

Highly Enantioselective Michael Reaction between α,β -Unsaturated Ketone and Malonic Acid Half-thioester

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Supporting Information

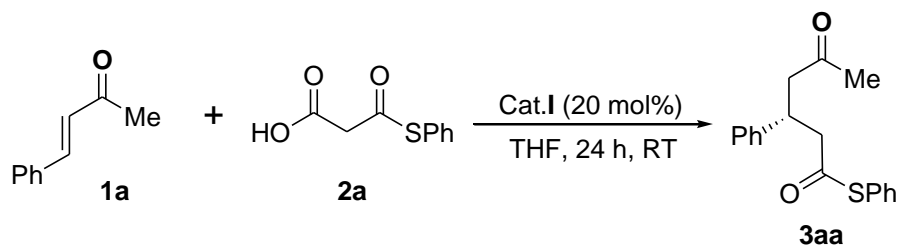
Contents:

1. General Information	S2
2. Experimental Procedure for Decarboxylative Reaction of MAHTs to Enones	S3
3. HPLC Chromatogram Profile and NMR Spectra of the Products	S11

1. General Information

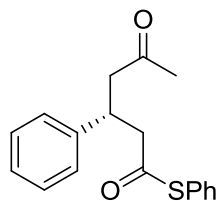
Chemicals and solvents were purchased from commercial suppliers and used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric excesses of products were determined by chiral phase HPLC analysis. Optical rotations were recorded on Jasco DIP-1000 polarimeter.

2. Experimental Procedure for Decarboxylative Reaction of MAHTs to Enones

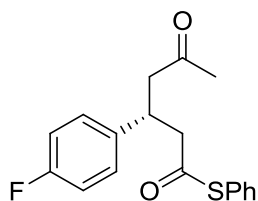


Typical procedure for the cascade reaction:

To a solution of *trans*-4-Phenyl-3-buten-2-one **1a** (29.2 mg, 0.2 mmol,) and catalyst **I** (12.9 mg, 0.04 mmol) in THF (1.0 mL) at room temperature, was added malonic acid half thioester **2a** (98.1 mg, 0.50 mmol) in one portion. The reaction mixture was kept stirring at room temperature for 24 h. The crude product was purified by silica gel flash chromatography, eluted by hexane/EtOAc = 10:1 to afford the desired product **3aa** as colorless oil (48.3 mg, 81% yield).



(R)-S-phenyl 5-oxo-3-phenylhexanethioate (3aa) (Table 2, entry 1). 48.3 mg, 81% yield; Colorless oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm): 7.40 – 7.36 (m, 3H), 7.33 – 7.29 (m, 4H), 7.24 – 7.21 (m, 3H), 3.77 (p, $J = 7.2$ Hz, 1H), 3.04 – 2.81 (m, 4H), 2.06 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm): 206.53, 195.84, 142.40, 134.37, 129.37, 129.12, 128.65, 127.49, 127.36, 126.96, 49.36, 48.90, 37.81, 30.34; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 321.0920, found 321.0929; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 15.6 min, t_{R} (minor) = 20.5 min, $ee = 97\%$; $[\alpha]_{\text{D}}^{25} = -74.2$ ($c = 1.01$ in DCM).



(R)-S-phenyl 3-(4-fluorophenyl)-5-oxohexanethioate (3ba) (Table 2, entry 2). 48.1 mg, 76% yield;

Colorless oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm): 7.42 – 7.36 (m, 3H), 7.33 – 7.27 (m, 2H), 7.23 –

7.17 (m, 2H), 6.99 (t, $J = 8.6$ Hz, 2H), 3.76 (p, $J = 7.2$ Hz, 1H), 3.02 – 2.78 (m, 4H), 2.06 (s, 3H); ^{13}C

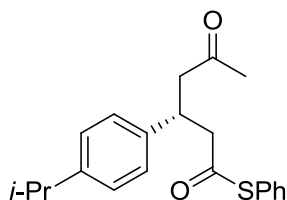
NMR (125 MHz, CDCl_3) δ (ppm): 206.25, 195.70, 162.66, 160.72, 138.12, 138.10, 134.34, 129.45,

129.17, 128.96, 128.90, 127.36, 115.54, 115.38, 49.34, 48.96, 37.04, 30.35; HRMS (ESI) calcd for

$\text{C}_{18}\text{H}_{17}\text{O}_2\text{FSNa}^+$ [$\text{M} + \text{Na}^+$] 339.0825, found 339.0831; HPLC (Chiralpak IC, *i*-propanol/hexane =

20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 9.9 min, t_{R} (minor) = 14.5 min, $ee = 97\%$;

$[\alpha]_{\text{D}}^{25} = -77.1$ ($c = 0.90$ in DCM).



(R)-S-phenyl 3-(4-isopropylphenyl)-5-oxohexanethioate (3ca) (Table 2, entry 3). 59.2 mg, 87%

yield; Colorless oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm): 7.38 – 7.36 (m, 3H), 7.30 (dd, $J = 6.6, 3.0$

Hz, 2H), 7.17 – 7.13 (m, 4H), 3.74 (p, $J = 7.2$ Hz, 1H), 3.02 – 2.80 (m, 5H), 2.06 (s, 3H), 1.24 (d, $J =$

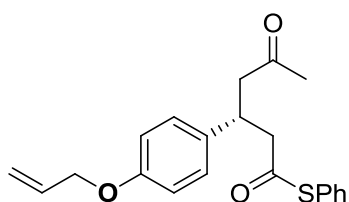
6.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.73, 195.99, 147.45, 139.72, 134.39, 129.35,

129.12, 127.60, 127.23, 126.66, 49.49, 49.02, 37.44, 33.65, 30.31, 23.94, 23.91; HRMS (ESI) calcd for

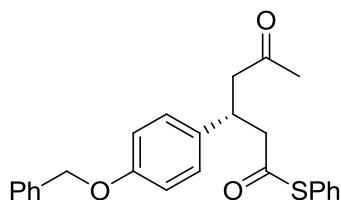
$\text{C}_{21}\text{H}_{24}\text{O}_2\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 363.1389, found 363.1407; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80,

flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 11.3 min, t_{R} (minor) = 16.9 min, $ee = 97\%$; $[\alpha]_{\text{D}}^{25} =$

-64.2 ($c = 1.23$ in DCM).

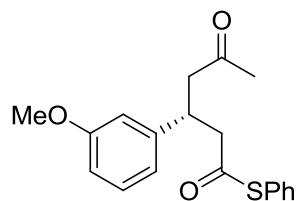


(R)-S-phenyl 3-(4-(allyloxy)phenyl)-5-oxohexanethioate (3da) (Table 2, entry 4). 50.4 mg, 71% yield; Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.17 – 7.11 (m, 2H), 6.89 – 6.83 (m, 2H), 6.05 (ddt, $J = 17.2, 10.5, 5.3$ Hz, 1H), 5.40 (ddd, $J = 17.2, 3.1, 1.5$ Hz, 1H), 5.28 (ddd, $J = 10.5, 2.6, 1.3$ Hz, 1H), 4.51 (dt, $J = 5.3, 1.4$ Hz, 2H), 3.71 (p, $J = 7.2$ Hz, 1H), 3.00 – 2.77 (m, 4H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.70, 195.90, 157.48, 134.59, 134.37, 133.28, 129.35, 129.11, 128.34, 127.55, 117.58, 114.84, 68.79, 49.60, 49.12, 37.15, 30.35; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 377.1182, found 377.1191; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 15.7 min, t_{R} (minor) = 24.6 min, $ee = 96\%$; $[\alpha]_{\text{D}}^{25} = -79.8$ ($c = 1.16$ in DCM).



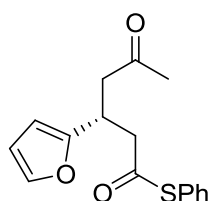
(R)-S-phenyl 3-(4-(benzyloxy)phenyl)-5-oxohexanethioate (3ea) (Table 2, entry 5). 63.1mg, 78% yield; White solid; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.44 – 7.42 (m, 2H), 7.39 – 7.37 (m, 5H), 7.34 – 7.29 (m, 3H), 7.15 (d, $J = 8.6$ Hz, 2H), 6.93 (d, $J = 8.6$ Hz, 2H), 5.04 (s, 2H), 3.72 (p, $J = 7.2$ Hz, 1H), 3.00 – 2.78 (m, 4H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.68, 195.90, 157.69, 136.99, 134.72, 134.37, 129.36, 129.13, 128.54, 128.39, 127.92, 127.55, 127.45, 114.97, 70.00, 49.60, 49.12, 37.15, 30.36; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 427.1338, found 427.1324; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 18.4

min, t_R (minor) = 28.4 min, $ee = 97\%$; $[\alpha]_D^{25} = -71.0$ ($c = 1.29$ in DCM).



(R)-S-phenyl 3-(3-methoxyphenyl)-5-oxohexanethioate (3fa) (Table 2, entry 6). 49.2 mg, 75% yield;

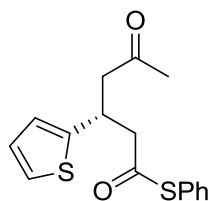
Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.39 – 7.37 (m, 3H), 7.32 – 7.30 (m, 2H), 7.23 (dd, $J = 8.8, 7.7$ Hz, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.77 (dd, $J = 3.8, 1.5$ Hz, 2H), 3.80 (s, 3H), 3.74 (p, $J = 7.2$ Hz, 1H), 3.01 – 2.80 (m, 4H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.51, 195.84, 159.78, 144.13, 134.40, 129.69, 129.40, 129.15, 127.55, 119.62, 113.38, 112.18, 55.19, 49.32, 48.87, 37.84, 30.36; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 351.1025, found 351.1009; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_R (major) = 25.2 min, t_R (minor) = 27.1 min, $ee = 97\%$; $[\alpha]_D^{25} = -69.5$ ($c = 0.96$ in DCM).



(R)-S-phenyl 3-(furan-2-yl)-5-oxohexanethioate (3ga) (Table 2, entry 7). 49.0mg, 85% yield;

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.40 – 7.38 (m, 3H), 7.37 – 7.34 (m, 2H), 7.32 (dd, $J = 1.8, 0.8$ Hz, 1H), 6.28 (dd, $J = 3.2, 1.9$ Hz, 1H), 6.07 (d, $J = 3.2$ Hz, 1H), 3.86 (p, $J = 6.9$ Hz, 1H), 3.06 – 2.97 (m, 2H), 2.92 – 2.83 (m, 2H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.21, 195.64, 155.15, 141.47, 134.41, 129.45, 129.18, 127.46, 110.23, 105.73, 46.54, 46.20, 31.38, 30.16; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 311.0712, found 311.0716; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_R (major) = 16.2 min, t_R (minor) = 39.8

min, $ee = 98\%$; $[\alpha]_{\text{D}}^{25} = -43.7$ ($c = 1.13$ in DCM).



(R)-S-phenyl 5-oxo-3-(thiophen-2-yl)hexanethioate (3ha) (Table 2, entry 8). 46.3 mg, 76% yield;

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.40 – 7.38 (m, 3H), 7.35 – 7.33 (m, 2H), 7.16 (d,

$J = 5.0$ Hz, 1H), 6.92 (dd, $J = 5.0, 3.5$ Hz, 1H), 6.88 (d, $J = 3.2$ Hz, 2H), 4.09 (p, $J = 6.9$ Hz, 1H), 3.08

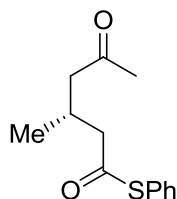
– 2.99 (m, 2H), 2.98 – 2.86 (m, 2H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.07,

195.59, 145.90, 134.41, 129.46, 129.18, 127.41, 126.76, 124.54, 123.66, 49.87, 49.58, 33.14, 30.35;

HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}_2\text{Na}^+$ [$\text{M} + \text{Na}^+$] 327.0484, found 327.0488; HPLC (Chiralpak IC,

i-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 14.6 min, t_{R} (minor) = 23.0

min, $ee = 97\%$; $[\alpha]_{\text{D}}^{25} = -56.5$ ($c = 1.05$ in DCM).



(R)-S-phenyl 3-methyl-5-oxohexanethioate (3ia) (Table 2, entry 9). 36.9 mg, 78% yield; Colorless

oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.40 (br, 5H), 2.68 (ddd, $J = 8.5, 6.3, 2.7$ Hz, 1H), 2.58 (ddd,

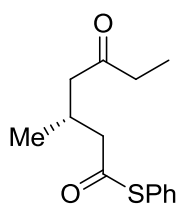
$J = 12.4, 11.4, 5.9$ Hz, 3H), 2.40 – 2.34 (m, 1H), 2.13 (s, 3H), 1.03 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (125

MHz, CDCl_3) δ (ppm): 207.50, 196.46, 134.38, 129.37, 129.16, 127.73, 49.55, 30.30, 29.65, 27.01,

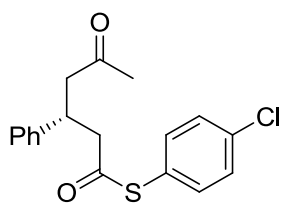
19.79; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 259.0763, found 259.0761; HPLC (Chiralpak

ID, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 10.4 min, t_{R} (minor) =

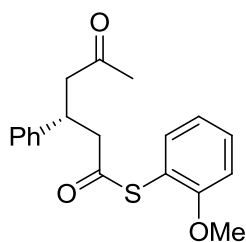
9.5 min, $ee = 97\%$; $[\alpha]_{\text{D}}^{25} = -5.7$ ($c = 0.90$ in DCM).



(R)-S-phenyl 3-methyl-5-oxoheptanethioate (3ja) (Table 2, entry 10). 35.1 mg, 70% yield; Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.40 (br, 5H), 2.71 – 2.66 (m, 1H), 2.63 – 2.52 (m, 3H), 2.45 – 2.33 (m, 3H), 1.04 (dd, $J = 12.8, 6.6$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 210.22, 196.53, 134.42, 129.38, 129.18, 127.81, 49.68, 48.28, 36.37, 27.15, 19.90, 7.71; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 273.0920, found 273.0920; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 8.2 min, t_{R} (minor) = 9.2 min, $ee = 98\%$; $[\alpha]_{\text{D}}^{25} = -6.5$ ($c = 1.20$ in DCM).

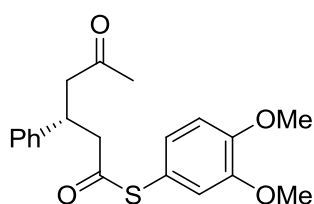


(R)-S-4-chlorophenyl 5-oxo-3-phenylhexanethioate (3ab) (Table 2, entry 11). 48.6 mg, 73% yield; White solid; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.35 – 7.30 (m, 4H), 7.24 – 7.20 (m, 5H), 3.76 (p, $J = 7.2$ Hz, 1H), 2.98 (qd, $J = 15.1, 7.2$ Hz, 2H), 2.87 (qd, $J = 16.9, 7.1$ Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 206.46, 195.34, 142.30, 135.81, 135.60, 129.38, 128.70, 127.36, 127.04, 125.95, 49.40, 48.92, 37.80, 30.37; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{ClSNa}^+$ [$\text{M} + \text{Na}^+$] 355.0530, found 355.0547; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 12.4 min, t_{R} (minor) = 16.1 min, $ee = 95\%$; $[\alpha]_{\text{D}}^{25} = -79.7$ ($c = 0.98$ in DCM).



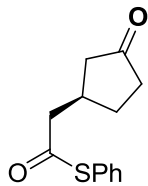
(R)-S-2-methoxyphenyl 5-oxo-3-phenylhexanethioate (3ac) (Table 2, entry 12). 52.6 mg, 80% yield;

Colorless oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm): 7.30 (td, $J = 8.4, 1.6$ Hz, 1H), 7.26 – 7.11 (m, 6H), 6.86 (dd, $J = 14.6, 7.9$ Hz, 2H), 3.73 – 3.65 (m, 4H), 2.94 – 2.73 (m, 4H), 1.95 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm): 206.59, 195.06, 159.08, 142.54, 136.53, 131.61, 128.56, 127.36, 126.82, 121.00, 115.74, 111.51, 55.84, 49.12, 48.83, 37.87, 30.29; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 351.1025, found 351.1035; HPLC (Chiralpak ID, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 15.4 min, t_{R} (minor) = 17.3 min, $ee = 98\%$; $[\alpha]_{\text{D}}^{25} = -66.4$ ($c = 1.15$ in DCM).



(R)-S-3,4-dimethoxyphenyl 5-oxo-3-phenylhexanethioate (3ad) (Table 2, entry 13). 50.9 mg, 71%

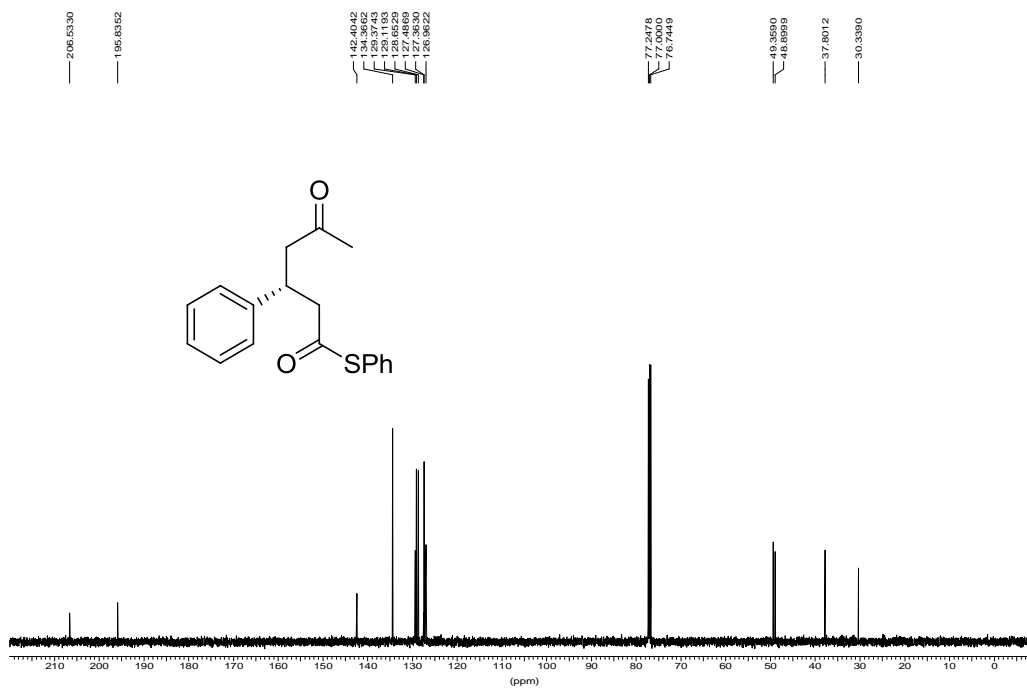
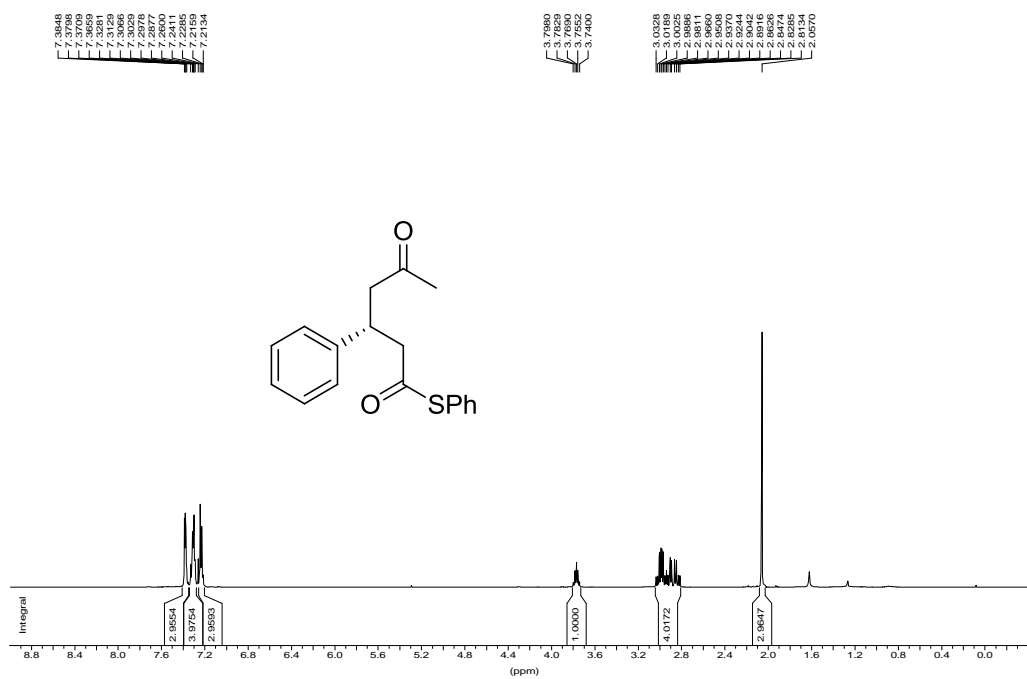
yield; Colorless oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm): 7.31 – 7.28 (m, 2H), 7.21 (dd, $J = 10.9, 4.4$ Hz, 3H), 6.86 (d, $J = 2.5$ Hz, 2H), 6.76 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.76 (p, $J = 7.1$ Hz, 1H), 3.00 – 2.80 (m, 4H), 2.05 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm): 206.53, 196.85, 150.22, 149.15, 142.46, 128.60, 127.60, 127.38, 126.90, 118.37, 117.23, 111.49, 55.92, 55.84, 49.11, 48.92, 37.82, 30.32; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 381.1131, found 381.1140; HPLC (Chiralpak IA, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 20.0 min, t_{R} (minor) = 22.2 min, $ee = 96\%$; $[\alpha]_{\text{D}}^{25} = -70.3$ ($c = 0.95$ in DCM).



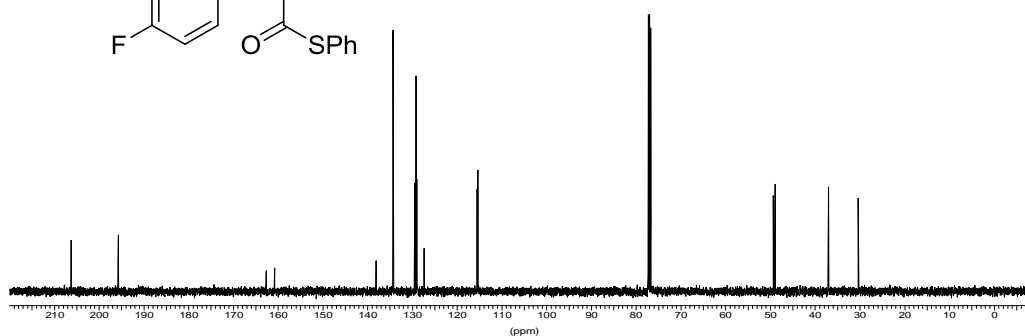
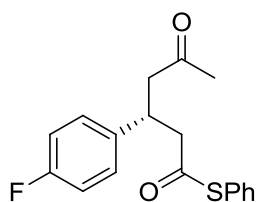
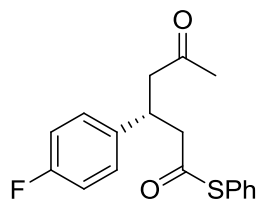
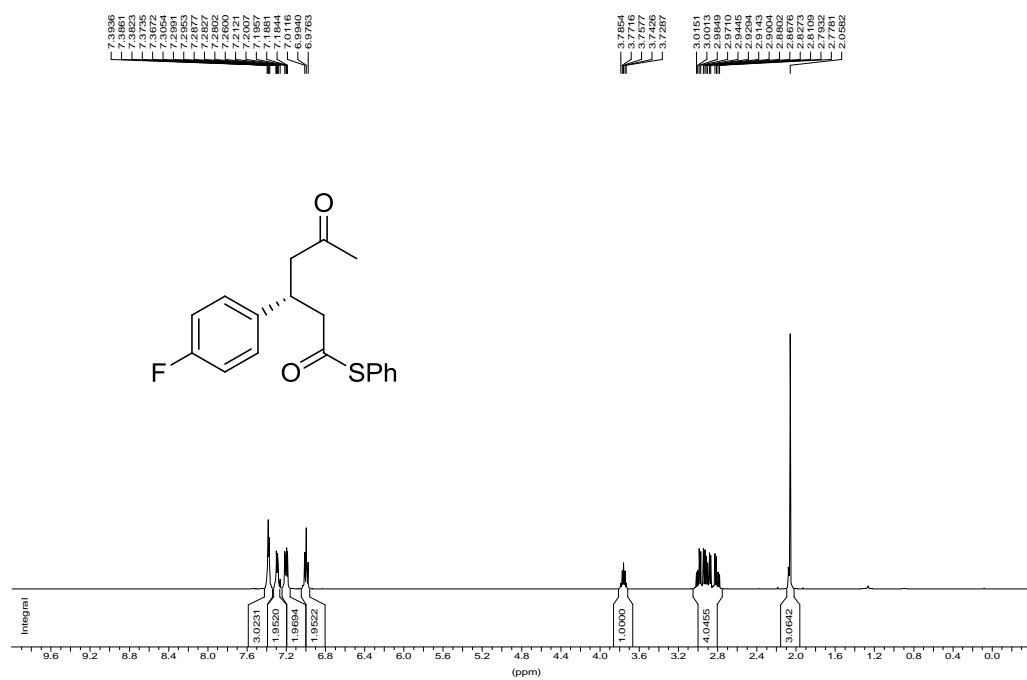
(R)-S-phenyl 2-(3-oxocyclopentyl)ethanethioate (3ka) (Table 2, entry 14). 29.1 mg, 62% yield; Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.43 – 7.40 (m, 5H), 2.85 – 2.75 (m, 2H), 2.75 – 2.65 (m, 1H), 2.51 (dd, $J = 18.3, 7.7$ Hz, 1H), 2.36 – 2.15 (m, 3H), 1.94 (dd, $J = 18.4, 9.8$ Hz, 1H), 1.70 – 1.61 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 217.75, 195.86, 134.40, 129.56, 129.27, 127.36, 48.58, 44.37, 38.16, 33.97, 29.12; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 257.0607, found 257.0609; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_{R} (major) = 27.0 min, t_{R} (minor) = 32.6 min, $ee = 80\%$; $[\alpha]_{\text{D}}^{25} = -73.0$ ($c = 0.86$ in DCM).

3. HPLC Chromatogram Profile and NMR Spectra of the Products

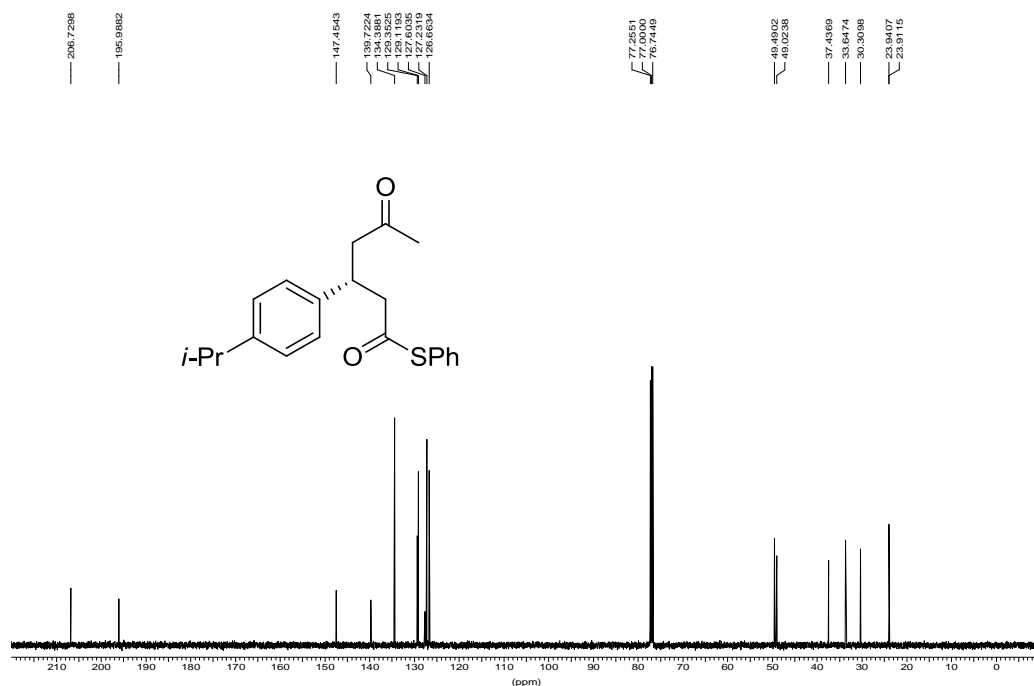
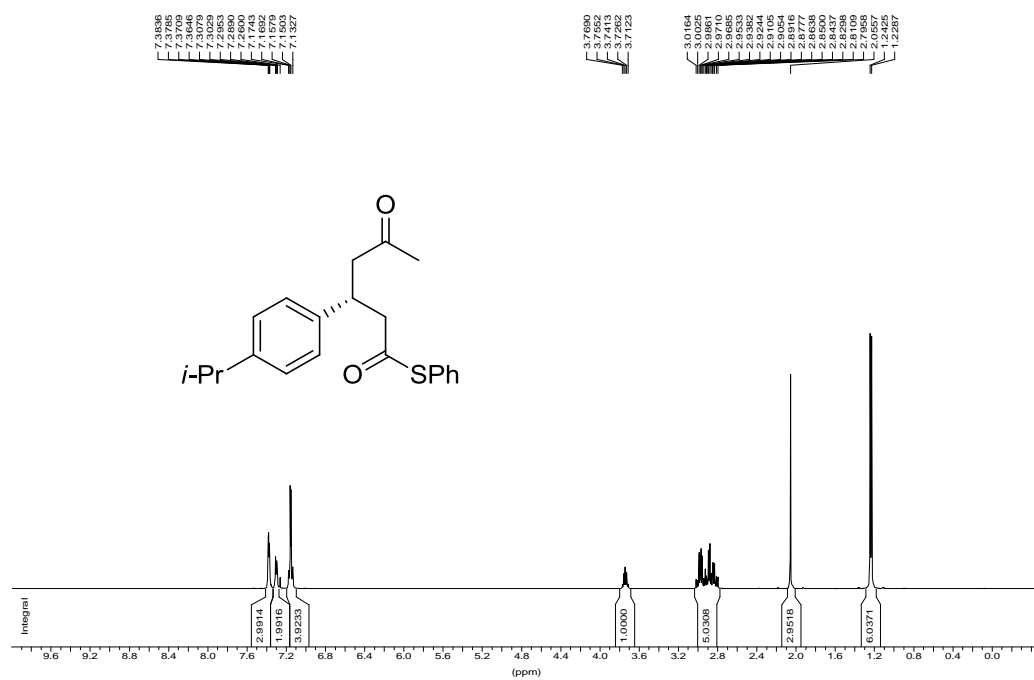
Compound 3aa



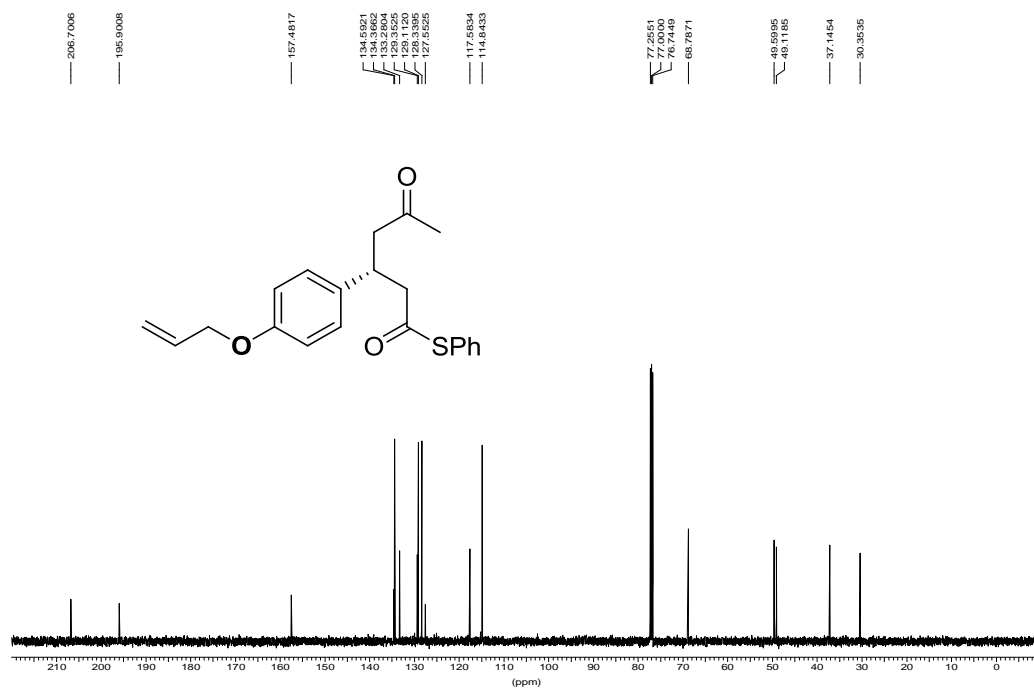
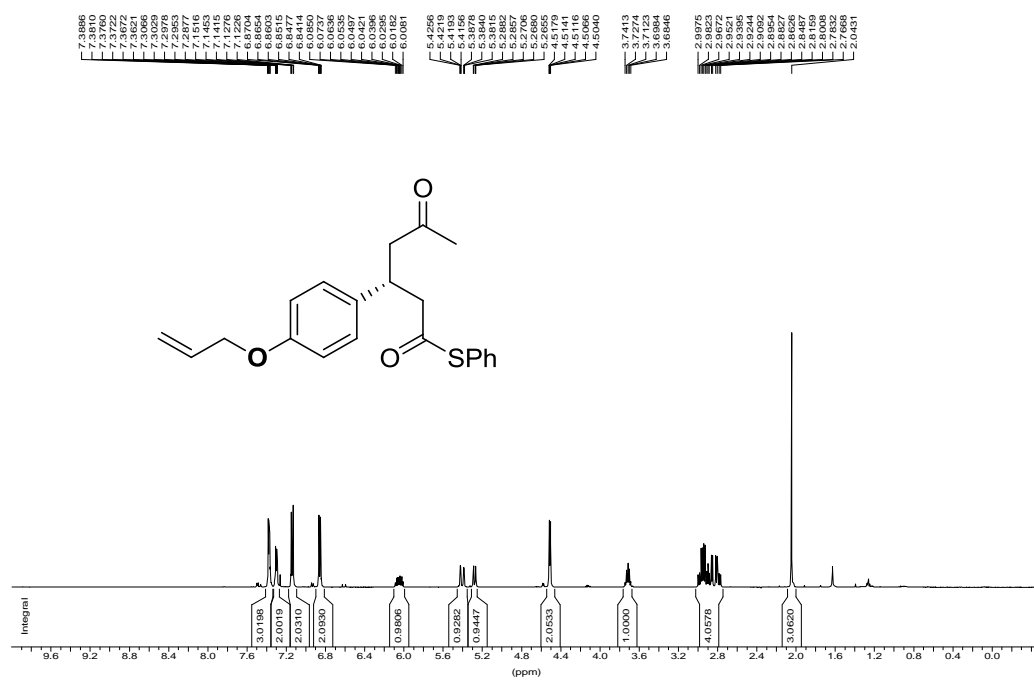
Compound 3ba



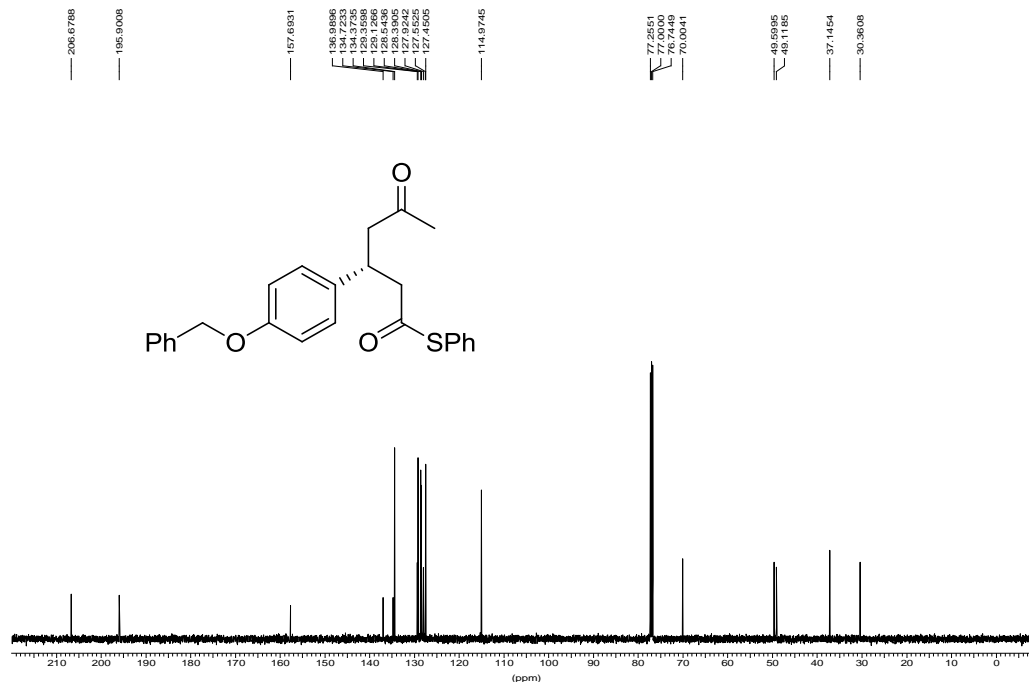
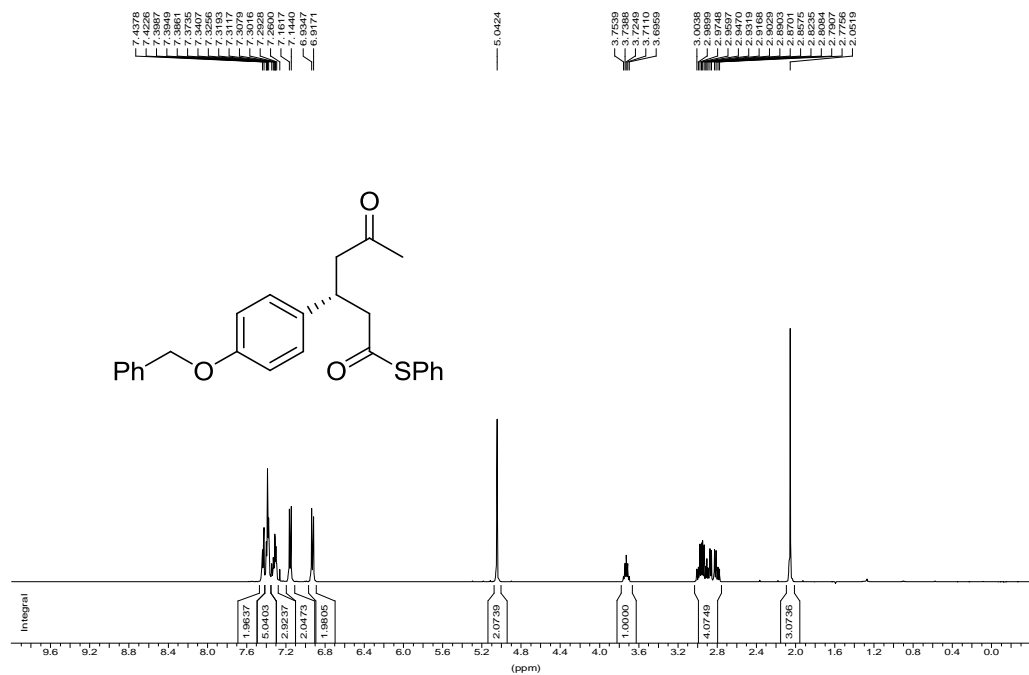
Compound 3ca



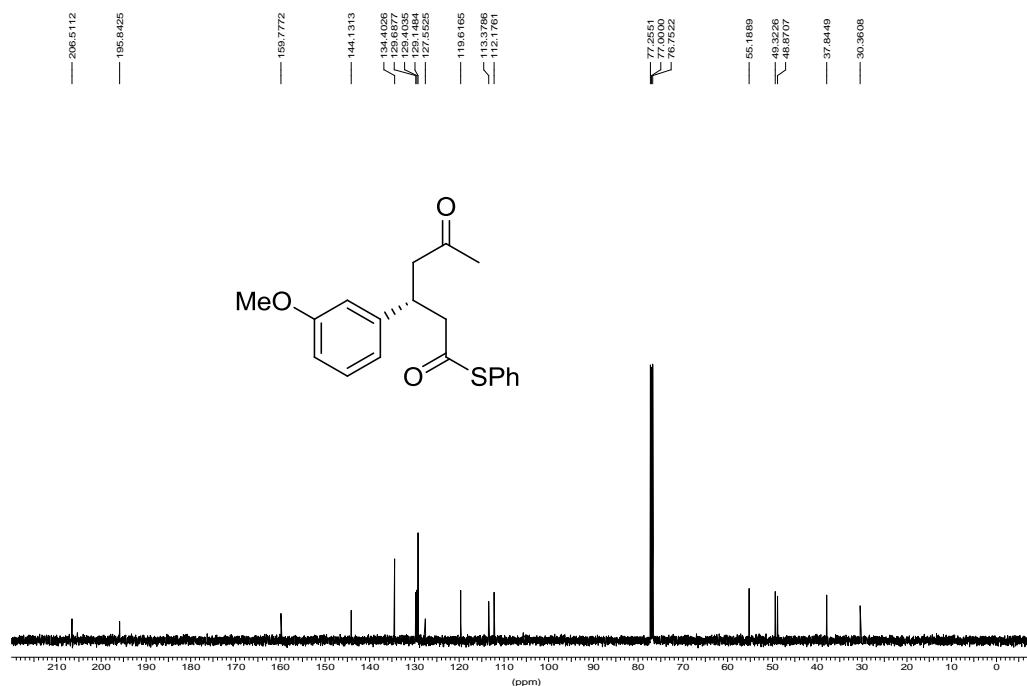
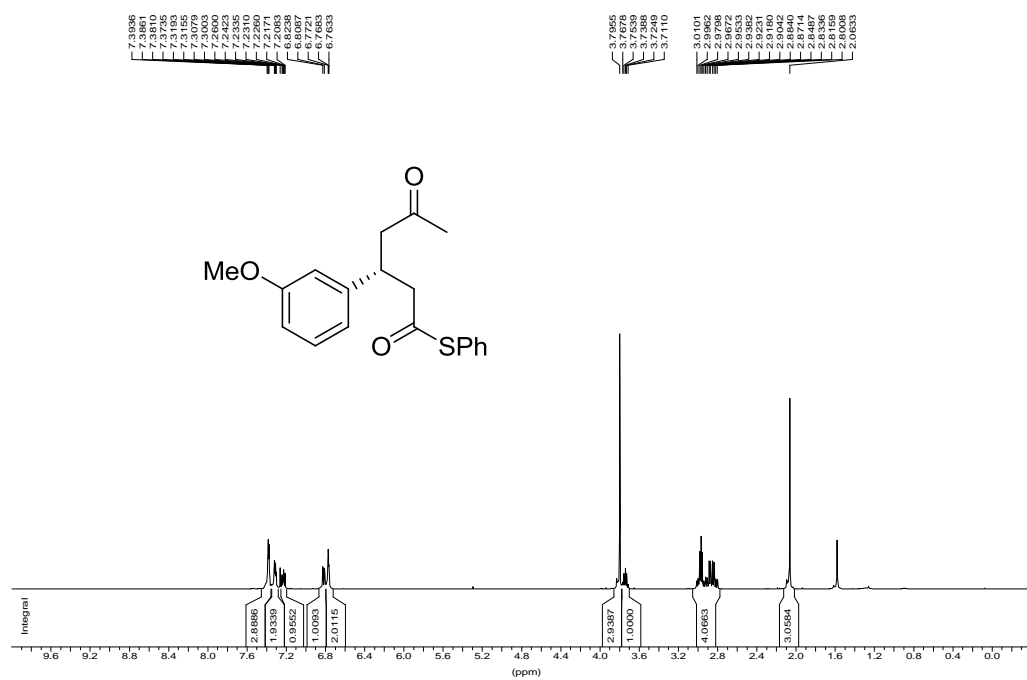
Compound 3da



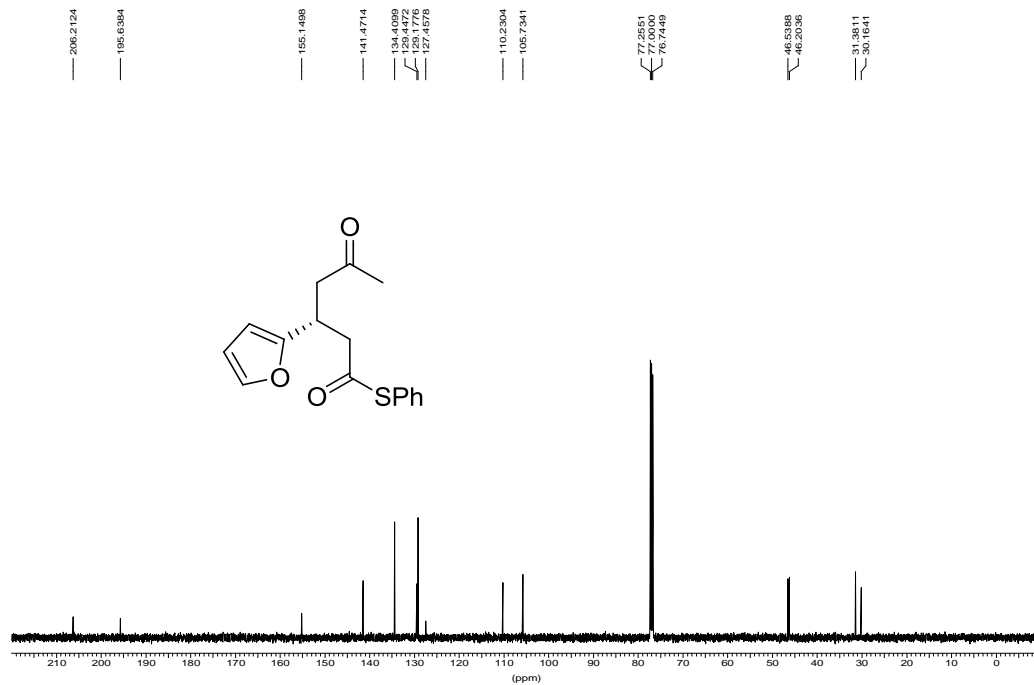
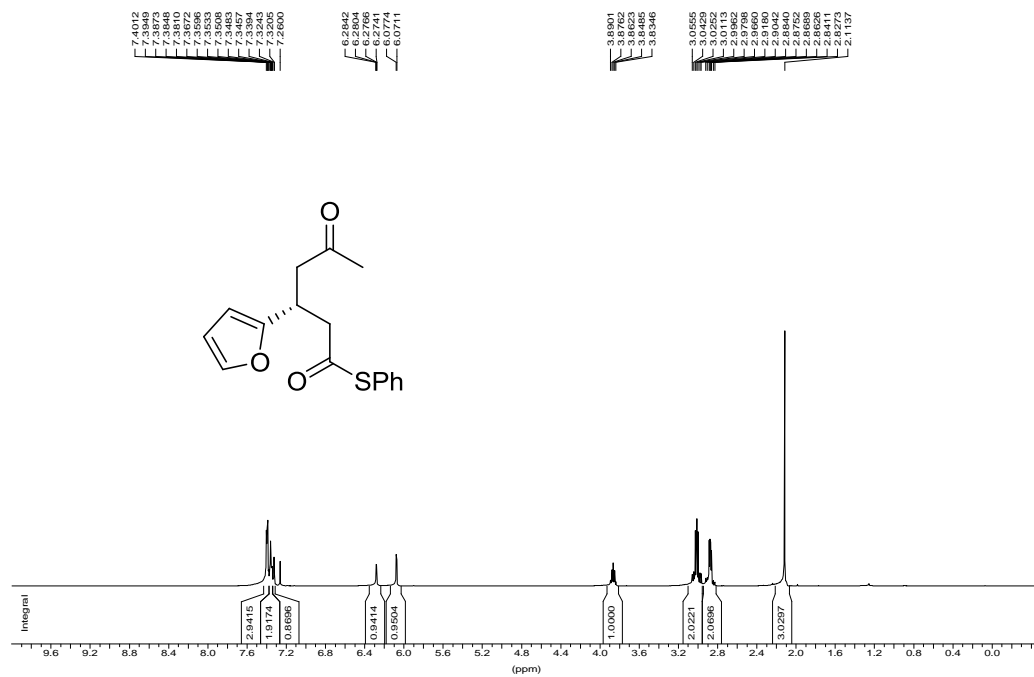
Compound 3ea



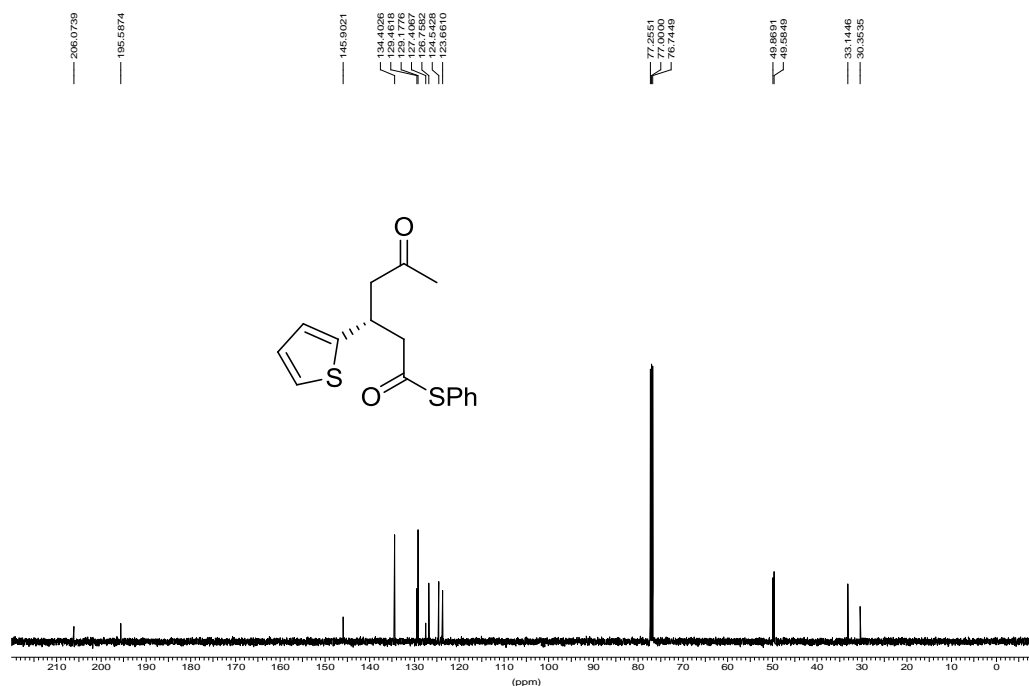
Compound 3fa



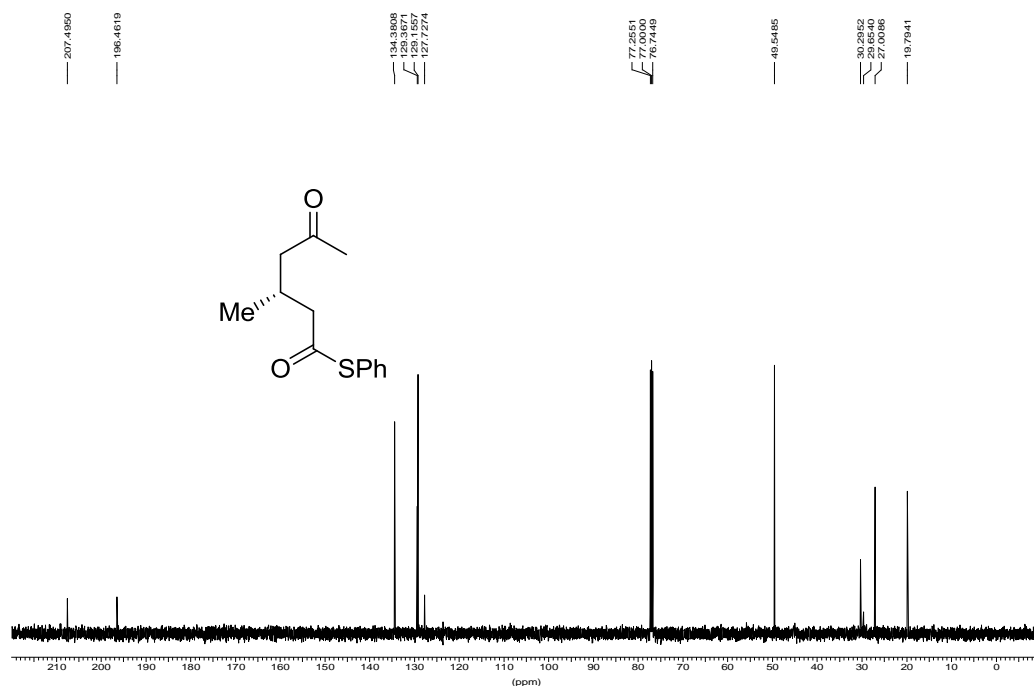
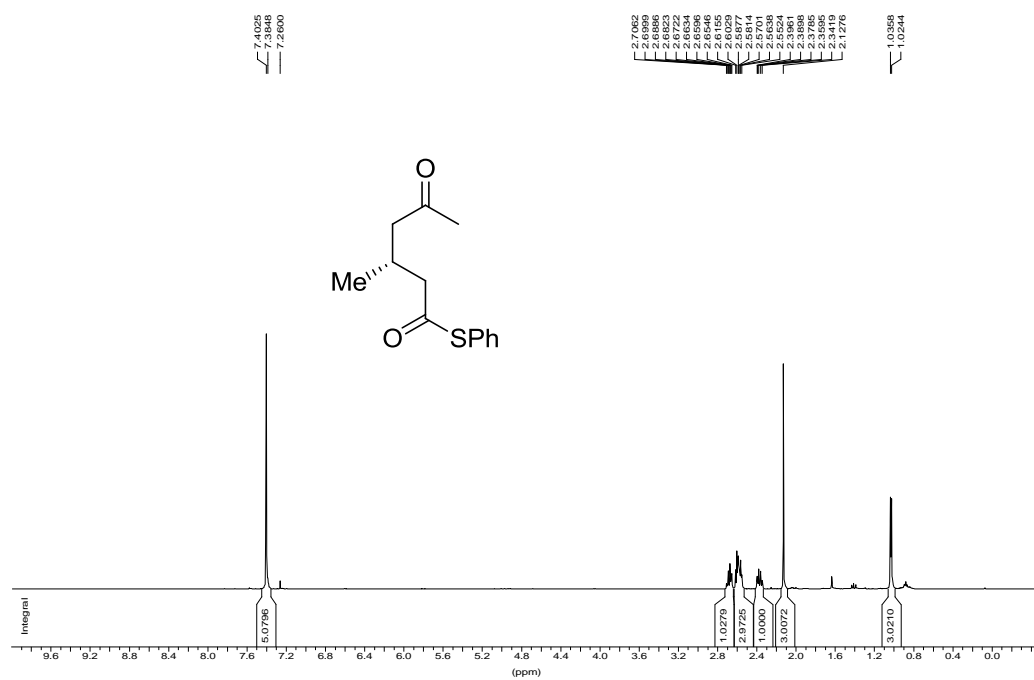
Compound 3ga



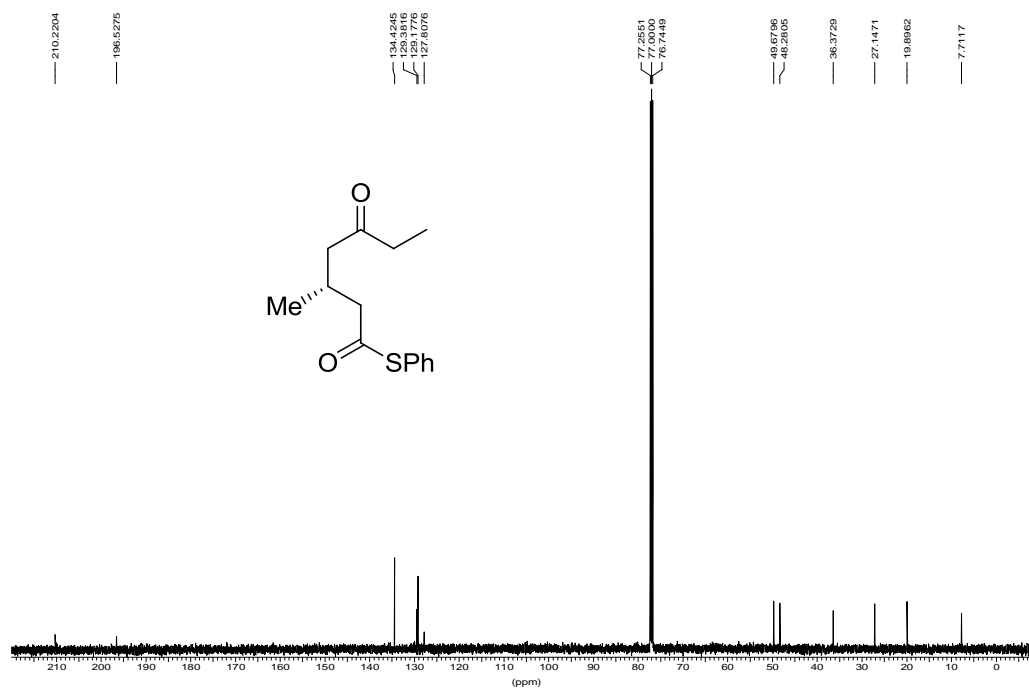
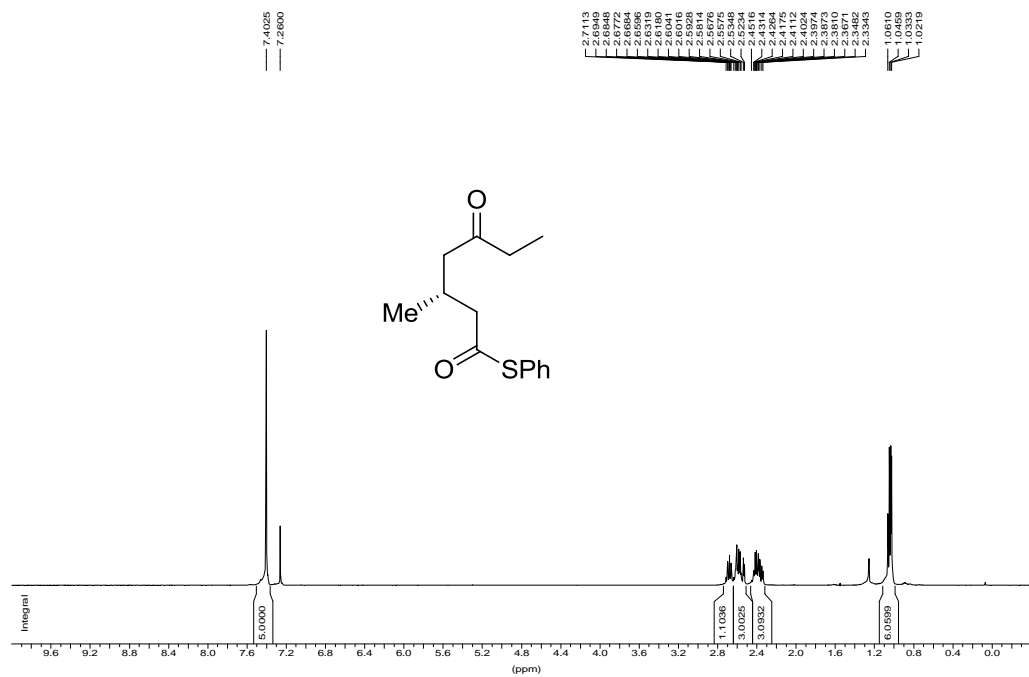
Compound 3ha



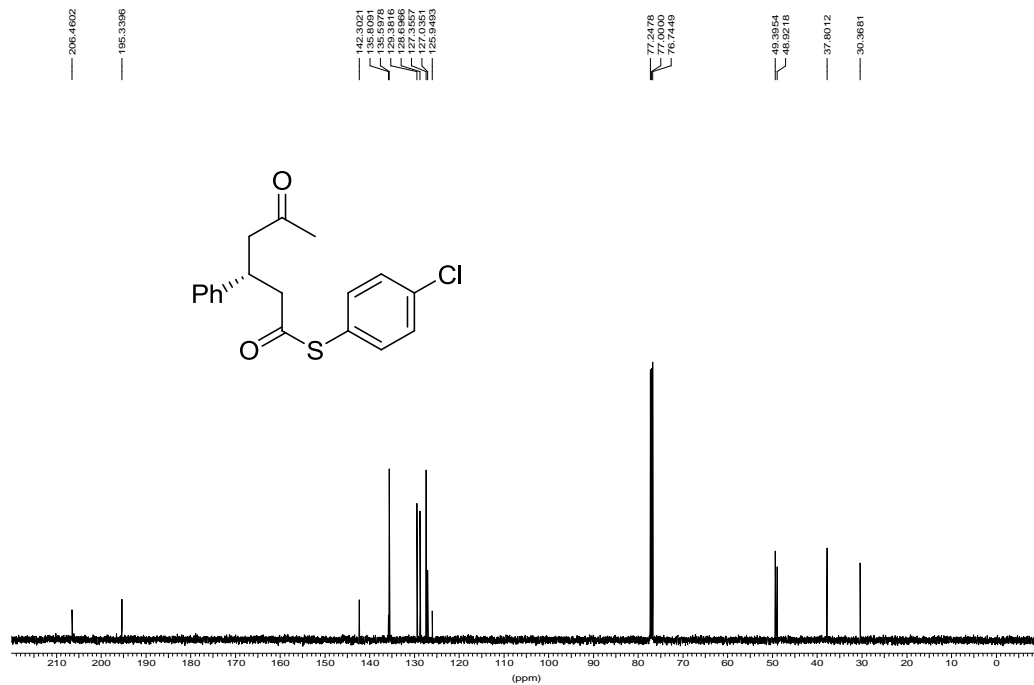
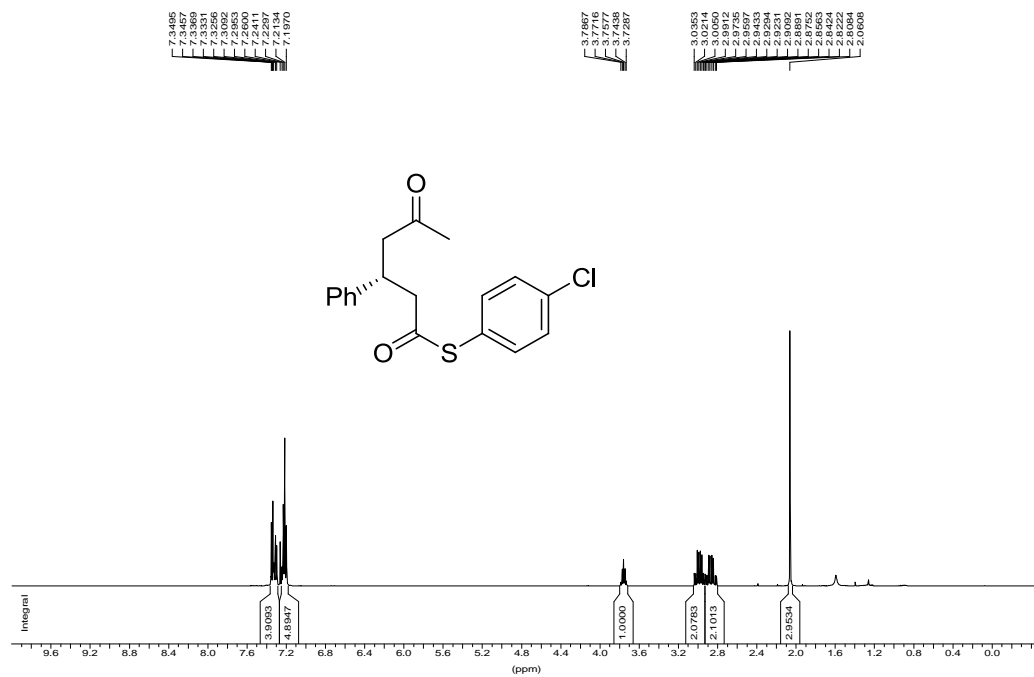
Compound 3ia



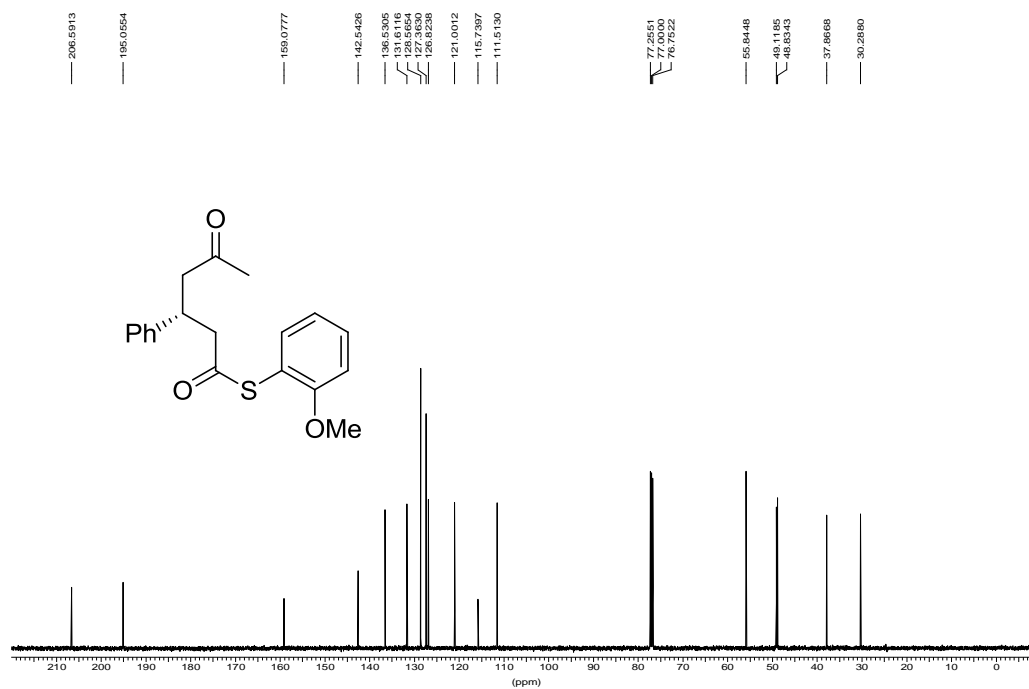
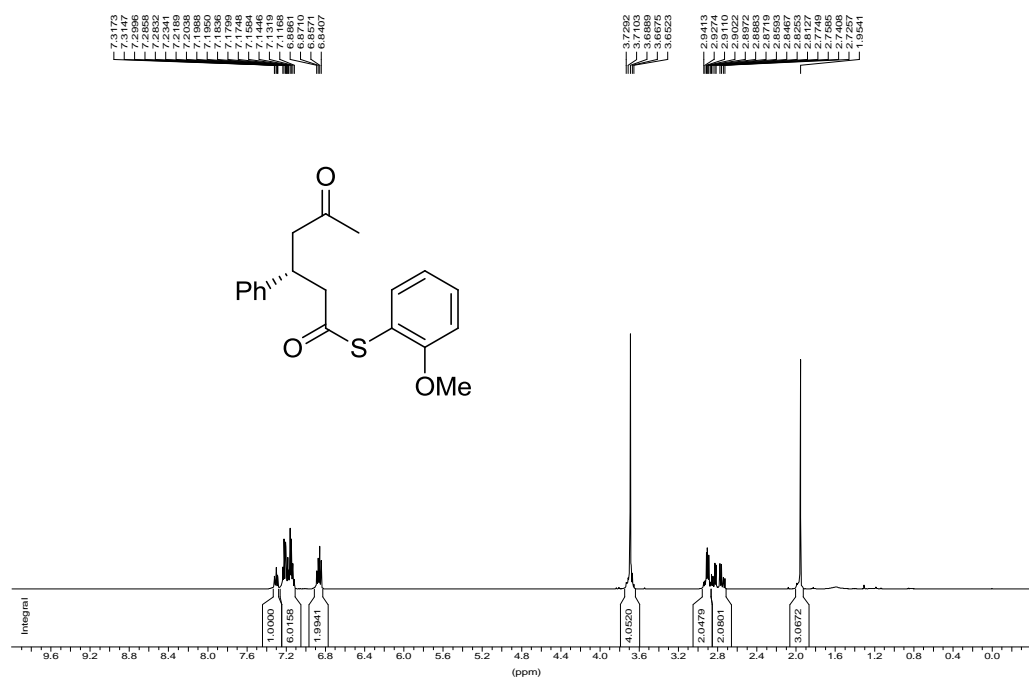
Compound 3ja



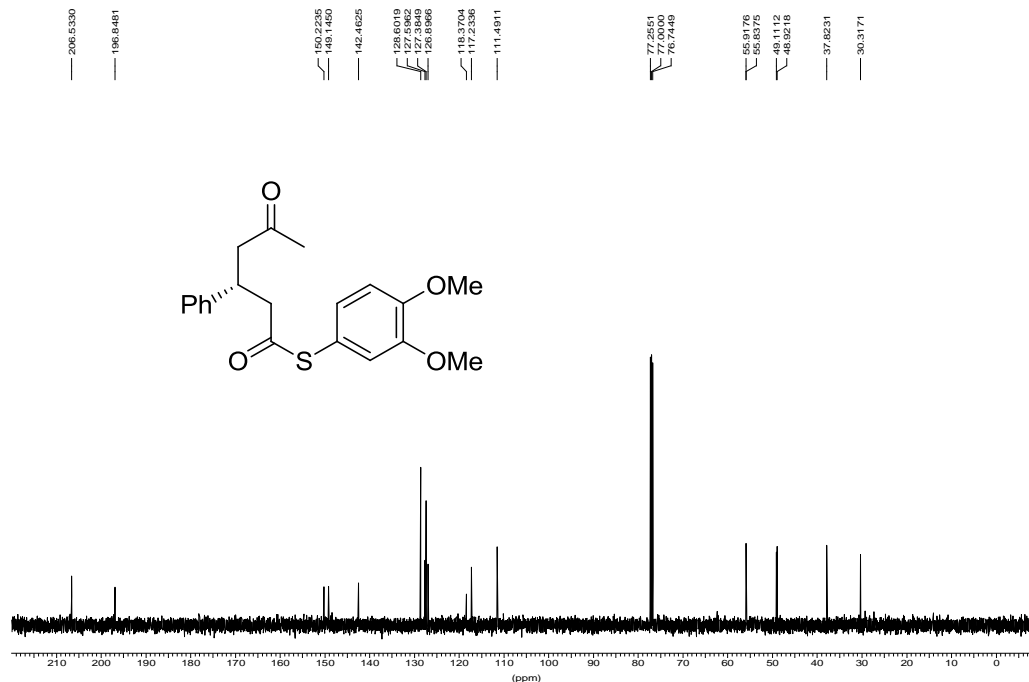
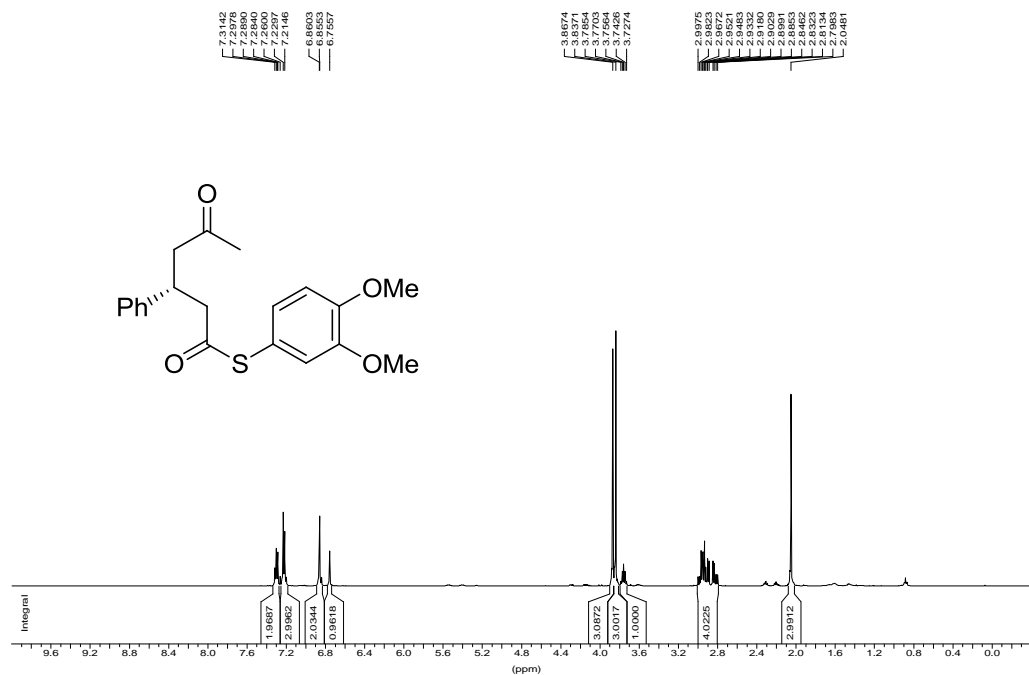
Compound 3ab



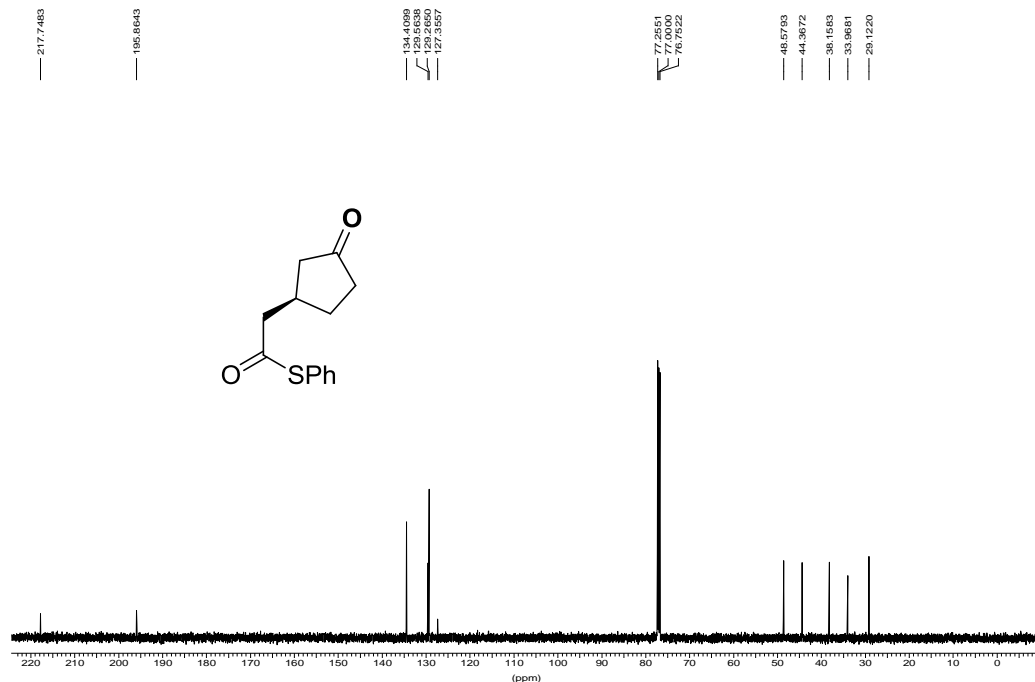
Compound 3ac



Compound 3ad



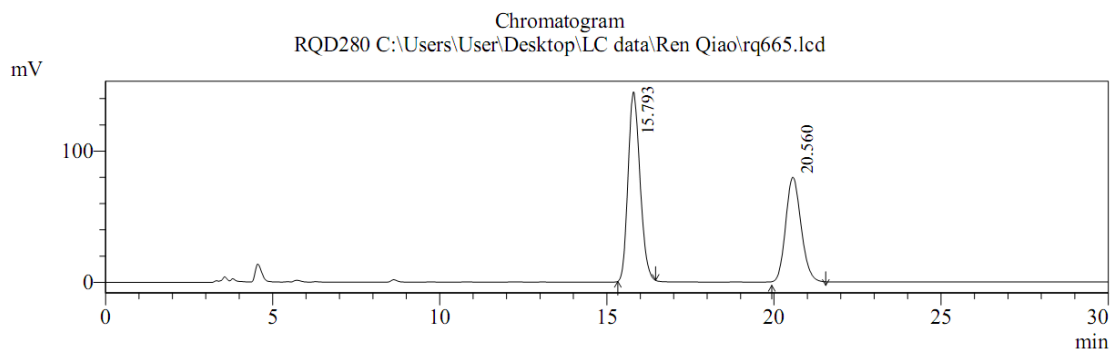
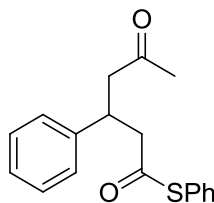
Compound 3ka



Racemic 3aa

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq665.lcd
Acquired by : Admin
Sample Name : RQD280
Sample ID : RQ
Data File Name : rq665.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



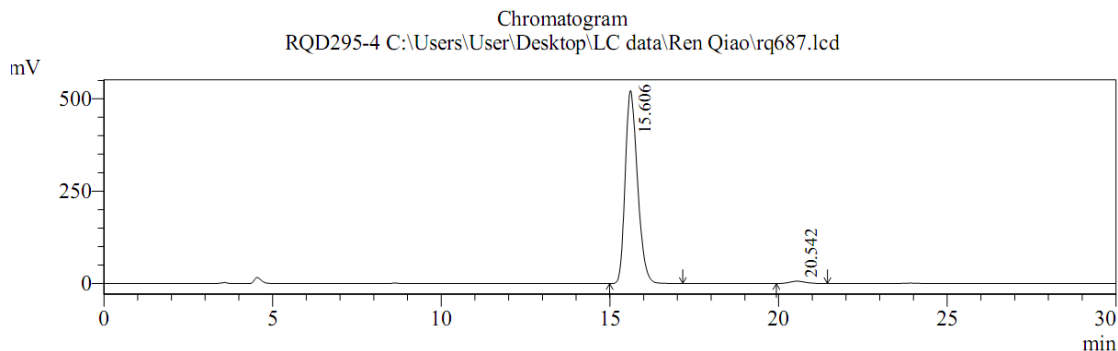
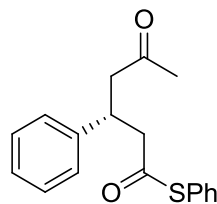
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.793	3561837	143991	55.958	63.624
2	20.560	2803335	82323	44.042	36.376
Total		6365171	226315	100.000	100.000

Enantiomeric enriched 3aa

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq687.lcd
Acquired by : Admin
Sample Name : RQD295-4
Sample ID : RQ
Data File Name : rq687.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



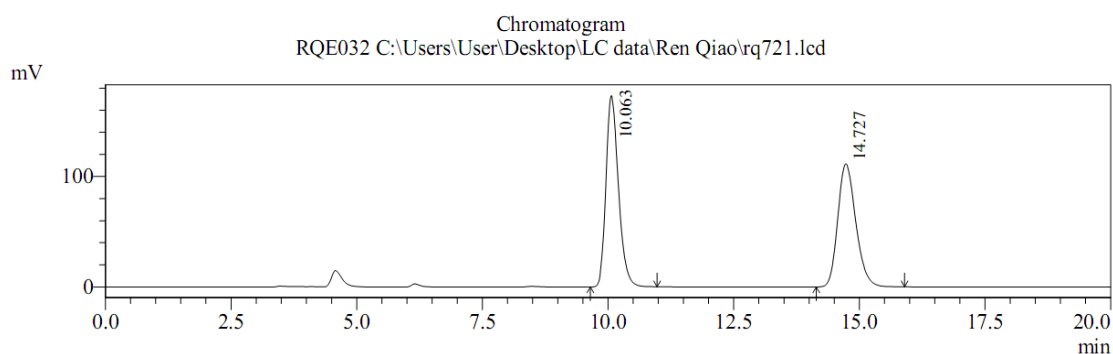
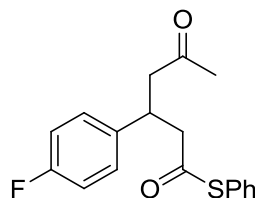
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.606	13206336	522074	98.508	98.804
2	20.542	199958	6322	1.492	1.196
Total		13406295	528396	100.000	100.000

Racemic 3ba

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq721.lcd
Acquired by : Admin
Sample Name : RQE032
Sample ID : RQ
Data File Name : rq721.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



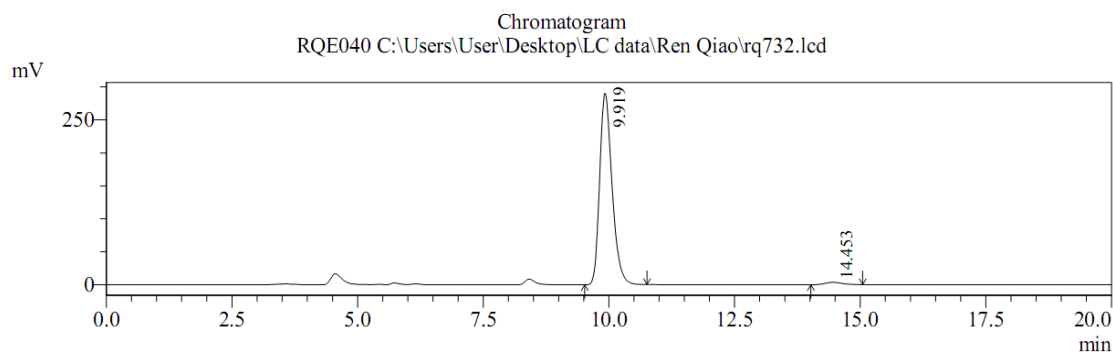
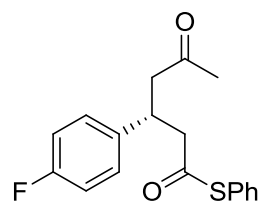
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.063	2992466	173286	51.823	60.857
2	14.727	2781985	111459	48.177	39.143
Total		5774451	284745	100.000	100.000

Enantiomeric enriched 3ba

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq732.lcd
Acquired by : Admin
Sample Name : RQE040
Sample ID : RQ
Data File Name : rq732.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



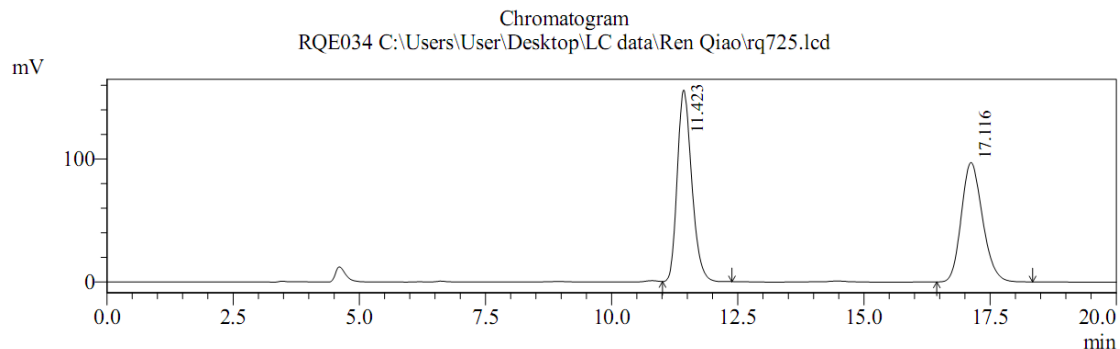
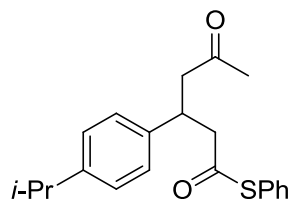
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.919	4969623	290271	98.357	98.762
2	14.453	83017	3638	1.643	1.238
Total		5052640	293909	100.000	100.000

Racemic 3ca

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq725.lcd
Acquired by : Admin
Sample Name : RQE034
Sample ID : RQ
Data File Name : rq725.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



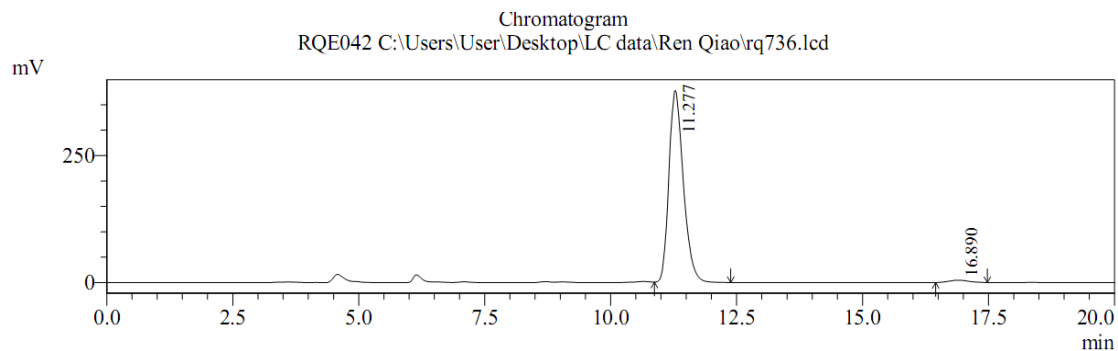
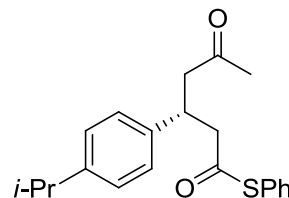
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.423	3115762	155856	52.294	61.601
2	17.116	2842384	97155	47.706	38.399
Total		5958146	253011	100.000	100.000

Enantiomeric enriched 3ca

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq736.lcd
Acquired by : Admin
Sample Name : RQE042
Sample ID : RQ
Data File Name : rq736.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



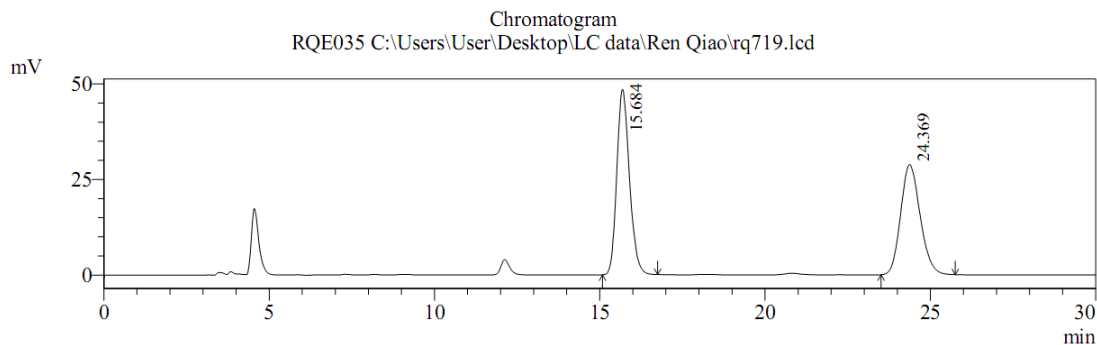
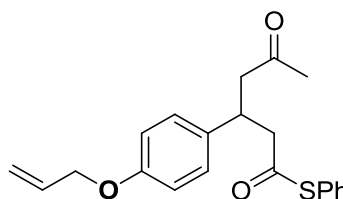
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.277	7514669	377523	98.368	98.799
2	16.890	124708	4589	1.632	1.201
Total		7639377	382112	100.000	100.000

Racemic 3da

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq719.lcd
 Acquired by : Admin
 Sample Name : RQE035
 Sample ID : RQ
 Data File Name : rq719.lcd
 Method File Name : 20%IPA, 1ml-min, 60min.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Description : IC column ;20%IPA ;1ml/min



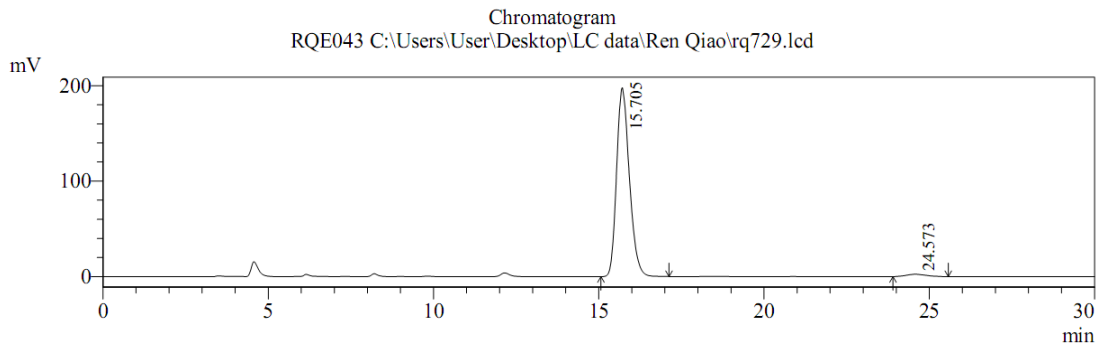
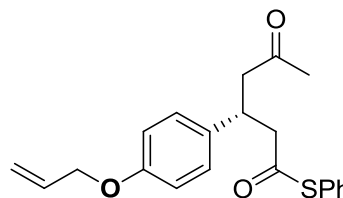
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.684	1291521	48446	52.284	62.706
2	24.369	1178670	28812	47.716	37.294
Total		2470191	77259	100.000	100.000

Enantiomeric enriched 3da

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq729.lcd
 Acquired by : Admin
 Sample Name : RQE043
 Sample ID : RQ
 Data File Name : rq729.lcd
 Method File Name : 20%IPA, 1ml-min, 60min.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Description : IC column ;20%IPA ;1ml/min



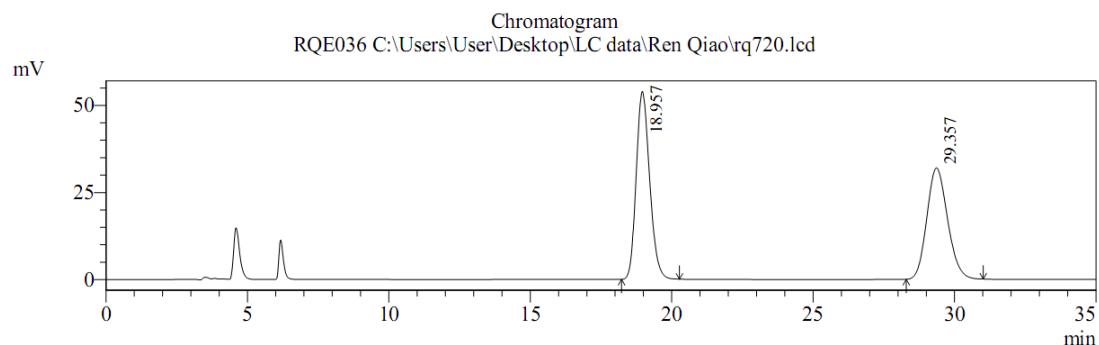
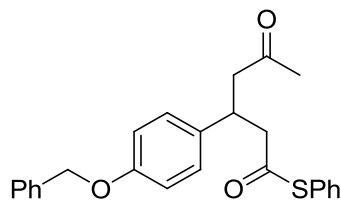
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.705	5328363	197841	98.141	98.793
2	24.573	100924	2417	1.859	1.207
Total		5429288	200258	100.000	100.000

Racemic 3ea

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq720.lcd
Acquired by : Admin
Sample Name : RQE036
Sample ID : RQ
Data File Name : rq720.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



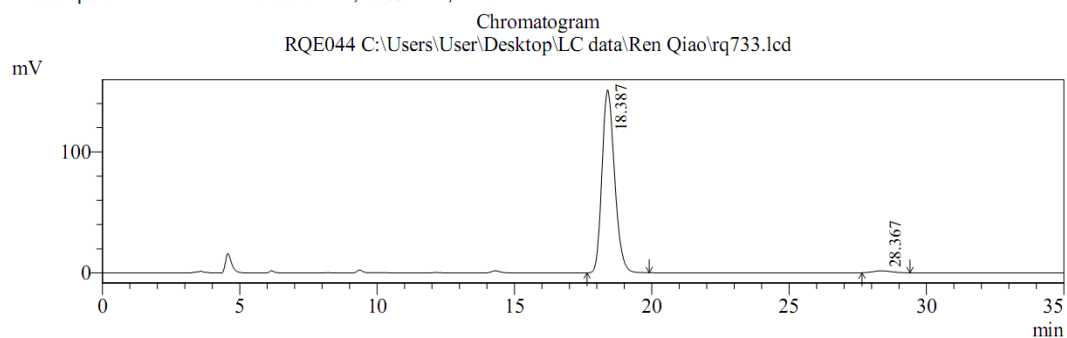
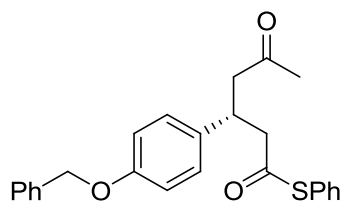
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.957	1784660	53936	52.329	62.797
2	29.357	1625798	31954	47.671	37.203
Total		3410458	85891	100.000	100.000

Enantiomeric enriched 3ea

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq733.lcd
Acquired by : Admin
Sample Name : RQE044
Sample ID : RQ
Data File Name : rq733.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



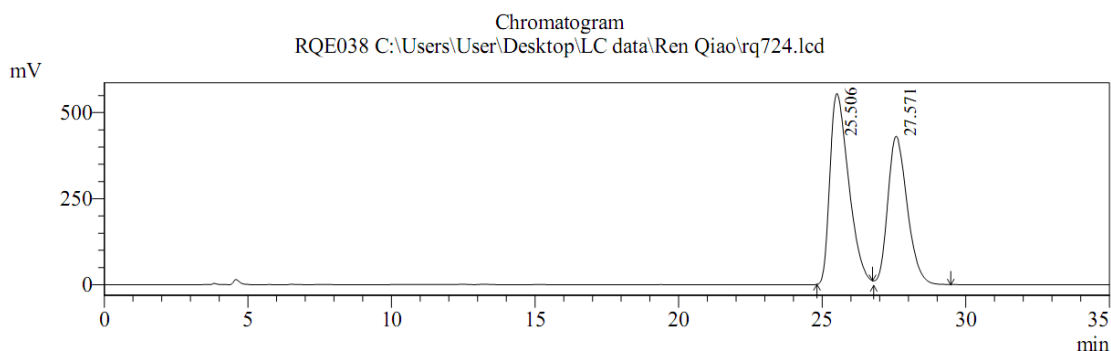
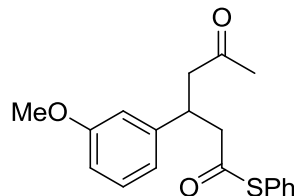
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.387	4818368	151211	98.435	98.920
2	28.367	76629	1650	1.565	1.080
Total		4894997	152862	100.000	100.000

Racemic 3fa

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq724.lcd
Acquired by : Admin
Sample Name : RQE038
Sample ID : RQ
Data File Name : rq724.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



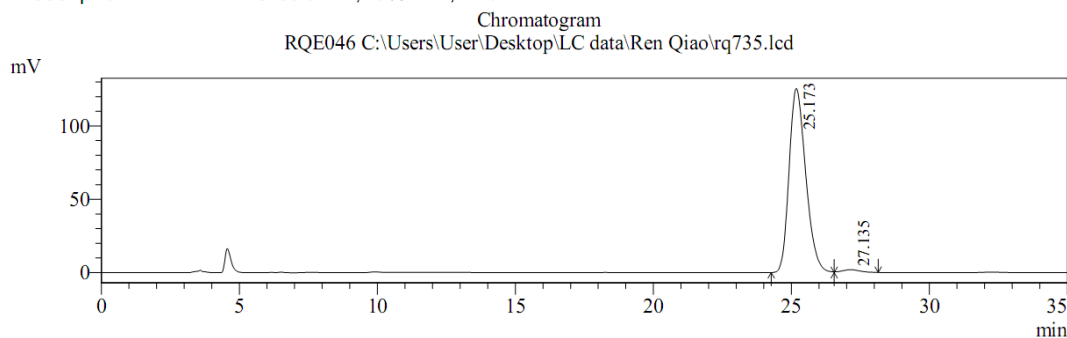
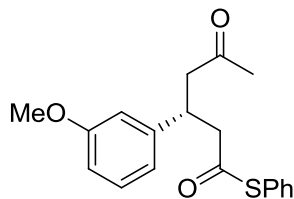
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.506	24735686	551014	54.506	55.996
2	27.571	20645943	433003	45.494	44.004
Total		45381629	984016	100.000	100.000

Enantiomeric enriched 3fa

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq735.lcd
Acquired by : Admin
Sample Name : RQE046
Sample ID : RQ
Data File Name : rq735.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



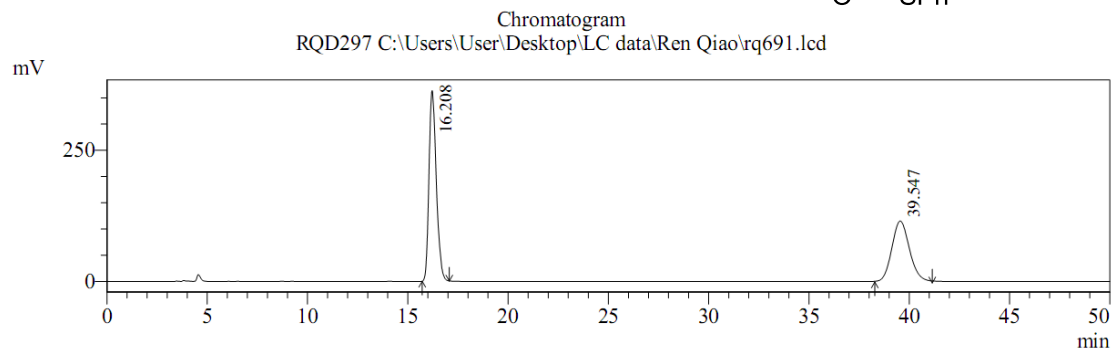
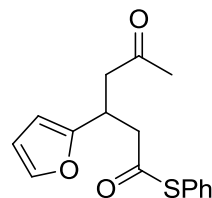
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.173	5270470	125457	98.400	98.502
2	27.135	85700	1908	1.600	1.498
Total		5356171	127364	100.000	100.000

Racemic 3ga

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq691.lcd
Acquired by : Admin
Sample Name : RQD297
Sample ID : RQ
Data File Name : rq691.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



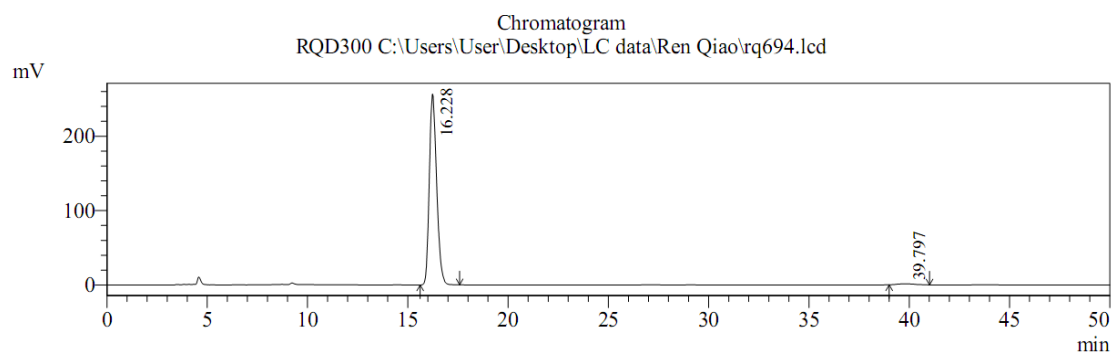
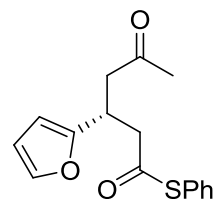
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.208	9222153	363123	55.596	75.624
2	39.547	7365720	117047	44.404	24.376
Total		16587873	480170	100.000	100.000

Enantiomeric enriched 3ga

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq694.lcd
Acquired by : Admin
Sample Name : RQD300
Sample ID : RQ
Data File Name : rq694.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



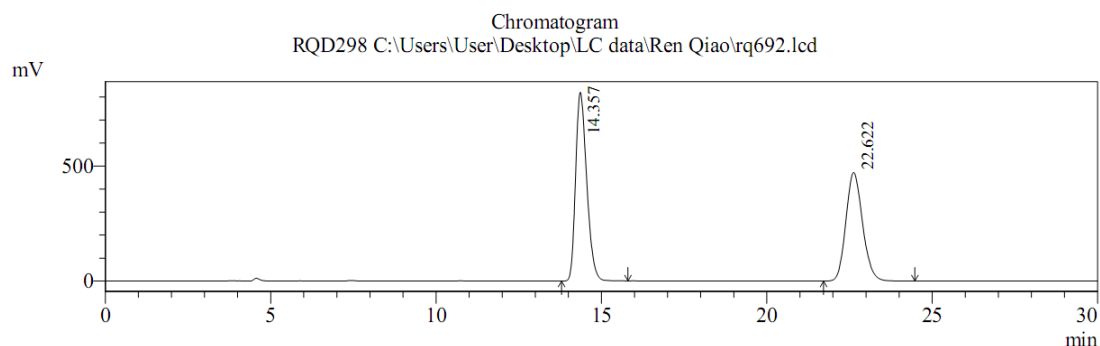
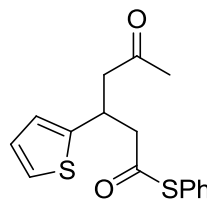
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.228	6515593	256557	98.830	99.467
2	39.797	77121	1376	1.170	0.533
Total		6592714	257933	100.000	100.000

Racemic 3ha

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq692.lcd
Acquired by : Admin
Sample Name : RQD298
Sample ID : RQ
Data File Name : rq692.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



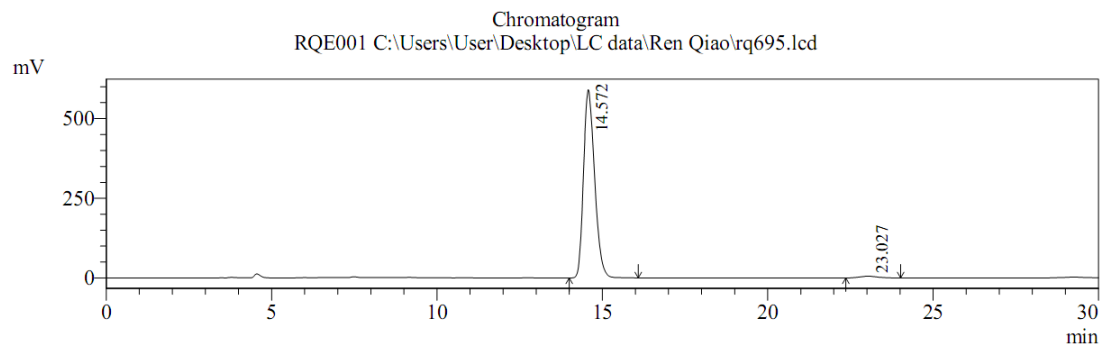
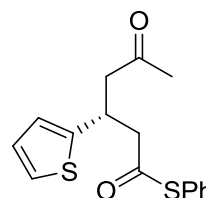
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.357	19099495	821168	53.658	63.520
2	22.622	16495351	471599	46.342	36.480
Total		35594847	1292767	100.000	100.000

Enantiomeric enriched 3ha

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq695.lcd
Acquired by : Admin
Sample Name : RQE001
Sample ID : RQ
Data File Name : rq695.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



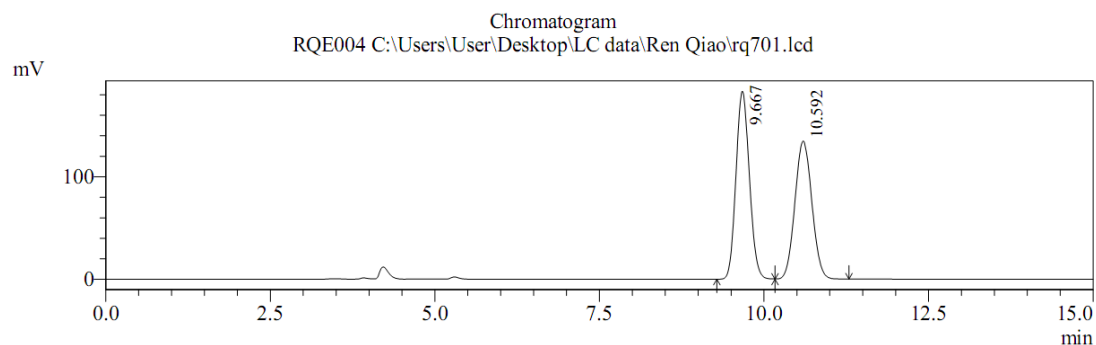
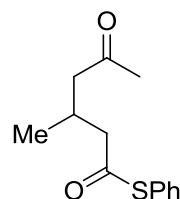
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.572	13742729	590527	98.588	99.056
2	23.027	196854	5626	1.412	0.944
Total		13939583	596153	100.000	100.000

Racemic 3ia

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq701.lcd
Acquired by : Admin
Sample Name : RQE004
Sample ID : RQ
Data File Name : rq701.lcd
Method File Name : 10%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : ID column ; 10%IPA ; 1ml/min



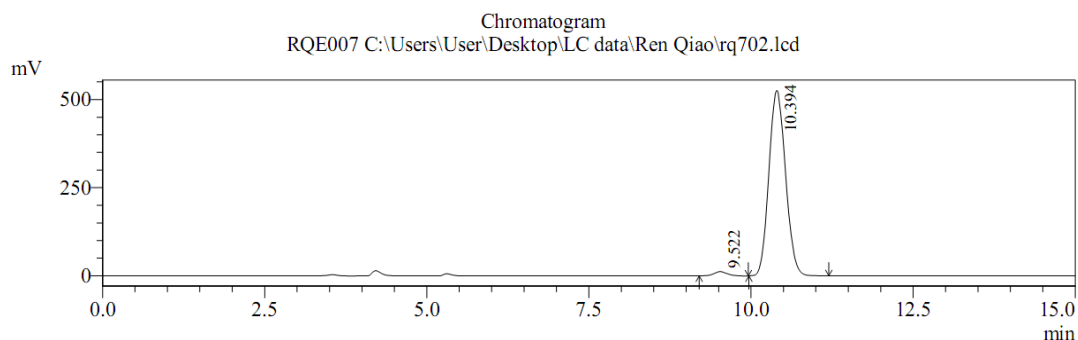
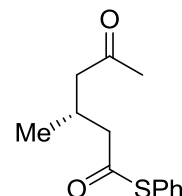
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.667	2594168	183166	51.751	57.642
2	10.592	2418598	134597	48.249	42.358
Total		5012767	317764	100.000	100.000

Enantiomeric enriched 3ia

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq702.lcd
Acquired by : Admin
Sample Name : RQE007
Sample ID : RQ
Data File Name : rq702.lcd
Method File Name : 10%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : ID column ; 10%IPA ; 1ml/min



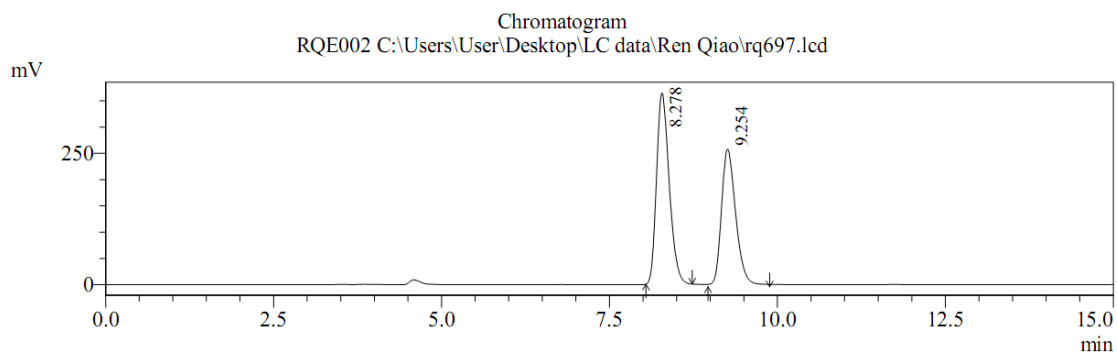
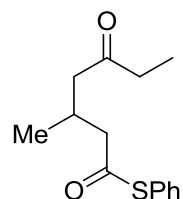
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.522	165012	12028	1.728	2.237
2	10.394	9383898	525632	98.272	97.763
Total		9548911	537660	100.000	100.000

Racemic 3ja

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq697.lcd
Acquired by : Admin
Sample Name : RQE002
Sample ID : RQ
Data File Name : rq697.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



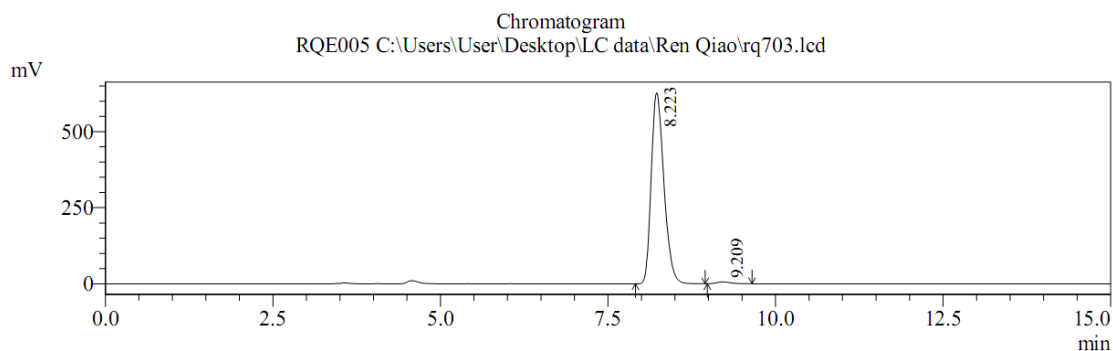
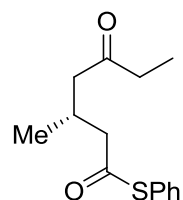
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.278	4776181	364045	54.487	58.130
2	9.254	3989620	262219	45.513	41.870
Total		8765801	626264	100.000	100.000

Enantiomeric enriched 3ja

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq703.lcd
Acquired by : Admin
Sample Name : RQE005
Sample ID : RQ
Data File Name : rq703.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



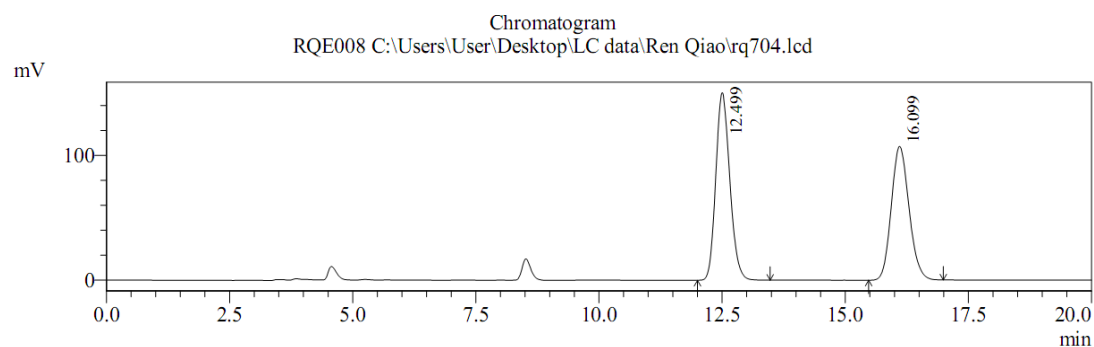
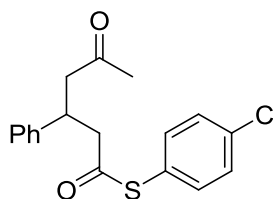
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.223	8286437	627879	98.955	99.007
2	9.209	87485	6299	1.045	0.993
Total		8373922	634178	100.000	100.000

Racemic 3ab

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq704.lcd
Acquired by : Admin
Sample Name : RQE008
Sample ID : RQ
Data File Name : rq704.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



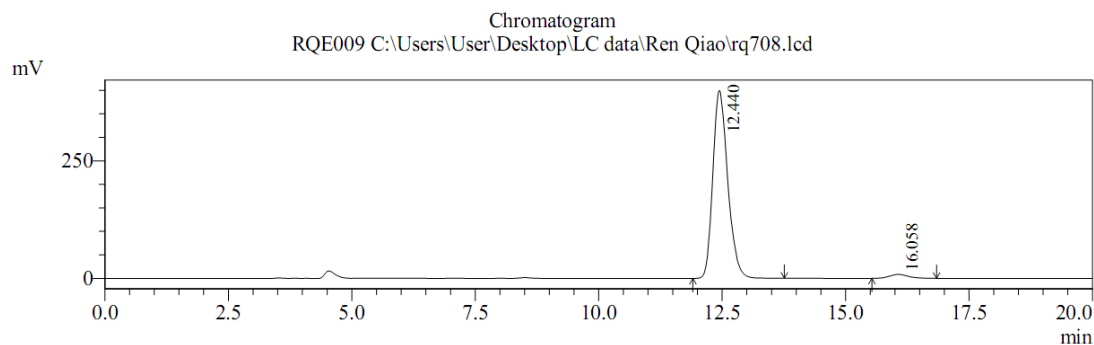
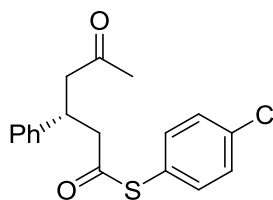
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.499	2985206	150425	52.662	58.372
2	16.099	2683446	107273	47.338	41.628
Total		5668652	257698	100.000	100.000

Enantiomeric enriched 3ab

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq708.lcd
Acquired by : Admin
Sample Name : RQE009
Sample ID : RQ
Data File Name : rq708.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



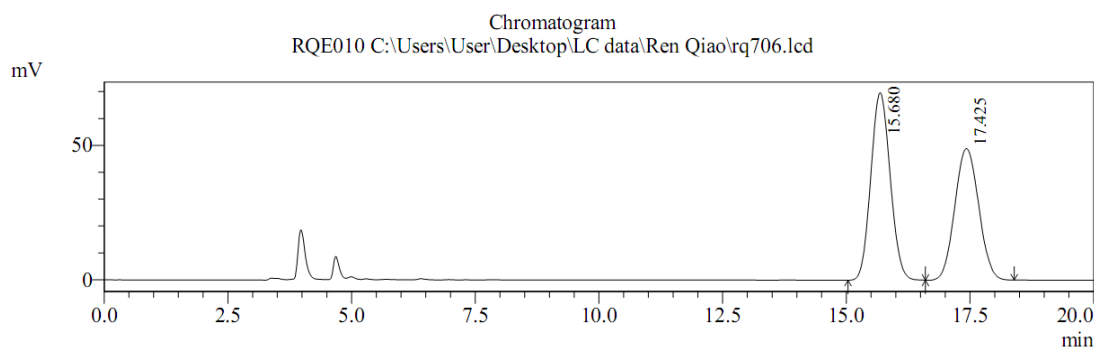
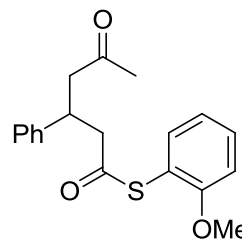
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.440	8379533	399331	97.486	97.952
2	16.058	216110	8350	2.514	2.048
Total		8595642	407681	100.000	100.000

Racemic 3ac

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq706.lcd
 Acquired by : Admin
 Sample Name : RQE010
 Sample ID : RQ
 Data File Name : rq706.lcd
 Method File Name : 20%IPA, 1ml-min, 60min.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Description : ID column ;20%IPA ;1ml/min



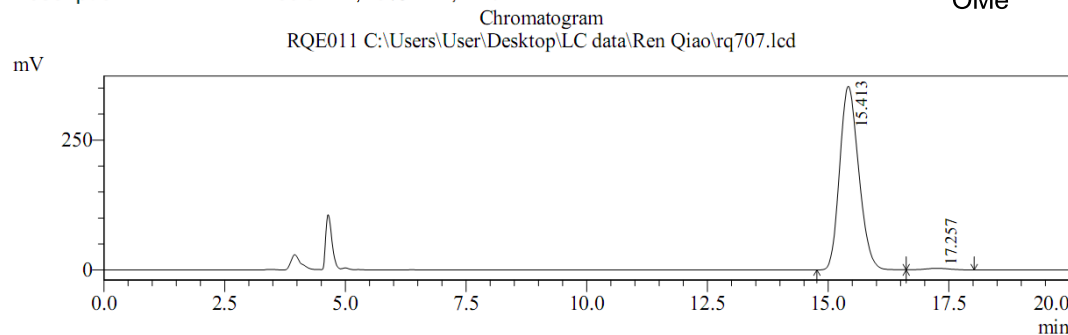
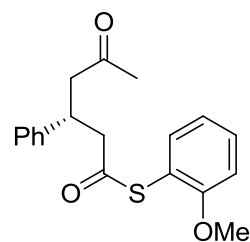
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.680	1895216	69771	53.573	58.773
2	17.425	1642440	48942	46.427	41.227
Total		3537656	118713	100.000	100.000

Enantiomeric enriched 3ac

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq707.lcd
 Acquired by : Admin
 Sample Name : RQE011
 Sample ID : RQ
 Data File Name : rq707.lcd
 Method File Name : 20%IPA, 1ml-min, 60min.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Description : ID column ;20%IPA ;1ml/min



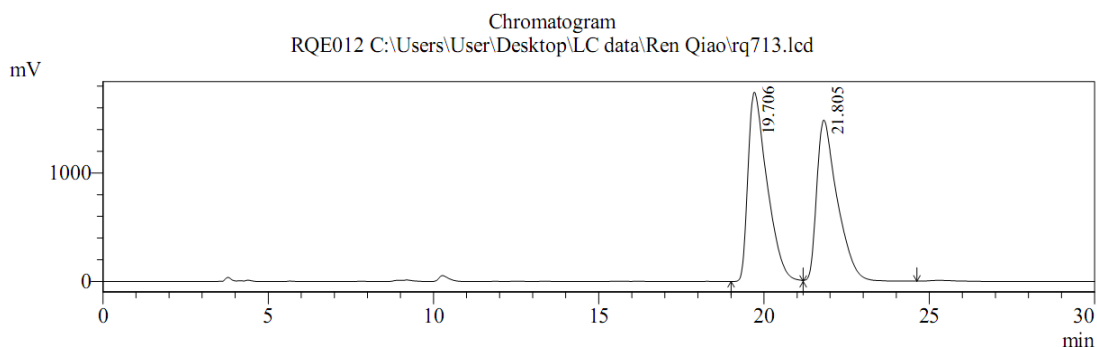
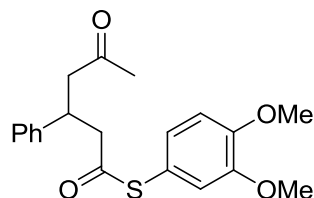
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.413	9695470	353306	98.910	99.114
2	17.257	106874	3159	1.090	0.886
Total		9802344	356465	100.000	100.000

Racemic 3ad

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq713.lcd
Acquired by : Admin
Sample Name : RQE012
Sample ID : RQ
Data File Name : rq713.lcd
Method File Name : 10%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IA column ;10%IPA ;1ml/min



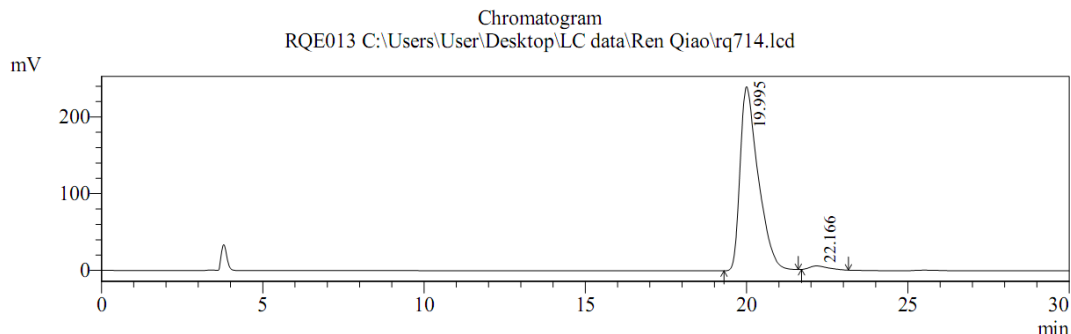
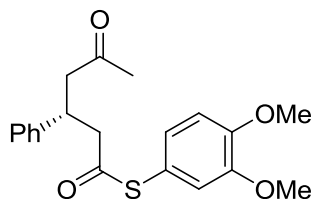
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.706	70072823	1742886	52.193	53.982
2	21.805	64184918	1485768	47.807	46.018
Total		134257741	3228655	100.000	100.000

Enantiomeric enriched 3ad

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq714.lcd
Acquired by : Admin
Sample Name : RQE013
Sample ID : RQ
Data File Name : rq714.lcd
Method File Name : 10%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IA column ;10%IPA ;1ml/min



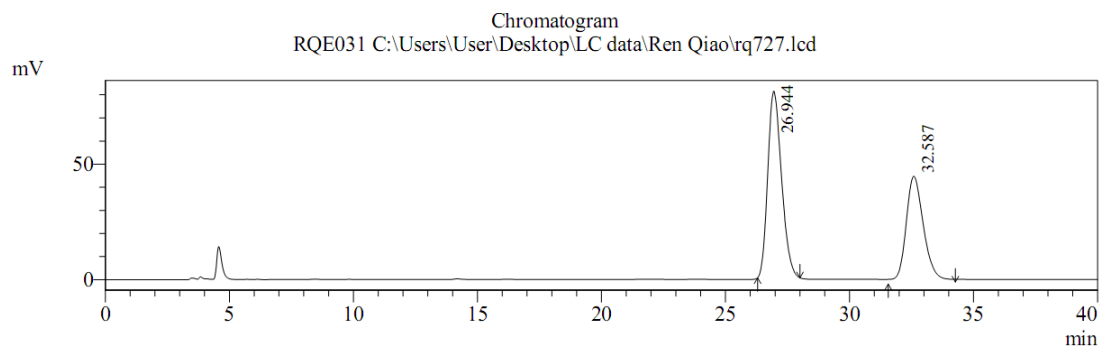
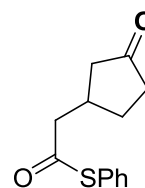
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.995	9306096	239413	97.986	97.981
2	22.166	191299	4933	2.014	2.019
Total		9497396	244347	100.000	100.000

Racemic 3ka

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq727.lcd
Acquired by : Admin
Sample Name : RQE031
Sample ID : RQ
Data File Name : rq727.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



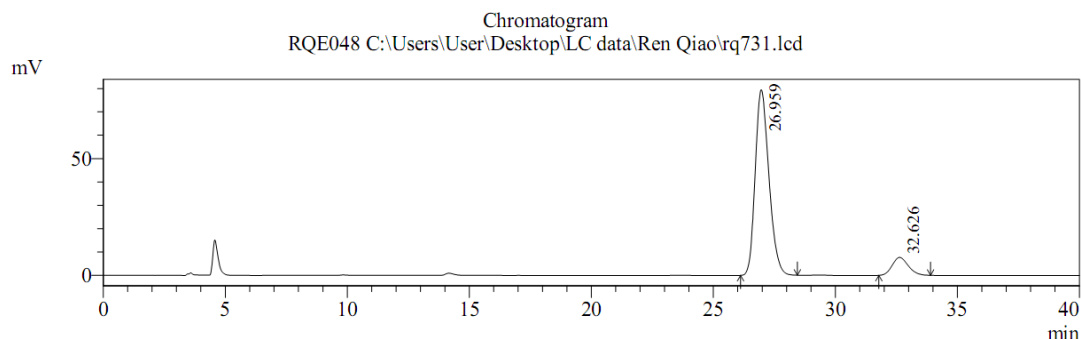
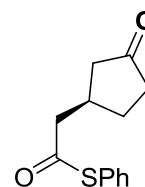
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.944	3112751	80811	56.847	63.553
2	32.587	2362930	46344	43.153	36.447
Total		5475681	127155	100.000	100.000

Enantiomeric enriched 3ka

==== Shimadzu LCsolution Analysis Report ====

C:\Users\User\Desktop\LC data\Ren Qiao\rq731.lcd
Acquired by : Admin
Sample Name : RQE048
Sample ID : RQ
Data File Name : rq731.lcd
Method File Name : 20%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column ;20%IPA ;1ml/min



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.959	3107383	79459	89.822	91.199
2	32.626	352125	7668	10.178	8.801
Total		3459508	87126	100.000	100.000