Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Catalyst-free hydrothiolation of alkynes with dithiocarbamic acids

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Experimental

General. All reactions were performed using Schlenk technique under argon. Chemicals were purchased from commercial suppliers and used without further purification. Dry THF and dioxane were applied in the reactions. For column chromatography a silica gel 60, (230–400 mesh, Machery-Nagel) was used. Ethyl acetate (EtOAc) was purified by distillation for chromatography before use. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica-gel 60 F254 (Merck). The TLC plates were visualized by UV fluorescence (λmax= 254 nm) and/or staining with $KMnO_4$ solution and heating. Routine ^{1}H-NMR analyses were measured with a Bruker Avance 300 (^{1}H-NMR: 300.13 MHz). For high field experiments a Bruker Avance 400 (^{1}H-NMR: 400.13 MHz, ^{13}C-NMR: 100.61 MHz, ^{1}H decoupled) or Bruker Avance 500 (^{1}H-NMR: 500.32 MHz, ^{13}C-NMR: 125.81 MHz, ^{1}H decoupled) were used. All NMR spectra were reported in parts per million (ppm) and measured relative to residual solvent $CHCl_3$ [$\delta(CHCl_3)$: 7.27 ppm or $\delta(CHCl_3)$: 77.16 ppm] or C_6H_6 [($\delta(C_6H_6)$: 7.15 ppm or $\delta(C_6H_6)$: 127.99)]. HRMS (High Resolution Mass Spectra) was measured on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument equipped with an APCI source in the positive-ion mode. tert-butyldimethyl(pent-4-yn-1-yloxy)silane and pent-4-yn-1-yl acetate were prepared from pent-4-yn-1-ol according to the literature [H. Tsukamoto, K. Ito and T. Doi, *Chem. Commun.*, 2018, **54**, 5102-5105. DOI: 10.1039/C8CC02589D; B. C. Ranu, S. S. Dey and A. Hajra, *Green Chem.*, 2003, **5**, 44–46. DOI: 10.1039/b211238h].

General procedure for the synthesis of vinyl dithiocarbamates

In a dry and argon-flushed Schlenk tube equipped with a magnetic stirring bar, an amine (1 mmol, 1 equivalent), THF or dioxane (2 mL), and CS_2 (2 mmol, 2 equivalents) were added and stirred for 5 minutes. Then, an alkyne (2 mmol, 2 equivalents) was added and the Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 110 °C for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography (*n*-pentane / ethyl acetate; 9:1).

Procedure for the synthesis of 2,2-dimethyldecane-4-thiol (5)

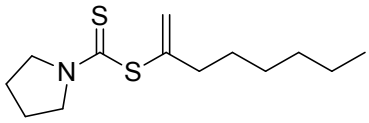
In a dry and argon-flushed Schlenk tube equipped with a septum and a magnetic stirring bar, oct-1-en-2-yl pyrrolidine-1-carbodithioate (**1a**, 1 mmol, 257 mg) was dissolved in THF (8 mL) and

the solution cooled to −90 °C. Then, *t*-BuLi (4 mmol) was added and the reaction mixture was stirred for 40 min. until the reaction temperature reached to -40 °C. The reaction mixture was quenched with sat. $NaHCO_3$ sol. (10 mL) and the resulting mixture was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash chromatography (SiO_2, pentane) yielded **5** (149 mg, 74%) as a colorless oil.

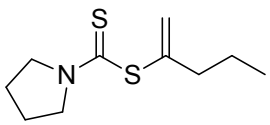
Procedure for the synthesis of 2-hydroxy-2-phenyl-1-(pyrrolidin-1-yl)ethanethione (6)

In a dry and argon-flushed Schlenk tube equipped with a septum and a magnetic stirring bar, oct-1-en-2-yl pyrrolidine-1-carbodithioate (**1a**, 1 mmol, 257 mg) was dissolved in THF (4 mL) and the solution cooled to −78 °C. Then, *t*-BuLi (1.6 mmol) was added and the reaction mixture was stirred for 10 min. Benzaldehyde (0.8 mmol) was added and the reaction mixture was stirred for 30 min. The reaction mixture was quenched with sat. $NaHCO_3$ sol. (10 mL) and the resulting mixture was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification was carried out by silica gel chromatography using ethyl acetate and petroleum ether gradient (EtOAc:PE, 1:9 to 1:1) to afford 2-hydroxy-2-phenyl-1-(pyrrolidin-1-yl)ethanethione **6** (151 mg, 62%) as a colorless oil and the thiol **5** (110 mg, 54%) as major products.

Characterization data for all products

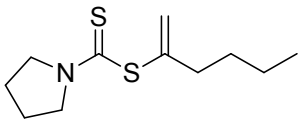


oct-1-en-2-yl pyrrolidine-1-carbodithioate **(1a):** Yield 172 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1H), 5.54 (s, 1H), 3.91 (t, J = 6.8 Hz, 2H), 3.66 (t, J = 6.9 Hz, 2H), 2.54 (dt, J = 7.0 and 1.2 Hz, 2H), 2.09 (m, 2H), 1.96 (m, 2H), 1.52 (m, 2H), 1.33 – 1.25 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 142.5, 127.1, 54.8, 51.2, 37.9, 31.7, 28.8, 28.2, 26.4, 24.5, 22.7, 14.1 ppm; HRMS Calcd for $C_{13}H_{24}NS_2$ $(M+H)^+$: 258.1350; Found: 258.1343.

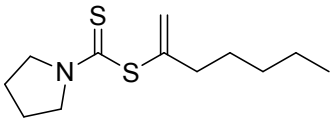


pent-1-en-2-yl pyrrolidine-1-carbodithioate **(1b)**: Yield 97 mg, 45%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (s, 1H), 5.55 (s, 1H), 3.90 (t, J = 6.9 Hz, 2H), 3.65 (t, J = 6.9

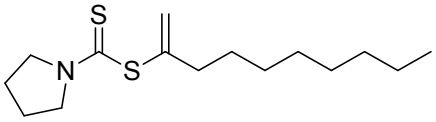
Hz, 2H), 2.51 (m, 2H), 2.08 (m, 2H), 1.95 (m, 2H), 1.54 (m, 2H), 0.91 (t, J = 7.35 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 142.1, 127.3, 54.8, 51.2, 39.8, 26.4, 24.5, 21.4, 13.6 ppm; HRMS Calcd for $C_{10}H_{18}NS_2$ $(M+H)^+$: 216.0881; Found: 216.0875.



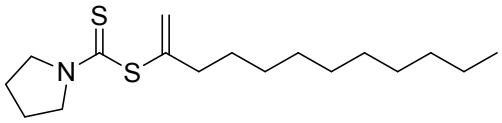
hex-1-en-2-yl pyrrolidine-1-carbodithioate **(1c)**: Yield 137 mg, 60%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.64 (s, 1H), 5.61 (s, 1H), 3.64 (t, J = 7.0 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H), 2.76 (m, 2H), 1.57 (m, 2H), 1.28 (m, 2H), 1.16 – 1.10 (m, 4H), 0.84 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 191.0, 142.9, 126.9, 54.5, 50.5, 38.1, 30.8, 25.9, 23.9, 22.6, 14.1 ppm. HRMS Calcd for $C_{11}H_{20}NS_2$ $(M+H)^+$: 230.1037; Found: 230.1032.



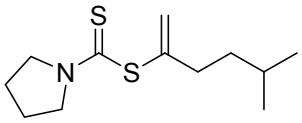
hept-1-en-2-yl pyrrolidine-1-carbodithioate **(1d)**: Yield 158 mg, 65%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.64 (s, 1H), 5.62 (s, 1H), 3.64 (t, J = 6.7 Hz, 2H), 3.11 (t, J = 6.9 Hz, 2H), 2.77 (t, J = 7.0 Hz, 2H), 1.61 (m, 2H), 1.24 – 1.22 (m, 4H), 1.13 – 1.06 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 191.0, 142.9, 126.9, 54.5, 50.5, 38.3, 31.6, 28.3, 25.9, 23.9, 22.9, 14.2 ppm; HRMS Calcd for $C_{12}H_{22}NS_2$ $(M+H)^+$: 244.1194; Found: 244.1188.



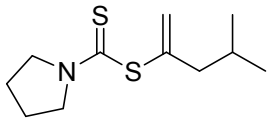
dec-1-en-2-yl pyrrolidine-1-carbodithioate **(1e)**: Yield 174 mg, 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71(s, 1H), 5.53 (s, 1H), 3.89 (t, J = 6.9 Hz, 2H), 3.65 (t, J = 6.9 Hz, 2H), 2.52 (dt, J = 6.8 and 1.5 Hz, 2H), 2.09 (m, 2H), 1.99 (m, 2H), 1.51 (m, 2H), 1.31 – 1.24 (m, 10 H), 0.86 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 142.4, 127.0, 54.8, 51.2, 37.8, 31.9, 29.4, 29.3, 29.1, 28.2, 26.4, 24.5, 22.7, 14.1 ppm; HRMS Calcd for $C_{15}H_{28}NS_2$ $(M+H)^+$: 286.1663; Found: 286.1657.



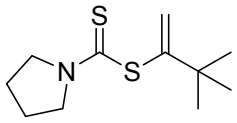
dodec-1-en-2-yl pyrrolidine-1-carbodithioate **(1f):** Yield 210 mg, 67%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.66 (s, 1H), 5.65 (s, 1H), 3.64 (t, J = 6.7 Hz, 2H), 3.11 (t, J = 7.0 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H), 1.66 (m, 2H), 1.33 – 1.25 (m, 14H), 1.13 – 1.04 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 191.1, 143.0, 126.9, 54.5, 50.5, 38.4, 32.3, 30.0 (2C), 29.9, 29.8, 29.6, 28.7, 25.9, 23.9, 23.1, 14.3 ppm; HRMS Calcd for $C_{17}H_{32}NS_2$ $(M+H)^+$: 314.1976; Found: 314.1971.



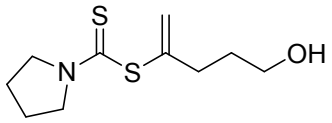
5-methylhex-1-en-2-yl pyrrolidine-1-carbodithioate **(1g):** Yield 146 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (s, 1H), 5.53 (s, 1H), 3.89 (t, J = 6.9 Hz, 2H), 3.65 (t, J = 7.0 Hz, 2H), 2.53 (dt, J = 7.0 and 1.5 Hz, 2H), 2.08 (m, 2H), 1.97 (m, 2H), 1.56 (m, 1H), 1.42 (m, 2H), 0.88 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 142.7, 126.8, 54.8, 51.2, 37.4, 35.8, 27.6, 26.4, 24.5, 22.6 ppm; HRMS Calcd for $C_{12}H_{22}NS_2$ $(M+H)^+$: 244.1194; Found: 244.1187.



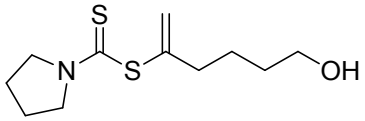
4-methylpent-1-en-2-yl pyrrolidine-1-carbodithioate **(1h)**: Yield 137 mg, 60%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.65 (s, 1H), 5.57 (s, 1H), 3.64 (t, J = 7.0 Hz, 2H), 3.10 (t, J = 6.9 Hz, 2H), 2.66 (d, J = 7.0 Hz, Hz), 2.0 (m, 1H), 1.12 – 1.04 (m, 4H), 0.90 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 190.9, 141.8, 128.5, 54.5, 50.5, 47.5, 27.1, 25.9, 23.9, 22.5 ppm; HRMS Calcd for $C_{11}H_{20}NS_2$ $(M+H)^+$: 230.1037; Found: 230.1032.



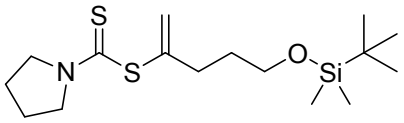
3,3-dimethylbut-1-en-2-yl pyrrolidine-1-carbodithioate **(1i+1i')**: Yield (**1i+1i'**) 34 mg, 15%; ^{1}H NMR for **1i** (500 MHz, C_6D_6) δ 6.04 (s, 1H), 5.76 (s, 1H), 3.71 (t, J = 7.0 Hz, 2H), 3.21 (t, J = 6.7 Hz, 2H), 1.26 (s, 9H), 1.17 – 1.05 (m, 4H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 192.5, 150.3, 128.9, 55.4, 50.5, 38.9, 29.4, 25.9, 23.9 ppm; HRMS Calcd for $C_{11}H_{20}NS_2$ $(M+H)^+$: 230.1037; Found: 230.1027.



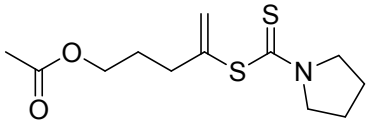
5-hydroxypent-1-en-2-yl pyrrolidine-1-carbodithioate **(1j):** Yield 145 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (s, 1H), 5.59 (s, 1H), 3.89 (t, J = 6.9 Hz, 2H), 3.71 – 3.62 (m, 4H), 2.64 (m, 2H), 2.07 (m, 2H), 1.96 (m, 2H), 1.80 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 141.2, 127.5, 61.9, 54.9, 51.3, 34.1, 30.8, 26.4, 24.5 ppm; HRMS Calcd for $C_{10}H_{18}NOS_2$ $(M+H)^+$: 232.0830; Found: 232.0824.



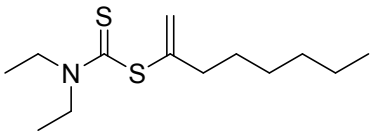
6-hydroxyhex-1-en-2-yl pyrrolidine-1-carbodithioate **(1k):** Yield 147 mg, 60%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.63 (s, 1H), 5.60 (s, 1H), 3.64 (t, J = 6.7 Hz, 2H), 3.35 (t, J = 6.4 Hz, 2H), 3.10 (t, J = 6.9 Hz, 2H), 2.73 (dt, J = 7.0 and 1.2 Hz, 2H), 1.62 (m, 2H), 1.39 (m, 2H), 1.14 – 1.03 (m, 4H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 191.1, 142.6, 127.1, 62.4, 54.5, 50.6, 38.0, 32.5, 25.9, 24.8, 23.9 ppm; HRMS Calcd for $C_{11}H_{20}NOS_2$ $(M+H)^+$: 246.0981; Found: 246.0986.



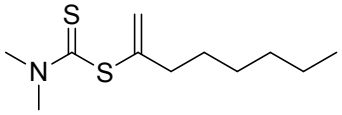
5-((tert-butyldimethylsilyl)oxy)pent-1-en-2-yl pyrrolidine-1-carbodithioate **(1l)**: Yield 217 mg, 63%; ^{1}H NMR (500 MHz, C_6D_6) δ 75.64 (s, 1H), 5.63 (s, 1H), 3.63 (t, J = 7.0 Hz, 2H), 3.57 (t, J = 6.3 Hz, 2H), 3.08 (t, J = 6.6 Hz, 2H), 2.89 (m, 2H), 1.86 (m, 2H), 1.12 – 1.05 (m, 4H), 0.96 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 190.9, 142.6, 128.2, 62.6, 54.5, 50.5, 34.8, 31.8, 26.2, 25.9, 23.9, 18.4, -5.2 ppm; HRMS Calcd for $C_{16}H_{32}NOS_2Si$ $(M+H)^+$: 346.1695; Found: 346.1689.



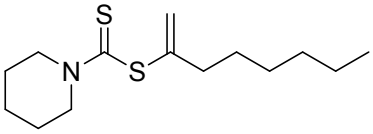
4-((pyrrolidine-1-carbonothioyl)thio)pent-4-en-1-yl acetate **(1m) 114-p**: Yield 191 mg, 70%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.57 (s, 1H), 5.54 (s, 1H), 3.99 (t, J = 6.6 Hz, 2H), 3.62 (t, J = 6.7 Hz, 2H), 3.09 (t, J = 6.9 Hz, 2H), 2.75 – 2.71 (m, 2H), 1.81 – 1.79 (m, 2H), 1.65 (s, 3H), 1.18 – 1.09 (m, 4H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 190.6, 170.0, 141.7, 127.8, 63.6, 54.6, 50.6, 34.6, 27.6, 25.9, 23.9, 20.5 ppm; HRMS Calcd for $C_{12}H_{20}NO_2S_2$ $(M+H)^+$: 274.0935; Found: 274.0930.



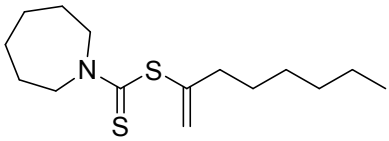
oct-1-en-2-yl diethylcarbamodithioate **(1n)**: Yield 129 mg, 50%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.63 (s, 1H), 5.61 (s, 1H), 4.00 (brs, 2H), 3.38 (brs, 2H), 2.73 (m, 2H), 1.58 (m, 2H), 1.27 – 1.01 (m, 12H), 0.84 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 194.0, 143.2, 127.0, 52.0 (2C), 38.5, 32.0, 29.2, 28.7, 26.2, 25.4, 24.1, 22.9, 14.2 ppm; HRMS Calcd for $C_{13}H_{26}NS_2$ $(M+H)^+$: 260.1507; Found: 260.1501.



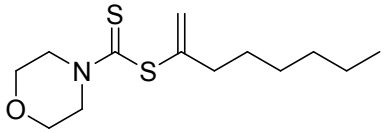
oct-1-en-2-yl dimethylcarbamodithioate **(1o):** Yield 138 mg, 60%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.59 (s, 2H), 2.96 (brs, 3H), 2.71 (t, J = 7.7 Hz, 2H), 2.54 (s, 3H), 1.60 – 1.54 (m, 2H), 1.28 – 1.18 (m, 6H), 0.84 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 195.3, 143.2, 127.0, 44.3 and 41.1 [$(CH_3)_2N$], 38.2, 32.0, 29.1, 28.6, 22.9, 14.2 ppm; HRMS Calcd for $C_{11}H_{22}NS_2$ $(M+H)^+$: 232.1194; Found: 232.1188.



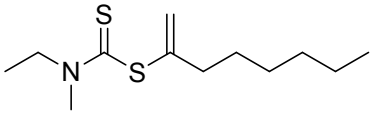
oct-1-en-2-yl piperidine-1-carbodithioate **(1p)**: Yield 149 mg, 55%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.60 (s,1H), 5.59 (s, 1H), 3.65 (brs, 2H) 3.18 (brs, 2H), 2.71 (t, J = 7.6 Hz, 2H), 1.58 (m, 2H), 1.26 – 1.15 (m, 6H), 0.99 – 0.96 (m, 3H), 0.85 – 0.82 (m, 6H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 193.9, 143.1, 127.0, 48.9, 47.0, 38.3, 32.0, 29.3, 29.1, 29.0, 28.6, 22.9, 22.8, 14.2 ppm; HRMS Calcd for $C_{14}H_{26}NS_2$ $(M+H)^+$: 272.1507; Found: 272.1501.



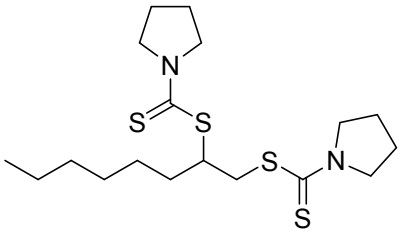
oct-1-en-2-yl azepane-1-carbodithioate **(1q)**: Yield 171 mg, 60%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.62 (s, 1H), 5.60 (s, 1H), 3.87 (t, J = 6.1 Hz, 2H), 3.36 (t, J = 6.2 Hz, 2H),, 2.74 (m, 2H), 1.62 – 1.54 (m, 4H), 1.39 (m, 2H), 1.26 – 1.14 (m, 10H), 0.84 (t, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 194.6, 143.1, 126.9, 54.9, 53.1, 38.3, 32.0, 29.1, 28.7, 27.7, 26.7, 26.4, 26.2, 22.9, 14.2 ppm; HRMS Calcd for $C_{15}H_{28}NS_2$ $(M+H)^+$: 286.1663; Found: 286.1658.



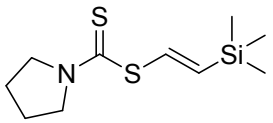
oct-1-en-2-yl morpholine-4-carbodithioate **(1r):** Yield 41 mg, 15%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.61 (s, 2H), 3.91 (brs, 2H), 3.34 (brs, 2H), 3.11 (brs, 4H), 2.70 (t, J = 7.6 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.27 – 1.19 (6H, m), 0.85 (t, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 195.7, 142.7, 127.4, 65.8 (2C), 50.7 (2C), 38.4, 32.0, 29.1, 28.7, 22.9, 14.2 ppm; HRMS Calcd for $C_{13}H_{24}NOS_2$ $(M+H)^+$: 274.1299; Found: 286.1294.



oct-1-en-2-yl ethyl(methyl)carbamodithioate **(1s)**: Yield 127 mg, 52%; ^{1}H NMR (500 MHz, C_6D_6) δ 5.60 (s, 1H), 5.59 (s, 1H), 3.67 (brs, 1H), 3.14 (brs, 1H), 3.01 (brs, 1.5H), 2.72 (t, J = 7.7 Hz, 2H), 2.59 (brs, 1.5H), 1.56 (m, 2H), 1.28 – 1.18 (m, 6H), 0.86 – 0.72 (m, 6H) ppm. ^{13}C NMR (126 MHz, C_6D6) δ 194.3, 143.4 and 143.1 (CH_2=C), 127.1 and 127.0 ($\underline{CH_2}$=C), 51.1 and 49.4 (CH_2N), 41.9 and 38.5 (CH_3N), 38.3, 32.0, 29.1, 28.6, 22.9, 14.2, 12.1 and 11.0 ($\underline{CH_3}CH_2N$) ppm; HRMS Calcd for $C_{12}H_{24}NS_2$ $(M+H)^+$: 246.1350; Found: 246.1345.

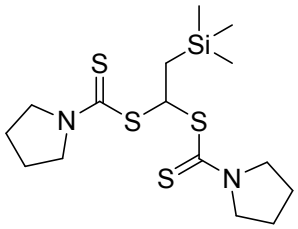


Octane-1,2-diyl bis(pyrrolidine-1-carbodithioate) **(C) :** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (m, 1H), 3.89 – 3.83 (m, 5H), 3.71 – 3.52 (m, 5H), 2.09 – 1.96 (m, 4H), 1.95 – 1.86 (m, 4H), 1.83 – 1.69 (m, 2H), 1.50 – 1.35 (m, 2H), 1.29 – 1.15 (m, 6H), 0.80 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 191.8, 55.2, 54.9, 51.1, 50.7, 41.8, 33.2, 31.7 (2C), 29.1, 26.9, 26.1, 26.1, 24.3, 24.3, 22.6, 14.1 ppm; HRMS Calcd for $C_{18}H_{32}N_2NaS_4$ $(M+Na)^+$: 427.1346; Found: 427.1340.

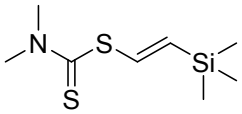


(E)-2-(trimethylsilyl)vinyl pyrrolidine-1-carbodithioate **(3a)**: Yield 154 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 18.7 Hz, 1H), 6.19 (d, J = 18.7 Hz, 1H),

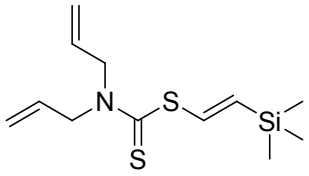
3.95 (t, J = 6.9 Hz, 2H), 3.65 (t, J = 6.9 Hz, 2H), 2.09 – 1.96 (m, 4H), 0.15 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 137.5, 132.0, 54.6, 50.7, 26.1, 24.3, -1.20 ppm. HRMS Calcd for $C_{10}H_{20}NS_2Si$ $(M+H)^+$: 246.0806; Found: 246.0801.



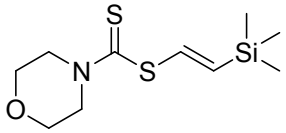
2-(trimethylsilyl)ethane-1,1-diyl bis(pyrrolidine-1-carbodithioate) **(4a):** Yield 59 mg, 15%; ^{1}H NMR (300 MHz, C_6D_6) δ 6.49 (t, J = 8.0 Hz, 1H), 3.37 – 3.32 (m, 4H), 2.87 – 2.80 (m, 4H), 2.03 (d, J = 8.0 Hz, 2H), 0.90 – 0.77 (m, 8H), 0.05 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 57.9, 54.6, 50.5, 26.2, 25.1, 24.3, -0.36 ppm; HRMS Calcd for $C_{15}H_{28}N_2NaS_4Si$ $(M+Na)^+$: 415.0802; Found: 415.0797.



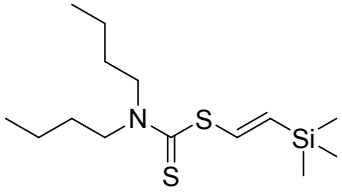
(E)-2-(trimethylsilyl)vinyl dimethylcarbamodithioate **(3b):** Yield 142 mg, 65%; ^{1}H NMR (500 MHz, C_6D_6) δ 8.08 (d, J = 18.8 Hz, 1H), 6.27 (d, J = 18.8 Hz, 1H), 2.93 (s, 3H), 2.41 (s, 3H), 0.08 (s, 9H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 193.5, 139.9, 131.3, 44.1, 40.2, -1.3 ppm; HRMS Calcd for $C_8H_{18}NS_2Si$ $(M+H)^+$: 220.0650; Found: 220.0644.



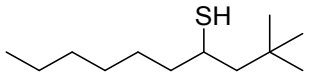
(E)-2-(trimethylsilyl)vinyl diallylcarbamodithioate **(3c):** Yield 136 mg, 50%; ^{1}H NMR (500 MHz, C_6D_6) δ 8.0 (d, J = 18.7 Hz, 1H), 6.22 (d, J = 18.7 Hz, 1H), 5.69 (brs, 1H), 5.37 (brs, 1H), 4.92 – 4.84 (m, 4H), 4.45 (brs, 2H), 3.83 (brs, 2H), 0.06 (s, 9H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 194.8, 139.4(SiCH=<u>CH</u>S-), 131.8 (Si<u>CH</u>=CHS-), 131.5 and 130.7 (CH_2=<u>CH</u>-CH_2N), 118.1 and 117.9 ((<u>CH_2</u>=CH-CH_2N), 56.2 (CH_2N), 53.3 (CH_2N), -1.4 ppm; HRMS Calcd for $C_{12}H_{22}NS_2Si$ $(M+H)^+$: 272.0963; Found: 272.0959.



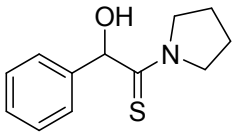
(E)-2-(trimethylsilyl)vinyl morpholine-4-carbodithioate **(3d):** Yield 78 mg, 30%; ^{1}H NMR (500 MHz, C_6D_6) δ 8.09 (d, J = 18.7 Hz, 1H), 6.32 (d, J = 18.7 Hz, 1H), 3.89 (brs, 2H), 3.40 –2.80 (brs, 6H), 0.09 (s, 9H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 193.9, 138.6, 132.4, 65.8 (2C), 50.8 (2C), -1.36 ppm; HRMS Calcd for $C_{10}H_{20}NOS_2Si$ $(M+H)^+$: 262.0756; Found: 262.0750.



(E)-2-(trimethylsilyl)vinyl dibutylcarbamodithioate **(3e):** Yield 197 mg, 65%; ^{1}H NMR (500 MHz, C_6D_6) δ 8.13 (d, J = 18.8 Hz, 1H), 6.25 (d, J = 18.8 Hz, 1H), 3.78 (t, J = 8.0 Hz, 2H), 3.23 3.78 (t, J = 7.8 Hz, 2H), 1.59 – 1.53 (m, 2H), 1.39 – 1.32 (m, 2H), 1.18 – 1.13 (m, 2H), 1.05 – 1.01 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H), 0.74 (t, J = 7.4 Hz, 3H), 0.08 (s, 9H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 192.7, 139.8, 131.1, 54.6, 52.3, 29.8, 28.7, 20.3, 20.2, 13.9, 13.7, -1.3 ppm; HRMS Calcd for $C_{14}H_{30}NS_2Si$ $(M+H)^+$: 304.1589; Found: 304.1583.

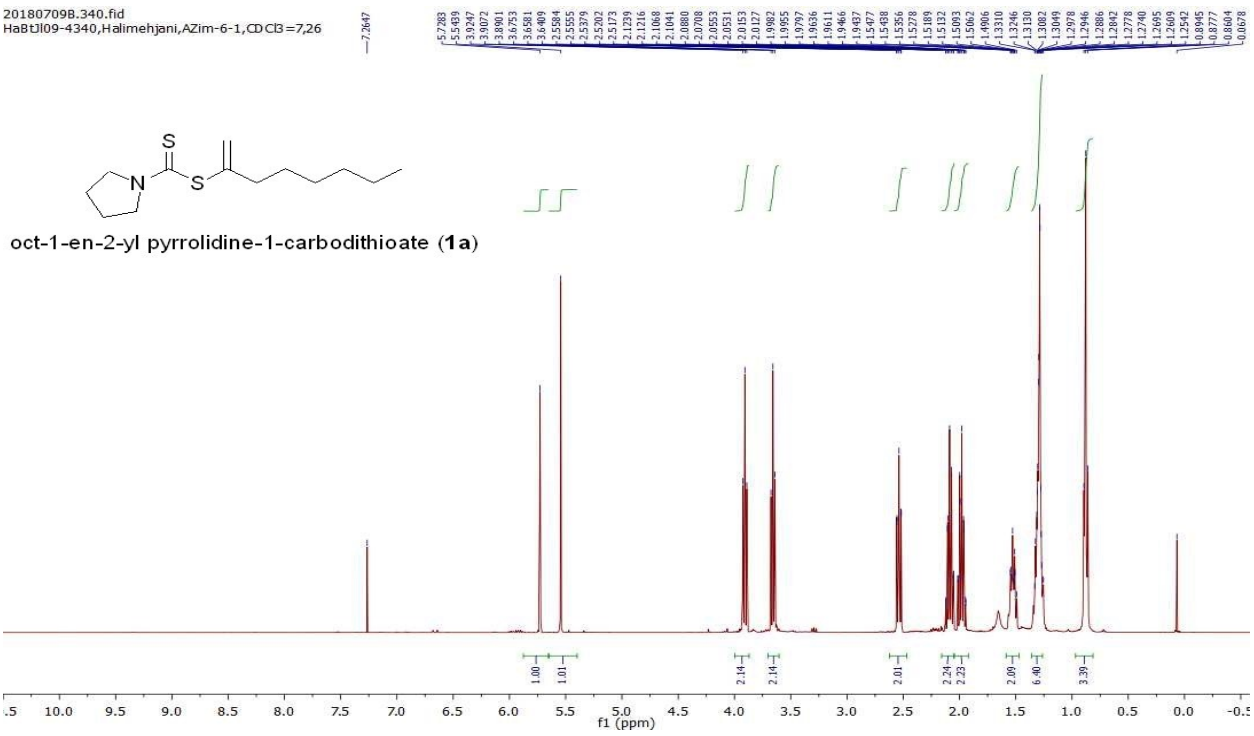


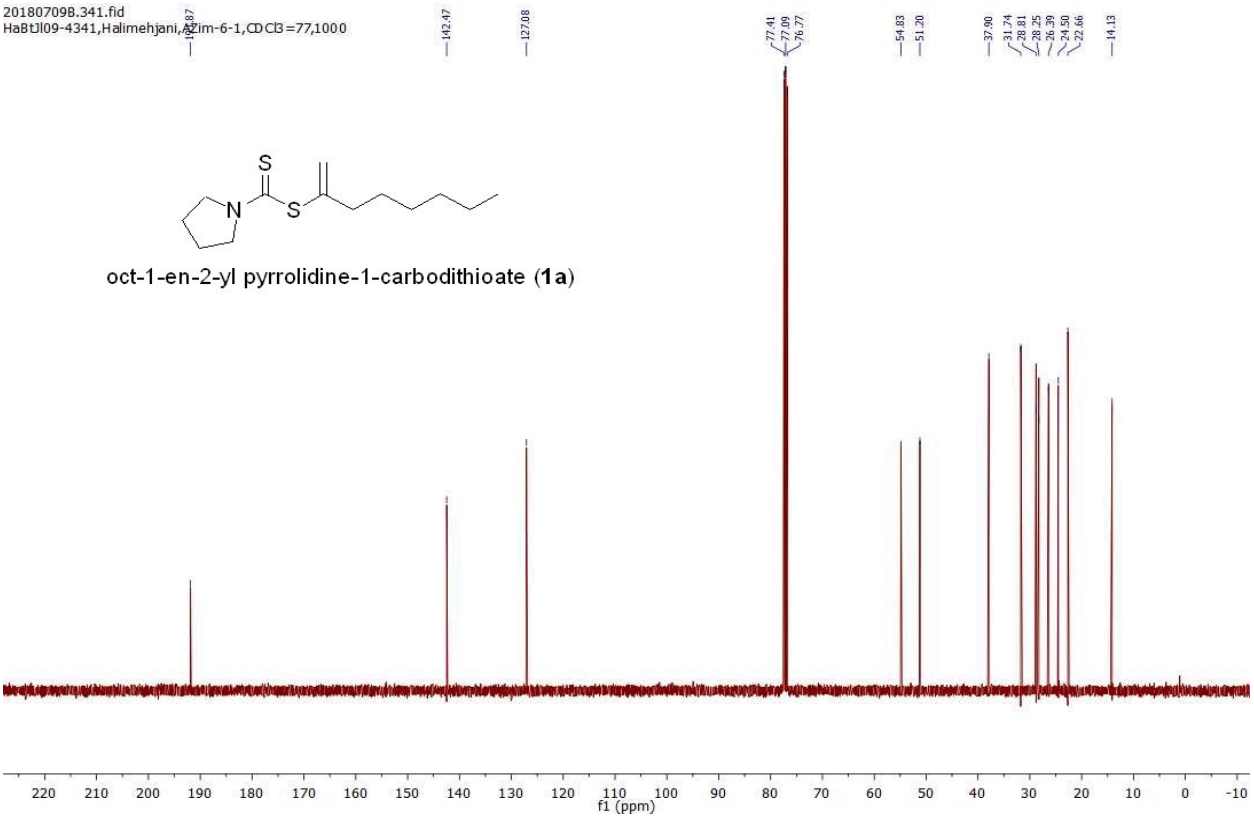
2,2-dimethyldecane-4-thiol **(5)**: Yield 149 mg, 74%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.85 (m, 1H), 1.62 – 1.40 (m, 6H), 1.32 – 1.27 (m, 6H), 0.95 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 53.1, 41.9, 36.9, 31.9, 31.2, 30.0, 29.1, 27.2, 22.7, 14.2 ppm; HRMS Calcd for $C_{12}H_{25}S$ $(M-H)^-$: 201.1677; Found: 201.1682.

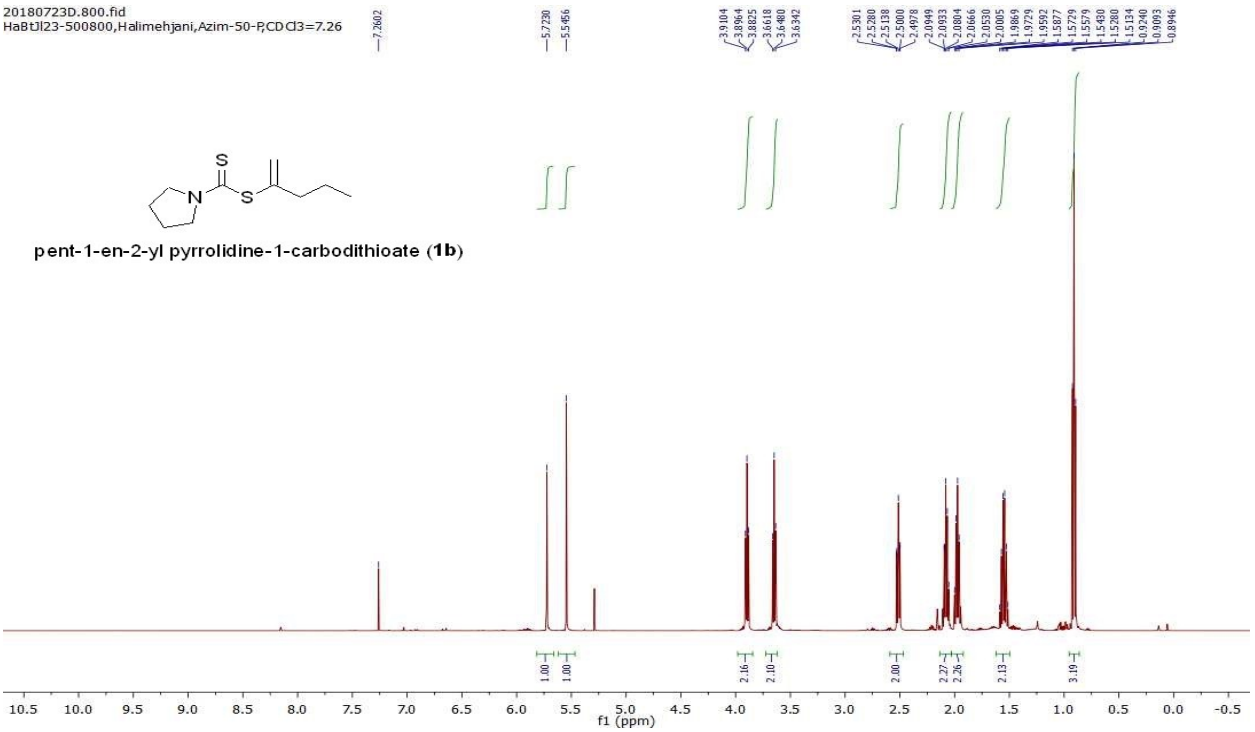


2-hydroxy-2-phenyl-1-(pyrrolidin-1-yl)ethanethione **(6)**: Yield 151 mg, 62%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 5H), 5.34 (d, J = 7.1 Hz, 1H), 5.16 (d, J = 6.0 Hz, 1H), 3.95 (m, 1H), 3.84 (m, 1H), 3.71 (m, 1H), 3.12 (m, 1H), 2.03 – 1.84 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 139.7, 128.9, 128.5, 127.8, 75.1, 54.9, 50.3, 26.1, 23.5 ppm; HRMS Calcd for $C_{12}H_{15}NNaOS_2$ $(M+H)^+$: 244.0772; Found: 244.0769.

^{1}H and ^{13}C NMR spectra for all the products:



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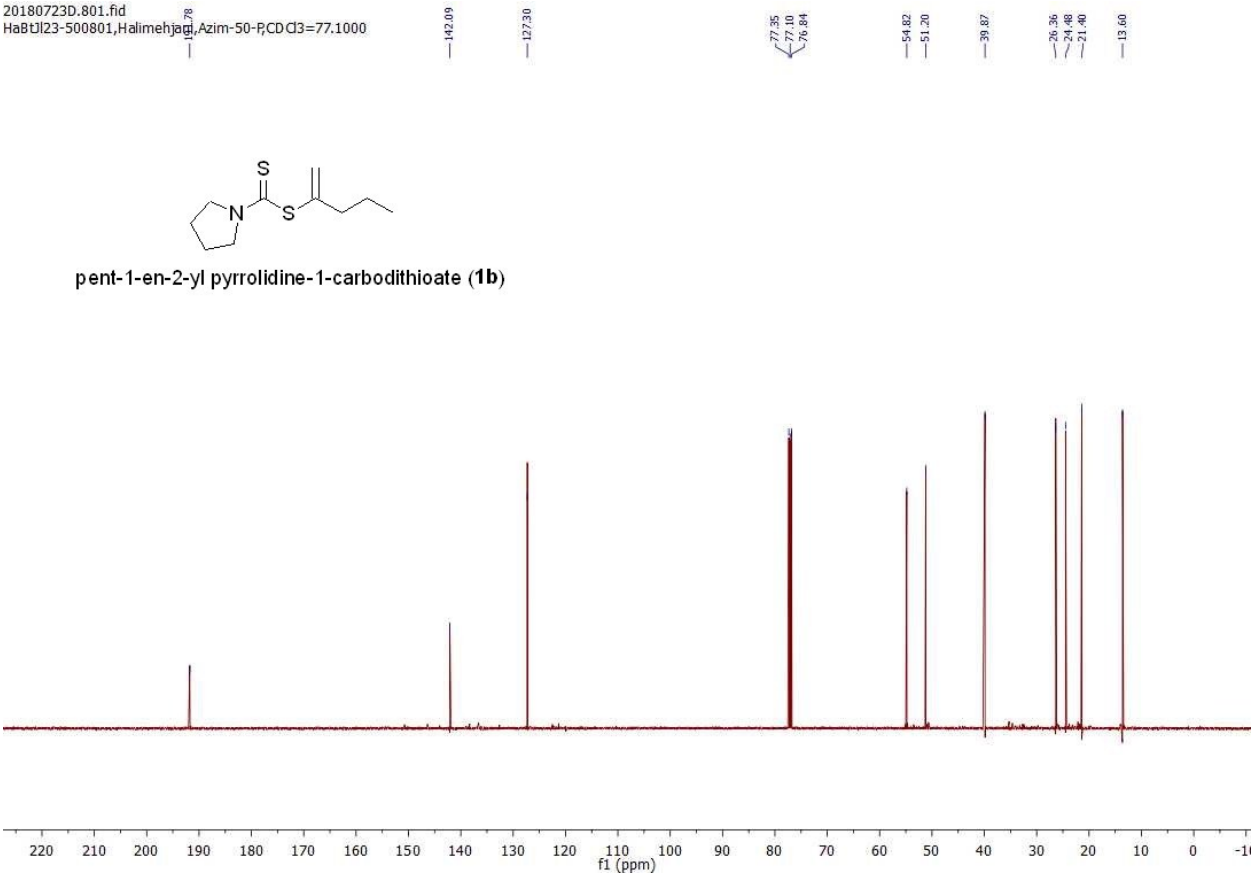
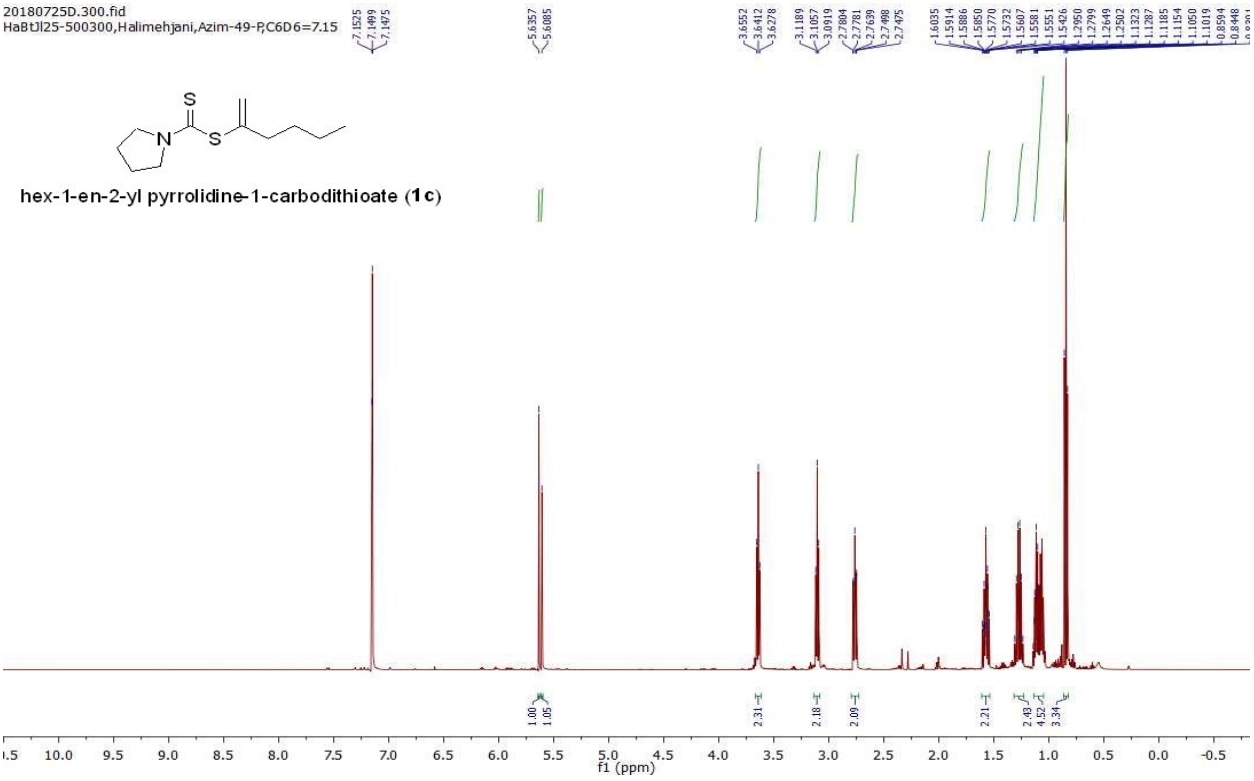
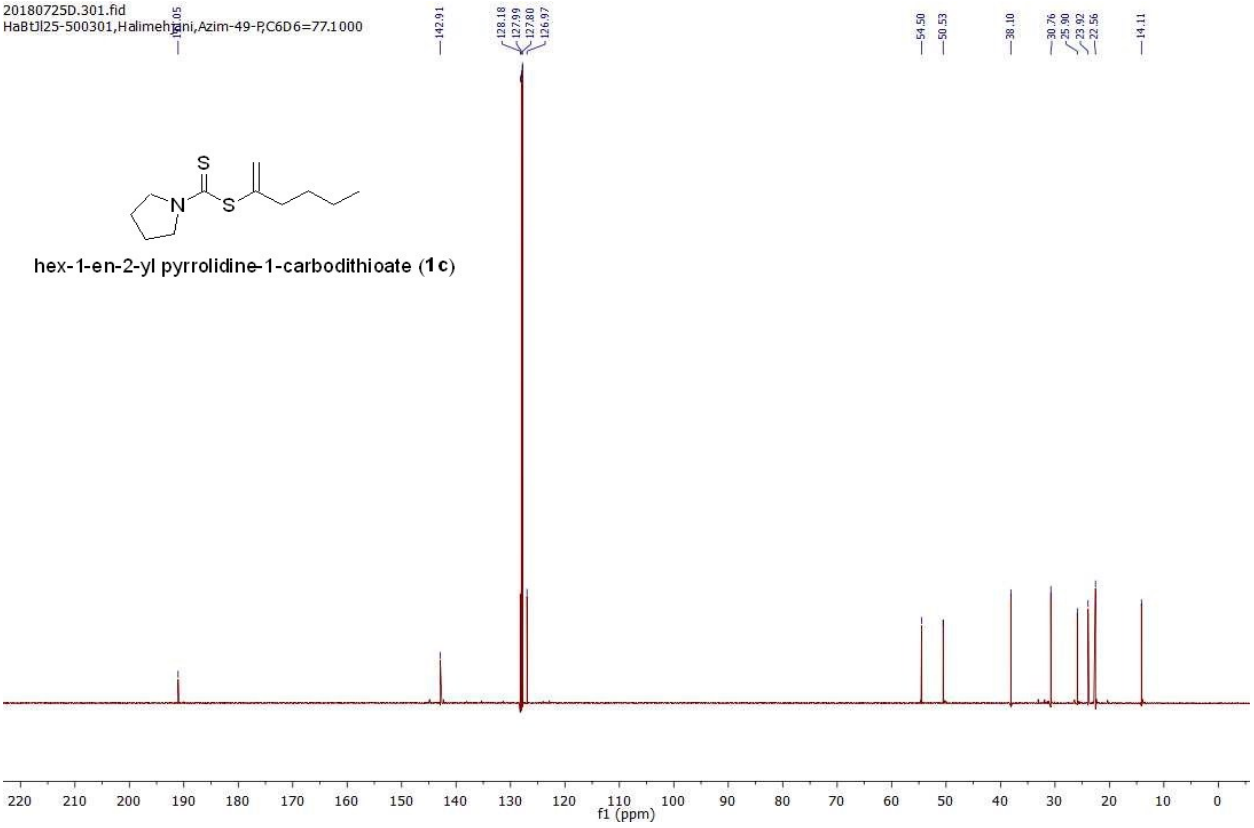
HaBtJl23-500800,Halimehjani,Azim-50-P,CDCl3=7.26
pent-1-en-2-yl pyrrolidine-1-carbodithioate (1b)
f1 (ppm)


20180723D.801.fid
HaBtJl23-500801,Halimehjani,Azim-50-P,CDCl3=77.1000
pent-1-en-2-yl pyrrolidine-1-carbodithioate (1b)
f1 (ppm)


20180725D.300.fid
HaBtJl25-500300,Halimehjani,Azim-49-P,C6D6=7.15
hex-1-en-2-yl pyrrolidine-1-carbodithioate (1c)
f1 (ppm)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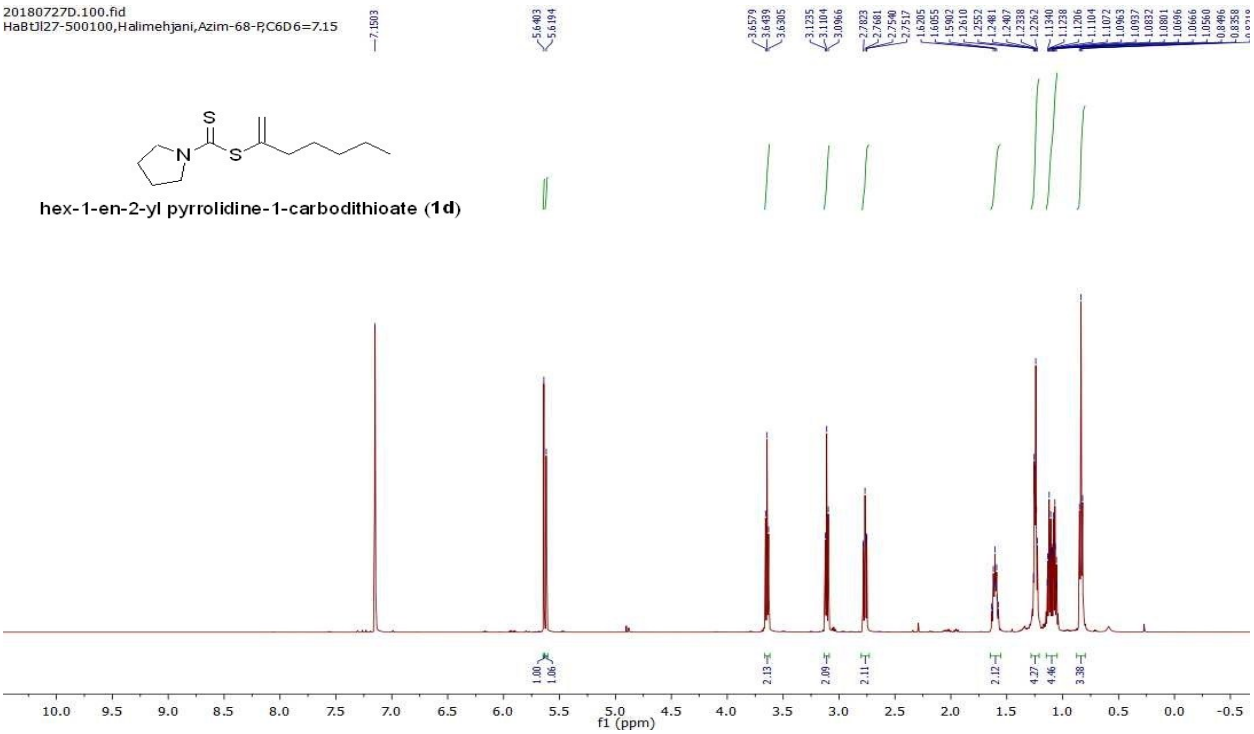
HaBtJl25-500301,Halimehjani,Azim-49-P,C6D6=77.1000
hex-1-en-2-yl pyrrolidine-1-carbodithioate (1c)
f1 (ppm)


20180727D.100.fid
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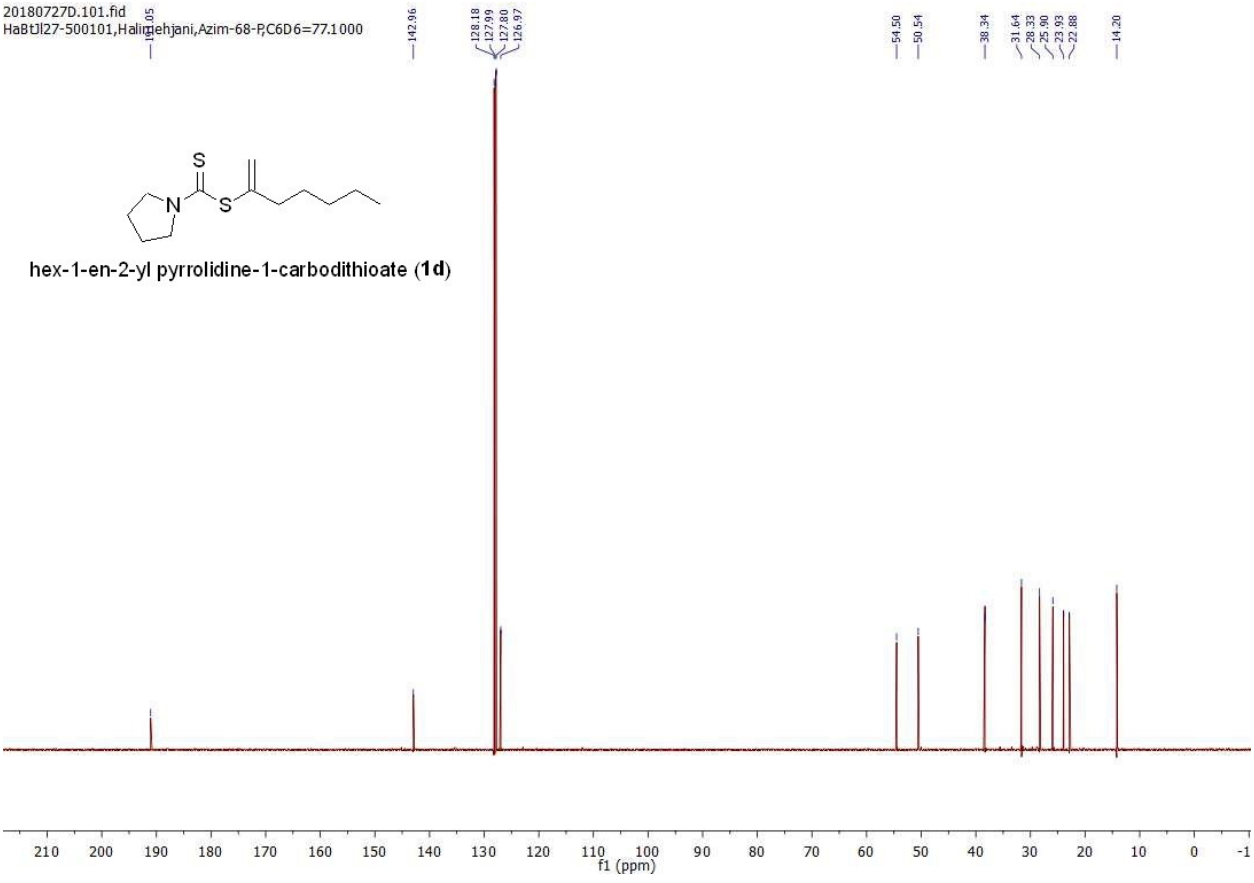
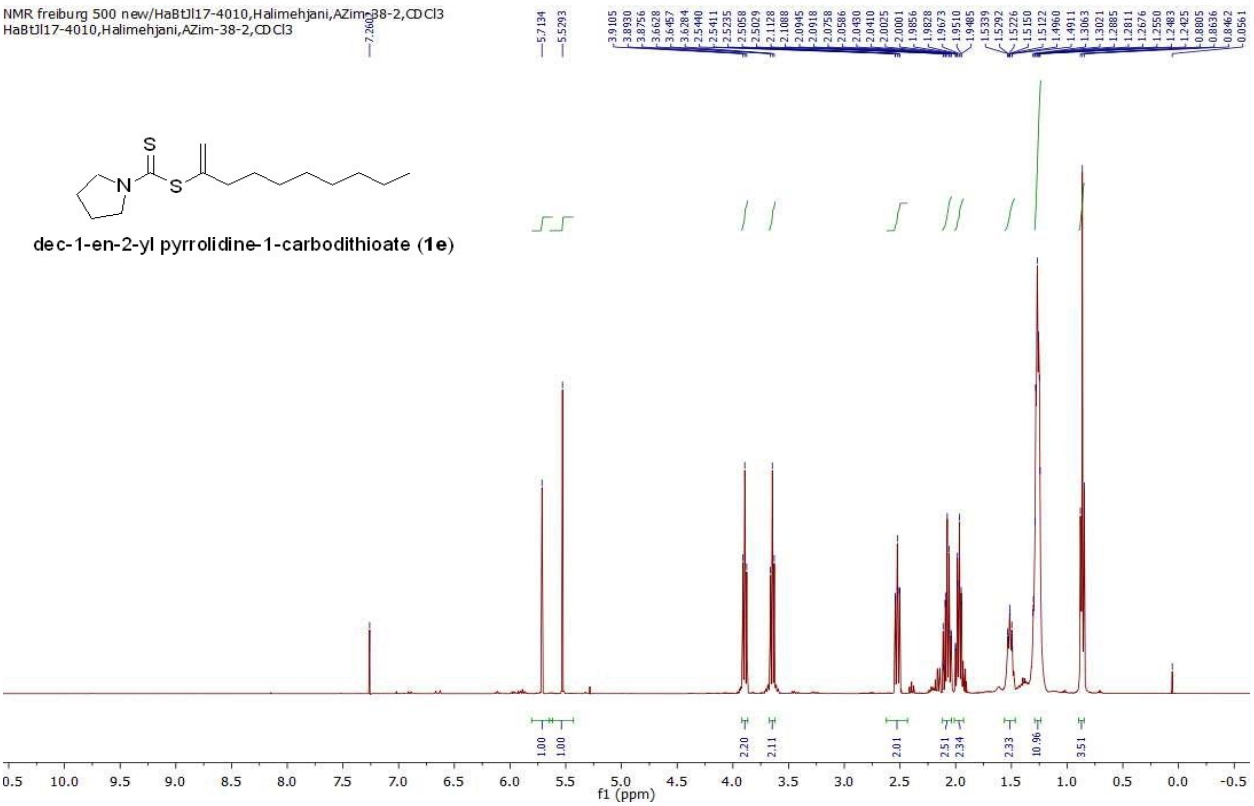
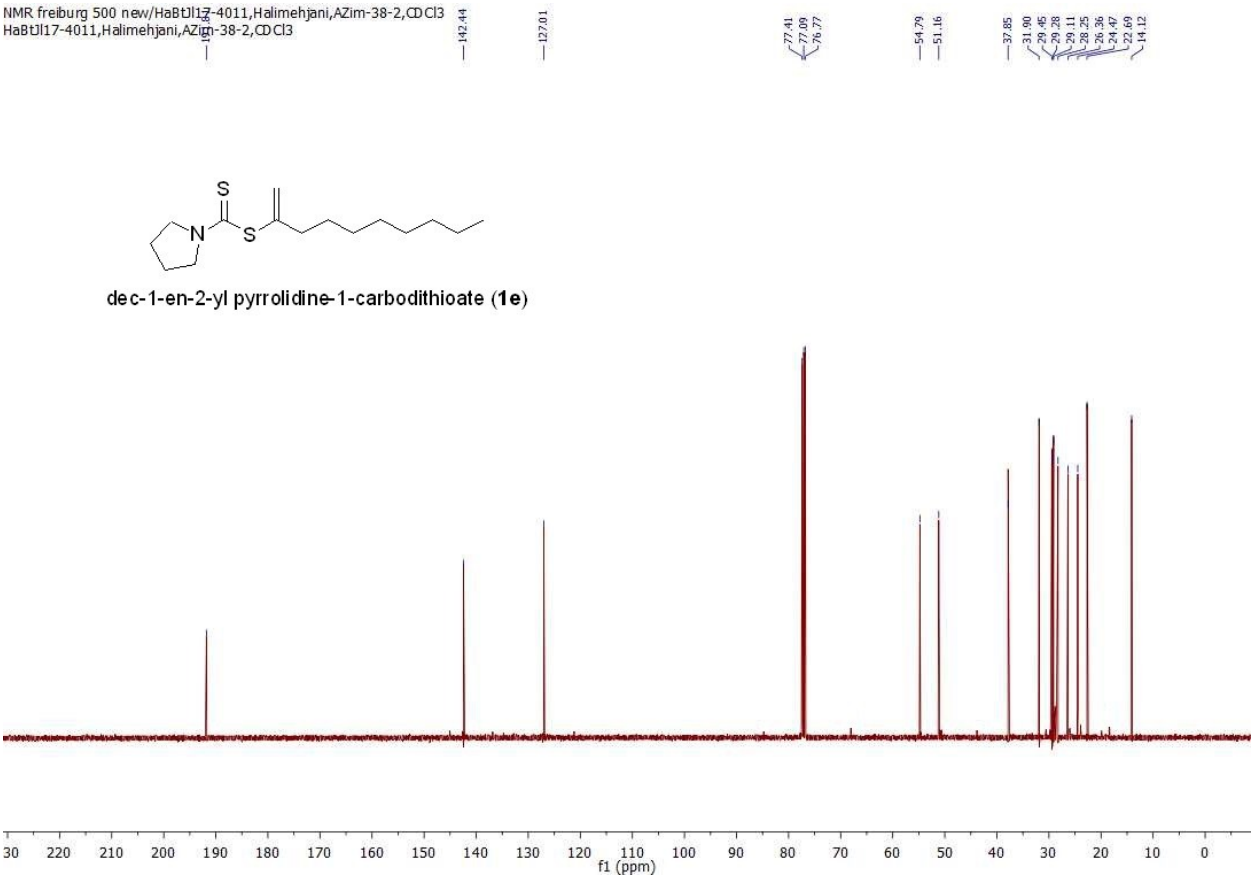
hex-1-en-2-yl pyrrolidine-1-carbodithioate (1d)
f1 (ppm)

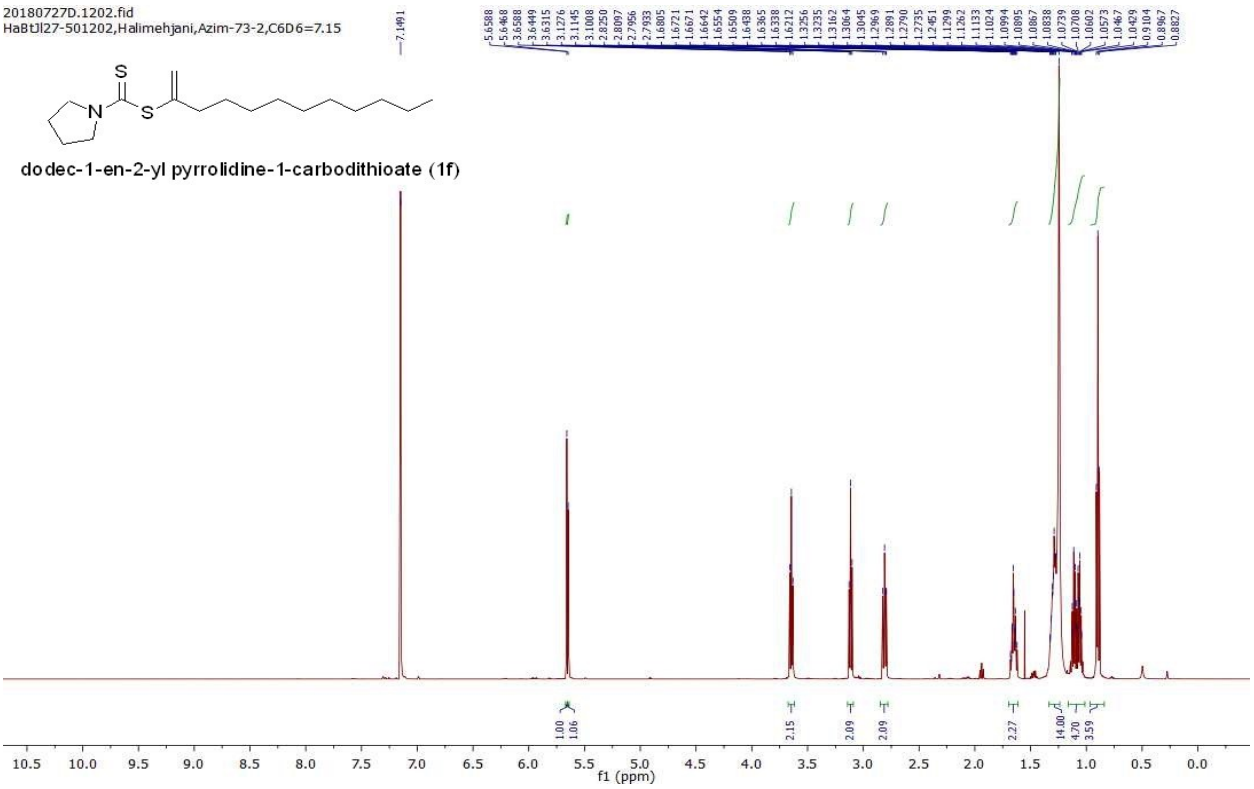

20180727D.101.fid
HaBtJl27-500101,Halimehjani,Azim-68-P,C6D6=77.1000
hex-1-en-2-yl pyrrolidine-1-carbodithioate (1d)
f1 (ppm)



dec-1-en-2-yl pyrrolidine-1-carbodithioate (**1e**)



dec-1-en-2-yl pyrrolidine-1-carbodithioate (**1e**)


20180727D.1202.fid
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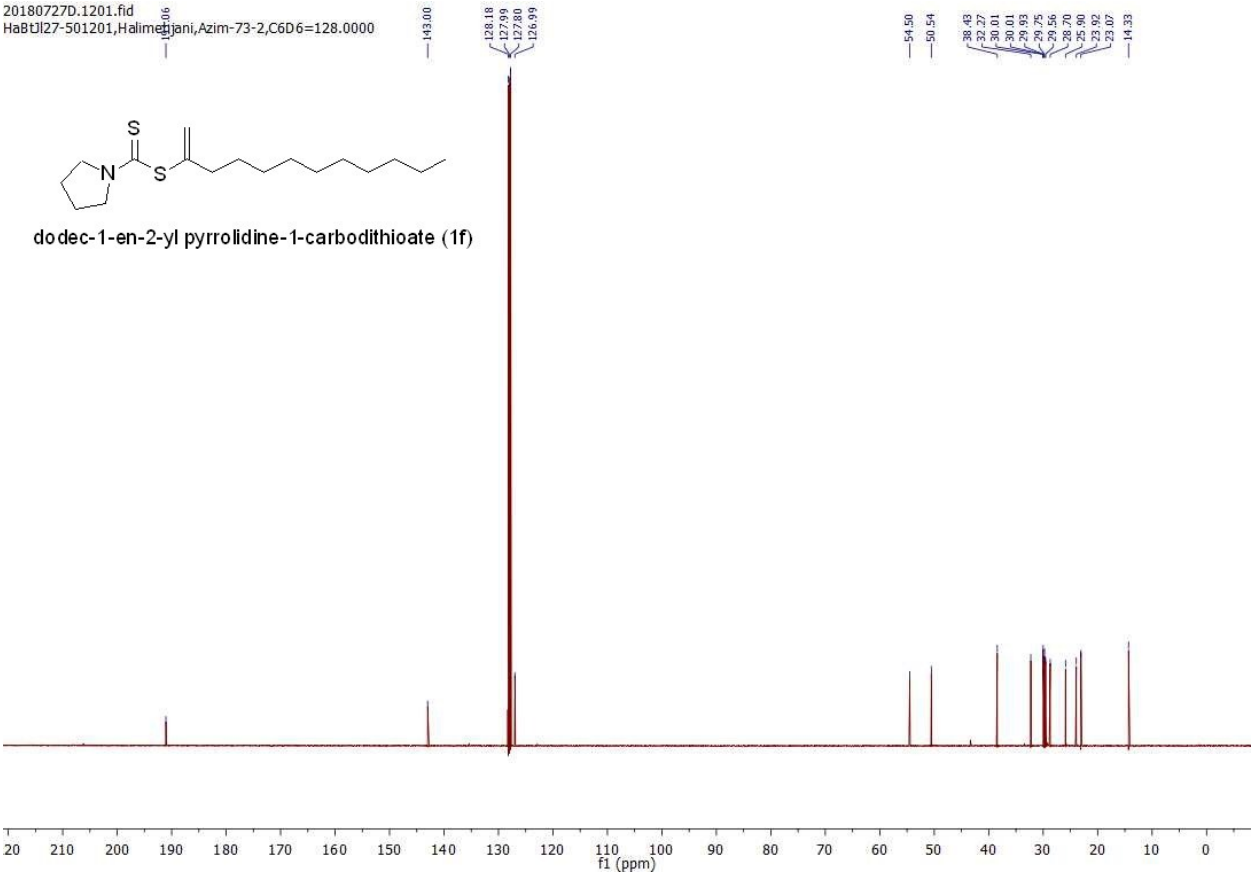
dodec-1-en-2-yl pyrrolidine-1-carbodithioate (1f)
f1 (ppm)


20180727D.1201.fid
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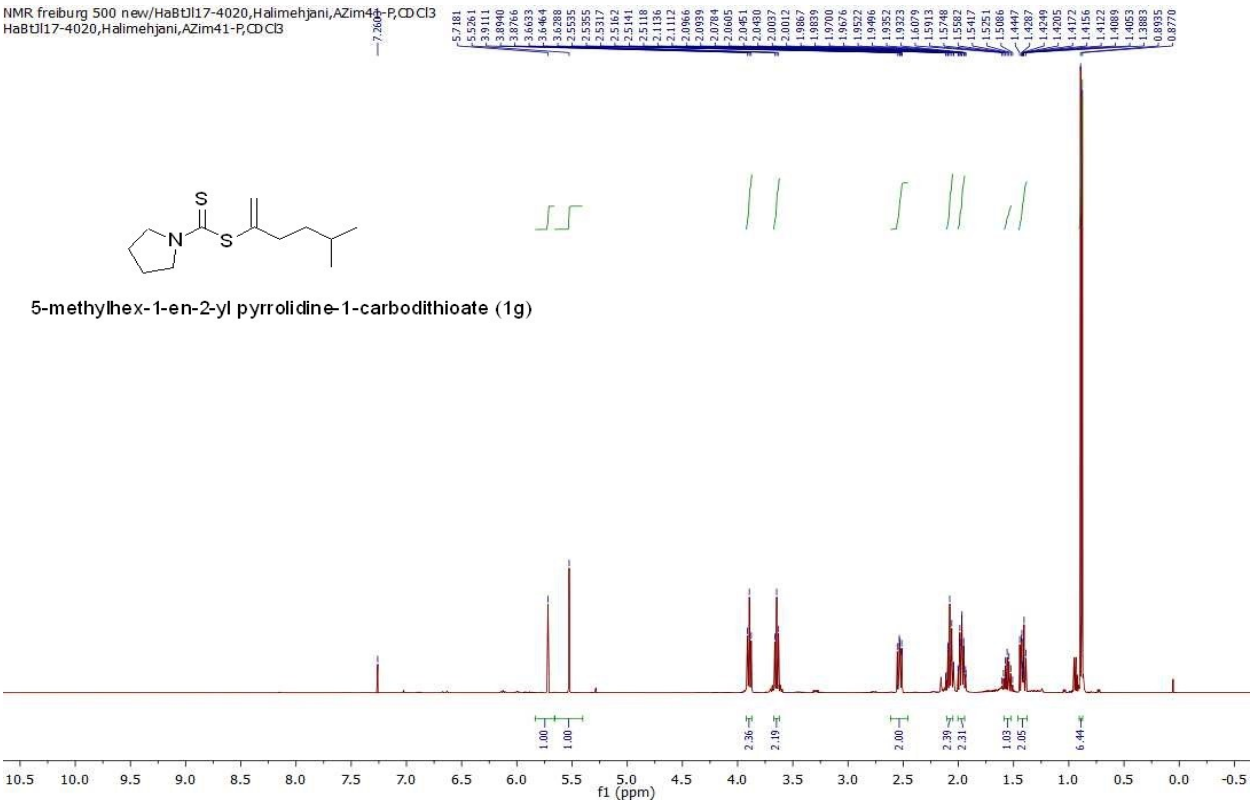
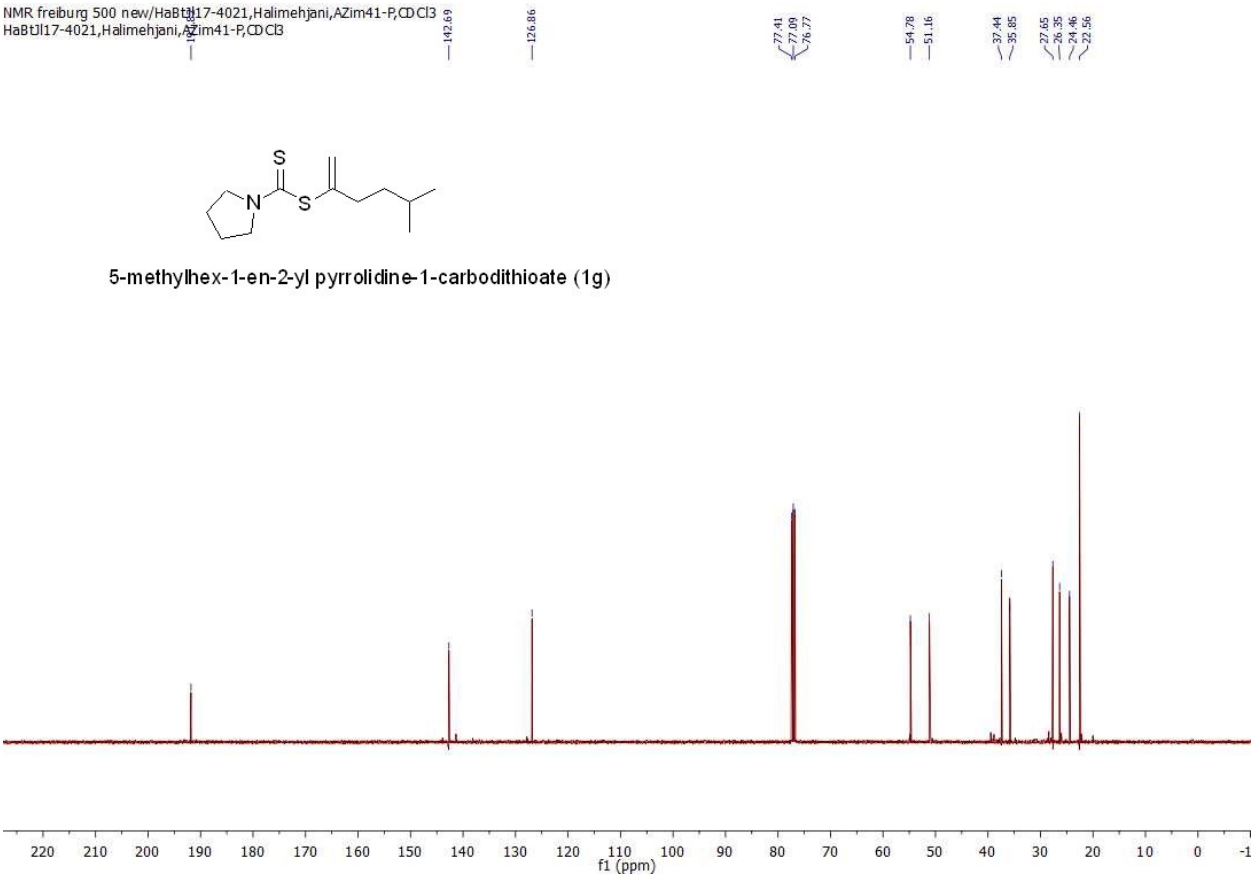
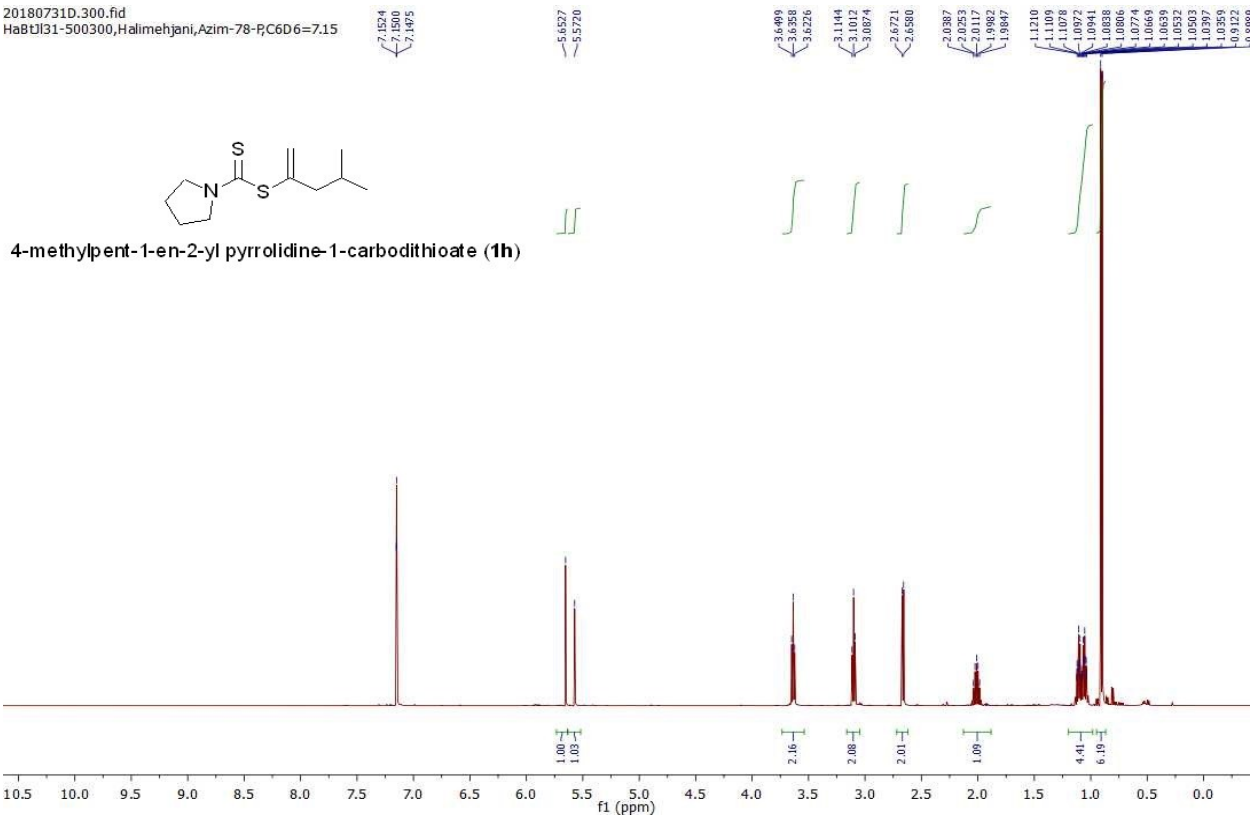
dodec-1-en-2-yl pyrrolidine-1-carbodithioate (1f)
f1 (ppm)



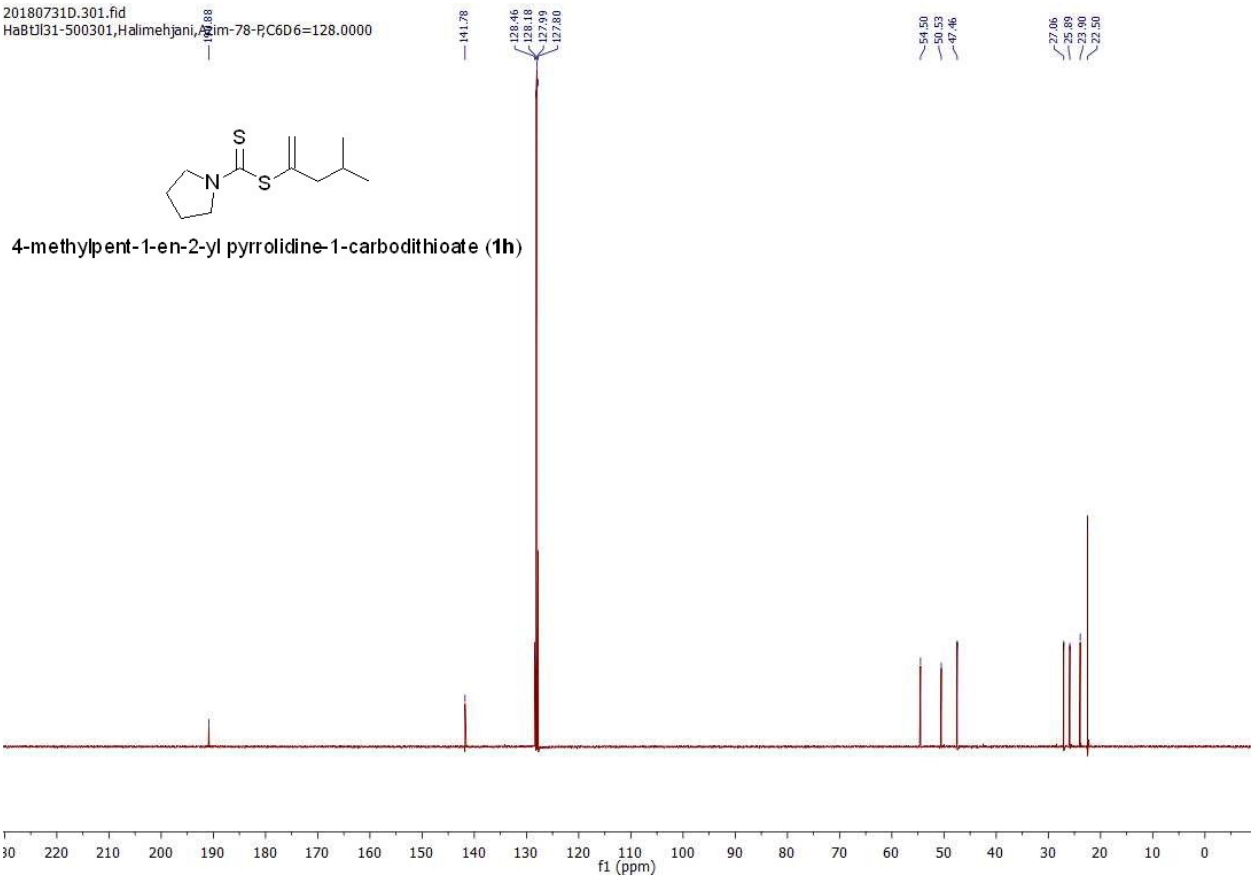
5-methylhex-1-en-2-yl pyrrolidine-1-carbodithioate (1g)



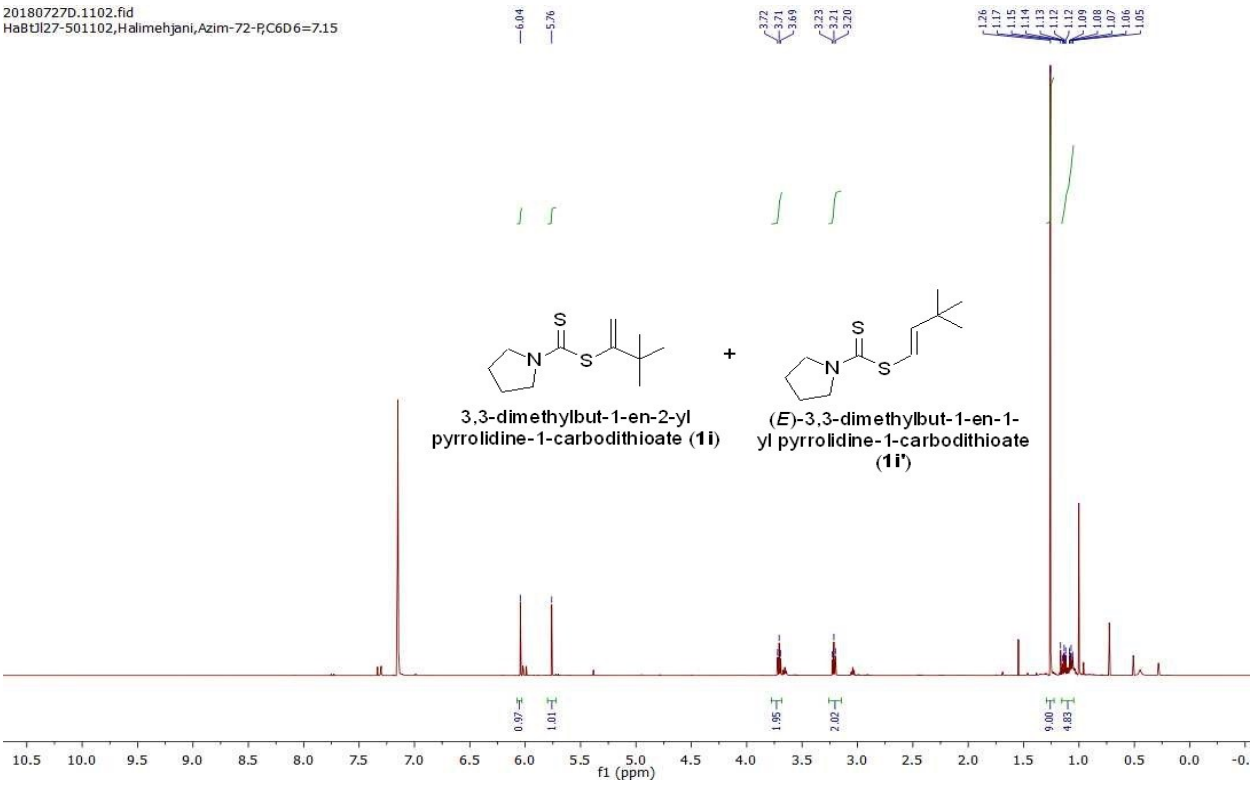
5-methylhex-1-en-2-yl pyrrolidine-1-carbodithioate (1g)

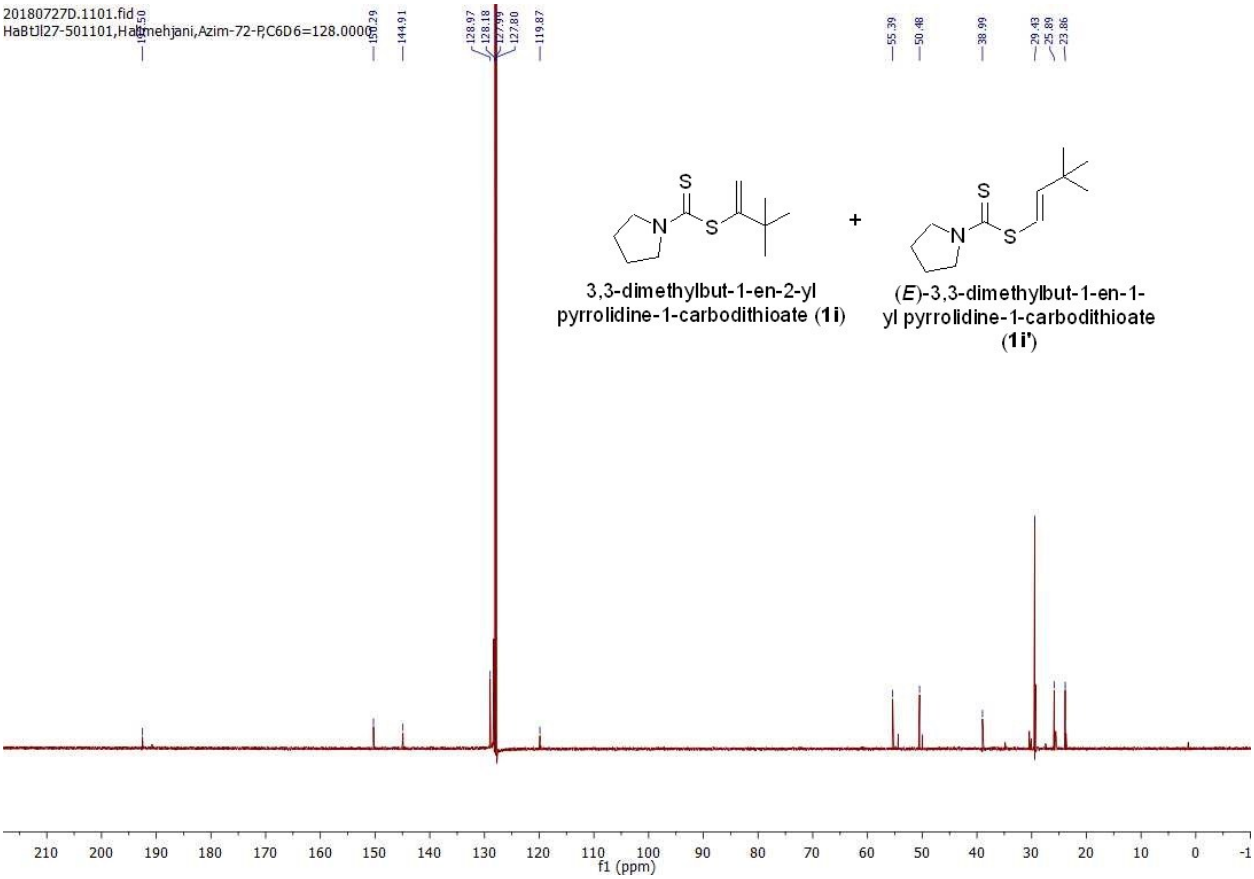


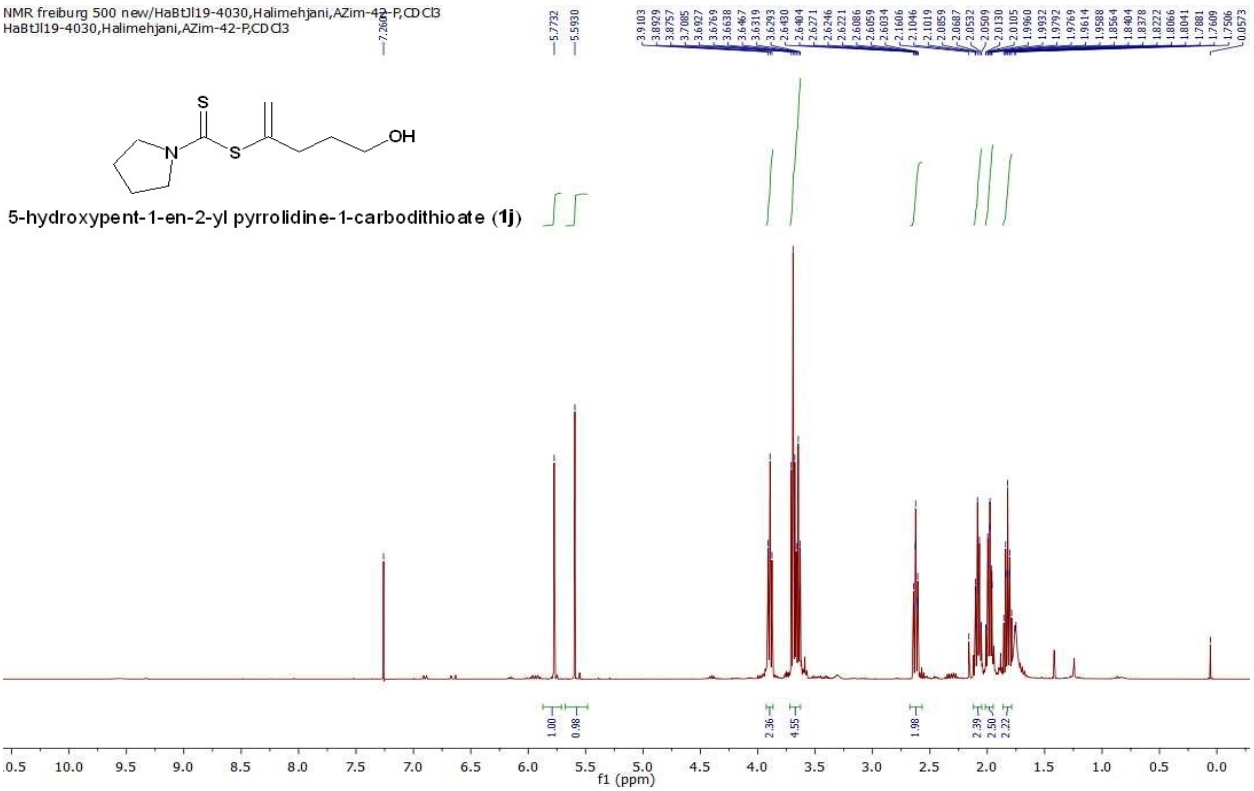
4-methylpent-1-en-2-yl pyrrolidine-1-carbodithioate (**1h**)



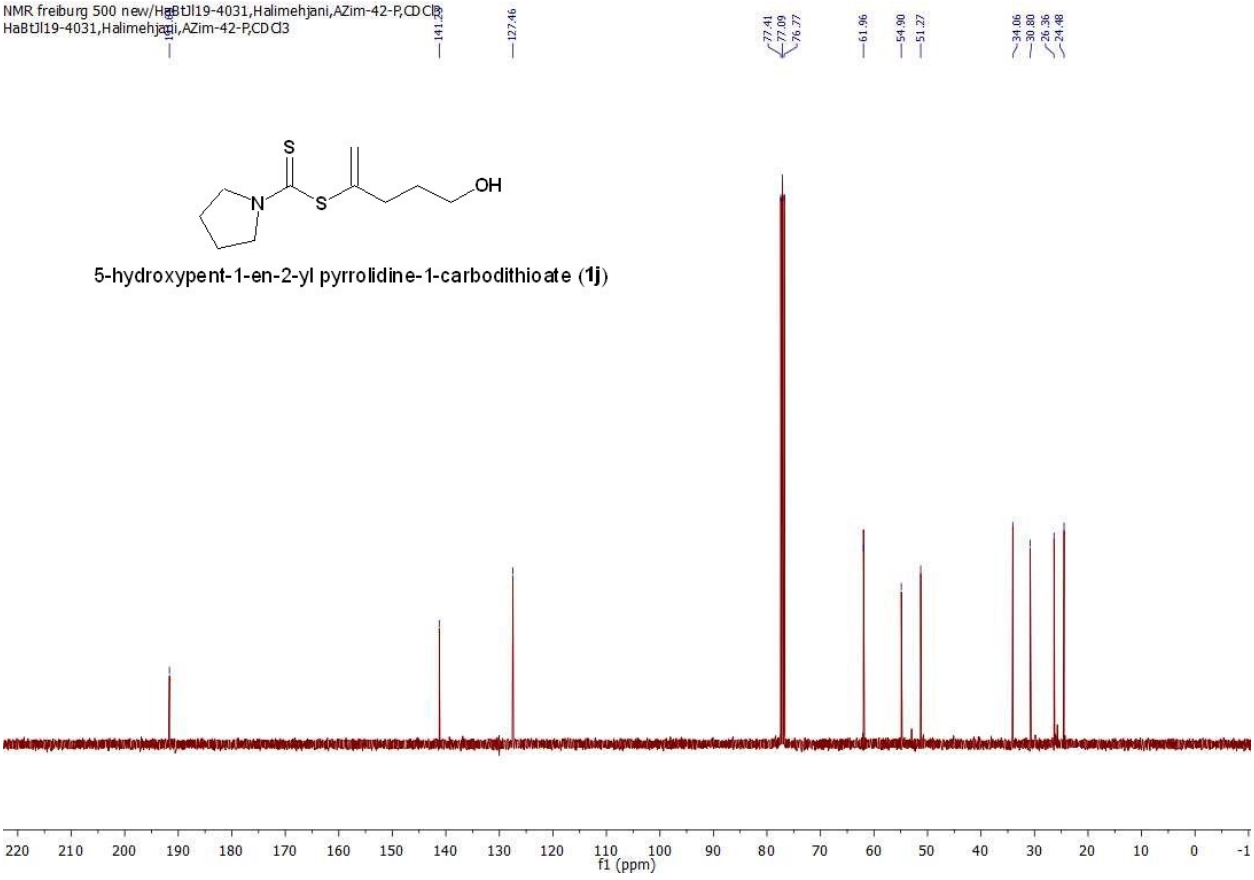
4-methylpent-1-en-2-yl pyrrolidine-1-carbodithioate (**1h**)


20180727D.1102.fid
HaBtJl27-501102,Halimehjani,Azim-72-P,C6D6=7.15
3,3-dimethylbut-1-en-2-yl pyrrolidine-1-carbodithioate (1i)
(E)-3,3-dimethylbut-1-en-1-yl pyrrolidine-1-carbodithioate (1i')
f1 (ppm)

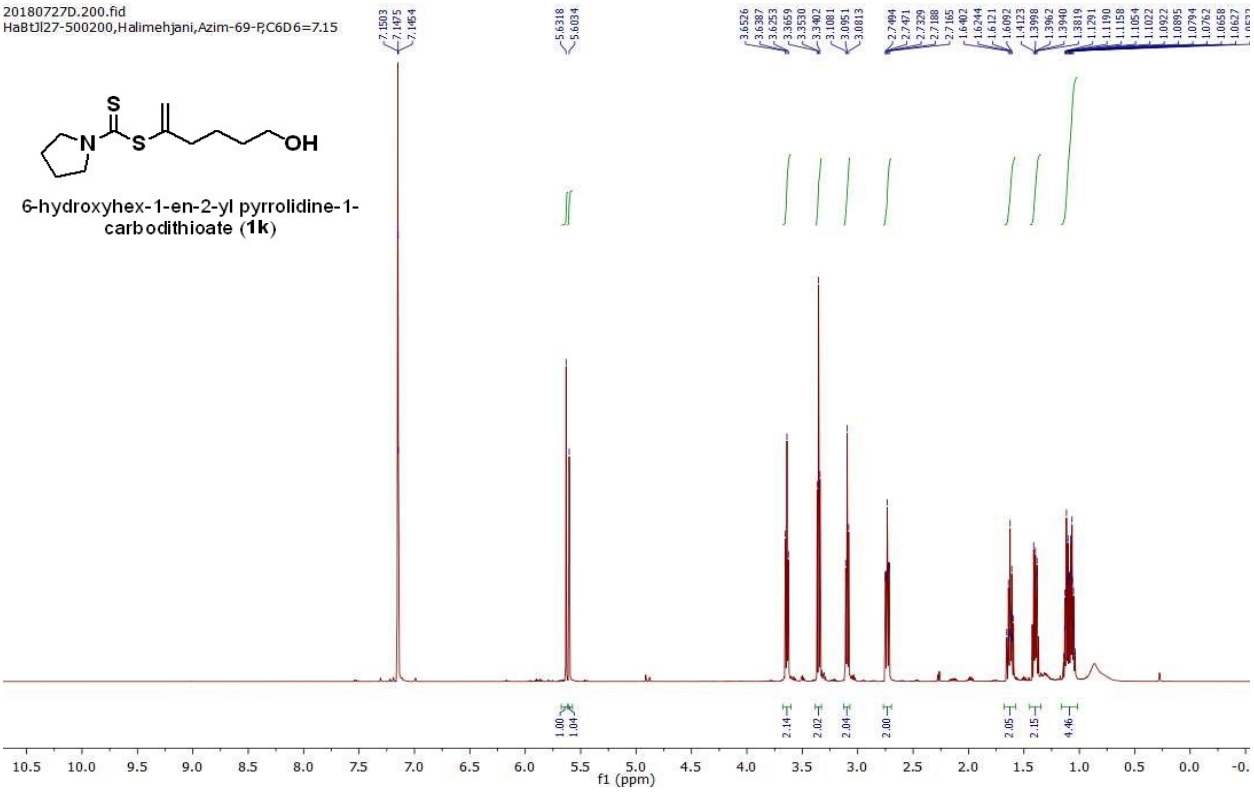

20180727D.1101.fid
HaBtJl27-501101,Halimehjani,Azim-72-P,C6D6=128.0000
3,3-dimethylbut-1-en-2-yl pyrrolidine-1-carbodithioate (1i)
(E)-3,3-dimethylbut-1-en-1-yl pyrrolidine-1-carbodithioate (1i')
f1 (ppm)

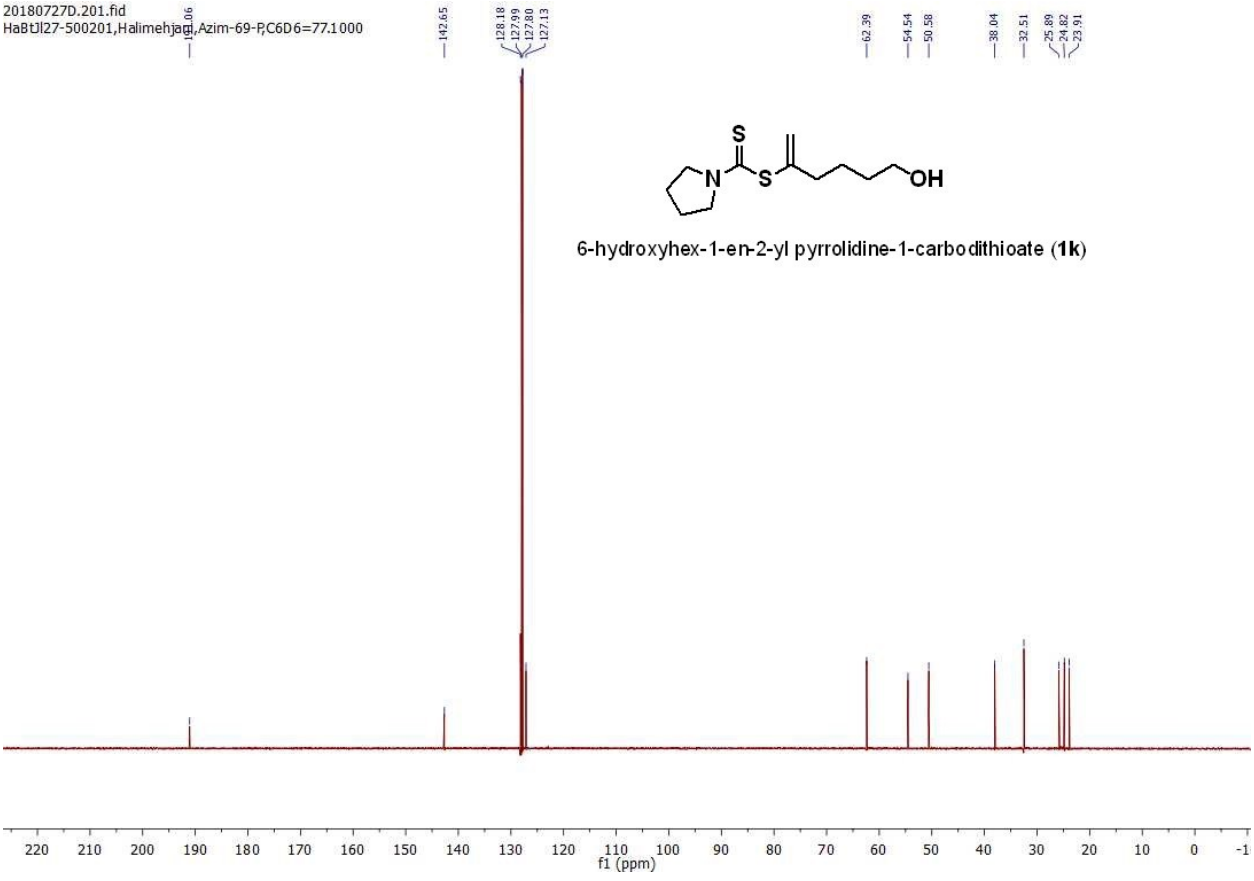


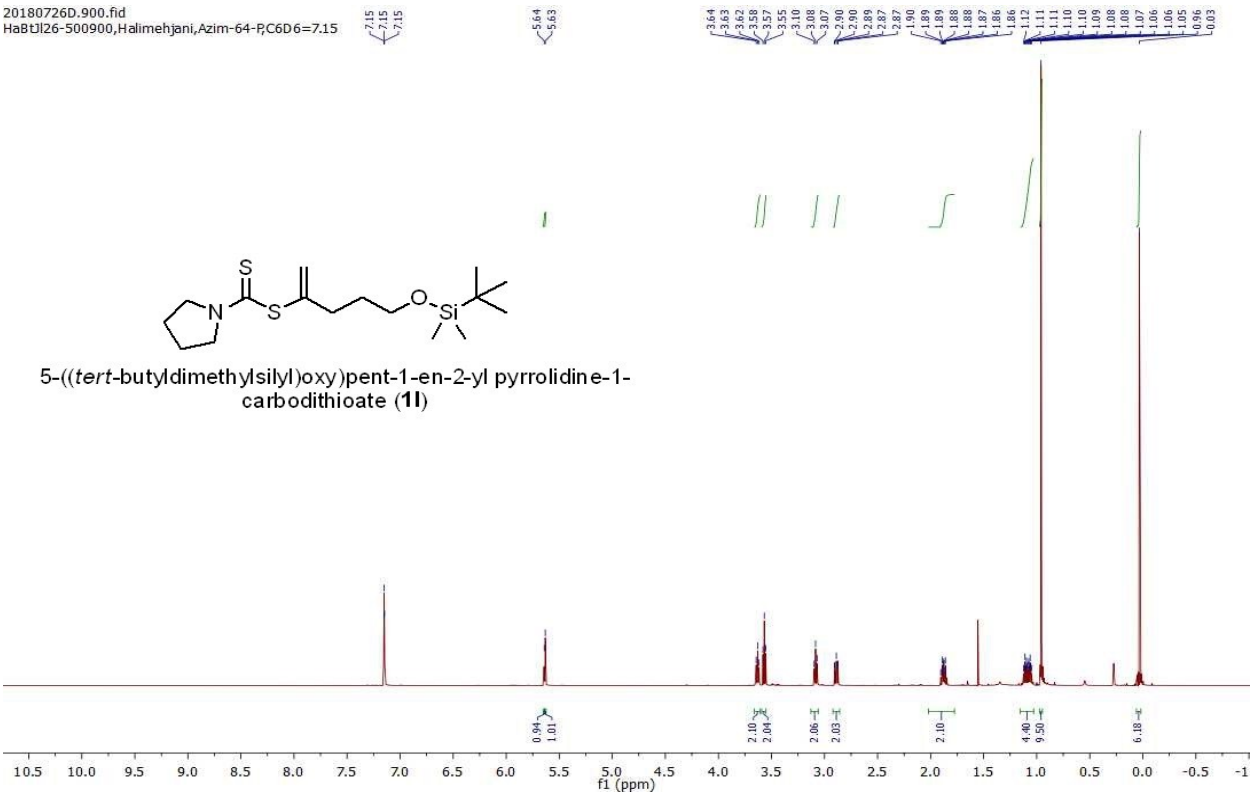
5-hydroxypent-1-en-2-yl pyrrolidine-1-carbodithioate (**1j**)



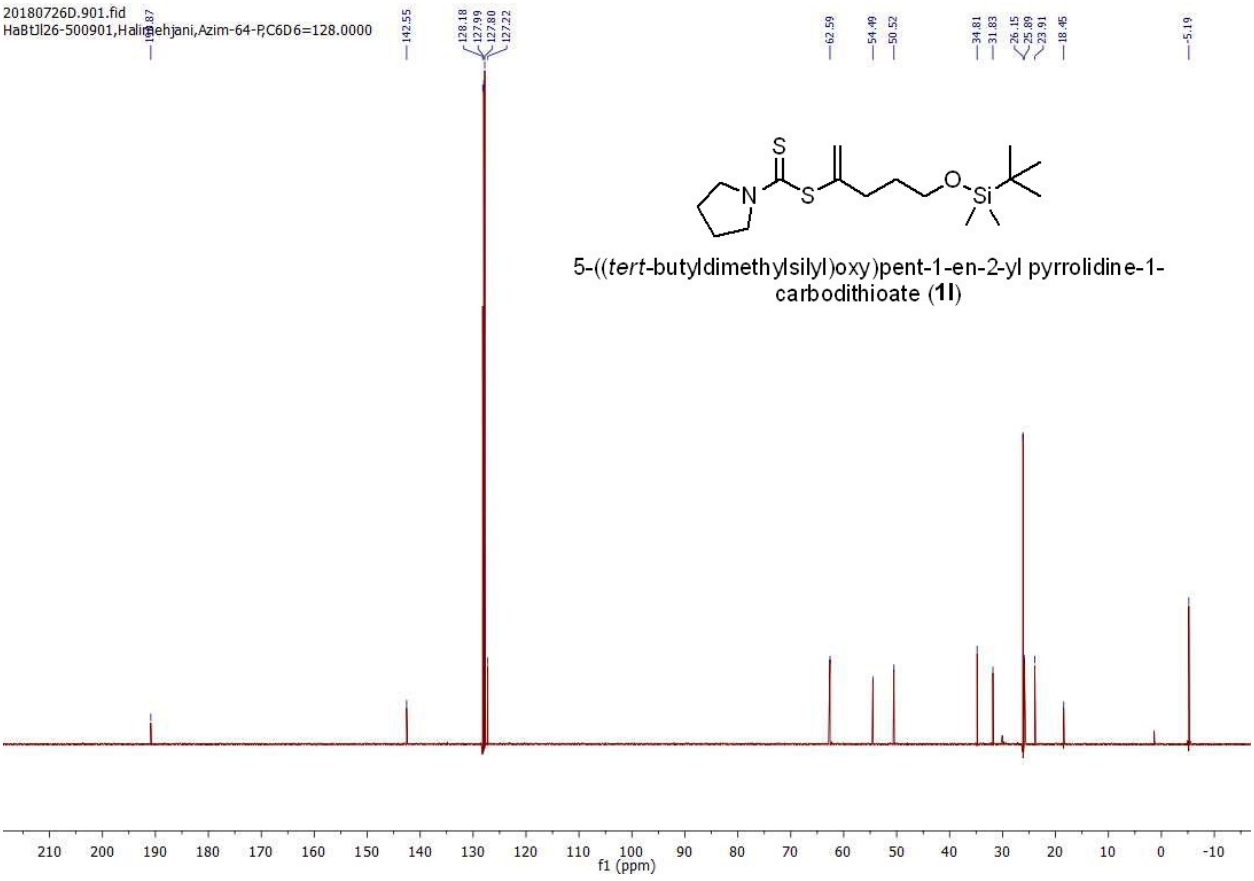
5-hydroxypent-1-en-2-yl pyrrolidine-1-carbodithioate (**1j**)


20180727D.200.fid
HaBtJl27-500200,Halimehjani,Azim-69-P,C6D6=7.15
6-hydroxyhex-1-en-2-yl pyrrolidine-1-carbodithioate (1k)
f1 (ppm)

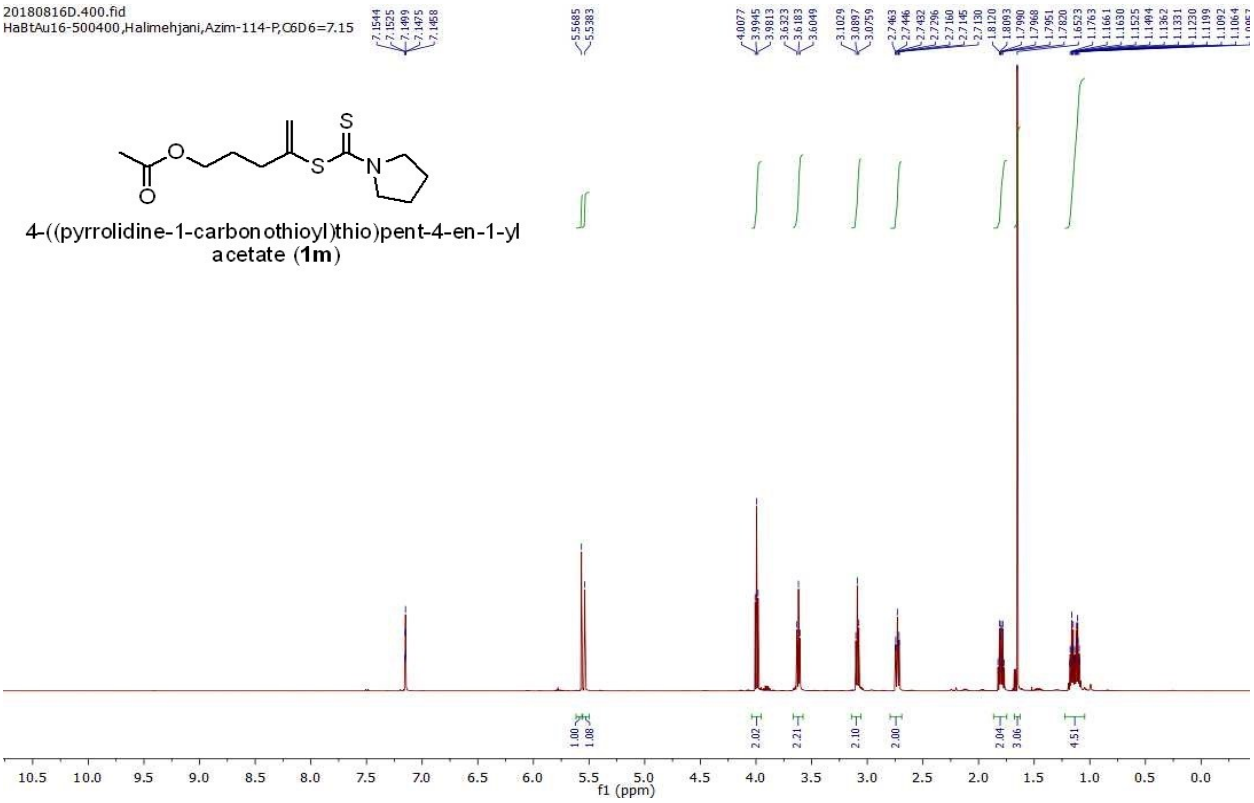

20180727D.201.fid
HaBtJl27-500201,Halimehjani,Azim-69-P,C6D6=77.1000
6-hydroxyhex-1-en-2-yl pyrrolidine-1-carbodithioate (1k)
f1 (ppm)

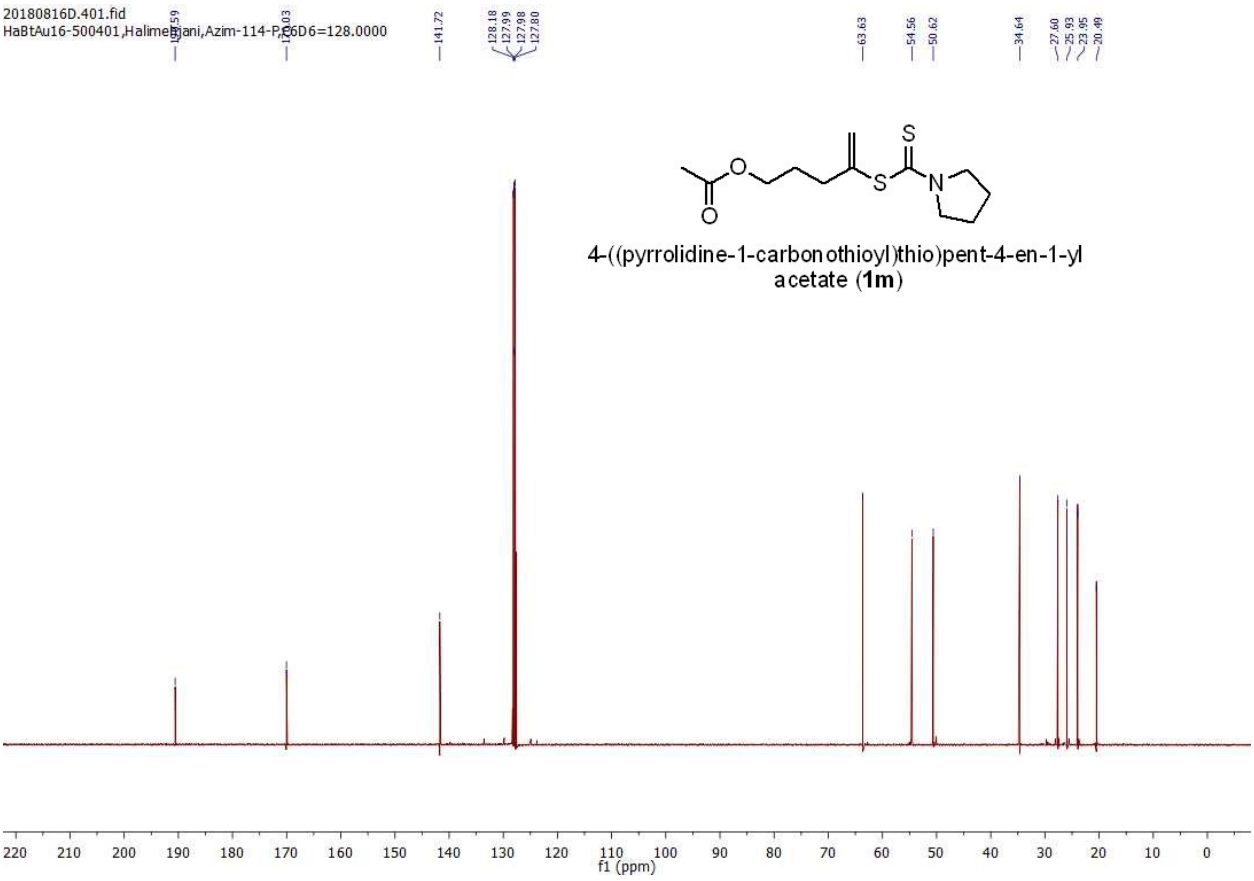


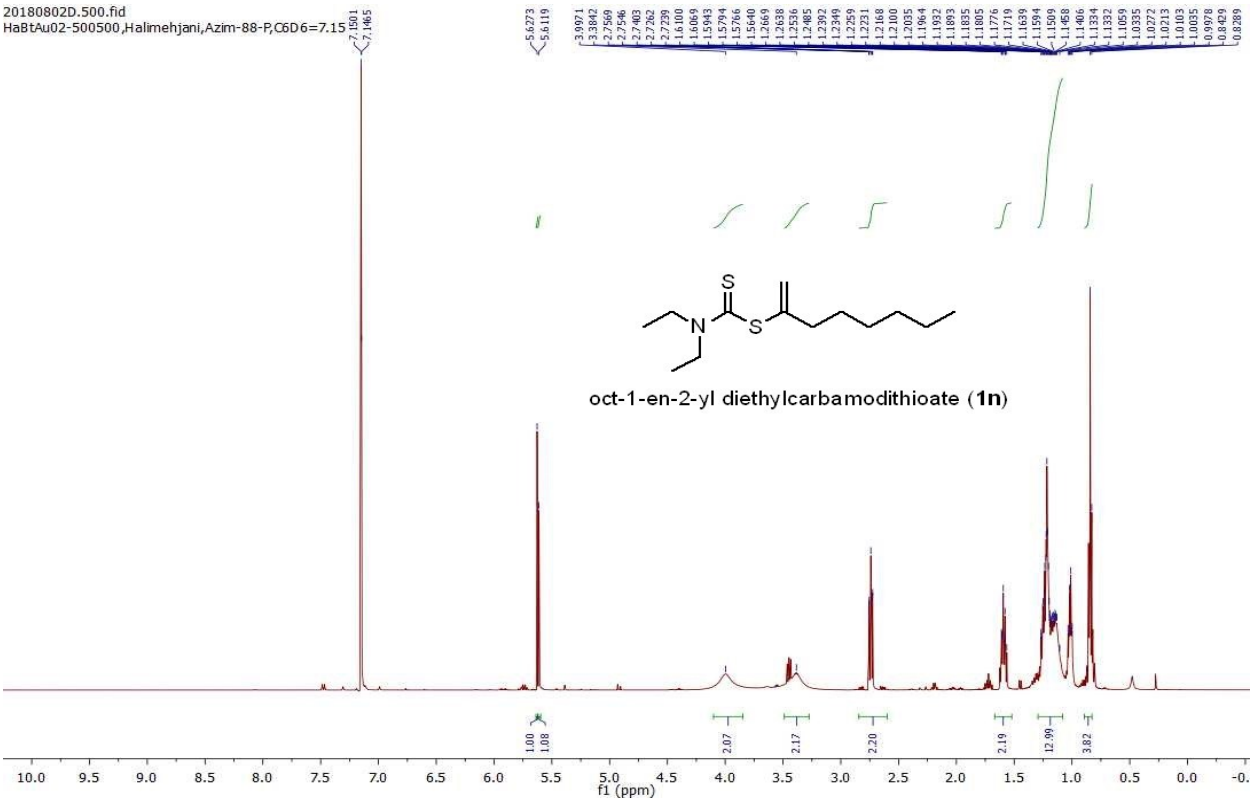
5-((*tert*-butyldimethylsilyl)oxy)pent-1-en-2-yl pyrrolidine-1-carbodithioate (**1l**)

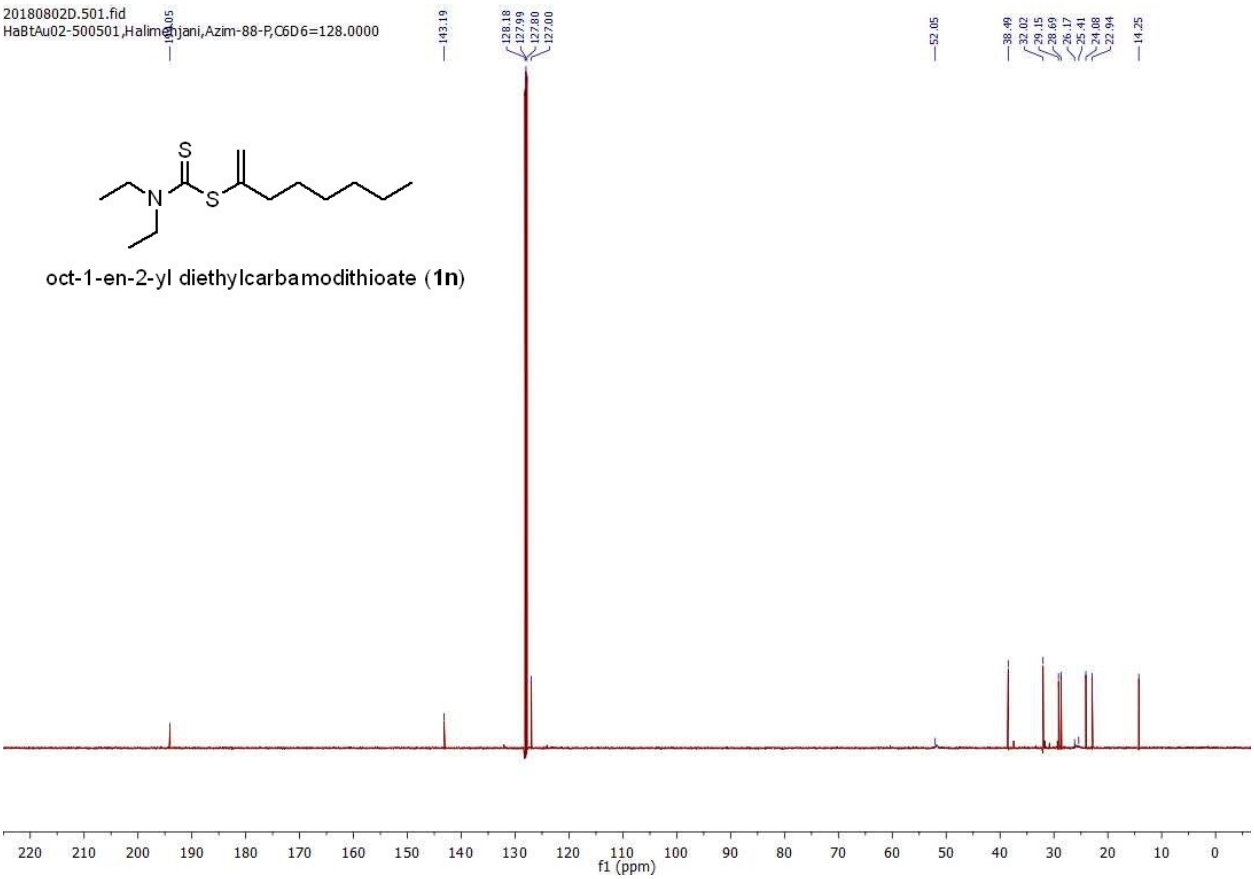


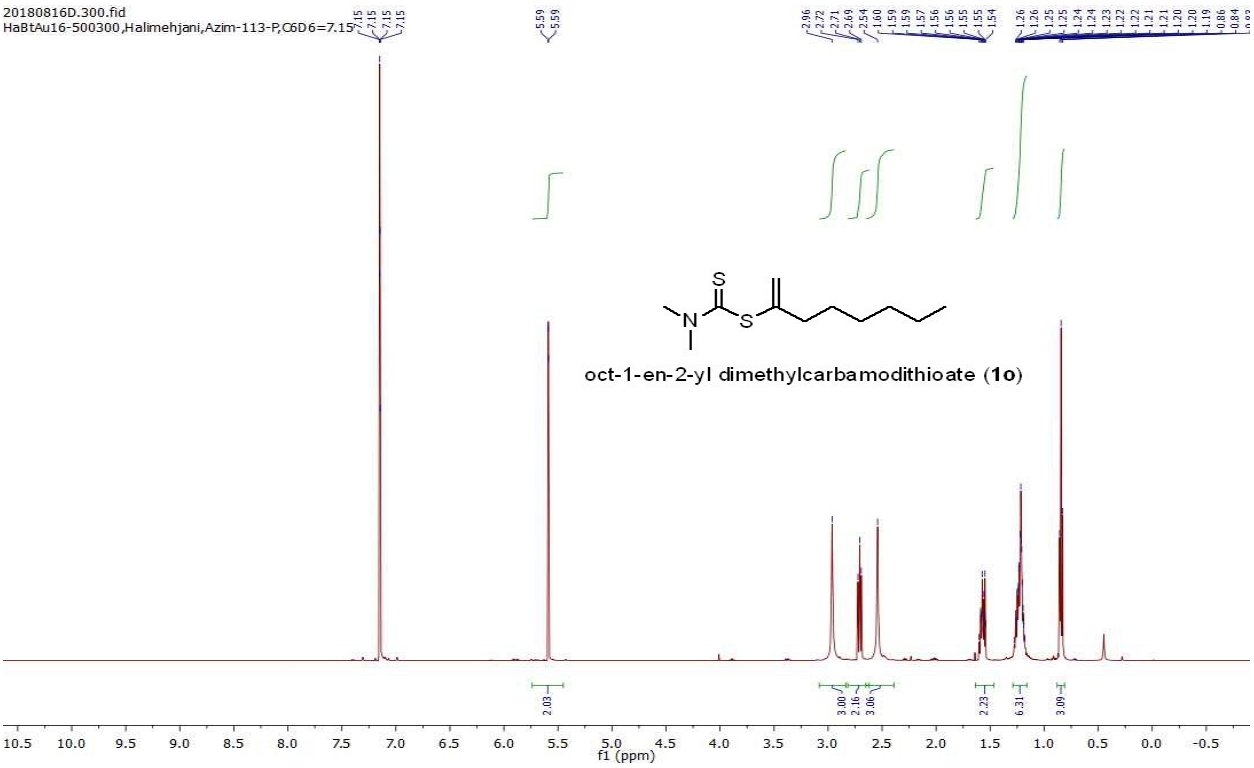
5-((*tert*-butyldimethylsilyl)oxy)pent-1-en-2-yl pyrrolidine-1-carbodithioate (**1l**)

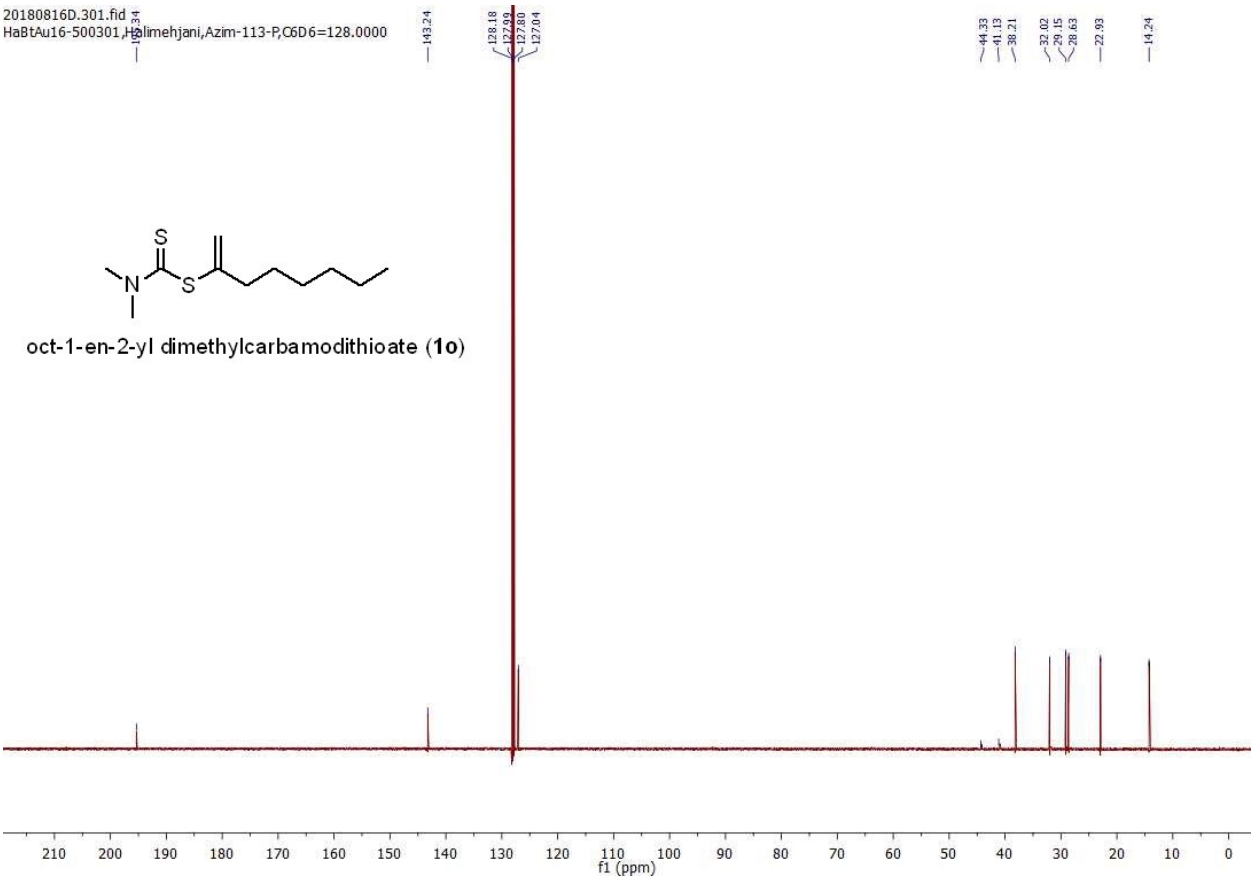

20180816D.400.fid
HaBtAu16-500400,Halimehjani,Azim-114-P,C6D6=7.15
4-((pyrrolidine-1-carbonothioyl)thio)pent-4-en-1-yl acetate (1m)
f1 (ppm)

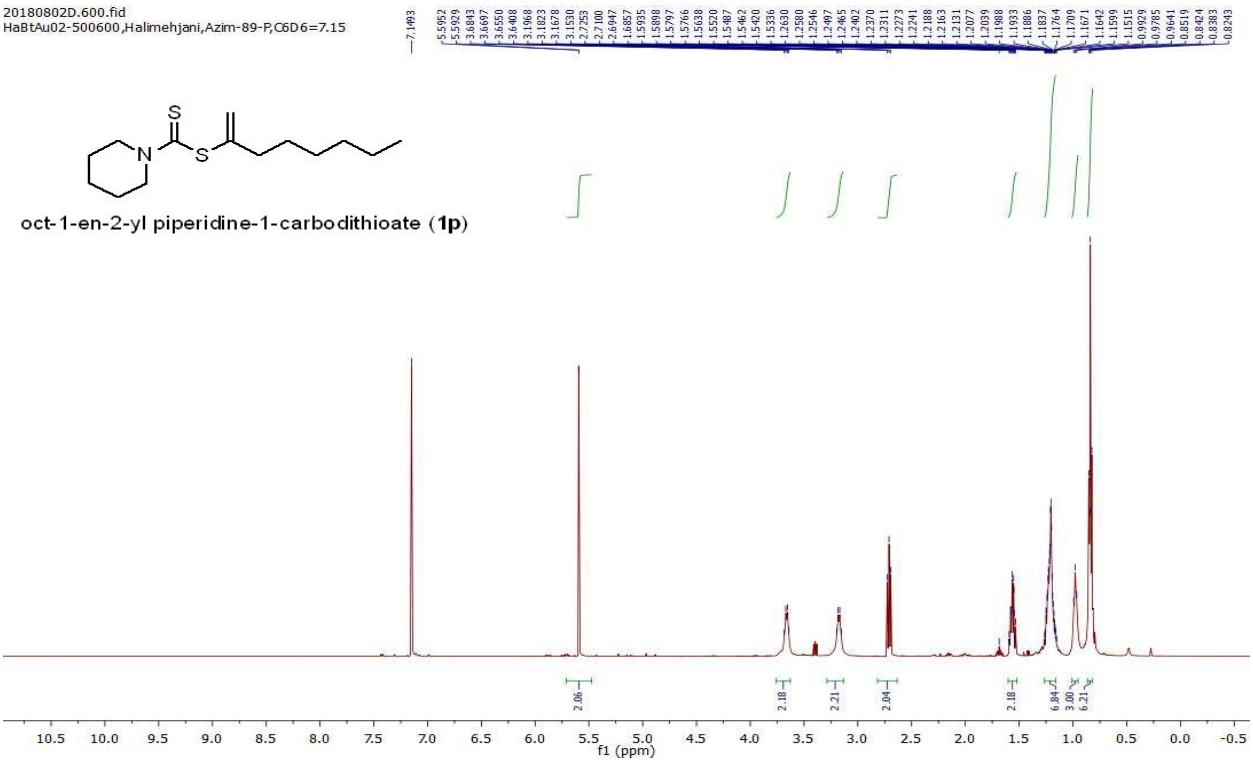

20180816D.401.fid
HaBtAu16-500401,Halimehjani,Azim-114-P,C6D6=128.0000
4-((pyrrolidine-1-carbonothioyl)thio)pent-4-en-1-yl acetate (1m)
f1 (ppm)

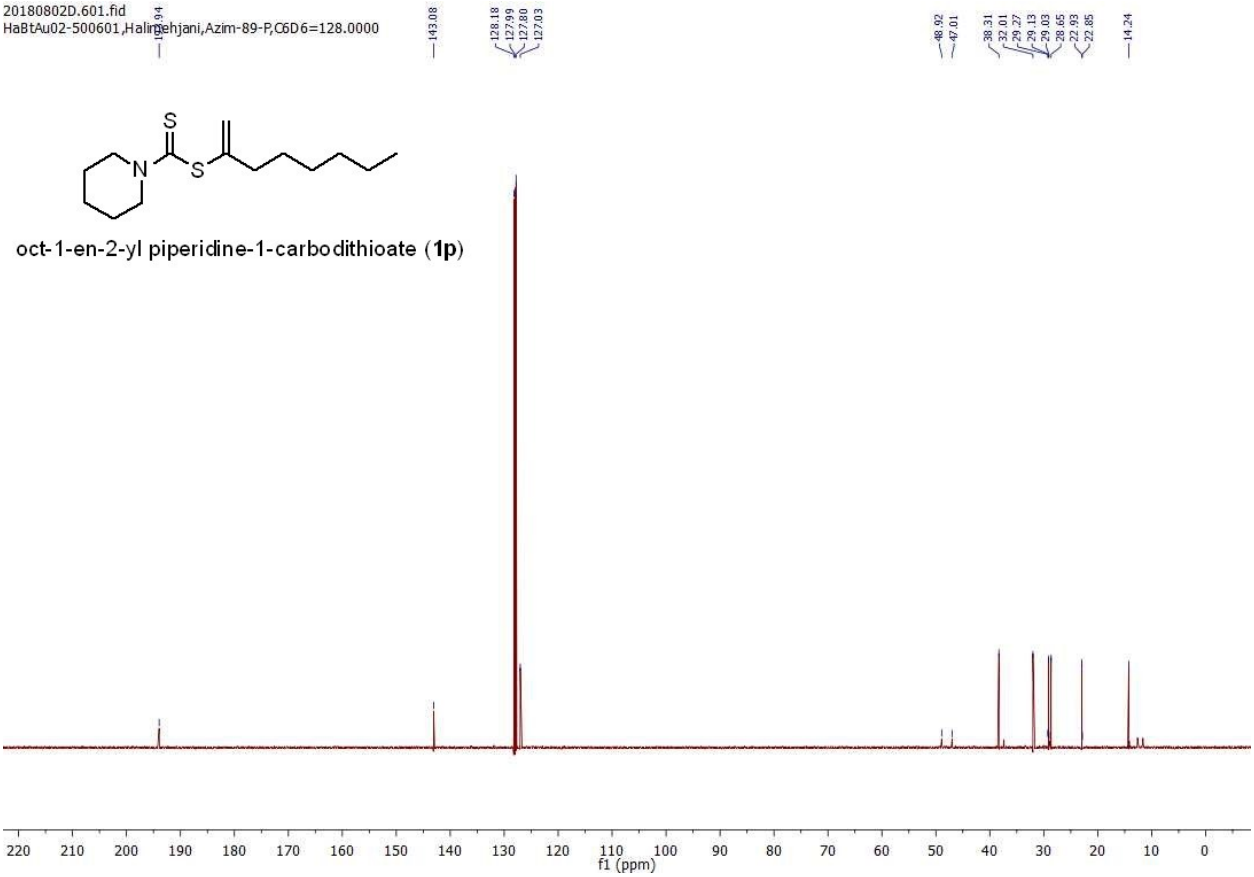

20180802D.500.fid
HaBtAu02-500500,Halimehjani,Azim-88-P,C6D6=7.15
oct-1-en-2-yl diethylcarbamodithioate (1n)
f1 (ppm)

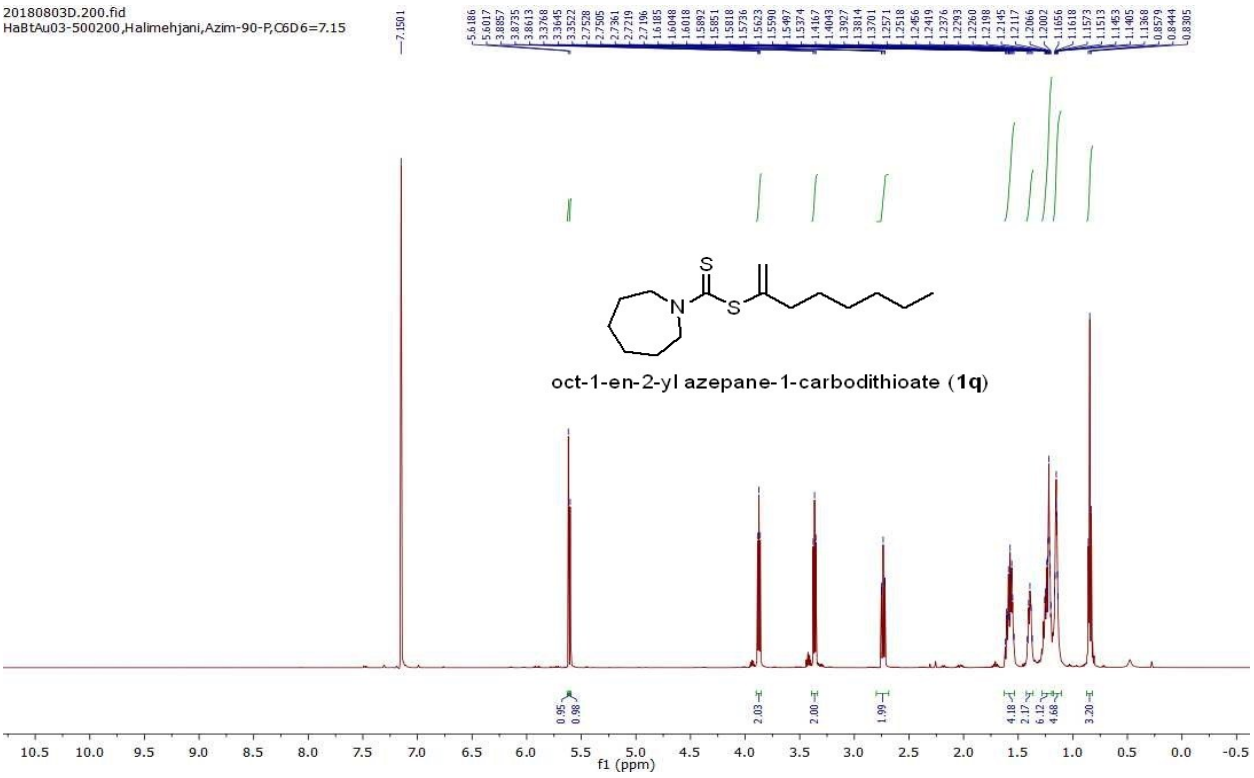

20180802D.501.fid
HaBtAu02-500501,Halimehjani,Azim-88-P,C6D6=128.0000
oct-1-en-2-yl diethylcarbamodithioate (1n)
f1 (ppm)

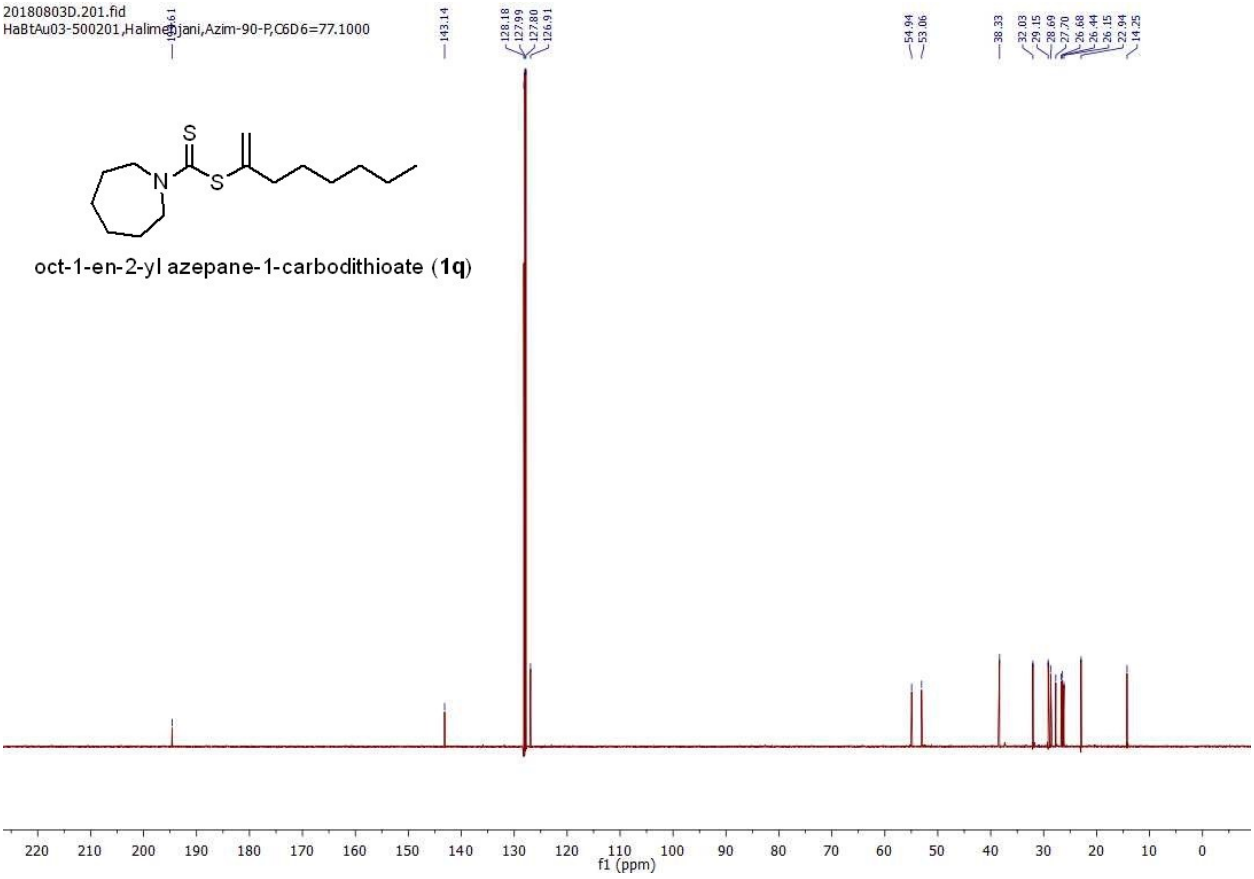

20180816D.300.fid
HaBtAu16-500300,Halimehjani,Azim-113-P,C6D6=7.15
oct-1-en-2-yl dimethylcarbamodithioate (1o)
f1 (ppm)

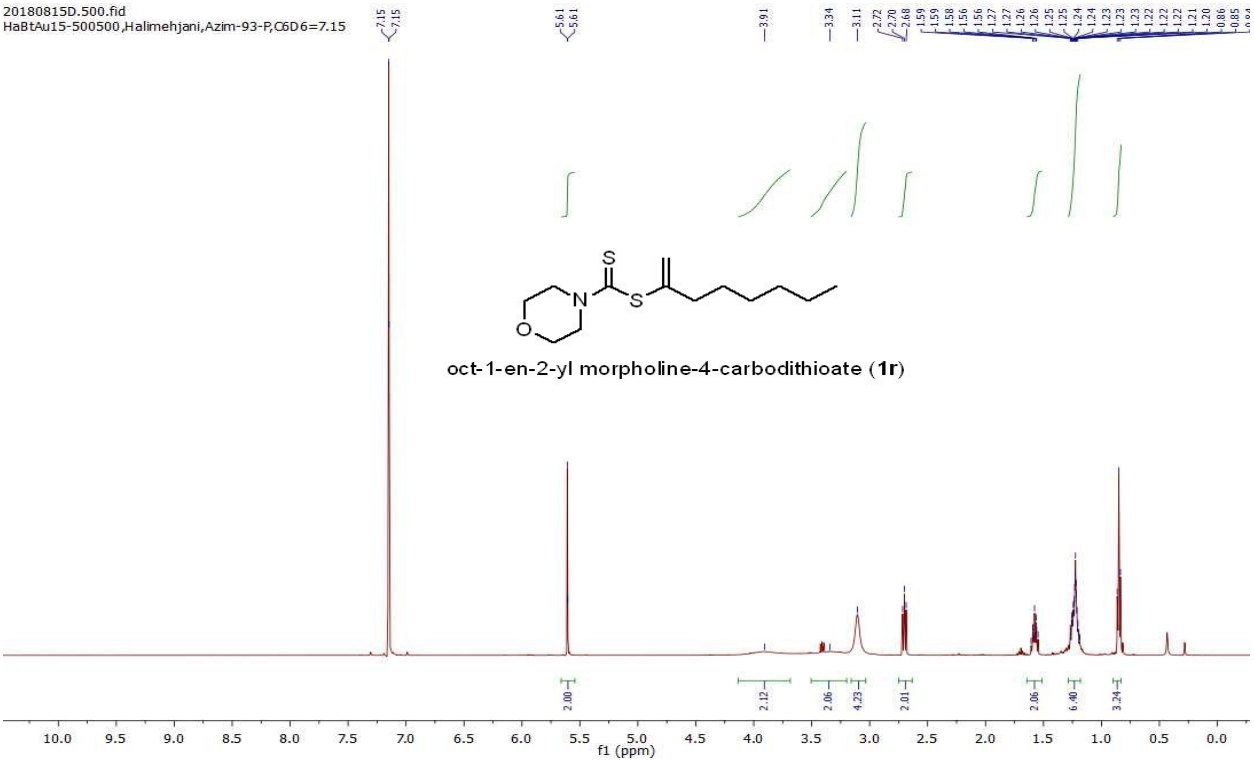

20180816D.301.fid
HaBtAu16-500301,Halimehjani,Azim-113-P,C6D6=128.0000
oct-1-en-2-yl dimethylcarbamodithioate (1o)
f1 (ppm)


20180802D.600.fid
HaBtAu02-500600,Halimehjani,Azim-89-P,C6D6=7.15
oct-1-en-2-yl piperidine-1-carbodithioate (1p)
f1 (ppm)

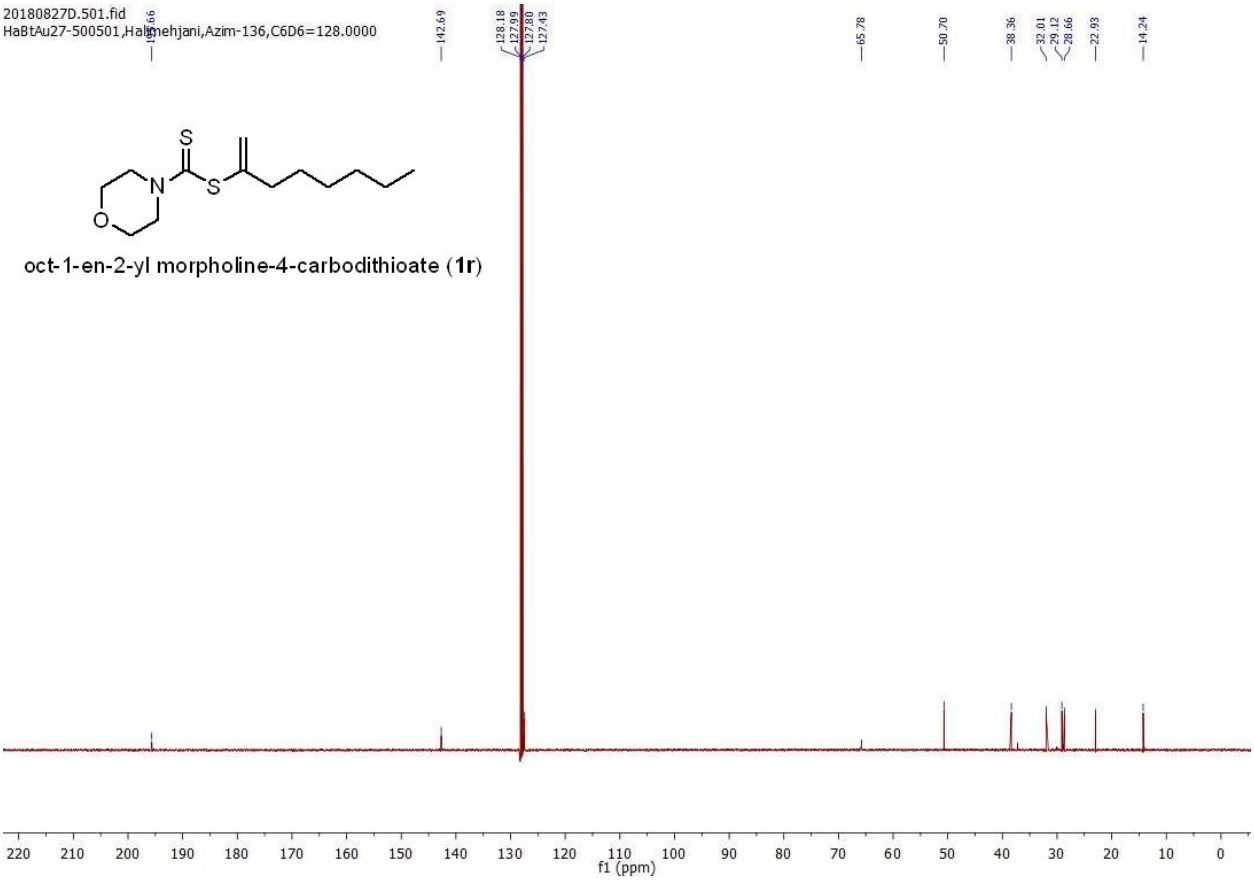

20180802D.601.fid
HaBtAu02-500601,Halimehjani,Azim-89-P,C6D6=128.0000
oct-1-en-2-yl piperidine-1-carbodithioate (1p)
f1 (ppm)


20180803D.200.fid
HaBtAu03-500200,Halimehjani,Azim-90-P,C6D6=7.15
oct-1-en-2-yl azepane-1-carbodithioate (1q)
f1 (ppm)

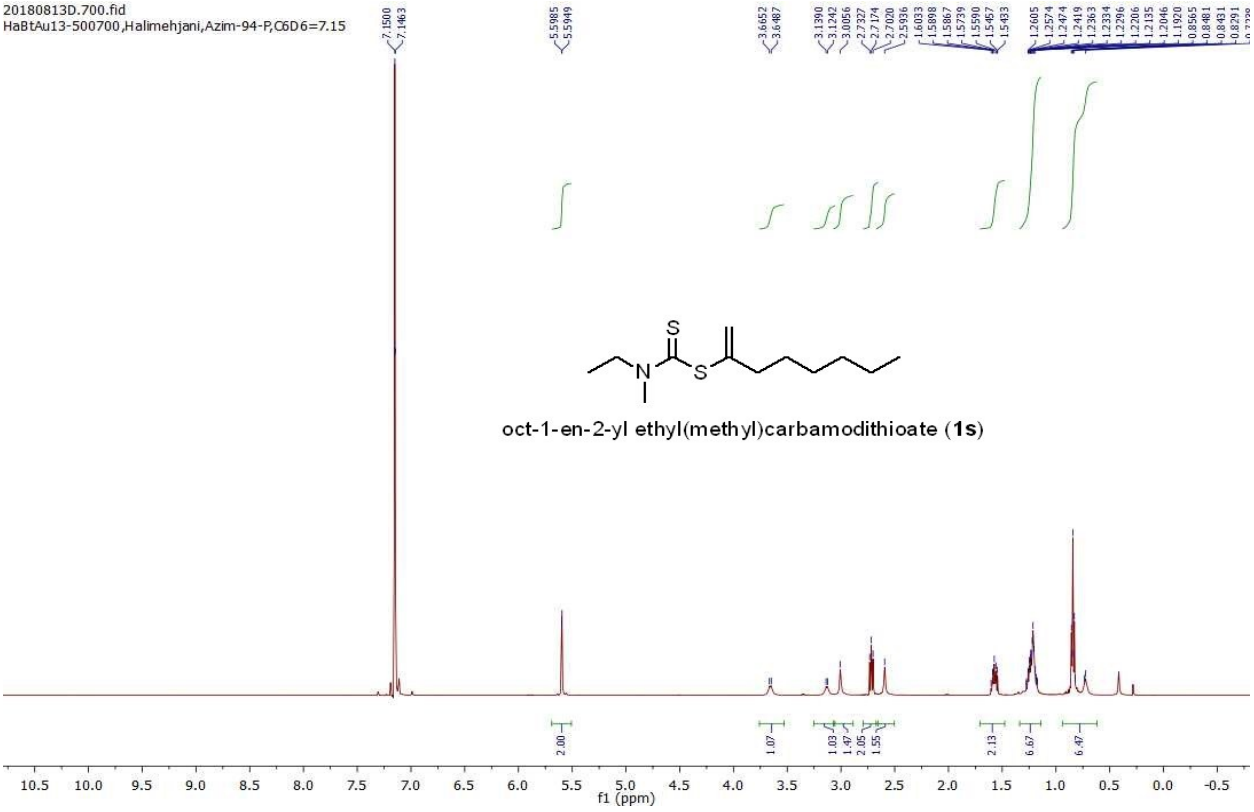

20180803D.201.fid
HaBtAu03-500201,Halimehjani,Azim-90-P,C6D6=77.1000
oct-1-en-2-yl azepane-1-carbodithioate (1q)
f1 (ppm)

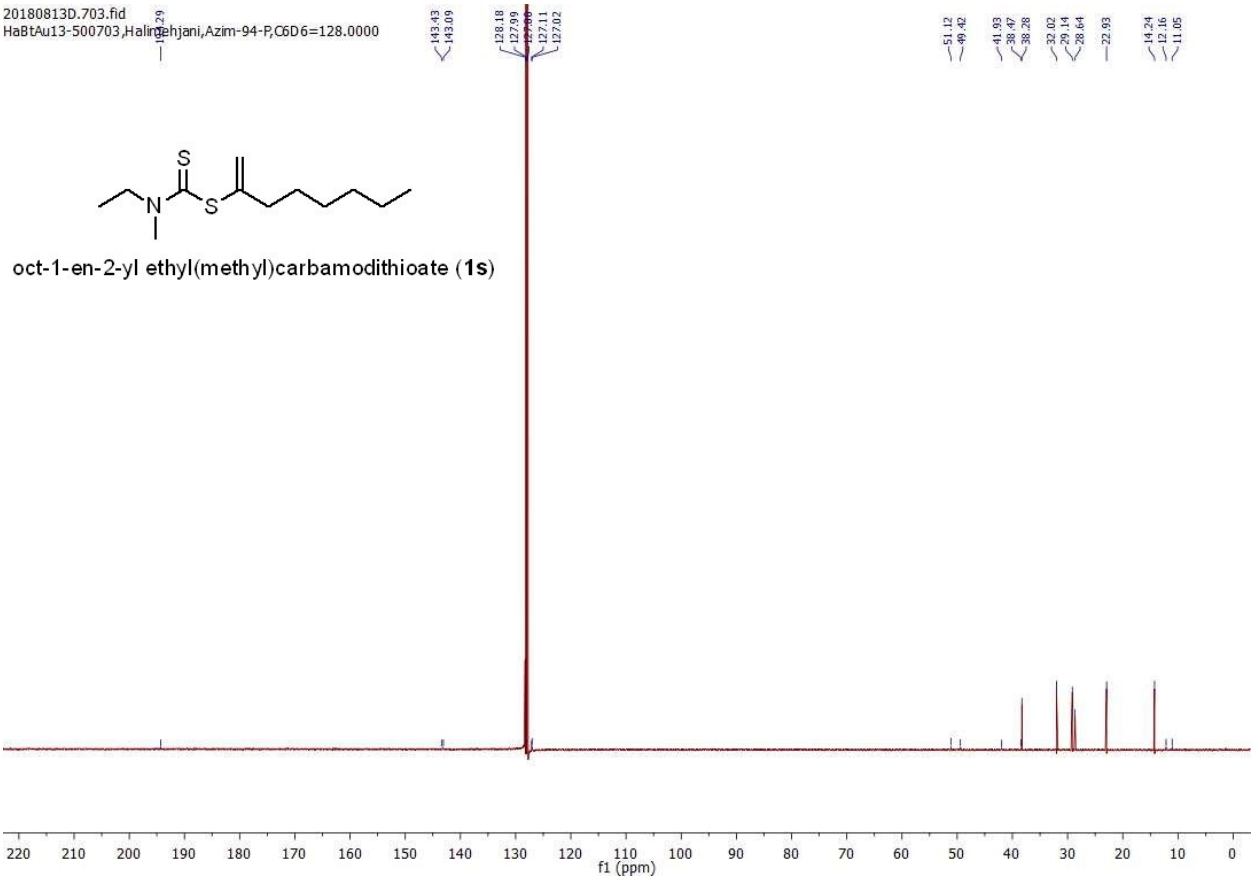


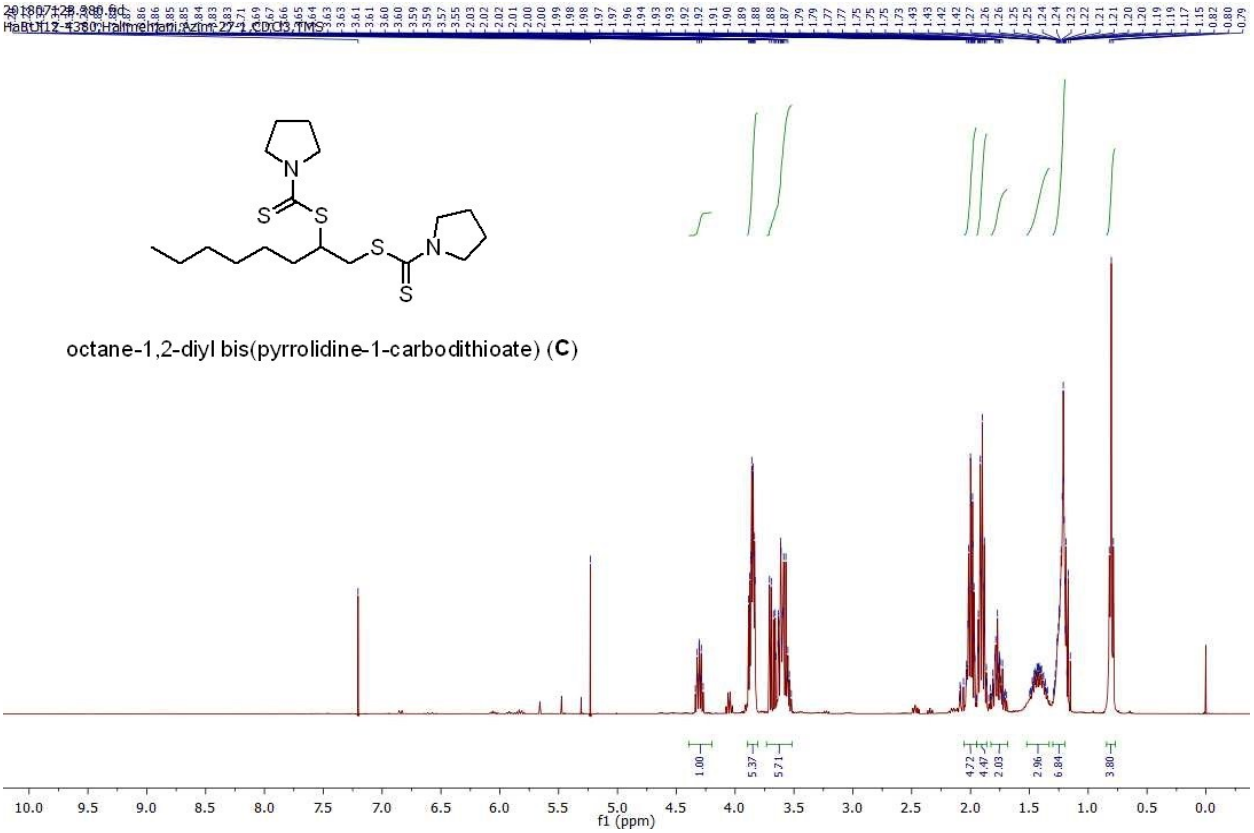
oct-1-en-2-yl morpholine-4-carbodithioate (**1r**)

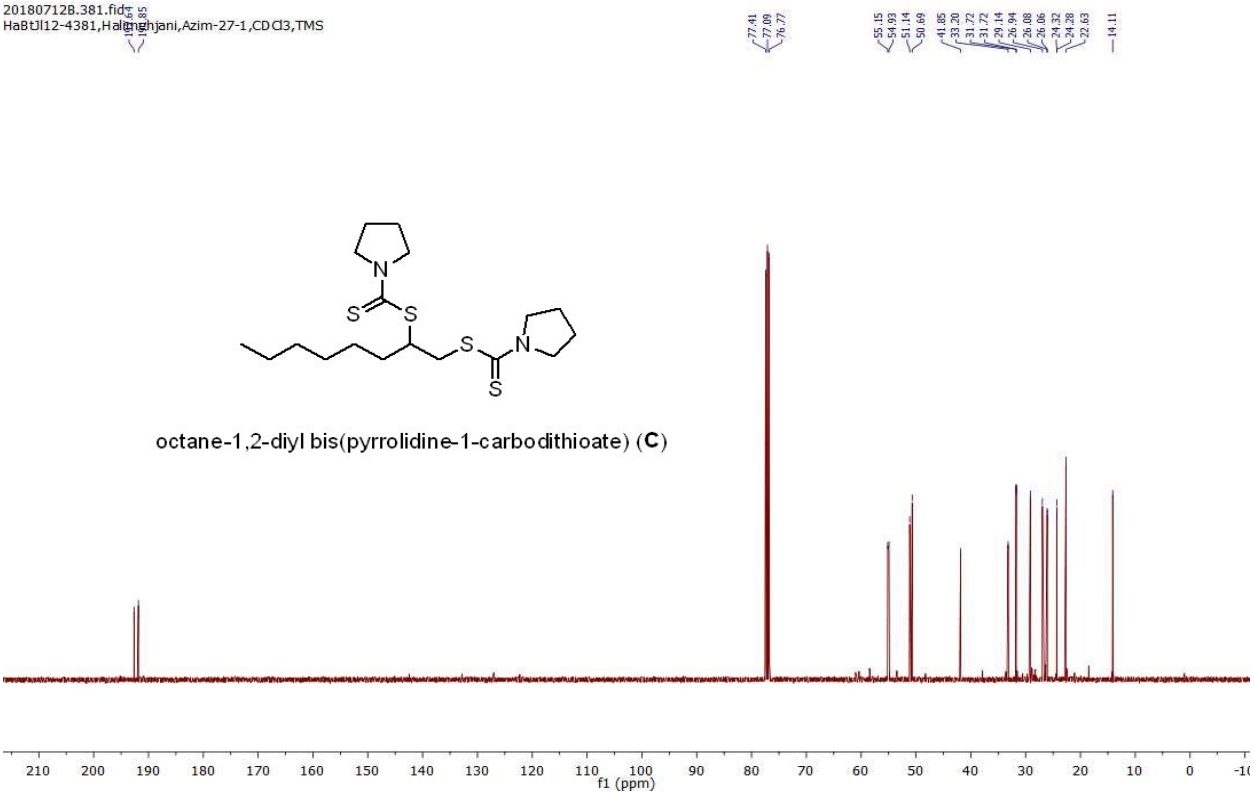


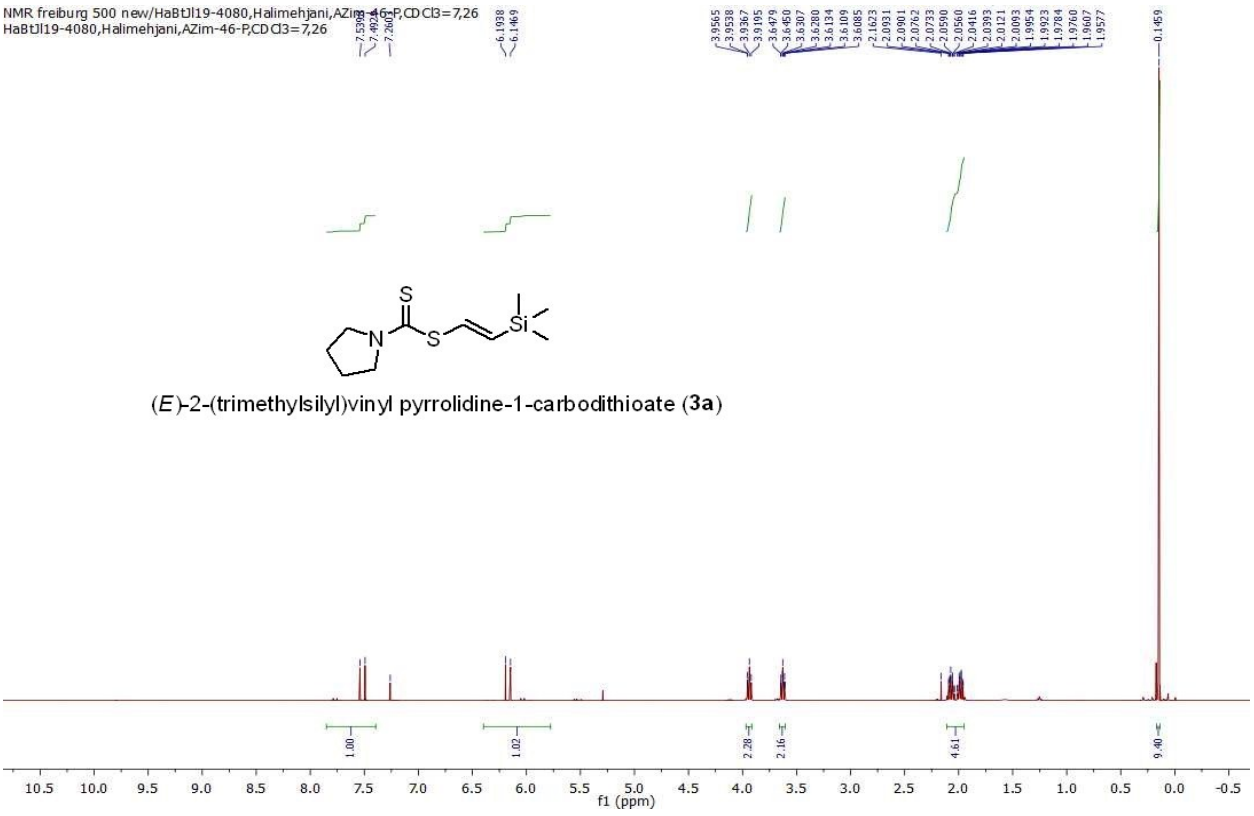
oct-1-en-2-yl morpholine-4-carbodithioate (**1r**)


20180813D.700.fid
HaBtAu13-500700,Halimehjani,Azim-94-P,C6D6=7.15
oct-1-en-2-yl ethyl(methyl)carbamodithioate (1s)
f1 (ppm)

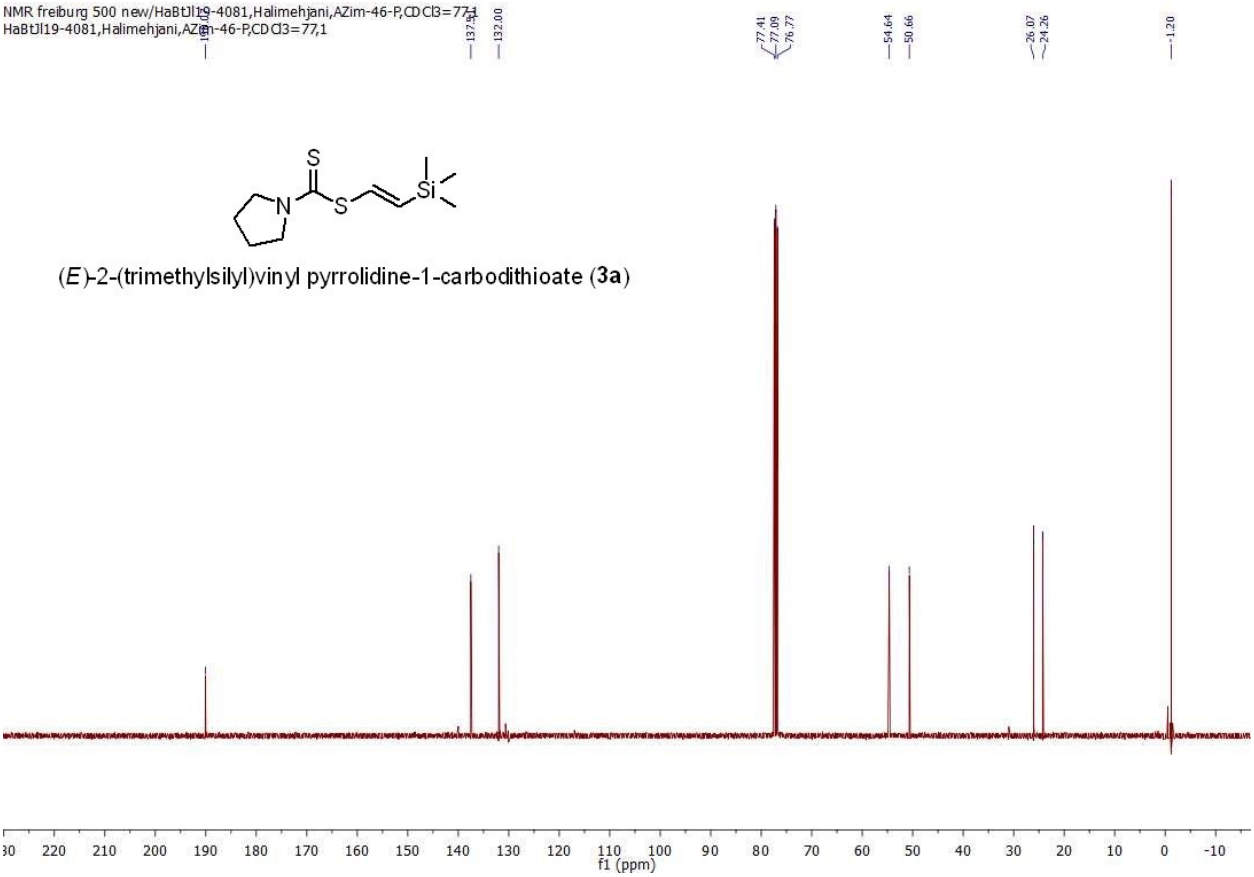

20180813D.703.fid
HaBtAu13-500703,Halimehjani,Azim-94-P,C6D6=128.0000
oct-1-en-2-yl ethyl(methyl)carbamodithioate (1s)
f1 (ppm)


20180712B.380.fid
HaBtJl12-4380,Hallmehjani,Azim-27-1,CDCl3,TMS
octane-1,2-diyl bis(pyrrolidine-1-carbodithioate) (C)
1.00
5.37
5.71
4.72
4.47
2.03
2.96
6.84
3.80
f1 (ppm)

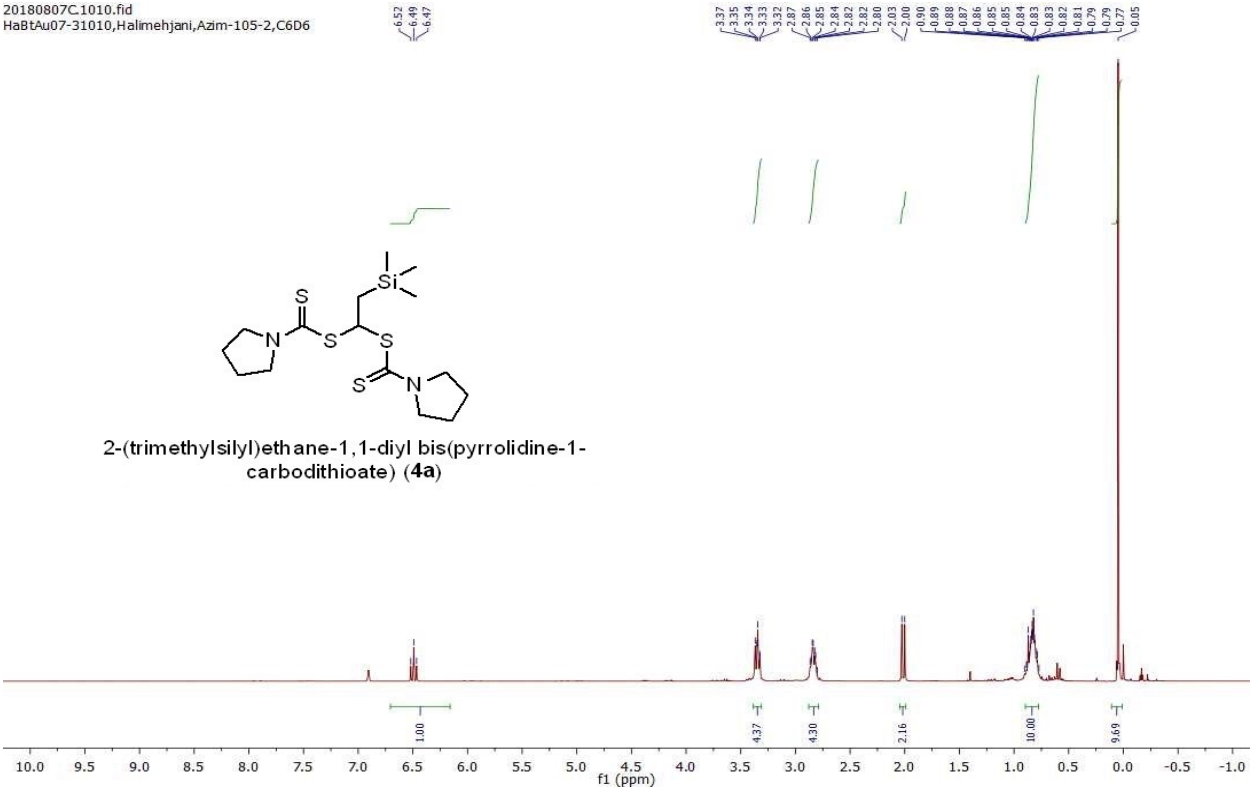

20180712B.381.fid
HaBtJl12-4381,Hallmehjani,Azim-27-1,CDCl3,TMS
77.41
77.09
76.77
55.15
54.93
51.14
50.69
41.85
33.20
31.72
31.72
29.14
26.94
26.08
26.06
24.32
24.28
22.63
14.11
octane-1,2-diyl bis(pyrrolidine-1-carbodithioate) (C)
f1 (ppm)



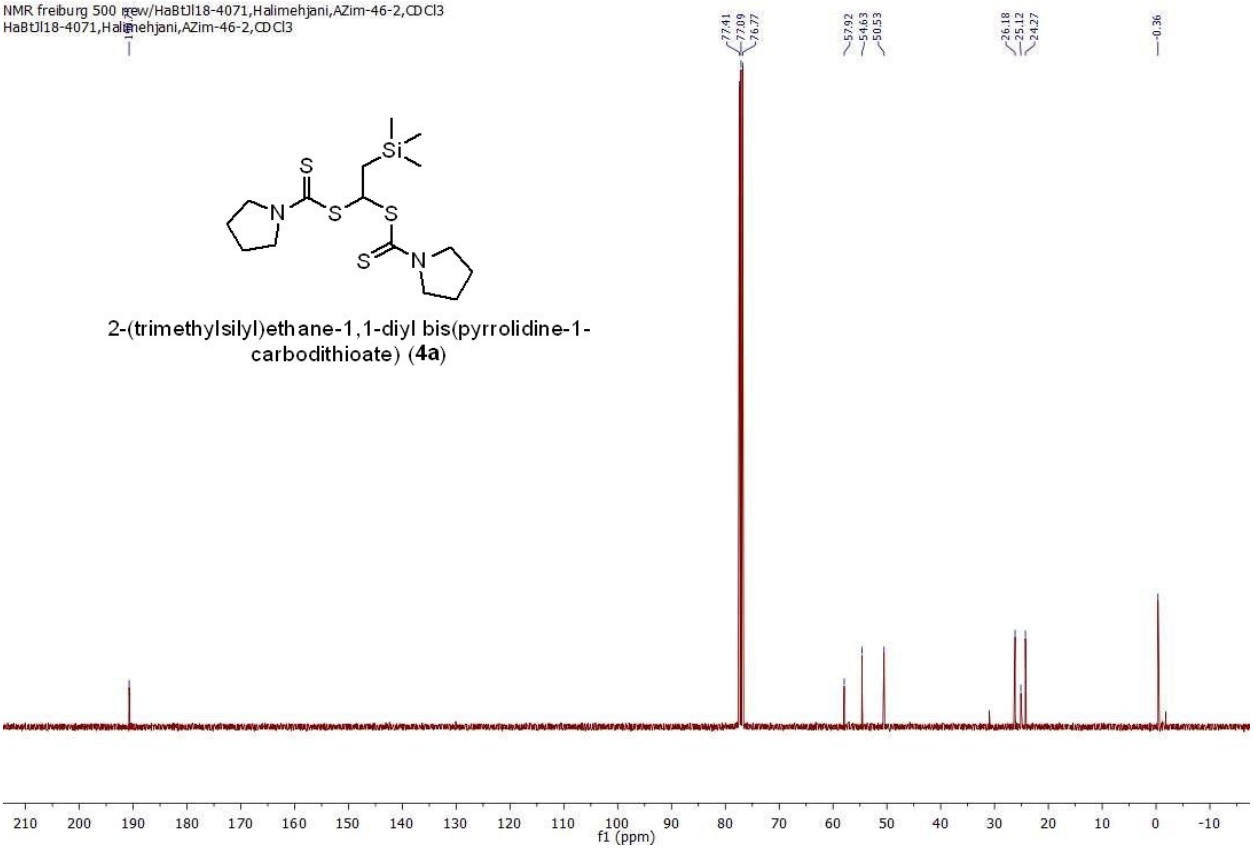
(*E*)-2-(trimethylsilyl)vinyl pyrrolidine-1-carbodithioate (**3a**)



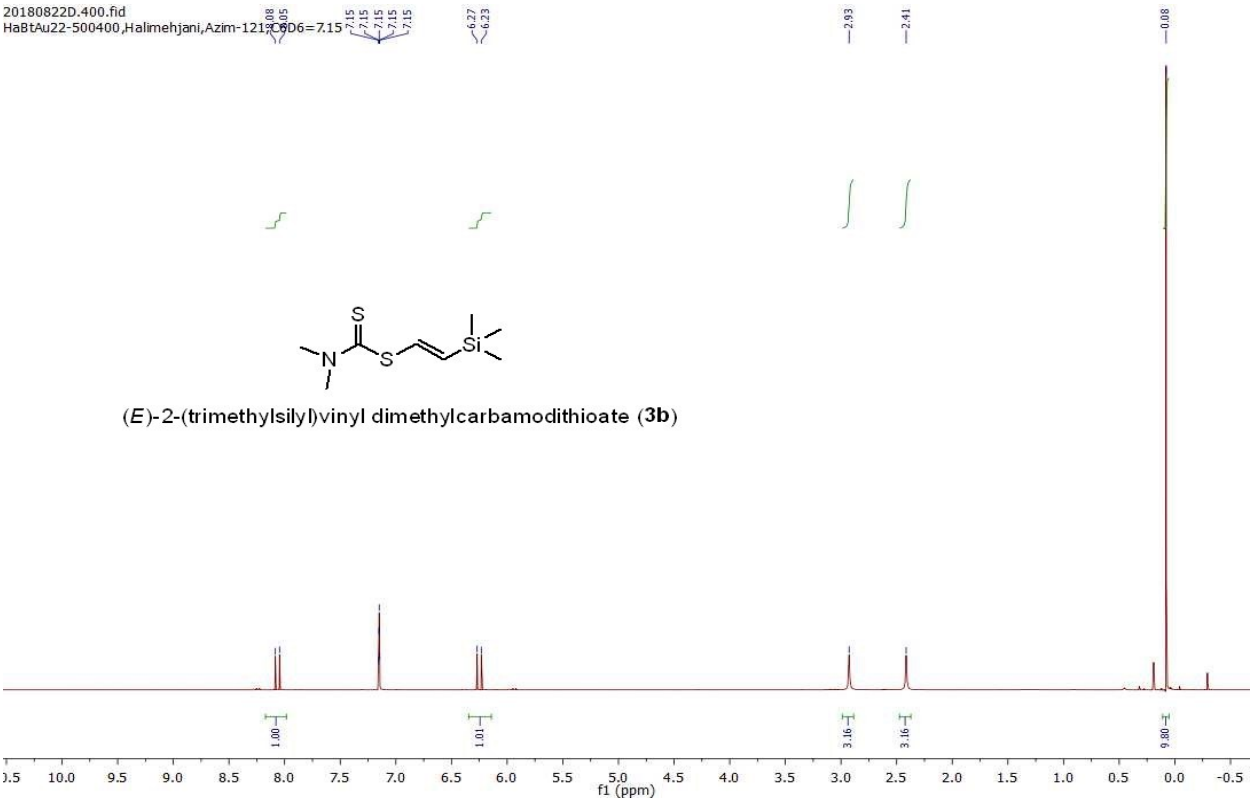
(*E*)-2-(trimethylsilyl)vinyl pyrrolidine-1-carbodithioate (**3a**)



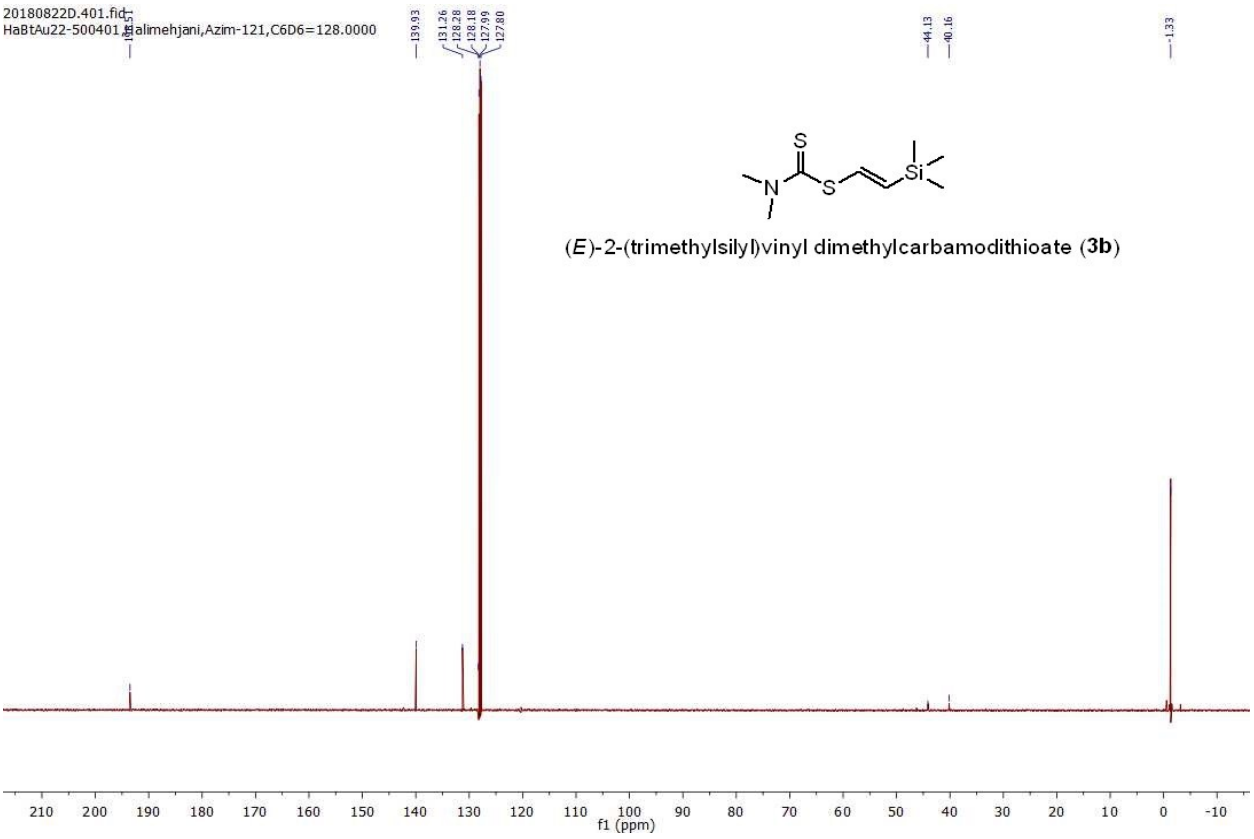
2-(trimethylsilyl)ethane-1,1-diyl bis(pyrrolidine-1-carbodithioate) (**4a**)



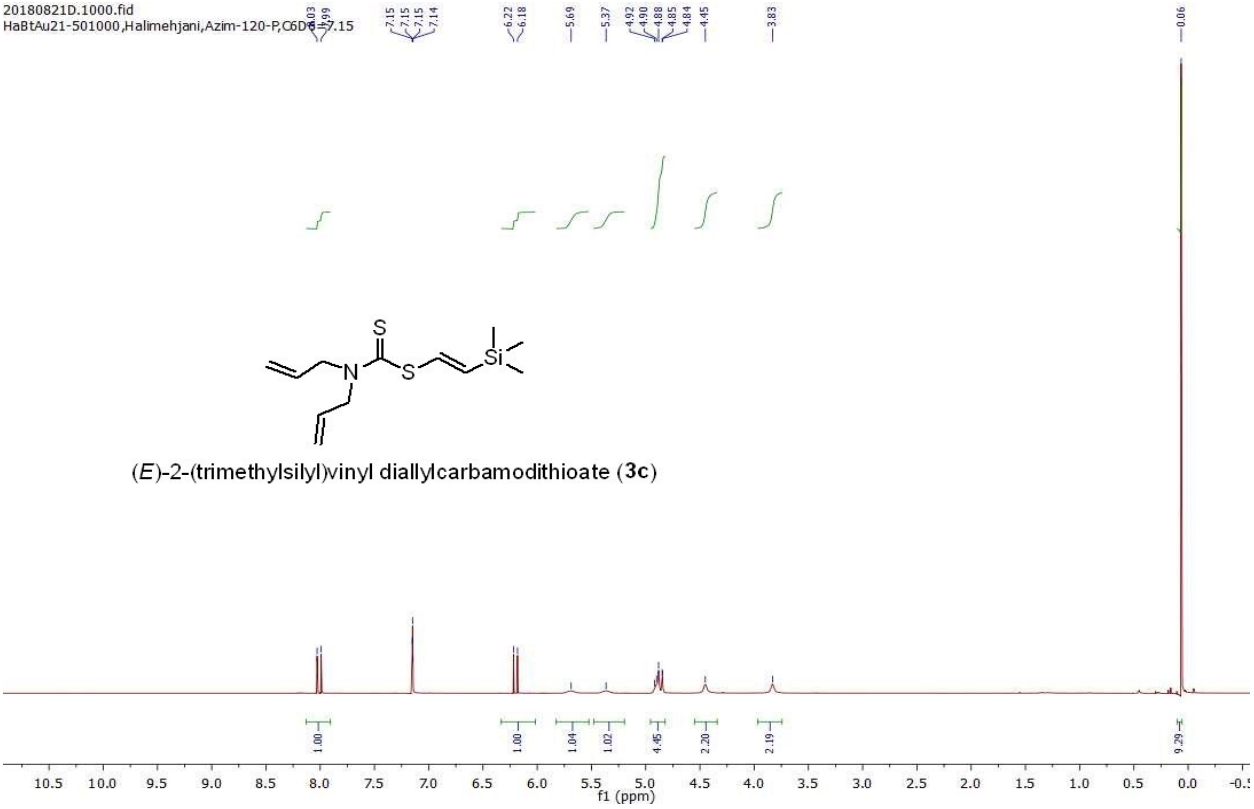
2-(trimethylsilyl)ethane-1,1-diyl bis(pyrrolidine-1-carbodithioate) (**4a**)



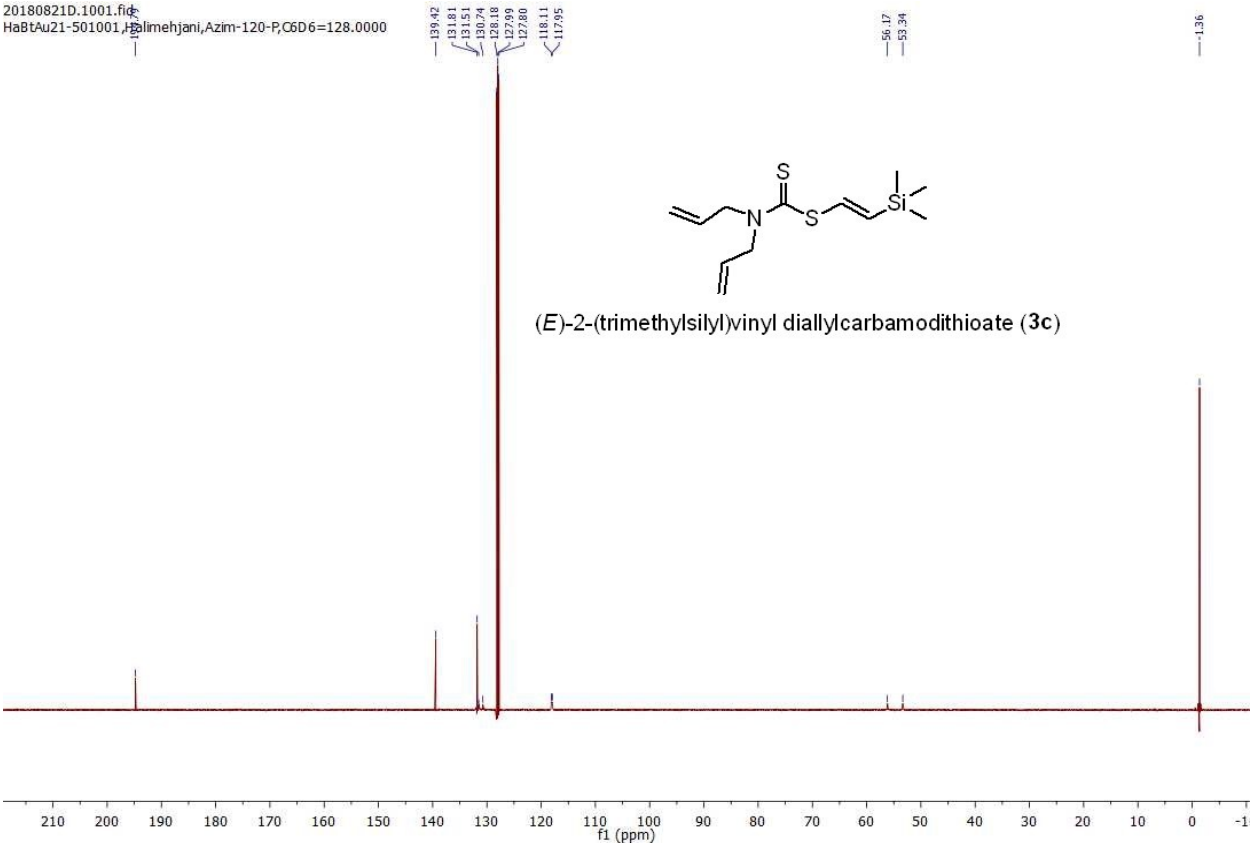
(*E*)-2-(trimethylsilyl)vinyl dimethylcarbamodithioate (**3b**)



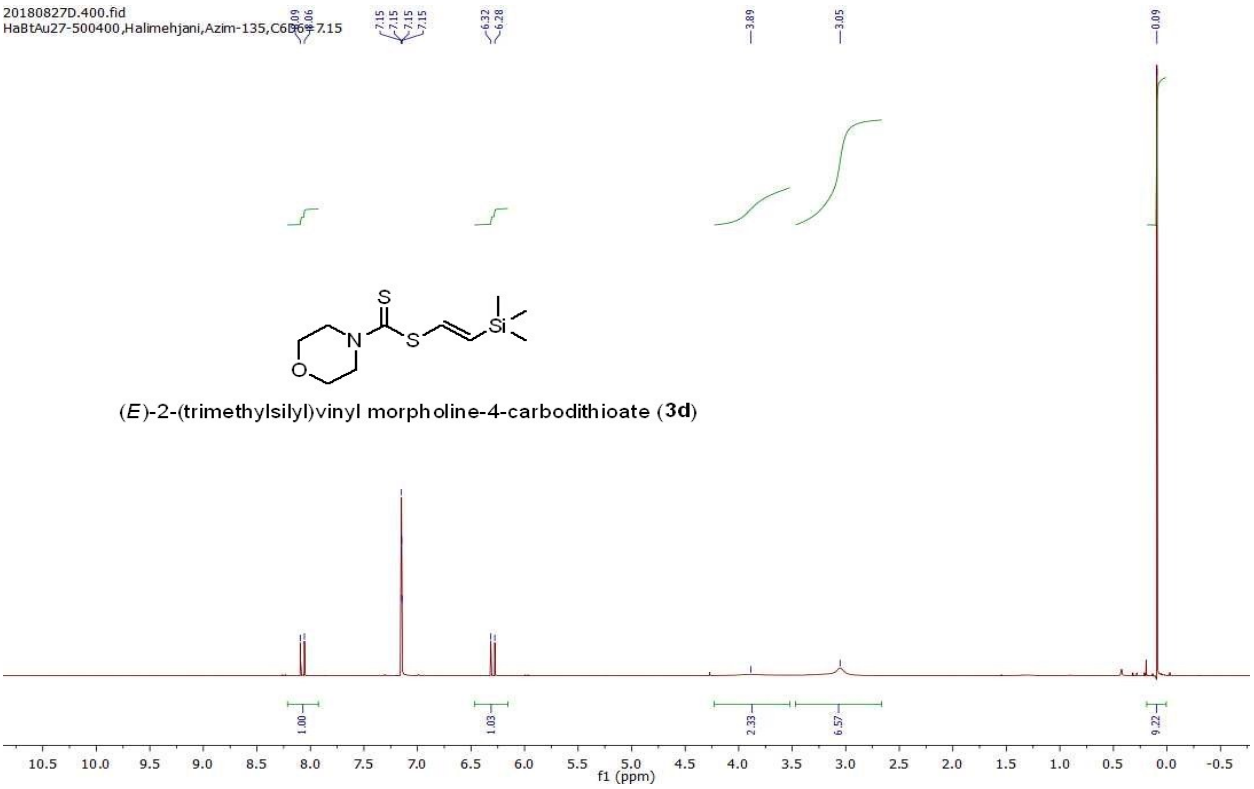
(*E*)-2-(trimethylsilyl)vinyl dimethylcarbamodithioate (**3b**)



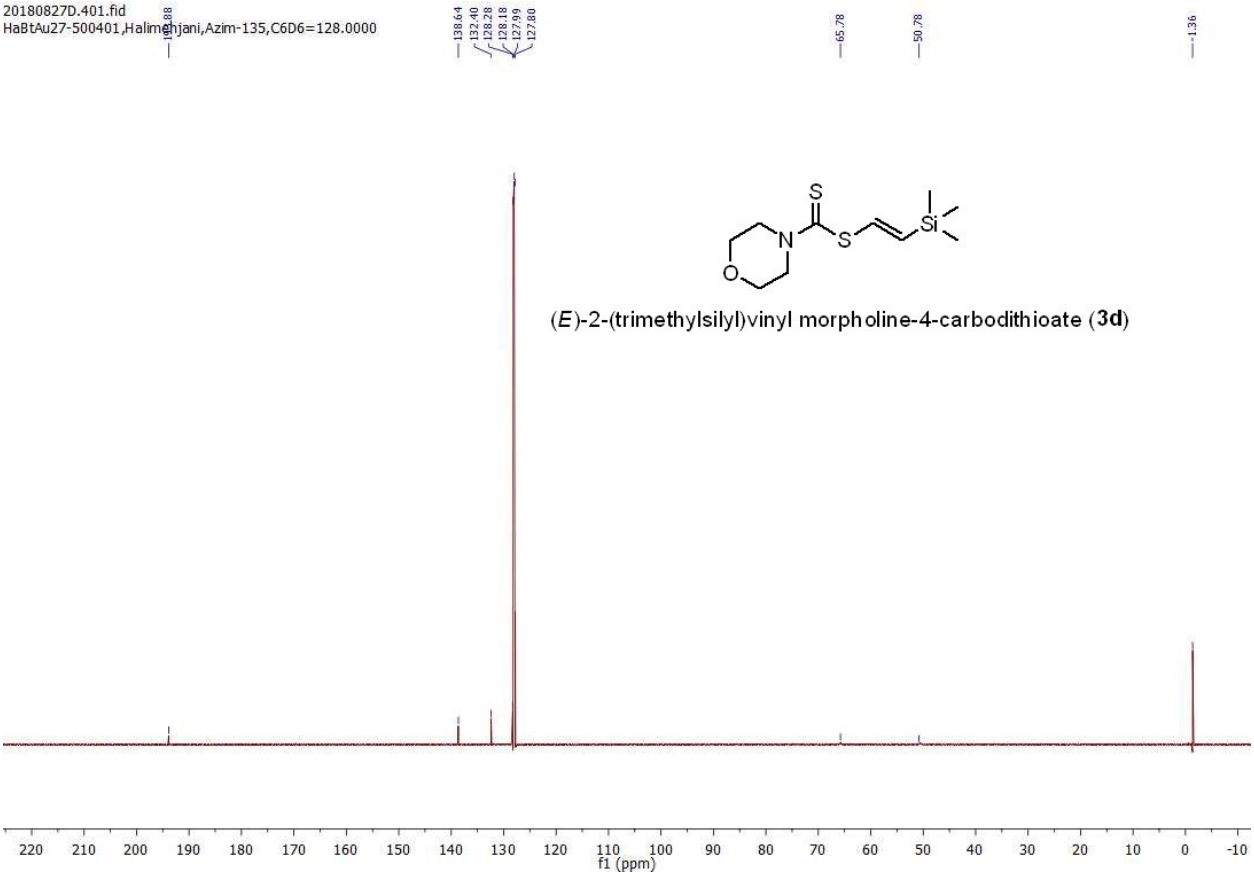
(*E*)-2-(trimethylsilyl)vinyl diallylcarbamodithioate (**3c**)



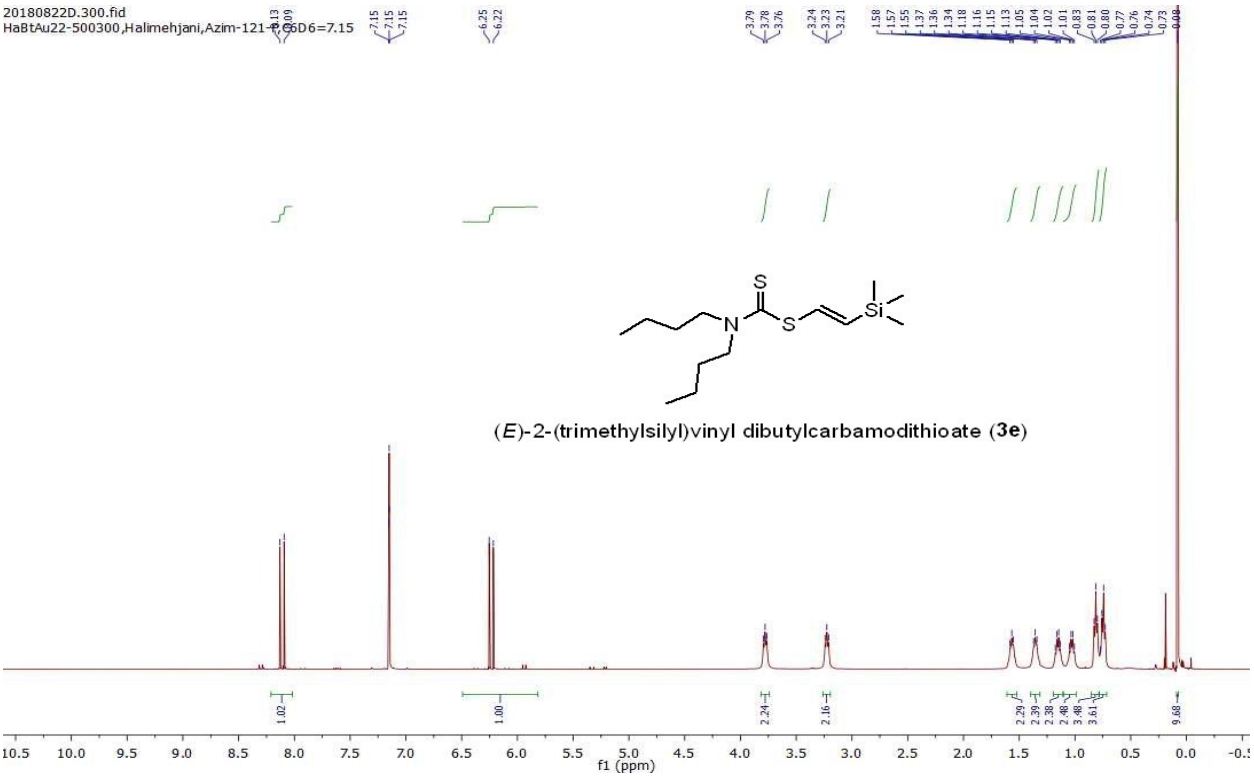
(*E*)-2-(trimethylsilyl)vinyl diallylcarbamodithioate (**3c**)



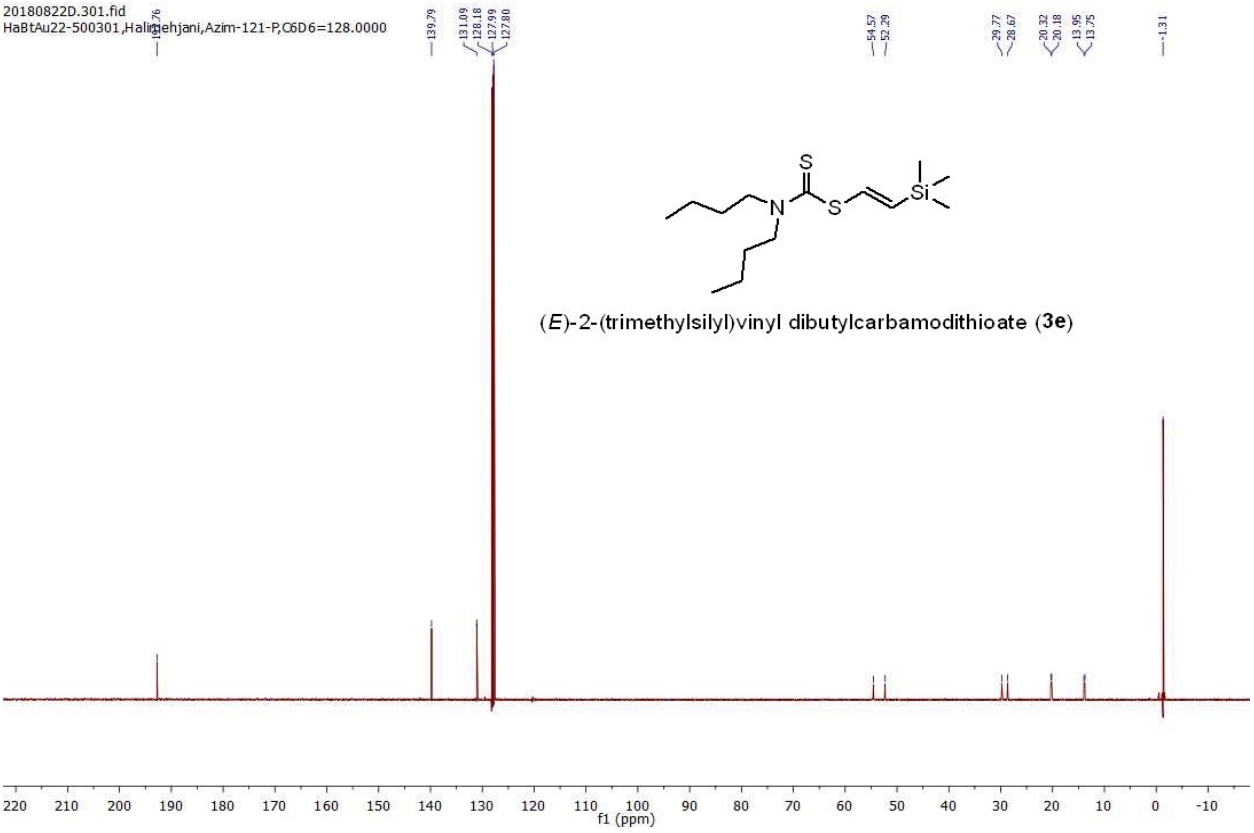
(*E*)-2-(trimethylsilyl)vinyl morpholine-4-carbodithioate (**3d**)



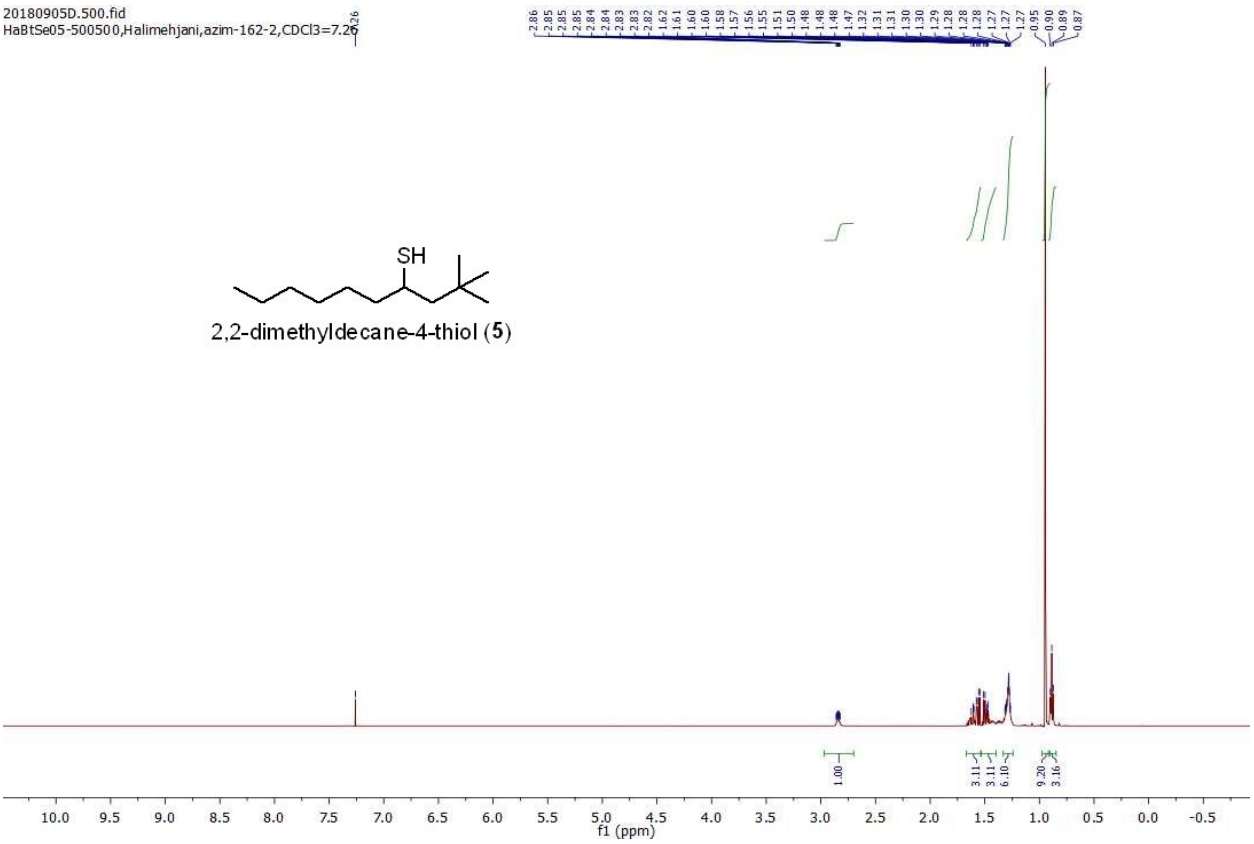
(*E*)-2-(trimethylsilyl)vinyl morpholine-4-carbodithioate (**3d**)

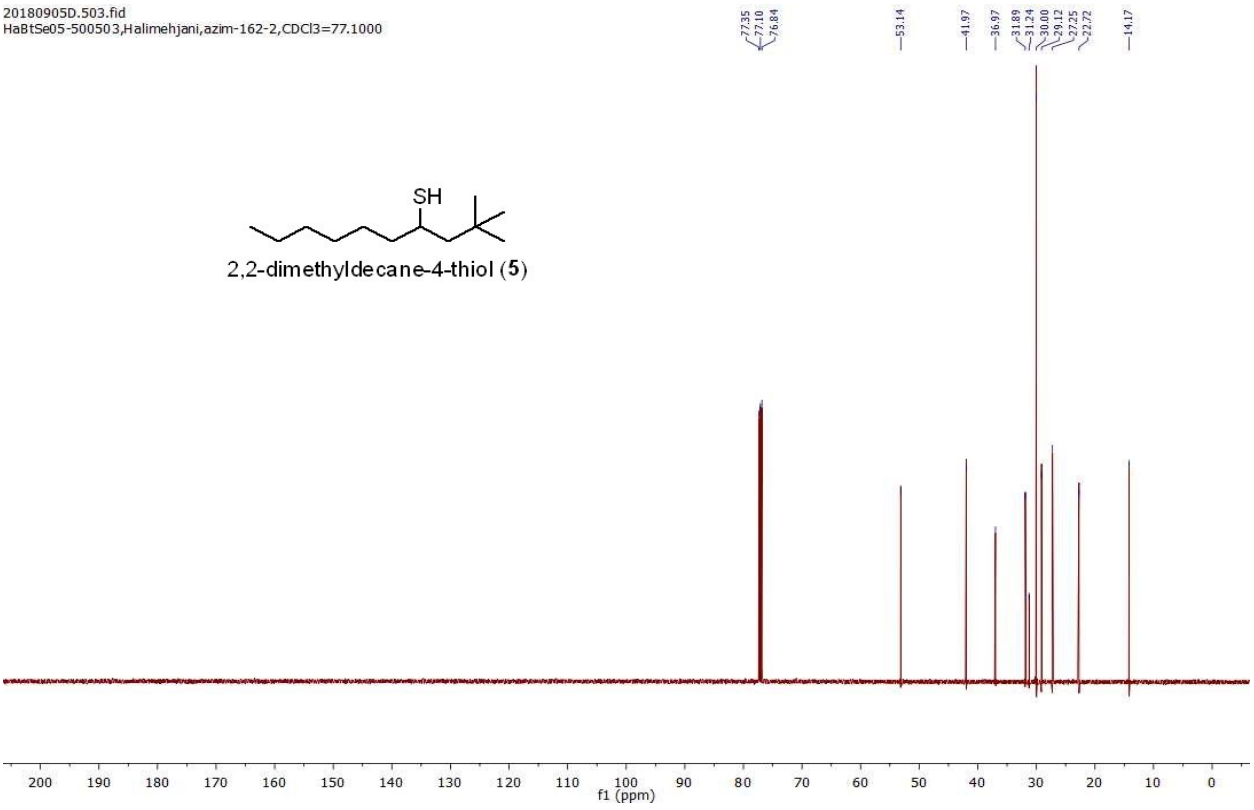


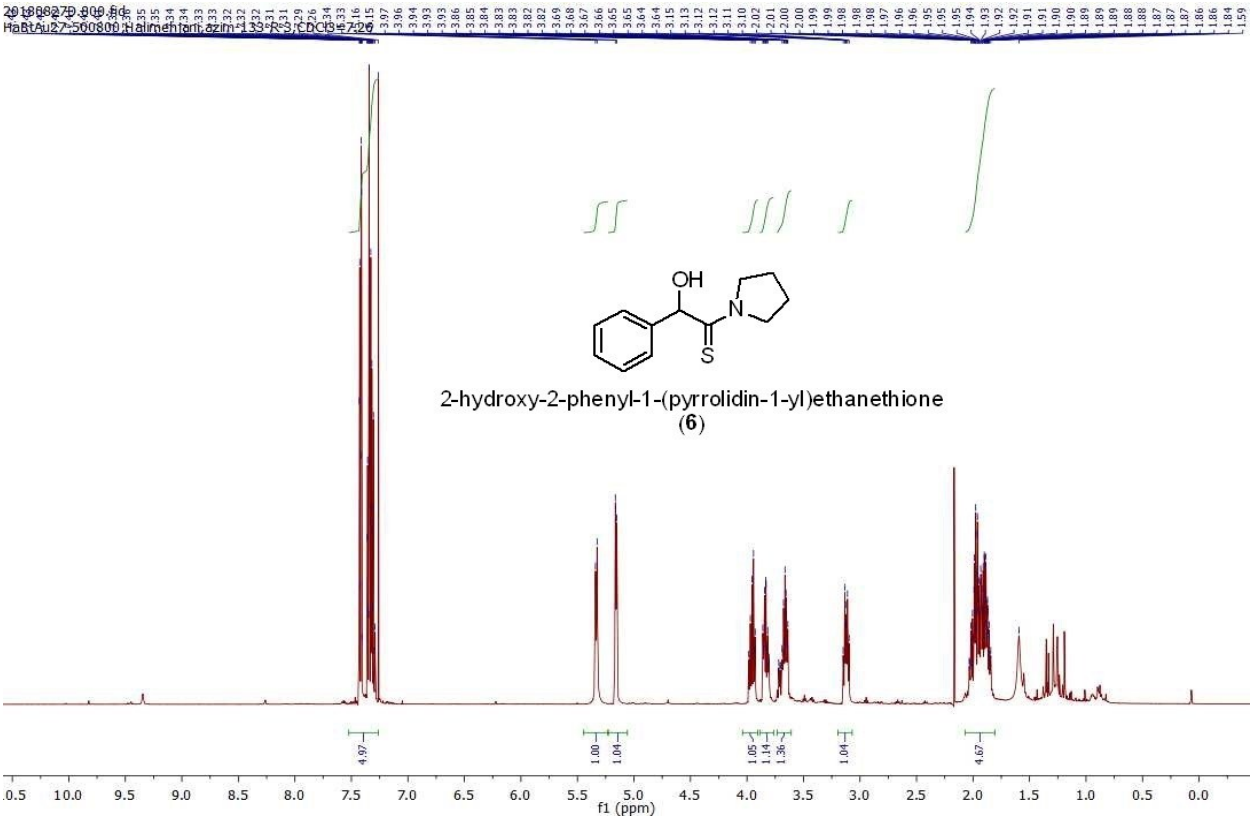
(*E*)-2-(trimethylsilyl)vinyl dibutylcarbamodithioate (**3e**)

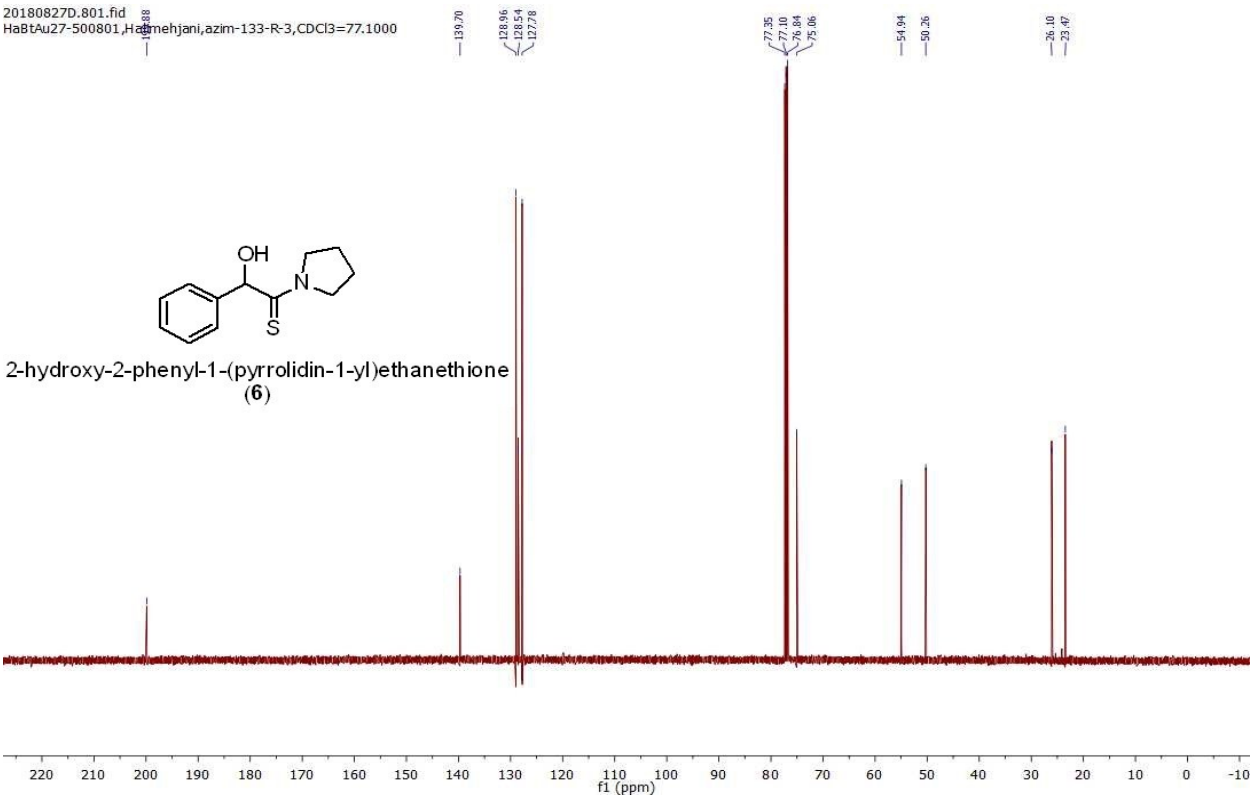


(*E*)-2-(trimethylsilyl)vinyl dibutylcarbamodithioate (**3e**)


20180905D.500.fid
HaBtSe05-500500,Halimehjani,azim-162-2,CDCl3=7.26
SH
2,2-dimethyldecane-4-thiol (5)
f1 (ppm)


20180905D.503.fid
HaBtSe05-500503,Halimehjani,azim-162-2,CDCl3=77.1000
SH
2,2-dimethyldecane-4-thiol (5)
f1 (ppm)


OH
N
S
2-hydroxy-2-phenyl-1-(pyrrolidin-1-yl)ethanethione
(6)
4.97
1.00
1.04
1.05
1.14
1.36
1.04
4.67
f1 (ppm)


20180827D.801.fid
HaBtAu27-500801,Hatimehjani,azim-133-R-3,CDCl3=77.1000
199.88
139.70
128.96
128.54
127.78
77.35
77.10
76.84
75.06
54.94
50.26
26.10
23.47
OH
N
S
2-hydroxy-2-phenyl-1-(pyrrolidin-1-yl)ethanethione
(6)
f1 (ppm)