Supporting Information

Selective Difunctionalization of Electron-Deficient Alkynes: Access to (*E*)-2-Iodo-3-(methylthio)acrylate

Ling-Hui Lu, Guangchuan Ou, Xiongjie Zhao, Yufei Wang, Xuelian Chen, Wenjun Liao, Shundan Li and Chao Wu*

Department of Chemistry, Hunan University of Science and Engineering, Yongzhou 425100, China

E-mail: chwu_chem@yeah.net

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1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. Chromatographic purifications were carried out on a Biotage Isolera Four instrument. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet.

X-ray structure determination: Single-crystal data for compound was collected on a Bruker Smart Apex II diffractometer, with Mo-K□ radiation (□ = 0.71073 Å). Empirical absorption corrections were applied by using the SADABS program[1]. All the structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs [2].

1. G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, **1996**.
2. G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112-122.

2. Experiment Section

General Procedure for the Synthesis of iodothiomethyl acrylates 2

A mixture of alkyne (0.3 mmol), 47% aqueous HI (0.66 mmol), DMSO (1.0 mL) was added successively in a round-bottom flask, and the resulting solution was stirred for 8 h at 105 °C. Upon completion, the reaction mixture was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford iodothiomethyl acrylates **2**.

3. Crystal data of 2s

Crystal data and structure refinement for compound **2s**

Compound	
Empirical formula	$C_{11}H_9IO_4S$
Formula weight	364.14
Temperature (K)	296(2)
crystal system	Monoclinic
space group	*P*2(1)/c
a / Å	11.705(4)
b / Å	15.007(5)
c / Å	7.459(2)
V /Å ^{3}	1264.1(7)
Z	4
D_c/g cm^{-3}	1.913
μ / mm^{-1}	2.697
F(000)	704
crystal size (mm)	0.45×0.36× 0.28
θ range / °	1.80 to 27.41
Refl. measured	13893
Refl. unique	2837
*R*int	0.0177
GooF	1.057
R_1, wR_2 (I >2σ (I))	0.0289, 0.0804
R_1, wR_2 (all data)	0.0342, 0.0838
Max. peak /hole (e. Å^{-3})	1.229/ –0.534

4. Characterization Data

***ethyl (E)-2-iodo-3-(methylthio)acrylate (2a)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 157.4, 71.6, 62.4, 19.7, 14.2. HRMS (ESI) *m/z* Calculated for $C_6H_9IO_2S$ $[M+H]^+$ 272.9441, found 272.9445.

***methyl (E)-2-iodo-3-(methylthio)acrylate (2b)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 3.80 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.1, 70.3, 53.2, 19.7. HRMS (ESI) *m/z* Calculated for $C_5H_7IO_2S$ $[M+H]^+$ 258.9284, found 258.9280.

***hexyl (E)-2-iodo-3-(methylthio)acrylate (2c)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 4.18 (t, J = 6.4 Hz, 2H), 2.43 (s, 3H), 1.73–1.66 (m, 2H), 1.42–1.31 (m, 6H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 157.2, 71.8, 66.6, 31.3, 28.4, 25.5, 22.5, 19.7, 14.0. HRMS (ESI) *m/z* Calculated for $C_{10}H_{17}IO_2S$ $[M+H]^+$ 329.0067, found 329.0070.

***decyl (E)-2-iodo-3-(methylthio)acrylate (2d)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 4.18 (t, J = 6.4 Hz, 2H), 2.43 (s, 3H), 1.73–1.66 (m, 2H), 1.41–1.26 (m, 14H), 0.898 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 157.3, 71.8, 66.7, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 28.5, 25.8, 22.7, 19.7, 14.1. HRMS (ESI) *m/z* Calculated for $C_{14}H_{25}IO_2S$ $[M+H]^+$ 385.0693, found 385.0695.

***cyclopentyl (E)-2-iodo-3-(methylthio)acrylate (2e)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 5.23–5.21 (m, 1H), 2.42 (s, 3H), 1.86–1.78 (m, 6H), 1.63–1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 156.5, 79.7, 73.1, 32.7, 23.6, 19.7. HRMS (ESI) *m/z* Calculated for $C_9H_{13}IO_2S$ $[M+H]^+$ 312.9754, found 312.9759.

***benzyl (E)-2-iodo-3-(methylthio)acrylate (2f)*:** White solid, m.p. 87-89 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.43–7.33 (m, 5H), 5.25 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.1, 135.4, 128.5, 128.2, 127.9, 70.9, 67.9, 19.7. HRMS (ESI) *m/z* Calculated for $C_{11}H_{11}IO_2S$ $[M+H]^+$ 334.9597, found 334.9599.

***phenyl (E)-2-iodo-3-(methylthio)acrylate (2g)*:** White solid, m.p. 92-93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.41–7.37 (m, 2H), 7.26–7.22 (m, 1H), 7.17–7.15 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.3, 150.8, 129.4, 126.0, 121.4, 69.3, 19.9. HRMS (ESI) *m/z* Calculated for $C_{10}H_9IO_2S$ $[M+H]^+$ 320.9441, found 320.9444.

***2-hydroxyethyl (E)-2-iodo-3-(methylthio)acrylate (2h)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 4.32 (t, J = 4.4 Hz, 2H), 3.89–3.85 (m, 2H), 2.45 (s, 3H), 2.16 (t, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 158.0, 71.2, 68.0, 60.9, 19.7. HRMS (ESI) *m/z* Calculated for $C_6H_9IO_3S$ $[M+H]^+$ 288.9390, found 288.9393.

***2-butoxyethyl (E)-2-iodo-3-(methylthio)acrylate (2i)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 4.32 (t, J = 4.8 Hz, 2H), 3.69 (t, J = 4.8 Hz, 2H), 3.51 (t, J = 6.4 Hz, 2H), 2.44 (s, 3H), 1.60–1.53 (m, 2H), 1.43–1.34 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 158.0, 71.2, 71.0, 68.1, 65.7, 31.7, 19.7, 19.2, 13.9. HRMS (ESI) *m/z* Calculated for $C_{10}H_{17}IO_3S$ $[M+H]^+$ 345.0016, found 345.0019.

***2-(benzyloxy)ethyl (E)-2-iodo-3-(methylthio)acrylate (2j)*:** White solid, m.p. 101-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.39–7.31 (m, 5H), 4.62 (s, 2H), 4.37 (t, J = 4.8 Hz, 2H), 3.75 (t, J = 4.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 158.1, 137.9, 128.4, 127.6, 127.6, 73.1, 70.8, 67.5, 65.6, 19.7. HRMS (ESI) *m/z* Calculated for $C_{13}H_{15}IO_3S$ $[M+H]^+$ 378.9859, found 378.9860.

***phenethyl (E)-2-iodo-3-(methylthio)acrylate (2k)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.36–7.28 (m, 5H), 4.41 (t, J = 6.8 Hz, 2H), 3.04 (t, J = 6.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 157.9, 137.5, 129.1, 128.4, 126.6, 71.0, 67.0, 35.0, 19.7. HRMS (ESI) *m/z* Calculated for $C_{12}H_{13}IO_2S$ $[M+H]^+$ 348.9754, found 348.9758.

***2-cyanoethyl (E)-2-iodo-3-(methylthio)acrylate (2l)*:** White solid, m.p. 88-90 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 4.37 (t, J = 6.4 Hz, 2H), 2.78 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 159.6, 116.5, 69.1, 60.4, 19.7, 17.9. HRMS (ESI) *m/z* Calculated for $C_7H_8INO_2S$ $[M+H]^+$ 297.9393, found 297.9398.

***2-bromoethyl (E)-2-iodo-3-(methylthio)acrylate (2m)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 4.32 (t, J = 4.4 Hz, 2H), 3.88 (t, J = 4.4 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 158.1, 71.2, 68.0, 60.9, 19.7. HRMS (ESI) *m/z* Calculated for $C_6H_8IBrO_2S$ $[M+H]^+$ 350.8546, found 350.8548.

***3,3,3-trifluoropropyl (E)-2-iodo-3-(methylthio)acrylate (2n)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 4.40 (t, J = 6.4 Hz, 2H), 2.60–2.52 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 159.1, 125.5 (q, J = 275.6 Hz), 69.5, 58.9 (q, J = 4.4 Hz), 33.3 (q, J = 29.2 Hz), 19.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.9. HRMS (ESI) *m/z* Calculated for $C_7H_8F_3IO_2S$ $[M+H]^+$ 340.9315, found 340.9318.

***naphthalen-2-yl (E)-2-iodo-3-(methylthio)acrylate (2o)*:** White solid, m.p. 115-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.89–7.81 (m, 3H), 7.67 (s, 1H), 7.50–7.48 (m, 2H), 7.33–7.31 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.6, 148.4, 133.6, 131.5, 129.3, 127.7, 127.6, 126.5, 125.7, 120.8, 118.4, 69.2, 19.9. HRMS (ESI) *m/z* Calculated for $C_{14}H_{11}IO_2S$ $[M+H]^+$ 370.9597, found 370.9563.

***thiophen-2-ylmethyl (E)-2-iodo-3-(methylthio)acrylate (2p)*:** Light yellow solid, m.p. 91-93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.36 (s, 1H), 7.32–7.30 (m, 1H), 7.14 (d, J = 4.8 Hz, 1H), 5.24 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.1, 136.3, 127.4, 126.1, 124.1, 70.9, 63.3, 19.8. HRMS (ESI) *m/z* Calculated for $C_9H_9IO_2S_2$ $[M+H]^+$ 340.9161, found 340.9165.

***furan-2-ylmethyl (E)-2-iodo-3-(methylthio)acrylate (2q)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.44 (s, 1H), 6.47 (d, J = 2.8 Hz, 1H), 6.37 (s, 1H), 5.18 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 158.4, 149.0, 143.3,

111.1, 110.6, 70.6, 59.7, 19.8. HRMS (ESI) *m/z* Calculated for $C_9H_9IO_3S$ $[M+H]^+$ 324.9390, found 324.9392.

***1-phenylethyl (E)-2-iodo-3-(methylthio)acrylate (2r)*:** Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.43–7.29 (m, 5H), 5.93 (q, J = 6.4 Hz, 1H), 2.43 (s, 3H), 1.61 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 157.6, 141.2, 128.4, 127.8, 126.0, 74.9, 72.0, 22.7, 19.4. HRMS (ESI) *m/z* Calculated for $C_{12}H_{13}IO_2S$ $[M+H]^+$ 348.9754, found 348.9755.

***benzo[d][1,3]dioxol-5-yl (E)-2-iodo-3-(methylthio)acrylate (2s)*:** White solid, m.p. 117-119 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.68 (s, 1H), 6.63–6.60 (m, 1H), 5.98 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.5, 147.9, 145.5, 145.1, 113.8, 107.9, 103.5, 101.7, 69.1, 19.9. HRMS (ESI) *m/z* Calculated for $C_{11}H_9IO_4S$ $[M+H]^+$ 364.9339, found 364.9344.

***benzo[d][1,3]dioxol-5-ylmethyl (E)-2-iodo-3-(methylthio)acrylate (2t)*:** Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 6.92–6.88 (m, 2H), 6.80–6.78 (m, 1H), 5.97 (s, 2H), 5.13 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.1, 147.7, 147.6, 129.1, 122.1, 108.9, 108.2, 101.1, 71.0, 67.9, 19.8. HRMS (ESI) *m/z* Calculated for $C_{12}H_{11}IO_4S$ $[M+H]^+$ 378.9495, found 378.9502.

***cinnamyl (E)-2-iodo-3-(methylthio)acrylate (2u)*:** Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.48–7.28 (m, 5H), 6.75 (d, J = 16.0 Hz, 1H), 6.38–6.31 (m, 1H), 4.87 (d, J = 6.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.0, 136.1, 134.3, 128.5, 128.0, 126.6, 122.6, 70.9, 66.8, 19.7. HRMS (ESI) *m/z* Calculated for $C_{13}H_{13}IO_2S$ $[M+H]^+$ 360.9754, found 360.9757.

***(1S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (E)-2-iodo-3-(methylthio)acrylate (2v)*:** White solid, m.p. 143-145 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 4.91 (d, J = 9.6 Hz, 1H), 2.44 (s, 3H), 2.43–2.35 (m, 1H), 2.19–2.13 (m, 1H), 1.79–1.69 (m, 2H), 1.33–1.24 (m, 2H), 1.08–1.03 (m, 1H), 0.90 (s, 3H), 0.89 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 156.9, 82.8, 72.4, 49.0, 47.8, 44.8, 36.7,

27.9, 27.2, 19.8, 19.7, 18.8, 13.5. HRMS (ESI) *m/z* Calculated for $C_{14}H_{21}IO_2S$ $[M+H]^+$ 381.0380, found 381.0382.

***(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl (E)-2-iodo-3-(methylthio)acrylate (2w)*:** Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 5.82 (s, 1H), 4.72 (d, J = 4.8 Hz, 2H), 4.58 (d, J = 3.2 Hz, 2H), 2.44 (s, 3H), 2.19–2.15 (m, 4H), 2.01–1.85 (m, 2H), 1.74 (s, 3H), 1.55–1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 157.5, 149.6, 132.1, 125.9, 108.7, 71.5, 70.3, 40.8, 30.4, 27.2, 26.3, 20.7, 19.8. HRMS (ESI) *m/z* Calculated for $C_{14}H1_9IO_2S$ $[M+H]^+$ 379.0223, found 379.0229.

***(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (E)-2-iodo-3-(methylthio)acrylate (2x)*:** Light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 5.38 (d, J = 3.6 Hz, 1H), 4.68–4.60 (m, 1H), 2.42 (s, 3H), 2.40 (s, 1H), 2.02–1.78 (m, 6H), 1.70–1.37 (m, 9H), 1.34–1.26 (m, 3H), 1.16–1.07 (m, 9H), 1.03 (s, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 2.0 Hz, 3H), 0.85 (d, J = 1.6 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 156.9, 139.4, 122.8, 76.6, 72.8, 56.6, 56.0, 49.9, 42.2, 39.6, 39.4, 38.0, 36.9, 36.5, 36.1, 35.7, 31.8, 31.8, 28.2, 28.0, 27.7, 24.2, 23.8, 22.8, 22.5, 21.0, 19.7, 19.3, 18.7, 11.8. HRMS (ESI) *m/z* Calculated for $C_{31}H4_9IO_2S$ $[M+H]^+$ 613.2581, found 613.2584.

***(S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl (E)-2-iodo-3-(methylthio)acrylate (2y)*:** Light brown solid, m.p. 121-123 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 2.59 (t, J = 6.0 Hz, 2H), 2.46 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.83–1.75 (m, 2H), 1.55–1.48 (m, 2H), 1.41–1.35 (m, 4H), 1.29–1.24 (m, 12H), 1.15–1.08 (m, 6H), 0.88–0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 159.5, 149.5, 141.0, 126.6, 124.8, 123.1, 117.4, 75.1, 69.6, 39.4, 37.4, 37.4, 37.3, 32.8, 32.7, 28.0, 24.8, 24.4, 24.1, 23.7, 22.7, 22.6, 21.0, 20.6, 19.8, 19.7, 19.7, 19.6, 13.1, 12.2, 11.8. HRMS (ESI) *m/z* Calculated for $C_{33}H_{53}IO_3S$ $[M+H]^+$ 657.2833, found 657.2838.

***S-(p-tolyl) (E)-2-iodo-3-(methylthio)prop-2-enethioate (2z)*:** Light yellow solid, m.p. 105-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 156.3, 139.8, 134.5, 130.1, 126.7, 77.8, 21.3, 20.4. HRMS (ESI) *m/z* Calculated for $C_{11}H_{11}IOS_2$ $[M+H]^+$ 350.9369, found 350.9375.

***S-benzyl (E)-2-iodo-3-(methylthio)prop-2-enethioate (2aa)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.35–7.23 (m, 5H), 4.14 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 155.2, 136.7, 129.0, 128.6, 127.3, 79.0, 37.4, 20.4. HRMS (ESI) *m/z* Calculated for $C_{11}H_{11}IOS_2$ $[M+H]^+$ 350.9369, found 350.9374.

***(E)-2-iodo-N-methyl-3-(methylthio)-N-phenylacrylamide (2ab)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 5H), 6.55 (s, 1H), 3.35 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 142.6, 139.2, 128.9, 127.7, 126.3, 78.6, 37.6, 17.5. HRMS (ESI) *m/z* Calculated for $C_{11}H_{12}INOS$ $[M+H]^+$ 333.9757, found 333.9763.

***dimethyl 2-(methylthio)maleate (2ac)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (s, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 164.1, 151.4, 111.7, 53.2, 51.8, 14.6. HRMS (ESI) *m/z* Calculated for $C_7H_{10}O_4S$ $[M+H]^+$ 191.0373, found 191.0376.

***diethyl 2-(methylthio)maleate (2ad)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (s, 1H), 4.35 (q, J = 7.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.5, 151.1, 112.1, 62.4, 60.7, 14.6, 14.1, 13.9. HRMS (ESI) *m/z* Calculated for $C_9H_{14}O_4S$ $[M+H]^+$ 219.0686, found 219.0689.

***ethyl (E)-2-iodo-3-((methyl-d_3)thio)acrylate (2a-d3)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.33(t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 157.3, 71.6, 62.5, 14.2. HRMS (ESI) *m/z* Calculated for $C_6H_6D_3IO_2S$ $[M+H]^+$ 275.9629, found 275.9636.

***methyl (E)-2-iodo-3-((methyl-d_3)thio)acrylate (2b-d3)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 3.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.0, 70.4, 53.2. HRMS (ESI) *m/z* Calculated for $C_5H_4D_3IO_2S$ $[M+H]^+$ 261.9472, found 261.9477.

***decyl (E)-2-iodo-3-((methyl-d_3)thio)acrylate (2d-d3)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 4.17 (t, J = 6.4 Hz, 2H), 1.72–1.63 (m, 2H), 1.39–1.26 (m, 14H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 158.2, 71.8, 66.6, 31.9, 29.5, 29.4, 29.3, 29.1, 28.4, 25.8, 22.6, 14.1. HRMS (ESI) *m/z* Calculated for $C_{14}H_{22}D_3IO_2S$ $[M+H]^+$ 388.0881, found 388.0884.

***benzyl (E)-2-iodo-3-((methyl-d_3)thio)acrylate (2f-d3)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.43–7.33 (m, 5H), 5.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.1, 135.4, 128.5, 128.2, 127.9, 70.9, 67.9. HRMS (ESI) *m/z* Calculated for $C_{11}H_8D_3IO_2S$ $[M+H]^+$ 337.9785, found 337.9792.

***thiophen-2-ylmethyl (E)-2-iodo-3-((methyl-d_3)thio)acrylate (2p-d3)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.36 (s, 1H), 7.32–7.30 (m, 1H), 7.15–7.14 (m, 1H), 5.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 158.0, 136.2, 127.3, 126.1, 124.1, 70.9, 63.2. HRMS (ESI) *m/z* Calculated for $C_9H_6D_3IO_2S_2$ $[M+H]^+$ 343.9350, found 343.9356.

***ethyl (E)-2-iodo-3-(phenylthio)acrylate (2ae)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.51–7.48 (m, 2H), 7.40–7.38 (m, 3H), 4.31 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 155.4, 135.5, 131.4, 129.5, 128.7, 72.2, 62.7, 14.2. HRMS (ESI) *m/z* Calculated for $C_{11}H_{11}IO_2S$ $[M+H]^+$ 334.9597, found 334.9600.

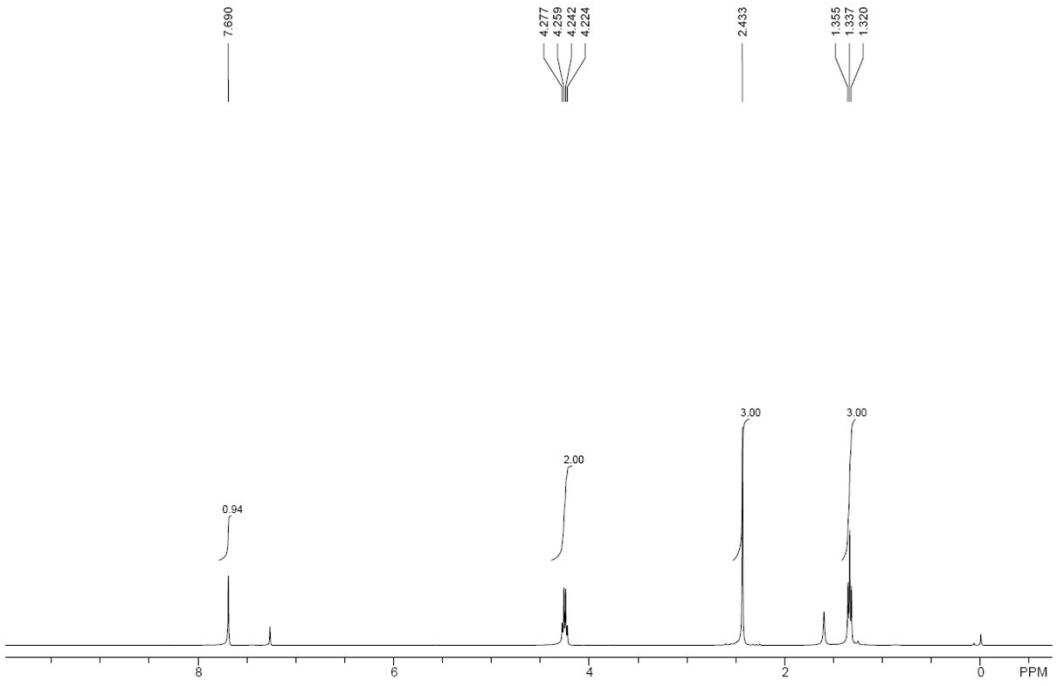
***ethyl (E)-2-iodo-3-(methylsulfonyl)acrylate (3a)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 4.36 (q, J = 7.2 Hz, 2H), 3.04 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 140.7, 103.3, 63.5, 43.4, 13.7. HRMS (ESI) *m/z* Calculated for $C_6H_9IO_4S$ $[M+H]^+$ 304.9339, found 304.9342.

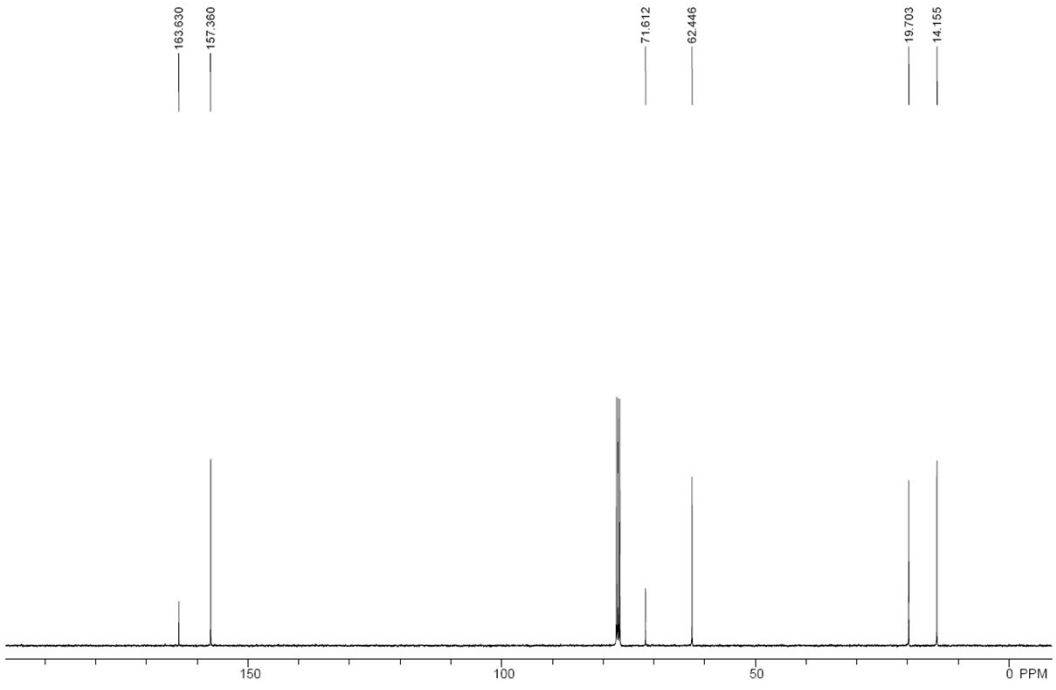
***ethyl (E)-2-iodo-3-(methylsulfinyl)acrylate (3b)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.83 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 162.1, 89.7, 63.9, 40.8, 13.9. HRMS (ESI) *m/z* Calculated for $C_6H_9IO_3S$ $[M+H]^+$ 288.9390, found 288.9391.

***ethyl (Z)-2-((methylthio)methylene)-4-phenylbut-3-ynoate (3c)*:** Light yellow solid, m.p. 165-167 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.46-7.44 (m, 2H), 7.33-7.31 (m, 3H), 4.31 (q, J = 7.2 Hz, 2H), 2.47 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 157.5, 131.3, 128.3, 128.1, 123.2, 108.8, 90.3, 85.5, 61.3, 20.0, 14.2. HRMS (ESI) *m/z* Calculated for $C_{14}H_{14}O_2S$ $[M+H]^+$ 247.0787, found 247.0793.

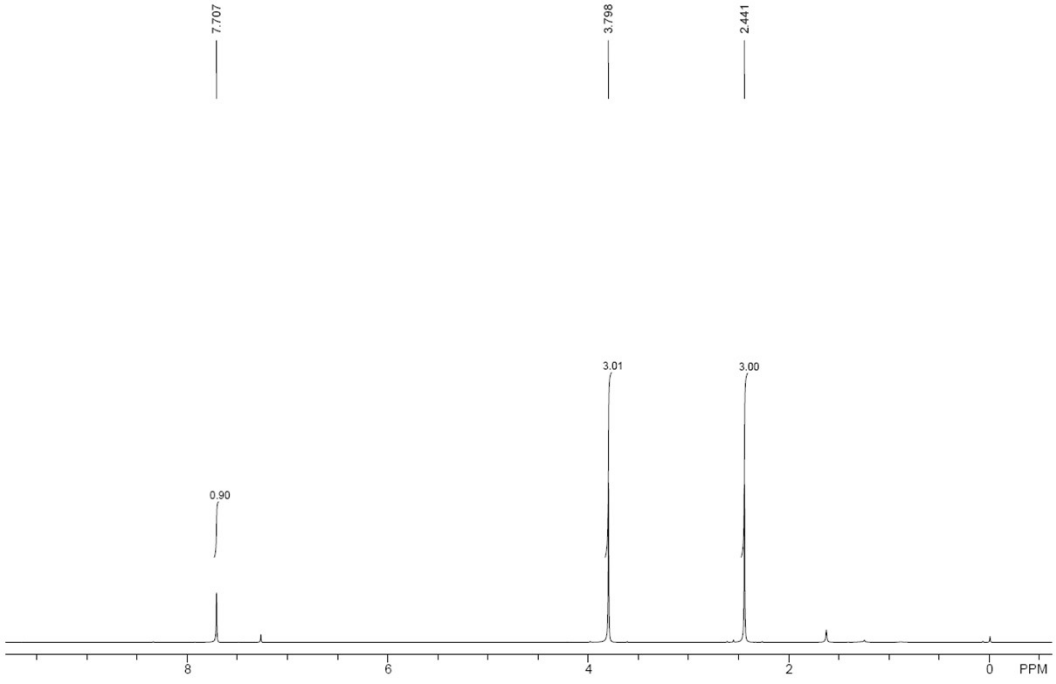
5. ^{1}H and ^{13}C NMR spectra

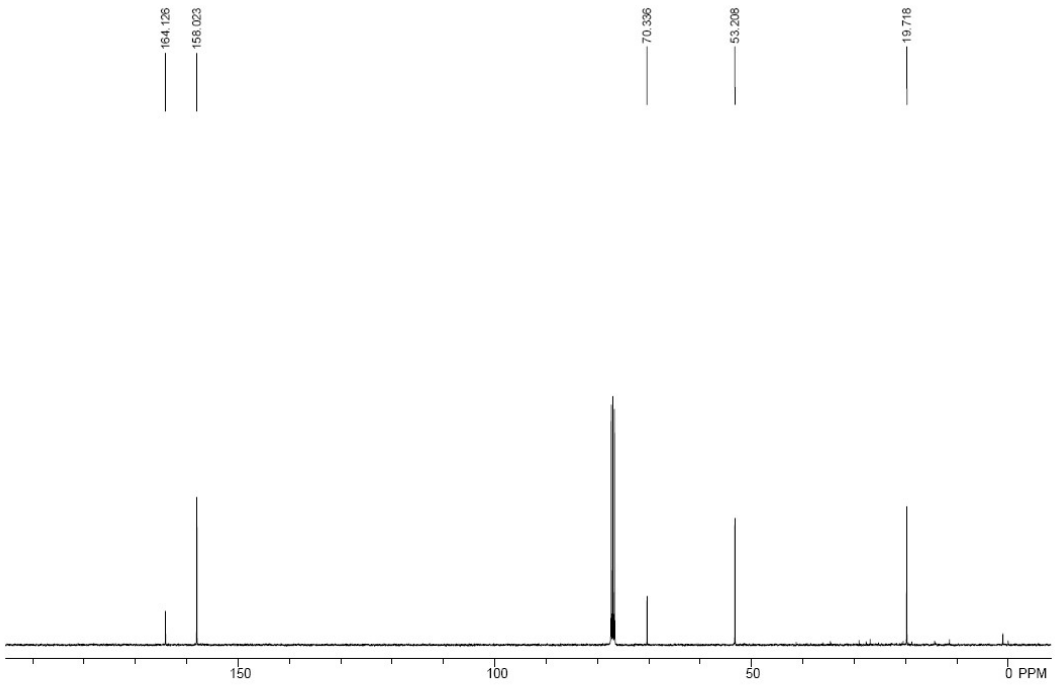
ethyl (*E*)-2-iodo-3-(methylthio)acrylate (2a)



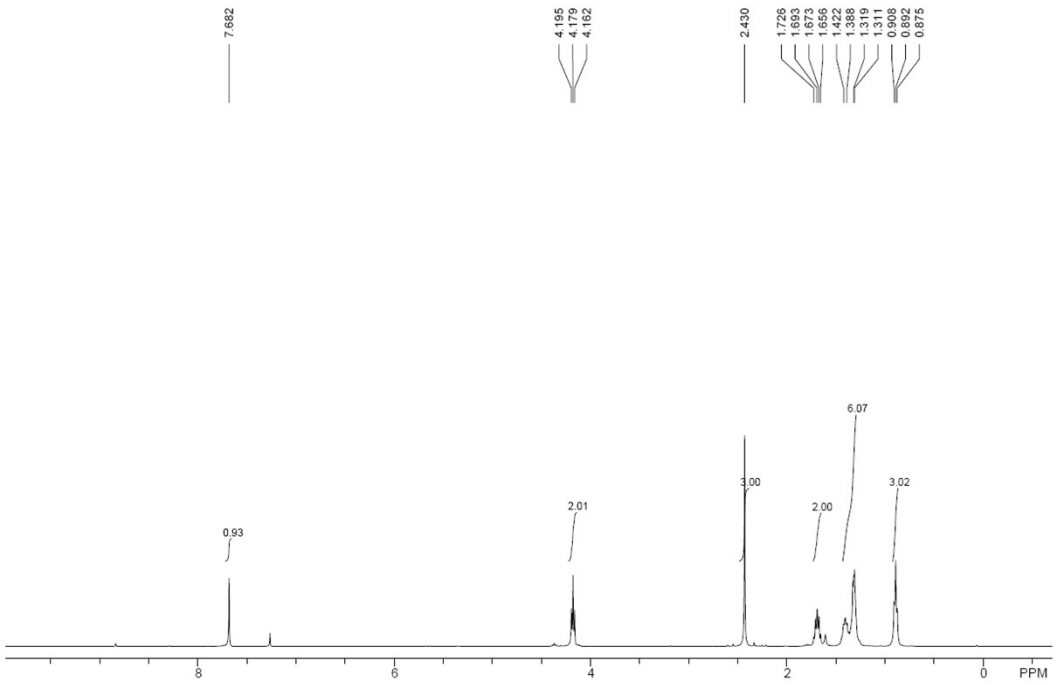


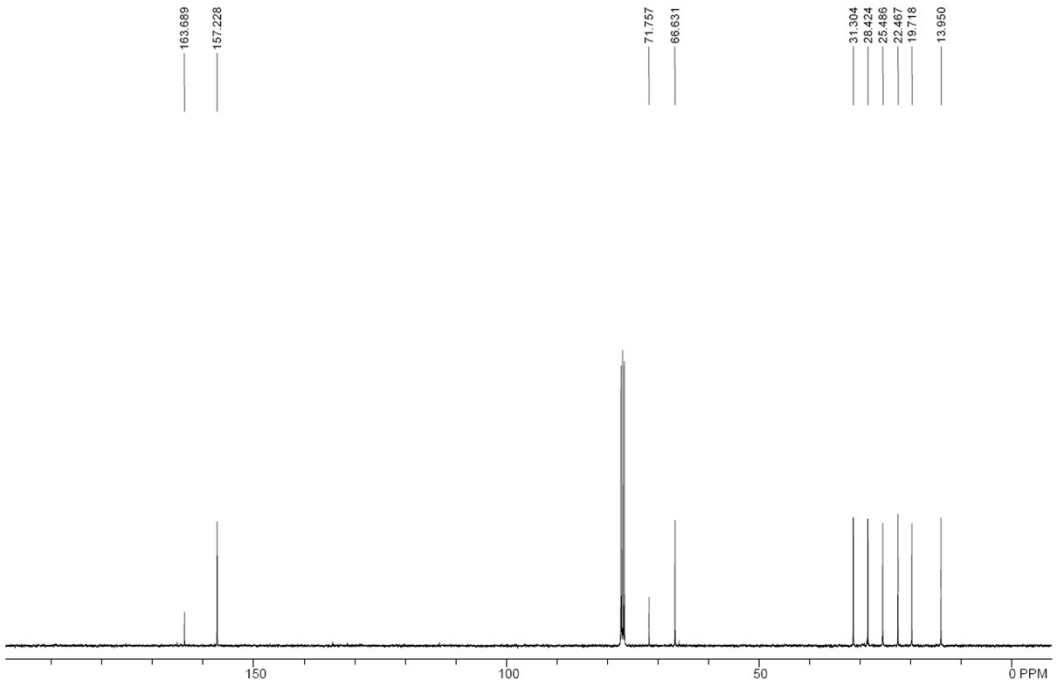
methyl (*E*)-2-iodo-3-(methylthio)acrylate (2b)



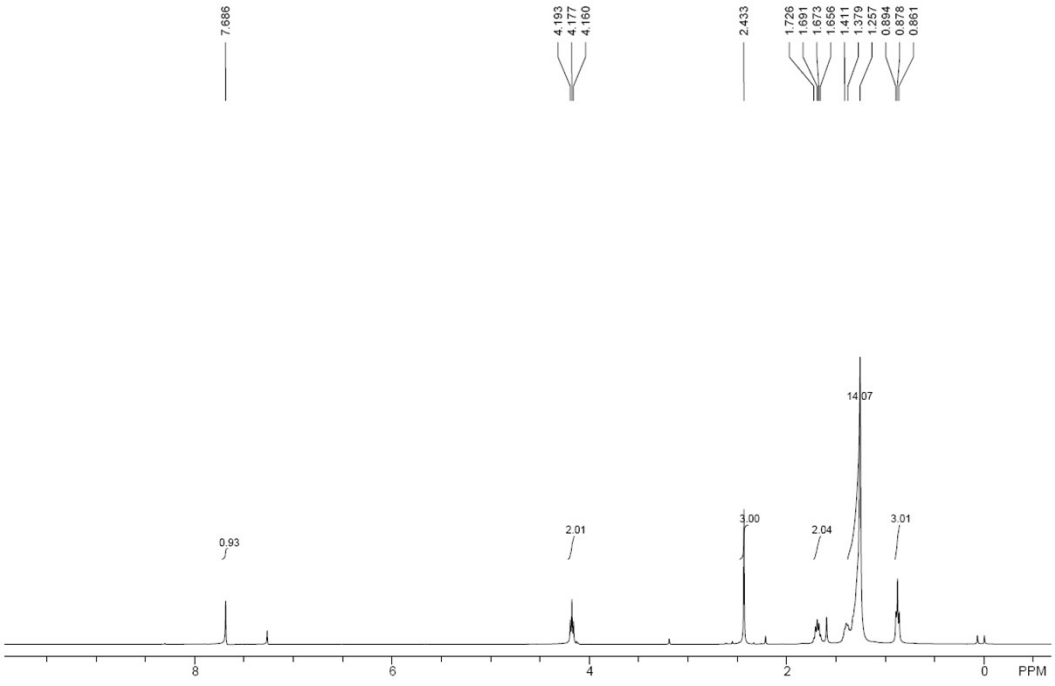


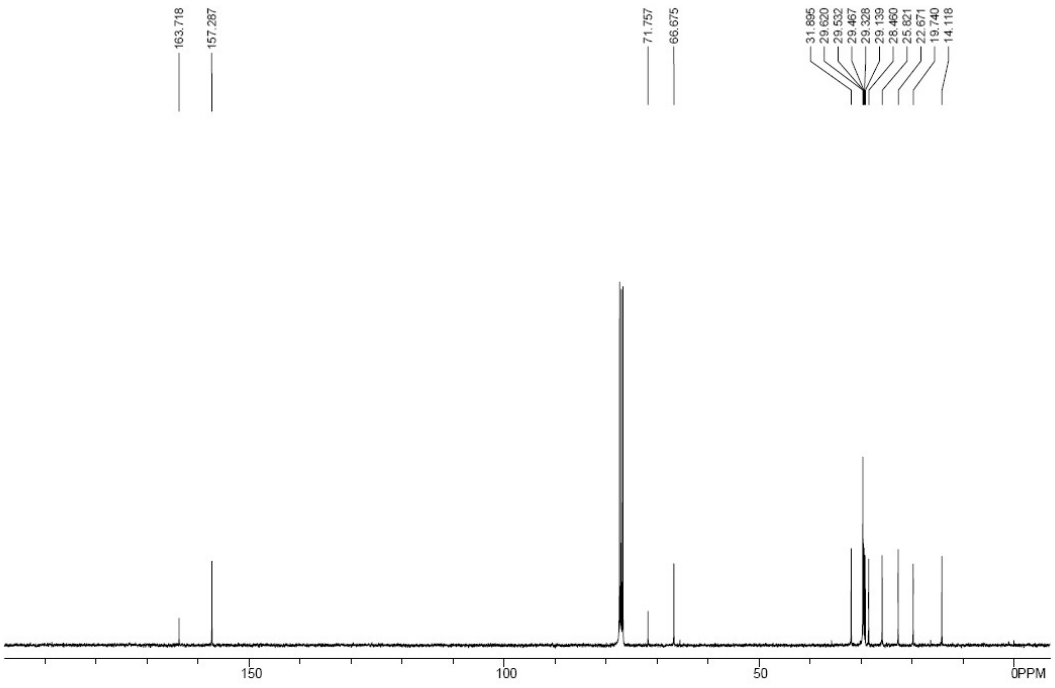
hexyl (*E*)-2-iodo-3-(methylthio)acrylate (2c)



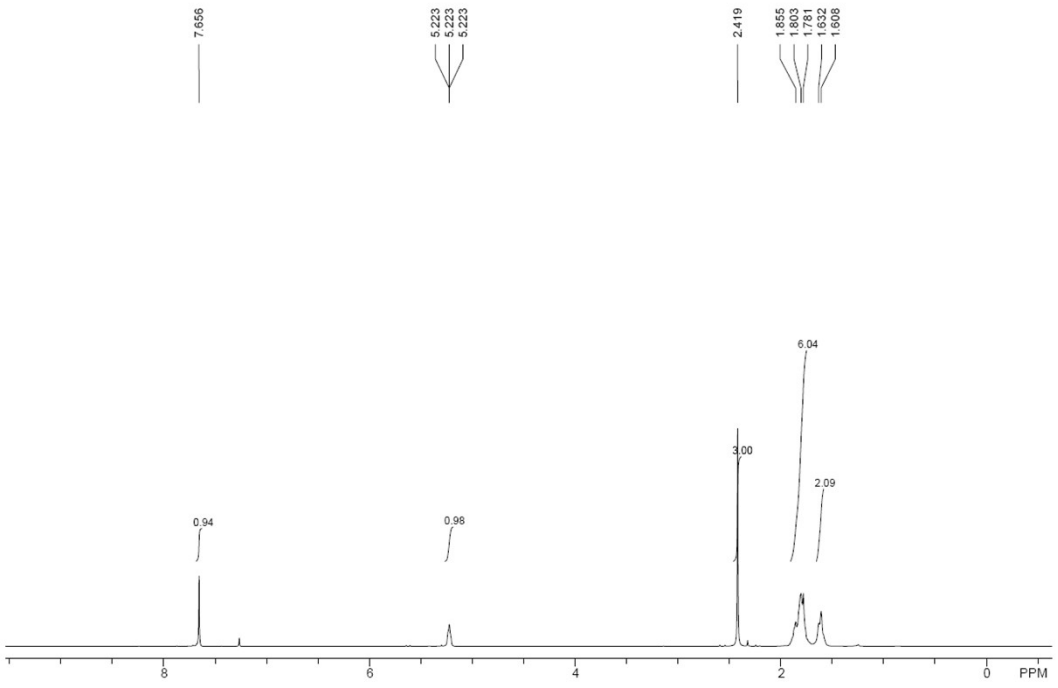


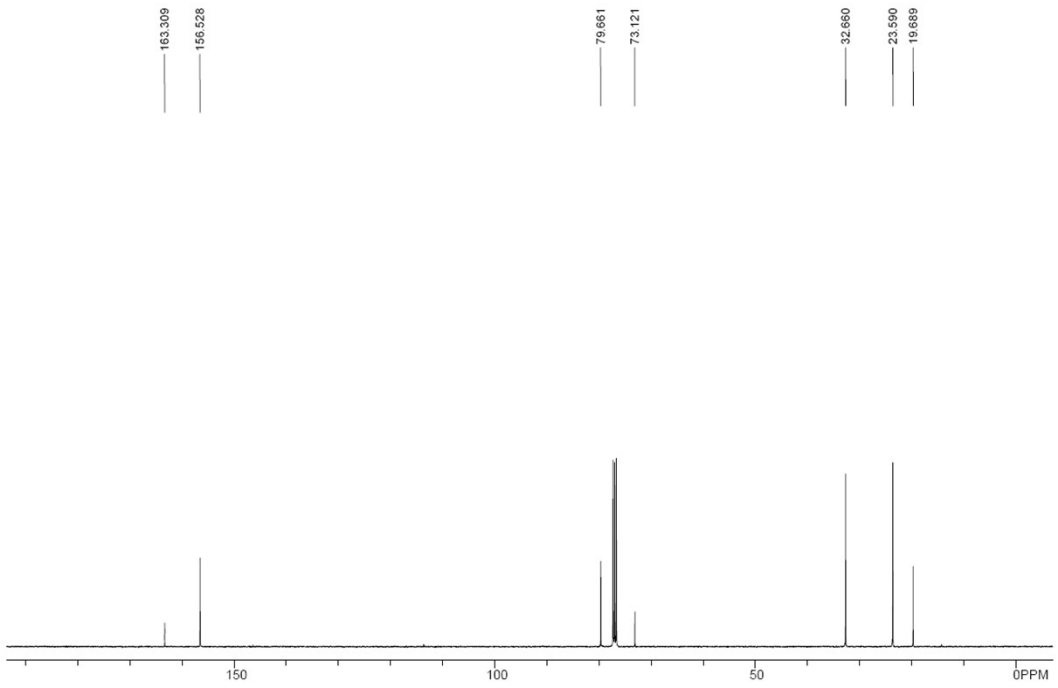
decyl (*E*)-2-iodo-3-(methylthio)acrylate (2d)



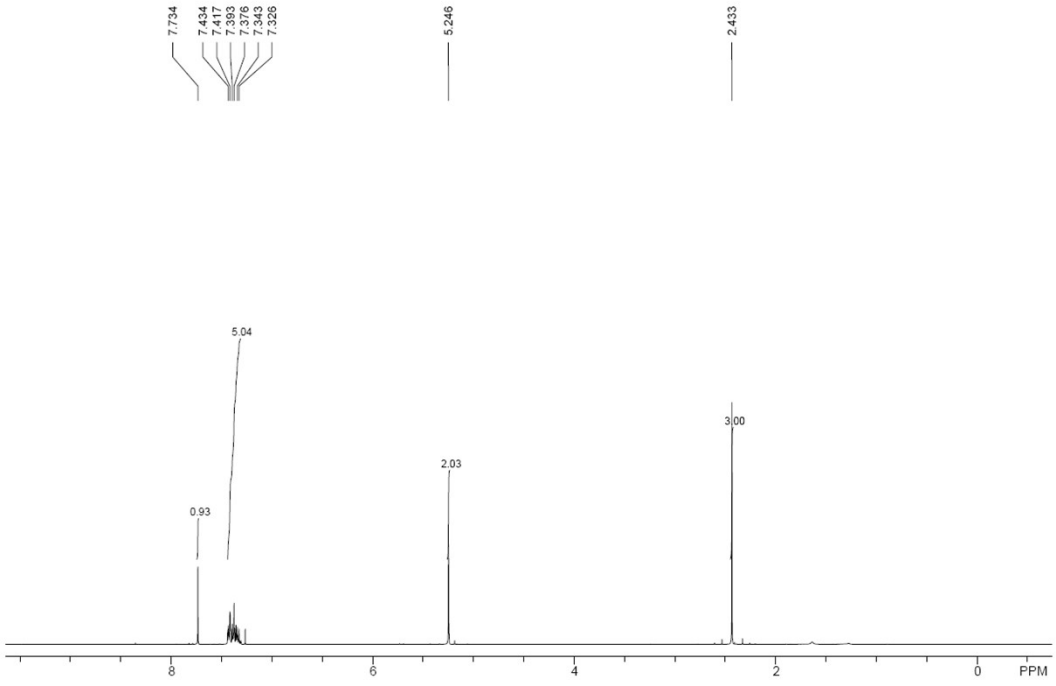


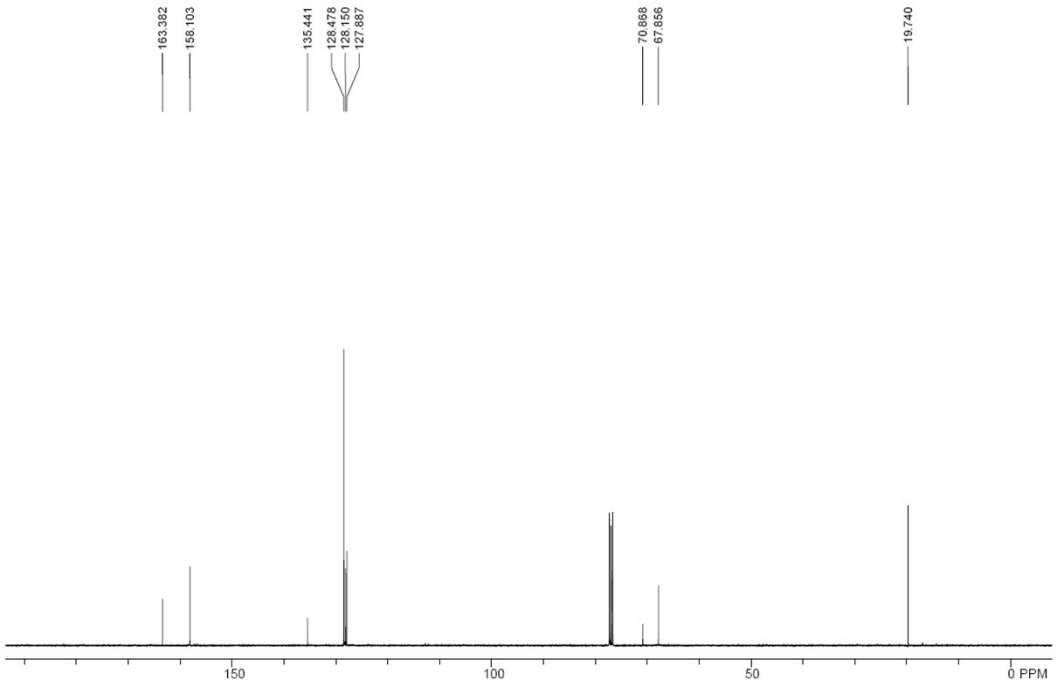
cyclopentyl (*E*)-2-iodo-3-(methylthio)acrylate (2e)



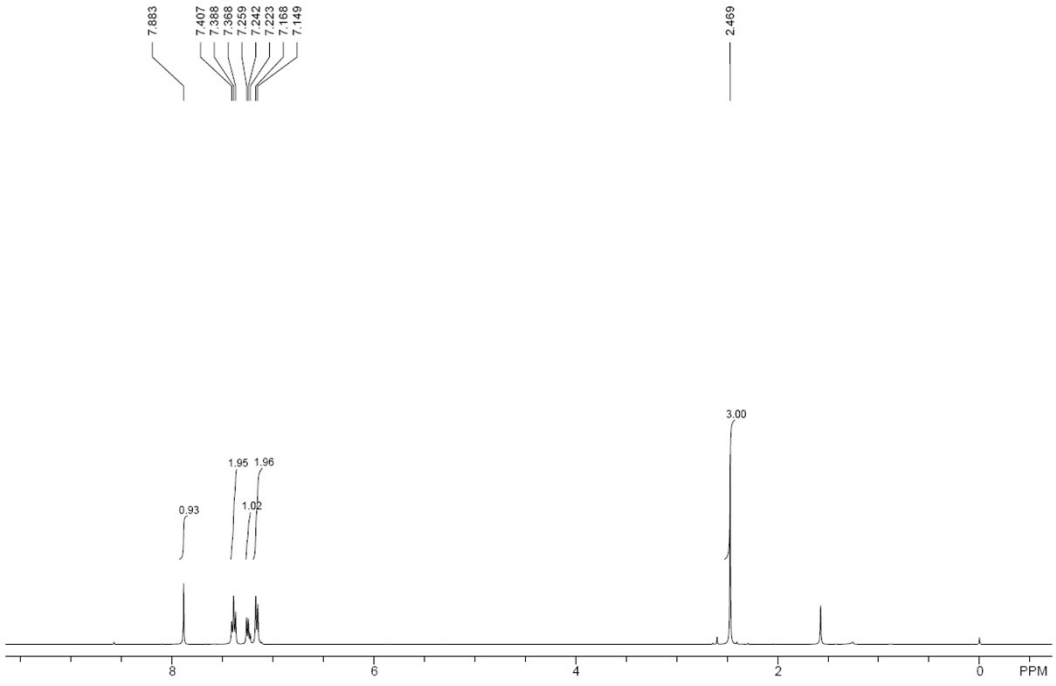


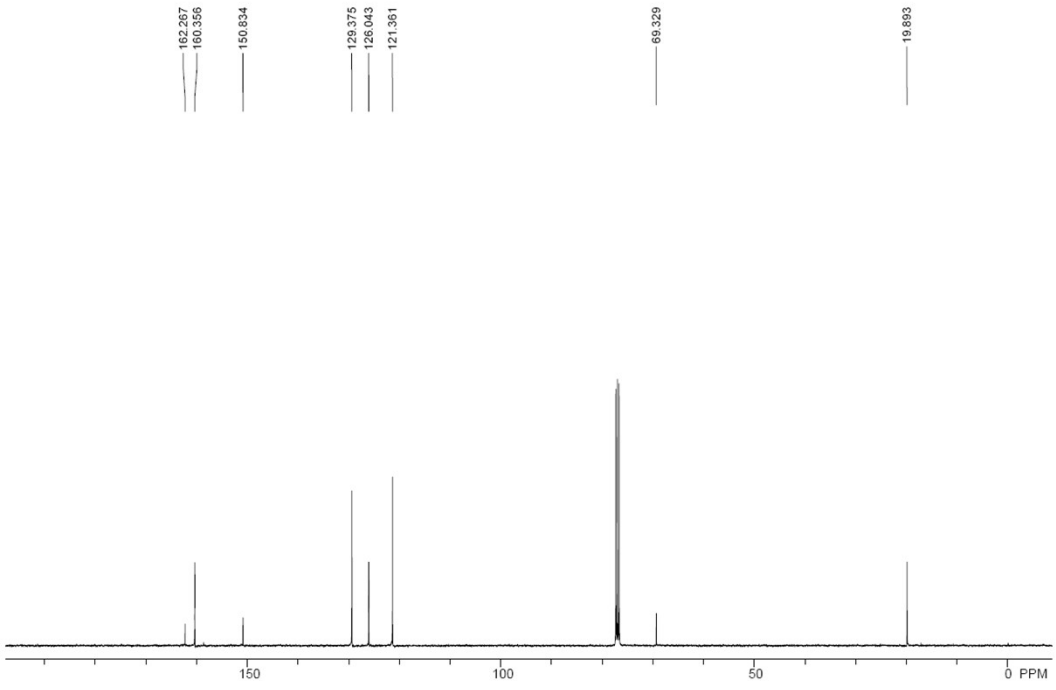
benzyl (*E*)-2-iodo-3-(methylthio)acrylate (2f)



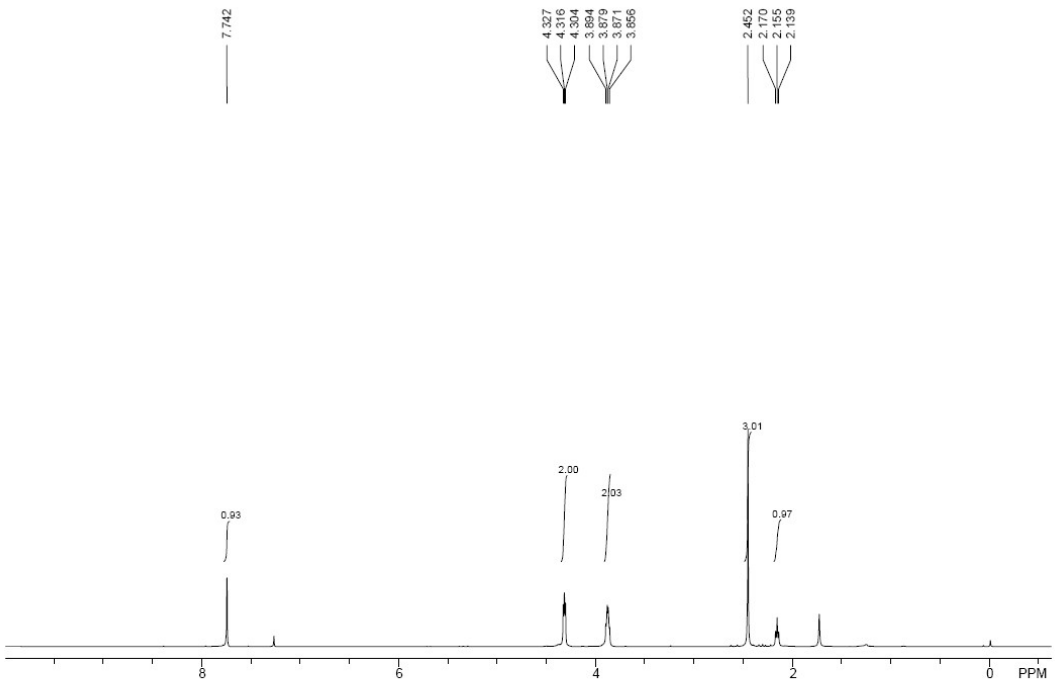


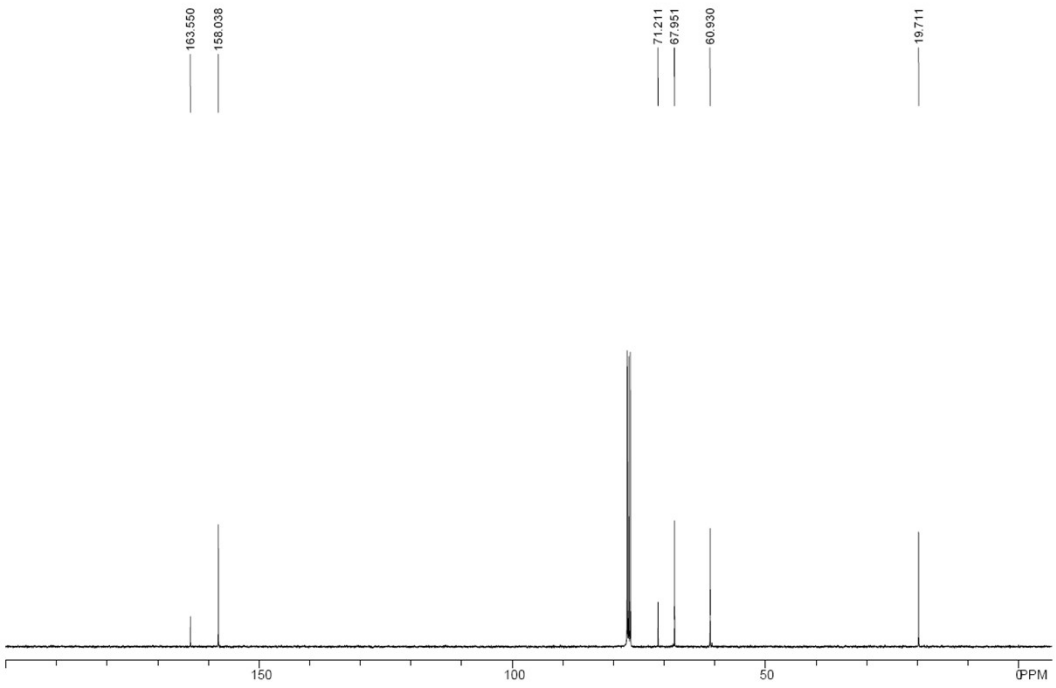
phenyl (*E*)-2-iodo-3-(methylthio)acrylate (2g)



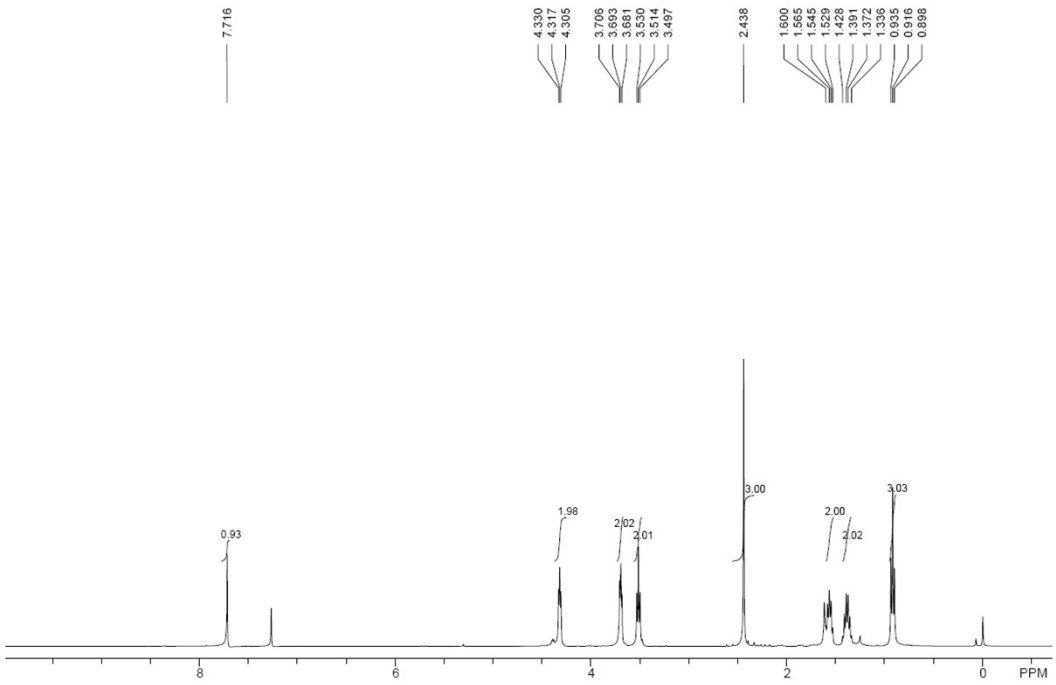


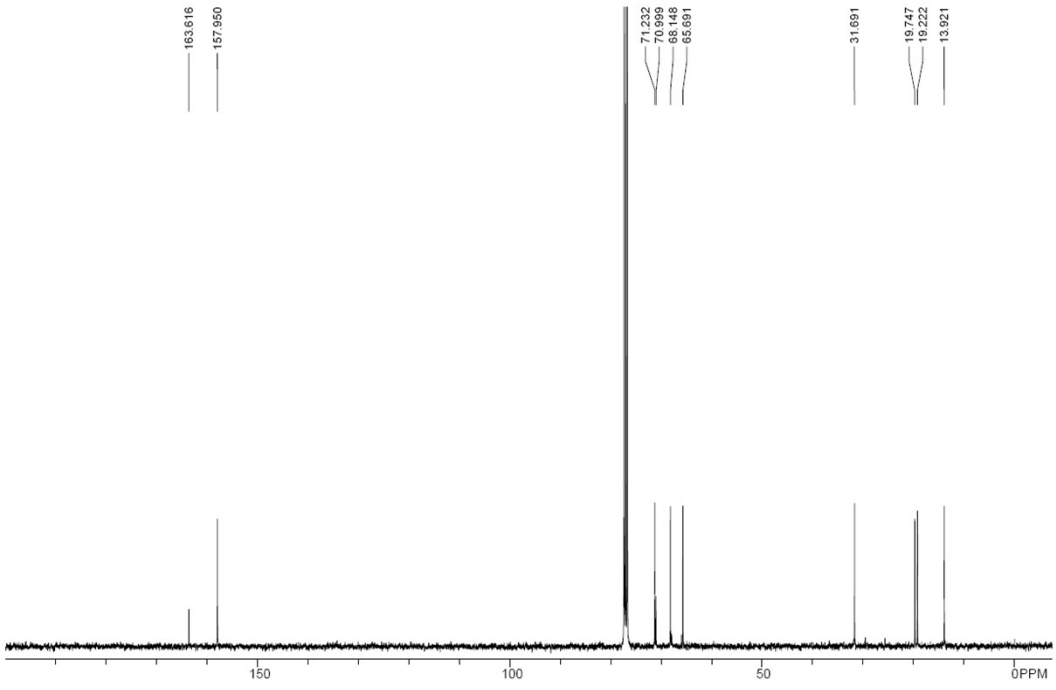
2-hydroxyethyl (*E*)-2-iodo-3-(methylthio)acrylate (2h)



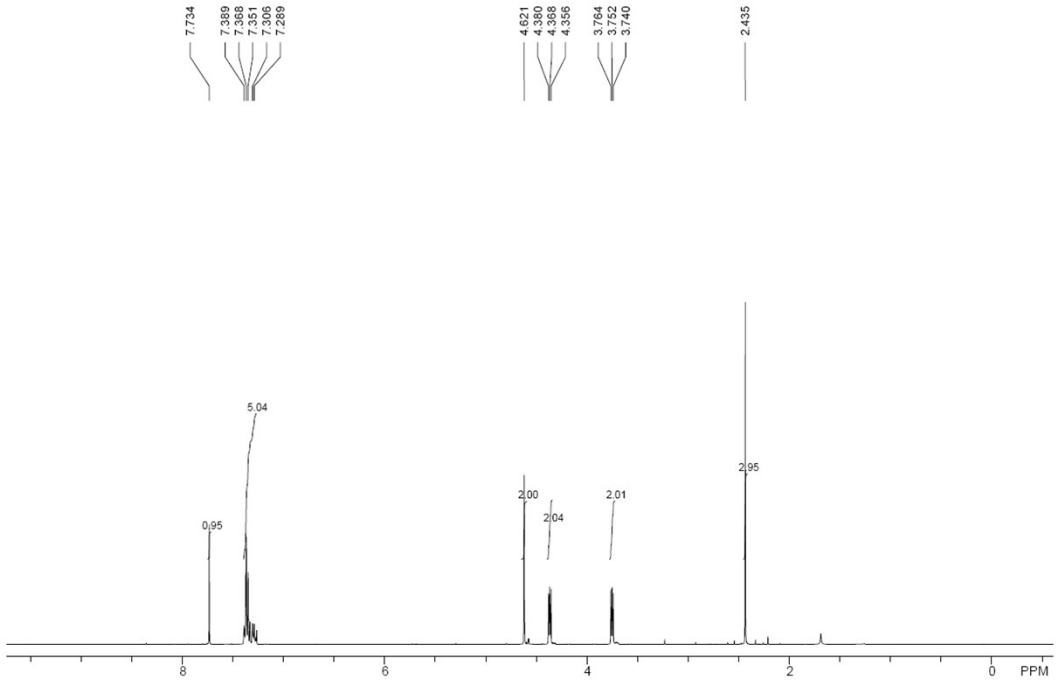


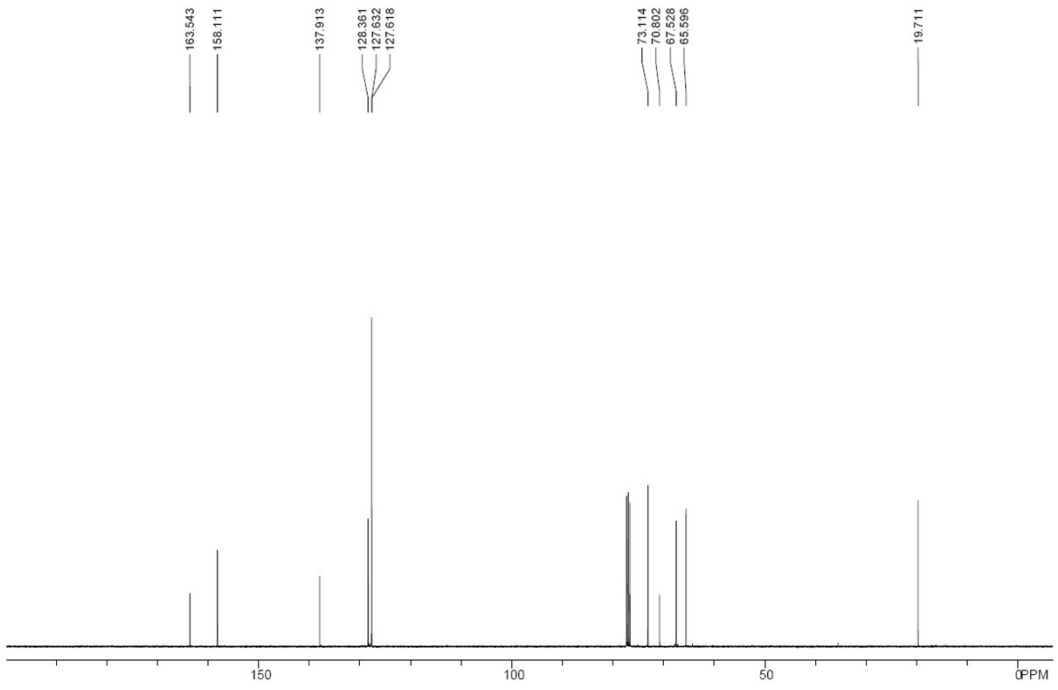
2-butoxyethyl (*E*)-2-iodo-3-(methylthio)acrylate (2i)



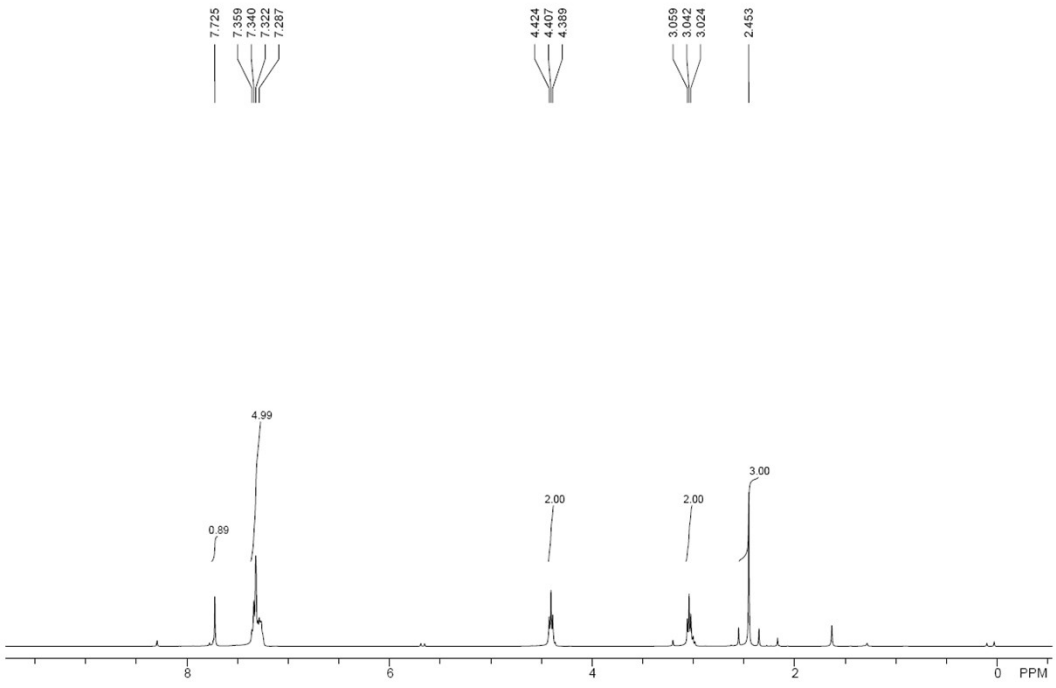


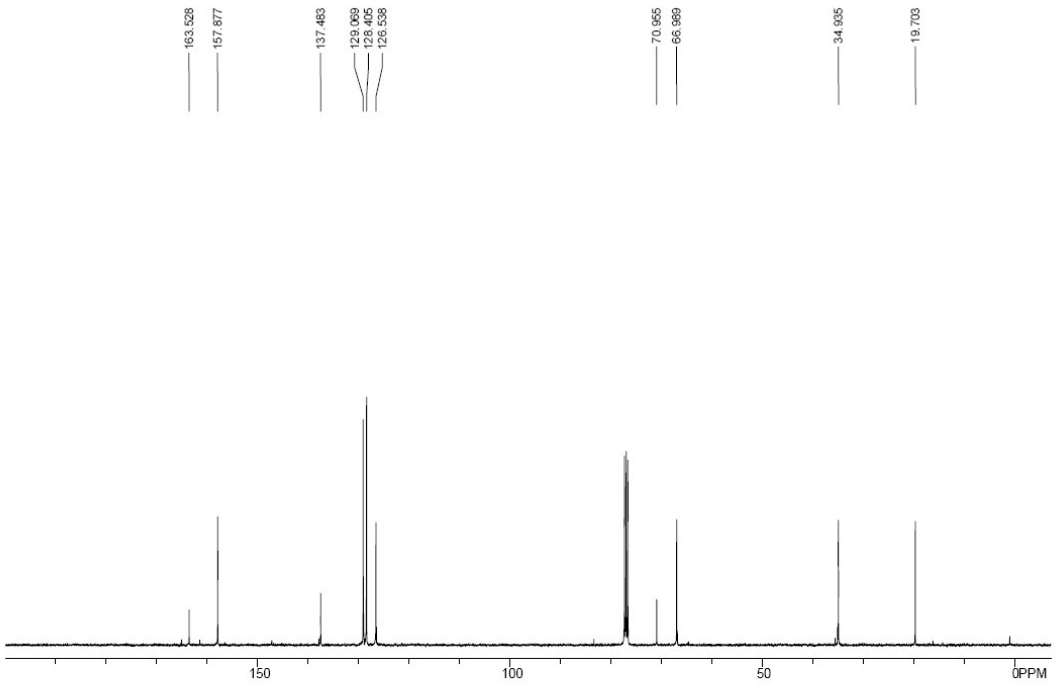
2-(benzyloxy)ethyl (*E*)-2-iodo-3-(methylthio)acrylate (2j)



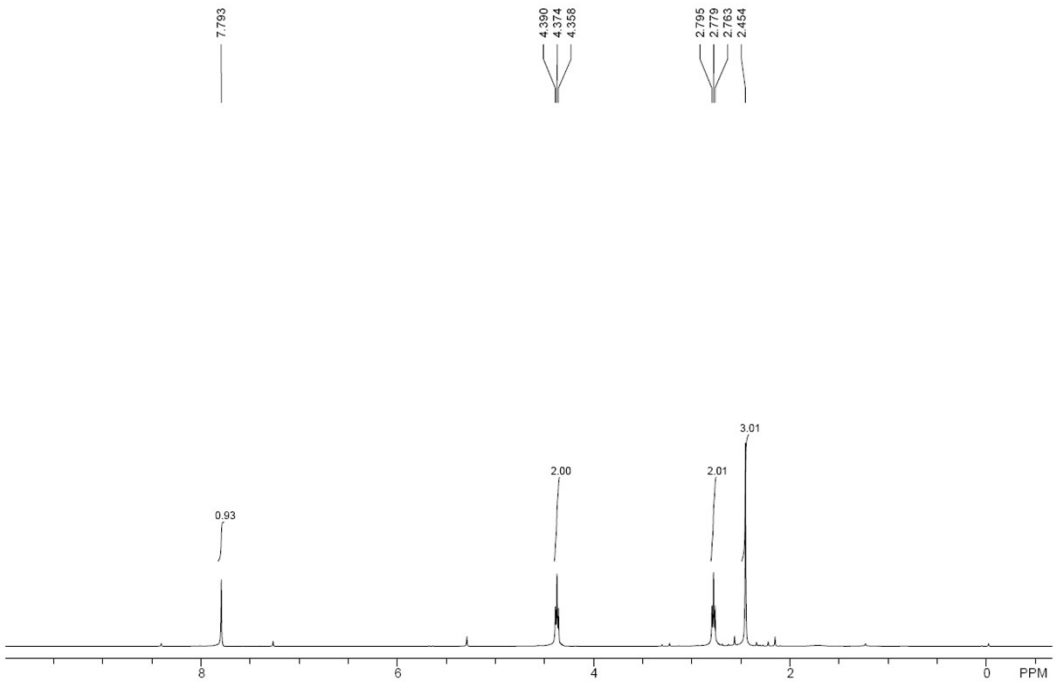


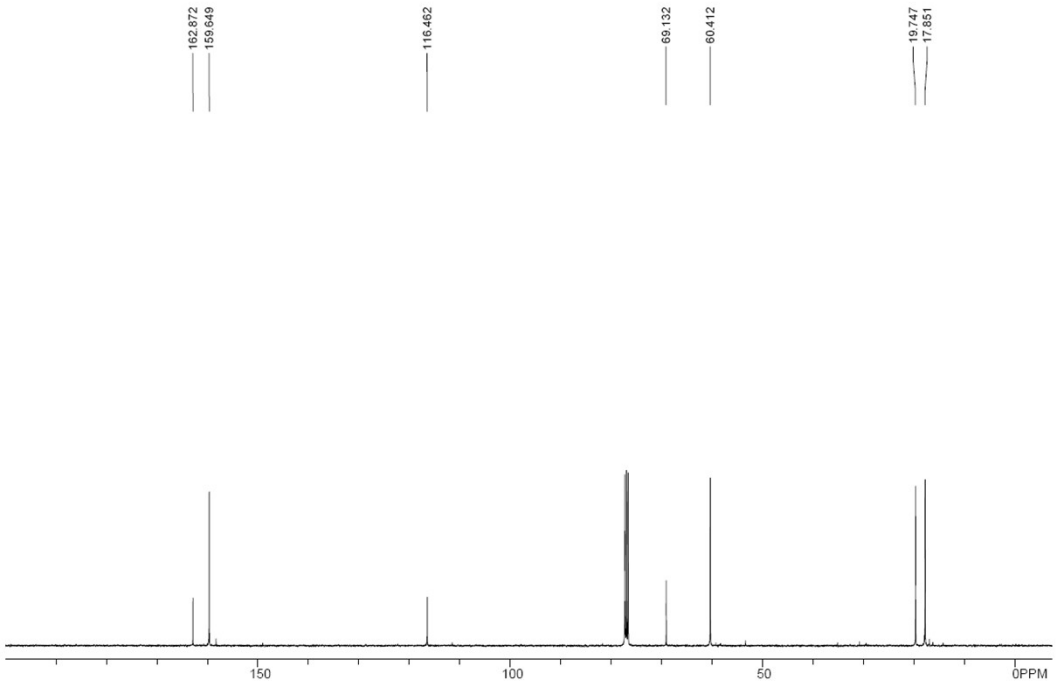
phenethyl (*E*)-2-iodo-3-(methylthio)acrylate (2k)



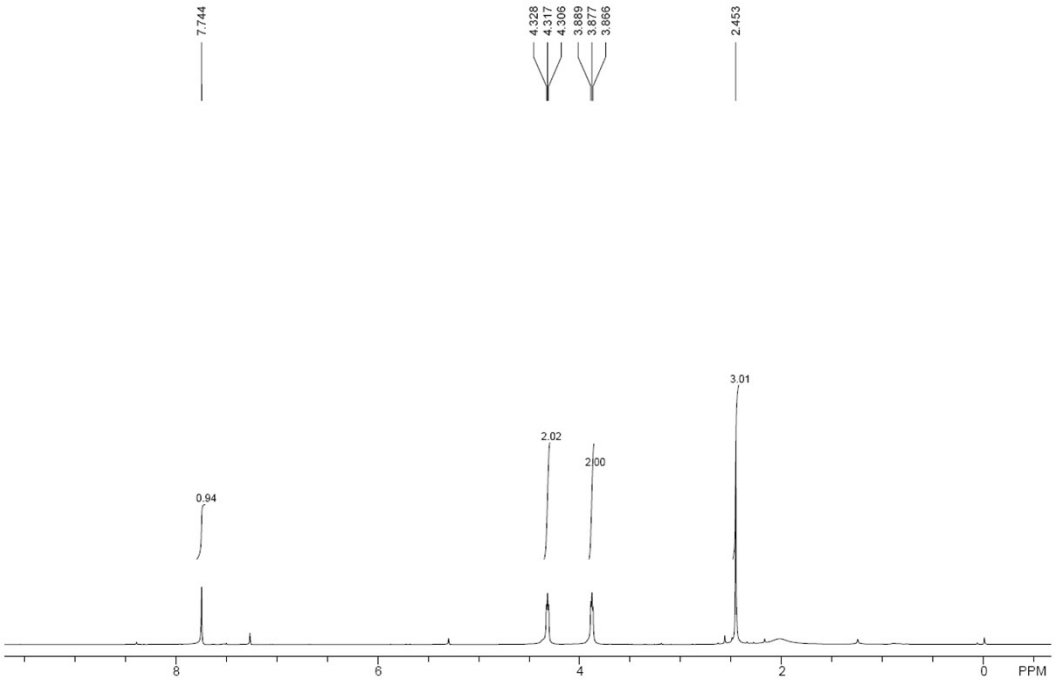


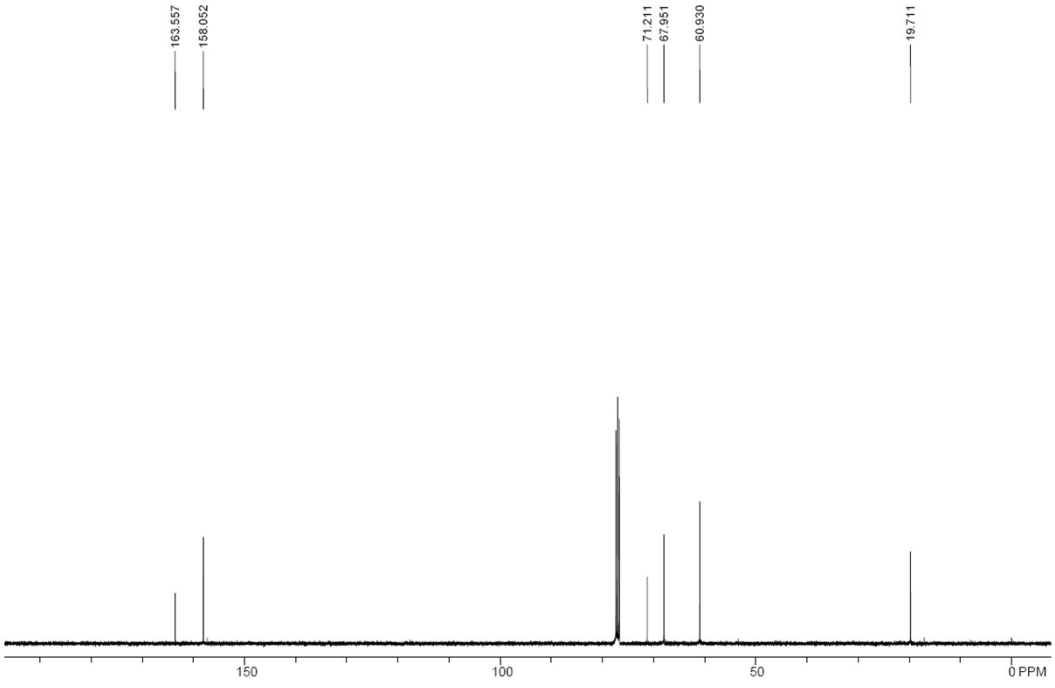
2-cyanoethyl (*E*)-2-iodo-3-(methylthio)acrylate (2l)



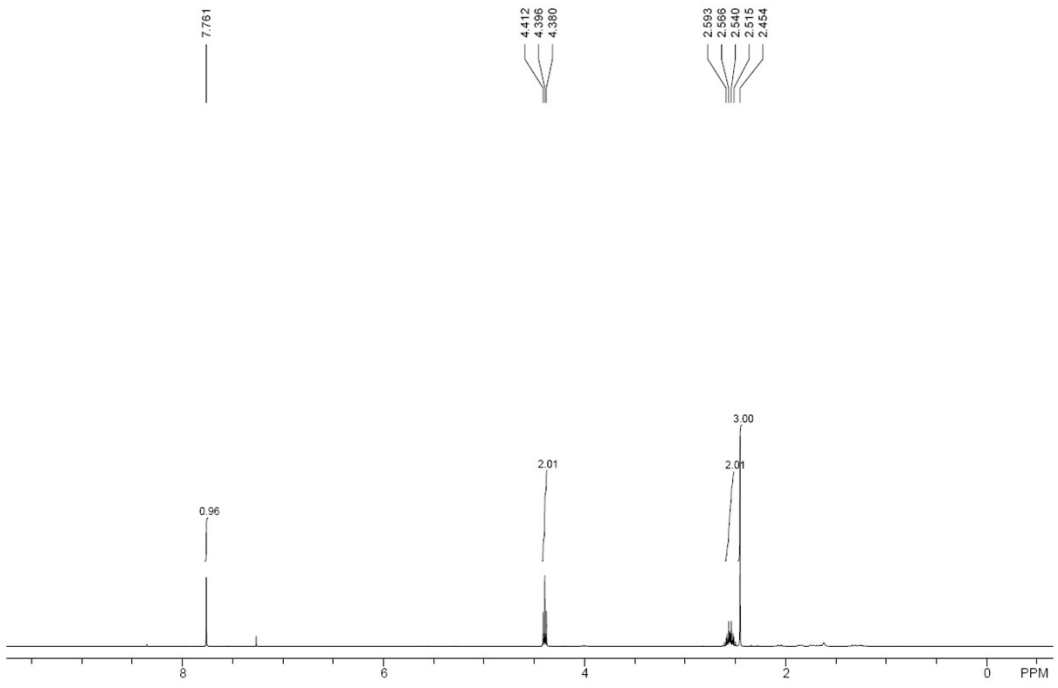


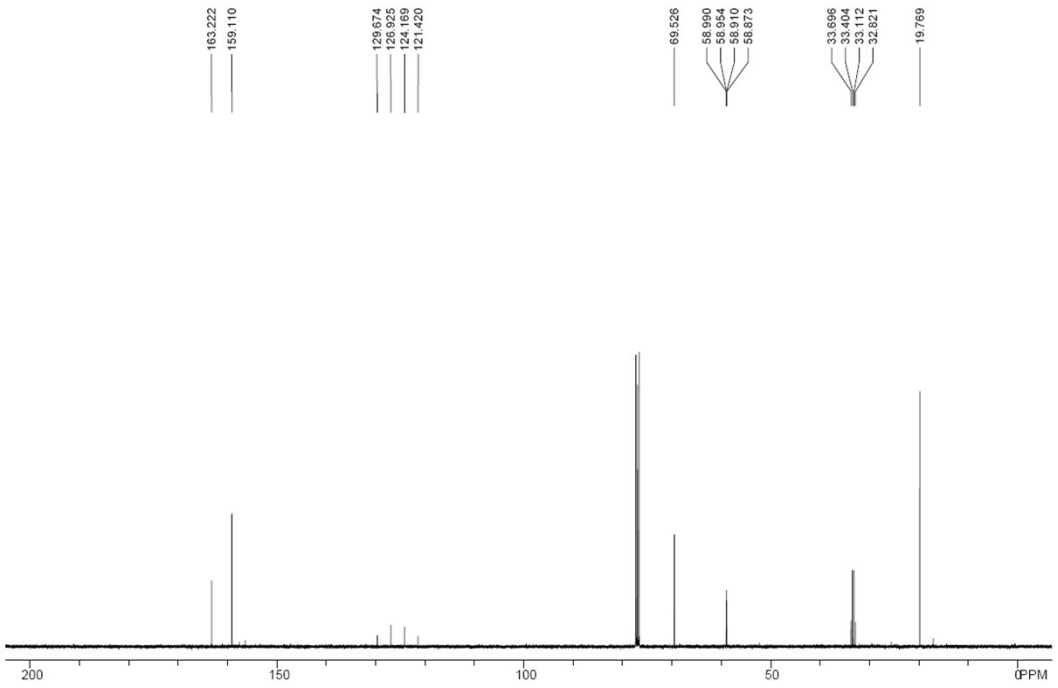
2-bromoethyl (*E*)-2-iodo-3-(methylthio)acrylate (2m)

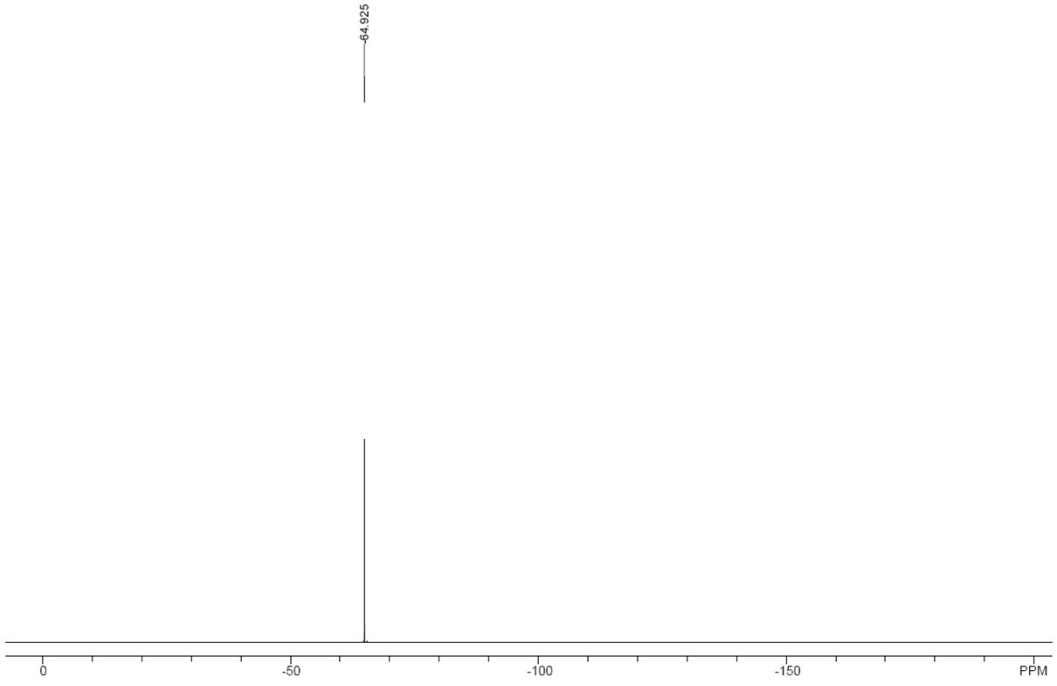




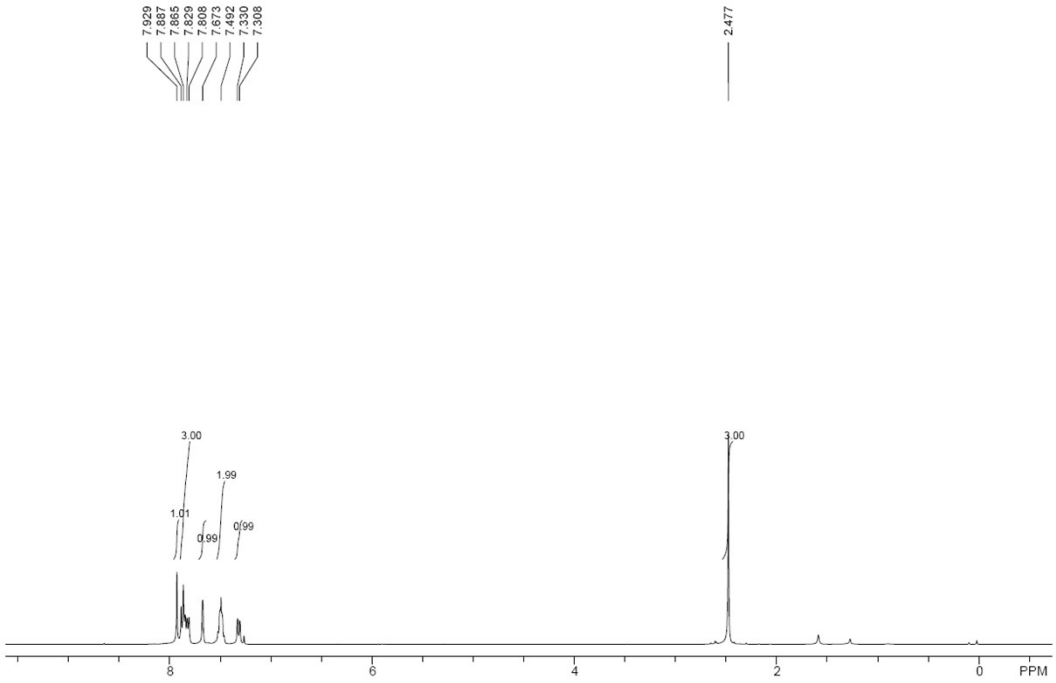
3,3,3-trifluoropropyl (*E*)-2-iodo-3-(methylthio)acrylate (2n)

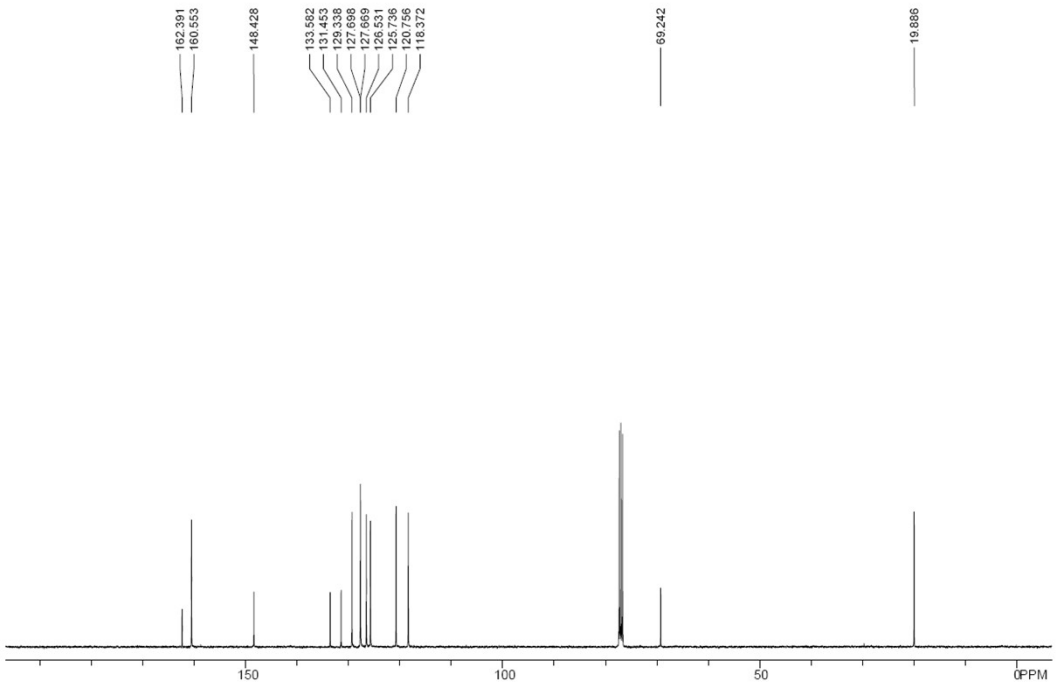




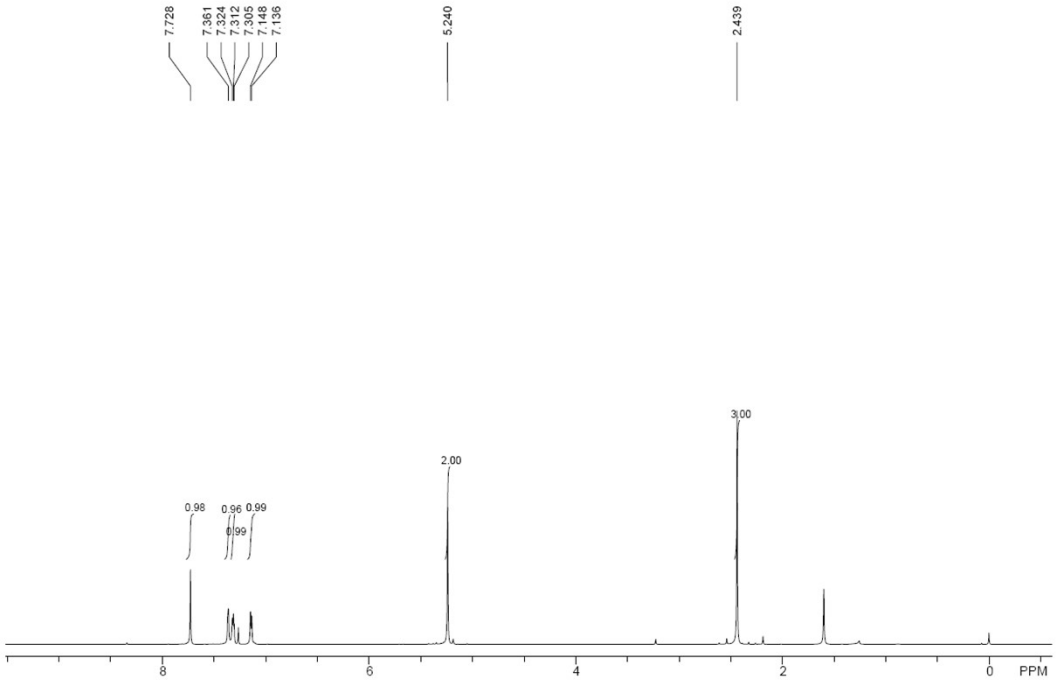

-64.925
0
-50
-100
-150
PPM

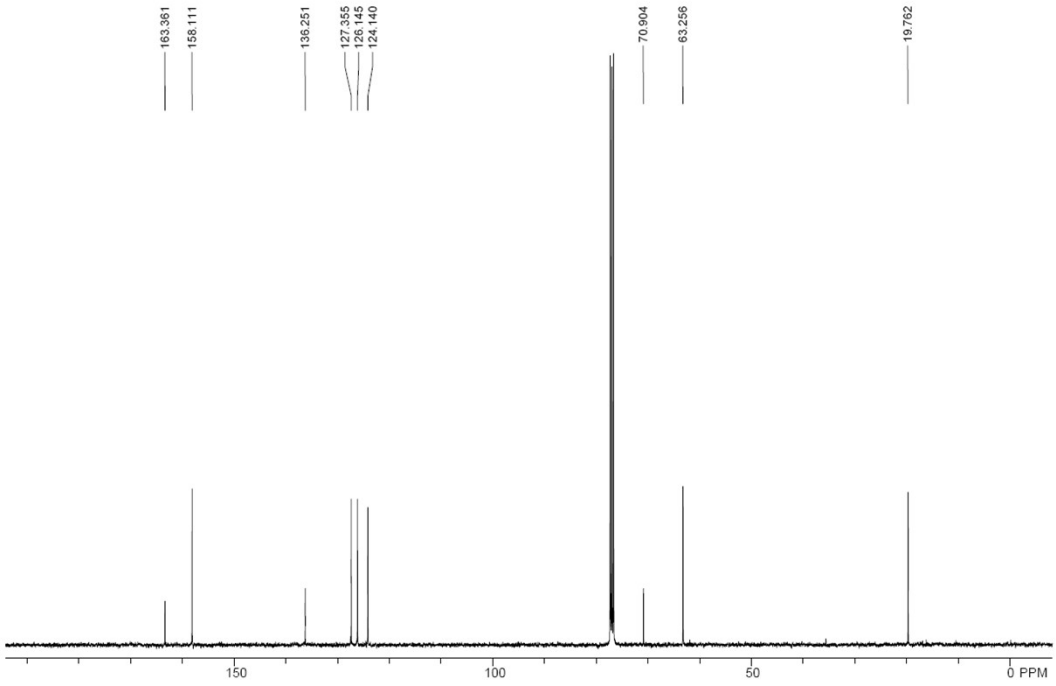
naphthalen-2-yl (*E*)-2-iodo-3-(methylthio)acrylate (2o)



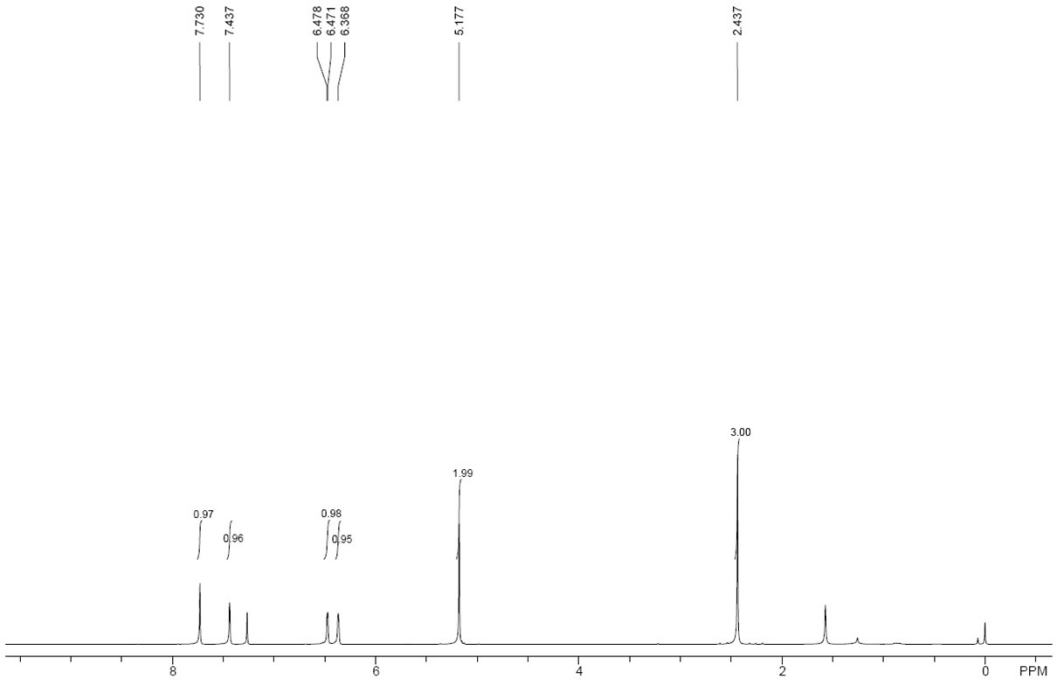


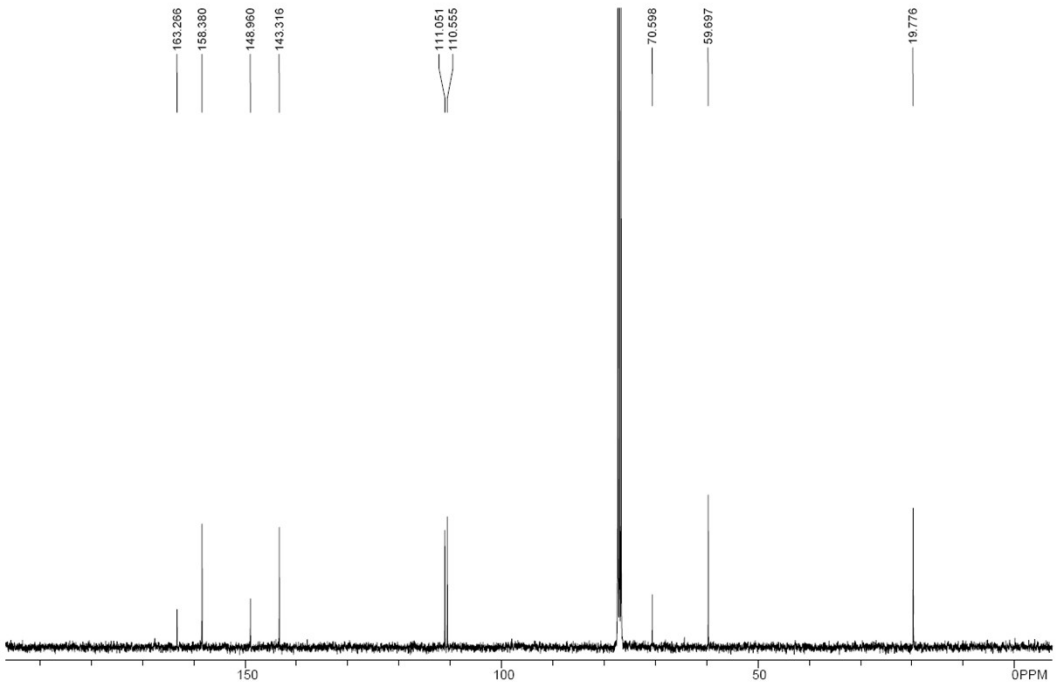
thiophen-2-ylmethyl (*E*)-2-iodo-3-(methylthio)acrylate (2p)



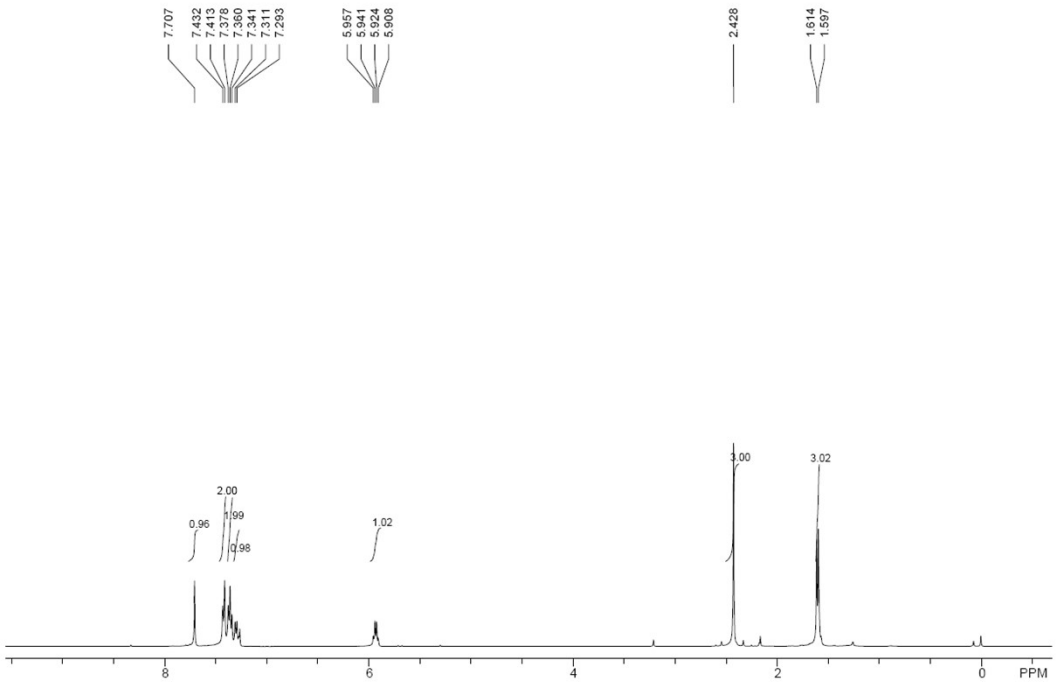


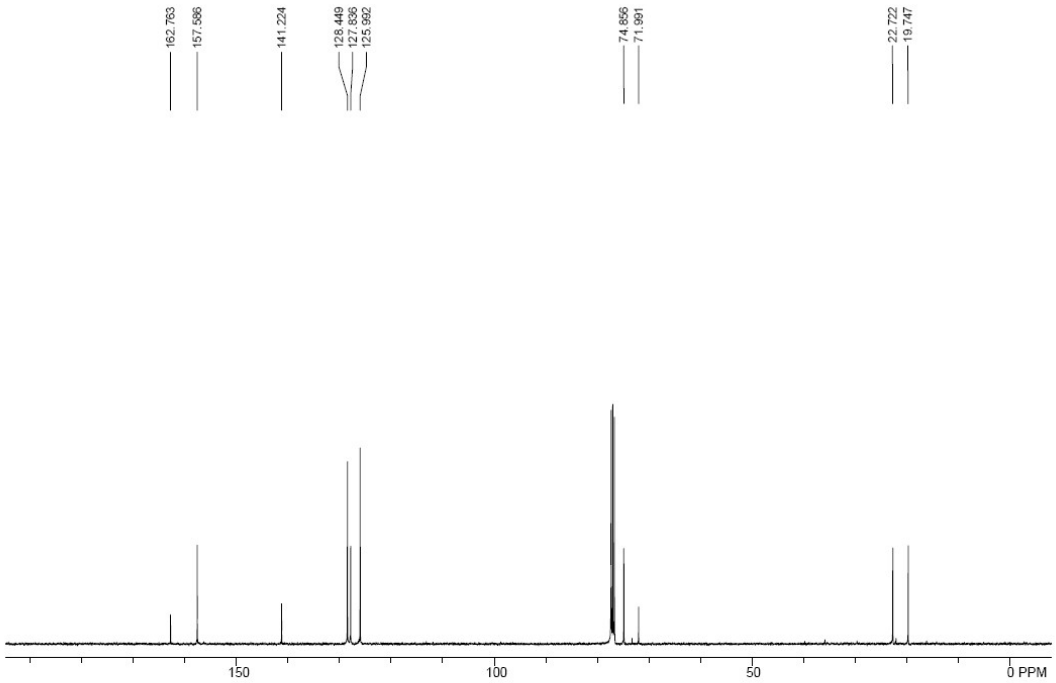
furan-2-ylmethyl (*E*)-2-iodo-3-(methylthio)acrylate (2q)



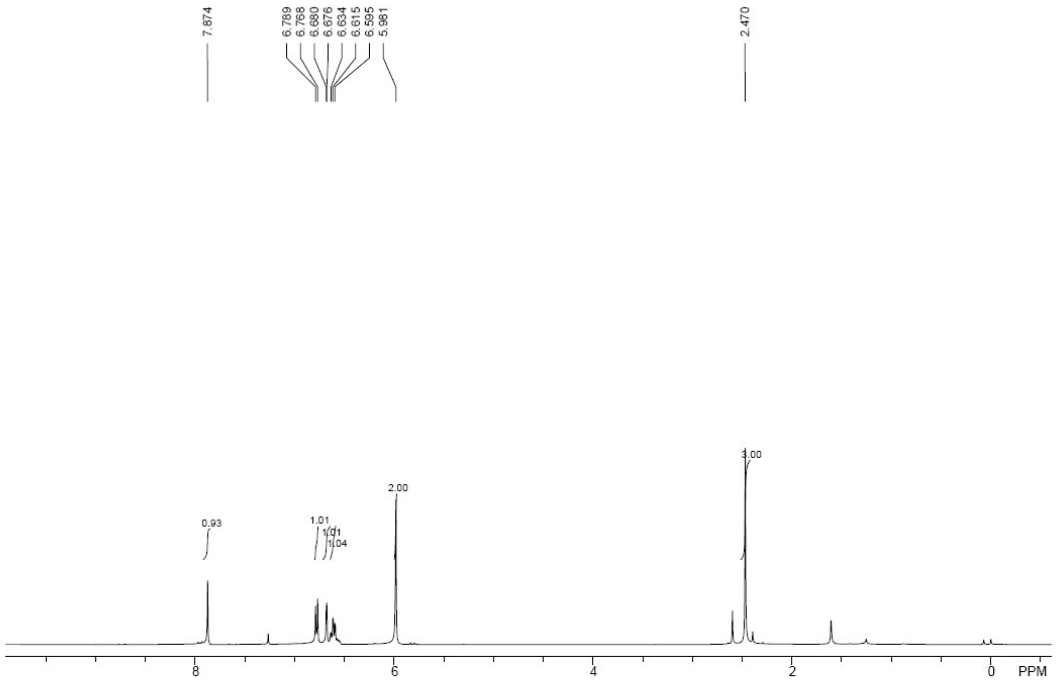


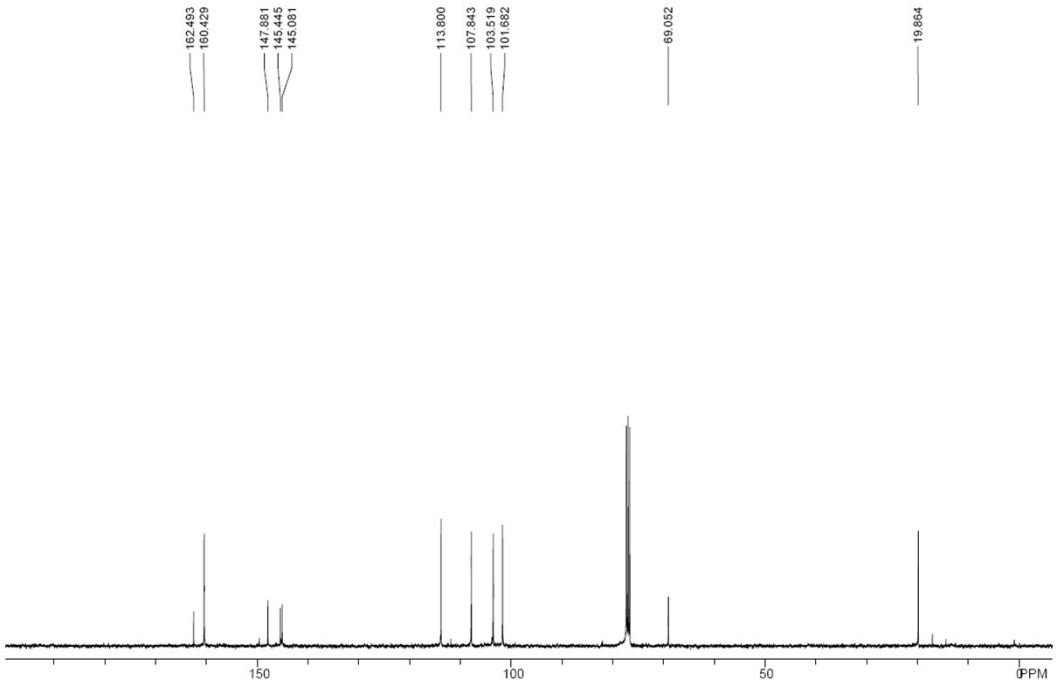
1-phenylethyl (*E*)-2-iodo-3-(methylthio)acrylate (2r)



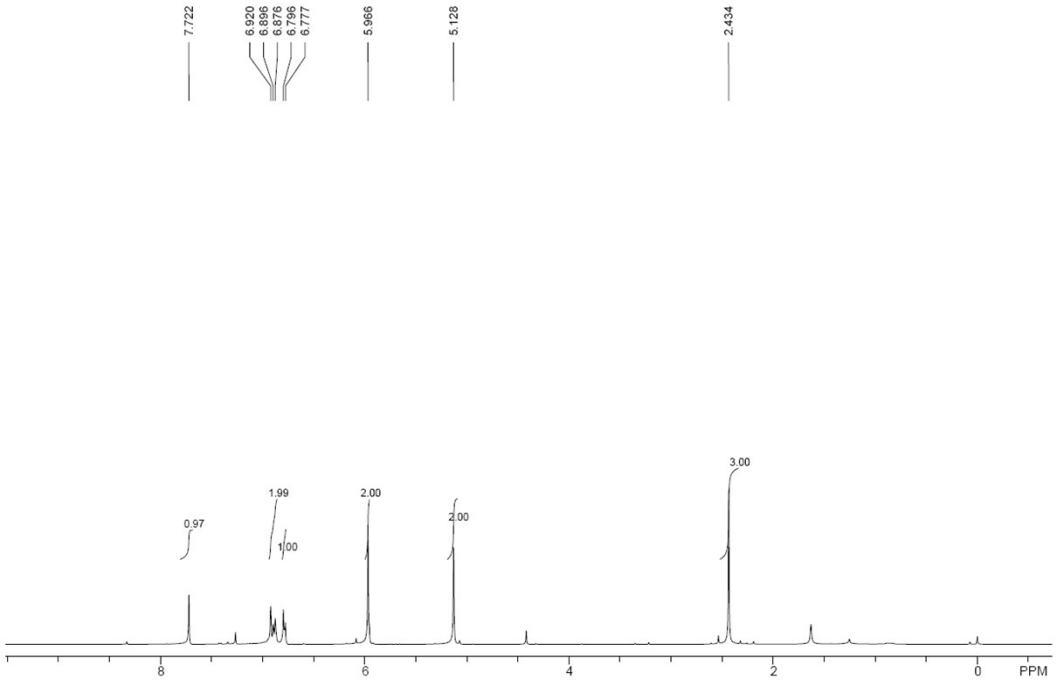


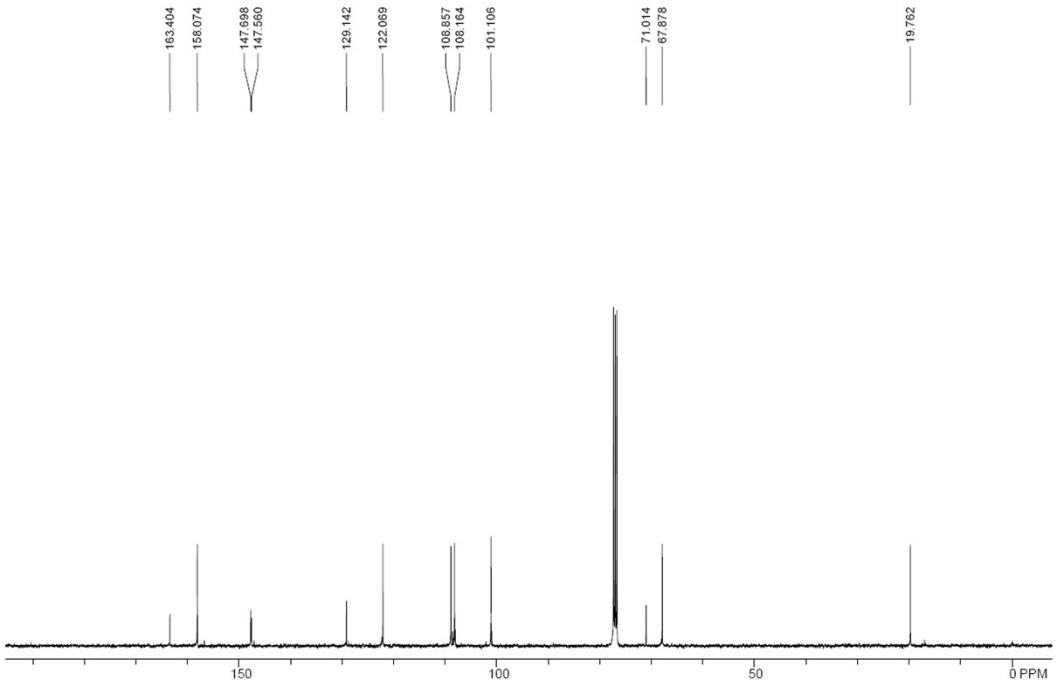
benzo[*d*][1,3]dioxol-5-yl (*E*)-2-iodo-3-(methylthio)acrylate (2s)



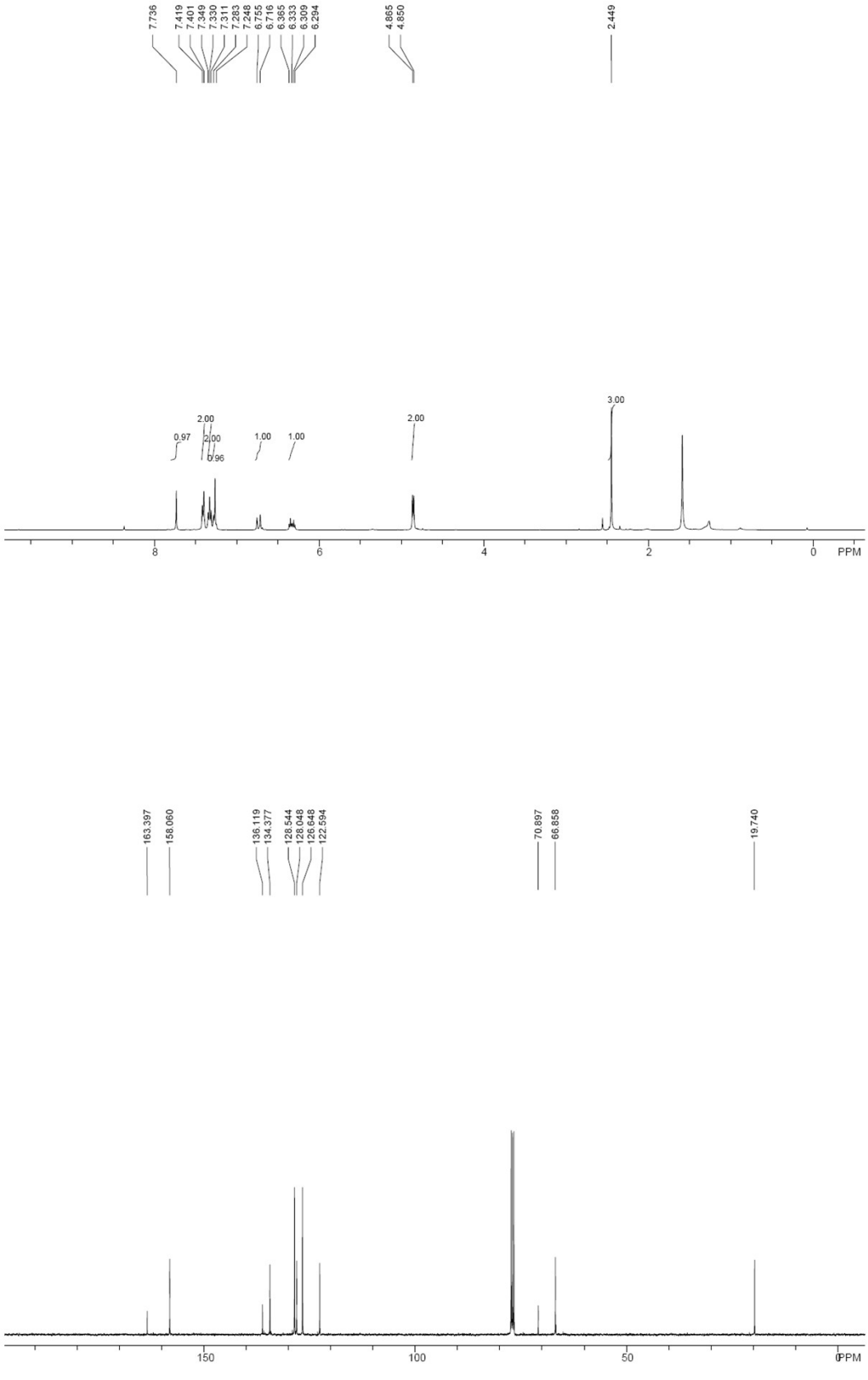


benzo[*d*][1,3]dioxol-5-ylmethyl (*E*)-2-iodo-3-(methylthio)acrylate (2t)

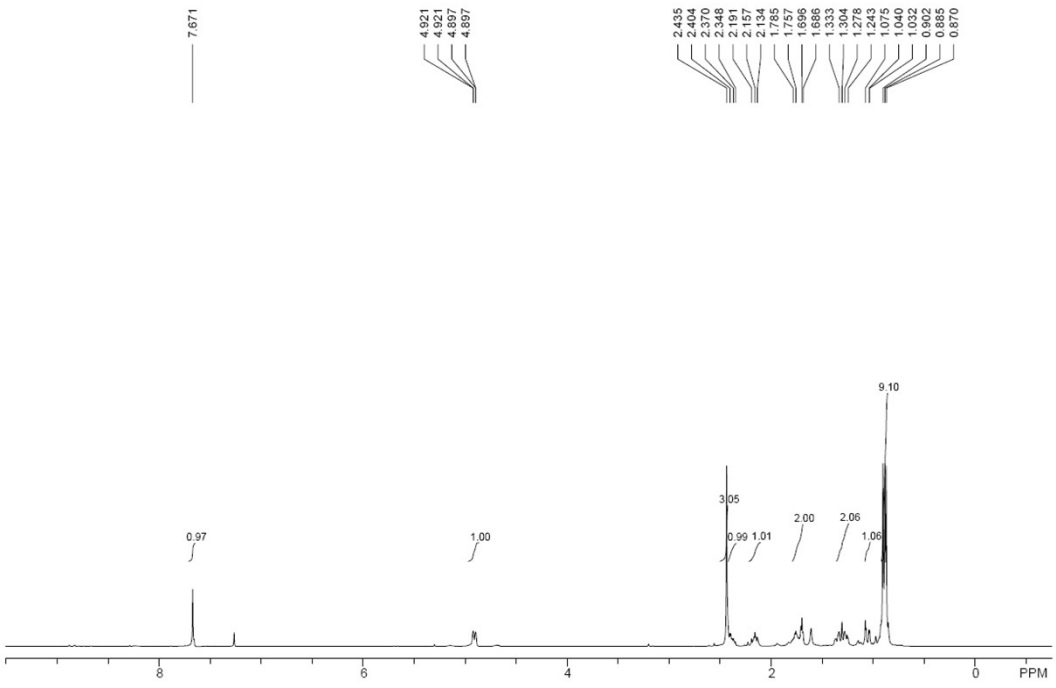


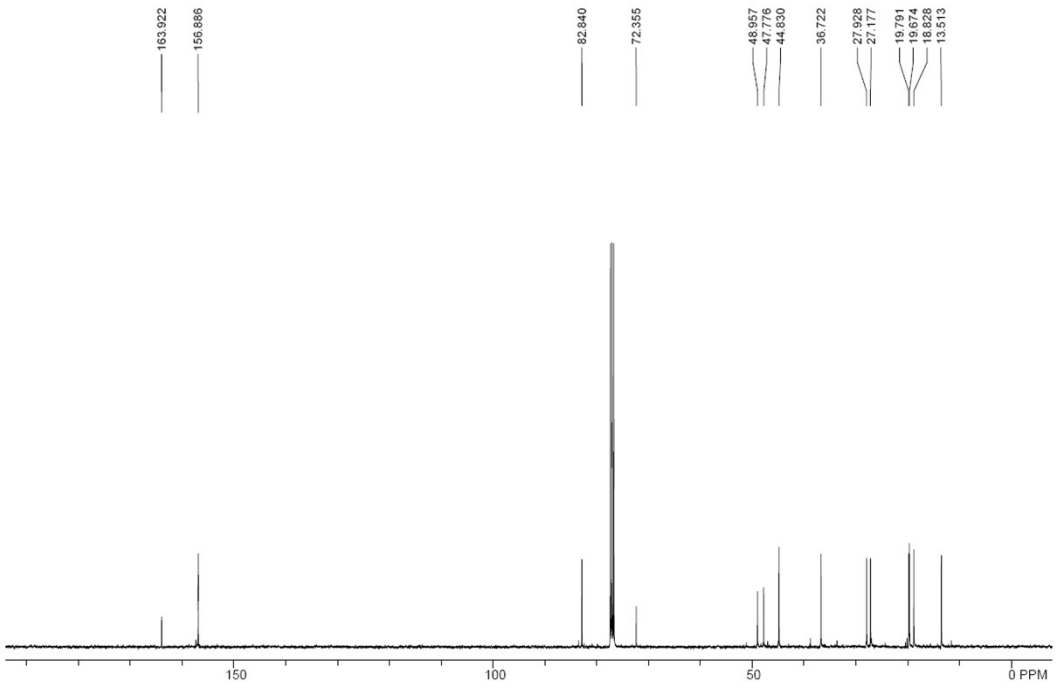


cinnamyl (*E*)-2-iodo-3-(methylthio)acrylate (2u)

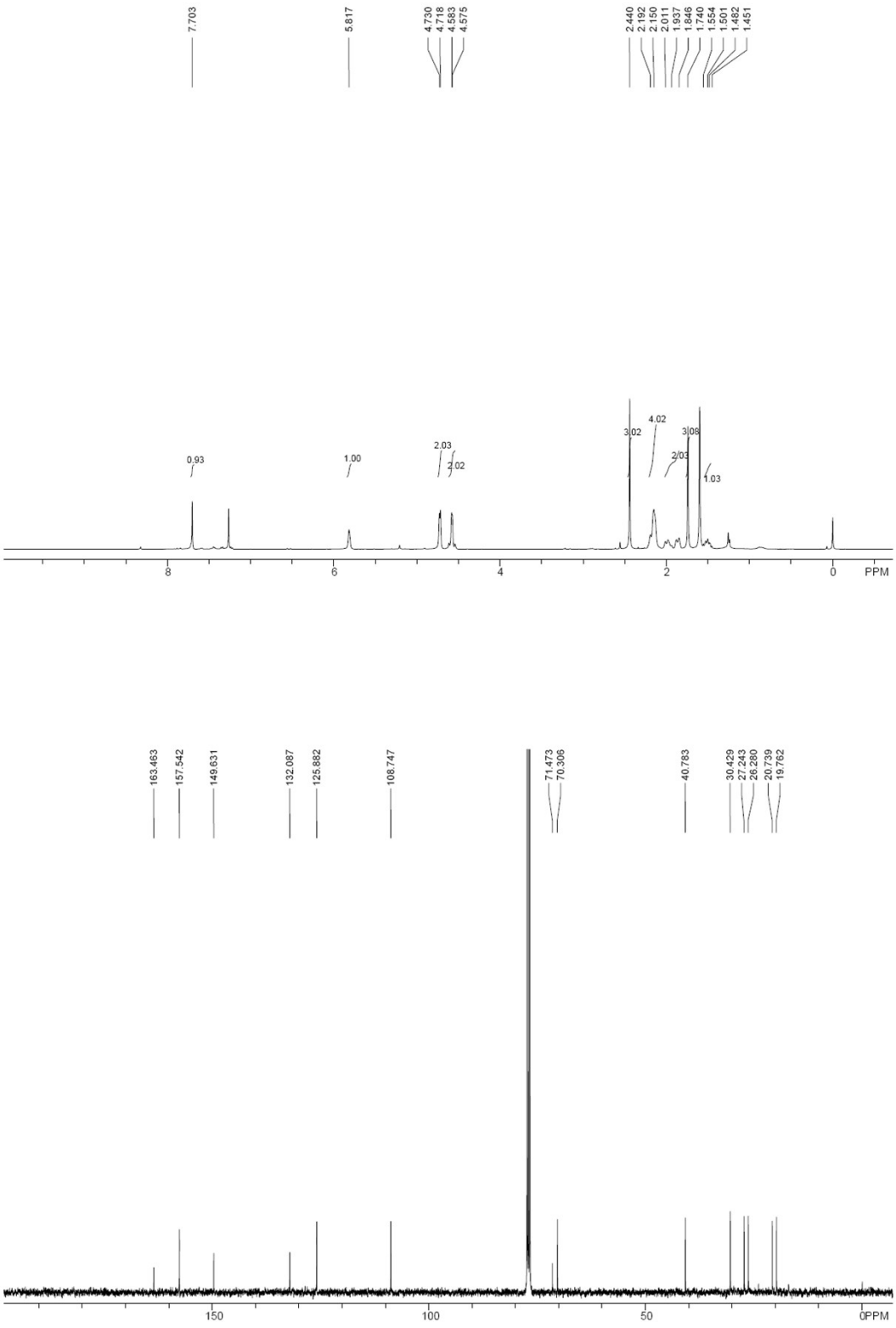


(1S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-2-iodo-3-(methylthio)acrylate (2v)

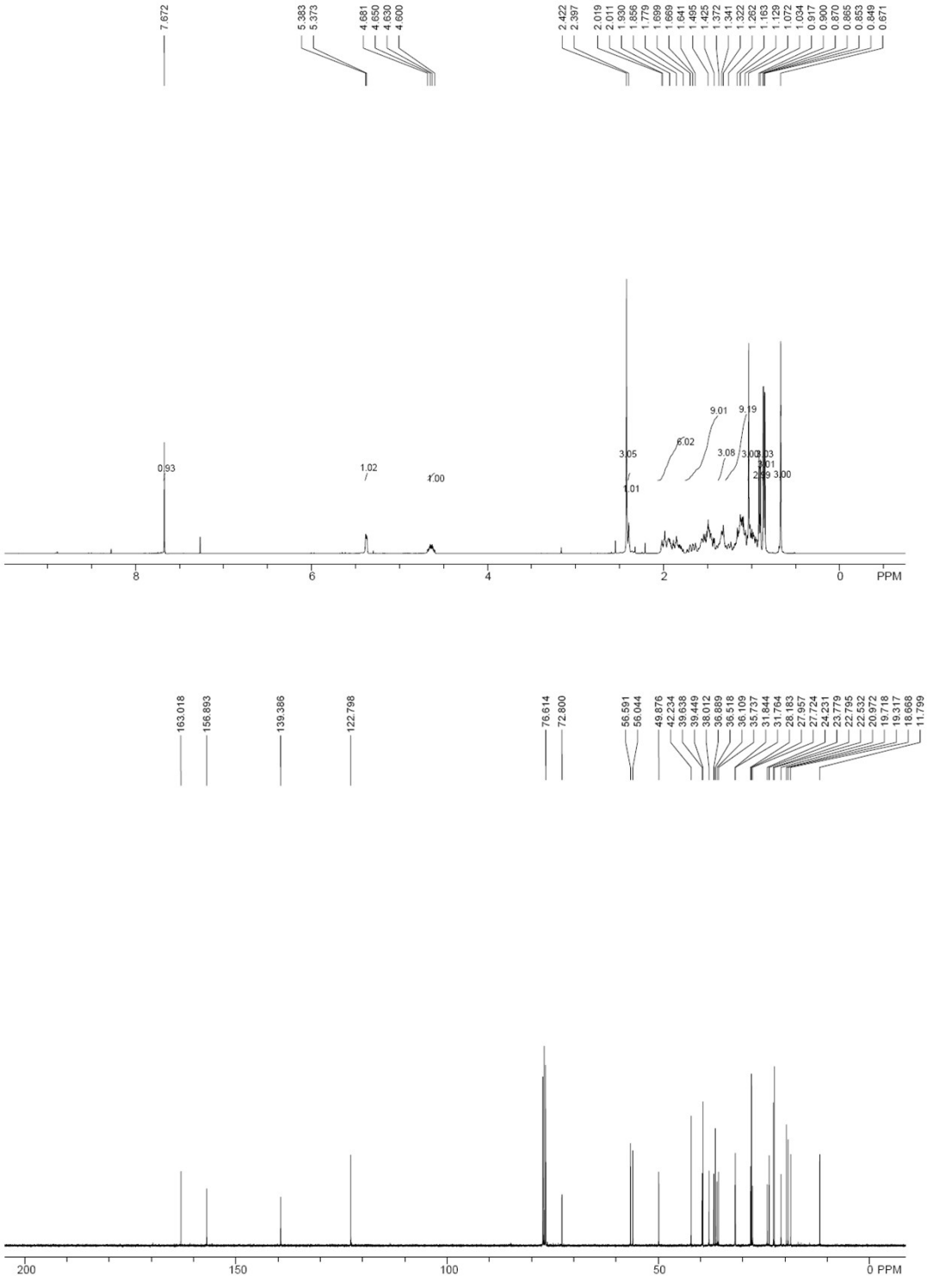




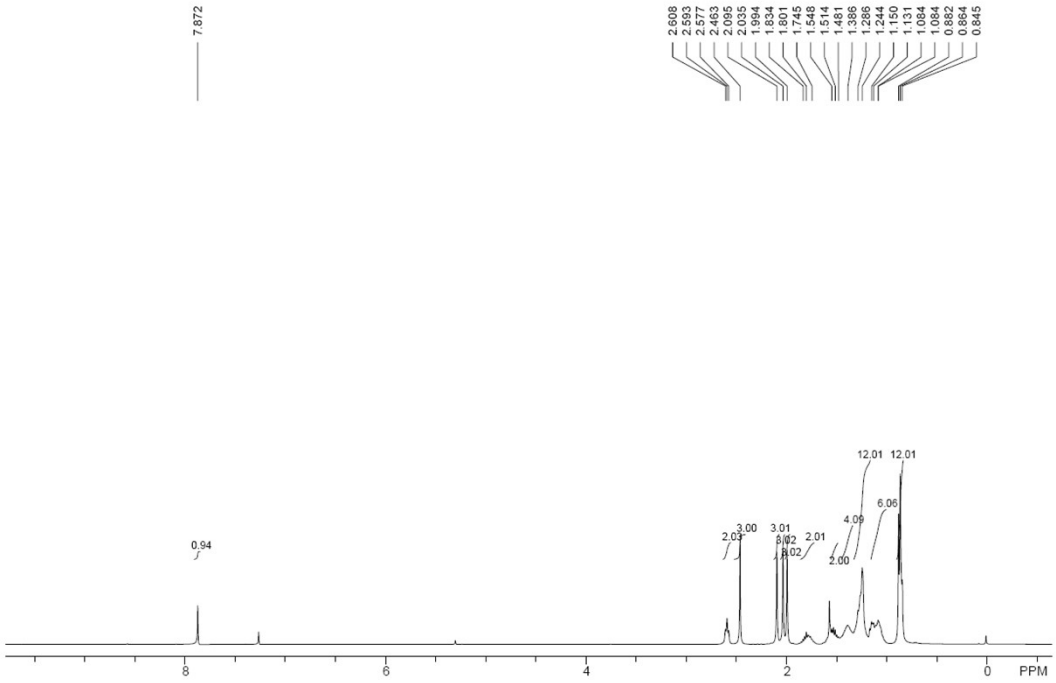
(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl (*E*)-2-iodo-3-(methylthio)acrylate (2w)

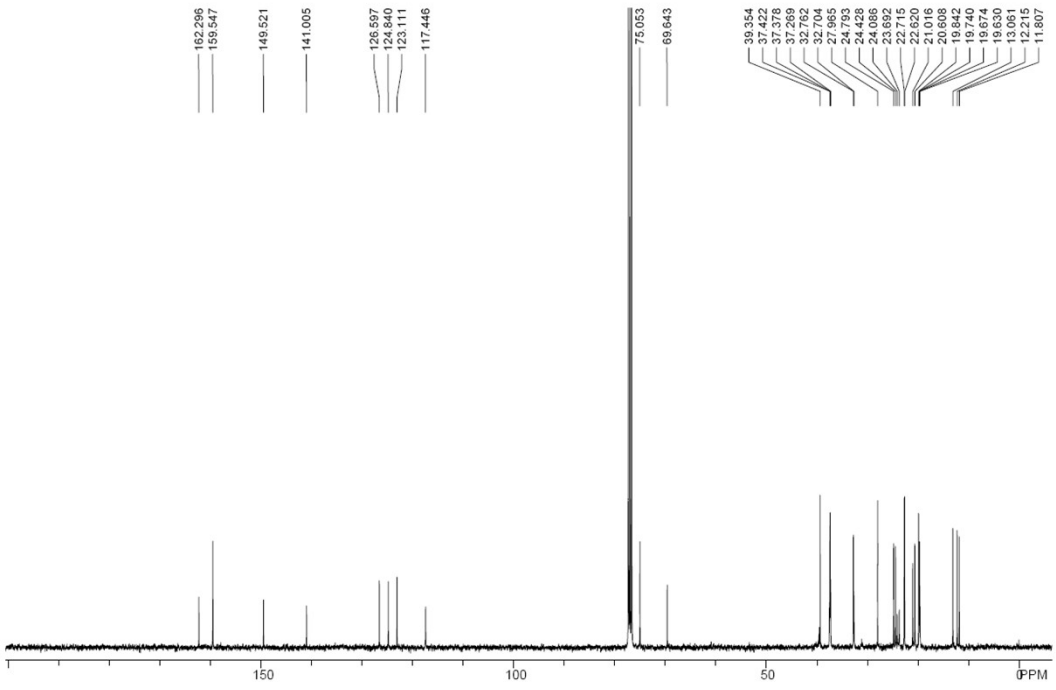


(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (*E*)-2-iodo-3-(methylthio)acrylate (2x)

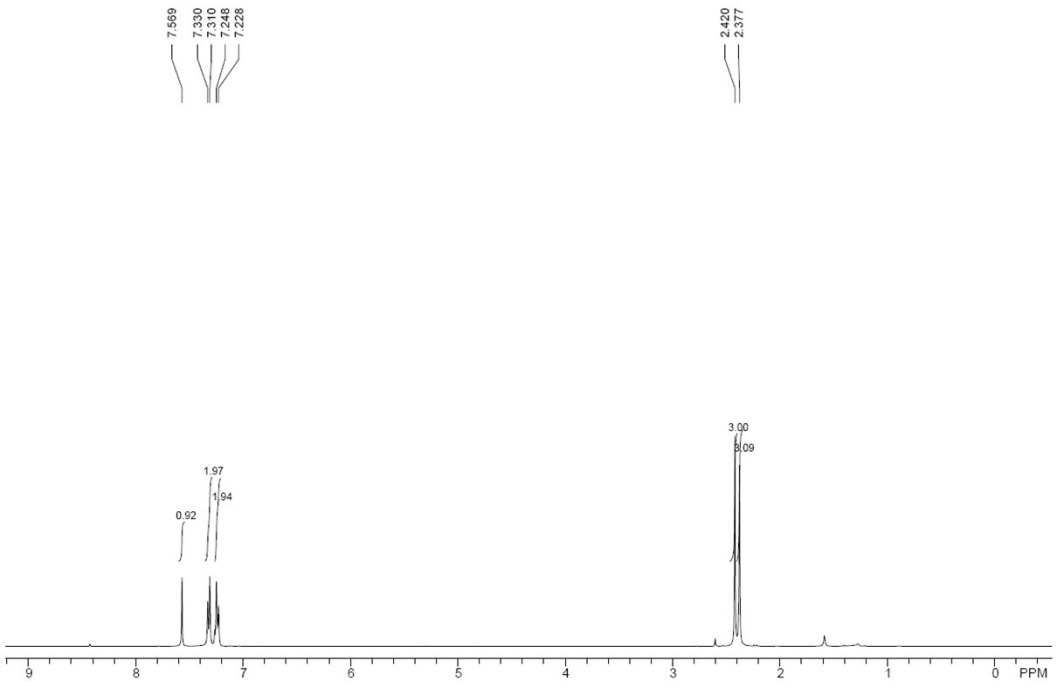


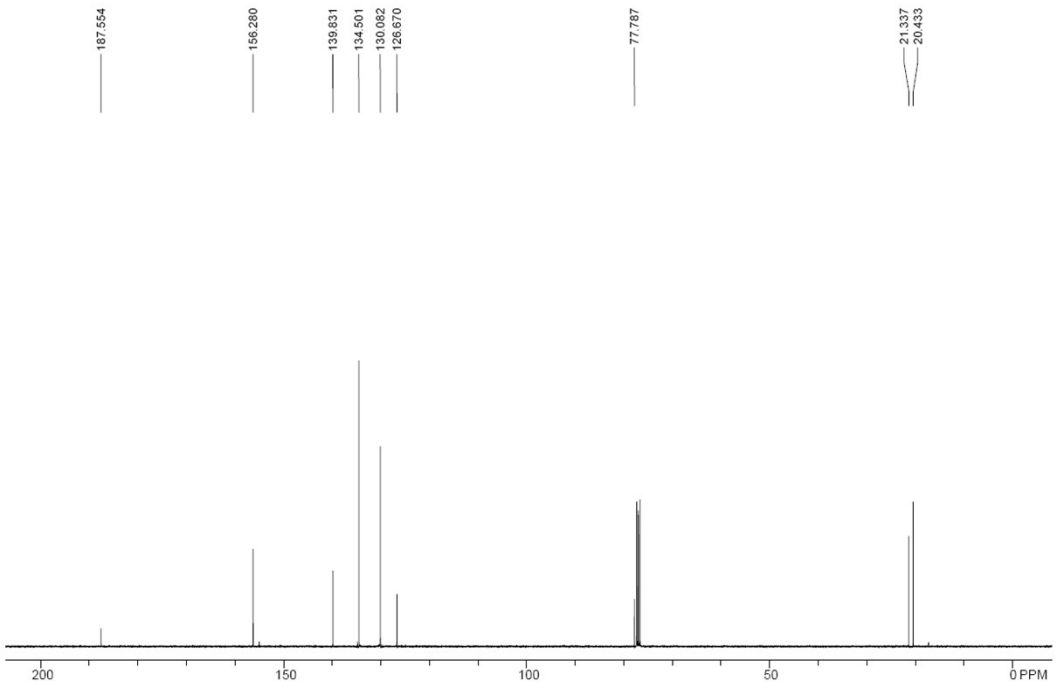
(S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl (*E*)-2-iodo-3-(methylthio)acrylate (2y)



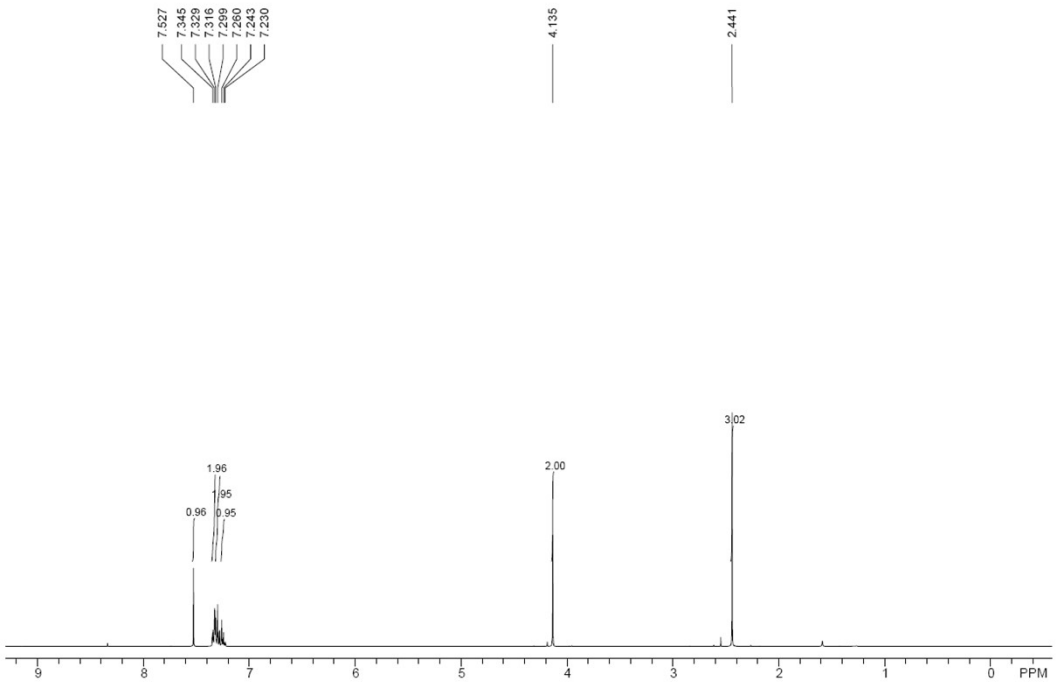


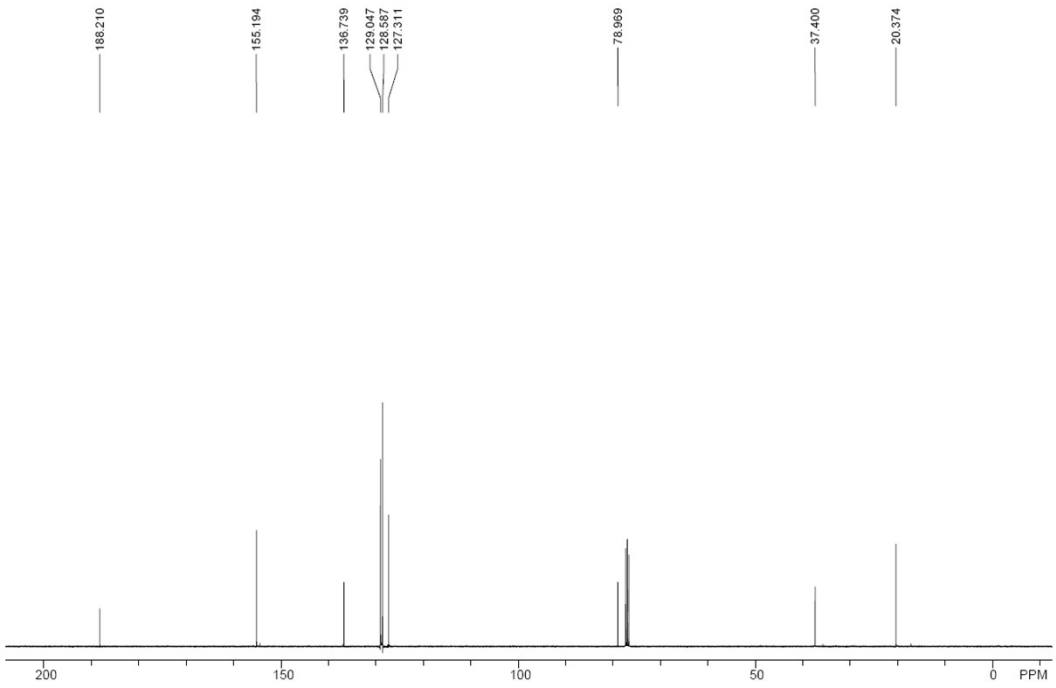
S-(p-tolyl) (*E*)-2-iodo-3-(methylthio)prop-2-enethioate (2z)



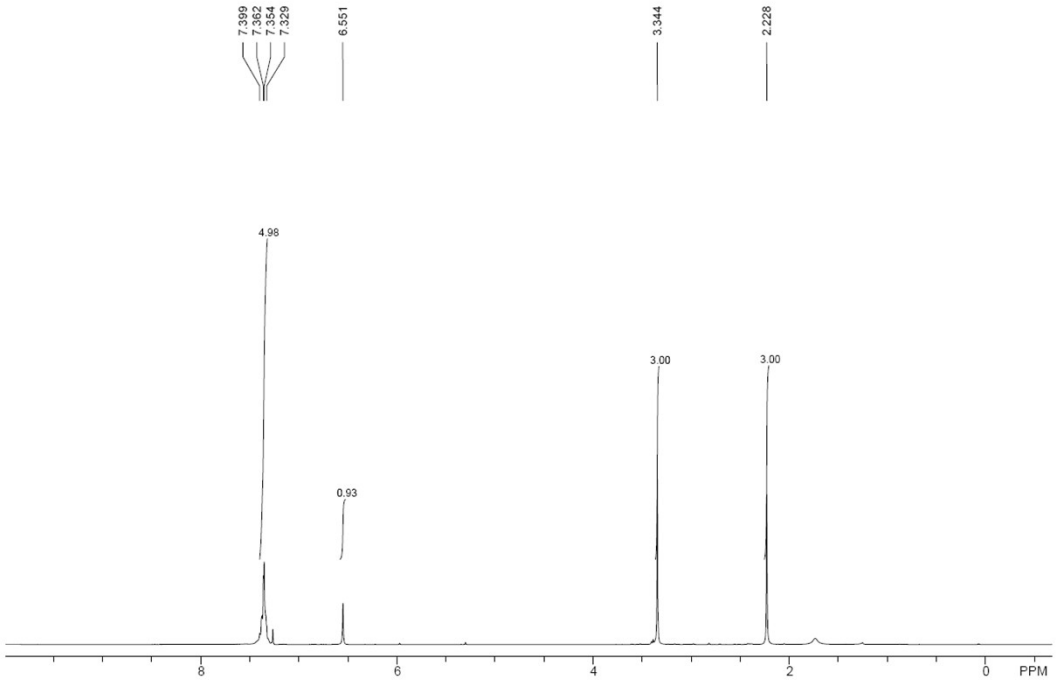


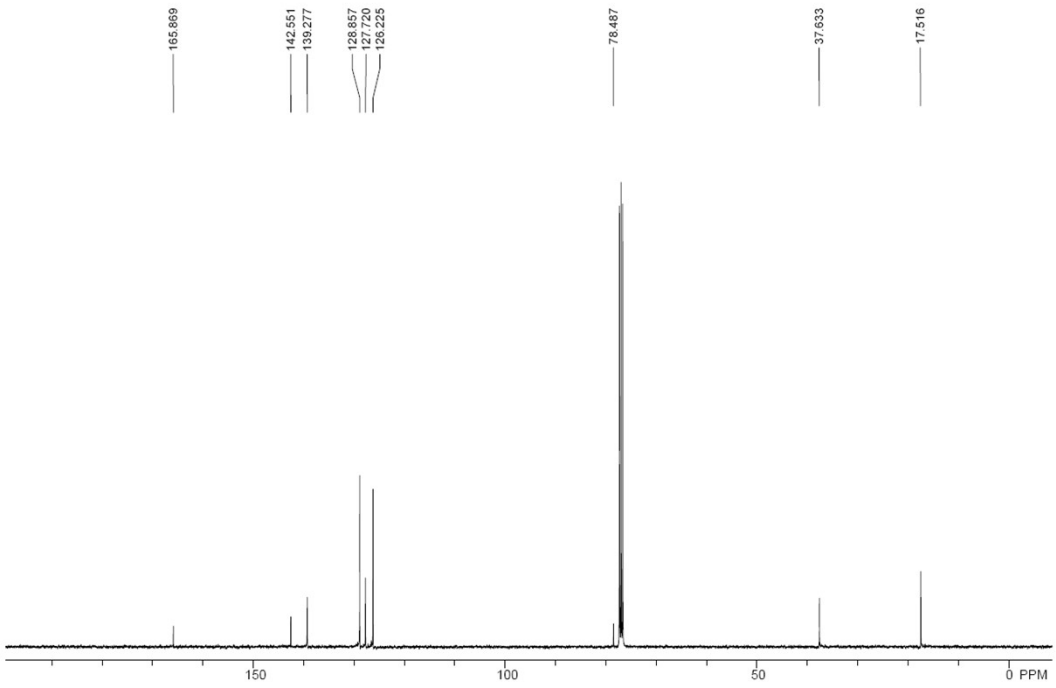
S-benzyl (*E*)-2-iodo-3-(methylthio)prop-2-enethioate (2aa)



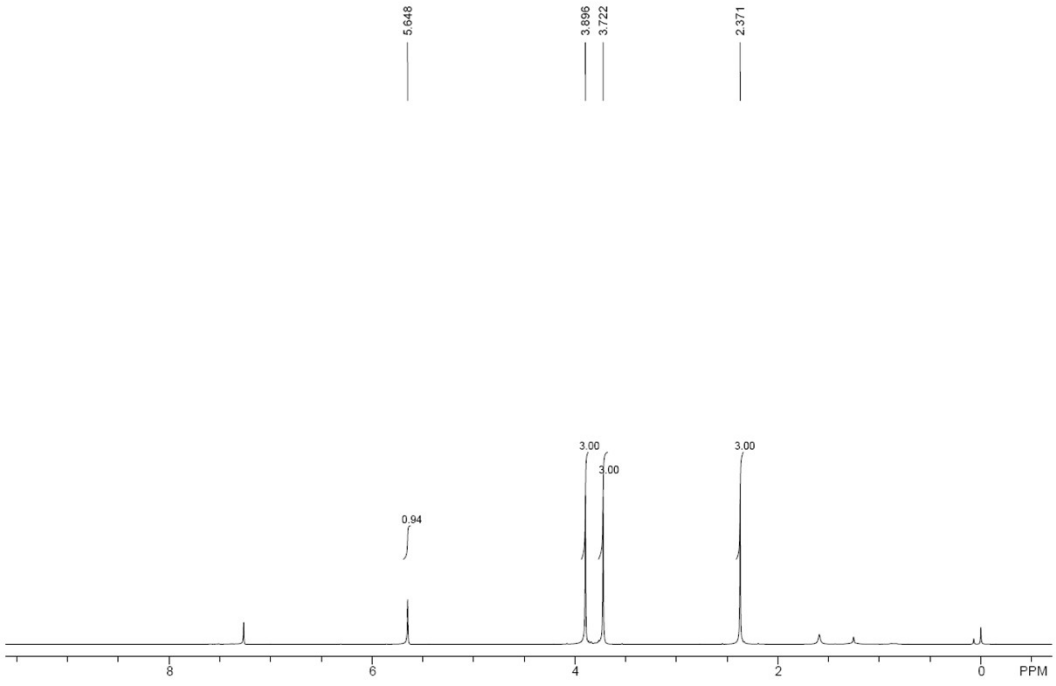


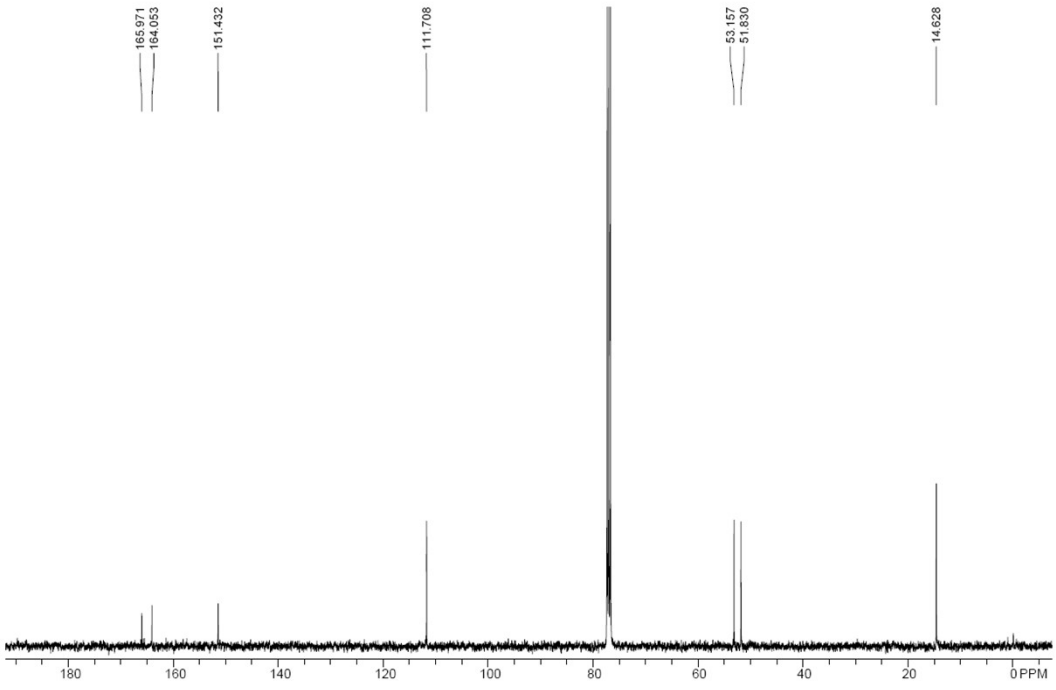
(*E*)-2-iodo-*N*-methyl-3-(methylthio)-*N*-phenylacrylamide (2ab)



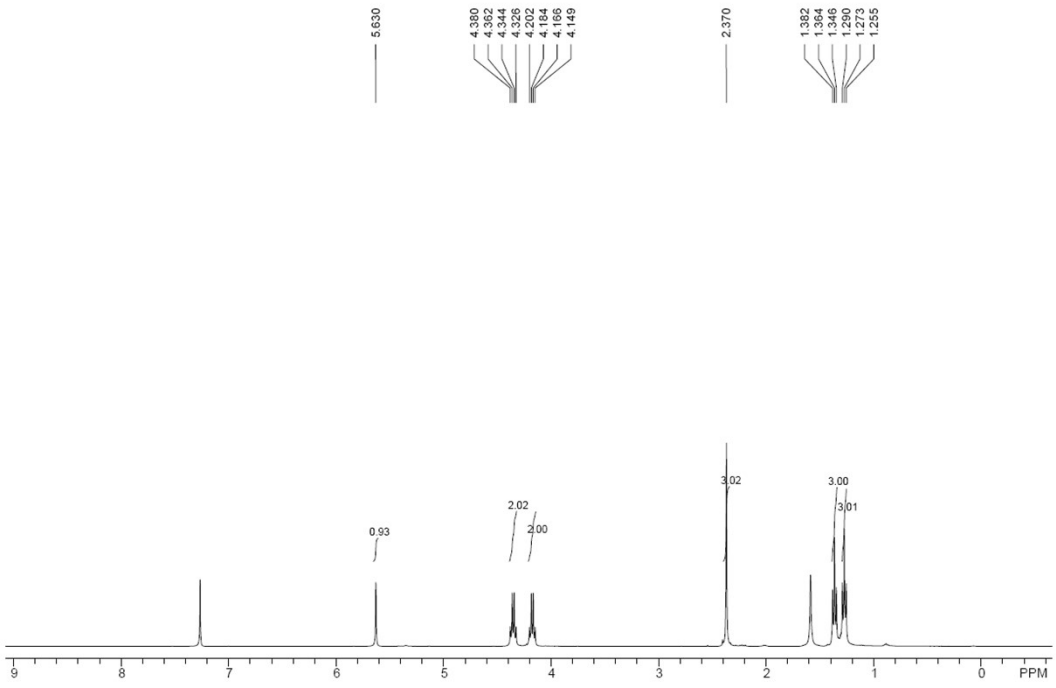


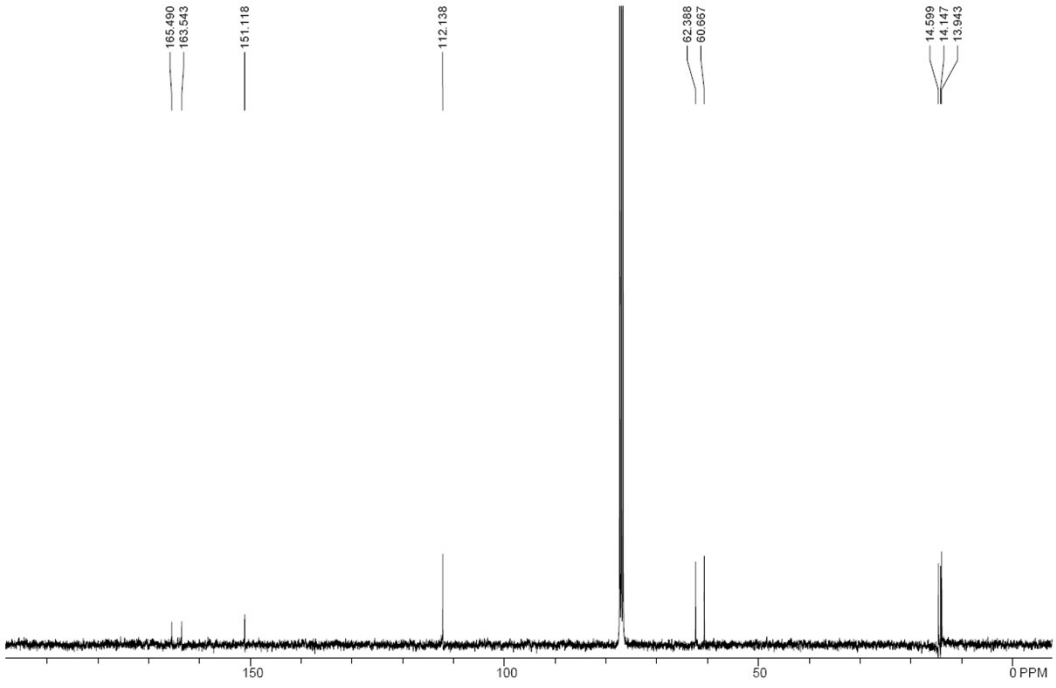
dimethyl 2-(methylthio)maleate (2ac)



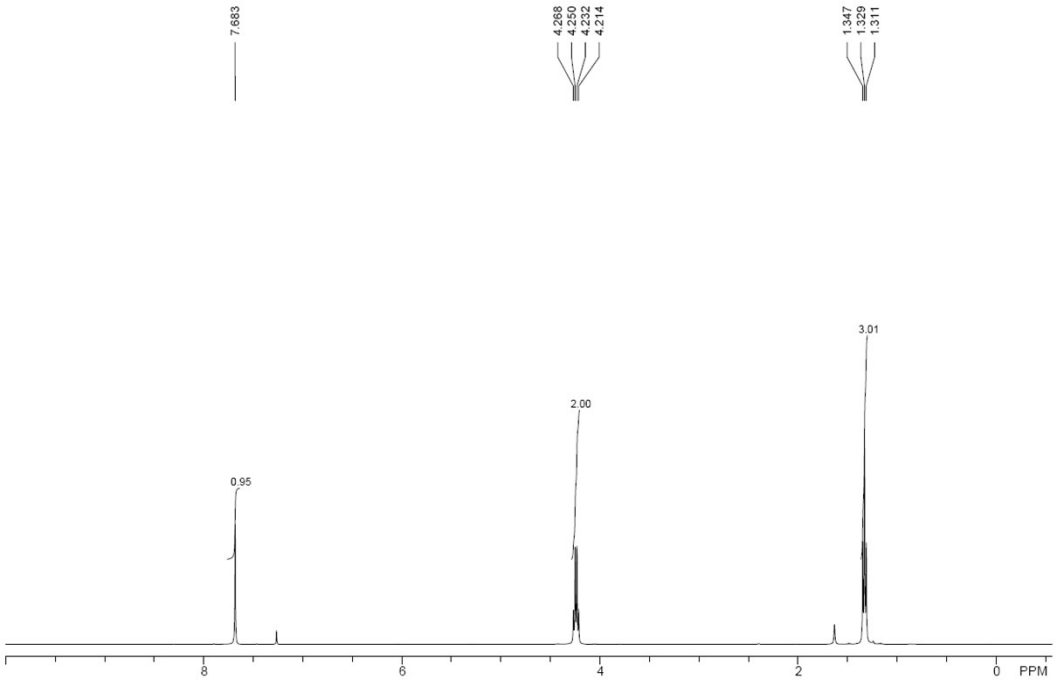


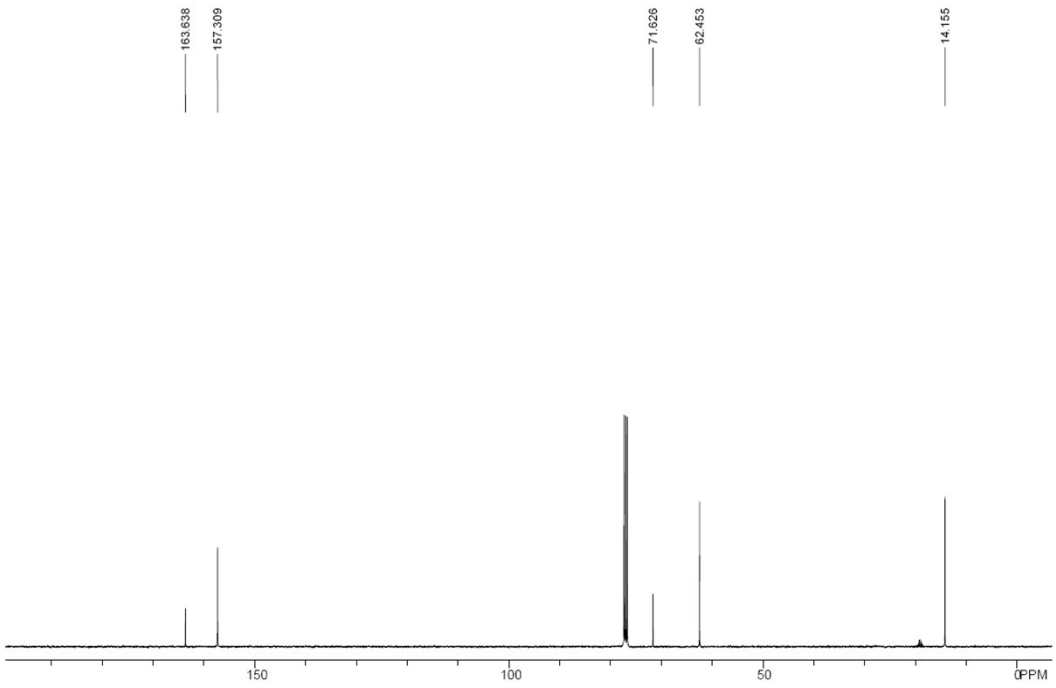
diethyl 2-(methylthio)maleate (2ad)



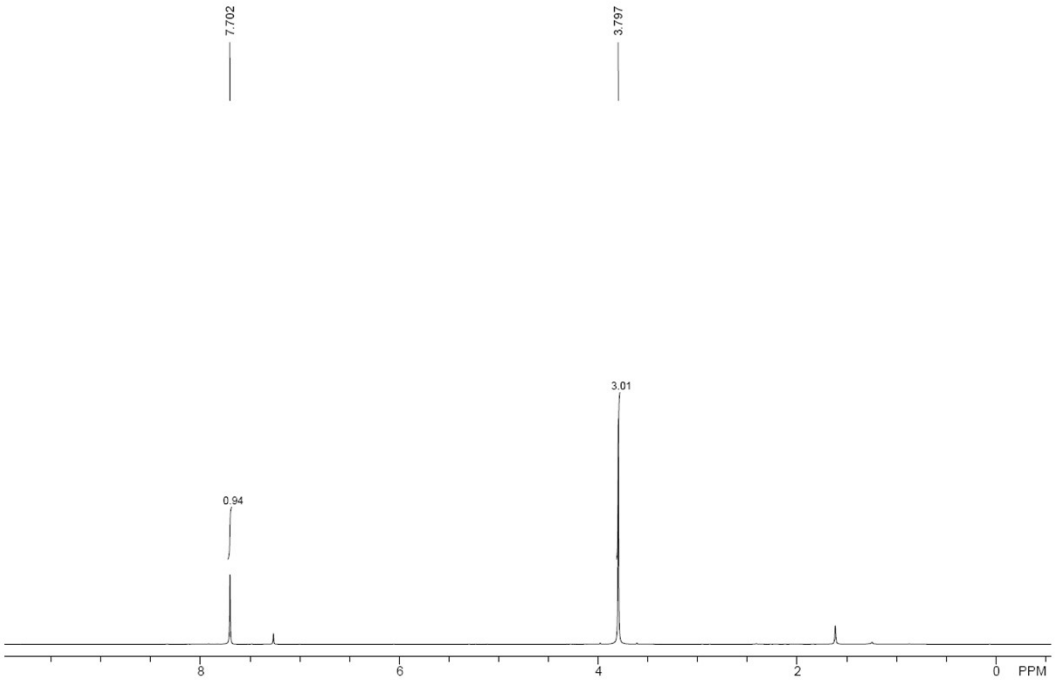


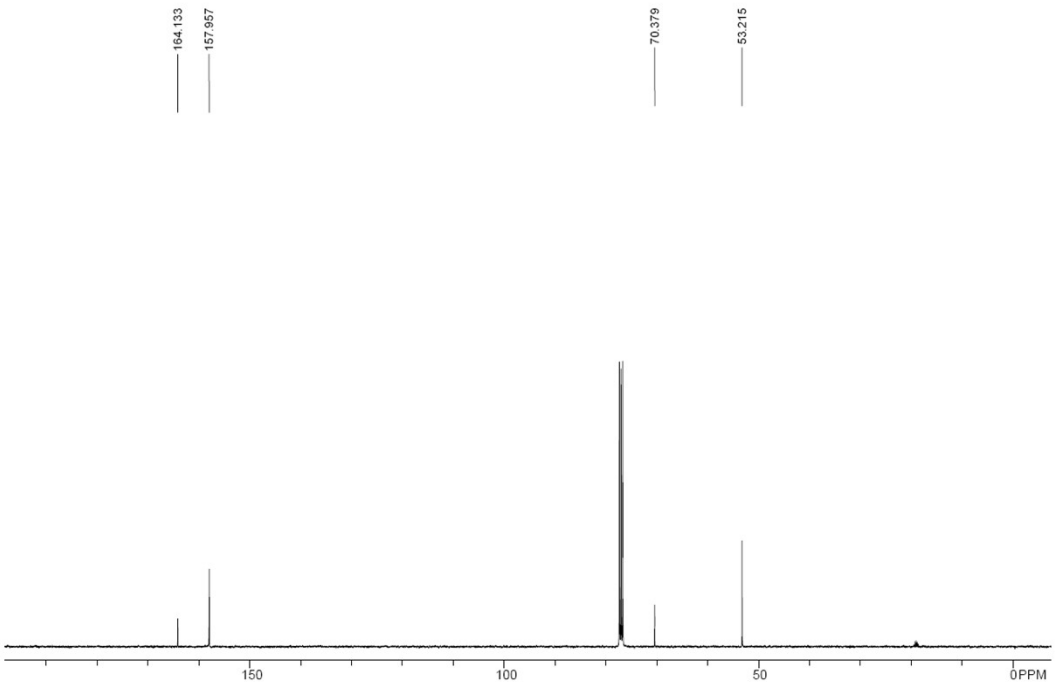
ethyl (*E*)-2-iodo-3-((methyl-d_3)thio)acrylate (2a-d3)



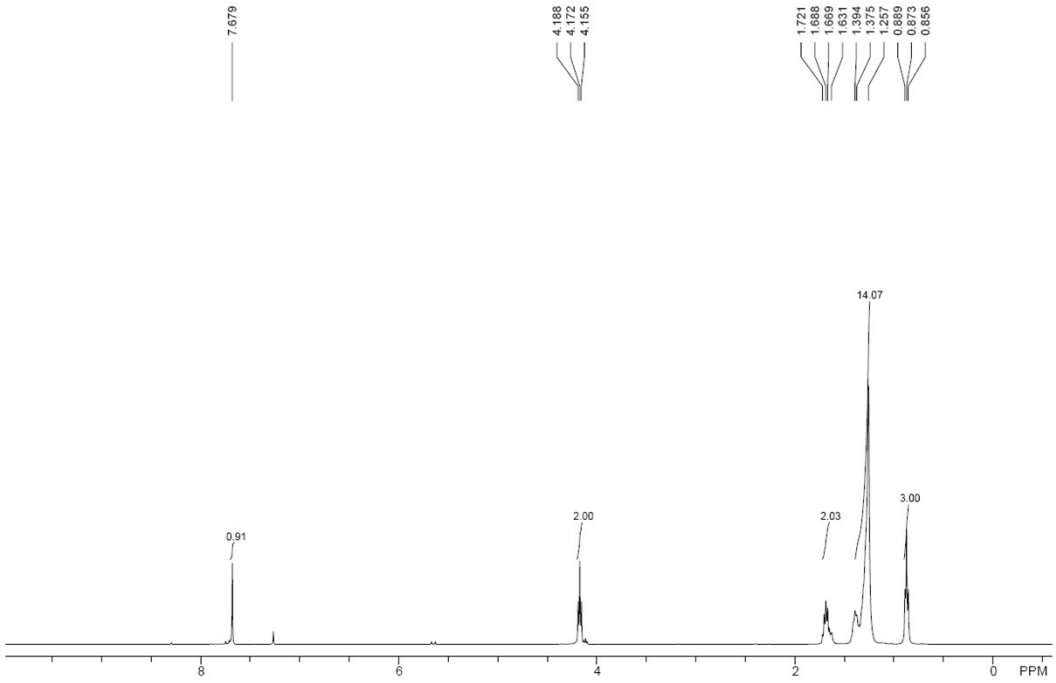


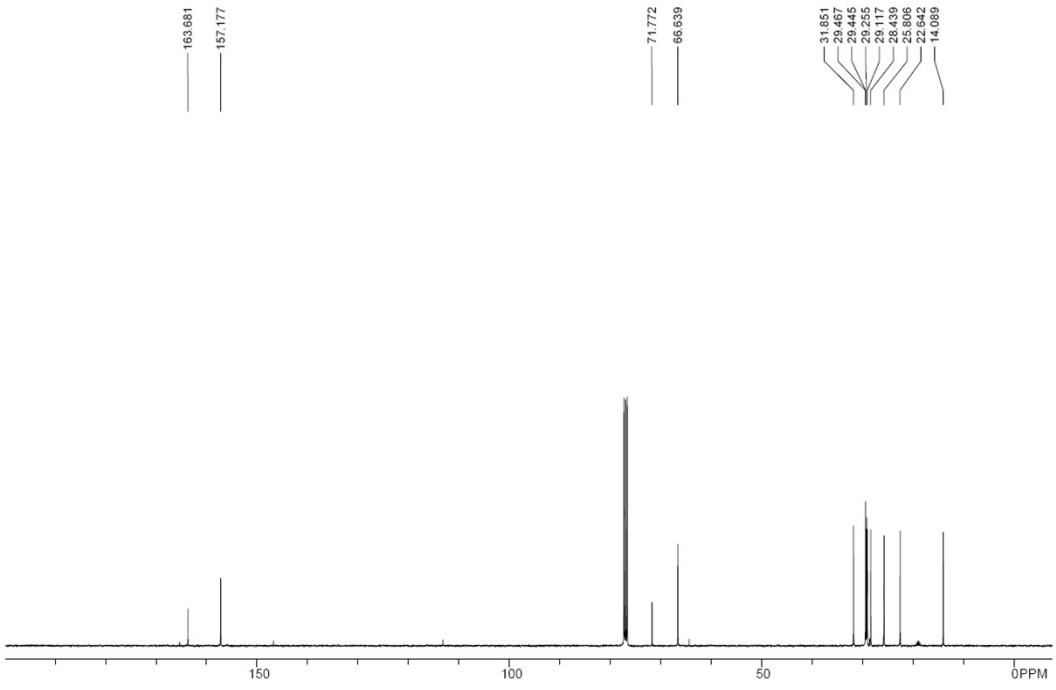
methyl (*E*)-2-iodo-3-((methyl-d_3)thio)acrylate (2b-d3)



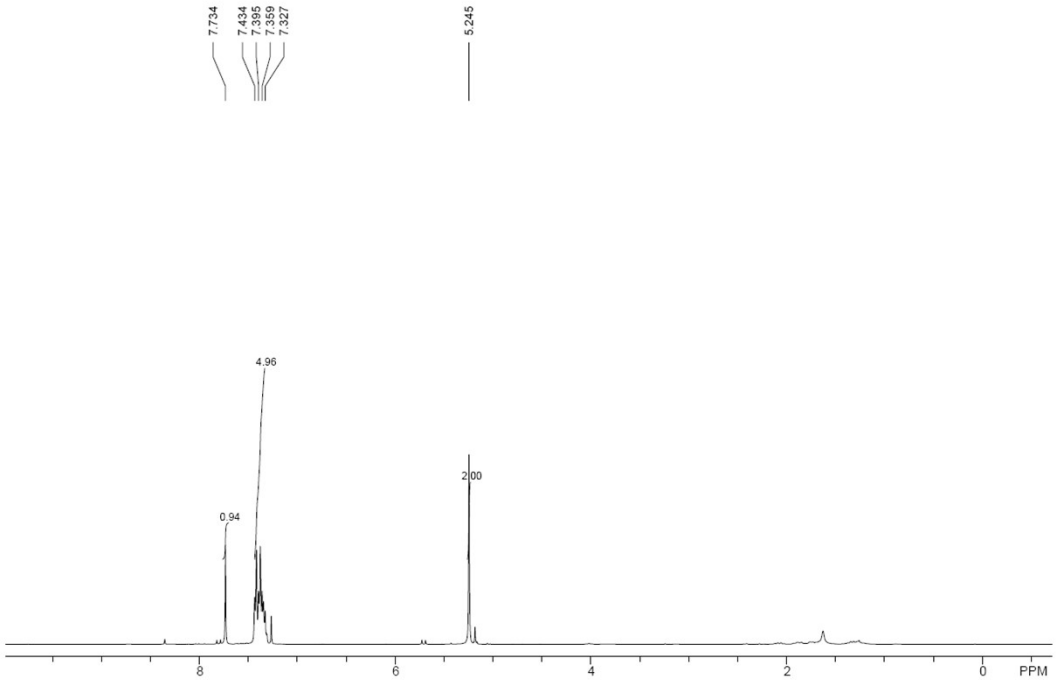


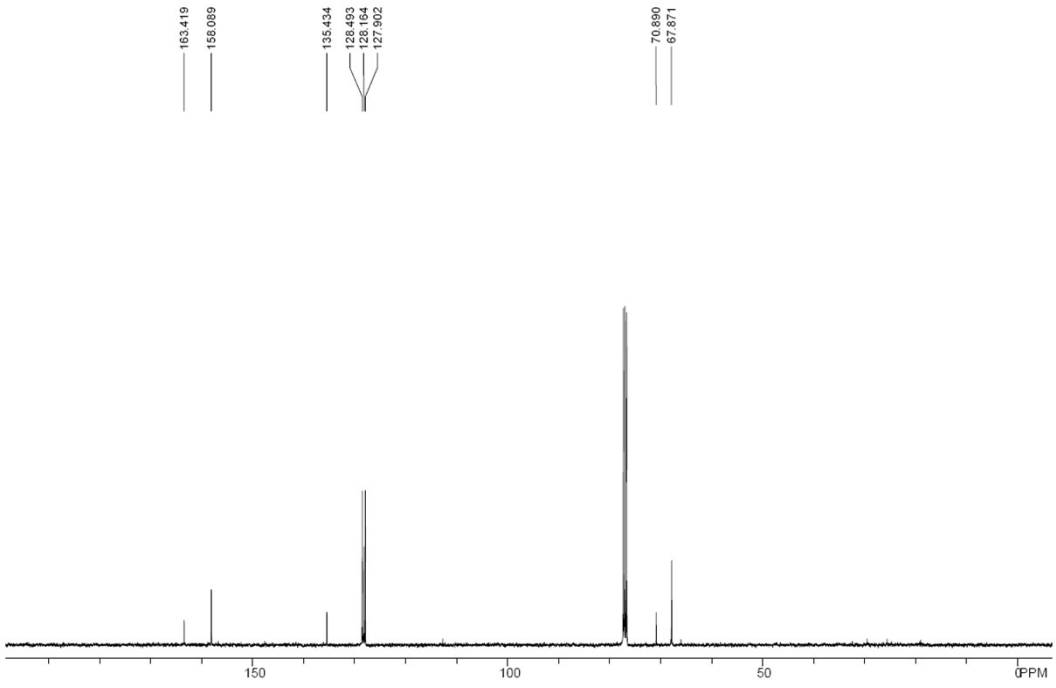
decyl (*E*)-2-iodo-3-((methyl-d_3)thio)acrylate (2d-d3)



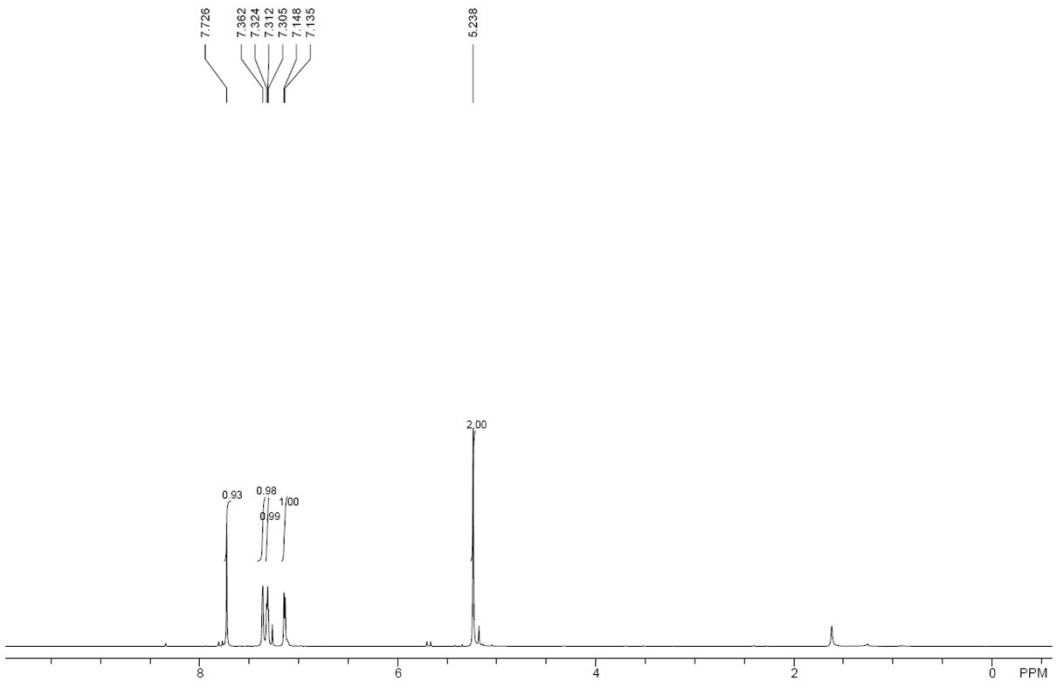


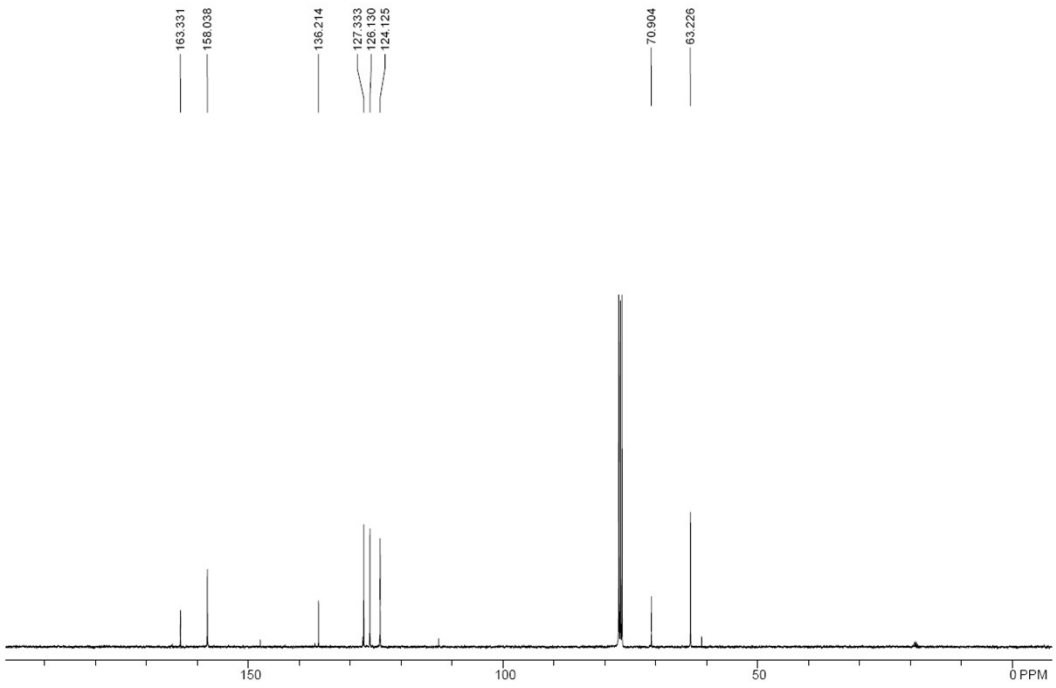
benzyl (*E*)-2-iodo-3-((methyl-d_3)thio)acrylate (2f-d3)



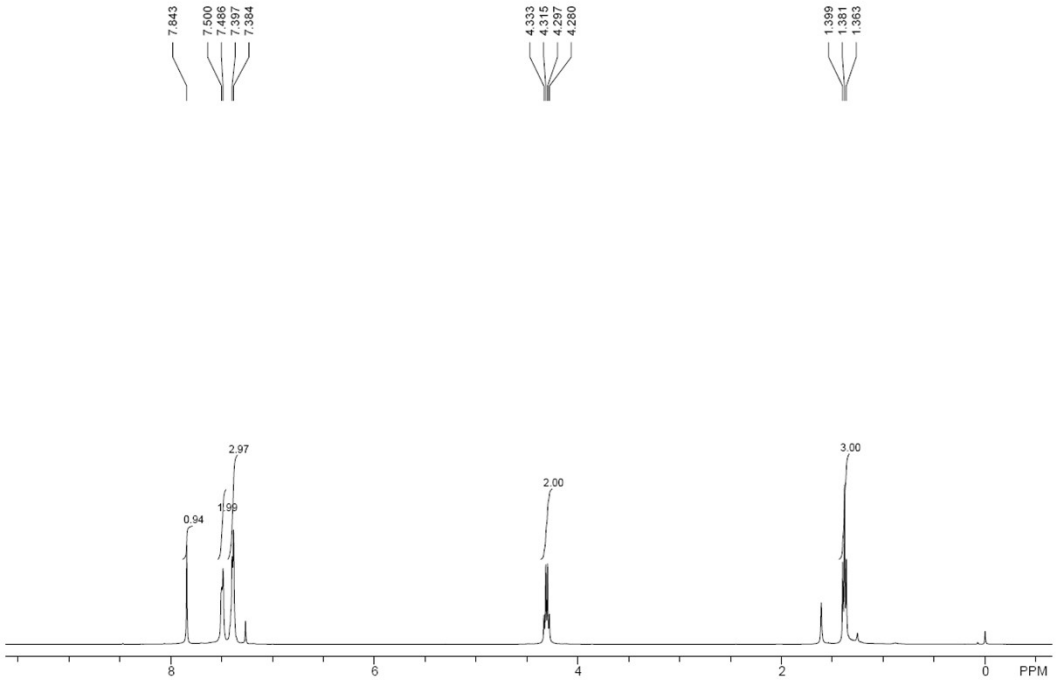


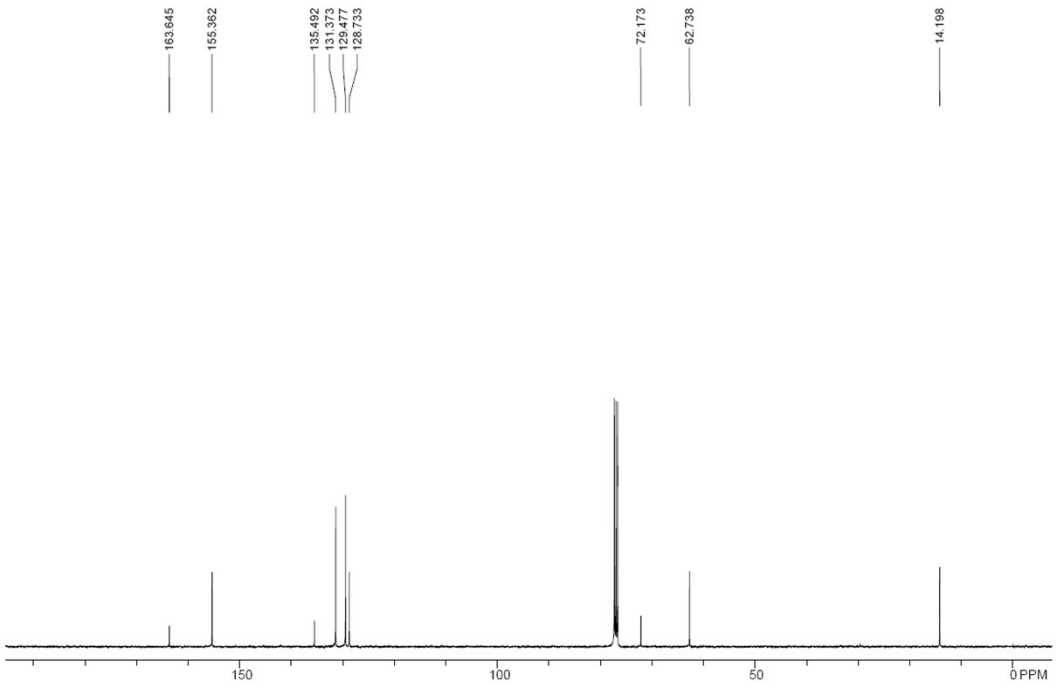
thiophen-2-ylmethyl (*E*)-2-iodo-3-((methyl-d_3)thio)acrylate (2p-d3)



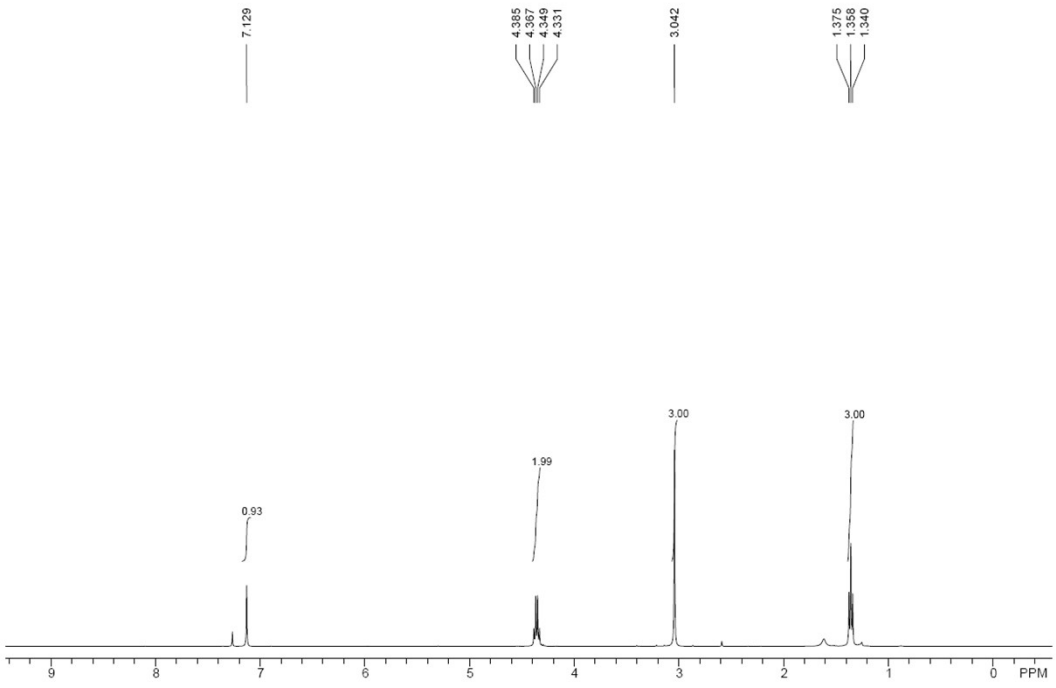


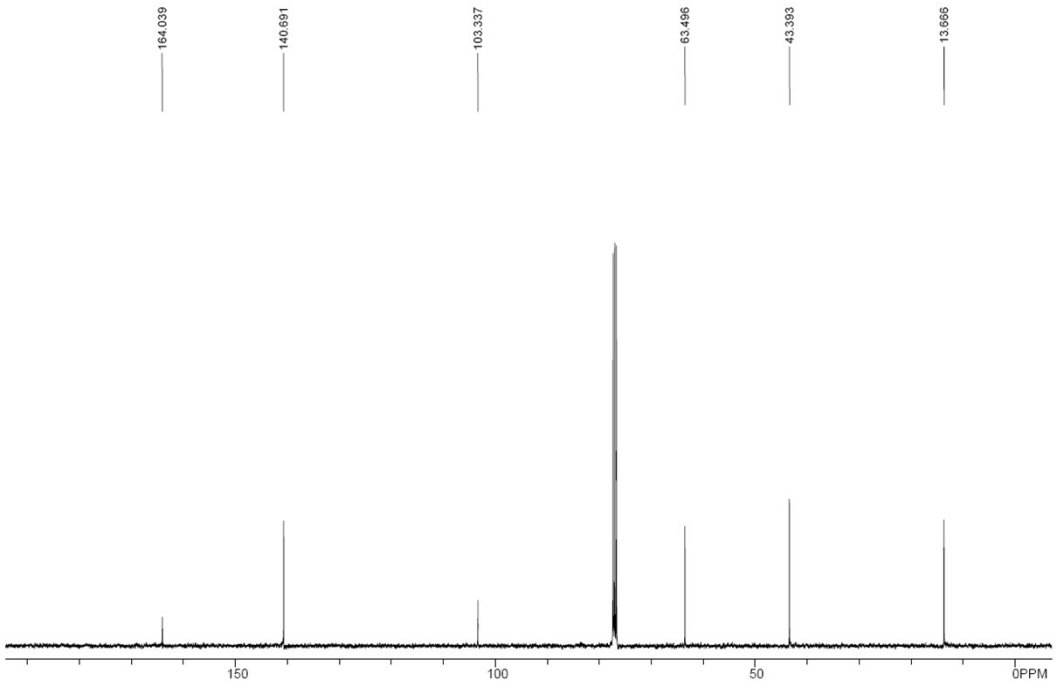
ethyl (*E*)-2-iodo-3-(phenylthio)acrylate (2ae)



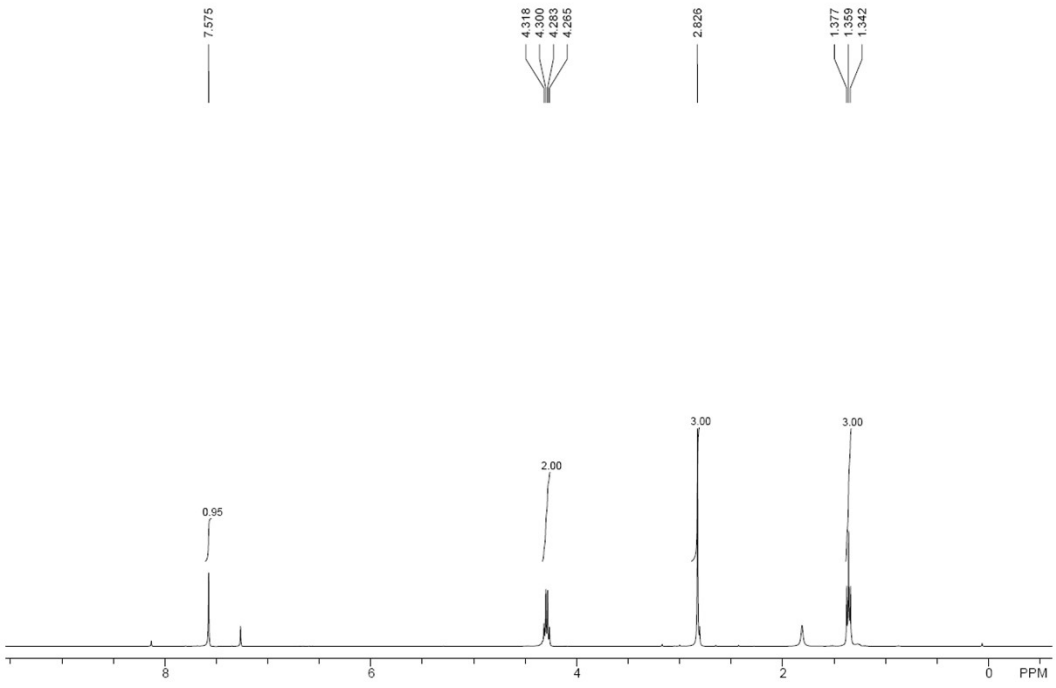


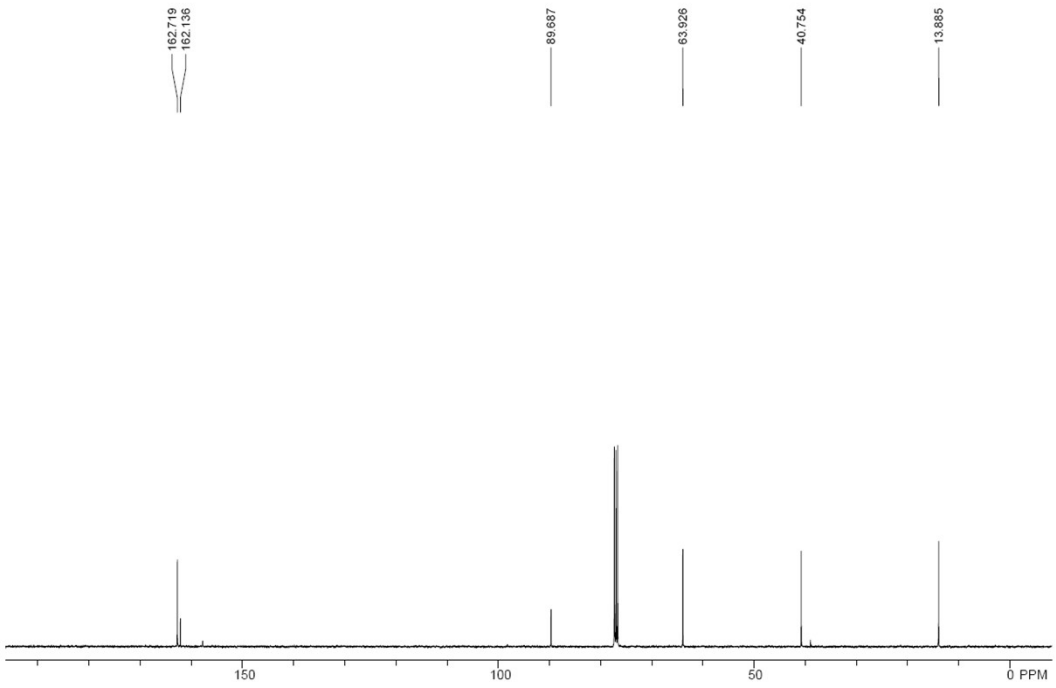
ethyl (*E*)-2-iodo-3-(methylsulfonyl)acrylate (3a)





ethyl (*E*)-2-iodo-3-(methylsulfinyl)acrylate (3b)





ethyl (*Z*)-2-((methylthio)methylene)-4-phenylbut-3-ynoate (3c)