Supporting Information for

Aqueous Hemin Catalyzed Sulfonium Ylide Formation and Subsequent [2, 3]-Sigmatropic Rearrangements

Xiaofei Xu,[a] Chang Li,[a] Zhihao Tao,[a] and Yuanjiang Pan*[a]

[a] Department of Chemistry, Zhejiang University, Hangzhou, 310028, Zhejiang, P. R. China

E-mail: panyuanjiang@zju.edu.cn.

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1. General Information and Materials

All reagents were purchased at the highest commercial quality and used without further purification. For chromatography, 100-200 mesh silica gel (Qingdao, China) was employed. Some ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX-400 instrument. The Other ^{1}H NMR and ^{13}C NMR spectra were recorded at 500MHz and 125 MHz with Bruker Avance DMX-500 instrument. High resolution mass spectra (HRMS) were recorded on a Shimadzu LC/MS IT-TOF. IR spectra were recorded on Bruker ALPHA FT-IR spectrometer.

2. Preparation of allylic thioether [1]

Allyl bromide/ benzyl bromide were added to an enthanolic solution of thiophenol/thiol (3 mmmol), K_2CO_3 (3.6 mmol) at r.t., and the resulting mixture was stirred for 12 h. The resulting mixture was concentrated and extracted with CH_2Cl_2. Then the extract was purified by column chromatography (hexane) to afford the desired sulfide.

3. Screening reaction conditions[a]

Table S1. Screening reaction conditions

entry	allyl phenyl sulfide (mmol)	EDA (mmol)	hemin (mol %)	β-CD (mol %)	Triton X-100 (mol %)	time (d)	yield (%)[b]
1	0.3	0.3	\	\	\	4	0
2	0.3	0.3	5	α-CD (20)	\	4	51
3	0.3	0.3	5	β-CD (20)	\	4	60
4	0.3	0.3	5	γ-CD (20)	\	4	53
5	0.3	0.45	1	20	\	4	65
6	0.3	0.45	2.5	20	\	4	77
7	0.3	0.45	5	20	\	4	71
8	0.3	0.45	10	20	\	4	78
9	0.3	0.45	20	20	\	4	77
10	0.3	0.3	2.5	20	\	4	33
11	0.3	0.45	2.5	20	\	4	77
12	0.3	0.6	2.5	20	\	4	83
13	0.3	0.9	2.5	20	\	4	86
14	0.3	1.2	2.5	20	\	4	84
15	0.3	1.5	2.5	20	\	4	84
16	0.3	0.9	2.5	20	\	1	79
17	0.3	0.9	2.5	20	\	2	85
18	0.3	0.9	2.5	20	\	3	83
19	0.3	0.9	2.5	20	\	4	83
20	0.3	0.9	2.5	20	\	5	84
21	0.3	0.6	2.5	20	10	2	90
22	0.3	0.6	2.5	20	5	2	92
23	0.3	0.6	2.5	20	2.5	2	93
24	0.3	0.6	2.5	20	1.5	2	85

[a]Reaction was carried out with 3 mL of H_2O at 40 ^oC for 48 h in a thermo shaker.

[b]Yield was determined by ^1H NMR analysis of the crude reaction mixture.

4. General procedures for [2,3]-sigmatropic rearrangement reactions

Sulfide (0.3 mmol) was added into 3 mL aqueous solution of 7.5 μmol hemin, 7.5 μmol Triton X-100 and 0.06 mmol β-CD, followed by adding 0.6 mmol diazo reagent in one portion. The reaction vial was then placed in a constant temperature shaker and left to shake at 200 rpm under 40 °C. After 2 days, the mixture was extracted twice with EtOAc (2×2 mL) in the reactor. The organic layer was further concentrated in vacuo, and then subjected to a short silica gel column, and eluted by petroleum ether to give the corresponding product.

5. Gram-scale reaction

Allyl phenyl sulfide (10 mmol) was added into 15mL aqueous solution of 0.25 mmol hemin, 0.25 mmol Triton X-100 and 2 mmol β-CD, followed by adding 20 mmol ethyl diazo acetate in one portion. The mixture was stirred for 20 h at 40 °C. After extracted twice with EtOAc (2×10 mL) in the reactor, the organic layer was further concentrated in vacuo. Finally the product was purified by silica gel chromatography with petroleum ether.

6. Calculation of E-factor

E-factor = waste(mg) / product(mg)

Calculation of E-factor has been performed according to the above equation, not accounting for the solvent of extraction, brine, drying agents and silica-gel column chromatography.

- *Simonneaux G, Galardon E, Paul-Roth C, et al.* ***J. Organomet. Chem.****, 2001, 617: 360-363.*

E-factor = [360mg (sulfide) + 57.1mg EDA + 741.81*0.005 mg (Ru (TPP)(CO)) + 1325*0.1 mg (DCM) – 9.5mg (product)] / 9.5mg = **57.2**

- *McMillen D W, Varga N, Reed B A, et al.* ***J. Org. Chem.****, 2000, 65(8): 2532-2536.*

E-factor = [315.5mg (sulfide) + 216.8mg (EDA) + 11mg (copper catalyst) + 11.8mg (ligand) + 1492*9mg ($CHCl_3$) – 264.9mg (product)] /264.9mg = **51.8**

- *Zhou C Y, Yu W Y, Chan P W H, et al.* ***J. Org. Chem.****, 2004, 69(21): 7072-7082.*

E-factor = [350mg (sulfide) + 57.1mg (EDA) +741.81*0.005 mg (Ru(TPP)(CO)) + 866*8mg (toluene) – 70.9mg (product)] / 70.9mg = **102.5**

- *Holzwarth M S, Alt I, Plietker B.* ***Angew. Chem. Int. Ed****., 2012, 51(22): 5351-5354*

E-factor = [150mg (sulfide) + 136.9mg (EDA)+ 10.3mg (TBAFe) + 1256mg (DCE) - 206mg (product)] / 206mg = **6.5**

- *Carter D S, Van Vranken D L.* ***Org. Lett.****, 2000, 2(9): 1303-1305.*

E-factor = [152mg (sulfide) + 229.3mg (EDA) + 18mg ($FeCl_2$dppe) + 1235.1*6.7mg (DCE) – 53.8mg (product)] /53.8mg = **160.2**

- *Tyagi V, Sreenilayam G, Bajaj P, et al.* ***Angew. Chem. Int. Ed.****, 2016, 55(43): 13562-13566.*

E-factor = [1.024mg/ μ L*14.8 μ L (sulfide) + 1.085 mg/ μ L*24 μ L (EDA) + 174.11*10/1000mg ($Na_2S_2O_4$) + 789*(250+250) /1000 mg (EtOH) + 10*394/1000000000*16700 mg (Mb) -19.5mg (product)] / 19.5mg = **21.4**

Not accounting for the potassium phosphate salt.

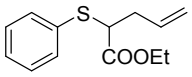
- **Our work:**

E-factor = [45.1mg (sulfide) + 68.5mg (EDA) + 68.1mg (β-CD) + 4.9mg (hemin) + 2.4mg (Triton X-100) – 70mg (product)] / 70mg = **1.7**

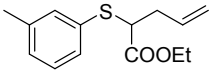
If the solvent and silica gel in the post-treatment stage were taken into consideration, assuming that 90% of the solvent petroleum ether could be recovered and re-used, the E-factor was calculated as following:

Complete E-factor = [45.1mg (sulfide) + 68.5mg (EDA) + 68.1mg (β -CD) + 4.9mg (hemin) + 2.4mg (Triton X-100) + 902*2mg (EtOAc) + 35mg (silica gel) + 650*45*0.1mg (petroleum ether) – 70mg (product)] / 70mg = **69.8**

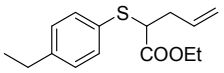
7. Experimental Characterization of Products

Ethyl-2-phenylthio-4-pentenoate (3a)[2]: 

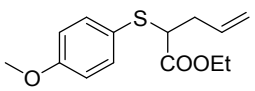
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.33 – 7.28 (m, 3H), 5.86 – 5.76 (m, 1H), 5.16 – 5.08 (m, 2H), 4.16 – 4.05 (m, 2H), 3.70 (dd, J = 8.7, 6.4 Hz, 1H), 2.67 – 2.48 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 134.0, 133.2, 129.0, 128.1, 118.1, 61.2, 50.3, 35.9, 14.2. IR (neat, cm^{-1}) 2982, 1733, 1439, 1368, 1232, 1155, 1025, 921, 749, 692. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{13}H_{17}O_2S)^+$: 237.0944, found: 237.0941.

Ethyl 2-((4-methyphenyl)thio)-4-pentenoate (3b): 

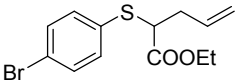
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 5.86 – 5.76 (m, 1H), 5.15 – 5.08 (m, 2H), 4.17 – 4.06 (m, 2H), 3.69 (dd, J = 8.7, 6.3 Hz, 1H), 2.64 – 2.49 (m, 2H), 2.33 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 138.8, 134.0, 133.7, 133.0, 130.1, 129.0, 128.9, 118.1, 61.2, 50.4, 36.0, 21.4, 14.2. IR (neat, cm^{-1}) 2981, 1733, 1592, 1475, 1368, 1232, 1154, 1039, 921, 780, 692. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{14}H_{19}O_2S)^+$: 251.1100, found: 251.1098.

Ethyl 2-((4-ethyphenyl)thio)-4-pentenoate (3c): 

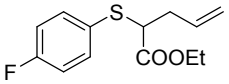
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.14 (d, J = 8.2 Hz, 2H), 5.86 – 5.75 (m, 1H), 5.15 – 5.07 (m, 2H), 4.16 – 4.05 (m, 2H), 3.63 (dd, J = 8.8, 6.3 Hz, 1H), 2.66 – 2.45 (m, 4H), 1.22 (t, J = 7.6 Hz, 1H), 1.16 (t, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 144.8, 134.1, 134.0, 129.5, 128.6, 118.0, 61.14, 50.6, 35.9, 28.6, 15.5, 14.2. IR (neat, cm^{-1}) 2967, 1734, 1494, 1368, 1232, 1155, 1017, 921, 829, 634, 532. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{15}H_{20}O_2SNa)^+$: 287.1076, found: 287.1073.

Ethyl 2-((4-methoxyphenyl)thio)-4-pentenoate (3d)[3]: 

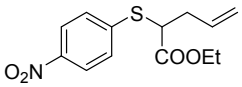
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 6.82 (d, J = 8.1 Hz, 2H), 5.81 – 5.73 (m, 1H), 5.08 (t, J = 13.5 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 3.52 (dd, J = 8.3, 6.8 Hz, 1H), 2.55 – 2.44 (m, 2H), 1.18 – 1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 160.3, 136.6, 134.1, 122.8, 117.9, 114.5, 61.0, 55.3, 50.9, 35.6, 14.2. IR (neat, cm^{-1}) 2981, 1731, 1593, 1494, 1368, 1287, 1248, 1173, 1032, 922, 830, 642, 527. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{14}H_{18}O_3SNa)^+$: 289.0869, found: 289.0866.

Ethyl 2-((4-bromophenyl)thio)-4-pentenoate (3e): 

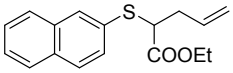
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 40.9, 8.4 Hz, 4H), 5.82 – 5.72 (m, 1H), 5.14 – 5.07 (m, 2H), 4.14 – 4.06 (m, 2H), 3.65 (dd, J = 8.6, 6.5 Hz, 1H), 2.63 – 2.44 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 134.6, 133.7, 132.3, 132.1, 122.4, 118.3, 61.3, 50.1, 35.7, 14.2. IR (neat, cm^{-1}) 2981, 1733, 1474, 1368, 1259, 1156, 1092, 1069, 1009, 922, 817, 730, 483. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{13}H_{15}B_rO_2SNa)^+$: 336.9868, found: 336.9867.

Ethyl 2-((4-fluorophenyl)thio)-4-pentenoate (3f): 

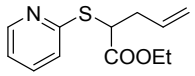
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 5.81 – 5.72 (m, 1H), 5.10 (t, J = 12.4 Hz, 2H), 4.09 (q, J = 7.2 Hz, 2H), 3.59 (dd, J = 8.6, 6.5 Hz, 1H), 2.61 – 2.42 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 164.3, 161.8, 136.3, 136.3, 133.8, 127.9, 127.8, 118.2, 116.2, 116.0, 61.2, 50.7, 35.7, 14.2. IR (neat, cm^{-1}) 2983, 1732, 1590, 1491, 1369, 1231, 1156, 922, 834, 635, 518. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{13}H_{16}FO_2S)^+$: 255.0850, found: 255.0847.

Ethyl 2-((4-nitrophenyl)thio)-4-pentenoate (3g): 

Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.11 (m, 2H), 7.50 – 7.47 (m, 2H), 5.84 – 5.74 (m, 1H), 5.19 – 5.12 (m, 2H), 4.20 – 4.12 (m, 2H), 3.92 (dd, *J* = 8.3, 6.7 Hz, 1H), 2.74 – 2.54 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 146.1, 144.5, 133.0, 129.1, 124.0, 119.0, 61.9, 48.6, 35.7, 14.2. IR (neat, cm^{-1}) 2983, 1733, 1579, 1516, 1479, 1342, 1156, 1093, 853, 743. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{13}H_{15}NO_4SNa)^+$: 304.0614, found: 304.0612.

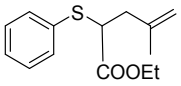
Ethyl-2-((2-naphthyl)thio)-4-pentenoate (3h): 

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 0.8 Hz, 1H), 7.83 – 7.77 (m, 3H), 7.56 – 7.47 (m, 3H), 5.92 –5.81 (m, 1H), 5.20 – 5.13 (m, 2H), 4.19 – 4.07 (m, 2H), 3.85 (dd, *J* = 8.6, 6.4 Hz, 1H), 2.74 – 2.56 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 133.9, 133.6, 132.7, 132.0, 130.6, 130.0, 128.6, 127.8, 127.6, 126.6, 126.6, 118.2, 61.3, 50.2, 36.0, 14.1. IR (neat, cm^{-1}) 2981, 1732, 1368, 1336, 1233, 1155, 1037, 922, 857, 815, 746, 476. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{17}H_{19}O_2S)^+$: 287.1100, found: 287.1096.

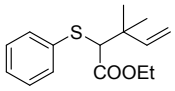
Ethyl-2-((2-pyridyl)thio)-4-pentenoate (3i): 

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.37 (m, 1H), 7.48 – 7.44 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.98 – 6.95 (m, 1H), 5.88 – 5.78 (m, 1H), 5.16 – 5.06 (m, 2H), 4.63 (t, *J* = 7.2 Hz, 1H), 4.21 – 4.10 (m, 2H), 2.76 – 2.61 (m, 2H), 1.22 – 1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 157.2, 149.4, 136.2, 134.0, 122.5, 120.0, 118.1, 61.4, 46.3, 36.2, 14.2. IR (neat, cm^{-1})

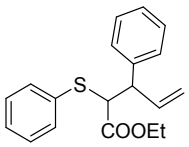
2981, 1734, 1579, 1558, 1454, 1416, 1368, 1232, 1156, 1123, 1041, 921, 760, 725. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{12}H_{16}NO_2S)^+$: 238.0896, found: 238.0894.

Ethyl 4-methyl-2-(phenylthio)pent-4-enoate (3j)[2]: 

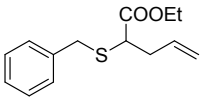
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.33 – 7.27 (m, 3H), 4.83 (s, 1H), 4.77 (s, 1H), 4.08 (q, J = 7.1 Hz, 2H), 3.85 (dd, J = 9.6, 6.1 Hz, 1H), 2.66 – 2.43 (m, 2H), 1.74 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 141.5, 133.3, 133.1, 129.0, 128.1, 113.3, 61.2, 49.1, 39.8, 22.4, 14.1. IR (neat, cm^{-1}) 2980, 1734, 1440, 1369, 1262, 1153, 1025, 897, 749, 692. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{14}H_{19}O_2S)^+$: 251.1100, found: 251.1094.

Ethyl 3,3-Dimethyl-2-(phenylthio)pent-4-enoate (3k)[2]: 

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.29 – 7.20 (m, 3H), 6.03 (dd, J = 17.4, 10.7 Hz, 1H), 5.12 – 5.07 (m, 2H), 4.15 – 4.02 (m, 2H), 3.59 (s, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 144.1, 135.3, 132.0, 129.0, 127.5, 113.3, 62.2, 60.9, 40.1, 25.4, 24.4, 14.2. IR (neat, cm^{-1}) 2972, 1737, 1580, 1440, 1366, 1304, 1262, 1147, 1028, 918, 741, 691. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{15}H_{21}O_2S)^+$: 265.1257, found: 265.1255.

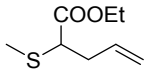
Ethyl 2-phenylsulfanyl-3-phenylpent-4-enoate (3l)[2]: 

(mixture of anti- and syn-isomers): yellowish oil;^{1}H NMR (400 MHz, $CDCl_3$) major isomer δ 7.51 – 7.48 (m, 1H), 7.34 – 7.17 (m,9H), 6.17 – 6.09 (m, 1H), 5.19 (dd, J = 19.8, 8.8 Hz, 2H), 4.07 (q, J = 7.1 Hz, 1H), 4.00 (d, J = 11.2 Hz,1H), 3.82 – 3.76 (m, 2H), 0.85 (t, J = 7.1 Hz, 3H), minor isomer δ 7.51 – 7.48 (m, 1H), 7.34 – 7.17 (m, 9H), 6.05 – 5.96 (m, 1H), 5.09 (dd, J = 10.3, 5.6 Hz, 2H), 4.07 (q, J = 7.1 Hz, 1H), 4.00 (d, J = 11.2 Hz, 1H), 3.80 – 3.74 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer δ 171.0, 140.9, 138.0, 133.6, 133.2, 129.0, 128.7, 128.1, 128.1, 127.2, 117.8, 60.9, 56.1, 51.8, 13.8, minor isomer δ 171.4, 139.9, 138.1, 133.6, 133.3, 128.9, 128.7, 128.4, 128.0, 127.3, 117.1, 61.2, 56.5, 52.1, 14.1. IR (neat, cm^{-1}) 2981, 1733, 1583, 1440, 1368, 1263, 1152, 1026, 922, 750, 700. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{19}H_{21}O_2S)^+$: 313.1257, found: 313.1256.

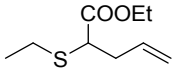
Ethyl-2-(benzylthio)-4-pentenoate (3m): 

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.27 – 7.23 (m, 1H), 5.77 – 5.66 (m, 1H), 5.09 – 5.03 (m, 2H), 4.24 – 4.12 (m, 2H), 3.83 (q, J = 13.3 Hz, 2H), 3.24 (dd, J = 8.7, 6.5

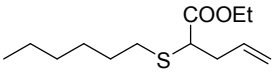
Hz, 1H), 2.63 – 2.35 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 137.5, 134.1, 129.1, 129.1, 128.6, 128.5, 127.3, 117.7, 61.2, 45.6, 35.9, 35.4, 14.3. IR (neat, cm^{-1}) 2981, 1733, 1454, 1261, 1155, 1029, 920, 702. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{14}H_{19}O_2S)^+$: 251.1100, found: 251.1094.

Ethyl 2-methylthio-4-pentenoate (3n)[3]: 

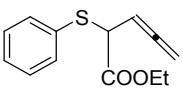
Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.69 (m, 1H), 5.10 – 5.02 (m, 2H), 4.20 – 4.09 (m, 2H), 3.19 (dd, *J* = 8.6, 6.7 Hz, 1H), 2.62 – 2.34 (m, 2H), 2.10 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 134.2, 117.6, 61.0, 46.8, 34.9, 14.2, 13.8. IR (neat, cm^{-1}) 2982, 1729, 1438, 1369, 1232, 1158, 920. HRMS (ESI) calcd. for $(M+H)^+$ $(C_8H_{15}O_2S)^+$: 175.0787, found: 175.0785.

Ethyl 2-ethylthio-4-pentenoate (3o)[4]: 

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.70 (m, 1H), 5.10 – 5.02 (m, 2H), 4.21 – 4.09 (m, 2H), 3.29 – 3.26 (m, 1H), 2.67 – 2.35 (m, 4H), 1.26 – 1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 134.3, 117.6, 61.1, 46.0, 35.7, 25.5, 14.5, 14.3. IR (neat, cm^{-1}) 2980, 1731, 1446, 1368, 1259, 1155, 1035, 920. HRMS (ESI) calcd. for $(M+H)^+$ $(C_9H_{17}O_2S)^+$: 189.0944, found: 189.0940.

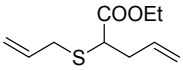
Ethyl 2-(hexylthio)-4-pentenoate (3p): 

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.74 (m, 1H), 5.14 – 5.06 (m, 2H), 4.25 – 4.13 (m, 2H), 3.29 (dd, *J* = 8.8, 6.5 Hz, 1H), 2.67 – 2.39 (m, 4H), 1.63 – 1.22 (m, 11H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 134.5, 117.7, 61.2, 46.4, 35.8, 31.5, 29.4, 28.7, 22.7, 14.4, 14.2. IR (neat, cm^{-1}) 2929, 1731, 1465, 1368, 1259, 1154, 919. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{13}H_{24}O_2SNa)^+$: 267.1389, found: 267.1386.

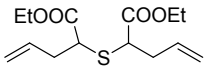
Ethyl 2-(phenylthio) pent-3,4-dienoate (3r): 

Colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.48 – 7.46 (m, 2H), 7.31 – 7.29 (m, 3H), 5.39 – 5.34 (m, 1H), 4.84 – 4.71 (m, 2H), 4.32 – 4.29 (m, 1H), 4.13 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 209.1, 169.9, 133.9, 132.6, 128.9, 128.4, 87.3, 77.5, 61.7,

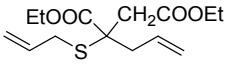
50.9, 14.1. IR (neat, cm^{-1}) 2983, 1954, 1734, 1439, 1368, 1277, 1155, 1027, 855, 747, 692. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{13}H_{14}O_2SNa)^+$: 257.0607, found: 257.0604.

Ethyl 2-allylthio-4-pentenoate (3s-1)[2]: 

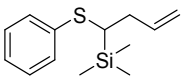
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 5.81 – 5.72 (m, 2H), 5.17 – 5.04 (m, 4H), 4.23 – 4.12 (m, 2H), 3.29 – 3.17 (m, 3H), 2.62 – 2.56 (m, 1H), 2.43 – 2.38 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 134.3, 133.5, 118.1, 117.8, 61.2, 45.1, 35.6, 34.7, 14.3. IR (neat, cm^{-1}) 2981, 1733, 1583, 1440, 1368, 1263, 1152, 1026, 922, 750, 700. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{10}H_{17}O_2S)^+$: 201.0944, found: 201.0941.

Ethyl 2-((allylethoxyacetyl)thio)-4-pentenoate (3s-2): 

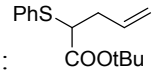
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 5.80 –5.72 (m, 2H), 5.13 – 5.06 (m, 4H), 4.24 – 4.15 (m, 4H), 3.57 –3.46 (m, 2H), 2.65 – 2.55 (m, 2H), 2.49 –2.39 (m, 2H), 1.29 –1.26 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 171.9, 133.9, 118.2, 118.1, 61.5, 61.4, 46.5, 46.4, 36.5, 35.7, 14.3, 14.3. IR (neat, cm^{-1}) 2982, 1735, 1642, 1439, 1369, 1260, 1158, 1037, 922. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{14}H_{22}O_4SNa)^+$: 309.1131, found: 309.1130.

Ethyl 2-allylthio-2-ethoxyformyl-4-pentenoate (3s-3): 

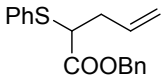
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 5.82 – 5.74 (m, 2H), 5.16 – 5.13 (dd, J = 13.6, 1.6 Hz, 4H), 4.22 – 4.14 (m, 4H), 3.38 (s, 2H), 2.85 – 2.51 (m, 4H), 1.28 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 170.0, 132.4, 119.5, 61.7, 61.6, 54.0, 37.9, 31.9, 14.3, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{14}H_{23}O_4S)^+$: 287.1312, found: 287.1309.

(1-Phenylsulfanylbut-3-enyl)trimethylsilane (3t): 

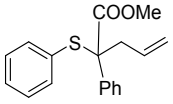
Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 5.95– 5.85 (m, 1H), 5.07 – 4.99 (m, 2H), 2.59 (t, *J* = 5.9 Hz, 1H), 2.54 – 2.38 (m, 2H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.2, 129.7, 128.9, 125.9, 116.3, 35.9, 33.7, -1.8. IR (neat, cm^{-1}) 2956, 1583, 1479, 1438, 1249, 912, 839, 739, 690. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{13}H_{21}SSi)^+$: 237.1128, found: 237.1122.

2-(Phenylthio)-4-pentenoic acid tert-butyl ester (3u): 

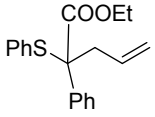
Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.32 – 7.24 (m, 3H), 5.87 – 5.77 (m, 1H), 5.16 – 5.08 (m, 2H), 3.63 (dd, *J* = 8.8, 6.2 Hz, 1H), 2.63 – 2.44 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 134.2, 133.7, 132.9, 128.9, 127.8, 117.9, 81.6, 51.0, 36.0, 28.0. IR (neat, cm^{-1}) 2979, 1729, 1439, 1368, 1341, 1258, 1145, 920, 846, 747, 691. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{15}H_{20}O_2SNa)^+$: 287.1076, found: 287.1073.

2-(Phenylthio)-4-pentenoic acid benzyl ester (3v): 

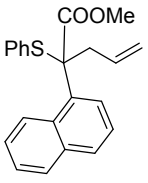
Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 7.27 – 7.22 (m, 5H), 5.84 – 5.74 (m, 1H), 5.13 – 5.05 (m, 4H), 3.74 (dd, *J* = 8.6, 6.5 Hz, 1H), 2.67 – 2.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.65, 135.56, 133.86, 133.35, 132.95, 129.08, 128.59, 128.44, 128.38, 128.23, 118.27, 67.00, 50.34, 35.87. IR (neat, cm^{-1}) 3064, 1734, 1455, 1438, 1335, 1264, 1229, 1151, 992, 921, 749, 694. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{18}H_{18}O_2SNa)^+$: 321.0920, found: 321.0915.

2-(Phenylthio)-2-phenyl-4-pentenoic acid methyl ester (3w)[4]: 

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 6H), 7.21 – 7.15 (m, 4H), 5.96 – 5.86 (m, 1H), 5.13 – 5.04 (m, 2H), 3.70 (s, 3H), 2.93 – 2.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 139.9, 137.0, 133.3, 130.8, 129.4, 128.6, 128.2, 127.7, 127.6, 119.0, 64.6, 52.8, 40.8. IR (KBr, cm^{-1}) 3071, 2951, 1721, 1436, 1316, 1261, 1222, 1120, 1013, 933, 753, 696, 513. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{18}H_{19}O_2S)^+$: 299.1100, found: 299.1092.

2-(Phenylthio)-2-phenyl-4-pentenoic acid ethyl ester (3x): 

Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 6H), 7.19 – 7.13 (m, 4H), 5.98 – 5.88 (m, 1H), 5.13 – 5.05 (m, 2H), 4.25 – 4.10 (m, 2H), 2.94 – 2.80 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 140.1, 136.9, 133.3, 131.0, 129.3, 128.5, 128.1, 127.6, 127.5, 118.9, 64.4, 61.9, 40.6, 14.1. IR (neat, cm^{-1}) 3052, 2980, 1727, 1473, 1440, 1255, 1212, 1122, 1025, 919, 750, 695. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{19}H_{20}O_2SNa)^+$: 335.1076, found: 335.1082.

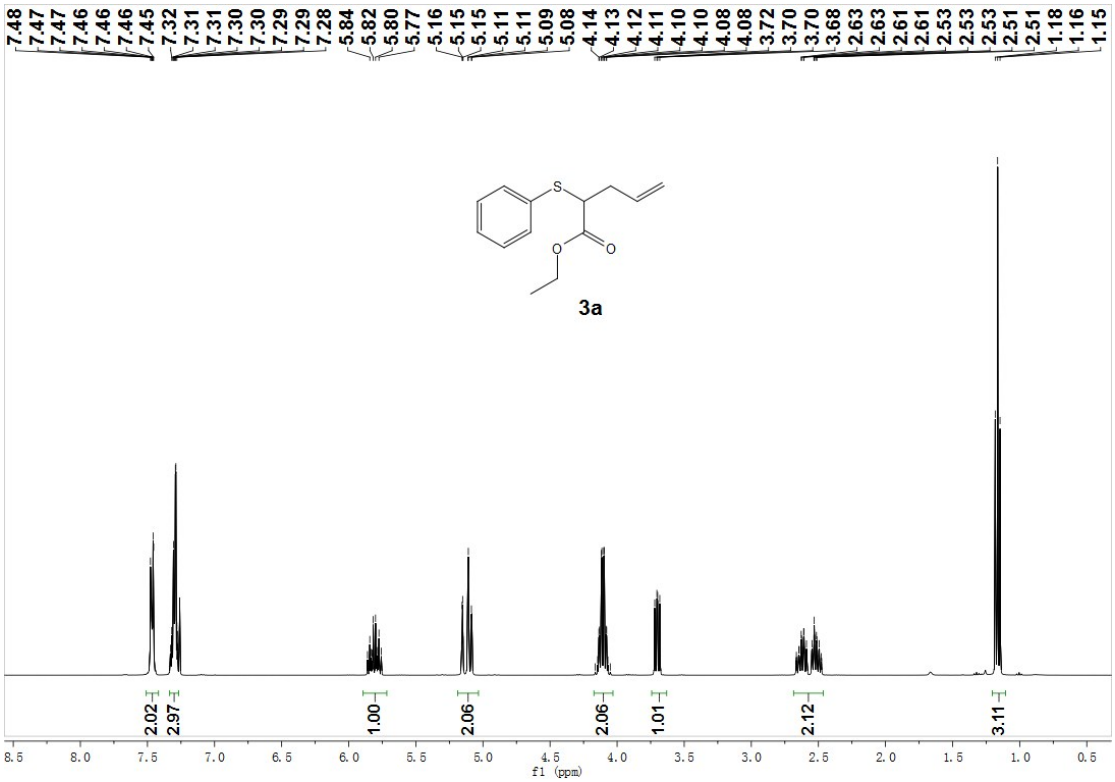
2-Naphthyl-2-(phenylthio)- 4-pentenoic acid methyl ester (3y): 

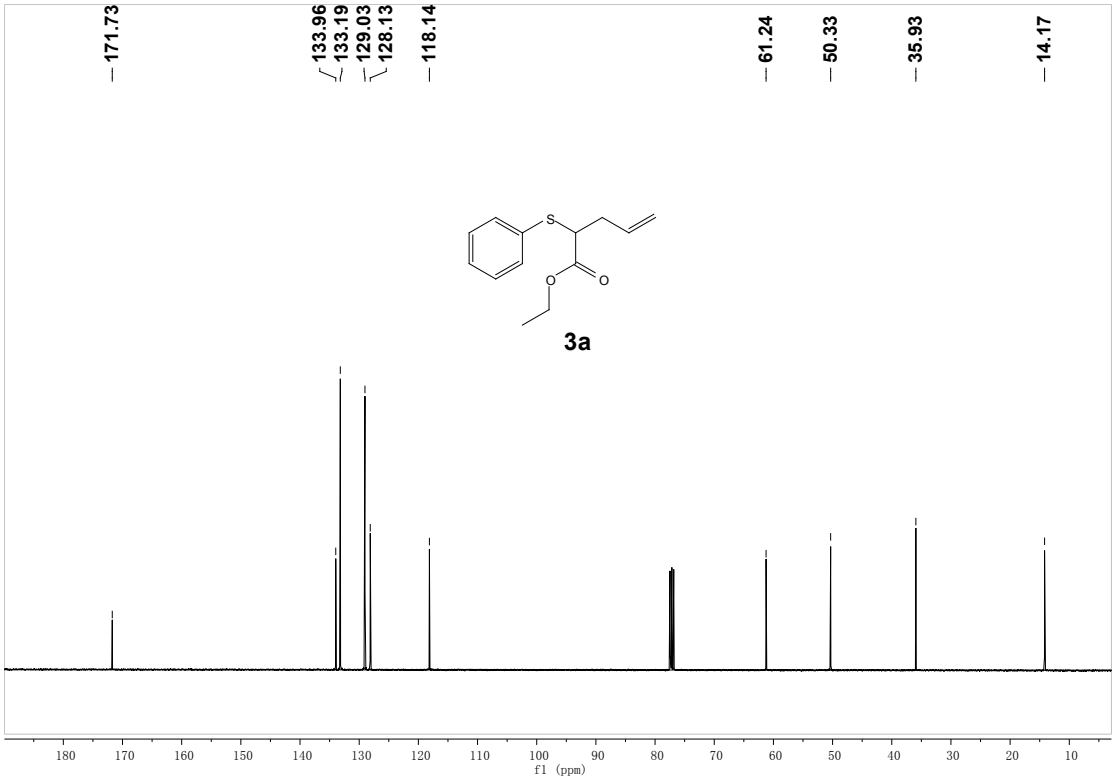
Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.5 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.77 – 7.75 (m, 1H), 7.54 – 7.48 (m, 2H), 7.22 (t, J = 8.0 Hz, 3H), 7.06 (t, J = 7.7 Hz, 2H), 6.91 (d, J = 7.4 Hz, 2H), 6.19 – 6.08 (m, 1H), 5.14 (dd, J = 17.0, 13.8 Hz, 2H), 3.56 (s, 3H), 3.10 – 2.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 137.3, 135.0, 134.3, 133.2, 131.1, 130.6, 129.4, 129.4, 129.2, 128.3, 126.2, 125.5, 125.5, 124.6, 124.3, 118.8, 64.0, 52.7, 41.4. IR (neat, cm^{-1}) 3059, 2949, 1732, 1437, 1237, 1215, 1123, 1042, 993, 920, 794, 779, 753, 694, 432. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{22}H_{20}O_2SNa)^+$: 371.1076, found: 371.1084.

8. References

1. Screttas, C. G.; Heropoulos, G. A.; Micha-Screttas, M.; Steele, B. R., *Tetrahedron Lett.,* **2005,** *46* (25), 4357-4360.
2. Holzwarth, M. S.; Alt, I.; Plietker, B., *Angew. Chem. Int. Ed.,* **2012,** *51* (22), 5351-5354.
3. McMillen, D. W.; Varga, N.; Reed, B. A.; King, C., *J. Org. Chem.,* **2000,** *65* (8), 2532-2536.
4. Zhou, C.-Y.; Yu, W.-Y.; Chan, P. W. H.; Che, C.-M., *J. Org. Chem.,* **2004,** *69* (21), 7072-7082.

9. Copies for ^{1}H NMR and ^{1}C NMR

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O
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60
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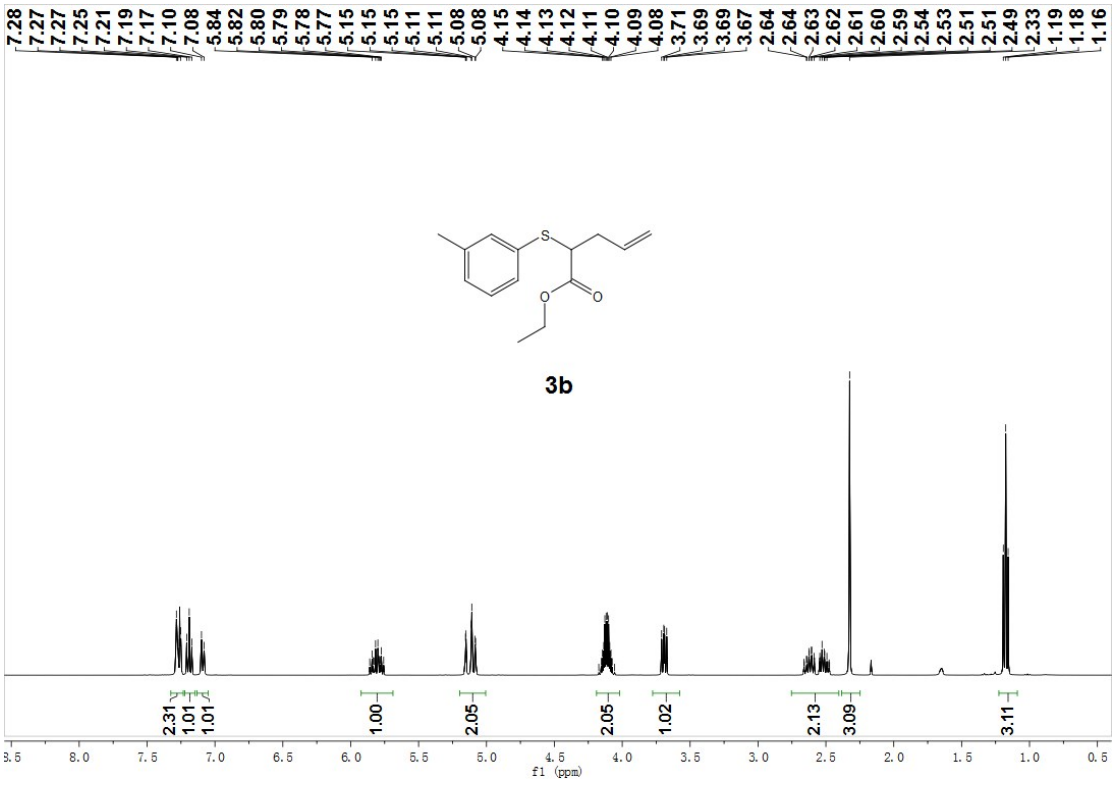
f1 (ppm)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3b
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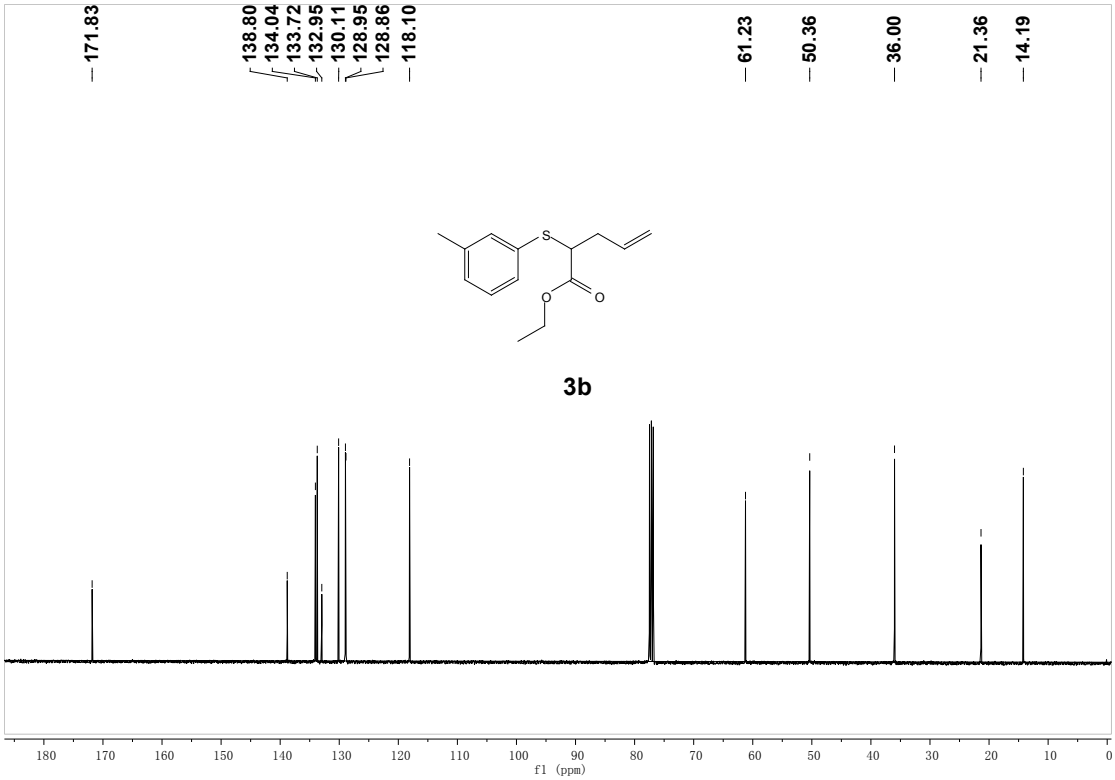
0.5
f1 (ppm)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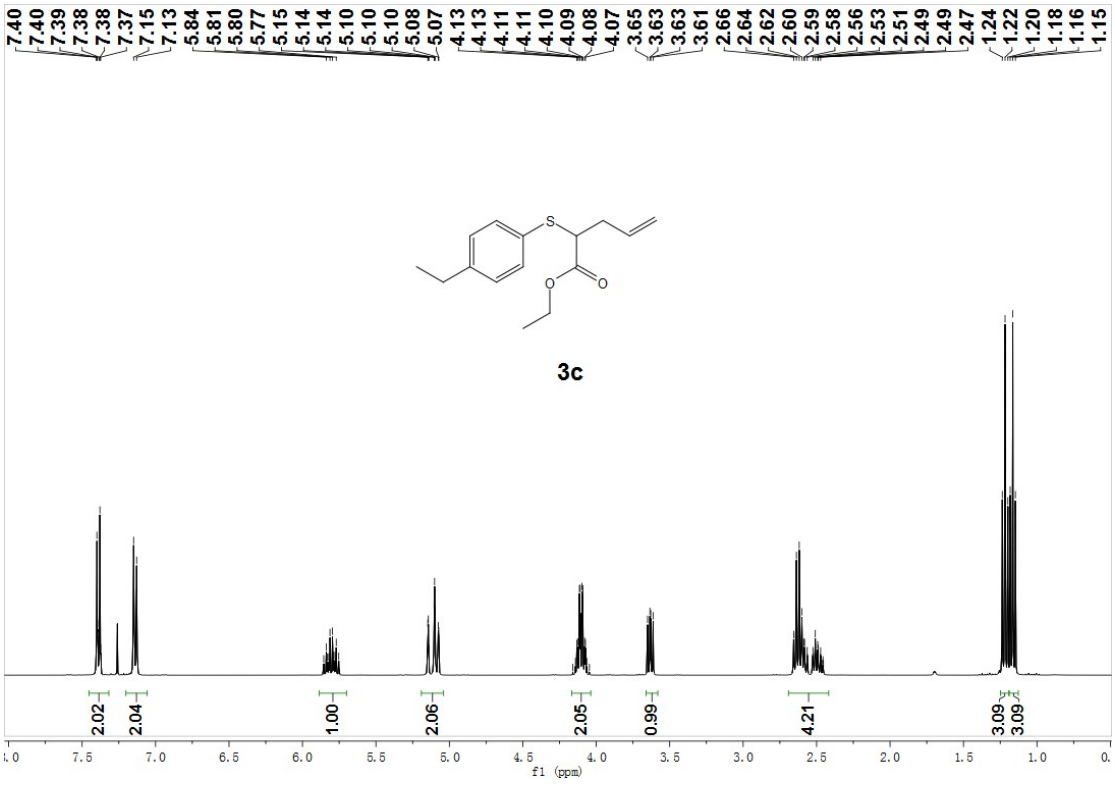
f1 (ppm)

3b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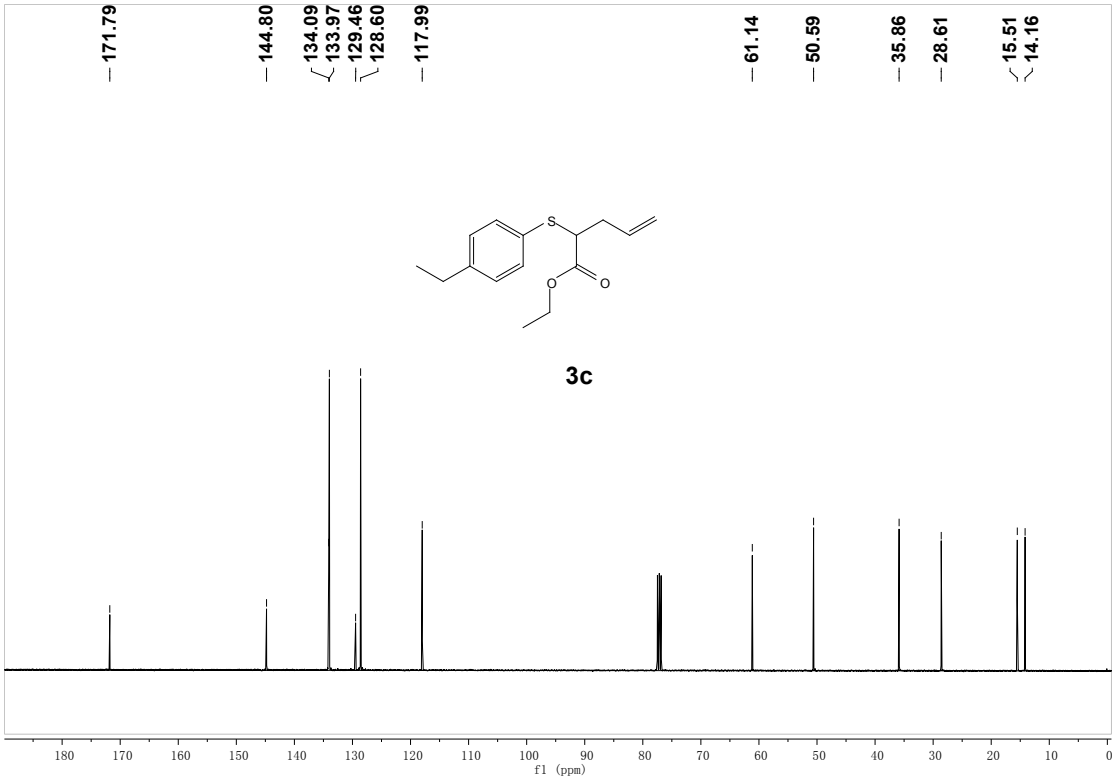
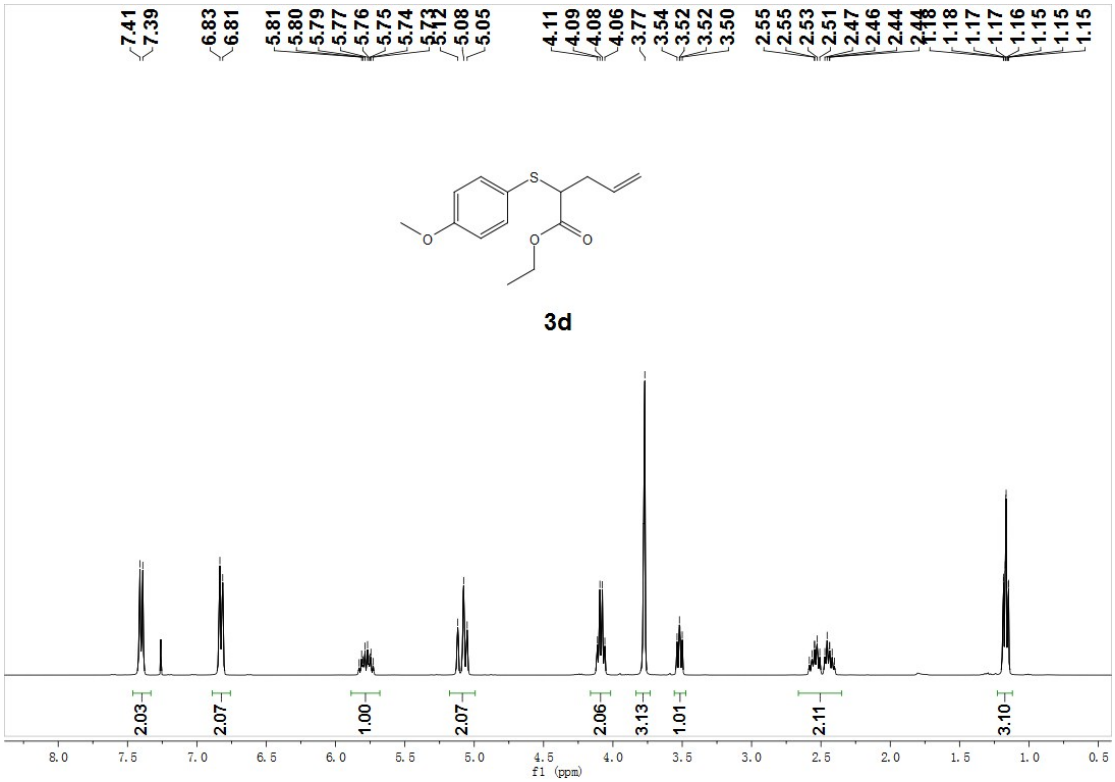
1.00
2.06
2.05
0.99
4.21
3.09
3.09
f1 (ppm)

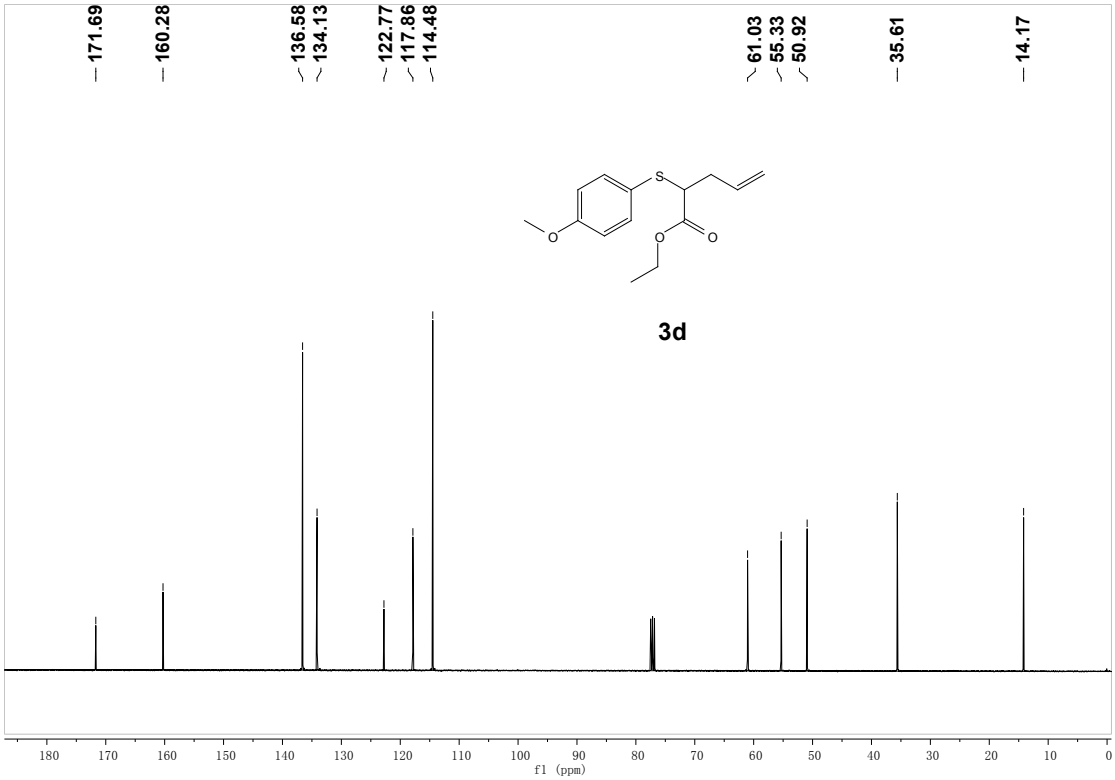
3c


171.79
144.80
134.09
133.97
129.46
128.60
117.99
61.14
50.59
35.86
28.61
15.51
14.16
S
O
O
f1 (ppm)

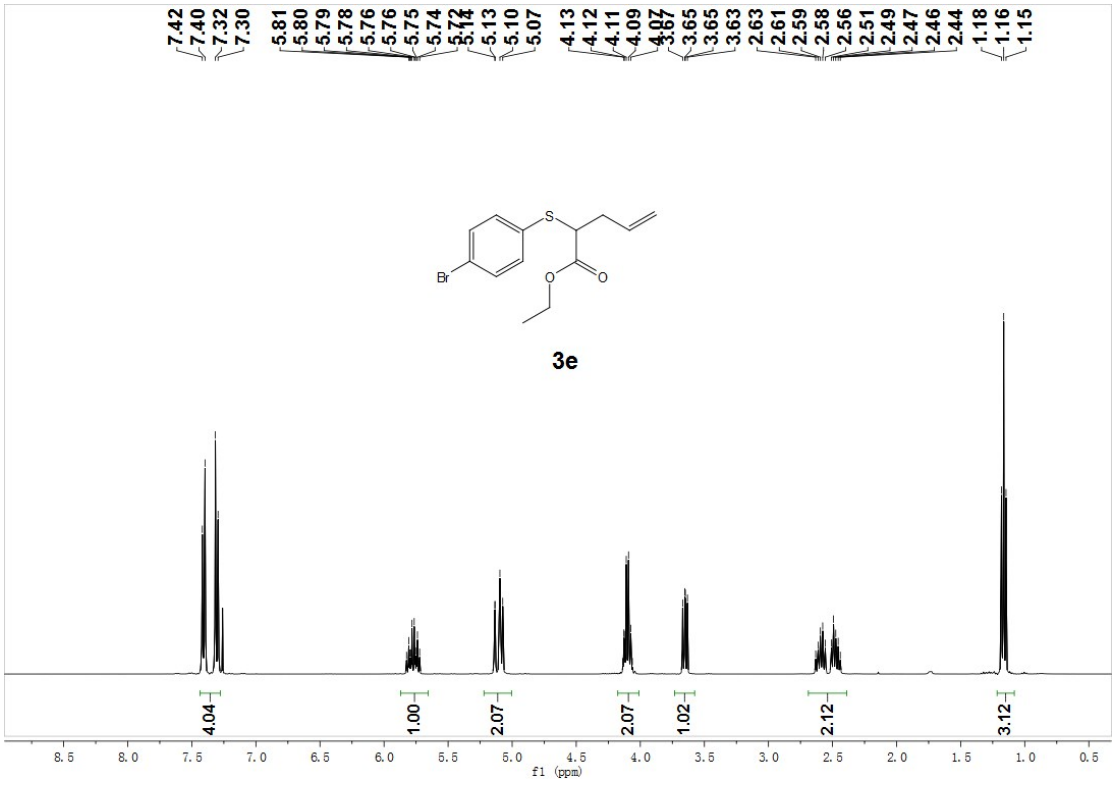
3c


7.41
7.39
6.83
6.81
5.81
5.80
5.79
5.77
5.76
5.75
5.74
5.08
5.05
4.11
4.09
4.08
4.06
3.77
3.54
3.52
3.52
3.50
2.55
2.55
2.53
2.51
2.47
2.46
2.44
1.18
1.17
1.17
1.16
1.15
1.15
1.15
S
O
O
O
2.03
2.07
1.00
2.07
2.06
3.13
1.01
2.11
3.10
f1 (ppm)

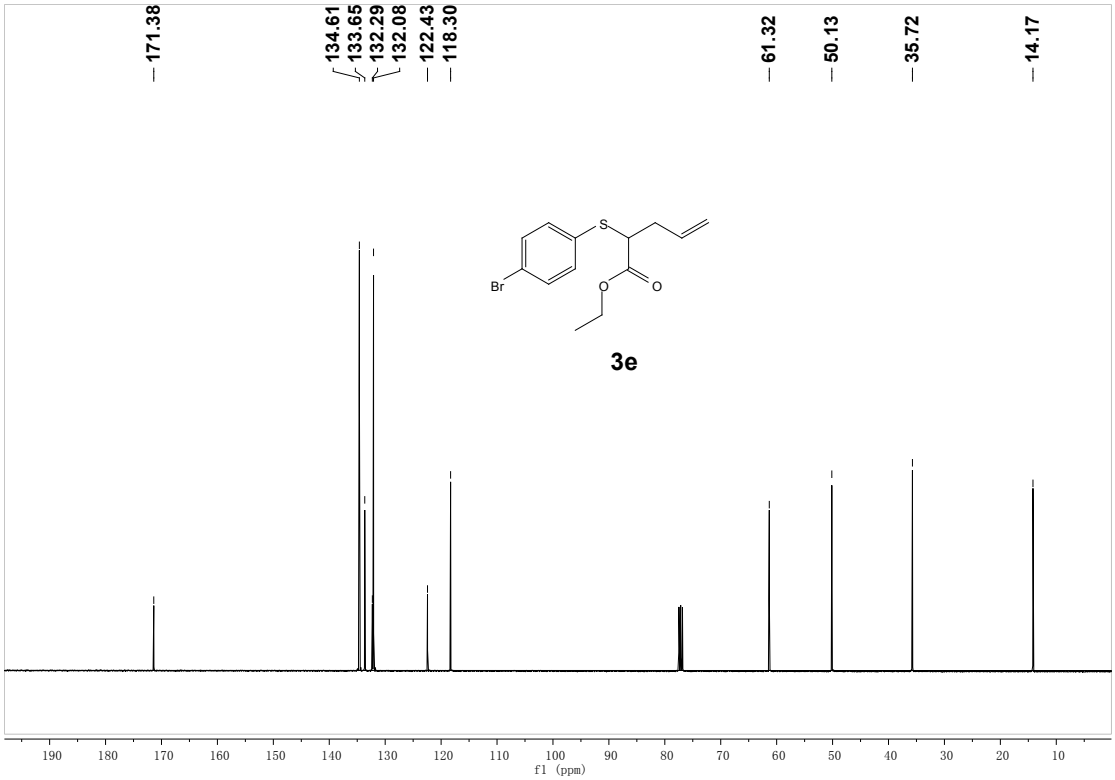
3d


171.69
160.28
136.58
134.13
122.77
117.86
114.48
61.03
55.33
50.92
35.61
14.17
S
O
O
O
f1 (ppm)

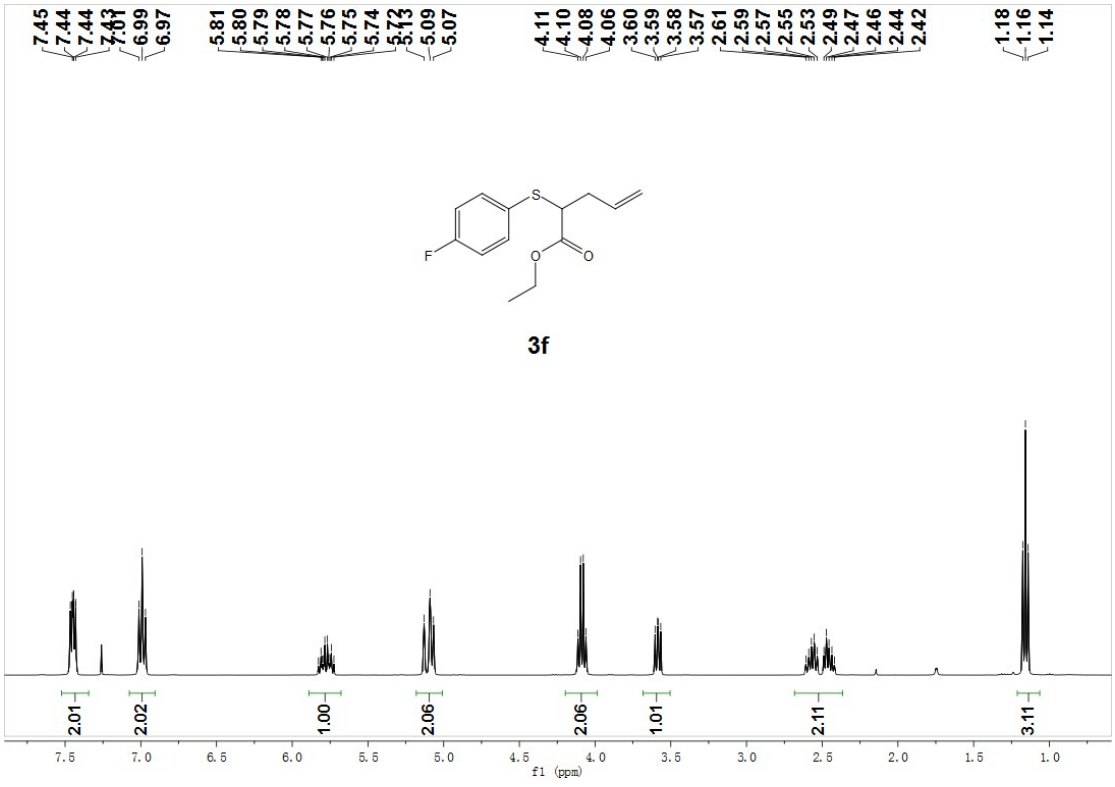
3d


7.42
7.40
7.32
7.30
5.81
5.80
5.79
5.78
5.76
5.76
5.75
5.74
5.13
5.10
5.07
4.13
4.12
4.11
4.09
3.65
3.65
3.63
2.63
2.61
2.59
2.58
2.56
2.51
2.49
2.47
2.46
2.44
1.18
1.16
1.15
S
Br
O
O
4.04
1.00
2.07
2.07
1.02
2.12
3.12
f1 (ppm)

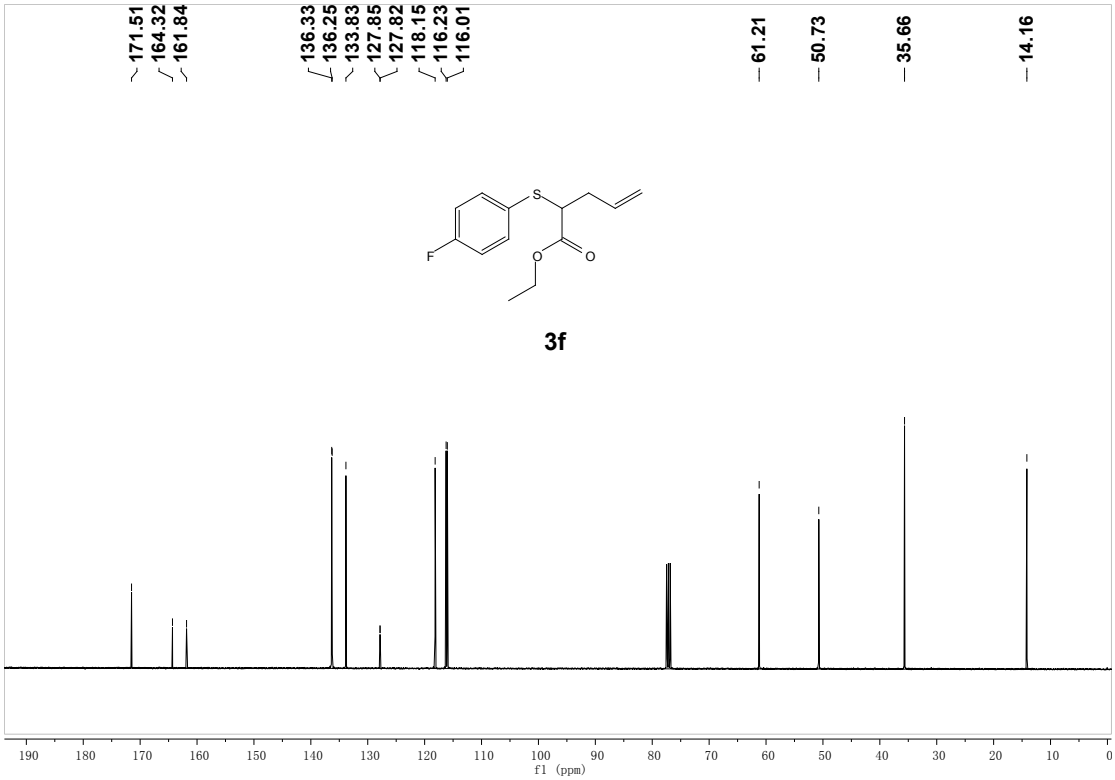
3e


171.38
134.61
133.65
132.29
132.08
122.43
118.30
61.32
50.13
35.72
14.17
S
Br
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

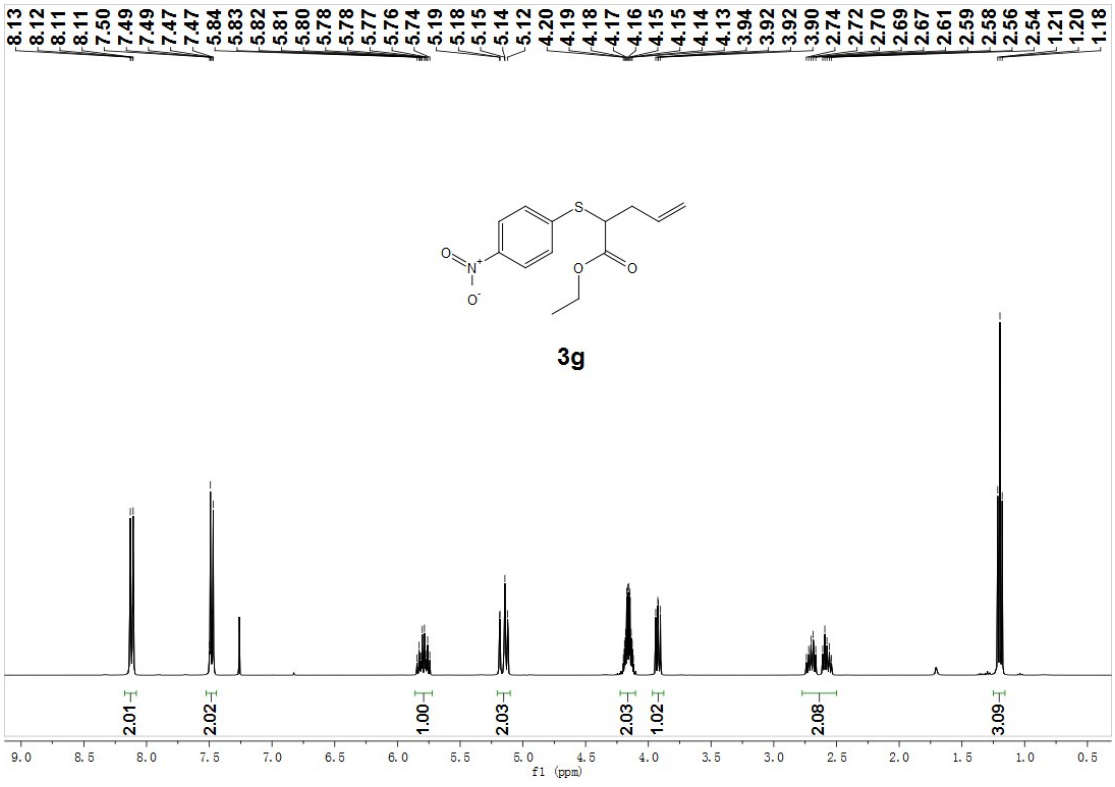
3e


7.45
7.44
7.44
7.43
7.01
6.99
6.97
5.81
5.80
5.79
5.78
5.77
5.76
5.75
5.74
5.72
5.13
5.09
5.07
4.11
4.10
4.08
4.06
3.60
3.59
3.58
3.57
2.61
2.59
2.57
2.55
2.53
2.49
2.47
2.46
2.44
2.42
1.18
1.16
1.14
S
F
O
O
2.01
2.02
1.00
2.06
2.06
1.01
2.11
3.11
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

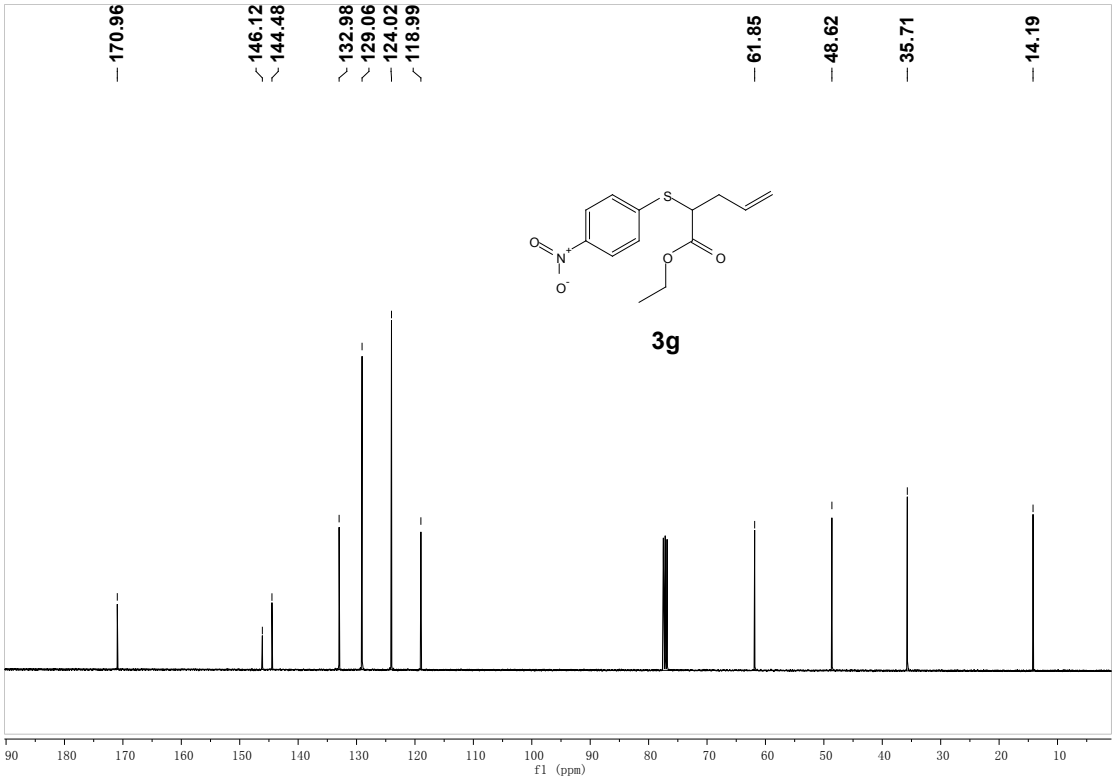
3f


171.51
164.32
161.84
136.33
136.25
133.83
127.85
127.82
118.15
116.23
116.01
61.21
50.73
35.66
14.16
S
F
O
O
f1 (ppm)

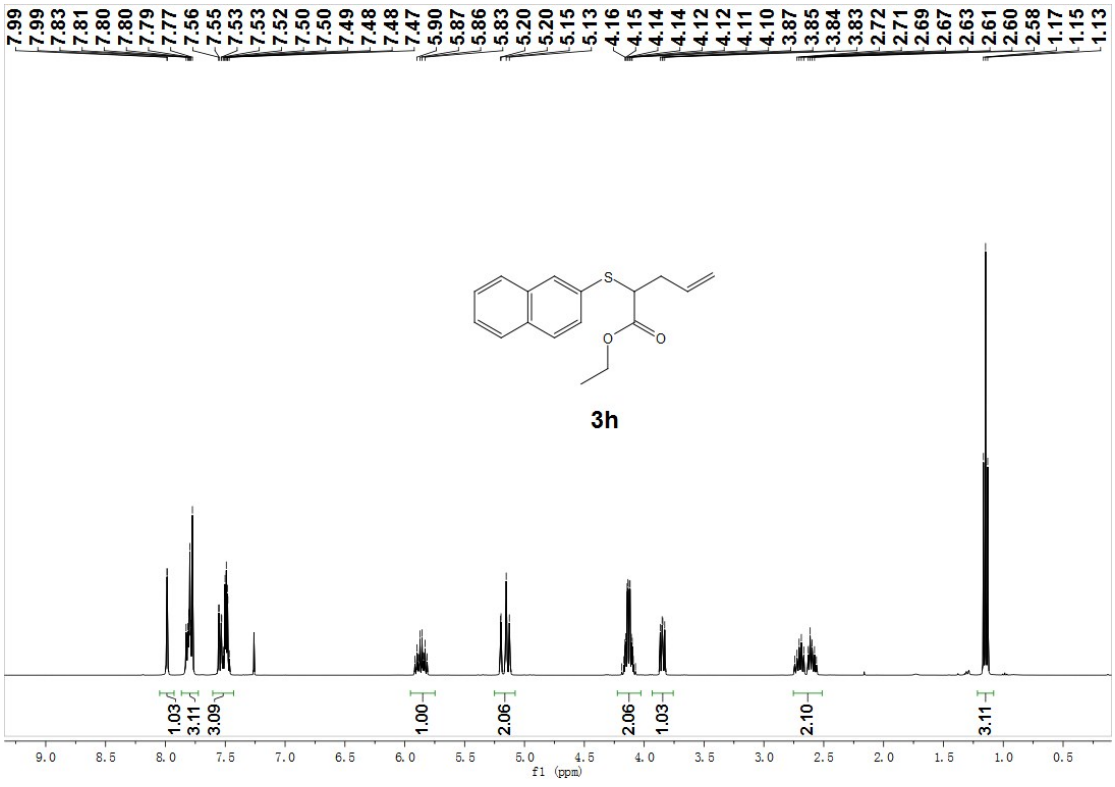
3f


8.13
8.12
8.11
8.11
7.50
7.49
7.49
7.47
7.47
5.84
5.83
5.82
5.81
5.80
5.78
5.78
5.77
5.76
5.74
5.19
5.18
5.15
5.14
5.12
4.20
4.19
4.18
4.17
4.16
4.15
4.15
4.14
4.13
3.94
3.92
3.92
3.90
2.74
2.72
2.70
2.69
2.67
2.61
2.59
2.58
2.56
2.54
1.21
1.20
1.18
S
O
N
O
O
O
2.01
2.02
1.00
2.03
2.03
1.02
2.08
3.09
f1 (ppm)

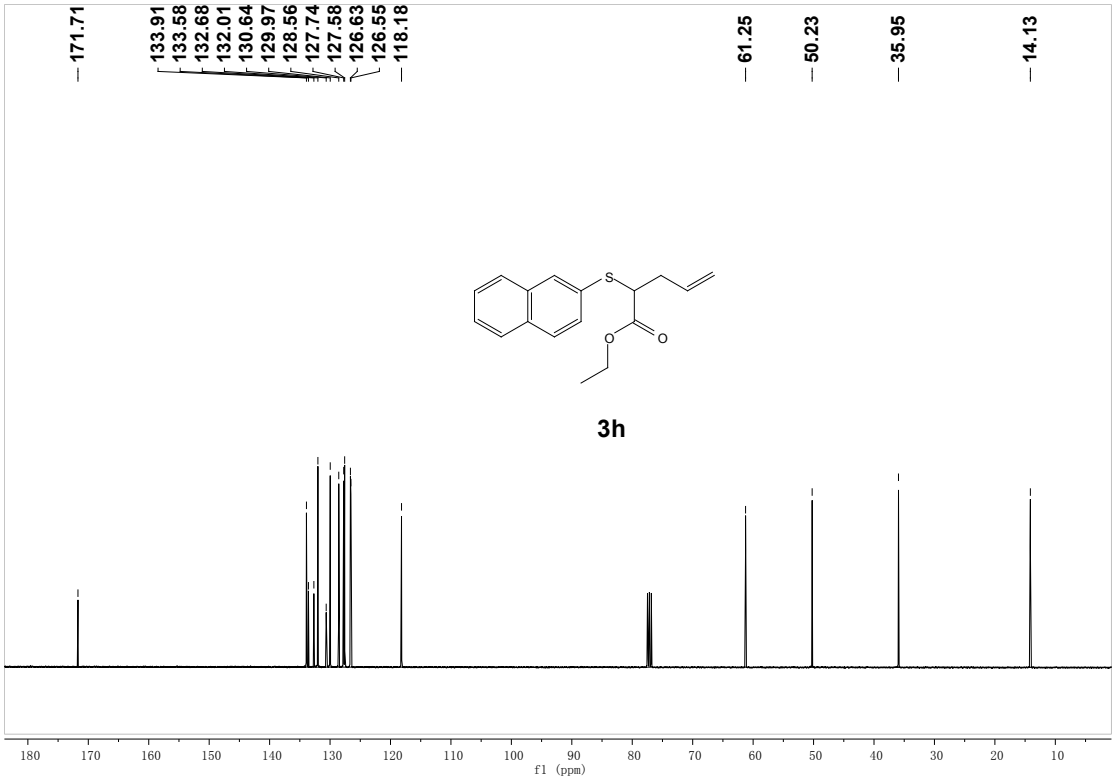
3g


170.96
146.12
144.48
132.98
129.06
124.02
118.99
61.85
48.62
35.71
14.19
S
O
N+
O-
O
O
f1 (ppm)

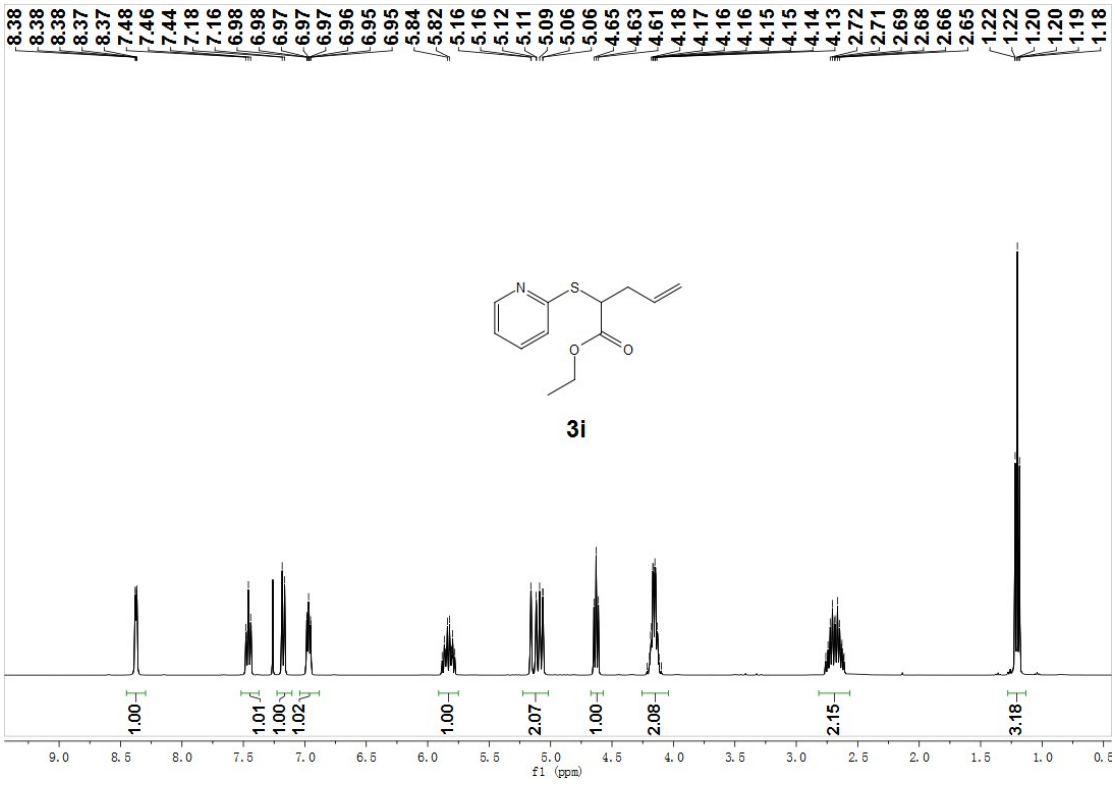
3g


7.99
7.99
7.83
7.81
7.80
7.80
7.79
7.77
7.56
7.55
7.53
7.53
7.52
7.50
7.50
7.49
7.48
7.48
7.47
5.90
5.87
5.86
5.83
5.20
5.20
5.15
5.13
4.16
4.15
4.14
4.14
4.12
4.12
4.11
4.10
3.87
3.85
3.84
3.83
2.72
2.71
2.69
2.67
2.63
2.61
2.60
2.58
1.17
1.15
1.13
S
O
O
1.03
3.11
3.09
1.00
2.06
2.06
1.03
2.10
3.11
f1 (ppm)

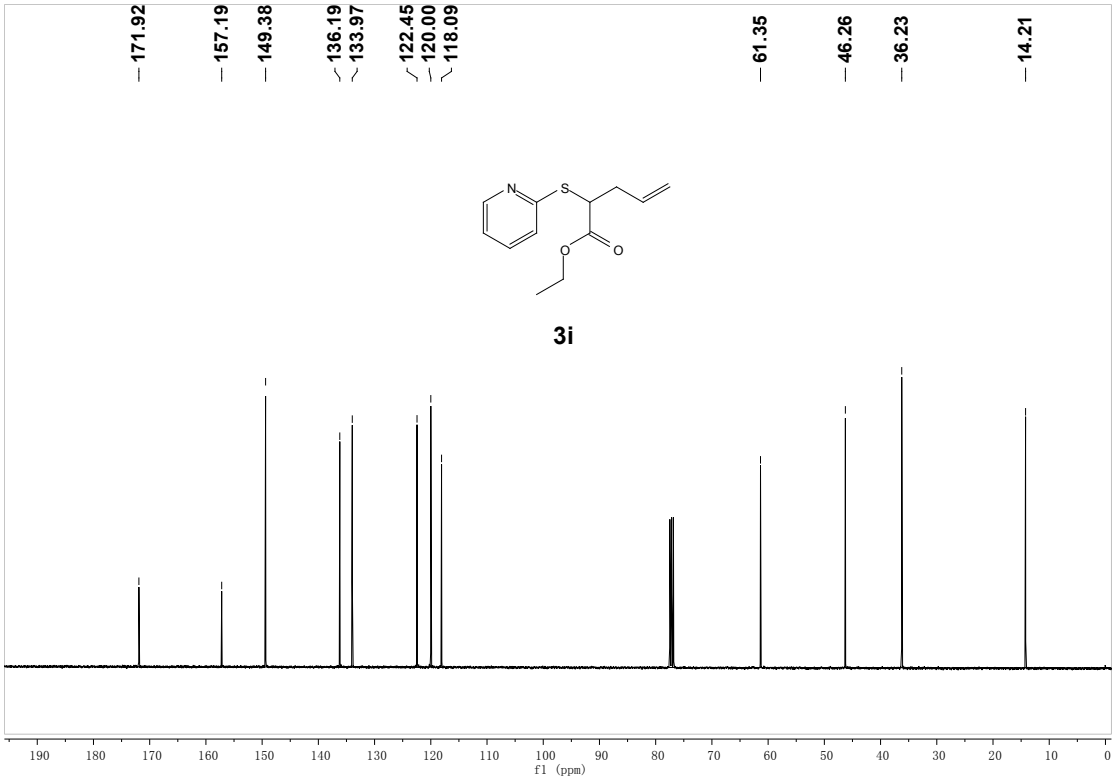
3h

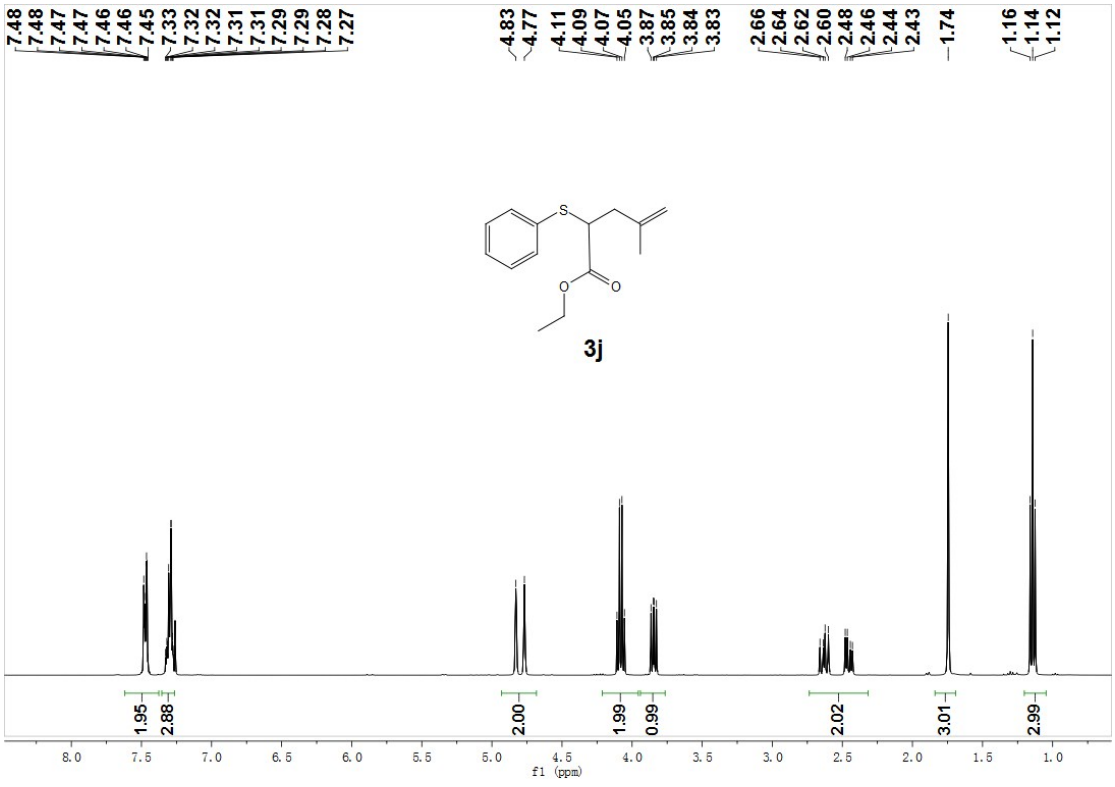

171.71
133.91
133.58
132.68
132.01
130.64
129.97
128.56
127.74
127.58
126.63
126.55
118.18
61.25
50.23
35.95
14.13
S
O
O
f1 (ppm)

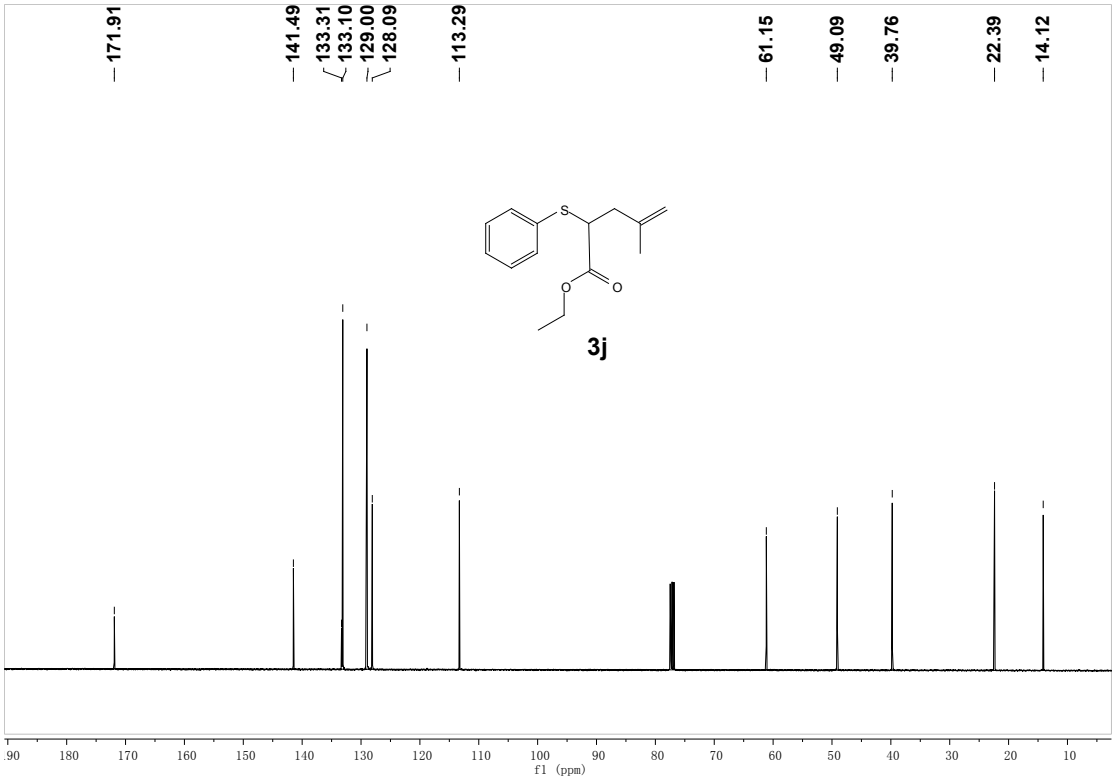
3h


8.38
8.38
8.38
8.37
8.37
7.48
7.46
7.44
7.18
7.16
6.98
6.98
6.97
6.97
6.97
6.96
6.95
6.95
5.84
5.82
5.16
5.16
5.12
5.11
5.09
5.06
5.06
4.65
4.63
4.61
4.18
4.17
4.16
4.16
4.15
4.15
4.14
4.13
2.72
2.71
2.69
2.68
2.66
2.65
1.22
1.22
1.20
1.20
1.19
1.18
N
S
O
O
1.00
1.01
1.00
1.02
1.00
2.07
1.00
2.08
2.15
3.18
f1 (ppm)

3i


171.92
157.19
149.38
136.19
133.97
122.45
120.00
118.09
61.35
46.26
36.23
14.21
N
S
O
O
O
3i
f1 (ppm)


7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.33
7.32
7.32
7.31
7.31
7.29
7.29
7.28
7.27
4.83
4.77
4.11
4.09
4.07
4.05
3.87
3.85
3.84
3.83
2.66
2.64
2.62
2.60
2.48
2.46
2.44
2.43
1.74
1.16
1.14
1.12
S
O
O
O
3j
1.95
2.88
2.00
1.99
0.99
2.02
3.01
2.99
f1 (ppm)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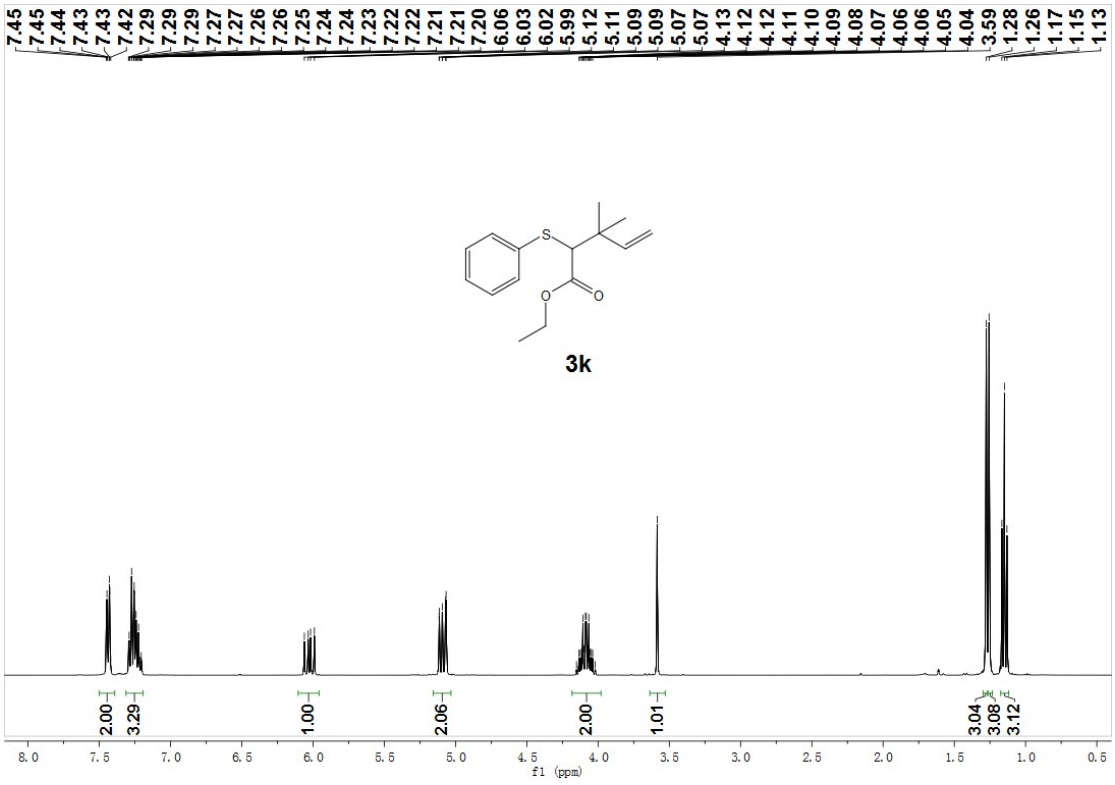
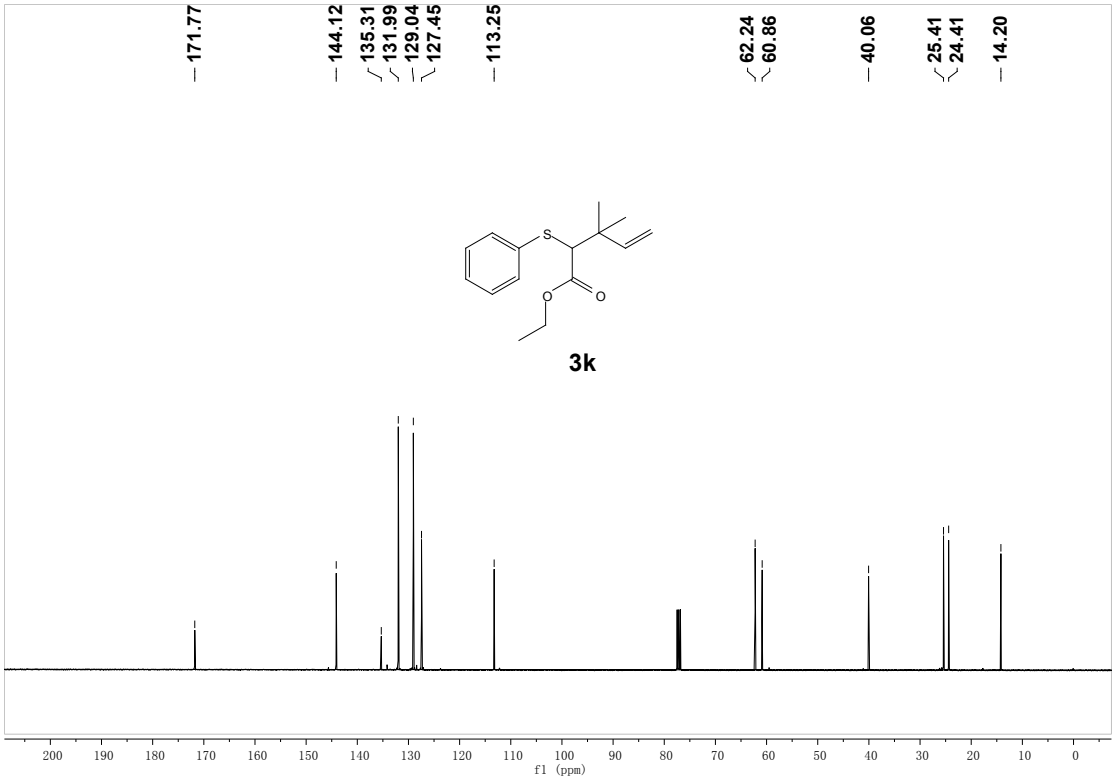
141.49
133.31
133.10
129.00
128.09
113.29
61.15
49.09
39.76
22.39
14.12
S
O
O
f1 (ppm)

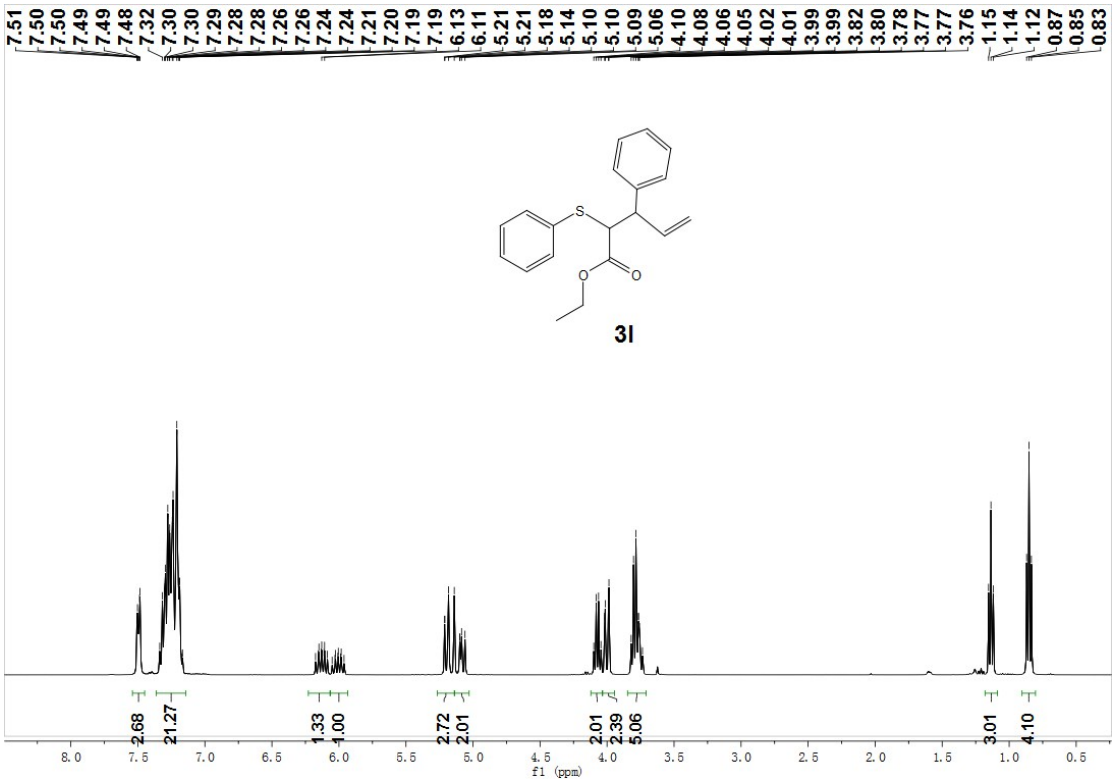
3j


7.45
7.45
7.44
7.43
7.43
7.42
7.29
7.29
7.29
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
6.06
6.03
6.02
5.99
5.12
5.11
5.09
5.09
5.07
5.07
4.13
4.12
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.06
4.05
4.04
3.59
1.28
1.26
1.17
1.15
1.13
S
O
O
2.00
3.29
1.00
2.06
2.00
1.01
3.04
3.08
3.12
f1 (ppm)

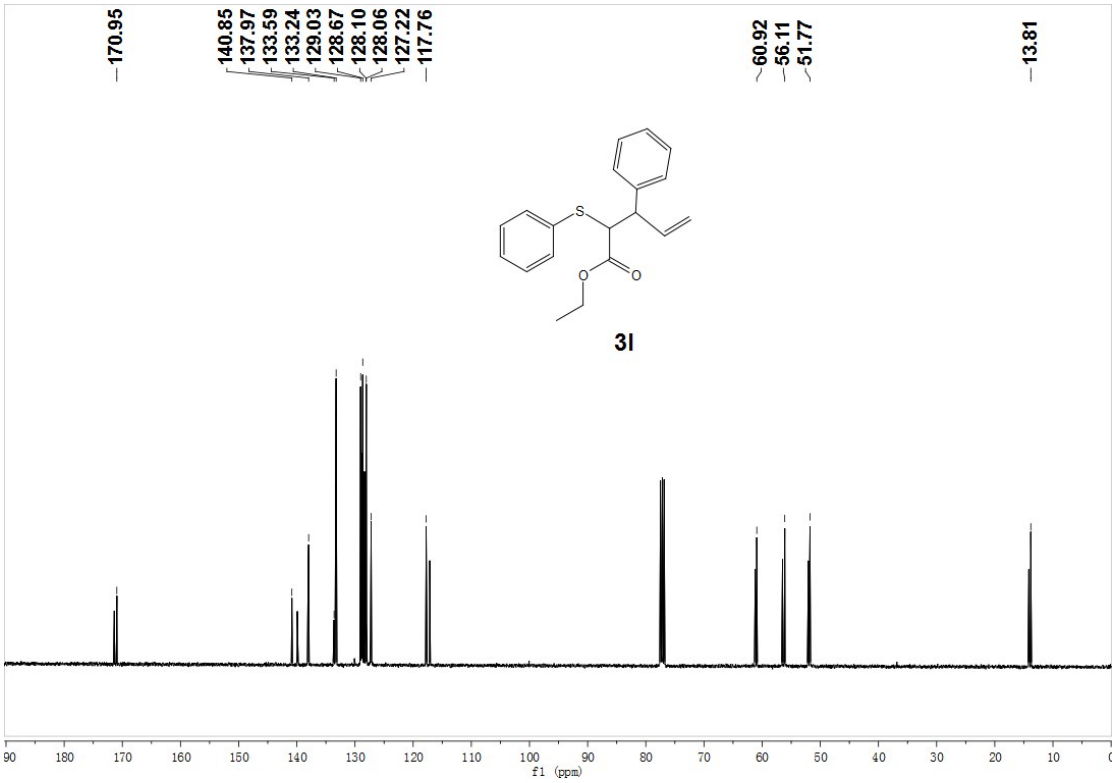
3k

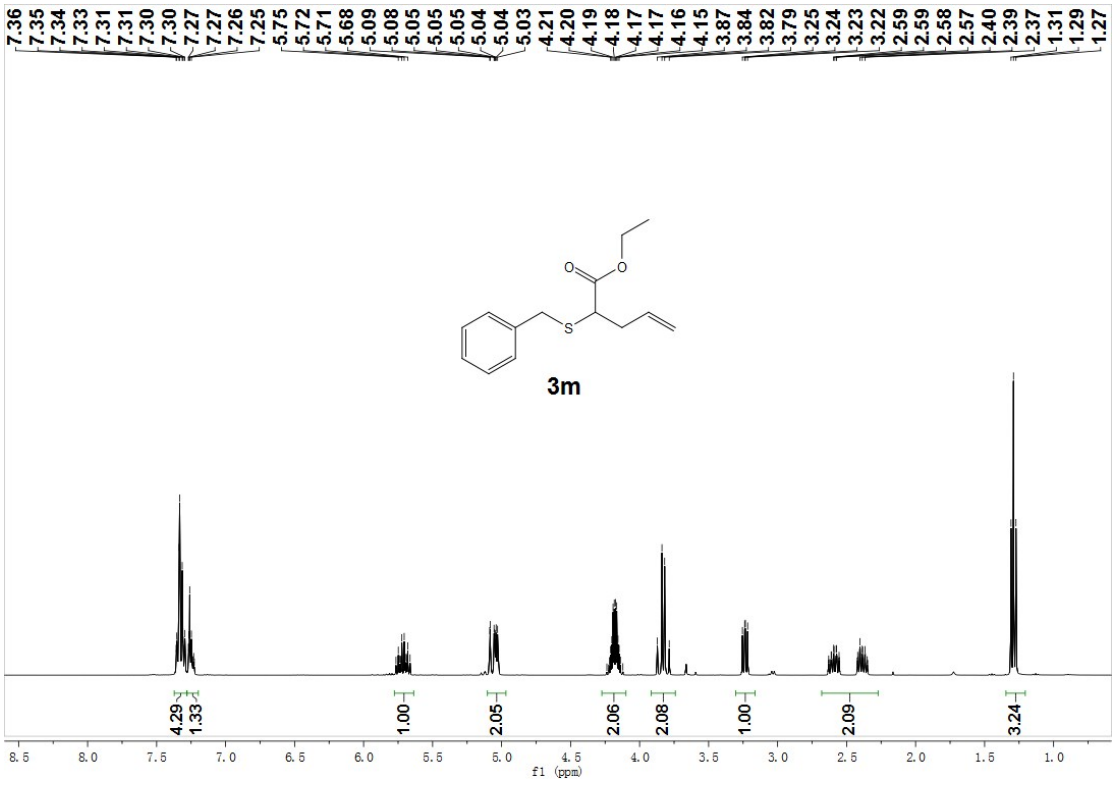

171.77
144.12
135.31
131.99
129.04
127.45
113.25
62.24
60.86
40.06
25.41
24.41
14.20
S
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

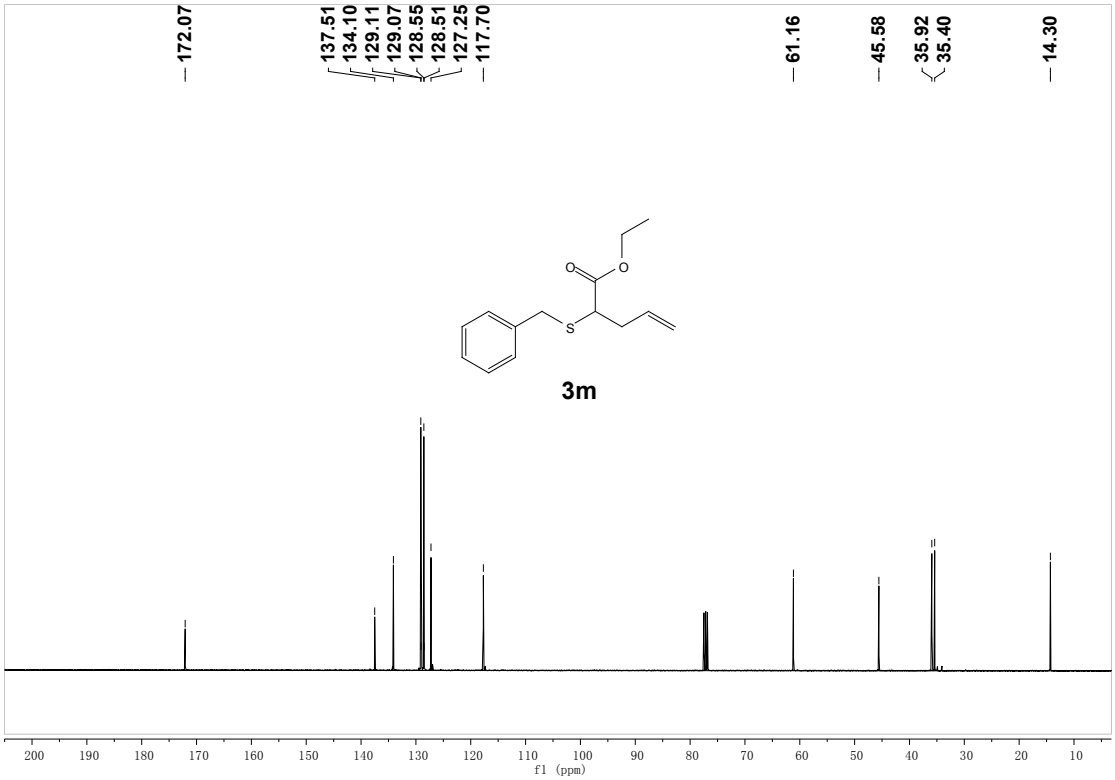
3k

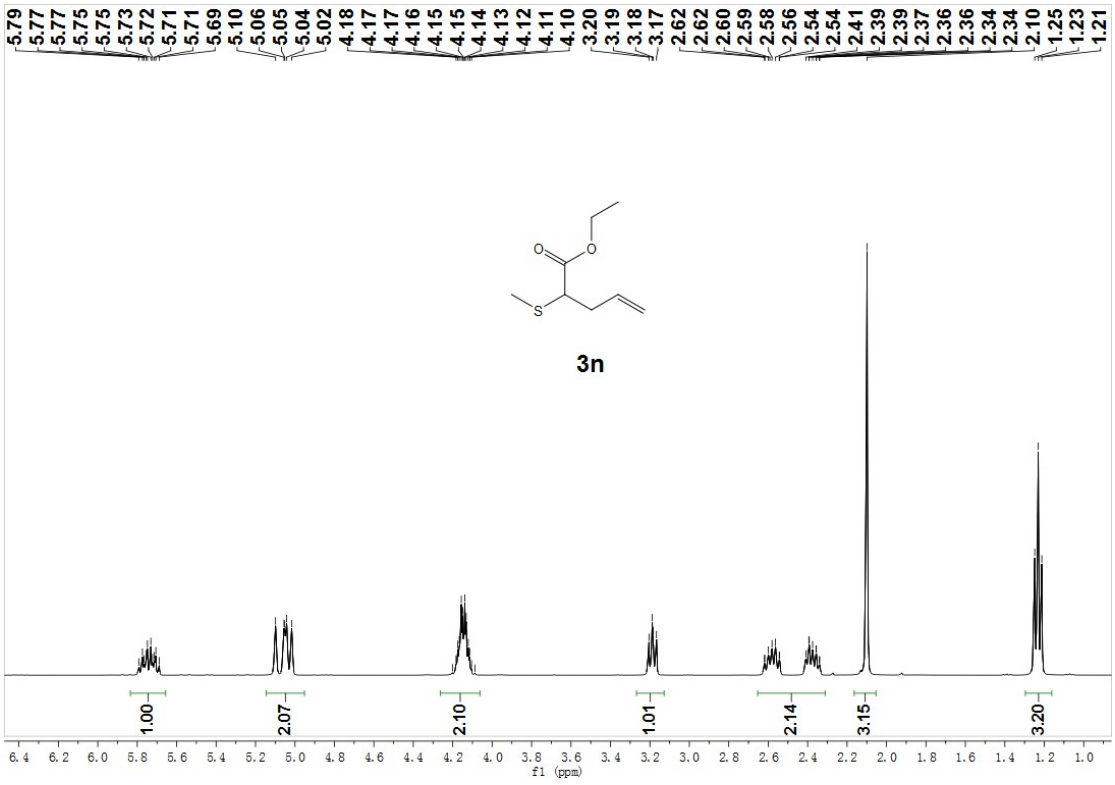

7.51 7.50 7.50 7.49 7.49 7.48 7.32 7.30 7.30 7.29 7.28 7.28 7.26 7.26 7.24 7.24 7.21 7.20 7.19 7.19 6.13 6.11 5.21 5.21 5.18 5.14 5.10 5.10 5.09 5.06 4.10 4.08 4.06 4.05 4.02 4.01 3.99 3.99 3.82 3.80 3.78 3.77 3.77 3.76 1.15 1.14 1.12 0.87 0.85 0.83
S
O
O
2.68 21.27 1.33 1.00 2.72 2.01 2.01 2.39 5.06 3.01 4.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

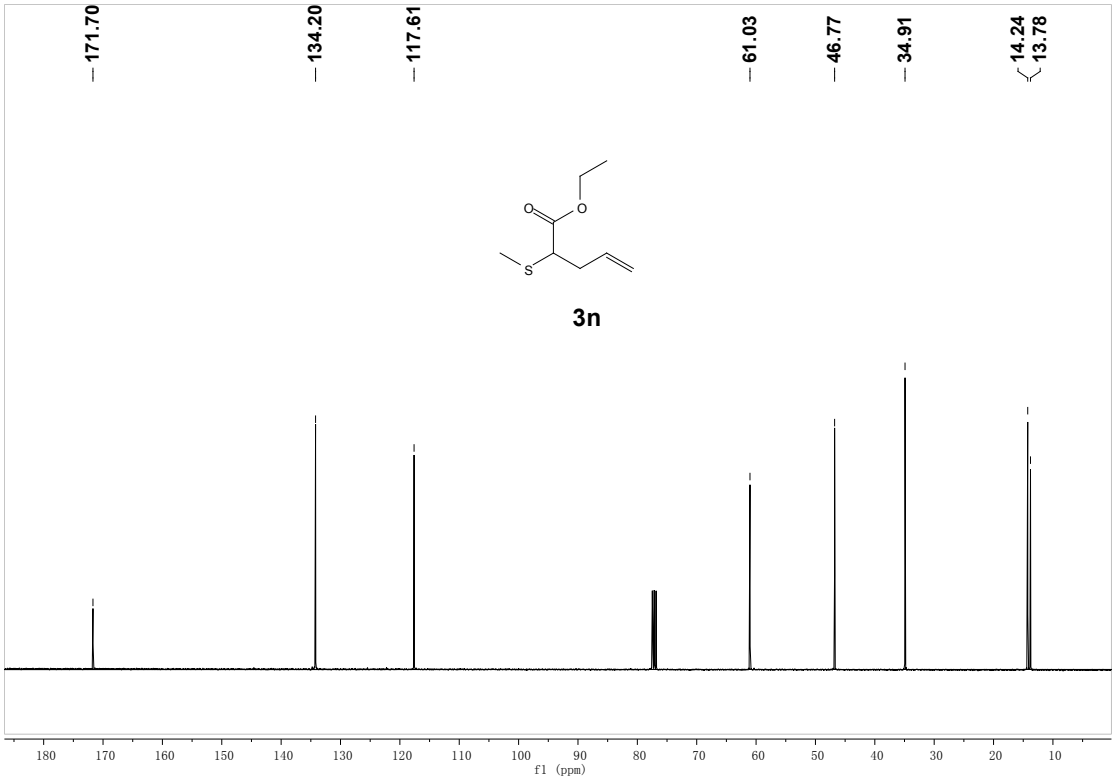
3l


170.95
140.85
137.97
133.59
133.24
129.03
128.67
128.10
128.06
127.22
117.76
60.92
56.11
51.77
13.81
S
O
O
3l
f1 (ppm)

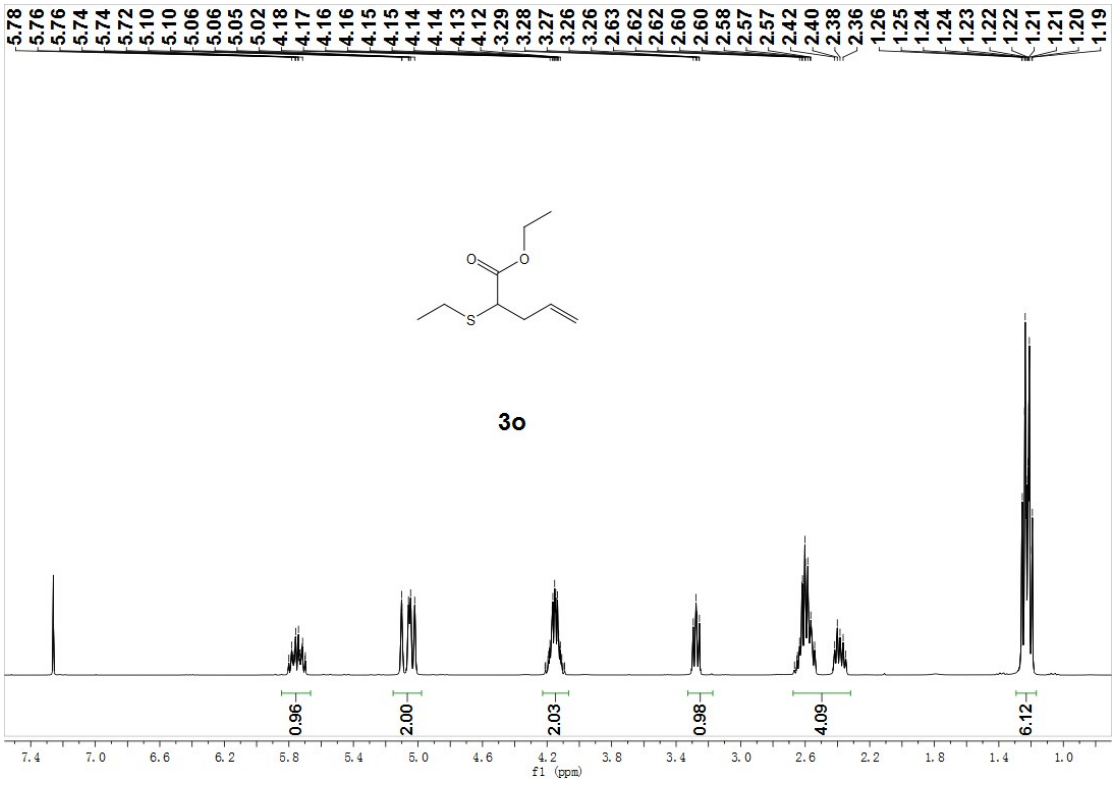

7.36
7.35
7.34
7.33
7.31
7.31
7.30
7.30
7.27
7.27
7.26
7.25
5.75
5.72
5.71
5.68
5.09
5.08
5.05
5.05
5.05
5.04
5.04
5.03
4.21
4.20
4.19
4.18
4.17
4.17
4.16
4.15
3.87
3.84
3.82
3.79
3.25
3.24
3.23
3.22
2.59
2.59
2.58
2.57
2.40
2.39
2.37
1.31
1.29
1.27
O
O
S
3m
4.29
1.33
1.00
2.05
2.06
2.08
1.00
2.09
3.24
f1 (ppm)


172.07
137.51
134.10
129.11
129.07
128.55
128.51
127.25
117.70
61.16
45.58
35.92
35.40
14.30
O
O
S
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

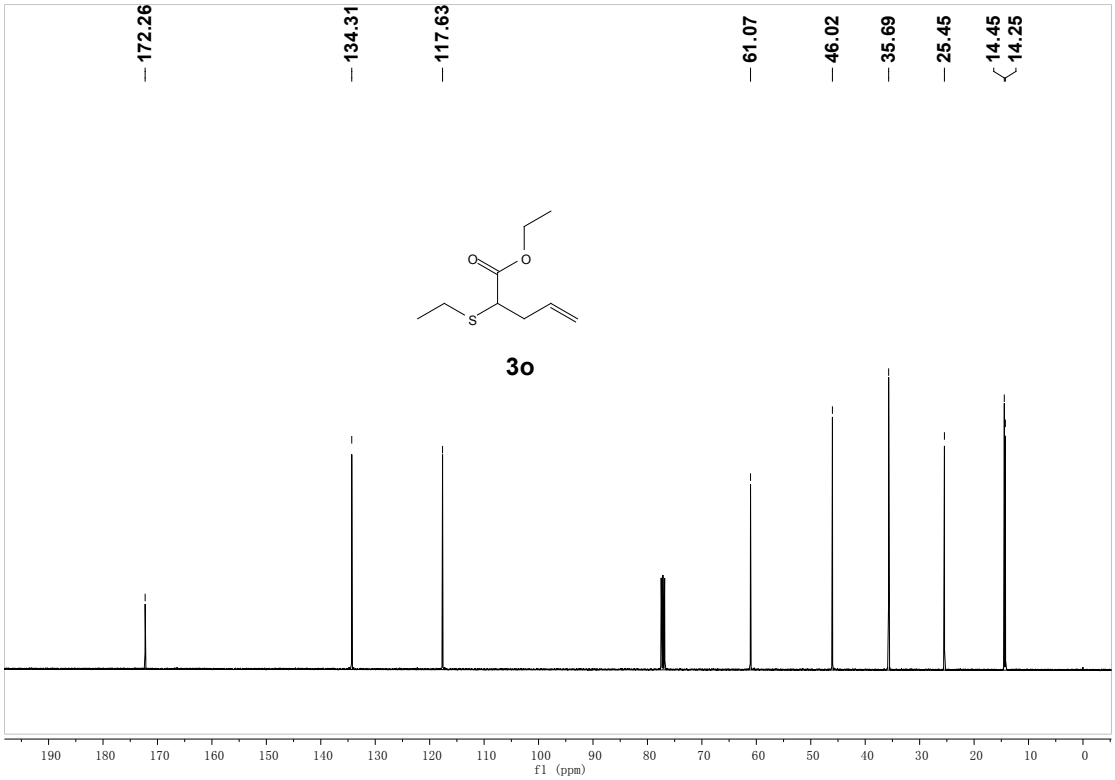

5.79 5.77 5.77 5.75 5.75 5.73 5.72 5.71 5.71 5.69
5.10 5.06 5.05 5.04 5.02
4.18 4.17 4.17 4.16 4.15 4.15 4.14 4.13 4.12 4.11 4.10
3.20 3.19 3.18 3.17
2.62 2.62 2.60 2.59 2.58 2.56 2.54 2.54 2.41 2.39 2.39 2.37 2.36 2.36 2.34 2.34
2.10 1.25 1.23 1.21
O
O
S
3n
1.00
2.07
2.10
1.01
2.14
3.15
3.20
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)


171.70
134.20
117.61
61.03
46.77
34.91
14.24
13.78
O
O
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

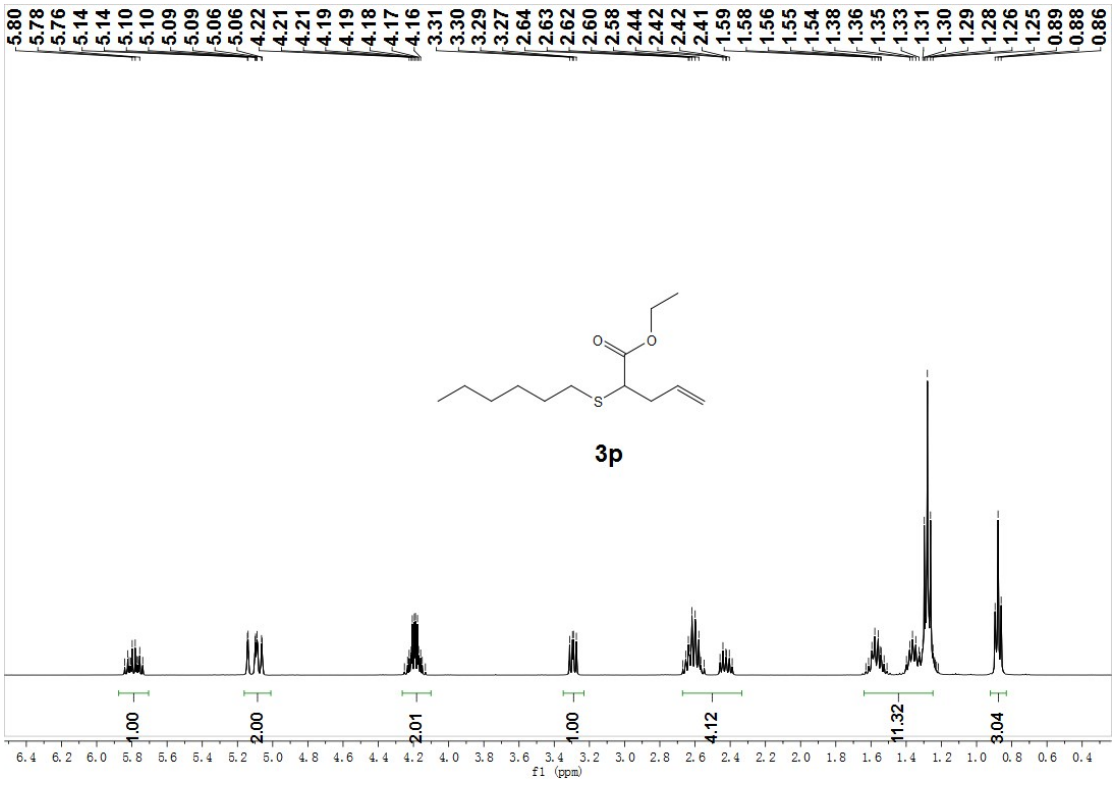
3n


5.78 5.76 5.76 5.74 5.74 5.72 5.10 5.10 5.06 5.06 5.05 5.02 4.18 4.17 4.16 4.16 4.15 4.15 4.14 4.14 4.13 4.12 3.29 3.28 3.27 3.26 3.26 2.63 2.62 2.62 2.60 2.60 2.58 2.57 2.57 2.42 2.40 2.38 2.36 1.26 1.25 1.24 1.24 1.23 1.22 1.22 1.21 1.21 1.20 1.19
O
O
S
0.96
2.00
2.03
0.98
4.09
6.12
7.4 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0
f1 (ppm)

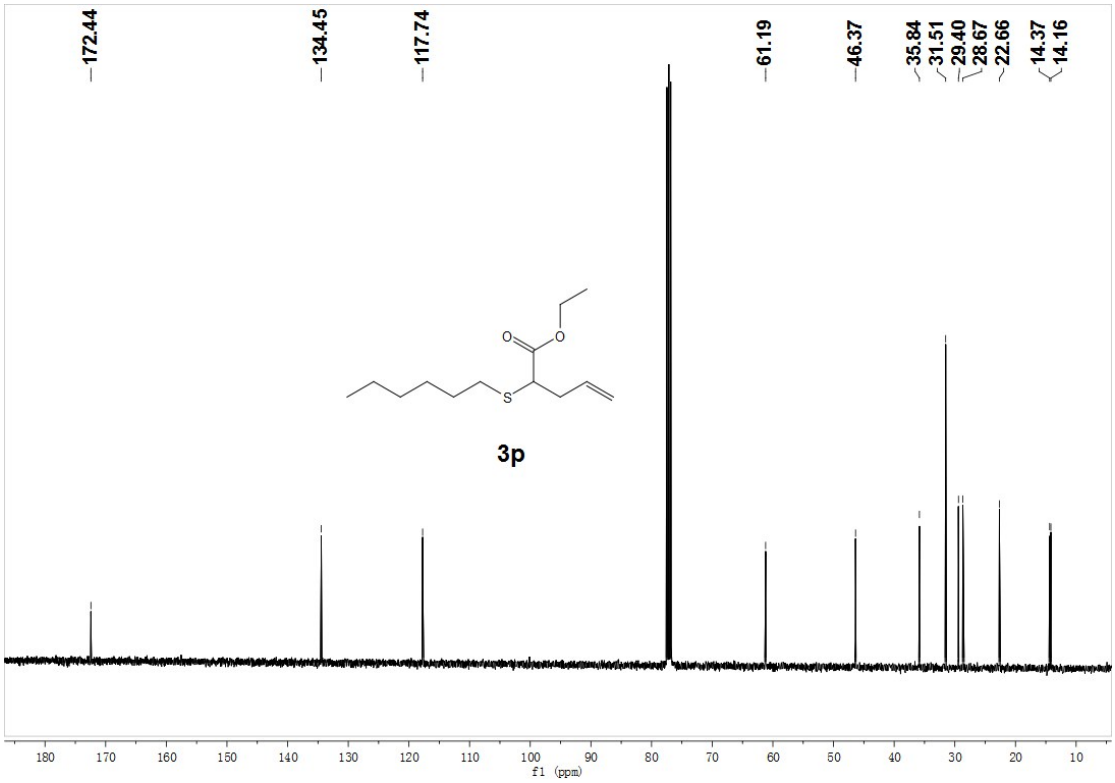
3o

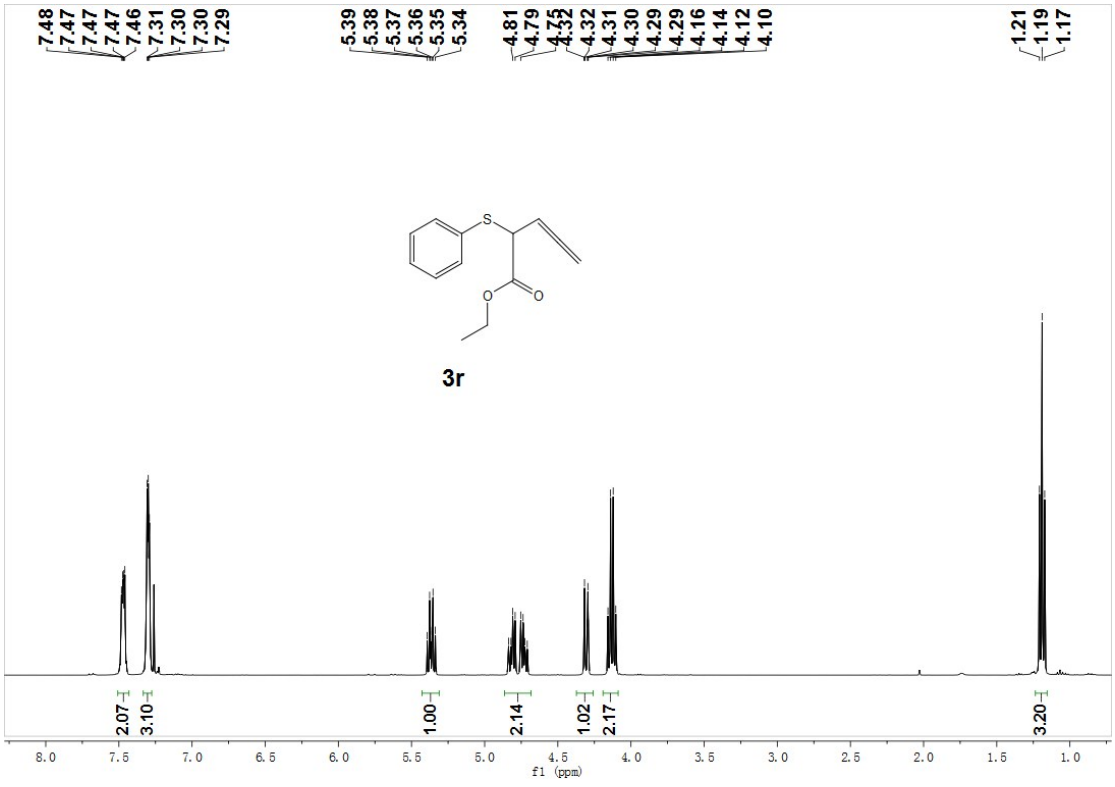

172.26
134.31
117.63
61.07
46.02
35.69
25.45
14.45
14.25
O
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3o


5.80 5.78 5.76 5.14 5.14 5.10 5.10 5.09 5.09 5.06 5.06 4.22 4.21 4.21 4.19 4.19 4.18 4.17 4.16 3.31 3.30 3.29 3.27 2.64 2.63 2.62 2.60 2.58 2.44 2.42 2.42 2.41 1.59 1.58 1.56 1.55 1.54 1.38 1.36 1.35 1.33 1.31 1.30 1.29 1.28 1.26 1.25 0.89 0.88 0.86
O
O
S
1.00 2.00 2.01 1.00 4.12 11.32 3.04
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)

3p


172.44
134.45
117.74
61.19
46.37
35.84
31.51
29.40
28.67
22.66
14.37
14.16
O
O
S
3p
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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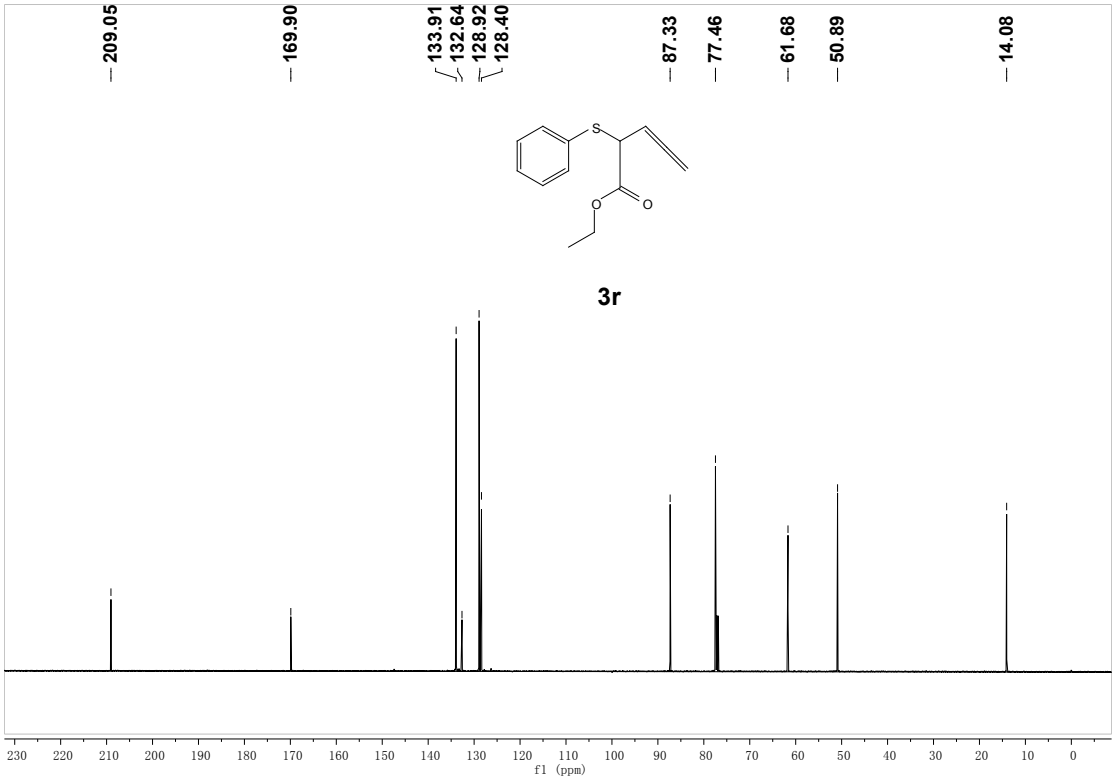
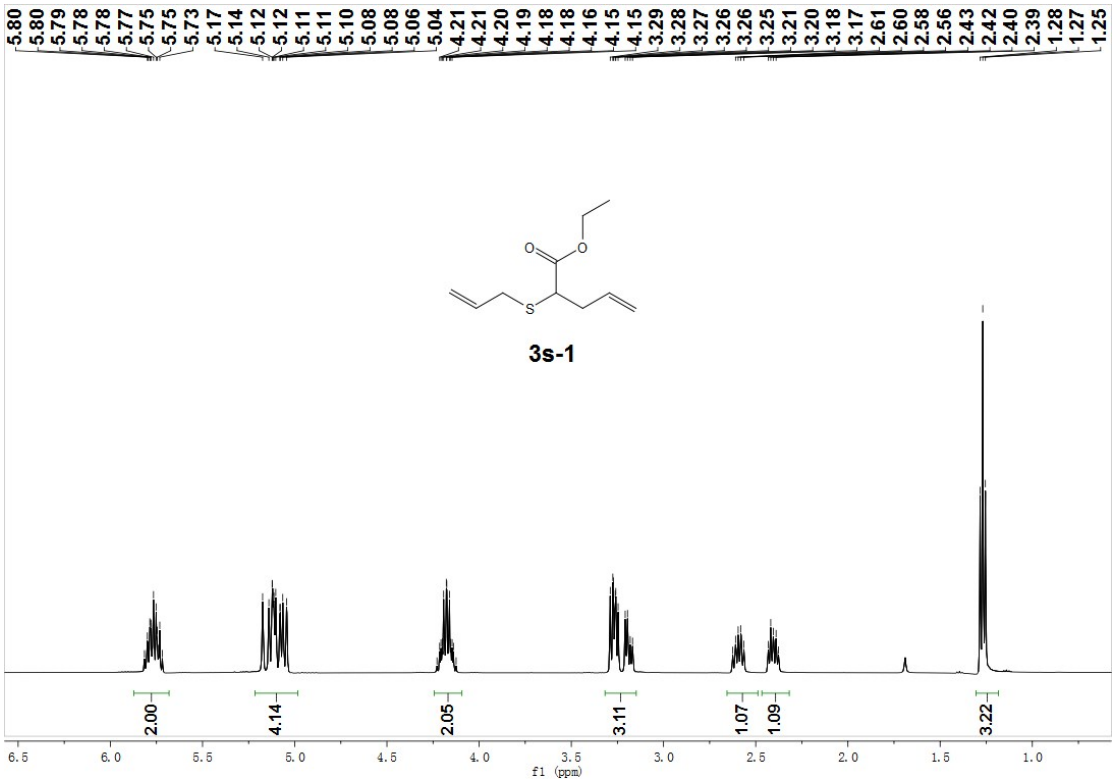
7.47
7.47
7.47
7.46
7.31
7.30
7.30
7.29
5.39
5.38
5.37
5.36
5.35
5.34
4.81
4.79
4.32
4.32
4.31
4.30
4.29
4.29
4.16
4.14
4.12
4.10
1.21
1.19
1.17
S
O
O
3r
2.07
3.10
1.00
2.14
1.02
2.17
3.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


209.05
169.90
133.91
132.64
128.92
128.40
87.33
77.46
61.68
50.89
14.08
S
O
O
3r
f1 (ppm)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5.80
5.79
5.78
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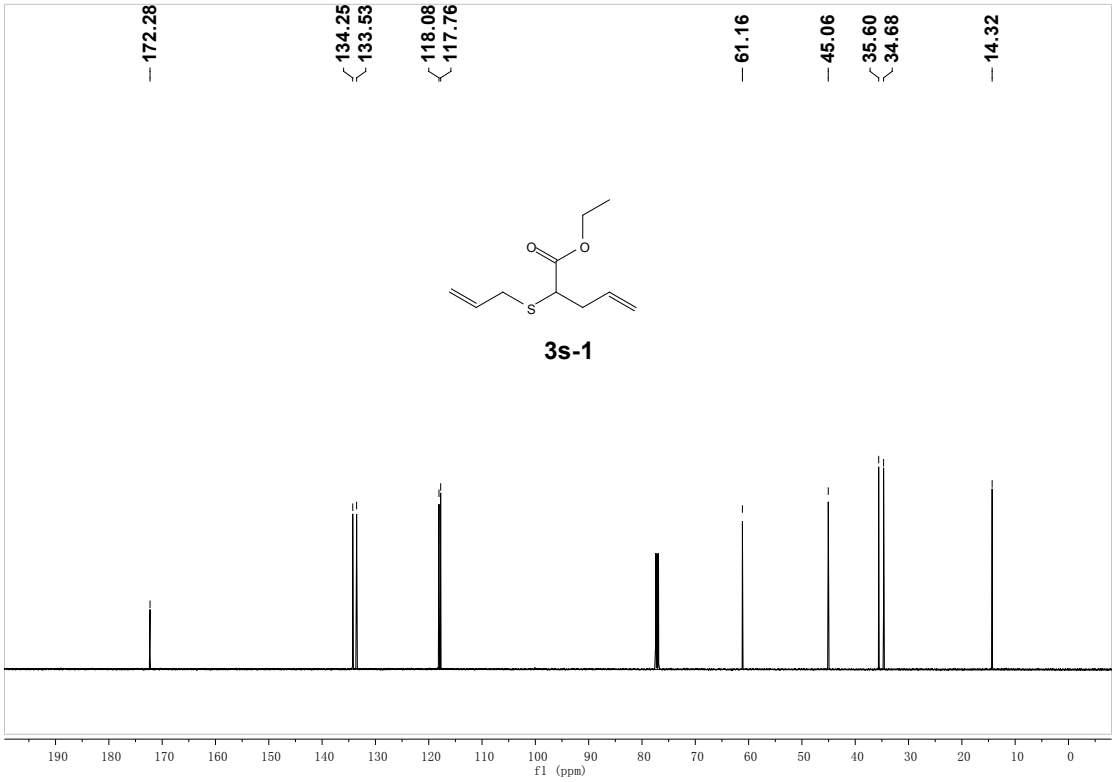
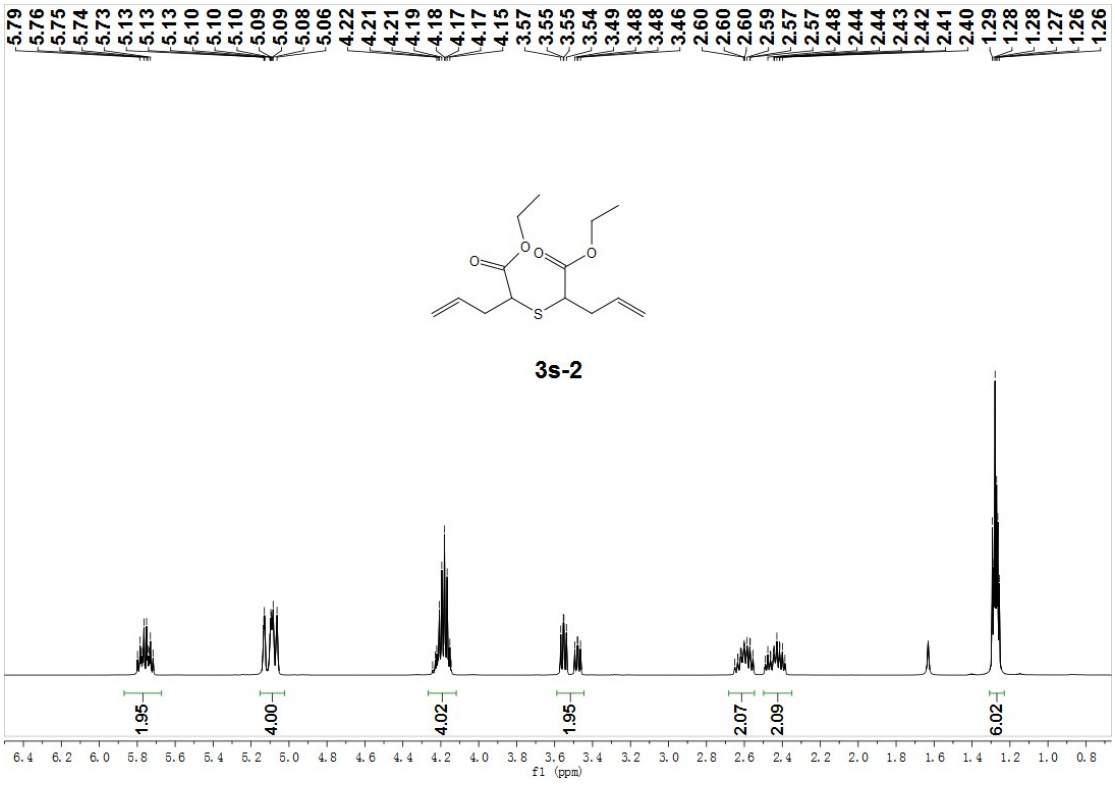
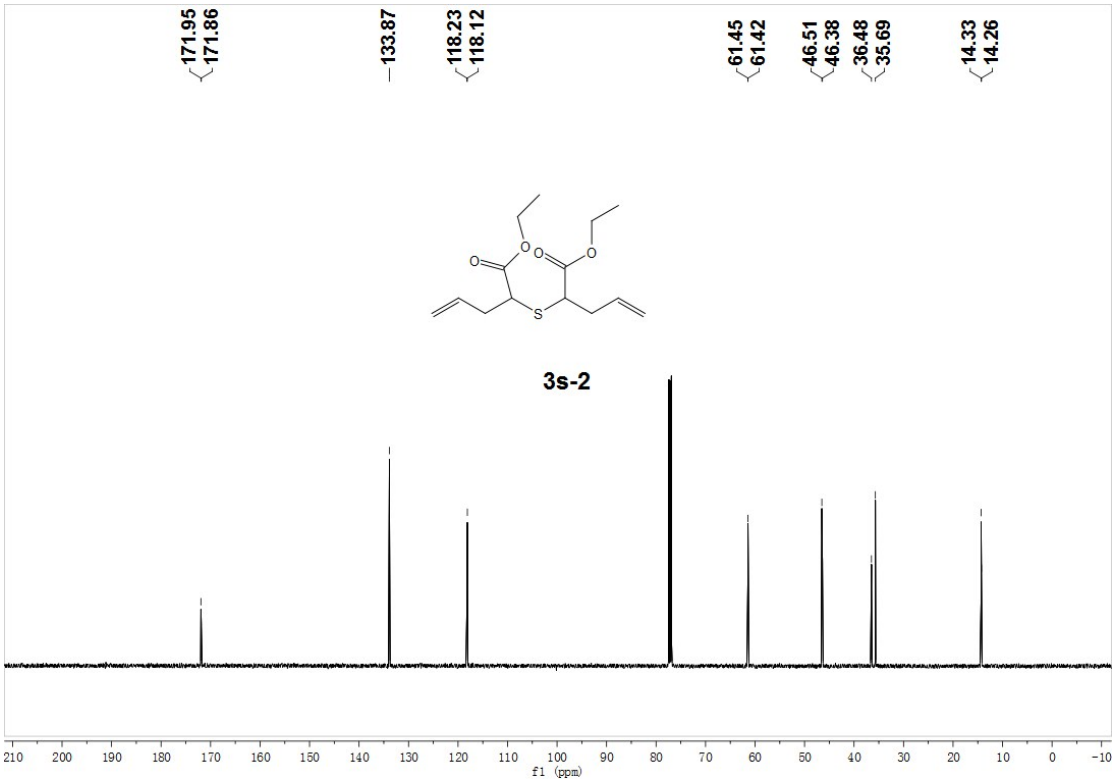
5.77
5.75
5.75
5.73
5.17
5.14
5.12
5.12
5.11
5.11
5.10
5.08
5.08
5.06
5.04
4.21
4.21
4.20
4.19
4.18
4.18
4.16
4.15
4.15
3.29
3.28
3.27
3.26
3.26
3.25
3.21
3.20
3.18
3.17
2.61
2.60
2.58
2.56
2.43
2.42
2.40
2.39
1.28
1.27
1.25
O
O
S
3s-1
2.00
4.14
2.05
3.11
1.07
1.09
3.22
f1 (ppm)

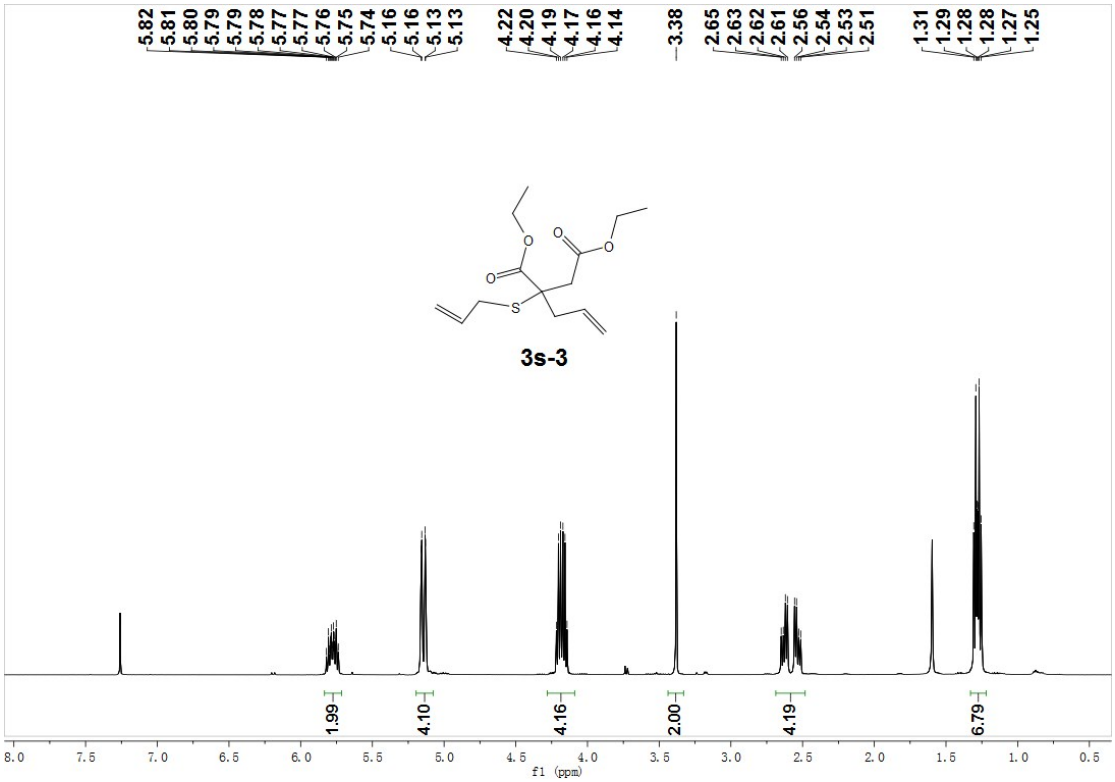

172.28
134.25
133.53
118.08
117.76
61.16
45.06
35.60
34.68
14.32
O
O
S
f1 (ppm)

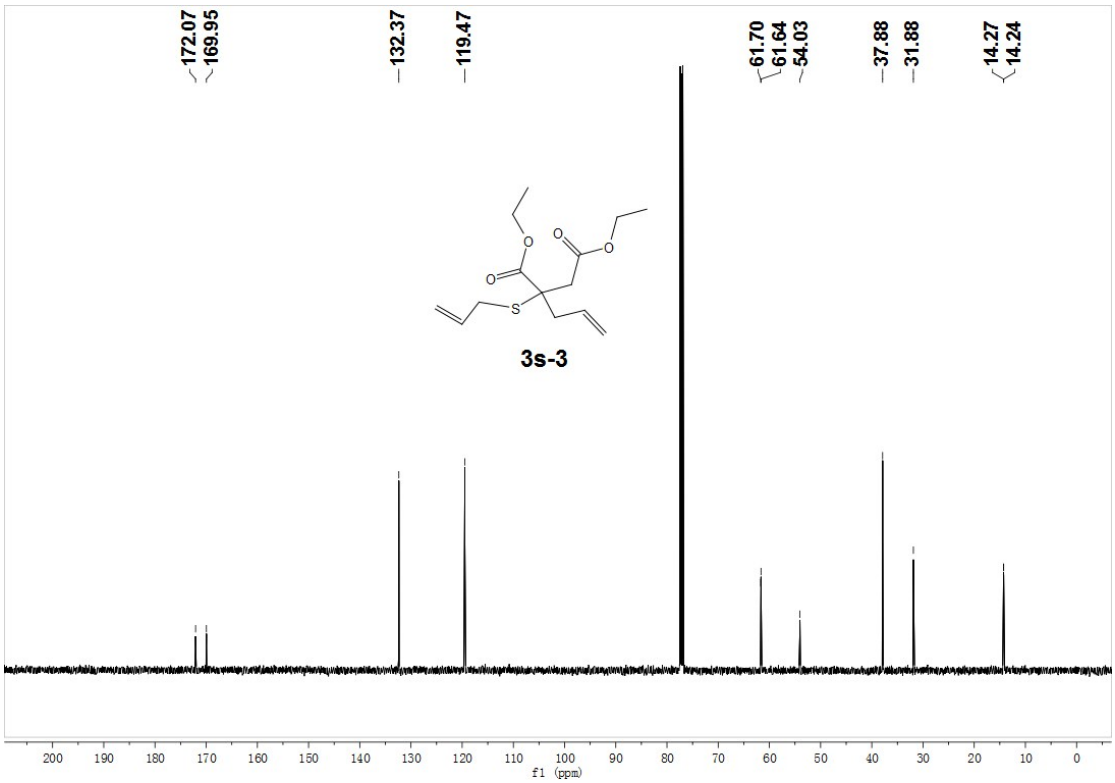
3s-1


5.79
5.76
5.75
5.74
5.73
5.13
5.13
5.13
5.10
5.10
5.09
5.09
5.08
5.06
4.22
4.21
4.21
4.19
4.18
4.17
4.17
4.15
3.57
3.55
3.55
3.54
3.49
3.48
3.48
3.46
2.60
2.60
2.60
2.59
2.57
2.57
2.48
2.44
2.44
2.43
2.42
2.41
2.40
1.29
1.28
1.28
1.27
1.26
1.26
O
O
O
O
O
S
1.95
4.00
4.02
1.95
2.07
2.09
6.02
f1 (ppm)

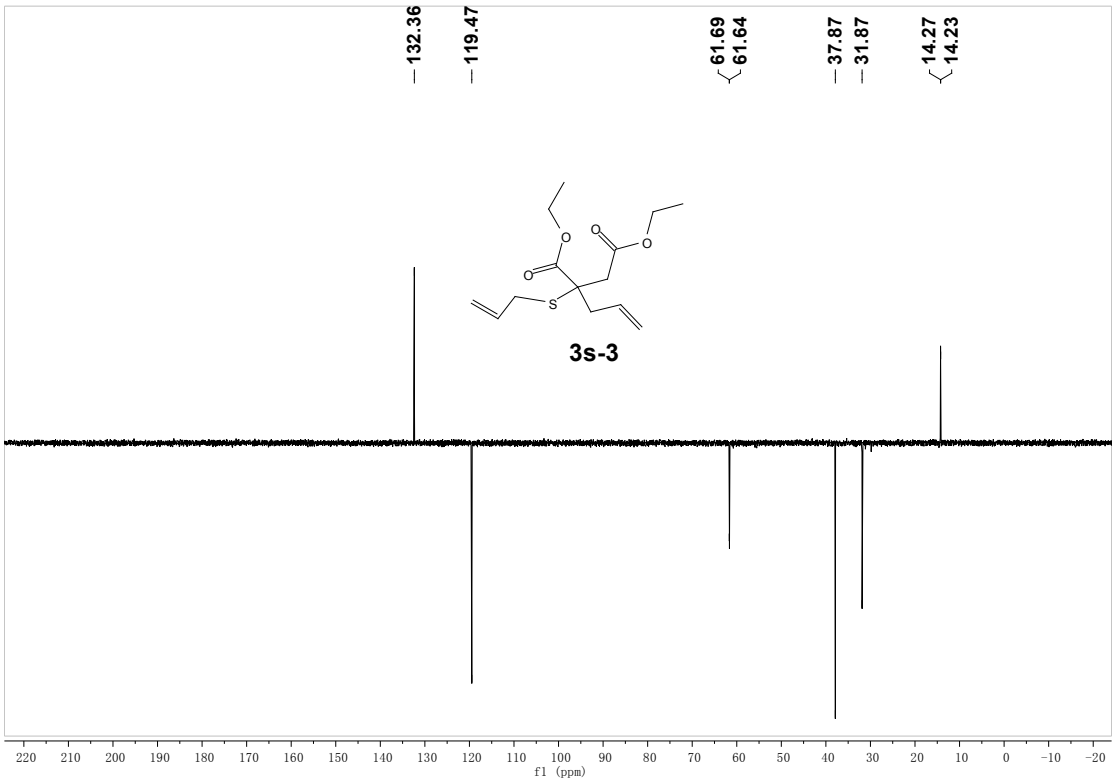
3s-2


171.95
171.86
133.87
118.23
118.12
61.45
61.42
46.51
46.38
36.48
35.69
14.33
14.26
3s-2
f1 (ppm)

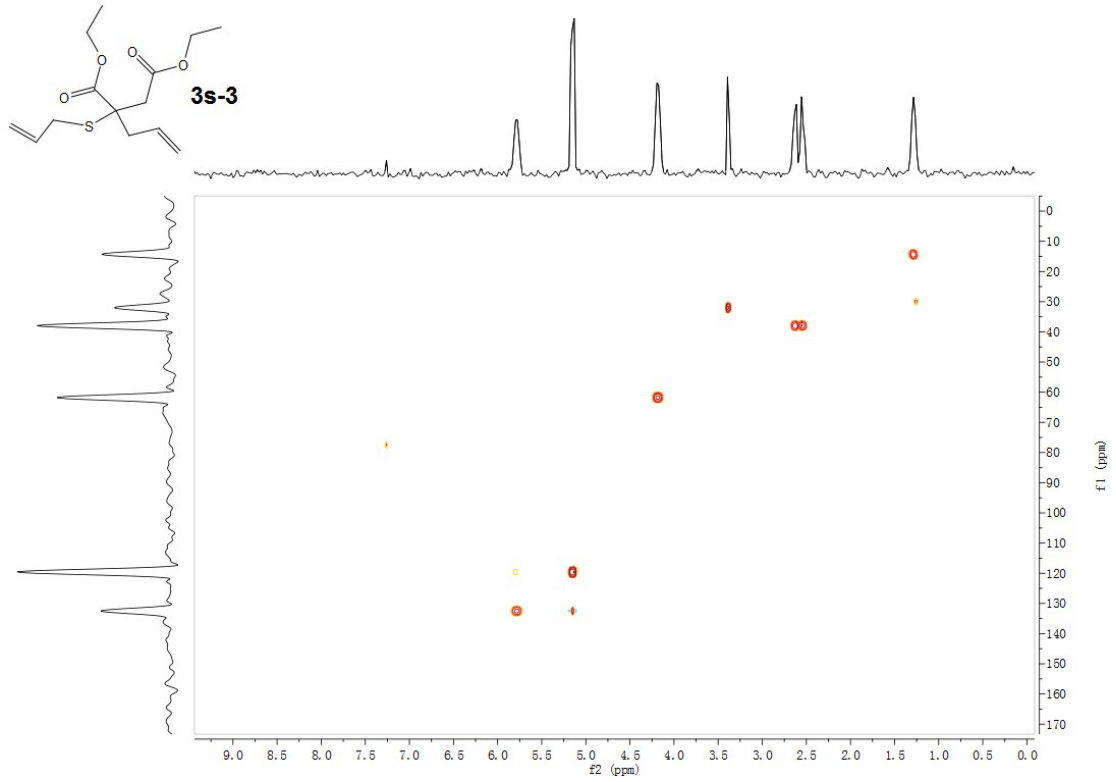

5.82
5.81
5.80
5.79
5.79
5.78
5.77
5.77
5.76
5.75
5.74
5.16
5.16
5.13
5.13
4.22
4.20
4.19
4.17
4.16
4.14
3.38
2.65
2.63
2.62
2.61
2.56
2.54
2.53
2.51
1.31
1.29
1.28
1.28
1.27
1.25
3s-3
1.99
4.10
4.16
2.00
4.19
6.79
f1 (ppm)



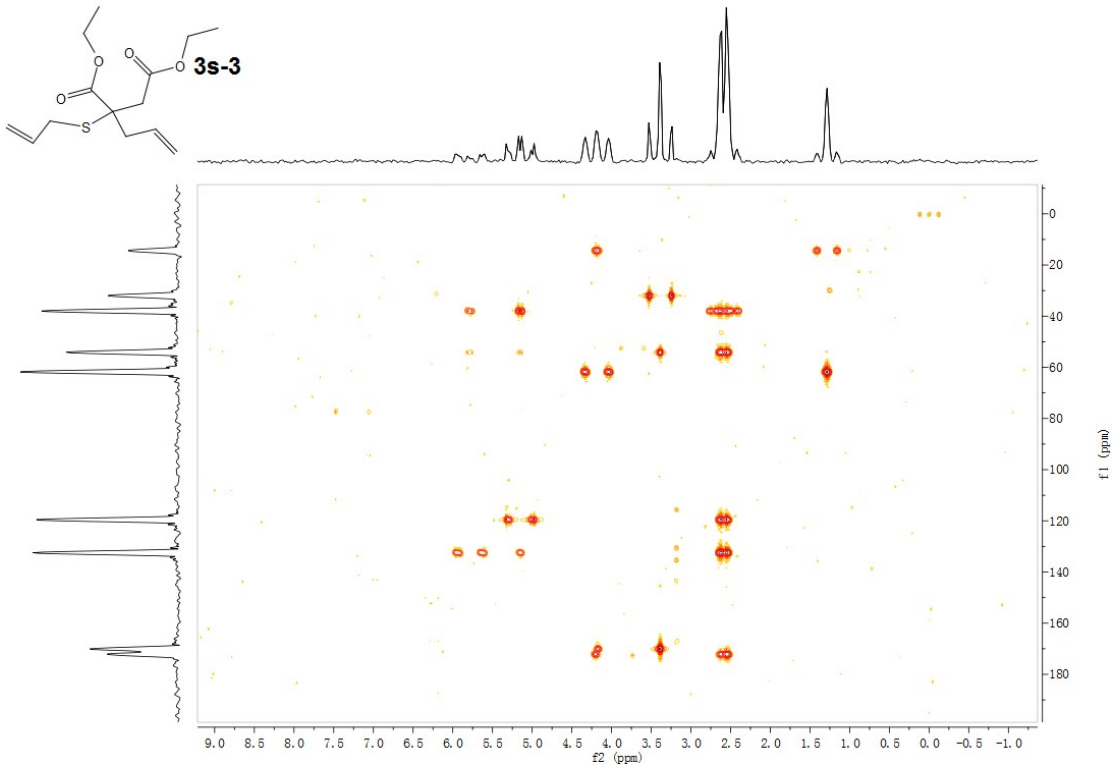
Distortionless Enhancement by Polarisation Transfer (DEPT)



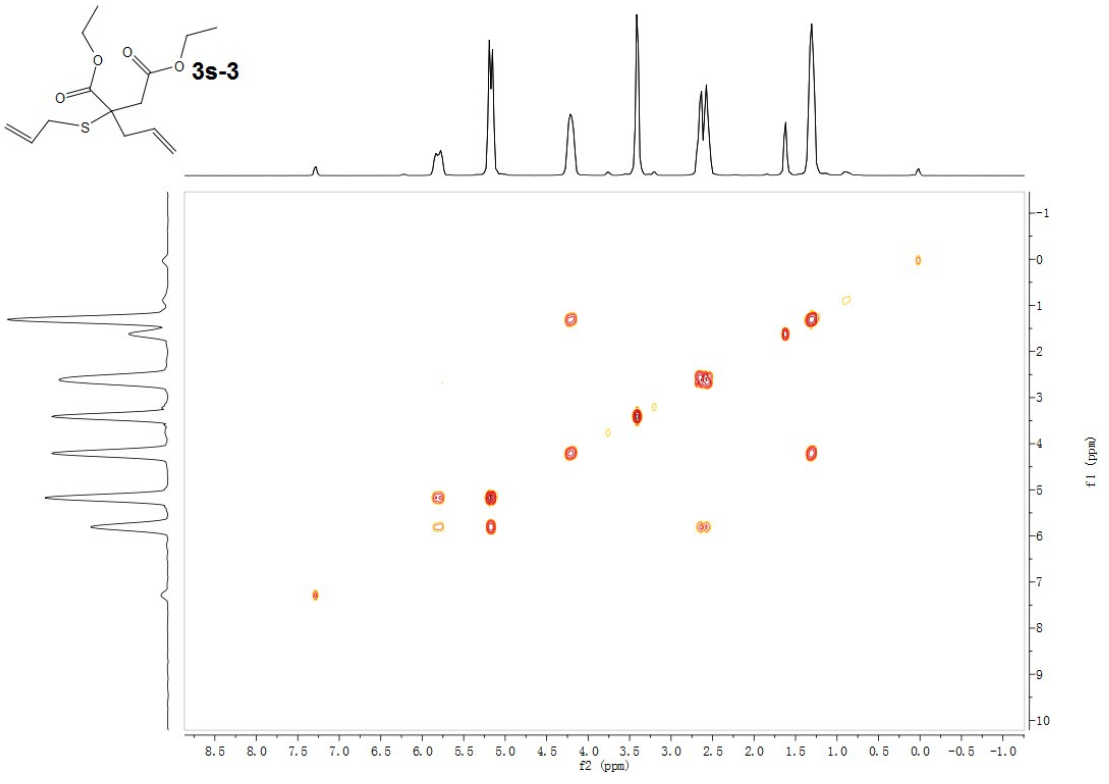
Heteronuclear single-quantum correlation spectroscopy (HSQC)

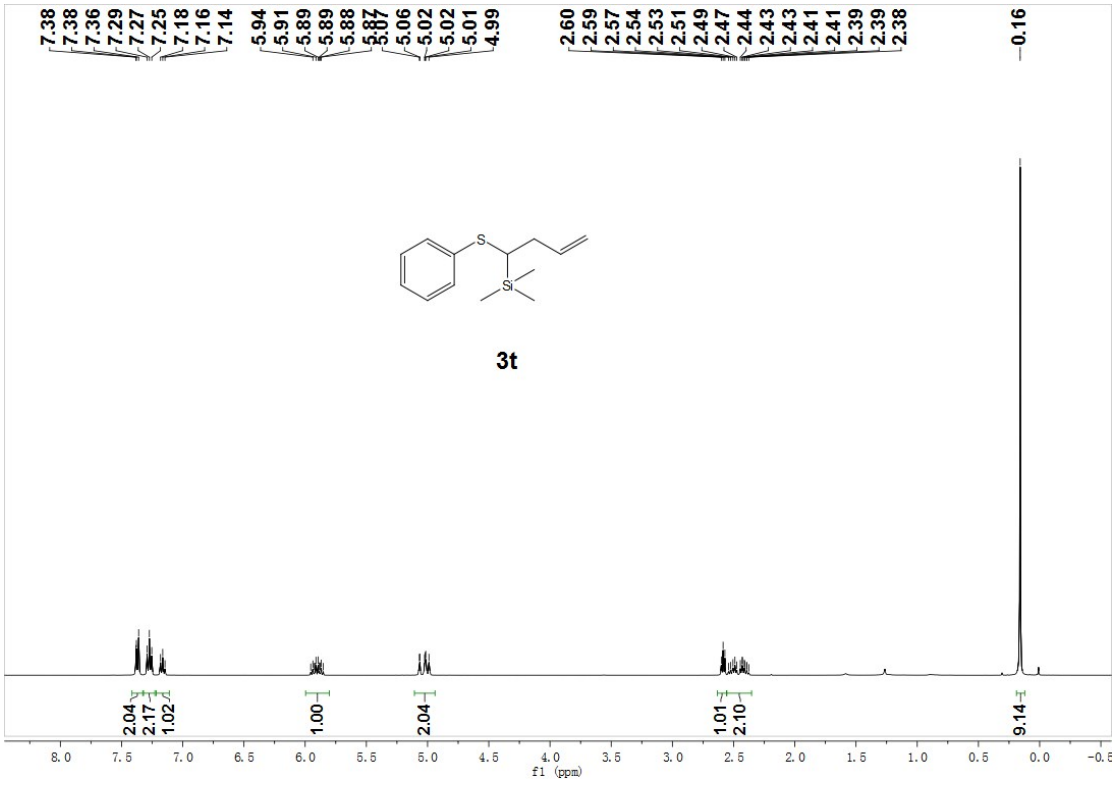


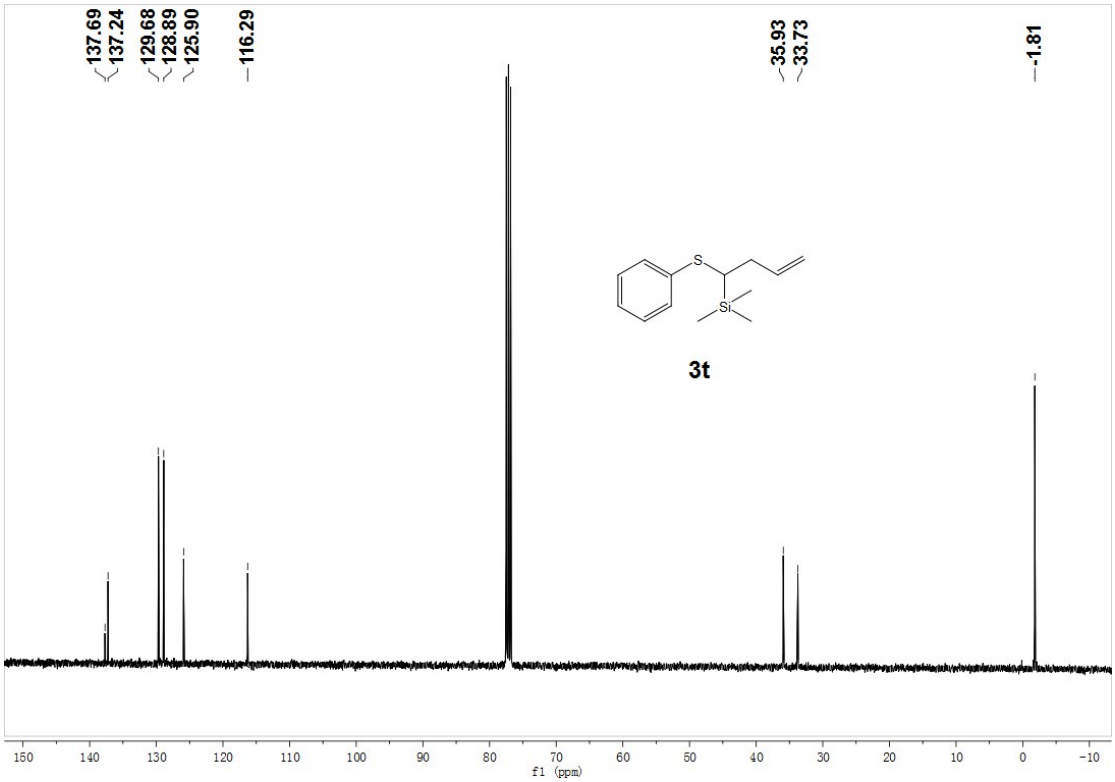
Heteronuclear multiple-bond correlation spectroscopy (HMBC)

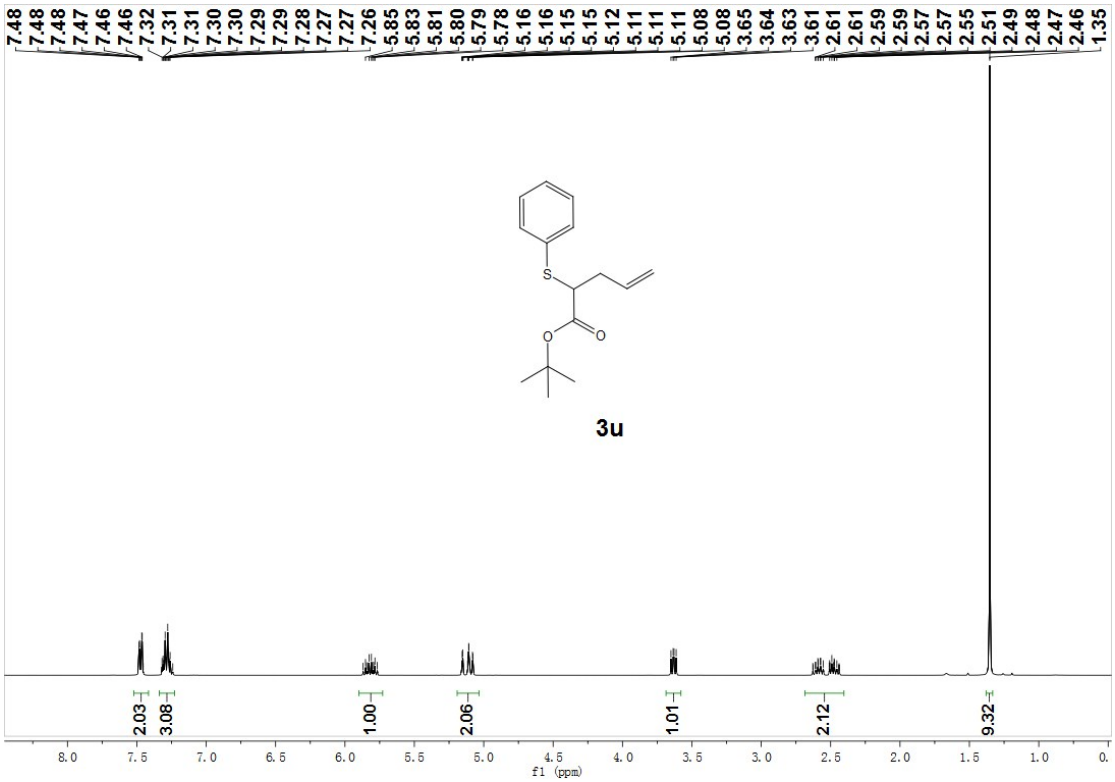


Correlation Spectroscopy (COSY)


3s-3
f2 (ppm)
f1 (ppm)


7.38
7.38
7.36
7.29
7.27
7.25
7.18
7.16
7.14
5.94
5.91
5.89
5.89
5.88
5.87
5.87
5.06
5.02
5.02
5.01
4.99
2.60
2.59
2.57
2.54
2.53
2.51
2.49
2.47
2.44
2.43
2.43
2.41
2.41
2.39
2.39
2.38
0.16
3t
2.04
2.17
1.02
1.00
2.04
1.01
2.10
9.14
f1 (ppm)


137.69
137.24
129.68
128.89
125.90
116.29
35.93
33.73
-1.81
S
Si
3t
f1 (ppm)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7.48
7.48
7.47
7.46
7.46
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
5.85
5.83
5.81
5.80
5.79
5.78
5.16
5.15
5.15
5.12
5.11
5.11
5.11
5.08
5.08
3.65
3.64
3.63
3.61
2.61
2.61
2.59
2.59
2.57
2.57
2.55
2.51
2.49
2.48
2.47
2.46
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O
3u
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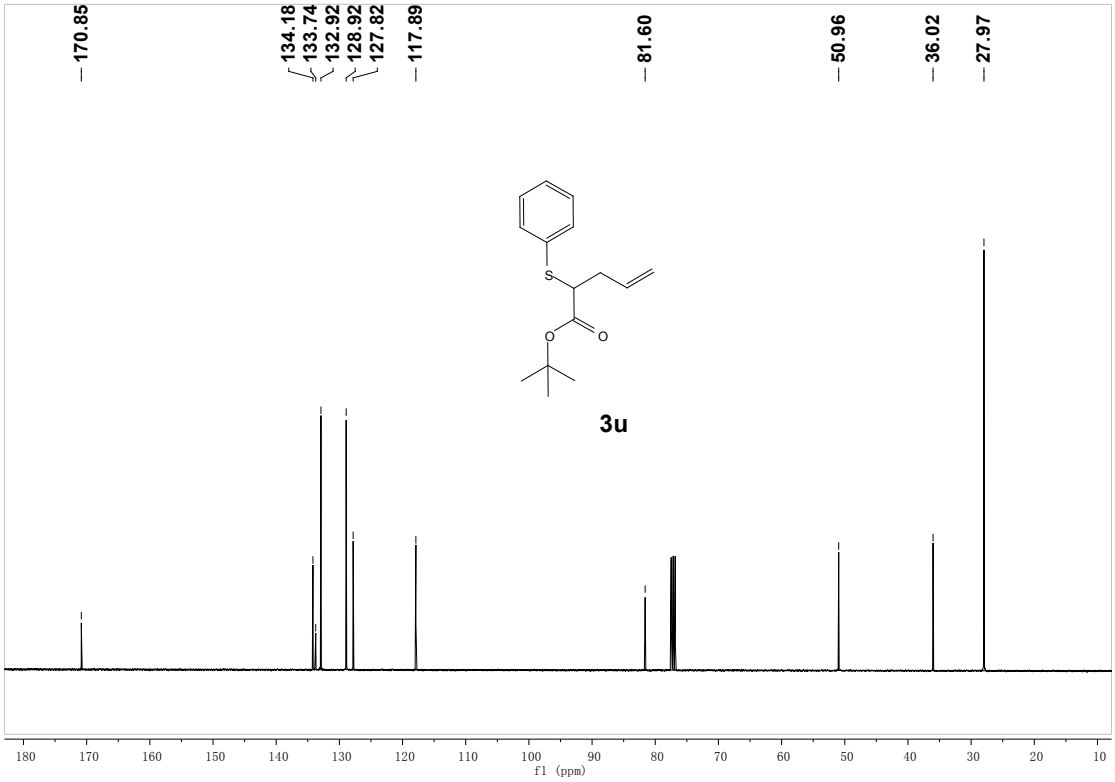
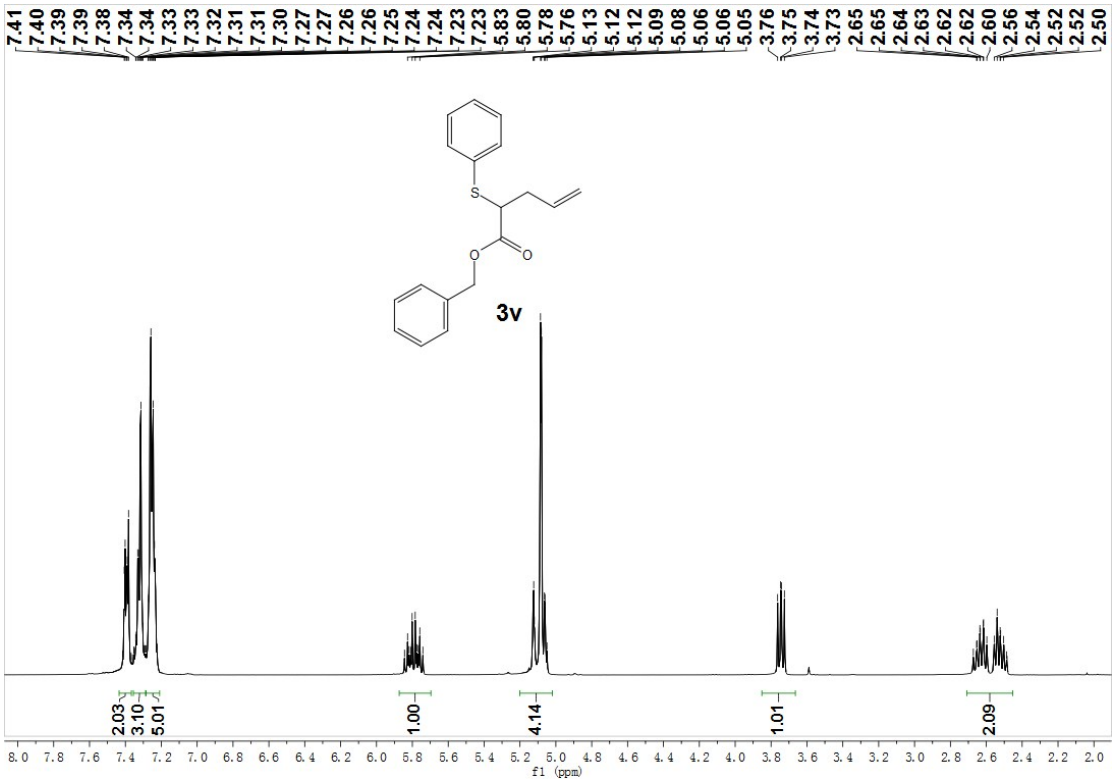
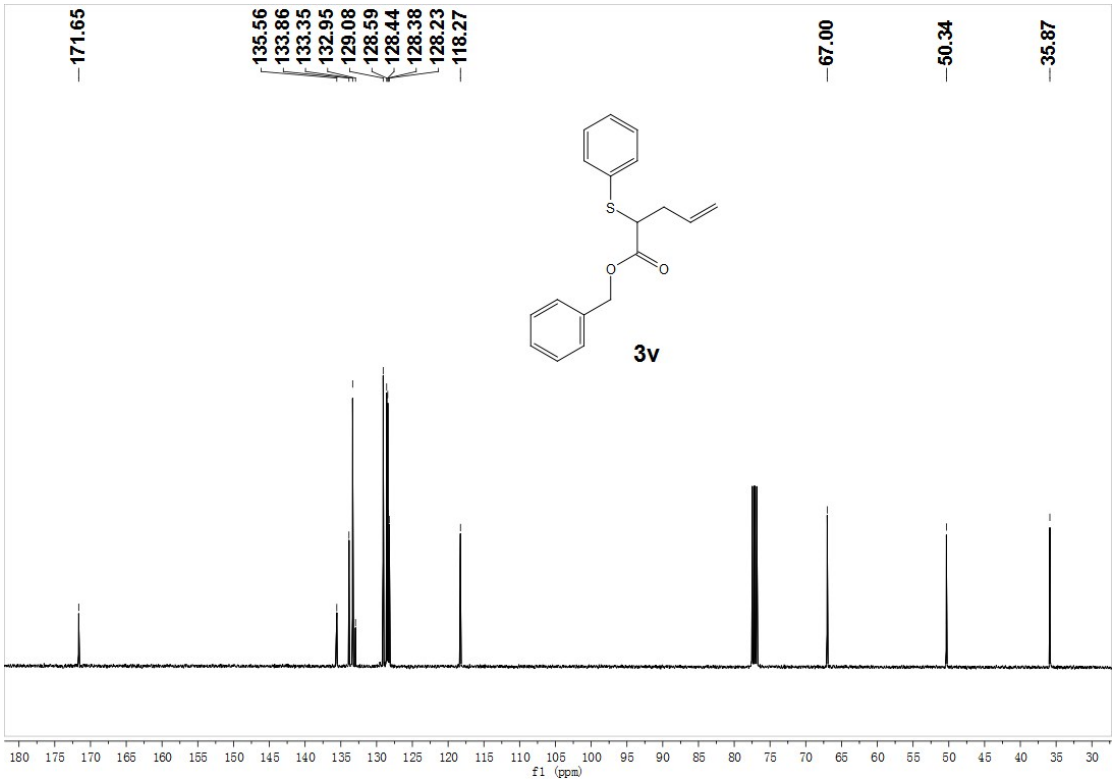
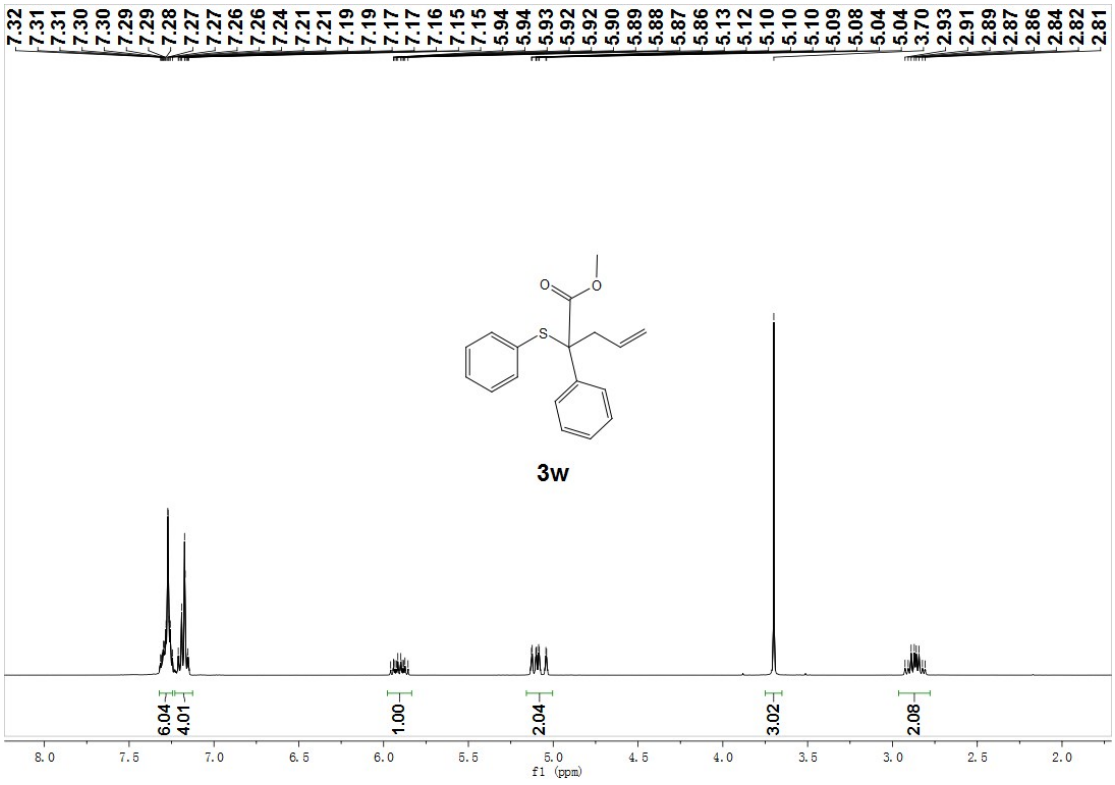
3.08
1.00
2.06
1.01
2.12
9.32
f1 (ppm)


170.85
134.18
133.74
132.92
128.92
127.82
117.89
81.60
50.96
36.02
27.97
S
O
O
3u
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.41 7.40 7.39 7.39 7.38 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.23 5.83 5.80 5.78 5.76 5.13 5.12 5.12 5.09 5.08 5.06 5.06 5.05 3.76 3.75 3.74 3.73 2.65 2.65 2.64 2.63 2.62 2.62 2.60 2.56 2.54 2.52 2.52 2.50
S
O
O
3v
2.03
3.10
5.01
1.00
4.14
1.01
2.09
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)


171.65
135.56
133.86
133.35
132.95
129.08
128.59
128.44
128.38
128.23
118.27
67.00
50.34
35.87
S
O
O
O
3v
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)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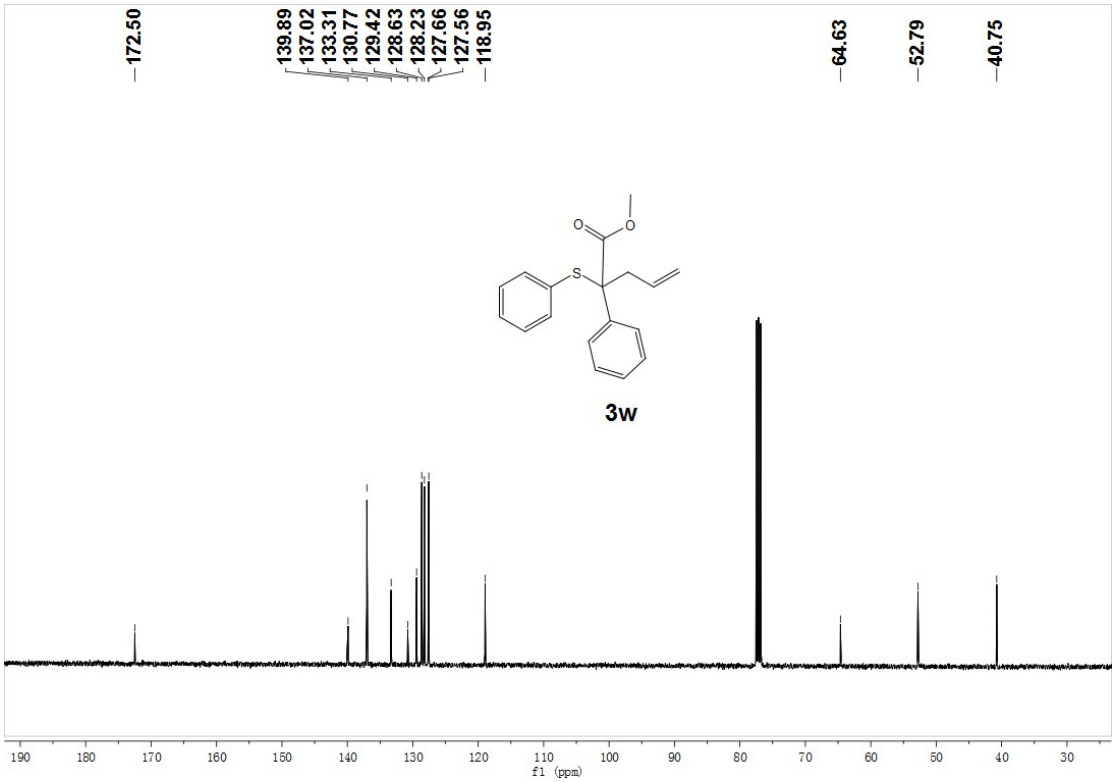
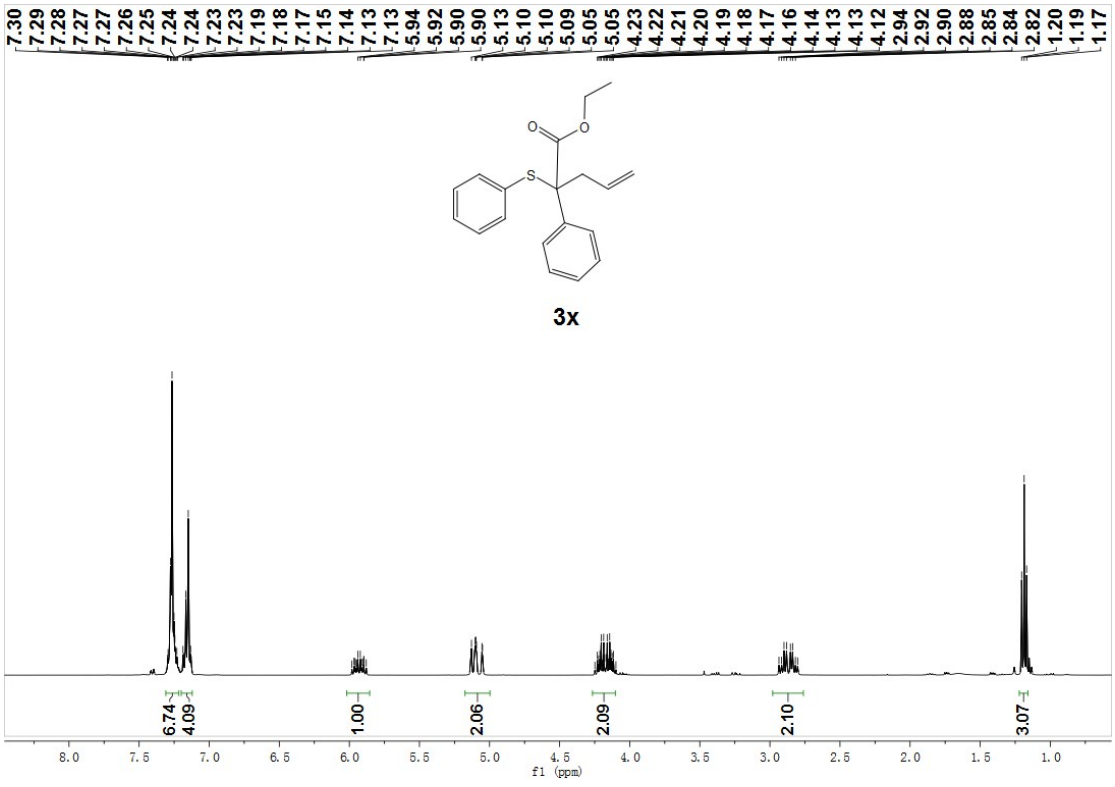
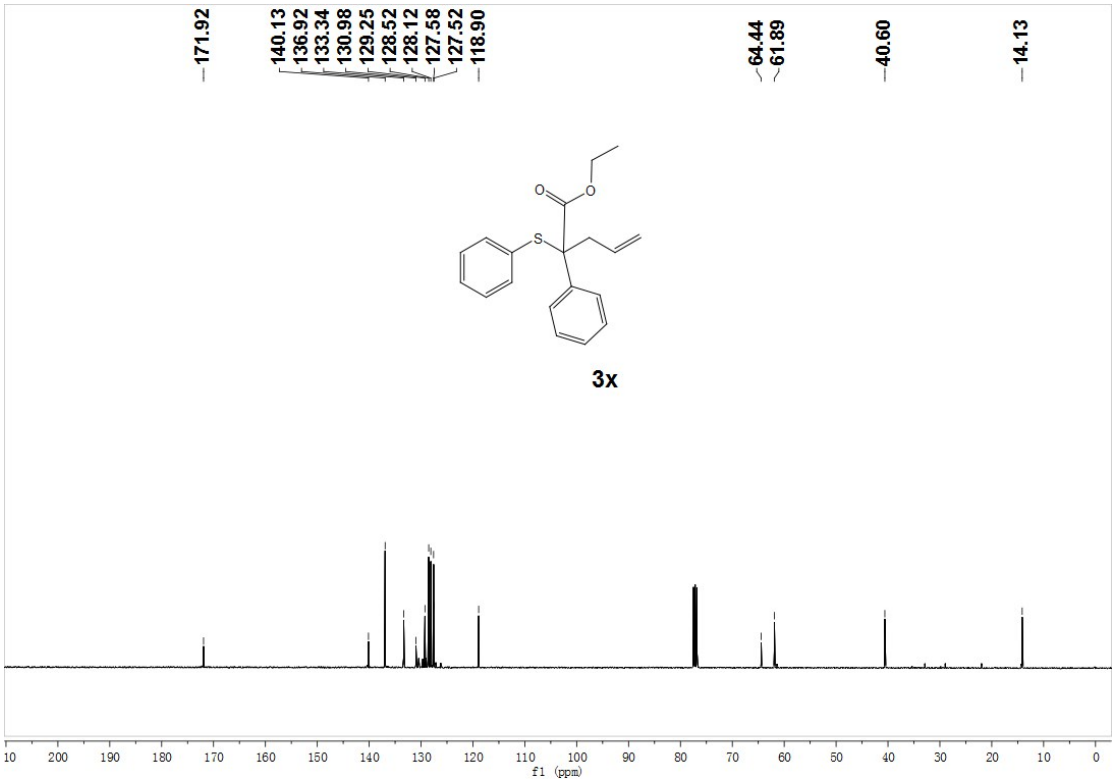
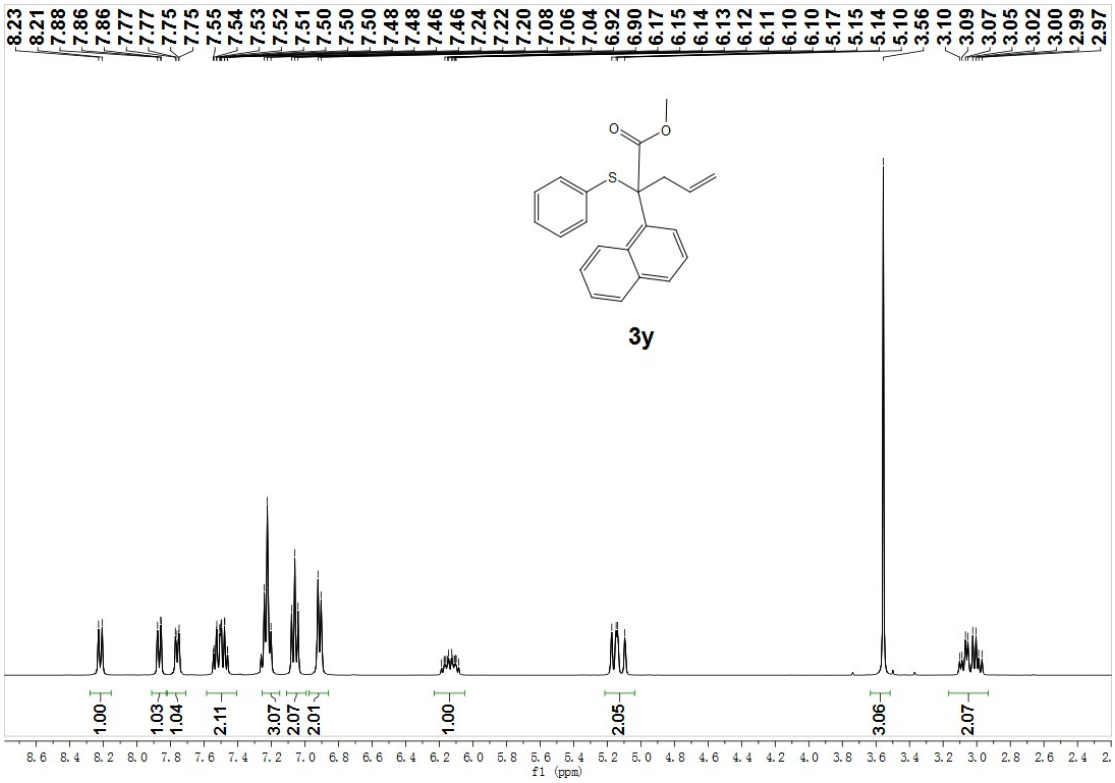
7.29
7.28
7.27
7.27
7.26
7.26
7.24
7.21
7.21
7.19
7.19
7.17
7.17
7.16
7.15
7.15
5.94
5.93
5.92
5.92
5.90
5.89
5.88
5.87
5.86
5.13
5.12
5.10
5.10
5.10
5.09
5.08
5.04
5.04
3.70
2.93
2.91
2.89
2.87
2.86
2.84
2.82
2.81
O
O
S
3w
6.04
4.01
1.00
2.04
3.02
2.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)


172.50
139.89
137.02
133.31
130.77
129.42
128.63
128.23
127.66
127.56
118.95
64.63
52.79
40.75
3w
f1 (ppm)

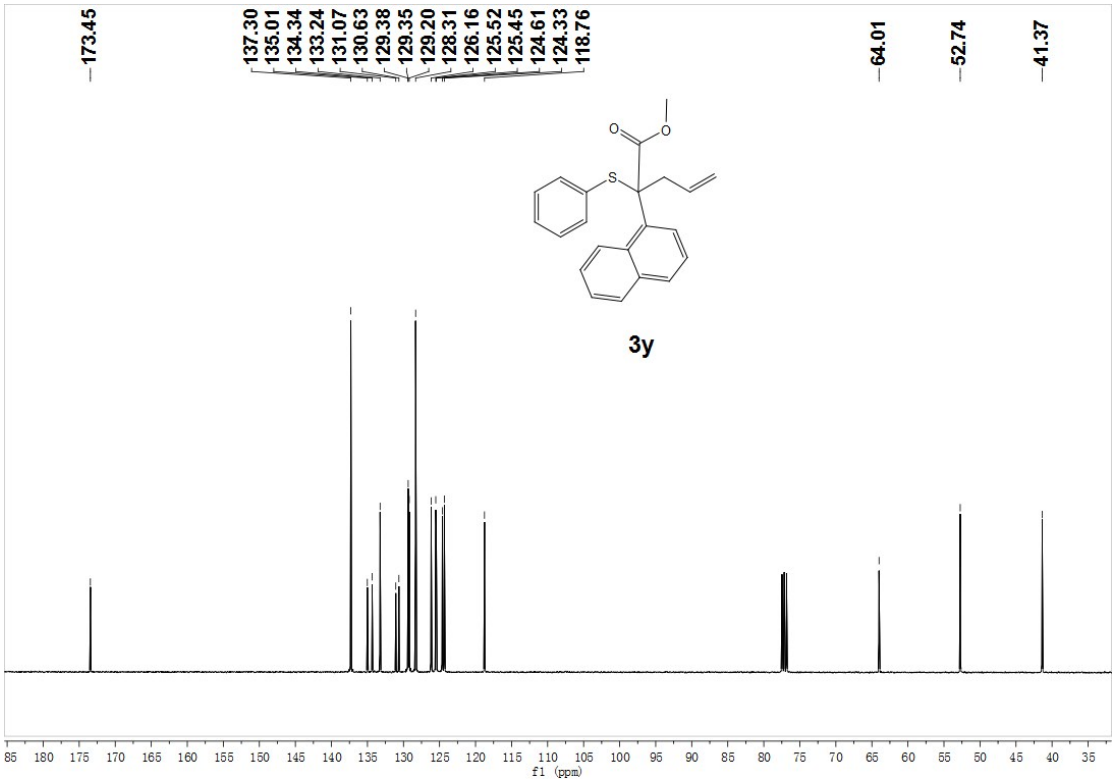

7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.19
7.18
7.17
7.15
7.14
7.13
7.13
5.94
5.92
5.90
5.90
5.13
5.10
5.10
5.09
5.05
5.05
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.14
4.13
4.13
4.12
2.94
2.92
2.90
2.88
2.85
2.84
2.82
1.20
1.19
1.17
3x
6.74
4.09
1.00
2.06
2.09
2.10
3.07
f1 (ppm)


171.92
140.13
136.92
133.34
130.98
129.25
128.52
128.12
127.58
127.52
118.90
64.44
61.89
40.60
14.13
O
O
S
f1 (ppm)

3x


8.23
8.21
7.88
7.86
7.86
7.77
7.77
7.75
7.75
7.55
7.54
7.53
7.52
7.51
7.50
7.50
7.50
7.48
7.48
7.46
7.46
7.24
7.22
7.20
7.08
7.06
7.04
6.92
6.90
6.17
6.15
6.14
6.13
6.12
6.11
6.10
6.10
5.17
5.15
5.14
5.10
3.56
3.10
3.09
3.07
3.05
3.02
3.00
2.99
2.97
1.00
1.03
1.04
2.11
3.07
2.07
2.01
1.00
2.05
3.06
2.07
O
O
S
f1 (ppm)

3y


173.45
137.30
135.01
134.34
133.24
131.07
130.63
129.38
129.35
129.20
128.31
126.16
125.52
125.45
124.61
124.33
118.76
64.01
52.74
41.37
O
O
S
3y
f1 (ppm)