CORE
Metadata
Provided by University

ELECTRONIC SUPPORTING INFORMATION

Straightforward synthesis of α,β-unsaturated thioesters via ruthenium catalysed olefin cross-metathesis with thioacrylate.

Anthoni W. van Zijl, Adriaan J. Minnaard, Ben L. Feringa**

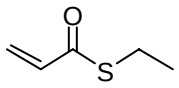
TABLE OF CONTENTS:

General Remarks:

^{1}H-NMR spectra were recorded at 300 or 400 MHz with $CDCl_3$ as solvent. ^{13}C-NMR spectra were obtained at 75.4 or 100.59 MHz in $CDCl_3$. Chemical shifts were determined relative to the residual solvent peaks ($CHCl_3$, δ = 7.26 ppm for hydrogen atoms, δ = 77.0 for carbon atoms). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad signal. Thin-layer chromatography (TLC) was performed using commercial Kieselgel $60F_{254}$ silica gel plates, and components were visualized with $KMnO_4$ or phosphomolybdic acid reagent. Flash chromatography was performed on silica gel. Solvent removal was conducted with a rotary evaporator.

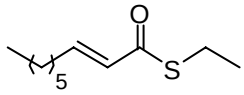
Metathesis catalysts were purchased from commercial sources and used as such, except for **Gre-2**, which was synthesised according to a literature procedure.[1] Wittig reagent **1** was synthesised according to a literature procedure.[2] Paraformaldehyde and all cross-metathesis partners were purchased from chemical suppliers and used without further purification, with the exception of methyl 4-pentenoate, which was synthesised from 4-pentenoic acid and trimethylsilyldiazomethane, and allyl tosylamide, which was synthesised from allylamine and tosylchloride. CH_2Cl_2 was distilled from CaH_2 under a N_2-atmosphere and used as such. All other solvents were used as purchased. Reactions were conducted under nitrogen atmosphere using standard Schlenk techniques.

[1] Grela, K.; Harutyunyan, S.; Michrowska, A., *Angew. Chem.-Int. Ed.* **2002,** 41, 4038-4040.
[2] Keck, G. E.; Boden, E. P.; Mabury, S. A., *J. Org. Chem.* **1985,** 50, 709-710.



_S_-Ethyl thioacrylate (2):

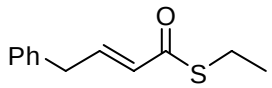
A flame dried Schlenk-flask under N_2-atmosphere was charged with Wittig reagent **1** (29.8 g, 82 mmol), paraformaldehyde (12.3 g, 410 mmol) and CH_2Cl_2 (200 mL). The resulting suspension was stirred for 30 min at reflux temperature. The mixture was concentrated in vacuo and the residue was suspended in pentane (100 mL) and filtered over silica. The filtercake was washed (10:90 Et_2O/pentane, 250 mL) and the filtrates combined. Hydroquinone (ca. 30 mg) was added to the solution to prevent polymerisation and the solvents were removed by distillation at atmospheric pressure using an efficient fractionating column. The crude thioacrylate was further purified by distillation at reduced pressure (50 mbar, 56-58°C), which afforded **2** (6.93 g, 73% yield) as a colorless oil. The compound was stored without stabilizer and used as such in the metathesis reactions; to prevent decomposition it was shielded from light and stored at 5-8 °C. ^{1}H-NMR δ 6.37 (dd, *J* = 17.2, 9.7 Hz, 1H), 6.28 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.66 (dd, *J* = 9.7, 1.6 Hz, 1H), 2.96 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (400 MHz, CDCl3) δ 190.0, 134.9, 125.7, 22.9, 14.4; MS (EI) *m/z* 116 (M^+, 37), 91 (6), 89 (6), 86 (17), 84 (25), 62 (10), 61 (16), 55 (100); HRMS Calcd. for C_5H_8OS 116.0296, found 116.0299.



(_E_)-_S_-ethyl non-2-enethioate (3):

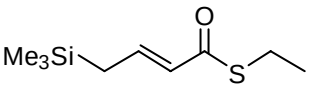
A flame dried Schlenk-flask under N_2-atmosphere was charged with *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg), 1-octene (2.5 mmol, 395 µl) and CH_2Cl_2 (2.5 mL). Hoveyda-Grubbs 2nd generation catalyst (2 mol%, 20 µmol, 12.5 mg) was added and the resulting solution was stirred for 60 min at reflux temperature. The mixture was then concentrated in vacuo and the residue purified by flash column chromatography (SiO_2, 0.5 : 99.5 to 5 : 95 Et_2O / pentane gradient, R_f (2 : 98) = 0.45), which afforded **3** (188 mg, 94% yield) as a colorless oil; ^{1}H-NMR δ 6.89 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.10 (dt, *J* = 15.5, 1.6 Hz, 1H), 2.94 (q, *J* = 7.4 Hz, 2H), 2.22-2.14 (m, 2H), 1.50-1.38 (m, 2H), 1.35-1.24 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 1H); ^{13}C-NMR δ 190.0, 145.3, 128.5, 32.1, 31.5, 28.7, 27.8, 22.9, 22.4, 14.7, 13.9; MS (EI) *m/z* 200 (M^+, 11), 140 (10), 139 (100), 81 (6), 69 (36), 68 (11), 67 (7), 55 (66), 53 (9); HRMS Calcd. for $C_{11}H_{20}OS$ 200.1235, found 200.1236.

(*E*)-*S*-ethyl 4-phenylbut-2-enethioate (4):



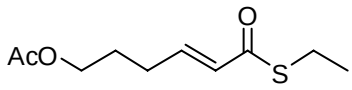
The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and allylbenzene (2.5 mmol, 330 µl) following the procedure described for **3** (reaction time: 60 min). Purification by flash column chromatography (SiO_2, 1 : 99 to 5 : 95 Et_2O / pentane gradient, R_f (1 : 99) = 0.15) afforded **4** (195 mg, 95% yield) as a colorless oil; ^{1}H-NMR δ 7.47-7.11 (m, 5H), 7.03 (dt, *J* = 15.4, 6.8 Hz, 1H), 6.10 (dt, *J* = 15.4, 1.6 Hz, 1H), 3.52 (d, *J* = 6.8 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 2H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.9, 143.1, 137.3, 129.4, 128.7, 128.6, 126.6, 38.3, 23.0, 14.7; MS (EI) *m/z* 206 (M^+, 19), 146 (11), 145 (100), 127 (28), 117 (22), 116 (6), 115 (31), 91 (10); HRMS Calcd. for $C_{12}H_{14}OS$ 206.0765, found 206.0756.

(*E*)-*S*-Ethyl 4-(trimethylsilyl)but-2-enethioate (5):



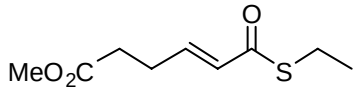
The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and allyltrimethylsilane (2.5 mmol, 397 µl) following the procedure described for **3** (reaction time: 2 h). Purification by flash column chromatography (SiO_2, 0.5 : 99.5 to 2 : 98 Et_2O / pentane gradient, R_f (2 : 98) = 0.4) afforded **5** (187 mg, 92% yield) as a colorless oil; ^{1}H-NMR δ 6.99 (dt, *J* = 15.3, 8.9 Hz, 1H), 5.97 (dt, *J* = 15.2, 1.3 Hz, 1H), 2.93 (q, *J* = 7.4 Hz, 2H), 1.72 (dd, *J* = 8.9, 1.3 Hz, 2H), 1.27 (t, *J* = 7.4 Hz, 3H), 0.06 (s, 9H); ^{13}C-NMR δ 189.4, 144.2, 126.7, 24.9, 22.8, 14.8, -1.8, MS (EI) *m/z* 205 (8), 173 ($[M-C_2H_5]^+$, 48), 141 (60), 119 (21), 91 (5), 84 (5), 75 (7), 74 (9), 73 (100); HRMS Calcd. for $C_7H_{13}OSiS$ = $[M-C_2H_5]^+$ 173.0456, found 173.0449.

(*E*)-6-(Ethylthio)-6-oxohex-4-enyl acetate (6):

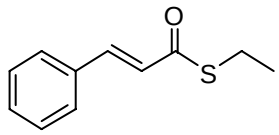


The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 4-pentenyl acetate (2.5 mmol, 353 µl) following the procedure described for **3** (reaction time: 4 h). Purification by flash column chromatography (SiO_2, 5 : 95 to 10 : 90 Et_2O / pentane gradient, R_f (10 : 90) = 0.25) afforded **6** (186 mg, 86% yield) as a colorless oil; ^{1}H-NMR δ 6.86 (dt, *J* = 15.5, 6.9 Hz, 1H), 6.11 (dt, *J* = 15.5, 1.6 Hz, 1H), 4.07 (t, *J* = 6.4 Hz, 2H), 2.93 (q, *J* = 7.4 Hz, 2H), 2.33-2.22 (m, 2H), 2.04 (s, 3H), 1.86-1.74 (m, 2H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.9, 170.9, 143.4, 129.2, 63.4, 28.6, 26.9, 23.0, 20.8, 14.7; MS (EI) *m/z*

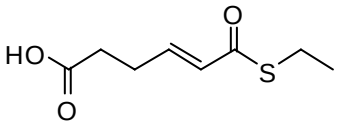
216 (M^+, 2), 155 (19), 114 (6), 113 (100), 95 (31), 71 (6), 68 (6), 67 (45), 55 (6); HRMS Calcd. for $C_{10}H_{16}O_3S$ 216.0820, found 216.0816.



(*E*)-Methyl 6-(ethylthio)-6-oxohex-4-enoate (7): The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and methyl 4-pentenoate (2.5 mmol, 285 mg) following the procedure described for **3** (reaction time: 4 h). Purification by flash column chromatography (SiO_2, 5 : 95 to 10 : 90 Et_2O / pentane gradient, R_f (10 : 90) = 0.25) afforded **7** (184 mg, 91% yield) as a colorless oil; ^{1}H-NMR δ 6.85 (dt, *J* = 15.6, 6.5 Hz, 1H), 6.12 (dt, *J* = 15.6, 1.5 Hz, 1H), 3.68 (s, 3H), 2.93 (q, *J* = 7.4 Hz, 2H), 2.60-2.41 (m, 4H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.8, 172.5, 142.2, 129.3, 51.7, 32.1, 27.0, 23.0, 14.6; MS (EI) *m/z* 202 (M^+, 4), 142 (8), 141 (100), 113 (21), 109 (29), 81 (13), 71 (45), 59 (10), 53 (8); HRMS Calcd. for $C_9H_{14}O_3S$ 202.0664, found 202.0673.

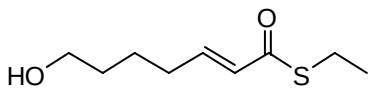


(*E*)-*S*-ethyl 3-phenylprop-2-enethioate (8): The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and styrene (2.5 mmol, 287 μl) following the procedure described for **3** (reaction time: 18 h). Purification by flash column chromatography (SiO_2, 0.5 : 99.5 to 1 : 99 Et_2O / pentane gradient, R_f (1 : 99) = 0.10) afforded **8** (139 mg, 72% yield) as a colorless oil; ^{1}H-NMR δ 7.61 (d, *J* = 15.8 Hz, 1H), 7.57-7.51 (m, 2H), 7.42-7.36 (m, 3H), 6.71 (d, *J* = 15.8 Hz, 1H), 3.02 (q, *J* = 7.4 Hz, 2H), 1.32 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.9, 140.1, 134.1, 130.4, 128.9, 128.3, 125.0, 23.3, 14.8; MS (EI) *m/z* 192 (M^+, 12), 132 (10), 131 (100), 103 (27), 77 (13); HRMS Calcd. for $C_{11}H_{12}OS$ 192.0609, found 192.0599.



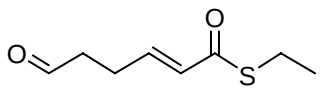
(*E*)-6-(ethylthio)-6-oxohex-4-enoic acid (9): The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 4-pentenoic acid (2.5 mmol, 258 μl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 0.5 : 5 : 95 to 2 : 20 : 80 AcOH / EtOAc / pentane gradient, R_f (1 : 10 : 90) = 0.2) afforded **9** (156 mg, 83% yield) as an off-white solid. Traces of

AcOH could be removed by trituration from $CHCl_3$ with pentane; mp = 69.5-69.8 °C; ^{1}H-NMR δ 10.20 (br s, 1H), 6.84 (dt, *J* = 15.4, 6.7 Hz, 1H), 6.15 (dt, *J* = 15.5, 1.5 Hz, 1H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.59-2.49 (m, 4H), 1.28 (t, *J* = 7.4 Hz, 1H); ^{13}C-NMR δ 190.0, 178.2, 141.9, 129.3, 32.0, 26.6, 23.0, 14.6; MS (EI) *m/z* 188 (M^+, 12), 128 (7), 127 (100), 109 (14), 99 (52), 81 (14), 71 (7), 57 (39), 55 (9), 53 (22); HRMS Calcd. for $C_8H_{12}O_3S$ 188.0507, found 188.0516.



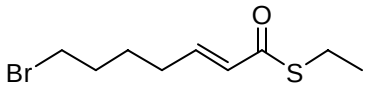
(*E*)-*S*-Ethyl 7-hydroxyhept-2-enethioate (10):

The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 5-hexen-1-ol (2.5 mmol, 300 µl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 40 : 60 to 70 : 30 Et_2O / pentane gradient, R_f (50 : 50) = 0.25) afforded **10** (175 mg, 93% yield) as a colorless oil; ^{1}H-NMR δ 6.88 (dt, *J* = 15.5, 6.9 Hz, 1H), 6.11 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.65 (t, *J* = 5.2 Hz, 2H), 2.93 (q, *J* = 7.4 Hz, 2H), 2.28-2.19 (m, 2H), 1.66-1.50 (m, 4H), 1.36 (br s, 1H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 190.2, 144.7, 128.6, 62.0, 31.8, 31.6, 24.0, 22.8, 14.6; MS (EI) *m/z* 188 (M^+, 7), 127 (31), 99 (5), 82 (7), 81 (100), 79 (8), 68 (9), 57 (6), 55 (16), 53 (10); HRMS Calcd. for $C_9H_{16}O_2S$ 188.0871, found 188.0876.

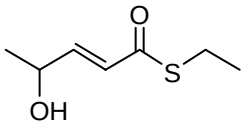


(*E*)-*S*-Ethyl 6-oxohex-2-enethioate (11):

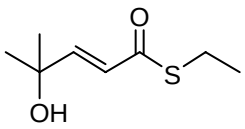
The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 1-pentenal (2.5 mmol, 247 µl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 10 : 90 to 20 : 80 Et_2O / pentane gradient, R_f (10 : 90) = 0.2) afforded **11** (129 mg, 75% yield) as a colorless oil; ^{1}H-NMR δ 9.79 (t, *J* = 1.1 Hz, 1H), 6.84 (dt, *J* = 15.4, 6.7 Hz, 1H), 6.12 (dt, *J* = 15.5, 1.5 Hz, 1H), 2.93 (q, *J* = 7.4 Hz, 2H), 2.67-2.61 (m, 2H), 2.55-2.47 (m, 2H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 200.0, 189.5, 142.0, 129.2, 41.5, 24.1, 22.9, 14.5; MS (EI) *m/z* 172 (M^+, 29), 112 (8), 111 (100), 83 (49), 55 (46), 53 (7); HRMS Calcd. for $C_8H_{12}O_2S$ 172.0558, found 172.0557.



(*E*)-*S*-Ethyl 7-bromohept-2-enethioate (12): The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 6-bromohex-1-ene (2.5 mmol, 337 µl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 0.5 : 99.5 to 2 : 98 Et_2O / pentane gradient, R_f (1 : 99) = 0.10) afforded **12** (180 mg, 72% yield) as a colorless oil; ^{1}H-NMR δ 6.86 (dt, *J* = 15.5, 6.9 Hz, 1H), 6.12 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.41 (t, *J* = 6.6 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 2H), 2.28-2.18 (m, 2H), 1.95-1.83 (m, 2H), 1.71-1.58 (m, 2H), 1.28 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.9, 143.9, 129.0, 33.1, 31.9, 31.1, 26.4, 23.0, 14.7; MS (EI) *m/z* 252 (M^+, 11), 250 (M^+, 11), 192 (7), 191 (98), 190 (8), 189 (100), 177 (9), 175 (9), 81 (13), 55 (58); HRMS Calcd. for $C_9H_{15}OSBr$ 250.0027, found 250.0034.

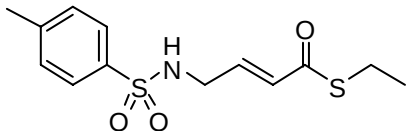


(*E*)-*S*-Ethyl 4-hydroxypent-2-enethioate (13): The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 3-buten-2-ol (2.5 mmol, 217 µl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 10 : 90 to 50 : 50 Et_2O / pentane gradient, R_f (30 : 70) = 0.25) afforded **13** (106 mg, 66% yield) as a yellowish oil; ^{1}H-NMR δ 6.79 (dd, *J* = 15.5, 4.5 Hz, 1H), 6.22 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.39 (qdd, *J* = 6.6, 4.6, 1.6 Hz, 1H), 3.27 (br s, 1H), 2.87 (q, *J* = 7.4 Hz, 2H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.20 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 190.6, 146.8, 126.0, 66.6, 23.1, 22.3, 14.4; MS (EI) *m/z* 160 (M^+, 5), 115 (7), 100 (5), 99 (100), 71 (20), 55 (9); HRMS Calcd. for $C_7H_{12}O_2S$ 160.0558, found 160.0550.



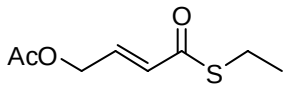
(*E*)-*S*-Ethyl 4-hydroxy-4-methylpent-2-enethioate (14): The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and 2-methyl-3-buten-2-ol (2.5 mmol, 261 µl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 20 : 80 to 40 : 60 Et_2O / pentane gradient, R_f (30 : 70) = 0.3) afforded **14** (124 mg, 71% yield) as a yellowish oil; ^{1}H-NMR δ 6.86 (d, *J* = 15.5 Hz, 1H), 6.26 (d, *J* = 15.5 Hz, 1H), 2.90 (q, *J* = 7.4 Hz, 2H), 2.35 (br s, 1H), 1.33 (s, 6H), 1.23 (t, *J* = 7.4 Hz,

3H); ^{13}C-NMR δ 190.6, 150.2, 124.7, 70.6, 29.1, 23.1, 14.6; MS (EI) *m/z* 174 (M^+, 6), 131 (12), 116 (16), 114 (7), 113 (100), 95 (15), 85 (16), 69 (8), 67 (9), 59 (7), 57 (7), 55 (8); HRMS Calcd. for $C_8H_{14}O_2S$ 174.0715, found 174.0721.



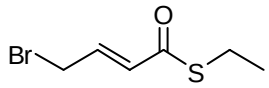
(*E*)-*S*-Ethyl 4-(4-methylphenylsulfonamido) but-2-enethioate (15):

The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and *N*-allyl-4-methylbenzenesulfonamide (2.5 mmol, 528 mg) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 20 : 80 to 60 : 40 Et_2O / pentane gradient, R_f (40 : 60) = 0.2) afforded **15** (176 mg, 71% yield) as a white solid; mp = 68.5-69.4 °C; ^{1}H-NMR δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.63 (dt, *J* = 15.5, 5.1 Hz, 1H), 6.14 (dt, *J* = 15.5, 1.7 Hz, 1H), 5.20 (t, *J* = 6.3 Hz, 1H), 3.77-3.69 (m, 2H), 2.89 (q, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 1.23 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.4, 143.7, 137.9, 136.5, 129.8, 129.2, 127.0, 43.6, 23.2, 21.4, 14.5; MS (EI) *m/z* 299 (M^+, 0.7), 239 (6), 238 (40), 156 (7), 155 (89), 144 (23), 92 (9), 91 (100), 82 (10), 65 (13), 55 (7); HRMS Calcd. for $C_{13}H_{17}NS_2O_3$ 299.0650, found 299.0666.



(*E*)-4-(Ethylthio)-4-oxobut-2-enyl acetate (16):

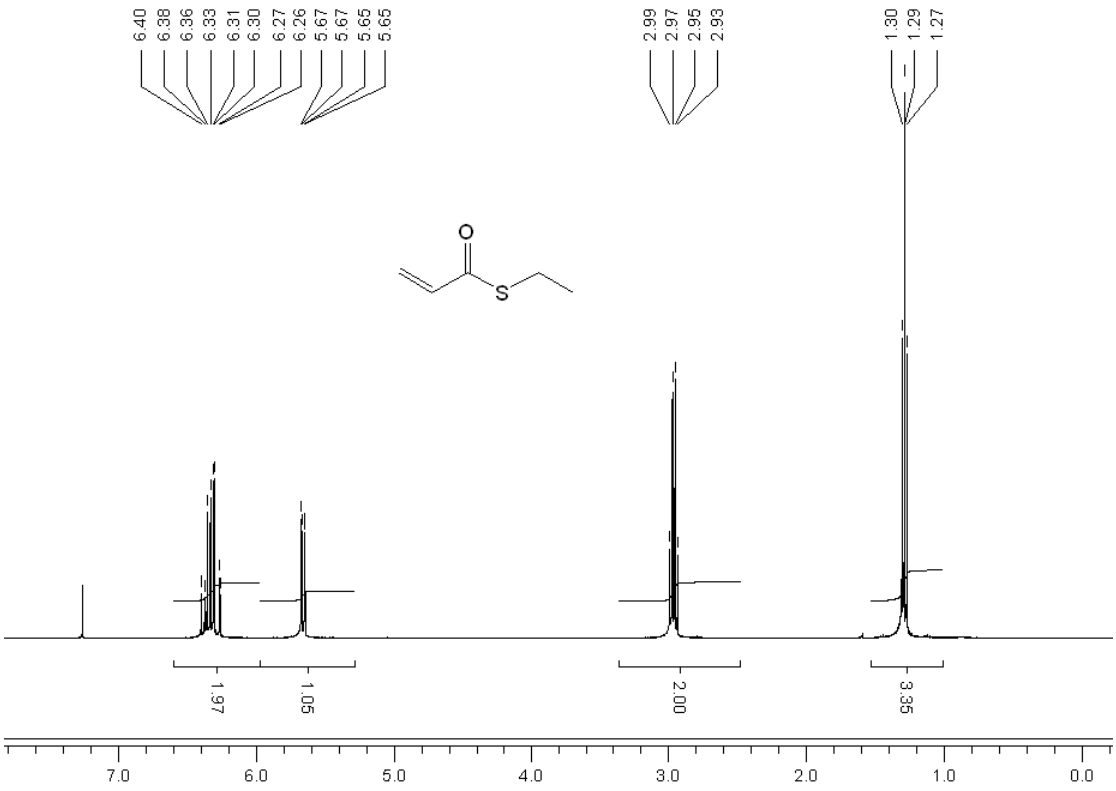
The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and *cis*-1,4-diacetoxy 2-butene (1.5 mmol, 239 µl) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 5 : 95 to 10 : 90 Et_2O / pentane gradient, R_f (10 : 90) = 0.30) afforded **16** (123 mg, 65% yield) as a colorless oil; ^{1}H-NMR δ 6.82 (dt, *J* = 15.6, 4.6 Hz, 1H), 6.27 (dt, *J* = 15.6, 1.9 Hz, 1H), 4.72 (dd, *J* = 4.6, 1.9 Hz, 2H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.3, 170.1, 136.6, 128.7, 62.3, 23.2, 20.6, 14.6; MS (EI) *m/z* 234 (6), 188 (M+, 10), 159 (23), 132 (10), 131 (15), 127 (34), 111 (17), 85 (100), 71 (10), 57 (5); HRMS Calcd. for $C_8H_{12}O_3S$ 188.0507, found 188.0514.

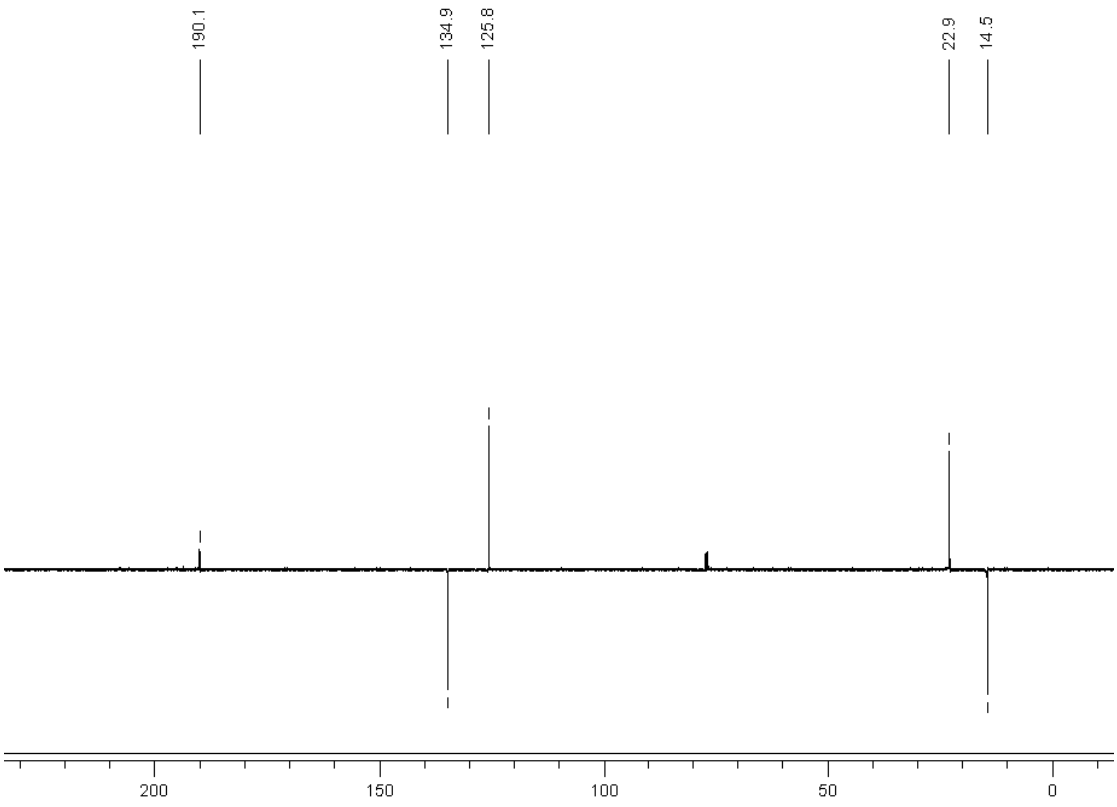


(*E*)-*S*-ethyl 4-bromobut-2-enethioate (17):

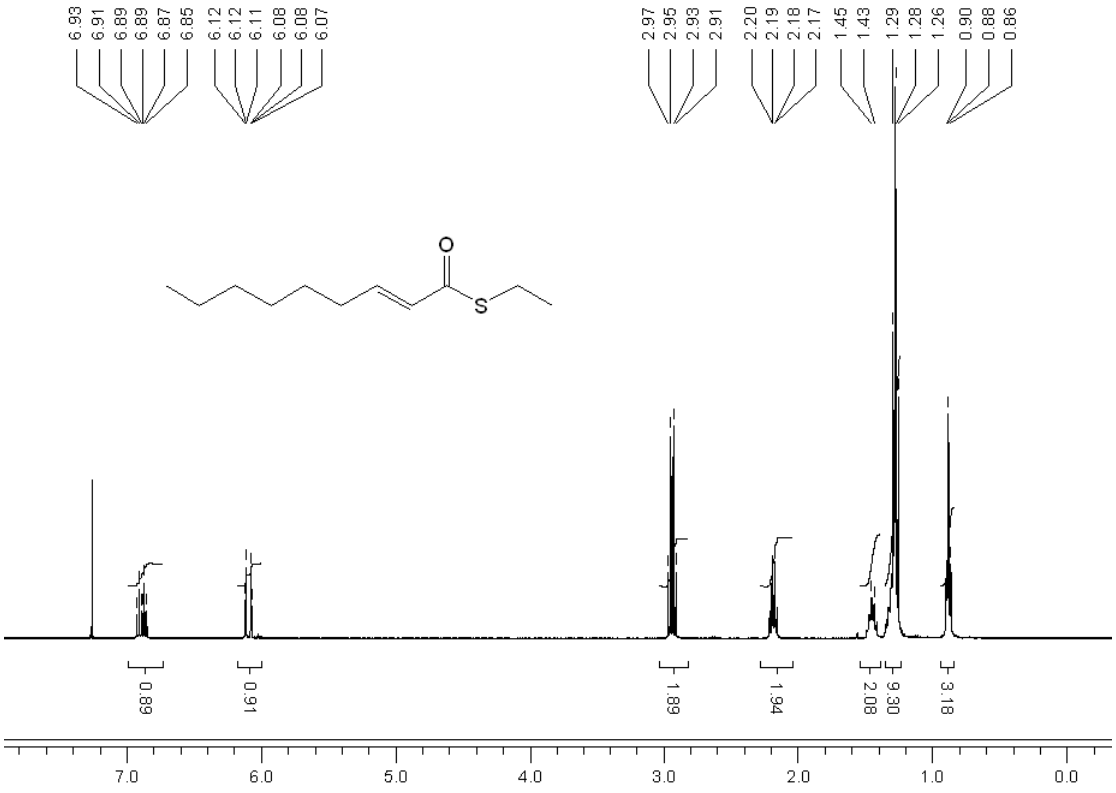
The title compound was prepared from *S*-ethyl thioacrylate **2** (1.0 mmol, 116 mg) and *trans*-1,4-dibromo 2-butene (1.5 mmol, 321 mg) following the procedure described for **3** (2nd portion of 2 mol% catalyst added after 16 h; total reaction time: 24 h). Purification by flash column chromatography (SiO_2, 0.5 : 99.5 to 2 : 98 Et_2O / pentane gradient, R_f (2 : 98) = 0.25) afforded **17** (134 mg, 64% yield) as a yellowish oil; ^{1}H-NMR δ 6.91 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.27 (dt, *J* = 15.2, 1.2 Hz, 1H), 4.00 (dd, *J* = 7.3, 1.2 Hz, 2H), 2.97 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR δ 189.0, 137.1, 130.8, 29.1, 23.2, 14.5; MS (EI) *m/z* 250 (7), 210 (M^+, 6), 208 (M^+, 7), 189 (22), 149 (55), 147 (100), 129 (12), 121 (5), 119 (6), 113 (9), 103 (9), 91 (7), 85 (6), 83 (8), 69 (6), 68 (22), 57 (7), 55 (5); HRMS Calcd. for $C_6H_9OSBr^{79}$ 207.9557, found 207.9563.

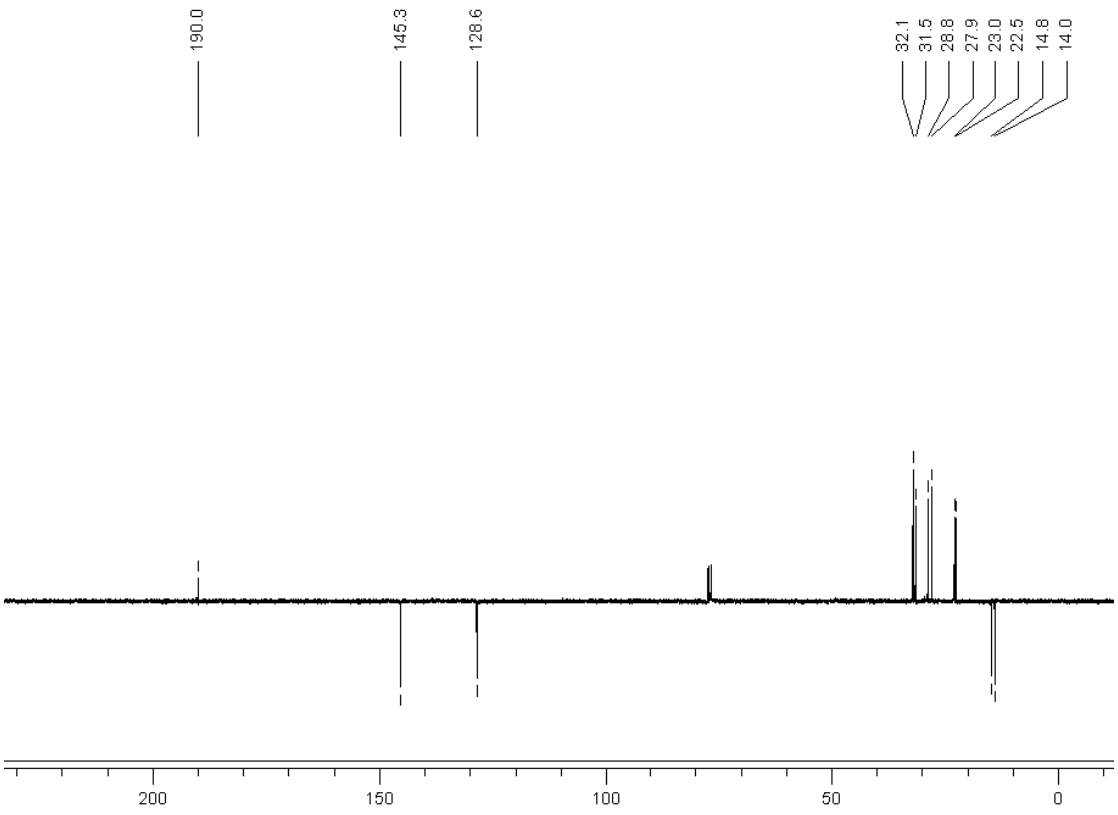
_S_-Ethyl thioacrylate (2):



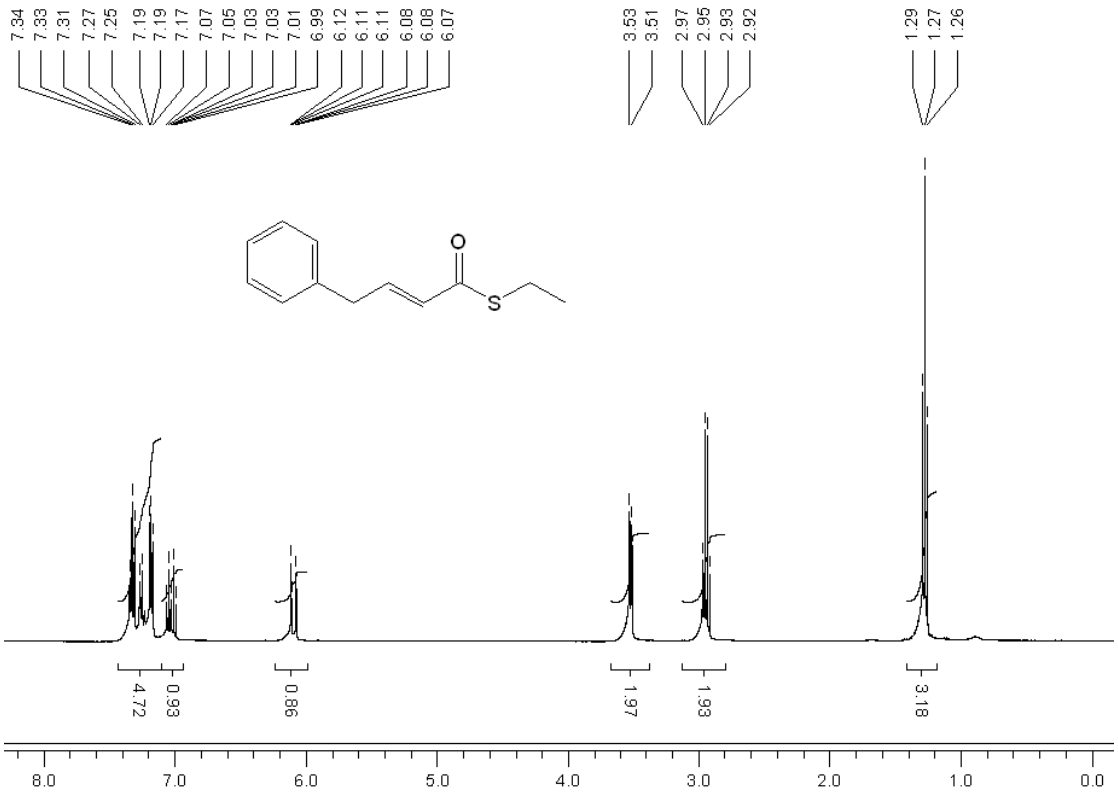


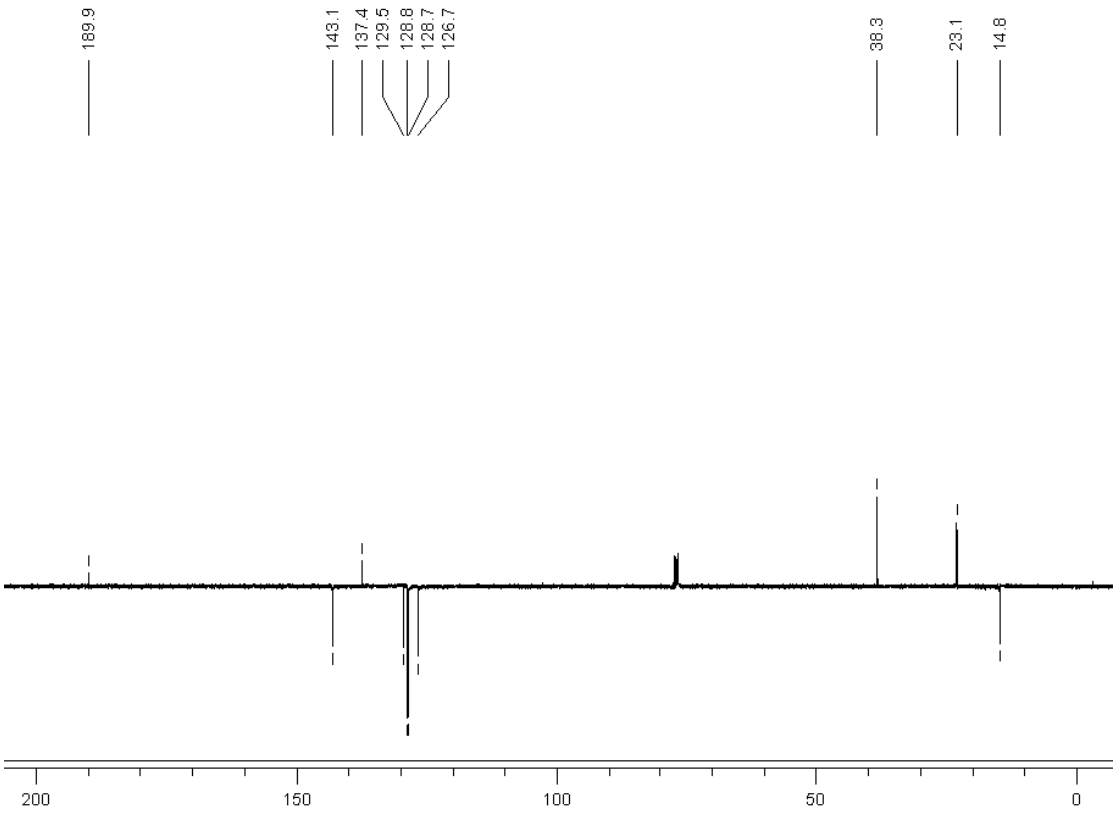
(*E*)-*S*-ethyl non-2-enethioate (3):



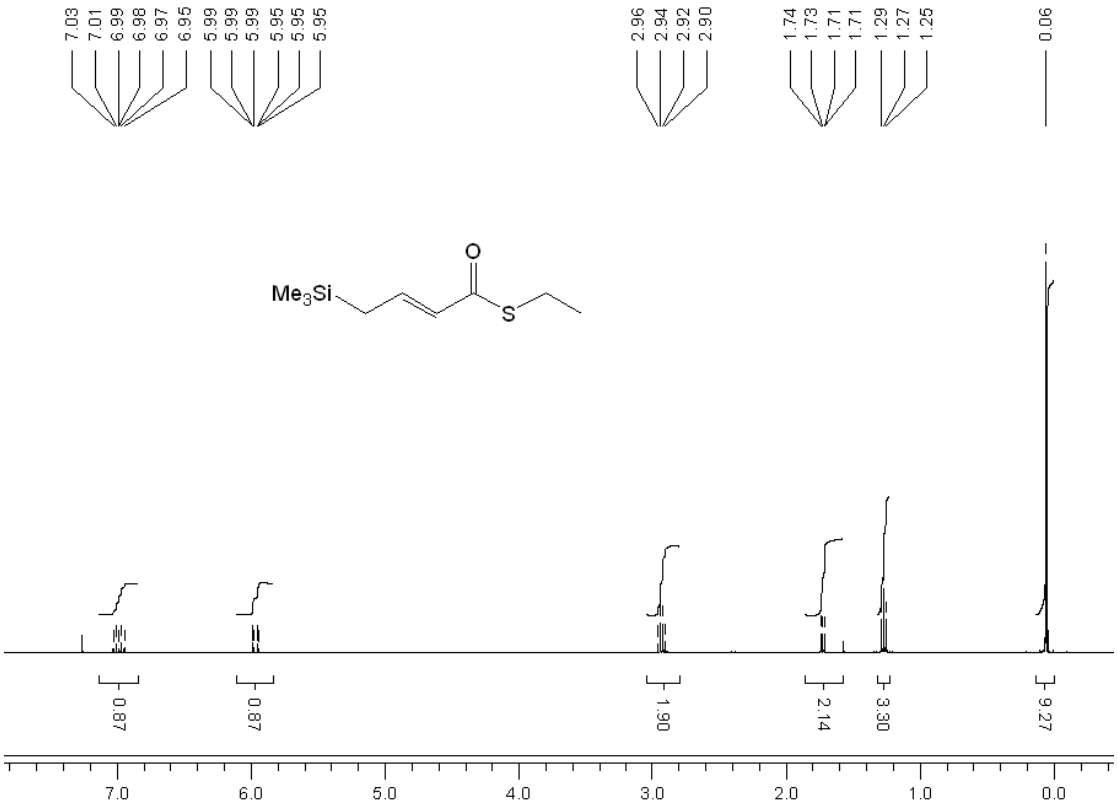


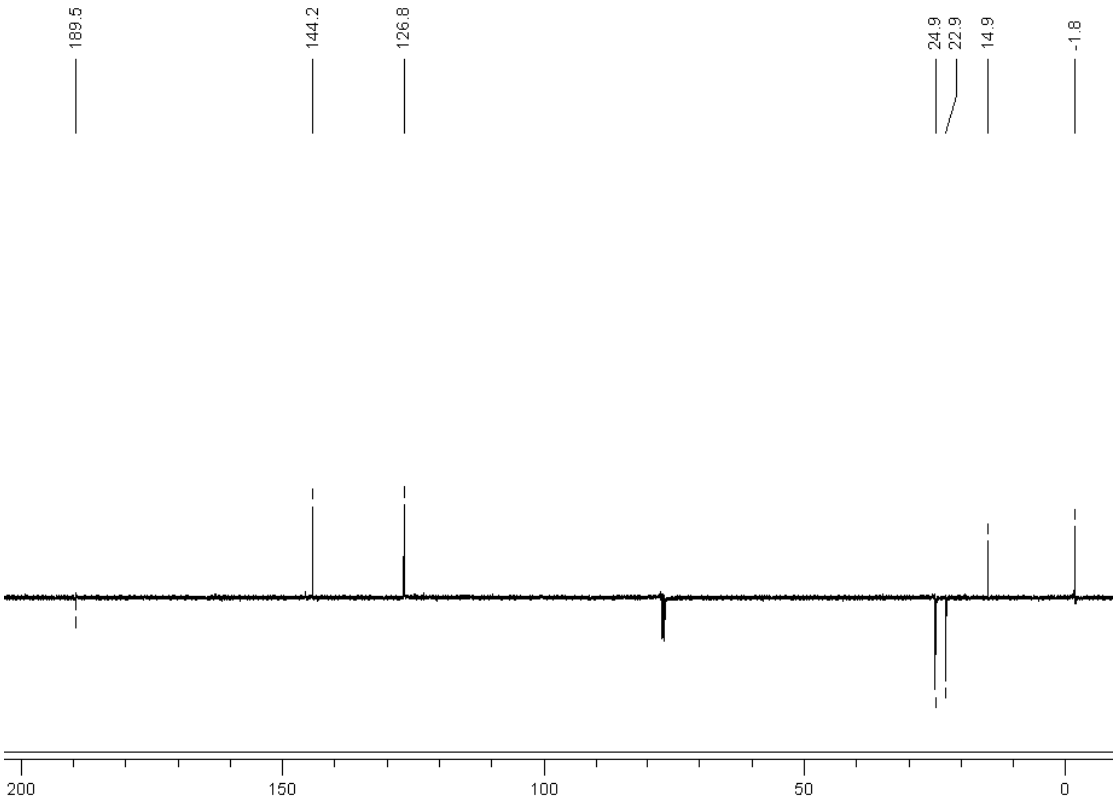
(*E*)-*S*-ethyl 4-phenylbut-2-enethioate (4):



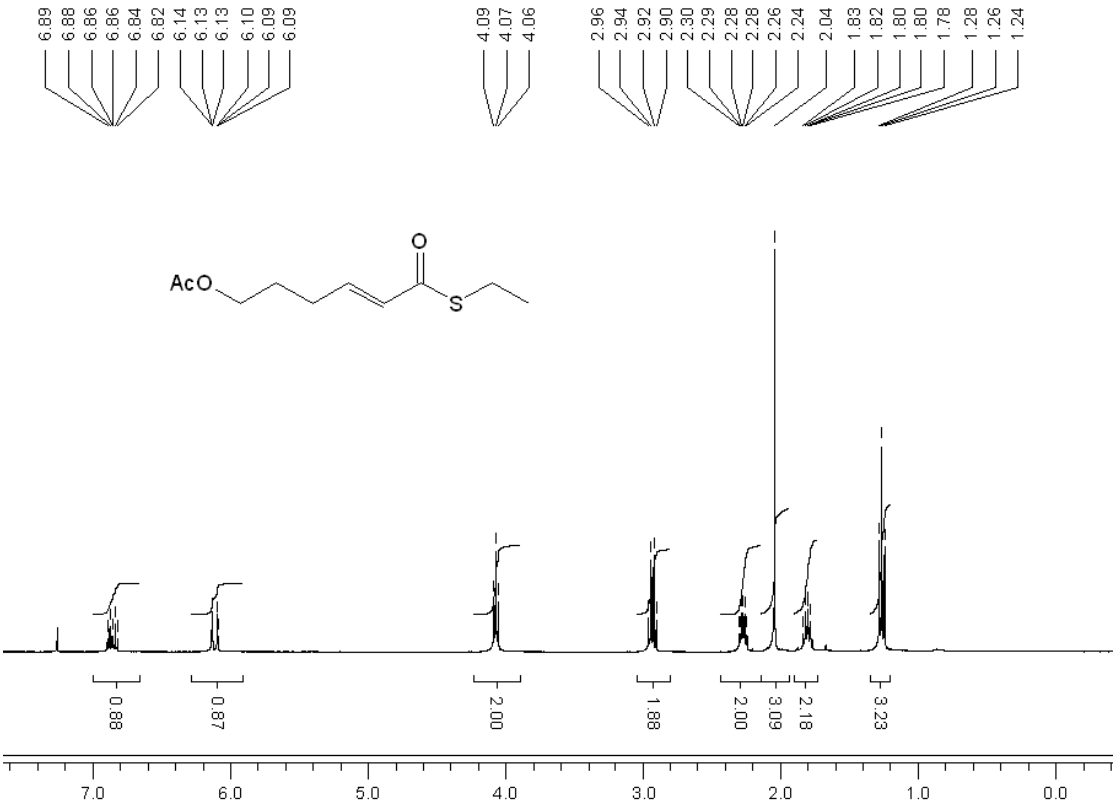


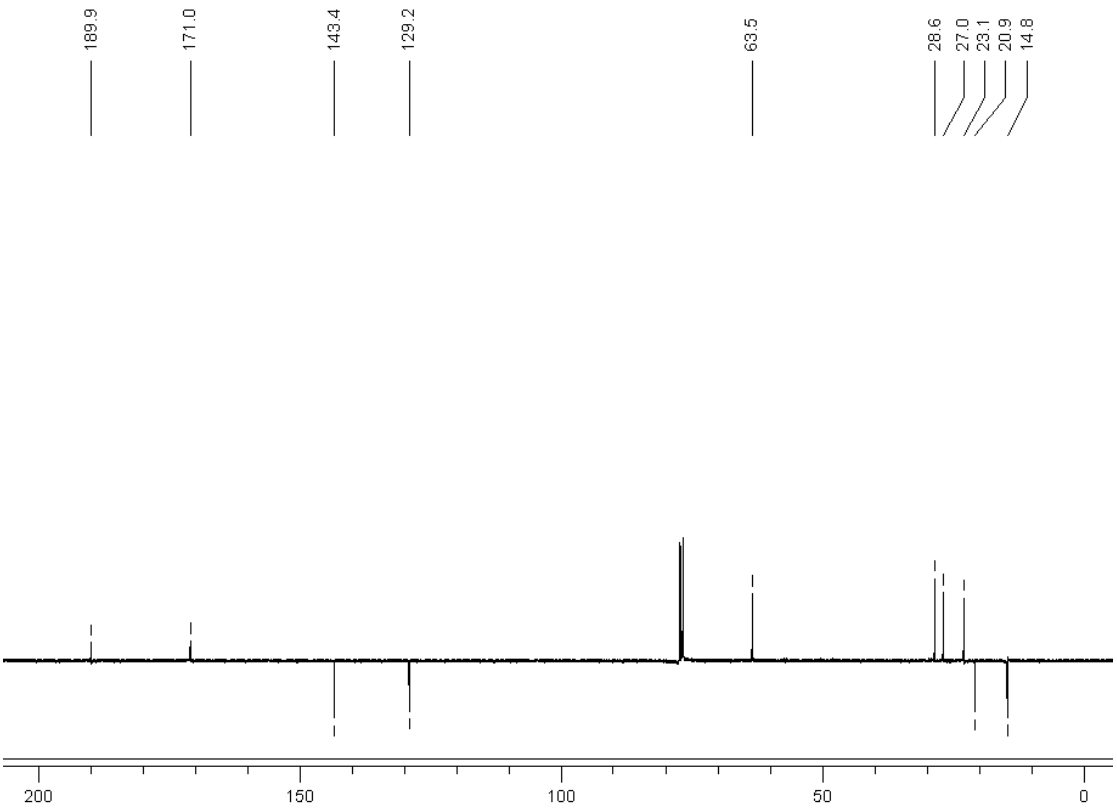
(*E*)-*S*-Ethyl 4-(trimethylsilyl)but-2-enethioate (5):



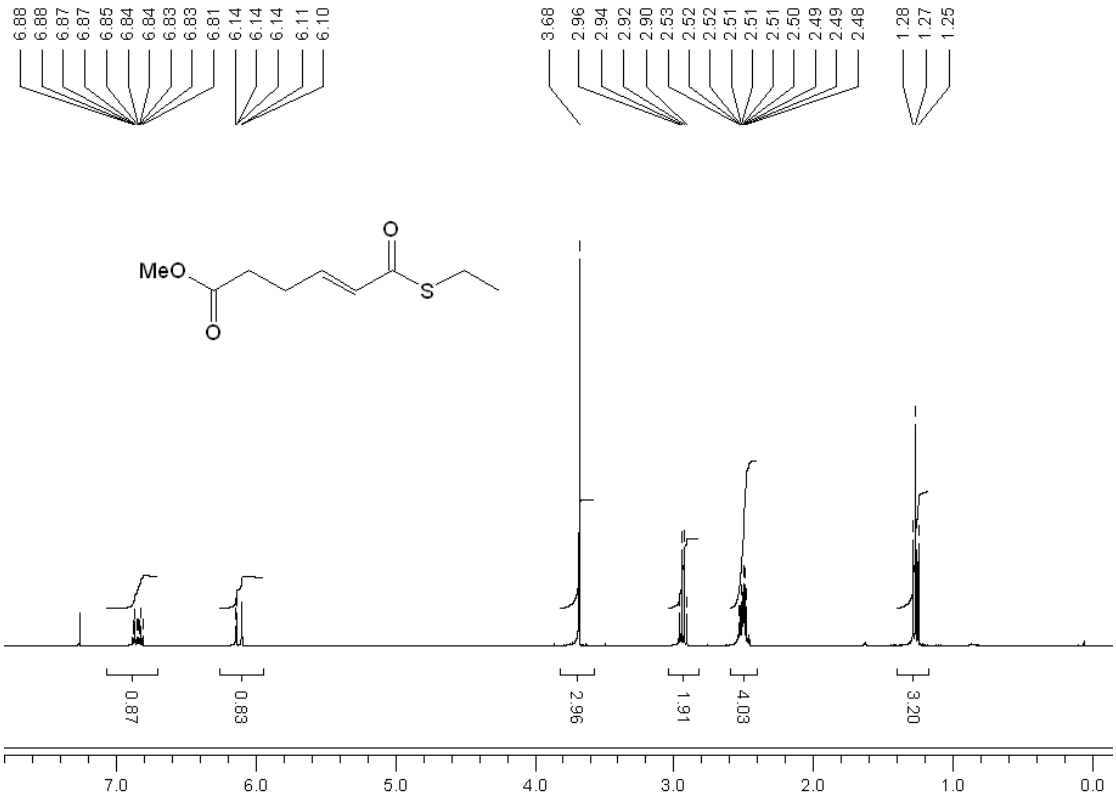


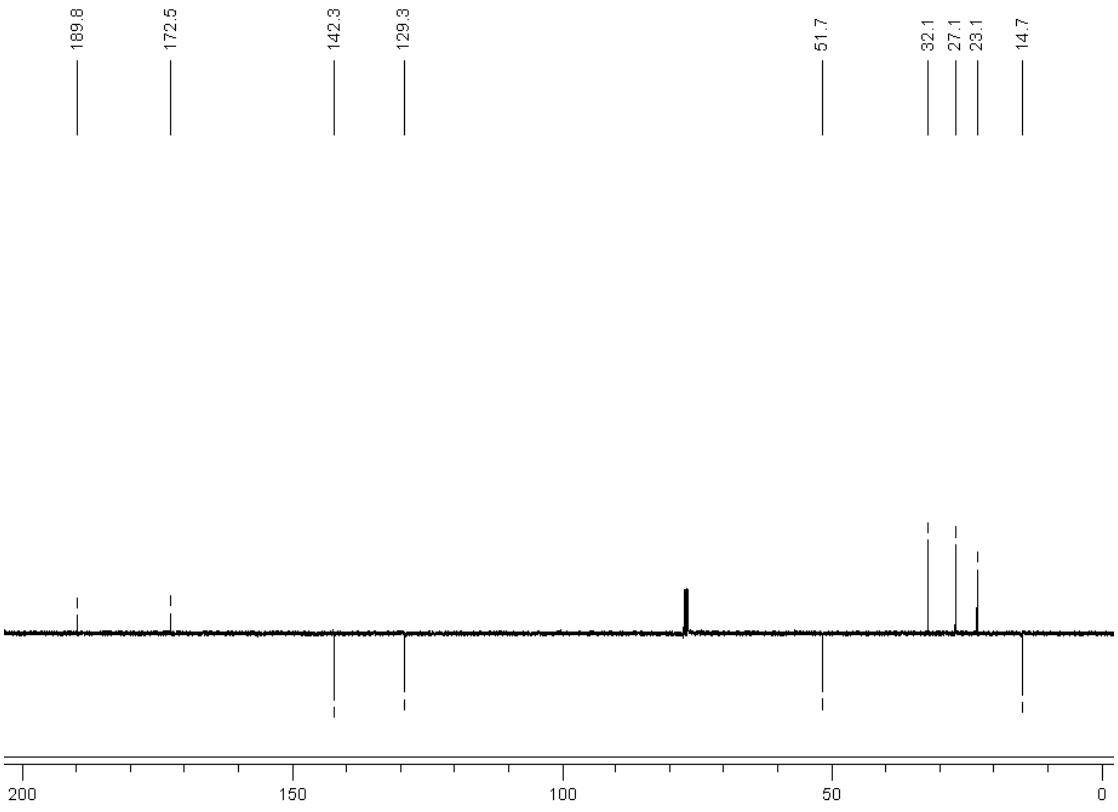
(*E*)-6-(Ethylthio)-6-oxohex-4-enyl acetate (6):



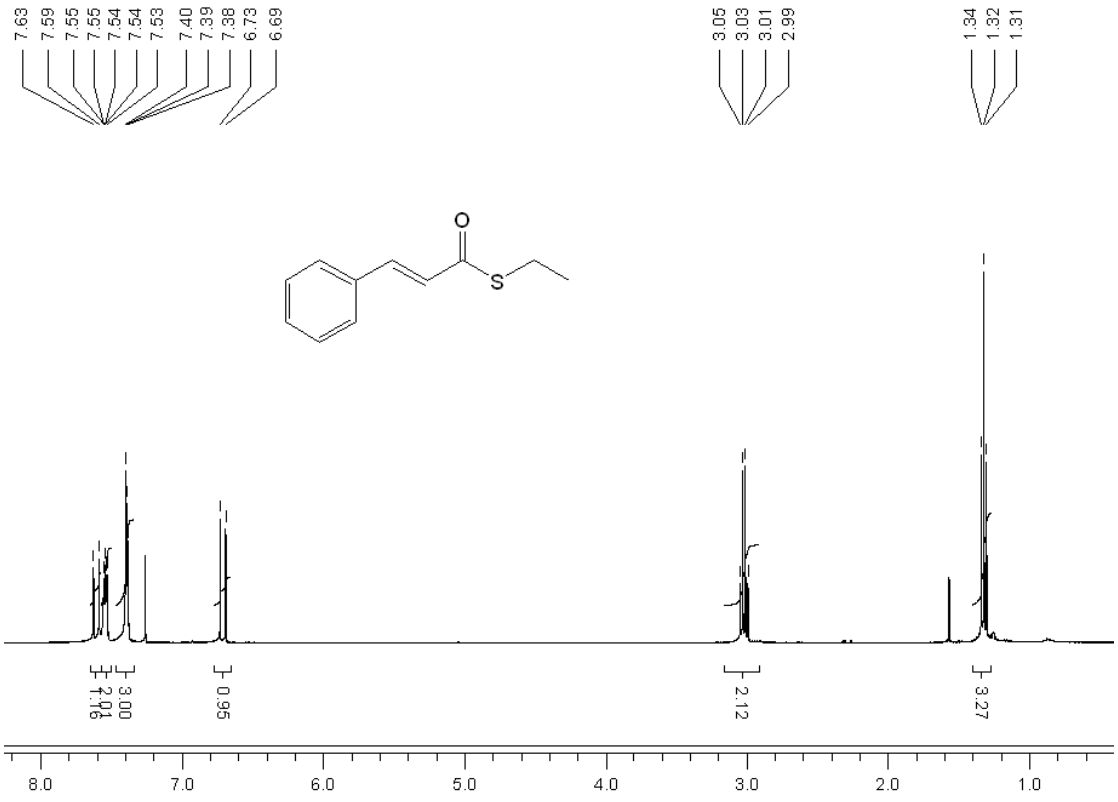


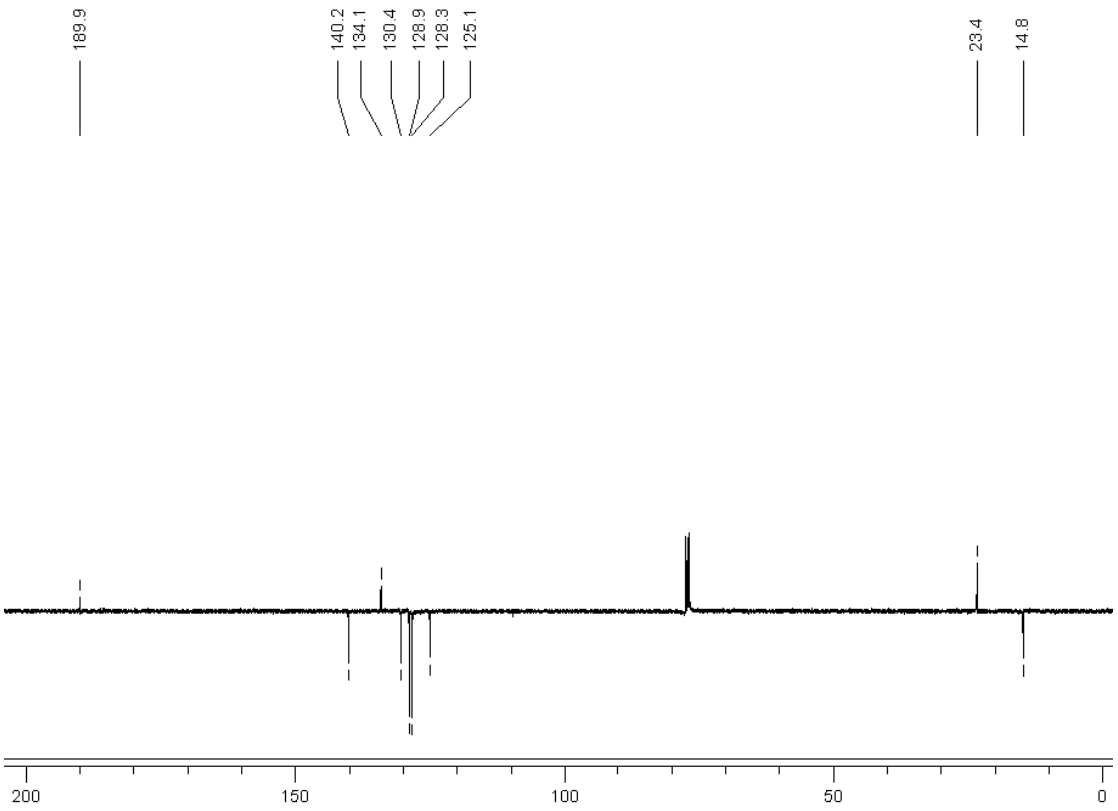
(*E*)-Methyl 6-(ethylthio)-6-oxohex-4-enoate (7):



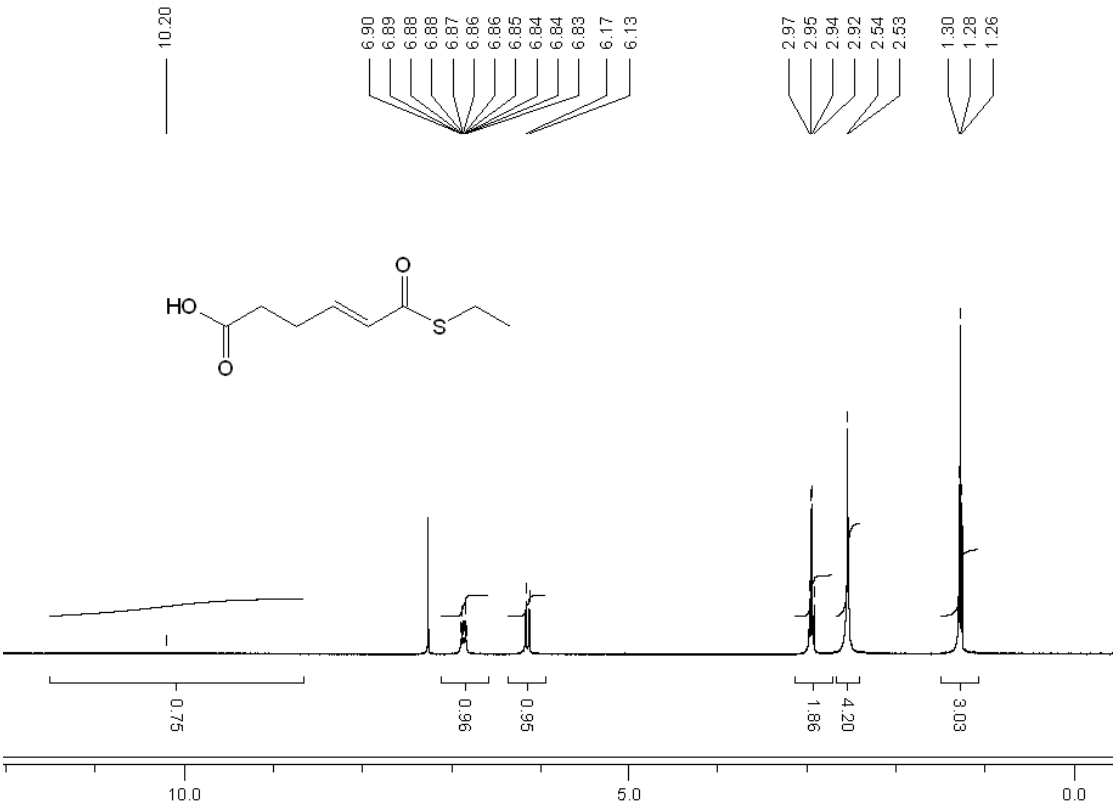


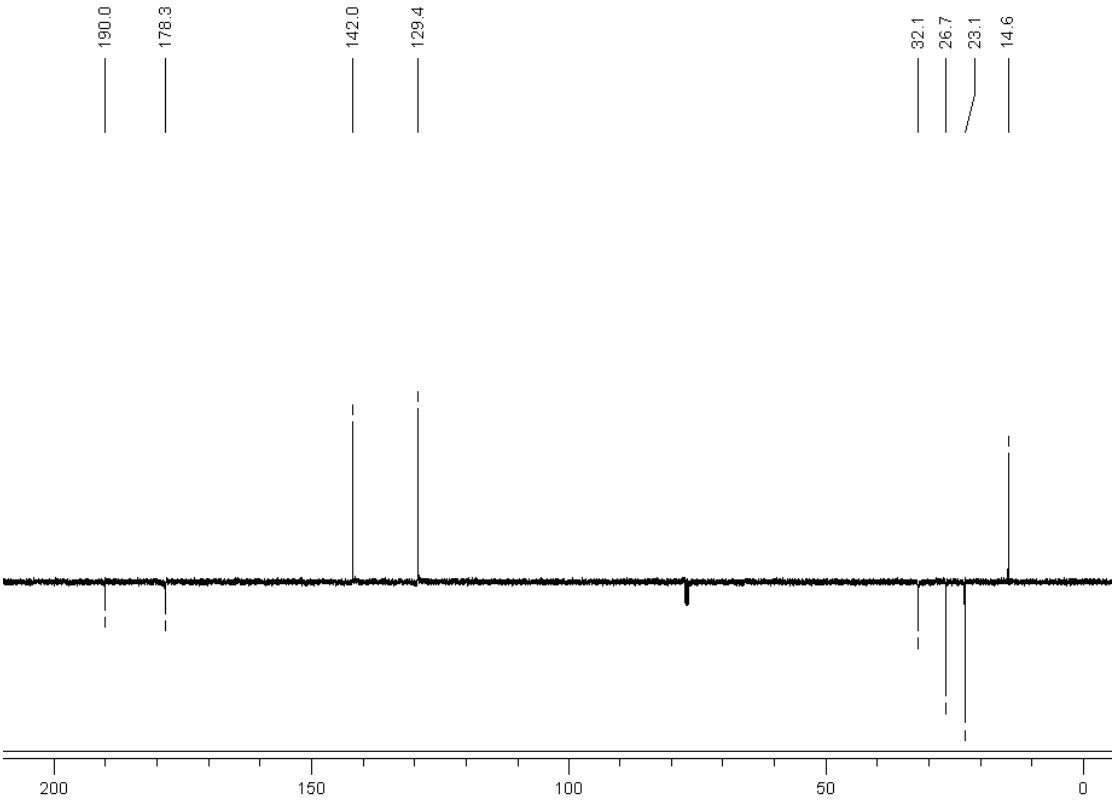
(*E*)-*S*-ethyl 3-phenylprop-2-enethioate (8):



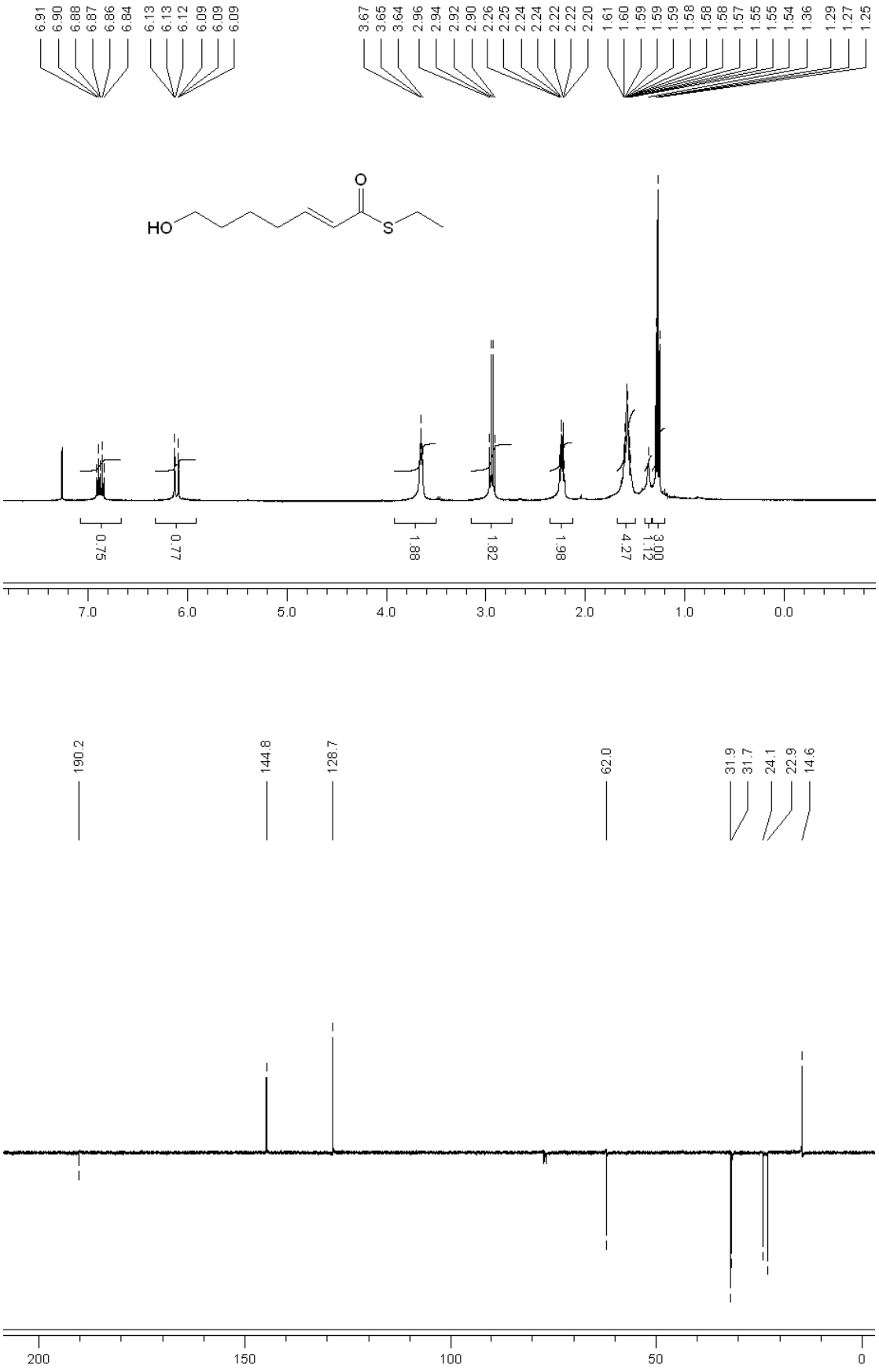


(*E*)-6-(ethylthio)-6-oxohex-4-enoic acid (9):

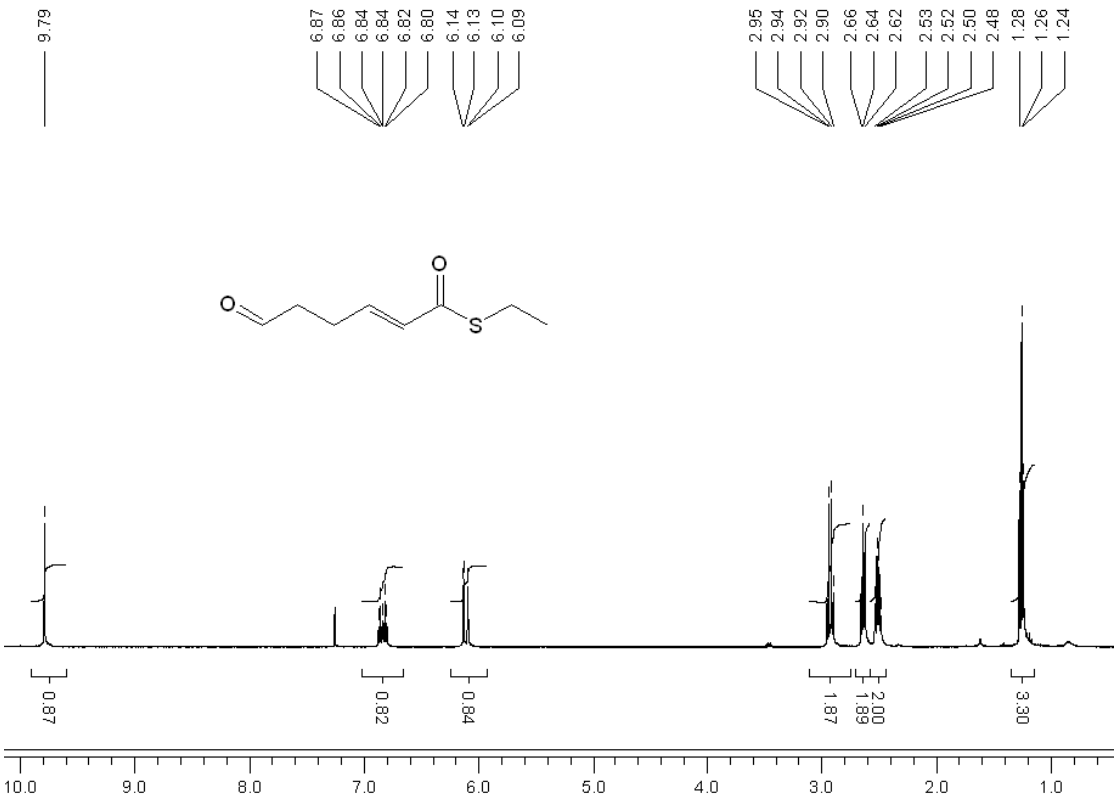


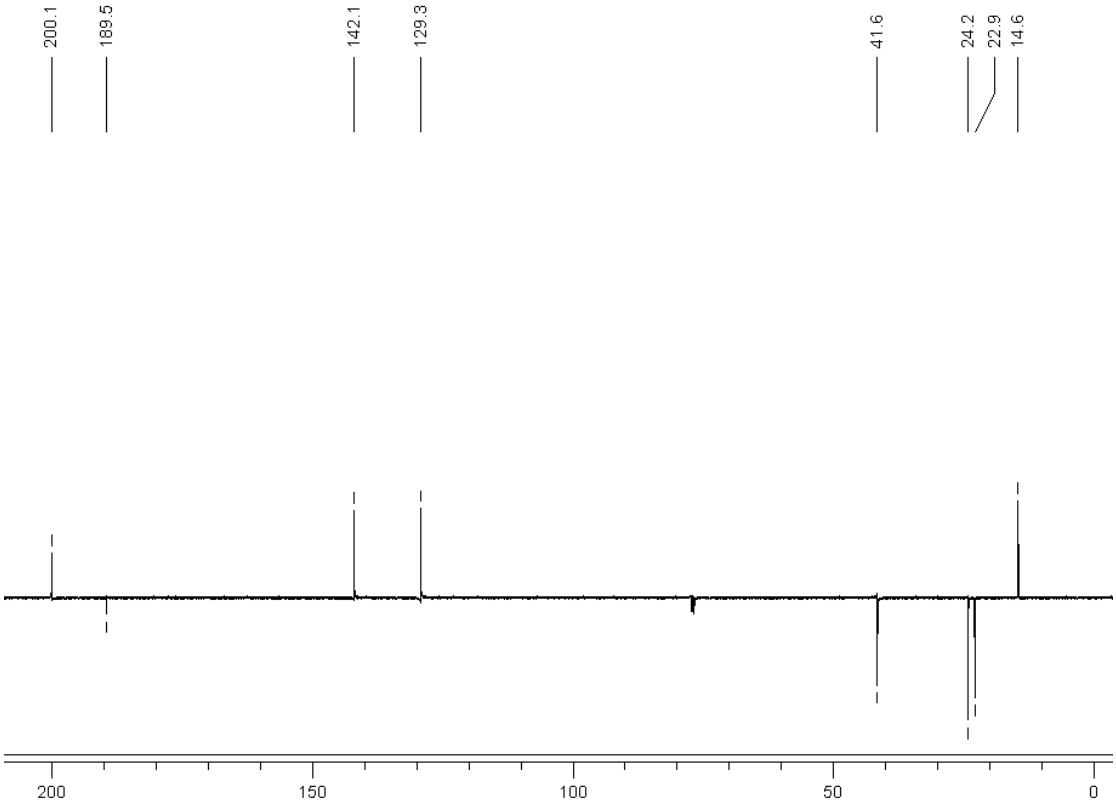


(*E*)-*S*-Ethyl 7-hydroxyhept-2-enethioate (10):

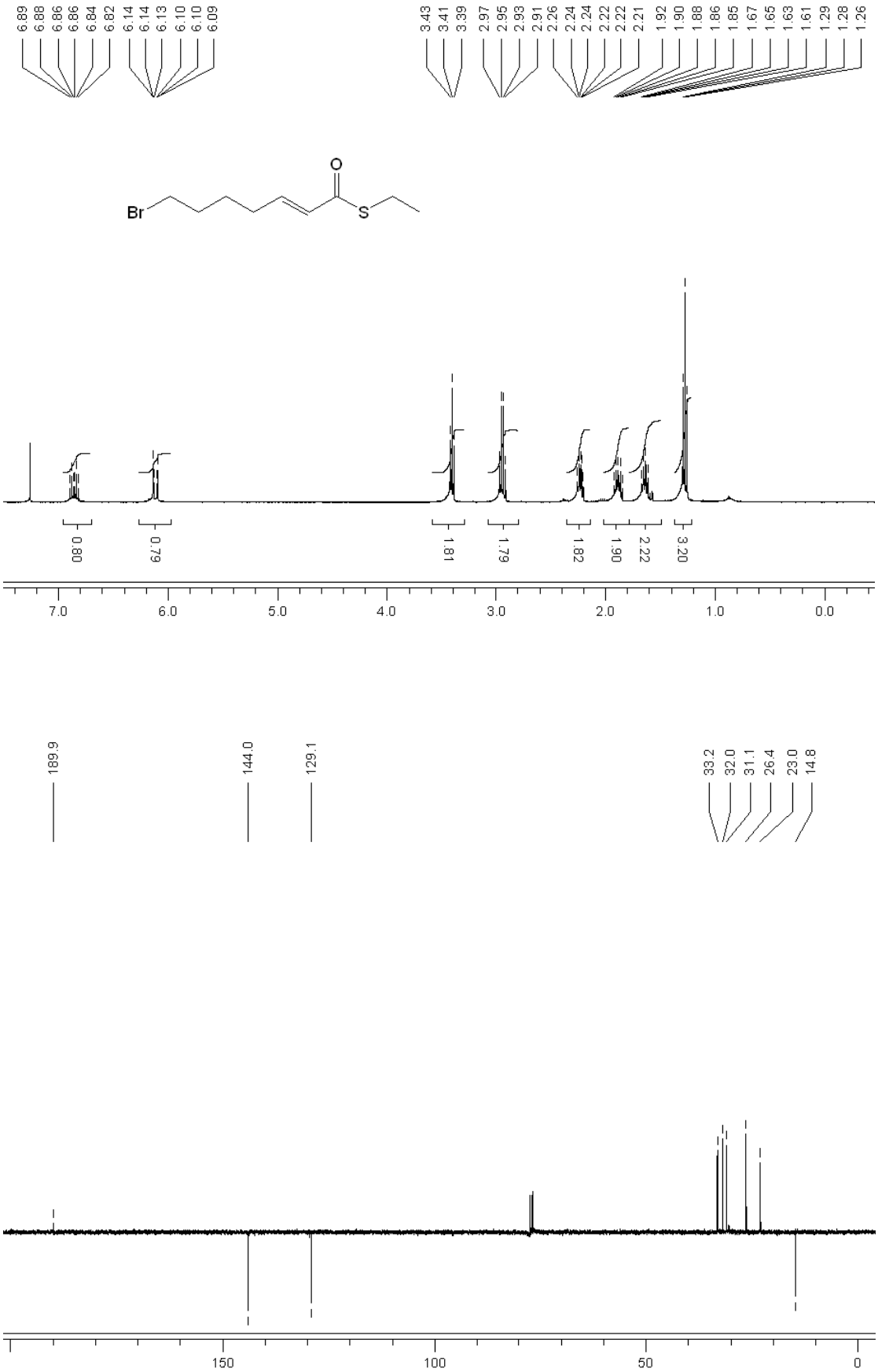


(*E*)-*S*-Ethyl 6-oxohex-2-enethioate (11):

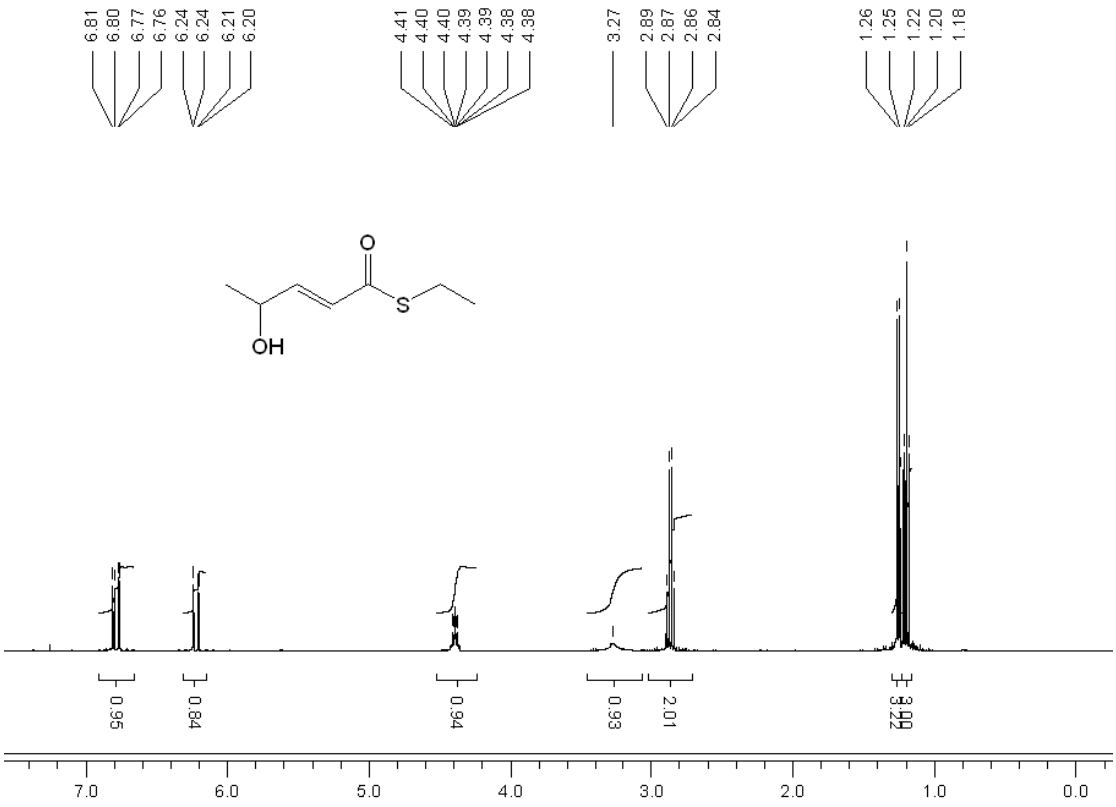


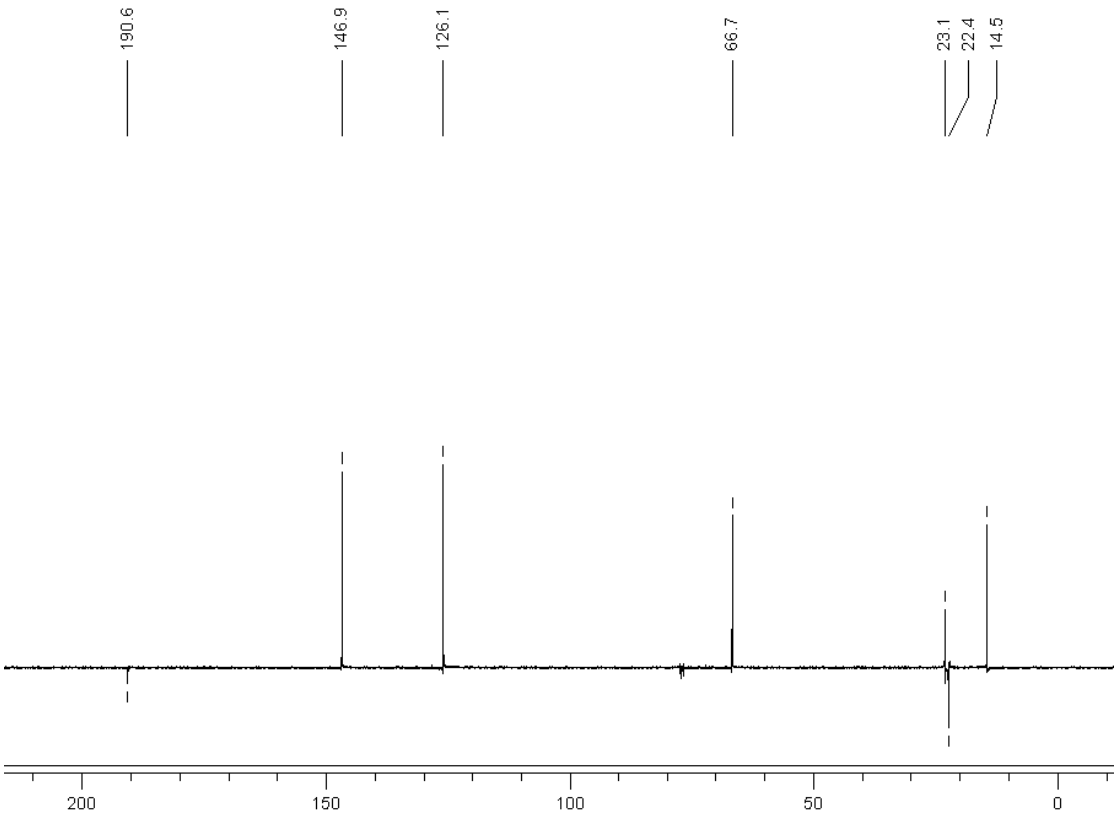


(*E*)-*S*-Ethyl 7-bromohept-2-enethioate (12):

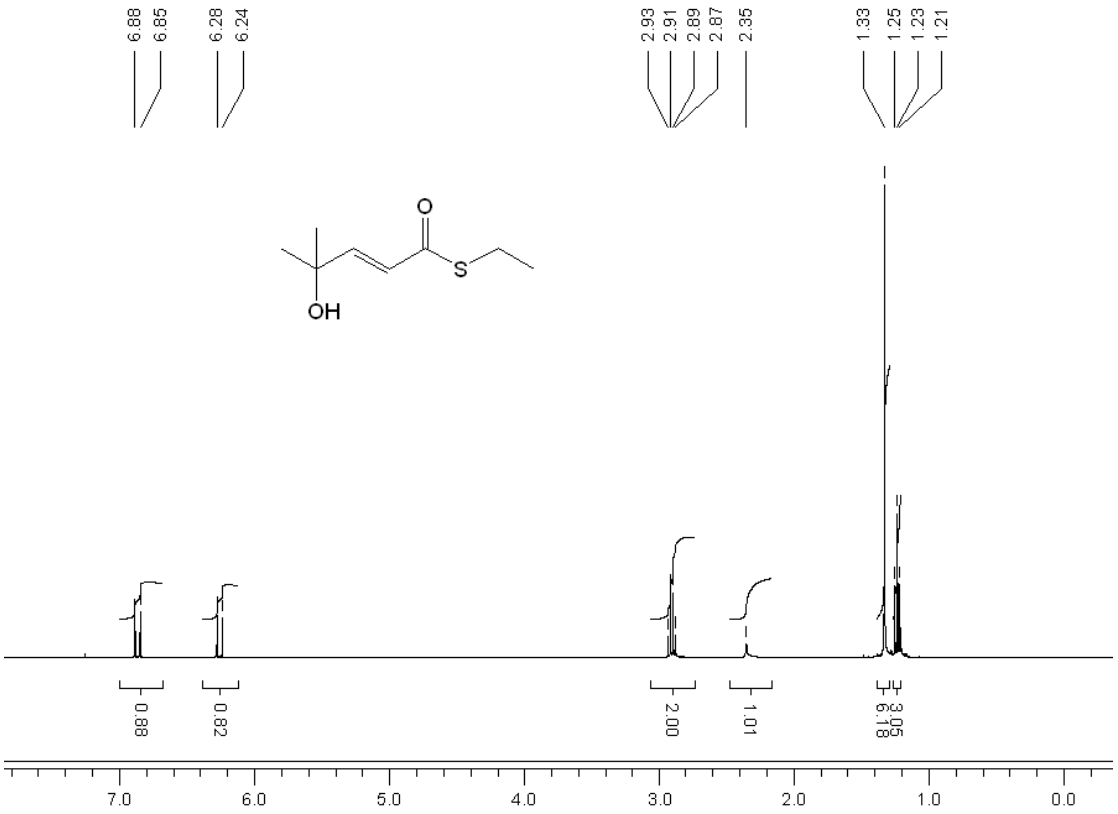


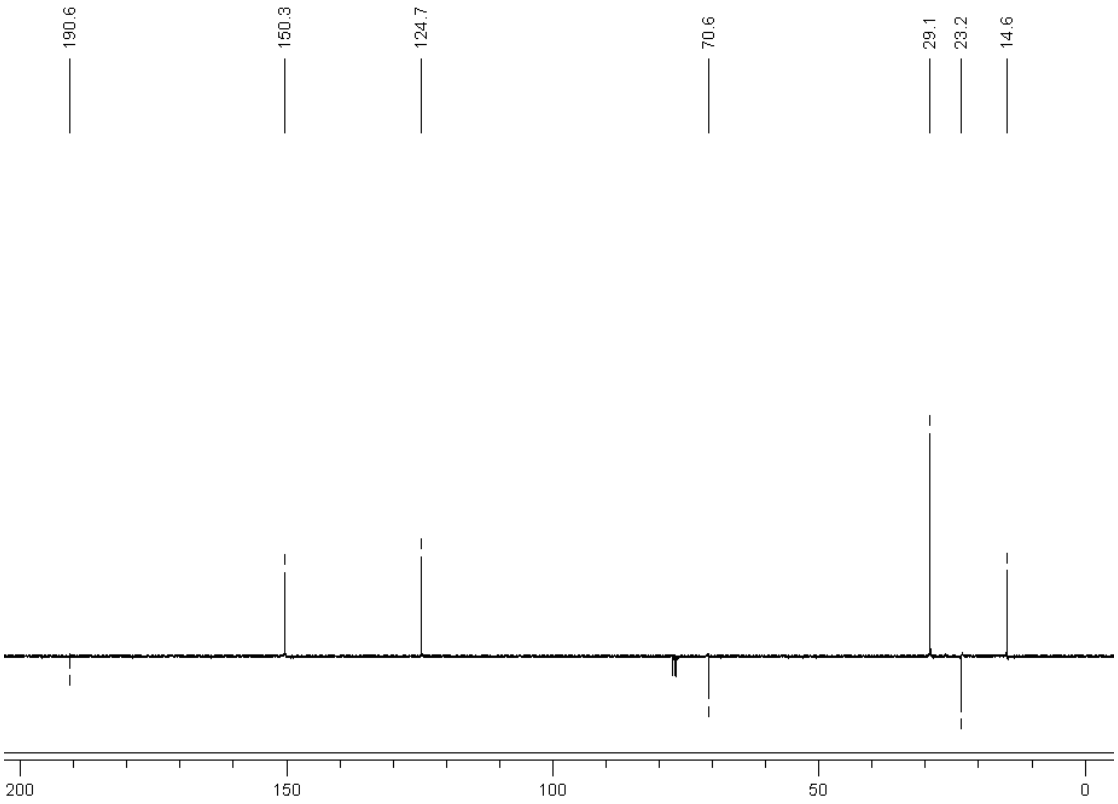
(*E*)-*S*-Ethyl 4-hydroxypent-2-enethioate (13):



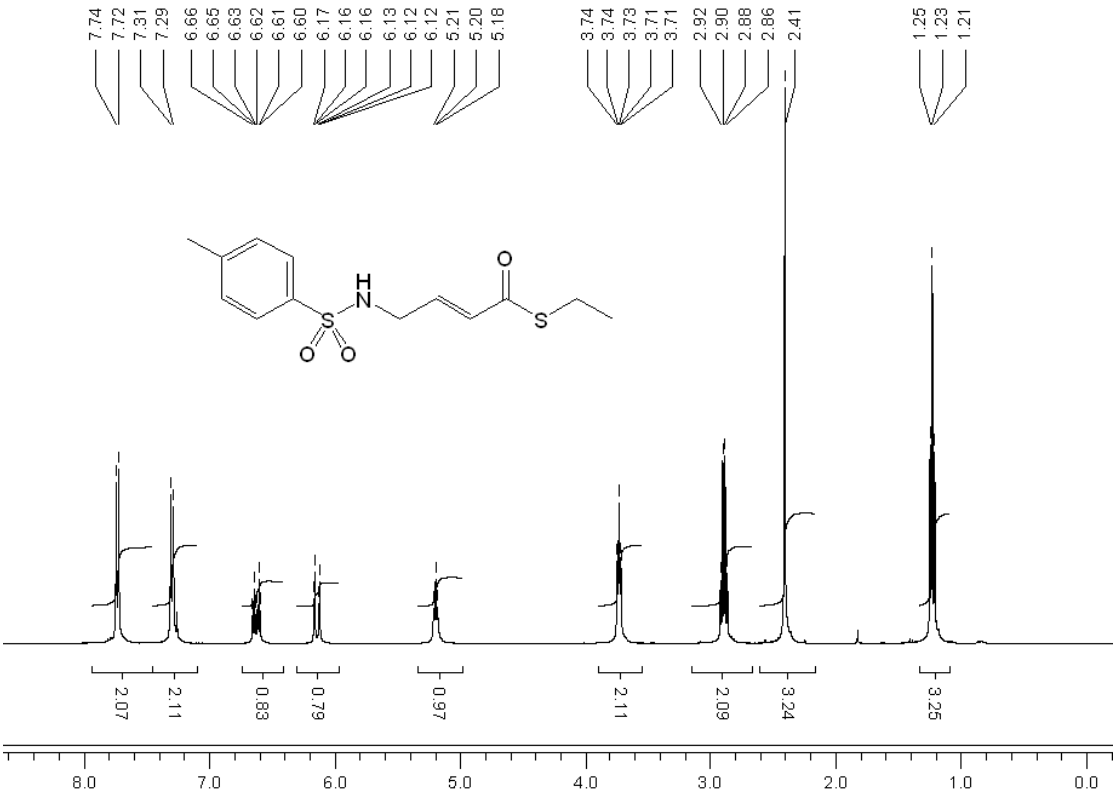


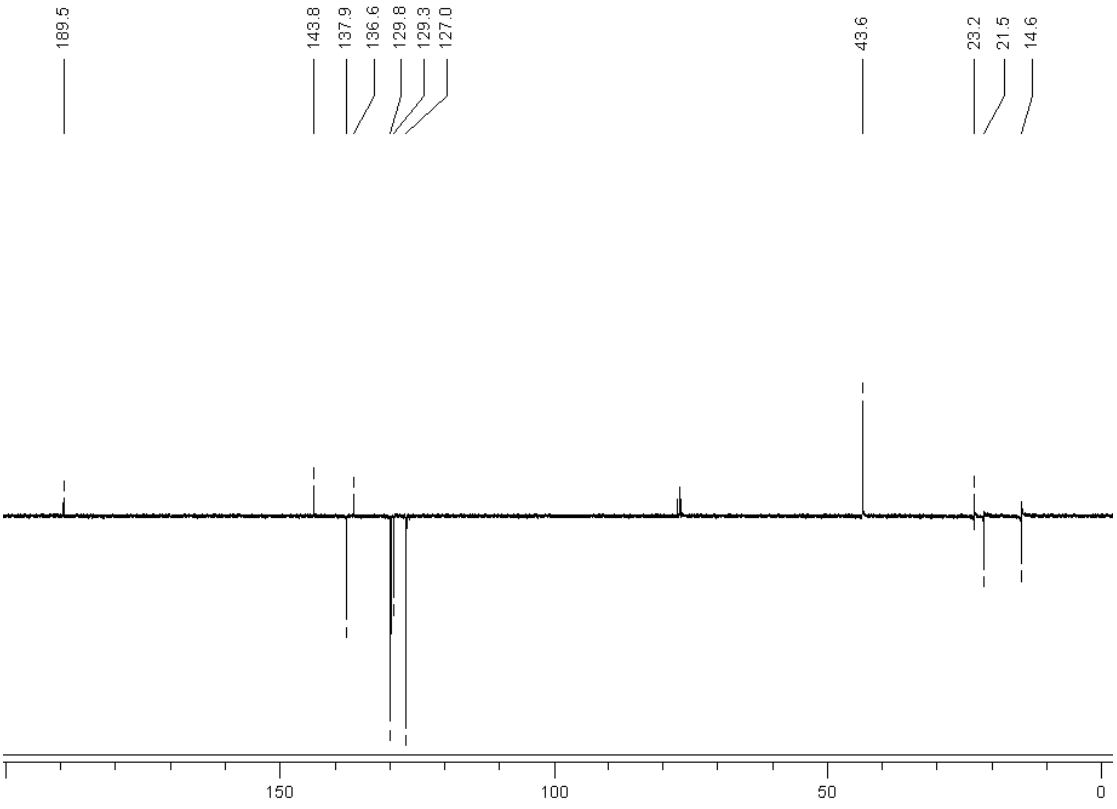
(*E*)-*S*-Ethyl 4-hydroxy-4-methylpent-2-enethioate (14):



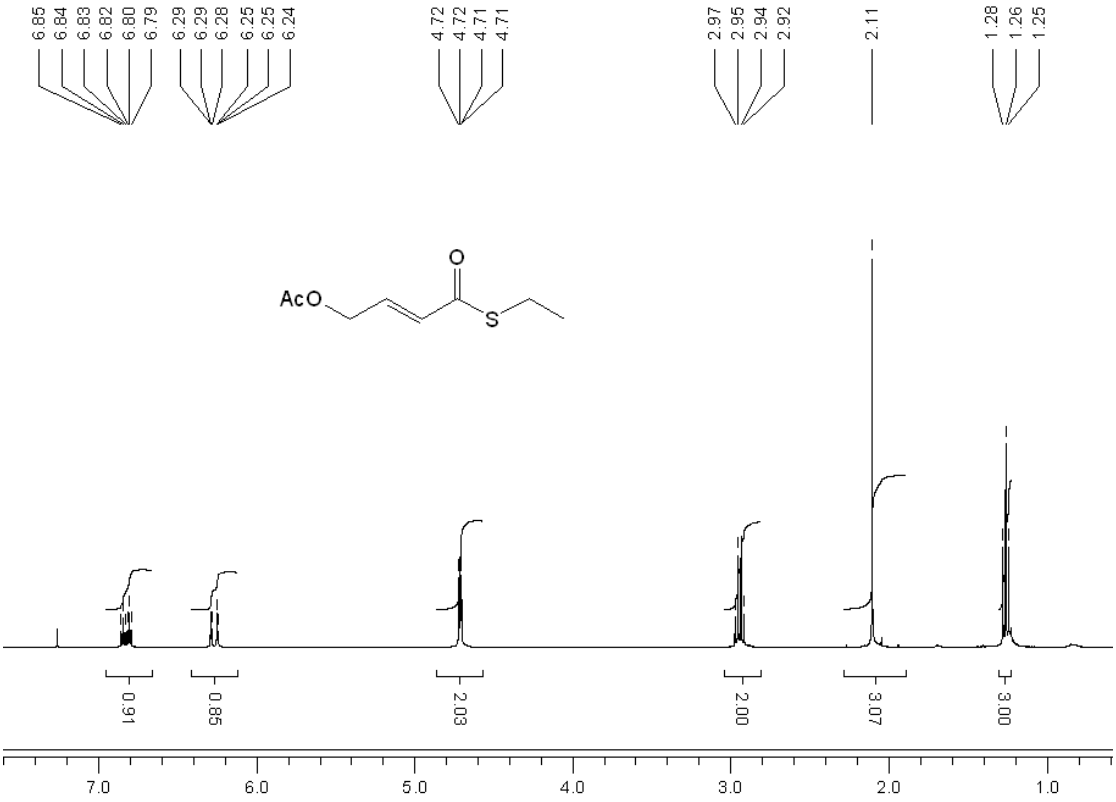


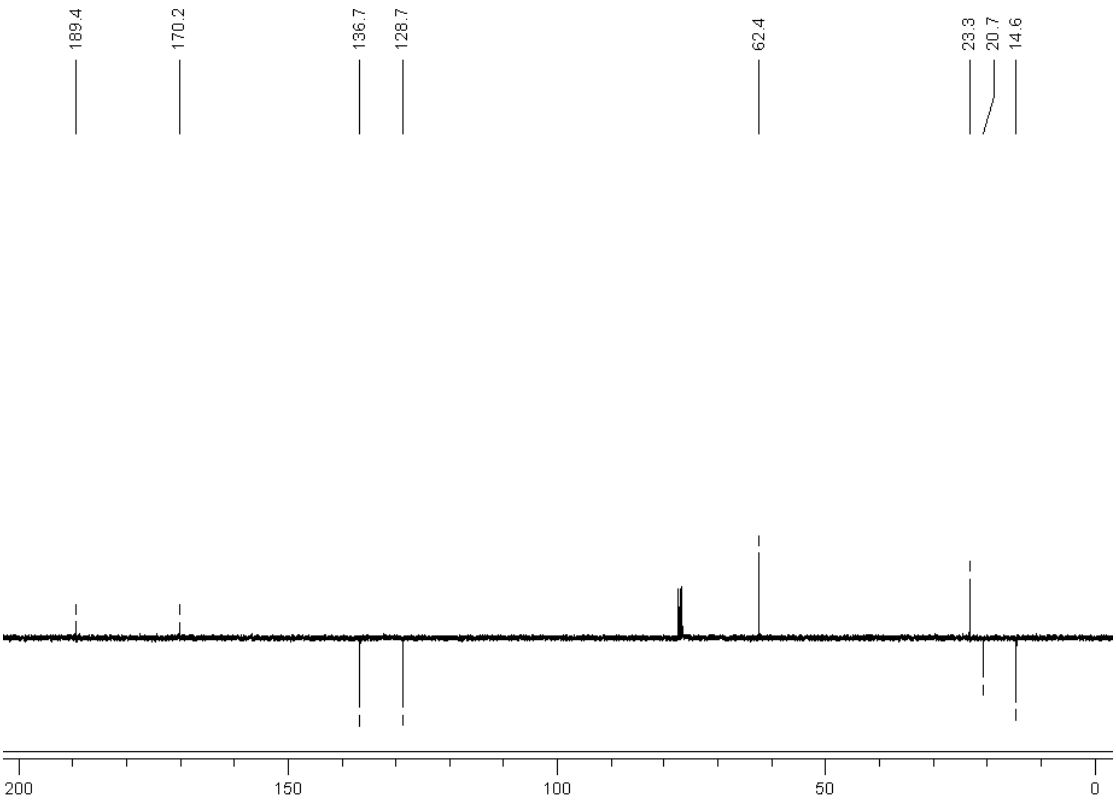
(*E*)-*S*-Ethyl 4-(4-methylphenylsulfonamido)but-2-enethioate (15):





(*E*)-4-(Ethylthio)-4-oxobut-2-enyl acetate (16):





(*E*)-*S*-ethyl 4-bromobut-2-enethioate (17):