Supporting Information

Ultrasound-promoted Brønsted acidic ionic liquid-catalyzed hydrothiocyanation of activated alkynes under minimal solvent conditions

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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. HRMS spectra spectra were performed on a spectrometer operating on EI.

The specification and details of the ultrasound set-up, processing parameters used during the experiments are:

Make: Yinyu Gaoke, China.

Operating frequency: 40 kHz.

Rated output power: 50 W.

Inner tank size: 150×135×65 mm.

2.1 General Procedure for the Synthesis of *Z*-vinyl thiocyanates 2

In a vial was placed alkyne (0.2 mmol), BAIL-1 (13mg, 0.04 mmol), KSCN (25mg, 0.26 mmol), water (4mg, 0.2 mmol), then the contents were reacted under ultrasound irradiation. Upon completion, the reaction mixture was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford **2**.

2.2 Recycling research of BAIL-1

In a pressure tube was consecutively placed ethyl propiolate (0.97 g, 10 mmol), BAIL-1 (0.60 g, 2 mmol), KSCN (1.27 g, 13 mmol) and H_2O (0.18 g, 10 mmol), then the mixtures were shaken at room temperature under ultrasound conditions, The progress of the reaction was monitored by TLC. Upon completion, 10 ml EtOAc was added to the reaction mixture. Then the mixture was filtered and the filtrate was product with high purity. The yield was estimated by gas chromatography. To the recycled BAIL-1, only 10 mmol of 1a, 13 mmol of KSCN, 10 mmol of H_2O were added to the filter residue, and the next cycle was carried out under the same reaction conditions.

3. Characterization Data

***ethyl (Z)-3-thiocyanatoacrylate (2a)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.8 Hz, 1H), 6.27 (d, J = 8.8 Hz, 1H), 4.26 (q, J = 6.8 Hz, 2H), 1.33 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 138.0, 119.8, 112.3, 61.6, 14.0. HRMS Calcd (EI) m/z for $C_6H_7NO_2S$: $[M]^+$ 157.0197, found: 157.0199.

***methyl (Z)-3-thiocyanatoacrylate (2b)*[1]:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 9.2 Hz, 1H), 6.27 (d, J = 9.2 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 138.4, 119.4, 112.1, 52.3.

***tert-butyl (Z)-3-thiocyanatoacrylate (2c)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 9.2 Hz, 1H), 6.17 (d, J = 9.2 Hz, 1H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 136.6, 121.6, 112.8, 83.0, 28.0. HRMS Calcd (EI) m/z for $C_8H_{11}NO_2S$: $[M]^+$ 185.0510, found: 185.0513.

***decyl (Z)-3-thiocyanatoacrylate (2d)*:** White solid, m.p. 68-70 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 9.2 Hz, 1H), 6.26 (d, J = 9.2 Hz, 1H), 4.19 (q, J = 4.0 Hz, 2H), 1.70–1.63(m, 2H), 1.26 (s, 14H), 0.88 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 138.1, 120.0, 112.4, 65.8, 31.9, 29.5, 29.4, 29.3, 29.1, 28.4, 25.8, 22.7, 14.1. HRMS Calcd (EI) m/z for $C_{14}H_{23}NO_2S$: $[M]^+$ 269.1449, found: 269.1447.

***benzyl (Z)-3-thiocyanatoacrylate (2e)*:** White solid, m.p. 91-92 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 5H), 7.17 (d, J = 9.2 Hz, 1H), 6.30 (d, J = 9.2 Hz, 1H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.7, 134.7, 128.7, 128.6, 128.5, 119.6, 112.1, 67.3. HRMS Calcd (EI) m/z for $C_{11}H_9NO_2S$: $[M]^+$ 219.0354, found: 219.0350.

***phenethyl (Z)-3-thiocyanatoacrylate (2f)*:** White solid, m.p. 85-86 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 2H), 7.28–7.26 (m, 1H), 7.24–7.22 (m, 2H), 7.14 (d, J = 9.6 Hz, 1H), 6.26 (d, J = 9.6 Hz, 1H), 4.42 (d, J = 6.8 Hz, 2H), 3.00 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 138.4, 137.1, 128.8, 128.6, 126.8, 119.6, 112.3, 66.0. HRMS Calcd (EI) m/z for $C_{12}H_{11}NO_2S$: $[M]^+$ 233.0510, found: 233.0514.

***cyclohexyl (Z)-3-thiocyanatoacrylate (2g)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 9.2 Hz, 1H), 6.25 (d, J = 9.2 Hz, 1H), 4.87–4.82 (m, 1H), 1.92–1.87 (m, 2H),

1.77–1.73 (m, 2H), 1.51–1.25 (m, 6H),. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 137.7, 120.4, 112.6, 74.5, 31.5, 25.2, 23.7. HRMS Calcd (EI) m/z for $C_{10}H_{13}NO_2S$: $[M]^+$ 211.0667, found: 211.0665.

phenyl (Z)-3-thiocyanatoacrylate (2h)[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.35 (d, J = 9.2 Hz, 1H), 7.30–7.26 (m, 1H), 7.15–7.13 (m, 2H), 6.51 (d, J = 9.2 Hz 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 149.8, 140.7, 129.6, 126.5, 121.1, 119.1, 111.8.

2-hydroxyethyl (Z)-3-thiocyanatoacrylate (2i)**:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 9.2 Hz, 1H), 6.32 (d, J = 9.2 Hz, 1H), 4.34 (t, J = 4.8 Hz, 2H), 3.89 (t, J = 4.8 Hz, 2H), 1.80 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 139.1, 119.4, 112.1, 67.0, 60.8. HRMS Calcd (EI) m/z for $C_6H_7NO_3S$: $[M]^+$ 173.0147, found: 173.0142.

2-butoxyethyl (Z)-3-thiocyanatoacrylate (2j)**:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 9.2 Hz, 1H), 6.32 (d, J = 9.2 Hz, 1H), 4.34 (t, J = 4.8 Hz, 2H), 3.66 (t, J = 4.8 Hz, 2H), 3.48 (t, J = 6.8 Hz, 2H), 1.60–1.53 (m, 2H), 1.41–1.32 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 138.5, 119.7, 112.2, 71.2, 68.1, 64.7, 31.6, 19.2, 13.9. HRMS Calcd (EI) m/z for $C_{10}H_{15}NO_3S$: $[M]^+$ 229.0773, found: 229.0776.

2-(benzyloxy)ethyl (Z)-3-thiocyanatoacrylate (2k)**:** White solid, m.p. 104-106 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H), 7.17 (d, J = 9.2 Hz, 1H), 6.31 (d, J = 9.2 Hz, 1H), 4.57 (s, 2H), 4.37 (t, J = 4.8 Hz, 2H), 3.71 (t, J = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 138.6, 137.5, 128.5, 127.9, 127.8, 119.6, 112.2, 73.2, 67.4, 64.6. HRMS Calcd (EI) m/z for $C_{13}H_{13}NO_3S$: $[M]^+$ 263.0616, found: 263.0618.

2-(tosyloxy)ethyl (Z)-3-thiocyanatoacrylate (2l)**:** White solid, m.p. 112-113 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 9.2 Hz, 1H), 6.20 (d, J = 9.2 Hz, 1H), 4.36 (t, J = 4.4 Hz, 2H), 4.25 (t, J = 4.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 145.3, 139.4, 132.4, 130.0, 127.9, 119.0, 111.8, 66.9, 62.6. HRMS Calcd (EI) m/z for $C_{13}H_{13}NO_5S_2$: $[M]^+$ 327.0235, found: 327.0232.

***2-cyanoethyl (Z)-3-thiocyanatoacrylate (2m)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 9.2 Hz, 1H), 6.32 (d, J = 9.2 Hz, 1H), 4.40 (t, J = 6.4 Hz, 2H), 3.77 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 140.2, 118.6, 116.3, 111.6, 59.6, 17.9. HRMS Calcd (EI) m/z for $C_7H_6N_2O_2S$: $[M]^+$ 182.0150, found: 182.0145.

***2-bromoethyl (Z)-3-thiocyanatoacrylate (2n)*:** Light yellow solid, m.p. 94-96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 9.6 Hz, 1H), 6.31 (d, J = 9.6 Hz, 1H), 4.49 (t, J = 6.0 Hz, 2H), 3.54 (t, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.4, 119.1, 111.8, 64.6, 27.9. HRMS Calcd (EI) m/z for $C_6H_6NO_2SBr$: $[M]^+$ 234.9303, found: 234.9300.

***2-azidoethyl (Z)-3-thiocyanatoacrylate (2o)*:** White solid, m.p. 82-83 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 9.2 Hz, 1H), 6.32 (d, J = 9.2 Hz, 1H), 4.36 (t, J = 5.2 Hz, 2H), 3.56 (t, J = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.6, 119.1, 63.9, 49.5. HRMS Calcd (EI) m/z for $C_6H_6N_4O_2S$: $[M]^+$ 198.0211, found: 198.0207.

***naphthalen-2-yl (Z)-3-thiocyanatoacrylate (2p)*:** White solid, m.p. 110-112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.82 (m, 3H), 7.63 (d, J = 2.4 Hz, 1H), 7.55–7.49 (m, 2H), 7.38 (d, J = 9.2 Hz, 1H), 7.28–7.25 (m, 1H), 6.56 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 147.5, 140.9, 133.6, 131.7, 129.7, 127.8, 127.7, 126.8, 126.1, 120.3, 119.1, 118.3, 111.8. HRMS Calcd (EI) m/z for $C_{14}H_9NO_2S$: $[M]^+$ 255.0354, found: 255.0352.

***furan-2-ylmethyl (Z)-3-thiocyanatoacrylate (2q)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.44 (m, 1H), 7.18 (d, J = 9.2 Hz, 1H), 6.46 (d, J = 3.2 Hz, 1H), 6.39–6.38 (m, 1H), 6.28 (d, J = 9.2 Hz, 1H), 5.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 148.3, 143.7, 139.0, 119.4, 112.1, 111.5, 110.7, 58.9. HRMS Calcd (EI) m/z for $C_9H_7NO_3S$: $[M]^+$ 209.0147, found: 209.0149.

***thiophen-2-ylmethyl (Z)-3-thiocyanatoacrylate (2r)*:** White solid, m.p. 83-84 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 2H), 7.17 (d, J = 9.2 Hz, 1H), 7.12–7.10 (m, 1H), 6.29 (d, J = 9.2 Hz, 1H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.7,

135.5, 127.6, 126.6, 125.3, 119.5, 112.2, 62.1. HRMS Calcd (EI) m/z for $C_9H_7NO_2S_2$: $[M]^+$ 224.9918, found: 224.9914.

***quinolin-5-yl (Z)-3-thiocyanatoacrylate (2s)*:** White solid, m.p. 117-119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99–8.97 (m, 1H), 8.20–8.17 (m, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.77–7.73 (m, 1H), 7.48 (d, J = 9.2 Hz, 1H), 7.48–7.42 (m, 1H), 7.41 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 151.1, 142.1, 129.6, 128.7, 128.2, 121.7, 121.6, 120.7, 118.5, 118.4, 111.5. HRMS Calcd (EI) m/z for $C_{13}H_8N_2O_2S$: $[M]^+$ 256.0306, found: 256.0301.

***benzo[d][1,3]dioxol-5-yl (Z)-3-thiocyanatoacrylate (2t)*:** White solid, m.p. 91-92 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 9.2 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 2.4 Hz, 1H), 6.60–6.57 (m, 1H), 6.47 (d, J = 9.2 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 148.1, 145.9, 144.1, 140.8, 119.0, 113.6, 108.1, 103.2, 101.9. HRMS Calcd (EI) m/z for $C_{11}H_7NO_4S$: $[M]^+$ 249.0096, found: 249.0099.

***cinnamyl (Z)-3-thiocyanatoacrylate (2u)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.40 (m, 2H), 7.37–7.29 (m, 3H), 7.18 (d, J = 9.6 Hz, 1H), 6.71 (d, J = 16.0 Hz, 1H), 6.33–6.26 (m, 1H), 6.31 (d, J = 9.6 Hz, 1H), 4.86 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.6, 135.7, 135.4, 128.6, 128.3, 126.6, 121.8, 119.5, 112.2, 66.1. HRMS Calcd (EI) m/z for $C_{13}H_{11}NO_2S$: $[M]^+$ 245.0510, found: 245.0507.

***(4-(prop-1-en-2-yl)cyclohex-2-en-1-yl)methyl (Z)-3-thiocyanatoacrylate (2v)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.30 (m, 1H), 7.25–7.23 (m, 1H), 7.16 (d, J = 9.2 Hz, 1H), 6.29 (d, J = 9.2 Hz, 1H), 4.74 (t, J = 1.4 Hz, 1H), 4.71 (t, J = 1.4 Hz, 1H), 4.58 (s, 2H), 2.94–2.88 (m, 1H), 2.02–1.98 (m, 1H), 1.89–1.85 (m, 2H), 1.74 (s, 3H), 1.53–1.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 149.3, 138.3, 131.5, 127.5, 126.8, 119.8, 112.3, 70.3, 40.6, 30.4, 27.2, 26.3, 20.7. HRMS Calcd (EI) m/z for $C_{14}H_{17}NO_2S$: $[M]^+$ 263.0980, found: 263.0974.

***ethyl (Z)-3-thiocyanatobut-2-enoate (2x)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (q, J = 1.2 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 2.47 (d, J = 1.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 146.7, 117.3, 110.3, 61.2, 25.8, 14.1.

HRMS Calcd (EI) m/z for $C_7H_9NO_2S$: $[M]^+$ 171.0354, found: 171.0352. The long range coupling constant for methyl and C-H is 1.2 Hz, which is very close to the similar structure ((*Z*)-(2-thiocyanatoprop-1-en-1-yl)benzene) reported in the literature (1.4 Hz).[1] The coupling constant is slightly different because there is a different substituent group on the olefin.

***ethyl (E)-3-bromo-3-thiocyanatoacrylate (2y)*:** White solid, m.p. 88-90 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 126.2, 124.8, 109.4, 61.9, 14.0. HRMS Calcd (EI) m/z for $C_6H_6NO_2SBr$: $[M]^+$ 234.9303, found: 234.9307.

***ethyl (Z)-4,4,4-trifluoro-3-thiocyanatobut-2-enoate (2z)*:** White solid, m.p. 94-95 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 136.0 (q, J = 35.0 Hz), 124.1, 123.6 (q, J = 5.1 Hz), 120.0 (q, J = 174.2 Hz), 106.6, 62.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5. HRMS Calcd (EI) m/z for $C_7H_6NO_2SF_3$: $[M]^+$ 225.0071, found: 225.0074.

***diethyl 2-thiocyanatofumarate (2aa)*:** White solid, m.p. 77-79 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 4.40 (q, J = 7.2 Hz, 2H), 4.27 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 161.3, 138.0, 126.3, 108.7, 63.9, 62.2, 14.0, 13.8. HRMS Calcd (EI) m/z for $C_9H_{11}NO_4S$: $[M]^+$ 229.0409, found: 229.0404.

***(Z)-4-thiocyanatobut-3-en-2-one (2ab)*[3]:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 138.2, 124.8, 113.5, 29.9.

***S-phenyl (Z)-3-thiocyanatoprop-2-enethioate (2ac)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 5H), 7.04 (d, J = 8.8 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 135.3, 134.4, 130.2, 129.5, 125.7, 124.1, 112.3. HRMS Calcd (EI) m/z for $C_{10}H_7NOS_2$: $[M]^+$ 220.9969, found: 220.9974.

***S-benzyl (Z)-3-thiocyanatoprop-2-enethioate (2ad)*:** Light yellow solid, m.p. 87-88 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 5H), 6.96 (d, J = 9.2 Hz, 1H), 6.55 (d, J = 9.2 Hz, 1H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 136.2, 134.0, 128.9, 128.8, 127.7, 124.7, 112.4, 33.5. HRMS Calcd (EI) m/z for $C_{11}H_9NOS_2$: $[M]^+$ 235.0126, found: 235.0124.

***(Z)-N-phenyl-3-thiocyanatoacrylamide (2ae)*:** White solid, m.p. 74-76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 6.4 Hz, 1H), 7.59–7.56 (m, 2H), 7.47–7.43 (m, 2H), 7.36–7.31 (m, 1H), 6.34 (d, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 139.5, 136.4, 129.4, 128.9, 127.5, 124.8, 114.9. HRMS Calcd (EI) m/z for $C_{10}H_8N_2OS$: $[M]^+$ 204.0357, found: 204.0353.

***(Z)-N-octyl-3-thiocyanatoacrylamide (2af)*:** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 10.0 Hz, 1H), 6.32 (d, J = 10.0 Hz, 1H), 5.83 (brs, 1H), 3.33 (q, J = 6.8 Hz, 2H), 1.57–1.50 (m, 2H), 1.34–1.27 (m, 2H), 2.55 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 126.3, 125.9, 107.4, 39.9, 31.7, 29.4, 29.2, 29.1, 26.9, 22.6, 14.1. HRMS Calcd (EI) m/z for $C_{12}H_{20}N_2OS$: $[M]^+$ 240.1296, found: 240.1298.

***(Z)-N-methyl-N-phenyl-3-thiocyanatoacrylamide (2ag)*:** White solid, m.p. 77-78 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.37 (m, 3H), 7.20–7.17 (m, 2H), 6.87 (d, J = 8.8 Hz, 1H), 6.10 (d, J = 8.8 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.3, 136.0, 130.0, 128.4, 128.3, 127.0, 118.8, 37.1. HRMS Calcd (EI) m/z for $C_{11}H_{10}N_2OS$: $[M]^+$ 218.0514, found: 218.0511.

***(Z)-1-methyl-4-((2-thiocyanatovinyl)sulfonyl)benzene (2ah)*:** White solid, m.p. 95-97 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 9.6 Hz, 1H), 6.60 (d, J = 9.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 136.0, 133.4, 130.3, 130.0, 127.6, 110.8, 21.7. HRMS Calcd (EI) m/z for $C_{10}H_9NO_2S_2$: $[M]^+$ 239.0075, found: 239.0081.

***ethyl (Z)-3-thiocyanatoacrylate-2-d (2a-d1)*:** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 166.23, 138.0, 119.6 (t, J = 26.2 Hz), 112.4, 61.6, 14.0. HRMS Calcd (EI) m/z for $C_6H_6DNO_2S$: $[M]^+$ 158.0260, found: 158.0258.

***ethyl (E)-3-bromo-3-thiocyanatoacrylate-d (2y-d1)*:** White solid, m.p. 88-89 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 4.24 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 126.1, 124.5 (t, J = 27.7 Hz), 109.5, 61.9, 14.0. HRMS Calcd (EI) m/z for $C_6H_5DNO_2SBr$: $[M]^+$ 235.9365, found: 235.9361.

***diethyl 2-thiocyanatofumarate-d (2aa-d1)*:** White solid, m.p. 77-79 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 4.40 (q, J = 7.2 Hz, 2H), 4.27 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 161.3, 138.0, 126.0 (t, J = 26.3 Hz), 109.7, 63.9, 62.2, 14.0, 13.8. HRMS Calcd (EI) m/z for $C_9H_{10}DNO_4S$: $[M]^+$ 230.0472, found: 230.0471.

4. References

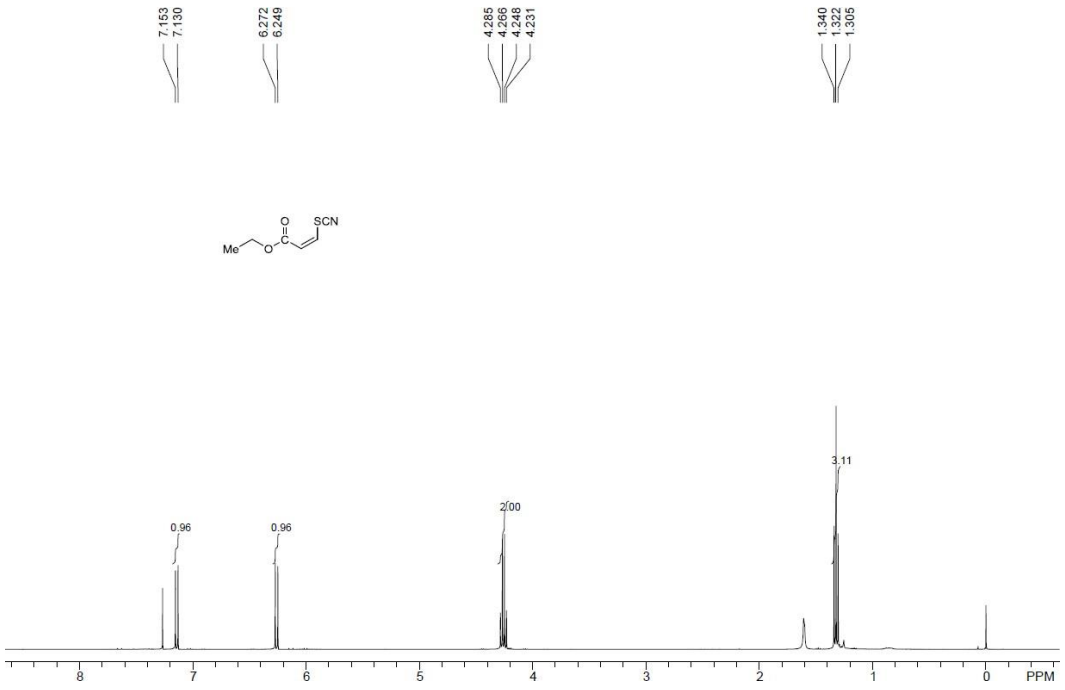
(1) Giffard, M.; Cousseau, J.; Gouin, L. *Tetrahedron* **1985**, *41*, 801–810.

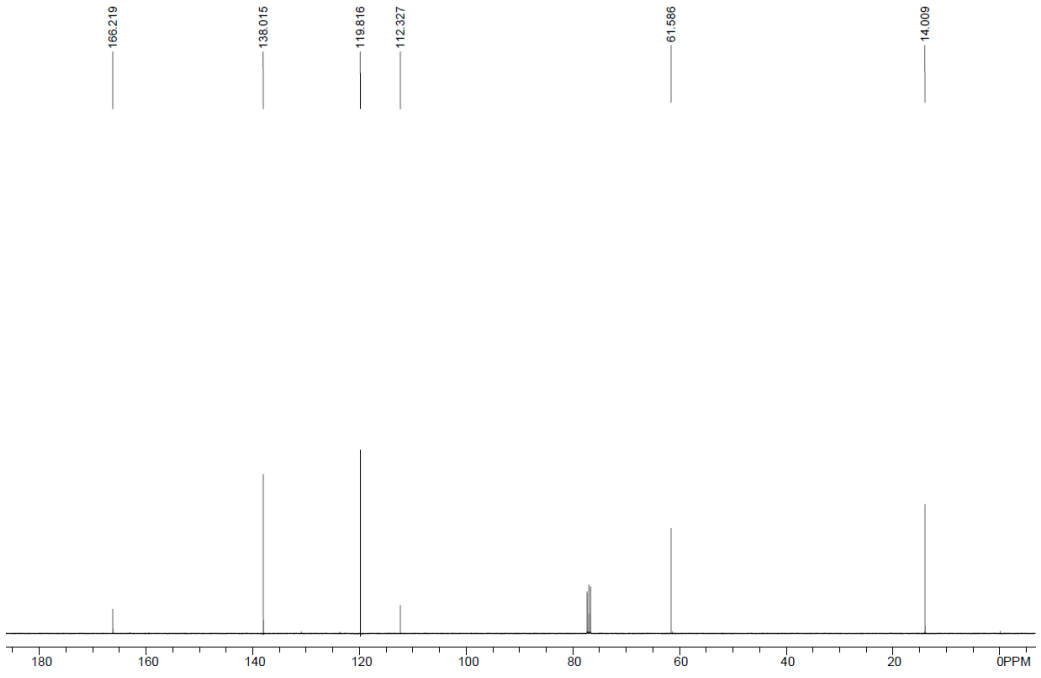
(2) Jiang, G. B.; Zhu, C. L.; Li, J. X.; Wu, W. Q.; Jiang, H. F. *Adv. Synth. Catal.* **2017**, 359,1208–1212.

(3)Dwivedi, V.; Rajesh, M.; Kumar, R.; Kant, R.; Reddy, M. S. *Chem. Commun.* **2017**, *53*, 11060–11063.

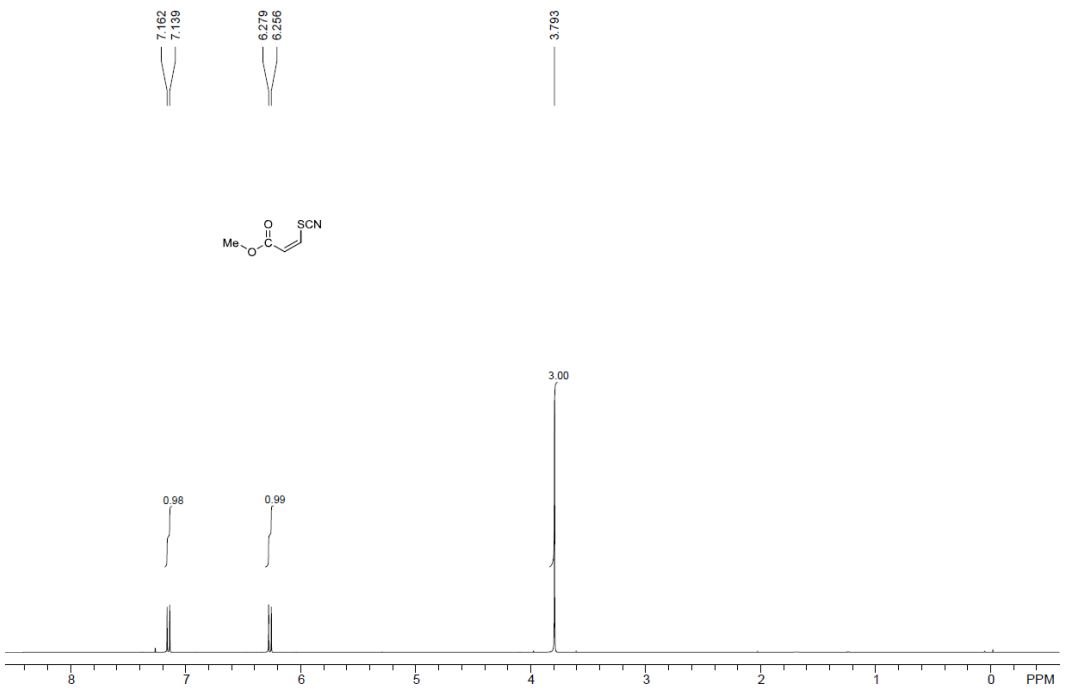
5. ^{1}H and ^{13}C NMR spectra

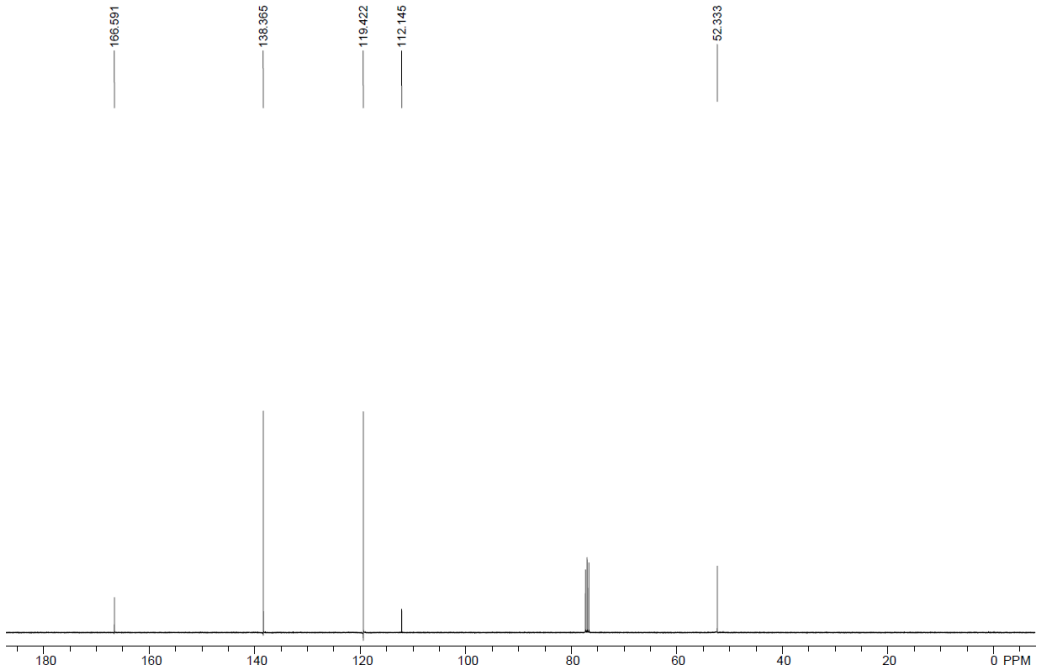
ethyl (*Z*)-3-thiocyanatoacrylate (2a)



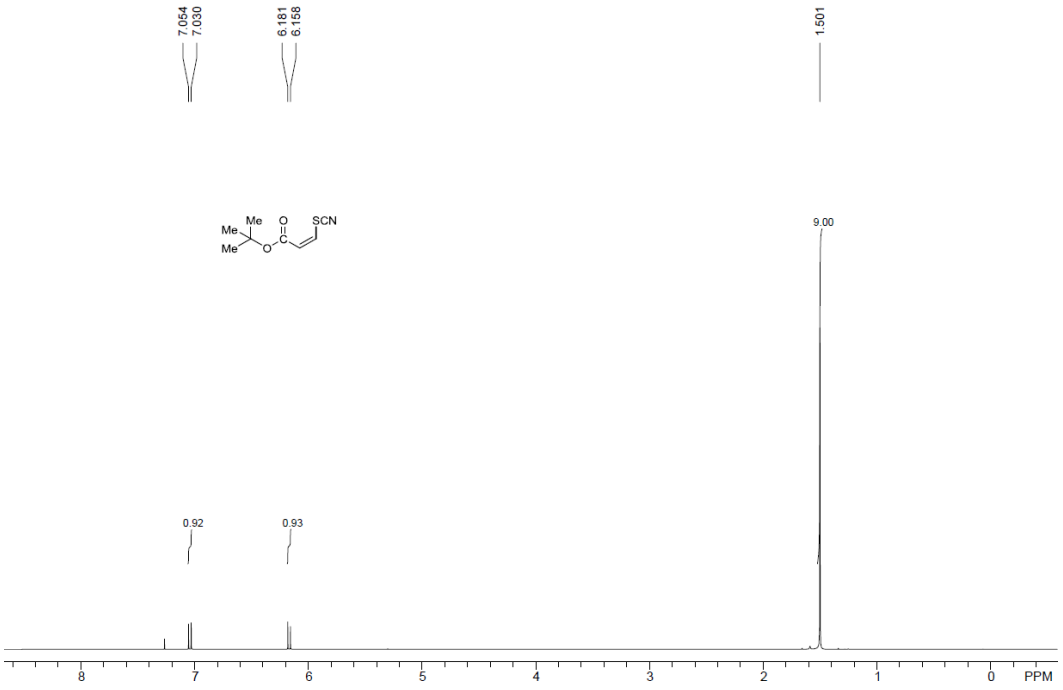


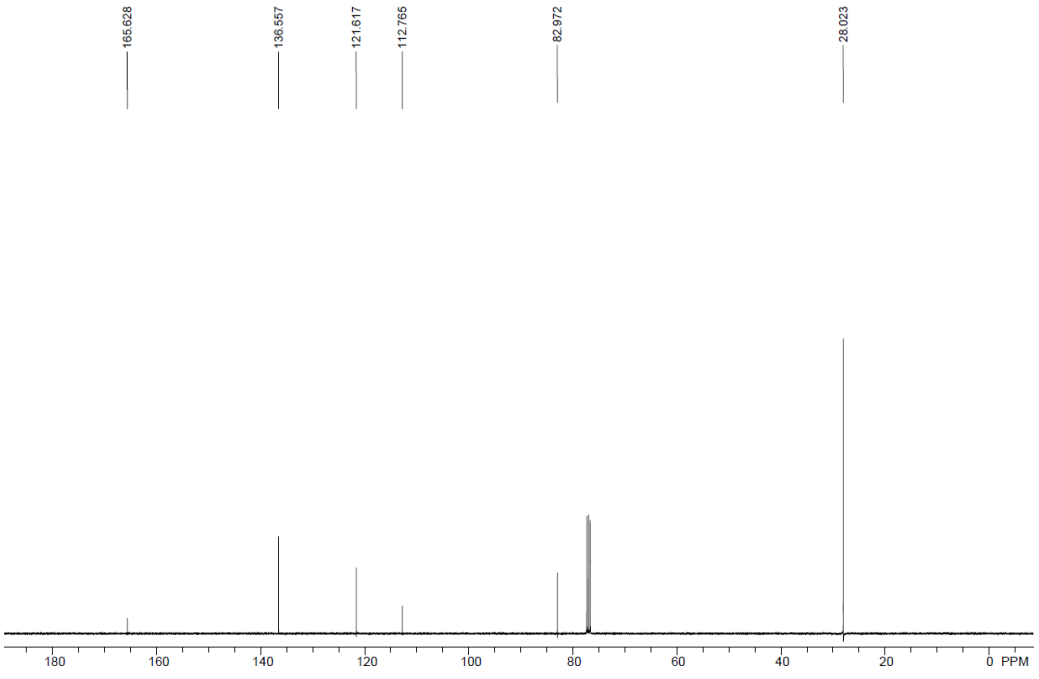
methyl (*Z*)-3-thiocyanatoacrylate (2b)



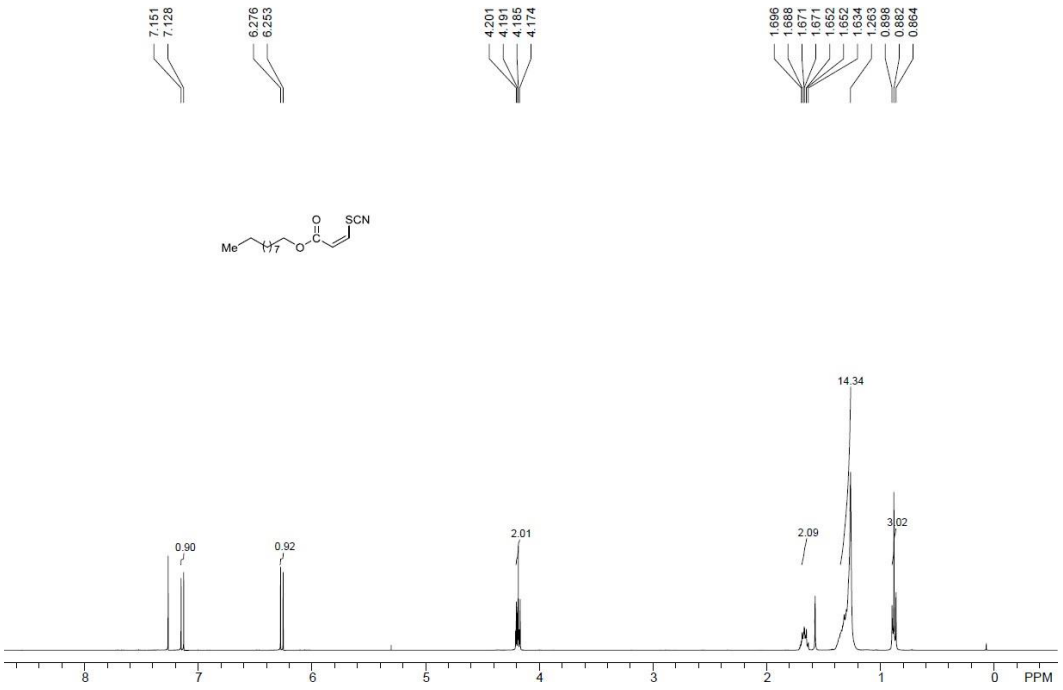


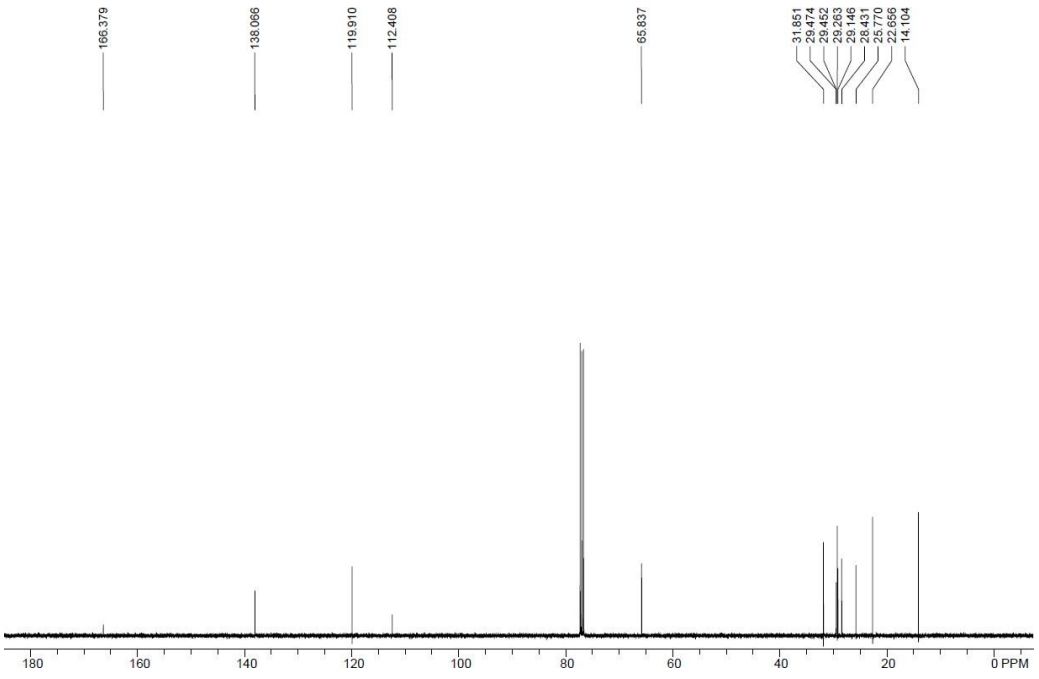
tert-butyl (*Z*)-3-thiocyanatoacrylate (2c)



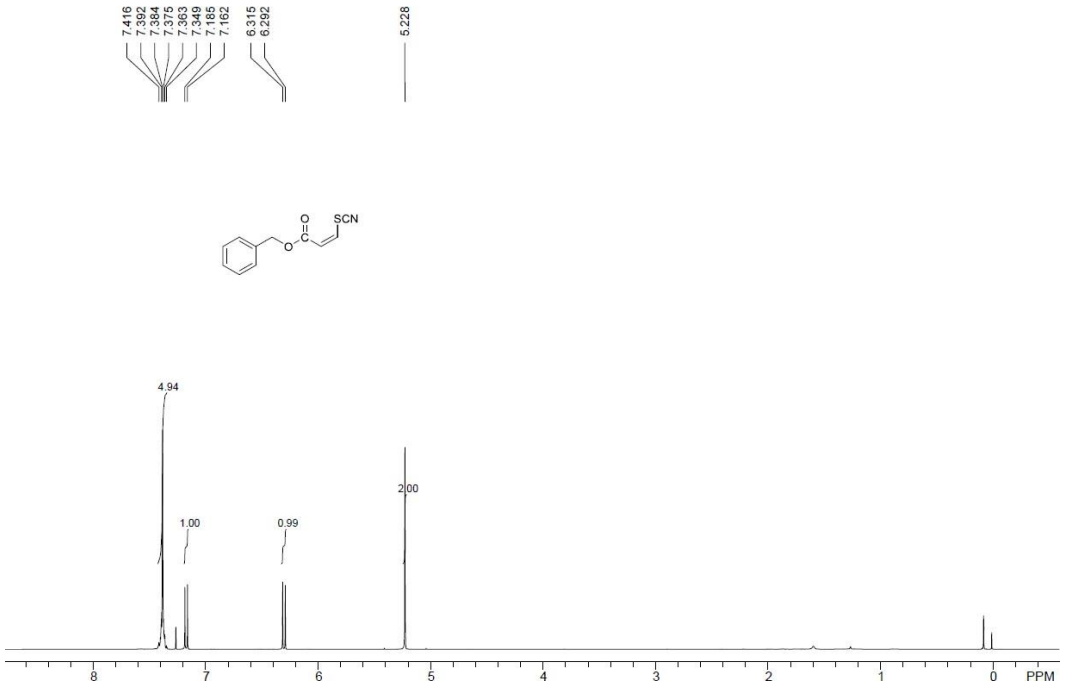


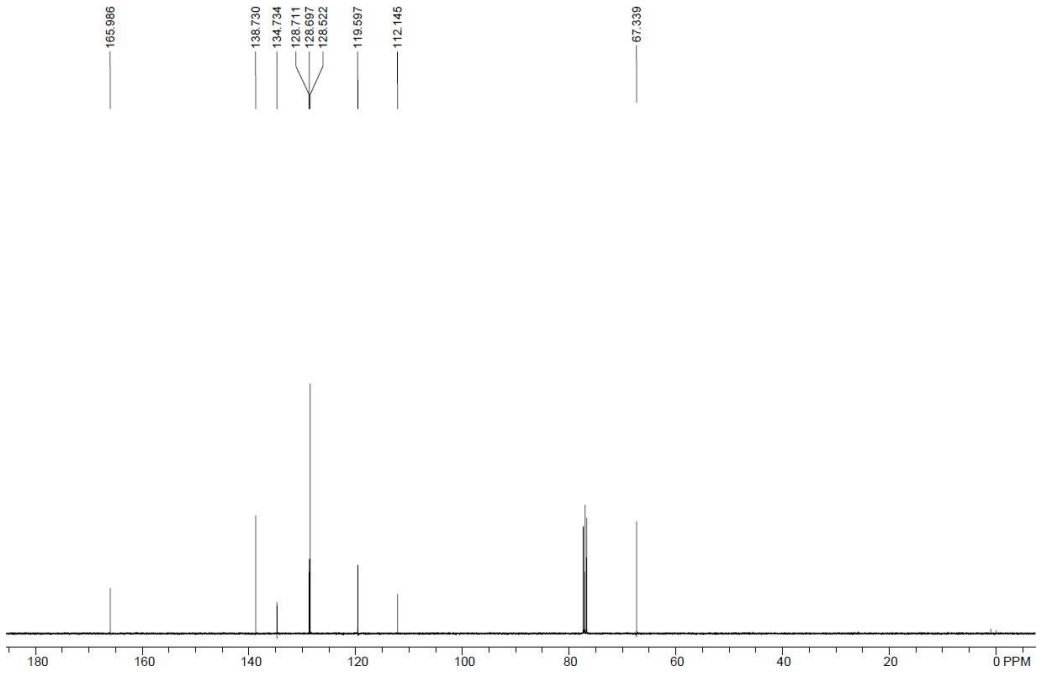
decyl (*Z*)-3-thiocyanatoacrylate (2d)



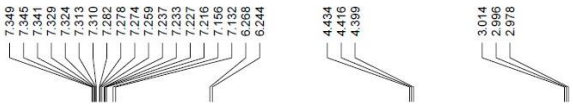


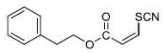
benzyl (*Z*)-3-thiocyanatoacrylate (2e)

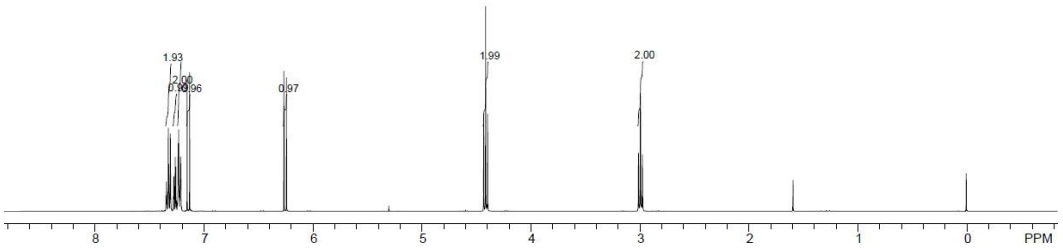


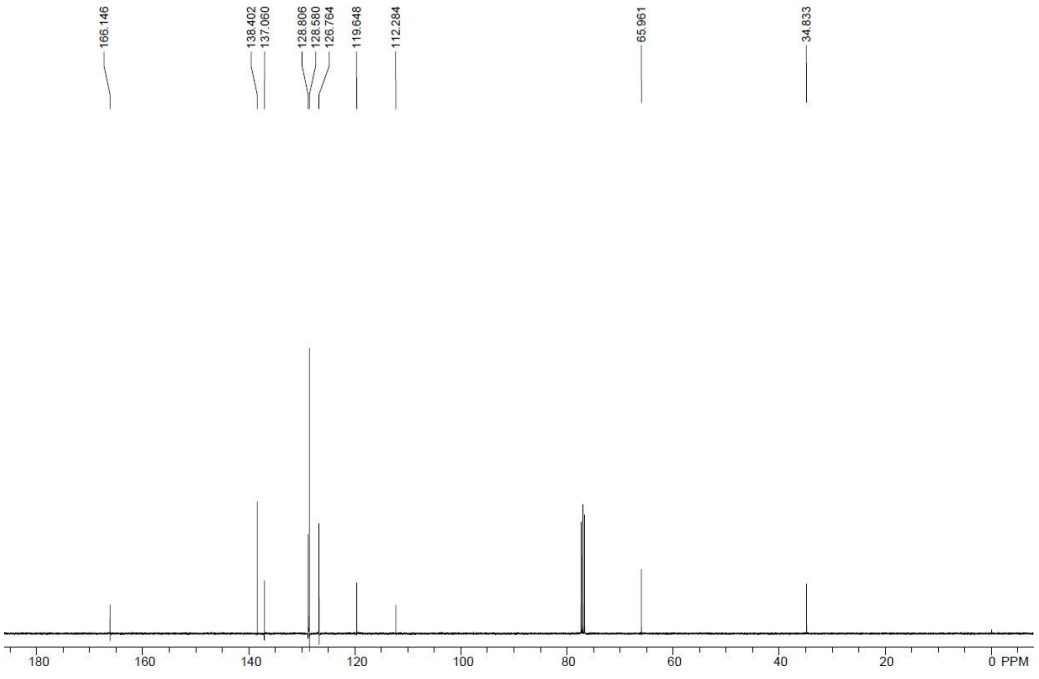


phenethyl (*Z*)-3-thiocyanatoacrylate (2f)

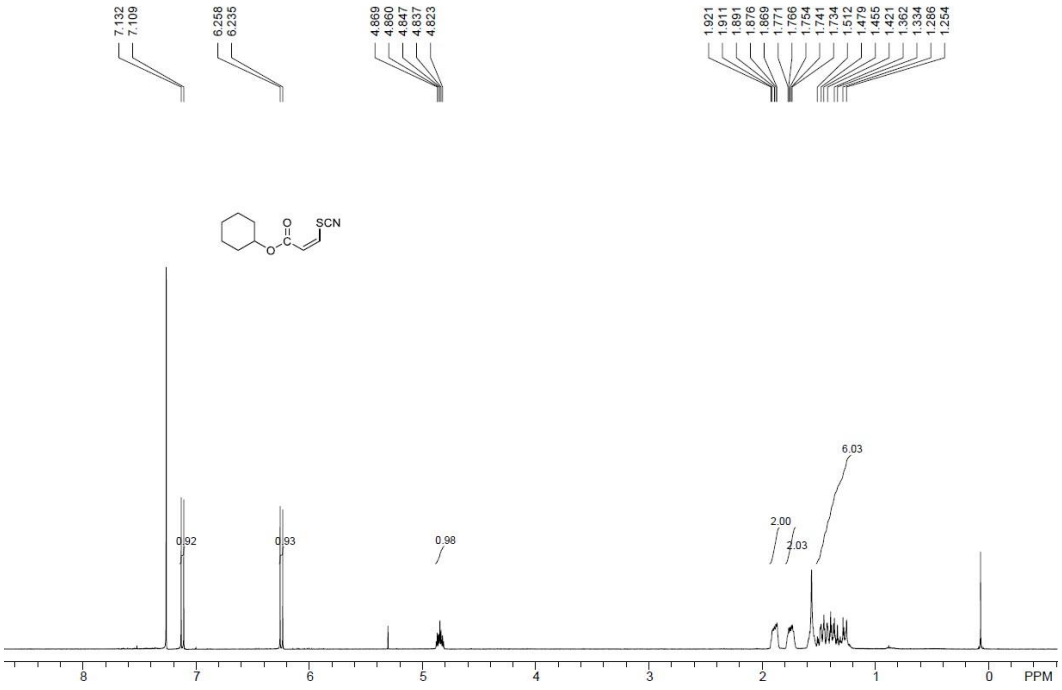


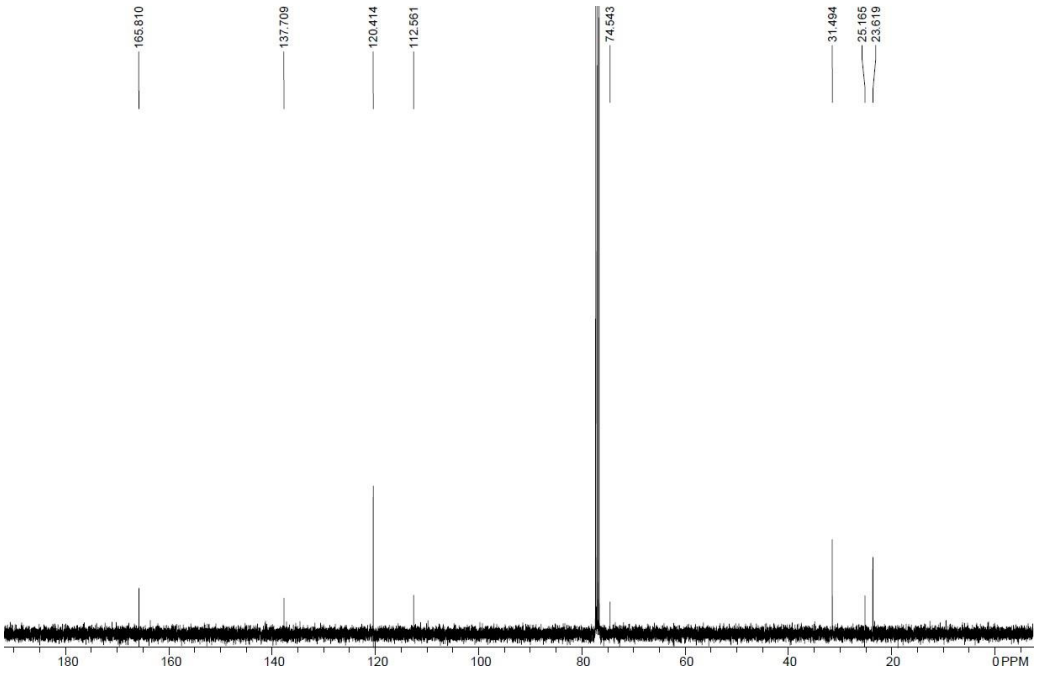




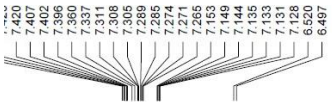


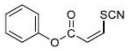
cyclohexyl (*Z*)-3-thiocyanatoacrylate (2g)

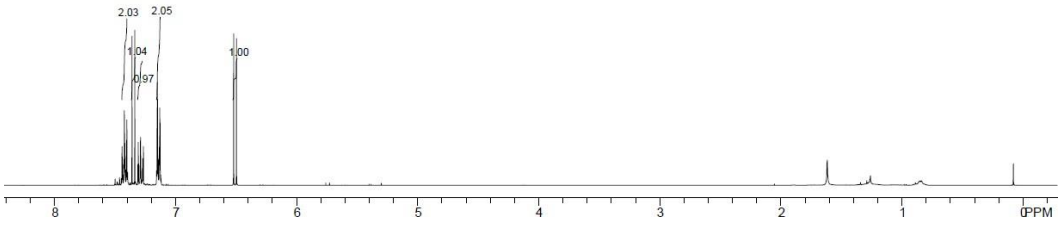


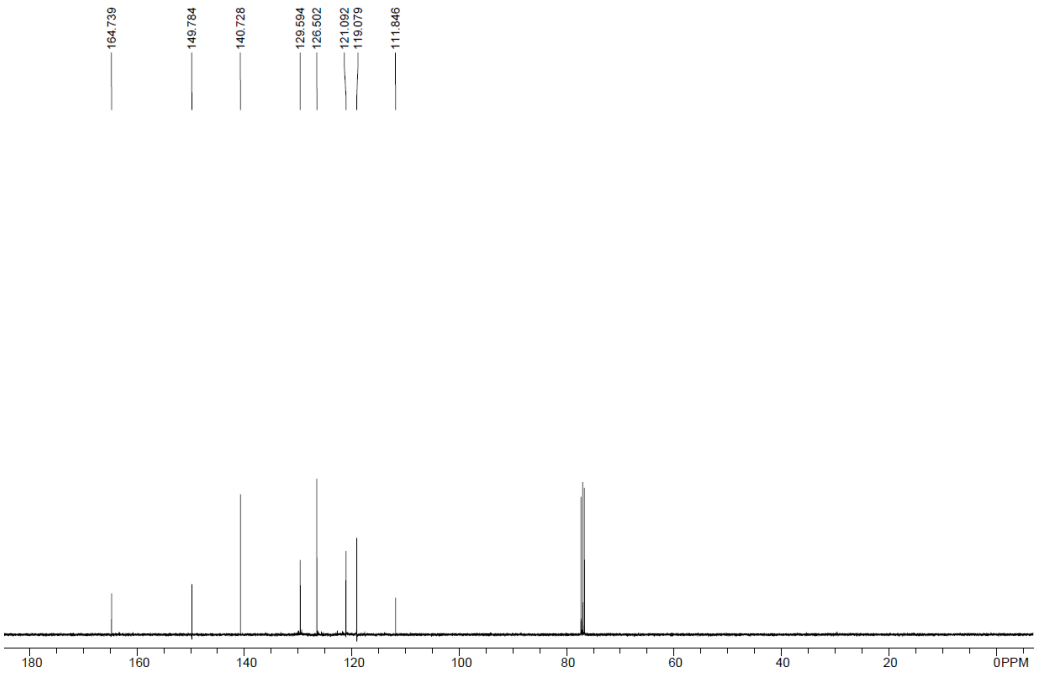


phenyl (*Z*)-3-thiocyanatoacrylate (2h)

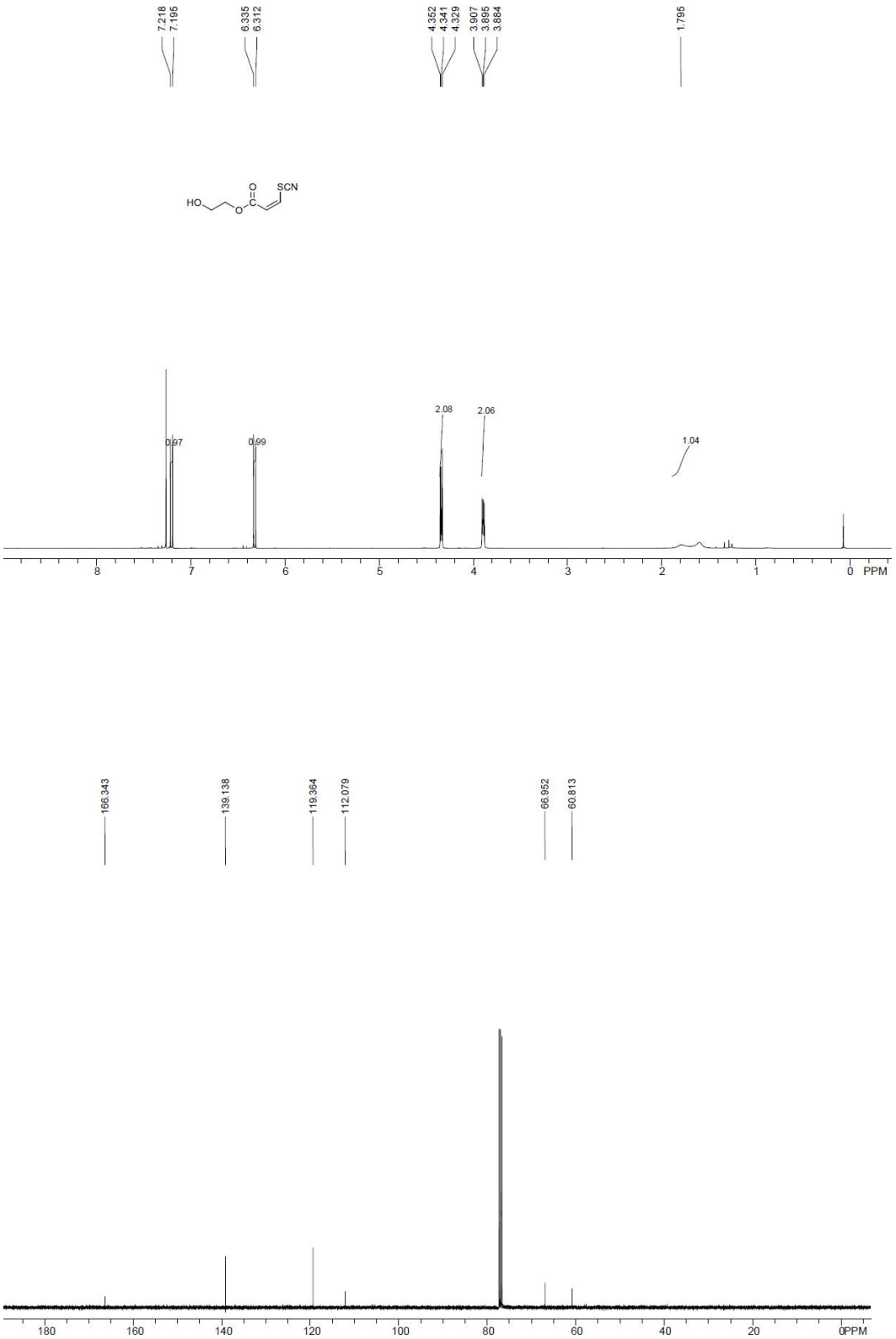




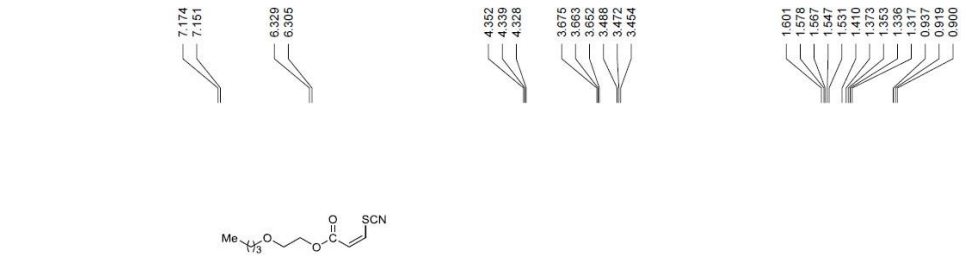


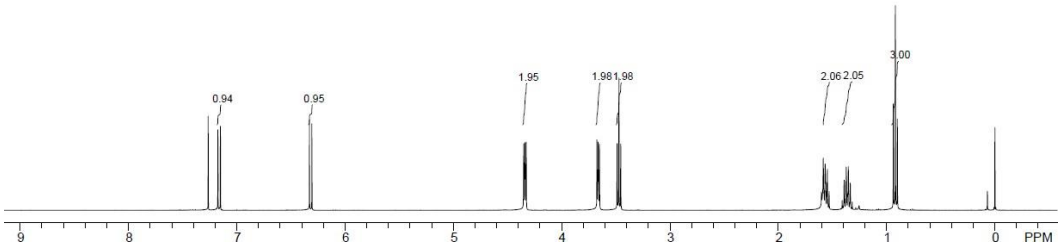


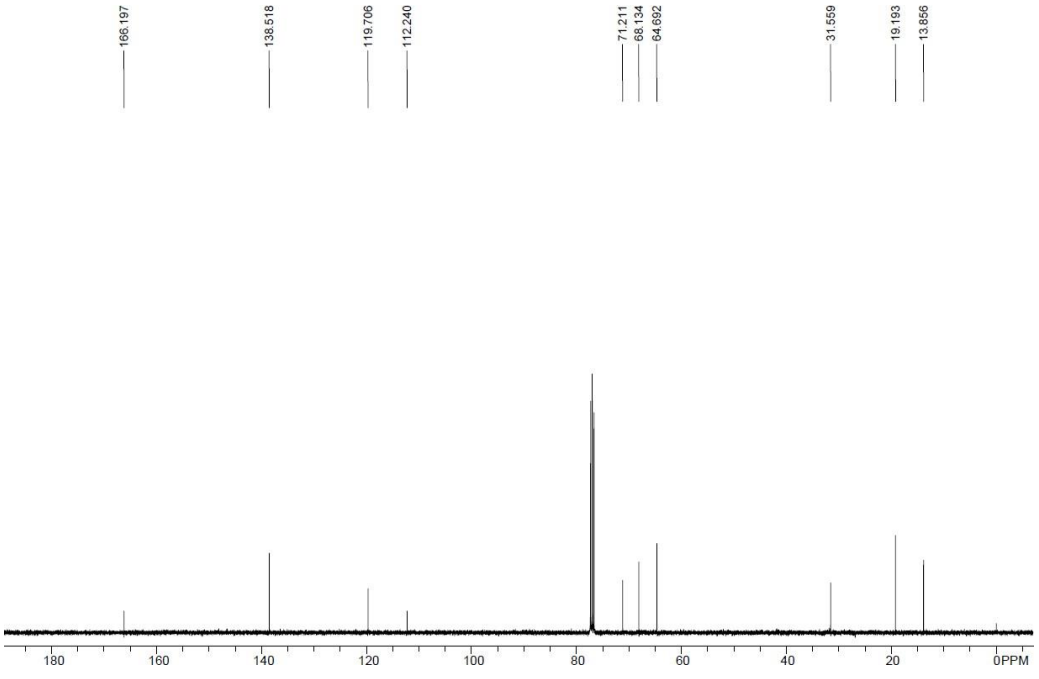
2-hydroxyethyl (*Z*)-3-thiocyanatoacrylate (2i)



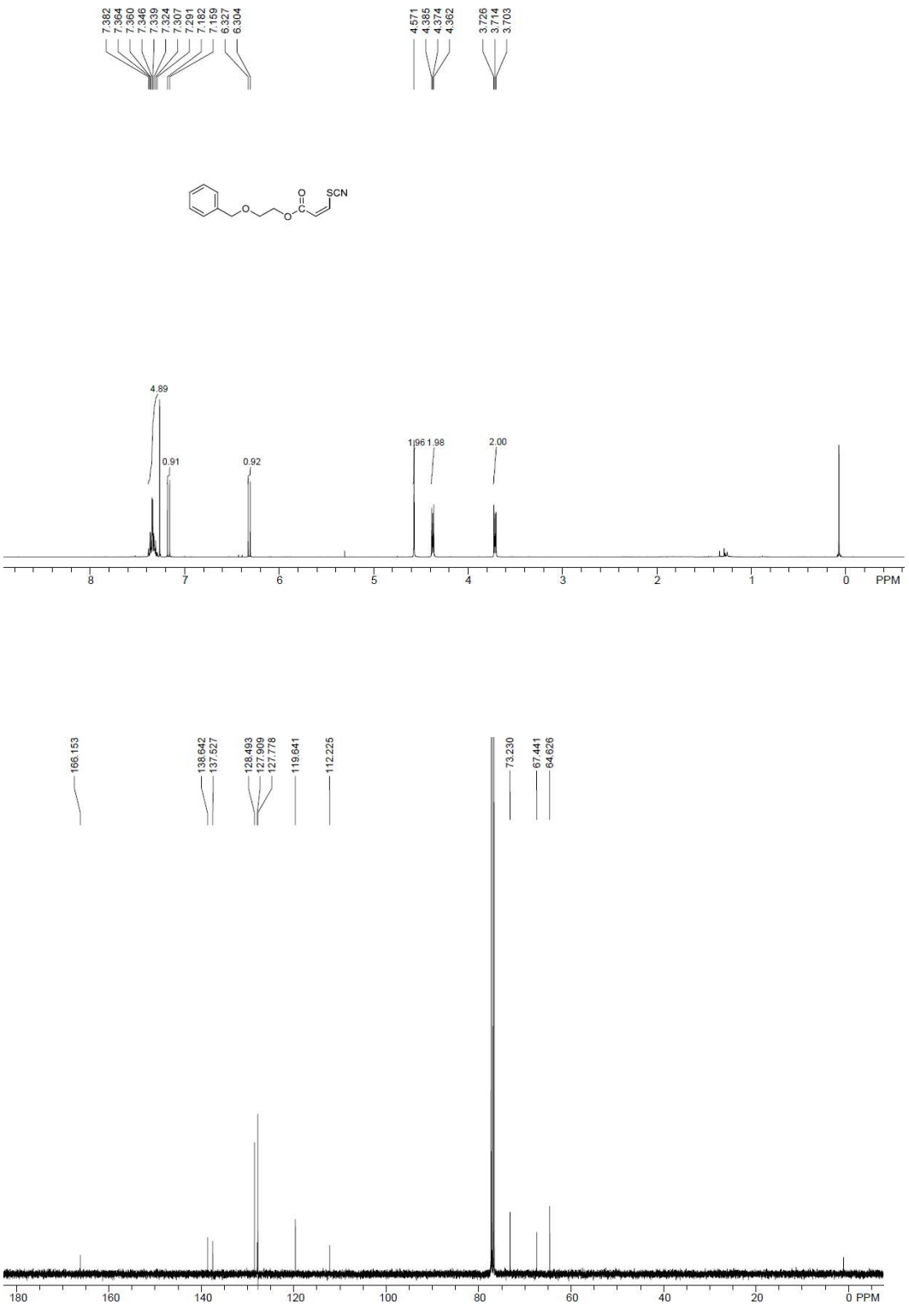
2-butoxyethyl (*Z*)-3-thiocyanatoacrylate (2j)



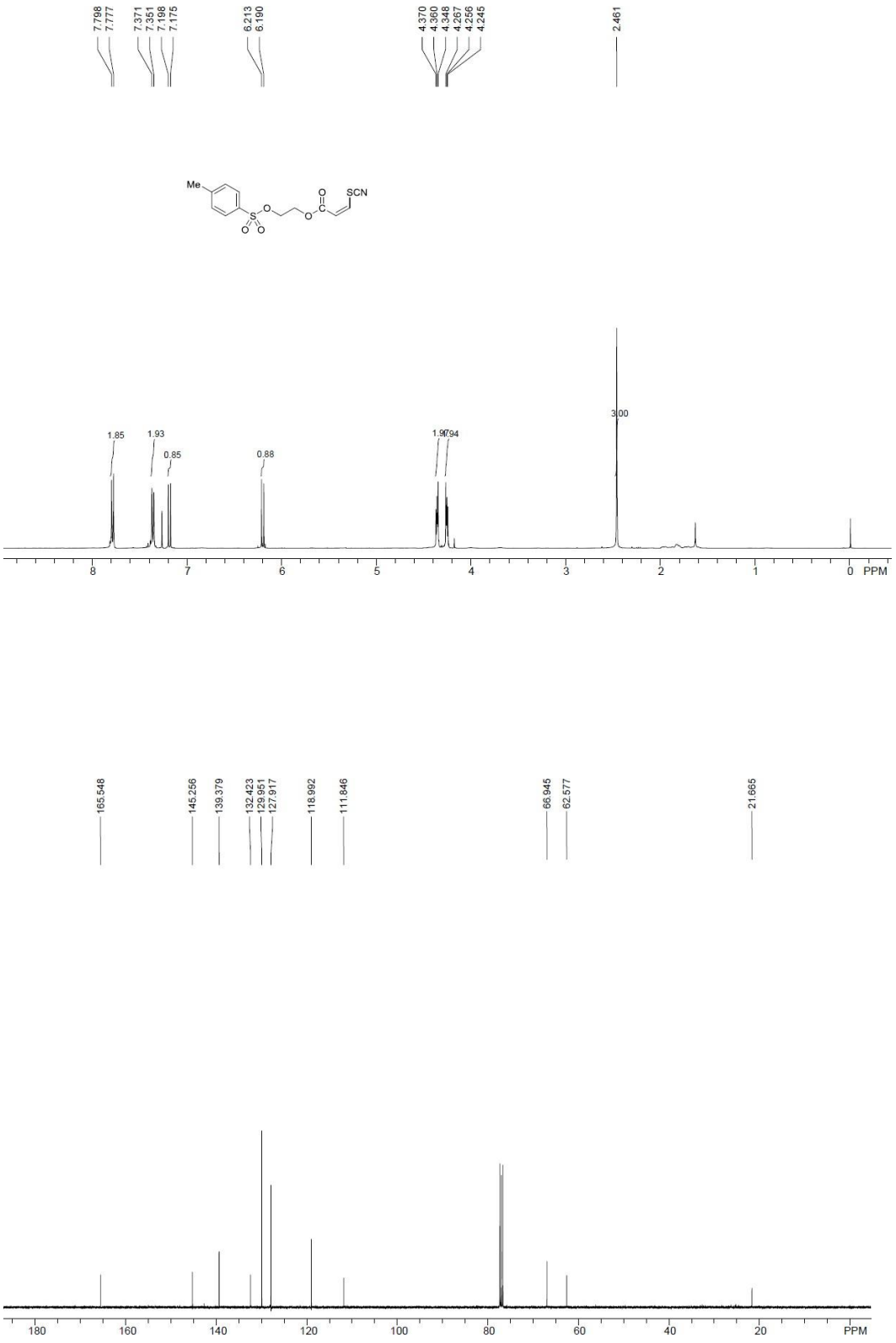




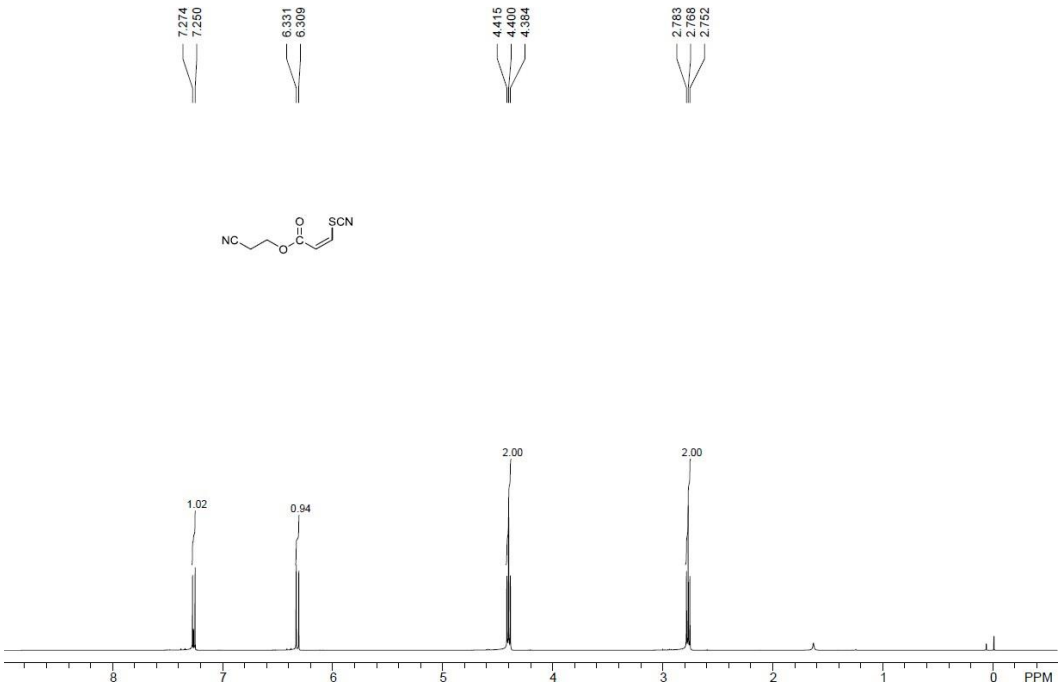
2-(benzyloxy)ethyl (*Z*)-3-thiocyanatoacrylate (2k)

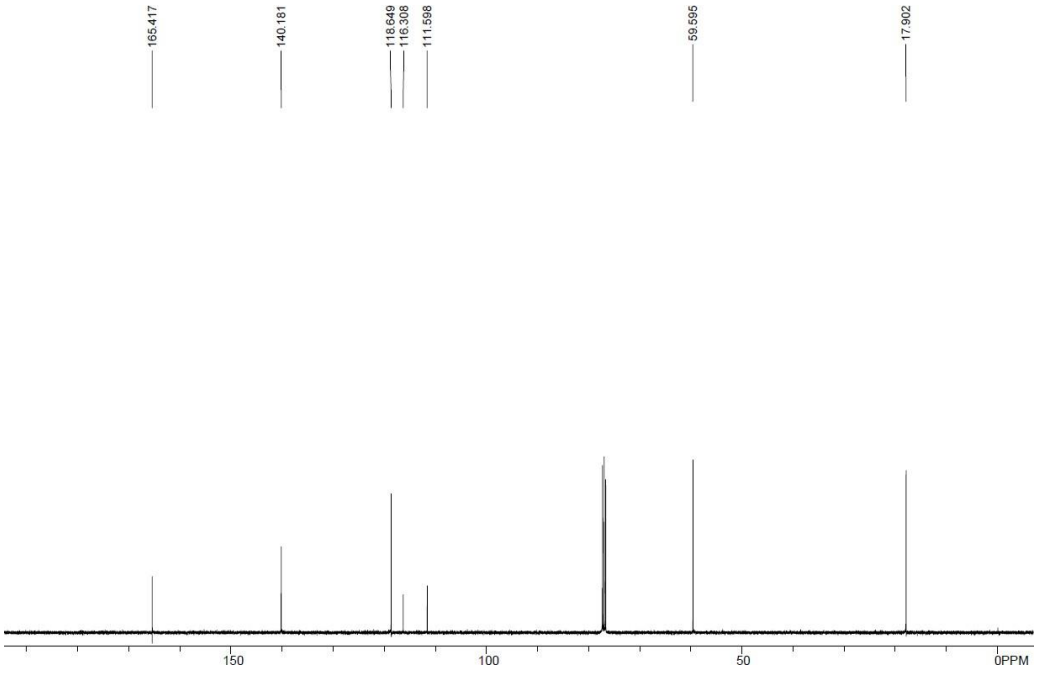


2-(tosyloxy)ethyl (*Z*)-3-thiocyanatoacrylate (2l)

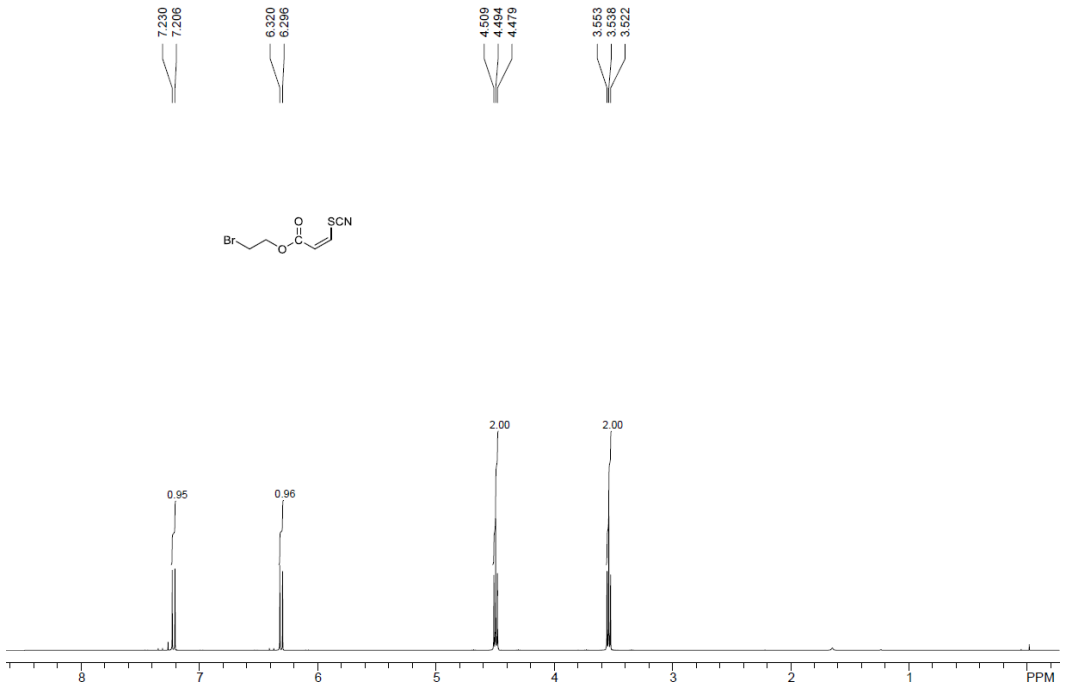


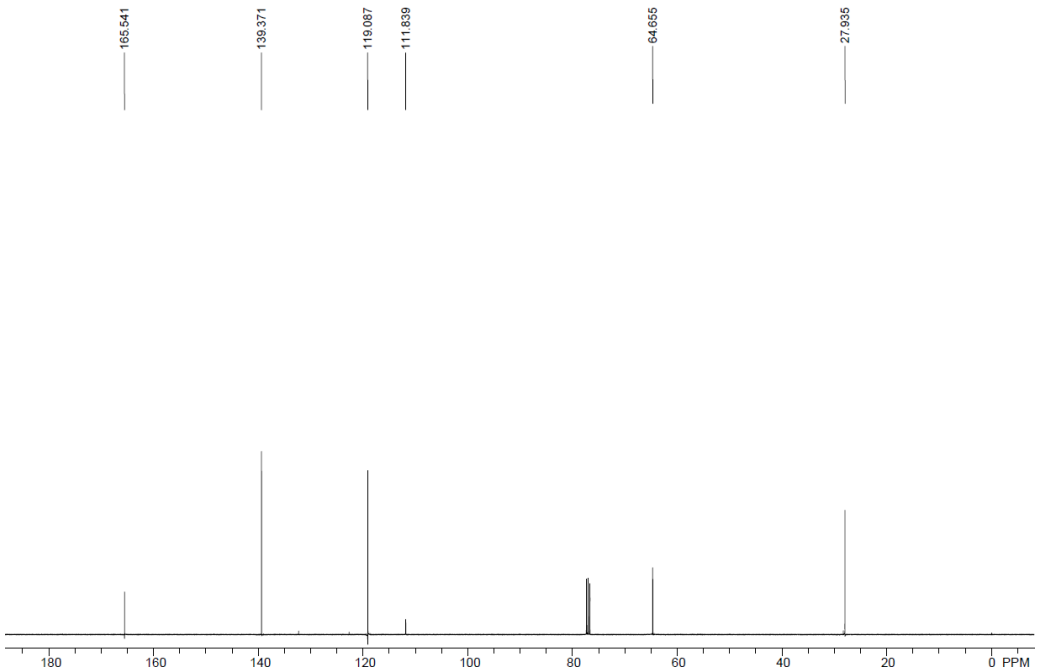
2-cyanoethyl (*Z*)-3-thiocyanatoacrylate (2m)



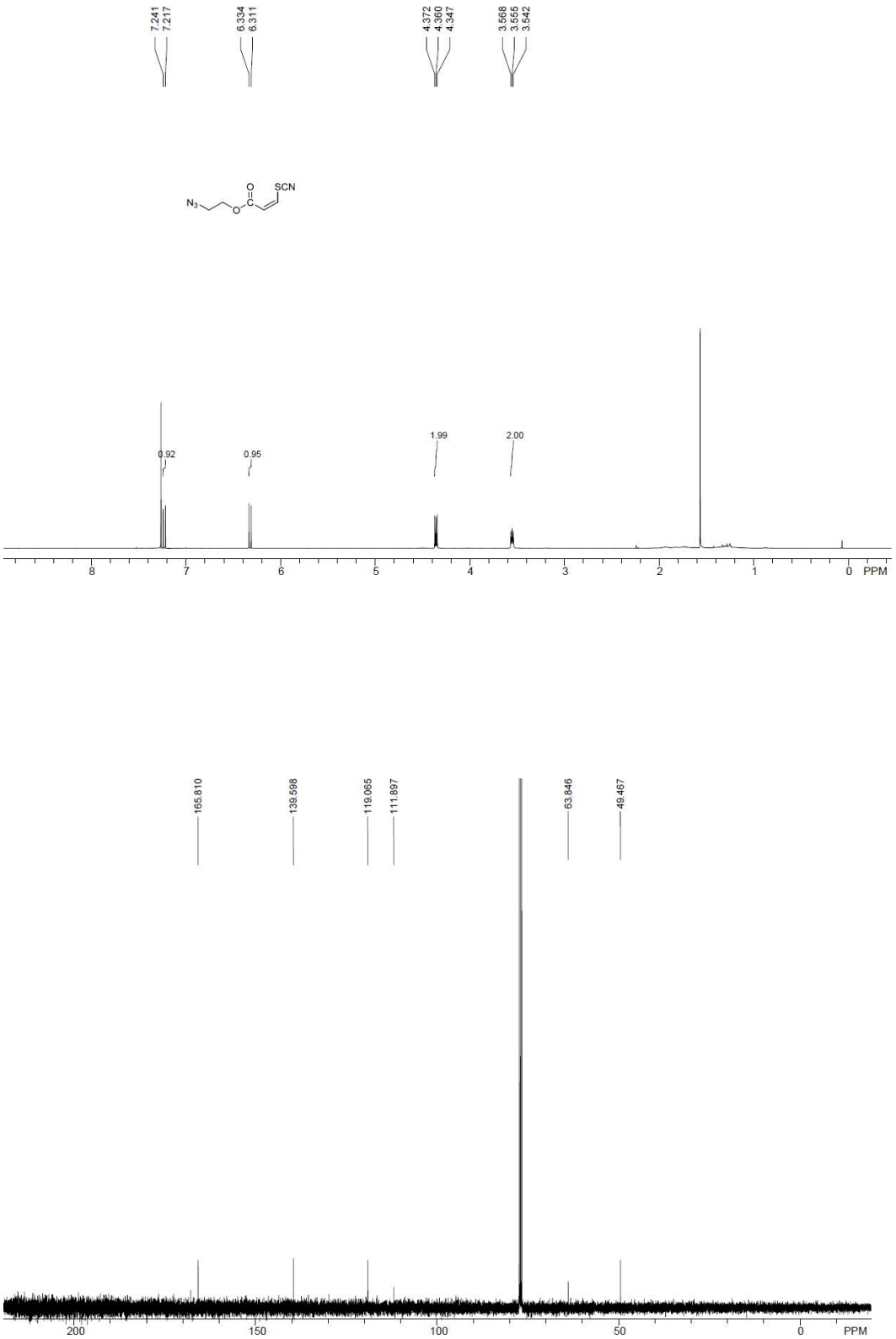


2-bromoethyl (*Z*)-3-thiocyanatoacrylate (2n)

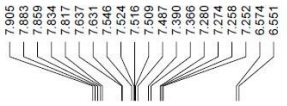


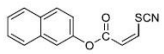


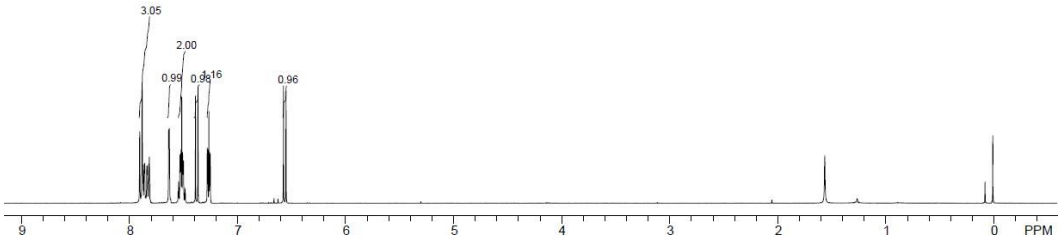
2-azidoethyl (*Z*)-3-thiocyanatoacrylate (2o)

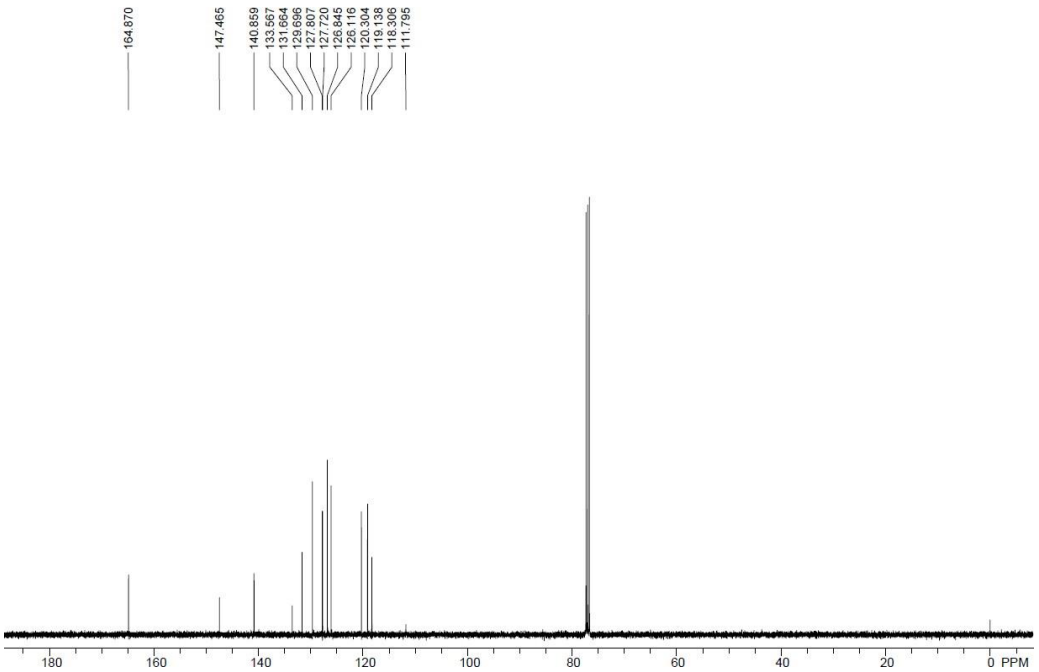


naphthalen-2-yl (*Z*)-3-thiocyanatoacrylate (2p)

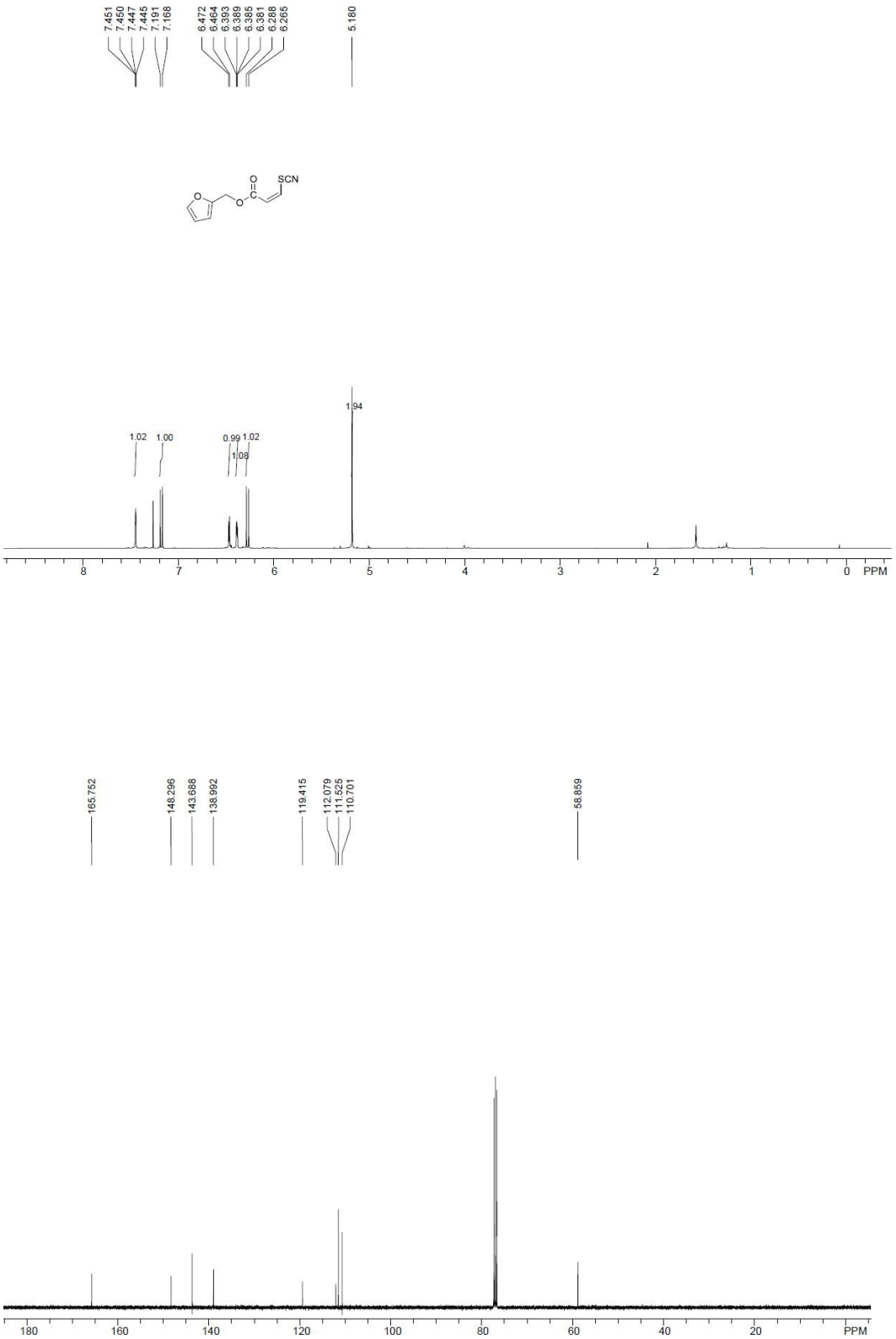




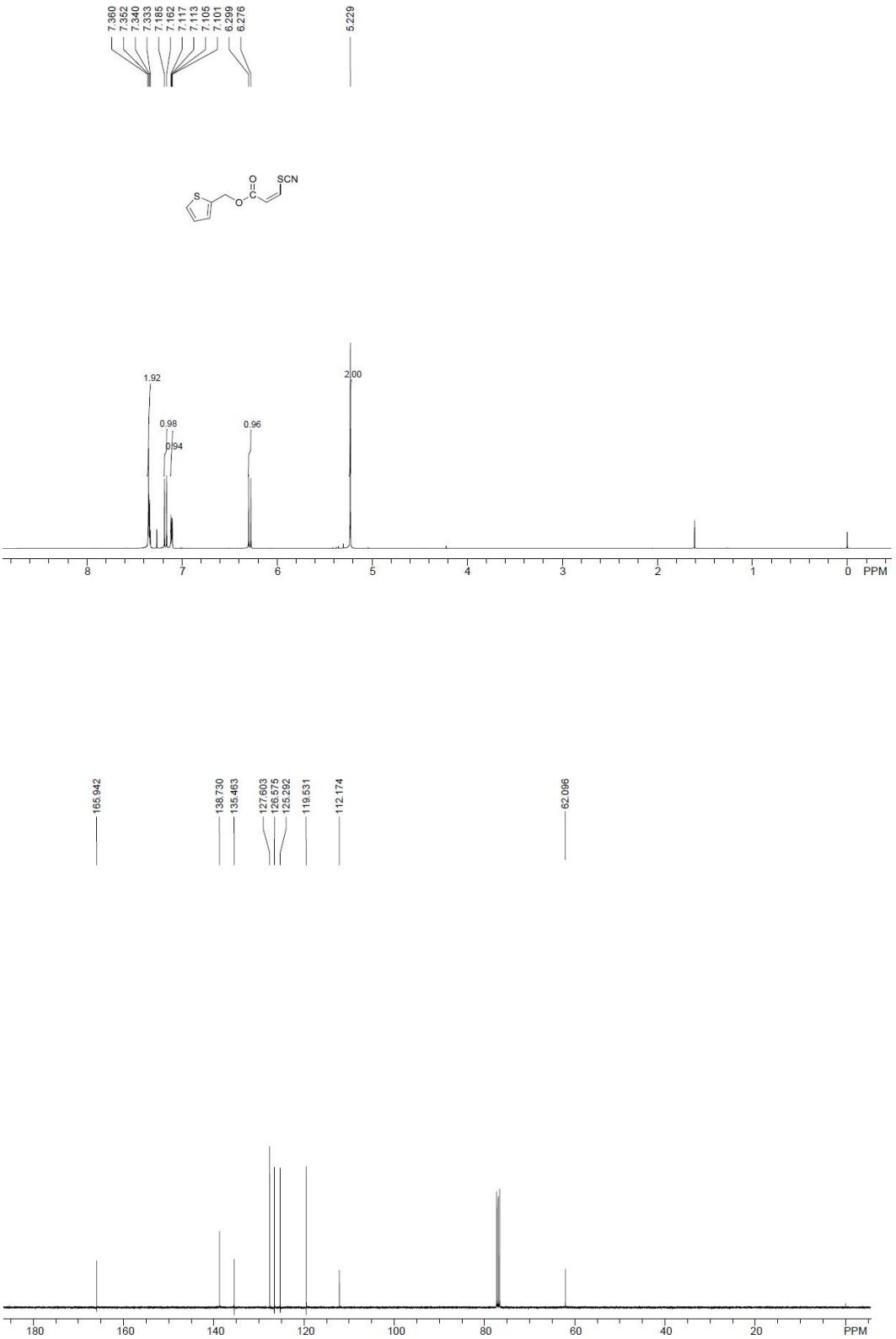




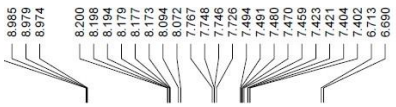
furan-2-ylmethyl (*Z*)-3-thiocyanatoacrylate (2q)

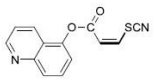


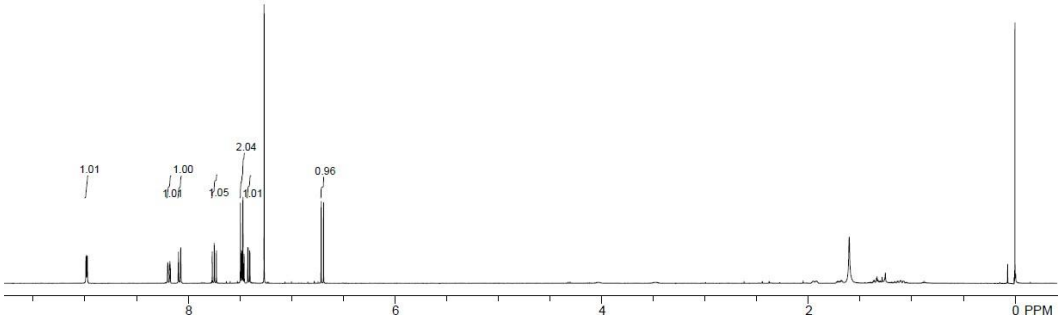
thiophen-2-ylmethyl (*Z*)-3-thiocyanatoacrylate (2r)

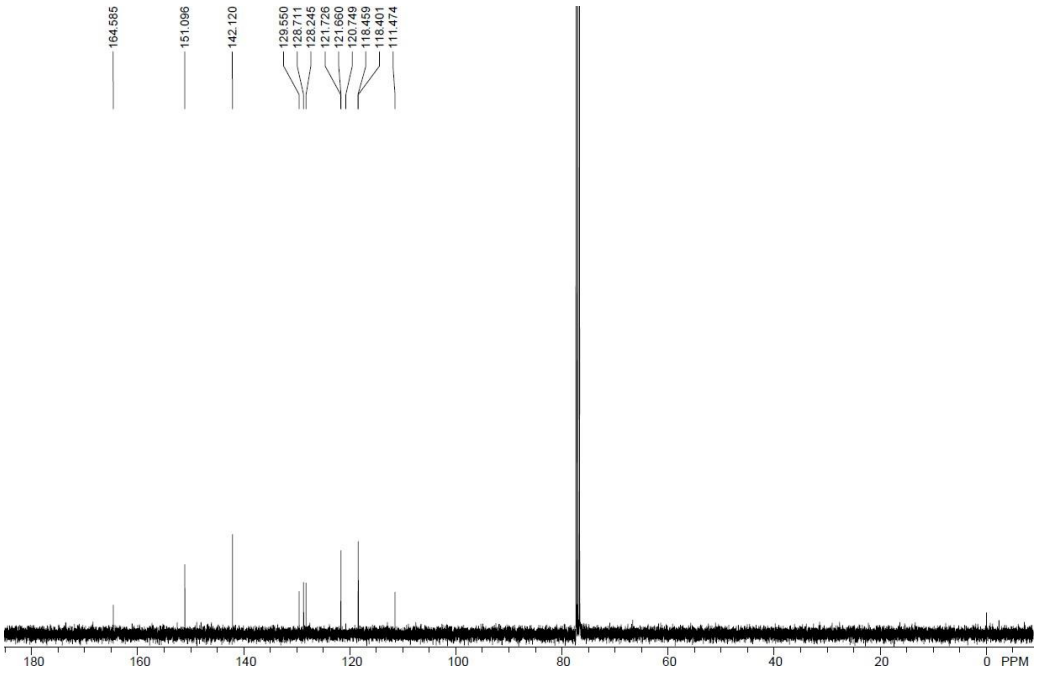


quinolin-5-yl (Z)-3-thiocyanatoacrylate (2s)

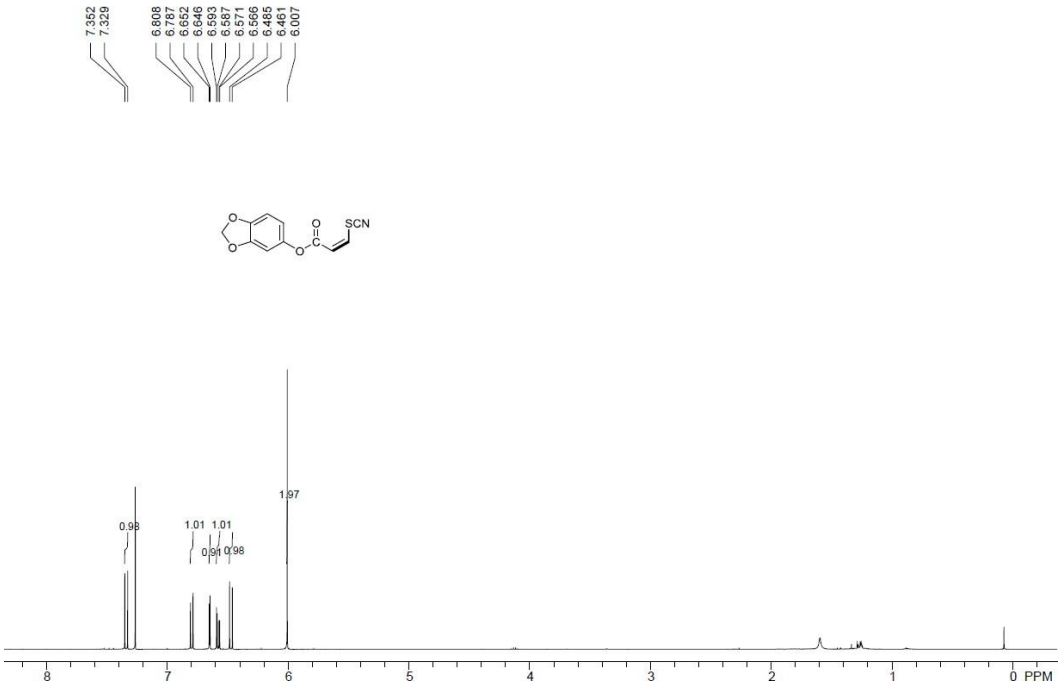


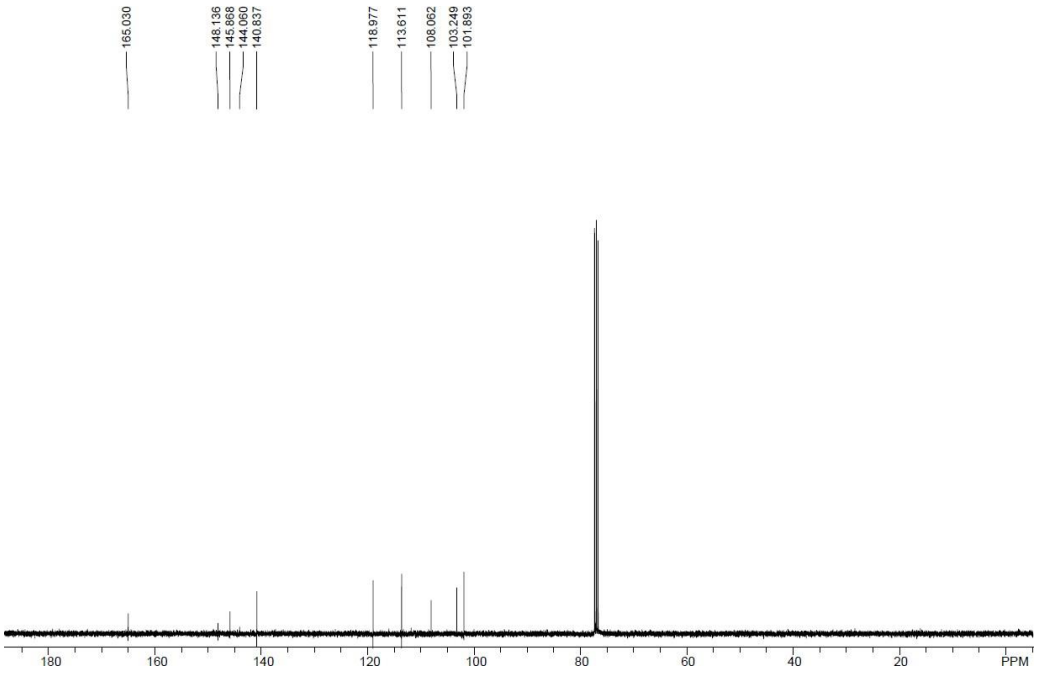




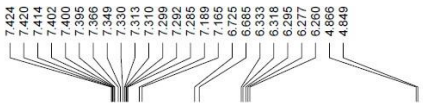


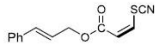
benzo[d][1,3]dioxol-5-yl (*Z*)-3-thiocyanatoacrylate (2t)

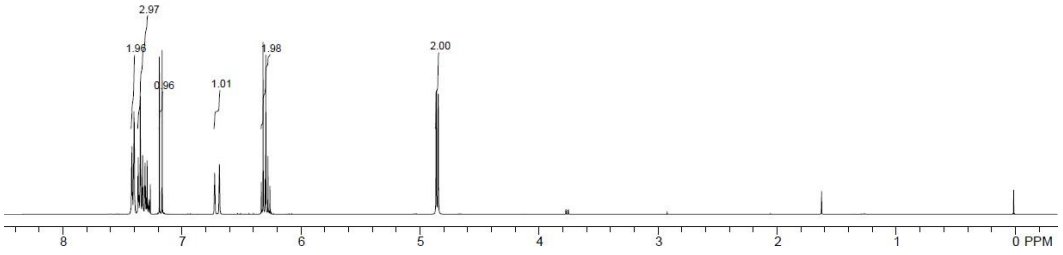


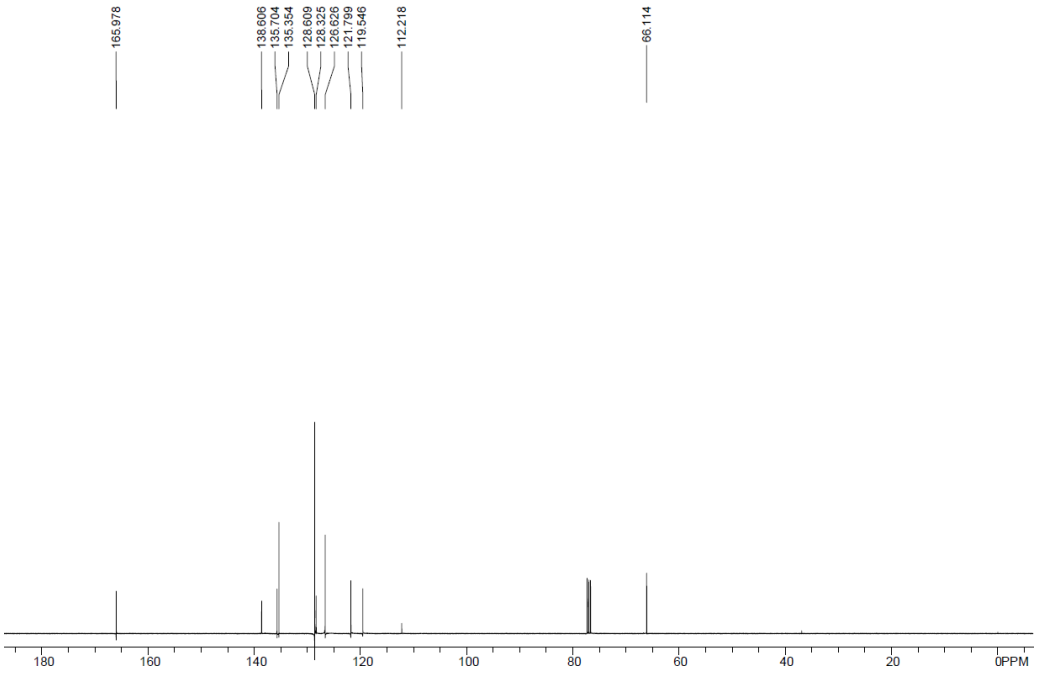


cinnamyl (*Z*)-3-thiocyanatoacrylate (2u)

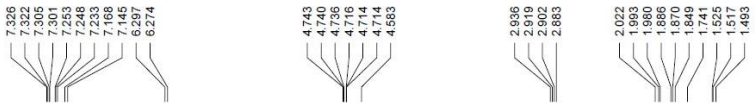


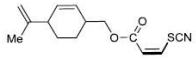


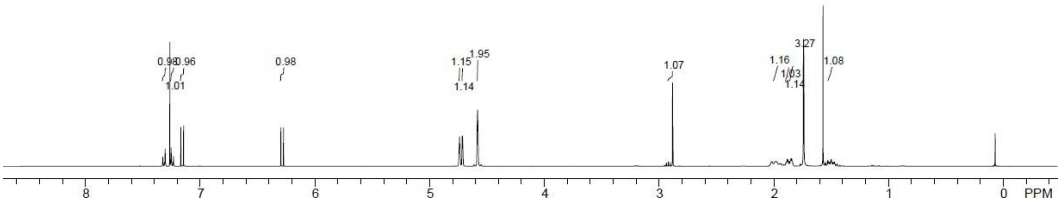


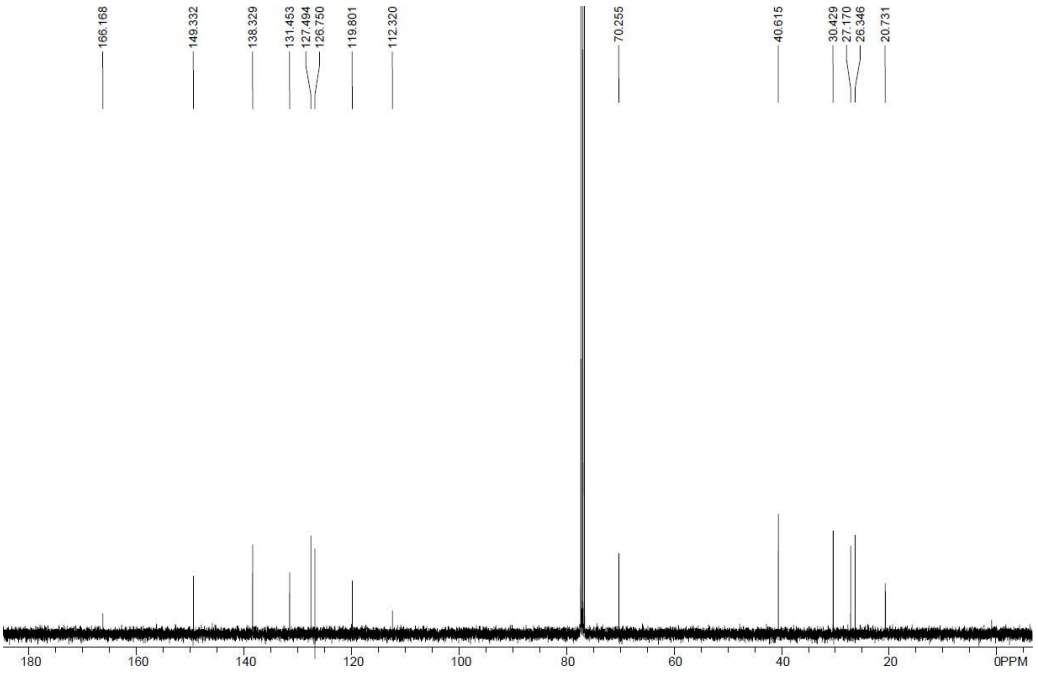


(4-(prop-1-en-2-yl)cyclohex-2-en-1-yl)methyl (*Z*)-3-thiocyanatoacrylate (2v)

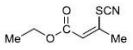


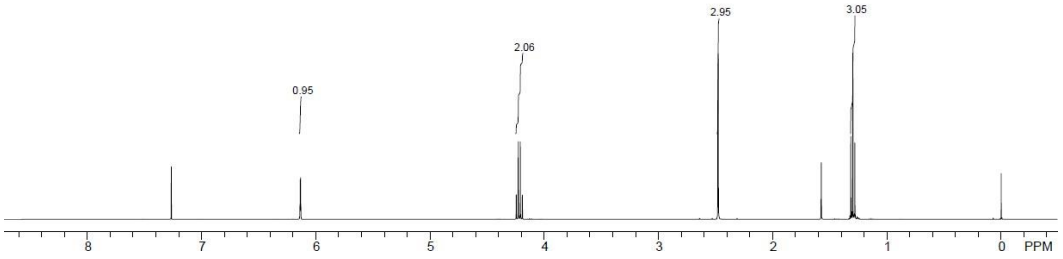


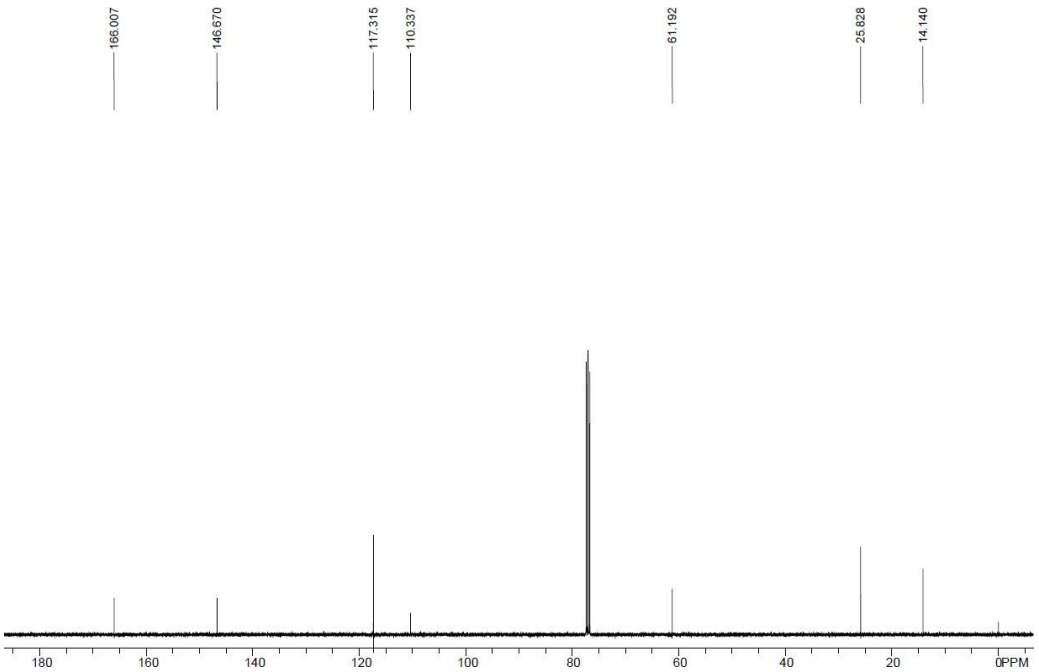




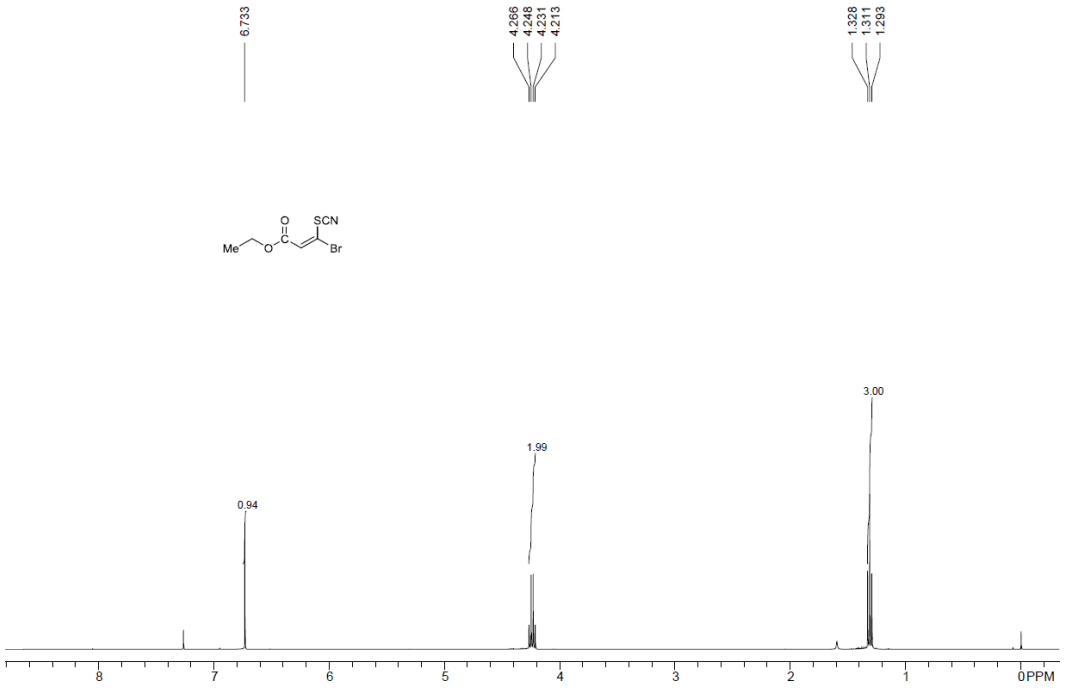
ethyl (*Z*)-3-thiocyanatobut-2-enoate (2x)

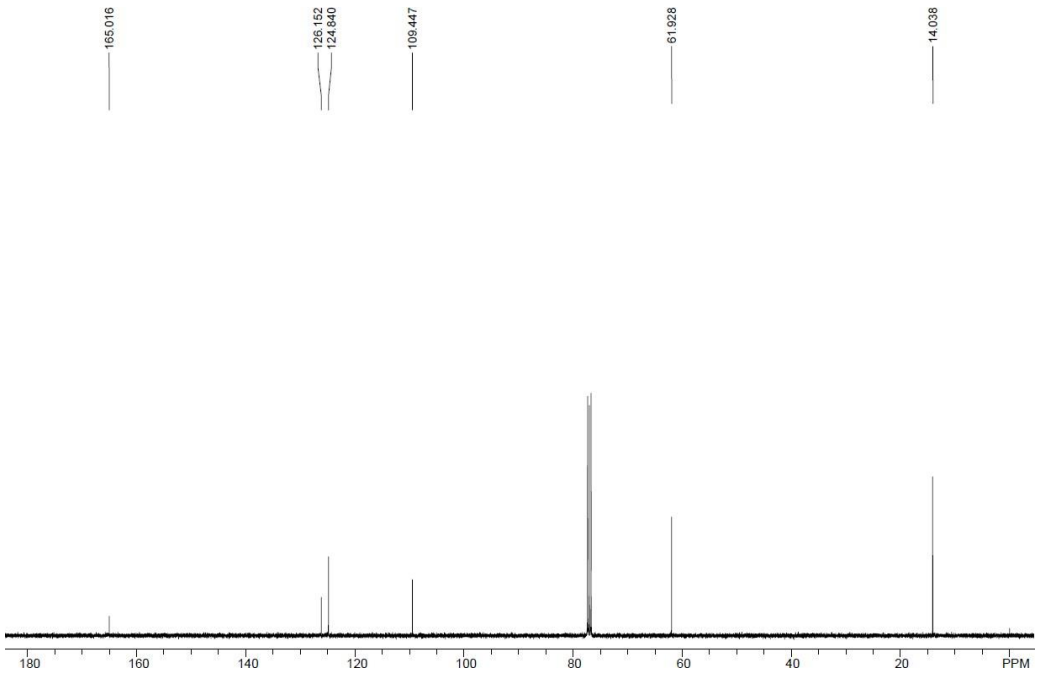




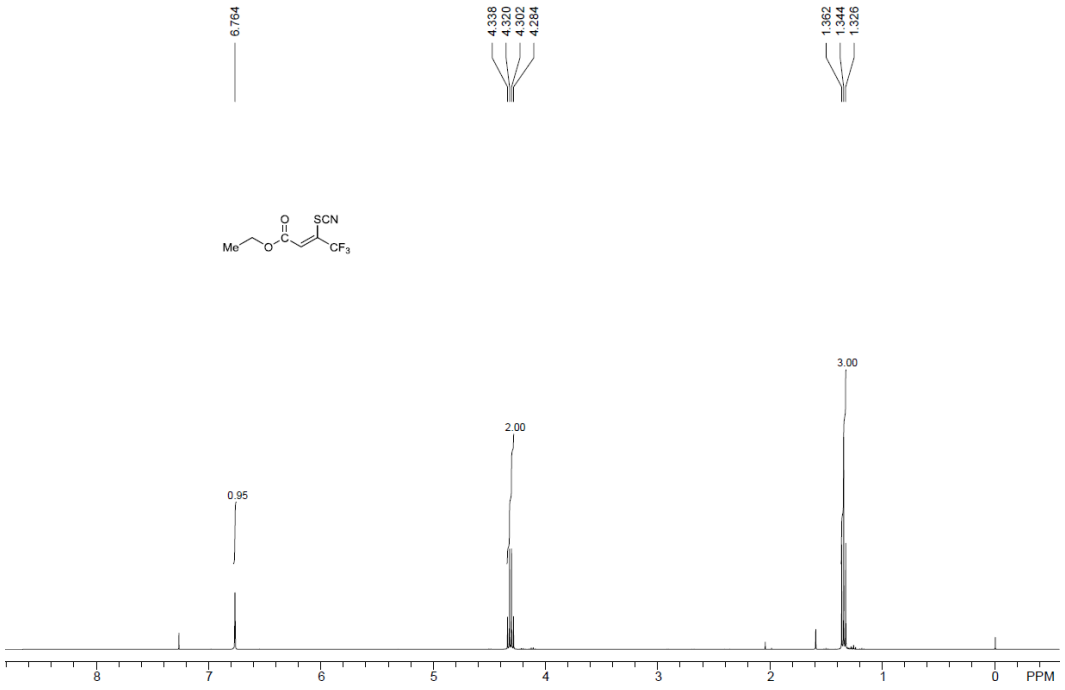


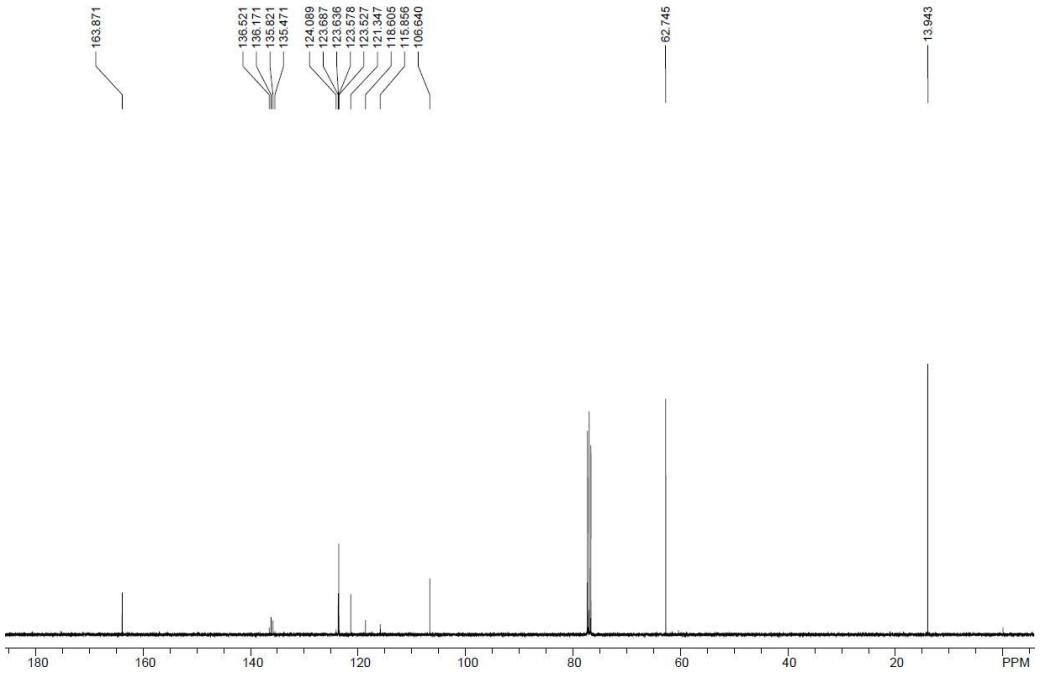
ethyl (*E*)-3-bromo-3-thiocyanatoacrylate (2y)

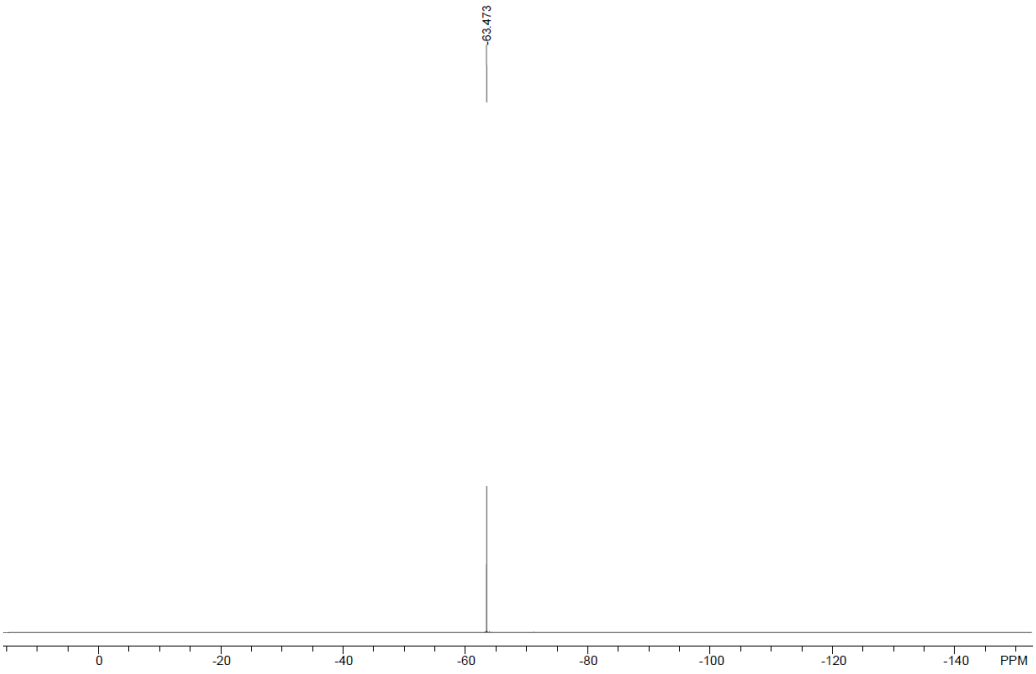




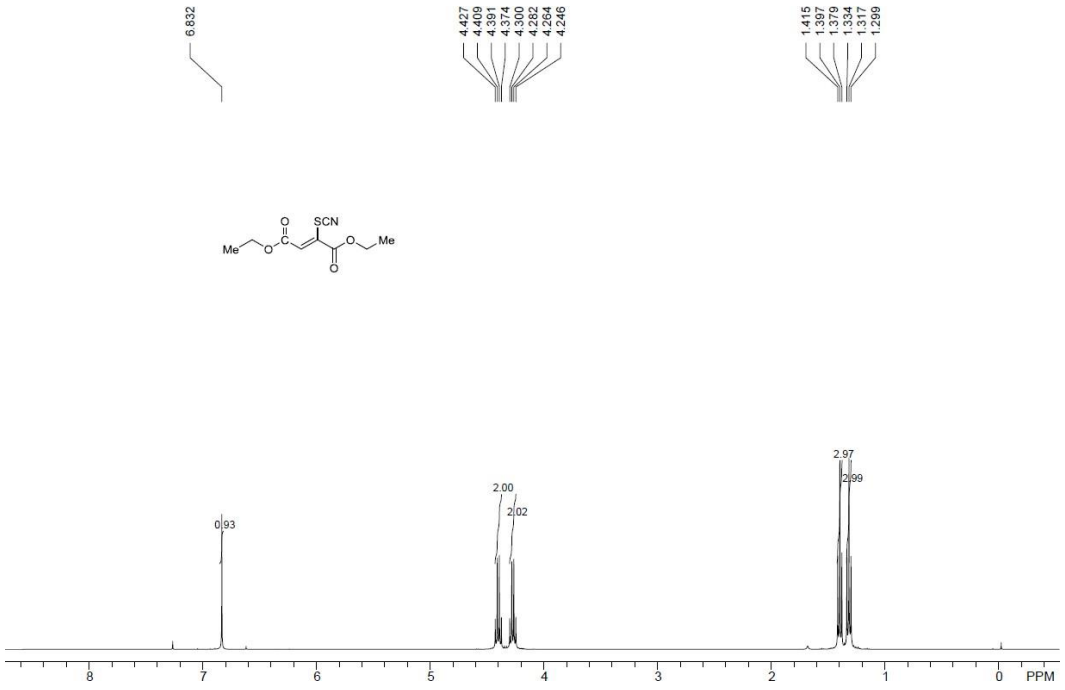
ethyl (*Z*)-4,4,4-trifluoro-3-thiocyanatobut-2-enoate (2z)

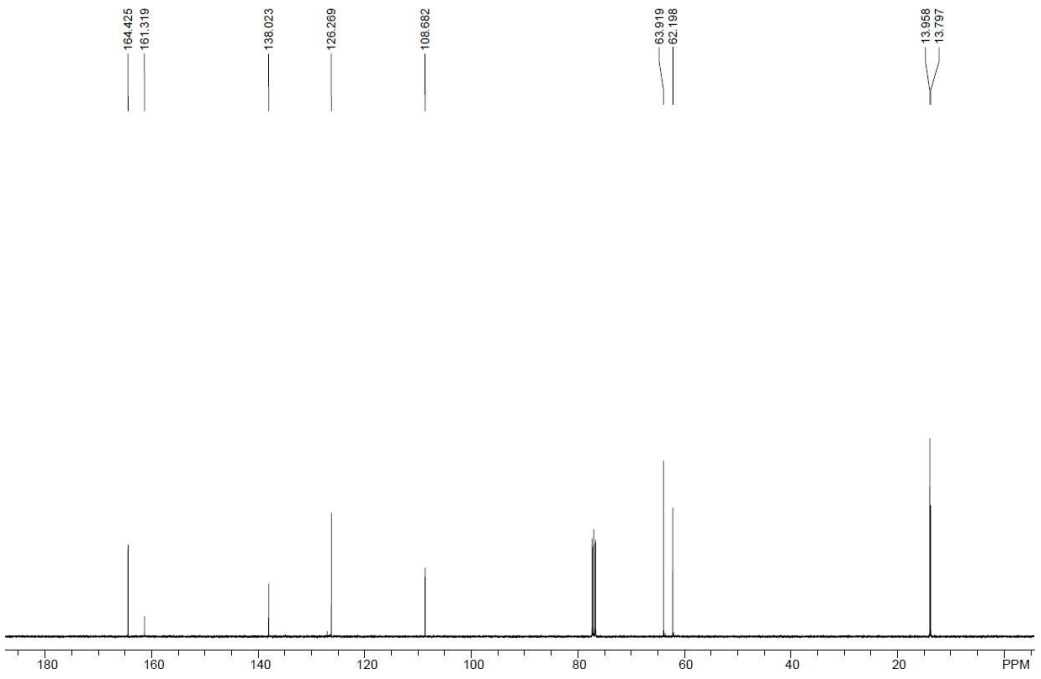




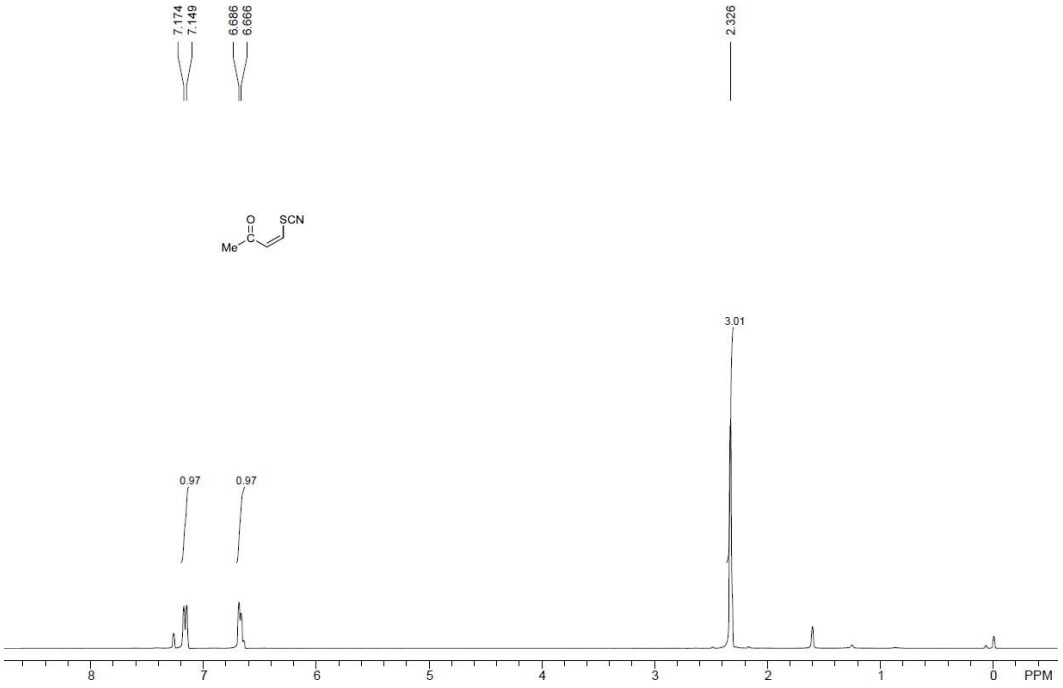

-63.473
0
-20
-40
-60
-80
-100
-120
-140
PPM

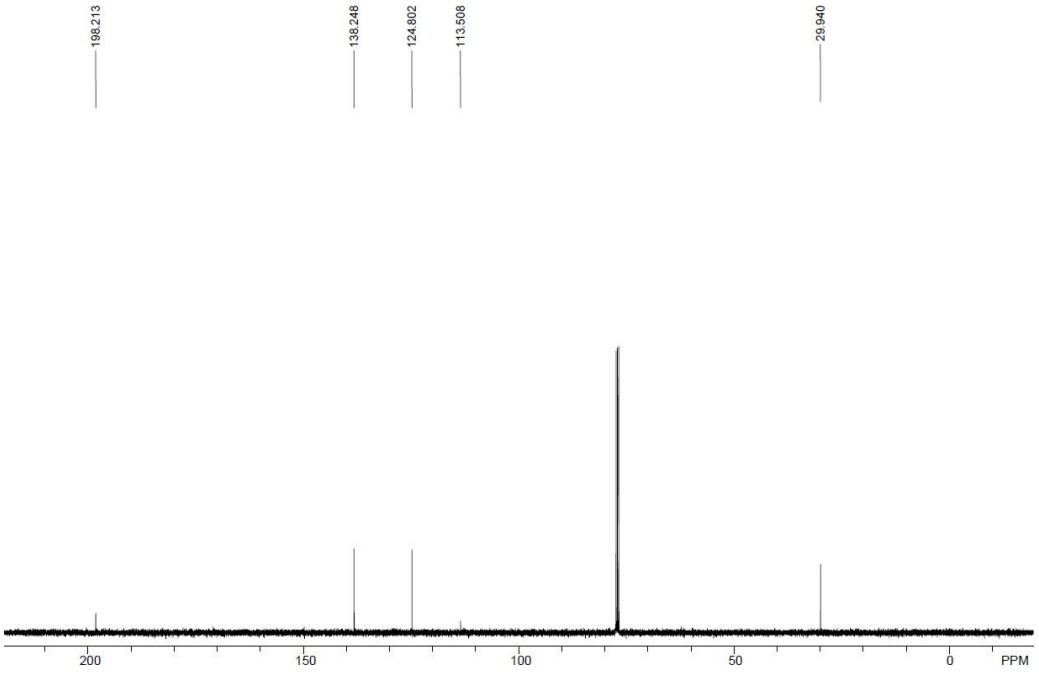
diethyl 2-thiocyanatofumarate (2aa)



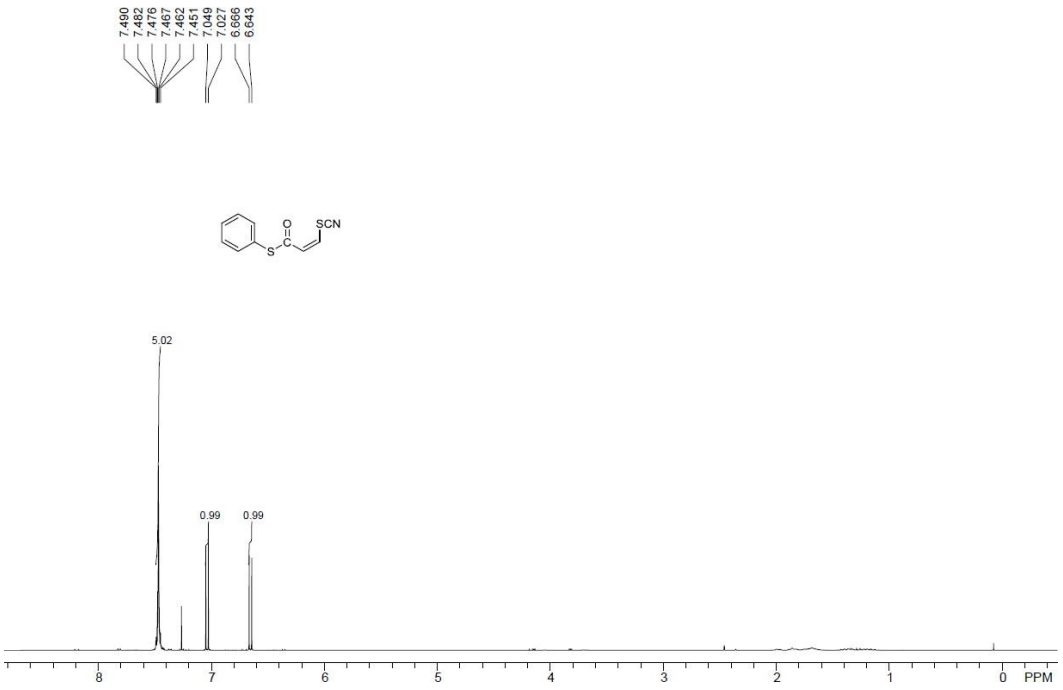


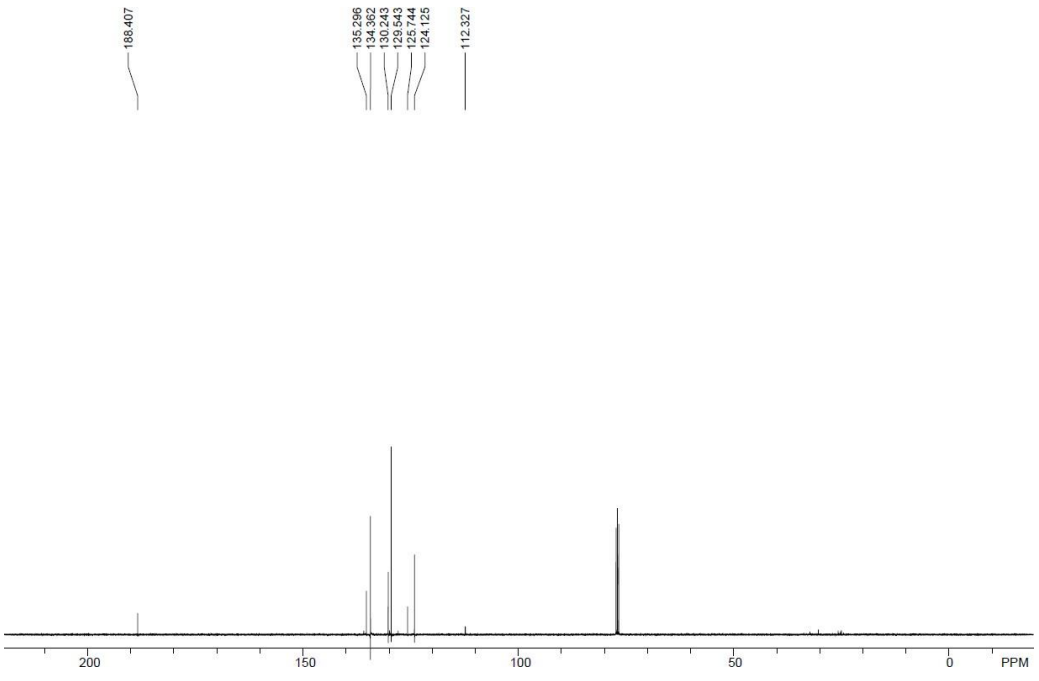
(*Z*)-4-thiocyanatobut-3-en-2-one (2ab)



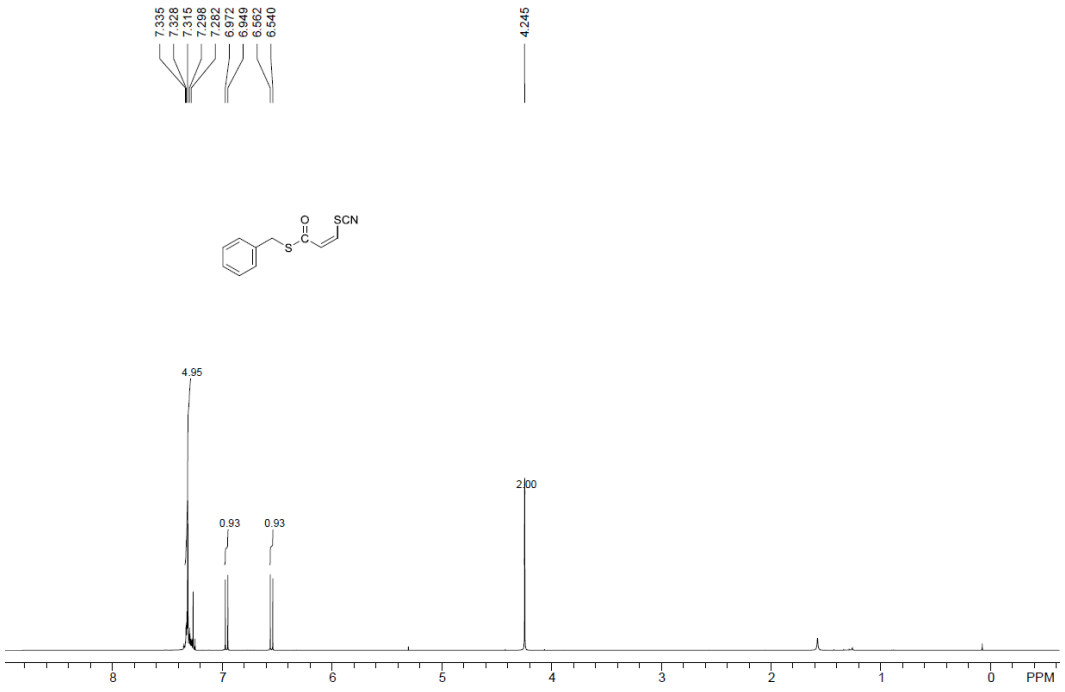


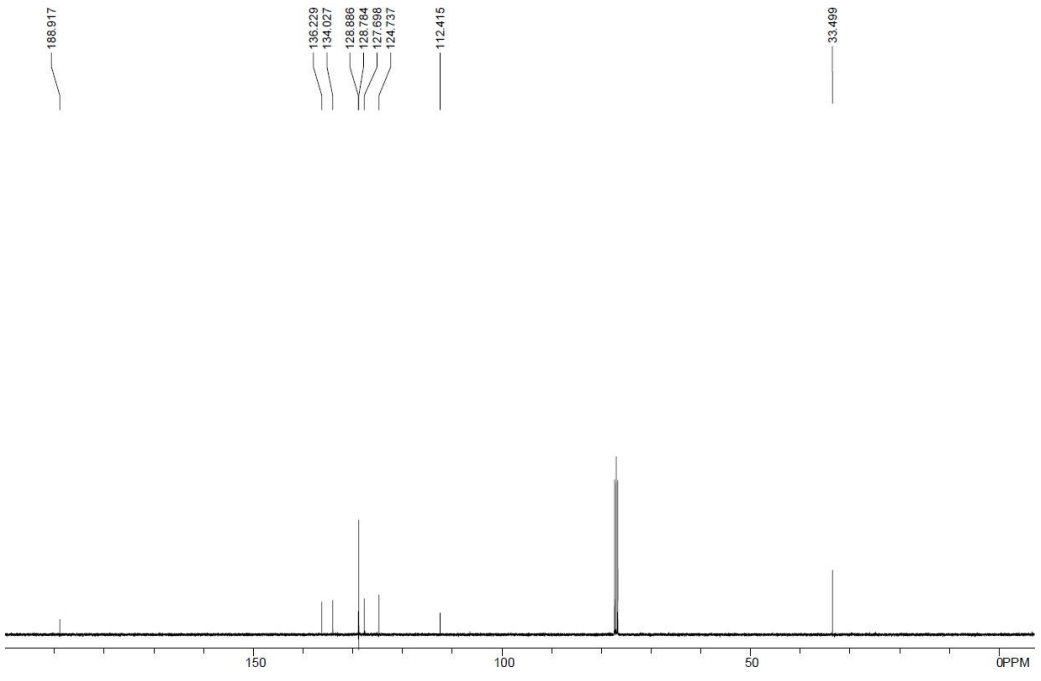
S-phenyl (Z)-3-thiocyanatoprop-2-enethioate (2ac)



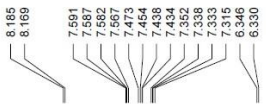


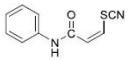
S-benzyl (Z)-3-thiocyanatoprop-2-enethioate (2ad)

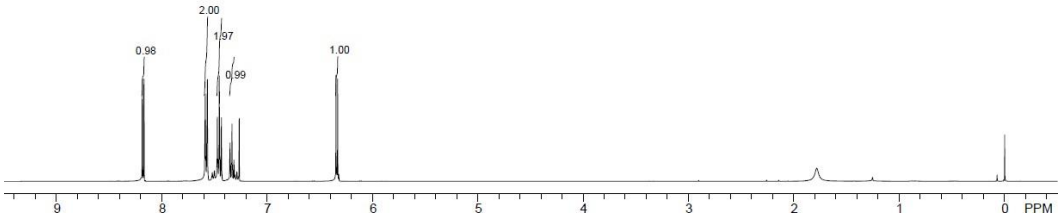


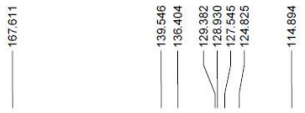


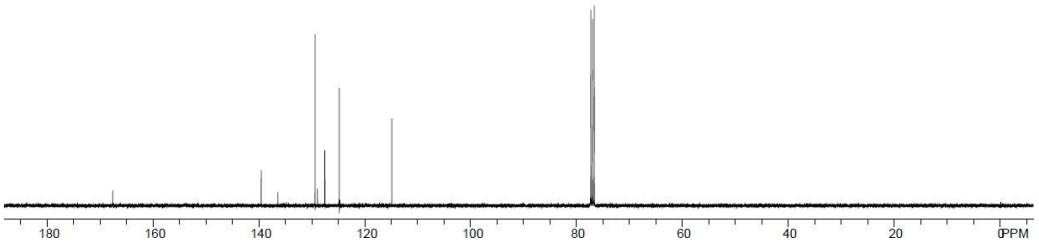
(*Z*)-*N*-phenyl-3-thiocyanatoacrylamide (2ae)



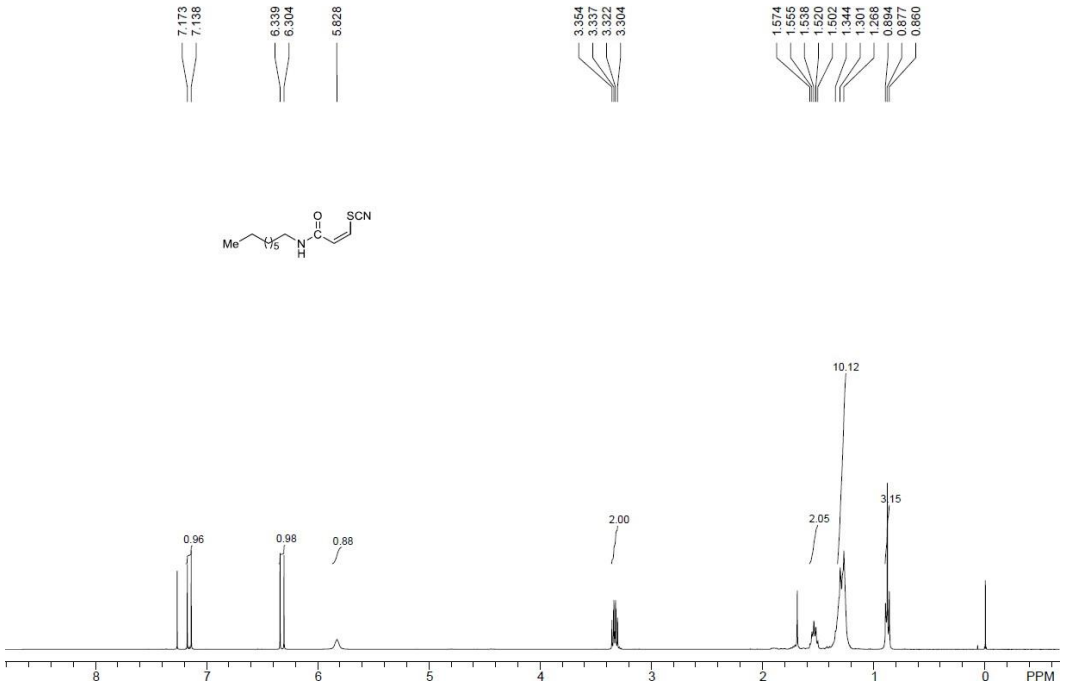


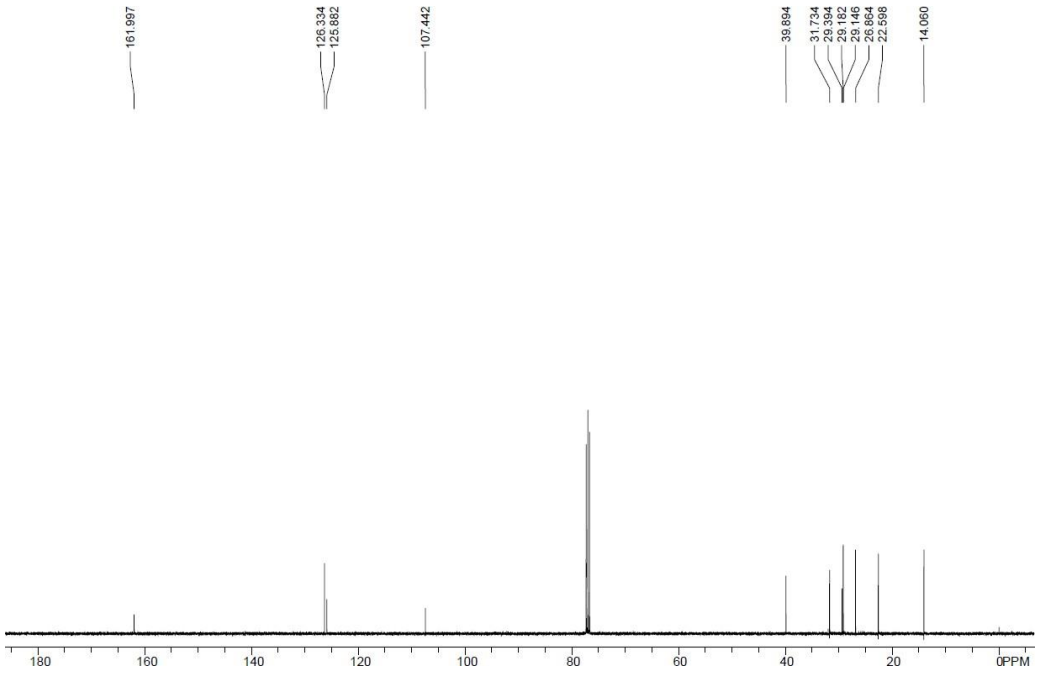




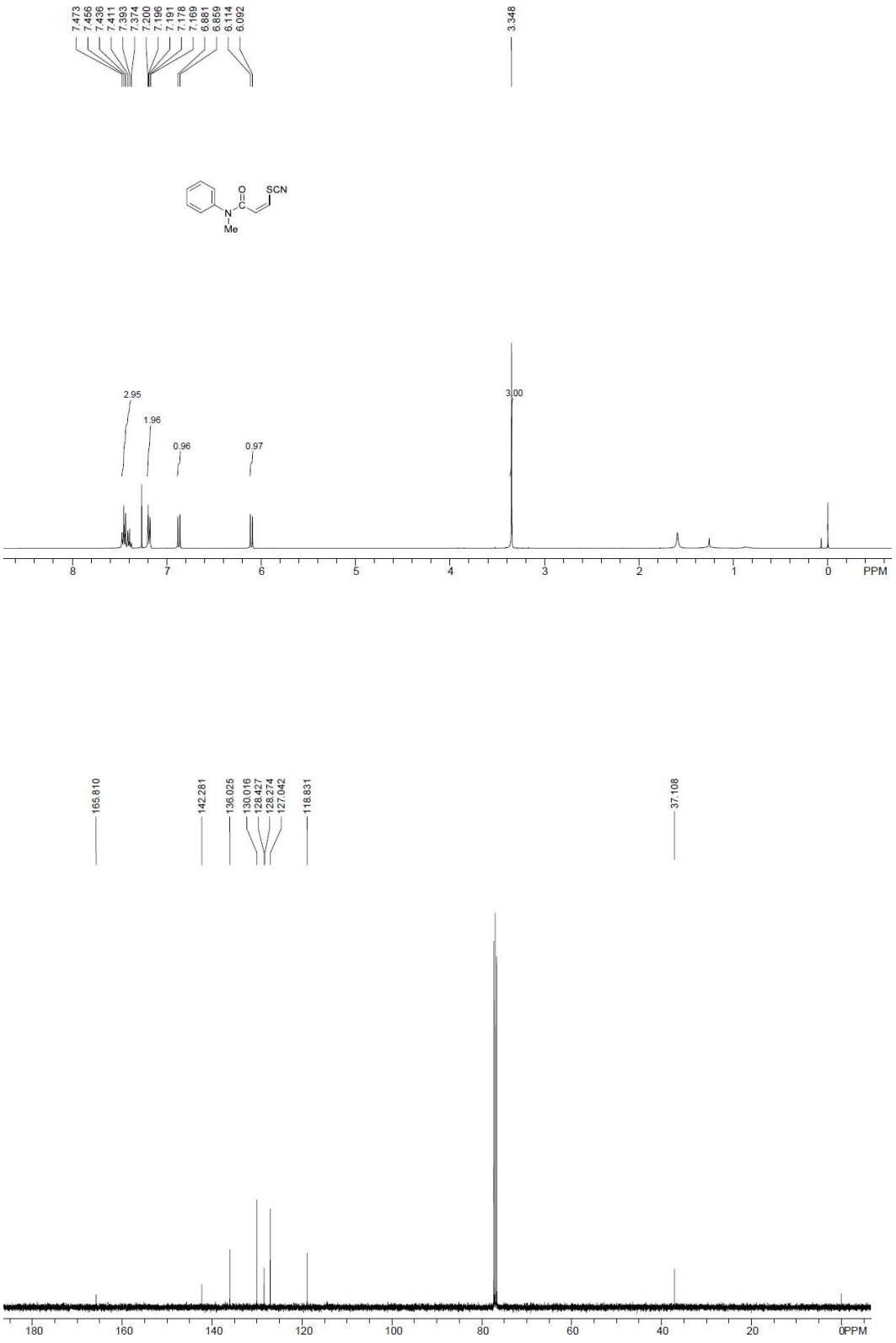


(*Z*)-*N*-octyl-3-thiocyanatoacrylamide (2af)

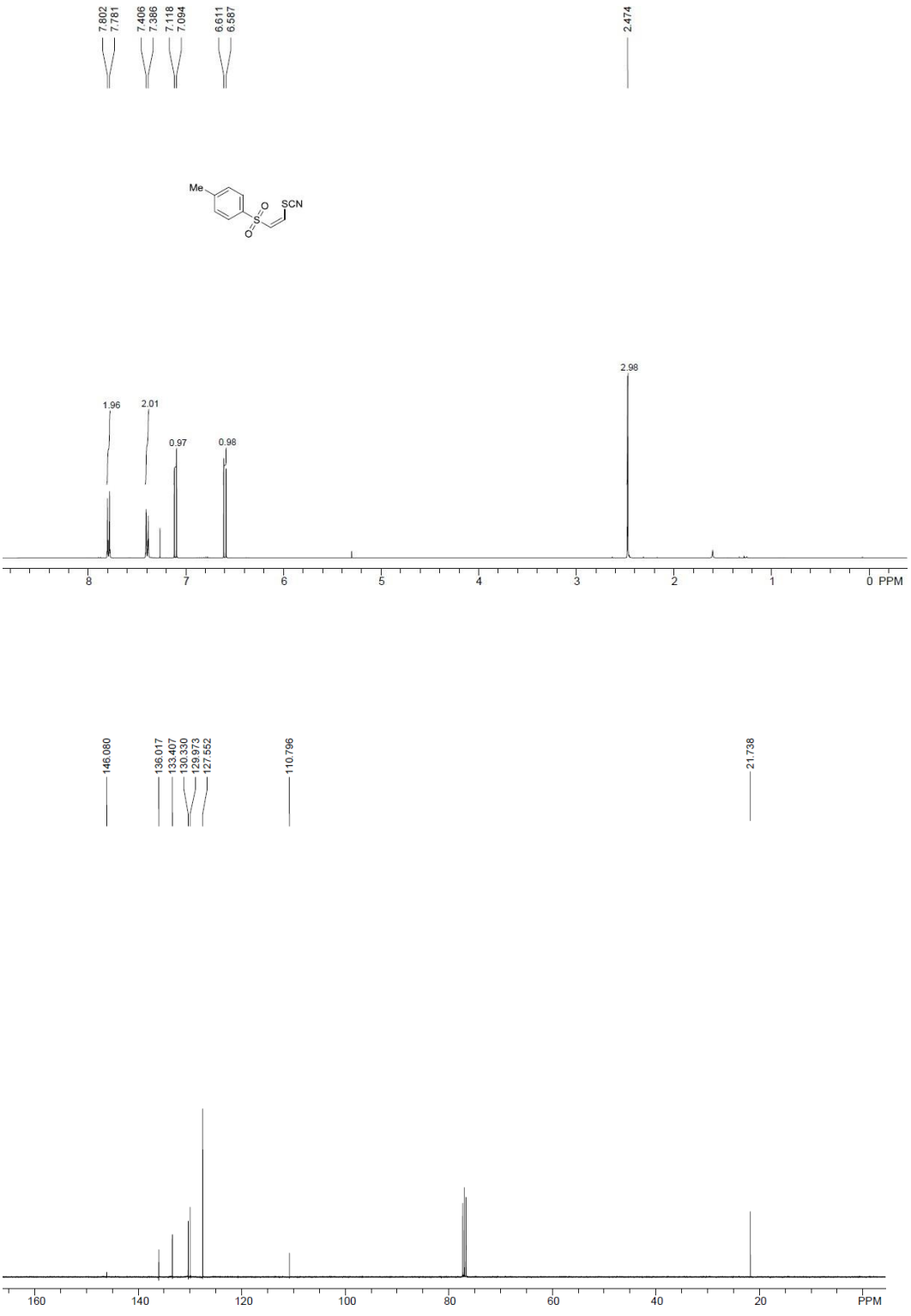




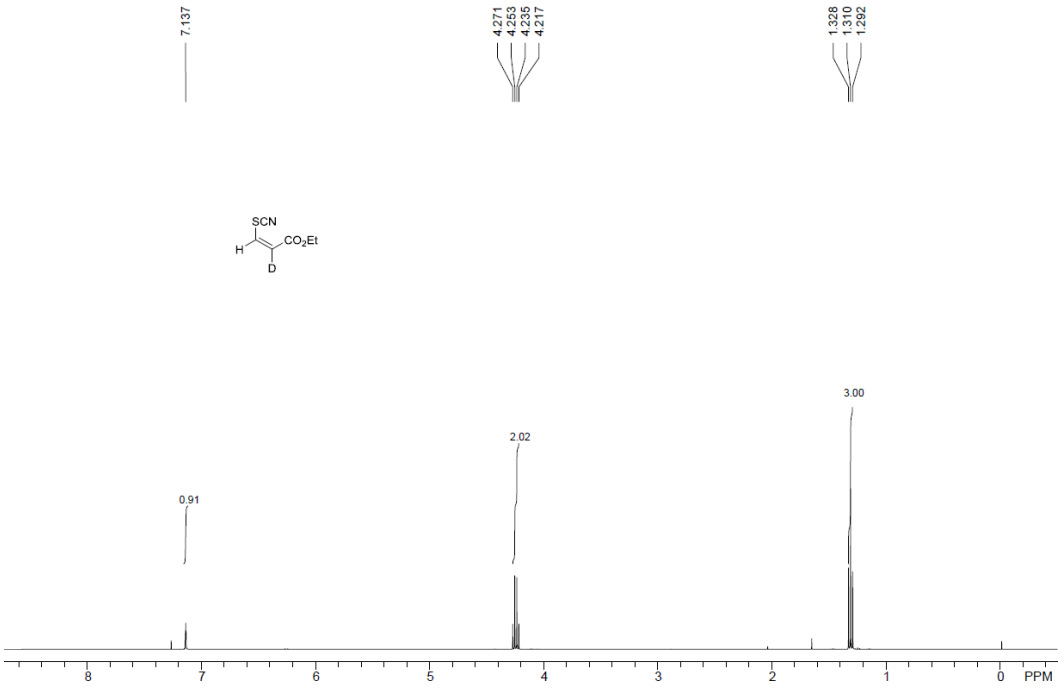
(*Z*)-*N*-methyl-*N*-phenyl-3-thiocyanatoacrylamide (2ag)

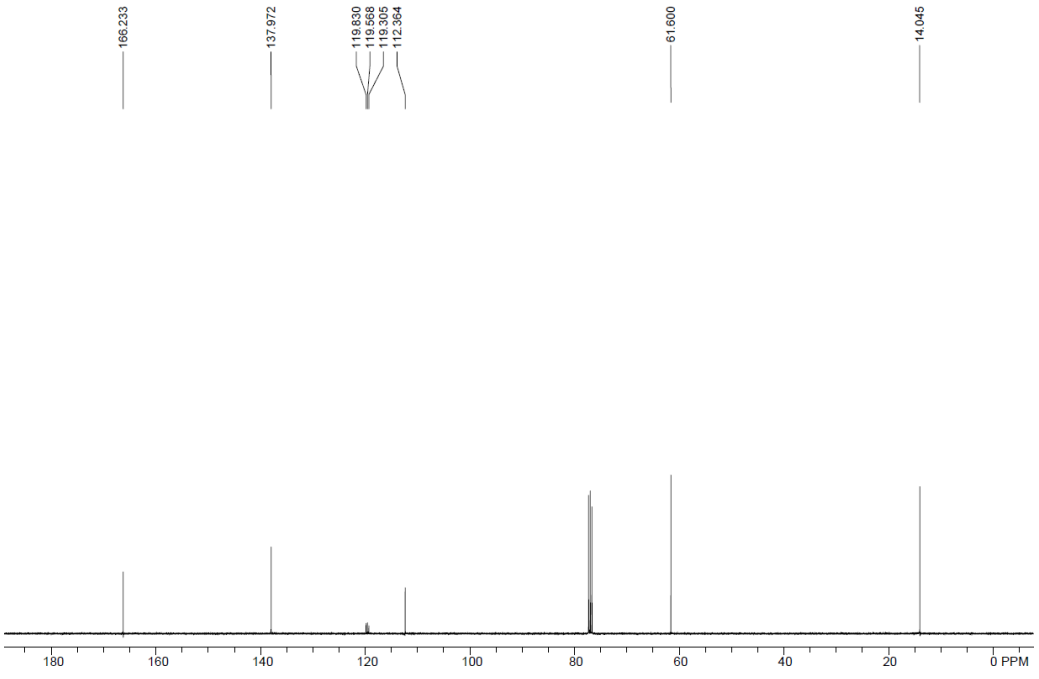


(*Z*)-1-methyl-4-((2-thiocyanatovinyl)sulfonyl)benzene (2ah)

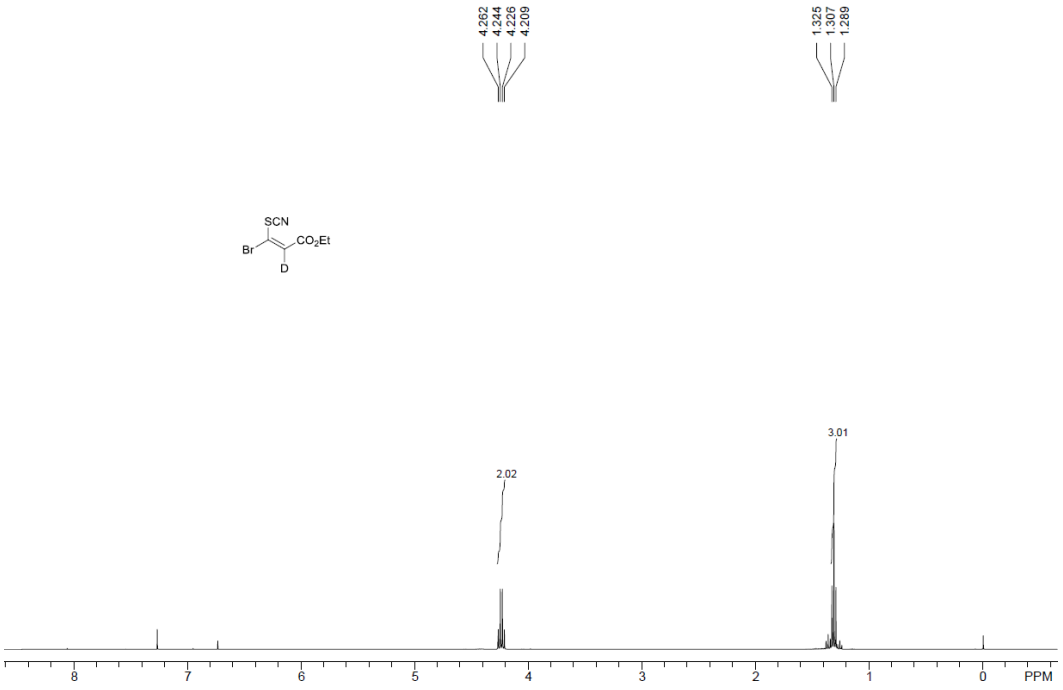


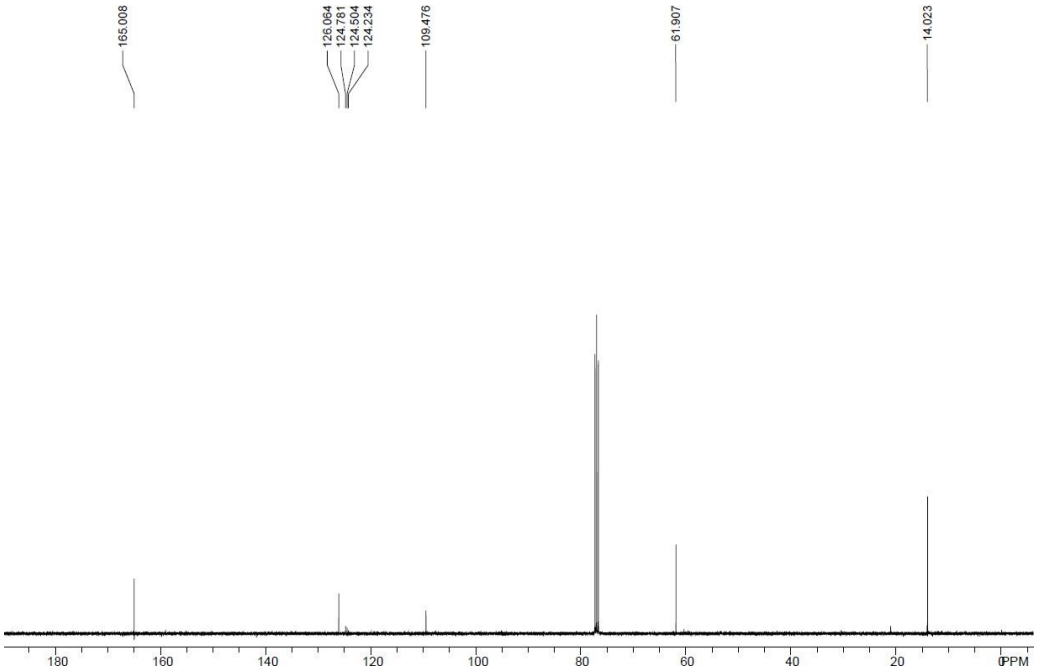
ethyl (*Z*)-3-thiocyanatoacrylate-2-d (2a-d1)





ethyl (*E*)-3-bromo-3-thiocyanatoacrylate-d (2y-d1)





diethyl 2-thiocyanatofumarate-d (2aa-d1)