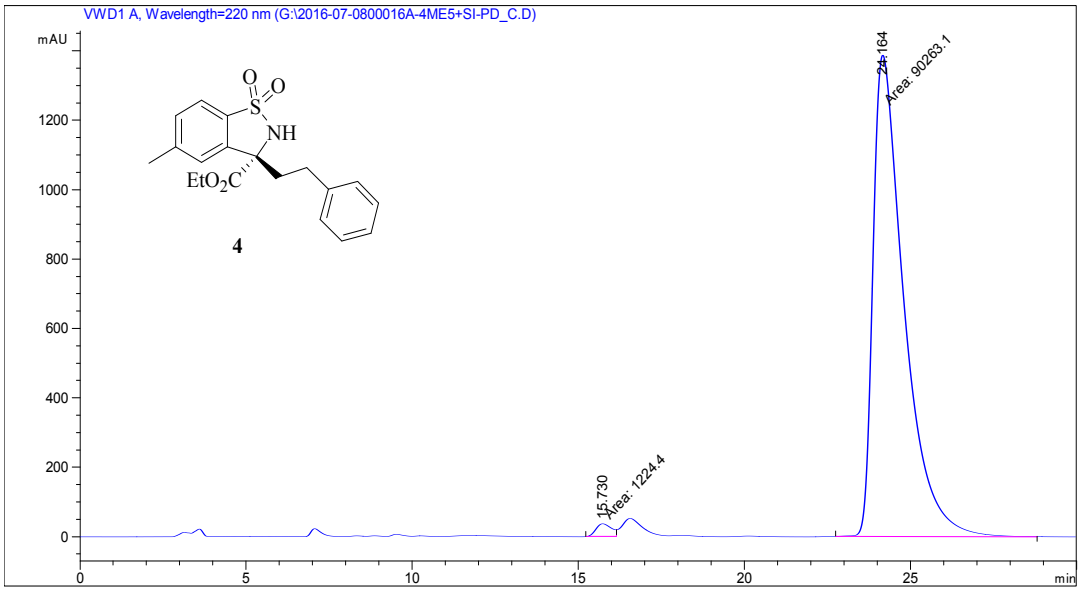


#	Time	Area	Height	Width	Area%	Symmetry
1	14.949	498.5	12.4	0.67	64.810	0.599
2	25.562	270.7	3.9	1.1591	35.190	0.617

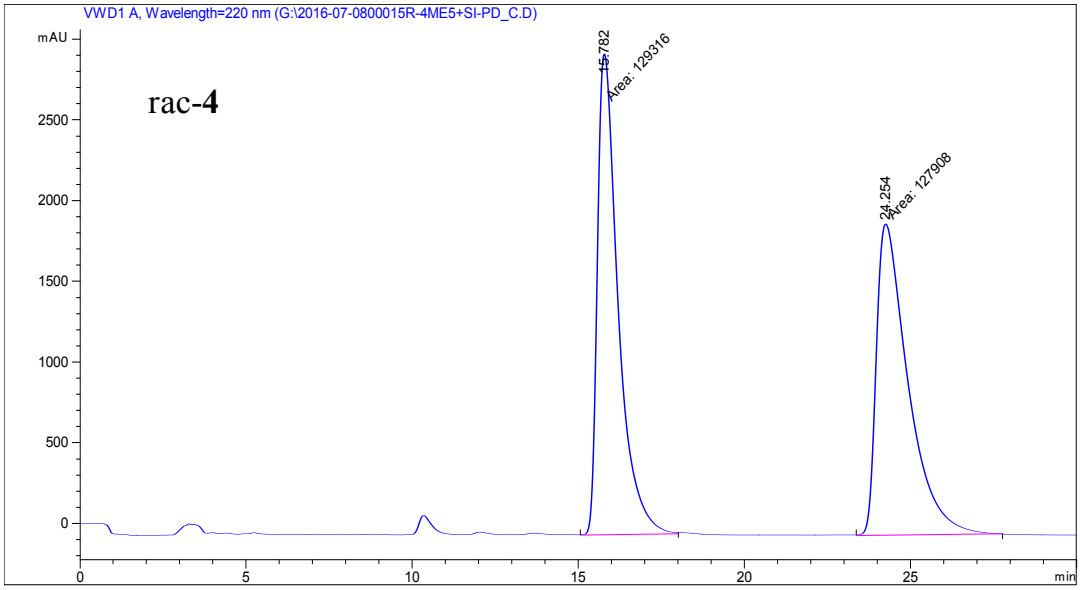


#	Time	Area	Height	Width	Area%	Symmetry
1	14.911	6861.5	172.8	0.5923	50.308	0.529
2	25.458	6777.4	96.1	1.0471	49.692	0.488

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 15.73 min, t_R (major) = 24.16 min; 97% ee.

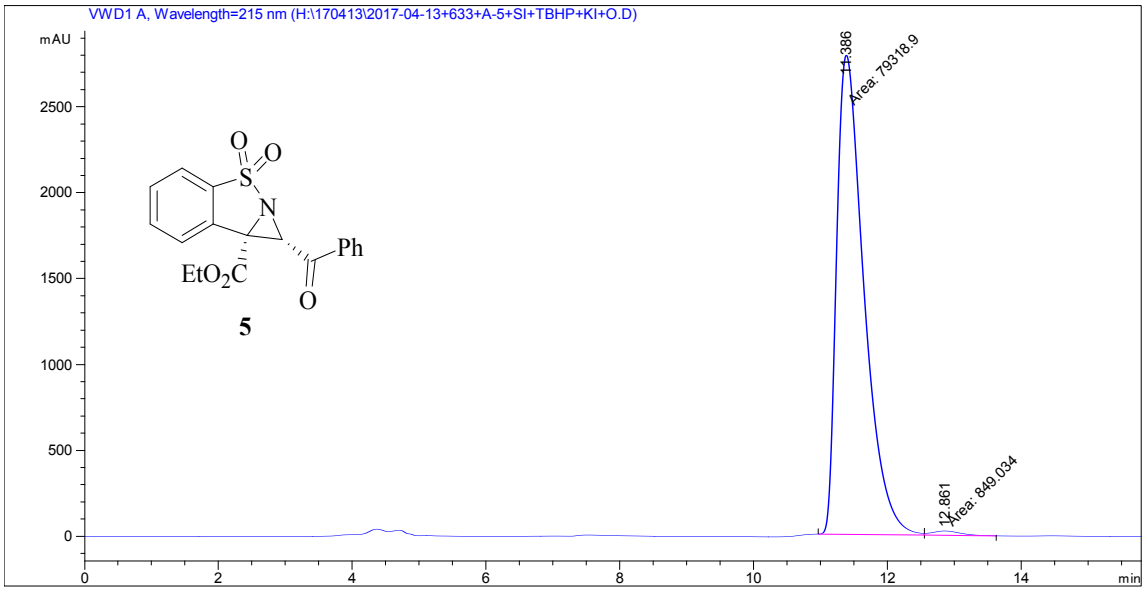


#	Time	Area	Height	Width	Area%	Symmetry
1	15.73	1224.4	37.1	0.5506	1.338	0.741
2	24.164	90263.1	1388.3	1.0836	98.662	0.44

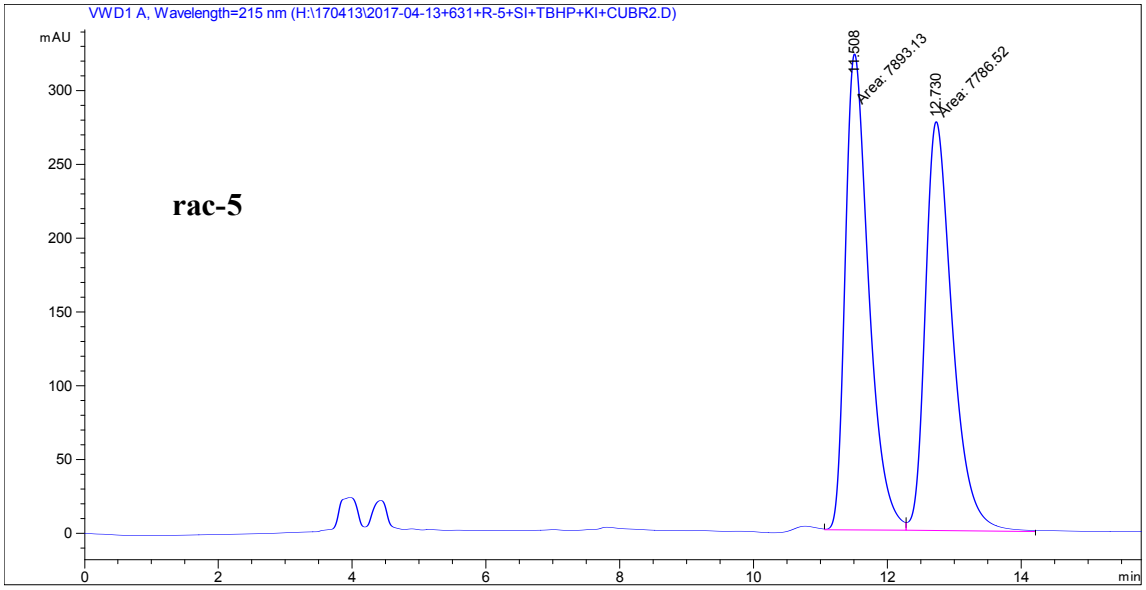


#	Time	Area	Height	Width	Area%	Symmetry
1	15.782	129316.5	2980.1	0.7232	50.274	0.48
2	24.254	127907.7	1929.2	1.105	49.726	0.405

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 70:30, 0.8 mL/min, 215 nm; t_R (major) = 11.39 min, t_R (minor) = 12.86 min; 98% ee.

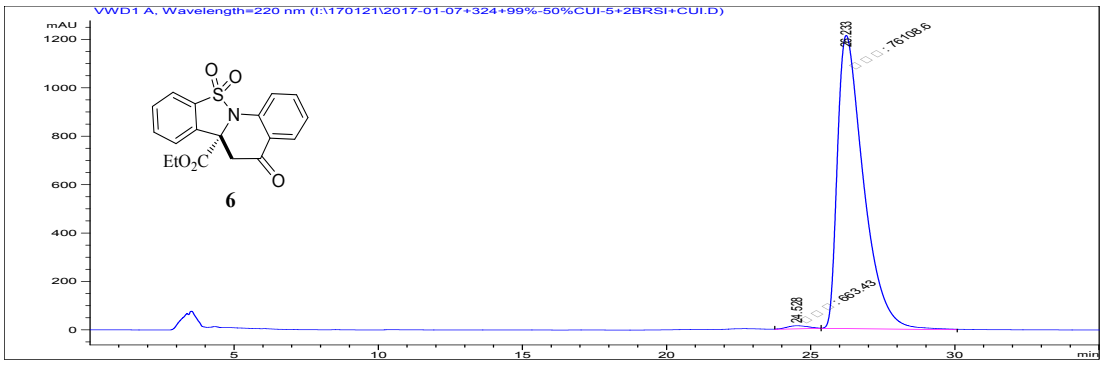


#	Time	Area	Height	Width	Area%	Symmetry
1	11.386	79318.9	2790.7	0.4737	98.941	0.527
2	12.861	849	26.9	0.5251	1.059	0.7

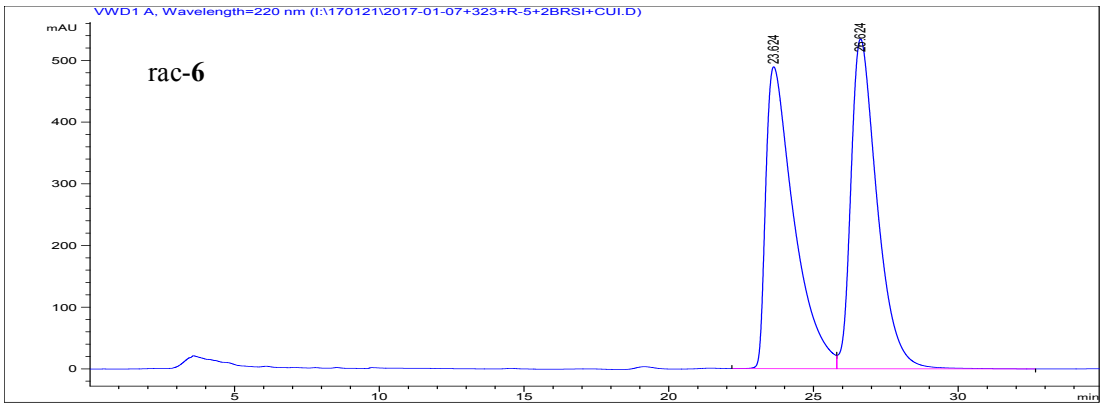


#	Time	Area	Height	Width	Area%	Symmetry
1	11.508	7893.1	322.9	0.4074	50.340	0.625
2	12.73	7786.5	277.4	0.4678	49.660	0.646

Daicel Chiralcel OD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t_R (minor) = 24.53 min, t_R (major) = 26.23 min; 98% ee.

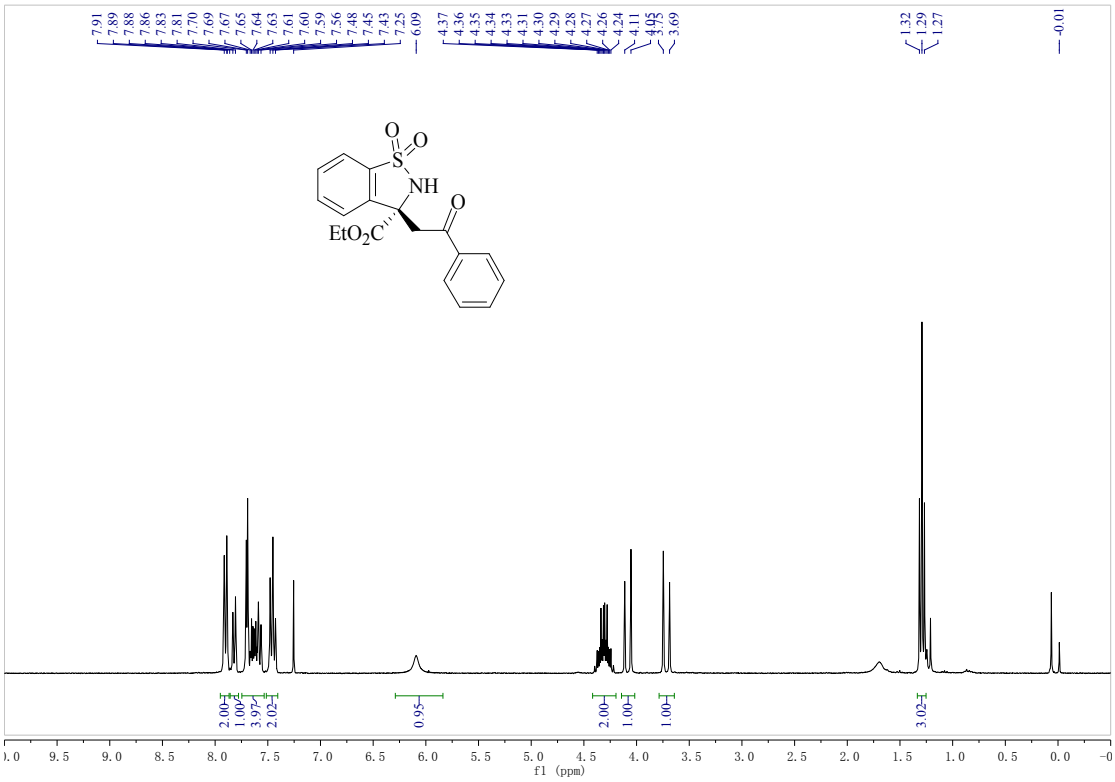


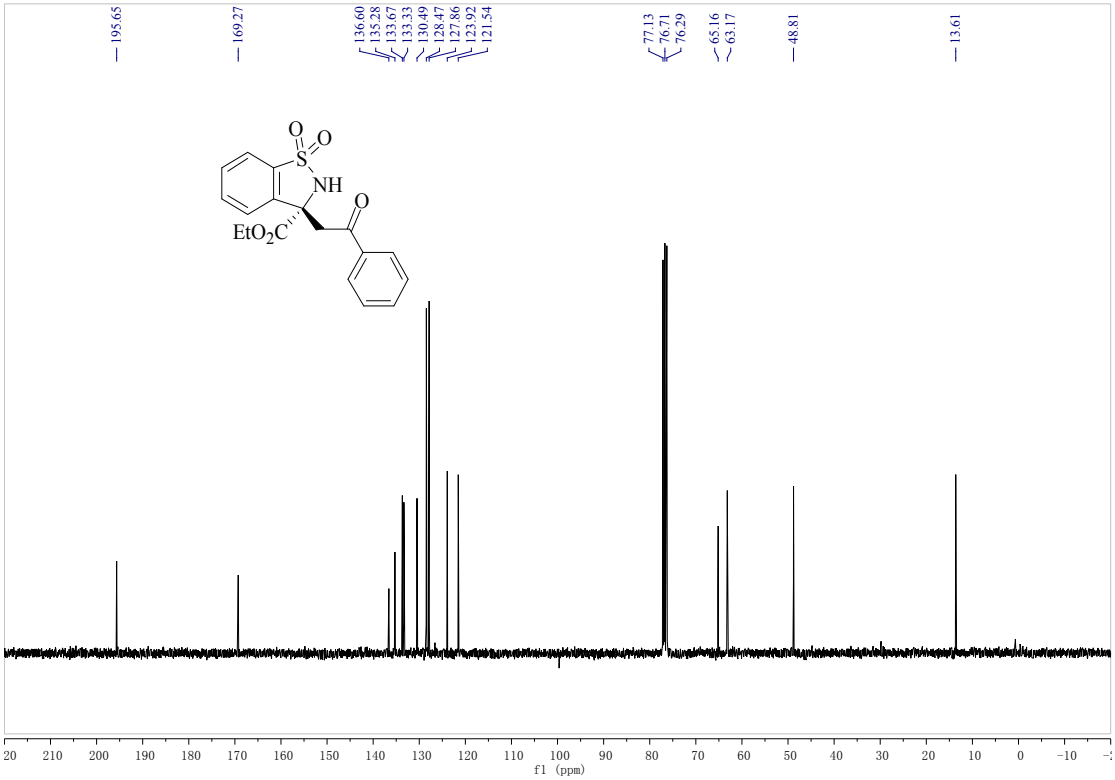
#	Time	Area	Height	Width	Area%	Symmetry
1	24.528	663.4	12.8	0.8664	0.864	0.892
2	26.233	76108.6	1211.4	1.0471	99.136	0.486

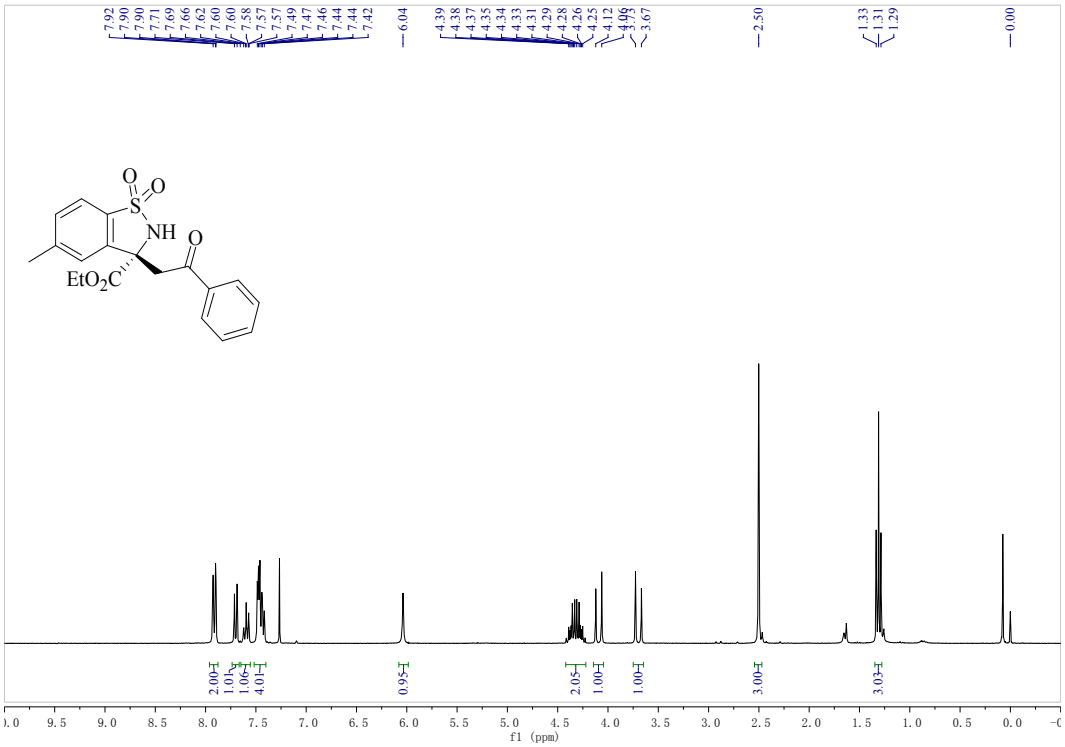


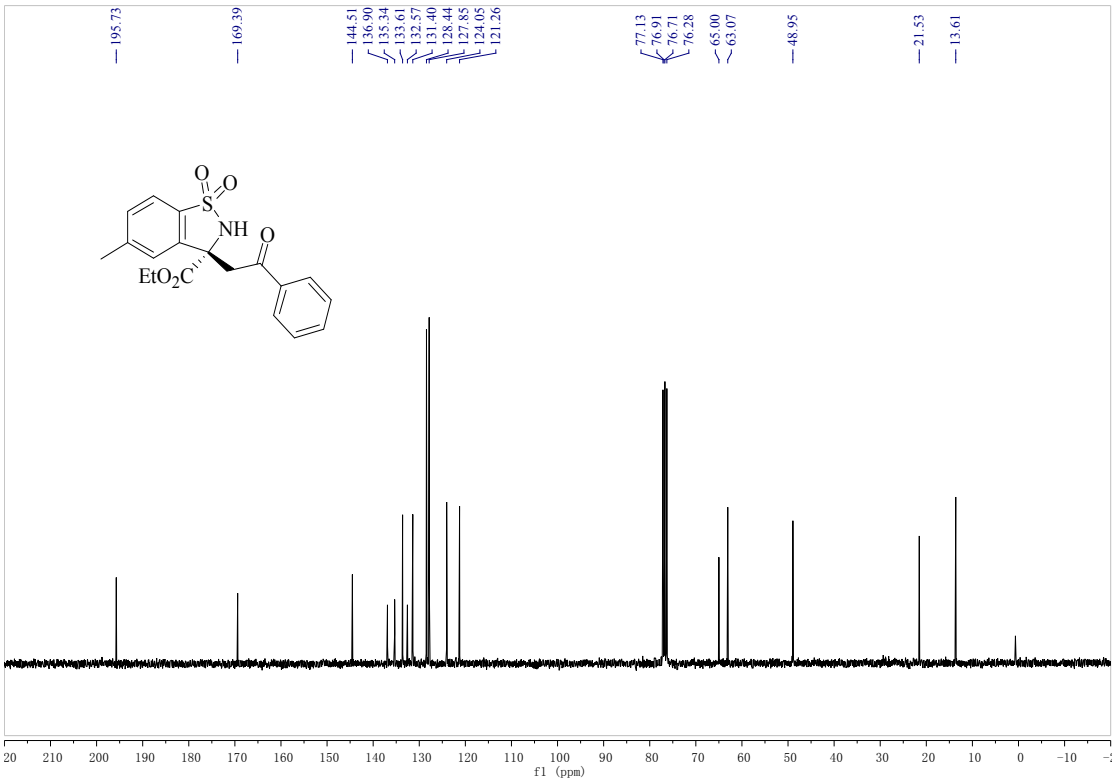
#	Time	Area	Height	Width	Area%	Symmetry
1	23.624	33157.2	489.4	0.9944	49.619	0.357
2	26.624	33666.7	534.7	0.9535	50.381	0.537

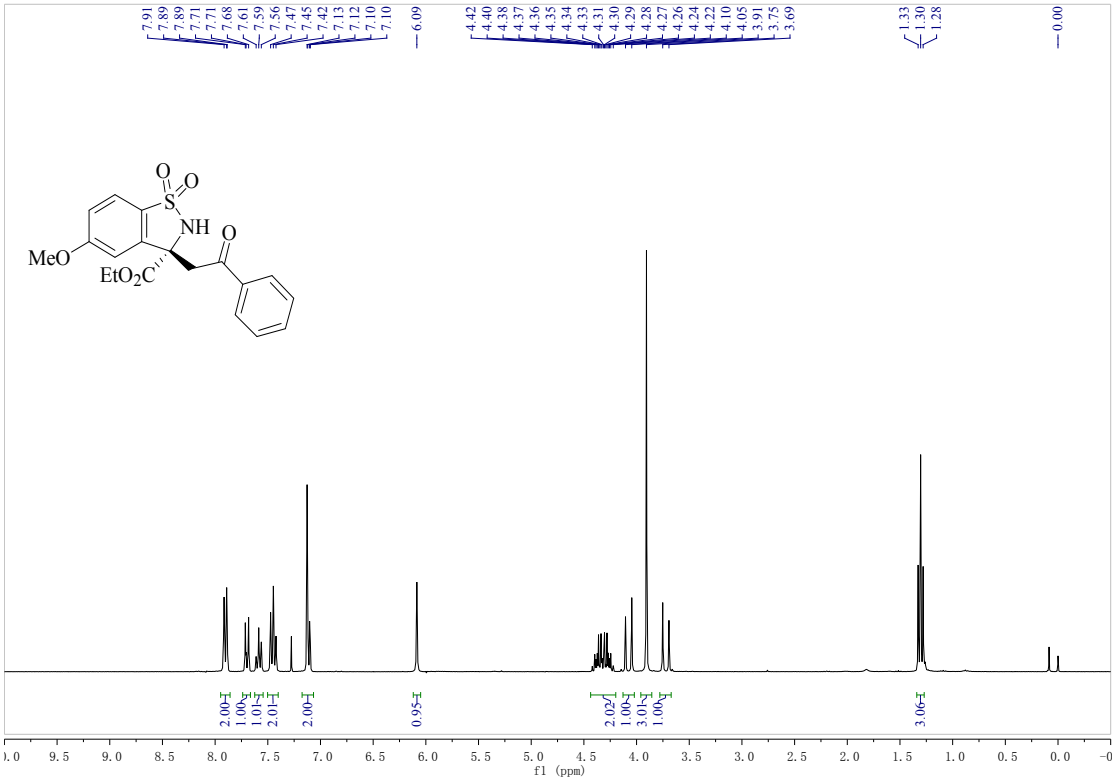
8. ^{1}H and ^{13}C NMR Spectra for Products 3~6.

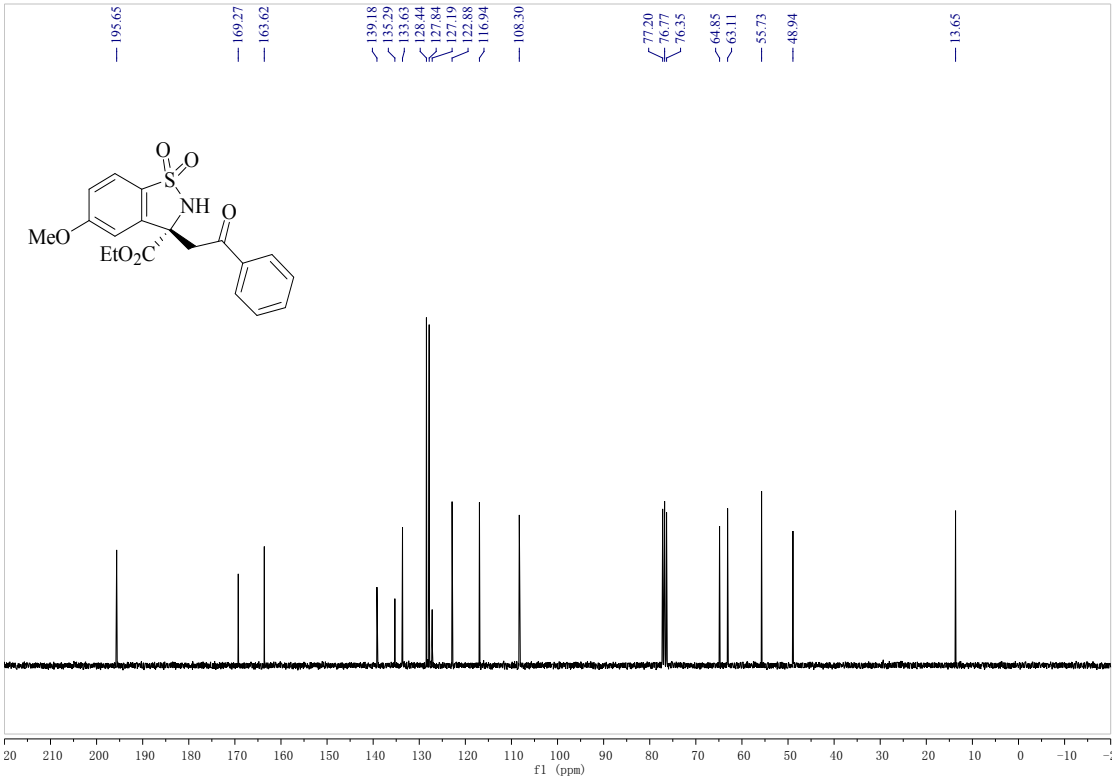


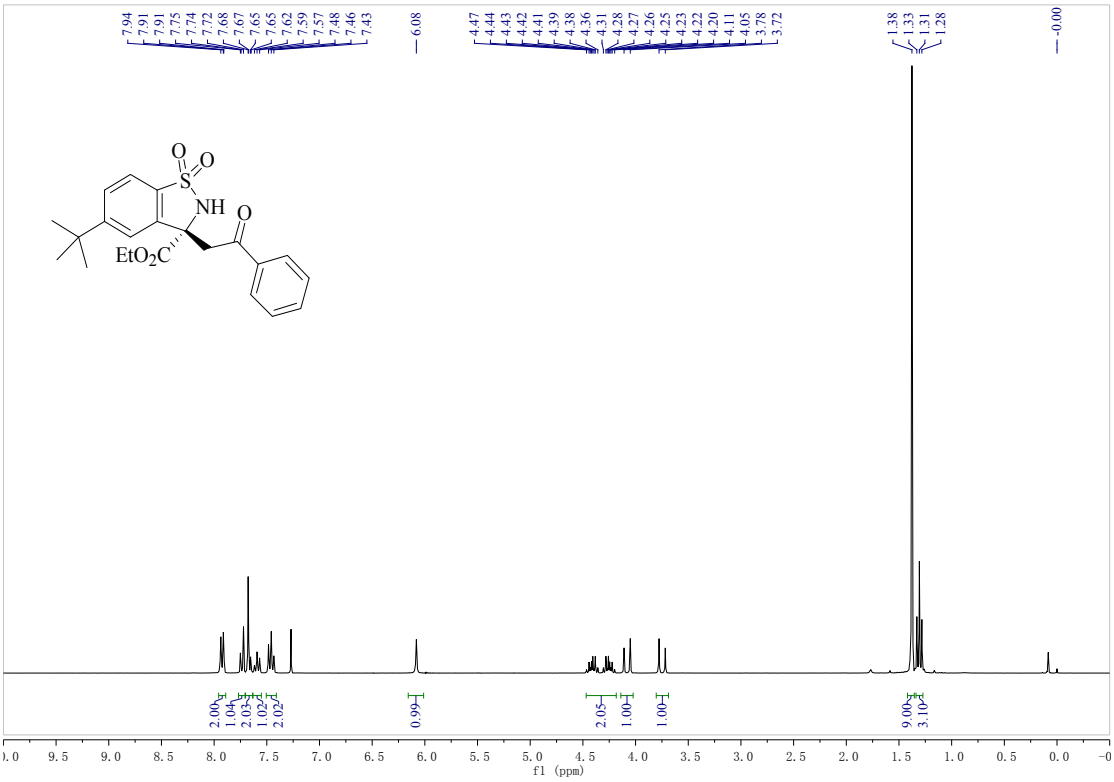


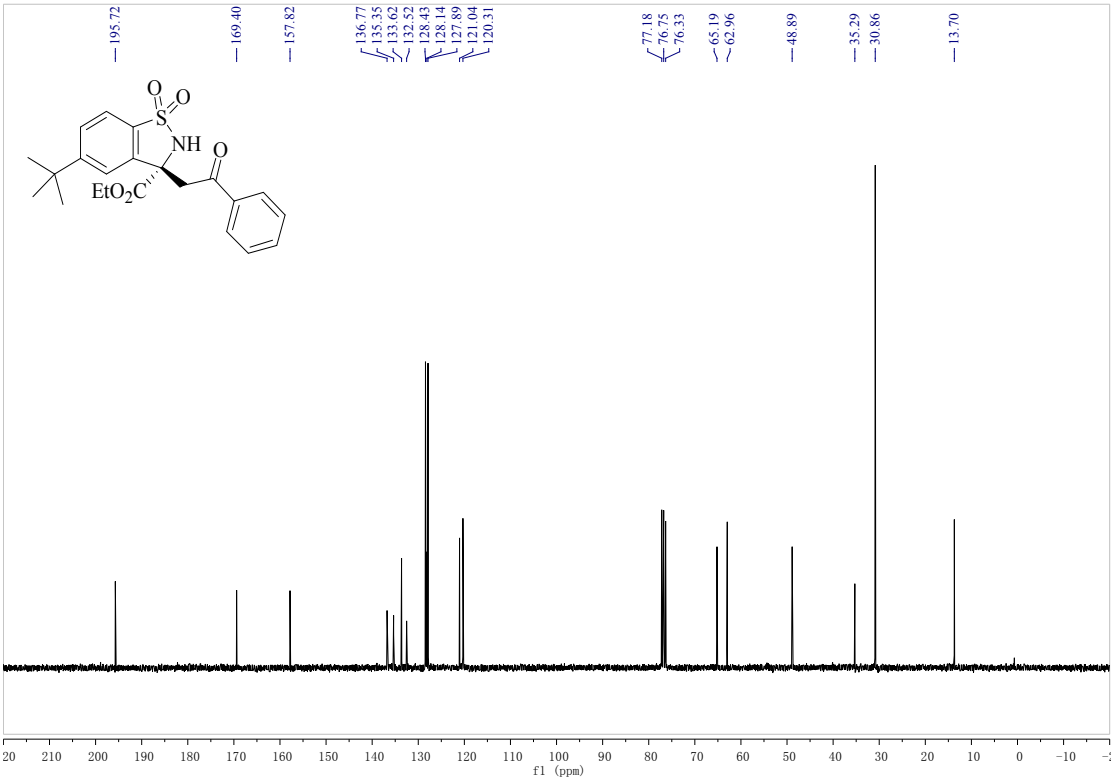

7.92
7.90
7.90
7.71
7.69
7.66
7.62
7.60
7.60
7.58
7.57
7.57
7.49
7.47
7.46
7.44
7.44
7.42
6.04
4.39
4.38
4.37
4.35
4.34
4.33
4.31
4.29
4.28
4.26
4.25
4.12
3.67
2.50
1.33
1.31
1.29
0.00
O
O
S
NH
O
EtO2C
2.00
1.01
1.06
4.01
0.95
2.05
1.00
1.00
3.00
3.03
f1 (ppm)

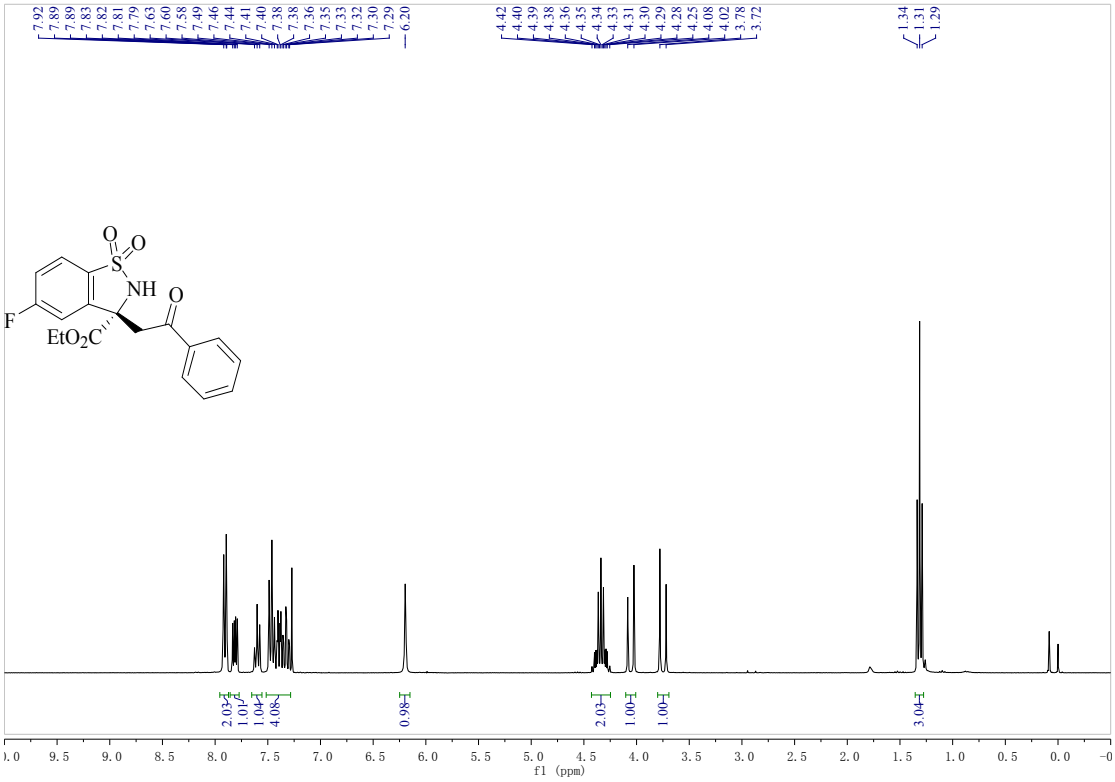

195.73
169.39
144.51
136.90
135.34
133.61
132.57
131.40
128.44
127.85
124.05
121.26
77.13
76.91
76.71
76.28
65.00
63.07
48.95
21.53
13.61
O
O
S
NH
O
EtO2C
f1 (ppm)

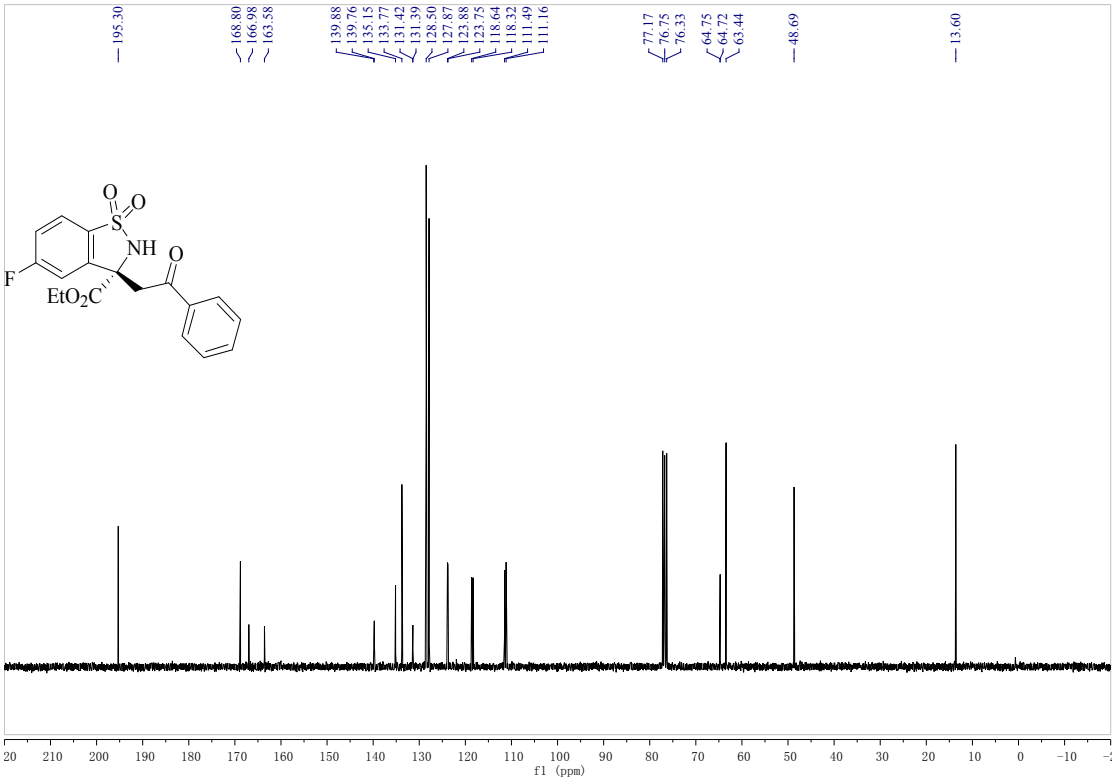

7.91
7.89
7.89
7.71
7.71
7.68
7.61
7.59
7.56
7.47
7.45
7.42
7.13
7.12
7.10
7.10
6.09
4.42
4.40
4.38
4.37
4.36
4.35
4.34
4.33
4.31
4.30
4.29
4.28
4.27
4.26
4.24
4.22
4.10
4.05
3.91
3.75
3.69
1.33
1.30
1.28
0.00
O
O
S
NH
O
MeO
EtO2C
2.00
1.00
1.01
2.01
2.00
0.95
2.02
1.00
3.01
1.00
3.06
f1 (ppm)


195.65
169.27
163.62
139.18
135.29
133.63
128.44
127.84
127.19
122.88
116.94
108.30
77.20
76.77
76.35
64.85
63.11
55.73
48.94
13.65
O
O
S
NH
O
MeO
EtO2C
f1 (ppm)


7.94 7.91 7.91 7.75 7.74 7.72 7.68 7.67 7.65 7.65 7.62 7.59 7.57 7.48 7.46 7.43
6.08
4.47 4.44 4.43 4.42 4.41 4.39 4.38 4.36 4.31 4.28 4.27 4.26 4.25 4.23 4.22 4.20 4.11 4.05 3.78 3.72
1.38 1.33 1.31 1.28
-0.00
O
O
S
NH
O
EtO2C
2.00 1.04 2.03 1.02 2.02 0.99 2.05 1.00 1.00 9.00 3.10
f1 (ppm)


195.72
169.40
157.82
136.77 135.35 133.62 132.52 128.43 128.14 127.89 121.04 120.31
77.18 76.75 76.33
65.19 62.96
48.89
35.29 30.86
13.70
O
O
S
NH
O
EtO2C
f1 (ppm)


7.92
7.89
7.89
7.83
7.82
7.81
7.79
7.63
7.60
7.58
7.49
7.46
7.44
7.41
7.40
7.38
7.38
7.36
7.35
7.33
7.32
7.30
7.29
6.20
4.42
4.40
4.39
4.38
4.36
4.35
4.34
4.33
4.31
4.30
4.29
4.28
4.25
4.08
4.02
3.78
3.72
1.34
1.31
1.29
O
O
S
NH
O
F
EtO2C
2.03
1.01
1.04
4.08
0.98
2.03
1.00
1.00
3.04
f1 (ppm)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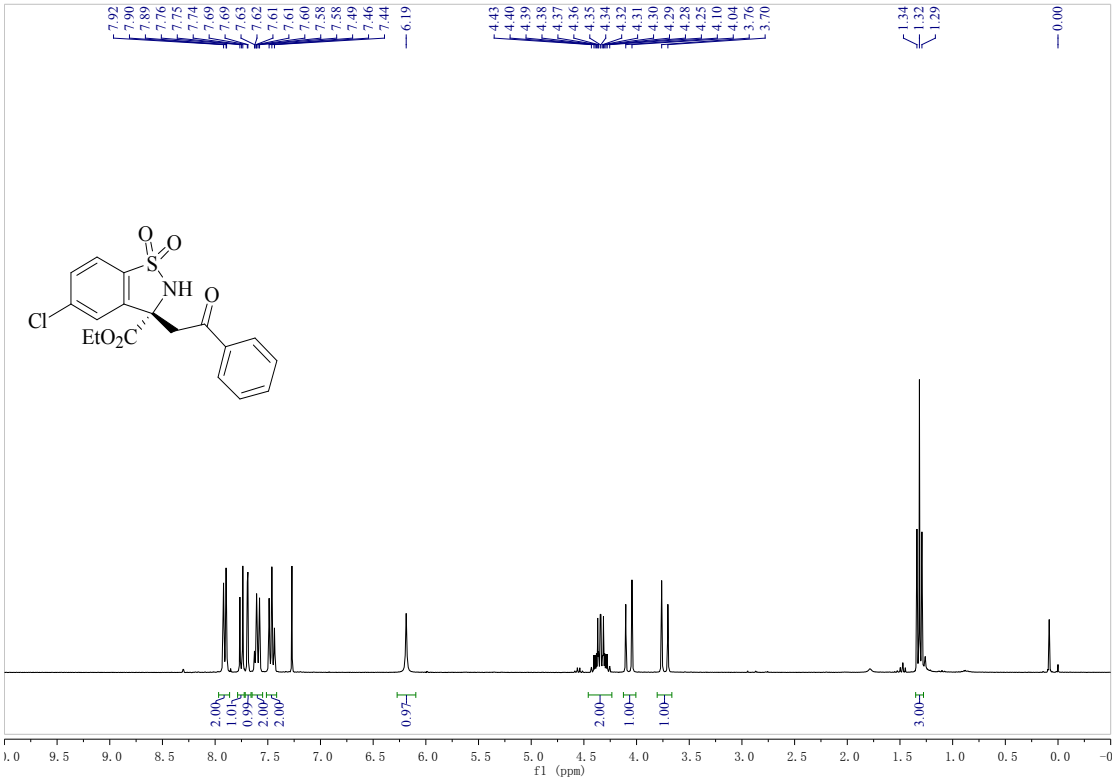
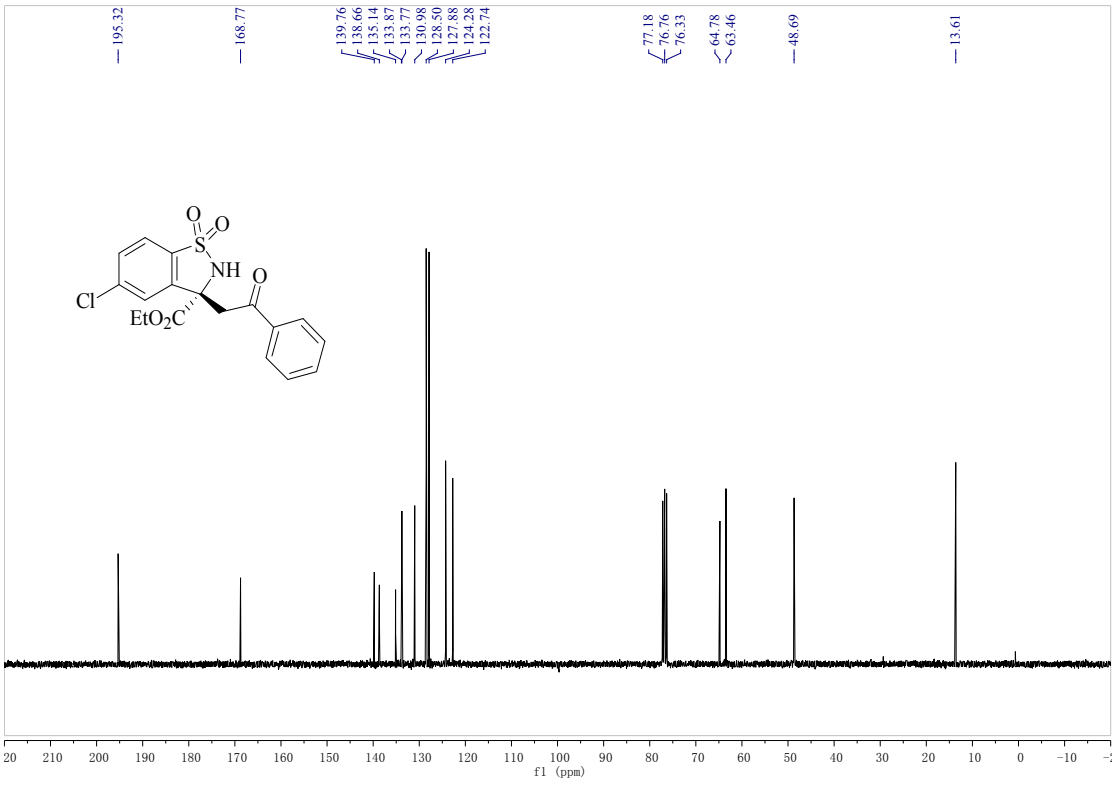
168.80
166.98
163.58
139.88
139.76
135.15
133.77
131.42
131.39
128.50
127.87
123.88
123.75
118.64
118.32
111.49
111.16
77.17
76.75
76.33
64.75
64.72
63.44
48.69
13.60
O
O
S
NH
O
F
EtO2C
f1 (ppm)


7.92
7.90
7.89
7.76
7.75
7.74
7.69
7.69
7.63
7.62
7.61
7.61
7.60
7.58
7.58
7.49
7.46
7.44
6.19
4.43
4.40
4.39
4.38
4.37
4.36
4.35
4.34
4.32
4.31
4.30
4.29
4.28
4.25
4.10
4.04
3.76
3.70
1.34
1.32
1.29
0.00
O
O
S
NH
O
Cl
EtO2C
2.00
1.01
0.99
2.00
2.00
0.97
2.00
1.00
1.00
3.00
f1 (ppm)


195.32
168.77
139.76
138.66
135.14
133.87
133.77
130.98
128.50
127.88
124.28
122.74
77.18
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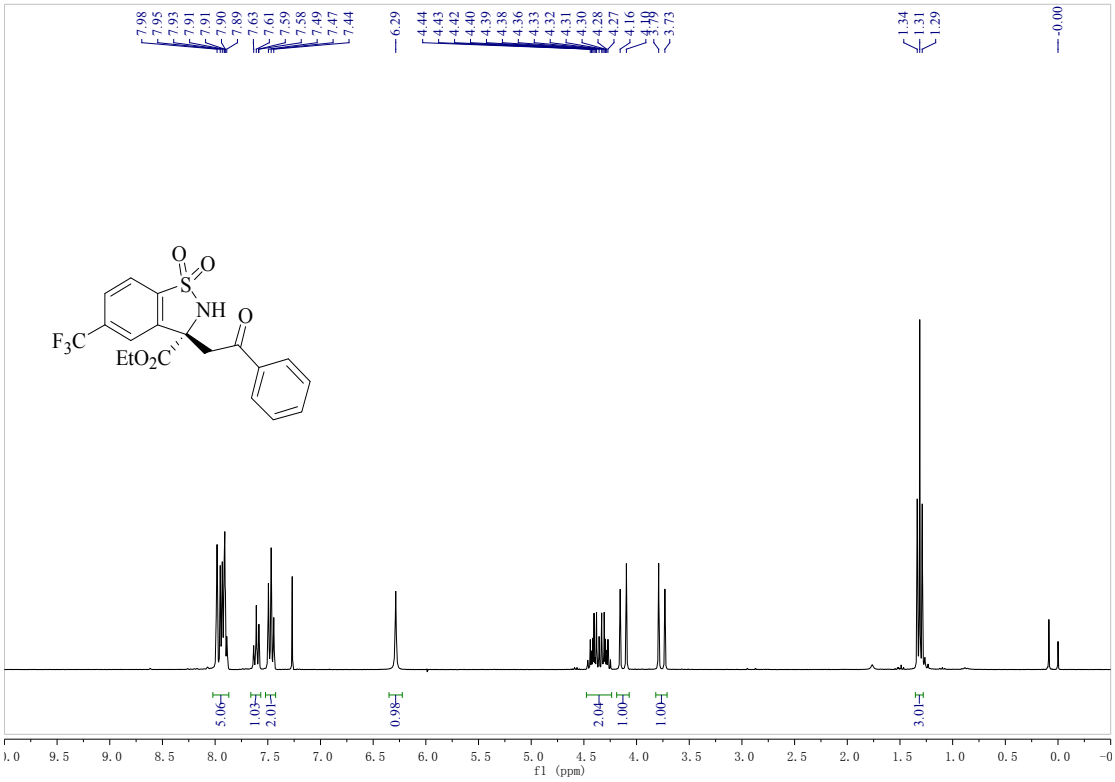
48.69
13.61
O
O
S
NH
O
Cl
EtO2C
f1 (ppm)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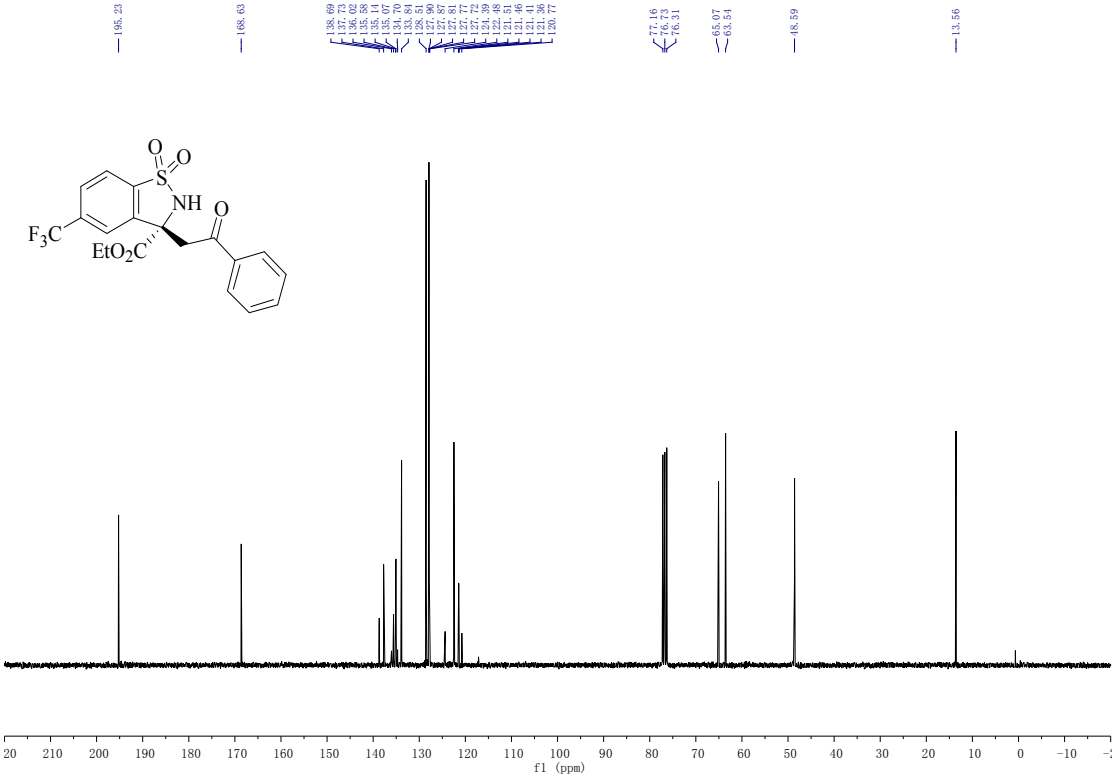
7.95
7.93
7.91
7.91
7.90
7.89
7.63
7.61
7.59
7.58
7.49
7.47
7.44
6.29
4.44
4.43
4.42
4.40
4.39
4.38
4.36
4.33
4.32
4.31
4.30
4.28
4.27
4.16
3.73
1.34
1.31
1.29
-0.00
O
O
S
NH
O
F3C
EtO2C
5.06
1.03
2.01
0.98
2.04
1.00
1.00
3.01
f1 (ppm)


195.23
168.63
138.69
137.73
136.62
136.35
135.14
135.07
134.70
133.84
128.51
127.90
127.87
127.81
127.77
127.72
124.39
122.48
121.51
121.46
121.41
121.36
120.77
77.16
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48.59
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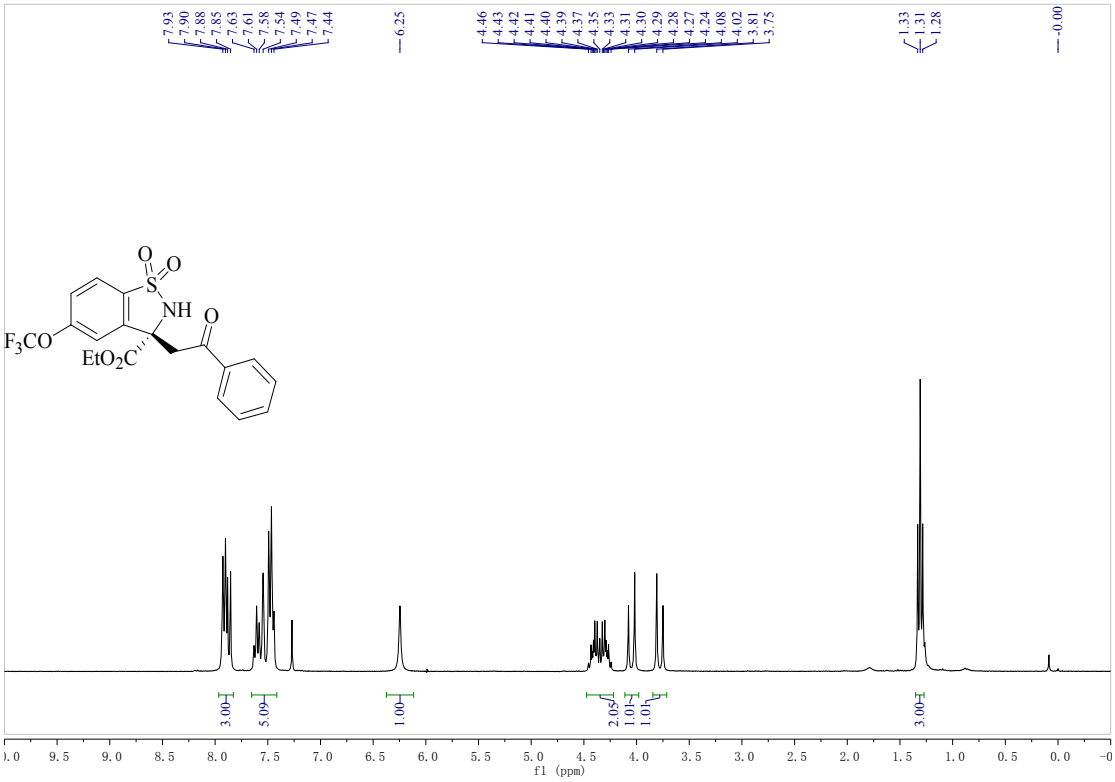
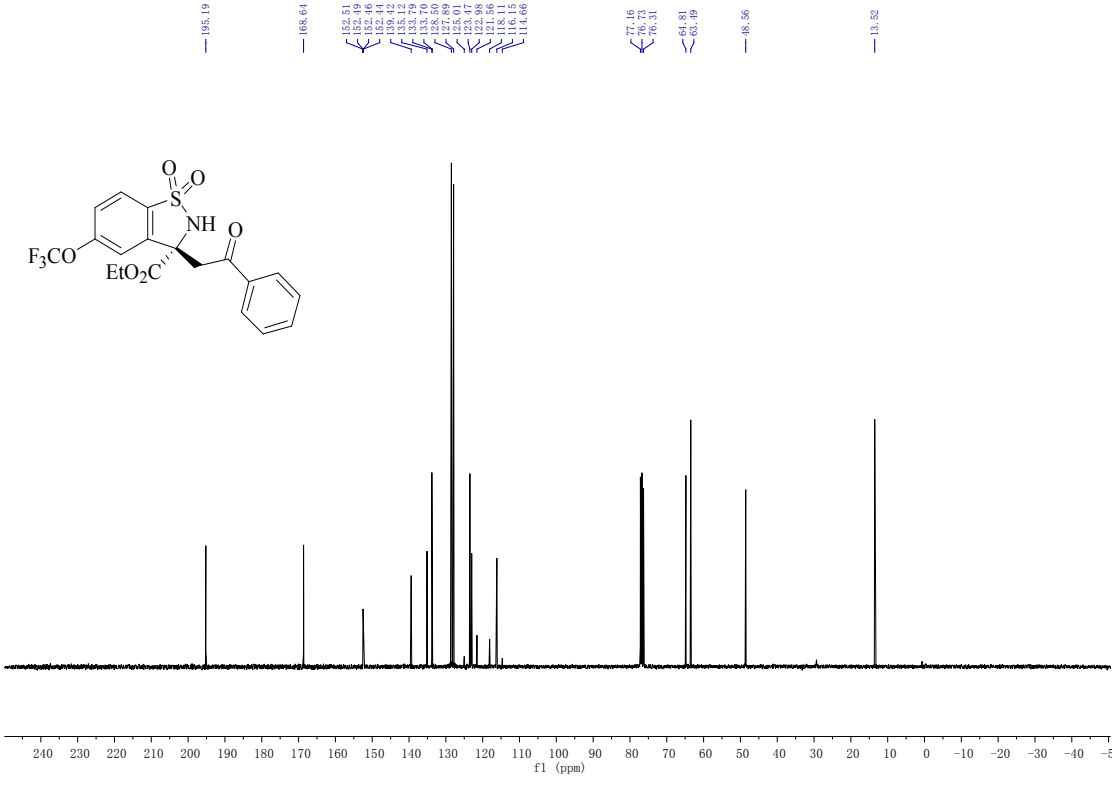
O
O
S
NH
O
F3C
EtO2C
f1 (ppm)


7.93
7.90
7.88
7.85
7.63
7.61
7.58
7.54
7.49
7.47
7.44
6.25
4.46
4.43
4.42
4.41
4.40
4.39
4.37
4.35
4.33
4.31
4.30
4.29
4.28
4.27
4.24
4.08
4.02
3.81
3.75
1.33
1.31
1.28
0.00
O
O
S
NH
O
F3CO
EtO2C
3.00
5.09
1.00
2.05
1.01
1.01
3.00
f1 (ppm)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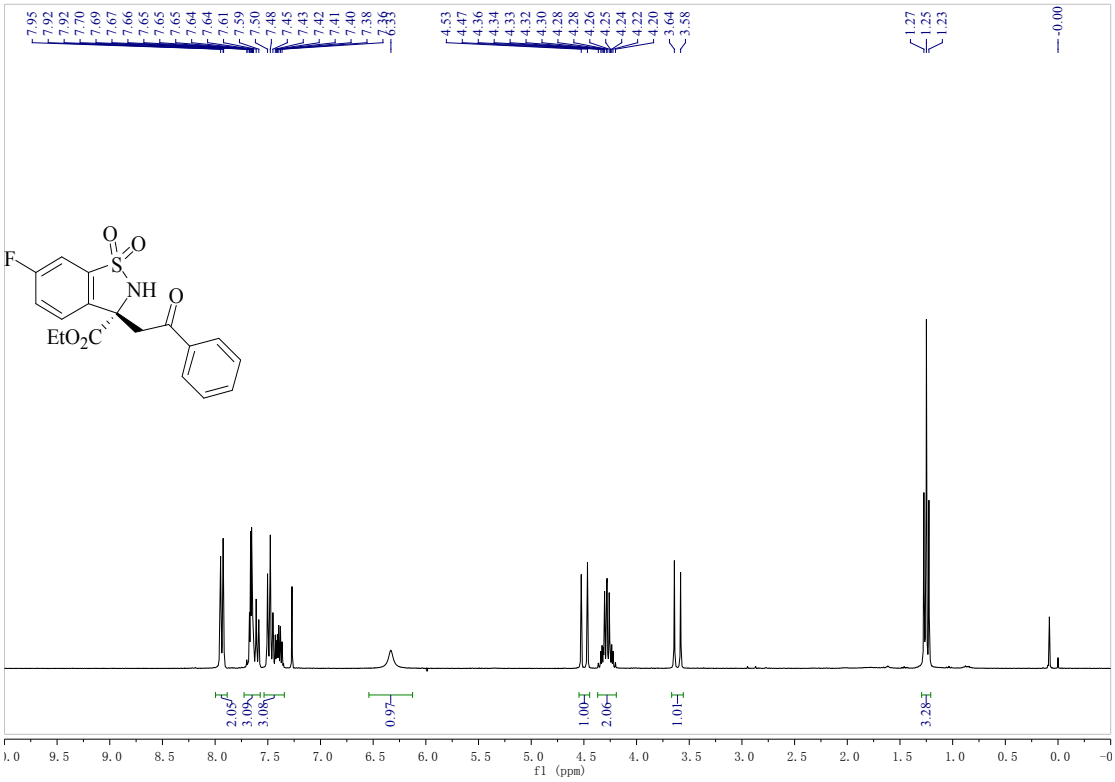
168.64
152.51
152.49
152.46
152.44
139.42
135.12
133.79
133.70
128.69
127.89
125.01
123.47
122.98
121.96
118.11
116.15
114.66
77.16
76.73
76.31
64.81
63.49
48.56
13.52
O
O
S
NH
O
F3CO
EtO2C
f1 (ppm)


7.95
7.92
7.92
7.70
7.69
7.67
7.66
7.65
7.65
7.65
7.64
7.64
7.61
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4.22
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1.25
1.23
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F
O
O
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1.01
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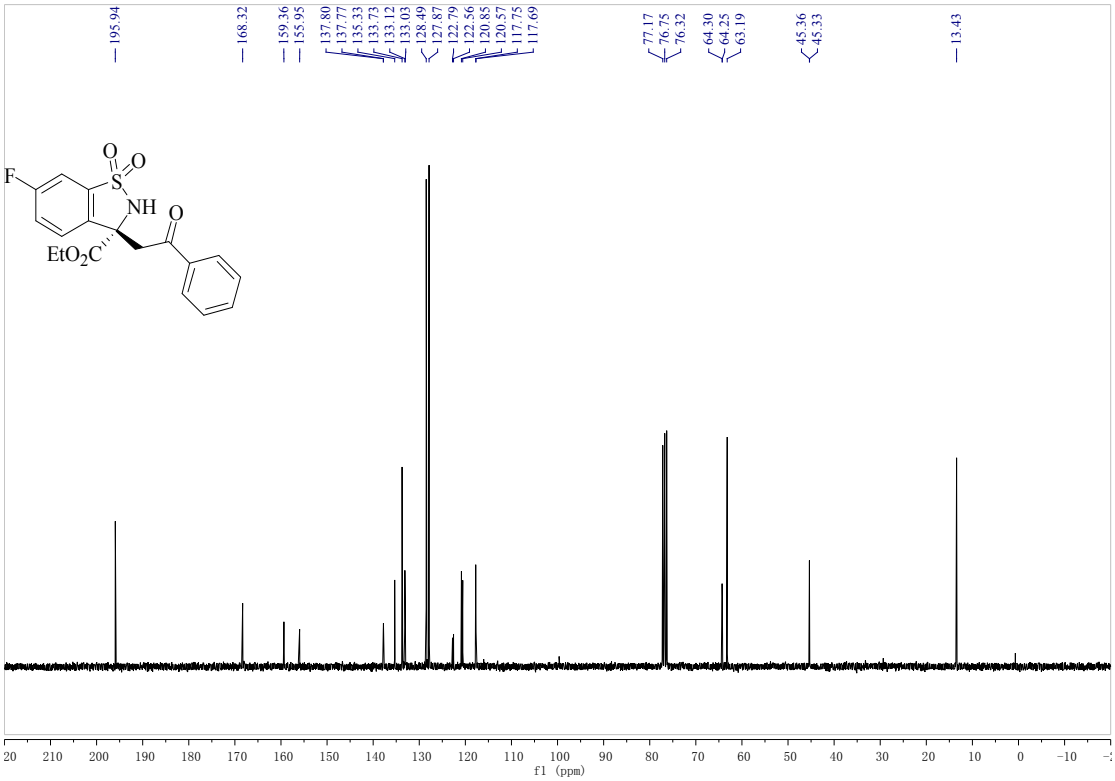
f1 (ppm)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120.57
117.75
117.69
77.17
76.75
76.32
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13.43
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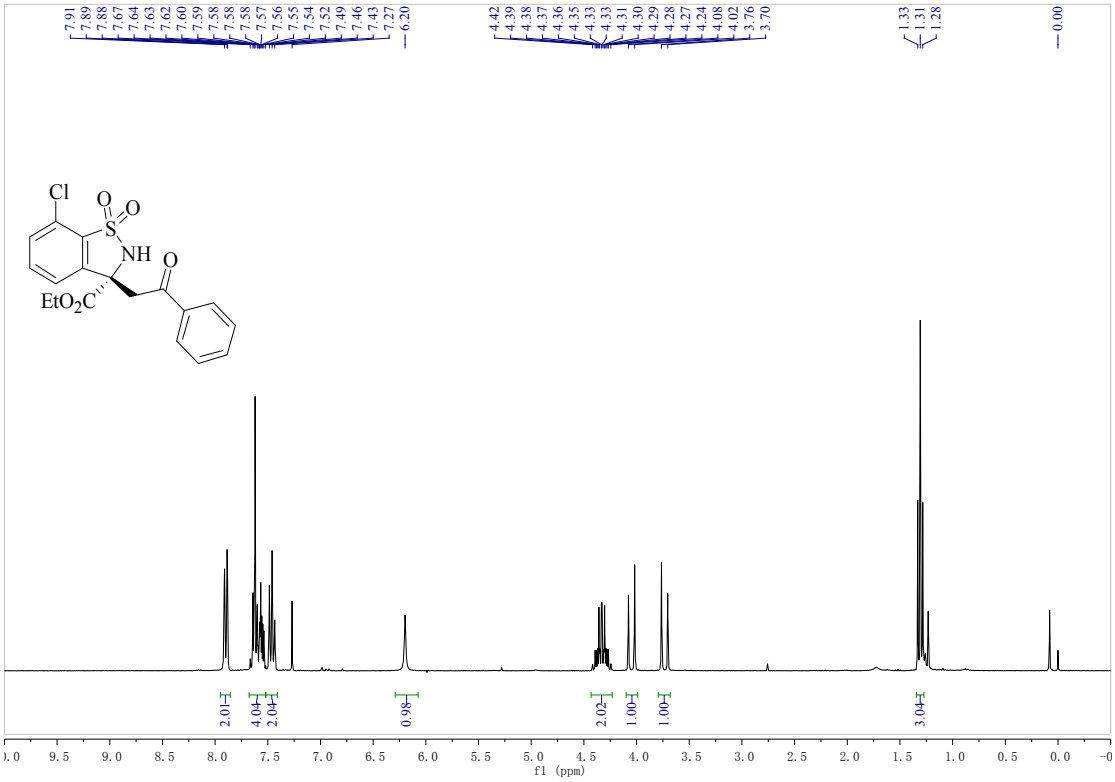
O
S
NH
O
EtO2C
f1 (ppm)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4.33
4.31
4.30
4.29
4.28
4.27
4.24
4.08
4.02
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1.33
1.31
1.28
0.00
Cl
O
O
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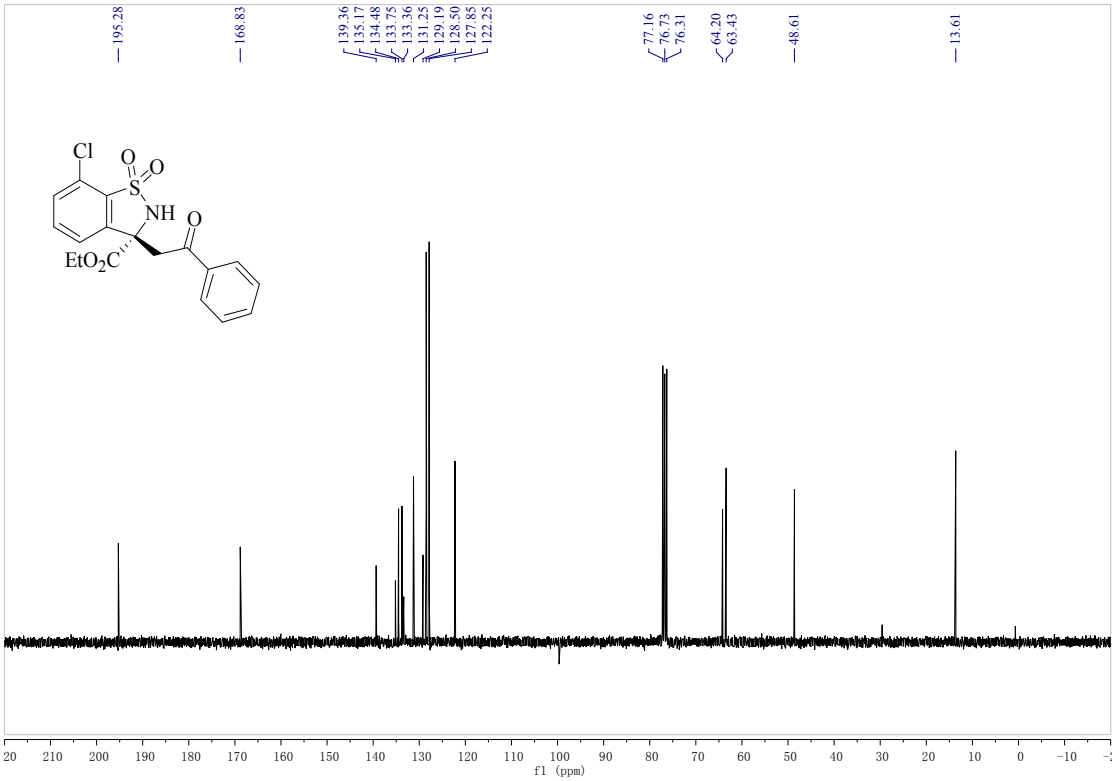
1.00
1.00
3.04
f1 (ppm)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13.61
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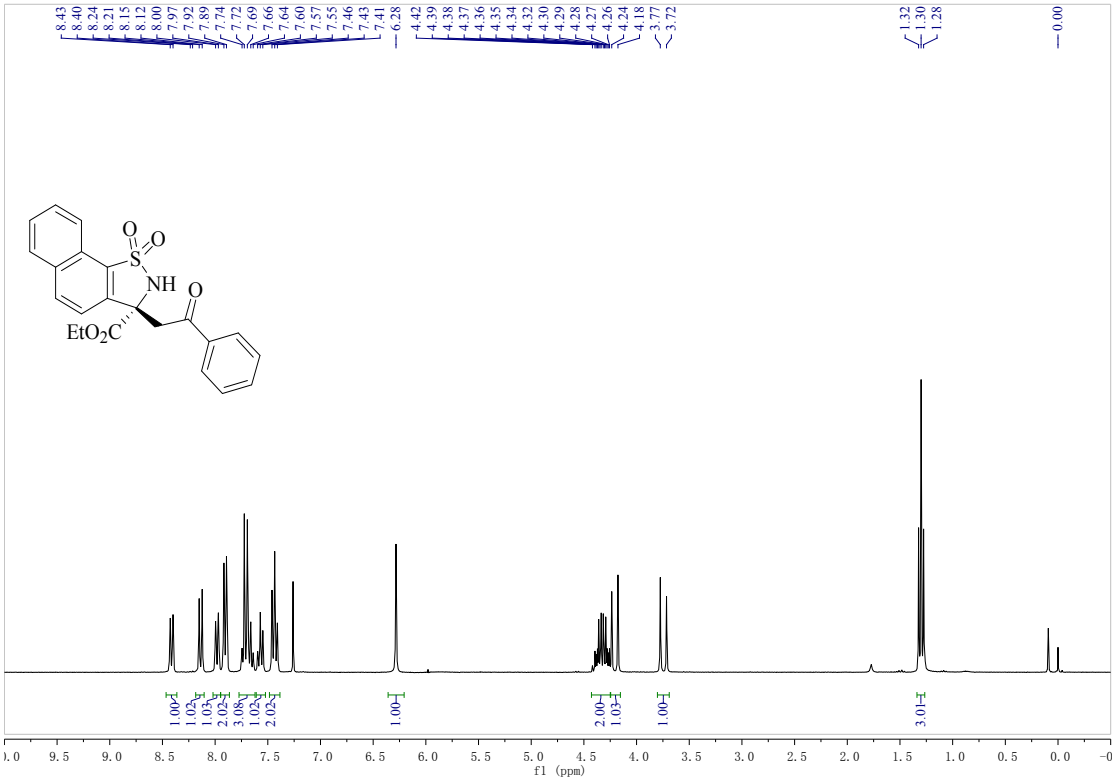
O
S
NH
O
EtO2C
f1 (ppm)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7.66
7.64
7.60
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7.55
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4.28
4.27
4.26
4.24
4.18
3.77
3.72
1.32
1.30
1.28
0.00
O
O
S
NH
O
EtO2C
1.00
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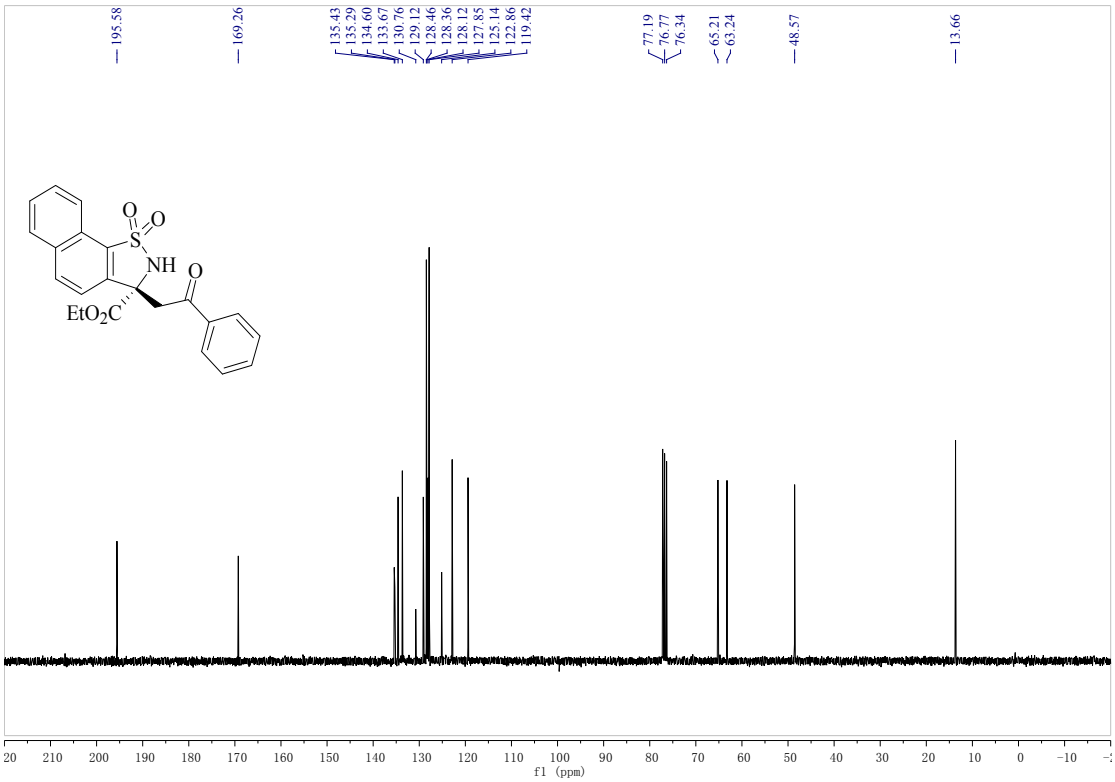
2.02
1.00
2.00
1.03
1.00
3.01
f1 (ppm)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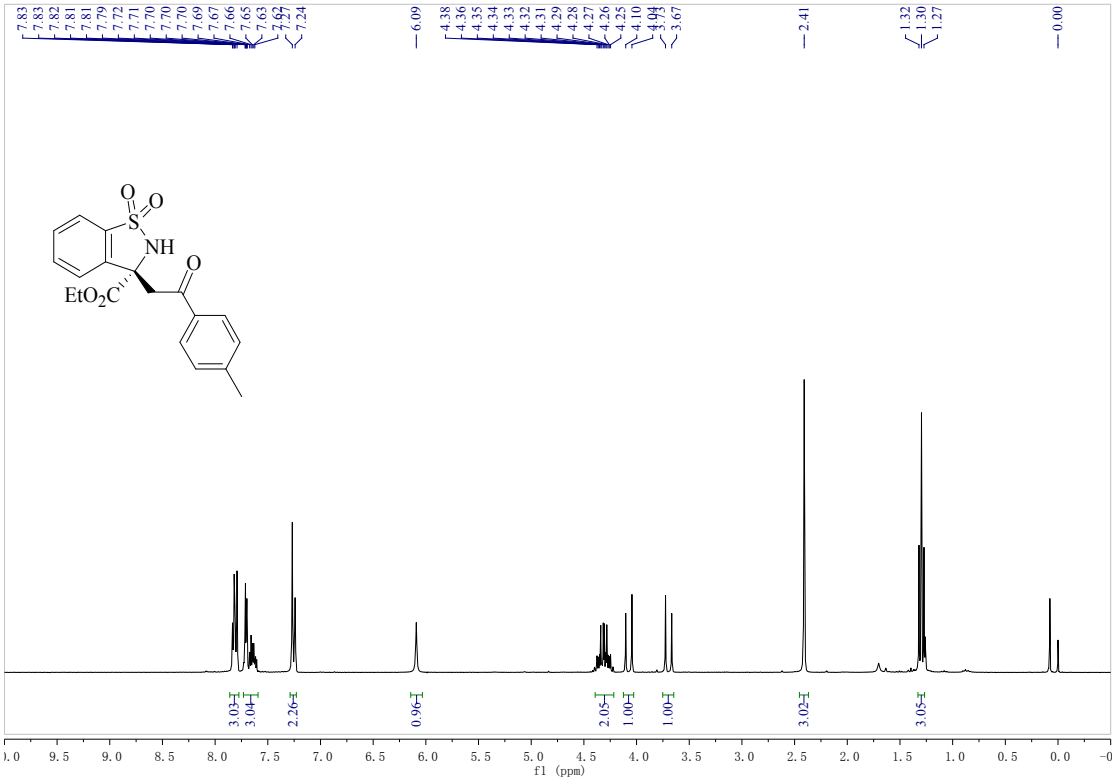
O
S
NH
O
EtO2C
f1 (ppm)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7.65
7.63
7.62
7.27
7.24
6.09
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4.33
4.32
4.31
4.29
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4.27
4.26
4.25
4.10
4.04
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3.67
2.41
1.32
1.30
1.27
0.00
O
O
S
NH
O
EtO2C
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3.04
2.26
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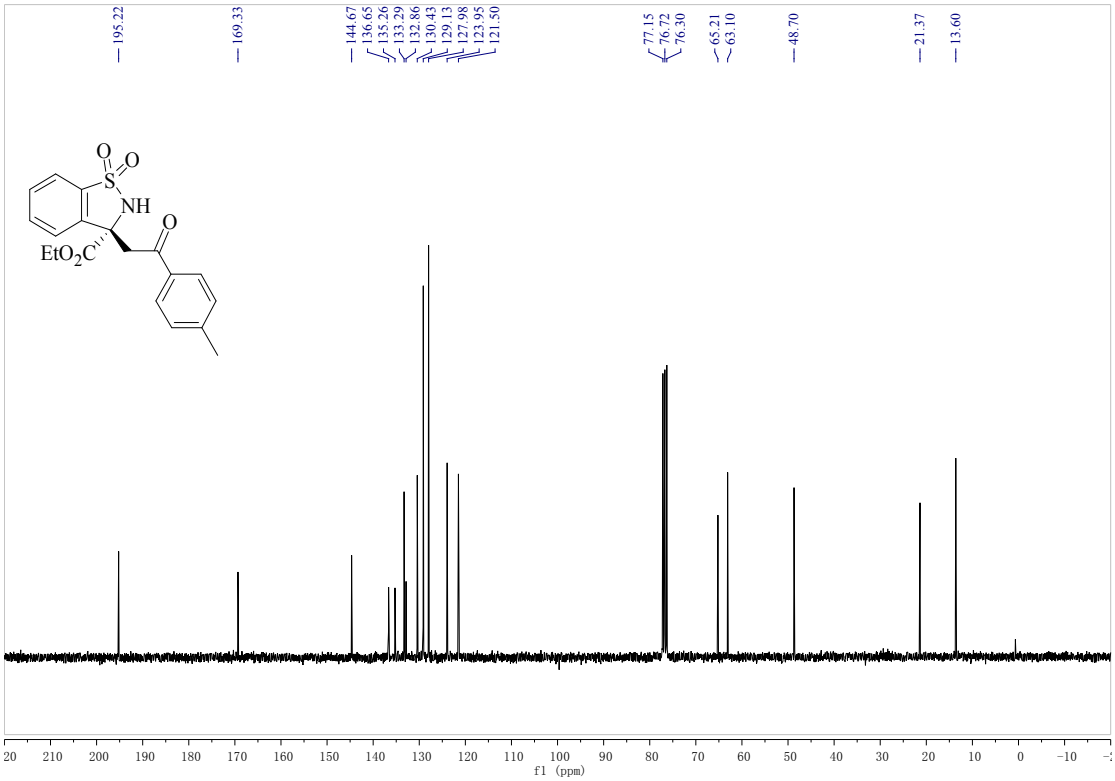
1.00
3.02
3.05
f1 (ppm)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130.43
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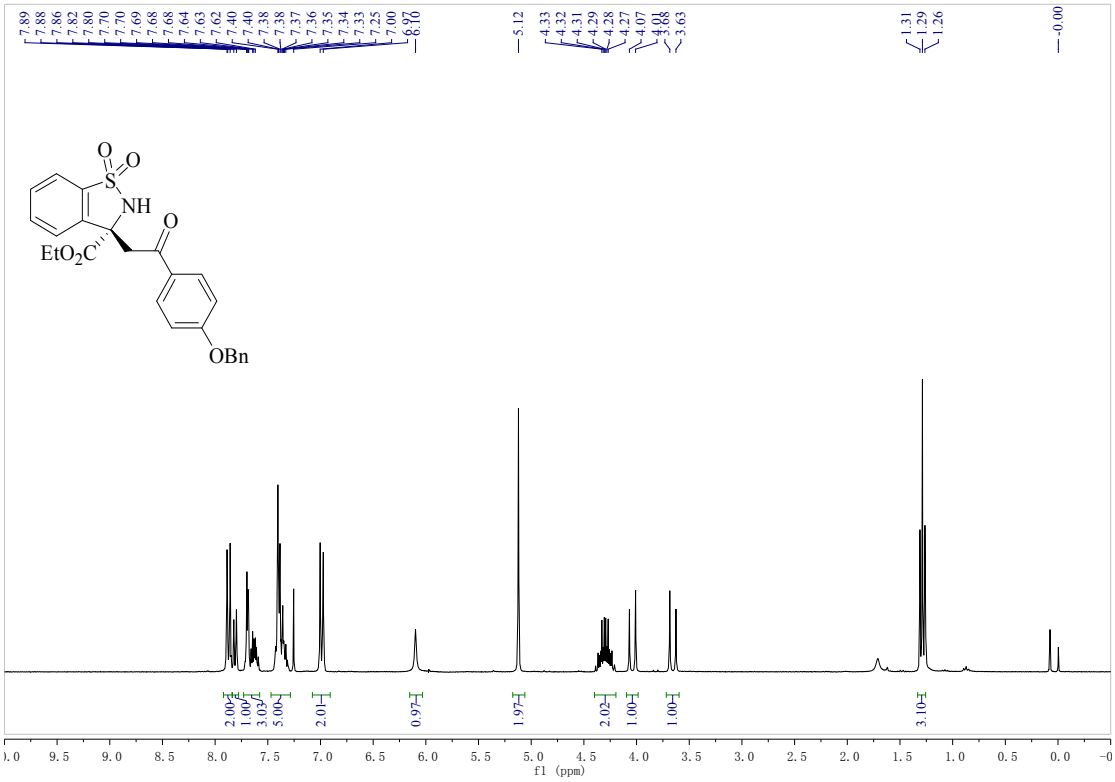
123.95
121.50
77.15
76.72
76.30
65.21
63.10
48.70
21.37
13.60
O
O
S
NH
O
EtO2C
f1 (ppm)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7.62
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.25
7.00
6.97
6.10
5.12
4.33
4.32
4.31
4.29
4.28
4.27
4.07
4.01
3.68
3.63
1.31
1.29
1.26
-0.00
O
O
S
NH
O
EtO2C
OBn
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1.00
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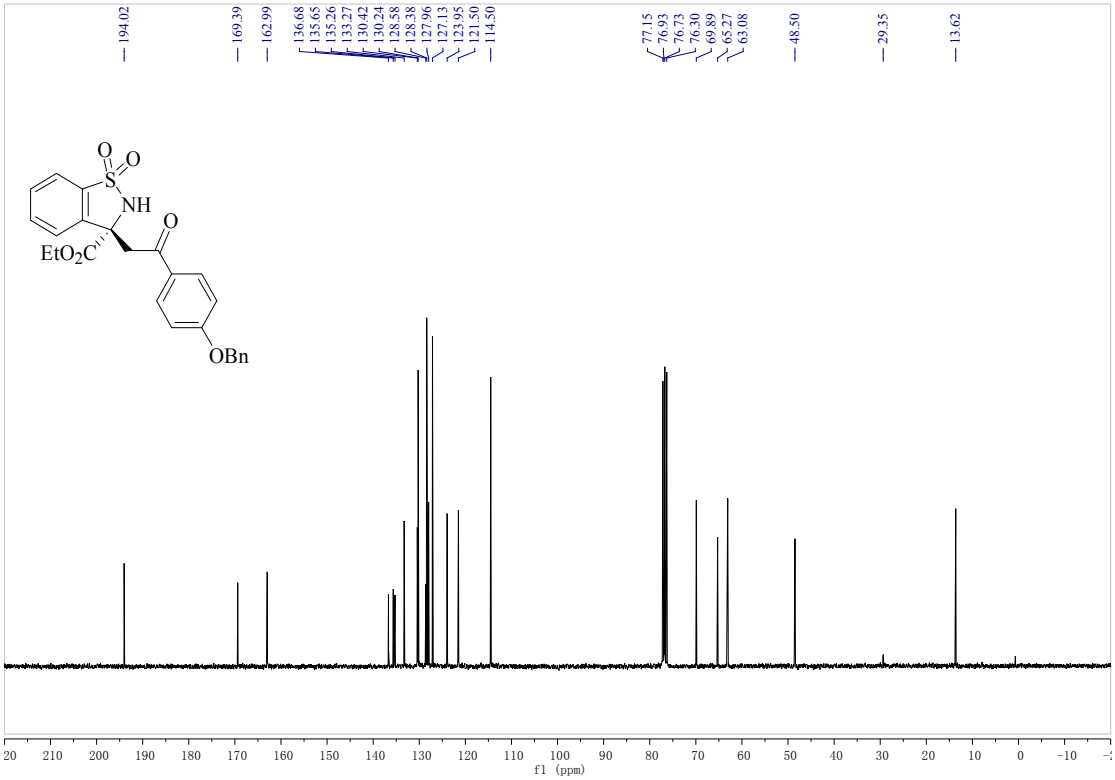
5.00
2.01
0.97
1.97
2.02
1.00
1.00
3.10
f1 (ppm)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127.96
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123.95
121.50
114.50
77.15
76.93
76.73
76.30
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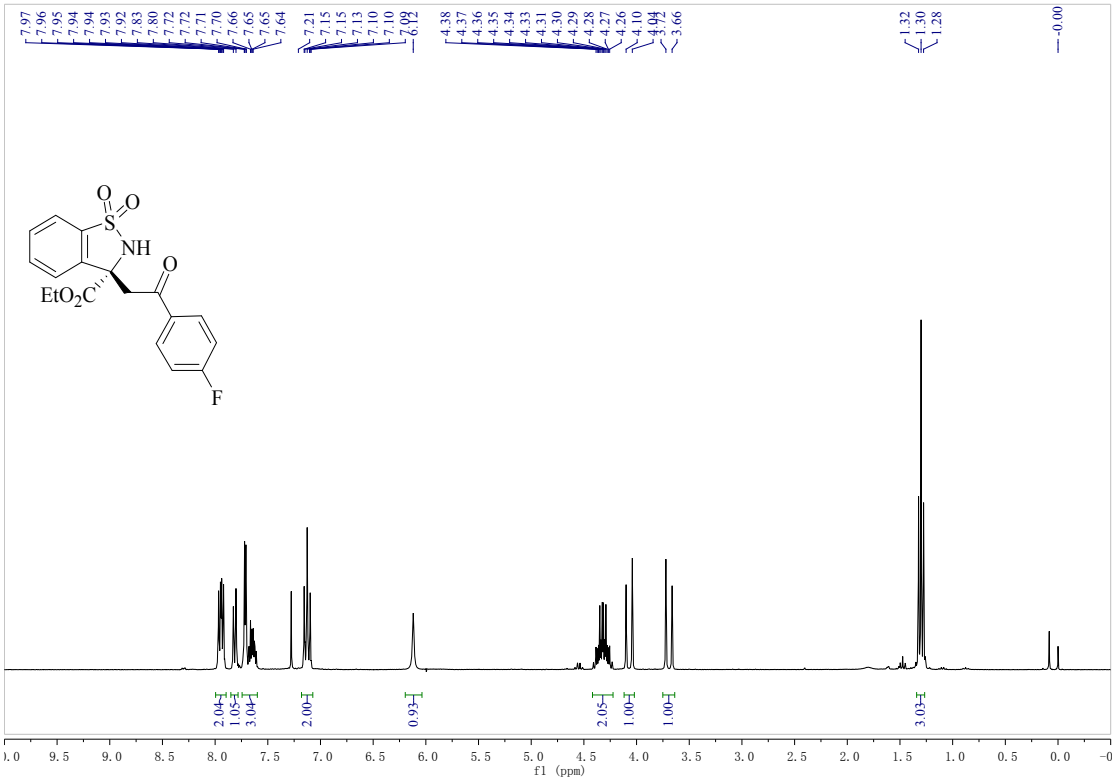
48.50
29.35
13.62
O
O
S
NH
O
EtO2C
OBn
f1 (ppm)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7.10
7.09
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4.28
4.27
4.26
4.10
4.04
3.72
3.66
1.32
1.30
1.28
0.00
O
O
S
NH
O
EtO2C
F
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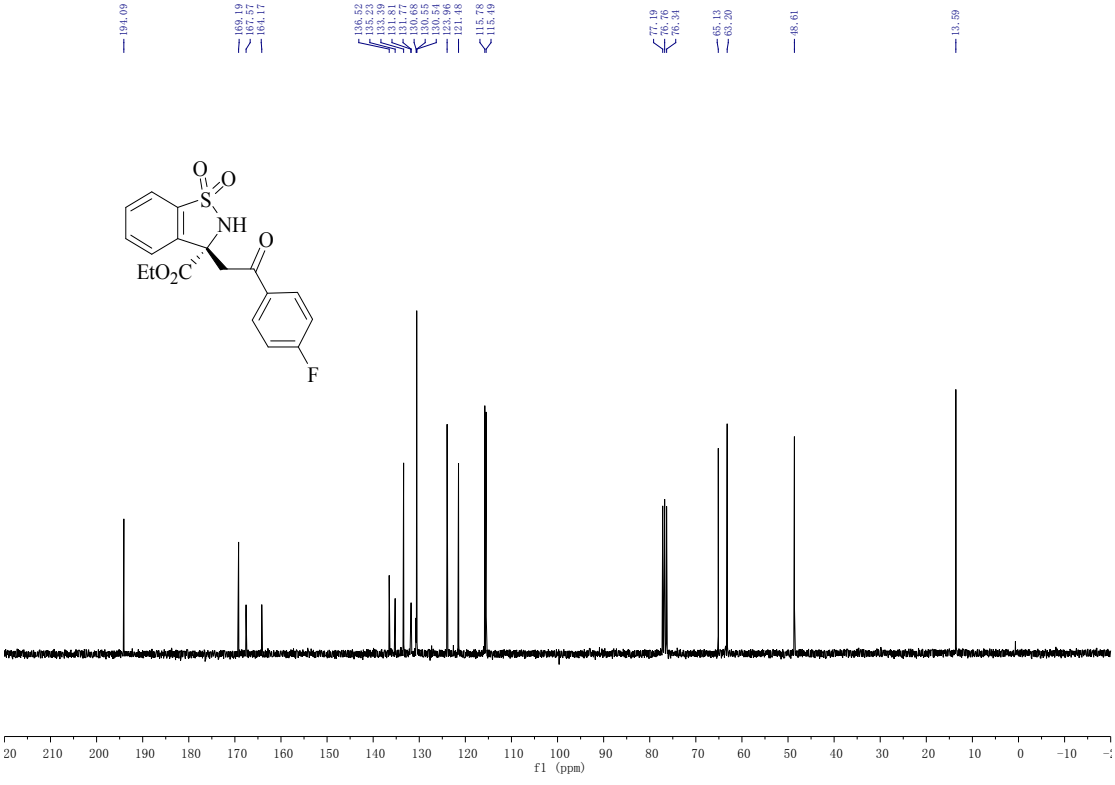
1.05
3.04
2.00
0.93
2.05
1.00
1.00
3.03
f1 (ppm)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121.48
115.78
115.49
77.19
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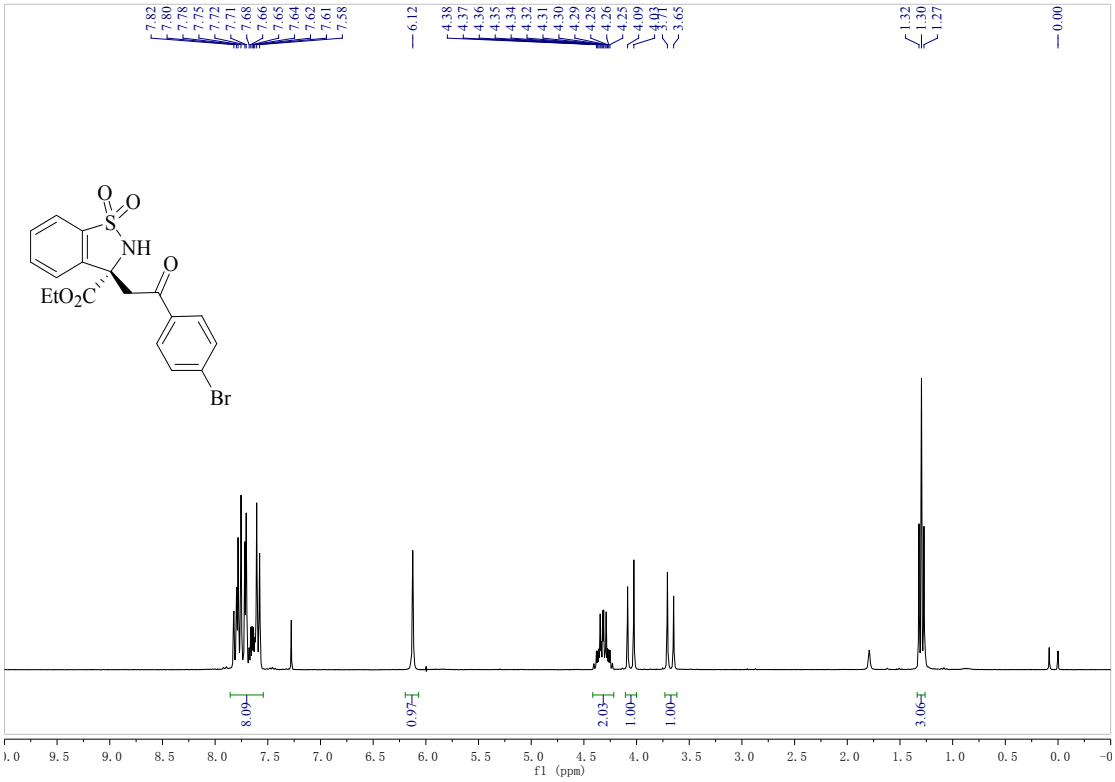
63.20
48.61
13.59
O
O
S
NH
O
EtO2C
F
f1 (ppm)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7.62
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6.12
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4.37
4.36
4.35
4.34
4.32
4.31
4.30
4.29
4.28
4.26
4.25
4.09
4.03
3.71
3.65
1.32
1.30
1.27
0.00
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NH
O
EtO2C
Br
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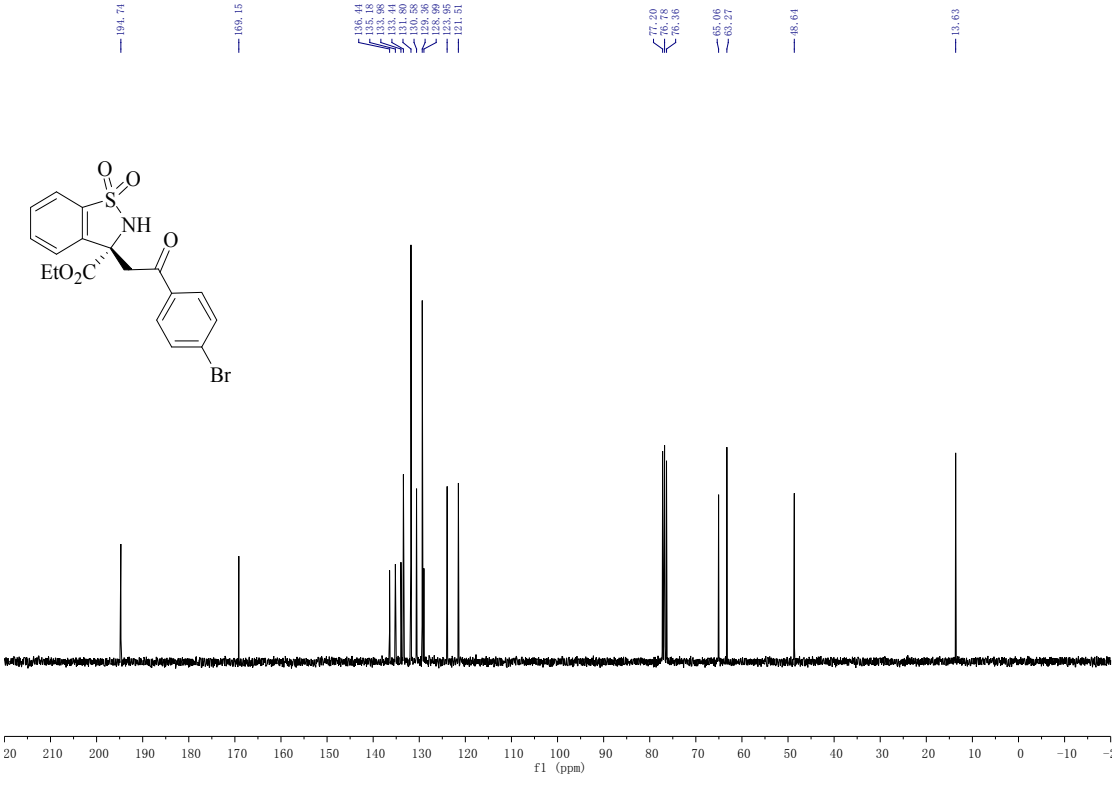
1.00
1.00
3.06
f1 (ppm)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128.98
123.95
121.51
77.20
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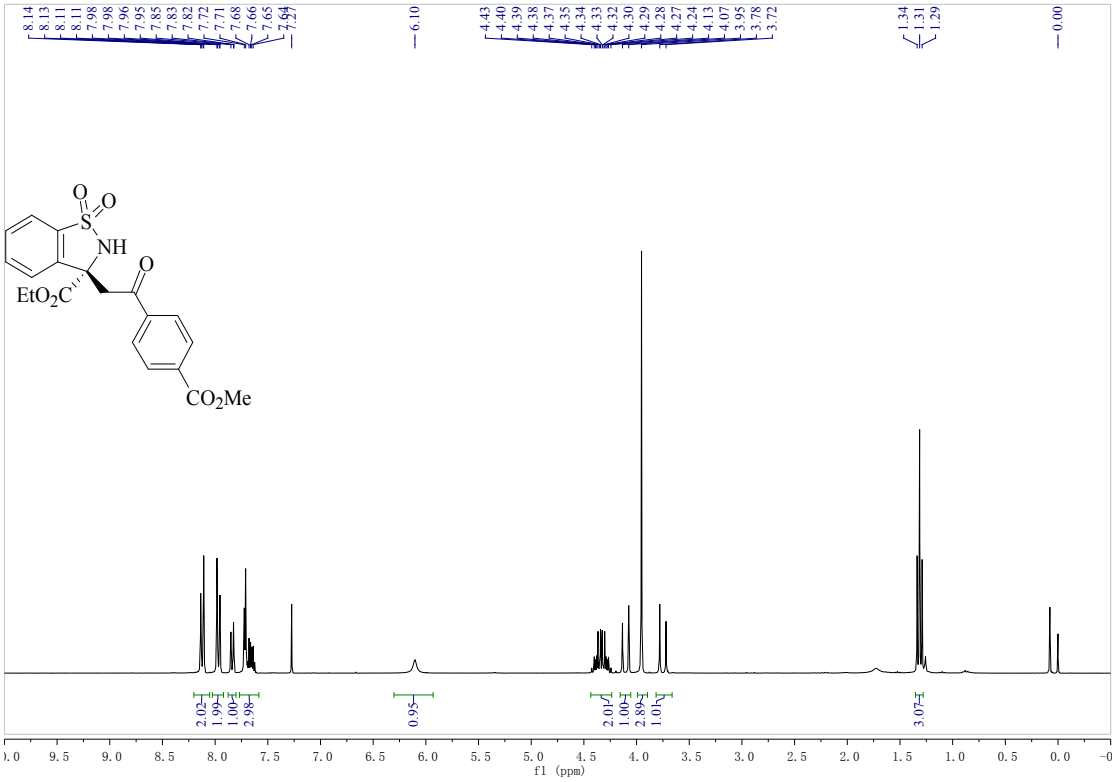
76.36
65.06
63.27
48.64
13.63
O
O
S
NH
O
EtO2C
Br
f1 (ppm)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7.71
7.68
7.66
7.65
7.64
6.10
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4.40
4.39
4.38
4.37
4.35
4.34
4.33
4.32
4.30
4.29
4.28
4.27
4.24
4.13
4.07
3.95
3.78
3.72
1.34
1.31
1.29
0.00
O
O
S
NH
O
EtO2C
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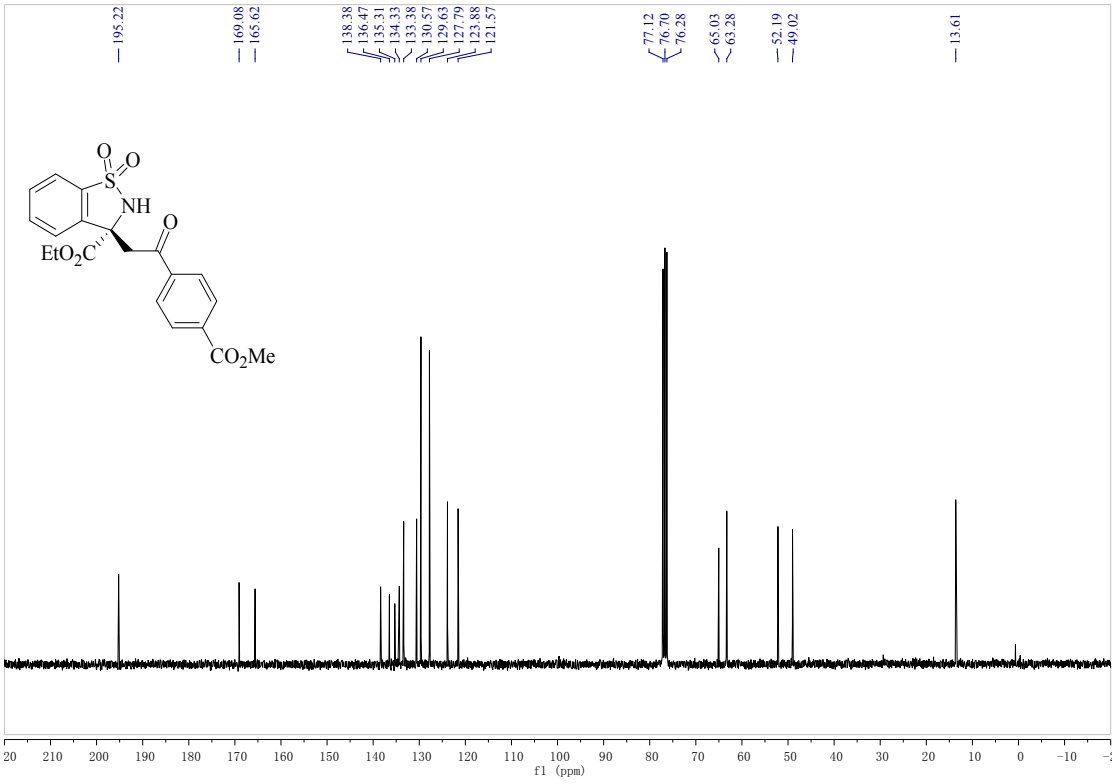
f1 (ppm)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76.70
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49.02
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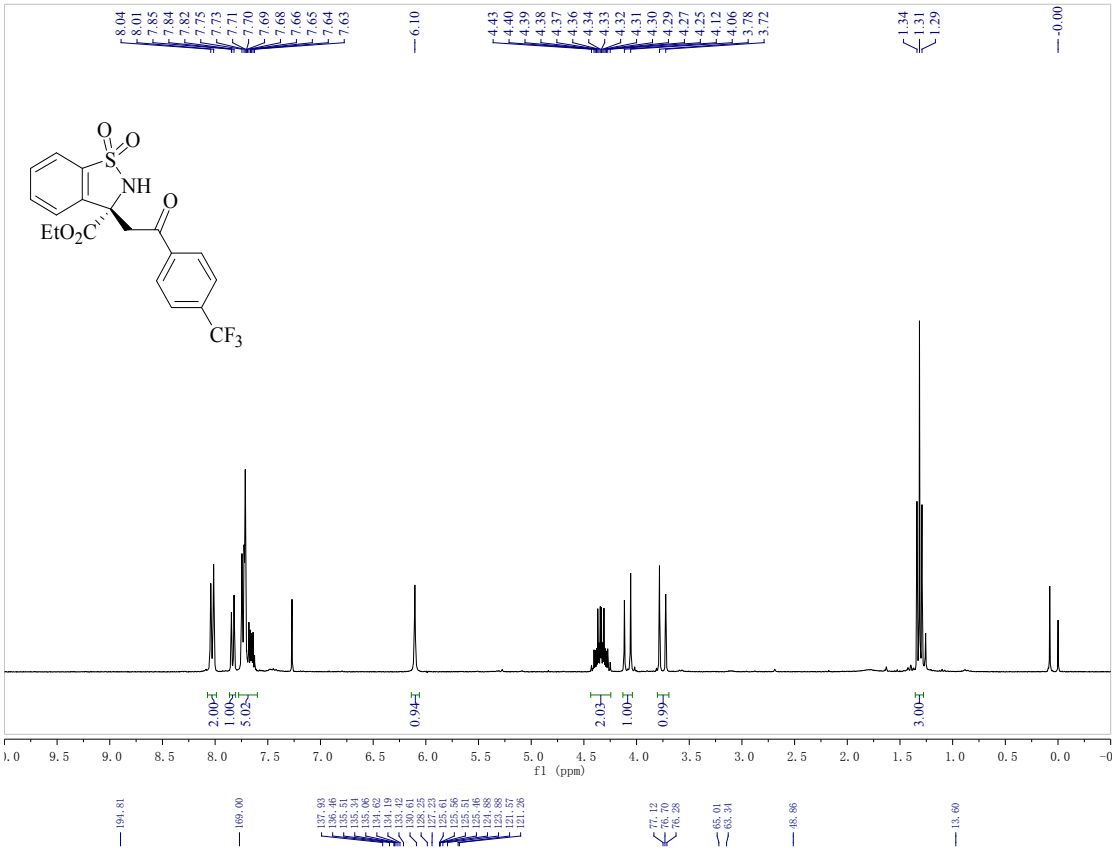
O
S
NH
O
EtO2C
CO2Me
f1 (ppm)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4.36
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4.32
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4.30
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4.25
4.12
4.06
3.78
3.72
1.34
1.31
1.29
0.00
O
O
S
NH
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CF3
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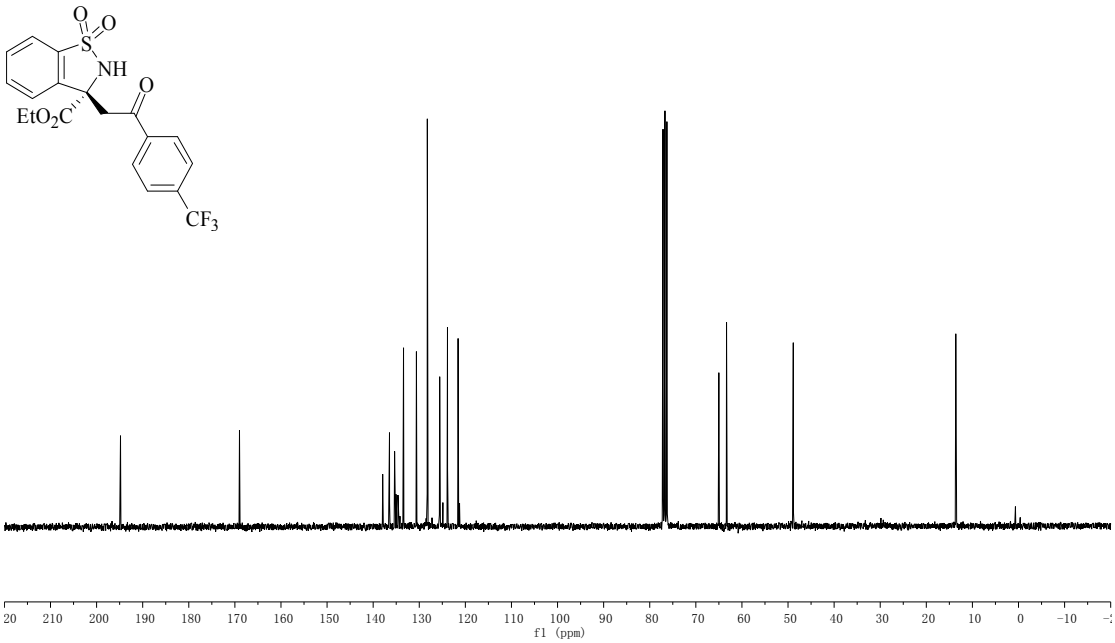
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121.26
77.12
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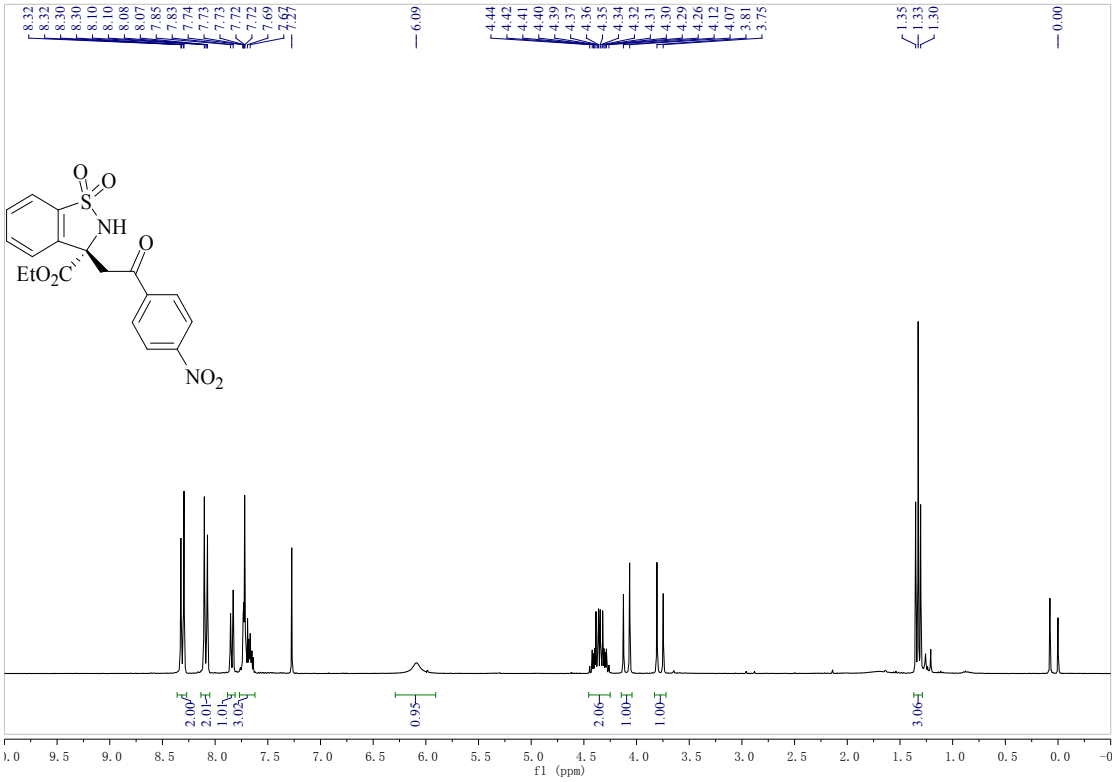
S
NH
O
EtO2C
CF3
f1 (ppm)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7.67
7.67
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4.32
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4.29
4.26
4.12
4.07
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3.75
1.35
1.33
1.30
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O
O
S
NH
O
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1.00
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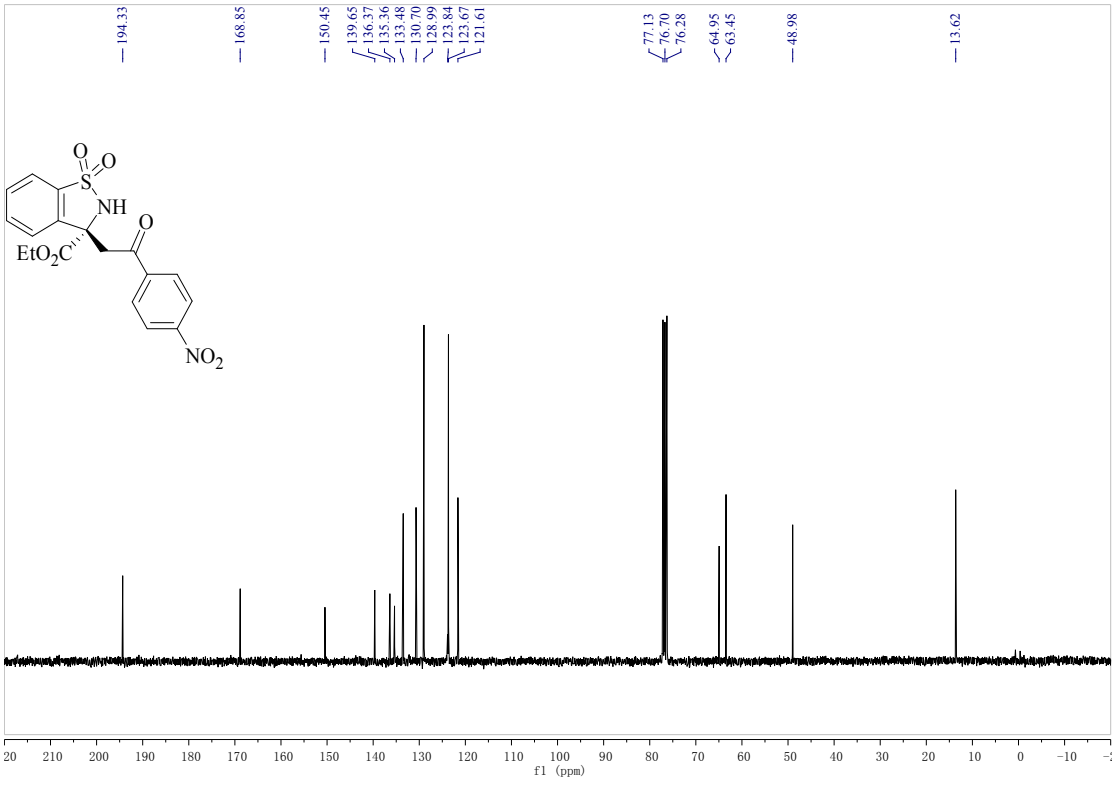
3.06
f1 (ppm)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77.13
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63.45
48.98
13.62
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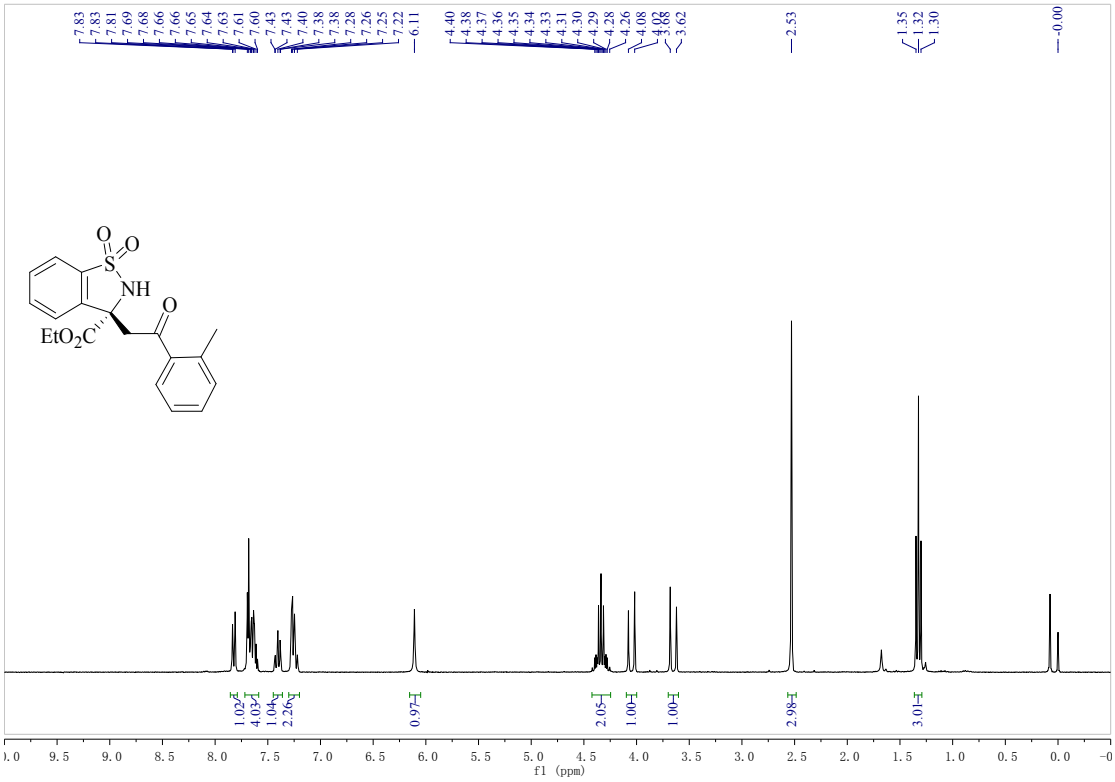
O
S
NH
O
EtO2C
NO2
f1 (ppm)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4.38
4.37
4.36
4.35
4.34
4.33
4.31
4.30
4.29
4.28
4.26
4.08
4.02
3.68
3.62
2.53
1.35
1.32
1.30
0.00
O
O
S
NH
O
EtO2C
1.02
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1.04
2.26
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2.05
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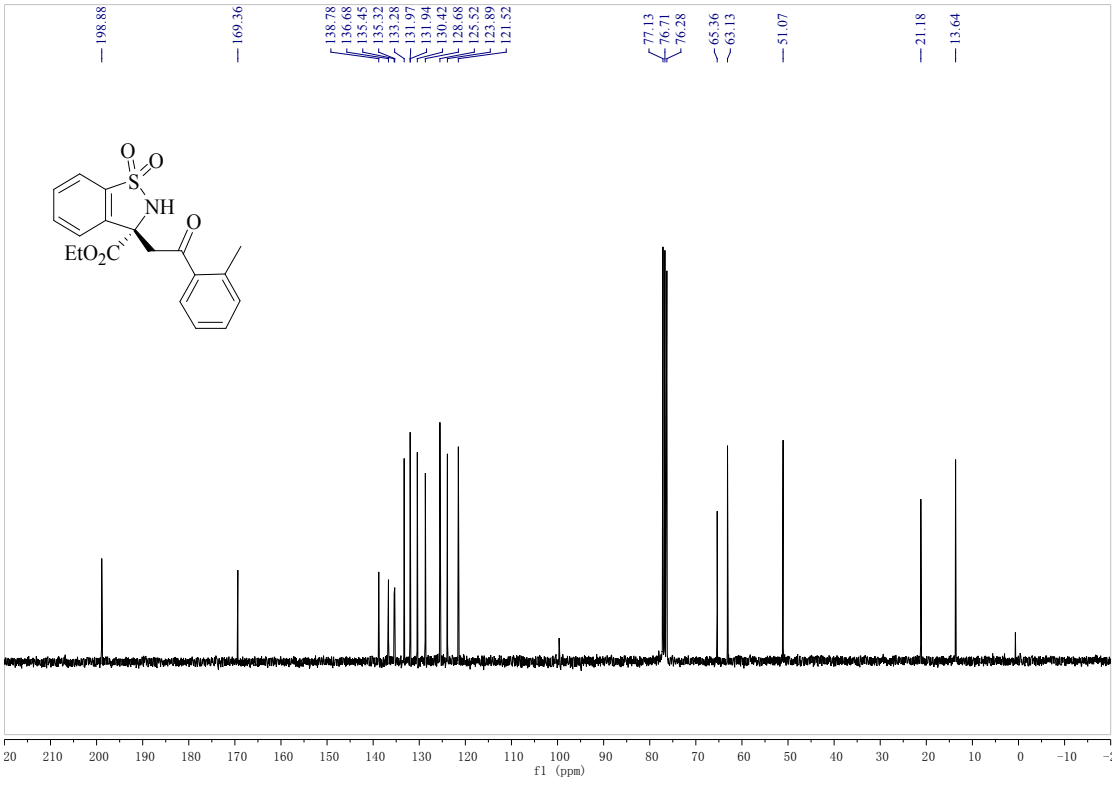
1.00
2.98
3.01
f1 (ppm)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123.89
121.52
77.13
76.71
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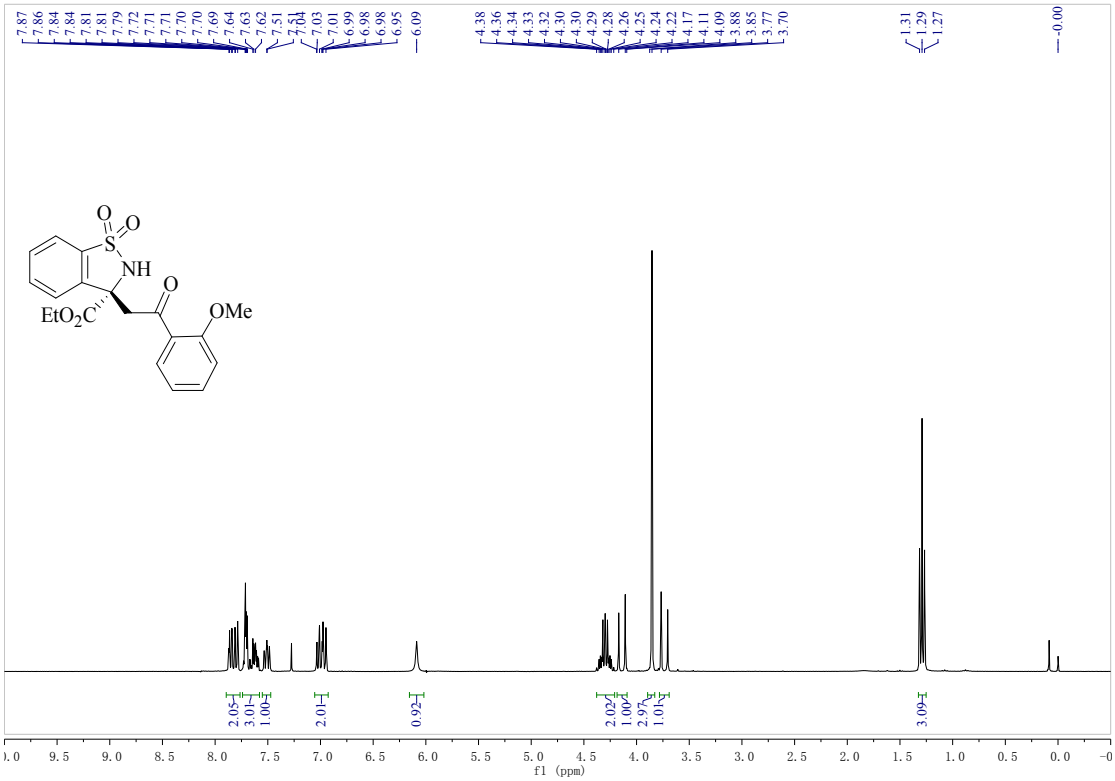
63.13
51.07
21.18
13.64
O
O
S
NH
O
EtO2C
f1 (ppm)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7.64
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7.62
7.51
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7.03
7.01
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6.98
6.95
6.09
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4.25
4.24
4.22
4.17
4.11
4.09
3.88
3.85
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3.70
1.31
1.29
1.27
0.00
O
O
S
NH
O
EtO2C
OMe
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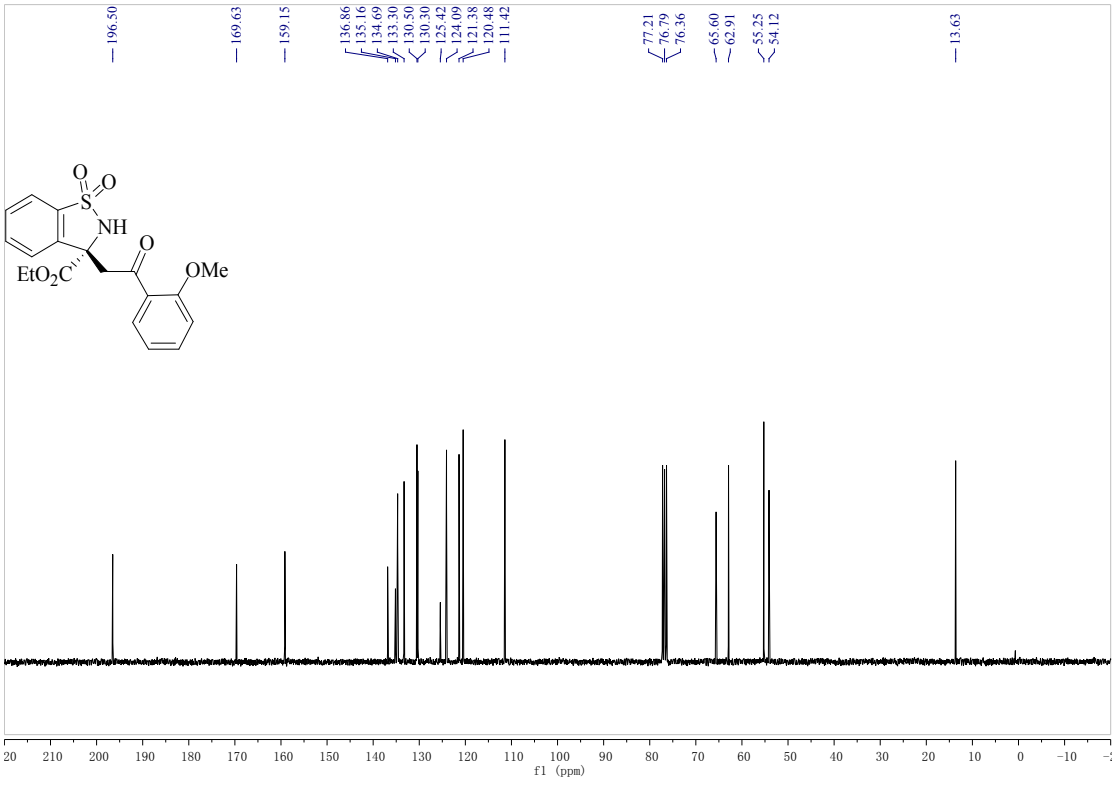
1.00
2.01
0.92
2.02
1.00
2.97
1.01
3.09
f1 (ppm)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130.50
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125.42
124.09
121.38
120.48
111.42
77.21
76.79
76.36
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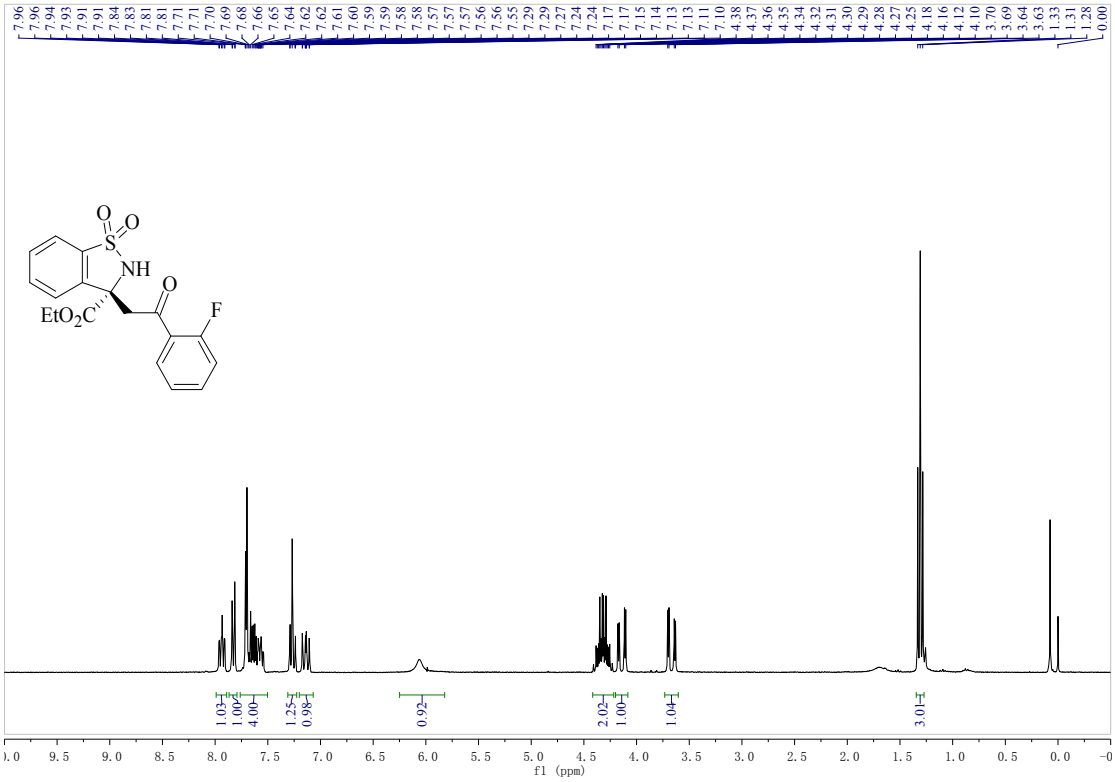
55.25
54.12
13.63
O
O
S
NH
O
EtO2C
OMe
f1 (ppm)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S
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O
EtO2C
F
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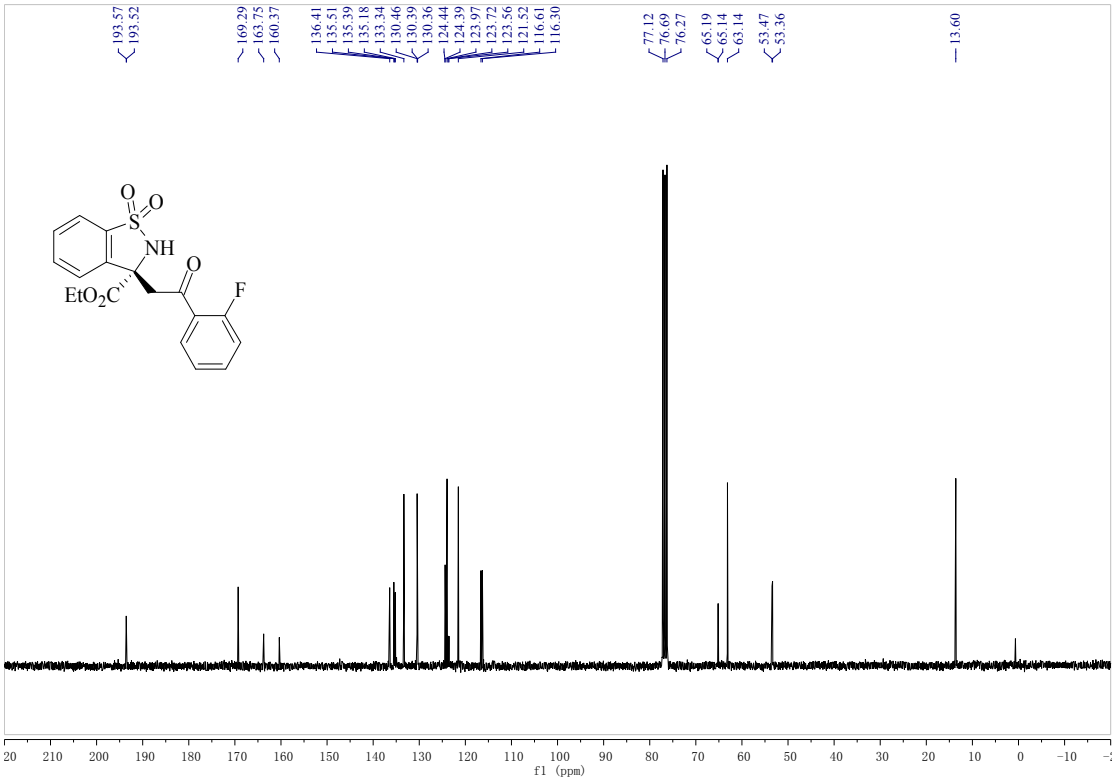
f1 (ppm)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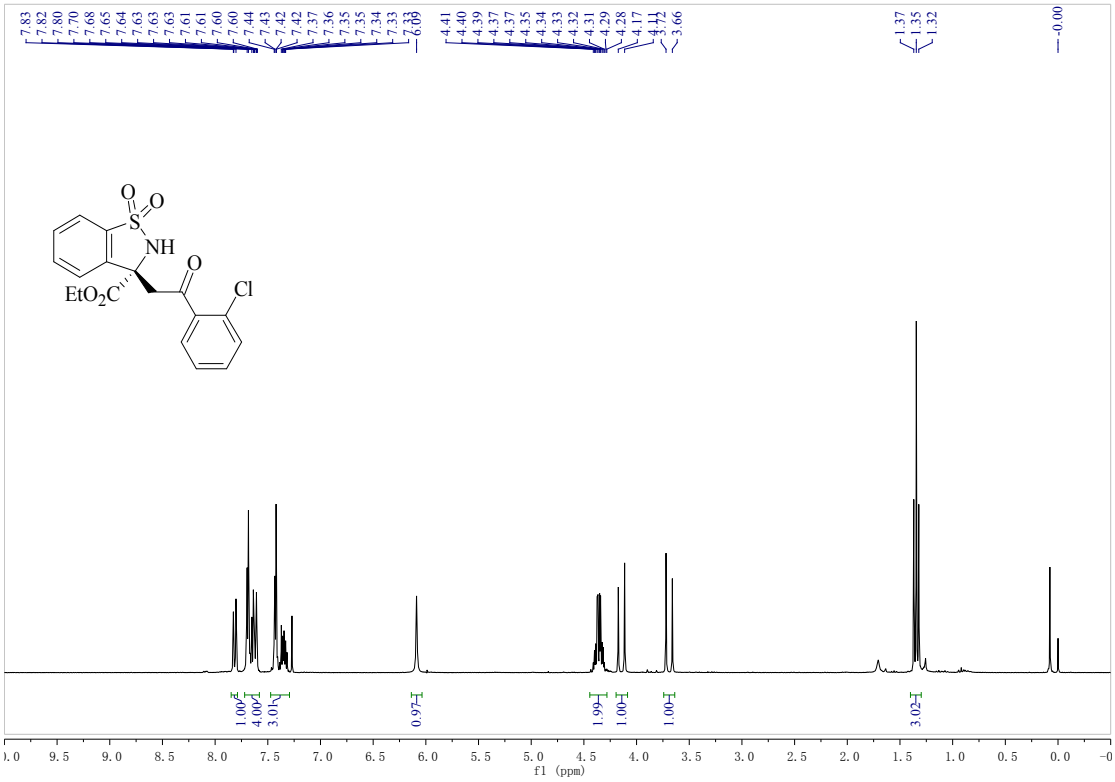
O
S
NH
O
EtO2C
F
f1 (ppm)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4.41 4.40 4.39 4.37 4.37 4.35 4.34 4.33 4.32 4.31 4.29 4.28 4.17 4.11 3.72 3.66
1.37 1.35 1.32
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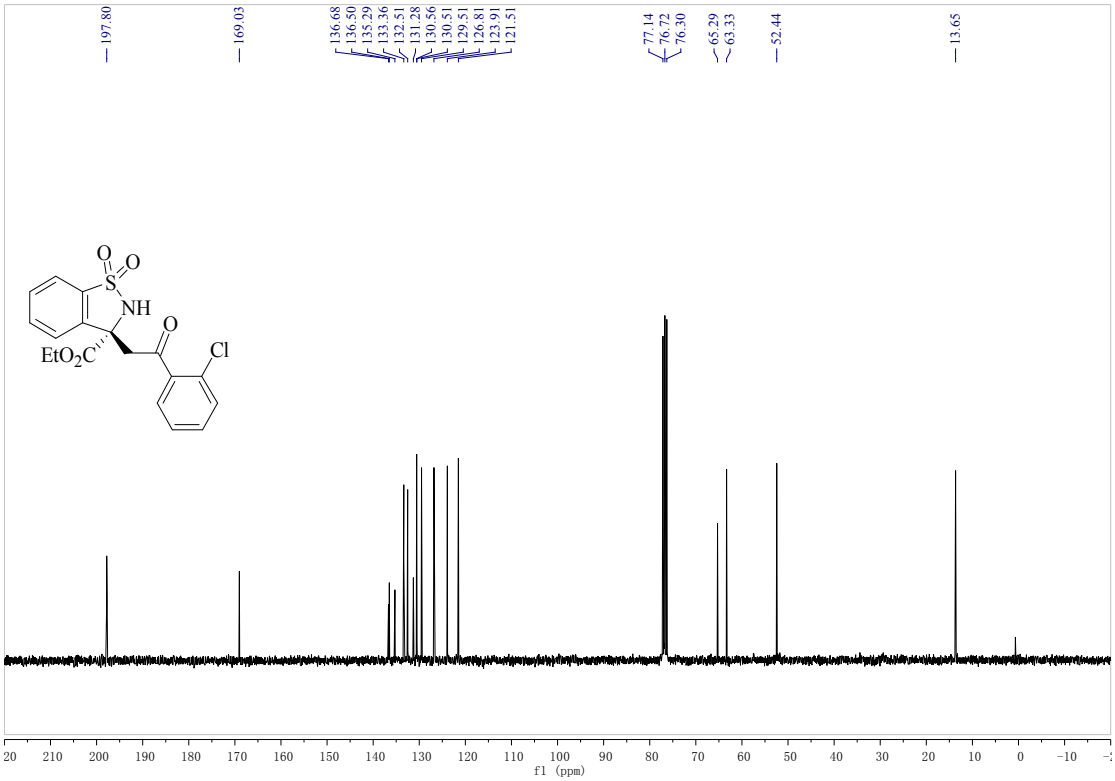
O
EtO2C
Cl
1.00 4.00 3.01 0.97 1.99 1.00 1.00 3.02
f1 (ppm)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169.03
136.68 136.50 135.29 133.36 132.51 131.28 130.56 130.51 129.51 126.81 123.91 121.51
77.14 76.72 76.30
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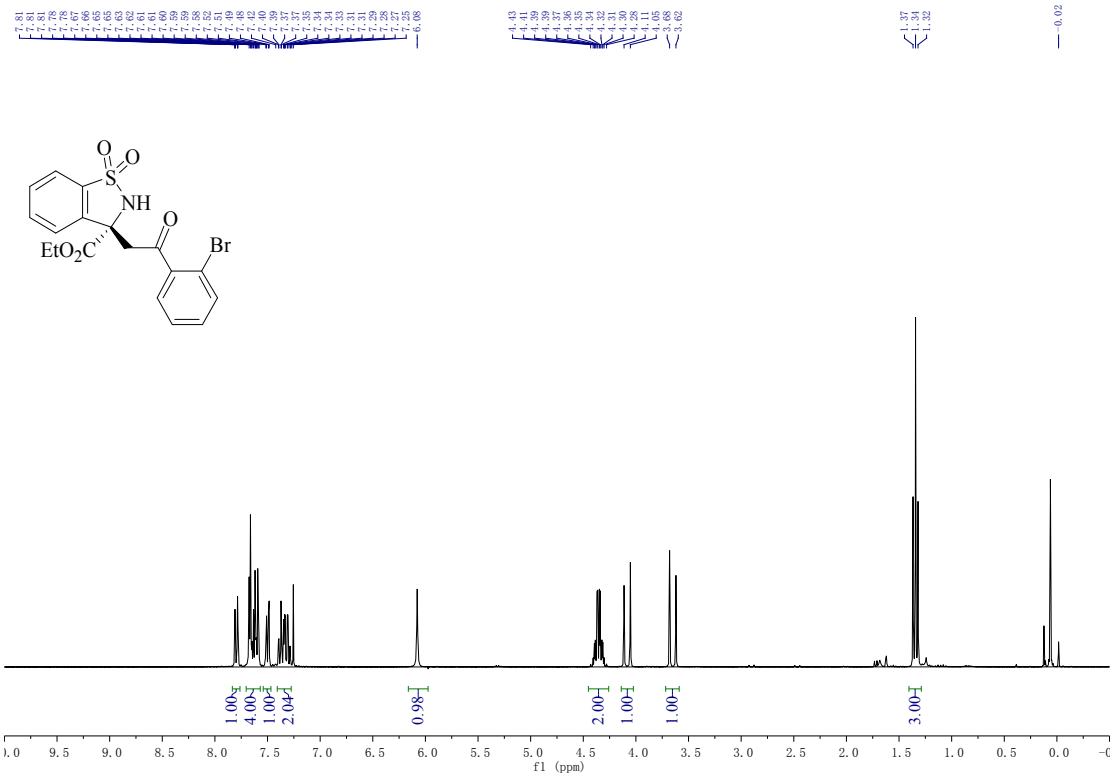
52.44
13.65
O
O
S
NH
O
EtO2C
Cl
f1 (ppm)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4.43 4.41 4.39 4.39 4.37 4.36 4.35 4.34 4.32 4.31 4.30 4.28 4.11 4.05 3.68 3.62
1.37 1.34 1.32
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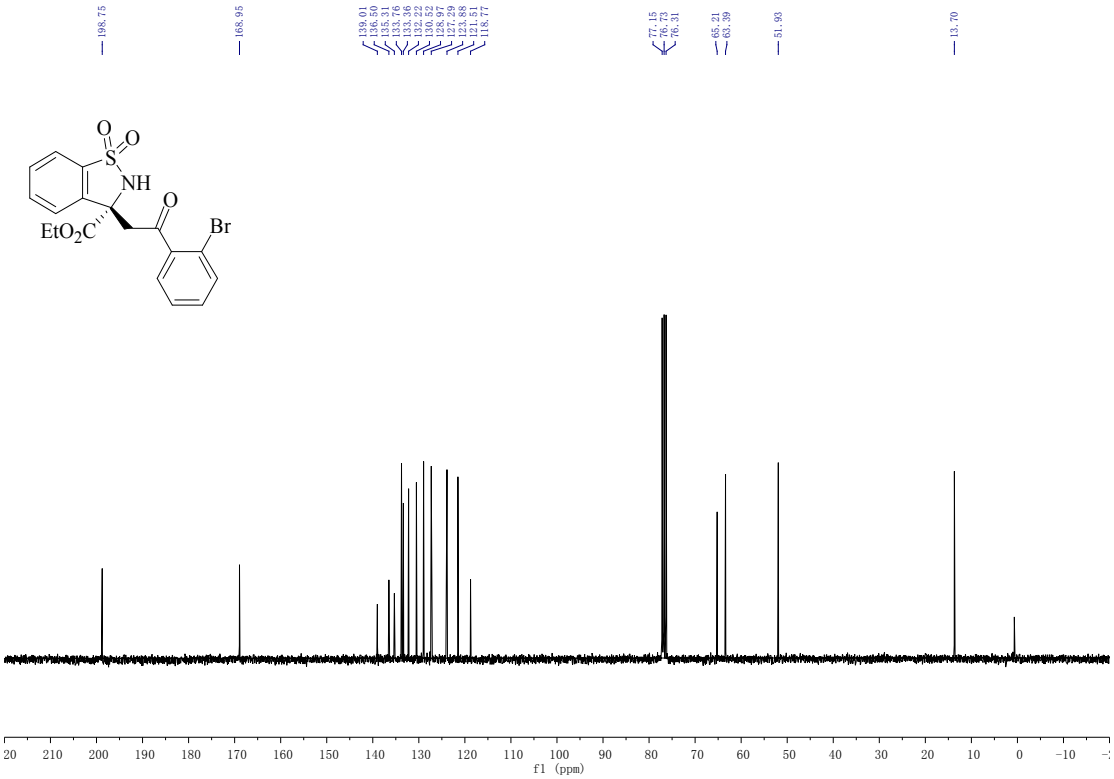
O O S NH O EtO2C Br
1.00 4.00 1.00 2.04 0.98 2.00 1.00 1.00 3.00
f1 (ppm)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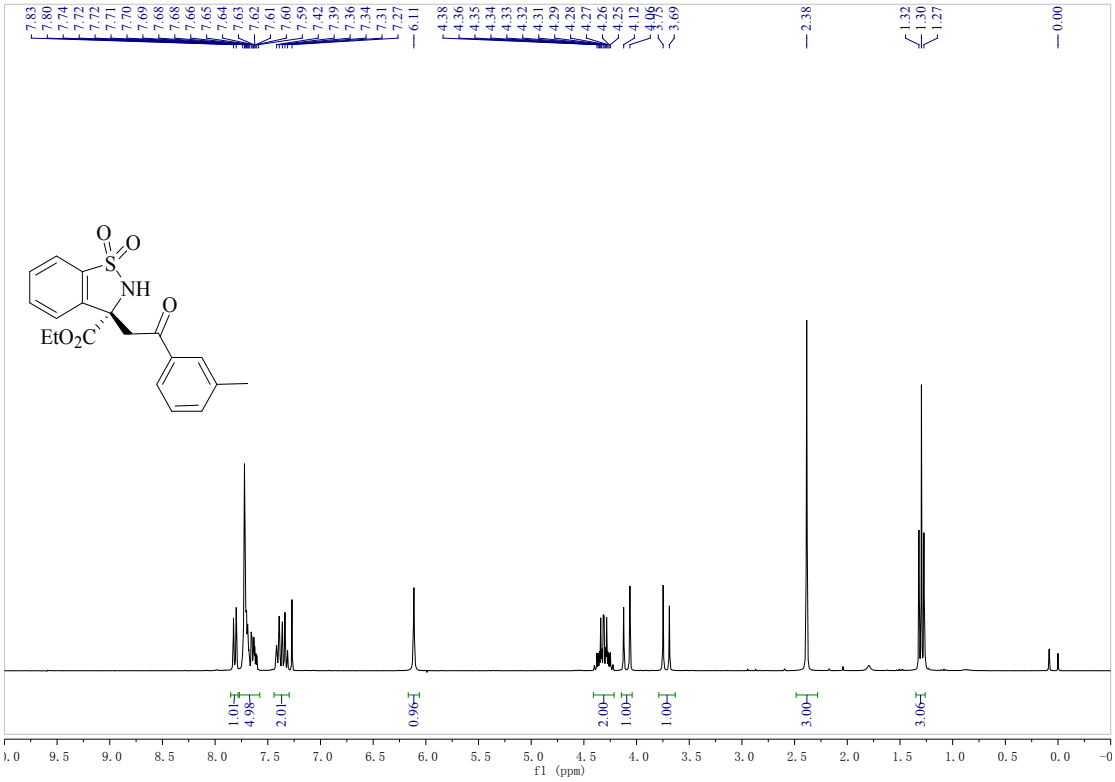
168.95
139.01 136.50 135.31 133.76 133.45 132.22 130.52 128.97 127.89 121.58 121.51 118.77
77.15 76.73 76.31
65.21 63.39
51.93
13.70
O O S NH O EtO2C Br
f1 (ppm)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7.65
7.64
7.63
7.62
7.61
7.60
7.59
7.42
7.39
7.36
7.34
7.31
7.27
6.11
4.38
4.36
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4.33
4.32
4.31
4.29
4.28
4.27
4.26
4.25
4.12
3.69
2.38
1.32
1.30
1.27
0.00
O
O
S
NH
O
EtO2C
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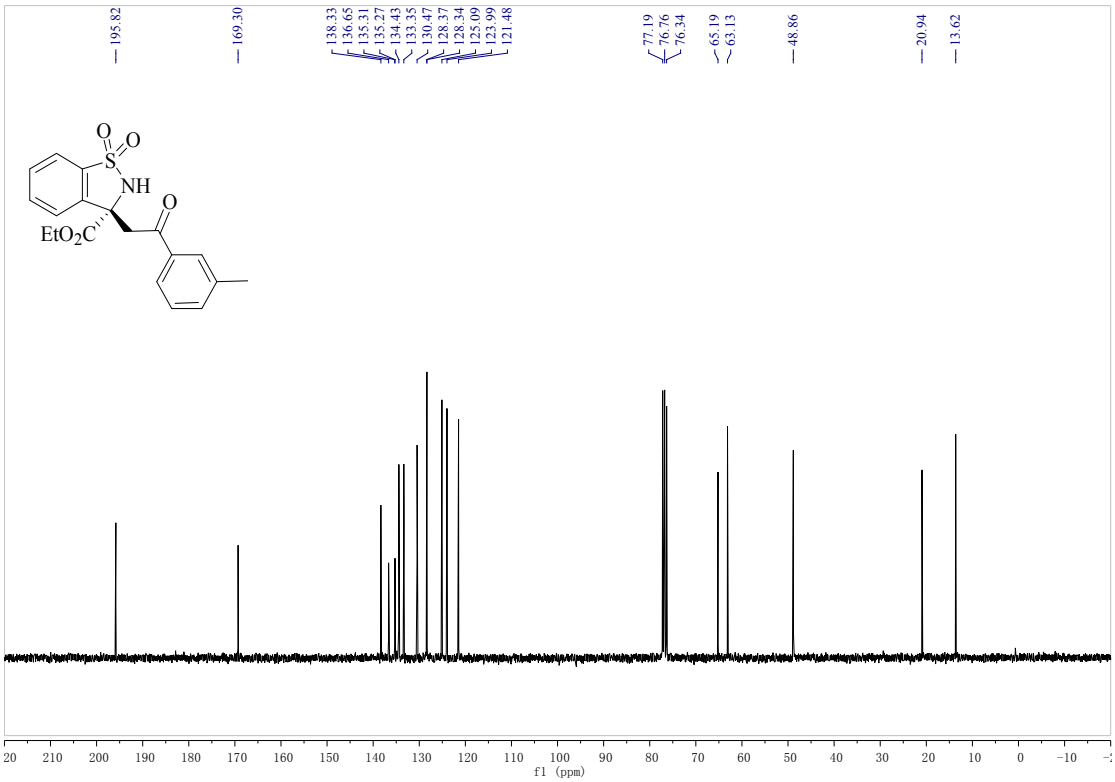
4.98
2.01
0.96
2.00
1.00
1.00
3.00
3.00
f1 (ppm)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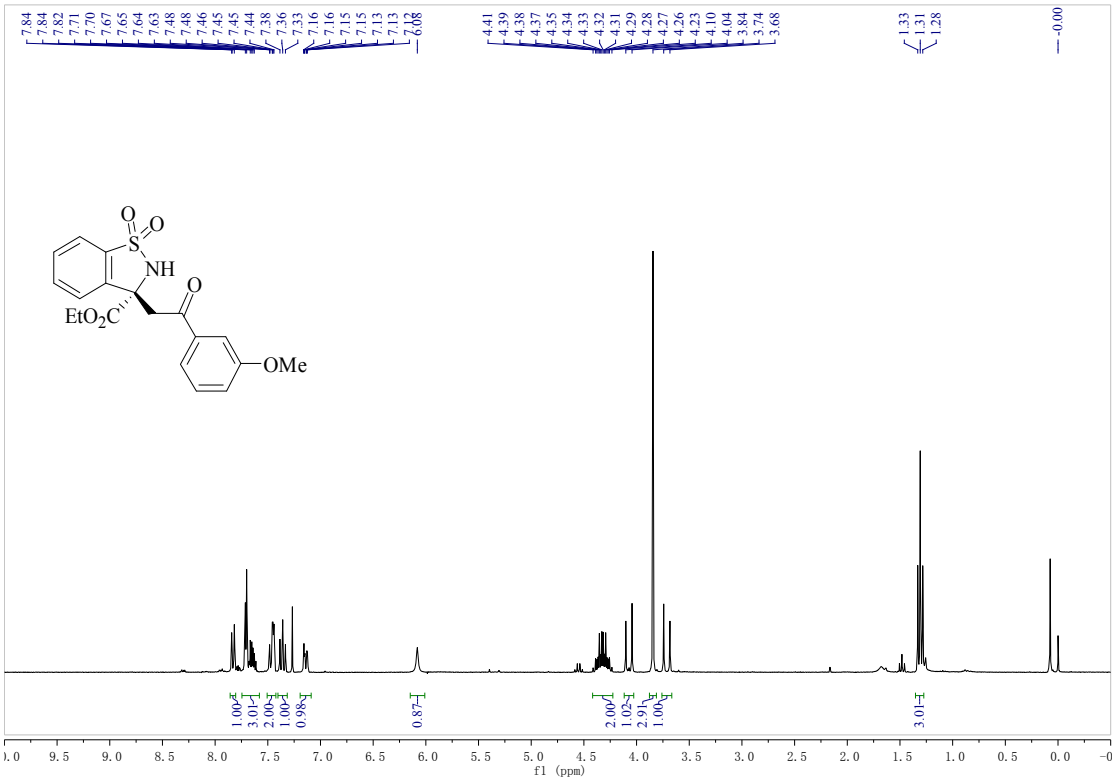
135.27
134.43
133.35
130.47
128.37
128.34
125.09
123.99
121.48
77.19
76.76
76.34
65.19
63.13
48.86
20.94
13.62
O
O
S
NH
O
EtO2C
f1 (ppm)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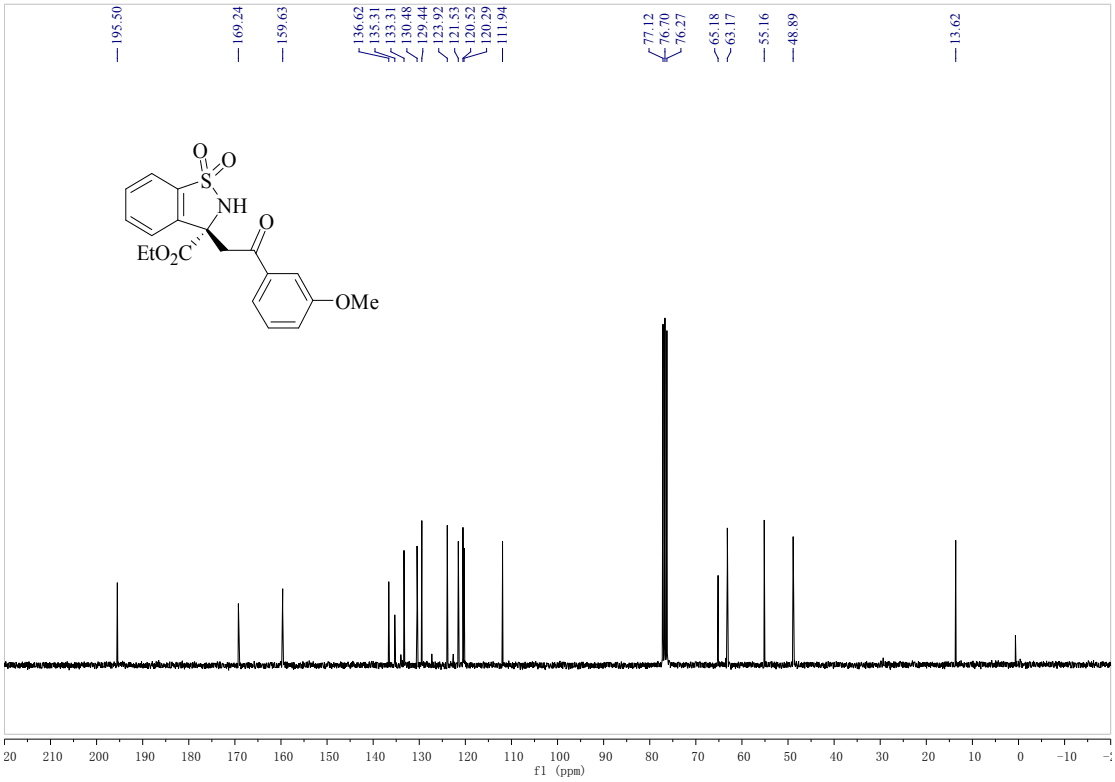
7.65
7.64
7.63
7.48
7.48
7.46
7.45
7.45
7.44
7.38
7.36
7.33
7.16
7.16
7.15
7.15
7.13
7.13
7.12
6.08
4.41
4.39
4.38
4.37
4.35
4.34
4.33
4.32
4.31
4.29
4.28
4.27
4.26
4.23
4.10
4.04
3.84
3.74
3.68
1.33
1.31
1.28
-0.00
O
O
S
NH
O
EtO2C
OMe
1.00
3.01
2.00
1.00
0.98
0.87
2.00
1.02
2.91
1.00
3.01
f1 (ppm)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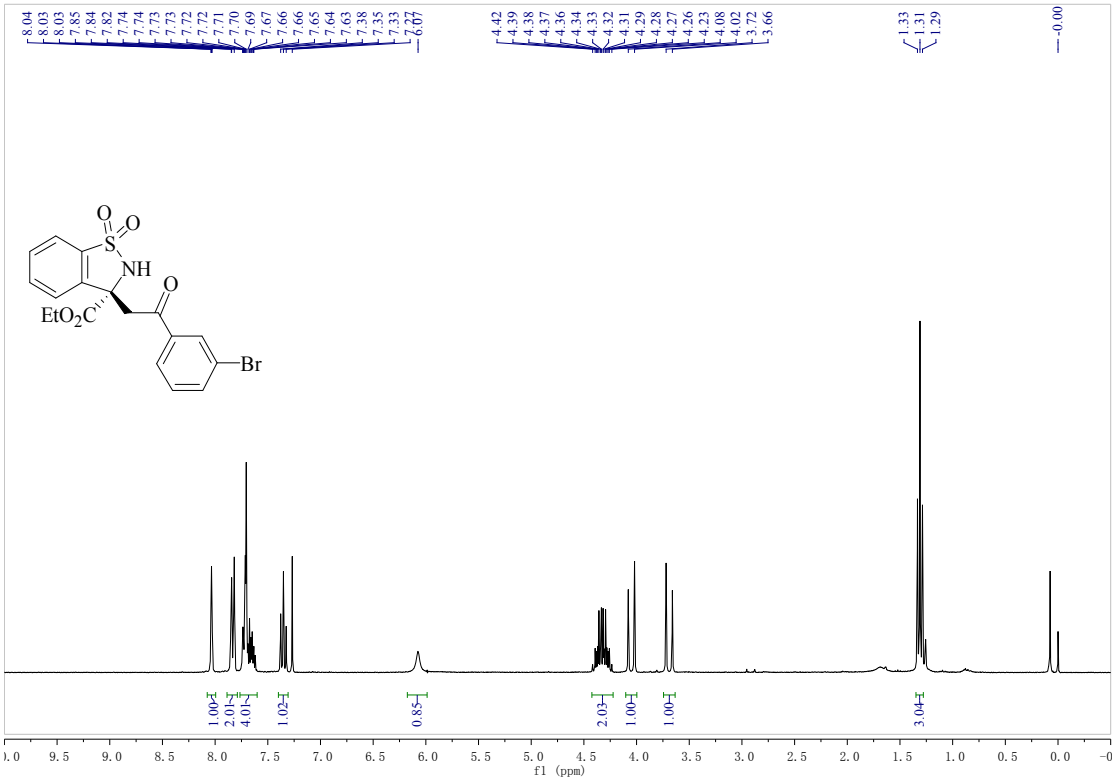
133.31
130.48
129.44
123.92
121.53
120.52
120.29
111.94
77.12
76.70
76.27
65.18
63.17
55.16
48.89
13.62
O
O
S
NH
O
EtO2C
OMe
f1 (ppm)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8.03
8.03
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7.82
7.74
7.74
7.73
7.73
7.72
7.72
7.71
7.70
7.69
7.67
7.66
7.66
7.65
7.64
7.63
7.38
7.35
7.33
7.27
6.07
4.42
4.39
4.38
4.37
4.36
4.34
4.33
4.32
4.31
4.29
4.28
4.27
4.26
4.23
4.08
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3.66
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1.31
1.29
-0.00
O
O
S
NH
O
EtO2C
Br
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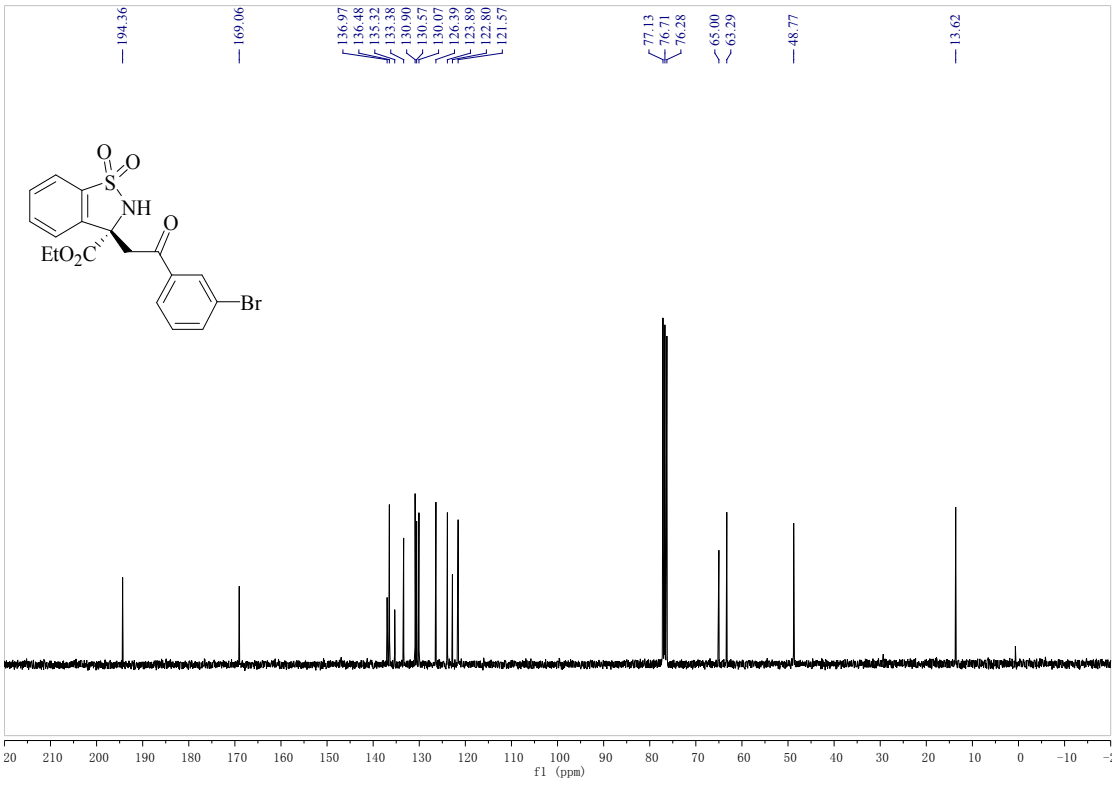
2.01
4.01
1.02
0.85
2.03
1.00
1.00
3.04
f1 (ppm)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135.32
133.38
130.90
130.57
130.07
126.39
123.89
122.80
121.57
77.13
76.71
76.28
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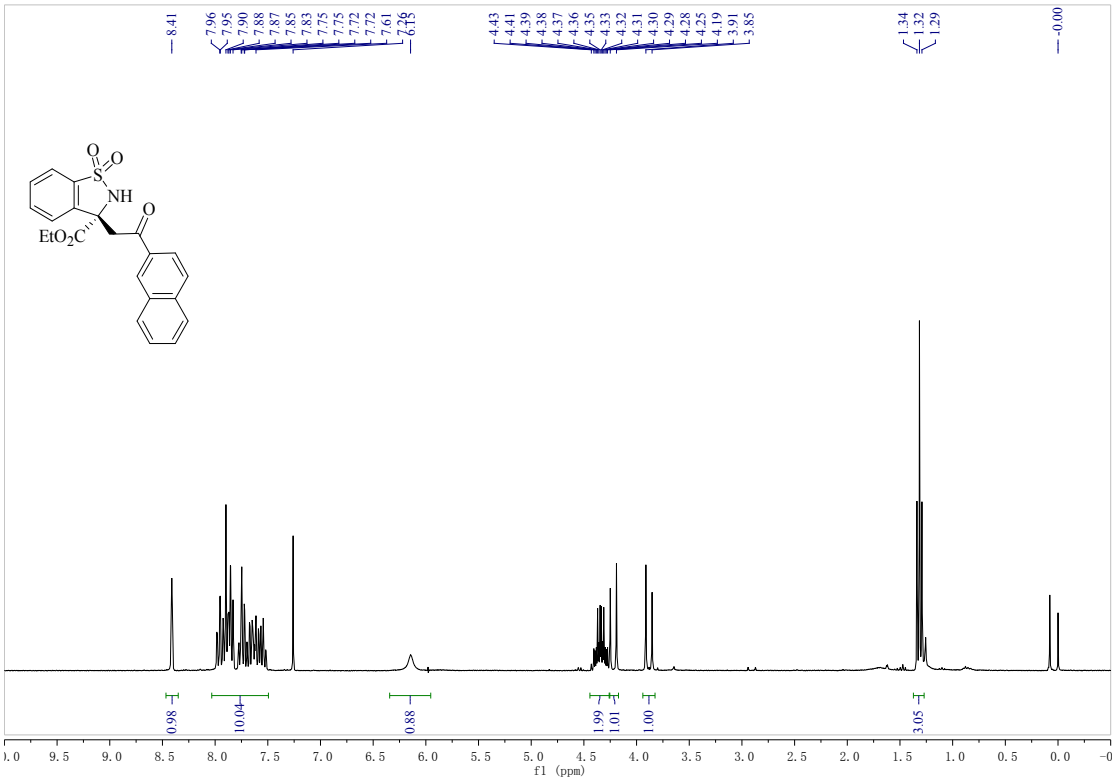
63.29
48.77
13.62
O
O
S
NH
O
EtO2C
Br
f1 (ppm)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7.95
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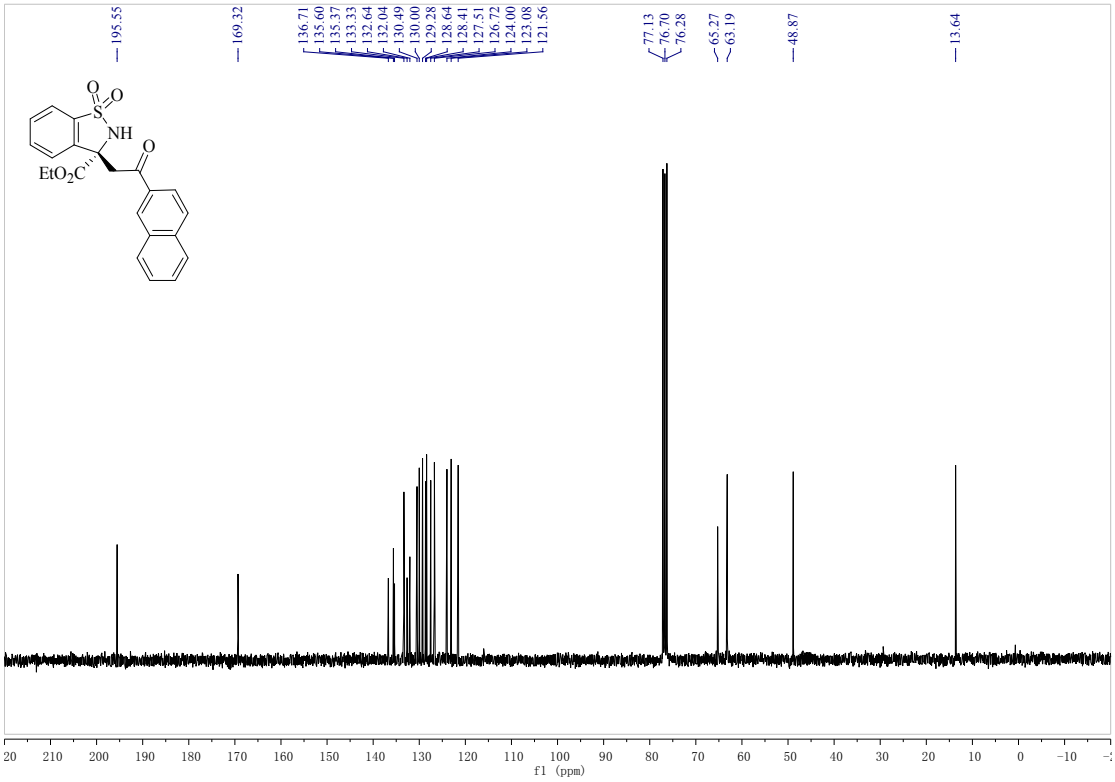
7.87
7.85
7.83
7.75
7.75
7.72
7.72
7.61
7.26
6.15
4.43
4.41
4.39
4.38
4.37
4.36
4.35
4.33
4.32
4.31
4.30
4.29
4.28
4.25
4.19
3.91
3.85
1.34
1.32
1.29
-0.00
O
O
S
NH
O
EtO2C
0.98
10.04
0.88
1.99
1.01
1.00
3.05
f1 (ppm)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132.04
130.49
130.00
129.28
128.64
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126.72
124.00
123.08
121.56
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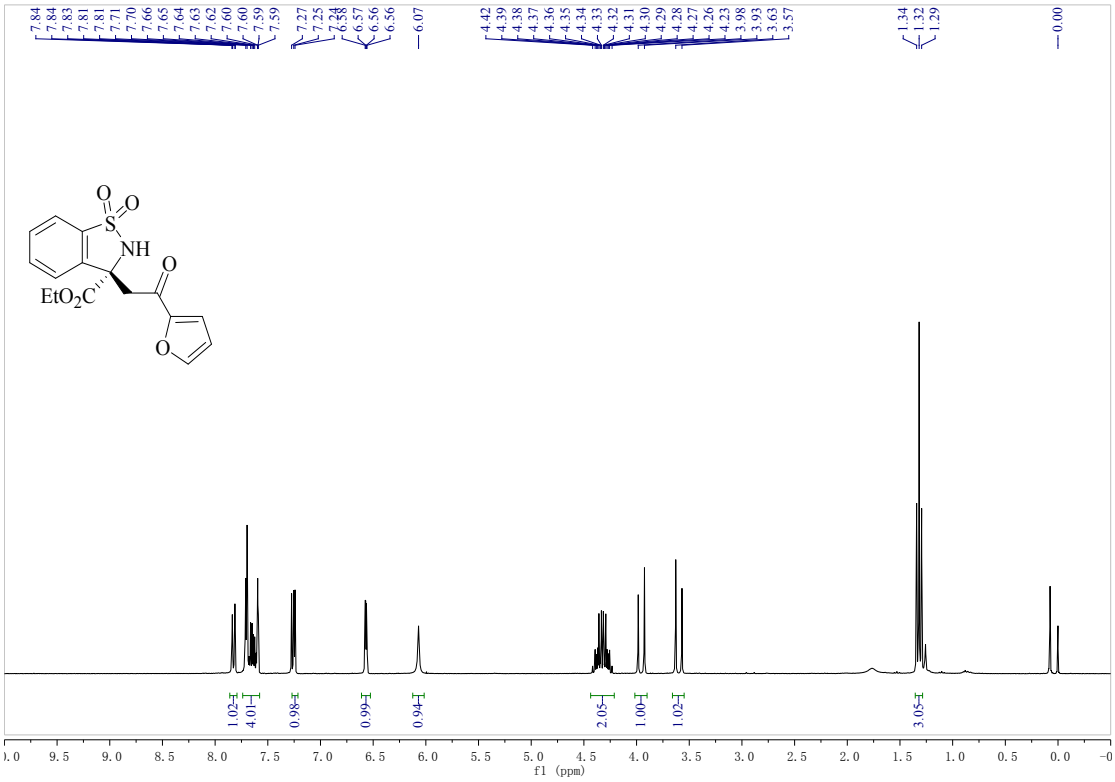
76.70
76.28
65.27
63.19
48.87
13.64
O
O
S
NH
O
EtO2C
f1 (ppm)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7.83
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7.64
7.63
7.62
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7.59
7.27
7.25
7.24
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6.57
6.56
6.56
6.07
4.42
4.39
4.38
4.37
4.36
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4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.23
3.98
3.93
3.63
3.57
1.34
1.32
1.29
0.00
O
O
S
NH
O
EtO2C
O
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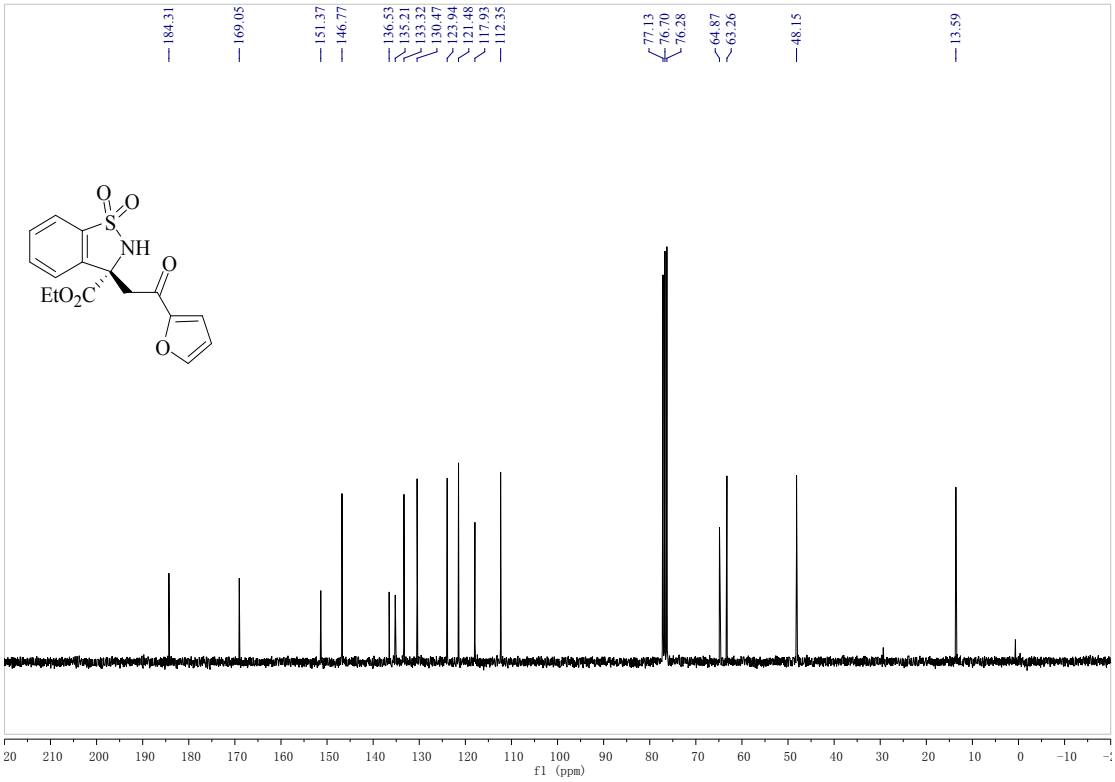
4.01
0.98
0.99
0.94
2.05
1.00
1.02
3.05
f1 (ppm)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133.32
130.47
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121.48
117.93
112.35
77.13
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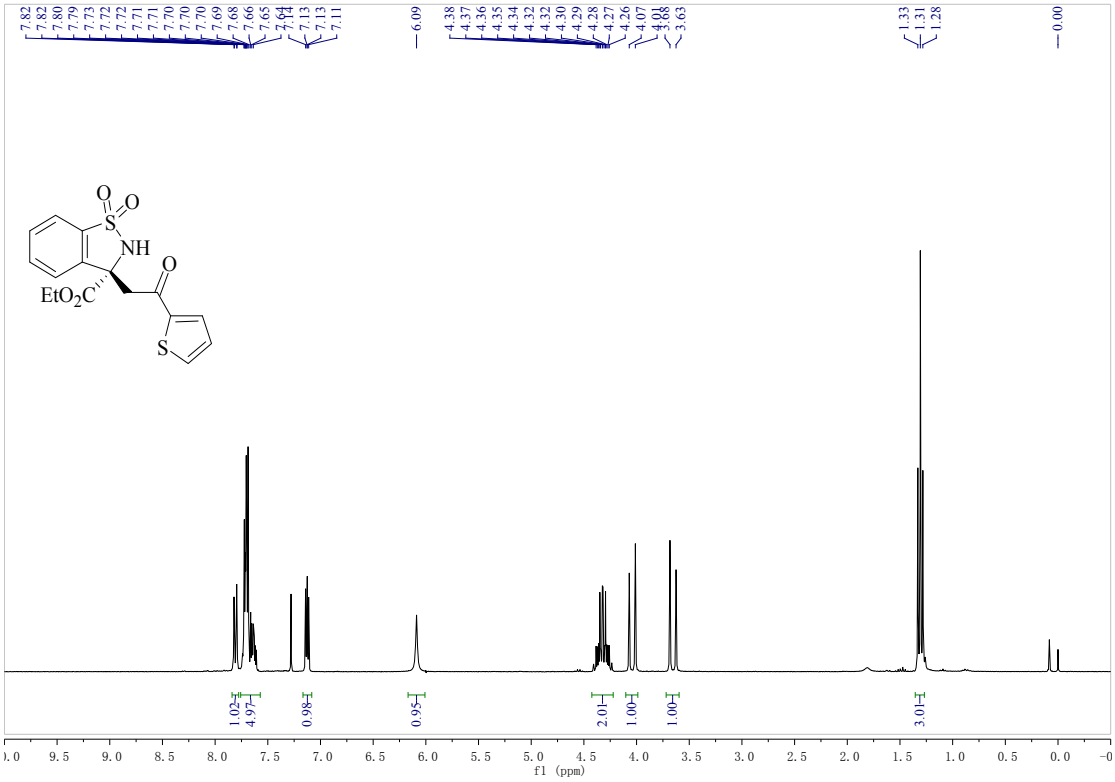
76.28
64.87
63.26
48.15
13.59
O
O
S
NH
O
EtO2C
O
f1 (ppm)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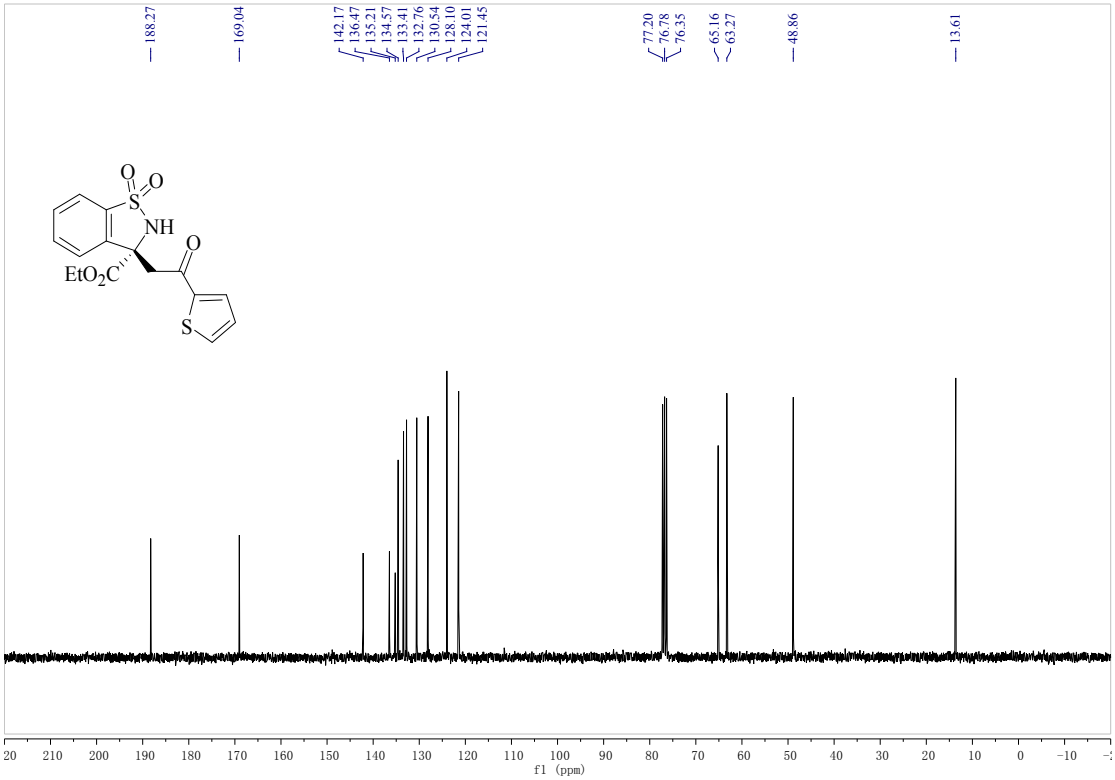
7.70
7.69
7.68
7.66
7.65
7.64
7.14
7.13
7.13
7.11
6.09
4.38
4.37
4.36
4.35
4.34
4.32
4.32
4.30
4.29
4.28
4.27
4.26
4.07
4.01
3.68
3.63
1.33
1.31
1.28
0.00
O
O
S
NH
O
EtO2C
S
1.02
4.97
0.98
0.95
2.01
1.00
1.00
3.01
f1 (ppm)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128.10
124.01
121.45
77.20
76.78
76.35
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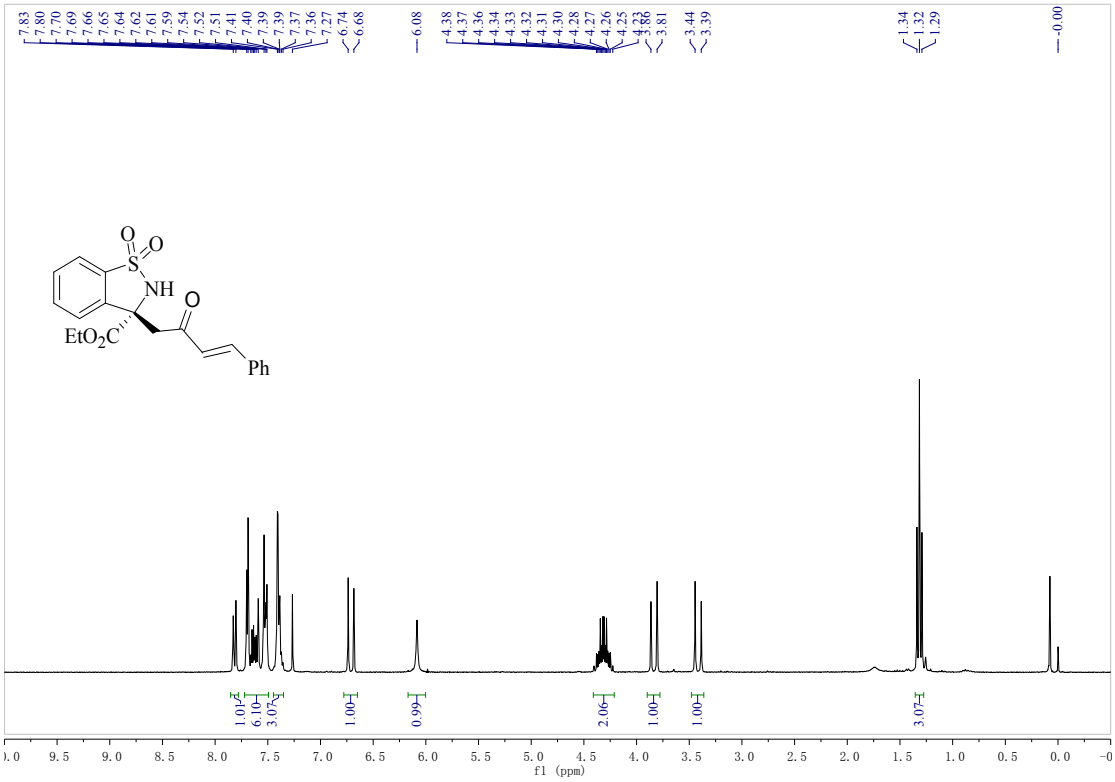
63.27
48.86
13.61
O
O
S
NH
O
EtO2C
S
f1 (ppm)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7.62
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7.41
7.40
7.39
7.39
7.37
7.36
7.27
6.74
6.68
6.08
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4.37
4.36
4.34
4.33
4.32
4.31
4.30
4.28
4.27
4.26
4.25
4.23
3.86
3.81
3.44
3.39
1.34
1.32
1.29
0.00
O
O
S
NH
O
EtO2C
Ph
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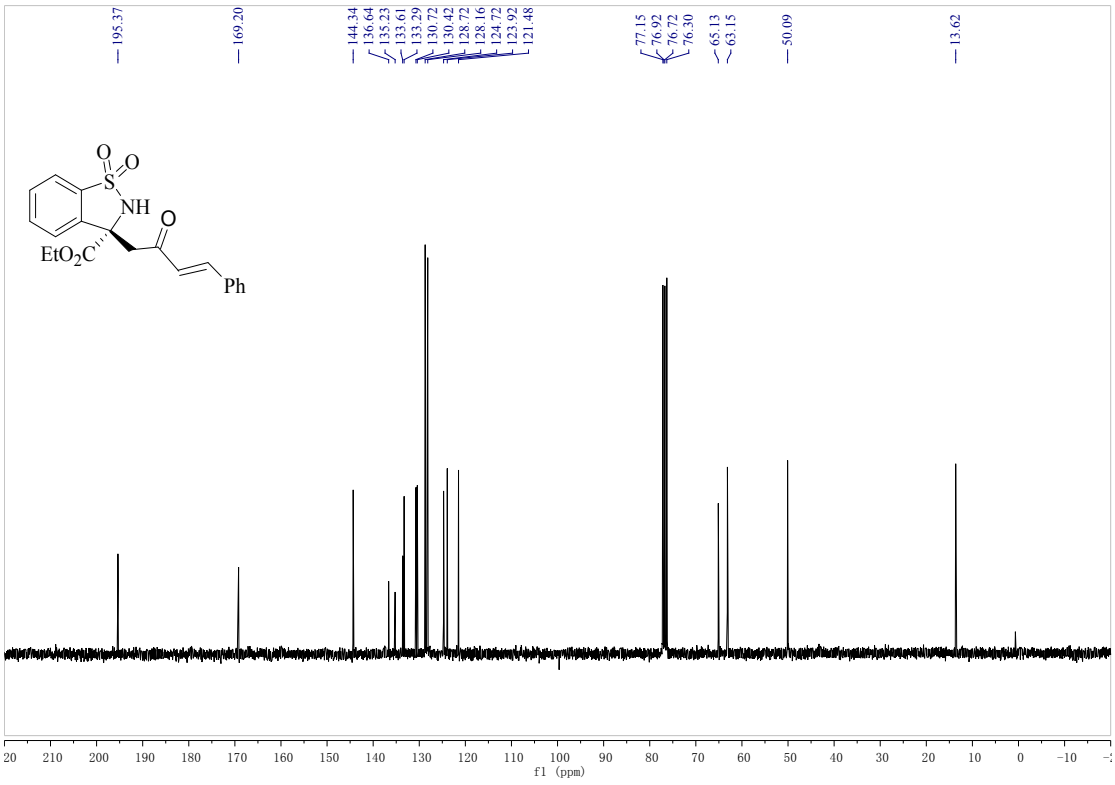
6.10
3.07
1.00
0.99
2.06
1.00
1.00
3.07
f1 (ppm)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130.72
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128.72
128.16
124.72
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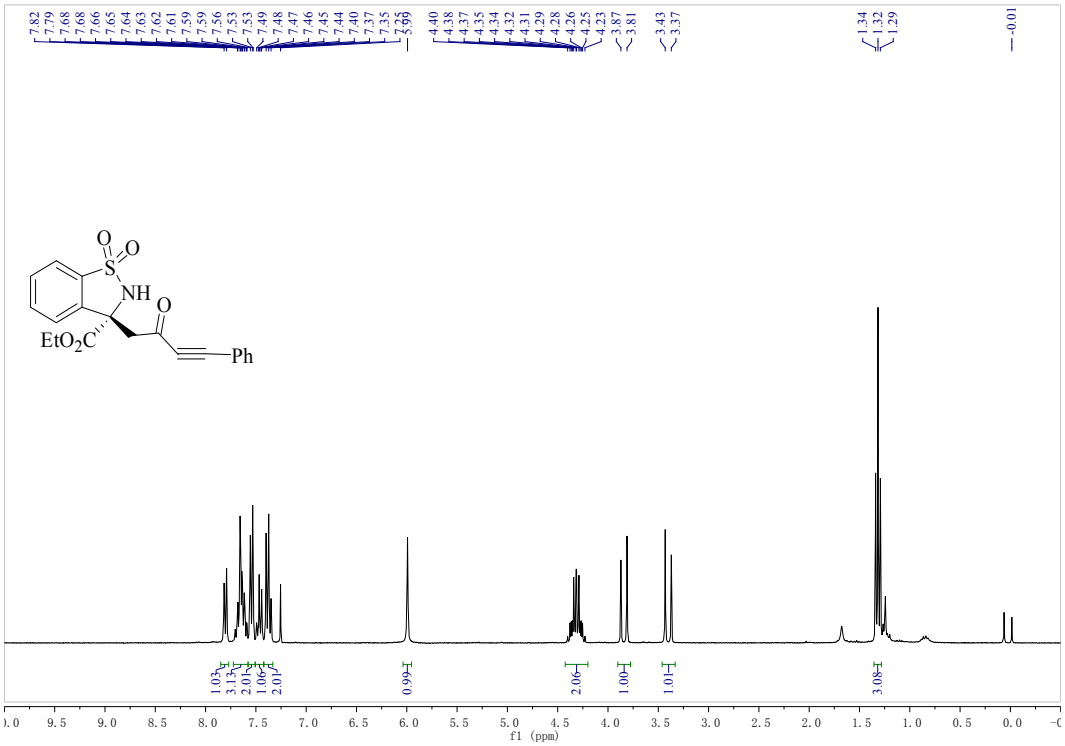
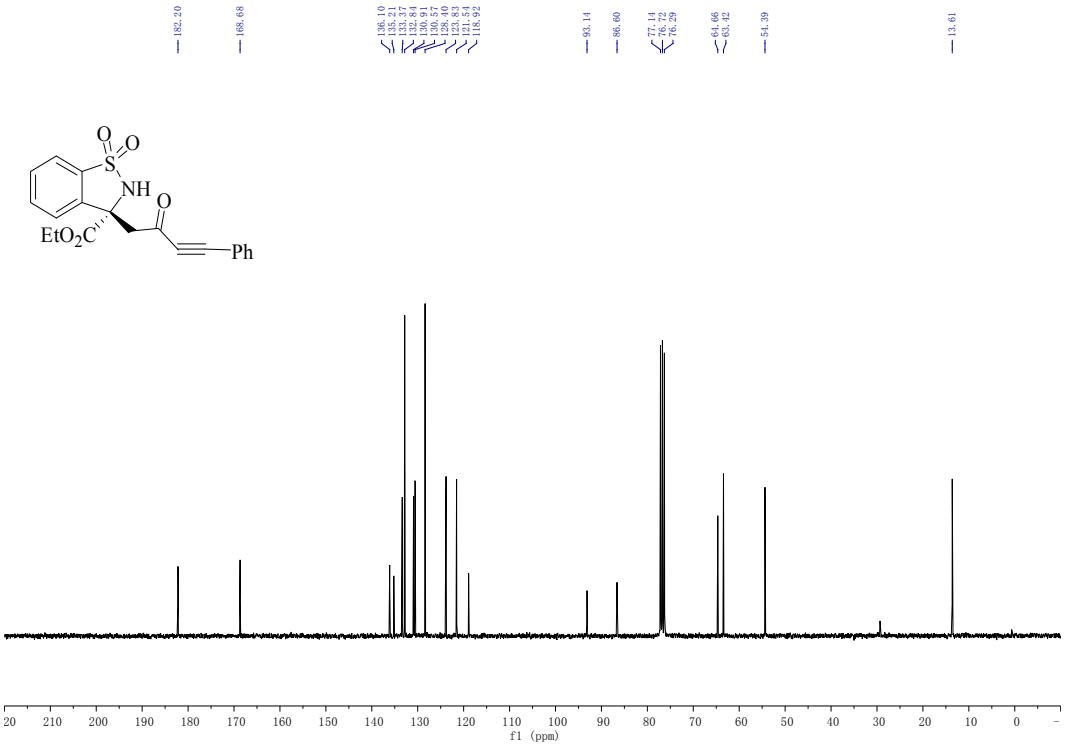
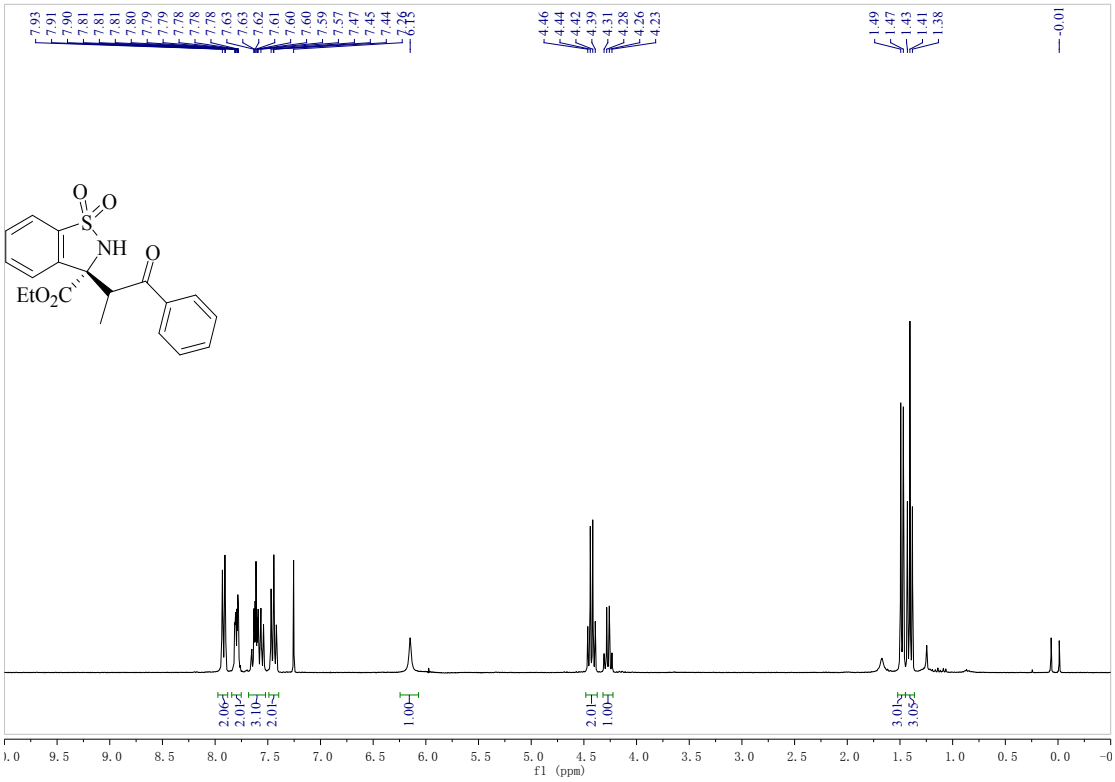
121.48
77.15
76.92
76.72
76.30
65.13
63.15
50.09
13.62
O
O
S
NH
O
EtO2C
Ph
f1 (ppm)


7.82 7.79 7.68 7.68 7.66 7.65 7.64 7.63 7.62 7.61 7.59 7.59 7.56 7.53 7.53 7.49 7.48 7.47 7.46 7.45 7.44 7.40 7.37 7.35 7.25 5.99 4.40 4.38 4.37 4.35 4.34 4.32 4.31 4.29 4.28 4.26 4.25 4.23 3.87 3.81 3.43 3.37 1.34 1.32 1.29 0.01
O
O
S
NH
O
EtO2C
Ph
1.03 3.13 2.01 1.06 2.01 0.99 2.06 1.00 1.01 3.08
f1 (ppm)


182.20 168.68 136.10 135.21 133.37 132.84 130.91 130.57 128.40 123.83 121.54 118.92 93.14 86.60 77.14 76.72 76.29 64.66 63.42 54.39 13.61
O
O
S
NH
O
EtO2C
Ph
f1 (ppm)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7.63
7.62
7.61
7.60
7.60
7.59
7.57
7.47
7.45
7.44
7.26
6.15
4.46
4.44
4.42
4.39
4.31
4.28
4.26
4.23
1.49
1.47
1.43
1.41
1.38
-0.01
O
O
S
NH
O
EtO2C
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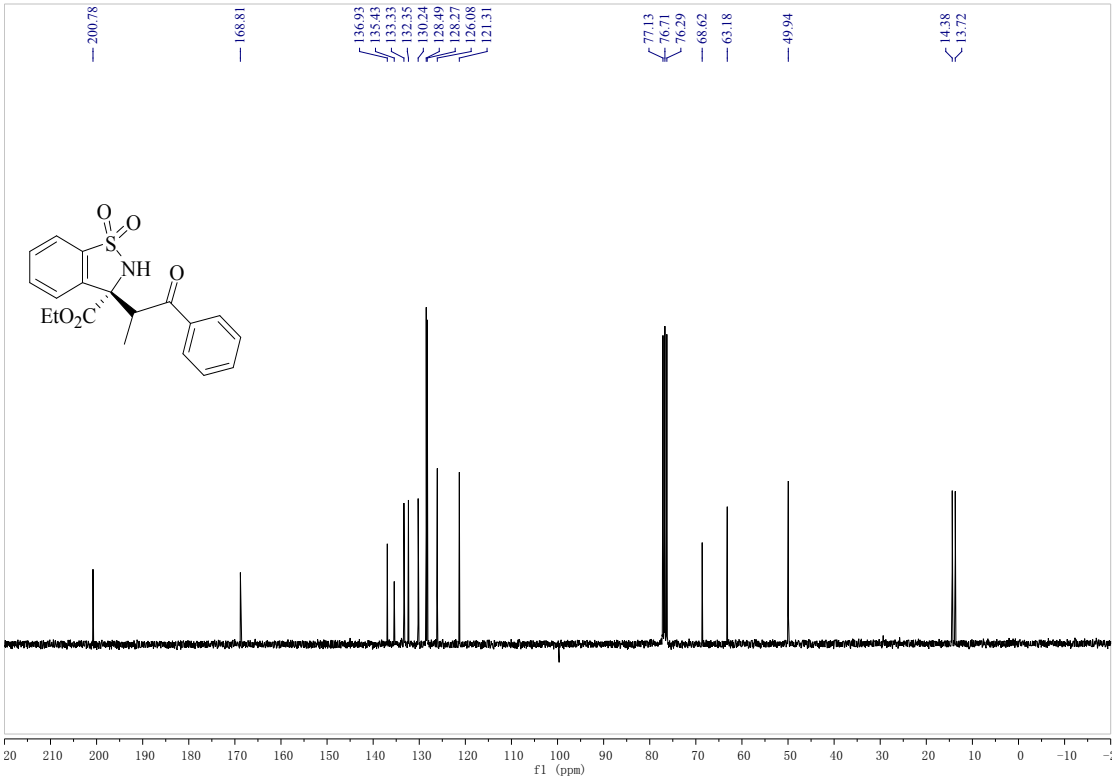
2.01
3.10
2.01
1.00
2.01
1.00
3.01
3.05
f1 (ppm)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130.24
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126.08
121.31
77.13
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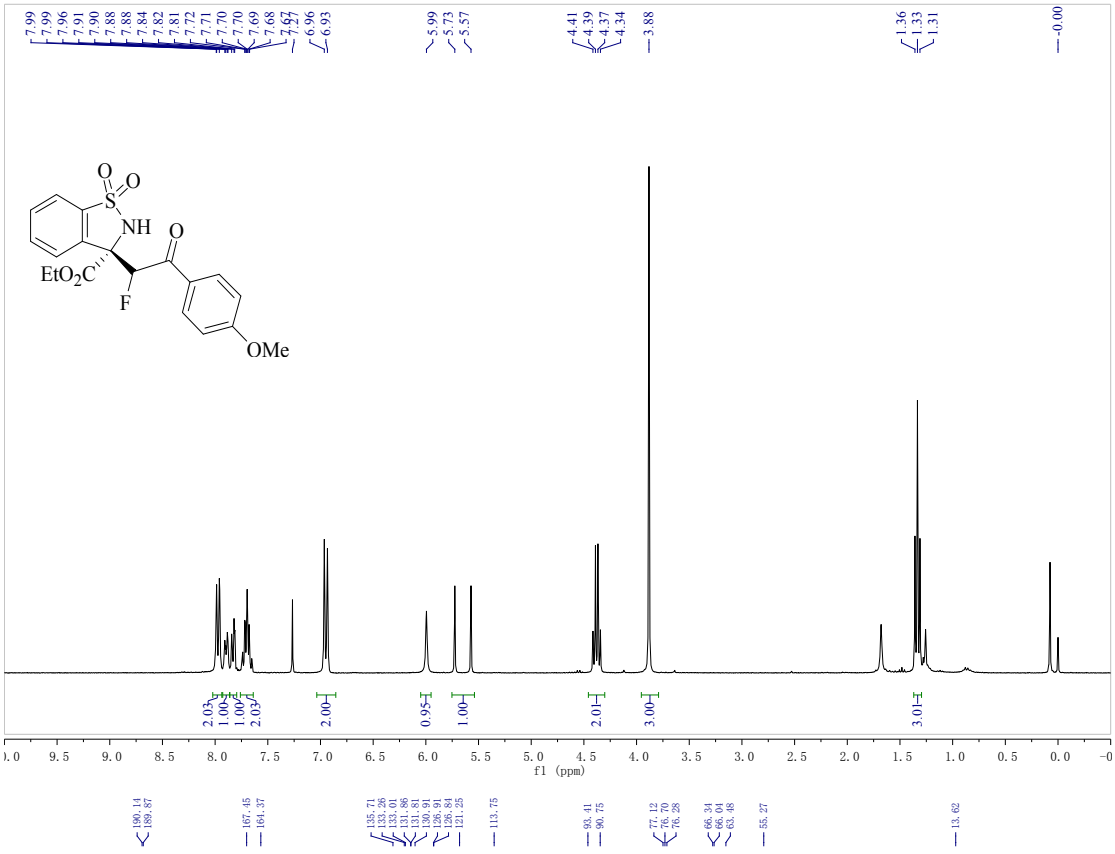
76.29
68.62
63.18
49.94
14.38
13.72
O
O
S
NH
O
EtO2C
f1 (ppm)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7.88
7.88
7.84
7.82
7.81
7.72
7.71
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7.70
7.69
7.68
6.96
6.93
5.99
5.73
5.57
4.41
4.39
4.37
4.34
3.88
1.36
1.33
1.31
-0.00
O
O
S
NH
O
EtO2C
F
OMe
2.03
1.00
1.00
2.03
2.00
0.95
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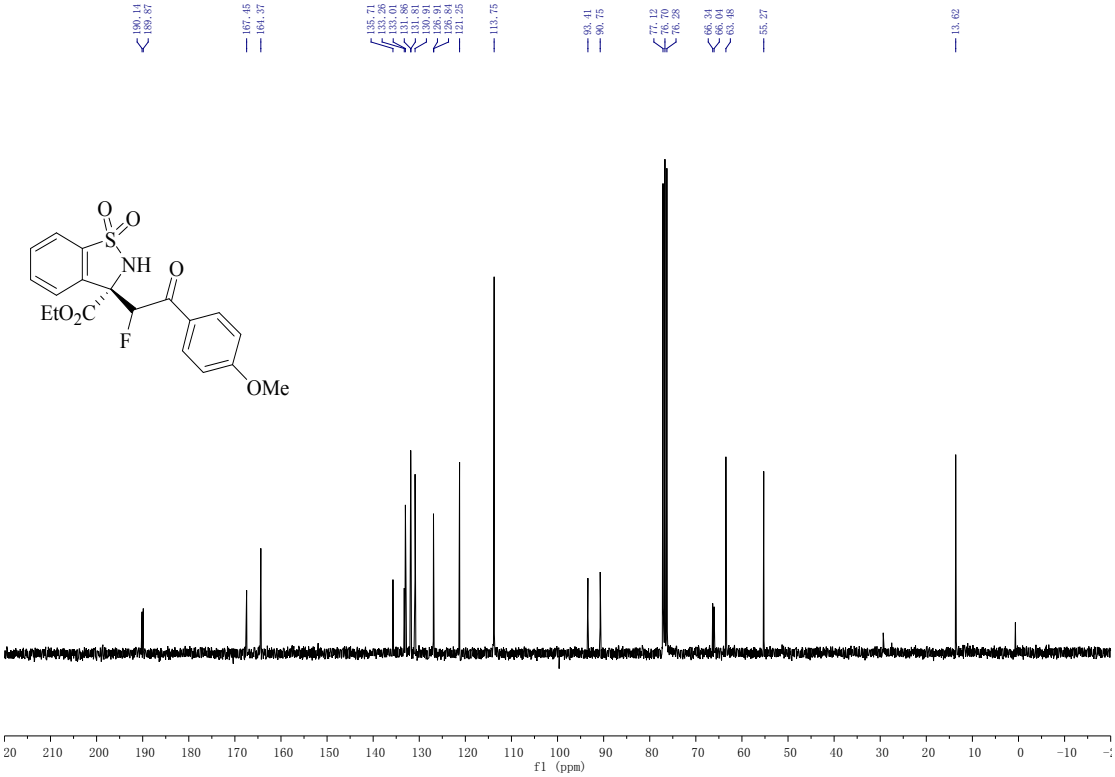
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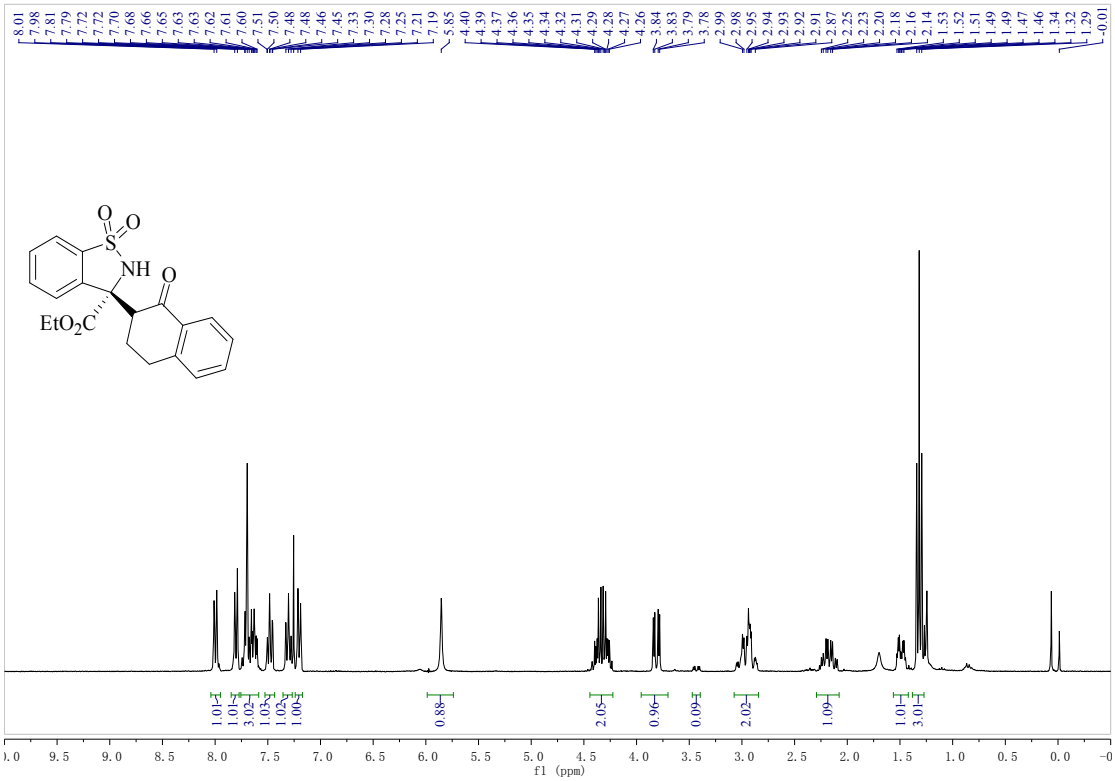
NH
O
EtO2C
F
OMe
f1 (ppm)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O
O
S
NH
O
EtO2C
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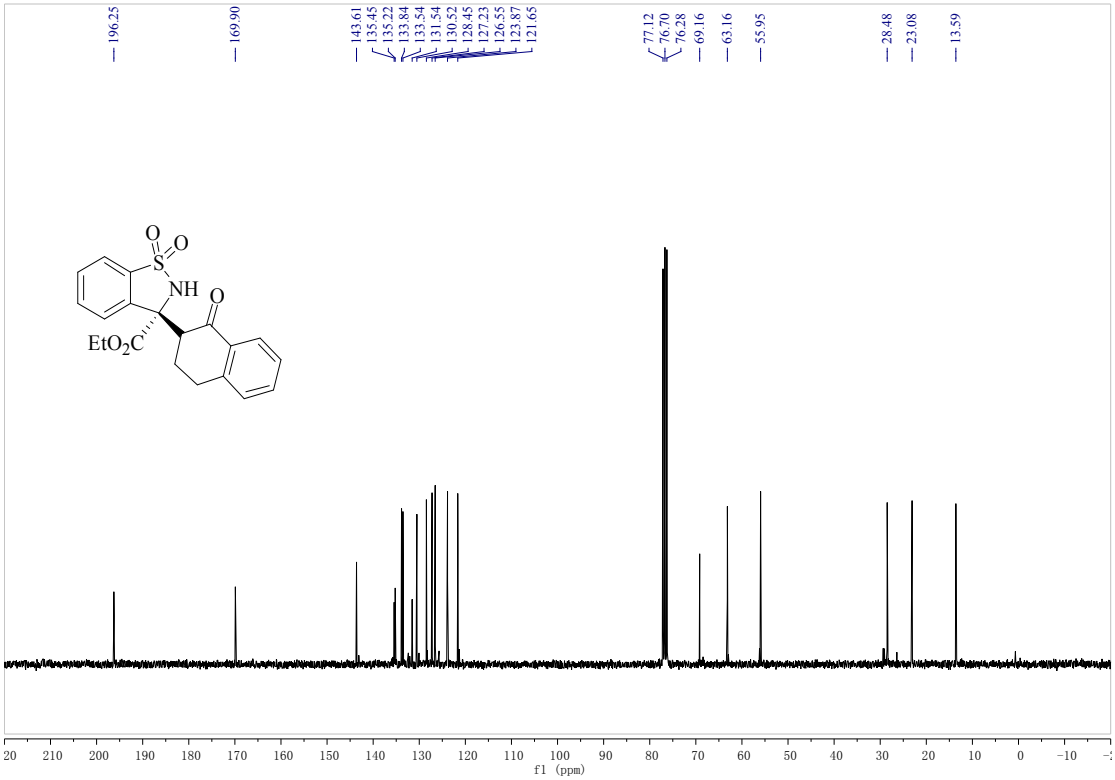
f1 (ppm)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NH
O
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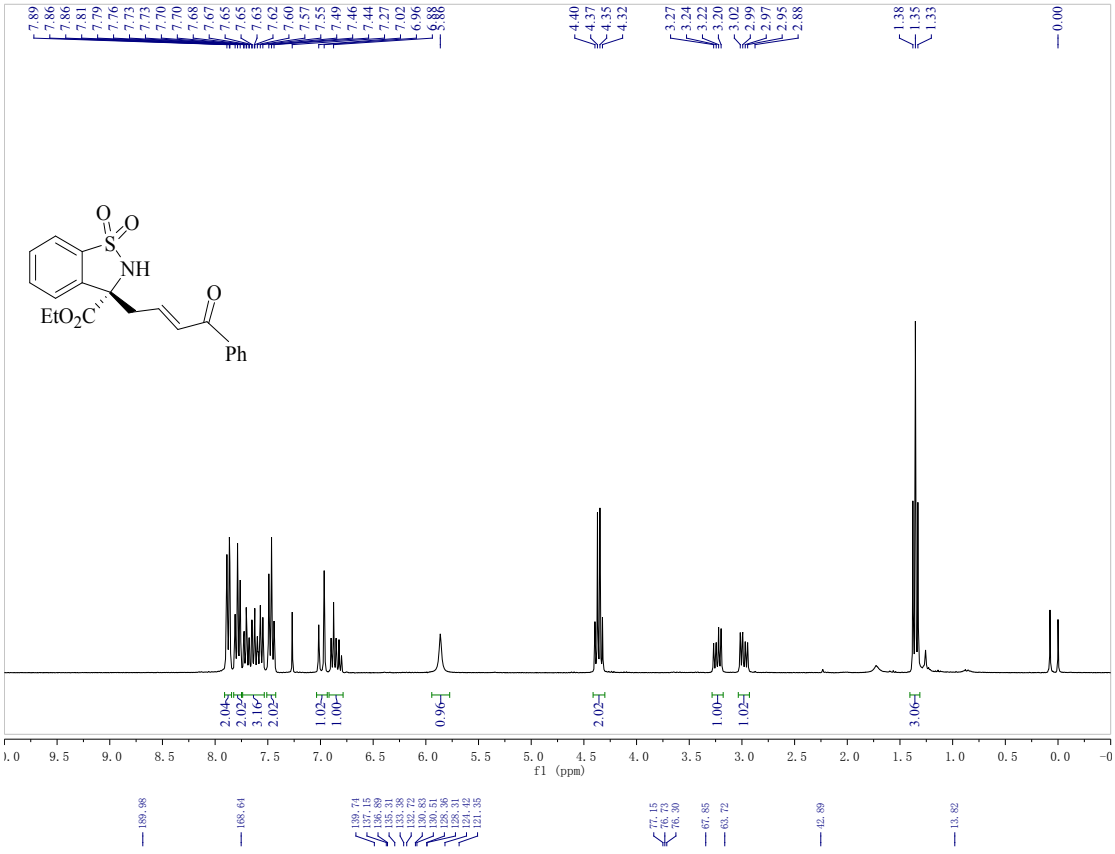
f1 (ppm)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3.24
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3.20
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2.97
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1.35
1.33
0.00
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O
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NH
EtO2C
O
Ph
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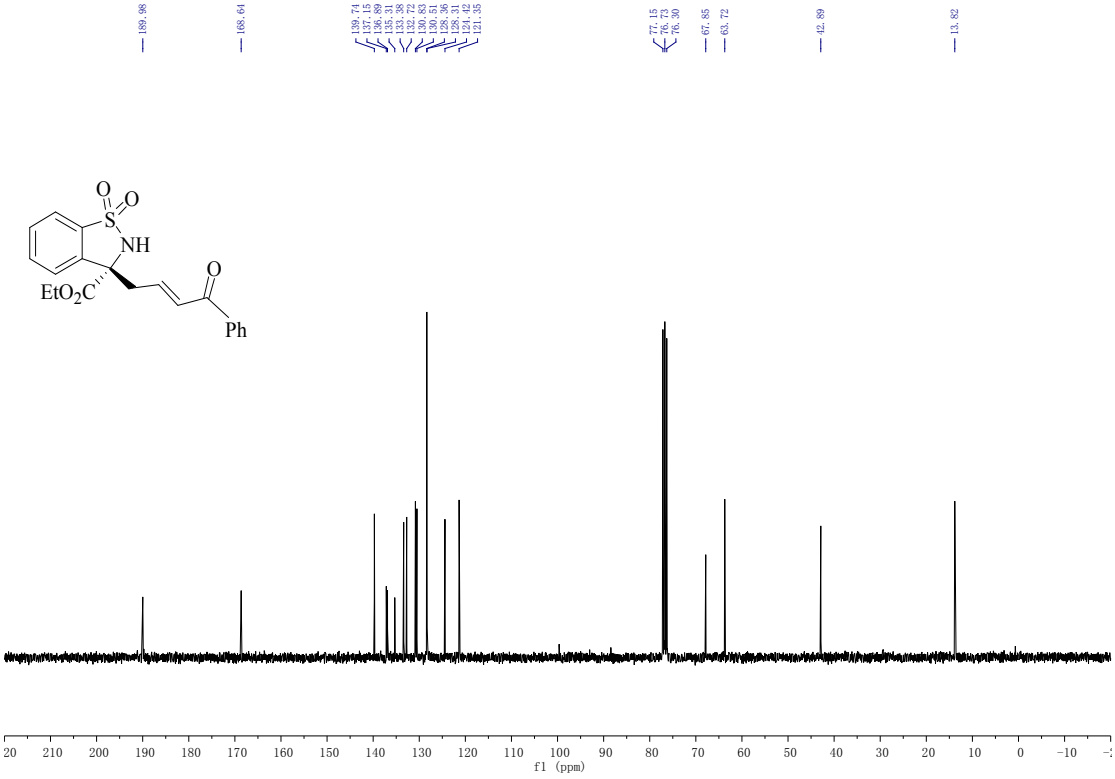
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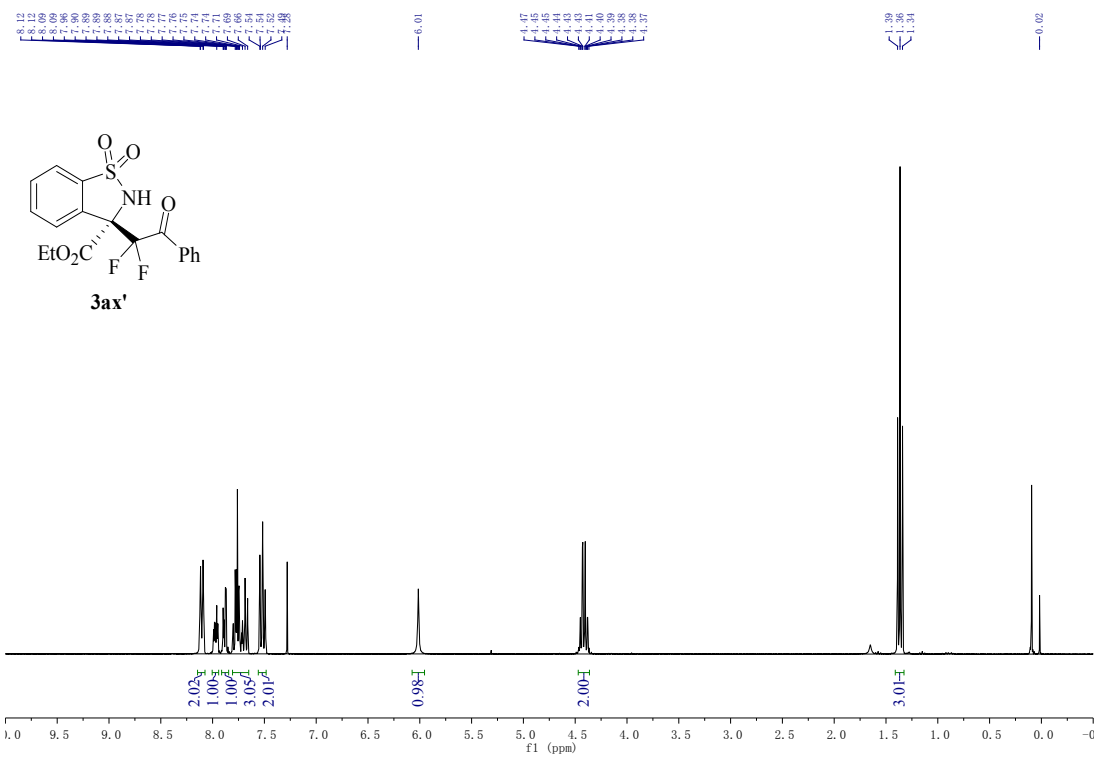
O
S
NH
EtO2C
O
Ph
f1 (ppm)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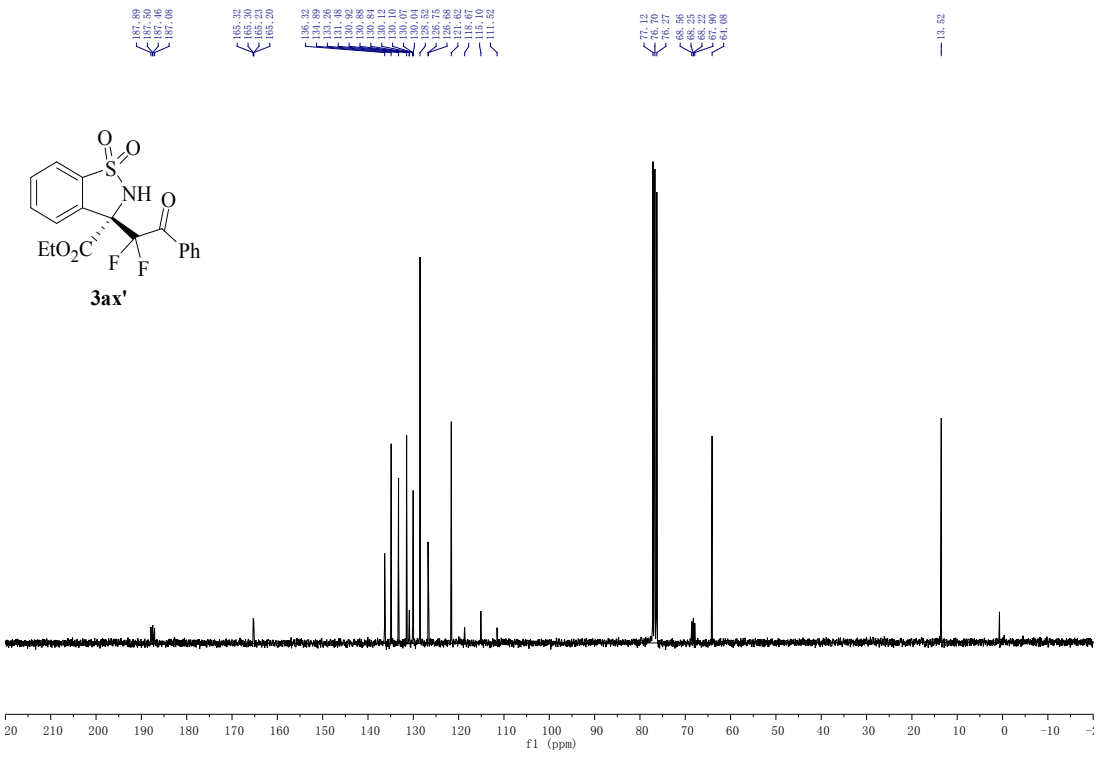
f1 (ppm)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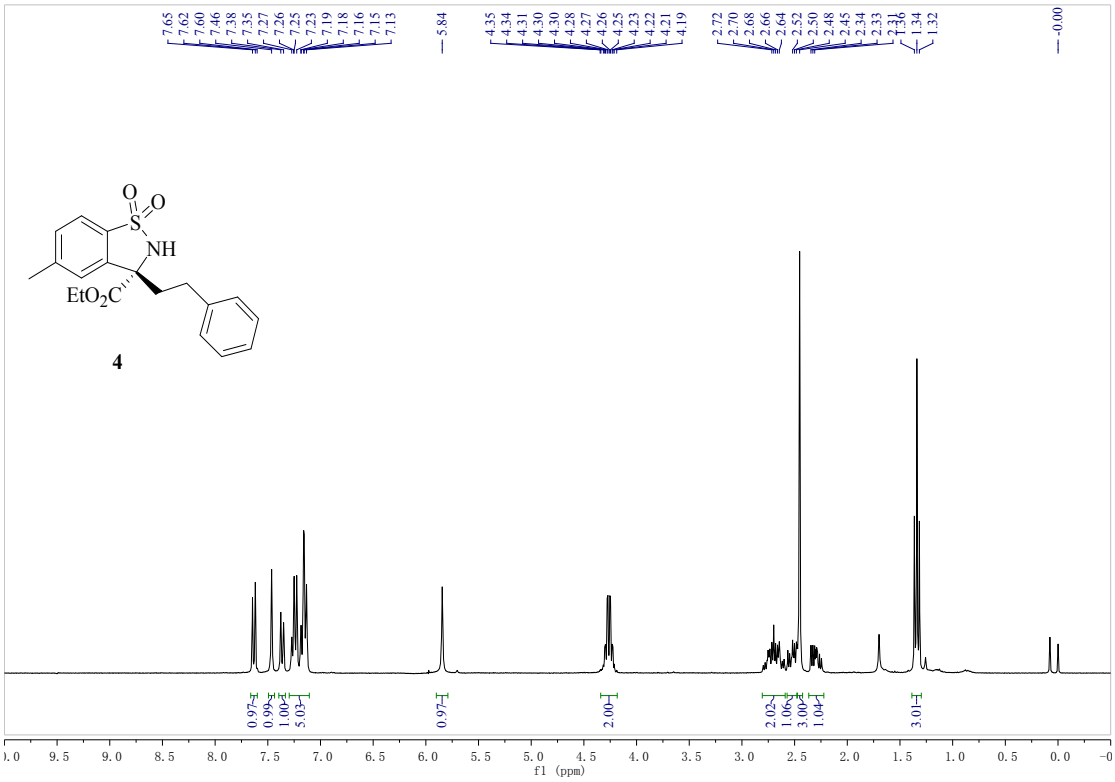
f1 (ppm)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4.34
4.31
4.30
4.30
4.28
4.27
4.26
4.25
4.23
4.22
4.21
4.19
2.72
2.70
2.68
2.66
2.64
2.52
2.50
2.48
2.45
2.34
2.33
2.31
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1.34
1.32
-0.00
O
O
S
NH
EtO2C
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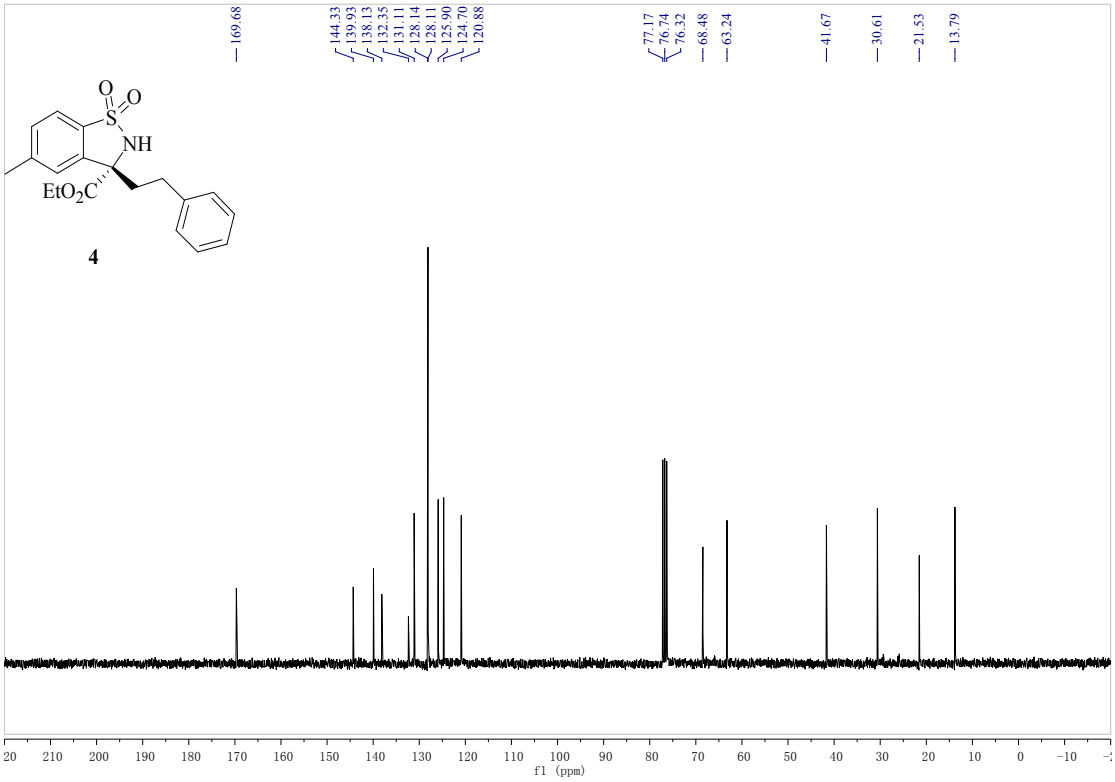
f1 (ppm)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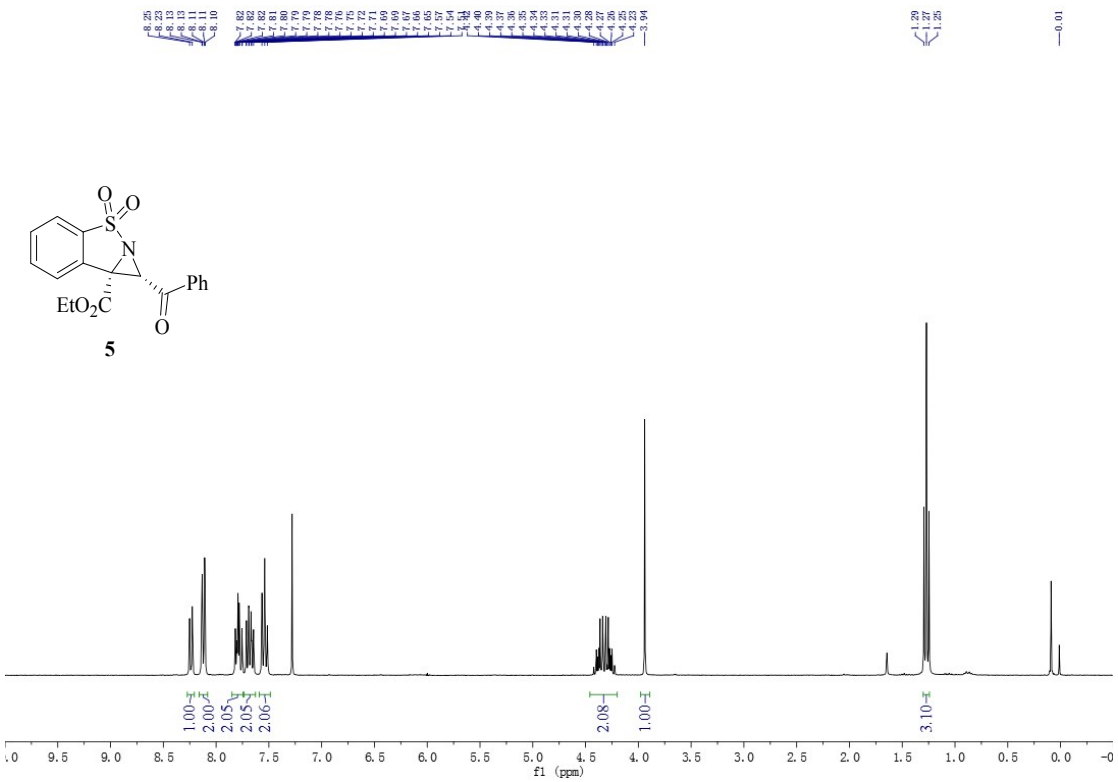
4
f1 (ppm)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4.27
4.26
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O
S
N
Ph
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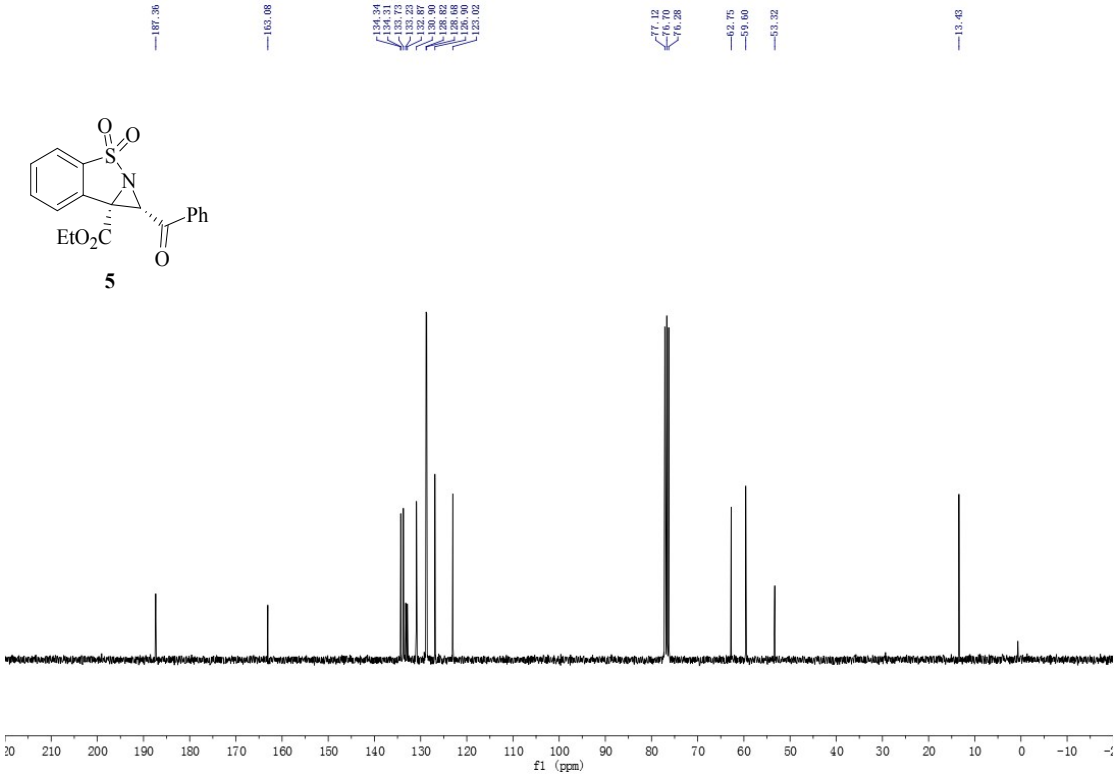
f1 (ppm)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76.70
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53.32
13.43
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O
S
N
Ph
EtO2C
O
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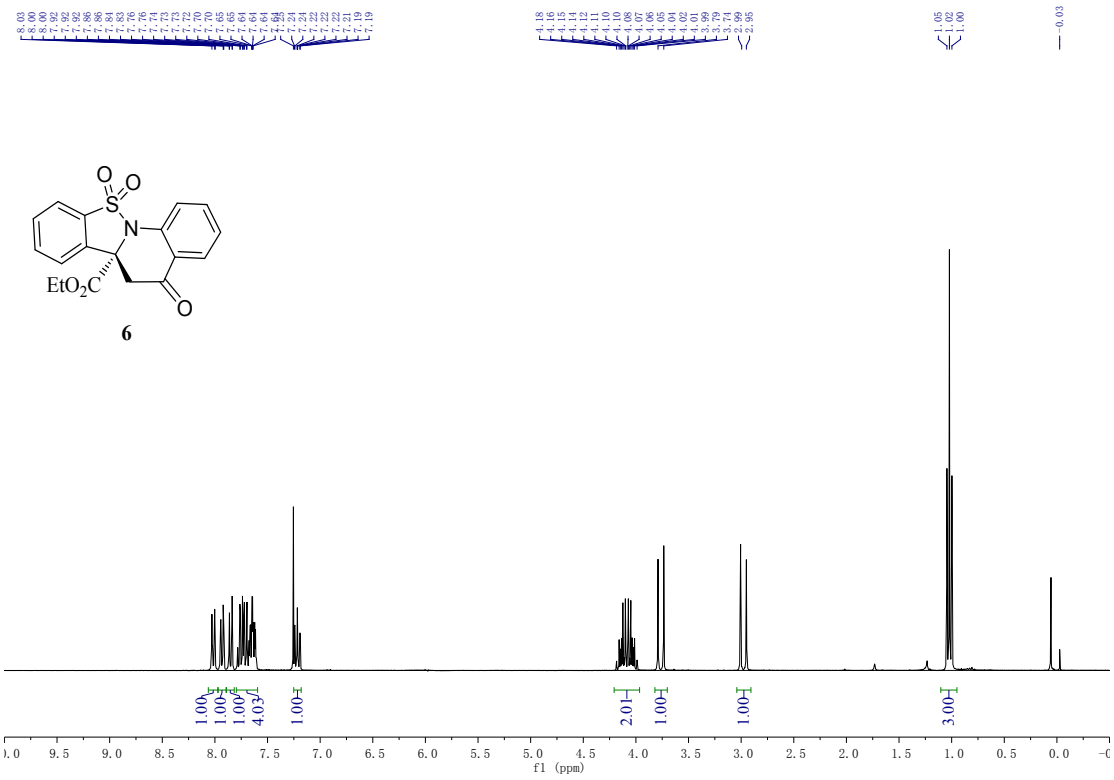
f1 (ppm)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O
S
N
EtO2C
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1.00
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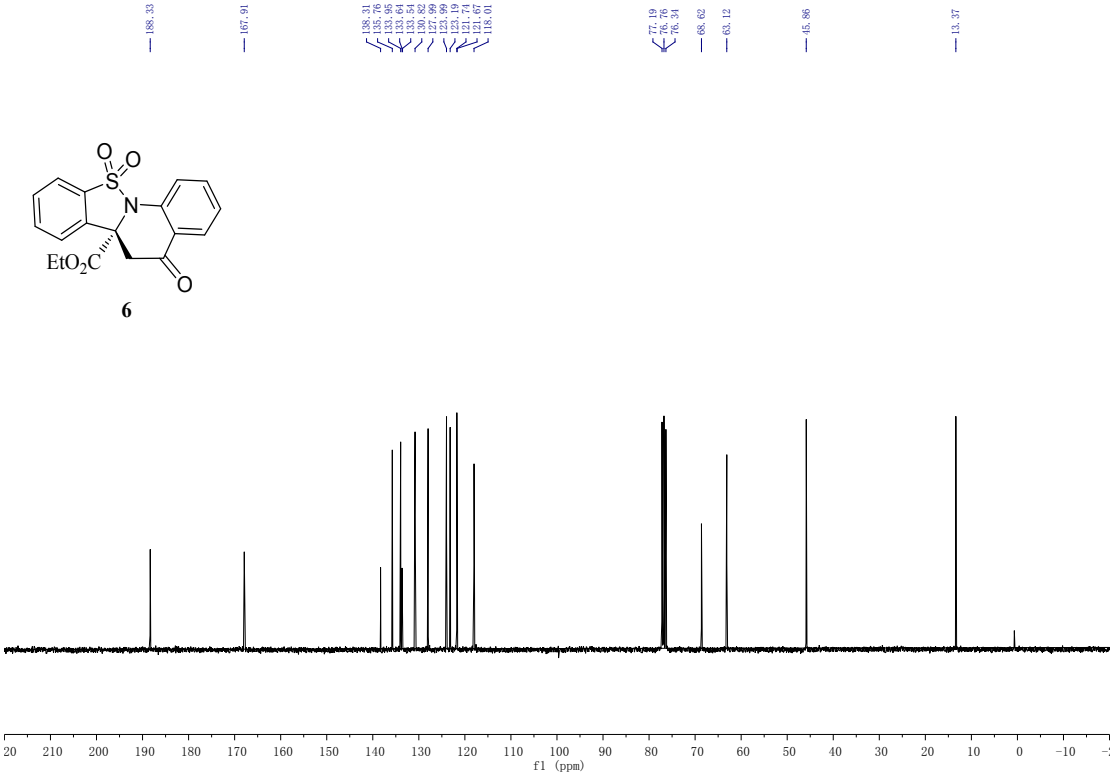
3.00
f1 (ppm)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77.19
76.76
76.34
68.62
63.12
45.86
13.37
O
O
S
N
EtO2C
O
6
f1 (ppm)

9. The structure of **3ka** and **3aw'** by X-ray diffraction analysis

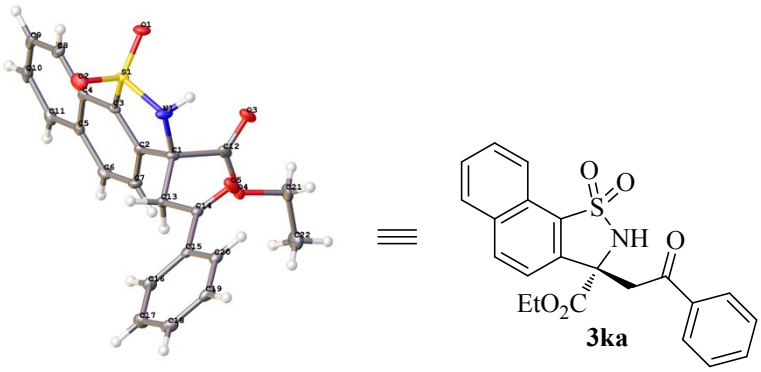
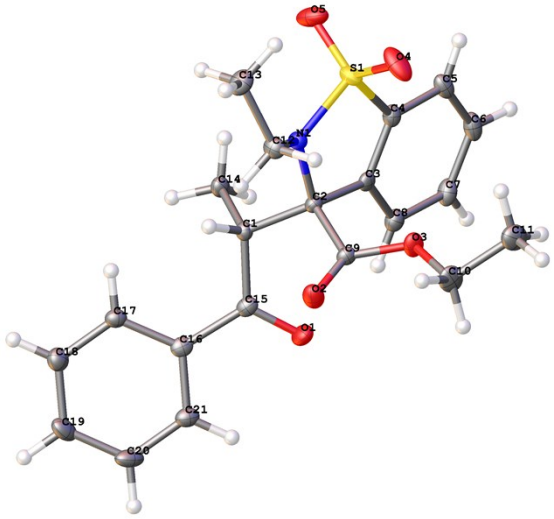
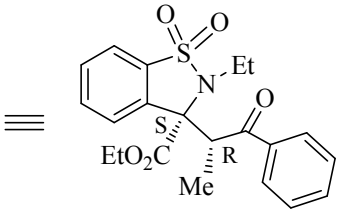


Table S3. Crystal data and structure refinement for **(S)-*3ka*** (**CCDC 1522074**)

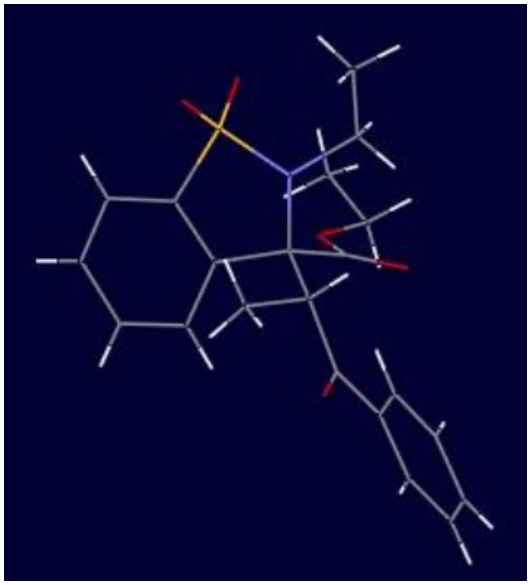
Empirical formula	C22H19NO5S
Formula weight	409.44
Temperature / K	105.8
Crystal system	orthorhombic
Space group	P212121
a / Å, b / Å, c / Å	8.8173(4), 14.3926(7), 15.3659(7)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume / $Å^3$	1950.00(15)
Z	4
ρ_{calc} / mg mm^{-3}	1.395
μ / mm^{-1}	1.775
F(000)	856
Crystal size / mm3	0.25 × 0.24 × 0.23
2Θ range for data collection	8.42 to 141.9°
Index ranges	-10 ≤ h ≤ 9, -17 ≤ k ≤ 17, -17 ≤ l ≤ 18
Reflections collected	6453
Independent reflections	3678[R(int) = 0.0210 (inf-0.9Å)]
Data/restraints/parameters	3678/0/264
Goodness-of-fit on F^2	1.061
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0271, wR_2 = 0.0686
Final R indexes [all data]	R_1 = 0.0275, wR_2 = 0.0689
Largest diff. peak/hole / e $Å^{-3}$	0.330/-0.306
Flack Parameters	0.003(12)
Completeness	0.989

Crystal structure for ***3aw'*** **(** CCDC 1536298)





3aw'



3aw' from different perspective