Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Aryne Triggered [2,3]-Sigmatropic Rearrangement of Allyl and Propargyl Thioethers

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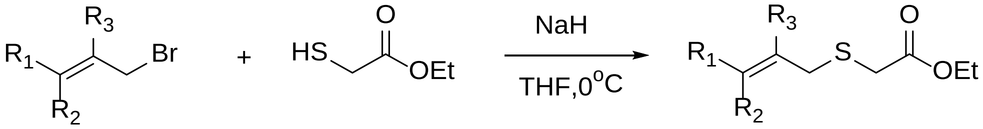
I. General Methods.

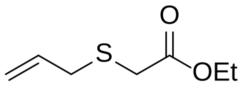
All reactions were carried out in schlenk tubes. The reactions were monitored either by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates (Yantai Chemical Industry Research Institute) or GC-MS（Thermo Fisher Trace 1300-ISQ）. Visualization was accomplished by UV light (254 nm). The crude products were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical). ^{1}H NMR spectra was recorded on a 400/500 MHz spectrometer at ambient temperature. Data are reported as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm) (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100/125 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.16 ppm). HR-MS data were obtained on a QTOF mass spectrometer. All commercial materials were used as received unless otherwise noted. Aryne precursors are all prepared following the literature procedures.

II. Substrates Preparation

1) General procedure A:

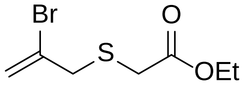


A mixture of sodium hydride (NaH, 5.25 mmol, 60% in mineral, 0.21 g, 1.05 equiv.) and anhydrous tetrahydrofuran (THF) was added ethyl 2-mercaptoacetate (5 mmol, 0.55 mL, 1 equiv.) under nitrogen atmosphere at 0 ^{o}C in a flame-dried schlenk tube with a magnetic stir bar. The minutes was kept stirring for 30 minutes until allyl bromide (5.25 mmol, 1.05 equiv.) was added to the solution dropwise. The reaction was kept stirring overnight at 0 ^{o}C. The reaction was then quenched with saturated NH_4Cl (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (petroleum ether (PE) and ethyl acetate (EA) as the eluent).



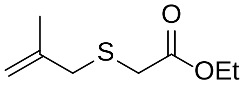
Ethyl 2-(allylthio)acetate (2d)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **2d** (95% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.76 (td, *J* = 16.4, 7.7 Hz, 1H), 5.20-5.10 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 7.3 Hz, 2H), 3.16 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.45, 132.93, 118.27, 61.22, 34.93, 31.74, 14.16. HR-MS (ESI): Calcd for $C_7H_{13}O_2S^+$ [M+H]$^+$ requires 161.0631; found 161.0623.



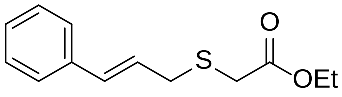
Ethyl 2-((2-bromoallyl)thio)acetate (2i)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **2i** (98% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.84 (s, 1H), 5.59 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 2H), 3.20 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.98, 128.29, 120.18, 61.45, 42.17, 31.91, 14.17. HR-MS (ESI): Calcd for $C_7H_{12}BrO_2S^+$ [M+H]$^+$ requires 238.9736; found 238.9723.



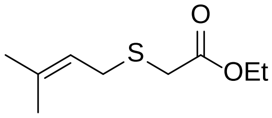
Ethyl 2-((2-methylallyl)thio)acetate (2j)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give **2j** (85% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.91 (s, 1H), 4.87 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.23 (s, 2H), 3.14 (s, 2H), 1.82 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.50, 139.96, 114.72, 61.21, 39.53, 31.98, 20.55, 14.18. HR-MS (ESI): Calcd for $C_8H_{15}O_2S^+$ [M+H]$^+$ requires 175.0787; found 175.0783.



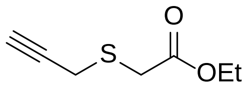
Ethyl 2-(cinnamylthio)acetate (2k)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **2k** (70% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.14 (dt, *J* = 15.3, 7.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 7.5 Hz, 2H), 3.17 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.55, 136.54, 133.77, 128.62, 127.75, 126.42, 124.47, 61.30, 34.64, 31.87, 14.21. HR-MS (ESI): Calcd for $C_{13}H_{17}O_2S^+$ [M+H]$^+$ requires 237.0944; found 237.0948.



Ethyl 2-((3-methylbut-2-en-1-yl)thio)acetate (2l)

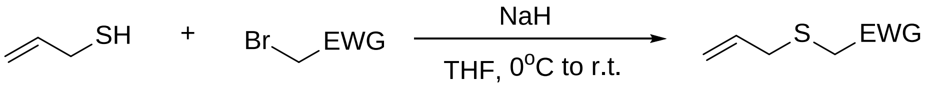
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give **2l** (85% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.26-5.15 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.27 (d, *J* = 7.8 Hz, 2H), 3.16 (s, 2H), 1.75 (s, 3H), 1.67 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.78, 136.78, 119.51, 61.23, 32.44, 30.06, 25.71, 17.67, 14.18. HR-MS (ESI): Calcd for $C_9H_{17}O_2S^+$ $[M+H]^+$ requires 189.0944; found 189.0948.



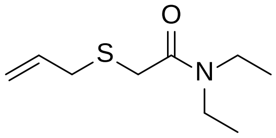
Ethyl 2-(prop-2-yn-1-ylthio)acetate (5b)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **5b** (81% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21 (q, *J* = 7.1 Hz, 2H), 3.42 (s, 2H), 3.41 (d, *J* = 2.7 Hz, 2H), 2.28 (t, *J* = 2.5 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.95, 78.95, 71.78, 61.47, 32.63, 19.91, 14.15. HR-MS (ESI): Calcd for $C_7H_{11}O_2S^+$ $[M+H]^+$ requires 159.0474; found 159.0477.

2) General procedure B:

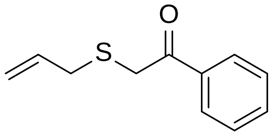


A mixture of NaH (5.25 mmol, 60% in mineral, 0.21 g, 1.05 equiv.) in anhydrous THF was added prop-2-ene-1-thiol (5 mmol, wt% =50%, 0.74 g, 1 equiv.) under nitrogen atmosphere at 0 °C for 30 minutes in a flame-dried schlenk tube with a magnetic stir bar. The reaction was kept stirring for 30 minutes until the electrophile compound (5.25 mmol, 1.05 equiv.) was added dropwise. The resultant solution was kept stirring overnight and then quenched with saturated NH_4Cl solution (30 mL), extracted with EA (3×30 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was then further purified by silica gel flash chromatography (PE and EA as the eluent).



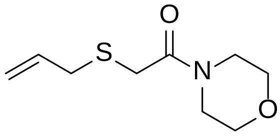
2-(Allylthio)-N,N-diethylacetamide (2b)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=5:1 as the eluent) to give **2b** (85% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.87-5.73 (m, 1H), 5.15 (dd, *J* = 25.2, 13.5 Hz, 2H), 3.43-3.30 (m, 4H), 3.23 (dd, *J* = 12.9, 4.8 Hz, 4H), 1.19 (td, *J* = 7.0, 2.3 Hz, 4H), 1.11 (td, *J* = 6.9, 2.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.32, 133.35, 117.98, 42.52, 40.31, 34.72, 31.73, 14.39, 12.88. HR-MS (ESI): Calcd for $C_9H_{18}NOS^+$ $[M+H]^+$ requires 188.1104; found 188.1114.



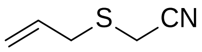
2-(Allylthio)-1-phenylethan-1-one (2c)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give **2c** (45% yield) as a deep yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99-7.93 (m, 2H), 7.57 (dd, *J* = 10.9, 3.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.77 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.25-5.12 (m, 2H), 3.76 (s, 2H), 3.18 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 194.49, 135.52, 133.32, 132.97, 128.68, 118.49, 35.58, 34.75. HR-MS (ESI): Calcd for $C_{11}H_{13}OS^+$ $[M+H]^+$ requires 193.0682; found 193.0689.



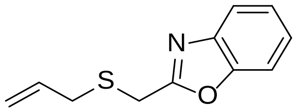
2-(Allylthio)-1-morpholinoethan-1-one (2e)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=5:1 as the eluent) to give **2e** (46% yield) as an orange oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.66 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.05 (ddd, *J* = 13.5, 10.6, 1.0 Hz, 2H), 3.59-3.50 (m, 4H), 3.49-3.43 (m, 2H), 3.40-3.34 (m, 2H), 3.13 (s, 2H), 3.10 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.68, 133.04, 118.13, 66.61, 66.45, 46.66, 42.04, 34.66, 31.50. HR-MS (ESI): Calcd for $C_9H_{16}NO_2S^+$ [M+H]$^+$ requires 202.0896; found 202.0902.



2-(Allylthio)acetonitrile (2f)

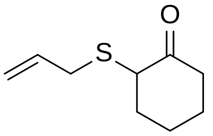
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give **2f** (49% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.81-5.66 (m, 1H), 5.31-5.20 (m, 2H), 3.39-3.31 (m, 2H), 3.23 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 131.74, 119.51, 116.33, 34.76, 15.40. HR-MS (ESI): Calcd for $C_5H_8NS^+$ [M+H]$^+$ requires 114.0372; found 114.0382.



2-((Allylthio)methyl)benzo[d]oxazole (2h)

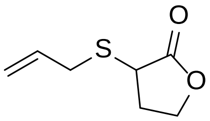
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **2h** (58% yield) as a white solid. ^{1}H NMR (400 MHz, CDCl3): δ 7.70 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.51 (dd, *J* = 6.2, 3.0 Hz, 1H), 7.33 (dt, *J* = 4.8, 3.6 Hz, 2H), 5.81 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.23 (dd, *J* = 25.5, 13.5 Hz, 2H), 3.87 (s, 2H), 3.27 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 163.72, 151.04, 141.25, 132.77, 125.06, 124.39, 120.00, 118.66, 110.59, 34.71, 26.69.

HR-MS (ESI): Calcd for $C_{11}H_{12}NOS^+$ [M+H]$^+$ requires 206.0634; found 206.0630.



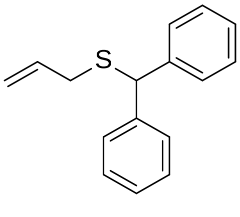
2-(Allylthio)cyclohexan-1-one (2m)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give **2m** (28% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.24-5.06 (m, 2H), 3.33 (t, *J* = 4.8 Hz, 1H), 3.11 (d, *J* = 7.2 Hz, 2H), 2.95 (ddd, *J* = 14.5, 10.7, 5.8 Hz, 1H), 2.29-1.67 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.73, 133.32, 117.99, 50.53, 37.97, 34.20, 32.96, 26.94, 22.09. HR-MS (ESI): Calcd for $C_9H_{15}OS^+$ $[M+H]^+$ requires 171.0838; found 171.0848.



3-(Allylthio)dihydrofuran-2(3H)-one (2n)

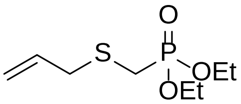
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give **2n** (38% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (ddd, *J* = 16.4, 9.2, 6.0 Hz, 1H), 5.23 (dd, *J* = 30.3, 13.5 Hz, 2H), 4.42 (dd, *J* = 16.1, 7.9 Hz, 1H), 4.33 (td, *J* = 8.5, 4.6 Hz, 1H), 3.57 (dd, *J* = 13.8, 8.5 Hz, 1H), 3.48 (dd, *J* = 8.6, 4.8 Hz, 1H), 3.23 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.65 (dq, *J* = 13.7, 8.1 Hz, 1H), 2.13 (ddt, *J* = 11.9, 7.1, 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.56, 132.69, 118.74, 66.74, 37.47, 33.93, 29.74. HR-MS (ESI): Calcd for $C_7H_{11}O_2S^+$ $[M+H]^+$ requires 159.0474; found 159.0480.



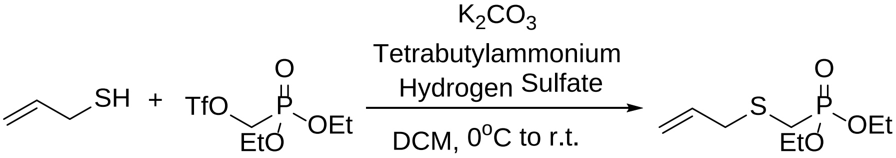
Allyl(benzhydryl)sulfane (2o)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE as the eluent) to give **2o** (48% yield) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 (d, *J* = 7.5 Hz, 4H), 7.30 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.1 Hz, 2H), 5.82 (td, *J* = 17.0, 7.2 Hz, 1H), 5.11 (s, 1H), 5.11-4.92 (m, 2H), 2.98 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.21, 133.97, 128.58, 128.53, 127.18, 117.39, 52.73, 35.10. HR-MS (ESI): Calcd for $C_{16}H_{17}S^+$ $[M+H]^+$ requires 241.1045; found 241.1050.

3) Synthesis of 2g



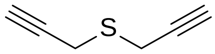
Diethyl ((allylthio)methyl)phosphonate (2g)



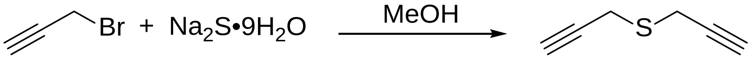
A mixture of anhydrous potassium carbonate (K$_2$CO$_3$, 10 mmol, 1.38 g, 2.0 equiv.) and Tetrabutylammonium Hydrogen Sulfate (1 mmol, 0.34 g, 0.1 equiv.) in 10mL anhydrous dichloromethane (DCM) was added prop-2-ene-1-thiol (5 mmol, wt% =50%, 0.74 g, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube with a magnetic stir bar. After 30 minutes, the triflate (5 mmol, 1.0 equiv.) was added to the solution dropwise and stirred at room temperature until TLC indicate the reactant was over. The mixture was then treated with water (30 mL), extracted with EA (3×30 mL), washed by brine (30 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was then purified by Aluminum oxide flash chromatography (PE: EA=4:1 as the eluent) to give **2g** (56% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.74 (ddd, *J* = 14.5, 9.5, 7.3 Hz, 1H), 5.20-5.13 (m, 2H), 4.20-4.15 (m, 4H), 3.31 (dd, *J* = 7.2, 0.6 Hz, 2H), 2.66 (d, *J* = 13.1

Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.80. ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.99, 118.52, 62.59, 62.53, 35.65, 35.61, 23.98, 22.49, 16.51, 16.45. HR-MS (ESI): Calcd for $C_8H_{18}O_3PS^+$ $[M+H]^+$ requires 225.0709; found 225.0719.

4) Synthesis of 5a

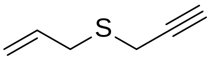


Di(prop-2-yn-1-yl)sulfane (5a)

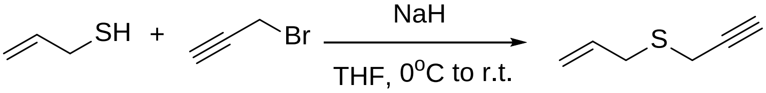


3-Bromoprop-1-yne (80 wt% in toluene, 1.25 mL, 11.2 mmol) was added dropwise to a solution of $Na_2S \cdot H_2O$ (1.24 g, 5.2 mmol) in methanol at 0 °C. The mixture was stirred at room temperature for 1 hour and the solvent was evaporated. The residue was treated with water (20 mL), extracted with Et_2O (3×30 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE: EA=20:1) to give **5a** (23%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.44 (d, *J* = 2.5 Hz, 1H), 2.27 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 78.98, 71.47, 18.85. HR-MS (ESI): Calcd for $C_6H_7S^+$ $[M+H]^+$ requires 111.0263; found 111.0268.

5) Synthesis of 5c



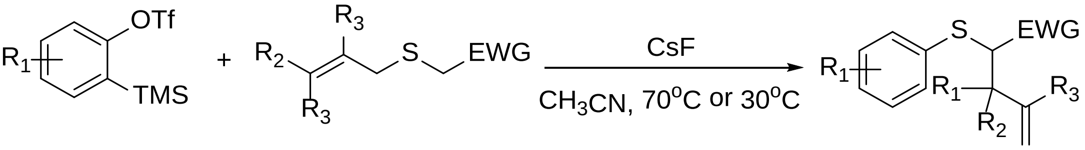
allyl(prop-2-yn-1-yl)sulfane (5c)



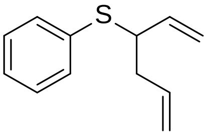
A mixture of NaH (5.25 mmol, 60% in mineral, 0.21 g, 1.05 equiv.) in anhydrous THF was added prop-2-ene-1-thiol (5 mmol, wt% =50%, 0.74 g, 1 equiv.)

under nitrogen atmosphere at 0 °C for 30 minutes in a flame-dried schlenk tube with a magnetic stir bar. The reaction was kept stirring for 30 minutes until 3-Bromoprop-1-yne (80 wt% in toluene, 1.25 mL, 11.2 mmol) was added dropwise. The resultant solution was kept stirring overnight and then quenched with saturated NH_4Cl solution (30 mL), extracted with EA (3×30 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was then further purified by vacuum distillation to give **5c** (25%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.71 (m, 1H), 5.20-5.06 (m, 2H), 3.32-3.28 (m, 2H), 3.18 (d, J = 2.6 Hz, 2H), 2.23 (t, J = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.94, 117.95, 79.91, 70.99, 33.87, 17.77.

III. General Procedure for Aryne Reaction

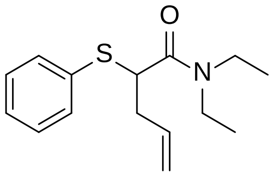


A mixture of cesium fluoride (CsF, 0.5 mmol, 0.076 g, 0.25 equiv.) in 1 mL anhydrous acetonitrile was added aryne (0.2 mmol, 49 μL, 1.0 equiv.) dropwise under nitrogen atmosphere at room temperature in a flame-dried schlenk tube with a magnetic stir bar. After 10 minutes, the sulfide (0.4 mmol, 2.0 equiv.) was added to the solution dropwise, which was then kept stirring at 30 °C or 70 °C (18 h or 48 h). The reaction mixture was then treated with water (20 mL), extracted with EA (3×20 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography.



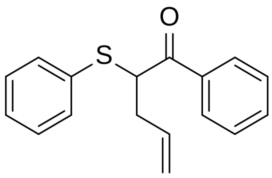
Hexa-1,5-dien-3-yl(phenyl)sulfane (3a)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give **3a** (90% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42-7.37 (m, 2H), 7.29 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.26-7.16 (m, 1H), 5.84 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.71 (ddd, *J* = 17.0, 10.1, 8.7 Hz, 1H), 5.16-5.03 (m, 2H), 5.01-4.85 (m, 2H), 3.65 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.53-2.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 138.14, 135.03, 134.47, 132.91, 128.72, 127.21, 117.24, 116.03, 51.77, 38.62. HR-MS (ESI): Calcd for $C_{12}H_{15}S^+$ $[M+H]^+$ requires 191.0889; found 191.0900.



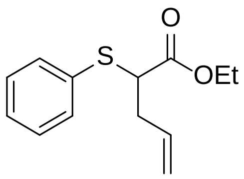
N,N-Diethyl-2-(phenylthio)pent-4-enamide (3b)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=10:1 as the eluent) to give **3b** (84% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.54-7.46 (m, 2H), 7.35-7.30 (m, 3H), 5.88-5.74 (m, 1H), 5.19-5.01 (m, 2H), 3.82 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.50 (dq, *J* = 13.9, 7.1 Hz, 1H), 3.41-3.18 (m, 2H), 3.11 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.87-2.72 (m, 1H), 2.49 (td, *J* = 13.2, 6.6 Hz, 1H), 1.11 (q, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.46, 135.01, 134.14, 132.83, 128.91, 128.31, 117.60, 47.37, 42.01, 40.82, 37.05, 14.75, 12.94. HR-MS (ESI): Calcd for $C_7H_{13}O_2S^+$ $[M+H]^+$ requires 161.0631; found 161.0623.



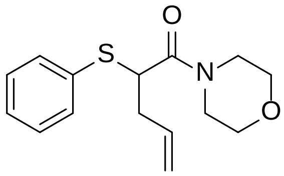
1-Phenyl-2-(phenylthio)pent-4-en-1-one (3c)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3c** (71% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.87 (m, 1H), 7.60-7.22 (m, 8H), 5.88 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.17-5.04 (m, 2H), 4.50 (dd, *J* = 7.7, 6.9 Hz, 1H), 2.76 (ddd, *J* = 14.6, 7.7, 6.8 Hz, 1H), 2.66-2.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.19, 136.11, 134.83, 133.10, 131.51, 128.98, 128.81, 128.60, 117.78, 50.83, 35.08. HR-MS (ESI): Calcd for $C1_7H_{17}OS^+$ $[M+H]^+$ requires 269.0995; found 269.0998.



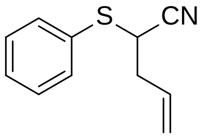
Ethyl 2-(phenylthio)pent-4-enoate (3d)

Following the general procedure, ethyl 2-(allylthio)acetate (0.2 mmol, 0.032 g, 1.0 equiv.) was added and the mixture was stirred at 70 °C for 18 h. The crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give **3d** (51% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.38 (m, 2H), 7.36-7.16 (m, 3H), 5.81 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.20-5.04 (m, 2H), 4.14-4.07 (m, 2H), 3.70 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.70-2.40 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.63, 133.90, 133.16, 133.11, 128.95, 128.04, 118.03, 61.15, 50.27, 35.86, 14.09. HR-MS (ESI): Calcd for $C_{13}H_{17}O_2S^+$ $[M+H]^+$ requires 237.0944; found 237.0958.



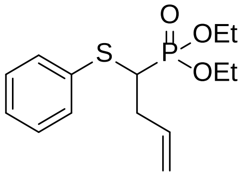
1-Morpholino-2-(phenylthio)pent-4-en-1-one (3e)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=5:1 as the eluent) to give **3e** (72% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53-7.40 (m, 2H), 7.36-7.29 (m, 3H), 5.88-5.75 (m, 1H), 5.10 (dd, *J* = 22.5, 5.4 Hz, 2H), 3.86 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.77-3.35 (m, 8H), 2.87-2.42 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.00, 134.89, 134.11, 132.31, 129.09, 128.60, 117.72, 66.88, 66.51, 46.69, 46.39, 42.47, 36.36. HR-MS (ESI): Calcd for $C_{15}H_{20}NO_2S^+$ [M+H]$^+$ requires 278.1209; found 278.1219.



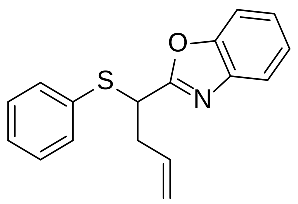
2-(Phenylthio)pent-4-enenitrile (3f)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give **3f** (84% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66-7.57 (m, 2H), 7.44-7.35 (m, 3H), 5.96-5.79 (m, 1H), 5.24 (dd, *J* = 8.5, 6.7 Hz, 2H), 3.73 (t, *J* = 7.3 Hz, 1H), 2.61-2.55 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 134.70, 131.83, 130.48, 129.64, 129.52, 120.02, 118.79, 36.91, 36.62. HR-MS (ESI): Calcd for $C_{11}H_{12}NS^+$ [M+H]$^+$ requires 190.0685; found 190.0685.



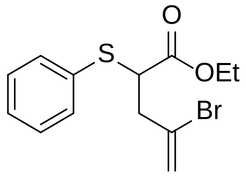
Diethyl (1-(phenylthio)but-3-en-1-yl)phosphonate (3g)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=5:1 as the eluent) to give **3g** (81% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (m, 2H), 7.33-7.26 (m, 3H), 5.98 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.20-5.11 (m, 2H), 4.17 (ddd, *J* = 22.0, 14.5, 7.2 Hz, 4H), 3.19 (ddd, *J* = 16.3, 9.3, 4.6 Hz, 1H), 2.78 (ddd, *J* = 19.8, 14.3, 5.6 Hz, 1H), 2.50 (td, *J* = 16.3, 9.3 Hz, 1H), 1.31 (td, *J* = 7.0, 1.8 Hz, 6H). ^{31}P NMR (162 MHz, CDCl3): δ 24.87. ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.86, 134.82, 134.59, 134.47, 131.99, 128.93, 127.45, 117.84, 63.08, 63.01, 62.76, 62.69, 45.39, 43.92, 34.44, 16.49, 16.44, 16.39. HR-MS (ESI): Calcd for $C_{14}H_{22}O_3PS^+$ $[M+H]^+$ requires 301.1022; found 301.1014.



2-(1-(Phenylthio)but-3-en-1-yl)benzo[d]oxazole (3h)

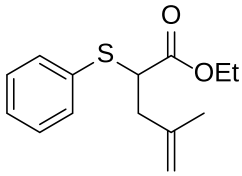
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3h** (86% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.62 (m, 1H), 7.52-7.46 (m, 1H), 7.40-7.34 (m, 2H), 7.33-7.28 (m, 2H), 7.27-7.23 (m, 3H), 5.86 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.11 (dd, *J* = 28.7, 13.6 Hz, 2H), 4.51-4.36 (m, 1H), 2.90 (ddt, *J* = 27.9, 14.2, 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.50, 150.74, 140.94, 133.72, 133.38, 132.55, 129.03, 128.28, 125.06, 124.36, 120.08, 118.44, 110.61, 46.14, 37.07. HR-MS (ESI): Calcd for $C_{17}H_{16}NOS^+$ $[M+H]^+$ requires 282.0947; found 282.0940.



Ethyl 4-bromo-2-(phenylthio)pent-4-enoate (3i)

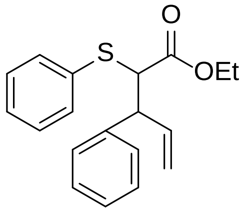
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3i** (94% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 2H), 7.32 (m, 3H), 5.68 (s, 1H), 5.52 (d, *J* = 1.7 Hz, 1H), 4.12 (q, *J* = 7.1, 2H), 3.98 (dd, *J* = 8.4, 6.7 Hz, 1H), 2.91

(ddd, *J* = 21.0, 14.6, 7.3 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.97, 133.61, 132.39, 129.16, 129.03, 128.44, 120.16, 61.39, 48.76, 43.18, 14.04. HR-MS (ESI): Calcd for $C_{13}H_{16}BrO_2S^+$ $[M+H]^+$ requires 315.0049; found 315.0060.



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

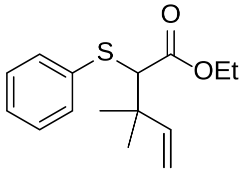
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3j** (93% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.43 (m, 2H), 7.31 (m, 3H), 4.83 (s, 1H), 4.77 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.84 (dd, *J* = 9.5, 6.1 Hz, 1H), 2.63 (dd, *J* = 14.6, 9.6 Hz, 1H), 2.45 (dd, *J* = 14.6, 6.0 Hz, 1H), 1.75 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.85, 141.45, 133.30, 133.03, 128.93, 128.01, 113.21, 61.09, 49.07, 39.72, 22.31, 14.05. HR-MS (ESI): Calcd for $C_{14}H_{19}O_2S^+$ $[M+H]^+$ requires 251.1100; found 251.1105.



Ethyl 3-phenyl-2-(phenylthio)pent-4-enoate (3k)

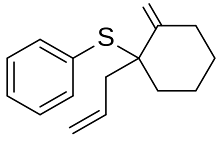
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3k** (88% yield) as a deep yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.43 (m, 2H), 7.37-7.15 (m, 18 h), 6.13 (ddd, *J* = 17.0, 10.1, 8.4 Hz, 1H), 6.01 (ddd, *J* = 17.2, 10.1, 8.3 Hz, 1H), 5.15 (m, 4H), 4.11-3.96 (m, 4H), 3.83-3.72 (m, 4H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1

Hz, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.32, 170.88, 140.79, 139.85, 138.00, 137.90, 133.58, 133.54, 133.23, 133.17, 128.95, 128.79, 128.63, 128.59, 128.30, 127.99, 127.95, 127.23, 127.15, 117.69, 117.06, 61.12, 60.85, 56.44, 56.05, 52.00, 51.70, 14.07, 13.73. HR-MS (ESI): Calcd for $C_{19}H_{21}O_2S^+$ $[M+H]^+$ requires 313.1257; found 313.1260.



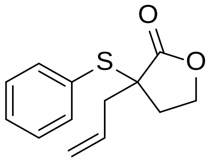
Ethyl 3,3-dimethyl-2-(phenylthio)pent-4-enoate (3l)

Following the general procedure at 70 °C for 48 h, the mixture was stirred for 48 h and the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3l** (83% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 (m, 2H), 7.33-7.14 (m, 3H), 6.03 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.13-5.04 (m, 2H), 4.10 (m, 2H), 3.58 (s, 1H), 2.17 (s, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 171.72, 144.09, 135.29, 131.94, 128.98, 127.38, 113.17, 62.20, 60.81, 40.01, 25.35, 24.37, 14.13. HR-MS (ESI): Calcd for $C_{15}H_{21}O_2S^+$ $[M+H]^+$ requires 265.1257; found 265.1255.



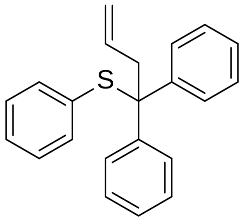
2-Allyl-2-(phenylthio)cyclohexan-1-one (3m)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3m** (43% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.27 (m, 5H), 5.85 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.07 (dd, *J* = 21.7, 13.6 Hz, 2H), 3.37 (td, *J* = 14.3, 5.8 Hz, 1H), 2.34 (m, 1H), 2.35-1.53 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 207.15, 136.28, 133.89, 130.27, 129.43, 128.91, 118.42, 60.18, 39.67, 37.73, 36.74, 26.93, 21.22. HR-MS (ESI): Calcd for $C_7H_{11}O_2S^+$ [M+H]$^+$ requires 247.1151; found 247.1147.



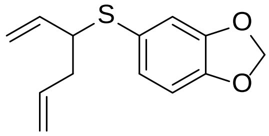
3-Allyl-3-(phenylthio)dihydrofuran-2(3H)-one (3n)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **3n** (81% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 5.80 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.22 - 5.13 (m, 2H), 4.26-4.19 (m, 2H), 2.59-2.52 (m, 2H), 2.50 (m, 1H), 2.19 (ddd, *J* = 13.9, 5.2, 3.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.56, 137.27, 132.15, 130.17, 129.05, 120.14, 65.05, 52.95, 39.44, 33.48. HR-MS (ESI): Calcd for $C_{13}H_{15}O_2S^+$ [M+H]$^+$ requires 235.0787; found 235.0786.



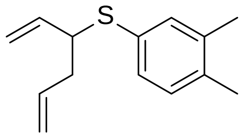
(1,1-Diphenylbut-3-en-1-yl)(phenyl)sulfane (3o)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give **3o** (33% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.01 (m, 15H), 5.65 (dt, *J* = 13.8, 9.8 Hz, 1H), 4.75 (dd, *J* = 43.8, 13.4 Hz, 2H), 4.44-4.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.26, 135.26, 133.51, 132.10, 131.25, 128.61, 128.53, 128.50, 128.39, 128.35, 128.14, 127.75, 127.50, 127.34, 126.78, 126.63, 126.58, 125.85, 116.46, 57.19, 55.92. HR-MS (ESI): Calcd for $C_{22}H_{21}S^+$ [M+H]$^+$ requires 317.1358; found 317.1360.



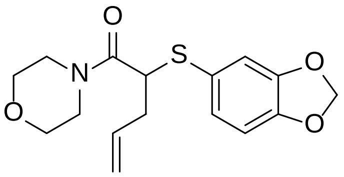
5-(Hexa-1,5-dien-3-ylthio)benzo[d][1,3]dioxole (4a)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give **4a** (73% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-6.88 (m, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.98 (s, 2H), 5.85 (ddt, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.71 (ddd, *J* = 17.1, 9.9, 9.0 Hz, 1H), 5.12 (dd, *J* = 13.1, 5.6 Hz, 2H), 4.93 (dd, *J* = 51.4, 13.6 Hz, 2H), 3.51 (dd, *J* = 14.6, 8.3 Hz, 1H), 2.54-2.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.74, 147.65, 138.19, 135.12, 128.70, 125.96, 117.10, 115.93, 114.72, 108.45, 101.31, 53.03, 38.37. HR-MS (ESI): Calcd for $C_{13}H_{15}O_2S^+$ [M+H]$^+$ requires 235.0787; found 235.0786.



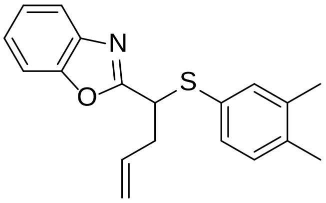
(3,4-Dimethylphenyl)(hexa-1,5-dien-3-yl)sulfane (4b)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **4b** (78% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-6.99 (m, 3H), 5.83 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.70 (ddd, *J* = 17.0, 10.1, 8.8 Hz, 1H), 5.12-5.03 (m, 2H), 4.93 (dd, *J* = 30.9, 13.6 Hz, 2H), 3.58 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.51-2.39 (m, 2H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.30, 137.04, 136.06, 135.23, 134.56, 130.87, 130.74, 129.98, 117.04, 115.80, 51.94, 38.59, 19.66, 19.44. HR-MS (ESI): Calcd for $C_{14}H_{19}S^+$ [M+H]$^+$ requires 219.1202; found 219.1207.



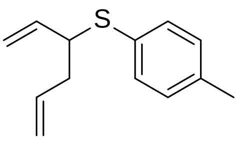
2-(Benzo[d][1,3]dioxol-5-ylthio)-1-morpholinopent-4-en-1-one (4c)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **4c** (69% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 5.88-5.76 (m, 1H), 5.17-5.02 (m, 2H), 3.80-3.72 (m, 1H), 3.70-3.41 (m, 8H), 2.79-2.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.93, 147.76, 146.90, 133.96, 128.75, 122.40, 116.61, 114.32, 107.68, 100.54, 65.92, 65.54, 46.05, 45.36, 41.40, 34.99, 28.67. HR-MS (ESI): Calcd for $C_{16}H_{20}NO_4S^+$ $[M+H]^+$ requires 322.1108; found 322.1116.



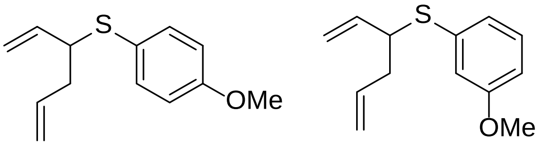
2-(1-((3,4-Dimethylphenyl)thio)but-3-en-1-yl)benzo[d]oxazole (4d)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **4d** (65% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 1H), 7.42 (ddd, *J* = 4.2, 2.1, 0.5 Hz, 1H), 7.27-7.19 (m, 2H), 7.00 (d, *J* = 4.9 Hz, 2H), 6.95-6.88 (m, 1H), 5.78 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.10-4.95 (m, 2H), 4.32-4.26 (m, 1H), 2.91-2.67 (m, 2H), 2.11 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.62, 149.68, 139.95, 136.37, 134.33, 132.91, 130.63, 129.22, 127.57, 123.92, 123.24, 118.97, 117.19, 109.52, 45.43, 35.91, 18.47, 18.44. HR-MS (ESI): Calcd for $C_{18}H_{20}NOS^+$ $[M+H]^+$ requires 298.1260; found 298.1260.



Hexa-1,5-dien-3-yl(p-tolyl)sulfane(4e) and hexa-1,5-dien-3-yl(m-tolyl)sulfane (4e')

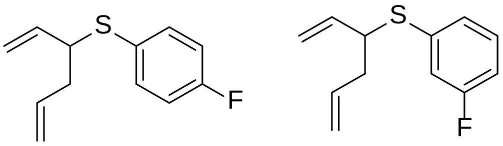
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **4e** and **4e'** (4e:4e'=1.3:1, 92% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (t, *J* = 5.9 Hz, 2.3H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 11.5, 4.9 Hz, 2.3H), 6.86 (t, *J* = 5.8 Hz, 2.6H), 6.80 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.91-5.81 (m, 2.3H), 5.73 (ddd, *J* = 18.6, 9.6, 5.1 Hz, 2.3H), 5.15-5.09 (m, 4.6H), 5.05-4.92 (m, 3.3H), 4.82 (d, *J* = 17.0 Hz, 1.3H), 3.82 (s, 3.9H), 3.82 (s, 3H), 3.71 (dd, *J* = 14.4, 8.0 Hz, 1H), 3.50 (dd, *J* = 14.6, 8.2 Hz, 1.3H), 2.45 (ddt, *J* = 16.0, 14.7, 7.1 Hz, 4.6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.31, 138.15, 136.27, 135.25, 134.96, 129.47, 124.64, 124.40, 117.61, 117.26, 117.00, 116.11, 115.76, 114.25, 112.97, 55.28, 52.93, 51.46, 38.62, 38.40. HR-MS (ESI): Calcd for $C_{13}H_{17}S^+$ $[M+H]^+$ requires 205.1045; found 205.1049.



Hexa-1,5-dien-3-yl(4-methoxyphenyl)sulfane (4f) and hexa-1,5-dien-3-yl(3-methoxyphenyl)sulfane (4f')

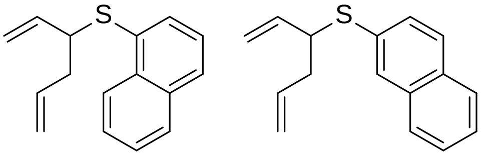
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **4f** and **4f'** (4f:4f'=1.3:1,75% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.8 Hz, 2.6H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.04-6.93 (m, 2H), 6.88-6.82 (m, 2.6H), 6.82-6.75 (m, 1H), 5.94-5.80 (m, 2.3H), 5.78-5.63 (m, 2.3H), 5.18-5.07 (m, 4.6H), 5.05-4.77 (m, 4.6H), 3.82 (s, 3.9H), 3.82 (s, 3H), 3.71 (dd, *J* = 14.4, 8.1 Hz, 1H), 3.50 (dd, *J* = 14.6, 8.3 Hz, 1.3H), 2.55-2.34 (m, 4.6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ

138.30, 138.14, 136.27, 135.25, 134.96, 129.46, 124.64, 124.39, 117.61, 117.26, 116.99, 116.12, 115.76, 114.25, 112.97, 55.28, 52.93, 51.47, 38.62, 38.40. HR-MS (ESI): Calcd for $C_{13}H_{17}OS^+$ $[M+H]^+$ requires 221.0995; found 221.0999.



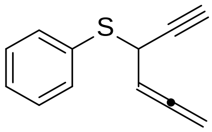
(4-Fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (4g) and (3-fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (4g')

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **4g** and **4g'** (4g:4g'=2.4:1, 86% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 4.4H), 7.25-7.20 (m, 1H), 7.10 (ddd, *J* = 10.9, 9.3, 4.7 Hz, 2.4H), 7.03-6.94 (m, 4.8H), 6.91 (td, *J* = 8.3, 1.7 Hz, 1H), 5.89-5.77 (m, 3.4H), 5.74-5.59 (m, 3.4H), 5.15-5.06 (m, 6.8H), 5.03-4.93 (m, 4.4H), 4.80 (d, *J* = 17.0 Hz, 2.4H), 3.68 (dd, *J* = 14.7, 7.9 Hz, 1H), 3.52 (dd, *J* = 14.7, 8.1 Hz, 2.4H), 2.49-2.33 (m, 6.8H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.66, -113.97. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.76, 161.30, 138.02, 137.79, 136.01, 135.93, 134.91, 134.66, 129.92, 129.83, 129.17, 127.72, 118.89, 118.67, 117.49, 117.26, 116.42, 116.06, 115.89, 115.67, 114.06, 113.85, 52.79, 51.51, 38.55, 38.41. HR-MS (ESI): Calcd for $C_{12}H_{14}FS^+$ $[M+H]^+$ requires 209.0795; found 209.0788.



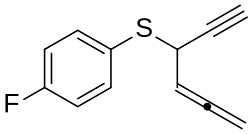
Hexa-1,5-dien-3-yl(naphthalen-1-yl)sulfane (4h) and hexa-1,5-dien-3-yl(naphthalen-2-yl)sulfane (4h')

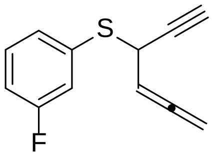
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give **4h** and **4h'** (4h:4h'=1:1, 71% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.52 (d, *J* = 8.4 Hz, 1H), 7.91-7.81 (m, 2H), 7.80-7.70 (m, 4H), 7.66 (dd, *J* = 7.1, 0.8 Hz, 1H), 7.58-7.36 (m, 6H), 5.95-5.79 (m, 2H), 5.72 (ddd, *J* = 18.4, 9.7, 5.2 Hz, 2H), 5.15-5.05 (m, 4H), 5.01-4.65 (m, 4H), 3.77 (dd, *J* = 14.5, 8.1 Hz, 1H), 3.67 (dd, *J* = 14.6, 8.2 Hz, 1H), 2.58-2.40 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.07, 138.03, 135.07, 135.00, 134.55, 134.08, 133.62, 133.28, 132.35, 131.95, 131.66, 131.55, 130.18, 128.71, 128.56, 128.18, 127.70, 127.43, 126.54, 126.41, 126.12, 125.88, 125.40, 117.32, 117.27, 116.22, 116.03, 52.14, 51.68, 38.90, 38.67. HR-MS (ESI): Calcd for $C_{16}H_{17}S^+$ [M+H]$^+$ requires 241.1045; found 241.1050.



Hexa-4,5-dien-1-yn-3-yl(phenyl)sulfane (6a)

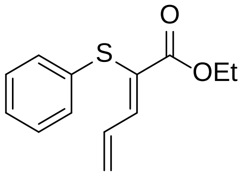
Following the general procedure at 30 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give **6a** (75% yield) as a yellow oil. For 1mmol scale reaction, the same procedure was followed. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60-7.49 (m, 2H), 7.38-7.29 (m, 3H), 5.27 (dd, *J* = 13.9, 6.6 Hz, 1H), 4.78 (dt, *J* = 6.4, 2.1 Hz, 1H), 4.38 (ddd, *J* = 7.1, 4.5, 2.2 Hz, 1H), 2.46 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 208.65, 134.20, 132.82, 128.76, 128.41, 89.92, 81.13, 78.26, 73.49, 38.29. HR-MS (ESI): Calcd for $C_{12}H_{11}S^+$ [M+H]$^+$ requires 187.0576; found 187.0566.





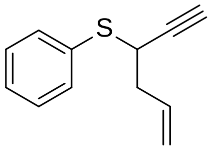
(4-fluorophenyl)(hexa-4,5-dien-1-yn-3-yl)sulfane (6b) and (3-fluorophenyl)(hexa-4,5-dien-1-yn-3-yl)sulfane (6b')

Following the general procedure at 30 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give **6b** and **6b'** (6b:6b'=5.5:1, 61% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.44 (m, 12H), 7.25-7.20 (m, 2H), 7.00-6.92 (m, 12H), 5.22-5.18 (m, 1H), 5.17 (dd, *J* = 7.3, 6.6 Hz, 5.5H), 4.77 (dd, *J* = 6.5, 2.3 Hz, 2H), 4.71-4.68 (m, 11H), 4.35 (dq, *J* = 7.1, 2.3 Hz, 1H), 4.22 (dq, *J* = 7.1, 2.3 Hz, 5.5H), 2.42 (d, *J* = 2.4 Hz, 1H), 2.39 (d, *J* = 2.4 Hz, 5.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.67, 137.40, 137.32, 115.95, 115.73, 89.83, 80.90, 78.26, 73.76, 38.87. HR-MS (ESI): Calcd for $C_{12}H_9FS^+$ $[M+H]^+$ requires 204.0409; found 204.0418.



Ethyl (Z)-2-(phenylthio)penta-2,4-dienoate (6c)

Following the general procedure at 30 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **6c** (56% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 10.9 Hz, 1H), 7.27-7.15 (m, 5H), 7.14-7.04 (m, 1H), 5.78 (dd, *J* = 17.0, 0.7 Hz, 1H), 5.64 (dd, *J* = 10.1, 1.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.60, 147.39, 135.82, 133.29, 128.94, 128.54, 127.66, 126.30, 126.24, 61.64, 13.92. HR-MS (ESI): Calcd for $C_{13}H_{15}O_2S^+$ $[M+H]^+$ requires 235.0787; found 235.0758.

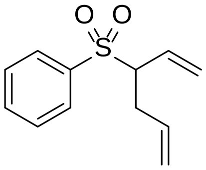


hex-5-en-1-yn-3-yl(phenyl)sulfane (6d)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give **6c** (80% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, *J* = 4.3, 2.3 Hz, 1H), 7.37-7.27 (m, 2H), 6.00-5.87 (m, 1H), 5.21-5.10 (m, 1H), 3.82 (ddd, *J* = 8.3, 6.1, 2.4 Hz, 1H), 2.57-2.48 (m, 1H), 2.37 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.98, 133.45, 133.00, 128.91, 127.91, 118.09, 83.13, 72.73, 39.16, 38.16. HR-MS (ESI): Calcd for $C_{12}H_{13}S^+$ $[M+H]^+$ requires 189.0732; found 188.0760.

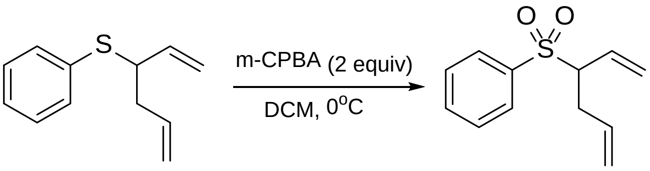
IV. Sulfide Oxidation

To demonstrate the synthetic utility of our method, we have further studied the rearrangement product functionalization. Oxidation reaction of **3a** using commercially available hydrogen peroxide or MCPBA gave the corresponding sulfone product in moderate yield respectively.



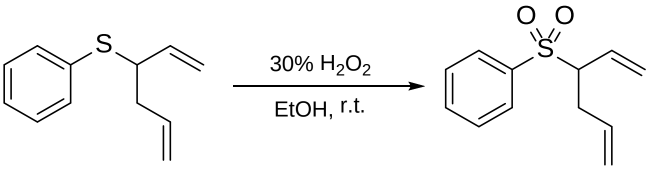
(hexa-1,5-dien-3-ylsulfonyl)benzene (7)

Procedure A:



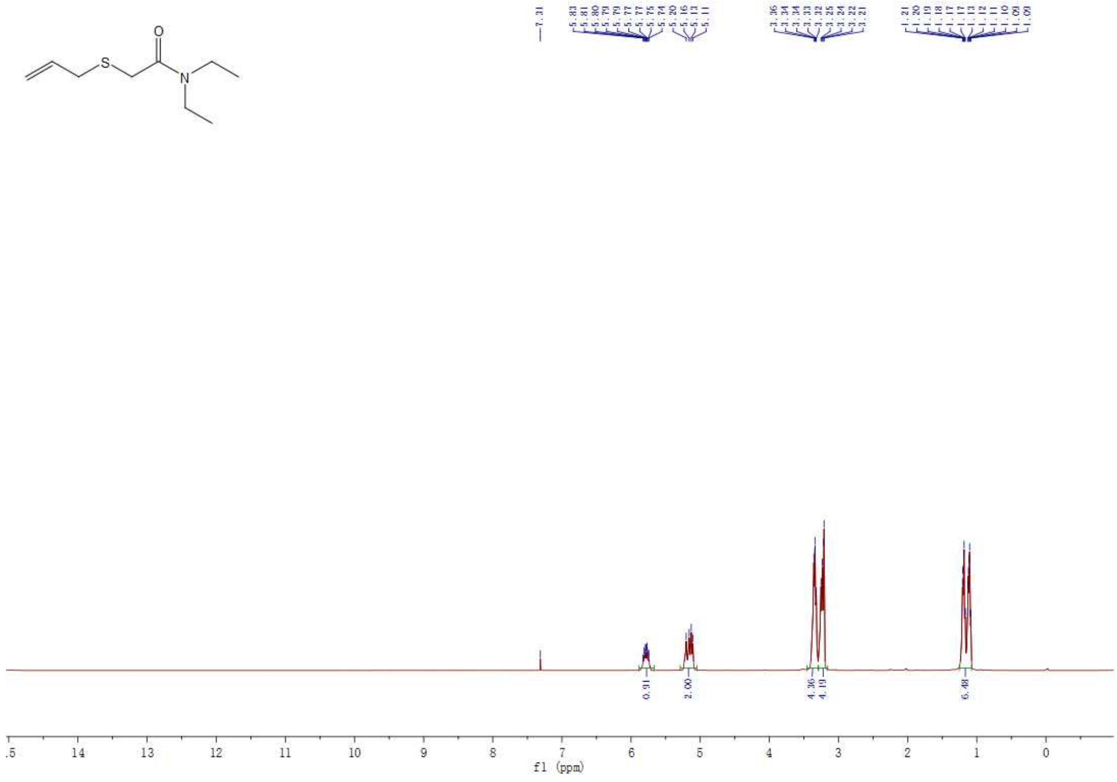
To a stirred solution of the sulfide **3a** (0.019g, 0.1mmol, 1 equiv.) in 1mL CH_2Cl_2 was added m-CPBA (0.041g, 0.2mmol, 2 equiv.) at 0°C. The reaction was kept stirring for 4h at 0 °C. The reaction was then quenched with saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (20 mL), washed with saturated $NaHCO_3$ (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give **7** (60% yield) as a white solid.

Procedure B:

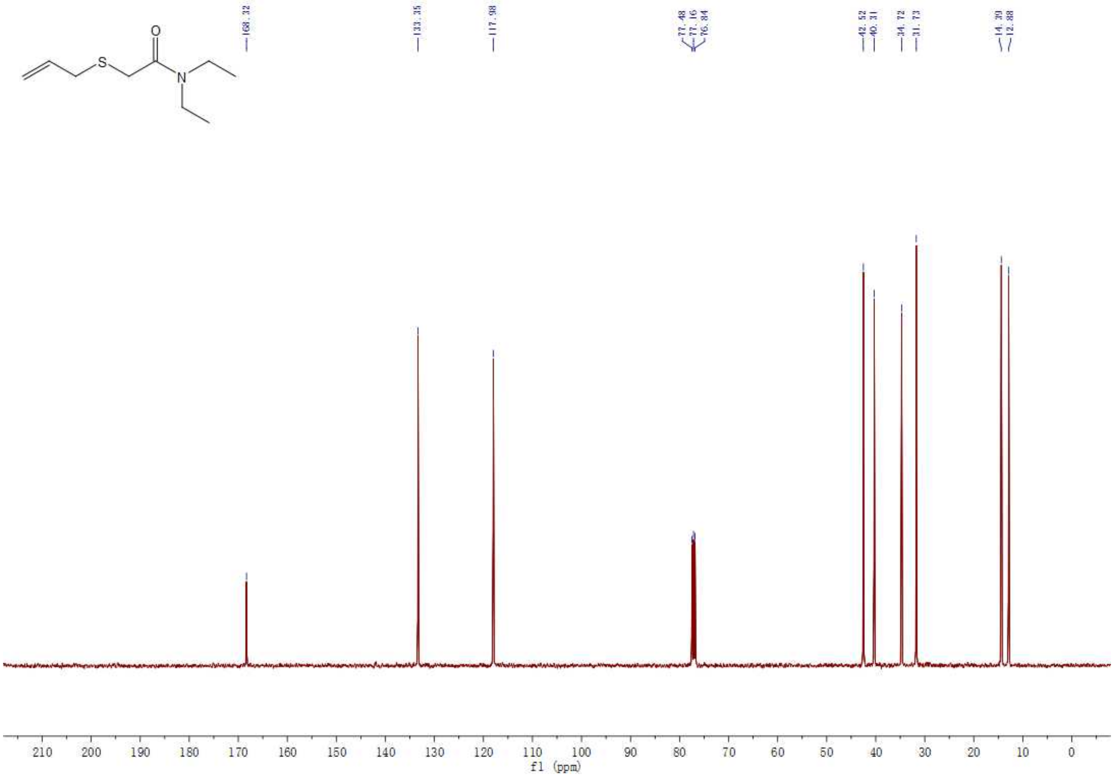


To a stirred solution of the sulfide **3a** (0.019g, 0.1mmol, 1 equiv.) in 1mL ethanol was added H_2O_2 (30% in water, 0.05 mL, 0.5mmol, 5.0 equiv.) at room temperature. The reaction was stirred for 24h and then concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give **7** (61% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.80 (m, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 5.72-5.57 (m, 1H), 5.33-4.98 (m, 2H), 3.57 (td, *J* = 10.3, 3.5 Hz, 1H), 2.94-2.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.21, 133.72, 132.90, 129.85, 129.29, 128.85, 123.83, 118.44, 69.30, 31.59. HR-MS (ESI): Calcd for $C_{12}H_{13}O_2S^+$ $[M+H]^+$ requires 221.0631; found 221.0656.

V. Spectrum



7.31
5.83
5.81
5.80
5.79
5.79
5.77
5.77
5.75
5.74
5.20
5.16
5.13
5.11
3.36
3.34
3.34
3.33
3.32
3.25
3.24
3.22
3.21
1.21
1.20
1.19
1.18
1.17
1.13
1.12
1.11
1.10
1.09
1.09
0.91
2.00
4.36
4.19
6.48
.5
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
S
O
N



O
S
N
168.32
133.35
117.98
77.48
77.16
76.84
42.52
40.31
34.72
31.73
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12.88
210
200
190
180
170
160
150
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130
120
110
100
90
80
70
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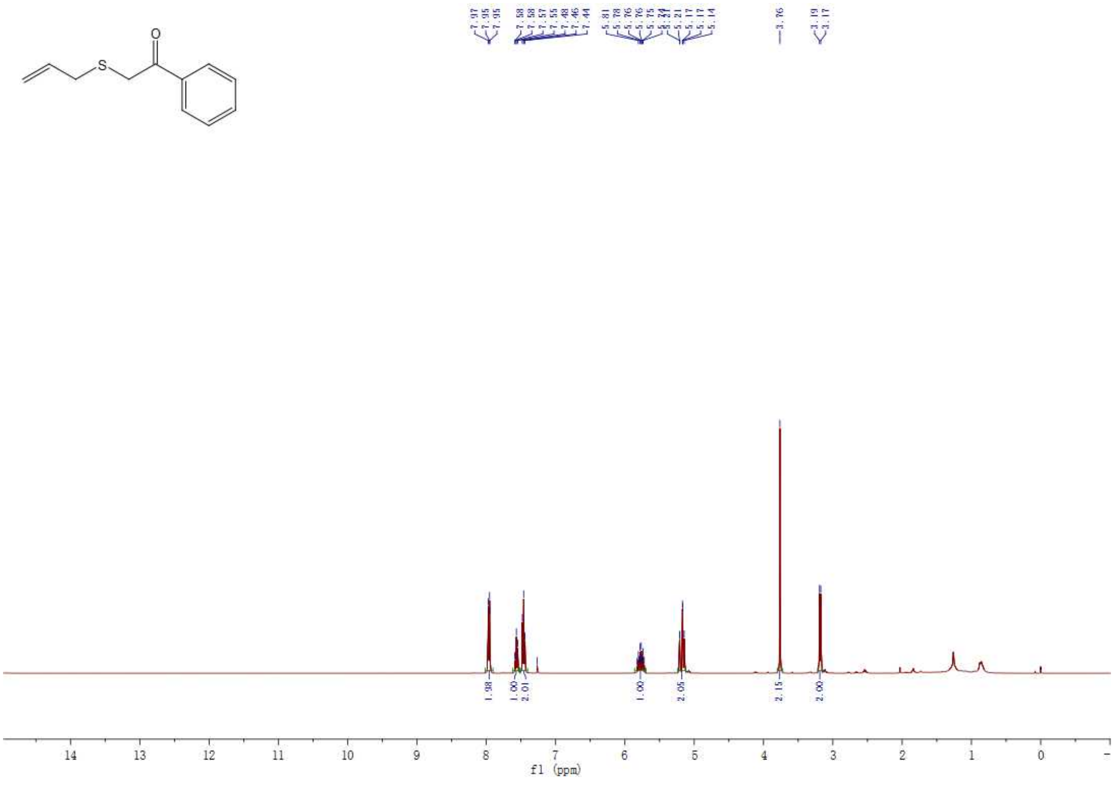
50
40
30
20
10
0
f1 (ppm)



O
S
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7.95
7.58
7.58
7.57
7.55
7.48
7.46
7.44
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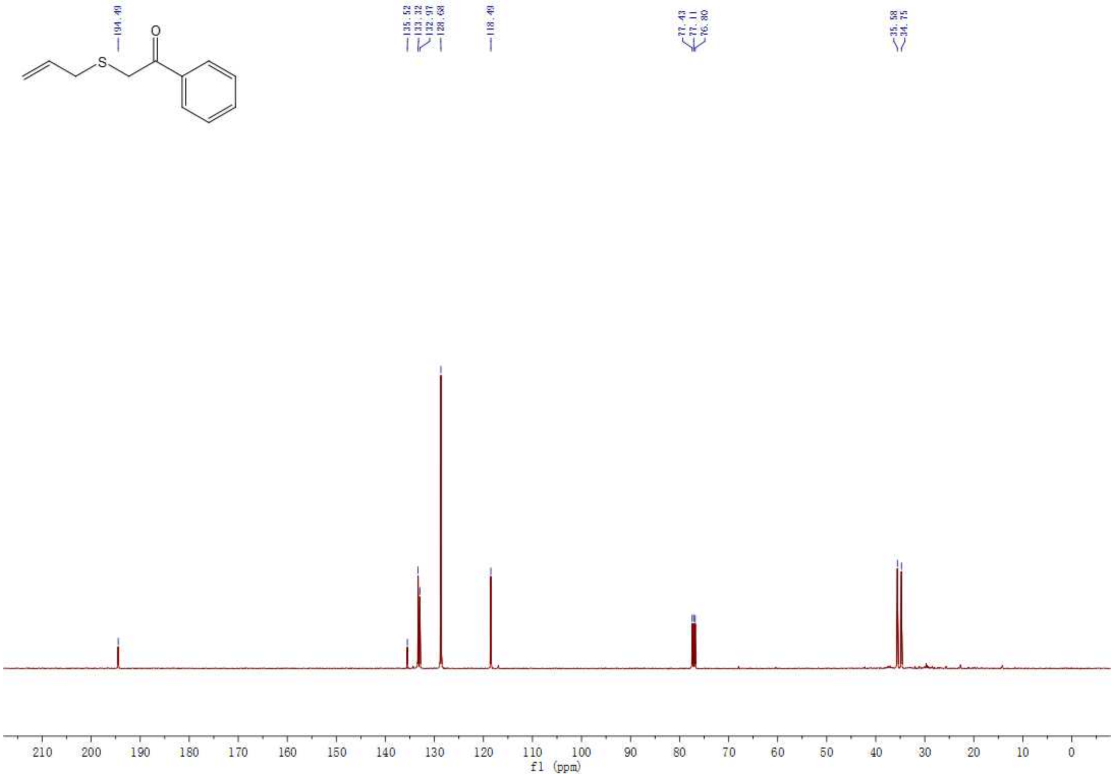
5.78
5.76
5.76
5.75
5.74
5.21
5.21
5.17
5.17
5.14
3.76
3.19
3.17
1.98
1.00
2.01
1.00
2.05
2.15
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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128.68
118.49
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77.11
76.80
35.58
34.75
S
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200
190
180
170
160
150
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120
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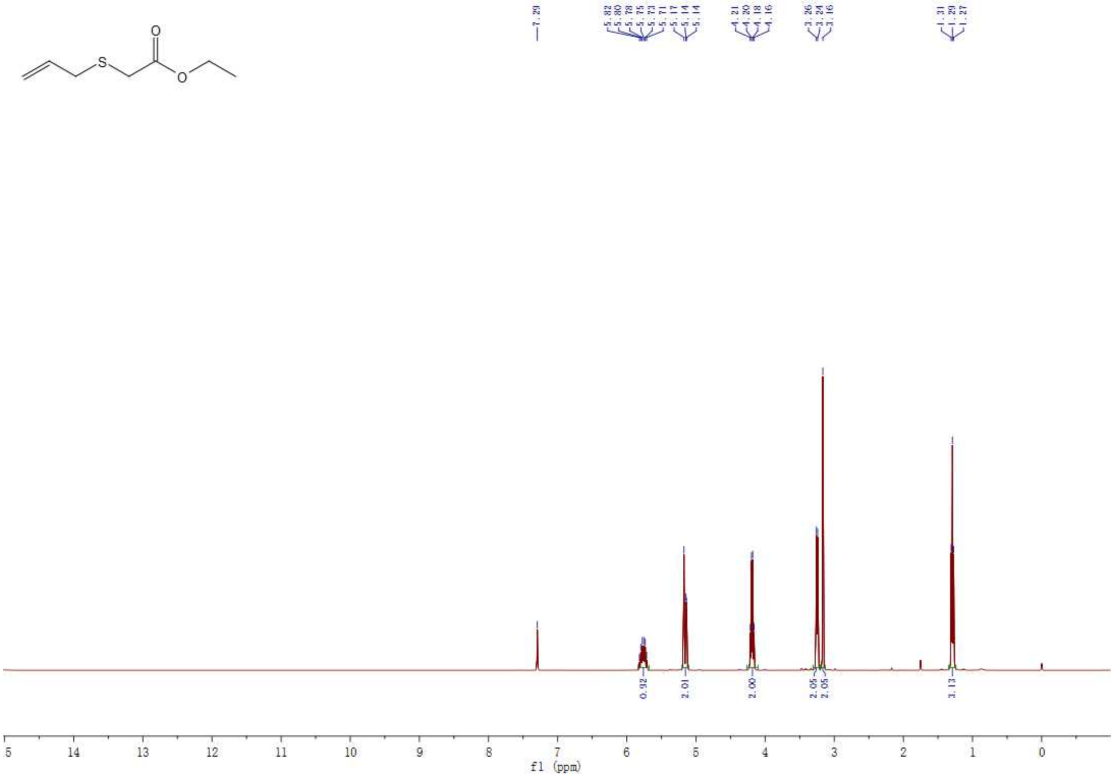
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
O
O
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5.80
5.78
5.75
5.73
5.71
5.17
5.14
5.14
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4.20
4.18
4.16
3.26
3.24
3.16
1.31
1.29
1.27
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2.00
2.05
2.05
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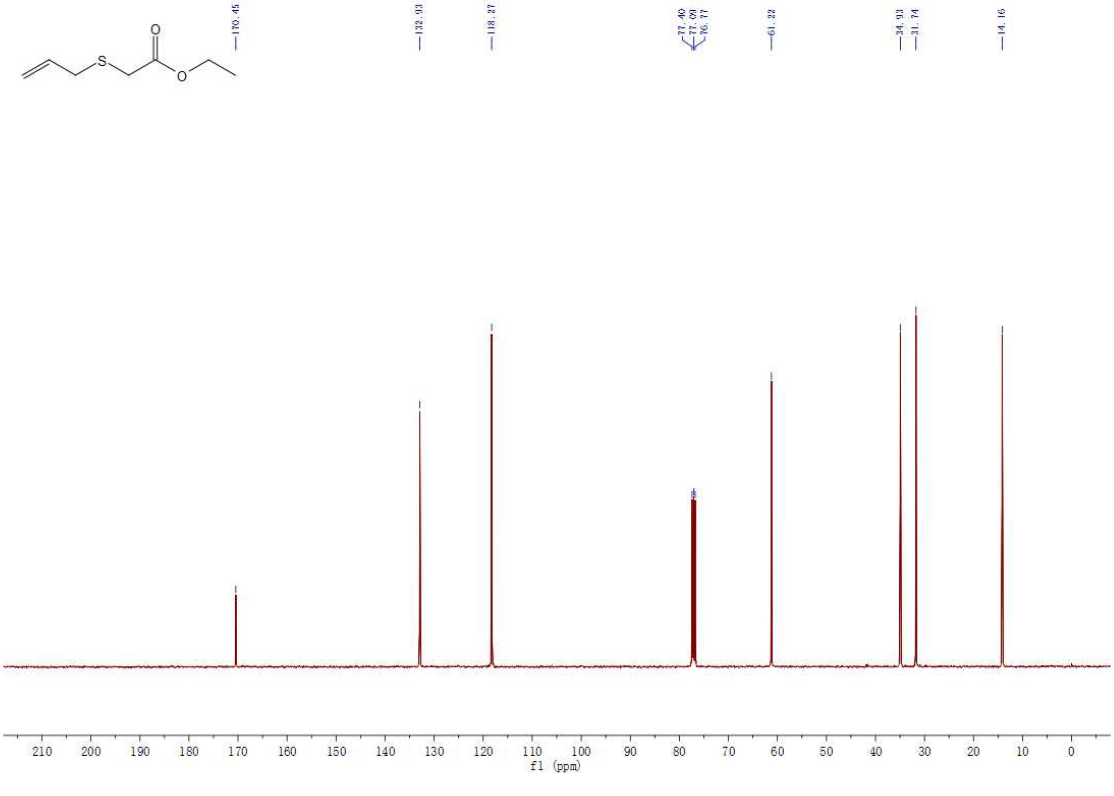
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200
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180
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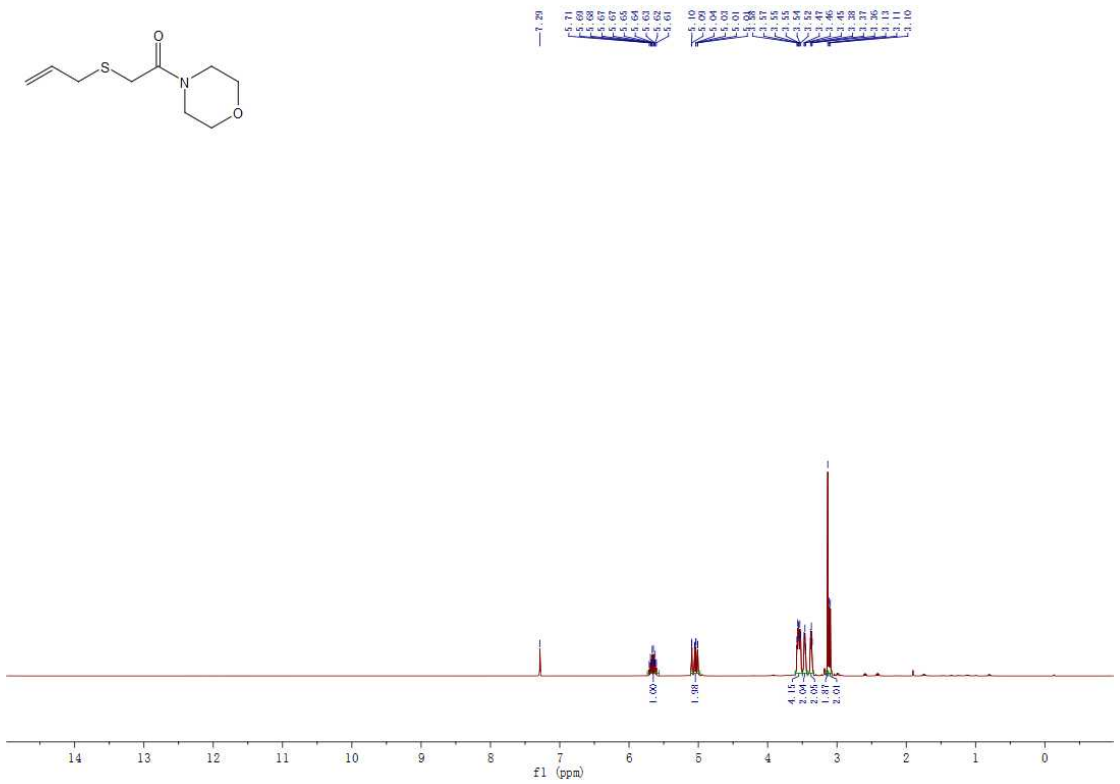
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5.03
5.01
5.00
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3.54
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3.45
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3.13
3.11
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2.05
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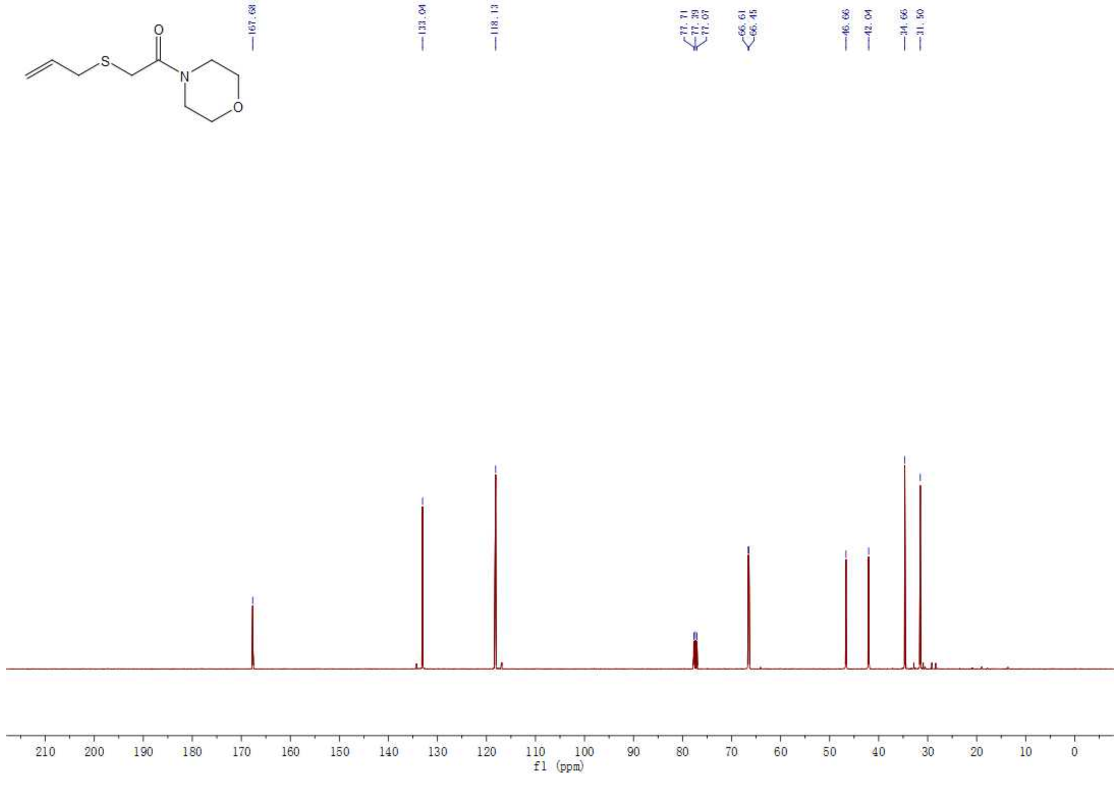
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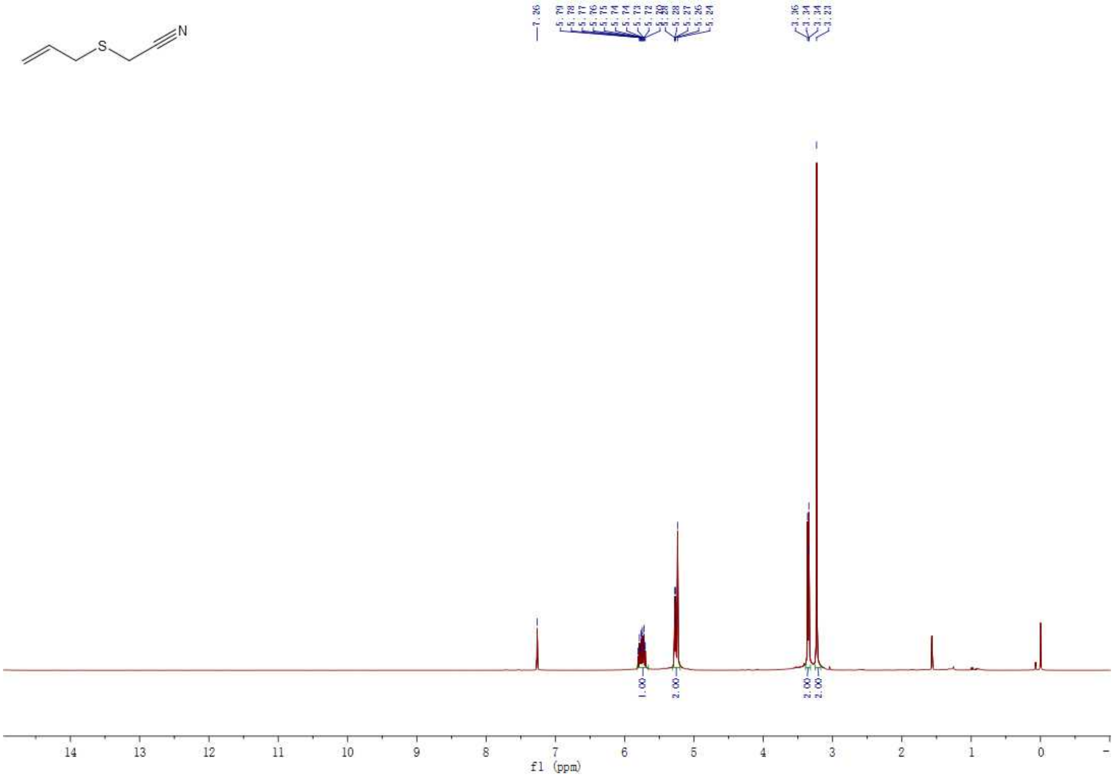
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5.29
5.28
5.27
5.26
5.24
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3.34
3.34
3.23
1.00
2.00
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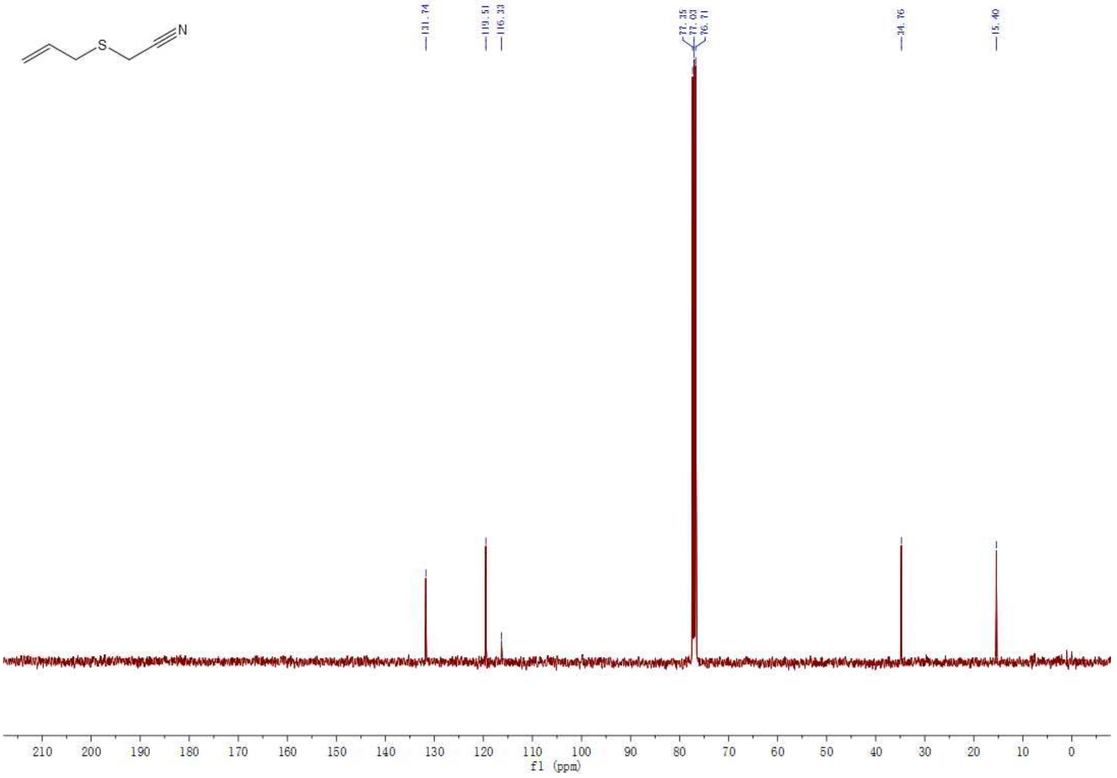
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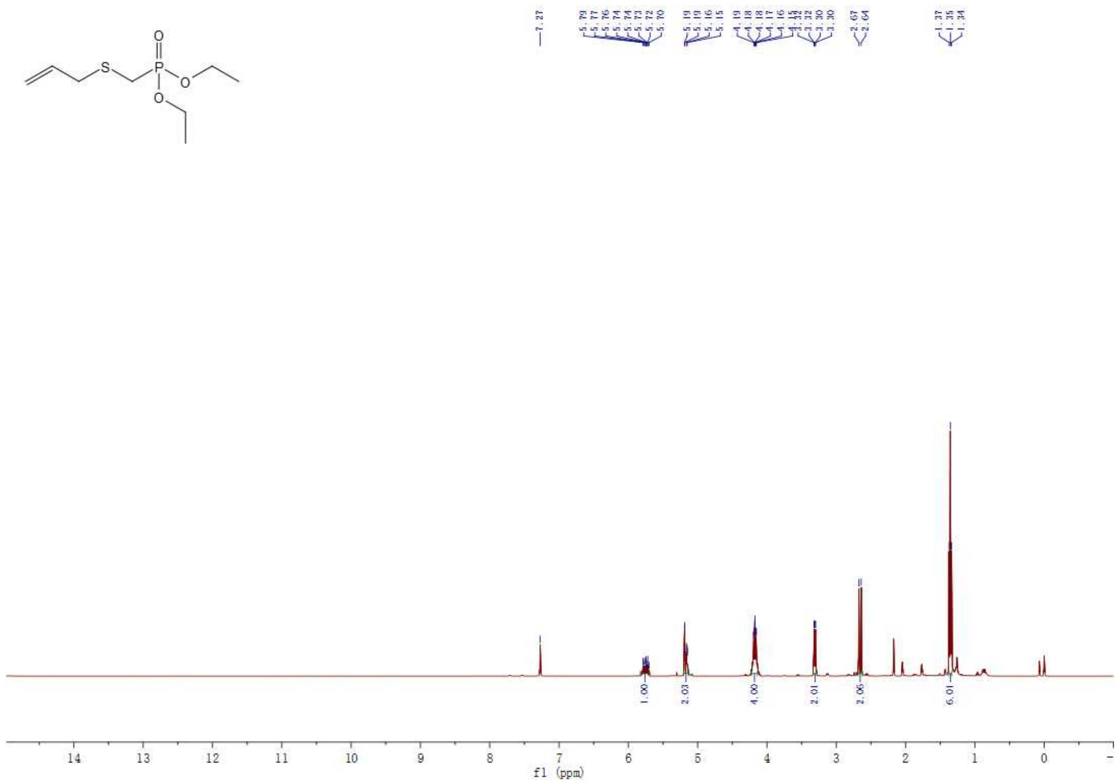
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5.19
5.16
5.15
4.19
4.18
4.18
4.17
4.16
4.15
3.32
3.32
3.30
3.30
2.67
2.64
1.37
1.35
1.34
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2.03
4.00
2.01
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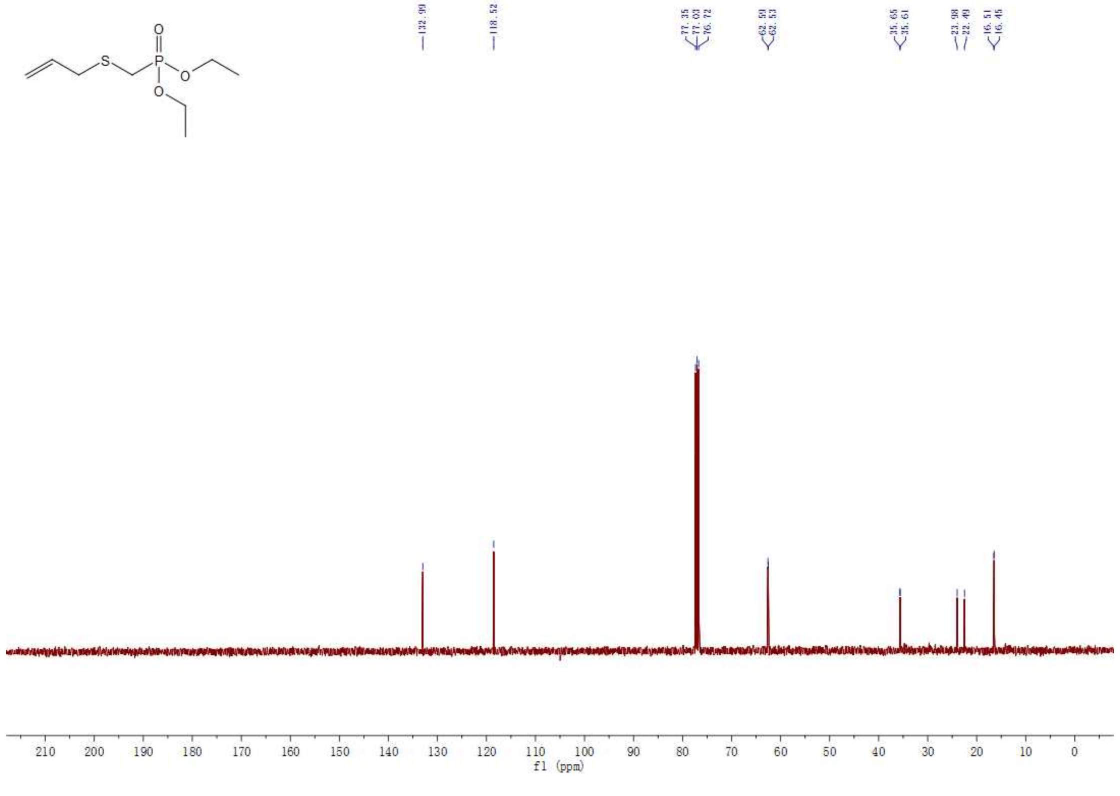
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23.98
22.49
16.51
16.45
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200
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180
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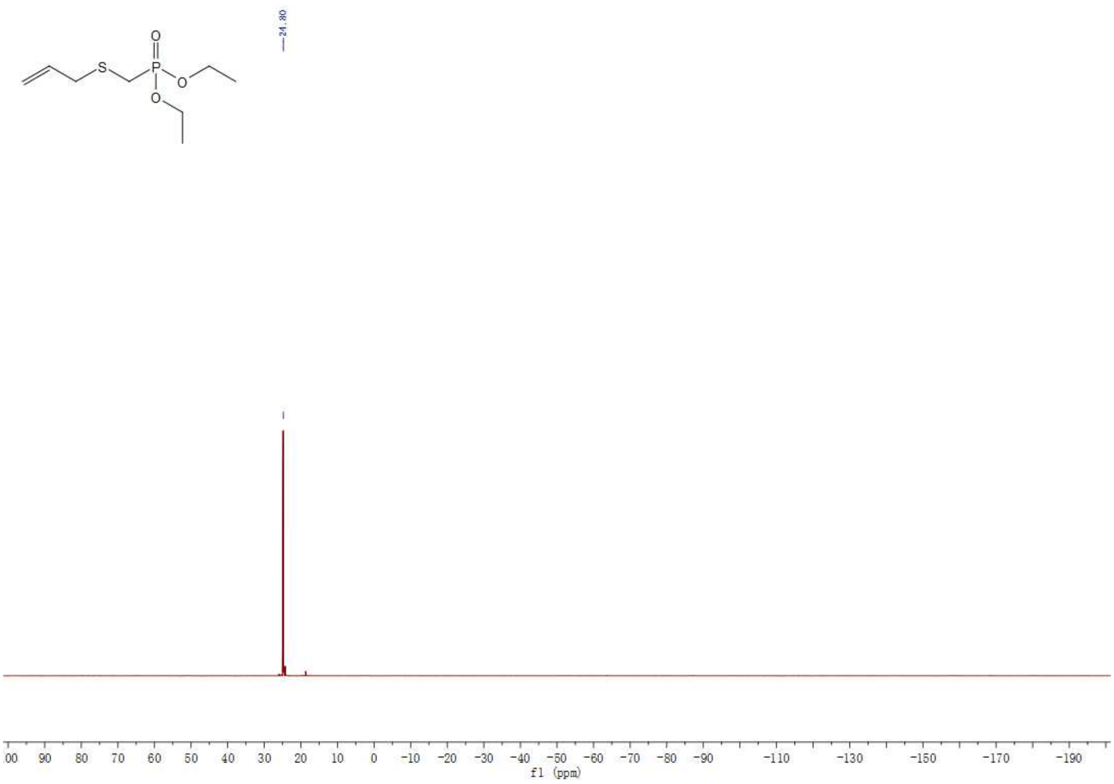

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P
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O
O
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20
10
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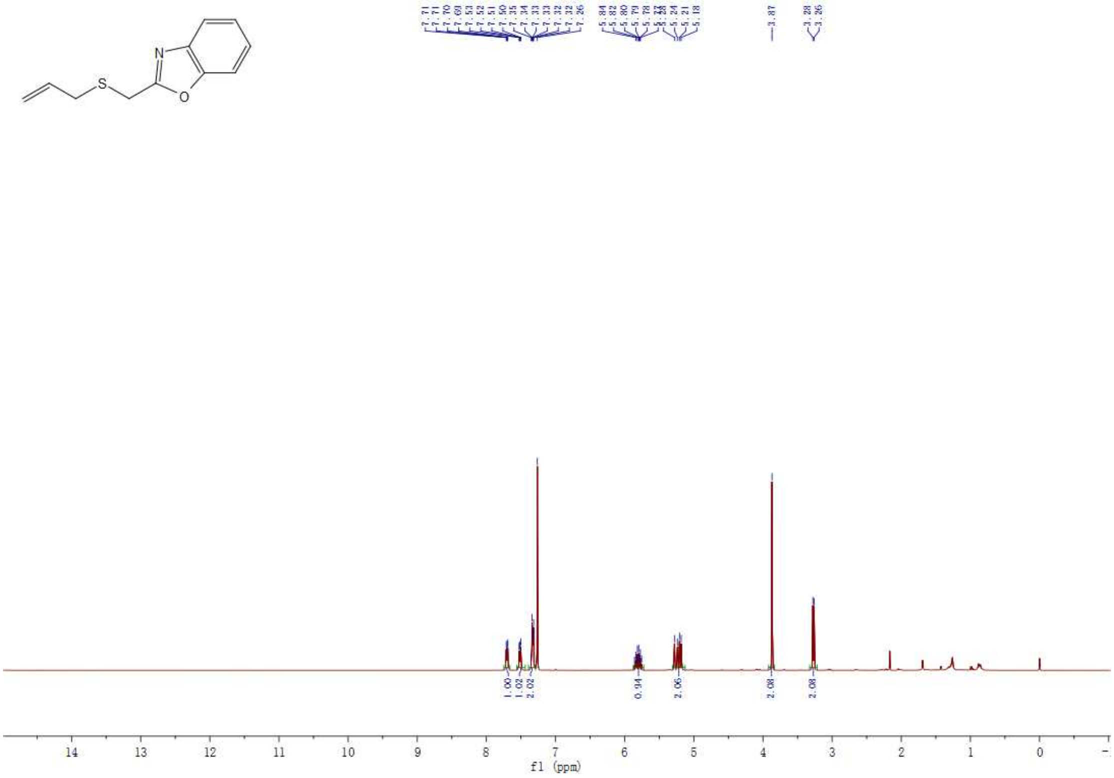
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)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7.33
7.33
7.32
7.32
7.26
5.84
5.82
5.80
5.79
5.78
5.77
5.28
5.24
5.21
5.18
3.87
3.28
3.26
1.00
1.02
2.02
0.94
2.06
2.08
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12
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10
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8
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6
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3
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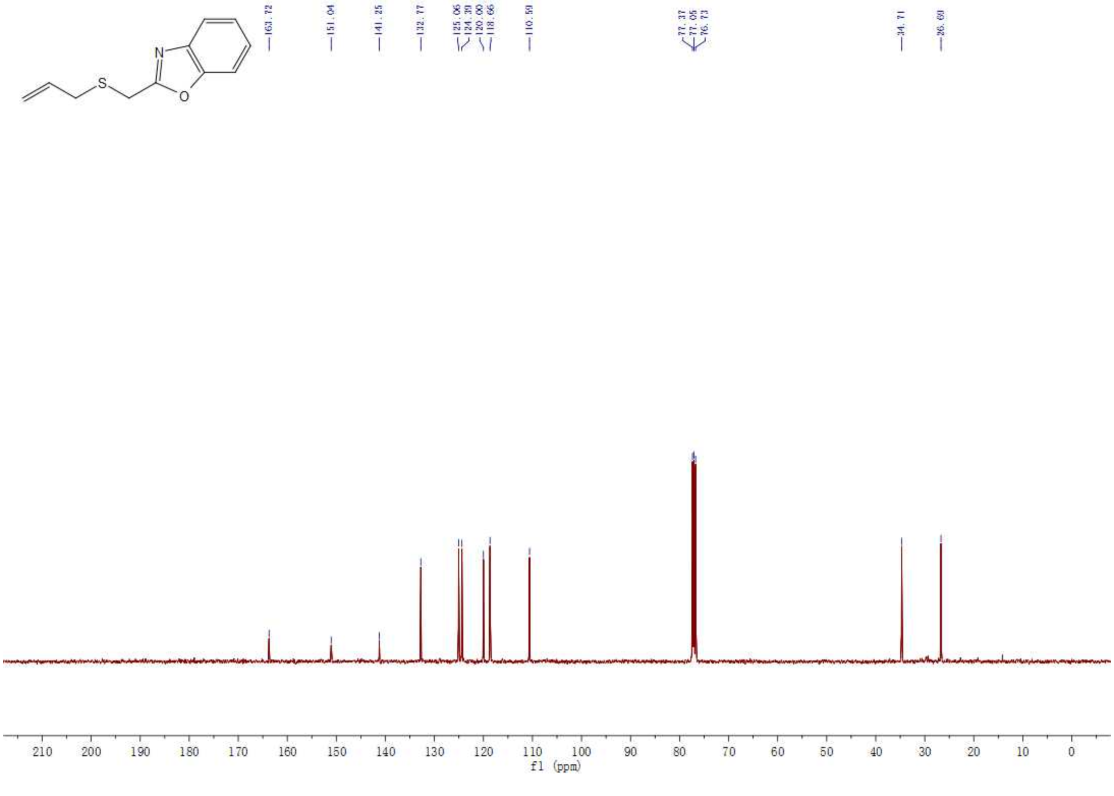
-1
f1 (ppm)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S
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132.77
125.06
124.39
120.00
118.66
110.59
77.37
77.05
76.73
34.71
26.69
210
200
190
180
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150
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130
120
110
100
90
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10
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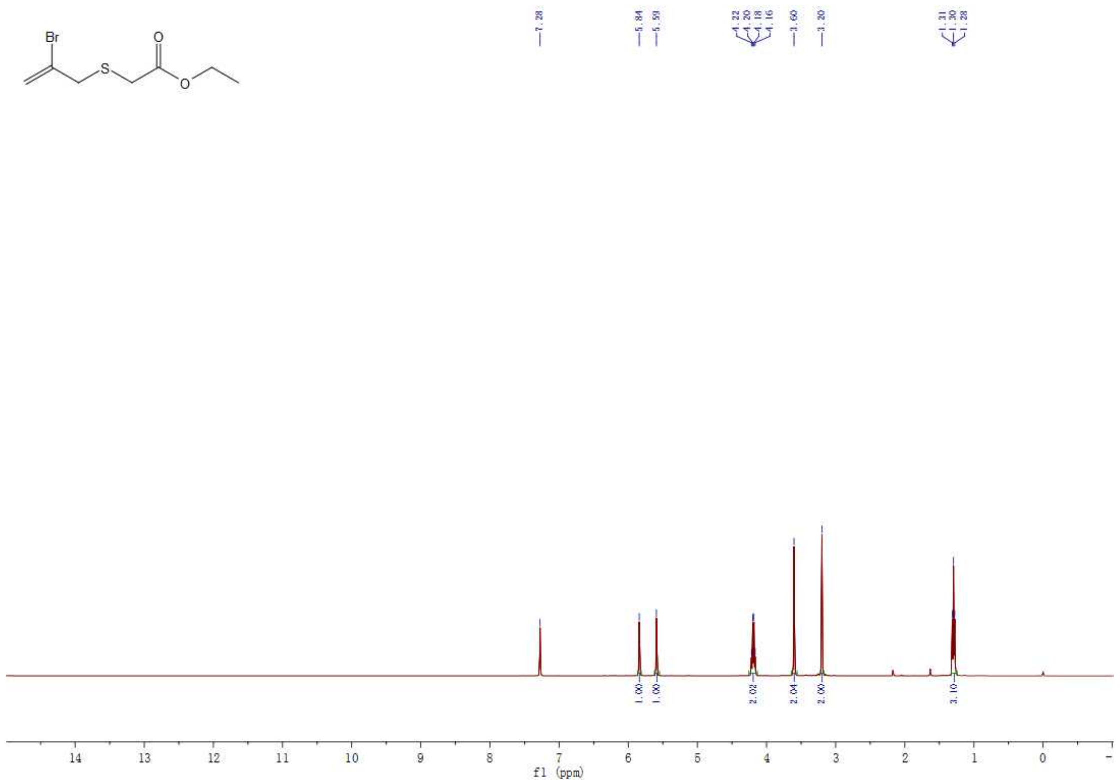
f1 (ppm)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S
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O
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4.22
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4.18
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3.60
3.20
1.31
1.30
1.28
1.00
1.00
2.02
2.04
2.00
3.10
14
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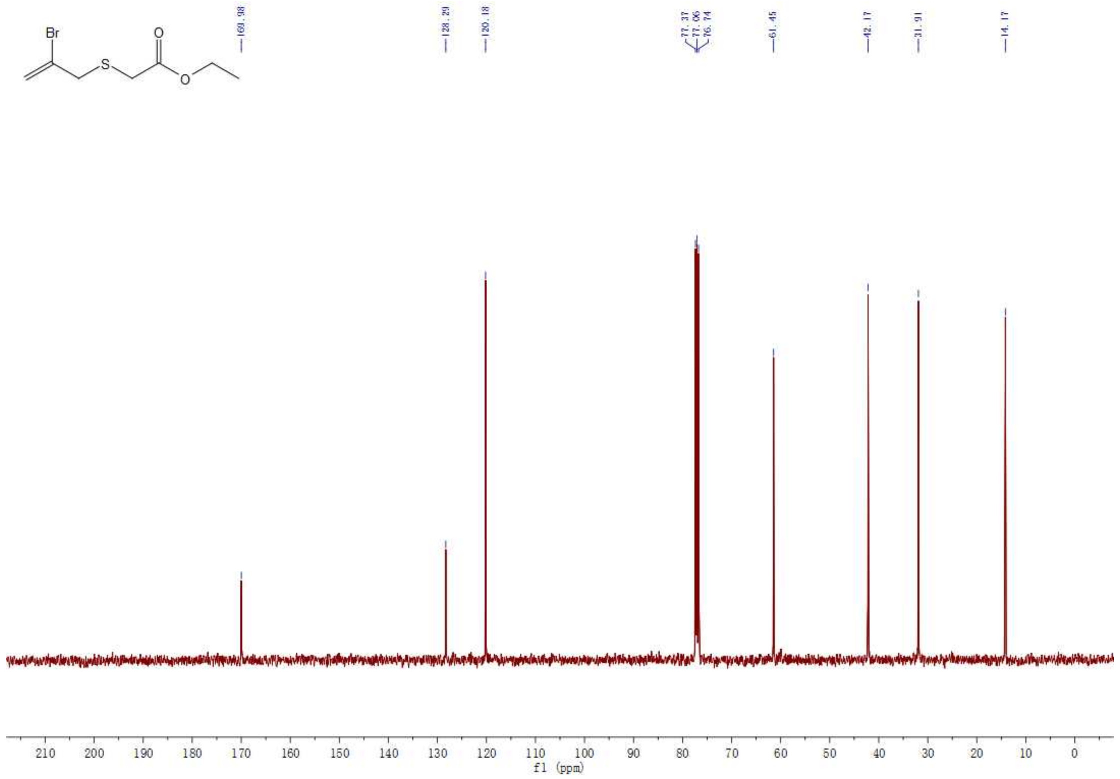
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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S
O
O
169.98
128.29
120.18
77.37
77.06
76.74
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42.17
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210
200
190
180
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130
120
110
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90
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10
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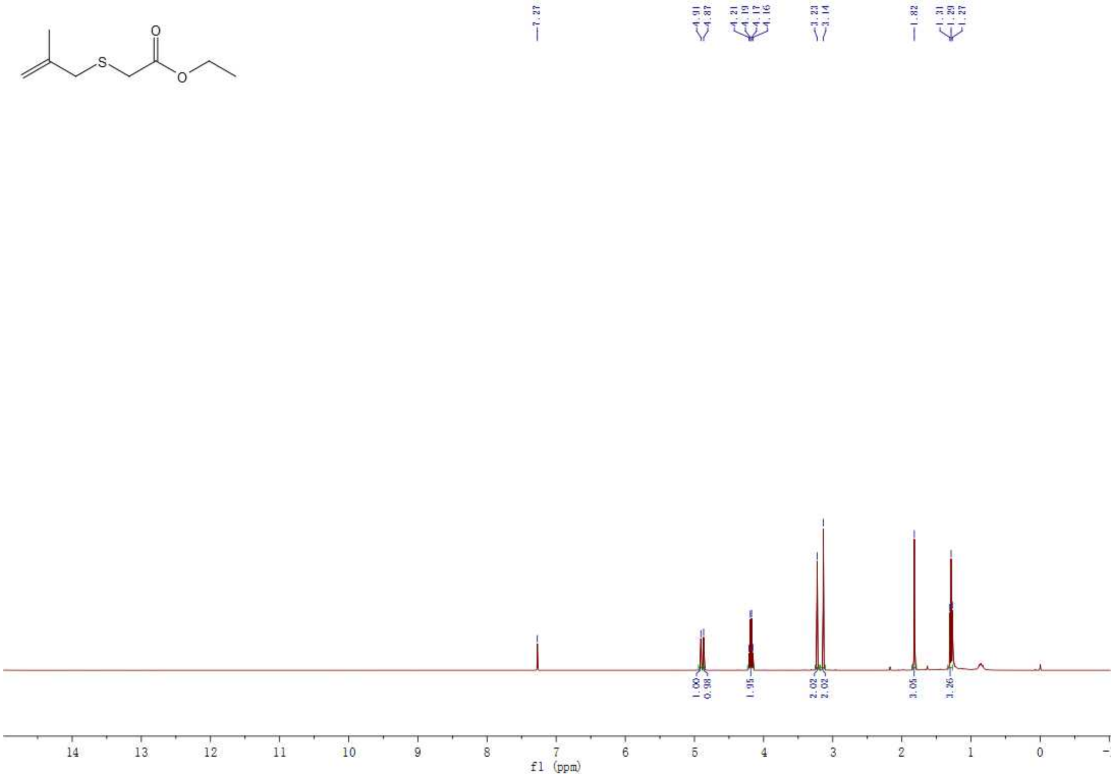
f1 (ppm)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S
O
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3.23
3.14
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1.31
1.29
1.27
1.00
0.98
1.95
2.02
2.02
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11
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9
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7
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5
4
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1
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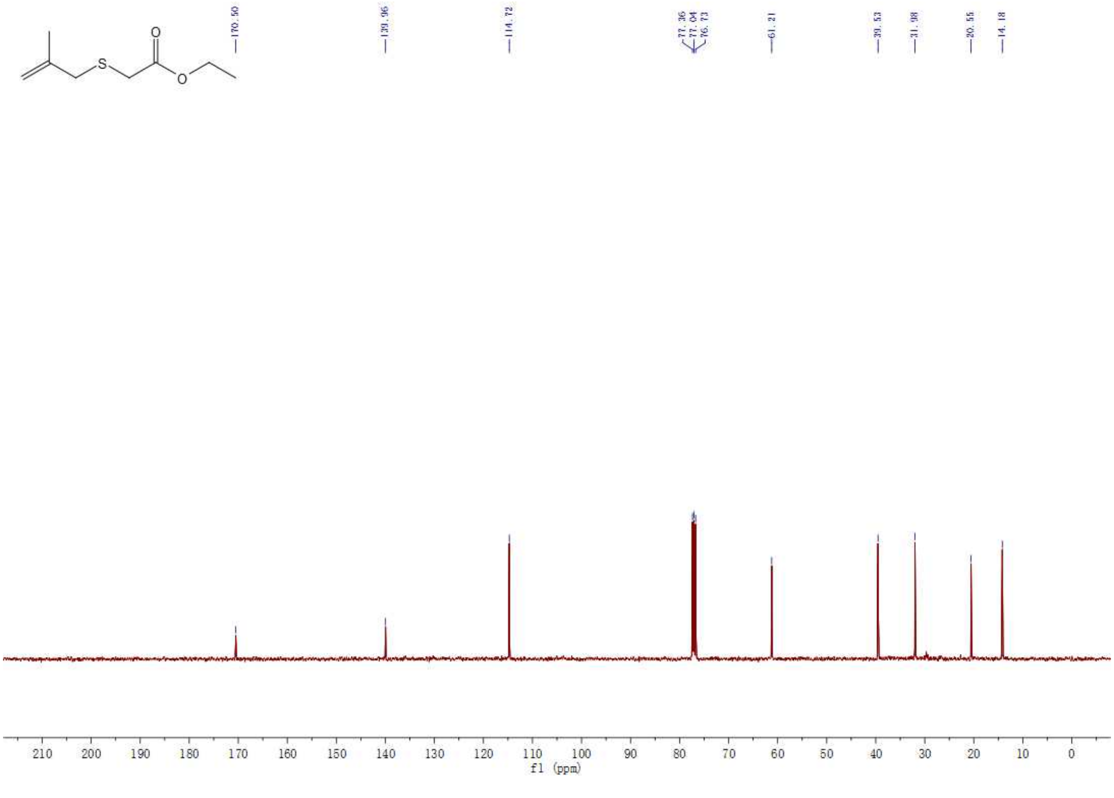
f1 (ppm)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76.73
61.21
39.53
31.98
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14.18
210
200
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180
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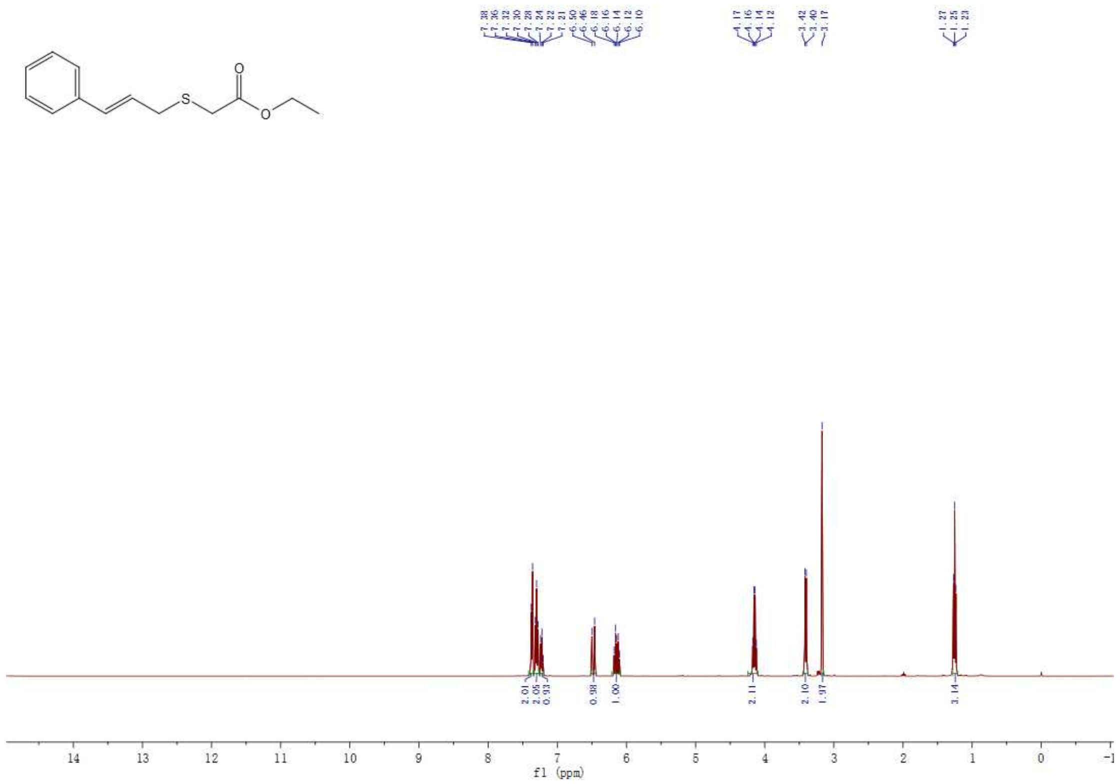
O
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O
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6.18
6.16
6.14
6.12
6.10
4.17
4.16
4.14
4.12
3.42
3.40
3.17
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1.25
1.23
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2.05
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0.98
1.00
2.11
2.10
1.97
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14
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10
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8
7
6
5
4
3
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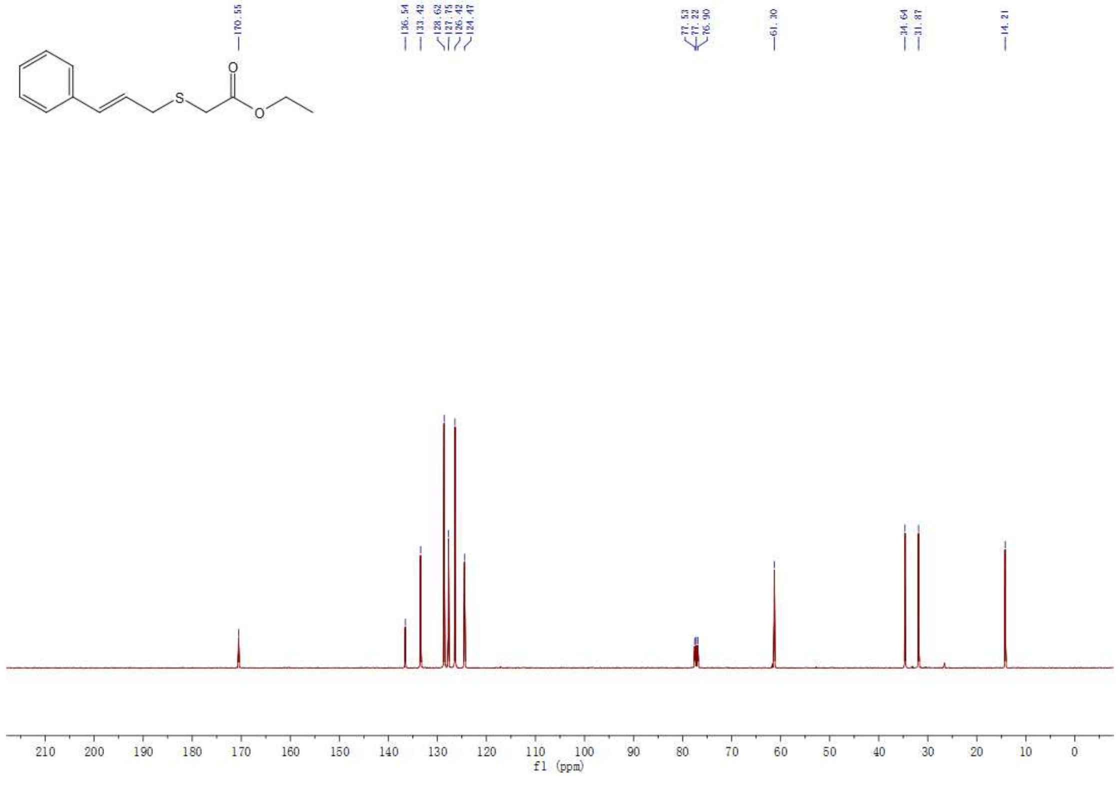
f1 (ppm)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61.30
34.64
31.87
14.21
210
200
190
180
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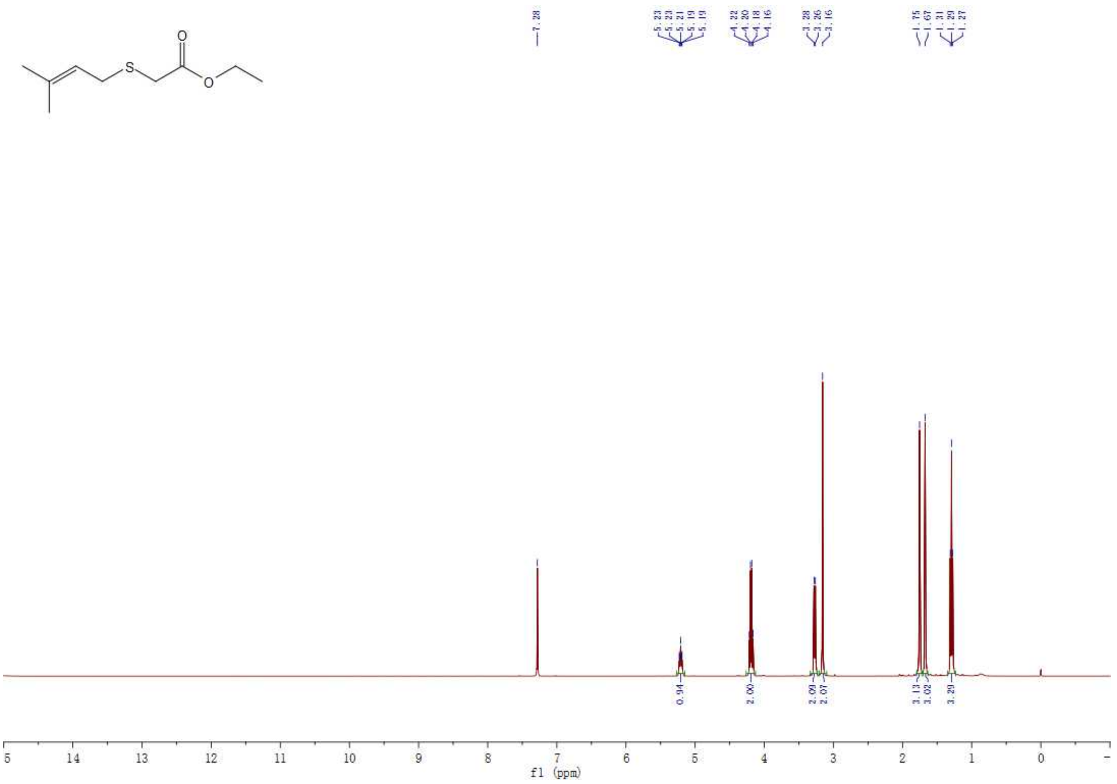
f1 (ppm)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5.19
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3.28
3.26
3.16
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1.67
1.31
1.29
1.27
0.94
2.00
2.09
2.07
3.13
3.02
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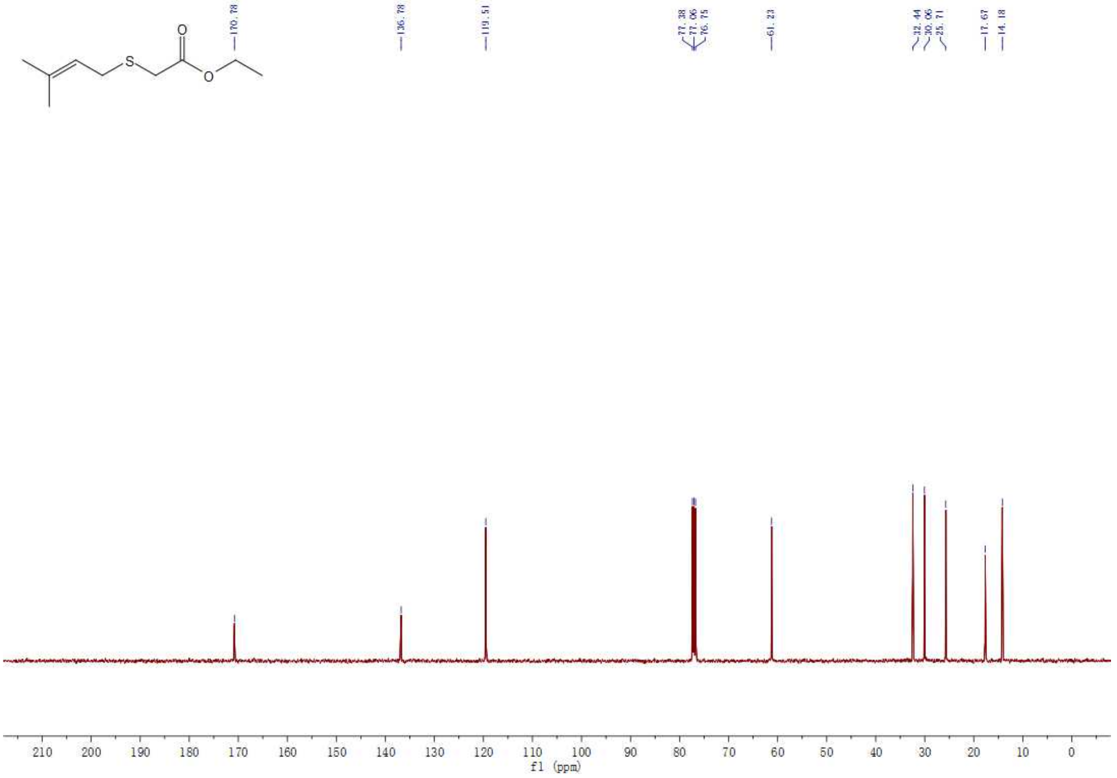
f1 (ppm)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14.18
210
200
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180
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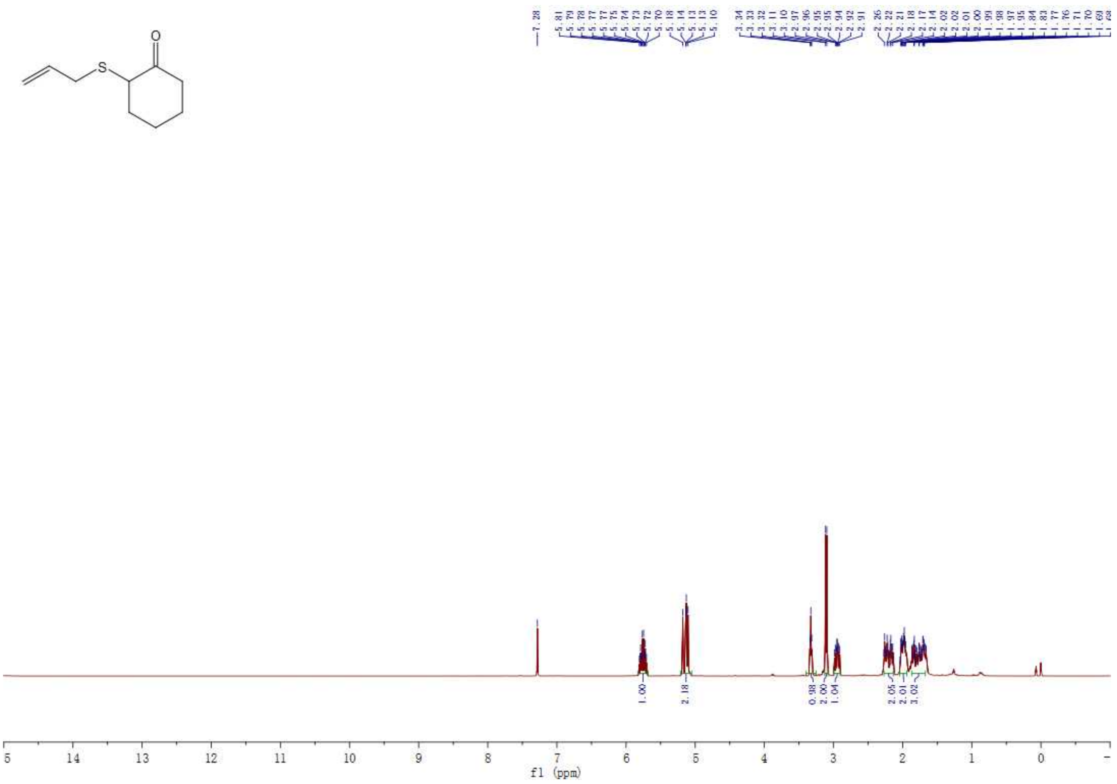
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3.33
3.32
3.11
3.10
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2.96
2.95
2.95
2.94
2.92
2.91
2.26
2.22
2.21
2.18
2.17
2.14
2.02
2.02
2.01
2.00
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1.83
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1.71
1.70
1.69
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2.00
1.04
2.05
2.01
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8
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4
3
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0
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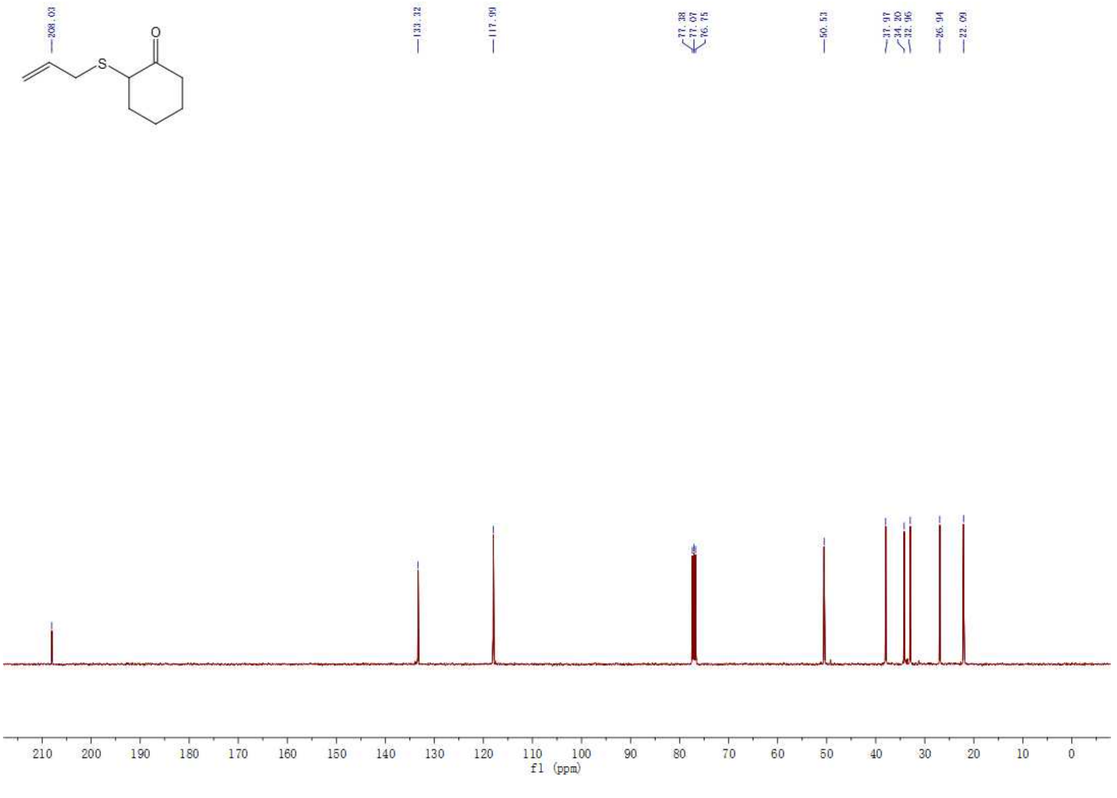
f1 (ppm)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34.20
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22.09
210
200
190
180
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100
90
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70
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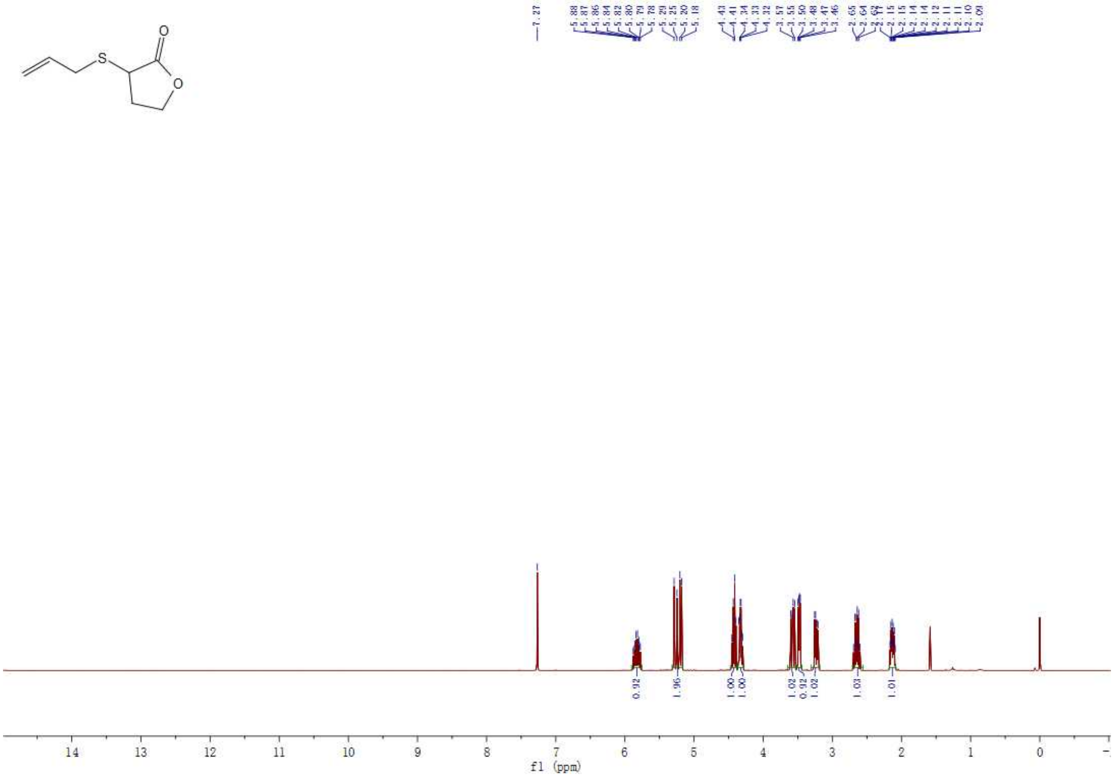
10
0
f1 (ppm)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4.32
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3.48
3.47
3.46
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2.64
2.62
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2.15
2.14
2.14
2.12
2.11
2.11
2.10
2.09
0.92
1.96
1.00
1.00
1.02
0.92
1.02
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9
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4
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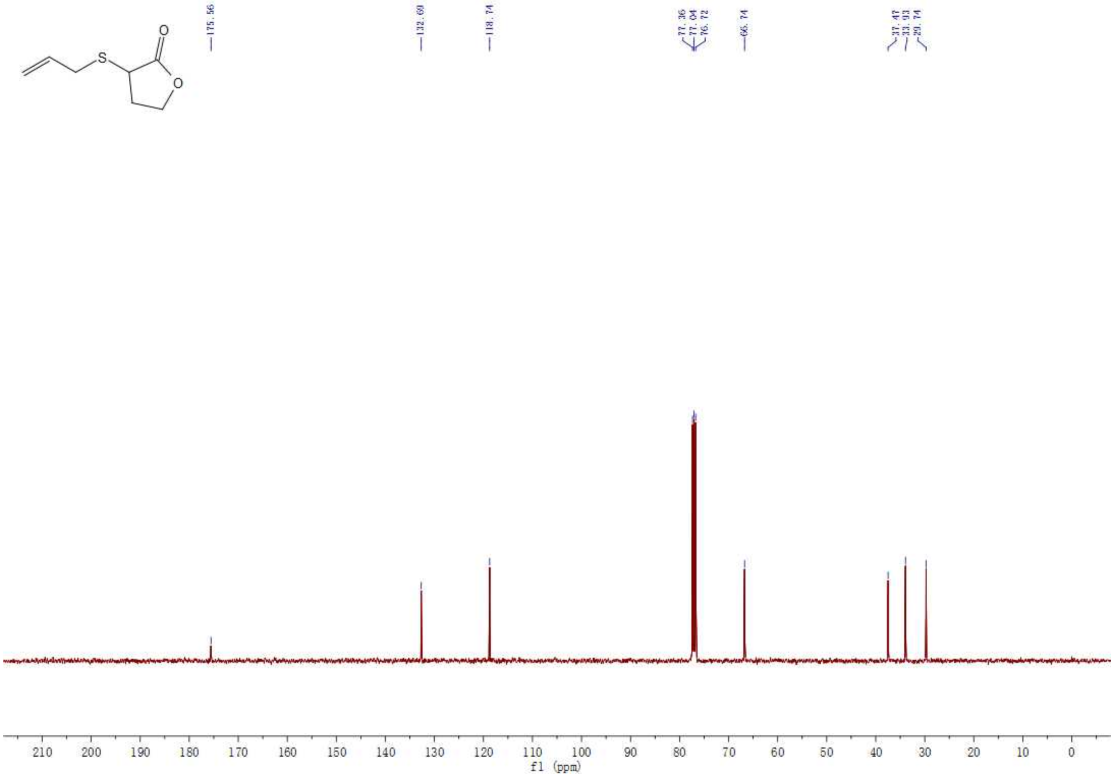
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200
190
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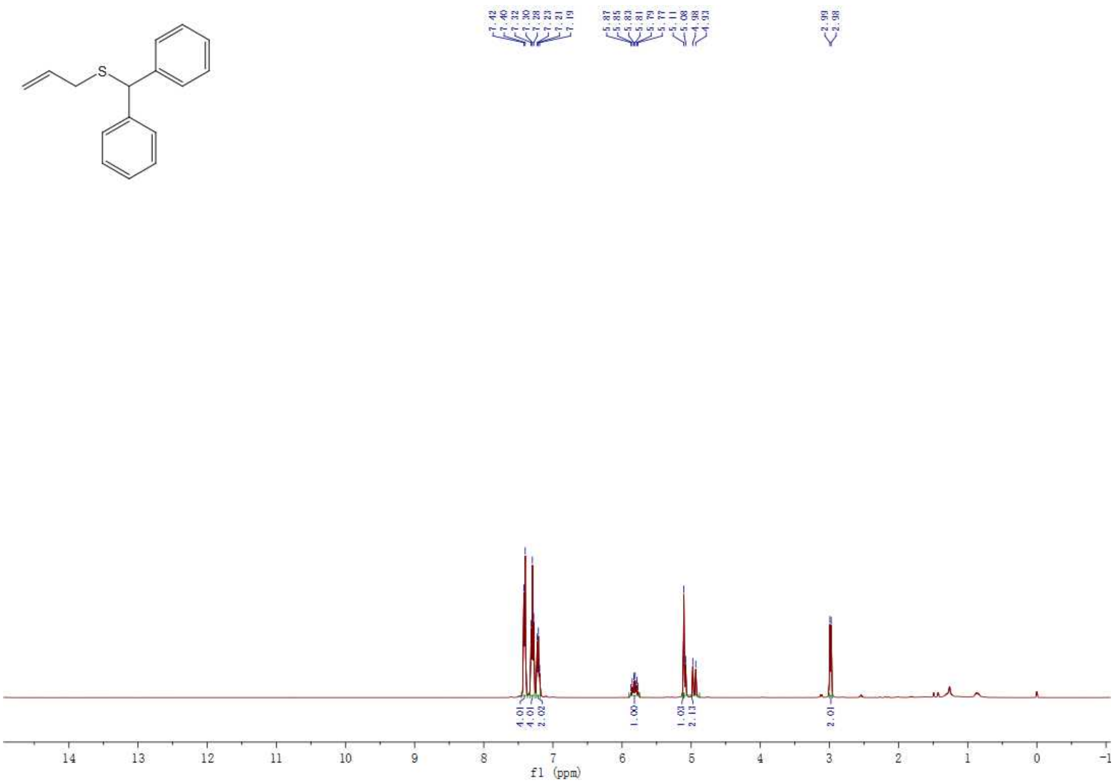
f1 (ppm)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5.79
5.77
5.11
5.08
4.98
4.93
2.99
2.98
4.01
4.01
2.02
1.00
1.03
2.11
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10
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8
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3
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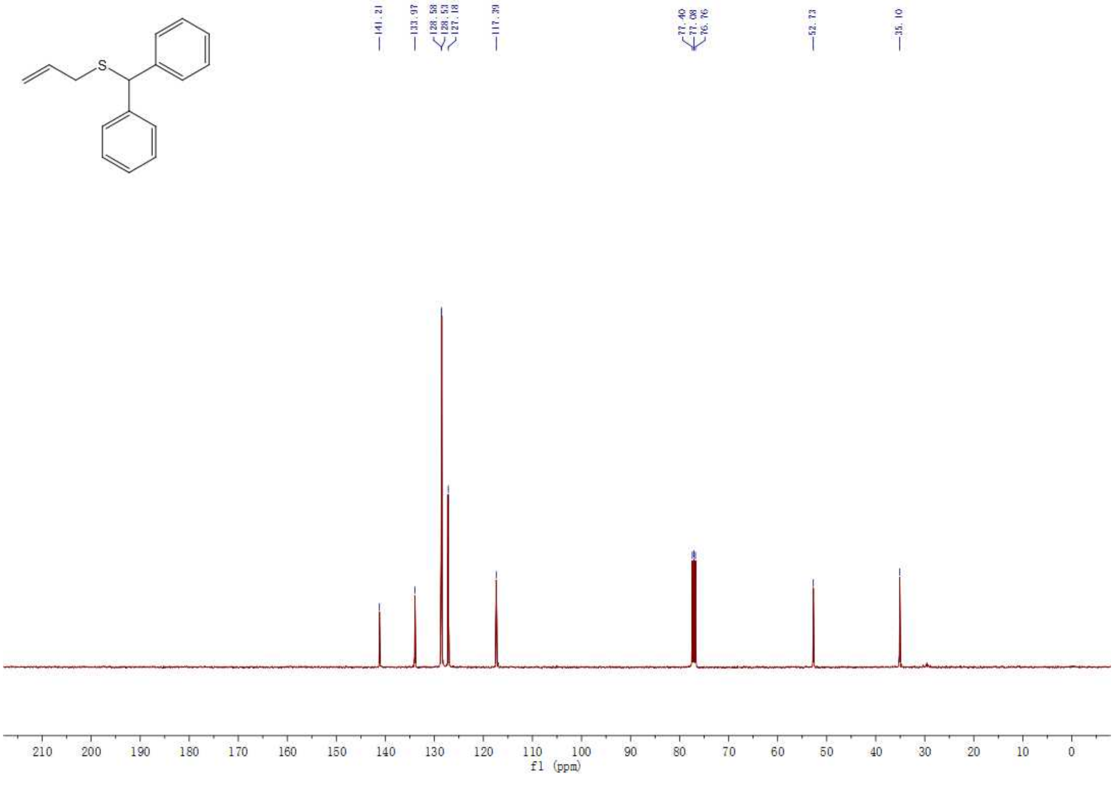
f1 (ppm)


S
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52.73
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200
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90
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10
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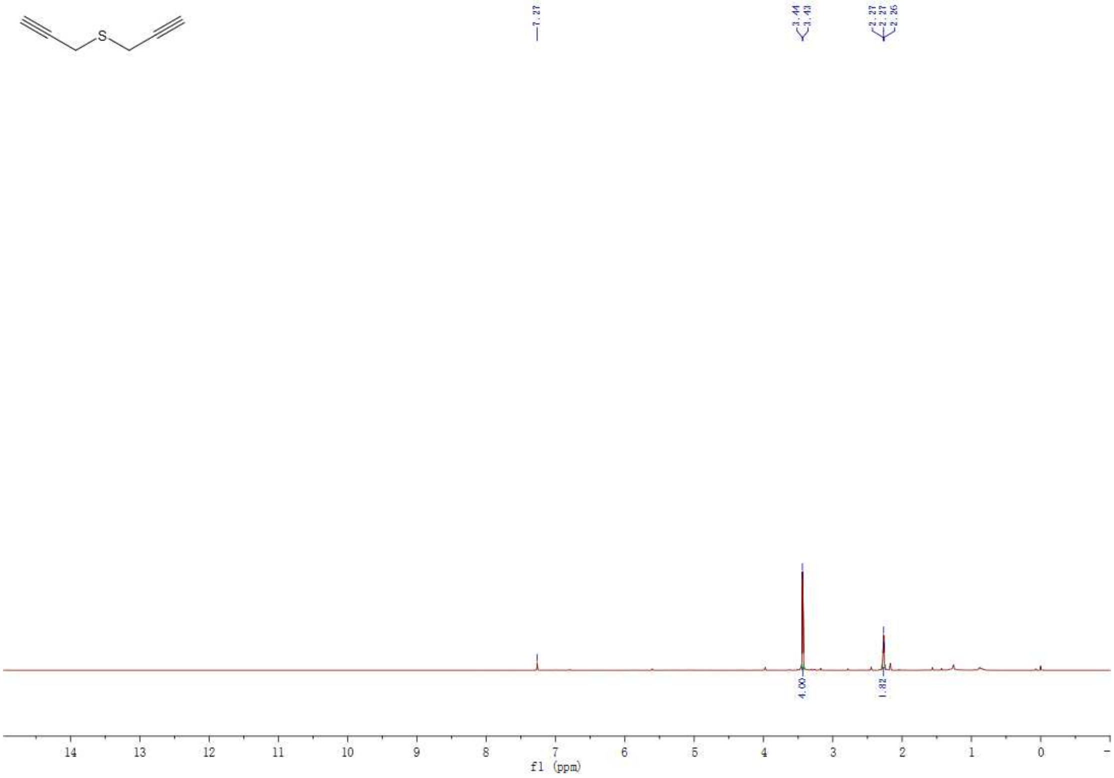
f1 (ppm)


S
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11
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9
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5
4
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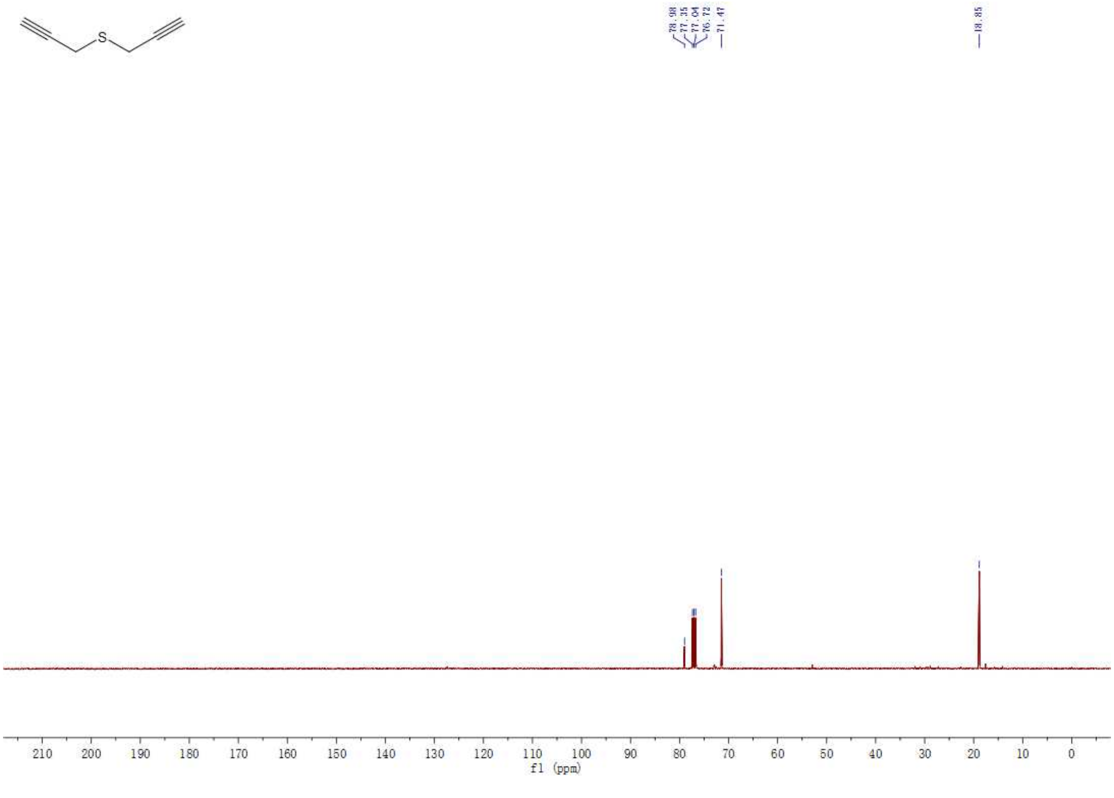
0
f1 (ppm)


S
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76.72
71.47
18.85
210
200
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130
120
110
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80
70
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50
40
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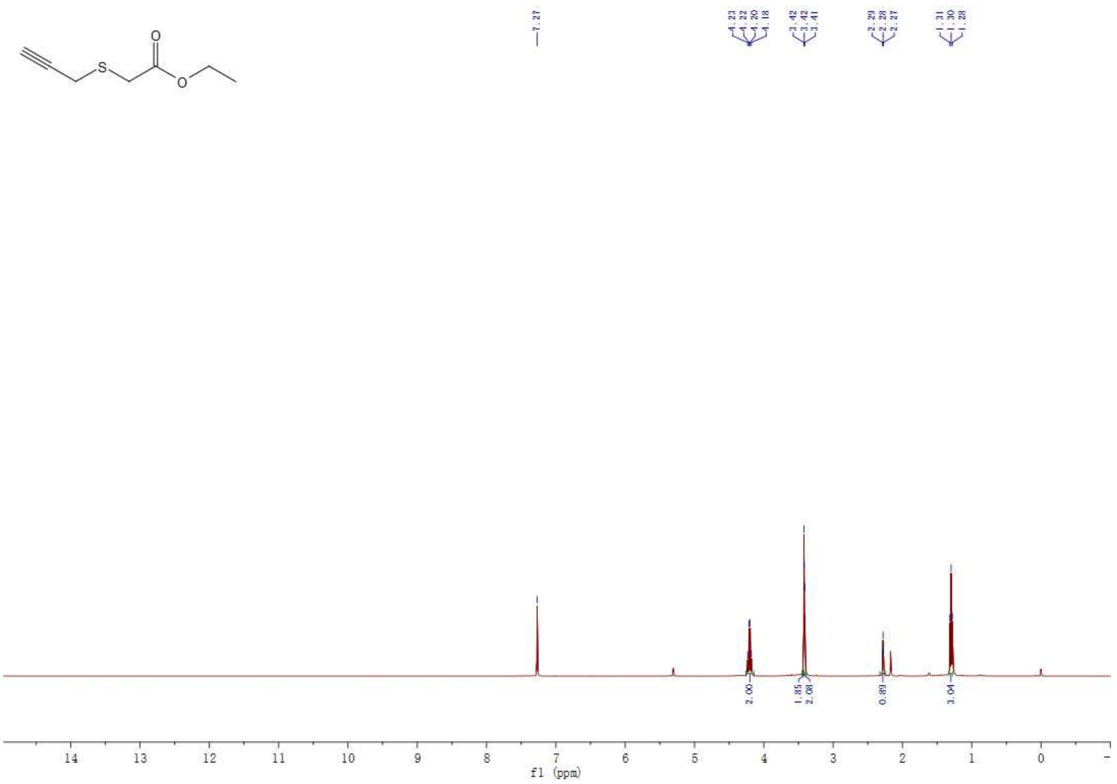
10
0
f1 (ppm)



O
S
O
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4.23
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4.20
4.18
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3.42
3.41
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2.27
1.31
1.30
1.28
2.00
1.85
2.08
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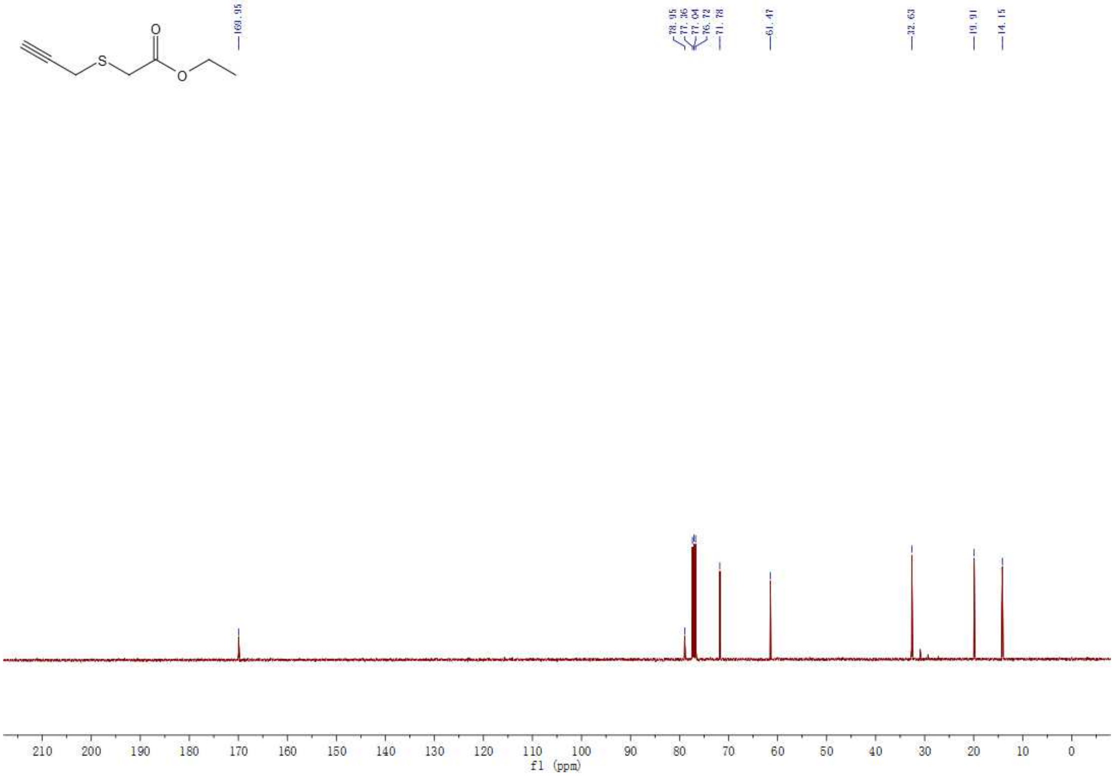

O
S
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210
200
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180
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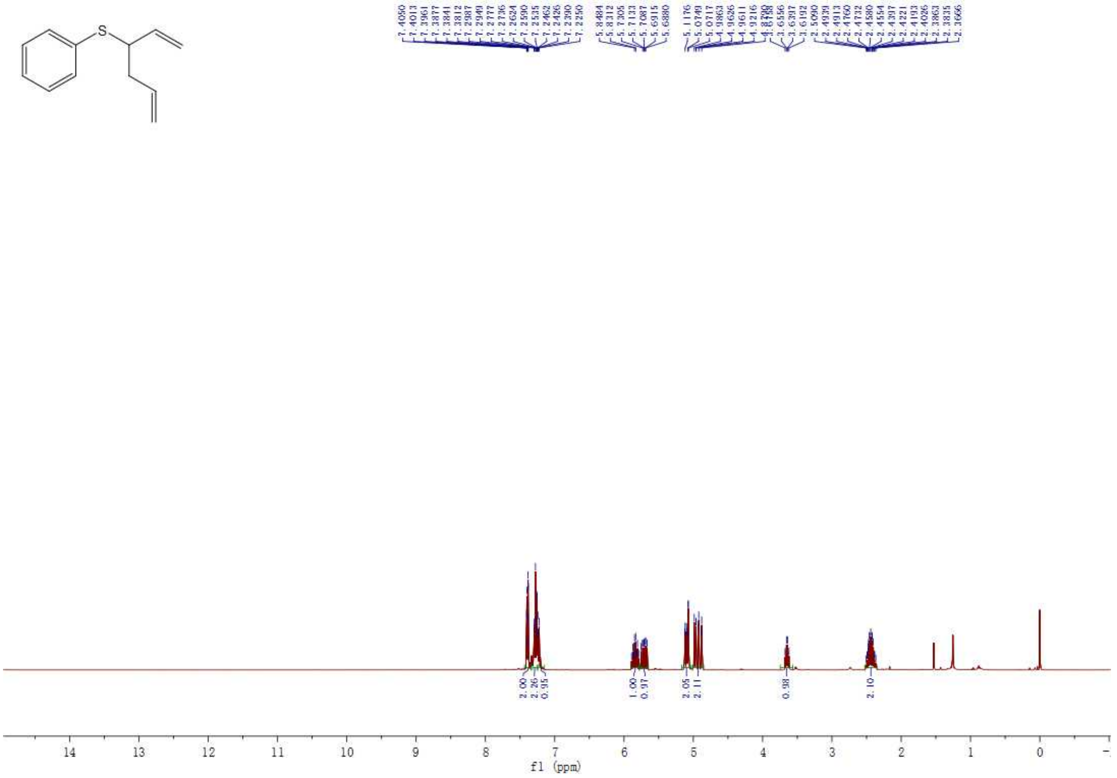
f1 (ppm)


S
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7.2590
7.2535
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7.2426
7.2390
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5.7133
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2.4732
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2.4193
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2.3863
2.3835
2.3666
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1.00
0.97
2.05
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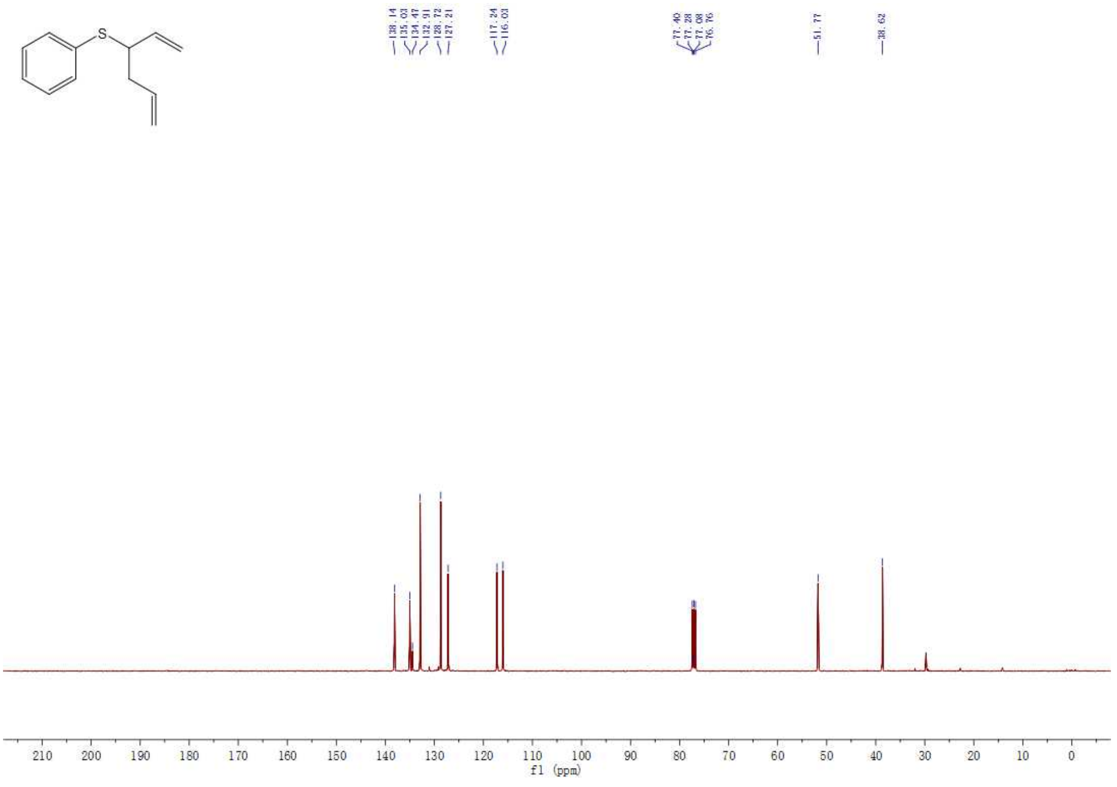
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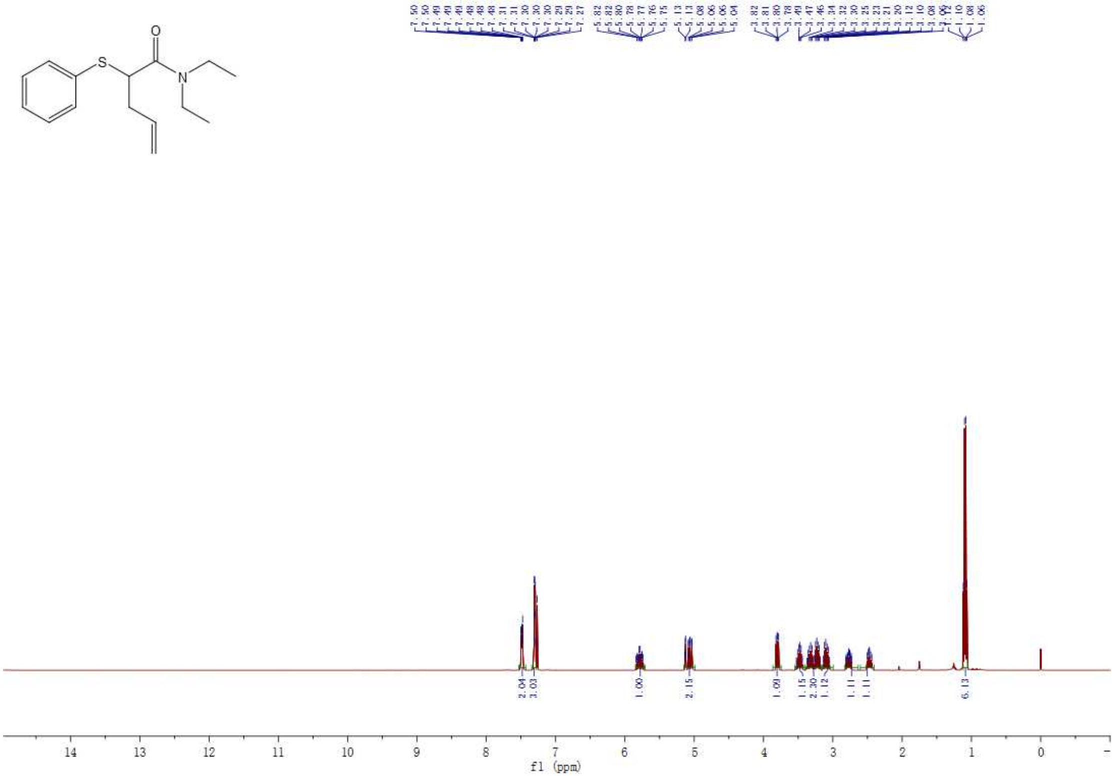
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7.30
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7.29
7.27
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5.82
5.80
5.78
5.77
5.76
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5.13
5.13
5.08
5.06
5.06
5.04
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3.80
3.78
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3.08
3.06
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1.08
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3.03
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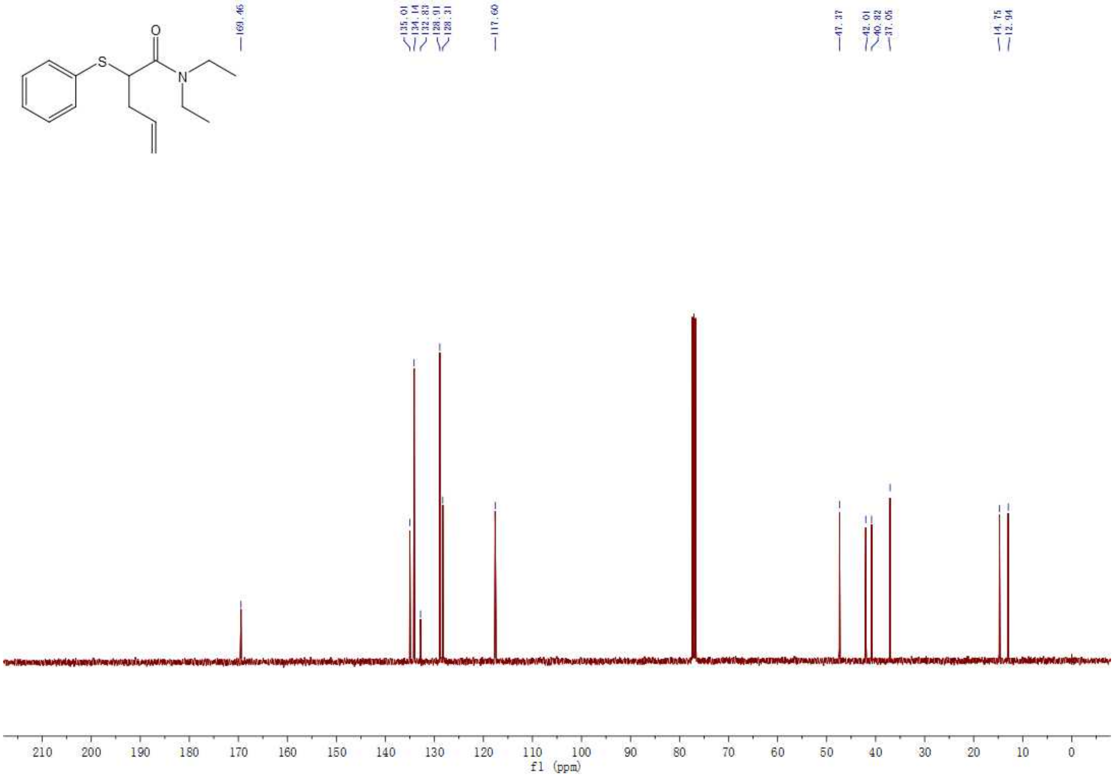
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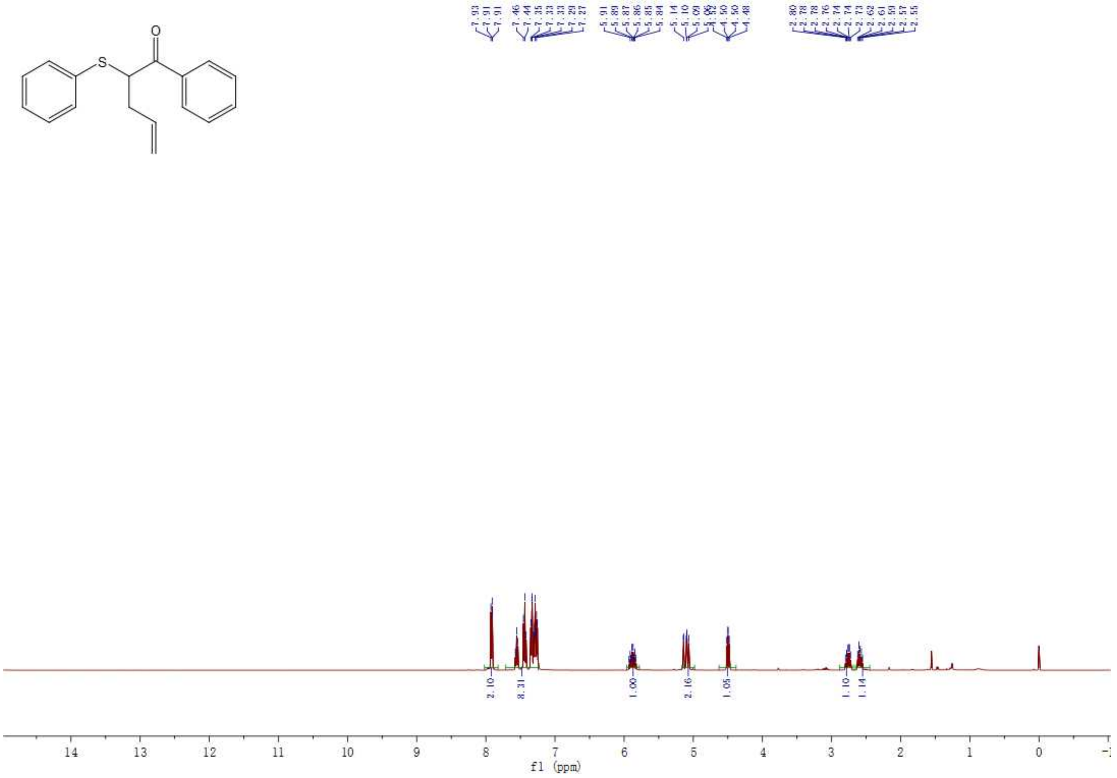
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5.86
5.85
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5.08
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4.50
4.48
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2.78
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2.74
2.74
2.73
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2.61
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2.57
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1.05
1.10
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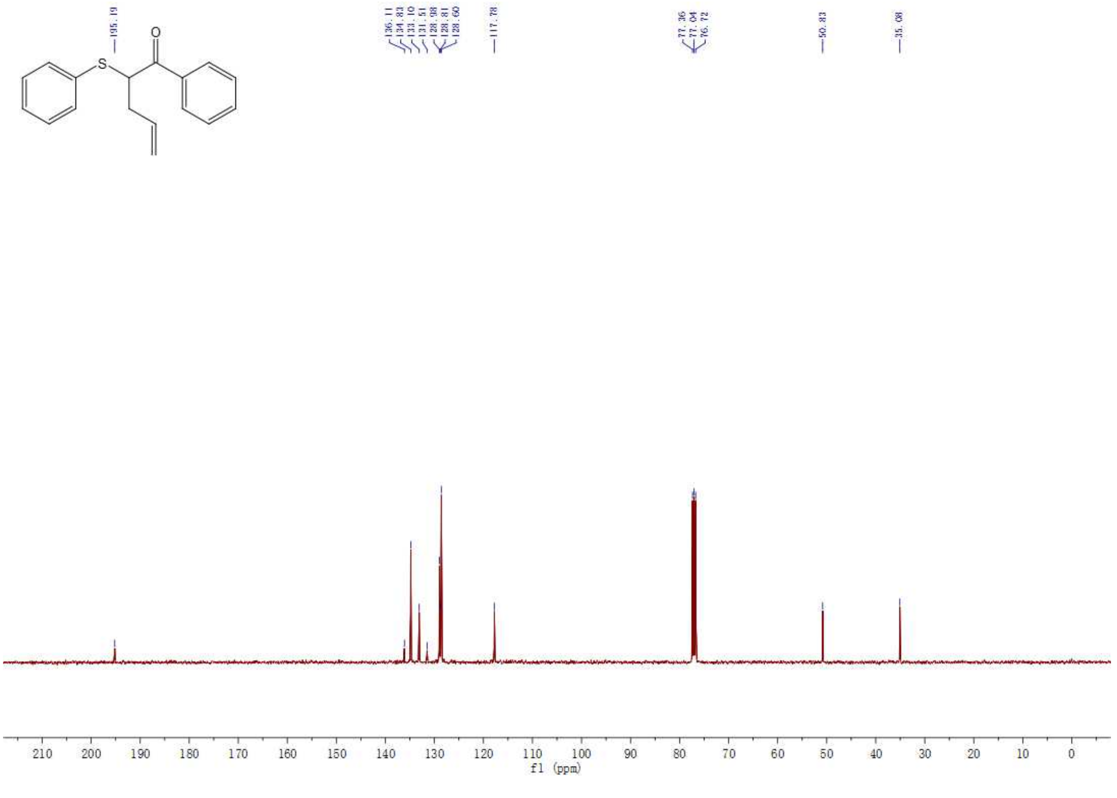
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200
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180
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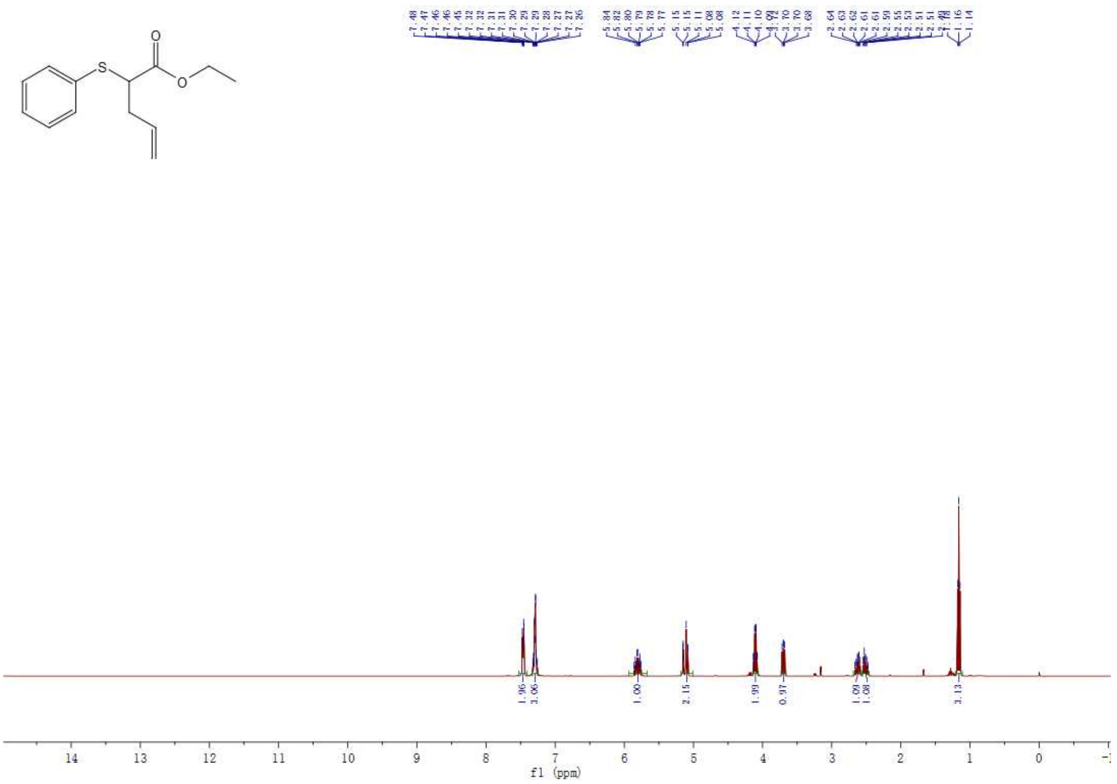
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7.27
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5.15
5.11
5.08
5.08
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4.11
4.10
4.09
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2.63
2.62
2.61
2.61
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2.55
2.53
2.51
2.51
2.48
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1.16
1.14
1.96
3.06
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2.15
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0.97
1.09
1.08
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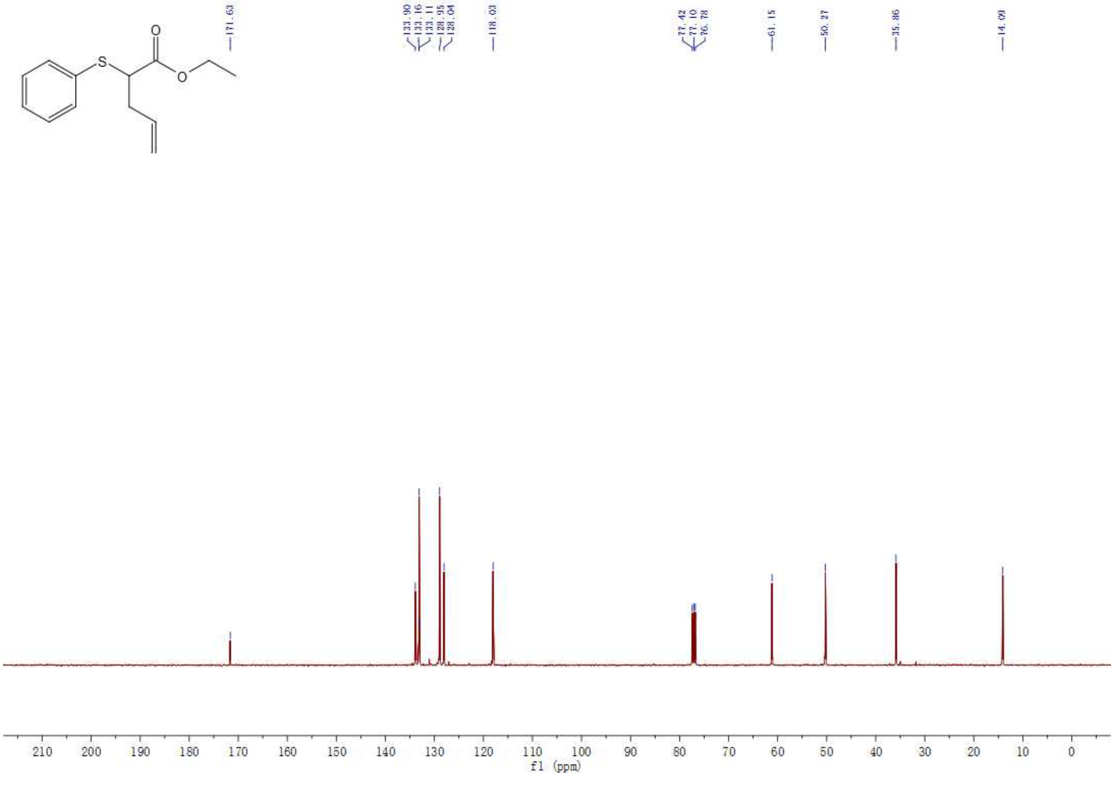
f1 (ppm)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76.78
61.15
50.27
35.86
14.09
210
200
190
180
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110
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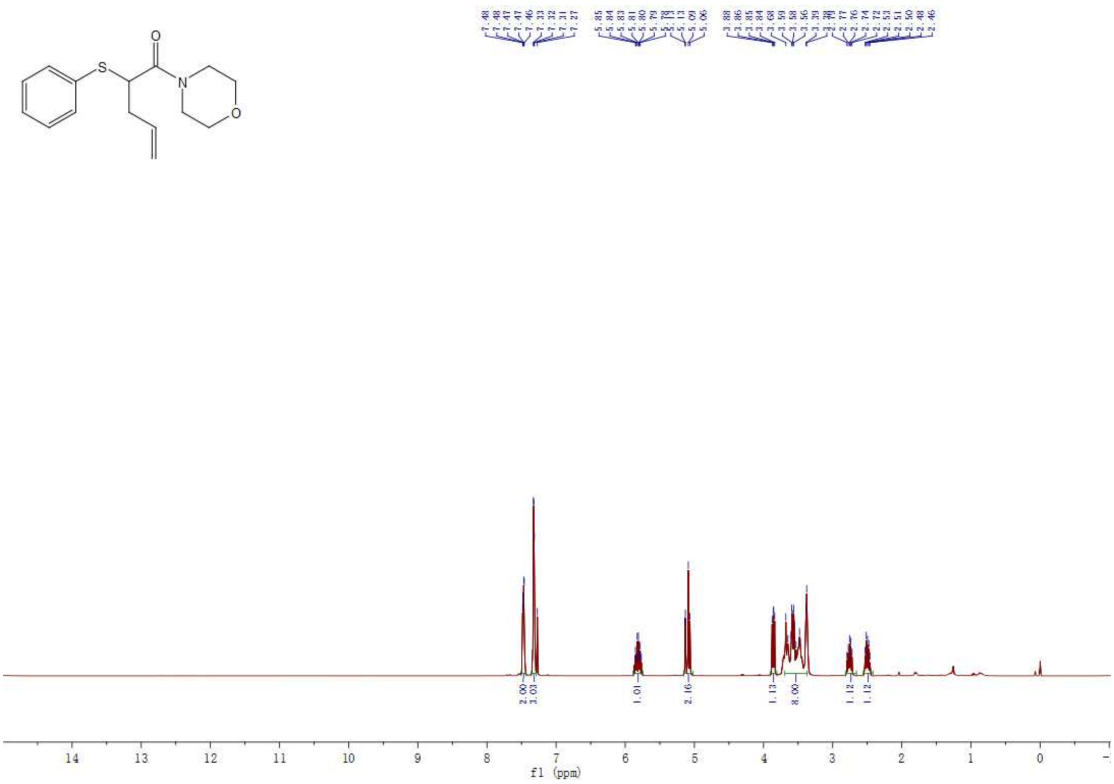
f1 (ppm)



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5.83
5.81
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5.79
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3.84
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3.59
3.58
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2.76
2.74
2.72
2.53
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2.50
2.48
2.46
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3.03
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8.00
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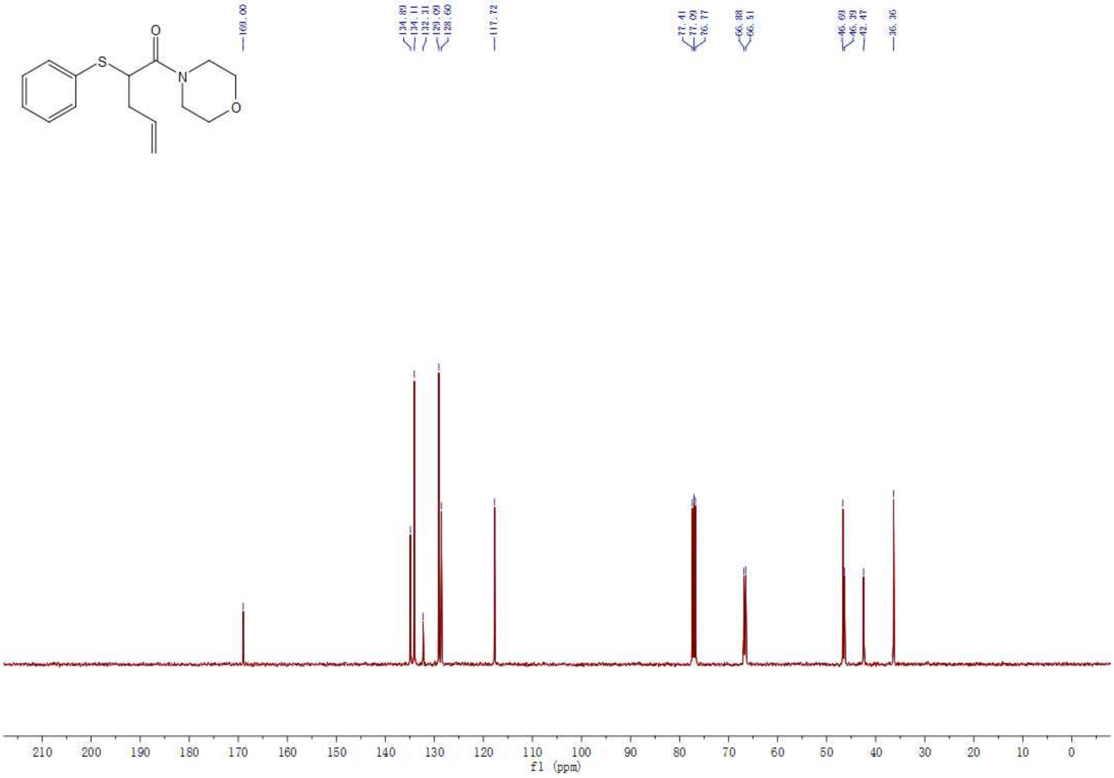
f1 (ppm)



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66.88
66.51
46.69
46.39
42.47
36.36
210
200
190
180
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120
110
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50
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10
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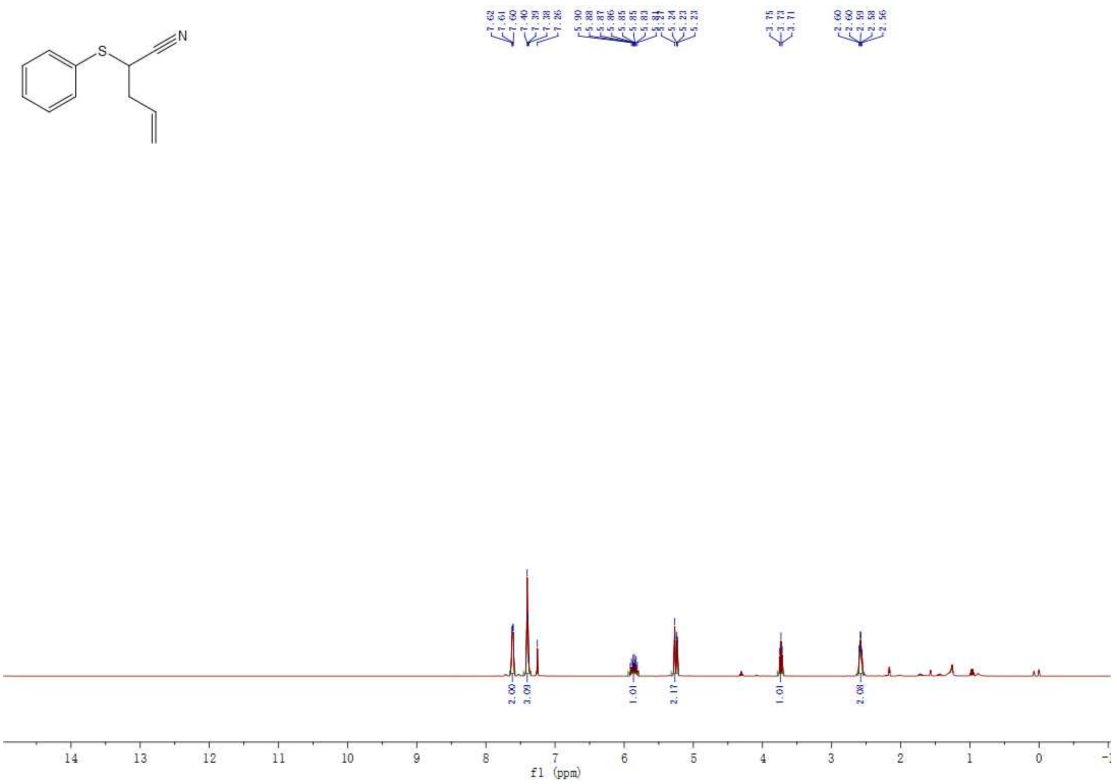
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5.86
5.85
5.85
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5.81
5.24
5.24
5.23
5.23
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2.60
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2.56
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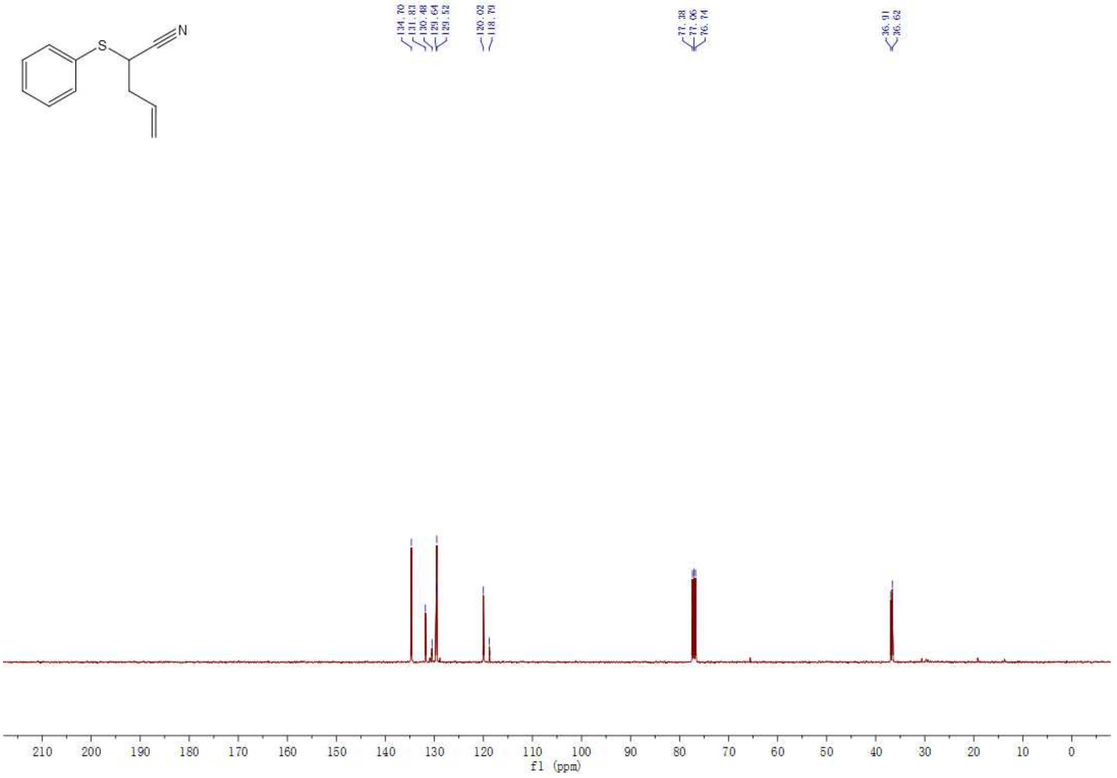
f1 (ppm)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200
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180
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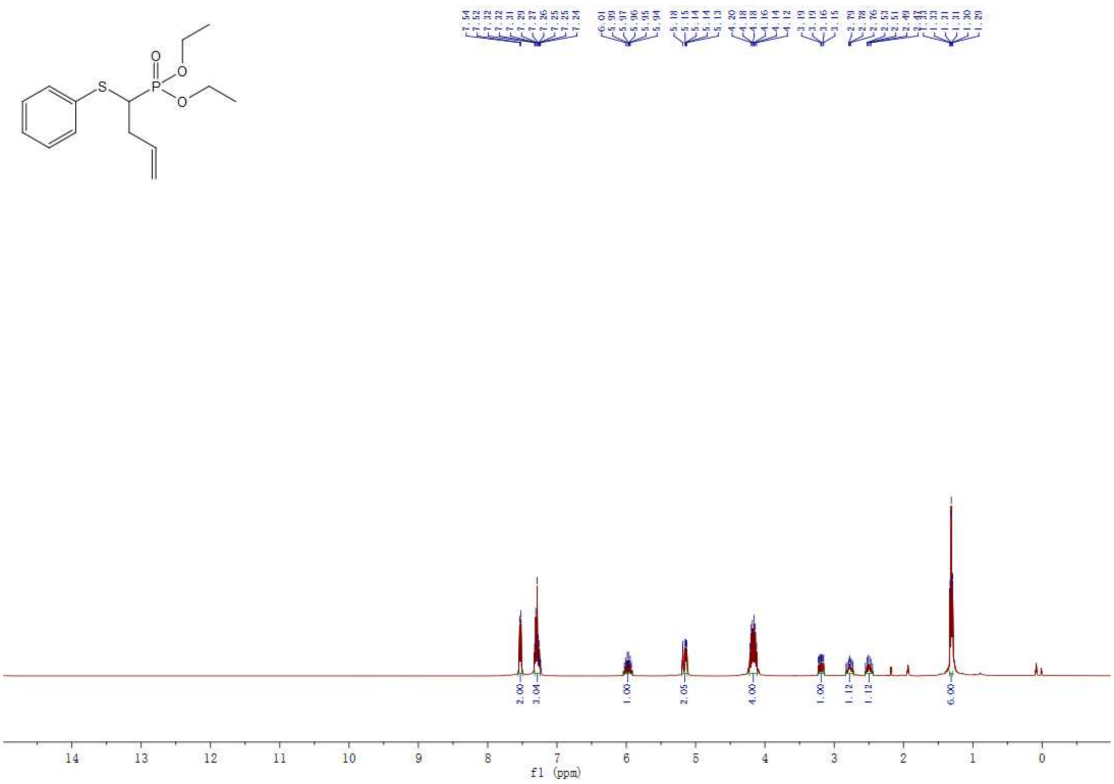
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O
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7.25
7.24
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5.94
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3.15
2.79
2.78
2.76
2.53
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2.49
2.48
1.33
1.31
1.31
1.30
1.29
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1.00
2.05
4.00
1.00
1.12
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5
4
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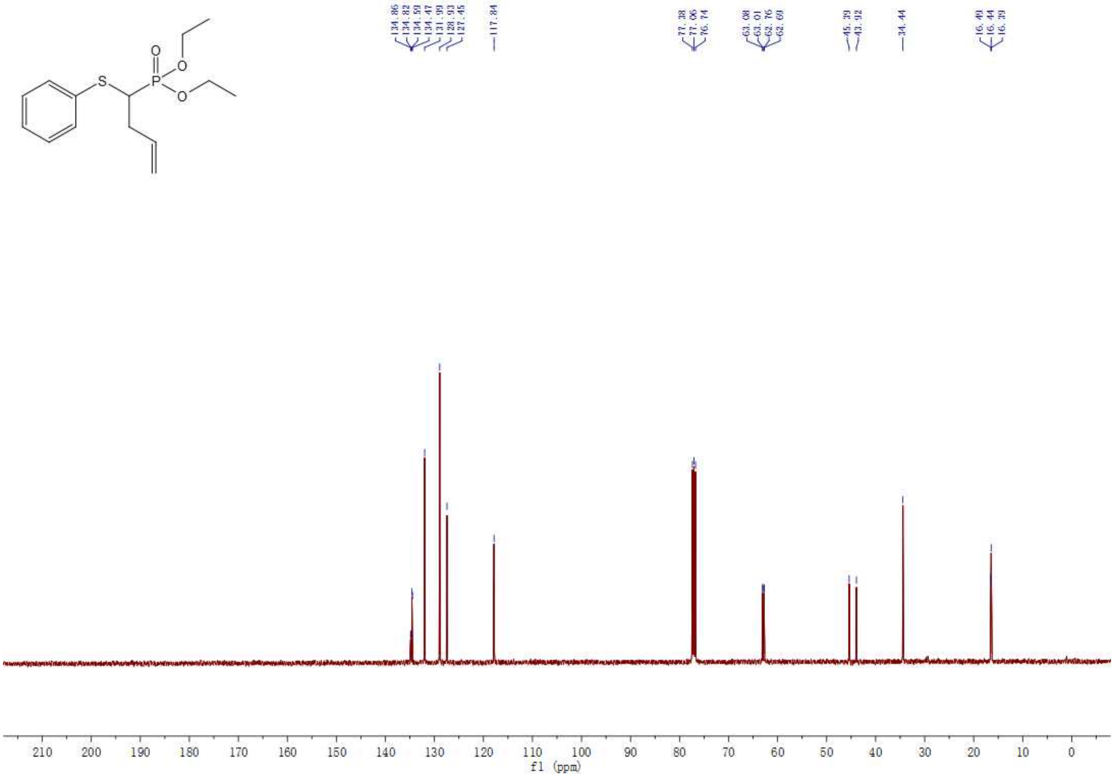
0
f1 (ppm)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P
O
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127.45
117.84
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77.06
76.74
63.08
63.01
62.76
62.69
45.39
43.92
34.44
16.49
16.44
16.39
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200
190
180
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120
110
100
90
80
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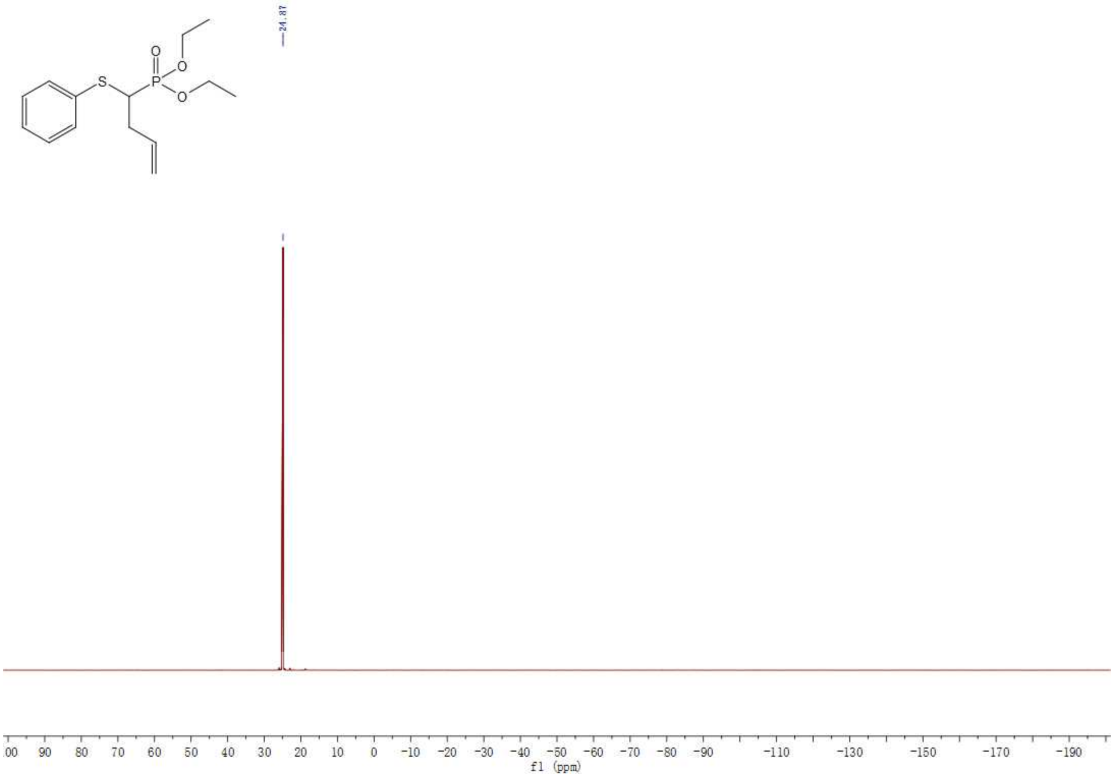
f1 (ppm)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P
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10
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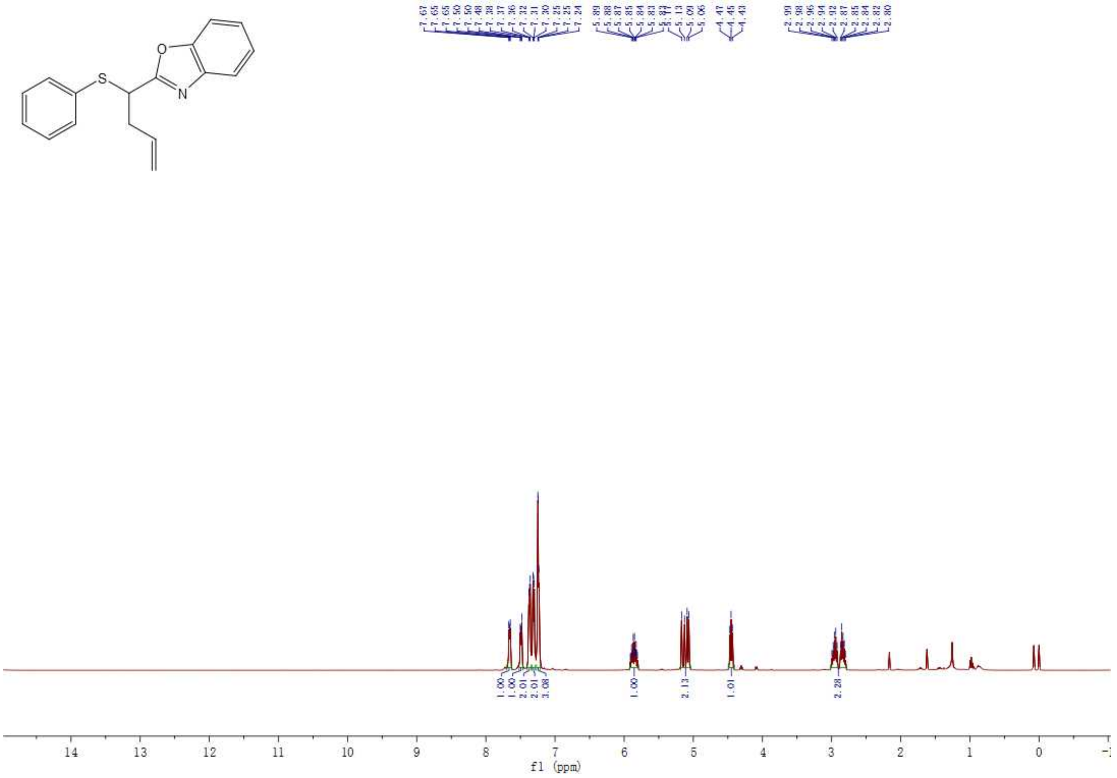
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)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5.83
5.82
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5.09
5.06
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2.96
2.94
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2.87
2.85
2.84
2.82
2.80
1.00
1.00
2.01
2.01
3.08
1.00
2.13
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4
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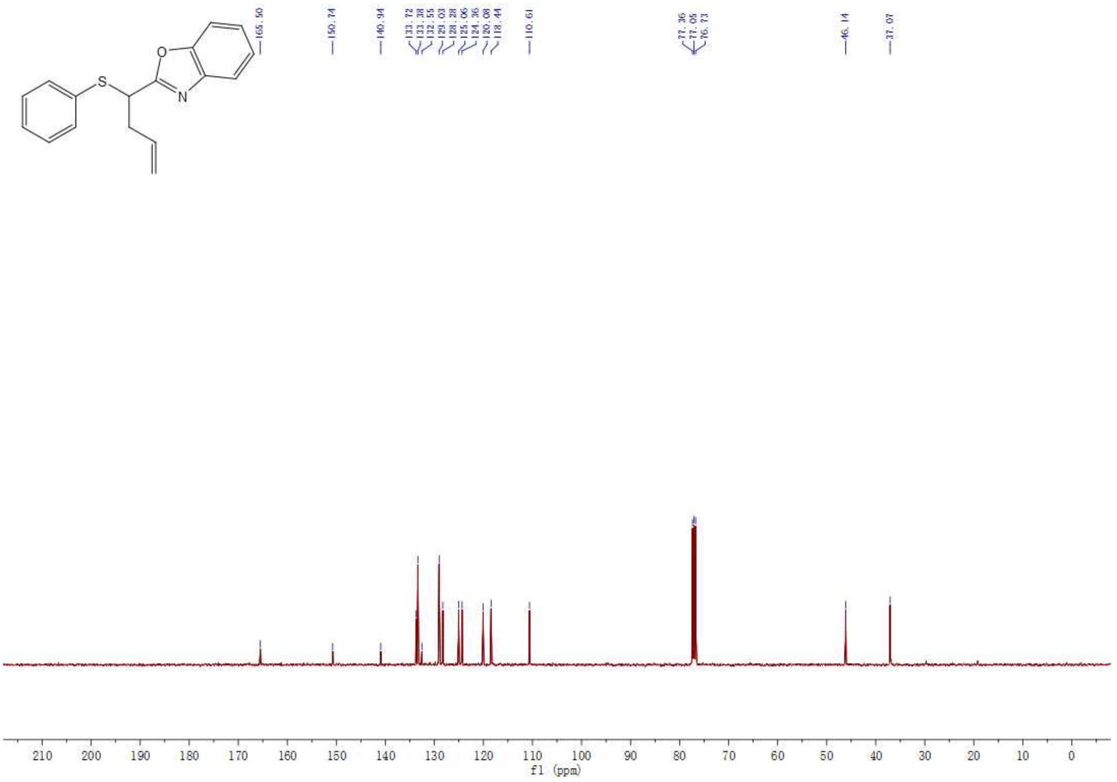
f1 (ppm)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110.61
77.36
77.05
76.73
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37.07
210
200
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180
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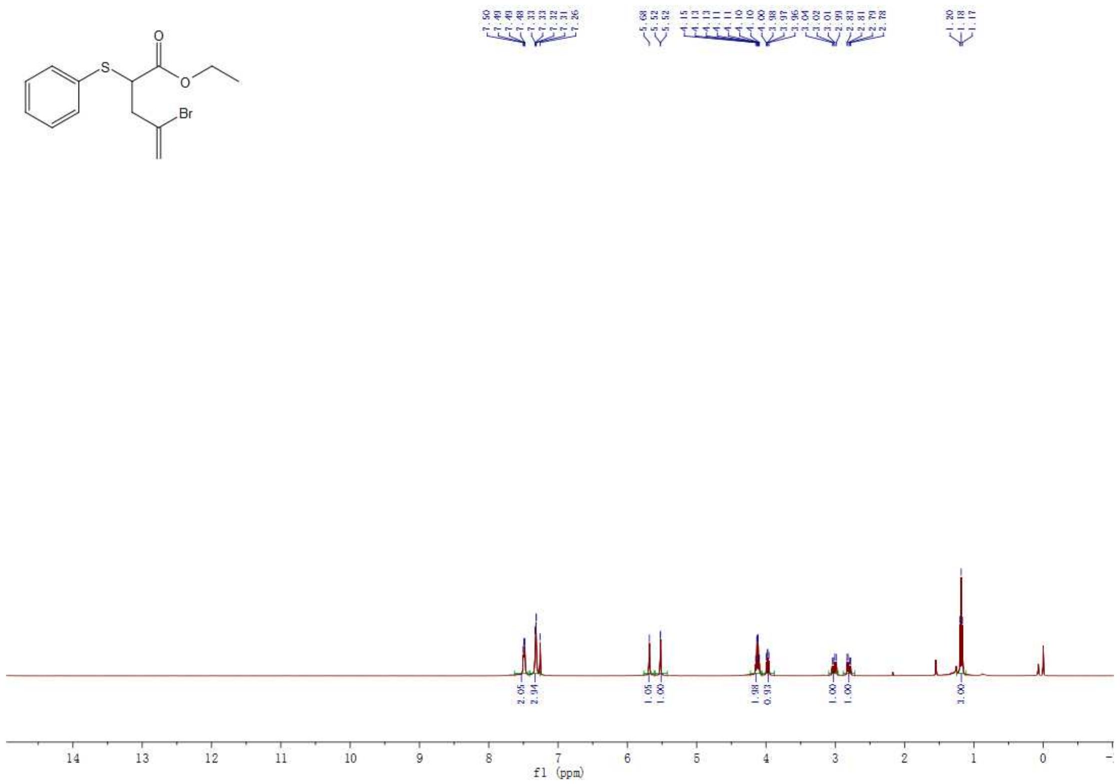
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5.52
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4.13
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4.11
4.10
4.10
4.00
3.98
3.97
3.96
3.04
3.02
3.01
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2.83
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2.78
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1.18
1.17
2.05
2.94
1.05
1.00
1.98
0.93
1.00
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9
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5
4
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1
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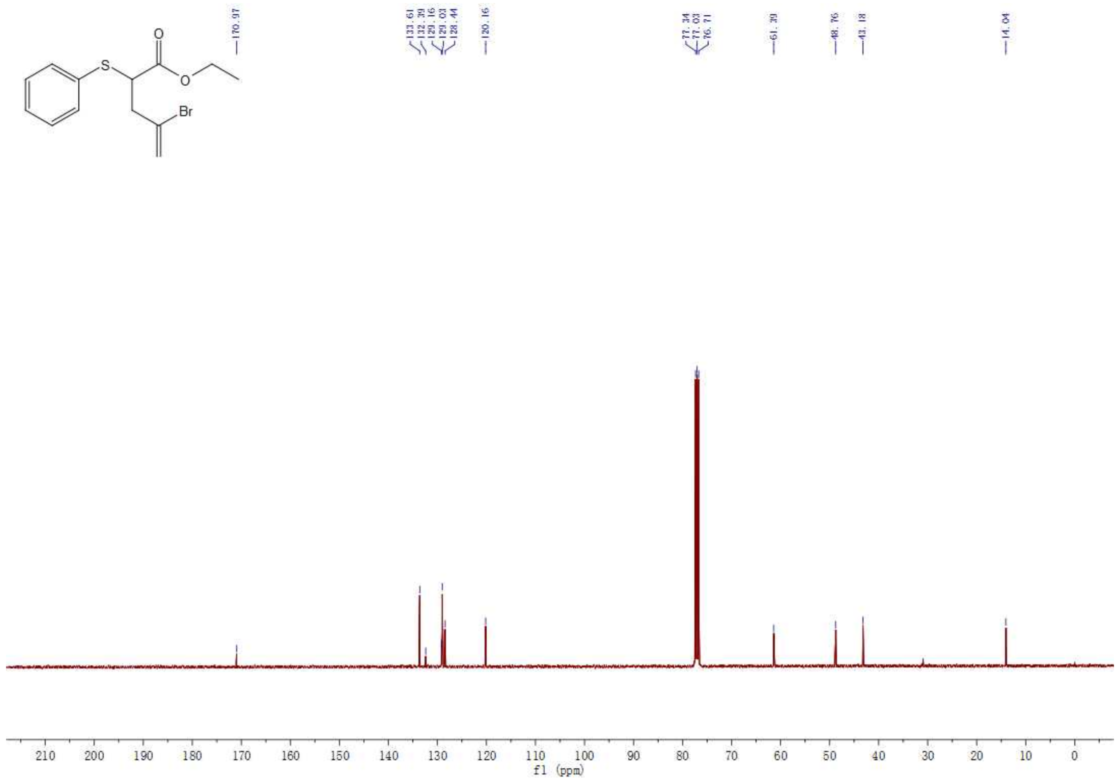
f1 (ppm)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77.03
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200
190
180
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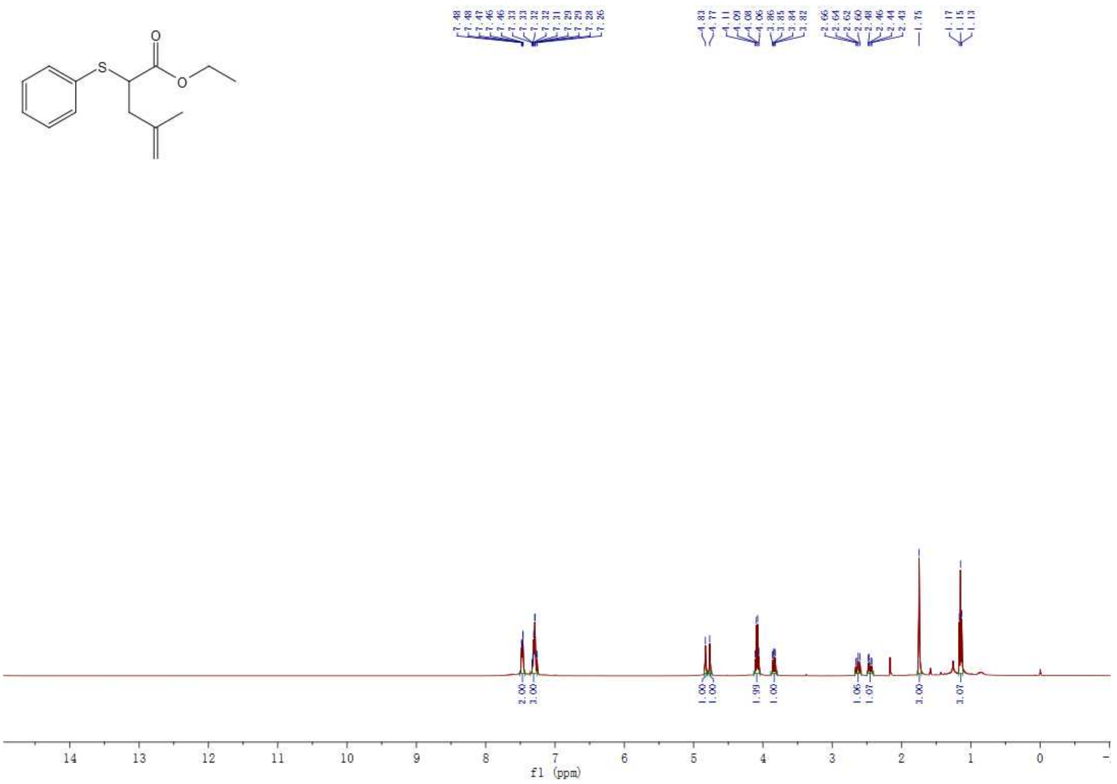
f1 (ppm)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4.08
4.06
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1.00
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1.00
1.06
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4
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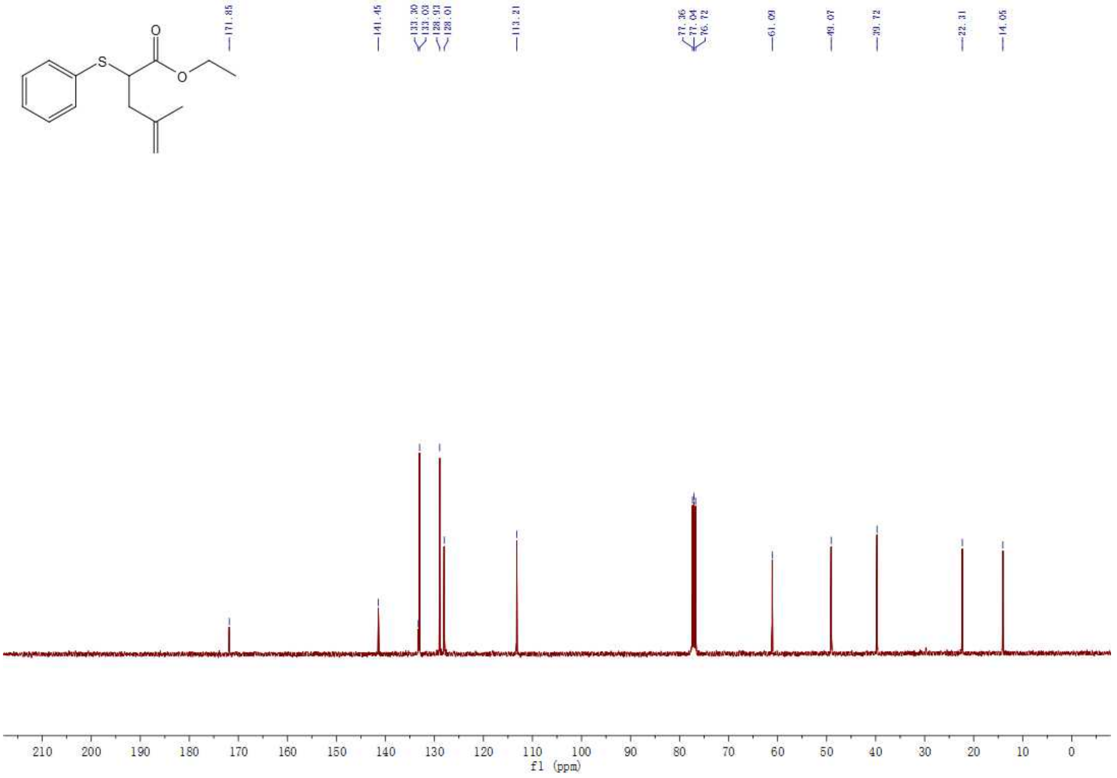
f1 (ppm)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49.07
39.72
22.31
14.05
210
200
190
180
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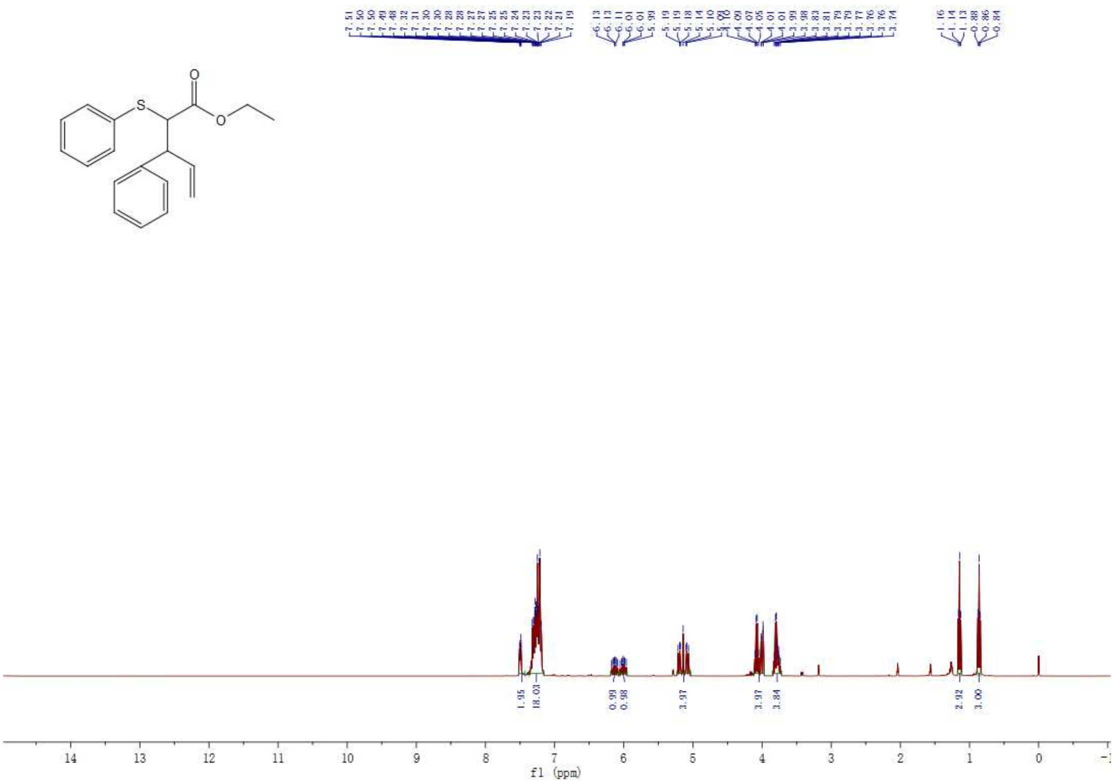
f1 (ppm)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6.01
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5.18
5.14
5.10
5.09
4.10
4.09
4.07
4.05
4.01
4.01
3.99
3.98
3.83
3.81
3.79
3.79
3.77
3.76
3.76
3.74
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1.13
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0.84
S
O
O
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2.92
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8
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4
3
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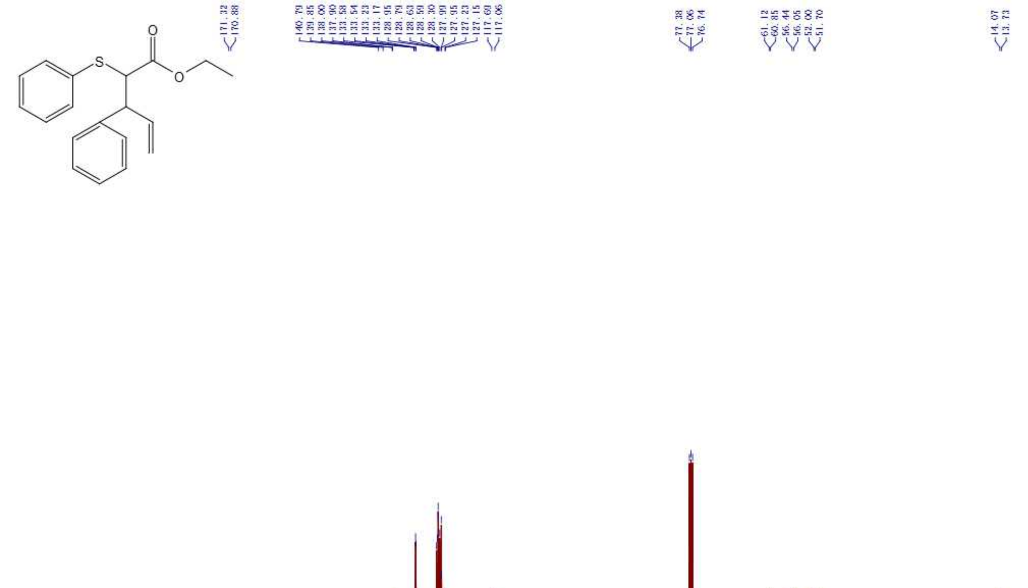
-1
f1 (ppm)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127.95
127.23
127.15
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117.06
77.38
77.06
76.74
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60.85
56.44
56.05
52.00
51.70
14.07
13.73
S
O
O
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200
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180
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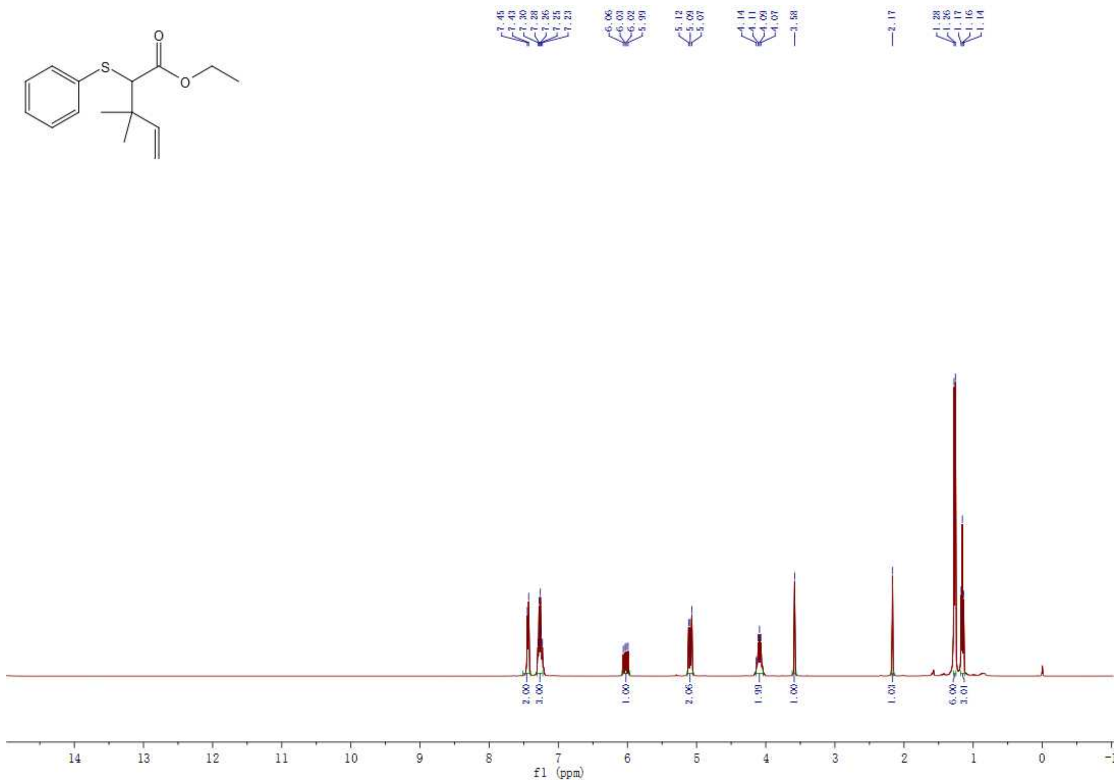
f1 (ppm)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5.12
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1.00
1.03
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4
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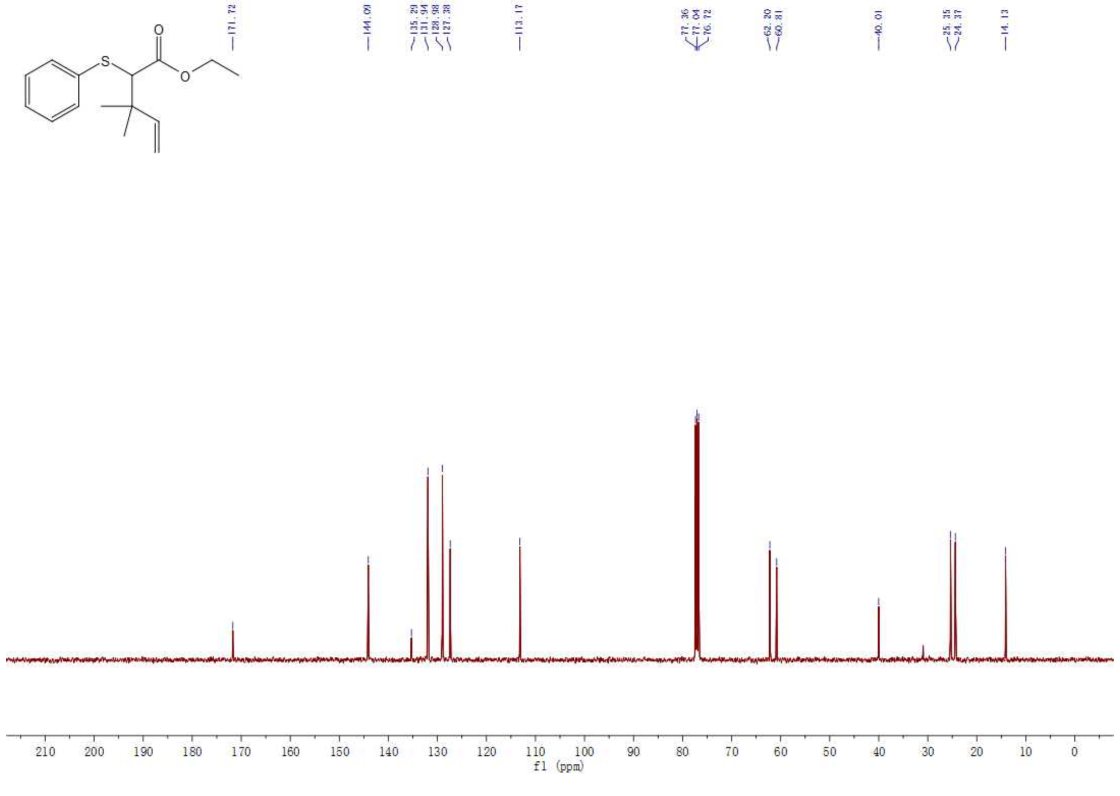
f1 (ppm)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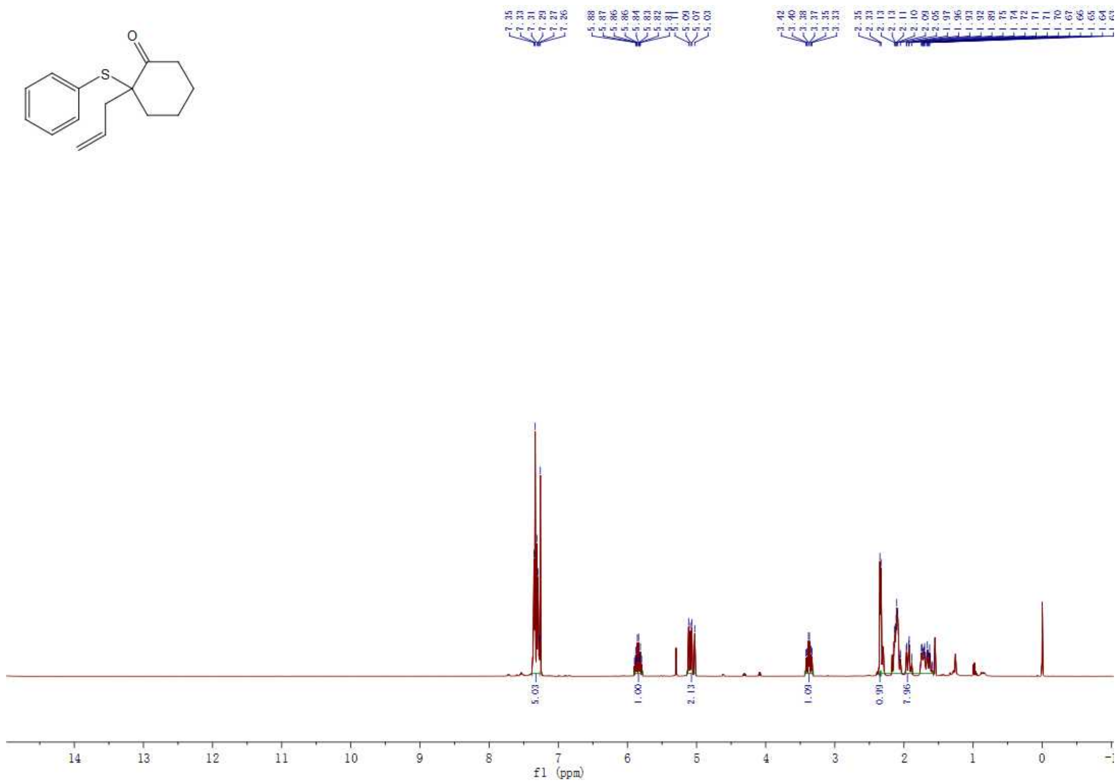
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.83
5.82
5.81
5.09
5.07
5.03
3.42
3.40
3.38
3.37
3.35
3.33
2.35
2.33
2.13
2.13
2.11
2.10
2.09
2.05
1.97
1.96
1.93
1.92
1.89
1.75
1.74
1.72
1.71
1.71
1.70
1.67
1.66
1.65
1.64
O
S
5.03
1.00
2.13
1.09
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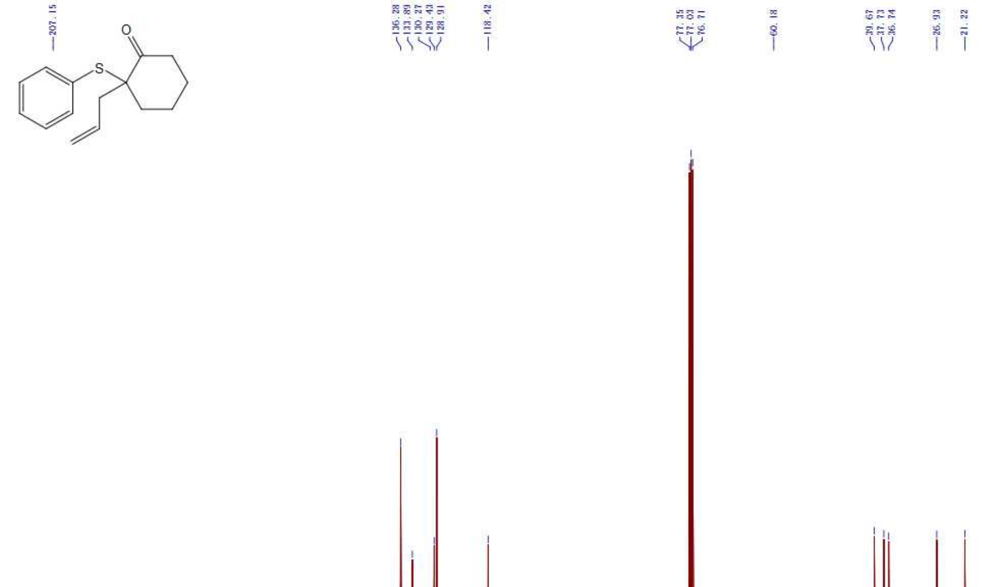
f1 (ppm)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76.71
60.18
39.67
37.73
36.74
26.93
21.22
O
S
210
200
190
180
170
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90
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70
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50
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10
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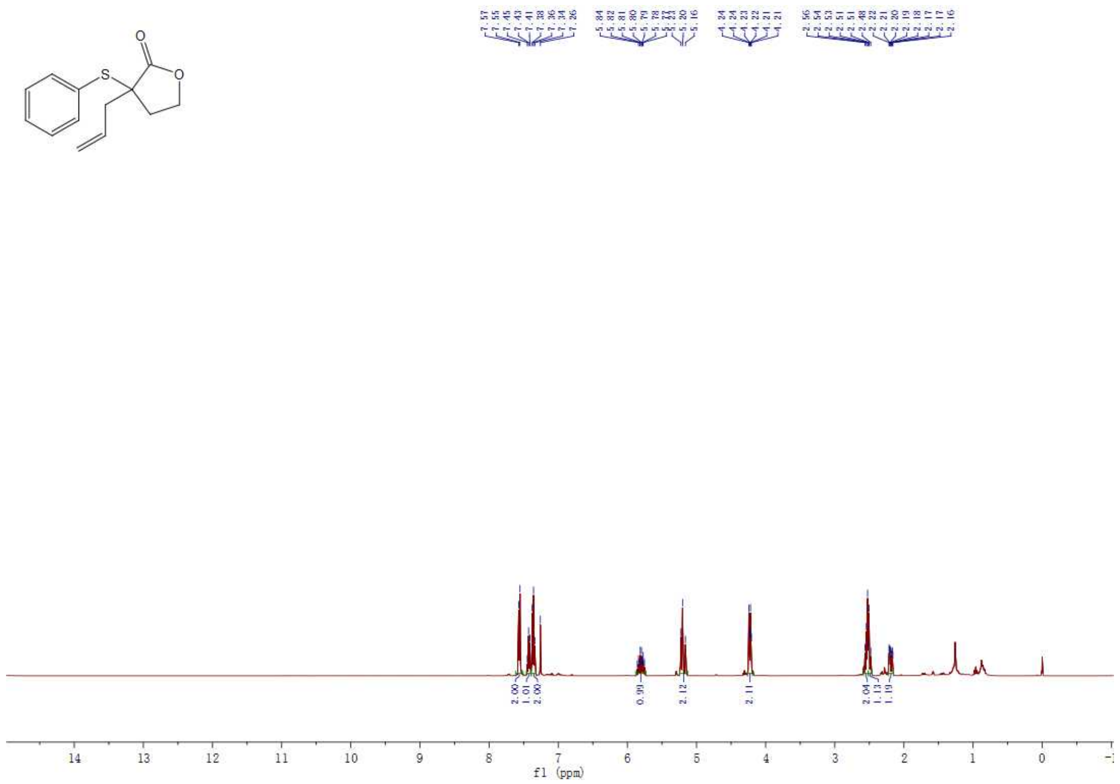
f1 (ppm)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5.82
5.81
5.80
5.79
5.78
5.77
5.21
5.20
5.16
4.24
4.24
4.23
4.22
4.21
4.21
2.56
2.54
2.53
2.51
2.51
2.48
2.22
2.21
2.20
2.19
2.18
2.17
2.17
2.16
2.00
1.01
2.00
0.99
2.12
2.11
2.04
1.13
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13
12
11
10
9
8
7
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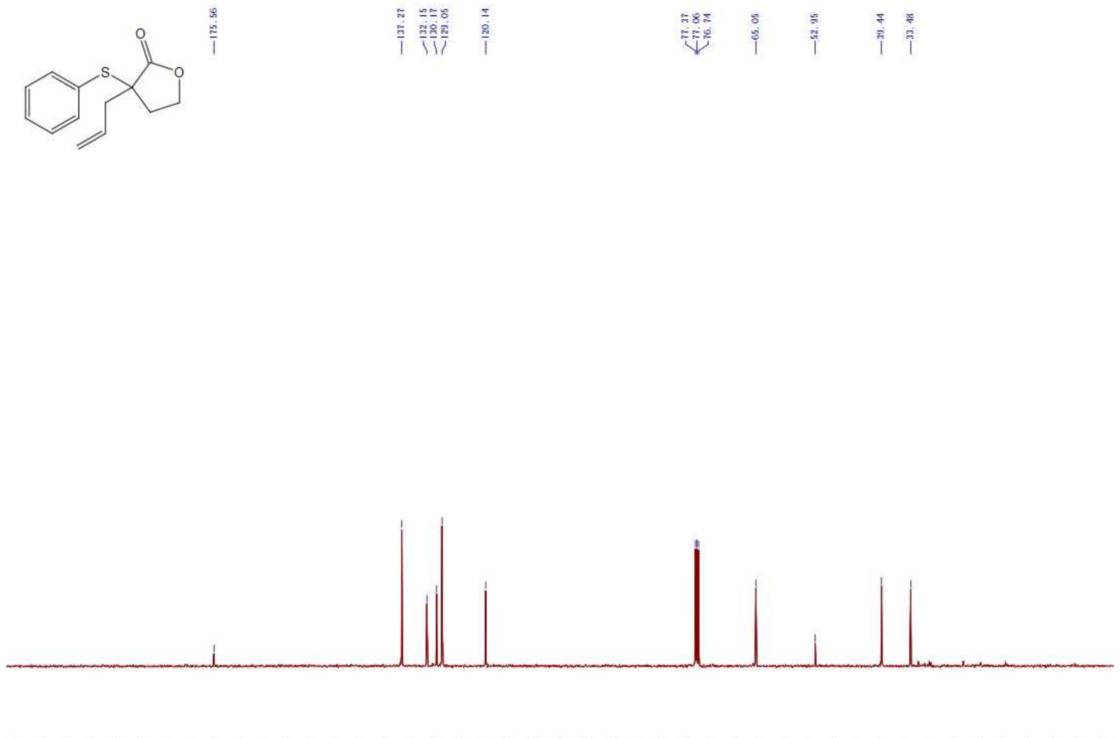
5
4
3
2
1
0
f1 (ppm)


O
S
O
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130.17
129.05
120.14
77.37
77.06
76.74
65.05
52.95
39.44
33.48
210
200
190
180
170
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150
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130
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110
100
90
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70
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50
40
30
20
10
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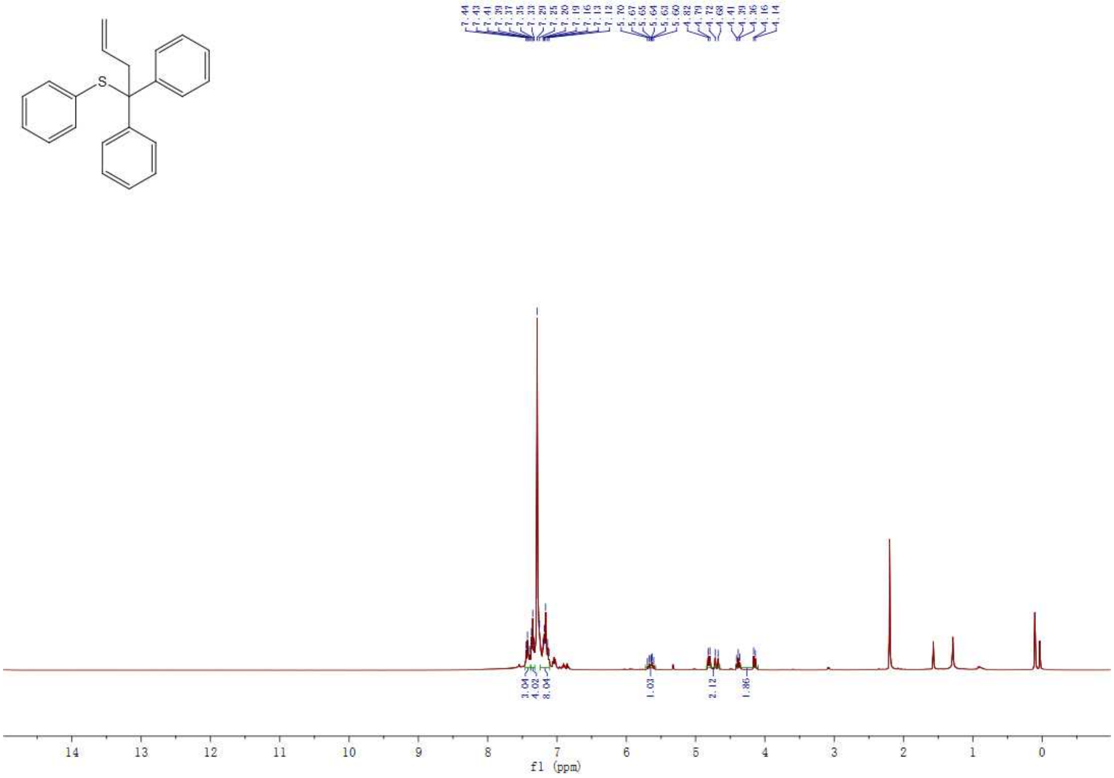
f1 (ppm)


S
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7.43
7.41
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7.37
7.35
7.33
7.29
7.25
7.20
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7.16
7.13
7.12
5.70
5.67
5.65
5.64
5.63
5.60
4.82
4.79
4.72
4.68
4.41
4.39
4.36
4.16
4.14
3.04
4.02
8.04
1.03
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13
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11
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9
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5
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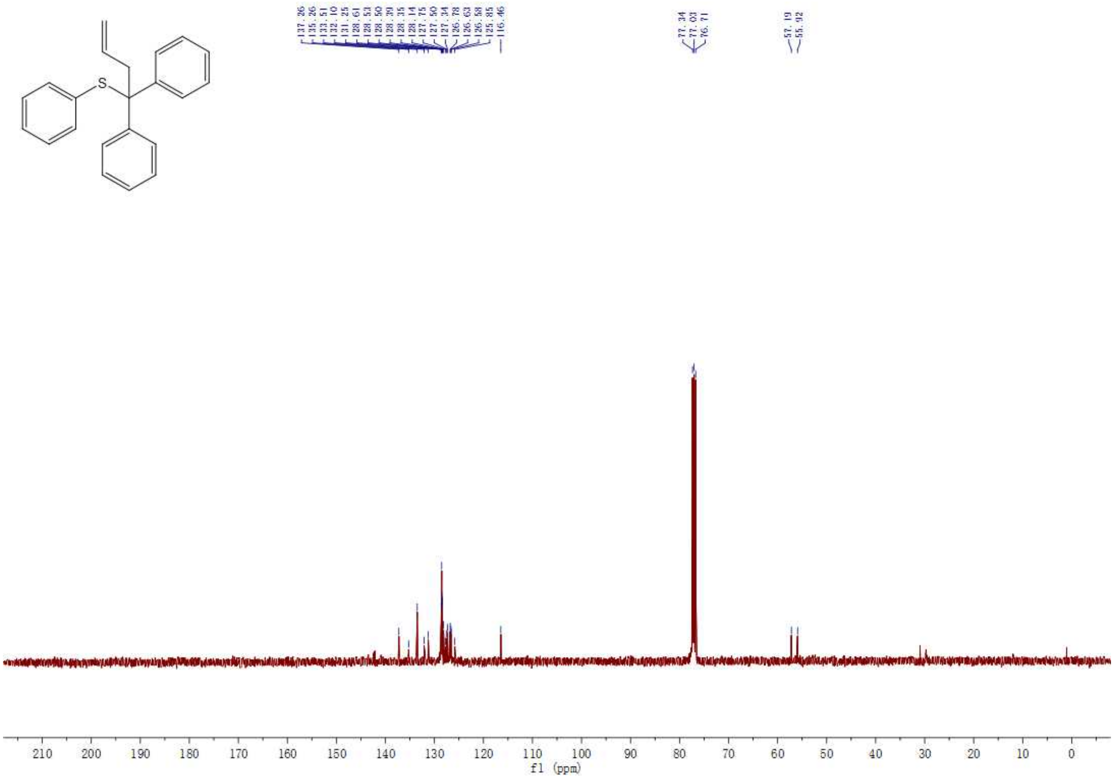
f1 (ppm)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132.10
131.25
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128.53
128.50
128.39
128.35
128.14
127.75
127.50
127.34
126.78
126.63
126.58
125.85
116.46
77.34
77.03
76.71
57.19
55.92
210
200
190
180
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130
120
110
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90
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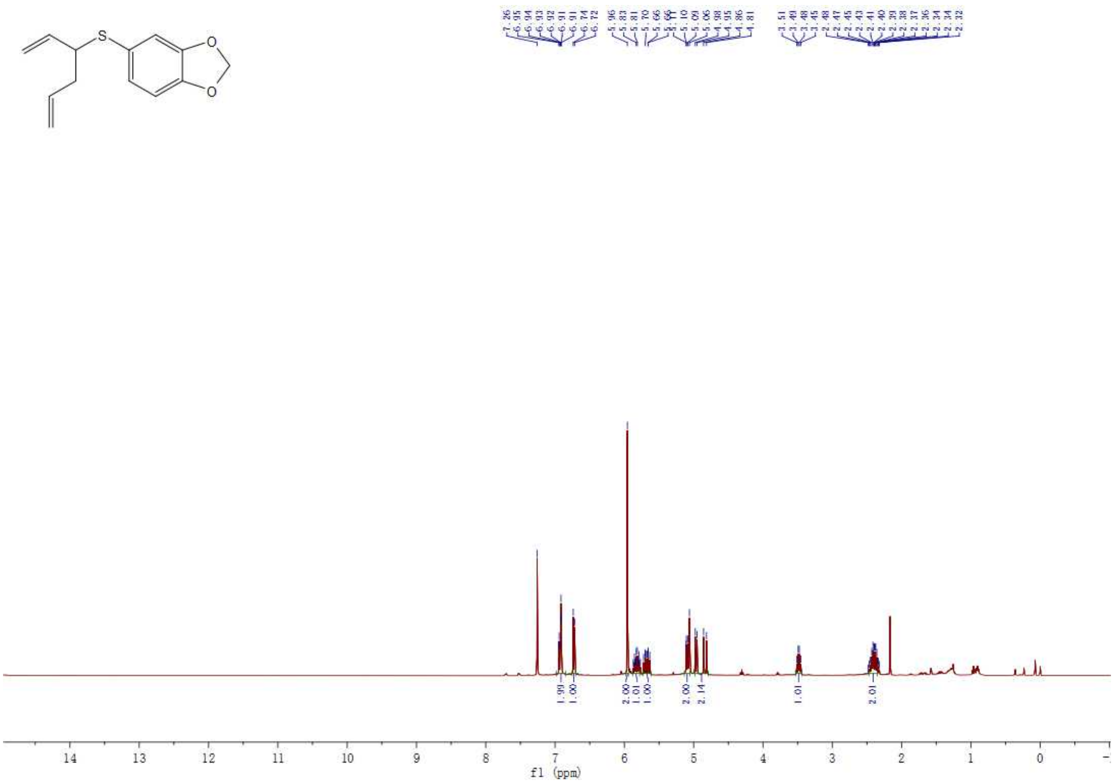
10
0
f1 (ppm)


S
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O
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6.94
6.93
6.92
6.91
6.91
6.74
6.72
5.96
5.83
5.81
5.70
5.66
5.66
5.11
5.10
5.09
5.06
4.98
4.95
4.86
4.81
3.51
3.49
3.48
3.45
2.48
2.47
2.45
2.43
2.41
2.40
2.39
2.38
2.37
2.36
2.34
2.34
2.32
1.99
1.00
2.00
1.01
1.00
2.00
2.14
1.01
2.01
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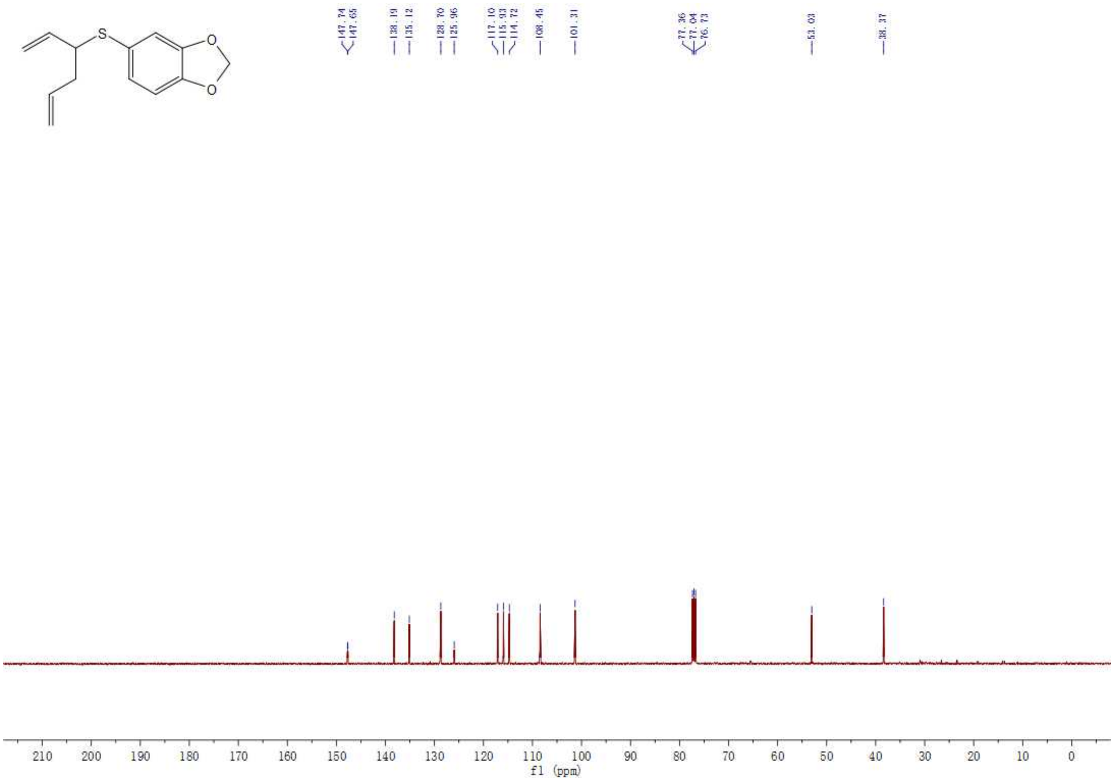
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


S
O
O
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147.65
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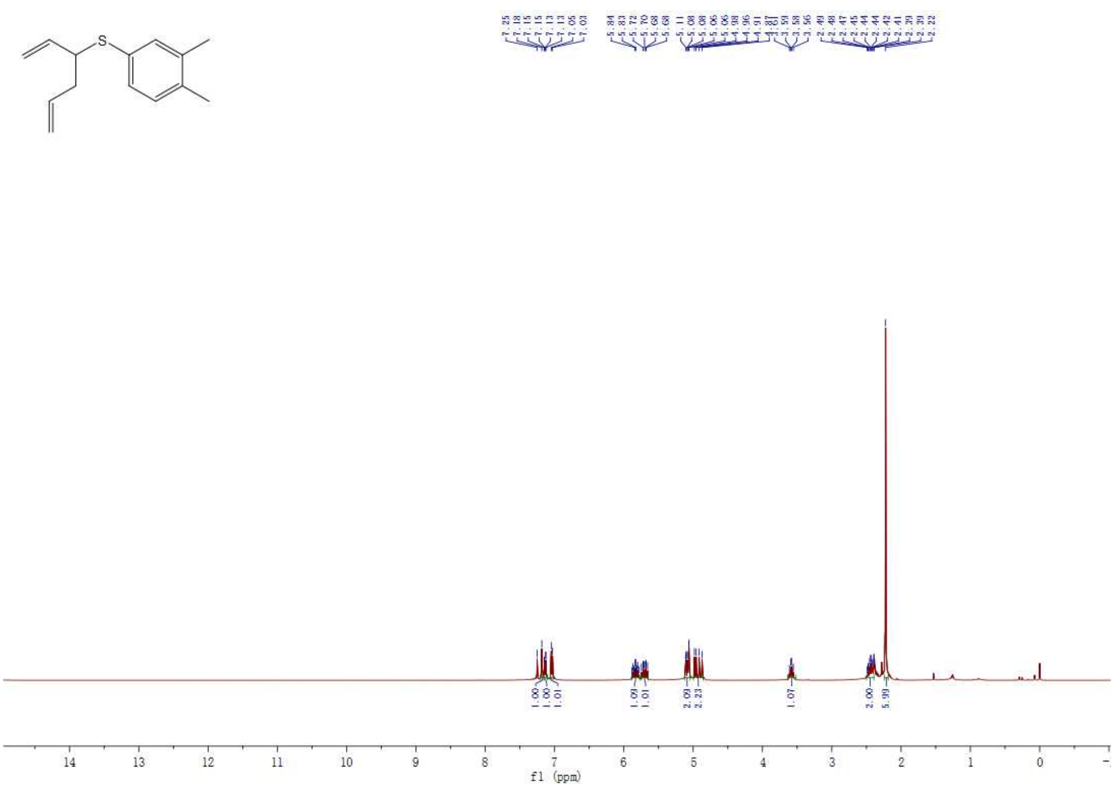
135.12
128.70
125.96
117.10
115.93
114.72
108.45
101.31
77.36
77.04
76.73
53.03
38.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
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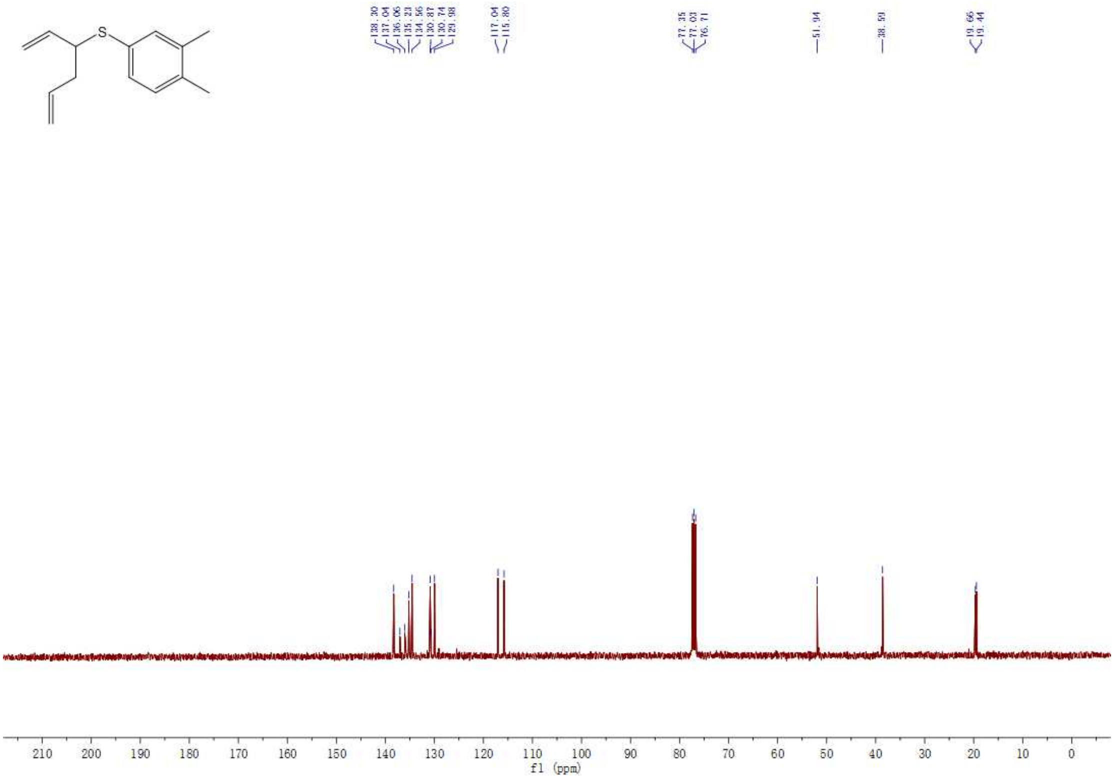
7.18
7.15
7.15
7.13
7.13
7.05
7.03
5.84
5.83
5.72
5.70
5.68
5.68
5.11
5.08
5.08
5.06
5.06
4.98
4.96
4.91
4.87
3.61
3.59
3.58
3.56
2.49
2.48
2.47
2.45
2.44
2.44
2.42
2.41
2.39
2.39
2.22
1.00
1.00
1.01
1.00
1.01
2.09
2.23
1.07
2.00
5.99
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


S
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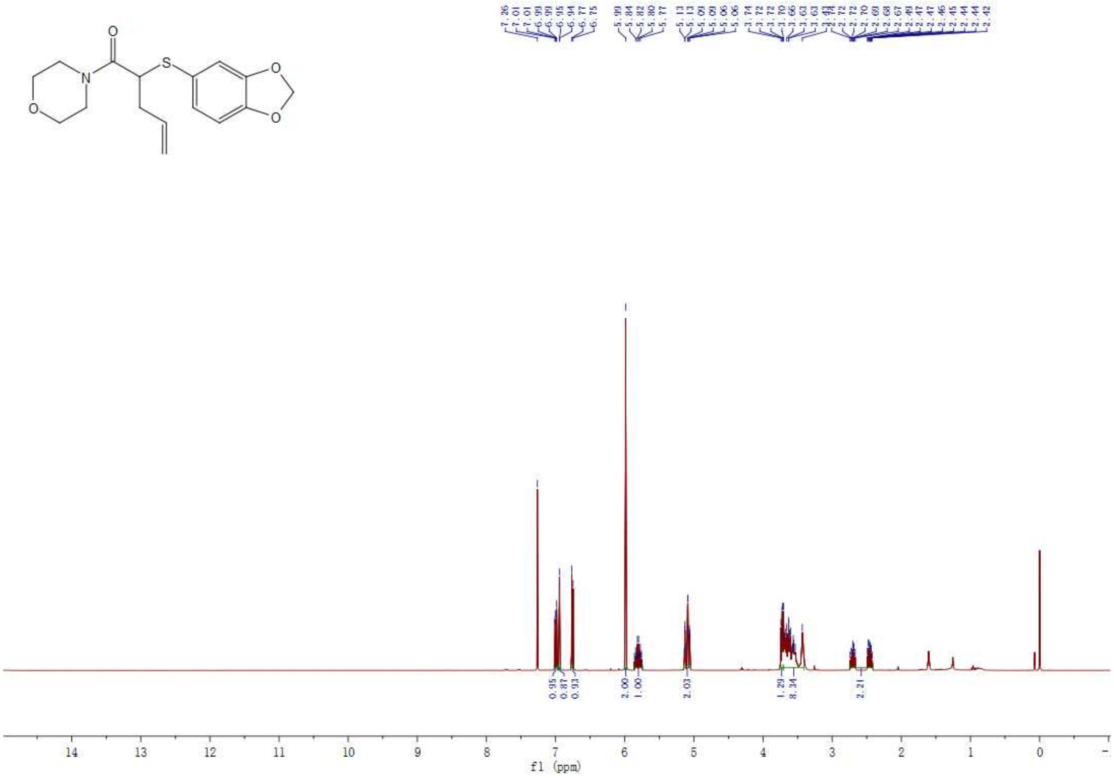
137.04
136.06
135.23
134.56
130.87
130.74
129.98
117.04
115.80
77.35
77.03
76.71
51.94
38.59
19.66
19.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
S
O
O
O
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7.01
7.01
6.99
6.99
6.95
6.94
6.77
6.75
5.99
5.84
5.82
5.80
5.77
5.13
5.13
5.09
5.09
5.06
5.06
3.74
3.72
3.72
3.70
3.66
3.63
3.63
3.43
2.72
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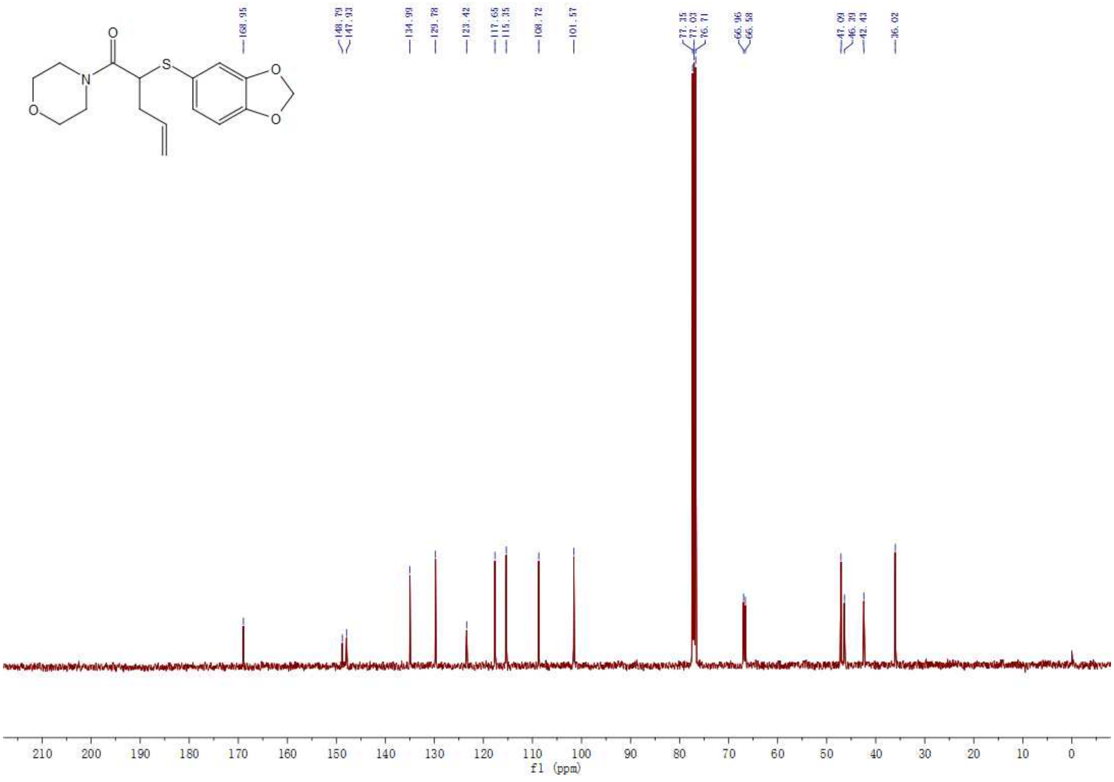
2.70
2.69
2.68
2.67
2.49
2.47
2.47
2.46
2.45
2.44
2.44
2.42
0.95
0.87
0.93
2.00
1.00
2.03
1.29
8.34
2.21
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


O
N
S
O
O
O
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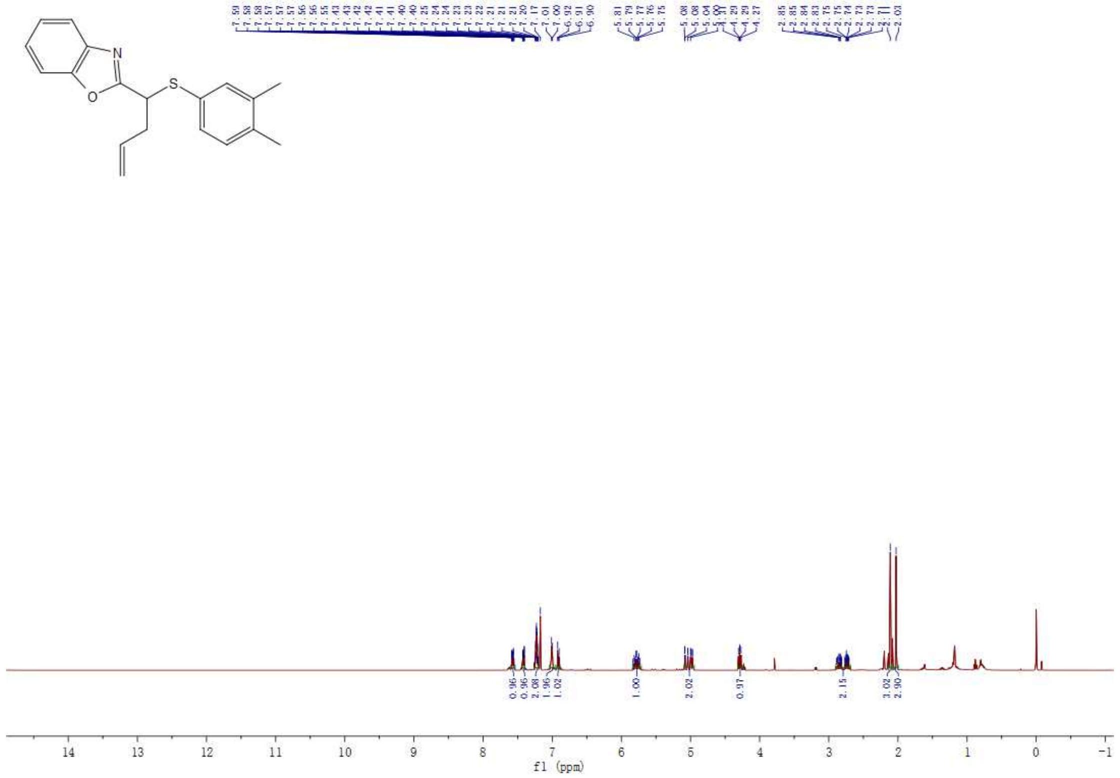
148.79
147.93
134.99
129.78
123.42
117.65
115.35
108.72
101.57
77.35
77.03
76.71
66.96
66.58
47.09
46.39
42.43
36.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
S
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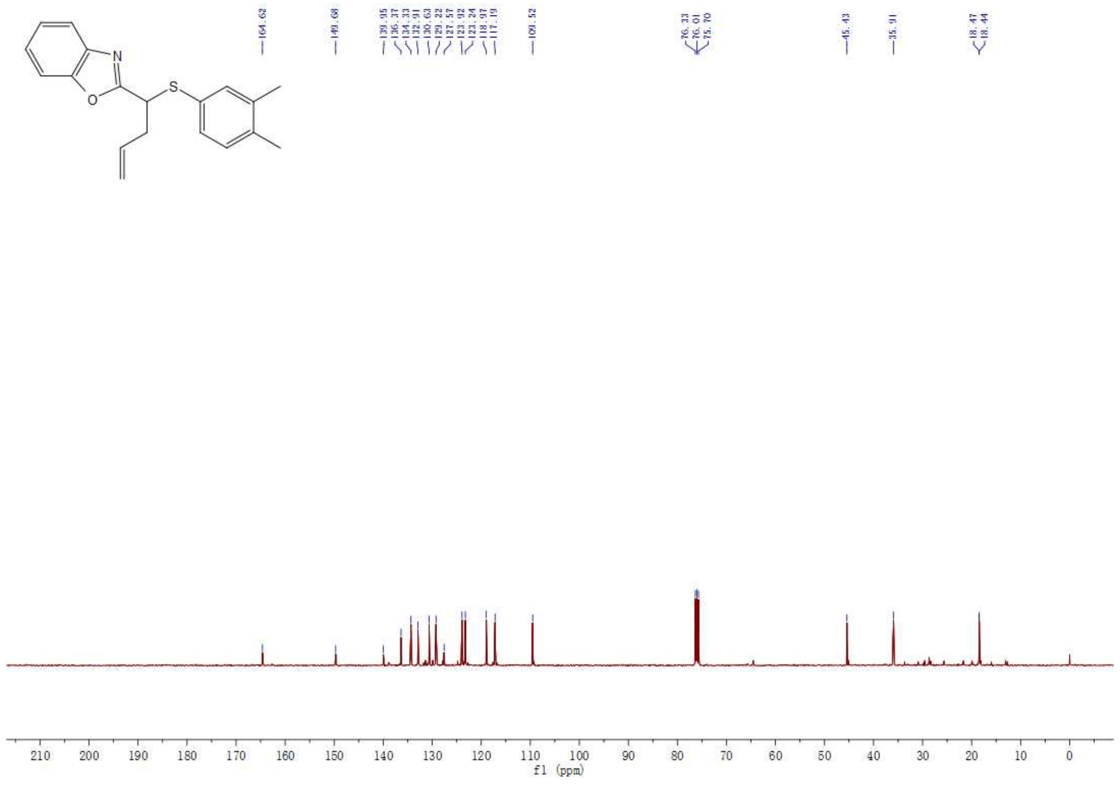
7.58
7.58
7.57
7.57
7.57
7.56
7.56
7.55
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.17
7.01
7.00
6.92
6.91
6.90
5.81
5.79
5.77
5.76
5.75
5.08
5.08
5.04
5.00
4.91
4.29
4.29
4.27
2.85
2.85
2.84
2.83
2.75
2.75
2.74
2.73
2.73
2.71
2.03
0.96
0.96
2.08
1.96
1.02
1.00
2.02
0.97
2.15
3.02
2.90
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


N
O
S
164.62
149.68
139.95
136.37
134.33
132.91
130.63
129.22
127.57
123.92
123.24
118.97
117.19
109.52
76.33
76.01
75.70
45.43
35.91
18.47
18.44
210
200
190
180
170
160
150
140
130
120
110
100
90
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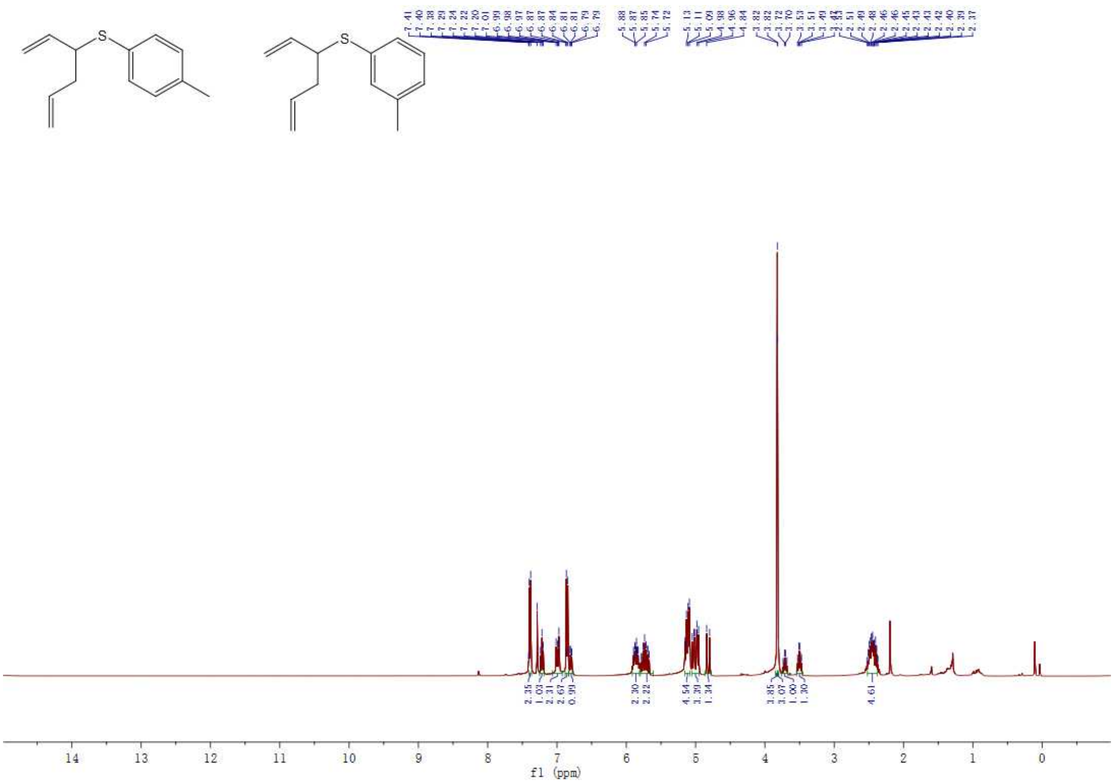
70
60
50
40
30
20
10
0
f1 (ppm)


S
S
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5.88 5.87 5.85 5.74 5.72
5.13 5.11 5.09 4.98 4.96 4.84
3.82 3.82 3.72 3.70 3.53 3.51 3.49 3.48
2.51 2.49 2.48 2.46 2.46 2.45 2.43 2.43 2.42 2.40 2.39 2.37
2.35 1.03 2.31 2.67 0.99
2.30 2.22
4.54 3.39 1.34
3.85 3.07 1.00 1.30
4.61
14
13
12
11
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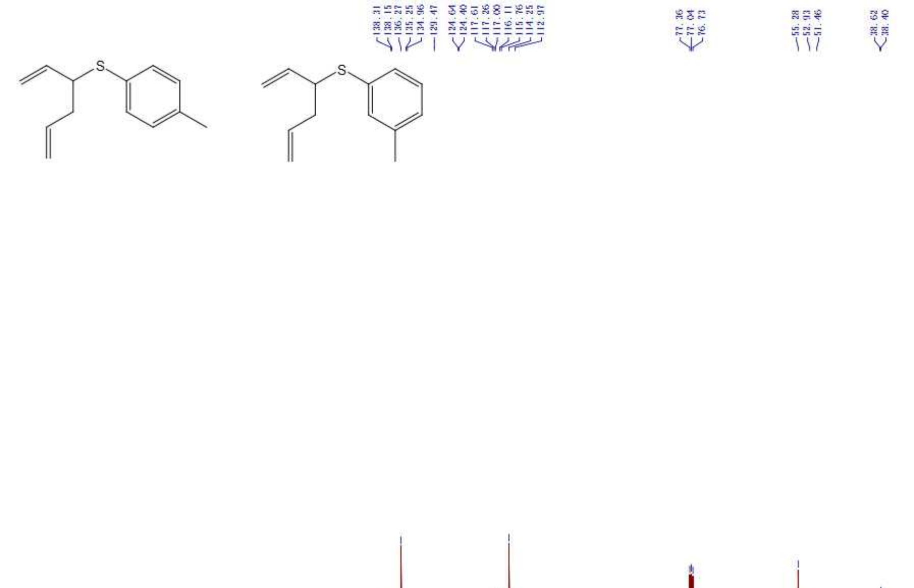
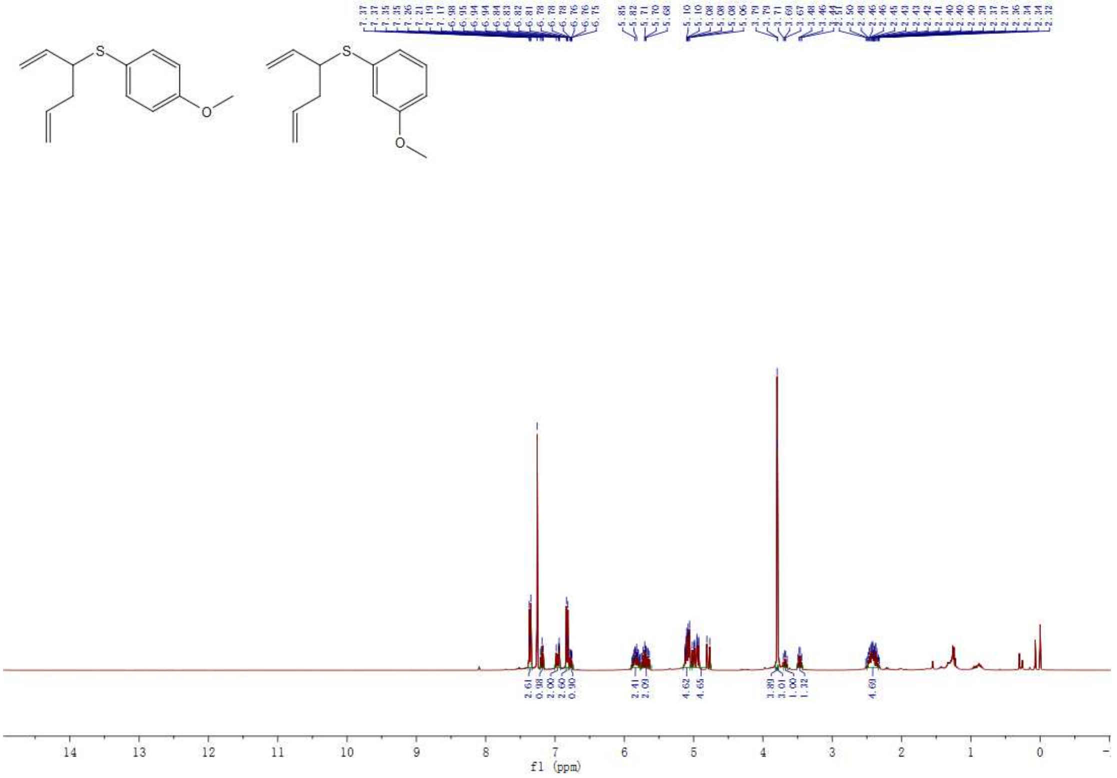
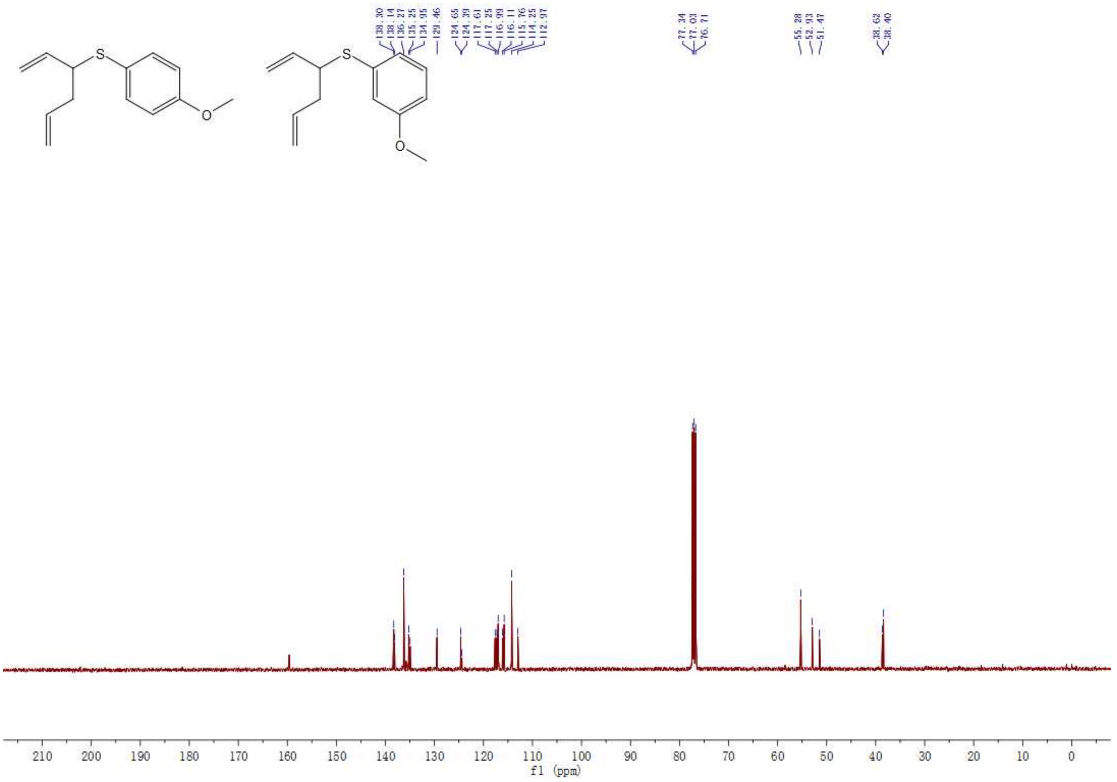
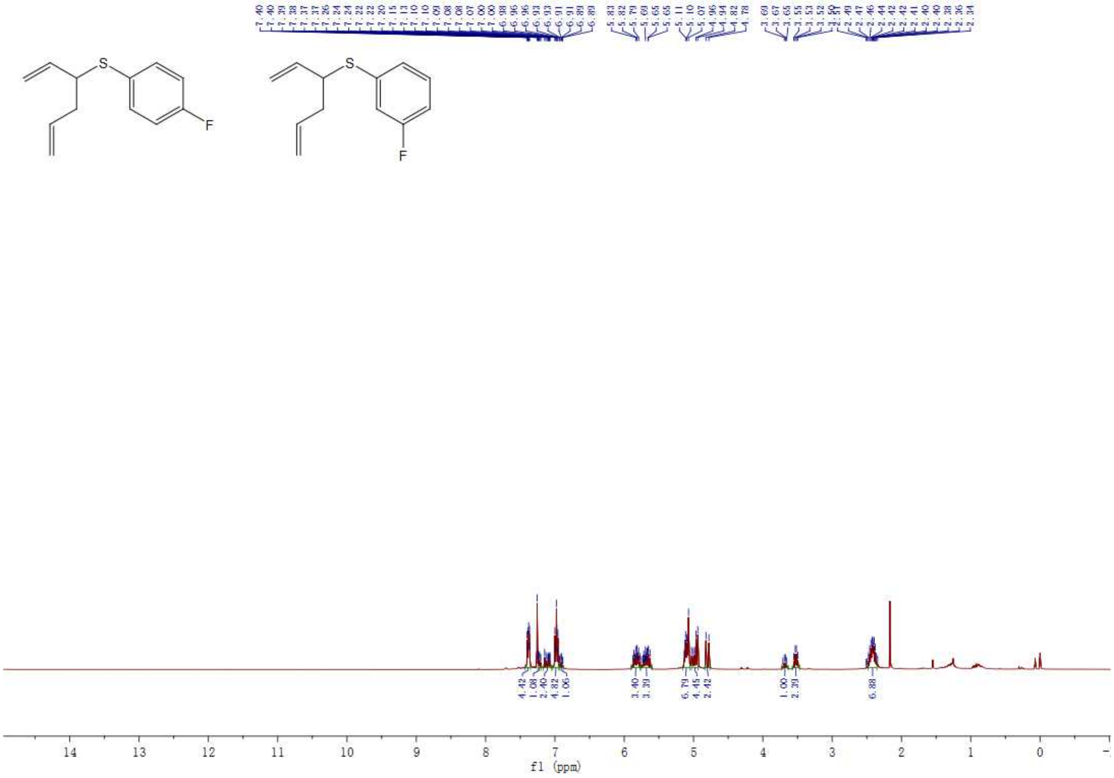
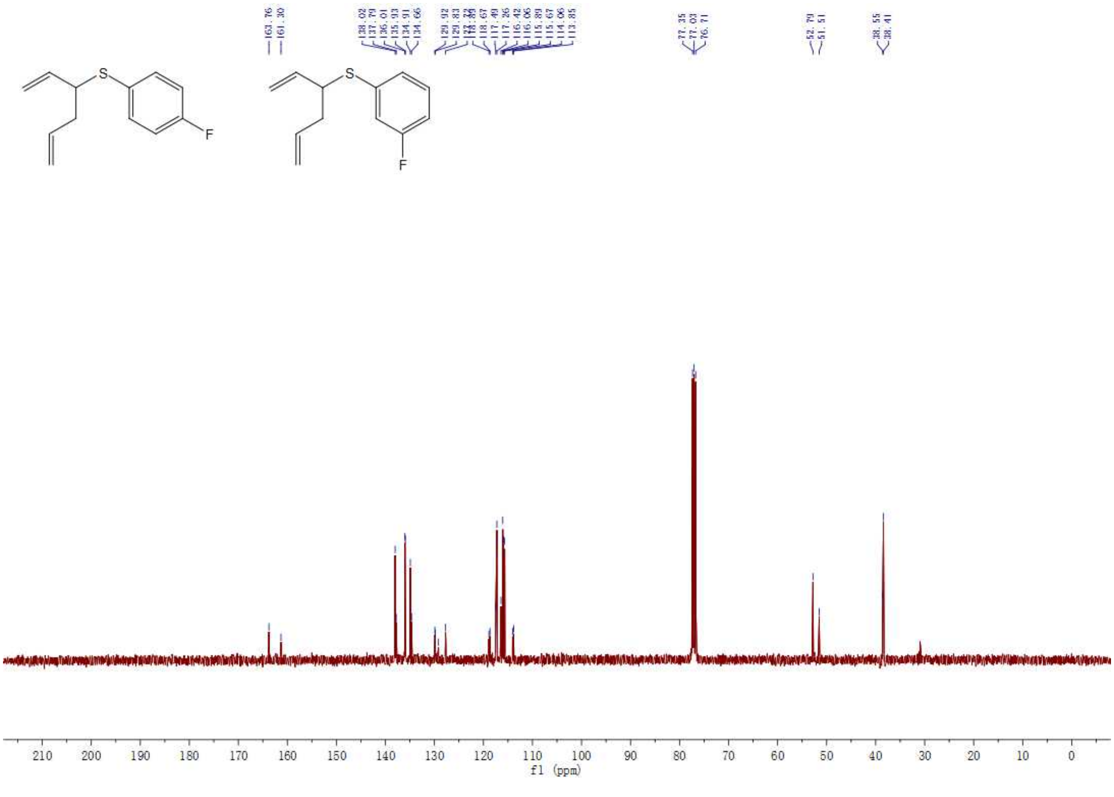
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

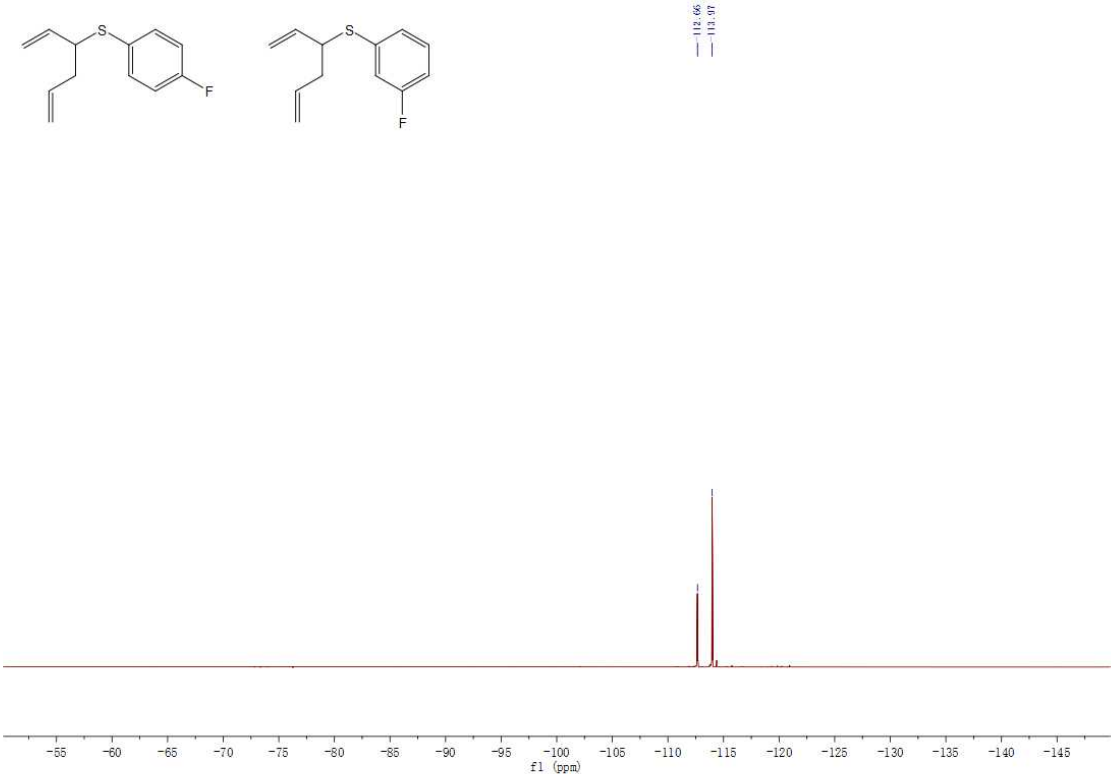

S
S
138.31 138.15 136.27 135.25 134.96
129.47
124.64 124.40
117.61 117.26 117.00 116.11 115.76 114.25 112.97
77.36 77.04 76.73
55.28 52.93 51.46
38.62 38.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

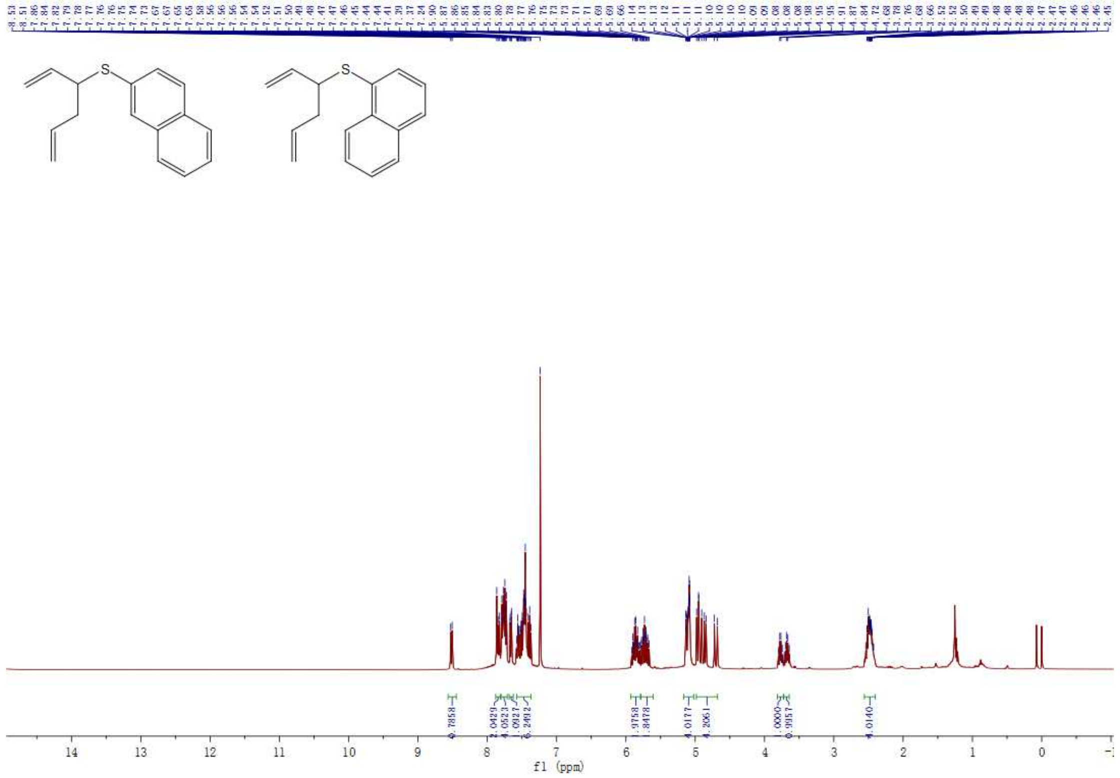

S
O
7.37 7.37 7.35 7.35 7.26 7.21 7.19 7.17 6.98 6.95 6.94 6.94 6.84 6.83 6.82 6.81 6.78 6.78 6.78 6.76 6.76 6.75
5.85 5.82 5.71 5.70 5.68
5.10 5.10 5.08 5.08 5.08 5.06
3.79 3.79 3.71 3.69 3.67 3.48 3.46 3.44 2.51 2.50 2.48 2.46 2.46 2.45 2.43 2.43 2.42 2.41 2.40 2.40 2.40 2.39 2.37 2.37 2.36 2.34 2.34 2.32
2.61 0.98 2.00 2.60 0.90 2.41 2.09 4.62 4.65 3.89 3.01 1.00 1.32 4.69
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


S
O
138.30 138.14 136.27 135.25 134.95 129.46 124.65 124.39 117.61 117.25 116.91 116.11 115.76 114.25 112.97
77.34 77.03 76.71
55.28 52.93 51.47
38.62 38.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.40 7.40 7.39 7.38 7.37 7.37 7.26 7.24 7.24 7.22 7.22 7.20 7.15 7.13 7.10 7.10 7.09 7.08 7.08 7.07 7.00 7.00 6.98 6.96 6.96 6.93 6.93 6.91 6.91 6.89 6.89
5.83 5.82 5.79 5.69 5.65 5.65 5.11 5.10 5.07 4.96 4.94 4.82 4.78
3.69 3.67 3.65 3.55 3.53 3.52 3.50 2.51 2.49 2.47 2.46 2.44 2.42 2.42 2.41 2.40 2.40 2.38 2.36 2.34
S
F
S
F
4.42 1.08 2.40 4.82 1.06
3.40 3.39
6.79 4.45 2.42
1.00 2.39
6.88
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


163.76 161.30
138.02 137.79 136.01 135.93 134.91 134.66
129.92 129.83 118.67 117.49 117.26 116.42 116.06 115.89 115.67 114.06 113.85
77.35 77.03 76.71
52.79 51.51
38.55 38.41
S
F
S
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
F
S
F
−112.66
−113.97
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)


8.53 8.51 7.86 7.84 7.82 7.79 7.78 7.77 7.76 7.76 7.75 7.74 7.73 7.67 7.67 7.65 7.65 7.58 7.56 7.56 7.56 7.54 7.54 7.52 7.51 7.50 7.49 7.48 7.47 7.47 7.46 7.45 7.44 7.44 7.41 7.39 7.37 7.24 5.90 5.87 5.86 5.85 5.84 5.83 5.80 5.78 5.77 5.76 5.75 5.73 5.73 5.71 5.71 5.69 5.69 5.66 5.14 5.13 5.13 5.12 5.11 5.11 5.11 5.10 5.10 5.10 5.10 5.09 5.09 5.08 5.08 5.08 4.98 4.95 4.95 4.91 4.87 4.84 4.72 4.68 3.78 3.76 3.68 3.66 2.52 2.52 2.50 2.49 2.49 2.48 2.48 2.48 2.48 2.47 2.47 2.47 2.46 2.46 2.46 2.45
S
S
0.7858
2.0429
4.0523
4.0927
6.2492
.9758
.8478
4.0177
4.2061
.0000
0.9957
4.0140
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13
12
11
10
9
8
7
6
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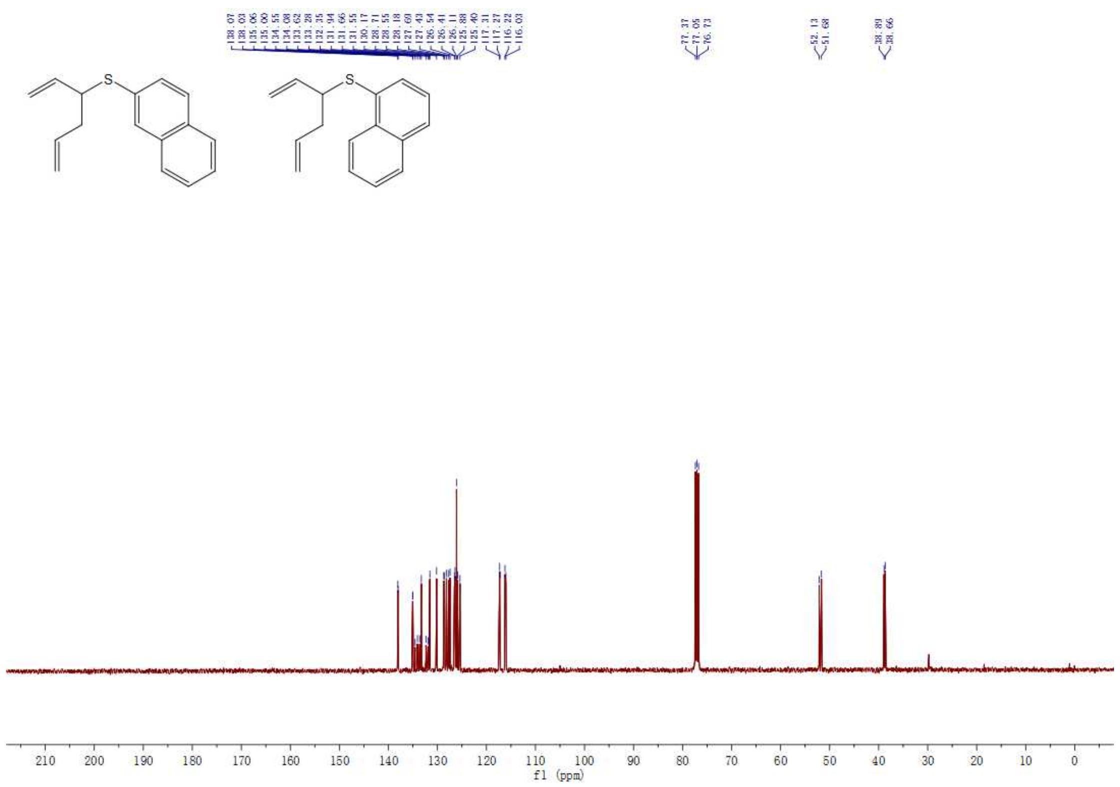
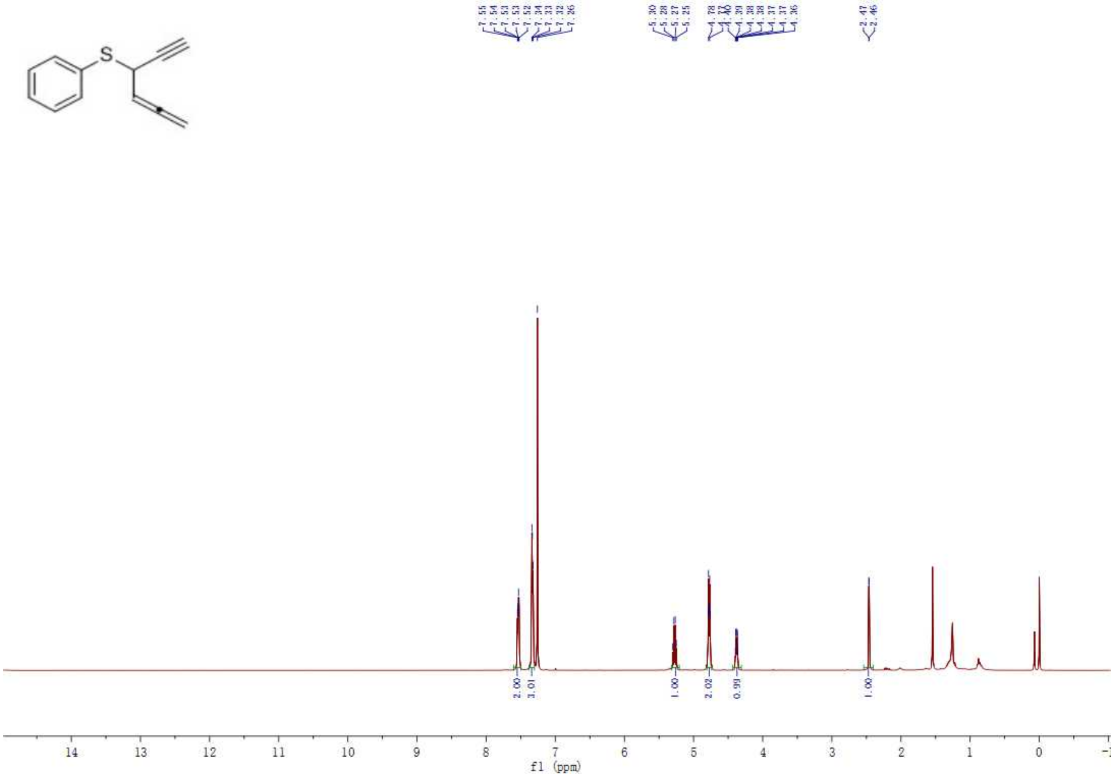
4
3
2
1
0
-1
f1 (ppm)


138.07 138.03 135.06 135.00 134.55 134.08 133.62 133.28 132.35 131.94 131.66 131.55 130.17 128.71 128.55 128.18 127.69 127.43 126.54 126.41 126.11 125.88 125.40 117.31 117.27 116.22 116.03
77.37 77.05 76.73
52.13 51.68
38.89 38.66
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
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7.54
7.53
7.53
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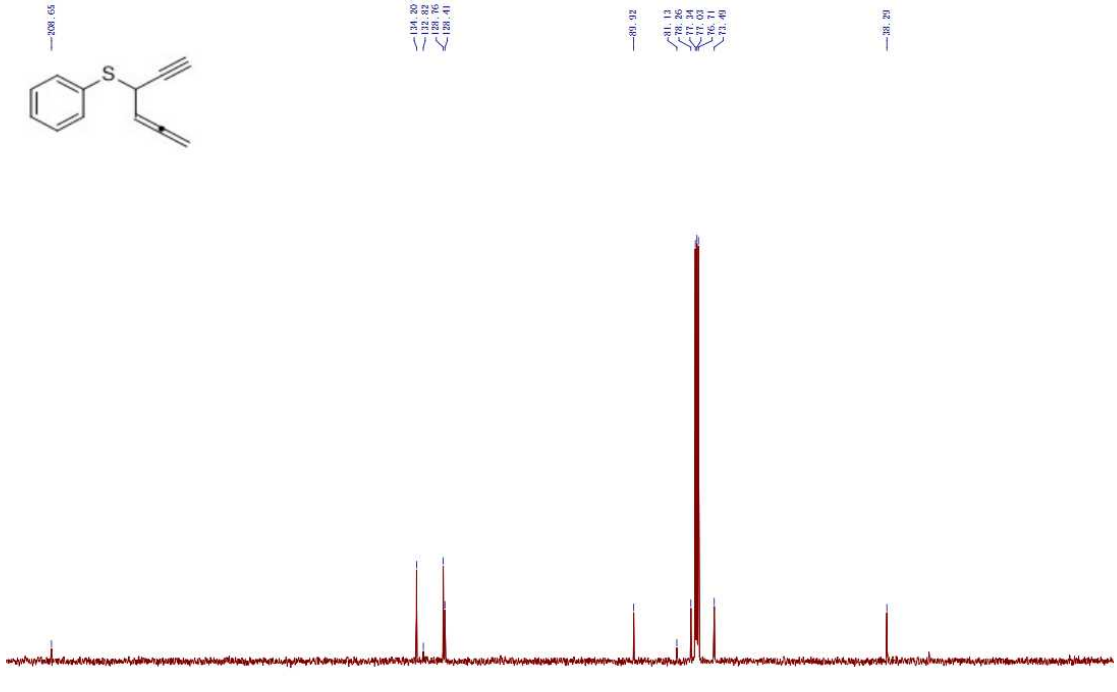
7.34
7.33
7.32
7.26
5.30
5.28
5.27
5.25
4.78
4.77
4.40
4.39
4.38
4.38
4.37
4.37
4.36
2.47
2.46
2.00
3.01
1.00
2.02
0.99
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


S
208.65
134.20
132.82
128.76
128.41
89.92
81.13
78.26
77.34
77.03
76.71
73.40
38.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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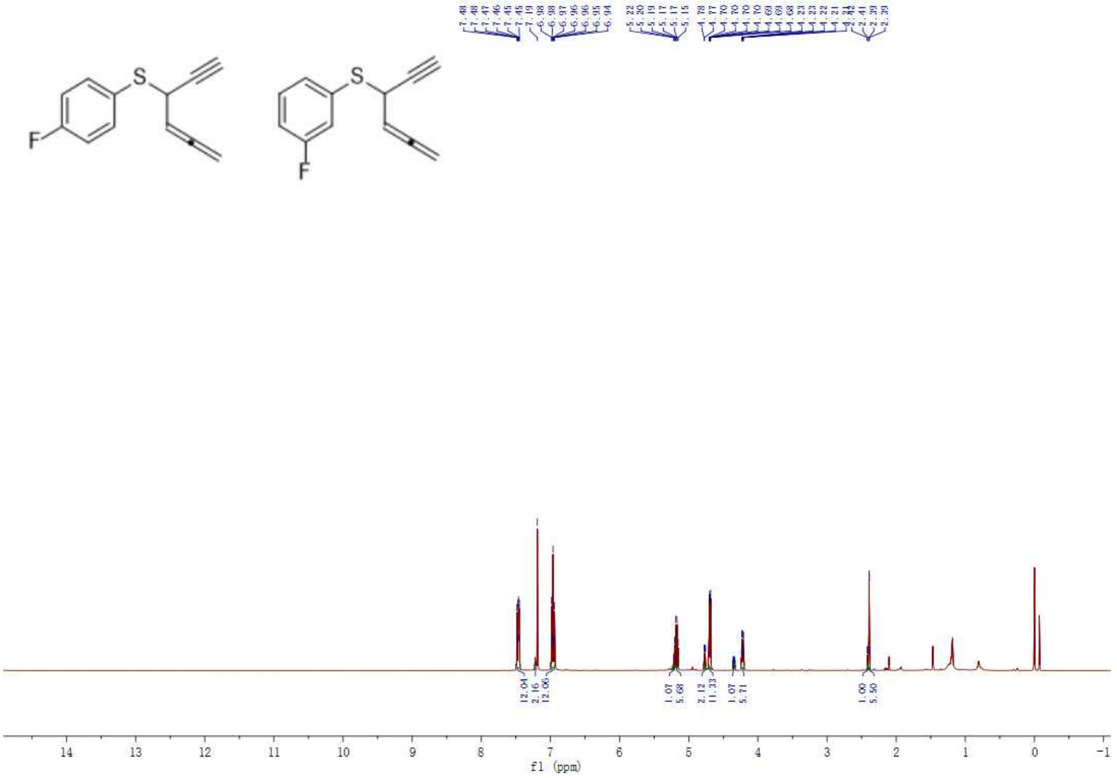
50
40
30
20
10
0
f1 (ppm)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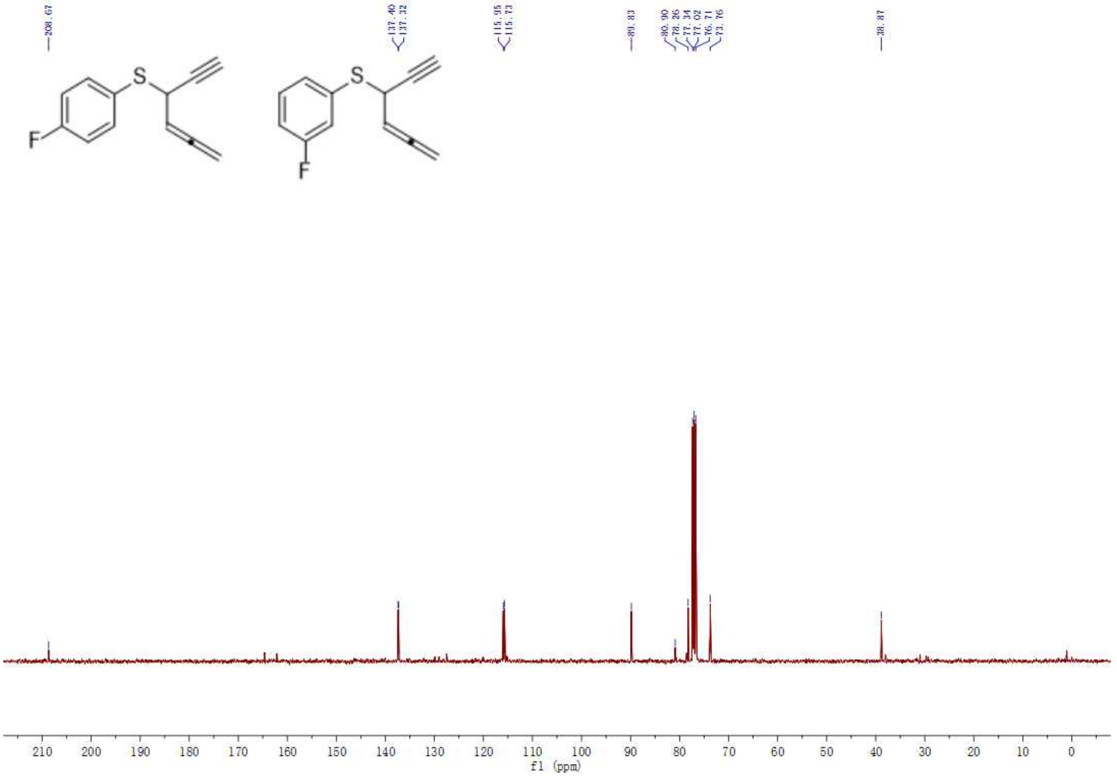
7.48
7.47
7.46
7.45
7.45
7.19
6.98
6.98
6.97
6.96
6.96
6.95
6.94
5.22
5.20
5.19
5.17
5.17
5.15
4.78
4.77
4.70
4.70
4.70
4.70
4.69
4.69
4.68
4.23
4.23
4.22
4.21
4.21
2.42
2.41
2.39
2.39
S
F
S
F
12.04
2.16
12.06
1.07
5.68
2.12
11.33
1.07
5.71
1.00
5.50
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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115.73
89.83
80.90
78.26
77.34
77.02
76.71
73.76
38.87
S
F
S
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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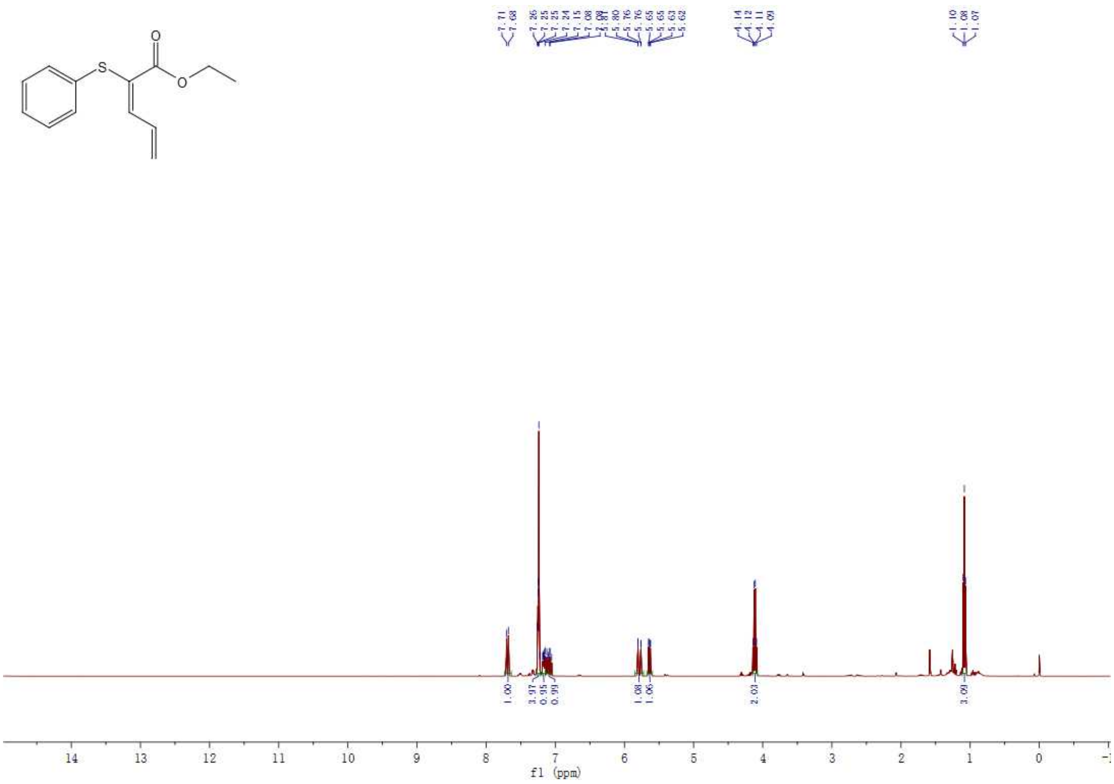
50
40
30
20
10
0
f1 (ppm)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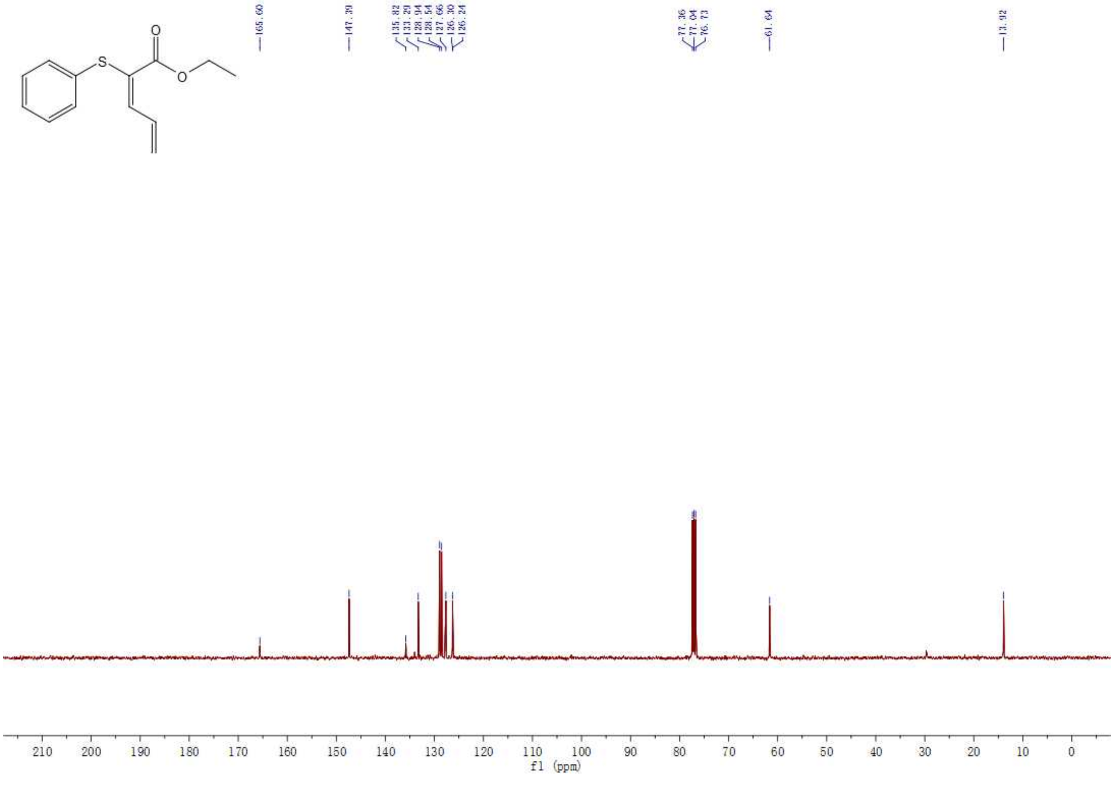
7.68
7.26
7.25
7.25
7.24
7.15
7.08
7.09
5.81
5.80
5.76
5.76
5.65
5.65
5.63
5.62
4.14
4.12
4.11
4.09
1.10
1.08
1.07
S
O
O
1.00
3.97
0.95
0.99
1.08
1.06
2.03
3.09
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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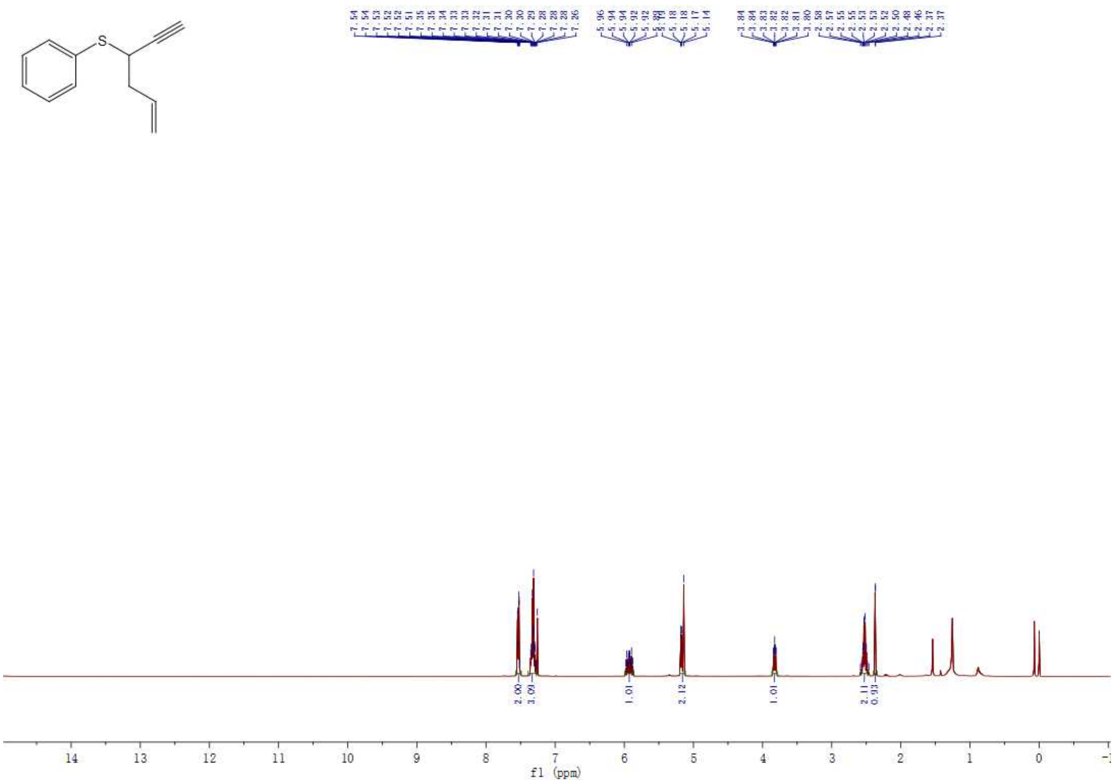
147.39
135.82
133.29
128.94
128.54
127.66
126.30
126.24
77.36
77.04
76.73
61.64
13.92
S
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
7.54
7.54
7.53
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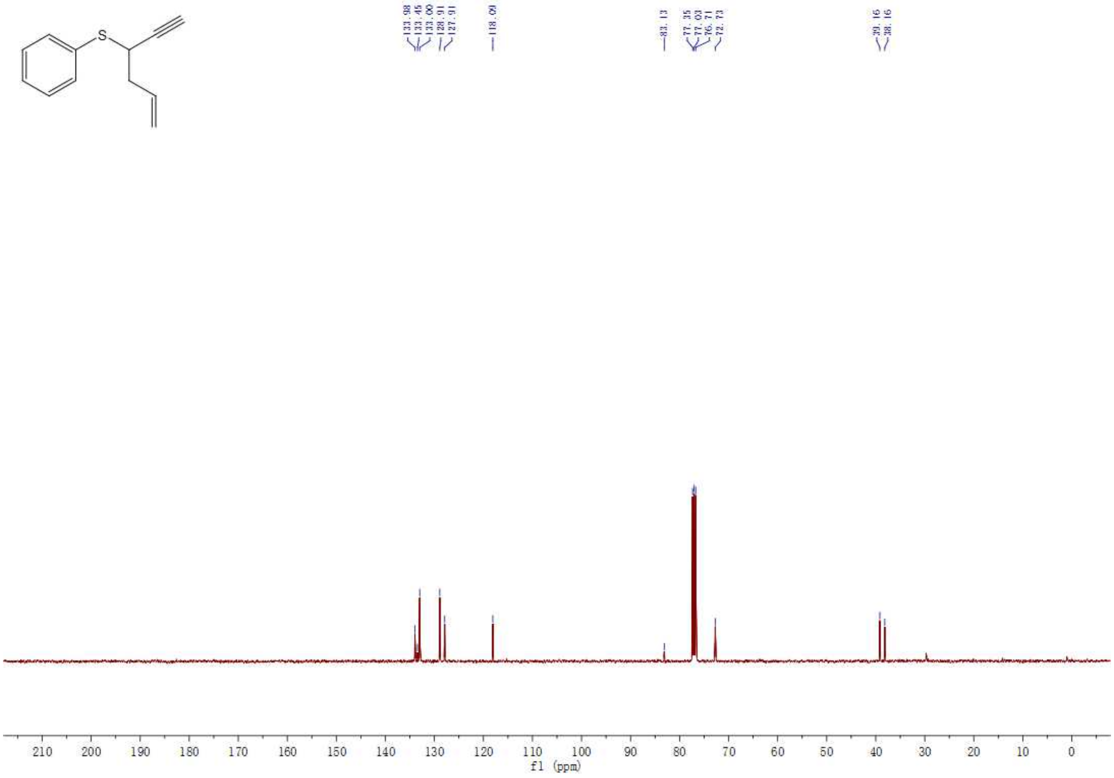
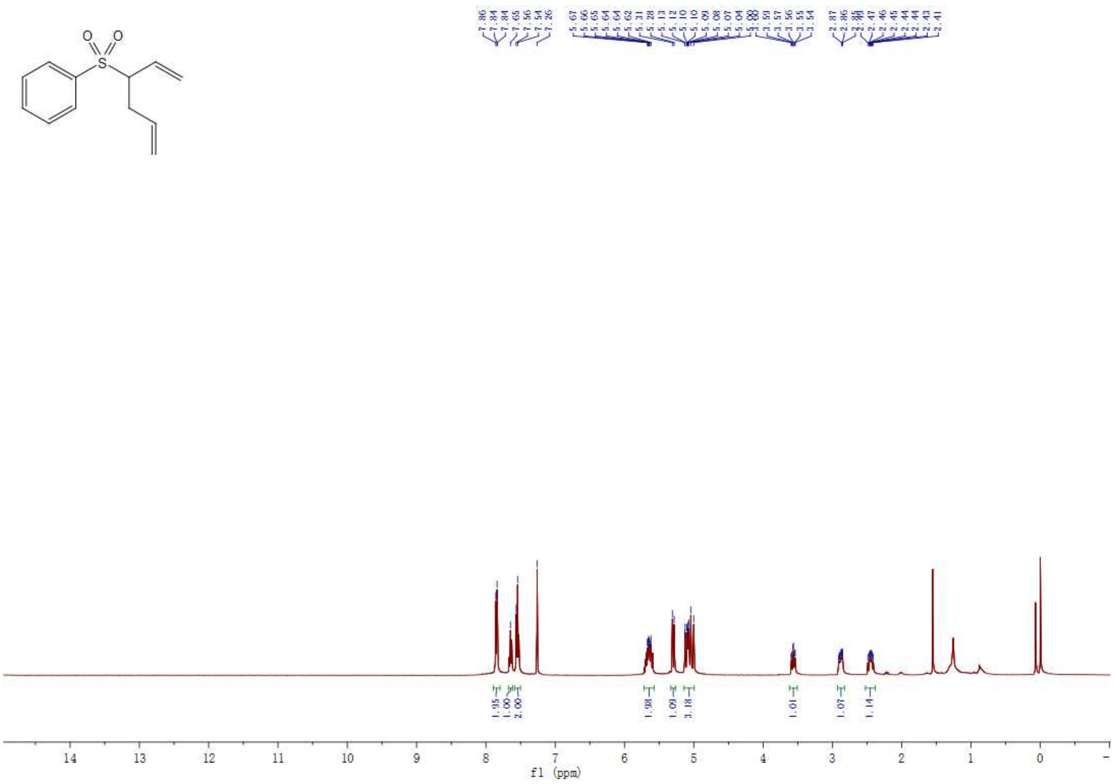
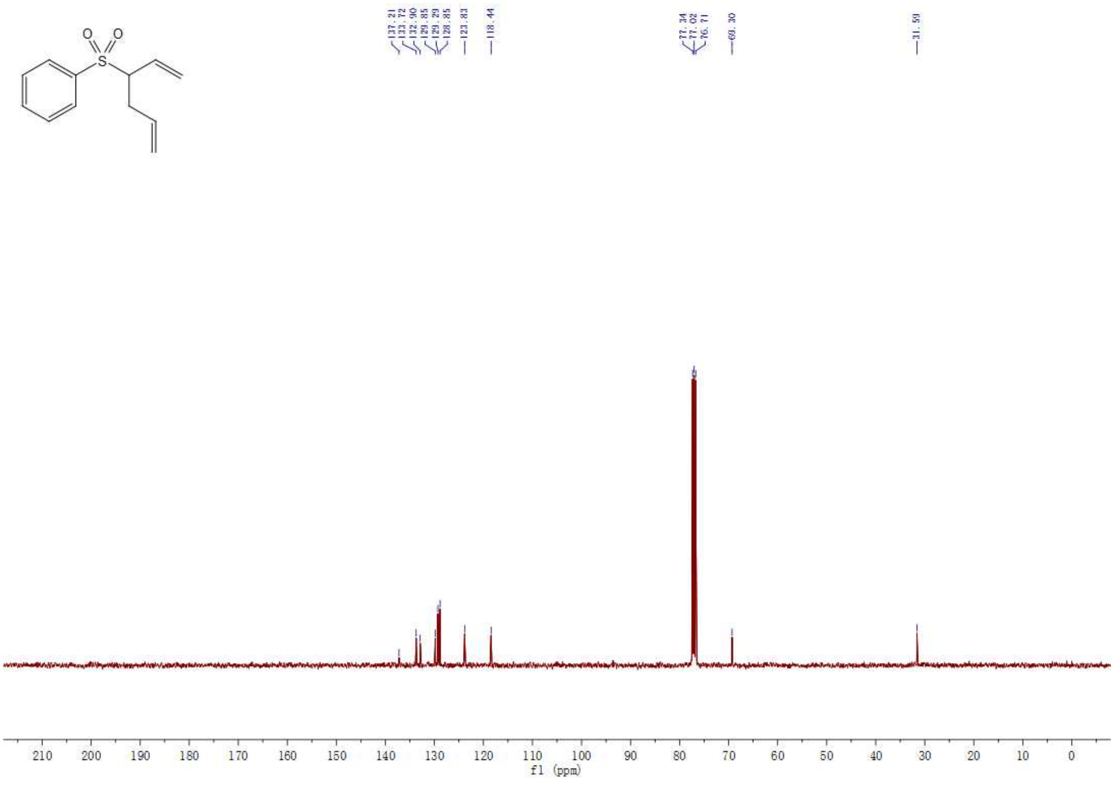
7.52
7.51
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.28
7.26
5.96
5.94
5.94
5.92
5.92
5.89
5.18
5.18
5.17
5.14
3.84
3.84
3.83
3.82
3.82
3.81
3.80
2.58
2.57
2.55
2.55
2.53
2.53
2.52
2.50
2.48
2.46
2.37
2.37
2.00
3.09
1.01
2.12
1.01
2.11
0.93
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


S
133.98
133.45
133.00
128.91
127.91
118.09
83.13
77.35
77.03
76.71
72.73
39.16
38.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.86
7.84
7.84
7.65
7.56
7.54
7.26
5.67
5.66
5.65
5.64
5.64
5.62
5.31
5.28
5.13
5.12
5.10
5.10
5.09
5.08
5.07
5.04
3.60
3.59
3.57
3.56
3.55
3.54
2.87
2.86
2.85
2.47
2.46
2.45
2.44
2.44
2.43
2.41
1.95
1.00
2.00
1.98
1.09
3.18
1.01
1.07
1.14
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


137.21
133.72
132.90
129.85
129.29
128.85
123.83
118.44
77.34
77.02
76.71
69.30
31.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)