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Supporting Information

Accessing chiral sulfones with an all-carbon quaternary stereocenter via photoinduced asymmetric Truce-Smiles rearrangement and radical sulfur dioxide insertion

Chenxin Wang,[a] Wei Xiao,*[a] and Jie Wu *[a, b]

[a] School of Pharmaceutical and Chemical Engineering & Institute for Advanced Studies, Taizhou University, Taizhou 318000, China.
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.
Corresponding author: xiaowei1992@tzc.edu.cn; jie_wu@fudan.edu.cn

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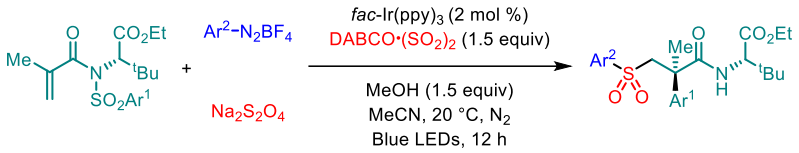
1. General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; brs = broad singlet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The enantiomeric excess values were determined by chiral HPLC with an Shimadzu instrument and a Daicel CHIRALCEL and CHIRALPAK column. High resolution mass spectroscopy (HRMS) analyses were performed at a Q-Exactive (Thermo Scientific) Inc mass instrument (HESI).

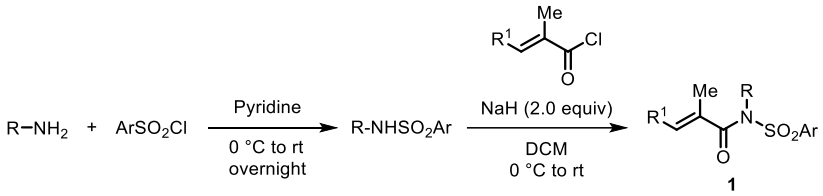
2. General procedure for the preparation of compound 3.



In a glove box, a dry vial equipped with a magnetic stir bar is charged sequentially with **1a** (0.2 mmol), **2a** (0.3 mmol), $Na_2S_2O_4$ (0.4 mmol), DABCO·$(SO_2)_2$ (0.3 mmol), MeOH (0.3 mmol), $Ir(ppy)_3$ (2 mol%) and dry MeCN (4.0 mL). The reaction mixture is stirred for 12 h at 900 rpm in a thermostatic water bath at 20 °C under 35 W blue LEDs light. When the reaction is completed (monitored by TLC), the mixture is purified by flash chromatography on silica gel and eluted with PE/EA (4/1) to afford the corresponding product **3**. The diastereomers showed one spot by TLC with different developers. However, they can be partially separated by flash chromatography on silica gel.

3. General procedure for the preparation of compound 1

The amides **1** were synthesized through a procedure from reported literature procedures.[1-2]

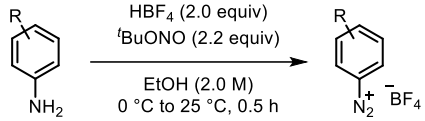


To a solution of the corresponding amine (1.0 equiv) in pyridine (c = 0.1M) was added aryl sulfonyl chloride (1.2 equiv) in several portions at 0 °C. The resulting solution was warmed to room temperature and stirred overnight. Then the reaction was concentrated under reduced pressure to remove pyridine and the crude mixture was purified by flash chromatography on silica gel (eluent: PET/EtOAc 4/1). Subsequently, the product was dissolved in distilled DCM (c = 0.5 M) at 0 °C. To this solution was added NaH (2 equiv) in one portion. The resulting solution was allowed to proceed until no further gas evolution was observed. At this point, the corresponding acryloyl chloride (2 equiv) was added slowly and the resulting solution was warmed to room temperature. Once the amine was fully consumed, the mixture was filtered, concentrated under reduced pressure and purified by flash chromatography on silica gel (eluent PET/EtOAc 4/1) to afford the corresponding amide **1**.

4. General procedure for the preparation of compound 2

Procedure A:

Aryldiazonium salts were prepared according to the **Procedure A** of Hanson.[3]

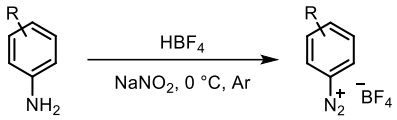


2

To a solution of aniline in ethanol (2.0 M) was added fluoroboric acid (2.0 equiv) at 0 °C. Then, a solution of ^{t}BuONO (2.2 equiv) was added slowly and the mixture was stirred for 30 min at room temperature. After completion, the thick precipitate was collected by filtration and washed with Et_2O. The diazonium tetrafluoroborate was then redissolved in minimal amount of acetone and precipitated by the addition of Et_2O. Then the product **2** was filtered and washed with Et_2O, dried under high vacuum and stored under argon in the freezer.

Procedure B:

General **Procedure B** for the synthesis of aryldiazonium salts **2**.[4]

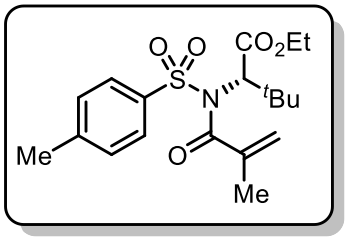


2

An oven-dried 100 mL round-bottom-flask equipped with a magnetic stir bar was charged with the corresponding aniline (1.0 equiv, 20 mmol). The flask was sealed with a rubber septum and connected to a Schlenk line though a needle. The flask was then evacuated and backfilled with argon (This sequence was repeated a total of three times). The solution of HBF_4 (6.8 ml HBF_4 (50% wt) in 8 mL H_2O) was added via syringe. The mixture was the cooled to 0 °C, and $NaNO_2$ aqueous (1.4 g in 3 mL H_2O) was added dropwise via a syringe on 0 °C. The resulting mixture was stirred for 40 min at 0 °C on argon atmosphere. Then, the solvent was removed by filtered, and the result solid was dissolved in acetone, crystallized from the solution by adding ice cold diethyl ether. The remaining solid was washed by ice cold diethyl ether (25 mL) three times to afford the product **2**.

5. Characterization data of substrate 1

Ethyl (*S*)-3,3-dimethyl-2-(*N*-tosylmethacrylamido)butanoate (1a)

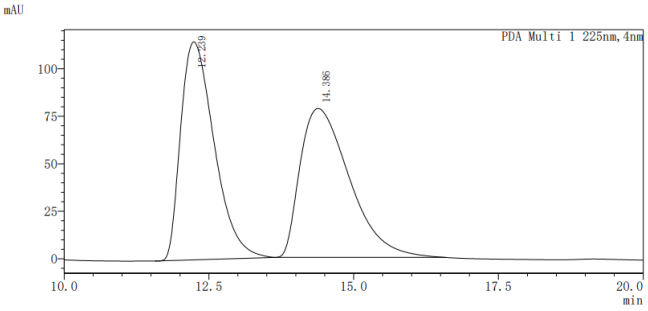


89% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.43 (s, 1H), 5.32 (d, *J* = 1.6 Hz, 1H), 4.83 (s, 1H), 4.28–4.19 (m, 2H), 2.44 (s, 3H), 1.40 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.7, 168.3, 145.0, 139.0, 136.3, 129.8, 129.3, 122.1, 66.1, 60.9, 36.2, 28.4, 21.7, 18.8, 14.2.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 13.4 min (minor), 15.3 min (major).

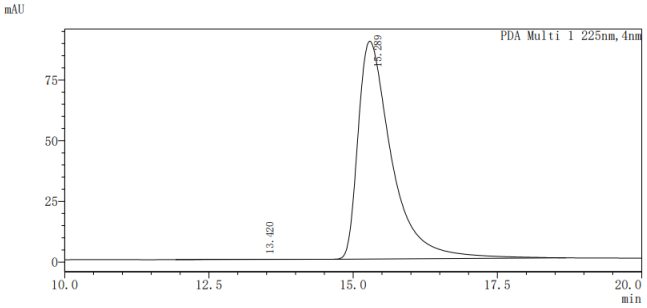
Chiral HPLC spectrum of (*rac*)-**1a**



PDA Ch1 225nm

Peak	Ret.Time	Area	Area%
1	12.239	4627246	49.844
2	14.386	4656138	50.156

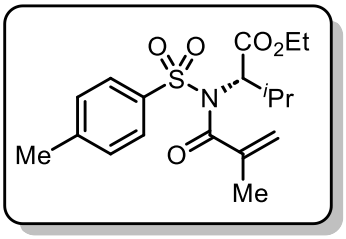
Chiral HPLC spectrum of (*S*)-**1a**



PDA Ch1 225nm

Peak	Ret.Time	Area	Area%
1	13.420	8542	0.234
2	15.289	3641806	99.766

Ethyl N-methacryloyl-N-tosyl-L-valinate (1a')

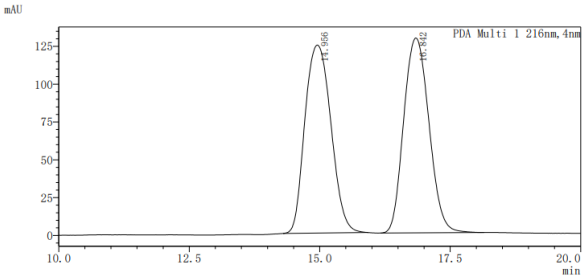


75% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.10 (d, *J* = 1.2 Hz, 1H), 4.85 (s, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.24 – 4.08 (m, 2H), 2.82 – 2.65 (m, 1H), 2.44 (s, 3H), 1.76 (s, 3H), 1.31 – 1.10 (m, 6H), 1.00 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 169.3, 145.0, 139.6, 136.6, 129.2, 129.1, 118.5, 65.9, 61.3, 28.6, 22.4, 21.7, 19.9, 19.7, 14.0.

HPLC analysis: Chiralcel IA column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 216 nm, t_R = 15.3 min (minor), 17.1 min (major).

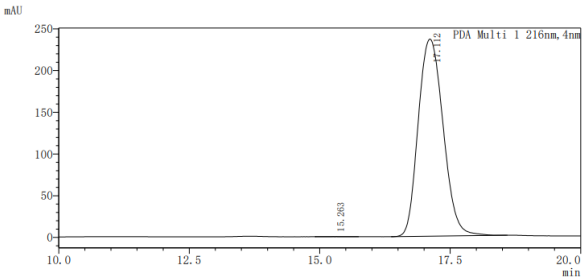
Chiral HPLC spectrum of (*rac*)- **1a'**



PDA Ch1 216nm

Peak	Ret. Time	Area	Area%
1	14.956	4323305	49.874
2	16.842	4345130	50.126

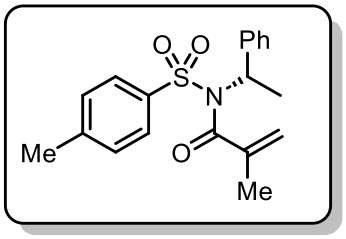
Chiral HPLC spectrum of (*S*)- **1a'**



PDA Ch1 216nm

Peak	Ret. Time	Area	Area%
1	15.263	2617	0.033
2	17.112	7850050	99.967

(S)-N-(1-phenylethyl)-N-tosylmethacrylamide (1a'')



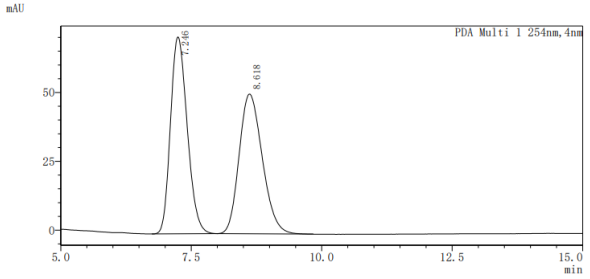
80% yield, 98% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.26 (m, 7H), 5.44 (dd, *J* = 14.0, 6.8 Hz, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 4.95 (s, 1H), 2.43 (s, 3H), 1.92 (d, *J* = 6.8 Hz, 3H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 144.7, 129.4, 128.7, 128.3, 127.7, 127.6, 119.0, 58.0, 21.7, 19.1, 18.6.

HPLC analysis: Chiralcel IA column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 7.3 min (minor), 8.8 min (major).

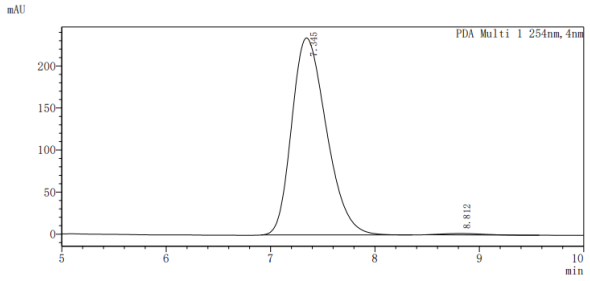
Chiral HPLC spectrum of (*rac*)- **1a''**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	7.246	1595888	50.418
2	8.618	1569397	49.582

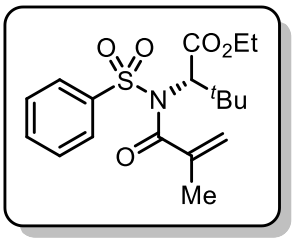
Chiral HPLC spectrum of (*S*)- **1a''**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	7.345	5412466	99.197
2	8.812	43796	0.803

Ethyl (*S*)-3,3-dimethyl-2-(*N*-(phenylsulfonyl)methacrylamido)butanoate (1b)

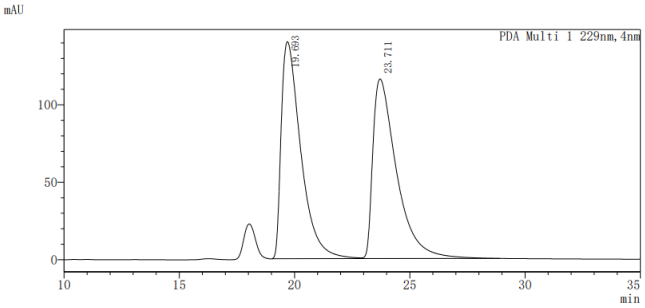


88% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.05–8.03 (m, 2H), 7.65–7.61 (m, 1H), 7.55–7.50 (m, 2H), 5.43 (s, 1H), 5.33 (d, *J* =1.6 Hz, 1H), 4.85 (s, 1H), 4.28–4.17 (m, 2H), 1.40 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.6, 168.2, 139.2, 138.9, 133.9, 129.7, 128.8, 122.3, 66.2, 60.9, 36.2, 28.4, 18.8, 14.2.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 229 nm, t_R = 18.8 min (minor), 22.8 min (major).

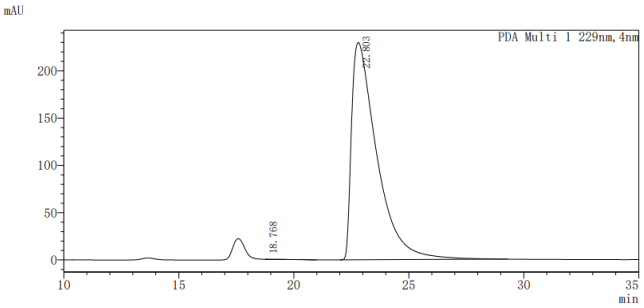
Chiral HPLC spectrum of (*rac*)-**1b**



PDA Ch1 229nm

Peak	Ret. Time	Area	Area%
1	19.693	8287001	49.878
2	23.711	8327629	50.122

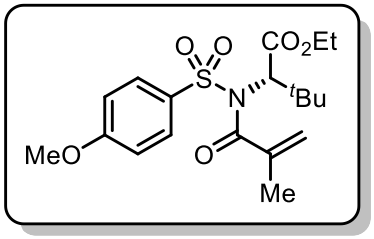
Chiral HPLC spectrum of (*S*)-**1b**



PDA Ch1 229nm

Peak	Ret. Time	Area	Area%
1	18.768	5335	0.030
2	22.803	17602651	99.970

Ethyl (*S*)-2-(*N*-((4-methoxyphenyl)sulfonyl)methacrylamido)-3,3-dimethylbutanoate (1c)

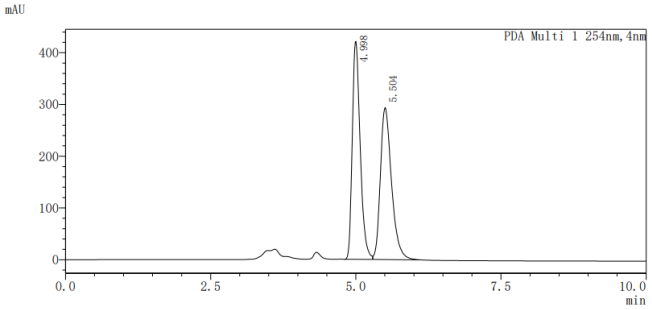


92% yield, > 99% ee

1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.96 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 9.2 Hz, 2H), 5.46 (s, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 4.83 (s, 1H), 4.28–4.19 (m, 2H), 3.88 (s, 3H), 1.43 (s, 3H), 1.28 (t, *J* = 7.2 Hz 3H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.7, 168.4, 163.8, 139.0, 132.1, 130.5, 122.0, 113.8, 66.2, 60.9, 55.8, 36.2, 28.4, 18.9, 14.2.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 5.2 min (minor), 5.8 min (major).

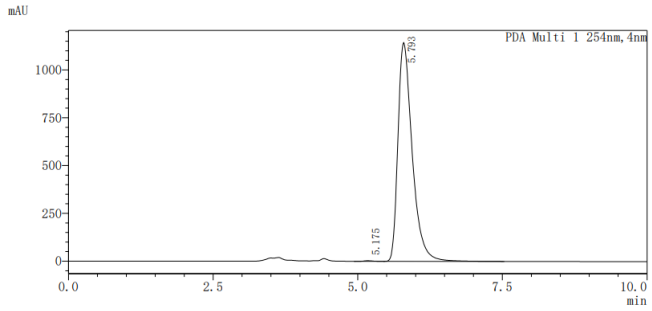
Chiral HPLC spectrum of (*rac*)-**1c**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	4.998	4006762	50.506
2	5.504	3926437	49.494

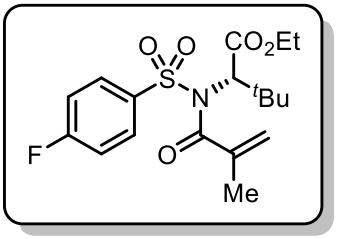
Chiral HPLC spectrum of (*S*)-**1c**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	5.175	32352	0.164
2	5.793	19635400	99.836

Ethyl (*S*)-2-(*N*-((4-fluorophenyl)sulfonyl)methacrylamido)-3,3-dimethylbutanoate (1d)

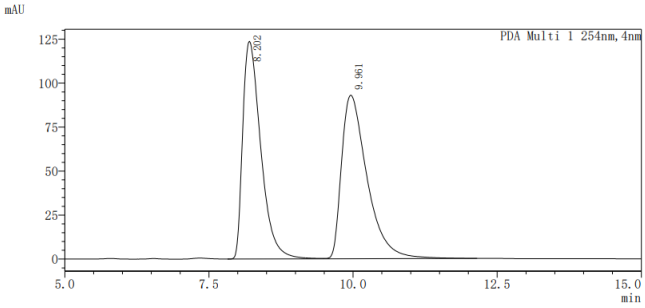


88% yield, 98% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.10–8.07 (m, 2H), 7.24–7.20 (m, 2H), 5.43 (s, 1H), 5.36 (d, *J* = 1.2 Hz, 1H), 4.83 (s, 1H), 4.28–4.19 (m, 2H), 1.51 (s, 3H), 1.27 (t, *J* = 6.8 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.4, 168.0, 165.6 (*J* = 256.0 Hz), 138.9, 135.1 (*J* = 3.1 Hz), 132.6 (*J* = 9.6 Hz), 122.1, 116.0 (*J* = 22.6 Hz), 66.6, 60.9, 36.2, 28.3, 18.9, 14.1.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 7.7 min (minor), 9.3 min (major).

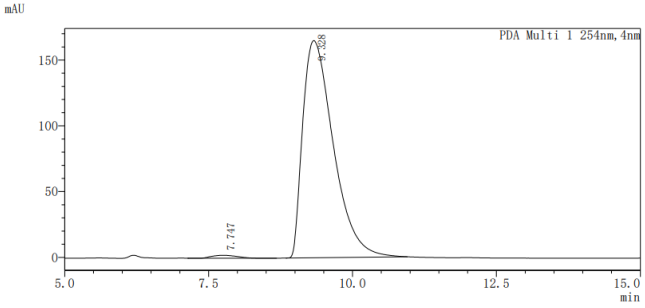
Chiral HPLC spectrum of (*rac*)-**1d**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	8.202	2703456	48.545
2	9.961	2865555	51.455

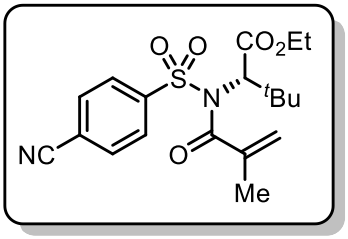
Chiral HPLC spectrum of (*S*)-**1d**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	7.747	66254	1.072
2	9.328	6112916	98.928

Ethyl (*S*)-2-(*N*-((4-cyanophenyl)sulfonyl)methacrylamido)-3,3-dimethylbutanoate (1e)

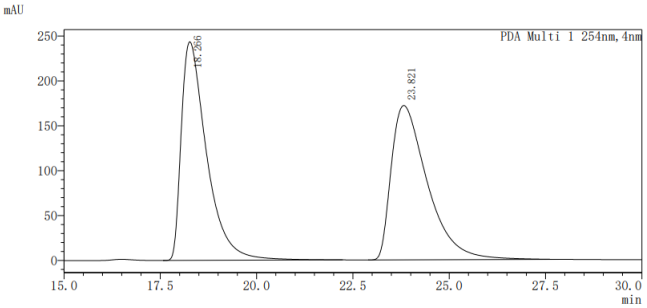


85% yield, 98% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.19 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 5.38 (d, *J* = 1.2 Hz), 4.82 (s, 1H), 4.27 (q, *J* = 6.8 Hz, 2H), 1.61 (s, 3H), 1.30 (t, *J* = 6.8 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.4, 168.2, 143.3, 138.9, 132.4, 130.1, 122.5, 117.4, 117.0, 67.8, 61.4, 36.3, 28.4, 19.2, 14.2.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 17.9 min (minor), 22.3 min (major).

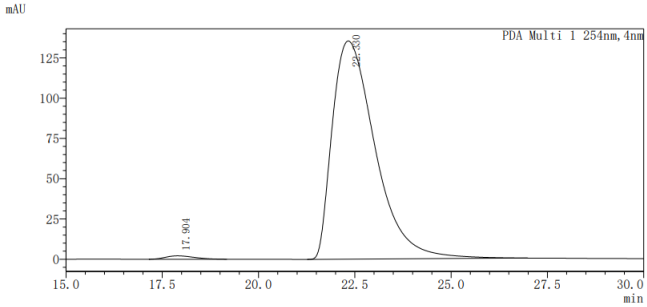
Chiral HPLC spectrum of (*rac*)-**1e**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	18.266	11159942	49.820
2	23.821	11240390	50.180

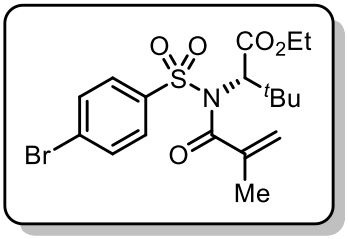
Chiral HPLC spectrum of (*S*)-**1e**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	17.904	109577	1.032
2	22.330	10504252	98.968

Ethyl (*S*)-2-(*N*-((4-bromophenyl)sulfonyl)methacrylamido)-3,3-dimethylbutanoate (1f)

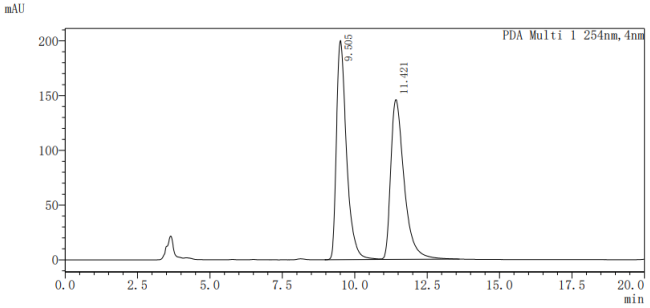


79% yield, 99% ee

1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.92–7.89 (m, 2H), 7.68–7.65 (m, 2H), 5.42 (s, 1H), 5.36 (d, *J* = 1.4 Hz, 1H), 4.81 (s, 1H), 4.27–4.21 (m, 2H), 1.54 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 168.2, 139.0, 138.2, 132.0, 131.1, 129.2, 122.4, 66.9, 61.1, 36.2, 28.4, 19.0, 14.2.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.8 min (minor), 12.0 min (major).

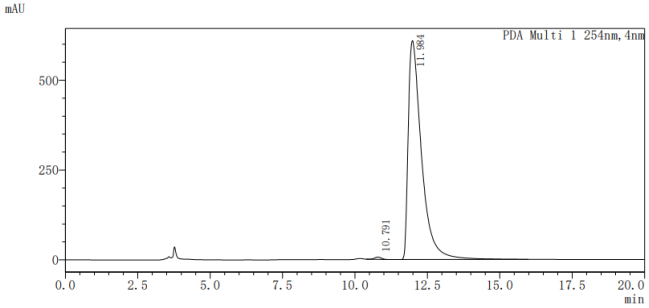
Chiral HPLC spectrum of (*rac*)-**1f**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	9.505	4852533	50.754
2	11.421	4708337	49.246

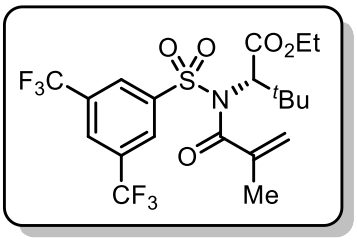
Chiral HPLC spectrum of (*S*)-**1f**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	10.791	101113	0.516
2	11.984	19493850	99.484

Ethyl (*S*)-2-(*N*-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)methacrylamido)-3,3-dimethylbutanoate (1g)

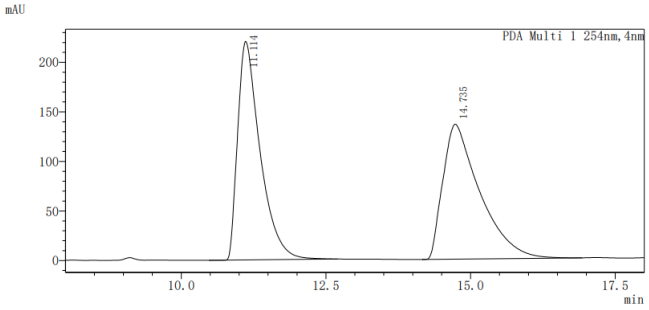


80% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.50 (s, 2H), 8.13 (s, 1H), 5.40 (d, *J* = 1.6 Hz, 1H), 5.35 (s, 1H), 4.81 (s, 1H), 4.31–4.21 (m, 2H), 1.72 (s, 3H), 1.25–1.21 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.3, 167.6, 141.8, 139.2, 132.6 (*J* = 34.5 Hz), 129.8 (*J* = 3.2 Hz), 127.1 (*J* = 3.5 Hz), 122.3 (*J* = 271.6 Hz), 122.1, 68.1, 61.3, 36.4, 28.4, 19.3, 14.0.

HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate = 0.8 mL/min, λ = 254 nm, t_R = 10.9 min (minor), 14.0 min (major).

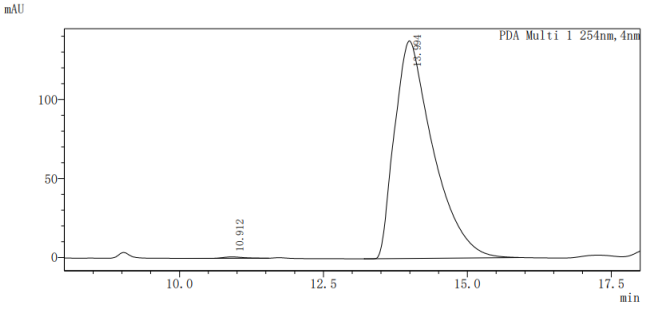
Chiral HPLC spectrum of (*rac*)-**1g**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	11.114	5945675	49.572
2	14.735	6048372	50.428

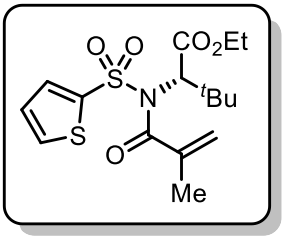
Chiral HPLC spectrum of (*S*)-**1g**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	10.912	20653	0.321
2	13.994	6409153	99.679

Ethyl (*S*)-3,3-dimethyl-2-(*N*-(thiophen-2-ylsulfonyl)methacrylamido)butanoate (1h)

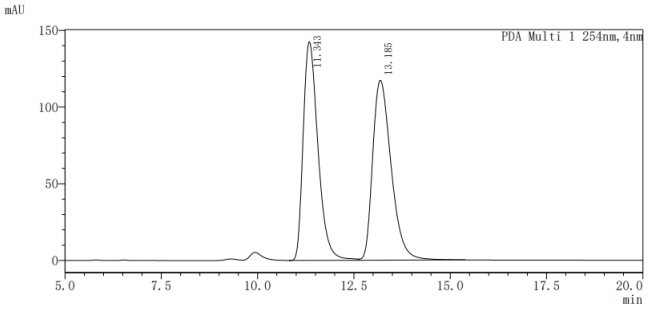


70% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.82 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.73 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.11 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.47 (s, 1H), 5.39 (d, *J* = 1.6 Hz, 1H), 4.80 (s, 1H), 4.27–4.20 (m, 2H), 1.65 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.9, 168.0, 139.5, 139.2, 136.4, 134.6, 127.1, 121.8, 67.1, 61.0, 36.2, 28.4, 19.1, 14.2.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.9 min (minor), 14.0 min (major).

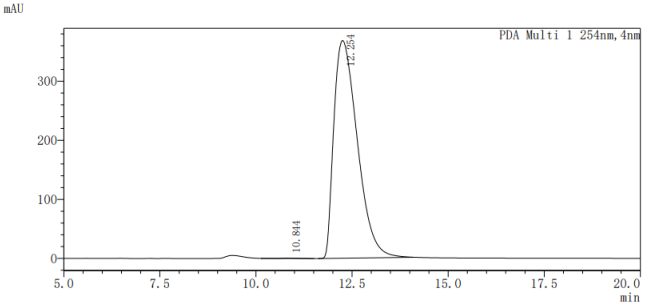
Chiral HPLC spectrum of (*rac*)-**1h**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	11.343	3817625	49.359
2	13.185	3916779	50.641

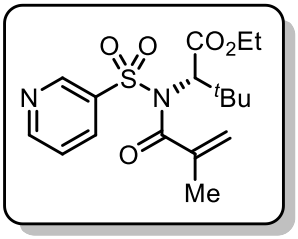
Chiral HPLC spectrum of (*S*)-**1h**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	10.844	15770	0.101
2	12.254	15673164	99.899

Ethyl (*S*)-3,3-dimethyl-2-(*N*-(pyridin-3-ylsulfonyl)methacrylamido)butanoate (1i)

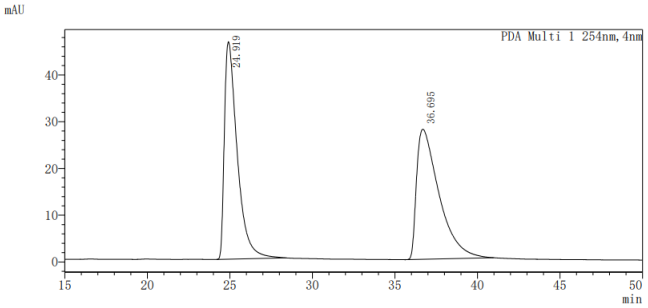


73% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.17 (d, *J* = 2.0 Hz, 1H), 8.85 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.37–8.34 (m, 1H), 7.52–7.49 (m, 1H), 5.40–5.39 (m, 2H), 4.82 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.62 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.4, 167.9, 153.9, 150.2, 139.2, 137.3, 136.0, 123.4, 122.3, 67.3, 61.2, 36.3, 28.4, 19.2, 14.1.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 24.8 min (minor), 35.9 min (major).

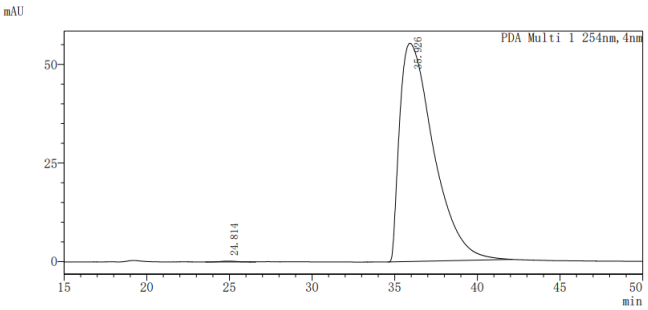
Chiral HPLC spectrum of (*rac*)-**1i**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	24.919	2515773	48.851
2	36.695	2634102	51.149

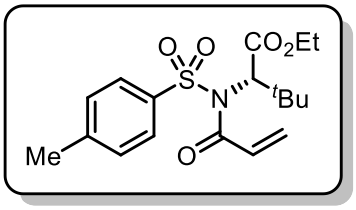
Chiral HPLC spectrum of (*S*)-**1i**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	24.814	12699	0.161
2	35.926	7878545	99.839

Ethyl (*S*)-3,3-dimethyl-2-(*N*-tosylacrylamido)butanoate (1j)

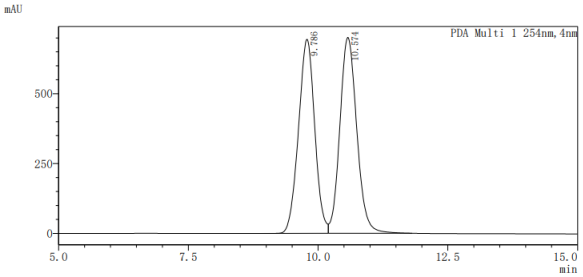


88% yield, 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.95 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.06 (q, *J* = 10.4 Hz, 1H), 6.18 (dd, *J* = 16.4, 1.2 Hz, 1H), 5.64 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.81 (s, 1H), 4.15–4.09 (m, 2H), 2.43 (s, 3H), 1.21 (s, 9H), 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 168.0, 165.8, 145.1, 136.9, 131.8, 129.4, 128.7, 128.6, 66.6, 60.7, 36.4, 28.5, 21.7, 14.1.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 9.78 min (minor), 10.57 min (major).

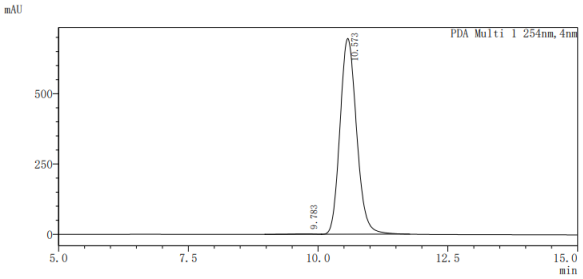
Chiral HPLC spectrum of (*rac*)-**1j**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	9.786	15085272	48.693
2	10.574	15894804	51.307

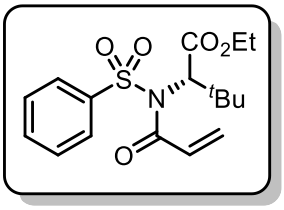
Chiral HPLC spectrum of (*S*)-**1j**



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	9.783	42534	0.274
2	10.573	15473467	99.726

Ethyl (*S*)-3,3-dimethyl-2-(*N*-(phenylsulfonyl)acrylamido)butanoate (1k)

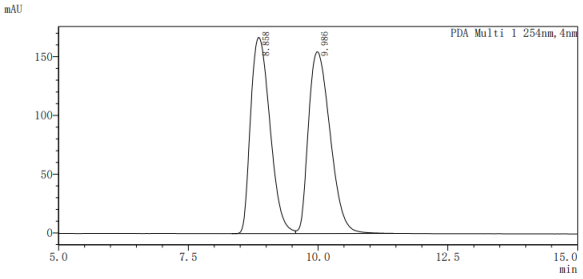


80% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.09–8.07 (m, 2H), 7.65–7.61 (m, 1H), 7.54–7.50 (m, 2H), 7.08 (dd, *J* = 16.4, 10.4 Hz, 1H), 6.18 (dd, *J* = 16.8, 1.6 Hz, 1H), 5.65 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.81 (s, 1H), 4.15–4.06 (m, 2H), 1.22 (s, 9H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 167.9, 165.8 139.8, 134.0, 131.9, 128.8, 128.7, 128.6, 66.7, 60.7, 36.4, 28.5, 14.0.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.28 min (minor), 10.99 min (major).

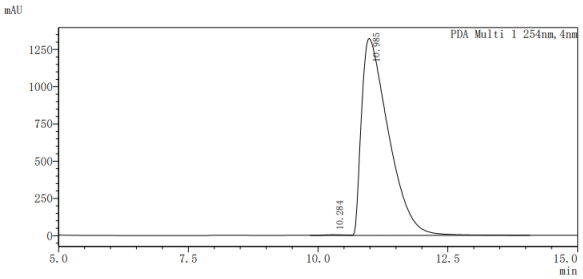
Chiral HPLC spectrum of (*rac*)-**1k**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	8.858	4344115	49.125
2	9.986	4498815	50.875

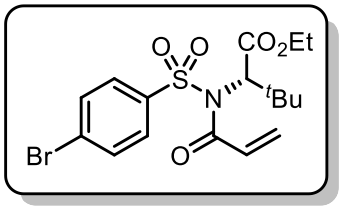
Chiral HPLC spectrum of (*S*)-**1k**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	10.284	111830	0.234
2	10.985	47756744	99.766

Ethyl (S)-2-(N-((4-bromophenyl)sulfonyl)acrylamido)-3,3-dimethylbutanoate (1l)

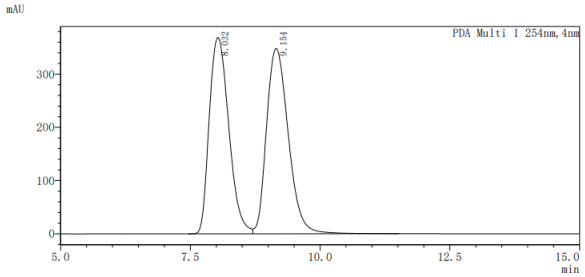


78% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.95 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.02 (q, *J* = 10.4 Hz, 1H), 6.22 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.69 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.78 (s, 1H), 4.16–4.10 (m, 2H), 1.21 (s, 9H), 1.14 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 167.9, 165.6, 138.8, 132.5, 132.1, 130.1, 129.3, 128.5, 66.9, 60.9, 36.4, 28.5, 14.1.

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 7.94 min (minor), 8.74 min (major).

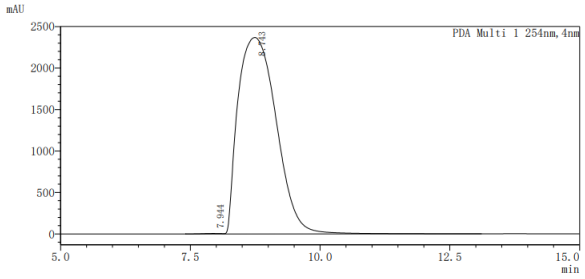
Chiral HPLC spectrum of (*rac*)-**1l**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	8.032	9650500	48.693
2	9.154	10168619	51.307

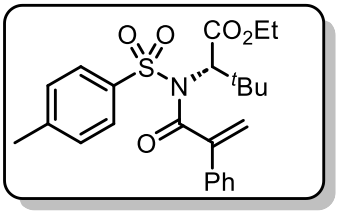
Chiral HPLC spectrum of (*S*)-**1l**



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	7.944	128236	0.105
2	8.743	121520198	99.895

Ethyl (S)-3,3-dimethyl-2-(2-phenyl-N-tosylacrylamido)butanoate (1m)

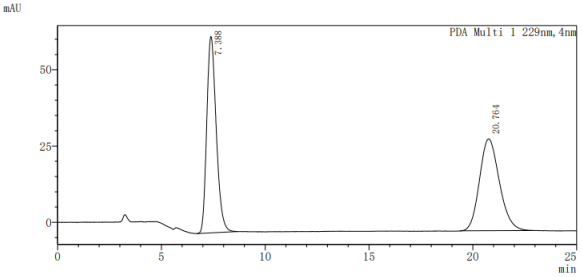


70% yield, > 99% ee

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.6 Hz, 2H), 7.22–6.99 (m, 7H), 5.90 (s, 1H), 5.55 (s, 1H), 4.92 (s, 1H), 4.31–4.16 (m, 2H), 2.26 (s, 3H), 1.32–1.26 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 168.2, 145.0, 135.8, 134.1, 129.7, 129.2, 128.1, 125.8, 119.3, 61.1, 36.5, 28.8, 21.5, 14.2.

HPLC analysis: Chiralcel ID column, n-hexane/i-PrOH = 99/1, flow rate = 0.5 mL·min-1 , λ = 254 nm, tR = 7.34 min (major), 20.77 min (minor).

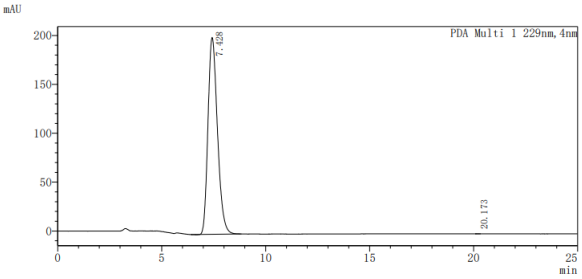
Chiral HPLC spectrum of (rac)-**1m**



PDA Ch1 229nm

Peak	Ret.Time	Area	Area%
1	7.388	2041104	50.487
2	20.764	2001748	49.513

Chiral HPLC spectrum of (S)-**1m**

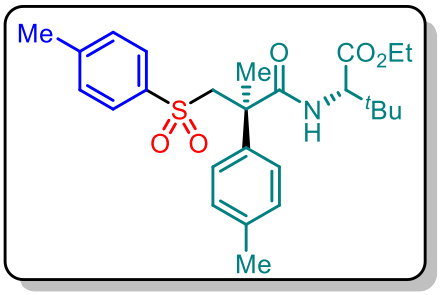


PDA Ch1 229nm

Peak	Ret.Time	Area	Area%
1	7.428	6378603	99.996
2	20.173	231	0.004

6. Characterization data of compound 3.

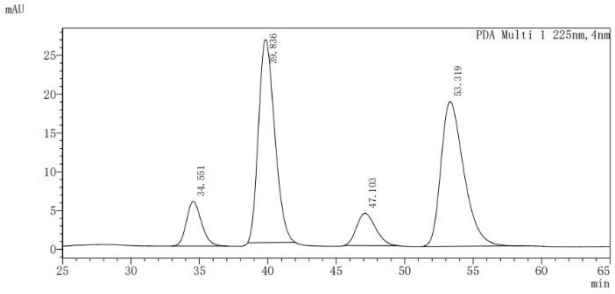
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(*p*-tolyl)-3-tosylpropanamido)butanoate (3a)



3a: 63.4 mg, 64% yield, > 99% ee_1, 99% ee_2, 83:17 dr, yellow solid.

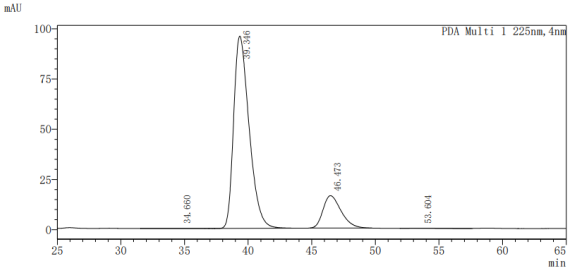
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.48 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 16.4, 8.0 Hz, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.74 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 4.0 Hz, 1H), 4.17–4.02 (m, 3H), 3.75 (d, *J* = 14.8 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.03 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 143.8, 138.3, 137.7, 136.1, 129.4, 129.4, 127.5, 126.9, 64.0, 60.9, 60.4, 49.4, 34.8, 26.5, 22.9, 21.5, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{35}NO_5S, M+Na]^+$: 496.2134, found: 496.2141. $[\alpha]_D^{25}$ = –1.1 (c = 0.64, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_1(major) = 39.3 min, t_1(minor) = 53.6 min, ee = > 99%; t_2(major) = 46.5 min, t_2(minor) = 34.7 min, ee = 99%.



PDA Ch1 225nm

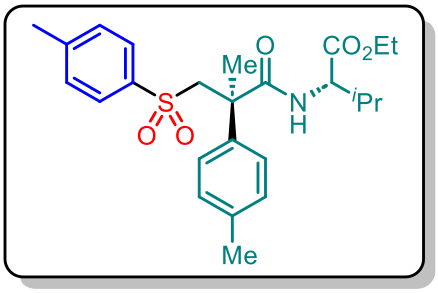
Peak	Ret. Time	Area	Area%
1	34.551	438500	8.483
2	39.836	2159042	41.768
3	47.103	403063	7.798
4	53.319	2168500	41.951



PDA Ch1 225nm

Peak	Ret. Time	Area	Area%
1	34.660	8347	0.086
2	39.346	8103993	83.436
3	46.473	1585791	16.327
4	53.604	14693	0.151

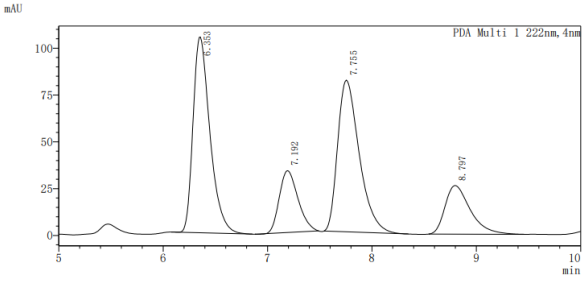
Ethyl ((R)-2-methyl-2-(p-tolyl)-3-tosylpropanoyl)-L-valinate (3a')



3a': 50.5 mg, 55% yield, > 99% ee_1, > 99% ee_2, 75:25 dr, yellow oil.

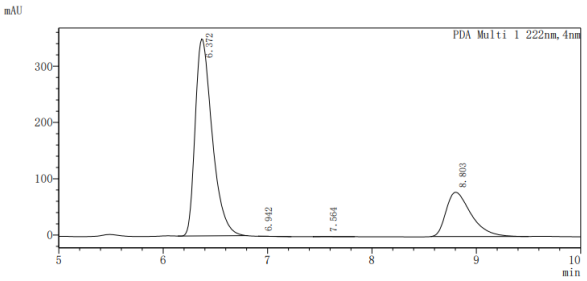
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.17–7.12 (m, 4H), 7.04–7.00 (m, 2H), 5.76 (d, *J* = 8.4 Hz, 1H), 4.41 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.17–4.02 (m, 3H) , 3.73 (d, *J* = 14.8 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 2.14–2.02 (m, 1H), 2.03 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 171.4, 143.8, 138.3, 137.7, 136.3, 129.4, 129.4, 127.6, 126.9, 64.1, 61.2, 57.4, 49.4, 31.1, 22.9, 21.6, 21.0, 18.9, 17.7, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{33}NO_5S+H^+$: M+H$]^+$: 460.2153, found: 460.2149. $[\alpha]_D^{25}$ = +4.3 (c = 0.24, $CHCl_3$).

HPLC analysis: Chiralcel IB column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 222 nm, t_1(major) = 6.4 min, t_1(minor) = 6.9 min, ee = > 99%; t_2(minor) = 7.6 min, t_2(major) = 8.8 min, ee = = > 99%.



PDA Ch1 222nm

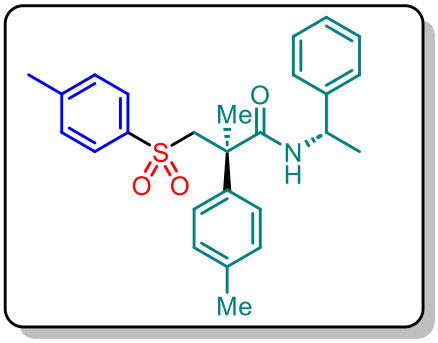
Peak	Ret. Time	Area	Area%
1	6.353	1176556	36.889
2	7.192	411335	12.897
3	7.755	1165599	36.545
4	8.797	435971	13.669



PDA Ch1 222nm

Peak	Ret. Time	Area	Area%
1	6.372	3967478	75.164
2	6.942	564	0.011
3	7.564	2068	0.039
4	8.803	1308318	24.786

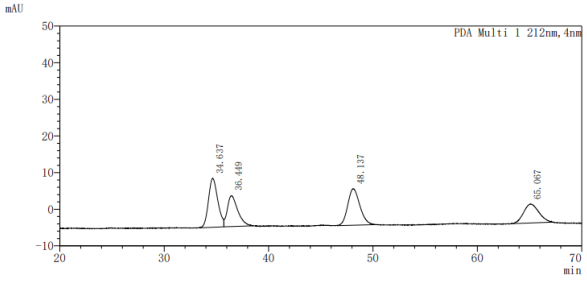
(R)-2-methyl-N-((S)-1-phenylethyl)-2-(p-tolyl)-3-tosylpropanamide (3a'')



3a'': 41.8 mg, 48% yield, 98% ee_1, > 99% ee_2, 59:41 dr, yellow oil.

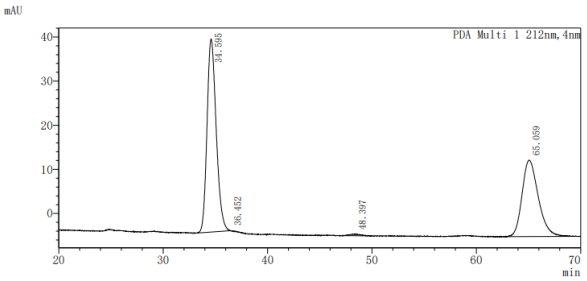
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.33–7.29 (m, 1H), 7.24–7.12 (m, 6H), 7.05 – 6.97 (m, 4H), 5.49 (d, *J* = 8.0 Hz, 1H), 5.06–5.00 (m, 1H), 4.10–4.04 (m, 1H), 3.69 (d, *J* = 14.4 Hz, 1H), 2.38 (s, 3H), 2.30 (d, *J* = 6.0 Hz, 3H), 2.02 (s, 3H), 1.30 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 143.8, 143.0, 138.4, 137.6, 136.8, 129.4, 129.3, 128.5, 127.6, 127.2, 126.8, 125.9, 64.2, 49.2, 49.1, 22.5, 21.8, 21.5, 21.0. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{29}NO_3S+H^+$: M+H$]^+$: 436.1941, found: 436.1942. $[\alpha]_D^{25}$ = +3.2 (c = 0.20, $CHCl_3$).

HPLC analysis: Chiralcel IA column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.8 mL/min, λ = 212 nm, t_1(major) = 34.6 min, t_1(minor) = 36.5 min, ee = 98%; t_2(major) = 48.4 min, t_2(minor) = 65.0 min, ee = > 99%.



PDA Ch1 212nm

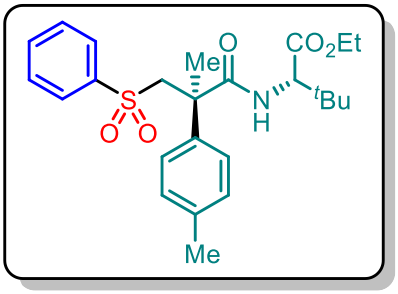
Peak	Ret. Time	Area	Area%
1	34.637	832985	30.353
2	36.449	585281	21.327
3	48.137	802183	29.231
4	65.067	523848	19.089



PDA Ch1 212nm

Peak	Ret. Time	Area	Area%
1	34.595	2671021	58.453
2	36.452	2510	0.055
3	48.397	28344	0.620
4	65.059	1867634	40.872

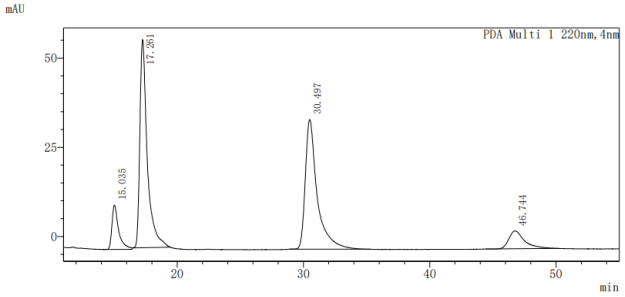
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-3-(phenylsulfonyl)-2-(*p*-tolyl)propanamido)butanoate (3b)



3b: 56.0 mg, 61% yield, > 99% ee_1, 99% ee_2, 84:16 dr, yellow oil.

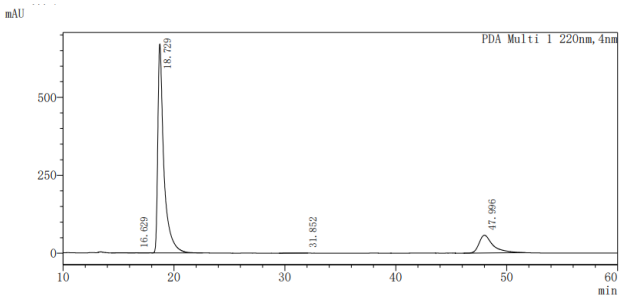
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.53 (d, *J* = 7.6 Hz, 2H), 7.45–7.41 (m, 1H), 7.30–7.25 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.68 (d, *J* = 9.2 Hz, 1H), 4.22 (d, *J* = 8.8 Hz, 1H), 4.11–3.95 (m, 3H), 3.72 (d, *J* = 14.8 Hz, 1H), 2.22 (s, 3H), 1.98 (s, 3H), 1.10 (t, *J* = 6.8 Hz, 3H), 0.81 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 141.2, 137.7, 136.0, 132.8, 129.4, 128.8, 127.5, 127.0, 64.0, 61.0, 60.4, 49.4, 34.8, 26.5, 23.0, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{33}NO_5S+H^+$: M+H$]^+$: 460.2152, found: 460.2157. $[\alpha]_D^{25}$ = –7.9 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 220 nm, t_1(major) = 18.7 min, t_1(minor) = 31.9 min, ee = > 99%; t_2(major) = 48.0 min, t_2(minor) = 16.6 min, ee = 99%.



PDA Ch1 220nm

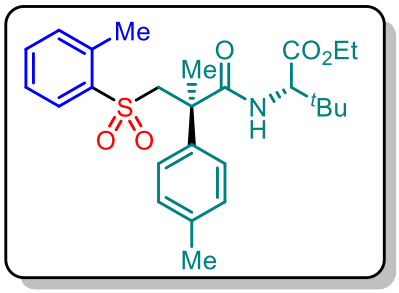
Peak	Ret. Time	Area	Area%
1	15.035	457538	8.100
2	17.261	2384882	42.219
3	30.497	2374291	42.032
4	46.744	432065	7.649



PDA Ch1 220nm

Peak	Ret. Time	Area	Area%
1	16.629	19130	0.063
2	18.729	25471592	83.637
3	31.852	4457	0.015
4	47.996	4959666	16.285

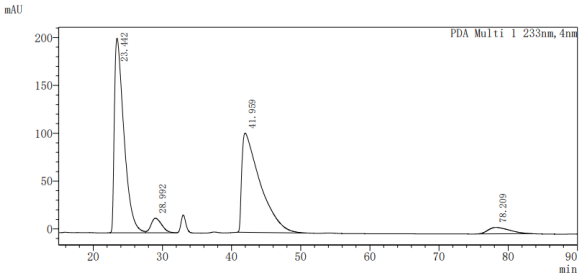
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(*p*-tolyl)-3-(*o*-tolylsulfonyl)propanamido)butanoate (3c)



3c: 39.8 mg, 42% yield, > 99% ee_1, > 99% ee_2, 85:15 dr, yellow oil.

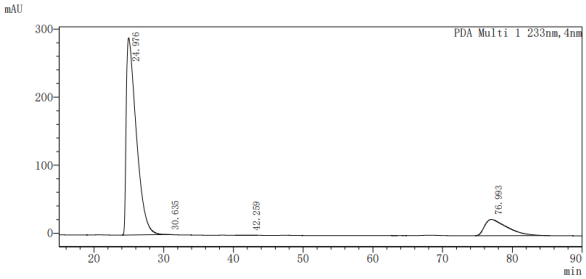
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.60–7.55 (m, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19–7.11 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.77 (d, *J* = 9.2 Hz, 1H), 4.29 (d, *J* = 9.2 Hz, 1H), 4.20–4.01 (m, 3H), 3.77 (d, *J* = 14.8 Hz, 1H), 2.62 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.88 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 139.1, 137.7, 137.5, 136.2, 133.0, 132.3, 129.6, 129.4, 126.8, 126.3, 62.9, 60.9, 60.3, 49.4, 34.8, 26.5, 23.0, 21.0, 20.3, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{35}NO_5S+H^+$: M+H$]^+$: 474.2309, found: 474.2320. $[\alpha]_D^{25}$ = +2.3 (c = 0.16, $CHCl_3$).

HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.6 mL/min, λ = 233 nm, t_1(major) = 25.0 min, t_1(minor) = 42.3 min, ee = > 99%; t_2(major) = 77.0 min, t_2(minor) = 30.6 min, ee = > 99%.



PDA Ch1 233nm

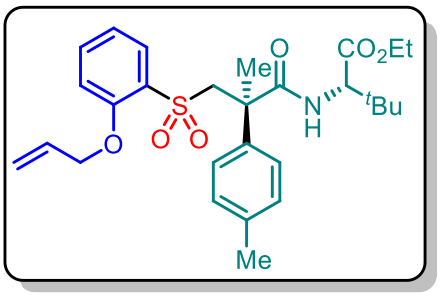
Peak	Ret. Time	Area	Area%
1	23.442	19552678	46.850
2	28.992	1632183	3.911
3	41.959	19123392	45.821
4	78.209	1426684	3.418



PDA Ch1 233nm

Peak	Ret. Time	Area	Area%
1	24.976	29144130	84.490
2	30.635	3958	0.011
3	42.259	14026	0.041
4	76.993	5332053	15.458

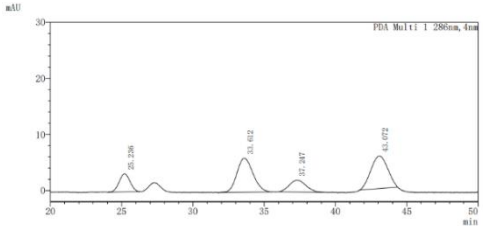
Ethyl (*S*)-2-((*R*)-3-((2-(allyloxy)phenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3d)



3d: 51.5 mg, 50% yield, > 99% ee_1, 98% ee_2, 78:22 dr, yellow oil.

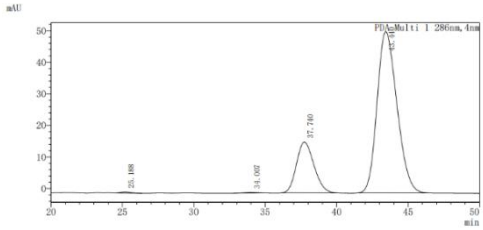
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.40–7.20 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.87–6.81 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.86 (dd, *J* = 8.8, 4.0 Hz, 1H), 4.66 (dd, *J* = 20.4, 9.6 Hz, 1H), 4.43–4.30 (m, 2H), 4.22–4.05 (m, 2H), 3.92–3.82 (m, 2H), 3.60 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.94–2.80 (m, 1H), 2.57–2.48 (m, 1H), 2.36 - 2.32 (m, 3H), 2.03 (d, *J* = 2.8 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 1.6 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.5, 174.4, 170.7, 159.7. 159.7, 138.5, 136.6, 136.5, 129.9, 129.2, 129.1, 127.1, 127.0, 124.1, 124.0, 120.7, 120.6, 109.9, 76.1, 75.9, 63.2, 63.0, 61.0, 60.4, 60.4, 58.7, 58.6, 49.6, 49.5, 36.0, 35.5, 34.8, 26.5, 23.0, 23.0, 21.0, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{28}H_{37}NO_6S+H^+$: M+H$]^+$: 516.2414, found: 516.2430. $[\alpha]_D^{25}$ = +16.4 (c= 0.14, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 286 nm, t_1(major) = 43.4 min, t_1(minor) = 34.0 min, ee = > 99%; t_2(major) = 37.7 min, t_2(minor) = 25.2 min, ee = 98%.



PDA Ch1 286nm

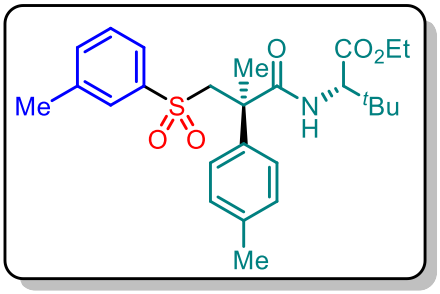
Peak	Ret. Time	Area	Area%
1	25.236	171308	13.197
2	33.612	477860	36.813
3	37.247	173089	13.334
4	43.072	475801	36.655



PDA Ch1 286nm

Peak	Ret. Time	Area	Area%
1	25.188	17891	0.282
2	34.007	13193	0.208
3	37.740	1374119	21.651
4	43.440	4941457	77.859

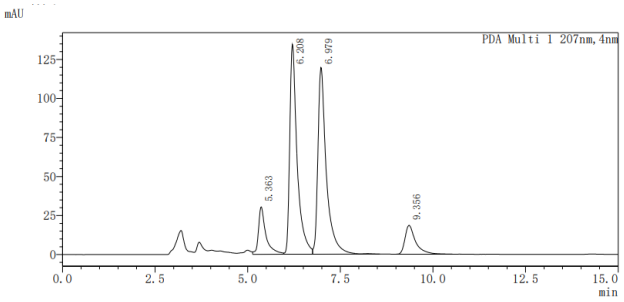
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(*p*-tolyl)-3-(*m*-tolylsulfonyl)propanamido)butanoate (3e)



3e: 53.0 mg, 56% yield, 98% ee_1, 91% ee_2,79:21 dr, yellow solid.

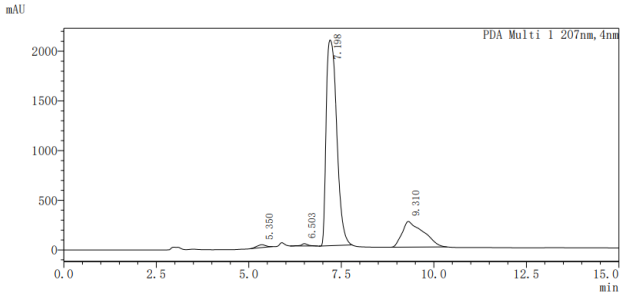
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43 (d, *J* = 7.6 Hz, 1H), 7.32–7.20 (m, 3H), 7.11–7.10 (m, 4H), 5.71 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 4.17–4.01 (m, 3H), 3.80 (d, *J* = 14.8 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.05 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.8, 8 170.7, 140.9, 138.9, 137.6, 135.9, 133.6, 129.3, 128.7, 127.9, 127.0, 124.6, 63.8, 60.9, 60.3, 49.4, 34.7, 26.5, 23.0, 21.2, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{35}NO_5S+H^+$: M+H$]^+$: 474.2309, found: 474.2319. $[\alpha]_D^{25}$ = +6.7 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 207 nm, t_1(major) = 7.2 min, t_1(minor) = 6.5 min, ee = 98%; t_2(major) = 9.3 min, t_2(minor) = 5.4 min, ee = 91%.



PDA Ch1 207nm

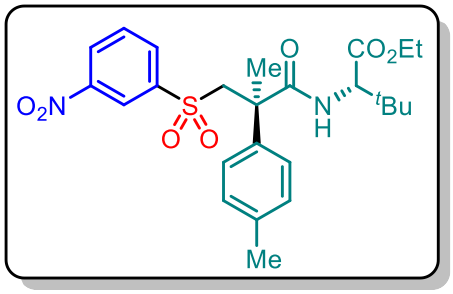
Peak	Ret.Time	Area	Area%
1	5.363	424048	9.299
2	6.208	1871698	41.047
3	6.979	1898713	41.639
4	9.356	365473	8.015



PDA Ch1 207nm

Peak	Ret.Time	Area	Area%
1	5.350	492422	0.945
2	6.503	311847	0.598
3	7.198	41074431	78.810
4	9.310	10239694	19.647

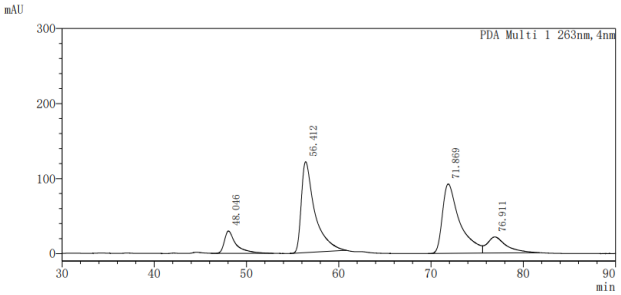
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-3-((3-nitrophenyl)sulfonyl)-2-(*p*-tolyl)propanamido)butanoate (3f)



3f: 26.2 mg, 26% yield, > 99% ee_1, > 99% ee_2, 82:18 dr, yellow oil.

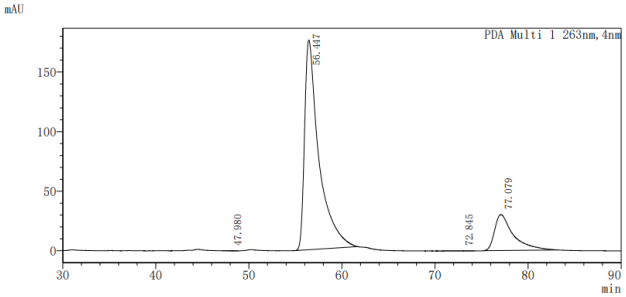
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.14–8.10 (m, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.05–7.02 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.61 (d, *J* = 8.8 Hz, 1H), 4.28 (d, *J* = 9.2 Hz, 1H), 4.21–4.02 (m, 3H), 3.90 (d, *J* = 15.2 Hz, 1H), 2.27 (s, 3H), 2.05 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.4, 170.6, 150.0, 146.2, 138.5, 135.3, 129.4, 129.0, 127.2, 123.8, 64.4, 61.0, 60.3, 49.3, 34.7, 26.5, 22.9, 20.9, 14.1. **HRMS** (ESI) m/z Calcd for [$C_{25}H_{32}N_2O_7S$+H^+: M+H]$^+$: 505.2003, found: 505.2015. $[\alpha]_D^{25}$ = +13.1 (c= 0.06, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.8 mL/min, λ = 263 nm, t_1(major) = 56.4 min, t_1(minor) = 72.8 min, ee = > 99%; t_2(major) = 77.1 min, t_2(minor) = 48.0 min, ee = > 99%.



PDA Ch1 263nm

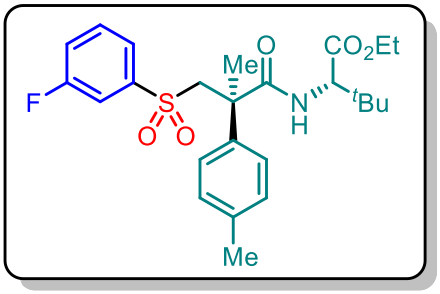
Peak	Ret. Time	Area	Area%
1	48.046	2614595	8.653
2	56.412	12359084	40.902
3	71.869	12121621	40.116
4	76.911	3121206	10.329



PDA Ch1 263nm

Peak	Ret. Time	Area	Area%
1	47.980	1267	0.005
2	56.447	18827773	81.698
3	72.845	275	0.001
4	77.079	4216293	18.295

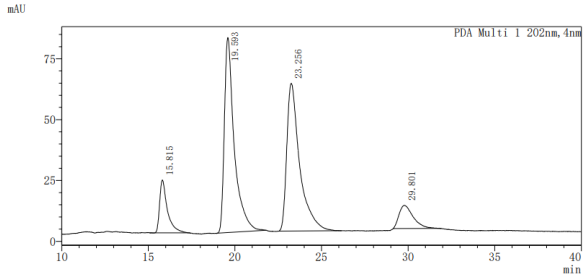
Ethyl (*S*)-2-((*R*)-3-((3-fluorophenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3g)



3g: 42.9 mg, 45% yield, 99% ee_1, 98% ee_2, 84:16 dr, yellow oil.

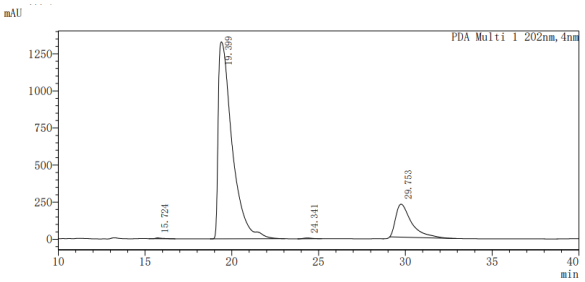
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.42–7.30 (m, 2H), 7.19–7.06 (m, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.69 (d, *J* = 8.8 Hz, 1H), 4.28 (d, *J* = 9.2 Hz, 1H), 4.20–3.97 (m, 3H), 3.86 (d, *J* = 14.8 Hz, 1H), 2.29 (s, 3H), 2.04 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 162.0 (*J* = 250.2 Hz), 143.0 (*J* = 6.4 Hz), 138.1, 135.4, 130.6 (*J* = 7.4 Hz), 129.4, 127.1, 123.2 (*J* = 3.2 Hz), 119.9 (*J* = 21.1 Hz), 115.0 (*J* = 24.4 Hz), 64.2, 60.9, 60.3, 49.4, 34.7, 26.5, 23.0, 20.9, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{32}FNO_5S+H^+$: M+H$]^+$: 478.2058, found: 478.2070. $[\alpha]_D^{25}$ = +2.5 (c = 0.24, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.8 mL/min, λ = 202 nm, t_1(major) = 19.4 min, t_1(minor) = 24.3 min, ee = 99%; t_2(major) = 29.8 min, t_2(minor) = 15.7 min, ee = 98%.



PDA Ch1 202nm

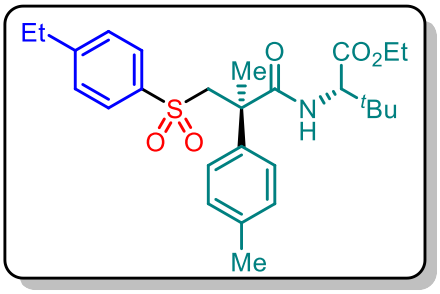
Peak	Ret.Time	Area	Area%
1	15.815	672622	8.918
2	19.593	3182804	42.200
3	23.256	3148052	41.739
4	29.801	538754	7.143



PDA Ch1 202nm

Peak	Ret.Time	Area	Area%
1	15.724	141124	0.159
2	19.399	74168606	83.660
3	24.341	188591	0.213
4	29.753	14156938	15.969

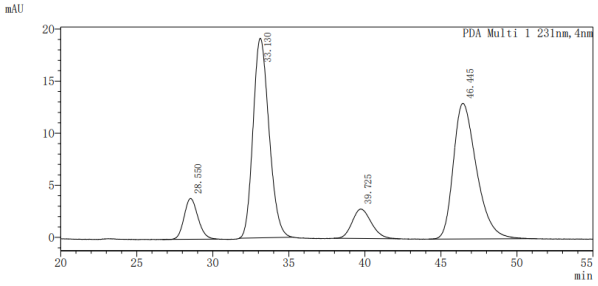
Ethyl (*S*)-2-((*R*)-3-((4-ethylphenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3h)



3h: 63.3 mg, 65% yield, > 99% ee_1, > 99% ee_2, 83:17 dr, yellow solid.

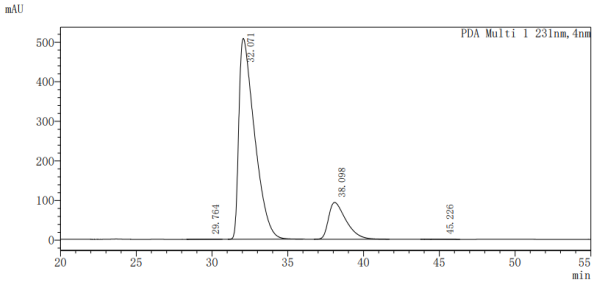
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (d, *J* = 8.0 Hz, 2H), 7.12–7.09 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.68 (d, *J* = 9.2 Hz, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 4.18–4.00 (m, 3H), 3.78 (d, *J* = 14.8 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.04 (s, 3H), 1.25–1.15 (m, 6H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 150.0, 138.4, 137.6, 136.1, 129.3, 128.3, 127.6, 127.0, 63.9, 60.9, 60.3, 49.4, 34.7, 28.8, 26.5, 22.9, 21.0, 15.3, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{27}H_{37}NO_5S+H^+$: M+H$]^+$: 488.2465, found: 488.2476. $[\alpha]_D^{25}$ = +1.9 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 231 nm, t_1(major) = 32.1min, t_1(minor) = 45.2 min, ee = > 99%; t_2(major) = 28.1 min, t_2(minor) = 29.8 min, ee = > 99%.



PDA Ch1 231nm

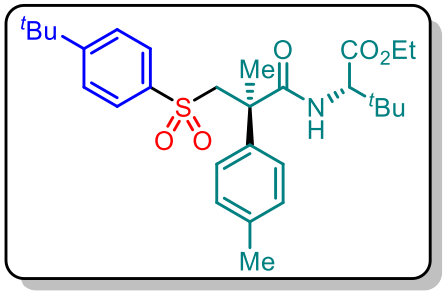
Peak	Ret.Time	Area	Area%
1	28.550	247847	7.559
2	33.130	1398364	42.650
3	39.725	247818	7.558
4	46.445	1384684	42.233



PDA Ch1 231nm

Peak	Ret.Time	Area	Area%
1	29.764	14903	0.034
2	32.071	36575872	83.072
3	38.098	7435304	16.887
4	45.226	2925	0.007

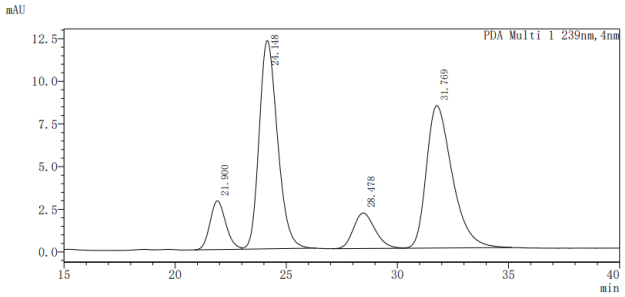
Ethyl (*S*)-2-((*R*)-3-((4-(*tert*-butyl)phenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3i)



3i: 58.7 mg, 57% yield, > 99% ee_1, > 99% ee_2, 81:19 dr, yellow solid.

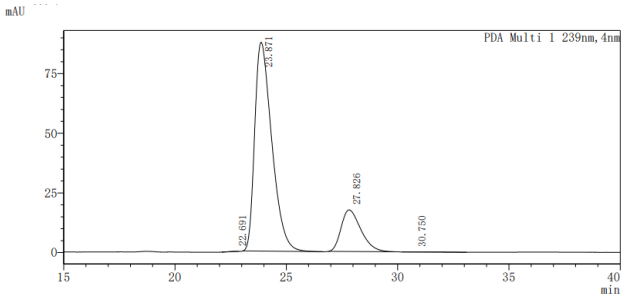
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43–7.38 (m, 2H), 7.28–7.24 (m, 2H), 7.04–7.01 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.63 (d, *J* = 9.2 Hz, 1H), 4.21 (d, *J* = 8.8 Hz, 1H), 4.10–3.94 (m, 3H), 3.73 (d, *J* = 14.8 Hz, 1H), 2.22 (s, 3H), 1.97 (s, 3H), 1.24 (s, 9H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.80 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.8, 170.7, 156.8, 138.1, 137.5, 136.0, 129.3, 127.3, 127.1, 125.8, 63.9, 60.9, 60.3, 49.4, 35.1, 34.7, 31.1, 26.5, 23.0, 21.1, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{29}H_{41}NO_5S+H^+$: M+H$]^+$: 516.2778, found: 516.2788. $[\alpha]_D^{25}$ = –10.7 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 239 nm, t_1(major) = 23.9 min, t_1(minor) = 30.9 min, ee = > 99%; t_2(major) = 27.8 min, t_2(minor) = 22.7 min, ee = > 99%.



PDA Ch1 239nm

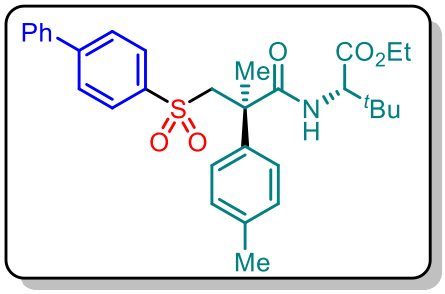
Peak	Ret.Time	Area	Area%
1	21.900	140914	8.482
2	24.148	701876	42.247
3	28.478	141084	8.492
4	31.769	677498	40.779



PDA Ch1 239nm

Peak	Ret.Time	Area	Area%
1	22.691	2206	0.038
2	23.871	4677720	81.187
3	27.826	1077571	18.702
4	30.750	4197	0.073

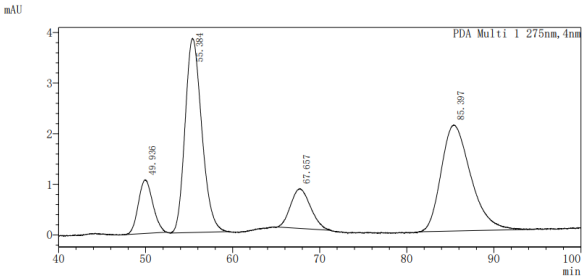
Ethyl (*S*)-2-((*R*)-3-([1,1'-biphenyl]-4-ylsulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3j)



3j: 48.2 mg, 45% yield, > 99% ee_1, > 99% ee_2, 82:18 dr, yellow oil.

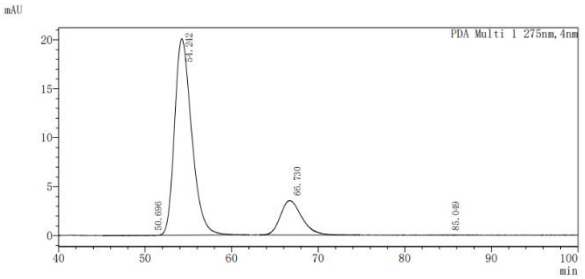
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65–7.60 (m, 2H), 7.57–7.51 (m, 4H), 7.49–7.40 (m, 3H), 7.14–7.10 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.73 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H), 4.20–4.02 (m, 3H), 3.84 (d, *J* = 14.8 Hz, 1H), 2.24 (s, 3H), 2.07 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 145.9, 139.6, 139.3, 137.8, 136.0, 129.4, 129.1, 128.5, 128.1, 127.4, 127.3, 127.0, 64.0, 61.9, 60.4, 49.5, 34.8, 26.5, 23.0, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{31}H_{37}NO_5S+H^+$: M+H$]^+$: 536.2465, found: 536.2477. $[\alpha]_D^{25}$ = –19.4 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 275 nm, t_1(major) = 54.2 min, t_1(minor) = 85.0 min, ee = > 99%; t_2(major) = 66.7 min, t_2(minor) = 50.7 min, ee = > 99%.



PDA Ch1 275nm

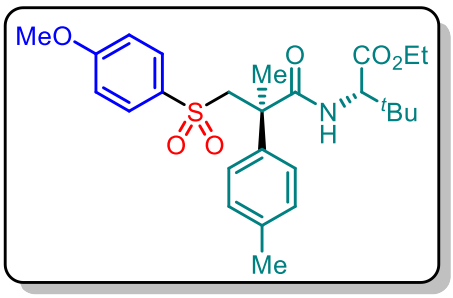
Peak	Ret.Time	Area	Area%
1	49.936	122112	9.734
2	55.384	512583	40.860
3	67.657	124732	9.943
4	85.397	495060	39.463



PDA Ch1 275nm

Peak	Ret.Time	Area	Area%
1	50.696	812	0.024
2	54.242	2766370	82.083
3	66.730	602994	17.892
4	85.049	44	0.001

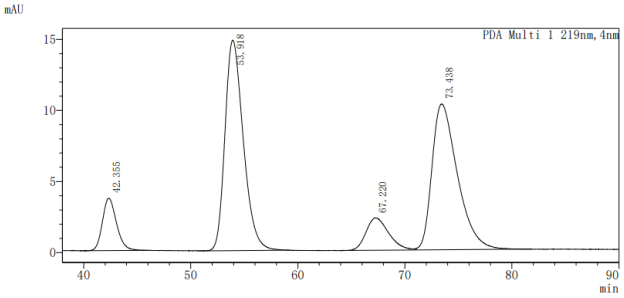
Ethyl (*S*)-2-((*R*)-3-((4-methoxyphenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3k)



3k: 68.5 mg, 70% yield, 99% ee_1, > 99% ee_2, 84:16 dr, yellow oil.

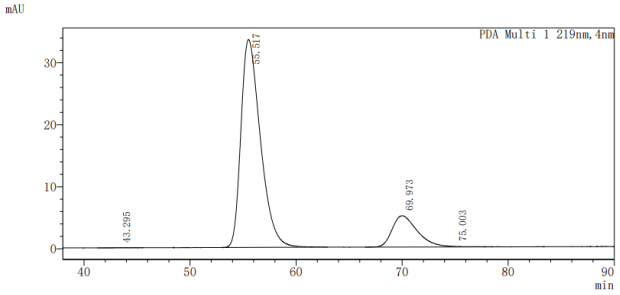
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.53–7.48 (m, 2H), 7.13–7.10 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.81–6.78 (m, 2H), 5.74 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 4.18–4.02 (m, 3H), 3.86–3.80 (m, 3H), 3.74 (d, *J* = 15.2 Hz, 1H), 2.30 (s, 3H), 2.03 (s, 3H), 1.17 (t, *J* = 6.8 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 163.2, 137.6, 136.2, 133.0, 129.7, 129.4, 127.0, 114.0, 64.1, 61.0, 60.3, 55.6, 49.4, 34.7, 26.5, 22.9, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{35}NO_6S+H^+$: M+H$]^+$: 490.2258, found: 490.2268. $[\alpha]_D^{25}$ = –5.5 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 219 nm, t_1(major) = 55.5 min, t_1(minor) = 75.0 min, ee = 99%; t_2(major) = 69.9 min, t_2(minor) = 43.3 min, ee = > 99%.



PDA Ch1 219nm

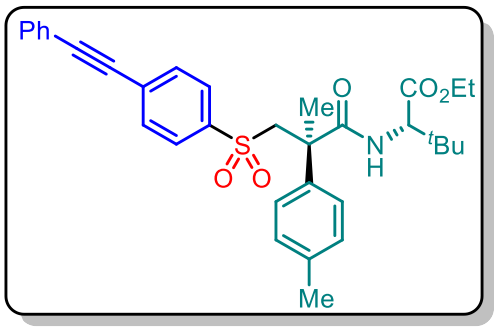
Peak	Ret. Time	Area	Area%
1	42.355	336152	8.136
2	53.918	1763682	42.685
3	67.220	335659	8.124
4	73.438	1696354	41.056



PDA Ch1 219nm

Peak	Ret. Time	Area	Area%
1	43.295	776	0.015
2	55.517	4280612	83.558
3	69.973	830807	16.217
4	75.003	10759	0.210

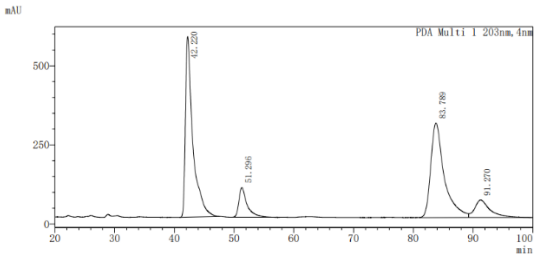
Ethyl (*R*)-3,3-dimethyl-2-((*R*)-2-methyl-3-((4-(phenylethynyl)phenyl)sulfonyl)-2-(*p*-tolyl)propanamido)butanoate (3l)



3l: 47.0 mg, 42% yield, > 99% ee_1, 99% ee_2, 81:19 dr, yellow oil.

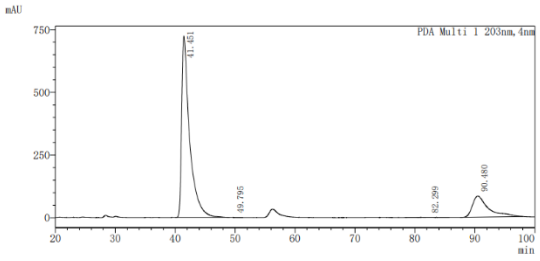
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.35–7.20 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.87–6.81 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.86 (dd, *J* = 8.8, 4.8 Hz, 1H), 4.66 (dd, *J* = 20.4, 9.6 Hz, 1H), 4.43–4.30 (m, 2H), 4.22–4.05 (m, 2H), 3.92–3.82 (m, 2H), 3.60 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.94–2.76 (m, 1H), 2.57–2.48 (m, 1H), 2.36–2.32 (m, 3H), 2.03 (d, *J* = 2.8 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 1.6 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 140.0, 138.1, 135.7, 131.8, 131.7, 129.5, 129.0, 128.5, 128.2, 127.5, 127.0, 122.4, 92.9, 87.8, 64.0, 60.9, 60.3, 49.4, 34.8, 26.5, 22.9, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{33}H_{37}NO_5S+H^+$: M+H$]^+$: 560.2465, found: 560.2479. $[\alpha]_D^{25}$ = –4.2 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 88/12, flow rate = 0.8 mL/min, λ = 203 nm, t_1(major) = 41.5 min, t_1(minor) = 82.3 min, ee = > 99%; t_2(major) = 90.5 min, t_2(minor) = 49.8 min, ee = 99%.



PDA Ch1 203nm

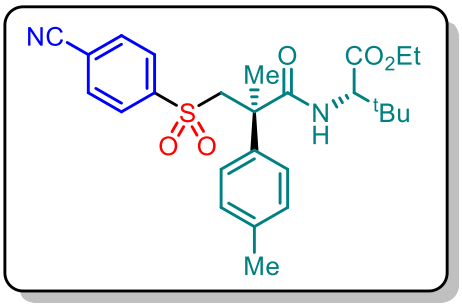
Peak	Ret.Time	Area	Area%
1	42.220	49306929	42.797
2	51.296	8971594	7.787
3	83.789	46965856	40.765
4	91.270	9967717	8.652



PDA Ch1 203nm

Peak	Ret.Time	Area	Area%
1	41.451	66521980	80.902
2	49.795	2299	0.003
3	82.299	112161	0.136
4	90.480	15589425	18.959

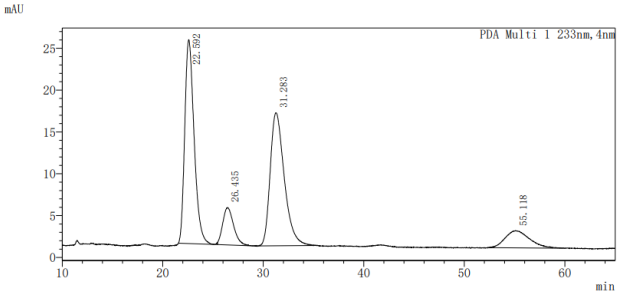
Ethyl (*S*)-2-((*R*)-3-((4-cyanophenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3m)



3m: 38.7 mg, 40% yield, > 99% ee_1, > 99% ee_2, 83:17 dr, yellow oil.

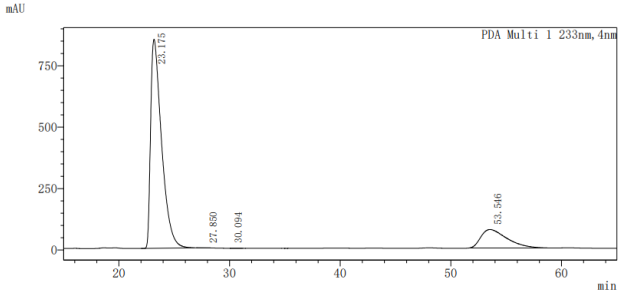
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65–7.57 (m, 4H), 7.06–6.97 (m, 4H), 5.67 (d, *J* = 9.2 Hz, 1H), 4.28 (d, *J* = 8.8 Hz, 1H), 4.21–4.02 (m, 3H), 3.86 (d, *J* = 15.2 Hz, 1H), 2.31 (s, 3H), 2.04 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.4, 170.6, 144.8, 138.3, 135.4, 132.4, 129.5, 128.3, 127.1, 117.2, 116.3, 64.2, 61.0, 60.4, 49.4, 34.7, 26.5, 22.9, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{32}N_2O_5S+H^+$: M+H$]^+$: 485.2105, found: 485.2116. $[\alpha]_D^{25}$ = +2.3 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 233 nm, t_1(major) = 23.2 min, t_1(minor) = 30.1 min, ee = > 99%; t_2(major) = 53.5 min, t_2(minor) = 27.9 min, ee = > 99%.



PDA Ch1 233nm

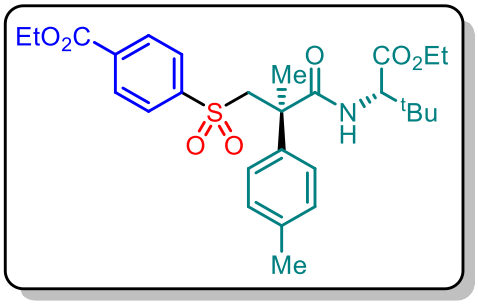
Peak	Ret. Time	Area	Area%
1	22.592	1574214	41.325
2	26.435	336609	8.836
3	31.283	1552263	40.748
4	55.118	346309	9.091



PDA Ch1 233nm

Peak	Ret. Time	Area	Area%
1	23.175	58398161	82.609
2	27.850	30660	0.043
3	30.094	921	0.001
4	53.546	12262560	17.346

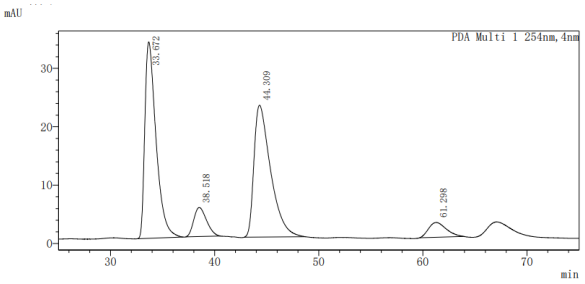
Ethyl 4-(((*R*)-3-(((*S*)-1-ethoxy-3,3-dimethyl-1-oxobutan-2-yl)amino)-2-methyl-3-oxo-2-(*p*-tolyl)propyl)sulfonyl)benzoate (3n)



3n: 53.1 mg, 50% yield, 98% ee_1, > 99% ee_2, 83:17 dr, yellow oil.

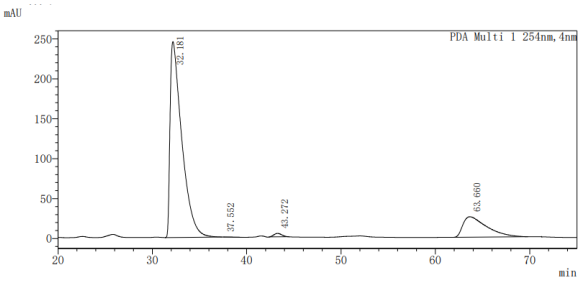
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.97–7.94 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.06–7.03 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.68 (d, *J* = 8.8 Hz, 1H), 4.45–4.38 (m, 2H), 4.28 (d, *J* = 8.8 Hz, 1H), 4.22–3.99 (m, 3H), 3.86 (d, *J* = 15.2 Hz, 1H), 2.27 (s, 3H), 2.04 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.6, 170.6, 165.1, 144.5, 138.1, 135.4, 134.1, 129.8, 129.4, 127.5, 127.1, 64.0, 61.7, 60.9, 60.3, 49.3, 34.7, 26.5, 22.9, 20.9, 14.3, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{28}H_{37}NO_7S+H^+$: M+H$]^+$: 532.2363, found: 532.2378. $[\alpha]_D^{25}$ = +5.4 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, t_1(major) = 32.2 min, t_1(minor) = 43.3 min, ee = 98%; t_2(major) = 63.7 min, t_2(minor) = 37.6 min, ee = > 99%.



PDA Ch1 254nm

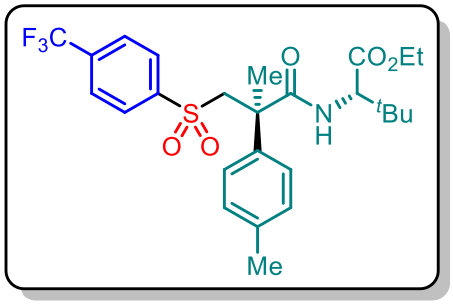
Peak	Ret.Time	Area	Area%
1	33.672	2517387	43.807
2	38.518	425249	7.400
3	44.309	2507032	43.627
4	61.298	296808	5.165



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	32.181	21185606	81.695
2	37.552	3291	0.013
3	43.272	255373	0.985
4	63.660	4488134	17.307

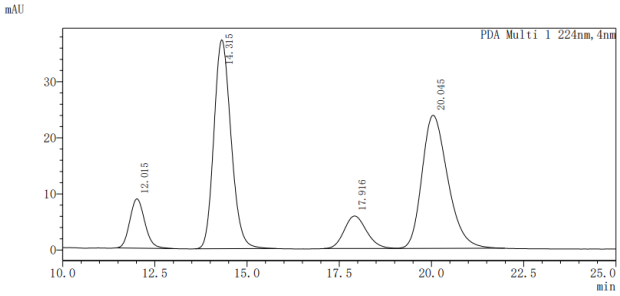
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(*p*-tolyl)-3-((4-(trifluoromethyl)phenyl)sulfonyl)propanamido)butanoate (3o)



3o: 64.3 mg, 61% yield, > 99% ee_1, 99% ee_2, 82:18 dr, yellow oil.

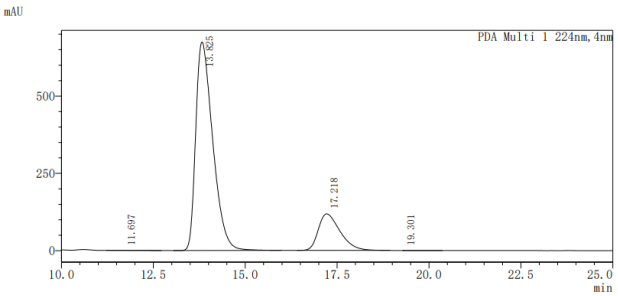
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.54–4.44 (m, 4H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.56 (d, *J* = 8.8 Hz, 1H), 4.19 (d, *J* = 8.8 Hz, 1H), 4.10–3.94 (m, 3H), 3.84 (d, *J* = 15.6 Hz, 1H), 2.18 (s, 3H), 1.97 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.78 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.6, 144.0, 138.1, 135.1, 134.3 (*J* = 32.9 Hz), 129.4, 128.1, 127.2, 125.7 (*J* = 3.6 Hz), 123.2 (*J* = 271.1 Hz), 64.0, 61.0, 60.3, 49.3, 34.7, 26.5, 22.9, 20.8, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{32}F_3NO_5S+H^+$: M+H$]^+$: 528.2026, found: 528.2037. $[\alpha]_D^{25}$ = +10.4 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 224 nm, t_1(major) = 13.8 min, t_1(minor) = 19.3 min, ee = > 99%; t_2(major) = 17.2 min, t_2(minor) = 11.7 min, ee = 99%.



PDA Ch1 224nm

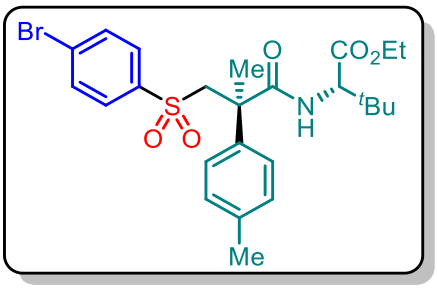
Peak	Ret. Time	Area	Area%
1	12.015	249000	8.712
2	14.315	1205377	42.174
3	17.916	245495	8.589
4	20.045	1158225	40.524



PDA Ch1 224nm

Peak	Ret. Time	Area	Area%
1	11.697	25439	0.096
2	13.825	21684474	81.602
3	17.218	4863280	18.301
4	19.301	223	0.001

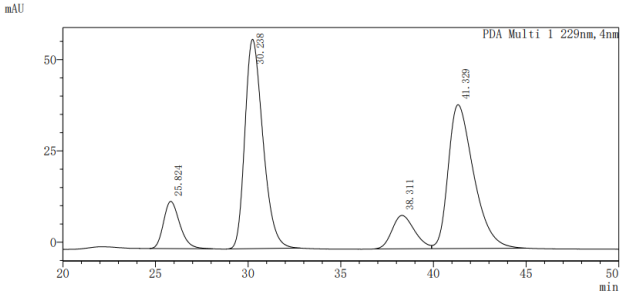
Ethyl (*S*)-2-((*R*)-3-((4-bromophenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3p)



3p: 55.8 mg, 52% yield, > 99% ee_1, > 99% ee_2, 85:15 dr, yellow solid.

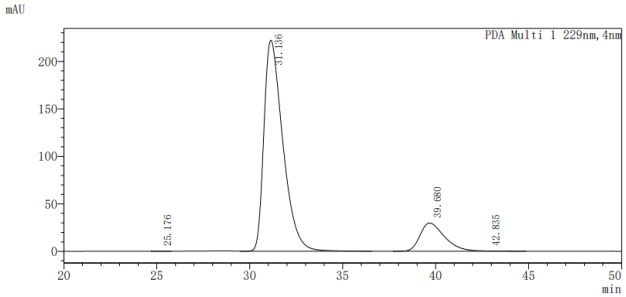
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.45–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.05–7.03 (m, 2H), 7.00–6.98 (m, 2H), 5.67 (d, *J* = 9.2 Hz, 1H), 4.28 (d, *J* = 8.8 Hz, 1H), 4.16–4.01 (m, 3H), 3.81 (d, *J* = 15.2 Hz, 1H), 2.32 (s, 3H), 2.03 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.6, 170.7, 139.9, 138.1, 135.5, 132.0, 129.4, 129.1, 128.0, 127.1, 64.1, 60.9, 60.3, 49.3, 34.7, 26.5, 22.8, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for [$C_{25}H_{32}BrNO_5S$+H^+: M+H]$^+$: 538.1257, found: 538.1271. $[\alpha]_D^{25}$ = –11.5 (c = 0.16, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 229 nm, t_1(major) = 31.1 min, t_1(minor) = 42.8 min, ee = > 99%; t_2(major) = 39.7 min, t_2(minor) = 25.2 min, ee = > 99%.



PDA Ch1 229nm

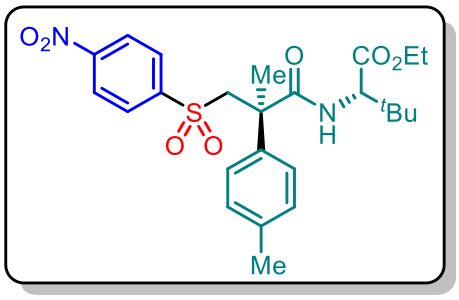
Peak	Ret. Time	Area	Area%
1	25.824	789340	8.573
2	30.238	3873609	42.071
3	38.311	770717	8.371
4	41.329	3773706	40.986



PDA Ch1 229nm

Peak	Ret. Time	Area	Area%
1	25.176	916	0.005
2	31.136	15714495	85.104
3	39.680	2736198	14.818
4	42.835	13350	0.072

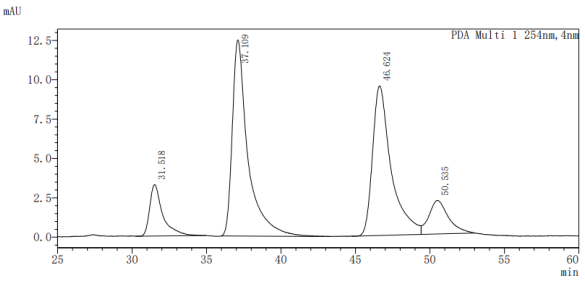
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-3-((4-nitrophenyl)sulfonyl)-2-(*p*-tolyl)propanamido)butanoate (3q)



3q: 33.3 mg, 33% yield, > 99% ee_1, > 99% ee_2, 83:17 dr, yellow oil.

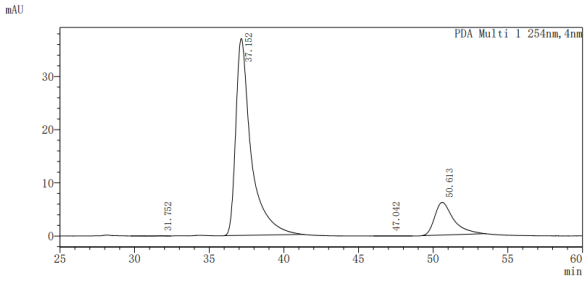
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.14–8.10 (m, 2H), 7.70–7.65 (m, 2H), 7.05–7.02 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.65 (d, *J* = 8.8 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 4.18–4.02 (m, 3H), 3.90 (d, *J* = 15.2 Hz, 1H), 2.27 (s, 3H), 2.05 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.4, 170.6, 150.0, 146.2, 138.5, 135.3, 129.4, 129.0, 127.2, 123.8, 64.4, 61.0, 60.3, 49.3, 34.7, 26.5, 22.9, 20.9, 14.1. **HRMS** (ESI) m/z Calcd for [$C_{25}H_{32}N_2O_7S$+H^+: M+H]$^+$: 505.2003, found: 505.2011. $[\alpha]_D^{25}$ = +9.6 (c = 0.20, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 254 nm, t_1(major) = 37.2 min, t_1(minor) = 47.0 min, ee = > 99%; t_2(major) = 50.6 min, t_2(minor) = 31.8 min, ee = > 99%.



PDA Ch1 254nm

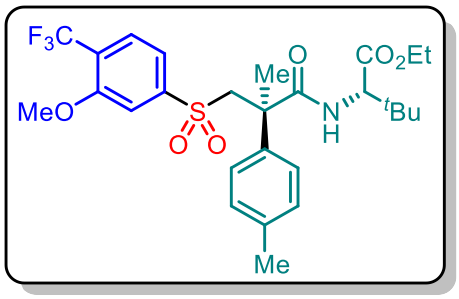
Peak	Ret.Time	Area	Area%
1	31.518	199471	9.353
2	37.109	909666	42.654
3	46.624	828039	38.827
4	50.535	195476	9.166



PDA Ch1 254nm

Peak	Ret.Time	Area	Area%
1	31.752	139	0.004
2	37.152	2647046	82.979
3	47.042	963	0.030
4	50.613	541879	16.987

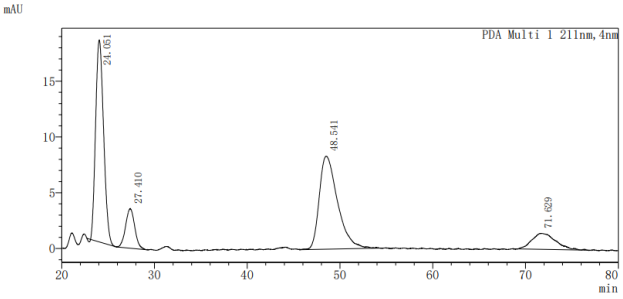
Ethyl (*S*)-2-((*R*)-3-((3-methoxy-4-(trifluoromethyl)phenyl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3r)



3r: 66.8 mg, 60% yield, > 99% ee_1, > 99% ee_2, 81:19 dr, yellow oil.

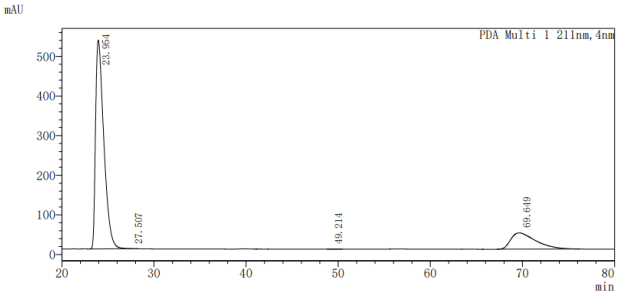
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.73–7.69 (m, 1H), 7.65–7.61 (m, 1H), 7.07–7.05 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.64 (d, *J* = 8.8 Hz, 1H), 4.27 (d, *J* = 9.2 Hz, 1H), 4.17–4.02 (m, 3H), 3.94 (s, 3H), 3.85 (d, *J* = 15.2 Hz, 1H), 2.27 (s, 3H), 2.04 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.6, 160.8, 138.0, 135.4, 133.4, 132.6, 129.5, 127.4 (*J* = 5.3 Hz), 127.1, 122.5 (*J* = 271.2 Hz), 119.1 (*J* = 31.9 Hz), 111.8, 64.1, 60.9, 60.3, 56.5, 49.4, 34.7, 26.4, 22.9, 20.9, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{27}H_{34}F_3NO_6S+H^+]$: M+H]$^+$: 558.2132, found: 558.2144. $[\alpha]_D^{25}$ = +3.1 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 94/6, flow rate = 0.8 mL/min, λ = 211 nm, t_1(major) = 24.0 min, t_1(minor) = 49.2 min, ee = > 99%; t_2(major) = 69.6 min, t_2(minor) = 27.5 min, ee = > 99%.



PDA Ch1 211nm

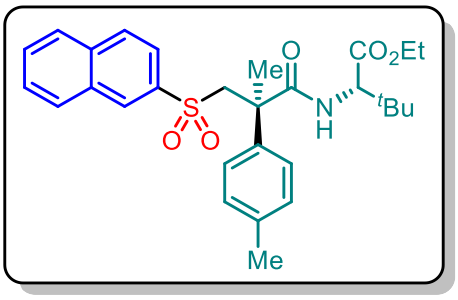
Peak	Ret. Time	Area	Area%
1	24.051	1084193	39.723
2	27.410	244059	8.942
3	48.541	1144021	41.915
4	71.629	257095	9.420



PDA Ch1 211nm

Peak	Ret. Time	Area	Area%
1	23.954	32819487	80.828
2	27.507	828	0.002
3	49.214	1783	0.004
4	69.649	7782213	19.166

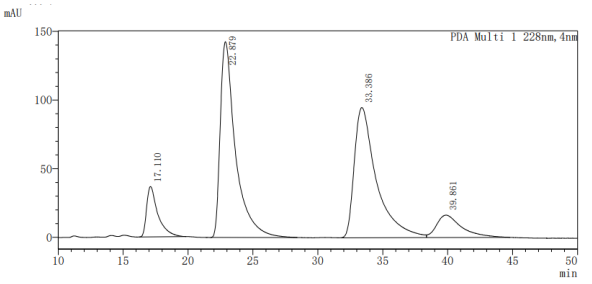
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-3-(naphthalen-2-ylsulfonyl)-2-(*p*-tolyl)propanamido)butanoate (3s)



3s: 66.2 mg, 65% yield, > 99% ee_1, 98% ee_2, 83:17 dr, yellow solid.

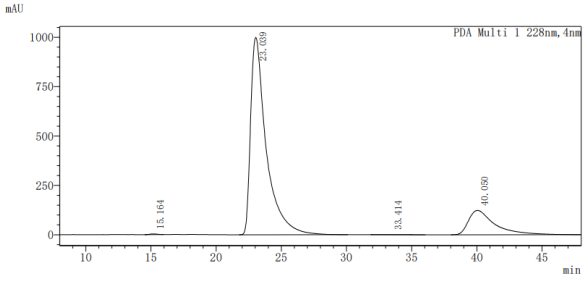
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.94 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.81–7.76 (m, 2H), 7.63–7.55 (m, 3H), 7.03 (d, *J* = 10.8 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 5.65 (d, *J* = 9.2 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 4.19–4.00 (m, 3H), 3.94 (d, *J* = 15.2 Hz, 1H), 2.08 (s, 3H), 1.97 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.85 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.9, 170.6, 137.9, 137.6, 135.3, 134.8, 131.9, 129.4, 129.2, 129.1, 128.9, 127.8, 127.3, 127.1, 122.3, 63.6, 60.9, 60.3, 49.4, 34.7, 26.5, 23.0, 20.7, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{29}H_{35}NO_5S+H^+$: M+H$]^+$: 510.2309, found: 510.2323. $[\alpha]_D^{25}$ = +29.4 (c = 0.16, $CHCl_3$).

HPLC analysis: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 228 nm, t_1(major) = 23.0 min, t_1(minor) = 33.4 min, ee = > 99%; t_2(major) = 40.1 min, t_2(minor) = 15.2 min, ee = 98%.



PDA Ch1 228nm

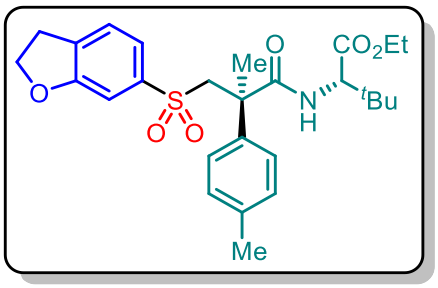
Peak	Ret.Time	Area	Area%
1	17.110	2210988	8.087
2	22.879	11666134	42.673
3	33.386	11257686	41.178
4	39.861	2203952	8.062



PDA Ch1 228nm

Peak	Ret.Time	Area	Area%
1	15.164	138112	0.137
2	23.039	83357524	82.657
3	33.414	18209	0.018
4	40.050	17333542	17.188

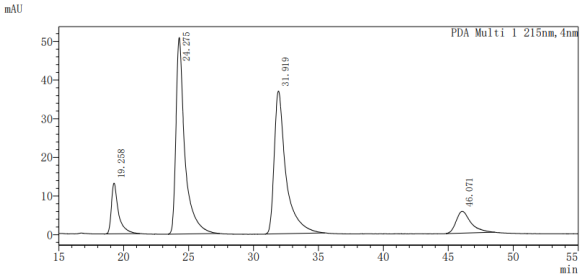
Ethyl (*S*)-2-((*R*)-3-((2,3-dihydrobenzofuran-6-yl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3t)



3t: 55.1 mg, 55% yield, > 99% ee_1, 97% ee_2, 84:16 dr, yellow solid.

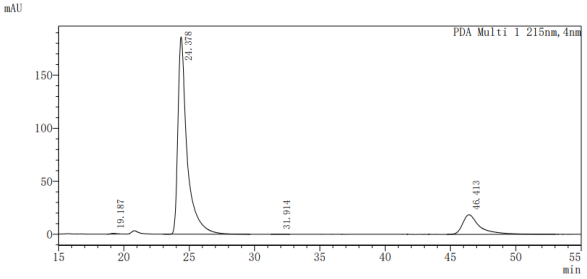
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43–7.38 (m, 1H), 7.35 (s, 1H), 7.31 (s, 1H), 7.14–7.10 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.73 (d, *J* = 8.8 Hz, 1H), 4.63 (t, *J* = 8.8 Hz, 2H), 4.29 (d, *J* = 8.8 Hz, 1H), 4.18–4.02 (m, 3H), 3.74 (d, *J* = 14.8 Hz, 1H), 3.20–3.07 (m, 2H), 2.31 (s, 3H), 2.03 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.7, 170.7, 164.1, 137.5, 136.3, 132.9, 129.3, 129.2, 128.0, 127.0, 124.9, 109.3, 72.3, 64.1, 60.9, 60.4, 49.4, 34.7, 28.9, 26.5, 22.8, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{27}H_{35}NO_6S+H^+]$: M+H]$^+$: 502.2258, found: 502.2267. $[\alpha]_D^{25}$ = –1.5 (c = 0.20, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 215 nm, t_1(major) = 24.4 min, t_1(minor) = 31.9 min, ee = > 99%; t_2(major) = 46.4 min, t_2(minor) = 19.2 min, ee = 97%.



PDA Ch1 215nm

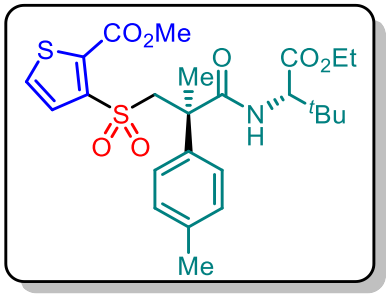
Peak	Ret. Time	Area	Area%
1	19.258	495920	8.746
2	24.275	2419919	42.677
3	31.919	2309672	40.733
4	46.071	444789	7.844



PDA Ch1 215nm

Peak	Ret. Time	Area	Area%
1	19.187	22317	0.206
2	24.378	9101286	84.189
3	31.914	631	0.006
4	46.413	1686274	15.598

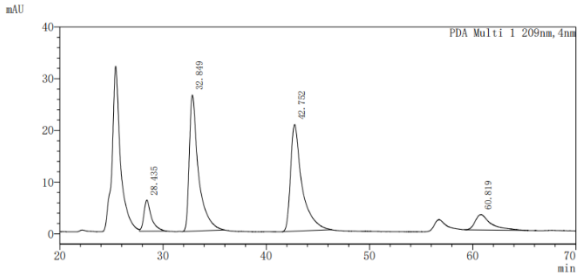
Methyl 3-(((*R*)-3-(((*S*)-1-ethoxy-3,3-dimethyl-1-oxobutan-2-yl)amino)-2-methyl-3-oxo-2-(*p*-tolyl)propyl)sulfonyl)thiophene-2-carboxylate (3u)



3u: 40.8 mg, 39% yield, 97% ee_1, 64% ee_2, 89:11 dr, yellow oil.

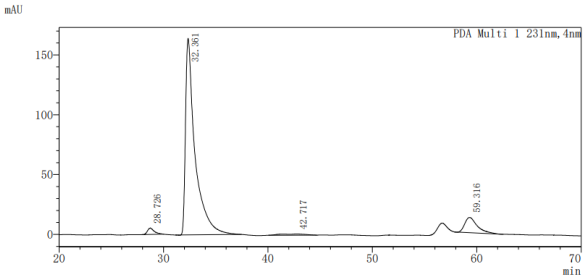
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.22 (d, *J* = 5.2 Hz, 1H), 7.14–7.05 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.62 (d, *J* = 9.2 Hz, 1H), 4.70 (d, *J* = 15.2 Hz, 1H), 4.31–4.22 (m, 2H), 4.17–4.01 (m, 2H), 3.92 (s, 3H), 2.27 (s, 3H), 2.03 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.85 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.9, 170.7, 159.9, 144.9, 137.8, 135.5, 133.5, 131.2, 129.2, 128.9, 127.3, 62.7, 60.9, 60.2, 53.0, 49.5, 34.8, 26.5, 23.3, 21.0, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{33}NO_7S_2+H^+$: M+H$]^+$: 524.1771, found: 524.1775. $[\alpha]_D^{25}$ = –1.6 (c = 0.20, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.8 mL/min, n, λ = 209 nm, t_1(major) = 32.4 min, t_1(minor) = 42.7 min, ee = 97%; t_2(major) = 59.3 min, t_2(minor) = 28.7 min, ee = 64%.



PDA Ch1 209nm

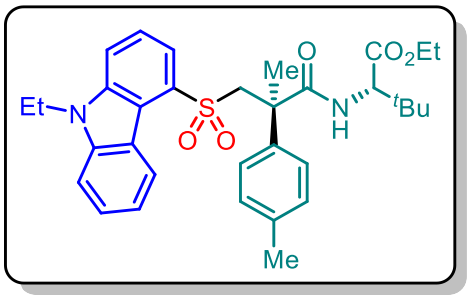
Peak	Ret.Time	Area	Area%
1	28.435	305103	7.945
2	32.849	1628991	42.418
3	42.752	1590536	41.417
4	60.819	315680	8.220



PDA Ch1 231nm

Peak	Ret.Time	Area	Area%
1	28.726	236084	1.984
2	32.361	10435328	87.688
3	42.717	163700	1.376
4	59.316	1065434	8.953

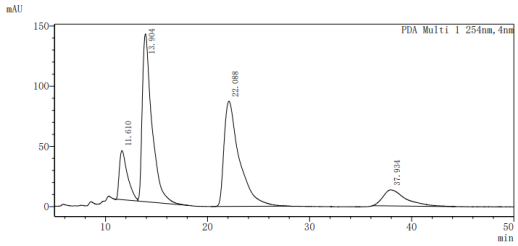
Ethyl (*S*)-2-((*R*)-3-((9-ethyl-9H-carbazol-4-yl)sulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3v)



3v: 43.8 mg, 38% yield, > 99% ee_1, 96% ee_2, 80:20 dr, brown oil.

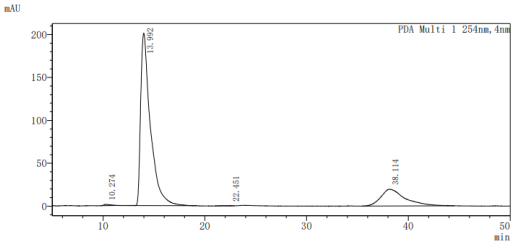
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.09 (d, *J* = 1.2 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.73–7.69 (m, 1H), 7.55–7.51 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33–7.29 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.64 (d, *J* = 8.8 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.26 (d, *J* = 9.2 Hz, 1H), 4.18–4.09 (m, 2H), 4.06–3.98 (m, 2H), 3.93 (d, *J* = 14.8 Hz, 1H), 2.07 (s, 3H), 1.73 (s, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 175.1, 170.7, 141.8, 140.6, 137.6, 135.5, 130.5, 129.0, 126.9, 126.8, 124.6, 122.5, 122.5, 121.4, 121.0, 120.2, 109.0, 108.3, 64.1, 60.8, 60.3, 49.4, 37.8, 34.7, 26.5, 23.0, 20.4, 14.0, 13.7. **HRMS** (ESI) m/z Calcd for $[C_{33}H_{40}N_2O_5S+H^+$: M+H$]^+$: 577.2731, found: 577.2746. $[\alpha]_D^{25}$ = +35.4 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel IA column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 254 nm, t_1(major) = 14.0 min, t_1(minor) = 22.5 min, ee = > 99%; t_2(major) = 38.1 min, t_2(minor) = 10.3 min, ee = 96%.



PDA Ch1 254nm

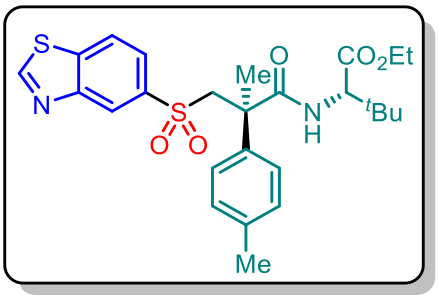
Peak	Ret. Time	Area	Area%
1	11.610	2270076	10.031
2	13.904	9179764	40.564
3	22.088	9094445	40.187
4	37.934	2085778	9.217



PDA Ch1 254nm

Peak	Ret. Time	Area	Area%
1	10.274	66720	0.399
2	13.992	13405605	80.153
3	22.451	15329	0.092
4	38.114	3237301	19.356

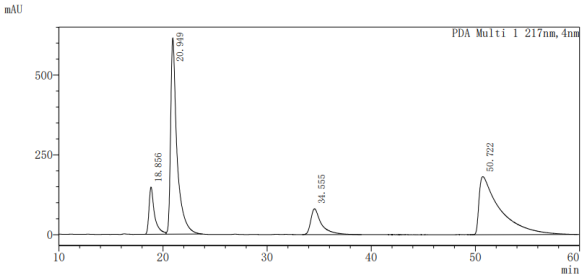
Ethyl (*S*)-2-((*R*)-3-(benzo[d]thiazol-5-ylsulfonyl)-2-methyl-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3w)



3w: 61.9 mg, 60% yield, > 99% ee_1, > 99% ee_2, 81:19 dr, yellow solid.

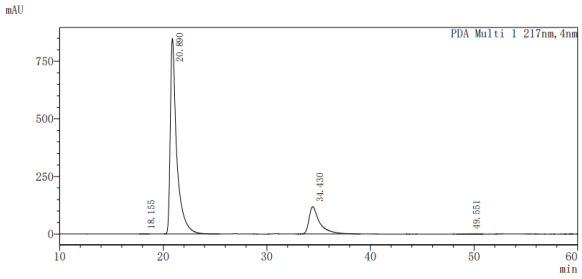
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.11 (s, 1H), 8.22 (s, 1H), 7.95–7.91 (m, 1H), 7.69–7.64 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.61 (d, *J* = 9.2 Hz, 1H), 4.27 (d, *J* = 9.2 Hz, 1H), 4.20–4.01 (m, 3H), 3.93 (d, *J* = 15.2 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.85 (s, 9H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm) = 174.7, 170.6, 156.1, 152.6, 139.3, 138.5, 137.9, 135.4, 129.2, 129.1, 127.1, 123.7, 122.5, 64.1, 60.9, 60.3, 49.4, 34.7, 26.5, 23.1, 20.8, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{32}N_2O_5S_2, M+Na]^+$: 517.1825, found: 517.1837. $[\alpha]_D^{25}$ = +15.5 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 217 nm, t_1(major) = 20.9 min, t_1(minor) = 49.6 min, ee = > 99%; t_2(major) = 34.6 min, t_2(minor) = 18.9 min, ee = > 99%.



PDA Ch1 217nm

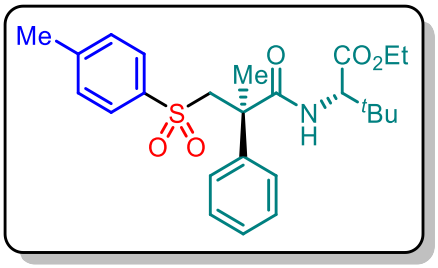
Peak	Ret.Time	Area	Area%
1	18.856	5458537	8.694
2	20.949	26112563	41.589
3	34.555	5712326	9.098
4	50.722	25504135	40.620



PDA Ch1 217nm

Peak	Ret.Time	Area	Area%
1	18.155	5928	0.013
2	20.890	36622338	81.165
3	34.430	8488571	18.813
4	49.551	4071	0.009

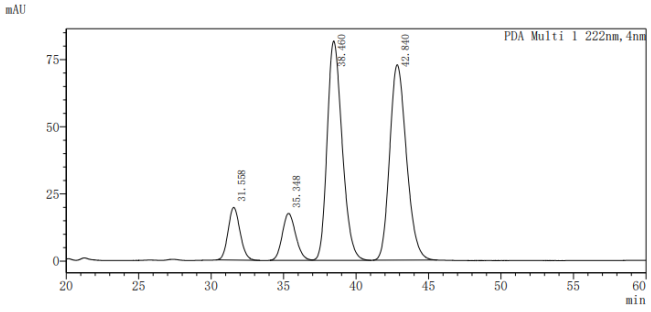
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-phenyl-3-tosylpropanamido)butanoate (3x)



3x: 51.4 mg, 56% yield, > 99% ee_1, > 99% ee_2, 86:14 dr, yellow solid.

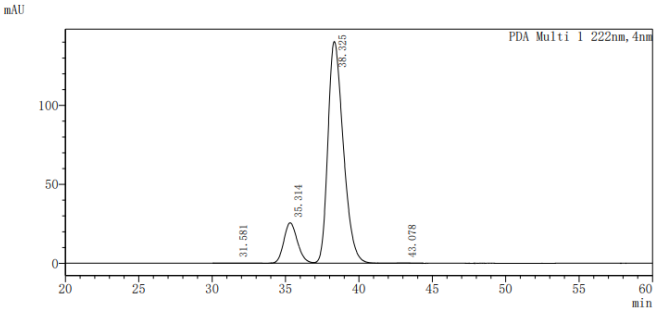
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.53–7.47 (m, 2H), 7.25 (s, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.73 (d, *J* = 9.2 Hz, 1H), 4.29 (d, *J* = 9.2 Hz, 1H), 4.18–4.02 (m, 3H), 3.75 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 2.07 (s, 3H), 1.17 (t, *J* = 6.8 Hz, 3H), 0.88 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.4, 171.0, 144.0, 139.5 138.3, 129.5, 128.8, 127.9, 127.5, 127.0, 63.9, 61.1, 60.4, 49.8, 34.7, 26.5, 22.8, 21.5, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{33}NO_5S+H^+$: M+H$]^+$: 460.2152, found: 460.2164. $[\alpha]_D^{25}$ = +1.8 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel IG column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 222 nm, t_1(major) = 38.3 min, t_1(minor) = 43.1 min, ee = > 99%; t_2(major) = 35.3min, t_2(minor) = 31.6 min, ee = > 99%.



PDA Ch1 222nm

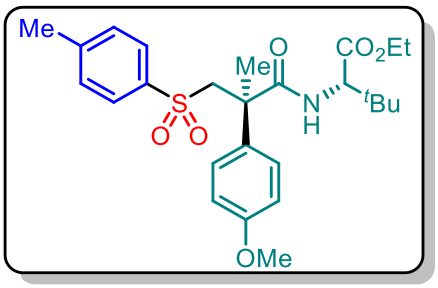
Peak	Ret.Time	Area	Area%
1	31.558	1125635	8.056
2	35.348	1122835	8.036
3	38.460	5868830	42.004
4	42.840	5854637	41.903



PDA Ch1 222nm

Peak	Ret.Time	Area	Area%
1	31.581	164	0.001
2	35.314	1647380	13.869
3	38.325	10224266	86.075
4	43.078	6460	0.054

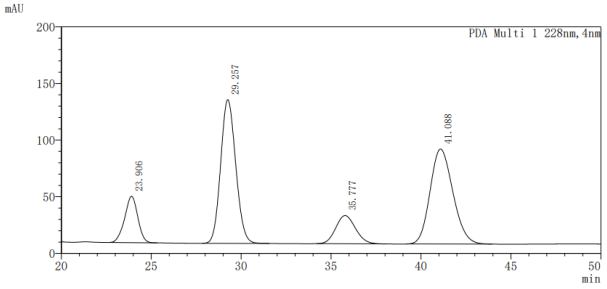
Ethyl (*S*)-2-((*R*)-2-(4-methoxyphenyl)-2-methyl-3-tosylpropanamido)-3,3-dimethylbutanoate (3y)



3y: 76.3 mg, 78% yield, > 99% ee_1, 99% ee_2, 81:19 dr, yellow oil.

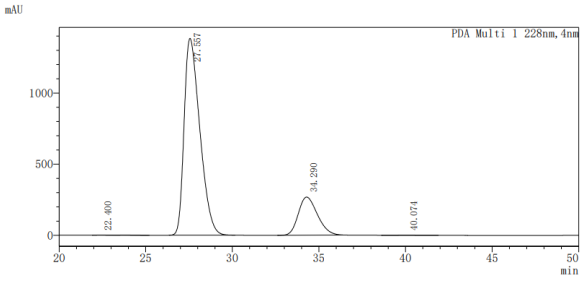
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47 (d, *J* = 8.0 Hz, 2H), 7.16–7.12 (m, 4H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.75 (d, *J* = 9.2 Hz, 1H), 4.28 (d, *J* = 9.2 Hz, 1H), 4.16–4.00 (m, 3H), 3.86–3.74 (m, 4H), 2.38 (s, 3H), 2.03 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.8, 170.7, 159.1, 143.8, 138.3, 130.9, 129.4, 128.3, 127.5, 114.0, 64.0, 60.9, 60.4, 55.2, 49.1, 34.7, 26.5, 23.1, 21.5, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{35}NO_6S+H^+$: $M+H]^+$: 490.2258, found: 490.2271. $[\alpha]_D^{25}$ = +2.3 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 228 nm, t_1(major) = 27.6 min, t_1(minor) = 40.1 min, ee = > 99%; t_2(major) = 34.3 min, t_2(minor) = 22.4 min, ee = 99%.



PDA Ch1 228nm

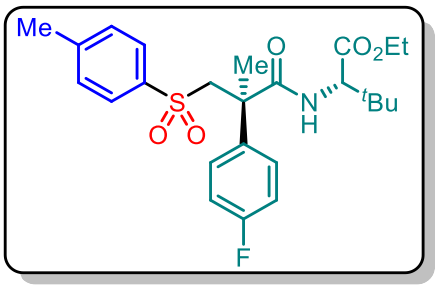
Peak	Ret. Time	Area	Area%
1	23.906	2077339	11.053
2	29.257	7405726	39.403
3	35.777	1902921	10.125
4	41.088	7408633	39.419



PDA Ch1 228nm

Peak	Ret. Time	Area	Area%
1	22.400	152559	0.142
2	27.557	87083321	80.782
3	34.290	20504279	19.021
4	40.074	59775	0.055

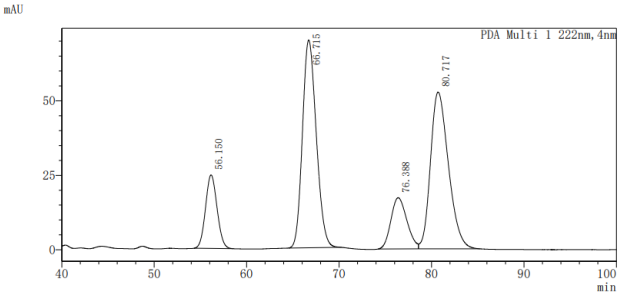
Ethyl (*S*)-2-((*R*)-2-(4-fluorophenyl)-2-methyl-3-tosylpropanamido)-3,3-dimethylbutanoate (3z)



3z: 48.7 mg, 51% yield, 99% ee_1, > 99% ee_2, 82:18 dr, yellow oil.

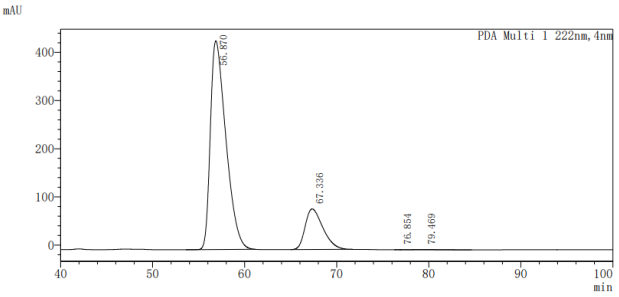
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50 (d, *J* = 8.4 Hz, 2H), 7.25–7.16 (m, 4H), 6.95–6.90 (m, 2H), 5.72 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 9.2 Hz, 1H), 4.19–4.02 (m, 3H), 3.74 (d, *J* = 14.8 Hz, 1H), 2.39 (s, 3H), 2.06 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 174.2, 170.7, 162.3 (*J* = 162.3 Hz), 144.2, 138.2, 135.1, 129.6, 128.9 (*J* = 8.2 Hz), 127.5, 115.6 (*J* = 21.4 Hz), 63.9, 61.0, 60.4, 49.2, 34.7, 26.5, 23.0, 21.5, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{32}FNO_5S+H^+$: M+H$]^+$: 478.2058, found: 478.2073. $[\alpha]_D^{25}$ = +3.5 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 88/12, flow rate = 0.8 mL/min, λ = 222 nm, t_1(major) = 67.3 min, t_1(minor) = 79.5 min, ee = 99%; t_2(major) = 56.8 min, t_2(minor) = 76.9 min, ee = > 99%.



PDA Ch1 222nm

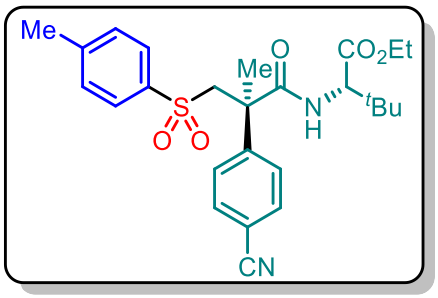
Peak	Ret. Time	Area	Area%
1	56.150	2142819	11.541
2	66.715	7246190	39.027
3	76.388	2068181	11.139
4	80.717	7109876	38.293



PDA Ch1 222nm

Peak	Ret. Time	Area	Area%
1	56.870	50813479	81.718
2	67.336	11284011	18.147
3	76.854	355	0.001
4	79.469	83557	0.134

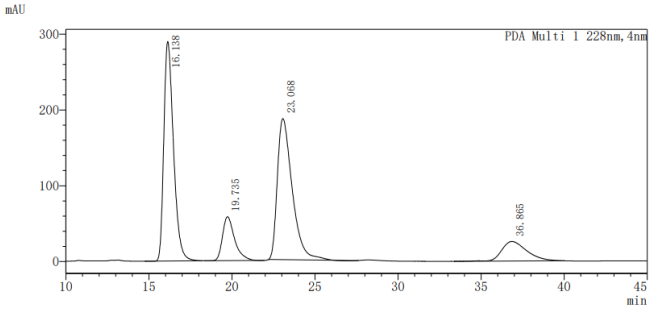
Ethyl (*S*)-2-((*R*)-2-(4-cyanophenyl)-2-methyl-3-tosylpropanamido)-3,3-dimethylbutanoate (3aa)



3aa: 33.9 mg, 35% yield, > 99% ee_1, 98% ee_2, 81:19 dr, yellow oil.

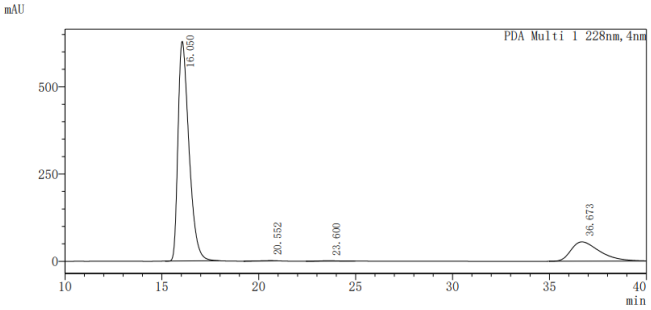
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.49–7.42 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.67 (d, *J* = 8.8 Hz, 1H), 4.24 (d, *J* = 8.8 Hz, 1H), 4.16–3.88 (m, 3H), 3.66 (d, *J* = 14.8 Hz, 1H), 2.34 (s, 3H), 2.02 (s, 3H), 1.12 (t, *J* = 6.8 Hz, 3H), 0.84 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 172.9, 170.7, 144.9, 144.6, 138.0, 132.4, 129.7, 127.9, 127.5, 118.2, 112.0, 63.6, 61.2, 60.5, 49.9, 34.8, 26.5, 22.4, 21.6, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{32}N_2O_5S+H^+$: M+H$]^+$: 485.2105, found: 485.2119. $[\alpha]_D^{25}$ = –1.5 (c = 0.16, $CHCl_3$).

HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 228 nm, t_1(major) = 16.1 min, t_1(minor) = 23.6 min, ee = > 99%; t_2(major) = 36.7 min, t_2(minor) = 20.6 min, ee = 98%.



PDA Ch1 228nm

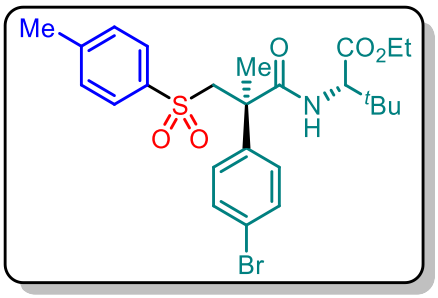
Peak	Ret.Time	Area	Area%
1	16.138	11729290	40.557
2	19.735	2936060	10.152
3	23.068	11548033	39.930
4	36.865	2707436	9.362



PDA Ch1 228nm

Peak	Ret.Time	Area	Area%
1	16.050	24747521	80.840
2	20.552	45757	0.149
3	23.600	77643	0.254
4	36.673	5742031	18.757

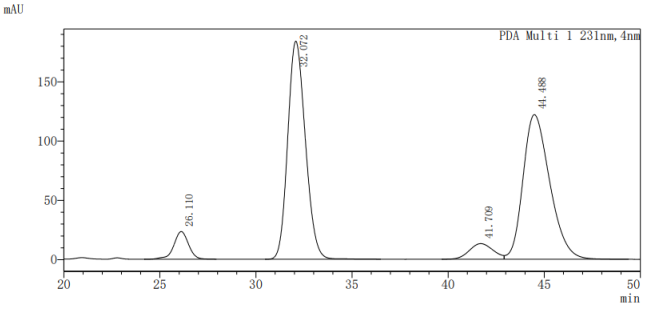
Ethyl (*S*)-2-((*R*)-2-(4-bromophenyl)-2-methyl-3-tosylpropanamido)-3,3-dimethylbutanoate (3ab)



3ab: 66.9 mg, 62% yield, > 99% ee_1, 99% ee_2, 85:15 dr, yellow oil.

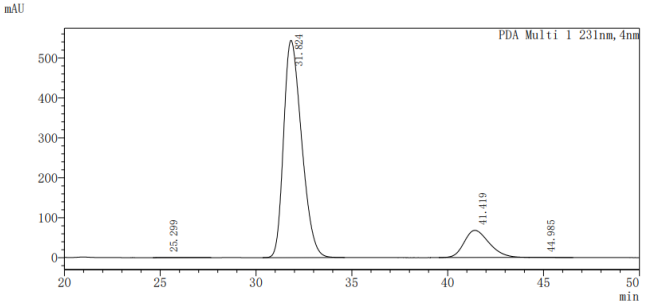
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.69 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 9.2 Hz, 1H), 4.19–3.95 (m, 3H), 3.77 (d, *J* = 15.2 Hz, 1H), 2.41 (s, 3H), 2.04 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 173.9, 170.6, 144.2, 138.1, 137.9, 131.7, 129.6, 128.9, 127.4, 122.4, 63.7, 61.0, 60.4, 49.3, 34.8, 26.5, 22.7, 21.6, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{32}Br^{81}NO_5S+H^+$: M+H$]^+$: 540.1237, found: 540.1243. $[\alpha]_D^{25}$ = –2.3 (c = 0.24, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 231 nm, t_1(major) = 31.8 min, t_1(minor) = 45.0 min, ee = > 99%; t_2(major) = 41.4 min, t_2(minor) = 25.3 min, ee = 99%.



PDA Ch1 231nm

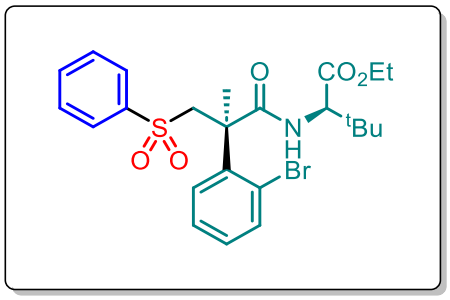
Peak	Ret. Time	Area	Area%
1	26.110	1238614	4.771
2	32.072	11764237	45.313
3	41.709	1133324	4.365
4	44.488	11826197	45.551



PDA Ch1 231nm

Peak	Ret. Time	Area	Area%
1	25.299	34679	0.083
2	31.824	35546340	85.108
3	41.419	6172872	14.780
4	44.985	12059	0.029

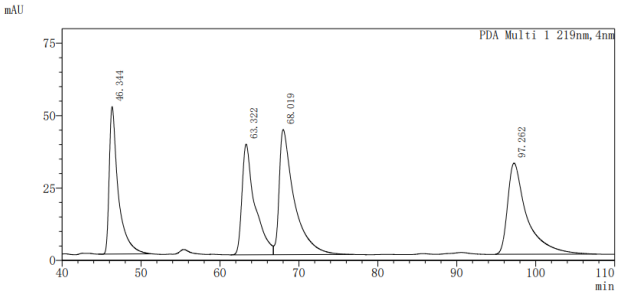
Ethyl (R)-2-((R)-2-(2-bromophenyl)-2-methyl-3-tosylpropanamido)-3,3-dimethylbutanoate (3ac)



3ac: 82.7 mg, 77% yield, > 99% ee_1, > 99% ee_2, 64:36 dr, yellow oil.

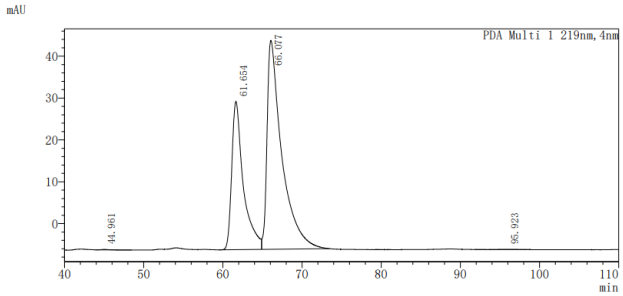
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.45–7.41 (m, 1H), 7.3–7.34 (m, 2H), 7.31–7.25 (m, 1H), 7.17–7.13 (m, 1H), 7.11–7.07 (m, 2H), 5.58 (d, *J* = 8.8 Hz, 1H), 4.62 (d, *J* = 15.6 Hz, 1H), 4.37 (d, *J* = 9.2 Hz, 1H), 4.19–3.99 (m, 2H), 3.85 (d, *J* = 15.6 Hz, 1H), 2.35 (s, 3H), 2.13 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.85 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 170.4, 143.8, 137.4, 136.6, 134.5, 131.1, 130.1, 129.3, 128.0, 127.4, 124.8, 61.2, 61.0, 60.1, 59.0, 50.5, 35.3, 26.4, 21.5, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{32}NO_5S+H^+$: M+H$]^+$: 540.1237, found: 540.1245 $[\alpha]_D^{25}$ = -3.5 (c= 0.28, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.8 mL·min^{-1}, n, λ = 219 nm, t_1(major) = 66.1 min, t_1(minor) = 95.9 min, ee = >99%; t_2(major) = 61.7 min, t_2(minor) = 45.0 min, ee = > 99%.



PDA Ch1 219nm

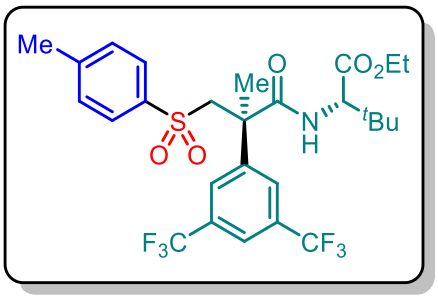
Peak	Ret. Time	Area	Area%
1	46.344	4052750	20.821
2	63.322	4345088	22.323
3	68.019	5711183	29.341
4	97.262	5355907	27.516



PDA Ch1 219nm

Peak	Ret. Time	Area	Area%
1	44.961	6279	0.062
2	61.654	3599254	35.738
3	66.077	6460109	64.144
4	95.923	5649	0.056

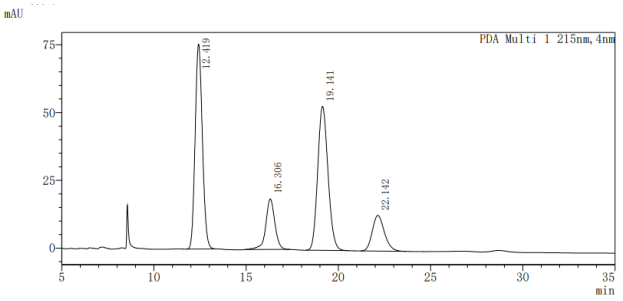
Ethyl (*S*)-2-((*R*)-2-(3,5-bis(trifluoromethyl)phenyl)-2-methyl-3-tosylpropanamido)-3,3-dimethylbutanoate (3ad)



3ad: 76.2 mg, 64% yield, 98% ee_1, 99% ee_2, 79:21 dr, yellow solid.

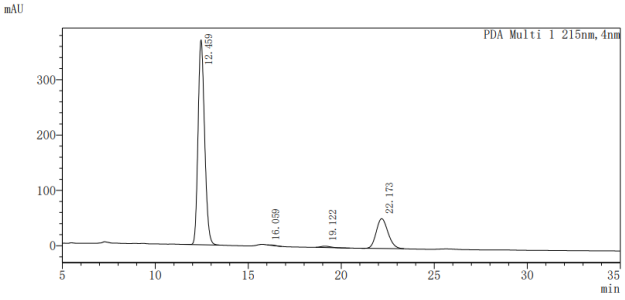
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.72–7.67 (m, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.79 (d, *J* = 8.8 Hz, 1H), 4.36 (d, *J* = 9.2, 1H), 4.25–4.03 (m, 3H), 3.82 (d, *J* = 14.8 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.94 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 172.6, 170.8, 144.7, 142.4, 137.5, 132.0 (*J* = 33.5 Hz), 129.8, 127.4, 122.9 (*J* = 273.0 Hz), 121.6, 63.5, 61.2, 60.6, 49.6, 34.8, 26.5, 22.4, 21.5, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{27}H_{31}F_6NO_5S+H^+$: M+H$]^+$: 596.1900, found: 496.1917. $[\alpha]_D^{25}$ = +7.3 (c = 0.16, $CHCl_3$).

HPLC analysis: Chiralcel IC column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 215 nm, t_1(major) = 12.5 min, t_1(minor) = 19.1 min, ee = 98%; t_2(major) = 22.1 min, t_2(minor) = 16.1 min, ee = 99%.



PDA Ch1 215nm

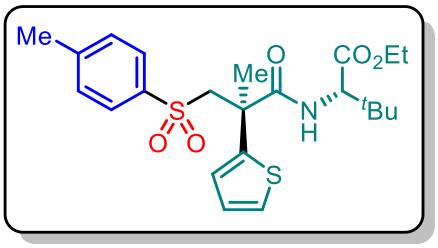
Peak	Ret. Time	Area	Area%
1	12.419	2056759	38.310
2	16.306	639299	11.908
3	19.141	2069785	38.552
4	22.142	602951	11.231



PDA Ch1 215nm

Peak	Ret. Time	Area	Area%
1	12.459	9093676	78.720
2	16.059	13346	0.116
3	19.122	87393	0.757
4	22.173	2357565	20.408

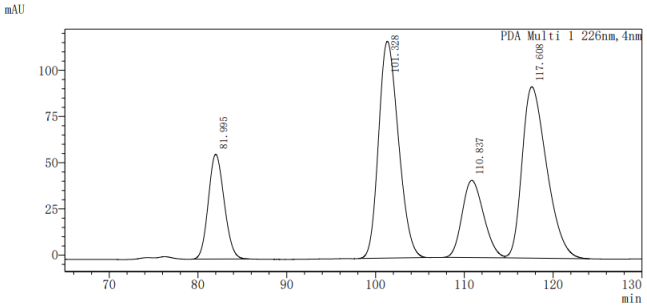
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(thiophen-2-yl)-3-tosylpropanamido)butanoate (3ae)



3ad: 65.1 mg, 70% yield, > 99% ee_1, > 99% ee_2, 72:28 dr, yellow oil.

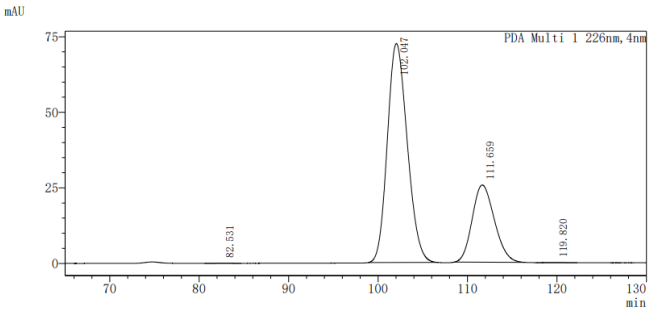
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 (d, *J* = 8.4 Hz, 2H), 7.26–7.24 (m, 3H), 7.03–6.98 (m, 1H), 6.95–6.92 (m, 1H), 6.17 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H), 4.23–4.06 (m, 3H), 3.67 (d, *J* = 14.4 Hz, 1H), 2.40 (s, 3H), 2.11 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 172.7, 170.8, 144.6, 144.3, 138.4, 129.7, 127.6, 127.2, 126.1, 125.8, 64.5, 61.0, 60.5, 48.0, 34.9, 26.5, 24.2, 21.6, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{23}H_{31}NO_5S_2+H^+$: $M+H]^+$: 466.1716, found: 466.1732. $[\alpha]_D^{25}$ = –6.8 (c = 0.25, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL/min, λ = 226 nm, t_1(major) = 102.0 min, t_1(minor) = 119.8 min, ee = > 99%; t_2(major) = 111.7 min, t_2(minor) = 82.5 min, ee = > 99%.



PDA Ch1 226nm

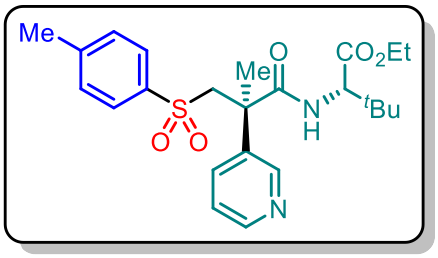
Peak	Ret.Time	Area	Area%
1	81.995	7037702	14.018
2	101.328	18239160	36.330
3	110.837	7037487	14.018
4	117.608	17889905	35.634



PDA Ch1 226nm

Peak	Ret.Time	Area	Area%
1	82.531	4475	0.029
2	102.047	11235114	71.779
3	111.659	4406891	28.155
4	119.820	5951	0.038

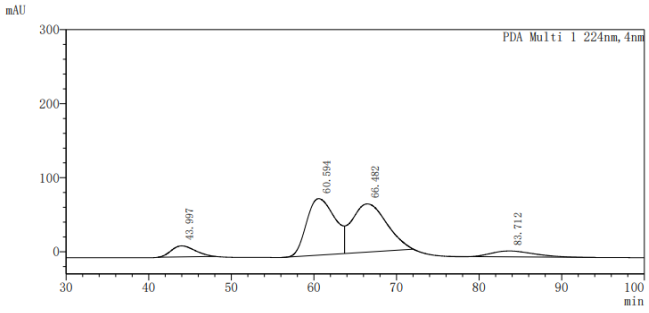
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(pyridin-3-yl)-3-tosylpropanamido)butanoate (3af)



3af: 44.2 mg, 48% yield, 97% ee_1, 99% ee_2, 80:20 dr, yellow oil.

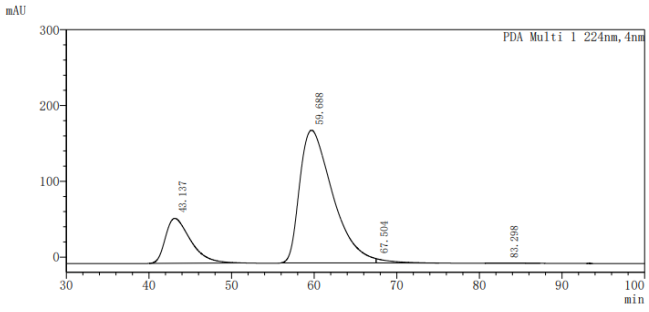
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.57 (s, 1H), 8.51 (s, 1H), 7.68–7.53 (m, 3H), 7.24–7.18 (m, 3H), 5.84 (d, *J* = 8.8 Hz, 1H), 4.35 (d, *J* = 8.0 Hz,1H), 4.21–4.01 (m, 3H), 3.71 (d, *J* = 14.8 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 173.0, 170.7, 149.1, 148.3, 144.5, 138.1, 135.6, 134.7, 129.8, 127.5, 123.3, 63.7, 61.1, 60.6, 48.4, 34.8, 26.6, 22.3, 21.6, 14.1. **HRMS** (ESI) m/z Calcd for $[C_{24}H_{32}N_2O_5S+H^+$: $M+H]^+$: 461.2105, found: 461.2109. $[\alpha]_D^{25}$ = +1.8 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 224 nm, t_1(major) = 59.7 min, t_1(minor) = 67.5 min, ee = 97%; t_2(major) = 84.7 min, t_2(minor) = 44.3 min, ee = 99%.



PDA Ch1 224nm

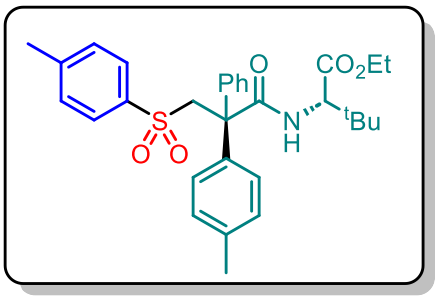
Peak	Ret. Time	Area	Area%
1	43.997	2981918	6.868
2	60.594	18332398	42.222
3	66.482	19257029	44.352
4	83.712	2847636	6.559



PDA Ch1 224nm

Peak	Ret. Time	Area	Area%
1	43.137	12554547	20.279
2	59.688	48625945	78.545
3	67.504	672780	1.087
4	83.298	54753	0.088

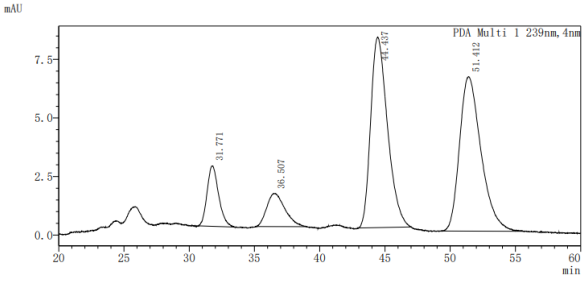
Ethyl (2S)-3,3-dimethyl-2-(2-phenyl-2-(p-tolyl)-3-tosylpropanamido)butanoate (3ag)



3ag: 40.7 mg, 38% yield, 99% ee_1, > 99% ee_2, 83:17 dr, yellow oil.

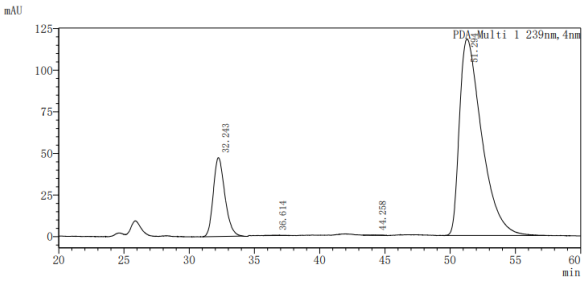
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 6H), 7.33 – 7.23 (m, 3H), 7.15 (s, 2H), 7.01 (s, 2H), 6.02 (s, 1H), 5.71 (s, 1H), 4.94 (s, 1H), 4.29 – 4.21 (m, 2H), 4.12 – 4.07 (m, 1H), 2.39 – 2.38 (m, 4H), 2.23 (s, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 168.0, 145.7, 144.4), 141.4, 138.3, 1356, 130.0, 129.6, 129.3, 128.0, 127.7, 127.2, 126.4, 61.2, 36.4, 28.8, 21.6, 21.4, 14.3. **HRMS** (ESI) m/z Calcd for $[C_{31}H_{37}NO_5S+H^+$: M+H$]^+$: 536.2466, found: 536.2469. $[\alpha]_D^{25}$ = –59.6 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel ID column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 239 nm, t_1(major) = 32.2 min, t_1(minor) = 36.6 min, ee_1 = 99%; t_2(minor) = 44.3 min, t_2(major) = 51.3 min, ee_2 = > 99%.



PDA Ch1 239nm

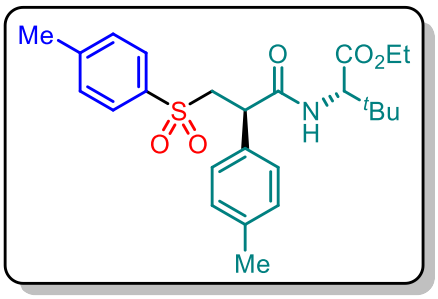
Peak	Ret. Time	Area	Area%
1	31.771	158557	8.888
2	36.507	137855	7.728
3	44.437	731238	40.991
4	51.412	756229	42.392



PDA Ch1 239nm

Peak	Ret. Time	Area	Area%
1	32.243	2930855	17.268
2	36.614	15183	0.089
3	44.258	12529	0.074
4	51.294	14014330	82.569

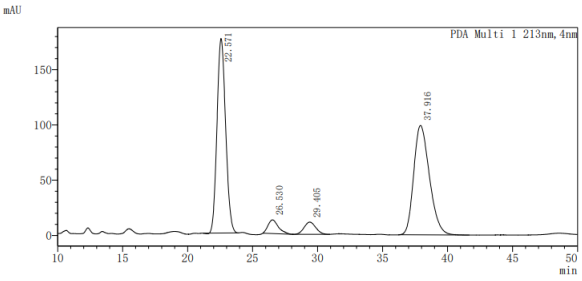
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-(*p*-tolyl)-3-tosylpropanamido)butanoate (3ah)



3ah: 72.6 mg, 79% yield, 97% ee_1, 98% ee_2, 91:9 dr, yellow oil.

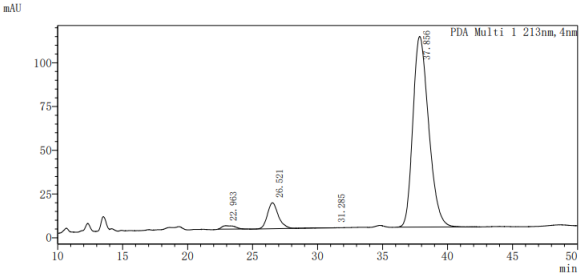
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (dd, *J* = 14.0, 8.4 Hz, 4H), 6.04 (d, *J* = 9.2 Hz, 1H), 4.26–4.16 (m, 4H), 4.03 (t, *J* = 6.4 Hz, 1H), 3.45–3.39 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.70 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.0, 169.7, 144.5, 137.8, 136.5, 134.3, 129.8, 129.6, 128.1, 127.6, 61.1, 59.8, 58.3, 47.0, 35.4, 26.3, 21.6, 21.1, 14.2. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{33}NO_5S+H^+]$: M+H]$^+$: 460.2152, found: 460.2156. $[\alpha]_D^{25}$ = –25.9 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 213 nm, t_1(minor) = 23.0 min, t_1(major) = 37.9 min, ee_1 = 97%; t_2(major) = 26.5 min, t_2(minor) = 31.3 min, ee_2 = 98%.



PDA Ch1 213nm

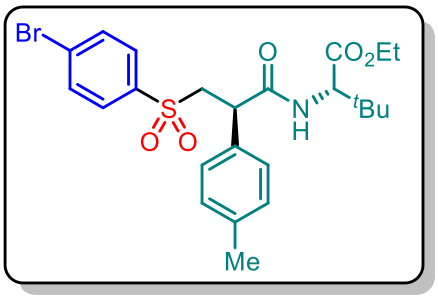
Peak	Ret.Time	Area	Area%
1	22.571	8146625	45.601
2	26.530	683748	3.827
3	29.405	691842	3.873
4	37.916	8342916	46.699



PDA Ch1 213nm

Peak	Ret.Time	Area	Area%
1	22.963	134154	1.316
2	26.521	861807	8.455
3	31.285	6489	0.064
4	37.856	9190151	90.165

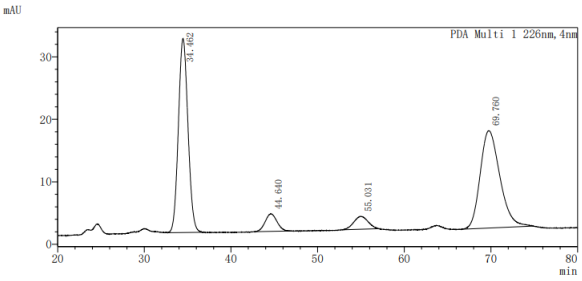
Ethyl (*S*)-2-((*R*)-3-((4-bromophenyl)sulfonyl)-2-(*p*-tolyl)propanamido)-3,3-dimethylbutanoate (3ai)



3ai: 69.0 mg, 66% yield, > 99% ee_1, > 99% ee_2, 89:11 dr, yellow oil.

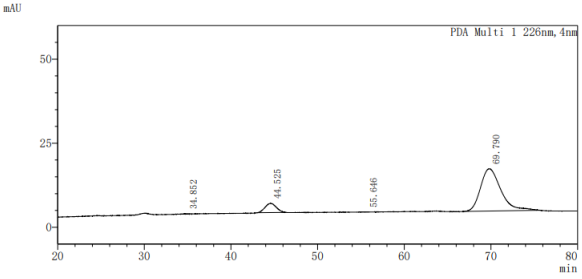
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56 (dd, *J* = 23.2, 8.4 Hz, 4H), 7.06 (s, 4H), 5.95 (d, *J* = 9.2 Hz, 1H), 4.25–4.16 (m, 4H), 4.02–3.99 (m, 1H), 3.46 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.31 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.69 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.1, 169.5, 138.4, 138.2, 133.7, 132.2, 129.9, 129.6, 128.8, 127.6, 61.3, 59.8, 58.3, 47.1, 35.3, 26.3, 21.1, 14.2. **HRMS** (ESI) m/z Calcd for $[C_{24}H_{30}BrNO_5S+H^+$: M+H$]^+$: 524.1101, found: 524.1102. $[\alpha]_D^{25}$ = –20.6 (c = 0.12, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 226 nm, t_1(minor) = 34.9 min, t_1(major) = 69.8 min, ee_1 = > 99%; t_2(major) = 44.3 min, t_2(minor) = 55.6 min, ee_2 = > 99%.



PDA Ch1 226nm

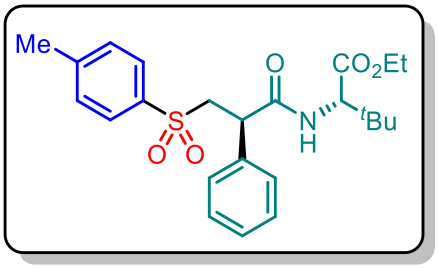
Peak	Ret. Time	Area	Area%
1	34.462	2387800	44.655
2	44.640	268252	5.017
3	55.031	235720	4.408
4	69.760	2455421	45.920



PDA Ch1 226nm

Peak	Ret. Time	Area	Area%
1	34.852	1174	0.051
2	44.525	248523	10.808
3	55.646	439	0.019
4	69.790	2049399	89.122

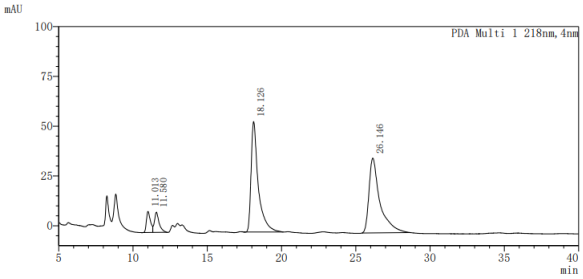
Ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-phenyl-3-tosylpropanamido)butanoate (3aj)



3aj: 49.0 mg, 55% yield, > 99% ee_1, > 99% ee_2, 90:10 dr, yellow oil.

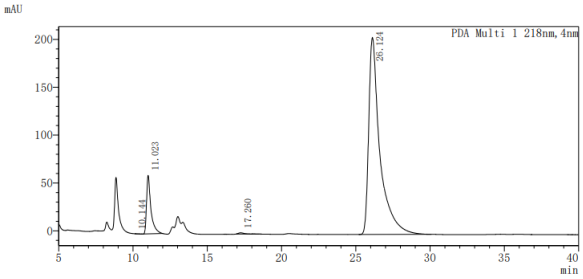
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 (d, *J* = 8.4 Hz, 2H), 7.28–7.21 (m, 7H), 5.99 (d, *J* = 9.6 Hz, 1H), 4.32– 4.14 (m, 4H), 4.07–4.04 (m, 1H), 3.44 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.68 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.0, 169.5, 144.6, 137.4, 136.4, 129.7, 129.2, 128.1, 127.8, 61.2, 59.8, 58.2, 47.4, 35.4, 26.2, 21.7, 14.2. **HRMS** (ESI) m/z Calcd for $[C_{24}H_{31}NO_5S+H^+$: M+H$]^+$: 446.1996, found: 446.2000. $[\alpha]_D^{25}$ = –27.2 (c = 0.18, $CHCl_3$).

HPLC analysis: Chiralcel AD-3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.8 mL/min, λ = 218 nm, t_1(minor) = 10.1 min, t_1(major) = 11.0 min, ee_1 = > 99%; t_2(minor) = 17.3 min, t_2(major) = 26.1 min, ee_2 = > 99%.



PDA Ch1 218nm

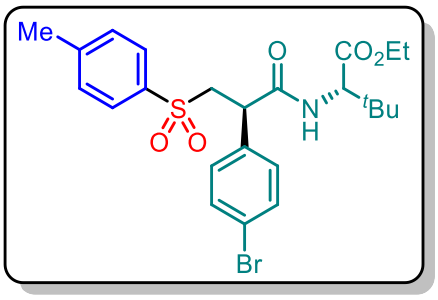
Peak	Ret. Time	Area	Area%
1	11.013	201696	4.790
2	11.580	222373	5.281
3	18.126	1867419	44.348
4	26.146	1919379	45.582



PDA Ch1 218nm

Peak	Ret. Time	Area	Area%
1	10.144	279	0.002
2	11.023	1234965	10.262
3	17.260	34766	0.289
4	26.124	10764441	89.447

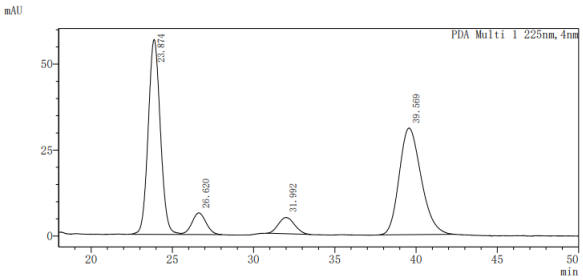
Ethyl (*S*)-2-((*R*)-2-(4-bromophenyl)-3-tosylpropanamido)-3,3-dimethylbutanoate (3ak)



3ak: 47.1 mg, 45% yield, 99% ee_1, > 99% ee_2, 89:11 dr, yellow oil.

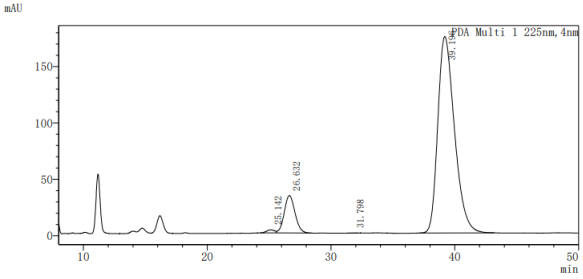
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.63 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.11 (d, *J* = 9.2 Hz, 1H), 4.32–4.03 (m, 5H), 3.45–3.32 (m, 1H), 2.42 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.72 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 171.0, 169.1, 144.8, 136.2, 132.2, 129.7, 129.5, 128.0, 122.2, 61.3, 59.9, 58.2, 46.8, 35.5, 26.3, 21.7, 14.2. **HRMS** (ESI) m/z Calcd for $[C_{24}H_{30}BrNO_5S+H^+]$: $M+H]^+$: 524.1101, found: 524.1100. $[\alpha]_D^{25}$ = –13.2 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel AZ-H column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_1(minor) = 25.1 min, t_1(major) = 39.2 min, ee_1 = 99%; t_2(major) = 26.6 min, t_2(minor) = 31.8 min, ee_2 = > 99%.



PDA Ch1 225nm

Peak	Ret. Time	Area	Area%
1	23.874	2946347	44.846
2	26.620	378798	5.766
3	31.992	327861	4.990
4	39.569	2916959	44.398

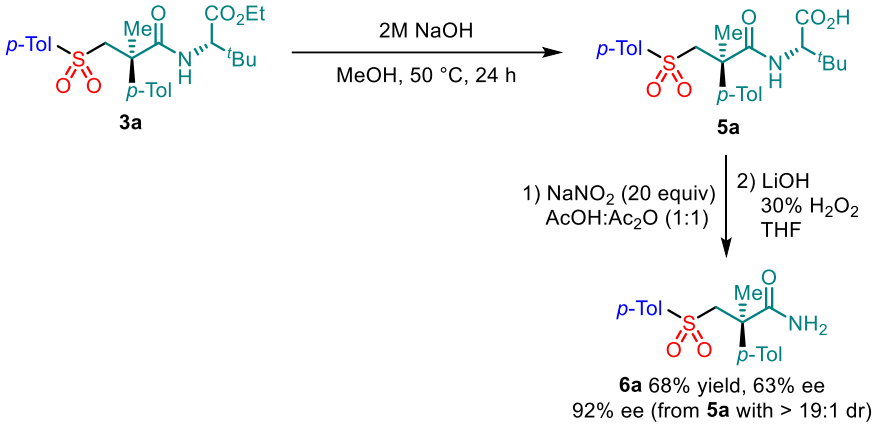


PDA Ch1 225nm

Peak	Ret. Time	Area	Area%
1	25.142	121686	0.660
2	26.632	2001348	10.859
3	31.798	2585	0.014
4	39.196	16304203	88.466

7. Chiral auxiliary cleavage: Synthesis of 6a

The amide **6a** were synthesized according to the reported literature procedure [5,6]



6a 68% yield, 63% ee
92% ee (from **5a** with > 19:1 dr)

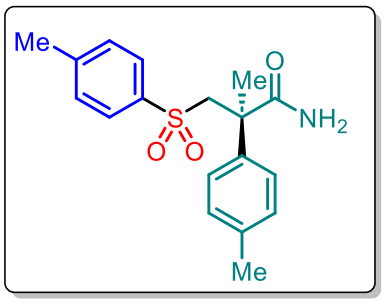
Conversion of **3a** to acid **5a**.

A 20 mL reaction tube equipped with a magnetic stirring bar was charged with ethyl (*S*)-3,3-dimethyl-2-((*R*)-2-methyl-2-(*p*-tolyl)-3-tosylpropanamido)butanoate 3a (37 mg, 0.5 mmol, 1 eq.) in methanol (2.5 mL). Next to it, an aqueous 2 M NaOH solution (1.0 mL) was added and the reaction mixture was stirred for 24 h at 50 °C till completion (monitored by TLC). After completion, crude mixture was acidified up to pH~1 with 1N HCl and extracted with EtOAc (3 x 20 mL). The organic layer was washed with 1N HCl, brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by flash chromatography to obtain the desired acid **5a.**

Conversion of **5a** to acid **6a**.

To a solution of purified **5a** (134 mg, 0.3 mmol) in glacial acetic acid (1.5 mL) and acetic anhydride (1.5 mL) was added $NaNO_2$ (6.0 mmol, 20 equiv.) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was poured into ice and the aqueous phase was extracted with diethyl ether twice. The organic phases were washed with a saturated aqueous solution of $NaHCO_3$ and with brine. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. The crude residue was passed through pad of SiO_2 using PET/AcOEt (2/1) as eluents. After concentration under reduce pressure, the product was dissolved in a 1:1 THF / 30% aqueous solution of H_2O_2 (1.0 mL) and a 1.0 M aqueous solution of LiOH (2.0 mL, 1.14 mmol) was added at room temperature. The mixture was monitored by TLC. Once the amide was no longer detectable, a saturated aqueous solution of Na_2SO_3 was added until peroxides were completely reduced. After concentration, the residual aqueous phase was washed with diethyl ether and acidified with a 2.0 M aqueous solution of $KHSO_4$. The aqueous phase was extracted with EA twice and the combined organic extracts were dried over Na_2SO_4. The crude residue was purified by flash chromatography using a gradient of Petroleum Ether, AcOEt and MeOH as eluents to deliver 66.2 mg of compound **6a** (White solid, 68%).

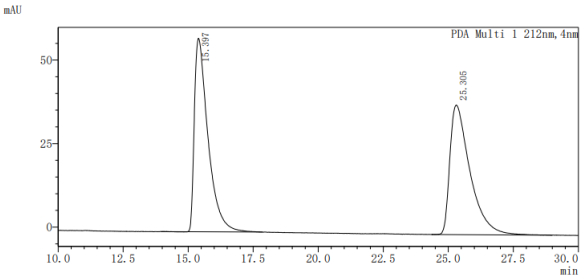
(*R*)-2-methyl-2-(p-tolyl)-3-tosylpropanamide (6a)



6a: 66.2 mg, 68% yield, 63% ee, 92% ee (from pure 5a), white solid.

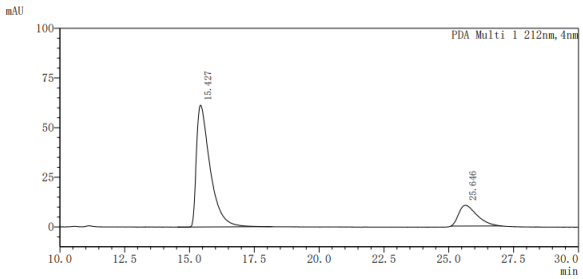
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.13 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 5.37 (s, 1H), 4.04 (d, *J* = 14.8 Hz, 1H), 3.72 (d, *J* = 14.8 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.4, 144.0, 138.3, 137.7, 136.7, 129.5, 1294, .127.6, 126.6, 64.1, 49.0, 22.5, 21.6, 21.0. **HRMS** (ESI) m/z Calcd for [$C_{18}H_{21}NO_3S$+Na^+: M+Na]$^+$: 354.1135, found: 354.1135. $[\alpha]_D^{25}$ = +4.6 (c = 0.10, $CHCl_3$).

HPLC analysis: Chiralcel IB column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 212 nm, t(major) = 15.43 min, t_1(minor) = 25.65 min, ee = 63%; t(major) = 15.67 min, t_2(minor) = 25.85 min, ee = 92% (from pure 5a).



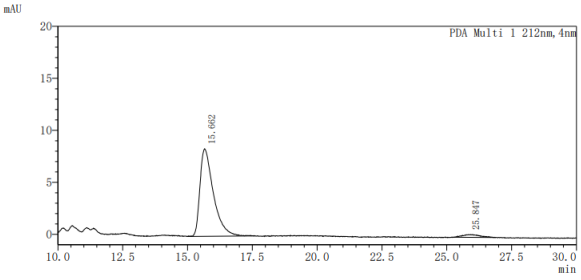
PDA Ch1 212nm

Peak	Ret. Time	Area	Area%
1	15.397	2114135	50.292
2	25.305	2089581	49.708



PDA Ch1 212nm

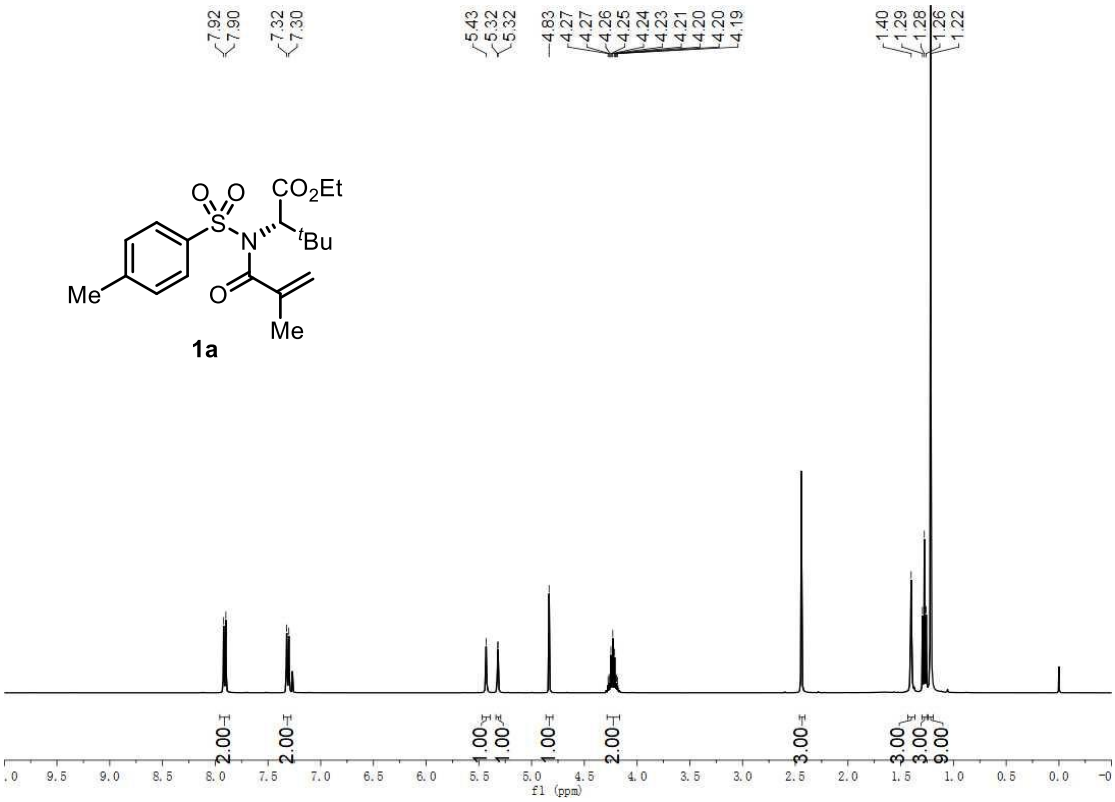
Peak	Ret. Time	Area	Area%
1	15.427	2261588	81.543
2	25.646	511890	18.457

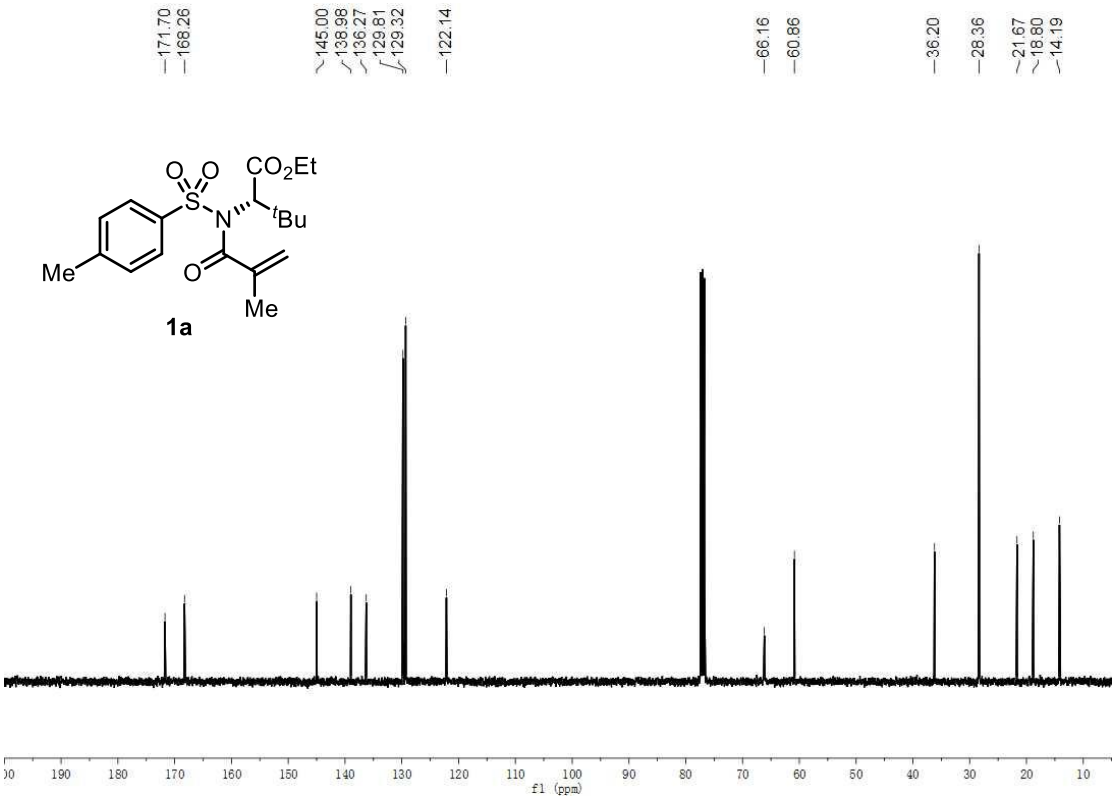


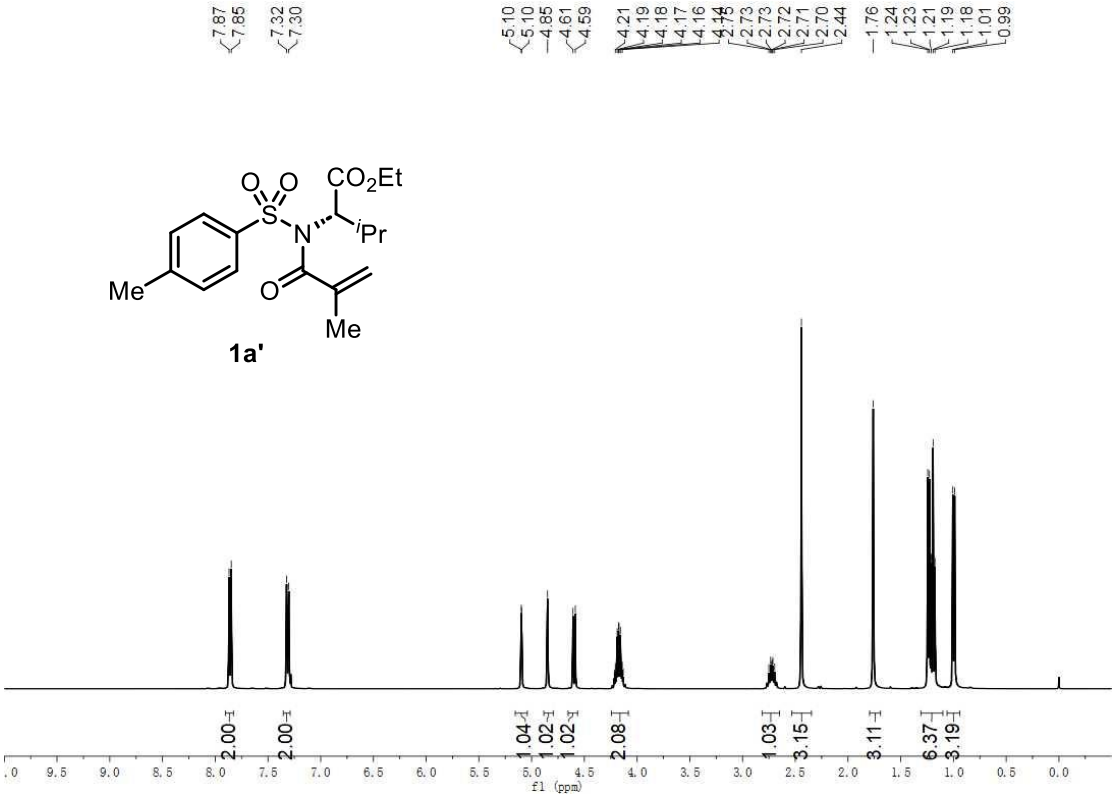
PDA Ch1 212nm

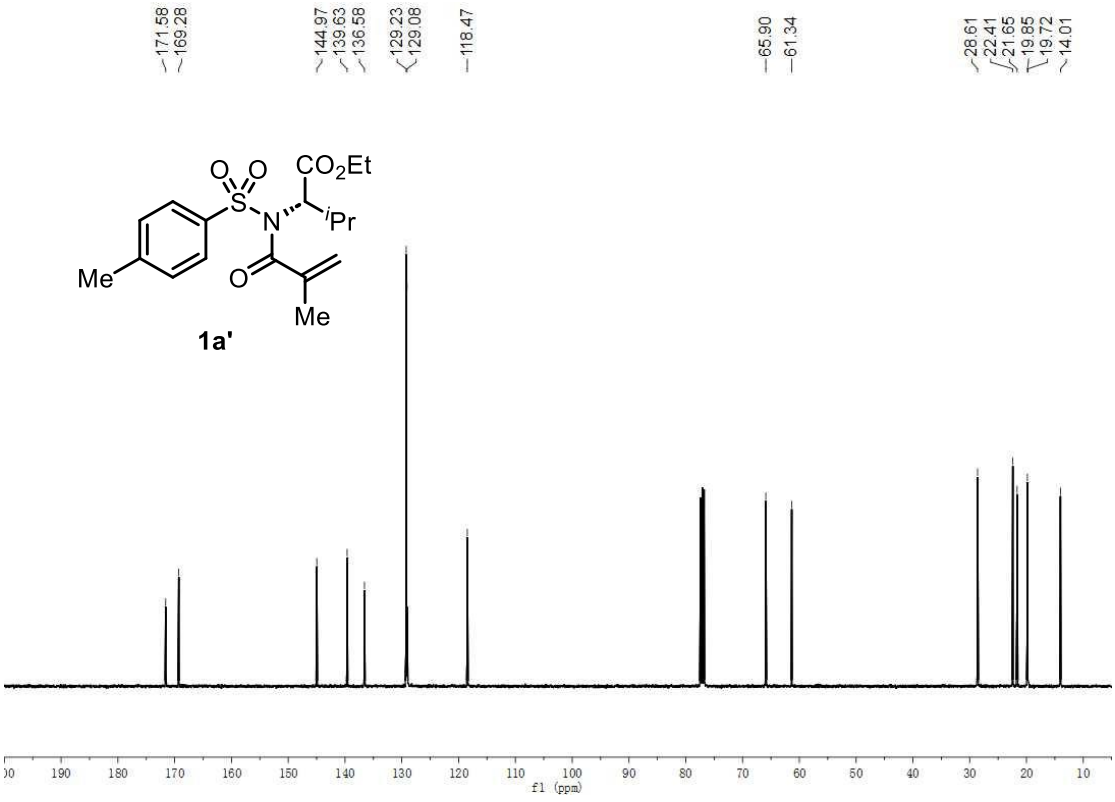
Peak	Ret.Time	Area	Area%
1	15.662	303581	95.927
2	25.847	12891	4.073

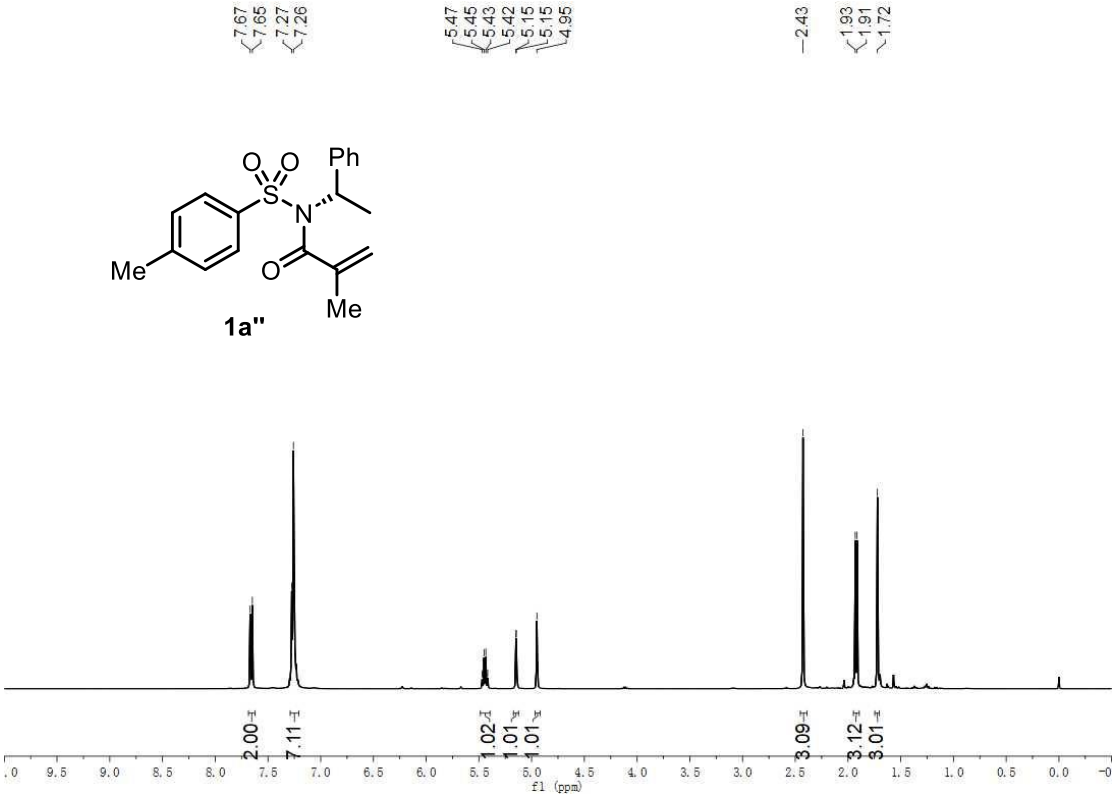
8. Copies of ^{1}H and ^{13}C NMR spectra

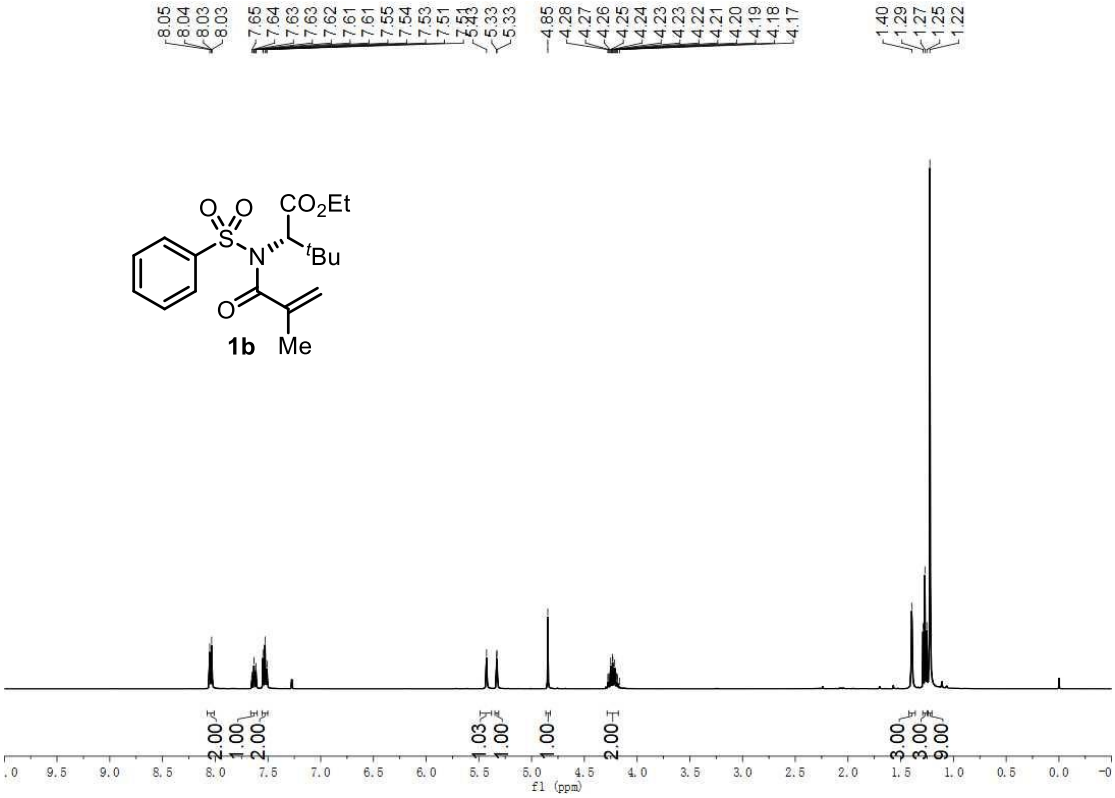


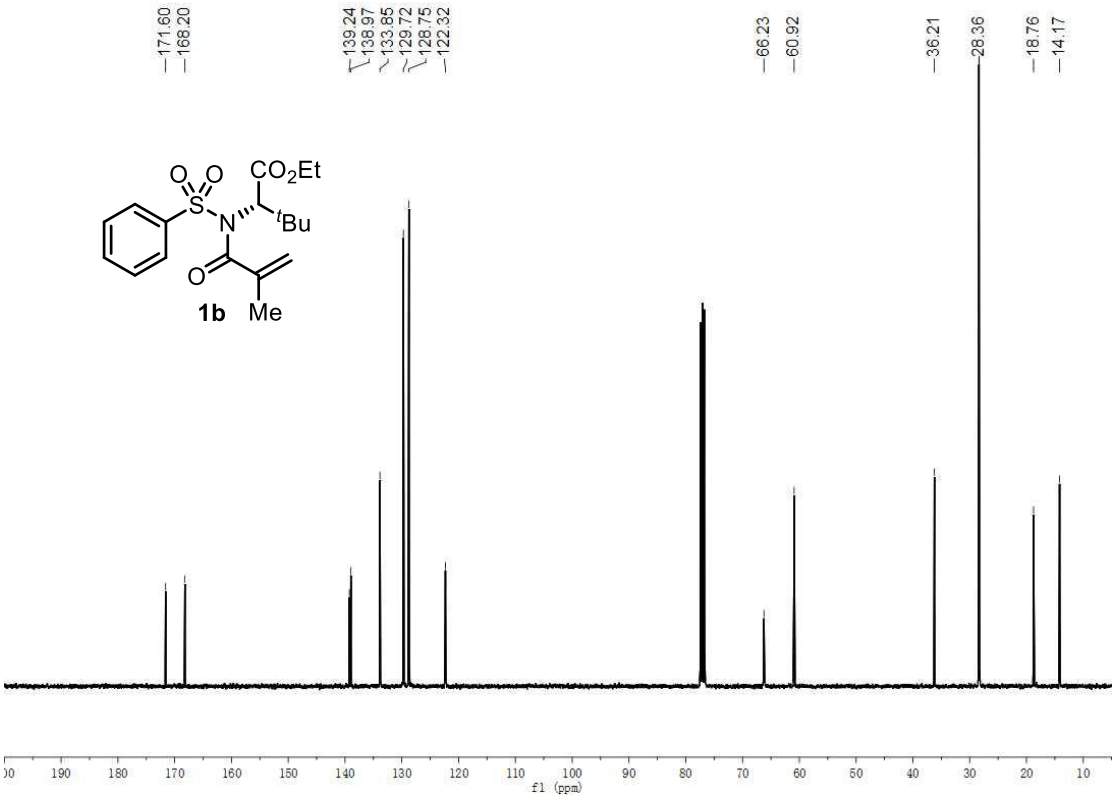


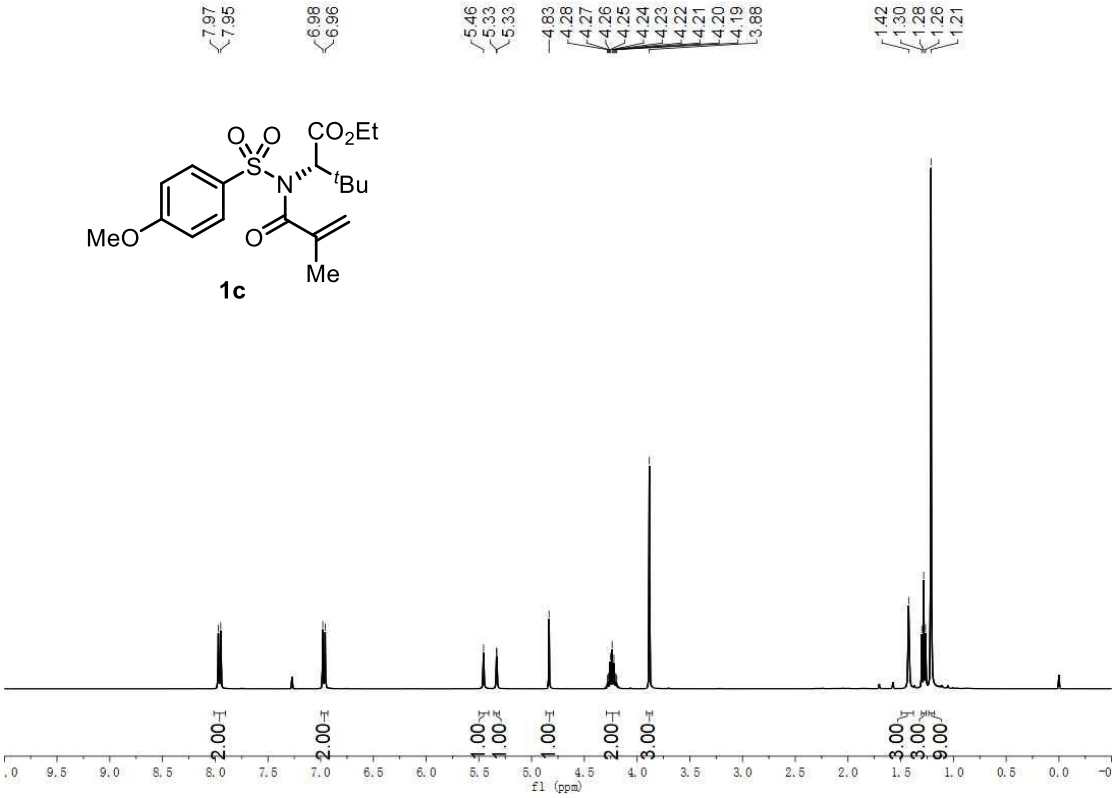

7.87
7.85
7.32
7.30
5.10
5.10
4.85
4.61
4.59
4.21
4.19
4.18
4.17
4.16
2.73
2.73
2.72
2.71
2.70
2.44
1.76
1.24
1.23
1.21
1.19
1.18
1.01
0.99
CO2Et
iPr
Me
Me
1a'
2.00
2.00
1.04
1.02
1.02
2.08
1.03
3.15
3.11
6.37
3.19
f1 (ppm)

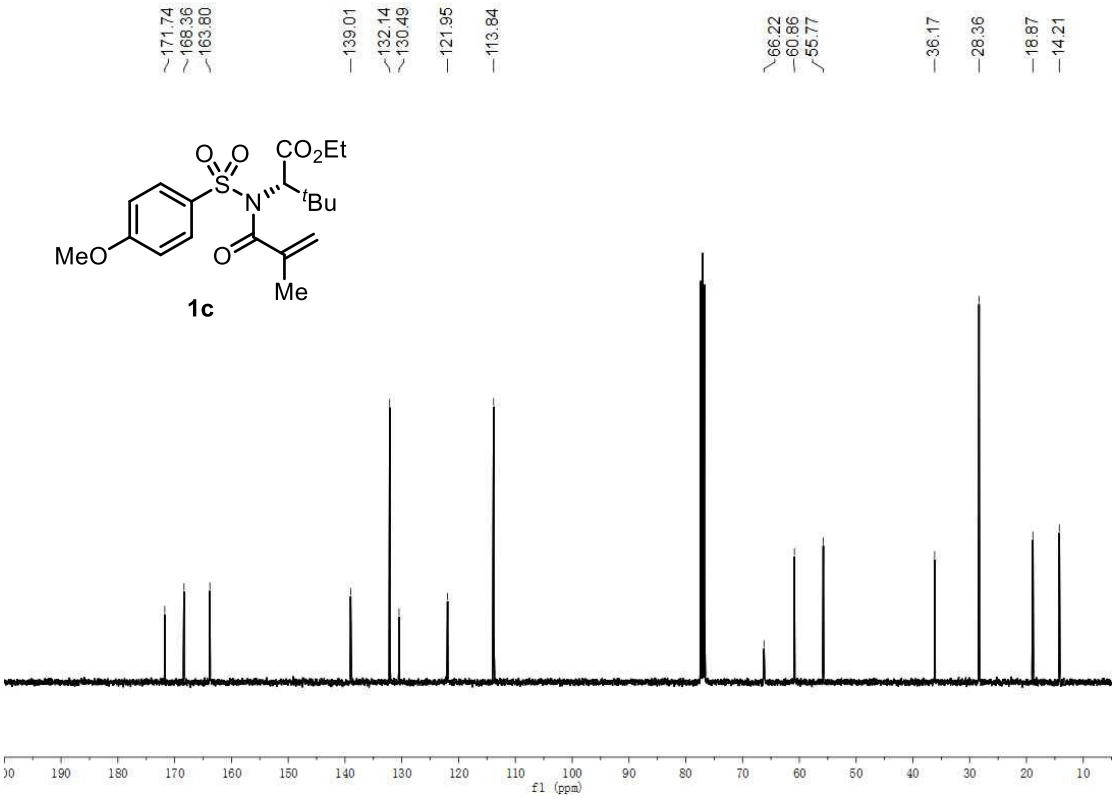

171.58
169.28
144.97
139.63
136.58
129.23
129.08
118.47
65.90
61.34
28.61
22.41
21.65
19.85
19.72
14.01
CO2Et
iPr
Me
Me
1a'
f1 (ppm)

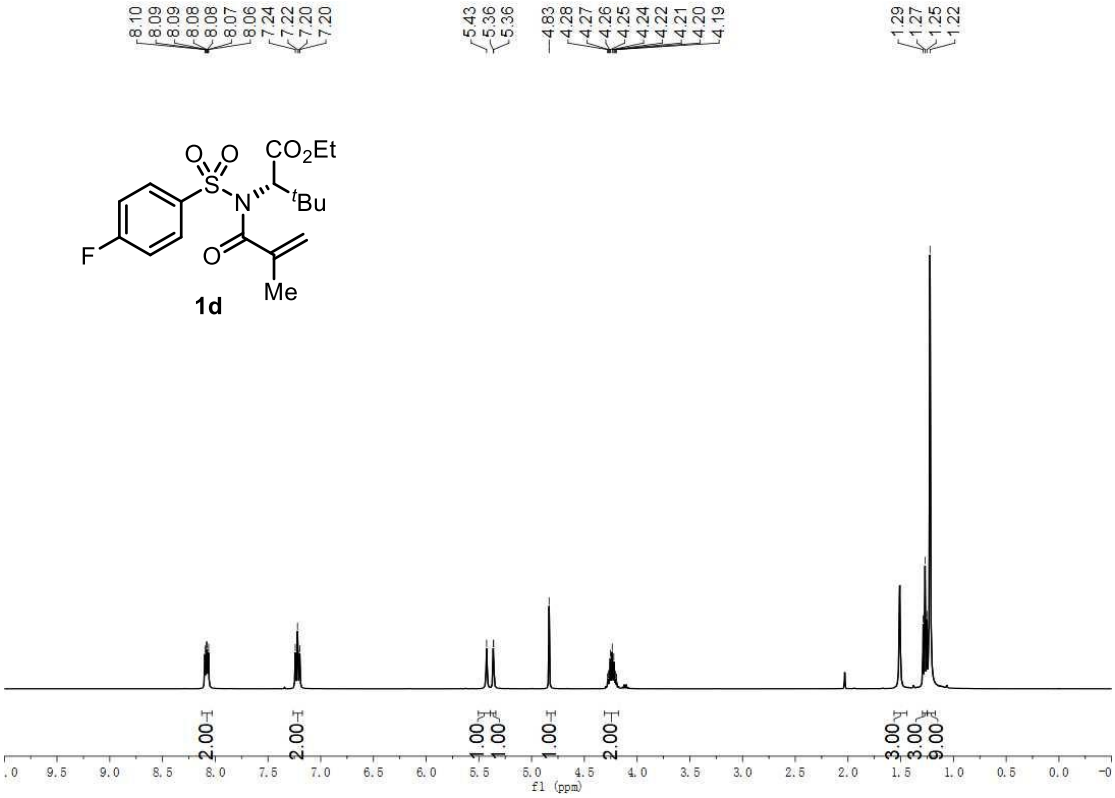

7.67
7.65
7.27
7.26
5.47
5.45
5.43
5.42
5.15
5.15
4.95
2.43
1.93
1.91
1.72
Ph
O
O
S
N
Me
O
Me
1a"
2.00
7.11
1.02
1.01
1.01
3.09
3.12
3.01
f1 (ppm)
172.9
144.7
129.4
128.6
128.3
127.7
127.6
119.0
58.0
21.7
19.1
18.6
Ph
O
O
S
N
Me
O
Me
1a"
f1 (ppm)

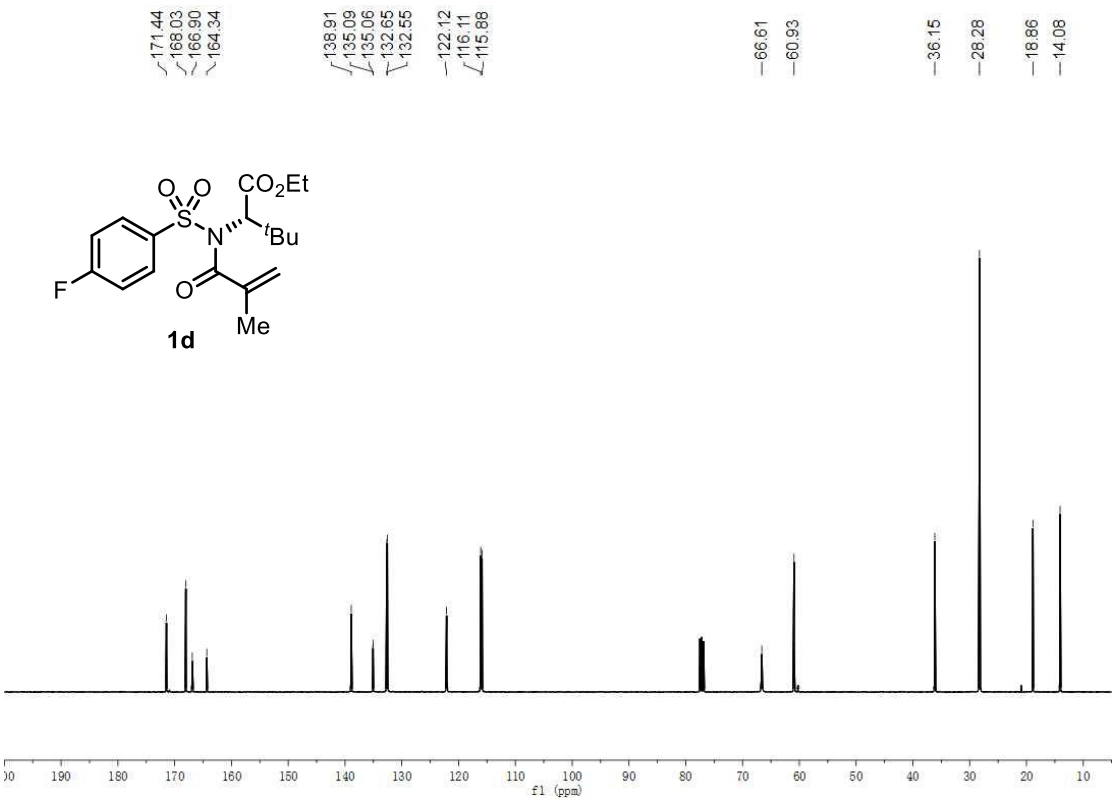

8.05
8.04
8.03
8.03
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.55
7.54
7.53
7.51
7.51
5.33
5.33
4.85
4.28
4.27
4.26
4.25
4.24
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.17
1.40
1.29
1.27
1.25
1.22
O
O
S
N
O
CO2Et
tBu
1b
Me
2.00
1.00
2.00
1.03
1.00
1.00
2.00
3.00
3.00
9.00
f1 (ppm)

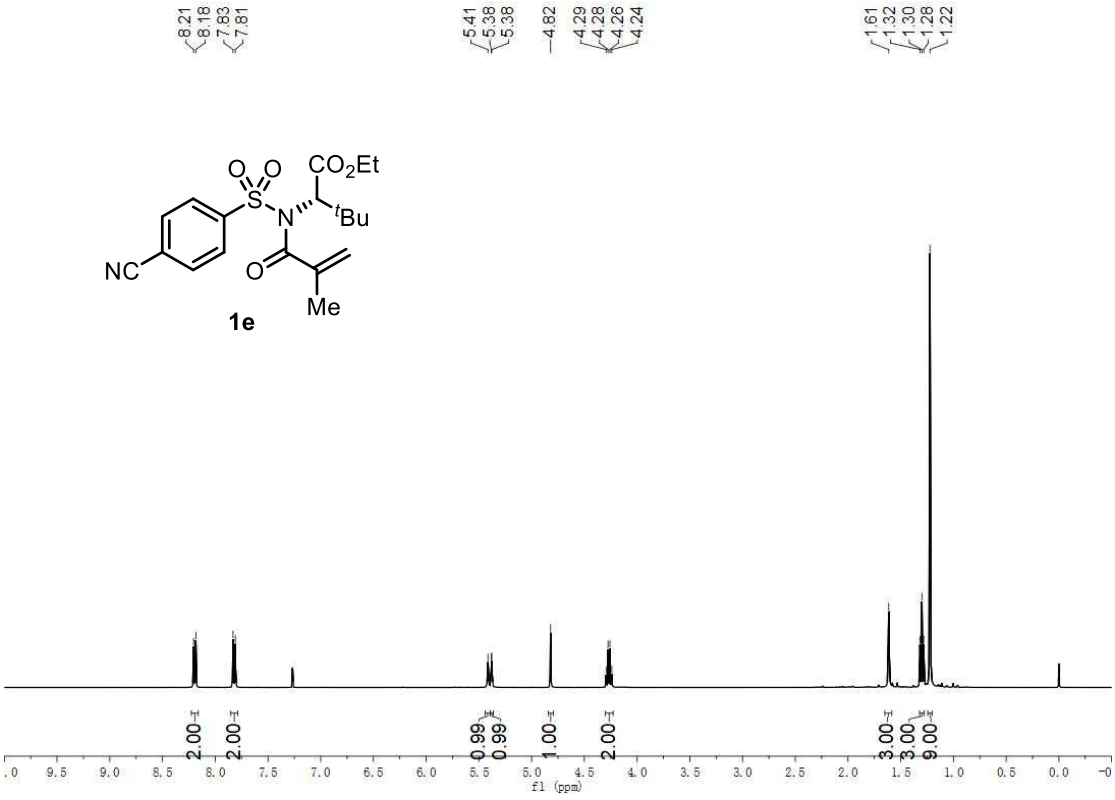

171.60
168.20
139.24
138.97
133.85
129.72
128.75
122.32
66.23
60.92
36.21
28.36
18.76
14.17
O
O
S
N
O
CO2Et
tBu
1b
Me
f1 (ppm)


7.97
7.95
6.98
6.96
5.46
5.33
5.33
4.83
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.20
4.19
3.88
1.42
1.30
1.28
1.26
1.21
MeO
Me
1c
2.00
2.00
1.00
1.00
1.00
2.00
3.00
3.00
3.00
3.00
f1 (ppm)


171.74
168.36
163.80
139.01
132.14
130.49
121.95
113.84
66.22
60.86
55.77
36.17
28.36
18.87
14.21
MeO
Me
1c
f1 (ppm)


8.10
8.09
8.09
8.08
8.08
8.07
8.06
7.24
7.22
7.20
7.20
5.43
5.36
5.36
4.83
4.28
4.27
4.26
4.25
4.24
4.22
4.21
4.20
4.19
1.29
1.27
1.25
1.22
O
O
S
N
CO2Et
tBu
F
O
Me
1d
2.00
2.00
1.00
1.00
1.00
2.00
3.00
3.00
9.00
f1 (ppm)


171.44
168.03
166.90
164.34
138.91
135.09
135.06
132.65
132.55
122.12
116.11
115.88
66.61
60.93
36.15
28.28
18.86
14.08
O
O
S
N
CO2Et
tBu
F
O
Me
1d
f1 (ppm)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4.28
4.26
4.24
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1.32
1.30
1.28
1.22
CO2Et
tBu
NC
Me
1e
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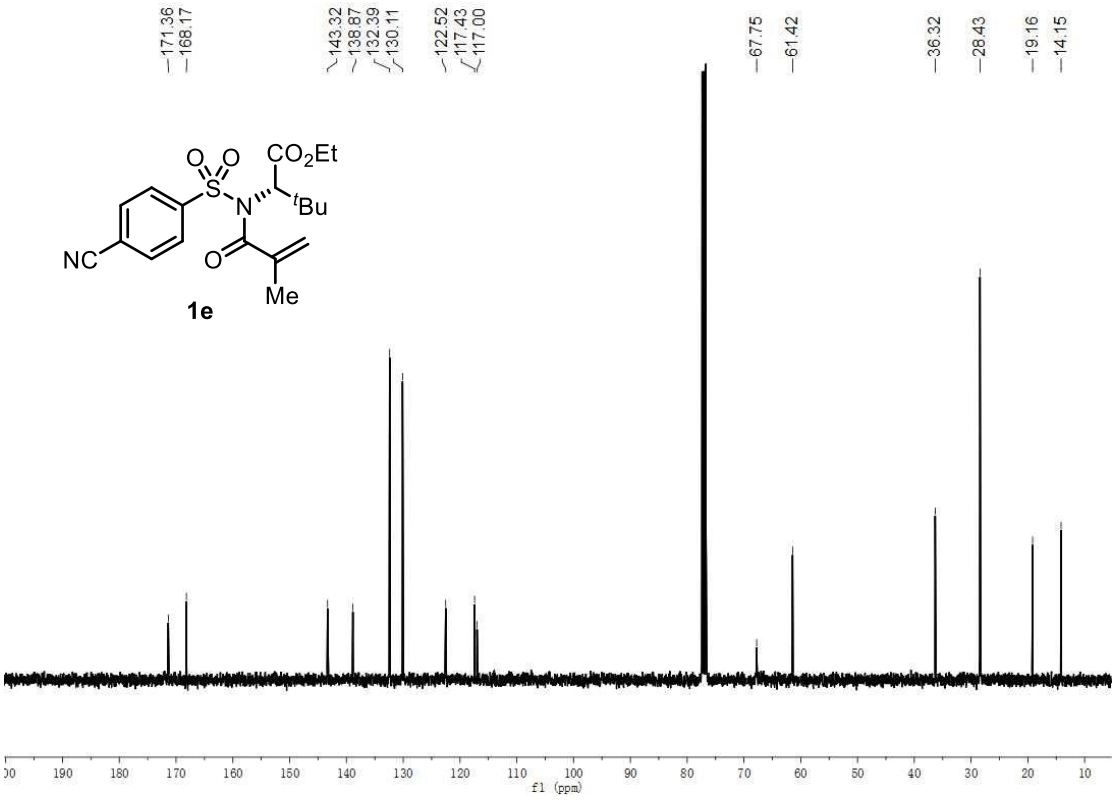
0.99
1.00
2.00
3.00
3.00
9.00
f1 (ppm)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117.43
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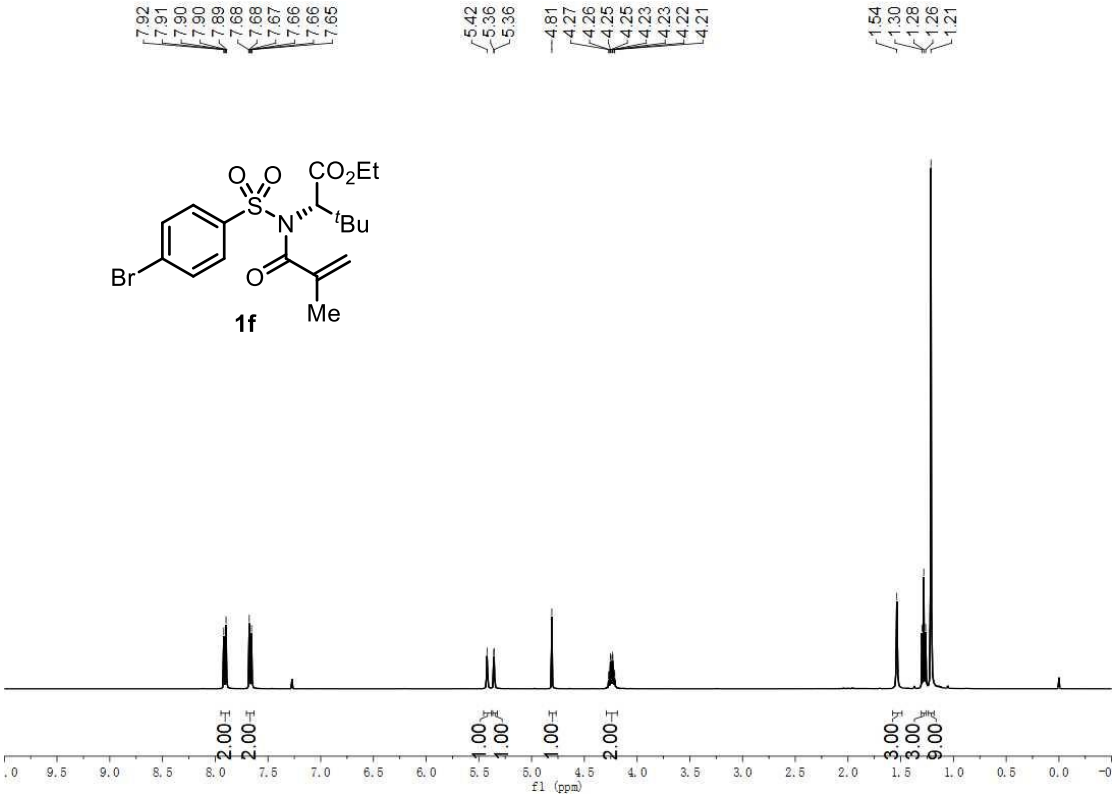
28.43
19.16
14.15
CO2Et
tBu
NC
Me
1e
f1 (ppm)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5.36
4.81
4.27
4.26
4.25
4.25
4.23
4.22
4.21
1.54
1.30
1.28
1.26
1.21
O
O
S
N
CO2Et
tBu
O
Br
Me
1f
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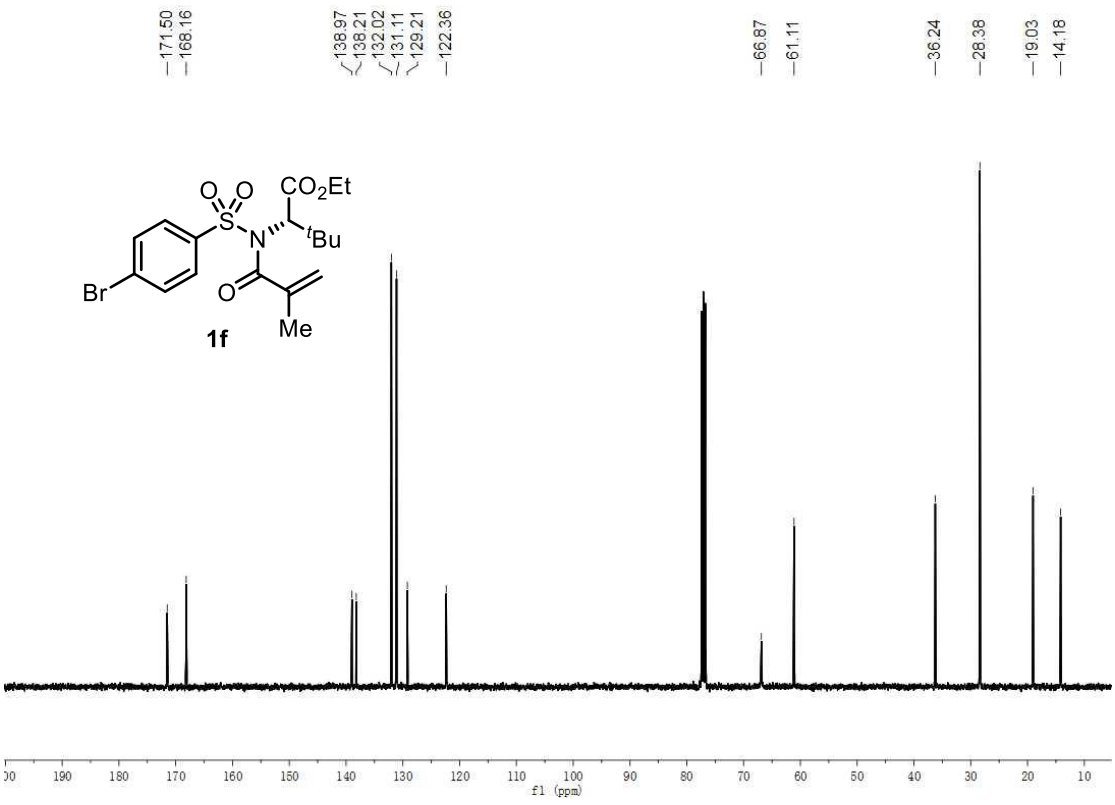
1.00
1.00
2.00
3.00
3.00
9.00
f1 (ppm)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122.36
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61.11
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14.18
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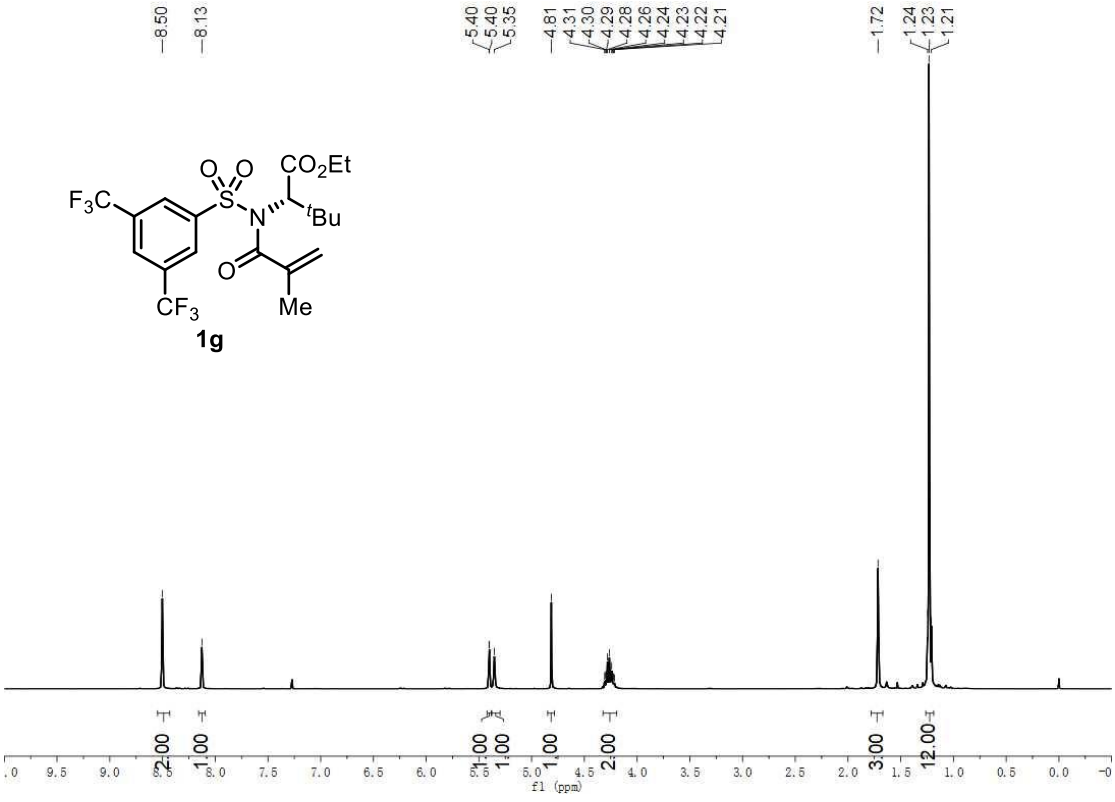
O
S
N
CO2Et
tBu
O
Br
Me
1f
f1 (ppm)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4.23
4.22
4.21
1.72
1.24
1.23
1.21
F3C
CO2Et
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1.00
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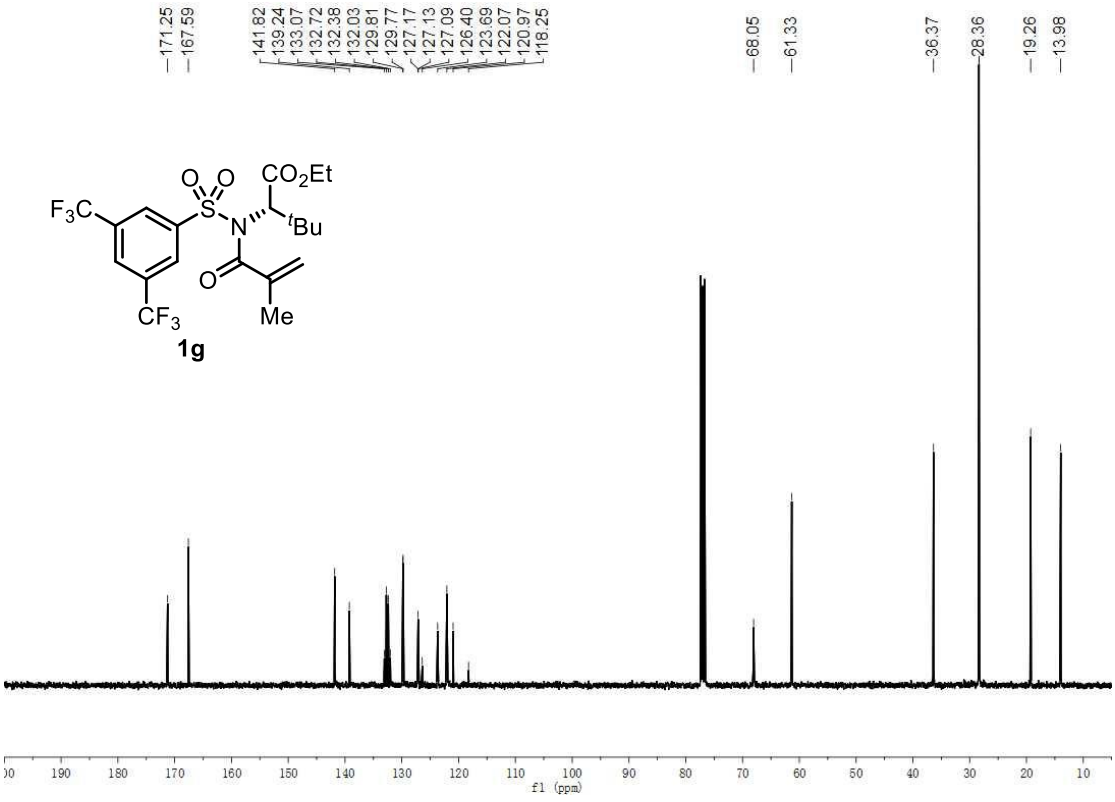
2.00
3.00
12.00
f1 (ppm)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126.40
123.69
122.07
120.97
118.25
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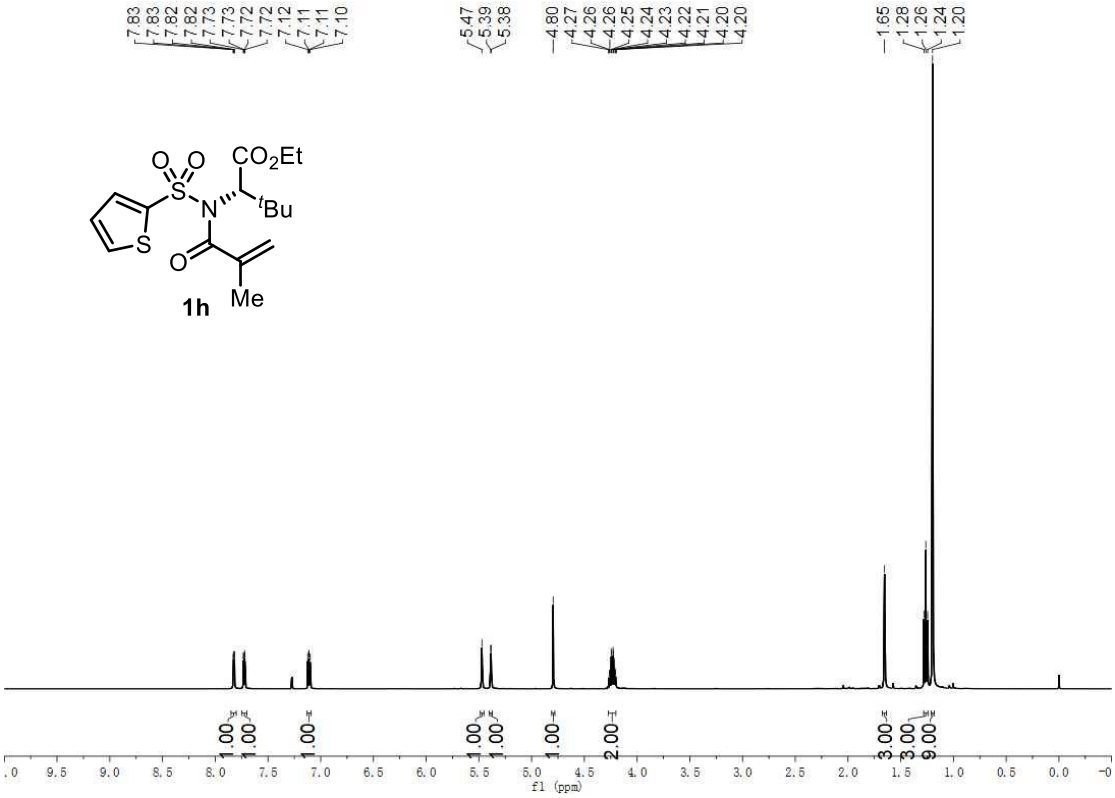
28.36
19.26
13.98
F3C
CO2Et
tBu
CF3
Me
1g
f1 (ppm)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7.10
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5.39
5.38
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4.27
4.26
4.26
4.25
4.24
4.23
4.22
4.21
4.20
4.20
1.65
1.28
1.26
1.24
1.20
CO2Et
tBu
Me
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1.00
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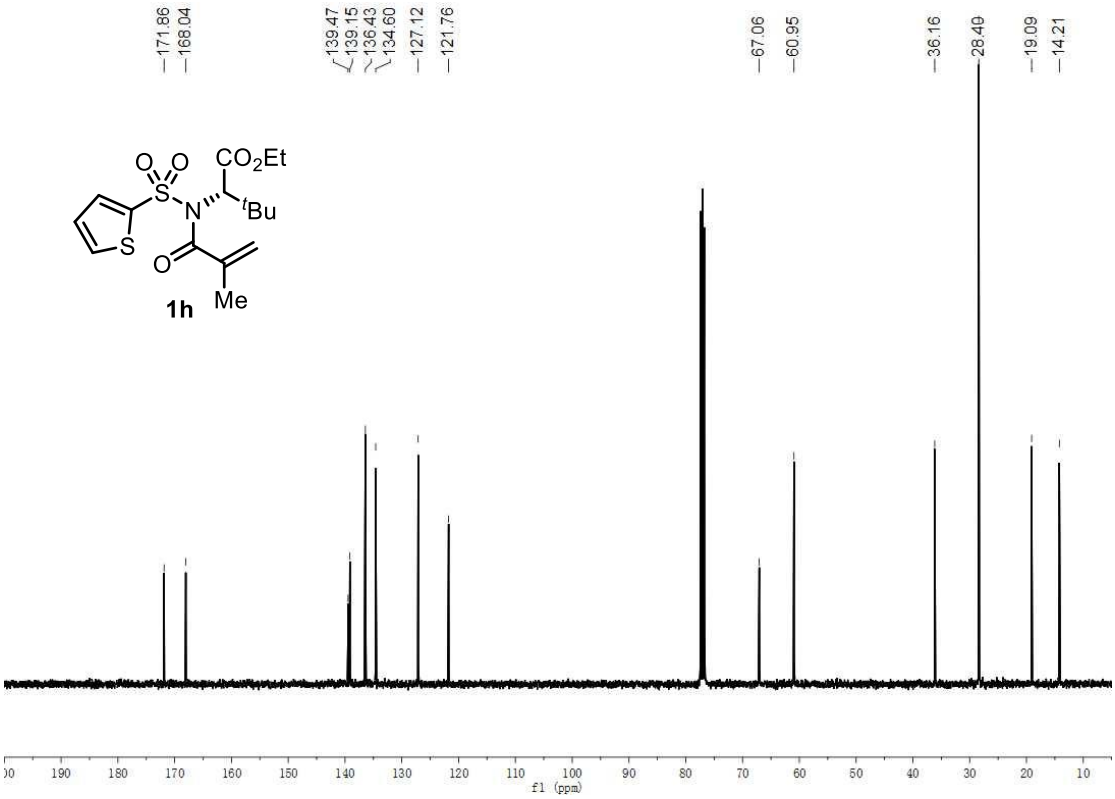
3.00
3.00
9.00
f1 (ppm)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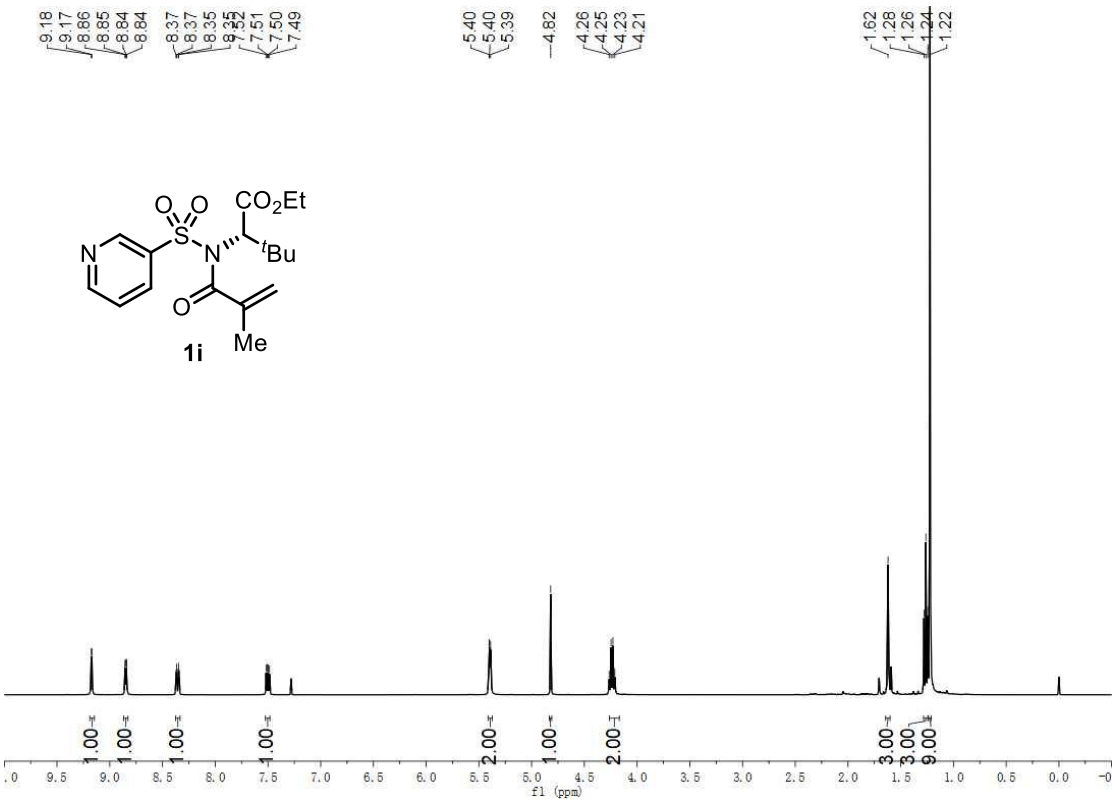
60.95
36.16
28.40
19.09
14.21
CO2Et
tBu
Me
1h
f1 (ppm)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9.17
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8.37
8.37
8.35
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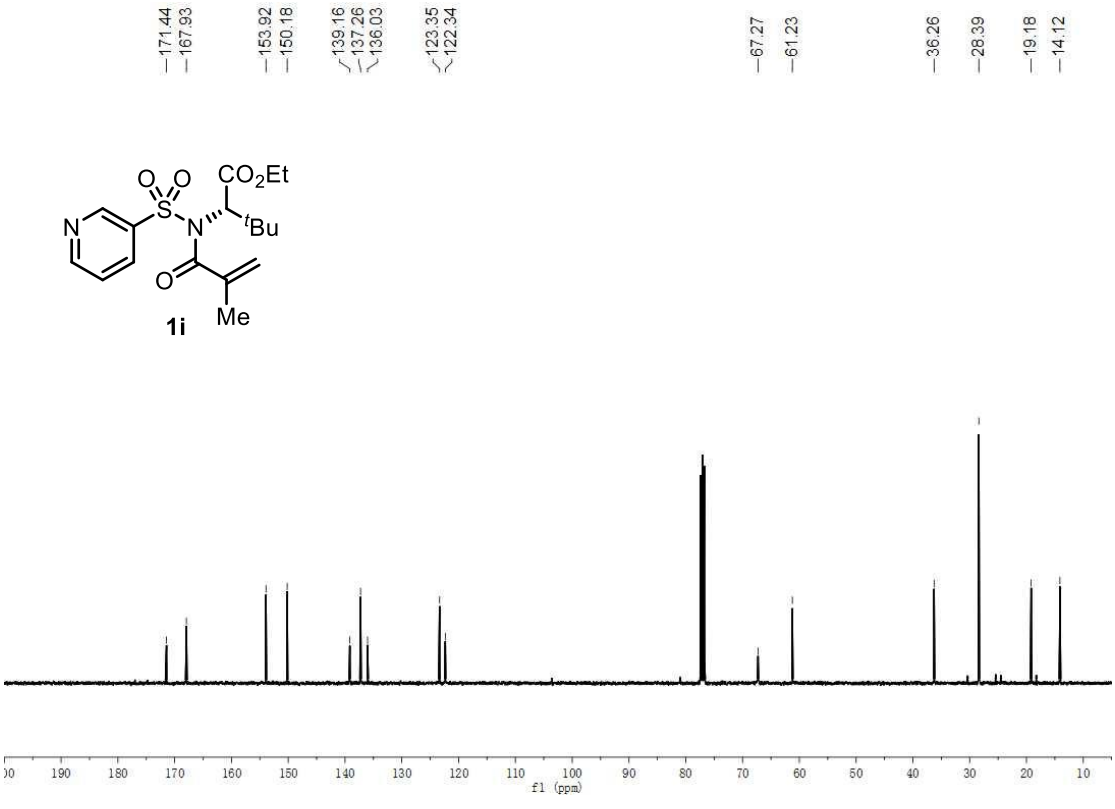
7.51
7.50
7.49
5.40
5.40
5.39
4.82
4.26
4.25
4.23
4.21
1.62
1.28
1.26
1.24
1.22
CO2Et
tBu
Me
1i
1.00
1.00
1.00
1.00
2.00
1.00
2.00
3.00
3.00
9.00
f1 (ppm)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137.26
136.03
123.35
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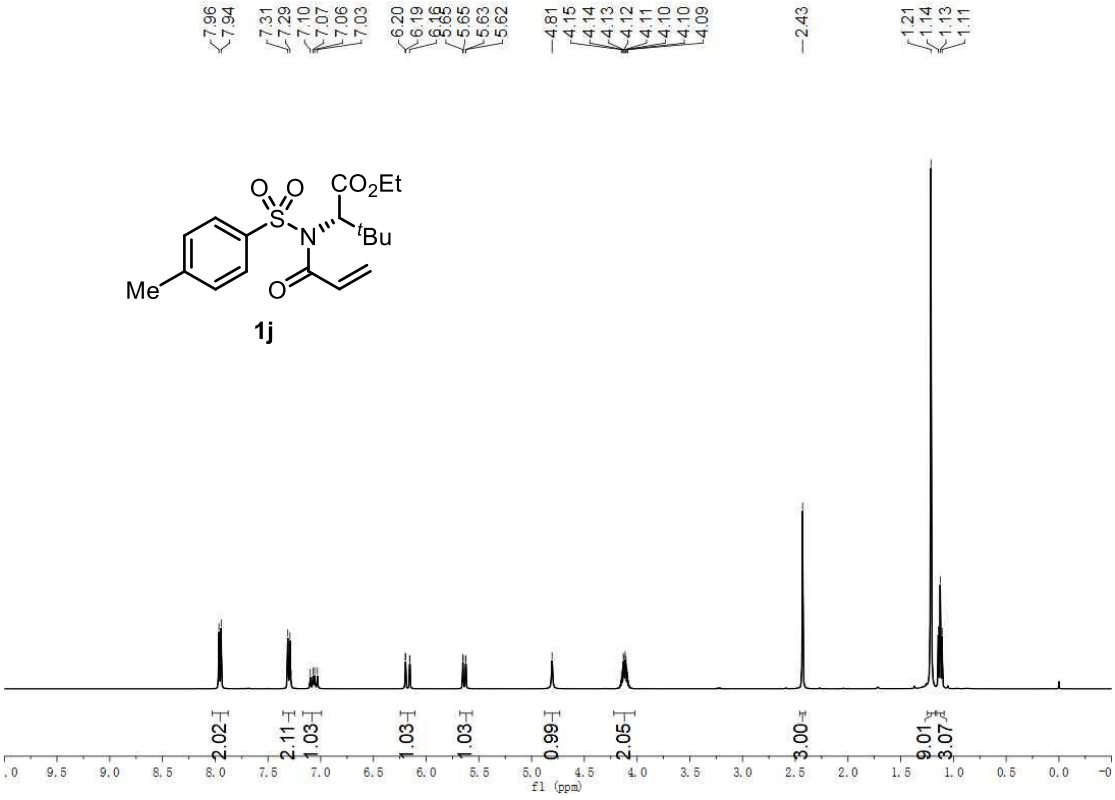
61.23
36.26
28.39
19.18
14.12
CO2Et
tBu
Me
1i
f1 (ppm)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7.03
6.20
6.19
6.16
6.15
5.65
5.63
5.62
4.81
4.15
4.14
4.13
4.12
4.11
4.10
4.09
2.43
1.21
1.14
1.13
1.11
Me
1j
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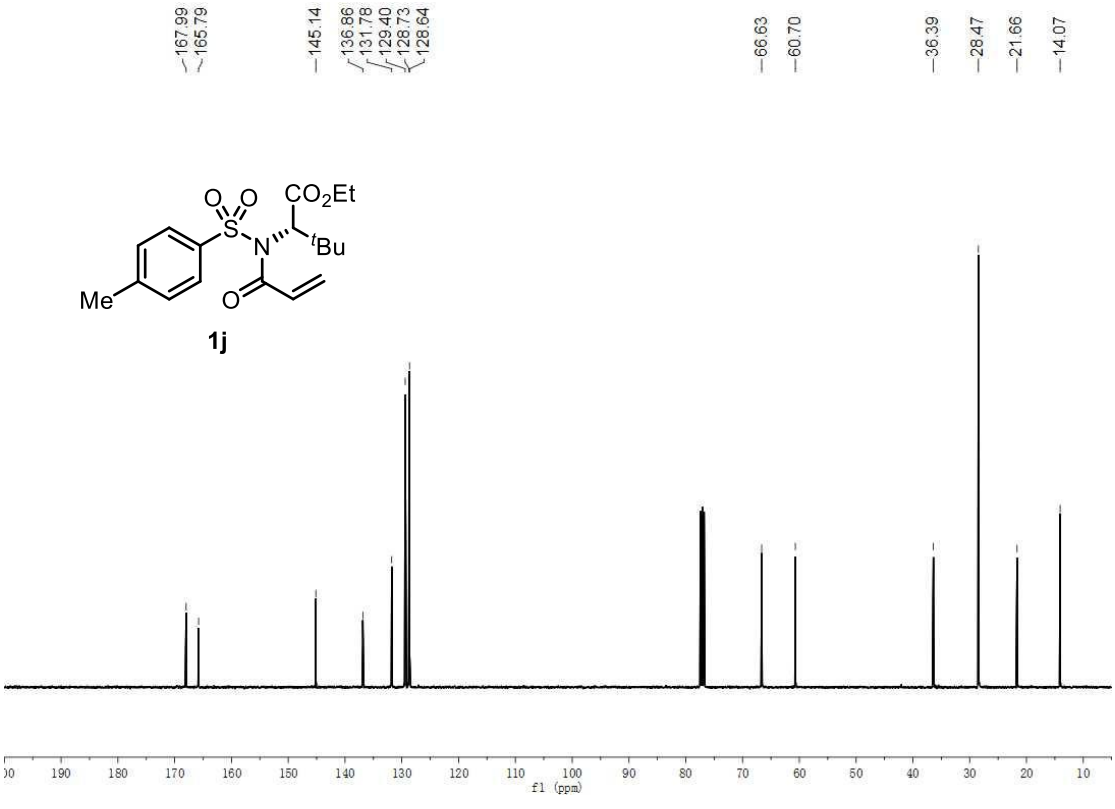
2.11
1.03
1.03
1.03
0.99
2.05
3.00
9.01
3.07
f1 (ppm)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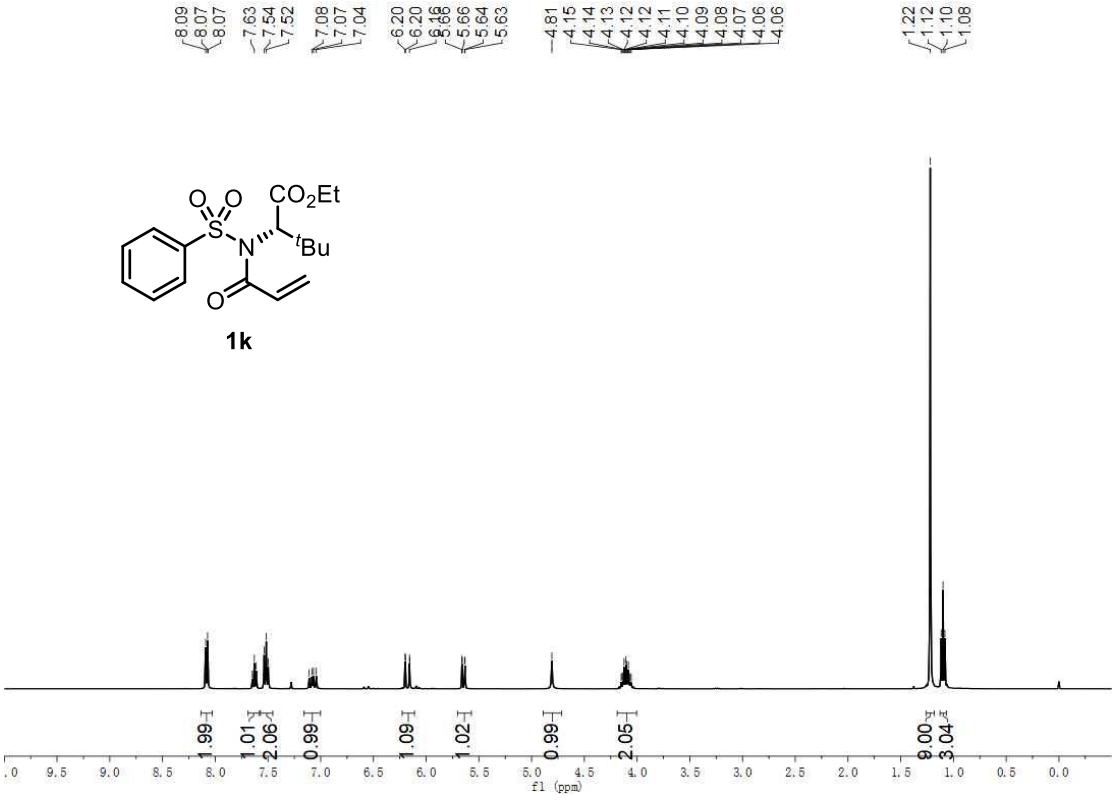
60.70
36.39
28.47
21.66
14.07
Me
1j
f1 (ppm)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8.07
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5.64
5.63
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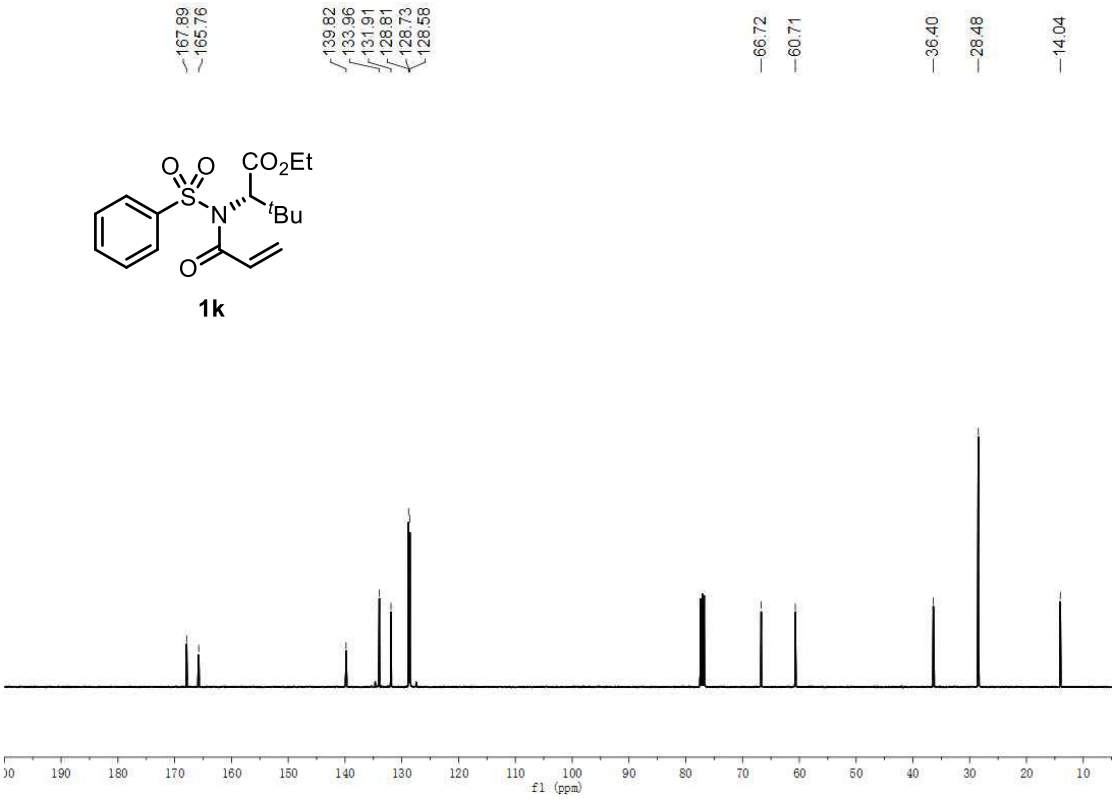
4.15
4.14
4.13
4.12
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.06
1.22
1.12
1.10
1.08
CO2Et
tBu
1k
1.99
1.01
2.06
0.99
1.09
1.02
0.99
2.05
9.00
3.04
f1 (ppm)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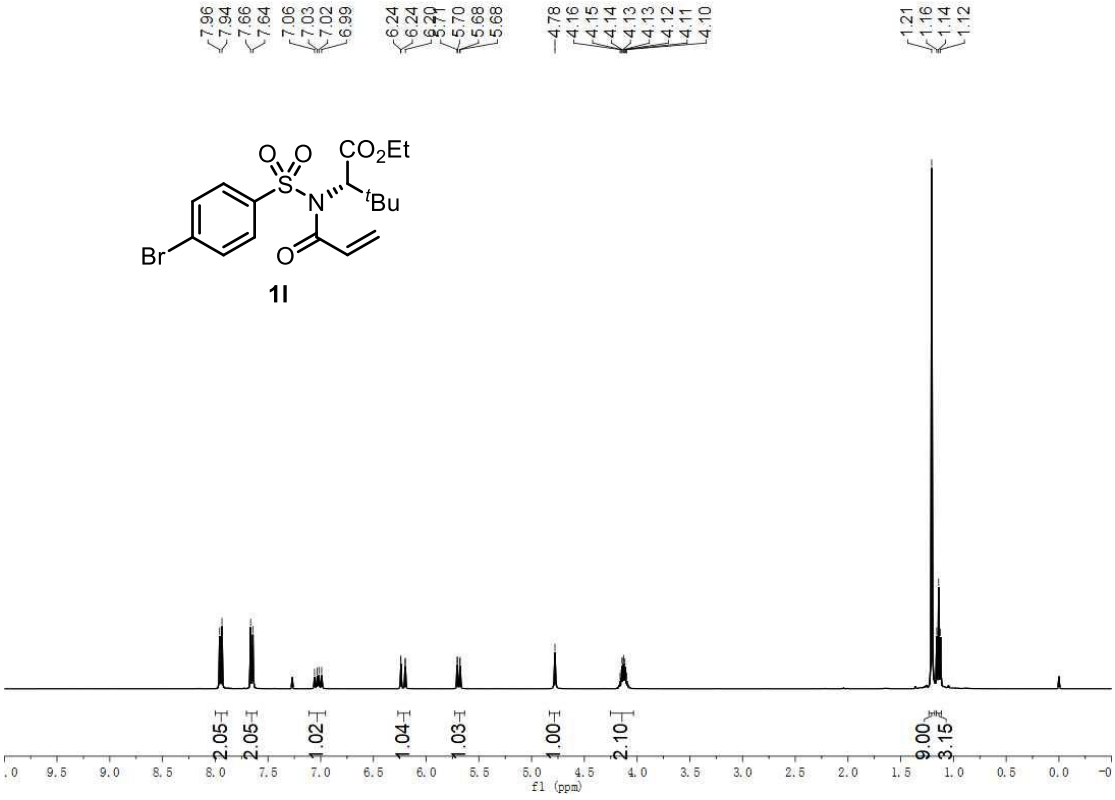
tBu
1k
f1 (ppm)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5.68
5.68
4.78
4.16
4.15
4.14
4.13
4.13
4.12
4.11
4.10
1.21
1.16
1.14
1.12
O
O
S
N
CO2Et
tBu
O
Br
1l
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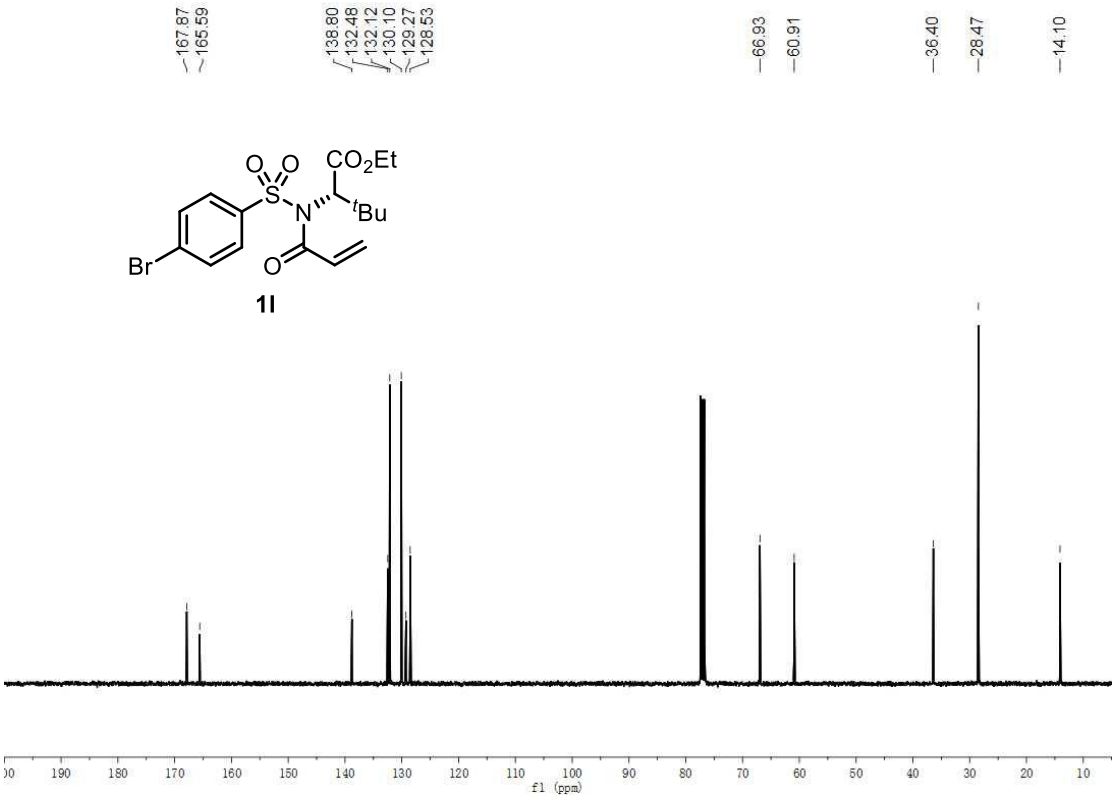
2.05
1.02
1.04
1.03
1.00
2.10
9.00
3.15
f1 (ppm)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130.10
129.27
128.53
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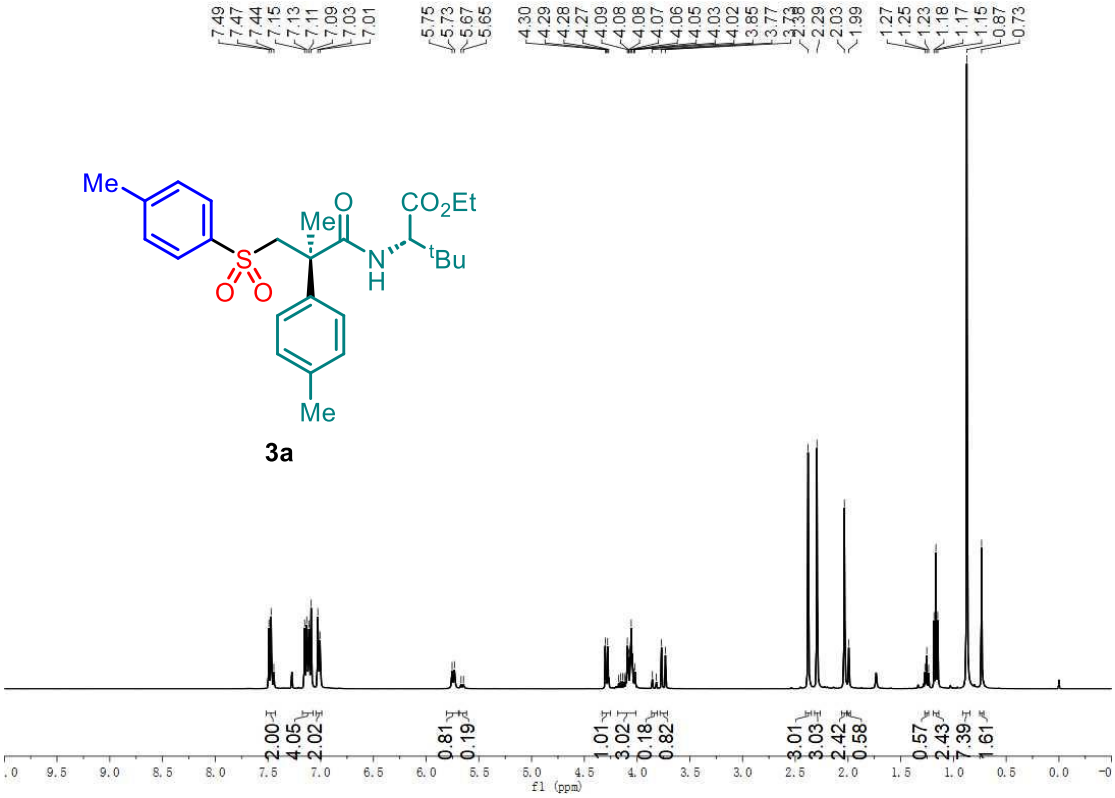
28.47
14.10
O
O
S
N
CO2Et
tBu
O
Br
1l
f1 (ppm)



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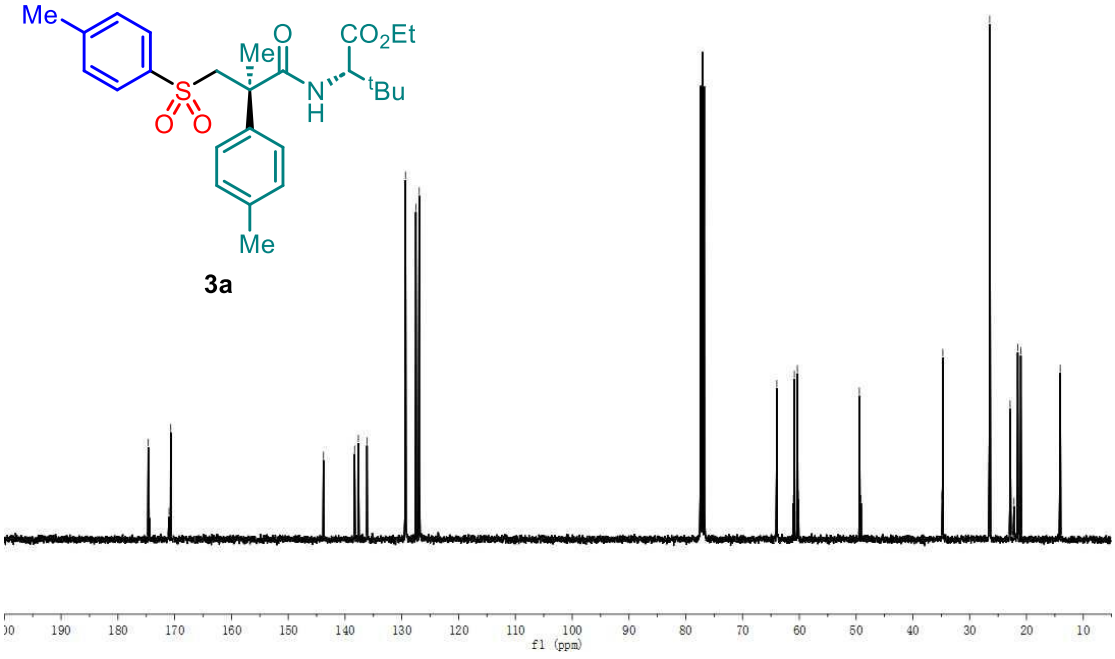

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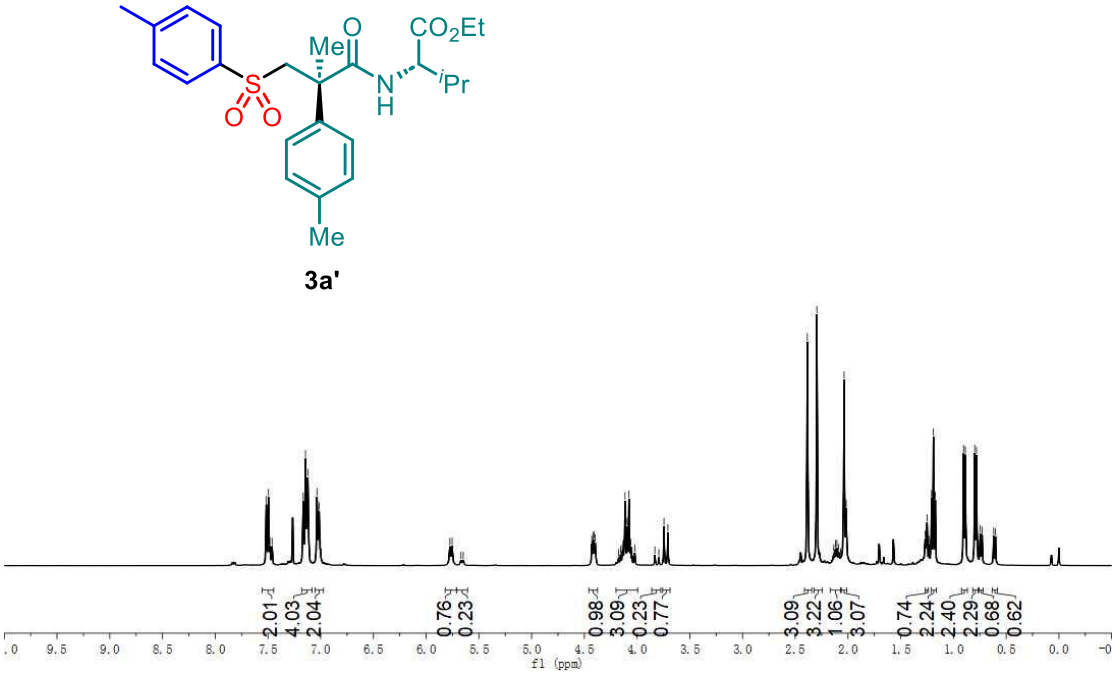

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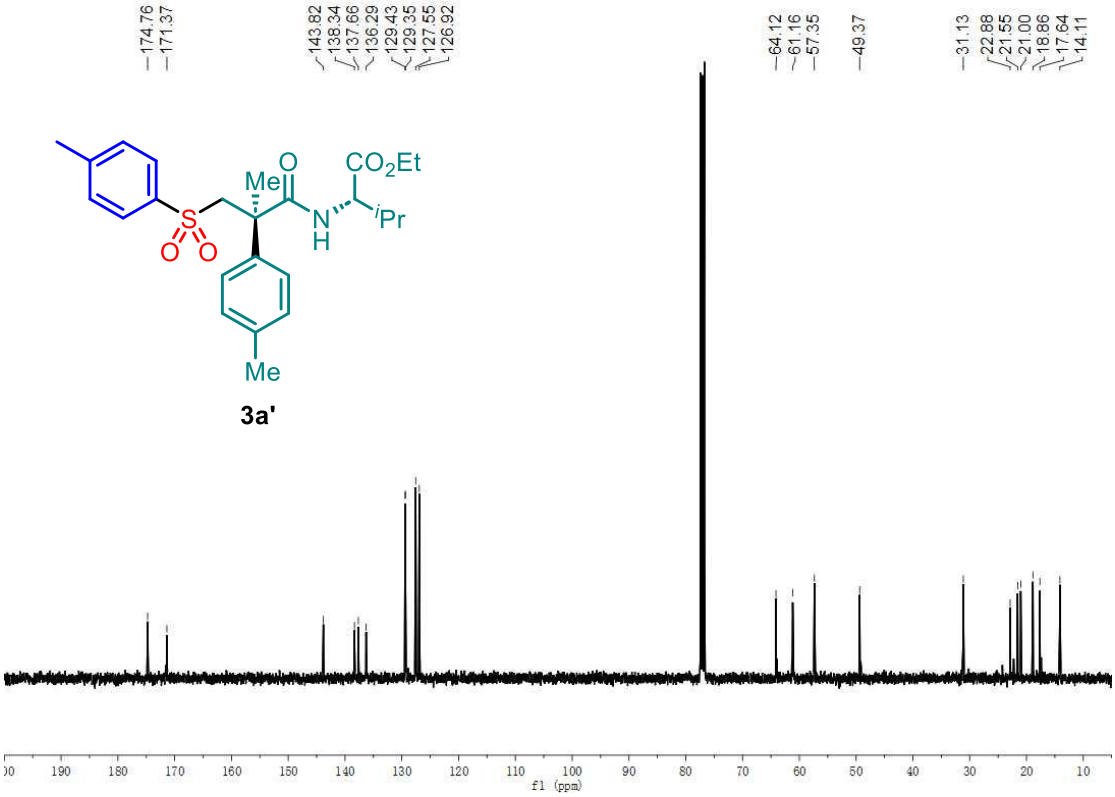

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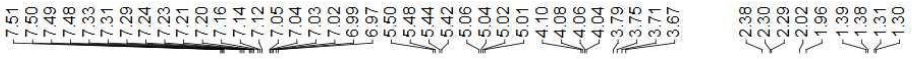
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7.12
7.05
7.04
7.03
7.02
6.99
6.97
5.50
5.48
5.44
5.42
5.06
5.04
5.02
5.01
4.10
4.08
4.06
4.04
3.79
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2.29
2.02
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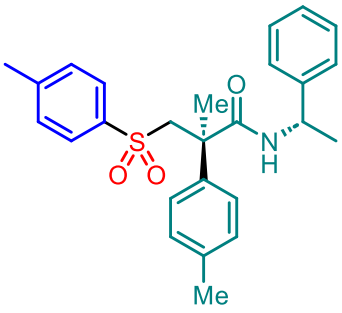
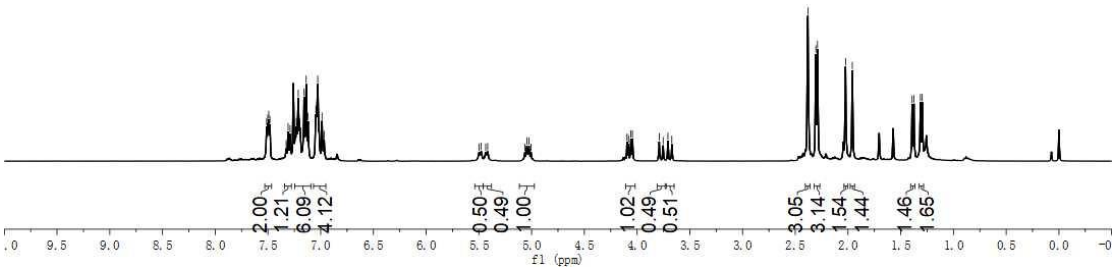
1.39
1.38
1.31
1.30


Me
O
S
O
O
N
H
Me

3a''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3.05
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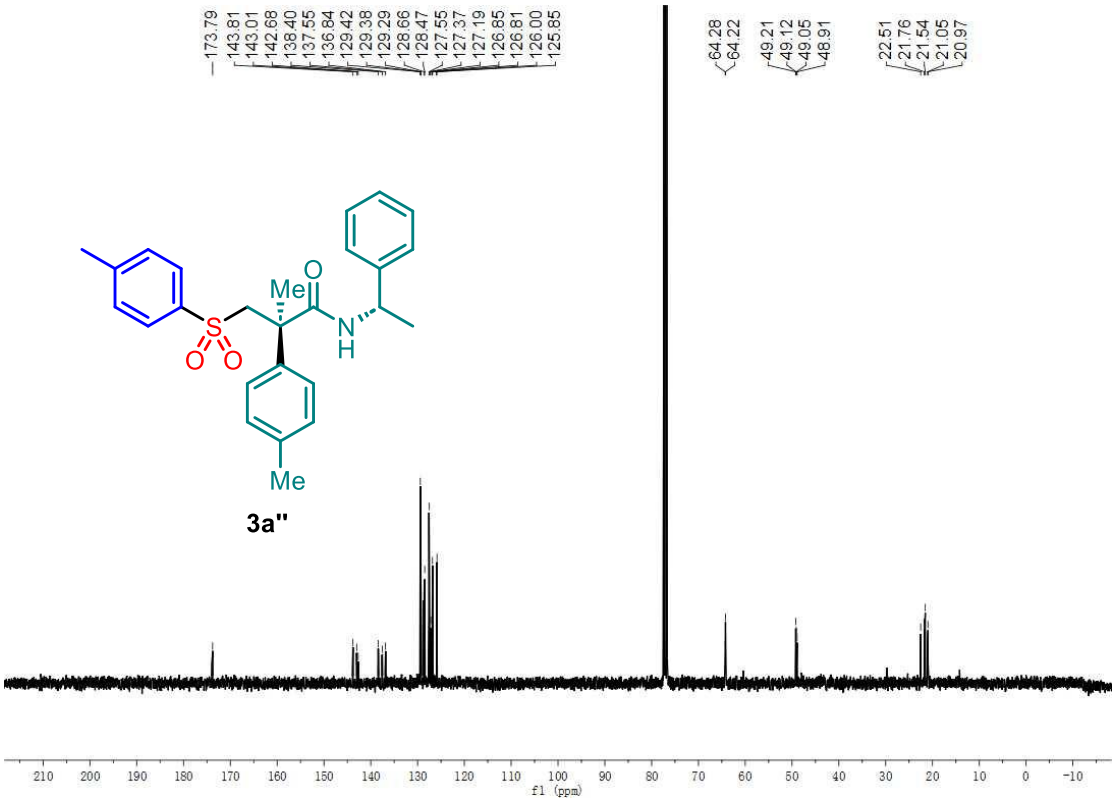
1.44
1.46
1.65
f1 (ppm)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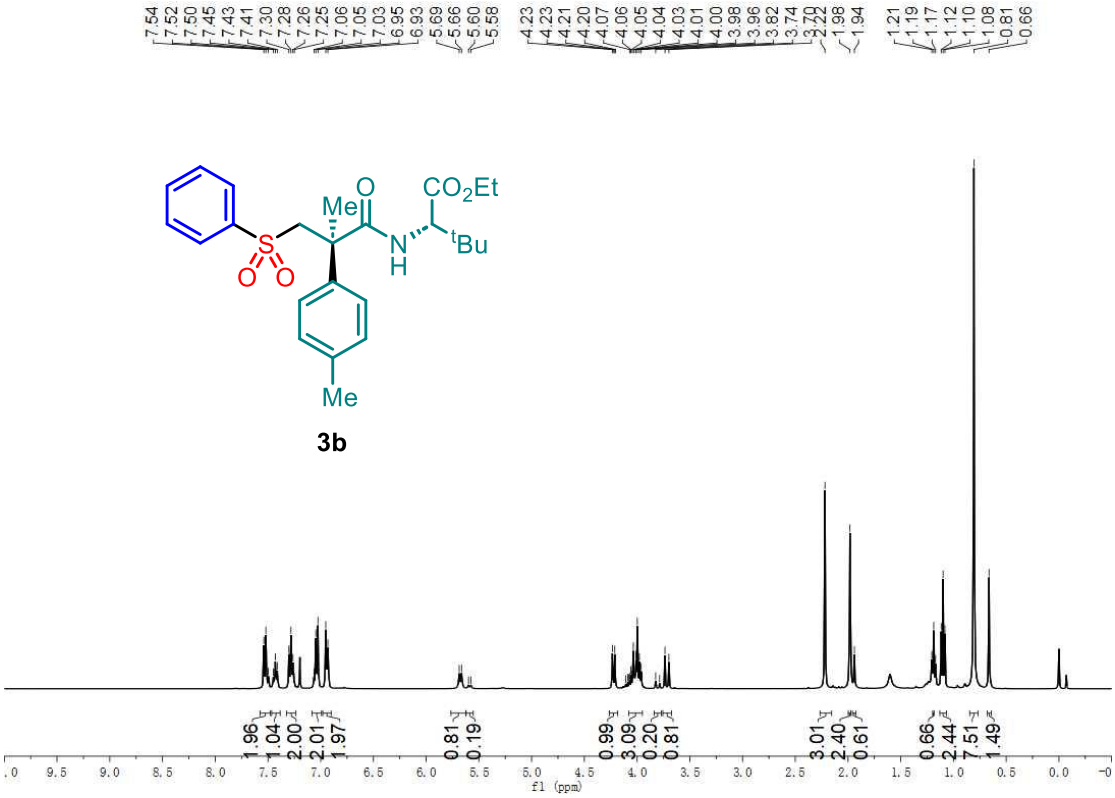
127.55
127.37
127.19
126.85
126.81
126.00
125.85
64.28
64.22
49.21
49.12
49.05
48.91
22.51
21.76
21.54
21.05
20.97
Me
O
S
O
O
N
H
Me
f1 (ppm)

3a''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7.03
6.95
6.93
5.69
5.66
5.60
5.58
4.23
4.23
4.21
4.20
4.07
4.06
4.05
4.04
4.03
4.01
4.00
3.98
3.96
3.82
3.74
3.70
2.22
1.98
1.94
1.21
1.19
1.17
1.12
1.10
1.08
0.81
0.66
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3b
1.96
1.04
2.00
2.01
1.97
0.81
0.19
0.99
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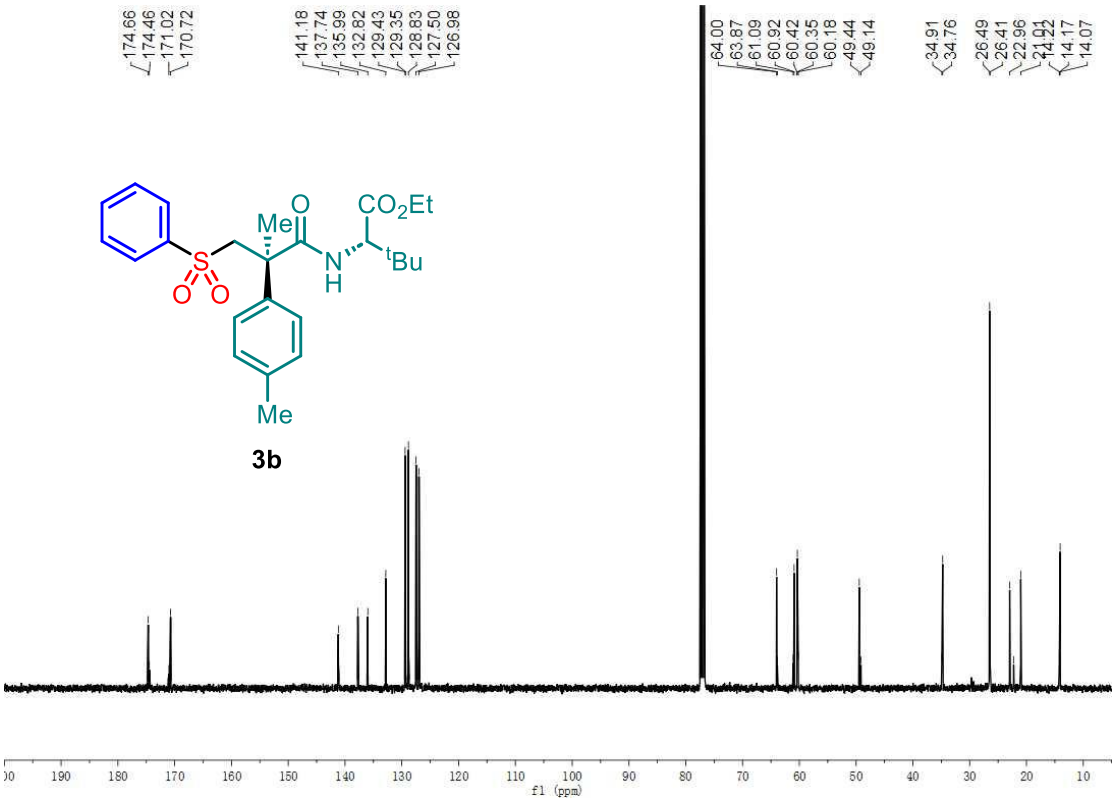
0.81
3.01
2.40
0.61
0.66
2.44
7.51
1.49
f1 (ppm)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60.18
49.44
49.14
34.91
34.76
26.49
26.41
22.96
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Me
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CO2Et
N
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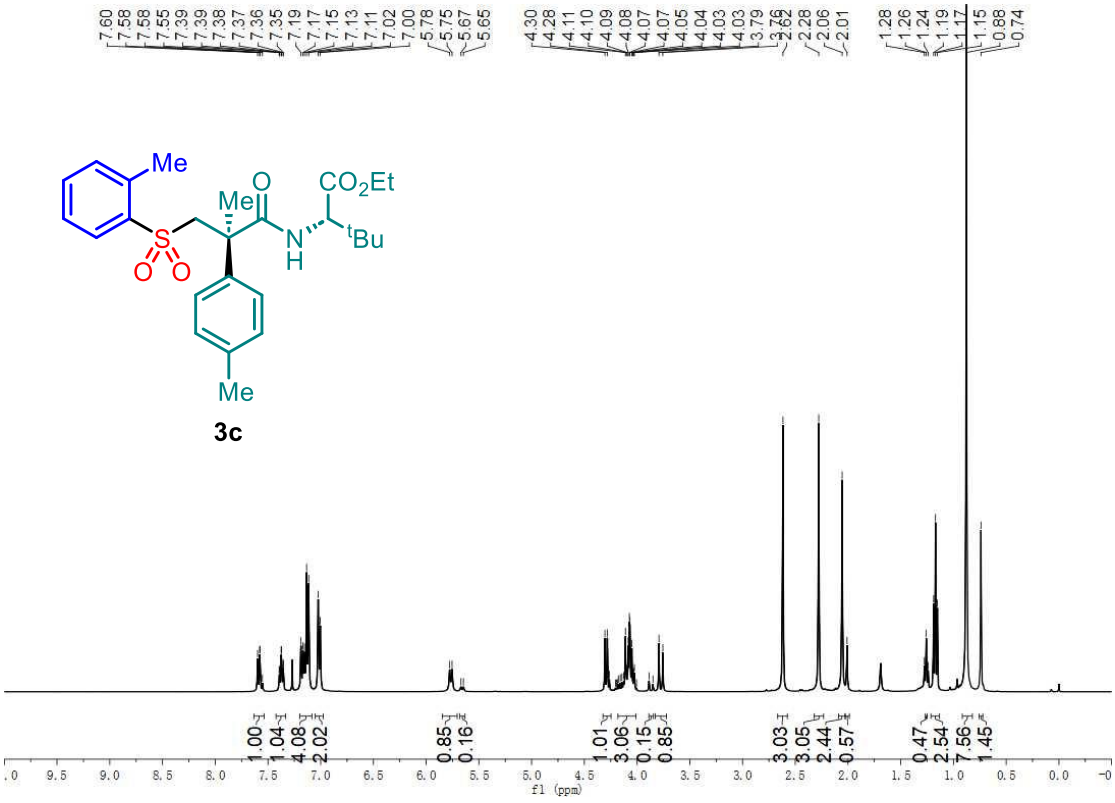
tBu
S
O
O
Me
3b
f1 (ppm)



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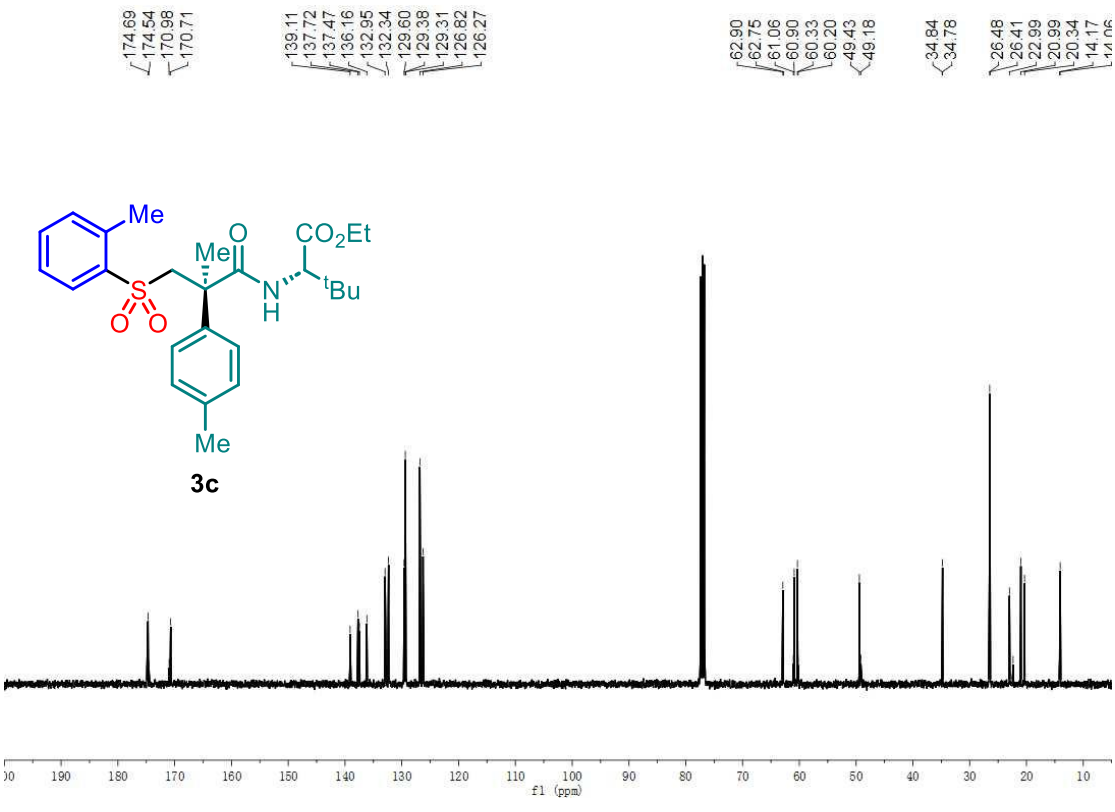

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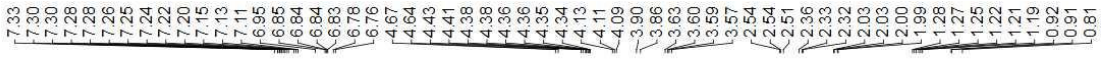

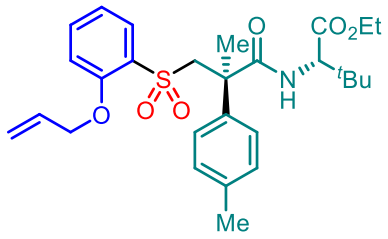

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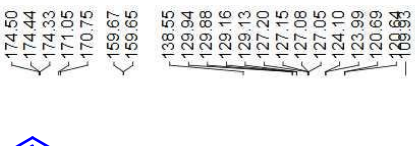

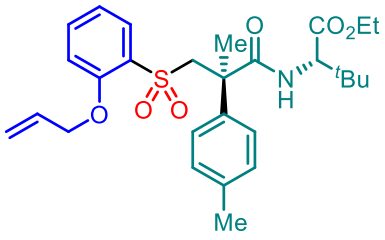

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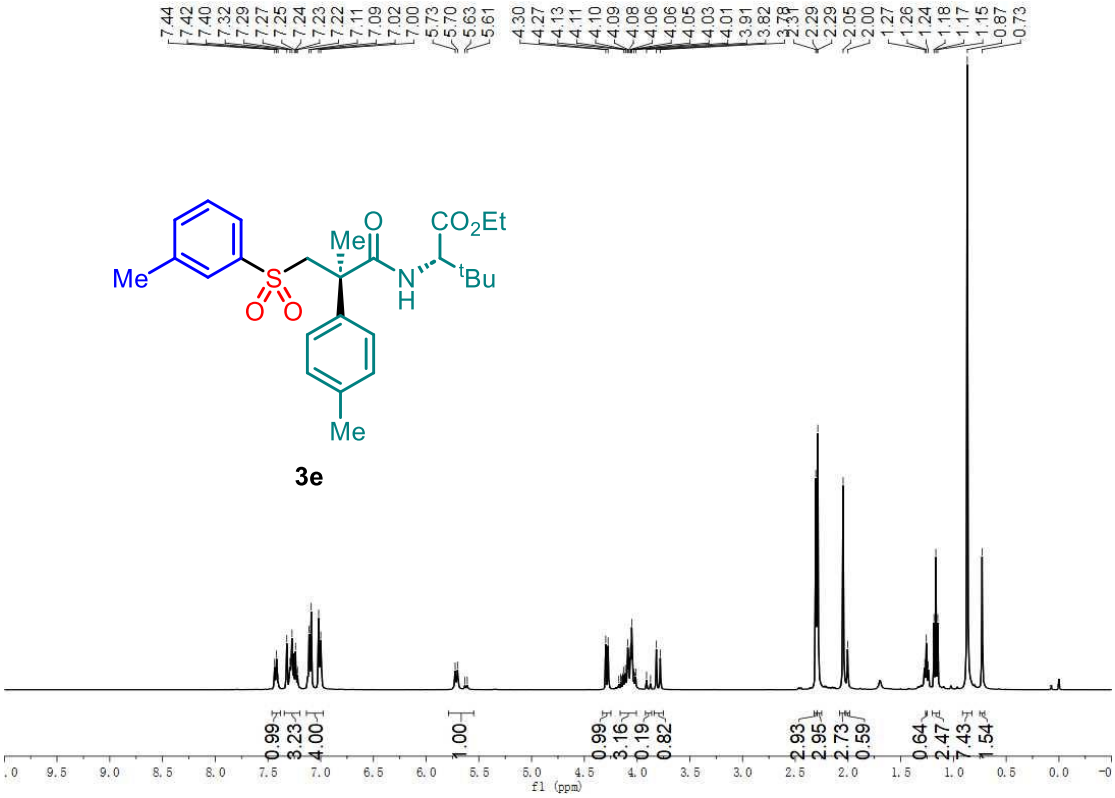
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4.11
4.10
4.09
4.08
4.06
4.06
4.05
4.03
4.01
3.91
3.82
3.78
2.31
2.29
2.29
2.05
2.00
1.27
1.26
1.24
1.18
1.17
1.15
0.87
0.73
Me
O
CO2Et
Me
S
N
H
tBu
O
O
Me
3e
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3.23
4.00
1.00
0.99
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2.95
2.73
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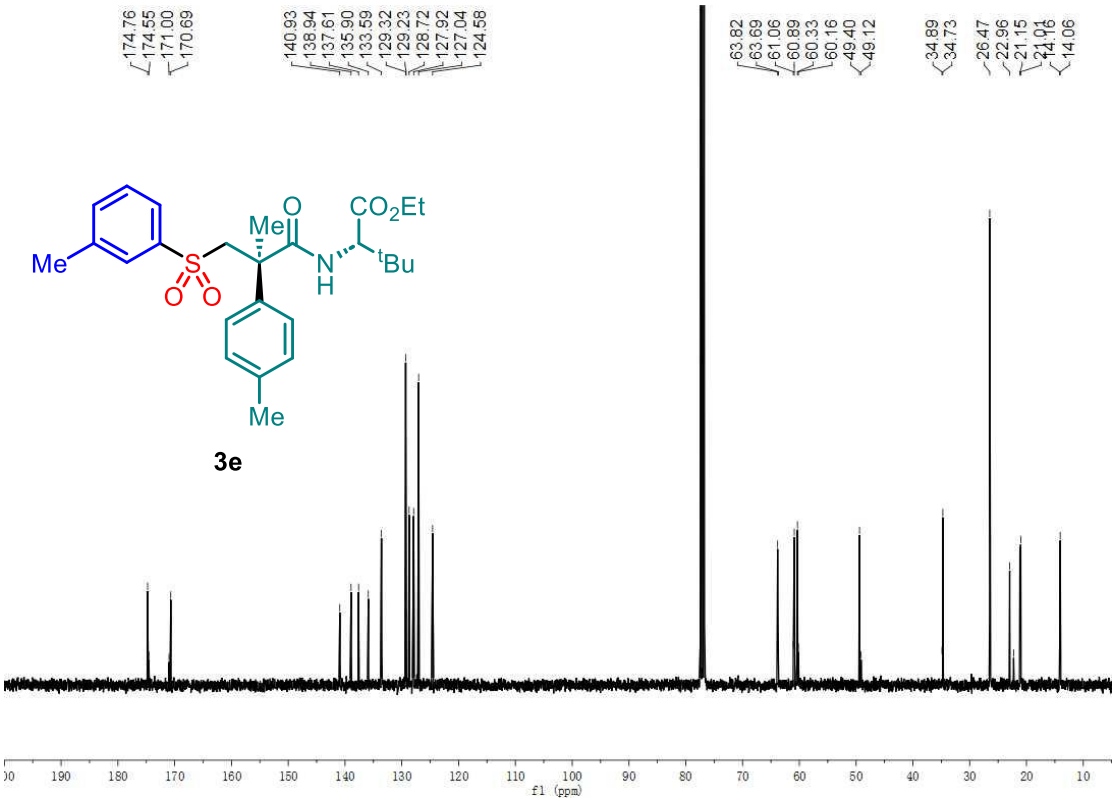
0.64
2.47
7.43
1.54
f1 (ppm)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124.58
63.82
63.69
61.06
60.89
60.33
60.16
49.40
49.12
34.89
34.73
26.47
22.96
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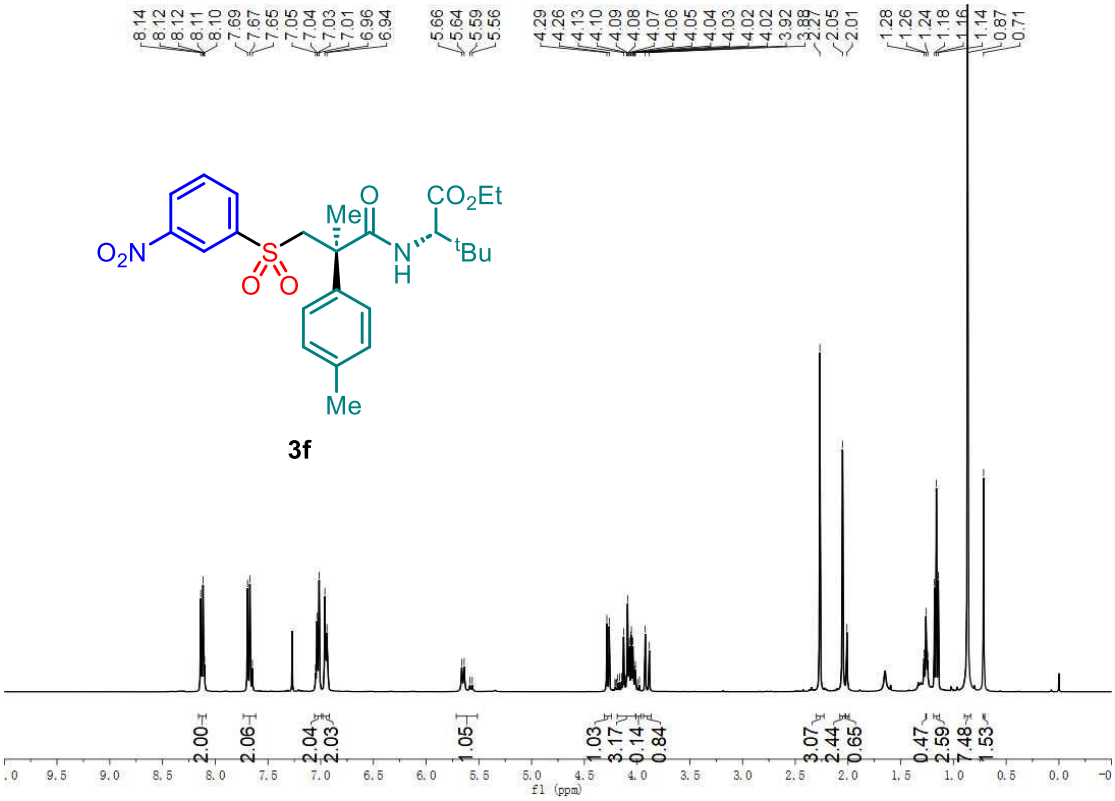
Me
O
CO2Et
Me
S
N
H
tBu
O
O
Me
3e
f1 (ppm)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5.64
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5.56
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4.26
4.13
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4.09
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.02
3.92
3.89
3.27
2.05
2.01
1.28
1.26
1.24
1.18
1.16
1.14
0.87
0.71
O2N
S
O
O
Me
O
N
H
CO2Et
tBu
Me
2.00
2.06
2.04
2.03
1.05
1.03
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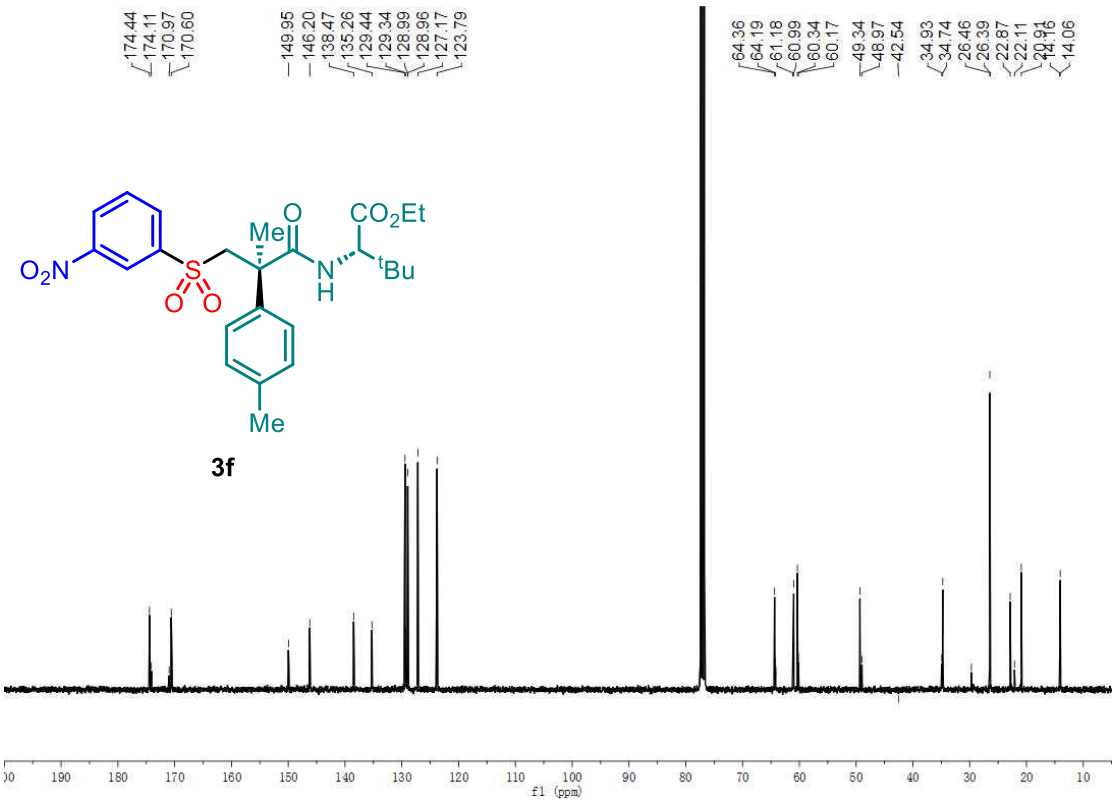
0.65
0.47
2.59
7.48
1.53
f1 (ppm)

3f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64.19
61.18
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60.34
60.17
49.34
48.97
42.54
34.93
34.74
26.46
26.39
22.87
22.11
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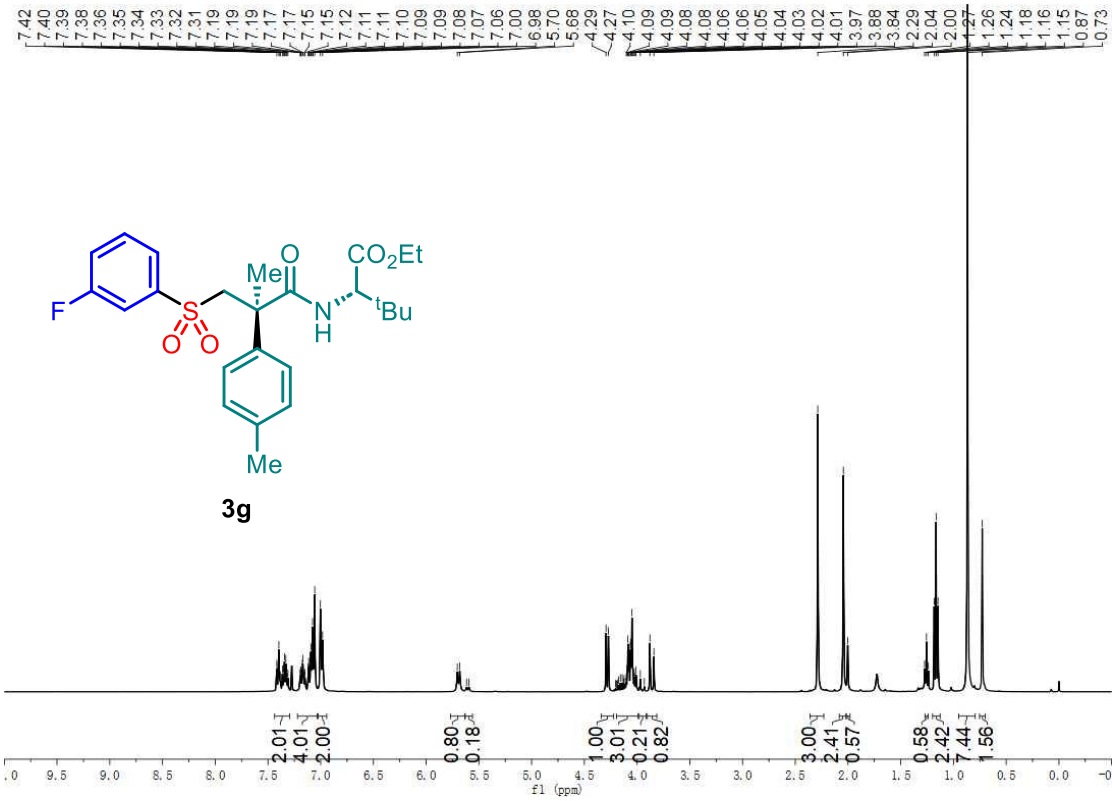
14.06
O2N
S
O
O
Me
O
N
H
CO2Et
tBu
Me
f1 (ppm)

3f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7.19
7.17
7.17
7.15
7.15
7.12
7.11
7.11
7.10
7.09
7.09
7.08
7.07
7.06
7.00
6.98
5.70
5.68
4.29
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4.09
4.09
4.08
4.08
4.06
4.06
4.05
4.04
4.03
4.02
4.01
3.97
3.88
3.84
2.29
2.04
2.00
1.27
1.26
1.24
1.18
1.16
1.15
0.87
0.73
F
S
O
O
Me
O
N
H
CO2Et
tBu
Me
2.01
4.01
2.00
0.80
0.18
1.00
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3.00
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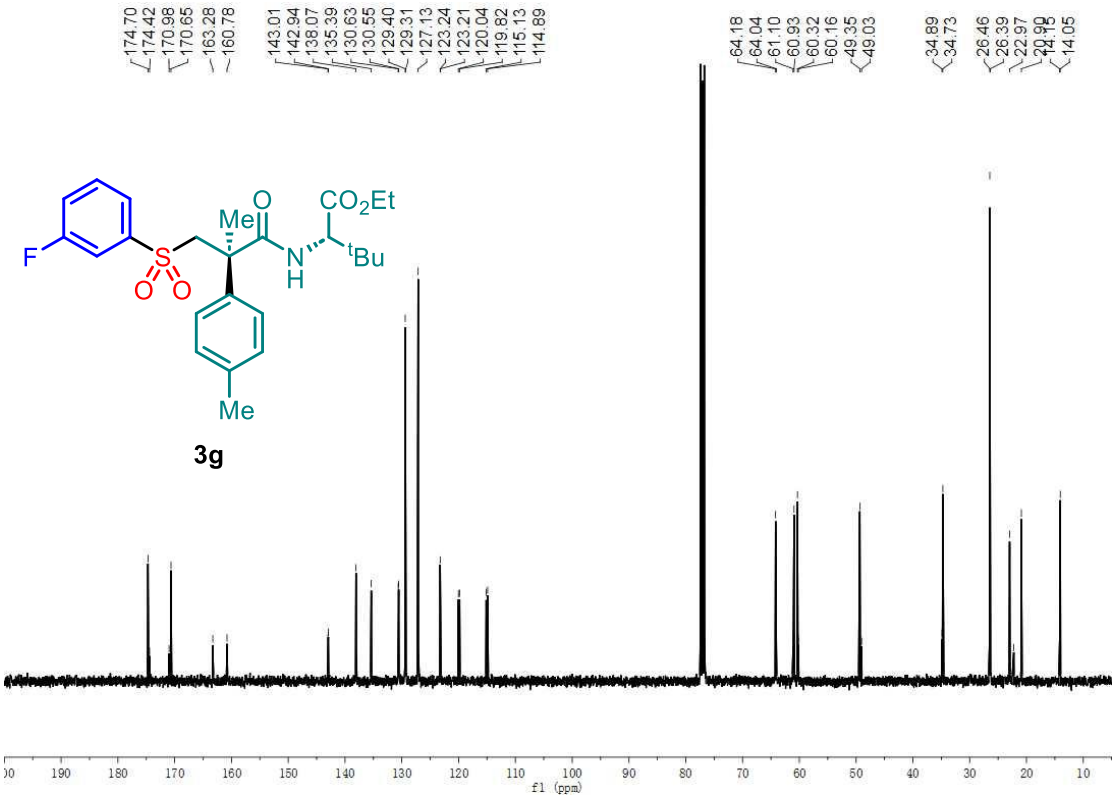
0.57
0.58
2.42
7.44
1.56
f1 (ppm)

3g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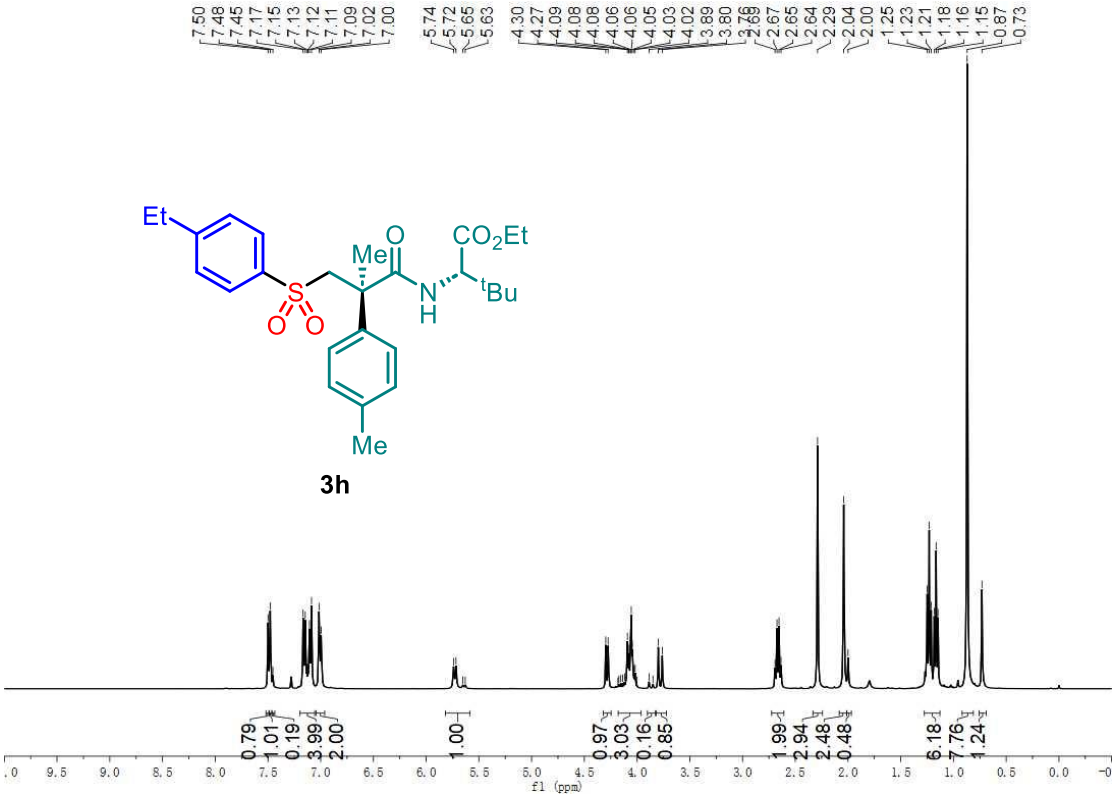
129.40
129.31
127.13
123.24
123.21
120.04
119.82
115.13
114.89
64.18
64.04
61.10
60.93
60.32
60.16
49.35
49.03
34.89
34.73
26.46
26.39
22.97
14.05
F
S
O
O
Me
O
N
H
CO2Et
tBu
Me
f1 (ppm)

3g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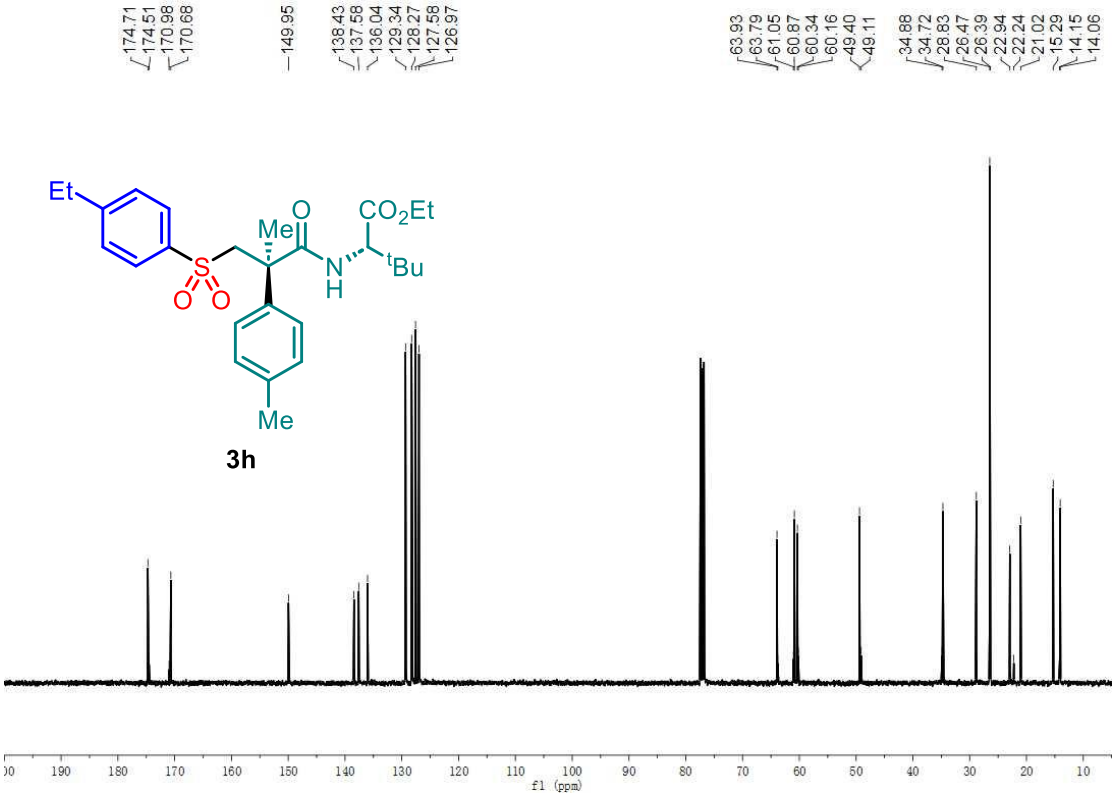
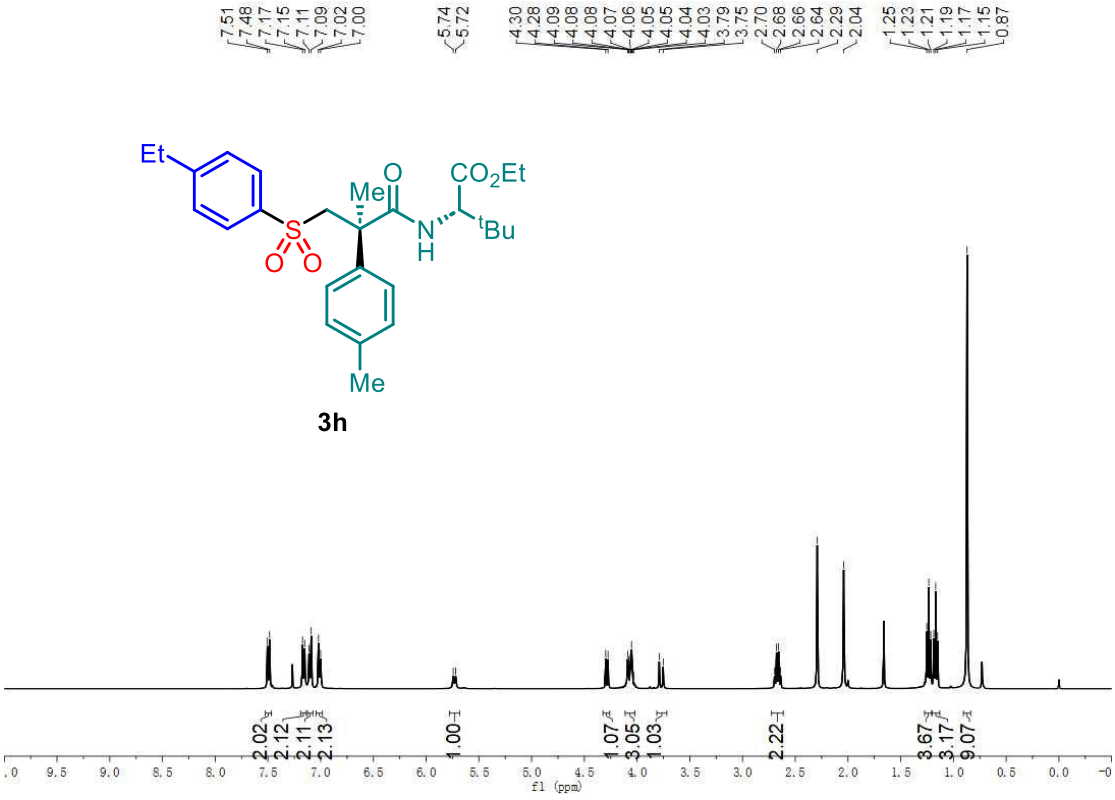
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3h
f1 (ppm)


Et
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3h
f1 (ppm)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4.28
4.09
4.08
4.08
4.07
4.06
4.05
4.05
4.04
4.03
3.79
3.75
2.70
2.68
2.66
2.64
2.29
2.04
1.25
1.23
1.21
1.19
1.17
1.15
0.87
Et
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3h
2.02
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1.00
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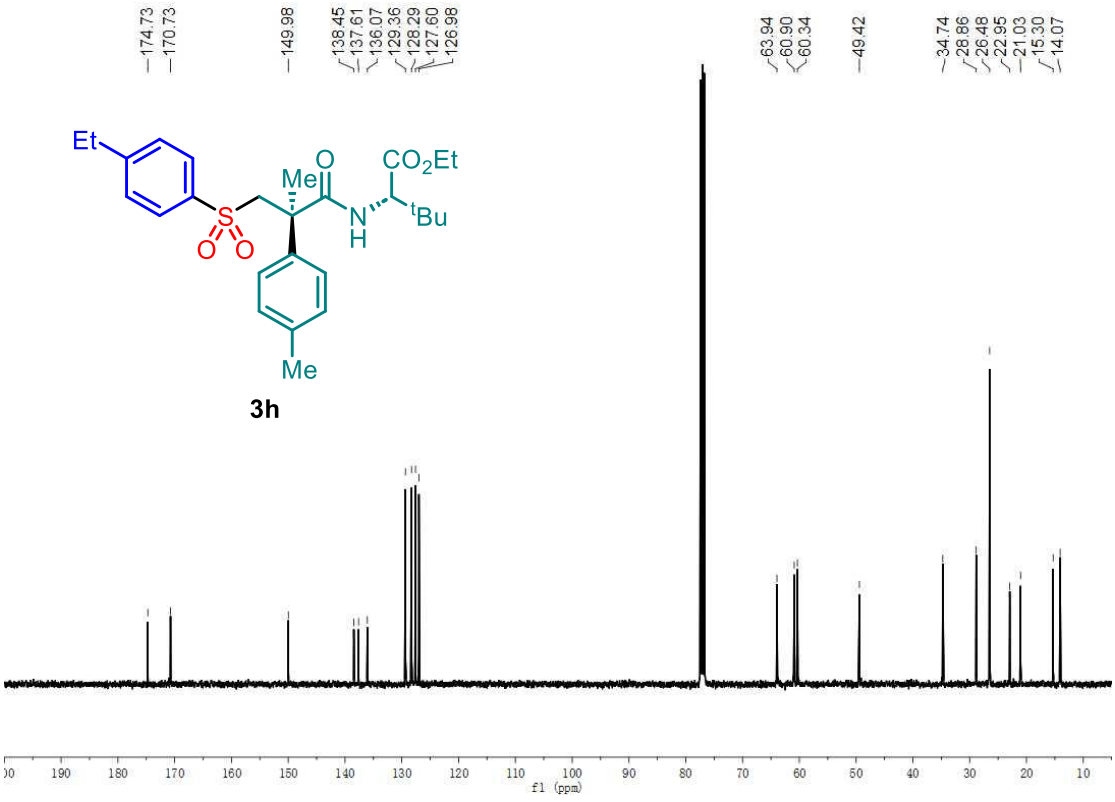
3.05
1.03
2.22
3.67
3.17
9.07
f1 (ppm)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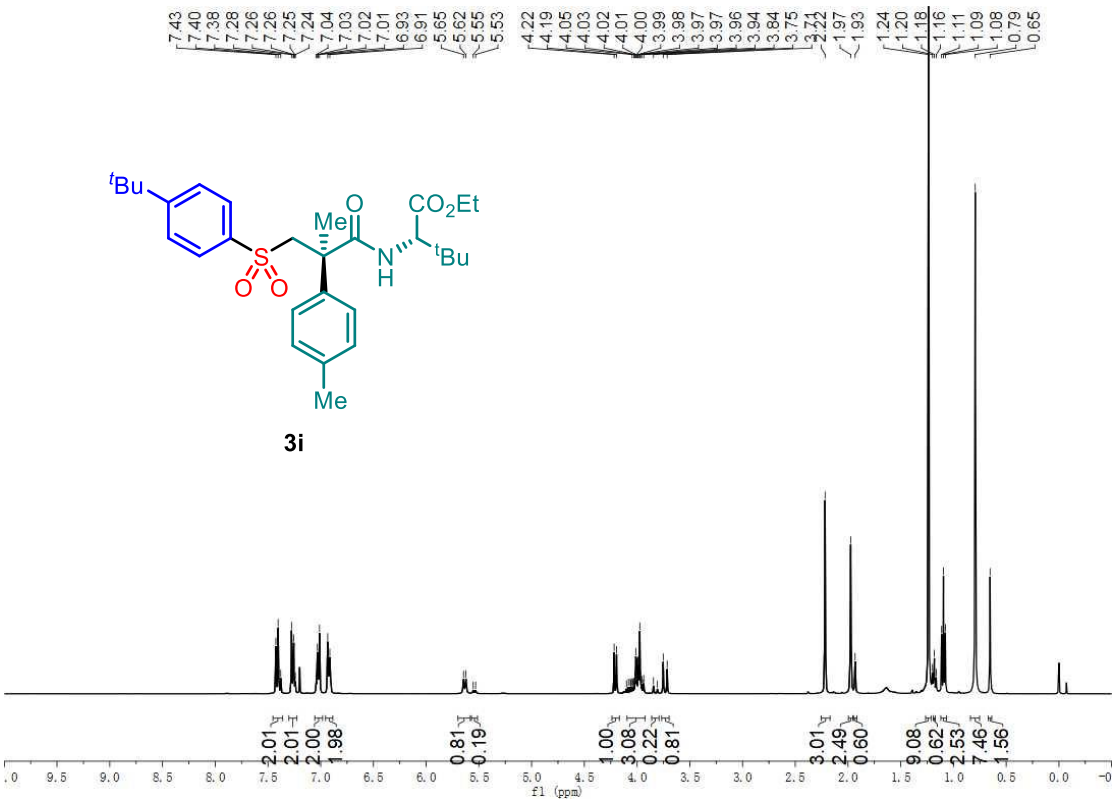
127.60
126.98
63.94
60.90
60.34
49.42
34.74
28.86
26.48
22.95
21.03
15.30
14.07
Et
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3h
f1 (ppm)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4.02
4.01
4.00
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3.96
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3.71
2.22
1.97
1.93
1.24
1.20
1.18
1.16
1.11
1.09
1.08
0.79
0.65
tBu
Me
O
CO2Et
N
H
tBu
S
O
O
Me
2.01
2.01
2.00
1.98
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0.19
1.00
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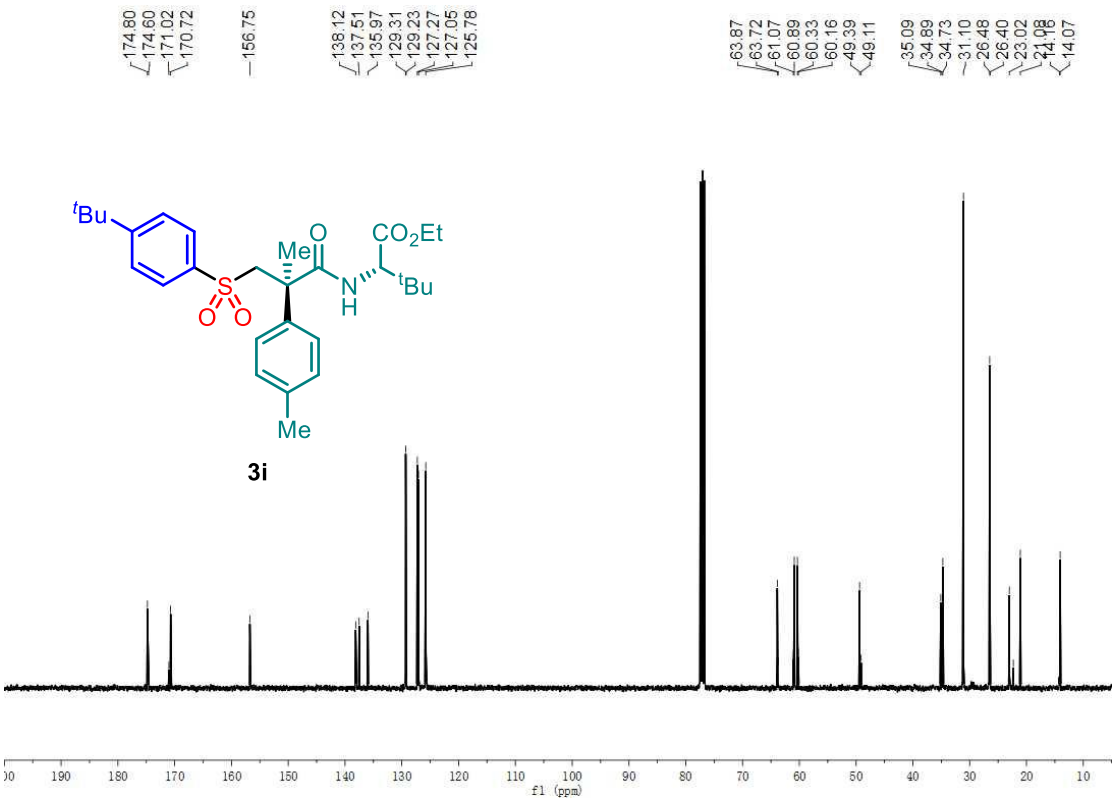
f1 (ppm)

3i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127.27
127.05
125.78
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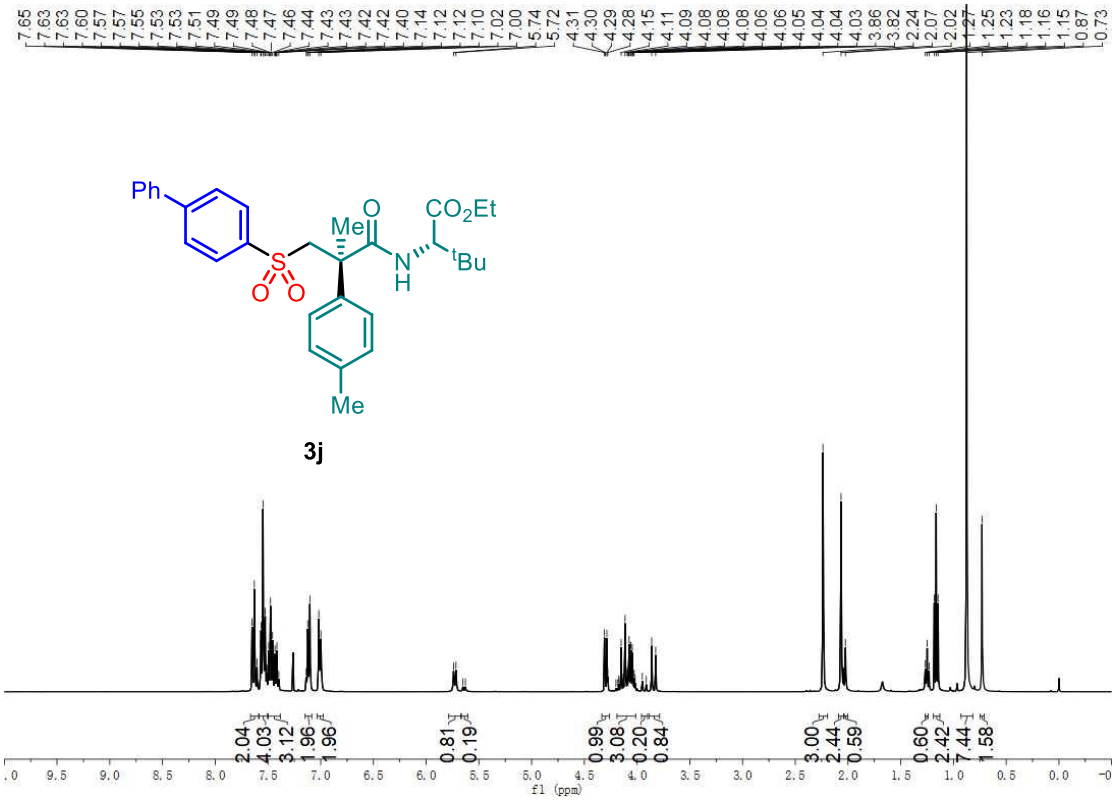
63.72
61.07
60.89
60.33
60.16
49.39
49.11
35.09
34.89
34.73
31.10
26.48
26.40
23.02
21.98
14.07
tBu
Me
O
CO2Et
N
H
tBu
S
O
O
Me
f1 (ppm)

3i



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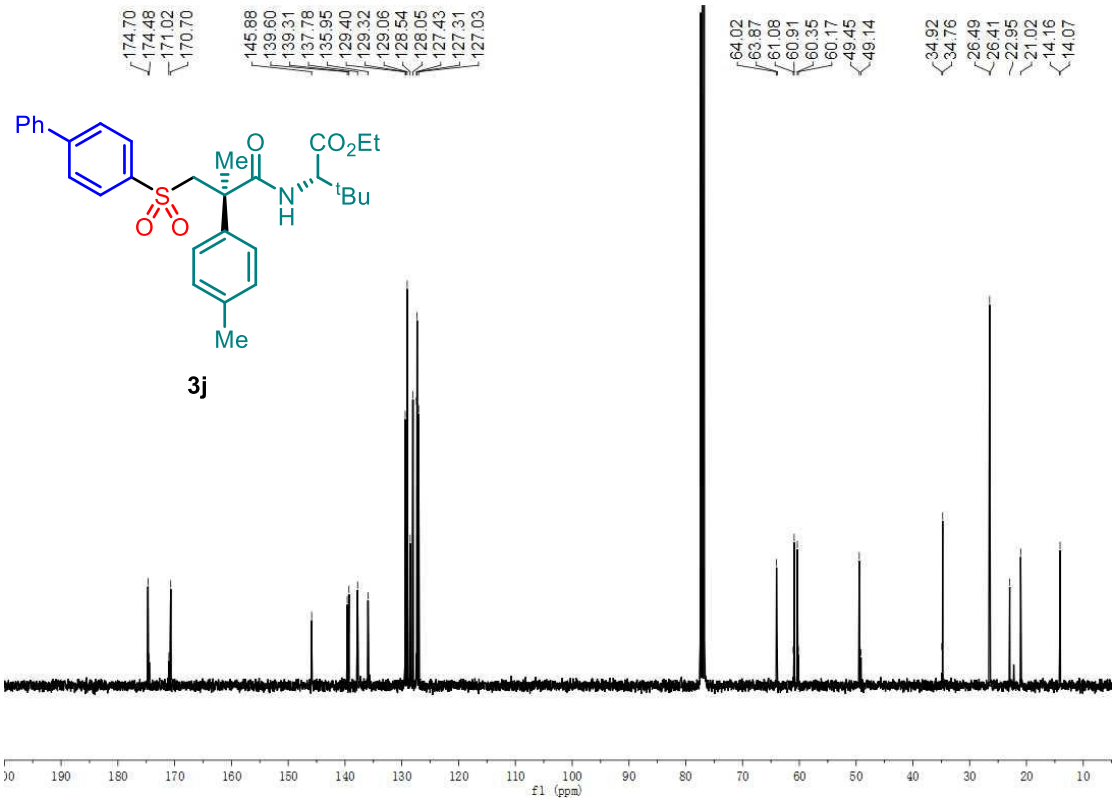

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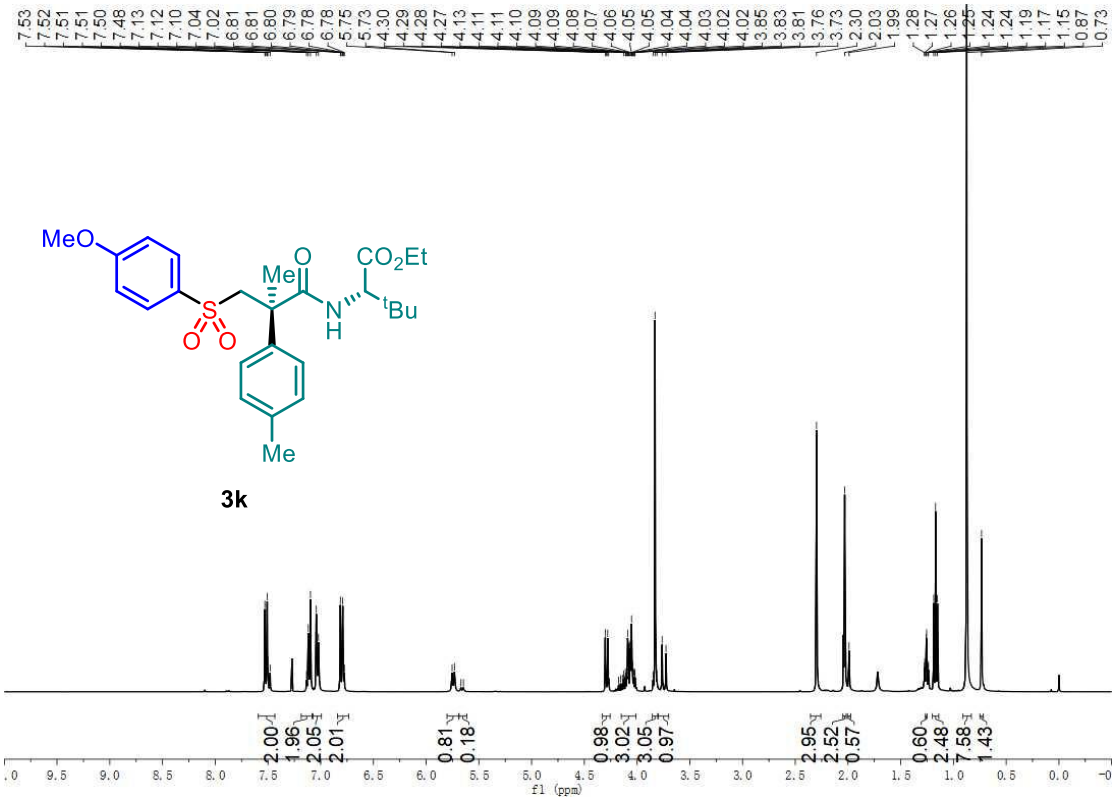
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CO2Et
N
H
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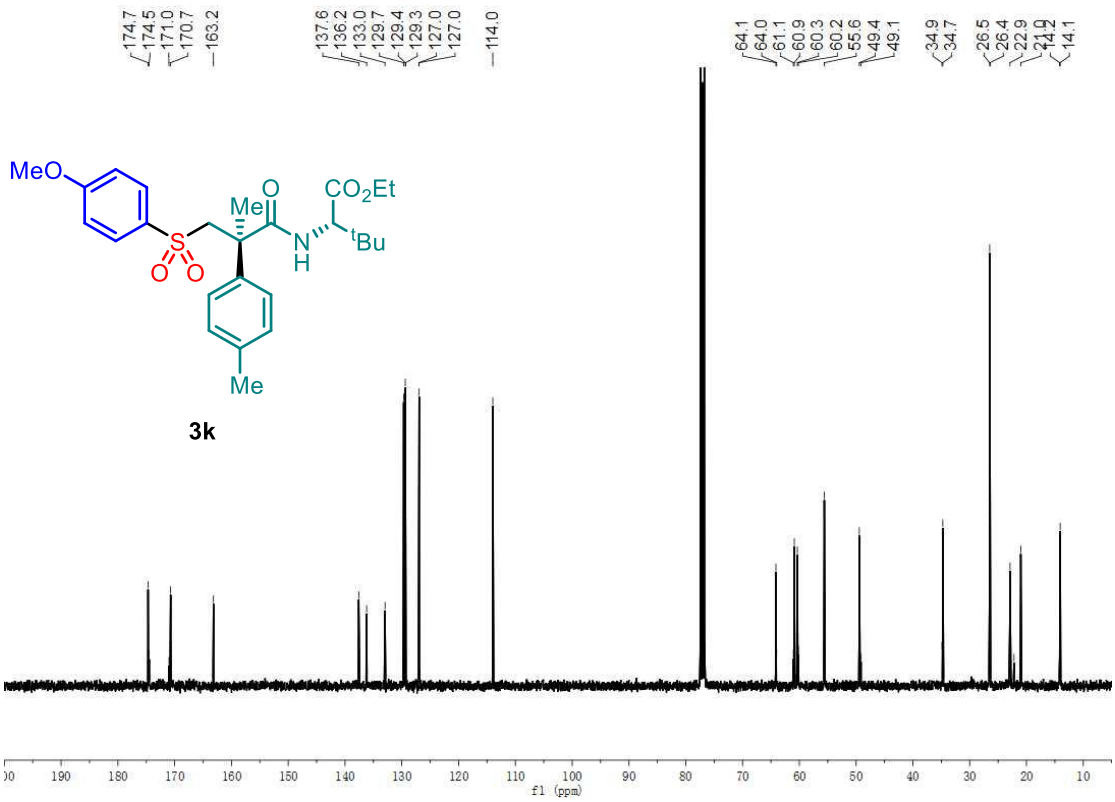
S
O
O
Me
3k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Me
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CO2Et
N
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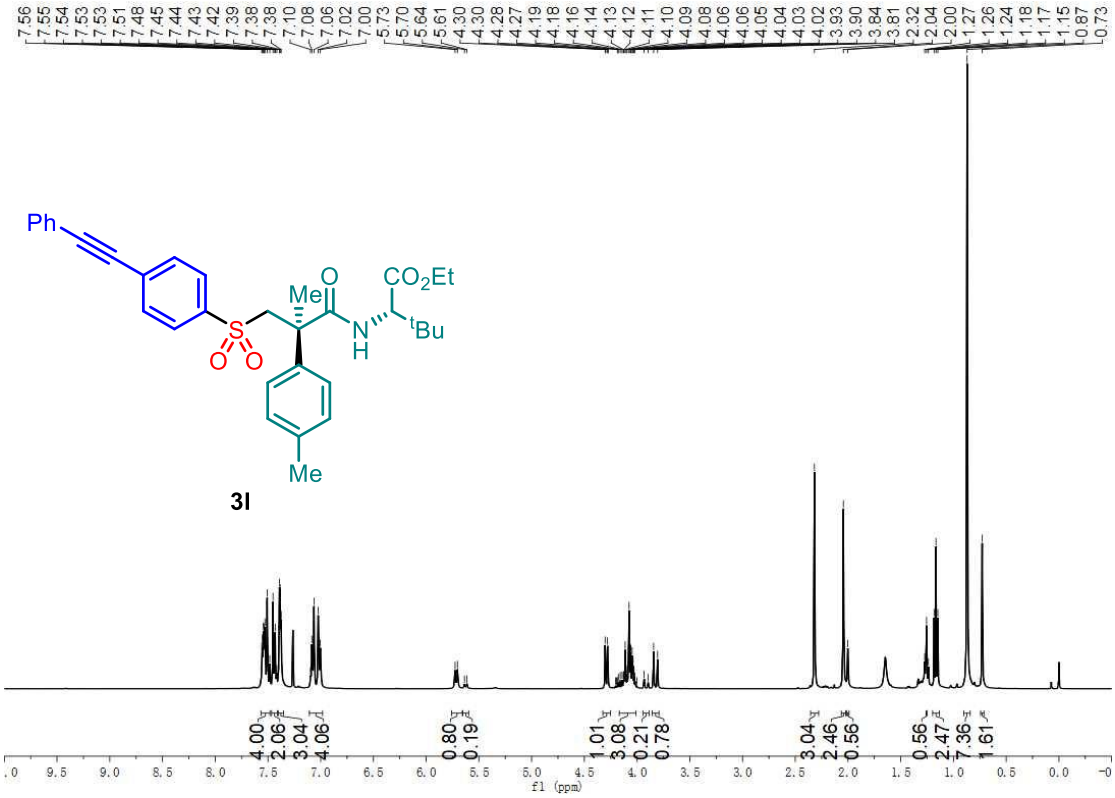
S
O
O
Me
3k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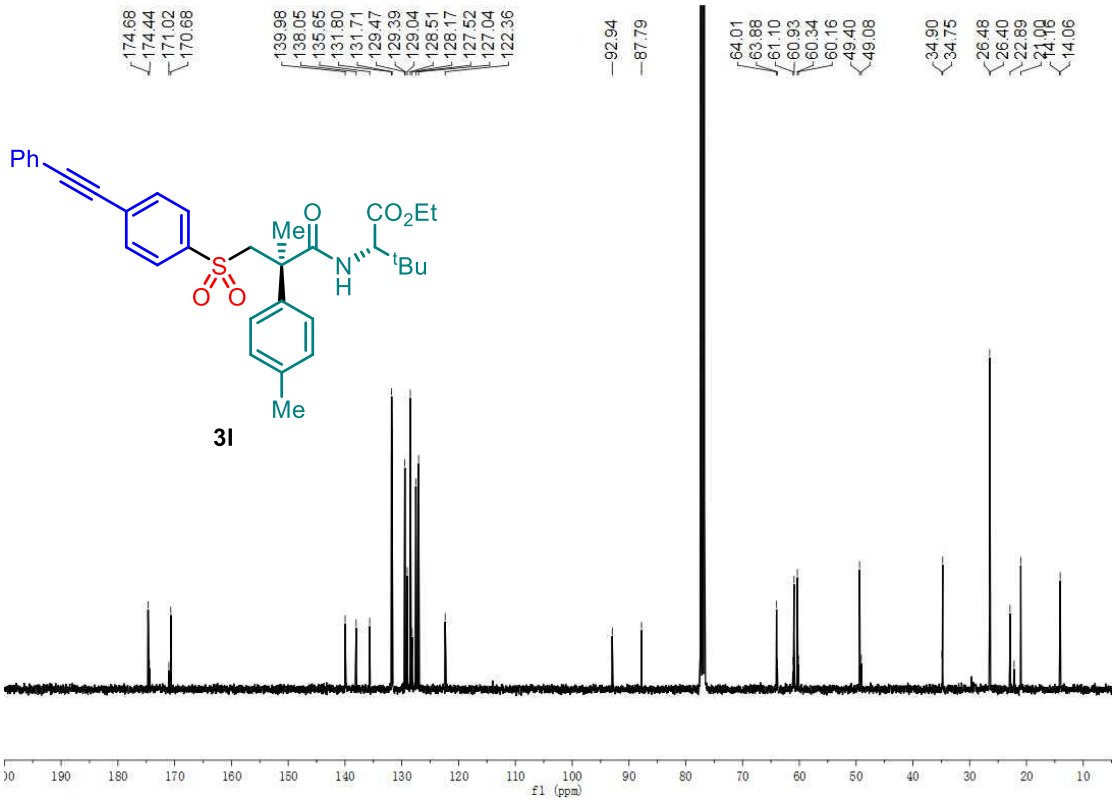
3l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CO2Et
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H
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S
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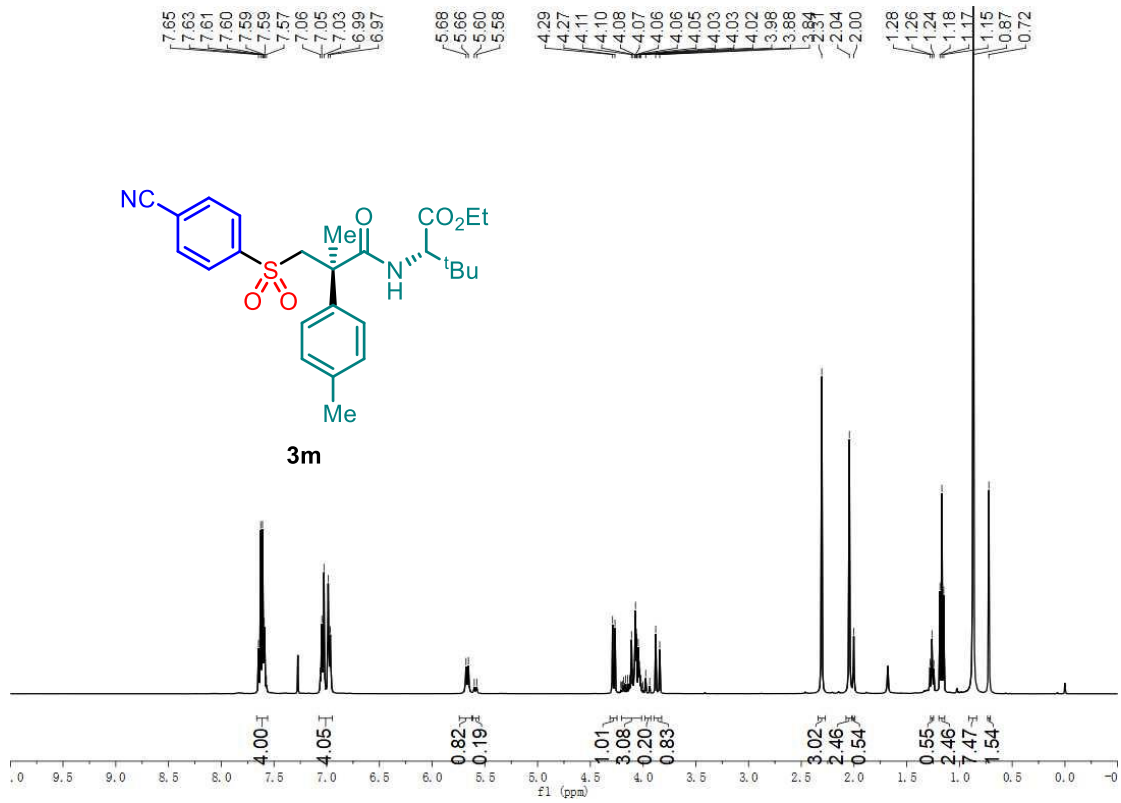
O
Me
3l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5.58
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4.27
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4.08
4.07
4.06
4.06
4.05
4.03
4.03
4.02
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2.04
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1.26
1.24
1.18
1.17
1.15
0.87
0.72
NC
Me
O
CO2Et
N
H
tBu
S
O
O
Me
4.00
4.05
0.82
0.19
1.01
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3.02
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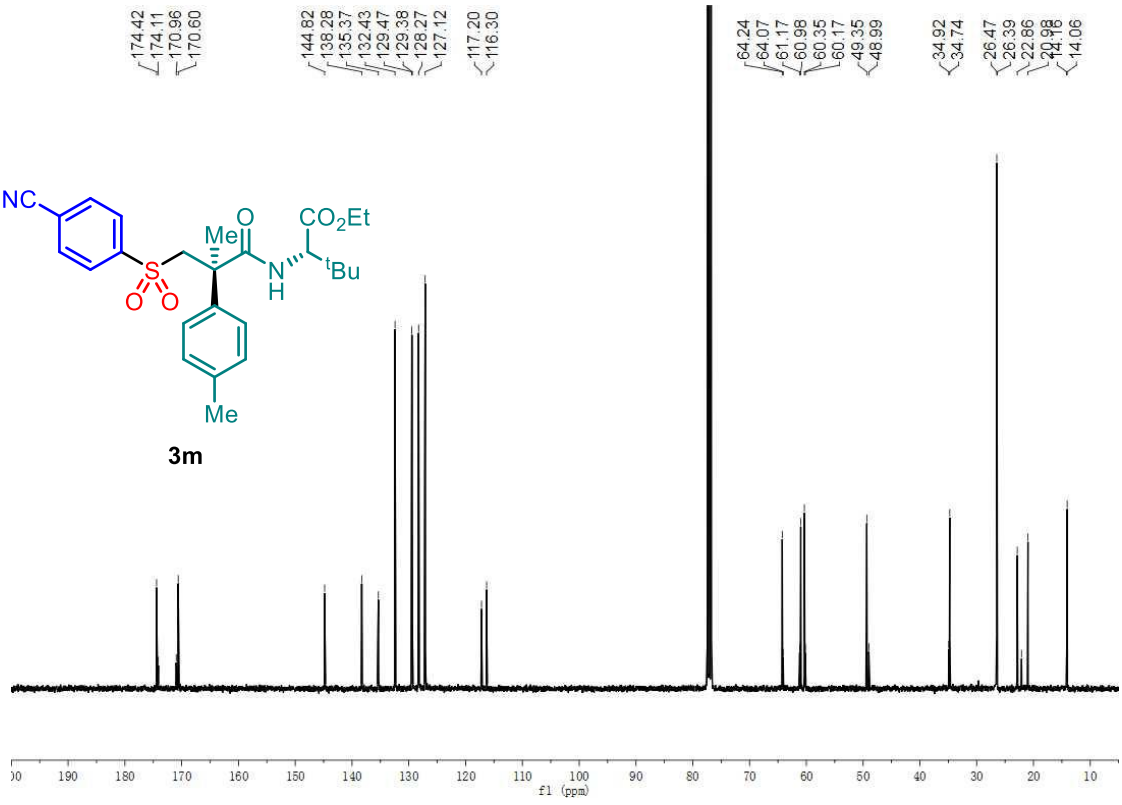
2.46
7.47
1.54
f1 (ppm)

3m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129.38
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127.12
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116.30
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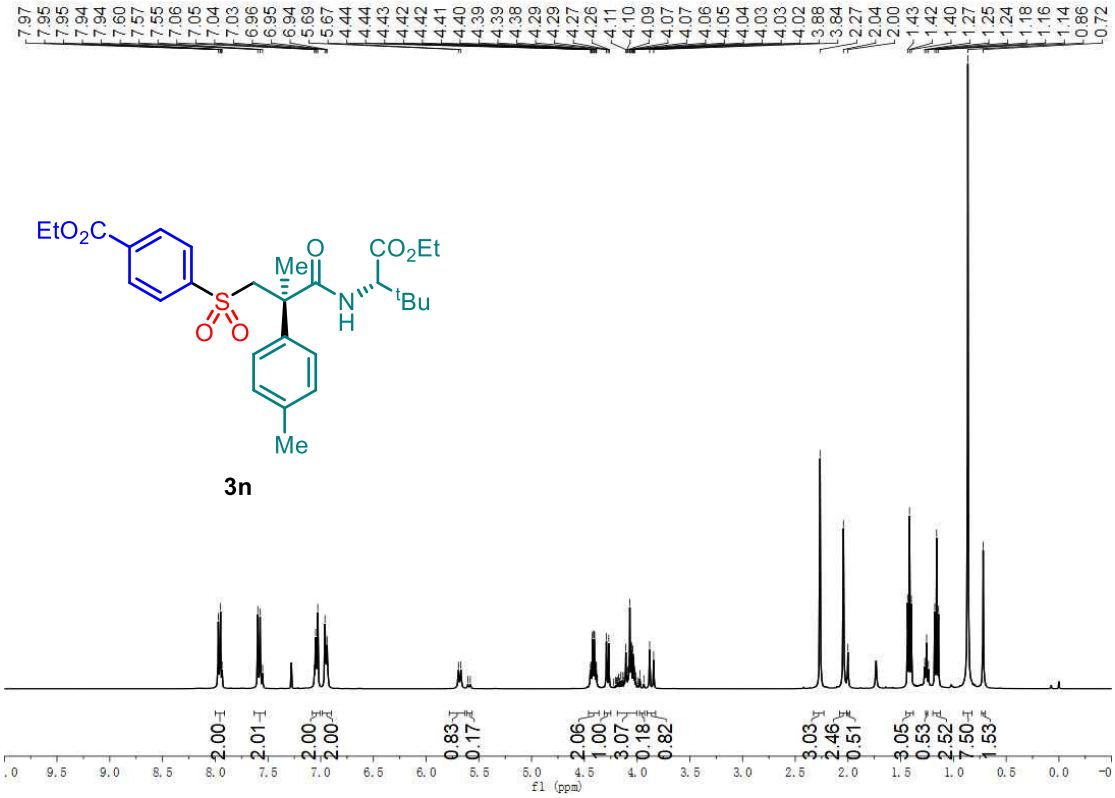
60.98
60.35
60.17
49.35
48.99
34.92
34.74
26.47
26.39
22.86
22.98
14.16
14.06
NC
Me
O
CO2Et
N
H
tBu
S
O
O
Me
f1 (ppm)

3m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4.09
4.07
4.07
4.06
4.05
4.04
4.03
4.02
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3.84
2.27
2.04
2.00
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1.42
1.40
1.27
1.25
1.24
1.18
1.16
1.14
0.86
0.72
EtO2C
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3n
2.00
2.01
2.00
2.00
0.83
0.17
2.06
1.00
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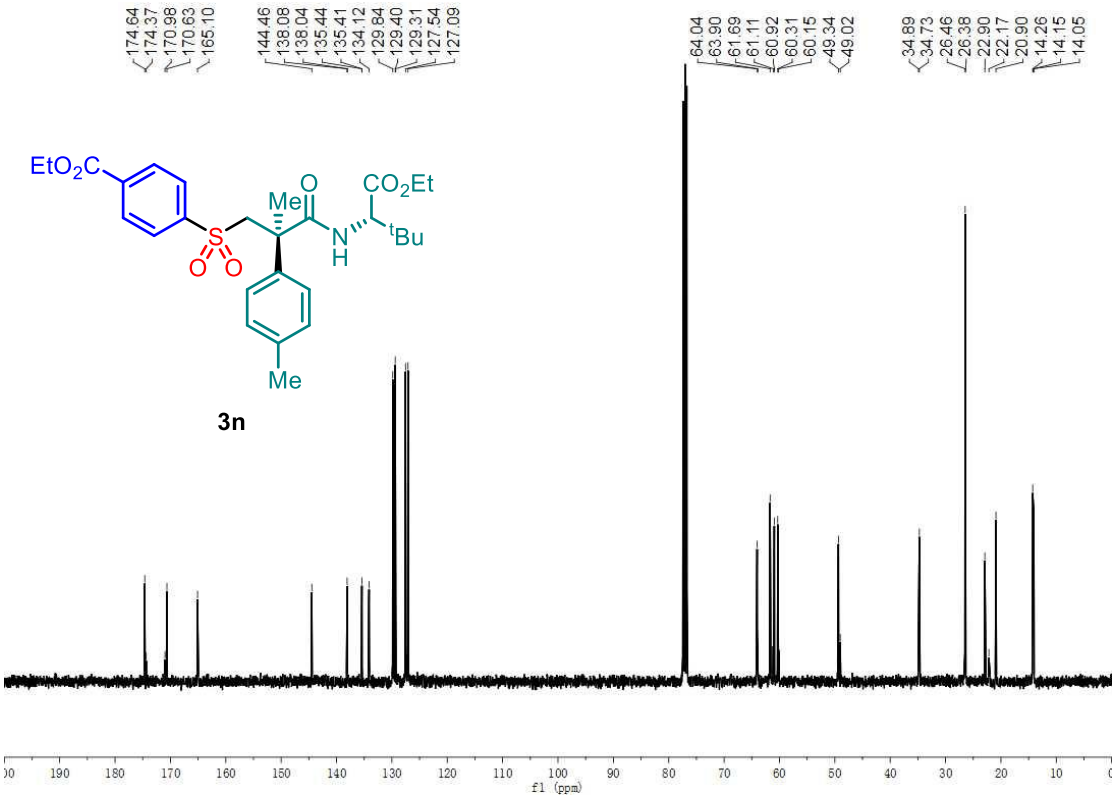
7.50
1.53
f1 (ppm)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127.54
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64.04
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34.73
26.46
26.38
22.90
22.17
20.90
14.26
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EtO2C
Me
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CO2Et
N
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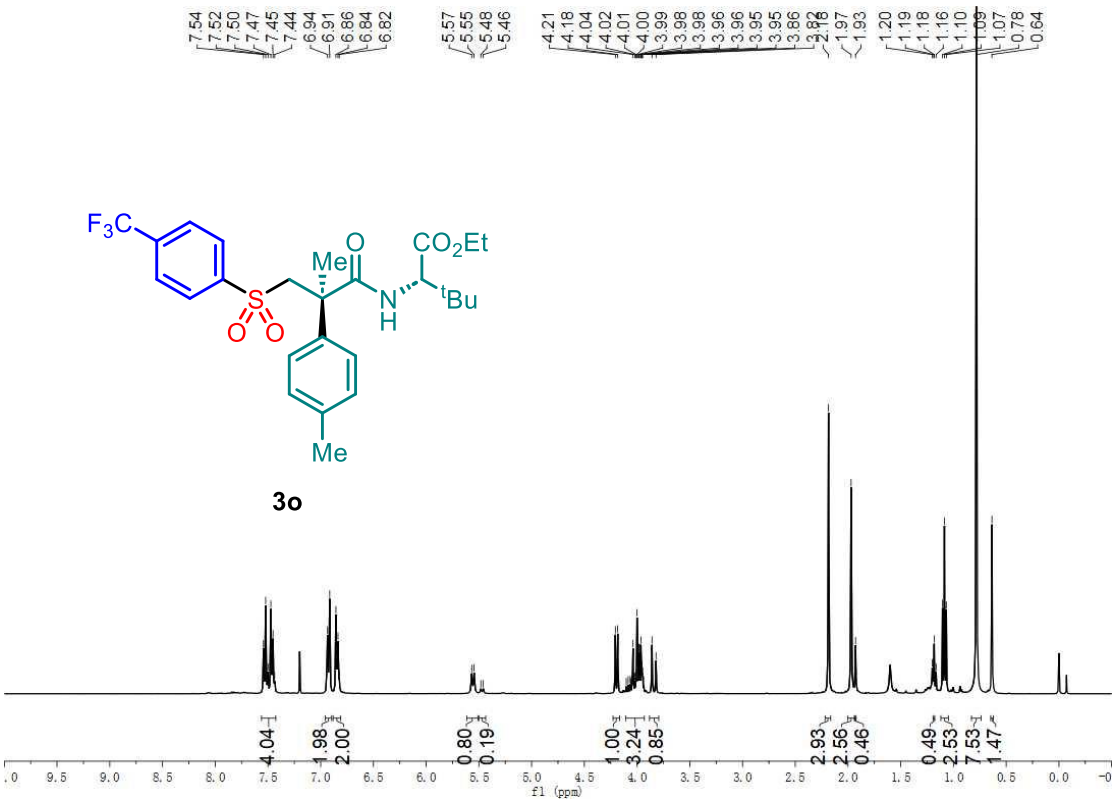
tBu
S
O
O
Me
3n
f1 (ppm)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5.55
5.48
5.46
4.21
4.18
4.04
4.02
4.01
4.00
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1.09
1.07
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S
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O
N
H
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3o
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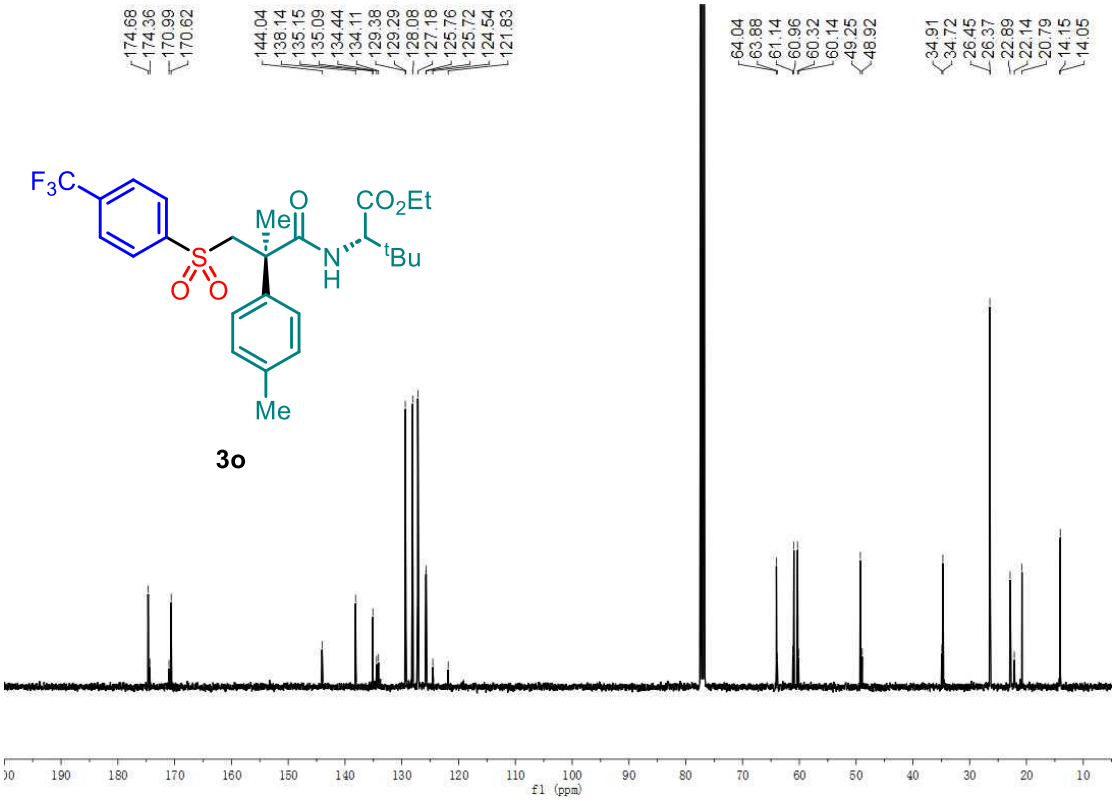
1.47
f1 (ppm)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61.14
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60.32
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34.91
34.72
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26.37
22.89
22.14
20.79
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O
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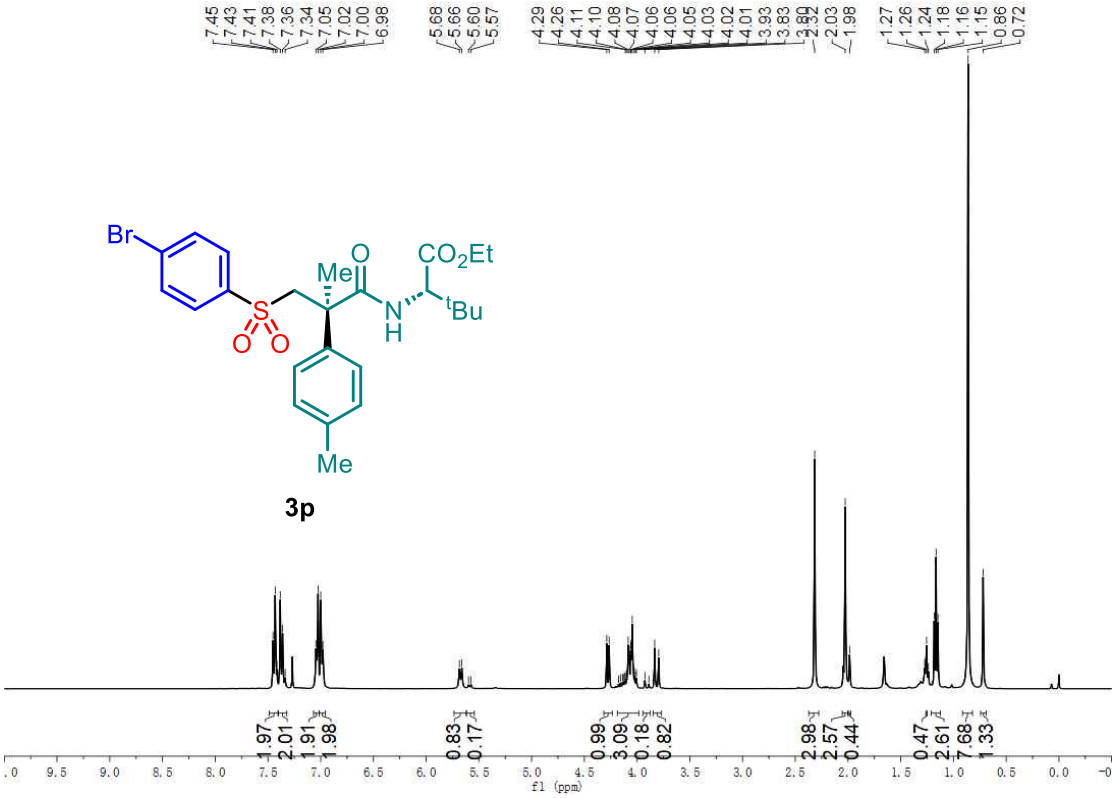
N
H
tBu
Me
3o
f1 (ppm)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N
H
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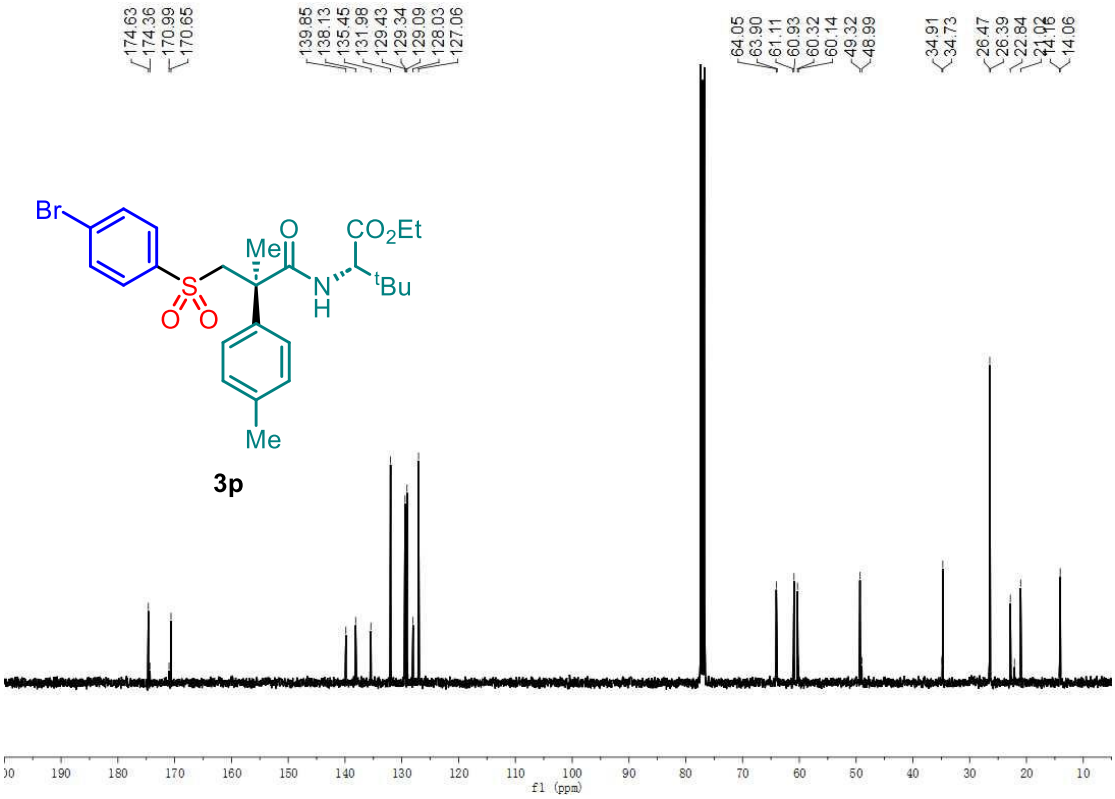
Me
3p
f1 (ppm)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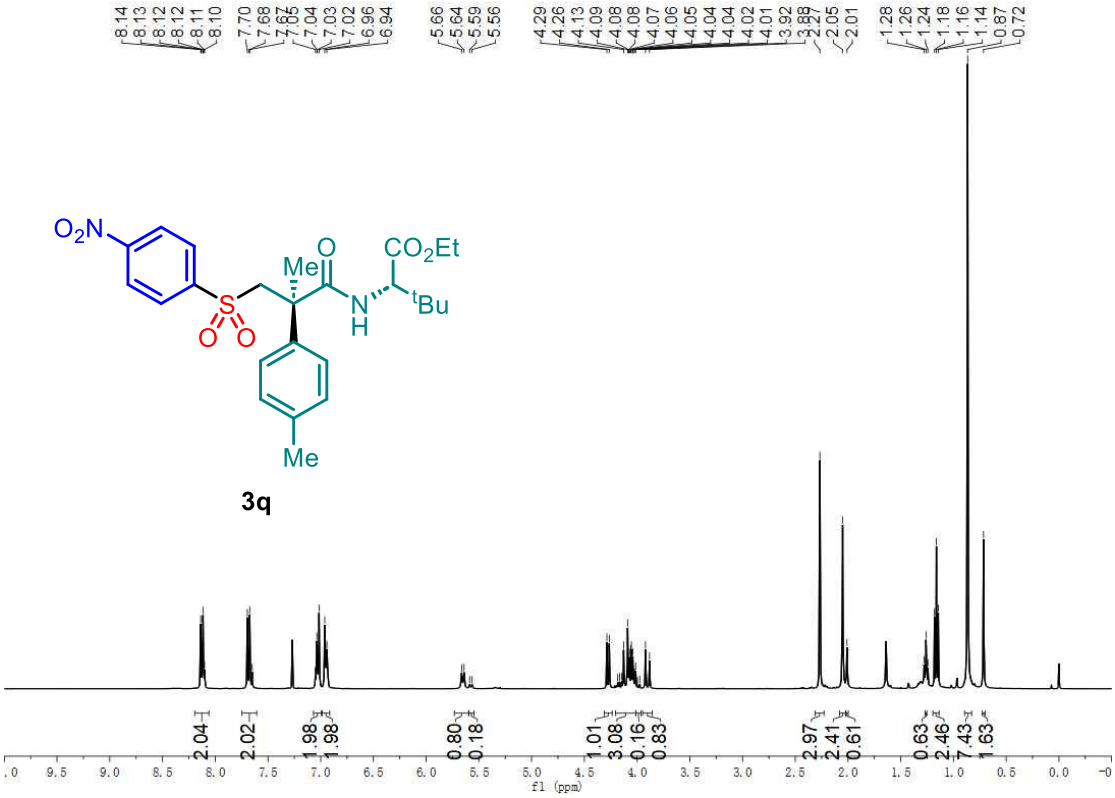
3p
f1 (ppm)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4.02
4.01
3.92
3.89
3.87
2.05
2.01
1.28
1.26
1.24
1.18
1.16
1.14
0.87
0.72
O2N
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3q
2.04
2.02
1.98
1.98
0.80
0.18
1.01
3.08
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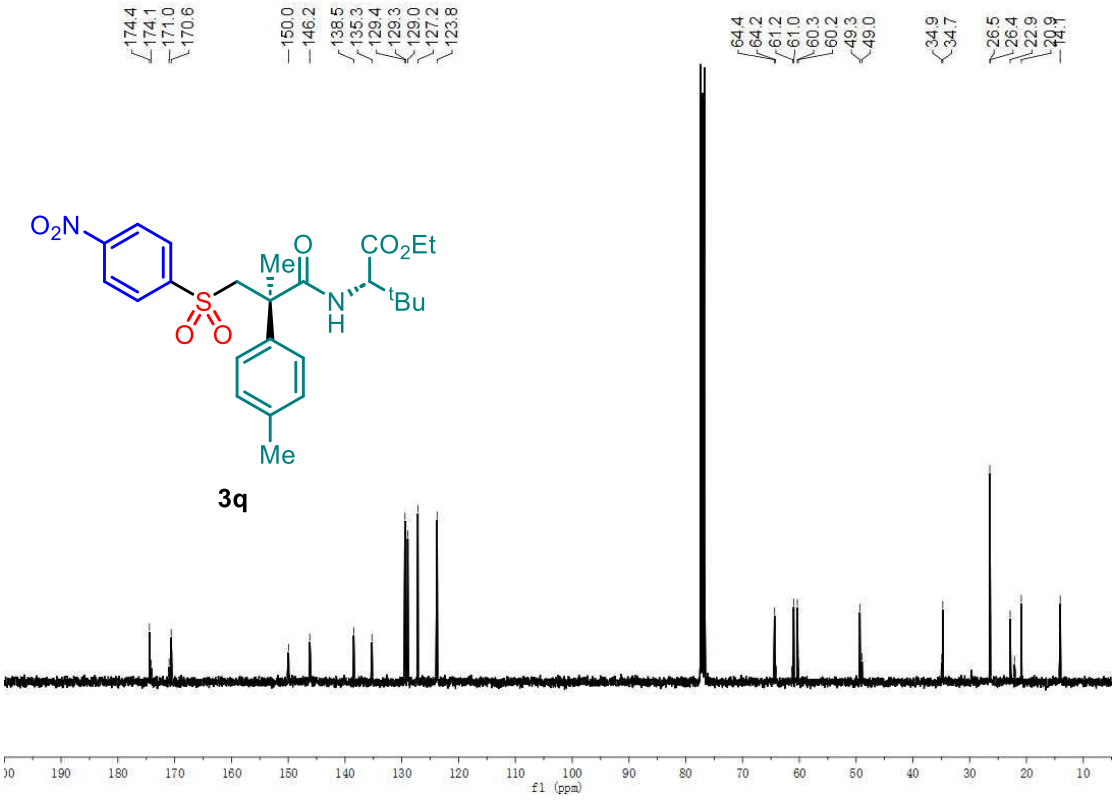
0.83
2.97
2.41
0.61
0.63
2.46
7.43
1.63
f1 (ppm)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146.2
138.5
135.3
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129.3
129.0
127.2
123.8
64.4
64.2
61.2
61.0
60.3
60.2
49.3
49.0
34.9
34.7
26.5
26.4
22.9
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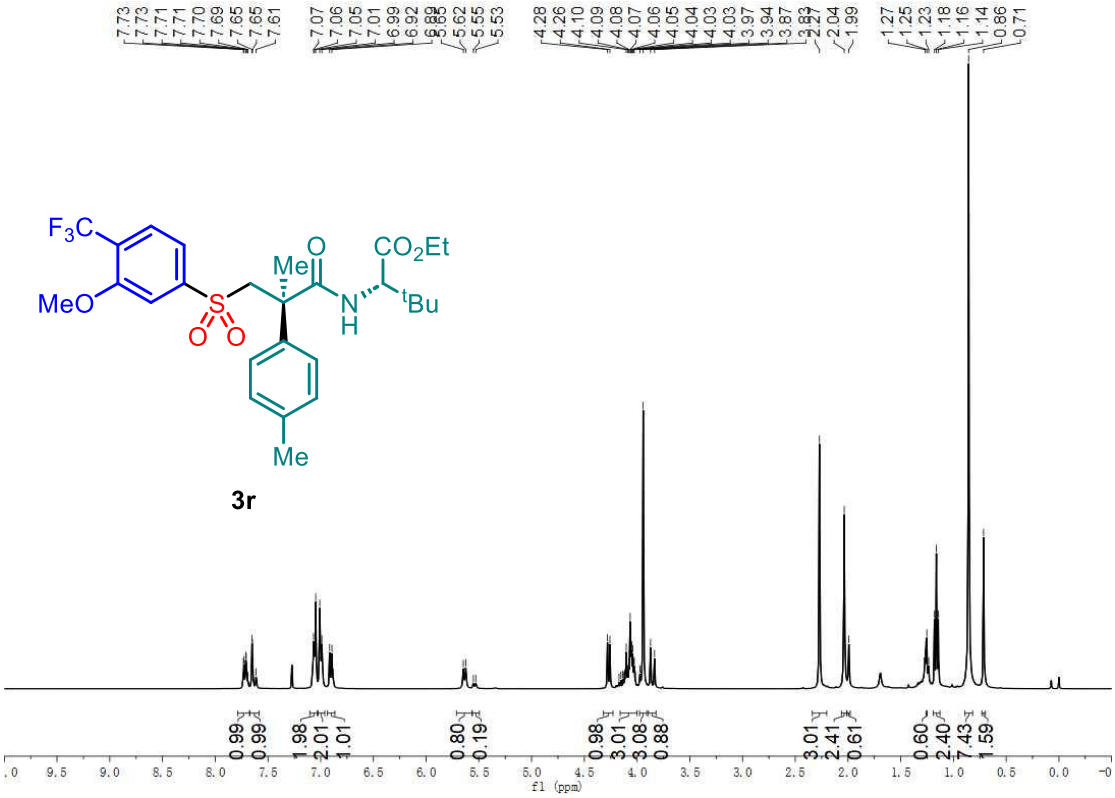
Me
O
CO2Et
N
H
tBu
S
O
O
Me
3q
f1 (ppm)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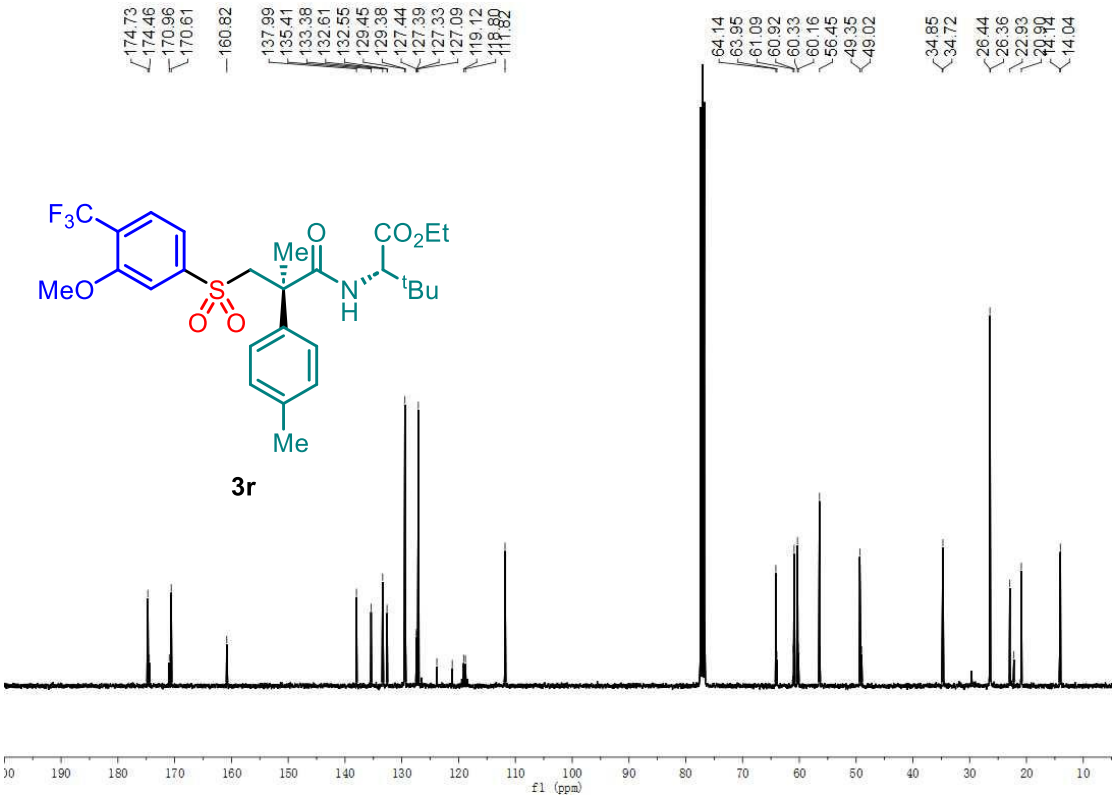
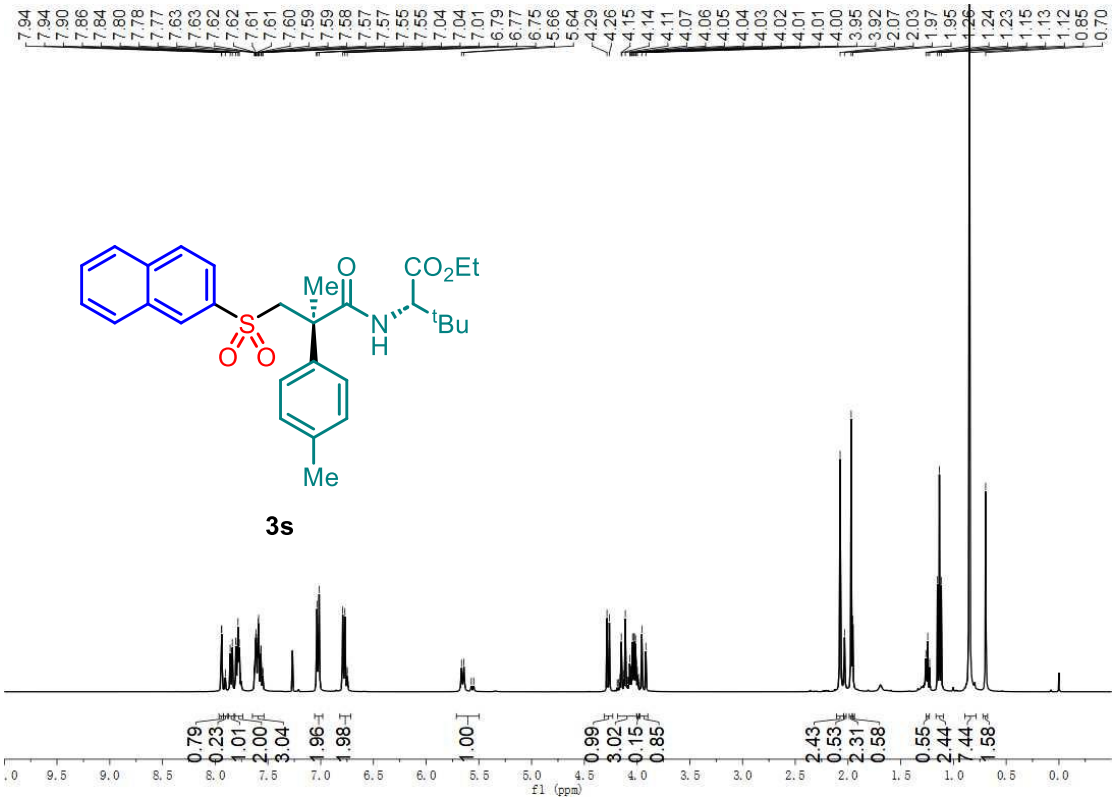
MeO
S
O
O
Me
O
N
H
CO2Et
tBu
Me
3r
f1 (ppm)


F3C
MeO
S
O
O
Me
O
N
H
CO2Et
tBu
Me
3r
f1 (ppm)



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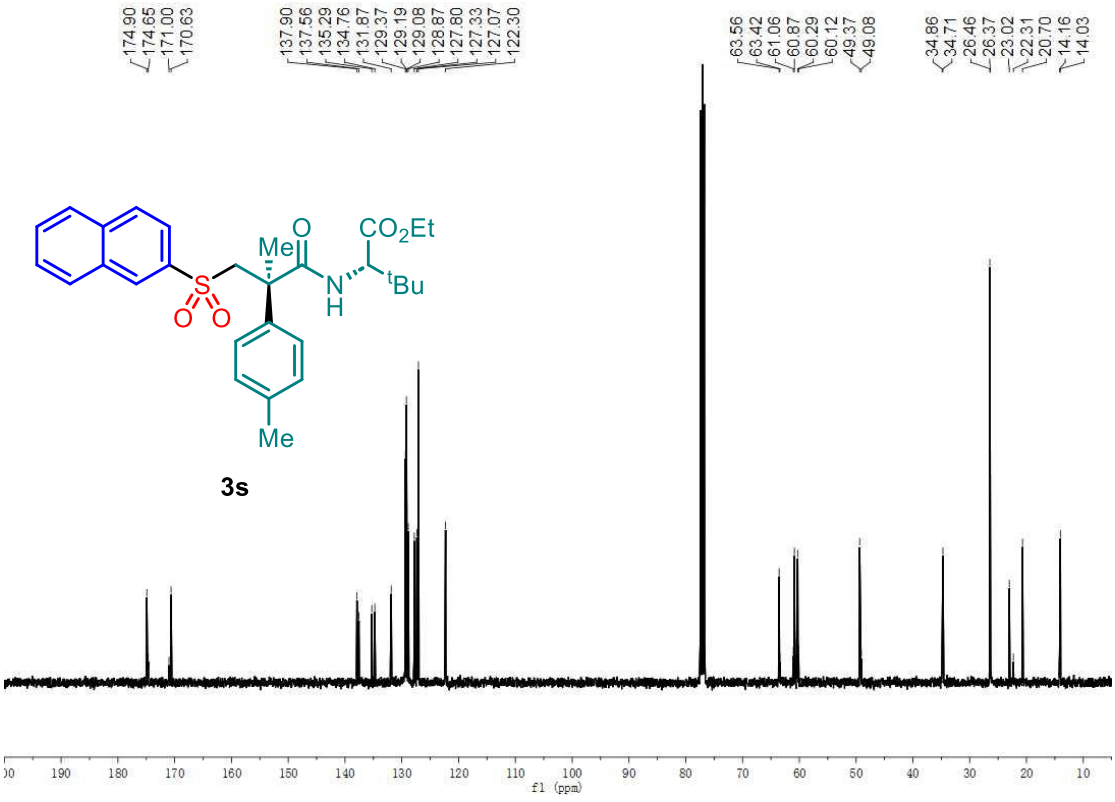

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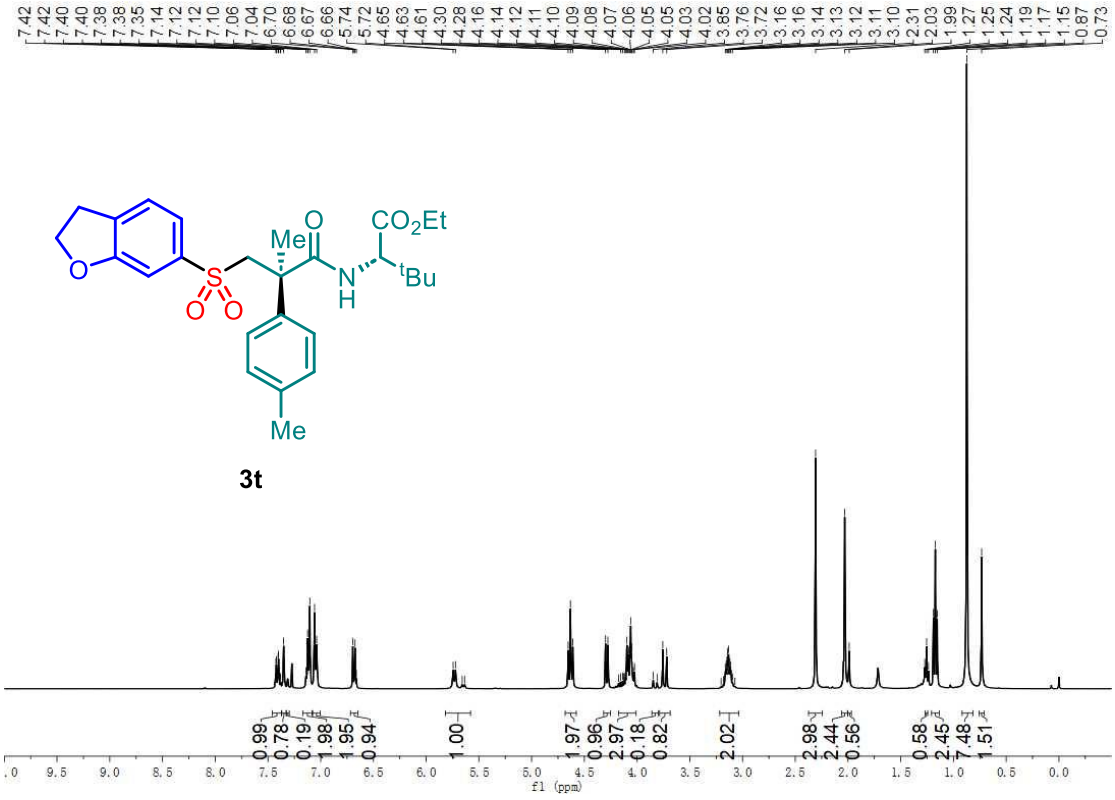
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7.14
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7.12
7.10
7.06
7.04
6.70
6.68
6.67
6.66
5.74
5.72
4.65
4.63
4.61
4.30
4.28
4.16
4.14
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.05
4.03
4.02
3.85
3.76
3.72
3.16
3.16
3.14
3.13
3.12
3.11
3.10
2.31
2.03
1.99
1.27
1.25
1.24
1.19
1.17
1.15
0.87
0.73
Me
O
CO2Et
N
H
tBu
O
S
O
O
Me
3t
0.99
0.78
0.19
1.98
1.95
0.94
1.00
1.97
0.96
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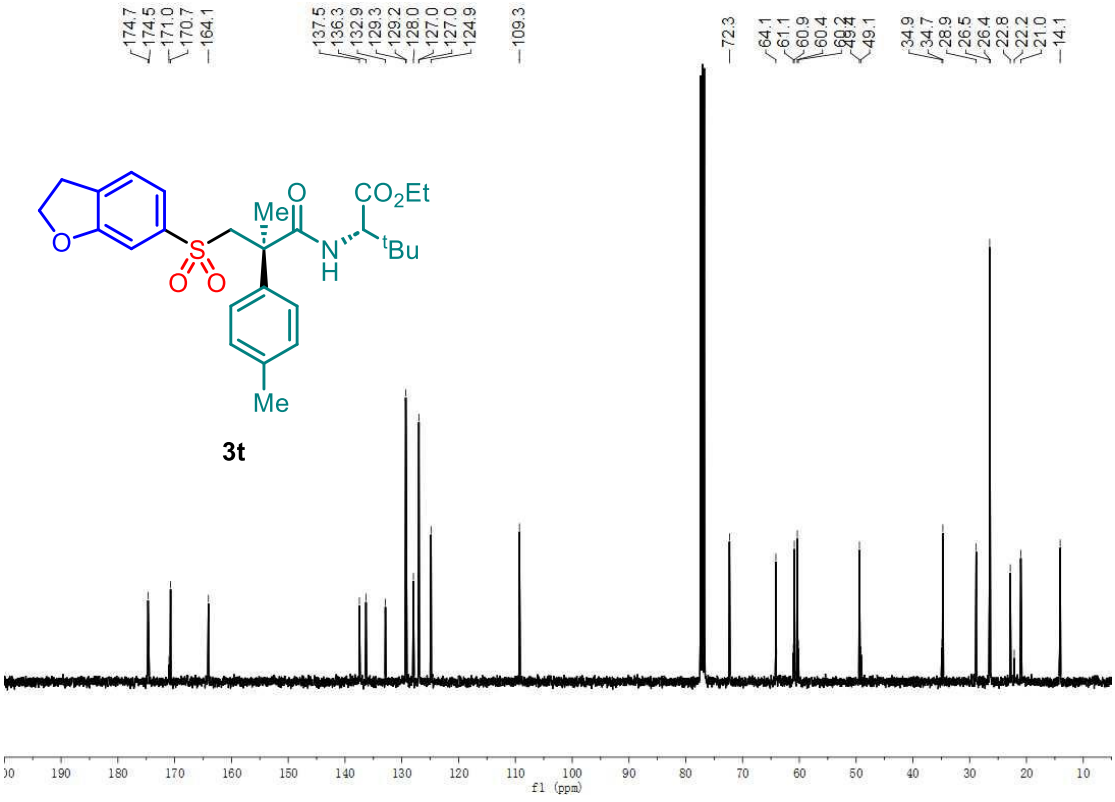
2.44
0.56
0.58
2.45
7.48
1.51
f1 (ppm)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127.0
127.0
124.9
109.3
72.3
64.1
61.1
60.9
60.4
49.4
49.1
34.9
34.7
28.9
26.5
26.4
22.8
22.2
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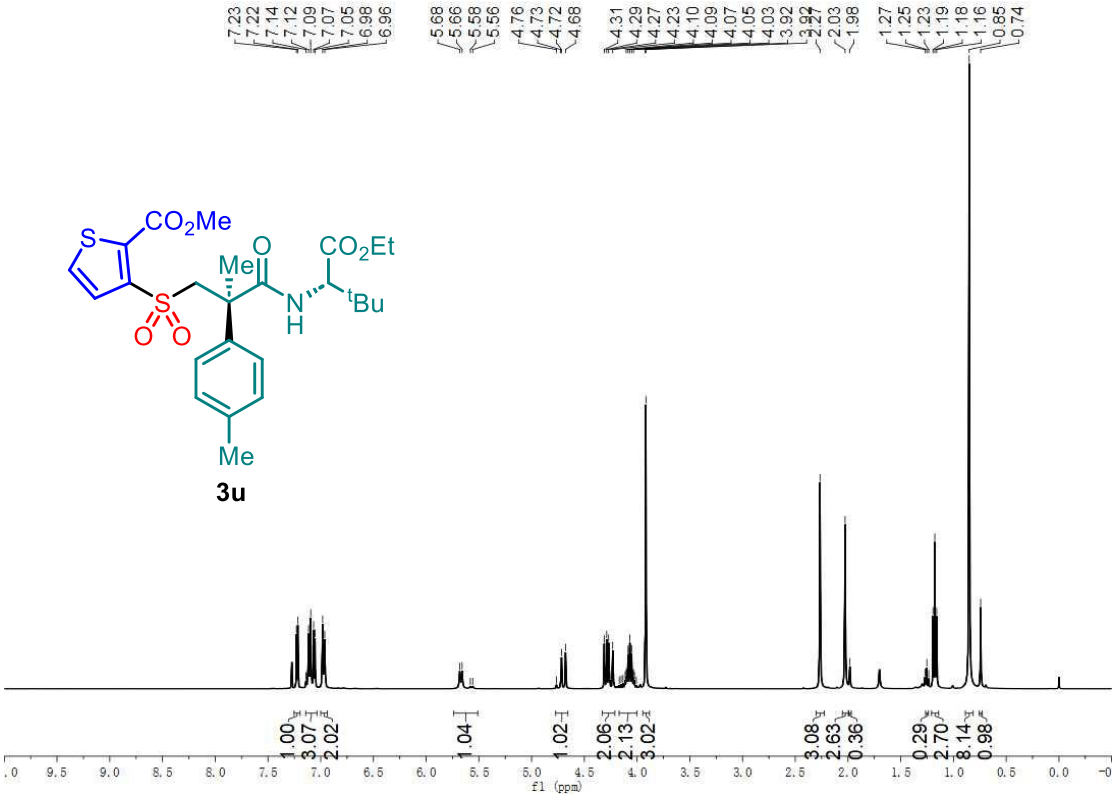
Me
O
CO2Et
N
H
tBu
O
S
O
O
Me
3t
f1 (ppm)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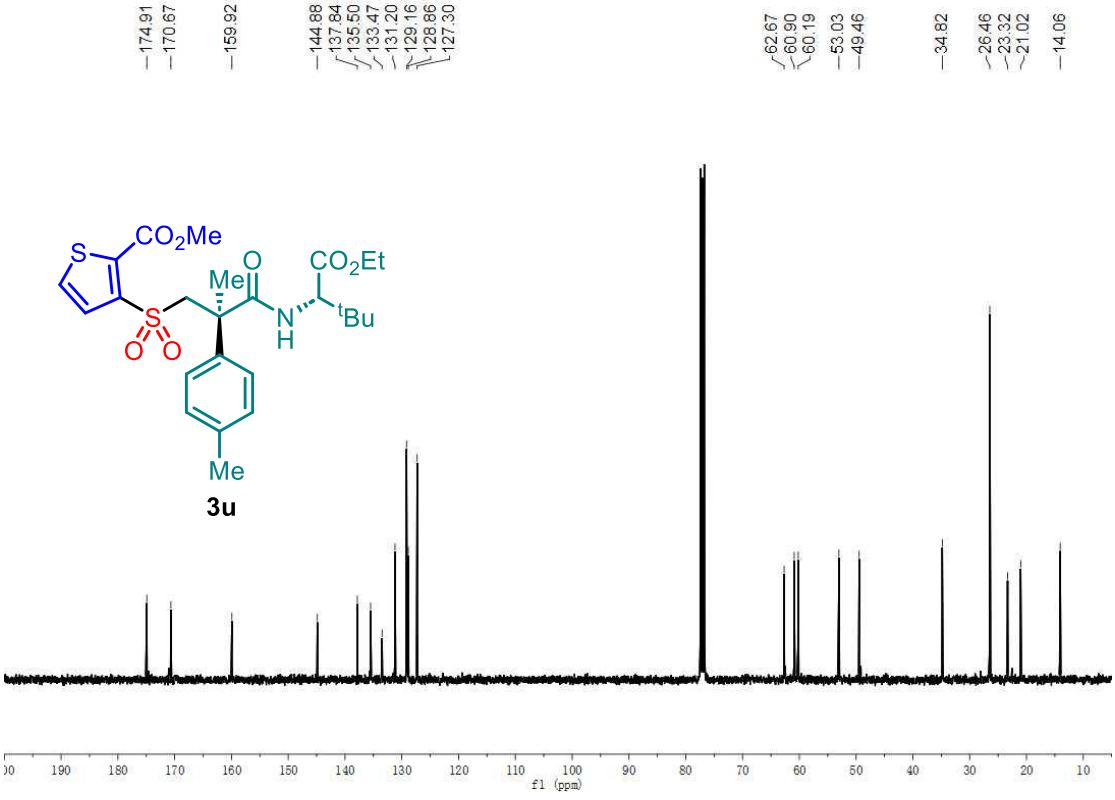
7.07
7.05
6.98
6.96
5.68
5.66
5.58
5.56
4.76
4.73
4.72
4.68
4.31
4.29
4.27
4.23
4.10
4.09
4.07
4.05
4.03
3.92
2.27
2.03
1.98
1.27
1.25
1.23
1.19
1.18
1.16
0.85
0.74
CO2Me
S
O
Me
CO2Et
N
H
tBu
O
O
Me
3u
1.00
3.07
2.02
1.04
1.02
2.06
2.13
3.02
3.08
2.63
0.36
0.29
2.70
8.14
0.98
f1 (ppm)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159.92
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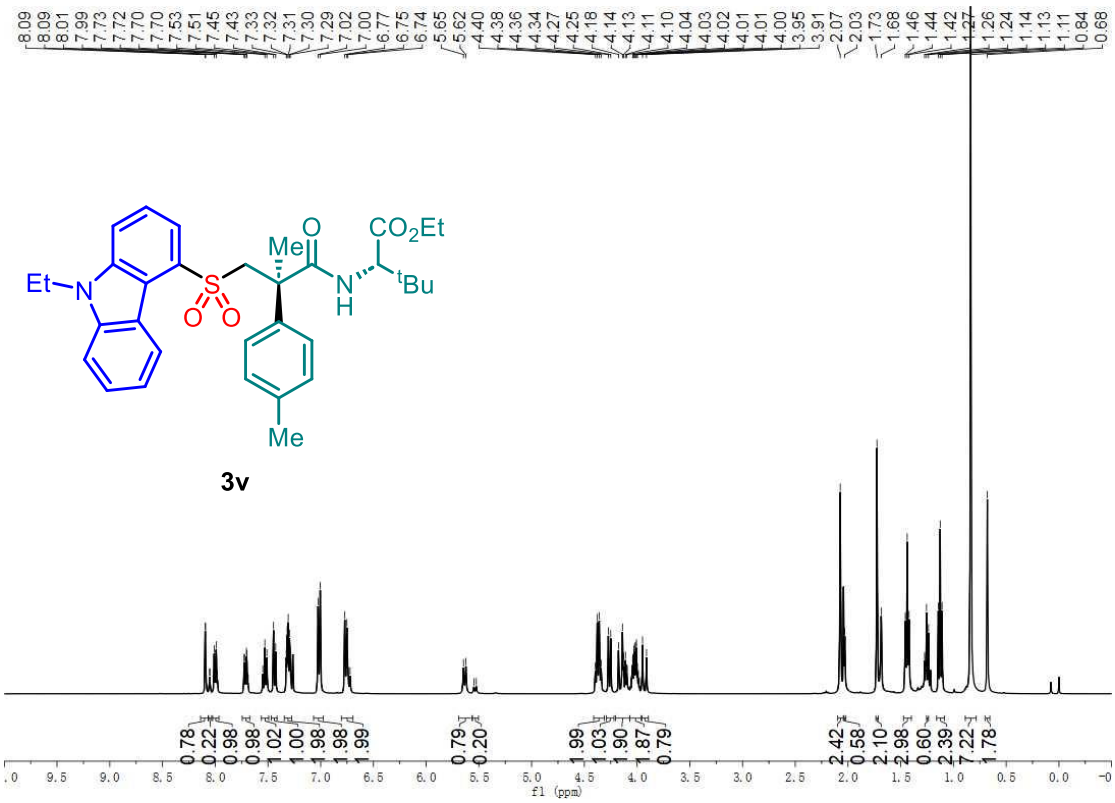
133.47
131.20
129.16
128.86
127.30
62.67
60.90
60.19
53.03
49.46
34.82
26.46
23.32
21.02
14.06
CO2Me
S
O
Me
CO2Et
N
H
tBu
O
O
Me
3u
f1 (ppm)



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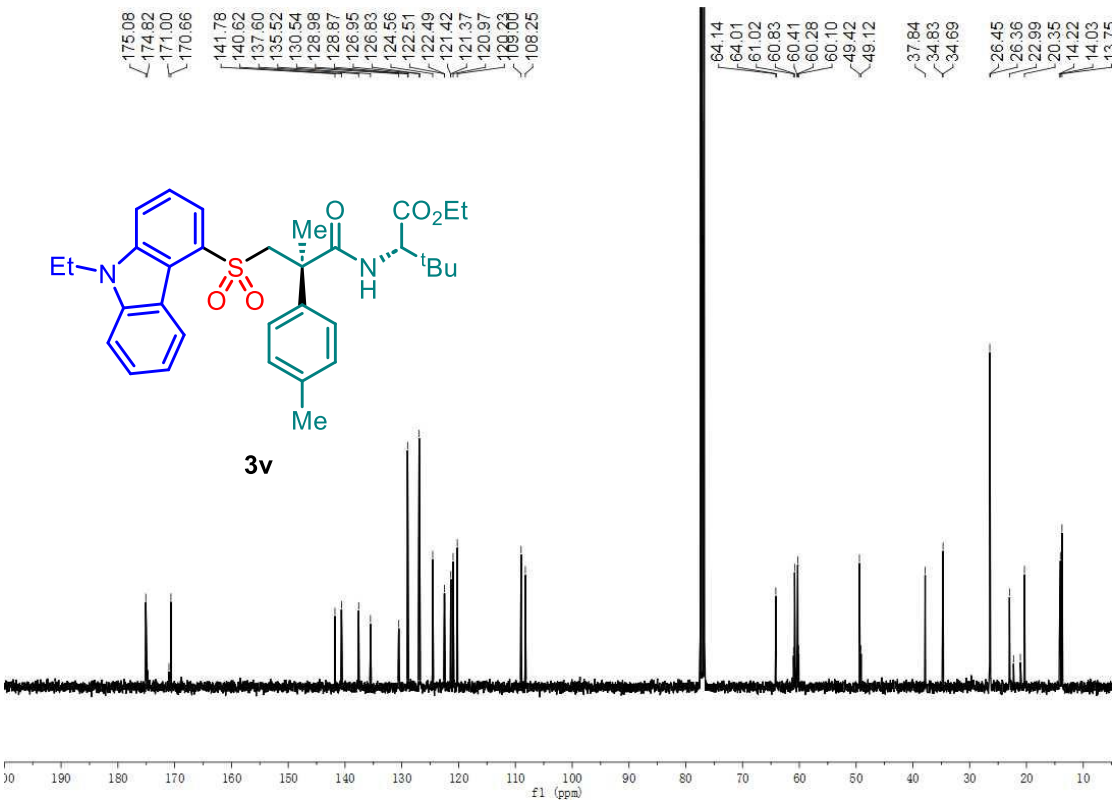

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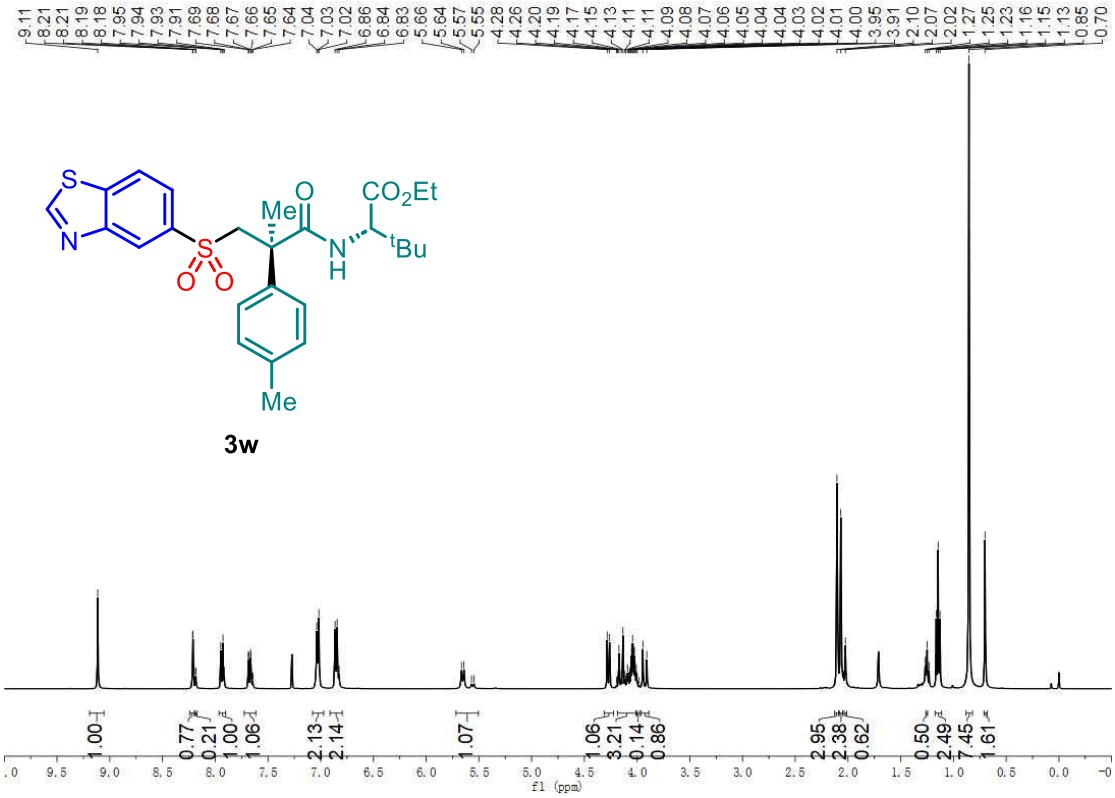
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8.21
8.19
8.18
7.95
7.94
7.93
7.91
7.69
7.68
7.67
7.66
7.65
7.64
7.04
7.03
7.02
6.86
6.84
6.83
5.66
5.64
5.57
5.55
4.28
4.26
4.20
4.19
4.17
4.15
4.13
4.11
4.11
4.09
4.08
4.07
4.06
4.05
4.04
4.04
4.03
4.02
4.01
4.00
3.95
3.91
2.10
2.07
2.02
1.27
1.25
1.23
1.16
1.15
1.13
0.85
0.70
S
N
Me
O
CO2Et
N
H
tBu
O
S
O
Me
1.00
0.77
0.21
1.00
1.06
2.13
2.14
1.07
1.06
3.21
0.14
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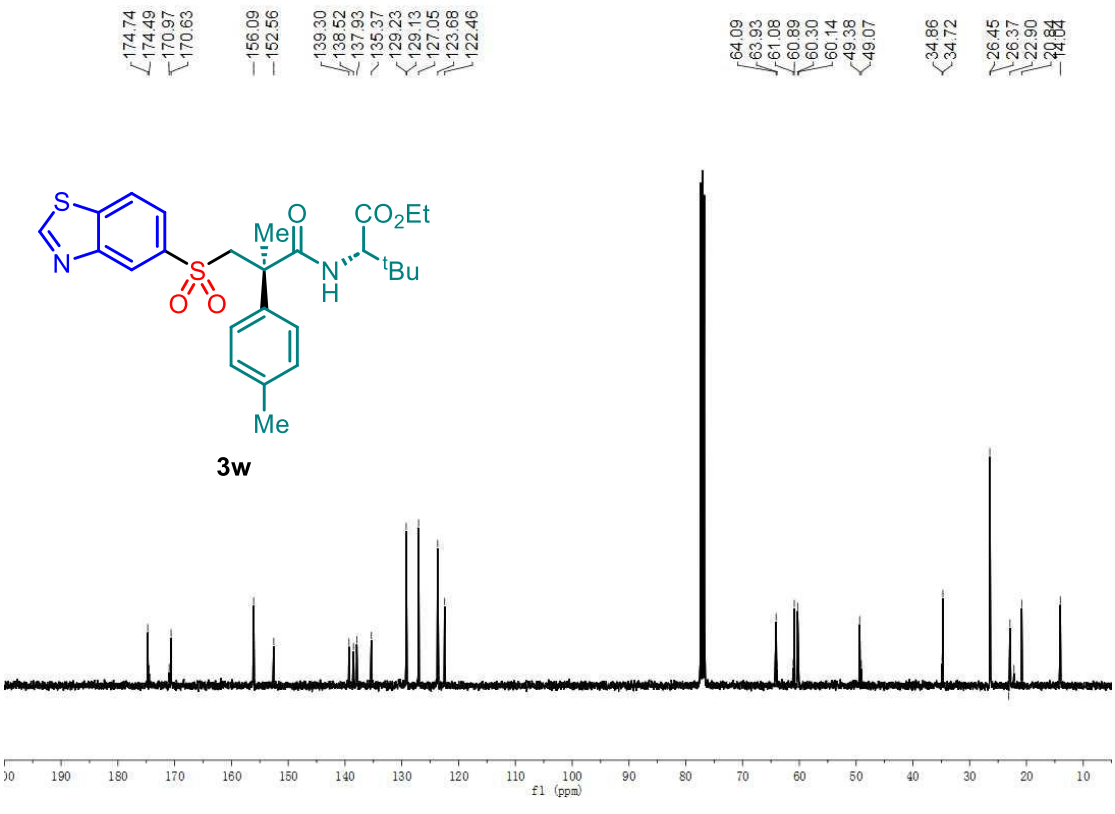
2.95
2.38
0.62
0.50
2.49
7.45
1.61
f1 (ppm)

3w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170.63
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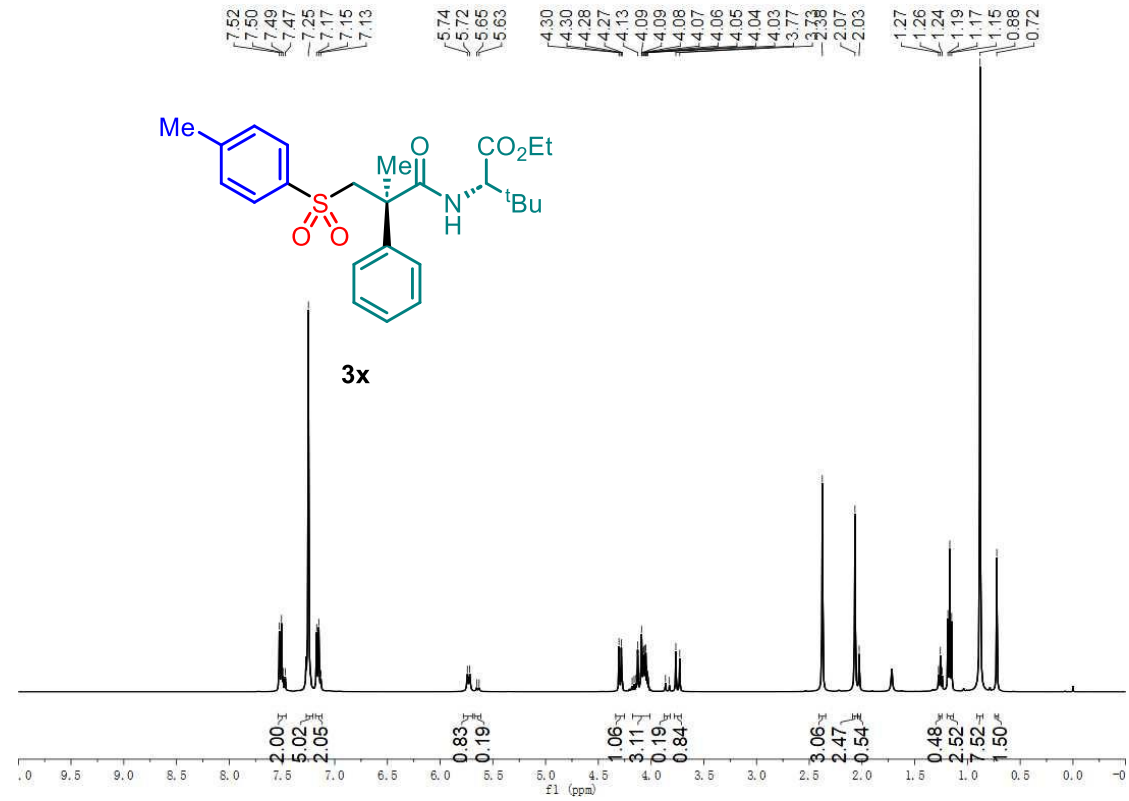
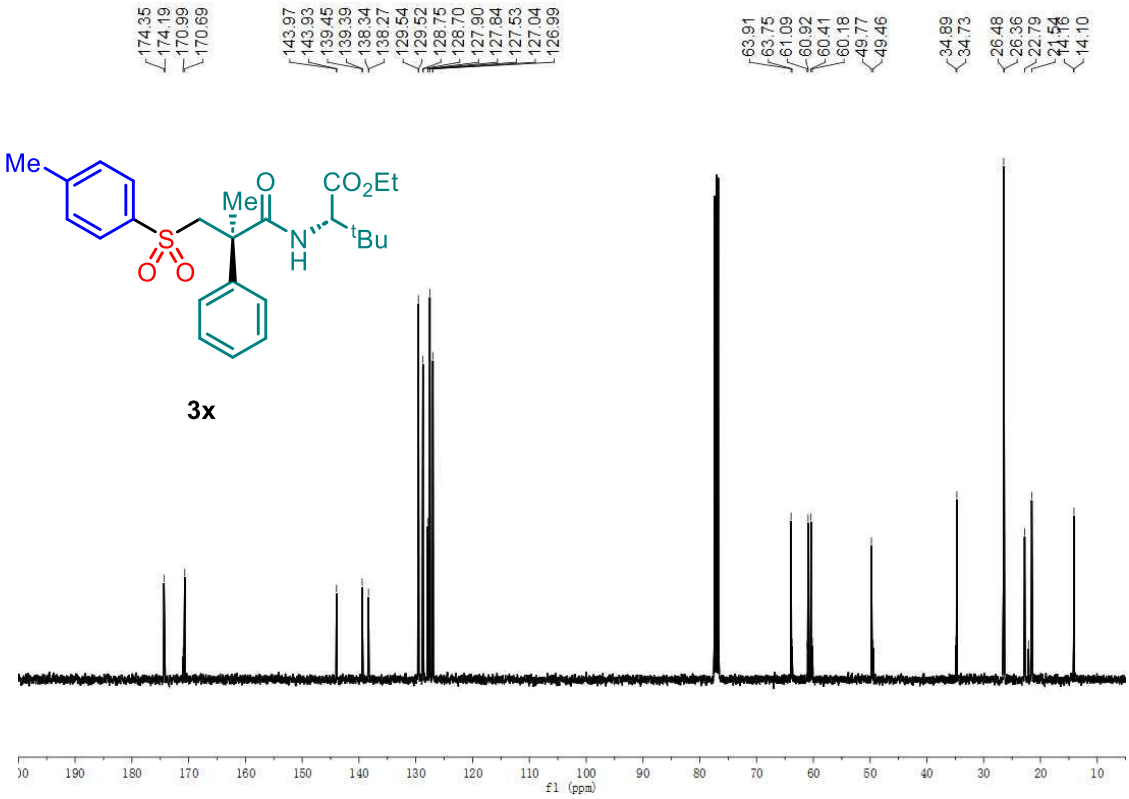
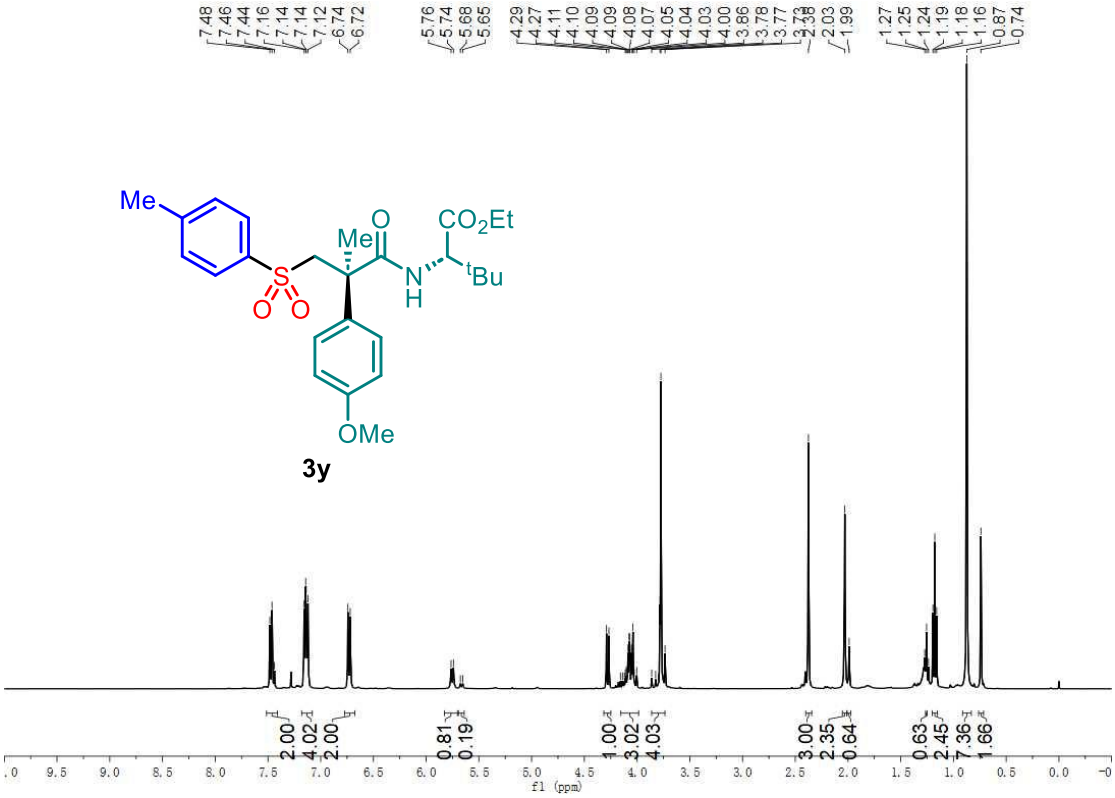
152.56
139.30
138.52
137.93
135.37
129.23
129.13
127.05
123.68
122.46
64.09
63.93
61.08
60.89
60.30
60.14
49.38
49.07
34.86
34.72
26.45
26.37
22.90
20.84
14.04
S
N
Me
O
CO2Et
N
H
tBu
O
S
O
Me
f1 (ppm)

3w


Me
O
Me
CO2Et
N
H
tBu
S
O
O
3x


Me
O
Me
CO2Et
N
H
tBu
S
O
O
3x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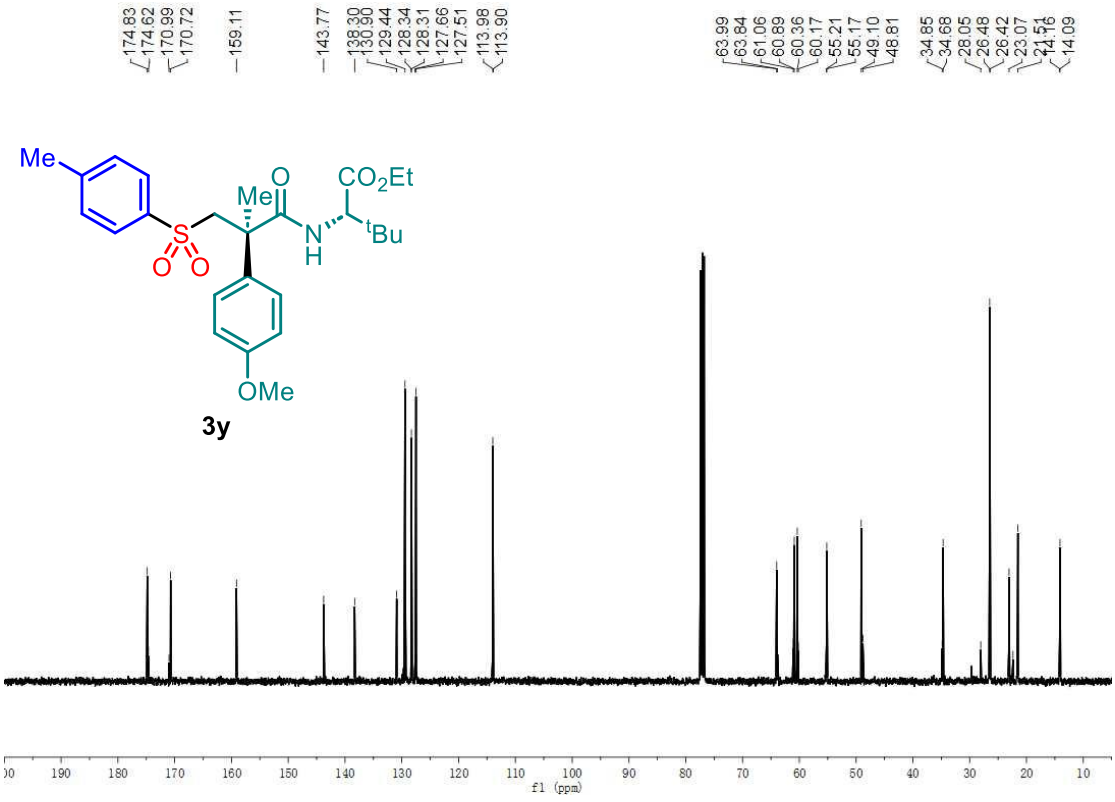
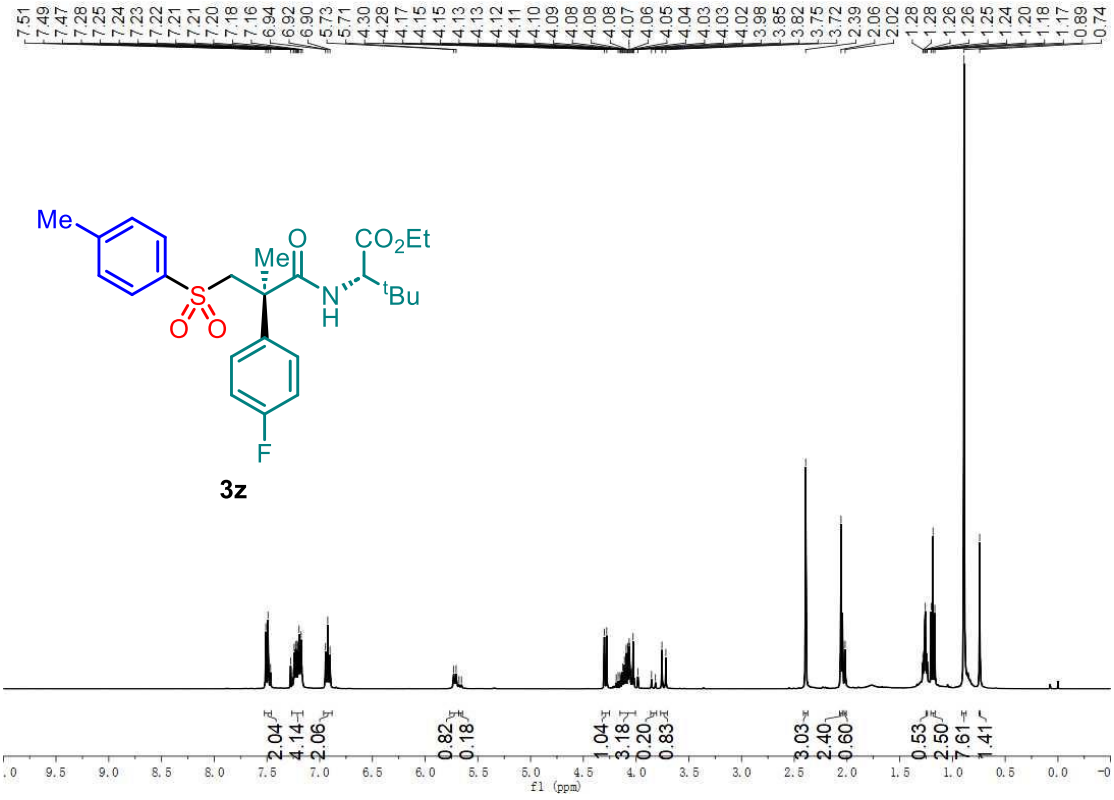
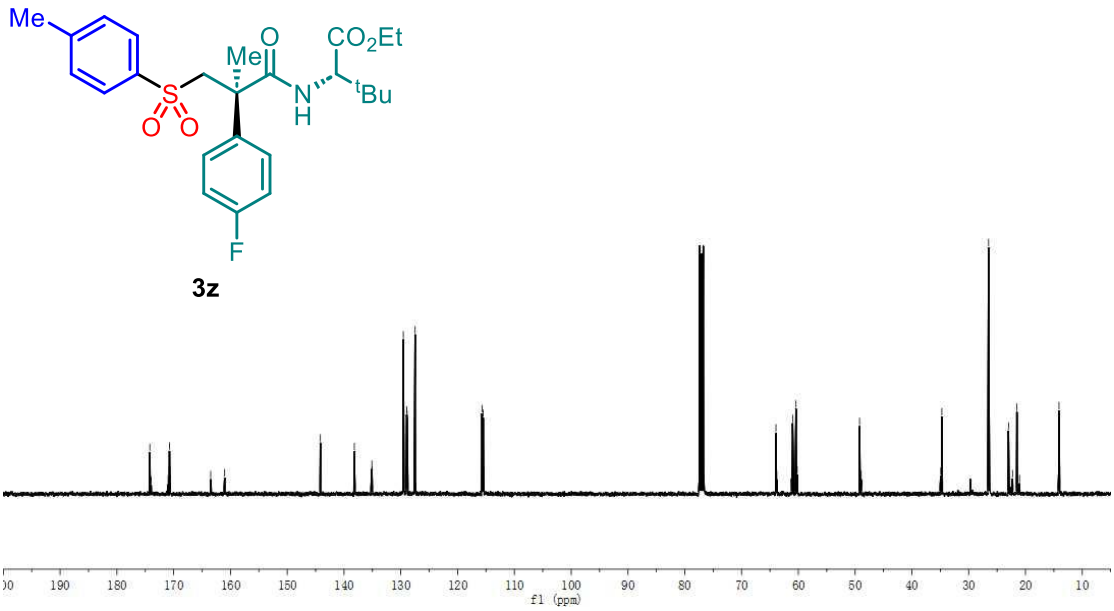
O
Me
CO2Et
S
O
O
N
H
tBu
OMe
3y
f1 (ppm)


Me
O
Me
CO2Et
S
O
O
N
H
tBu
OMe
3y
f1 (ppm)



3z



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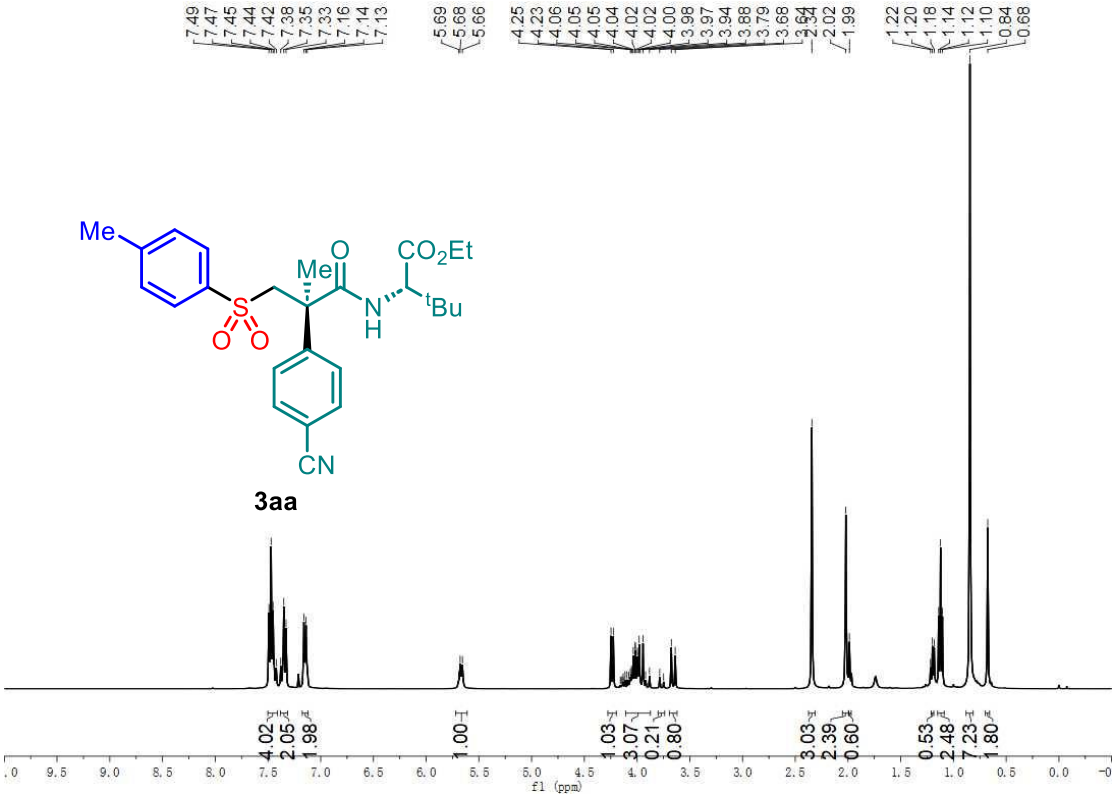
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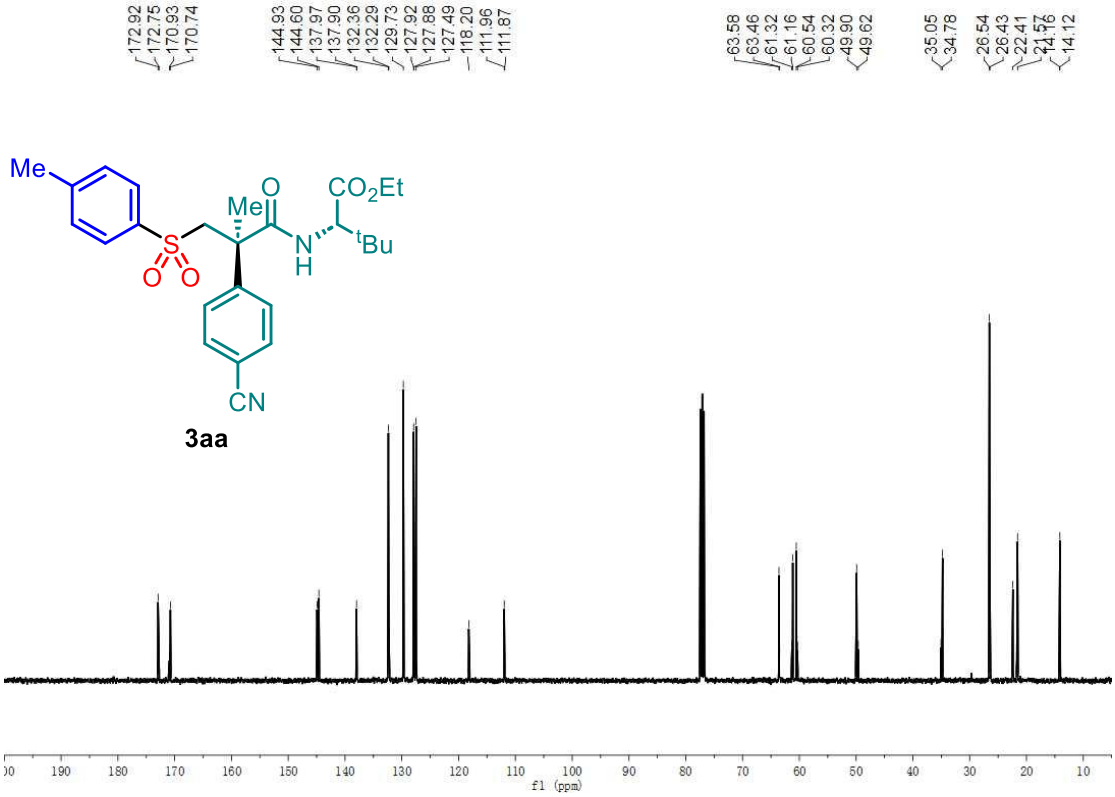
Me
CO2Et
N
H
tBu
S
O
O
CN
3aa
f1 (ppm)


Me
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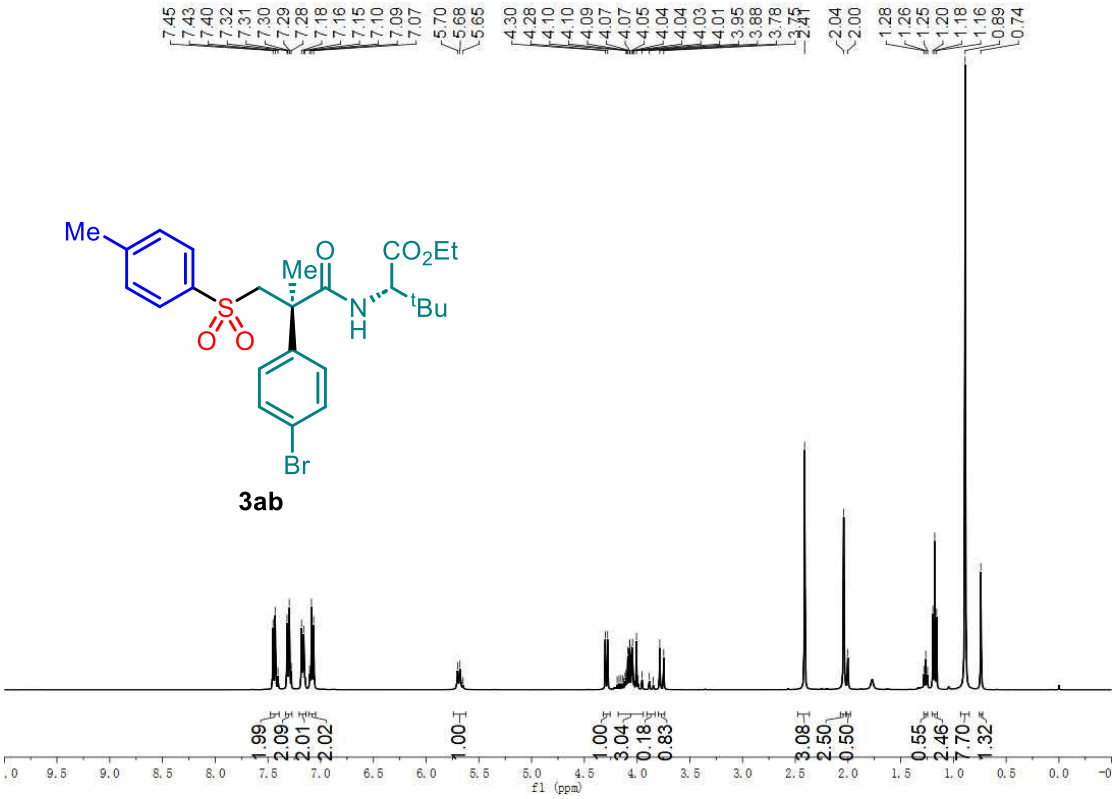
Me
CO2Et
N
H
tBu
S
O
O
CN
3aa
f1 (ppm)


Me
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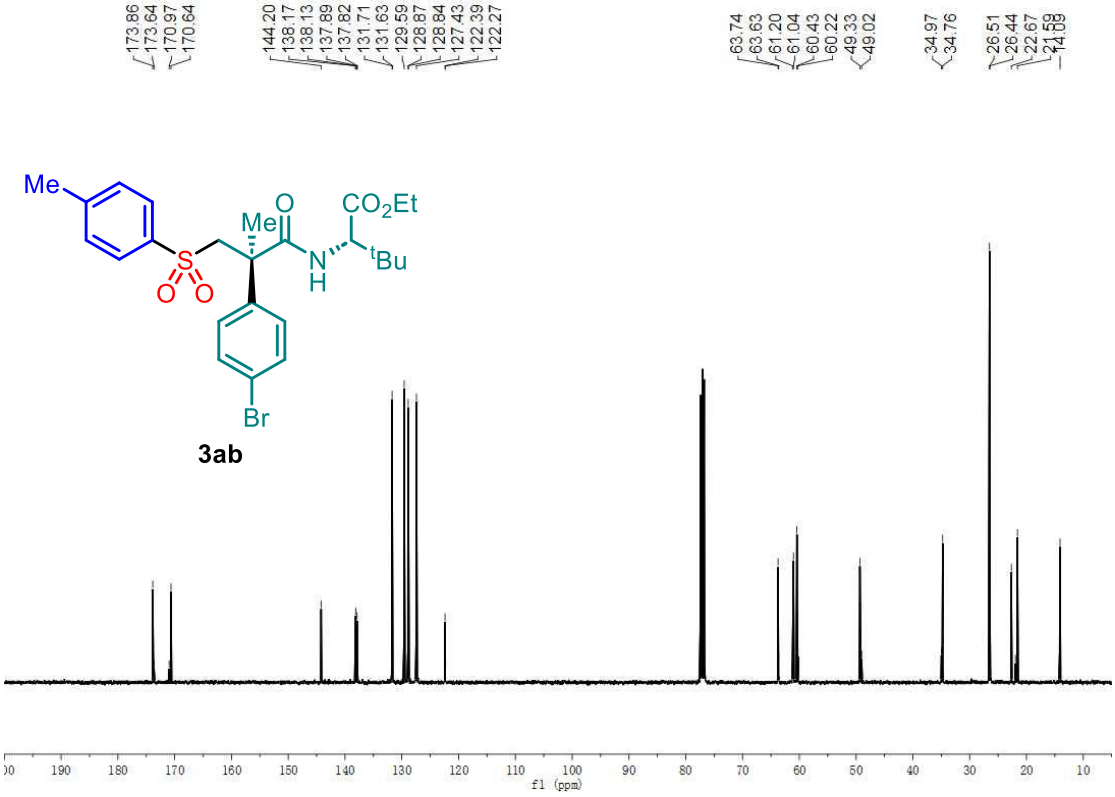
Me
CO2Et
S
N
H
tBu
O
O
Br
3ab
f1 (ppm)


Me
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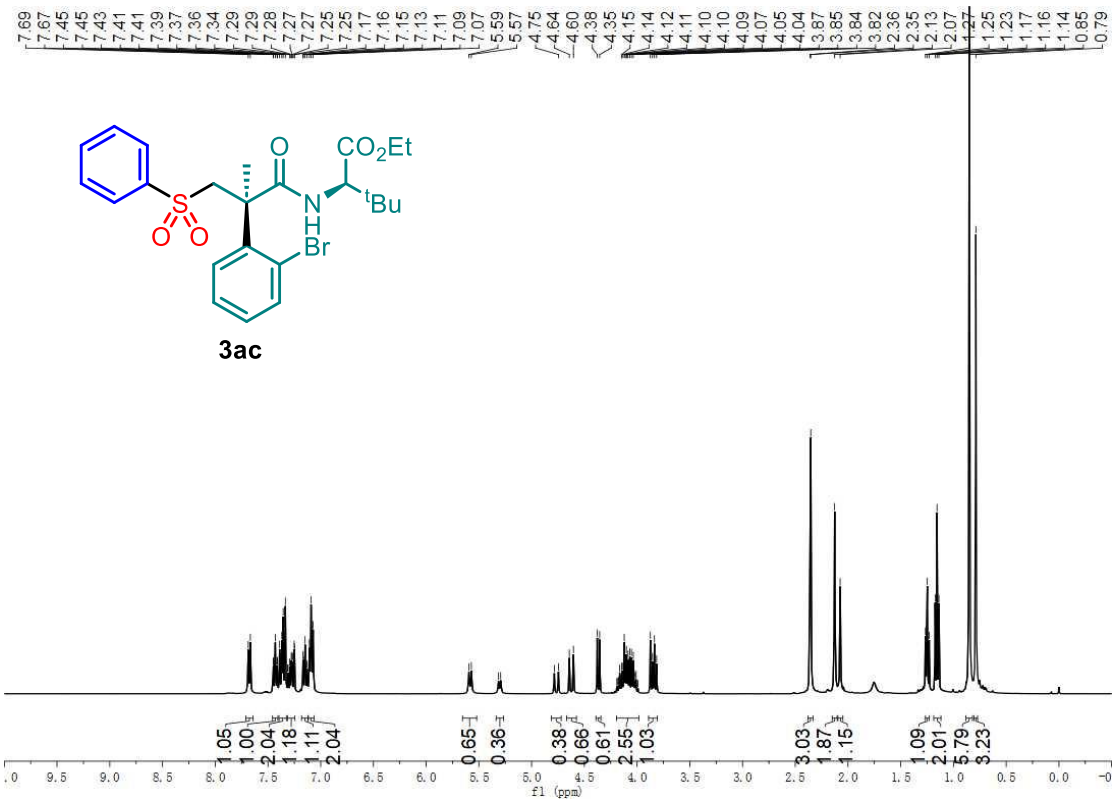
Me
CO2Et
S
N
H
tBu
O
O
Br
3ab
f1 (ppm)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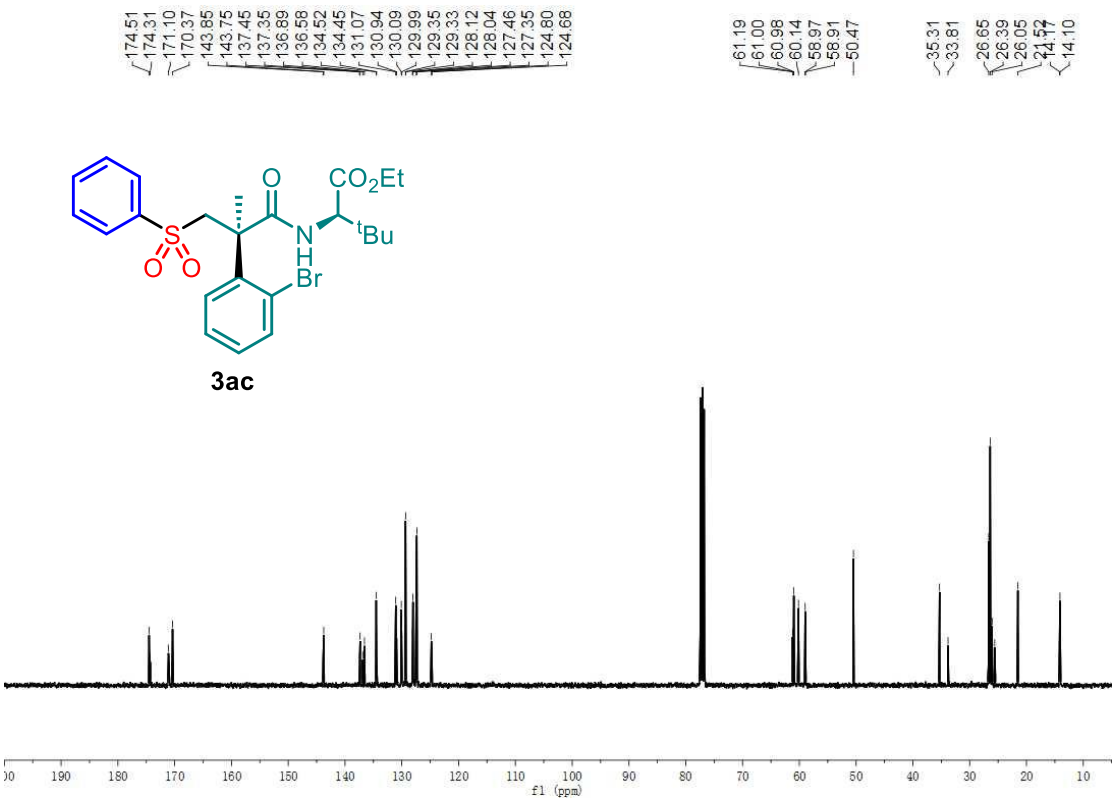
O
CO2Et
N
H
tBu
S
O
O
Br
3ac
1.05 1.00 2.04 1.18 1.11 2.04 0.65 0.36 0.38 0.66 0.61 2.55 1.03 3.03 1.87 1.15 1.09 2.01 5.79 3.23
f1 (ppm)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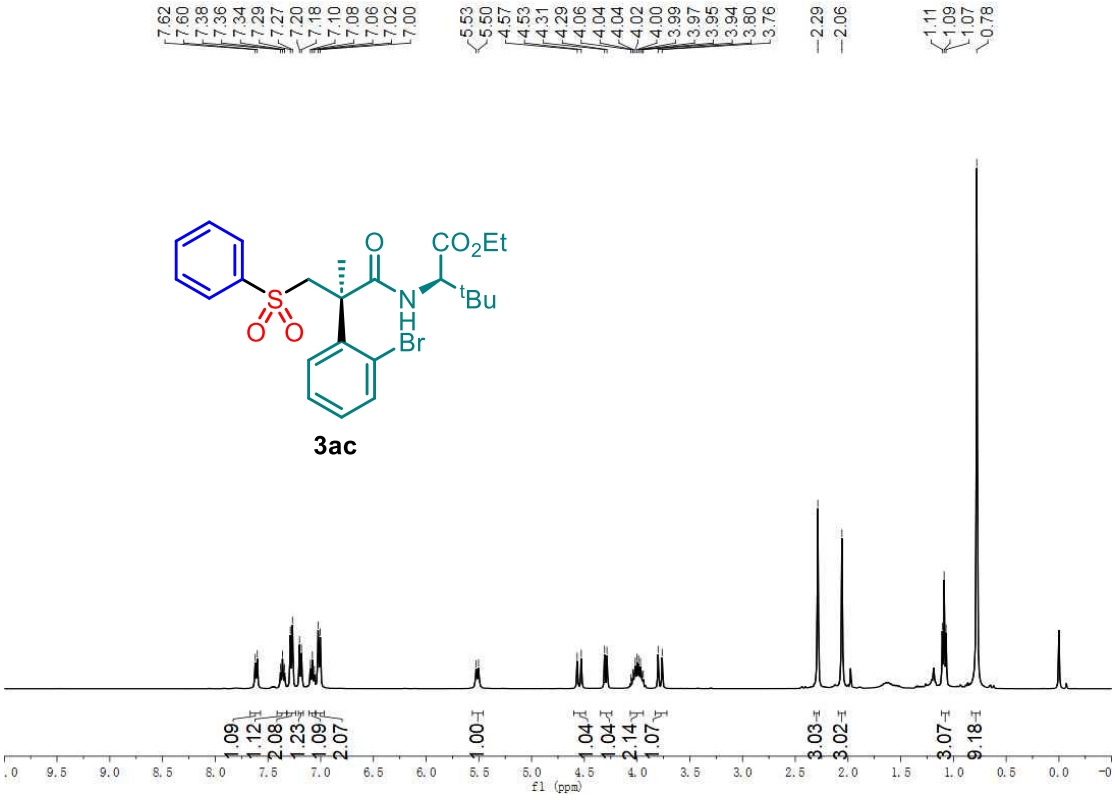
61.19 61.00 60.98 60.14 58.97 58.91 50.47
35.31 33.81 26.65 26.39 26.05 21.57 21.47 14.10
O
CO2Et
N
H
tBu
S
O
O
Br
3ac
f1 (ppm)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7.10
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7.02
7.00
5.53
5.50
4.57
4.53
4.31
4.29
4.06
4.04
4.04
4.02
4.00
3.99
3.97
3.95
3.94
3.80
3.76
2.29
2.06
1.11
1.09
1.07
0.78
O
CO2Et
S
O
O
N
H
tBu
Br
3ac
1.09
1.12
2.08
1.23
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2.07
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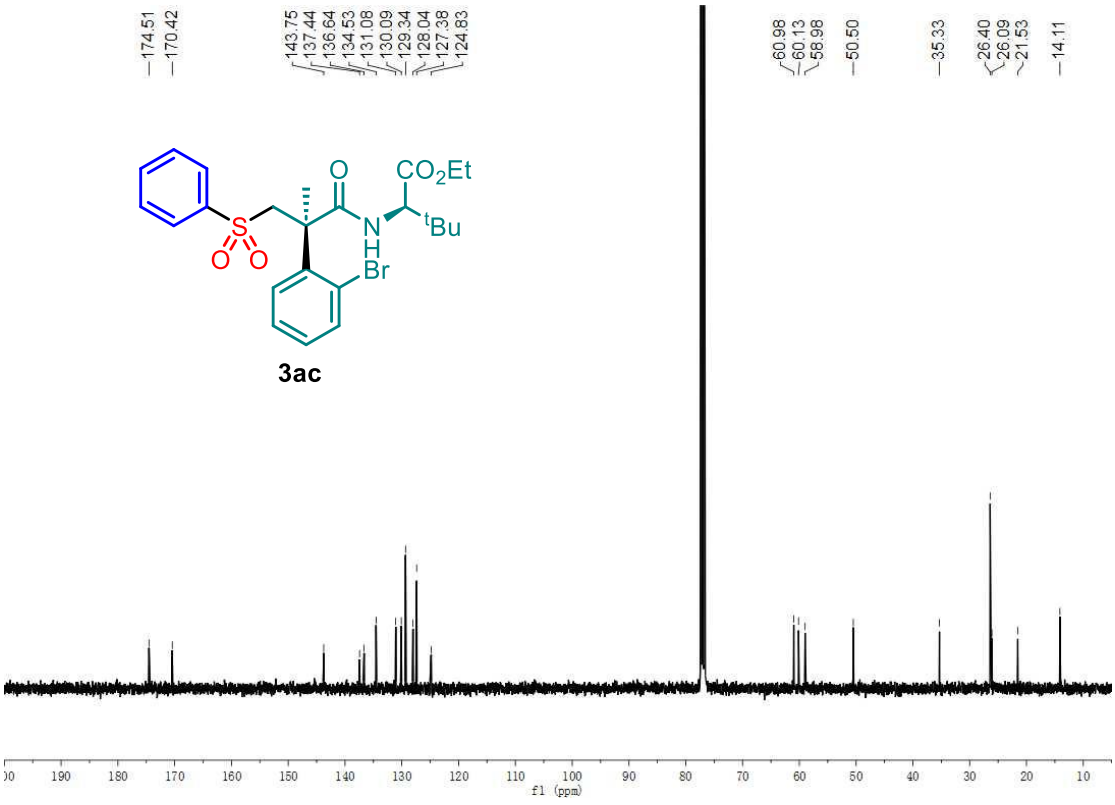
1.04
1.04
2.14
1.07
3.03
3.02
3.07
9.18
f1 (ppm)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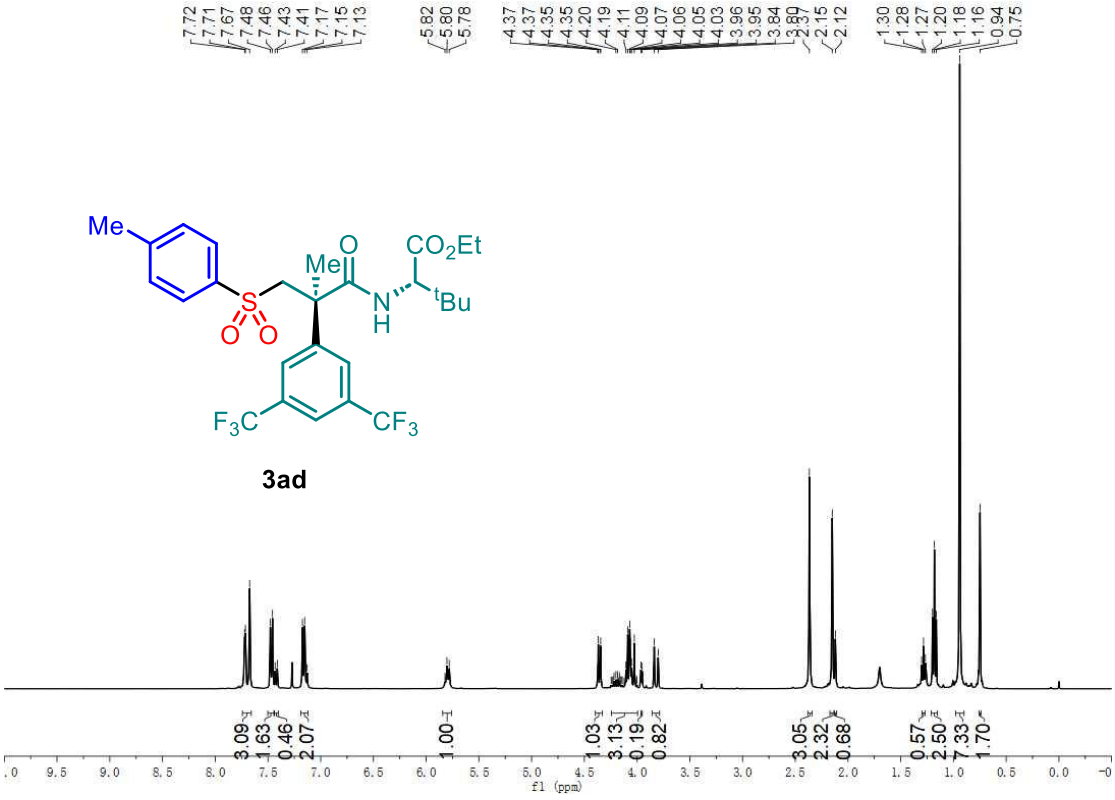
128.04
127.38
124.83
60.98
60.13
58.98
50.50
35.33
26.40
26.09
21.53
14.11
O
CO2Et
S
O
O
N
H
tBu
Br
3ac
f1 (ppm)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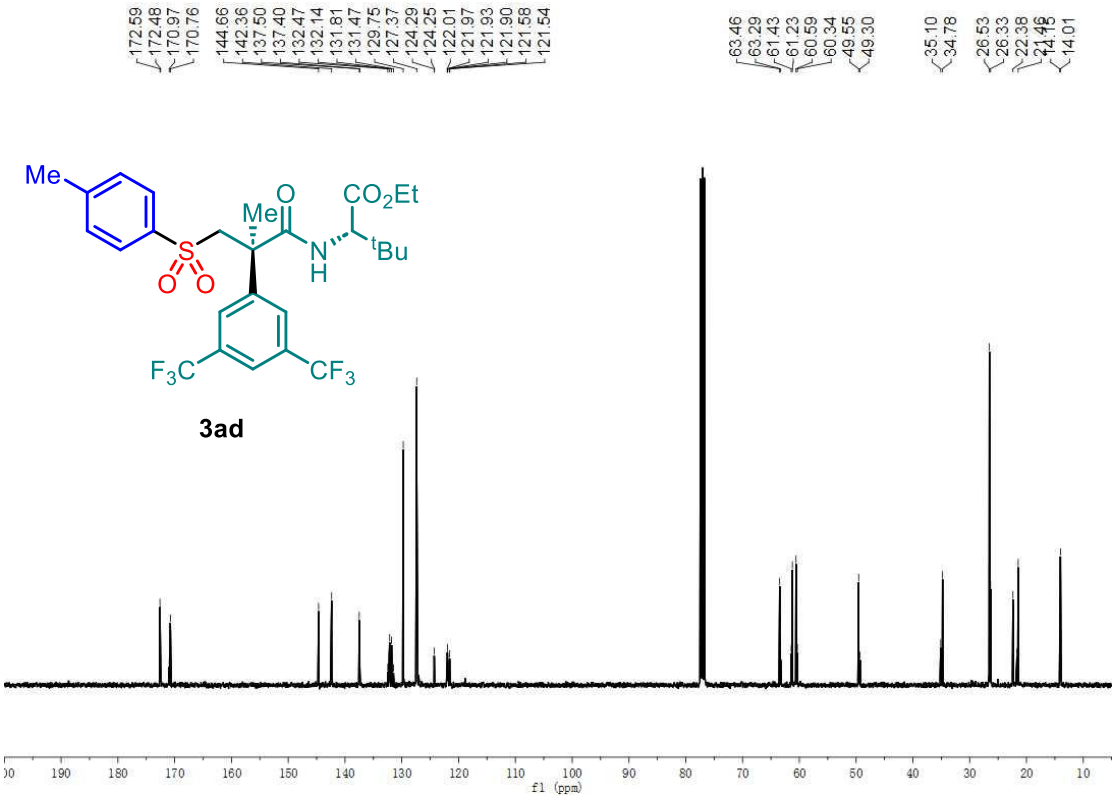
Me
CO2Et
N
H
tBu
S
O
O
F3C
CF3
3ad
f1 (ppm)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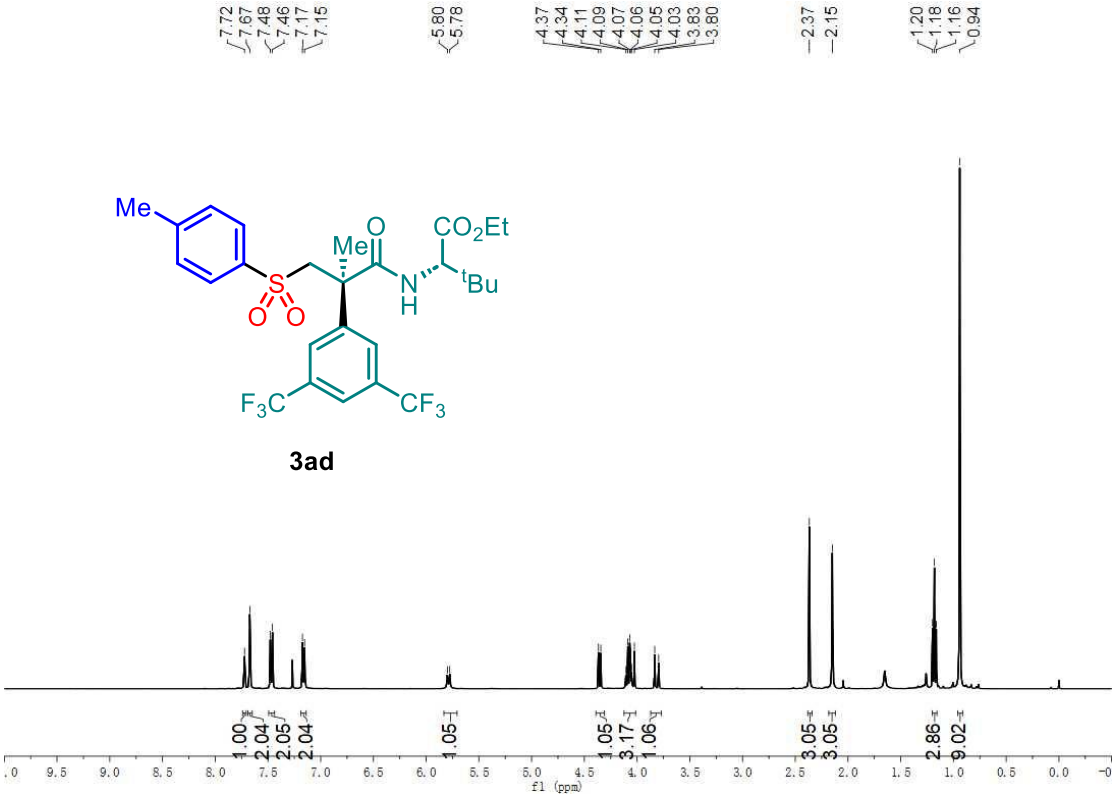
Me
CO2Et
N
H
tBu
S
O
O
F3C
CF3
3ad
f1 (ppm)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4.34
4.11
4.09
4.07
4.06
4.05
4.03
3.83
3.80
2.37
2.15
1.20
1.18
1.16
0.94
Me
O
CO2Et
Me
S
N
H
tBu
O
O
F3C
CF3
3ad
1.00
2.04
2.05
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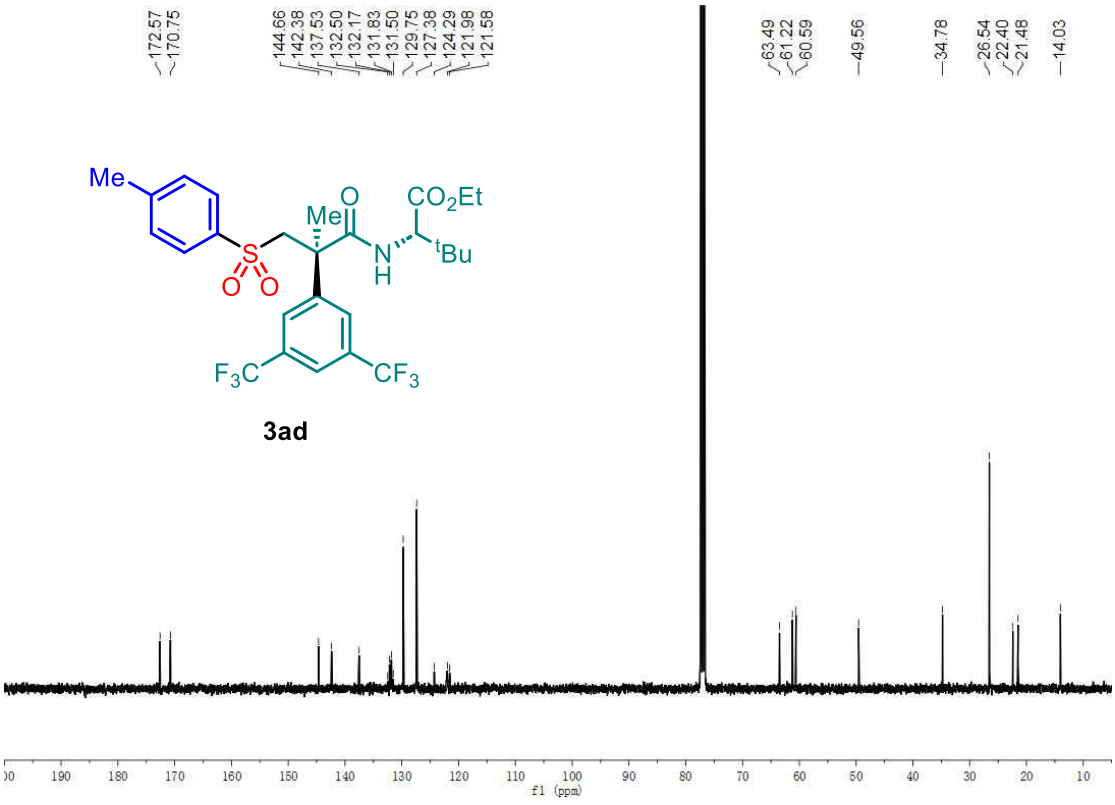
1.05
1.05
3.17
1.06
3.05
3.05
2.86
9.02
f1 (ppm)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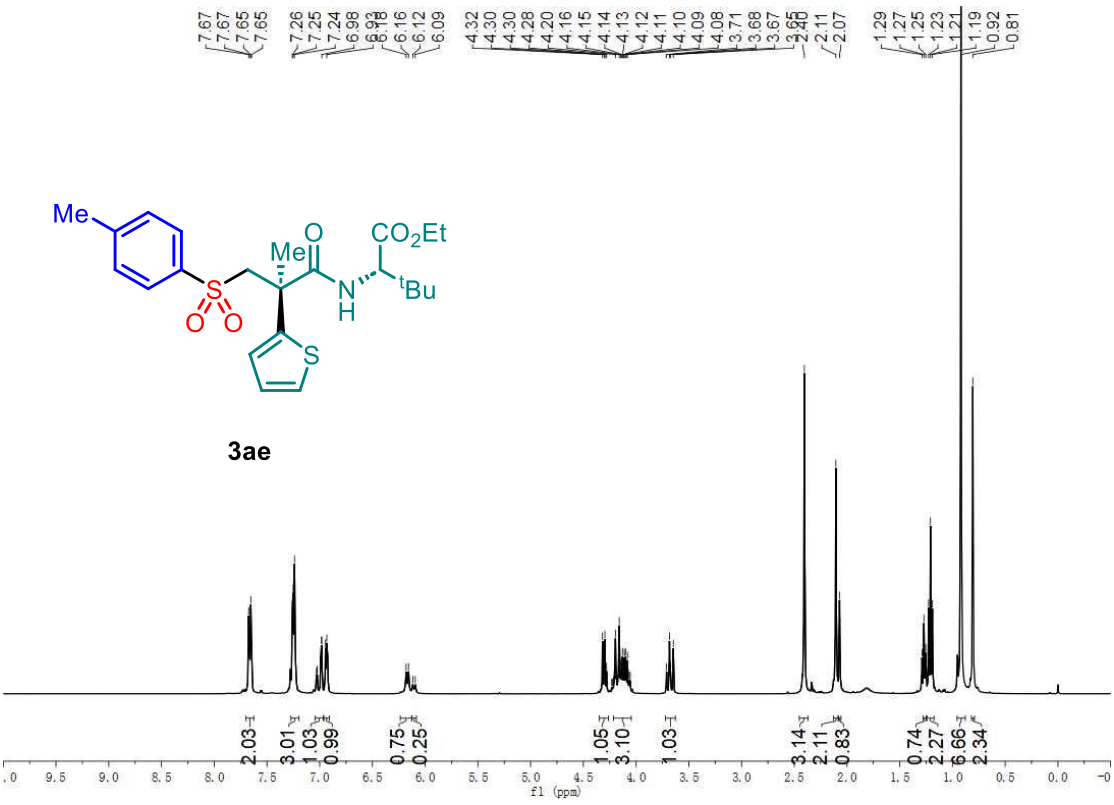
127.38
124.29
121.98
121.58
63.49
61.22
60.59
49.56
34.78
26.54
22.40
21.48
14.03
Me
O
CO2Et
Me
S
N
H
tBu
O
O
F3C
CF3
3ad
f1 (ppm)



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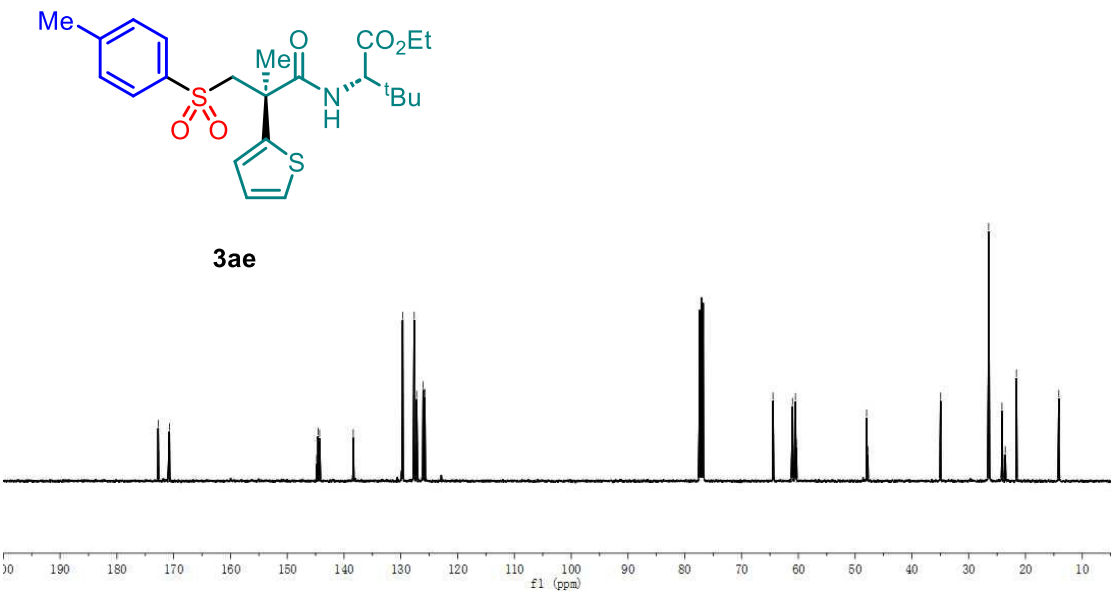

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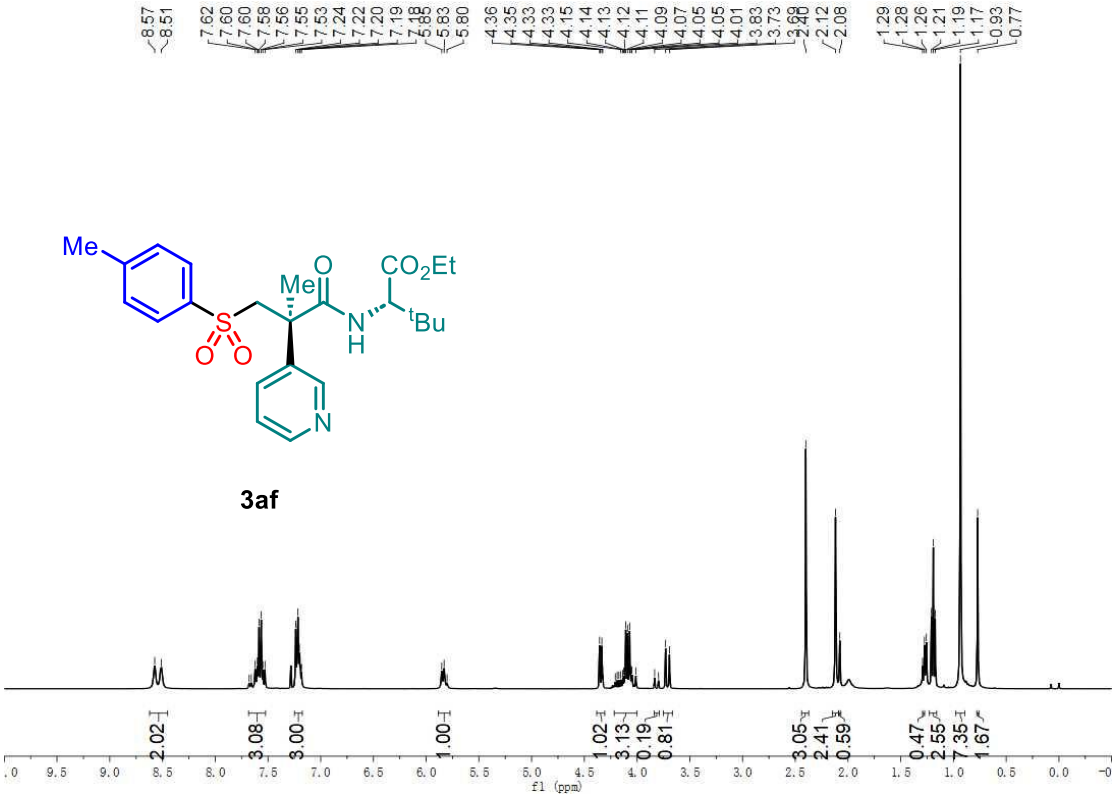
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S
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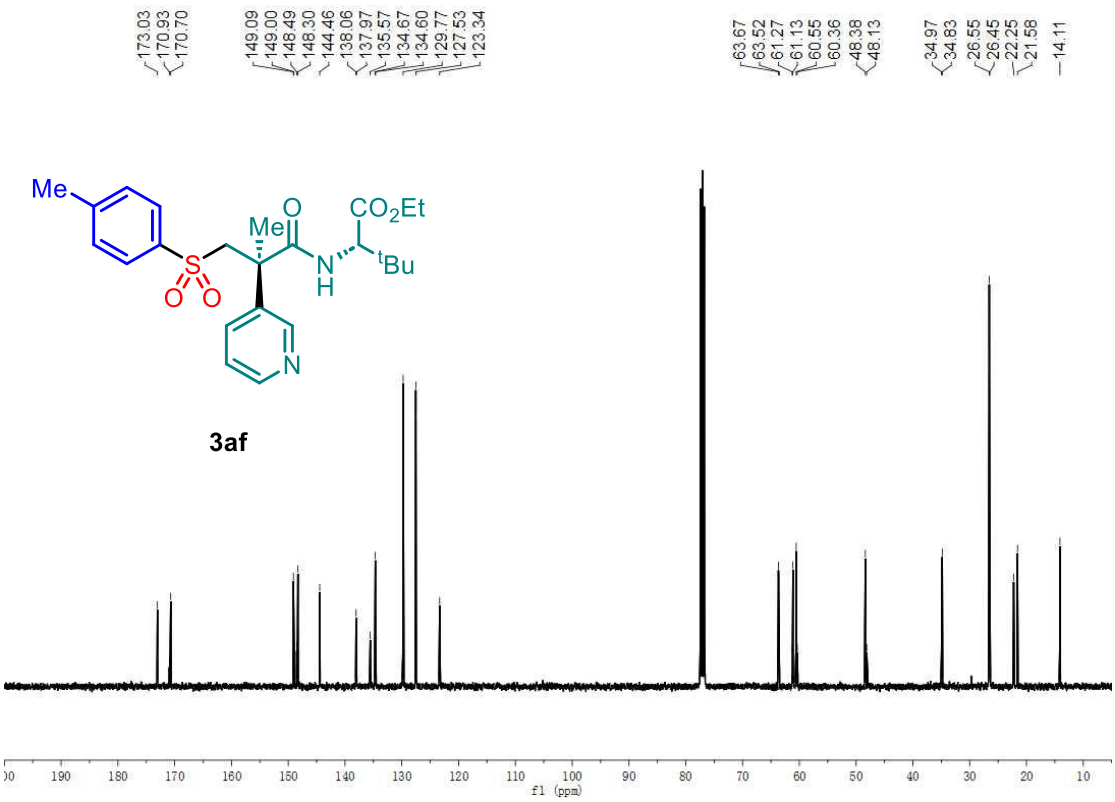
O
N
H
tBu
N
3af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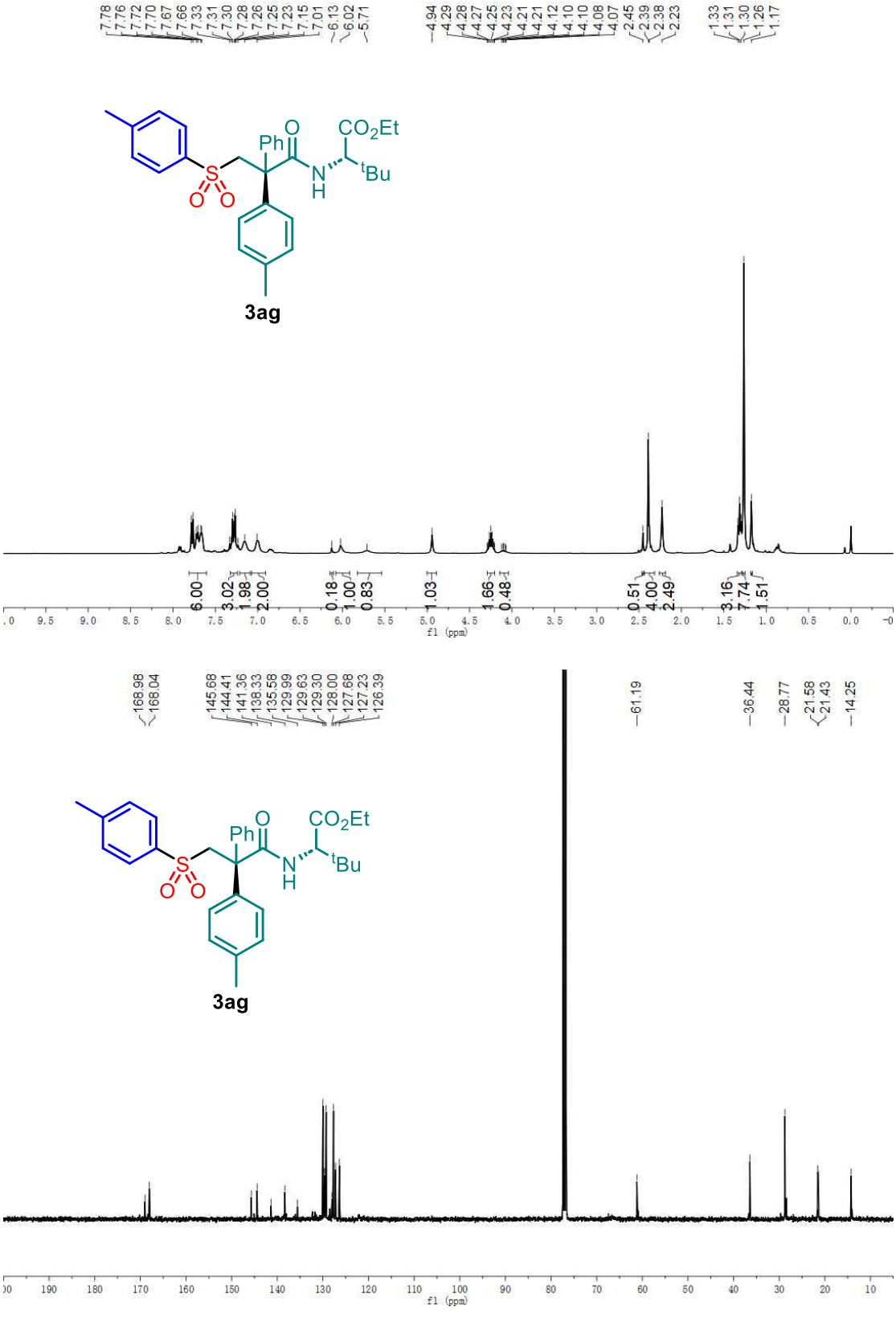
3af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7.23
7.15
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6.13
6.02
5.71
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4.29
4.28
4.27
4.25
4.23
4.21
4.21
4.12
4.10
4.10
4.08
4.07
2.45
2.39
2.38
2.23
1.33
1.31
1.30
1.26
1.17
Ph
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CO2Et
S
O
O
N
H
tBu
3ag
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3.02
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2.00
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1.00
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1.03
1.66
0.48
0.51
4.00
2.49
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1.51
f1 (ppm)
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168.04
145.68
144.41
141.36
138.33
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129.99
129.63
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128.00
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127.23
126.39
61.19
36.44
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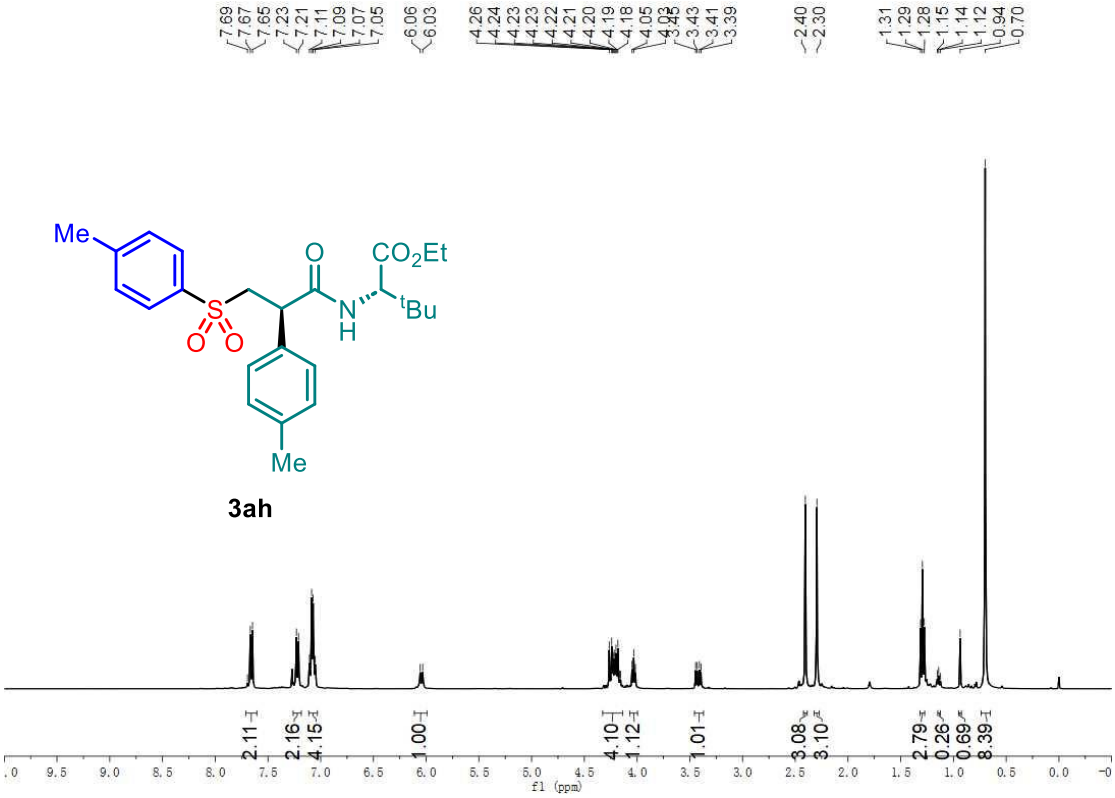
S
O
O
N
H
tBu
3ag
f1 (ppm)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7.07
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6.06
6.03
4.26
4.24
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.05
4.03
3.45
3.43
3.41
3.39
2.40
2.30
1.31
1.29
1.28
1.15
1.14
1.12
0.94
0.70
Me
O
CO2Et
S
O
O
N
H
tBu
Me
3ah
2.11
2.16
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4.10
1.12
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3.08
3.10
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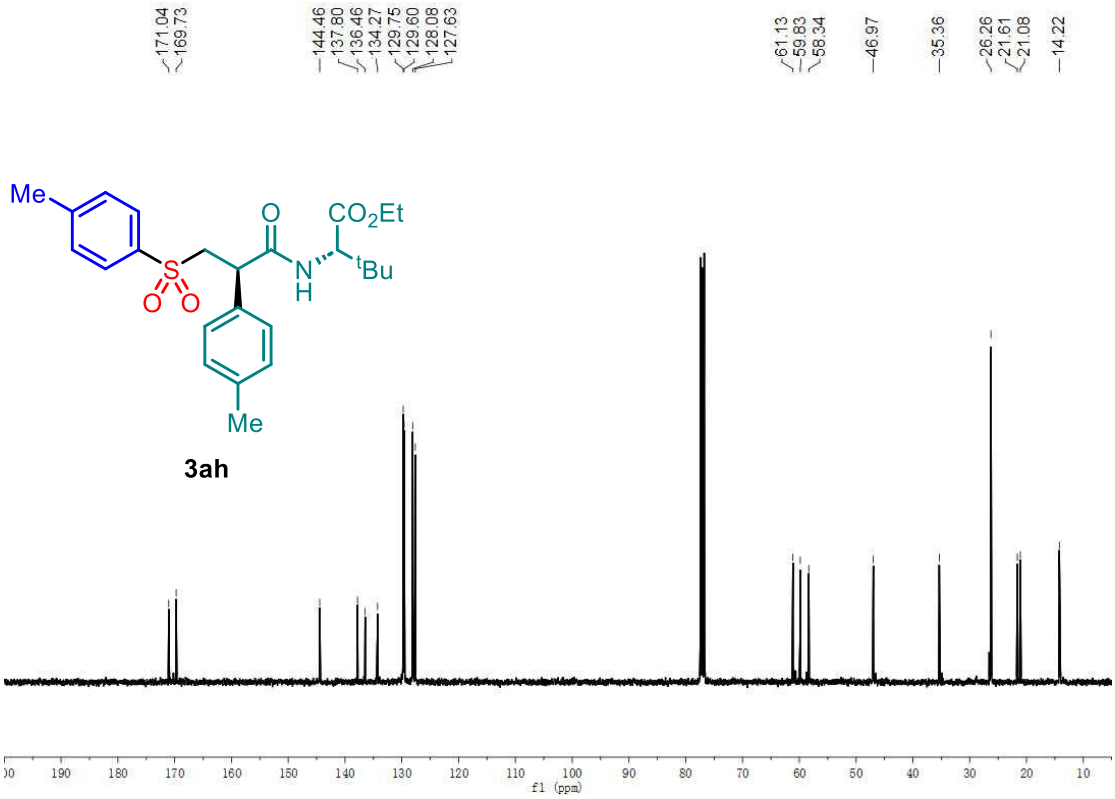
f1 (ppm)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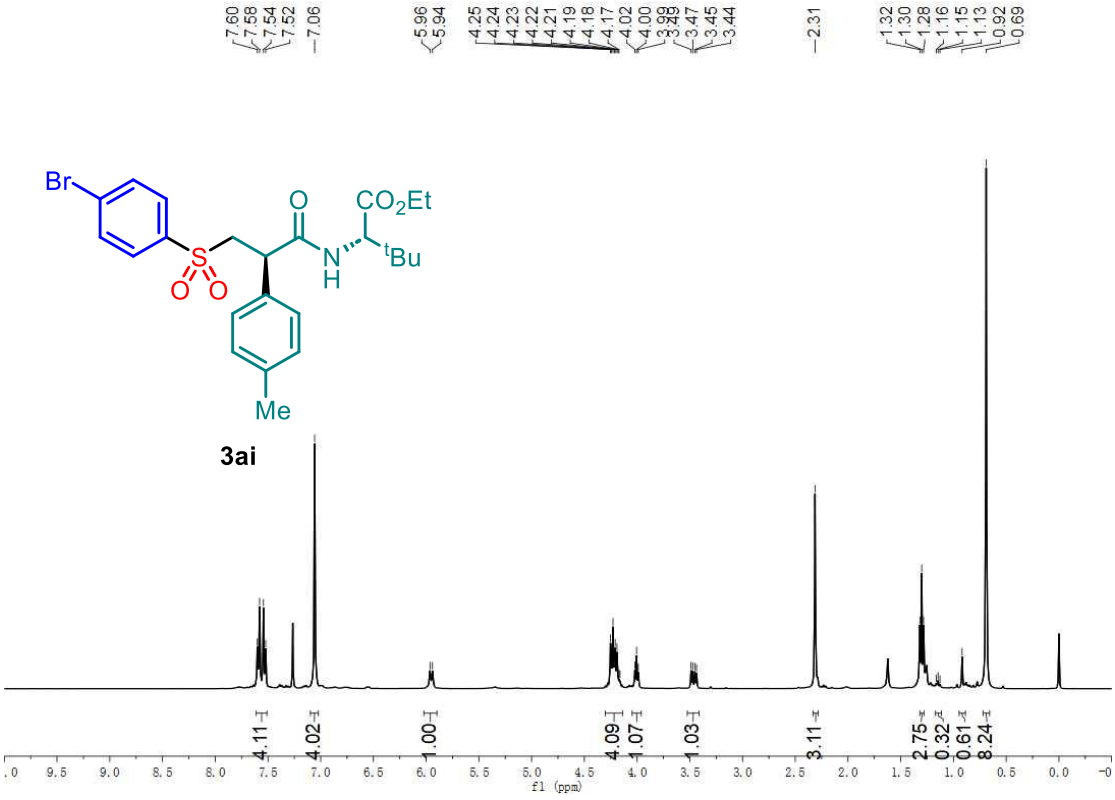
127.63
61.13
59.83
58.34
46.97
35.36
26.26
21.61
21.08
14.22
Me
O
CO2Et
S
O
O
N
H
tBu
Me
3ah
f1 (ppm)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5.94
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4.22
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4.19
4.18
4.17
4.02
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3.45
3.44
2.31
1.32
1.30
1.28
1.16
1.15
1.13
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0.69
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S
O
O
N
H
tBu
Me
3ai
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1.03
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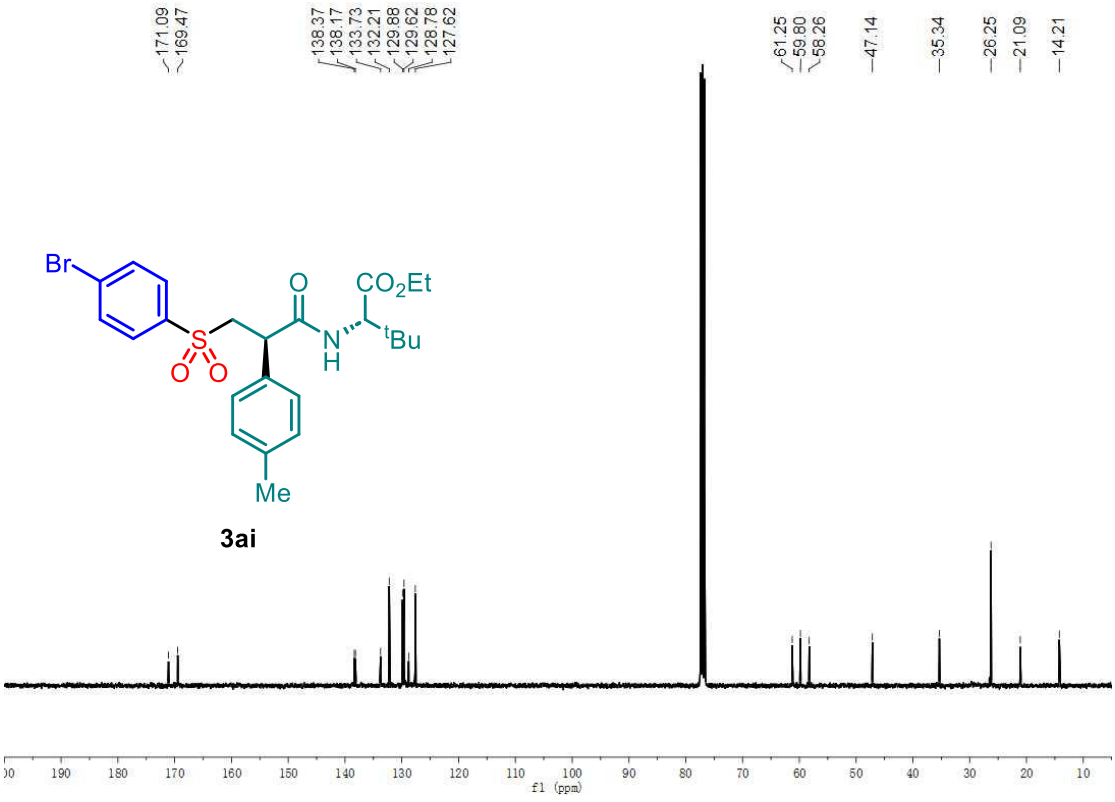
f1 (ppm)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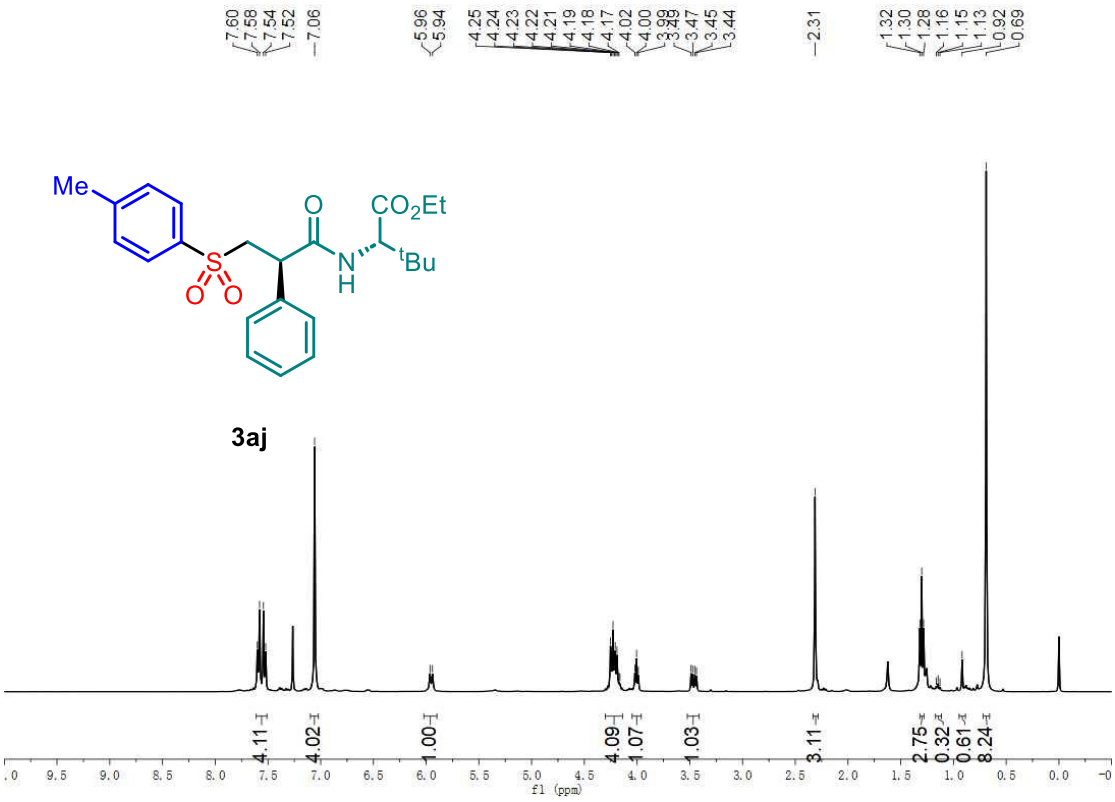
58.26
47.14
35.34
26.25
21.09
14.21
Br
O
CO2Et
S
O
O
N
H
tBu
Me
3ai
f1 (ppm)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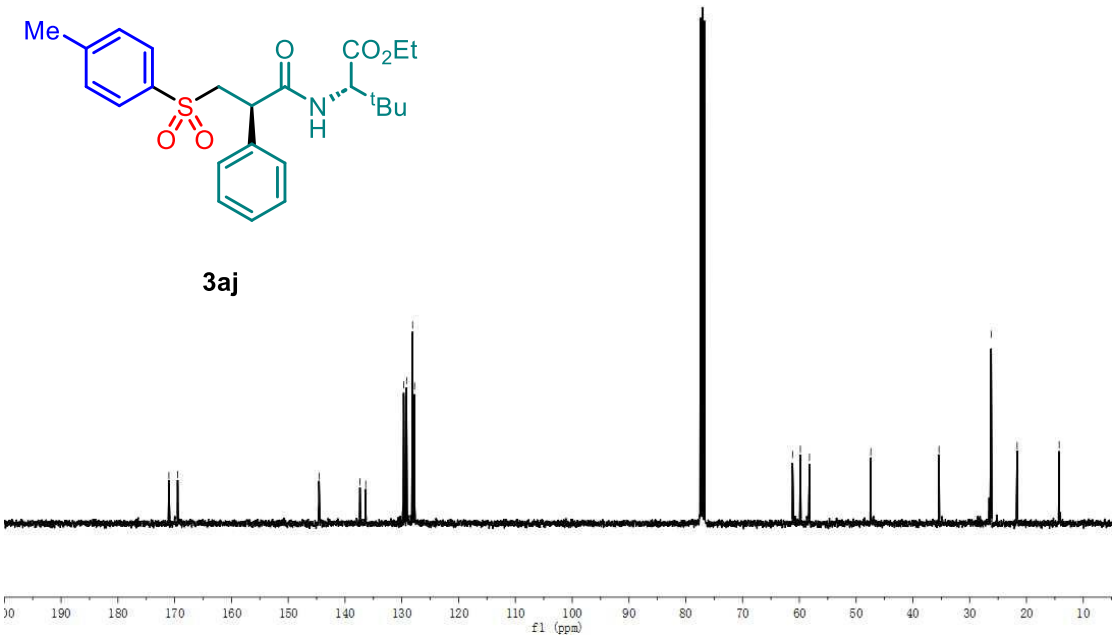
5.94
4.25
4.24
4.23
4.22
4.21
4.19
4.18
4.17
4.02
4.00
3.99
3.47
3.45
3.44
2.31
1.32
1.30
1.28
1.16
1.15
1.13
0.92
0.69
Me
O
CO2Et
S
O
O
N
H
tBu
4.11
4.02
1.00
4.09
1.07
1.03
3.11
2.75
0.32
0.61
8.24
f1 (ppm)

3aj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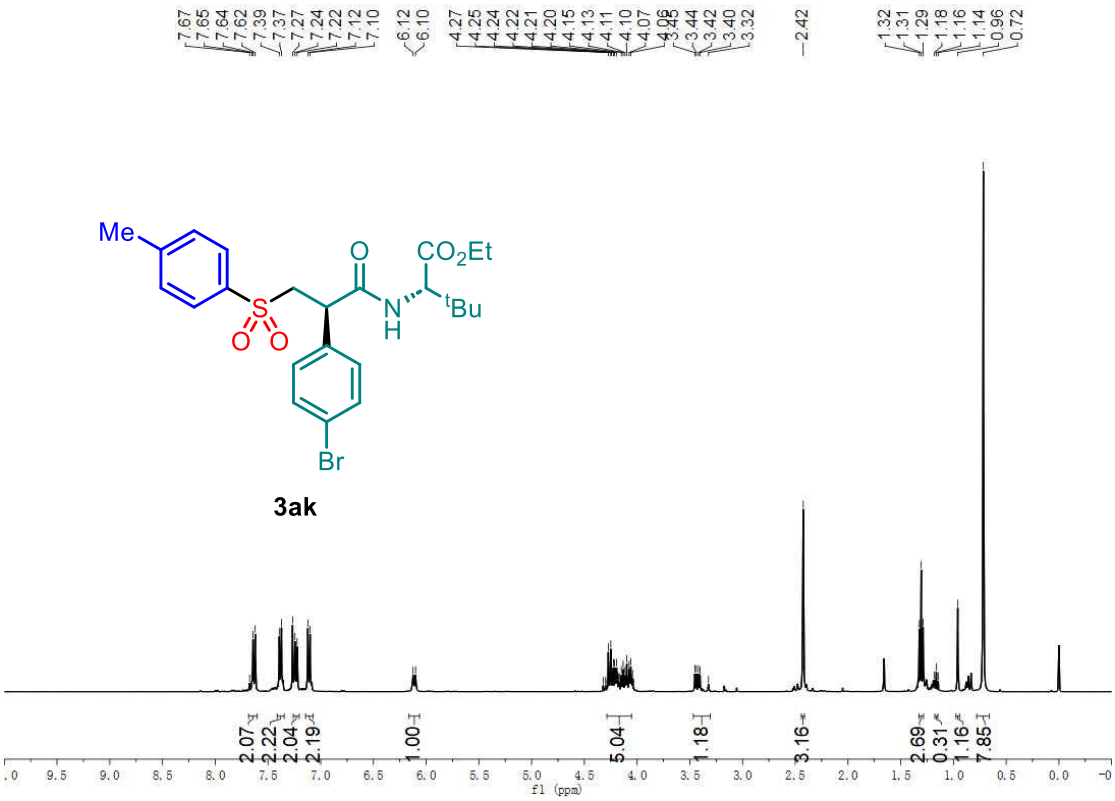
136.35
129.67
129.16
128.10
127.75
61.19
59.82
58.21
47.40
35.40
26.22
21.65
14.24
Me
O
CO2Et
S
O
O
N
H
tBu
f1 (ppm)

3aj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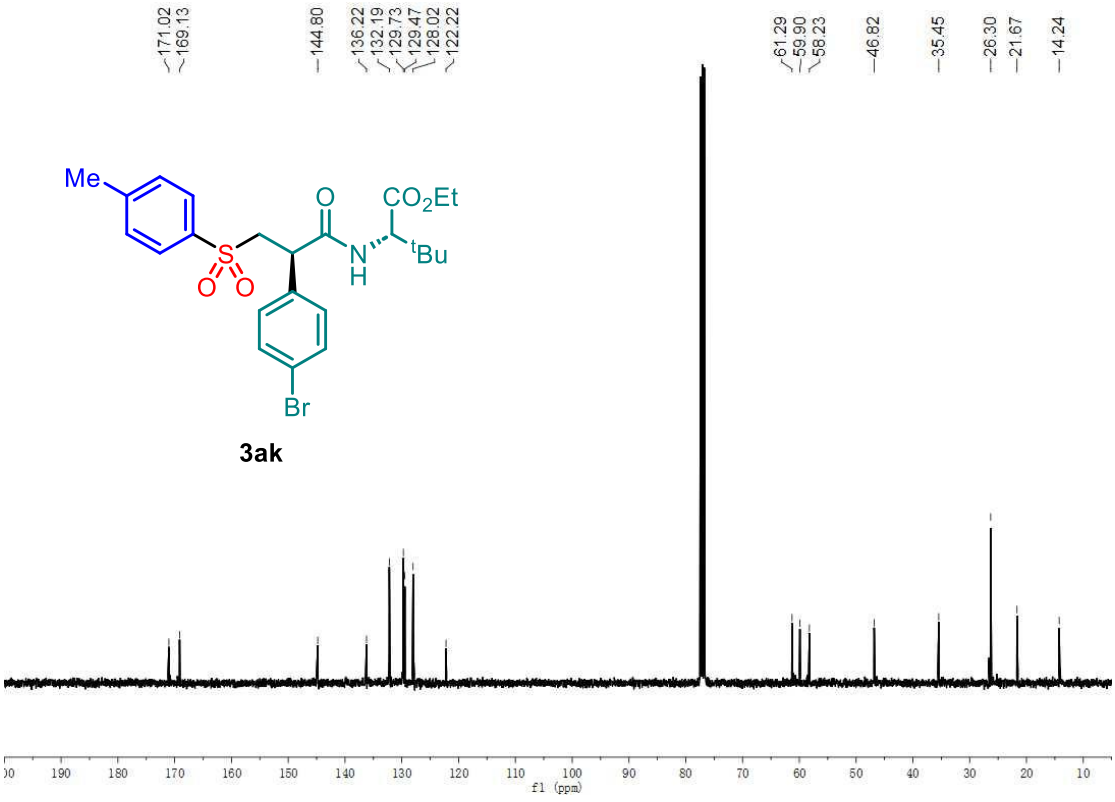
7.24
7.22
7.12
7.10
6.12
6.10
4.27
4.25
4.24
4.22
4.21
4.20
4.15
4.13
4.11
4.10
4.07
3.44
3.42
3.40
3.32
2.42
1.32
1.31
1.29
1.18
1.16
1.14
0.96
0.72
Me
O
CO2Et
S
O
O
N
H
tBu
Br
3ak
2.07
2.22
2.04
2.19
1.00
5.04
1.18
3.16
2.69
0.31
1.16
7.85
f1 (ppm)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132.19
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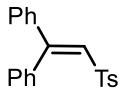
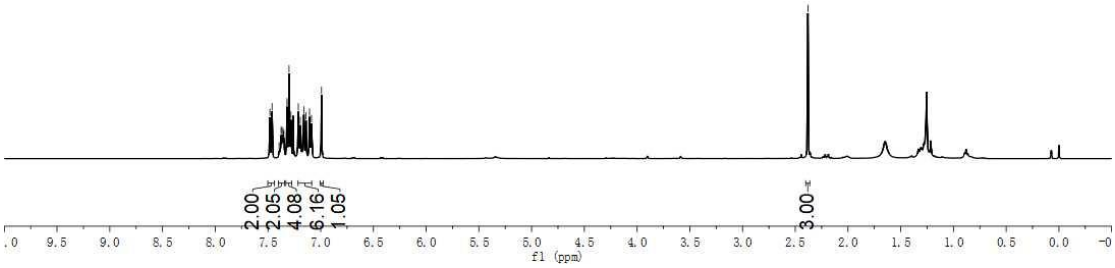
129.47
128.02
122.22
61.29
59.90
58.23
46.82
35.45
26.30
21.67
14.24
Me
O
CO2Et
S
O
O
N
H
tBu
Br
3ak
f1 (ppm)


7.48
7.46
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.32
7.30
7.28
7.21
7.19
7.16
7.14
7.11
7.09
6.99

2.38


Ph
Ph
Ts

4


2.00
2.05
4.08
6.16
1.05
3.00
f1 (ppm)


154.74
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139.23
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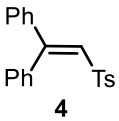
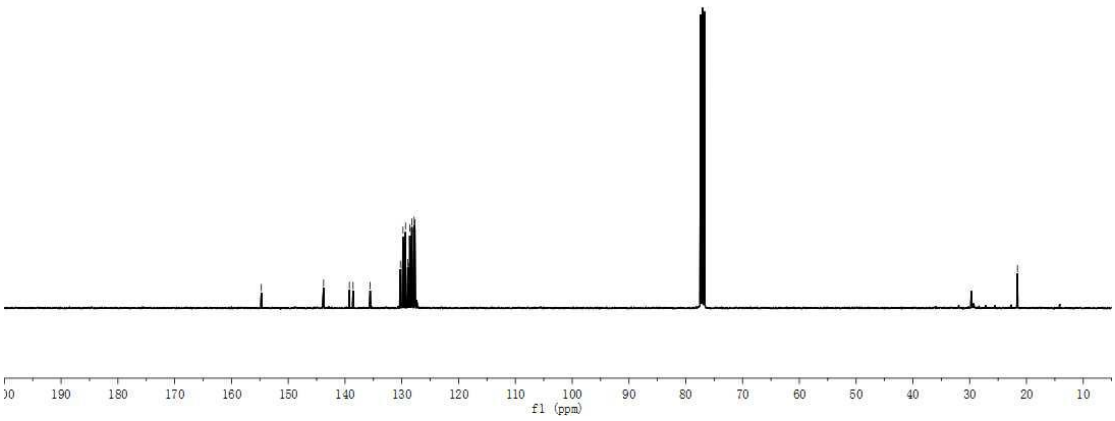
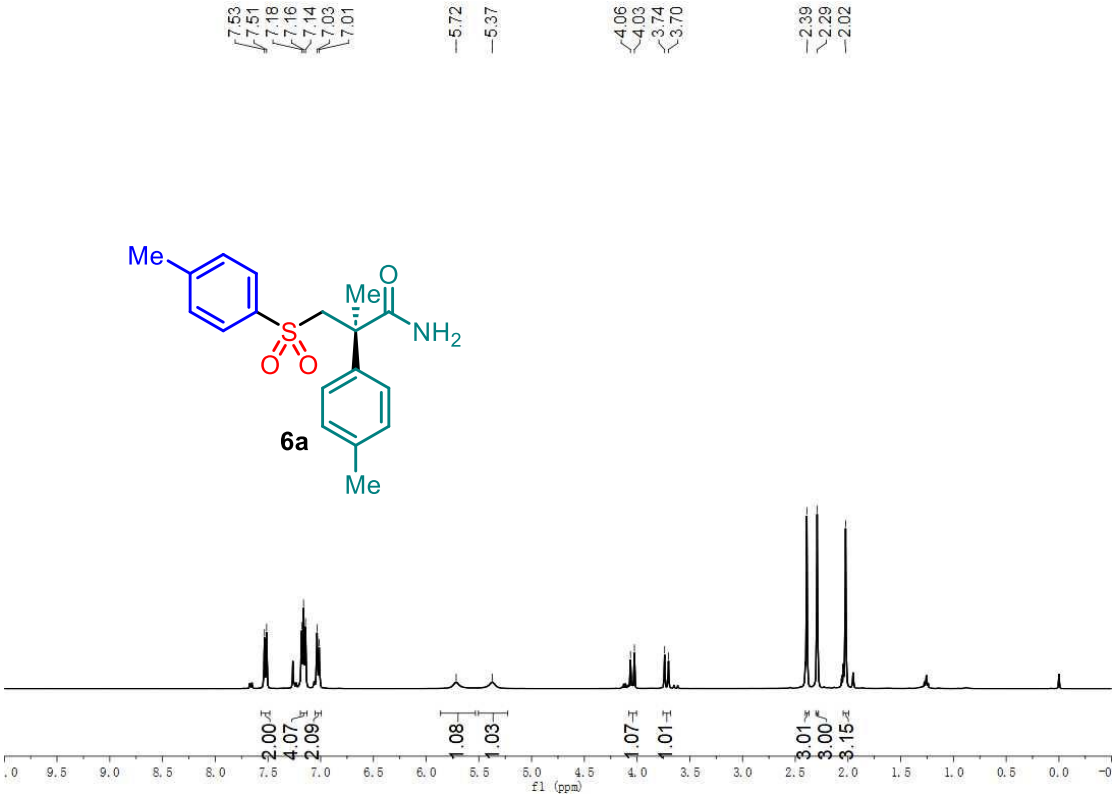
135.58
130.25
129.79
129.35
128.94
128.86
128.59
128.23
127.82
127.71


21.59


Ph
Ph
Ts

4


f1 (ppm)


7.53
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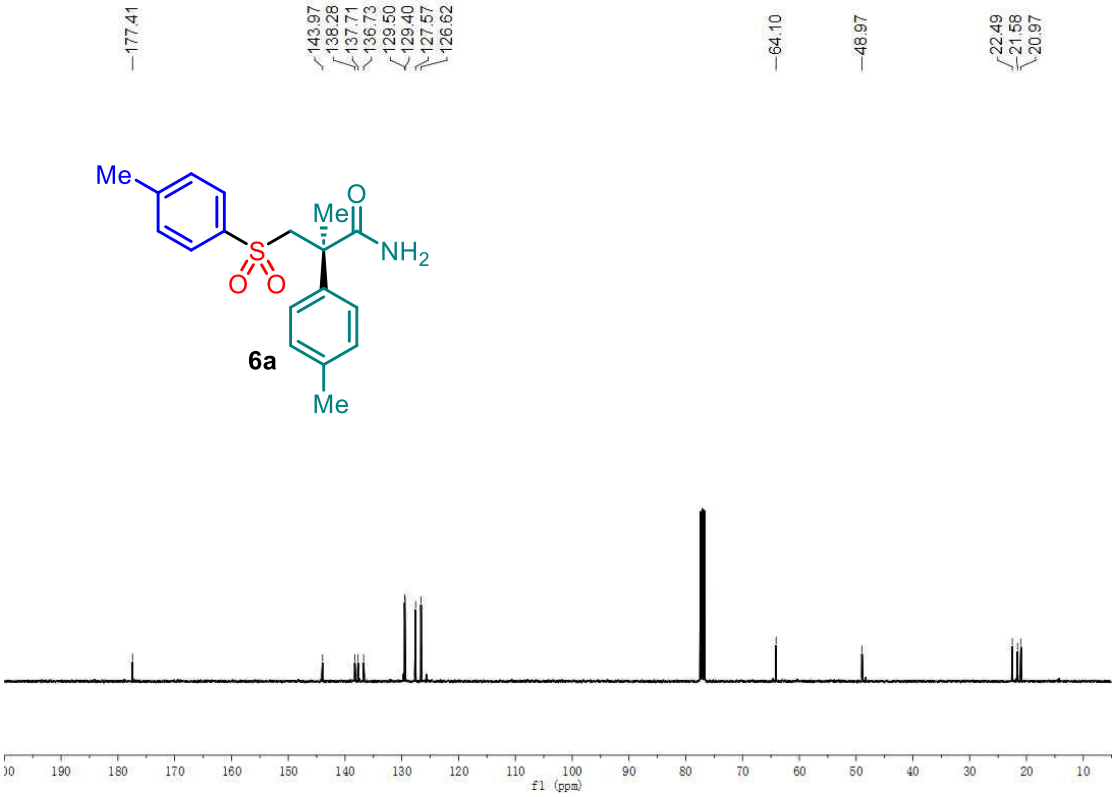
7.16
7.14
7.03
7.01
5.72
5.37
4.06
4.03
3.74
3.70
2.39
2.29
2.02
Me
O
Me
NH2
S
O
O
6a
Me
2.00
4.07
2.09
1.08
1.03
1.07
1.01
3.01
3.00
3.15
f1 (ppm)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136.73
129.50
129.40
127.57
126.62
64.10
48.97
22.49
21.58
20.97
Me
O
Me
NH2
S
O
O
6a
Me
f1 (ppm)

9. Crystal data and structure refinement for 3a

The crystal structure of compound **3a** has been deposited at the Cambridge Crystallographic Data Centre (**CCDC 2395343**).

The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

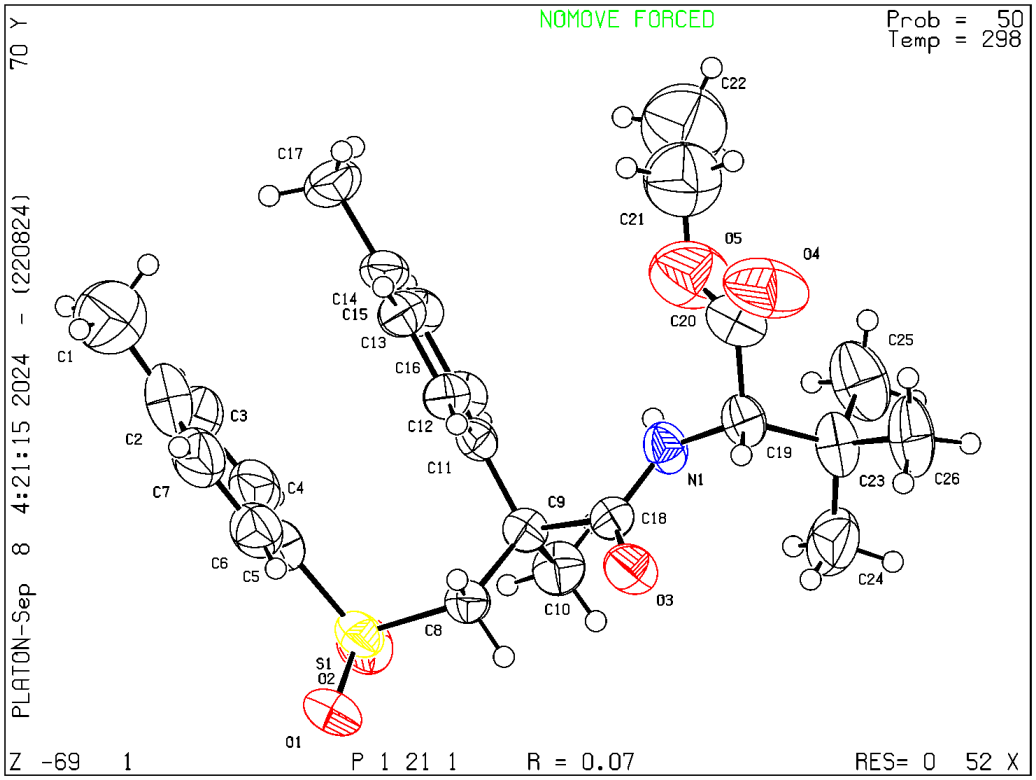

Table 1 Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{26}H_{35}NO_5S$
Formula weight	473.61
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.13820(10)
b/Å	16.9845(3)
c/Å	12.9091(2)
α/°	90
β/°	101.2190(10)
γ/°	90
Volume/Å^3	1320.11(4)
Z	2
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	1.367

F(000)	508.0
Crystal size/mm^3	0.23 × 0.22 × 0.21
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.98 to 136.832
Index ranges	-7 ≤ h ≤ 6, -20 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected	11135
Independent reflections	4358 [R_{int} = 0.0418, R_{sigma} = 0.0527]
Data/restraints/parameters	4358/105/305
Goodness-of-fit on F^2	1.172
Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1999
Final R indexes [all data]	R_1 = 0.0724, wR_2 = 0.2016
Largest diff. peak/hole / e Å^{-3}	0.40/-0.58
Flack parameter	0.168(11)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	5636.8(17)	3475.3(18)	9650.7(8)	53.5(4)
O3	8405(6)	2985(3)	6773(3)	61.2(9)
O2	3288(6)	3611(4)	9385(3)	73.2(11)
O1	6424(8)	2807(3)	10310(3)	75.5(11)
N1	7088(7)	4050(3)	5811(3)	52.4(9)
C11	6444(6)	4724(3)	7751(3)	39.5(7)
C9	5955(6)	3859(3)	7510(3)	42.3(8)
C18	7305(6)	3581(3)	6672(3)	41.8(7)
C19	8393(7)	3930(4)	5002(3)	51.4(9)
C16	8618(6)	4959(3)	8148(3)	43.9(8)
C15	9144(7)	5737(3)	8383(4)	48.6(9)
C10	3500(7)	3682(4)	7032(4)	58.0(13)
C8	6757(7)	3333(3)	8482(3)	46.1(9)
C5	6917(9)	4322(4)	10273(4)	55.1(9)
C12	4827(7)	5302(3)	7590(4)	51.2(9)
O4	11371(10)	4704(5)	4588(7)	118(2)
C14	7493(8)	6318(3)	8241(4)	50.9(9)
C6	9105(10)	4310(5)	10747(4)	68.6(13)
O5	8535(13)	5315(5)	5068(7)	123(2)
C17	8085(11)	7156(4)	8539(6)	70.8(14)
C13	5364(8)	6090(4)	7832(4)	57.7(10)
C23	7028(8)	3597(5)	3939(4)	65.1(12)
C20	9638(10)	4681(4)	4847(5)	72.3(13)

C26	8666(12)	3292(6)	3279(5)	95(3)
C25	5545(13)	4221(7)	3303(6)	98(3)
C24	5663(14)	2915(6)	4199(6)	95(2)
C7	10104(14)	4997(6)	11210(5)	89.2(18)
C4	5689(12)	5018(4)	10251(5)	72.2(14)
C3	6745(17)	5698(5)	10734(7)	95(2)
C2	8870(20)	5695(7)	11189(6)	112(2)
C21	9630(20)	6040(6)	4908(13)	135(3)
C1	10115(19)	6444(8)	11650(10)	122(3)
C22	7940(20)	6663(7)	4519(13)	160(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	55.5(6)	58.6(7)	50.5(6)	7.3(4)	20.1(4)	-5.3(5)
O3	71(2)	53(2)	66(2)	10.9(16)	29.2(17)	19.6(15)
O2	52.5(12)	99(3)	73(2)	-1(2)	26.4(15)	-12.7(17)
O1	100(3)	65(2)	65(2)	22.6(17)	24(2)	-6(2)
N1	61(2)	55(2)	43.4(17)	3.5(14)	16.2(14)	16.0(17)
C11	38.8(15)	43.6(18)	38.1(18)	3.7(14)	12.6(13)	3.1(13)
C9	35.1(15)	46.4(19)	45.6(18)	1.5(15)	8.5(13)	-0.5(15)
C18	40.1(16)	40.6(19)	44.5(16)	-1.1(13)	7.7(13)	0.0(13)
C19	48(2)	64(3)	44.3(19)	1.4(18)	12.5(14)	6.0(17)
C16	37.1(15)	44.4(18)	53(2)	-0.8(16)	14.4(15)	4.8(14)
C15	44.4(19)	47.3(19)	57(2)	-3.5(18)	16.8(18)	-1.6(14)
C10	38.7(17)	72(4)	62(3)	-5(2)	5.4(17)	-9.5(18)
C8	50.2(19)	42(2)	47.1(16)	1.3(15)	11.9(14)	-0.2(16)
C5	66(2)	63(2)	40(2)	0.2(16)	21.0(17)	-2.2(16)
C12	40.3(19)	53(2)	60(2)	6.0(19)	9.6(17)	7.7(15)
O4	98(3)	111(5)	163(6)	30(4)	66(4)	-11(3)
C14	63(2)	38(2)	56(2)	5.2(17)	22.6(18)	3.1(15)
C6	73(2)	75(3)	56(3)	7(2)	8(2)	-2(2)
O5	135(5)	94(3)	149(5)	22(4)	53(4)	32(3)
C17	88(4)	42(2)	87(4)	-9(2)	31(3)	-1(2)
C13	56.0(19)	48(2)	71(3)	8(2)	17(2)	13.9(16)
C23	60(2)	93(4)	42(2)	-5(2)	9.3(16)	11(2)
C20	72(3)	73(3)	74(3)	18(3)	19(2)	-1(2)
C26	97(4)	137(8)	56(3)	-17(4)	27(3)	27(4)
C25	81(4)	145(7)	63(3)	19(4)	-1(3)	33(4)
C24	99(5)	109(6)	73(4)	-29(4)	10(3)	-31(4)

C7	102(5)	107(4)	54(3)	1(3)	5(3)	-38(3)
C4	92(4)	70(3)	64(3)	2(2)	38(3)	11(2)
C3	143(5)	66(4)	89(5)	-13(3)	57(4)	5(4)
C2	161(6)	126(4)	52(3)	-9(4)	32(4)	-8(3)
C21	137(3)	132(3)	137(3)	2.9(14)	28.2(14)	-9.4(13)
C1	122(3)	122(3)	122(3)	-0.1(3)	23.6(6)	-0.2(3)
C22	159(4)	156(4)	164(4)	6(3)	27(3)	10(3)

Table 4 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.434(4)	C5	C6	1.363(8)
S1	O1	1.444(4)	C5	C4	1.399(9)
S1	C8	1.791(4)	C12	C13	1.398(8)
S1	C5	1.756(6)	O4	C20	1.176(9)
O3	C18	1.209(5)	C14	C17	1.501(7)
N1	C18	1.352(6)	C14	C13	1.367(7)
N1	C19	1.449(6)	C6	C7	1.398(10)
C11	C9	1.519(6)	O5	C20	1.333(10)
C11	C16	1.392(5)	O5	C21	1.436(15)
C11	C12	1.384(6)	C23	C26	1.530(8)
C9	C18	1.559(5)	C23	C25	1.528(9)
C9	C10	1.543(5)	C23	C24	1.506(12)
C9	C8	1.541(6)	C7	C2	1.402(15)
C19	C23	1.568(7)	C4	C3	1.410(11)
C19	C20	1.520(8)	C3	C2	1.324(14)
C16	C15	1.381(7)	C2	C1	1.542(16)
C15	C14	1.400(7)	C21	C22	1.4993(14)

Table 5 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	O1	118.2(3)	C6	C5	C4	120.1(6)
O2	S1	C8	110.7(2)	C4	C5	S1	119.4(5)
O2	S1	C5	108.5(3)	C11	C12	C13	121.0(4)
O1	S1	C8	104.5(2)	C15	C14	C17	120.1(5)
O1	S1	C5	107.8(3)	C13	C14	C15	117.7(5)
C5	S1	C8	106.5(2)	C13	C14	C17	122.2(5)
C18	N1	C19	122.0(4)	C5	C6	C7	119.4(7)
C16	C11	C9	119.3(3)	C20	O5	C21	113.0(8)
C12	C11	C9	123.3(4)	C14	C13	C12	121.6(4)
C12	C11	C16	117.4(4)	C26	C23	C19	108.2(4)

C11	C9	C18	108.9(3)	C25	C23	C19	112.4(6)
C11	C9	C10	114.1(4)	C25	C23	C26	108.9(6)
C11	C9	C8	112.1(3)	C24	C23	C19	107.9(5)
C10	C9	C18	105.8(3)	C24	C23	C26	108.5(7)
C10	C9	C8	110.2(4)	C24	C23	C25	110.8(6)
C8	C9	C18	105.1(3)	O4	C20	C19	124.8(7)
O3	C18	N1	123.0(4)	O4	C20	O5	124.0(7)
O3	C18	C9	122.6(4)	O5	C20	C19	111.2(6)
N1	C18	C9	114.3(4)	C6	C7	C2	120.5(8)
N1	C19	C23	113.9(4)	C5	C4	C3	118.9(7)
N1	C19	C20	109.9(4)	C2	C3	C4	121.5(8)
C20	C19	C23	112.6(4)	C7	C2	C1	117.7(9)
C15	C16	C11	121.5(4)	C3	C2	C7	119.6(9)
C16	C15	C14	120.9(4)	C3	C2	C1	122.6(10)
C9	C8	S1	119.5(3)	O5	C21	C22	109.9(11)
C6	C5	S1	120.5(5)				

Table 6 Torsion Angles for 1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C5	C6	C7	178.2(5)	C15	C14	C13	C12	1.8(7)
S1	C5	C4	C3	-178.7(5)	C10	C9	C18	O3	-105.4(5)
O2	S1	C8	C9	41.6(4)	C10	C9	C18	N1	72.8(5)
O2	S1	C5	C6	170.2(4)	C10	C9	C8	S1	-67.6(5)
O2	S1	C5	C4	-11.7(5)	C8	S1	C5	C6	-70.6(5)
O1	S1	C8	C9	169.9(3)	C8	S1	C5	C4	107.5(4)
O1	S1	C5	C6	41.1(5)	C8	C9	C18	O3	11.2(5)
O1	S1	C5	C4	-140.8(4)	C8	C9	C18	N1	-170.5(4)
N1	C19	C23	C26	-164.8(6)	C5	S1	C8	C9	-76.2(4)
N1	C19	C23	C25	74.9(7)	C5	C6	C7	C2	0.0(10)
N1	C19	C23	C24	-47.5(7)	C5	C4	C3	C2	1.2(10)
N1	C19	C20	O4	149.3(8)	C12	C11	C9	C18	120.0(4)
N1	C19	C20	O5	-29.2(7)	C12	C11	C9	C10	2.1(6)
C11	C9	C18	O3	131.5(4)	C12	C11	C9	C8	-124.1(4)
C11	C9	C18	N1	-50.3(4)	C12	C11	C16	C15	0.6(6)
C11	C9	C8	S1	60.7(4)	C6	C5	C4	C3	-0.6(8)
C11	C16	C15	C14	0.8(7)	C6	C7	C2	C3	0.5(11)
C11	C12	C13	C14	-0.4(8)	C6	C7	C2	C1	-176.0(7)
C9	C11	C16	C15	-179.7(4)	C17	C14	C13	C12	-177.9(5)
C9	C11	C12	C13	179.5(4)	C23	C19	C20	O4	-82.6(9)

C18	N1	C19	C23	108.3(5)	C23	C19	C20	O5	98.9(7)
C18	N1	C19	C20	-124.4(5)	C20	C19	C23	C26	69.3(7)
C18	C9	C8	S1	178.8(3)	C20	C19	C23	C25	-51.0(6)
C19	N1	C18	O3	-8.3(7)	C20	C19	C23	C24	-173.5(6)
C19	N1	C18	C9	173.5(4)	C20	O5	C21	C22	145.6(11)
C16	C11	C9	C18	-59.7(4)	C4	C5	C6	C7	0.1(8)
C16	C11	C9	C10	-177.6(4)	C4	C3	C2	C7	-1.1(12)
C16	C11	C9	C8	56.2(5)	C4	C3	C2	C1	175.3(8)
C16	C11	C12	C13	-0.8(7)	C21	O5	C20	C19	-178.6(9)
C16	C15	C14	C17	177.7(5)	C21	O5	C20	O4	2.8(14)
C16	C15	C14	C13	-2.0(7)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	*x*	*y*	*z*	U(eq)
H1	6146	4430	5741	63
H19	9518	3533	5275	62
H16	9742	4583	8258	53
H15	10614	5878	8639	58
H10A	2608	3775	7553	87
H10B	3354	3142	6810	87
H10C	3012	4019	6435	87
H8A	8356	3392	8679	55
H8B	6470	2790	8261	55
H12	3360	5166	7317	61
H6	9926	3848	10762	82
H17A	7916	7247	9253	106
H17B	7121	7503	8073	106
H17C	9598	7253	8482	106
H13	4246	6468	7712	69
H26A	9719	3697	3212	143
H26B	7872	3145	2590	143
H26C	9435	2841	3619	143
H25A	4582	4443	3730	147
H25B	4667	3983	2685	147
H25C	6453	4629	3094	147
H24A	6591	2565	4677	142
H24B	5041	2637	3562	142
H24C	4486	3107	4523	142
H7	11596	4992	11535	107

H4	4199	5031	9923	87
H3	5930	6160	10733	114
H21A	10576	5960	4396	162
H21B	10559	6207	5567	162
H1A	11412	6299	12158	183
H1B	9156	6759	11986	183
H1C	10552	6741	11091	183
H22A	6616	6421	4131	241
H22B	8527	7021	4067	241
H22C	7593	6946	5110	241

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