Supporting Information

The C(sp^3)-H Bond Functionalization of Thioethers with Styrenes with Insight into the Mechanism

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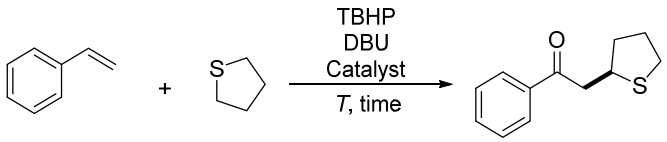
1. Additional Experiments on Reaction Condition Optimization[a]



1a 2a 3a

Entry	Peroxide (equiv)	Base (equiv)	Catalyst (mol%)	Yield (%)[b]
1	TBHP (5.0)	DBU (1.5)	$Cu(OTf)_2$ (40)	16
2	TBHP (5.0)	DBU (1.5)	$Co(OAc)_2{\cdot}4H_2O$ (40)	18
3	TBHP (5.0)	DBU (1.5)	$MnCl_2{\cdot}4H_2O$ (40)	21
4	TBHP (5.0)	DBU (1.5)	$Ni(OAc)_2{\cdot}4H_2O$ (40)	26
5	TBHP (5.0)	DBU (1.5)	$NiSO_4{\cdot}6H_2O$ (40)	27
6[c]	TBHP (40)	DBU (6.0)	-	29
7[d]	TBHP (40)	DBU (6.0)	-	36
8[e]	TBHP (40)	DBU (6.0)	-	31

[a] Reaction conditions: Styrene **1a** (21 mg, 0.2 mmol, 1.0 equiv), Tetrahydrothiophene **2a** (3.0 mL), TBHP (70% aqueous solution), in sealed tube at 60 ºC for 12 h, unless otherwise noted.

[b] Isolated yields.

[c] Styrene **1a** (31 mg, 0.3 mmol, 1.0 equiv), Tetrahydrothiophene **2a** (6.0 mL), at 80 ºC for 24 h.

[d] Styrene **1a** (42 mg, 0.4 mmol, 1.0 equiv), Tetrahydrothiophene **2a** (6.0 mL), at 80 ºC for 24 h.

[e] Styrene **1a** (52 mg, 0.5 mmol, 1.0 equiv), Tetrahydrothiophene **2a** (6.0 mL), at 80 ºC for 24 h.

2. General Information

All of the reagents were purchased from commercial sources without additional purification. The TBHP was 70% aqueous solution. The ^1H NMR and ^{13}C NMR spectra of the products were measured at the spectrometer of 400 MHz (300 MHz for **3o**) and 100 MHz. And high resolution mass spectroscopy (HRMS) spectra were acquired by EI and ESI.

3. Experimental Section

General Procedure for the C(sp^3)-H Bond Functionalization of Thioethers with Styrenes

In a 15 mL tube with a stir bar, firstly it was charged with 6 mL thioether, then DBU (182 mg, 1.2 mmol, 6.0 equiv) and TBHP (1032 mg, 8.0 mmol, 40.0 equiv) were added. At last, styrene (0.2 mmol, 1.0 equiv) was added into the reaction system. The tube was sealed with a teflon coated cap and then the reaction mixture was stirred at 80 ℃ for 24

h. When the reaction got complete, the solvent was evaporated off and the residue was flash chromatographed (petroleum ether/ ethyl acetate 10/1, v/v) to deliver the final pure products.

Inductive Effect Index Calculation of the C(sp^3)-H Bond in Thioethers

Table S1 The Results of Inductive Index Calculation of C(sp^3)-H Bond in Thioethers

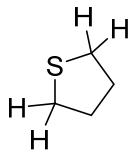
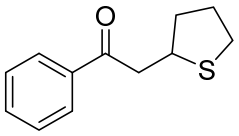
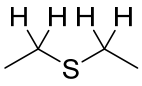
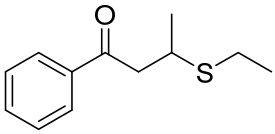
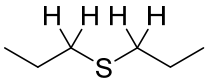
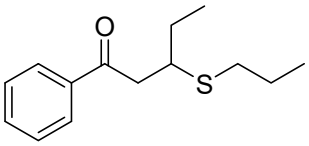
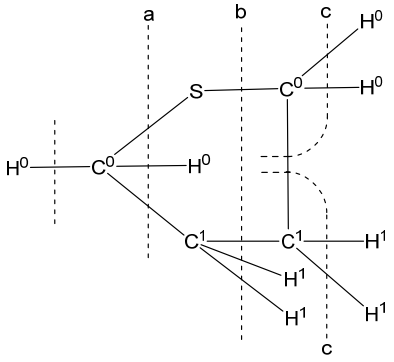
C(sp^3)-H	Inductive Effect Index	Products and Yields
	0.0110	 39%
	0.00859	 21%
	0.00757	 12%

Table S2. Parameters of Bond Length and Atom Electronegativity of Tetrahydrothiophene

Tetrahydrothiophene			
Bond Length /Å	C_0H_0	SC_0	C_1H_1
	1.09232	1.85365	1.09447
Atom	C	H	S
Electronegativity	2.55	2.20	2.58



$I=i_0+i$

$=\frac{\delta C0H0}{rC0H0}+i$

$=\frac{\delta C0H0}{rC0H0}+\frac{1}{\alpha}\sum(\frac{\delta}{r})a+\frac{1}{\alpha^2}\sum(\frac{\delta}{r})b+\frac{1}{\alpha^3}\sum(\frac{\delta}{r})c$

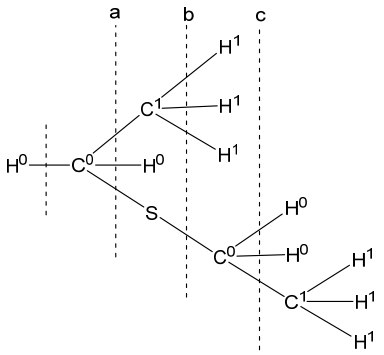
$=\frac{\delta C0H0}{rC0H0}+\frac{1}{\alpha}(\frac{\delta SC0}{rSC0}+\frac{\delta H0C0}{rH0C0}+\frac{\delta C1C0}{rC1C0})+\frac{1}{\alpha^2}(\frac{\delta C0S}{rC0S}+\frac{\delta C1C1}{rC1C1}+2\frac{\delta H1C1}{rH1C1})+\frac{1}{\alpha^3}(2\frac{\delta C0H0}{rC0H0}+\frac{\delta C1C0}{rC1C0}+2\frac{\delta H1C1}{rH1C1}+\frac{\delta C0C1}{rC0C1})$

$=\frac{\frac{2.55-2.20}{2.55+2.20}}{1.09232}+\frac{1}{2.7}\times(\frac{\frac{2.58-2.55}{2.58+2.55}}{1.85365}+\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09232}+0)+\frac{1}{2.7^2}\times(\frac{\frac{2.55-2.58}{2.55+2.58}}{1.85365}+0+2\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09447})+\frac{1}{2.7^3}\times(2\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09232}+0+2\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09447}+0)$

$=0.0110$

Table S3. Parameters of Bond Length and Atom Electronegativity of Diethyl Sulfide

Diethyl Sulfide			
Bond Length /Å	C_0H_0	SC_0	C_1H_1
	1.09343	1.83688	1.09313
Atom	C	H	S
Electronegativity	2.55	2.20	2.58



$I=i_0+i$

$=\frac{\delta C0H0}{rC0H0}+i$

$=\frac{\delta C0H0}{rC0H0}+\frac{1}{\alpha}\sum(\frac{\delta}{r})a+\frac{1}{\alpha^2}\sum(\frac{\delta}{r})b+\frac{1}{\alpha^3}\sum(\frac{\delta}{r})c$

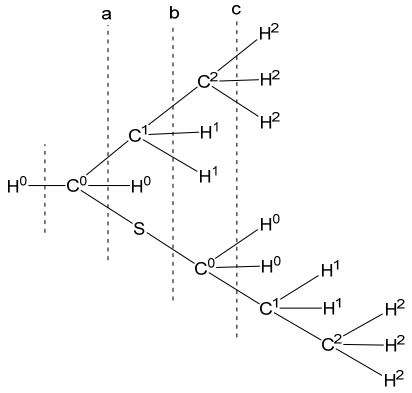
$=\frac{\delta C0H0}{rC0H0}+\frac{1}{\alpha}(\frac{\delta C1C0}{rC1C0}+\frac{\delta H0C0}{rH0C0}+\frac{\delta SC0}{rSC0})+\frac{1}{\alpha^2}(3\frac{\delta H1C1}{rH1C1}+\frac{\delta C0S}{rC0S})+\frac{1}{\alpha^3}(2\frac{\delta H0C0}{rH0C0}+\frac{\delta C1C0}{rC1C0})$

$=\frac{\frac{2.55-2.20}{2.55+2.20}}{1.09343}+\frac{1}{2.7}\times(0+\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09343}+\frac{\frac{2.58-2.55}{2.58+2.55}}{1.83688})+\frac{1}{2.7^2}\times(3\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09313}+\frac{\frac{2.55-2.58}{2.55+2.58}}{1.83688})+\frac{1}{2.7^3}\times(2\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09343}+0)$

$=0.00859$

Table S4. Parameters of Bond Length and Atom Electronegativity of Dipropyl Sulfide

Dipropyl Sulfide				
Bond Length /Å	C_0H_0	SC_0	C_1H_1	C_2H_2
	1.09430	1.83665	1.09500	1.09401
Atom	C	H	S	
Electronegativity	2.55	2.20	2.58	



$I=i_0+i$

$=\frac{\delta C0H0}{rC0H0}+i$

$=\frac{\delta C0H0}{rC0H0}+\frac{1}{\alpha}\sum(\frac{\delta}{r})a+\frac{1}{\alpha^2}\sum(\frac{\delta}{r})b+\frac{1}{\alpha^3}\sum(\frac{\delta}{r})c$

$=\frac{\delta C0H0}{rC0H0}+\frac{1}{\alpha}(\frac{\delta C1C0}{rC1C0}+\frac{\delta H0C0}{rH0C0}+\frac{\delta SC0}{rSC0})+\frac{1}{\alpha^2}(\frac{\delta C2C1}{rC2C1}+2\frac{\delta H1C1}{rH1C1}+\frac{\delta C0S}{rC0S})+\frac{1}{\alpha^3}(3\frac{\delta H2C2}{rH2C2}+2\frac{\delta H0C0}{rH0C0}+\frac{\delta C1C0}{rC1C0})$

$=\frac{\frac{2.55-2.20}{2.55+2.20}}{1.09430}+\frac{1}{2.7}\times(0+\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09430}+\frac{\frac{2.58-2.55}{2.58+2.55}}{1.83665})+\frac{1}{2.7^2}\times(0+2\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09500}+\frac{\frac{2.55-2.58}{2.55+2.58}}{1.83665})+\frac{1}{2.7^2}\times(3\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09401}+2\times\frac{\frac{2.20-2.55}{2.20+2.55}}{1.09430}+0)$

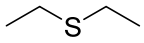
=0.00757

Computational Method

DFT calculations were performed for all the molecular structures at B3LYP/6-311+G** level[S1] using Gaussian 09 program[S2], All the structures were optimized with no imaginary frequency under the environmental effect provided by CPCM model[S3] with diethyl ether as the solvent.

C	0.04885000	1.34800400	-0.13606800
C	-1.28493200	0.71635100	0.27273000
C	-1.28493400	-0.71634800	-0.27273000

C	0.04884600	-1.34800500	0.13606800
S	1.31777900	-0.00000100	0.00000000
H	0.34231300	2.17335800	0.51218600
H	0.02335700	1.70196100	-1.16789800
H	-1.36592400	0.69603400	1.36417600
H	-2.12546000	1.30033600	-0.11278200
H	-2.12546300	-1.30033100	0.11278100
H	-1.36592500	-0.69603100	-1.36417600
H	0.02335400	-1.70196100	1.16789900
H	0.34230800	-2.17335900	-0.51218500



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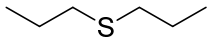
C	0.00000000	1.41108400	-0.62015400
S	0.00000000	0.00000000	0.56005400
C	0.00000000	-1.41108400	-0.62015400
C	0.00000000	-2.73880700	0.13274800
H	0.00000000	3.56922300	-0.57854500
H	0.88535500	2.83827500	0.76580200
H	-0.88535500	2.83827500	0.76580200
H	0.88569000	1.32809800	-1.25452800
H	-0.88569000	1.32809800	-1.25452800
H	0.88569000	-1.32809800	-1.25452800
H	-0.88569000	-1.32809800	-1.25452800
H	0.00000000	-3.56922300	-0.57854500
H	0.88535500	-2.83827500	0.76580200
H	-0.88535500	-2.83827500	0.76580200



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C	0.00000000	-2.74487000	0.35835200
C	0.00000000	3.94071000	-0.60028400
C	0.00000000	-3.94071000	-0.60028400
H	0.87821700	2.79645000	1.01043300
H	-0.87821700	2.79645000	1.01043300
H	0.88634900	1.32836700	-1.02325500
H	-0.88634900	1.32836700	-1.02325500
H	0.88634900	-1.32836700	-1.02325500
H	-0.88634900	-1.32836700	-1.02325500
H	0.87821700	-2.79645000	1.01043300
H	-0.87821700	-2.79645000	1.01043300
H	-0.88416600	3.93209200	-1.24487600
H	0.88416600	3.93209200	-1.24487600

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H	0.88416600	-3.93209200	-1.24487600
H	0.00000000	-4.88344700	-0.04684100
H	-0.88416600	-3.93209200	-1.24487600

References

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S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J, Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O. Ehara, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Gaussian: Wallingford, CT, USA, Revision D.01, 2013.

S3. V. Barone, M. Cossi, Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, *J. Phys. Chem. A* 1998**, 102**, 1995-2001.

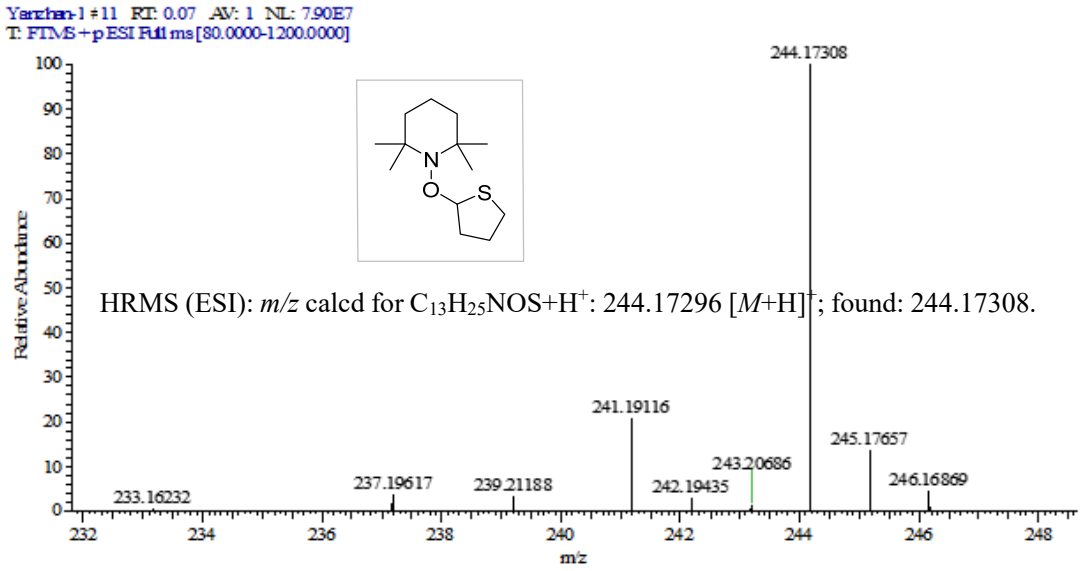
4. Mechanism Studies

4.1.Radical Capture Experiments

Reaction Procedure at the Beginning

In a 10 mL tube with a stir bar, firstly it was charged with 3.0 mL tetrahydrothiophene, then TEMPO (312 mg, 2.0 mmol, 2.0 equiv), DBU (152 mg, 1.0 mmol, 1.0 equiv) and TBHP (643 mg, 5.0 mmol, 5.0 equiv) were added. At last, styrene (104 mg, 1.0 mmol, 1.0 equiv) was added into the reaction system. The tube was sealed with a teflon coated cap and then the reaction mixture was stirred at 60 ℃ for 24 h. When the reaction got complete, get the reaction mixture sample and measure HRMS.

Copy of the HRMS spectrum



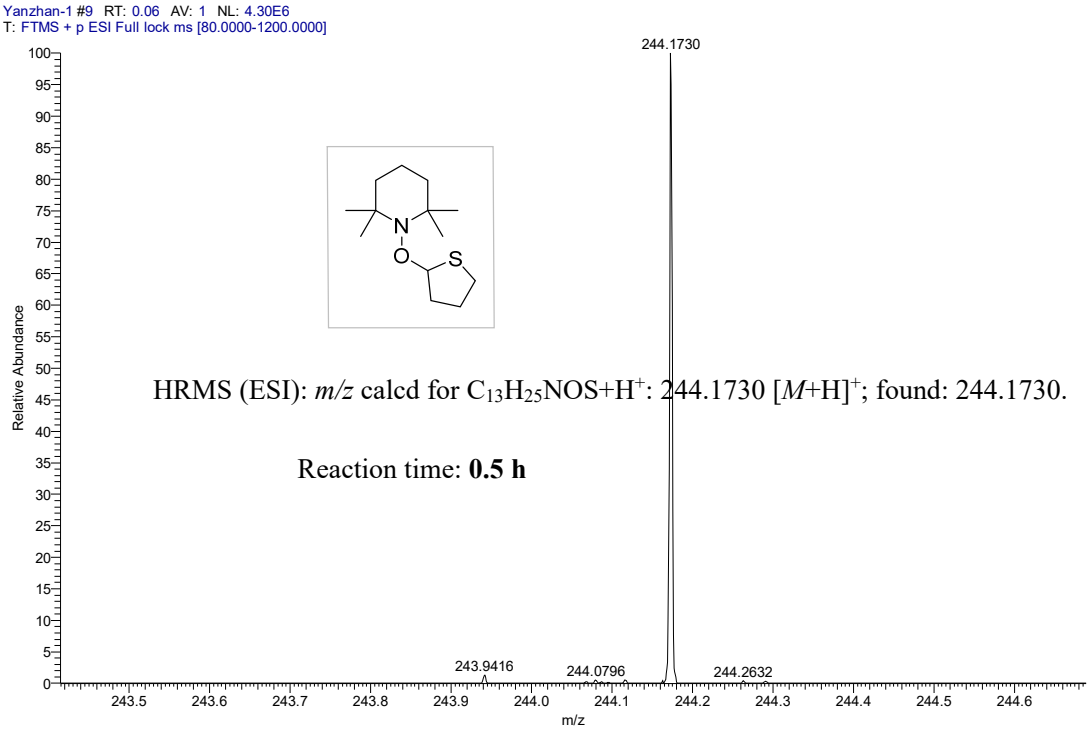
HRMS (ESI): *m/z* calcd for $C_{13}H_{25}NOS+H^+$: 244.17296 $[M+H]^+$; found: 244.17308.

HRMS spectrum of Adduct **D**

Reaction Procedure Modified

In a 15 mL tube with a stir bar, firstly it was charged with 6.0 mL tetrahydrothiophene, then TEMPO (78 mg, 0.5 mmol, 0.5 equiv), DBU (152 mg, 1.0 mmol, 1.0 equiv) and TBHP (1287 mg, 10.0 mmol, 10.0 equiv) were added. At last, styrene (104 mg, 1.0 mmol, 1.0 equiv) was added into the reaction system. The tube was sealed with a teflon coated cap and then the reaction mixture was stirred at 60 ℃ for 0.5 h, 1.0 h, 3.0 h and 6.0 h, respectively. When the reaction got complete, get the reaction mixture sample and measure HRMS.

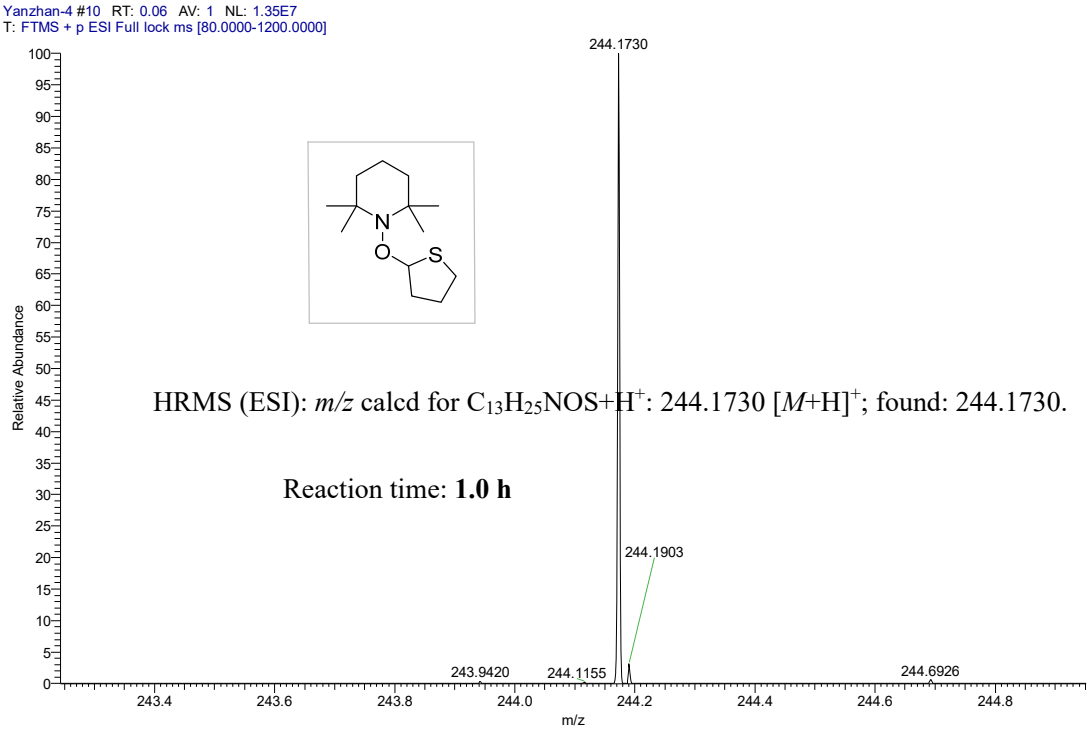
Copies of the HRMS spectra



HRMS (ESI): *m/z* calcd for $C_{13}H_{25}NOS+H^+$: 244.1730 $[M+H]^+$; found: 244.1730.

Reaction time: **0.5 h**

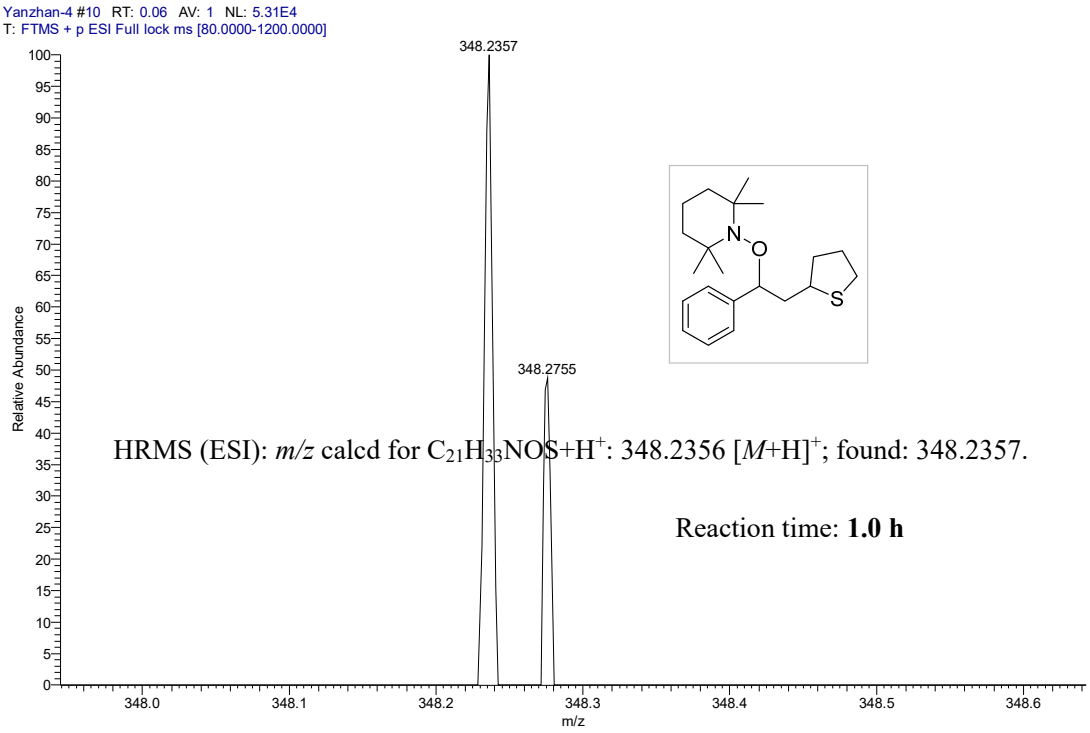
HRMS spectrum of Adduct **D** (after **0.5** h reaction)



HRMS (ESI): *m/z* calcd for $C_{13}H_{25}NOS+H^+$: 244.1730 $[M+H]^+$; found: 244.1730.

Reaction time: **1.0 h**

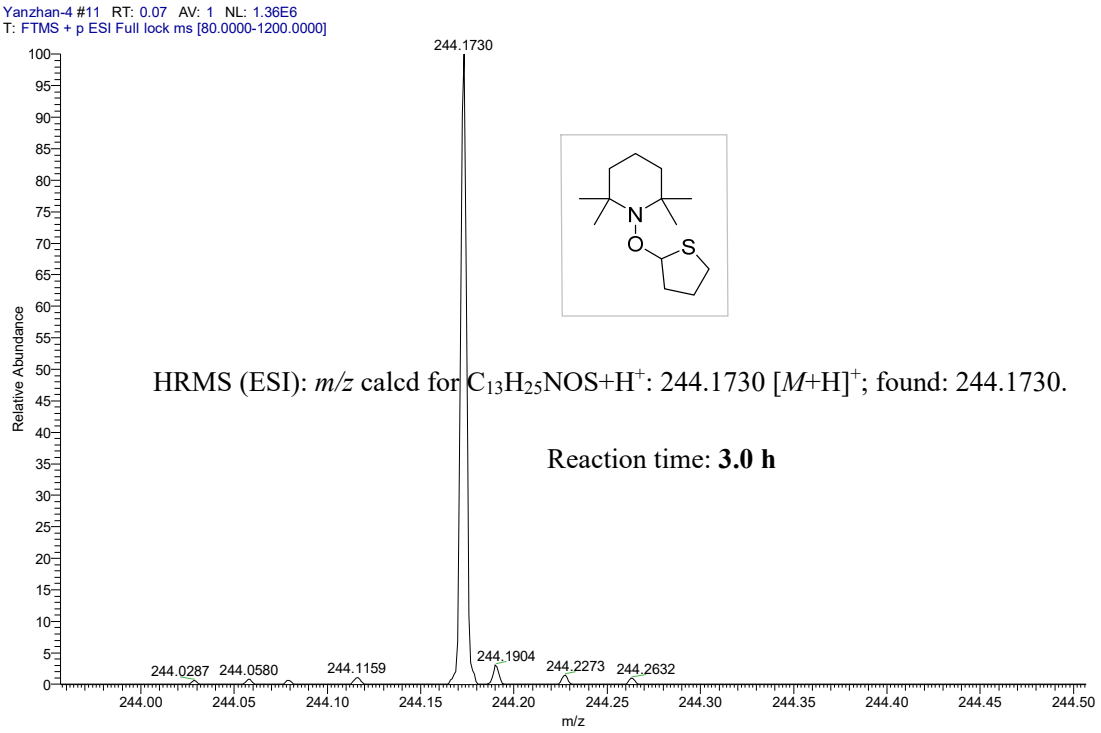
HRMS spectrum of Adduct **D** (after **1.0** h reaction)



HRMS (ESI): *m/z* calcd for $C_{21}H_{33}NOS+H^+$: 348.2356 $[M+H]^+$; found: 348.2357.

Reaction time: **1.0 h**

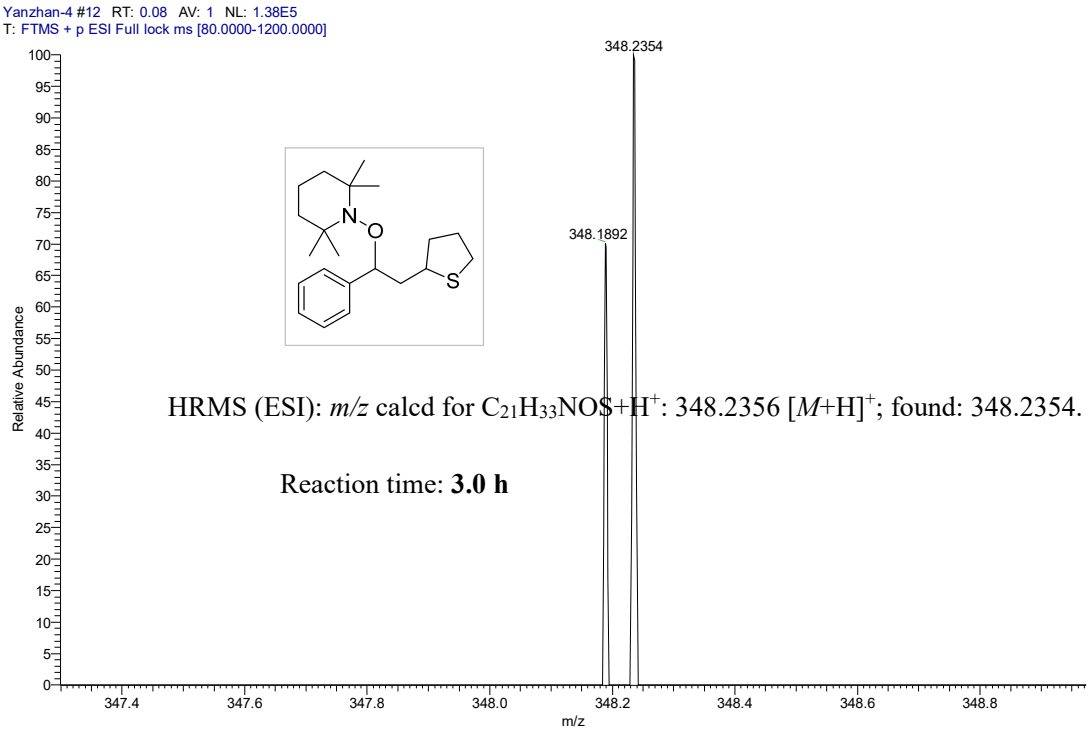
HRMS spectrum of Adduct **E** (after **1.0 h** reaction)



HRMS (ESI): *m/z* calcd for $C_{13}H_{25}NOS+H^+$: 244.1730 $[M+H]^+$; found: 244.1730.

Reaction time: **3.0 h**

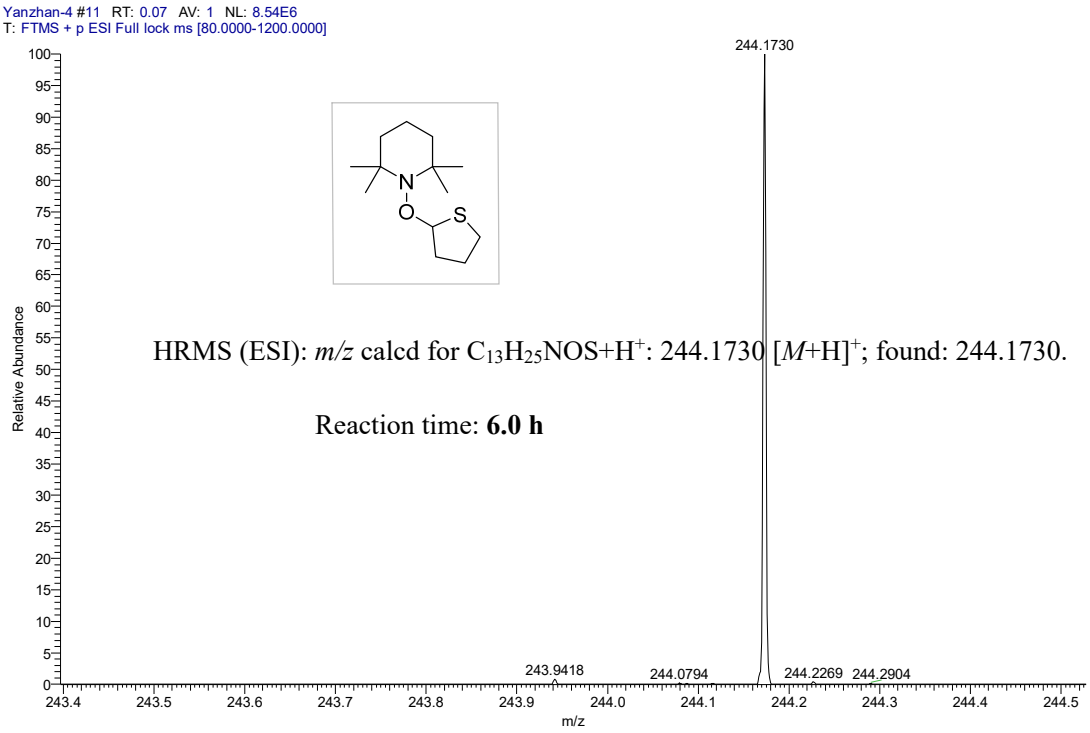
HRMS spectrum of Adduct **D** (after **3.0 h** reaction)



HRMS (ESI): *m/z* calcd for $C_{21}H_{33}NOS+H^+$: 348.2356 $[M+H]^+$; found: 348.2354.

Reaction time: **3.0 h**

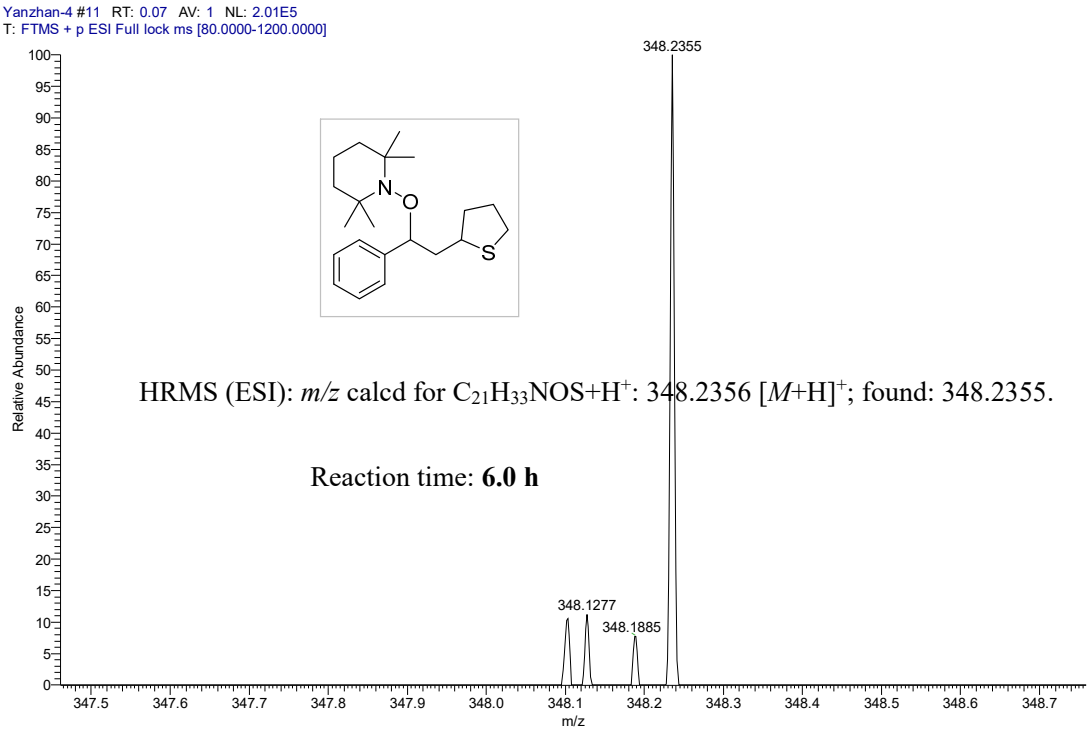
HRMS spectrum of Adduct **E** (after **3.0 h** reaction)



HRMS (ESI): *m/z* calcd for $C_{13}H_{25}NOS+H^+$: 244.1730 $[M+H]^+$; found: 244.1730.

Reaction time: **6.0 h**

HRMS spectrum of Adduct **D** (after **6.0 h** reaction)



HRMS (ESI): *m/z* calcd for $C_{21}H_{33}NOS+H^+$: 348.2356 $[M+H]^+$; found: 348.2355.

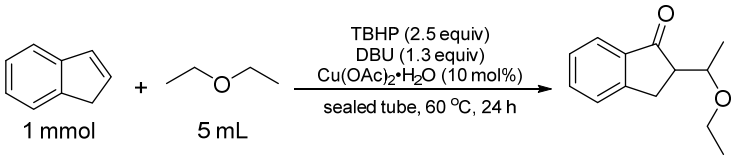
Reaction time: **6.0 h**

HRMS spectrum of Adduct **E** (after **6.0 h** reaction)

4.2.HMBC Spectrum Evidence for Site Selectivity

Synthetic procedure

A mixture of $Cu(OAc)_2 \cdot H_2O$ (20 mg, 0.1 mmol, 10 mol%), TBHP (320 mg, 2.5 mmol, 2.5 equiv, 70% aqueous solution), DBU (200 mg, 1.3 mmol, 1.3 equiv) and indene (116 mg, 1.0 mmol, 1.0 equiv) were added in sequence to an oven-dried 15 mL sealed tube with a stir bar filled with 5 mL diethyl ether. The tube was sealed with a teflon coated cap and then the reaction mixture was stirred at 60 ºC for 24 h. When the reaction got completed, evaporated the reaction solution to get the reaction residue. Made column separation using elute (petroleum ether/ethyl acetate = 20/1, v/v) and silicon gel (200-300 mesh), collected the desired component and evaporated to get the final product.



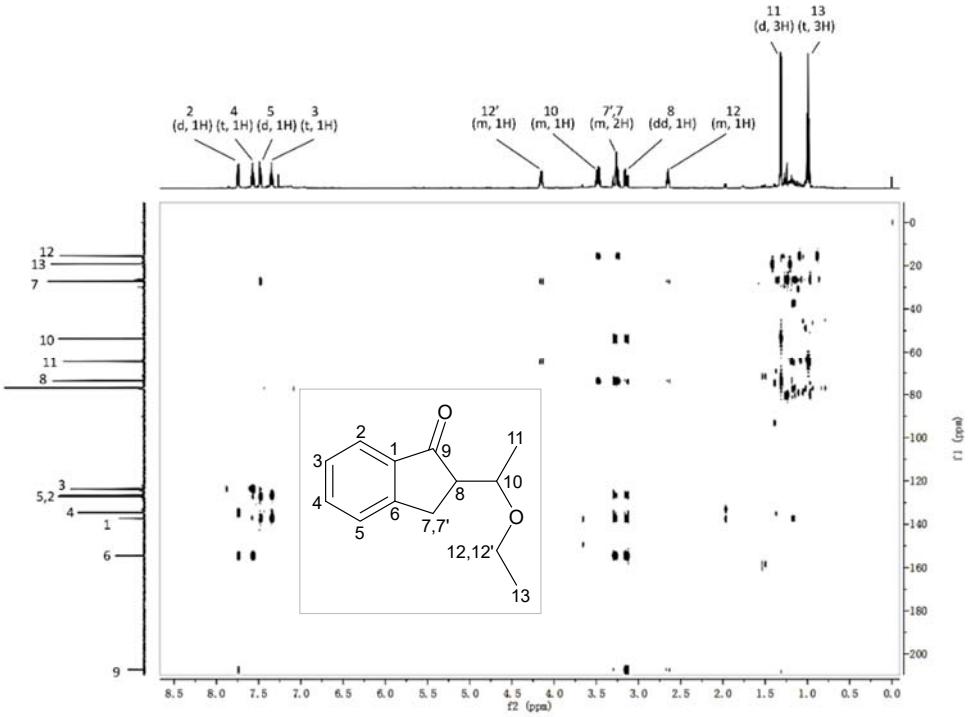


Figure S1 HMBC Spectrum of Compound **F**

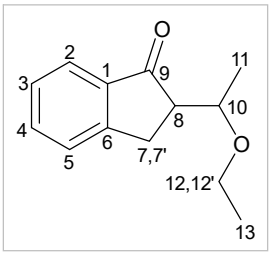
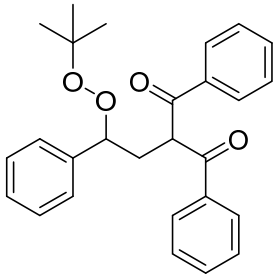


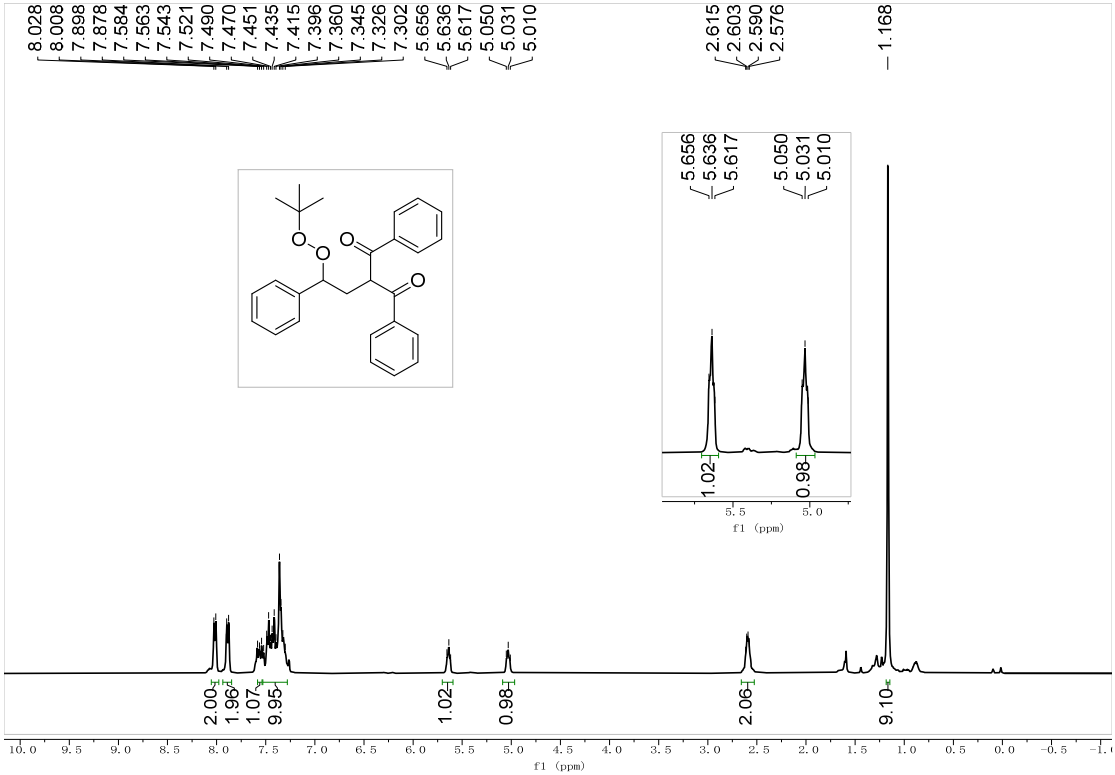
Table S5 Heteronuclear Correlation of Compound **F**

C / H		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
		137.22	126.59	123.69	134.56	127.08	154.58	27.25	73.75	207.23	53.77	64.65	15.38	19.18
H2	7.75		Bonding		β		β			β				
H3	7.35	β	α	Bonding	α	β								
H4	7.57			α	Bonding		β							
H5	7.49	β		β		Bonding		β						
H7	3.24	β					α	Bonding	α		β			
H7'	3.26	β					α	Bonding	α		β			
H8	3.15	β					β		Bonding	α	α			
H10	3.48								α		Bonding		β	
H11	1.32								β		α	Bonding		
H12	2.65												Bonding	
H12'	4.16												Bonding	
H13	0.99													Bonding

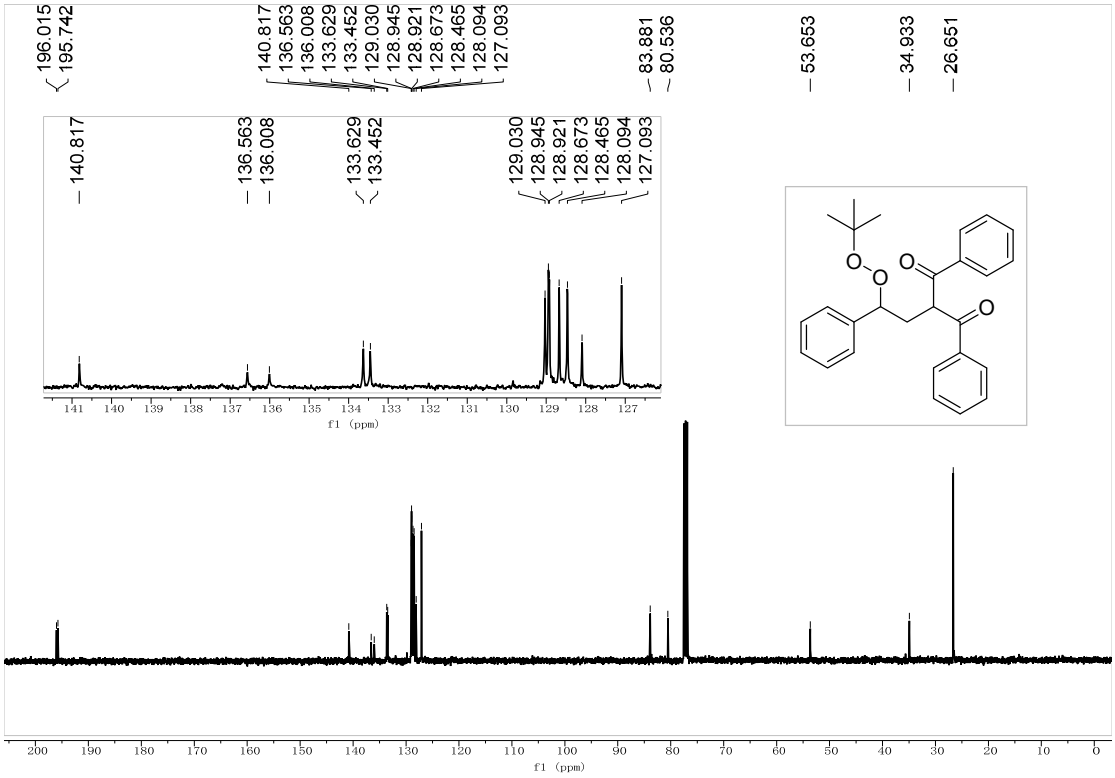
4.3.Relevant Products in Other Research Groups



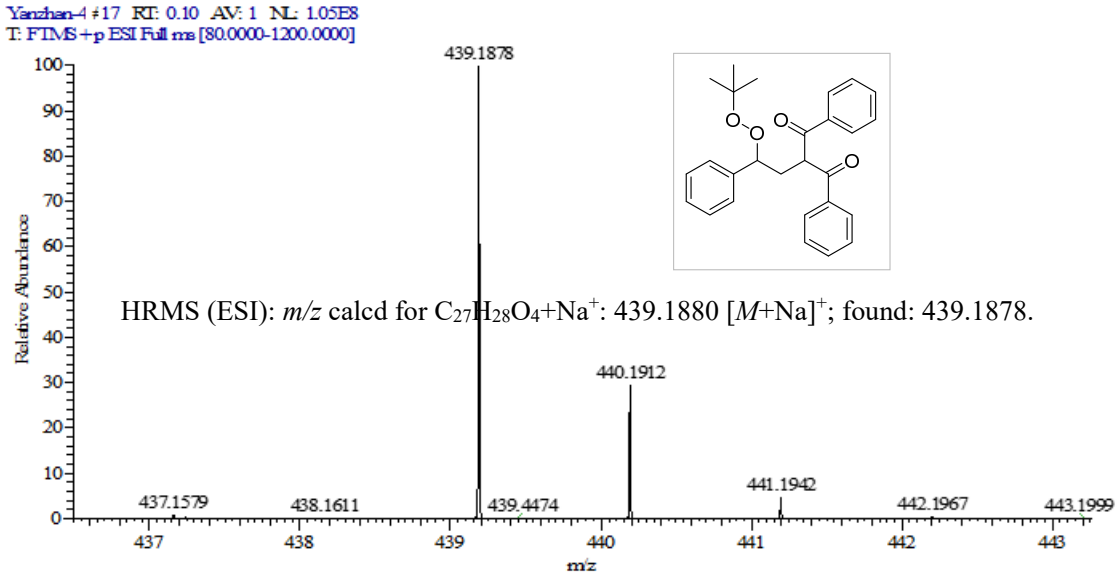
2-(2-(*tert*-butylperoxy)-2-phenylethyl)-1,3-diphenylpropane-1,3-dione: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.52 – 7.30 (m, 10H), 5.64 (t, *J* = 8.0 Hz, 1H), 5.03 (t, *J* = 7.6 Hz, 1H), 2.62 – 2.58 (m, 2H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.02, 195.74, 140.82, 136.56, 136.01, 133.63, 133.45, 129.03, 128.95, 128.92, 128.67, 128.47, 128.09, 127.09, 83.88, 80.54, 53.65, 34.93, 26.65. HRMS (ESI): *m/z* calcd for $C_{27}H_{28}O_4$+Na^+: 439.1880 [*M*+Na]$^+$; found: 439.1878.



^{1}H NMR of *α-tert*-butylperoxyl functionalized product

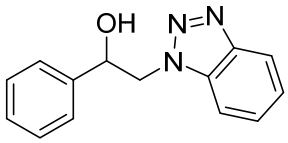


^{13}C NMR of *α-tert*-butylperoxyl functionalized product

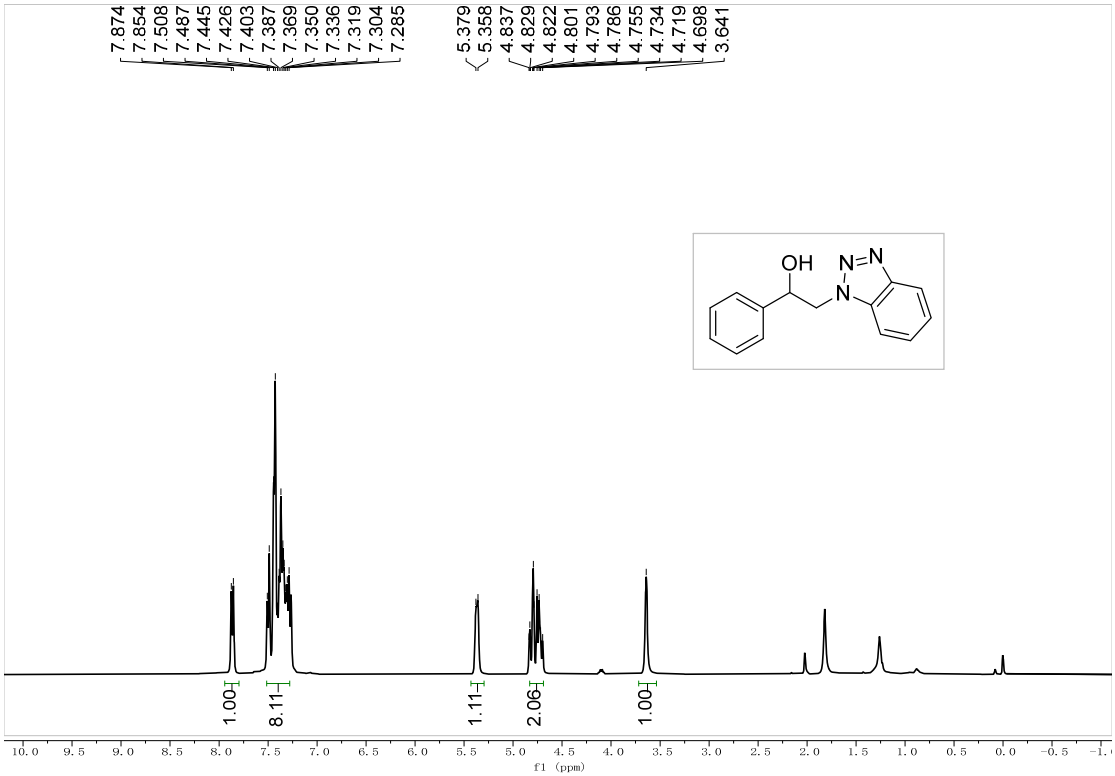


HRMS (ESI): *m/z* calcd for $C_{27}H_{28}O_4$+Na^+: 439.1880 [*M*+Na]$^+$; found: 439.1878.

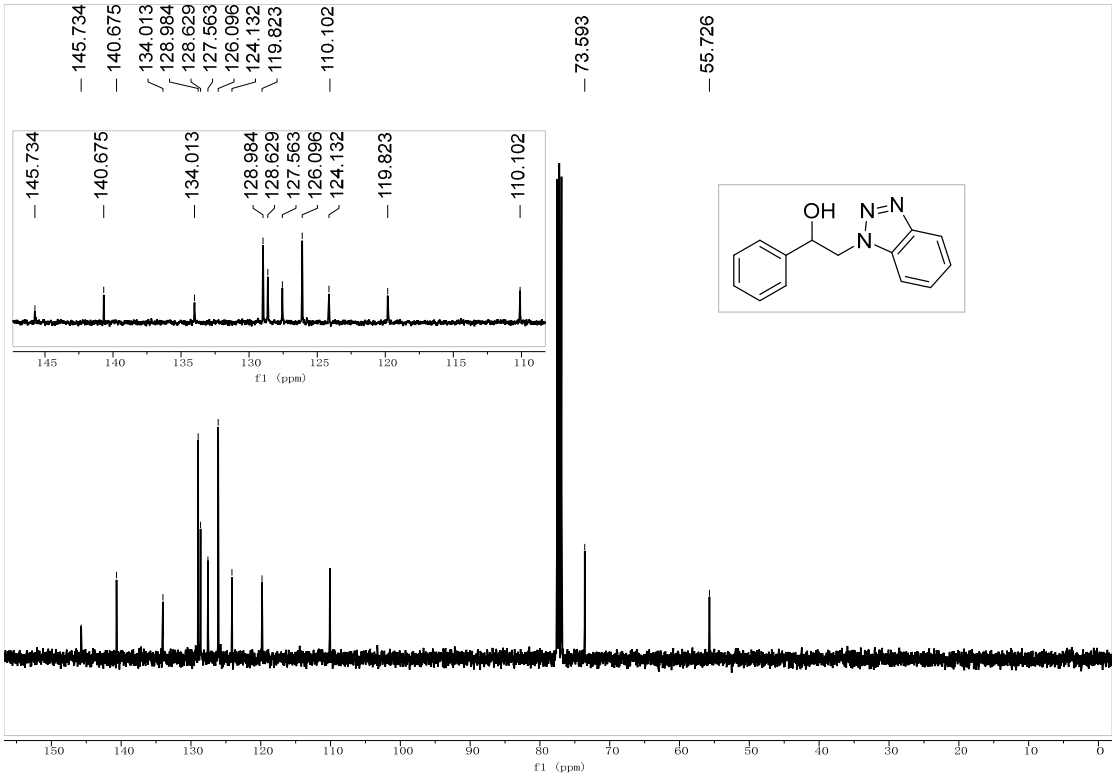
HRMS of *α-tert*-butylperoxyl functionalized product



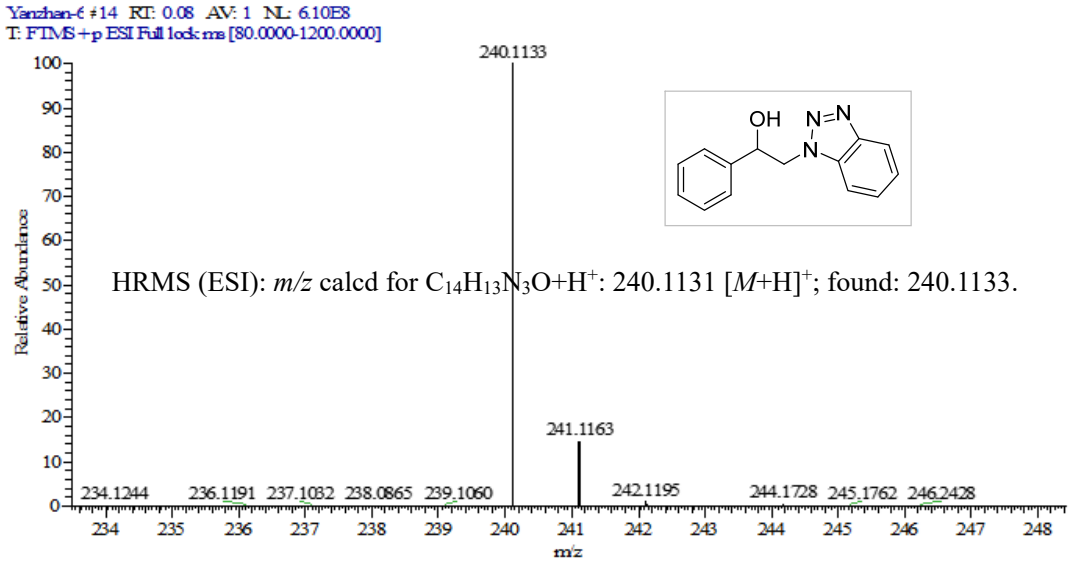
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethan-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.29 (m, 8H), 5.37 (d, *J* = 8.4 Hz, 1H), 4.84 – 4.70 (m, 2H), 3.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.73, 140.68, 134.01, 128.98, 128.63, 127.56, 126.10, 124.13, 119.82, 110.10, 73.59, 55.73. HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_3O+H^+$: 240.1131 $[M+H]^+$; found: 240.1133.



^{1}H NMR of *α*-hydroxyl functionalized product



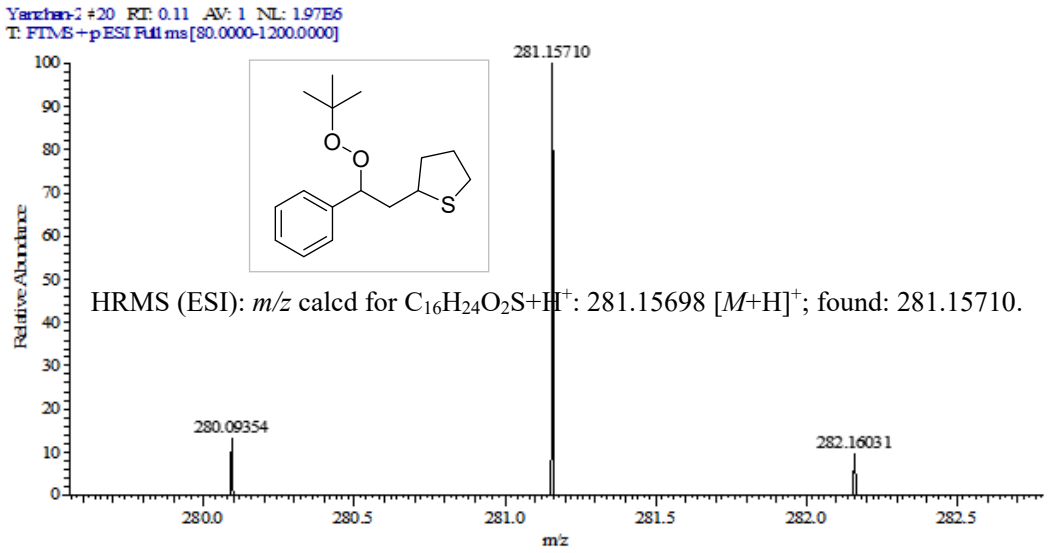
^{13}C NMR of α-hydroxyl functionalized product



HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_3O+H^+$: 240.1131 $[M+H]^+$; found: 240.1133.

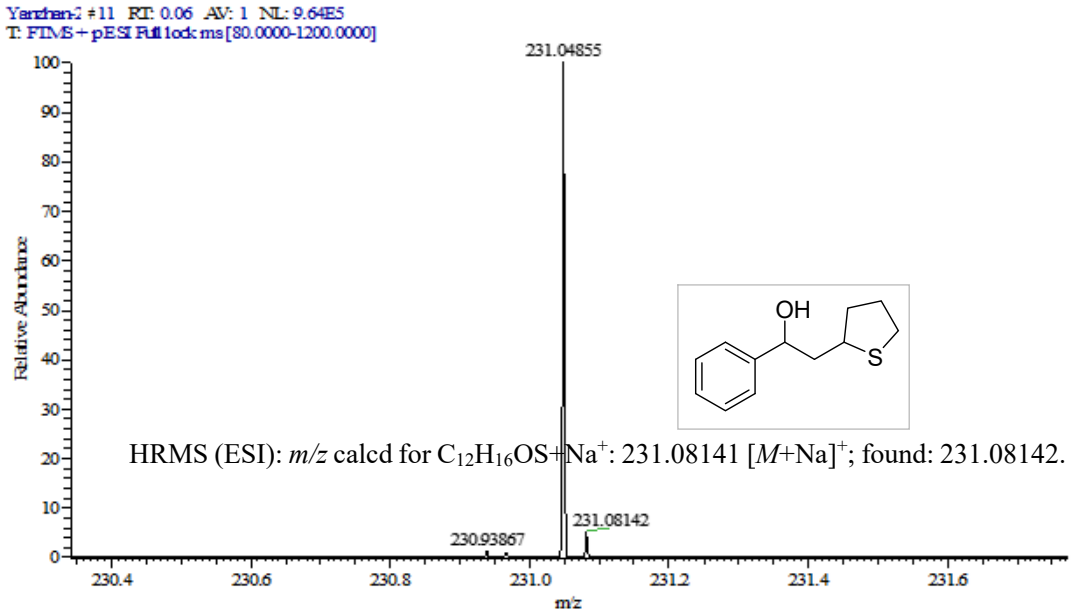
HRMS of α-hydroxyl functionalized product

4.4.Intermediate Study



HRMS (ESI): *m/z* calcd for $C_{16}H_{24}O_2S+H^+$: 281.15698 $[M+H]^+$; found: 281.15710.

HRMS spectrum of product Compound **J**



HRMS (ESI): *m/z* calcd for $C_{12}H_{16}OS+Na^+$: 231.08141 $[M+Na]^+$; found: 231.08142.

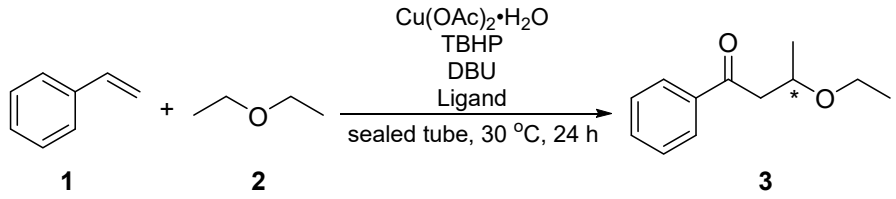
HRMS spectrum of product Compound **K**

4.5.Studies on Reaction Stereo Selectivity

Asymmetric Synthesis

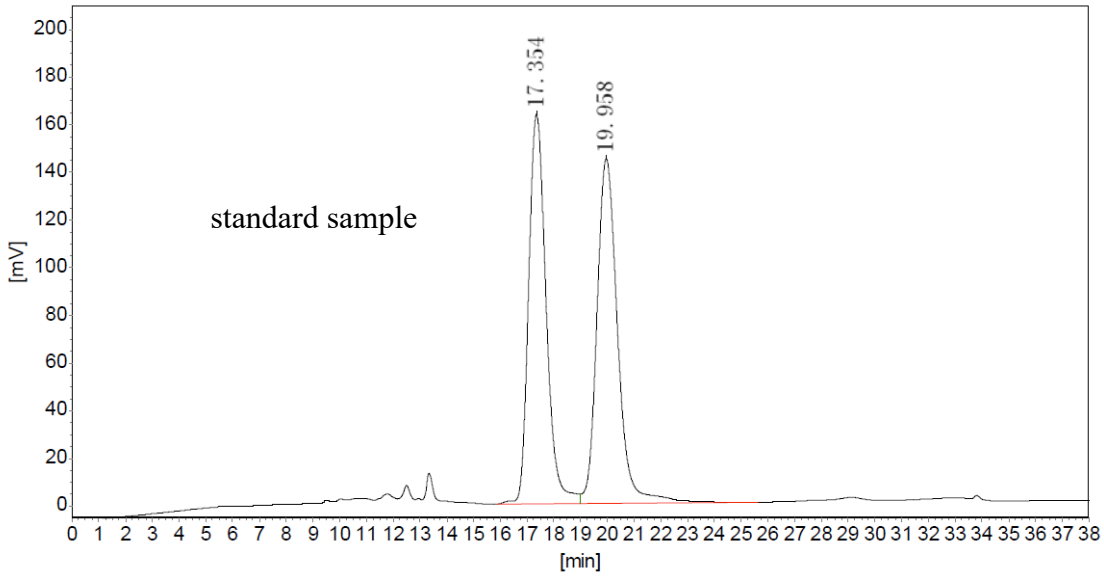
In a 15 mL tube with a stir bar, firstly $Cu(OAc)_2 \cdot H_2O$ (20 mg, 0.1 mmol, 20 mol%) and chiral ligand (10 mol%) were added, and it was charged with 3.0 mL diethyl ether. Then DBU (152 mg, 1.0 mmol, 2.0 equiv) and TBHP (643 mg, 5.0 mmol, 10.0 equiv) were added. At last, styrene (52 mg, 0.5 mmol, 1.0 equiv) was added into the reaction system.

The tube was sealed with a teflon coated cap and then the reaction mixture was stirred at 30 ℃ for 24 h. When the reaction got complete, take the reaction mixture to be analyzed by HPLC, using elute (*n*-hexane/isopropanol=200/1, v/v), and the flow rate was 0.4 mL/min.

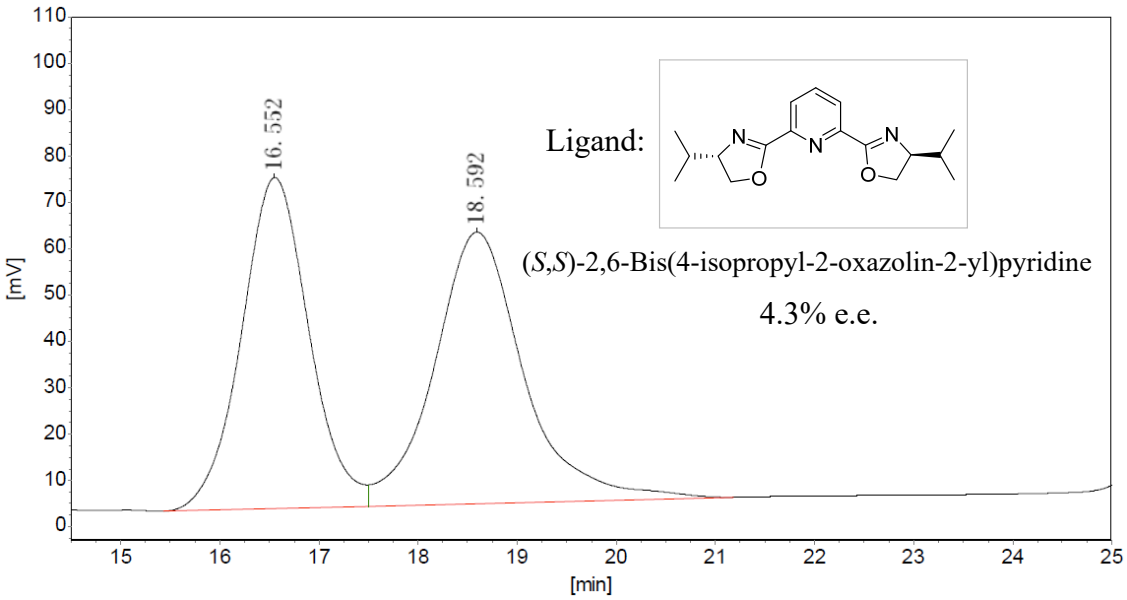


1 **2** **3**

Copies of the HPLC Spectra

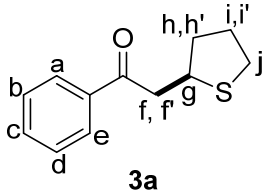


RT/min	Contents/%
17.354	48.8850
19.958	51.1150



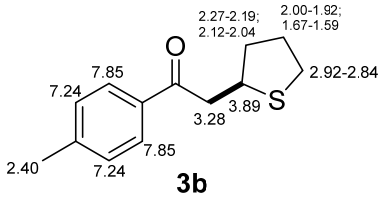
RT/min	Contents/%
16.552	47.8578
18.592	52.1422

5. Characterization Data of All Products



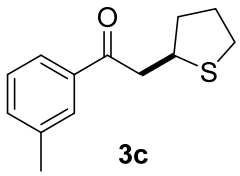
3a

phenyl-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3a**): yellow oil, 39% yield (16.1 mg), R_f = 0.46 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H, H_a, H_e), 7.58 – 7.53 (m, 1H, H_c), 7.48 – 7.43 (m, 2H, H_b, H_d), 3.90 (m, 1H, H_g), 3.31 (d, *J* = 6.8 Hz, 2H, H_f, $H_{f'}$), 2.94 – 2.84 (m, 2H, H_j), 2.28 – 2.21 (m, 1H, H_h), 2.14 – 2.05 (m, 1H, $H_{h'}$), 2.01 – 1.91 (m, 1H, H_i), 1.68 – 1.59 (m, 1H, $H_{i'}$).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.42, 136.71, 133.20, 128.63, 128.08, 46.66, 43.23, 37.02, 32.46, 30.27. HRMS (ESI): *m/z* calcd for $C_{12}H_{14}OS+Na^+$: 229.0658 [*M*+Na]$^+$; found: 229.0660.



3b

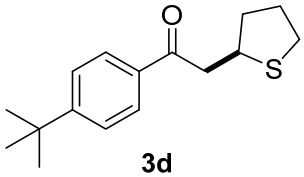
2-(tetrahydrothiophen-2-yl)-1-(*p*-tolyl)ethan-1-one (**3b**): colorless oil, 48% yield (21.1 mg), R_f = 0.39 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.89 (m, 1H), 3.28 (d, *J* = 6.8 Hz, 2H), 2.92 – 2.84 (m, 2H), 2.40 (s, 3H), 2.27 – 2.19 (m, 1H), 2.12 – 2.04 (m, 1H), 2.00 – 1.92 (m, 1H), 1.67 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.01, 143.94, 134.29, 129.27, 128.19, 46.49, 43.35, 37.02, 32.43, 30.25, 21.64. HRMS (ESI): *m/z* calcd for $C_{13}H_{16}OS+Na^+$: 243.0814 [*M*+Na]$^+$; found: 243.0815.



3c

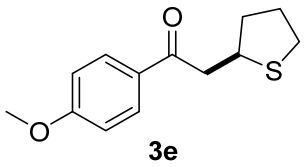
2-(tetrahydrothiophen-2-yl)-1-(*m*-tolyl)ethan-1-one (**3c**): light yellow oil, 52% yield (23.0 mg), R_f = 0.43 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 2H), 7.38 – 7.32 (m, 2H), 3.90 (m, 1H), 3.29 (d, *J* = 6.8 Hz,

2H), 2.92 – 2.83 (m, 2H), 2.40 (s, 3H), 2.28 – 2.20 (m, 1H), 2.14 – 2.05 (m, 1H), 2.01 – 1.91 (m, 1H), 1.67 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.58, 138.39, 136.78, 133.92, 128.59, 128.48, 125.29, 46.68, 43.29, 37.01, 32.43, 30.25, 21.35. HRMS (EI): *m/z* calcd for $C_{13}H_{16}OS^+$: 220.09164 $[M]^+$; found: 220.09145.



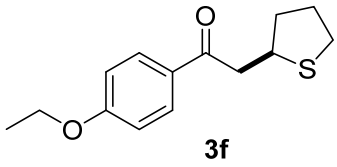
3d

1-(4-(*tert*-butyl)phenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3d**): yellow oil, 65% yield (34.1 mg), R_f = 0.45 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 3.91 (m, 1H), 3.29 (dd, *J* = 7.0, 1.6 Hz, 2H), 2.92 – 2.84 (m, 2H), 2.27 – 2.20 (m, 1H), 2.12 – 2.06 (m, 1H), 2.00 – 1.91 (m, 1H), 1.68 – 1.59 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.01, 156.88, 134.21, 128.05, 125.54, 46.49, 43.36, 37.03, 35.10, 32.42, 31.09, 30.25. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}OS+Na^+$: 285.1284 $[M+Na]^+$; found: 285.1284.



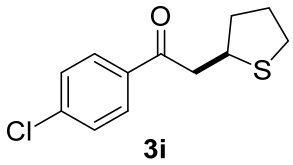
3e

1-(4-methoxyphenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3e**): orange oil, 33% yield (15.6 mg), R_f = 0.36 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.93 – 3.87 (m, 1H), 3.86 (s, 3H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.89 – 2.85 (m, 2H), 2.27 – 2.19 (m, 1H), 2.12 – 2.06 (m, 1H), 1.99 – 1.92 (m, 1H), 1.68 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.92, 163.54, 130.34, 129.87, 113.73, 55.47, 46.23, 43.47, 37.03, 32.42, 30.24. HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_2S+Na^+$: 259.0763 $[M+Na]^+$; found: 259.0764.



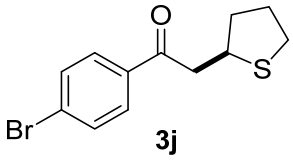
3f

1-(4-ethoxyphenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3f**): brown oil, 34% yield (17.0 mg), R_f = 0.27 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.09 (q, *J* = 6.8 Hz, 2H), 3.89 (m, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.94 – 2.83 (m, 2H), 2.27 – 2.20 (m, 1H), 2.14 – 2.05 (m, 1H), 2.01 – 1.90 (m, 1H), 1.68 – 1.59 (m, 1H), 1.44 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.06, 163.18, 130.53, 129.98, 114.39, 63.95, 46.39, 43.72, 37.24, 32.58, 30.42, 14.82. HRMS (EI): *m/z* calcd for $C_{14}H_{18}O_2S^+$: 250.10220 $[M]^+$; found: 250.10217.



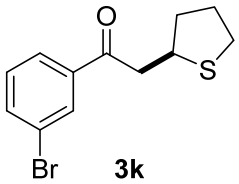
3i

1-(4-chlorophenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3i**): yellow oil, 42% yield (20.2 mg), R_f = 0.38 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 3.88 (m, 1H), 3.28 (d, *J* = 7.2 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.27 – 2.21 (m, 1H), 2.13 – 2.05 (m, 1H), 2.00 – 1.91 (m, 1H), 1.67 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.15, 139.61, 135.03, 129.49, 128.92, 46.62, 43.11, 36.99, 32.45, 30.24. HRMS (EI): *m/z* calcd for $C_{12}H_{13}ClOS^+$: 240.03701 $[M]^+$; found: 240.03690.



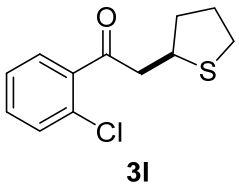
3j

1-(4-bromophenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3j**): yellow oil, 58% yield (32.9 mg), R_f = 0.41 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.60 – 7.57 (m, 2H), 3.91 – 3.84 (m, 1H), 3.27 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.91 – 2.85 (m, 2H), 2.26 – 2.21 (m, 1H), 2.11 – 2.06 (m, 1H), 2.00 – 1.94 (m, 1H), 1.66 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.33, 135.43, 131.91, 129.60, 128.35, 46.61, 43.10, 36.99, 32.46, 30.25. HRMS (EI): *m/z* calcd for $C_{12}H_{13}BrOS^+$: 283.98650 $[M]^+$; found: 283.98630.



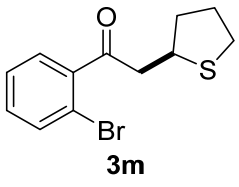
3k

1-(3-bromophenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3k**): yellow oil, 57% yield (32.4 mg), R_f = 0.38 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.34 (td, *J* = 7.4, 3.2 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.28 (dd, *J* = 7.0, 2.4 Hz, 2H), 2.90 – 2.88 (m, 2H), 2.28 – 2.21 (m, 1H), 2.13 – 2.05 (m, 1H), 2.01 – 1.93 (m, 1H), 1.68 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.00, 138.44, 136.01, 131.15, 130.23, 126.59, 122.99, 46.76, 43.01, 36.97, 32.47, 30.25. HRMS (EI): *m/z* calcd for $C_{12}H_{13}BrOS^+$: 283.98650 $[M]^+$; found: 283.98621.



3l

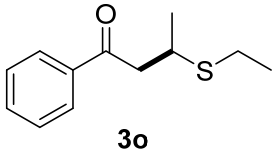
1-(2-chlorophenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3l**): yellow oil, 50% yield (24.0 mg), R_f = 0.48 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 1H), 7.43 – 7.35 (m, 2H), 7.34 – 7.30 (m, 1H), 3.87 (m, 1H), 3.28 (m, 2H), 2.93 – 2.82 (m, 2H), 2.26 – 2.19 (m, 1H), 2.12 – 2.03 (m, 1H), 2.00 – 1.91 (m, 1H), 1.69 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.49, 139.14, 131.79, 130.90, 130.53, 129.07, 126.96, 50.88, 43.25, 36.94, 32.49, 30.19. HRMS (EI): *m/z* calcd for $C_{12}H_{13}ClOS^+$: 240.03701 $[M]^+$; found: 240.03688.



3m

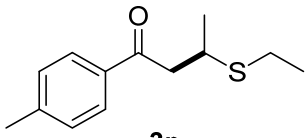
1-(2-bromophenyl)-2-(tetrahydrothiophen-2-yl)ethan-1-one (**3m**): yellow oil, 31% yield (17.6 mg), R_f = 0.45 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 3.87 (m, 1H), 3.26 (m, 2H), 2.94 – 2.83 (m, 2H), 2.28 – 2.20 (m, 1H), 2.13 – 2.03 (m, 1H),

2.01 – 1.92 (m, 1H), 1.71 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.32, 141.43, 133.70, 131.64, 128.60, 127.45, 118.67, 50.57, 43.18, 36.95, 32.51, 30.20. HRMS (EI): *m/z* calcd for $C_{12}H_{13}BrOS^+$: 283.98650 $[M]^+$; found: 283.98627.



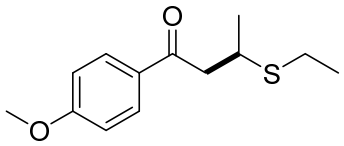
3o

3-(ethylthio)-1-phenylbutan-1-one (**3o**): light yellow oil, 21% yield (8.7 mg), R_f = 0.57 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 3.54 – 3.43 (m, 1H), 3.30 (dd, *J* = 16.8, 5.1 Hz, 1H), 3.10 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.61 (q, *J* = 7.2 Hz, 2H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.27 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.24, 137.03, 133.20, 128.66, 128.10, 46.16, 35.12, 24.87, 21.71, 14.80. HRMS (ESI): *m/z* calcd for $C_{12}H_{16}OS+Na^+$: 231.0814 $[M+Na]^+$; found: 231.0816.



3p

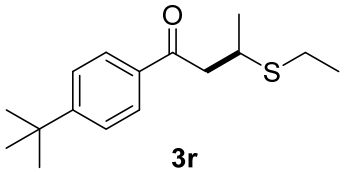
3-(ethylthio)-1-(*p*-tolyl)butan-1-one (**3p**): yellow oil, 33% yield (14.7 mg), R_f = 0.54 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.53 – 3.45 (m, 1H), 3.28 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.08 (dd, *J* = 16.6, 8.8 Hz, 1H), 2.62 (q, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.01, 144.14, 134.90, 129.49, 128.42, 46.30, 35.51, 25.05, 21.89, 21.74, 14.98. HRMS (EI): *m/z* calcd for $C_{13}H_{18}OS^+$: 222.10729 $[M]^+$; found: 222.10706.



3q

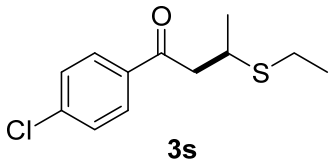
3-(ethylthio)-1-(4-methoxyphenyl)butan-1-one (**3q**): yellow oil, 28% (13.3 mg), R_f = 0.33 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.51 – 3.43 (m, 1H), 3.24 (dd, *J* = 16.4, 5.2 Hz, 1H), 3.03 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.60 (q, *J* = 7.2 Hz, 2H),

1.34 (d, J = 6.8 Hz, 3H), 1.26 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.88, 163.83, 130.57, 130.50, 114.00, 55.63, 46.07, 35.64, 25.06, 21.91, 14.98. HRMS (EI): *m/z* calcd for $C_{13}H_{18}O_2S^+$: 238.10220 $[M]^+$; found: 238.10201.



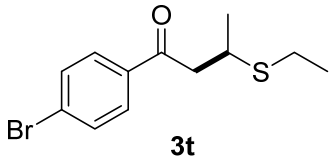
3r

1-(4-(*tert*-butyl)phenyl)-3-(ethylthio)butan-1-one (**3r**): yellow oil, 48% yield (25.3 mg), R_f = 0.56 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 3.53 – 3.44 (m, 1H), 3.27 (dd, J = 16.8, 5.2 Hz, 1H), 3.07 (dd, J = 16.6, 8.8 Hz, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.34 (s, 12H), 1.27 (t, J = 8.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.00, 157.14, 134.78, 128.27, 125.75, 46.33, 35.49, 35.29, 31.26, 25.05, 21.89, 14.99. HRMS (EI): *m/z* calcd for $C_{16}H_{24}OS^+$: 264.15424 $[M]^+$; found: 264.15417.



3s

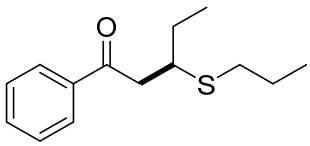
1-(4-chlorophenyl)-3-(ethylthio)butan-1-one (**3s**): yellow oil, 19% yield (9.2 mg), R_f = 0.59 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 5.6 Hz, 2H), 7.44 (d, J = 6.0 Hz, 2H), 3.45 (q, J = 6.8 Hz, 1H), 3.26 (dd, J = 16.8, 3.2 Hz, 1H), 3.05 (dd, J = 16.8, 8.4 Hz, 1H), 2.60 (q, J =9.6 Hz, 2H), 1.35 (d, J = 4.0 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.13, 139.87, 135.67, 129.69, 129.15, 46.39, 35.42, 25.11, 21.94, 14.96. HRMS (EI): *m/z* calcd for $C_{12}H_{15}ClOS^+$: 242.05266 $[M]^+$; found: 242.05259.



3t

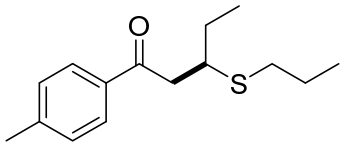
1-(4-bromophenyl)-3-(ethylthio)butan-1-one (**3t**): yellow oil, 34% yield (19.4 mg), R_f = 0.51 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.81 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 3.45 (h, J = 6.8 Hz, 1H), 3.25 (dd, J = 16.8, 5.2 Hz, 1H), 3.04 (dd, J = 16.8, 8.0 Hz, 1H), 2.59 (q, J = 7.2 Hz, 2H), 1.35 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.33, 136.04, 132.16, 129.80, 128.56, 46.36, 35.40, 25.11, 21.94, 14.96. HRMS (EI): *m/z* calcd for $C_{12}H_{15}BrOS^+$: 286.00215 $[M]^+$; found: 286.00194.



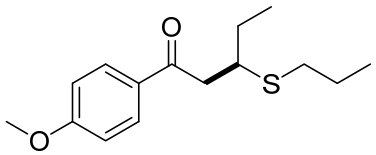
3u

phenyl-3-(propylthio)pentan-1-one (**3u**): yellow oil, 12% yield (5.7 mg), R_f = 0.59 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 6.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 3.33 – 3.29 (m, 2H), 3.21 – 3.15 (m, 1H), 2.54 (t, J = 6.8 Hz, 2H), 1.73 – 1.61 (m, 4H), 1.05 (t, J = 7.6 Hz, 3H), 0.98 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.77, 137.48, 133.25, 128.80, 128.31, 44.81, 42.86, 33.53, 28.45, 23.36, 13.71, 11.43. HRMS (EI): *m/z* calcd for $C_{14}H_{20}OS^+$: 236.12294 $[M]^+$; found: 236.12266.



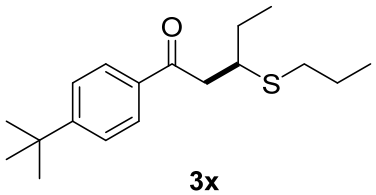
3v

3-(propylthio)-1-(*p*-tolyl)pentan-1-one (**3v**): yellow oil, 24% yield (12.0 mg), R_f = 0.53 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 2H), 7.27 – 7.24 (m, 2H), 3.25 – 3.22(m, 1H), 3.16 – 3.10 (m, 1H), 2.95 – 2.92 (m, 1H), 2.51 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.64 – 1.55 (m, 4H), 1.03 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.36, 144.02, 135.06, 129.46, 128.43, 44.70, 42.99, 33.53, 28.44, 23.37, 21.73, 13.68, 11.40. HRMS (EI): *m/z* calcd for $C_{15}H_{22}OS^+$: 250.13859 $[M]^+$; found: 250.13832.



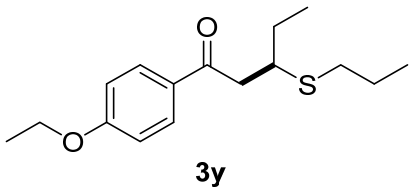
3w

1-(4-methoxyphenyl)-3-(propylthio)pentan-1-one (**3w**): brown oil, 21% yield (11.2 mg), R_f = 0.32 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.29 – 3.25 (m, 1H), 3.21 – 3.11 (m, 1H), 3.10 – 2.89 (m, 1H), 2.53 – 2.49 (m, 2H), 1.70 – 1.55 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.29, 163.77, 130.58, 130.46, 113.98, 55.62, 44.45, 43.11, 33.54, 28.45, 23.37, 13.67, 11.39. HRMS (EI): *m/z* calcd for $C_{15}H_{22}O_2S^+$: 266.13350 $[M]^+$; found: 266.13328.



3x

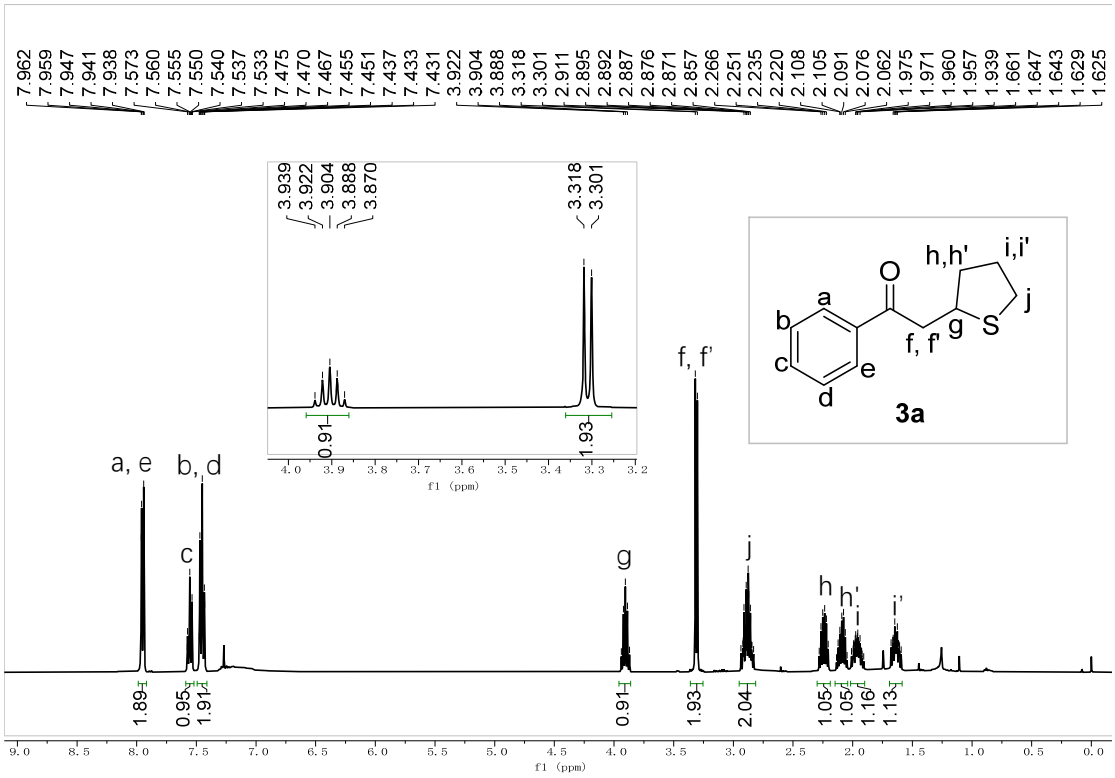
1-(4-(*tert*-butyl)phenyl)-3-(propylthio)pentan-1-one (**3x**): colorless oil, 27% yield (15.8 mg), R_f = 0.68 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 3.31 – 3.25 (m, 2H), 3.20 – 3.15 (m, 1H), 2.54 (td, *J* = 7.2, 2.4 Hz, 2H), 1.76 – 1.59 (m, 4H), 1.36 (s, 9H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.41, 157.05, 134.90, 128.29, 125.73, 44.72, 42.92, 35.29, 33.52, 31.27, 28.43, 23.37, 13.70, 11.42. HRMS (EI): *m/z* calcd for $C_{18}H_{28}OS^+$: 292.18554 $[M]^+$; found: 292.18533.



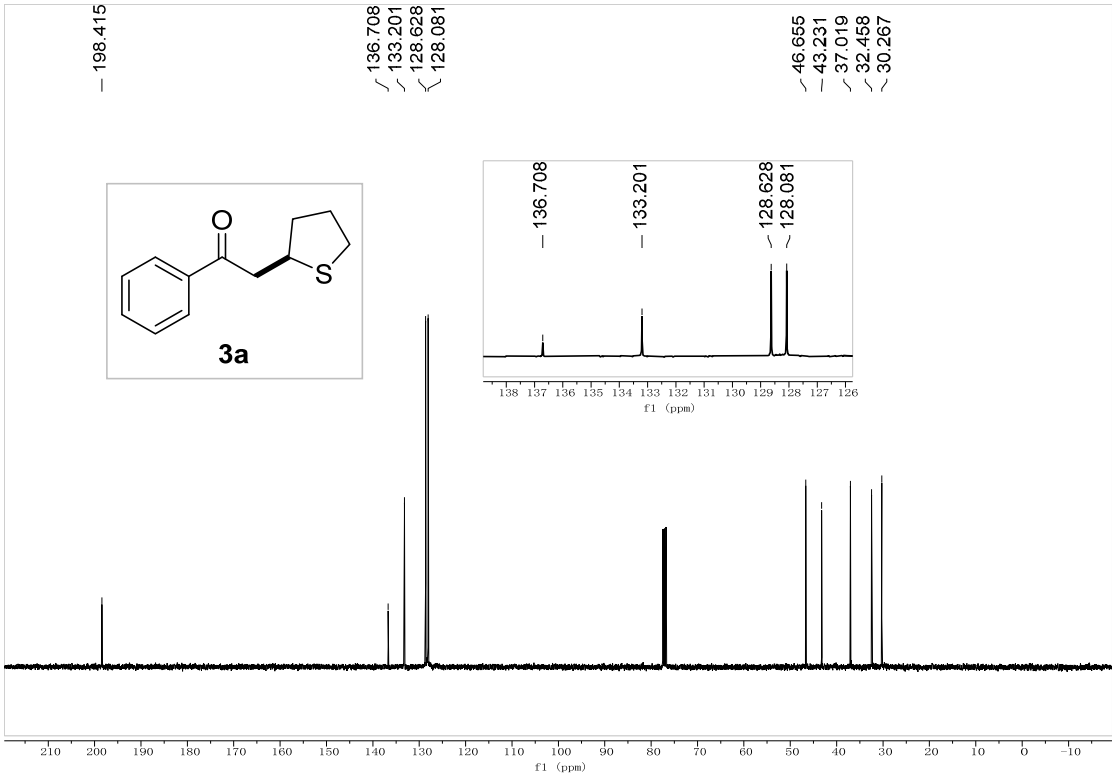
3y

1-(4-ethoxyphenyl)-3-(propylthio)pentan-1-one (**3y**): orange oil, 21% yield (11.8 mg), R_f = 0.38 (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 4.10 (q, *J* = 6.4 Hz, 2H), 3.29 – 3.25 (m, 1H), 3.21 – 3.11 (m, 1H), 3.09 – 2.89 (m, 1H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.70 – 1.55 (m, 4H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.23, 163.18, 130.58, 130.46, 114.44, 63.95, 44.43, 43.11, 33.53, 28.45, 23.37, 14.81, 13.68, 11.40. HRMS (ESI): *m/z* calcd for $C_{15}H_{25}O_2S+H^+$: 281.1570 $[M+H]^+$; found: 281.1563.

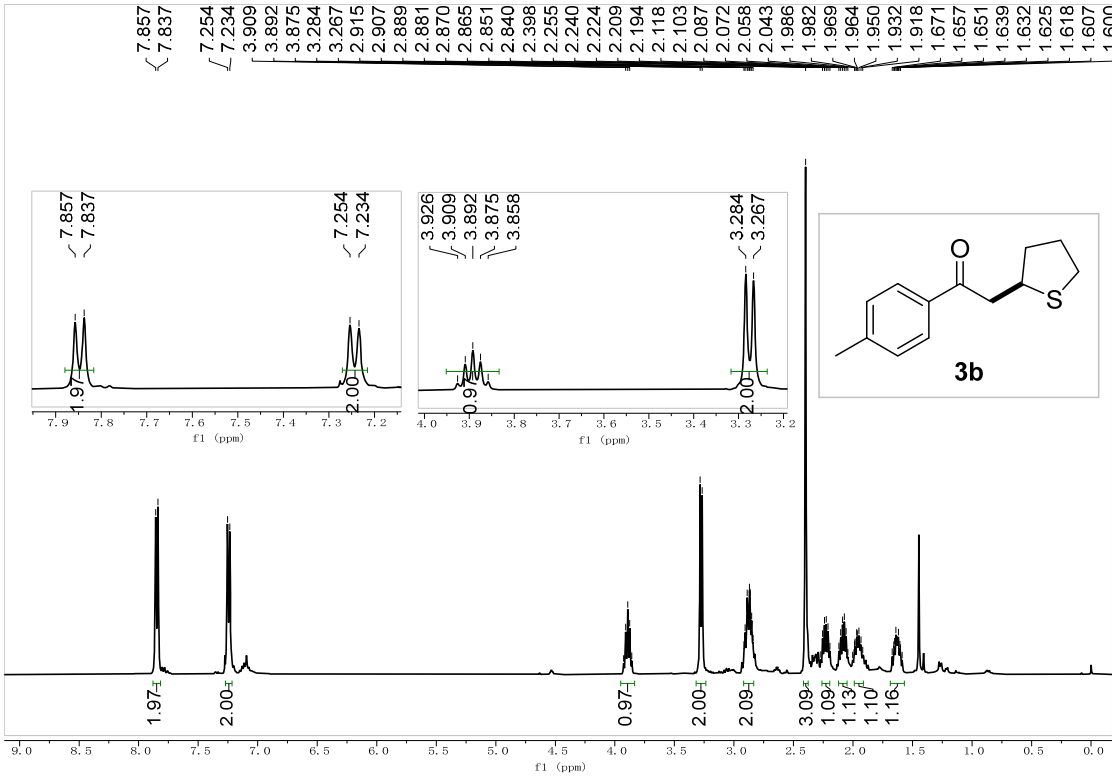
6. Copies of NMR Spectra of All Products



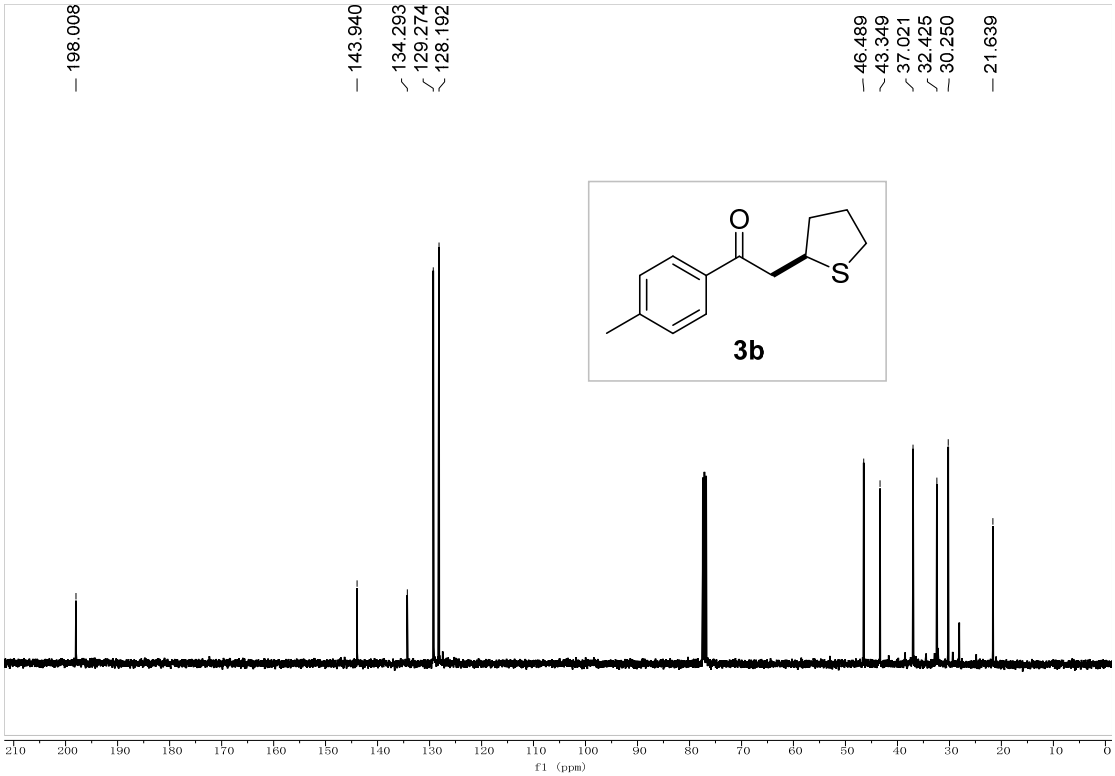
^{1}H NMR spectrum of product **3a**



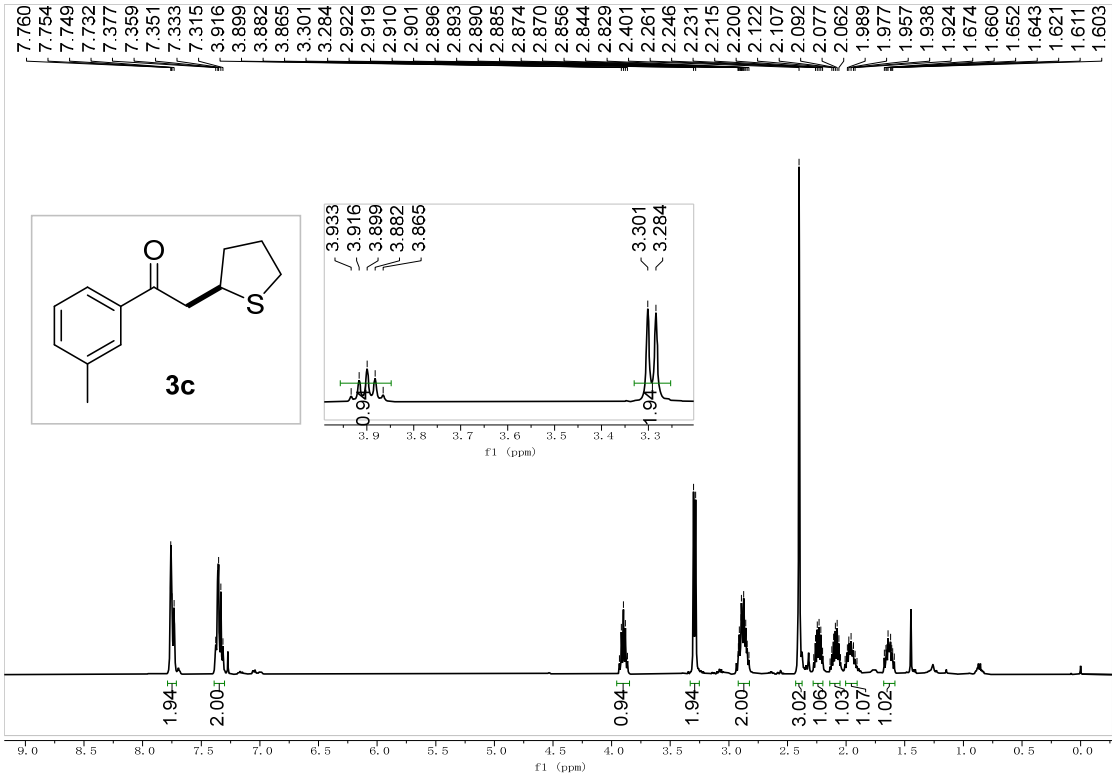
^{13}C NMR spectrum of product **3a**



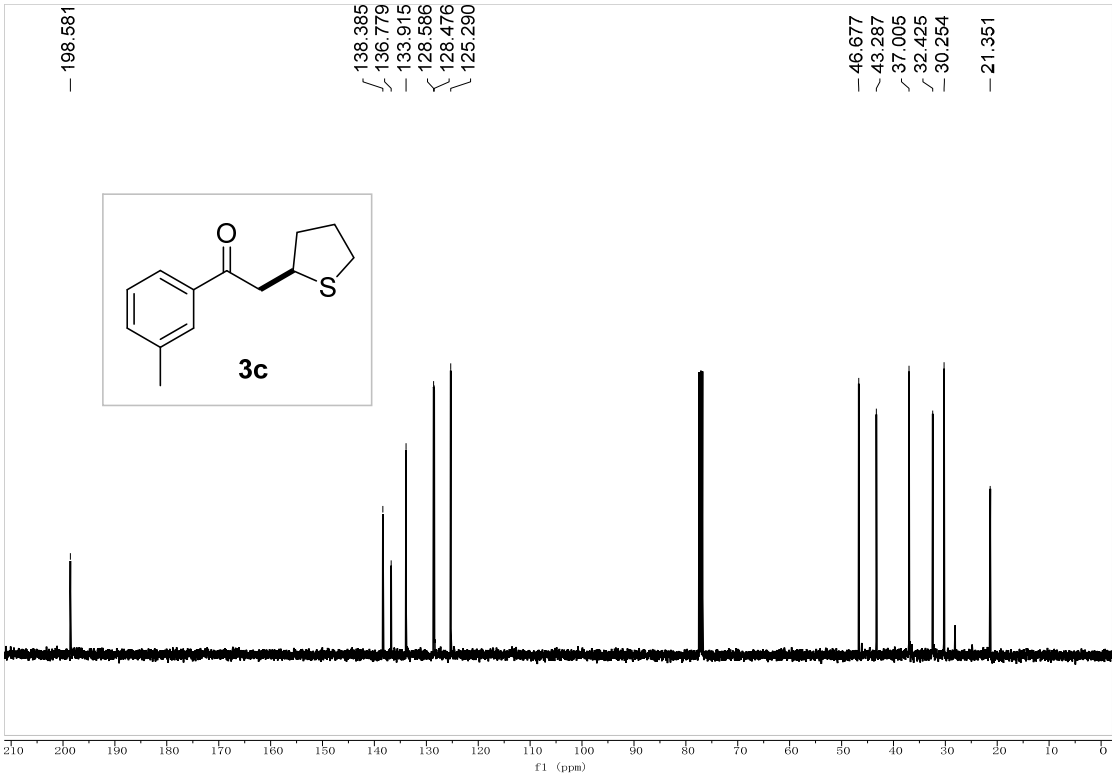
^{1}H NMR spectrum of product **3b**



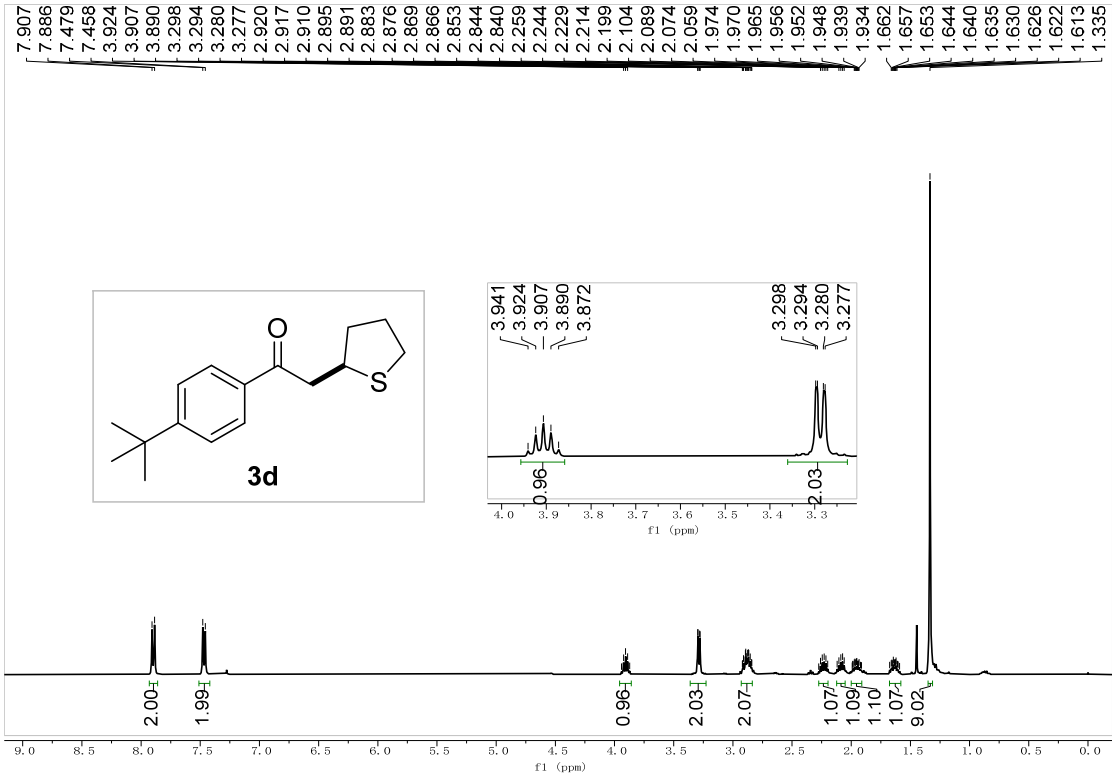
^{13}C NMR spectrum of product **3b**



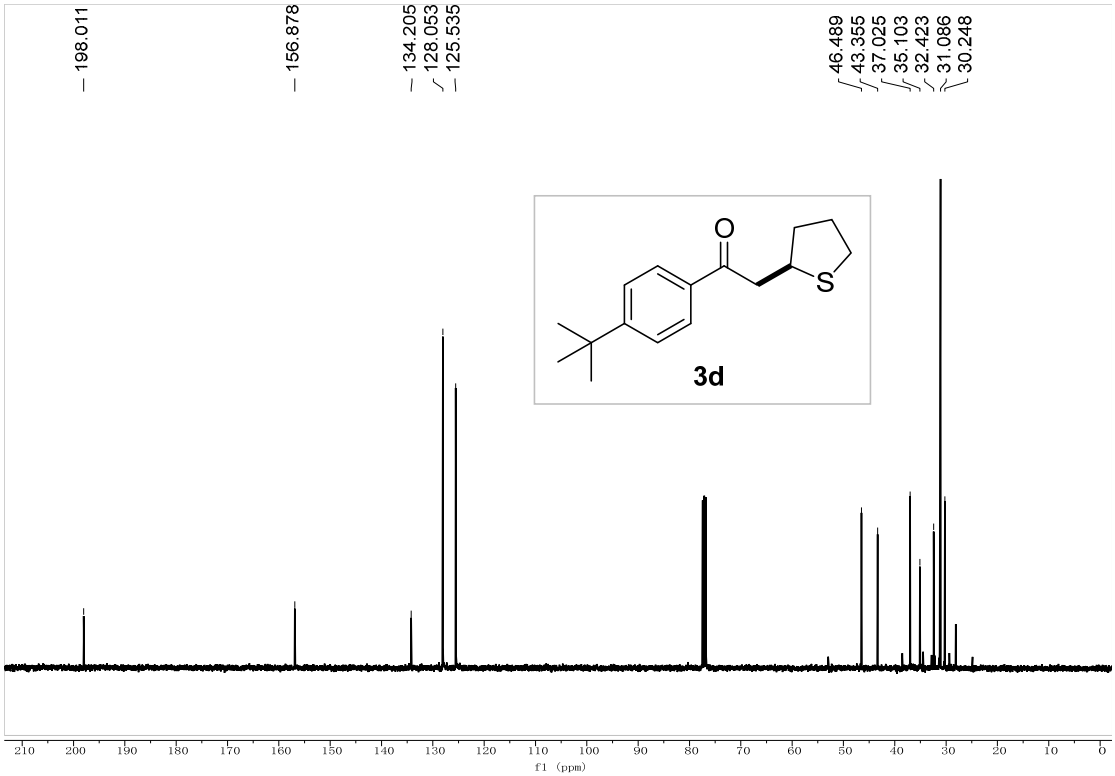
^{1}H NMR spectrum of product **3c**



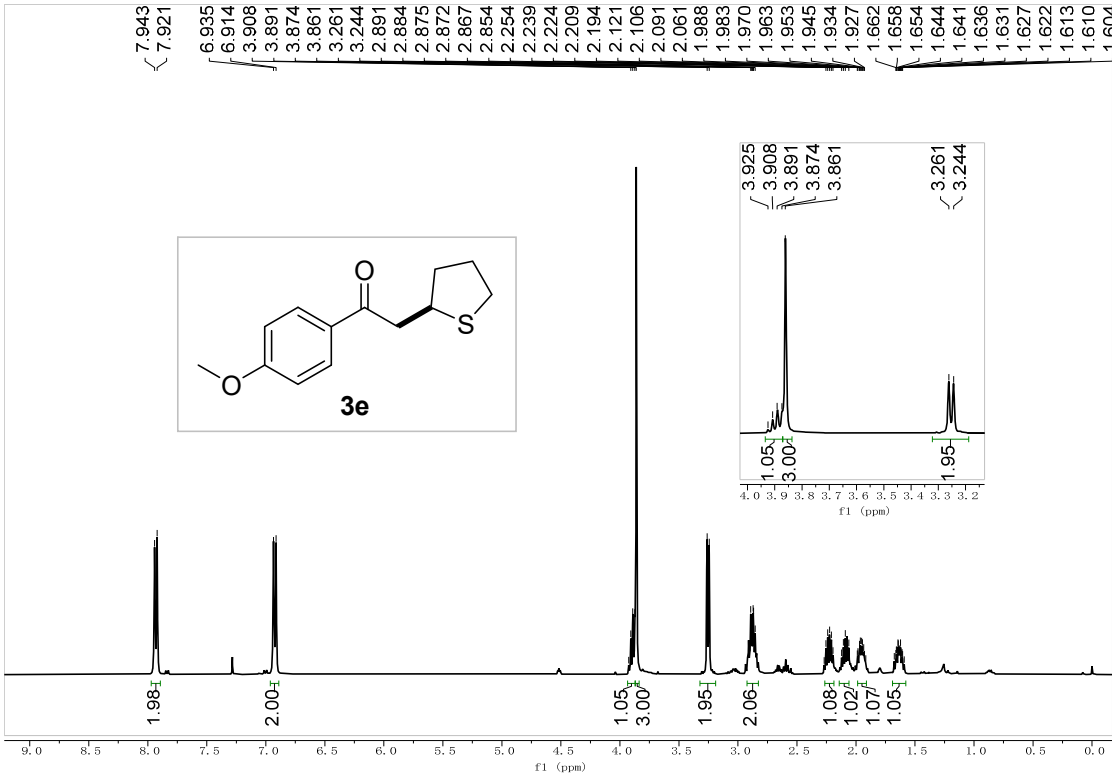
^{13}C NMR spectrum of product **3c**



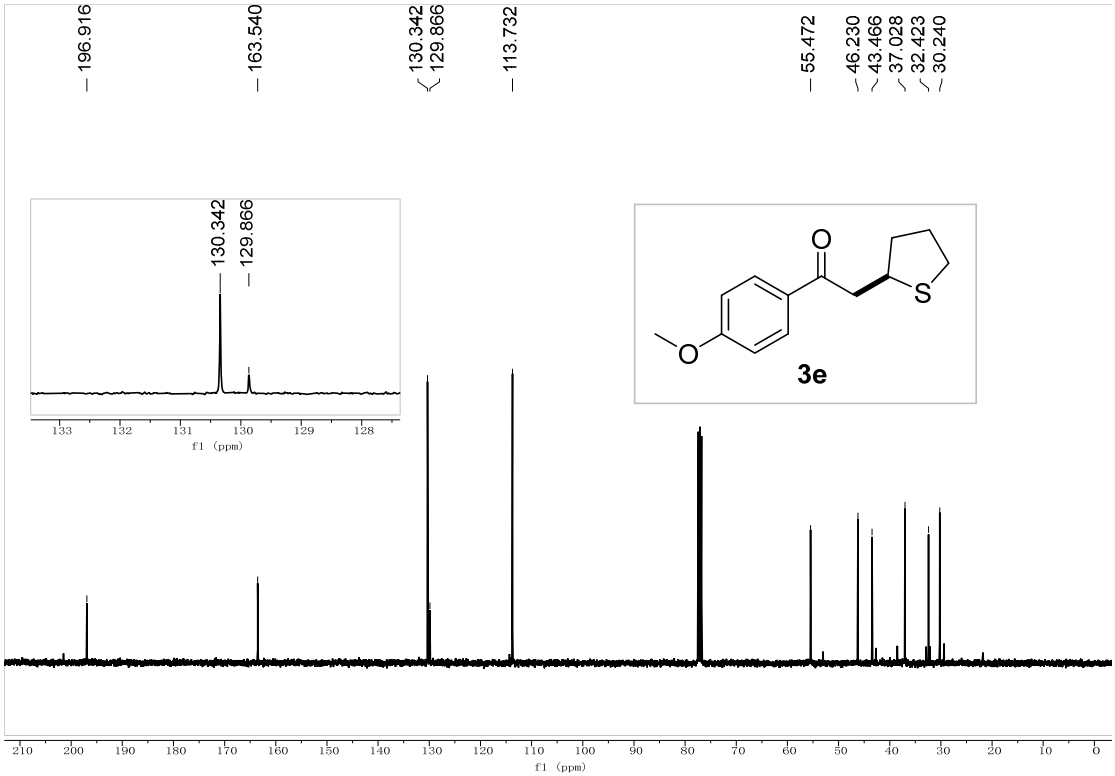
^{1}H NMR spectrum of product **3d**



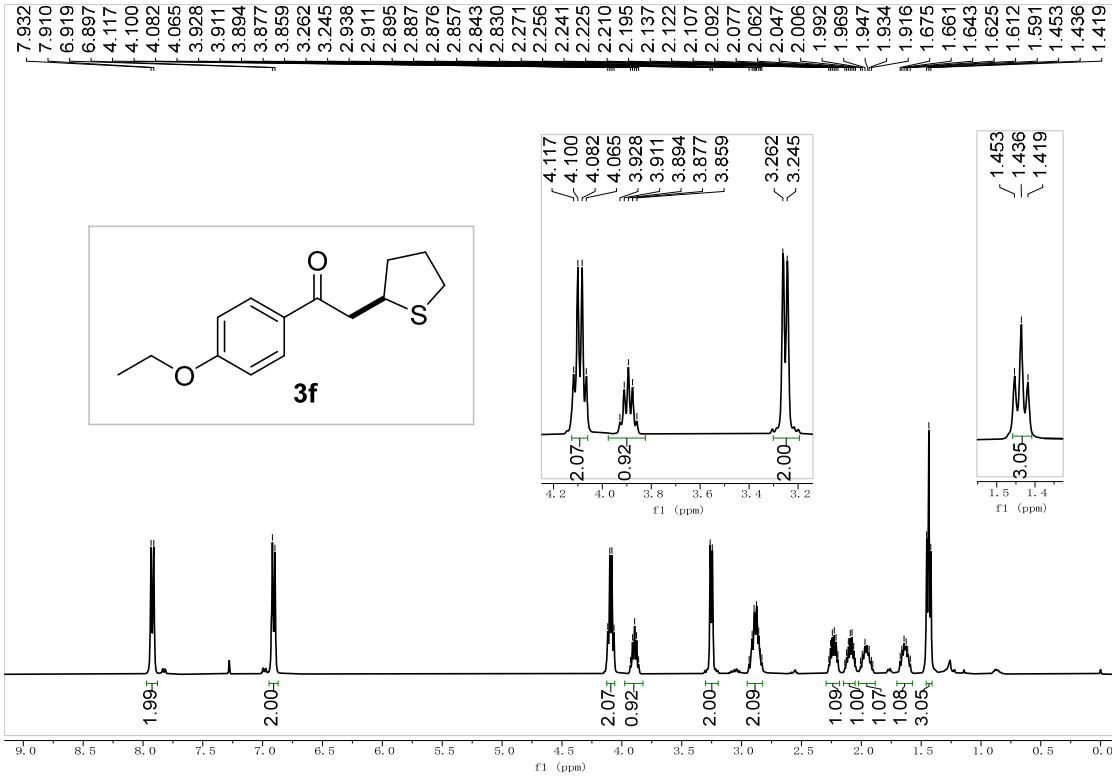
^{13}C NMR spectrum of product **3d**



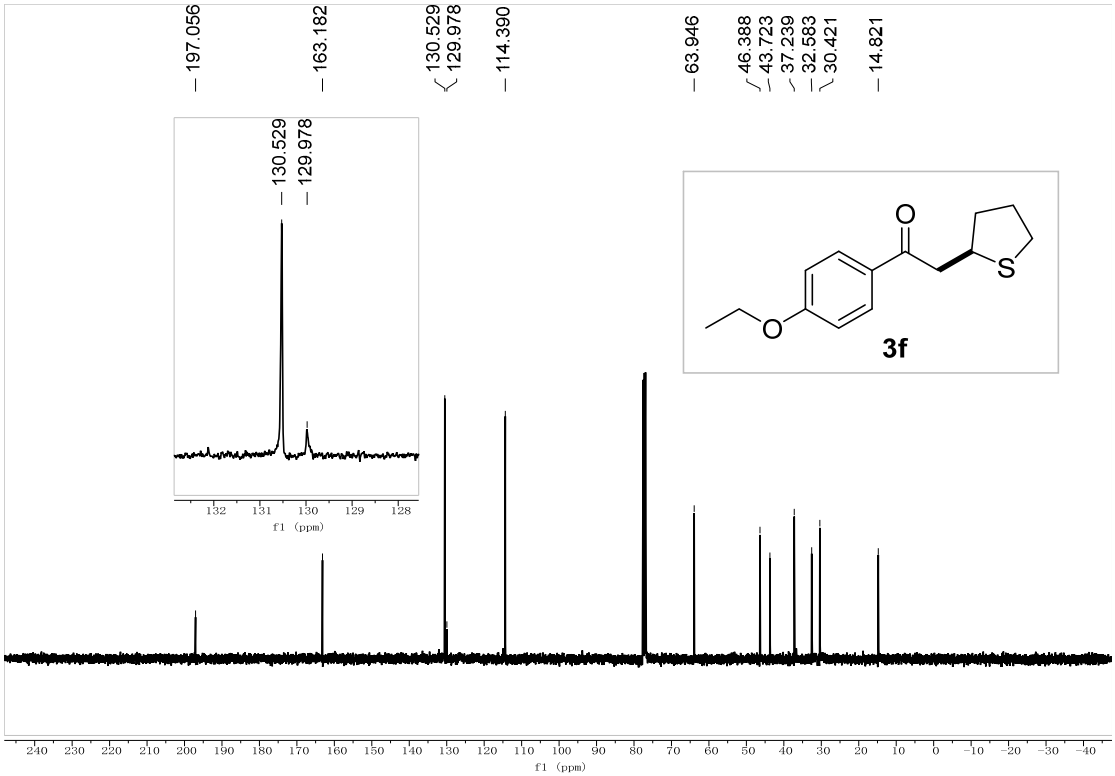
^{1}H NMR spectrum of product **3e**



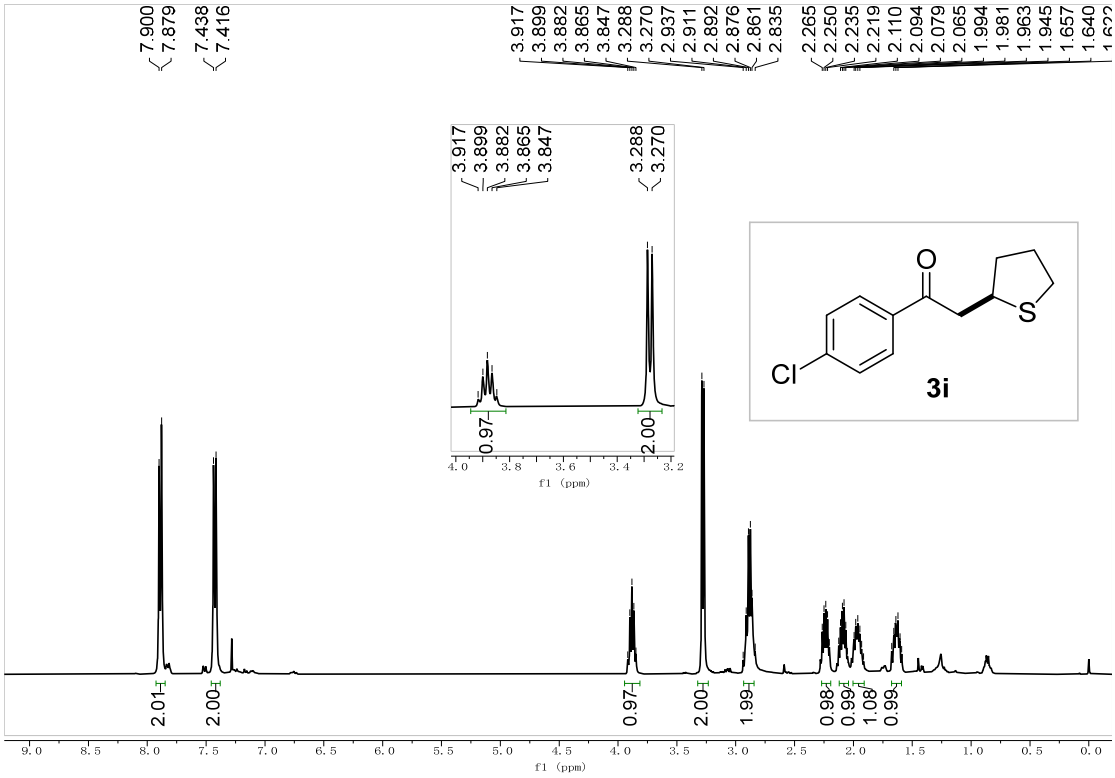
^{13}C NMR spectrum of product **3e**



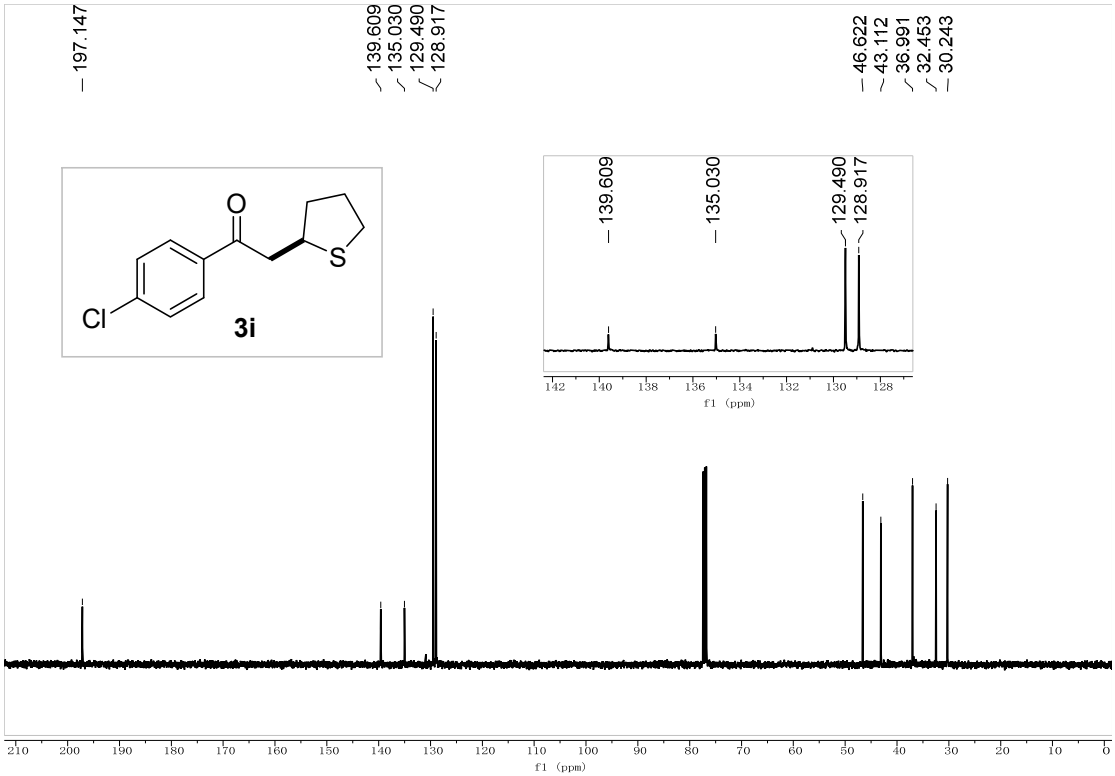
^{1}H NMR spectrum of product **3f**



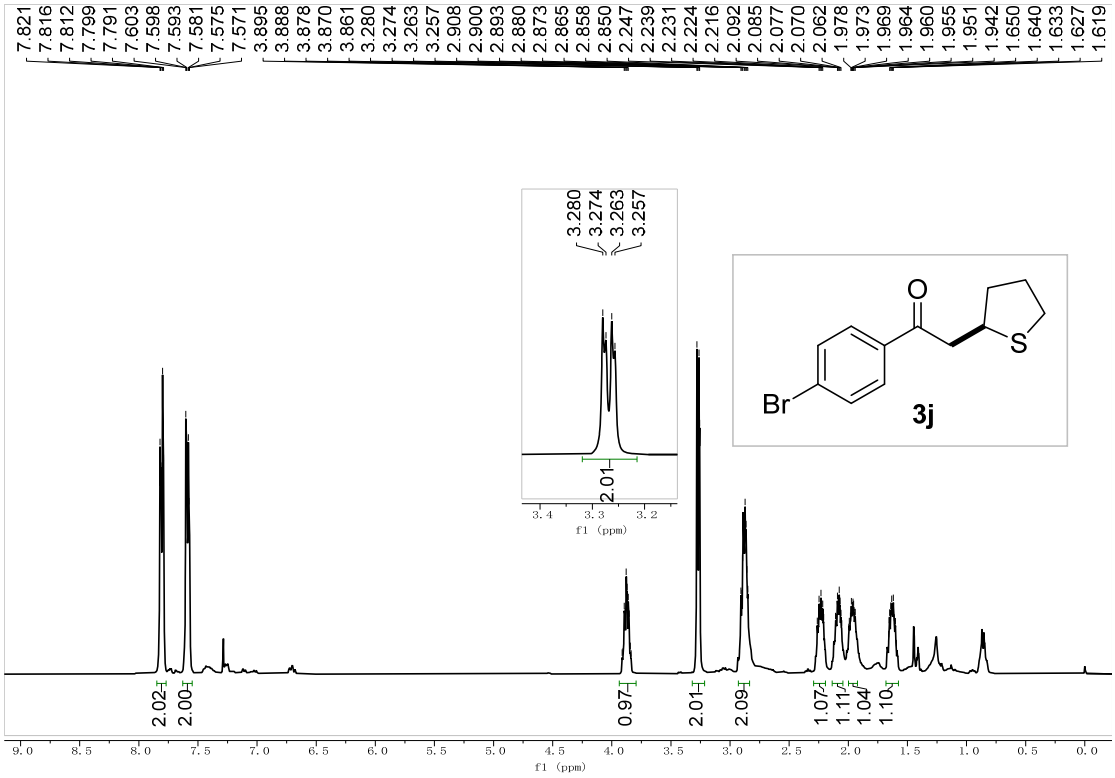
^{13}C NMR spectrum of product **3f**



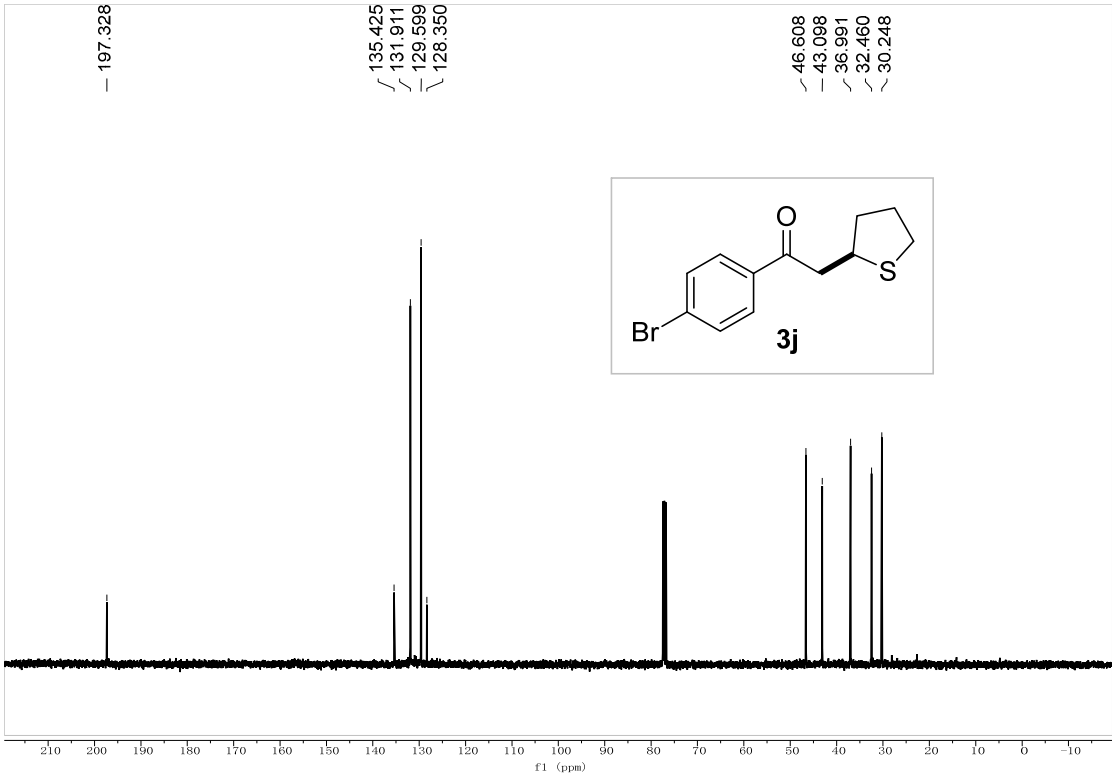
^{1}H NMR spectrum of product **3i**



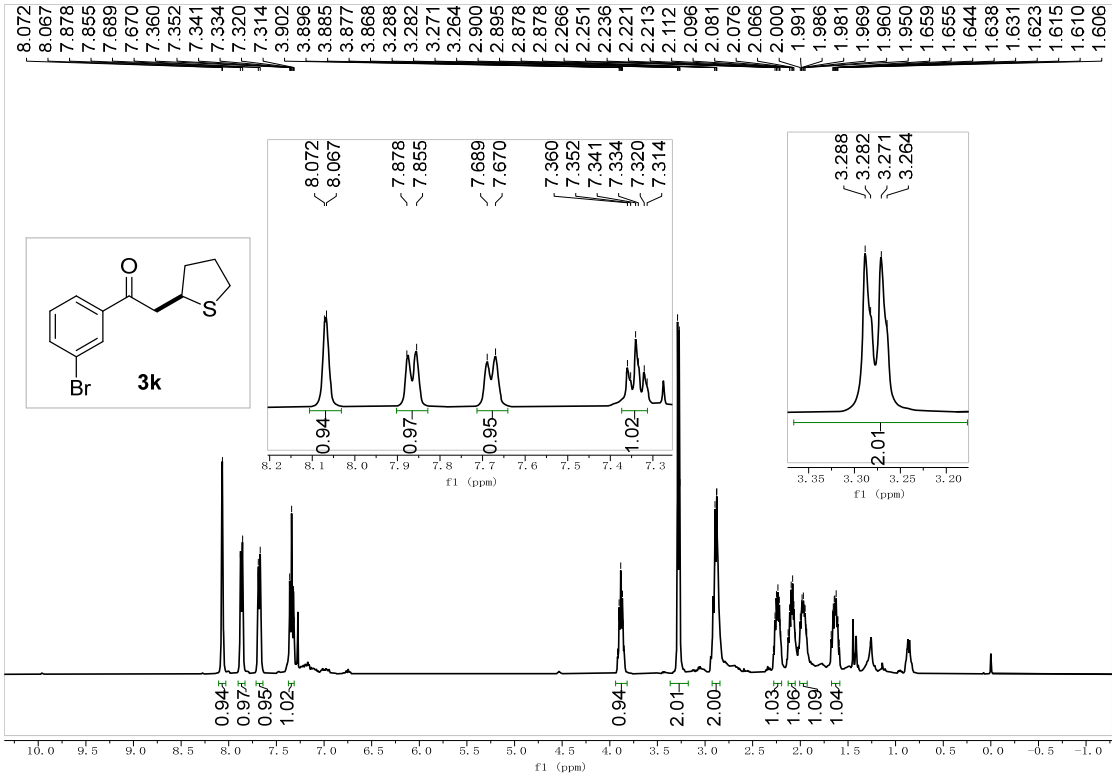
^{13}C NMR spectrum of product **3i**



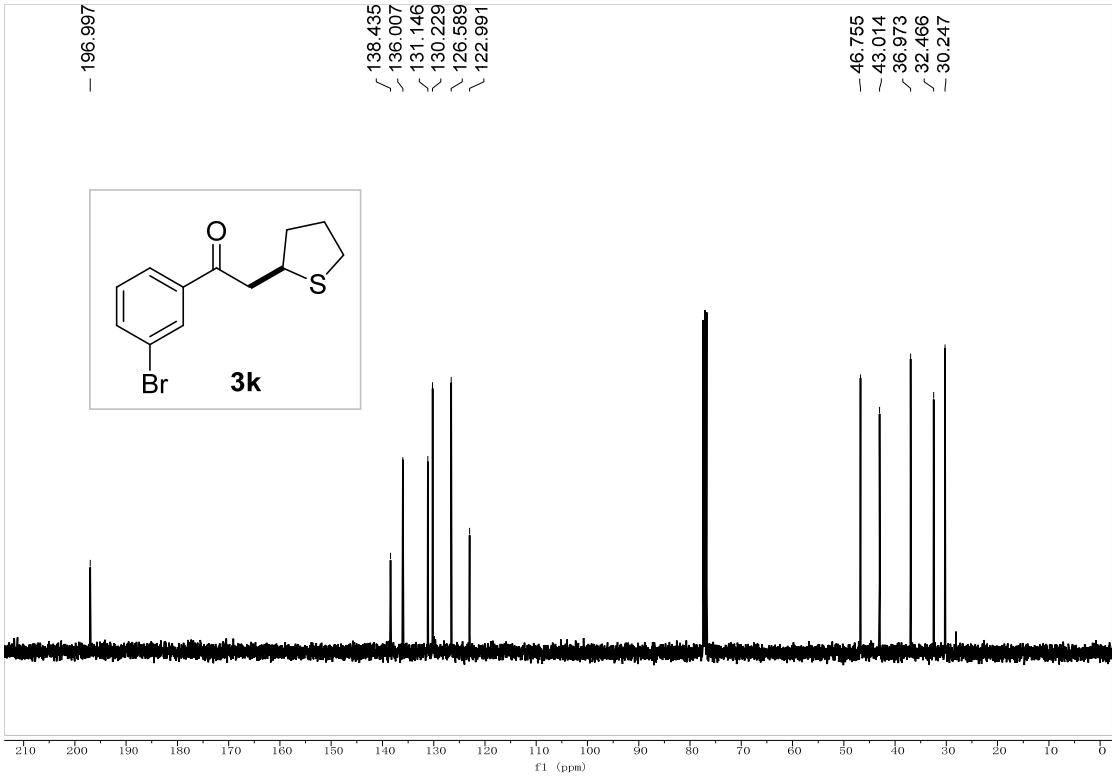
^{1}H NMR spectrum of product **3j**



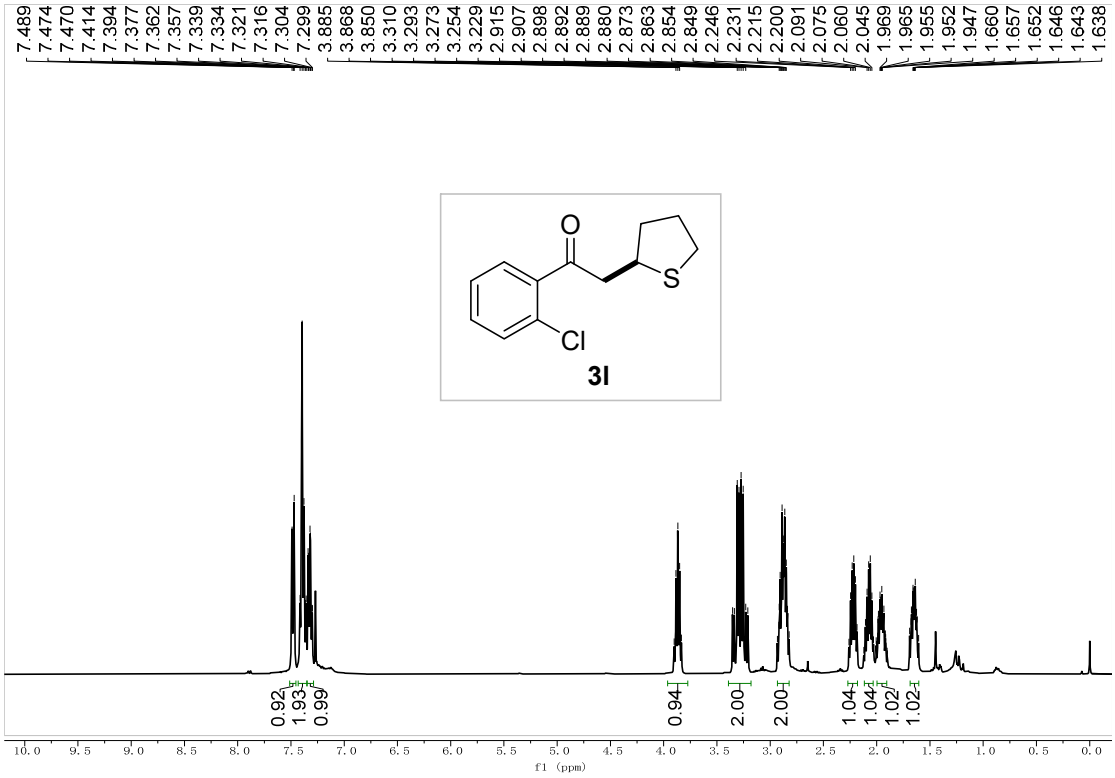
^{13}C NMR spectrum of product **3j**



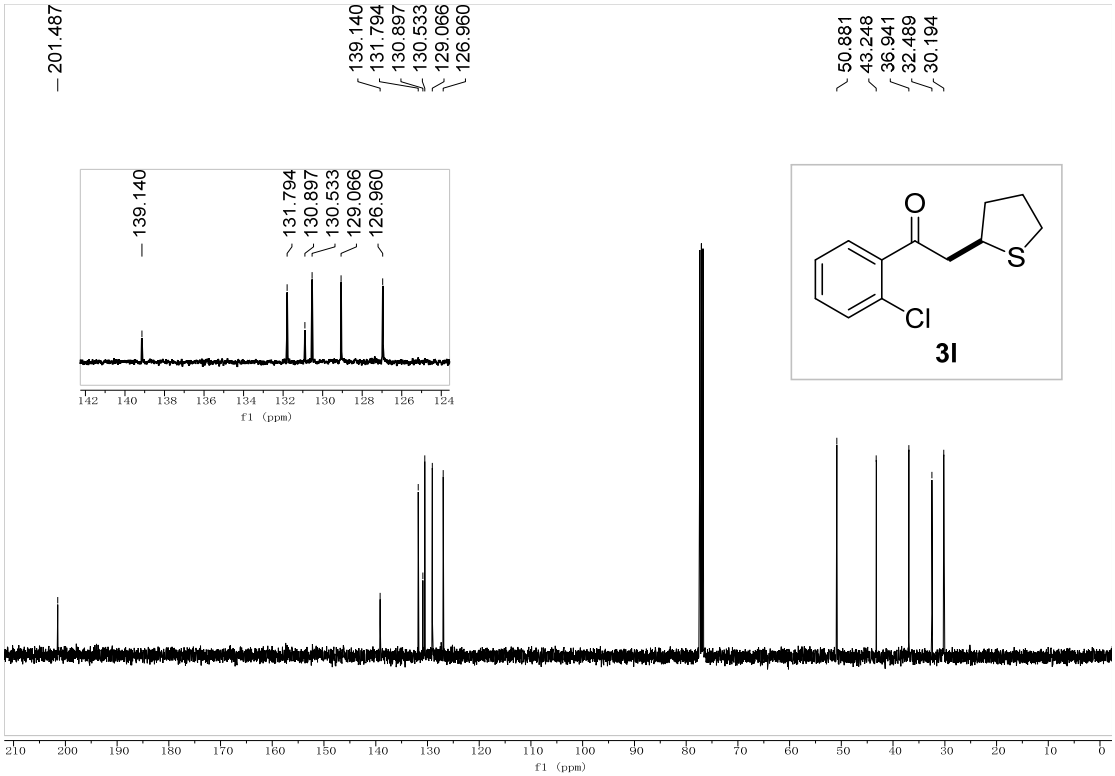
^{1}H NMR spectrum of product **3k**



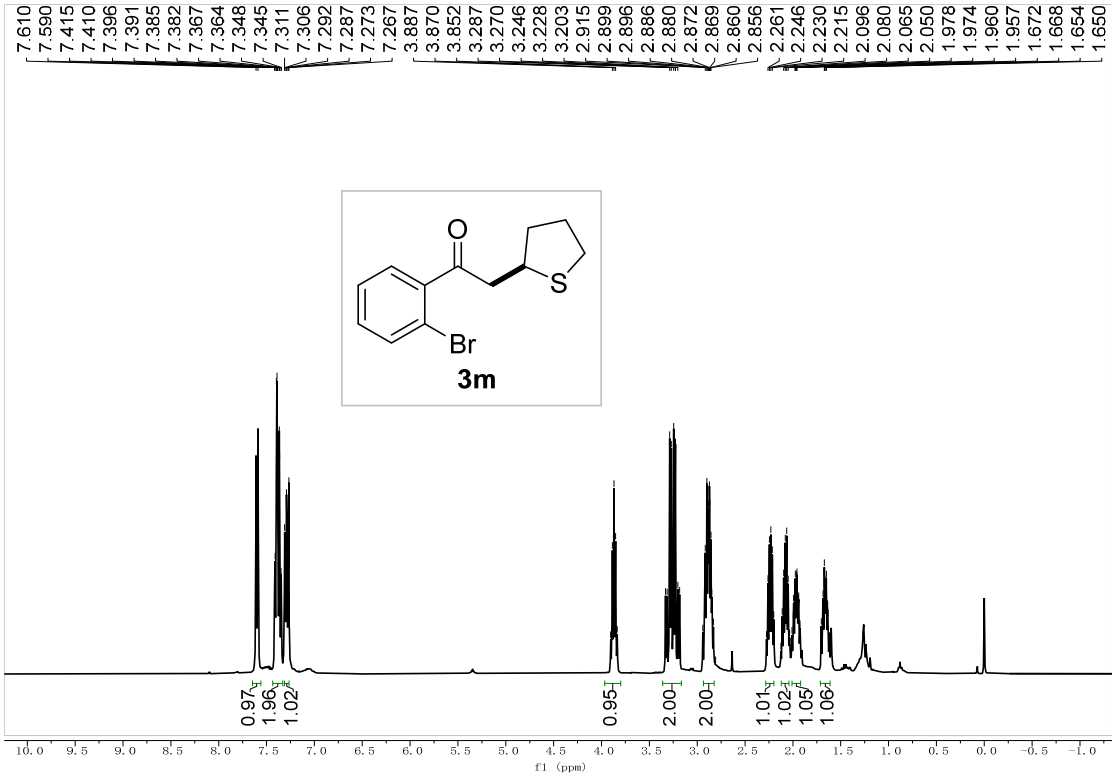
^{13}C NMR spectrum of product **3k**



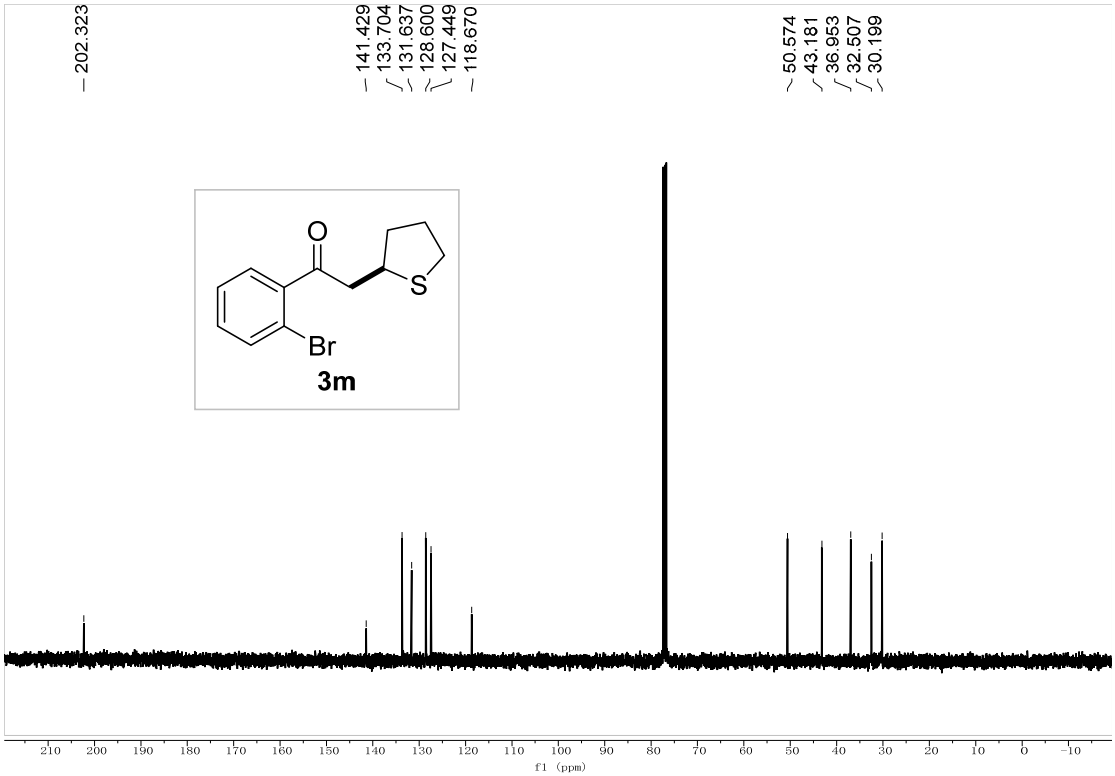
^{1}H NMR spectrum of product **3l**



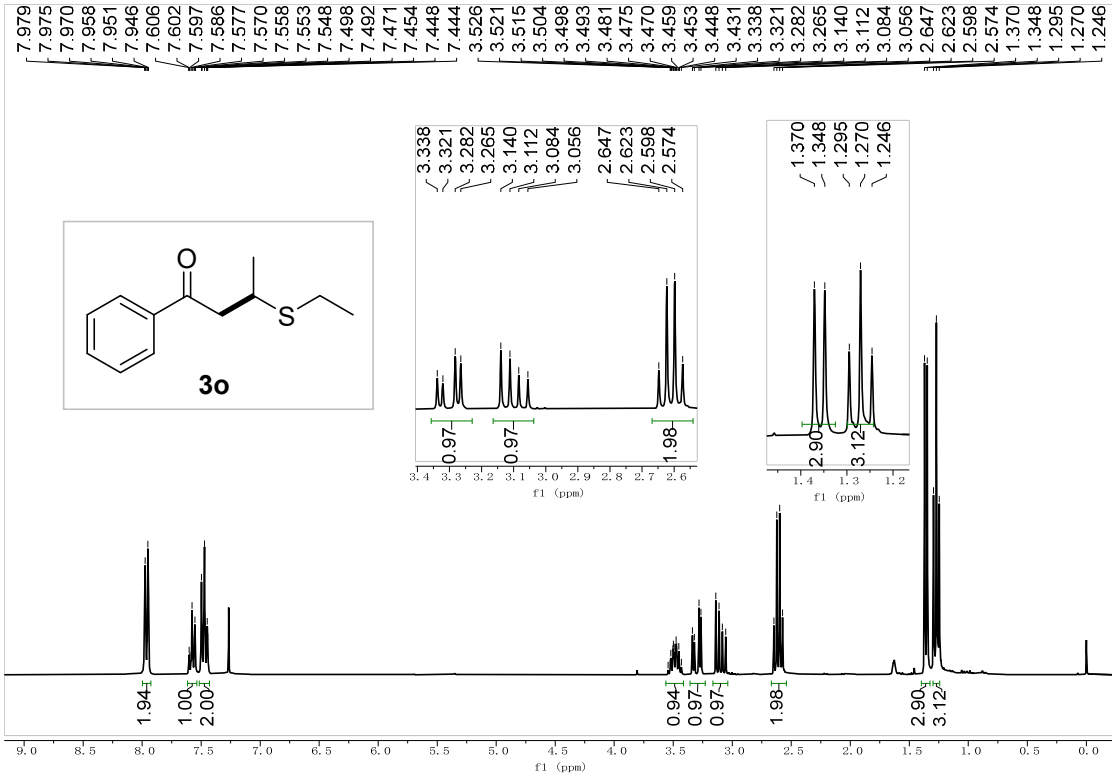
^{13}C NMR spectrum of product **3l**



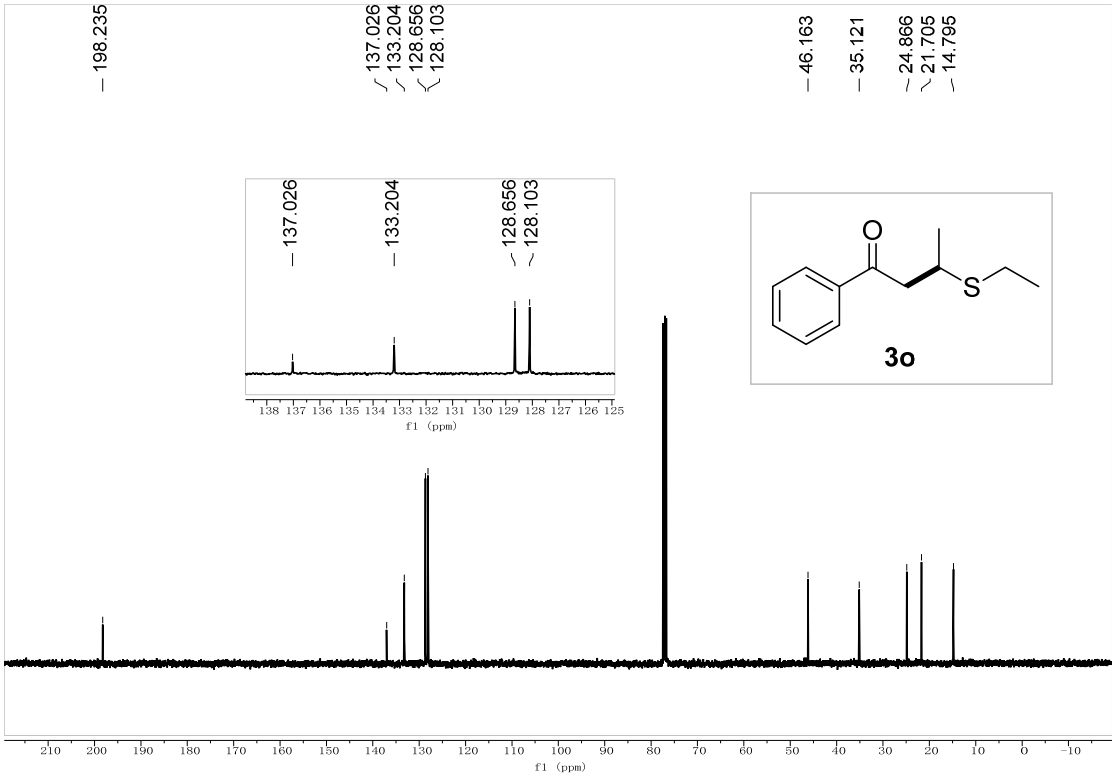
^{1}H NMR spectrum of product **3m**



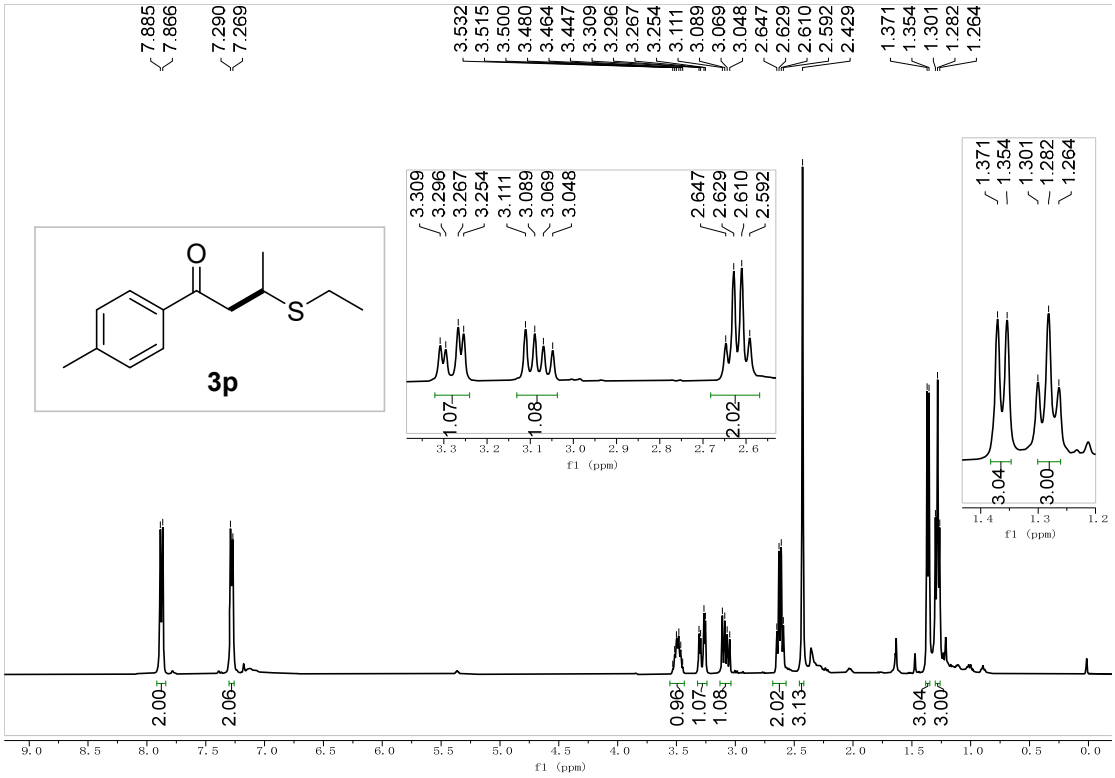
^{13}C NMR spectrum of product **3m**



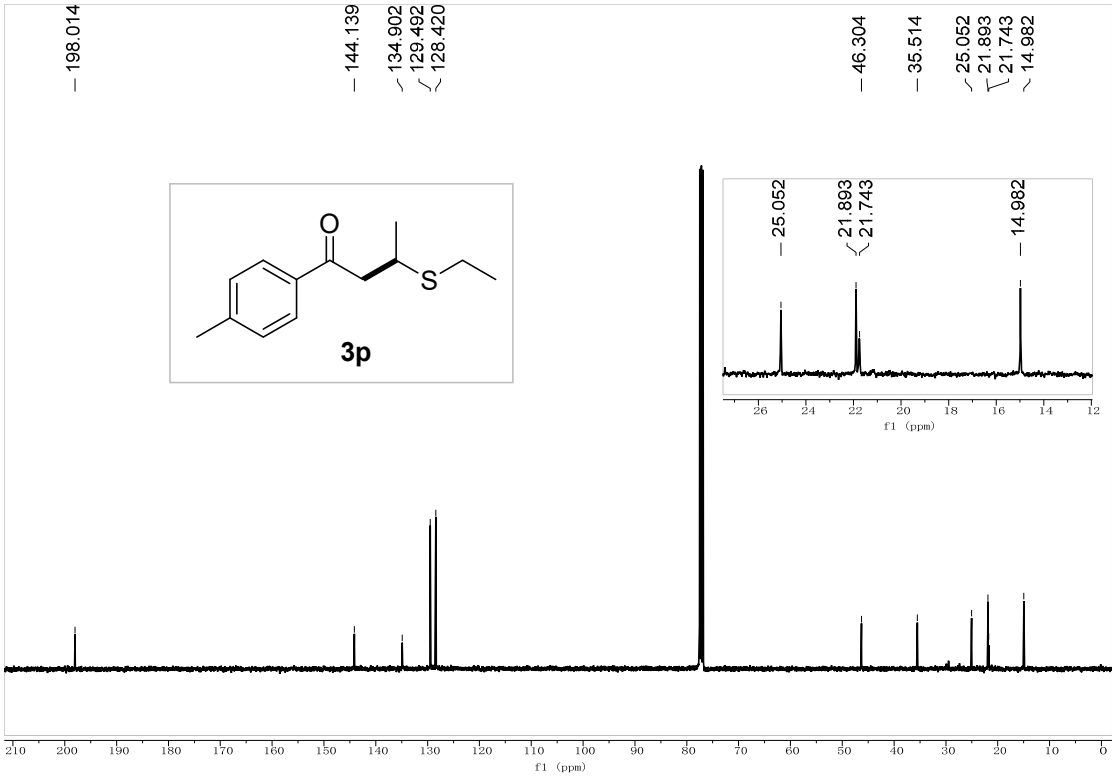
^{1}H NMR spectrum of product **3o**



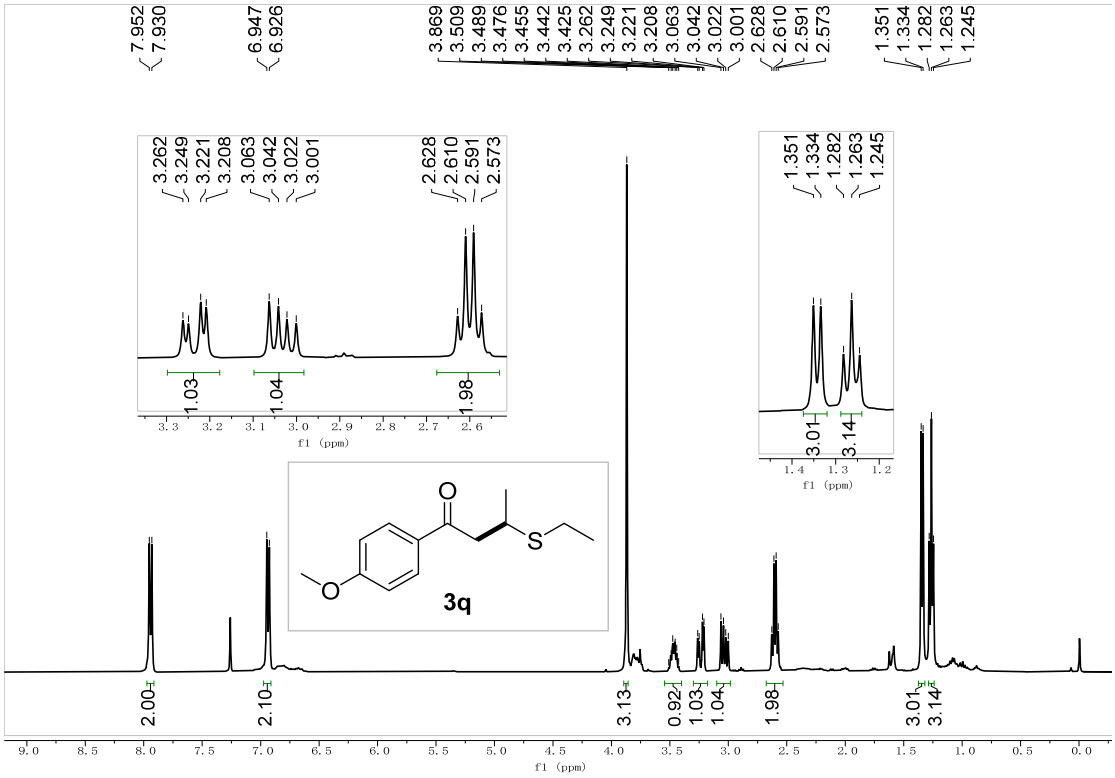
^{13}C NMR spectrum of product **3o**



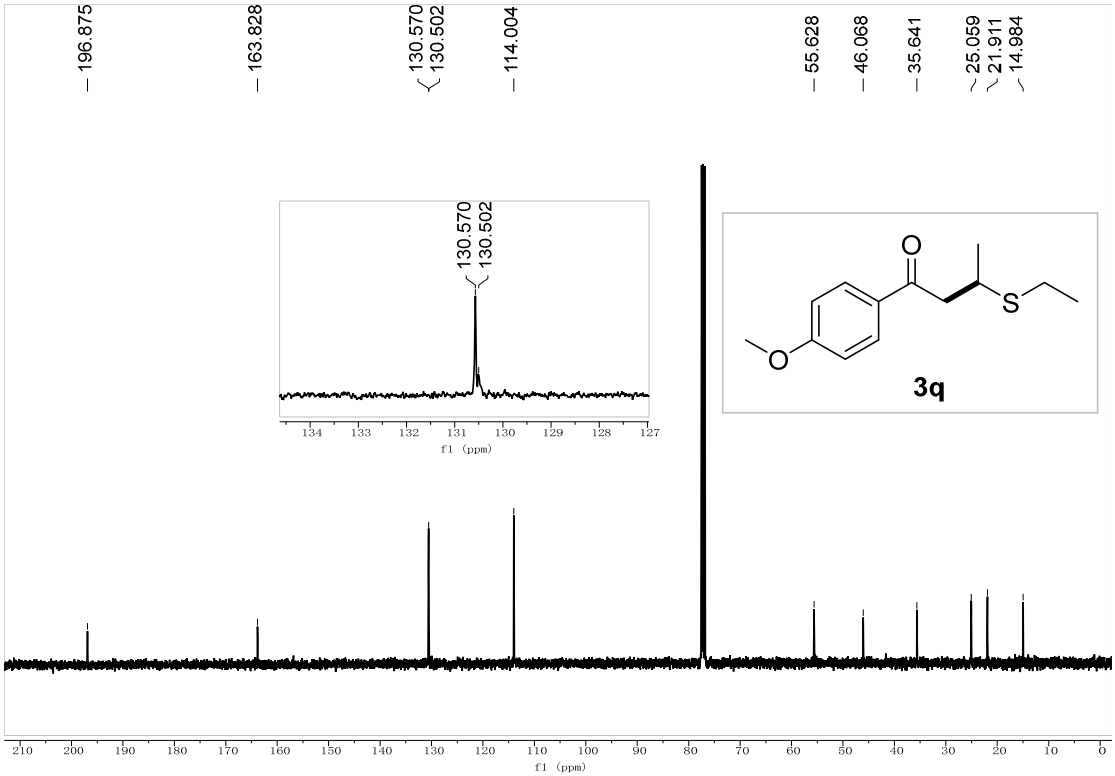
^{1}H NMR spectrum of product **3p**



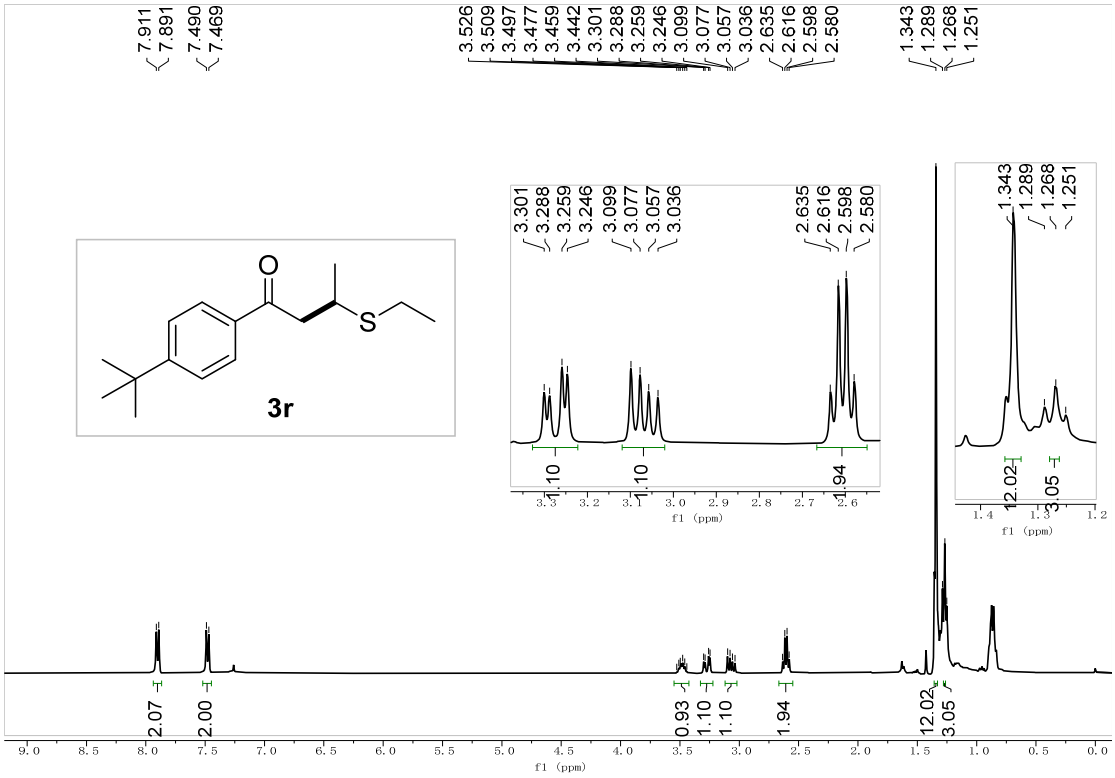
^{13}C NMR spectrum of product **3p**



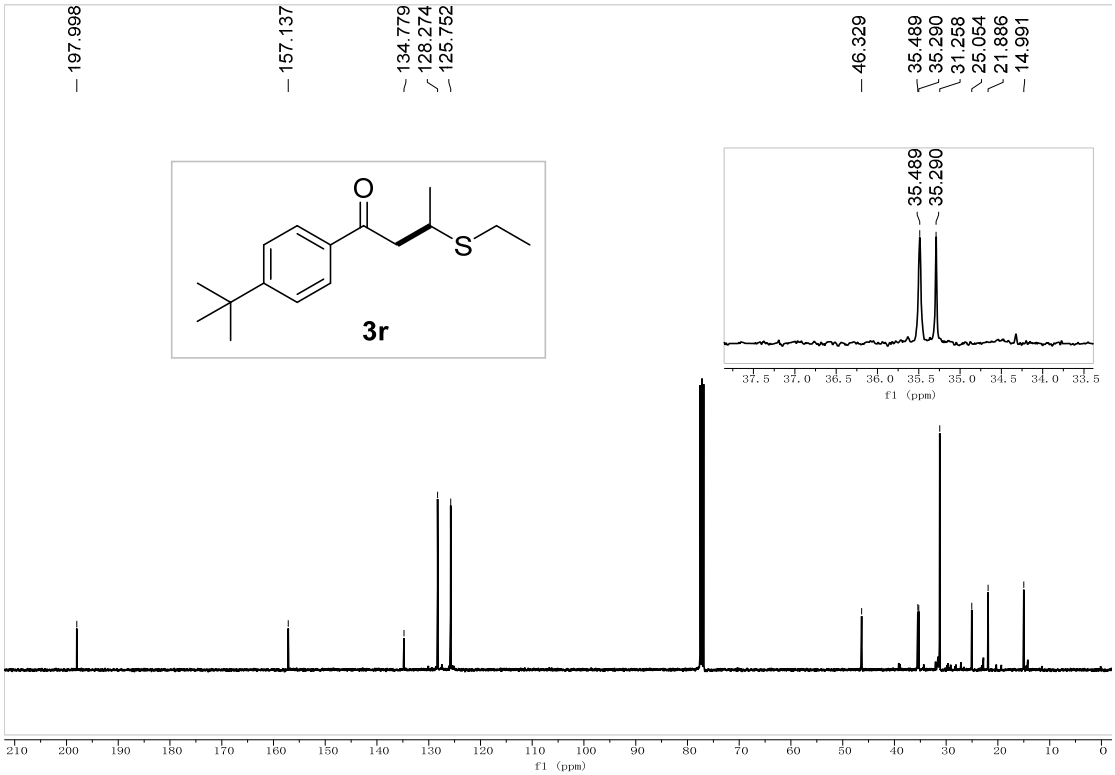
^{1}H NMR spectrum of product **3q**



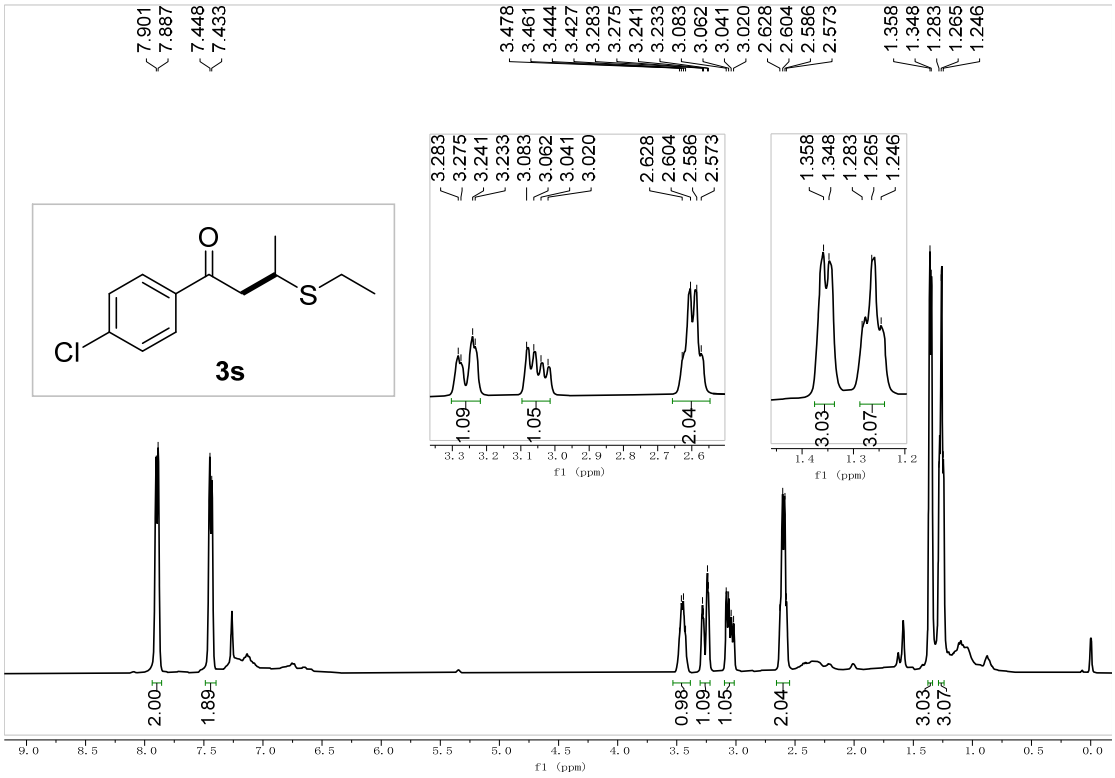
^{13}C NMR spectrum of product **3q**



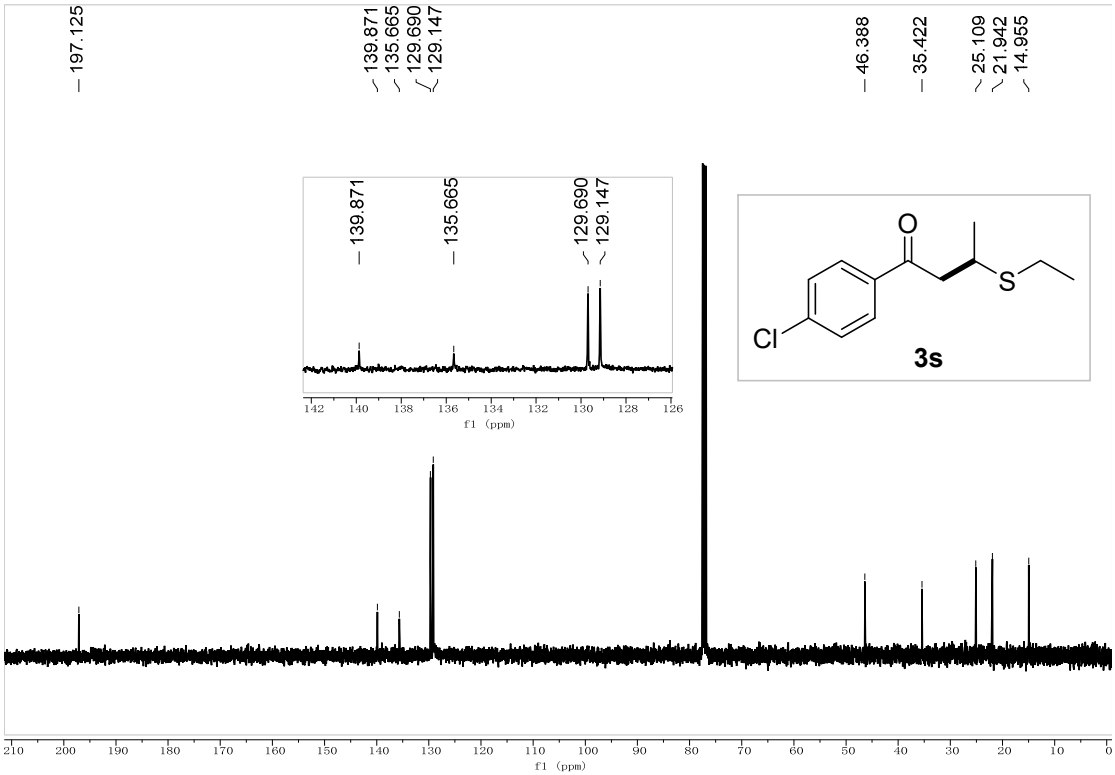
^{1}H NMR spectrum of product **3r**



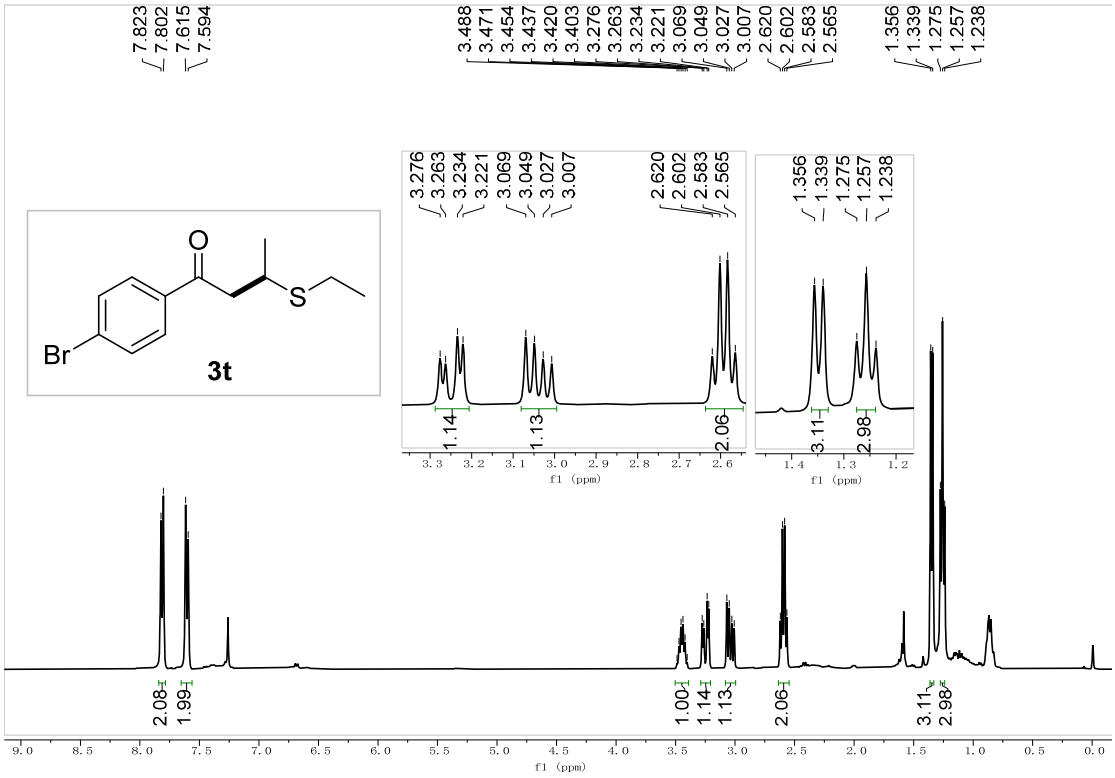
^{13}C NMR spectrum of product **3r**



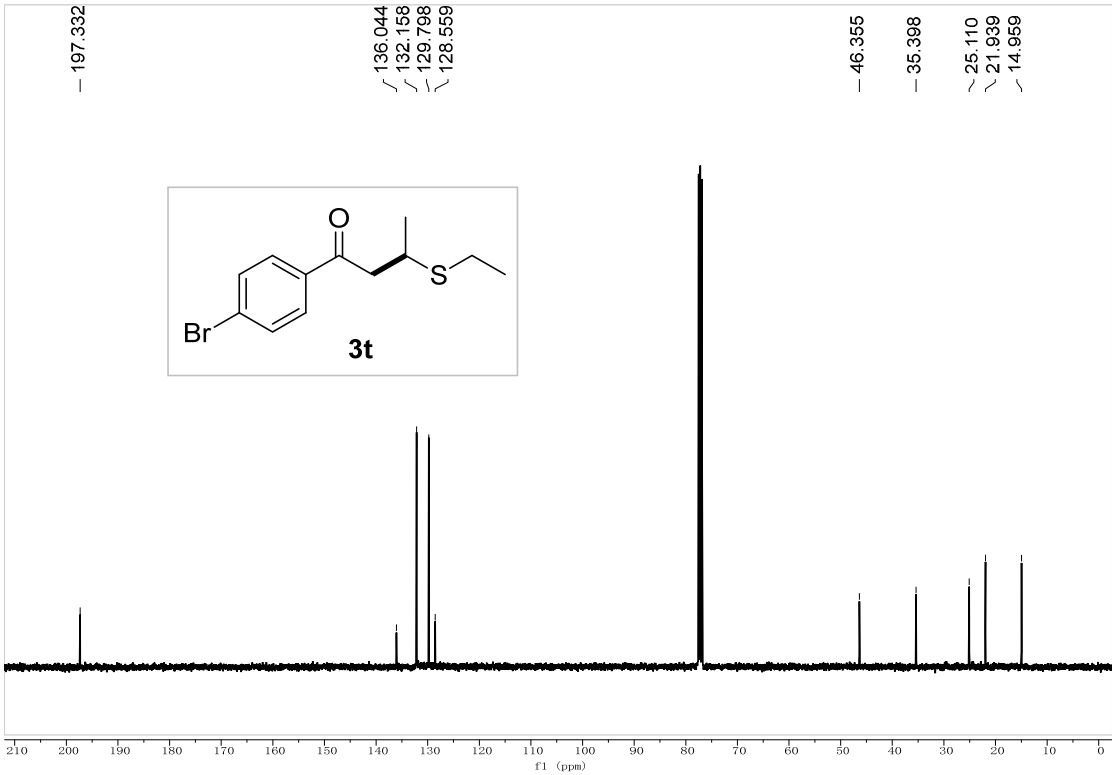
^{1}H NMR spectrum of product **3s**



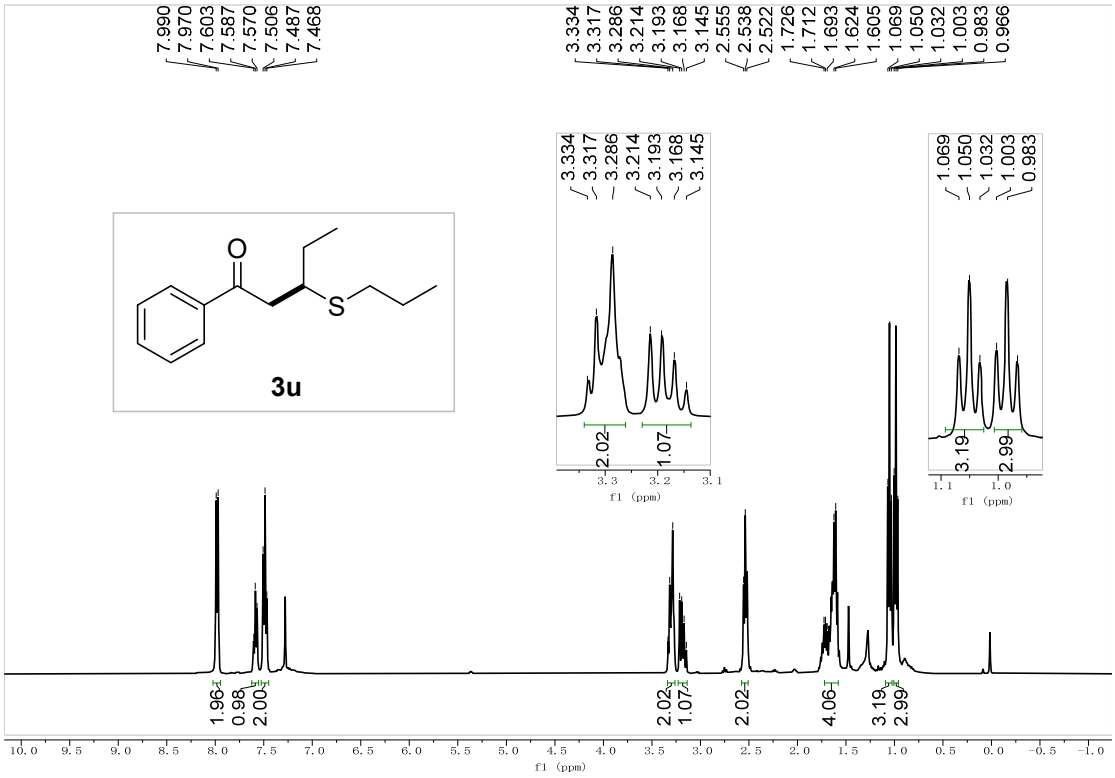
^{13}C NMR spectrum of product **3s**



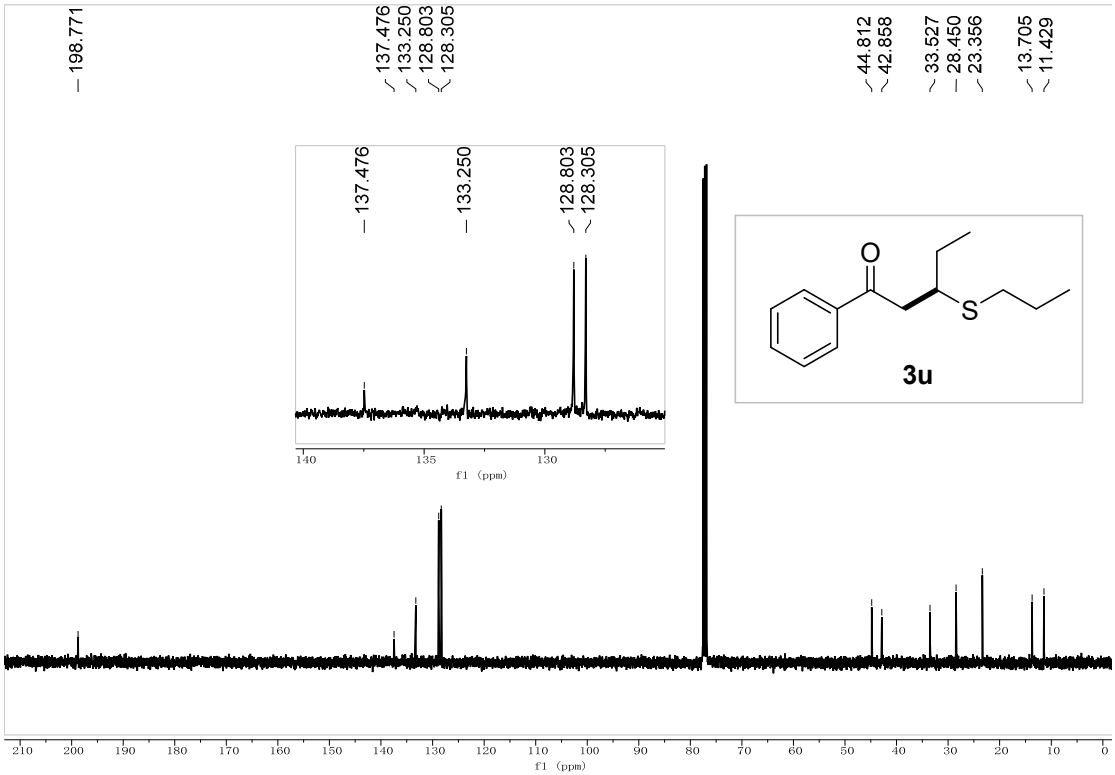
^{1}H NMR spectrum of product **3t**



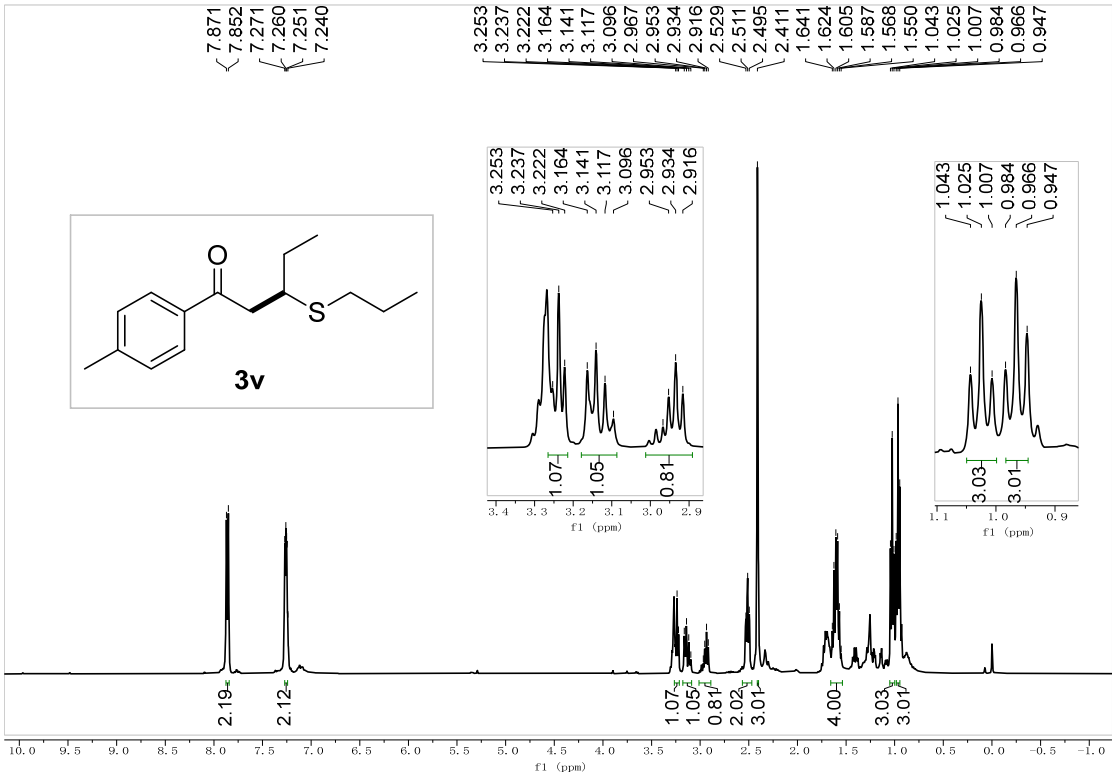
^{13}C NMR spectrum of product **3t**



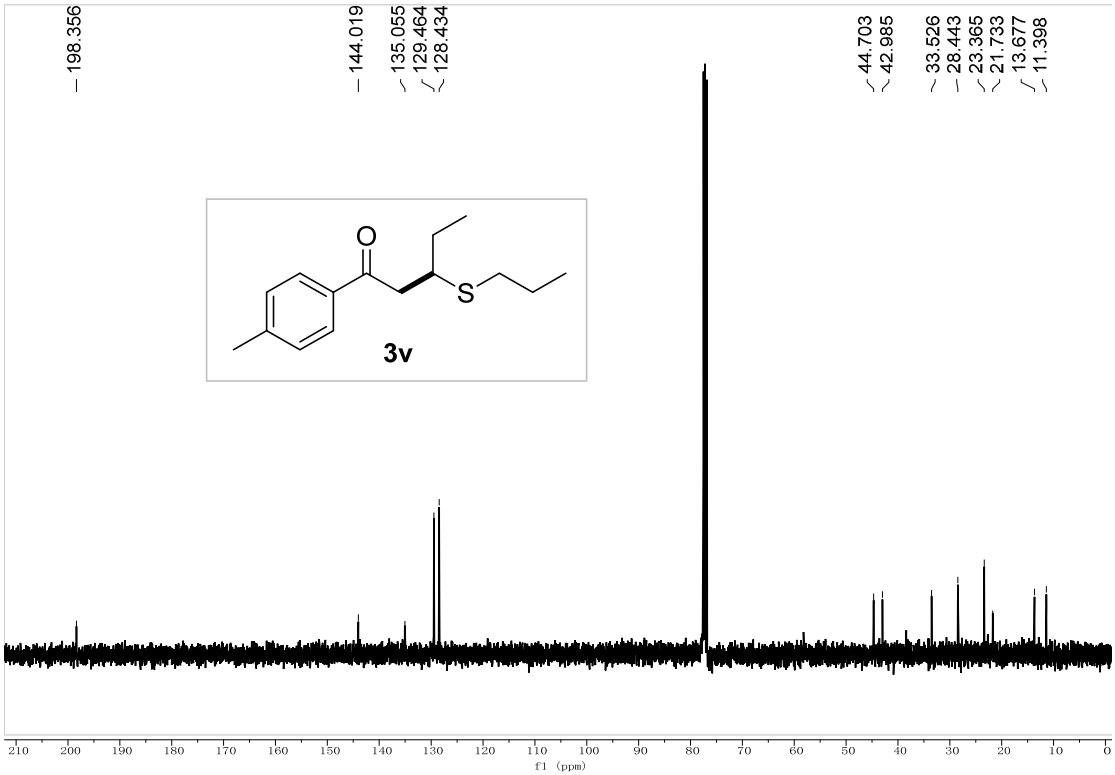
^{1}H NMR spectrum of product **3u**



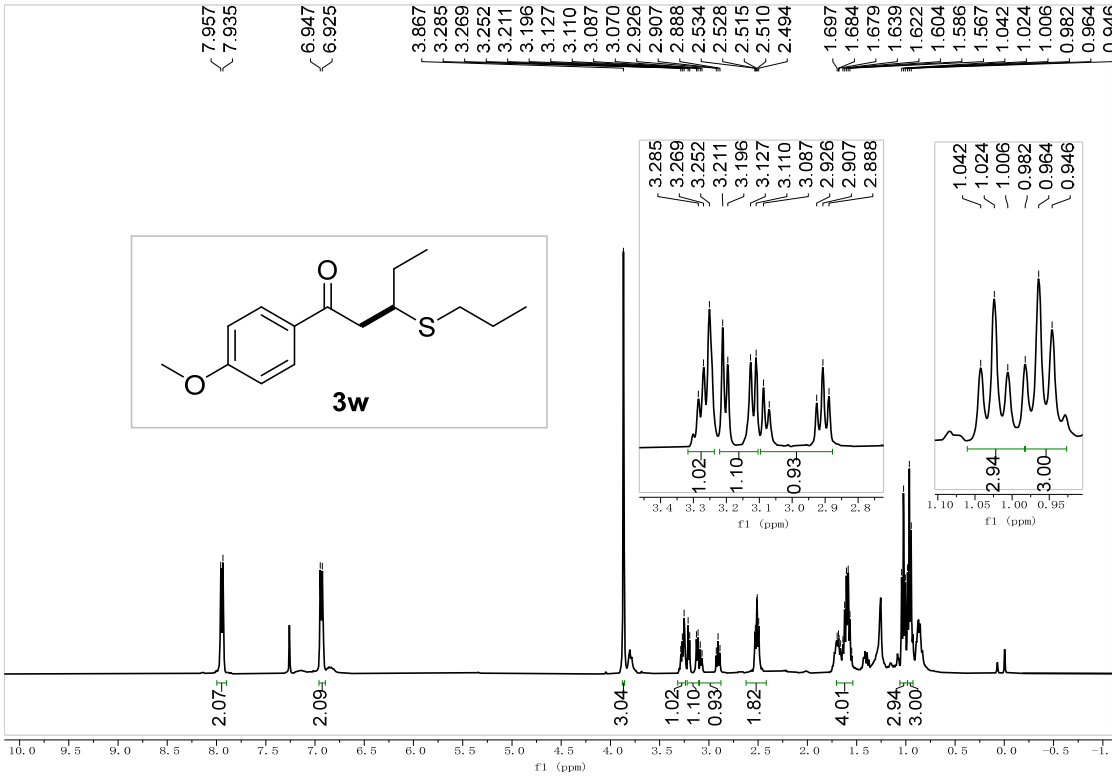
^{13}C NMR spectrum of product **3u**



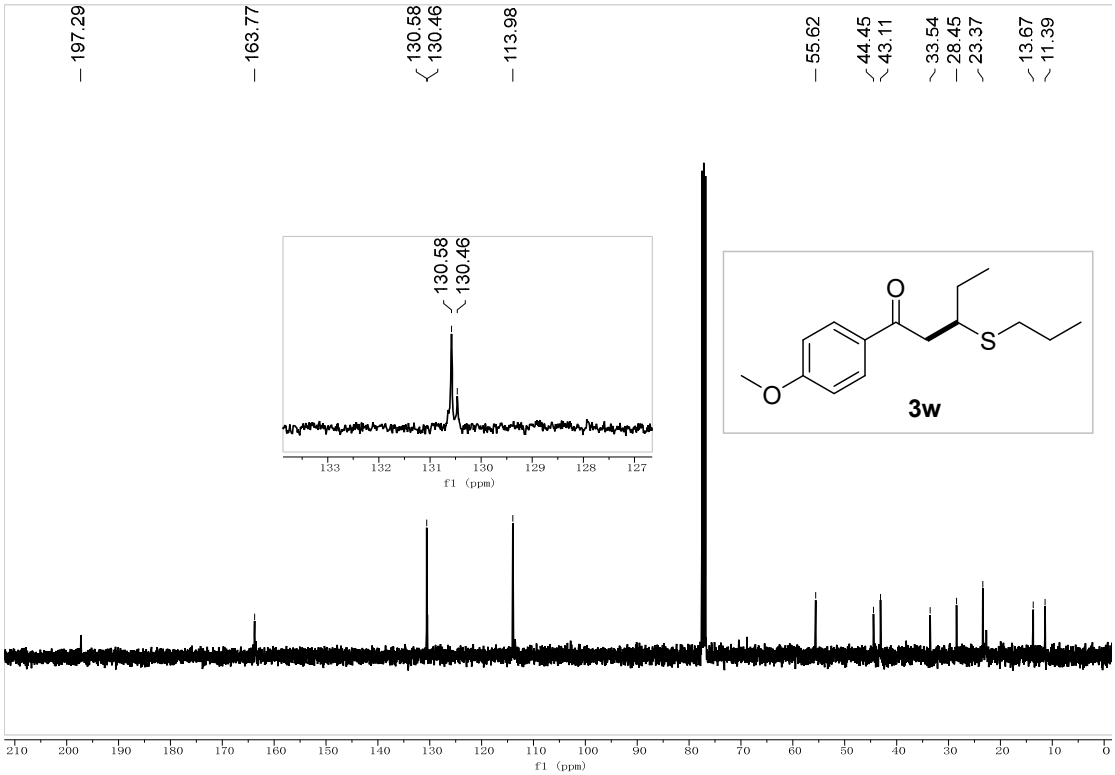
^{1}H NMR spectrum of product **3v**



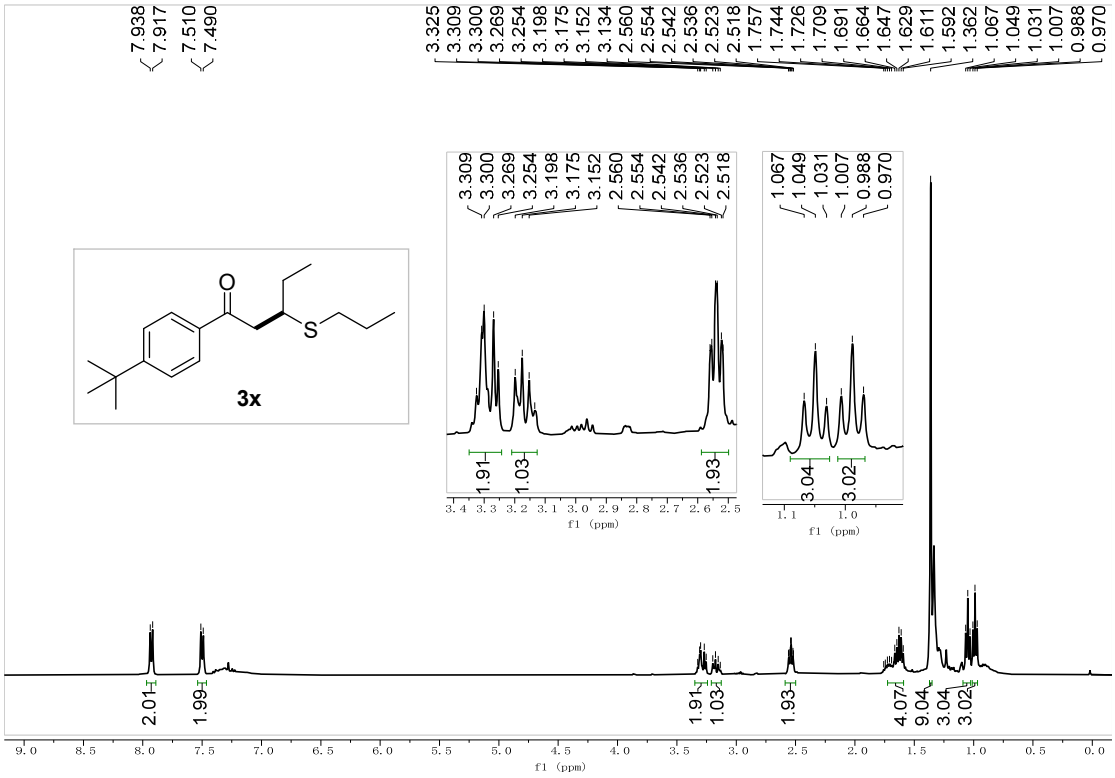
^{13}C NMR spectrum of product **3v**



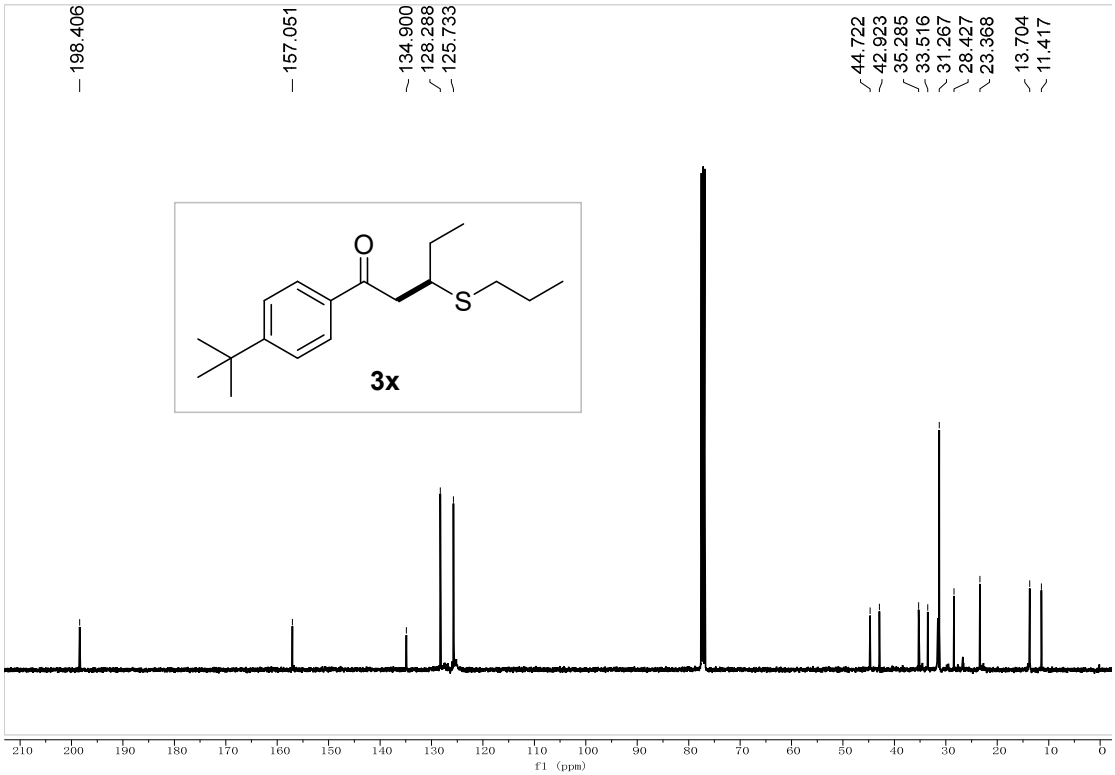
^{1}H NMR spectrum of product **3w**



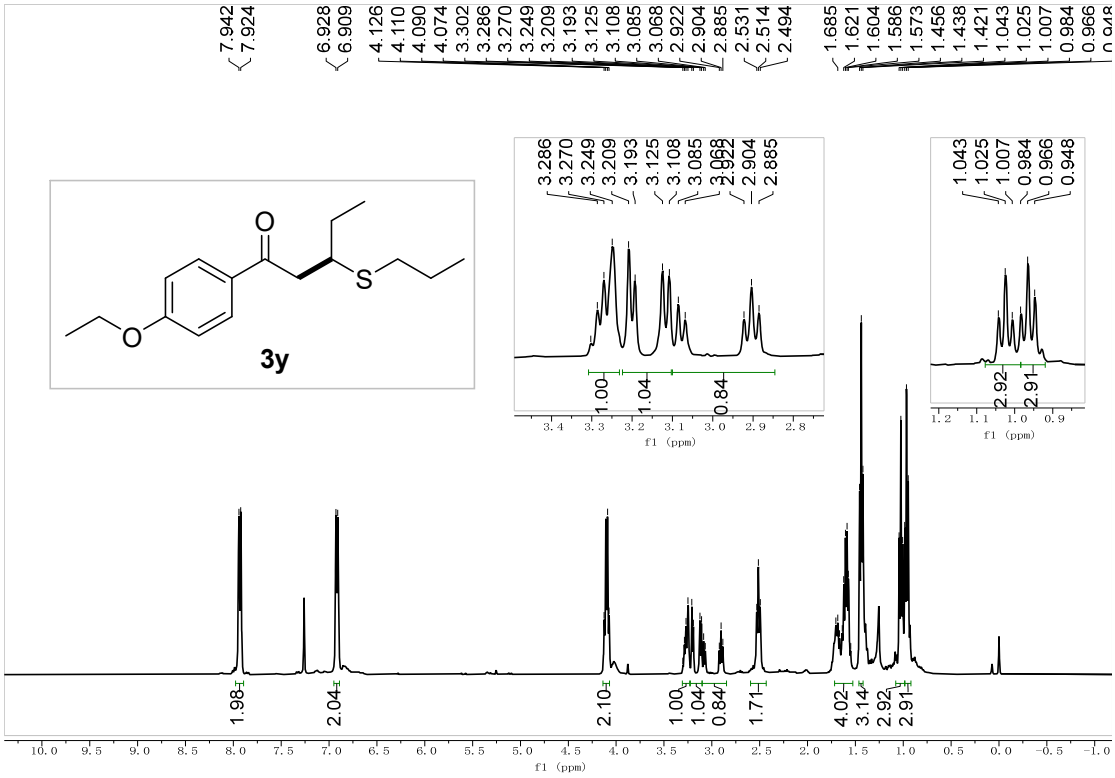
^{13}C NMR spectrum of product **3w**



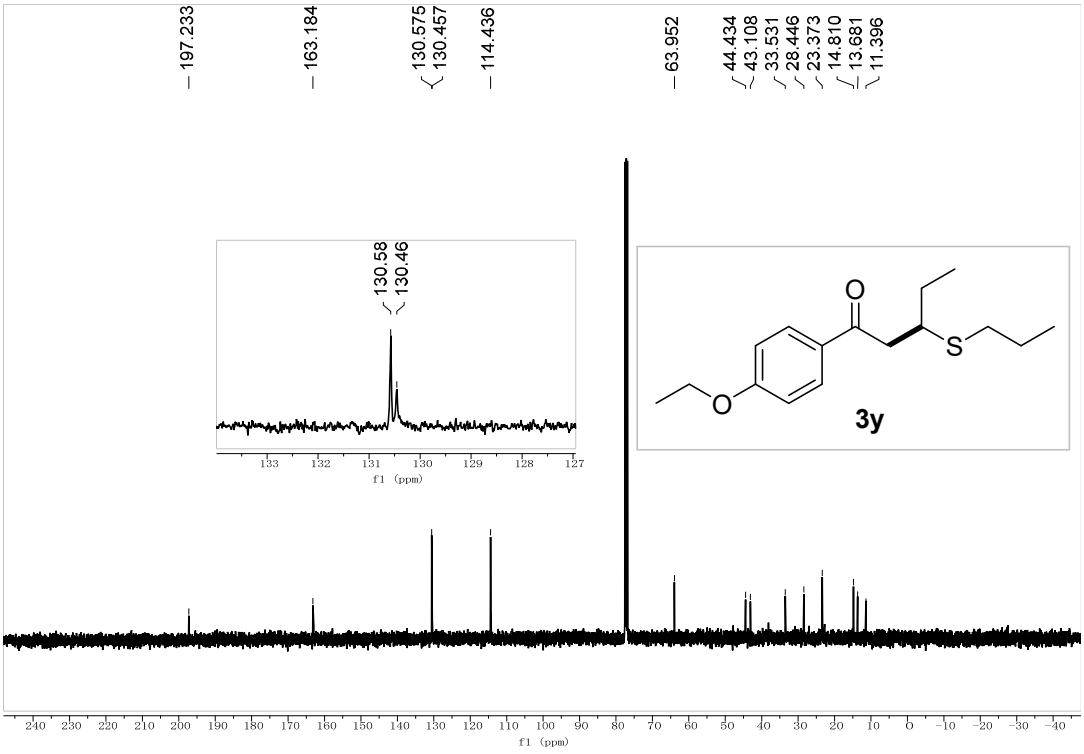
^{1}H NMR spectrum of product **3x**



^{13}C NMR spectrum of product **3x**

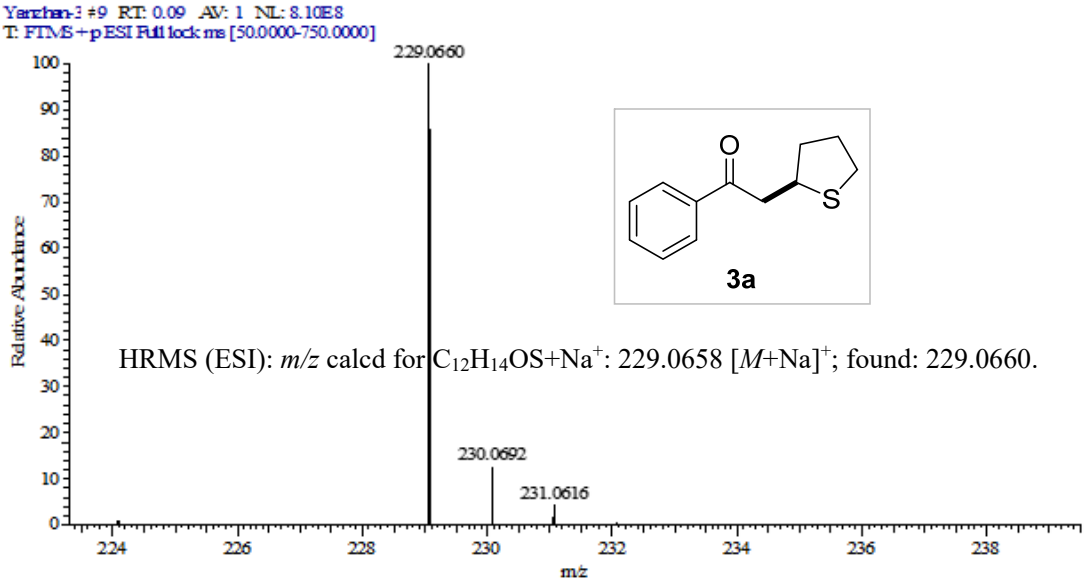


^{1}H NMR spectrum of product **3y**



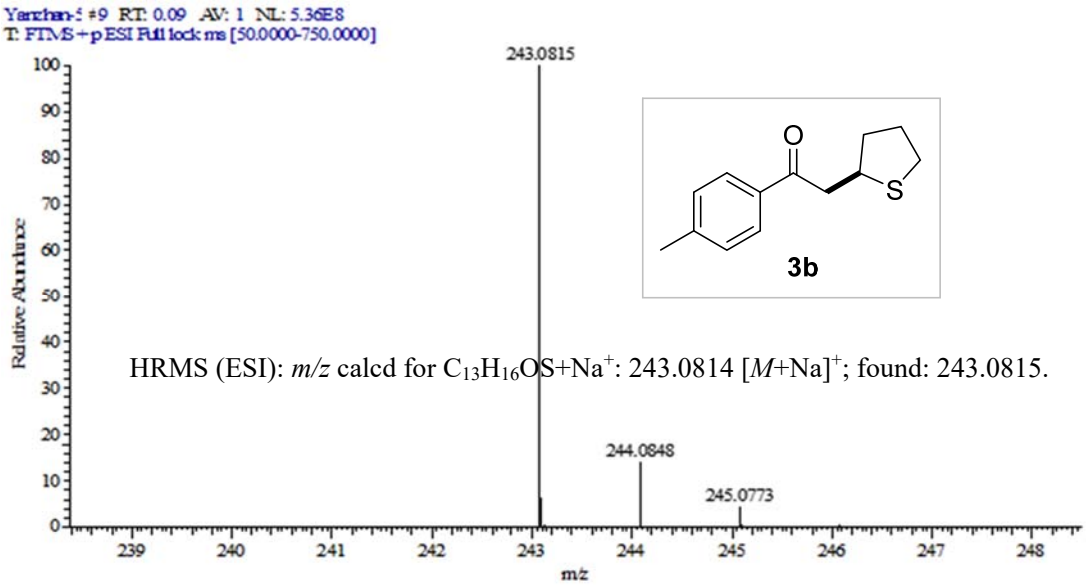
^{13}C NMR spectrum of product **3y**

7. Copies of HRMS Spectra of All Products



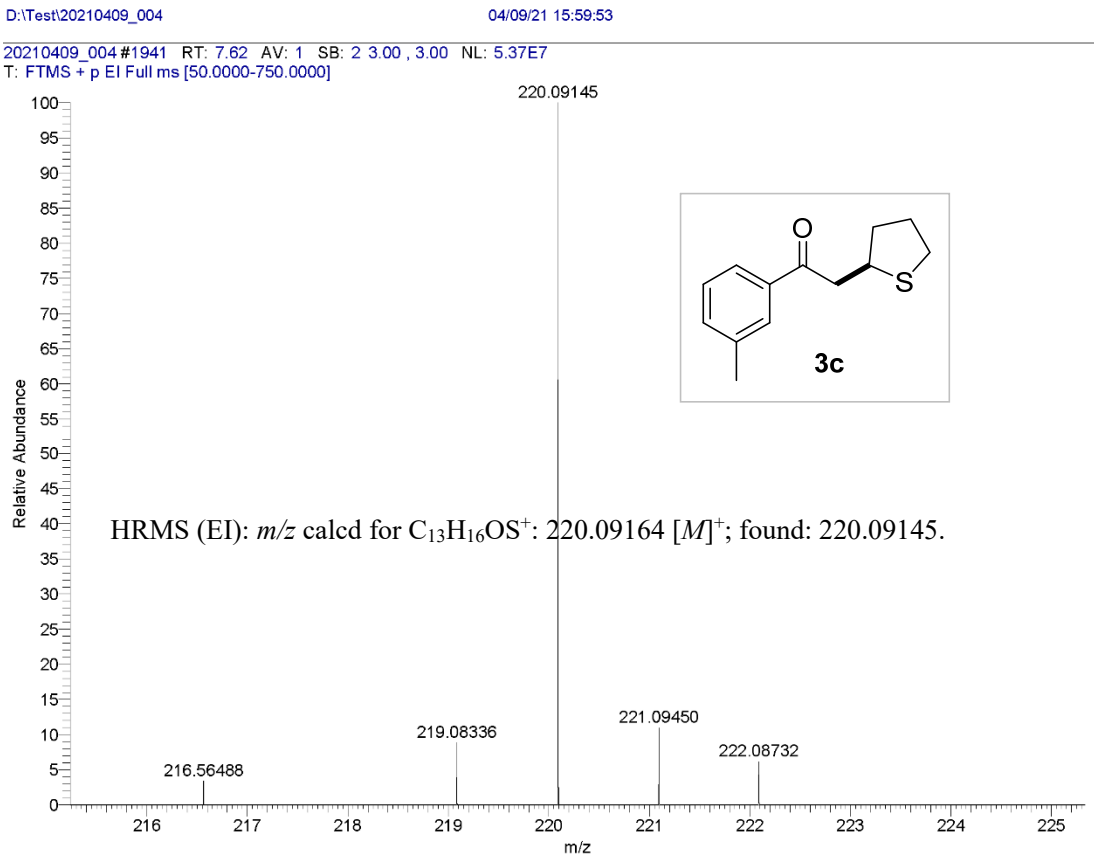
HRMS (ESI): *m/z* calcd for $C_{12}H_{14}OS+Na^+$: 229.0658 $[M+Na]^+$; found: 229.0660.

HRMS spectrum of product **3a**



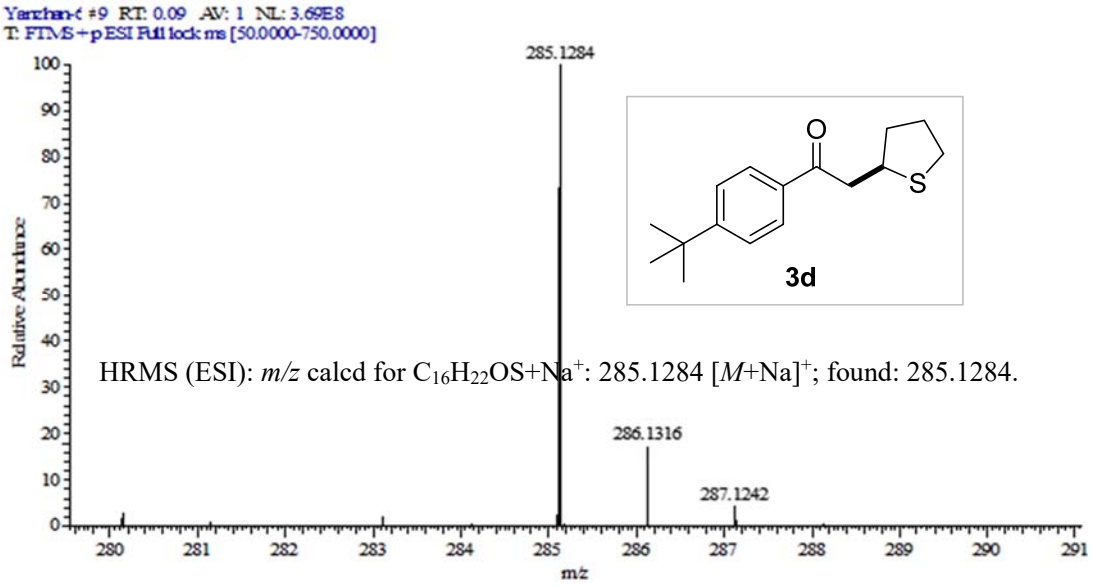
HRMS (ESI): *m/z* calcd for $C_{13}H_{16}OS+Na^+$: 243.0814 $[M+Na]^+$; found: 243.0815.

HRMS spectrum of product **3b**



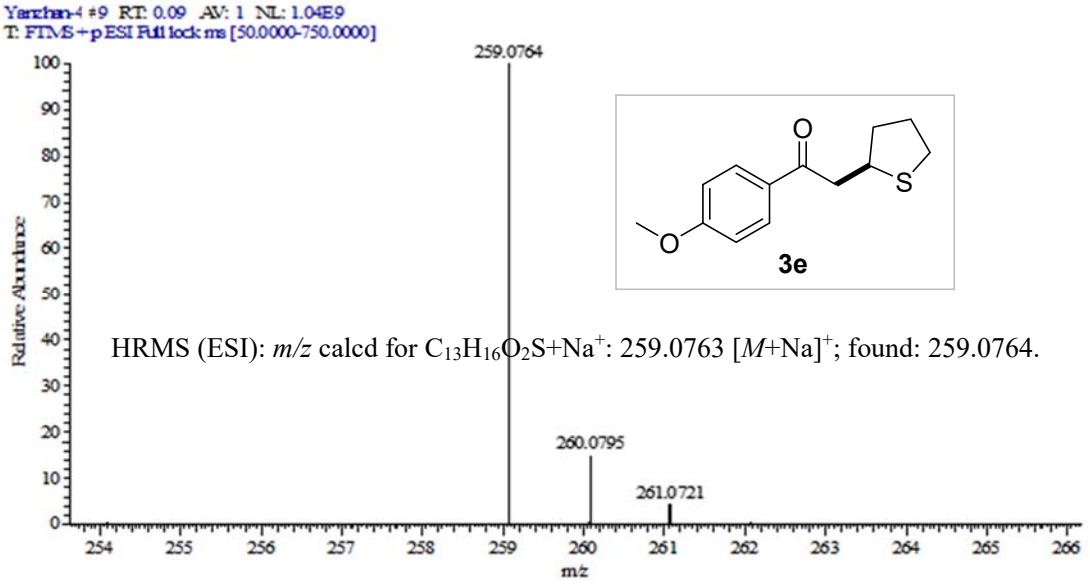
HRMS (EI): *m/z* calcd for $C_{13}H_{16}OS^{+}$: 220.09164 $[M]^{+}$; found: 220.09145.

HRMS spectrum of product **3c**



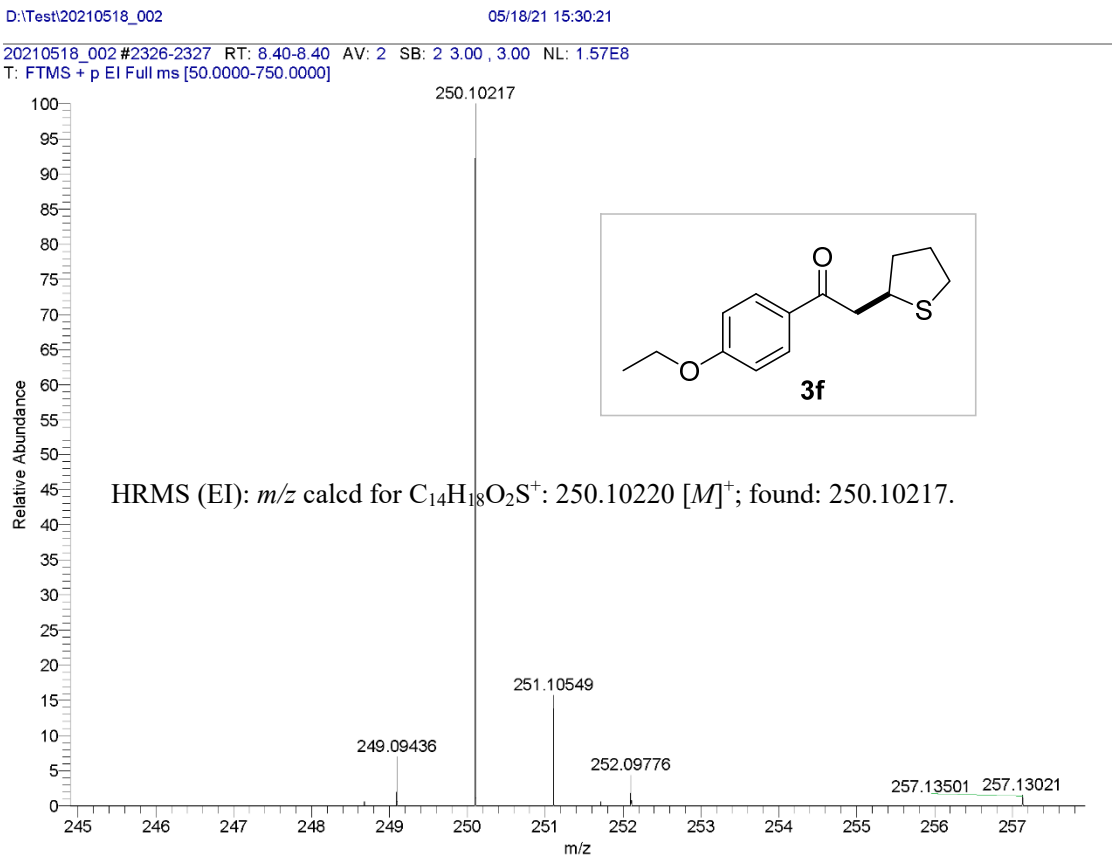
HRMS (ESI): *m/z* calcd for $C_{16}H_{22}OS+Na^{+}$: 285.1284 $[M+Na]^{+}$; found: 285.1284.

HRMS spectrum of product **3d**



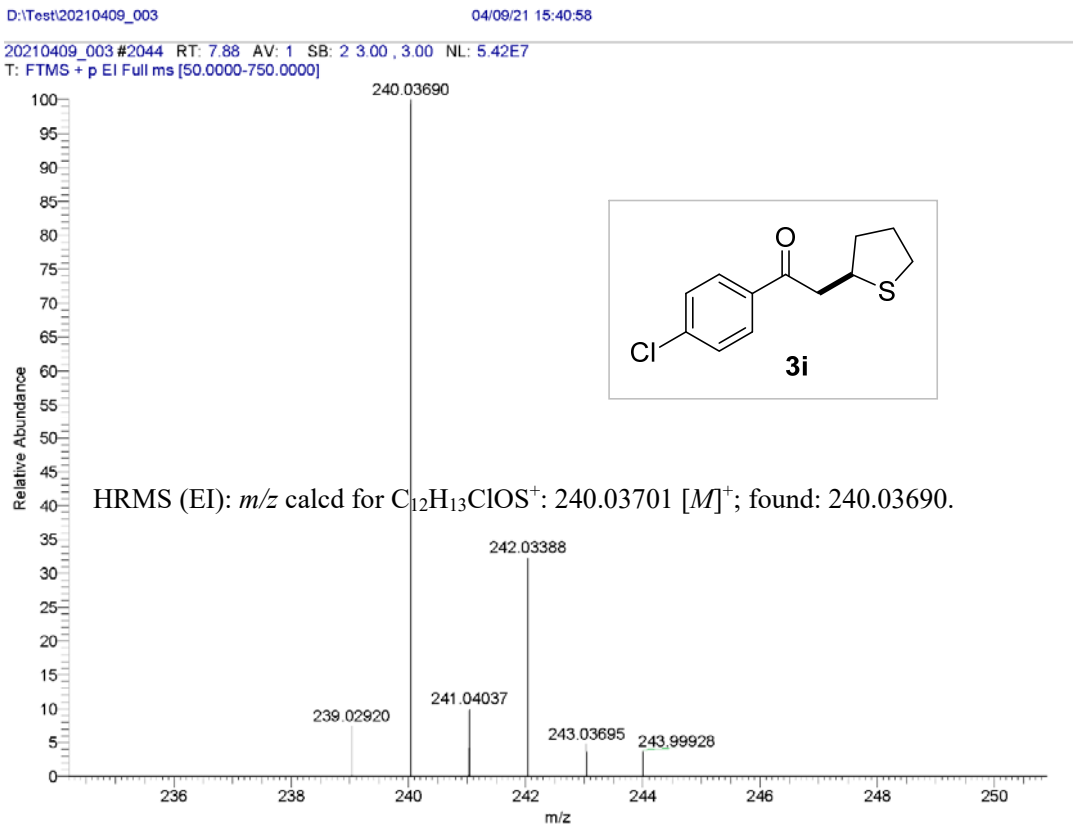
HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_2S+Na^+$: 259.0763 $[M+Na]^+$; found: 259.0764.

HRMS spectrum of product **3e**



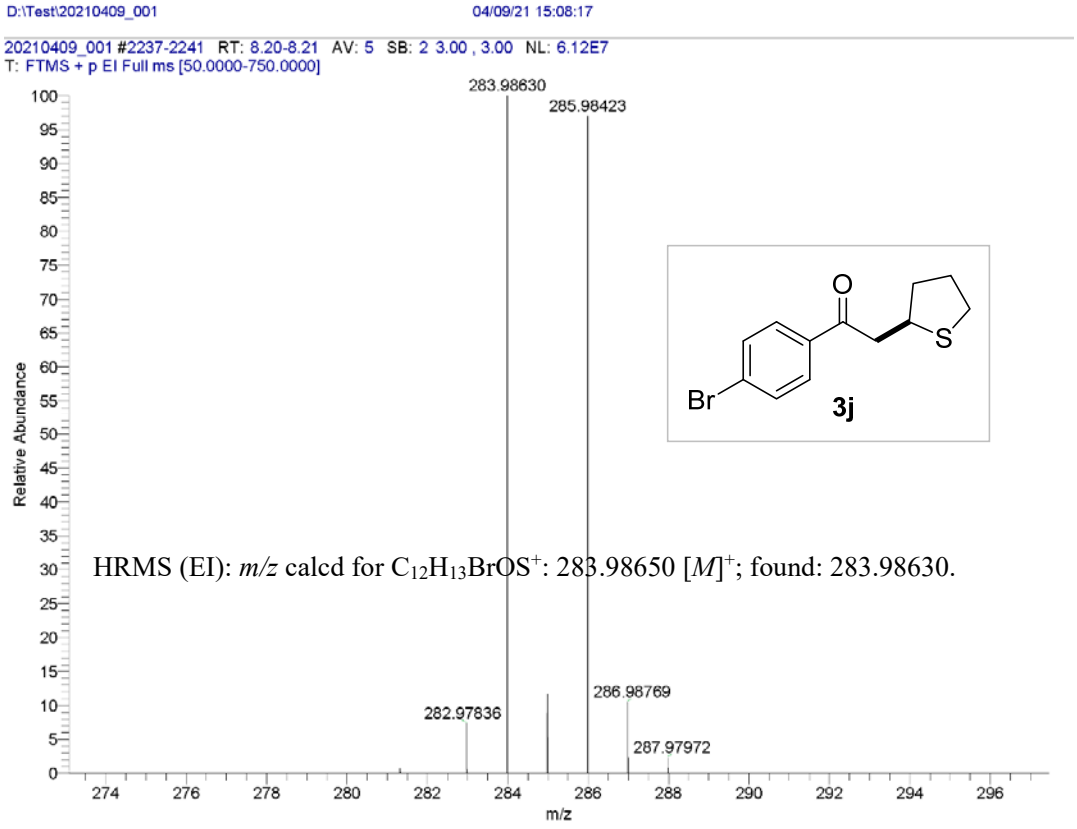
HRMS (EI): *m/z* calcd for $C_{14}H_{18}O_2S^+$: 250.10220 $[M]^+$; found: 250.10217.

HRMS spectrum of product **3f**



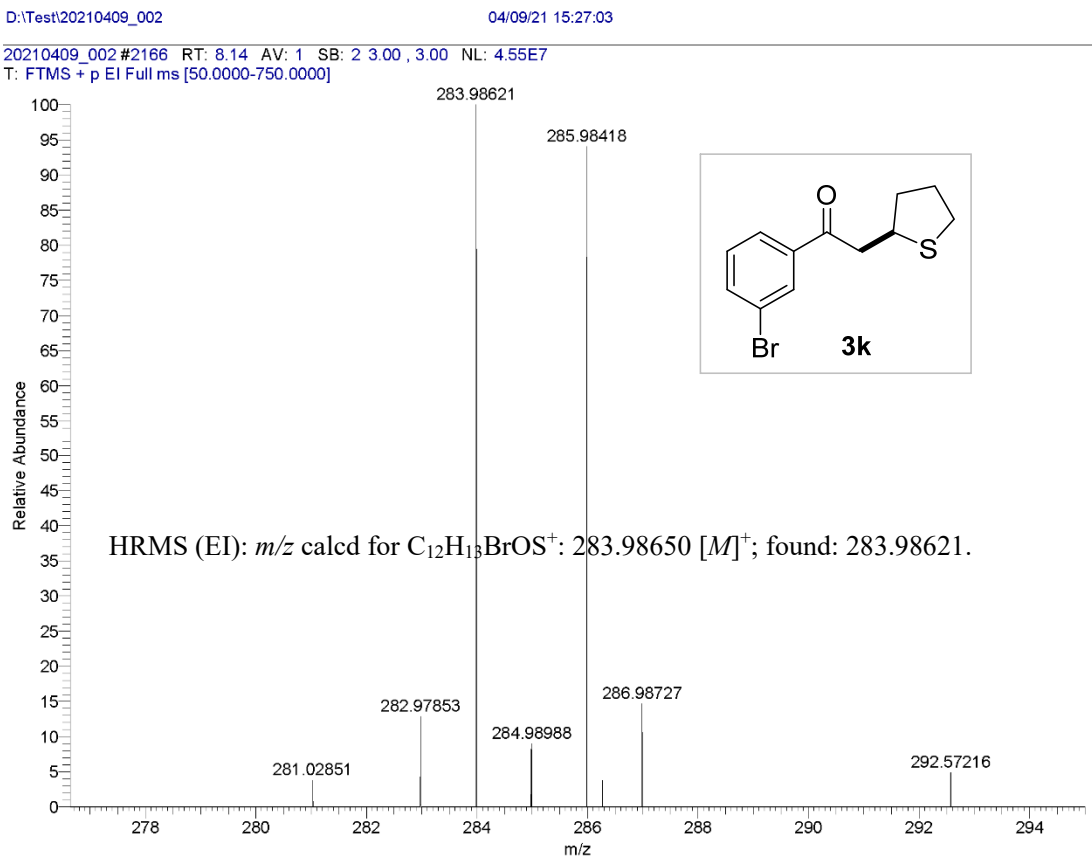
HRMS (EI): *m/z* calcd for $C_{12}H_{13}ClOS^{+}$: 240.03701 $[M]^{+}$; found: 240.03690.

HRMS spectrum of product **3i**



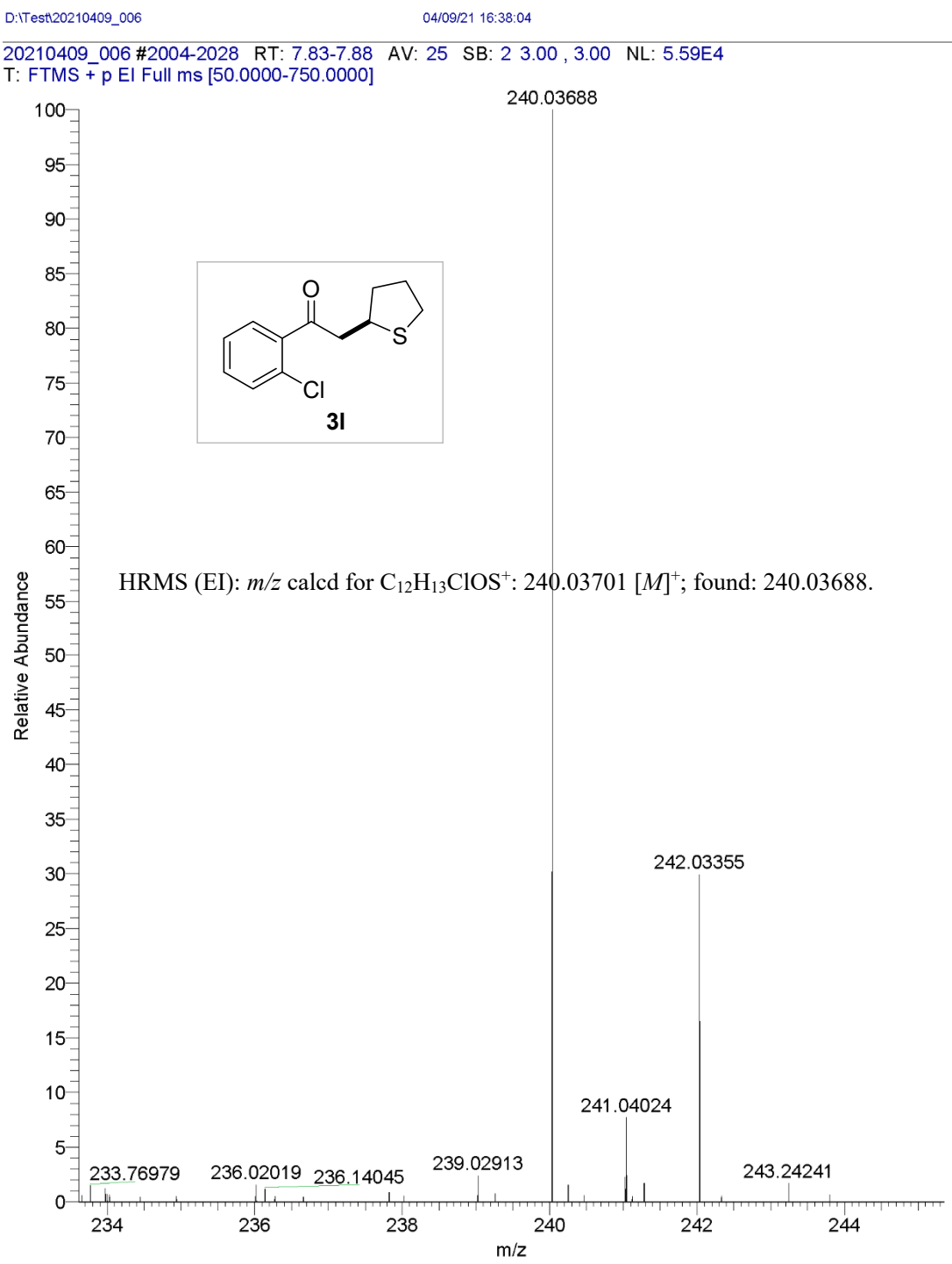
HRMS (EI): *m/z* calcd for $C_{12}H_{13}BrOS^{+}$: 283.98650 $[M]^{+}$; found: 283.98630.

HRMS spectrum of product **3j**



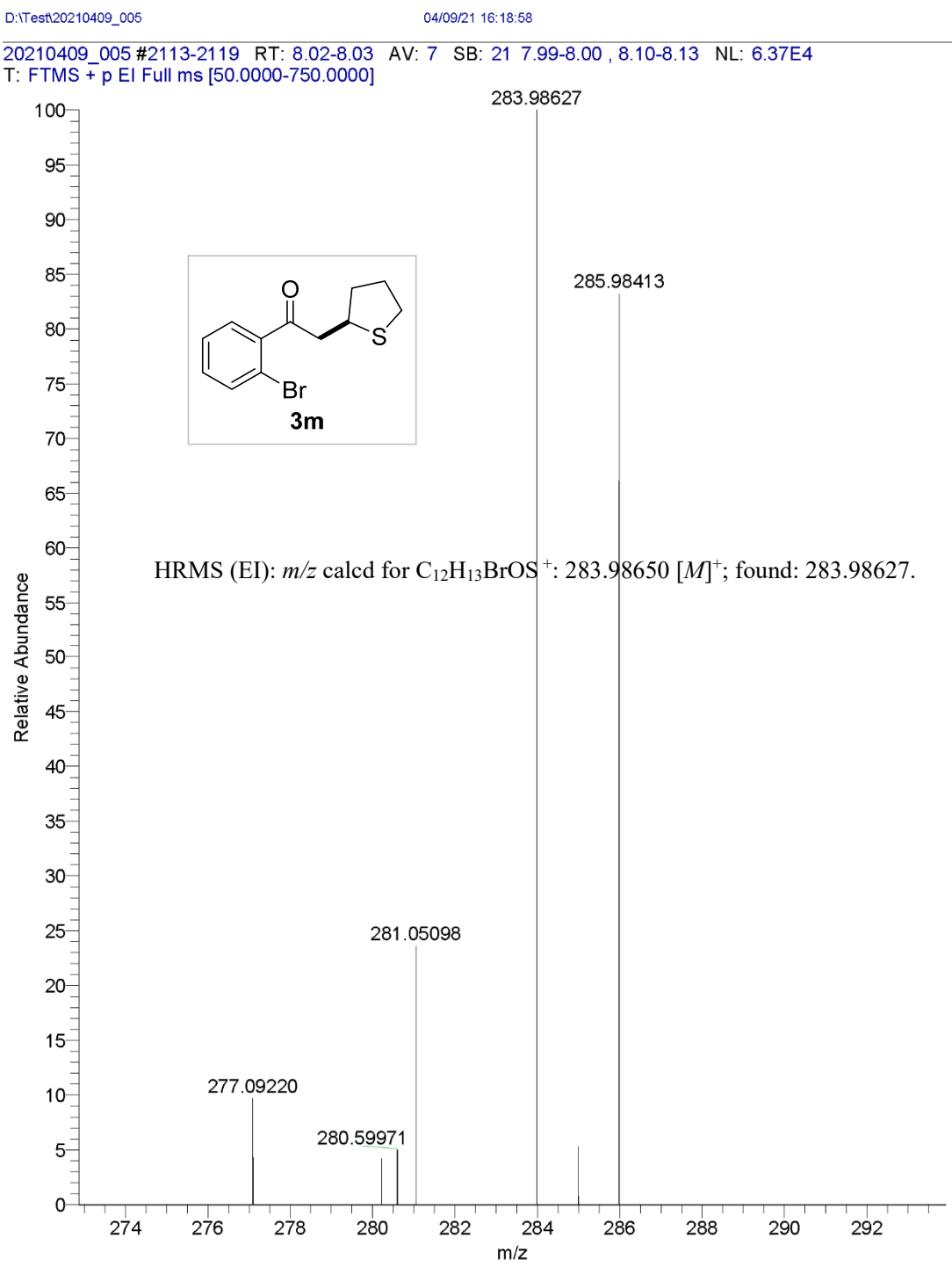
HRMS (EI): *m/z* calcd for $C_{12}H_{13}BrOS^{+}$: 283.98650 $[M]^{+}$; found: 283.98621.

HRMS spectrum of product **3k**



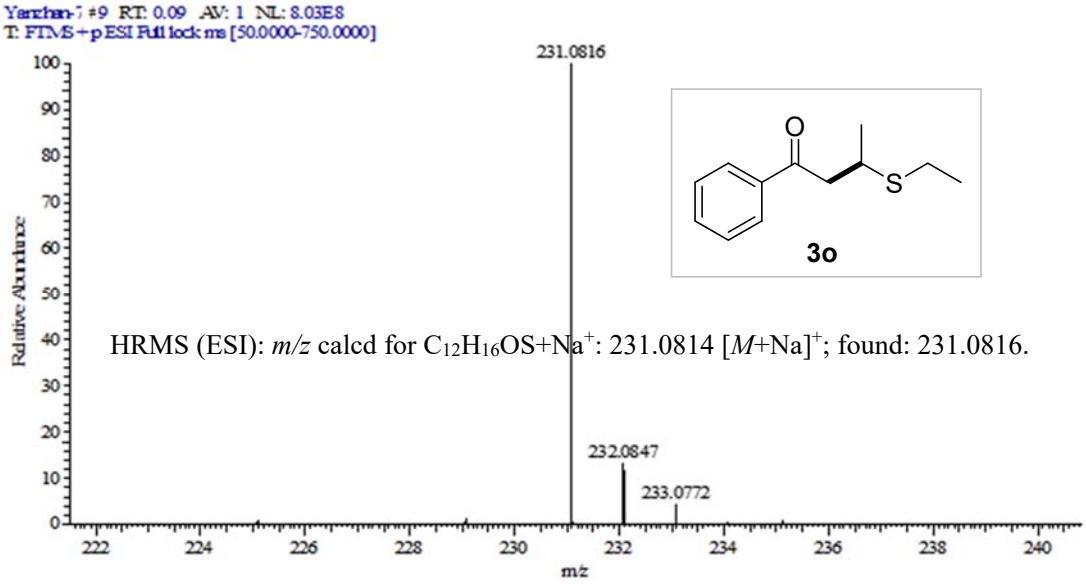
HRMS (EI): *m/z* calcd for $C_{12}H_{13}ClOS^{+}$: 240.03701 $[M]^{+}$; found: 240.03688.

HRMS spectrum of product **3l**



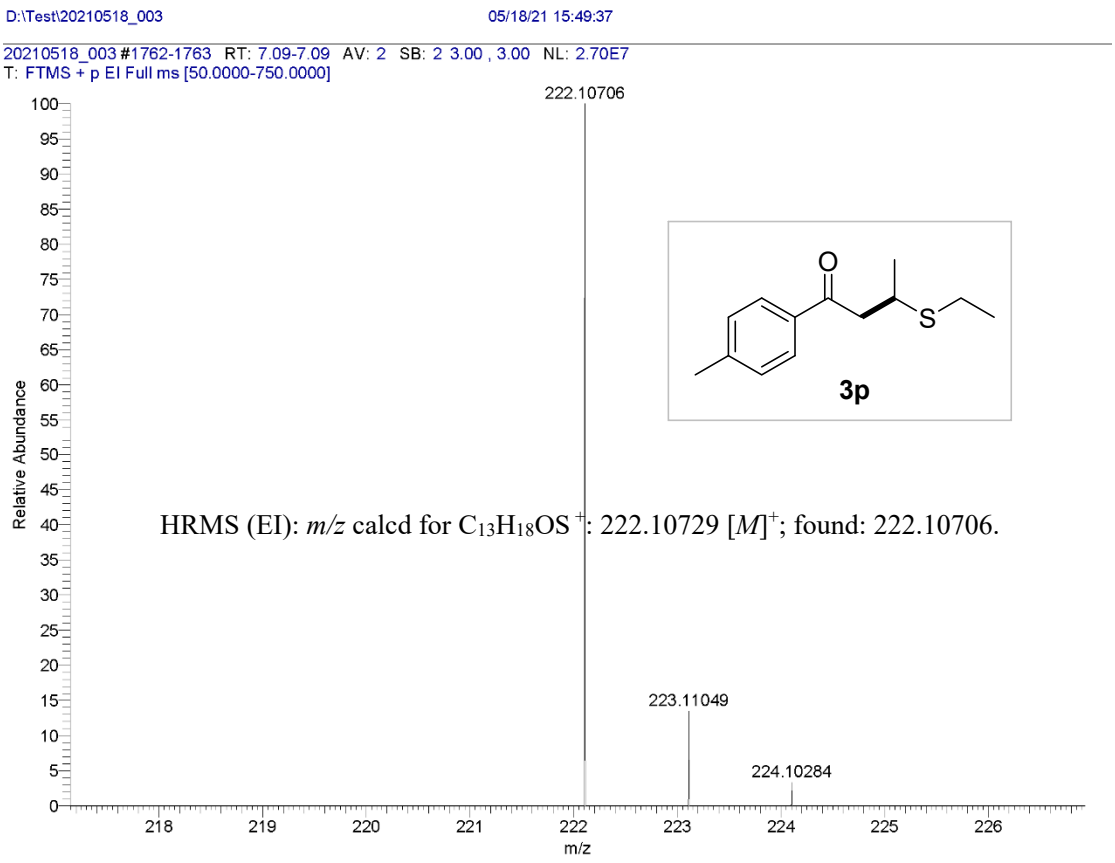
HRMS (EI): *m/z* calcd for $C_{12}H_{13}BrOS^{+}$: 283.98650 $[M]^{+}$; found: 283.98627.

HRMS spectrum of product **3m**



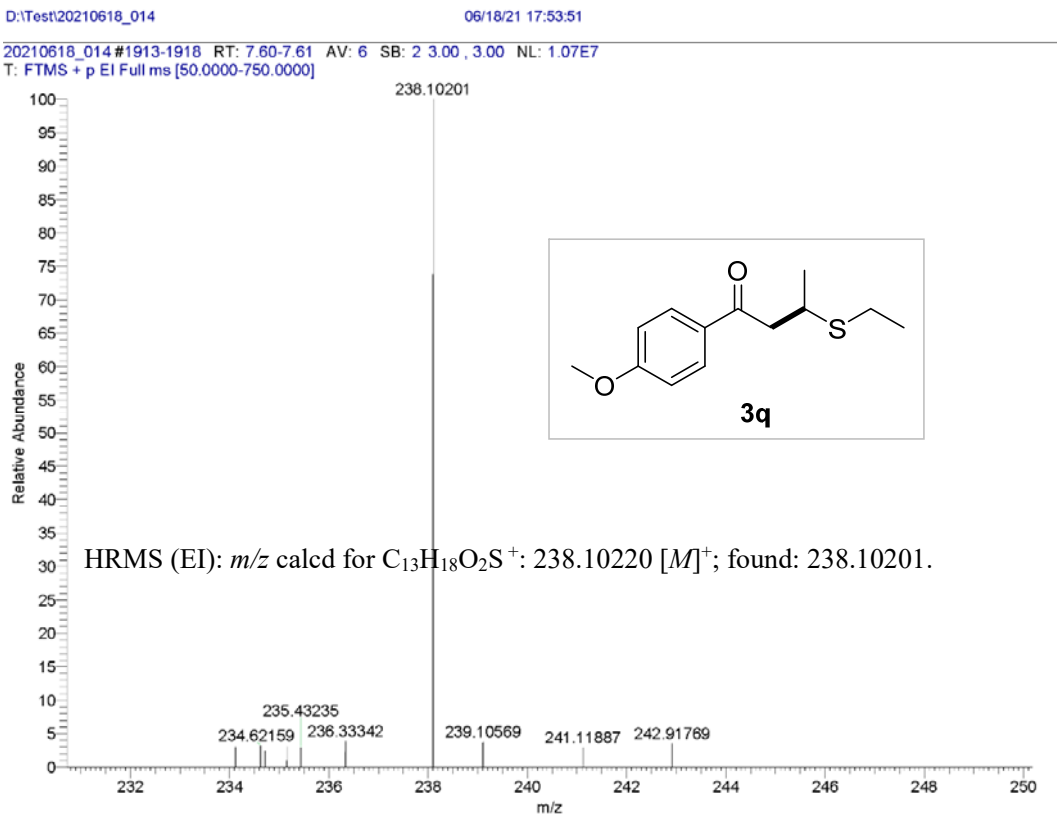
HRMS (ESI): *m/z* calcd for $C_{12}H_{16}OS+Na^+$: 231.0814 $[M+Na]^+$; found: 231.0816.

HRMS spectrum of product **3o**



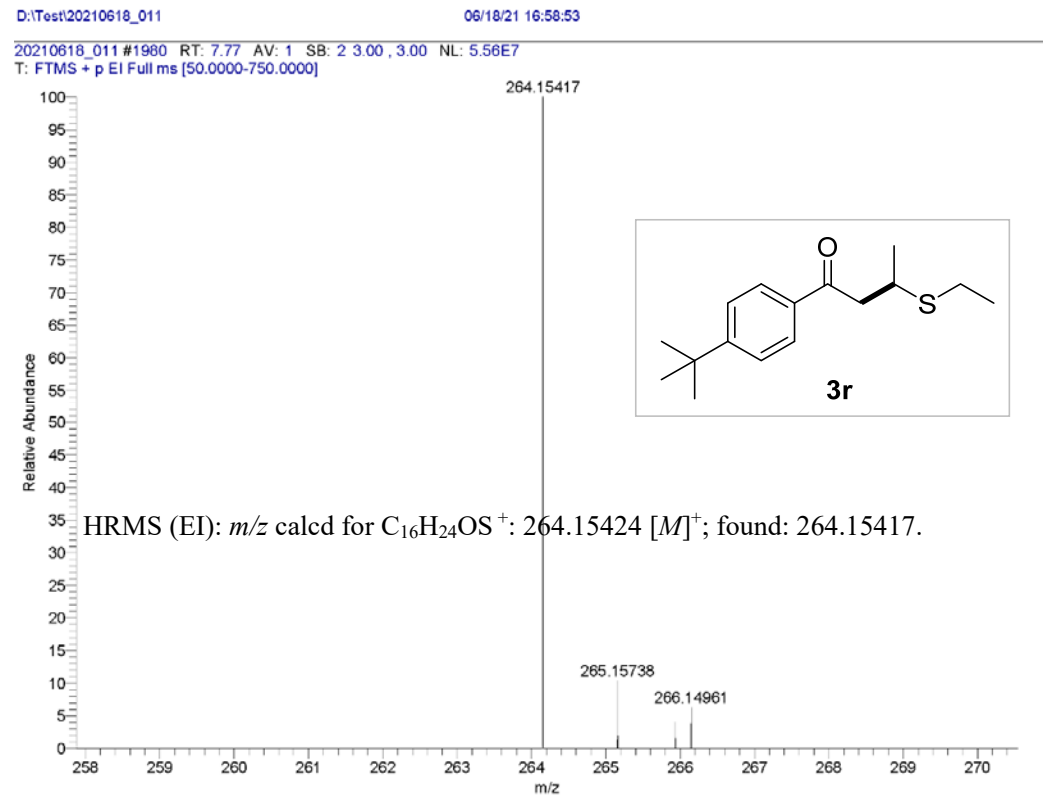
HRMS (EI): *m/z* calcd for $C_{13}H_{18}OS^+$: 222.10729 $[M]^+$; found: 222.10706.

HRMS spectrum of product **3p**



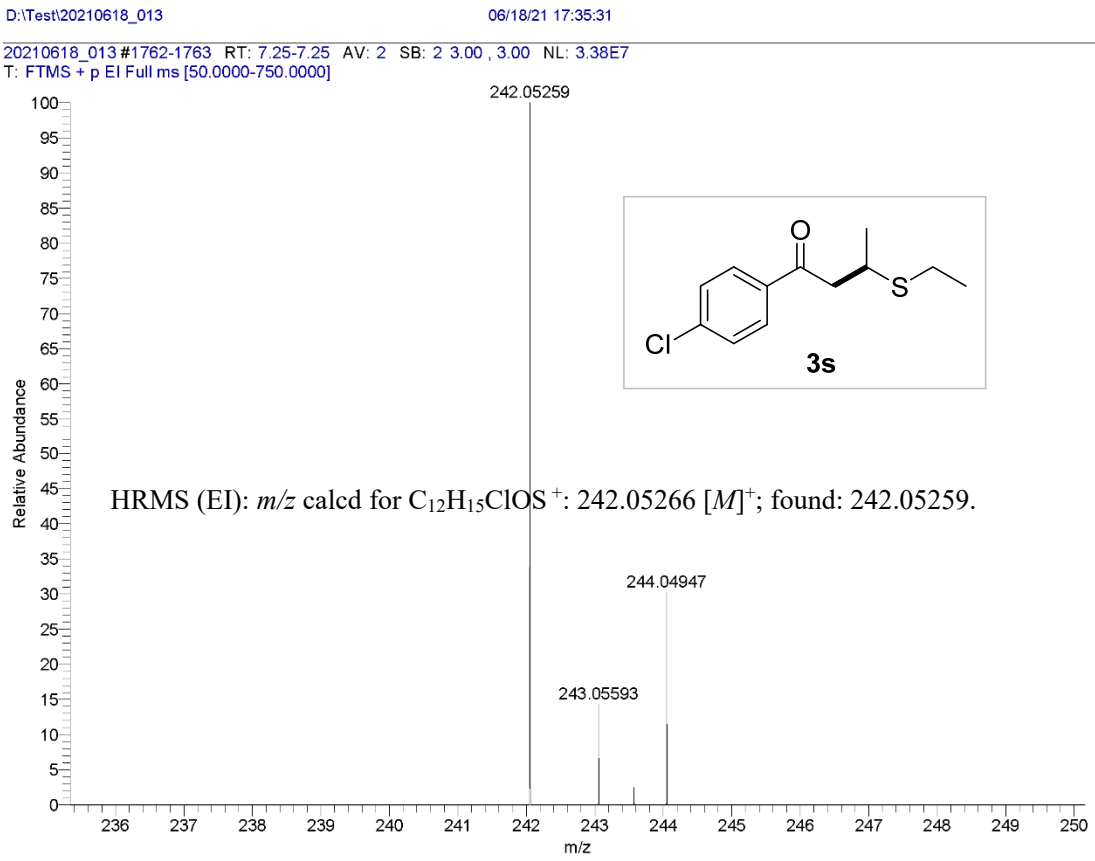
HRMS (EI): *m/z* calcd for $C_{13}H_{18}O_2S^+$: 238.10220 $[M]^+$; found: 238.10201.

HRMS spectrum of product **3q**



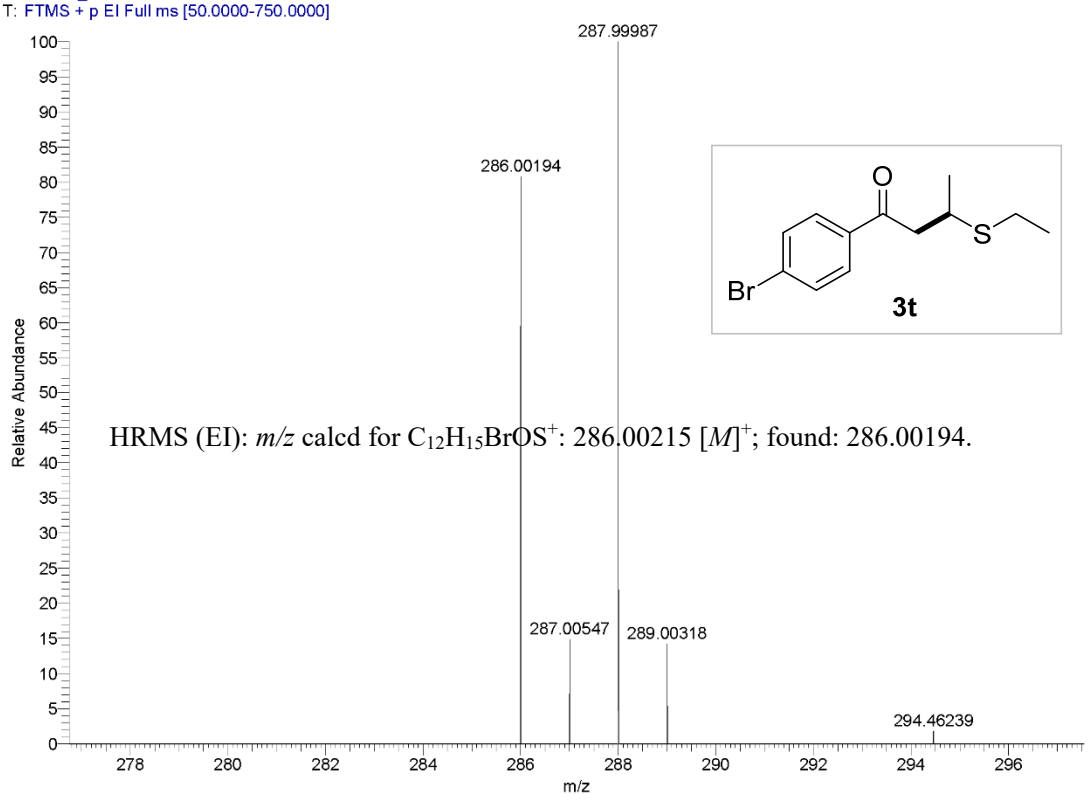
HRMS (EI): *m/z* calcd for $C_{16}H_{24}OS^+$: 264.15424 $[M]^+$; found: 264.15417.

HRMS spectrum of product **3r**



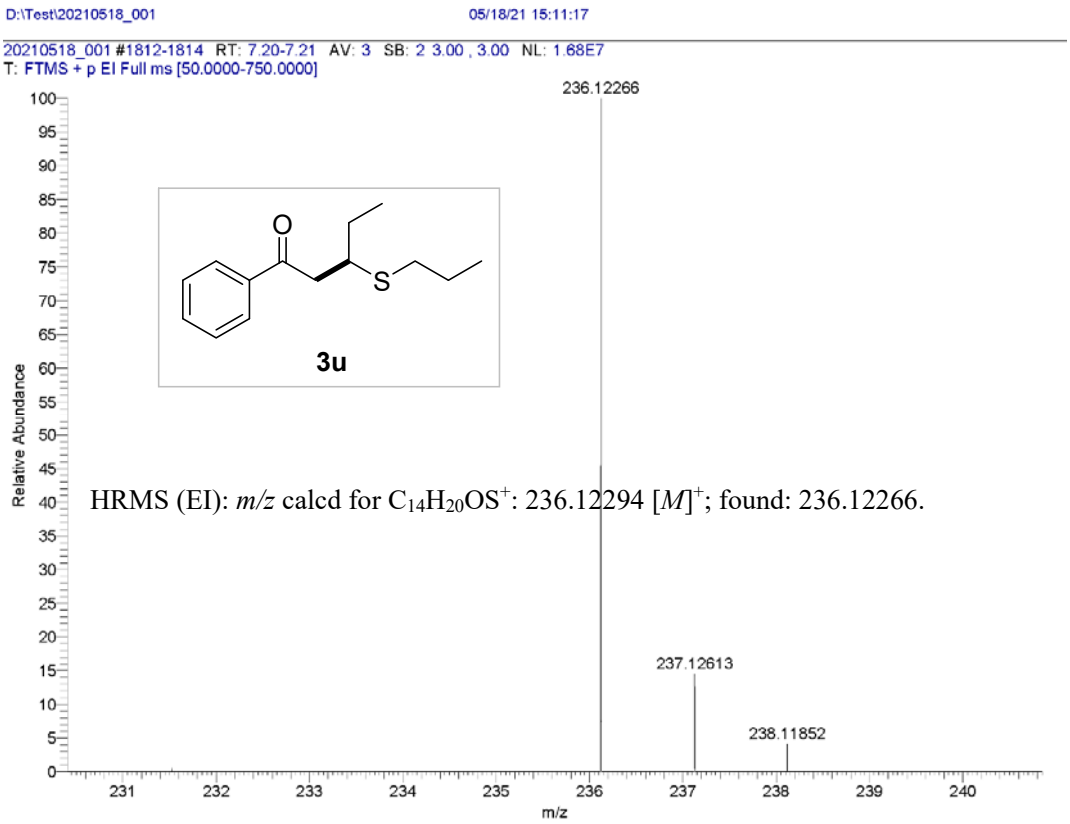
HRMS (EI): *m/z* calcd for $C_{12}H_{15}ClOS^{+}$: 242.05266 $[M]^{+}$; found: 242.05259.

HRMS spectrum of product **3s**



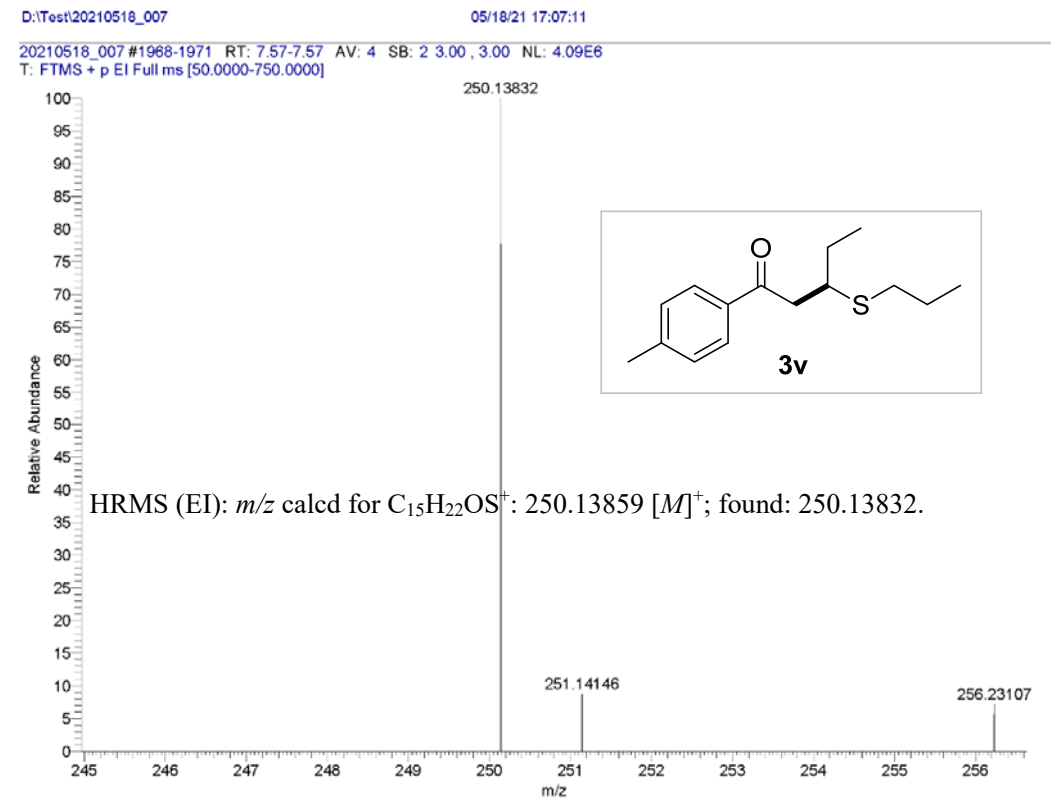
HRMS (EI): *m/z* calcd for $C_{12}H_{15}BrOS^{+}$: 286.00215 $[M]^{+}$; found: 286.00194.

HRMS spectrum of product **3t**



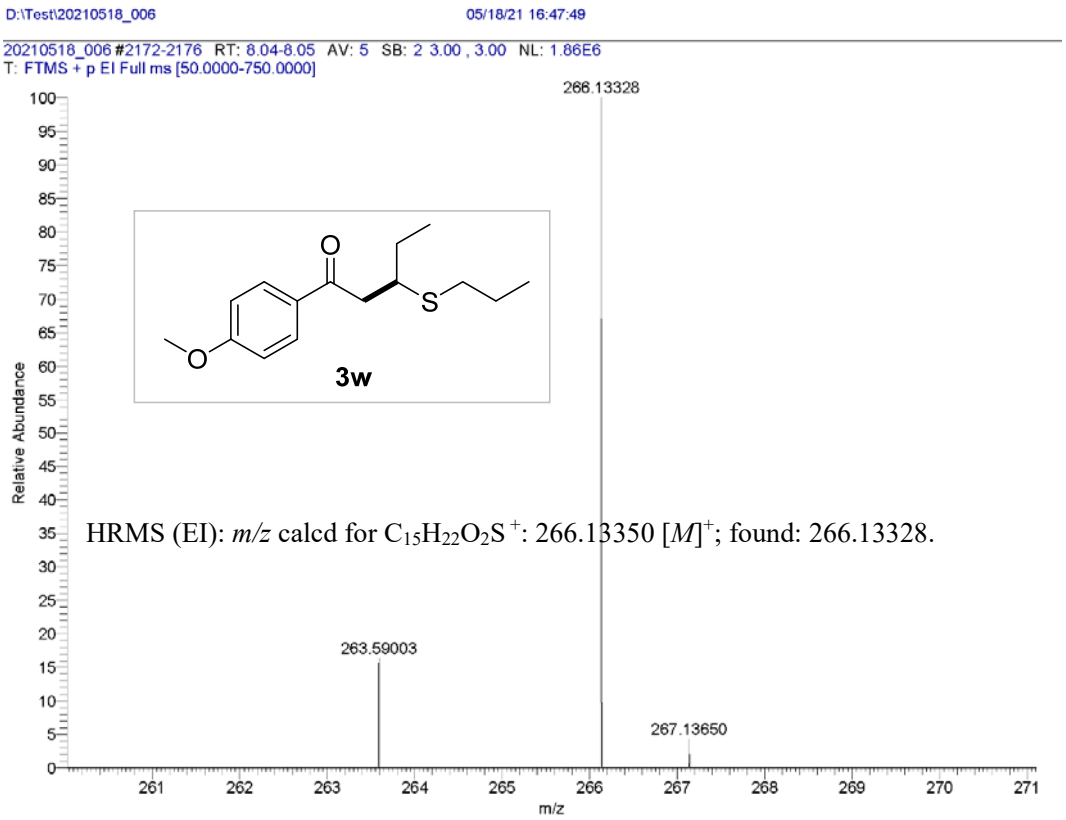
HRMS (EI): *m/z* calcd for $C_{14}H_{20}OS^{+}$: 236.12294 $[M]^{+}$; found: 236.12266.

HRMS spectrum of product **3u**



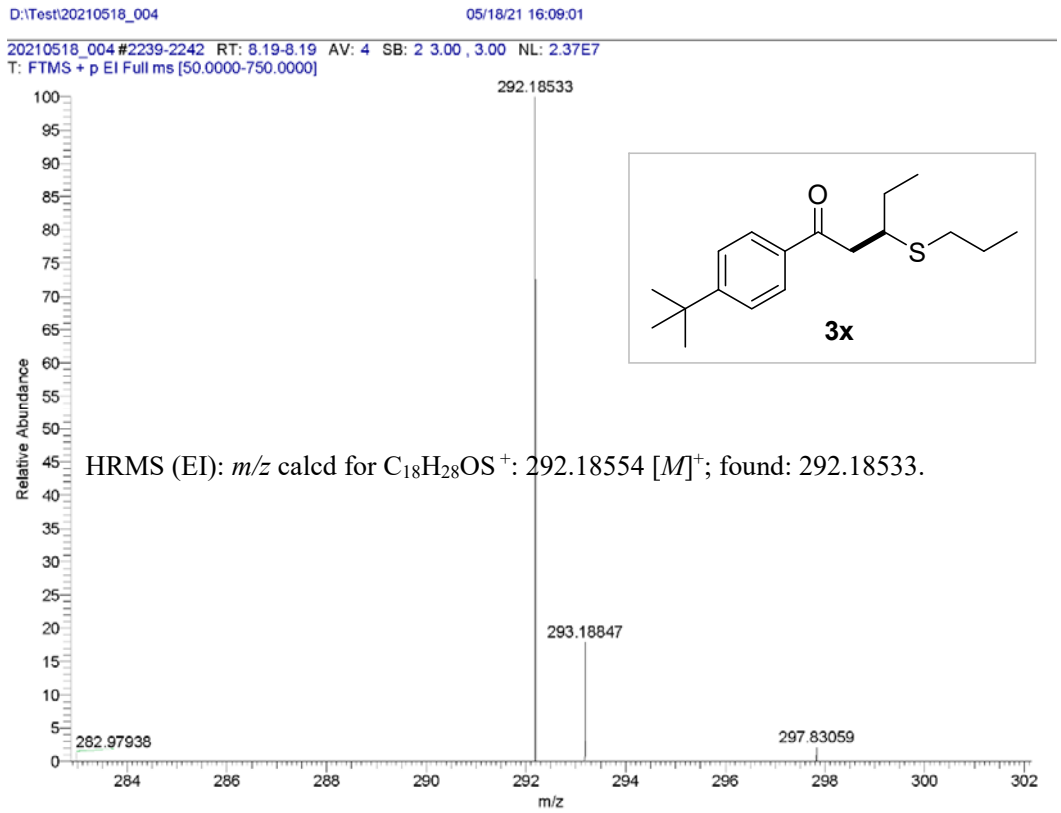
HRMS (EI): *m/z* calcd for $C_{15}H_{22}OS^{+}$: 250.13859 $[M]^{+}$; found: 250.13832.

HRMS spectrum of product **3v**



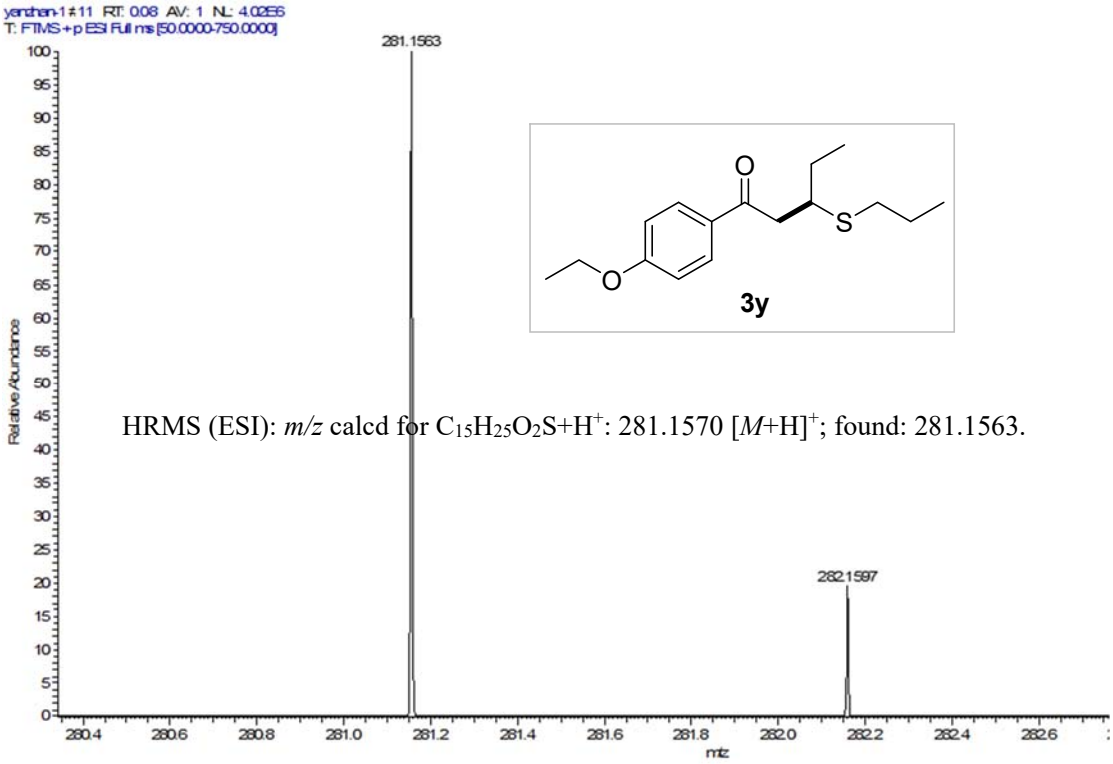
HRMS (EI): *m/z* calcd for $C_{15}H_{22}O_2S^+$: 266.13350 $[M]^+$; found: 266.13328.

HRMS spectrum of product **3w**



HRMS (EI): *m/z* calcd for $C_{18}H_{28}OS^+$: 292.18554 $[M]^+$; found: 292.18533.

HRMS spectrum of product **3x**



HRMS (ESI): *m/z* calcd for $C_{15}H_{25}O_2S+H^+$: 281.1570 $[M+H]^+$; found: 281.1563.

HRMS spectrum of product **3y**