Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Transition Metal-Free sp^3C-H Bond Coupling among Three Methyl Groups

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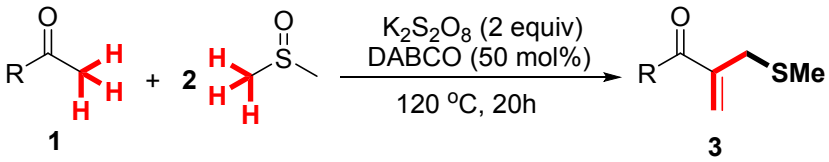
I. General Information

Except noted otherwise, all reactions were carried out in Schlenk tubes. Reagents and solvents were obtained from commercial sources and used without further purification. The ^{1}H and ^{13}C spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz and 100 MHz, and chemical shifts were reported in parts per million (ppm). Flash column chromatography was performed using silica gel of 300-400 μm. The GC-MS results were recorded on a GC-MS QP2010 equipmment, GC analysis was performed on GC 2010 Plus. The electron ionization (EI) method was used for HRMS measurement, and the mass analyzer type is TOF for EI. The HRMS (EI) was recorded on an Esquire 3000 plus instrument.

II. General Procedures



In a Schlenk tube of 25 mL, DABCO (0.1 mmol, 50 mol%) and acetophenone **1** (0.2 mmol, 1.0 equiv) were dissolved in DMSO (1.2 mL) and stirred at room temperature for 1 minutes. Then $K_2S_2O_8$ (0.4 mmol, 2 equiv) were added. The mixture was stirred at 120 ºC for 20 h under N_2 atmosphere. After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3×5 mL), and dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired product.

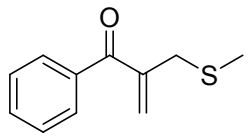
Gram scale synthesis

A round-bottomed of 250 mL flask equipped with a magnetic stir bar (20 mm) was charged with DABCO (5 mmol, 50 mol%) and ortho-hydroxyacetophenone (**1x**, 10 mmol) were dissolved in DMSO (60 mL) and stirred at room temperature for 1 minutes. Then $K_2S_2O_8$ (20 mmol, 2 equiv) were added. The mixture was stirred at 120

ºC for 35 h under N_2 atmosphere. After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (30 mL), washed with water (30 mL), extracted with ethyl acetate (3×30 mL), and dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired product **3x** in 68% yield (1414mg).

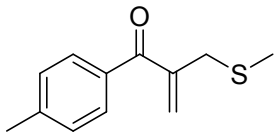
III. Spectra Data of the Products

2-(methylthiomethyl)-1-phenylprop-2-en-1-one (3a)



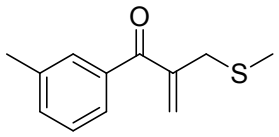
Prepared according to the general procedure to afford a yellow oil in 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 5.92 (s, 1H), 5.68 (s, 1H), 3.54 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0, 143.7, 137.5, 132.5, 129.5, 128.3, 126.0, 35.3, 15.5. **HRMS (EI)**: calcd for $C_{11}H_{12}OS$: 192.0609; found: 192.0602.

2-(methylthiomethyl)-1-(p-tolyl)prop-2-en-1-one (3b)



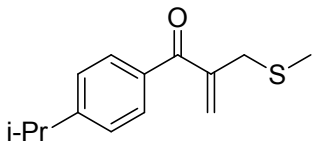
Following the general procedure to afford a yellow oil in 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 5.87 (s, 1H), 5.64 (s, 1H), 3.53 (s, 2H), 2.42 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 196.7, 143.9, 143.3, 134.8, 129.7, 129.0, 125.1, 100.0, 35.5, 21.6, 15.5. **HRMS (EI)**: calcd for $C_{12}H_{14}OS$: 206.0765; found: 206.0761.

2-(methylthiomethyl)-1-(m-tolyl)prop-2-en-1-one (3c)



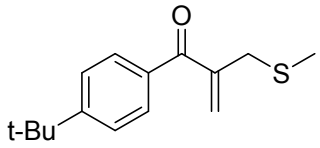
Following the general procedure to afford a yellow oil in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.37 (d, J = 7.3 Hz, 1H), 7.33 (t, J = 14.8 Hz, 1H), 5.91 (s, 1H), 5.67 (s, 1H), 3.53 (s, 2H), 2.41 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.2, 143.9, 138.1, 137.5, 133.2, 129.9, 128.1, 126.8, 125.8, 35.3, 21.3, 15.5. **HRMS (EI)**: calcd for $C_{12}H_{14}OS$: 206.0765; found: 206.0757.

1-(4-isopropylphenyl)-2-(methylthiomethyl)prop-2-en-1- one (3d)



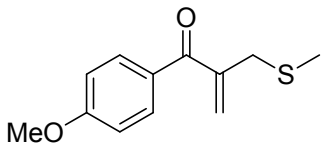
Following the general procedure to afford a yellow oil in 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.87 (s, 1H), 5.66 (s, 1H), 3.53 (s, 2H), 2.97 (dt, J = 13.8, 6.9 Hz, 1H), 2.12 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 154.1, 143.9, 135.1, 129.9, 126.4, 125.0, 35.5, 34.2, 23.7, 15.5. **HRMS (EI)**: calcd for $C_{14}H_{18}OS$: 234.1078; found: 234.1076.

1-(4-(tert-butyl)phenyl)-2-(methylthiomethyl)prop-2-en-1-one (3e)



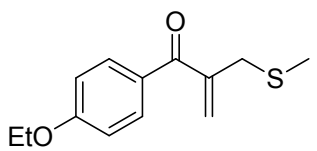
Following the general procedure to afford a yellow oil in 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 5.87 (s, 1H), 5.66 (s, 1H), 3.53 (s, 2H), 2.12 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 156.3, 143.8, 134.7, 129.6, 125.2, 125.1, 35.5, 35.0, 31.1, 15.4. **HRMS (EI)**: calcd for $C_{15}H_{20}OS$: 248.1235; found: 248.1231.

1-(4-methoxyphenyl)-2-(methylthiomethyl)prop-2-en-1-one (3f)



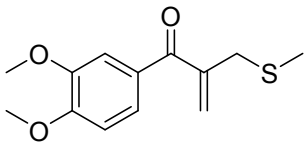
Following the general procedure to afford a yellow oil in 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 7.7 Hz, 2H), 5.82 (s, 1H), 5.60 (s, 1H), 3.87 (s, 3H), 3.54 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 163.3, 143.9, 132.0, 130.0, 123.9, 113.6, 55.5, 35.8, 15.5. **HRMS (EI)**: calcd for $C_{12}H_{14}O_2S$: 222.0715; found: 222.0706.

1-(4-ethoxyphenyl)-2-(methylthiomethyl)prop-2-en-1-one (3g)



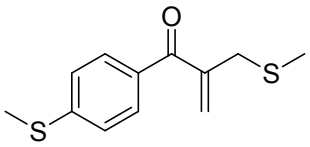
Following the general procedure to afford a yellow oil in 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 7.7 Hz, 2H), 5.82 (s, 1H), 5.60 (s, 1H), 3.87 (s, 3H), 3.54 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 163.3, 143.9, 132.0, 130.0, 123.9, 113.6, 55.5, 35.8, 15.5. **HRMS (EI)**: calcd for $C_{13}H_{16}O_2S$: 236.0871; found: 236.0864.

1-(3,4-dimethoxyphenyl)-2-(methylthiomethyl)prop-2-en-1-one (3h)



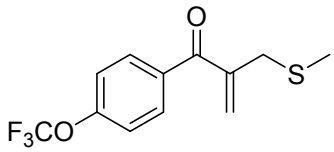
Following the general procedure to afford a yellow oil in 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.82 (s, 1H), 5.61 (s, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.54 (s, 2H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 153.2, 149.0, 143.8, 130.0, 124.7, 123.6, 111.6, 109.7, 56.0, 55.9, 35.9, 15.5. **HRMS (EI)**: calcd for $C_{13}H_{16}O_3S$: 252.0820; found: 252.0817.

2-(methylthiomethyl)-1-(4-methylthiophenyl)prop-2-en-1-one (3i)



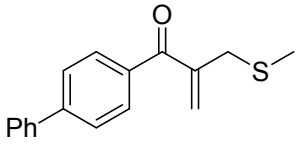
Following the general procedure to afford a yellow oil in 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.86 (s, 1H), 5.62 (s, 1H), 3.52 (s, 2H), 2.52 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.0, 145.4, 143.8, 133.5, 130.1, 124.8, 124.7, 35.6, 15.5, 14.8. **HRMS (EI)**: calcd for $C_{12}H_{14}OS_2$: 238.0486; found: 238.0481.

2-(methylthiomethyl)-1-(4-(trifluoromethoxy)phenyl) prop-2-en-1-one (3j)



Following the general procedure to afford a yellow oil in 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.93 (s, 1H), 5.66 (s, 1H), 3.53 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 152.2, 143.7, 135.7, 131.4, 125.9, 120.2, 35.3, 30.6 (d, *J* = 180.8 Hz), 15.5. **HRMS (EI)**: calcd for $C_{12}H_{11}F_3O_2S$: 276.0432; found: 276.0431.

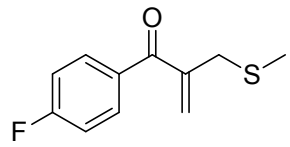
1-([1,1'-biphenyl]-4-yl)-2-(methylthiomethyl)prop-2-en-1-one (3k)



Following the general procedure to afford a yellow oil in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 5.93 (s, 1H), 5.72 (s, 1H), 3.57 (s, 2H), 2.15 (s, 3H); **^{13}C NMR**

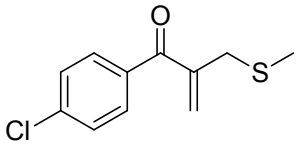
(100 MHz, $CDCl_3$) δ 196.6, 145.3, 143.9, 139.9, 136.1, 130.2, 129.0, 128.2, 127.3, 127.0, 125.5, 35.4, 15.5. **HRMS (EI)**: calcd for $C_{17}H_{16}OS$: 268.0922; found: 268.0914.

1-(4-fluorophenyl)-2-(methylthiomethyl)prop-2-en-1-one (3l)



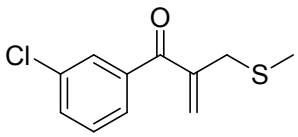
Following the general procedure to afford a yellow oil in 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.79 (m, 2H), 7.16-7.12 (m, 2H), 5.90 (s, 1H), 5.63 (s, 1H), 3.53 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 165.4 (d, J = 254.4 Hz), 143.7, 133.6 (d, J = 3.1 Hz), 132.1 (d, J = 9.2 Hz), 125.3, 115.5 (d, J = 21.9 Hz), 35.4, 15.5. **HRMS (EI)**: calcd for $C_{11}H_{11}FOS$: 210.0515; found: 210.0511.

1-(4-chlorophenyl)-2-(methylthiomethyl)prop-2-en-1-one (3m):



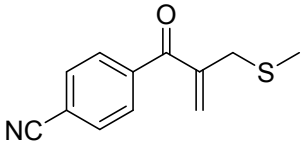
Following the general procedure to afford a yellow oil in 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 5.92 (s, 1H), 5.64 (s, 1H), 3.52 (s, 2H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 143.7, 138.9, 135.7, 130.9, 128.6, 125.8, 35.3, 15.6. **HRMS (EI)**: calcd for $C_{11}H_{11}ClOS$: 226.0219; found: 226.0213.

1-(3-chlorophenyl)-2-(methylthiomethyl)prop-2-en-1-one (3n)



Following the general procedure to afford a yellow oil in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 5.95 (s, 1H), 5.68 (s, 1H), 3.52 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 143.5, 139.1, 134.5, 132.4, 129.6, 129.4, 127.5, 126.5, 35.1, 15.5. **HRMS (EI)**: calcd for $C_{11}H_{11}ClOS$: 226.0219; found: 226.02161.

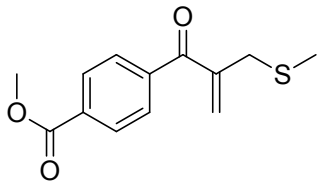
4-(2-(methylthiomethyl)acryloyl)benzonitrile (3o)



Following the general procedure to afford a yellow oil in 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 6.01 (s, 1H), 5.67 (s, 1H),

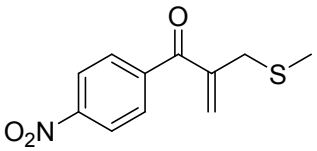
3.53 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.3, 143.5, 141.1, 132.2, 129.7, 127.3, 117.9, 115.7, 34.9, 15.6. **HRMS (EI)**: calcd for $C_{12}H_{11}NOS$: 217.0561; found: 217.0554.

4-(2-(methylthiomethyl)acryloyl)benzoate (3p)



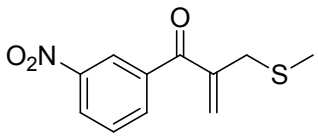
Following the general procedure to afford a yellow oil in 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 5.99 (s, 1H), 5.69 (s, 1H), 3.96 (s, 3H), 3.54 (s, 2H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 166.2, 143.7, 141.2, 133.2, 129.5, 129.2, 127.0, 52.4, 34.9, 15.6. **HRMS (EI)**: calcd for $C_{13}H_{14}O_3S$: 250.0664; found: 250.0661.

2-(methylthiomethyl)-1-(4-nitrophenyl)prop-2-en-1-one (3q)



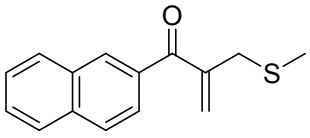
Following the general procedure to afford a yellow oil in 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.92 (s, 1H), 5.64 (s, 1H), 3.52 (s, 2H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 143.7, 138.9, 135.7, 130.9, 128.6, 125.8, 35.3, 15.6. **HRMS (EI)**: calcd for $C_{11}H_{11}NO_3S$: 237.0460; found: 237.0455.

2-(methylthiomethyl)-1-(3-nitrophenyl)prop-2-en-1-one(3r)



Following the general procedure to afford a yellow oil in 83% yield. **1H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 6.03 (s, 1H), 5.70 (s, 1H), 3.55 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.5, 148.1, 143.4, 138.9, 134.9, 129.6, 126.9, 126.8, 124.3, 35.1, 15.6. **HRMS (EI)**: calcd for $C_{11}H_{11}NO_3S$: 237.0460; found: 237.0455.

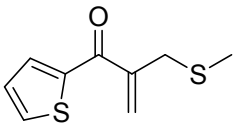
2-(methylthiomethyl)-1-(naphthalen-2-yl)prop-2-en-1-one (3s)



Following the general procedure to afford a yellow oil in 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.98–7.83 (m, 4H), 7.62–7.51 (m, 2H), 5.96 (s, 1H), 5.74 (s,

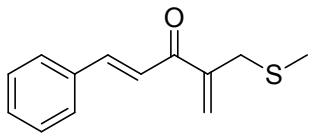
1H), 3.60 (s, 2H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 144.0, 135.3, 134.7, 132.2, 131.2, 129.4, 128.3, 128.3, 127.8, 126.8, 125.7, 125.3, 35.5, 15.6. **HRMS (EI)**: calcd for $C_{15}H_{14}O$: 242.0765; found: 242.0761.

2-(methylthiomethyl)-1-(thiophen-2-yl)prop-2-en-1-one (3t)



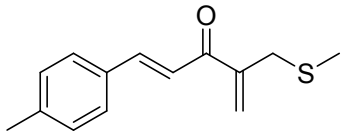
Following the general procedure to afford a yellow oil in 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72–7.66 (m, 2H), 7.14 (t, *J* = 4.3 Hz, 1H), 5.87 (s, 1H), 5.82 (s, 1H), 3.52 (s, 2H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.3, 144.2, 143.4, 134.3, 134.0, 127.9, 123.4, 35.6, 15.3. **HRMS (EI)**: calcd for $C_9H_{10}OS_2$: 198.0173; found: 198.0170.

(E)-4-(methylthiomethyl)-1-phenylpenta-1,4-dien-3-one (3u)



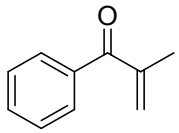
Following the general procedure to afford a yellow solid in 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.7 Hz, 1H), 7.53–7.49 (m, 2H), 7.35–7.30 (m, 3H), 7.22 – 7.16 (m, 1H), 6.05 (s, 1H), 5.82 (s, 1H), 3.39 (s, 2H), 1.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.7, 145.2, 144.3, 134.8, 130.5, 128.9, 128.4, 124.3, 121.6, 34.5, 15.4. **HRMS (EI)**: calcd for $C_{13}H_{14}OS$: 218.0765; found: 218.0760.

(E)-4-(methylthiomethyl)-1-(p-tolyl)penta-1,4-dien-3-one (3v)



Following the general procedure to afford a yellow solid in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.25–7.18 (m, 3H), 6.11 (s, 1H), 5.88 (s, 1H), 3.47 (s, 2H), 2.38 (s, 3H), 2.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 145.3, 144.4, 141.0, 132.0, 129.7, 128.4, 124.0, 120.7, 34.5, 21.5, 15.4. **HRMS (EI)**: calcd for $C_{14}H_{16}OS$: 232.0922; found: 232.0917.

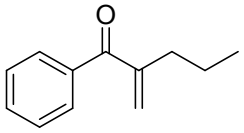
2-methyl-1-phenylprop-2-en-1-one (4a).



Following the general procedure to afford a pale yellow oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 5.83 (s, 1H), 5.54 (s, 1H),

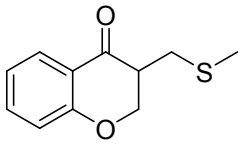
1.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.3, 143.7, 137.7, 132.0, 129.4, 128.1, 127.1, 18.6.

2-methylene-1-phenylpentan-1-one (4b).



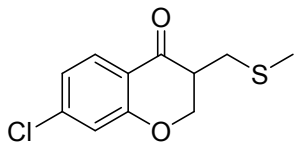
Following the general procedure to afford a yellow oil in 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 5.82 (s, 1H), 5.58 (s, 1H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.62–1.47 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.5, 148.2, 137.9, 132.1, 129.5, 128.1, 125.3, 34.3, 21.3, 13.8.

3-(methylthiomethyl)chroman-4-one (3x)



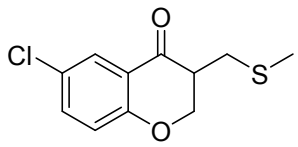
Following the general procedure to afford a yellow oil in 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.66 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.50–4.44 (m, 1H), 3.04 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.89 (ddd, *J* = 13.5, 9.0, 4.2 Hz, 1H), 2.66 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.8, 161.6, 136.1, 127.4, 121.5, 120.4, 117.8, 69.4, 45.4, 30.8, 16.2. **HRMS (EI)**: calcd for $C_{11}H_{12}O_2S$: 208.0558; found: 208.5553.

7-chloro-3-(methylthiomethyl)chroman-4-one (3y)



Following the general procedure to afford a pale yellow solid in 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 1H), 7.06–6.98 (m, 2H), 4.67 (dd, *J* = 11.5, 4.4 Hz, 1H), 4.48 (dd, *J* = 10.7, 9.6 Hz, 1H), 3.03 (dd, *J* = 13.7, 3.8 Hz, 1H), 2.89 (ddd, *J* = 13.1, 8.9, 4.1 Hz, 1H), 2.70–2.61 (m, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8, 161.9, 141.9, 128.6, 122.4, 119.0, 118.0, 69.8, 45.3, 30.7, 16.2. **HRMS (EI)**: calcd for $C_{11}H_{11}ClO_2S$: 242.0168; found: 242.0161.

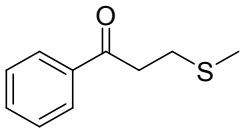
6-chloro-3-(methylthiomethyl)chroman-4-one (3z)



Following the general procedure to afford a pale yellow solid in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (s,

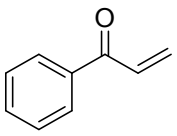
1H), 7.42 (dd, *J* = 8.9, 1.6 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 4.66 (dd, *J* = 11.5, 4.4 Hz, 1H), 4.47 (dd, *J* = 10.8, 9.5 Hz, 1H), 3.02 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.91 (dd, *J* = 9.4, 4.3 Hz, 1H), 2.65 (dd, *J* = 13.6, 9.9 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.7, 160.0, 135.9, 127.1, 126.7, 121.2, 119.6, 69.6, 45.2, 30.6, 16.2. **HRMS (EI)**: calcd for $C_{11}H_{11}ClO_2S$: 242.0168; found: 242.0161.

3-(methylthio)-1-phenylpropan-1-one (C)



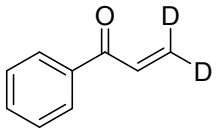
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 3.29 (t, J = 7.3 Hz, 2H), 2.91 (t, J = 7.4 Hz, 2H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.4, 136.6, 133.2, 128.6, 128.0, 38.6, 28.5, 15.9. **HRMS (EI)**: calcd for $C_{10}H_{12}OS$: 180.0609; found: 180.0603.

1-phenylprop-2-en-1-one (D)



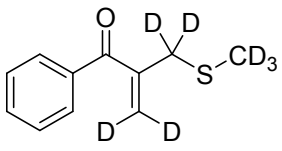
Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.16 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.44 (d, *J* = 17.1 Hz, 1H), 5.94 (d, *J* = 10.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.1, 137.2, 133.0, 132.4, 130.2, 128.7, 128.6.

1-phenylprop-2-en-1-one-3,3-d_2 (D-d_2)



Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.15 (s, 1H).

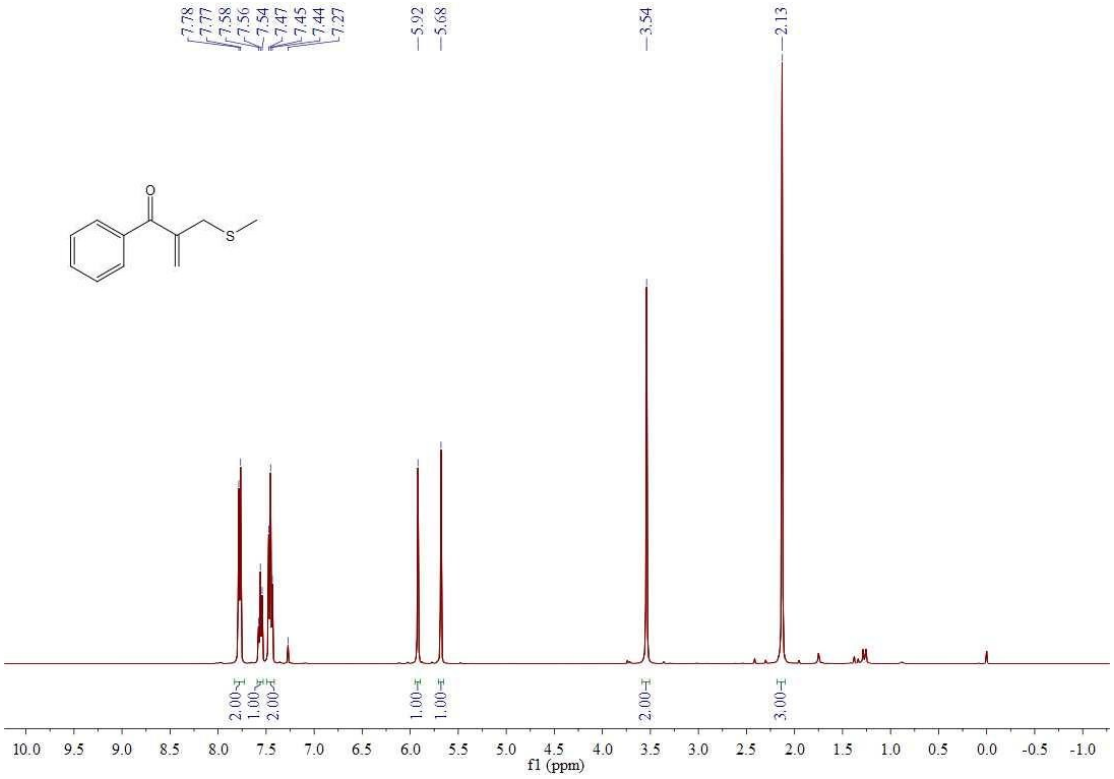
2-((methyl-d_3)thiomethyl-d_2)-1-phenylprop-2-en-1-one-3,3-d_2 (3a-d_7)

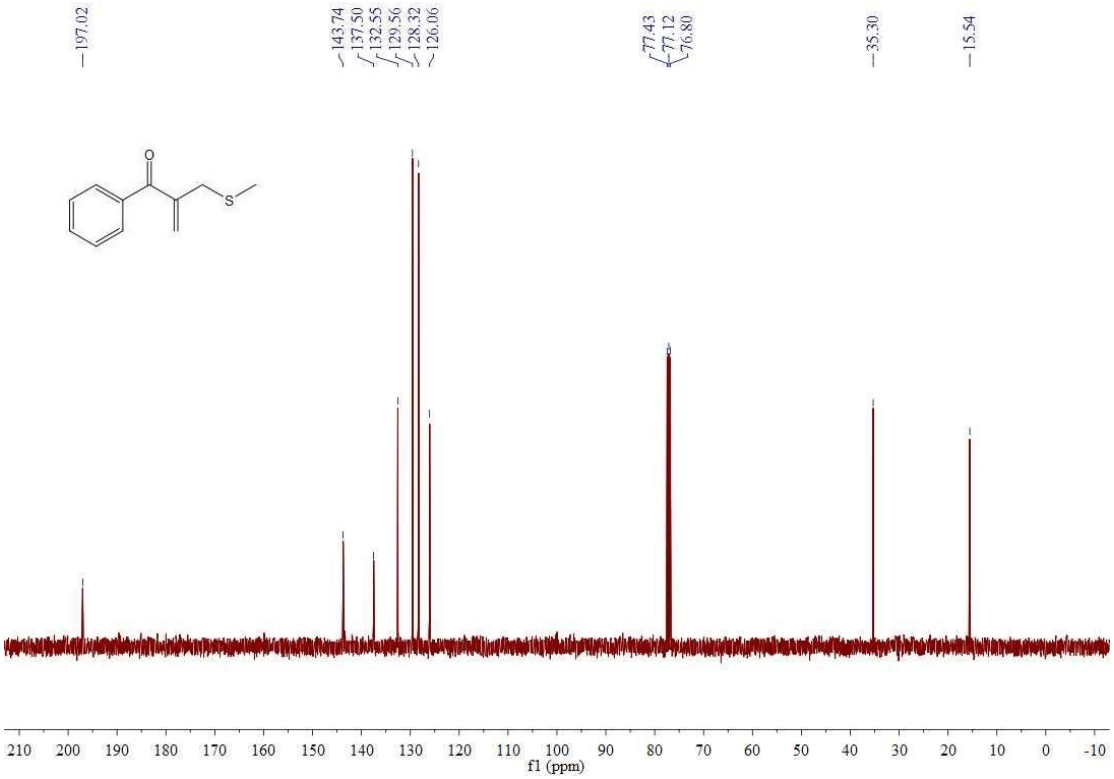


Following the general procedure to afford a yellow oil in 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 5.92 (s, 1H), 5.68 (s, 1H), 3.54 (s, 1H). **HRMS (EI)**: calcd for $C_{11}H_5D_7OS$: 199.1048; found: 199.1042.

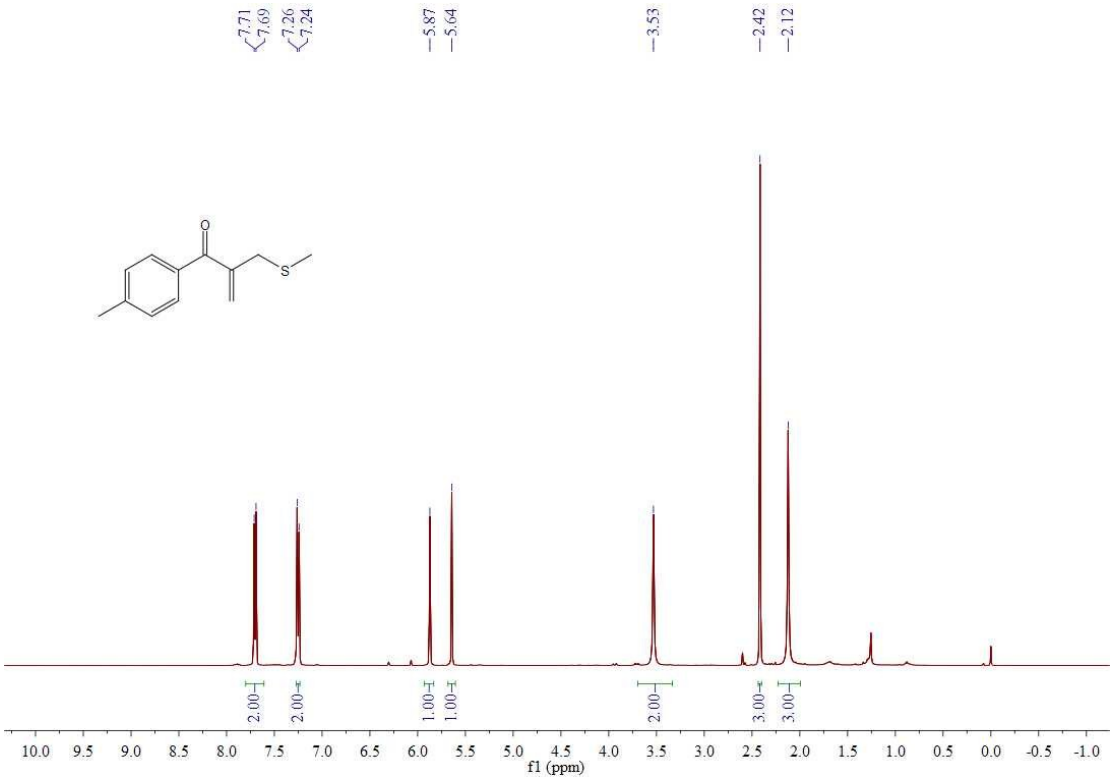
IV. NMR Spectra

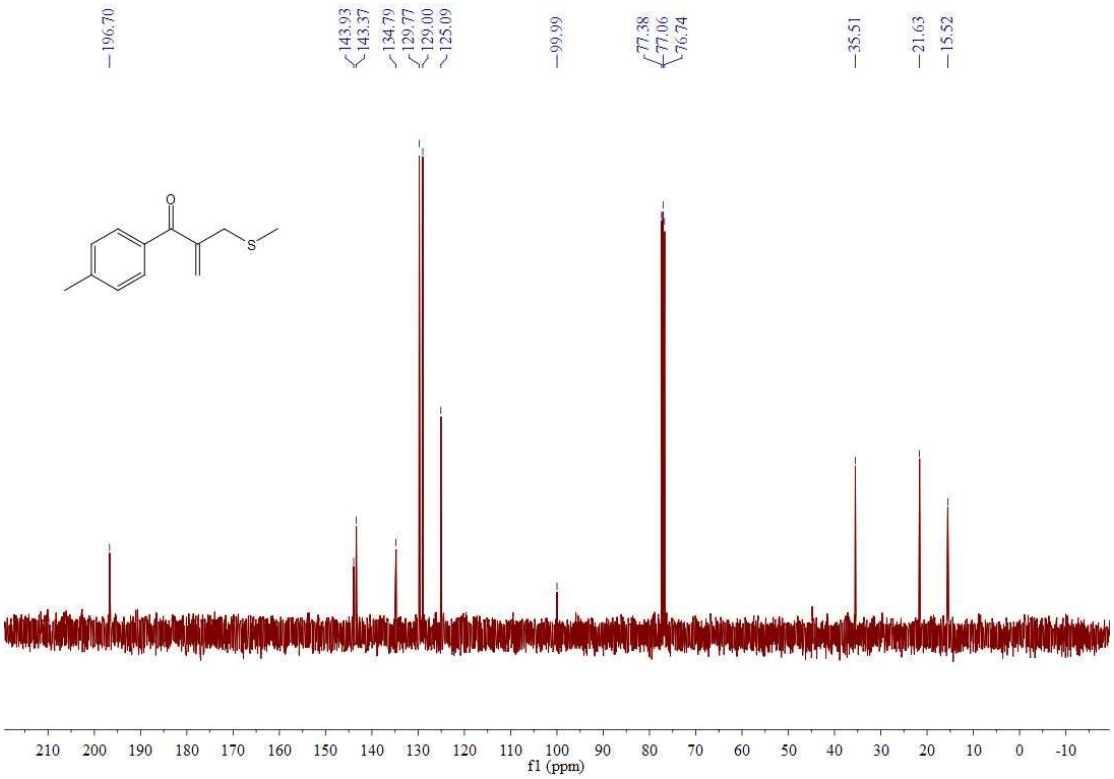
Compound 3a



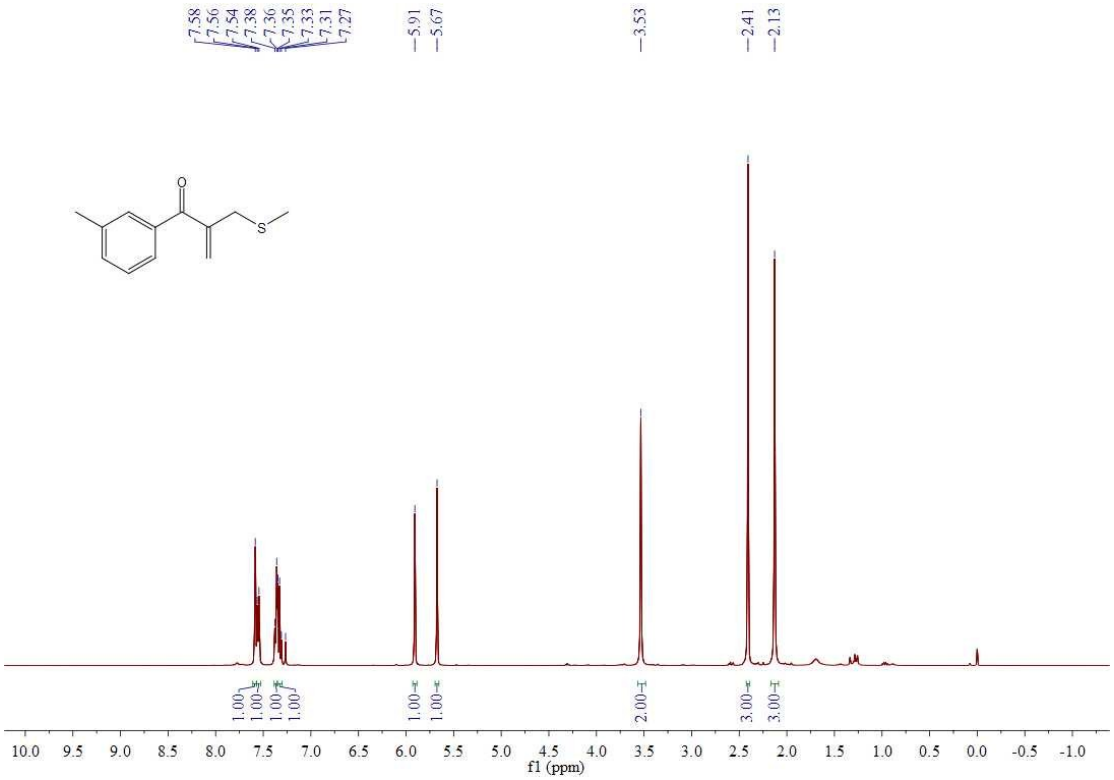


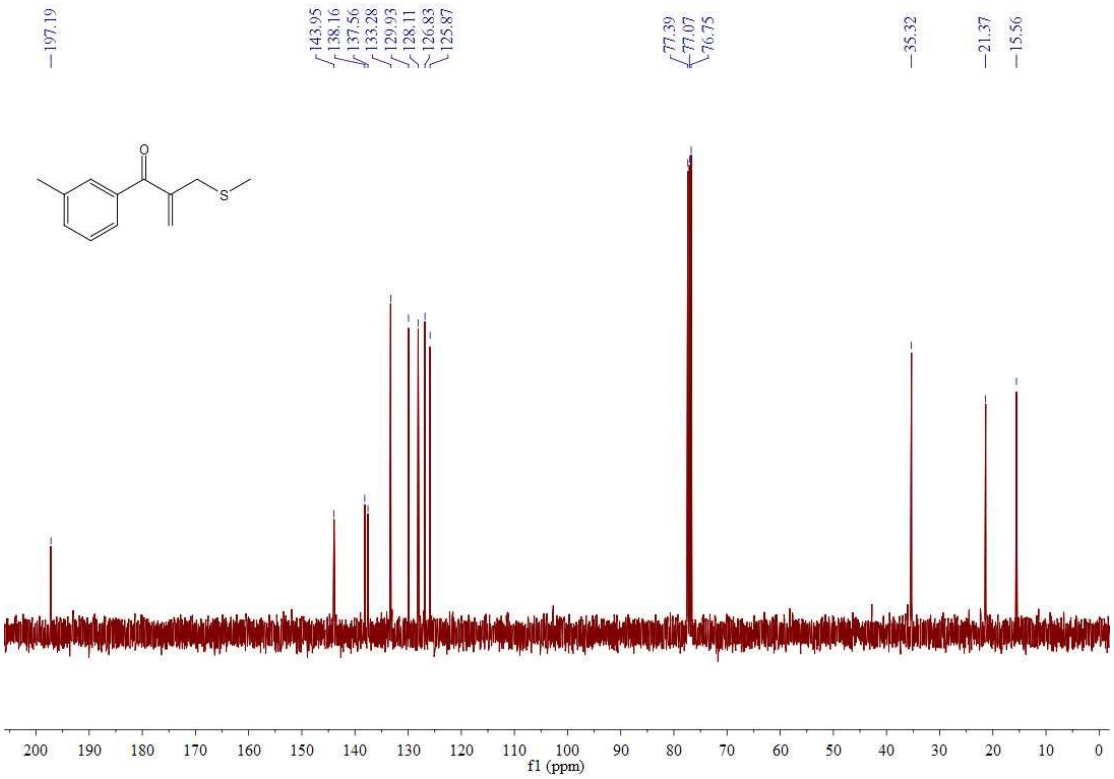
Compound 3b


7.71
7.69
7.26
7.24
5.87
5.64
3.53
2.42
2.12
O
S
2.00
2.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

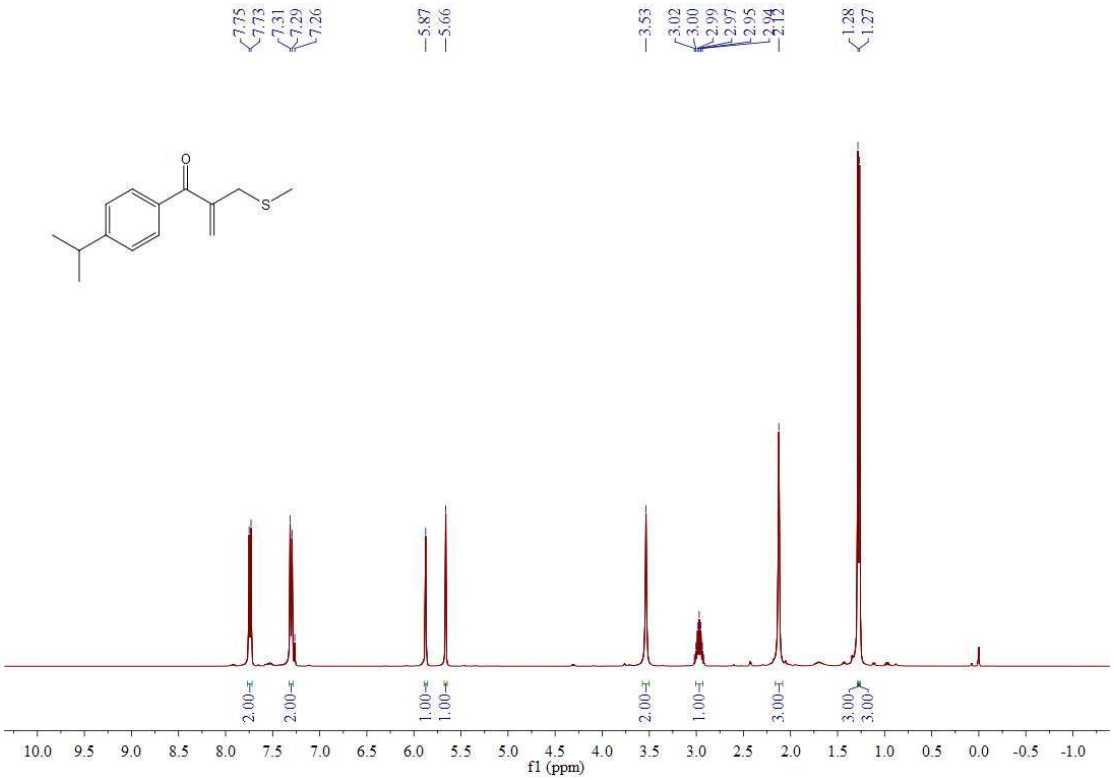

196.70
143.93
143.37
134.79
129.77
129.00
125.09
99.99
77.38
77.06
76.74
35.51
21.63
15.52
O
S
f1 (ppm)

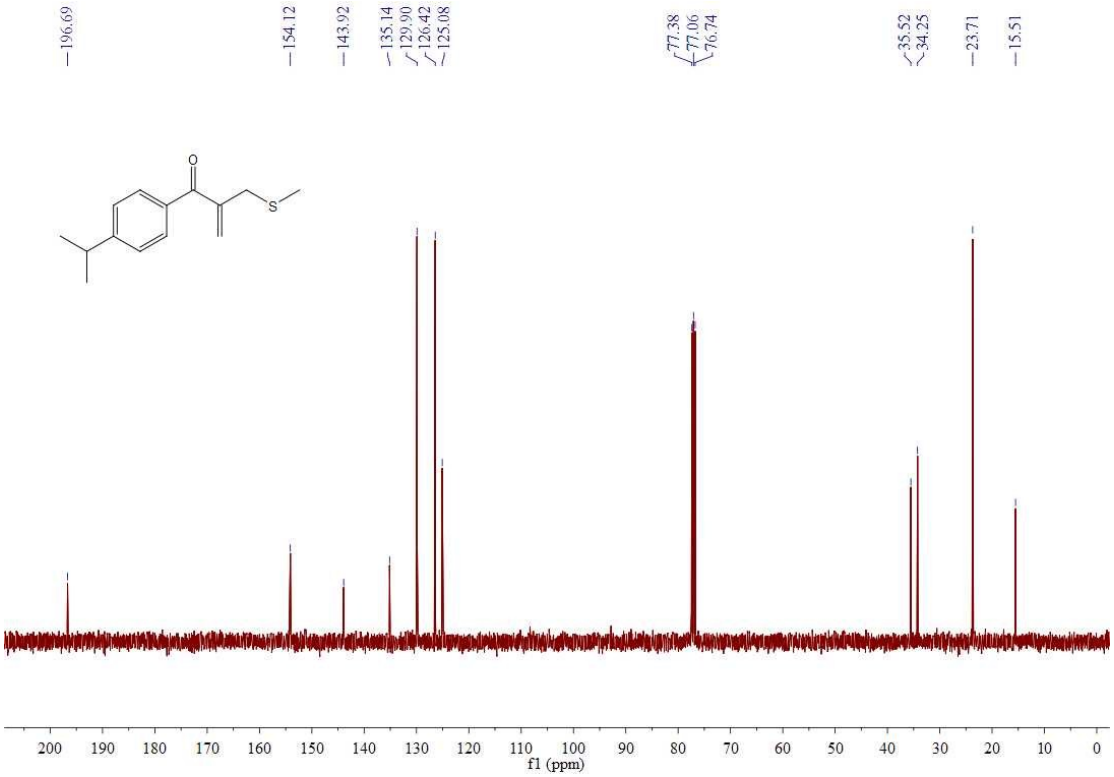
Compound 3c


7.58
7.56
7.54
7.38
7.36
7.35
7.33
7.31
7.27
5.91
5.67
3.53
2.41
2.13
O
S
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

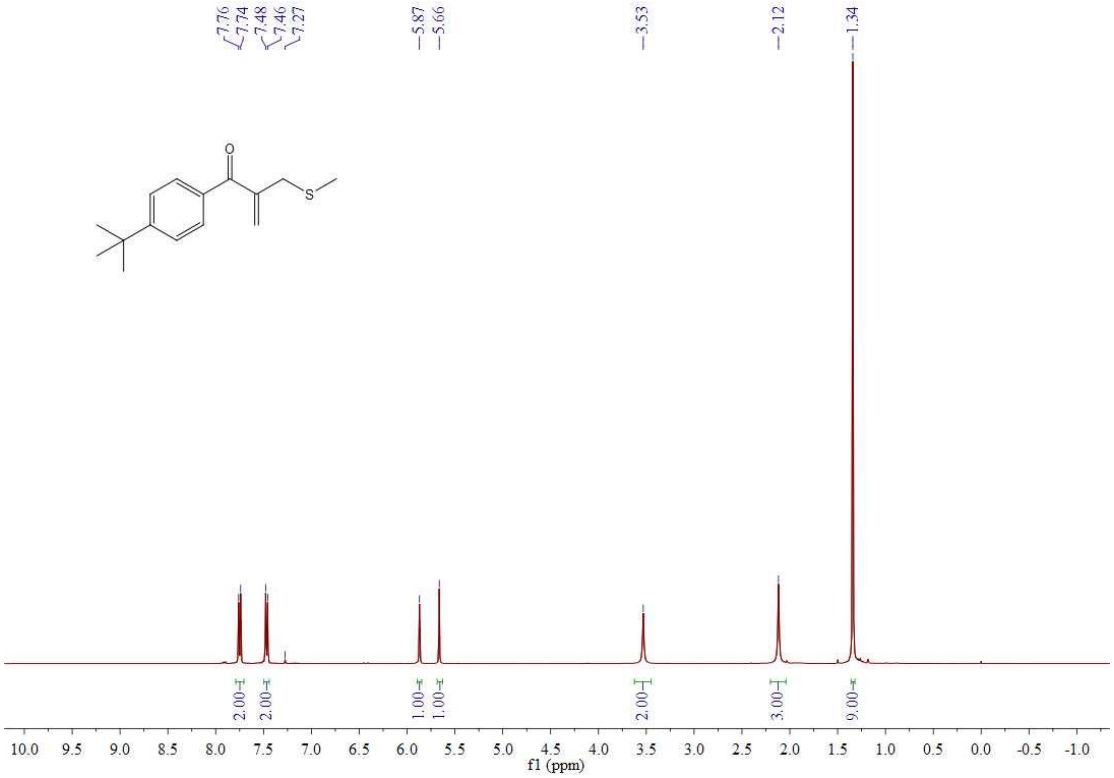

197.19
143.95
138.16
137.56
133.28
129.93
128.11
126.83
125.87
77.39
77.07
76.75
35.32
21.37
15.56
O
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

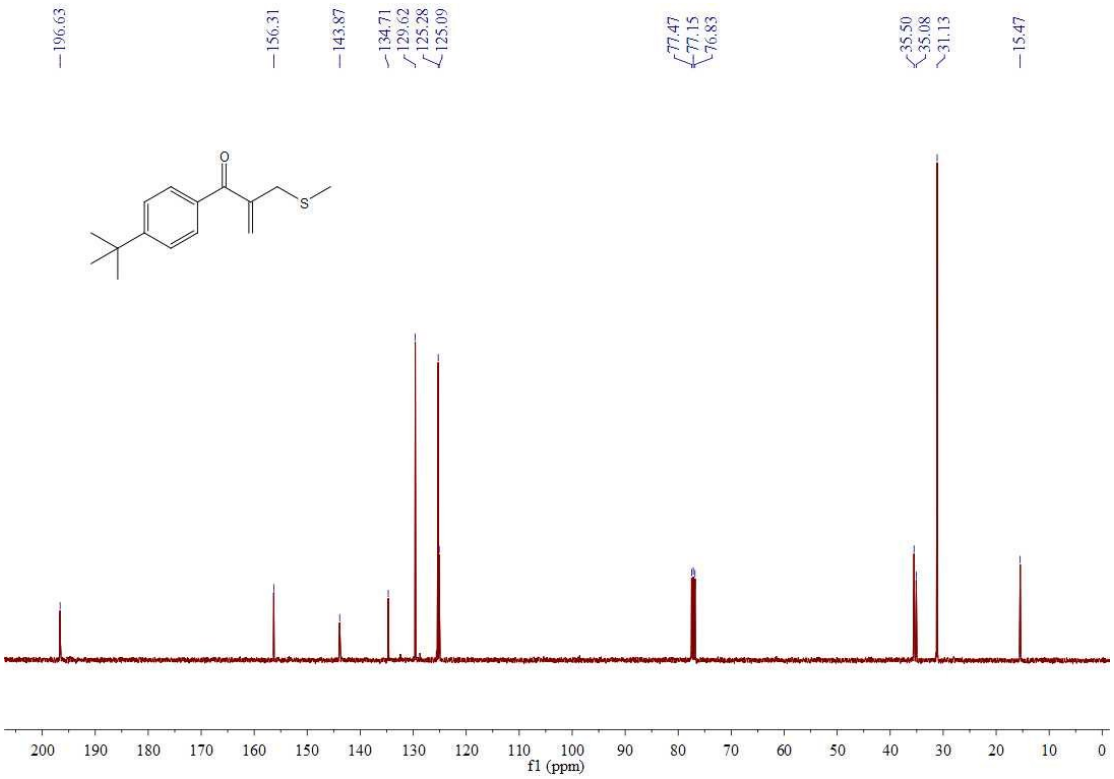
Compound 3d


7.75
7.73
7.31
7.29
7.26
5.87
5.66
3.53
3.02
3.00
2.99
2.97
2.95
2.94
2.12
1.28
1.27
O
S
2.00
2.00
1.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)

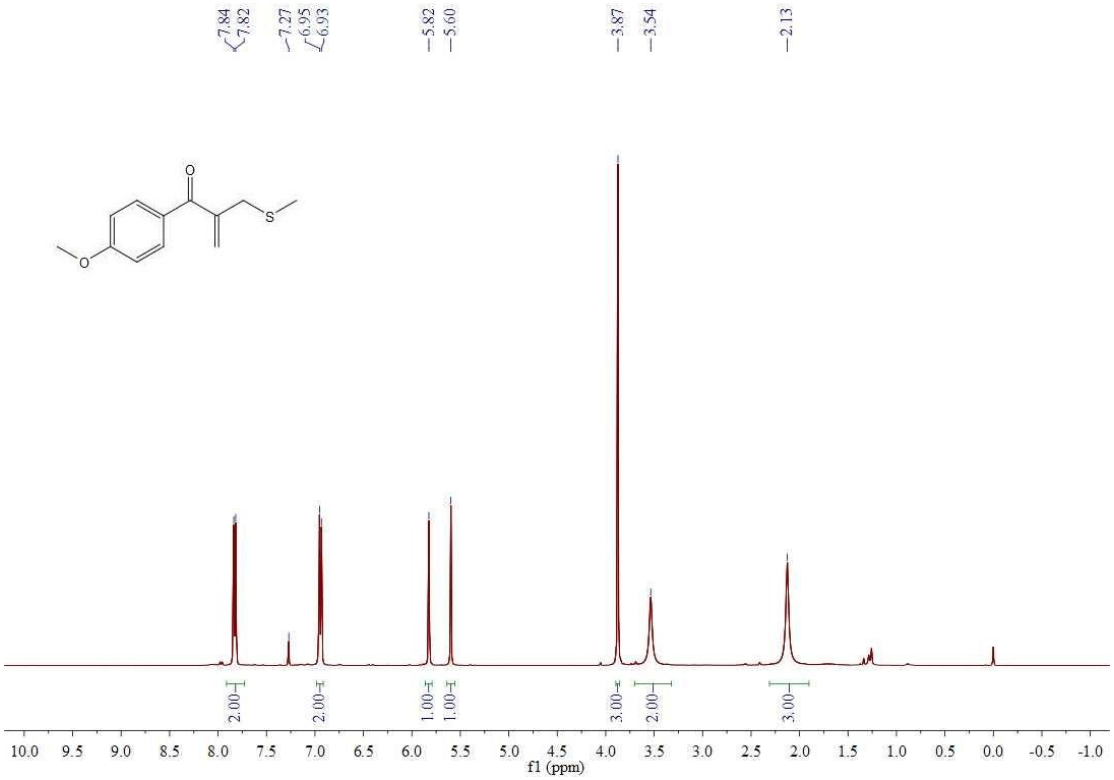

196.69
154.12
143.92
135.14
129.90
126.42
125.08
77.38
77.06
76.74
35.52
34.25
23.71
15.51
O
S
f1 (ppm)

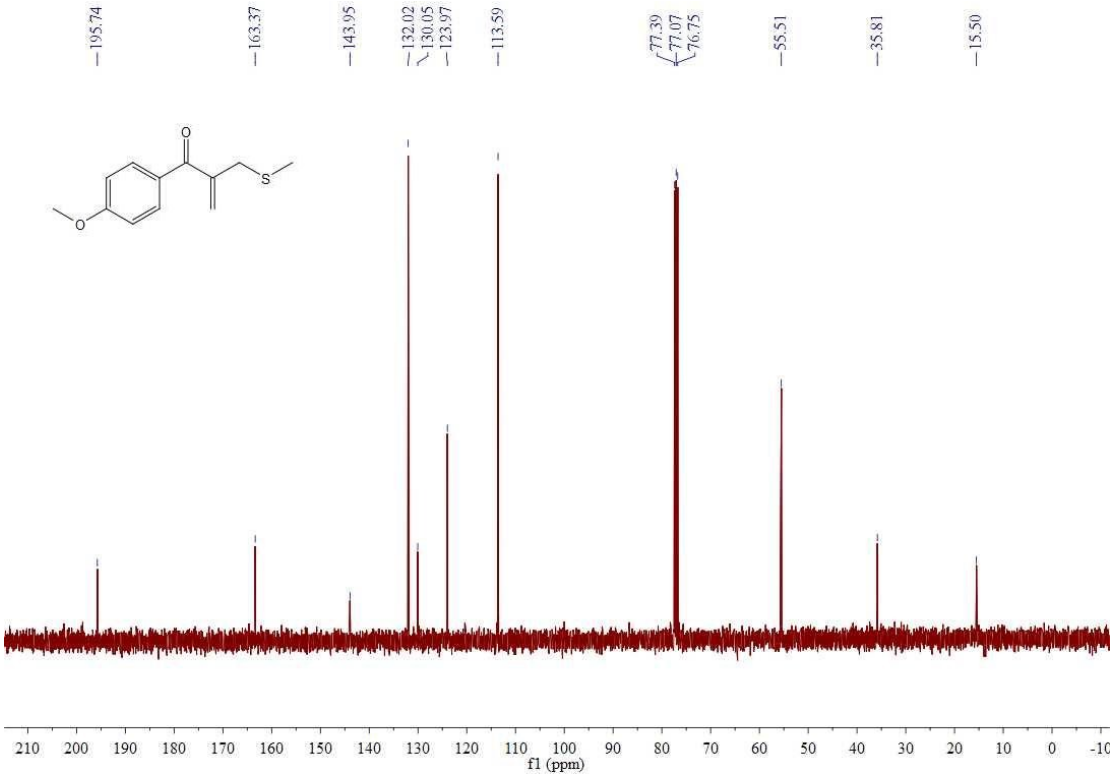
Compound 3e


7.76
7.74
7.48
7.46
7.27
5.87
5.66
3.53
2.12
1.34
O
S
2.00
2.00
1.00
1.00
2.00
3.00
9.00
f1 (ppm)

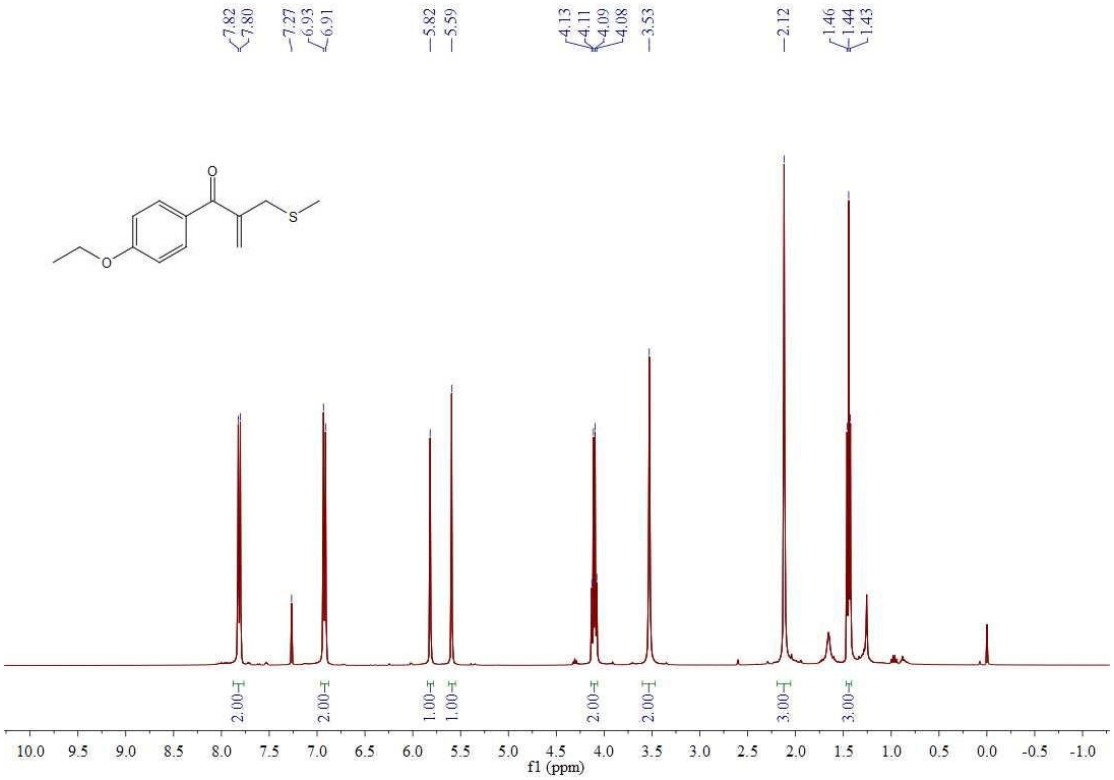

196.63
156.31
143.87
134.71
129.62
125.28
125.09
77.47
77.15
76.83
35.50
35.08
31.13
15.47
O
S
f1 (ppm)

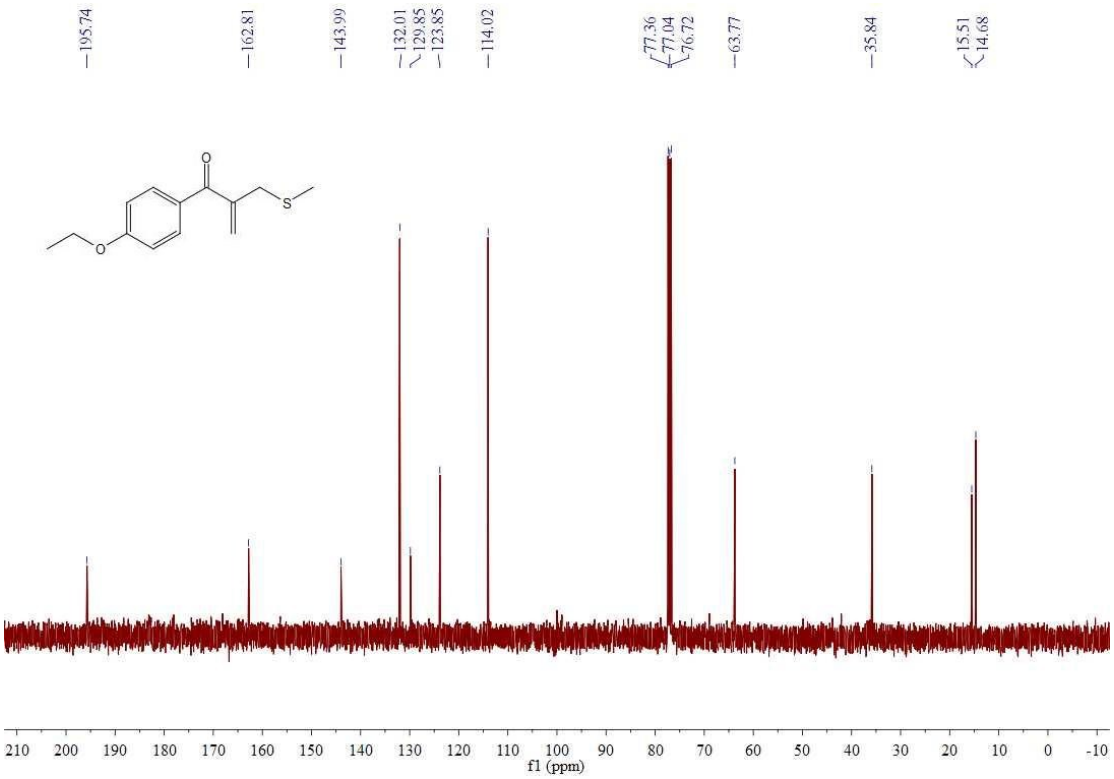
Compound 3f


7.84
7.82
7.27
6.95
6.93
5.82
5.60
3.87
3.54
2.13
O
S
O
2.00
2.00
1.00
1.00
3.00
2.00
3.00
f1 (ppm)

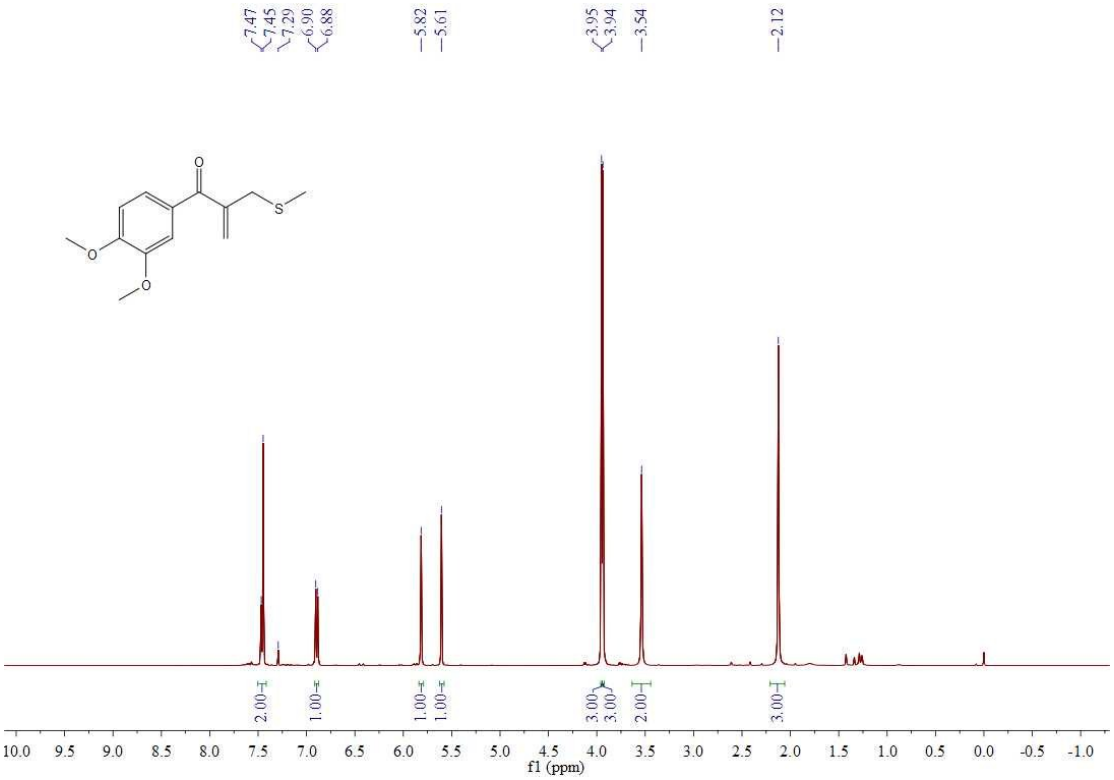

195.74
163.37
143.95
132.02
130.05
123.97
113.59
77.39
77.07
76.75
55.51
35.81
15.50
O
S
O
f1 (ppm)

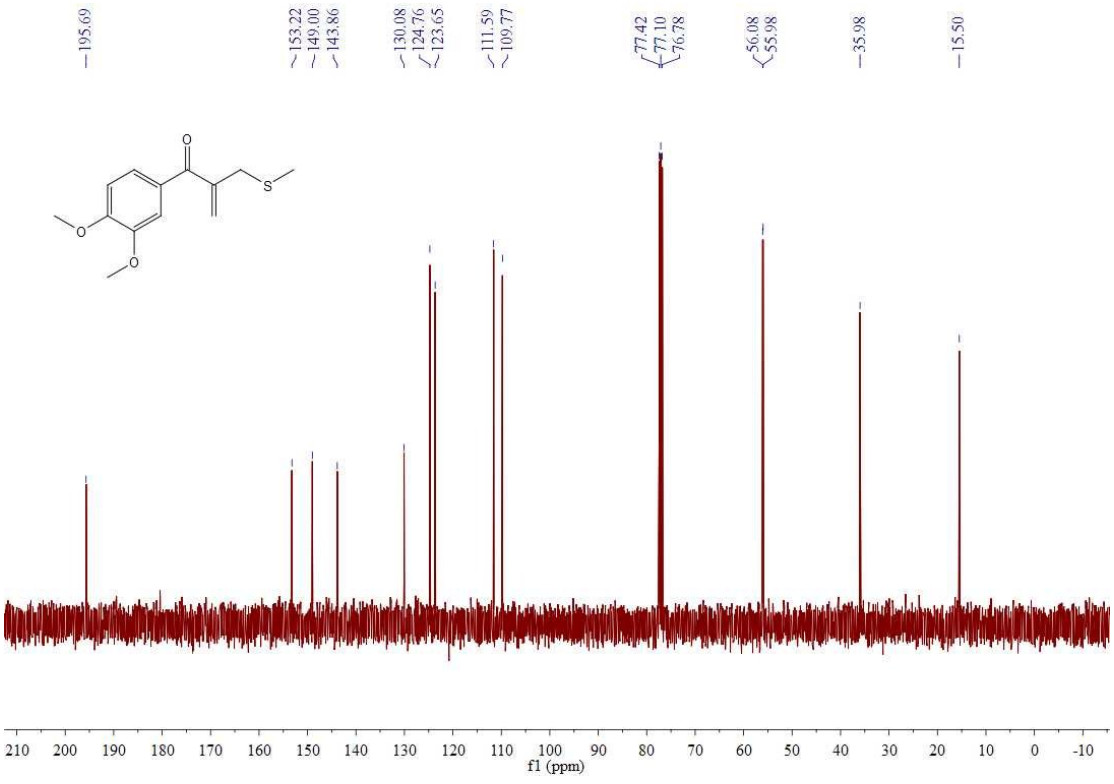
Compound 3g


7.82
7.80
7.27
6.93
6.91
5.82
5.59
4.13
4.11
4.09
4.08
3.53
2.12
1.46
1.44
1.43
O
S
O
2.00
2.00
1.00
1.00
2.00
2.00
3.00
3.00
f1 (ppm)


195.74
162.81
143.99
132.01
129.85
123.85
114.02
77.36
77.04
76.72
63.77
35.84
15.51
14.68
O
S
O
f1 (ppm)

Compound 3h


7.47
7.45
7.29
6.90
6.88
5.82
5.61
3.95
3.94
3.54
2.12
O
S
O
O
2.00
1.00
1.00
1.00
3.00
3.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


195.69
153.22
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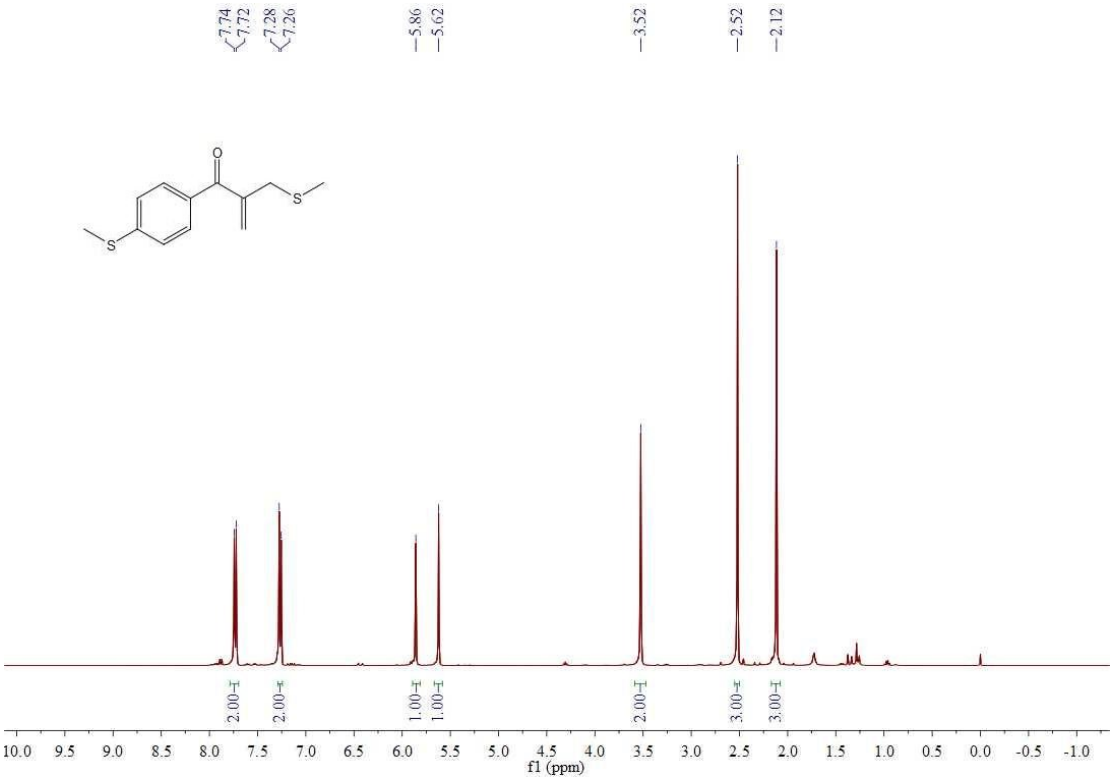
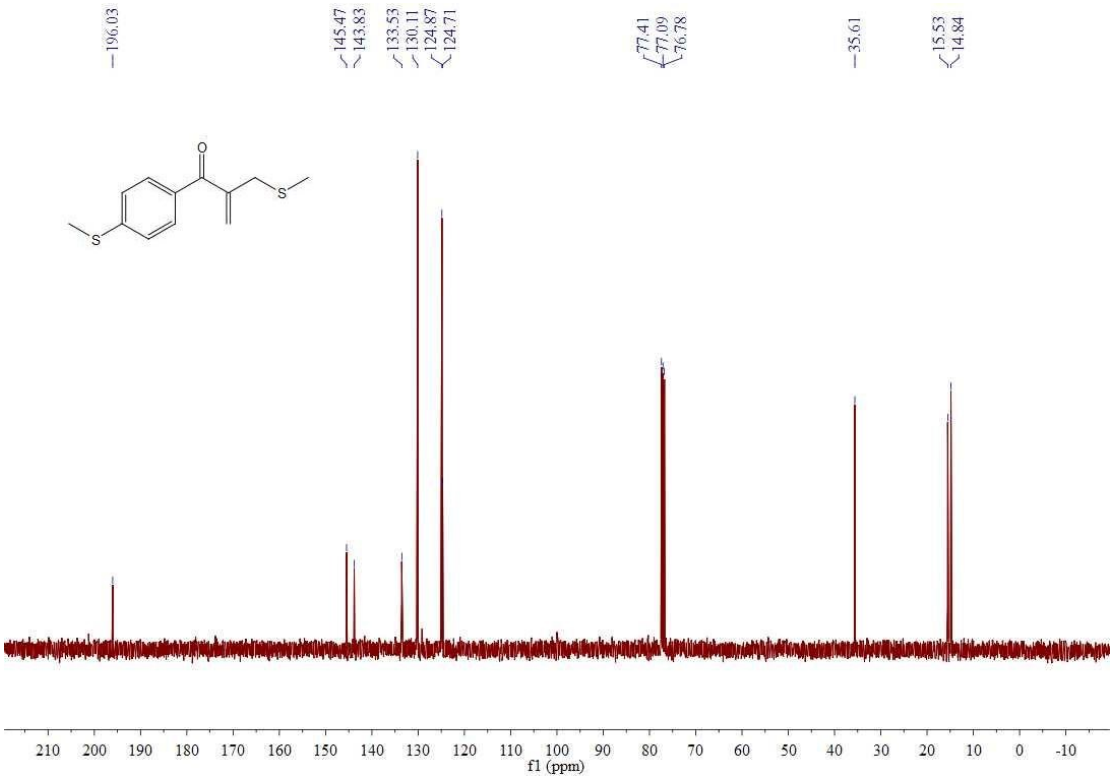
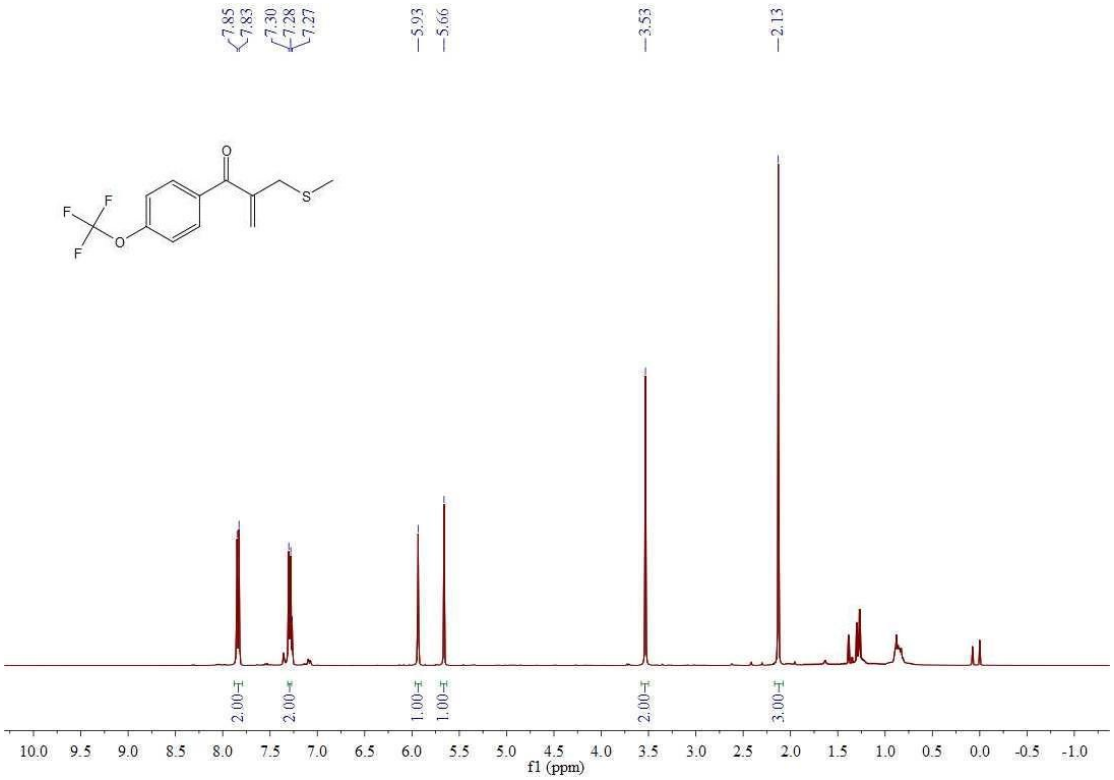
143.86
130.08
124.76
123.65
111.59
109.77
77.42
77.10
76.78
56.08
55.98
35.98
15.50
O
S
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

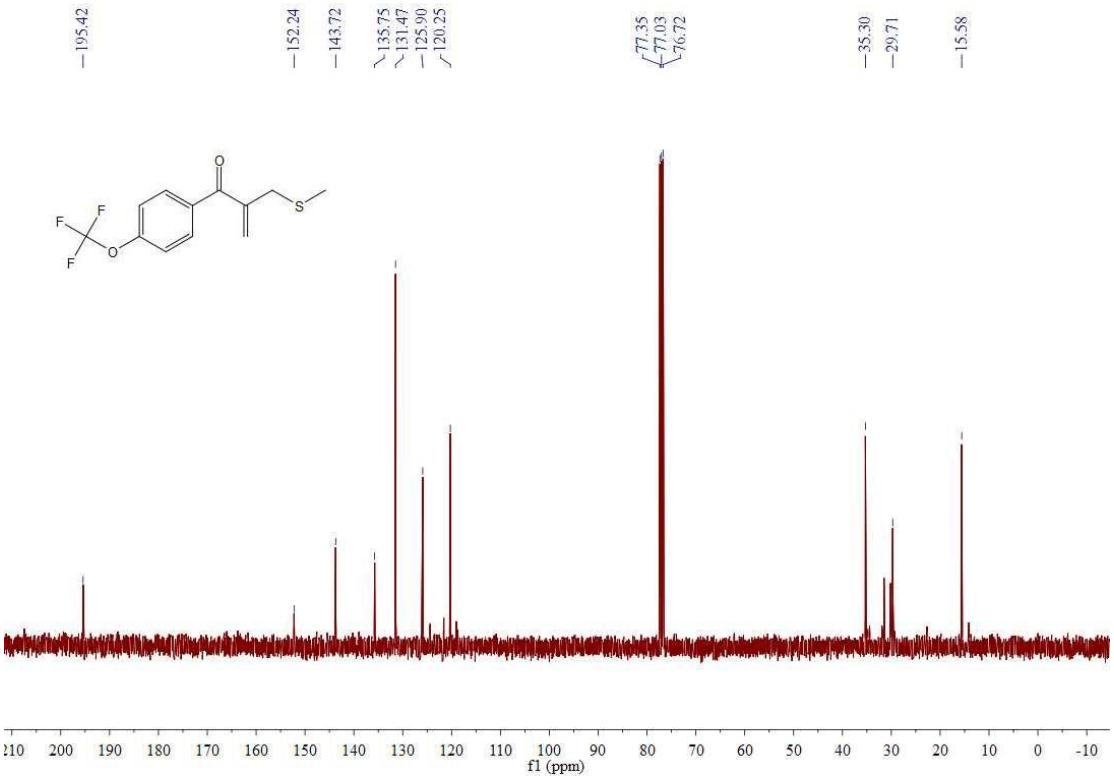
Compound 3i


7.74
7.72
7.28
7.26
5.86
5.62
3.52
2.52
2.12
O
S
S
2.00
2.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

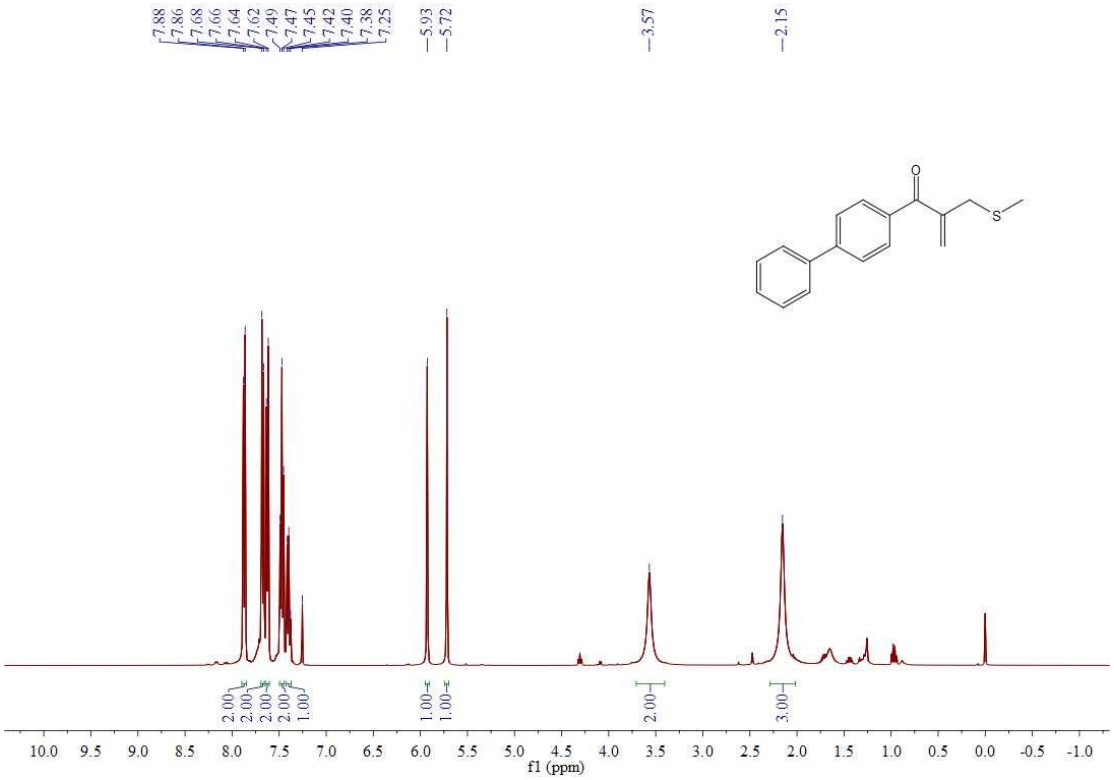

196.03
145.47
143.83
133.53
130.11
124.87
124.71
77.41
77.09
76.78
35.61
15.53
14.84
O
S
S
f1 (ppm)

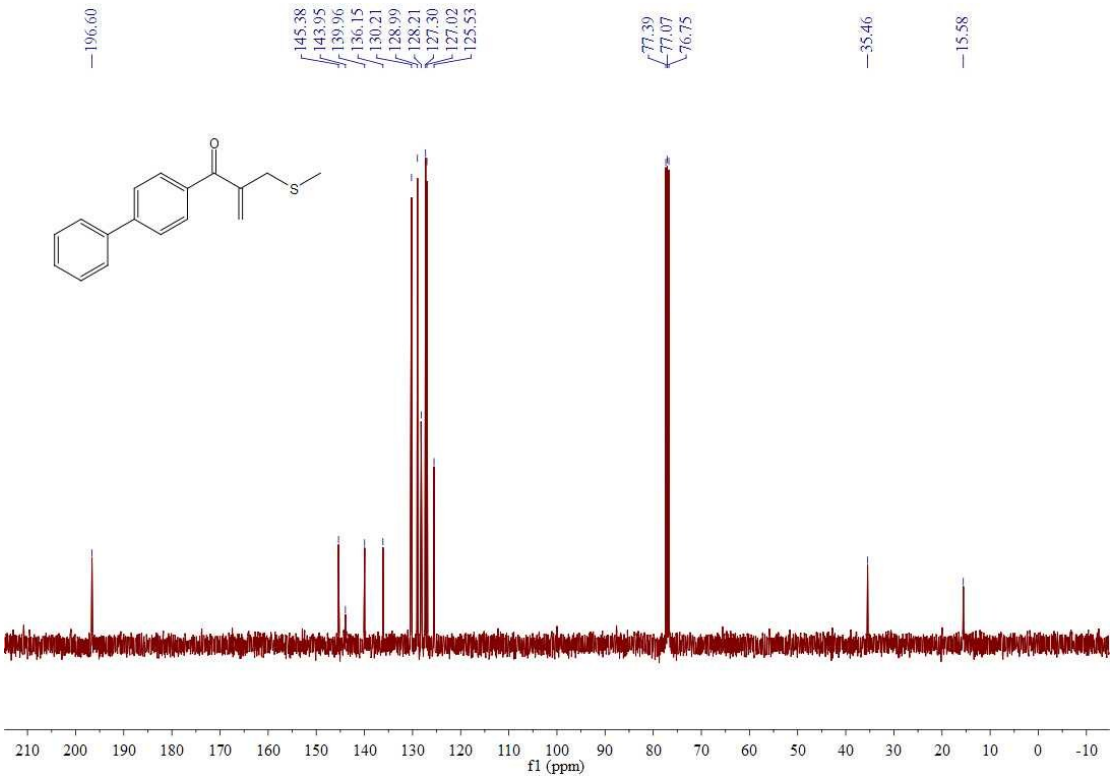
Compound 3j


7.85
7.83
7.30
7.28
7.27
5.93
5.66
3.53
2.13
O
S
F
F
F
O
2.00
2.00
1.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

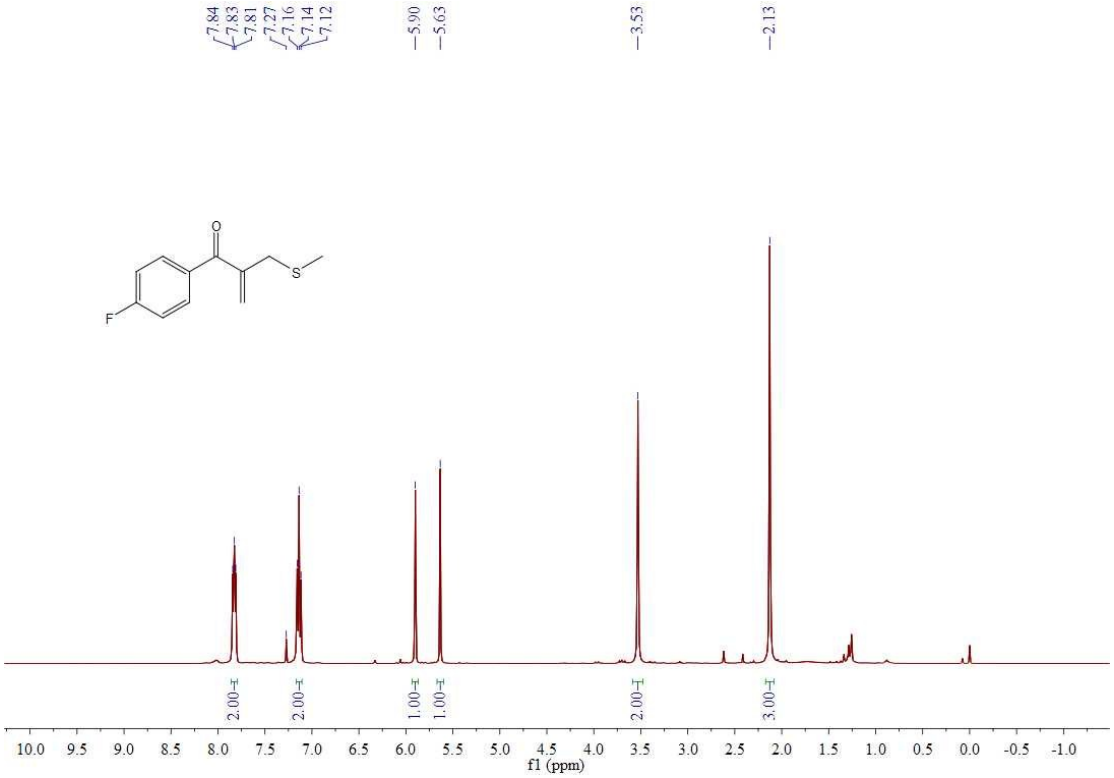

195.42
152.24
143.72
135.75
131.47
125.90
120.25
77.35
77.03
76.72
35.30
29.71
15.58
O
S
F
F
F
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

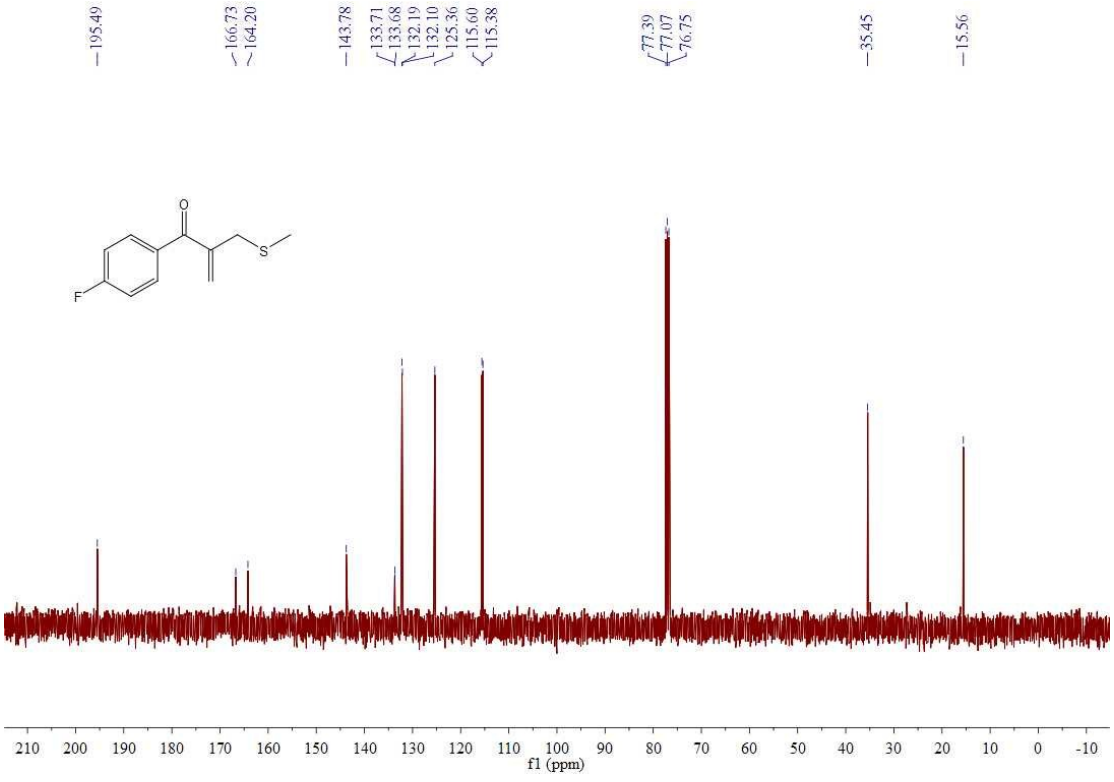
Compound 3k


7.88
7.86
7.68
7.66
7.64
7.62
7.49
7.47
7.45
7.42
7.40
7.38
7.25
5.93
5.72
3.57
2.15
O
S
2.00
2.00
2.00
2.00
1.00
1.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

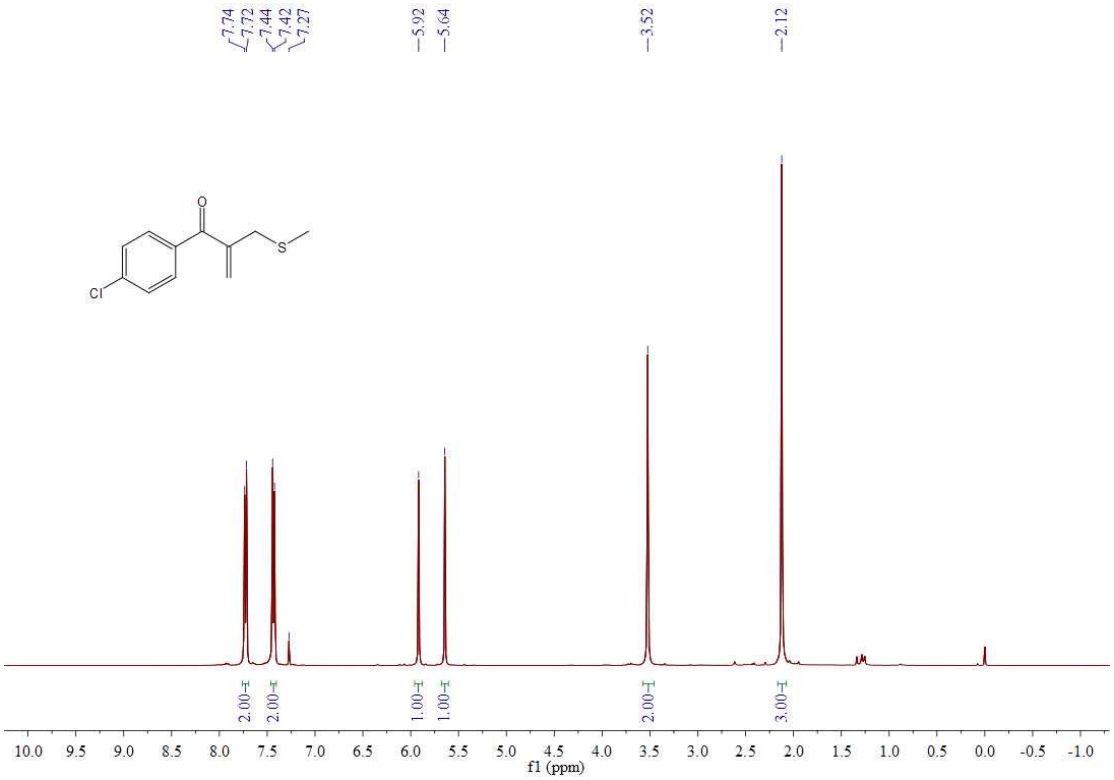

196.60
145.38
143.95
139.96
136.15
130.21
128.99
128.21
127.30
127.02
125.53
77.39
77.07
76.75
35.46
15.58
O
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

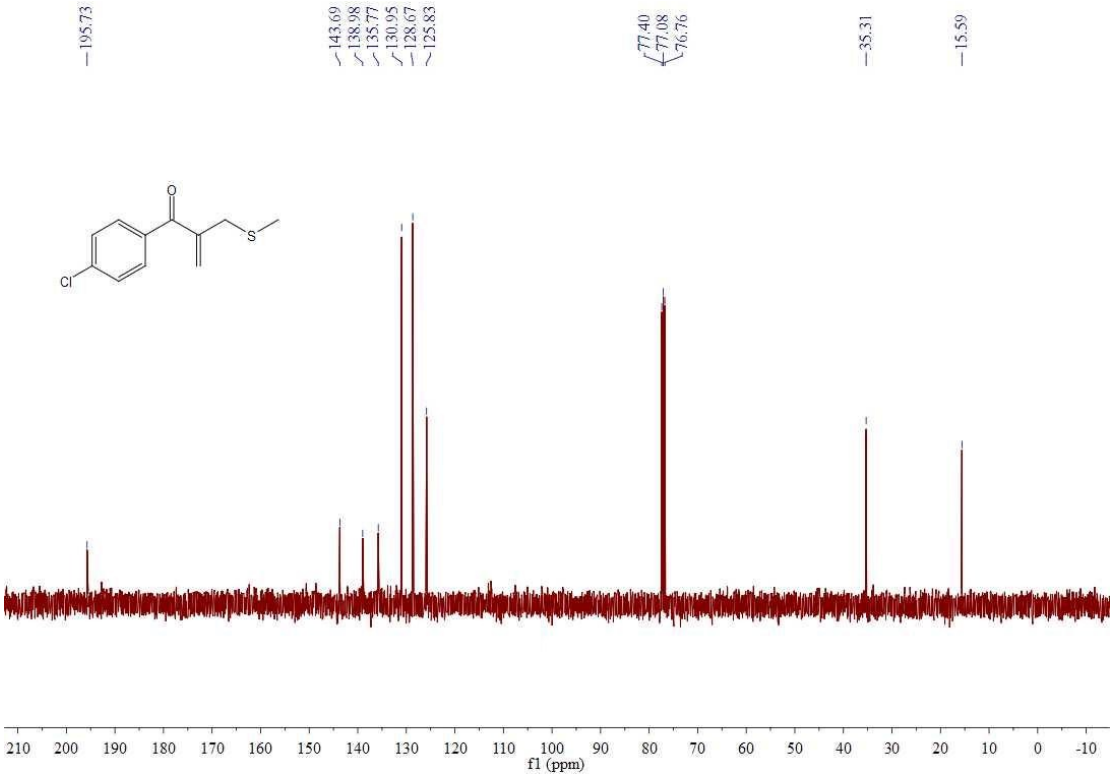
Compound 3l


7.84
7.83
7.81
7.27
7.16
7.14
7.12
5.90
5.63
3.53
2.13
O
S
F
2.00
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

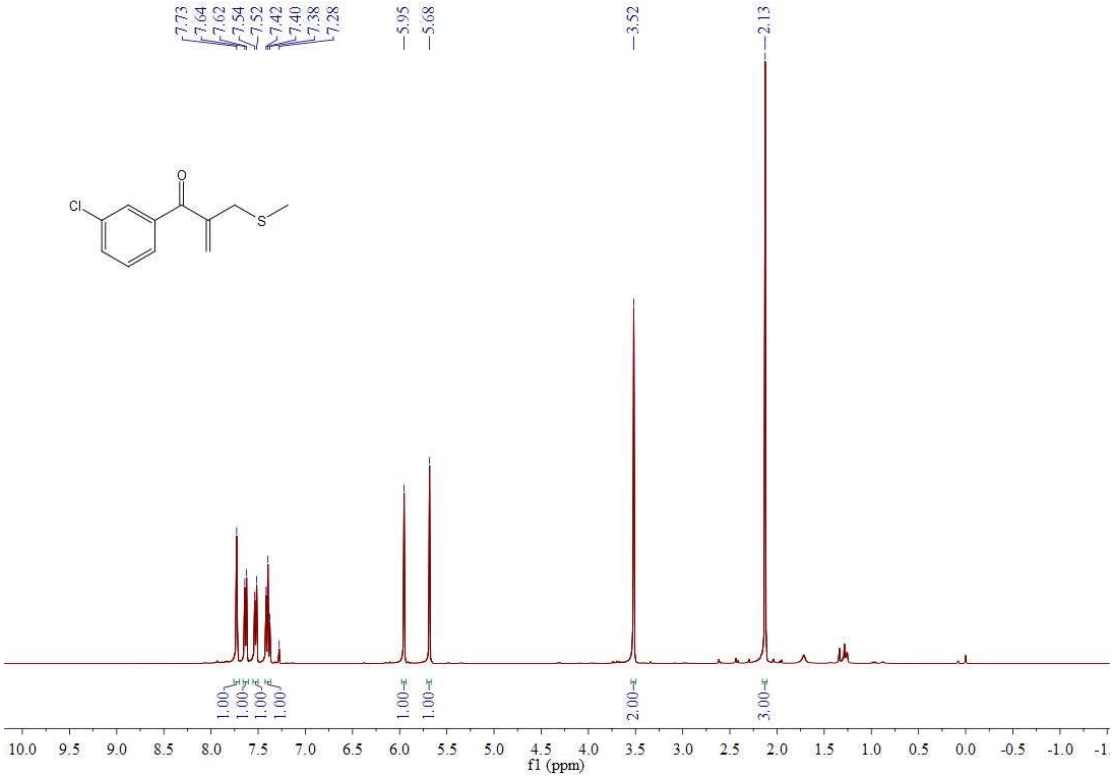

195.49
166.73
164.20
143.78
133.71
133.68
132.19
132.10
125.36
115.60
115.38
77.39
77.07
76.75
35.45
15.56
O
S
F
f1 (ppm)

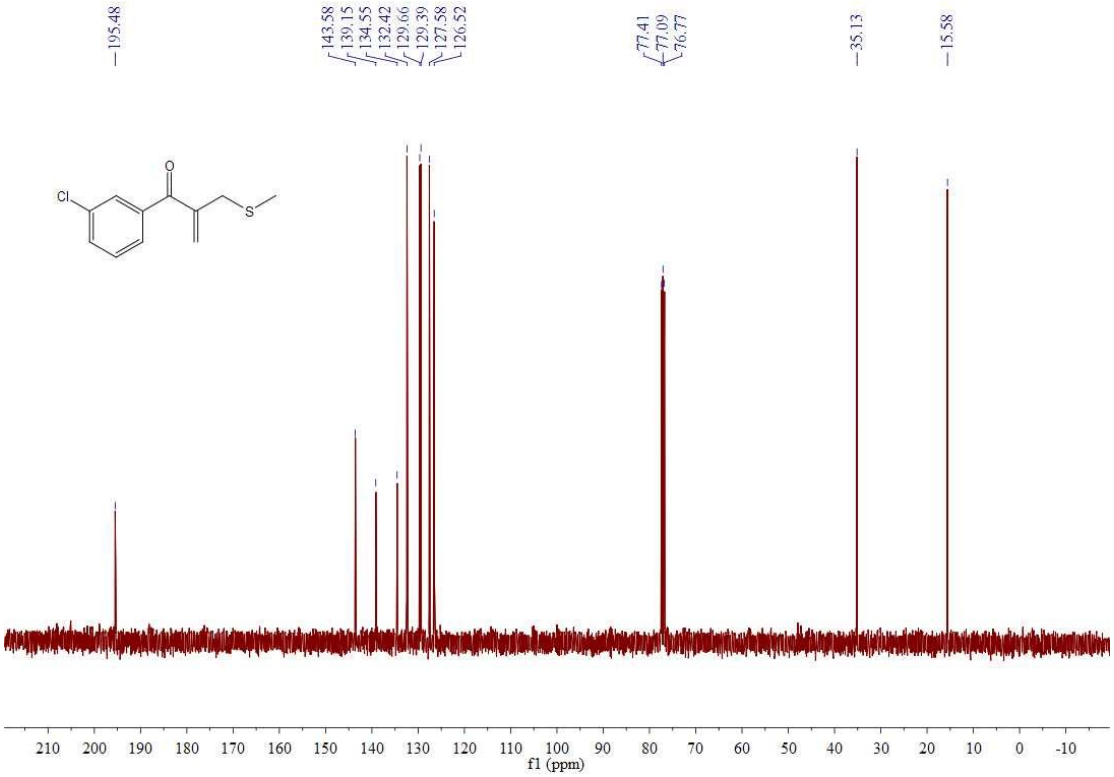
Compound 3m


7.74
7.72
7.44
7.42
7.27
5.92
5.64
3.52
2.12
O
S
Cl
2.00
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

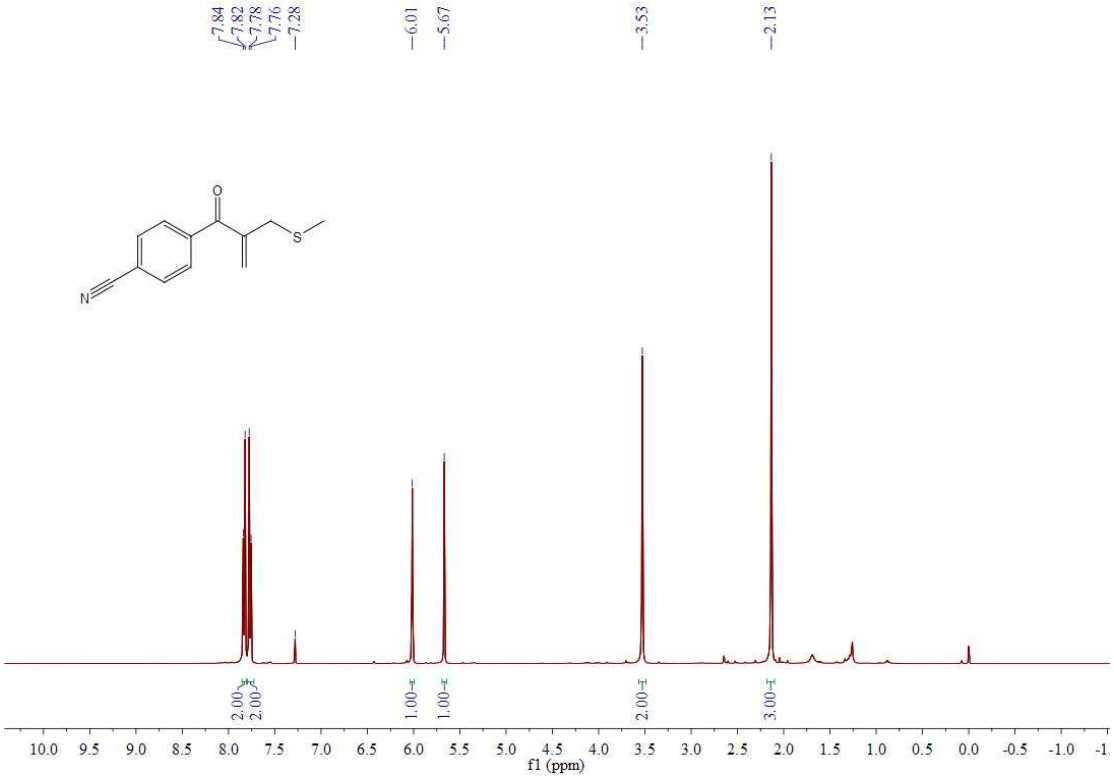

195.73
143.69
138.98
135.77
130.95
128.67
125.83
77.40
77.08
76.76
35.31
15.59
O
S
Cl
f1 (ppm)

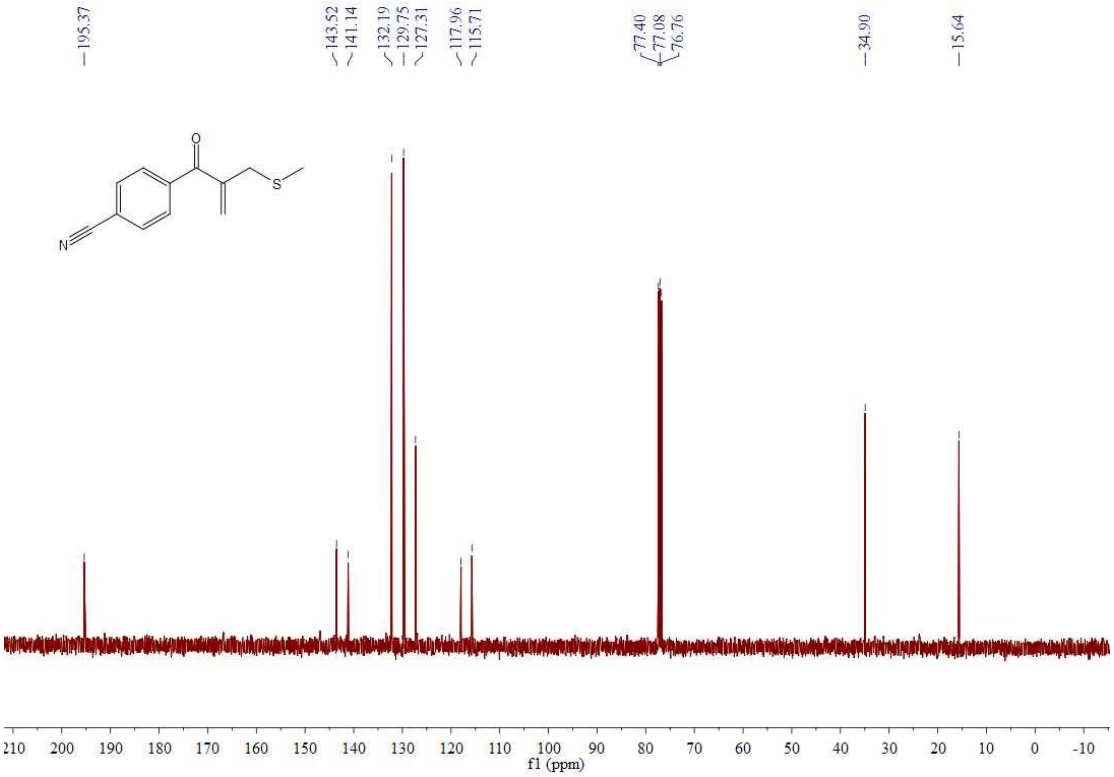
Compound 3n


7.73
7.64
7.62
7.54
7.52
7.42
7.40
7.38
7.28
5.95
5.68
3.52
2.13
Cl
O
S
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

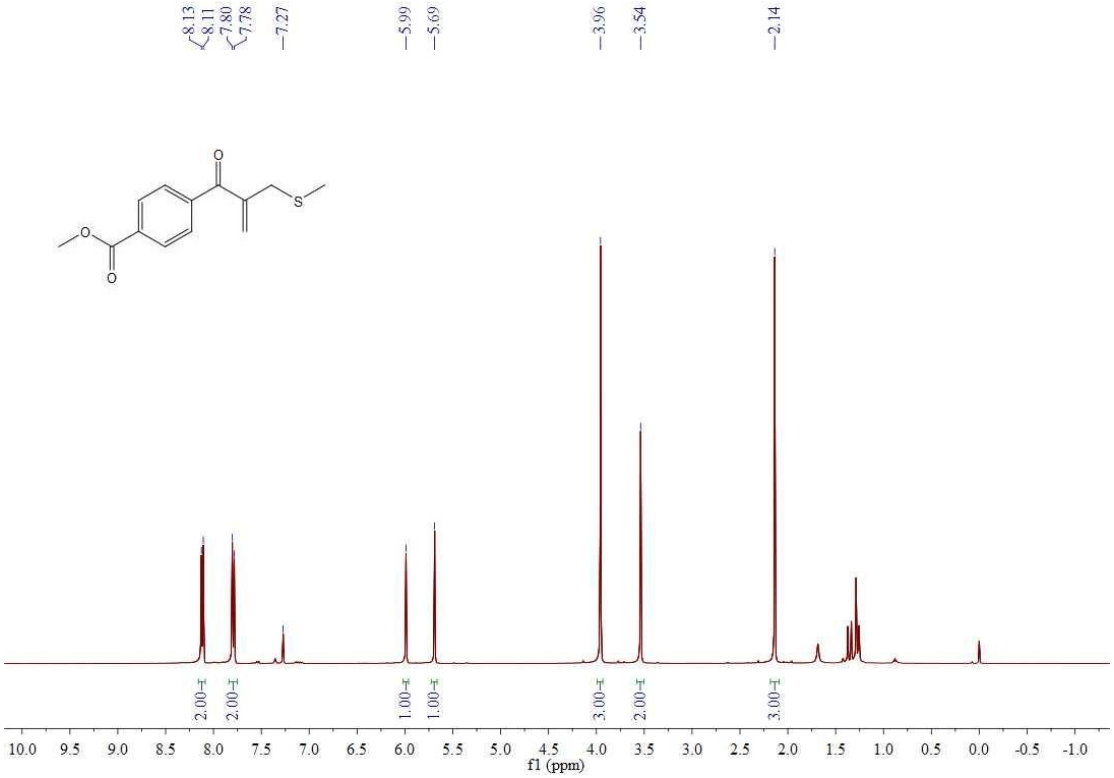

195.48
143.58
139.15
134.55
132.42
129.66
129.39
127.58
126.52
77.41
77.09
76.77
35.13
15.58
Cl
O
S
f1 (ppm)

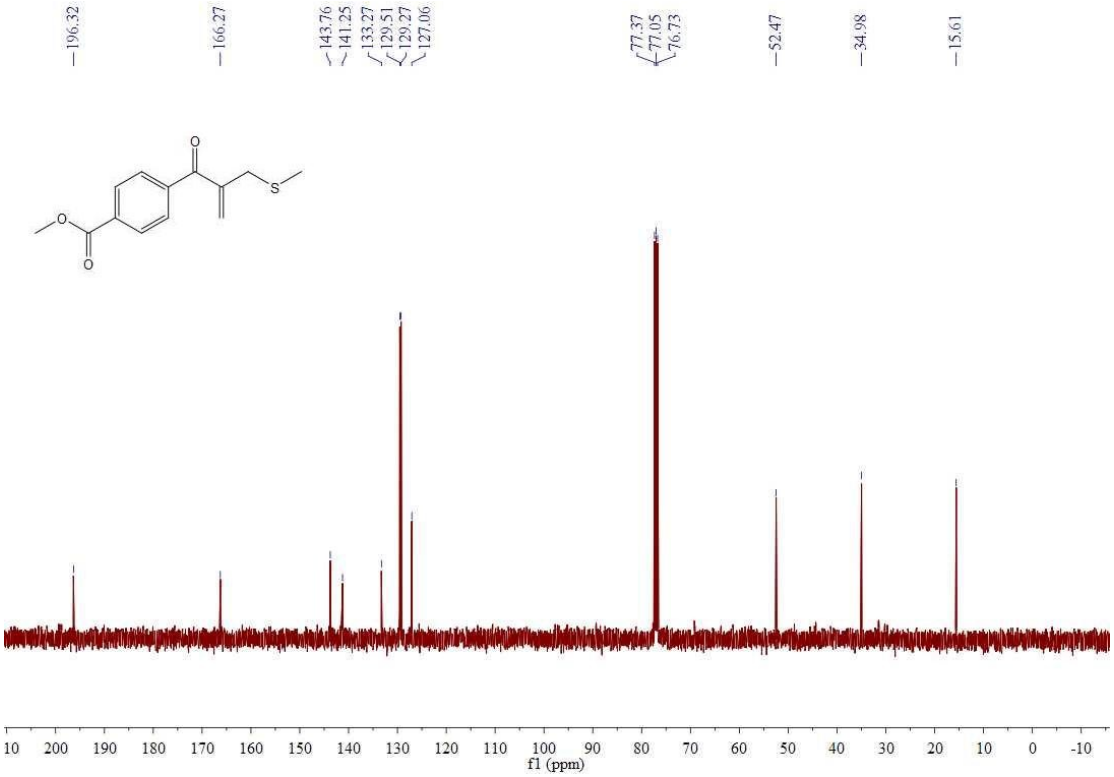
Compound 3o


7.84
7.82
7.78
7.76
7.28
6.01
5.67
3.53
2.13
O
S
N
2.00
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

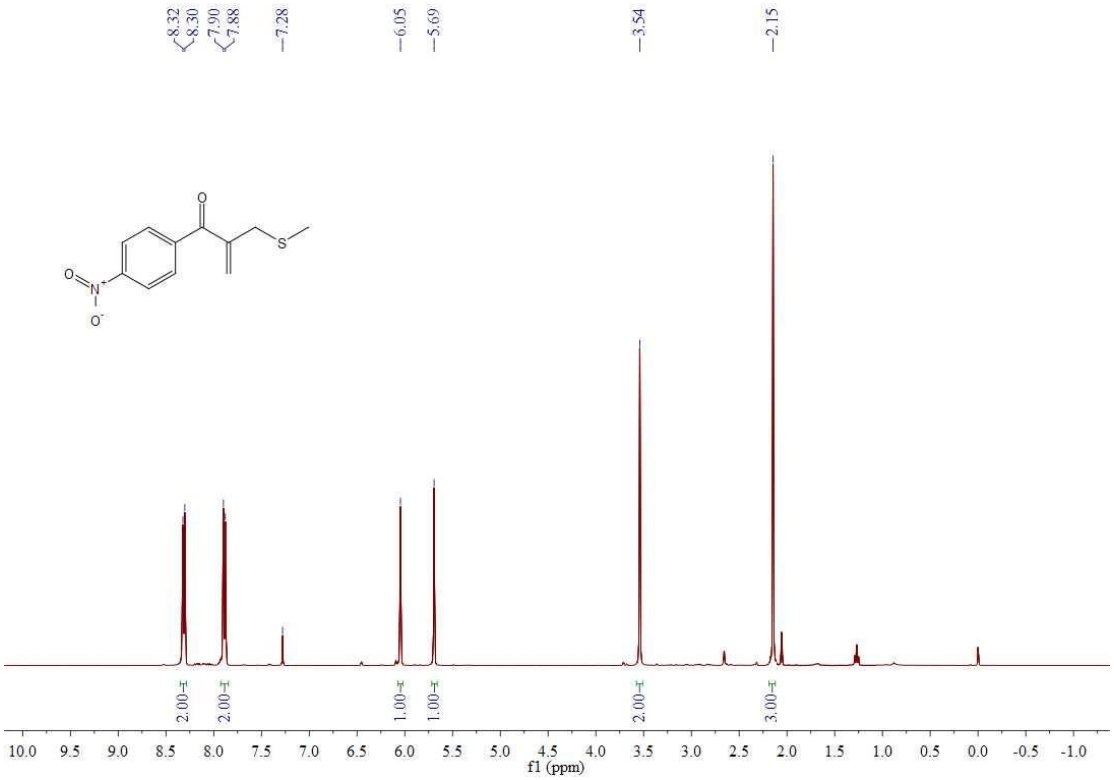

195.37
143.52
141.14
132.19
129.75
127.31
117.96
115.71
77.40
77.08
76.76
34.90
15.64
O
S
N
f1 (ppm)

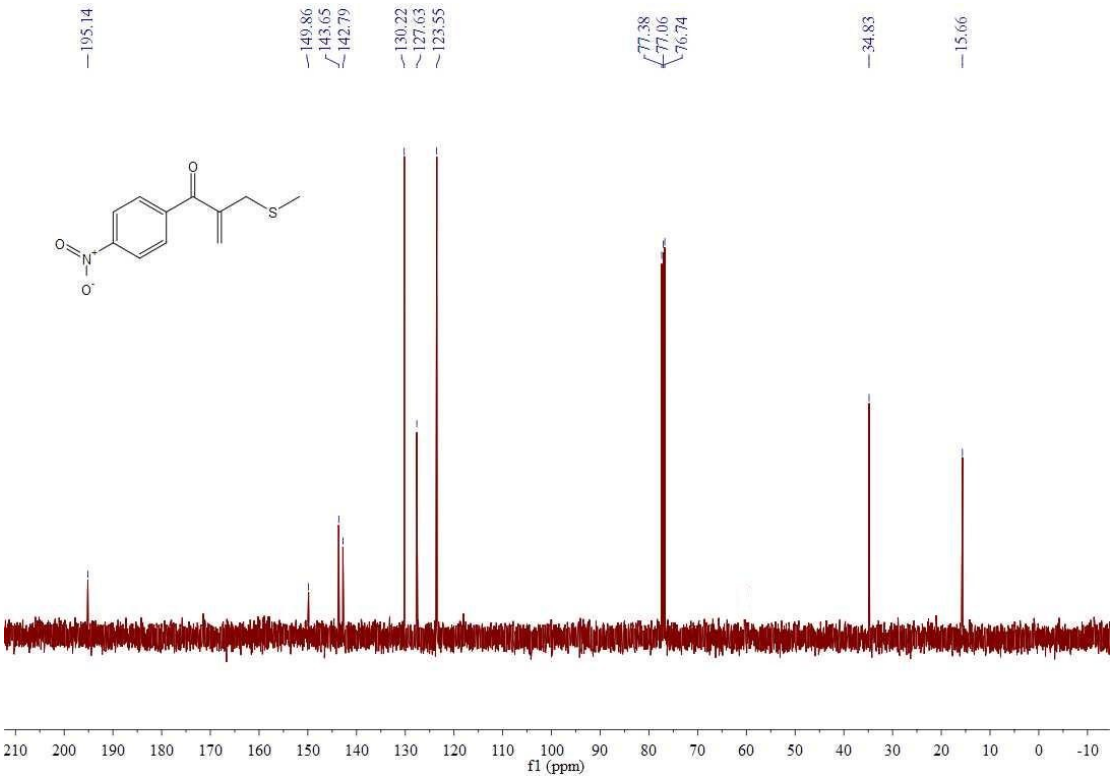
Compound 3p


8.13
8.11
7.80
7.78
7.27
5.99
5.69
3.96
3.54
2.14
2.00
2.00
1.00
1.00
3.00
2.00
3.00
f1 (ppm)

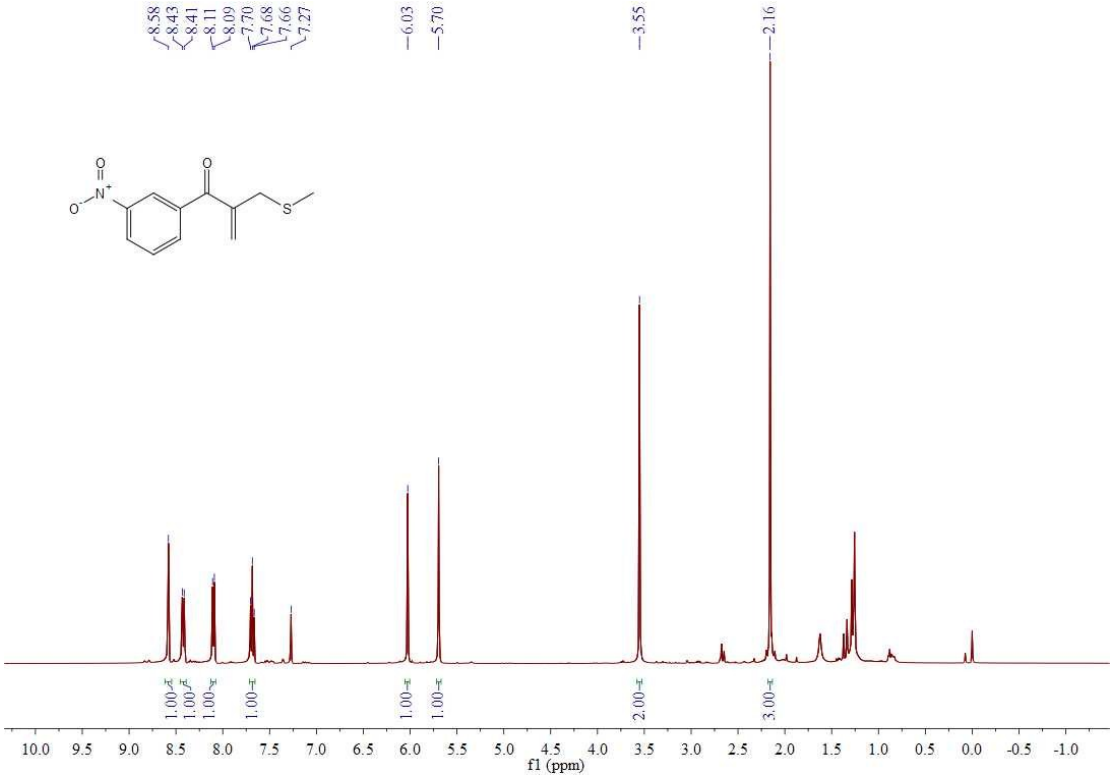

196.32
166.27
143.76
141.25
133.27
129.51
129.27
127.06
77.37
77.05
76.73
52.47
34.98
15.61
f1 (ppm)

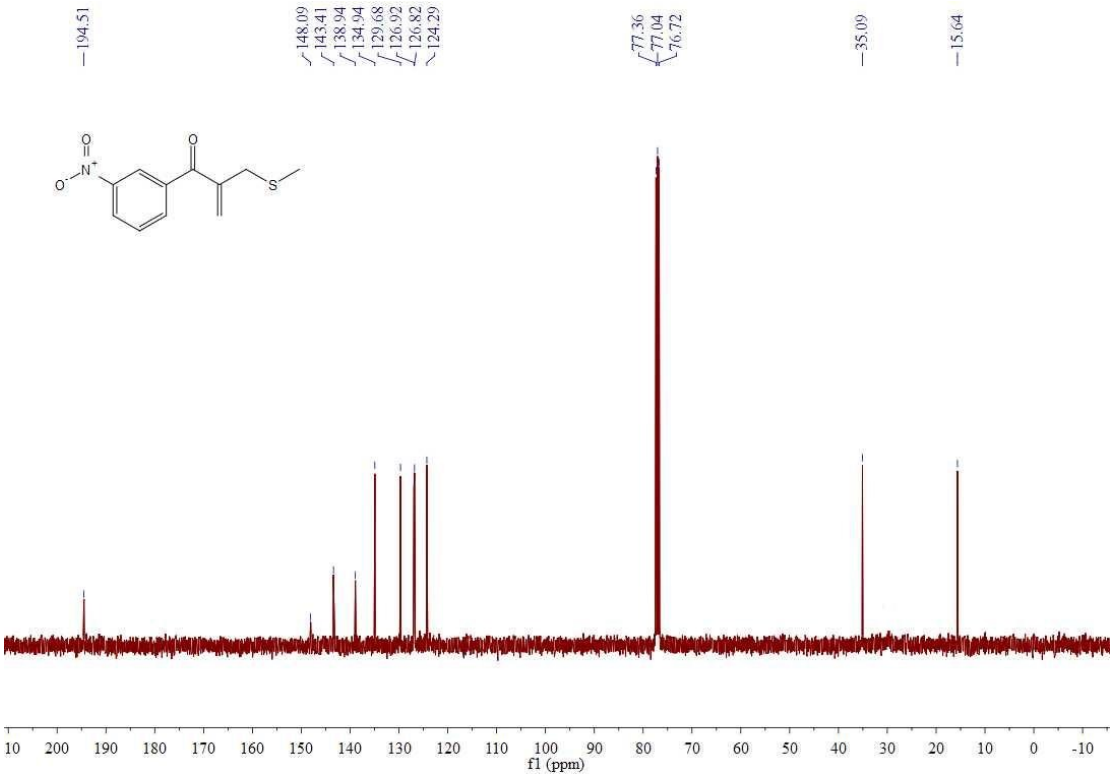
Compound 3q


8.32
8.30
7.90
7.88
7.28
6.05
5.69
3.54
2.15
O
S
O
N+
O-
2.00
2.00
1.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

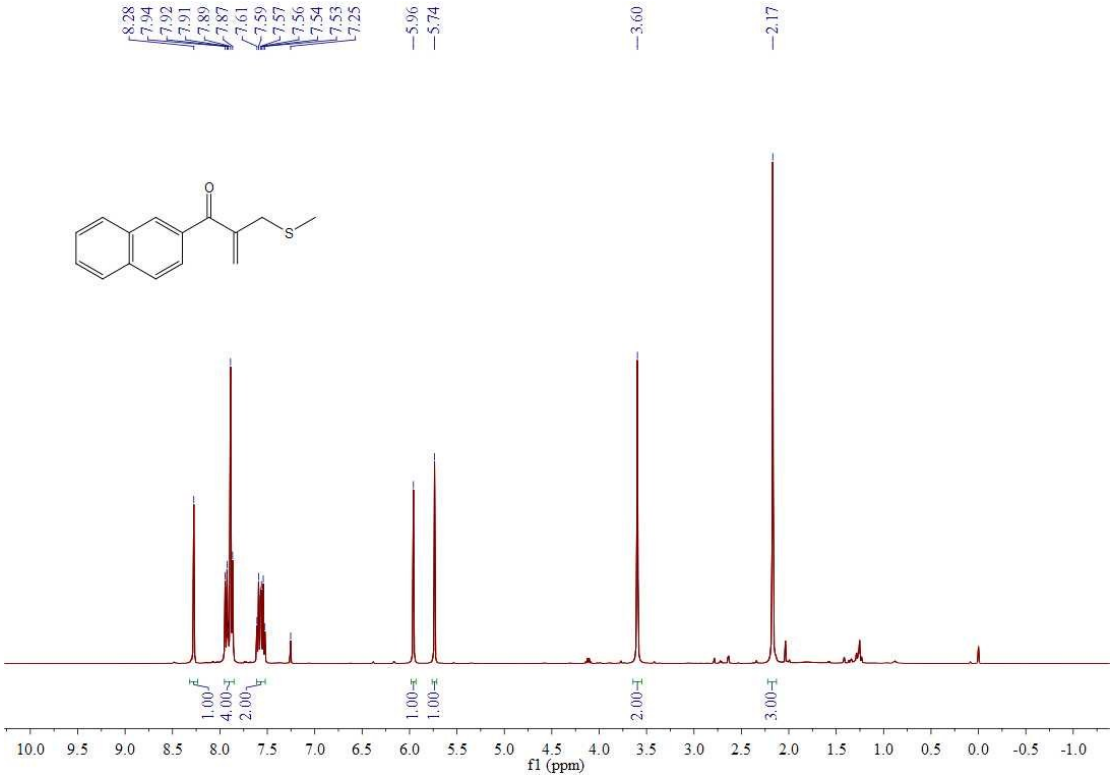

195.14
149.86
143.65
142.79
130.22
127.63
123.55
77.38
77.06
76.74
34.83
15.66
O
S
O
N+
O-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

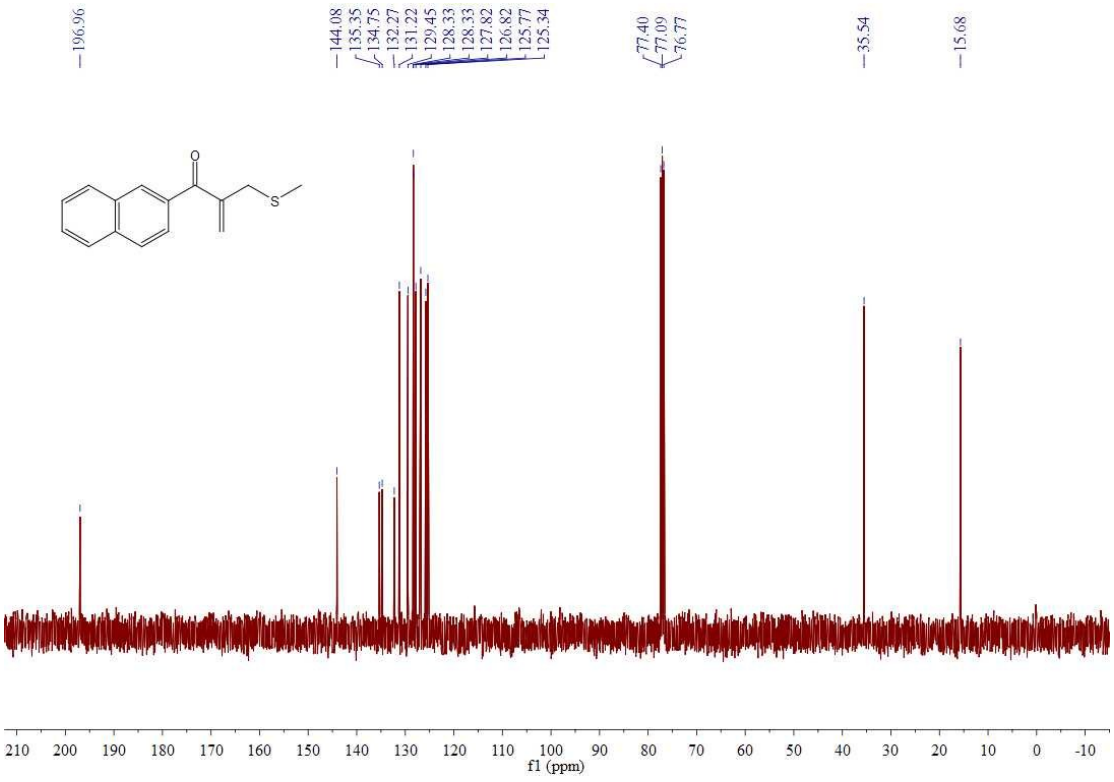
Compound 3r


8.58
8.43
8.41
8.11
8.09
7.70
7.68
7.66
7.27
6.03
5.70
3.55
2.16
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

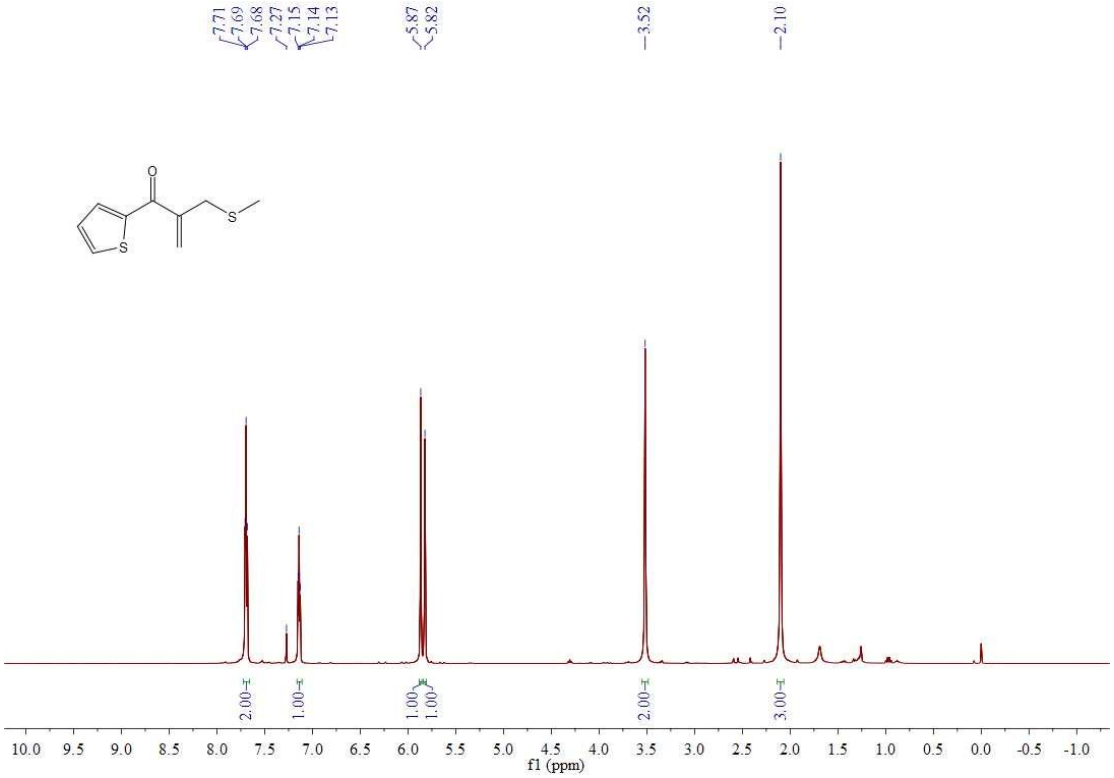

194.51
148.09
143.41
138.94
134.94
129.68
126.92
126.82
124.29
77.36
77.04
76.72
35.09
15.64
f1 (ppm)

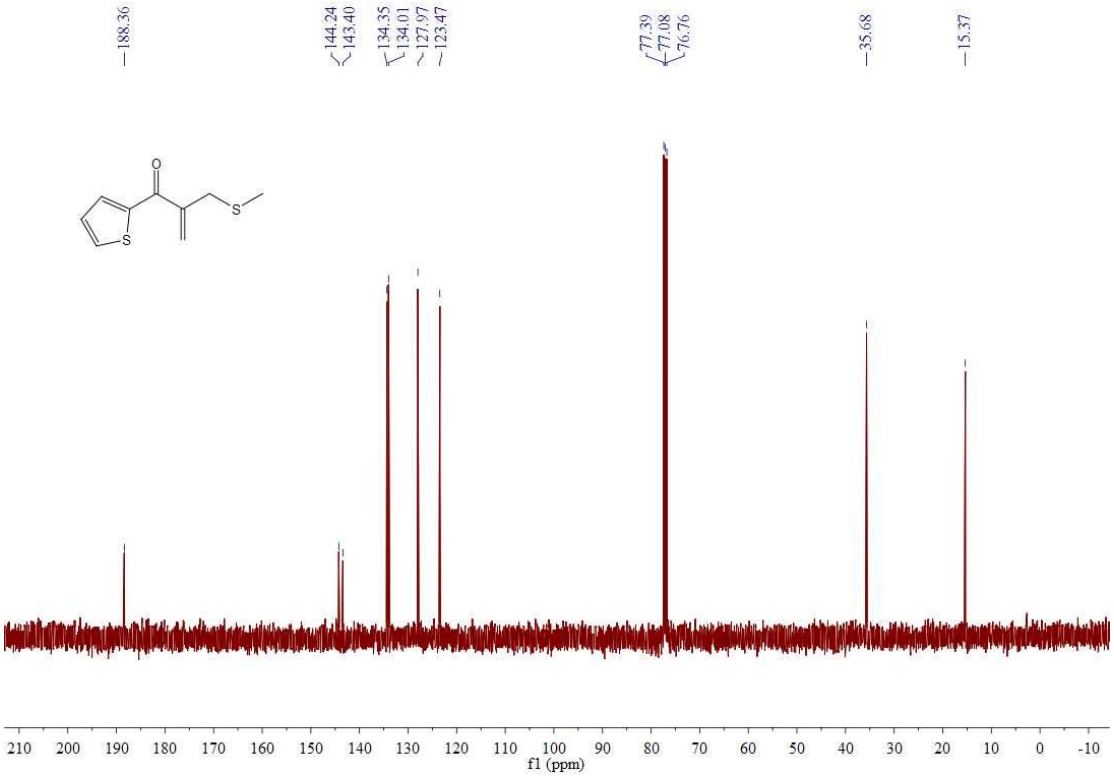
Compound 3s


8.28
7.94
7.92
7.91
7.89
7.87
7.61
7.59
7.57
7.56
7.54
7.53
7.25
5.96
5.74
3.60
2.17
O
S
1.00
4.00
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

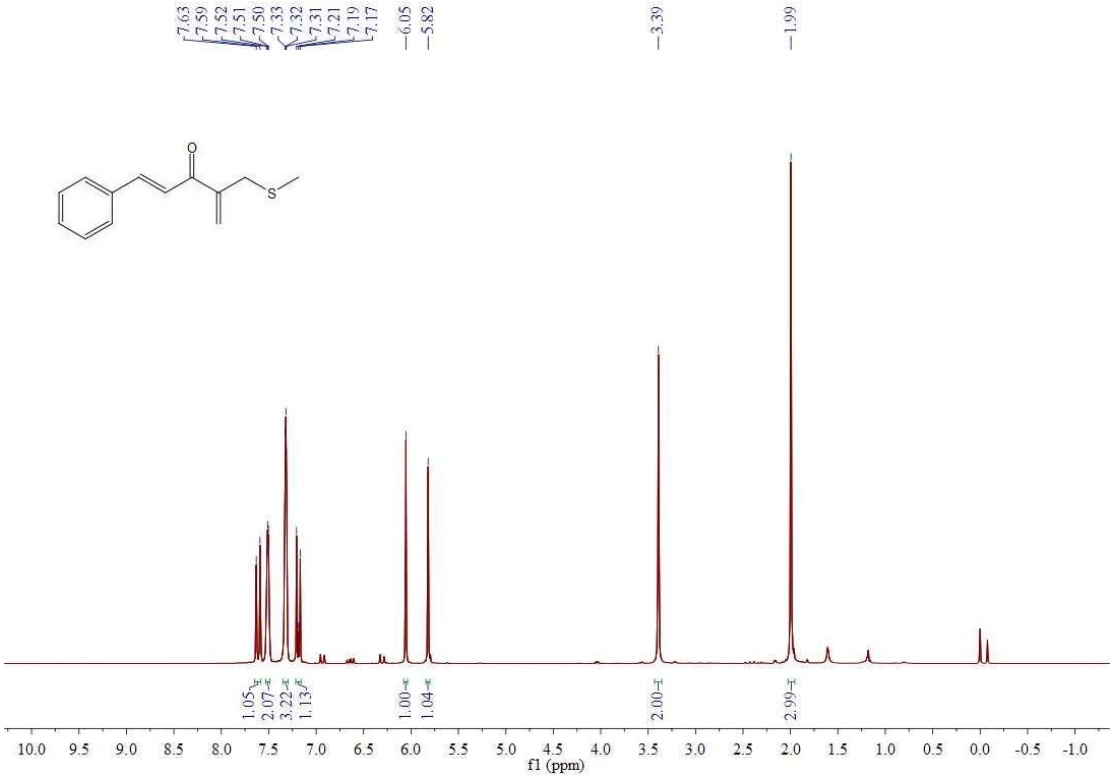

196.96
144.08
135.35
134.75
132.27
131.22
129.45
128.33
128.33
127.82
126.82
125.77
125.34
77.40
77.09
76.77
35.54
15.68
O
S
f1 (ppm)

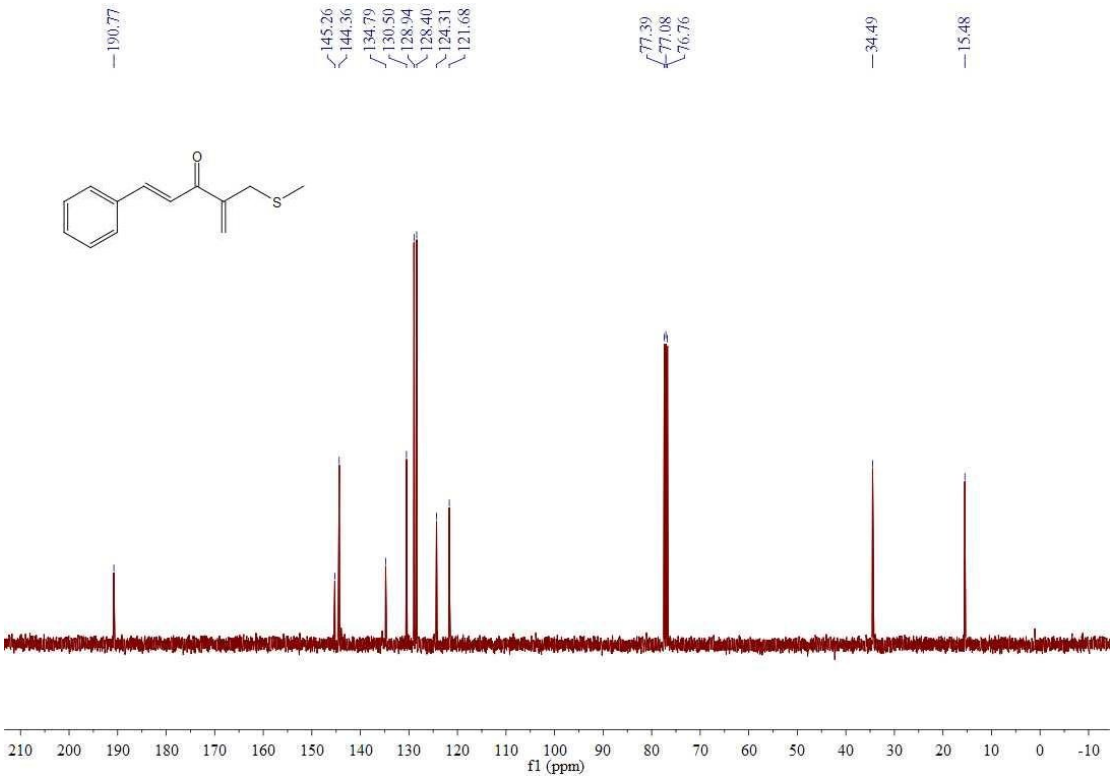
Compound 3t


7.71
7.69
7.68
7.27
7.15
7.14
7.13
5.87
5.82
3.52
2.10
2.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

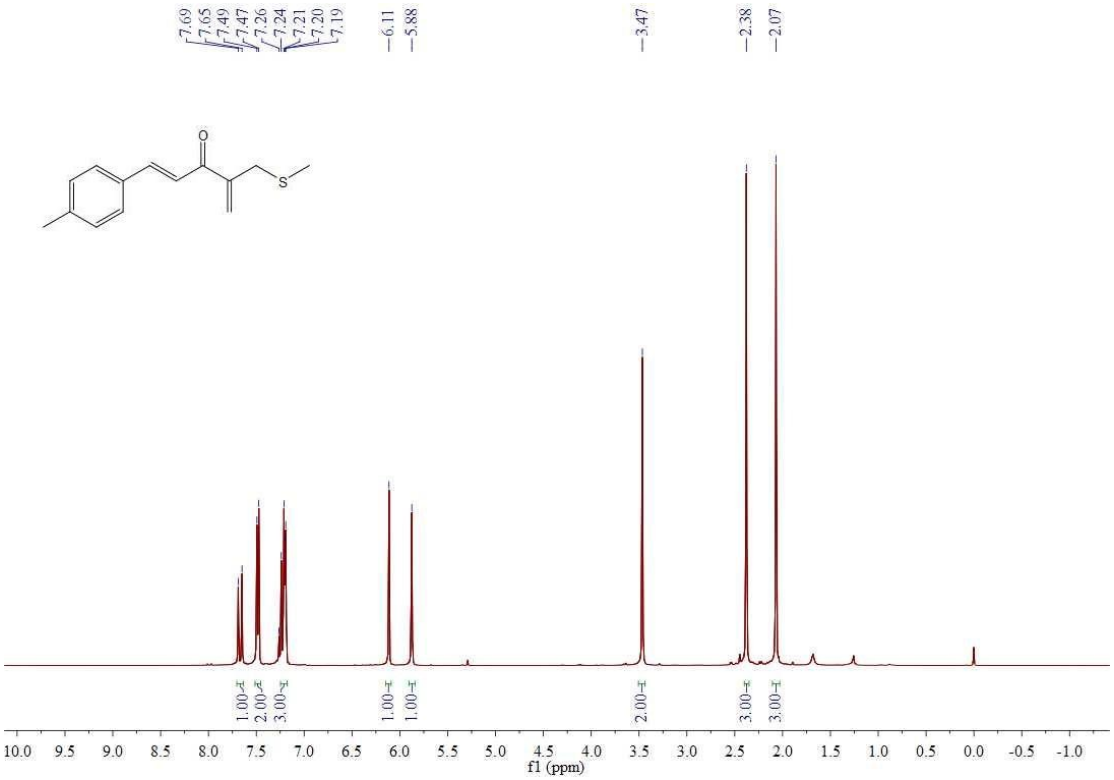

188.36
144.24
143.40
134.35
134.01
127.97
123.47
77.39
77.08
76.76
35.68
15.37
f1 (ppm)

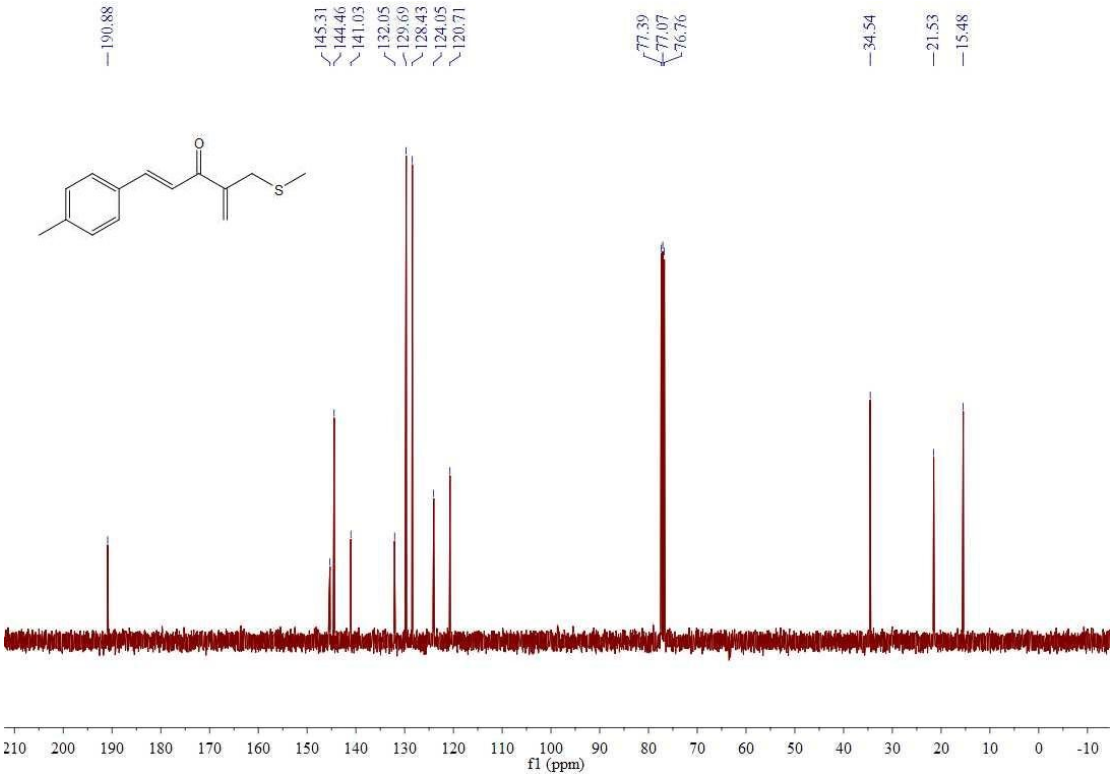
Compound 3u


7.63
7.59
7.52
7.51
7.50
7.33
7.32
7.31
7.21
7.19
7.17
6.05
5.82
3.39
1.99
O
S
1.05
2.07
3.22
1.13
1.00
1.04
2.00
2.99
f1 (ppm)

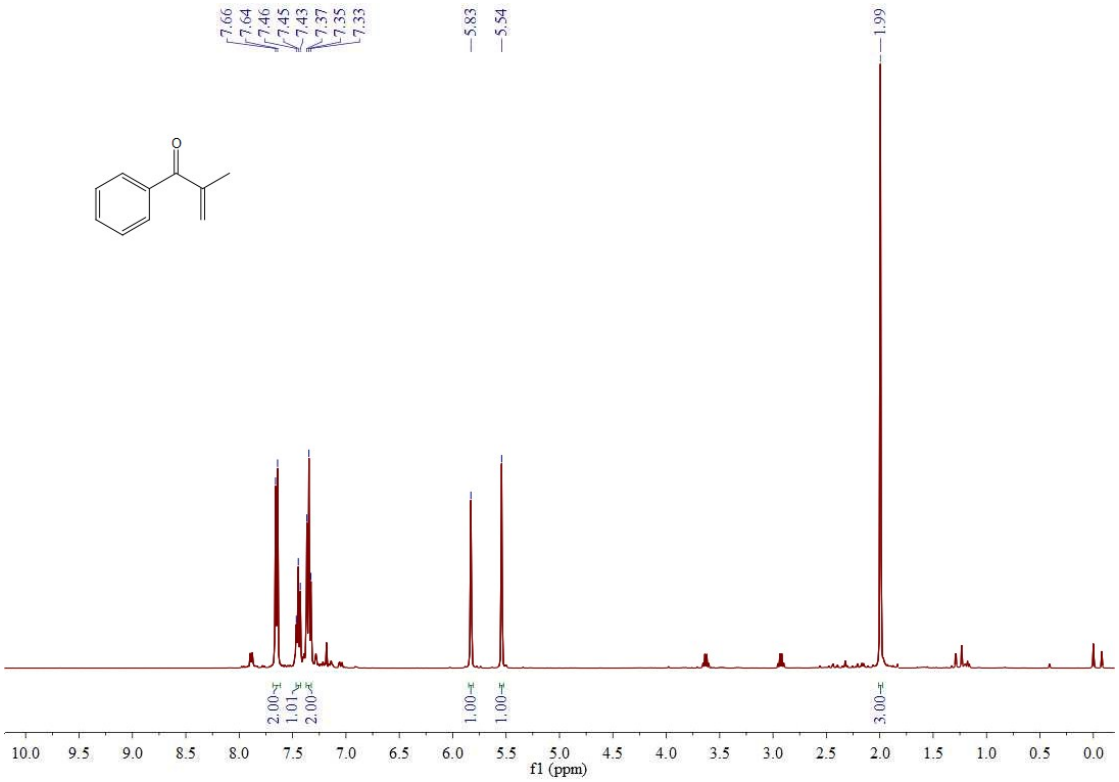

190.77
145.26
144.36
134.79
130.50
128.94
128.40
124.31
121.68
77.39
77.08
76.76
34.49
15.48
O
S
f1 (ppm)

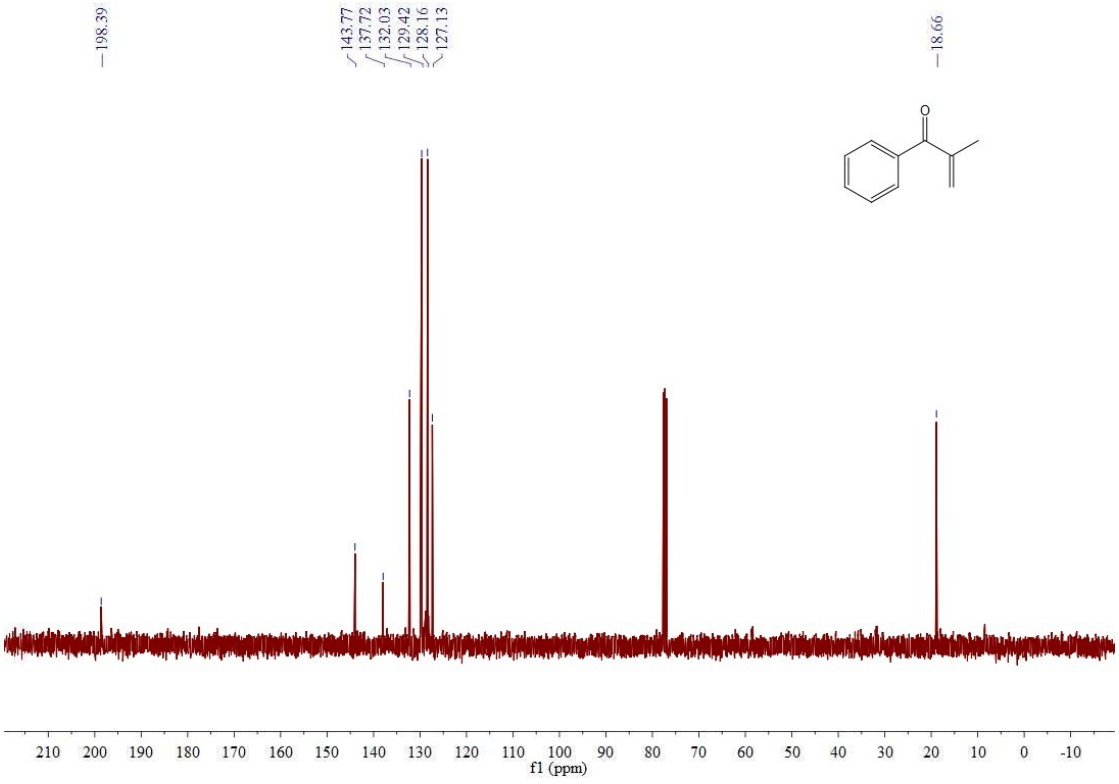
Compound 3v


7.69
7.65
7.49
7.47
7.26
7.24
7.21
7.20
7.19
6.11
5.88
3.47
2.38
2.07
O
S
1.00
2.00
3.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

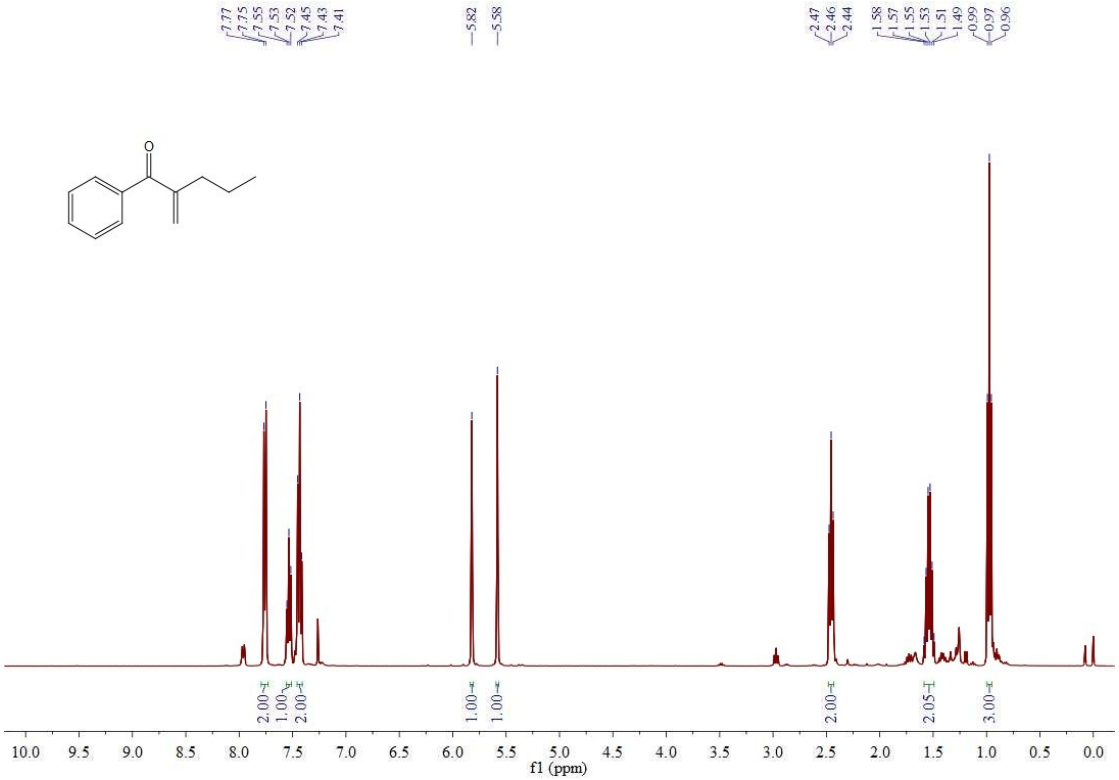

190.88
145.31
144.46
141.03
132.05
129.69
128.43
124.05
120.71
77.39
77.07
76.76
34.54
21.53
15.48
O
S
f1 (ppm)

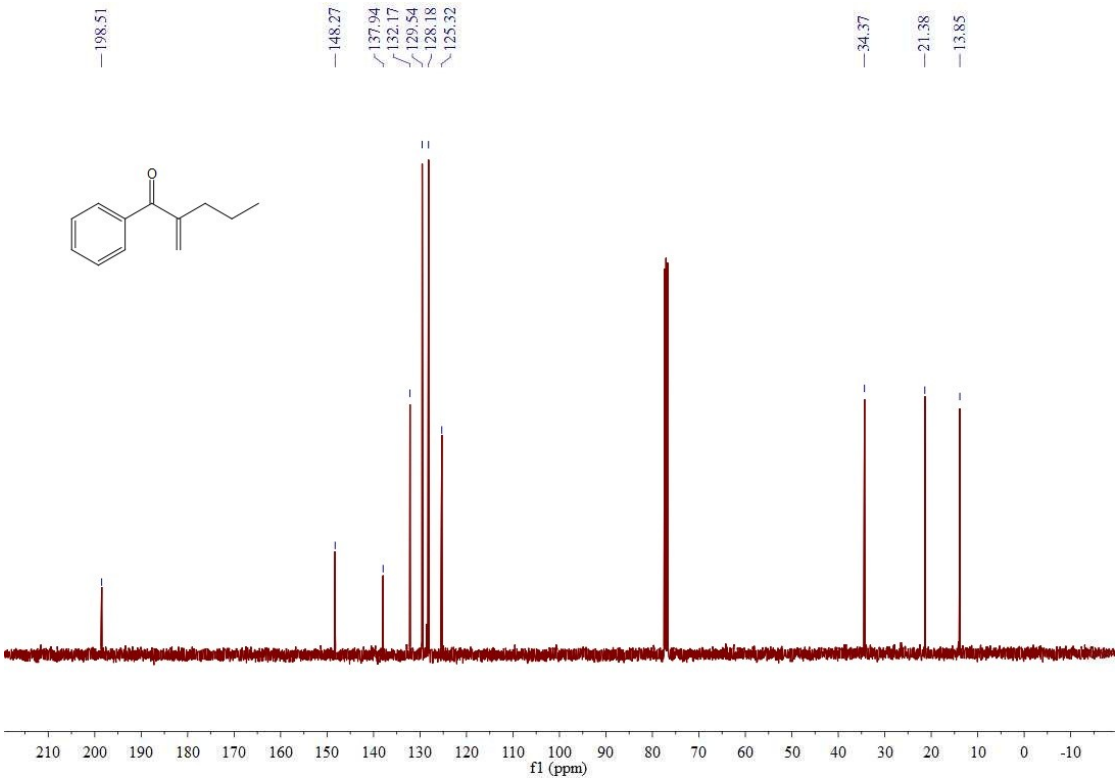
Compound 4a


7.66
7.64
7.46
7.45
7.43
7.37
7.35
7.33
5.83
5.54
1.99
2.00
1.01
2.00
1.00
1.00
3.00
f1 (ppm)

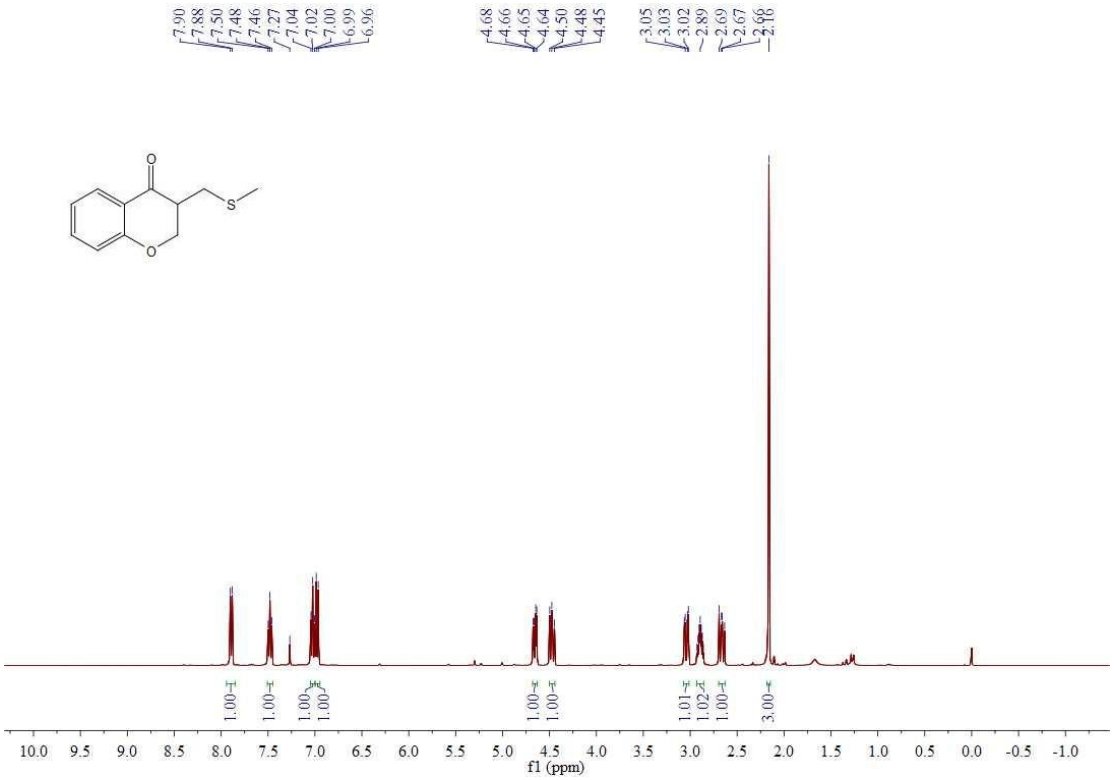

198.39
143.77
137.72
132.03
129.42
128.16
127.13
18.66
f1 (ppm)

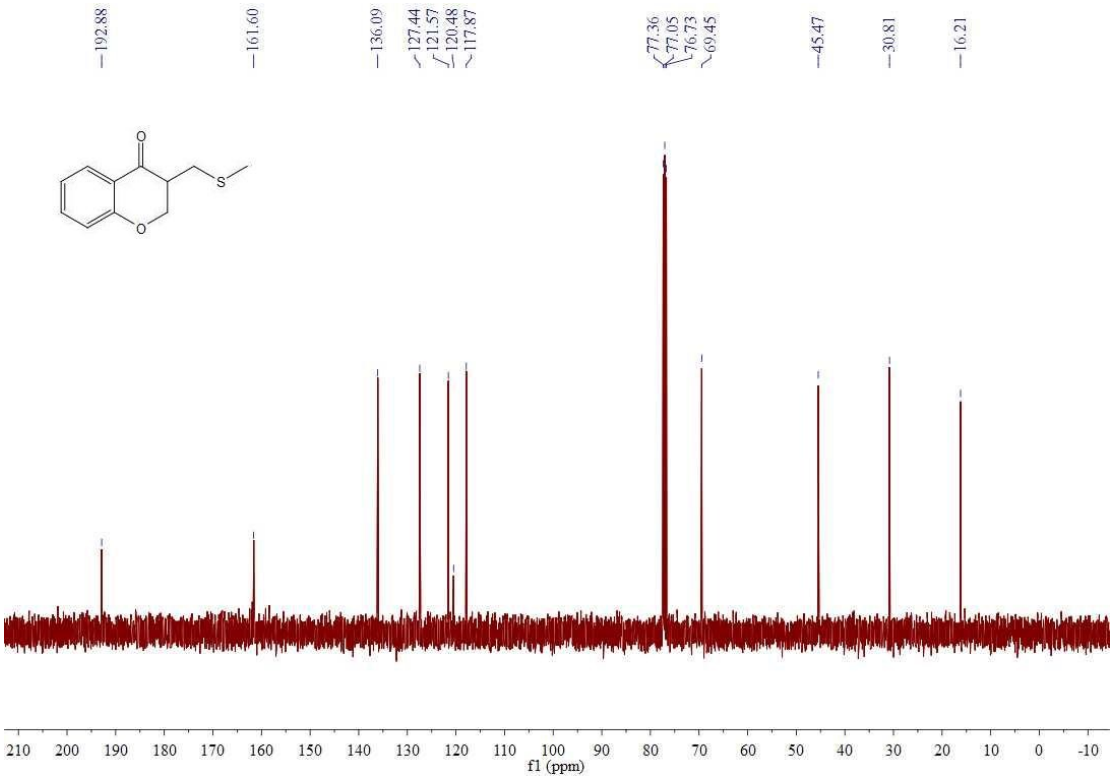
Compound 4b


7.77
7.75
7.55
7.53
7.52
7.45
7.43
7.41
5.82
5.58
2.47
2.46
2.44
1.58
1.57
1.55
1.53
1.51
1.49
0.99
0.97
0.96
2.00
1.00
2.00
1.00
1.00
2.00
2.05
3.00
f1 (ppm)

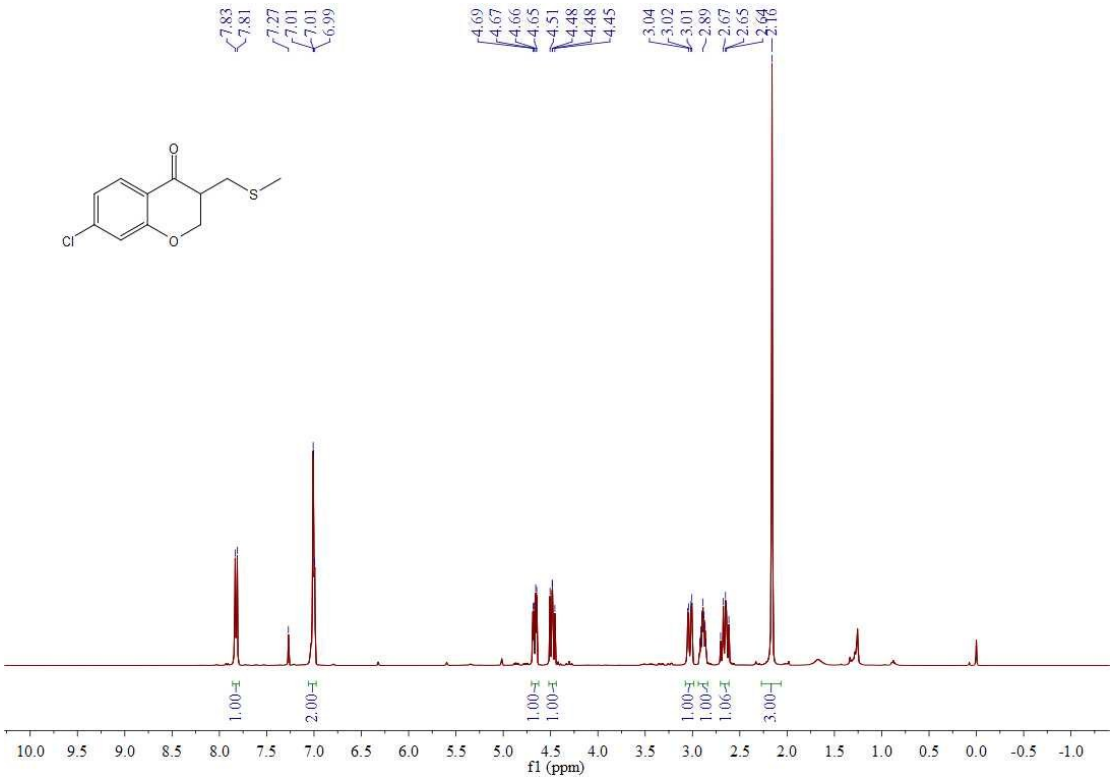

198.51
148.27
137.94
132.17
129.54
128.18
125.32
34.37
21.38
13.85
f1 (ppm)

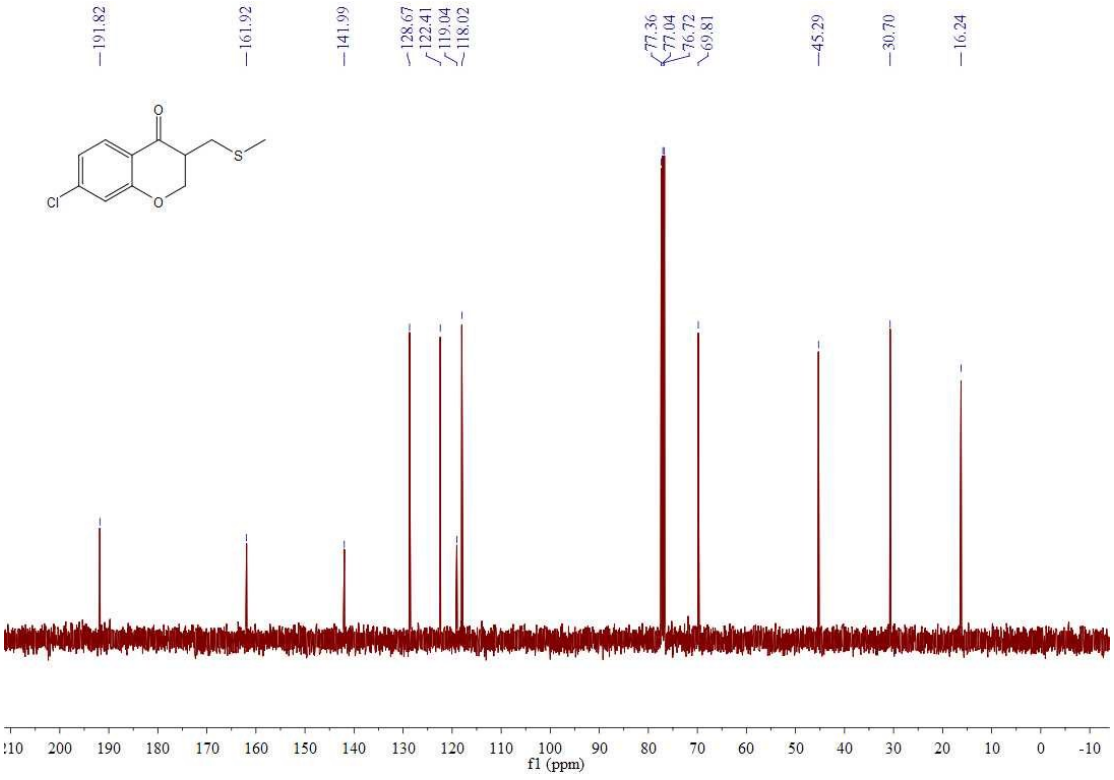
Compound 3x


7.90
7.88
7.50
7.48
7.46
7.27
7.04
7.02
7.00
6.99
6.96
4.68
4.66
4.65
4.64
4.50
4.48
4.45
3.05
3.03
3.02
2.89
2.69
2.67
2.66
2.16
O
S
O
1.00
1.00
1.00
1.00
1.00
1.00
1.01
1.02
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

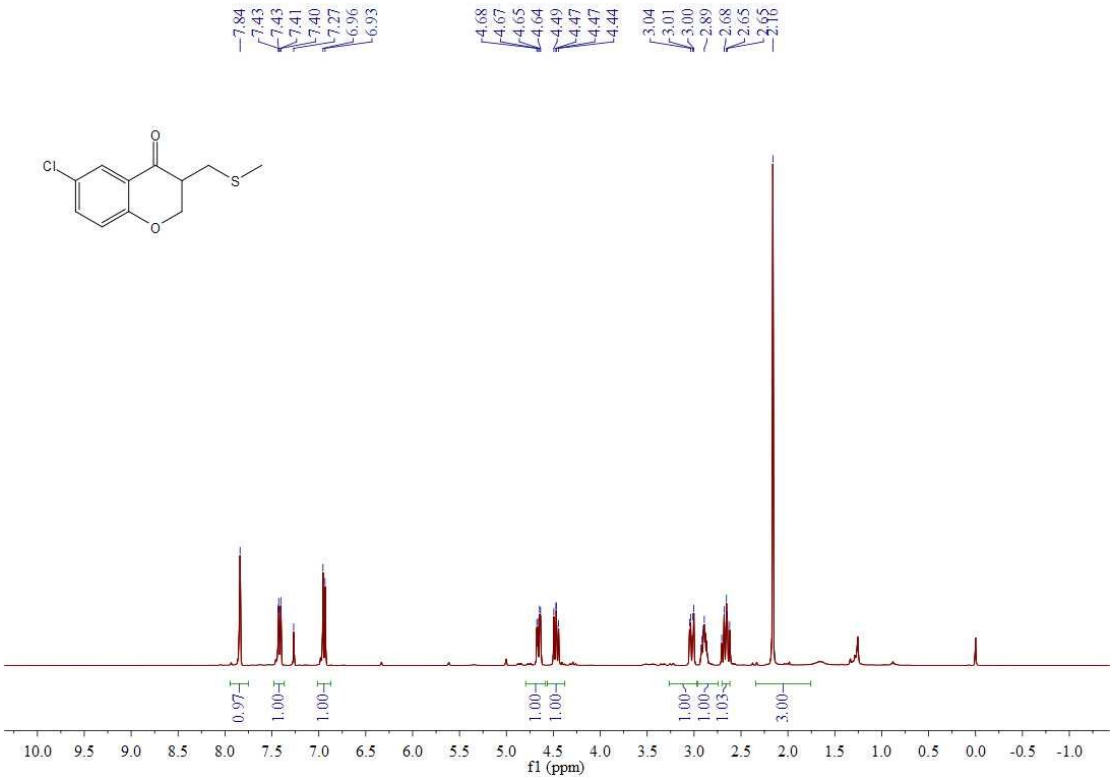

192.88
161.60
136.09
127.44
121.57
120.48
117.87
77.36
77.05
76.73
69.45
45.47
30.81
16.21
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

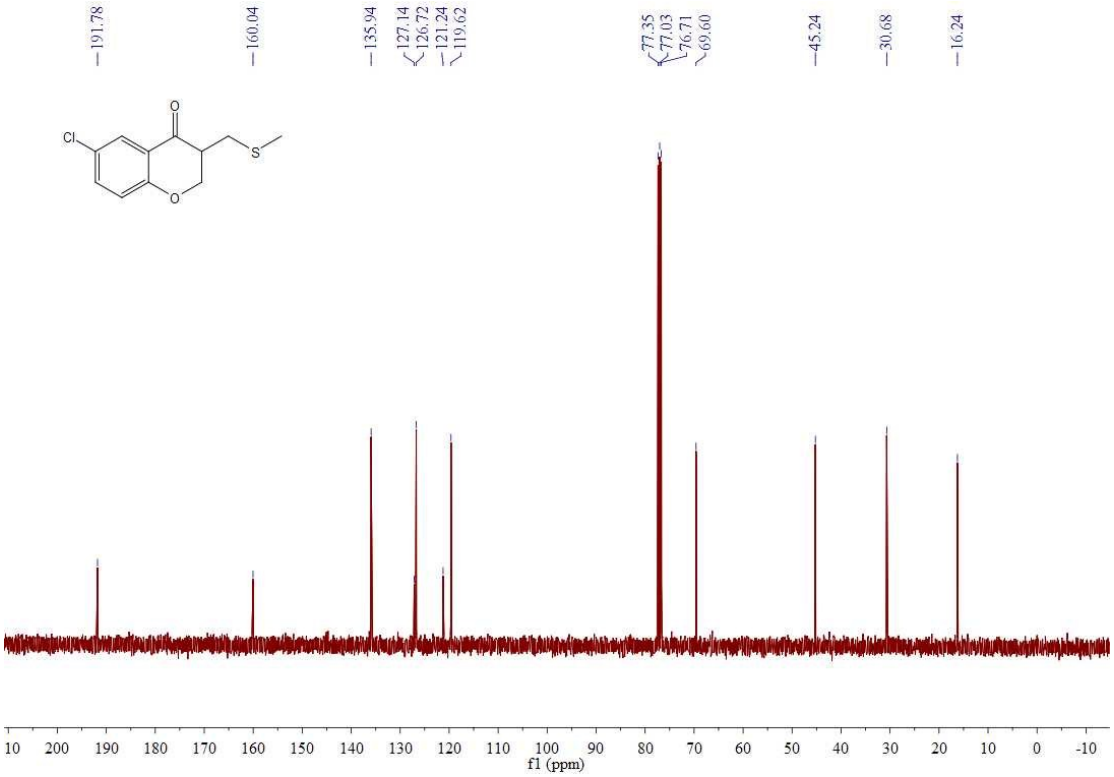
Compound 3y


7.83
7.81
7.27
7.01
7.01
6.99
4.69
4.67
4.66
4.65
4.51
4.48
4.48
4.45
3.04
3.02
3.01
2.89
2.67
2.65
2.64
2.16
O
S
Cl
O
1.00
2.00
1.00
1.00
1.00
1.00
1.06
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

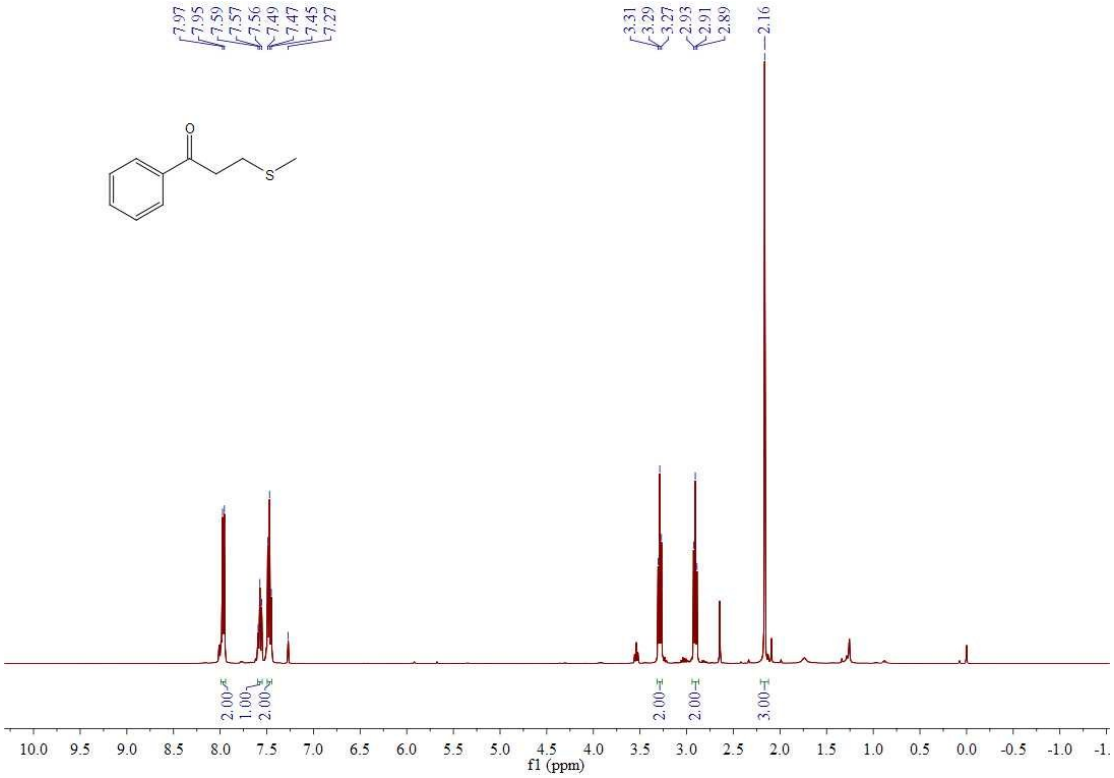

191.82
161.92
141.99
128.67
122.41
119.04
118.02
77.36
77.04
76.72
69.81
45.29
30.70
16.24
O
S
Cl
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

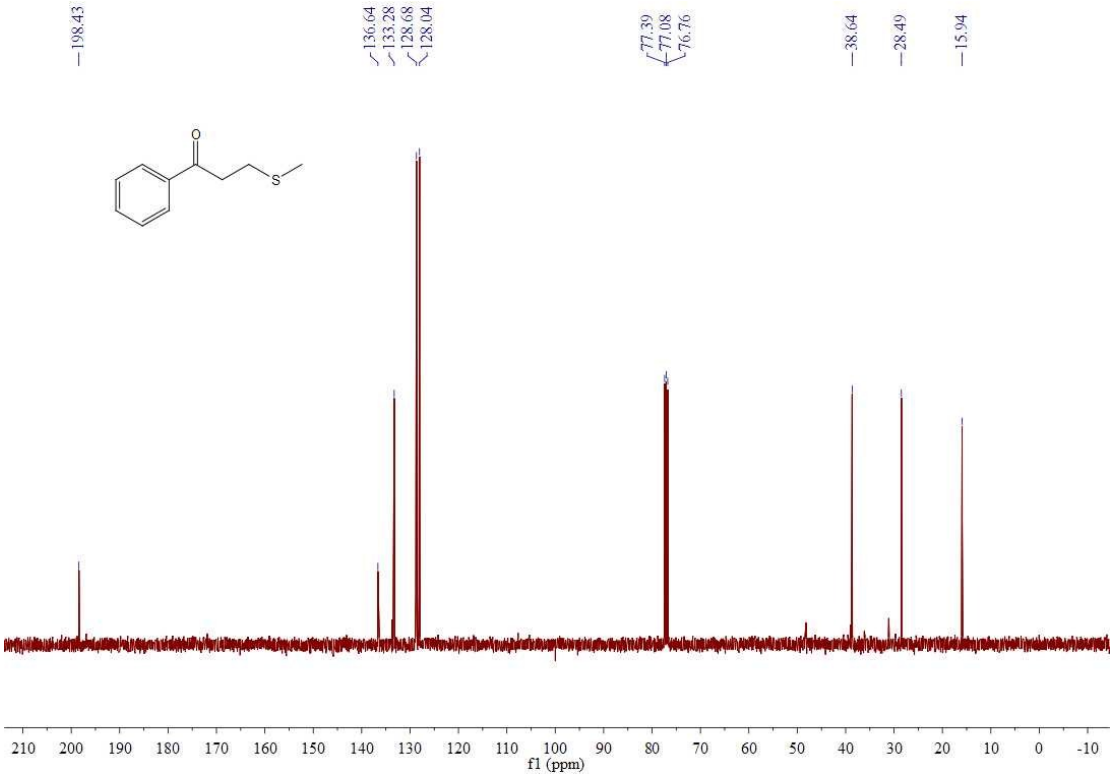
Compound 3z


7.84
7.43
7.43
7.41
7.40
7.27
6.96
6.93
4.68
4.67
4.65
4.64
4.49
4.47
4.47
4.44
3.04
3.01
3.00
2.89
2.68
2.65
2.65
2.16
Cl
O
S
O
0.97
1.00
1.00
1.00
1.00
1.00
1.00
1.03
3.00
f1 (ppm)

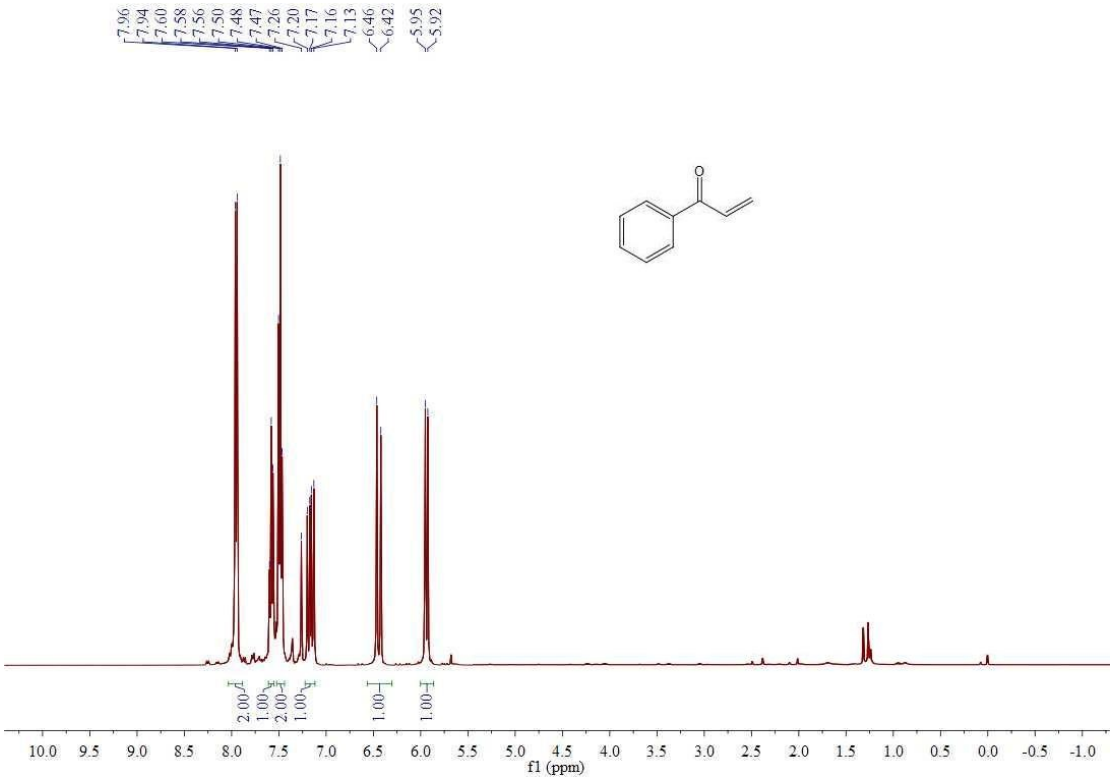

191.78
160.04
135.94
127.14
126.72
121.24
119.62
77.35
77.03
76.71
69.60
45.24
30.68
16.24
Cl
O
S
O
f1 (ppm)

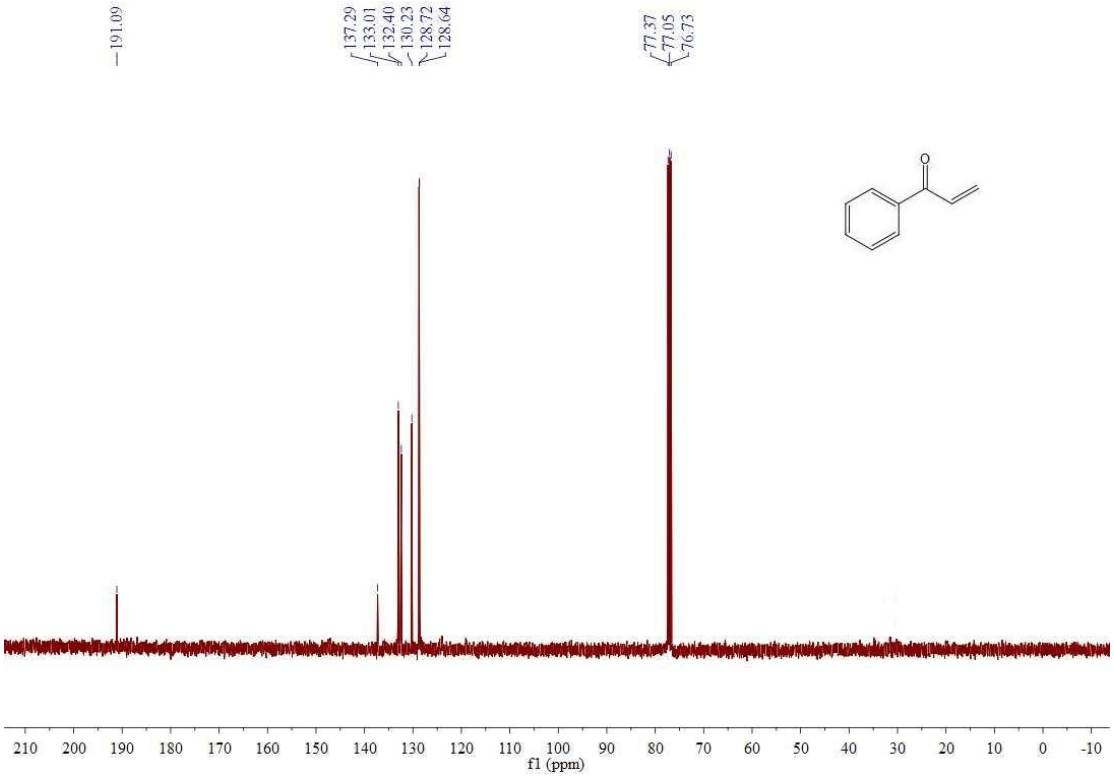
Compound C


7.97
7.95
7.59
7.57
7.56
7.49
7.47
7.45
7.27
3.31
3.29
3.27
2.93
2.91
2.89
2.16
O
S
2.00
1.00
2.00
2.00
2.00
3.00
f1 (ppm)

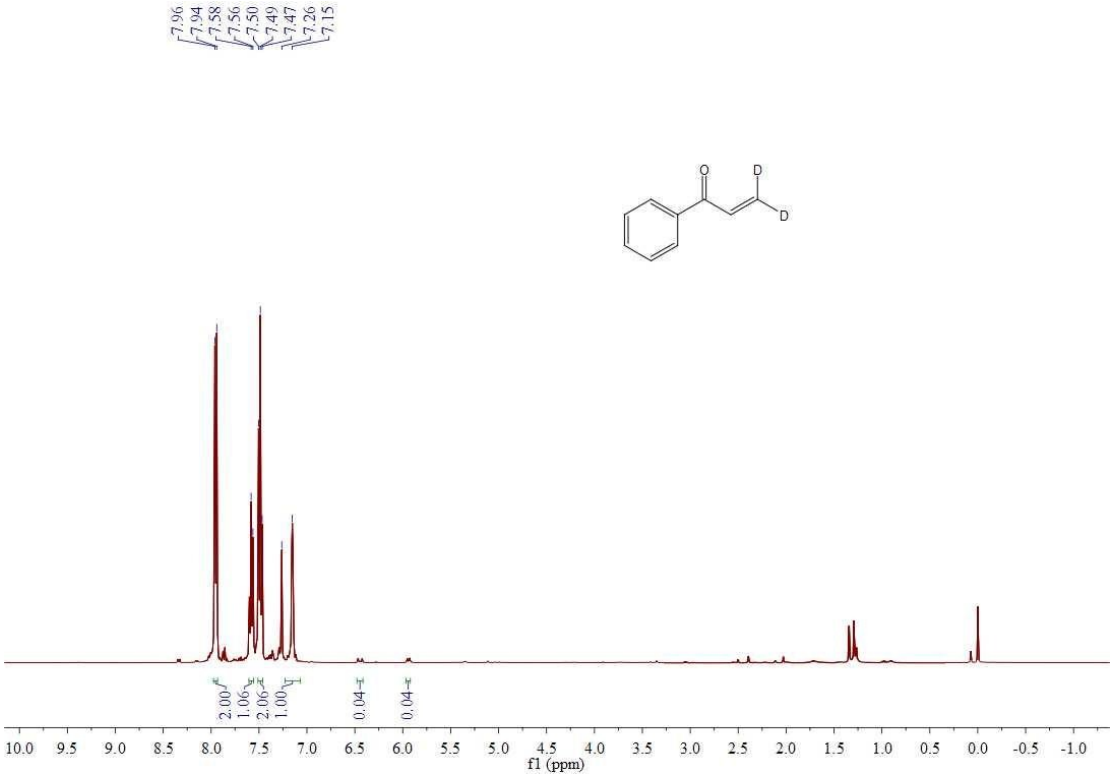

198.43
136.64
133.28
128.68
128.04
77.39
77.08
76.76
38.64
28.49
15.94
O
S
f1 (ppm)

Compound D


7.96
7.94
7.60
7.58
7.56
7.50
7.48
7.47
7.26
7.20
7.17
7.16
7.13
6.46
6.42
5.95
5.92
O
2.00
1.00
2.00
1.00
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


191.09
137.29
133.01
132.40
130.23
128.72
128.64
77.37
77.05
76.73
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound D-d_2



Compound 3a-d_7