Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Catalytic Asymmetric Oxidative Sulfenylation of β-Ketocarbonyls by Chiral Primary Amine

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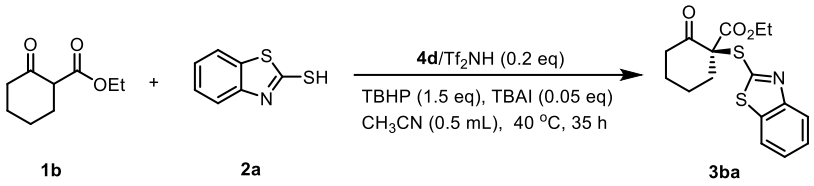
1. General information and materials

General information: All commercial reagents were used without further purification unless otherwise noted. ^{1}H, ^{13}C, ^{19}F NMR spectra were measured on NMR instrument (400 or 500 MHz for ^{1}H NMR, 101 or 126 MHz for ^{13}C NMR and 377 MHz for ^{19}F NMR). Tetramethylsilane (TMS) served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR. The following abbreviations were used to express the mutiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. The enantiomeric excesses were determined by HPLC analysis on Chiral Daicel Chiralpak OD-H, OJ-H, AS-H, AD-H. Optical rotations were measured on a commercial polarimeter and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). HRMS was recorded on a commercial instrument (ESI and APCI Source).

Materials: The corresponding 2-mercaptobenzothiazole derivatives **2b**, **2d**, **2g**, **2h, 2l, 2m, 2n, 2p**were prepared according to the procedures reported previously.[1,2] Others were from commercial Alfa-Aesar, Acros, TCI etc.

2. Optimization of reaction conditions

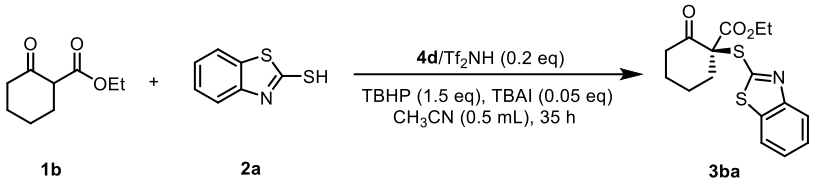
Table S1. Screening of atmosphere[a]



Entry	Atmosphere	Yield (%)	Ee (%)
1	Ar	83	86
2	Air	71	87

[a]All reactions were performed at 40 °C in MeCN (0.5 mL) with **1b** (0.10 mmol), **2a** (0.10 mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4d**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

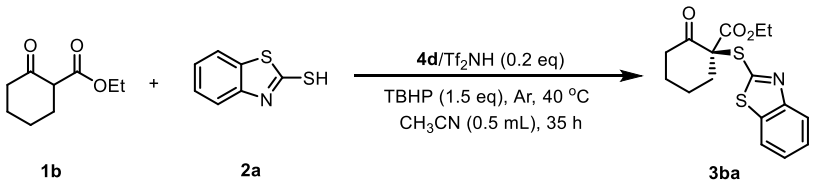
Table S2. Screening of temperature[a]



Entry	Temperature (°C)	Yield (%)	Ee (%)
1	50	81	85
2	40	89	86
3	R.T.	86	86
4	-5	10	24

[a]All reactions were performed in MeCN (0.5 mL) with **1b** (0.10 mmol), **2a** (0.10 mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4d**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

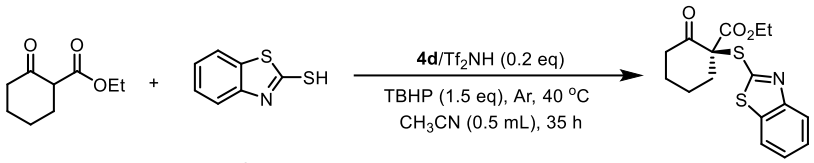
Table S3. Screening of iodide anion[a]



Entry	Iodide anion	Yield (%)	Ee (%)
1	NaI	88	81
2	KI	86	86
3	TBAI	89	86
4	TMAI	77	86
5	TEAI	84	86
6	NiI	94	5

[a]All reactions were performed at 40 °C in MeCN (0.5 mL) with **1b** (0.10 mmol), **2a** (0.10 mmol), iodide anion (0.05 eq), TBHP (1.5 eq), **4d**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

Table S4. Screening of the amount of TBAI[a]

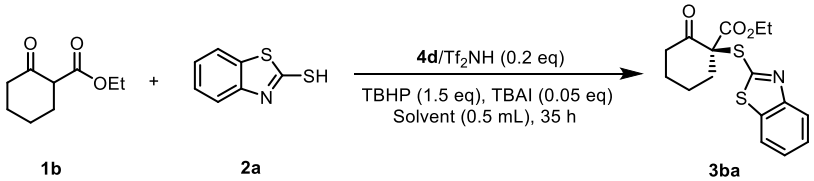


1b 2a 3ba

Entry	TBAI (x eq)	Yield (%)	Ee (%)
1	0.0125	62	76
2	0.025	89	84
3	0.05	89	86
4	0.1	52	88
5	0.2	69	88

[a]All reactions were performed at 40 °C in MeCN (0.5 mL) with **1b** (0.10 mmol), **2a** (0.10 mmol), TBAI (x eq), TBHP (1.5 eq), **4d**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

Table S5. Screening of the solvent[a]

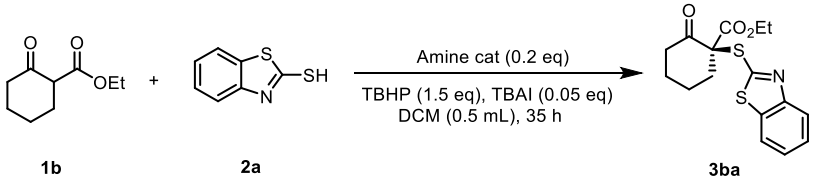


1b 2a 3ba

Entry	Solvent	Yield (%)	Ee (%)
1	EA	83	70
2	DCM	88	88
3	$CHCl_3$	84	86
4	THF	77	70
5	MeCN	86	86
6	CCl_4	18	60
7	PhF	49	80
8	MeOH	35	63
9	DMF	N.D.	/
10	DCE	86	88

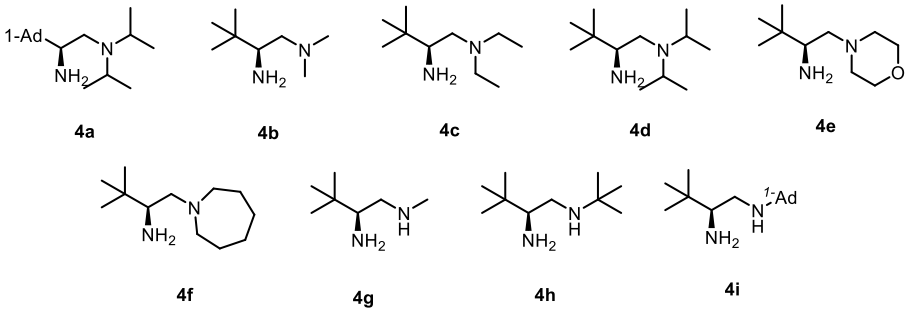
[a]All reactions were performed at 40 °C in solvent (0.5 mL) with **1b** (0.10 mmol), **2a** (0.10 mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4d**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

Table S6. Screening of the primary amines[a]



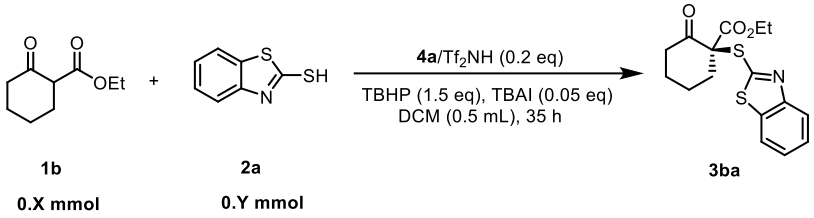
1b **2a** **3ba**

Entry	Primary amines	Yield (%)	Ee (%)
1	**4a** / Tf_2NH	81	90
2	**4a** / TfOH	81	84
3	**4b** / TfOH	72	2
4	**4c** / Tf_2NH	69	51
5	**4d** / Tf_2NH	88	86
6	**4e** / TfOH	72	-21
7	**4f** / TfOH	65	9
8	**4g** / Tf_2NH	trace	/
9	**4h** / Tf_2NH	75	-86
10	**4i** / TfOH	76	-86



[a]All reactions were performed at 40 °C in DCM (0.5 mL) with **1b** (0.10 mmol), **2a** (0.10 mmol), TBAI (0.05 eq), TBHP (1.5 eq), amine catalyst (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

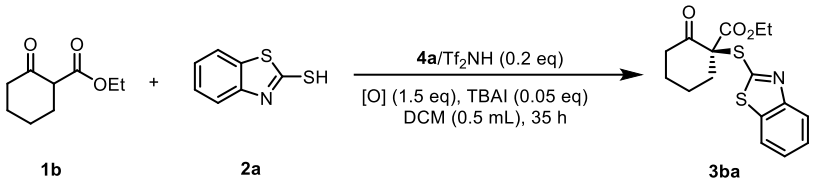
Table S7. Screening of the ratio between **1b** and **2a**[a]



Entry	X : Y	Yield (%)	Ee (%)
1	1.0 : 1.2	85	84
2	1.0 : 1.0	87	88
3	1.2 : 1.0	92	90
4	1.4 : 1.0	98	90
5	1.6 : 1.0	98	90
6	1.8 : 1.0	97	90

[a]All reactions were performed at 40 °C in DCM (0.5 mL) with **1b** (0.X mmol), **2a** (0.Y mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4a**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

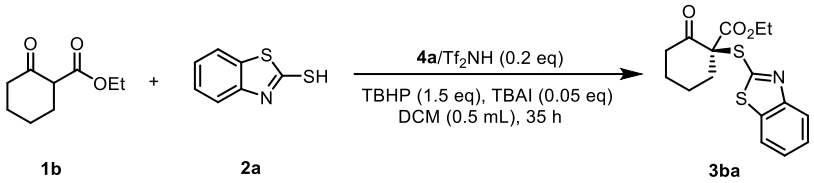
Table S8. Screening of the oxidant[a]



Entry	Oxidant	Yield (%)	Ee (%)
1	TBHP	95	90
2	DTBP	Trace	/
3	H_2O_2	N.R.	/

[a]All reactions were performed at 40 °C in DCM (0.5 mL) with **1b** (0.14 mmol), **2a** (0.1 mmol), TBAI (0.05 eq), oxidant (1.5 eq), **4a**/Tf_2NH (20 mol%) and pimelic acid (0.3 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

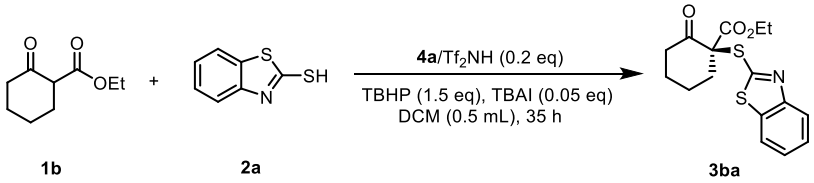
Table S9. Screening of the amount of acid[a]



Entry	Pimelic acid (X eq)	Yield (%)	Ee (%)
1	0.3	95	90
2	0.2	93	91
3	0.1	94	91

[a]All reactions were performed at 40 °C in DCM (0.5 mL) with **1b** (0.14 mmol), **2a** (0.1 mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4a**/Tf_2NH (20 mol%) and pimelic acid (X eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

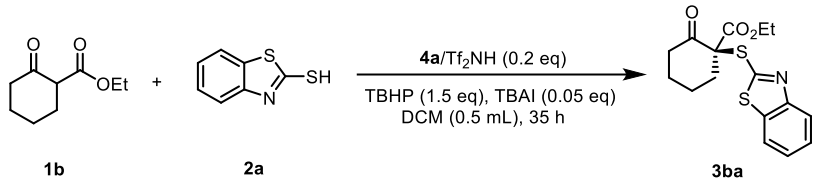
Table S10. Screening of the acid[a]



Entry	Acid (0.1 eq)	Yield (%)	Ee (%)
1	pimelic acid	93	91
2	TsOH	56	31
3	$BnCO_2H$	90	90
4	$C_6F_5CO_2H$	95	53
5	*m*-NO_2PhCO_2H	92	90
6	Malonic acid	95	51

[a]All reactions were performed at 40 °C in DCM (0.5 mL) with **1b** (0.14 mmol), **2a** (0.1 mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4a**/Tf_2NH (20 mol%) and acid (0.1 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

Table S11. Control experiments[a]

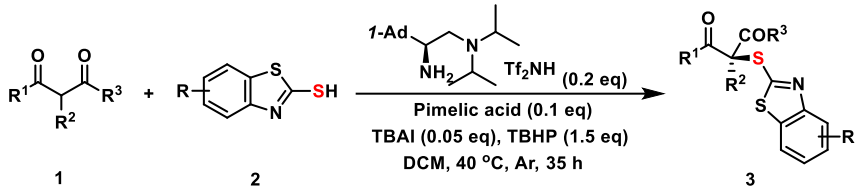


1b 2a 3ba

Entry	Conditions	Yield (%)	Ee (%)
1	No TBAI	N.R.	/
2	No TBHP	N.R.	/
3	No acid	87	89
4	BHT (3.0 eq)	94	91
5	TEMPO (3.0 eq)	75	82

[a]All reactions were performed at 40 °C in DCM (0.5 mL) with **1b** (0.14 mmol), **2a** (0.1 mmol), TBAI (0.05 eq), TBHP (1.5 eq), **4a**/Tf_2NH (20 mol%) and pimelic acid (0.1 eq) for 35 h at Ar atmosphere. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values base on HPLC analysis.

3. General procedure of the catalytic reactions



General procedure: To a 10 mL flame-dried Schlenk tube charged with a magnetic stir bar was added chiral primary amine catalyst (11.2 mg, 0.02 mmol), pimelic acid (1.6 mg, 0.01 mmol), TBAI (1.8 mg, 0.05 eq) and 2-mercaptobenzothiazoles (0.1 mmol), then a solution of β-ketocarbonyl **1** (0.14 mmol) in 0.5 mL anhydrous DCM was added via syringe under Ar. Finally, the TBHP (~5.5mol/L in decane (over molecular sieve 4Å), 27.3 uL, 0.15 mmol, 1.5 eq) was slowly added dropwise into the solution. After degassing 3 times by a standard freeze-thaw operation, the reaction was conducted at 40 °C for 35 h. Solvent was removed and purification by silica gel column to give the desired product (S)-**3**.

4. X-Ray crystallographic structure:

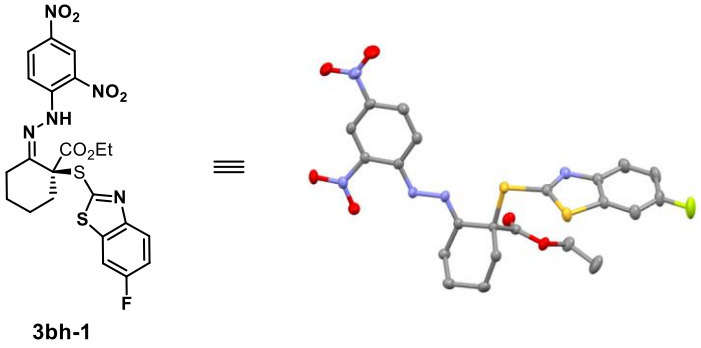


Table 1 Crystal data and structure refinement for 3bh-1 (CCDC 2090638).

Identification code	TX5103A
Empirical formula	$C_{16}H_{16}FNO_3S_2$
Formula weight	353.42
Temperature/K	220.01(15)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.57210(10)
b/Å	9.14670(10)
c/Å	26.7412(3)
α/°	90
β/°	90

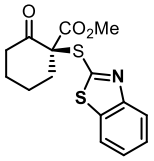
γ/°	90
Volume/Å^3	1607.49(4)
Z	4
ρ_{calc}g/cm^3	1.460
μ/mm^{-1}	3.228
F(000)	736.0
Crystal size/mm^3	0.11 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.61 to 150.696
Index ranges	-8 ≤ h ≤ 7, -11 ≤ k ≤ 6, -33 ≤ l ≤ 33
Reflections collected	9366
Independent reflections	3191 [R_{int} = 0.0270, R_{sigma} = 0.0268]
Data/restraints/parameters	3191/0/209
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0723
Final R indexes [all data]	R_1 = 0.0294, wR_2 = 0.0731
Largest diff. peak/hole / e Å^{-3}	0.17/-0.20
Flack parameter	-0.006(8)

5. Reference

(1) Wang, F.; Cai, S.; Wang, Z.; Xi, C. Synthesis of 2-Mercaptobenzothiazoles via DBU-Promoted Tandem Reaction of o-Haloanilines and Carbon Disulfide. *Org. Lett.* **2011**, *13*, 3202-33205.

(2) Gao, M.; Lou, C. Q.; Zhu, N.; Qin, W.; Suo, Q.; Han, L.; Hong, H. Efficient, Iron-Catalyzed Synthesis of 2-Mercaptobenzothiazole through S-Arylation/Heterocyclization of 2-Haloaniline with Potassium Xanthate. *Synth. Commun.* **2015**, *45*, 2378.

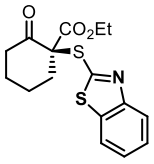
6. Spectra data for substrates and products



3aa

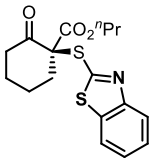
3aa: pale yellow oil, 72% yield, 89% ee. $[\alpha]_D^{20}$ = -12.8 (c = 2.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 2.89 (dd, *J* = 8.7, 5.3 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.53 (ddd, *J* = 14.4, 11.0, 5.7 Hz, 1H), 2.30 – 2.16 (m, 1H), 2.07 – 1.73 (m, 4H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 201.8, 168.6, 160.0, 153.2, 137.3, 126.2, 125.4, 122.9, 121.1, 69.5, 53.4, 40.5, 37.6, 26.9, 22.7. IR (thin film, cm^{-1}) 3019, 2400, 1718, 1431, 1428, 1311, 1214, 1126, 1078, 991, 929, 744, 668, 627, 555, 432. HRMS (ESI) calcd for $C_{15}H_{16}NO_3S_2^+$ ($M+H^+$) 322.05661 f ound 322.05587. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flo w rate = 1.0 mL/min, λ = 222 nm, retention time: 42.6 min (minor) and 46.1 min (maj or).



3ba

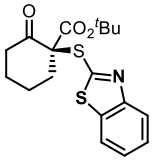
3ba: pale yellow oil, 90% yield, 91% ee. $[\alpha]_D^{20}$ = -22.4 (c = 3.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.91 (d, *J* = 13.8 Hz, 1H), 2.79 (dd, *J* = 10.1, 4.2 Hz, 1H), 2.63 – 2.48 (m, 1H), 2.31 – 2.16 (m, 1H), 2.05 – 1.75 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 168.0, 160.2, 153.2, 137.3, 126.2, 125.4, 122.9, 121.1, 69.5, 62.6, 40.5, 37.6, 26.8, 22.7, 13.9. IR (thin film, cm^{-1}) 3019, 2400, 1717, 1521, 1428, 1214, 929, 744, 668, 628, 556, 495. HRMS (ESI) calcd for $C_{16}H_{18}NO_3S_2^+$ ($M+H^+$) 336.07226 found 336.07123. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 24.9 min (minor) and 30.8 min (major).



3ca

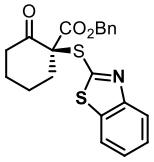
3ca: colorless oil, 68% yield, 89% ee. $[\alpha]_D^{20}$ = -24.1 (c = 2.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.01 – 2.86 (m, 1H), 2.80 (dt, *J* = 8.8, 4.1 Hz, 1H), 2.56 (ddd, *J* = 14.3, 11.1, 5.7 Hz, 1H), 2.34 – 2.18 (m, 1H), 2.08 – 1.77 (m, 4H), 1.61 (h, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.87 (s), 168.10 (s), 160.25 (s), 153.20 (s), 137.22 (s), 126.18 (s), 125.35 (s), 122.8, 121.1, 69.6, 68.2, 40.5, 37.6, 26.8, 22.7, 21.7, 10.3. IR (thin film, cm^{-1}) 3019, 2971, 2940, 2400, 1717, 1454, 1429, 1311, 1214, 1126, 1055, 991, 745, 668, 628, 557. HRMS (ESI) calcd for $C_{17}H_{20}NO_3S_2^+$ ($M+H^+$) 350.08791

found 350.08674. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 17.9 min (minor) and 22.9 min (major).



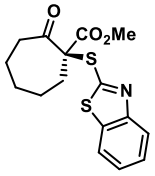
3da

3da: colorless oil, 77% yield, 91% ee. $[\alpha]_D^{20}$ = -34.8 (c = 2.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.75 (d, *J* = 14.3 Hz, 1H), 2.61 – 2.51 (m, 1H), 2.28 – 2.16 (m, 1H), 2.03 (s, 1H), 1.95 – 1.74 (m, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 166.8, 160.7, 153.1, 137.3, 126.1, 125.3, 122.7, 121.1, 83.7, 70.1, 40.6, 37.7, 27.7, 26.7, 22.9. IR (thin film, cm^{-1}) 3019, 2933, 2868, 2400, 1716, 1455, 1429, 1370, 1335, 1252, 1215, 1160, 1147, 989, 942, 840, 751, 668, 627, 558. HRMS (ESI) calcd for $C_{18}H_{22}NO_3S_2^+$ ($M+H^+$) 364.10356 found 364.10245. HPLC analysis: Daicel Chiralpak IC-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 21.2 min (major) and 22.5 min (minor).



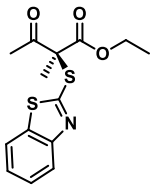
3ea

3ea: colorless oil, 45% yield, 86% ee. $[\alpha]_D^{20}$ = -28.2 (c = 1.7, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 1.4 Hz, 5H), 5.20 (q, *J* = 12.2 Hz, 2H), 2.92 (dt, *J* = 13.8, 5.4 Hz, 1H), 2.84 – 2.72 (m, 1H), 2.48 (ddd, *J* = 14.3, 10.9, 5.6 Hz, 1H), 2.26 (ddd, *J* = 14.2, 10.8, 3.6 Hz, 1H), 2.03 – 1.84 (m, 3H), 1.78 – 1.70 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 167.9, 160.2, 153.2, 137.2, 128.7, 128.1, 126.2, 125.3, 122.9, 121.1, 69.6, 68.2, 40.4, 37.6, 26.9, 22.6. IR (thin film, cm^{-1}) 3019, 1718, 1428, 1214, 1078, 991, 748, 668, 627. HRMS (ESI) calcd for $C_{21}H_{20}NO_3S_2^+$ ($M+H^+$) 398.08791 found 398.08664. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 205 nm, retention time: 15.6 min (minor) and 17.9 min (major).



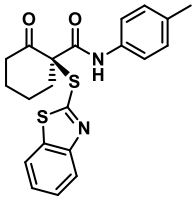
3fa

3fa: colorless oil, 70% yield, 57% ee. $[\alpha]_D^{20}$ = 5.4 (c = 2.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.39 (dd, *J* = 27.2, 6.7 Hz, 2H), 3.77 (s, 3H), 2.75 (dd, *J* = 20.2, 7.9 Hz, 2H), 2.66 – 2.41 (m, 2H), 1.84 (s, 2H), 1.76 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 168.9, 161.4, 153.3, 136.8, 126.2, 125.2, 122.7, 121.1, 73.9, 53.5, 40.7, 33.6, 29.8, 26.4, 24.5. IR (thin film, cm^{-1}) 3020, 2932, 2857, 1739, 174, 1455, 1312, 1215, 1127, 1005, 940, 750, 668, 627. HRMS (ESI) calcd for $C_{16}H_{18}NO_3S_2^+$ ($M+H^+$) 336.07226 found 336.07108. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 25.7 min (minor) and 32.9 min (major).



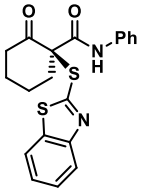
3ga

3ga: colorless oil, 51% yield, 76% ee. $[\alpha]_D^{20}$ = -33.6 (c = 2.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.94 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 168.7, 160.5, 153.3, 136.4, 126.3, 125.3, 122.6, 121.1, 68.2, 63.0, 26.0, 21.8, 13.9. IR (thin film, cm^{-1}) 3020, 1716, 1429, 1232, 1215,1122, 991, 906, 753, 728, 668, 650. HRMS (ESI) calcd for $C_{14}H_{16}NO_3S_2^+$ ($M+H^+$) 310.05661 found 310.05843. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 19.3 min (minor) and 22.3 min (major).



3ha

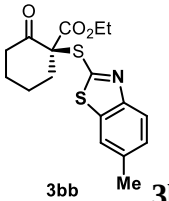
3ha: white solid, 83% yield, 83% ee. $[\alpha]_D^{20}$ = 44.6 (c = 3.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.05 (dd, *J* = 14.2, 6.3 Hz, 1H), 2.92 – 2.80 (m, 1H), 2.71 (dt, *J* = 9.2, 7.1 Hz, 1H), 2.31 (s, 3H), 2.25 (dd, *J* = 10.3, 6.2 Hz, 1H), 2.05 – 1.85 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 166.6, 163.1, 152.5, 135.7, 134.0, 129.5, 126.7, 125.5, 121.9, 121.3, 119.9, 69.2, 40.2, 36.6, 26.9, 22.1, 20.9. IR (thin film, cm^{-1}) 2927, 2253, 1715, 1673, 1612, 1552, 1414, 1513, 1276, 1260, 995, 903, 724, 649, 554, 509. HRMS (ESI) calcd for $C_{21}H_{21}N_2O_2S_2^+$ ($M+H^+$) 397.10390 found 397.10595. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 247 nm, retention time: 16.3 min (minor) and 20.9 min (major).



3ia

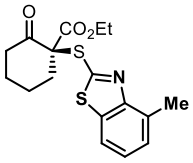
3ia: white solid, 84% yield, 77% ee. $[\alpha]_D^{20}$ = 63.8 (c = 3.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.87-7.77 (m, 1H), 7.60 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.54-7.47 (m, 1H), 7.42-7.36 (m, 1H), 7.34-7.28 (m, 2H), 7.14-7.04 (m, 1H), 3.14-2.96 (m, 1H), 3.12-2.94 (m, 1H), 2.86 (dd, *J* = 12.7, 6.9 Hz, 1H), 2.86 (dd, *J* = 12.7, 6.9 Hz, 1H), 2.70 (ddd, *J* = 14.4, 7.8, 3.9 Hz, 1H), 2.70 (ddd, *J* = 14.4, 7.8, 3.9 Hz, 1H), 2.26 (dd, *J* = 9.2, 4.3 Hz, 1H), 2.26 (dd, *J* = 9.2, 4.3 Hz, 1H), 2.11-1.90 (m, 4H), 1.99 (dddd, *J* = 20.8, 13.5, 9.8, 3.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 166.9, 163.2, 152.4, 138.3, 135.8, 129.0, 126.7, 125.5, 124.4, 121.8, 121.3, 119.8, 69.1, 40.1, 36.5, 26.9, 22.1.IR (thin film, cm^{-1}) 2947, 2253, 1716, 1676, 1600, 1499, 1455, 1313, 1262, 1125, 1080, 903,724, 649, 582. HRMS (ESI) calcd for $C_{20}H_{19}N_2O_2S_2^+$ ($M+H^+$) 383.08825 found 383.08491. HPLC analysis: Daicel Chiralpak AD-H,

hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 206 nm, retention time: 22.1 min (minor) and 24.0 min (major).



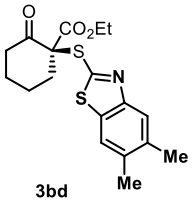
3bb

3bb: pale yellow oil, 81% yield, 90% ee. $[\alpha]_D^{20}$ = -13.9 (c = 2.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.78 (dd, *J* = 9.8, 4.4 Hz, 1H), 2.62 – 2.50 (m, 1H), 2.46 (s, 3H), 2.27 – 2.15 (m, 1H), 2.07 – 1.70 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 168.0, 158.5, 151.4, 137.7, 135.7, 127.8, 122.5, 120.8, 69.5, 62.6, 40.5, 37.6, 26.9, 22.8, 21.6, 13.9. IR (thin film, cm^{-1}) 3019, 1717, 1214, 744, 668, 628. HRMS (ESI) calcd for $C_{17}H_{20}NO_3S_2^+$ ($M+H^+$) 350.08791 found 350.08676. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 25.2 min (major) and 30.0 min (minor).



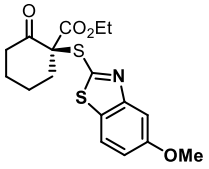
3bc

3bc: colorless oil, 67% yield, 89% ee. $[\alpha]_D^{20}$ = -10.2 (c = 2.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.47 (m, 1H), 7.23 (d, *J* = 6.8 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.82 (dd, *J* = 9.7, 4.7 Hz, 1H), 2.68 (s, 3H), 2.56 (ddd, *J* = 14.5, 10.8, 5.6 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.06 – 1.77 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 168.1, 158.9, 152.6, 136.9, 132.8, 126.7, 125.3, 118.5, 69.6, 62.5, 40.5, 37.5, 27.0, 22.7, 18.4, 13.9. IR (thin film, cm^{-1}) 3019, 1717, 1445, 1214, 1019, 986, 747, 688, 627, 557. HRMS (ESI) calcd for $C_{17}H_{20}NO_3S_2^+$ ($M+H^+$) 350.08791 found 350.08632. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 224 nm, retention time: 11.6 min (minor) and 13.6 min (major).



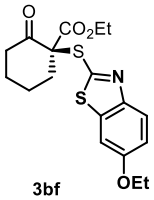
3bd

3bd: colorless oil, 82% yield, 88% ee. $[\alpha]_D^{20}$ = -15.3 (c = 3.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.54 (s, 1H), 7.26 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.82 (m, 1H), 2.82 – 2.72 (m, 1H), 2.51 (ddd, *J* = 14.3, 11.2, 5.7 Hz, 1H), 2.36 (d, *J* = 3.4 Hz, 6H), 2.24 – 2.15 (m, 1H), 2.02 – 1.69 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 168.0, 158.1, 152.1, 135.6, 135.1, 123.1, 121.0, 69.4, 62.6, 40.5, 37.6, 26.9, 22.8, 20.2, 13.9. IR (thin film, cm^{-1}) 3014, 2939, 2867, 1717, 1540, 1442, 1366, 1334, 1297, 1238, 1216, 1140, 1092, 1043, 1021, 980, 902, 867, 812, 753, 686, 667, 557, 519, 436. HRMS (ESI) calcd for $C_{18}H_{22}NO_3S_2^+$ ($M+H^+$) 364.10356 found 364.10239. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 224 nm, retention time: 10.3 min (major) and 11.6 min (minor).



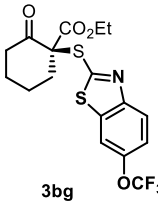
3be

3be: colorless oil, 89% yield, 90% ee. $[\alpha]_D^{20}$ = -27.9 (c = 3.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.89 (d, *J* = 14.2 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.61 – 2.46 (m, 1H), 2.27 – 2.13 (m, 1H), 2.07 – 1.67 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 168.0, 160.7, 159.0, 154.5, 129.2, 121.3, 115.9, 105.1, 69.5, 62.6, 55.6, 40.5, 37.6, 26.9, 22.7, 13.9. IR (thin film, cm^{-1}) 3019, 2942, 2918, 1716, 1601, 1470, 1430, 1407, 1328, 1276, 1214, 1161, 1078, 1030, 842, 747, 668, 641, 556. HRMS (ESI) calcd for $C_{17}H_{20}NO_4S_2^+$ ($M+H^+$) 366.08283 found 366.08173. HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 99:1, flow rate = 0.5 mL/min, λ = 226 nm, retention time: 106.7 min (major) and 110.6 min (minor).



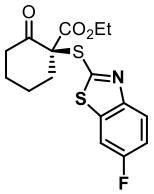
3bf

3bf: brown oil, 86% yield, 91% ee. $[\alpha]_D^{20}$ = -13.9 (c = 3.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 1H), 7.22 (s, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 4.23 (d, *J* = 6.7 Hz, 2H), 4.07 (d, *J* = 6.5 Hz, 2H), 2.82 (dd, *J* = 34.1, 13.4 Hz, 2H), 2.51 (d, *J* = 9.8 Hz, 1H), 2.16 (t, *J* = 10.7 Hz, 1H), 2.05 – 1.66 (m, 4H), 1.44 (t, *J* = 6.0 Hz, 3H), 1.20 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 168.0, 157.4, 155.9, 147.9, 139.3, 123.7, 116.3, 104.0, 69.4, 64.1, 62.6, 40.5, 37.6, 26.9, 22.8, 14.8, 13.9. IR (thin film, cm^{-1}) 3019, 1717, 1601, 1467, 1214, 1066, 1038, 938, 749, 668, 558. HRMS (ESI) calcd for $C_{18}H_{22}NO_4S_2^+$ ($M+H^+$) 380.09848 found 380.09774. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 219 nm, retention time: 12.3 min (minor) and 13.0 min (major).



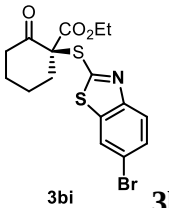
3bg

3bg: yellow oil, 79% yield, 90% ee. $[\alpha]_D^{20}$ = -15.6 (c = 3.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 1H), 7.66 (s, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.92 (d, *J* = 13.9 Hz, 1H), 2.79 (dd, *J* = 10.0, 4.3 Hz, 1H), 2.57 (ddd, *J* = 14.6, 11.2, 5.8 Hz, 1H), 2.33 – 2.18 (m, 1H), 2.05 (d, *J* = 5.4 Hz, 1H), 1.99 – 1.72 (m, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 167.9, 161.9, 151.6, 146.6, 137.9, 123.6, 120.5 (q, J = 257.8 Hz), 120.1 113.6, 69.7, 62.7, 40.5, 37.6, 26.8, 22.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.04 (s). IR (thin film, cm^{-1}) 3019, 1717, 1521, 1428, 1214, 744. 668, 626. HRMS (ESI) calcd for $C_{17}H_{17}F_3NO_4S_2^+$ ($M+H^+$) 420.05456 found 420.05286. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 225 nm, retention time: 10.8 min (major) and 11.9 min (minor).



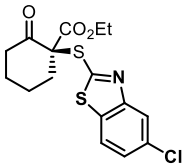
3bh

3bh: white solid, 59% yield, 85% ee. $[\alpha]_D^{20}$ = -17.5 (c = 2.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.45 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.15 (td, *J* = 8.9, 2.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.87 (d, *J* = 14.1 Hz, 1H), 2.75 (dt, *J* = 13.6, 4.2 Hz, 1H), 2.51 (ddd, *J* = 14.3, 11.2, 5.7 Hz, 1H), 2.24 – 2.12 (m, 1H), 2.07 – 1.96 (m, 1H), 1.96 – 1.67 (m, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 167.9, 160.6 (d, J = 246.9 Hz), 159.5 (d, J = 3.3 Hz), 149.9 (d, J = 1.4 Hz), 138.4 (d, J = 11.1 Hz), 123.9 (d, J = 9.4 Hz), 114.9 (d, J = 24.8 Hz), 107.3 (d, J = 26.8 Hz), 69.6, 62.7, 40.5, 37.6, 26.8, 22.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.09 (s). IR (thin film, cm^{-1}) 3019, 2942, 2869, 1717, 1601, 1563, 1467, 1449, 1367, 1335, 1312, 1240, 1214, 1141, 1091, 1002, 908, 851, 816, 751, 668, 606, 558. HRMS (ESI) calcd for $C_{16}H_{17}FNO_3S_2^+$ ($M+H^+$) 354.06284 found 354.06183. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 224 nm, retention time: 9.6 min (minor) and 10.4 min (major).



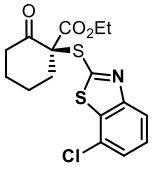
3bi

3bi: colorless oil, 70% yield, 82% ee. $[\alpha]_D^{20}$ = -13.1 (c = 2.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.55 (dd, *J* = 8.7, 1.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.92 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.57 (ddd, *J* = 14.4, 11.1, 5.8 Hz, 1H), 2.32 – 2.19 (m, 1H), 2.05 (dd, *J* = 10.4, 4.8 Hz, 1H), 2.02 – 1.78 (m, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 167.9, 161.2, 152.0, 138.7, 129.7, 123.8, 123.6, 119.1, 69.7, 62.7, 40.5, 37.6, 26.8, 22.7, 13.9. IR (thin film, cm^{-1}) 3019, 2938, 2850, 1717, 1584, 1449, 1432, 1388, 1236, 1214, 1094, 1019, 1000, 861, 749, 668, 558. HRMS (ESI) calcd for $C_{16}H_{17}BrNO_3S_2^+$ ($M+H^+$) 413.98277 found 413.98203. HPLC analysis: Daicel Chiralpak IC-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 224 nm, retention time: 32.9 min (minor) and 37.2 min (major).



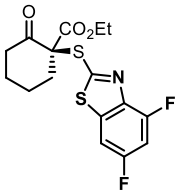
3bj

3bj: orange oil, 18% yield, 87% ee. $[\alpha]_D^{20}$ = -14.3 (c = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.28 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.90 (d, *J* = 14.1 Hz, 1H), 2.77 (dd, *J* = 10.4, 4.0 Hz, 1H), 2.56 (ddd, *J* = 14.5, 11.2, 5.8 Hz, 1H), 2.33 – 2.19 (m, 1H), 2.02 (d, *J* = 4.6 Hz, 1H), 1.97 – 1.75 (m, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 167.9, 162.9, 153.9, 135.2, 132.3, 125.7, 122.4, 121.8, 69.8, 62.7, 40.5, 37.6, 26.8, 22.7, 13.9. IR (thin film, cm^{-1}) 3020, 1718, 1431, 1214, 747, 668, 627. HRMS (ESI) calcd for $C_{16}H_{17}ClNO_3S_2^+$ ($M+H^+$) 370.03329 found 370.03232. HPLC analysis: Daicel Chiralpak OJ-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 230 nm, retention time: 17.7 min (minor) and 51.6 min (major).



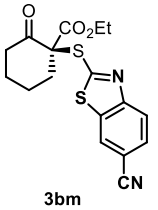
3bk

3bk: orange oil, 79% yield, 89% ee. $[\alpha]_D^{20}$ = -14.3 (c = 2.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.51 – 7.27 (m, 2H), 4.24 (d, *J* = 6.7 Hz, 2H), 2.92 (d, *J* = 13.0 Hz, 1H), 2.78 (d, *J* = 13.8 Hz, 1H), 2.56 (s, 1H), 2.24 (t, *J* = 10.9 Hz, 1H), 2.07 – 1.68 (m, 4H), 1.21 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 167.9, 161.7, 153.7, 137.2, 127.1, 126.3, 125.0, 121.0, 69.7, 62.8, 40.5, 37.6, 26.8, 22.7, 13.9. IR (thin film, cm^{-1}) 3019, 1717, 1455, 1395, 1309, 1237, 1091, 1017, 989, 929, 748, 668, 627, 557. HRMS (ESI) calcd for $C_{16}H_{17}ClNO_3S_2^+$ ($M+H^+$) 370.03329 found 370.03220. HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 223 nm, retention time: 8.4 min (minor) and 9.3 min (major).



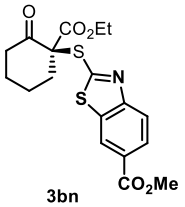
3bl

3bl: colorless oil, 68% yield, 91% ee. $[\alpha]_D^{20}$ = -9.2 (c = 2.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.98 – 2.76 (m, 2H), 2.65 – 2.51 (m, 1H), 2.43 – 2.26 (m, 1H), 2.14 – 1.91 (m, 3H), 1.90 – 1.71 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 167.9, 161.7 (d, J = 3.1 Hz), 159.7 (d, J = 250.2 Hz), 148.3 (d, J = 2.0 Hz), 137.8 (d, J = 11.4 Hz), 118.5 (d, J = 27.3 Hz), 116.1 (d, J = 11.0 Hz), 106.6 (d, J = 26.4 Hz), 70.0, 62.9, 40.5, 37.4, 26.4, 22.7, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.10 (s). IR (thin film, cm^{-1}) 3019, 2400, 1717, 1599, 1553, 1440, 1385, 1214, 1009, 930, 856, 744, 668, 627, 557, 497. HRMS (ESI) calcd for $C_{16}H_{16}F_2NO_3S_2^+$ ($M+H^+$) 372.05342 found 372.05641. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 283 nm, retention time: 10.3 min (major) and 11.0 min (minor).



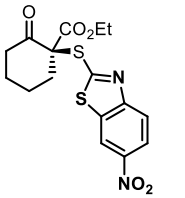
3bm

3bm: yellow oil, 60% yield, 90% ee. $[\alpha]_D^{20}$ = -11.2 (c = 2.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 4.25 (dd, *J* = 13.9, 6.9 Hz, 2H), 2.95 (d, *J* = 13.7 Hz, 1H), 2.79 (d, *J* = 14.5 Hz, 1H), 2.67 – 2.54 (m, 1H), 2.29 (t, *J* = 10.7 Hz, 1H), 2.05 (s, 1H), 2.00 – 1.81 (m, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 167.8, 167.0, 155.2, 136.9, 129.4, 125.7, 123.0, 118.6, 108.5, 70.1, 62.9, 40.5, 37.6, 26.7, 22.7, 13.9. IR (thin film, cm^{-1}) 3020, 2229, 1717, 1437, 1214, 1042, 1008, 745, 668, 558. HRMS (ESI) calcd for $C_{17}H_{17}N_2O_3S_2^+$ ($M+H^+$) 361.06751 found 361.06656. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 31.3 min (minor) and 33.3 min (major).



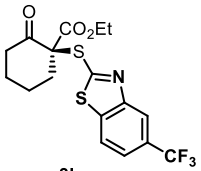
3bn

3bn: white solid, 79% yield, 90% ee. $[\alpha]_D^{20}$ = -8.7 (c = 3.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 4.27 (d, *J* = 6.8 Hz, 2H), 3.97 (s, 3H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.62 (s, 1H), 2.33 (t, *J* = 11.1 Hz, 1H), 2.13 – 1.76 (m, 4H), 1.23 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 167.9, 166.5, 165.3, 155.9, 136.6, 127.4, 126.9, 123.2, 122.1, 69.9, 62.8, 52.4, 40.5, 37.6, 26.7, 22.7, 13.9. IR (thin film, cm^{-1}) 3020, 2952, 2400, 1717, 1598, 1465, 1433, 1402, 1286, 1264, 1214, 1114, 1007, 977, 760, 668, 558, 491. HRMS (ESI) calcd for $C_{18}H_{20}NO_5S_2^+$ ($M+H^+$) 394.07774 found 394.07660. HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 216 nm, retention time: 20.1 min (minor) and 21.5 min (major).



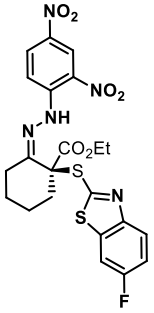
3bo

3bo: colorless oil, 74% yield, 85% ee. $[\alpha]_D^{20}$ = -11.9 (c = 2.7, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 4.27 (dd, *J* = 13.6, 6.7 Hz, 2H), 2.99 (d, *J* = 13.3 Hz, 1H), 2.81 (d, *J* = 14.3 Hz, 1H), 2.73 – 2.55 (m, 1H), 2.33 (t, *J* = 10.4 Hz, 1H), 1.97 (dd, *J* = 41.4, 30.4 Hz, 4H), 1.23 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 168.8, 167.7, 156.6, 144.7, 136.7, 122.3, 121.8, 117.5, 70.3, 62.9, 40.5, 37.6, 26.7, 22.7, 13.9. IR (thin film, cm^{-1}) 3200, 2400, 1718, 1522, 1435, 1341, 1214, 1125, 1049, 929, 744, 668, 627, 557, 493. HRMS (ESI) calcd for $C_{16}H_{17}N_2O_5S_2^+$ ($M+H^+$) 381.05734 found 381.05640. HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 222 nm, retention time: 27.6 min (minor) and 30.3 min (major).



3bp

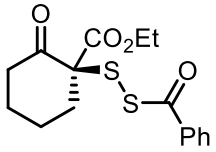
3bp: colorless oil, 74% yield, 89% ee. $[\alpha]_D^{20}$ = -13.7 (c = 3.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.95 (d, *J* = 14.2 Hz, 1H), 2.88 – 2.72 (m, 1H), 2.66 – 2.50 (m, 1H), 2.36 – 2.23 (m, 1H), 2.10 – 1.80 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 167.9, 163.8, 152.7, 140.2, 128.9 (q, J = 99 Hz), 124.1 (d, J = 272.3 Hz), 121.7, 121.5 (d, *J* = 10.2 Hz), 119.7 (d, *J* = 12.6 Hz). 69.9, 62.8, 40.5, 37.6, 26.7, 22.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.79 (s). IR (thin film, cm^{-1}) 3020, 2400, 1718, 1338, 1214, 1175, 1130, 1058, 989, 918, 745, 668, 627, 553. HRMS (ESI) calcd for $C_{17}H_{17}F_3NO_3S_2^+$ ($M+H^+$) 404.05965 found 404.05850. HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 281 nm, retention time: 8.3 min (major) and 9.0 min (minor).



3bh-1

3bh-1: red solid, 74% yield, 91% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 11.20 (s, 1H), 9.06 (d, *J* = 1.8 Hz, 1H), 8.24 (d, *J* = 9.5 Hz, 1H), 7.87 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.79 (d, *J* = 9.5 Hz, 1H), 7.56 – 7.36 (m, 1H), 7.15 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.27 (dt, *J* = 13.5, 6.8 Hz, 2H), 3.04 – 2.74 (m, 2H), 2.54 – 2.29 (m, 1H), 2.28 – 2.12 (m, 1H), 2.07 – 1.65 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 160.7 (d, J = 247.6 Hz), 159.9 (d, J = 3.3 Hz), 154.5, 149.8 (d, J = 1.5 Hz), 144.9, 138.5 (t, J = 5.5 Hz), 130.0, 129.7, 124.1 (d, J = 9.4 Hz), 123.2, 116.7, 115.1 (d, J = 24.9 Hz), 107.3 (d, J = 26.7 Hz), 65.7, 62.6, 36.6, 25.6, 25.1, 22.5, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.60 (s). IR (thin film, cm^{-1}) 2254, 1729, 1618, 1594, 1519, 1505, 1468, 1339, 1294, 1259, 1197, 1160, 1112, 903, 722, 650, 542. HRMS (ESI) calcd for $C_{22}H_{21}FN_5O_6S_2^+$ ($M+H^+$) 534.09118 found 534.09445. HPLC analysis: Daicel Chiralpak AS-

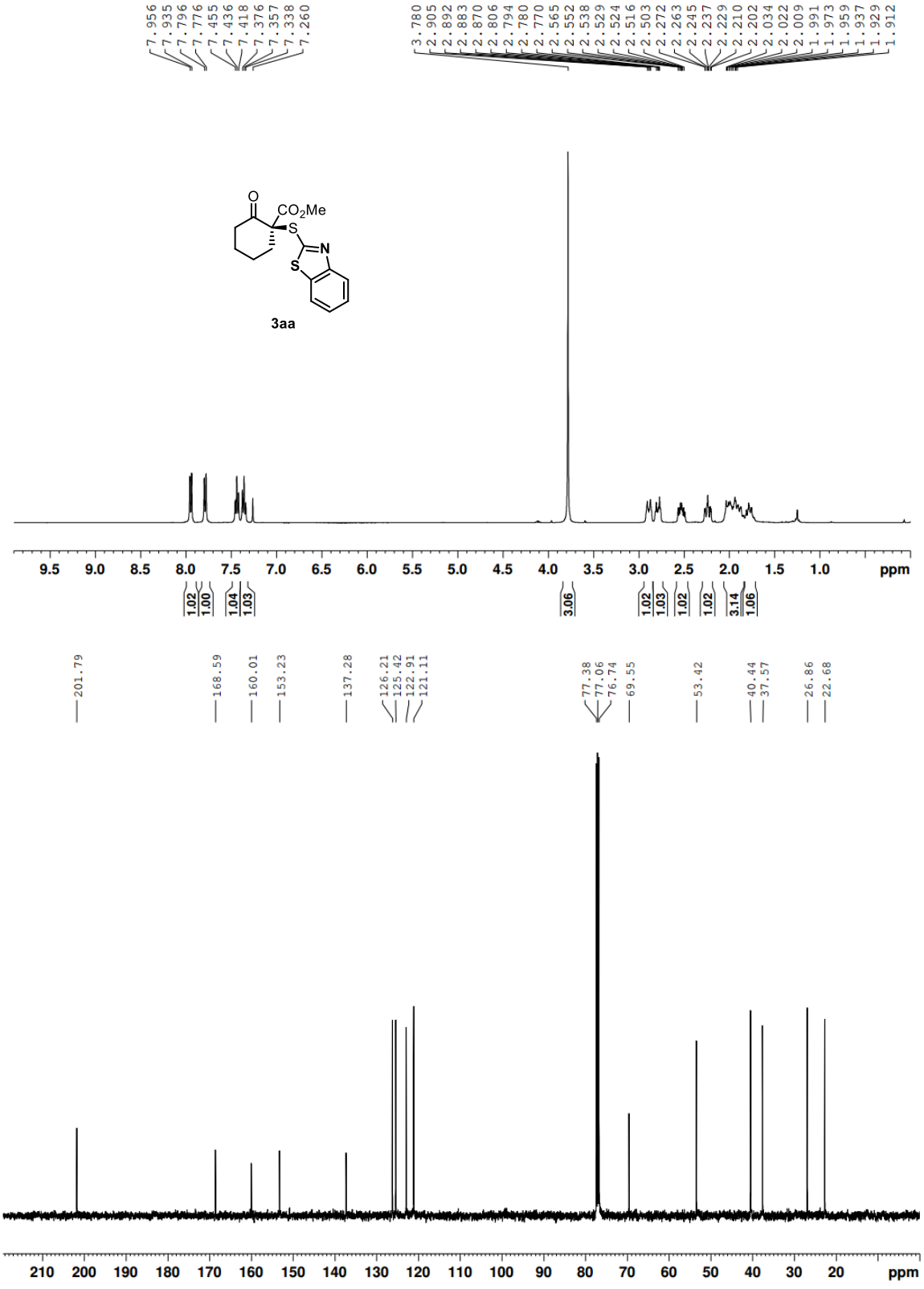
H, hexane/iso-propanol = 97:3, flow rate = 0.8 mL/min, λ = 222 nm, retention time: 35.4 min (minor) and 40.7 min (major).

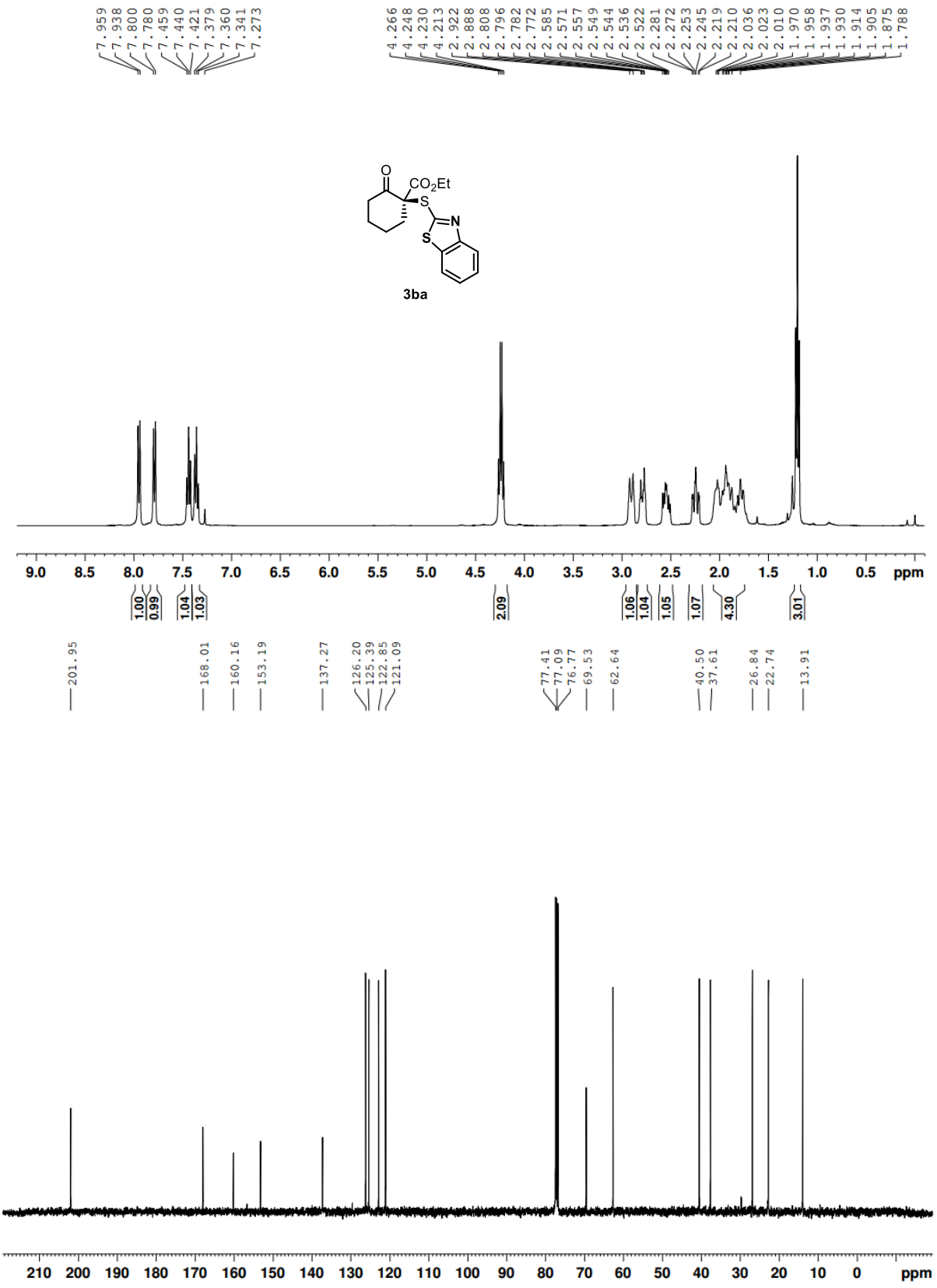


3bq

3bq: white solid. 17% yield, 90% ee.$[\alpha]_D^{20}$ = 34.1 (c = 0.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 4.23 (ddq, *J* = 14.6, 7.4, 3.6 Hz, 2H), 2.97-2.80 (m, 1H), 2.71 (dd, *J* = 14.1, 4.0 Hz, 1H), 2.49-2.37 (m, 1H), 2.12-1.96 (m, 1H), 1.91-1.58 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.20 (s), 188.81 (s), 167.12 (s), 135.57 (s), 134.1, 128.9, 127.8, 67.4, 62.6, 40.6, 36.3, 26.9, 22.9, 13.9. IR (thin film, cm^{-1}) 2927, 2866, 2369, 1713, 1698, 1448, 1264, 1243, 1204, 1176, 1126, 1096, 1021, 884, 736, 703, 679, 646, 551, 509, 442. HRMS (ESI) calcd for $C_{16}H_{18}NaO_4S_2^+$ ($M+Na^+$) 361.05387 found 361.05240. HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 95:5, flow rate = 1.0 mL/min, λ = 240 nm, retention time: 11.7 min (major) and 13.9 min (minor).

7. NMR spectra

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4.230
4.213
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2.888
2.808
2.796
2.782
2.772
2.585
2.571
2.557
2.549
2.544
2.536
2.522
2.281
2.272
2.253
2.245
2.219
2.210
2.036
2.023
2.010
1.970
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1.937
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1.914
1.905
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O
CO2Et
S
N
S
3ba
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.99
1.04
1.03
2.09
1.06
1.04
1.05
1.07
4.30
3.01
201.95
168.01
160.16
153.19
137.27
126.20
125.39
122.85
121.09
77.41
77.09
76.77
69.53
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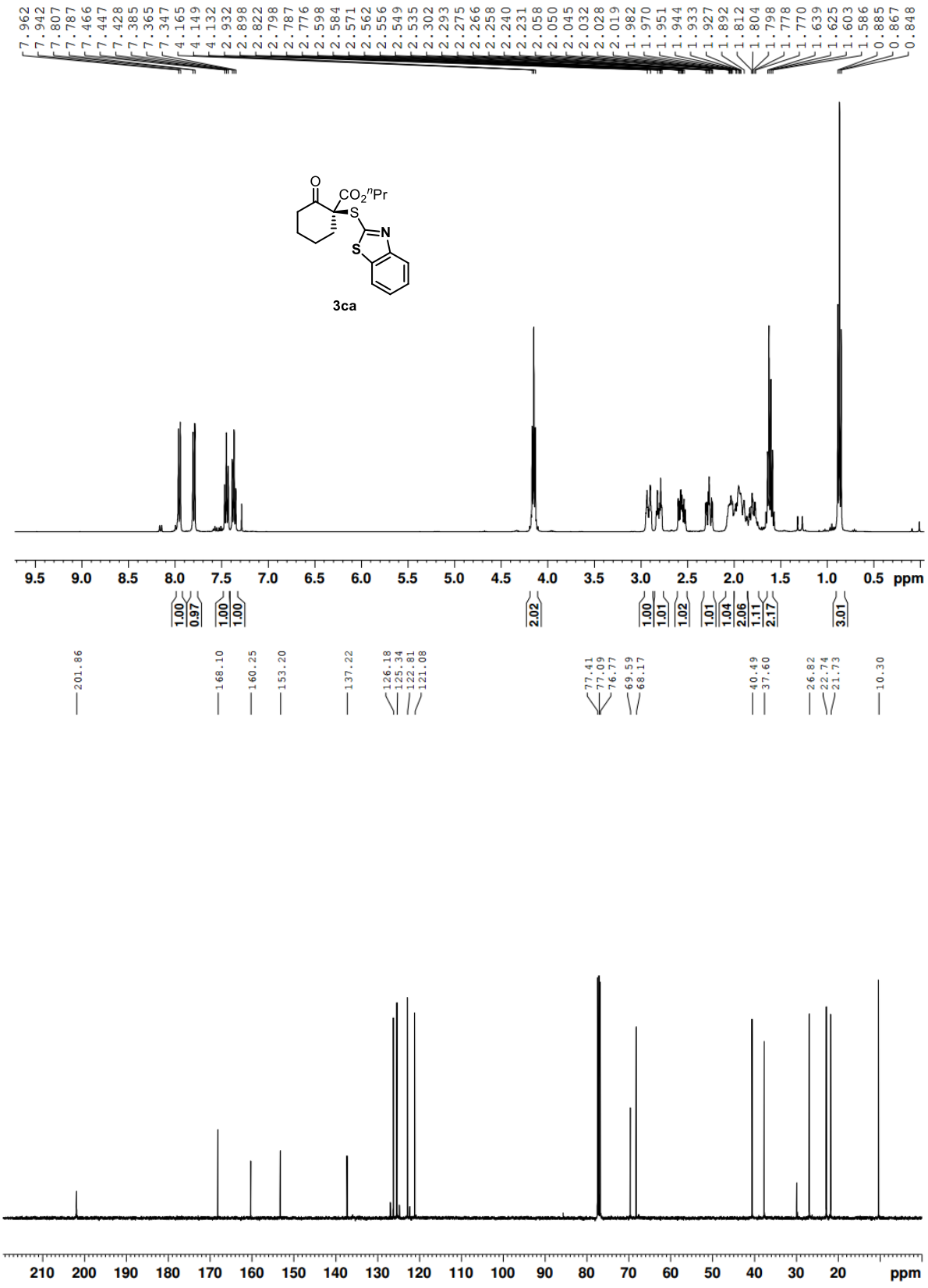
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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2.798
2.787
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2.584
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2.032
2.028
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1.927
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1.812
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1.798
1.778
1.770
1.639
1.625
1.603
1.586
0.885
0.867
0.848
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CO2nPr
S
N
S
3ca
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.97 1.00 1.00 2.02 1.00 1.01 1.02 1.01 1.04 2.06 1.11 2.17 3.01
201.86
168.10
160.25
153.20
137.22
126.18
125.34
122.81
121.08
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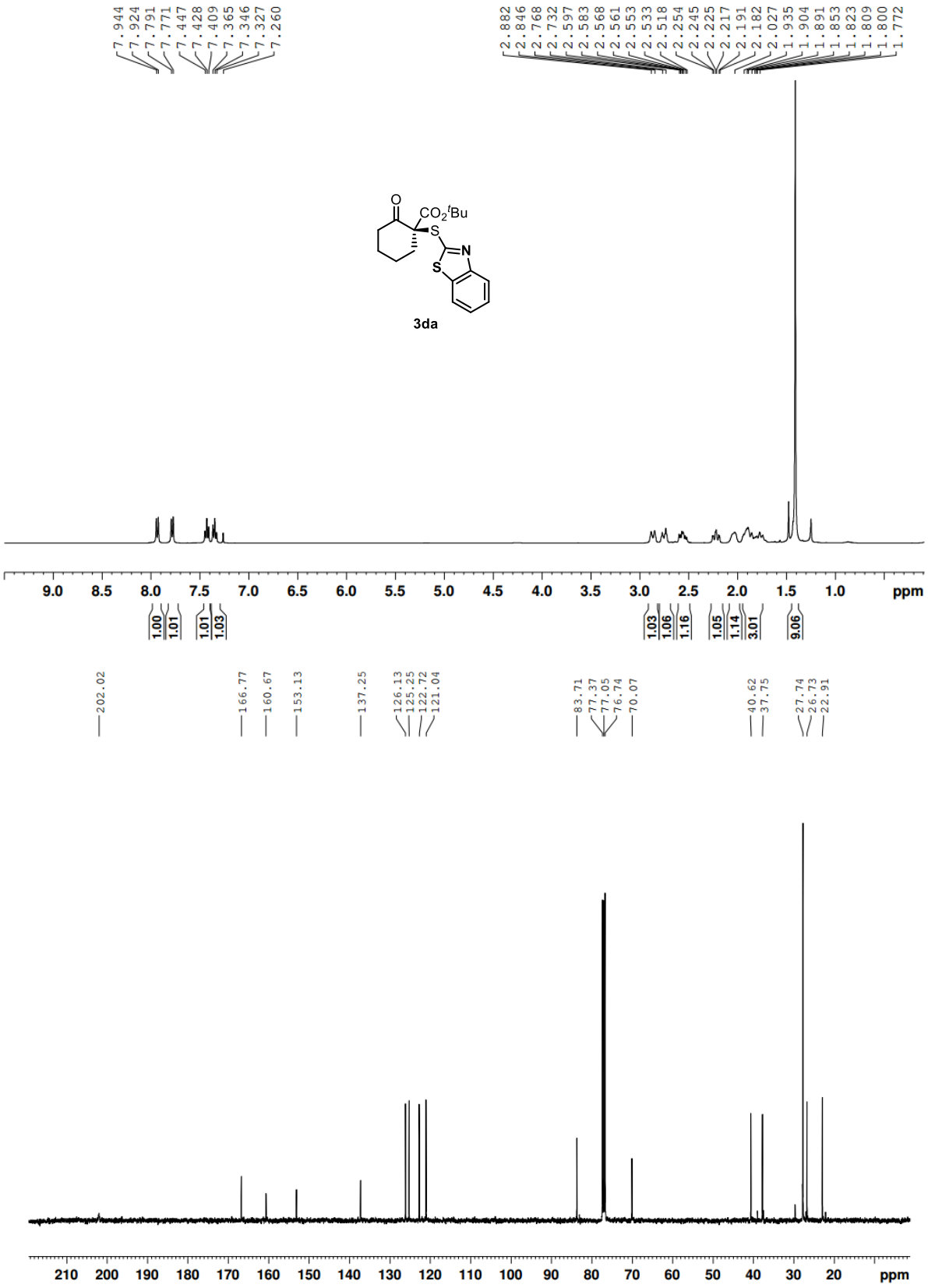
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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S
N
S
3da
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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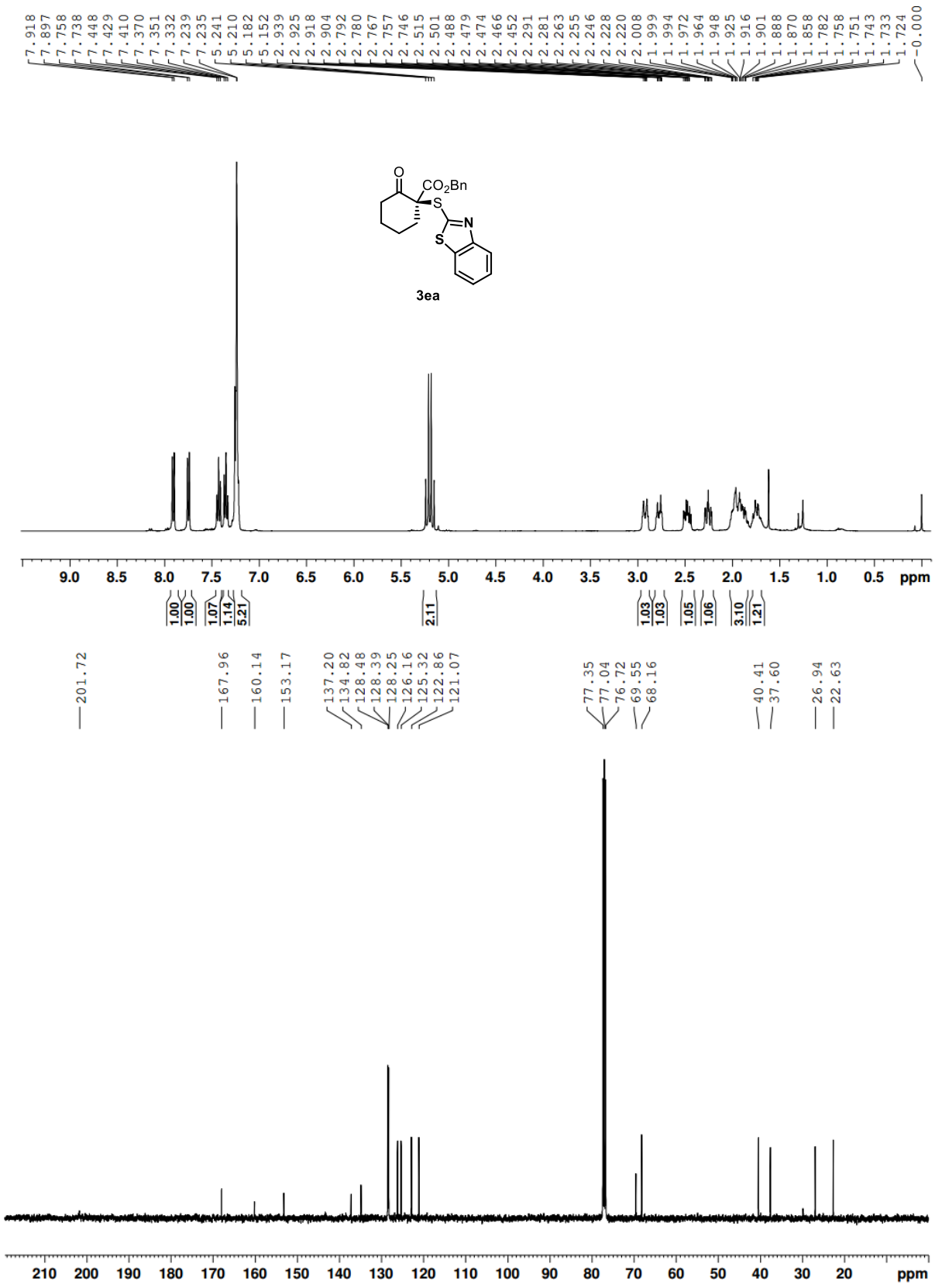
202.02
166.77
160.67
153.13
137.25
126.13
125.25
122.72
121.04
83.71
77.37
77.05
76.74
70.07
40.62
37.75
27.74
26.73
22.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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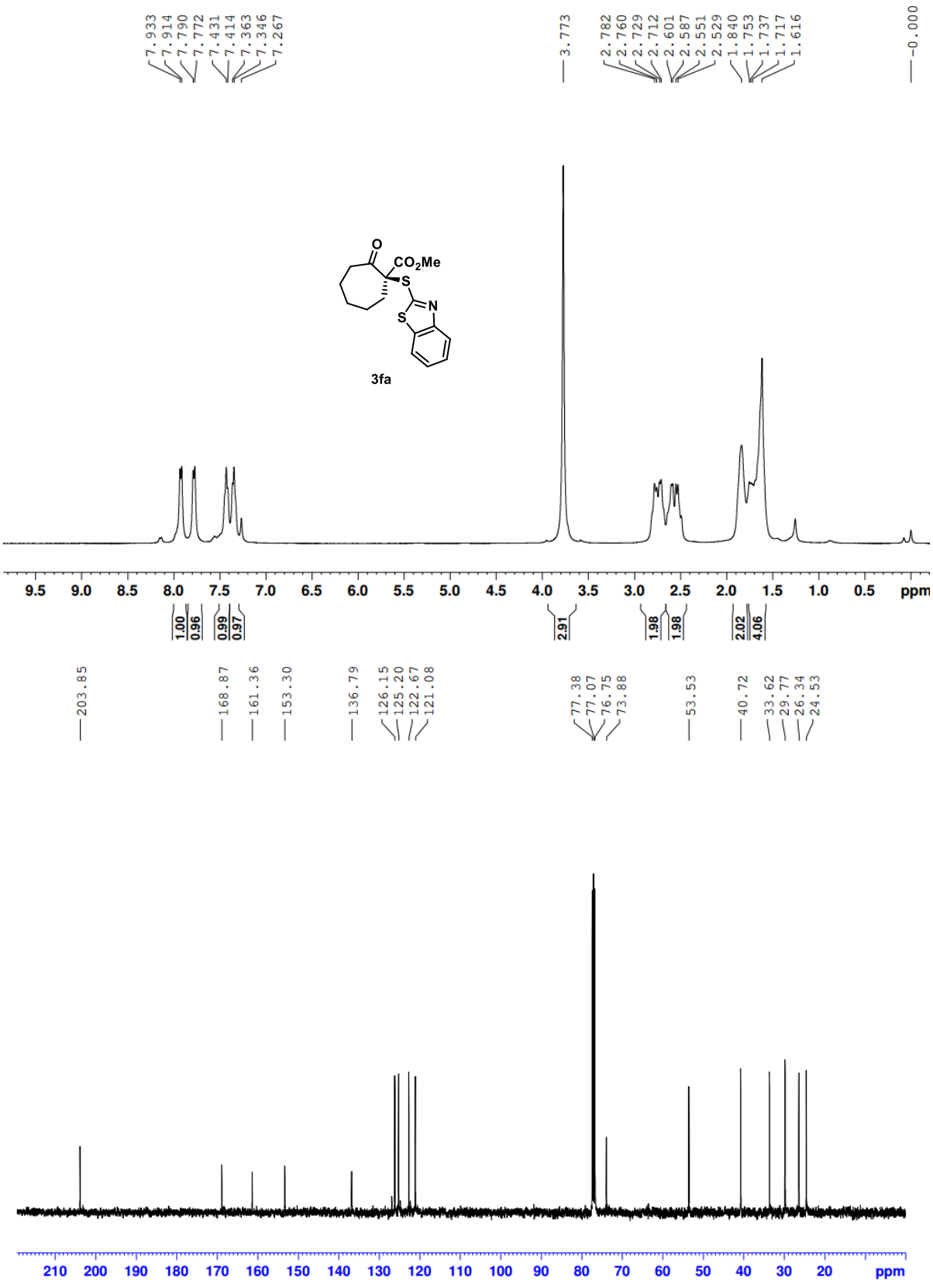
7.370
7.351
7.332
7.239
7.235
5.241
5.210
5.182
5.152
2.939
2.925
2.918
2.904
2.792
2.780
2.767
2.757
2.746
2.515
2.501
2.488
2.479
2.474
2.466
2.452
2.291
2.281
2.263
2.255
2.246
2.228
2.220
2.008
1.999
1.994
1.972
1.964
1.948
1.925
1.916
1.901
1.888
1.870
1.858
1.782
1.758
1.751
1.743
1.733
1.724
0.000
O
CO2Bn
S
N
S
3ea
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.00
1.07
1.14
5.21
2.11
1.03
1.03
1.05
1.06
3.10
1.21
201.72
167.96
160.14
153.17
137.20
134.82
128.48
128.39
128.25
126.16
125.32
122.86
121.07
77.35
77.04
76.72
69.55
68.16
40.41
37.60
26.94
22.63
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.414
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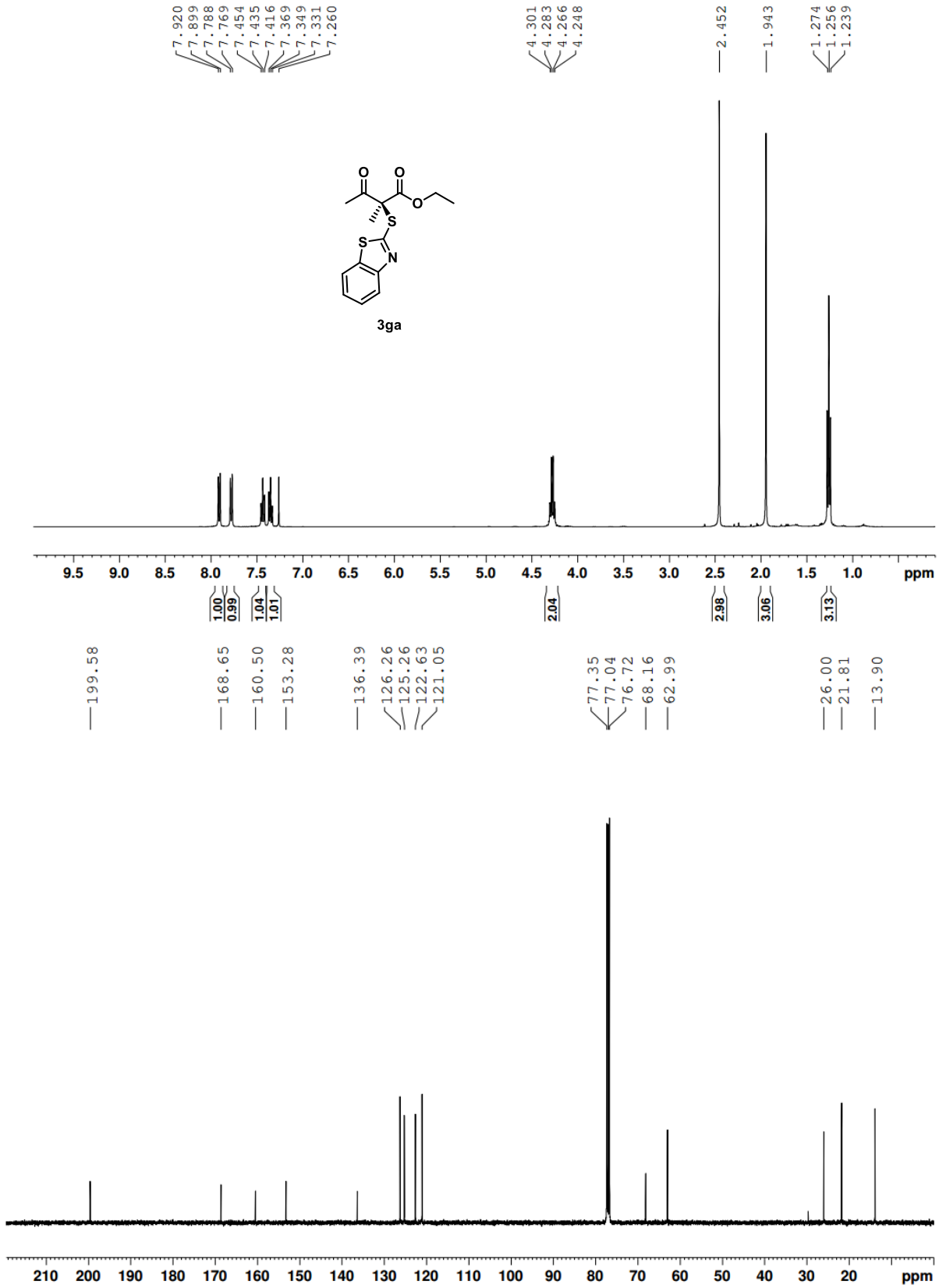
7.346
7.267
3.773
2.782
2.760
2.729
2.712
2.601
2.587
2.551
2.529
1.840
1.753
1.737
1.717
1.616
-0.000
O
CO2Me
S
N
S
3fa
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.96 0.99 0.97 2.91 1.98 1.98 2.02 4.06
203.85
168.87
161.36
153.30
136.79
126.15
125.20
122.67
121.08
77.38
77.07
76.75
73.88
53.53
40.72
33.62
29.77
26.34
24.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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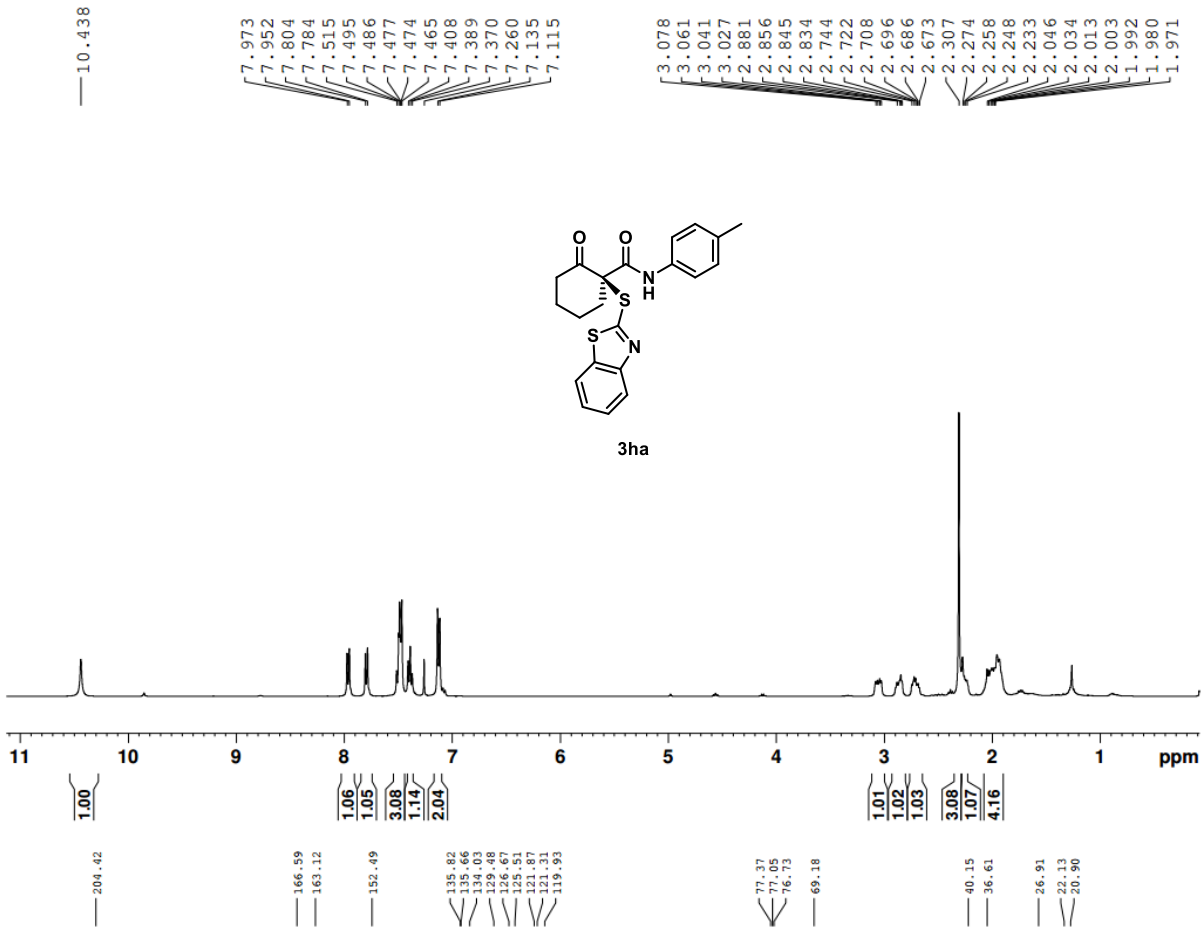
7.788
7.769
7.454
7.435
7.416
7.369
7.349
7.331
7.260
4.301
4.283
4.266
4.248
2.452
1.943
1.274
1.256
1.239
3ga
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.99
1.04
1.01
2.04
2.98
3.06
3.13
199.58
168.65
160.50
153.28
136.39
126.26
125.26
122.63
121.05
77.35
77.04
76.72
68.16
62.99
26.00
21.81
13.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.515
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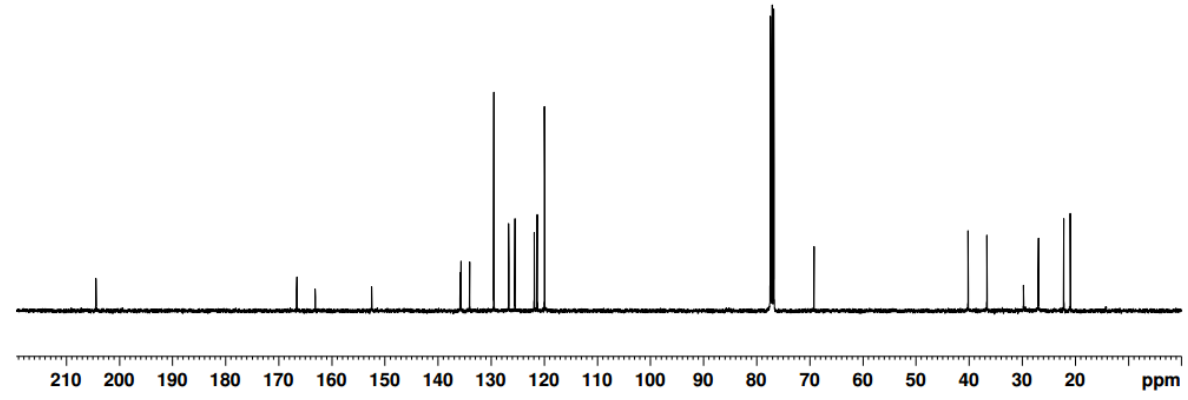
7.486
7.477
7.474
7.465
7.408
7.389
7.370
7.260
7.135
7.115
3.078
3.061
3.041
3.027
2.881
2.856
2.845
2.834
2.744
2.722
2.708
2.696
2.686
2.673
2.307
2.274
2.258
2.248
2.233
2.046
2.034
2.013
2.003
1.992
1.980
1.971
O
O
N
H
S
S
N
3ha
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
1.05
3.08
1.14
2.04
1.01
1.02
1.03
3.08
1.07
4.16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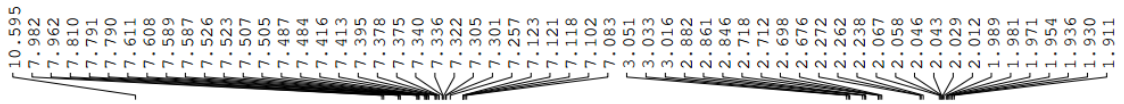
166.59
163.12
152.49
135.82
135.66
134.03
129.48
126.67
125.51
121.87
121.31
119.93
77.37
77.05
76.73
69.18
40.15
36.61
26.91
22.13
20.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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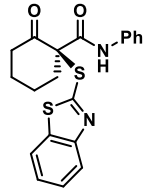
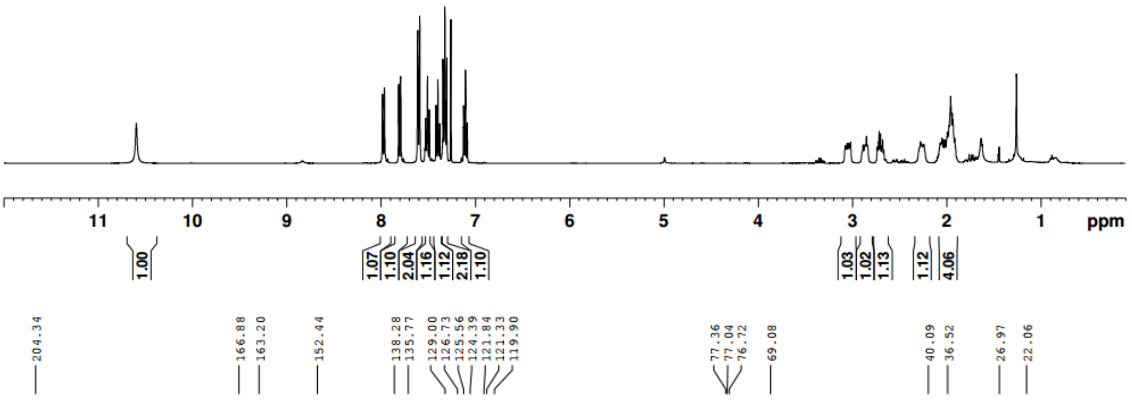
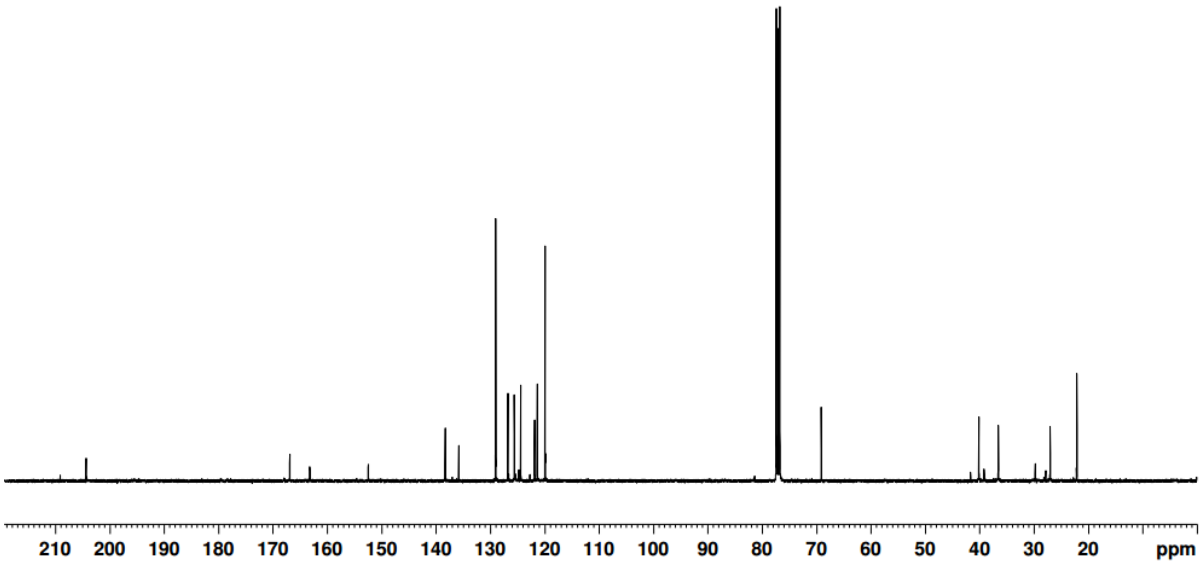
7.982
7.962
7.810
7.791
7.790
7.611
7.608
7.589
7.587
7.526
7.523
7.507
7.505
7.487
7.484
7.416
7.413
7.395
7.378
7.375
7.340
7.336
7.322
7.305
7.301
7.257
7.123
7.121
7.118
7.102
7.083
3.051
3.033
3.016
2.882
2.861
2.846
2.718
2.712
2.698
2.676
2.272
2.262
2.238
2.067
2.058
2.046
2.043
2.029
2.012
1.989
1.981
1.971
1.954
1.936
1.930
1.911

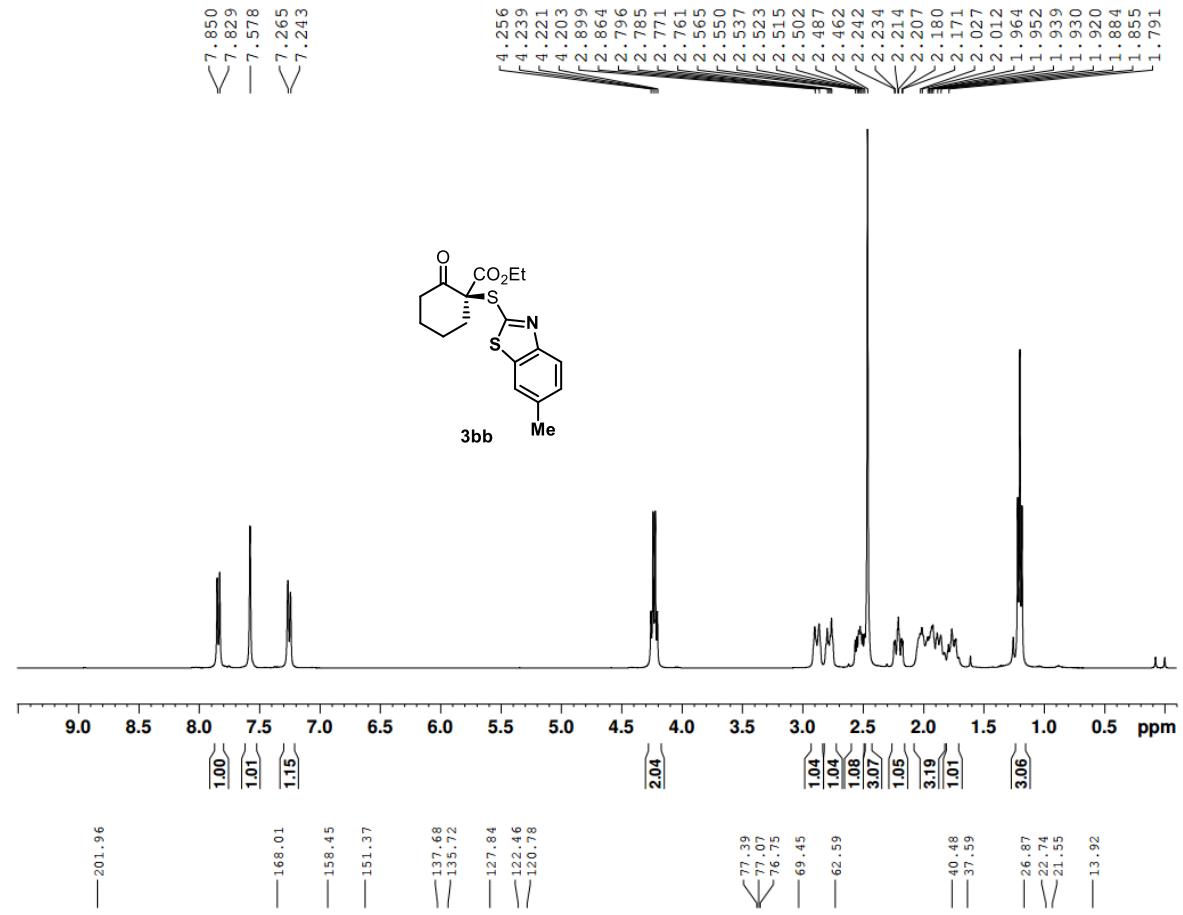

O
O
N
Ph
H
S
S
N

3ia


11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.07
1.10
2.04
1.16
1.12
2.18
1.10
1.03
1.02
1.13
1.12
4.06

204.34
166.88
163.20
152.44
138.28
135.77
129.00
126.73
125.56
124.39
121.84
121.33
119.90
77.36
77.04
76.72
69.08
40.09
36.52
26.97
22.06


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.850
7.829
7.578
7.265
7.243
4.256
4.239
4.221
4.203
2.899
2.864
2.796
2.785
2.771
2.761
2.565
2.550
2.537
2.523
2.515
2.502
2.487
2.462
2.242
2.234
2.214
2.207
2.180
2.171
2.027
2.012
1.964
1.952
1.939
1.930
1.920
1.884
1.855
1.791
CO2Et
S
N
S
Me
3bb
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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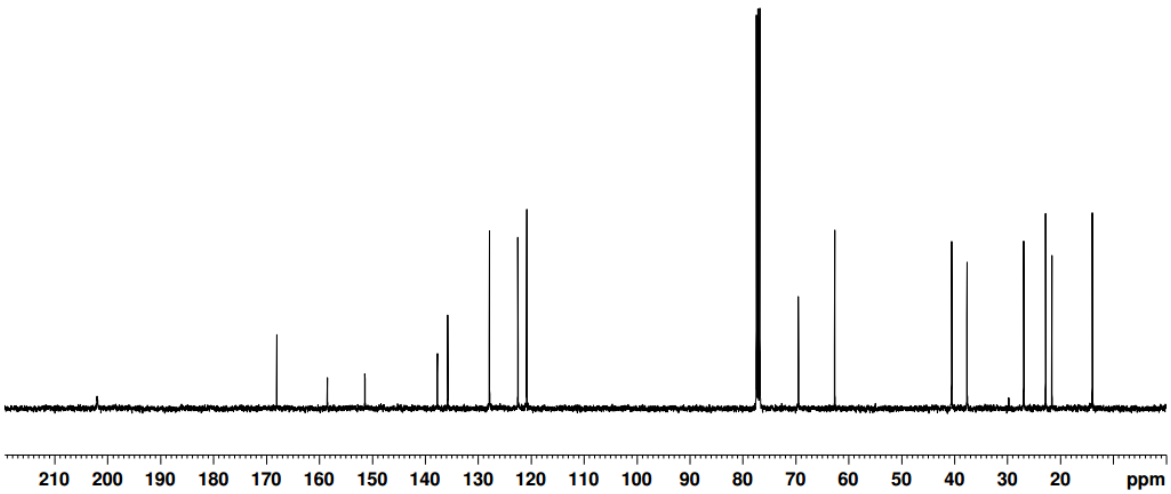
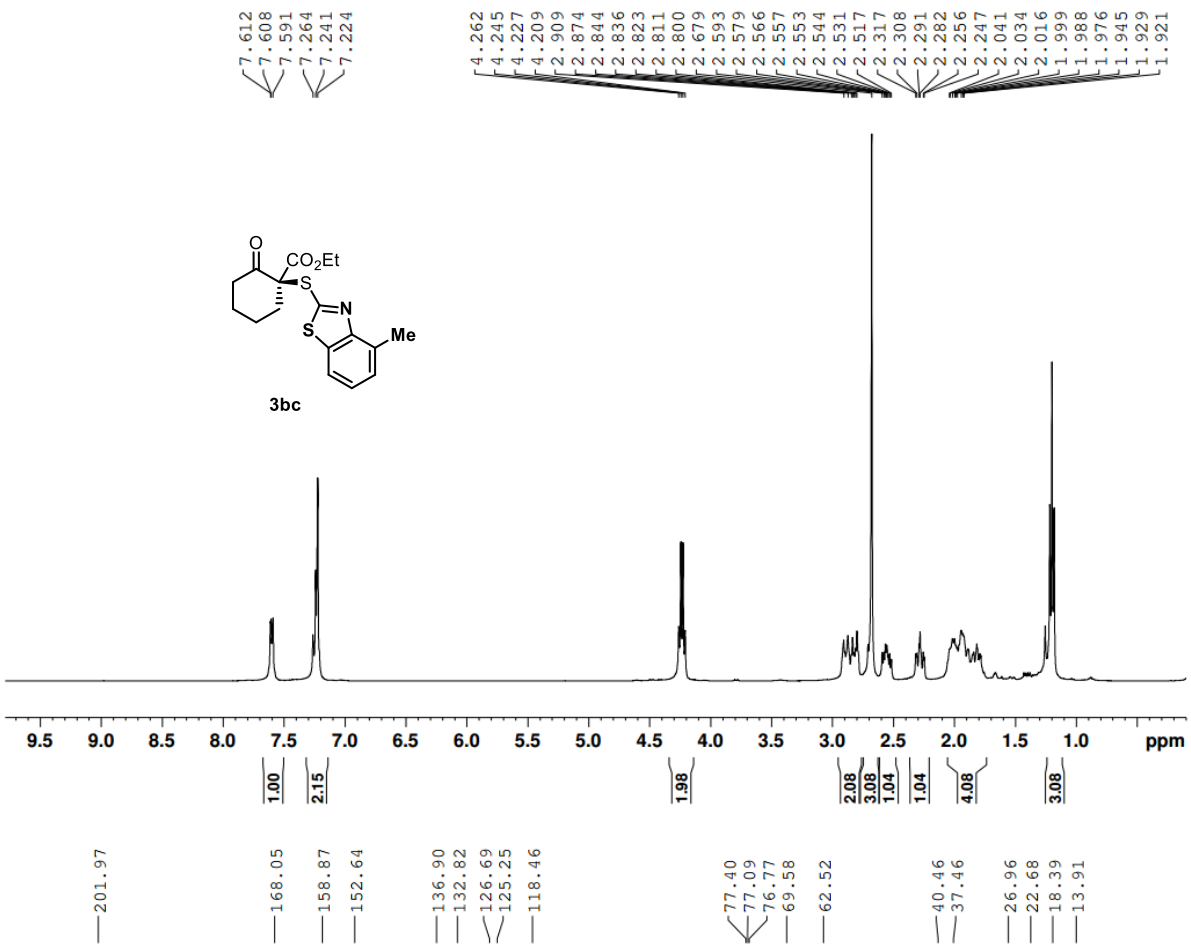
1.01
1.15
2.04
1.04
1.04
1.08
3.07
1.05
3.19
1.01
3.06


201.96
168.01
158.45
151.37
137.68
135.72
127.84
122.46
120.78
77.39
77.07
76.75
69.45
62.59
40.48
37.59
26.87
22.74
21.55
13.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.608
7.591
7.264
7.241
7.224
4.262
4.245
4.227
4.209
2.909
2.874
2.844
2.836
2.823
2.811
2.800
2.679
2.593
2.579
2.566
2.557
2.553
2.544
2.531
2.517
2.317
2.308
2.291
2.282
2.256
2.247
2.041
2.034
2.016
1.999
1.988
1.976
1.945
1.929
1.921
O
CO2Et
S
N
S
Me
3bc
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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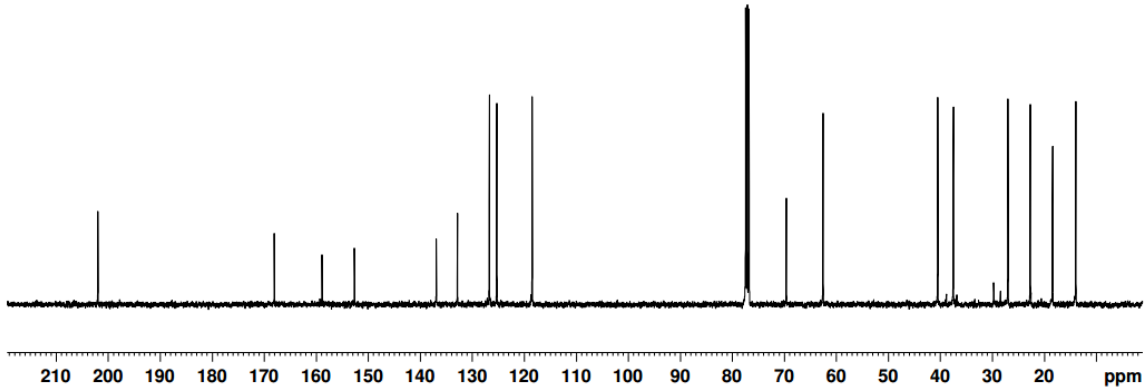
1.98
2.08
3.08
1.04
1.04
4.08
3.08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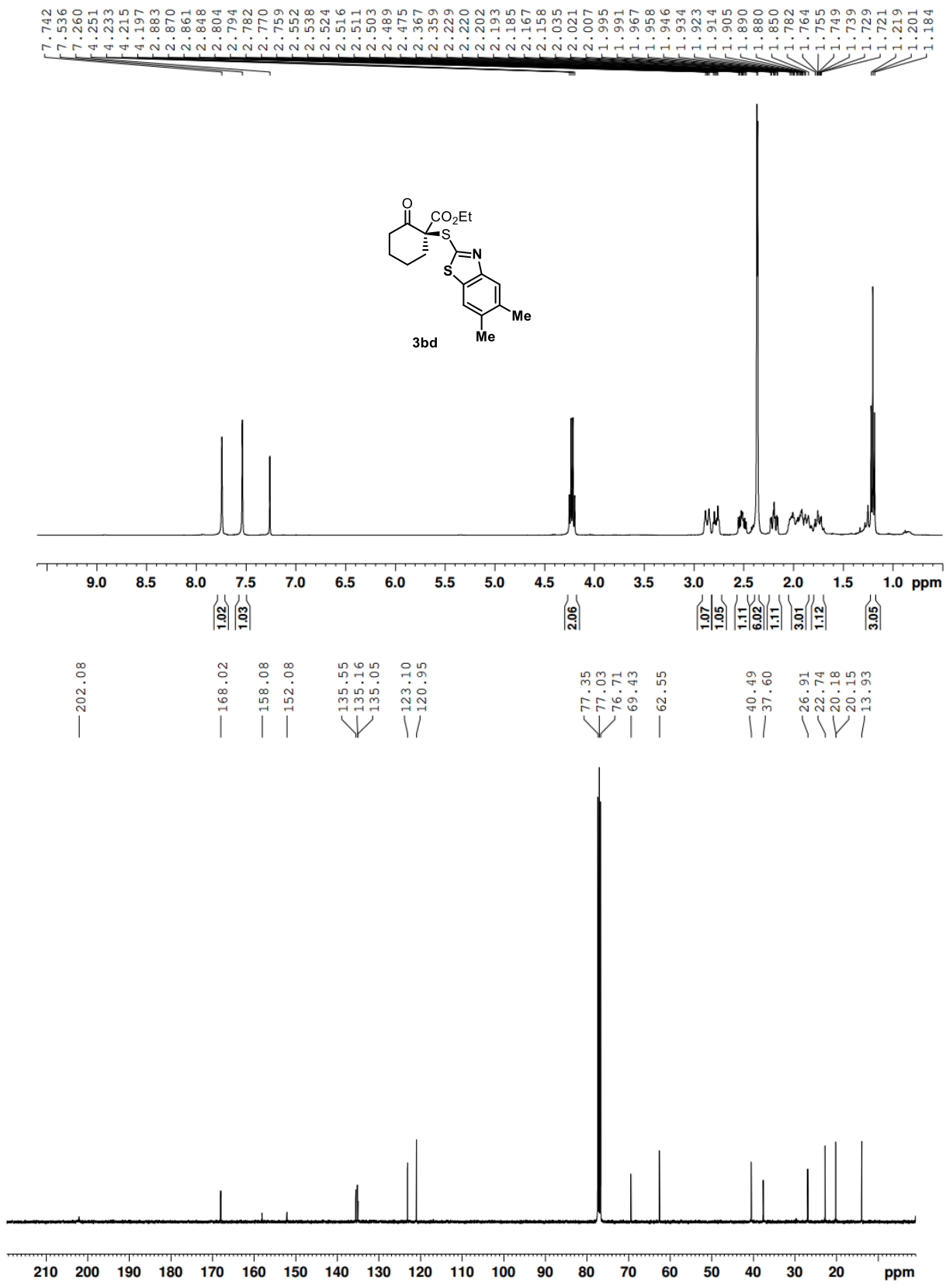
168.05
158.87
152.64
136.90
132.82
126.69
125.25
118.46
77.40
77.09
76.77
69.58
62.52
40.46
37.46
26.96
22.68
18.39
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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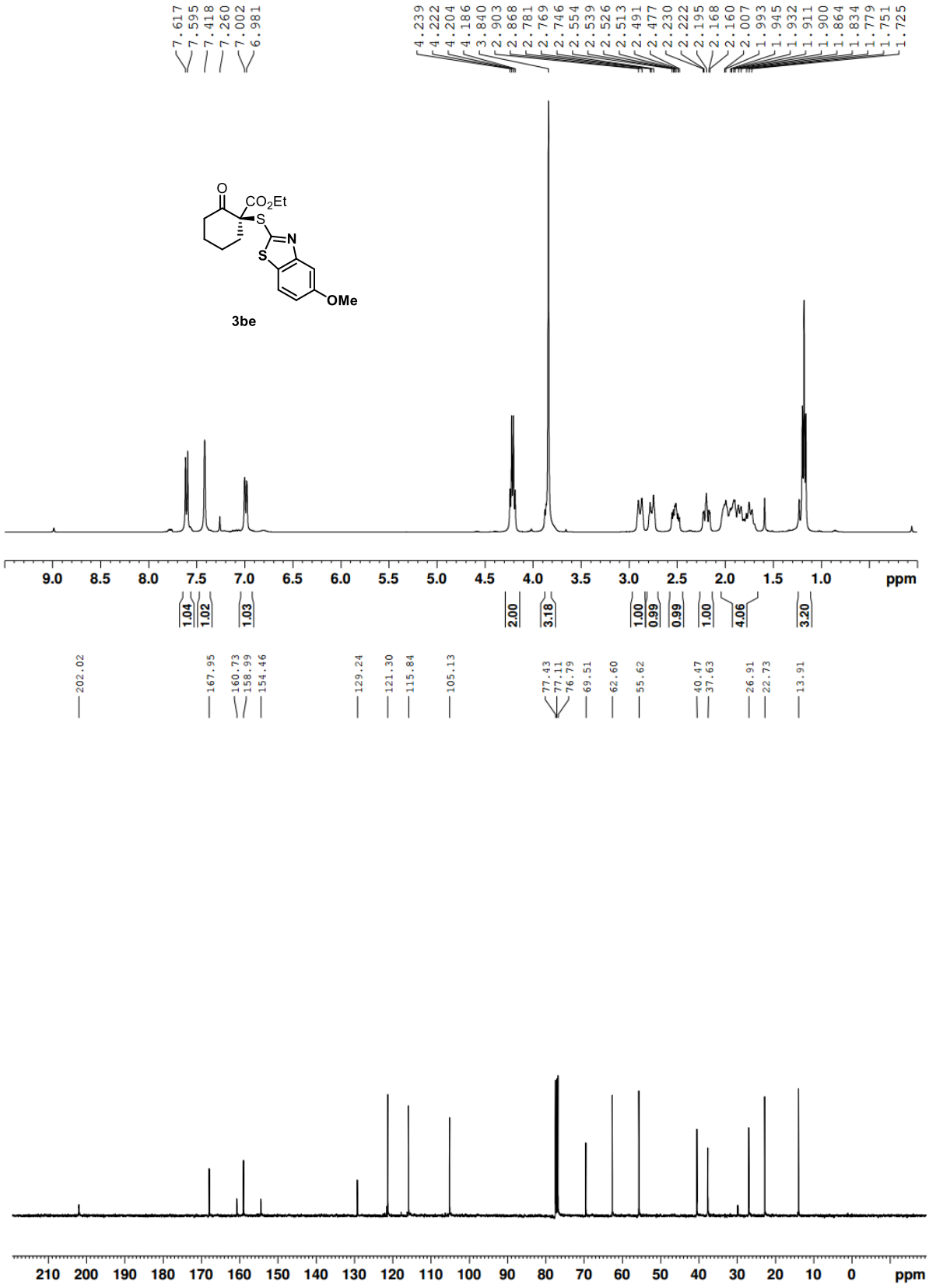
4.233
4.215
4.197
2.883
2.870
2.861
2.848
2.804
2.794
2.782
2.770
2.759
2.552
2.538
2.524
2.516
2.511
2.503
2.489
2.475
2.367
2.359
2.229
2.220
2.202
2.193
2.185
2.167
2.158
2.035
2.021
2.007
1.995
1.991
1.967
1.958
1.946
1.934
1.923
1.914
1.905
1.890
1.880
1.850
1.782
1.764
1.755
1.749
1.739
1.729
1.721
1.219
1.201
1.184
O
CO2Et
S
N
S
Me
Me
3bd
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.02
1.03
2.06
1.07
1.05
1.11
6.02
1.11
3.01
1.12
3.05
202.08
168.02
158.08
152.08
135.55
135.16
135.05
123.10
120.95
77.35
77.03
76.71
69.43
62.55
40.49
37.60
26.91
22.74
20.18
20.15
13.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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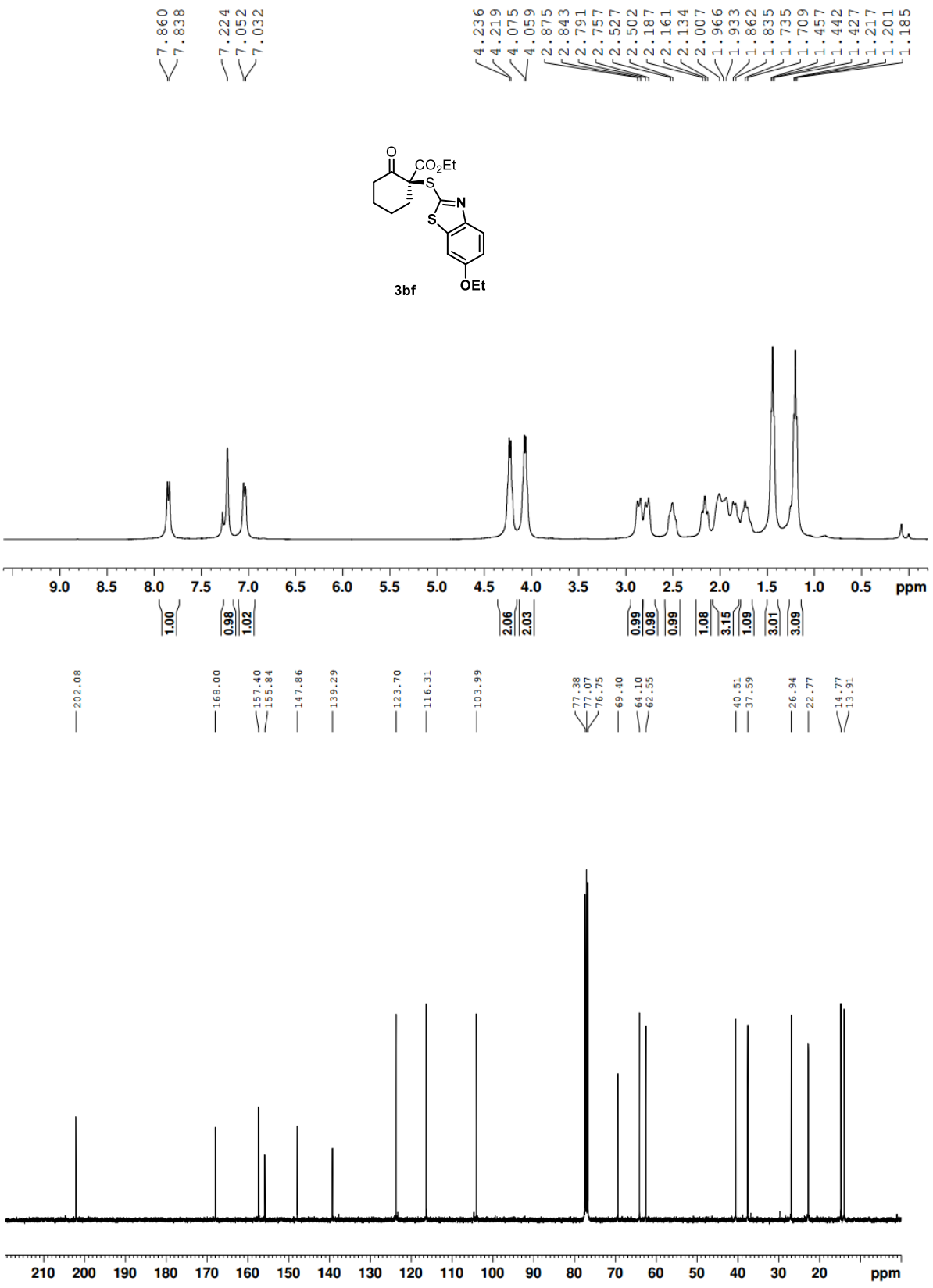
4.222
4.204
4.186
3.840
2.903
2.868
2.781
2.769
2.746
2.554
2.539
2.526
2.513
2.491
2.477
2.230
2.222
2.195
2.168
2.160
2.007
1.993
1.945
1.932
1.911
1.900
1.864
1.834
1.779
1.751
1.725
O
CO2Et
S
N
S
OMe
3be
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.04
1.02
1.03
2.00
3.18
1.00
0.99
0.99
1.00
4.06
3.20
202.02
167.95
160.73
158.99
154.46
129.24
121.30
115.84
105.13
77.43
77.11
76.79
69.51
62.60
55.62
40.47
37.63
26.91
22.73
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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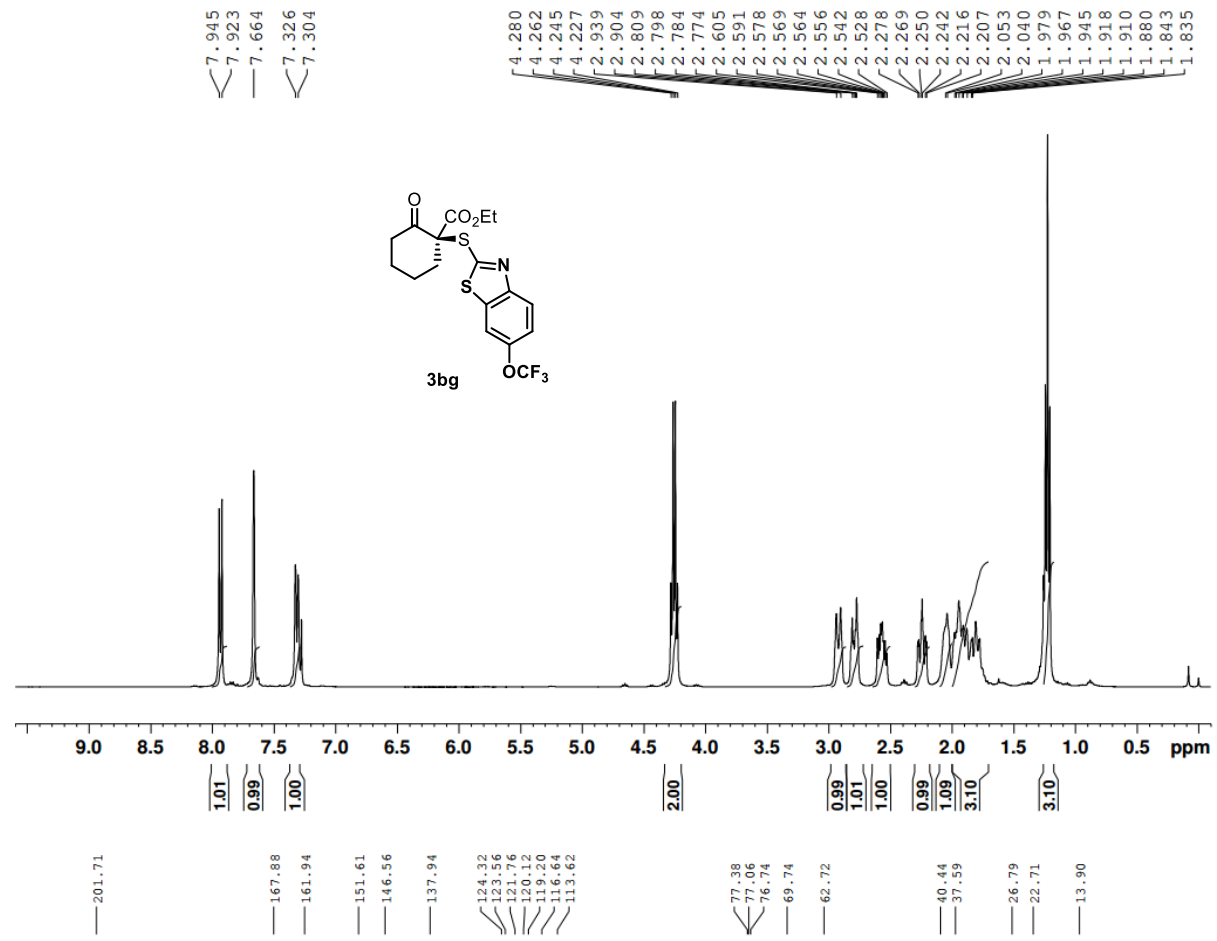
7.224
7.052
7.032
4.236
4.219
4.075
4.059
2.875
2.843
2.791
2.757
2.527
2.502
2.187
2.161
2.134
2.007
1.966
1.933
1.862
1.835
1.735
1.709
1.457
1.442
1.427
1.217
1.201
1.185
CO2Et
S
N
S
O
OEt
3bf
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.98
1.02
2.06
2.03
0.99
0.98
0.99
1.08
3.15
1.09
3.01
3.09
202.08
168.00
157.40
155.84
147.86
139.29
123.70
116.31
103.99
77.38
77.07
76.75
69.40
64.10
62.55
40.51
37.59
26.94
22.77
14.77
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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4.280
4.262
4.245
4.227
2.939
2.904
2.809
2.798
2.784
2.774
2.605
2.591
2.578
2.569
2.564
2.556
2.542
2.528
2.278
2.269
2.250
2.242
2.216
2.207
2.053
2.040
1.979
1.967
1.945
1.918
1.910
1.880
1.843
1.835
O
CO2Et
S
N
S
OCF3
3bg
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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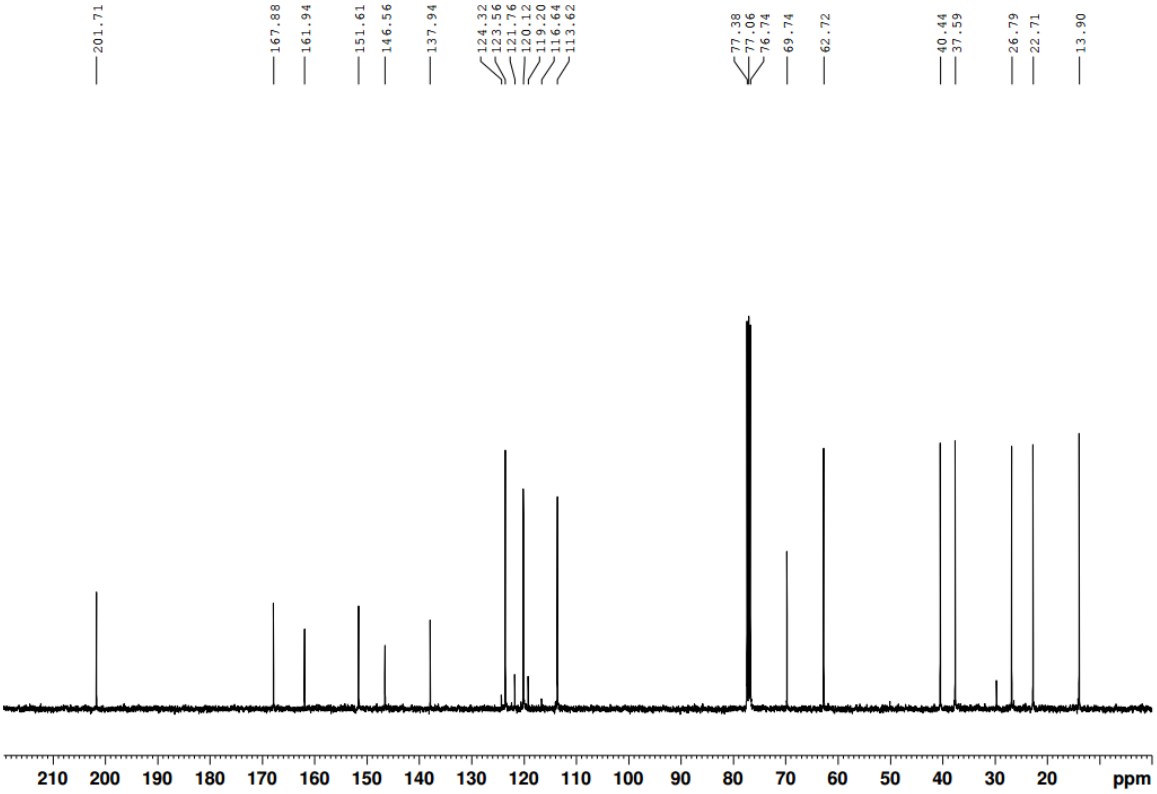
0.99
1.00
2.00
0.99
1.01
1.00
0.99
1.09
3.10
3.10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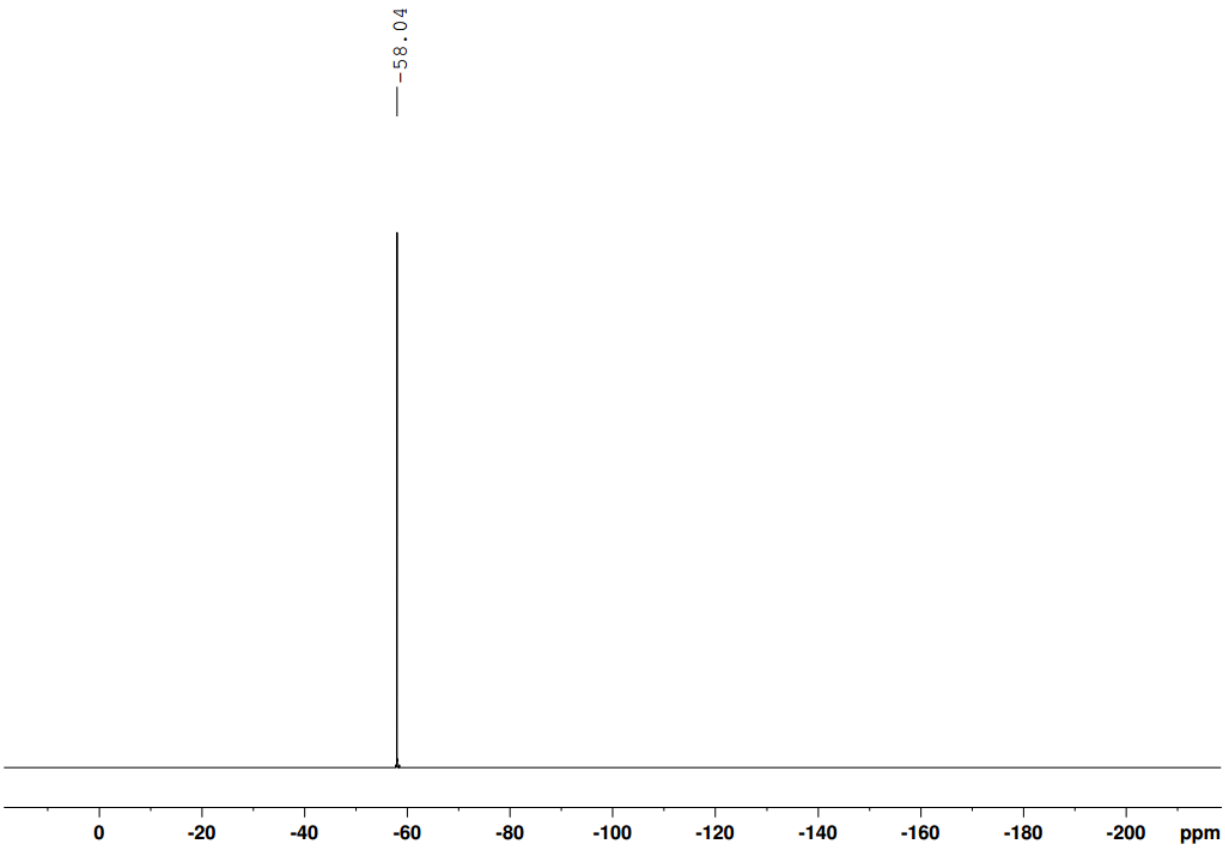
151.61
146.56
137.94
124.32
123.56
121.76
120.12
119.20
116.64
113.62
77.38
77.06
76.74
69.74
62.72
40.44
37.59
26.79
22.71
13.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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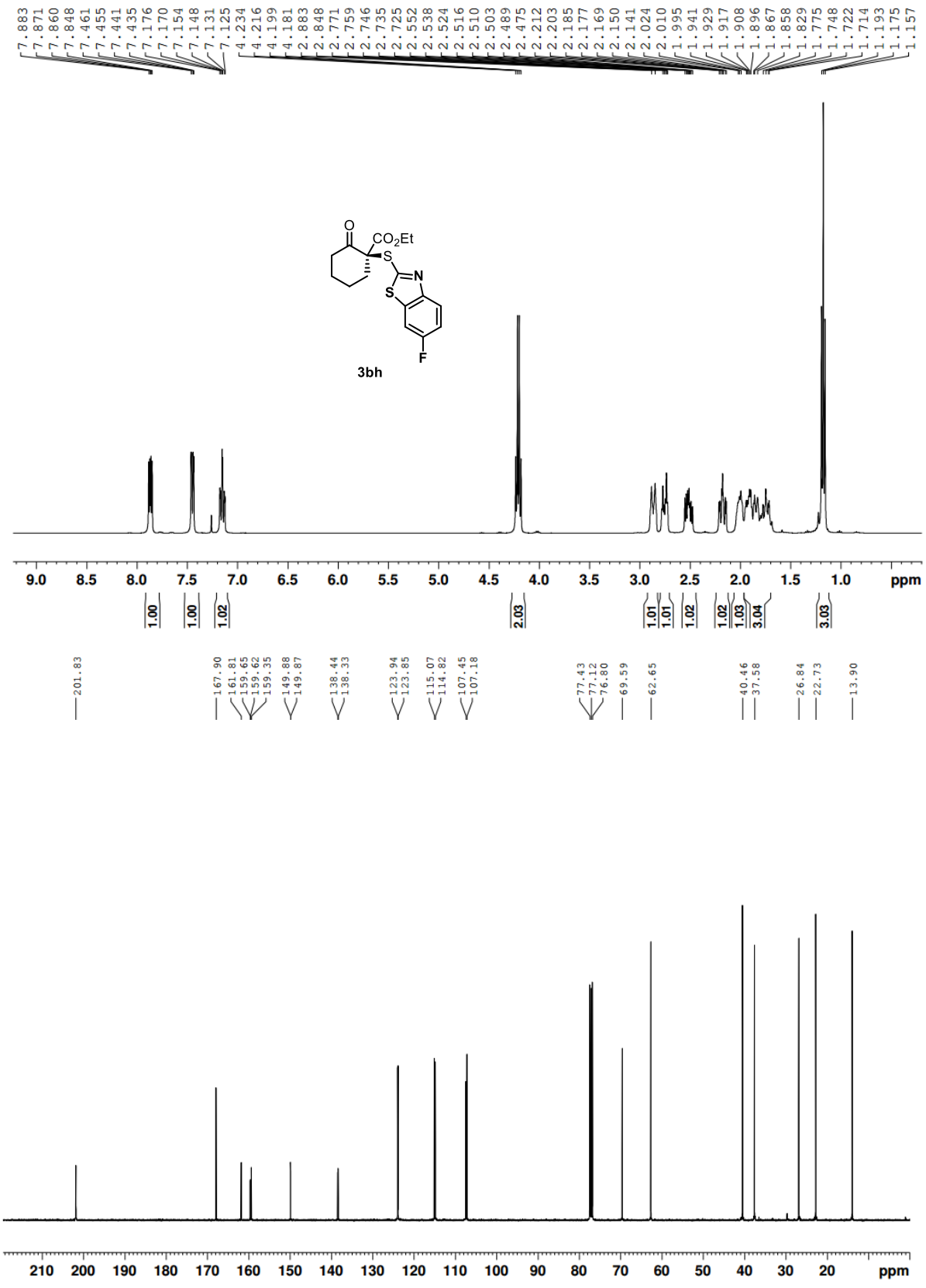
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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7.848
7.461
7.455
7.441
7.435
7.176
7.170
7.154
7.148
7.131
7.125
4.234
4.216
4.199
4.181
2.883
2.848
2.771
2.759
2.746
2.735
2.725
2.552
2.538
2.524
2.516
2.510
2.503
2.489
2.475
2.212
2.203
2.185
2.177
2.169
2.150
2.141
2.024
2.010
1.995
1.941
1.929
1.917
1.908
1.896
1.867
1.858
1.829
1.775
1.748
1.722
1.714
1.193
1.175
1.157
O
CO2Et
S
N
S
F
3bh
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
1.02
2.03
1.01
1.01
1.02
1.02
1.03
3.04
3.03
201.83
167.90
161.81
159.65
159.62
159.35
149.88
149.87
138.44
138.33
123.94
123.85
115.07
114.82
107.45
107.18
77.43
77.12
76.80
69.59
62.65
40.46
37.58
26.84
22.73
13.90
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150
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120
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80
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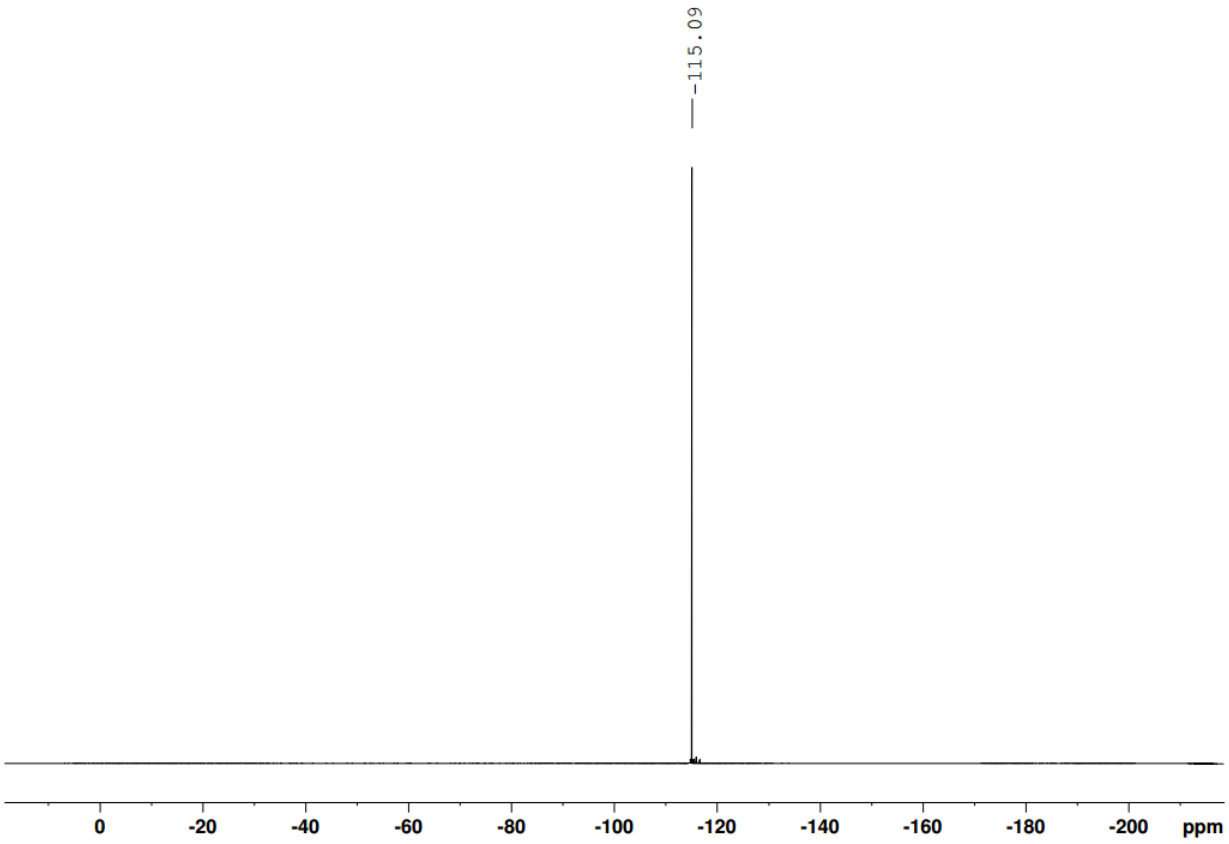
40
30
20
ppm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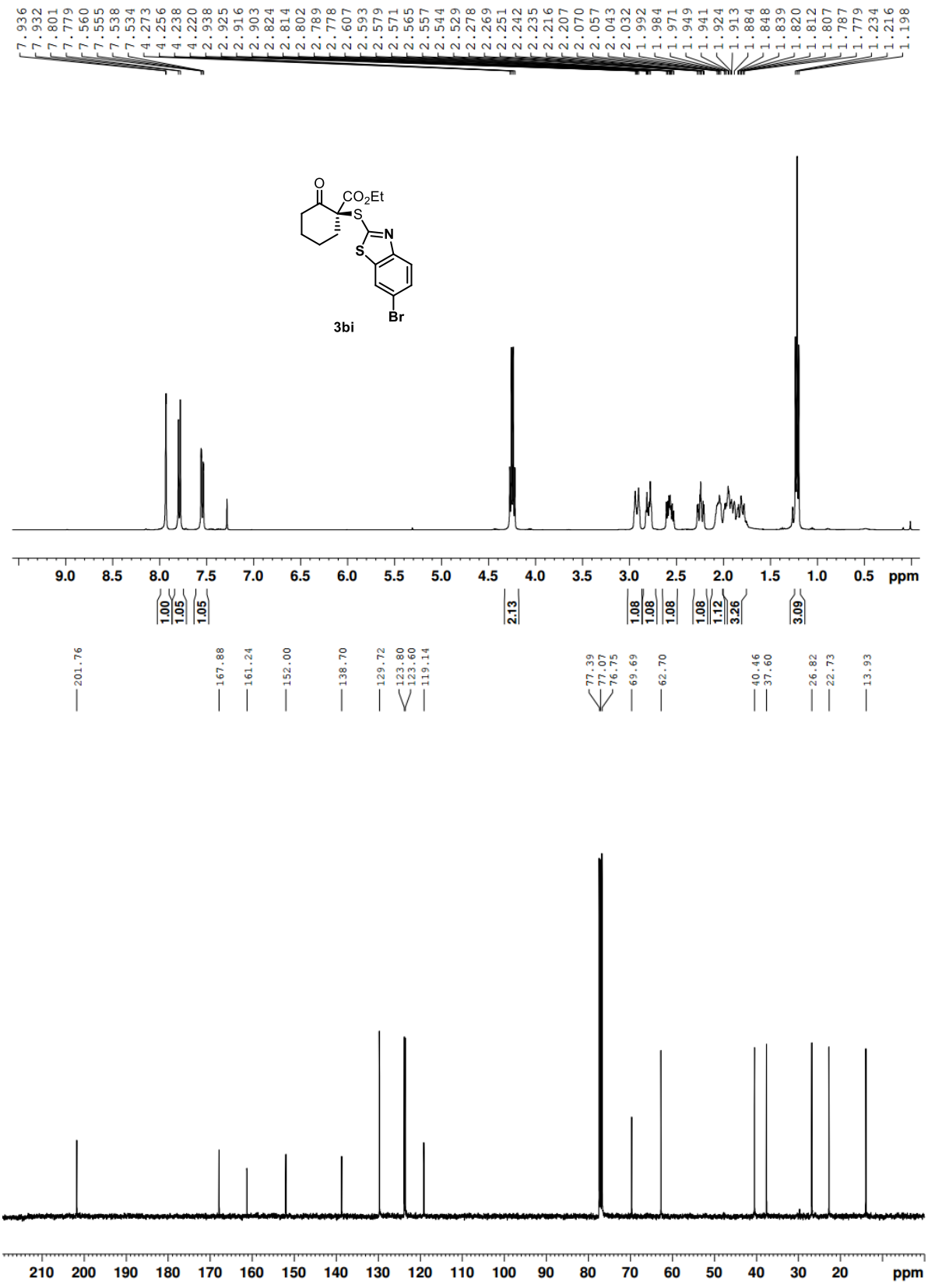
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4.256
4.238
4.220
2.938
2.925
2.916
2.903
2.824
2.814
2.802
2.789
2.778
2.607
2.593
2.579
2.571
2.565
2.557
2.544
2.529
2.278
2.269
2.251
2.242
2.235
2.216
2.207
2.070
2.057
2.043
2.032
1.992
1.984
1.971
1.949
1.941
1.924
1.913
1.884
1.848
1.839
1.820
1.812
1.807
1.787
1.779
1.234
1.216
1.198
O
CO2Et
S
N
S
Br
3bi
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.05 1.05 2.13 1.08 1.08 1.08 1.08 1.12 3.26 3.09
201.76
167.88
161.24
152.00
138.70
129.72
123.80
123.60
119.14
77.39
77.07
76.75
69.69
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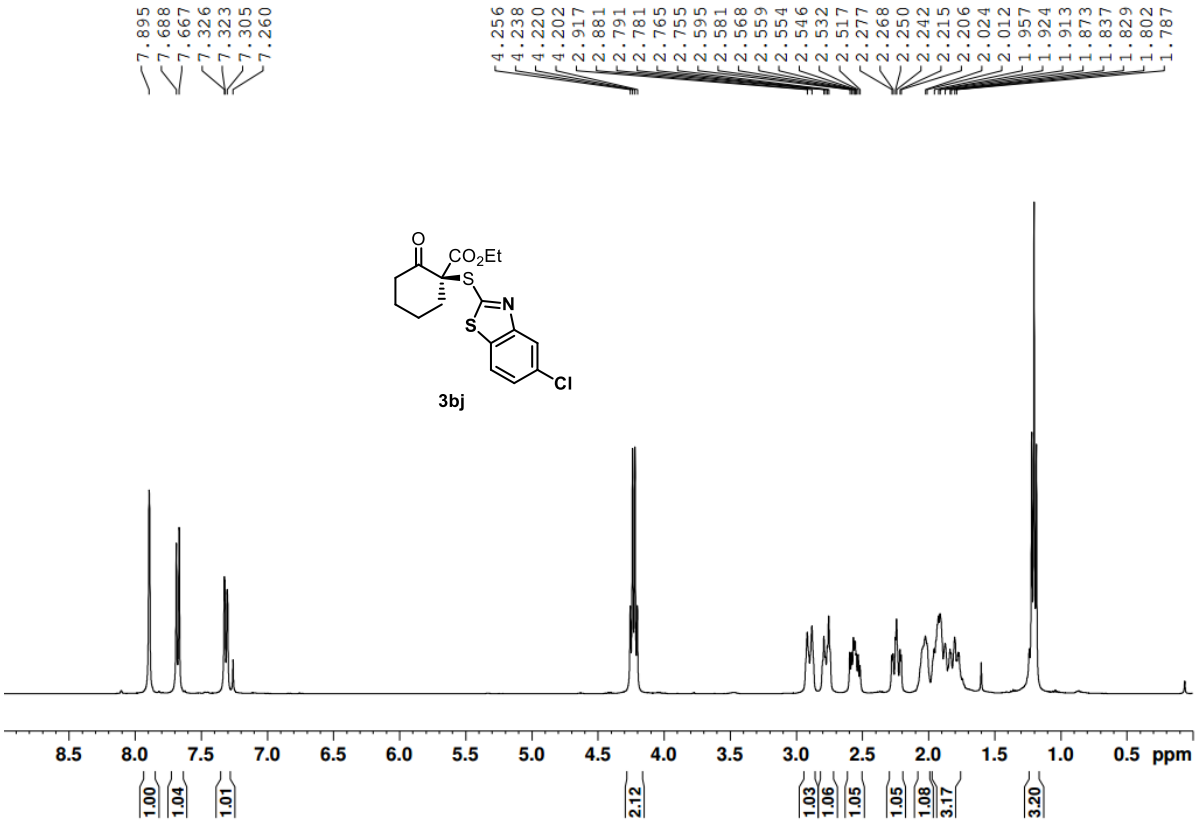
40.46
37.60
26.82
22.73
13.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.323
7.305
7.260
4.256
4.238
4.220
4.202
2.917
2.881
2.791
2.781
2.765
2.755
2.595
2.581
2.568
2.559
2.554
2.546
2.532
2.517
2.277
2.268
2.250
2.242
2.215
2.206
2.024
2.012
1.957
1.924
1.913
1.873
1.837
1.829
1.802
1.787
O
CO2Et
S
N
S
Cl
3bj
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.01
2.12
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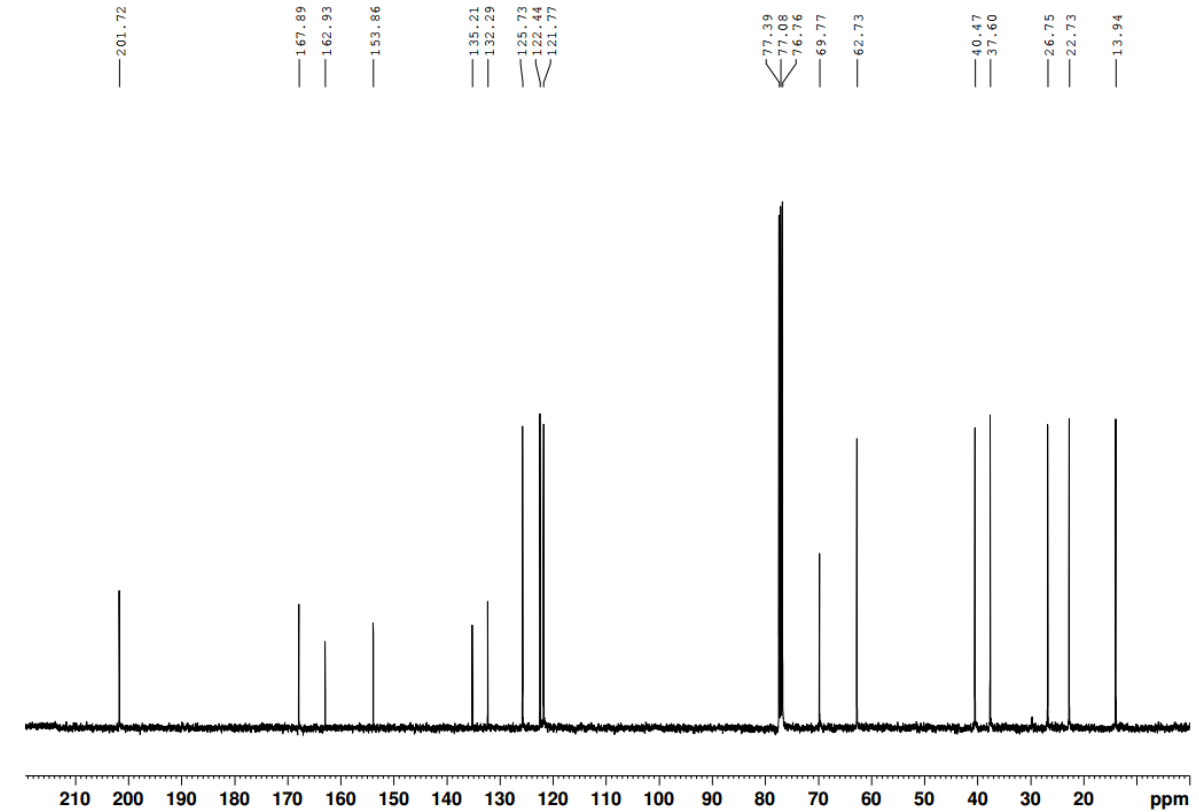
1.06
1.05
1.05
1.08
3.17
3.20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162.93
153.86
135.21
132.29
125.73
122.44
121.77
77.39
77.08
76.76
69.77
62.73
40.47
37.60
26.75
22.73
13.94
210
200
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180
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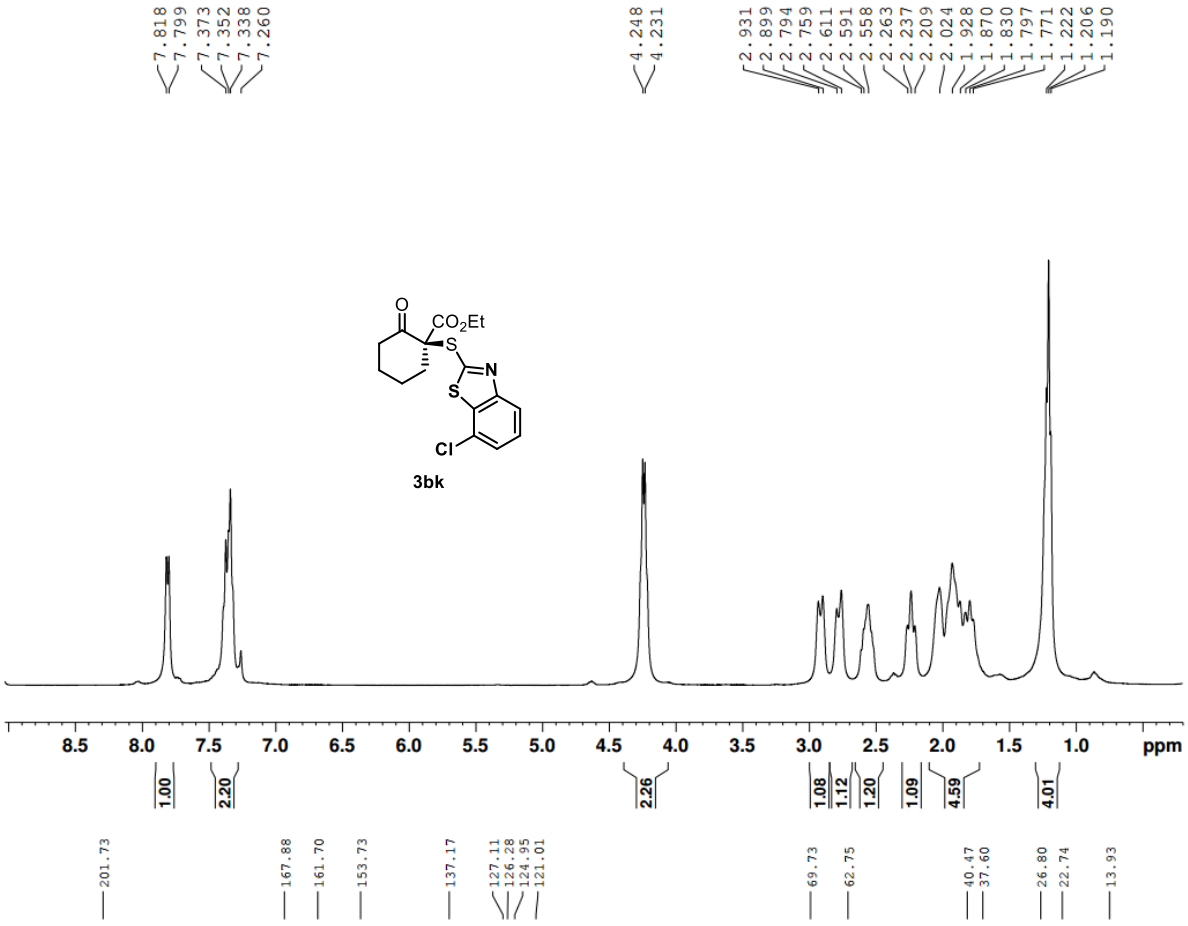
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.373
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7.260
4.248
4.231
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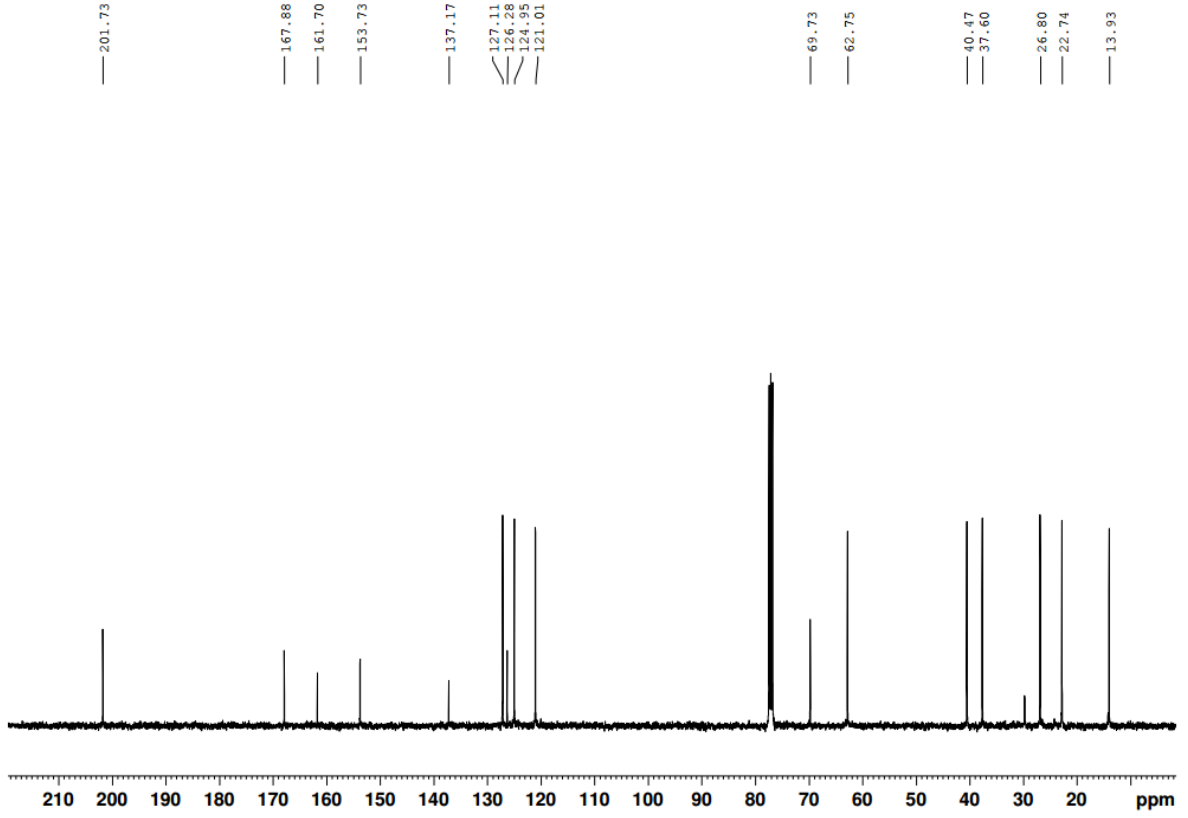
2.899
2.794
2.759
2.611
2.591
2.558
2.263
2.237
2.209
2.024
1.928
1.870
1.830
1.797
1.771
1.222
1.206
1.190
O
CO2Et
S
N
S
Cl
3bk
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.20
2.26
1.08
1.12
1.20
1.09
4.59
4.01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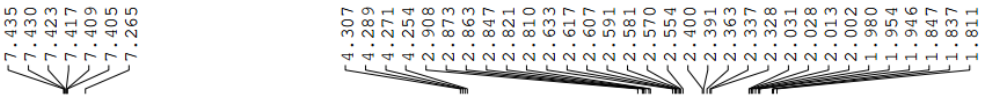
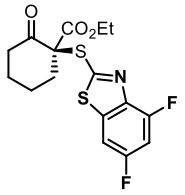
167.88
161.70
153.73
137.17
127.11
126.28
124.95
121.01
69.73
62.75
40.47
37.60
26.80
22.74
13.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.435
7.430
7.423
7.417
7.409
7.405
7.265
4.307
4.289
4.271
4.254
2.908
2.873
2.863
2.847
2.821
2.810
2.633
2.617
2.607
2.591
2.581
2.570
2.554
2.400
2.391
2.363
2.337
2.328
2.031
2.028
2.013
2.002
1.980
1.954
1.946
1.847
1.837
1.811


O
CO2Et
S
N
S
F
F

3bl

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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
ppm
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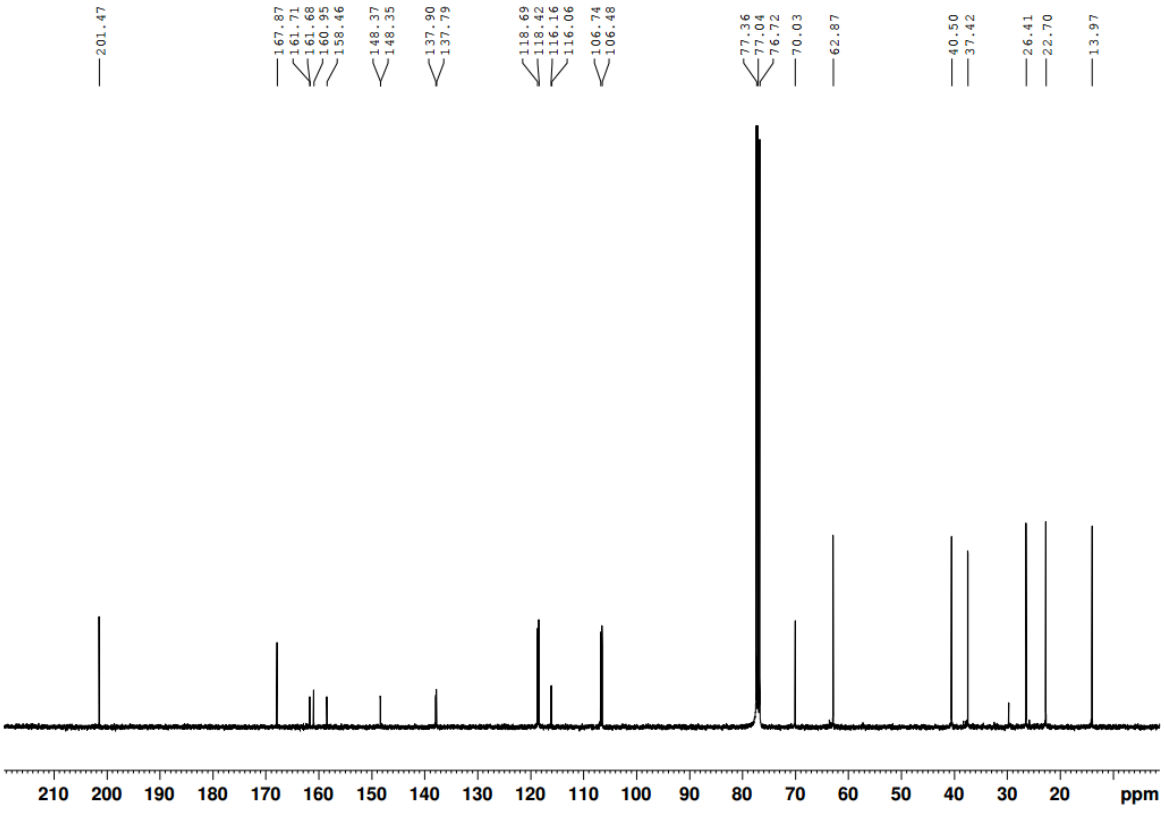
2.00
1.99
1.00
1.02
3.06
1.02
3.11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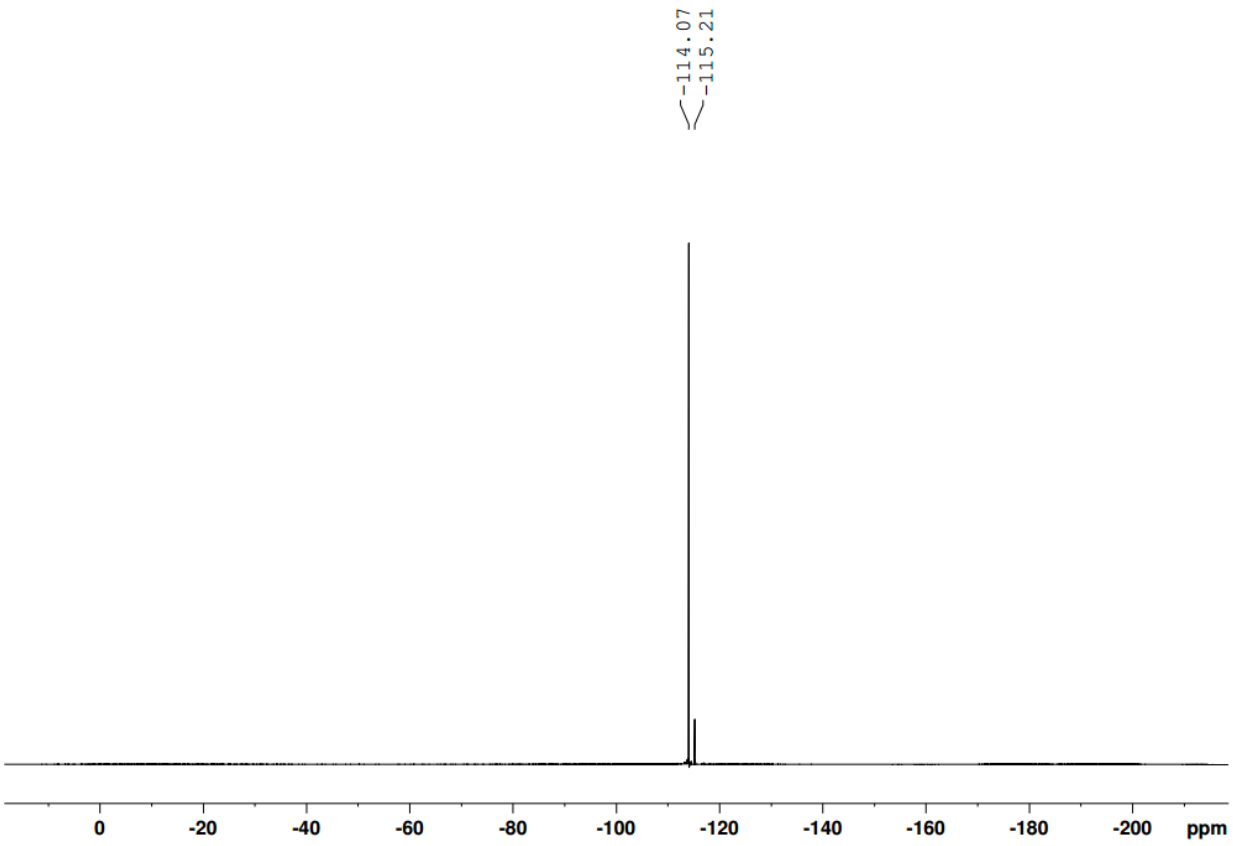
167.87
161.71
161.68
160.95
158.46
148.37
148.35
137.90
137.79
118.69
118.42
116.16
116.06
106.74
106.48
77.36
77.04
76.72
70.03
62.87
40.50
37.42
26.41
22.70
13.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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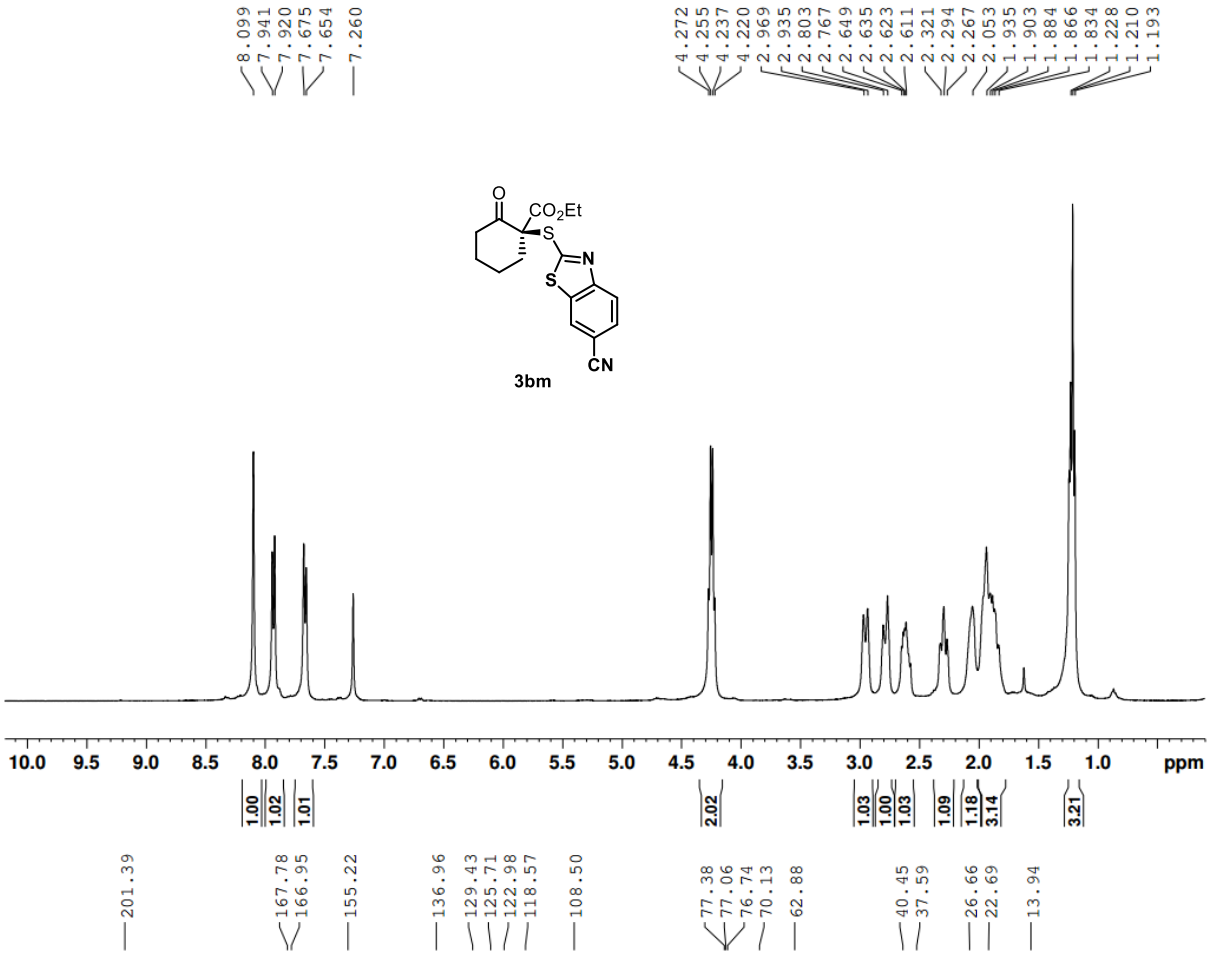
-115.21
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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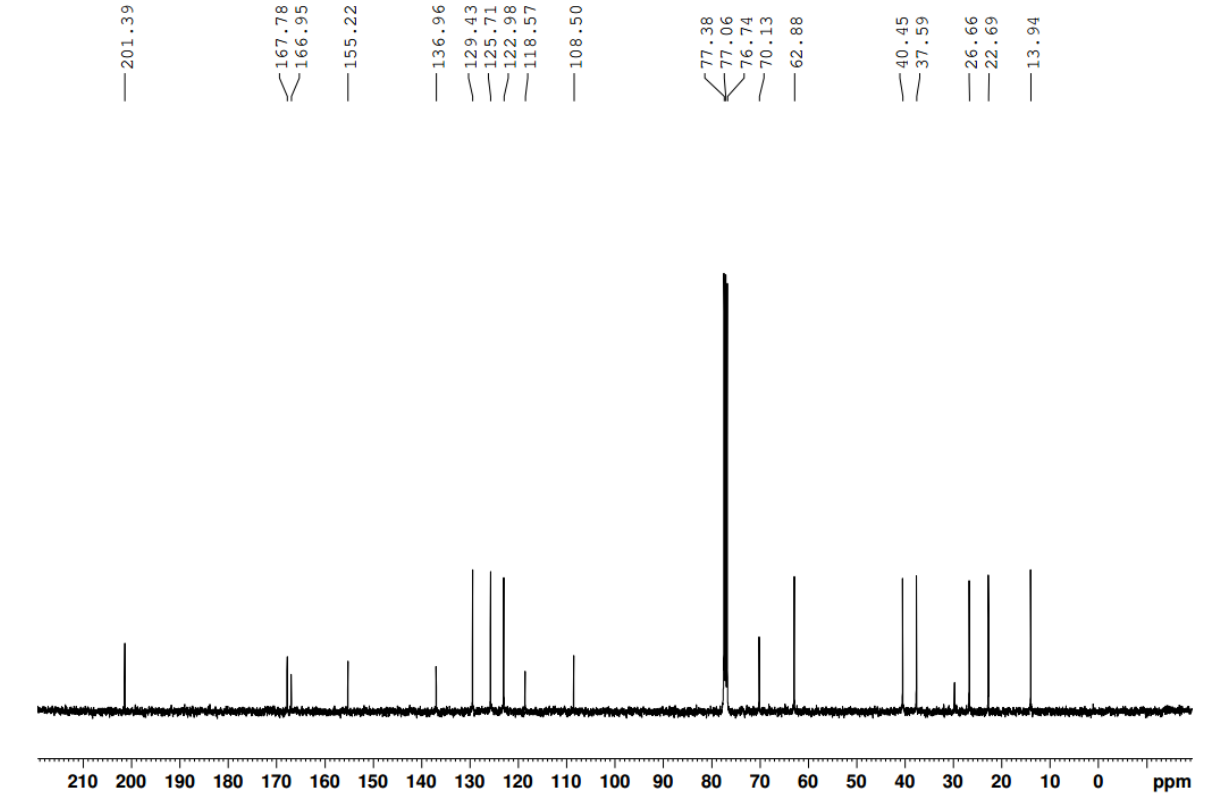
7.941
7.920
7.675
7.654
7.260
4.272
4.255
4.237
4.220
2.969
2.935
2.803
2.767
2.649
2.635
2.623
2.611
2.321
2.294
2.267
2.053
1.935
1.903
1.884
1.866
1.834
1.228
1.210
1.193
O
CO2Et
S
N
S
CN
3bm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.02 1.01 2.02 1.03 1.00 1.03 1.09 1.18 3.14 3.21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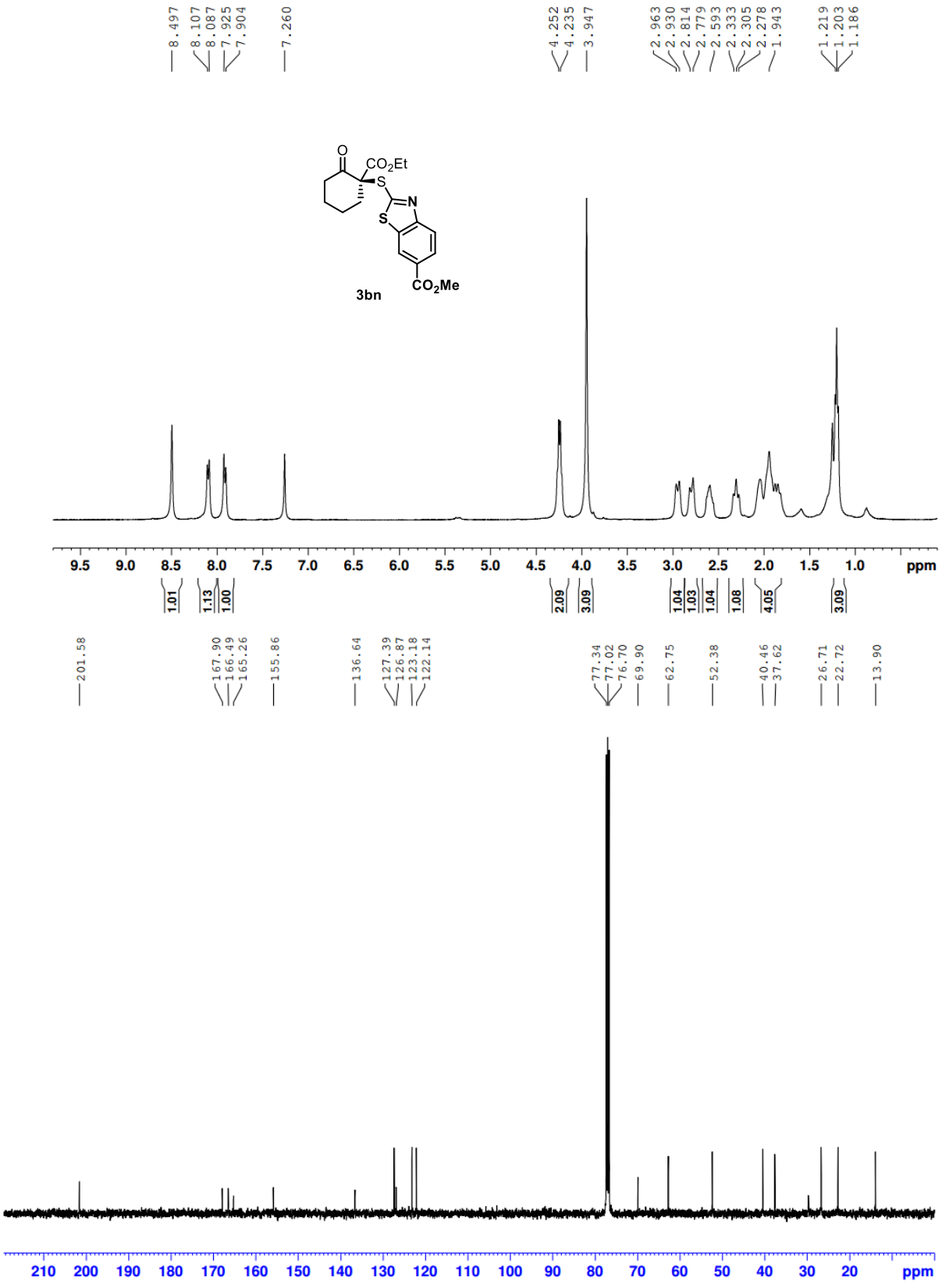
166.95
155.22
136.96
129.43
125.71
122.98
118.57
108.50
77.38
77.06
76.74
70.13
62.88
40.45
37.59
26.66
22.69
13.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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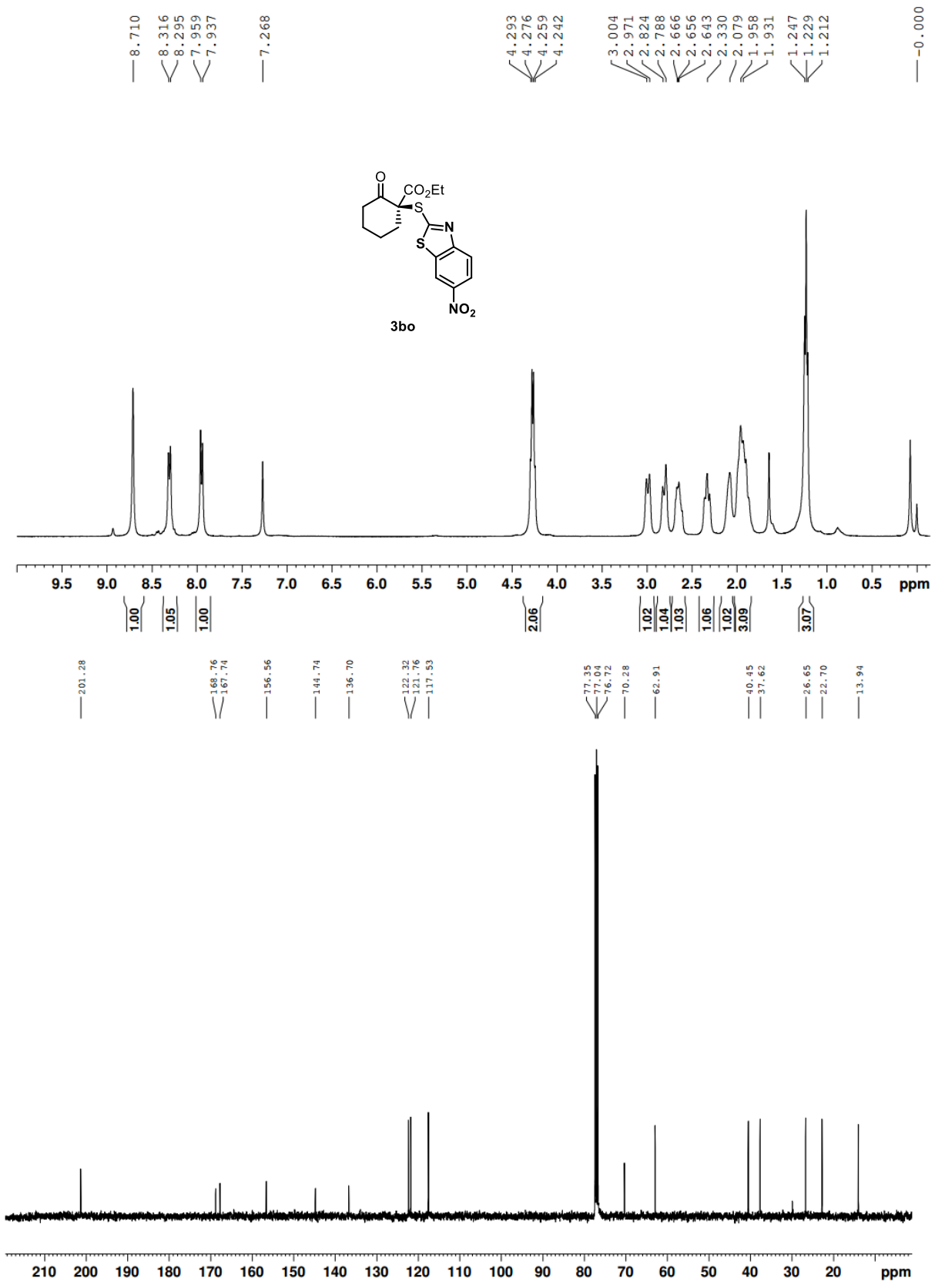
7.904
7.260
4.252
4.235
3.947
2.963
2.930
2.814
2.779
2.593
2.333
2.305
2.278
1.943
1.219
1.203
1.186
O
CO2Et
S
N
S
CO2Me
3bn
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.01
1.13
1.00
2.09
3.09
1.04
1.03
1.04
1.08
4.05
3.09
201.58
167.90
166.49
165.26
155.86
136.64
127.39
126.87
123.18
122.14
77.34
77.02
76.70
69.90
62.75
52.38
40.46
37.62
26.71
22.72
13.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.295
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7.937
7.268
4.293
4.276
4.259
4.242
3.004
2.971
2.824
2.788
2.666
2.656
2.643
2.330
2.079
1.958
1.931
1.247
1.229
1.212
0.000
O
CO2Et
S
N
S
NO2
3bo
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.05
1.00
2.06
1.02
1.04
1.03
1.06
1.02
3.09
3.07
201.28
168.76
167.74
156.56
144.74
136.70
122.32
121.76
117.53
77.35
77.04
76.72
70.28
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40.45
37.62
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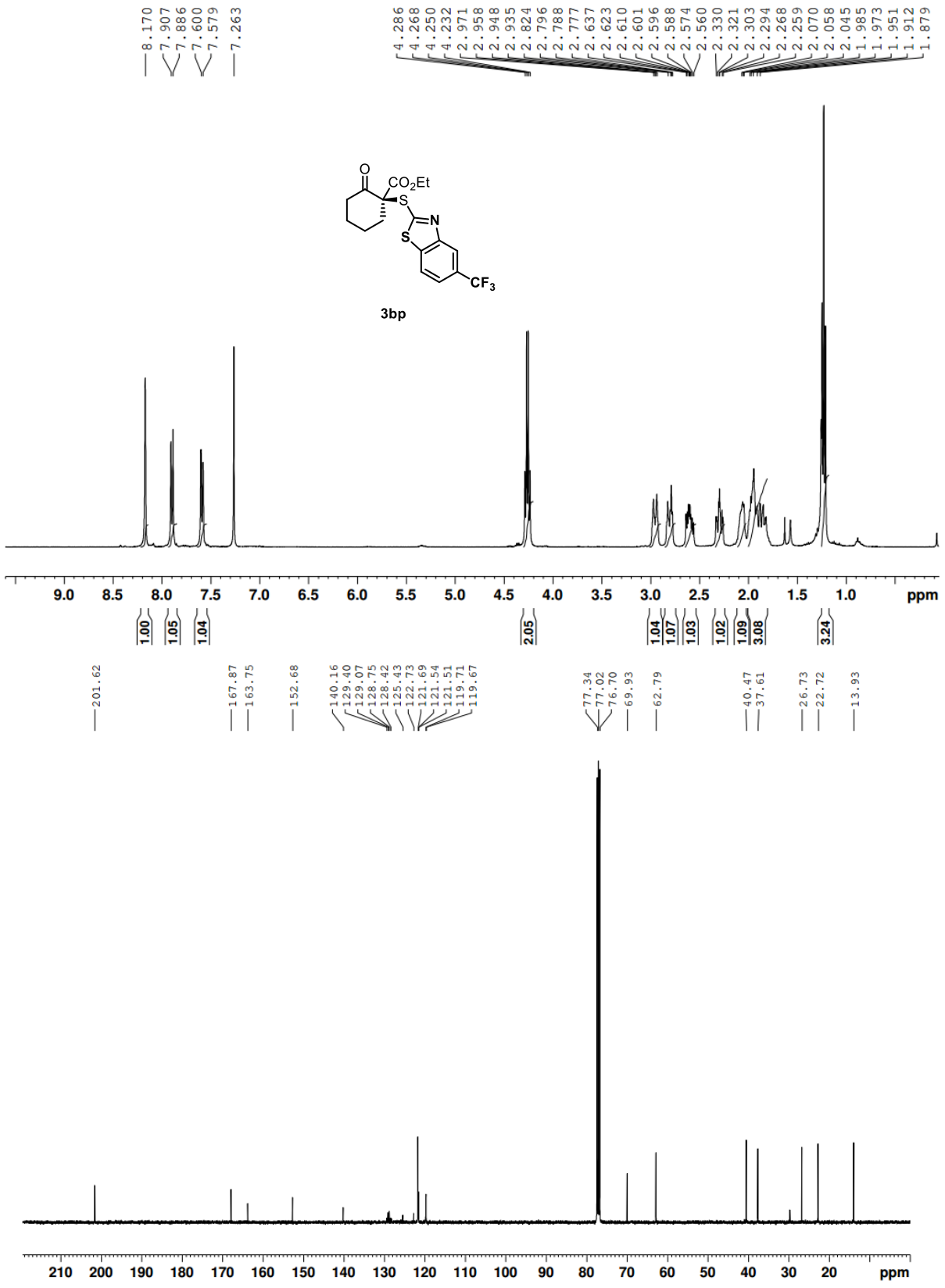
22.70
13.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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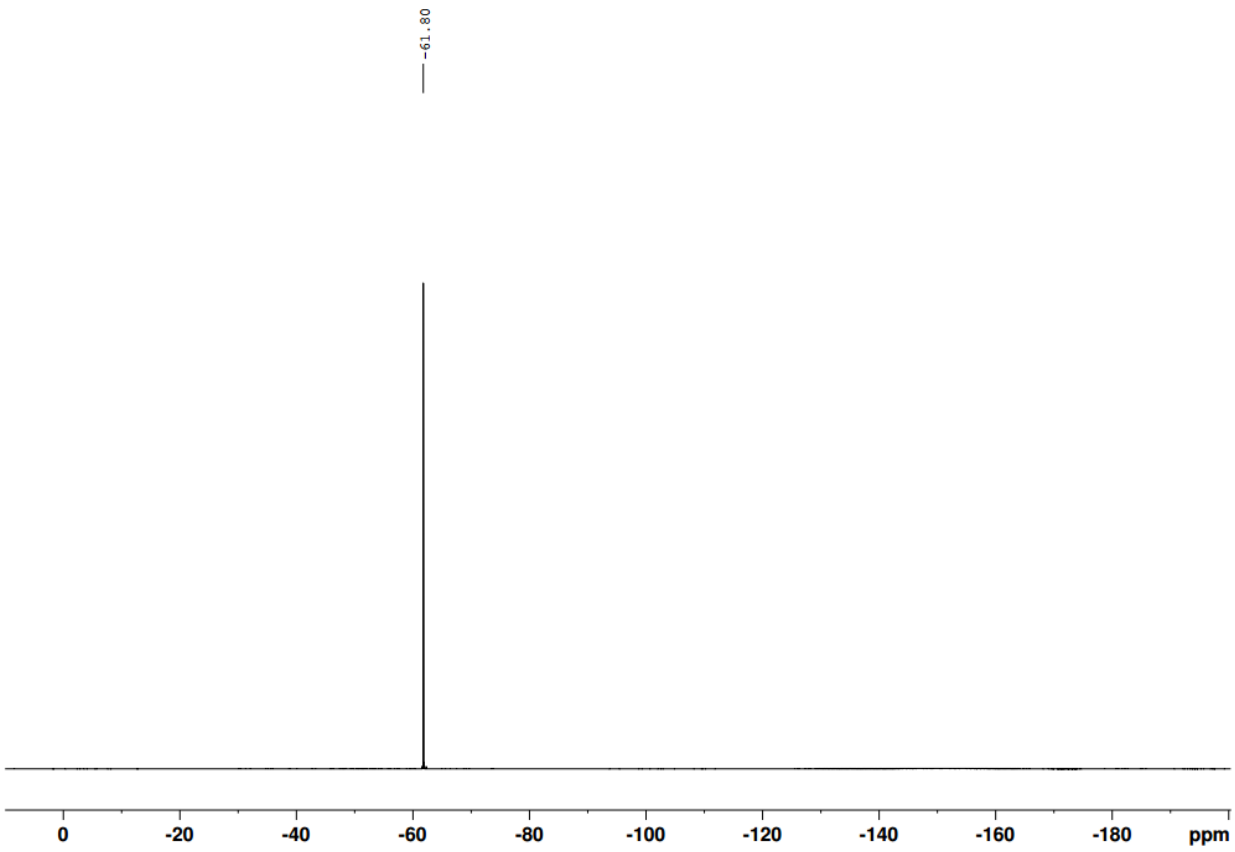
7.263
4.286
4.268
4.250
4.232
2.971
2.958
2.948
2.935
2.824
2.796
2.788
2.777
2.637
2.623
2.610
2.601
2.596
2.588
2.574
2.560
2.330
2.321
2.303
2.294
2.268
2.259
2.070
2.058
2.045
1.985
1.973
1.951
1.912
1.879
O
CO2Et
S
N
S
CF3
3bp
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.05 1.04 2.05 1.04 1.07 1.03 1.02 1.09 3.08 3.24
201.62
167.87
163.75
152.68
140.16
129.40
129.07
128.75
128.42
125.43
122.73
121.69
121.54
121.51
119.71
119.67
77.34
77.02
76.70
69.93
62.79
40.47
37.61
26.73
22.72
13.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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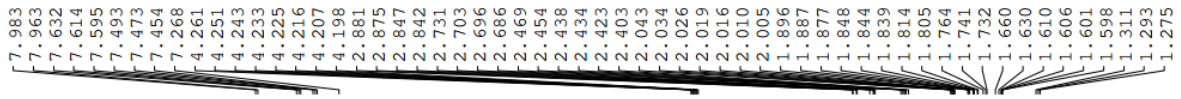
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm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7.632
7.614
7.595
7.493
7.473
7.454
7.268
4.261
4.251
4.243
4.233
4.225
4.216
4.207
4.198
2.881
2.875
2.847
2.842
2.731
2.703
2.696
2.686
2.469
2.454
2.438
2.434
2.423
2.403
2.043
2.034
2.026
2.019
2.016
2.010
2.005
1.896
1.887
1.877
1.848
1.844
1.839
1.814
1.805
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1.732
1.660
1.630
1.610
1.606
1.601
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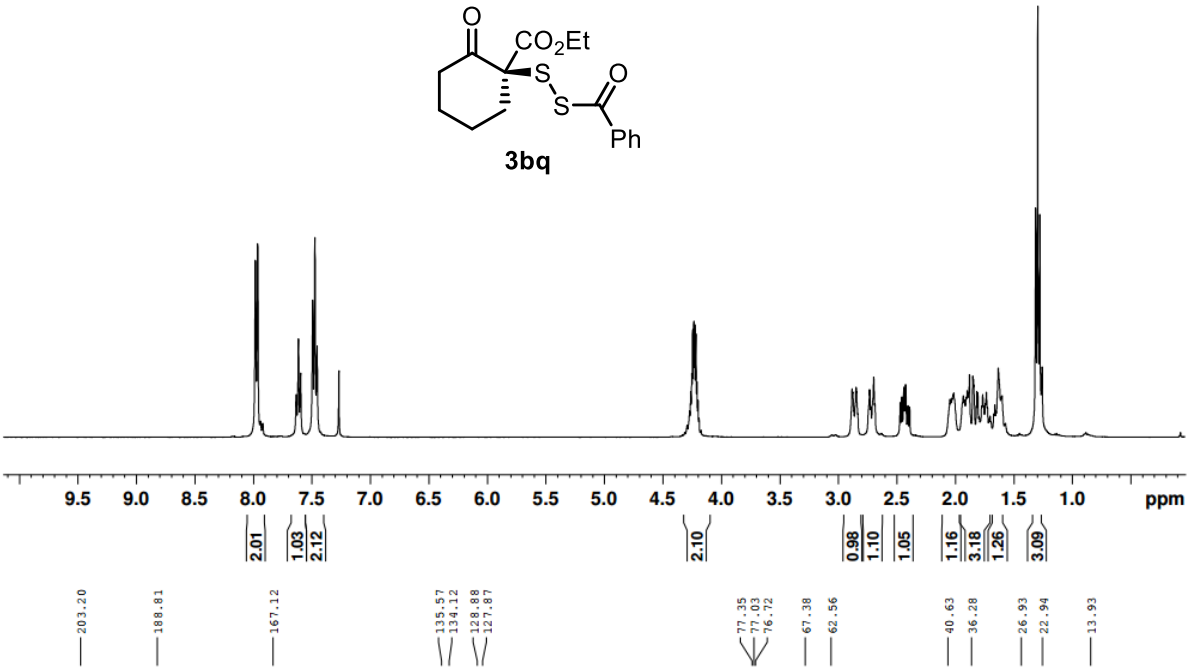
1.311
1.293
1.275


O
CO2Et
S
S
O
Ph
3bq
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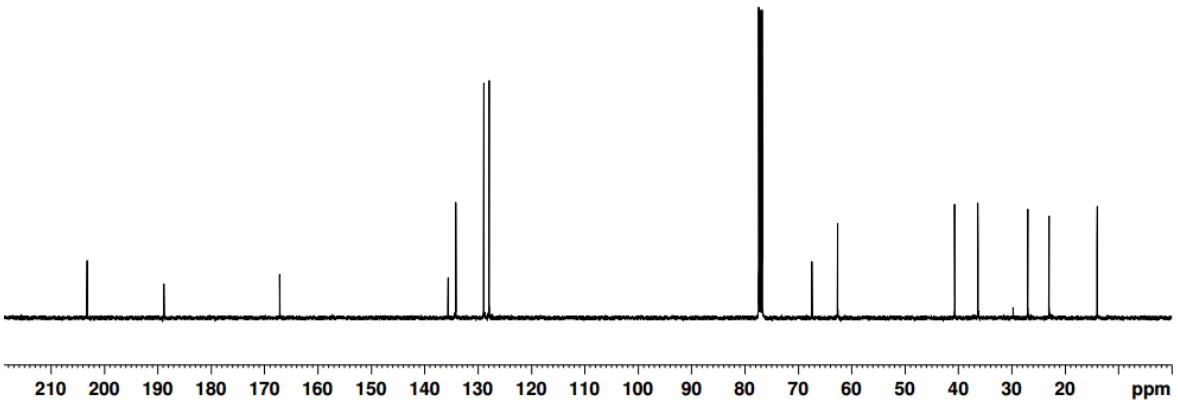
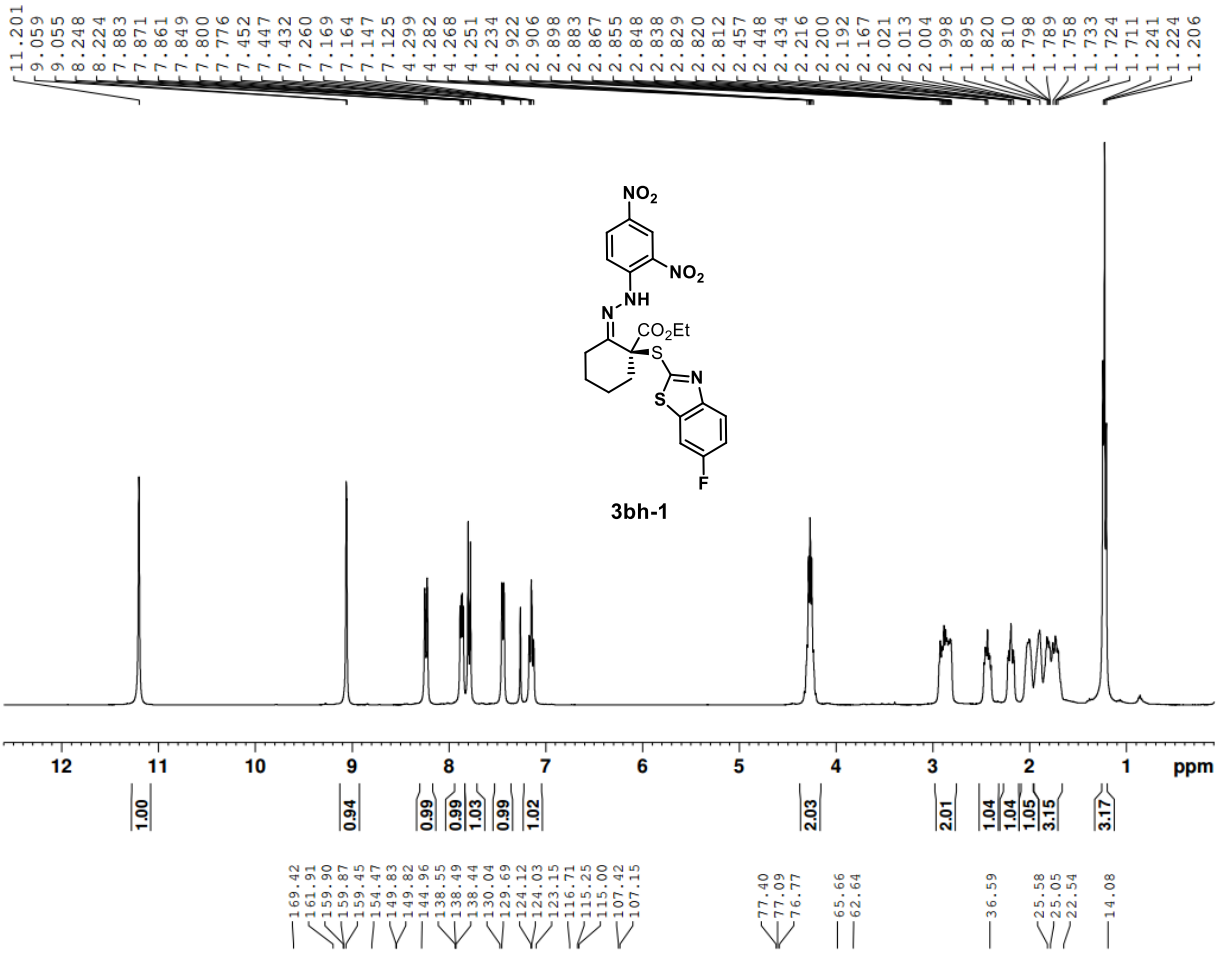
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.01
1.03
2.12
2.10
0.98
1.10
1.05
1.16
3.18
1.26
3.09
203.20
188.81
167.12
135.57
134.12
128.88
127.87
77.35
77.03
76.72
67.38
62.56
40.63
36.28
26.93
22.94
13.93


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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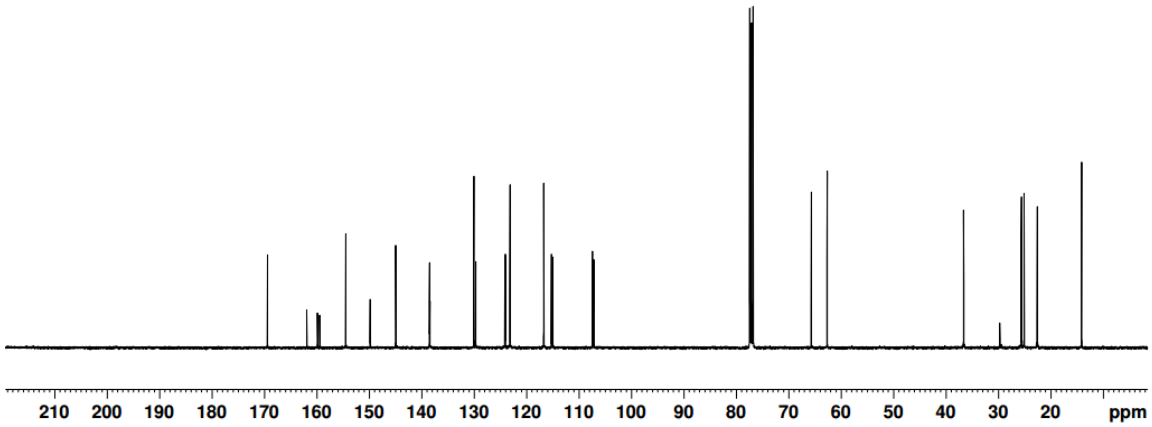
9.055
8.248
8.224
7.883
7.871
7.861
7.849
7.800
7.776
7.452
7.447
7.432
7.260
7.169
7.164
7.147
7.125
4.299
4.282
4.268
4.251
4.234
2.922
2.906
2.898
2.883
2.867
2.855
2.848
2.838
2.829
2.820
2.812
2.457
2.448
2.434
2.216
2.200
2.192
2.167
2.021
2.013
2.004
1.998
1.895
1.820
1.810
1.798
1.789
1.758
1.733
1.724
1.711
1.241
1.224
1.206
NO2
NO2
NH
N
CO2Et
S
N
S
F
3bh-1
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.94
0.99
0.99
1.03
0.99
1.02
2.03
2.01
1.04
1.04
1.05
3.15
3.17

169.42
161.91
159.90
159.87
159.45
154.47
149.83
149.82
144.96
138.55
138.49
138.44
130.04
129.69
124.12
124.03
123.15
116.71
115.25
115.00
107.42
107.15
77.40
77.09
76.77
65.66
62.64
36.59
25.58
25.05
22.54
14.08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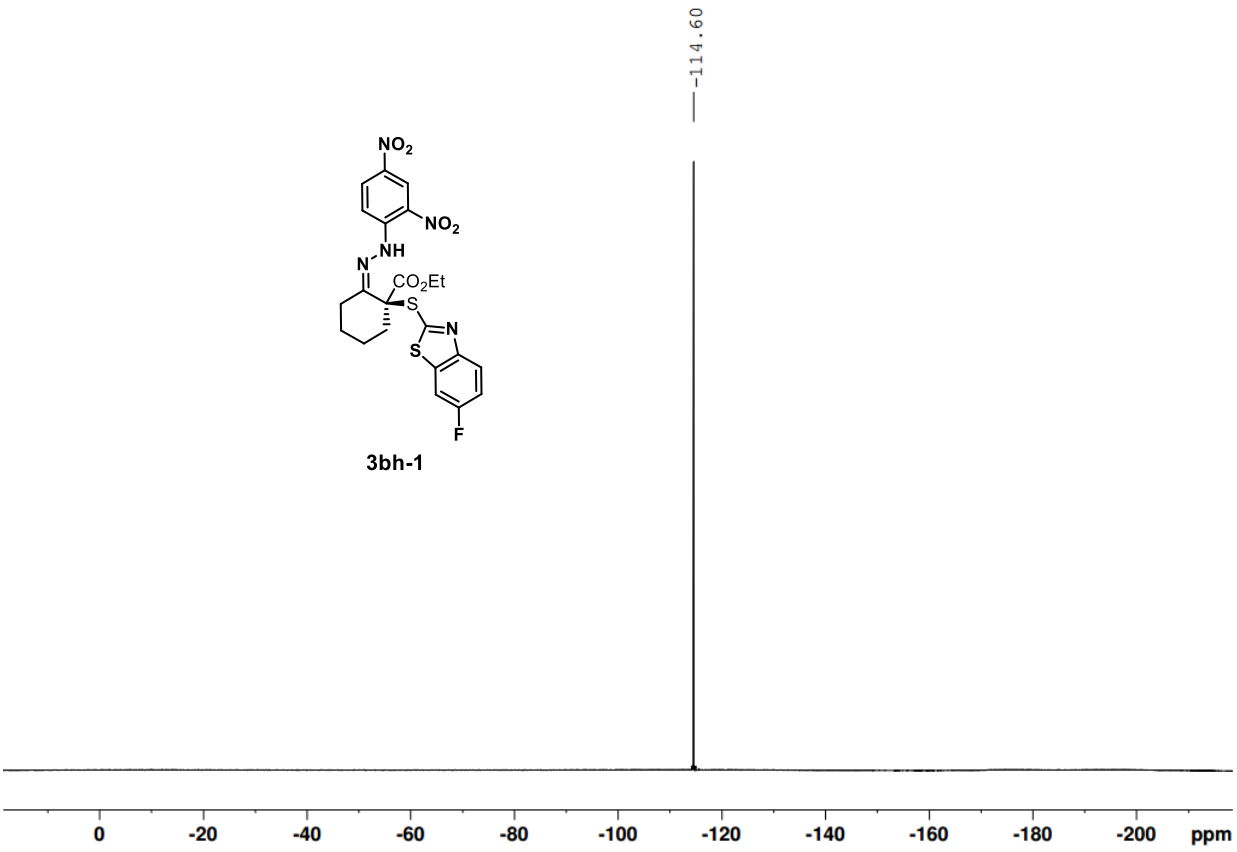
-114.60
NO2
NO2
NH
N
CO2Et
S
N
S
F
3bh-1
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-80
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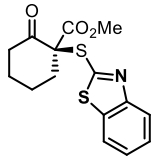
-120
-140
-160
-180
-200
ppm

8. HPLC spectra



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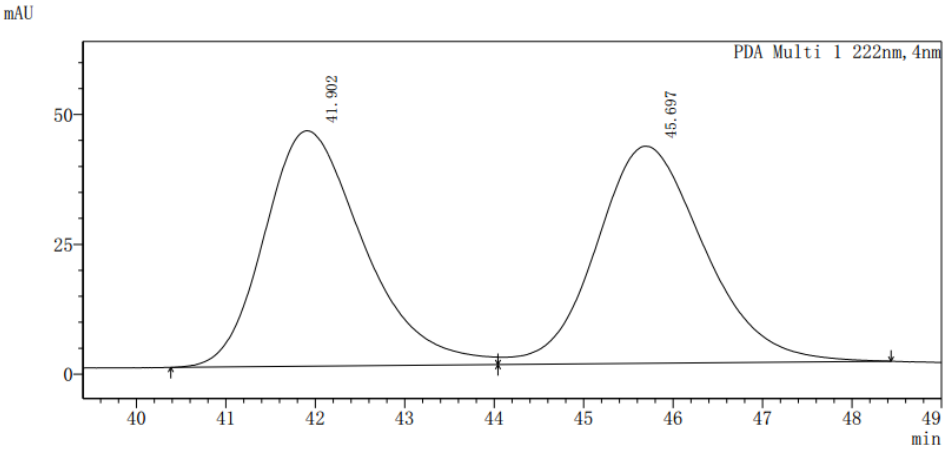
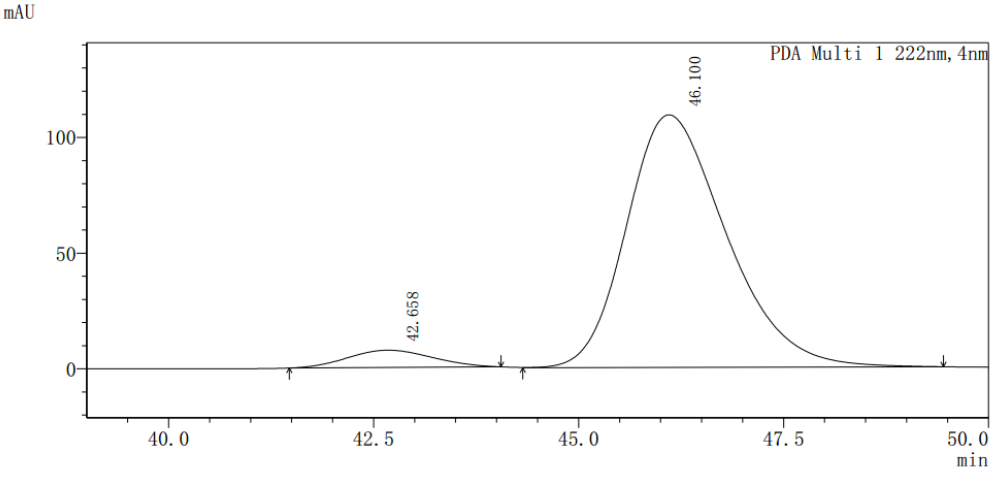


<Peak Results>

PDA Ch1 222nm

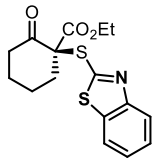
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	41.902	45326	3512359	49.893
2	45.697	41819	3527375	50.107



<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	42.658	7478	535728	5.463
2	46.100	109212	9271131	94.537



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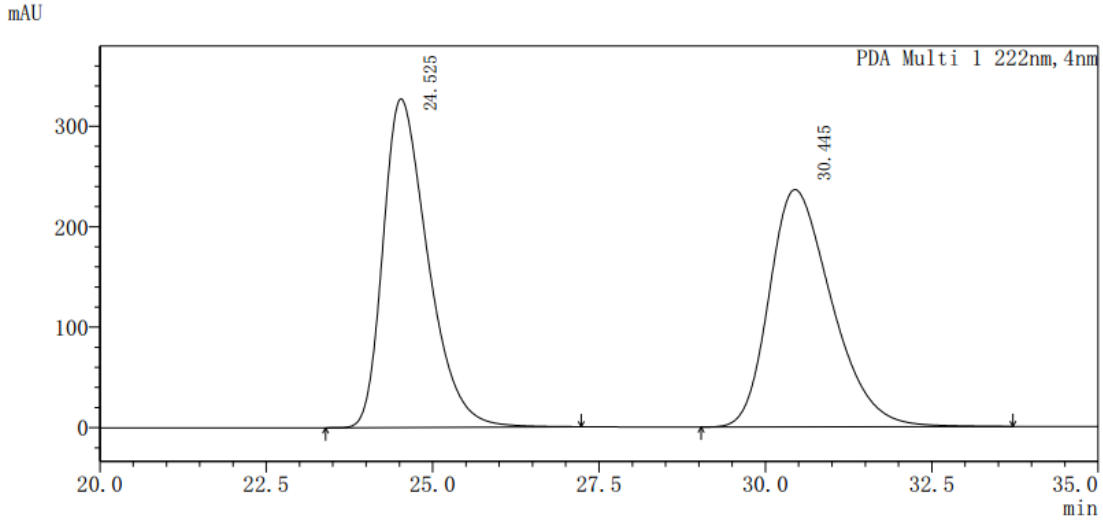
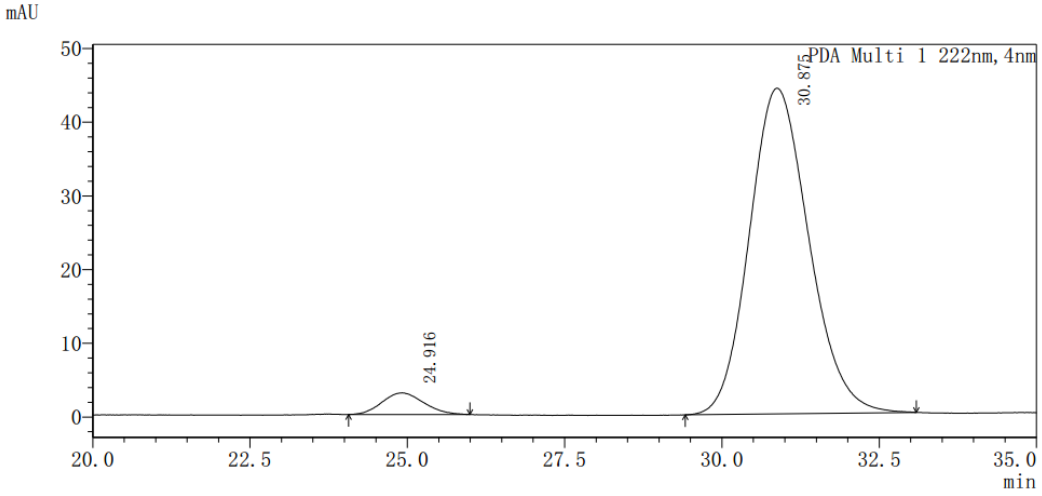


<Peak Results>

PDA Ch1 222nm

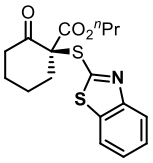
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.525	327142	15337055	49.808
2	30.445	236194	15455349	50.192



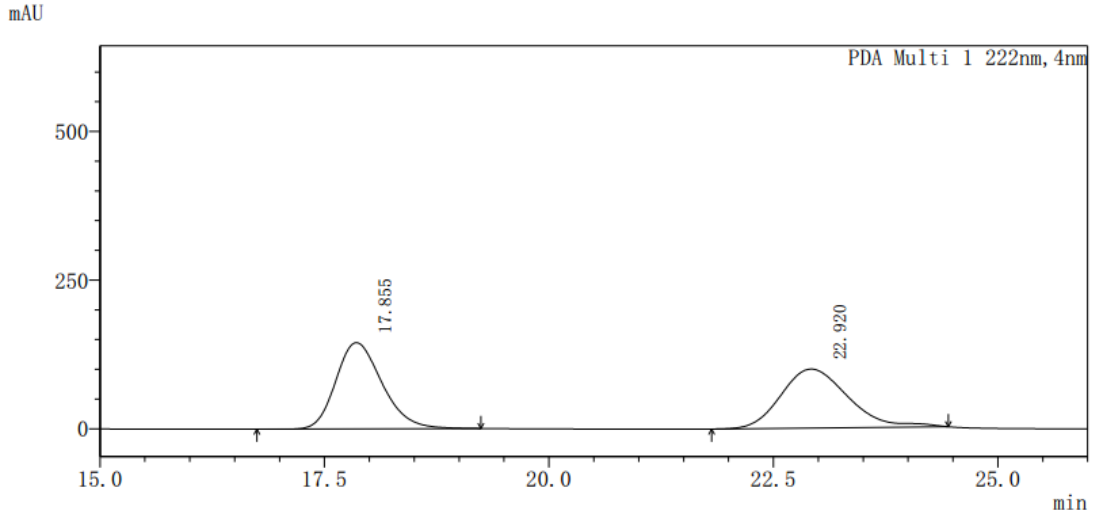
<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.916	2949	136070	4.473
2	30.875	44198	2905646	95.527



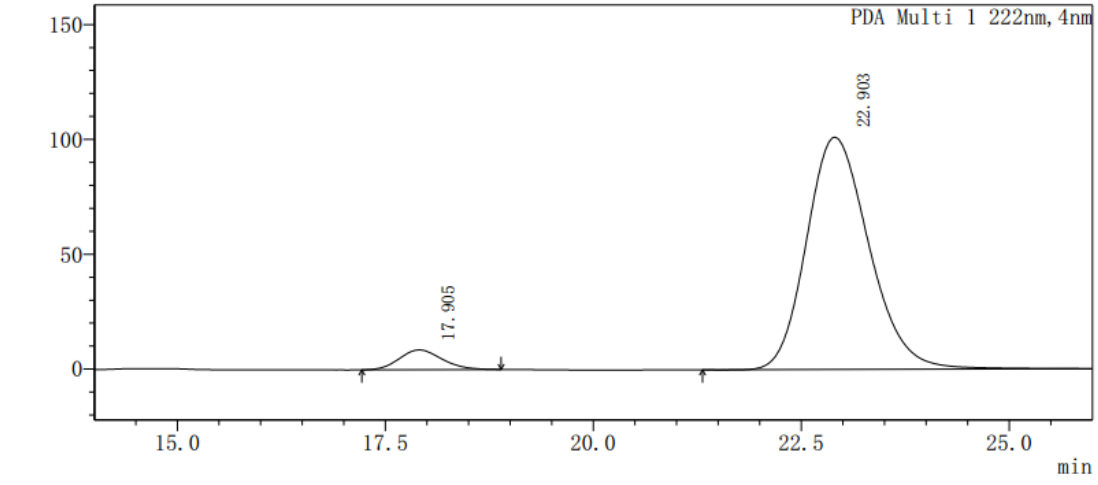
3ca



<Peak Results>

PDA Ch1 222nm

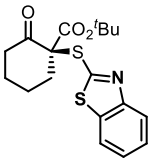
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.855	145092	5197620	50.163
2	22.920	99266	5163857	49.837



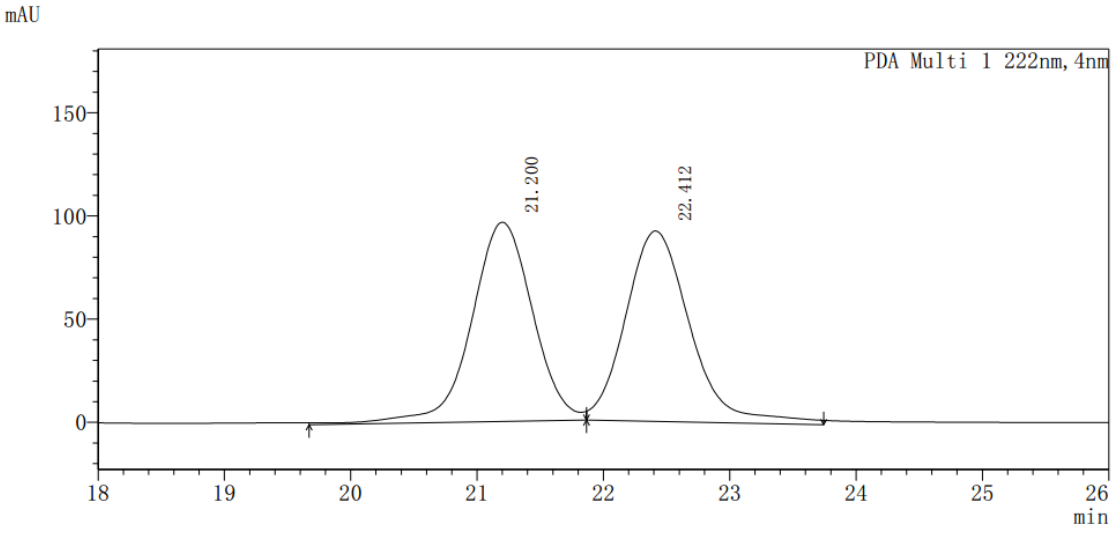
<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.905	8597	306266	5.452
2	22.903	101164	5311576	94.548



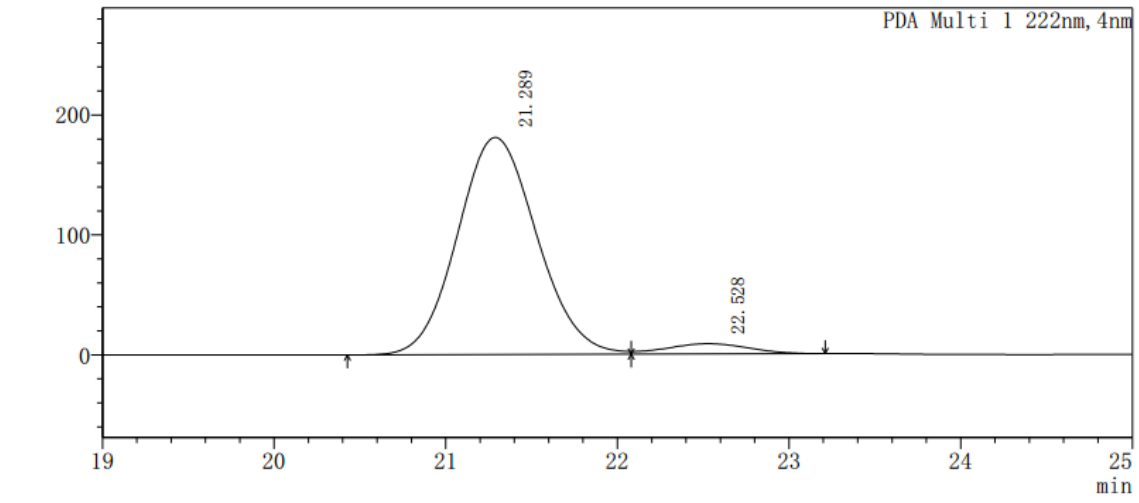
3da



<Peak Results>

PDA Ch1 222nm

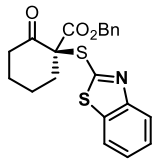
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	21.200	96588	3260085	49.913
2	22.412	92279	3271477	50.087



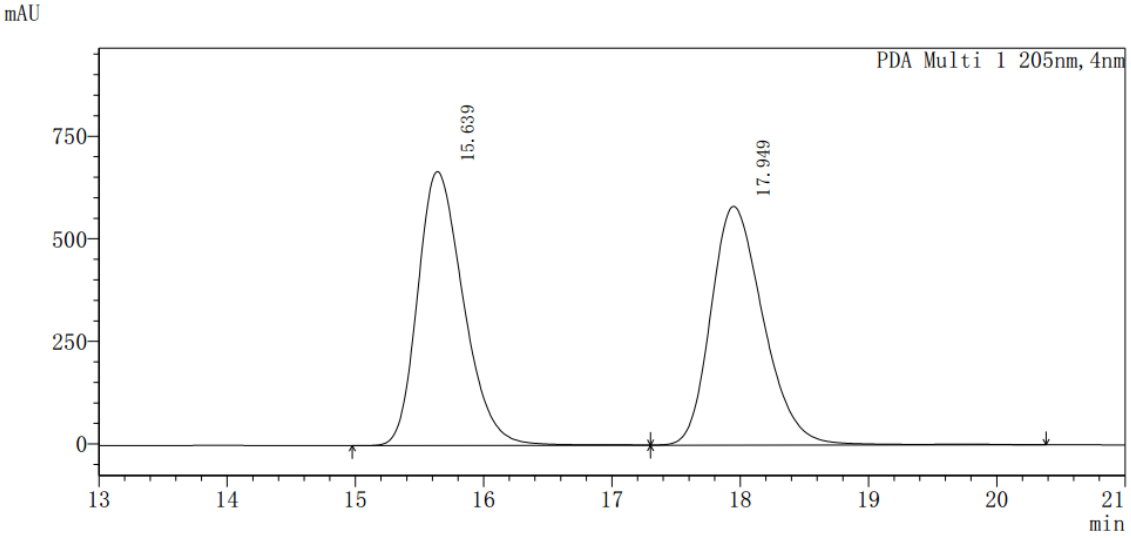
<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	21.289	181023	5820697	95.353
2	22.528	8565	283687	4.647



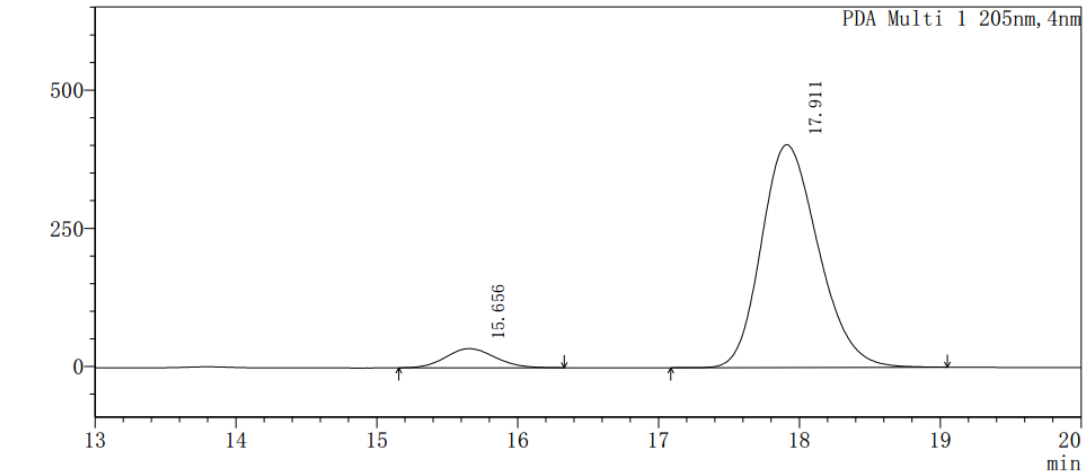
3ea



<Peak Results>

PDA Ch1 205nm

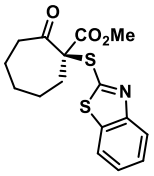
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	15.639	667930	16576846	49.972
2	17.949	582048	16595247	50.028



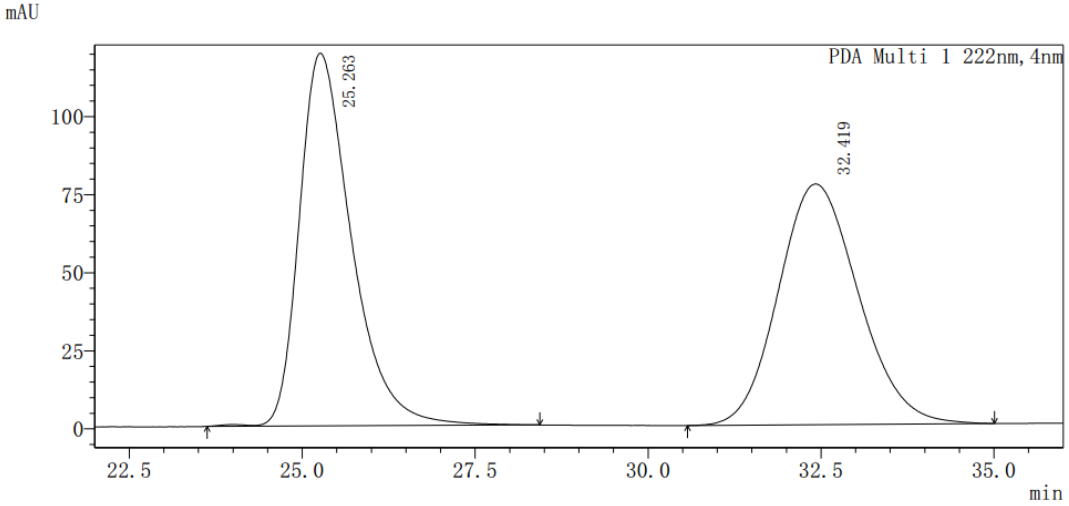
<Peak Results>

PDA Ch1 205nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	15.656	34597	842896	6.917
2	17.911	403031	11343153	93.083



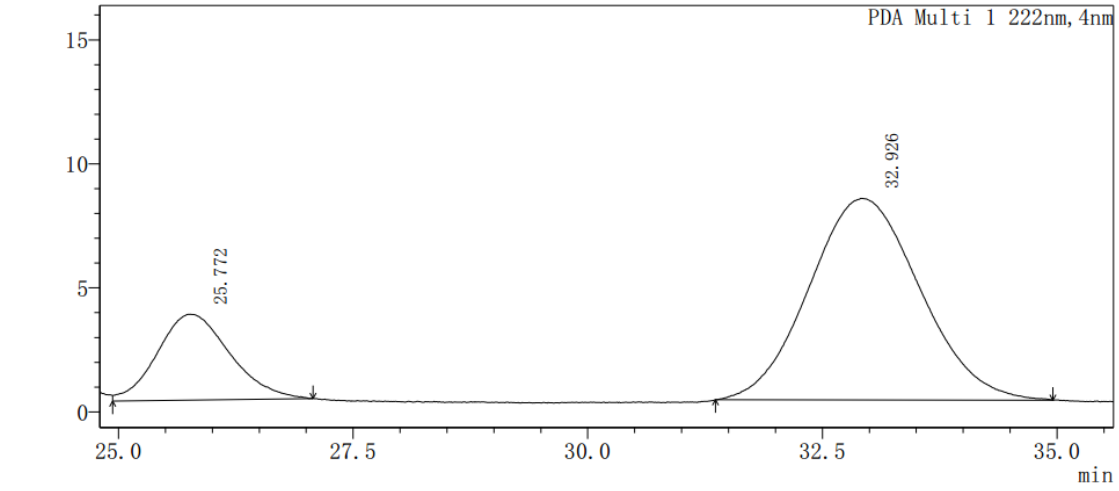
3fa



<Peak Results>

PDA Ch1 222nm

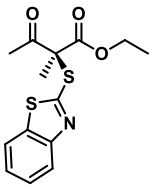
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.263	119372	6264426	50.199
2	32.419	77102	6214781	49.801



<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.772	3458	186047	21.798
2	32.926	8130	667451	78.202



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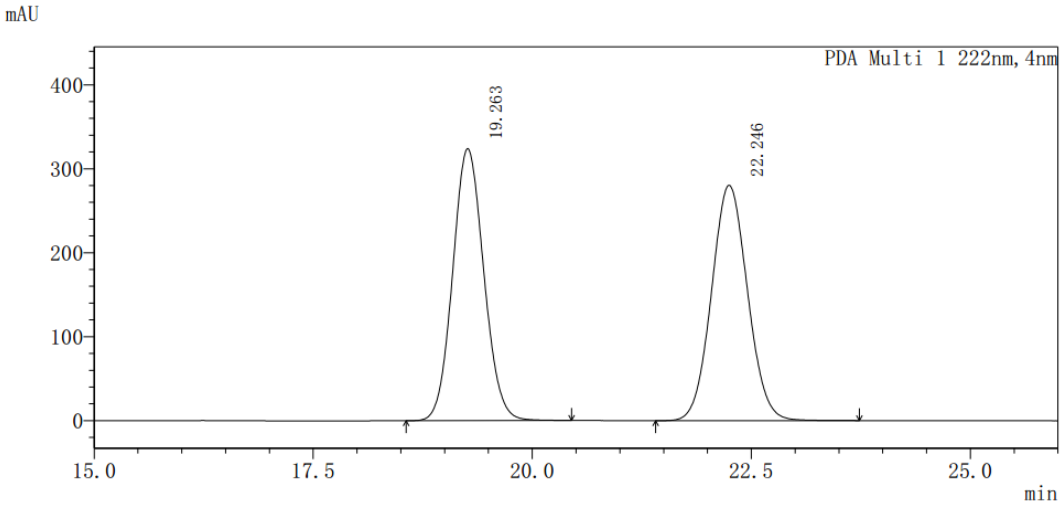
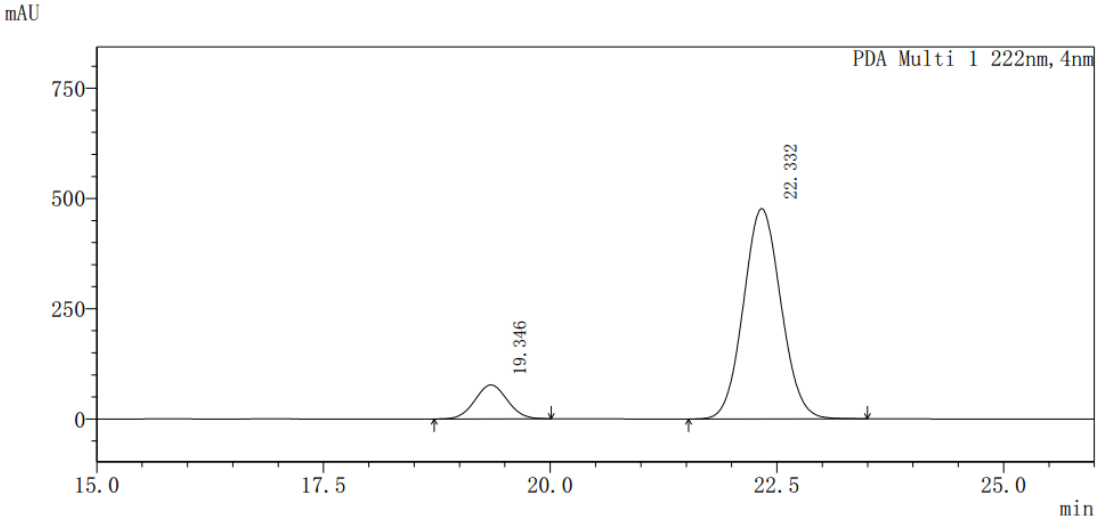


<Peak Results>

PDA Ch1 222nm

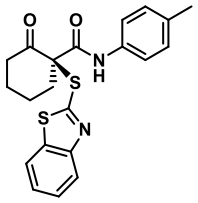
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.263	324067	8007448	49.954
2	22.246	280421	8022132	50.046



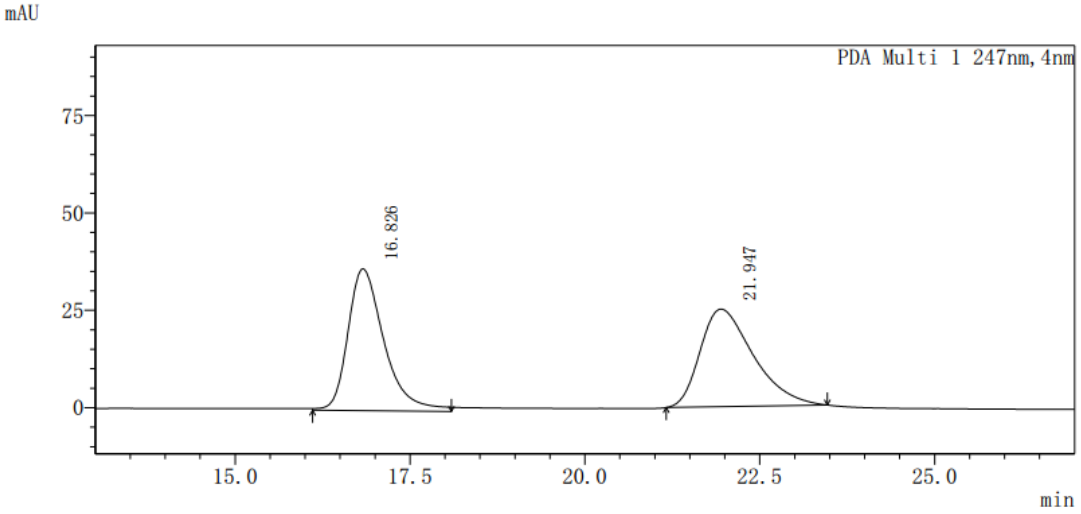
<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.346	76975	1917186	12.236
2	22.332	476831	13751831	87.764



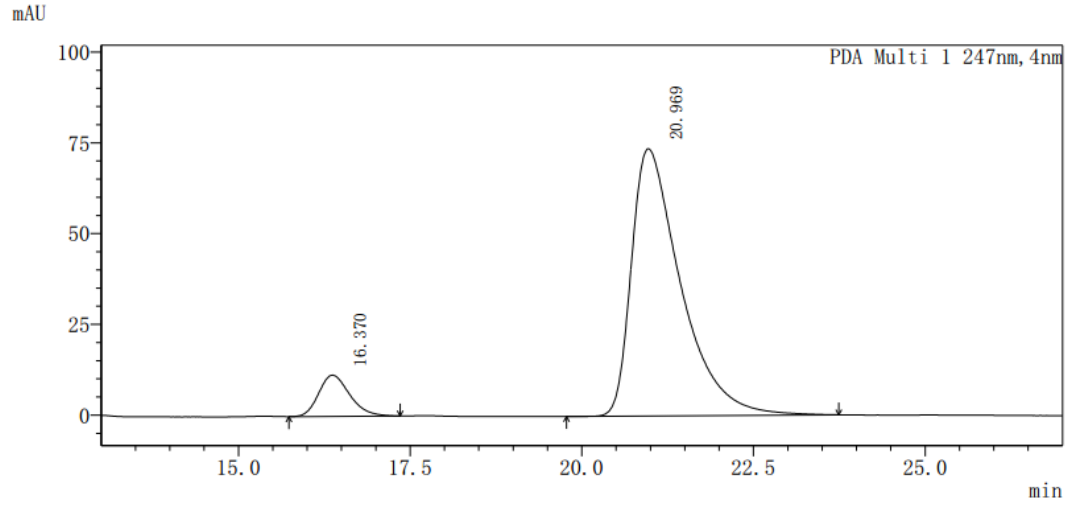
3ha



<Peak Results>

PDA Ch1 247nm

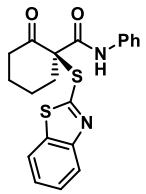
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.826	36411	1314109	49.754
2	21.947	25052	1327105	50.246



<Peak Results>

PDA Ch1 247nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.370	11358	357252	8.865
2	20.969	73608	3672454	91.135



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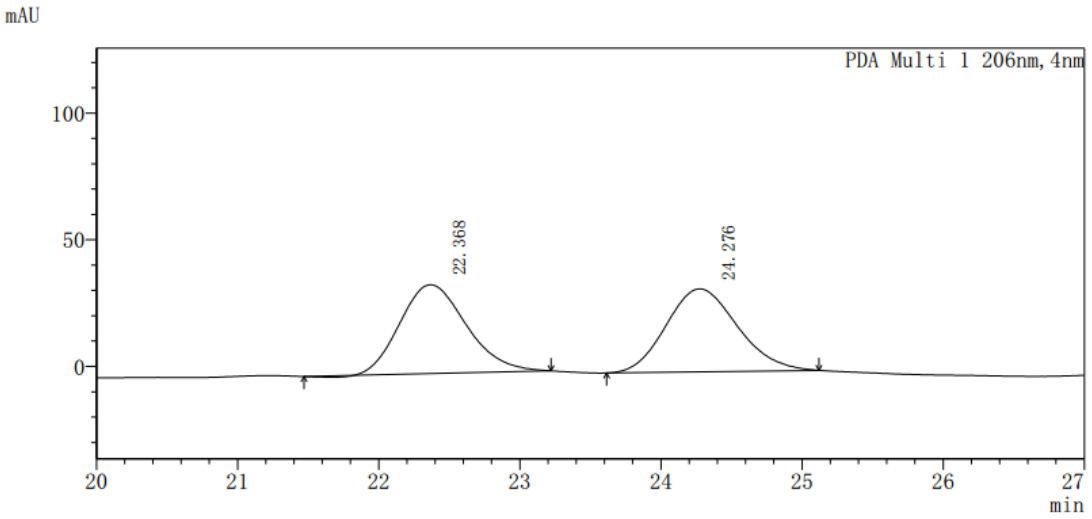
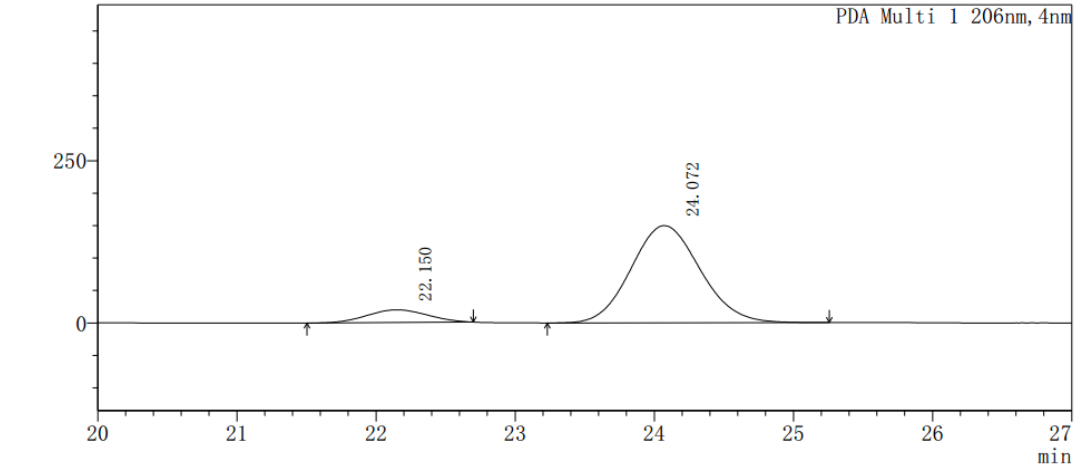


<Peak Results>

PDA Ch1 206nm

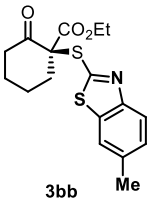
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	22.368	35111	1147582	49.923
2	24.276	32747	1151136	50.077



<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	22.150	19585	594575	10.288
2	24.072	149742	5184733	89.712



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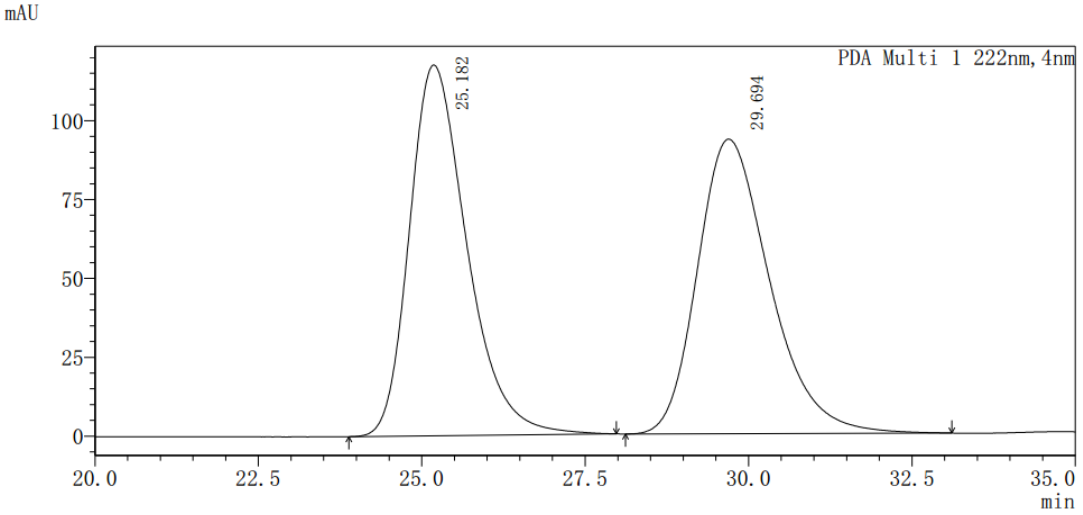
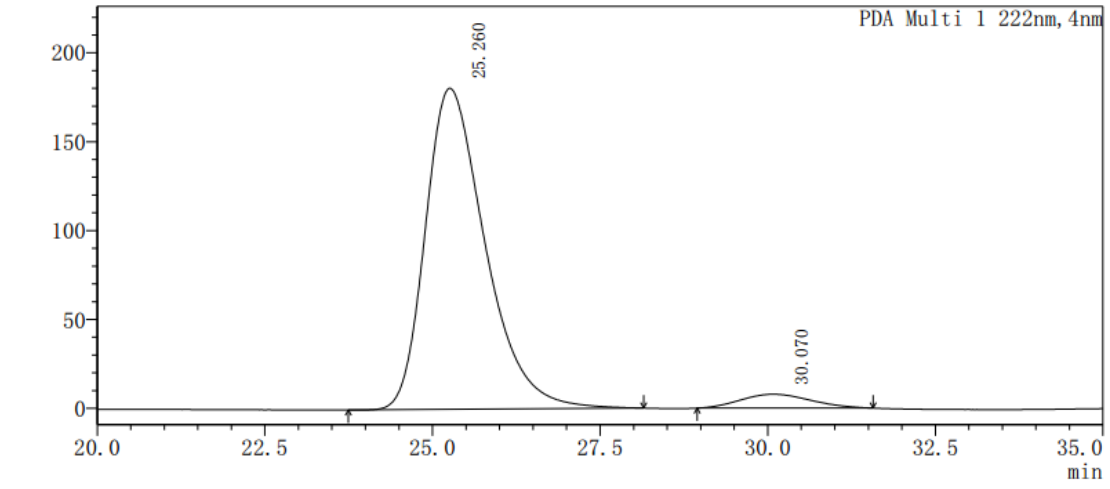


<Peak Results>

PDA Ch1 222nm

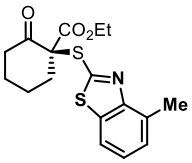
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.182	117549	7196131	50.004
2	29.694	93406	7195025	49.996



<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.260	180612	11218955	95.164
2	30.070	7804	570145	4.836



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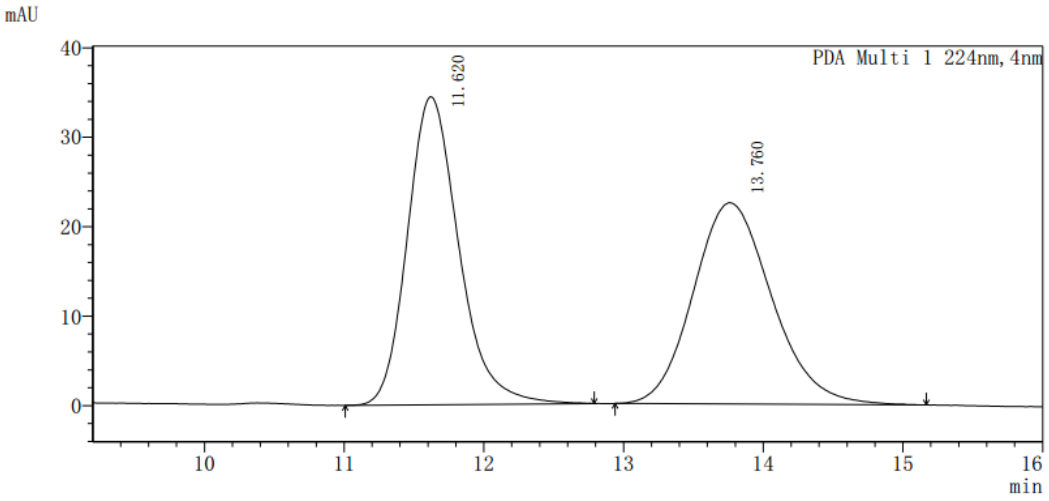
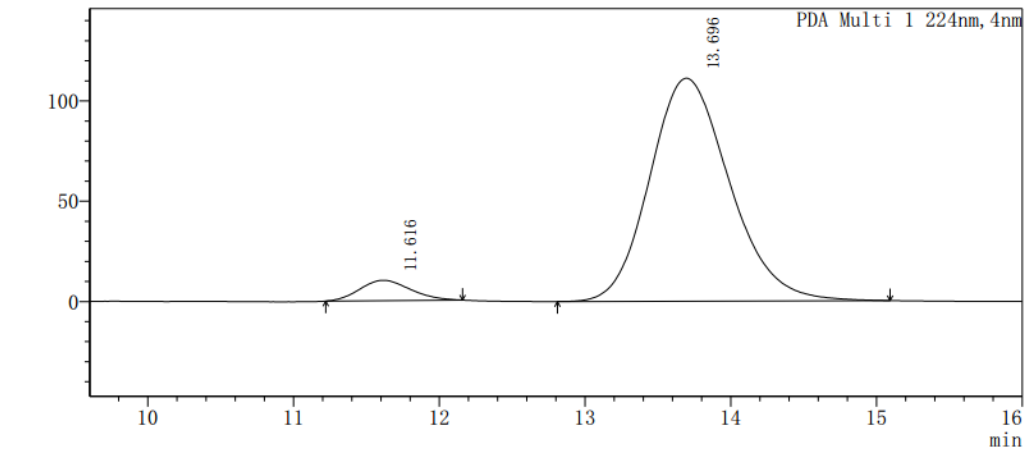


<Peak Results>

PDA Ch1 224nm

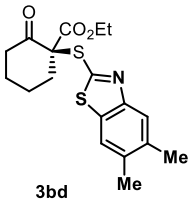
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.620	34424	881733	50.072
2	13.760	22497	879195	49.928



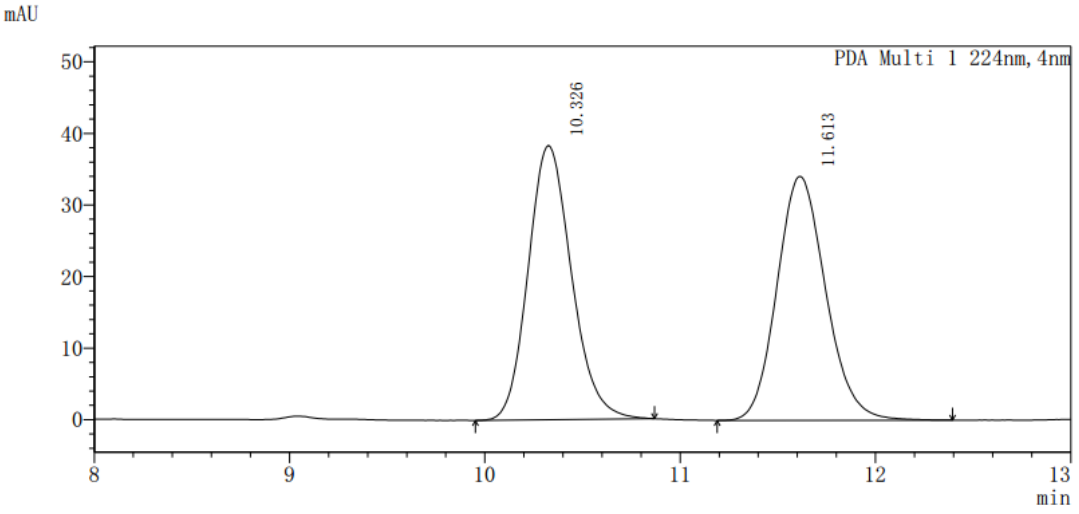
<Peak Results>

PDA Ch1 224nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.616	10143	245199	5.470
2	13.696	111117	4237590	94.530



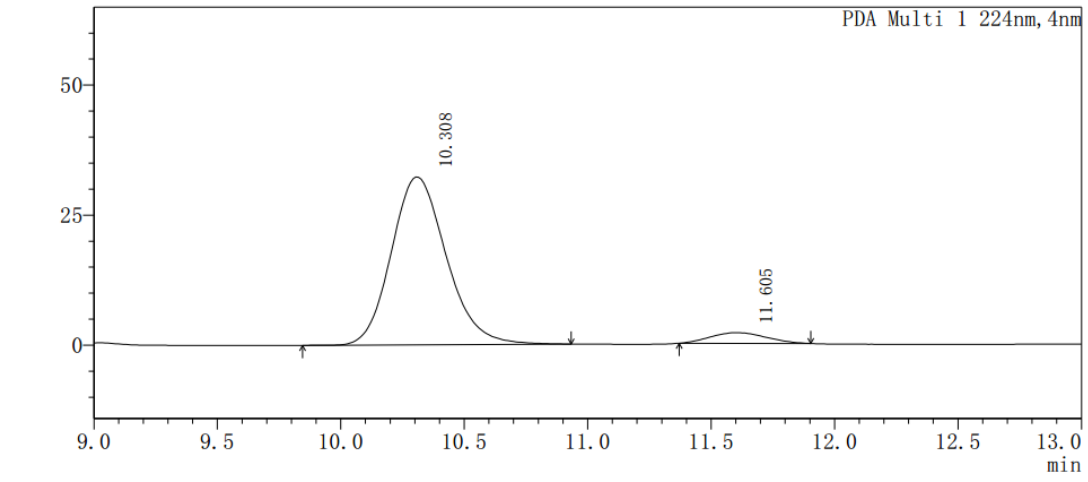
3bd



<Peak Results>

PDA Ch1 224nm

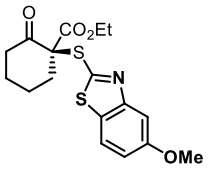
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.326	38322	591728	50.044
2	11.613	34078	590696	49.956



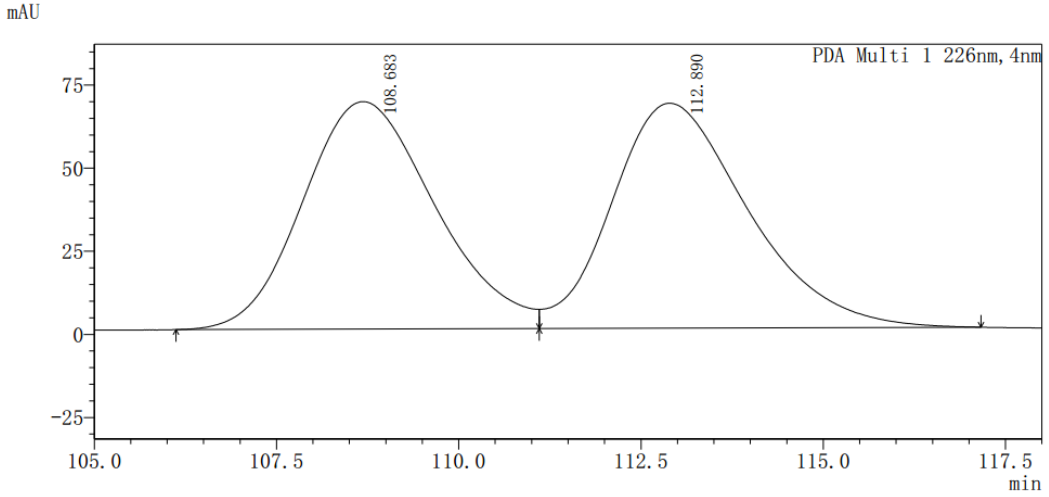
<Peak Results>

PDA Ch1 224nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.308	32256	500159	93.981
2	11.605	2056	32030	6.019



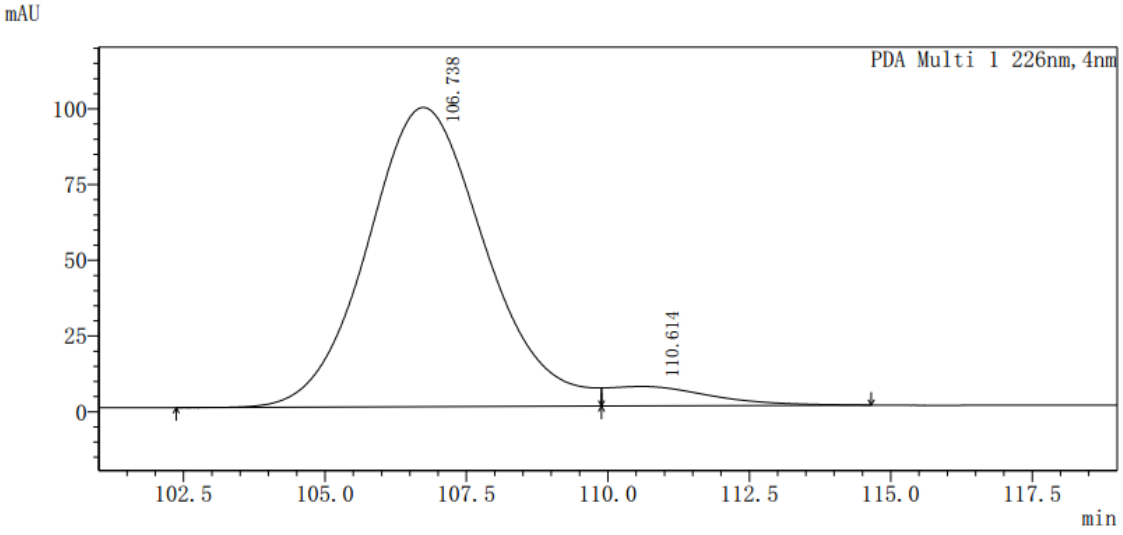
3be



<Peak Results>

PDA Ch1 226nm

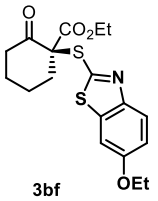
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	108.683	68443	8624886	49.536
2	112.890	67685	8786292	50.464



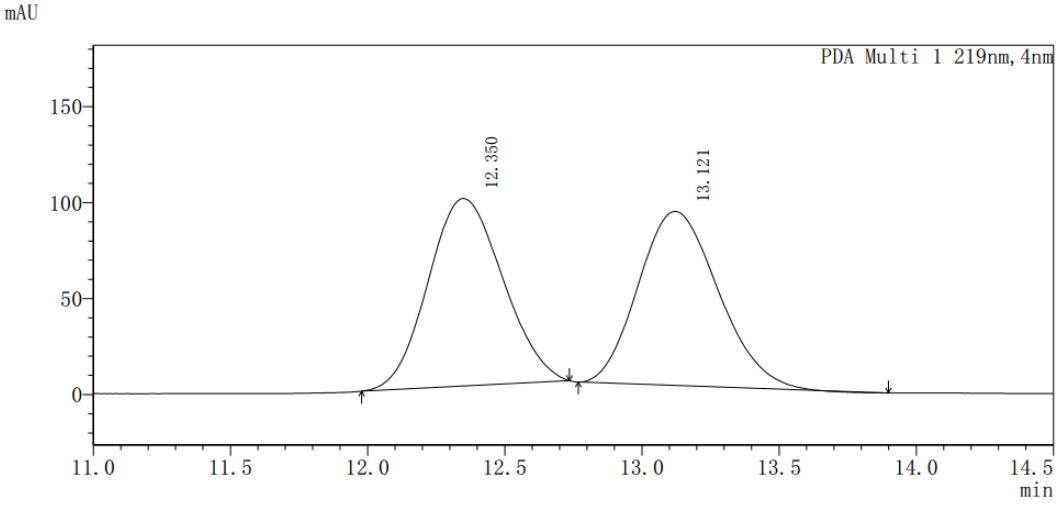
<Peak Results>

PDA Ch1 226nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	106.738	98803	14350802	94.701
2	110.614	6425	802974	5.299



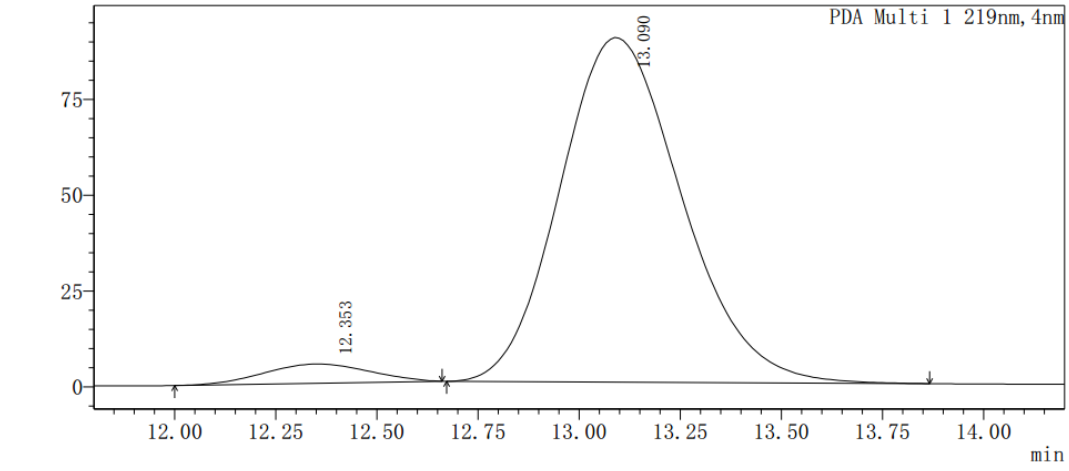
3bf



<Peak Results>

PDA Ch1 219nm

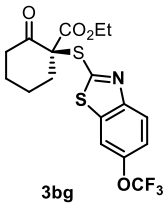
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.350	97793	1853583	50.247
2	13.121	90683	1835358	49.753



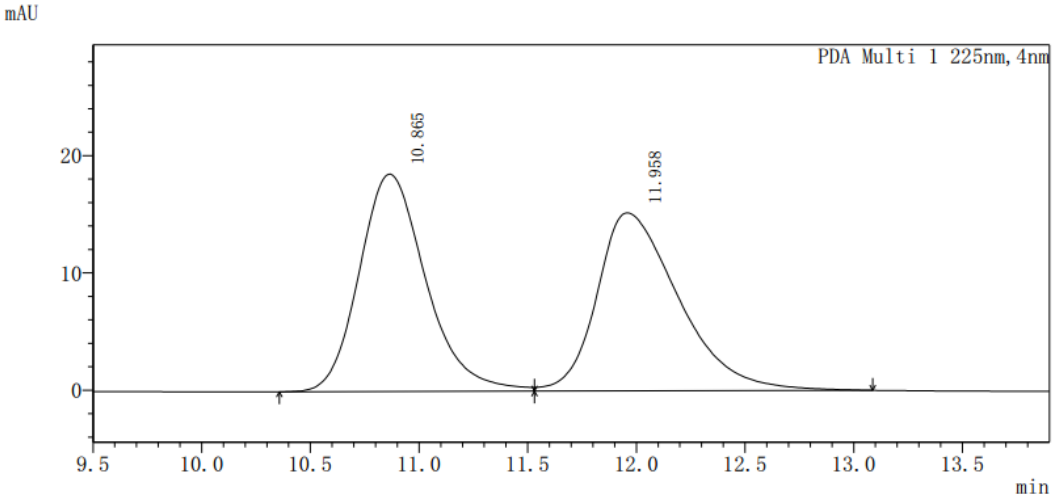
<Peak Results>

PDA Ch1 219nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.353	5017	91378	4.623
2	13.090	89904	1885362	95.377



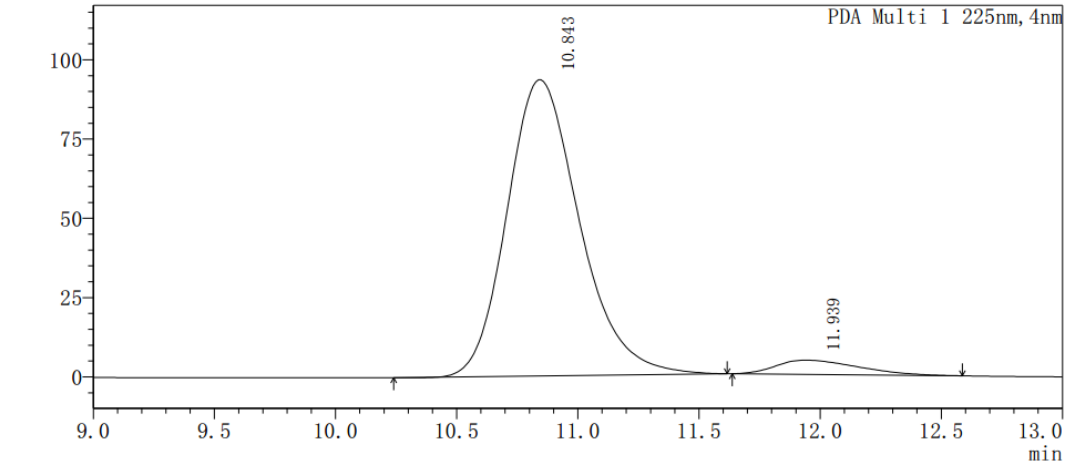
3bg



<Peak Results>

PDA Ch1 225nm

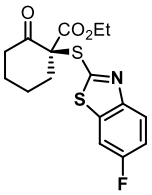
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.865	18537	395651	49.828
2	11.958	15187	398381	50.172



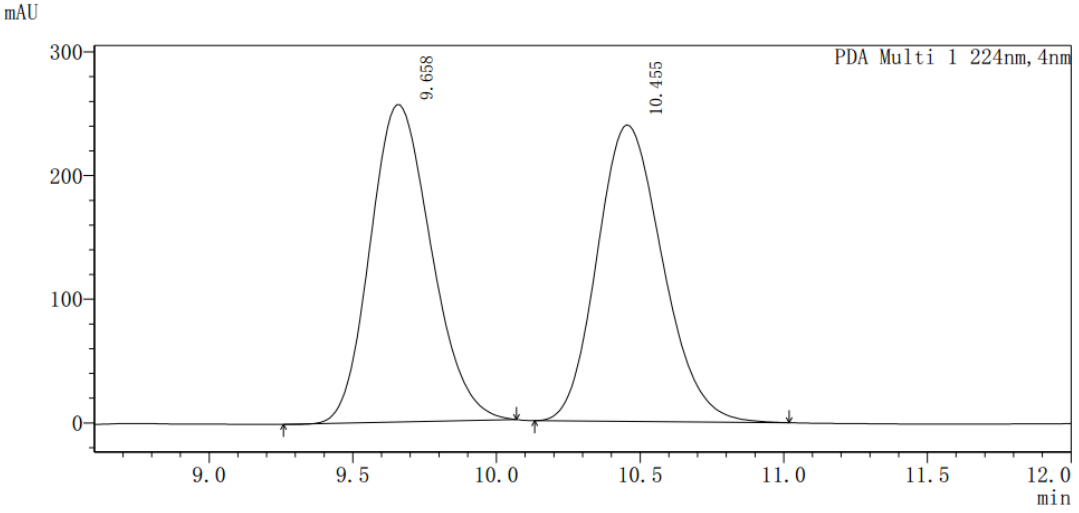
<Peak Results>

PDA Ch1 225nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.843	93413	1944909	94.857
2	11.939	4467	105457	5.143



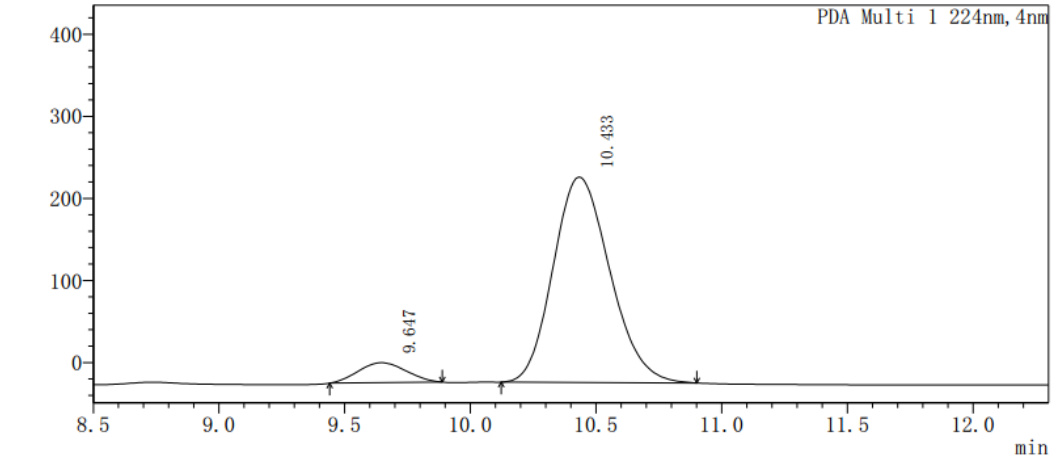
3bh



<Peak Results>

PDA Ch1 224nm

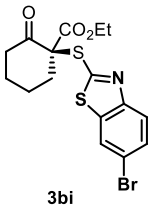
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.658	256717	3799393	49.989
2	10.455	239786	3801125	50.011



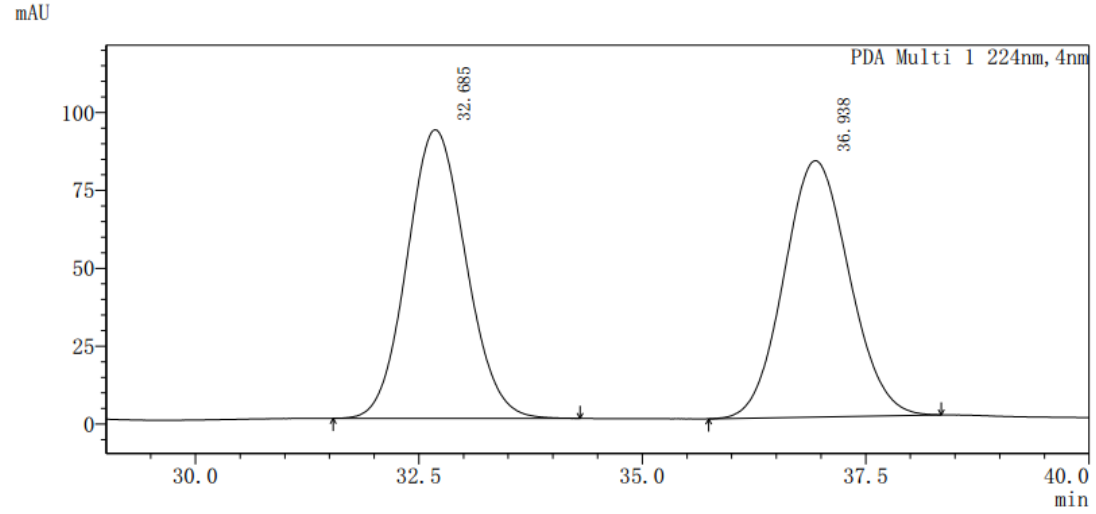
<Peak Results>

PDA Ch1 224nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.647	24278	321586	7.563
2	10.433	250416	3930638	92.437



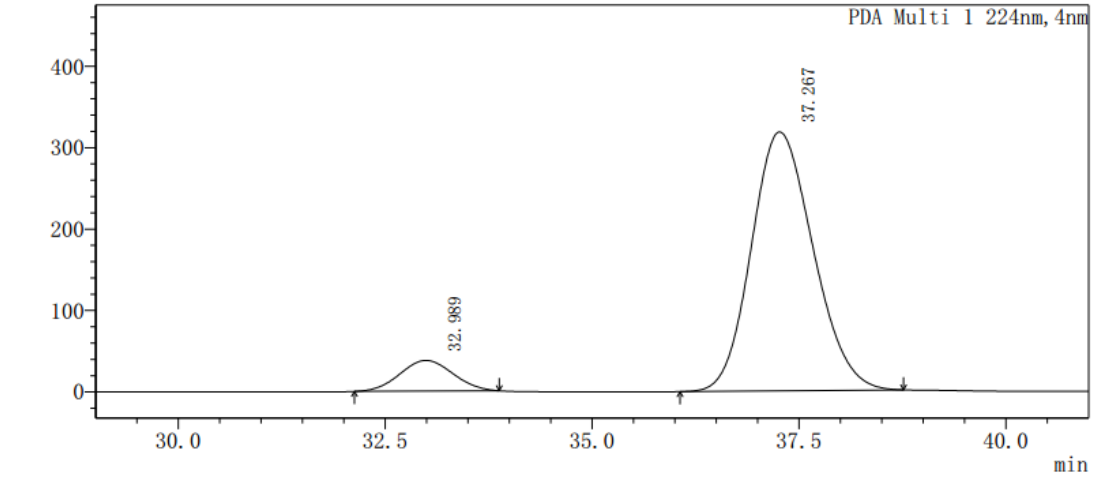
3bi



<Peak Results>

PDA Ch1 224nm

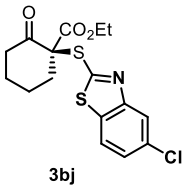
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.685	92609	4249499	50.380
2	36.938	82276	4185462	49.620



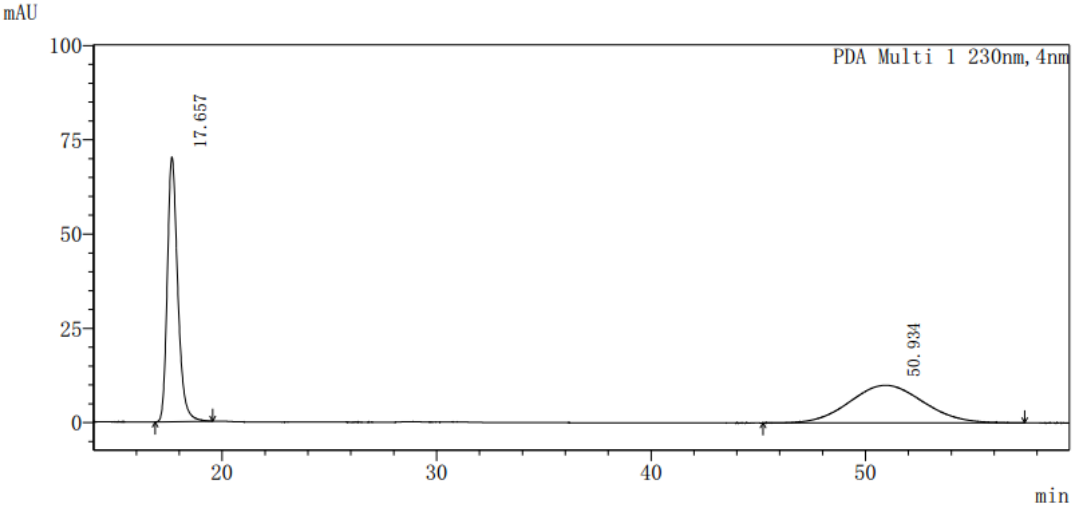
<Peak Results>

PDA Ch1 224nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.989	37689	1679381	9.217
2	37.267	317960	16541660	90.783



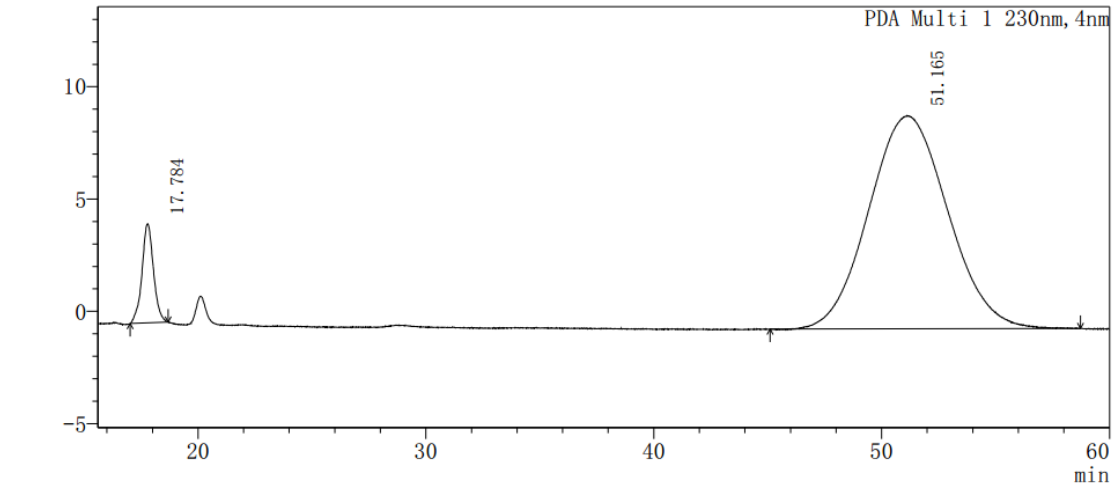
3bj



<Peak Results>

PDA Ch1 230nm

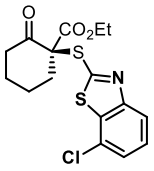
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.657	70179	2380349	49.872
2	50.934	9975	2392532	50.128



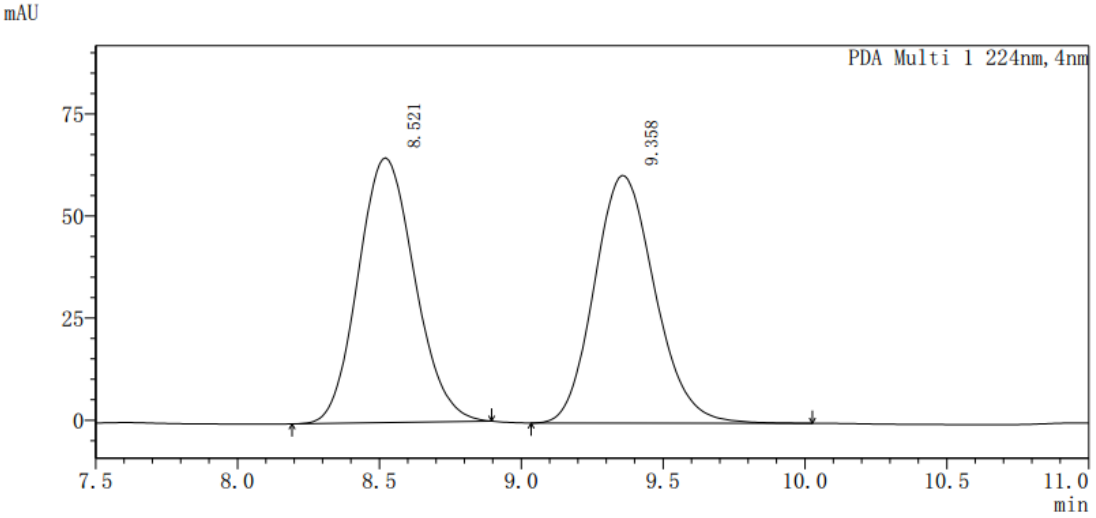
<Peak Results>

PDA Ch1 230nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.784	4408	155080	6.347
2	51.165	9487	2288394	93.653



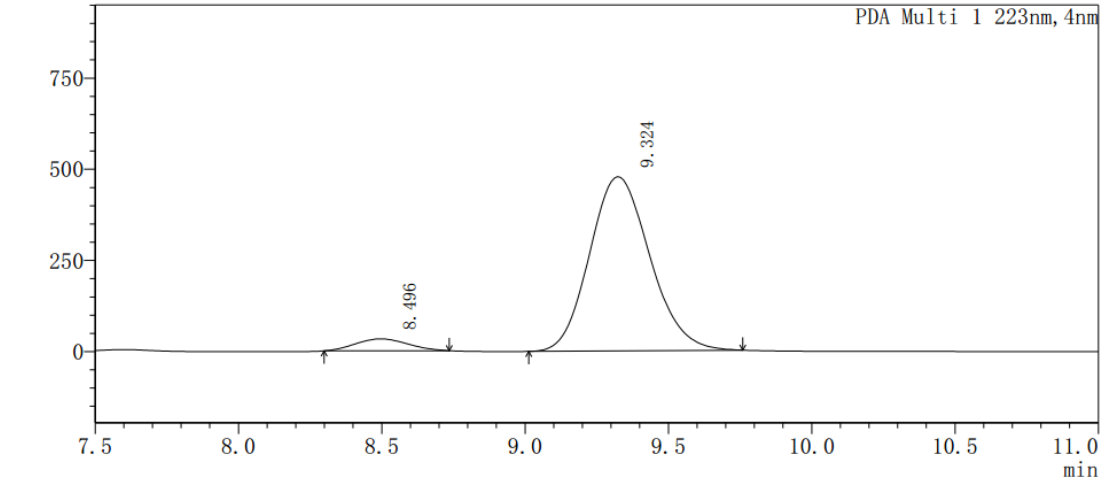
3bk



<Peak Results>

PDA Ch1 224nm

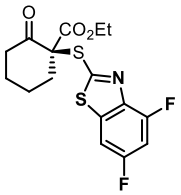
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.521	64875	900521	49.963
2	9.358	60646	901851	50.037



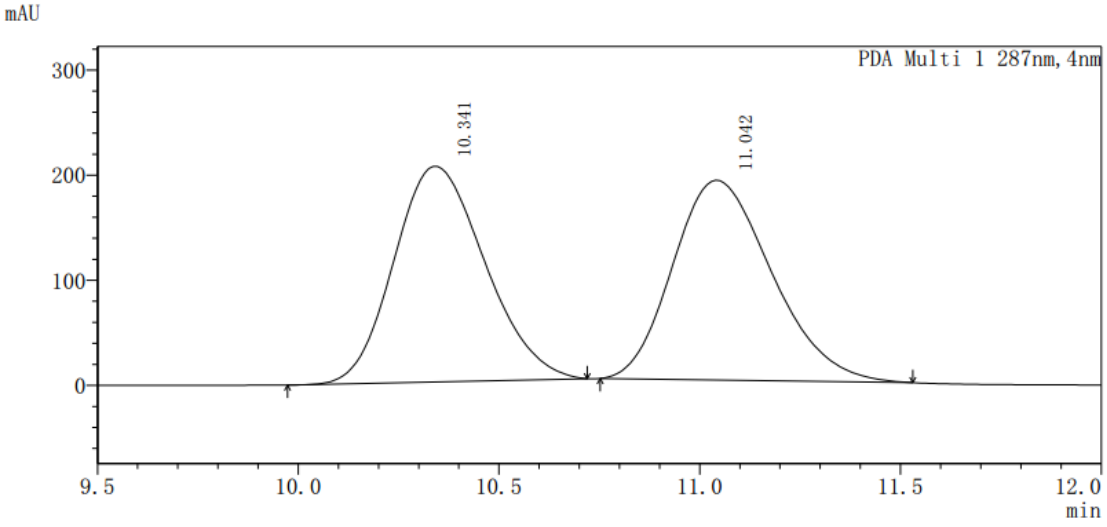
<Peak Results>

PDA Ch1 223nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.496	32614	414398	5.595
2	9.324	477723	6991934	94.405



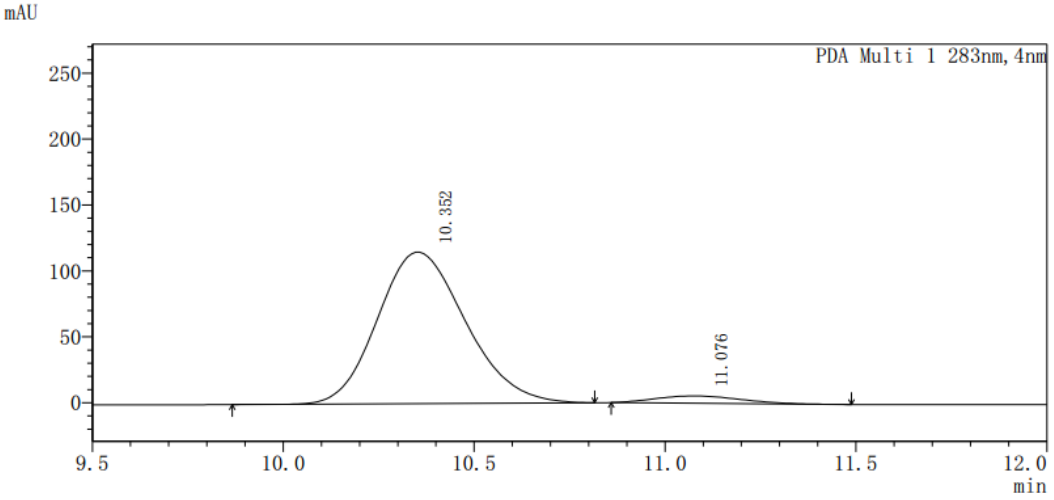
3bl



<Peak Results>

PDA Ch1 287nm

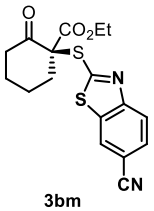
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.341	205020	3234859	49.809
2	11.042	190197	3259711	50.191



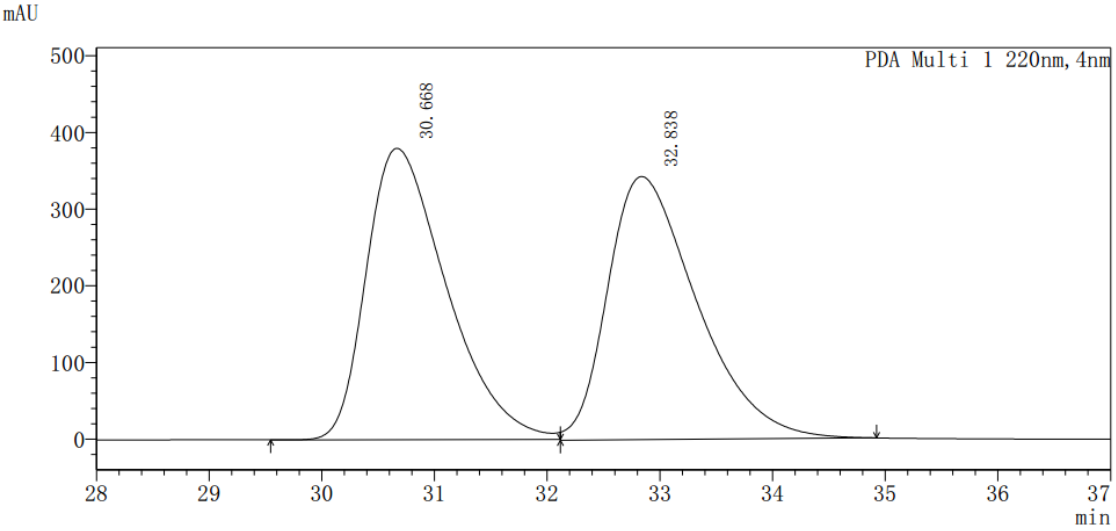
<Peak Results>

PDA Ch1 283nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.352	114877	1841517	95.578
2	11.076	5551	85200	4.422



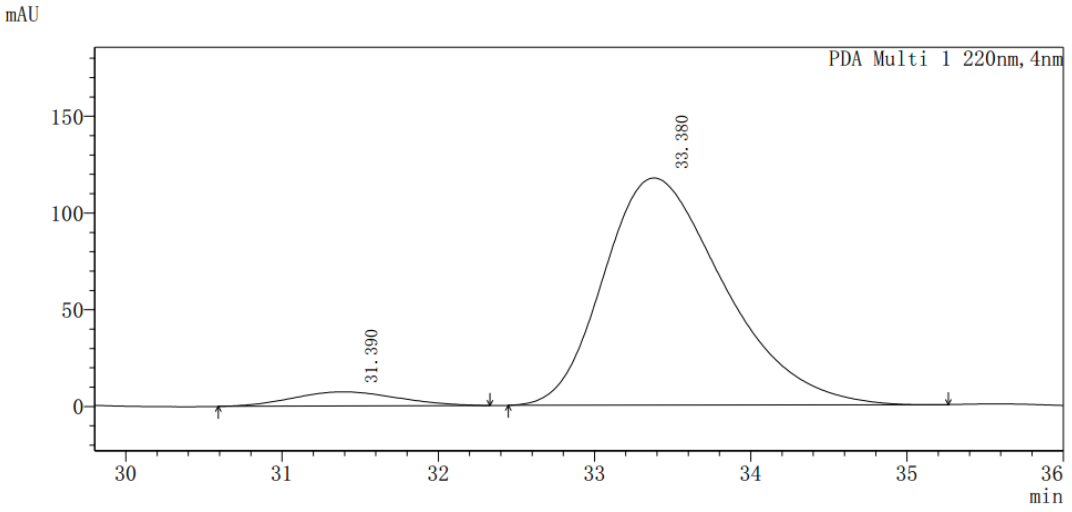
3bm



<Peak Results>

PDA Ch1 220nm

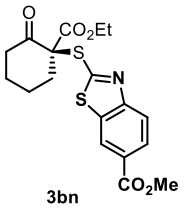
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	30.668	380149	18853336	49.967
2	32.838	343143	18878448	50.033



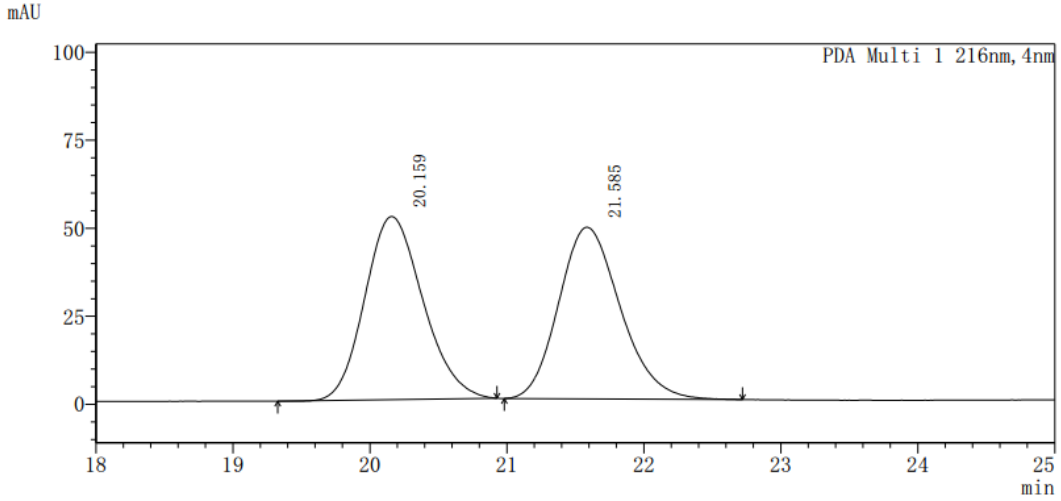
<Peak Results>

PDA Ch1 220nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.390	7330	341917	5.152
2	33.380	117412	6294566	94.848



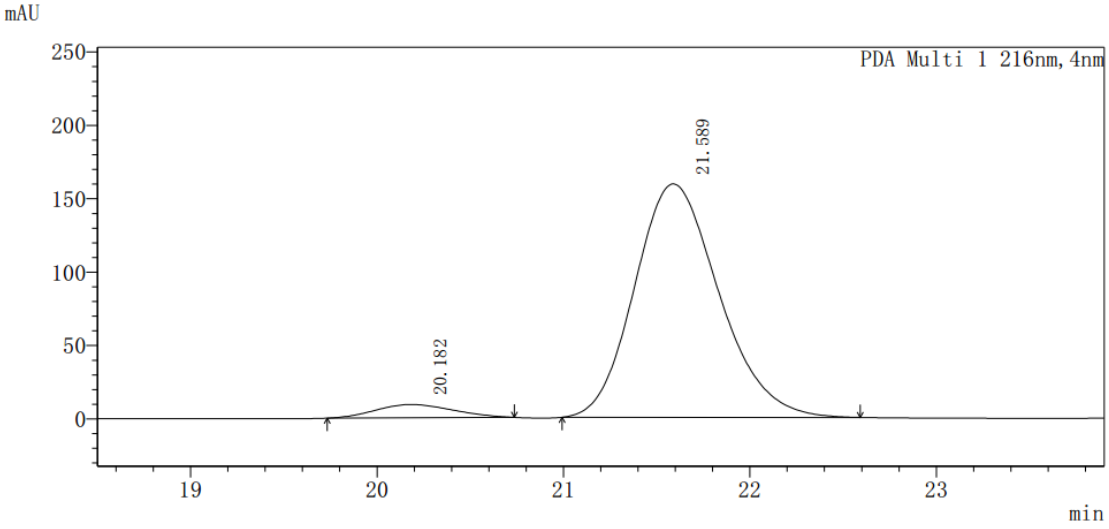
3bn



<Peak Results>

PDA Ch1 216nm

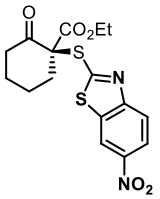
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.159	52023	1535761	50.161
2	21.585	48718	1525887	49.839



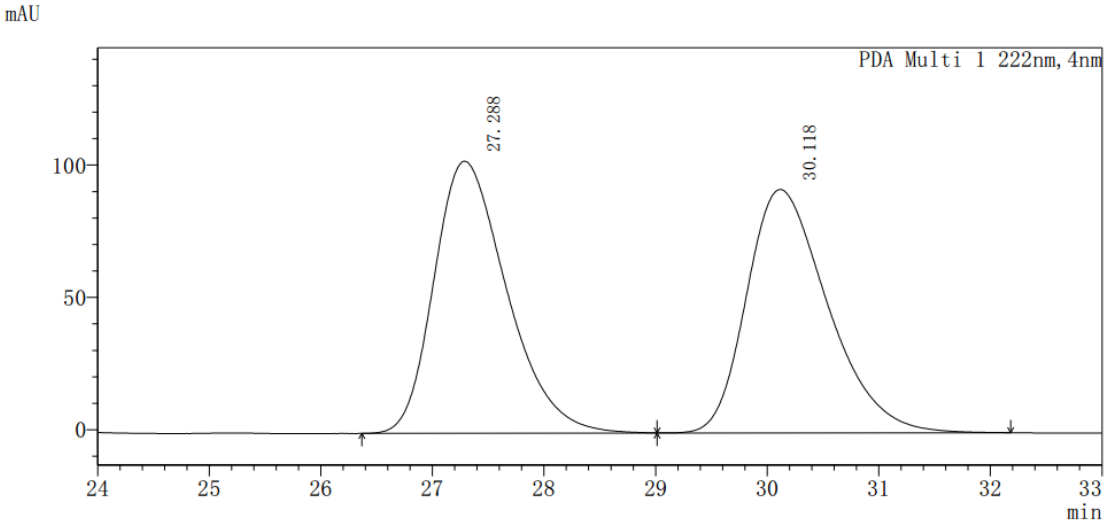
<Peak Results>

PDA Ch1 216nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.182	9085	260965	4.960
2	21.589	159076	5000591	95.040



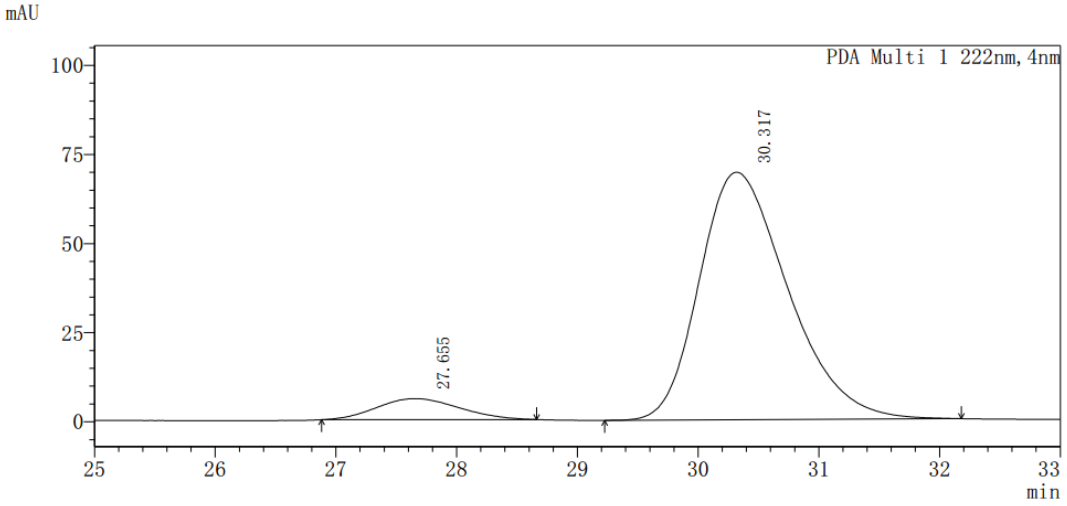
3bo



<Peak Results>

PDA Ch1 222nm

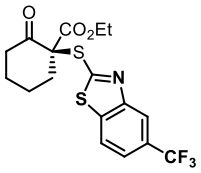
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.288	102836	4668741	50.097
2	30.118	91978	4650645	49.903



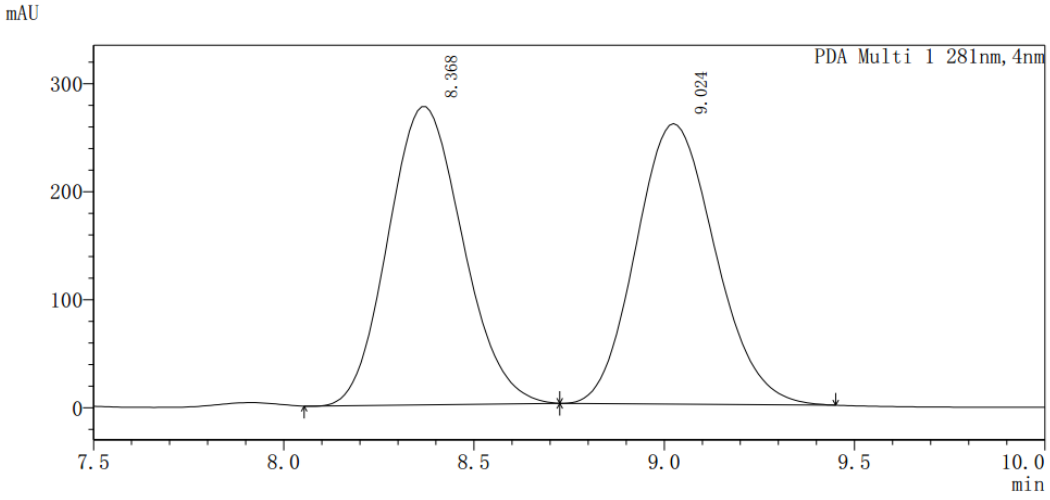
<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.655	5894	281736	7.375
2	30.317	69456	3538230	92.625



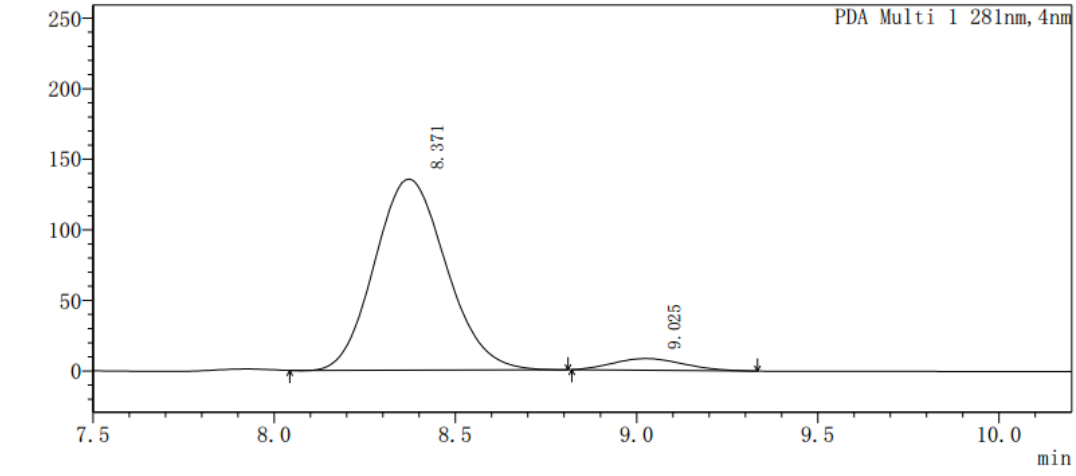
3bp



<Peak Results>

PDA Ch1 281nm

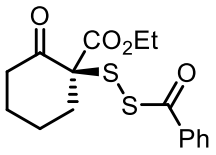
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.368	275968	3769841	50.036
2	9.024	259601	3764397	49.964

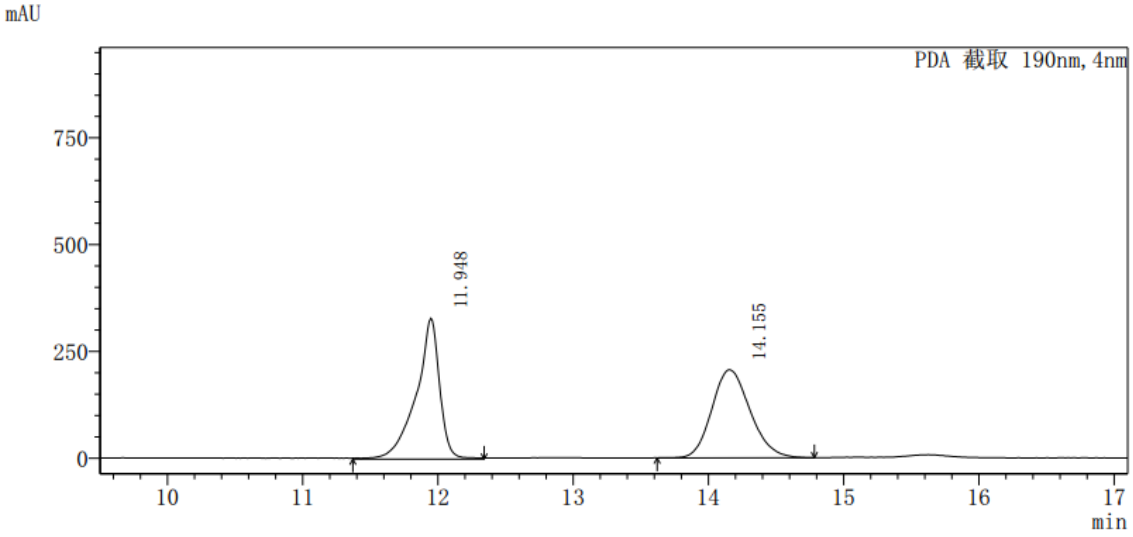


<Peak Results>

PDA Ch1 281nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.371	135518	1862480	94.354
2	9.025	8270	111441	5.646

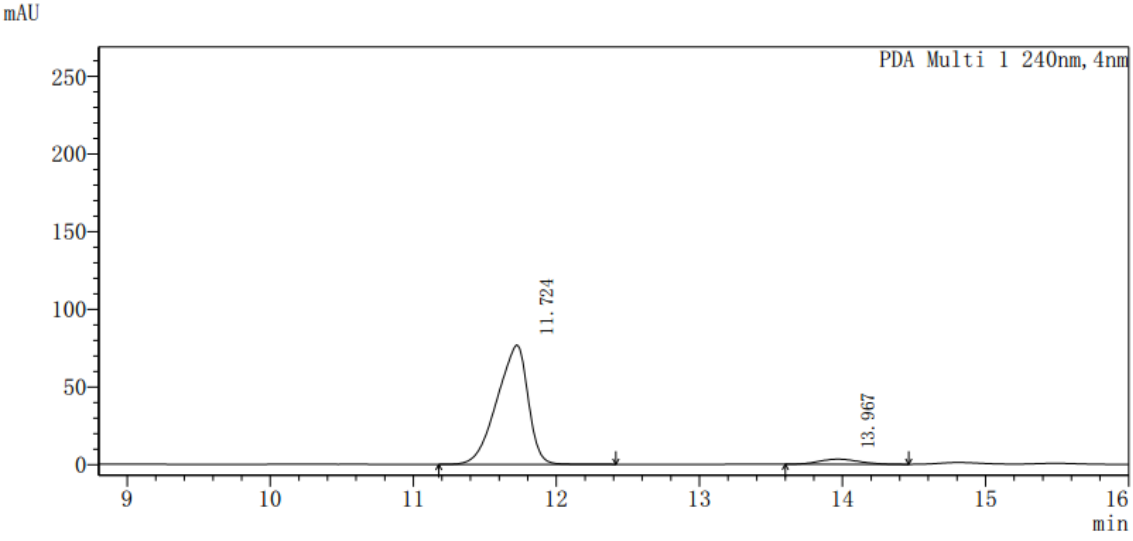




<Peak Results>

PDA Ch1 240nm

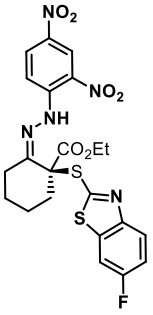
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.948	327069	3837623	49.442
2	14.156	202379	3924318	50.558



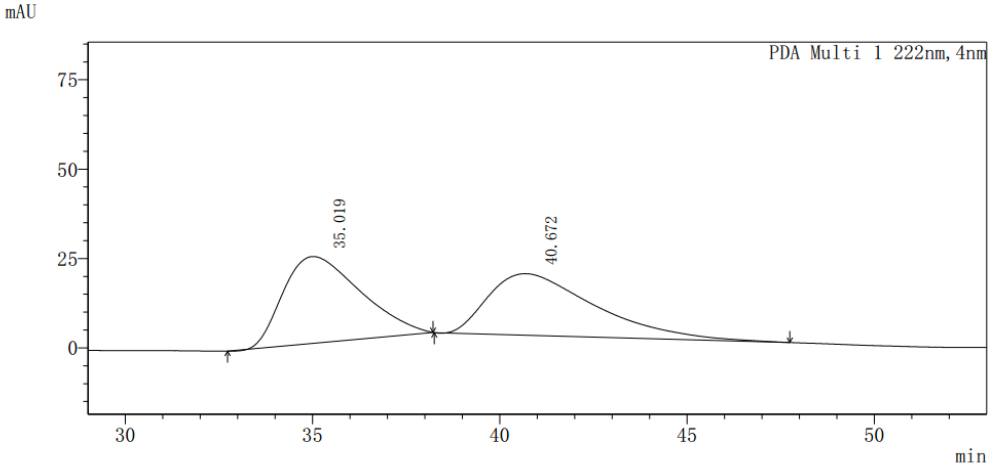
<Peak Results>

PDA Ch1 240nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.724	76791	1155570	94.837
2	13.967	3295	62912	5.163



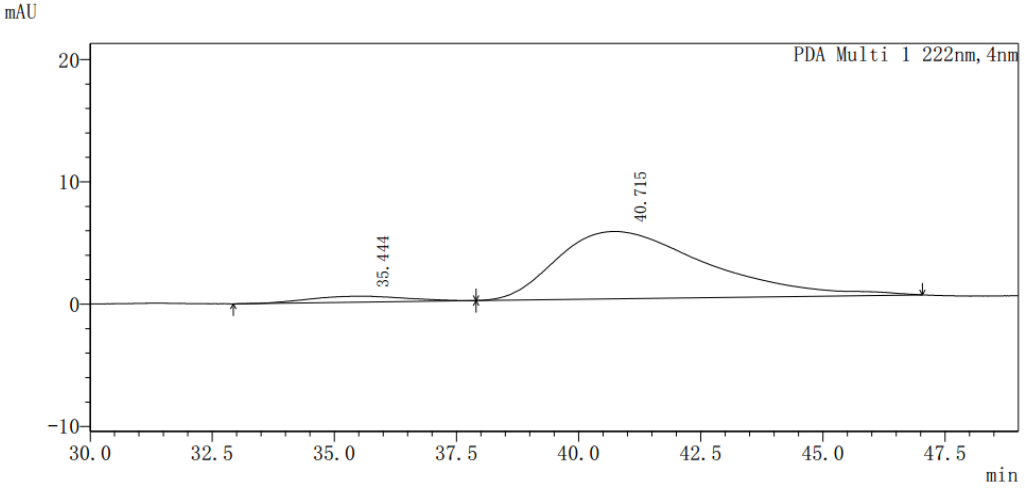
3bh-1



<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	35.019	24291	3477252	50.443
2	40.672	17200	3416223	49.557



<Peak Results>

PDA Ch1 222nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	35.444	489	65712	5.289
2	40.715	5505	1176757	94.711