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

SUPPORTING INFORMATION

for

Chemoselective Reduction of Isothiocyanates to Thioformamides Mediated by the Schwartz Reagent

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1. Instrumental and General Analytical Method

Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 40 MHz for ^{15}N, 376 MHz for ^{19}F) and with a Bruker DRX 200 spectrometer (200 MHz for ^{1}H, 50 MHz for ^{13}C) at 297 K using a "directly" detecting broadband observe (BBFO) probe. The center of the solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 2.49 ppm (^{1}H in DMSO-d_6), δ 77.0 ppm (^{13}C in $CDCl_3$), and δ 39.5 ppm (^{13}C in DMSO-d_6). ^{15}N NMR spectra (gs-HMBC, gs-HSQC) were referenced against neat, external nitromethane, ^{19}F NMR spectra by absolute referencing via *Ξ* ratio. Spin-spin coupling constants (*J*) are given in Hz. In nearly all cases, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, COSY and NOESY experiments. Due to the restricted rotation around the N–CS bond in many cases two separate signal sets were observed in the NMR spectra of the thioformanilides which can be attributed to the s-*cis* and the s-*trans* rotameric form, respectively. The rotamers were discriminated by NOE-experiments, suitable γ-effects and by considering the size of the vicinal **H**-CS-N**H** coupling (Karplus-relationship).

THF and 2-MeTHF were distilled over Na / benzophenone. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar and TCI Europe, otherwise specified. Solutions were evaporated under reduced pressure with a rotary evaporator. TLC was carried out on aluminium sheets precoated with silica gel 60F254 (Macherey-Nagel, Merk); the spots were visualised under UV light (λ = 254 nm) and/or $KMnO_4$ (aq.) was used as revealing system.

2. General Procedures

Reduction of 3-acetylphenyl isothiocyanate; General Procedure 1

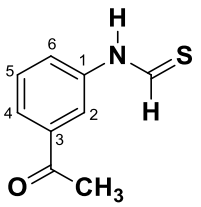
To a solution of 3-acetylphenyl isothiocyanate **1** (0.177 g, 1.0 mmol, 1.0 equiv) in dry THF (5 mL) at the proper temperature, the corresponding reducing agents were added dropwise (*see conditions indicated in Table 1 of the manuscript)*. After the appropriate time, the reactions were quenched with the following reagents: H_2O and 2.5 M NaOH (entries 1-3) / H_2O (entry 4) / NH_4Cl (entry 5) / H_2O and 1 M HCl (entries 6-14), respectively. The aqueous layers were extracted with Et_2O (3×) and the organic phases were combined. The organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crudes were purified by flash SiO_2 column chromatography to yield the products indicated in Table 1.

Reduction of Isothiocyanates to Thioformamides with the *in situ* generated Schwartz Reagent; General Procedure 2

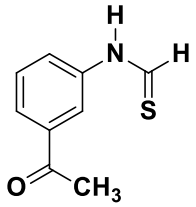
To an oven-dried and argon-flushed flask was added the isothiocyanate and Cp_2ZrCl_2. The reagents were dissolved in anhydrous 2-MeTHF at rt and then the mixture was cooled at 0 °C. $LiAl(O\text{-}t\text{-}Bu)_3H$ (1 M in THF) was added dropwise at 0 °C and then the cooling bath was removed, allowing the mixture to reach rt. After the appropriate time, the reaction was quenched with H_2O (5 mL) and stirred for 1-2 min. Then, a solution of 1 M HCl (4 mL) was added and the layers were separated. The aqueous layer was extracted with EtOAc (3×) and the organic layers were combined. The organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crudes were purified by flash SiO_2 column chromatography to yield the product, using *n*-hexane:EtOAc as mobile phase.

3. Characterization and Spectral Data of the Compounds

***N*-(3-acetylphenyl)thioformamide (2)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 3-acetylphenyl isothiocyanate (0.177 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **2** was obtained in 84% yield (0.151 g) as a brown solid; mp 111-114 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 9 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.90 (d, ^3J = 14.5 Hz, 1H, HC=S), 9.59 (br d, ^3J = 14.5 Hz, 1H, NH), 7.80 (ddd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, ^4J = 1.0 Hz, 1H, Ph H-4), 7.77 (m, 1H, Ph H-2), 7.51 (m, 1H, Ph H-5), 7.36 (ddd, ^3J = 8.1 Hz, ^4J = 2.4 Hz, ^4J = 1.0 Hz, 1H, Ph H-6), 2.63 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.8 (C=O), 187.7 (C=S), 139.0 (Ph C-1), 138.7 (Ph C-3), 130.4 (Ph C-5), 126.0 (Ph C-4), 121.6 (Ph C-6), 116.6 (Ph C-2), 26.7 (CH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -213.8 (NH).

s-*cis* rotamer:

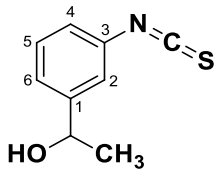
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.74 (d, ^3J = 6.6 Hz, 1H, HC=S), 9.31 (br s, 1H, NH), 7.94 (m, 1H, Ph H-2), 7.92 (m, 1H, Ph H-4), 7.58 (m, 2H, Ph H-5,6), 2.65 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.7 (C=O), 187.5 (C=S), 138.8 (Ph C-3), 130.9 (Ph C-5), 128.0 (Ph C-4), 124.4 (Ph C-6), 117.5 (Ph C-2), 26.8 (CH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -215.6 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for C_9H_9NNaOS: 202.0297; found: 202.0302.

1-(3-isothiocyanatophenyl)ethanol (3)



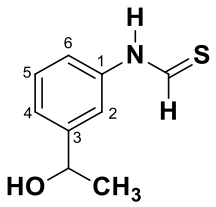
Obtained as a pale yellow oil, as reported in Table 1 of the manuscript.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.32 (m, 1H, Ph H-5), 7.27 (m, 2H, Ph H-2,6), 7.12 (m, 1H, Ph H-4), 4.89 (q, ^{3}J = 6.5 Hz, 1H, HOC*H*CH_3), 1.86 (br s, 1H, OH), 1.49 (d, ^{3}J = 6.5 Hz, 3H, HOCHC*H*$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.8 (Ph C-1), 131.5 (Ph C-3), 129.6 (Ph C-5), 124.5 (Ph C-4), 124.3 (Ph C-6), 122.8 (Ph C-2), 69.6 (HO*C*HCH_3), 25.3 (HOCH*C*H_3).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd. for $C_9H_{10}NOS$: 180.0478; found: 180.0476.

***N*-[3-(1-Hydroxyethyl)phenyl]thioformamide (4)**



s-*trans* rotamer

Obtained as a pale yellow oil, as reported in Table 1 of the manuscript.

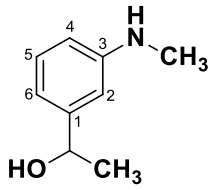
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.81 (d, ^{3}J = 14.6 Hz, 1H, HC=S), 9.46 (br s, 1H, NH), 7.36 (t, m, 1H, Ph H-5), 7.23 (d, ^{3}J = 7.6 Hz, 1H, Ph H-4), 7.20 (m, 1H, Ph H-2), 7.04 (ddd, ^{3}J = 7.9 Hz, ^{4}J = 2.4 Hz, ^{4}J = 1.0 Hz, 1H, Ph H-6), 4.93 (q, ^{3}J = 6.5 Hz, 1H, HOC*H*CH_3), 1.98 (br s, 1H, OH), 1.51 (d, ^{3}J = 6.5 Hz, 3H, HOCHC*H*$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.5 (C=S), 148.2 (Ph C-3), 138.7 (Ph C-1), 130.1 (Ph C-5), 123.3 (Ph C-4), 116.3 (Ph C-6), 114.4 (Ph C-2), 69.8 (HO*C*HCH_3), 25.5 (HOCH*C*H_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -212.0 (NH).

HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_9H_{12}NOS$: 182.0634; found: 182.0631.

1-[3-(Methylamino)phenyl]ethanol (5)



Obtained as a pale yellow oil, as reported in Table 1 of the manuscript.

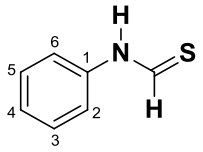
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.16 (t, ^{3}J = 7.8 Hz, 1H, Ph H-5), 6.70 (m, 1H, Ph H-6), 6.62 (s, 1H, Ph H-2), 6.52 (m, 1H, Ph H-4), 4.79 (q, ^{3}J = 6.5 Hz, 1H, HOC*H*CH_3), 2.95 (br s, 2H, OH and NH), 2.83 (s, 3H, $HNCH_3$), 1.47 (d, ^{3}J = 6.5 Hz, 3H, HOCHC*H*$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.4 (Ph C-3), 147.1 (Ph C-1), 129.2 (Ph C-5), 114.3 (Ph C-6), 111.4 (Ph C-4), 109.4 (Ph C-2), 70.4 (HO*C*HCH_3), 30.7 ($HNCH_3$), 24.9 ($HOCHCH_3$).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -329.2 (NH).

HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_9H_{14}NO$: 152.1070; found: 152.1073.

***N*-Phenylthioformamide (6)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of phenyl isothiocyanate (0.135 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **6** was obtained in 97% yield (0.133 g) as a pale orange solid; mp 137 °C (lit.,[1] 136 °C), without column chromatographic purification.

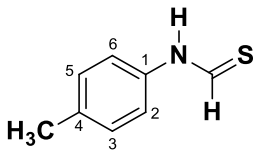
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.80 (d, ^3J = 14.7 Hz, 1H, HC=S), 9.47 (br s, 1H, NH), 7.40 (m, 2H, Ph H-3,5), 7.25 (m, 1H, Ph H-4), 7.15 (m, 2H, Ph H-2,6).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.4 (C=S), 138.5 (Ph C-1), 130.0 (Ph C-3,5), 126.3 (Ph C-4), 117.5 (Ph C-2,6).

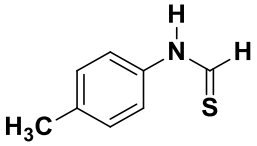
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -212.0 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for C_7H_7NNaS: 160.0191; found: 160.0190.

***N*-(4-Methylphenyl)thioformamide (7)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of *p*-tolyl isothiocyanate (0.149 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **7** was obtained in 89% yield (0.134 g) as a brown solid; mp 165-166 °C, after purification *via* column chromatography on silica gel (eluent hexane:EtOAc 8:2).

s-*trans* : s-*cis* ~ 24 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.92 (br s, 1H, NH), 9.73 (d, ^3J = 14.6 Hz, 1H, HC=S), 7.18 (m, 2H, Ph H-3,5), 7.05 (m, 2H, Ph H-2,6), 2.34 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.9 (C=S), 136.3 (Ph C-4), 136.2 (Ph C-1), 130.4 (Ph C-3,5), 117.5 (Ph C-2,6), 20.9 (CH_3).

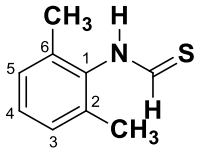
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -210.2 (NH).

s-*cis* rotamer:

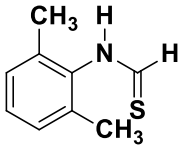
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.66 (d, ^3J = 6.8 Hz, 1H, HC=S), 7.10 (m, 2H, Ph H-3,5), 7.00 (m, 2H, Ph H-2,6), 2.31 (s, 3H, CH_3).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd. for $C_8H_{10}NS$: 152.0528; found: 152.0532.

***N*-(2,6-Dimethylphenyl)thioformamide (8)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 2,6-dimethylphenyl isothiocyanate (0.163 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **8** was obtained in 80% yield (0.132 g) as a pale orange solid; mp 130-133 °C, after purification by chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 2.6 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.56 (br s, 1H, NH), 9.20 (d, ^3J = 15.0 Hz, 1H, HC=S), 7.16 (m, 1H, Ph H-4), 7.11 (m, 2H, Ph H-3,5), 2.31 (s, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 193.1 (C=S), 136.9 (Ph C-1), 133.9 (Ph C-2,6), 128.8 (Ph C-3,5), 128.16 (Ph C-4), 18.5 (CH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -216.9 (NH).

s-*cis* rotamer:

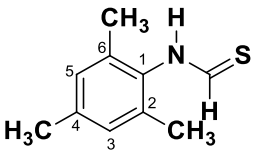
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.62 (d, ^3J = 6.0 Hz, 1H, HC=S), 8.84 (br s, 1H, NH), 7.17 (m, 1H, Ph H-4), 7.10 (m, 2H, Ph H-3,5), 2.23 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.1 (C=S), 135.1 (Ph C-2,6), 134.2 (Ph C-1), 128.5 (Ph C-4), 128.2 (Ph C-3,5), 18.1 (CH_3).

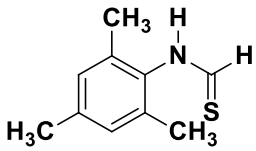
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -218.7 (NH).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd. for $C_9H_{11}NNaS$: 188.0504; found: 188.0510.

***N*-Mesitylthioformamide (9)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 2,4,6-trimethylphenyl isothiocyanate (0.177 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **9** was obtained in 83% yield (0.149 g) as a white solid; mp 197-198 °C, after purification by chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 2.7 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.25 (br d, ^3J = 15.0 Hz, 1H, HC=S), 8.87 (br s, 1H, NH), 6.92 (s, 2H, Ph H-3,5), 2.29 (s, 3H, Ph-4-C*H*$_3$), 2.26 (s, 6H, Ph-2,6-C*H*$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 193.1 (C=S), 138.2 (Ph C-4), 134.4 (Ph C-1), 133.7 (Ph C-2,6), 129.5 (Ph C-3,5), 20.9 (Ph-4-*C*H$_3$), 18.4 (Ph-2,6-*C*H$_3$).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -219.6 (NH).

s-*cis* rotamer:

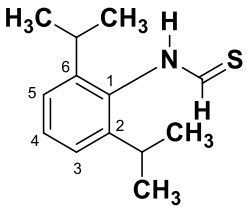
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.68 (d, ^3J = 5.9 Hz, 1H, HC=S), 8.38 (br s, 1H, NH), 6.94 (s, 2H, Ph H-3,5), 2.29 (s, 3H, Ph-4-C*H*$_3$), 2.22 (s, 6H, Ph-2,6-C*H*$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.2 (C=S), 138.5 (Ph C-4), 134.9 (Ph C-2,6), 131.6 (Ph C-1), 129.2 (Ph C-3,5), 21.0 (Ph-4-*C*H$_3$), 18.1 (Ph-2,6-*C*H$_3$).

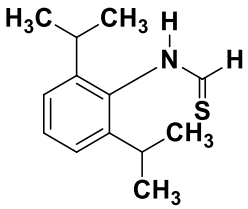
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -221.7 (NH).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd. for $C_{10}H_{14}NS$: 180.0841; found: 180.0843.

***N*-(2,6-Diisopropylphenyl)thioformamide (10)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 2,6-diisopropylphenyl isothiocyanate (0.219 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **10** was obtained in 99% yield (0.219 g) as a white solid; mp 143-145 °C, without column chromatographic purification.

s-*trans* : s-*cis* ~ 5 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.16 (br d, ^3J = 15.0 Hz, 1H, NH), 9.13 (d, ^3J = 15.0 Hz, 1H, HC=S), 7.36 (t, ^3J = 7.8 Hz, 1H, Ph H-4), 7.22 (d, ^3J = 7.8 Hz, 2H, Ph H-3,5), 3.17 (sept, ^3J = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.24 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 193.2 (C=S), 145.3 (Ph C-2,6), 134.4 (Ph C-1), 129.3 (Ph C-4), 123.9 (Ph C-3,5), 28.5 (*C*H$(CH_3)_2$), 23.5 (CH(*C*$H_3)_2$).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -217.5 (NH).

s-*cis* rotamer:

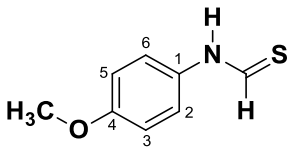
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.79 (d, ^3J = 6.1 Hz, 1H, HC=S), 8.96 (br d, ^3J = 6.1 Hz, 1H, NH), 7.37 (t, ^3J = 7.8 Hz, 1H, Ph H-4), 7.23 (d, ^3J = 7.8 Hz, 2H, Ph H-3,5), 3.03 (sept, ^3J = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.16 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.6 (C=S), 145.4 (Ph C-2,6), 131.6 (Ph C-1), 129.2 (Ph C-4), 123.7 (Ph C-3,5), 28.6 (*C*H$(CH_3)_2$), 24.2 (CH(*C*$H_3)_2$).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -220.7 (NH).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd. for $C_{13}H_{19}NNaS$: 244.1130; found: 244.1138.

***N*-(4-Methoxyphenyl)thioformamide (11)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of 4-methoxyphenyl isothiocyanate (0.165 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **11** was obtained in 91% yield (0.152 g) as a pale brown solid; mp 126 °C (lit.,[1] 125 °C), without column chromatographic purification.

Only traces of the s-*cis* isomer were detected (< 5%).

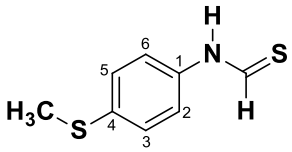
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.63 (d, ^3J = 14.6 Hz, 1H, HC=S), 9.55 (br s, 1H, NH), 7.09 (m, 2H, Ph H-2,6), 6.90 (m, 2H, Ph H-3,5), 3.81 (s, 3H, OCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.9 (C=S), 158.2 (Ph C-4), 132.1 (Ph C-1), 119.4 (Ph C-2,6), 115.1 (Ph C-3,5), 55.6 (OCH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -212.5 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for C_8H_9NNaOS: 190.0297; found: 190.0294.

***N*-[4-(Methylsulfanyl)phenyl)]thioformamide (12)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of 4-(methylthio)phenyl isothiocyanate (0.181 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **12** was obtained in 78% yield (0.143 g) as a brown solid; mp 65-67 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

Only traces of the s-*cis* isomer were detected.

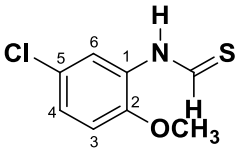
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.53 (br s, 1H, NH), 9.74 (d, ^3J = 14.4 Hz, 1H, HC=S), 7.21 (m, 2H, Ph H-3,5), 7.09 (m, 2H, Ph H-2,6), 2.45 (s, 3H, SCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.6 (C=S), 136.6 (Ph C-4), 135.9 (Ph C-1), 127.7 (Ph C-3,5), 118.0 (Ph C-2,6), 15.9 (SCH_3).

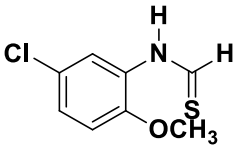
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -208.9 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_8H_9NNaS_2$: 206.0069; found: 206.0067.

***N*-(5-chloro-2-methoxyphenyl)thioformamide (13)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 5-chloro-2-methoxyphenyl isothiocyanate (0.199 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **13** was obtained in 83% yield (0.167 g) as a brown solid; mp 95-97 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 8.1 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.75 (d, ^3J = 14.4 Hz, 1H, HC=S), 9.56 (br s, 1H, NH), 7.20 (d, ^4J = 2.4 Hz, 1H, Ph H-6), 7.09 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H, Ph H-4), 6.83 (d, ^3J = 8.8 Hz, 1H, Ph H-3), 3.86 (s, 3H, OCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.1 (C=S), 146.0 (Ph C-2), 128.4 (Ph C-1), 126.2 (Ph C-5), 125.5 (Ph C-4), 115.5 (Ph C-6), 112.3 (Ph C-3), 56.0 (OCH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -223.4 (NH).

s-*cis* rotamer:

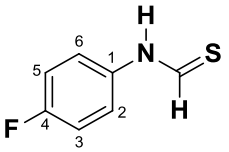
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.71 (d, ^3J = 6.5 Hz, 1H, HC=S), 9.46 (br s, 1H, NH), 9.30 (d, ^4J = 2.5 Hz, 1H, Ph H-6), 7.10 (dd, ^3J = 8.7 Hz, ^4J = 2.5 Hz, 1H, Ph H-4), 6.83 (d, ^3J = 8.8 Hz, 1H, Ph H-3), 3.87 (s, 3H, OCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.1 (C=S), 147.4 (Ph C-2), 128.3 (Ph C-1), 125.6 (Ph C-4), 125.0 (Ph C-5), 120.8 (Ph C-6), 111.0 (Ph C-3), 56.1 (OCH_3).

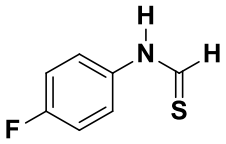
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -224.9 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_8H_8ClNNaOS$: 223.9907; found: 223.9908.

***N*-(4-Fluorophenyl)thioformamide (14)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 4-fluorophenyl isothiocyanate (0.153 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **14** was obtained in 81% yield (0.126 g) as a white solid; mp 182-183 °C (lit.,[1] 184 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 10 : 1

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.78 (br s, 1H, NH), 9.77 (br s, 1H, HC=S), 7.14 (m, 2H, Ph H-2,6), 7.09 (m, 2H, Ph H-3,5).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.5 (C=S), 160.9 (d, $^1J_{C,F}$ = 246.8 Hz, Ph C-4), 134.9 (d, $^4J_{C,F}$ = 3.1 Hz Ph C-1), 119.5 (d, $^3J_{C,F}$ = 8.3 Hz, Ph C-2,6), 116.9 (d, $^2J_{C,F}$ = 23.2 Hz, Ph C-3,5).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -213.3 (NH).

^{19}F NMR ($CDCl_3$, 376 MHz): δ = -115.1 (m).

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.83 (br s, 1H, NH), 9.70 (d, ^3J = 6.6 Hz, 1H, HC=S), 7.81 (m, 2H, Ph H-2,6), 7.10 (m, 2H, Ph H-3,5).

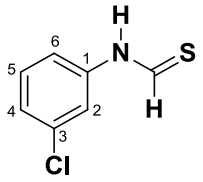
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.3 (C=S), 124.7 (d, $^3J_{C,F}$ = 8.1 Hz, Ph C-2,6), 115.9 (d, $^2J_{C,F}$ = 22.8 Hz,Ph C-3,5); Ph C-4 and Ph C-1 were not found.

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -217.4 (NH).

^{19}F NMR ($CDCl_3$, 376 MHz): δ = -113.5 (m).

HRMS (ESI): *m/z* $[M + H]^+$ calcd. for C_7H_7FNS: 156.0278; found: 156.0276.

***N*-(3-Chlorophenyl)thioformamide (15)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of 3-chlorophenyl isothiocyanate (0.169 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **15** was obtained in 79% yield (0.136 g) as a brown solid; mp 180 °C (lit.,[2] 178-181 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

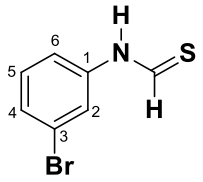
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.81 (d, ^3J = 14.3 Hz, 1H, HC=S), 9.48 (br s, 1H, NH), 7.32 (t, ^3J = 8.0 Hz, 1H, Ph H-5), 7.22 (ddd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, ^4J = 0.9 Hz, 1H, Ph H-4), 7.16 (t, ^4J = 2.0 Hz, 1H, Ph H-2), 7.03 (ddd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, ^4J = 0.9 Hz, 1H, Ph H-6).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.7 (C=S), 139.5 (Ph C-1), 135.8 (Ph C-3), 131.0 (Ph C-5), 126.3 (Ph C-4), 117.6 (Ph C-2), 115.5 (Ph C-6).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -214.3 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_7H_6ClNNaS$: 193.9802; found: 193.9803.

***N*-(3-Bromophenyl)thioformamide (16)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of 3-bromophenyl isothiocyanate (0.214 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **16** was obtained in 85% yield (0.184 g) as a pale yellow solid; mp 180 °C (lit.,[3] 180-181 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.79 (d, ^3J = 14.4 Hz, 1H, HC=S), 9.35 (br s, 1H, NH), 7.37 (m, 1H, Ph H-4), 7.31 (m, 1H, Ph H-2), 7.26 (m, 1H, Ph H-5), 7.07 (m, 1H, Ph H-6).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.7 (C=S), 139.6 (Ph C-1), 131.3 (Ph C-5), 129.2 (Ph C-4), 123.7 (Ph C-3), 120.5 (Ph C-2), 116.0 (Ph C-6).

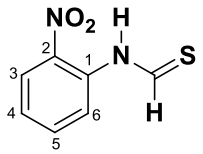
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -214.9 (NH).

Minor s-*cis* rotamer ≈ 4%

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.71 (d, ^3J = 6.5 Hz, 1H, HC=S), 8.13 (m, 1H, Ph H-2), other signals overlapped by those of the major isomer.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd. for C_7H_7BrNS: 215.9477; found: 215.9473.

***N*-(2-Nitrophenyl)thioformamide (17)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of 2-nitrophenyl isothiocyanate (0.180 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **17** was obtained in 80% yield (0.146 g) as an orange solid; mp 98-101 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

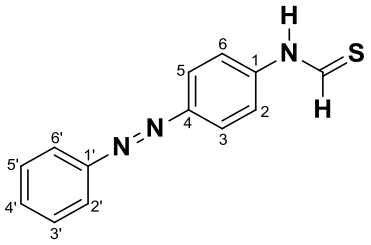
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 11.51 (br s, 1H, NH), 10.08 (d, ^3J = 13.6 Hz, 1H, HC=S), 8.27 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 1H, Ph H-3), 7.71 (m, 1H, Ph H-5), 7.56 (m, 1H, Ph H-6), 7.35 (m, 1H, Ph H-4).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.8 (C=S), 136.1 (Ph C-5), 135.7 (Ph C-2), 134.5 (Ph C-1), 126.7 (Ph C-3), 125.2 (Ph C-4), 117.8 (Ph C-6).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -223.6 (NH), -13.2 (NO_2).

HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_7H_7N_2O_2S$: 183.0223; found: 183.0221.

***N*-[4-(Phenyldiazenyl)phenyl]thioformamide (18)**



s-*trans* rotamer

By following the General Procedure 2, to a solution of 4-phenylazophenyl isothiocyanate (0.239 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **18** was obtained in 88% yield (0.212 g) as an orange solid; mp 157-160 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

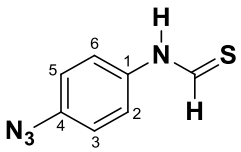
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.07 (d, ^3J = 14.2 Hz, 1H, HC=S), 9.58 (d, ^3J = 14.2 Hz, 1H, NH), 7.98 (m, 2H, Ph H-3,5), 7.92 (m, 2H, Ph H-2‘,6‘), 7.52 (m, 2H, Ph H-3‘,5‘), 7.50 (m, 1H, Ph H-4‘), 7.28 (m, 2H, Ph H-2,6).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.1 (C=S), 152.5 (Ph C-1‘), 150.4 (Ph C-4), 140.1 (Ph C-1), 131.3 (Ph C-4‘), 129.2 (Ph C-3‘,5‘), 124.8 (Ph C-3,5), 122.9 (Ph C-2‘,6‘), 117.5 (Ph C-2,6).

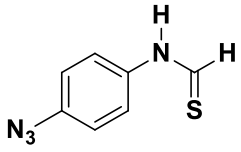
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -212.2 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{13}H_{11}N_3NaS$: 264.0566; found: 264.0566.

***N*-(4-Azidophenyl)thioformamide (19)**



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 4-azidophenyl isothiocyanate (0.176 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **19** was obtained in 94% yield (0.168 g) as a yellow solid; mp 184 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 6 : 1

s-*trans* rotamer:

^{1}H NMR (DMSO-d_6, 200 MHz): δ = 12.22 (d, ^3J = 14.0 Hz, 1H, NH), 9.93 (d, ^3J = 14.0 Hz, 1H, HC=S), 7.42 (m, 2H, Ph H-2,6), 7.10 (m, 2H, Ph H-3,5).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 188.4 (C=S), 136.8 (Ph C-1), 136.1 (Ph C-4), 120.2 (Ph C-3,5), 118.8 (Ph C-2,6).

^{15}N NMR (DMSO-d_6, 40 MHz): δ = -206.7 (NH).

s-*cis* rotamer:

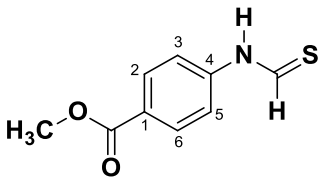
^{1}H NMR (DMSO-d_6, 200 MHz): δ = 12.07 (br d, ^3J = 6.8 Hz, 1H, NH), 9.50 (d, ^3J = 6.8 Hz, 1H, HC=S), 8.06 (m, 2H, Ph H-2,6), 7.15 (m, 2H, Ph H-3,5).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 186.5 (C=S), 136.3 (Ph C-4), 135.8 (Ph C-1), 123.2 (Ph C-2,6), 119.3 (Ph C-3,5).

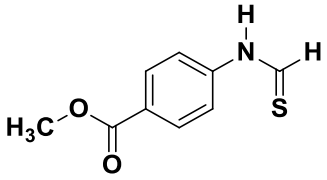
^{15}N NMR (DMSO-d_6, 40 MHz): δ = -206.5 (NH).

HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_7H_7N_4S$: 179.0386; found: 179.0387.

Methyl 4-(thioformylamino) benzoate (20)



s-*trans* rotamer



s-*cis* rotamer

By following the General Procedure 2, to a solution of 4-(methoxycarbonyl)phenyl isothiocyanate (0.193 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **20** was obtained in 80% yield (0.156 g) as a yellow solid; mp 217-218 °C (lit.,[2] 215-219 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*trans* : s-*cis* ~ 10 : 1

s-*trans* rotamer:

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.39 (br d, ^3J = 13.4 Hz, 1H, NH), 10.15 (d, ^3J = 13.7 Hz, 1H, HC=S), 7.92 (m, 2H, Ph H-2,6), 7.51 (m, 2H, Ph H-3,5), 3.82 (s, 3H, OCH_3).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 190.3 (C=S), 165.6 (OC=O), 143.2 (Ph C-4), 130.8 (Ph C-2,6), 125.8 (Ph C-1), 116.8 (Ph C-3,5), 52.06 (OCH_3).

^{15}N NMR (DMSO-d_6, 40 MHz): δ = -205.7 (NH).

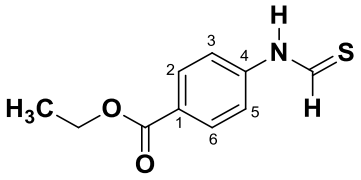
s-*cis* rotamer:

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.28 (br s, 1H, NH), 9.63 (s, 1H, HC=S), 8.20 (m, 2H, Ph H-3,5), 7.99 (m, 2H, Ph H-2,6), 3.83 (s, 3H, OCH_3).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 188.3 (C=S), 165.5 (OC=O), 142.7 (Ph C-4), 130.0 (Ph C-2,6), 126.5 (Ph C-1), 121.1 (Ph C-3,5), 52.10 (OCH_3).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_9H_9NNaO_2S$: 218.0246; found: 218.0246.

Ethyl 4-(thioformylamino) benzoate (21)



s-*trans* rotamer

By following the General Procedure 2, to a solution of 4-(ethoxycarbonyl)phenyl isothiocyanate (0.207 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **21** was obtained in 82% yield (0.172 g) as a brown solid; mp 109-112 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

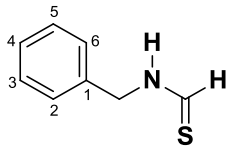
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.95 (br d, ^3J = 14.1 Hz, 1H, HC=S), 9.34 (br d, ^3J = 14.1 Hz, 1H, NH), 8.08 (m, 2H, Ph H-2,6), 7.18 (m, 2H, Ph H-3,5), 4.38 (q, ^3J = 7.1 Hz, 2H, OCH_2), 1.40 (t, ^3J = 7.1 Hz, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.5 (C=S), 165.5 (OC=O), 141.7 (Ph C-4), 131.7 (Ph C-2,6), 128.0 (Ph C-1), 116.5 (Ph C-3,5), 61.2 (OCH_2), 14.3 (CH_3).

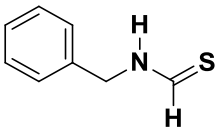
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -213.3 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{10}H_{11}NNaO_2S$: 232.0403; found: 232.0403.

***N*-Benzylthioformamide (22)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of benzyl isothiocyanate (0.149 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, LiAl(O-*t*-Bu)$_3$H (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **22** was obtained in 91% yield (0.138 g) as a brown solid; mp 62-64 °C (lit.,[4] 63-64 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 8:2).

s-*cis* : s-*trans* ~ 4 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.49 (dt, ^3J = 6.2 Hz, ^4J = 1.1 Hz, 1H, HC=S), 7.57 (br s, 1H, NH), 7.42-7.23 (m, 5H, Ph H), 4.87 (d, ^3J = 5.4 Hz, 2H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.8 (C=S), 135.6 (Ph C-1), 129.0 (Ph C-3,5), 128.3 (Ph C-2,6), 128.2 (Ph C-4), 47.6 (CH_2).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -219.4 (NH).

s-*trans* rotamer:

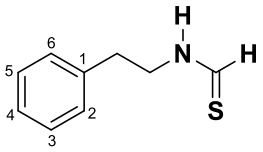
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.26 (d, ^3J = 15.0 Hz, 1H, HC=S), 7.89 (br s, 1H, NH), 7.42-7.23 (m, 5H, Ph H), 4.60 (d, ^3J = 6.2 Hz, 2H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.6 (C=S), 137.9 (Ph C-1), 129.1 (Ph C-3,5), 127.5 (Ph C-2,6), 53.4 (CH_2); Ph C-4 not unambiguously assigned.

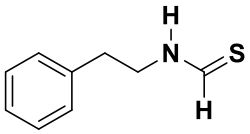
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -223.3 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for C_8H_9NNaS: 174.0348; found: 174.0347.

***N*-(2-Phenethyl)thioformamide (23)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of 2-phenetyl isothiocyanate (0.163 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **23** was obtained in 93% yield (0.153 g) as a brown oil, after purification by column chromatography on silica gel (eluent hexane:EtOAc 8:2).

s-*cis* : s-*trans* ~ 3.3 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.25 (d, ^3J = 6.4 Hz, 1H, HC=S), 7.91 (br s, 1H, NH), 7.31 (m, 2H, Ph H-3,5), 7.23 (m, 1H, Ph H-4), 7.21 (m, 2H, Ph H-2,6), 3.93 (m, 2H, HNC$\underline{H_2}$$CH_2$Ph), 2.96 (t, ^3J = 7.1 Hz, 2H, $HNCH_2C\underline{H_2}$Ph).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.8 (C=S), 137.7 (Ph C-1), 128.57 (Ph C-3,5), 128.5 (Ph C-2,6), 126.6 (Ph C-4), 44.1 (HN$\underline{C}H_2CH_2$Ph), 33.3 ($HNCH_2\underline{C}H_2$Ph).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -219.3 (NH).

s-*trans* rotamer:

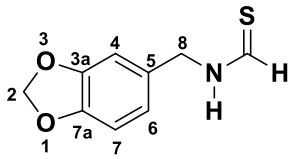
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.91 (d, ^3J = 15.1 Hz, 1H, HC=S), 8.22 (br s, 1H, NH), 7.32 (m, 2H, Ph H-3,5), 7.23 (m, 1H, Ph H-4), 7.16 (m, 2H, Ph H-2,6), 3.63 (q, ^3J = 6.8 Hz, 2H, HNC$\underline{H_2}$$CH_2$Ph), 2.88 (t, ^3J = 7.0 Hz, 2H, $HNCH_2C\underline{H_2}$Ph).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C=S), 136.7 (Ph C-1), 128.7 (Ph C-3,5), 128.60 (Ph C-2,6), 126.9 (Ph C-4), 50.8 (HN$\underline{C}H_2CH_2$Ph), 36.3 ($HNCH_2\underline{C}H_2$Ph).

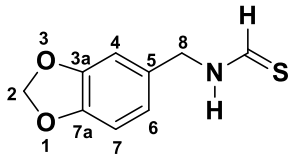
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -220.9 (NH).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd. for $C_9H_{11}NNaS$: 188.0504; found: 188.0508.

***N*-(1,3-Benzodioxol-5-ylmethyl)thioformamide (24)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of 1,3-benzodioxol-5-ylmethyl isothiocyanate (0.193 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **24** was obtained in 96% yield (0.187 g) as a yellow solid; mp 56 °C (lit.,[5] 56-58 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*cis* : s-*trans* ~ 3.6 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.43 (dt, ^3J = 6.3 Hz, ^4J = 1.2 Hz, 1H, HC=S), 7.67 (br s, 1H, NH), 6.81 (m, 1H, H-4), 6.78 (m, 2H, H-6,7), 5.95 (s, 2H, H-2), 4.74 (dd, ^3J = 5.4 Hz, ^4J = 1.1 Hz, 2H, H-8).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.6 (C=S), 148.0 (C-3a), 147.5 (C-7a), 129.3 (C-5), 121.9 (C-6), 108.8 (C-4), 108.5 (C-7), 101.2 (C-2), 47.3 (C-8).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -217.6 (NH).

s-*trans* rotamer:

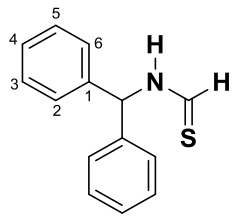
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.19 (d, ^3J = 15.0 Hz, 1H, HC=S), 8.04 (br s, 1H, NH), 6.70 (m, 2H, H-4,6), 5.96 (s, 2H, H-2), 4.47 (d, ^3J = 6.0 Hz, 2H, H-8); H-7 not unambiguously assigned due to overlap with other signals.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.1 (C=S), 148.3 (C-3a), 147.8 (C-7a), 128.8 (C-5), 121.2 (C-6), 108.6 (C-7), 108.0 (C-4), 101.3 (C-2), 53.3 (C-8).

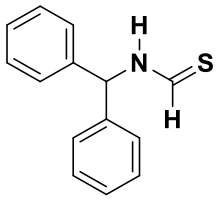
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -221.0 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_9H_9NNaO_2S$: 218.0246; found: 218.0249.

***N*-(Diphenylmethyl)thioformamide (25)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of benzhydryl isothiocyanate (0.225 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, LiAl(O-*t*-Bu)$_3$H (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **25** was obtained in 90% yield (0.204 g) as a yellow solid; mp 108-111 °C, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*cis* : s-*trans* ~ 2 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.57 (dd, ^3J = 6.1 Hz, ^4J = 1.1 Hz, 1H, HC=S), 7.83 (br s, 1H, NH), 7.42-7.22 (m, 10H, Ph-2-6), 6.97 (d, ^3J = 8.1 Hz, 1H, $Ph_2C\underline{H}NH$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.2 (C=S), 139.4 (Ph C-1), 128.9 (Ph C-3,5), 128.0 (Ph C-4), 127.7 (Ph C-2,6), 60.0 ($Ph_2\underline{C}HNH$).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -211.0 (NH).

s-*trans* rotamer:

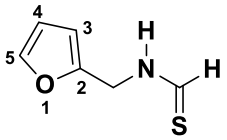
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.23 (dd, ^3J = 15.1 Hz, ^4J = 0.6 Hz, 1H, HC=S), 8.10 (br s, 1H, NH), 7.42-7.22 (m, 10H, Ph-2-6), 5.90 (d, ^3J = 6.7 Hz, 1H, $Ph_2C\underline{H}NH$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.6 (C=S), 139.1 (Ph C-1), 129.1 (Ph C-3,5), 128.5 (Ph C-4), 127.5 (Ph C-2,6), 66.9 ($Ph_2\underline{C}HNH$).

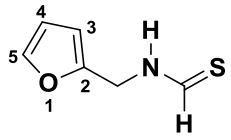
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -213.7 (NH).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd. for $C_{14}H_{13}NNaS$: 250.0661; found: 250.0666.

***N*-(2-Furylmethyl)thioformamide (26)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of furfuryl isothiocyanate (0.139 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **26** was obtained in 91% yield (0.128 g) as a brown oil, after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*cis* : s-*trans* ~ 4 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.43 (d, ^3J = 6.2 Hz, 1H, HC=S), 7.82 (br s, 1H, NH), 7.38 (m, 1H, Fur H-5), 6.35 (m, 1H, Fur H-4), 6.34 (m, 1H, Fur H-3), 4.85 (dd, ^3J = 5.2 Hz, ^4J = 1.0 Hz, 2H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.7 (C=S), 148.6 (Fur C-2), 142.7 (Fur C-5), 110.6 (Fur C-4), 109.1 (Fur C-3), 40.2 (CH_2).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -224.3 (NH).

s-*trans* rotamer:

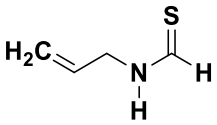
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.27 (d, ^3J = 14.9 Hz, 1H, HC=S), 8.02 (br s, 1H, NH), 7.40 (dd, ^3J = 1.9 Hz, ^4J = 0.8 Hz, 1H, Fur H-5), 6.35 (m, 1H, Fur H-4), 6.30 (m, 1H, Fur H-3), 4.55 (d, ^3J = 5.9 Hz, 2H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.5 (C=S), 148.2 (Fur C-2), 143.4 (Fur C-5), 110.6 (Fur C-4), 109.0 (Fur C-3), 45.8 (CH_2).

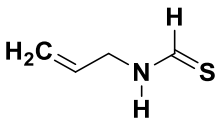
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -226.6 (NH).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd. for C_6H_8NOS: 142.0321; found: 148.0374.

***N*-Allylthioformamide (27)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of allyl isothiocyanate (0.099 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **27** was obtained in 95% yield (0.096 g) as a yellow oil,[6] after purification by column chromatography on silica gel (eluent hexane:EtOAc 9:1).

s-*cis* : s-*trans* ~ 2.9 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.40 (d, ^3J = 6.4 Hz, 1H, HC=S), 8.04 (br s, 1H, NH), 5.86 (m, 1H, CH_2=C*H*-CH_2), 5.30-5.20 (m, 2H, C*H*$_2$=CH-CH_2), 4.28 (m, 2H, CH_2=CH-C*H*$_2$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.8 (C=S), 131.0 (CH_2=*C*H-CH_2), 118.9 (*C*H_2=CH-CH_2), 45.5 (CH_2=CH-*C*H_2).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -220.8 (NH).

s-*trans* rotamer:

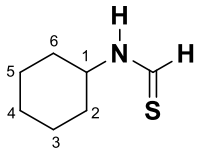
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.11 (d, ^3J = 15.0 Hz, 1H, HC=S), 8.31 (br s, 1H, NH), 5.82 (m, 1H, CH_2=C*H*-CH_2), 5.30-5.20 (m, 2H, C*H*$_2$=CH-CH_2), 4.01 (m, 2H, CH_2=CH-C*H*$_2$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.4 (C=S), 131.9 (CH_2=*C*H-CH_2), 118.5 (*C*H_2=CH-CH_2), 51.5 (CH_2=CH-*C*H_2).

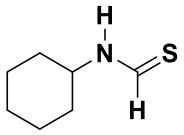
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -223.3 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for C_4H_7NNaS: 124.0191; found: 125.1078.

***N*-Cyclohexylthioformamide (28)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of cyclohexyl isothiocyanate (0.141 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **28** was obtained in 99% yield (0.142 g) as an orange oil,[7] without column chromatographic purification.

s-*cis* : s-*trans* ~ 1.1 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.34 (d, ^3J = 6.6 Hz, 1H, HC=S), 7.41 (br s, 1H, NH), 4.49 (m, 1H, Cy H-1), 2.06, 1.25 (m, 4H, Cy H-2,6), 1.82-1.11 (m, 6H, Cy H-3,4,5).

^{13}C NMR ($CDCl_3$, 100 MHz)*: δ = 187.3 (C=S), 51.6 (Cy C-1), 31.3 (Cy C-2,6).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -204.4 (NH).

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.22 (br d, ^3J = 15.0 Hz, 1H, HC=S), 8.12 (br s, 1H, NH), 3.45 (m, 1H, Cy H-1), 1.96, 1.34 (m, 4H, Cy H-2,6), 1.82-1.11 (m, 6H, Cy H-3,4,5).

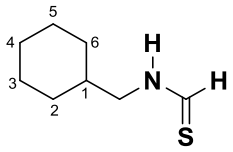
^{13}C NMR ($CDCl_3$, 100 MHz)*: δ = 188.8 (C=S), 58.8 (Cy C-1), 33.4 (Cy C-2,6).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -204.7 (NH).

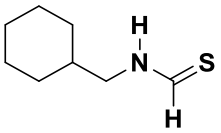
* Not assignable C signals: 25.30, 24.78, 24.43, 24.39.

HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_7H_{13}NNaS$: 166.0661; found: 166.0665.

***N*-(Cyclohexylmethyl)thioformamide (29)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of cyclohexylmethyl isothiocyanate (0.155 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, LiAl(O-*t*-Bu)$_3$H (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **29** was obtained in 99% yield (0.155 g) as an orange oil, without column chromatographic purification.

s-*cis* : s-*trans* ~ 1.7 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.35 (td, ^3J = 6.7 Hz, ^4J = 1.0 Hz, 1H, HC=S), 8.24 (br s, 1H, NH), 3.47 (dt, ^3J = 6.3 Hz, ^4J = 1.0 Hz, 2H, HNC$\underline{H_2}$Cy), 1.65 (m, 1H, Cy H-1), 1.73-0.81 (m, 10H, Cy H-2-6).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.5 (C=S), 49.5 (HN$\underline{C}H_2$Cy), 36.4 (Cy C-1), 30.7 (Cy C-2,6), 25.9 (Cy C-4), 25.4 (Cy C-3,5).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -217.6 (NH).

s-*trans* rotamer:

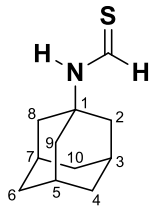
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.01 (d, ^3J = 15.1 Hz, 1H, HC=S), 8.61 (br s, 1H, NH), 3.20 (t, ^3J = 6.6 Hz, 2H, HNC$\underline{H_2}$Cy), 1.49 (m, 1H, Cy H-1), 1.73-0.81 (m, 10H, Cy H-2-6).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.6 (C=S), 56.1 (HN$\underline{C}H_2$Cy), 38.2 (Cy C-1), 30.1 (Cy C-2,6), 25.8 (Cy C-4), 25.3 (Cy C-3,5).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -219.5 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_8H_{15}NNaS$: 180.0817; found: 180.0822.

***N*-Adamantan-1-ylthioformamide (30)**



s-*trans* rotamer

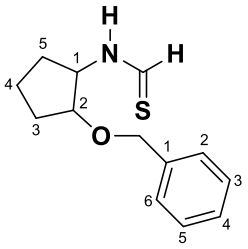
By following the General Procedure 2, to a solution of 1-adamantyl isothiocyanate (0.193 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **30** was obtained in 96% yield (0.187 g) as a white solid; mp 244-247 °C (lit.,[1] 246 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 85:15).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.35 (d, ^3J = 15.7 Hz, 1H, HC=S), 7.84 (br s, 1H, NH), 2.18 (m, 3H, Adam H-3,5,7), 1.85 (m, 6H, Adam H-2,8,9), 1.77-1.62 (m, 6H, Adam H-4,6,10).

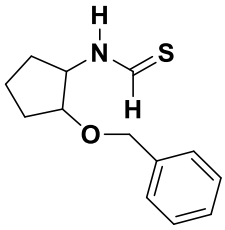
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.5 (C=S), 56.2 (Adam C-1), 43.1 (Adam C-2,8,9), 35.7 (Adam C-4,6,10), 29.2 (Adam C-3,5,7).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd. for $C_{11}H_{17}NNaS$: 218.0974; found: 218.0977.

***N*-[2-(Benzyloxy)cyclopentyl]thioformamide (31)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of (1*R*,2*R*)-(-)-2-benzyloxycyclopentyl isothiocyanate (0.233 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, LiAl(O-*t*-Bu)$_3$H (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **31** was obtained in 94% yield (0.221 g) as a pale brown oil, after purification by column chromatography silica gel (eluent hexane:EtOAc 9:1).

s-*cis* : s-*trans* ~ 1.7 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.32 (d, ^3J = 6.5 Hz, 1H, HC=S), 7.75 (br s, 1H, NH), 7.37-7.24 (m, 3H, Ph H-3,4,5), 7.33 (m, 2H, Ph H-2,6), 4.88 (m, 1H, Cp H-1), 4.68 (A-part of an AB-system, $^2J_{AB}$ = 12.1 Hz, OCH_2), 4.61 (B-part of an AB-system, $^2J_{AB}$ = 12.1 Hz, OCH_2), 3.95 (m, 1H, Cp H-2), 2.33, 1.49 (m, 2H, Cp H-5), 1.88, 1.78 (m, 2H, Cp H-3), 1.88, 1.72 (m, 2H, Cp H-4).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.1 (C=S), 138.3 (Ph C-1), 128.3 (Ph C-3,5), 127.8 (Ph C-4), 127.62 (Ph C-2,6), 83.7 (Cp C-2), 71.1 (O<u>C</u>H_2Ph), 59.0 (Cp C-1), 30.6 (Cp C-3), 29.4 (Cp C-5), 21.7 (Cp C-4).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -209.9 (NH).

s-*trans* rotamer:

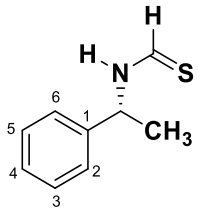
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.20 (d, ^3J = 15.0 Hz, 1H, HC=S), 8.55 (br s, 1H, NH), 7.37-7.24 (m, 3H, Ph H-3,4,5), 7.31 (m, 2H, Ph H-2,6),), 4.54 (A-part of an AB-system, $^2J_{AB}$ = 11.7 Hz, OCH_2), 4.46 (B-part of an AB-system, $^2J_{AB}$ = 11.7 Hz, OCH_2), 3.88 (m, 1H, Cp H-1), 3.79 (m, 1H, Cp H-2), 2.11, 1.62 (m, 2H, Cp H-5), 1.98, 1.67 (m, 2H, Cp H-3), 1.76, 1.73 (m, 2H, Cp H-4).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.3 (C=S), 137.7 (Ph C-1), 128.4 (Ph C-3,5), 127.56 (Ph C-2,6), 127.5 (Ph C-4), 84.3 (Cp C-2), 71.8 (O<u>C</u>H_2Ph), 65.9 (Cp C-1), 29.3 (Cp C-5), 29.2 (Cp C-3), 20.3 (Cp C-4).

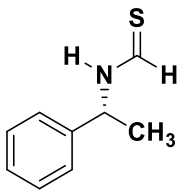
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -211.4 (NH).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{13}H_{17}NNaOS$: 258.0923; found: 258.0931.

***N*-[(1*R*)-1-Phenylethyl]thioformamide (32)**



s-*cis* rotamer



s-*trans* rotamer

By following the General Procedure 2, to a solution of (*R*)-(-)-1-phenylethyl isothiocyanate (0.163 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, LiAl(O-*t*-Bu)$_3$H (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction was allowed to warm to rt. Compound **32** was obtained in 99% yield (0.163 g) as a yellow solid; mp 50-52 °C, $[\alpha]_D^{20}$ +158 ° (*c* 0.5, $CHCl_3$), without column chromatographic purification.

s-*cis* : s-*trans* ~ 1.8 : 1

s-*cis* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.31 (s, 1H, HC=S), 8.19 (br s, 1H, NH), 7.34 (m, 4H, Ph H-2,3,5,6), 7.29 (m, 1H, Ph H-4), 5.81 (q, ^3J = 6.9 Hz, 1H, PhC*H*(CH$_3$)NH), 1.58 (d, ^3J = 6.9 Hz, 3H, PhCH(C*H*$_3$)NH).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.4 (C=S), 140.7 (Ph C-1), 128.7 (Ph C-3,5), 127.7 (Ph C-4), 126.4 (Ph C-2,6), 51.8 (Ph*C*H(CH$_3$)NH), 20.0 (PhCH(*C*H$_3$)NH).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -203.3 (NH).

s-*trans* rotamer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.12 (s, 1H, HC=S), 8.66 (br s, 1H, NH), 7.36 (m, 2H, Ph H-3,5), 7.31 (m, 1H, Ph H-4), 7.25 (m, 2H, Ph H-2,6), 4.75 (q, ^3J = 6.9 Hz, 1H, PhC*H*(CH$_3$)NH), 1.60 (d, ^3J = 6.9 Hz, 3H, PhCH(C*H*$_3$)NH).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.0 (C=S), 140.5 (Ph C-1), 129.0 (Ph C-3,5), 128.2 (Ph C-4), 126.1 (Ph C-2,6), 59.1 (Ph*C*H(CH$_3$)NH), 22.1 (PhCH(*C*H$_3$)NH).

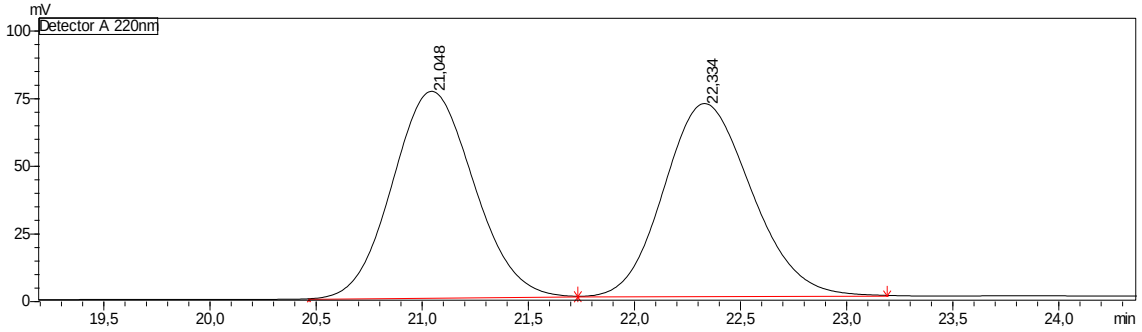
^{15}N NMR ($CDCl_3$, 40 MHz): δ = -206.3 (NH).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd. for $C_9H_{11}NNaS$: 188.0504; found: 188.0508.

HPLC Chiralpak® IG; λ = 220 nm; *n*-hexane/*i*-propanol 98/2; flow rate = 1.00 mL/min.

Racemate

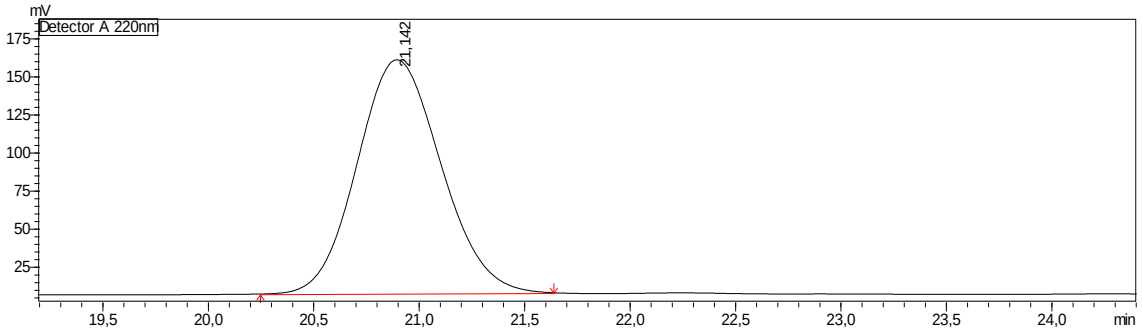
Datafile Name:KVH-040rac-12.lcd
Sample Name:KVH-040rac-11
Sample ID:KVH-040rac-11



Peaks	Retention time (min)	Area	Area (%)
1	21.048	2033727	49.952
2	22.334	2037667	50.048
Total		4071394	100.000

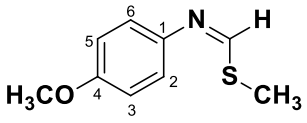
Enantioenriched

Datafile Name:KVH-012(+)_2.lcd
Sample Name:KVH-012(+)_1
Sample ID:KVH-012(+)_1



Peaks	Retention time (min)	Area	Area (%)
1	21.142	4241574	100.000
Total		4241574	100.000

Methyl (4-methoxyphenyl)imidothioformate (33)



To a solution of thioformanilide **11** (0.167 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL) at -78 °C was added MeI (0.19 mL, 3.0 mmol, 3.0 equiv), followed by the dropwise addition of MeLi·LiBr (1.5 M, 1.87 mL, 2.8 mmol, 2.8 equiv). After 1 h at -78 °C, a solution of 1 M HCl (4 mL) was added and the layers were separated. The aqueous layer was extracted with EtOAc (3x) and washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Compound **33** was obtained in 91% yield (0.165 g) as a yellow oil, after purification on column chromatography on silica gel (eluent hexane:EtOAc 95:5).

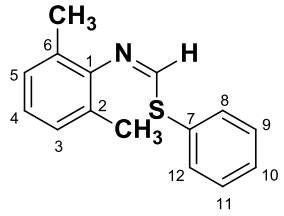
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.47 (s, HC=N), 7.01 (m, 2H, Ph H-2,6), 6.86 (m, 2H, Ph H-3,5), 3.80 (s, 3H, OCH_3), 2.51 (s, 3H, SCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.5 (Ph C-4), 156.9 (HC=N, $^1J_{C\text{-}H}$ = 175.1 Hz), 144.8 (Ph C-1), 121.6 (Ph C-2,6), 114.3 (Ph C-3,5), 55.5 (OCH_3), 11.7 (SCH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -77.8 (C=N).

HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_9H_{11}NOS$: 182.0634; found: 182.0636.

Phenyl (2,6-dimethylphenyl)imidothioformate (34)



To a solution of thioformanilide **8** (0.165 g, 1.0 mmol, 1.0 equiv) in 1,2-dichloroethane (DCE) (5.0 mL) was added Ph_2IOTf (0.860 g, 2.0 mmol, 2.0 equiv) and $Cu(OTf)_2$ (72 mg, 0.2 mmol, 0.2 equiv). The reaction was then heated at 70 °C for 3.5 h. Afterward, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with a saturated sodium bicarbonate solution (50 mL). The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to dryness. Compound **34** was obtained in 84% yield (0.206 g) as a yellow liquid, after purification by column chromatography on silica gel (eluent hexane:EtOAc 95:5).

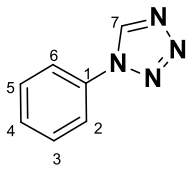
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.56 (s, HC=N), 7.50 (m, 2H, Ph H-8,12), 7.42 (m, 2H, Ph H-9,11), 7.41 (m, 1H, Ph H-10), 7.11 (d, ^3J = 7.5 Hz, 2H, Ph H-3,5), 7.02 (t, ^3J = 7.5 Hz, 1H, Ph H-4), 2.23 (s, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.7 (C=N), 147.9 (Ph C-1), 132.8 (Ph C-8,12), 131.2 (Ph C-7), 129.5 (Ph C-9,11), 128.9 (Ph C-10), 128.1 (Ph C-3,5), 126.0 (Ph C-2,6), 124.2 (Ph C-4), 17.6 (CH_3).

^{15}N NMR ($CDCl_3$, 40 MHz): δ = -56.8 (C=N).

HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{15}H_{16}NS$: 242.0998; found: 242.1001.

1-Phenyl-1*H*-tetrazole (35)



To a solution of thioformanilide **6** (0.137 g, 1.0 mmol, 1.0 equiv) in xylene (2 mL) was added Et_2AlN_3 (0.508 g, 4.0 mmol, 4.0 equiv). The reaction was heated at 100 °C for 24 h and then, when TLC analysis showed complete conversion, it was cooled to 0 °C and a solution of 15% aq NaOH (13.0 equiv) containing sodium nitrite (13.0 equiv, solution pH 13.5) was added. The pH value was then adjusted to 1.5 with 6N HCl and the mixture was exhaustively extracted with ethyl acetate (2x). The solvents were removed under reduced pressure to afford the crude product, which was re-dissolved in ethyl acetate and extracted with aq K_2CO_3 (10%) to the aqueous phase (pH 11). The combined basic aq. phases were cooled to 0 °C and carefully treated with 6N HCl to adjust the pH value to 2.5. The product was then extracted with AcOEt, the combined organic phases were dried over anhyd Na_2SO_4, filtered and concentrated under reduced pressure. Compound **35** was obtained in 86% yield (0.125 g) as a brown solid; mp 64 °C (lit.,[8] 64-66 °C), after purification by column chromatography on silica gel (eluent hexane:EtOAc 8:2).

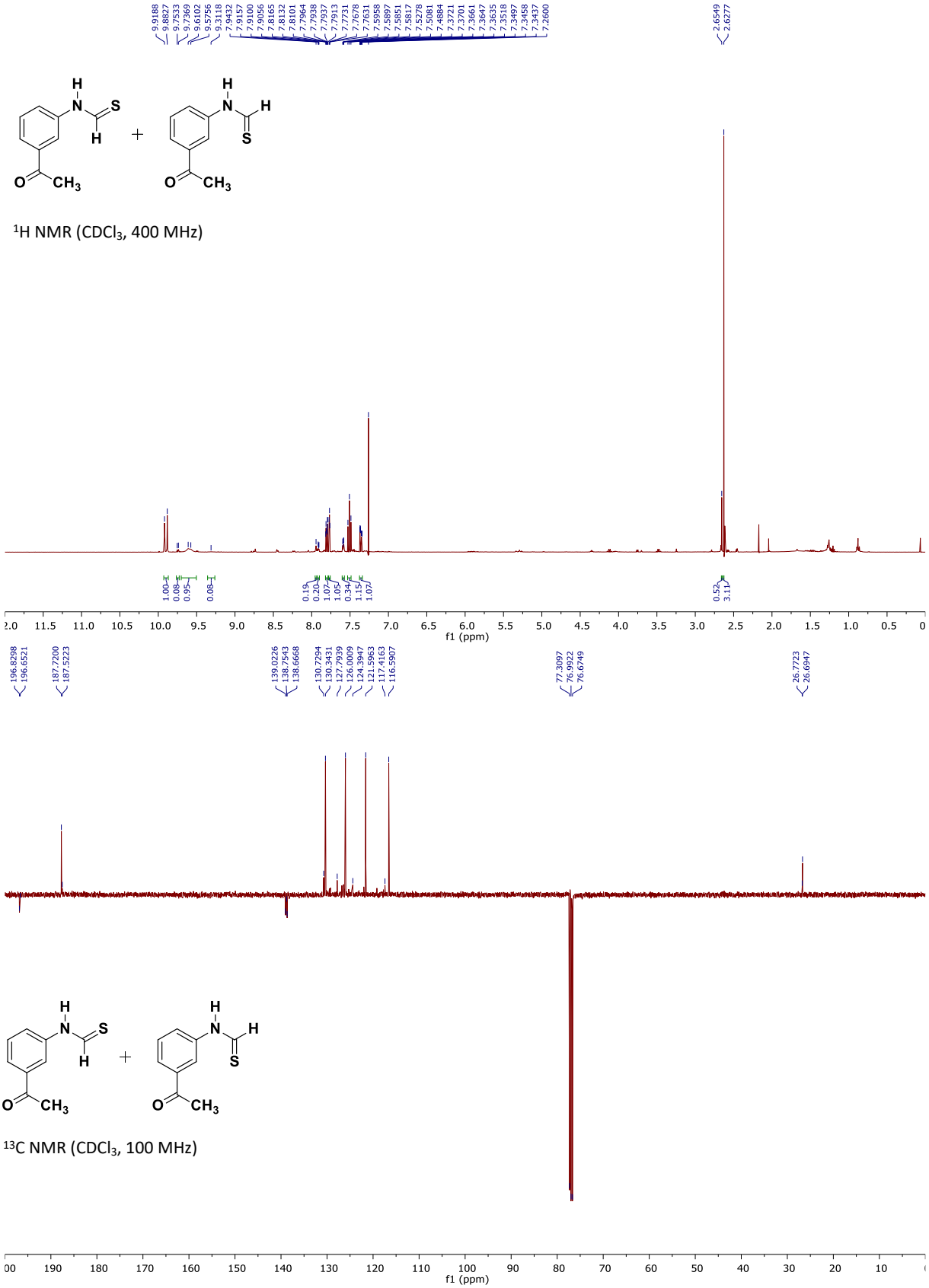
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.99 (s, tetrazole-H), 7.72 (m, 2H, Ph H-2,6), 7.60 (m, 2H, Ph H-3,5), 7.55 (m, 1H, Ph H-4).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.4 (tetrazole-C), 133.9 (Ph C-1), 130.2 (Ph C-3,5), 130.1 (Ph C-4), 121.3 (Ph C-2,6).

HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_7H_7N_4$: 147.0665; found: 147.0669.

4. Copies of ^{1}H- and ^{13}C-NMR Spectra

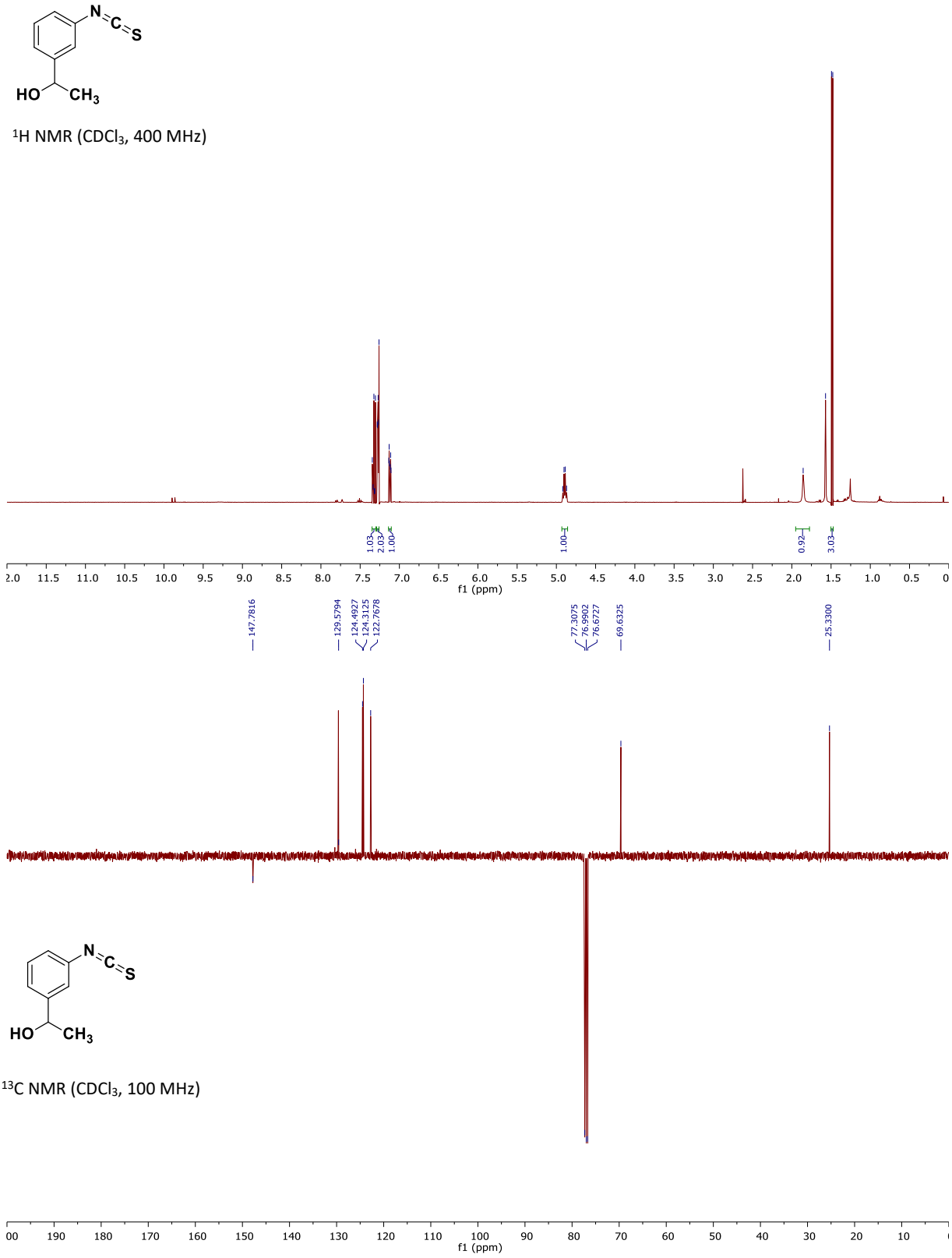
_N_-(3-acetylphenyl)thioformamide (2)



^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 100 MHz)

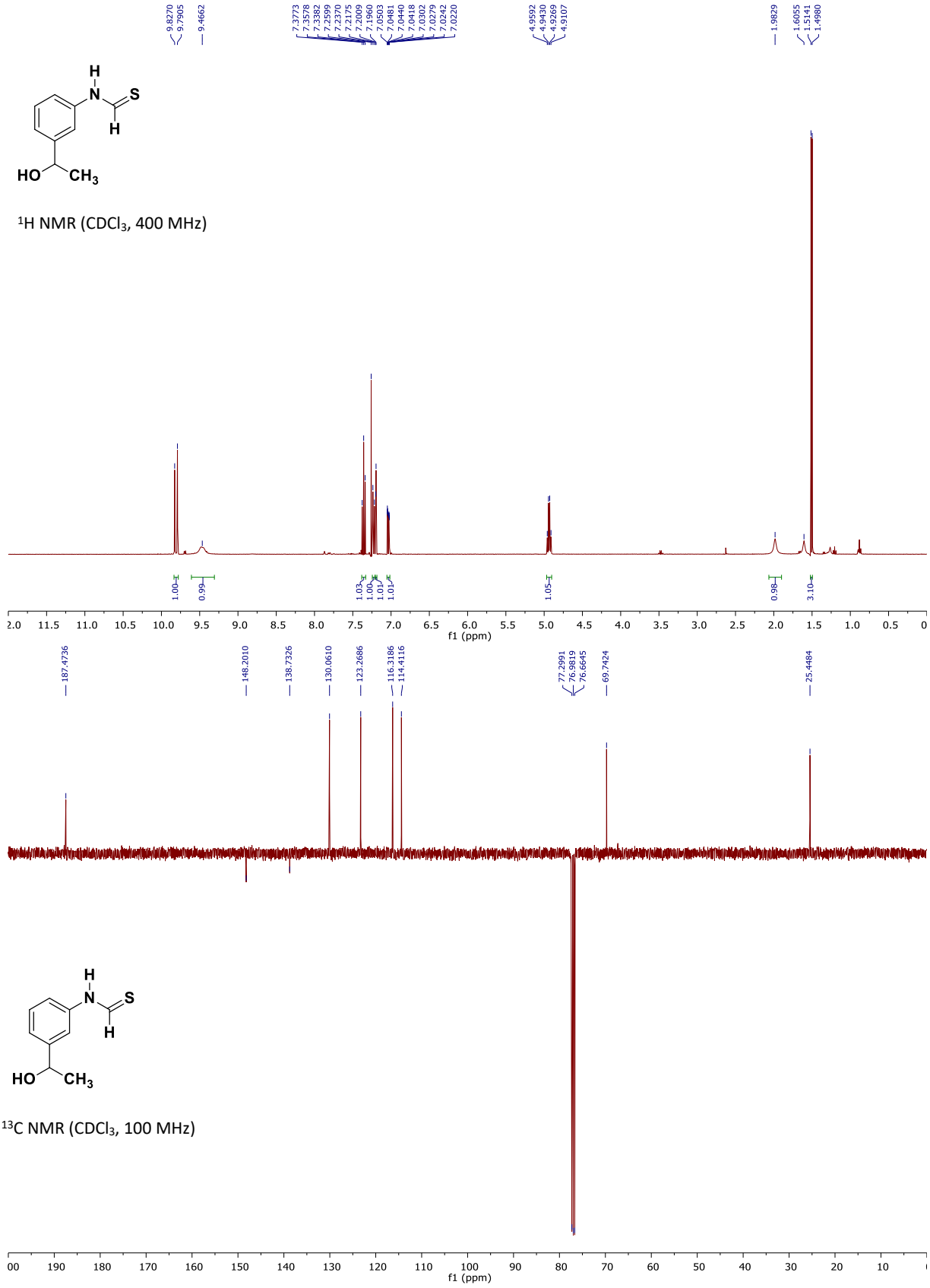
1-(3-isothiocyanatophenyl)ethanol (3)



^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 100 MHz)

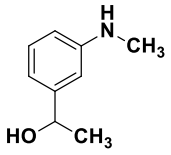
_N_-[3-(1-Hydroxyethyl)phenyl]thioformamide (4)



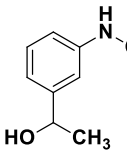
^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 100 MHz)

1-[3-(Methylamino)phenyl]ethanol (5)

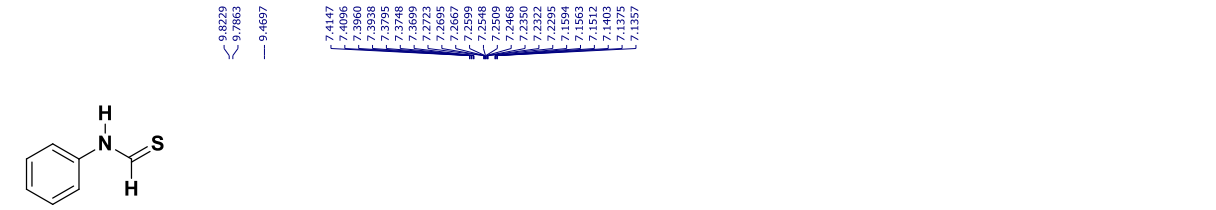


^{1}H NMR ($CDCl_3$, 400 MHz)

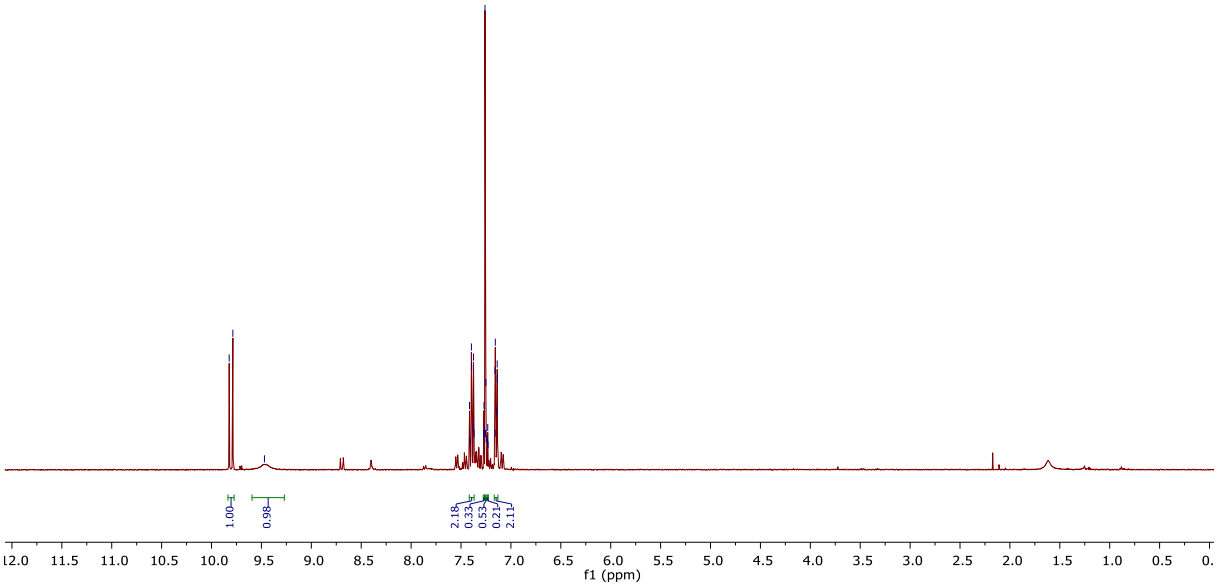


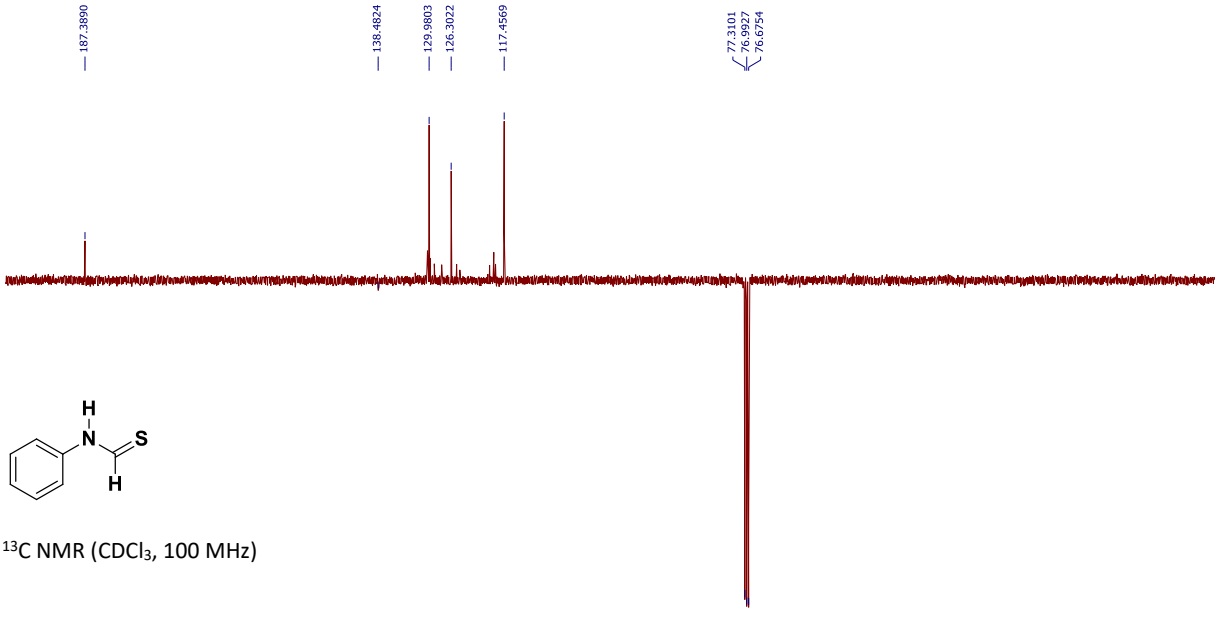
^{13}C NMR ($CDCl_3$, 100 MHz)

N-Phenylthioformamide (6)

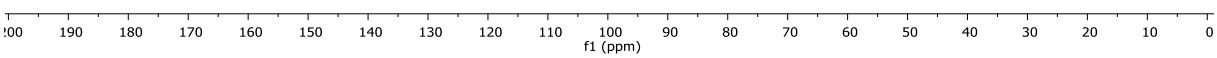


^{1}H NMR ($CDCl_3$, 400 MHz)

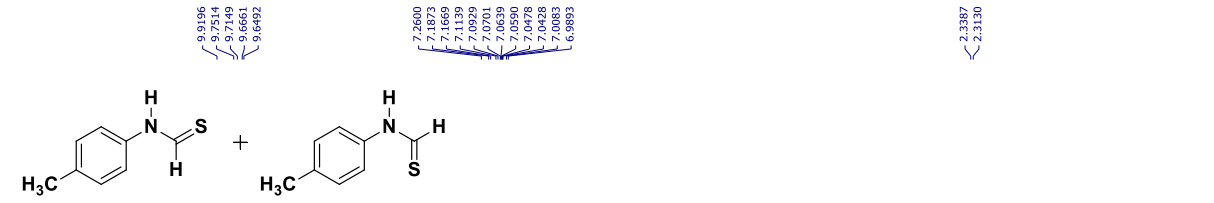




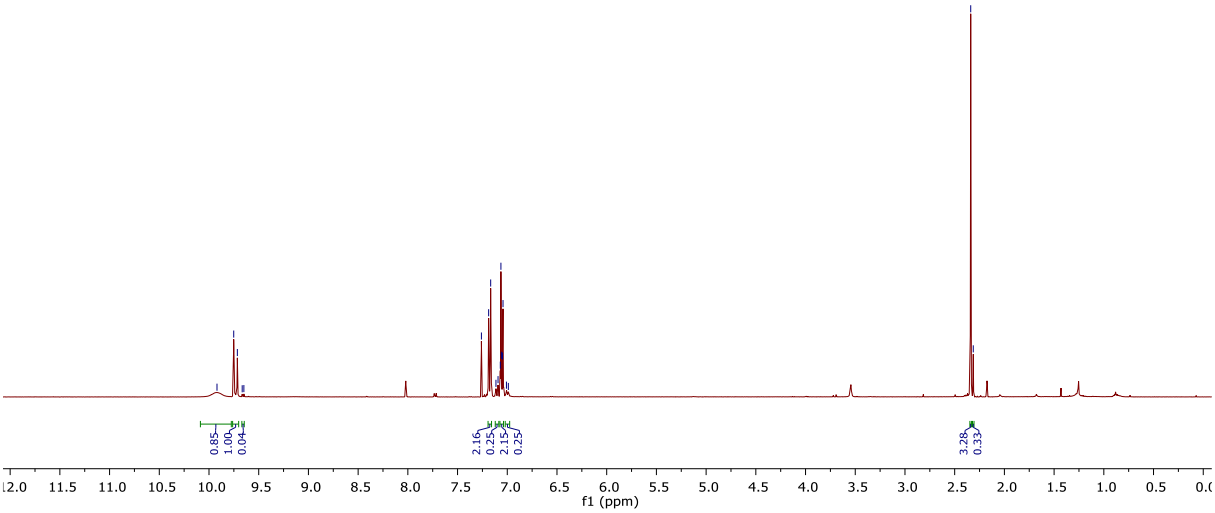
^{13}C NMR ($CDCl_3$, 100 MHz)



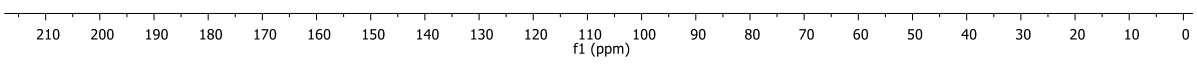
N-(4-Methylphenyl)thioformamide (7)



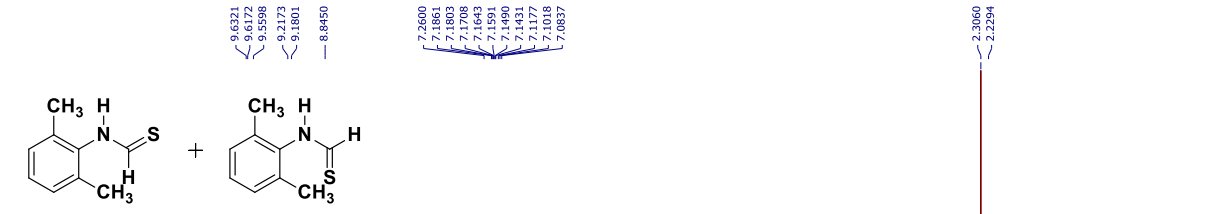
^{1}H NMR ($CDCl_3$, 400 MHz)



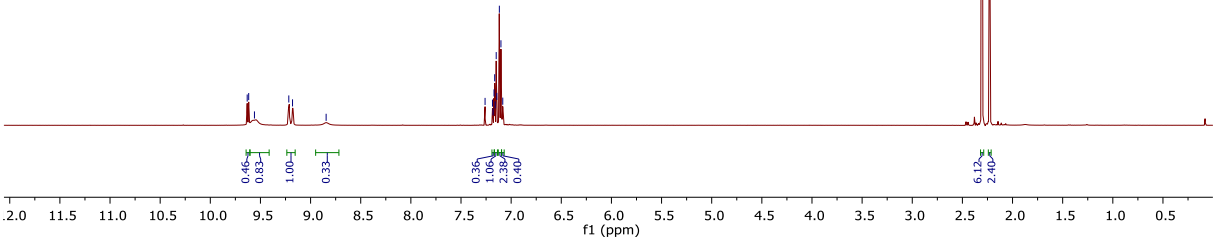
^{13}C NMR ($CDCl_3$, 100 MHz)

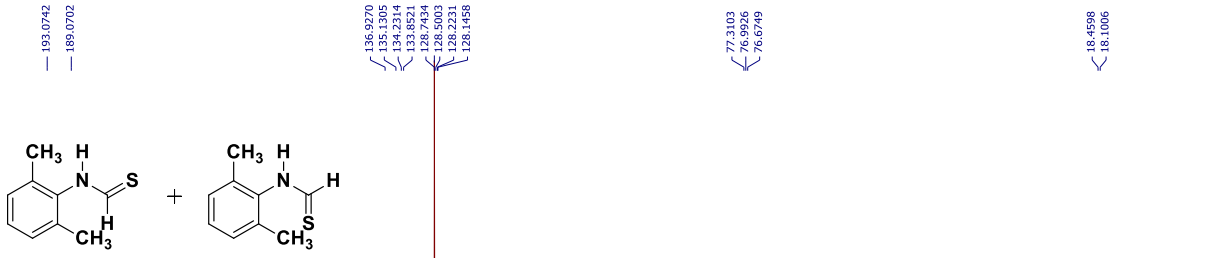


_N_-(2,6-Dimethylphenyl)thioformamide (8)

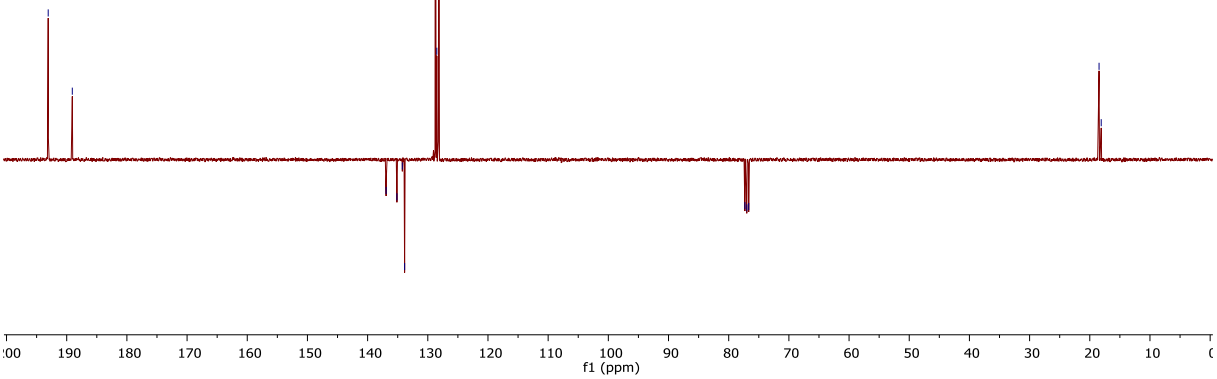


^{1}H NMR ($CDCl_3$, 400 MHz)

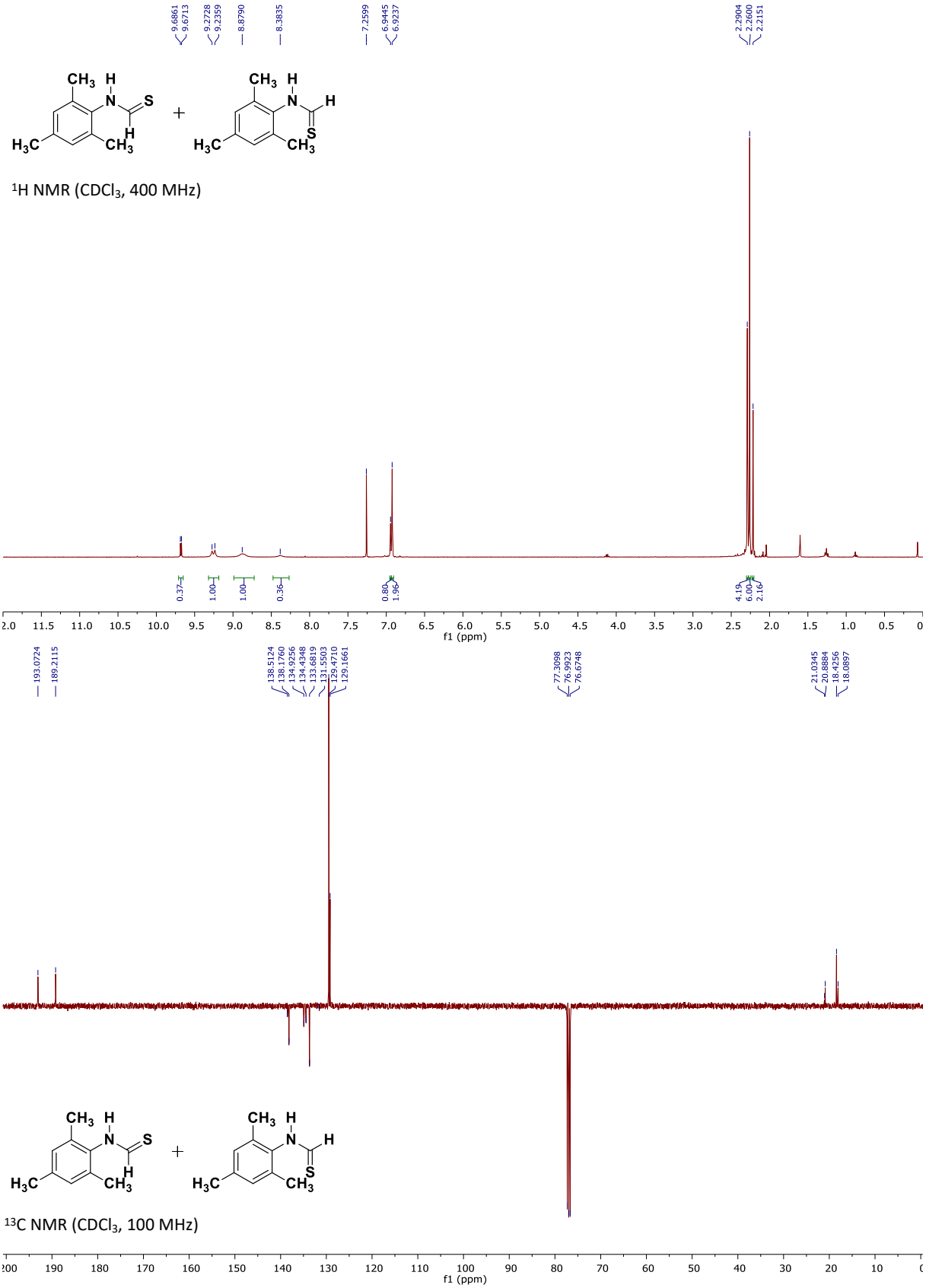




^{13}C NMR ($CDCl_3$, 100 MHz)



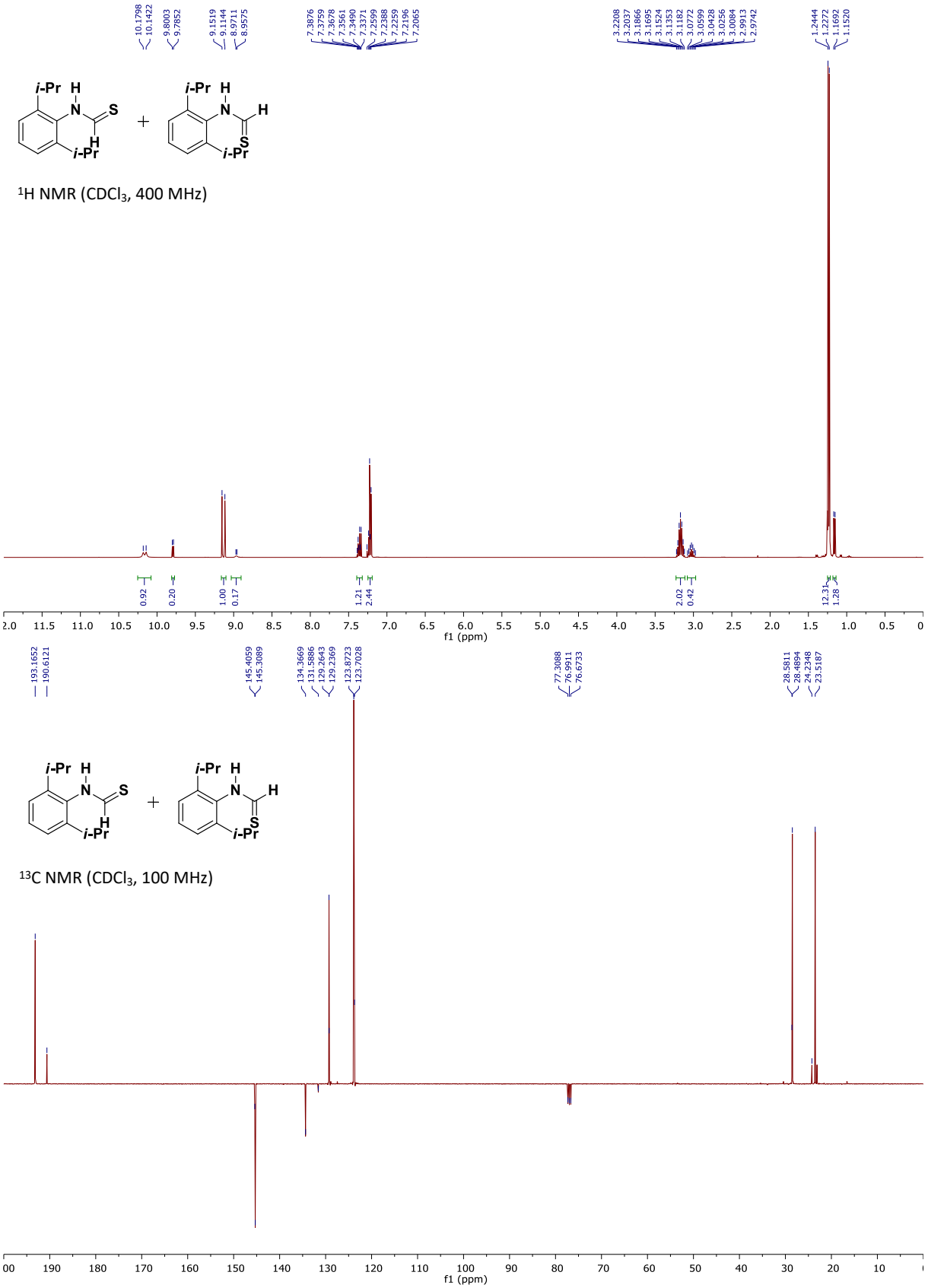
_N_-Mesitylthioformamide (9)



^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 100 MHz)

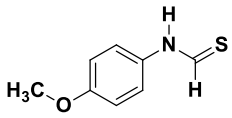
N-(2,6-Diisopropylphenyl)thioformamide (10)



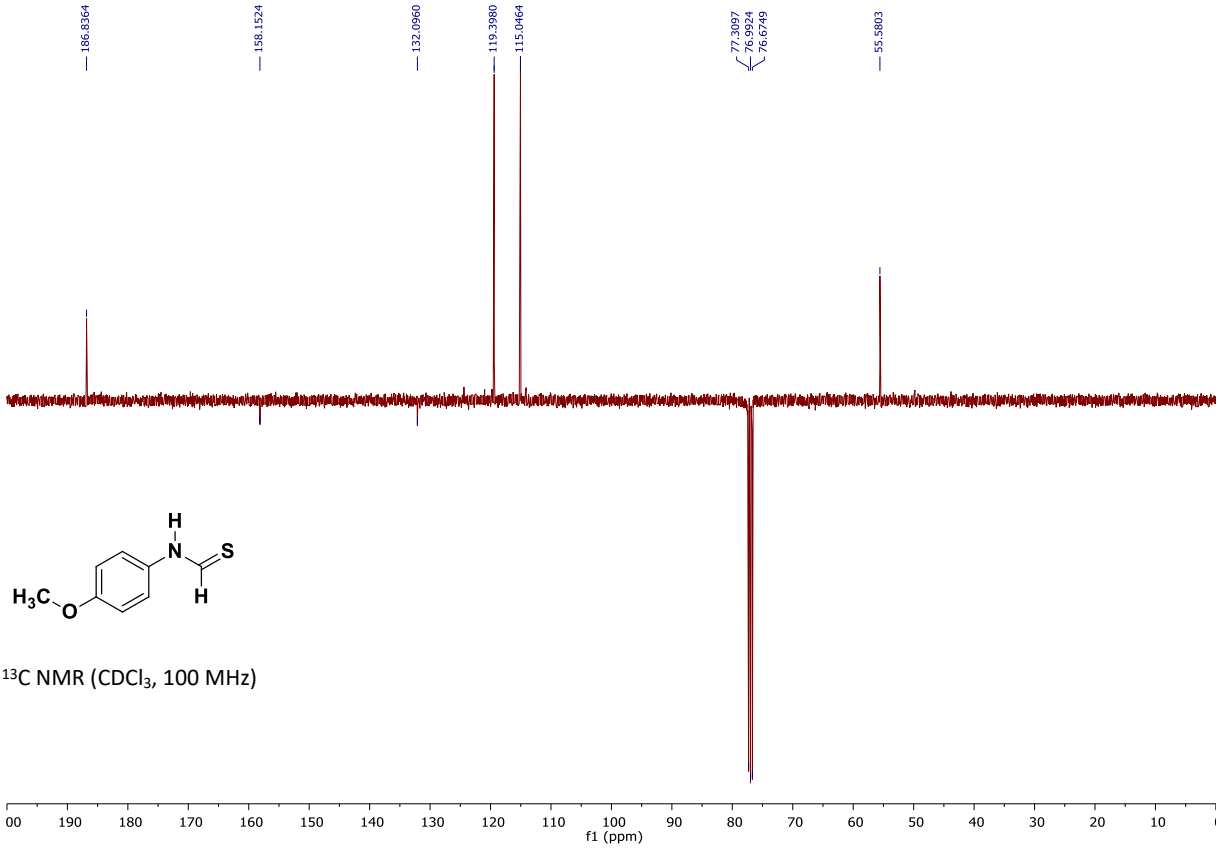
^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(4-Methoxyphenyl)thioformamide (11)

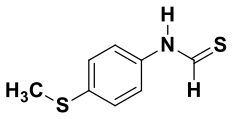


^{1}H NMR ($CDCl_3$, 400 MHz)

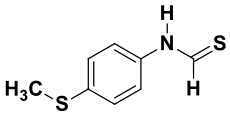


^{13}C NMR ($CDCl_3$, 100 MHz)

N-[4-(Methylsulfanyl)phenyl)]thioformamide (12)

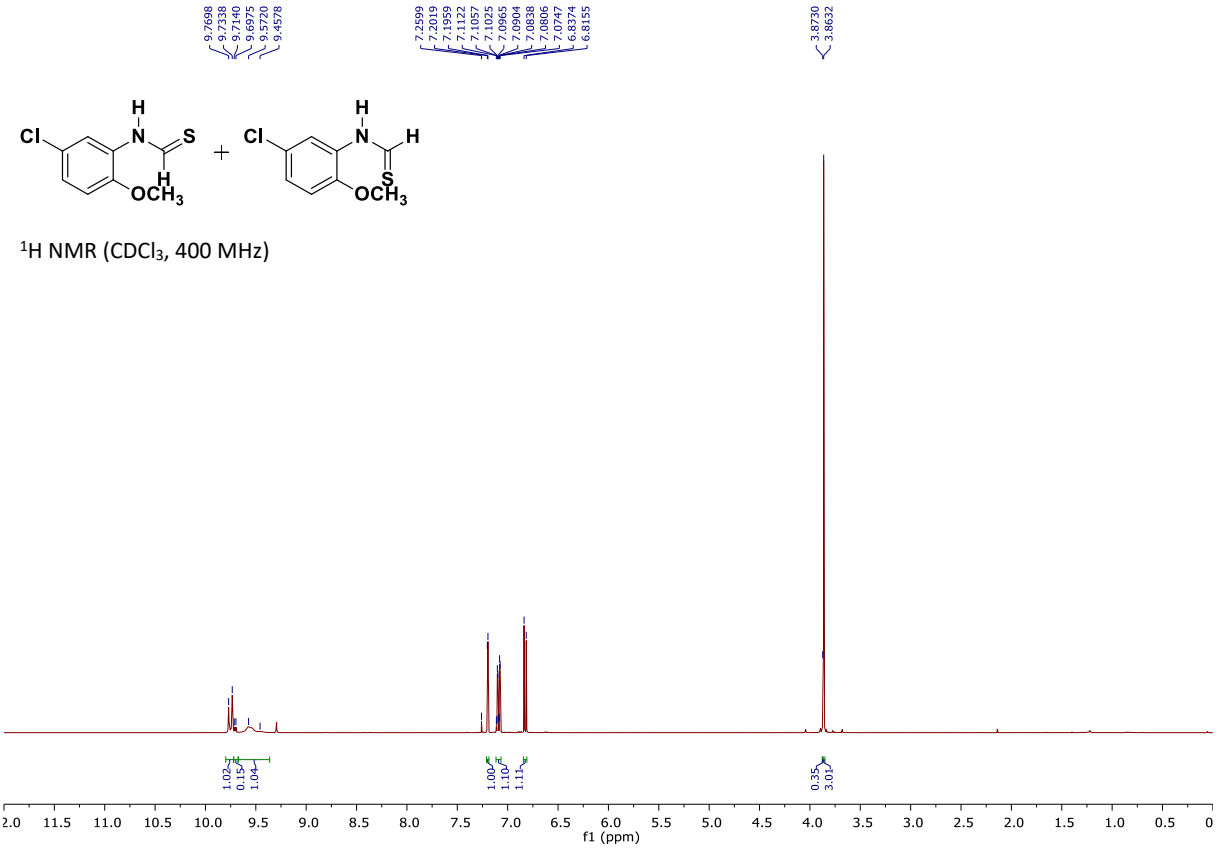


^{1}H NMR ($CDCl_3$, 400 MHz)

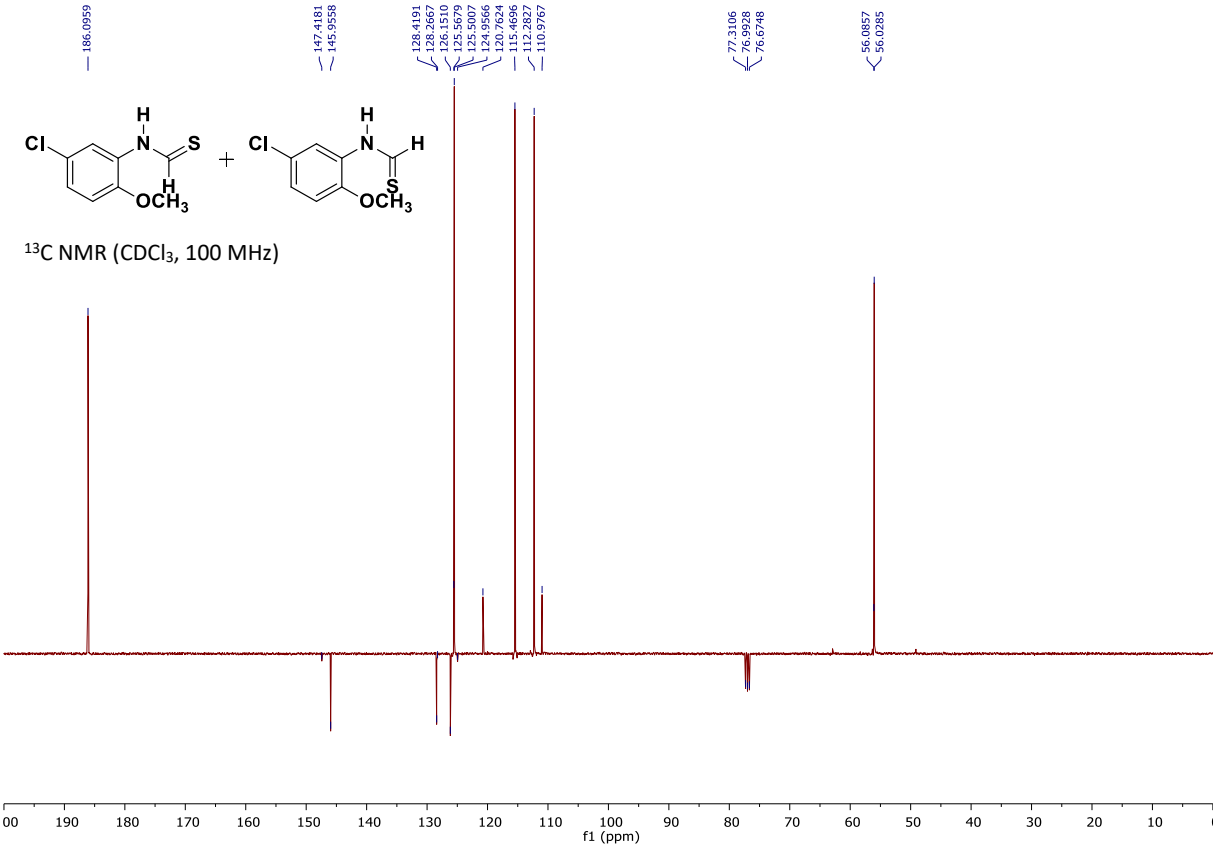


^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(5-chloro-2-methoxyphenyl)thioformamide (13)



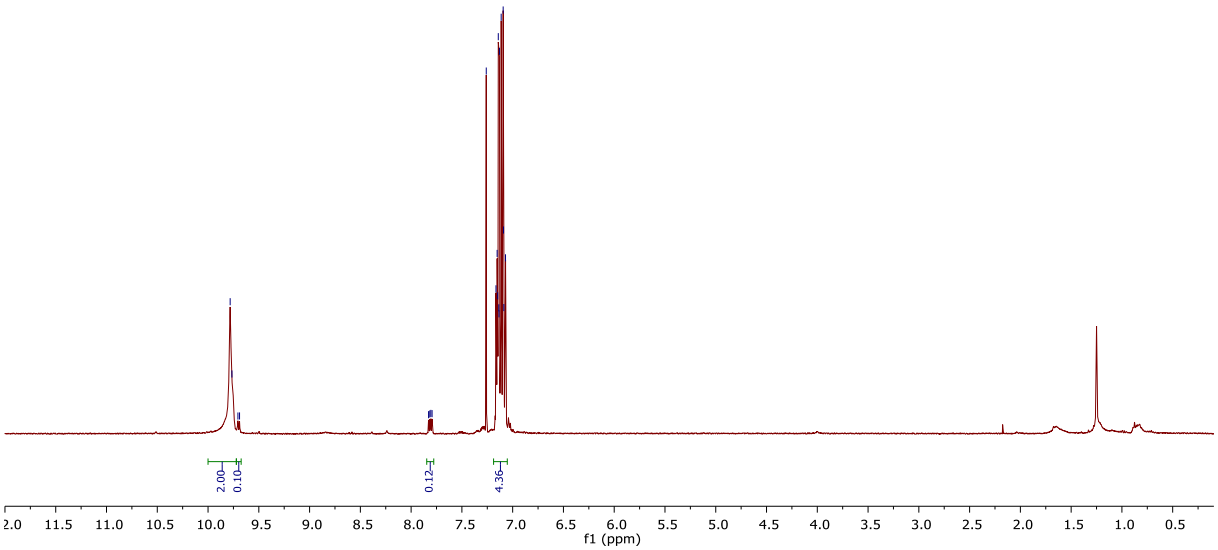
^{1}H NMR ($CDCl_3$, 400 MHz)

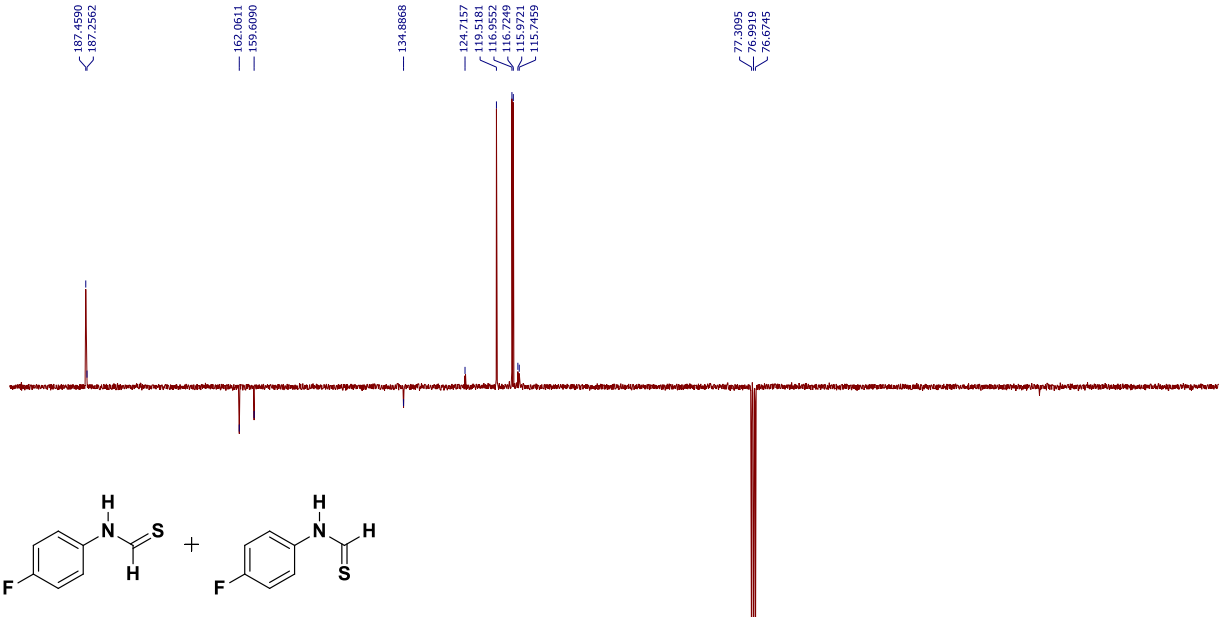


^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(4-Fluorophenyl)thioformamide (14)

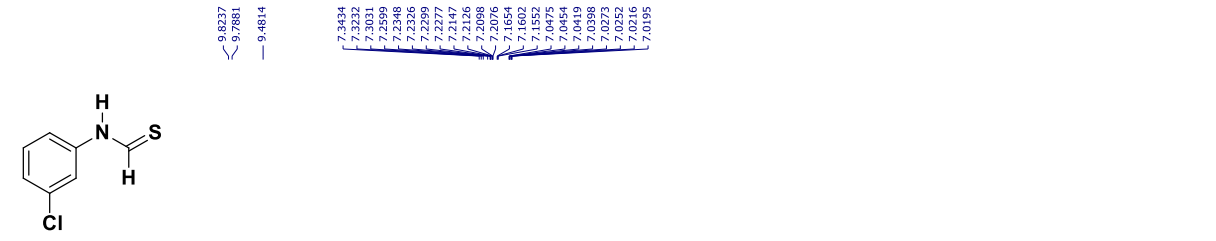
^{1}H NMR ($CDCl_3$, 400 MHz)



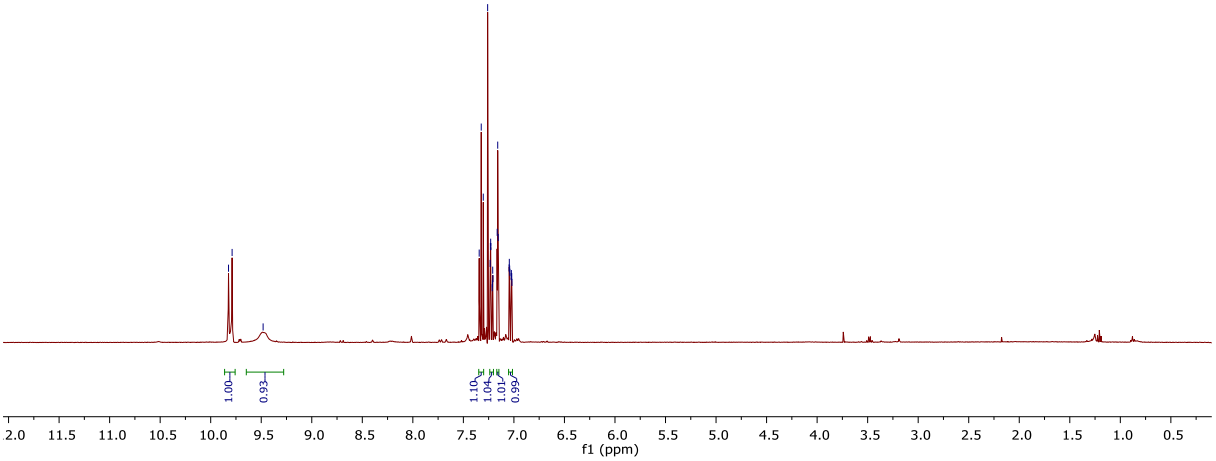


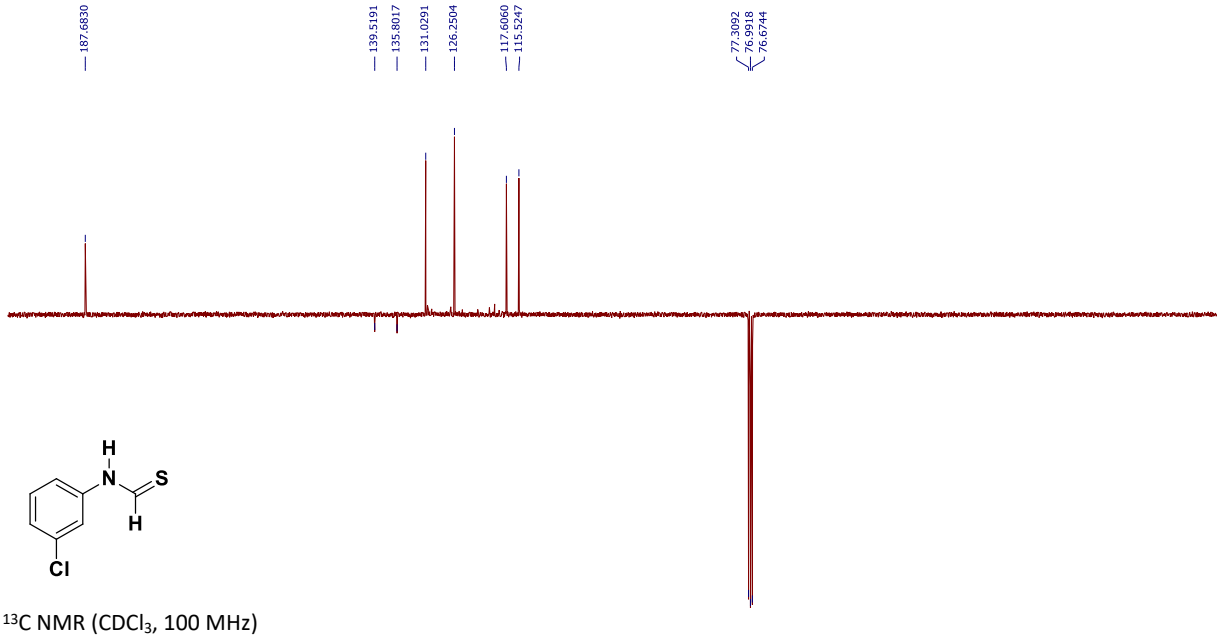
^{13}C NMR ($CDCl_3$, 100 MHz)

N-(3-Chlorophenyl)thioformamide (15)

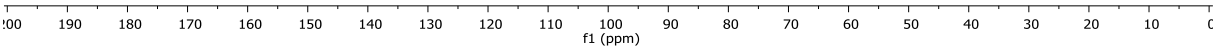


^{1}H NMR ($CDCl_3$, 400 MHz)

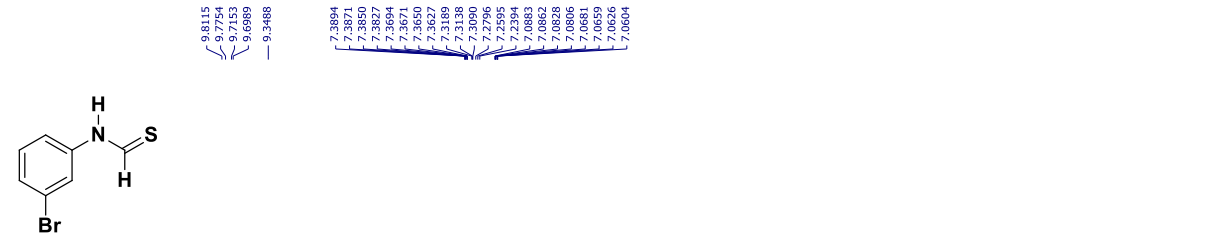




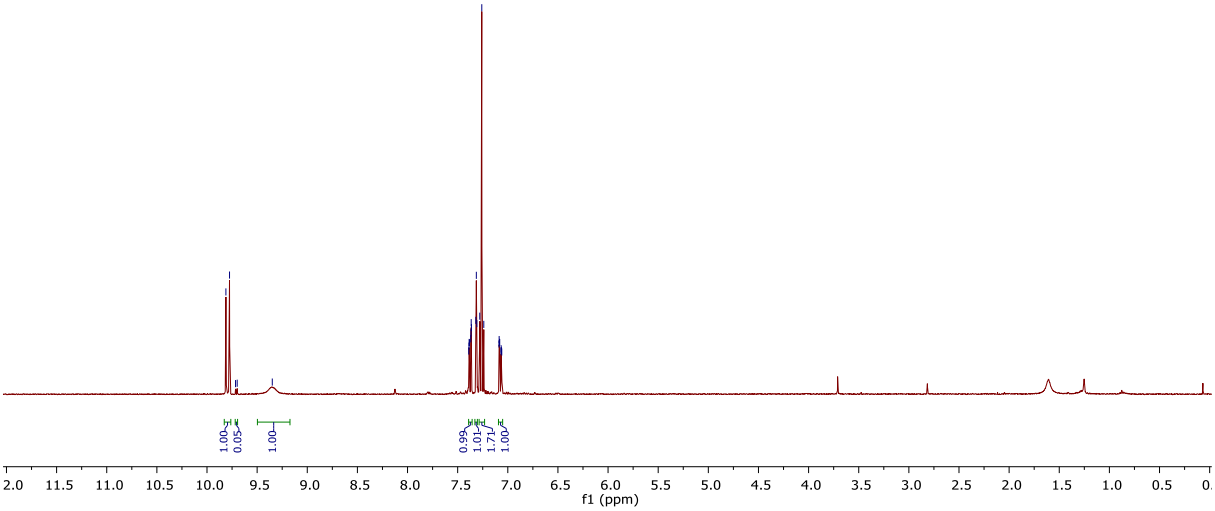
^{13}C NMR ($CDCl_3$, 100 MHz)

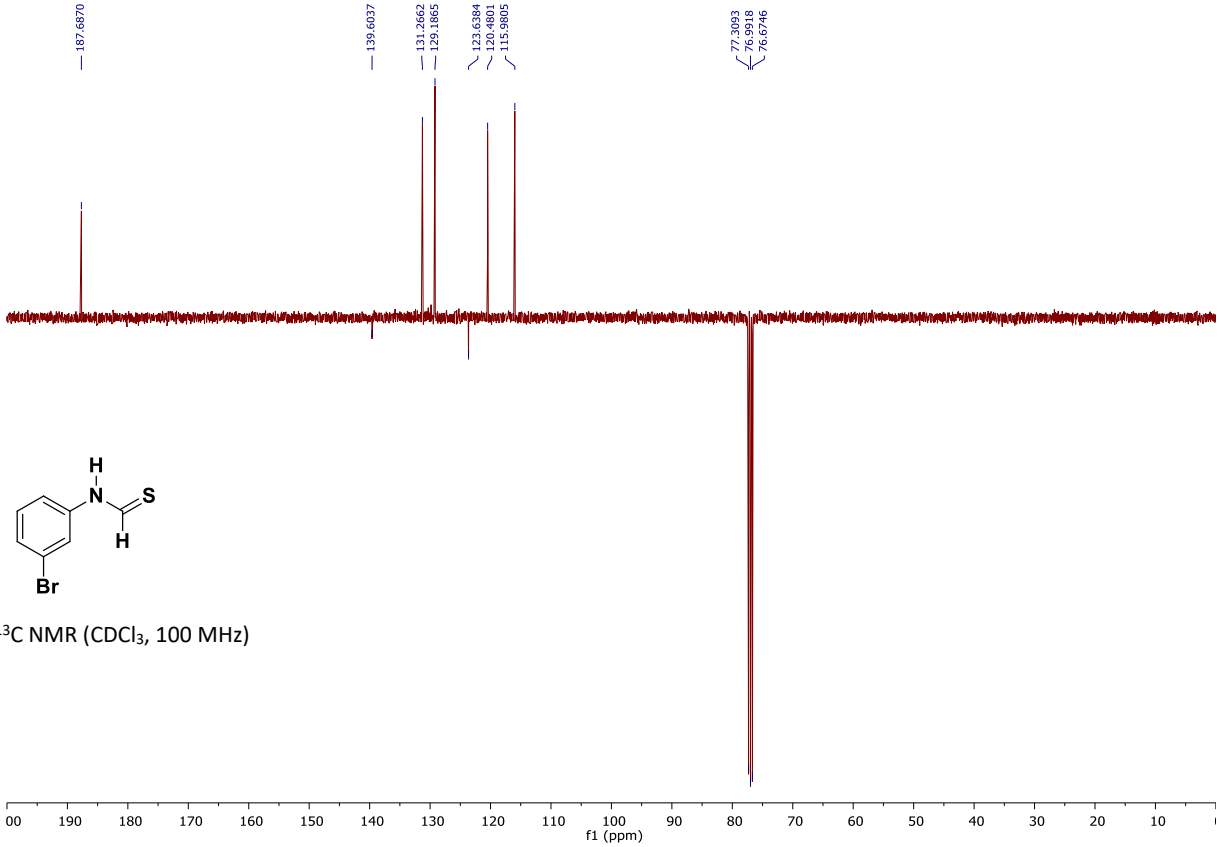


N-(3-Bromophenyl)thioformamide (16)



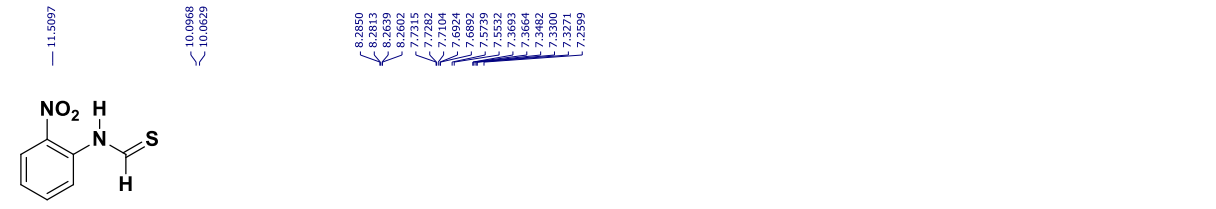
^{1}H NMR ($CDCl_3$, 400 MHz)



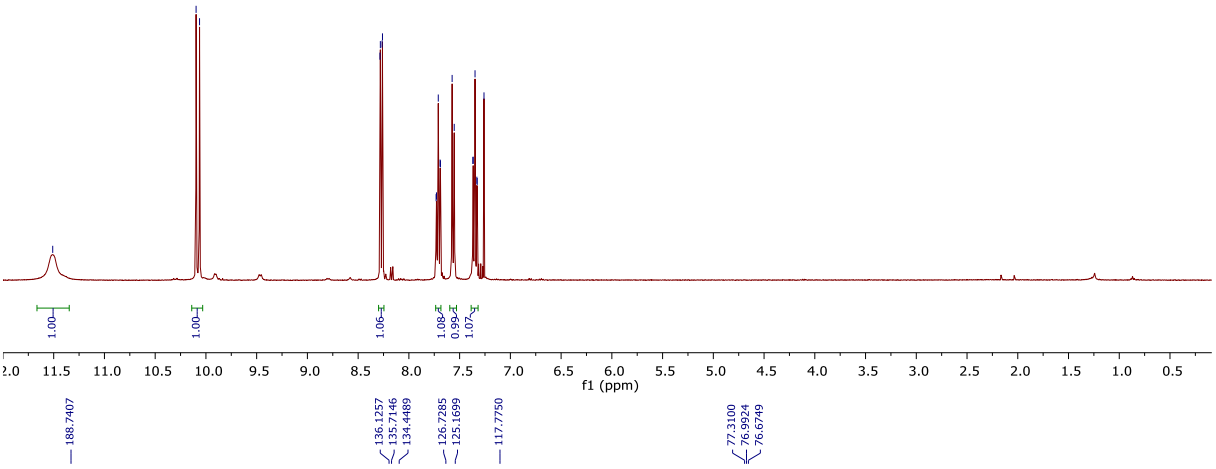


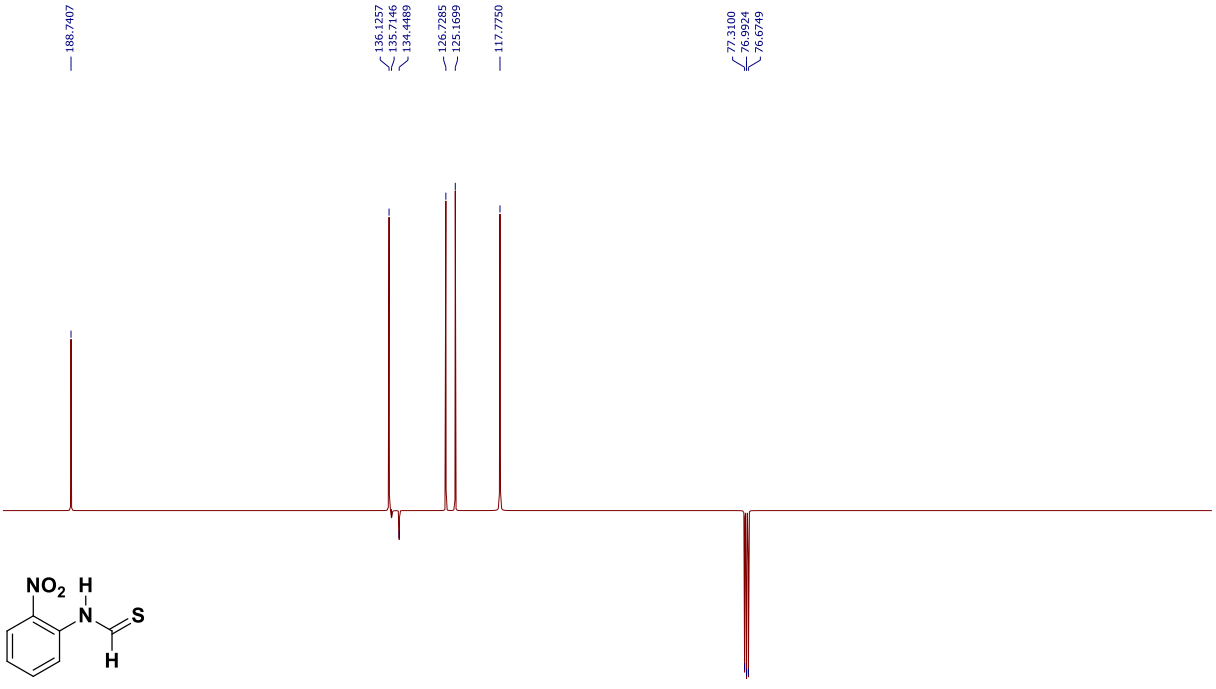
^{13}C NMR ($CDCl_3$, 100 MHz)

N-(2-Nitrophenyl)thioformamide (17)

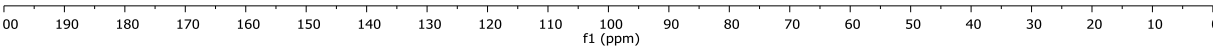


^{1}H NMR ($CDCl_3$, 400 MHz)

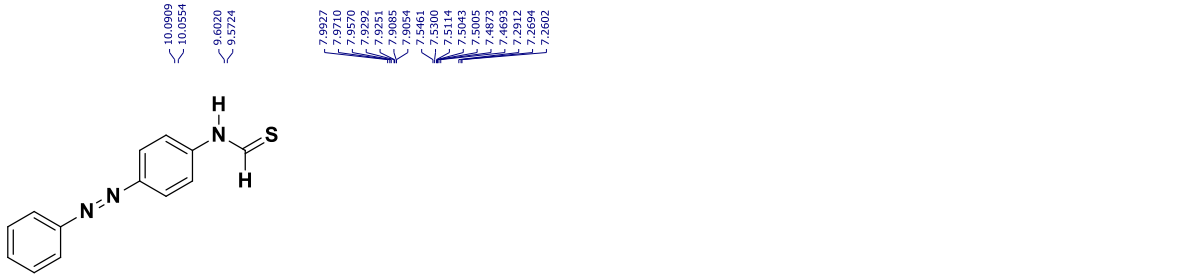




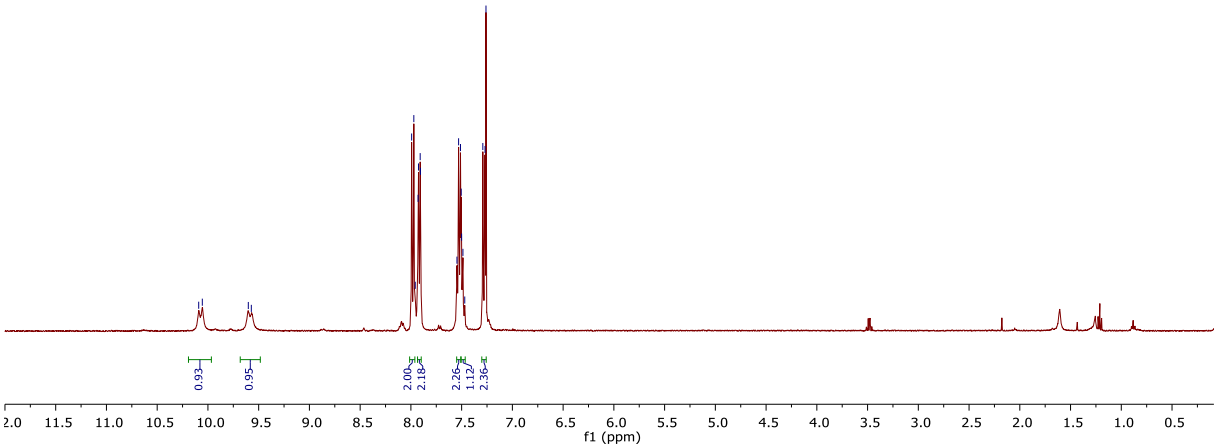
^{13}C NMR ($CDCl_3$, 100 MHz)

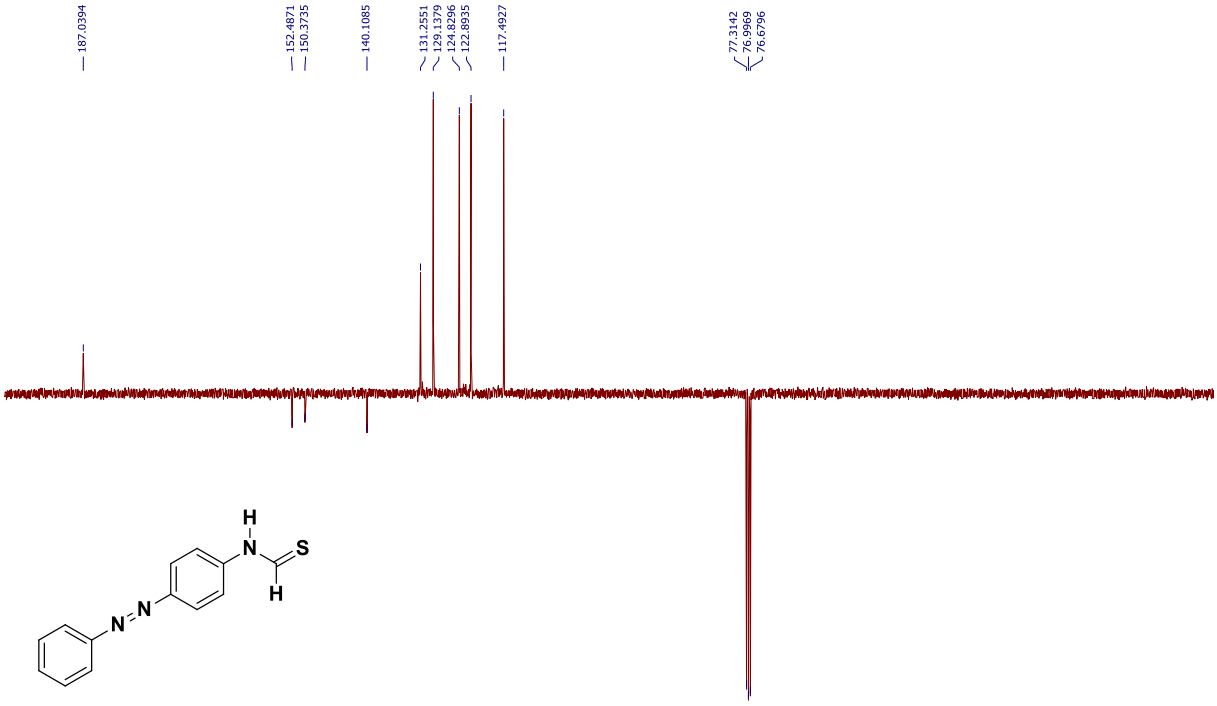


_N_-[4-(Phenyldiazenyl)phenyl]thioformamide (18)

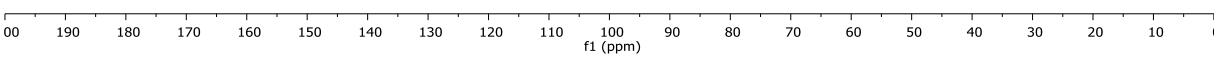


^{1}H NMR ($CDCl_3$, 400 MHz)

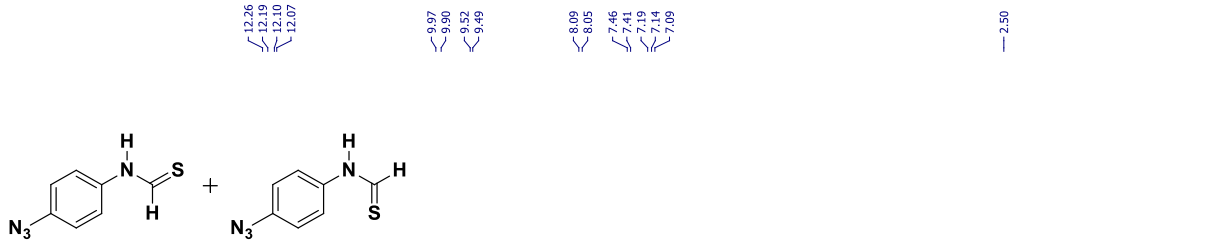




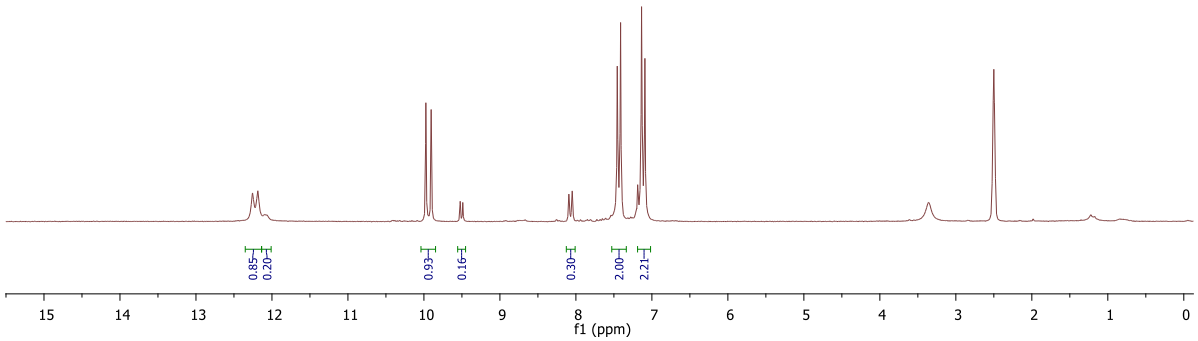
^{13}C NMR ($CDCl_3$, 100 MHz)

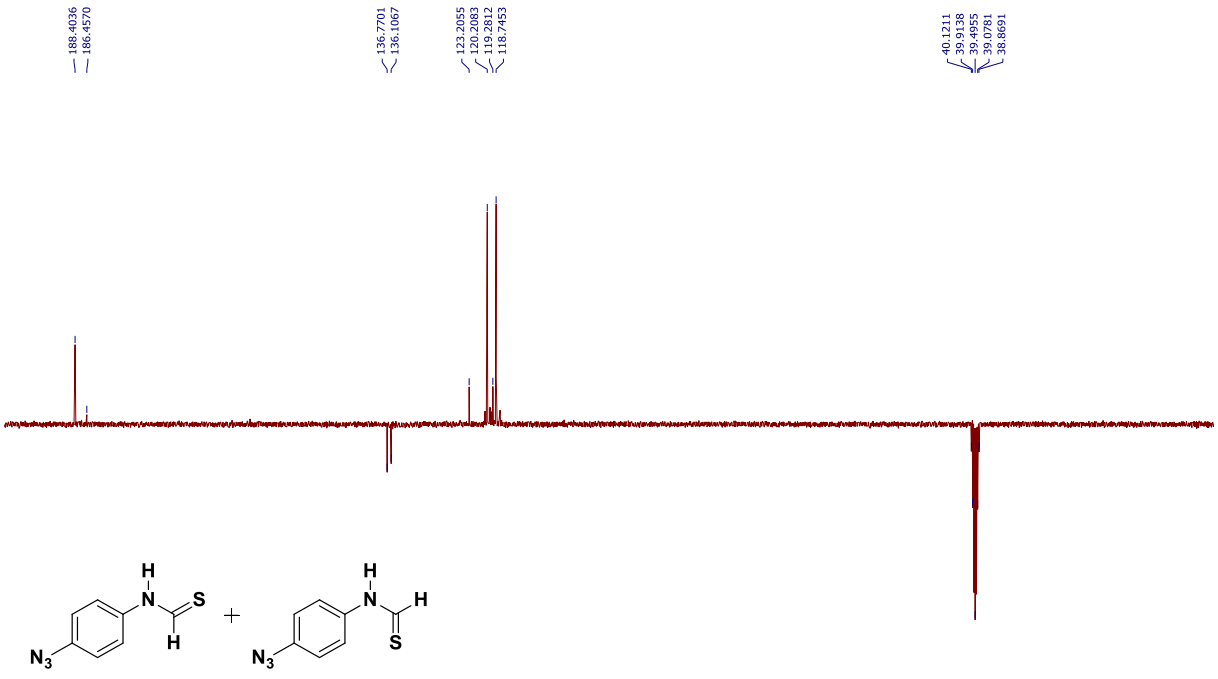


N-(4-Azidophenyl)thioformamide (19)

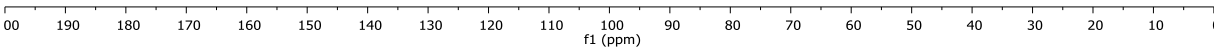


^{1}H NMR (DMSO-d_6, 200 MHz)

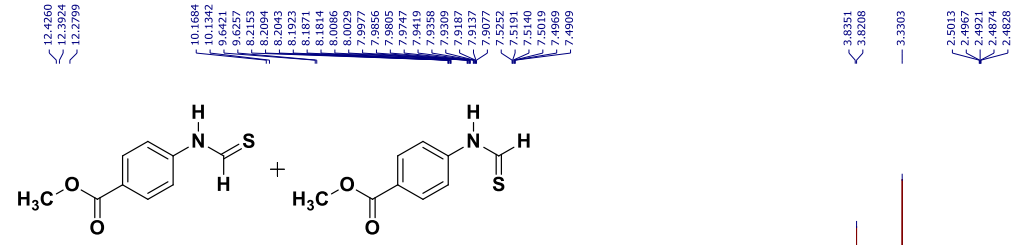




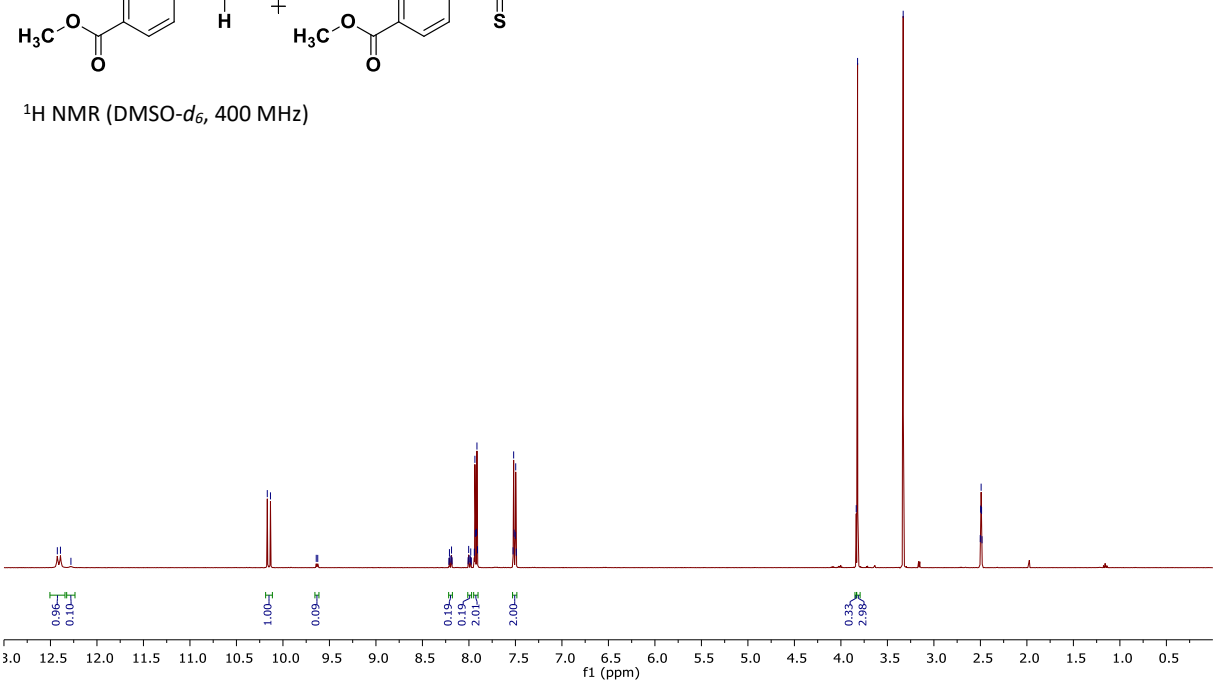
^{13}C NMR (DMSO-d_6, 100 MHz)

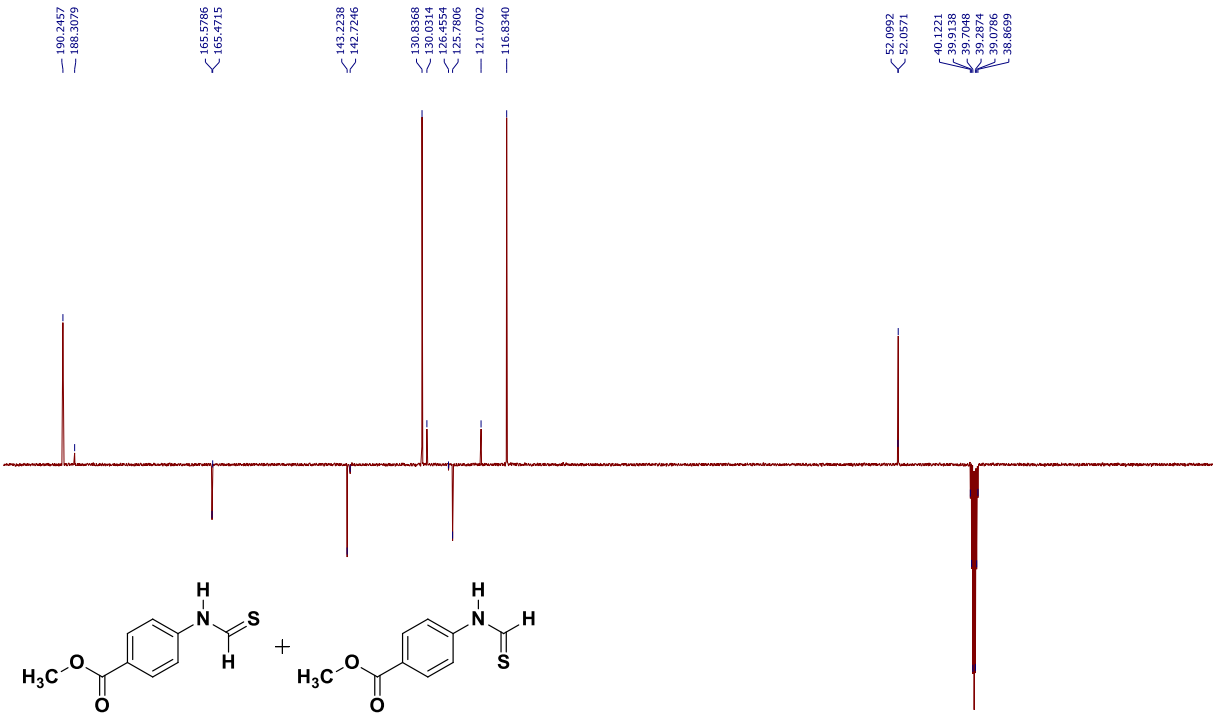


Methyl 4-(thioformylamino) benzoate (20)

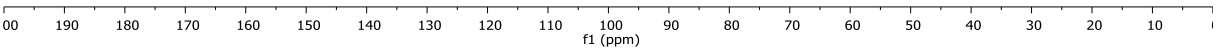


^{1}H NMR (DMSO-d_6, 400 MHz)

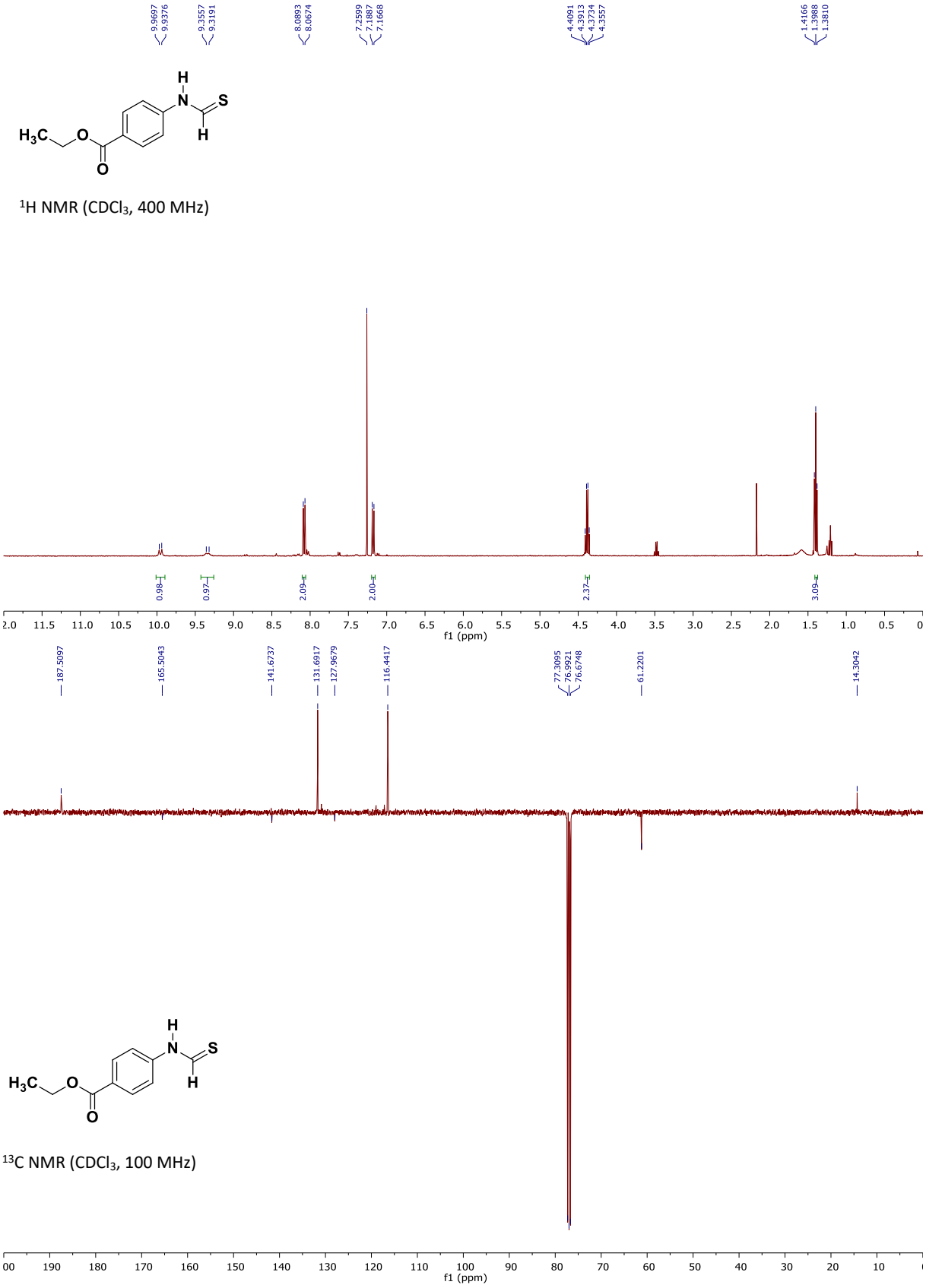




^{13}C NMR (DMSO-d_6, 100 MHz)



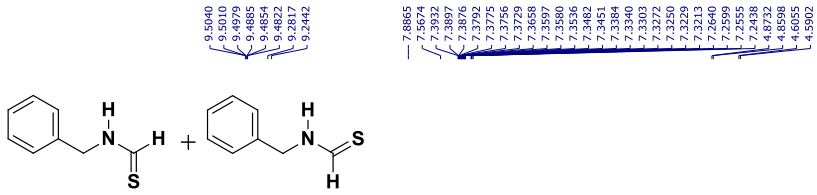
Ethyl 4-(thioformylamino) benzoate (21)



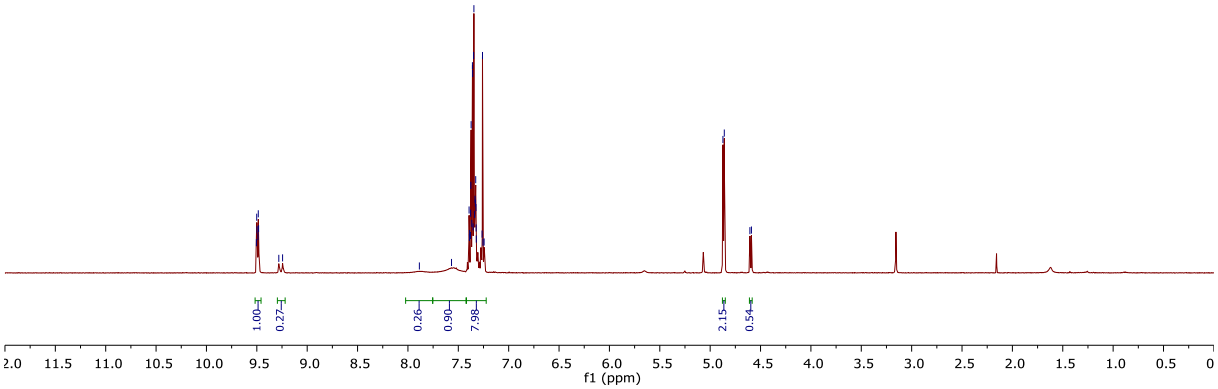
^{1}H NMR ($CDCl_3$, 400 MHz)

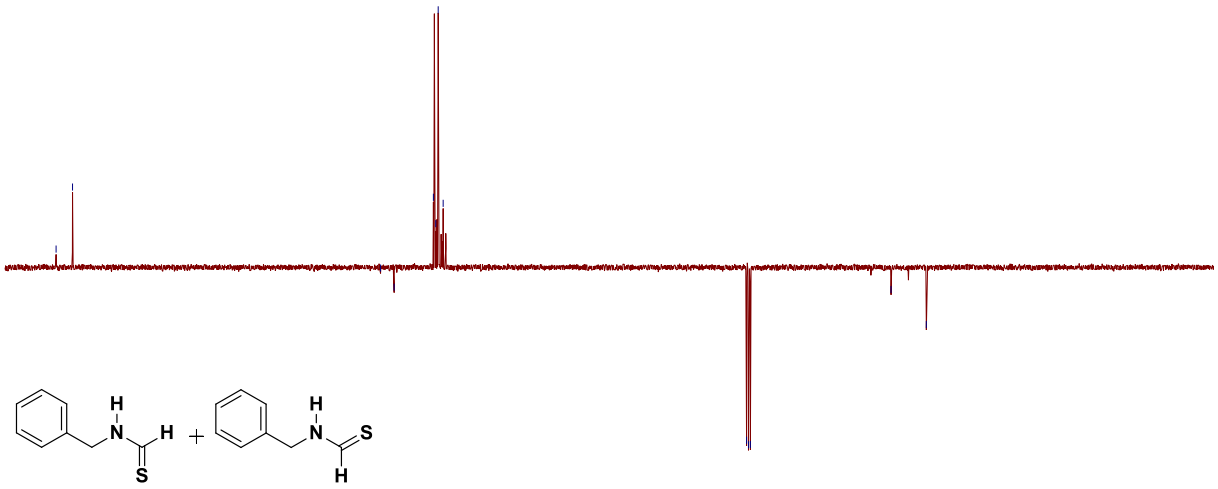
^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-Benzylthioformamide (22)

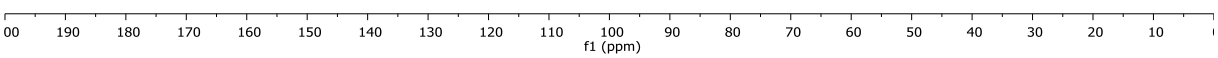


^{1}H NMR ($CDCl_3$, 400 MHz)

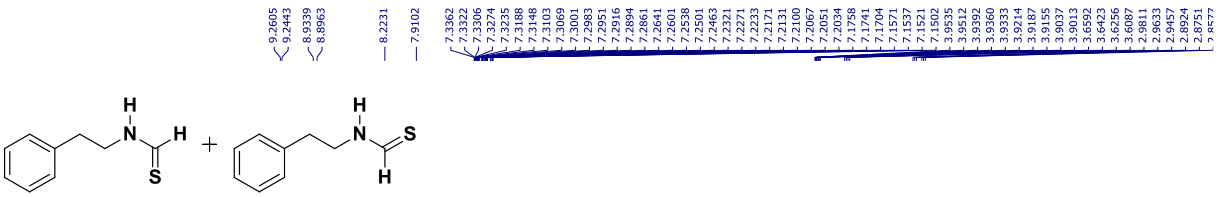




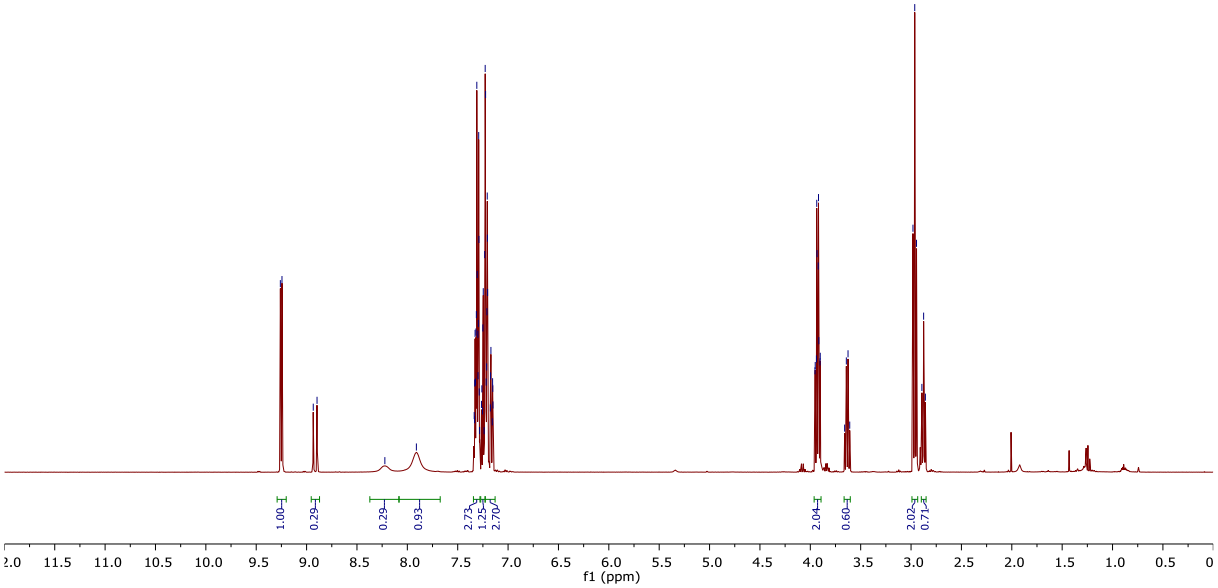
^{13}C NMR ($CDCl_3$, 100 MHz)

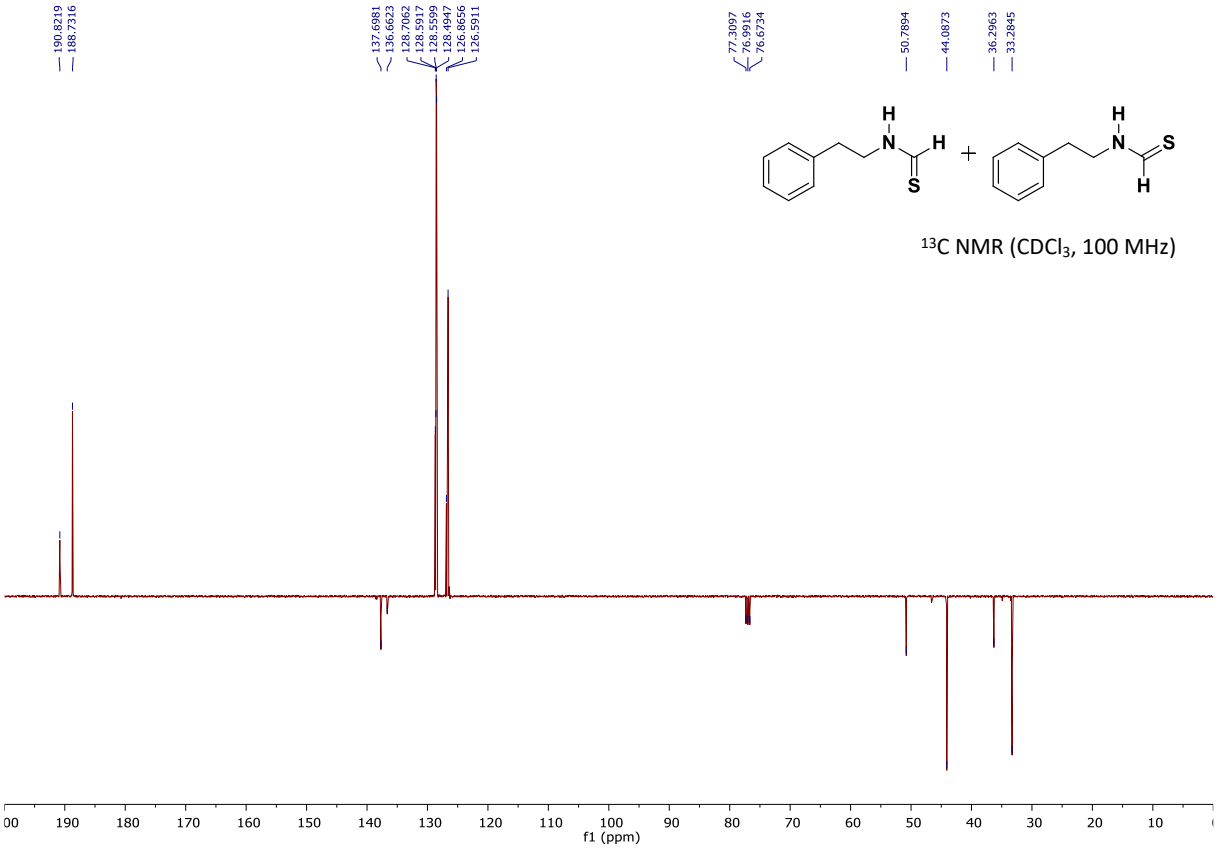


N-(2-Phenethyl)thioformamide (23)



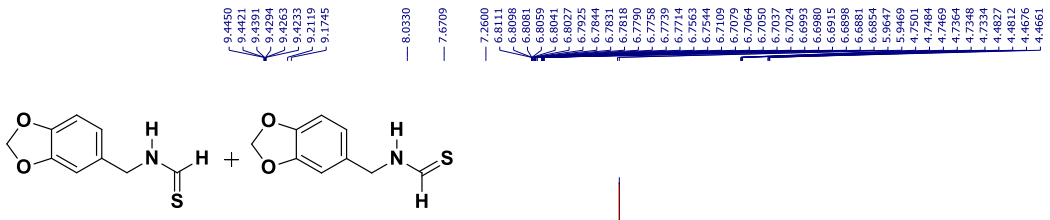
^{1}H NMR ($CDCl_3$, 400 MHz)



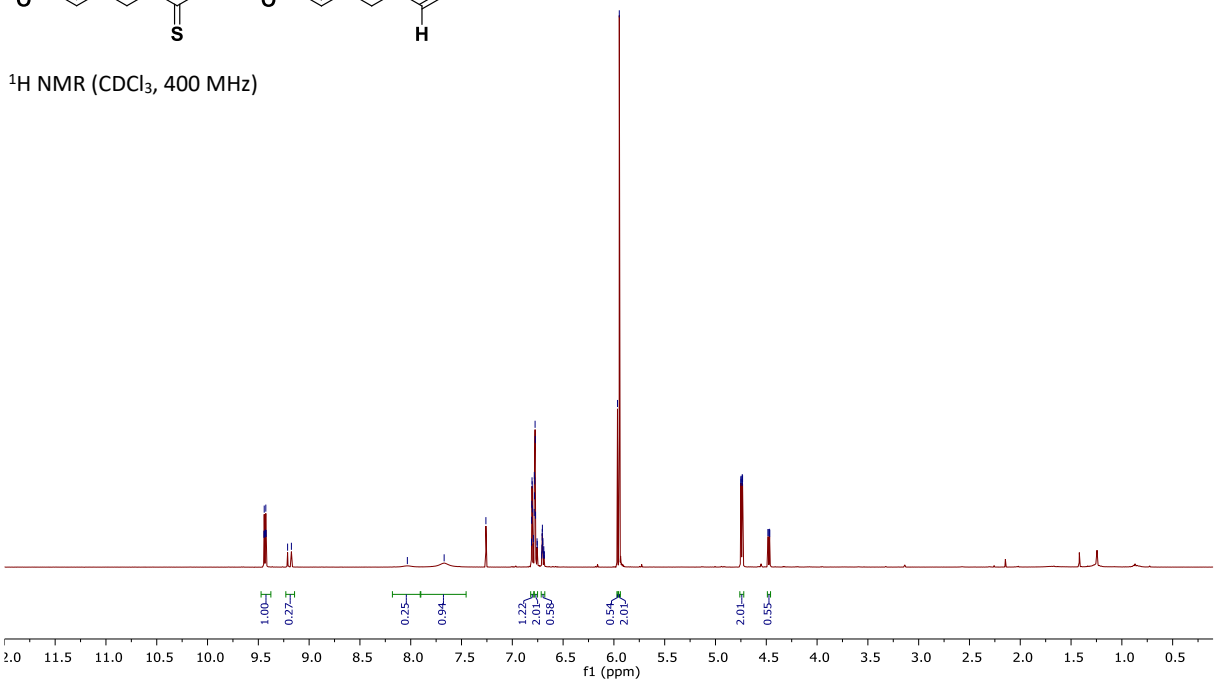


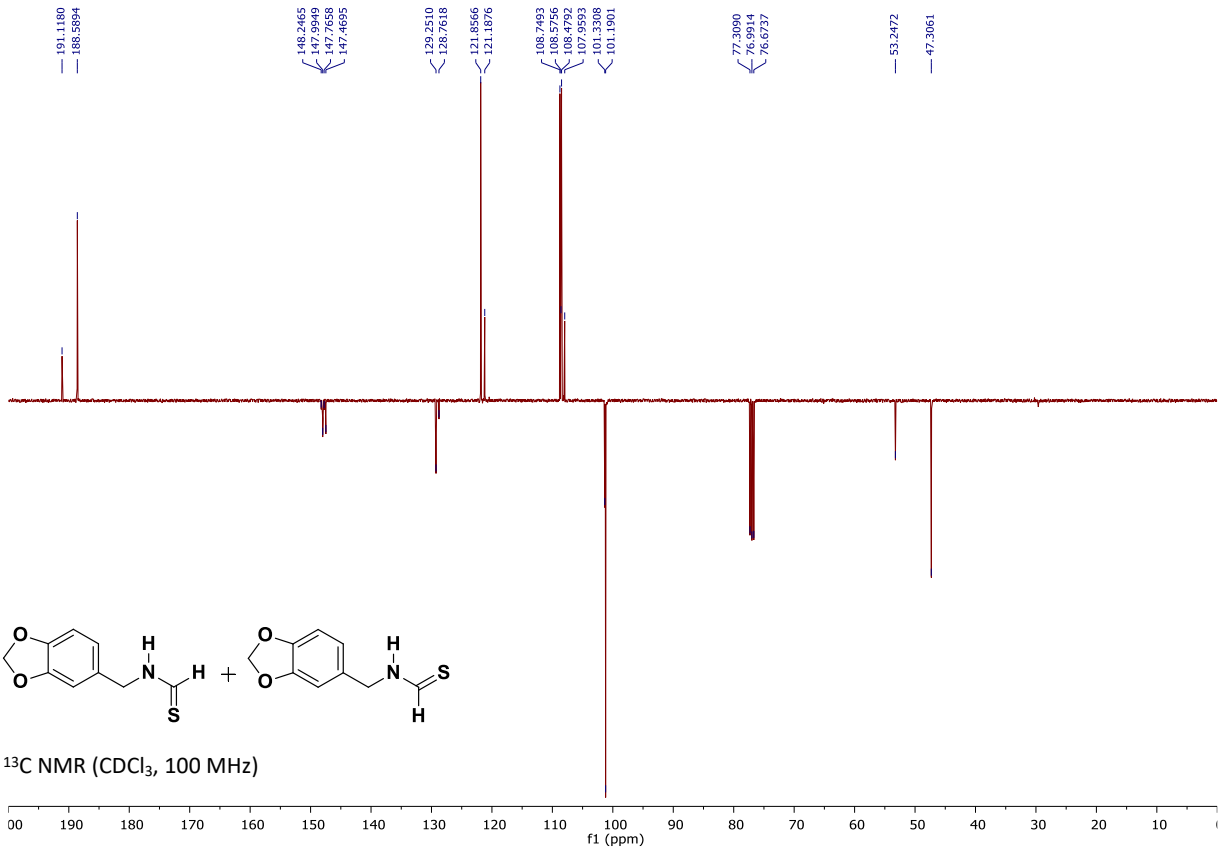
^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(1,3-Benzodioxol-5-ylmethyl)thioformamide (24)



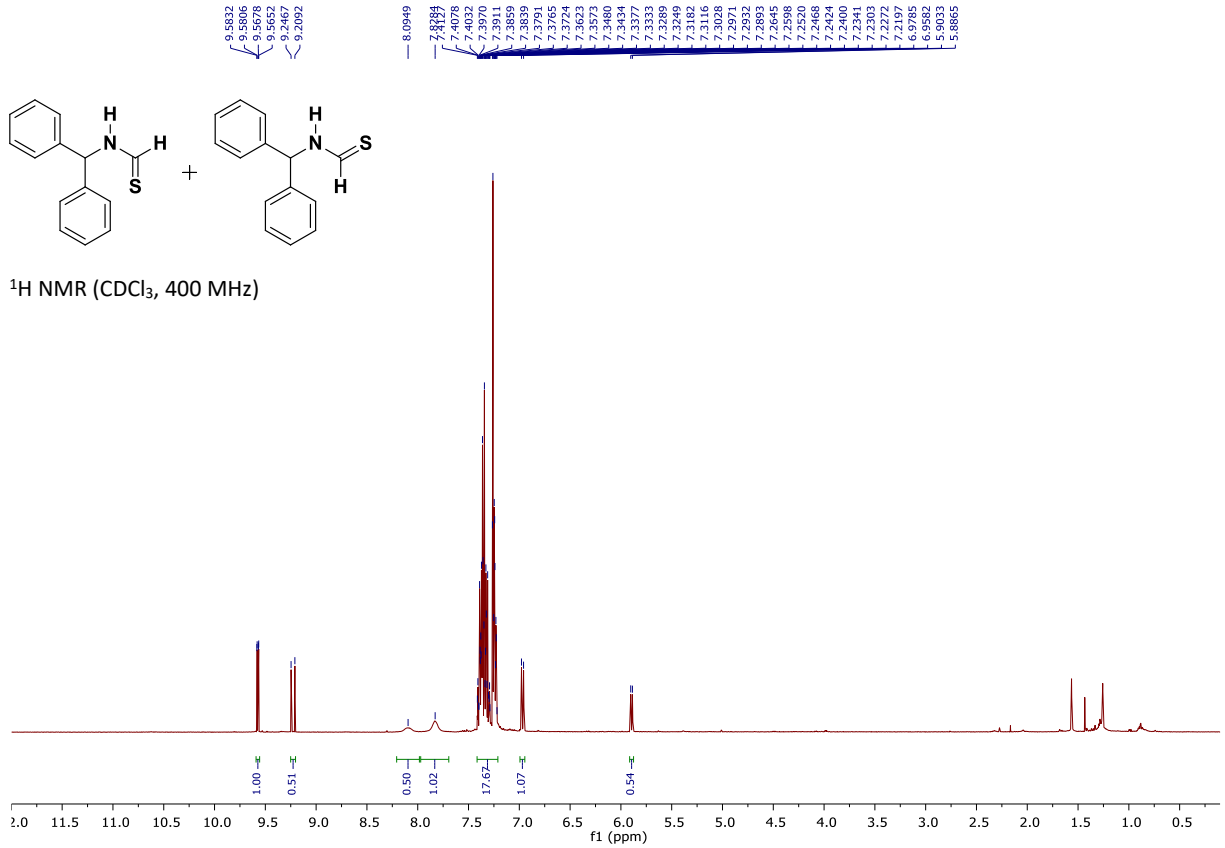
^{1}H NMR ($CDCl_3$, 400 MHz)



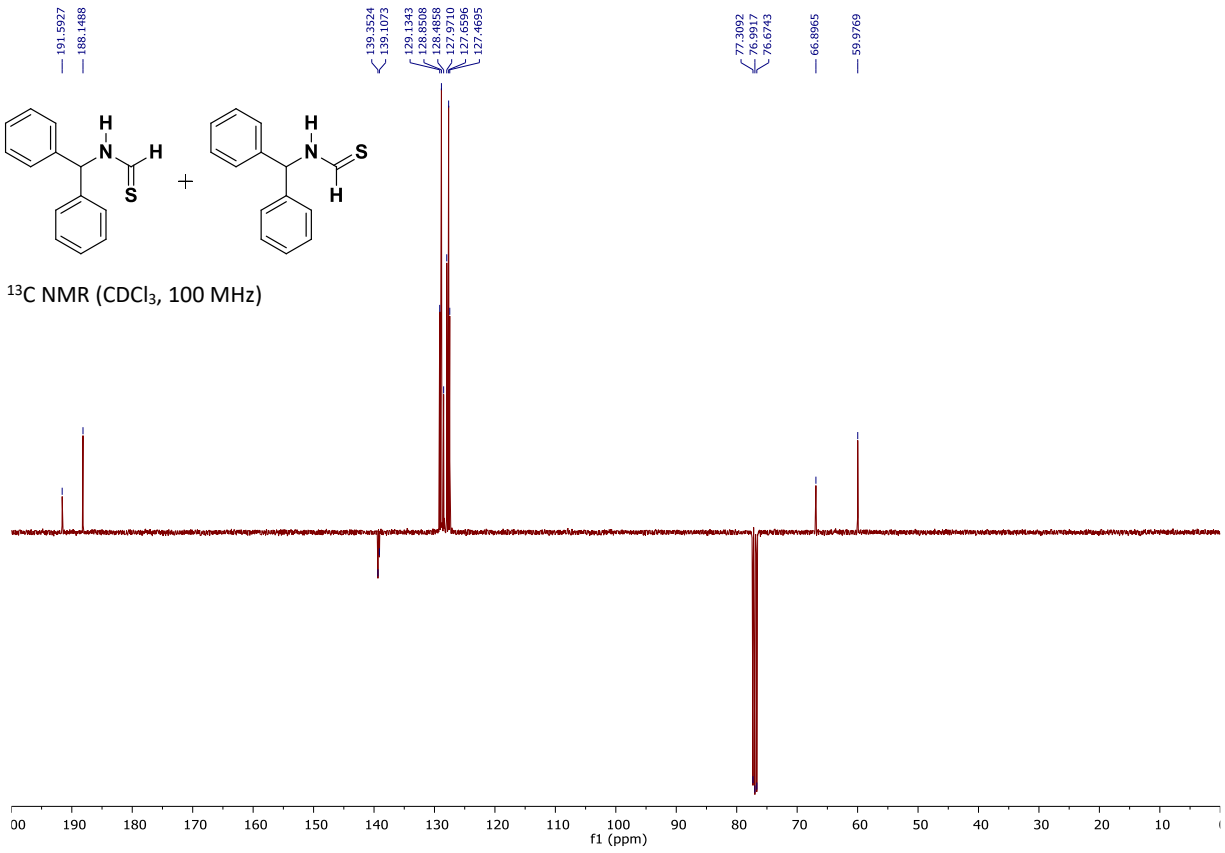


^{13}C NMR ($CDCl_3$, 100 MHz)

N-(Diphenylmethyl)thioformamide (25)

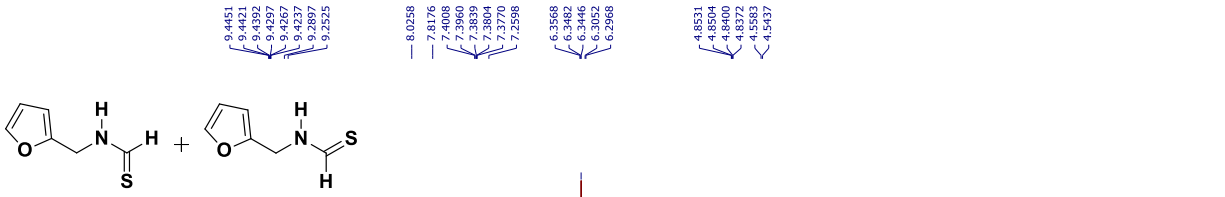


^{1}H NMR ($CDCl_3$, 400 MHz)

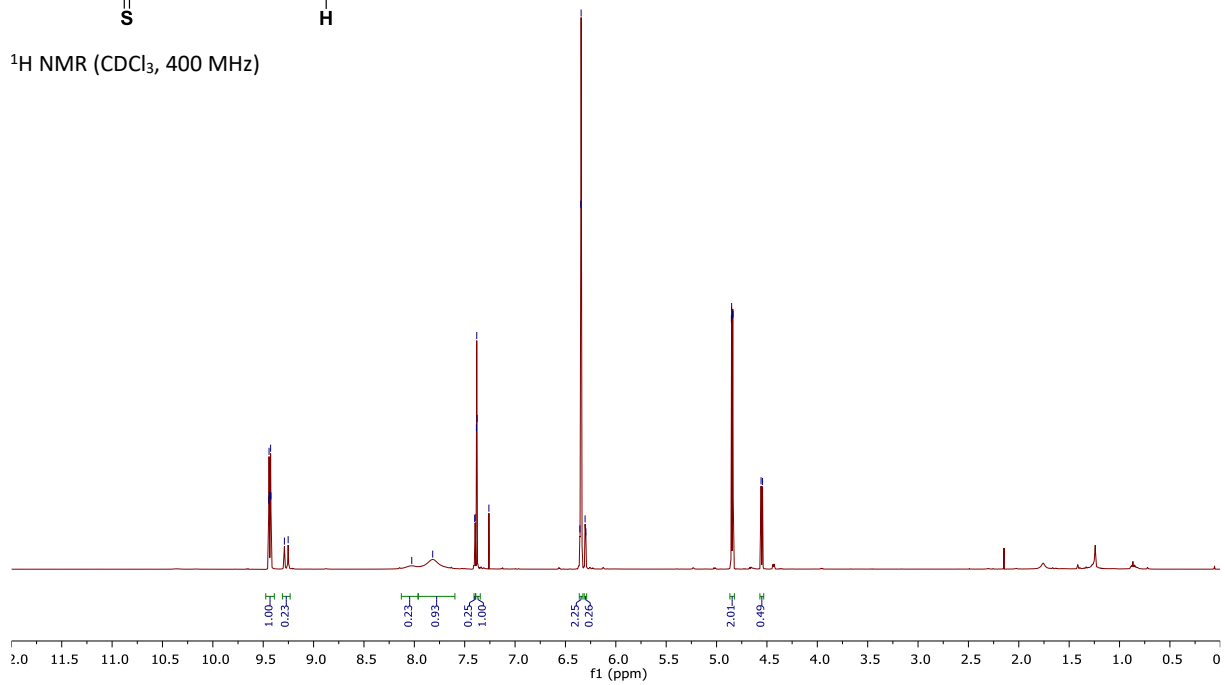


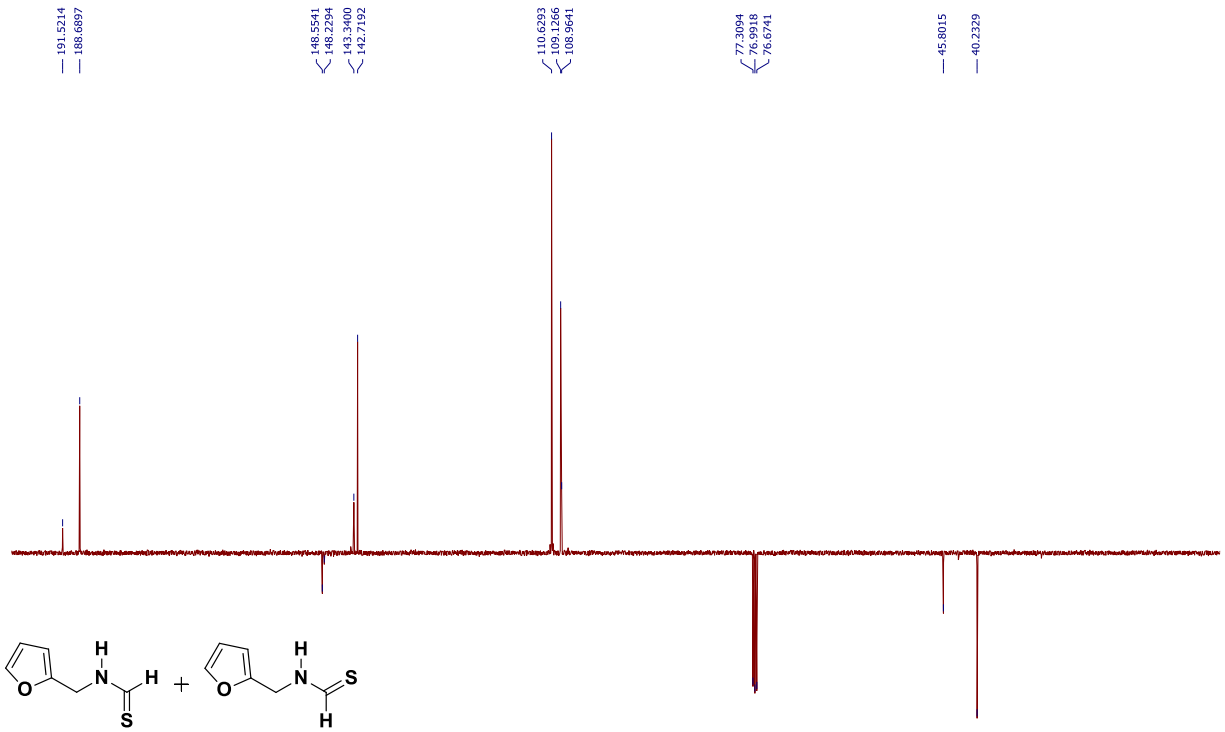
^{13}C NMR ($CDCl_3$, 100 MHz)

N-(2-Furylmethyl)thioformamide (26)



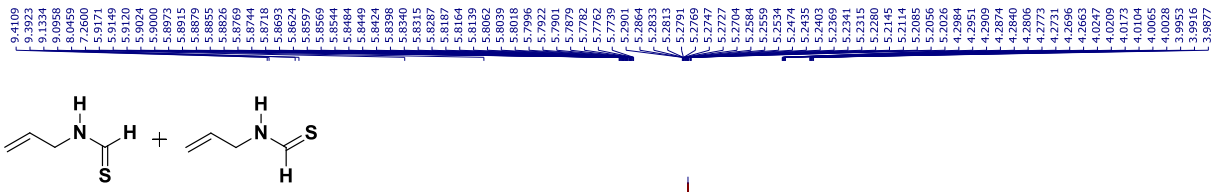
^{1}H NMR ($CDCl_3$, 400 MHz)



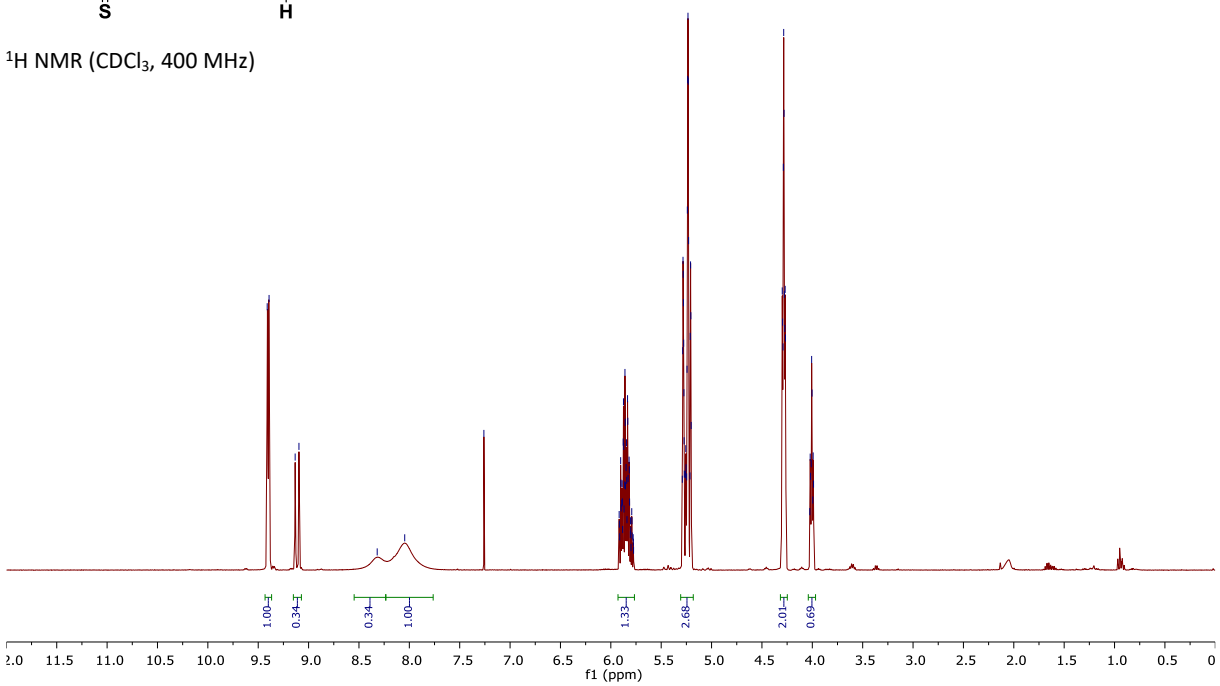


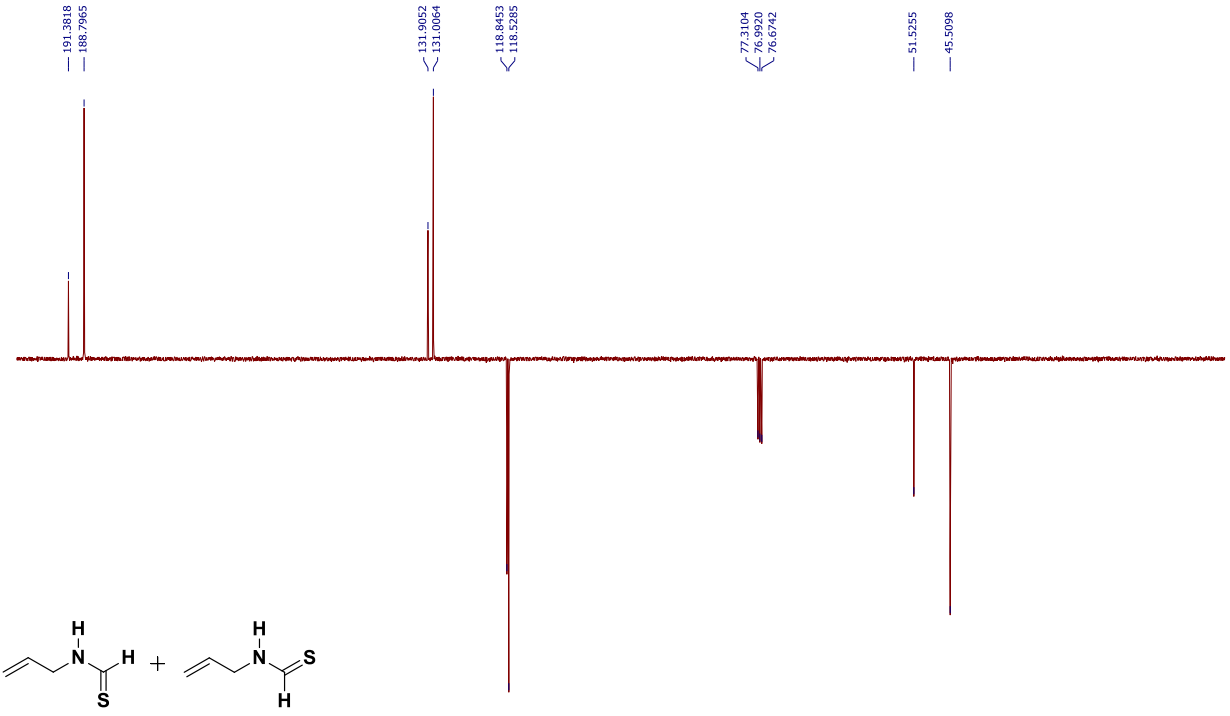
^{13}C NMR ($CDCl_3$, 100 MHz)

N-Allylthioformamide (27)

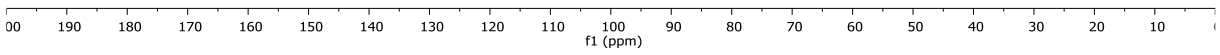


^{1}H NMR ($CDCl_3$, 400 MHz)

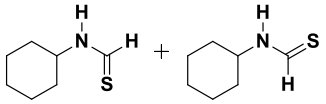




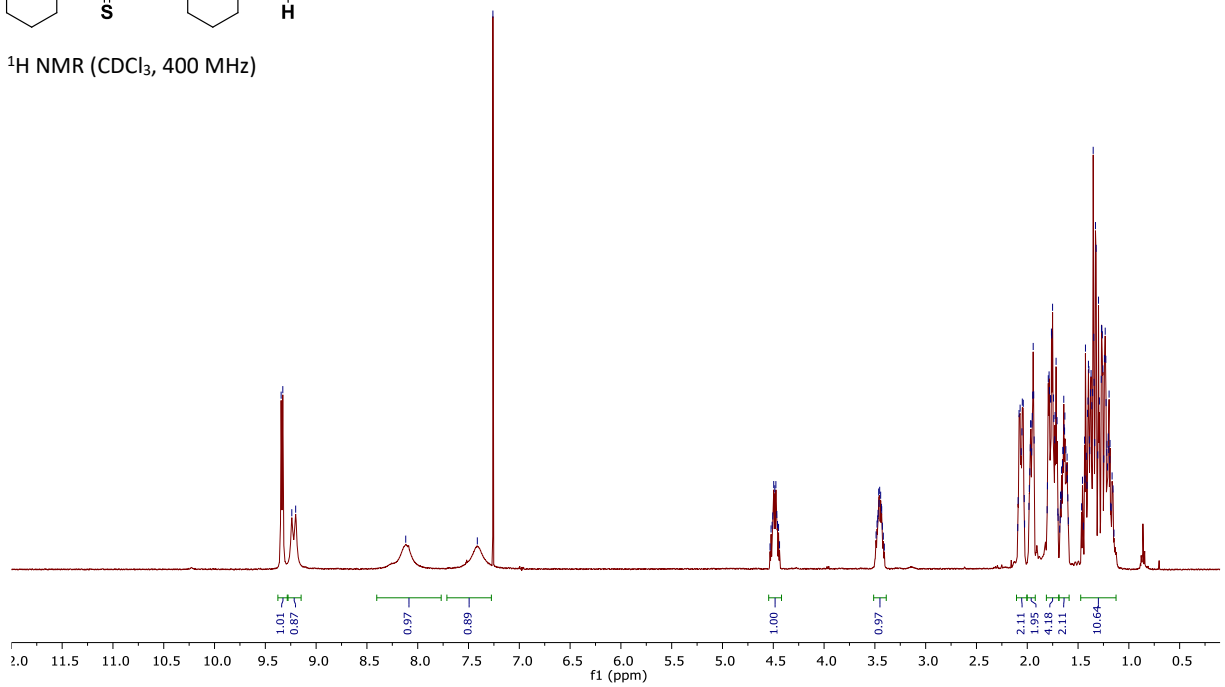
^{13}C NMR ($CDCl_3$, 100 MHz)

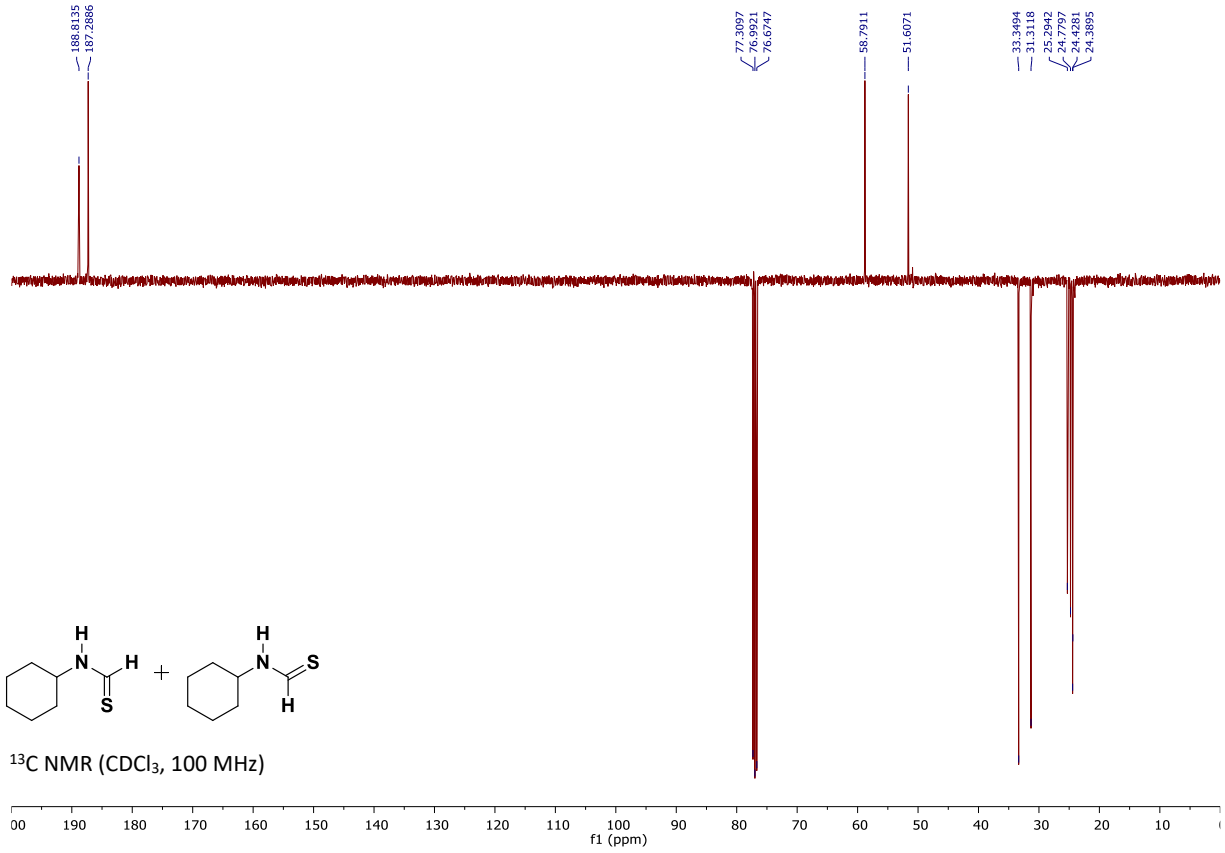


N-Cyclohexylthioformamide (28)



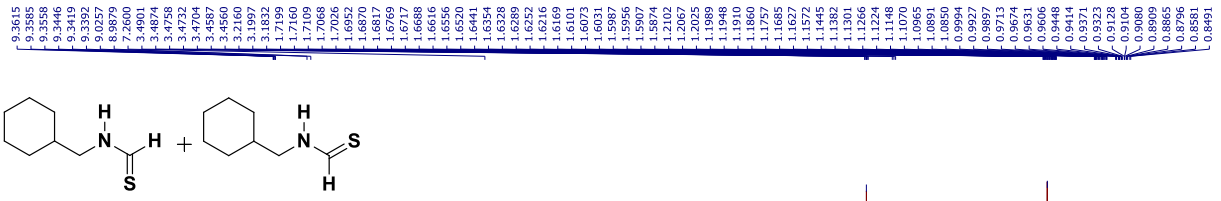
^{1}H NMR ($CDCl_3$, 400 MHz)



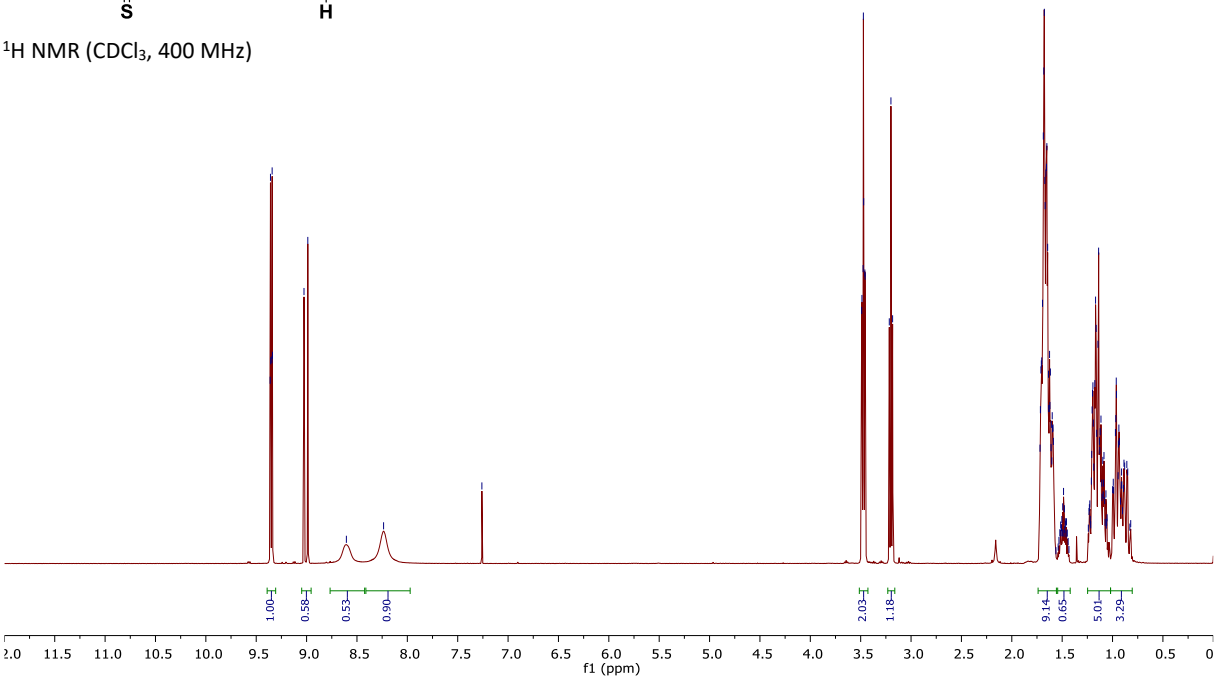


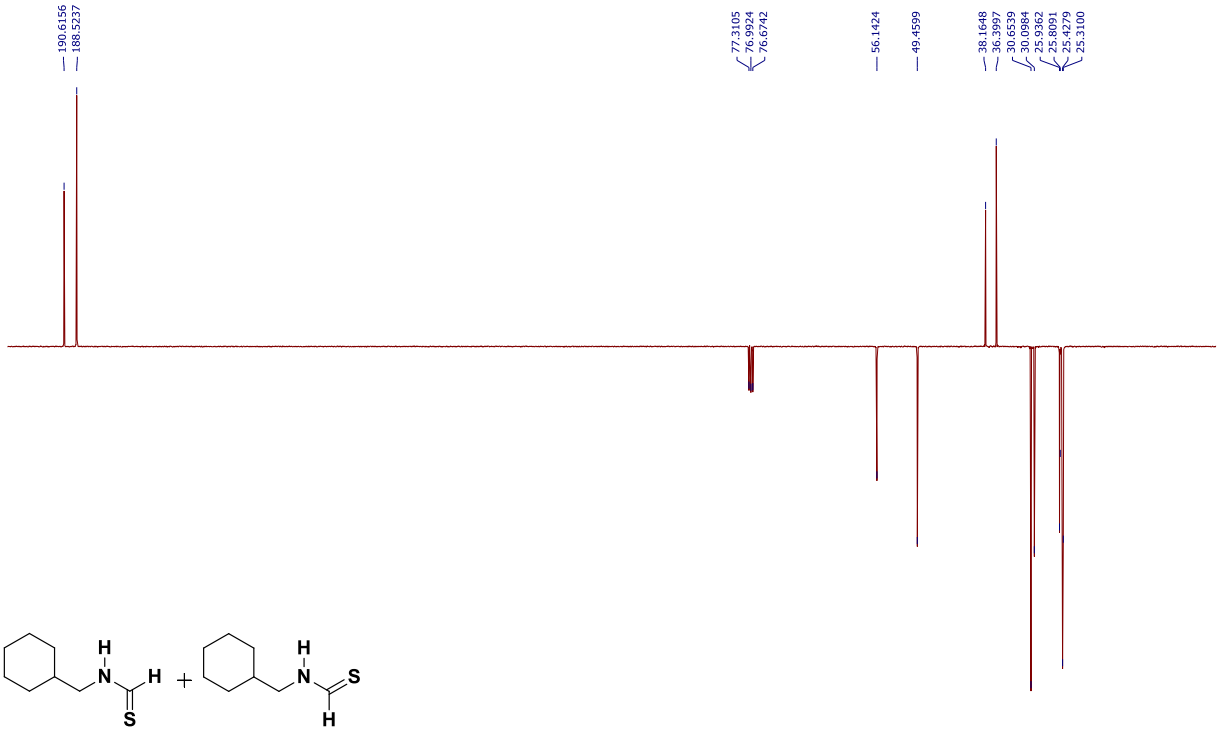
^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(Cyclohexylmethyl)thioformamide (29)

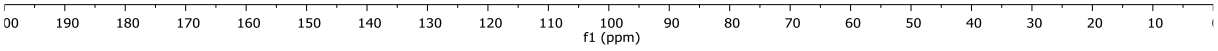


^{1}H NMR ($CDCl_3$, 400 MHz)

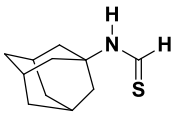




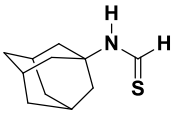
^{13}C NMR ($CDCl_3$, 100 MHz)



N-Adamantan-1-ylthioformamide (30)



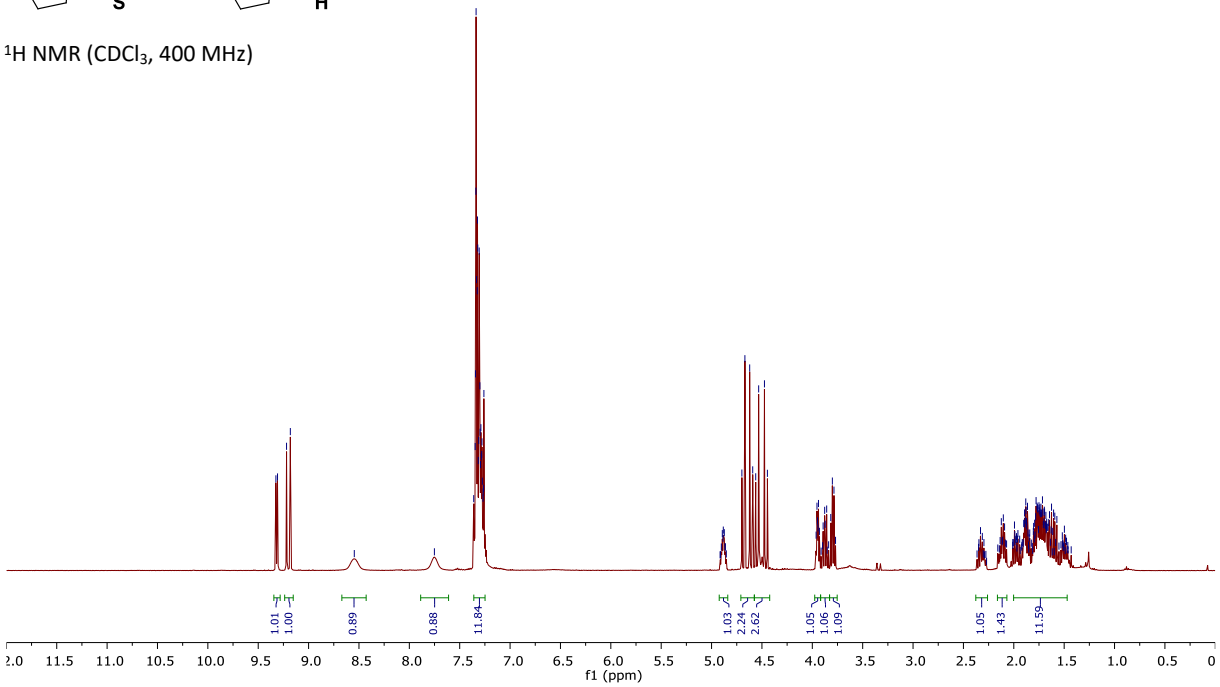
^{1}H NMR ($CDCl_3$, 400 MHz)

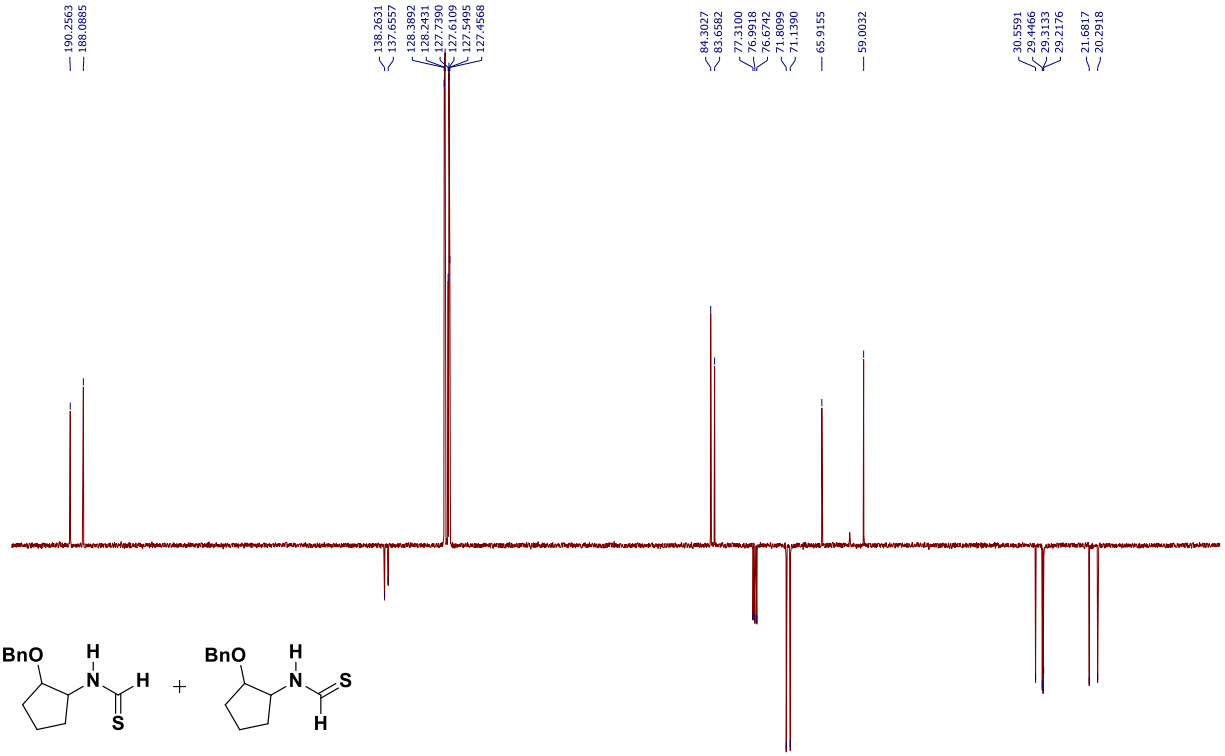


^{13}C NMR ($CDCl_3$, 100 MHz)

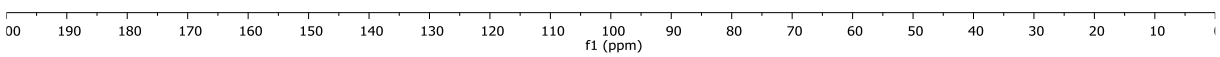
_N_-[2-(Benzyloxy)cyclopentyl]thioformamide (31)

^{1}H NMR ($CDCl_3$, 400 MHz)

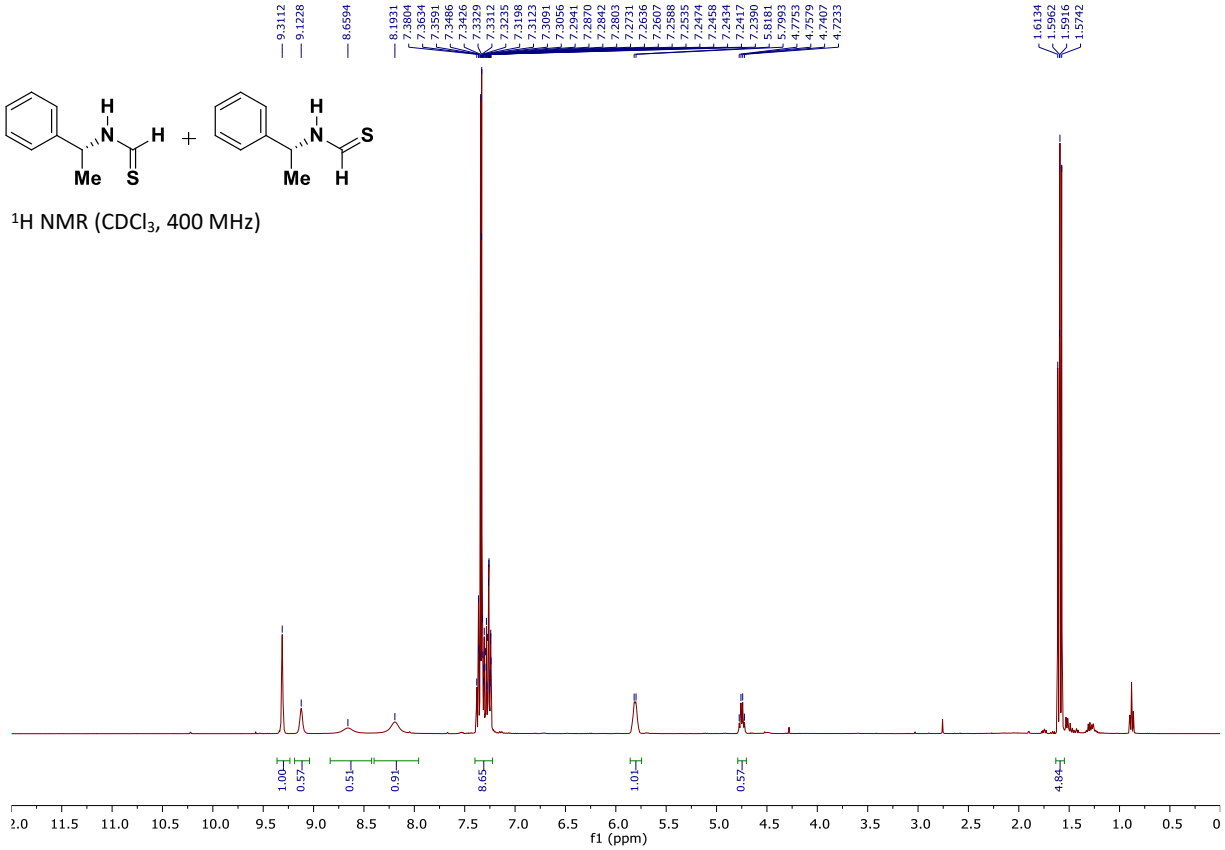




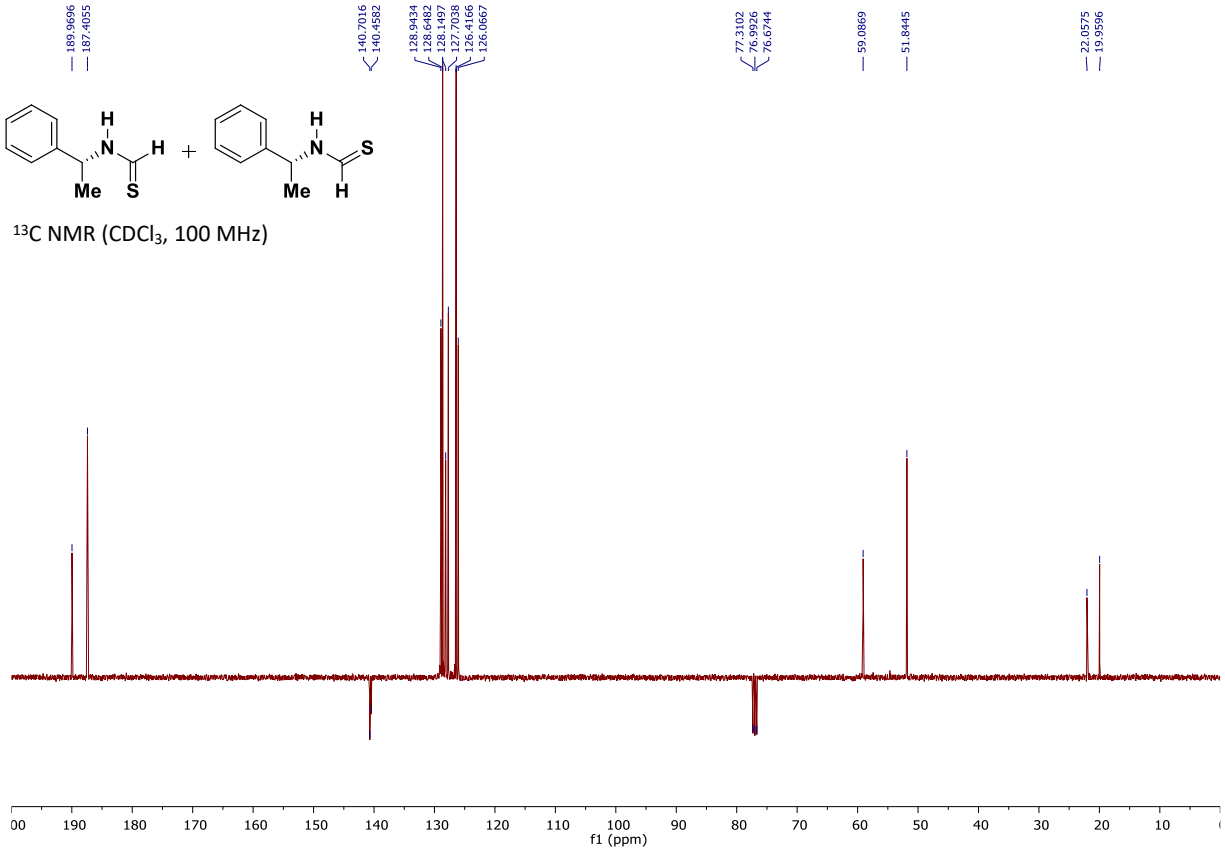
^{13}C NMR ($CDCl_3$, 100 MHz)



_N_-[(1_R_)-1-Phenylethyl]thioformamide (32)

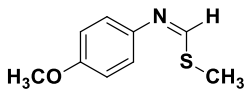


^{1}H NMR ($CDCl_3$, 400 MHz)

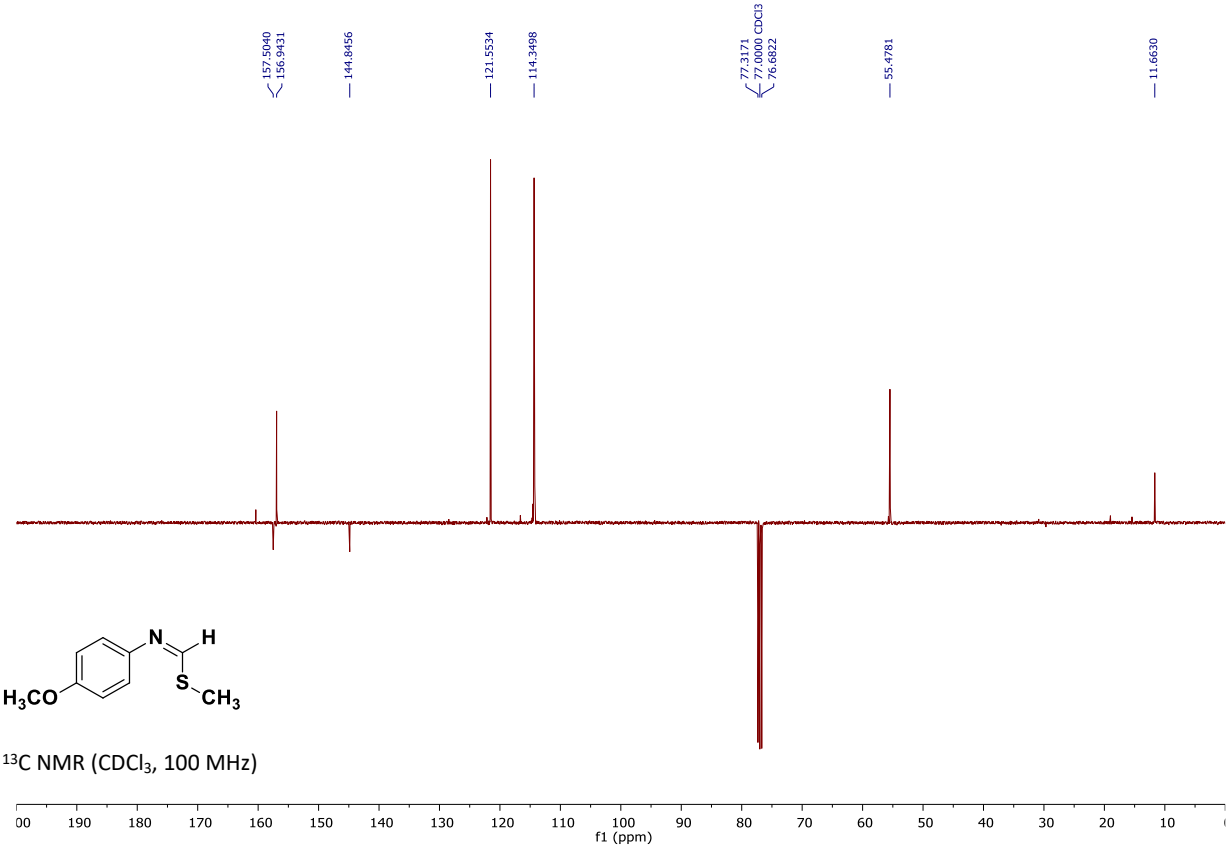


^{13}C NMR ($CDCl_3$, 100 MHz)

Methyl (4-methoxyphenyl)imidothioformate (33)

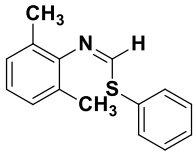


^{1}H NMR ($CDCl_3$, 400 MHz)

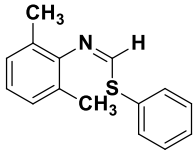


^{13}C NMR ($CDCl_3$, 100 MHz)

Phenyl (2,6-dimethylphenyl)imidothioformate (34)

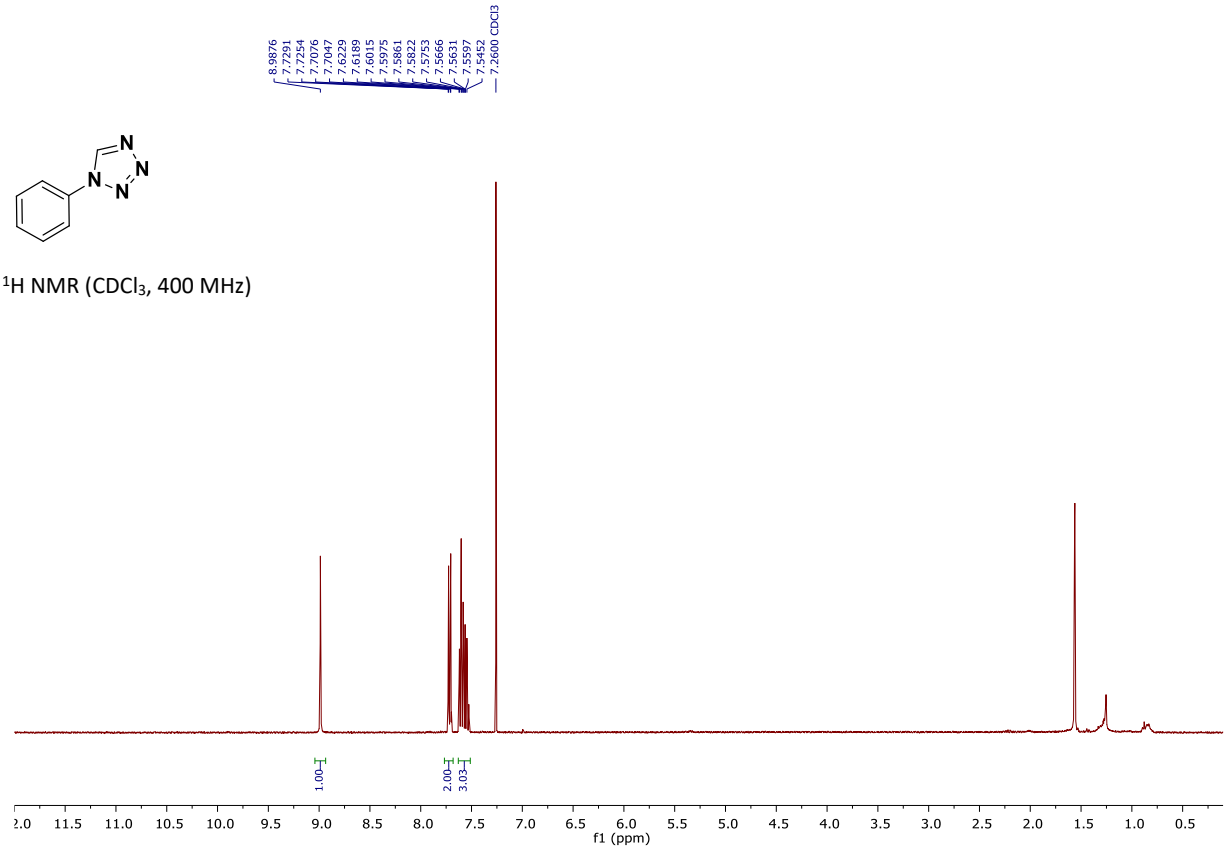


^{1}H NMR ($CDCl_3$, 400 MHz)

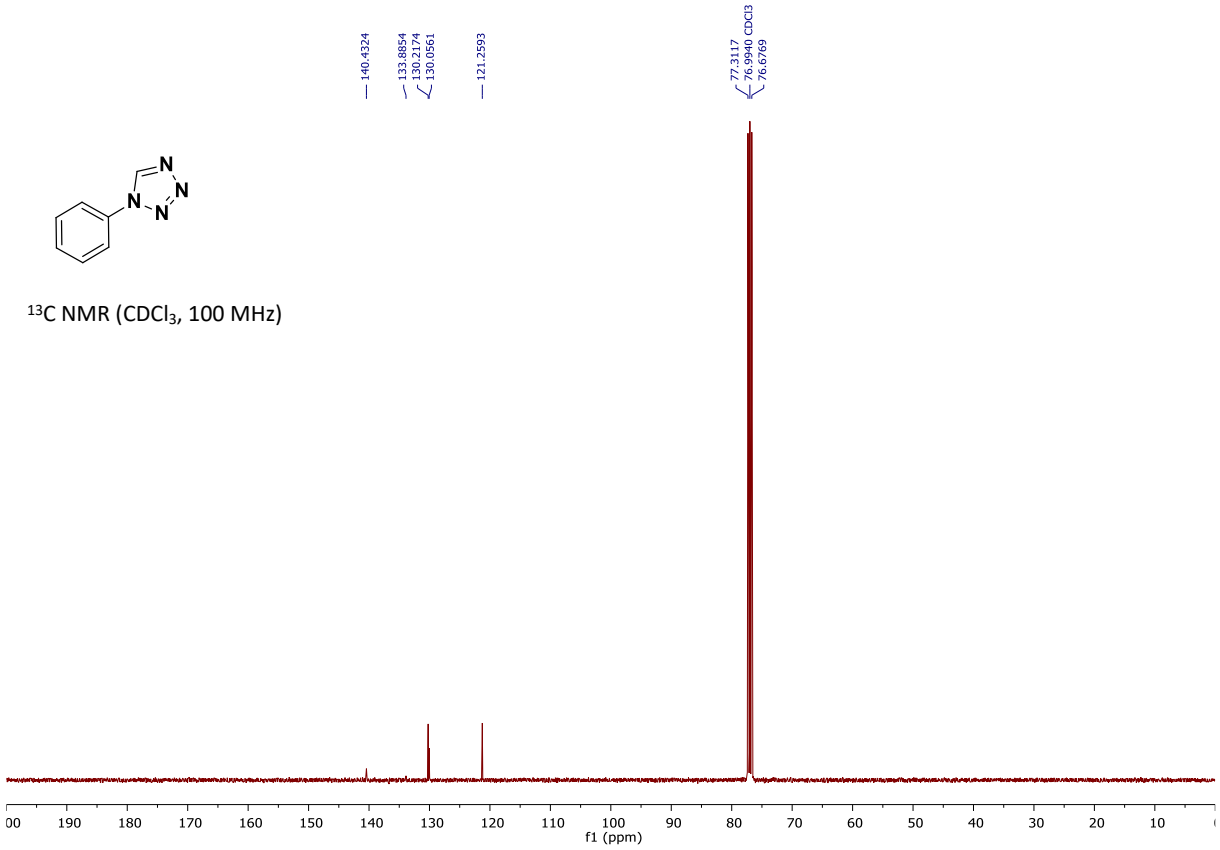


^{13}C NMR ($CDCl_3$, 100 MHz)

1-Phenyl-1*H*-tetrazole (35)



^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)

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