Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Catalytic Enantioselective α-Sulfenylation of β-Ketocarbonyls by Chiral Primary Amine

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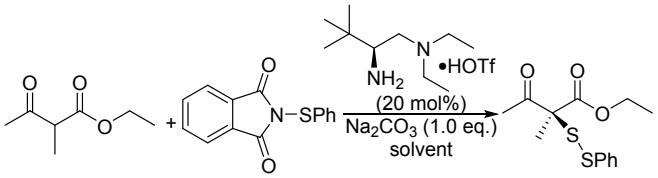
Supporting Imformation

General information: All commercial reagents were used without further purification unless otherwise noted. The corresponding β-Ketocarbonyls were prepared according to reported procedures.[1] NMR spectra were recorded on *Bruker AV 400* and *Bruker Avance 500* spectrometers. ^{1}H NMR spectra were obtained at 400 or 500 MHz in $CDCl_3$ unless otherwise noted. ^{13}C NMR spectra were obtained at 101 or 126 MHz using a proton-decoupled pulse sequence and are tabulated by observed peak. Chemical shifts were reported in parts per million (ppm) and referenced to 7.27 and 77.00 ppm respectively. Coupling constants were expressed in Hertz (Hz). The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad. ^{19}F spectra were obtained at 377 MHz using a proton-decoupled pulse sequence in the presence of fluorobenzene as an internal standard. High resolution mass spectra were obtained using electrospray ionization (ESI). The enantiomeric excesses were determined by HPLC analysis on Chiral Daicel Chiralpak OD-H, OJ-H, AS-H, AD-H or IC. Optical rotation were measured on a commercial polarimeter and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent).

Experimental section:

A) Optimization of reaction conditions

a) Screening of solvents[a]

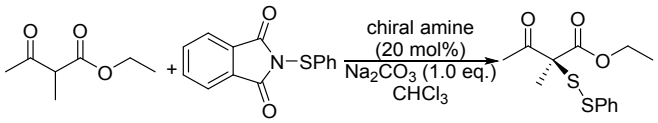


1a **2a** **3a**

Entry	Solvent	Yield[b]	*Ee*[c]
1	$CHCl_3$	**46%**	**53%**
2	MeCN	71%	35%
3	THF	68%	0
4	DCM	60%	51%
5	DCE	43%	50%
6	toluene	0	-
7	MTBE	14%	19%
8	Hexane	0	-
9	EA	70%	0
10	MeOH	0	-
11	EtOH	0	-
12	DMF	72%	0

[a]All reactions were carried out with 1.2 equivalents of *N*-(phenylthio)phthalimide **2a**, 1.0 equivalent of Na_2CO_3 and 20 mol% of amine catalyst **(II**/TfOH) respect to ethyl 2-methylacetoacetate **1a** (0.10 mmol) in 0.5 ml of solvents for 36 h unless otherwise noted. [b]Yields were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC on a chiral stationary phase.

b) Screening of primary amines[a]

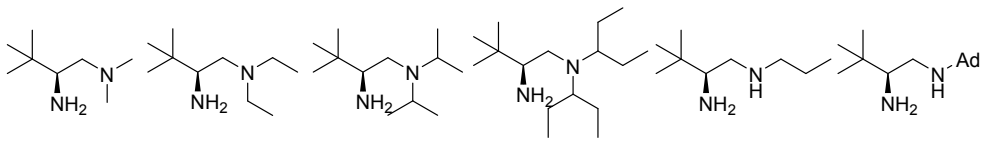


1a **2a** **3a**

Entry	Catalyst	Yield[b]	*Ee*[c]
1	**I**/TfOH	32%	9%
2	**II**/TfOH	62%	53%
3	**III**/TfOH	59%	89%
4	**IV/**TfOH	21%	82%
5	**V**/TfOH	20%	12%
6	**VI**/TfOH	42%	19%

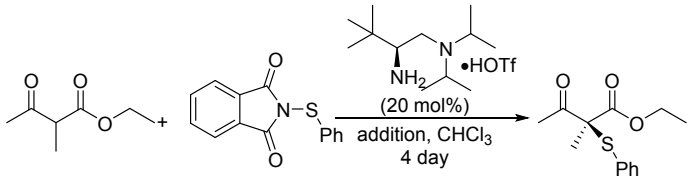
[a]All reactions were carried out with 1.2 equivalents of *N*-(phenylthio)phthalimide **2a**, 1.0 equivalent of Na_2CO_3 and 20 mol% of amine catalyst respect to ethyl 2-methylacetoacetate **1a** (0.10 mmol) in 0.5 ml of $CHCl_3$ for 68 h unless otherwise noted. [b]Yields were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC on a chiral stationary phase.

Chiral amines:



I II III IV V VI

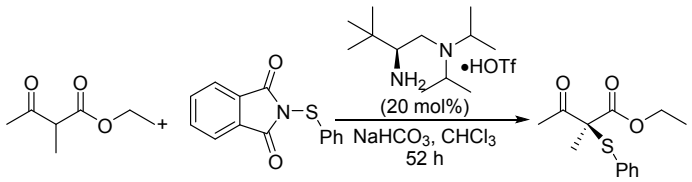
c) Screening of bases[a]



Entry	bases	Yield[b]	*Ee*[c]
1	$NaHCO_3$	**90%**	**93%**
2	TsONa	trace	-
3	KOAc	46%	72%
4	$KHCO_3$	59%	76%
5	K_2CO_3	90%	73%
6	$Na_3PO_4.12H_2O$	30%	55%
7	NaOAc	54%	89%
8	Na_2CO_3	80%	89%
9	Li_2CO_3	trace	-
10	LiOAc	trace	-

[a]All reactions were carried out with 1.2 equivalents of *N*-(phenylthio)phthalimide **2a**, 1.0 equivalent of bases and 20 mol% of amine catalyst **(III**/TfOH) respect to ethyl 2-methylacetoacetate **1a** (0.10 mmol) in 0.5 ml of $CHCl_3$ for 4 days unless otherwise noted. [b]Yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC on a chiral stationary phase.

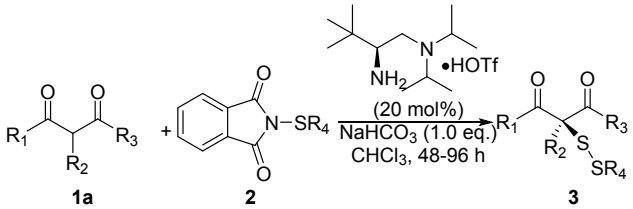
c) Screening of concentration[a]



Entry	c (mol/L)	Yield[b]	*Ee*[c]
1	0.20	33%	92%
2	0.33	50%	91%
3	0.50	**91%**	**93%**

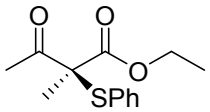
[a]All reactions were carried out with 1.2 equivalents of *N*-(phenylthio)phthalimide **2a**, 1.0 equivalents of $NaHCO_3$ and 20 mol% of amine catalyst **(III**/TfOH) respect to ethyl 2-methylacetoacetate **1a** (0.10 mmol) in $CHCl_3$ for 52 h unless otherwise noted. [b]Yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC on a chiral stationary phase.

B) General procedure for Sulfenylation reaction



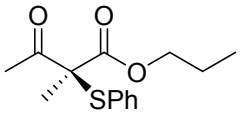
To a flame-dried tube equipped with a magnetic stir bar were added β-ketocarbonyl (**1**, 0.10 mmol), amine catalyst (**III**/HOTf, 7.0 mg, 0.02 mmol), Sulfenylation reagent (**2**, 0.12 mmol), and $NaHCO_3$ (8.4 mg, 0.10 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48-96 h, the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1 to 10:1) to give (*S*)-**3**.

C) Characterization data for new compounds:



3a

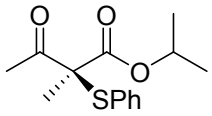
To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3a** (21.9 mg, 87%) as a colorless oil: IR (thin film, cm^{-1}) 2982, 2935, 1713, 1474, 1439, 1246, 1109, 1016, 752, 693; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2 H), 7.38 (d, *J* = 7.3 Hz, 1 H), 7.32 (t, *J* = 7.4 Hz, 2 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 2.37 (s, 3 H), 1.50 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 170.1, 137.1, 130.0, 129.5, 129.1, 65.9, 62.6, 26.2, 20.8, 14.1; HRMS (ESI) calcd for $C_{13}H_{16}O_3NaS^+$: 275.0712, found 275.0710; HPLC analysis: Daicel Chiralpak OD-H, flow rate = 0.5 ml/min, λ = 210 nm, hexane/iso-propanol = 97:3, (*S*)-**3a**: 93% *ee*; $[\alpha]_D^{25}$ = -55.7 (c = 1.4, CH_2Cl_2), retention time: 13.2 min (minor) and 13.8 min (major).



3b

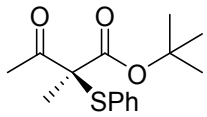
To a flame-dried tube equipped with a magnetic stir bar were added **1b** (15.8 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3b** (22.6 mg, 85%) as a colorless oil: IR (thin film, cm^{-1}) 2969, 2936, 1713, 1473, 1439, 1242, 1117, 967, 751, 692; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 4.21 – 4.06 (m, 2 H), 2.37 (s, 3 H), 1.73 – 1.60 (m, 2 H), 1.50 (s, 3 H), 0.94 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 170.1, 137.0, 130.0, 129.5, 129.1, 68.1, 65.9, 26.2, 21.9, 20.8, 10.4; HRMS (ESI) calcd for $C_{14}H_{18}O_3NaS^+$: 289.0869, found 289.0869; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol

= 70:30, (*S*)-**3b**: 90% *ee*; $[\alpha]_D^{25}$ = -51.4 (c = 1.00, CH_2Cl_2), retention time: 11.4 min (major) and 13.8 min (minor).



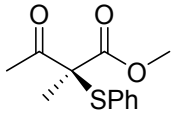
3c

To a flame-dried tube equipped with a magnetic stir bar were added **1c** (15.8 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3c** (22.1 mg, 83%) as a colorless oil: IR (thin film, cm^{-1}) 2982, 2934, 1711, 1473, 1439, 1374, 1249, 1099, 749, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 6.9, 5.5 Hz, 2 H), 7.37 (dd, J = 7.9, 1.9 Hz, 1 H), 7.31 (t, *J* = 7.3 Hz, 2 H), 5.11 (dt, *J* = 12.5, 6.3 Hz, 1 H), 2.37 (s, 3 H), 1.48 (s, 3 H), 1.27 (dd, *J* = 6.1, 4.9 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 169.5, 137.0, 129.9, 129.5, 129.1, 70.5, 66.0, 26.1, 21.6, 21.5, 20.7; HRMS (ESI) calcd for $C_{14}H_{18}O_3NaS^+$: 289.0869, found 289.0868; HPLC analysis: Daicel Chiralpak IC, flow rate = 0.5 ml/min, λ= 210 nm, hexane/*iso*-propanol = 97:3, (*S*)-**3c**: 97% *ee*; $[\alpha]_D^{25}$ = -60.8 (c = 0.95, CH_2Cl_2), retention time: 18.4 min (major) and 19.4 min (minor).



3d

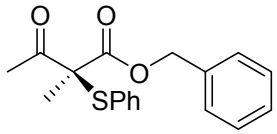
To a flame-dried tube equipped with a magnetic stir bar were added **1d** (17.2 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3d** (25.2 mg, 90%) as a colorless oil: IR (thin film, cm^{-1}) 2979, 2934, 1711, 1474, 1439, 1369, 1354, 1256, 1161, 1124, 850, 750, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 5.2, 3.1 Hz, 2 H), 7.38 – 7.33 (m, 1 H), 7.33 – 7.27 (m, 2 H), 2.38 (s, 3 H), 1.48 (s, 9 H), 1.45 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 169.0, 137.0, 129.8, 129.7, 129.0, 83.7, 66.6, 27.9, 26.1, 20.8; HRMS (ESI) calcd for $C_{15}H_{20}O_3NaS^+$: 303.1025, found 303.1026; HPLC analysis: Daicel Chiralpak IC, flow rate = 1 ml/min, λ = 210 nm, hexane/iso-propanol = 97:3, (*S*)-**3d**: 95% *ee*; $[\alpha]_D^{25}$ = -55.3 (c = 0.95, CH_2Cl_2), retention time: 7.3 min (major) and 7.9 min (minor); The spectroscopic data for **3d** matched those described in the literature; For the *S*-enantiomer 88% *ee*; $[\alpha]_D^{25}$ = -50.8 (c = 0.535, CH_2Cl_2) is reported in the literature. [2a]



3e

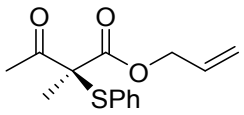
To a flame-dried tube equipped with a magnetic stir bar were added **1e** (13.0 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) NaHCO3 (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of CHCl3. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3e** (21.7 mg, 91%) as a colorless oil: IR (thin film, cm-

1) 2953, 1713, 1474, 1439, 1355, 1250, 1199, 974, 869, 752, 693; ^{1}H NMR (500 MHz, CDCl3) δ 7.44 – 7.40 (m, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 4.21 – 4.06 (m, 2 H), 2.37 (s, 3 H), 1.73 – 1.60 (m, 2 H), 1.50 (s, 3 H), 0.94 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, CDCl3) δ 199.5, 170.5, 137.0, 130.1, 129.4, 129.1, 65.8, 53.3, 26.1, 20.9; HRMS (ESI) calcd for $C_{12}H_{14}O_3NaS^+$: 261.0556, found 261.0556; HPLC analysis: Daicel Chiralpak IC, flow rate = 0.5 ml/min, λ = 210 nm, hexane/iso-propanol = 97:3, (S)-**3e**: 95% ee; $[\alpha]_D^{25}$ = -60.7 (c = 0.98, CH2Cl2), retention time: 24.4 min (major) and 25.5 min (minor).



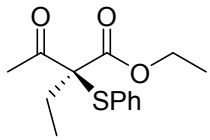
3f

To a flame-dried tube equipped with a magnetic stir bar were added **1f** (20.6 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3f** (30.8 mg, 98%) as a colorless oil: IR (thin film, cm^{-1}) 2933, 1712, 1473, 1455, 1439, 1354, 1235, 1115, 1093, 946, 750, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.2, 3.2 Hz, 8 H), 7.28 (dd, *J* = 10.5, 6.3 Hz, 2 H), 5.26 – 5.17 (m, 2 H), 2.27 (s, 3 H), 1.51 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 169.8, 137.1, 134.9, 130.0, 129.3, 129.1, 128.8, 128.7, 68.1, 65.9, 26.1, 20.8; HRMS (ESI) calcd for $C_{18}H_{18}O_3NaS^+$: 337.0869, found 337.0868; HPLC analysis: Daicel Chiralpak OD-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 95:5, (*S*)-**3f**: 87% *ee*; $[\alpha]_D^{25}$ = -59.9 (c = 1.25, CH_2Cl_2), retention time: 10.6 min (minor) and 11.5 min (major); The spectroscopic data for **3f** matched those described in the literature.[2b]



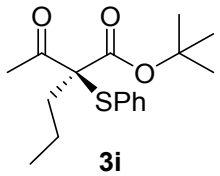
3g

To a flame-dried tube equipped with a magnetic stir bar were added **1g** (15.6 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3g** (25.1 mg, 95%) as a colorless oil: IR (thin film, cm^{-1}) 2935, 1713, 1474, 1439, 1355, 1238, 1118, 1093, 940, 750, 692; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.5, 7.3 Hz, 2 H), 7.39 – 7.34 (m, 1 H), 7.32 (t, *J* = 7.4 Hz, 2 H), 5.95 – 5.82 (m, 1 H), 5.37 (dd, *J* = 17.2, 1.2 Hz, 1 H), 5.29 (dd, *J* = 10.4, 0.8 Hz, 1 H), 4.68 (d, *J* = 5.9 Hz, 2 H), 2.37 (s, 3 H), 1.51 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 169.8, 137.1, 131.1, 130.1, 129.4, 129.1, 119.8, 67.0, 65.9, 26.2, 20.9; HRMS (ESI) calcd for $C_{14}H_{16}O_3NaS^+$: 287.0712, found 287.0716; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3g**: 89% *ee*; $[\alpha]_D^{25}$ = -58.4 (c = 1.15, CH_2Cl_2), retention time: 13.5 min (major) and 16.6 min (minor).



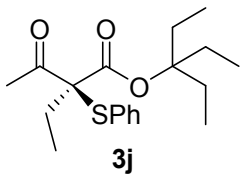
3h

To a flame-dried tube equipped with a magnetic stir bar were added **1h** (15.8 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 96 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3h** (18.9 mg, 71%) as a colorless oil: IR (thin film, cm^{-1}) 2974, 2923, 1710, 1439, 1382, 1354, 1281, 1229, 1183, 1126, 1024, 751, 692; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.1, 5.0 Hz, 3 H), 7.33 – 7.26 (m, 2 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 2.34 (s, 3 H), 1.94 (dq, *J* = 14.8, 7.4 Hz, 1 H), 1.74 (dq, *J* = 14.8, 7.4 Hz, 1 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.00 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 169.2, 136.7, 129.9, 129.3, 129.1, 72.0, 62.4, 26.5, 25.1, 14.2, 8.6; HRMS (ESI) calcd for $C_{14}H_{18}O_3NaS^+$: 289.0869, found 289.0871; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3h**: 92% *ee*; $[\alpha]_D^{25}$ = -35.8 (c = 0.55, CH_2Cl_2), retention time: 9.9 min (major) and 13.0 min (minor).



3i

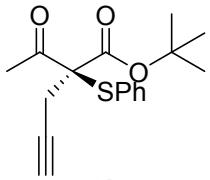
To a flame-dried tube equipped with a magnetic stir bar were added **1i** (20.0 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 96 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3i** (22.2 mg, 72%) as a colorless oil: IR (thin film, cm^{-1}) 2962, 2932, 2873, 1709, 1489, 1417, 1369, 1354, 1339, 1295, 1228, 1155, 1127, 1025, 837, 749, 693; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 3 H), 7.33 – 7.27 (m, 2 H), 2.37 (s, 3 H), 1.81 (ddd, *J* = 14.0, 12.2, 4.3 Hz, 1 H), 1.74 – 1.63 (m, 1 H), 1.61 – 1.51 (m, 2 H), 1.49 (s, 9 H), 1.32 – 1.24 (m, 1 H), 0.91 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 168.2, 136.7, 129.8, 129.7, 129.1, 83.7, 72.0, 33.7, 28.0, 26.3, 17.5, 14.2; HRMS (ESI) calcd for $C_{17}H_{24}O_3NaS^+$: 331.1338, found 331.1339; HPLC analysis: Daicel Chiralpak IC, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 97:3, (*S*)-**3i**: 95% *ee*; $[\alpha]_D^{25}$ = -41.7 (c = 0.81, CH_2Cl_2), retention time: 6.2 min (major) and 6.8 min (minor).



3j

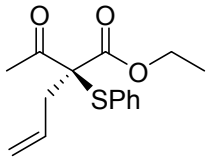
To a flame-dried tube equipped with a magnetic stir bar were added **1j** (22.8 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 96 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3j** (22.6 mg, 82%) as a colorless oil: IR (thin film, cm^{-1}) 2972, 2936, 2882, 1709, 1457, 1439, 1353, 1328, 1279, 1236, 1184, 1123, 1025, 869, 816, 750, 692; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3 H), 7.29 (t, *J* = 7.3 Hz, 2 H), 2.42 (s, 3 H), 1.97 – 1.83 (m, 7 H), 1.70 (dq, *J* = 14.9, 7.5 Hz, 1 H), 1.04 (t, *J* = 7.4 Hz, 3 H), 0.88 (t, *J* = 7.5 Hz, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 167.8, 136.4, 129.8, 129.7, 129.1, 92.7, 72.8, 27.3, 27.0, 25.2, 8.8, 8.0; HRMS (ESI) calcd for $C_{19}H_{28}O_3NaS^+$: 359.1651, found 359.1653; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1

ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3j**: 96% *ee*; $[\alpha]_D^{25}$ = -23.3 (c = 0.90, CH_2Cl_2), retention time: 7.2 min (major) and 11.9 min (minor).



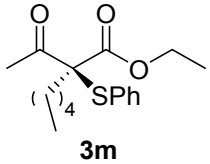
3k

To a flame-dried tube equipped with a magnetic stir bar were added **1k** (19.6 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 96 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3k** (16.4 mg, 54%) as a colorless oil: IR (thin film, cm^{-1}) 3285, 2979, 2930, 1734, 1712, 1369, 1310, 1258, 1147, 839, 753, 693, 647; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2 H), 7.40 (t, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.5 Hz, 2 H), 2.73 (dd, *J* = 17.7, 2.6 Hz, 1 H), 2.44 (d, *J* = 2.7 Hz, 1 H), 2.43 (s, 3 H), 2.41 (d, *J* = 2.6 Hz, 1 H), 2.18 (t, *J* = 2.6 Hz, 1 H), 1.52 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 166.7, 137.3, 130.4, 129.3, 128.7, 84.4, 79.17, 72.3, 70.1, 27.9, 25.8, 23.2; HRMS (ESI) calcd for $C_{17}H_{20}O_3NaS^+$: 327.1025, found 327.1027; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 90:10, (*S*)-**3k**: 82% *ee*; $[\alpha]_D^{25}$ = -40.6 (c = 0.68, CH_2Cl_2), retention time: 10.4 min (major) and 20.4 min (minor).



3l

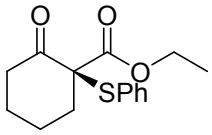
To a flame-dried tube equipped with a magnetic stir bar were added **1l** (17.0 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 96 h. Then, the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3l** (16.7 mg, 60%) as a colorless oil: IR (thin film, cm^{-1}) 2921, 2850, 1734, 1711, 1437, 1353, 1257, 1212, 1178, 1126, 1025, 922, 751, 692; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 4.21 – 4.06 (m, 2 H), 2.37 (s, 3 H), 1.73 – 1.60 (m, 2 H), 1.50 (s, 3 H), 0.94 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 170.1, 137.0, 123.0, 129.5, 129.1, 79.17 68.1, 65.9, 26.2, 21.9, 20.8, 10.4; HRMS (ESI) calcd for $C_{15}H_{18}O_3NaS^+$: 301.0869, found 301.0872; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 90:10, (*S*)-**3l**: 84% *ee*; $[\alpha]_D^{25}$ = -76.7 (c = 0.28, CH_2Cl_2), retention time: 12.1 min (major) and 16.6 min (minor).



3m

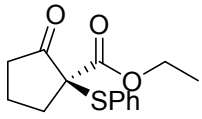
To a flame-dried tube equipped with a magnetic stir bar were added **1m** (20.2 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12

mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 96 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3m** (19.7 mg, 64%) as a colorless oil: IR (thin film, cm^{-1}) 2957, 2929, 2859, 1740, 1714, 1467, 1439, 1356, 1232, 1177, 1025, 751, 693; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 9.8, 4.4 Hz, 3 H), 7.31 (dd, *J* = 9.2, 5.7 Hz, 2 H), 4.34 – 4.15 (m, 2 H), 2.34 (s, 3 H), 1.94 – 1.80 (m, 1 H), 1.71 – 1.52 (m, 2 H), 1.37 – 1.16 (m, 8 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 169.3, 136.8, 129.9, 129.4, 129.1, 71.4, 62.4, 31.9, 31.80, 26.4, 23.8, 22.5, 14.2, 14.1; HRMS (ESI) calcd for $C_{17}H_{24}O_3NaS^+$: 331.1338, found 331.1340; HPLC analysis: Daicel Chiralpak IC, flow rate = 0.5 ml/min, λ= 210 nm, hexane/iso-propanol = 97:3, (*S*)-**3m**: 96% *ee*; $[\alpha]_D^{25}$ = -37.0 (c = 0.46, CH_2Cl_2), retention time: 29.9 min (major) and 30.1 min (minor).



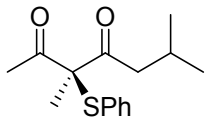
3n

To a flame-dried tube equipped with a magnetic stir bar were added **1n** (17.0 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 72 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3n** (18.4 mg, 66%) as a colorless oil: IR (thin film, cm^{-1}) 2937, 2865, 1716, 1473, 1439, 1237, 1203, 1125, 1071, 1023, 755, 703, 692; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 2 H), 7.37 (t, *J* = 7.3 Hz, 1 H), 7.30 (t, *J* = 7.4 Hz, 2 H), 4.24 – 4.02 (m, 2 H), 2.67 (dt, *J* = 13.9, 3.7 Hz, 1 H), 2.53 – 2.34 (m, 2 H), 2.06 – 1.92 (m, 1 H), 1.90 – 1.66 (m, 3 H), 1.63 – 1.48 (m, 1 H), 1.20 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 168.6, 137.3, 131.1, 129.8, 129.7, 129.5, 128.8, 67.7, 62.1, 41.0, 37.6, 27.2, 23.1, 14.1; HRMS (ESI) calcd for $C_{15}H_{18}O_3NaS^+$: 301.0869, found 301.0872; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 90:10, (*S*)-**3n**: 91% *ee*; $[\alpha]_D^{25}$ = -26.1 (c = 0.65, CH_2Cl_2), retention time: 33.0min (minor) and 49.7 min (major).



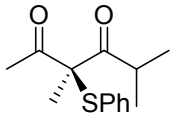
3o

To a flame-dried tube equipped with a magnetic stir bar were added **1o** (15.6 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3o** (24.6 mg, 93%) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2 H), 7.36 (dd, *J* = 8.5, 6.1 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 4.26 – 4.12 (m, 2 H), 2.57 (ddd, *J* = 15.8, 9.4, 3.9 Hz, 1 H), 2.51 – 2.42 (m, 1 H), 2.41 – 2.30 (m, 1 H), 2.16 – 2.02 (m, 2 H), 2.02 – 1.91 (m, 1 H), 1.24 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.3, 169.3, 136.4, 130.2, 129.7, 129.0, 64.8, 62.4, 36.9, 35.0, 19.2, 14.2; HPLC analysis: Daicel Chiralpak OD-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 90:10, (*S*)-**3o**: 32% *ee*, retention time: 6.5 min (minor) and 7.3 min (major); The spectroscopic data for **3o** matched those described in the literature.[2c]



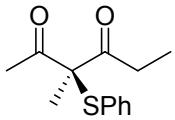
3p

To a flame-dried tube equipped with a magnetic stir bar were added **1p** (15.6 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 72 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3p** (20.3 mg, 77%) as a colorless oil: IR (thin film, cm^{-1}) 2959, 2930, 2872, 1699, 1683, 1458, 1367, 1288, 1196, 1166, 1069, 1024, 949, 749, 704, 692; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3 H), 7.34 – 7.28 (m, 2 H), 2.54 (qd, *J* = 17.7, 6.7 Hz, 2 H), 2.34 (s, 3 H), 2.21 (td, *J* = 13.4, 6.7 Hz, 1 H), 1.41 (s, 3 H), 0.95 (dd, *J* = 6.7, 1.2 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.7, 201.9, 136.6, 129.8, 129.4, 129.2, 72.7, 47.8, 27.0, 24.3, 22.7, 22.5, 20.0; HRMS (ESI) calcd for $C_{15}H_{20}O_2NaS^+$: 287.1076, found 287.1076; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 90:10, (*S*)-**3p**: 92% *ee*; $[\alpha]_D^{25}$ = -32.3 (c = 0.80, CH_2Cl_2), retention time: 17.1 min (major) and 24.4 min (minor).



3q

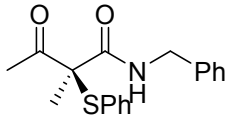
To a flame-dried tube equipped with a magnetic stir bar were added **1q** (14.2 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 72 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3q** (14.5 mg, 58%) as a colorless oil: IR (thin film, cm^{-1}). 2971, 2931, 1699, 1474, 1439, 1381, 1353, 1261, 1202, 1099, 1002, 800, 749, 692; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5 H), 3.22 – 3.08 (m, 1 H), 2.36 (s, 3 H), 1.41 (s, 3 H), 1.18 (dd, *J* = 23.5, 6.7 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 202.0, 136.5, 129.8, 129.4, 129.22, 72.6, 37.4, 27.3, 20.8, 20.4, 19.8; HRMS (ESI) calcd for $C_{14}H_{18}O_2NaS^+$: 273.0920, found 273.0924; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3q**: 92% *ee*; $[\alpha]_D^{25}$ = -15.0 (c = 0.50, CH_2Cl_2), retention time: 11.4 min (major) and 13.0 min (minor).



3r

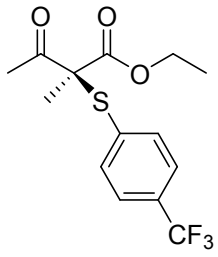
To a flame-dried tube equipped with a magnetic stir bar were added **1r** (12.8 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 72 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3r** (14.6 mg, 62%) as a colorless oil: IR (thin film, cm^{-1}) 2978, 2933, 1699, 1473, 1439, 1354, 1208, 1171, 1085, 1024, 969, 749, 704, 692; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5 H), 2.69 (ddq, *J* = 87.3, 17.9, 7.2 Hz, 2 H), 2.33 (s, 3 H), 1.43 (s, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.6, 202.2, 136.7, 129.9, 129.3, 129.2, 72.4,

32.5, 26.9, 20.1, 8.6; HRMS (ESI) calcd for $C_{13}H_{16}O_2NaS^+$: 259.0763, found 259.0767; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3r**: 88% *ee*; $[\alpha]_D^{25}$ = -17.1 (c = 0.48, CH_2Cl_2), retention time: 15.7 min (major) and 25.4 min (minor).



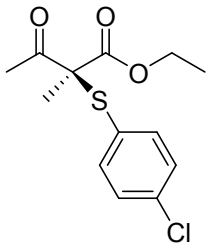
3s

To a flame-dried tube equipped with a magnetic stir bar were added **1s** (20.5 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2a** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 10:1) to afford **3s** (31.0 mg, 99%) as a colorless oil: IR (thin film, cm^{-1}) 3332 (br), 3061, 2929, 1712, 1658, 1515, 1454, 1439, 1262, 1204, 1081, 1025, 1000, 750, 693; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 6 H), 7.30 – 7.23 (m, 4 H), 4.46 (d, *J* = 5.8 Hz, 2 H), 2.35 (s, 3H), 1.57 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 169.2, 137.7, 136.3, 130.0, 129.3, 129.2, 128.9, 128.0, 127.8, 65.2, 44.3, 26.5, 21.40; HRMS (ESI) calcd for $C_{18}H_{19}O_2NNaS^+$: 336.1029, found 336.1030; HPLC analysis: Daicel Chiralpak OD-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 95:5, (*S*)-**3s**: 45% *ee*; $[\alpha]_D^{25}$ = -25.7 (c = 1.25, CH_2Cl_2), retention time: 24.3 min (major) and 26.1 min (minor).



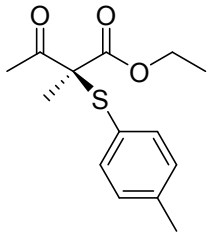
3t

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2b** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3t** (16.6 mg, 52%) as a colorless oil: IR (thin film, cm^{-1}) 2985, 2936, 1714, 1607, 1446, 1399, 1324, 1247, 1168, 1127, 1104, 1063, 1016, 841, 704, 599; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (q, *J* = 8.4 Hz, 4 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 2.36 (s, 3 H), 1.54 (s, 3 H), 1.28 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 169.7, 136.6, 134.7, 131.74 (q, *J* = 32.7 Hz), 125.9 (q, *J* = 3.6 Hz), 123.89 (q, *J* = 272.4 Hz), 66.1, 62.8, 26.0, 20.9, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.91; HRMS (ESI) calcd for $C_{14}H_{15}O_3F_3NaS^+$: 343.0586, found 343.0591; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 0.5 ml/min, λ= 210 nm, hexane/iso-propanol = 97:3, (*S*)-**3t**: 89% *ee*; $[\alpha]_D^{25}$ = -37.7 (c = 0.69, CH_2Cl_2), retention time: 18.5 min (major) and 19.9 min (minor).



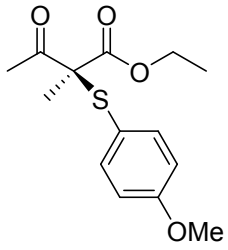
3u

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2c** (30.6mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3u** (23.5 mg, 82%) as a colorless oil: IR (thin film, cm^{-1}) 2982, 2935, 1711, 1573, 1476, 1444, 1389, 1355, 1246, 1197, 1109, 1091, 1013, 826, 747, 507; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 2.35 (s, 3 H), 1.49 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 169.8, 138.2, 136.7, 129.4, 128.0, 66.0, 62.7, 26.1, 20.8, 14.1; HRMS (ESI) calcd for $C_{13}H_{15}O_3ClNaS^+$: 309.0323, found 309.0329; HPLC analysis: Daicel Chiralpak IC, flow rate = 0.5 ml/min, λ= 210 nm, hexane/iso-propanol = 97:3, (*S*)-**3u**: 91% *ee*; $[\alpha]_D^{25}$ = -48.5 (c = 1.04, CH_2Cl_2), retention time: 39.2 min (major) and 41.0 min (minor).



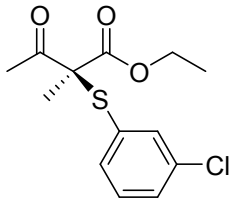
3v

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2d** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then, the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3v** (24.2 mg, 91%) as a colorless oil: IR (thin film, cm^{-1}) 2982, 2934, 1713, 1575, 1563, 1462, 1398, 1372, 1355, 1246, 1197, 1117, 1015, 864, 781, 684; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 2.36 (s, 3 H), 2.34 (s, 3 H), 1.48 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 170.1, 140.4, 137.1, 129.9, 125.8, 65.8, 62.5, 26.2, 21.4, 20.7, 14.1; HRMS (ESI) calcd for $C_{14}H_{18}O_3NaS^+$: 289.0869, found 289.0873; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3v**: 93% *ee*; $[\alpha]_D^{25}$ = -55.5 (c = 1.10, CH_2Cl_2), retention time: 9.5 min (major) and 13.0 min (minor).



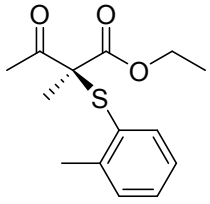
3w

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2e** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3w** (24.9 mg, 88%) as a colorless oil: IR (thin film, cm^{-1}) 2980, 2935, 2838, 1711, 1591, 1569, 1494, 1442, 1354, 1287, 1246, 1173, 1096, 1027, 832, 799, 720, 531; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.6 Hz, 2 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.79 (s, 3 H), 2.36 (s, 3 H), 1.46 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 170.2, 161.3, 138.8, 119.9, 114.6, 65.8, 62.5, 55.4, 26.2, 20.6, 14.1; HRMS (ESI) calcd for $C_{14}H_{18}O_4NaS^+$: 305.0818, found 305.0822; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 80:20, (*S*)-**3w**: 92% *ee*; $[\alpha]_D^{25}$ = -43.8 (c = 1.15, CH_2Cl_2), retention time: 21.8 min (minor) and 24.6 min (major).



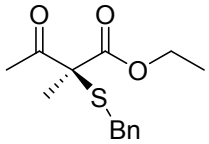
3x

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2f** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3x** (17.5 mg, 61%) as a colorless oil: IR (thin film, cm^{-1}) 2981, 2933, 1712, 1597, 1491, 1444, 1371, 1354, 1245, 1107, 1096, 1017, 865, 811, 510; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1 H), 7.37 (d, *J* = 7.8 Hz, 1 H), 7.31 (d, *J* = 7.7 Hz, 1 H), 7.26 (dd, *J* = 9.8, 5.6 Hz, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 2.36 (s, 3H), 1.53 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 169.8, 136.6, 135.0, 134.5, 131.5, 130.2, 130.1, 66.1, 62.7, 26.0, 20.9, 14.1; HRMS (ESI) calcd for $C_{13}H_{15}O_3ClNaS^+$: 309.0323, found 309.0328; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3x**: 86% *ee*; $[\alpha]_D^{25}$ = -46.0 (c = 0.55, CH_2Cl_2), retention time: 7.1 min (major) and 8.3 min (minor).



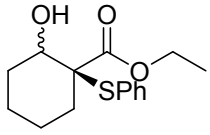
3y

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2g** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3y** (1.9 mg, 7%) as a colorless oil: IR (thin film, cm^{-1}) 2925, 1742, 1712, 1468, 1354, 1276, 1245, 1109, 1046, 1018, 865, 755, 716, 526; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 1 H), 7.30 – 7.22 (m, 2 H), 7.17 – 7.09 (m, 1 H), 4.25 (qd, *J* = 7.1, 3.4 Hz, 2 H), 2.46 (s, 3 H), 2.39 (s, 3 H), 1.44 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 170.2, 144.2, 138.2, 130.9, 130.1, 128.9, 126.5, 65.8, 62.5, 26.2, 21.5, 20.2, 14.1; HRMS (ESI) calcd for $C_{14}H_{18}O_3NaS^+$: 289.0869, found 289.0871; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3y**: 91% *ee*; $[\alpha]_D^{25}$ = -74.1 (c = 0.15, CH_2Cl_2), retention time: 7.7 min (major) and 15.0 min (minor).



3z

To a flame-dried tube equipped with a magnetic stir bar were added **1a** (14.4 mg, 0.10 mmol), **III**/TfOH (0.02 mmol) $NaHCO_3$ (8.4 mg, 0.10 mmol) and sulfenylation reagents **2h** (30.6 mg, 0.12 mmol). The resulting mixture was then diluted with 0.2 mL of $CHCl_3$. The reaction was conducted at room temperature for 48 h. Then the crude mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20:1) to afford **3z** (20.8 mg, 78%) as a colorless oil: IR (thin film, cm^{-1}) 2980, 2934, 1732, 1709, 1495, 1453, 1354, 1247, 1200, 1108, 1091, 1054, 1017, 864, 699, 468; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 5 H), 4.25 (q, *J* = 7.0 Hz, 2 H), 3.70 (s, 2 H), 2.29 (s, 3 H), 1.68 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 170.2, 136.5, 129.4, 128.7, 127.5, 63.2, 62.4, 34.7, 25.3, 20.7, 14.1; HRMS (ESI) calcd for $C_{14}H_{18}O_3NaS^+$: 289.0869, found 289.0875; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min, λ= 210 nm, hexane/iso-propanol = 70:30, (*S*)-**3z**: 87% *ee*; $[\alpha]_D^{25}$ = -5.8 (c = 0.45, CH_2Cl_2), retention time: 11.8 min (major) and 12.7 min (minor).



4n

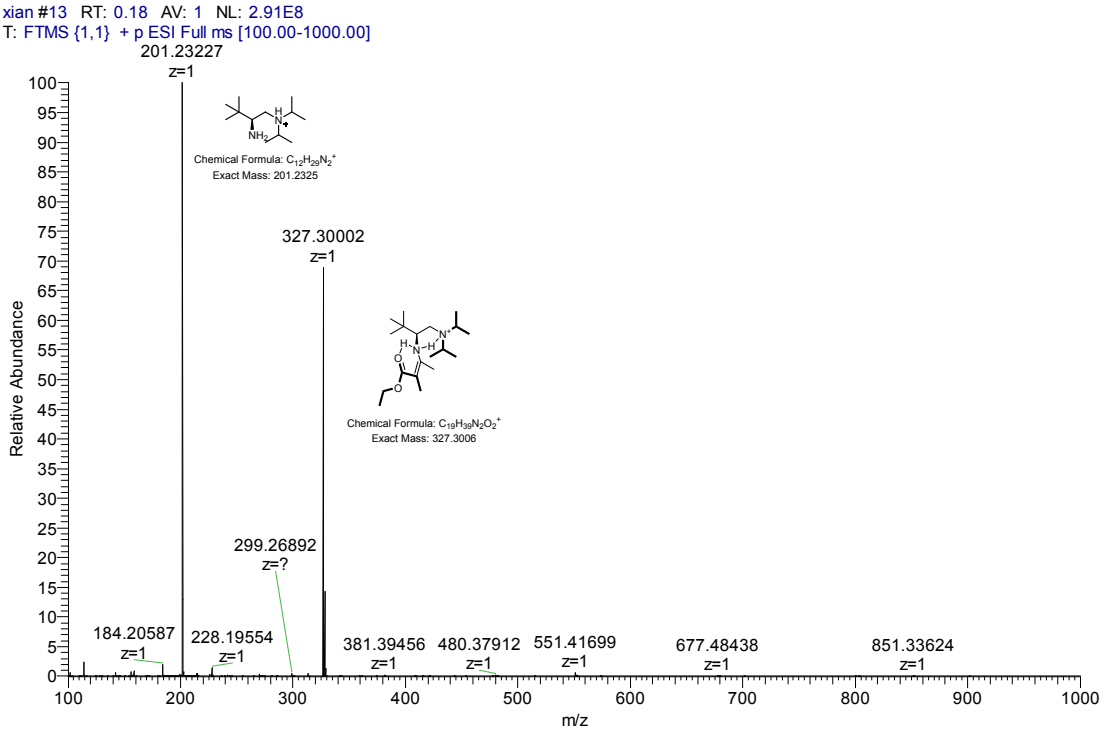
To a solution of α-sulfenylated β-keto ester (**3n**, 61mg, 0.22 mmol) in THF (0.3 ml) was added BH_3•DMS (0.66 mmol) at 0 °C, and the obtained mixture was stirred for 4 h. The reaction was quenched with saturated aq. NH_4Cl, and the mixture was extracted with Et_2O (5 mL x 3). The organic layers were combined, dried over Na_2SO_4, concentrated and chromatographed on silica gel (petroleum ether : ethyl acetate = 20:1) to give **4n** (31.8 mg, 52%) as a colorless oil: IR (thin film, cm^{-1}) 3446 (br), 2936, 1634, 1438, 1201, 1068, 967; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2 H), 7.38 (ddd, *J* = 6.3, 3.7, 1.3 Hz, 1 H), 7.35 – 7.28 (m, 2 H), 4.21 – 3.98 (m, 2 H), 3.85 (dt, *J* = 8.3, 3.5 Hz, 1 H), 3.45 (d, *J* = 7.5 Hz, 1 H), 2.16 – 2.03 (m, 2 H), 1.68 (td, *J* = 10.8, 9.3 Hz, 2 H), 1.60 – 1.50 (m, 2 H), 1.46 – 1.35 (m, 1 H), 1.28 (dd, *J* = 12.2, 8.8 Hz, 1 H), 1.18 (t, *J* = 7.1 Hz, 3 H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 137.5, 130.1, 129.5, 128.6, 73.5, 61.2, 59.3, 32.0, 31.4, 22.6, 22.4, 14.0; HRMS (ESI) calcd for $C_{15}H_{20}O_3NaS^+$: 303.1025, found 303.1023; HPLC analysis: Daicel Chiralpak OJ-H, flow rate = 1 ml/min,

λ= 254 nm, hexane/iso-propanol = 95:5, **4n**: 90% *ee*; $[\alpha]_D^{25}$ = -12.8 (c = 1.10, CH_2Cl_2), retention time: 9.0 min (major) and 10.2 min (minor).

Mechanism studies

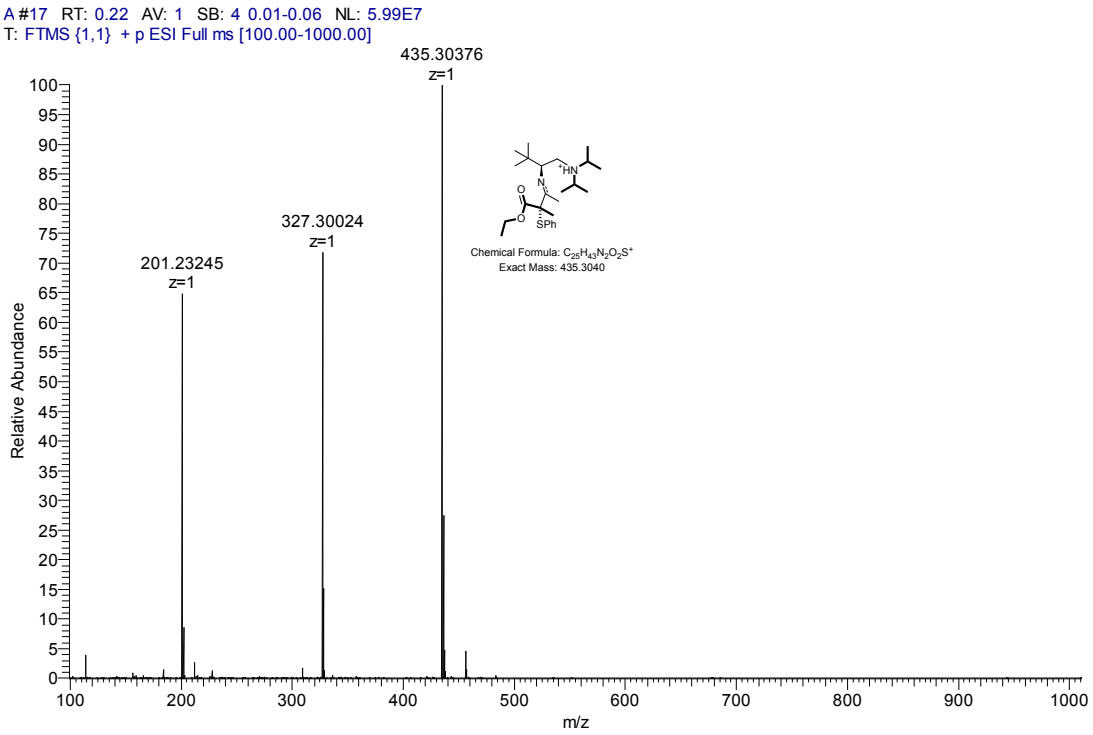
In-situ ESI-MS studies of the reaction mixture

An oven-dried 10 mL schlenk tube was charged with **1a** (0.10 mmol), amine catalyst (**III**/HOTf, 0.02 mmol) and $NaHCO_3$ (0.10 mmol) followed by $CHCl_3$ (0.2 mL). The mixture was stirred under air at room temperature for 30 min. Then an aliquot was taken for ESI-MS analysis.



Reaction with *N*-(phenylthio)phthalimide 2a:

To the above reaction mixture, N-(phenylthio)phthalimide (**2a**, 0.12 mmol) was added. The reaction was stirred under air at room temperature for 6 h. Then an aliquot was taken for ESI-MS analysis. It was found that a sulfenylated iminium ion was clearly noted, a clear indication of the enamine pathway.

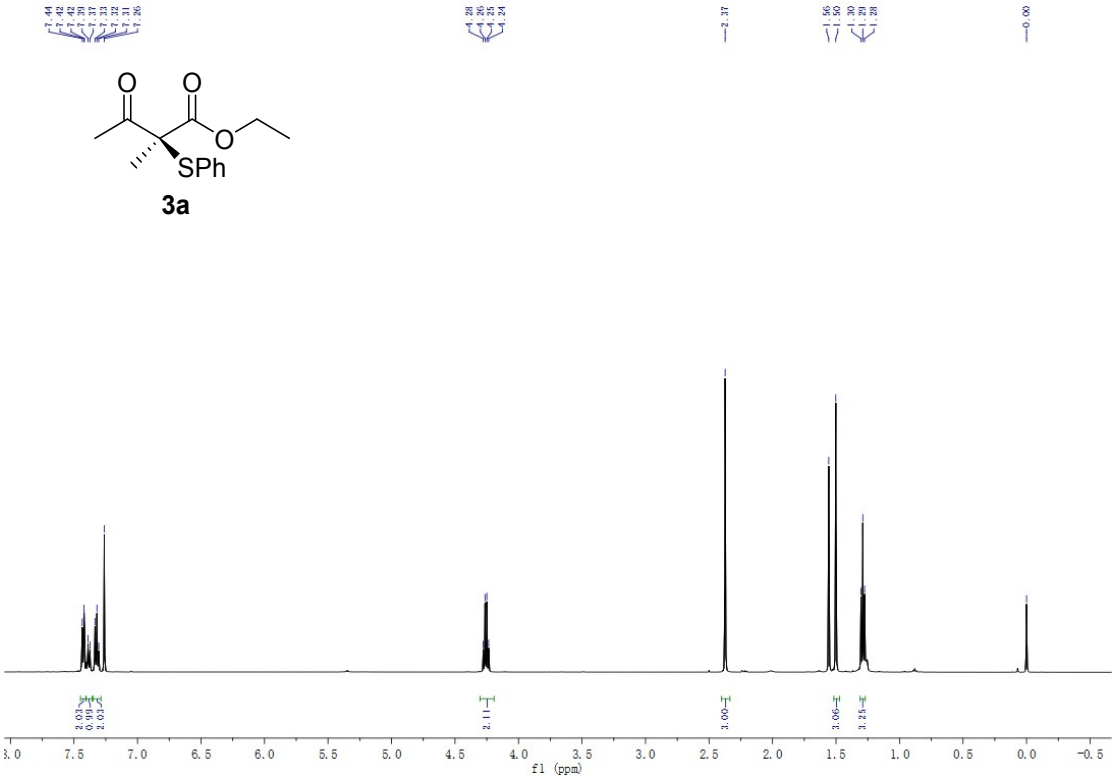


Reference

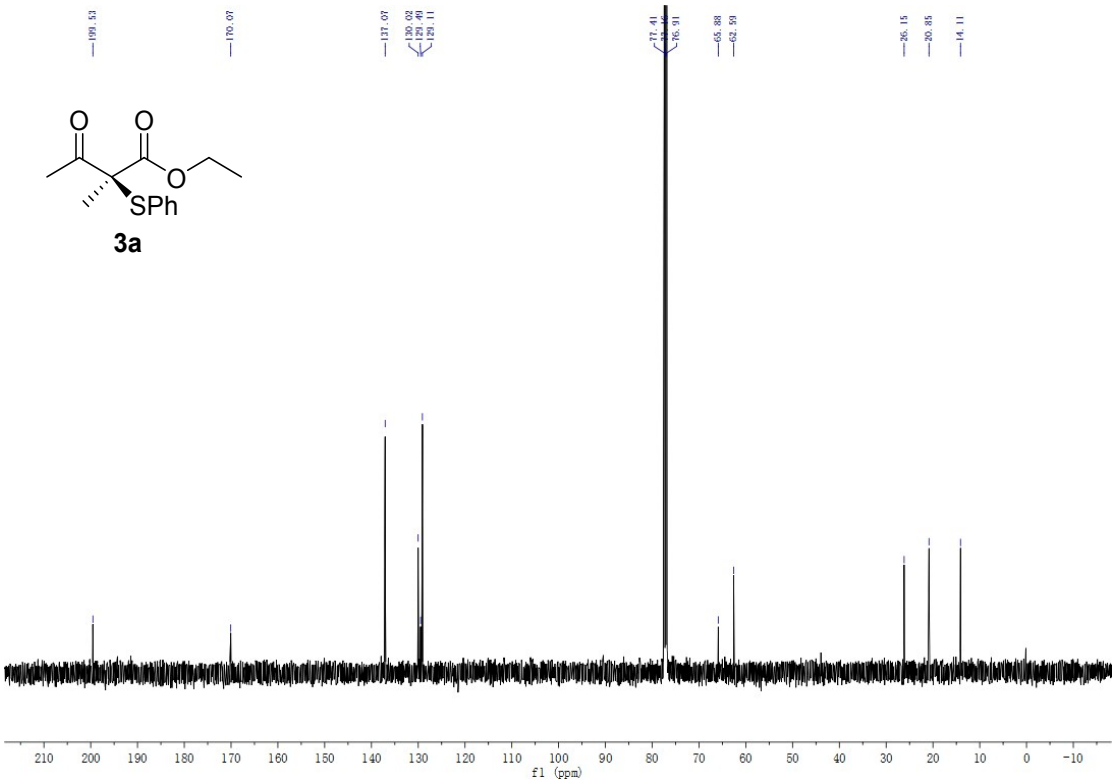
1. (a) H. -M. Gillis, L. Greene, A. Thompson, *Synlett.,* 2009, 112; (b) T.-C. Ollins, A.-M. Vijayakrishna, *Can. J. Chem*., 1987, **65**, 38.

2. (a) M. Jereb, A. Togni, *Org. Lett*., 2005, **7**, 4041; (b) M. Jereb, A. Togni, *Chem. Eur. J.,* 2007, **13**, 9384; (c) L. Fang, A. Lin, H. Hu, C. Zhu, *Chem. Eur. J.,* 2009, **15**, 7039.

NMR spectra



3a



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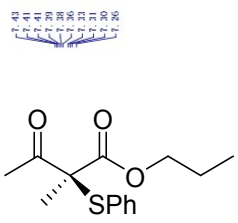
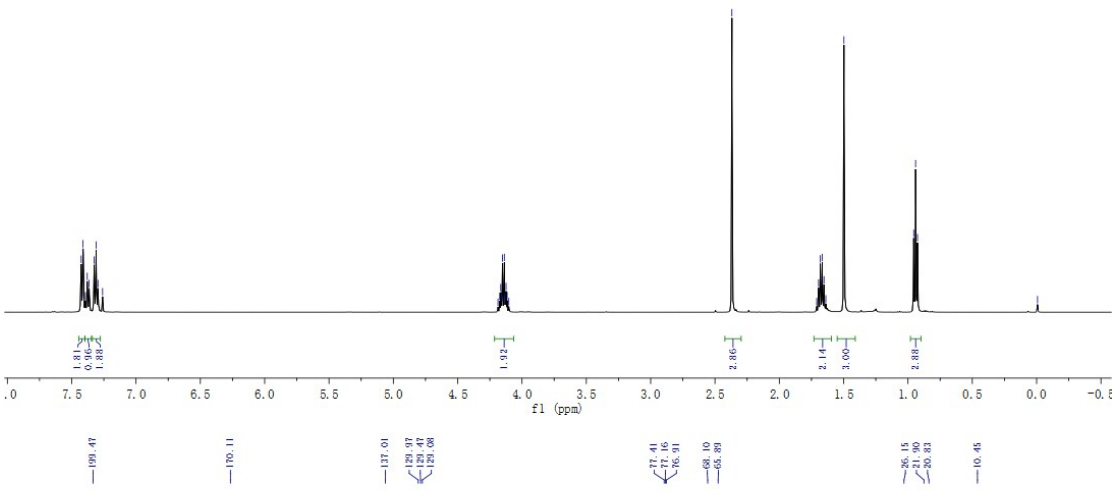
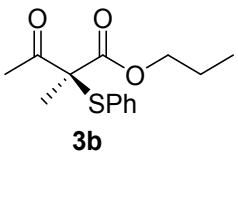


3b





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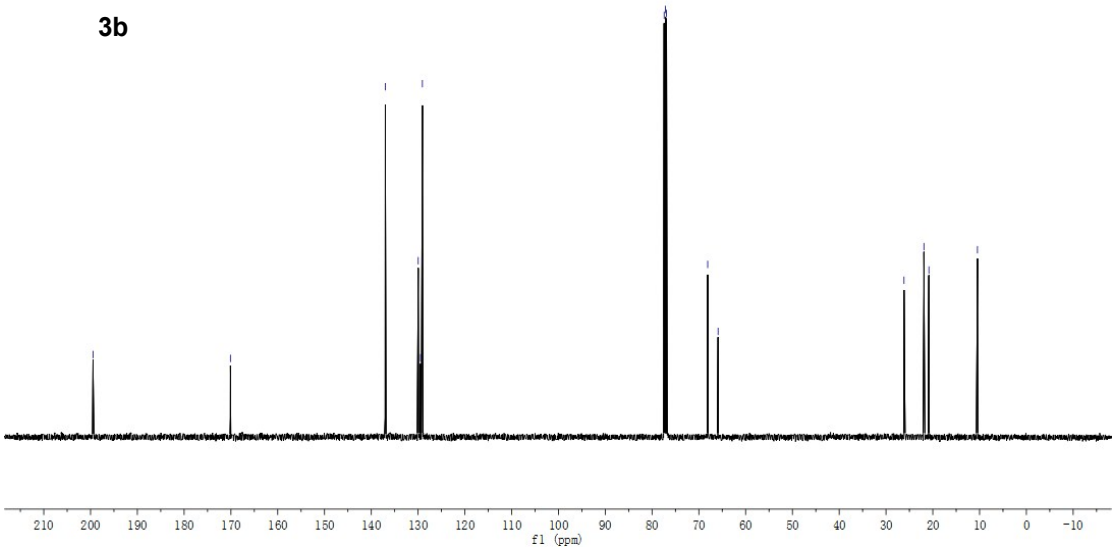

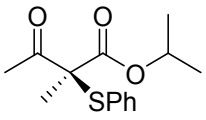

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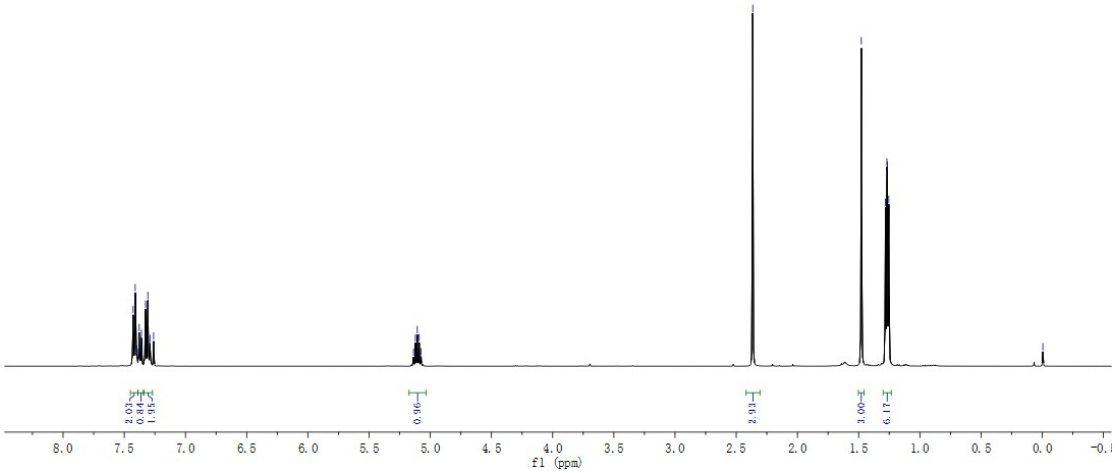

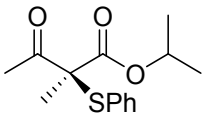

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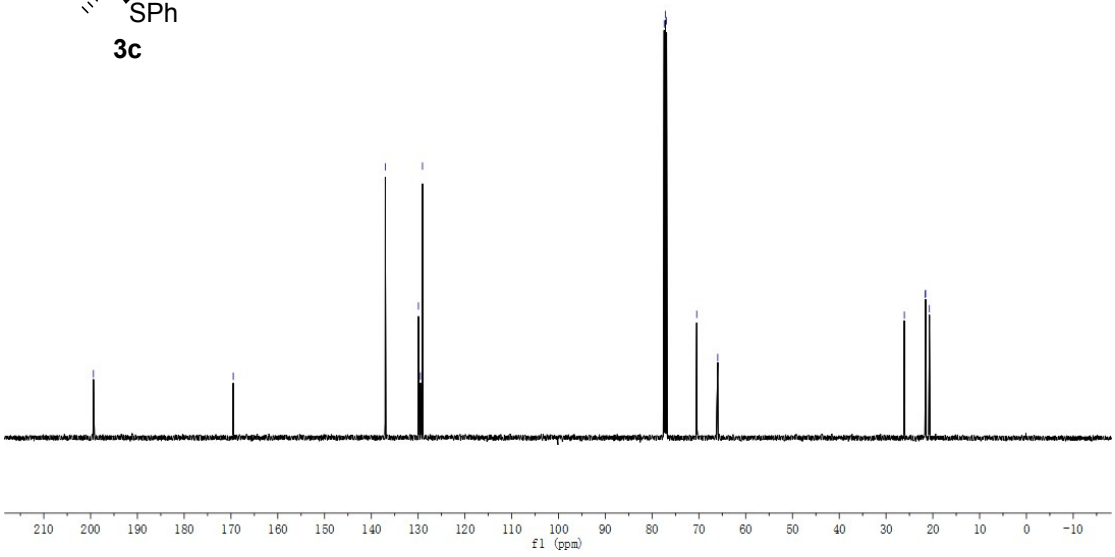

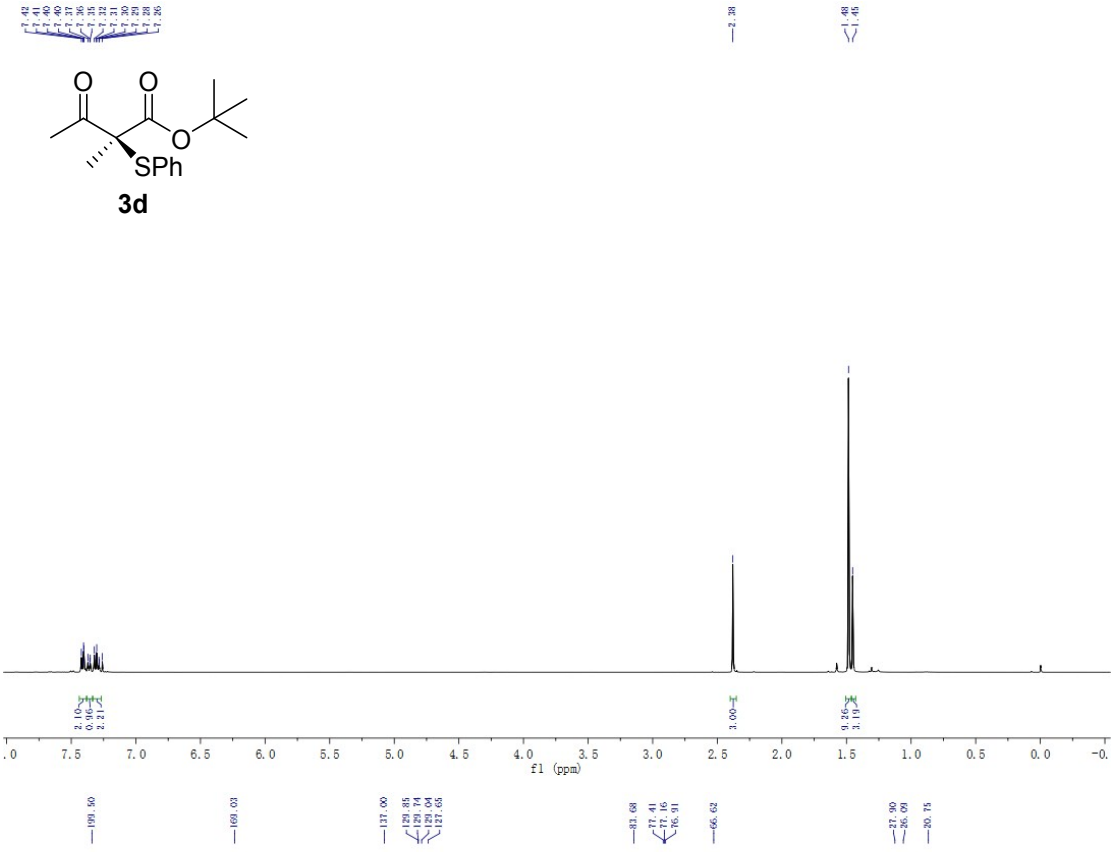
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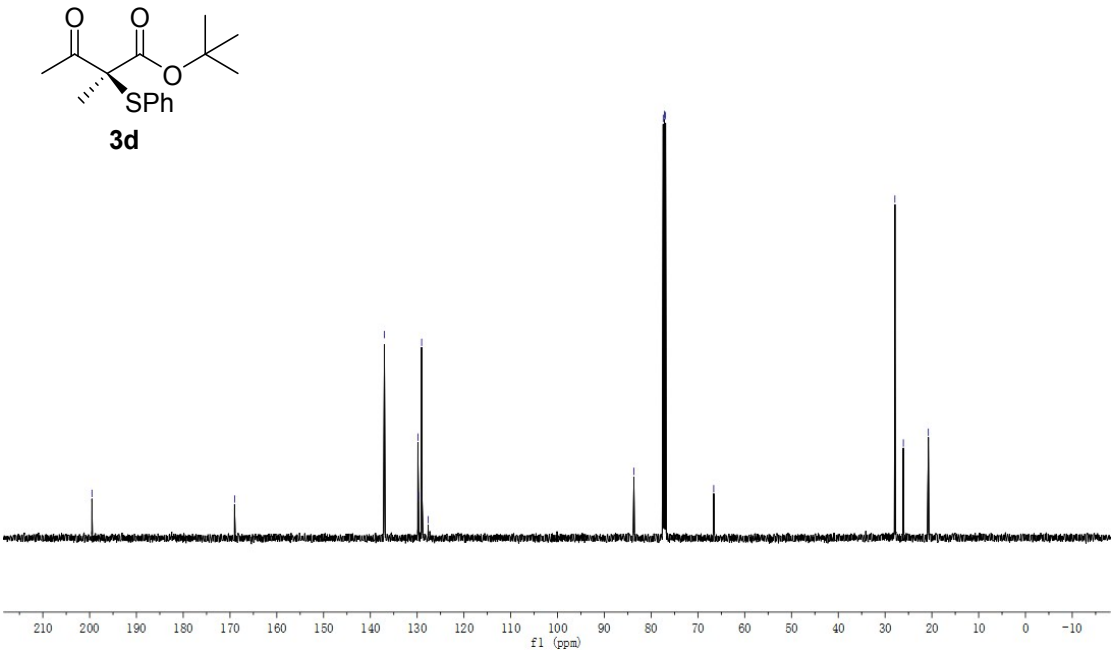
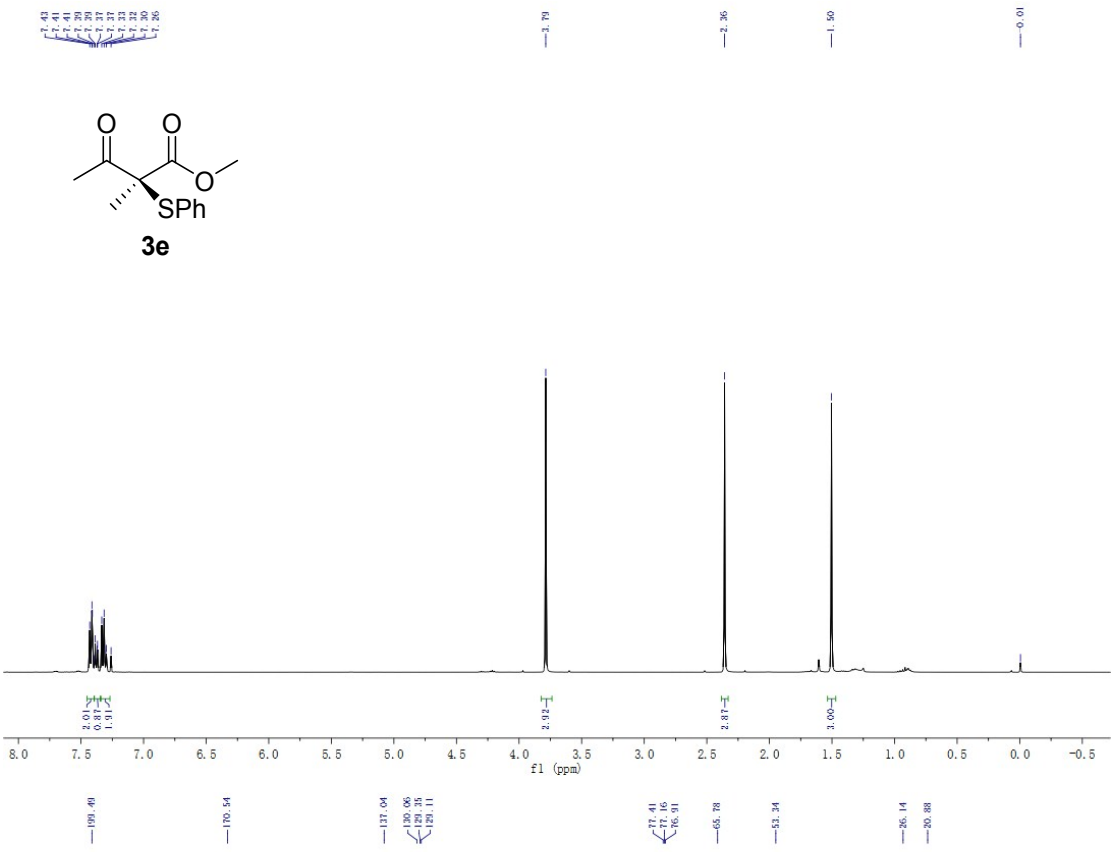
3d
f1 (ppm)


SPh
3d
f1 (ppm)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7.30
7.26
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1.50
0.01
O
O
O
SPh
2.01
2.03
1.91
2.93
2.87
3.00
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
0.0
-0.5
f1 (ppm)
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170.54
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129.35
129.11
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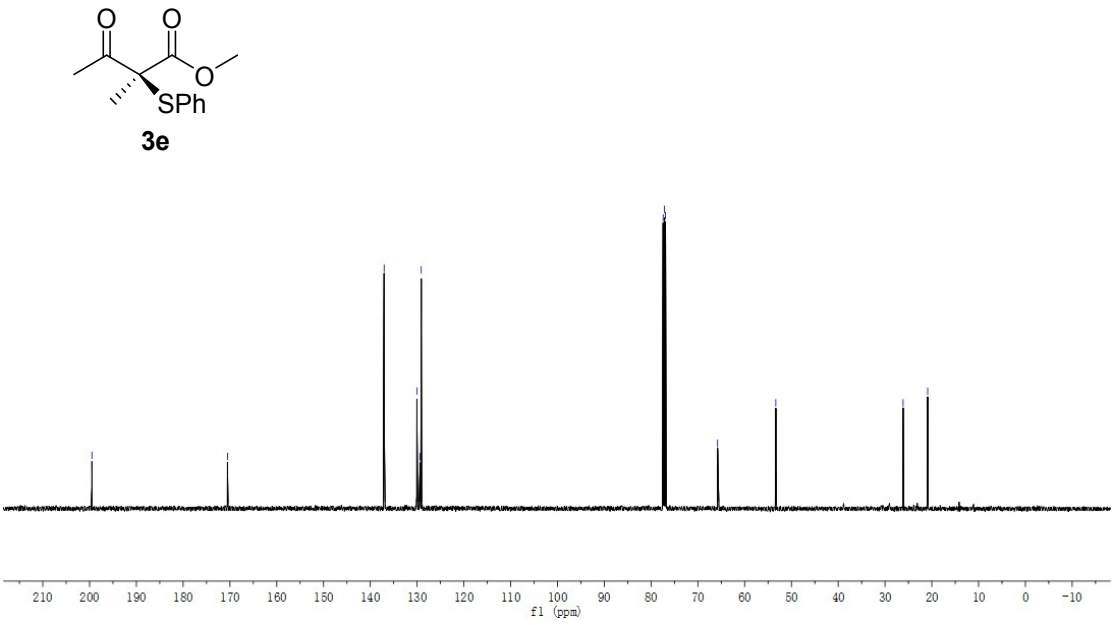
77.16
76.91
65.78
53.24
26.14
20.88

3e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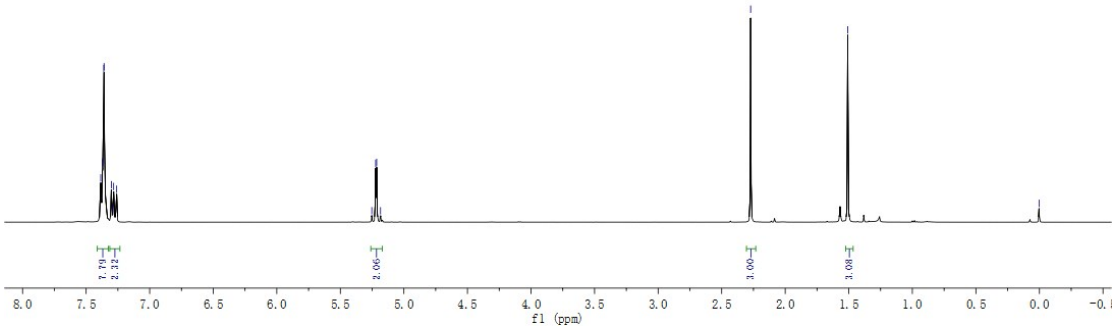
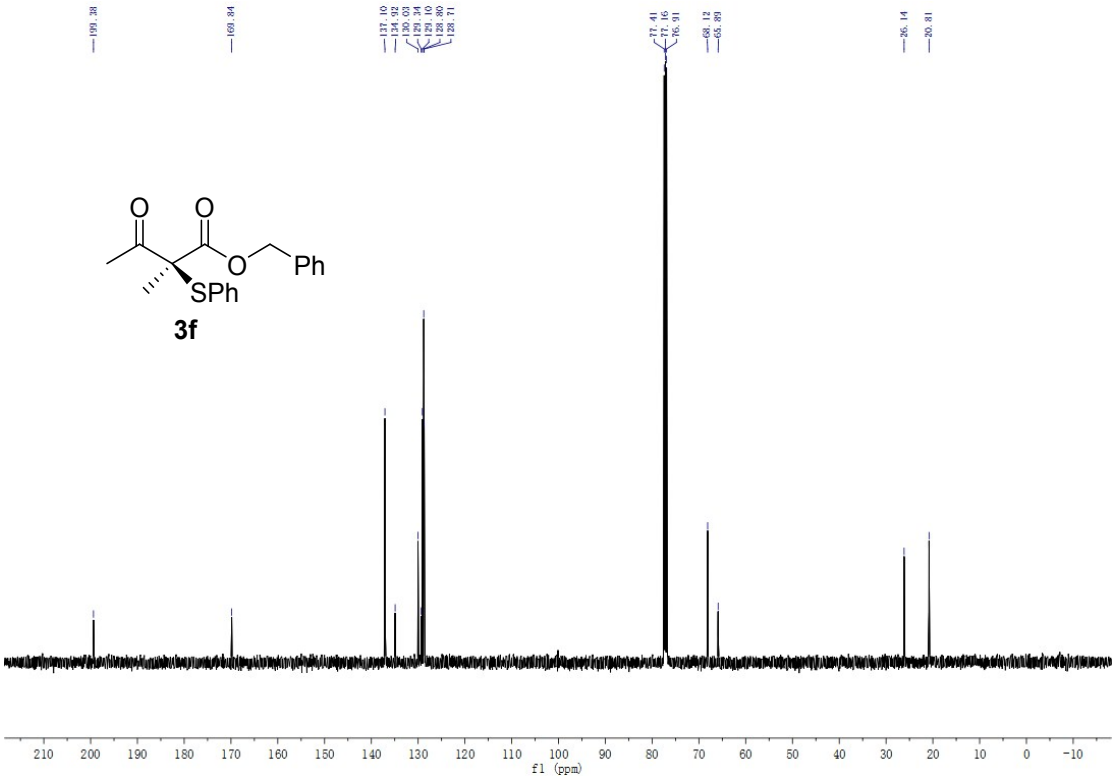
O
O
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3e

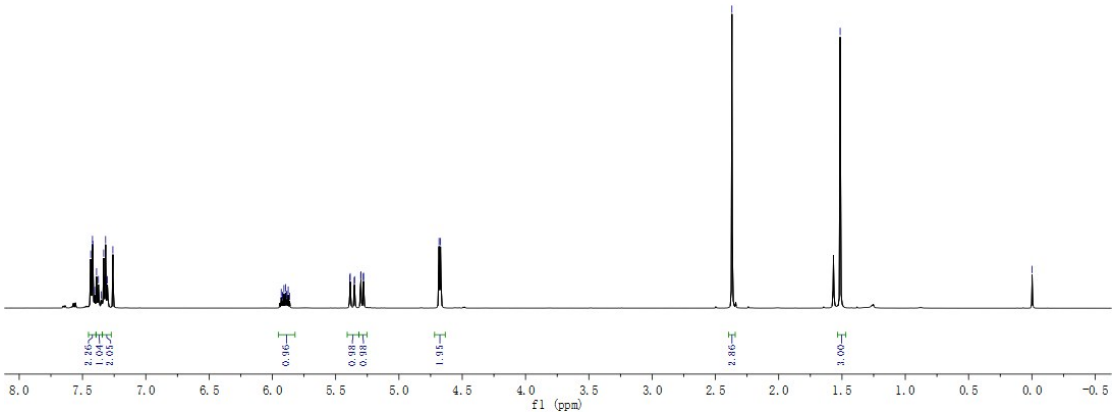
3f

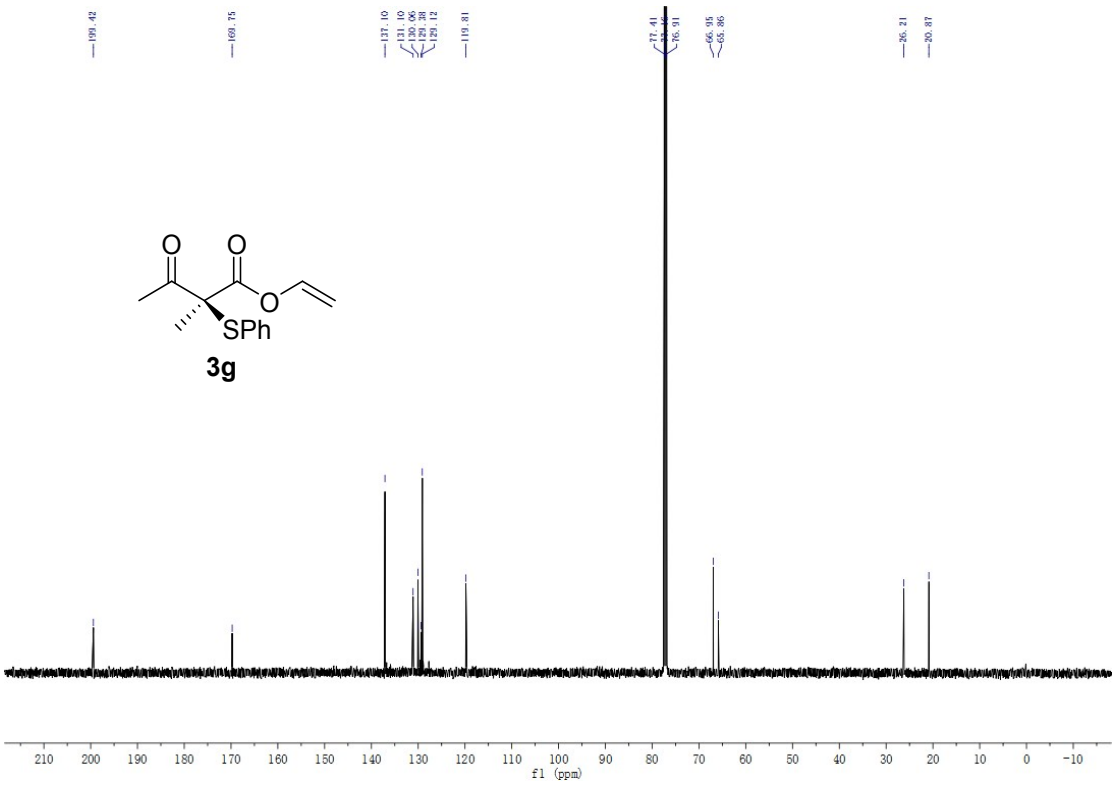




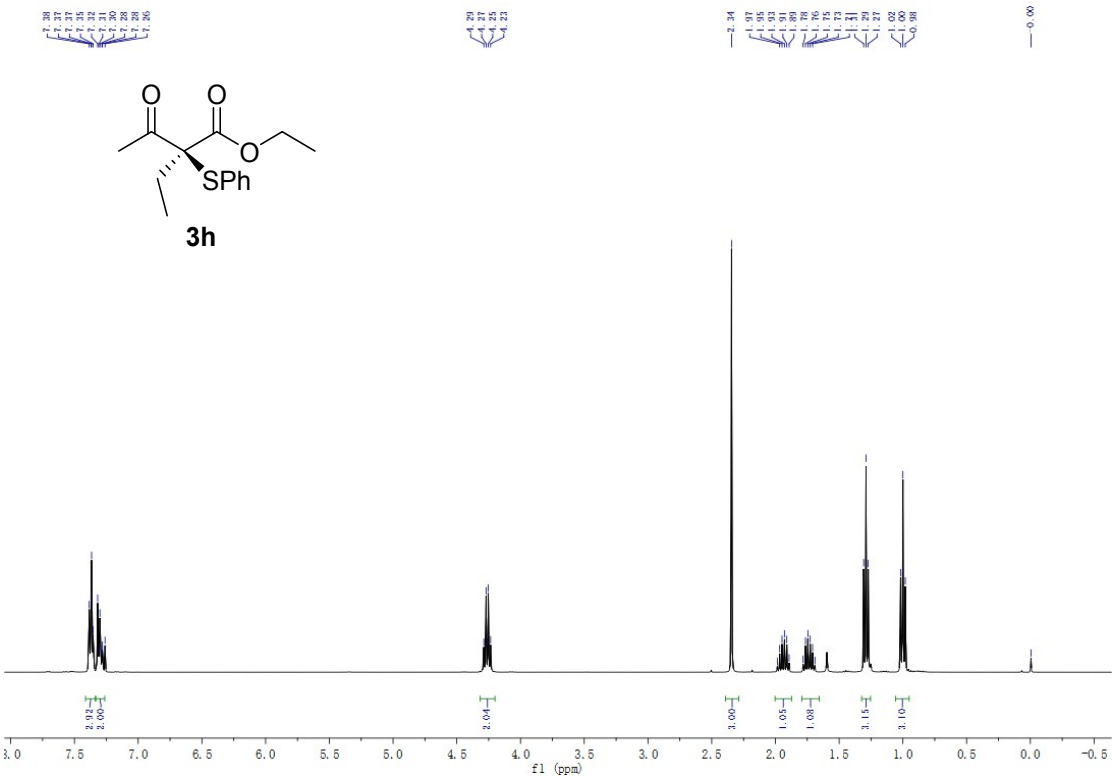
3f

3g





3g



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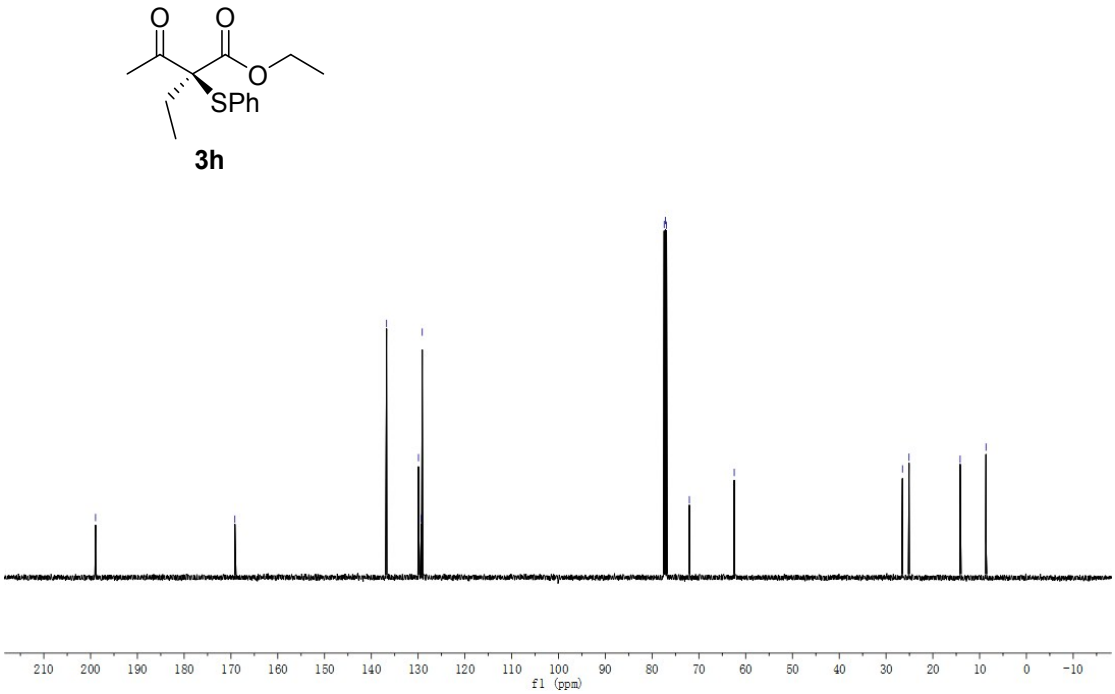

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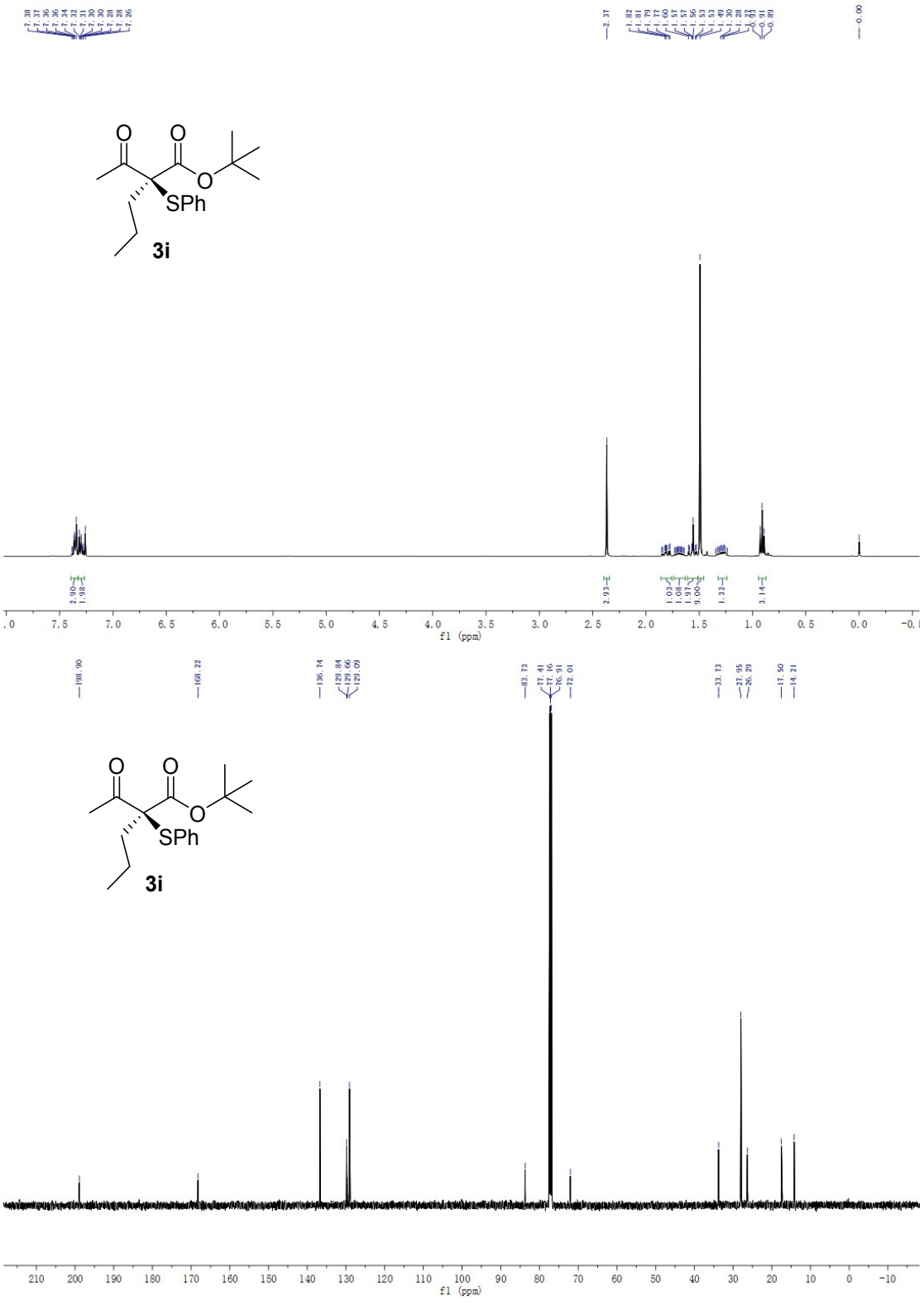
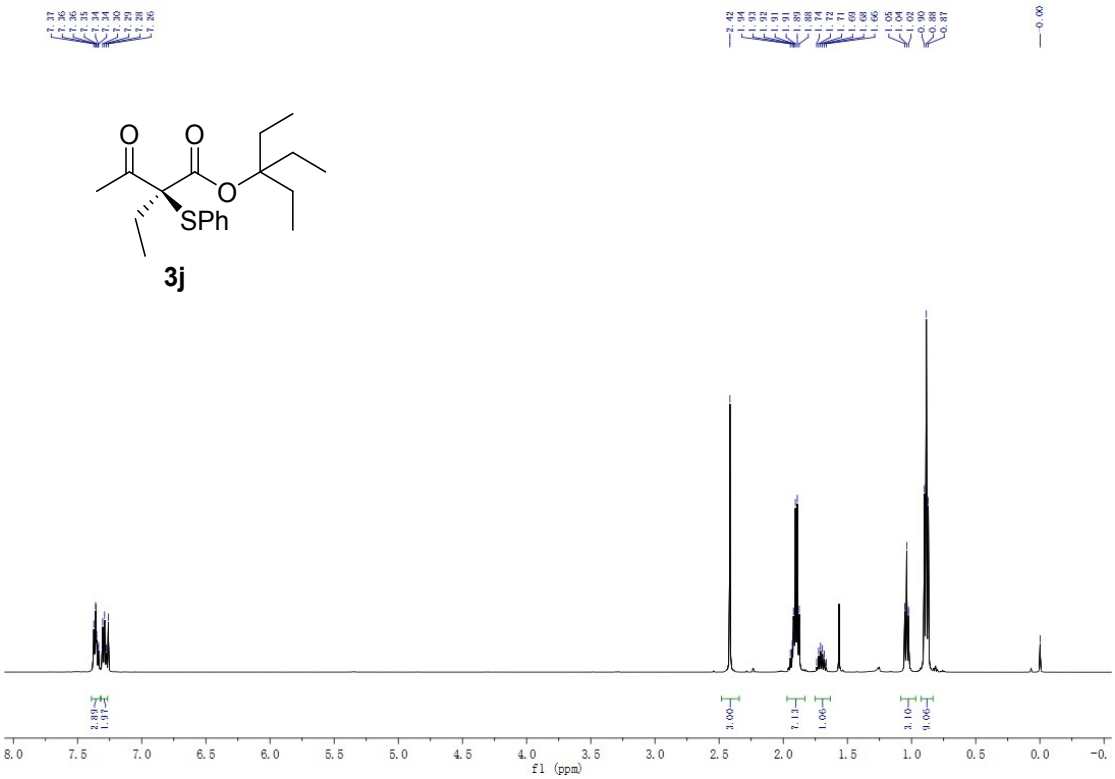

O
O
O
SPh
3i
f1 (ppm)
O
O
O
SPh
3i
f1 (ppm)



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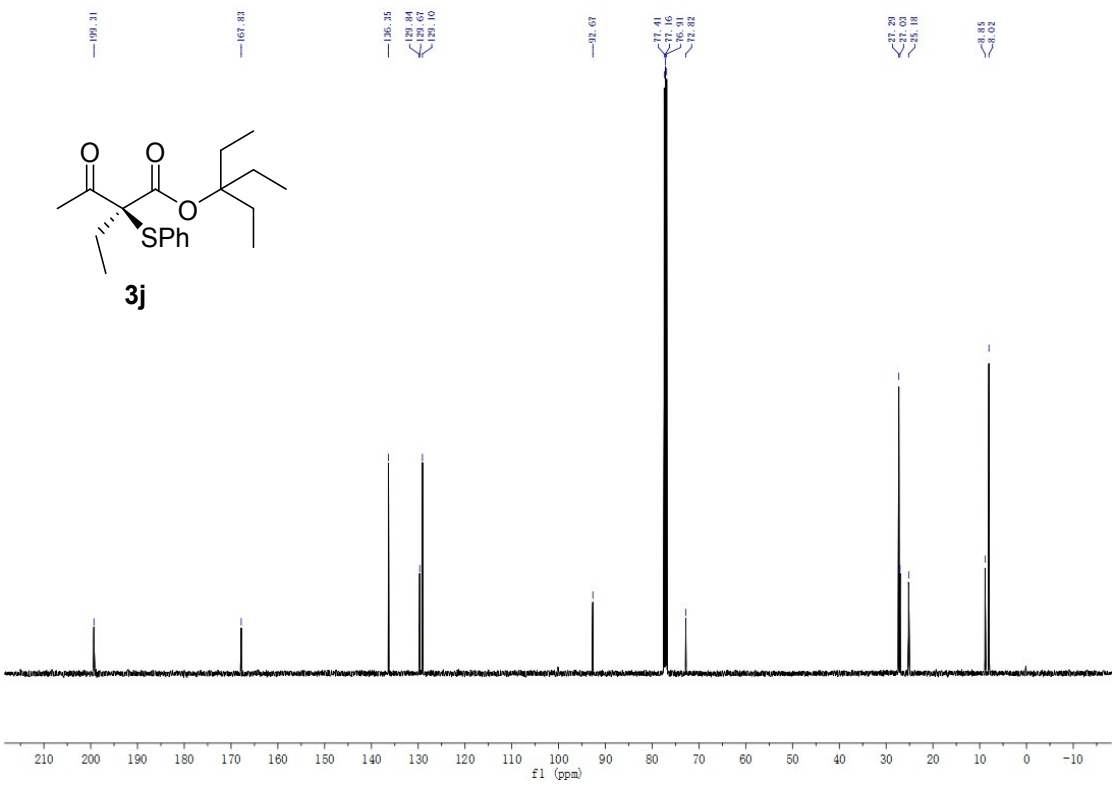

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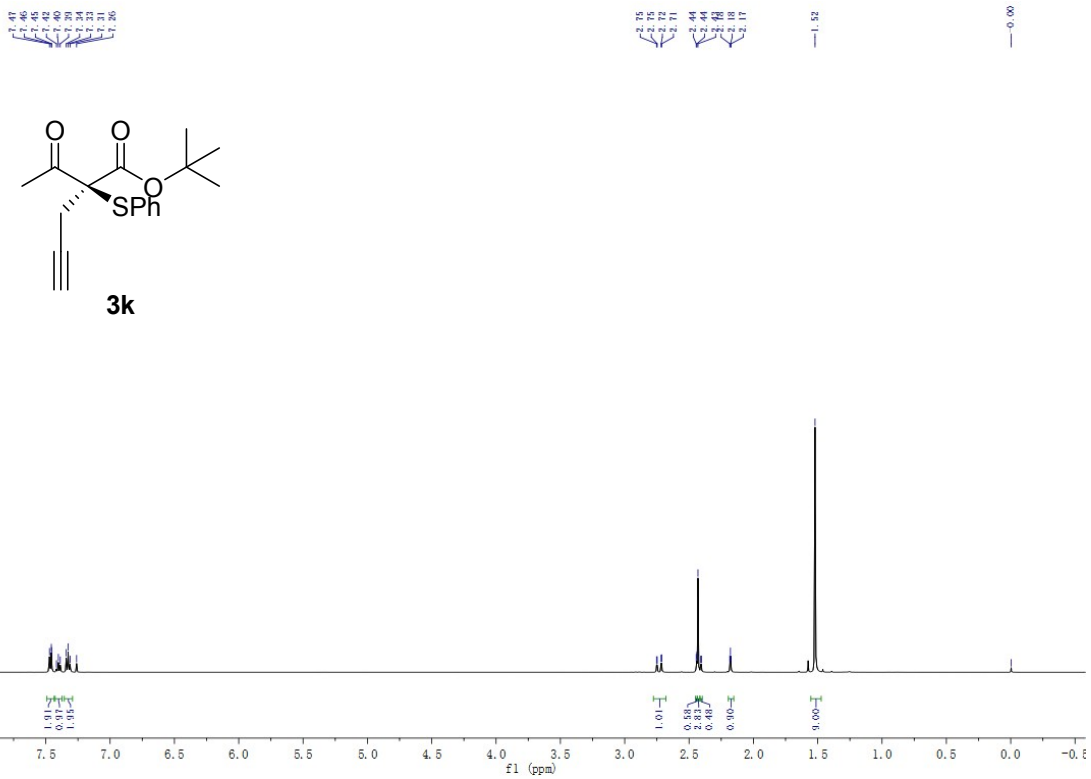

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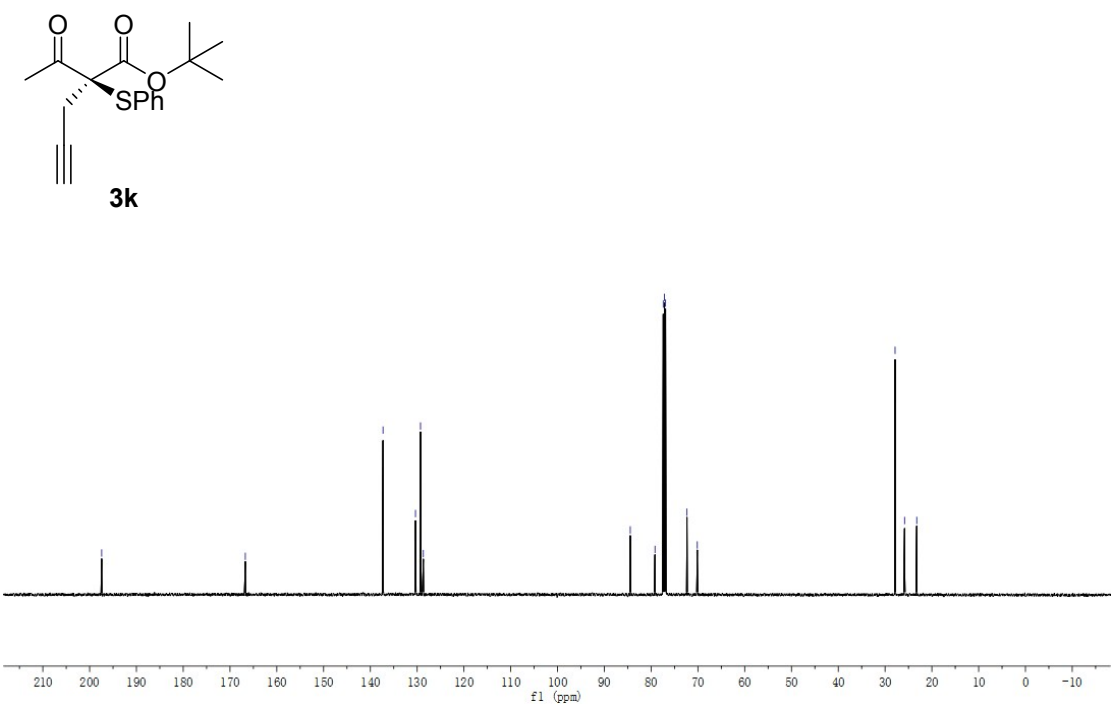

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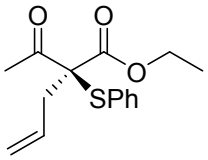

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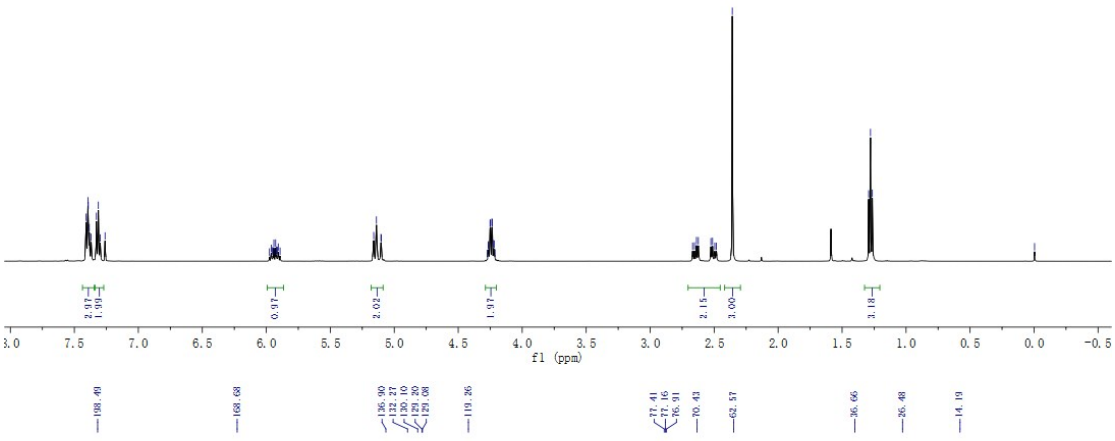

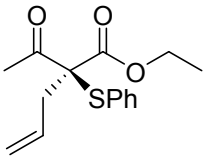

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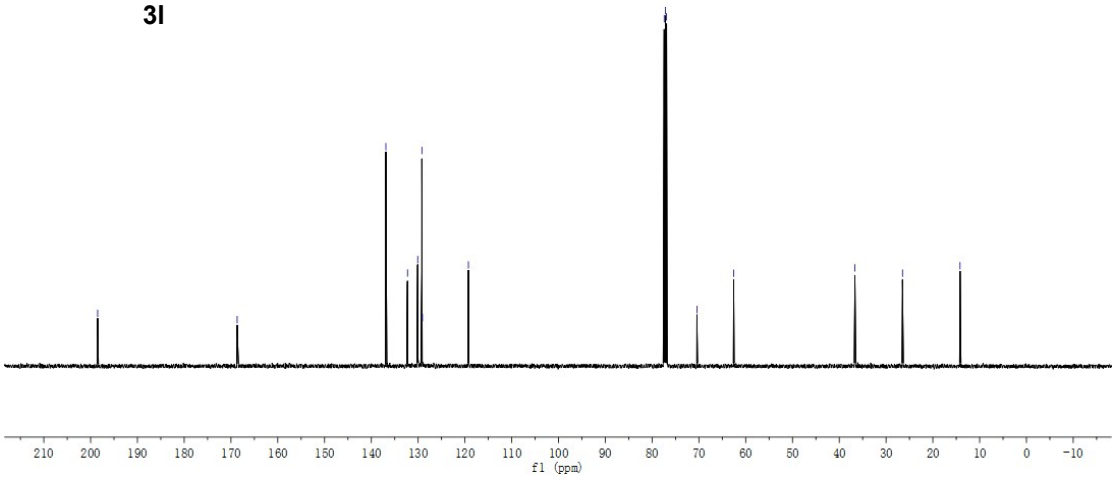
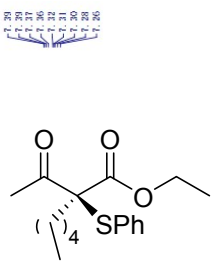
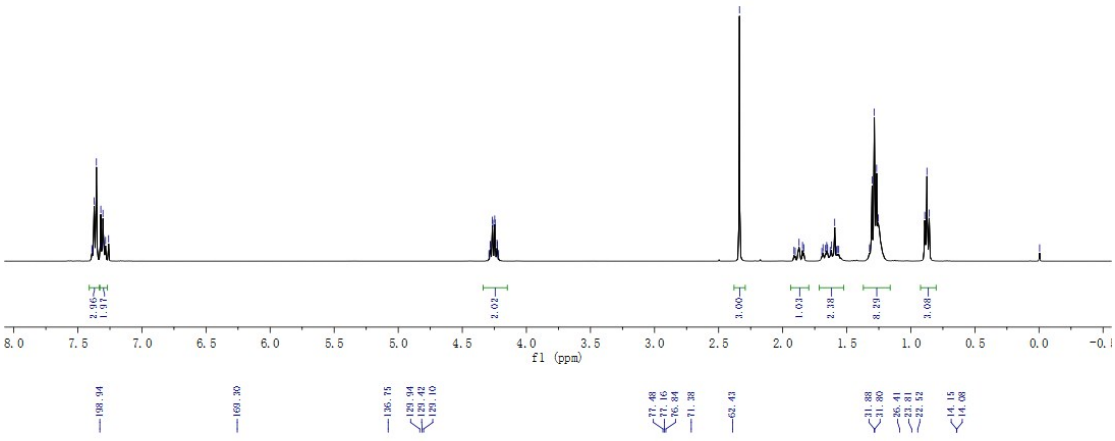
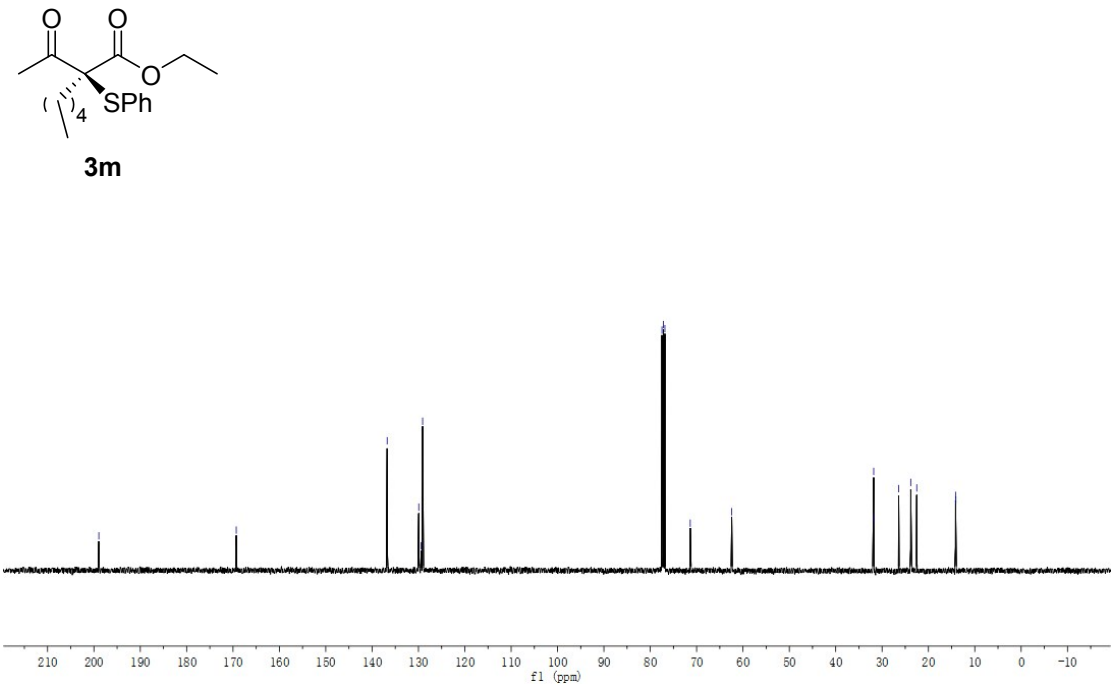




3m





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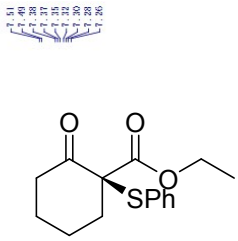

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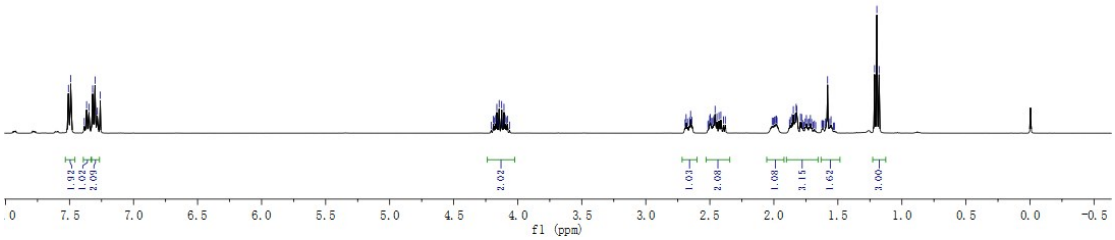

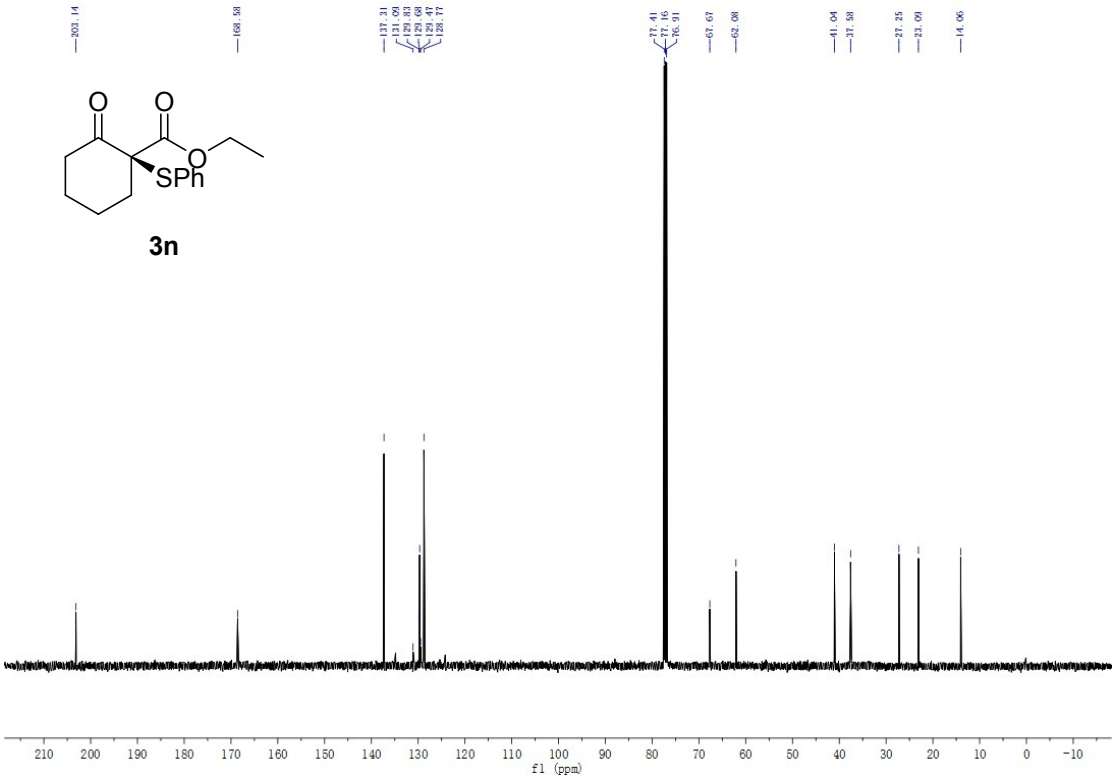

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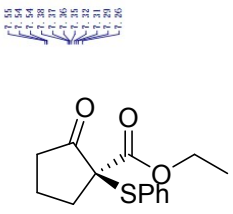
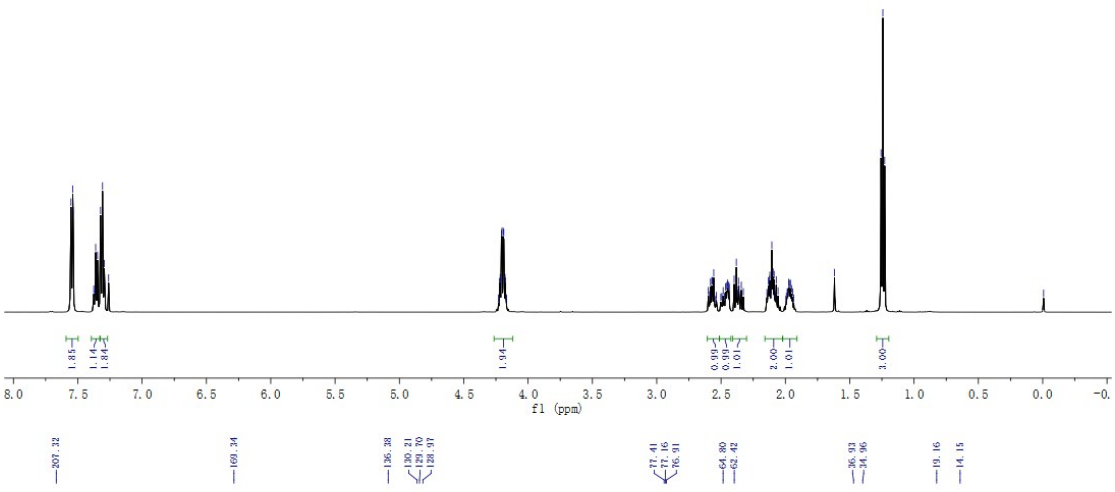
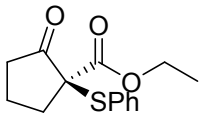


3o





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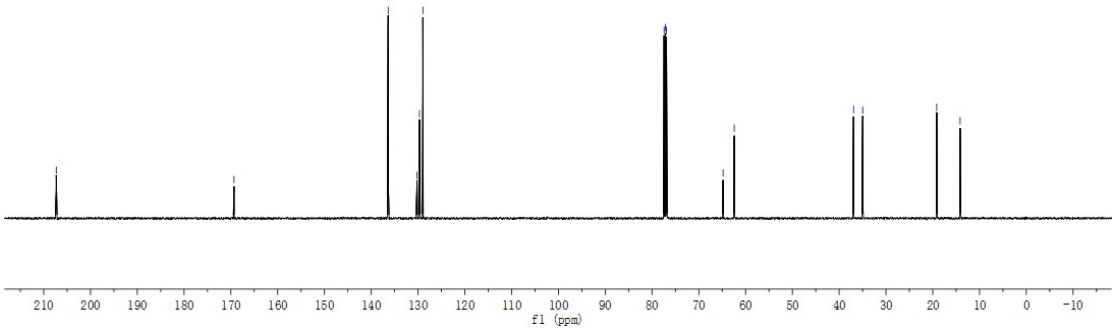
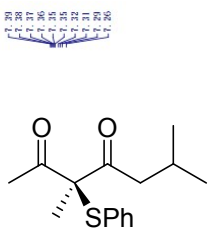
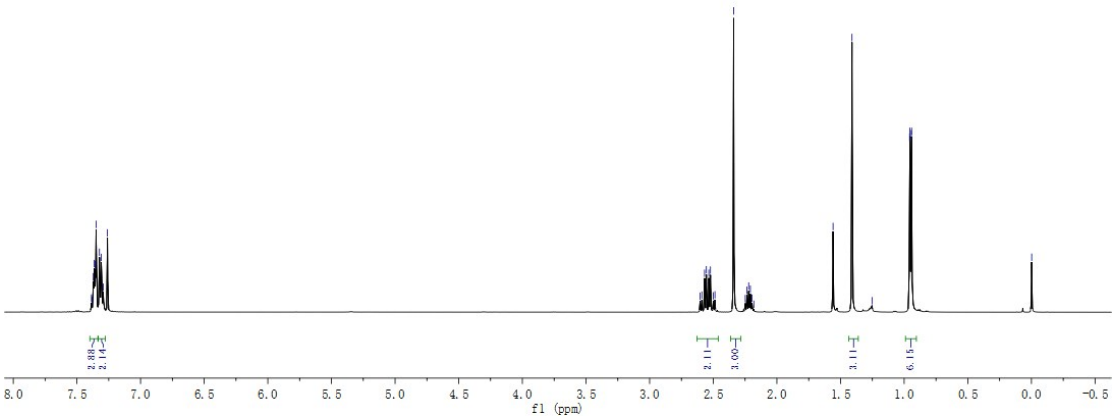
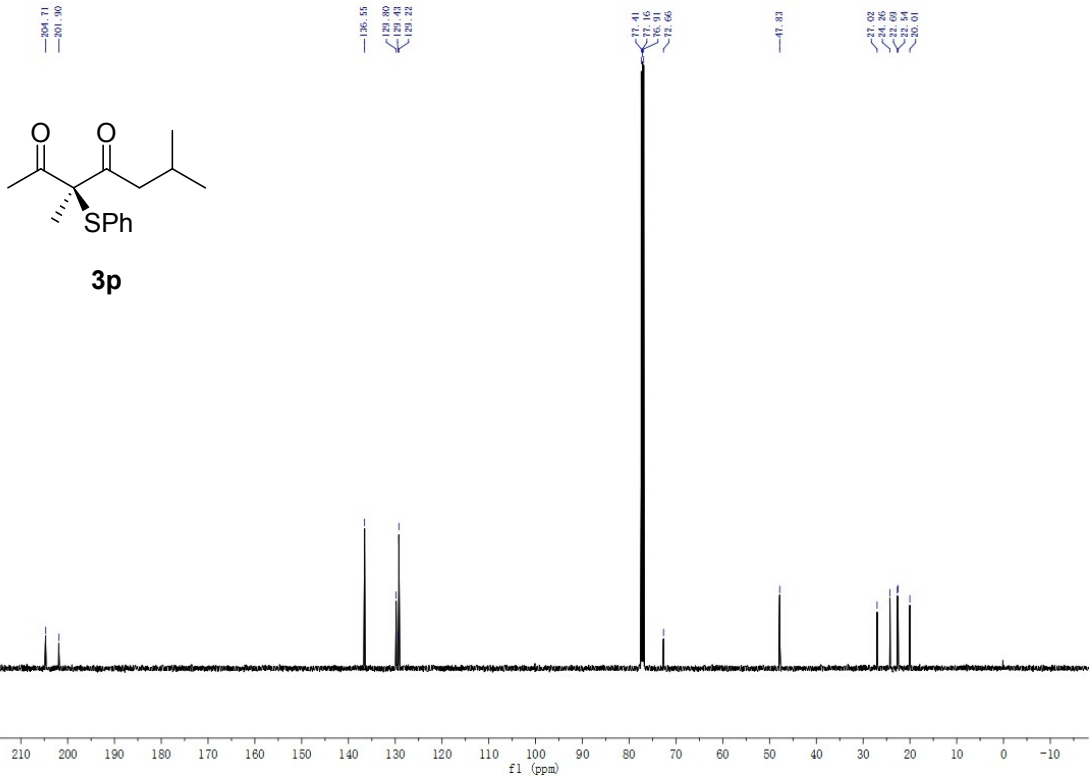


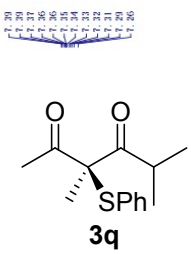


3p

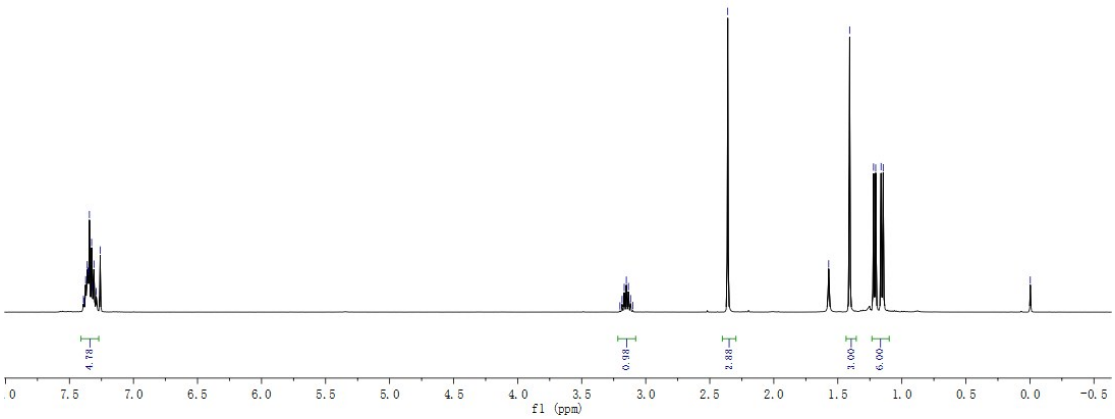


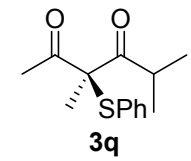


3p


O
O
SPh

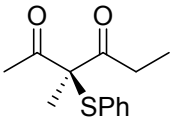
3q


4.78
0.98
2.83
3.00
6.00
f1 (ppm)

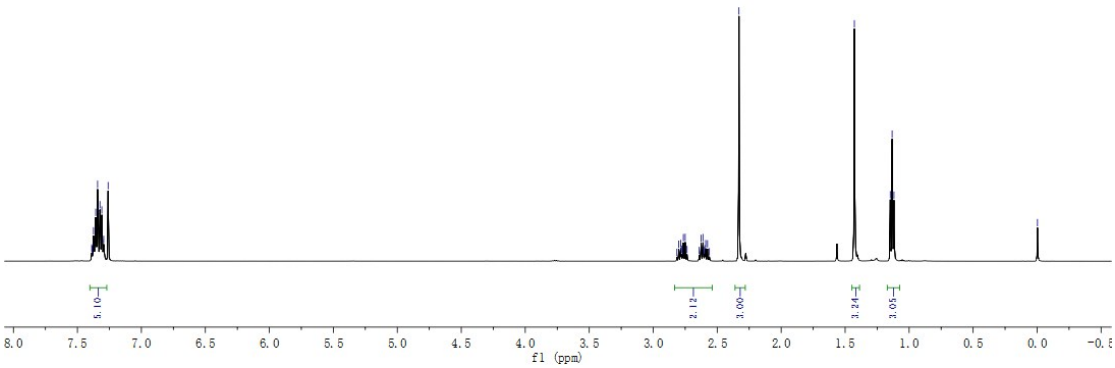

O
O
SPh

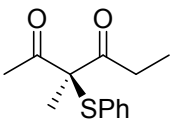
3q

209.93
201.98
136.52
129.79
129.35
129.23
77.41
77.16
76.91
72.99
37.36
27.26
20.79
20.43
19.80
f1 (ppm)

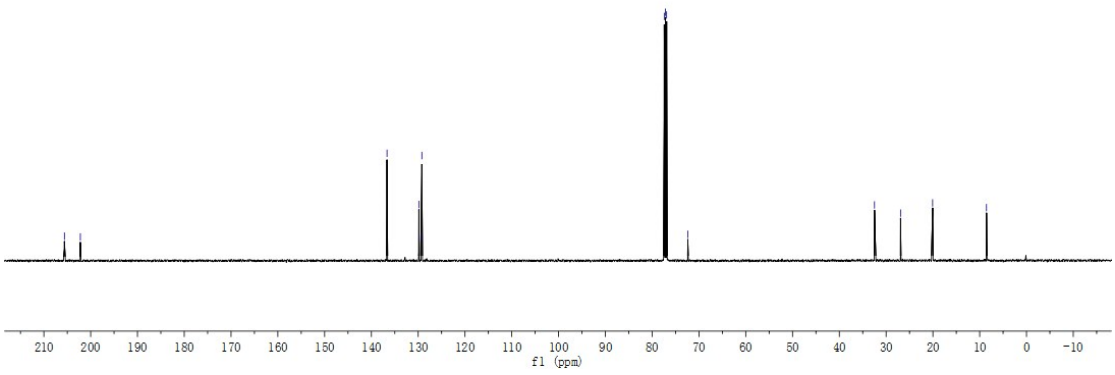


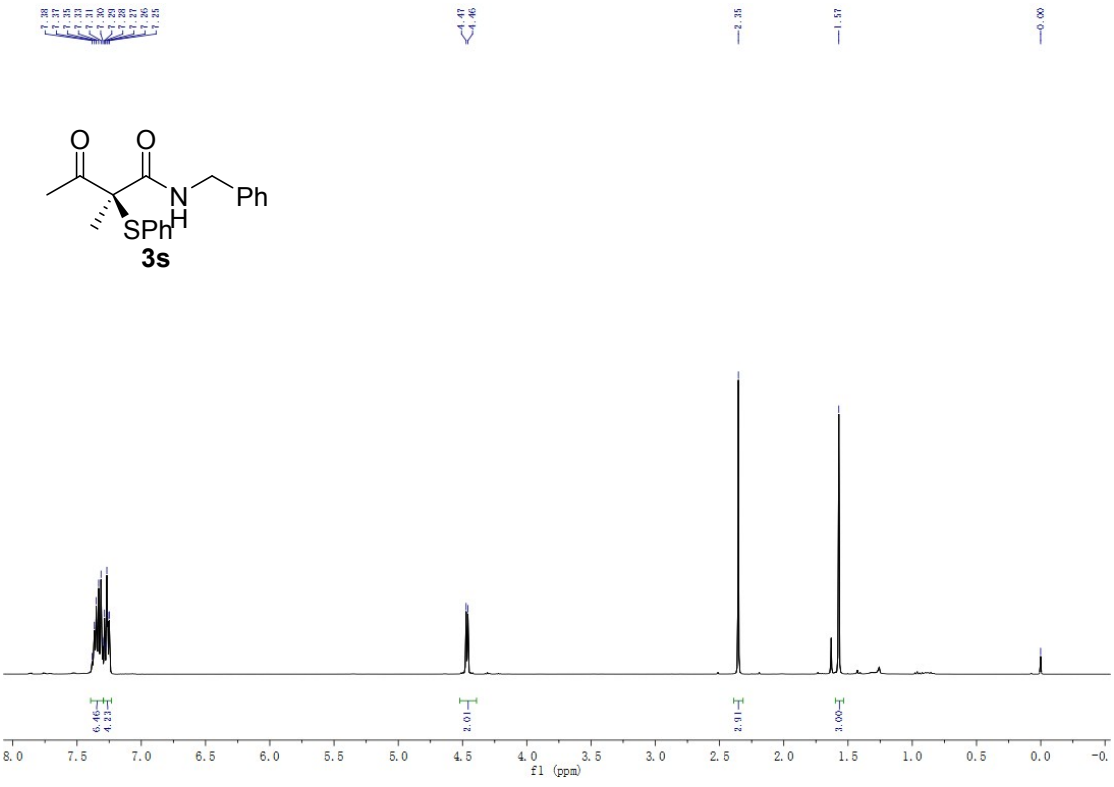
3r

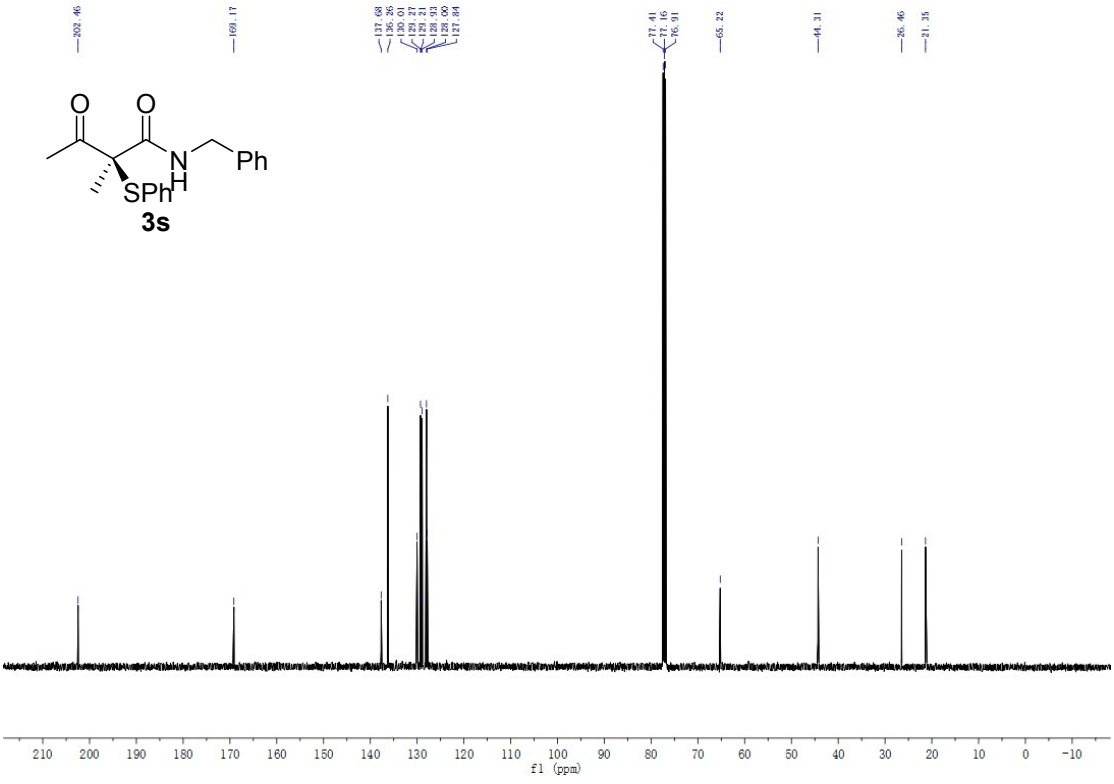


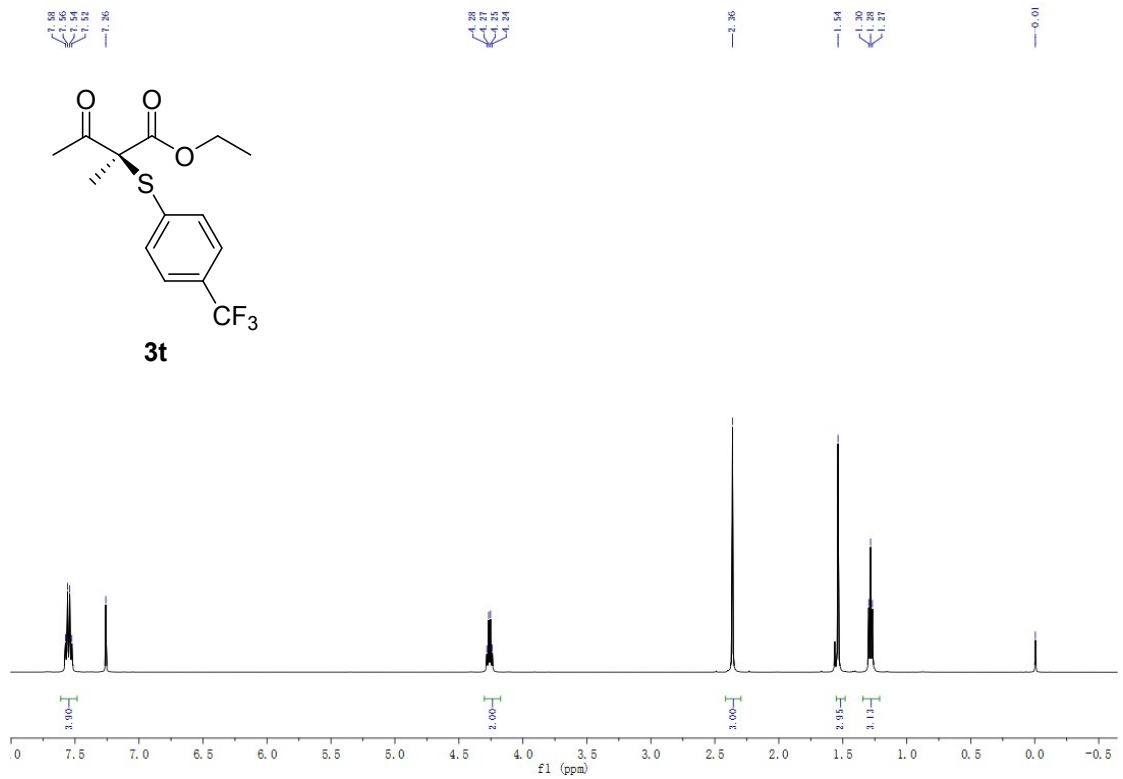


3r

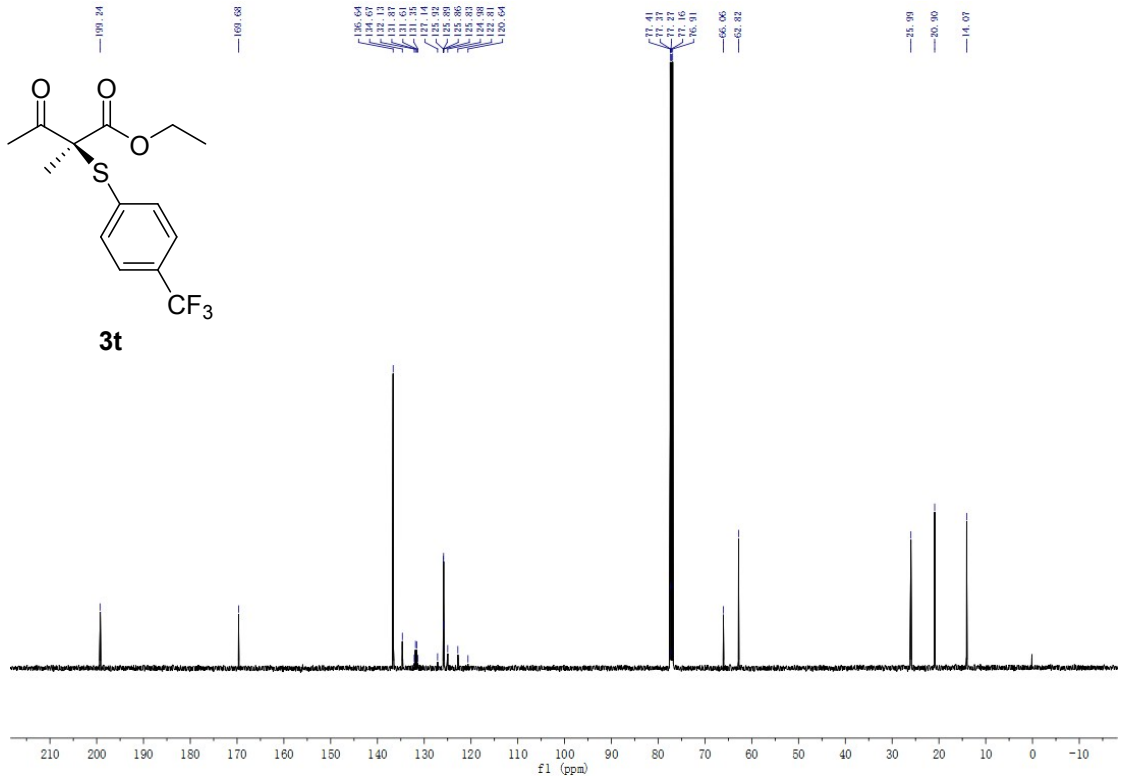



O
O
N
H
Ph
SPh
3s
f1 (ppm)

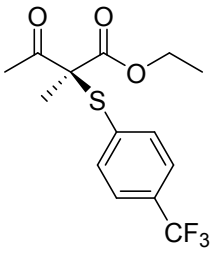

O
O
N
H
Ph
SPh
3s
f1 (ppm)


7.58
7.56
7.54
7.52
7.26
4.28
4.27
4.25
4.24
2.35
1.54
1.30
1.28
1.27
0.01
O
O
O
S
CF3
3.90
2.00
3.00
2.95
3.13
f1 (ppm)

3t

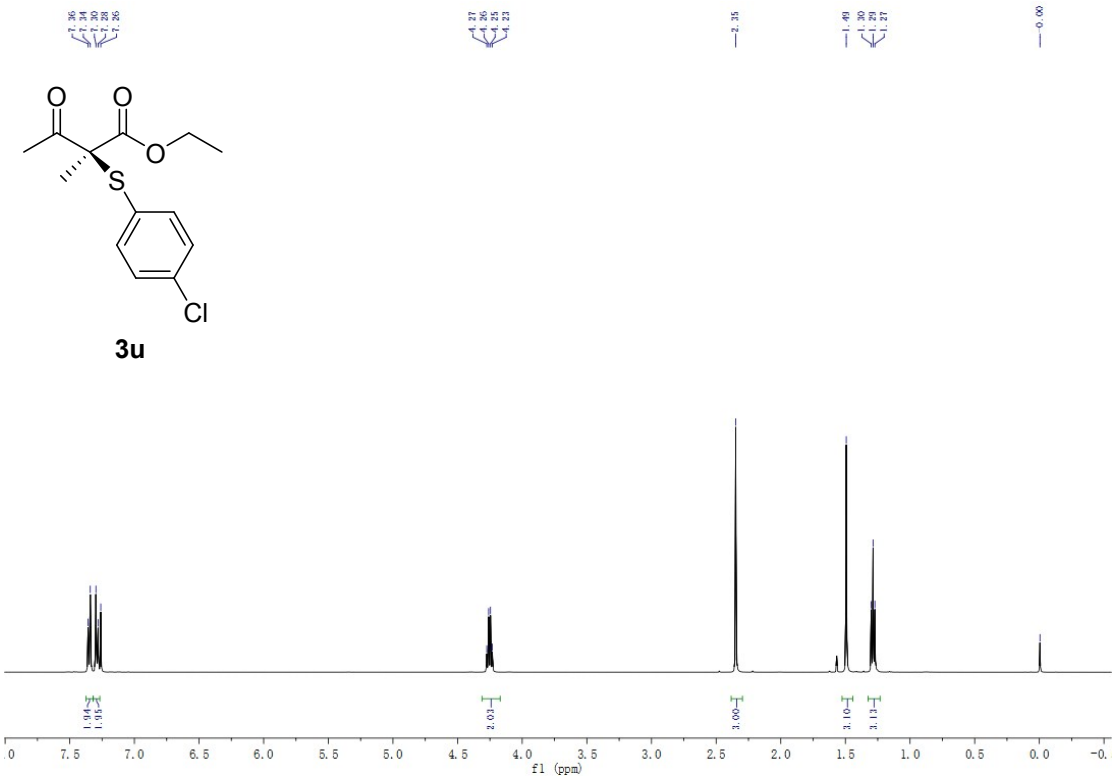

199.24
169.68
136.64
134.67
132.13
131.87
131.61
131.35
127.14
125.92
125.89
125.86
125.83
124.98
122.81
120.64
77.41
77.37
77.27
77.16
76.91
66.06
62.82
25.99
20.90
14.07
O
O
O
S
CF3
f1 (ppm)

3t

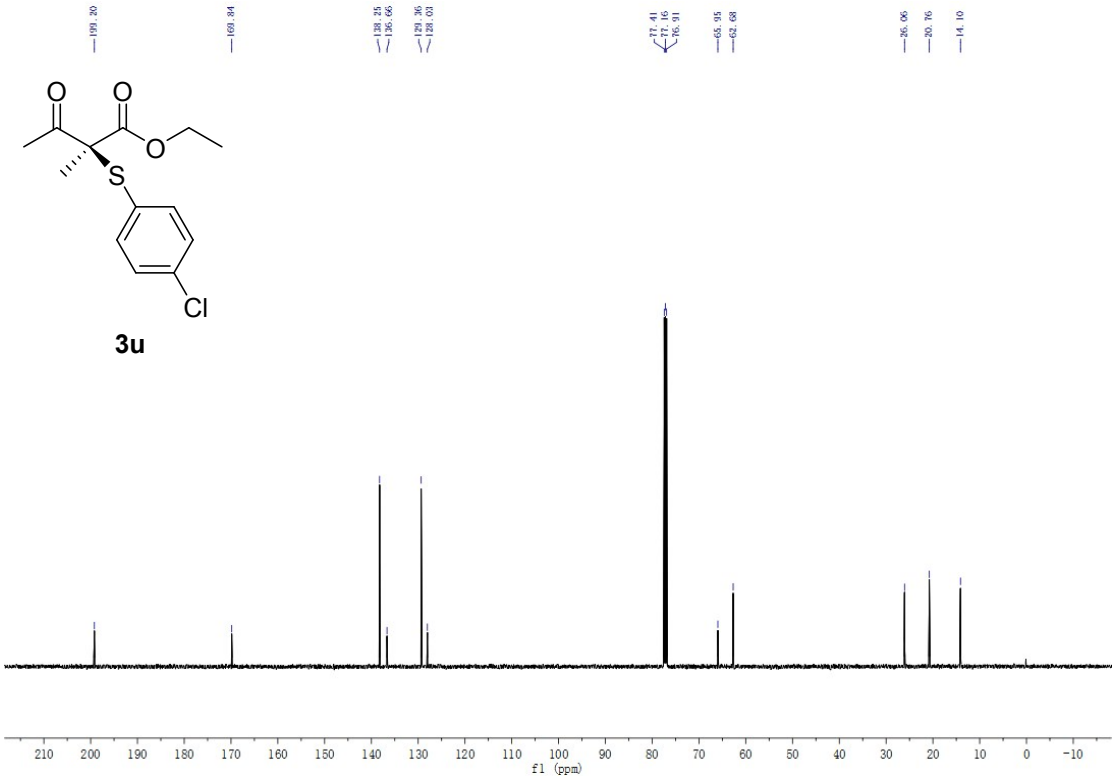

O
O
O
S
CF3

3t

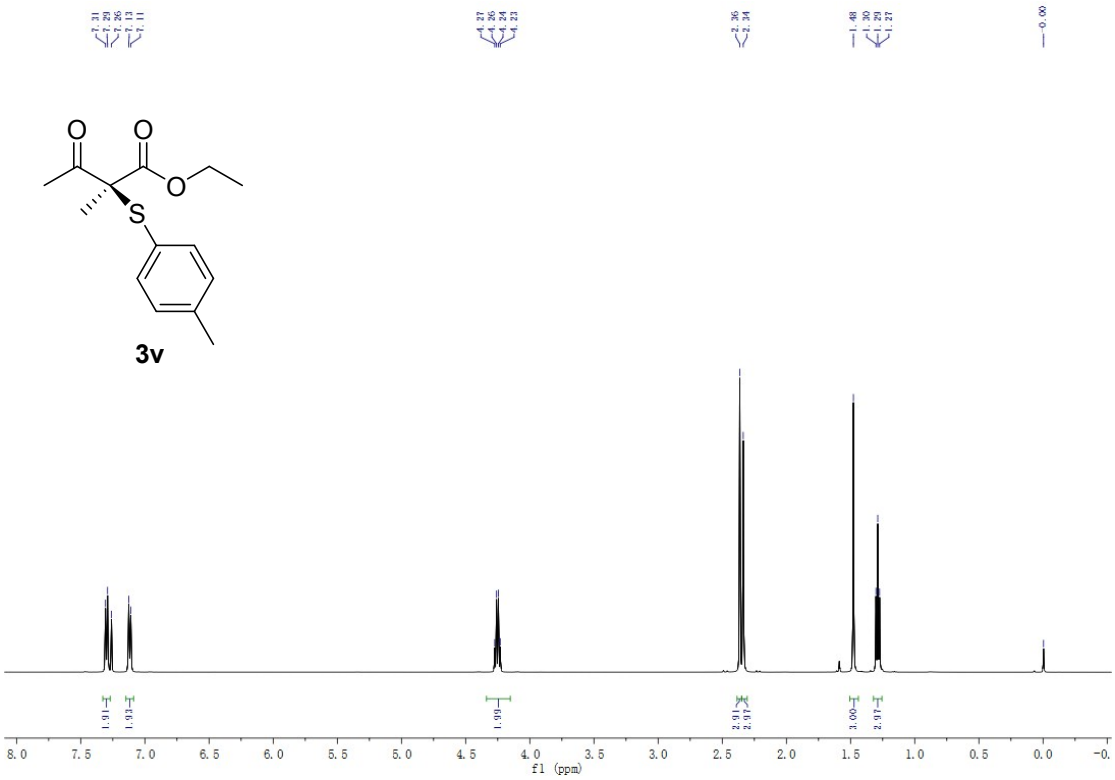
-62.91
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

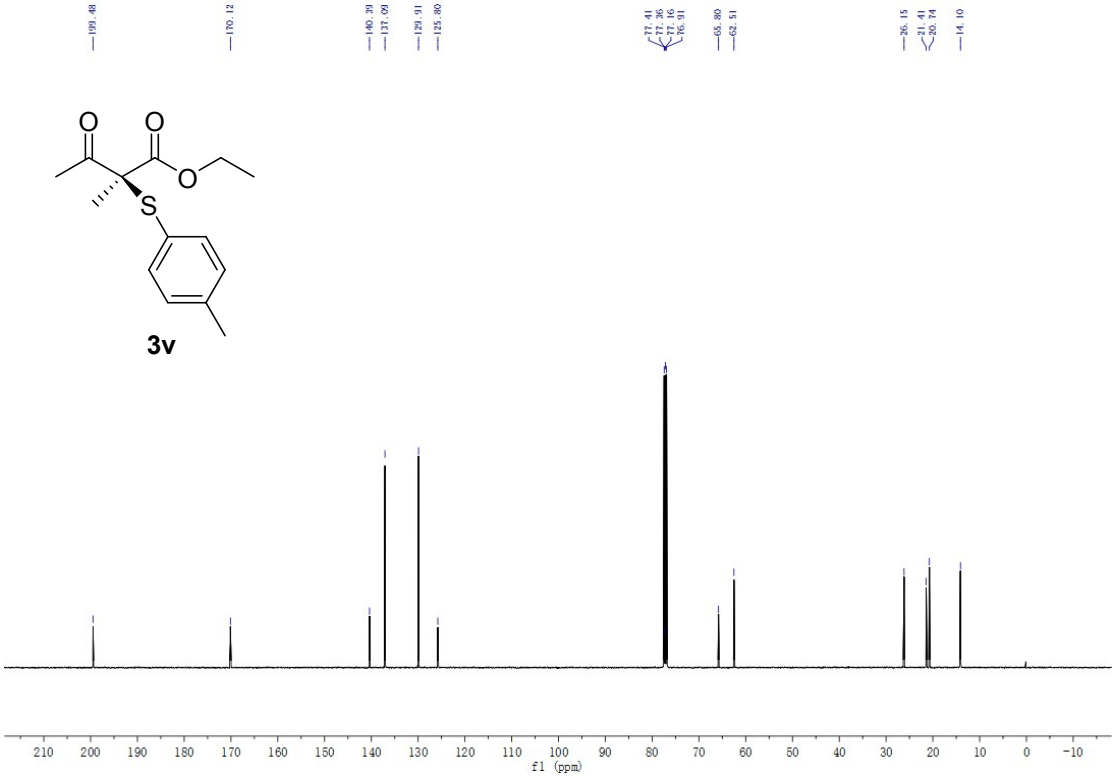

7.36
7.34
7.30
7.28
7.25
4.27
4.26
4.25
4.23
2.35
1.49
1.30
1.29
1.27
0.00
O
O
O
S
Cl
1.94
1.94
2.03
3.00
3.10
3.13
f1 (ppm)

3u


199.20
169.84
138.25
136.66
129.36
128.03
77.41
77.16
76.91
65.95
62.68
26.06
20.76
14.10
O
O
O
S
Cl
f1 (ppm)

3u


7.31
7.29
7.26
7.13
7.11
4.37
4.35
4.24
4.23
2.36
2.34
1.48
1.30
1.29
1.27
0.00
O
O
O
S
3v
1.91
1.93
1.99
2.91
2.97
3.00
2.97
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
0.0
f1 (ppm)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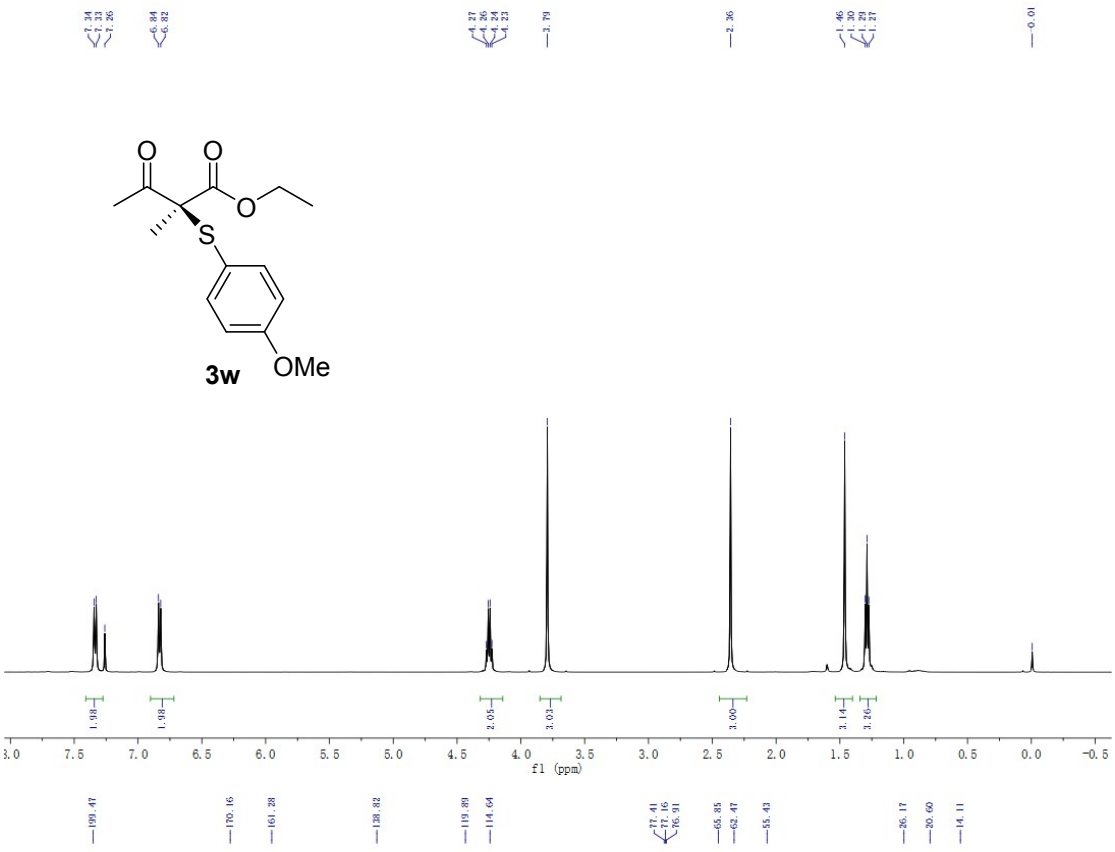
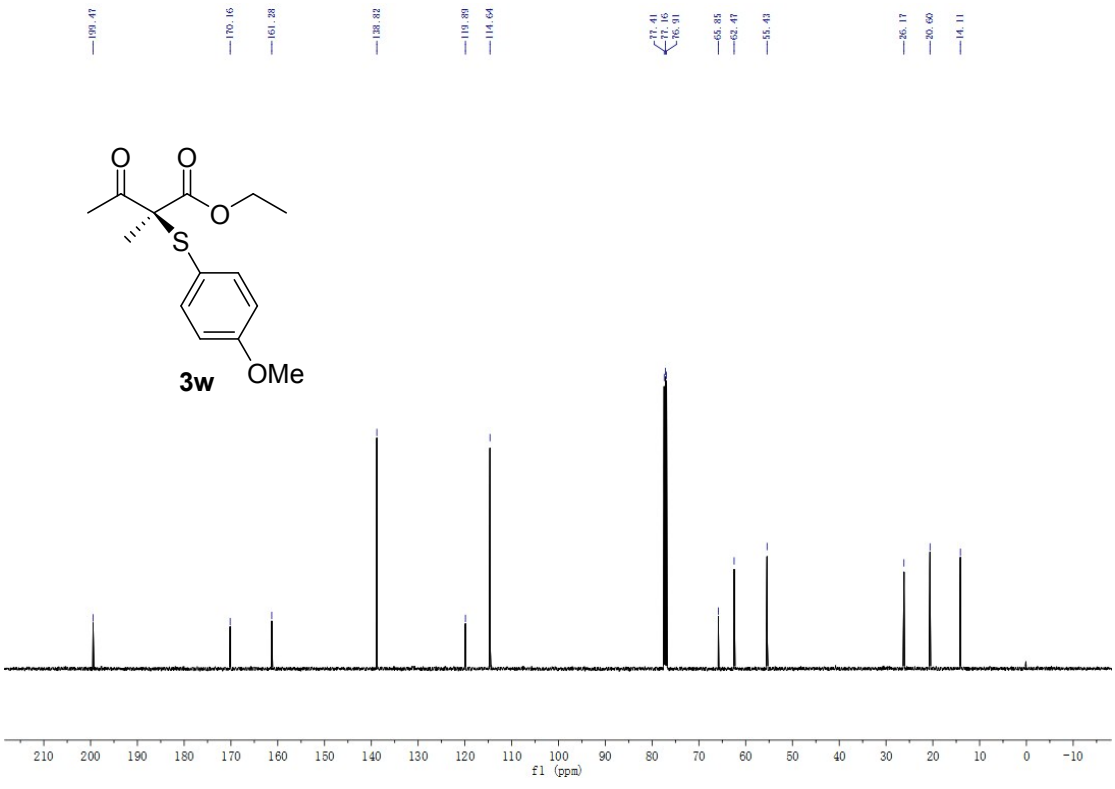
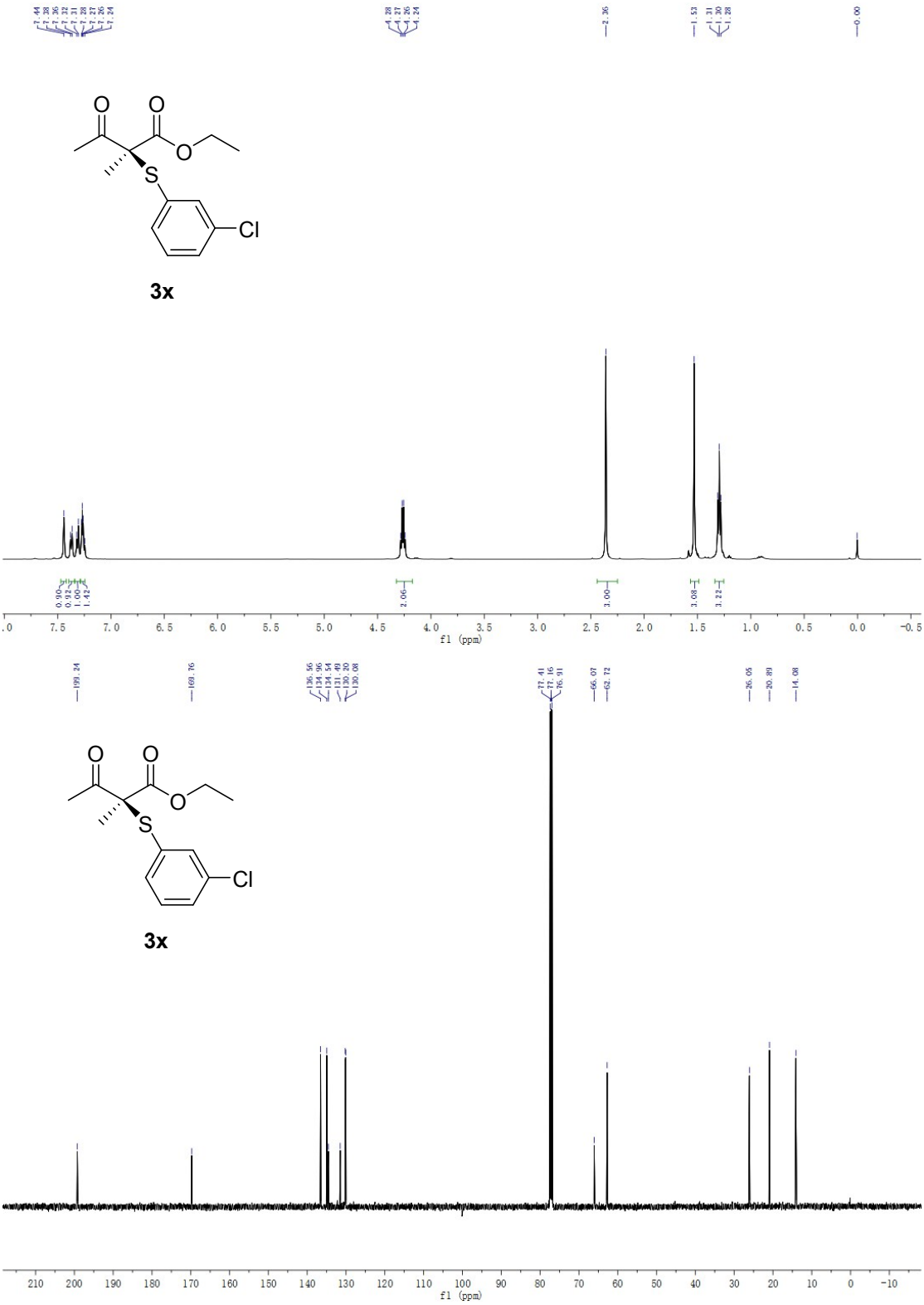
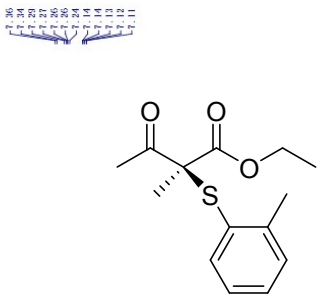
170.12
140.39
137.09
129.91
125.80
77.41
77.16
76.91
65.80
62.51
26.15
21.41
20.74
14.10
O
O
O
S
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

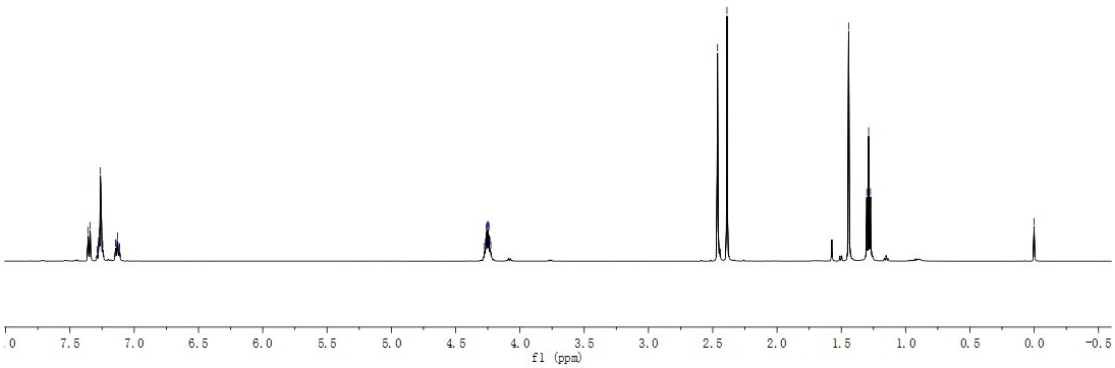

7.34
7.33
7.25
6.84
6.82
4.27
4.26
4.24
4.23
3.79
2.36
1.46
1.30
1.29
1.27
0.01
O
O
O
S
OMe
3w
1.98
1.98
2.05
3.03
3.00
3.14
3.26
f1 (ppm)


199.47
170.16
161.28
138.82
119.89
114.64
77.41
77.16
76.91
65.85
62.47
55.43
26.17
20.60
14.11
O
O
O
S
OMe
3w
f1 (ppm)

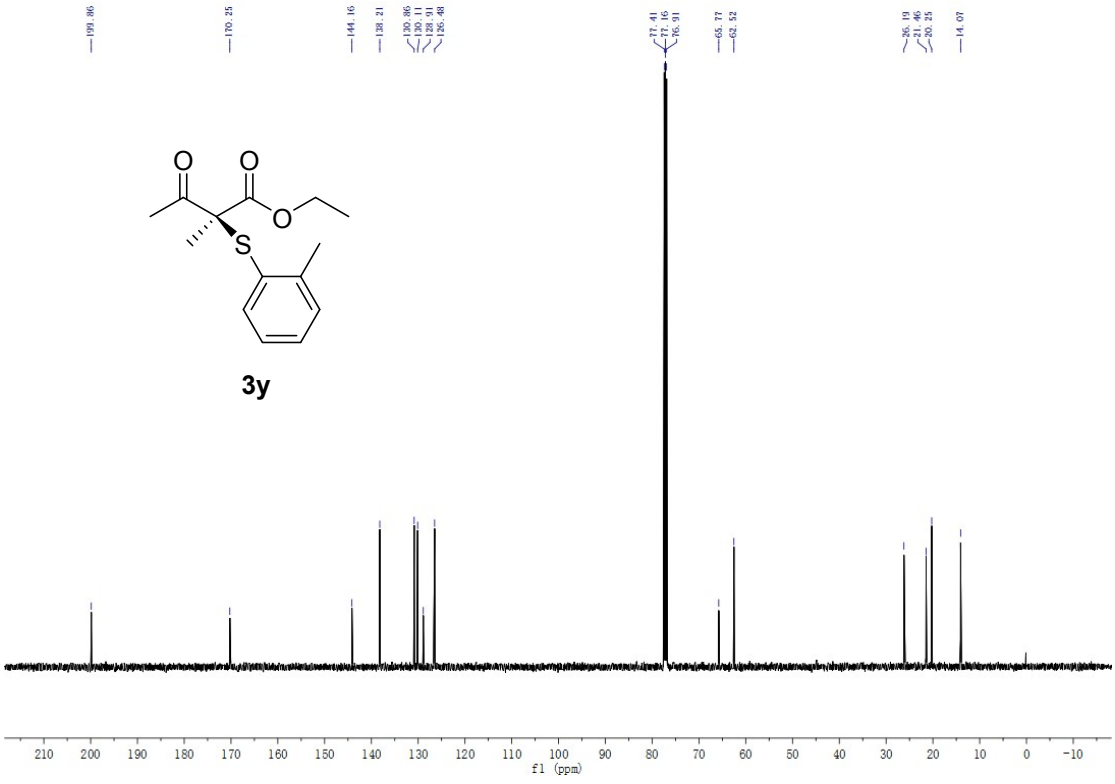

O
O
O
S
Cl
3x
f1 (ppm)
O
O
O
S
Cl
3x
f1 (ppm)

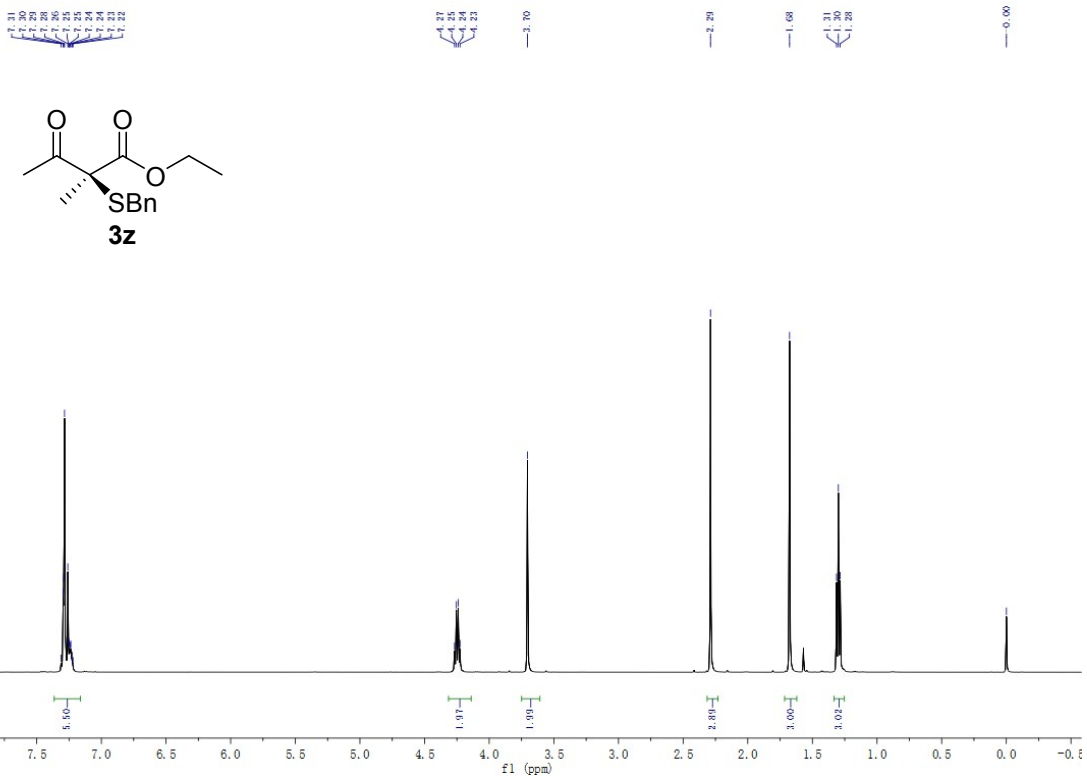


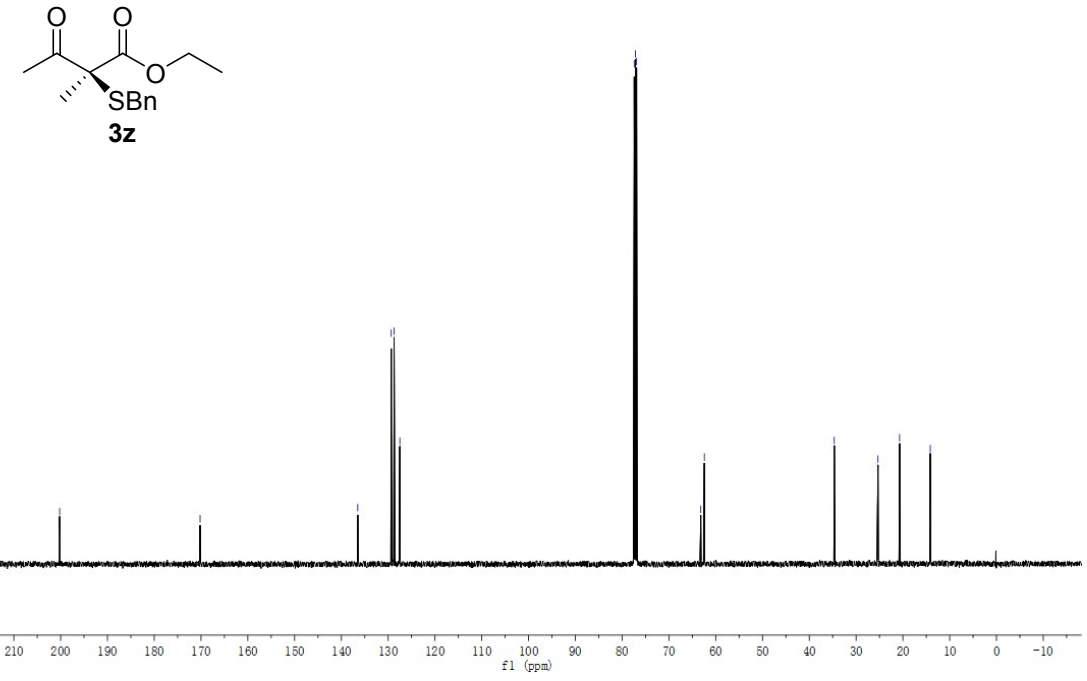
3y

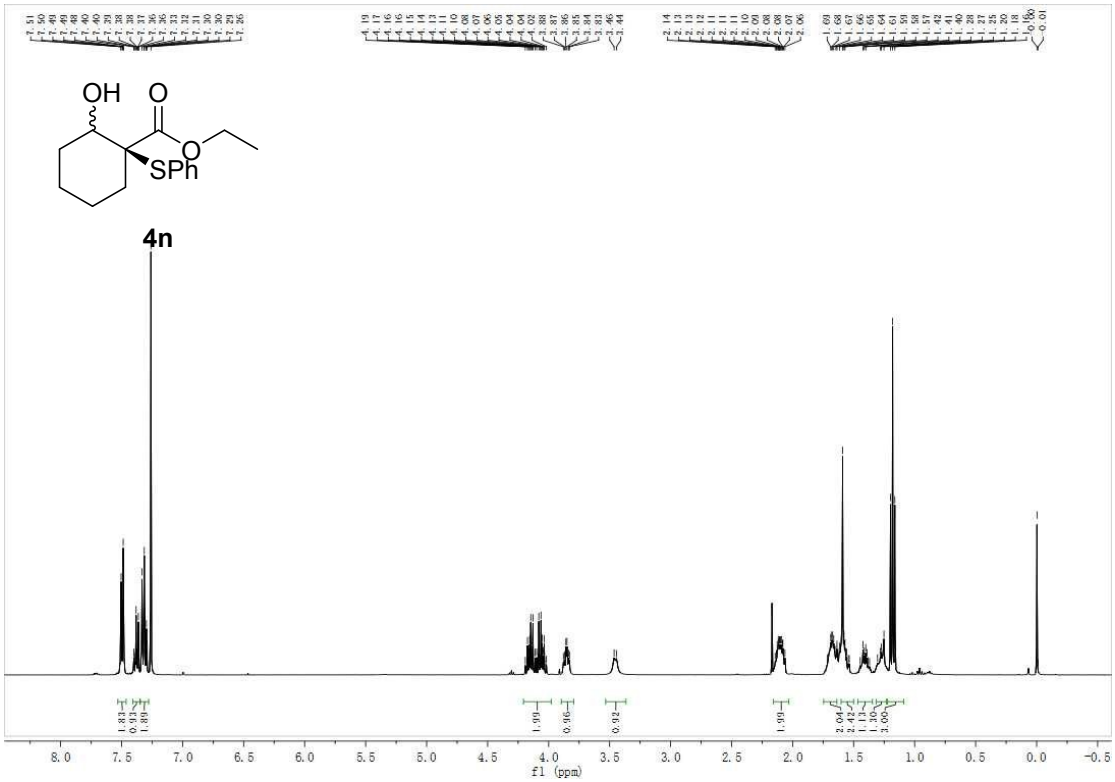


3y

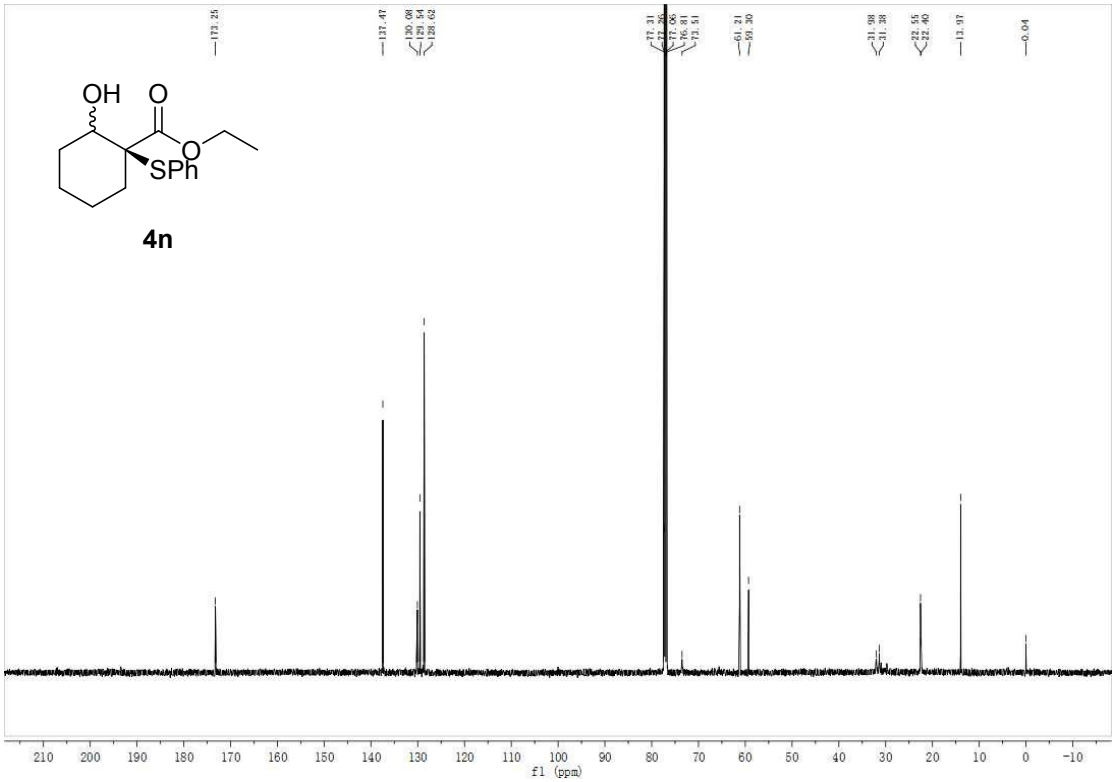



SBn
3z
f1 (ppm)


SBn
3z
f1 (ppm)

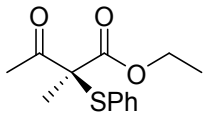


4n



4n

HPLC charts



3a

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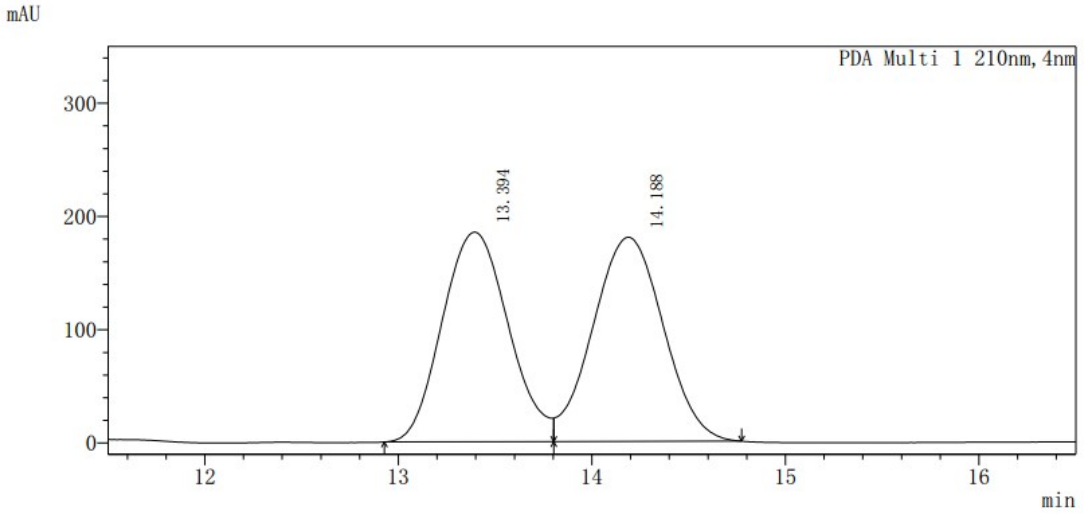
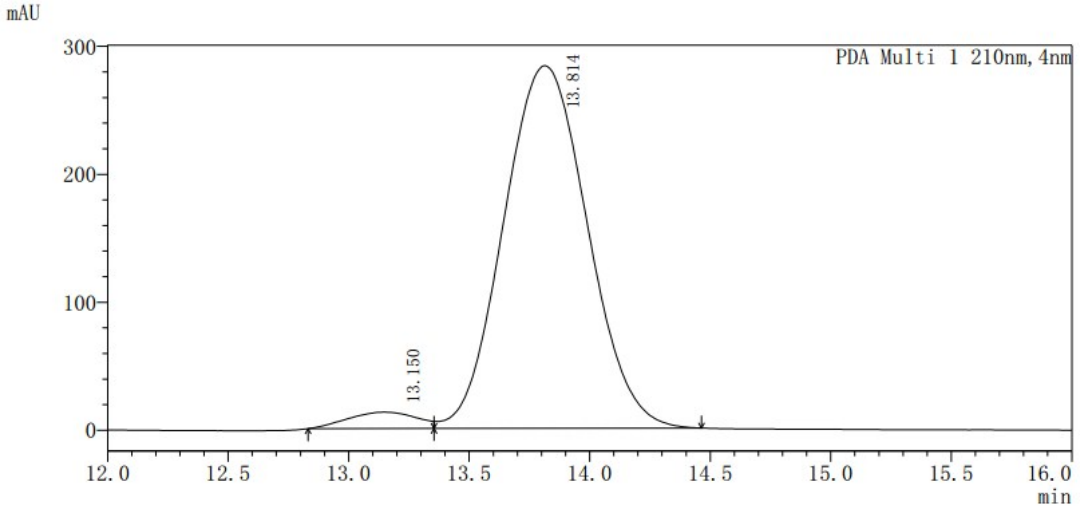


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.394	185094	4403491	49.153
2	14.188	180336	4555295	50.847

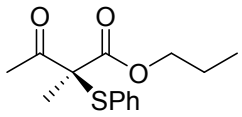
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.150	12754	253861	3.569
2	13.814	283389	6858829	96.431



3b

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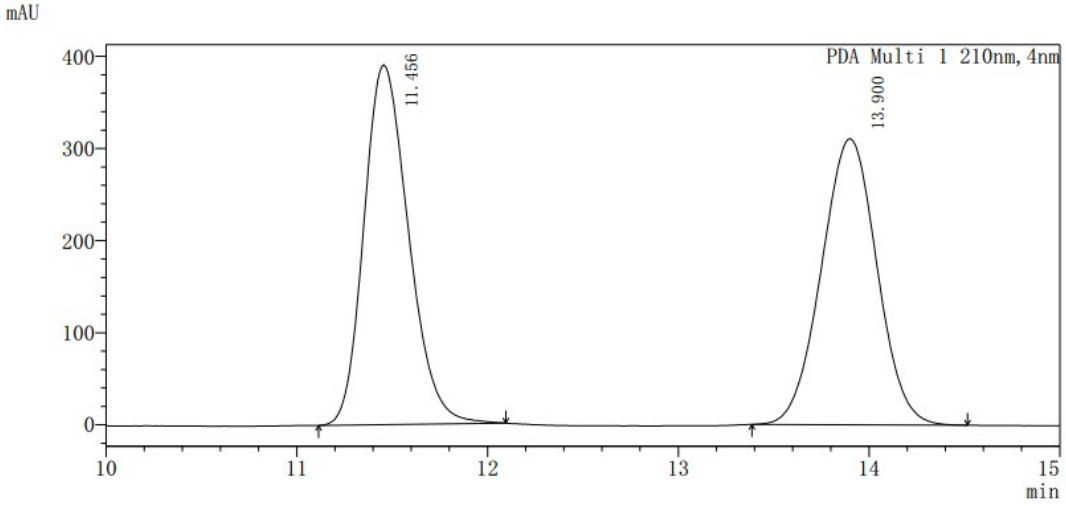
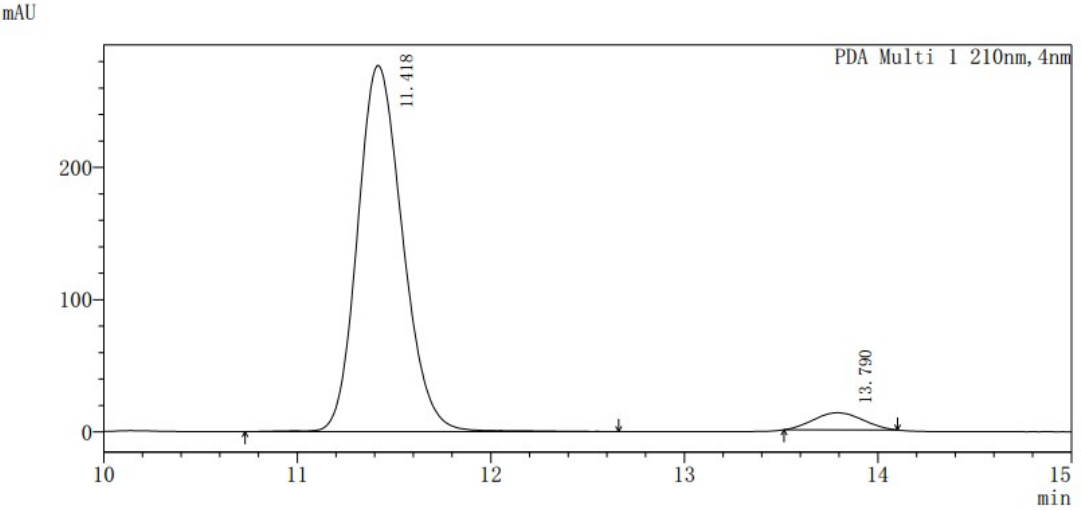


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.456	390559	6352540	50.267
2	13.900	310490	6285119	49.733

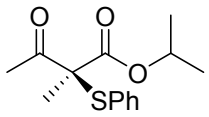
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.418	276855	4466518	95.093
2	13.790	13028	230484	4.907



3c

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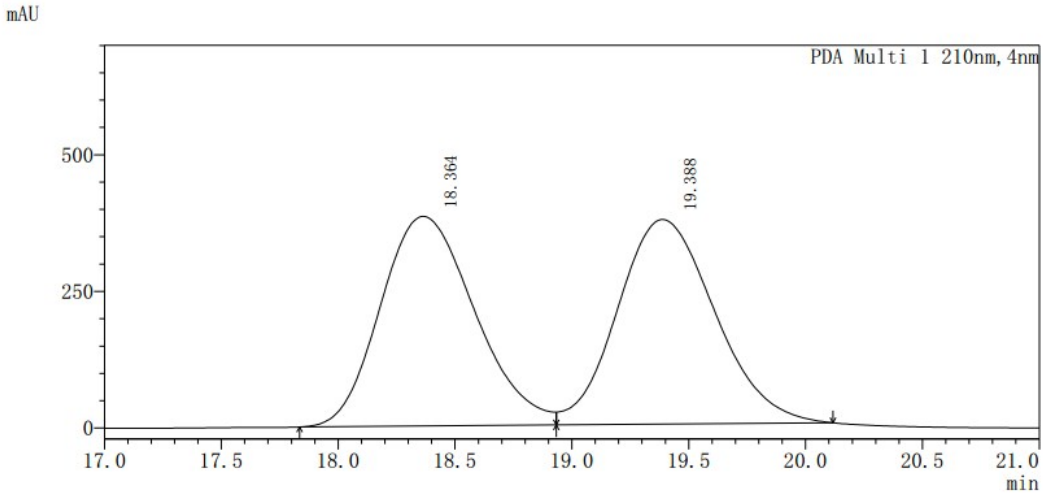
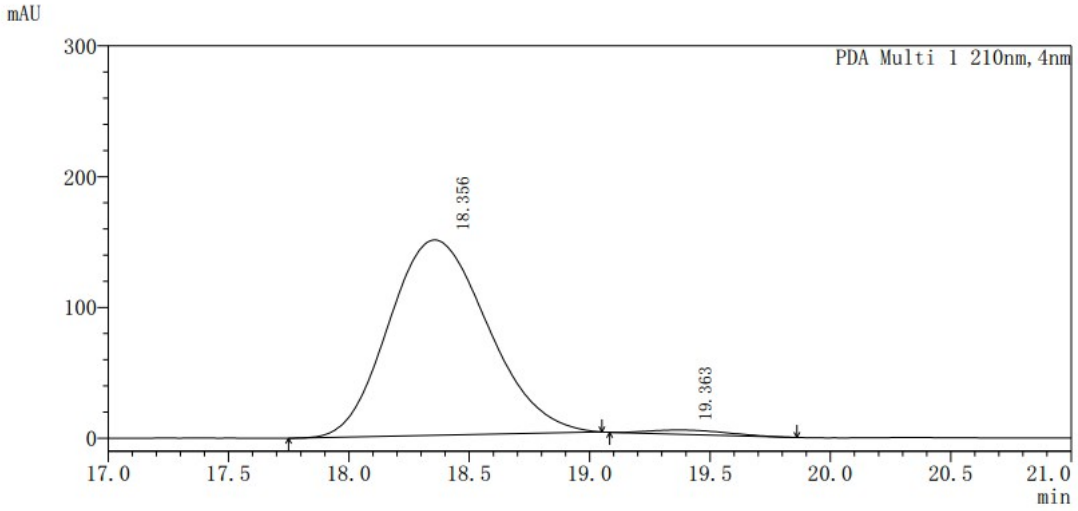


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	18.364	383462	10771442	49.840
2	19.388	374228	10840424	50.160

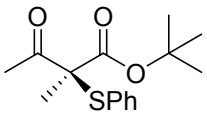
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	18.356	149492	4286393	98.321
2	19.363	3208	73214	1.679



3d

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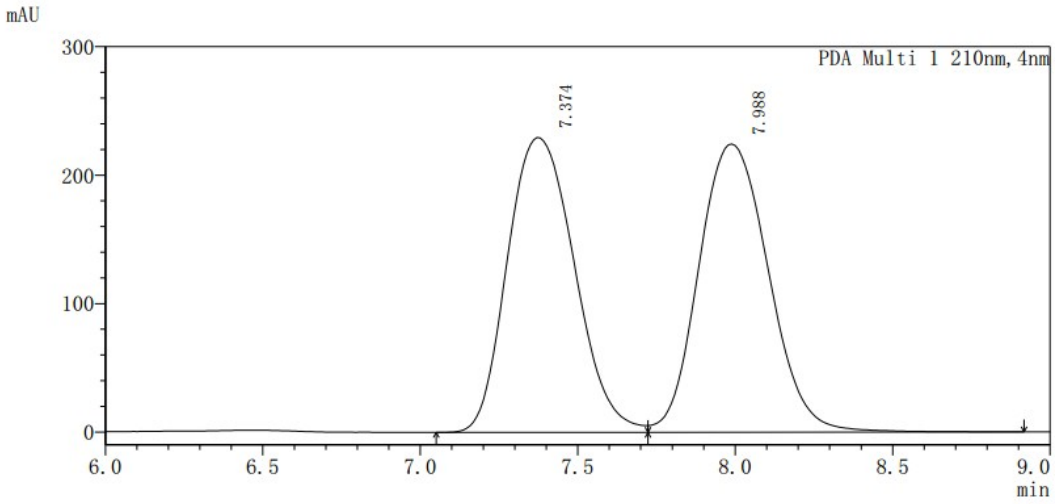
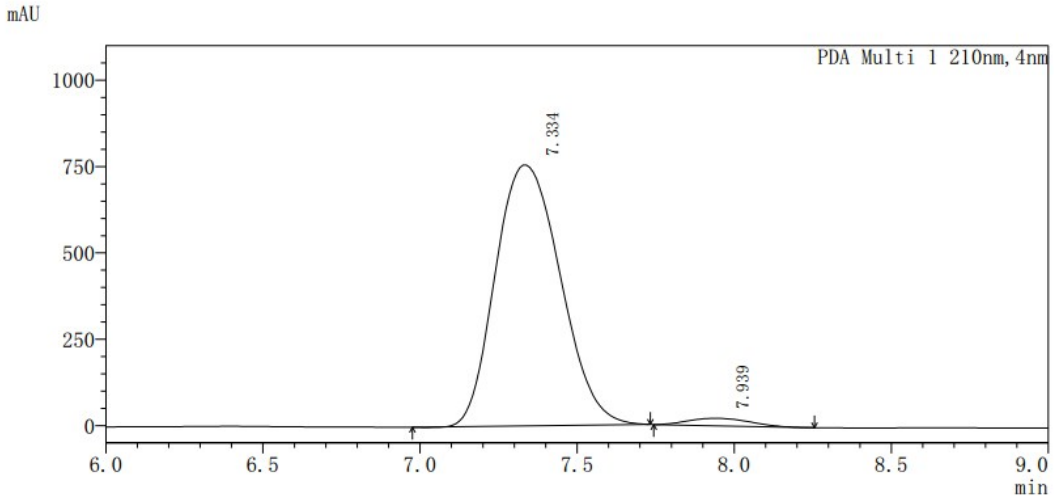


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.374	229580	3406668	49.639
2	7.988	224453	3456193	50.361

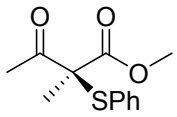
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.334	755838	10922182	97.417
2	7.939	21618	289632	2.583



3e

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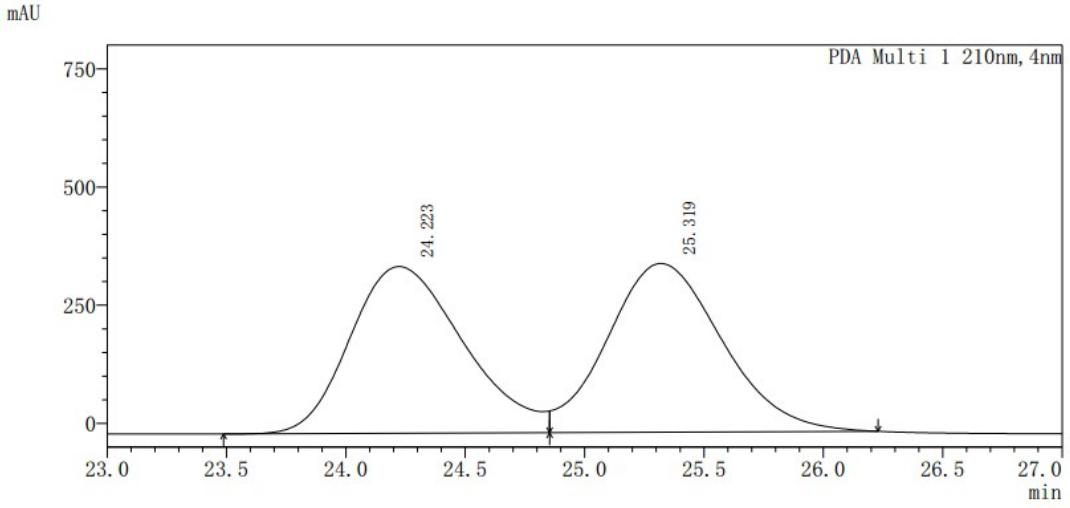

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.223	352661	11665011	49.481
2	25.319	356846	11909516	50.519

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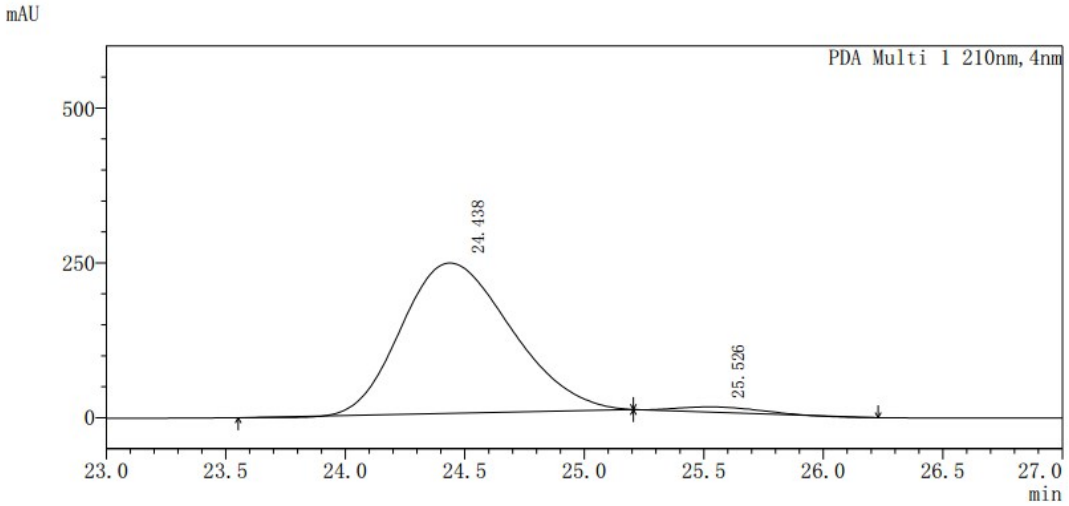
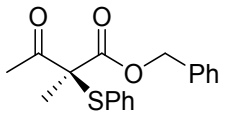


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.438	242770	7762476	97.658
2	25.526	8388	186184	2.342



3f

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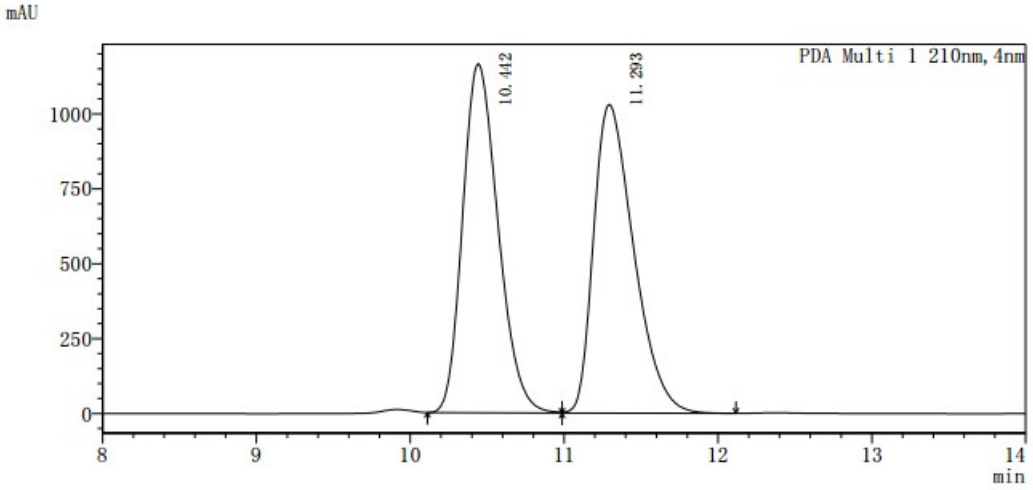
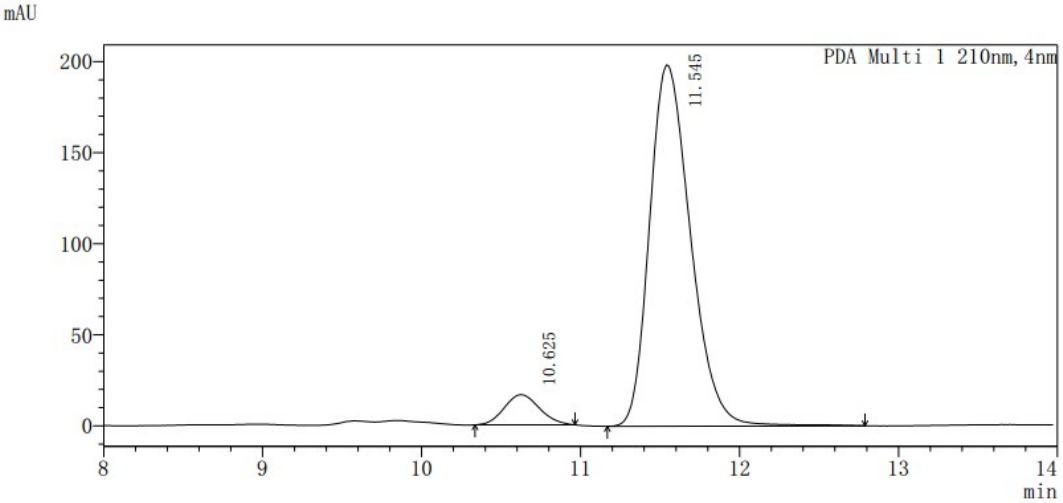


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.442	1164496	18654123	49.964
2	11.293	1029406	18680899	50.036

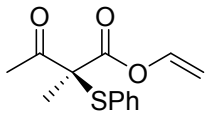
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.625	16535	254968	6.701
2	11.545	198208	3549835	93.299



3g

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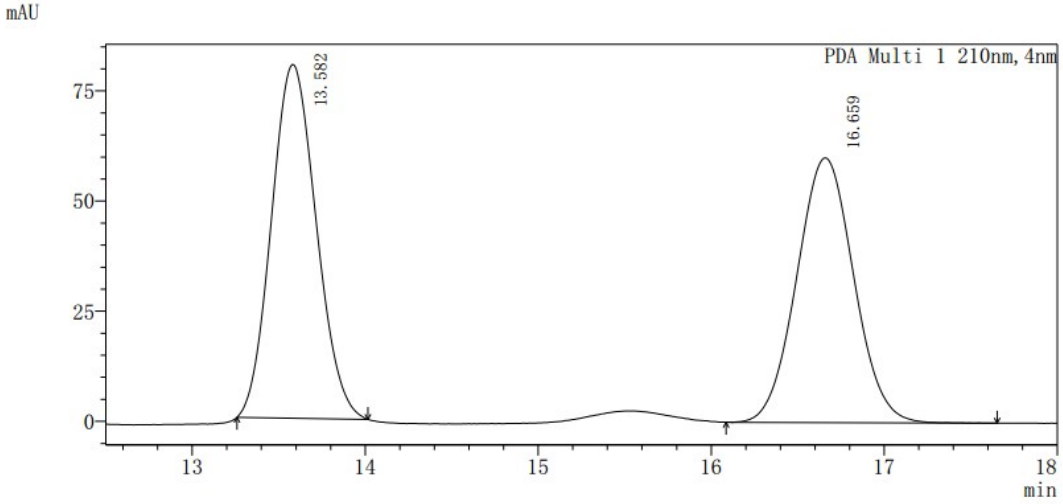

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.582	80294	1450974	51.354
2	16.659	60086	1374446	48.646

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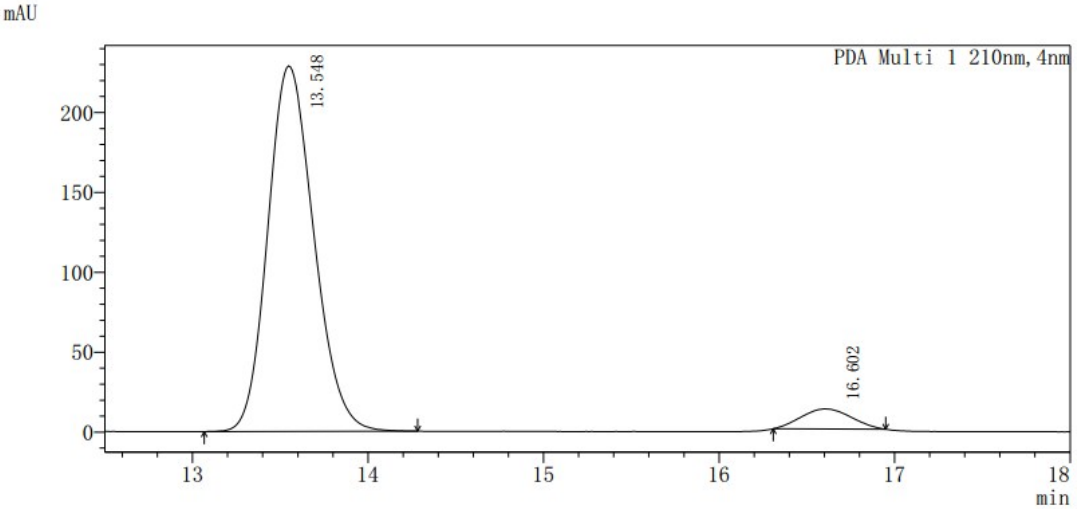
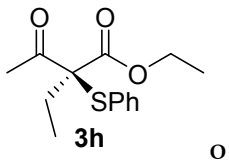


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.548	228693	4178667	94.362
2	16.602	12564	249666	5.638



3h

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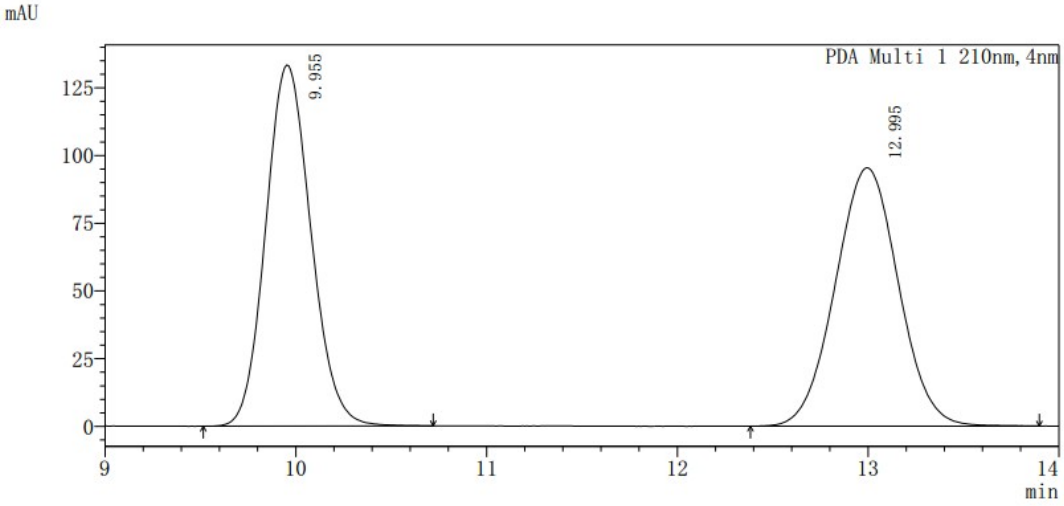
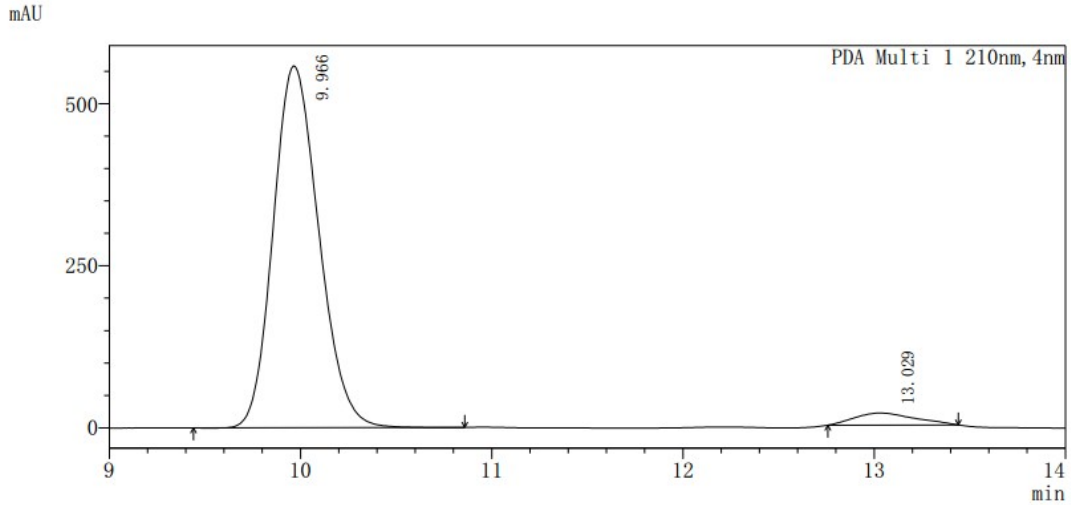


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.955	133267	2197114	50.008
2	12.995	95360	2196440	49.992

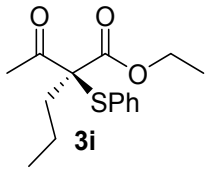
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.966	558089	9259004	95.792
2	13.029	18497	406769	4.208



3i

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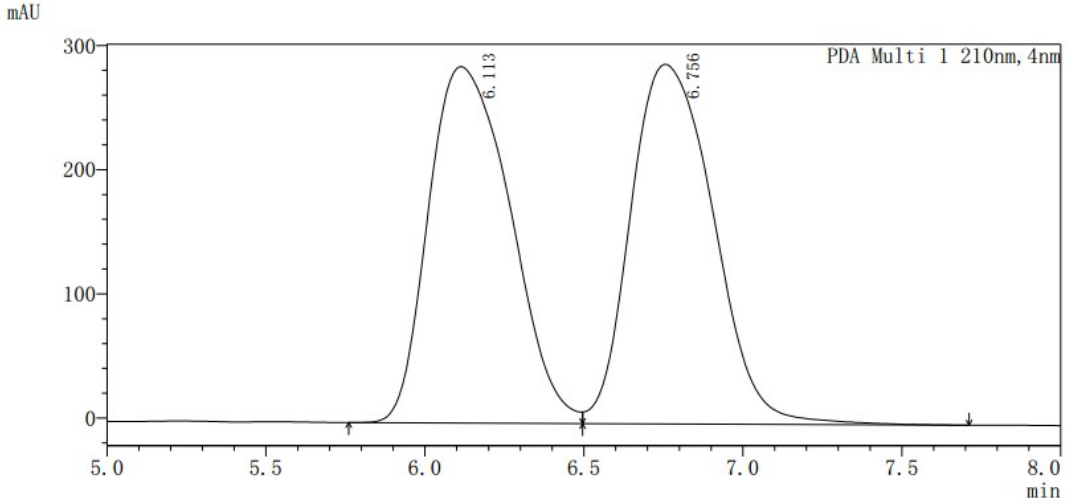

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.113	287044	5146677	49.463
2	6.756	289426	5258419	50.537

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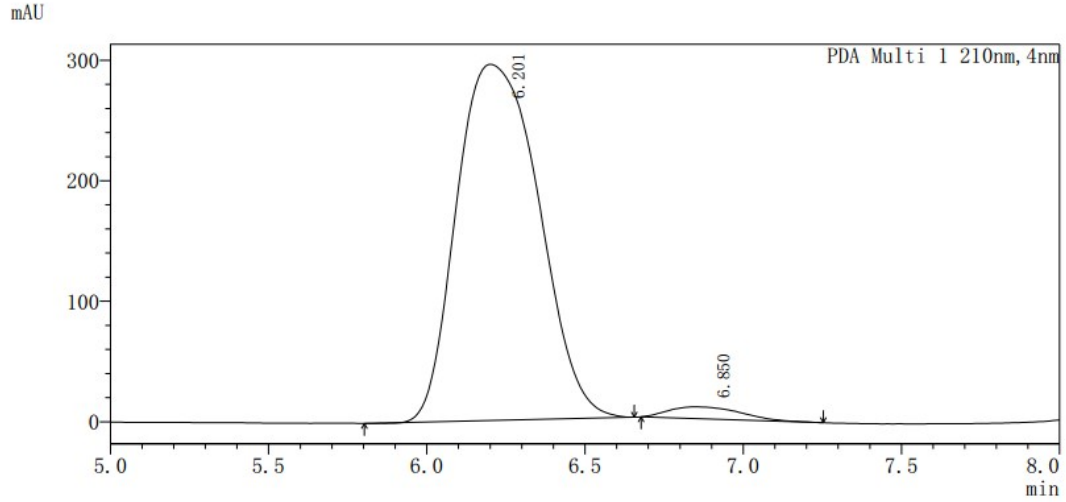
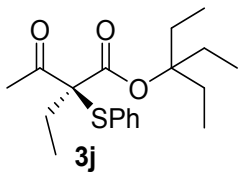


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.201	295505	5362433	97.227
2	6.850	9659	152916	2.773



3j

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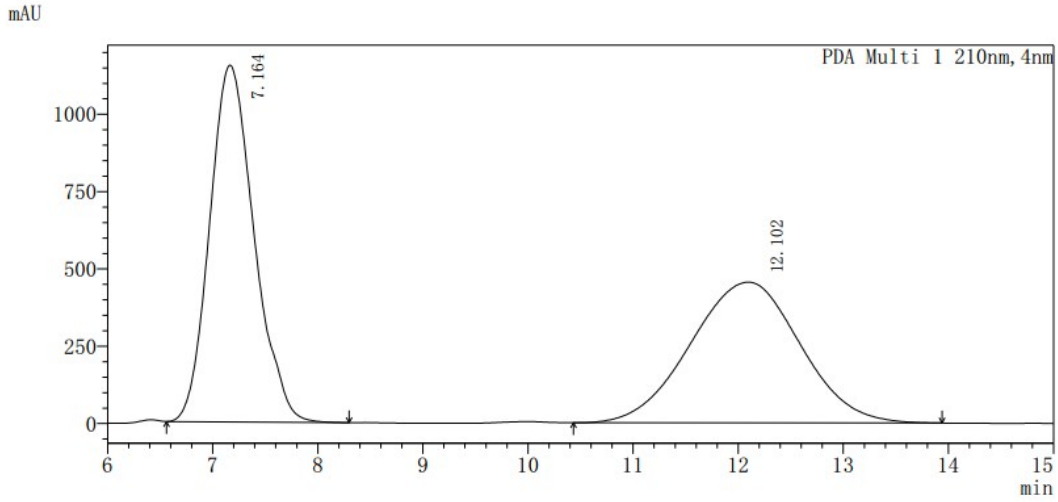

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.164	1153442	33905500	50.634
2	12.102	454960	33055994	49.366

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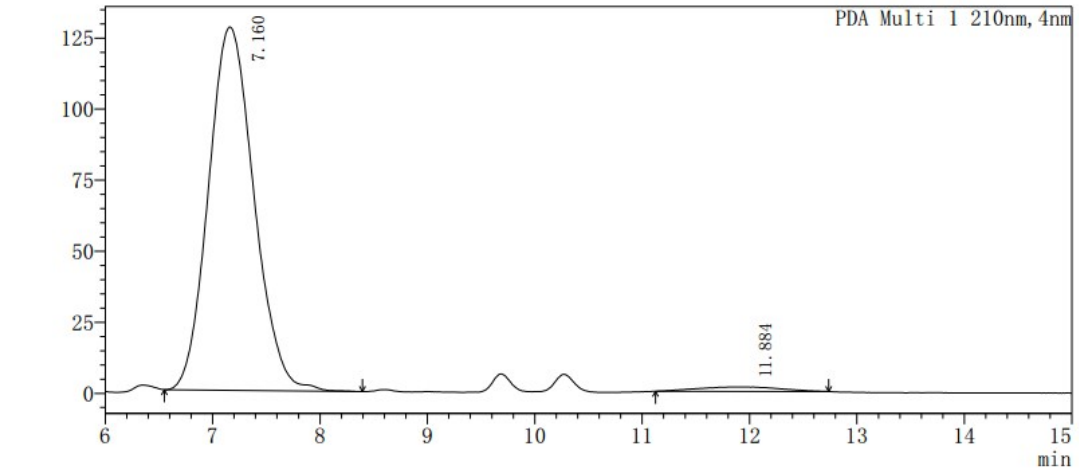
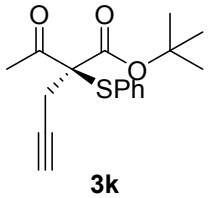


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.160	127843	3766424	97.791
2	11.884	1567	85085	2.209



3k

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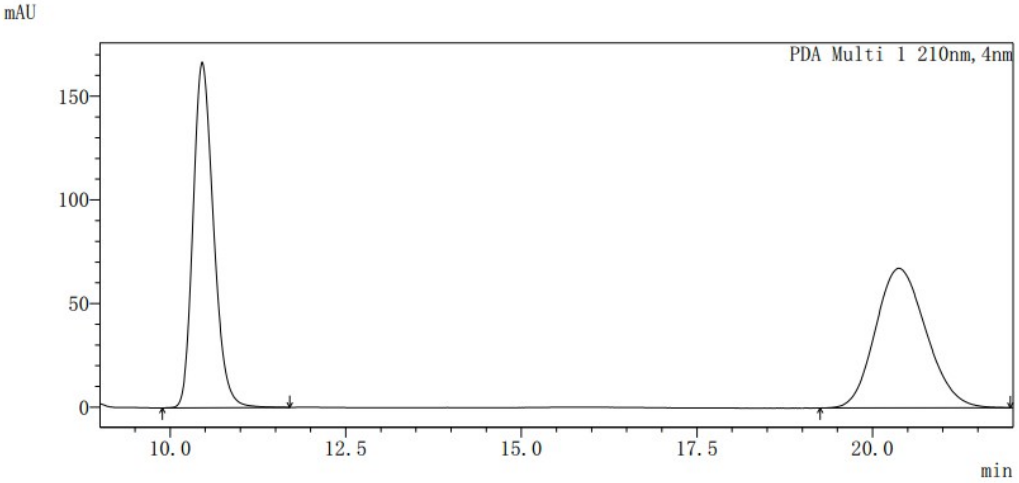
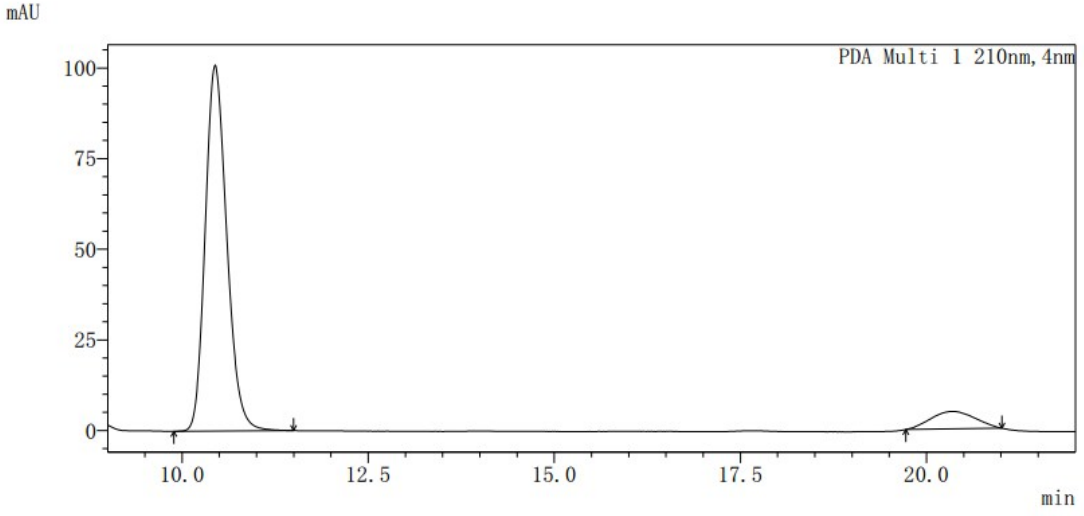


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.456	166612	3376968	49.978
2	20.375	67334	3379968	50.022

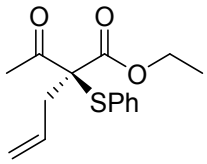
<Chromatogram>



<Peak Results>

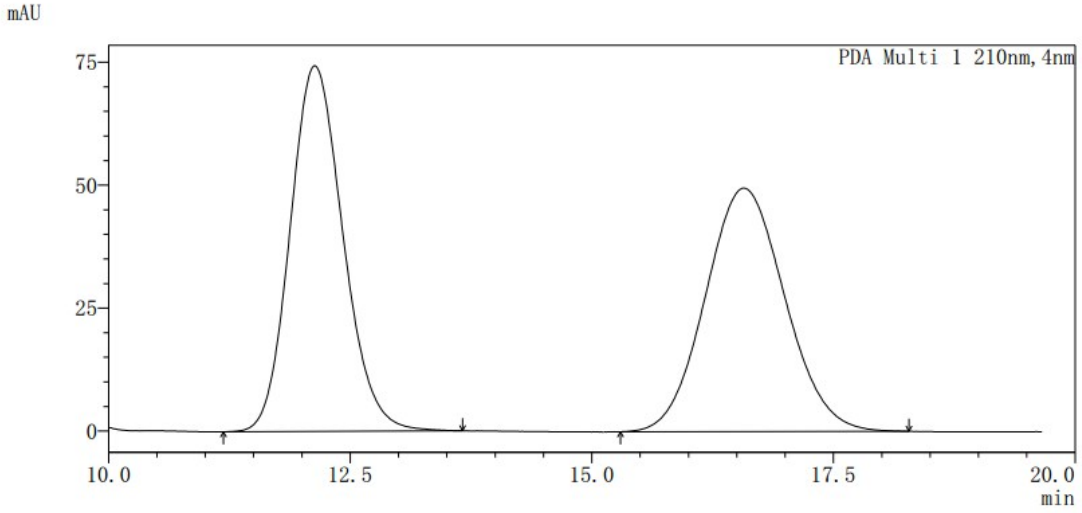
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.442	100907	2033950	91.071
2	20.354	4822	199411	8.929



3l

<Chromatogram>

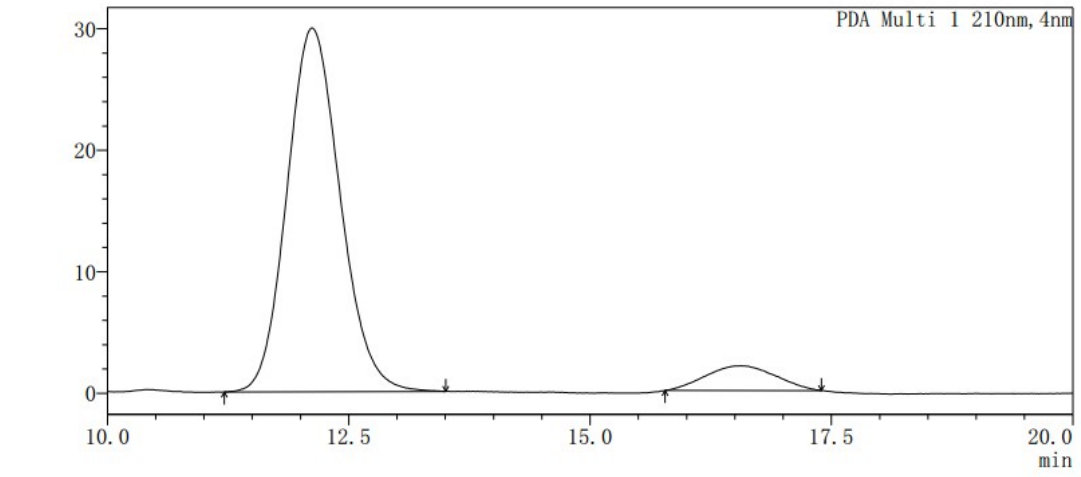


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.133	74358	2833083	50.026
2	16.574	49515	2830194	49.974

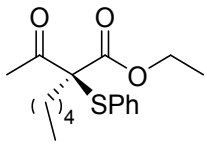
<Chromatogram>



<Peak Results>

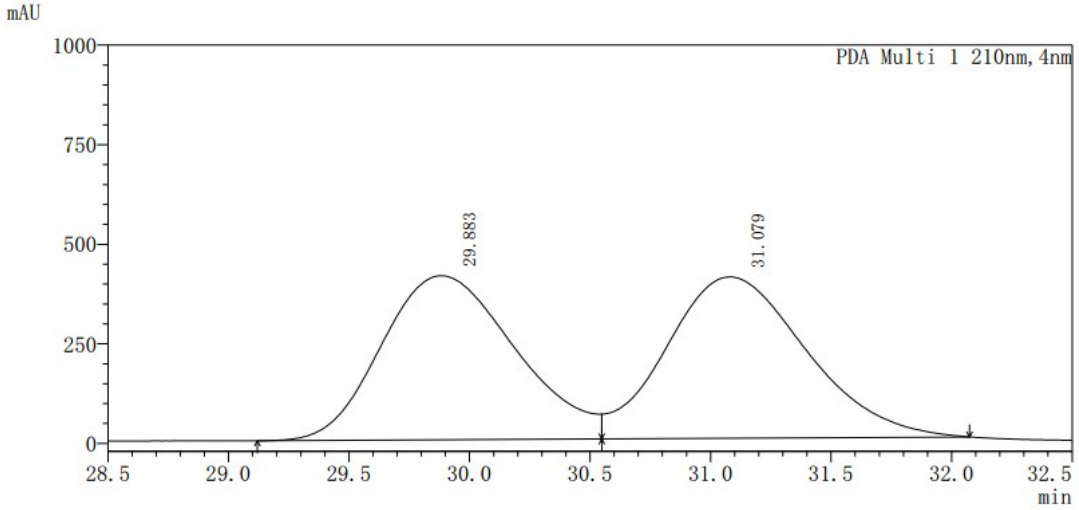
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.121	29932	1147664	91.772
2	16.567	2036	102896	8.228



3m

<Chromatogram>

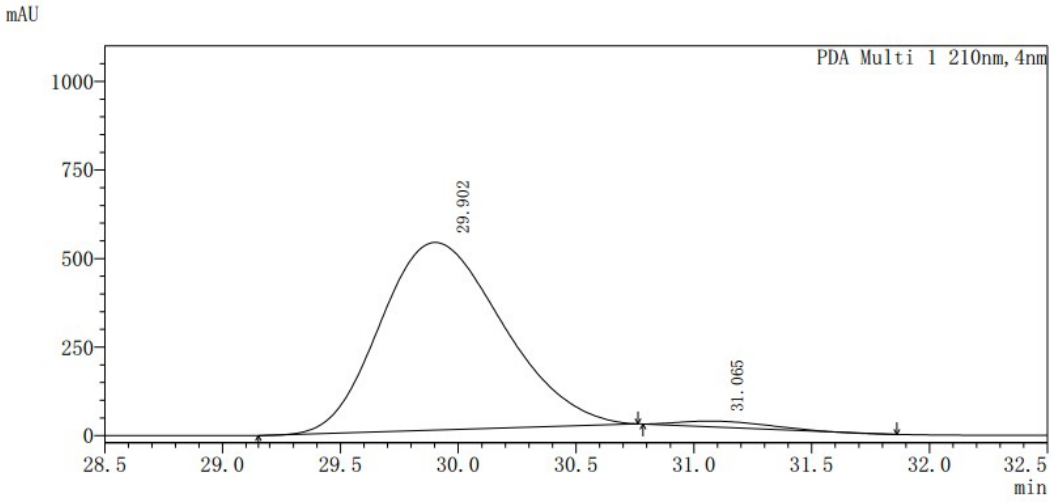


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	29.883	412088	15926621	49.383
2	31.079	405078	16324842	50.617

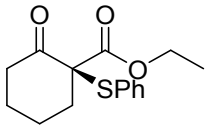
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	29.902	529723	19180398	97.933
2	31.065	15761	404779	2.067



3n

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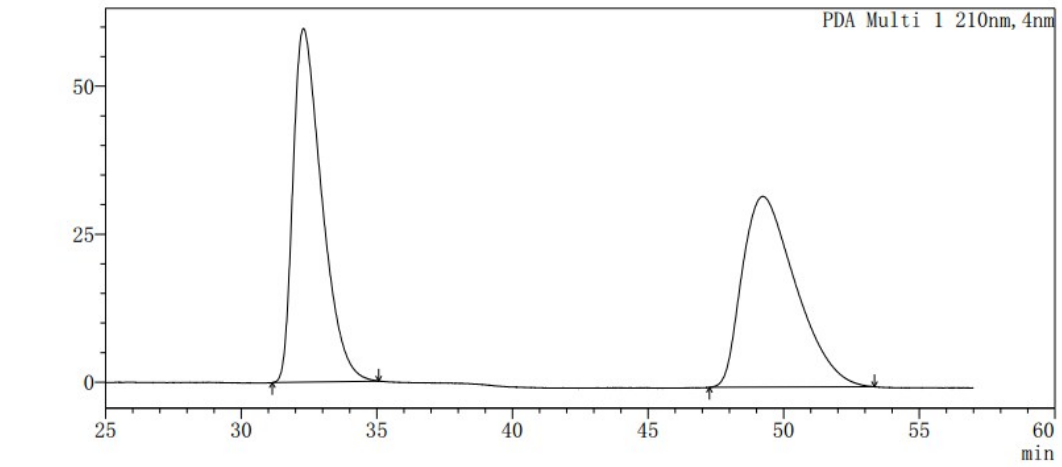
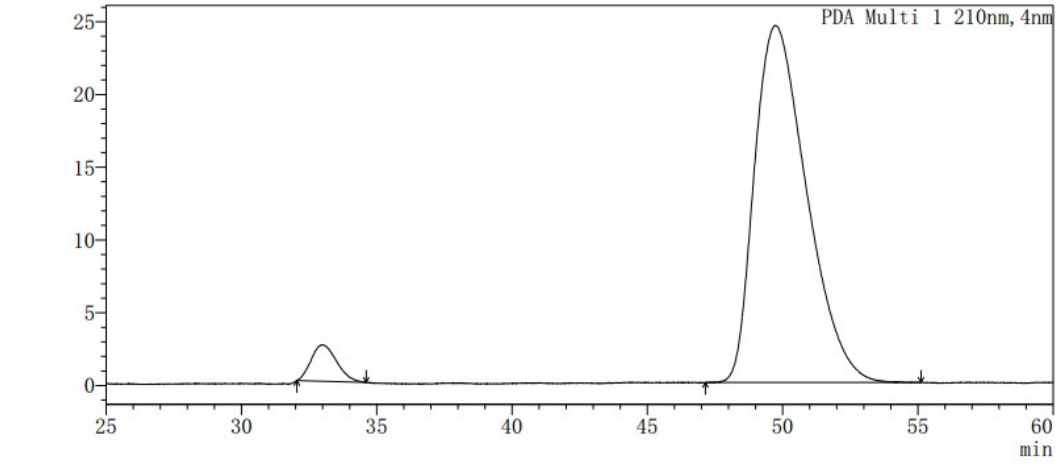


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.302	59749	4405795	49.892
2	49.231	32228	4424846	50.108

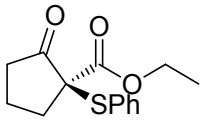
<Chromatogram>



<Peak Results>

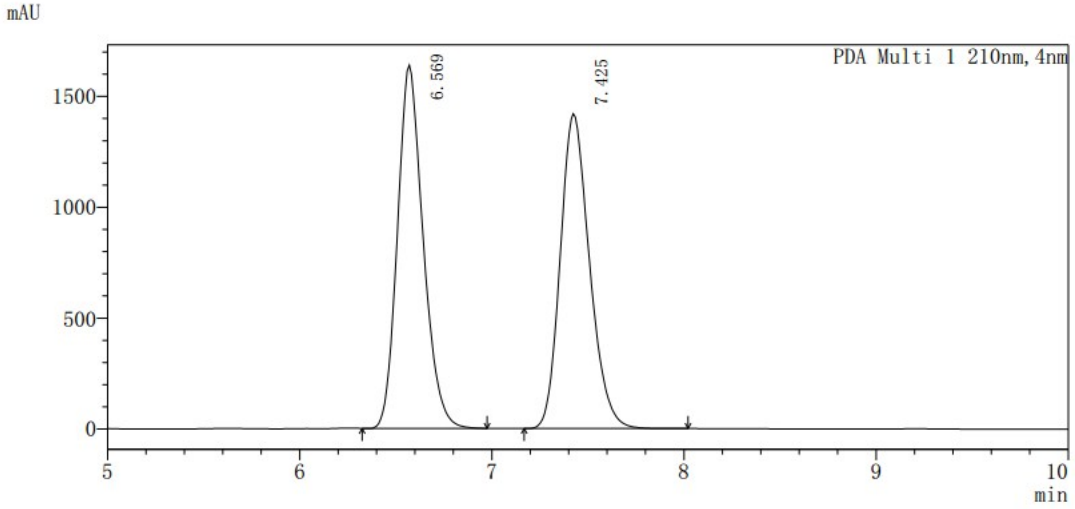
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	33.003	2499	163256	4.724
2	49.738	24536	3292722	95.276



3o

<Chromatogram>

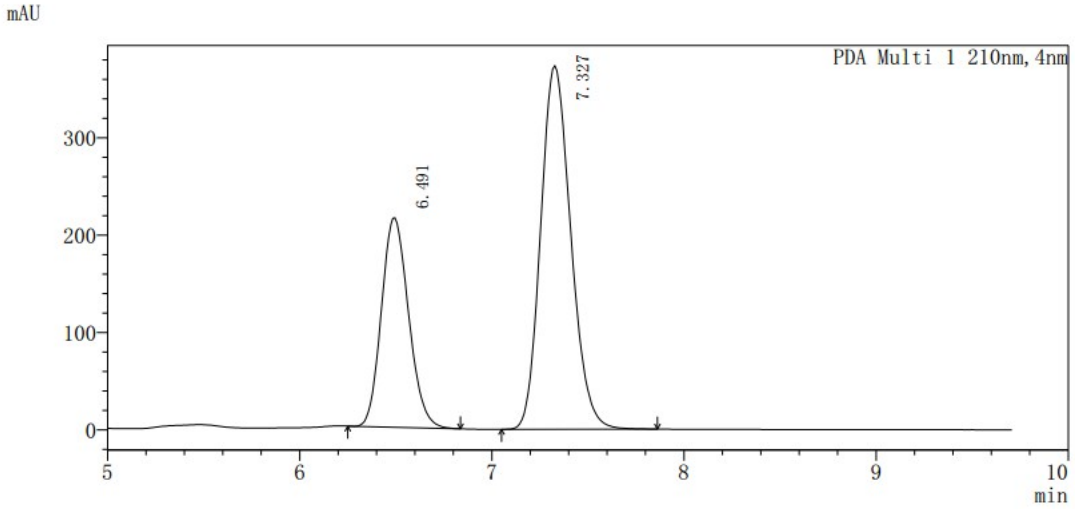


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.569	1638066	15206356	50.353
2	7.425	1419948	14992978	49.647

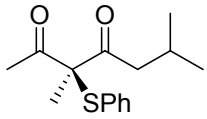
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.491	214925	2113829	34.193
2	7.327	373090	4068148	65.807



3p

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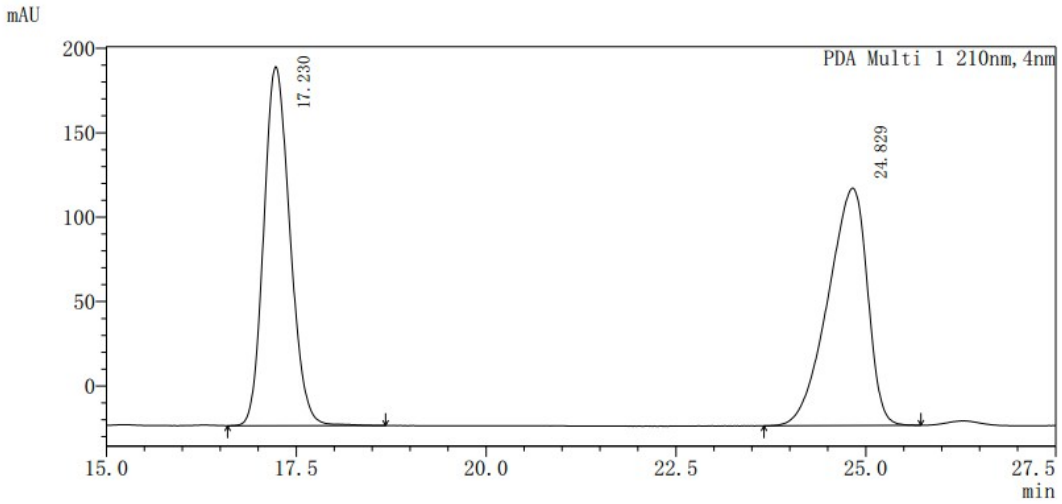

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.230	212519	5092845	50.052
2	24.829	140580	5082227	49.948

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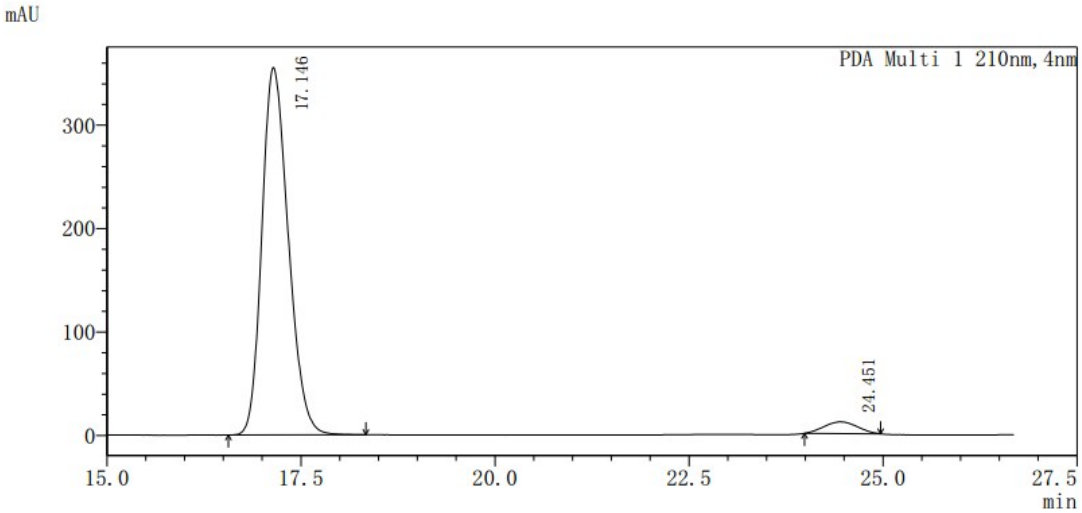
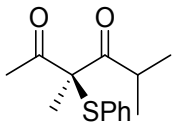


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.146	355095	8406987	96.136
2	24.451	11289	337880	3.864



3q

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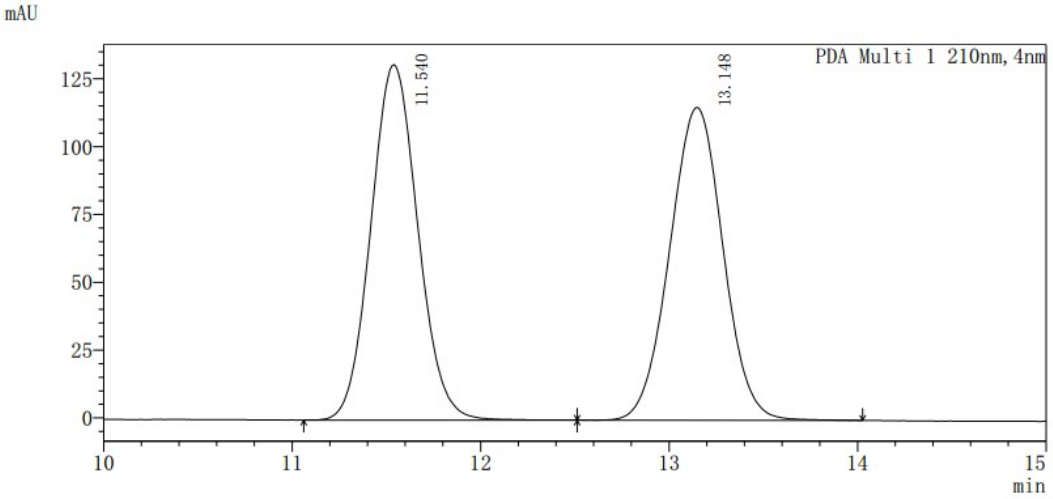

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.540	131018	2272540	50.028
2	13.148	115351	2270022	49.972

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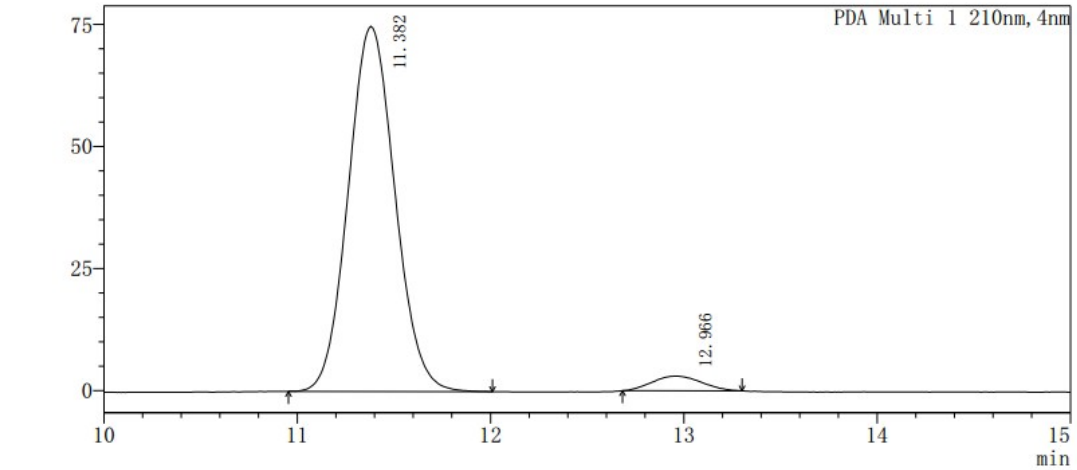
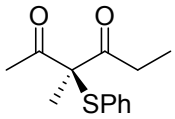


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.382	74806	1256870	95.915
2	12.966	3024	53523	4.085



3r

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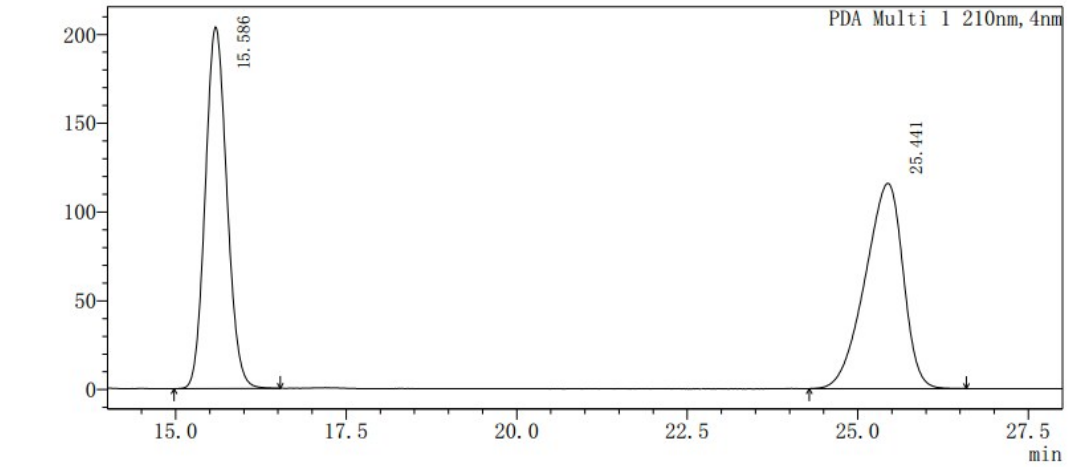
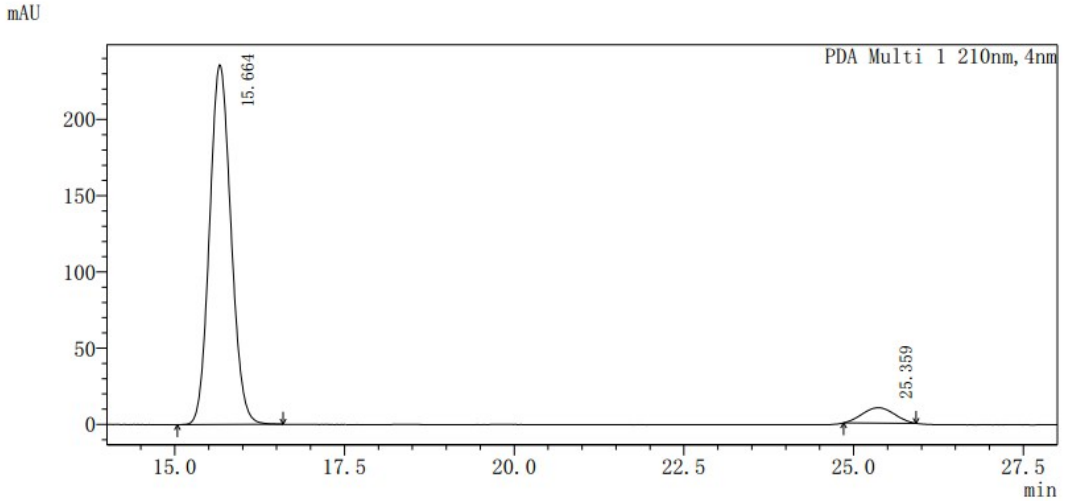


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	15.586	203621	4482230	49.991
2	25.441	115636	4483807	50.009

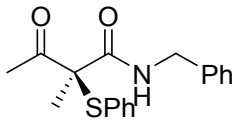
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	15.664	235817	5172497	94.020
2	25.359	10094	328997	5.980



3s

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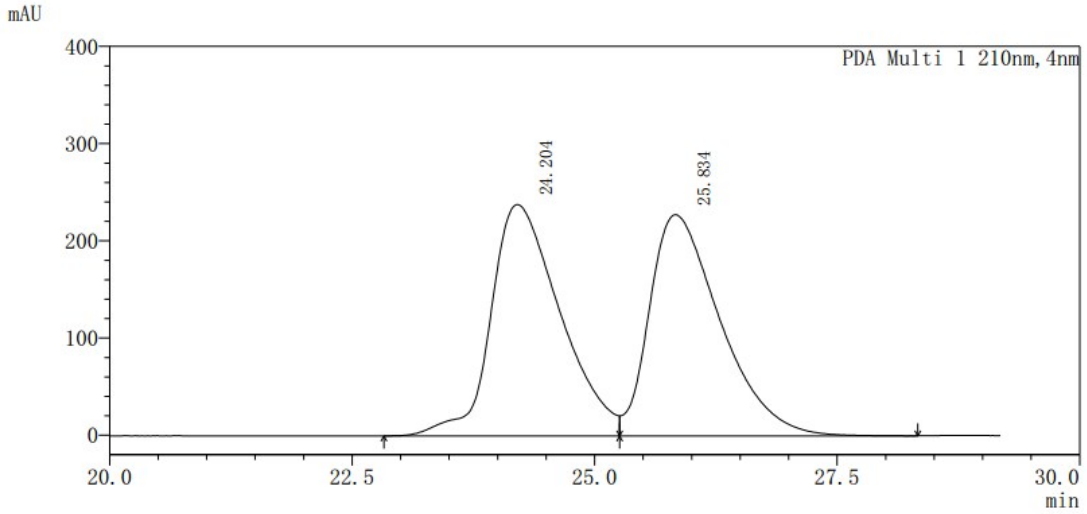

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.204	237999	11842353	50.615
2	25.834	227601	11554442	49.385

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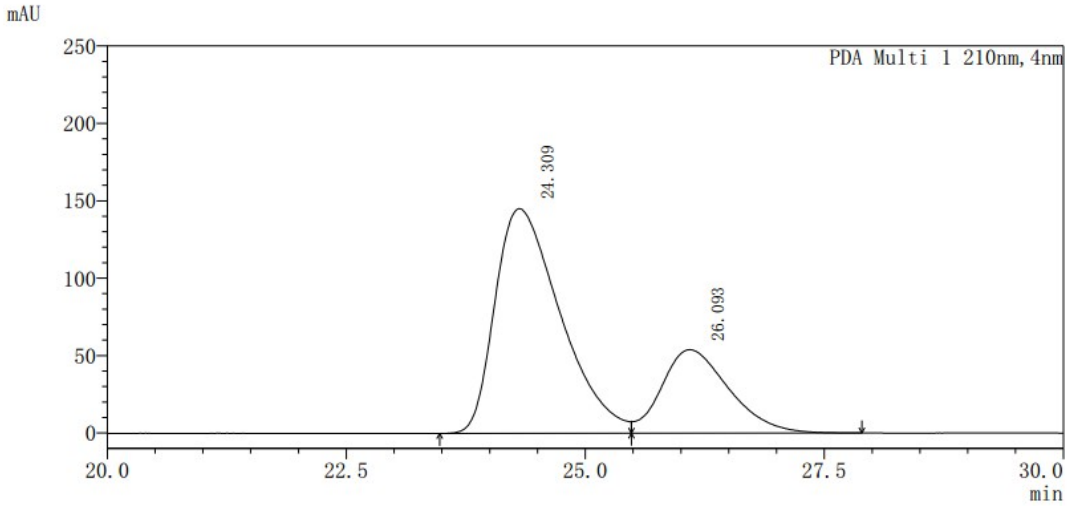
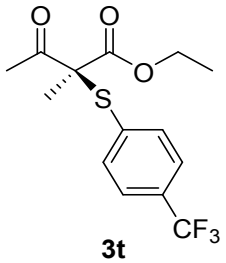


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.309	145141	6913175	72.413
2	26.093	53935	2633753	27.587



3t

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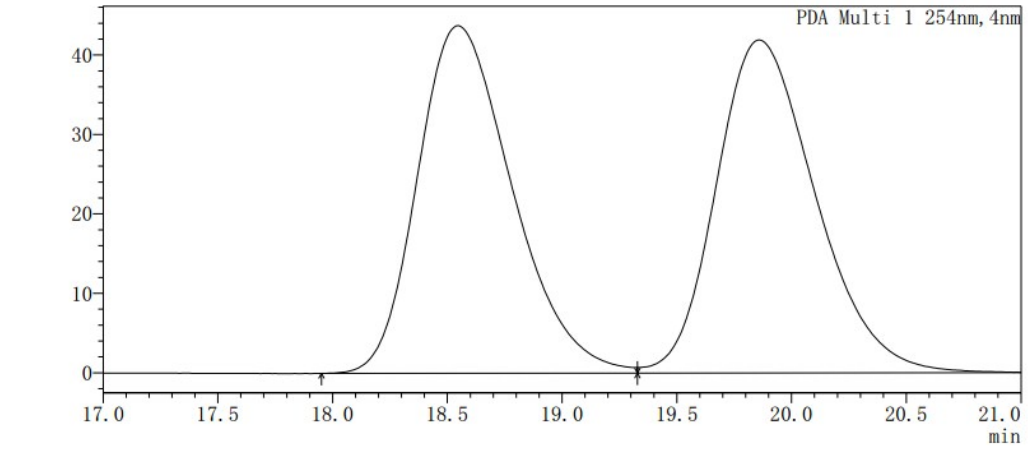
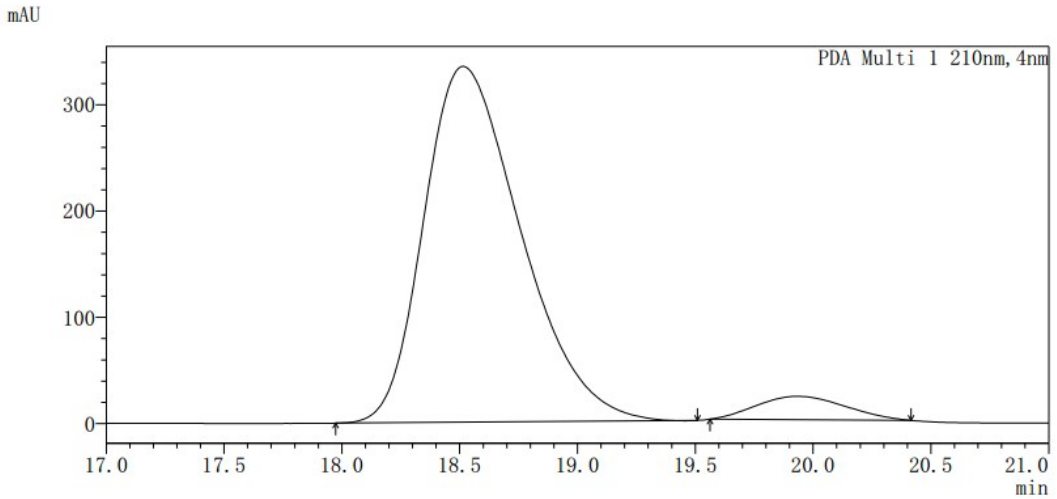


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	18.546	43757	1255395	49.827
2	19.859	41926	1264092	50.173

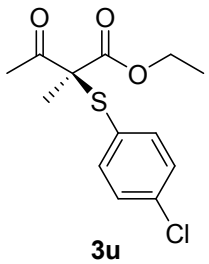
<Chromatogram>



<Peak Results>

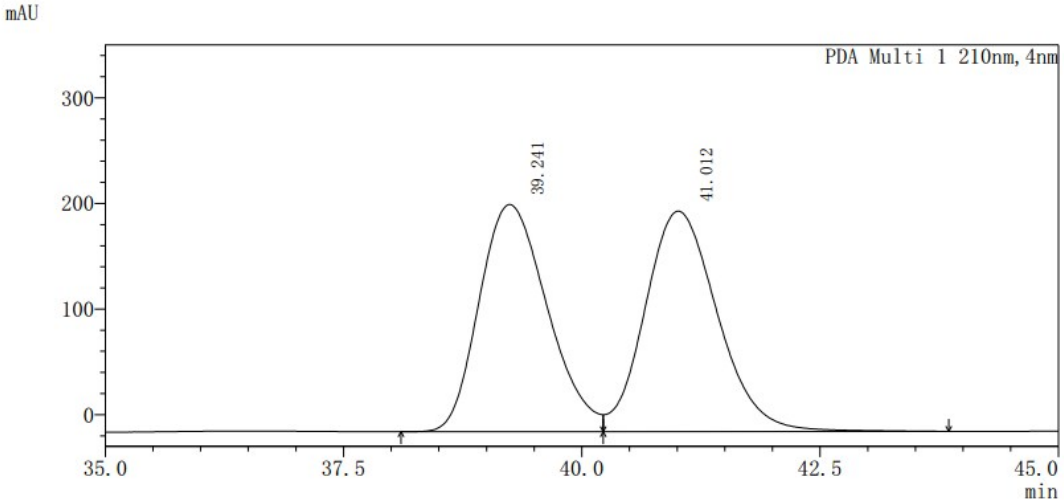
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	18.515	334832	9585753	94.323
2	19.934	22013	576943	5.677



3u

<Chromatogram>

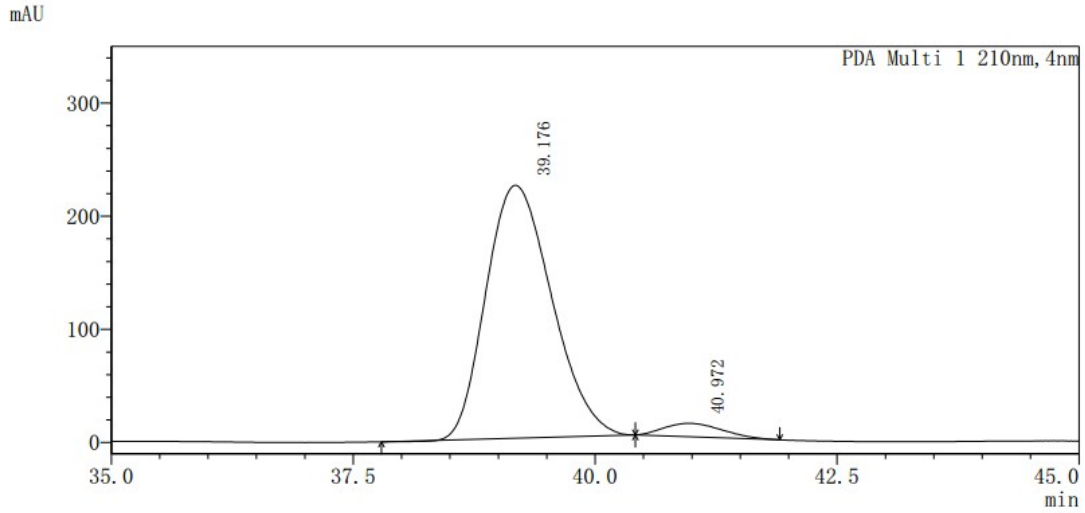


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	39.241	215099	10685957	49.222
2	41.012	208743	11023912	50.778

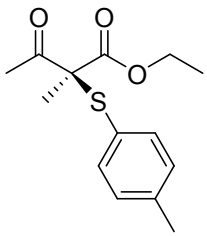
<Chromatogram>



<Peak Results>

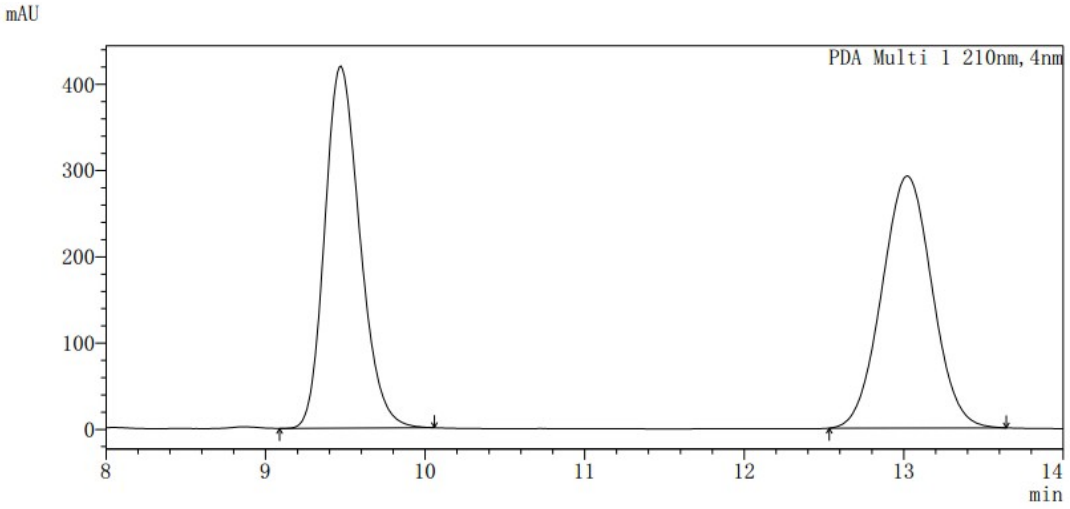
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	39.176	223493	10561044	95.516
2	40.972	11817	495801	4.484



3v

<Chromatogram>

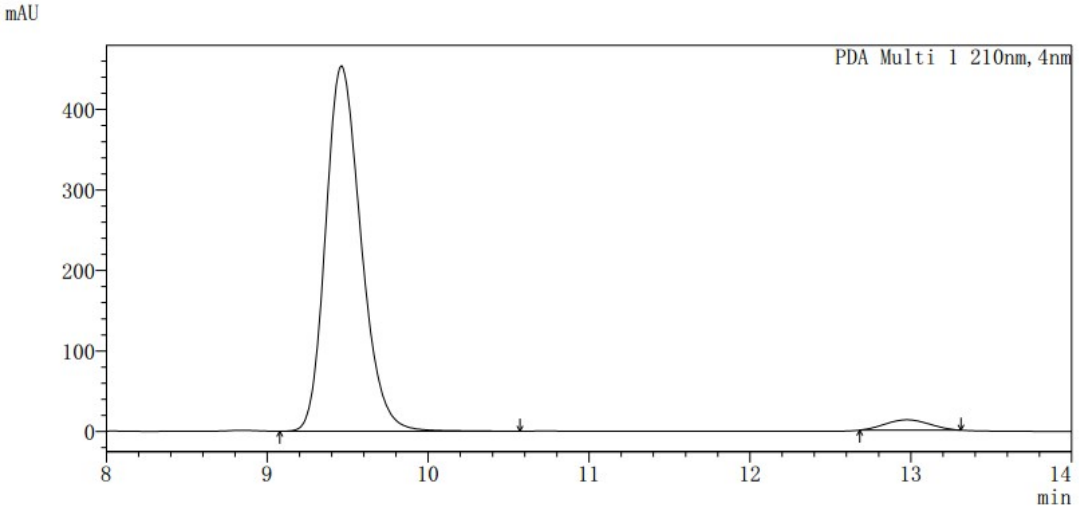


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.469	419766	6429756	50.122
2	13.022	292225	6398446	49.878

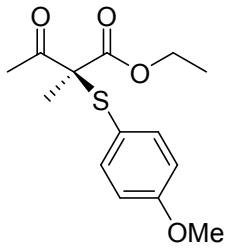
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.461	453891	6918766	96.581
2	12.975	12882	244920	3.419



3w

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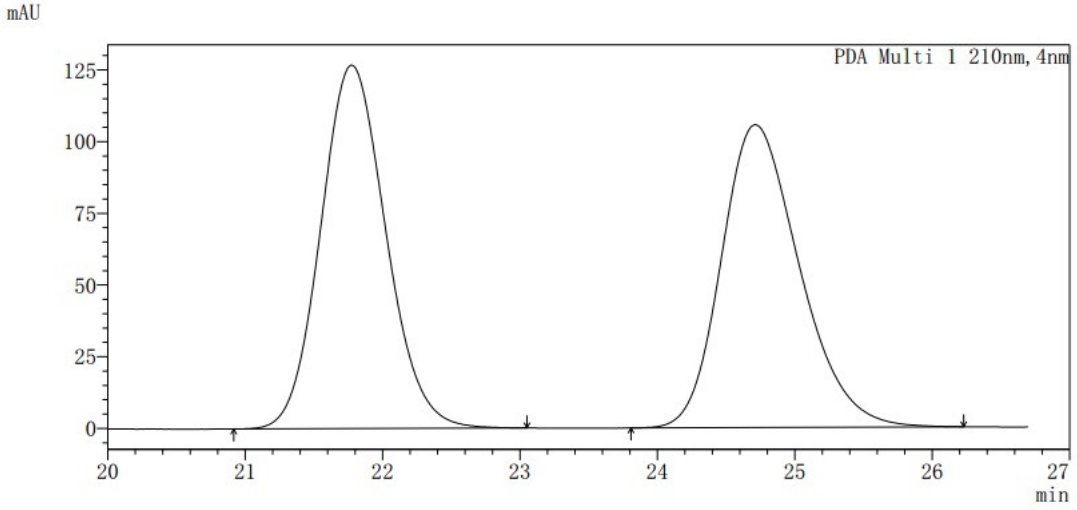
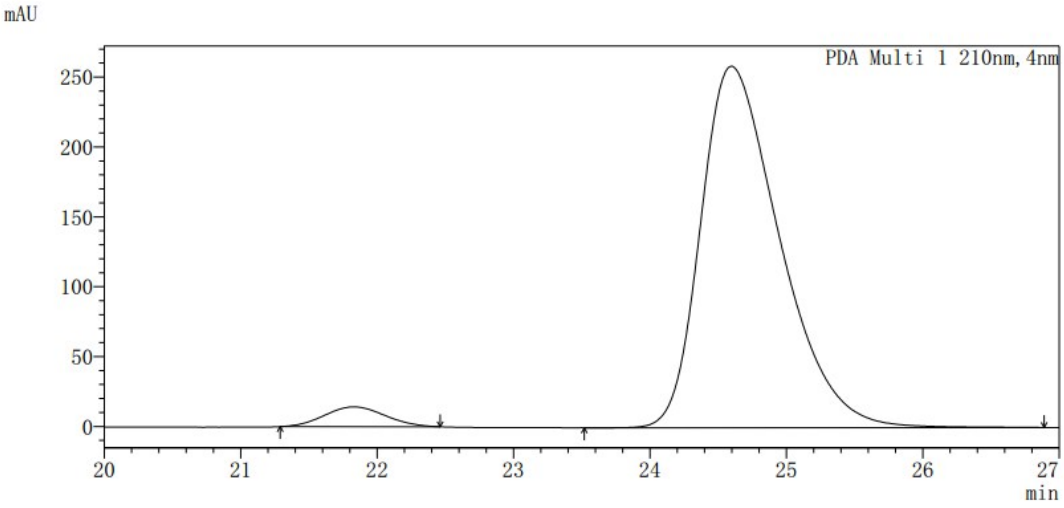


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	21.775	126750	4189161	50.080
2	24.712	105624	4175852	49.920

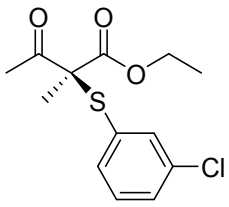
<Chromatogram>



<Peak Results>

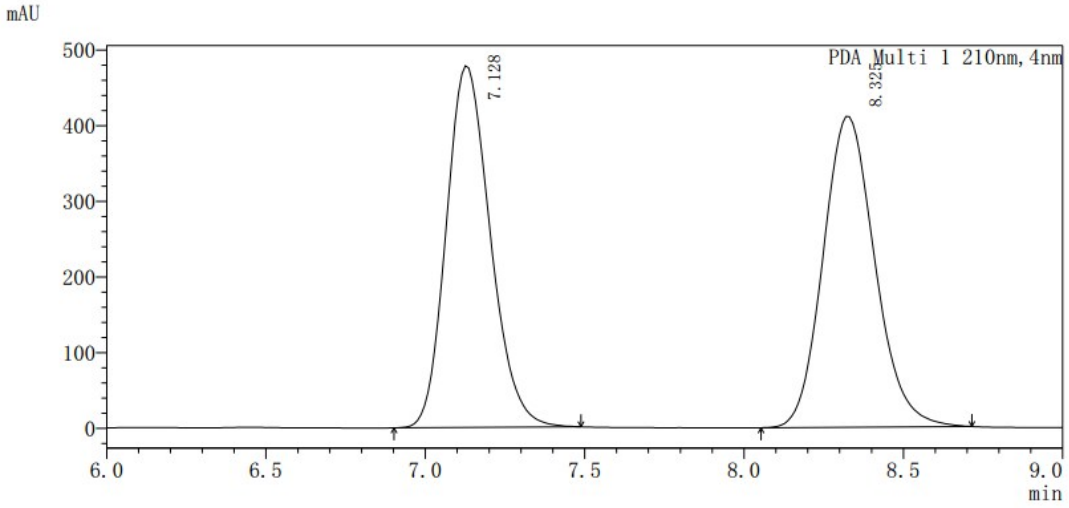
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	21.830	14192	438806	4.047
2	24.598	258635	10404828	95.953



3x

<Chromatogram>

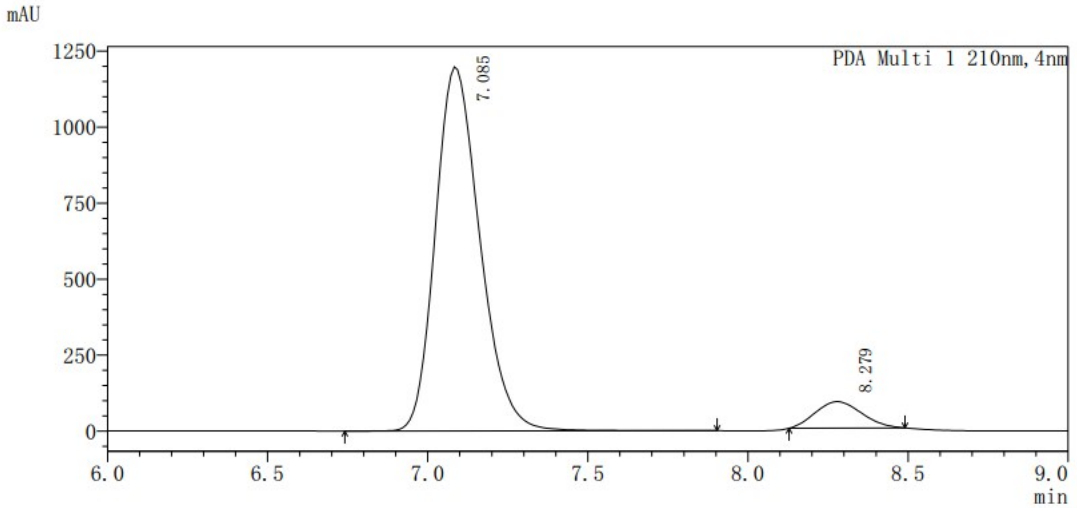


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.128	478277	4596199	49.717
2	8.325	411046	4648546	50.283

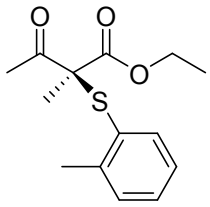
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.085	1197275	11572967	92.942
2	8.279	87243	878804	7.058



3y

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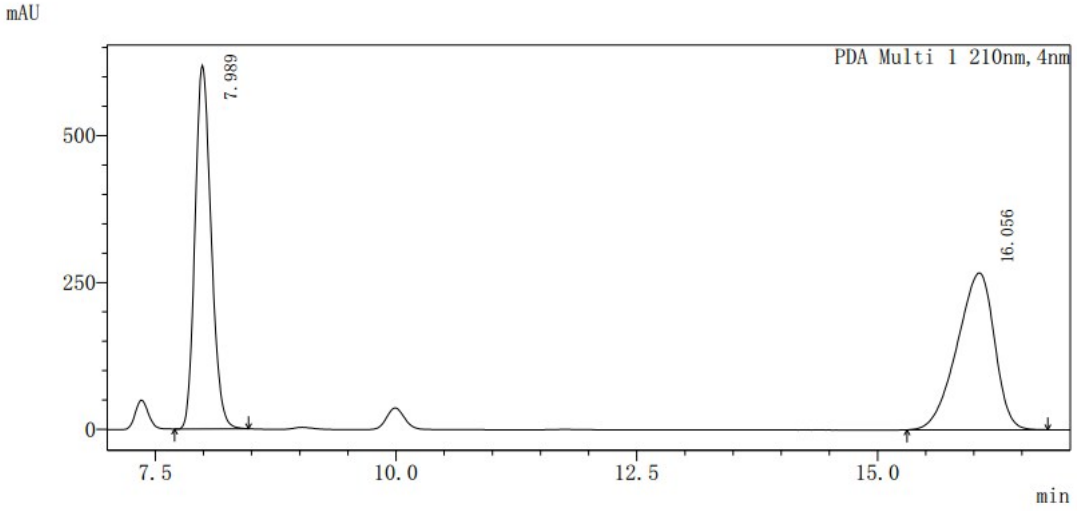
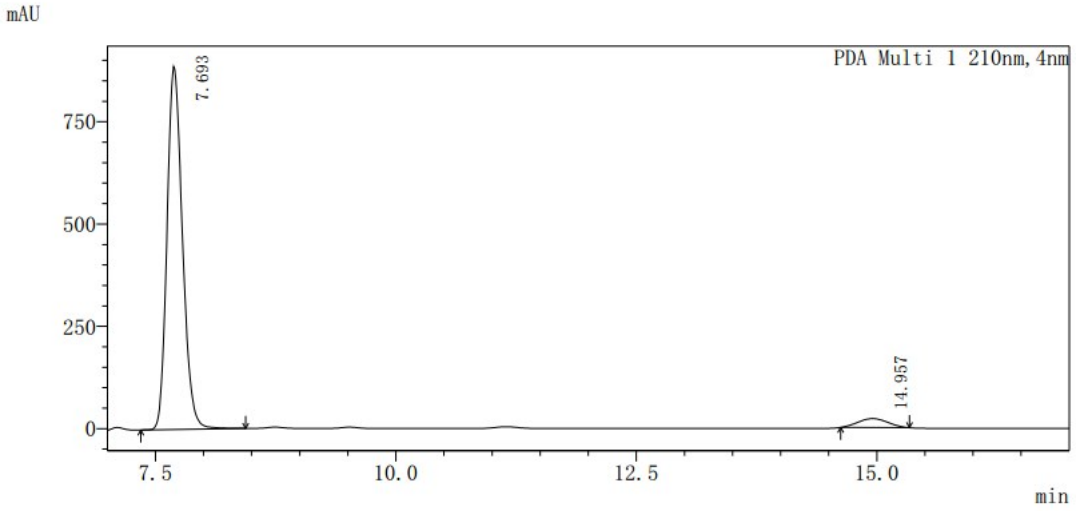


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.989	618851	7204030	49.950
2	16.056	267094	7218468	50.050

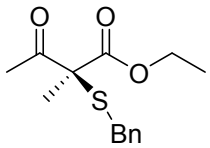
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.693	887113	9894686	95.449
2	14.957	21905	471788	4.551



3z

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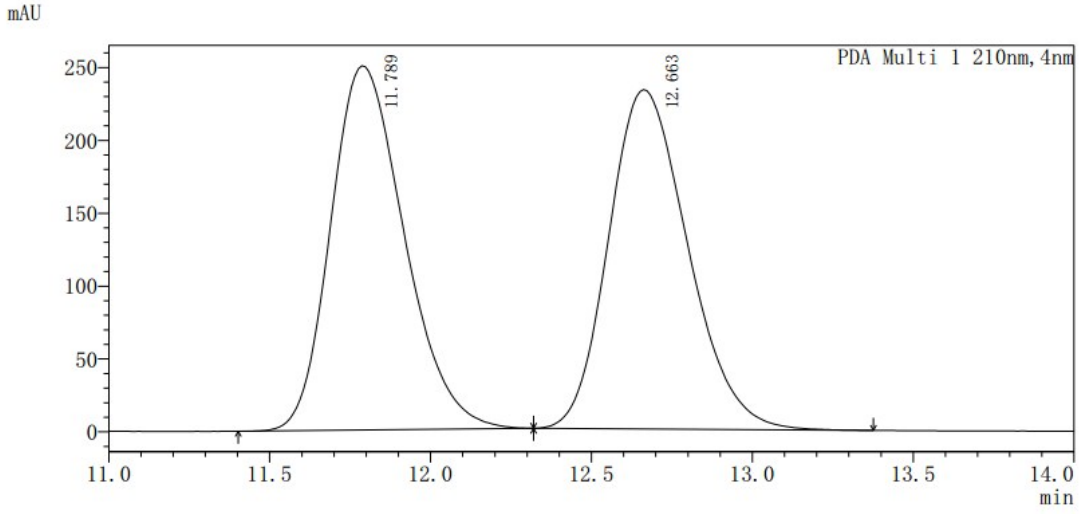
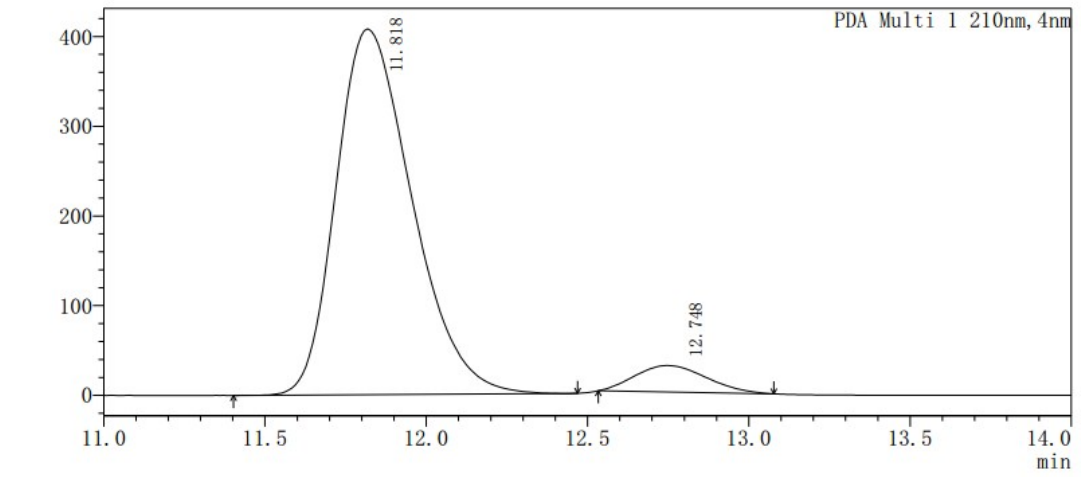


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.789	249937	3984155	49.977
2	12.663	232910	3987898	50.023

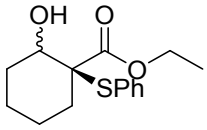
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.818	407640	6674103	93.646
2	12.748	29538	452884	6.354



4n

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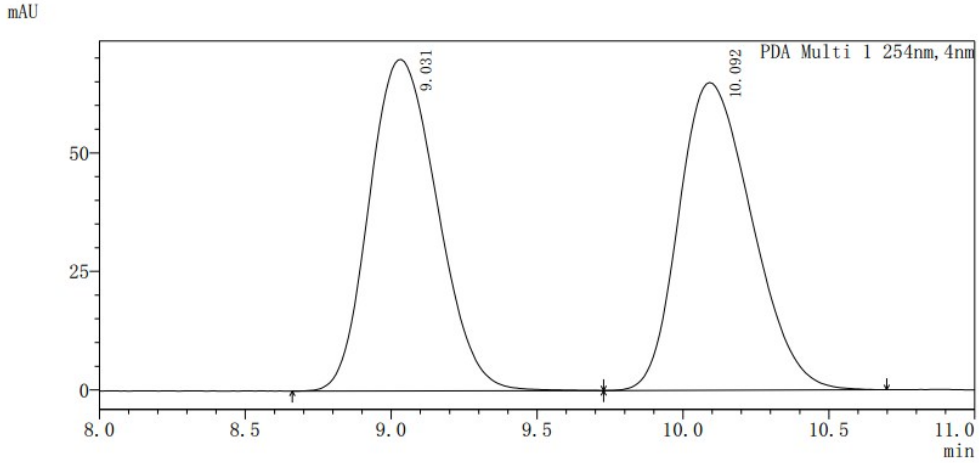
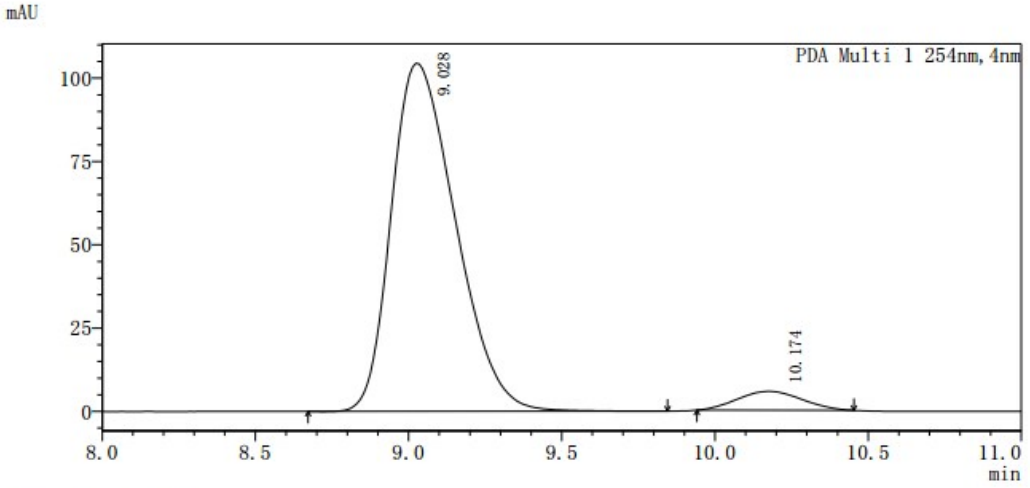


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.031	69889	1135105	50.108
2	10.092	64895	1130226	49.892

<Chromatogram>



<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.028	104453	1524529	94.837
2	10.174	5671	83004	5.163