

SUPPORTING INFORMATION

for

Chemoselective Reduction of Isothiocyanates to Thioformamides Mediated by the Schwartz Reagent

Karen de la Vega-Hernández,^{a,b} Raffaele Senatore,^a Margherita Miele,^a Ernst Urban,^a Wolfgang Holzer^a and Vittorio Pace^{*a}

^aDepartment of Pharmaceutical Chemistry, University of Vienna, Althanstrasse, 14, A-1090 Vienna, Austria.

^bNew address: Sorbonne Université, Institut Parisien de Chimie Moléculaire, 4 Place Jussieu, 75005, Paris, France.

e-mail: vittorio.pace@univie.ac.at.

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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). ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 spectrometer (400 MHz for ^1H , 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 ^1H , 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 (^1H in CDCl_3), δ 2.49 ppm (^1H 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-NH 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 ($\lambda = 254$ nm) and/or KMnO_4 (aq.) was used as revealing system.

2. General Procedures

Reduction of 3-acetylphenyl isothiocyanate; General Procedure 1

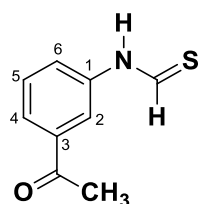
To a solution of 3-acetylphenyl isothiocyanate **1** (0.177 g, 1.0 mmol, 1.0 equiv) in dry THF (5 mL) at the proper temperature, the corresponding reducing agents were added dropwise (*see conditions indicated in Table 1 of the manuscript*). After the appropriate time, the reactions were quenched with the following reagents: H₂O and 2.5 M NaOH (entries 1-3) / H₂O (entry 4) / NH₄Cl (entry 5) / H₂O and 1 M HCl (entries 6-14), respectively. The aqueous layers were extracted with Et₂O (3×) and the organic phases were combined. The organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crudes were purified by flash SiO₂ 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

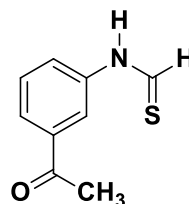
To an oven-dried and argon-flushed flask was added the isothiocyanate and Cp₂ZrCl₂. The reagents were dissolved in anhydrous 2-MeTHF at rt and then the mixture was cooled at 0 °C. LiAl(O-*t*-Bu)₃H (1 M in THF) was added dropwise at 0 °C and then the cooling bath was removed, allowing the mixture to reach rt. After the appropriate time, the reaction was quenched with H₂O (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 Na₂SO₄, filtered and concentrated under reduced pressure. The crudes were purified by flash SiO₂ 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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:

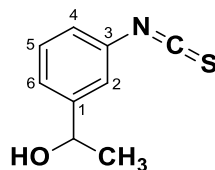
^1H NMR (CDCl_3 , 400 MHz): δ = 9.74 (d, 3J = 6.6 Hz, 1H, HC=S), 9.31 (br s, 1H, NH), 7.94 (m, 1H, Ph H-2), 7.92 (m, 1H, Ph H-4), 7.58 (m, 2H, Ph H-5,6), 2.65 (s, 3H, CH_3).

^{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 [$\text{M} + \text{Na}$] $^+$ calcd for $\text{C}_9\text{H}_9\text{NNaOS}$: 202.0297; found: 202.0302.

1-(3-isothiocyanatophenyl)ethanol (3)



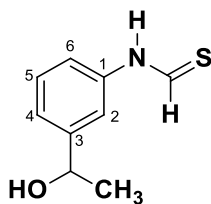
Obtained as a pale yellow oil, as reported in Table 1 of the manuscript.

¹H NMR (CDCl₃, 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, HOCH₂CH₃), 1.86 (br s, 1H, OH), 1.49 (d, ³*J* = 6.5 Hz, 3H, HOCHCH₃).

¹³C NMR (CDCl₃, 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 (HOCHCH₃), 25.3 (HOCH₂CH₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd. for C₉H₁₀NOS: 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.

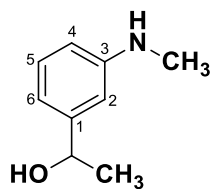
¹H NMR (CDCl₃, 400 MHz): δ = 9.81 (d, ³*J* = 14.6 Hz, 1H, HC=S), 9.46 (br s, 1H, NH), 7.36 (t, m, 1H, Ph H-5), 7.23 (d, ³*J* = 7.6 Hz, 1H, Ph H-4), 7.20 (m, 1H, Ph H-2), 7.04 (ddd, ³*J* = 7.9 Hz, ⁴*J* = 2.4 Hz, ⁴*J* = 1.0 Hz, 1H, Ph H-6), 4.93 (q, ³*J* = 6.5 Hz, 1H, HOCHHCH₃), 1.98 (br s, 1H, OH), 1.51 (d, ³*J* = 6.5 Hz, 3H, HOCHCH₃).

¹³C NMR (CDCl₃, 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 (HOCHCH₃), 25.5 (HOCHCH₃).

¹⁵N NMR (CDCl₃, 40 MHz): δ = -212.0 (NH).

HRMS (ESI): *m/z* [M + H]⁺ calcd. for C₉H₁₂NOS: 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.

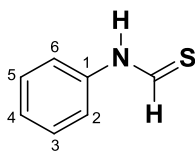
¹H NMR (CDCl₃, 400 MHz): δ = 7.16 (t, ³J = 7.8 Hz, 1H, Ph H-5), 6.70 (m, 1H, Ph H-6), 6.62 (s, 1H, Ph H-2), 6.52 (m, 1H, Ph H-4), 4.79 (q, ³J = 6.5 Hz, 1H, HOCHCH₃), 2.95 (br s, 2H, OH and NH), 2.83 (s, 3H, HNCH₃), 1.47 (d, ³J = 6.5 Hz, 3H, HOCHCH₃).

¹³C NMR (CDCl₃, 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 (HOCHCH₃), 30.7 (HNCH₃), 24.9 (HOCHCH₃).

¹⁵N NMR (CDCl₃, 40 MHz): δ = -329.2 (NH).

HRMS (ESI): *m/z* [M + H]⁺ calcd. for C₉H₁₄NO: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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.

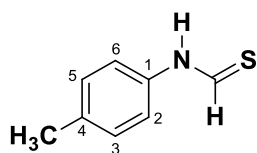
^1H NMR (CDCl_3 , 400 MHz): δ = 9.80 (d, 3J = 14.7 Hz, 1H, HC=S), 9.47 (br s, 1H, NH), 7.40 (m, 2H, Ph H-3,5), 7.25 (m, 1H, Ph H-4), 7.15 (m, 2H, Ph H-2,6).

^{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).

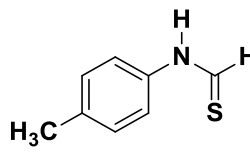
^{15}N NMR (CDCl_3 , 40 MHz): δ = -212.0 (NH).

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_7\text{H}_7\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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).

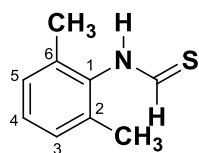
^{15}N NMR (CDCl_3 , 40 MHz): δ = -210.2 (NH).

s-cis rotamer:

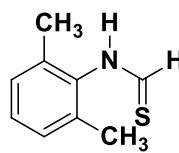
^1H NMR (CDCl_3 , 400 MHz): δ = 9.66 (d, 3J = 6.8 Hz, 1H, HC=S), 7.10 (m, 2H, Ph H-3,5), 7.00 (m, 2H, Ph H-2,6), 2.31 (s, 3H, CH_3).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_8\text{H}_{10}\text{NS}$: 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, $\text{LiAl(O-}i\text{-t-Bu)}_3\text{H}$ (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:

^1H 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:

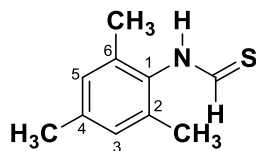
^1H NMR (CDCl_3 , 400 MHz): δ = 9.62 (d, 3J = 6.0 Hz, 1H, HC=S), 8.84 (br s, 1H, NH), 7.17 (m, 1H, Ph H-4), 7.10 (m, 2H, Ph H-3,5), 2.23 (s, 3H, CH_3).

^{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).

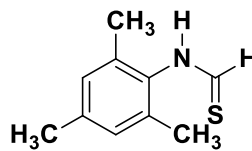
^{15}N NMR (CDCl_3 , 40 MHz): δ = -218.7 (NH).

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_9\text{H}_{11}\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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- CH_3), 2.26 (s, 6H, Ph-2,6- CH_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- CH_3), 18.4 (Ph-2,6- CH_3).

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

s-cis rotamer:

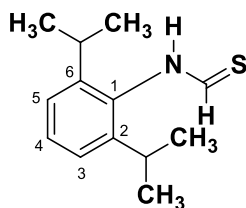
^1H NMR (CDCl_3 , 400 MHz): δ = 9.68 (d, 3J = 5.9 Hz, 1H, HC=S), 8.38 (br s, 1H, NH), 6.94 (s, 2H, Ph H-3,5), 2.29 (s, 3H, Ph-4- CH_3), 2.22 (s, 6H, Ph-2,6- CH_3).

^{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- CH_3), 18.1 (Ph-2,6- CH_3).

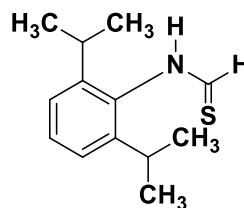
^{15}N NMR (CDCl_3 , 40 MHz): δ = -221.7 (NH).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{10}\text{H}_{14}\text{NS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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, $\text{CH}(\text{CH}_3)_2$), 1.24 (d, 3J = 6.9 Hz, 12H, $\text{CH}(\text{CH}_3)_2$).

^{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 ($\text{CH}(\text{CH}_3)_2$), 23.5 ($\text{CH}(\text{CH}_3)_2$).

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

s-cis rotamer:

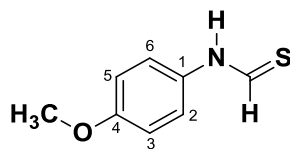
^1H NMR (CDCl_3 , 400 MHz): δ = 9.79 (d, 3J = 6.1 Hz, 1H, HC=S), 8.96 (br d, 3J = 6.1 Hz, 1H, NH), 7.37 (t, 3J = 7.8 Hz, 1H, Ph H-4), 7.23 (d, 3J = 7.8 Hz, 2H, Ph H-3,5), 3.03 (sept, 3J = 6.9 Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.16 (d, 3J = 6.9 Hz, 12H, $\text{CH}(\text{CH}_3)_2$).

^{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 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$).

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

HRMS (ESI): m/z [$\text{M} + \text{Na}$] $^+$ calcd. for $\text{C}_{13}\text{H}_{19}\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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%).

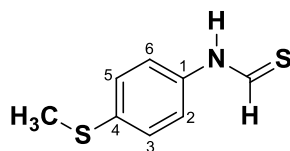
^1H NMR (CDCl_3 , 400 MHz): δ = 9.63 (d, 3J = 14.6 Hz, 1H, HC=S), 9.55 (br s, 1H, NH), 7.09 (m, 2H, Ph H-2,6), 6.90 (m, 2H, Ph H-3,5), 3.81 (s, 3H, OCH_3).

^{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 $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_8\text{H}_9\text{NNaOS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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.

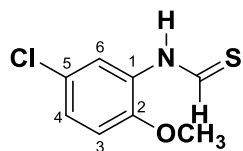
^1H NMR (CDCl_3 , 400 MHz): δ = 10.53 (br s, 1H, NH), 9.74 (d, 3J = 14.4 Hz, 1H, HC=S), 7.21 (m, 2H, Ph H-3,5), 7.09 (m, 2H, Ph H-2,6), 2.45 (s, 3H, SCH₃).

^{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 (SCH₃).

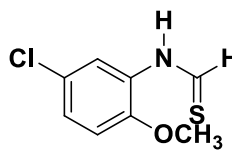
^{15}N NMR (CDCl_3 , 40 MHz): δ = -208.9 (NH).

HRMS (ESI): m/z [$\text{M} + \text{Na}$]⁺ calcd. for $\text{C}_8\text{H}_9\text{NNaS}_2$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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:

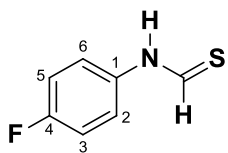
^1H NMR (CDCl_3 , 400 MHz): δ = 9.71 (d, 3J = 6.5 Hz, 1H, HC=S), 9.46 (br s, 1H, NH), 9.30 (d, 4J = 2.5 Hz, 1H, Ph H-6), 7.10 (dd, 3J = 8.7 Hz, 4J = 2.5 Hz, 1H, Ph H-4), 6.83 (d, 3J = 8.8 Hz, 1H, Ph H-3), 3.87 (s, 3H, OCH_3).

^{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).

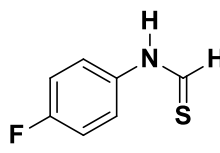
^{15}N NMR (CDCl_3 , 40 MHz): δ = -224.9 (NH).

HRMS (ESI): m/z [$\text{M} + \text{Na}$] $^+$ calcd. for $\text{C}_8\text{H}_8\text{ClNNaOS}$: 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, $\text{LiAl(O-}t\text{-Bu)}_3\text{H}$ (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:

¹H 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).

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

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

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

s-cis rotamer:

¹H 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).

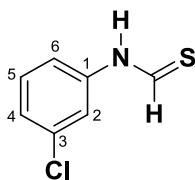
¹³C NMR (CDCl_3 , 100 MHz): δ = 187.3 (C=S), 124.7 (d, $^3J_{\text{C,F}}$ = 8.1 Hz, Ph C-2,6), 115.9 (d, $^2J_{\text{C,F}}$ = 22.8 Hz, Ph C-3,5); Ph C-4 and Ph C-1 were not found.

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

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

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_7\text{H}_7\text{FNS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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).

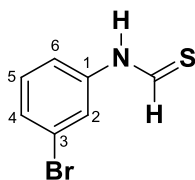
^1H NMR (CDCl_3 , 400 MHz): δ = 9.81 (d, 3J = 14.3 Hz, 1H, HC=S), 9.48 (br s, 1H, NH), 7.32 (t, 3J = 8.0 Hz, 1H, Ph H-5), 7.22 (ddd, 3J = 8.0 Hz, 4J = 1.9 Hz, 4J = 0.9 Hz, 1H, Ph H-4), 7.16 (t, 4J = 2.0 Hz, 1H, Ph H-2), 7.03 (ddd, 3J = 8.0 Hz, 4J = 2.0 Hz, 4J = 0.9 Hz, 1H, Ph H-6).

^{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 $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_7\text{H}_6\text{ClNNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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).

^1H 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).

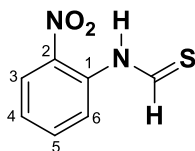
^{15}N NMR (CDCl_3 , 40 MHz): δ = -214.9 (NH).

Minor *s-cis* rotamer \approx 4%

^1H 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 $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_7\text{H}_7\text{BrNS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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).

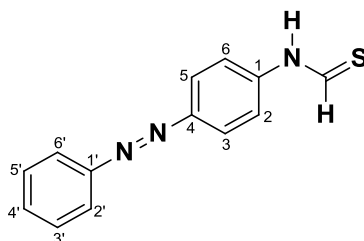
^1H NMR (CDCl_3 , 400 MHz): δ = 11.51 (br s, 1H, NH), 10.08 (d, 3J = 13.6 Hz, 1H, HC=S), 8.27 (dd, 3J = 8.4 Hz, 4J = 1.5 Hz, 1H, Ph H-3), 7.71 (m, 1H, Ph H-5), 7.56 (m, 1H, Ph H-6), 7.35 (m, 1H, Ph H-4).

^{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 $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_7\text{H}_7\text{N}_2\text{O}_2\text{S}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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).

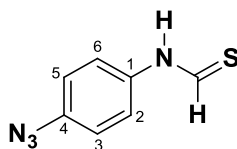
^1H NMR (CDCl_3 , 400 MHz): δ = 10.07 (d, 3J = 14.2 Hz, 1H, HC=S), 9.58 (d, 3J = 14.2 Hz, 1H, NH), 7.98 (m, 2H, Ph H-3,5), 7.92 (m, 2H, Ph H-2',6'), 7.52 (m, 2H, Ph H-3',5'), 7.50 (m, 1H, Ph H-4'), 7.28 (m, 2H, Ph H-2,6).

^{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).

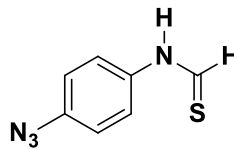
^{15}N NMR (CDCl_3 , 40 MHz): δ = -212.2 (NH).

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{NaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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:

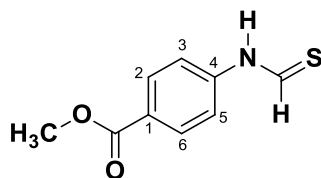
^1H NMR (DMSO- d_6 , 200 MHz): δ = 12.07 (br d, 3J = 6.8 Hz, 1H, NH), 9.50 (d, 3J = 6.8 Hz, 1H, HC=S), 8.06 (m, 2H, Ph H-2,6), 7.15 (m, 2H, Ph H-3,5).

^{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).

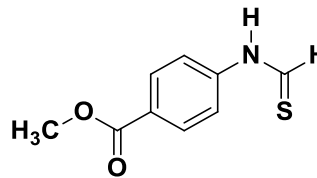
^{15}N NMR (DMSO- d_6 , 40 MHz): δ = -206.5 (NH).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_7\text{H}_7\text{N}_4\text{S}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

¹H 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, OCH₃).

¹³C 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 (OCH₃).

¹⁵N NMR (DMSO-*d*₆, 40 MHz): δ = -205.7 (NH).

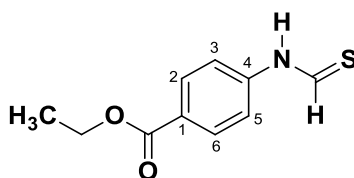
s-cis rotamer:

¹H 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, OCH₃).

¹³C 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 (OCH₃).

HRMS (ESI): m/z [M + Na]⁺ calcd. for C₉H₉NNaO₂S: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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).

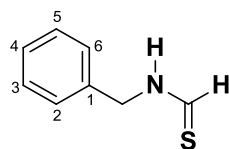
^1H NMR (CDCl_3 , 400 MHz): δ = 9.95 (br d, 3J = 14.1 Hz, 1H, HC=S), 9.34 (br d, 3J = 14.1 Hz, 1H, NH), 8.08 (m, 2H, Ph H-2,6), 7.18 (m, 2H, Ph H-3,5), 4.38 (q, 3J = 7.1 Hz, 2H, OCH_2), 1.40 (t, 3J = 7.1 Hz, 3H, CH_3).

^{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).

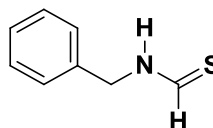
^{15}N NMR (CDCl_3 , 40 MHz): δ = -213.3 (NH).

HRMS (ESI): m/z [$\text{M} + \text{Na}$] $^+$ calcd. for $\text{C}_{10}\text{H}_{11}\text{NNaO}_2\text{S}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

¹H 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).

¹³C 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).

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

s-trans rotamer:

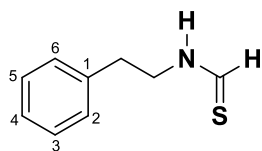
¹H NMR (CDCl_3 , 400 MHz): δ = 9.26 (d, 3J = 15.0 Hz, 1H, HC=S), 7.89 (br s, 1H, NH), 7.42–7.23 (m, 5H, Ph H), 4.60 (d, 3J = 6.2 Hz, 2H, CH_2).

¹³C 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.

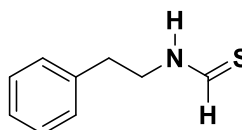
¹⁵N NMR (CDCl_3 , 40 MHz): δ = -223.3 (NH).

HRMS (ESI): m/z [$\text{M} + \text{Na}$]⁺ calcd. for $\text{C}_8\text{H}_9\text{NNaS}$: 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-phenethyl 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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, $\text{HNCH}_2\text{CH}_2\text{Ph}$), 2.96 (t, 3J = 7.1 Hz, 2H, $\text{HNCH}_2\text{CH}_2\text{Ph}$).

^{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 ($\text{HNCH}_2\text{CH}_2\text{Ph}$), 33.3 ($\text{HNCH}_2\text{CH}_2\text{Ph}$).

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

s-trans rotamer:

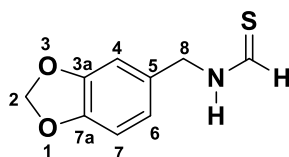
^1H NMR (CDCl_3 , 400 MHz): δ = 8.91 (d, 3J = 15.1 Hz, 1H, HC=S), 8.22 (br s, 1H, NH), 7.32 (m, 2H, Ph H-3,5), 7.23 (m, 1H, Ph H-4), 7.16 (m, 2H, Ph H-2,6), 3.63 (q, 3J = 6.8 Hz, 2H, $\text{HNCH}_2\text{CH}_2\text{Ph}$), 2.88 (t, 3J = 7.0 Hz, 2H, $\text{HNCH}_2\text{CH}_2\text{Ph}$).

^{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 ($\text{HNCH}_2\text{CH}_2\text{Ph}$), 36.3 ($\text{HNCH}_2\text{CH}_2\text{Ph}$).

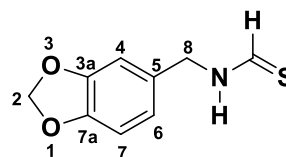
^{15}N NMR (CDCl_3 , 40 MHz): δ = -220.9 (NH).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_9\text{H}_{11}\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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:

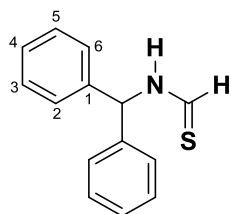
^1H NMR (CDCl_3 , 400 MHz): δ = 9.19 (d, 3J = 15.0 Hz, 1H, HC=S), 8.04 (br s, 1H, NH), 6.70 (m, 2H, H-4,6), 5.96 (s, 2H, H-2), 4.47 (d, 3J = 6.0 Hz, 2H, H-8); H-7 not unambiguously assigned due to overlap with other signals.

^{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).

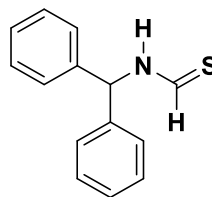
^{15}N NMR (CDCl_3 , 40 MHz): δ = -221.0 (NH).

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_9\text{H}_9\text{NNaO}_2\text{S}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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_2CHNH).

^{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_2CHNH).

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

s-trans rotamer:

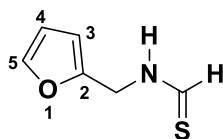
^1H NMR (CDCl_3 , 400 MHz): δ = 9.23 (dd, 3J = 15.1 Hz, 4J = 0.6 Hz, 1H, HC=S), 8.10 (br s, 1H, NH), 7.42-7.22 (m, 10H, Ph-2-6), 5.90 (d, 3J = 6.7 Hz, 1H, Ph_2CHNH).

^{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_2CHNH).

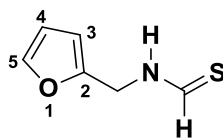
^{15}N NMR (CDCl_3 , 40 MHz): δ = -213.7 (NH).

HRMS (ESI): m/z [$\text{M} + \text{Na}$] $^+$ calcd. for $\text{C}_{14}\text{H}_{13}\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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:

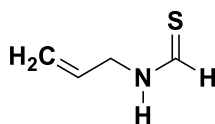
^1H NMR (CDCl_3 , 400 MHz): δ = 9.27 (d, 3J = 14.9 Hz, 1H, HC=S), 8.02 (br s, 1H, NH), 7.40 (dd, 3J = 1.9 Hz, 4J = 0.8 Hz, 1H, Fur H-5), 6.35 (m, 1H, Fur H-4), 6.30 (m, 1H, Fur H-3), 4.55 (d, 3J = 5.9 Hz, 2H, CH_2).

^{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).

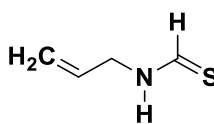
^{15}N NMR (CDCl_3 , 40 MHz): δ = -226.6 (NH).

HRMS (ESI): m/z [$\text{M} + \text{H}$] $^+$ calcd. for $\text{C}_6\text{H}_8\text{NOS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.30-5.20 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.28 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 188.8 (C=S), 131.0 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 118.9 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 45.5 ($\text{CH}_2=\text{CH}-\text{CH}_2$).

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

s-trans rotamer:

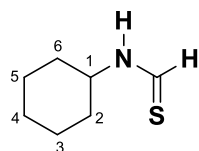
^1H NMR (CDCl_3 , 400 MHz): δ = 9.11 (d, 3J = 15.0 Hz, 1H, HC=S), 8.31 (br s, 1H, NH), 5.82 (m, 1H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.30-5.20 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.01 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 191.4 (C=S), 131.9 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 118.5 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 51.5 ($\text{CH}_2=\text{CH}-\text{CH}_2$).

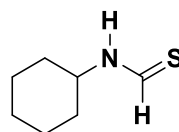
^{15}N NMR (CDCl_3 , 40 MHz): δ = -223.3 (NH).

HRMS (ESI): m/z [$\text{M} + \text{Na}$]⁺ calcd. for $\text{C}_4\text{H}_7\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

¹H 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).

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

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

s-trans rotamer:

¹H 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).

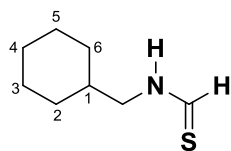
¹³C NMR (CDCl_3 , 100 MHz)*: δ = 188.8 (C=S), 58.8 (Cy C-1), 33.4 (Cy C-2,6).

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

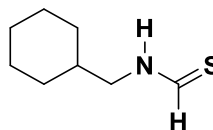
* Not assignable C signals: 25.30, 24.78, 24.43, 24.39.

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_7\text{H}_{13}\text{NNaS}$: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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:

^1H 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, HNCH_2Cy), 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 (HNCH_2Cy), 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:

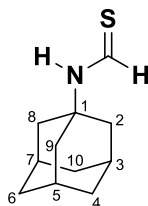
^1H NMR (CDCl_3 , 400 MHz): δ = 9.01 (d, 3J = 15.1 Hz, 1H, HC=S), 8.61 (br s, 1H, NH), 3.20 (t, 3J = 6.6 Hz, 2H, HNCH_2Cy), 1.49 (m, 1H, Cy H-1), 1.73-0.81 (m, 10H, Cy H-2-6).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 190.6 (C=S), 56.1 (HNCH_2Cy), 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 [$\text{M} + \text{Na}$] $^+$ calcd. for $\text{C}_8\text{H}_{15}\text{NNaS}$: 180.0817; found: 180.0822.

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



s-trans rotamer

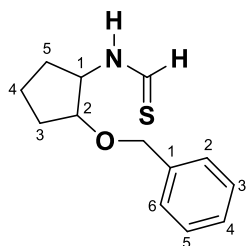
By following the General Procedure 2, to a solution of 1-adamantyl isothiocyanate (0.193 g, 1.0 mmol, 1.0 equiv) and Cp_2ZrCl_2 (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise, and then, the reaction 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).

^1H 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).

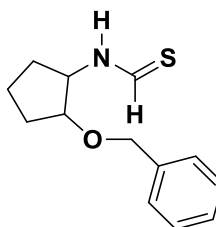
^{13}C NMR (CDCl_3 , 100 MHz): δ = 186.5 (C=S), 56.2 (Adam C-1), 43.1 (Adam C-2,8,9), 35.7 (Adam C-4,6,10), 29.2 (Adam C-3,5,7).

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{11}\text{H}_{17}\text{NNaS}$: 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 Cp₂ZrCl₂ (0.438 g, 1.5 mmol, 1.5 equiv) in dry 2-MeTHF (5 mL) at 0 °C, LiAl(O-*t*-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 **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:

¹H NMR (CDCl₃, 400 MHz): δ = 9.32 (d, ³*J* = 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, ²*J*_{AB} = 12.1 Hz, OCH₂), 4.61 (B-part of an AB-system, ²*J*_{AB} = 12.1 Hz, OCH₂), 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).

¹³C NMR (CDCl₃, 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 (OCH₂Ph), 59.0 (Cp C-1), 30.6 (Cp C-3), 29.4 (Cp C-5), 21.7 (Cp C-4).

¹⁵N NMR (CDCl₃, 40 MHz): δ = -209.9 (NH).

s-trans rotamer:

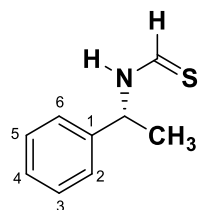
¹H NMR (CDCl₃, 400 MHz): δ = 9.20 (d, ³*J* = 15.0 Hz, 1H, HC=S), 8.55 (br s, 1H, NH), 7.37-7.24 (m, 3H, Ph H-3,4,5), 7.31 (m, 2H, Ph H-2,6), 4.54 (A-part of an AB-system, ²*J*_{AB} = 11.7 Hz, OCH₂), 4.46 (B-part of an AB-system, ²*J*_{AB} = 11.7 Hz, OCH₂), 3.88 (m, 1H, Cp H-1), 3.79 (m, 1H, Cp H-2), 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).

¹³C NMR (CDCl₃, 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 (OCH₂Ph), 65.9 (Cp C-1), 29.3 (Cp C-5), 29.2 (Cp C-3), 20.3 (Cp C-4).

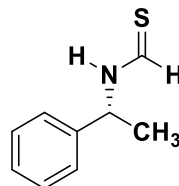
¹⁵N NMR (CDCl₃, 40 MHz): δ = -211.4 (NH).

HRMS (ESI): *m/z* [M + Na]⁺ calcd. for C₁₃H₁₇NNaOS: 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, $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ (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, $[\alpha]_D^{20} +158^\circ$ (c 0.5, CHCl_3), without column chromatographic purification.

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

s-cis rotamer:

^1H 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, PhCH(H)(CH₃)NH), 1.58 (d, 3J = 6.9 Hz, 3H, PhCH(CH₃)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 (PhCH(CH₃)NH), 20.0 (PhCH(CH₃)NH).

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

s-trans rotamer:

^1H 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, PhCH(H)(CH₃)NH), 1.60 (d, 3J = 6.9 Hz, 3H, PhCH(CH₃)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 (PhCH(CH₃)NH), 22.1 (PhCH(CH₃)NH).

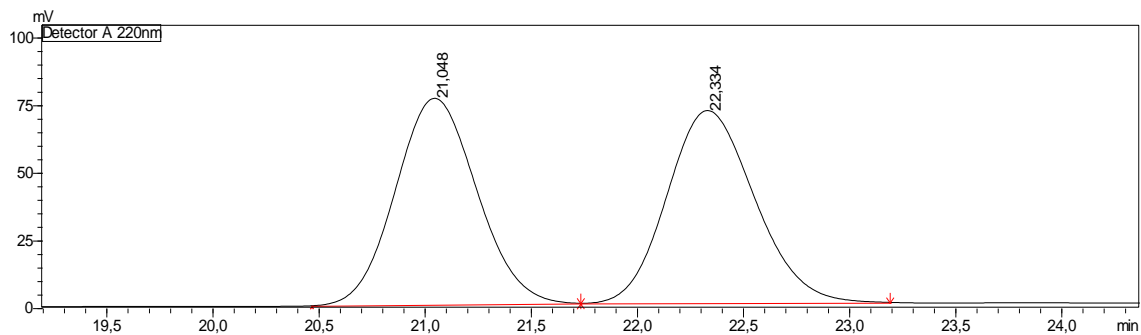
^{15}N NMR (CDCl_3 , 40 MHz): δ = -206.3 (NH).

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_9\text{H}_{11}\text{NNaS}$: 188.0504; found: 188.0508.

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

Racemate

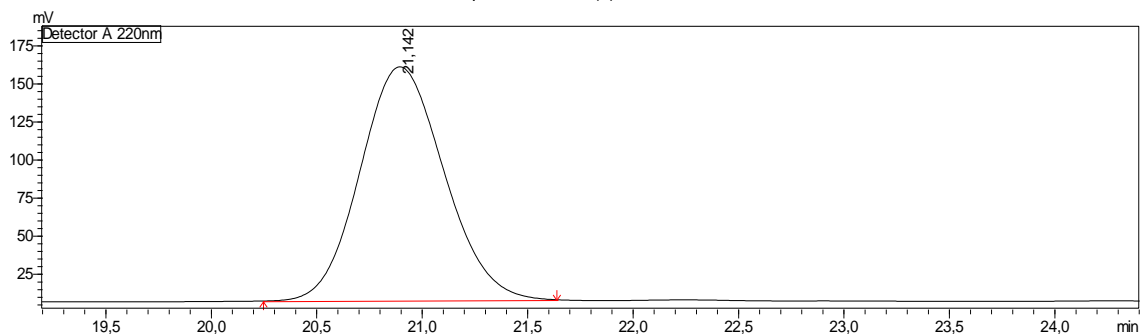
Datafile Name:KVH-040rac-12.lcd
Sample Name:KVH-040rac-11
Sample ID:KVH-040rac-11



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

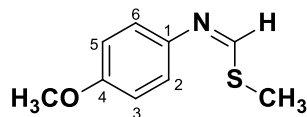
Enantioenriched

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 Na₂SO₄, 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).

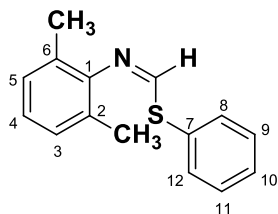
¹H NMR (CDCl₃, 400 MHz): δ = 8.47 (s, HC=N), 7.01 (m, 2H, Ph H-2,6), 6.86 (m, 2H, Ph H-3,5), 3.80 (s, 3H, OCH₃), 2.51 (s, 3H, SCH₃).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.5 (Ph C-4), 156.9 (HC=N, ¹J_{C-H} = 175.1 Hz), 144.8 (Ph C-1), 121.6 (Ph C-2,6), 114.3 (Ph C-3,5), 55.5 (OCH₃), 11.7 (SCH₃).

¹⁵N NMR (CDCl₃, 40 MHz): δ = -77.8 (C=N).

HRMS (ESI): m/z [M + H]⁺ calcd. for C₉H₁₁NOS: 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 Ph₂IOTf (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 CH₂Cl₂ (50 mL) and washed with a saturated sodium bicarbonate solution (50 mL). The aqueous phase was extracted with CH₂Cl₂ and the combined organic layers were dried over anhydrous Na₂SO₄, 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).

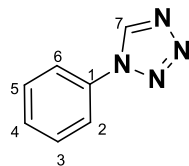
¹H NMR (CDCl₃, 400 MHz): δ = 8.56 (s, HC=N), 7.50 (m, 2H, Ph H-8,12), 7.42 (m, 2H, Ph H-9,11), 7.41 (m, 1H, Ph H-10), 7.11 (d, ³J = 7.5 Hz, 2H, Ph H-3,5), 7.02 (t, ³J = 7.5 Hz, 1H, Ph H-4), 2.23 (s, 6H, CH₃).

¹³C NMR (CDCl₃, 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 (CH₃).

¹⁵N NMR (CDCl₃, 40 MHz): δ = -56.8 (C=N).

HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₅H₁₆NS: 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).

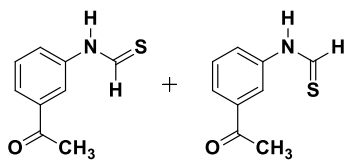
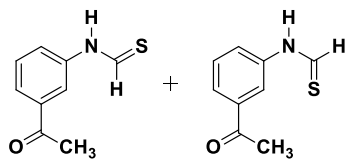
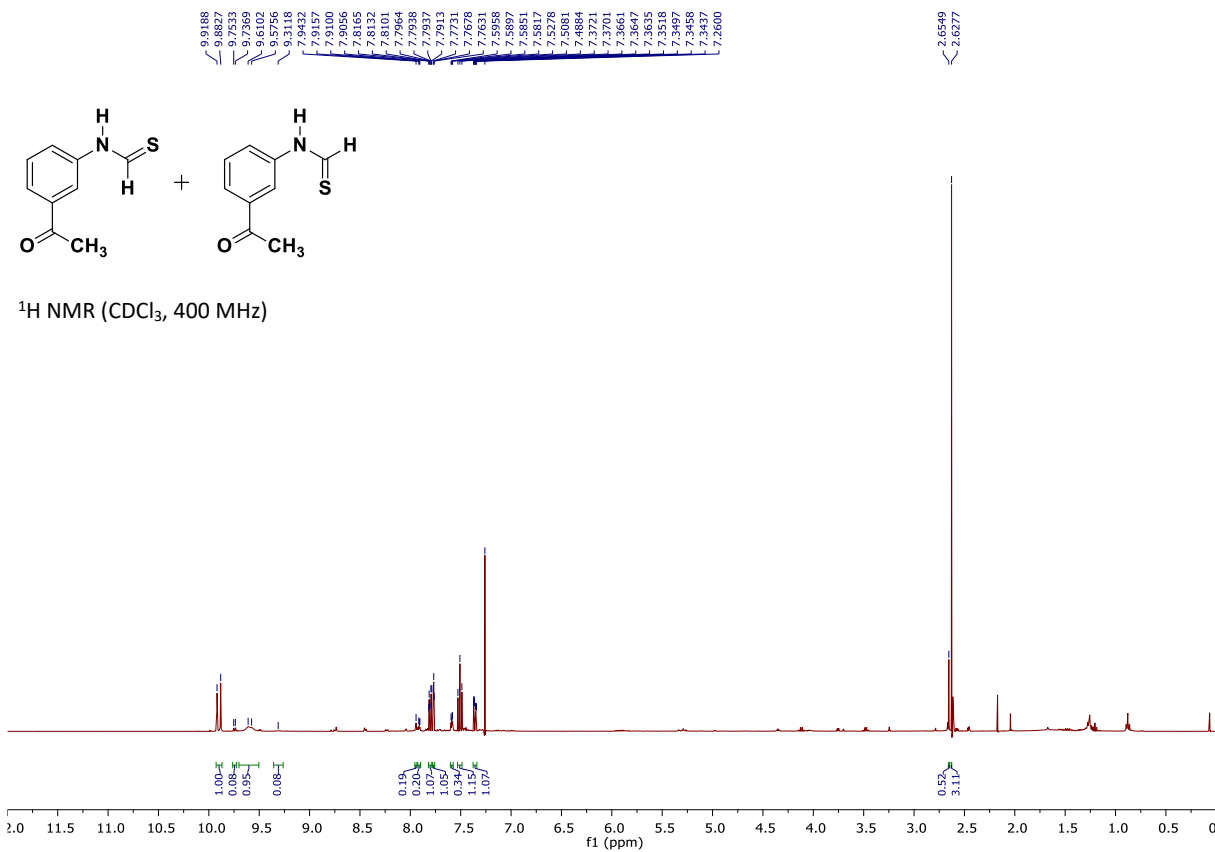
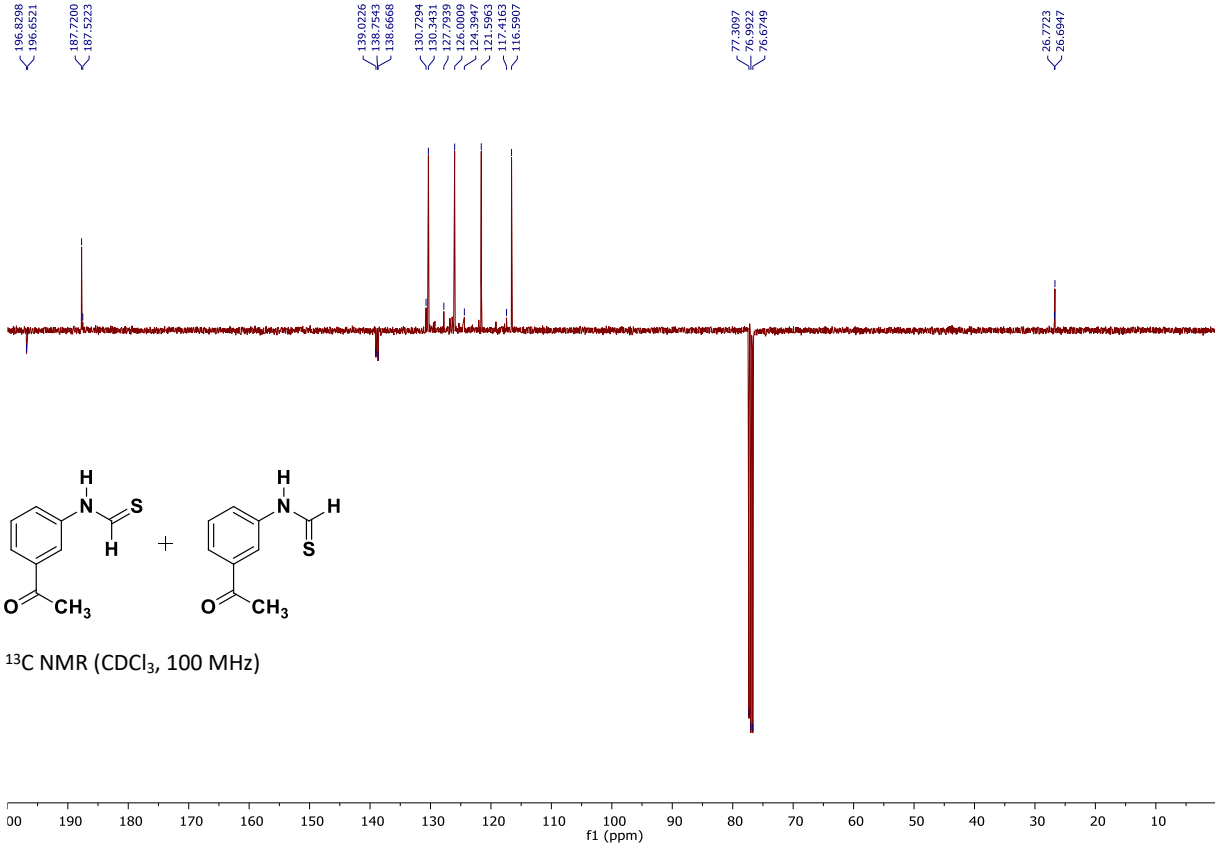
¹H NMR (CDCl_3 , 400 MHz): δ = 8.99 (s, tetrazole-H), 7.72 (m, 2H, Ph H-2,6), 7.60 (m, 2H, Ph H-3,5), 7.55 (m, 1H, Ph H-4).

¹³C 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).

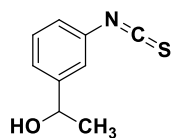
HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_7\text{H}_7\text{N}_4$: 147.0665; found: 147.0669.

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

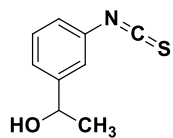
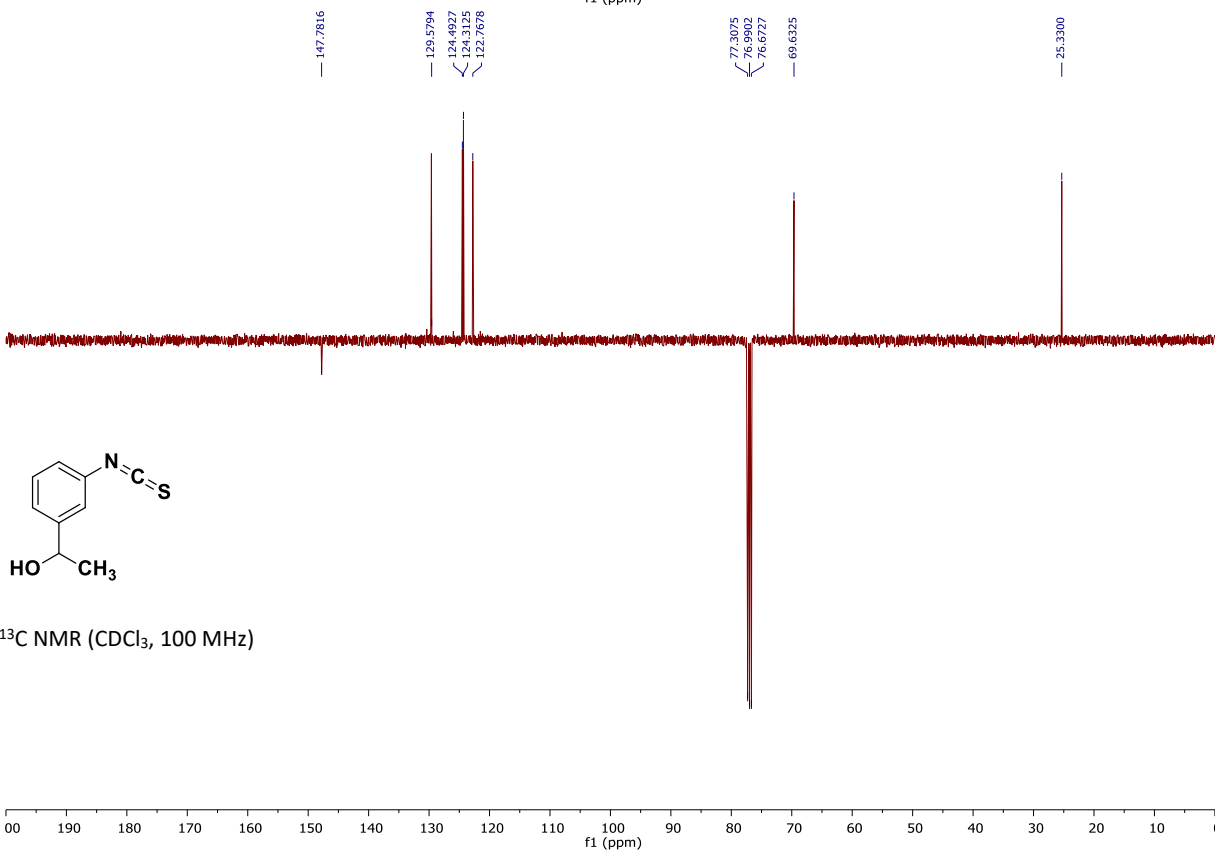
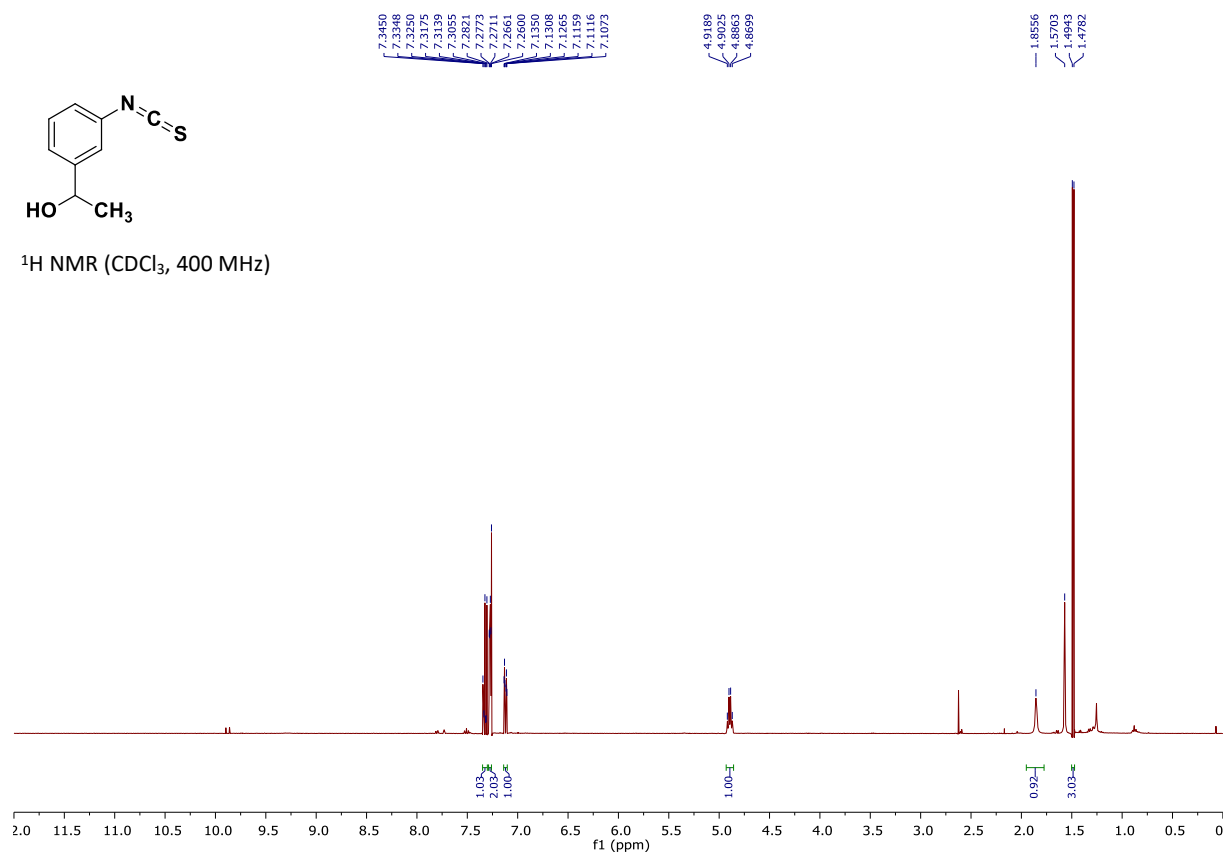
***N*-(3-acetylphenyl)thioformamide (2)**

¹H NMR (CDCl₃, 400 MHz) ^{13}C NMR (CDCl_3 , 100 MHz)

1-(3-isothiocyanatophenyl)ethanol (3)

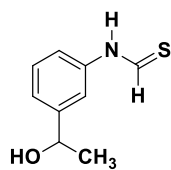


^1H NMR (CDCl_3 , 400 MHz)

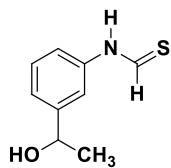
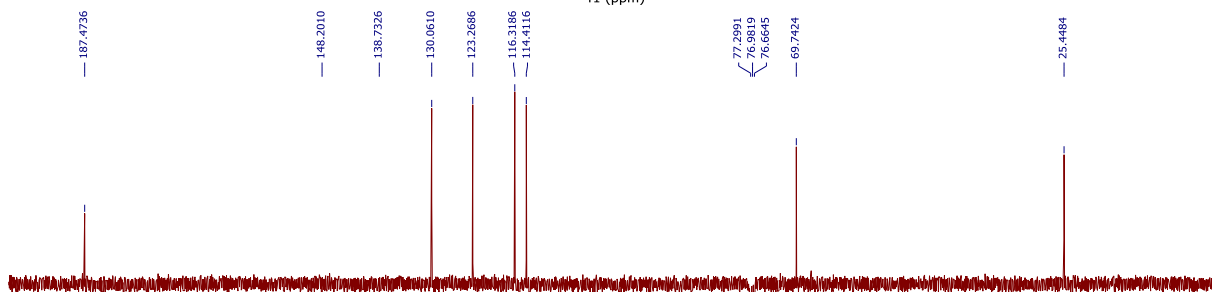
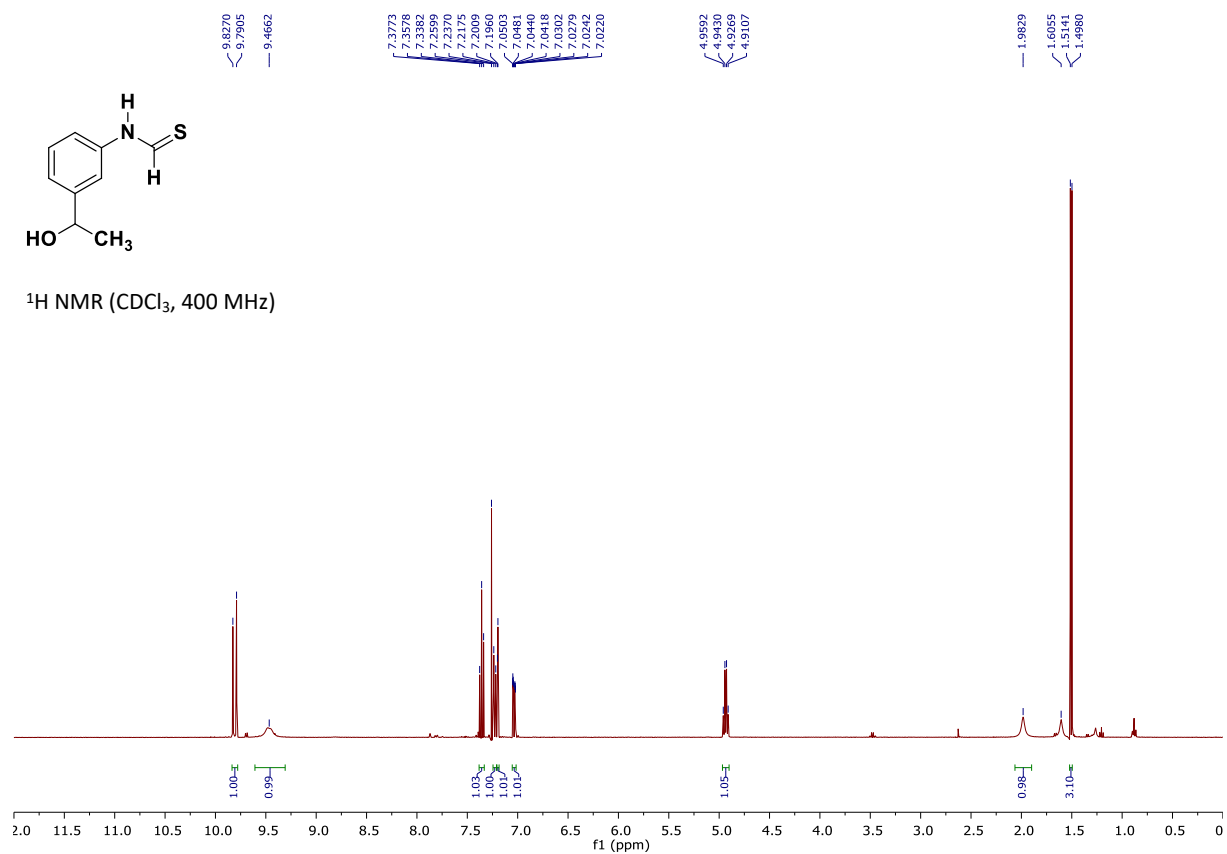


^{13}C NMR (CDCl_3 , 100 MHz)

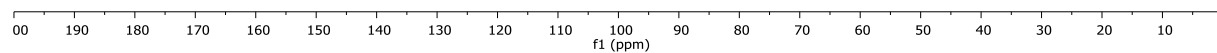
***N*-[3-(1-Hydroxyethyl)phenyl]thioformamide (4)**



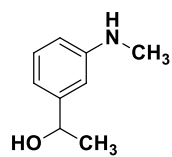
¹H NMR (CDCl₃, 400 MHz)



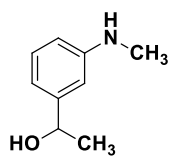
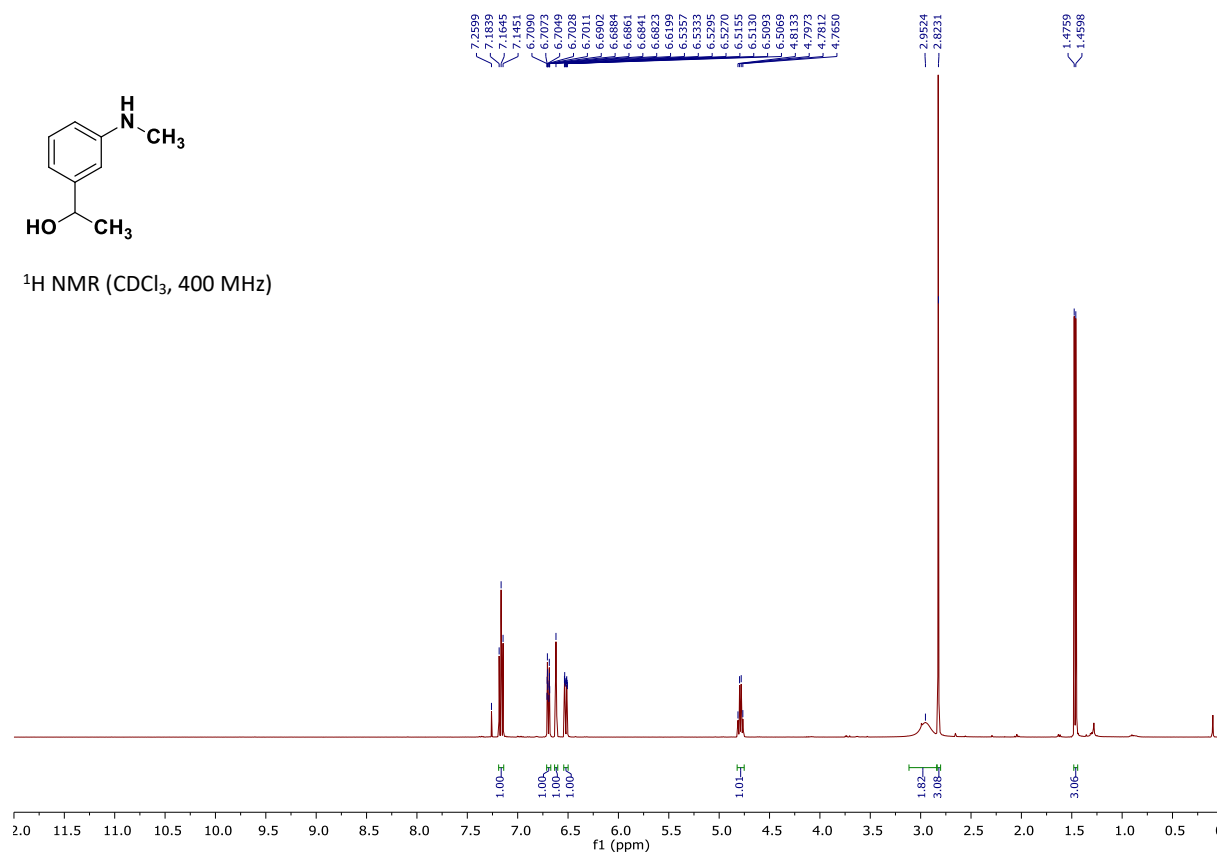
¹³C NMR (CDCl₃, 100 MHz)



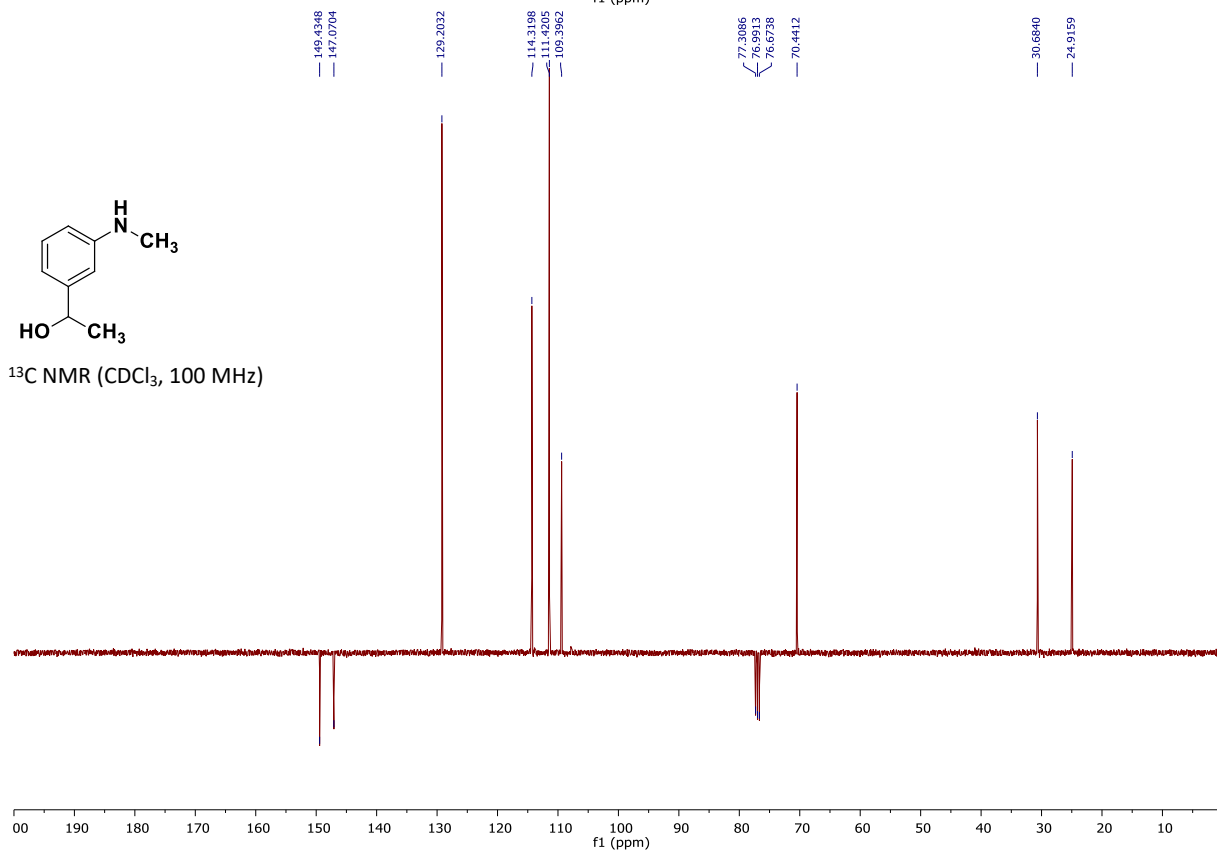
1-[3-(Methylamino)phenyl]ethanol (5)



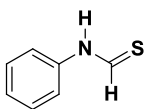
^1H NMR (CDCl_3 , 400 MHz)



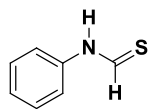
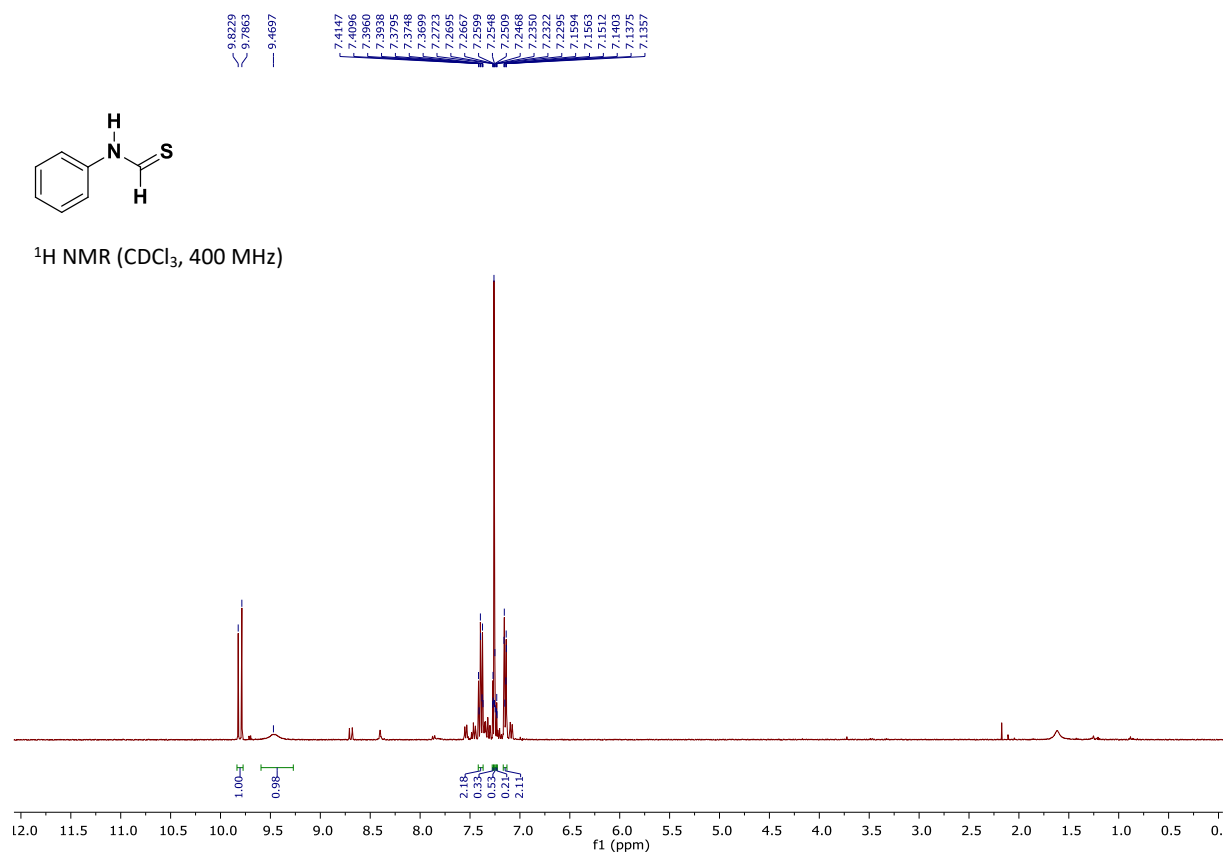
^{13}C NMR (CDCl_3 , 100 MHz)



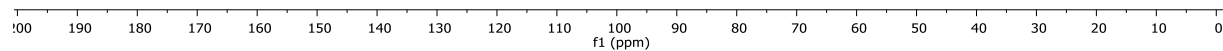
N-Phenylthioformamide (6)



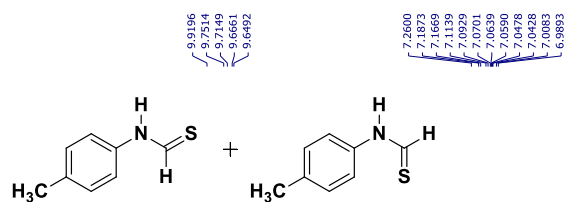
¹H NMR (CDCl₃, 400 MHz)



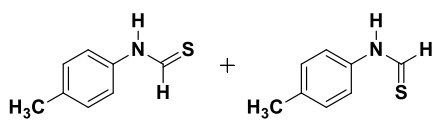
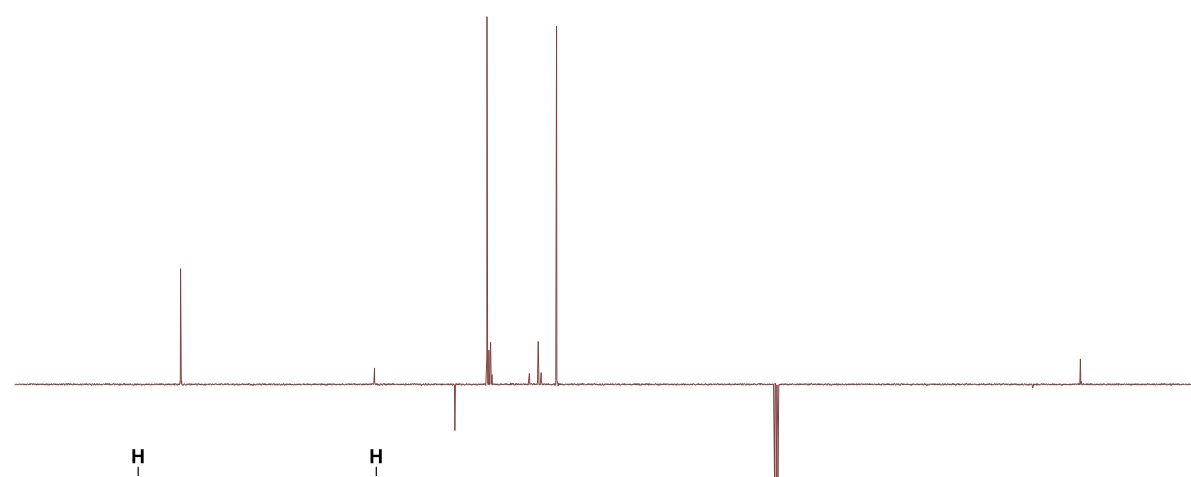
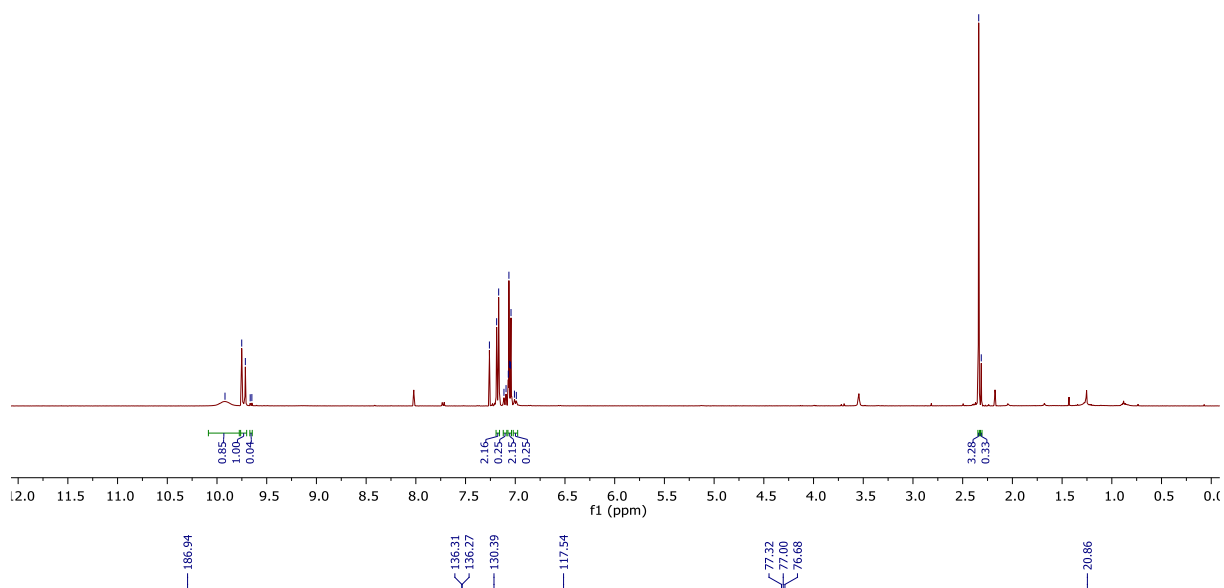
¹³C NMR (CDCl₃, 100 MHz)



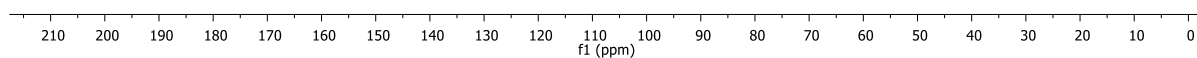
***N*-(4-Methylphenyl)thioformamide (7)**



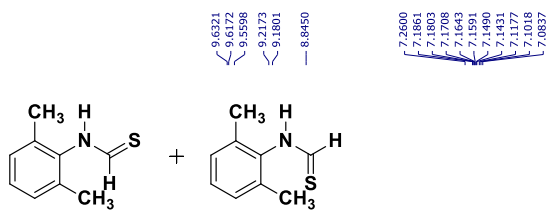
^1H NMR (CDCl_3 , 400 MHz)



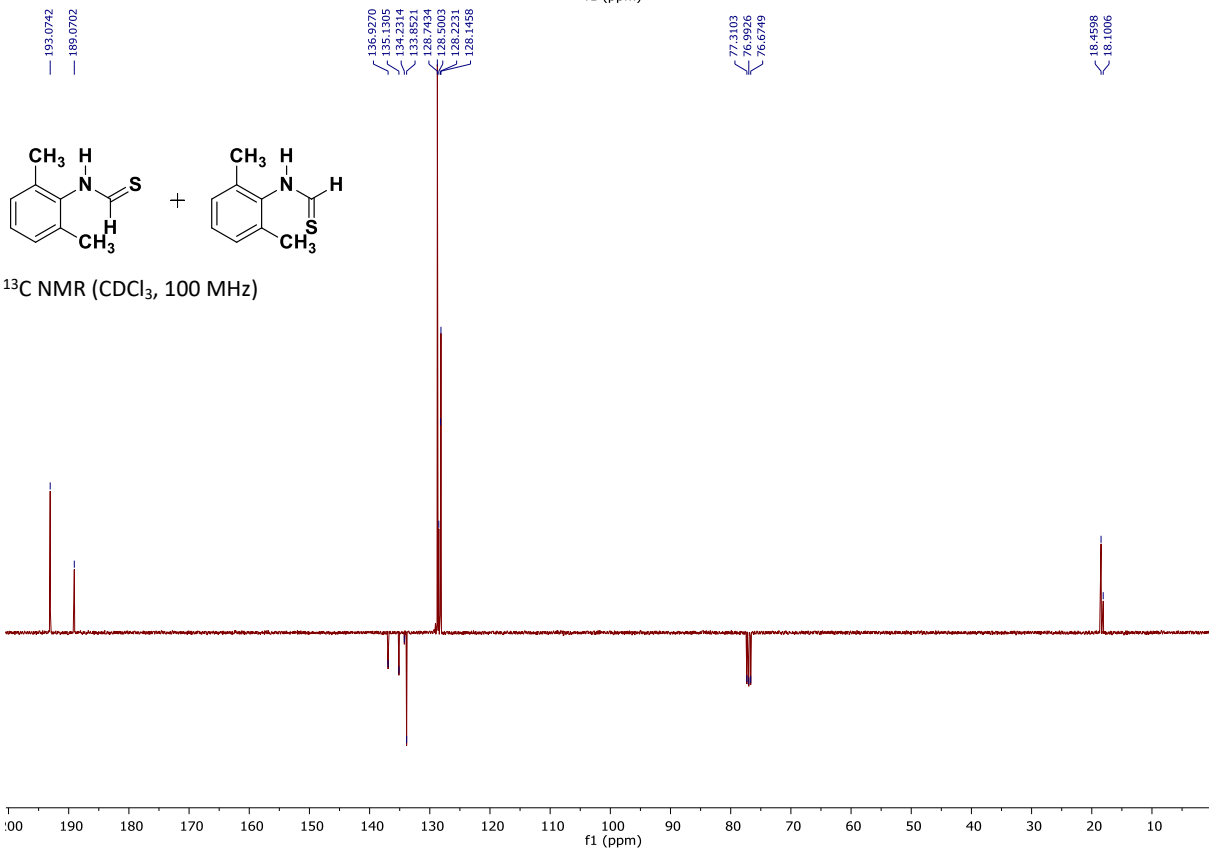
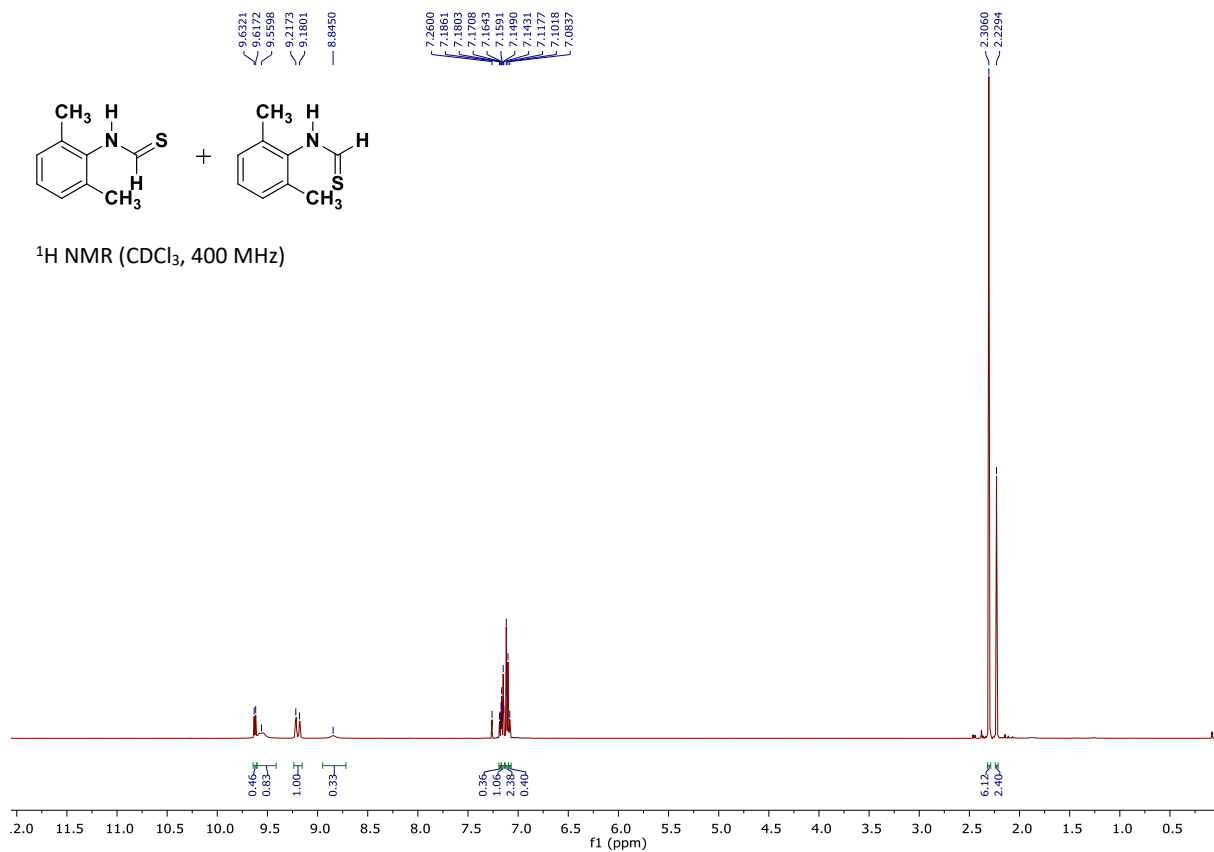
^{13}C NMR (CDCl_3 , 100 MHz)



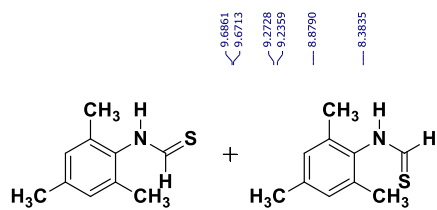
***N*-(2,6-Dimethylphenyl)thioformamide (8)**



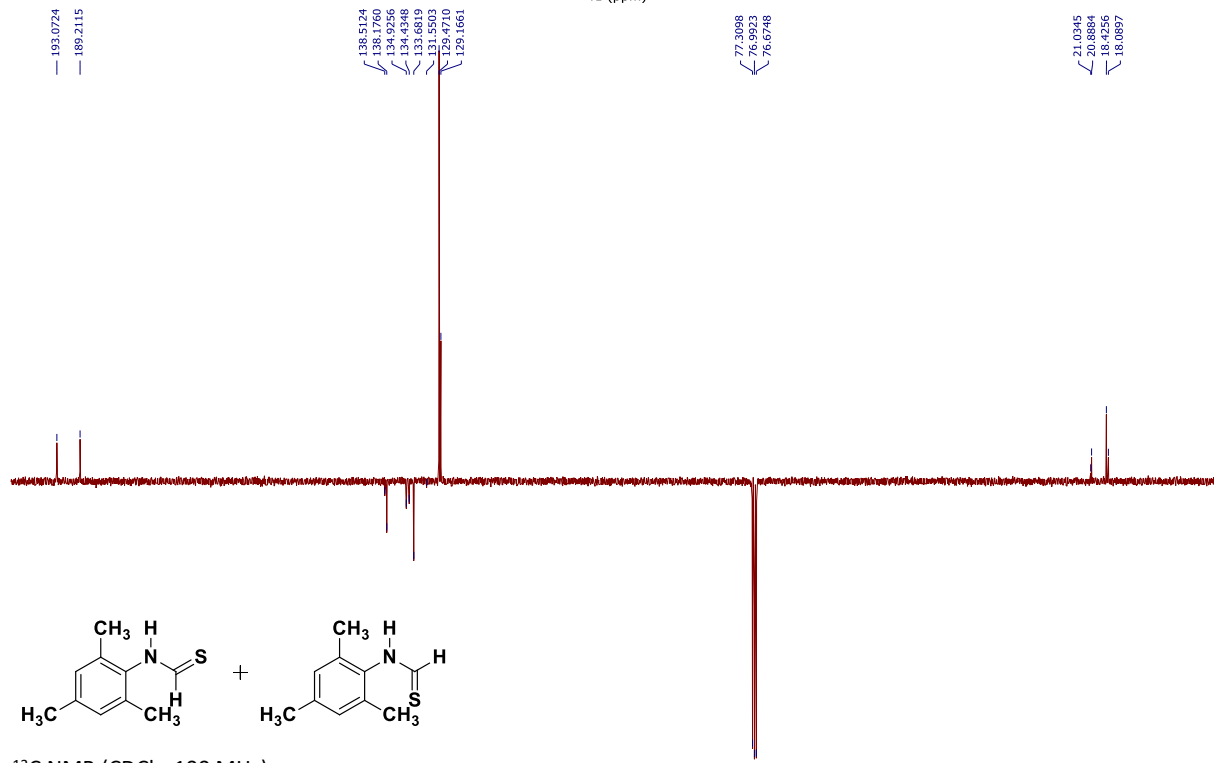
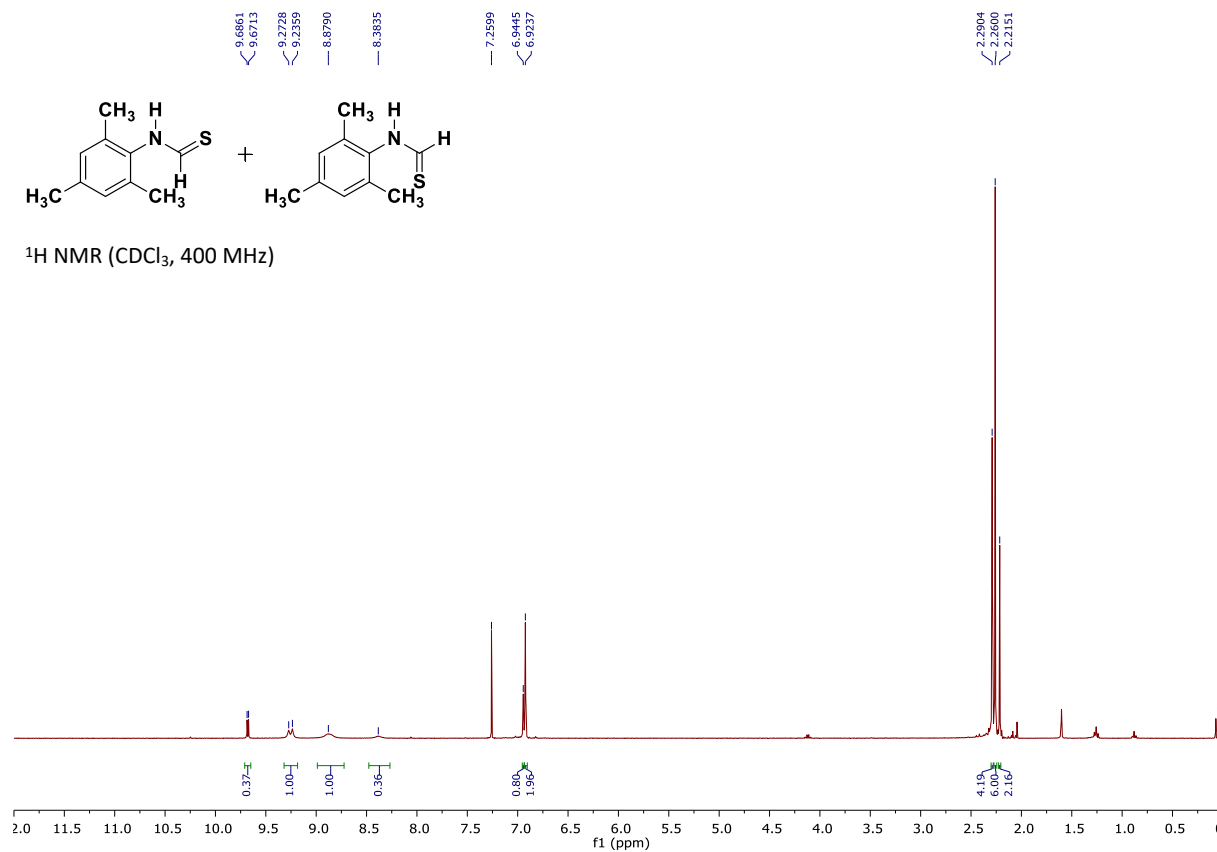
¹H NMR (CDCl₃, 400 MHz)



N-Mesitylthioformamide (9)

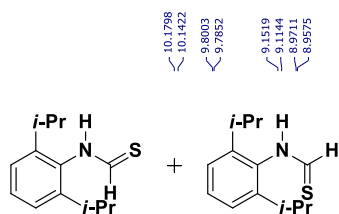


^1H NMR (CDCl_3 , 400 MHz)

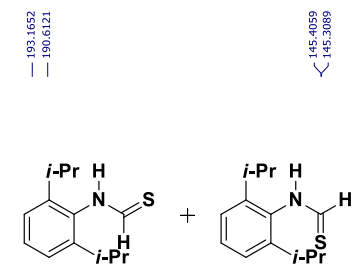
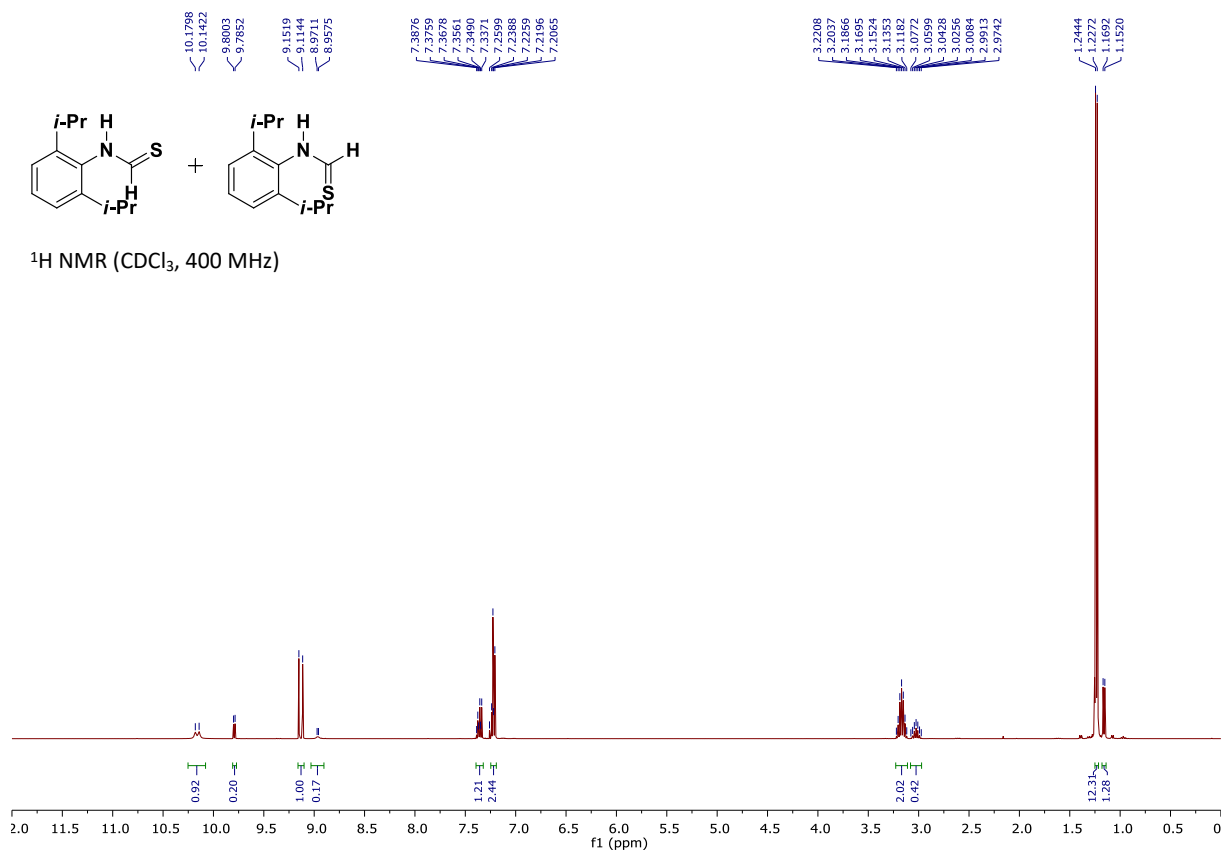


^{13}C NMR (CDCl_3 , 100 MHz)

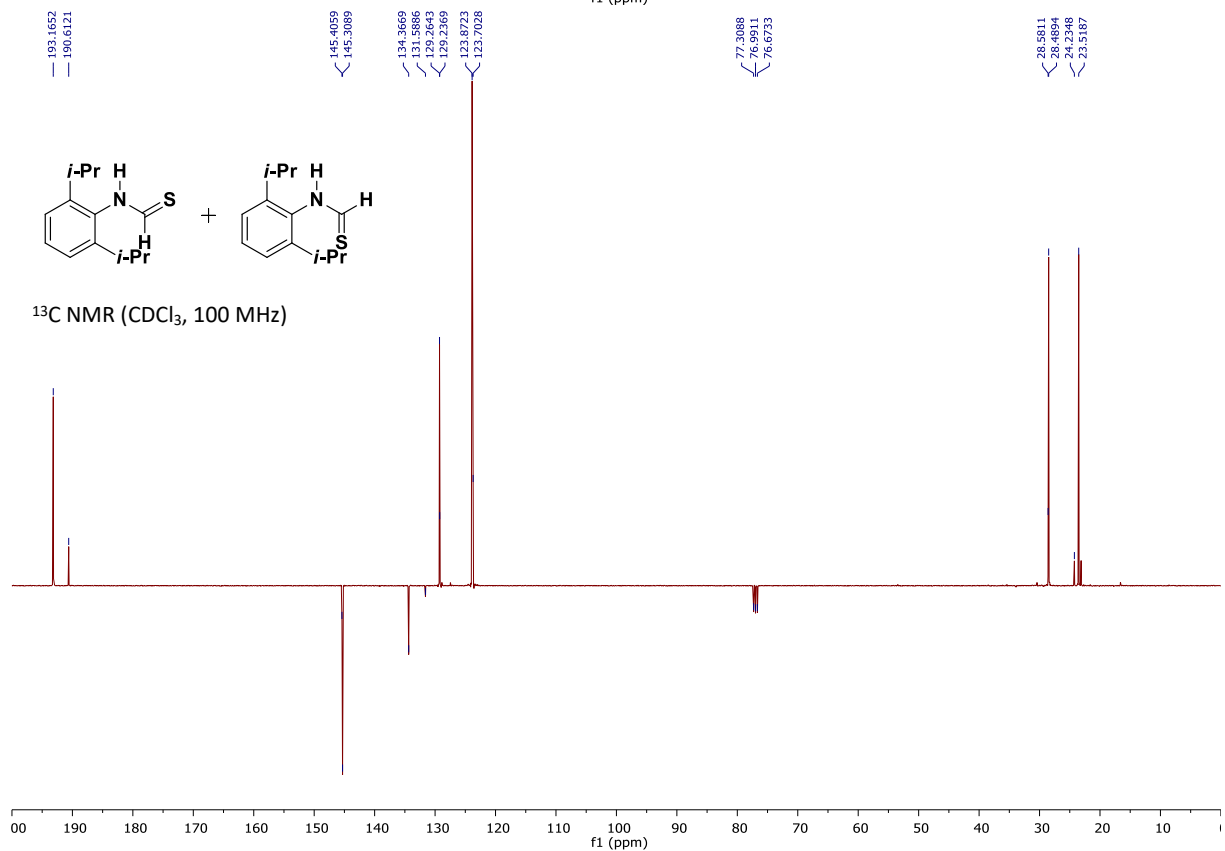
***N*-(2,6-Diisopropylphenyl)thioformamide (10)**



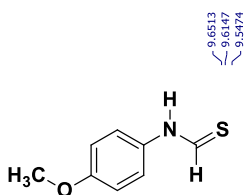
^1H NMR (CDCl_3 , 400 MHz)



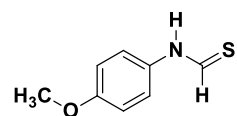
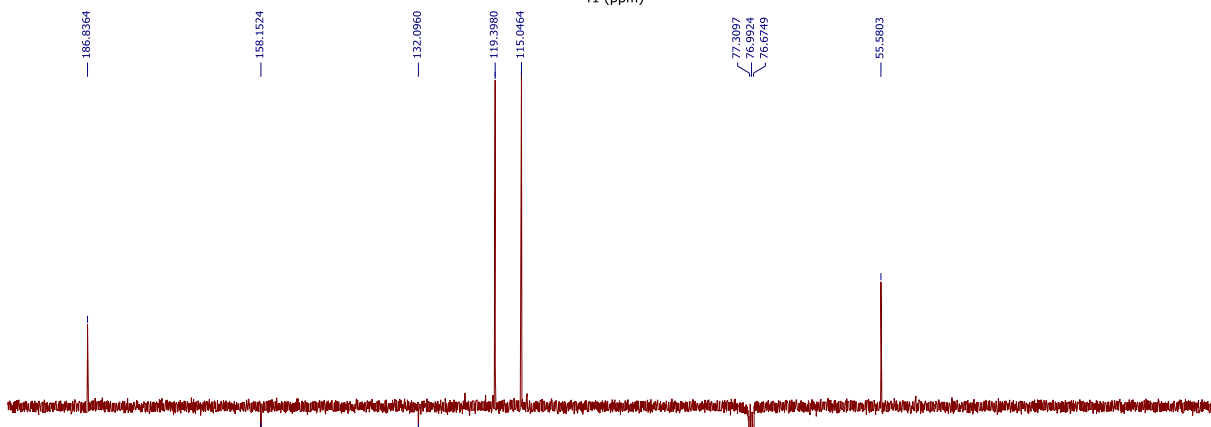
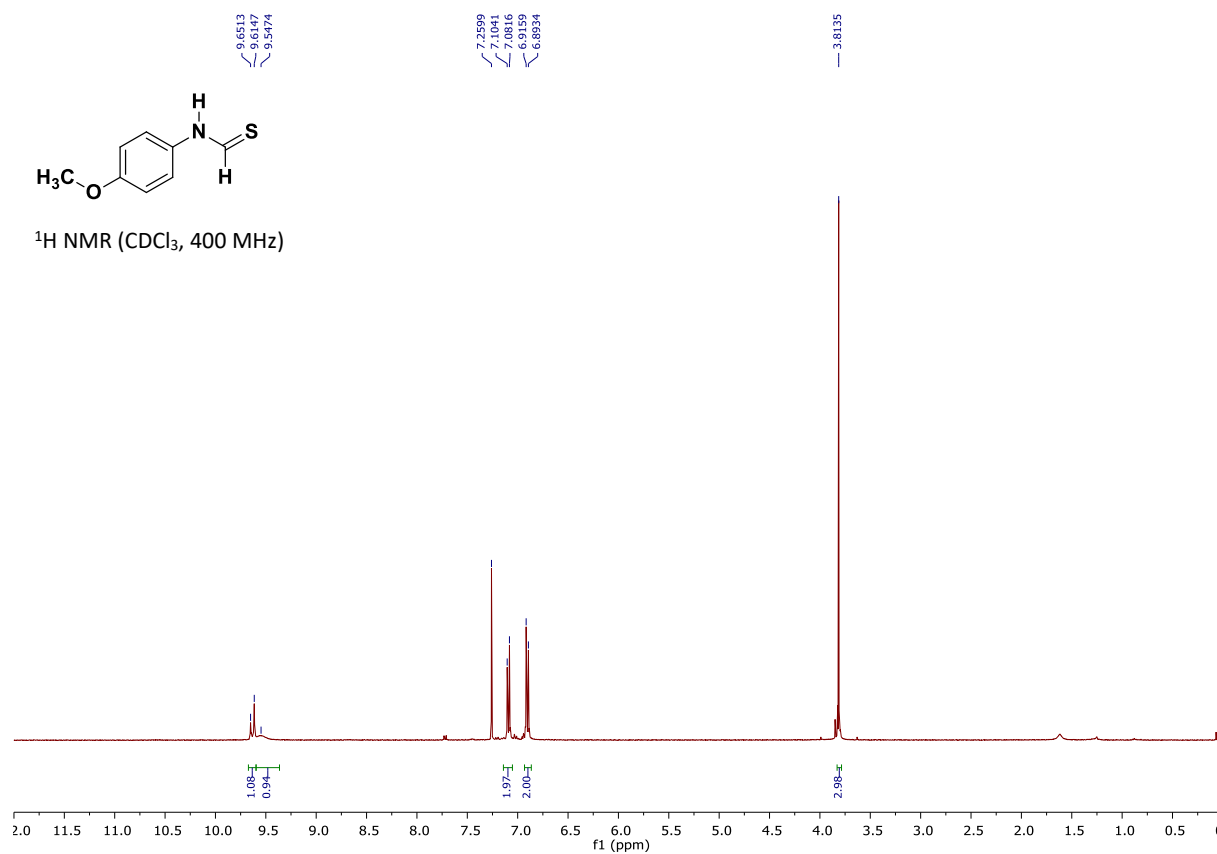
^{13}C NMR (CDCl_3 , 100 MHz)



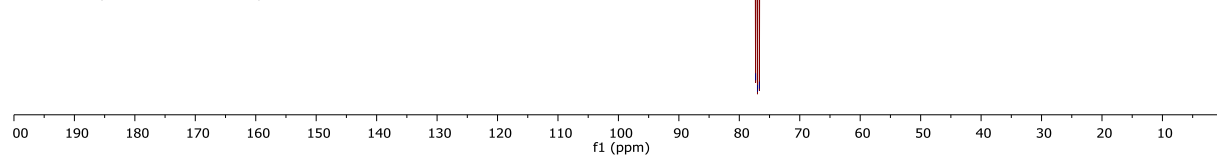
***N*-(4-Methoxyphenyl)thioformamide (11)**



^1H NMR (CDCl_3 , 400 MHz)



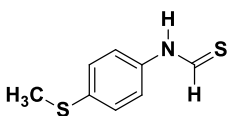
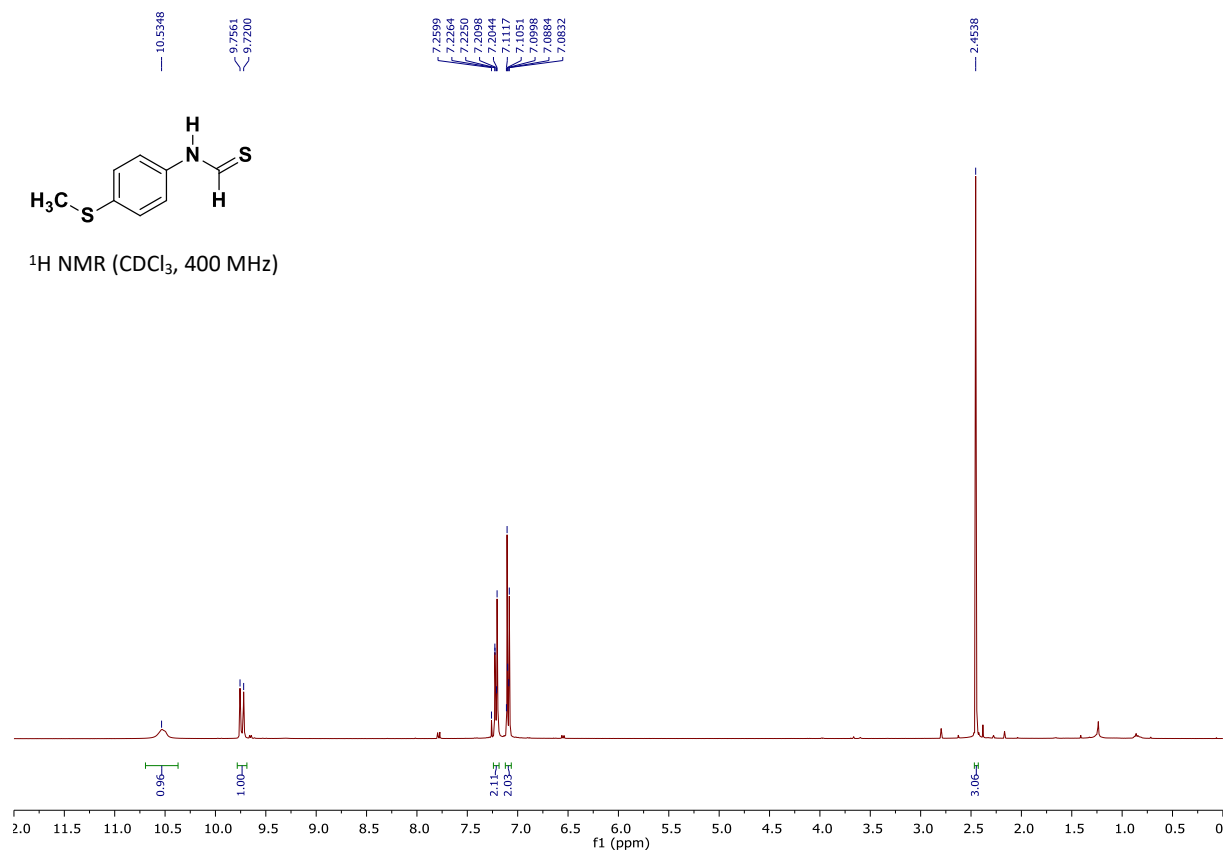
^{13}C NMR (CDCl_3 , 100 MHz)



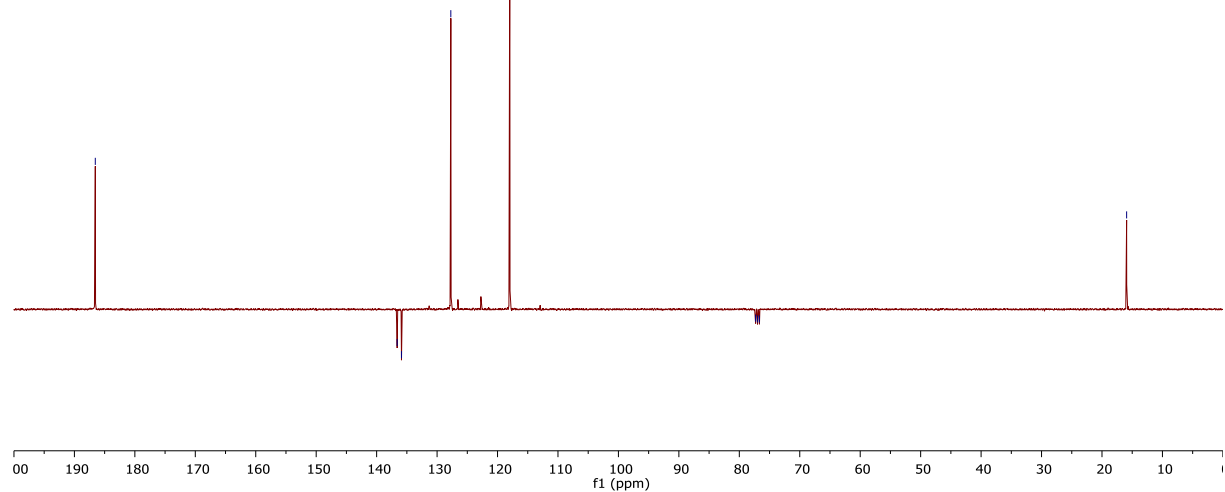
***N*-[4-(Methylsulfanyl)phenyl]thioformamide (12)**



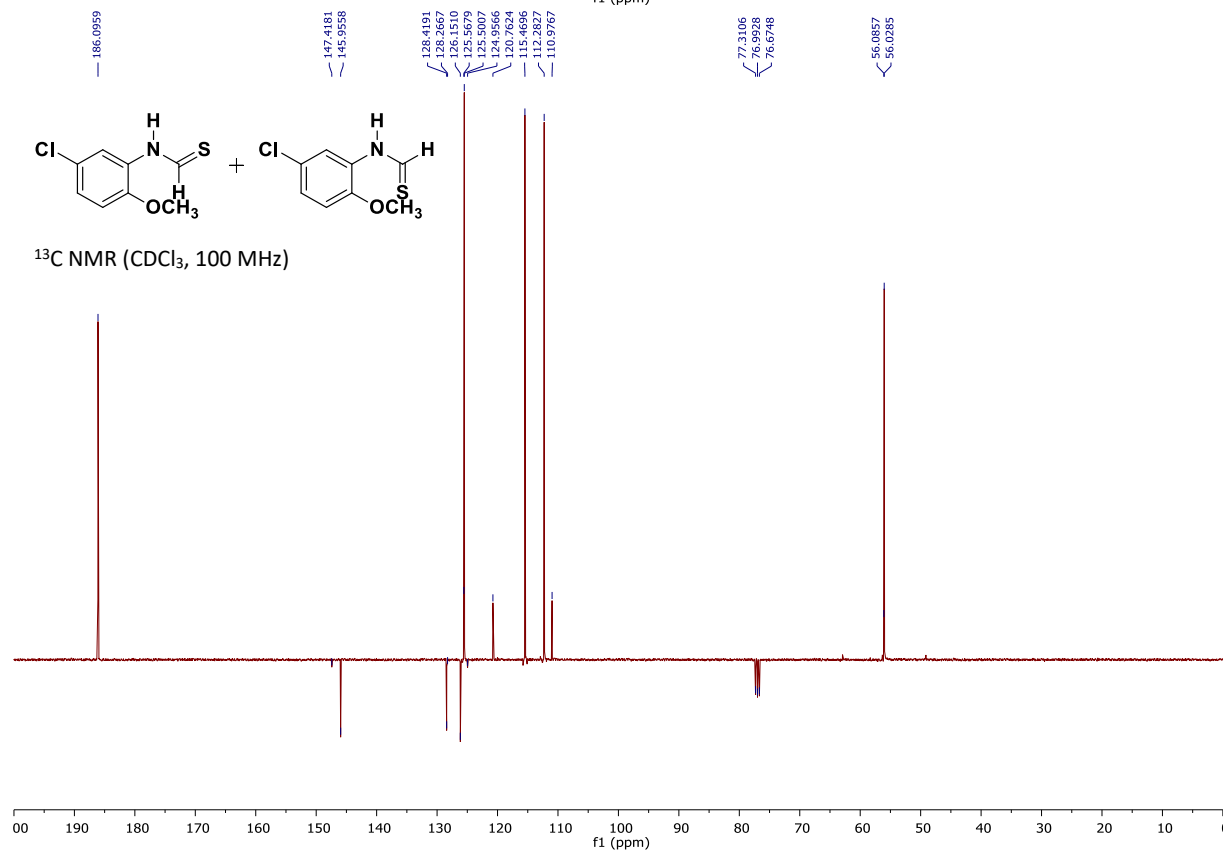
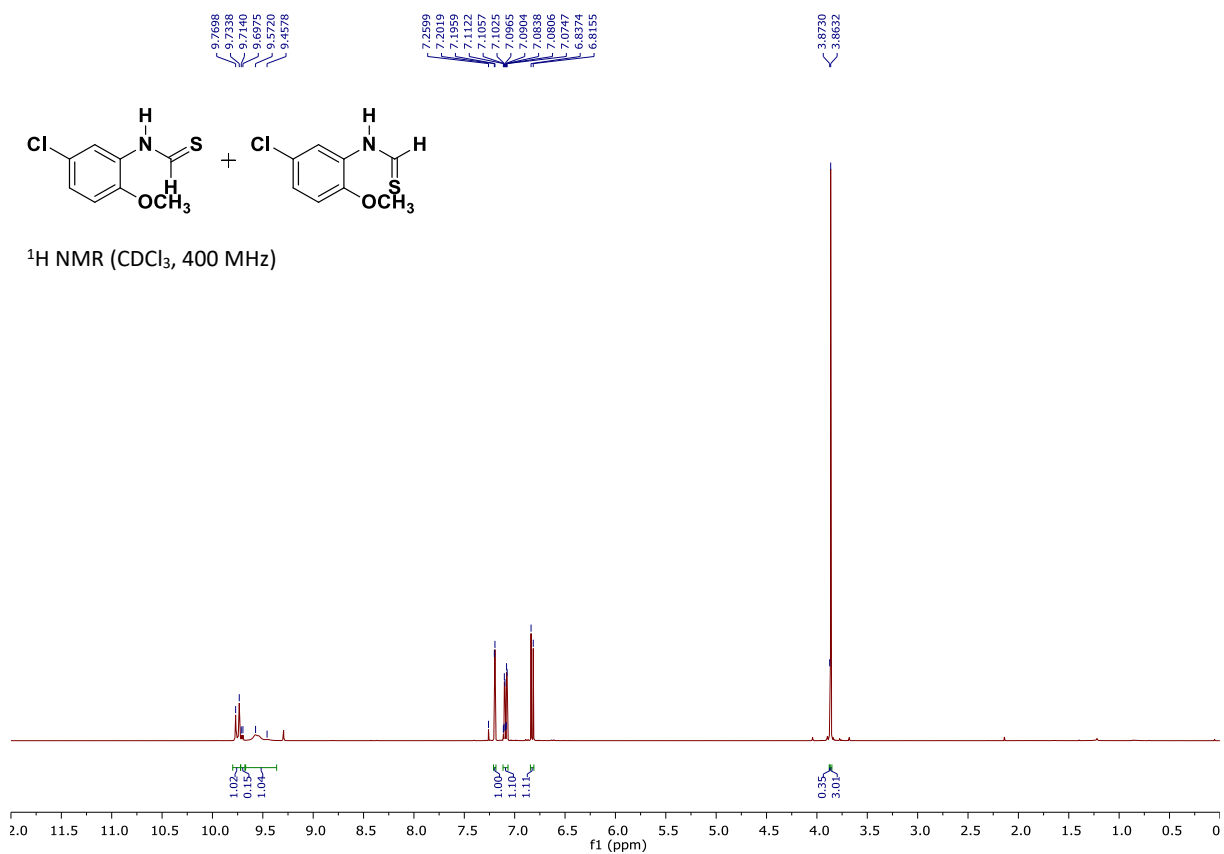
^1H NMR (CDCl_3 , 400 MHz)



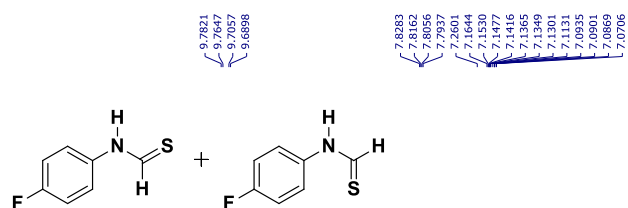
^{13}C NMR (CDCl_3 , 100 MHz)



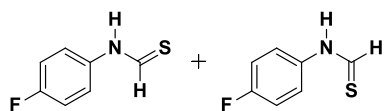
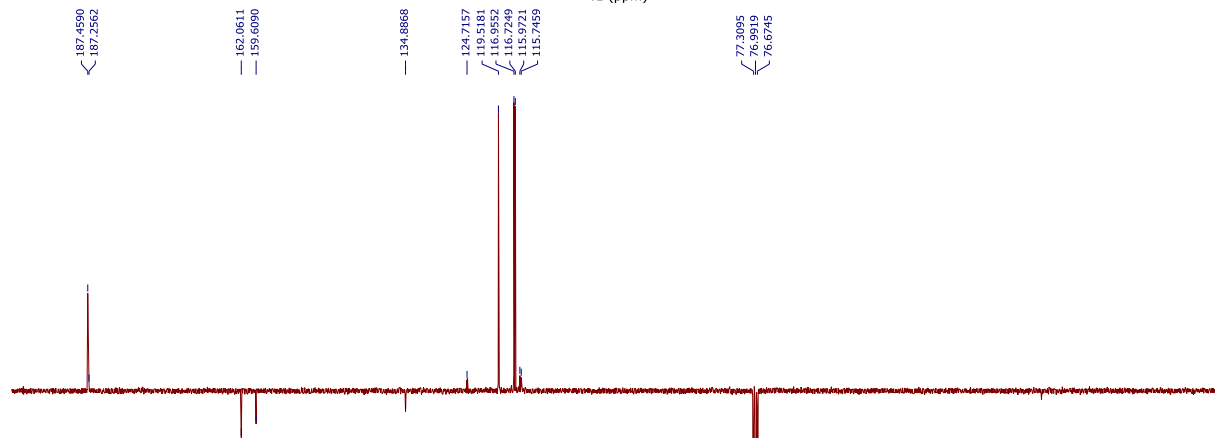
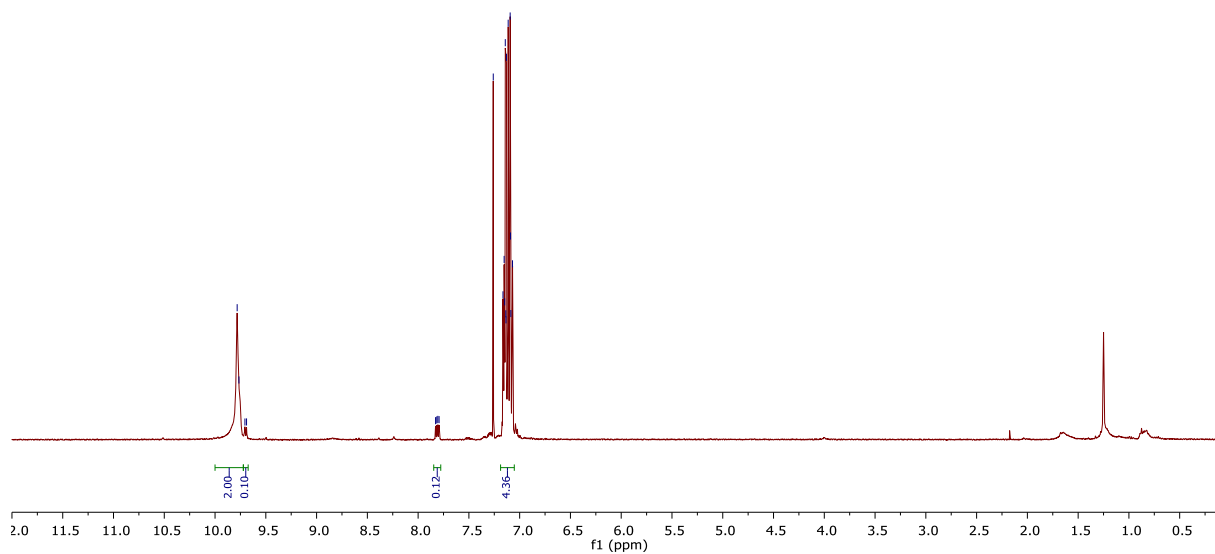
***N*-(5-chloro-2-methoxyphenyl)thioformamide (13)**



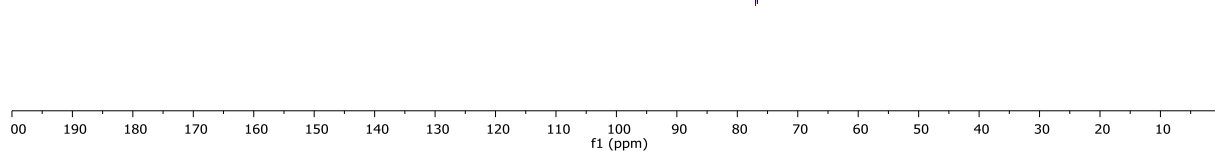
***N*-(4-Fluorophenyl)thioformamide (14)**



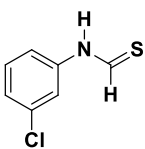
¹H NMR (CDCl₃, 400 MHz)



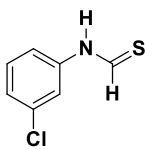
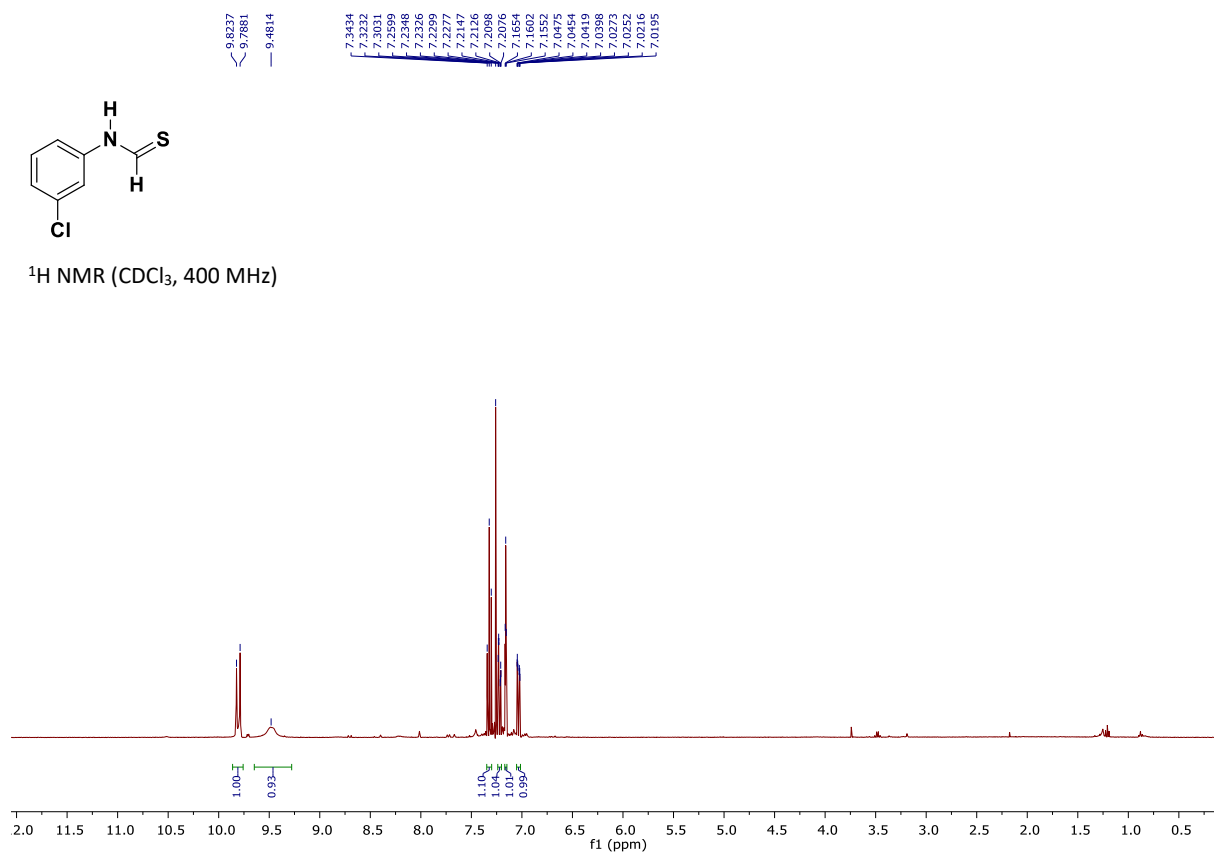
¹³C NMR (CDCl₃, 100 MHz)



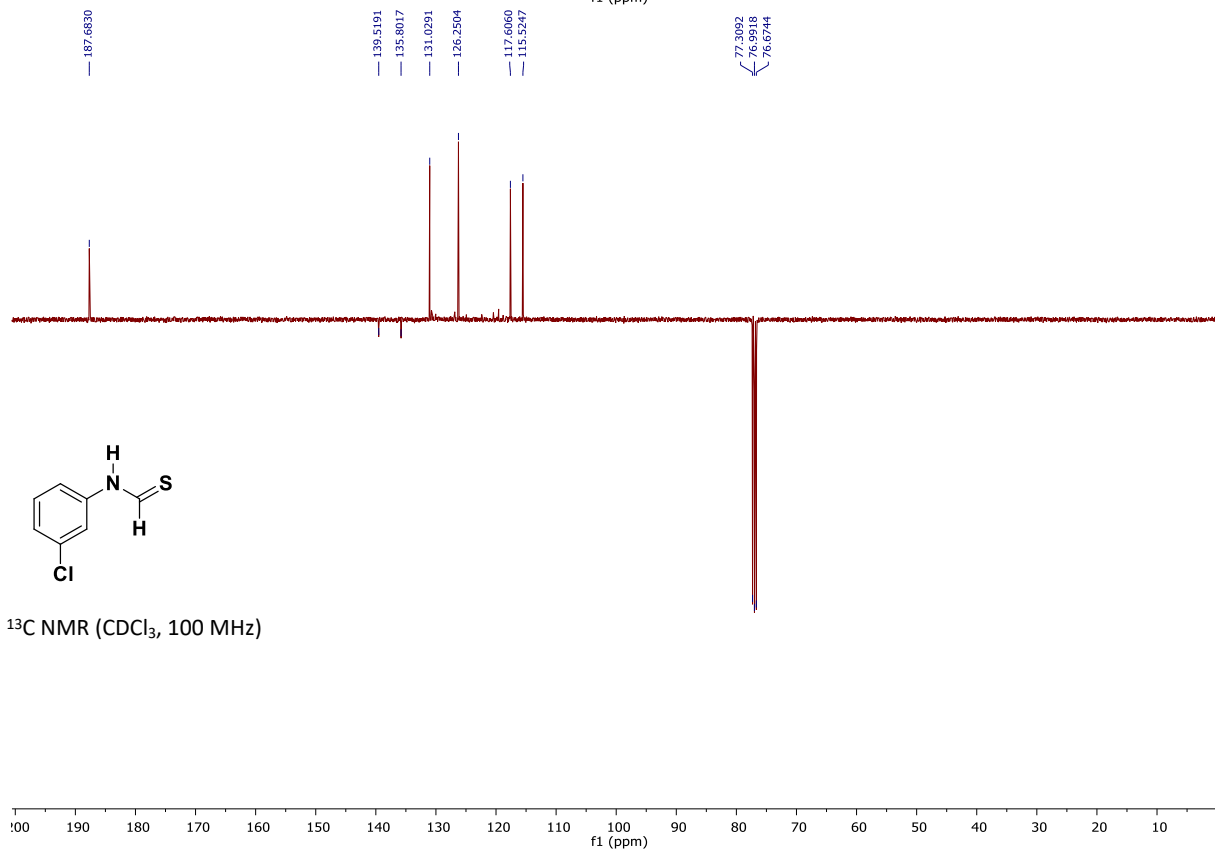
***N*-(3-Chlorophenyl)thioformamide (15)**



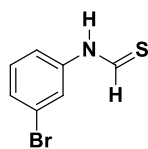
^1H NMR (CDCl_3 , 400 MHz)



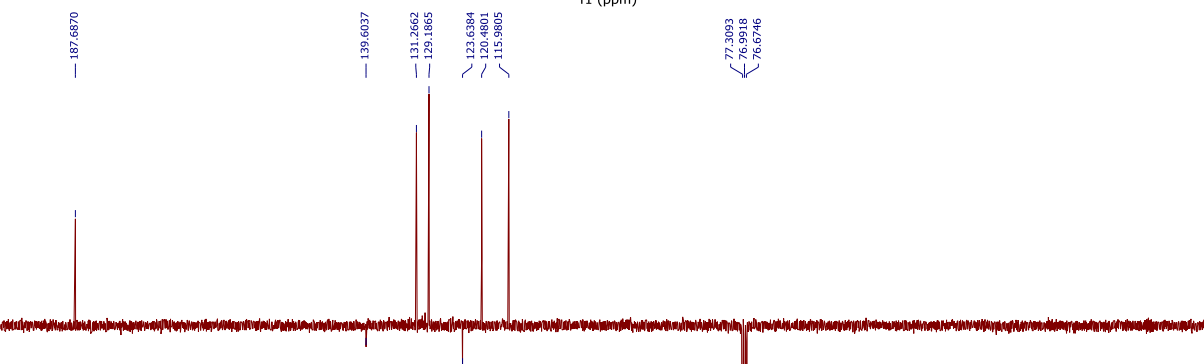
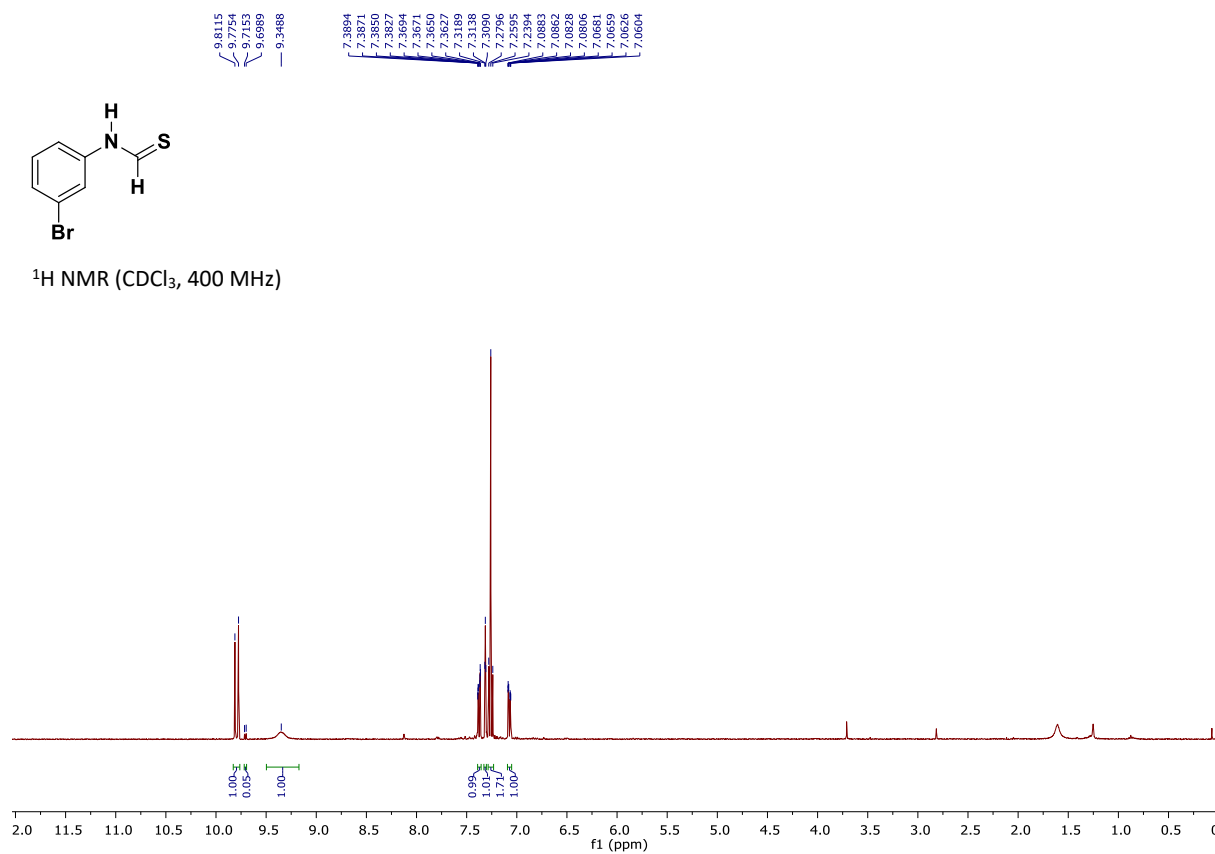
^{13}C NMR (CDCl_3 , 100 MHz)



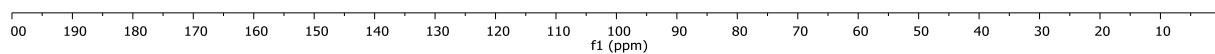
***N*-(3-Bromophenyl)thioformamide (16)**



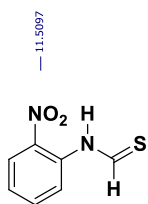
^1H NMR (CDCl_3 , 400 MHz)



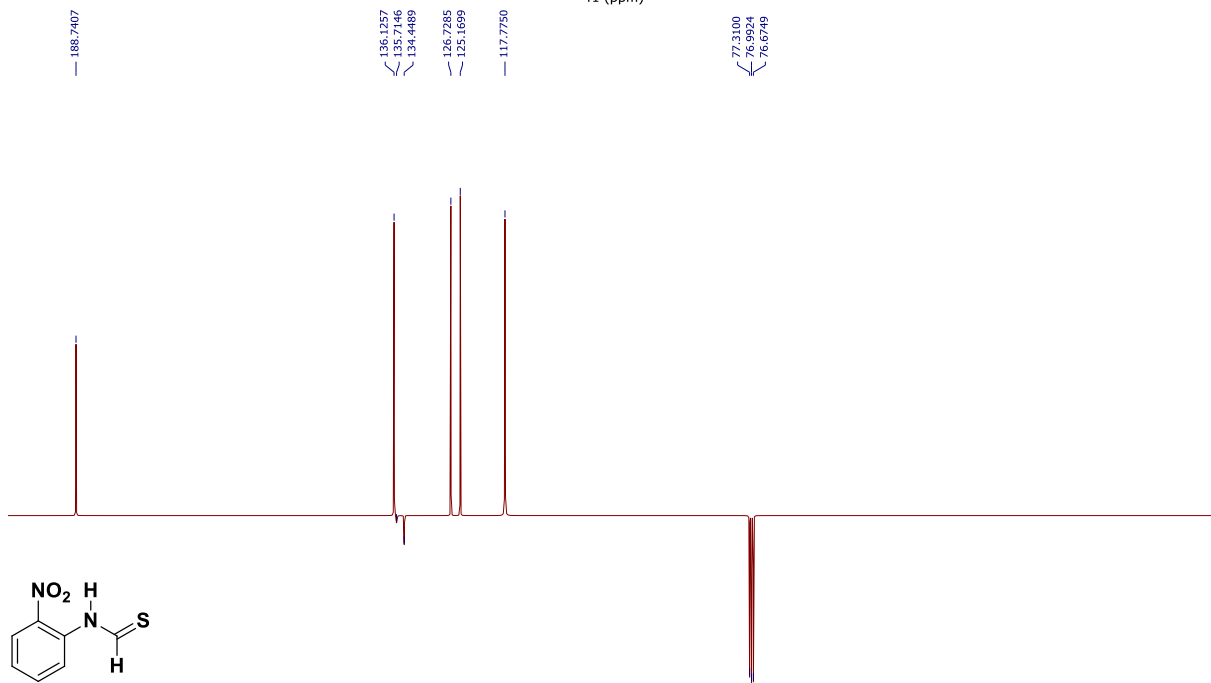
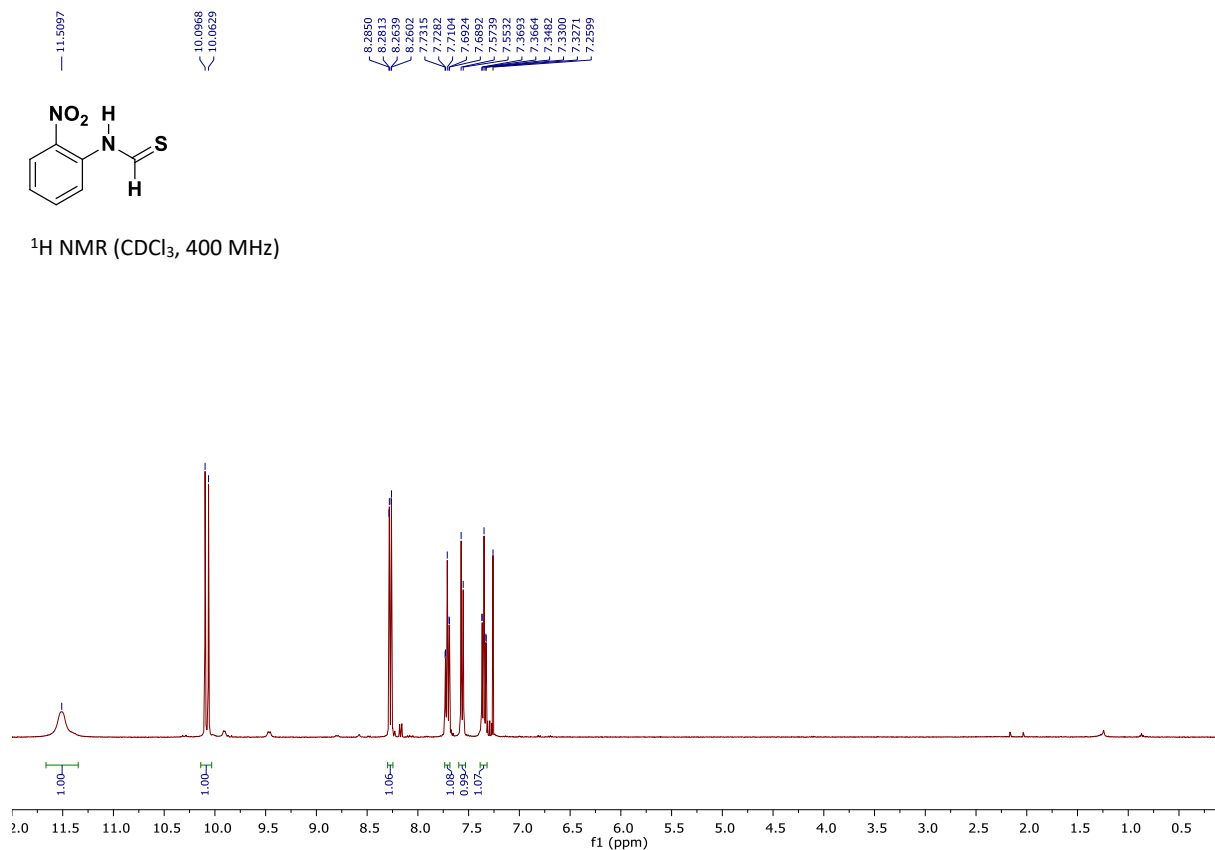
^{13}C NMR (CDCl_3 , 100 MHz)



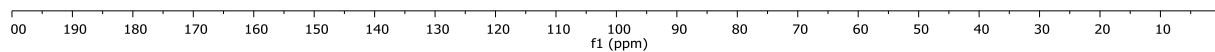
***N*-(2-Nitrophenyl)thioformamide (17)**



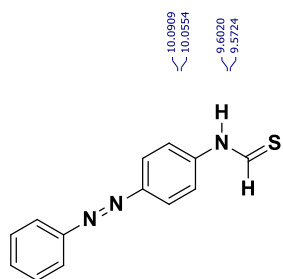
¹H NMR (CDCl₃, 400 MHz)



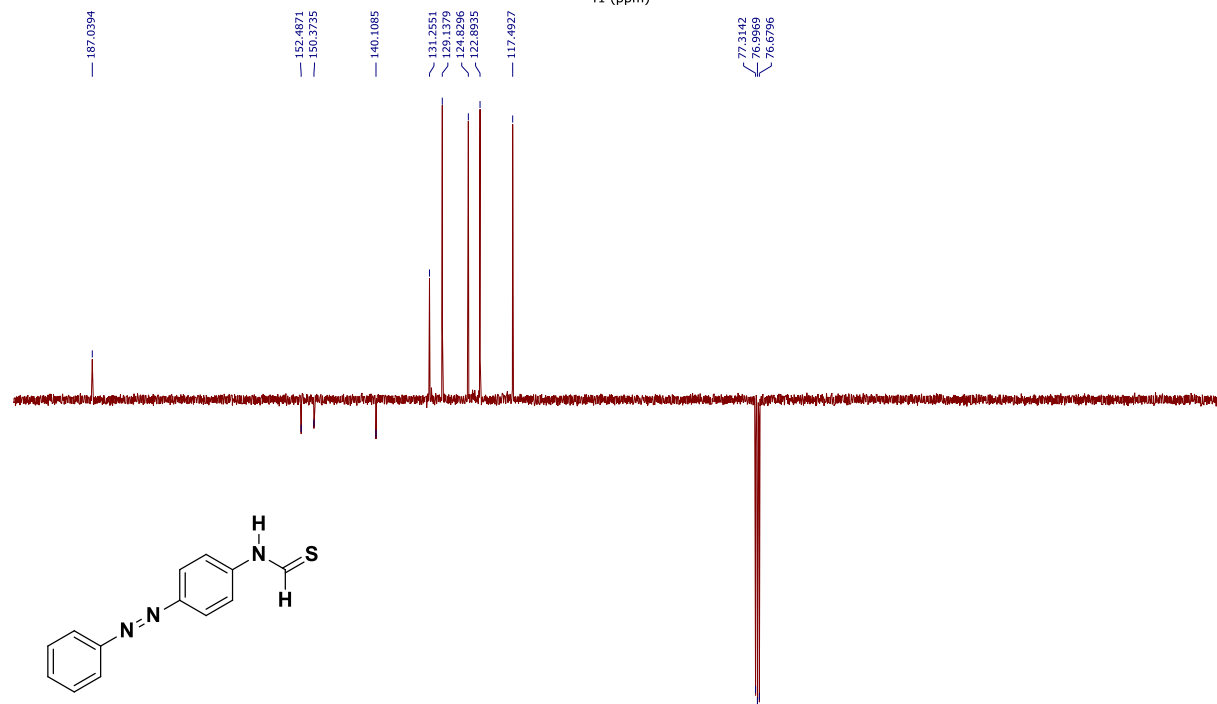
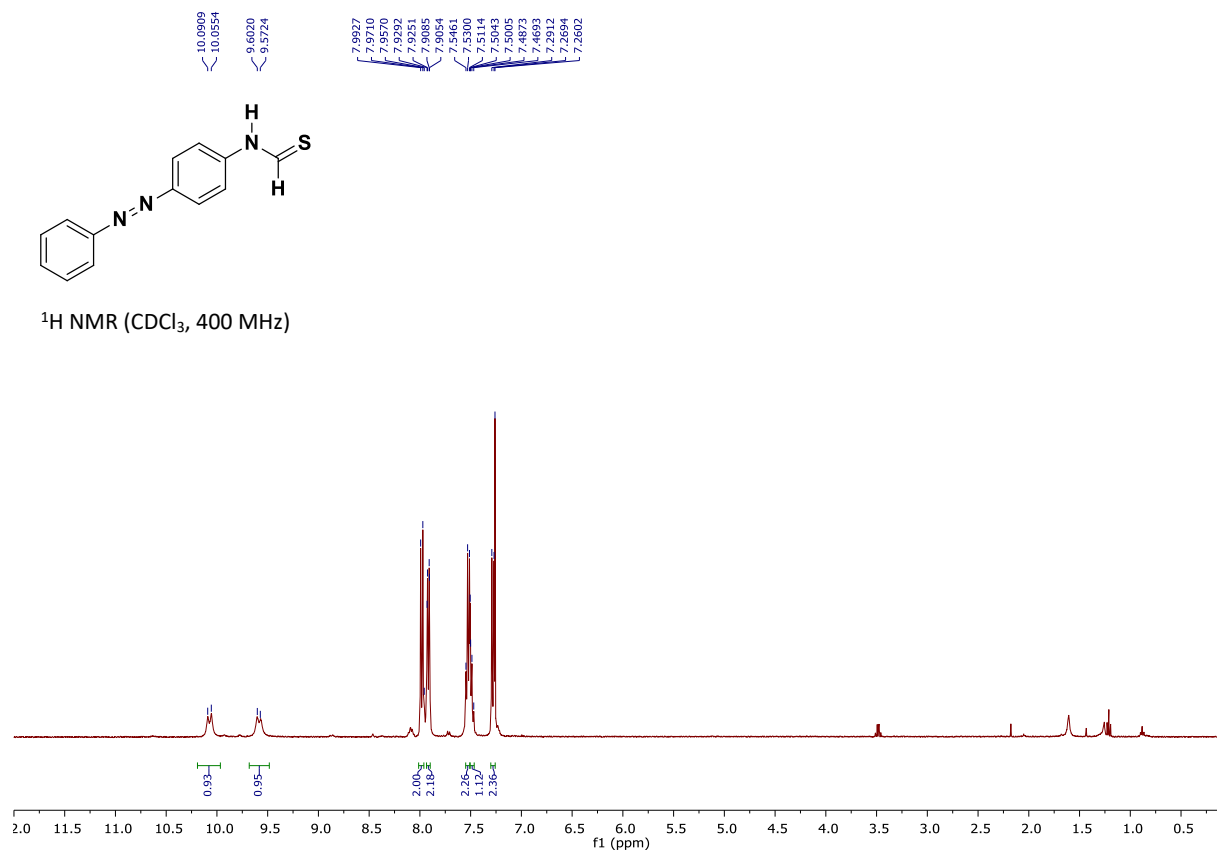
¹³C NMR (CDCl₃, 100 MHz)



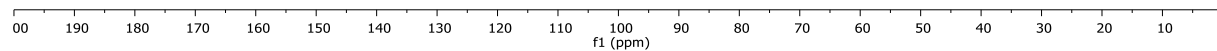
***N*-[4-(Phenyldiazenyl)phenyl]thioformamide (18)**



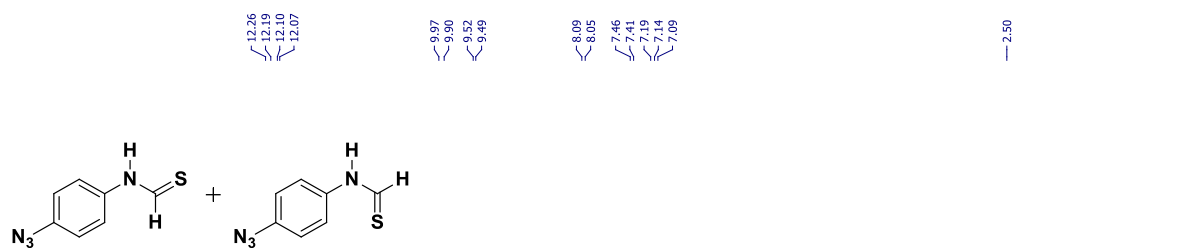
^1H NMR (CDCl_3 , 400 MHz)



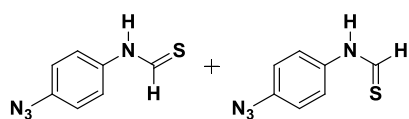
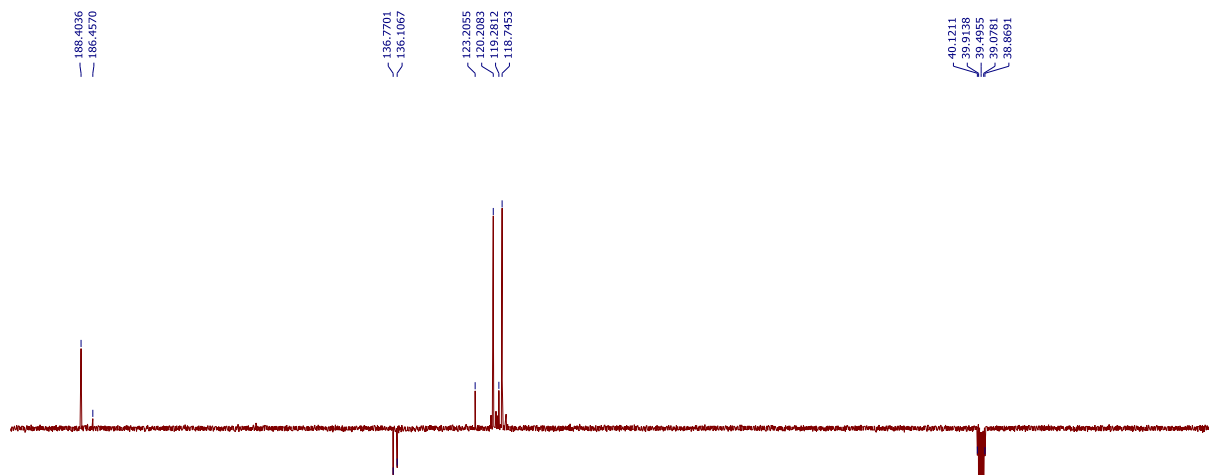
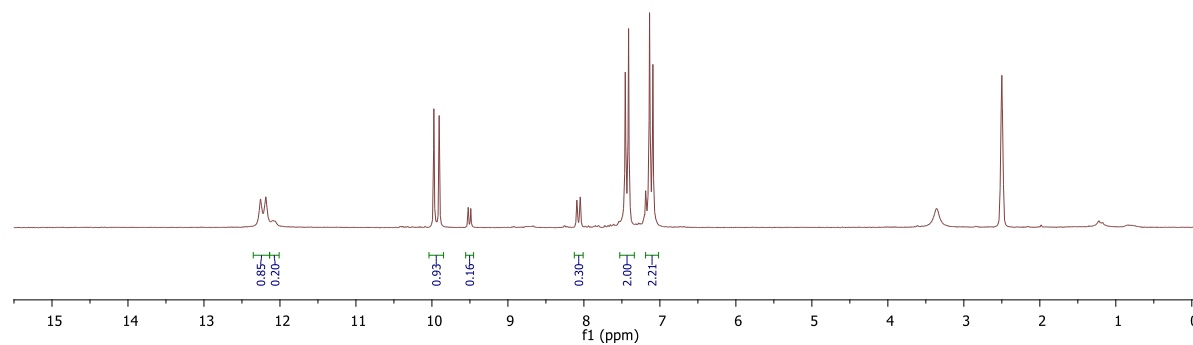
^{13}C NMR (CDCl_3 , 100 MHz)



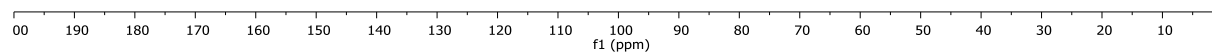
***N*-(4-Azidophenyl)thioformamide (19)**



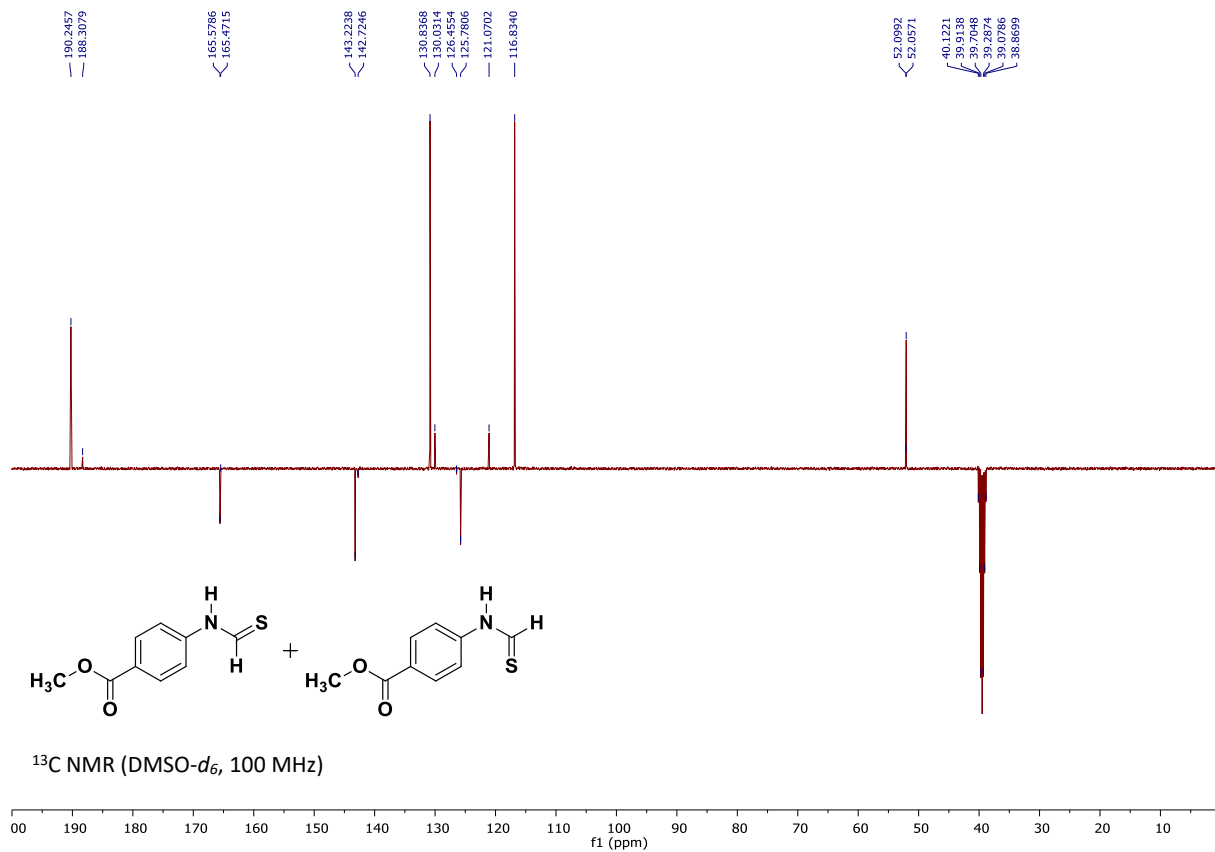
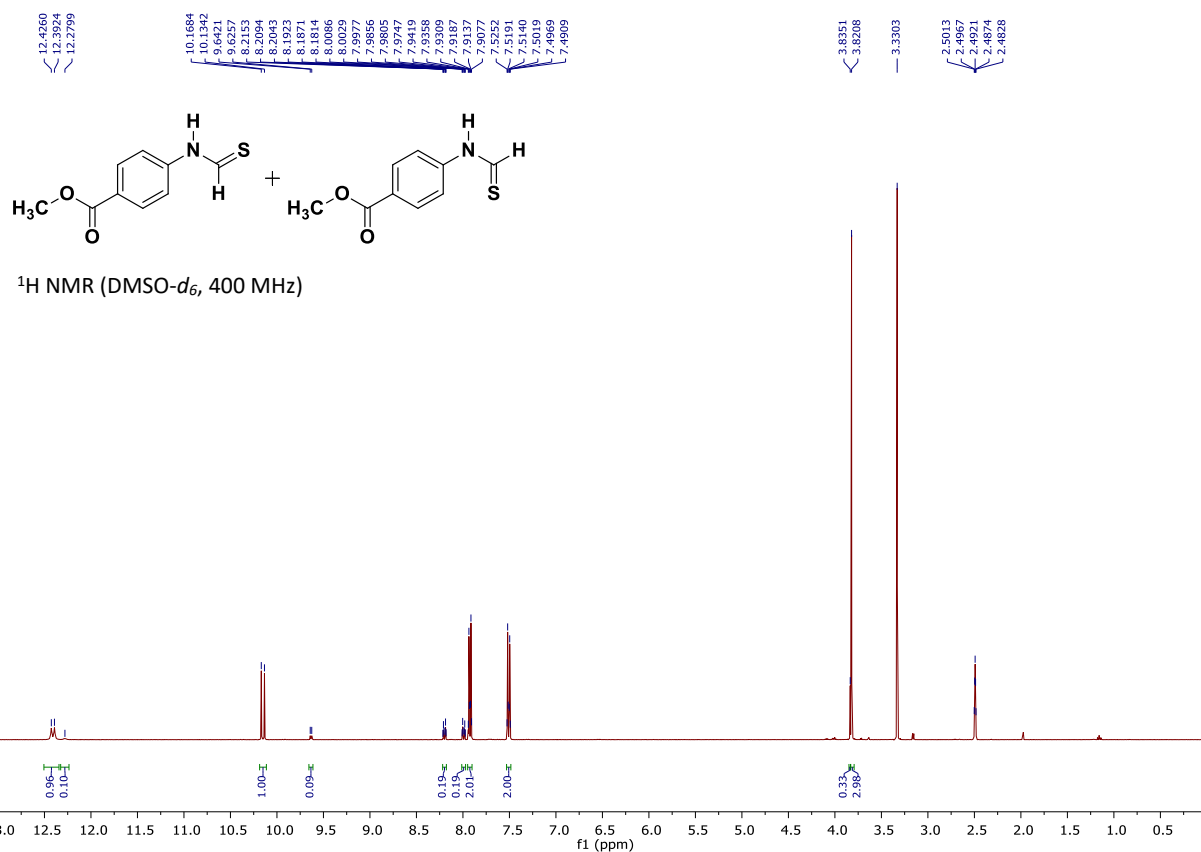
¹H NMR (DMSO-*d*₆, 200 MHz)



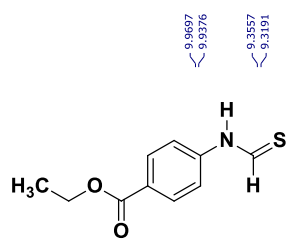
¹³C NMR (DMSO-*d*₆, 100 MHz)



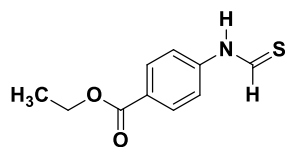
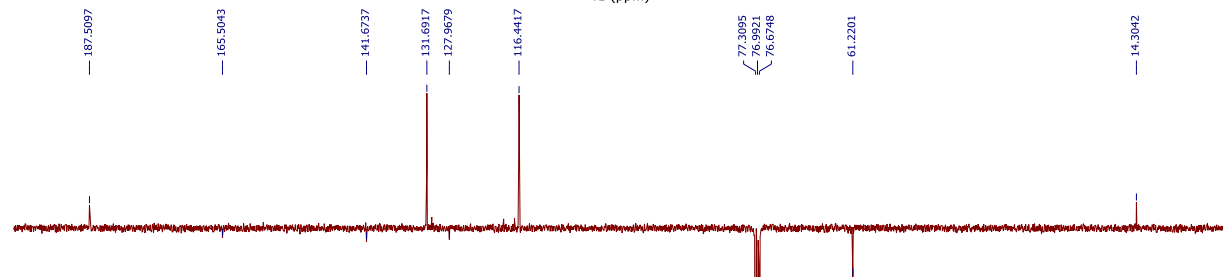
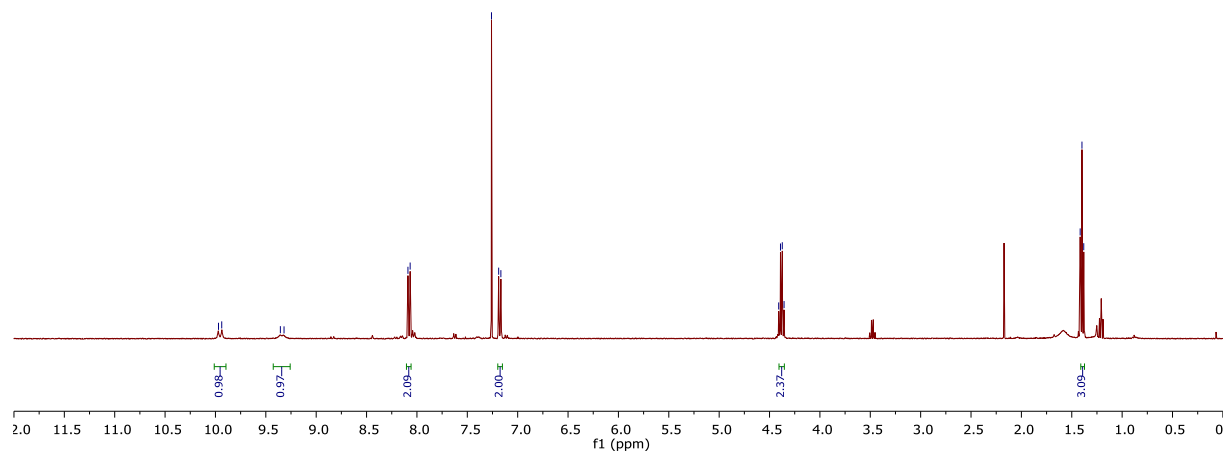
Methyl 4-(thioformylamino) benzoate (20)



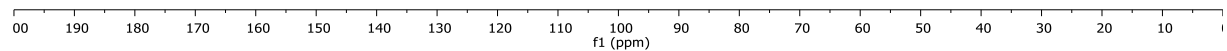
Ethyl 4-(thioformylamino) benzoate (21)

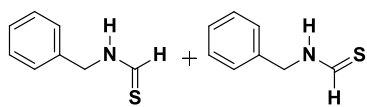
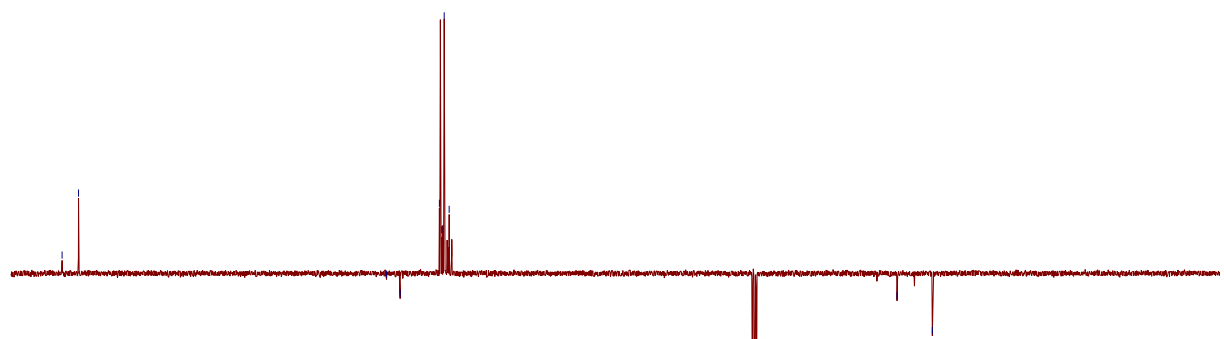


¹H NMR (CDCl₃, 400 MHz)

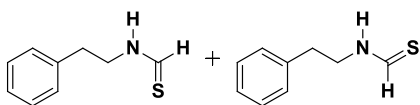


¹³C NMR (CDCl₃, 100 MHz)

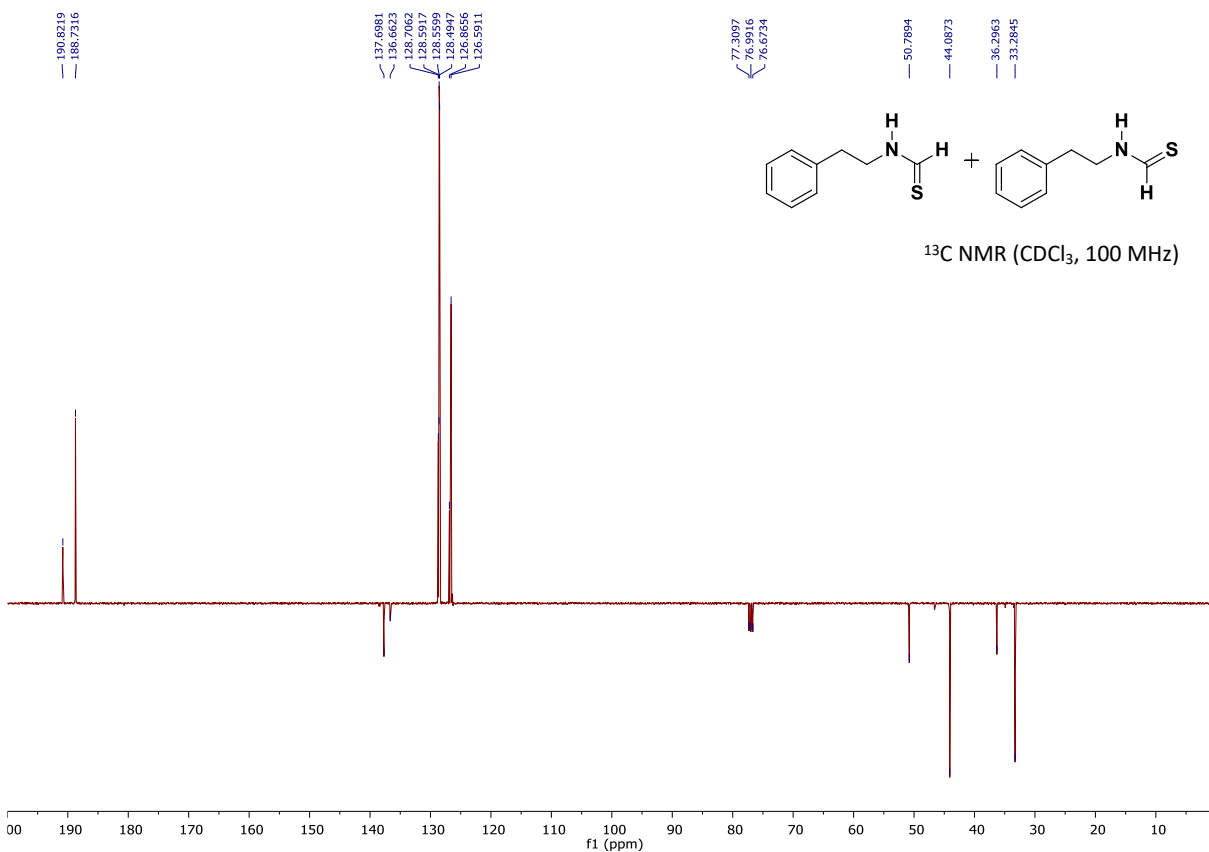
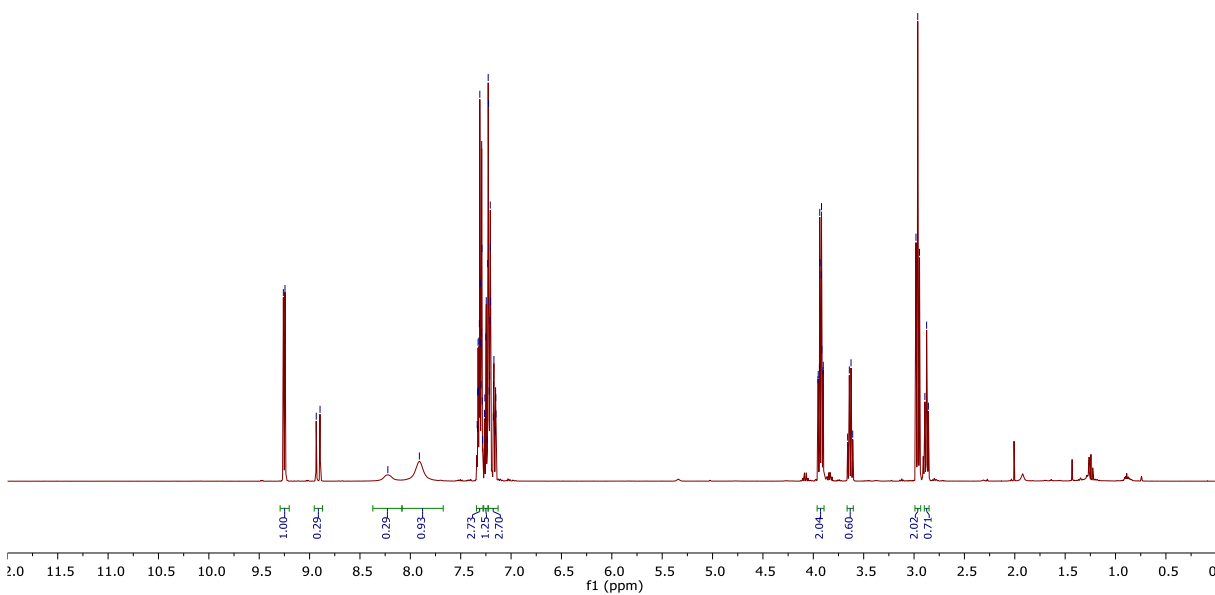




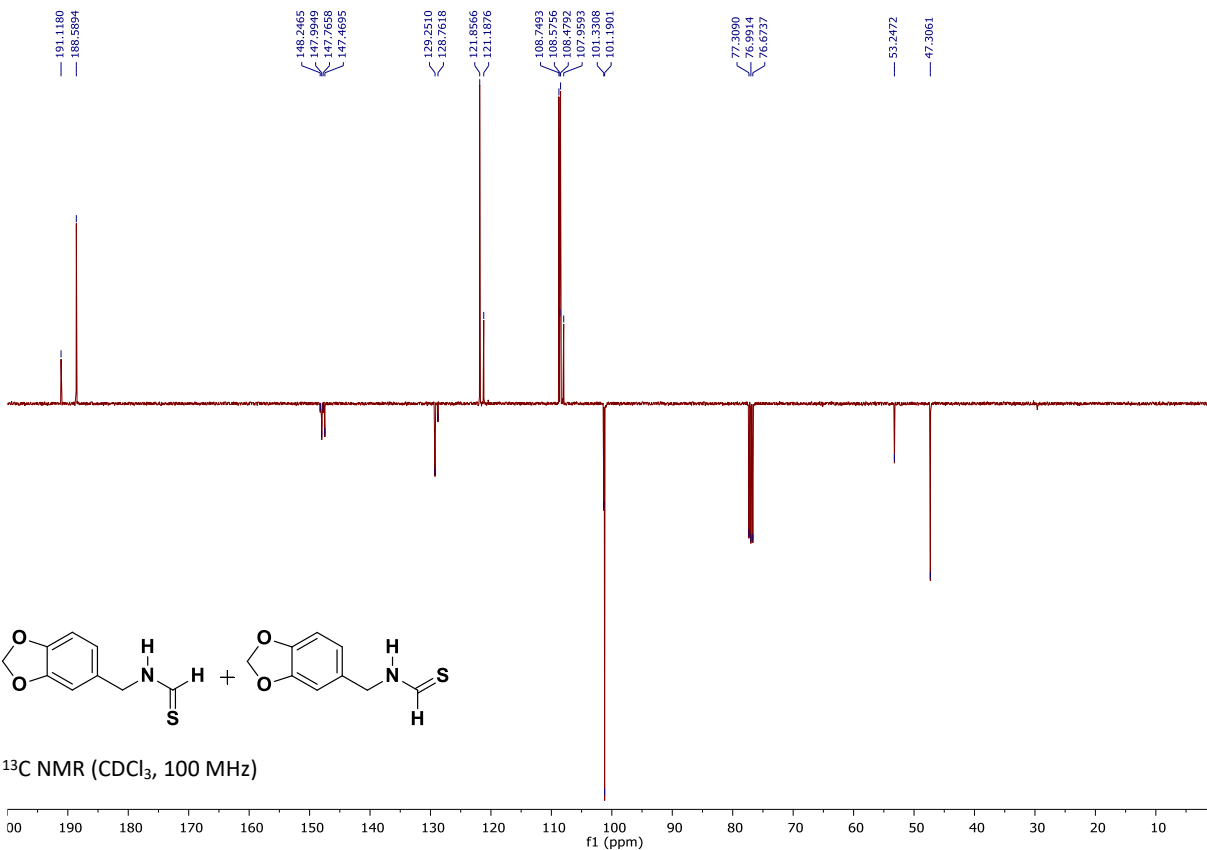
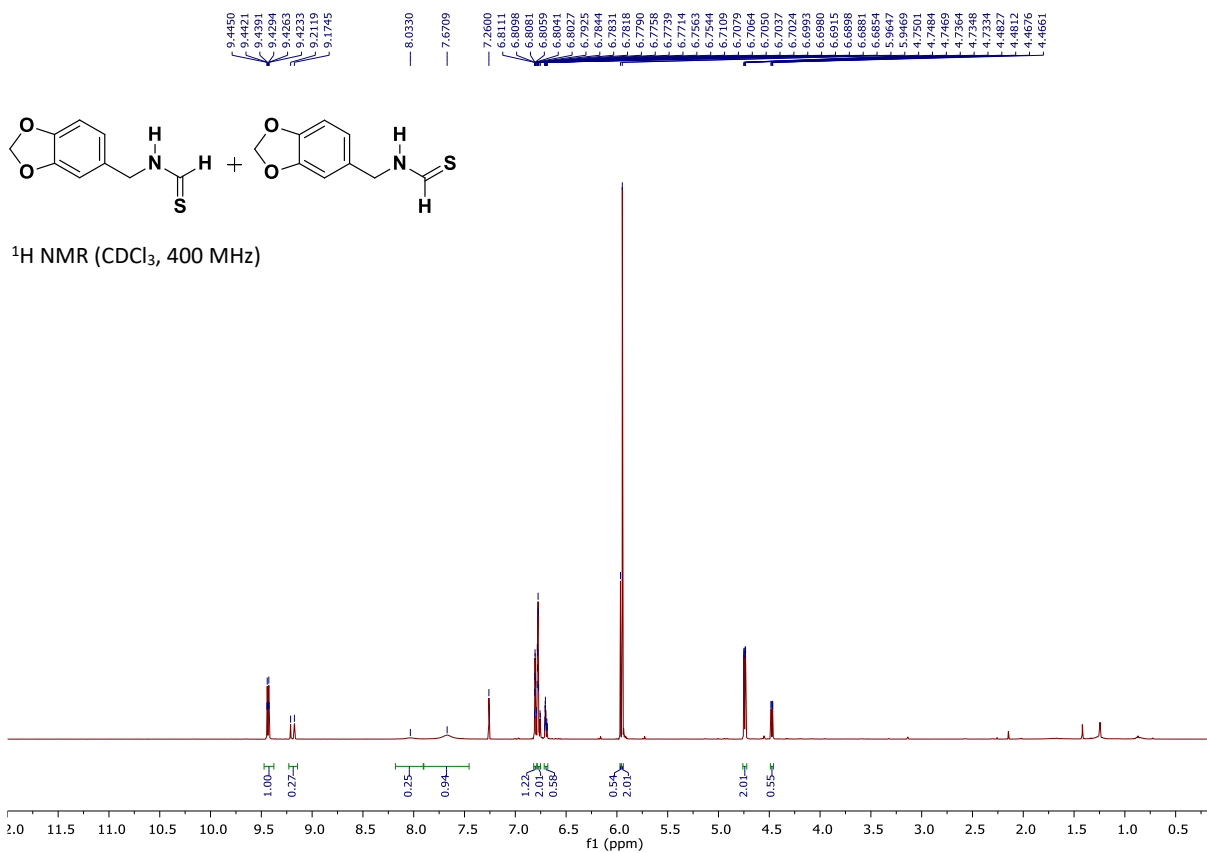
***N*-(2-Phenethyl)thioformamide (23)**



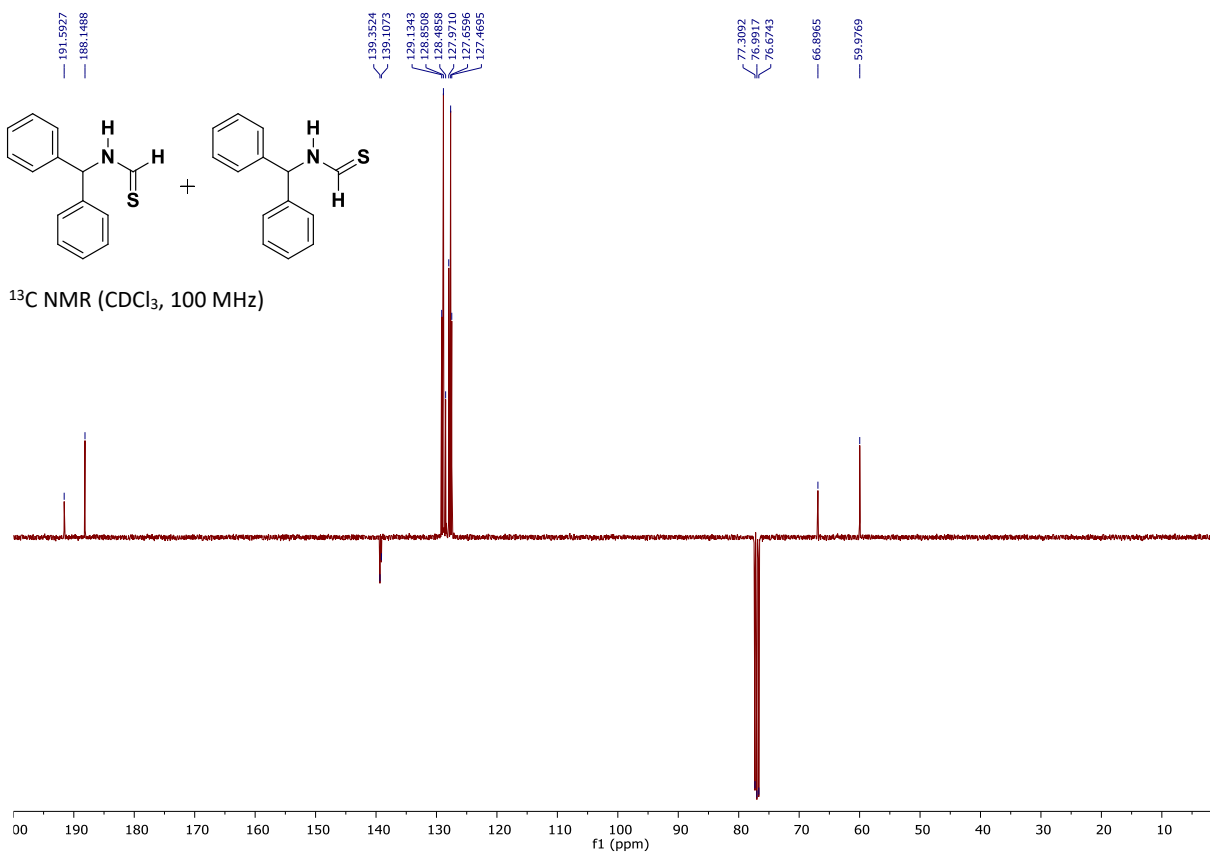
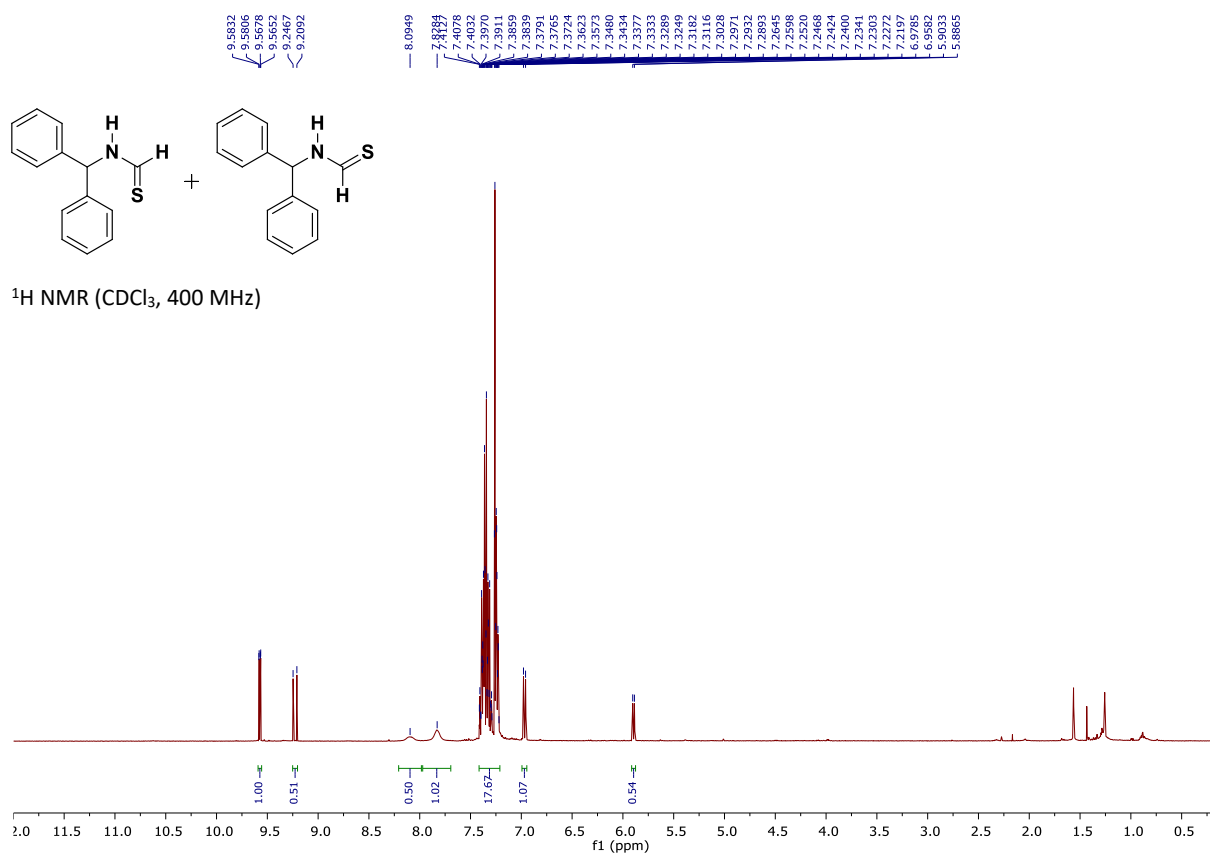
^1H NMR (CDCl_3 , 400 MHz)



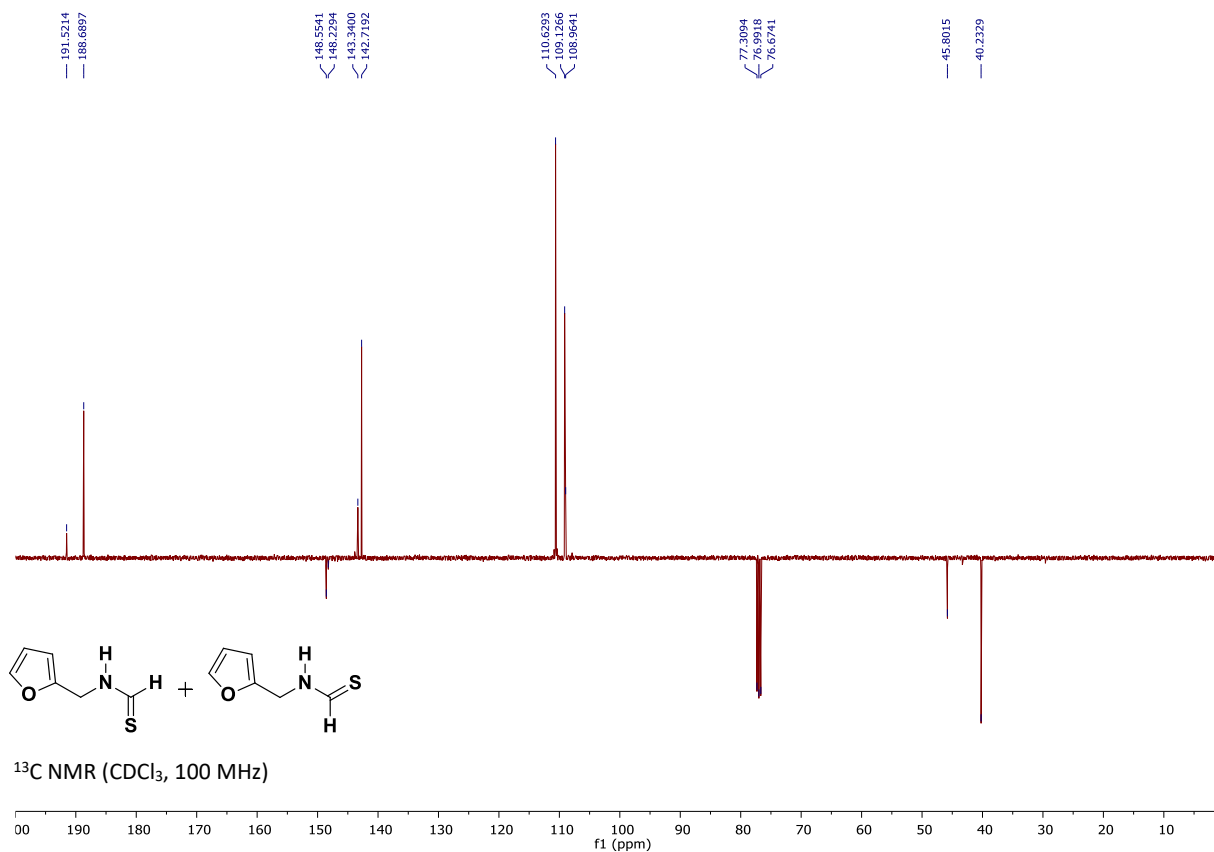
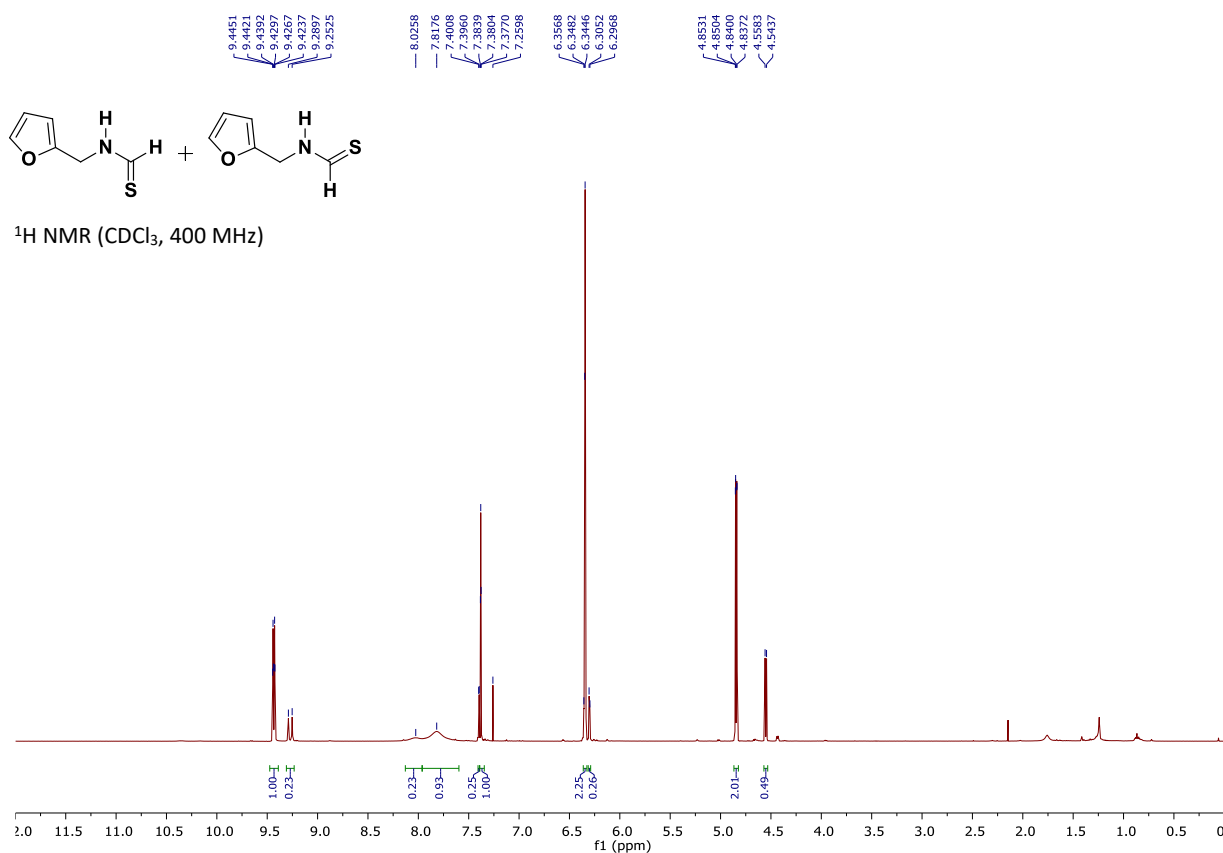
***N*-(1,3-Benzodioxol-5-ylmethyl)thioformamide (24)**



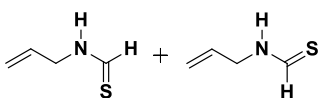
***N*-(Diphenylmethyl)thioformamide (25)**



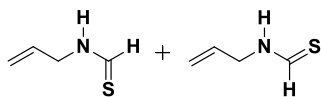
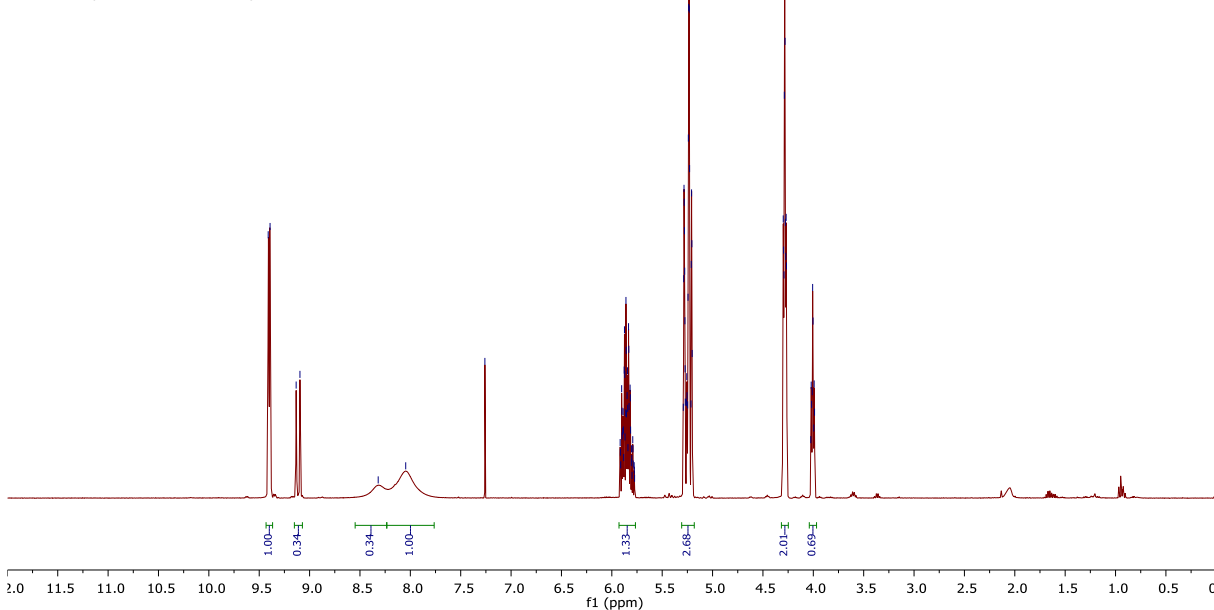
***N*-(2-Furylmethyl)thioformamide (26)**



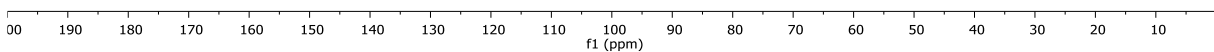
N-Allylthioformamide (27)



¹H NMR (CDCl₃, 400 MHz)



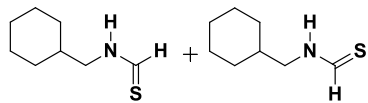
¹³C NMR (CDCl₃, 100 MHz)



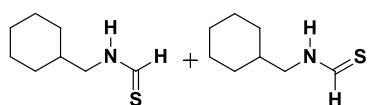
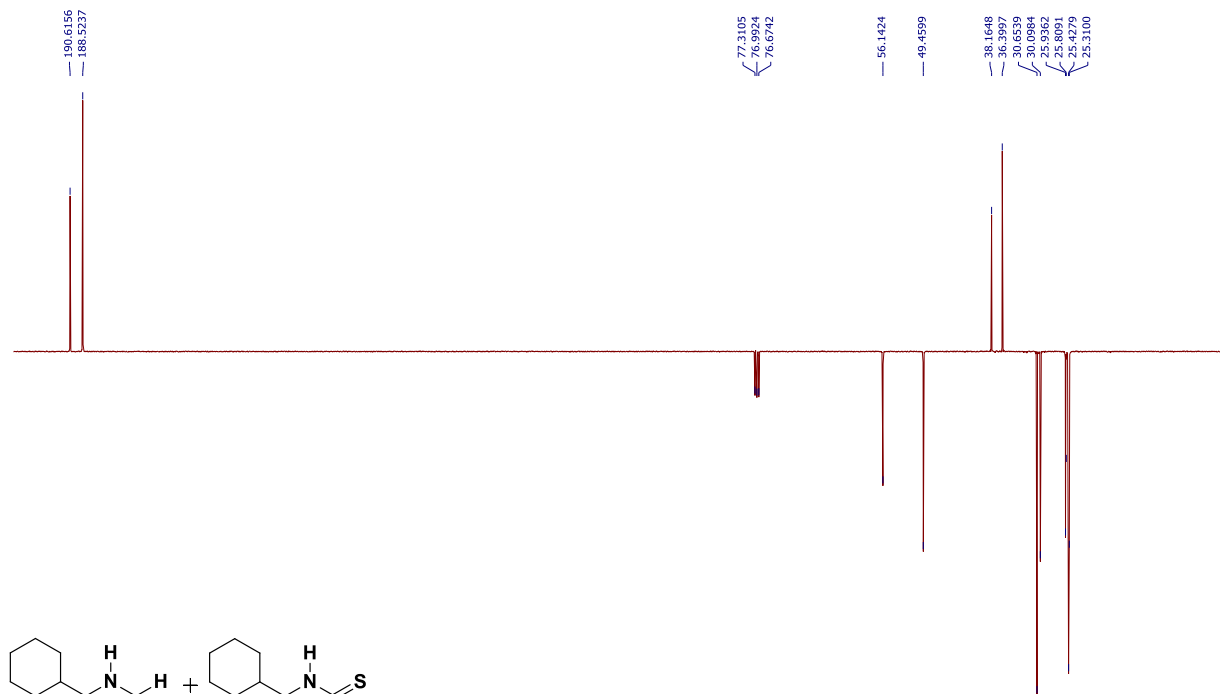
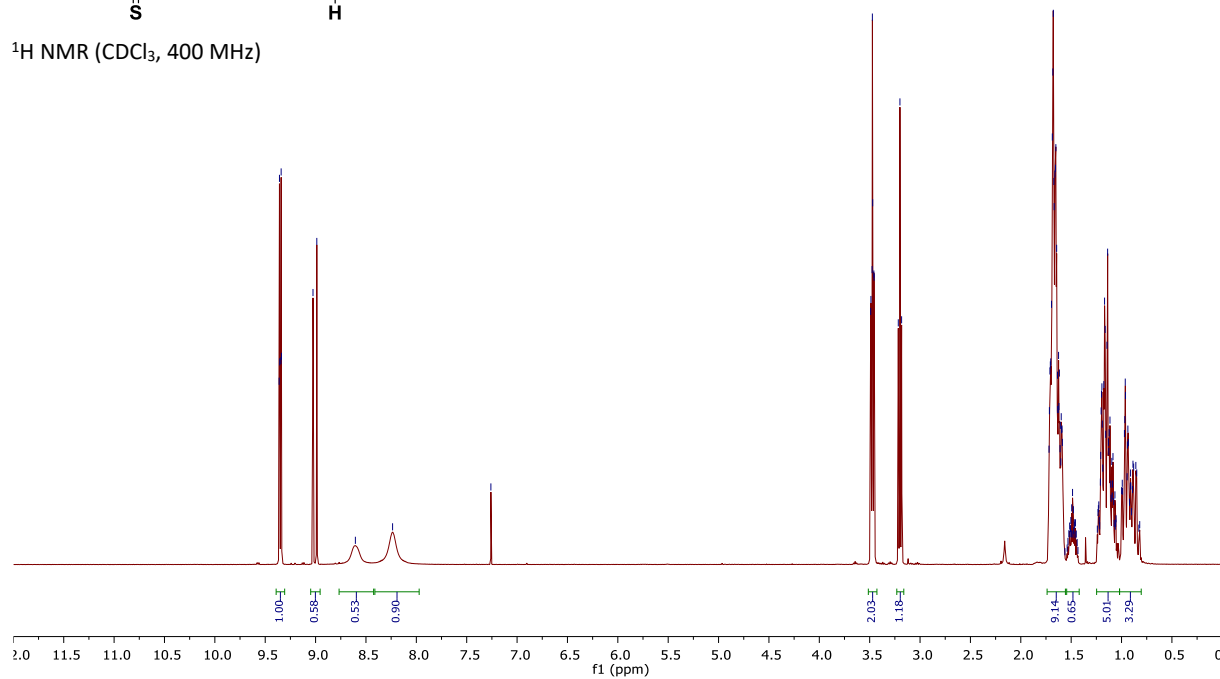
***N*-Cyclohexylthioformamide (28)**

9.3445, 9.3281, 7.2599, 2.0807, 2.0703, 2.0546, 2.0524, 2.0488, 2.0395, 1.9747, 1.9705, 1.9658, 1.9655, 1.9629, 1.9539, 1.9508, 1.9460, 1.9416, 1.9368, 1.9324, 1.9281, 1.9252, 1.9183, 1.9152, 1.9120, 1.9087, 1.9054, 1.9021, 1.8988, 1.8955, 1.8922, 1.8889, 1.8856, 1.8823, 1.8790, 1.8757, 1.8724, 1.8691, 1.8658, 1.8625, 1.8592, 1.8559, 1.8526, 1.8493, 1.8460, 1.8427, 1.8394, 1.8361, 1.8328, 1.8295, 1.8262, 1.8229, 1.8196, 1.8163, 1.8130, 1.8097, 1.8064, 1.8031, 1.7998, 1.7965, 1.7932, 1.7899, 1.7866, 1.7833, 1.7800, 1.7767, 1.7734, 1.7701, 1.7668, 1.7635, 1.7602, 1.7569, 1.7536, 1.7503, 1.7470, 1.7437, 1.7404, 1.7371, 1.7338, 1.7305, 1.7272, 1.7239, 1.7206, 1.7173, 1.7140, 1.7107, 1.7074, 1.7041, 1.7008, 1.6975, 1.6942, 1.6909, 1.6876, 1.6843, 1.6810, 1.6777, 1.6744, 1.6711, 1.6678, 1.6645, 1.6612, 1.6579, 1.6546, 1.6513, 1.6480, 1.6447, 1.6414, 1.6381, 1.6348, 1.6315, 1.6282, 1.6249, 1.6216, 1.6183, 1.6150, 1.6117, 1.6084, 1.6051, 1.6018, 1.5985, 1.5952, 1.5919, 1.5886, 1.5853, 1.5820, 1.5787, 1.5754, 1.5721, 1.5688, 1.5655, 1.5622, 1.5589, 1.5556, 1.5523, 1.5490, 1.5457, 1.5424, 1.5391, 1.5358, 1.5325, 1.5292, 1.5259, 1.5226, 1.5193, 1.5160, 1.5127, 1.5094, 1.5061, 1.5028, 1.4995, 1.4962, 1.4929, 1.4896, 1.4863, 1.4830, 1.4797, 1.4764, 1.4731, 1.4698, 1.4665, 1.4632, 1.4599, 1.4566, 1.4533, 1.4500, 1.4467, 1.4434, 1.4401, 1.4368, 1.4335, 1.4302, 1.4269, 1.4236, 1.4203, 1.4170, 1.4137, 1.4104, 1.4071, 1.4038, 1.4005, 1.3972, 1.3939, 1.3906, 1.3873, 1.3840, 1.3807, 1.3774, 1.3741, 1.3708, 1.3675, 1.3642, 1.3609, 1.3576, 1.3543, 1.3510, 1.3477, 1.3444, 1.3411, 1.3378, 1.3345, 1.3312, 1.3279, 1.3246, 1.3213, 1.3180, 1.3147, 1.3114, 1.3081, 1.3048, 1.3015, 1.2982, 1.2949, 1.2916, 1.2883, 1.2850, 1.2817, 1.2784, 1.2751, 1.2718, 1.2685, 1.2652, 1.2619, 1.2586, 1.2553, 1.2520, 1.2487, 1.2454, 1.2421, 1.2388, 1.2355, 1.2322, 1.2289, 1.2256, 1.2223, 1.2190, 1.2157, 1.2124, 1.2091, 1.2058, 1.2025, 1.1992, 1.1959, 1.1926, 1.1893, 1.1860, 1.1827, 1.1794, 1.1761, 1.1728, 1.1695, 1.1662, 1.1629, 1.1596, 1.1563, 1.1530, 1.1497, 1.1464, 1.1431, 1.1398, 1.1365, 1.1332, 1.1299, 1.1266, 1.1233, 1.1200, 1.1167, 1.1134, 1.1101, 1.1068, 1.1035, 1.1002, 1.0969, 1.0936, 1.0903, 1.0870, 1.0837, 1.0804, 1.0771, 1.0738, 1.0705, 1.0672, 1.0639, 1.0606, 1.0573, 1.0540, 1.0507, 1.0474, 1.0441, 1.0408, 1.0375, 1.0342, 1.0309, 1.0276, 1.0243, 1.0210, 1.0177, 1.0144, 1.0111, 1.0078, 1.0045, 1.0012, 0.9979, 0.9946, 0.9913, 0.9880, 0.9847, 0.9814, 0.9781, 0.9748, 0.9715, 0.9682, 0.9649, 0.9616, 0.9583, 0.9550, 0.9517, 0.9484, 0.9451, 0.9418, 0.9385, 0.9352, 0.9319, 0.9286, 0.9253, 0.9220, 0.9187, 0.9154, 0.9121, 0.9088, 0.9055, 0.9022, 0.8989, 0.8956, 0.8923, 0.8890, 0.8857, 0.8824, 0.8791, 0.8758, 0.8725, 0.8692, 0.8659, 0.8626, 0.8593, 0.8560, 0.8527, 0.8494, 0.8461, 0.8428, 0.8395, 0.8362, 0.8329, 0.8296, 0.8263, 0.8230, 0.8197, 0.8164, 0.8131, 0.8098, 0.8065, 0.8032, 0.7999, 0.7966, 0.7933, 0.7900, 0.7867, 0.7834, 0.7801, 0.7768, 0.7735, 0.7702, 0.7669, 0.7636, 0.7603, 0.7570, 0.7537, 0.7504, 0.7471, 0.7438, 0.7405, 0.7372, 0.7339, 0.7306, 0.7273, 0.7240, 0.7207, 0.7174, 0.7141, 0.7108, 0.7075, 0.7042, 0.7009, 0.6976, 0.6943, 0.6910, 0.6877, 0.6844, 0.6811, 0.6778, 0.6745, 0.6712, 0.6679, 0.6646, 0.6613, 0.6580, 0.6547, 0.6514, 0.6481, 0.6448, 0.6415, 0.6382, 0.6349, 0.6316, 0.6283, 0.6250, 0.6217, 0.6184, 0.6151, 0.6118, 0.6085, 0.6052, 0.6019, 0.5986, 0.5953, 0.5920, 0.5887, 0.5854, 0.5821, 0.5788, 0.5755, 0.5722, 0.5689, 0.5656, 0.5623, 0.5590, 0.5557, 0.5524, 0.5491, 0.5458, 0.5425, 0.5392, 0.5359, 0.5326, 0.5293, 0.5260, 0.5227, 0.5194, 0.5161, 0.5128, 0.5095, 0.5062, 0.5029, 0.4996, 0.4963, 0.4930, 0.4897, 0.4864, 0.4831, 0.4798, 0.4765, 0.4732, 0.4699, 0.4666, 0.4633, 0.4600, 0.4567, 0.4534, 0.4501, 0.4468, 0.4435, 0.4402, 0.4369, 0.4336, 0.4303, 0.4270, 0.4237, 0.4204, 0.4171, 0.4138, 0.4105, 0.4072, 0.4039, 0.4006, 0.3973, 0.3940, 0.3907, 0.3874, 0.3841, 0.3808, 0.3775, 0.3742, 0.3709, 0.3676, 0.3643, 0.3610, 0.3577, 0.3544, 0.3511, 0.3478, 0.3445, 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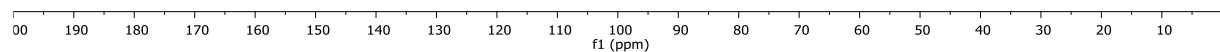
***N*-(Cyclohexylmethyl)thioformamide (29)**



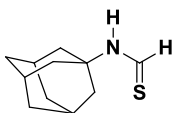
¹H NMR (CDCl₃, 400 MHz)



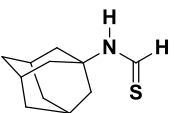
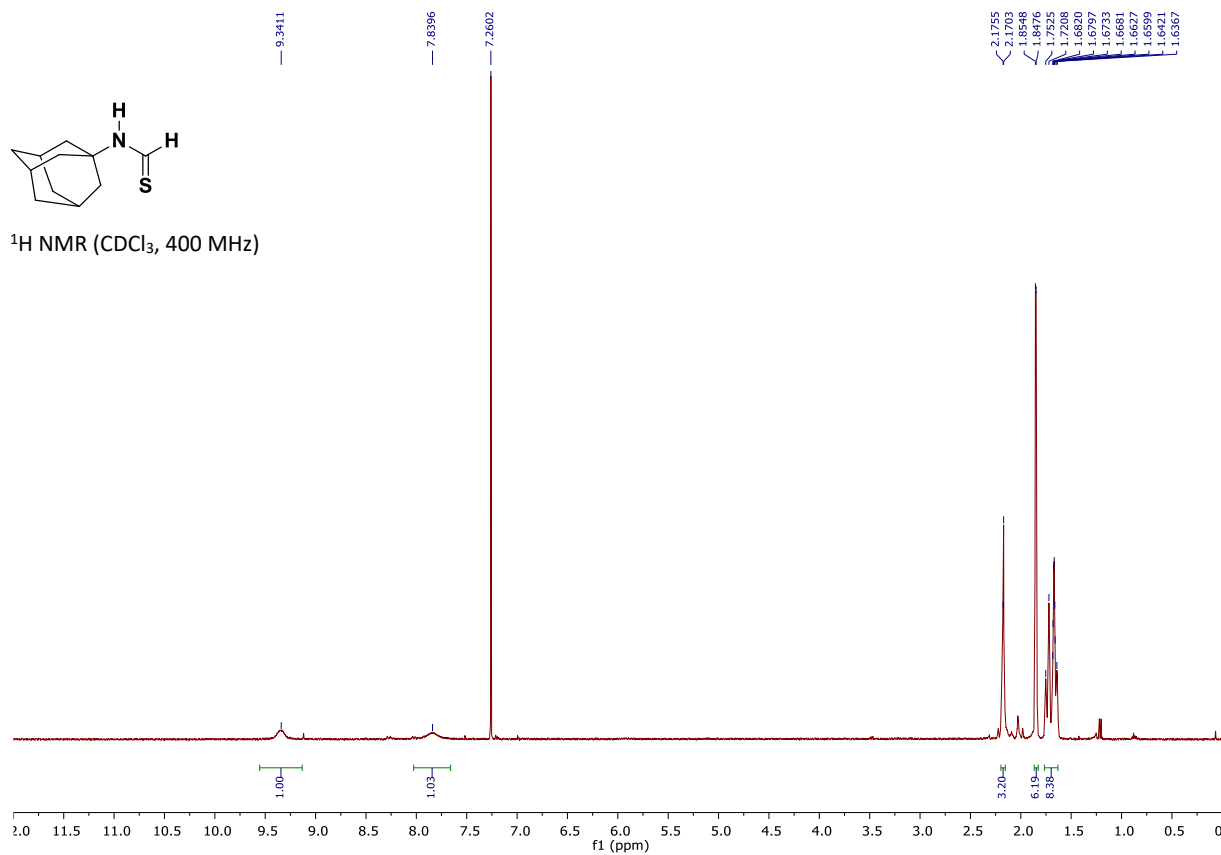
¹³C NMR (CDCl₃, 100 MHz)



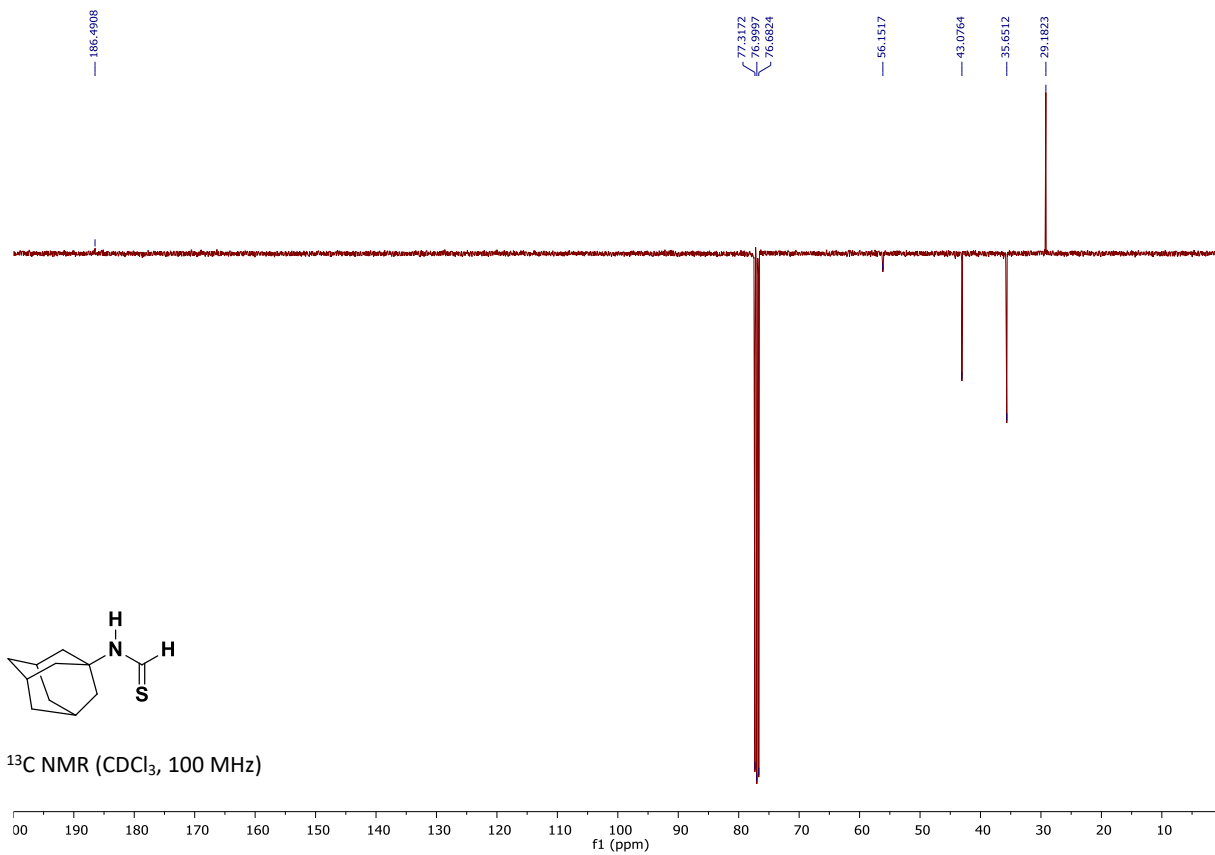
***N*-Adamantan-1-ylthioformamide (30)**



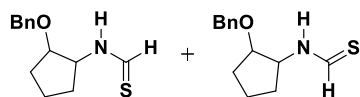
^1H NMR (CDCl_3 , 400 MHz)



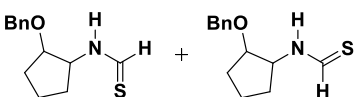
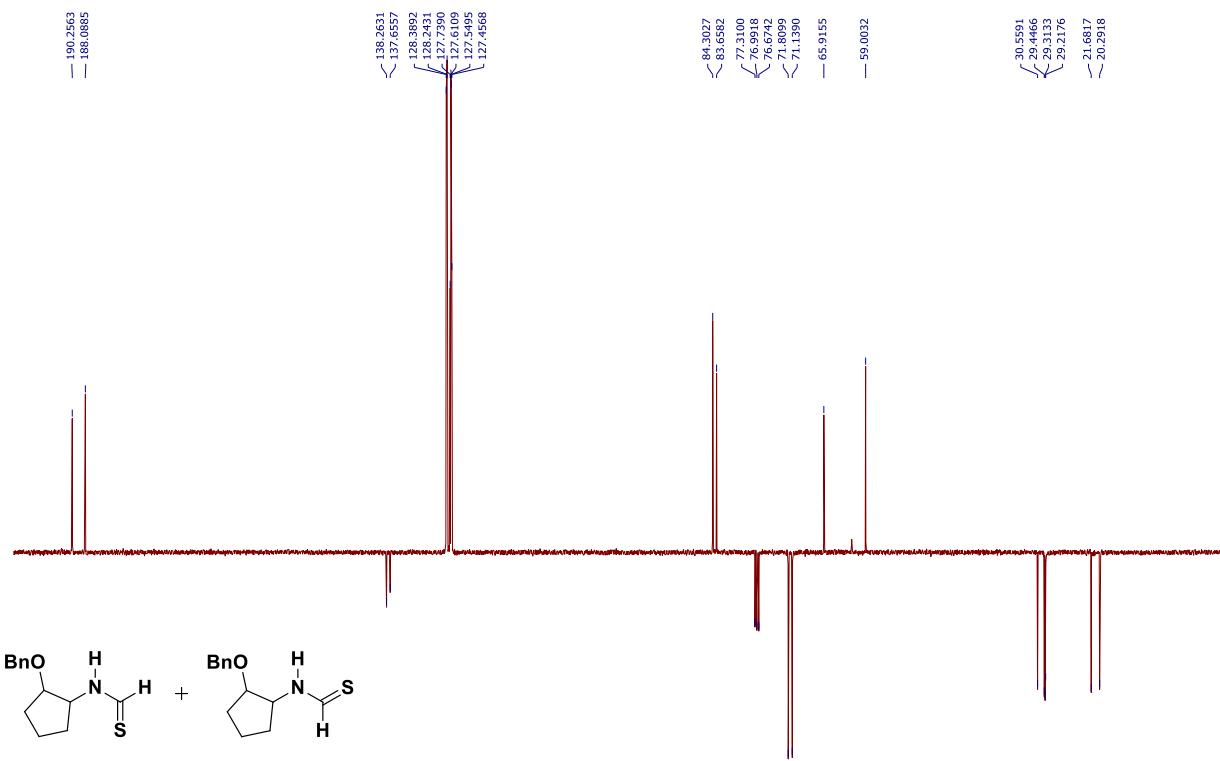
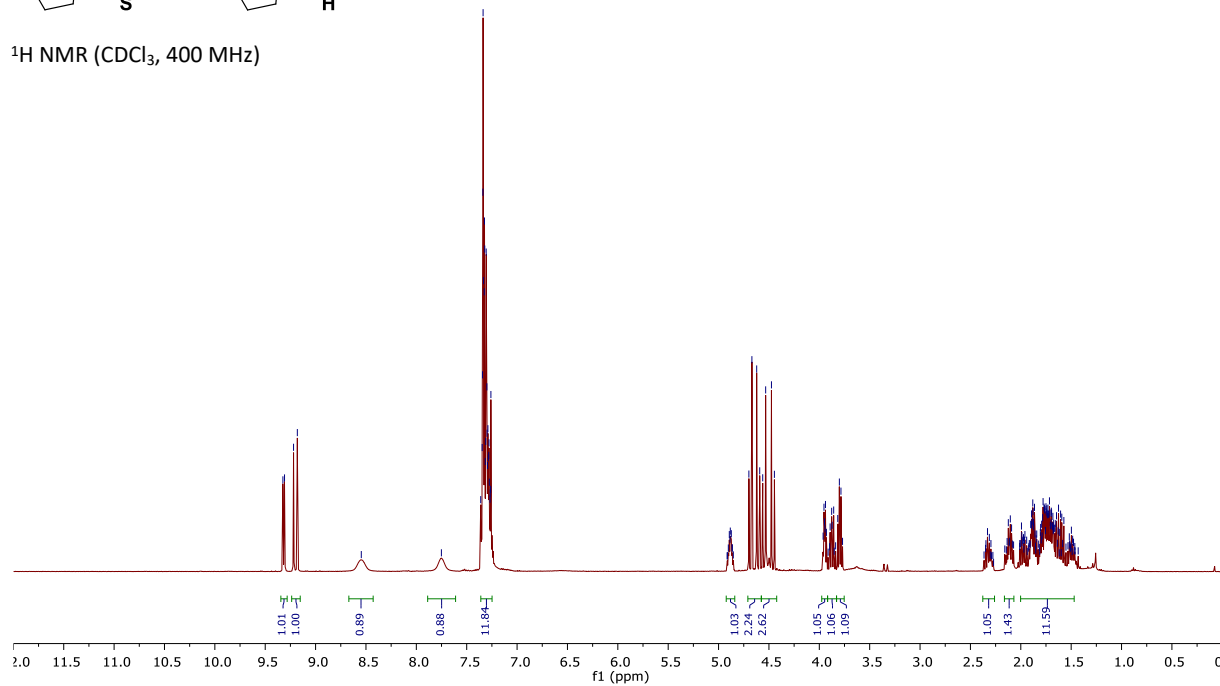
^{13}C NMR (CDCl_3 , 100 MHz)



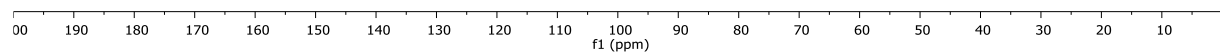
***N*-[2-(Benzyloxy)cyclopentyl]thioformamide (31)**



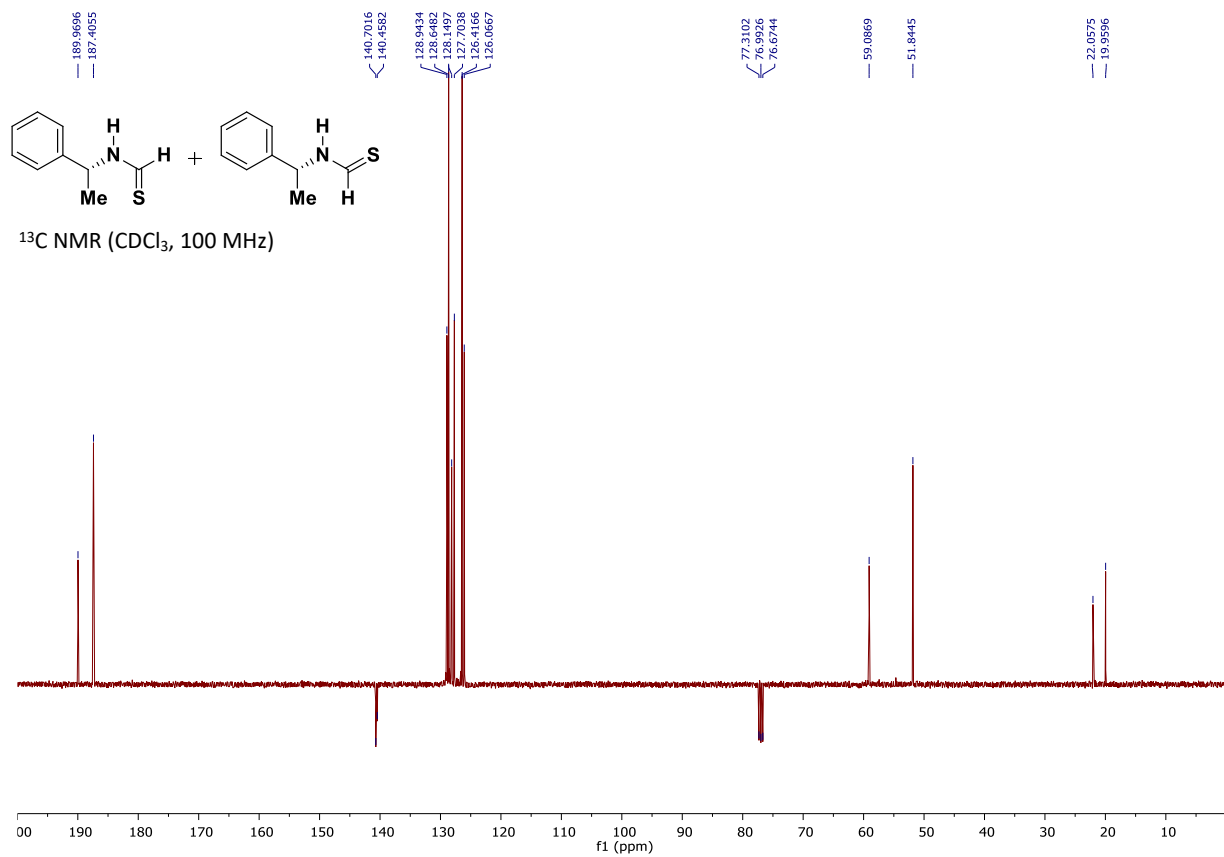
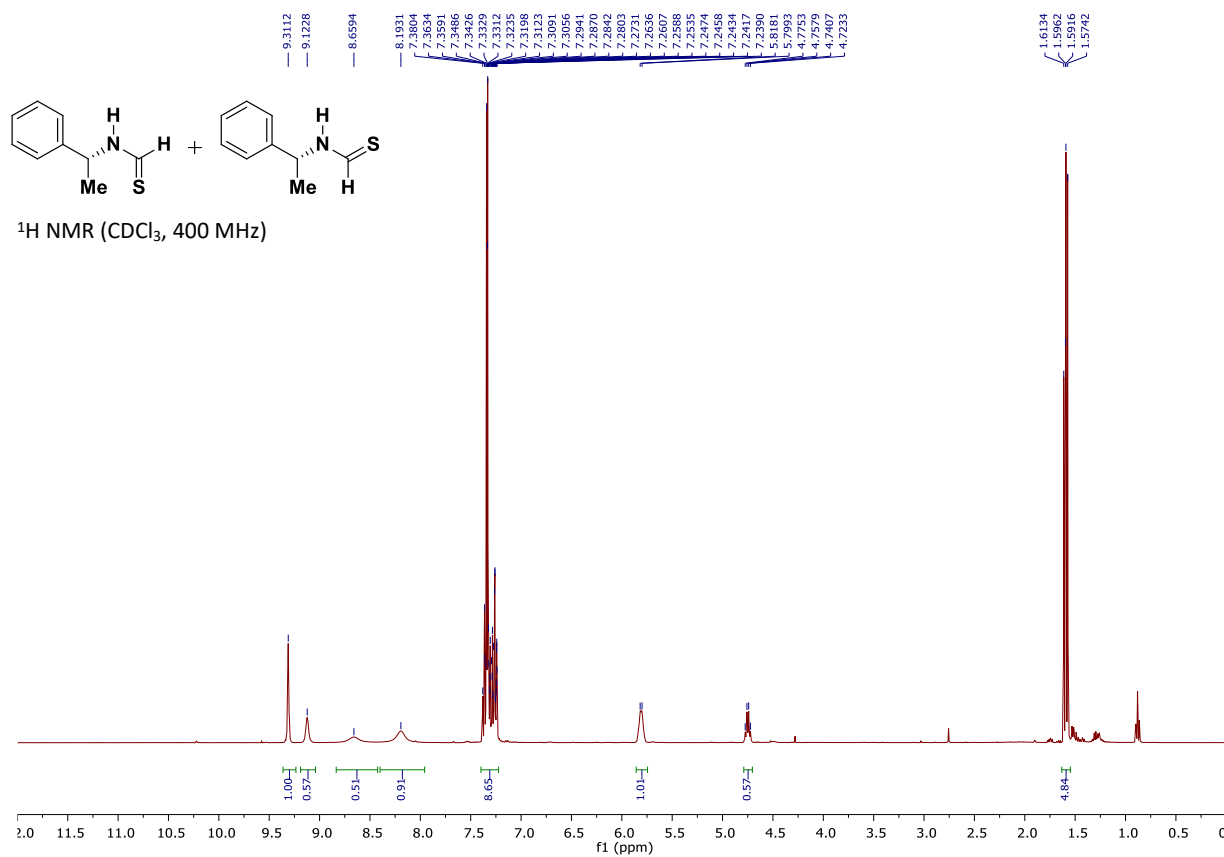
¹H NMR (CDCl₃, 400 MHz)



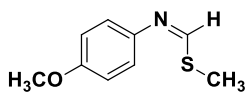
¹³C NMR (CDCl₃, 100 MHz)



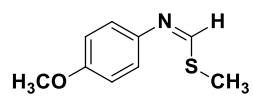
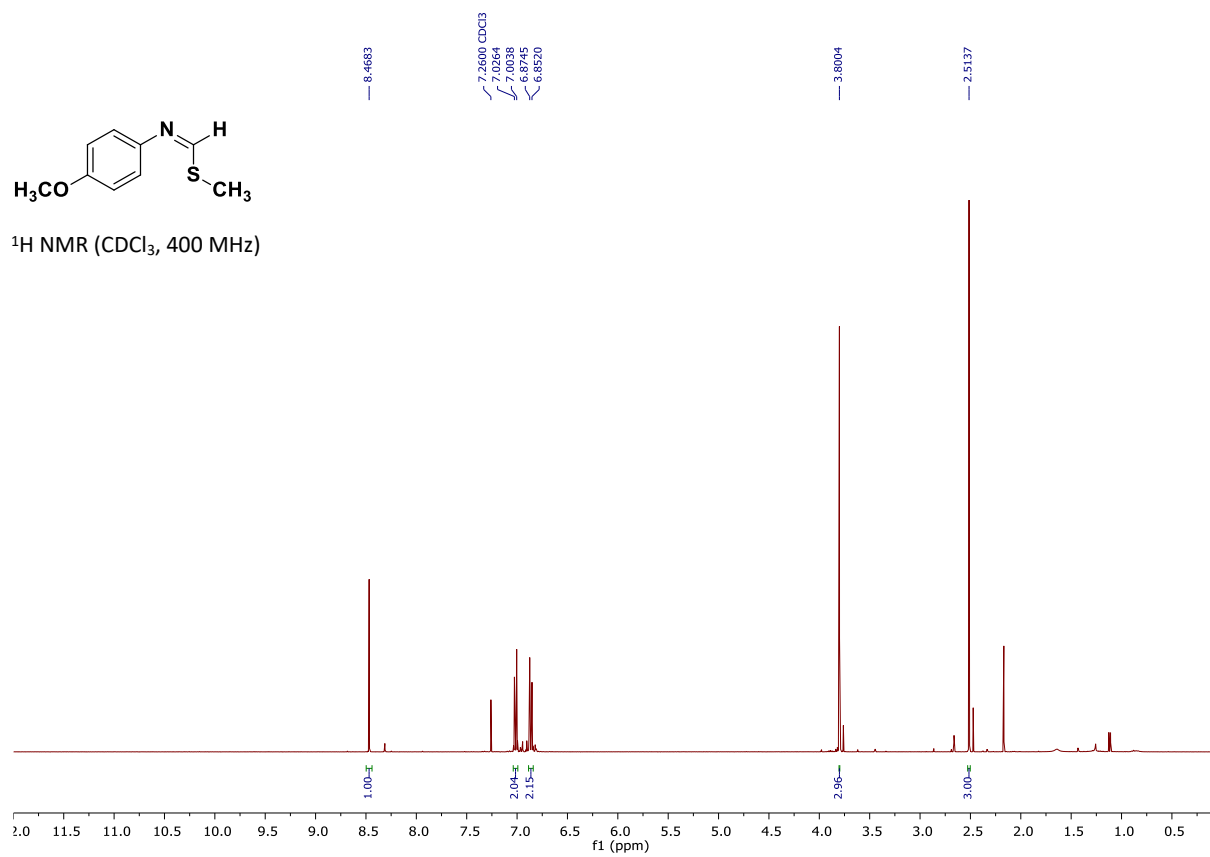
***N*-[(1*R*)-1-Phenylethyl]thioformamide (32)**



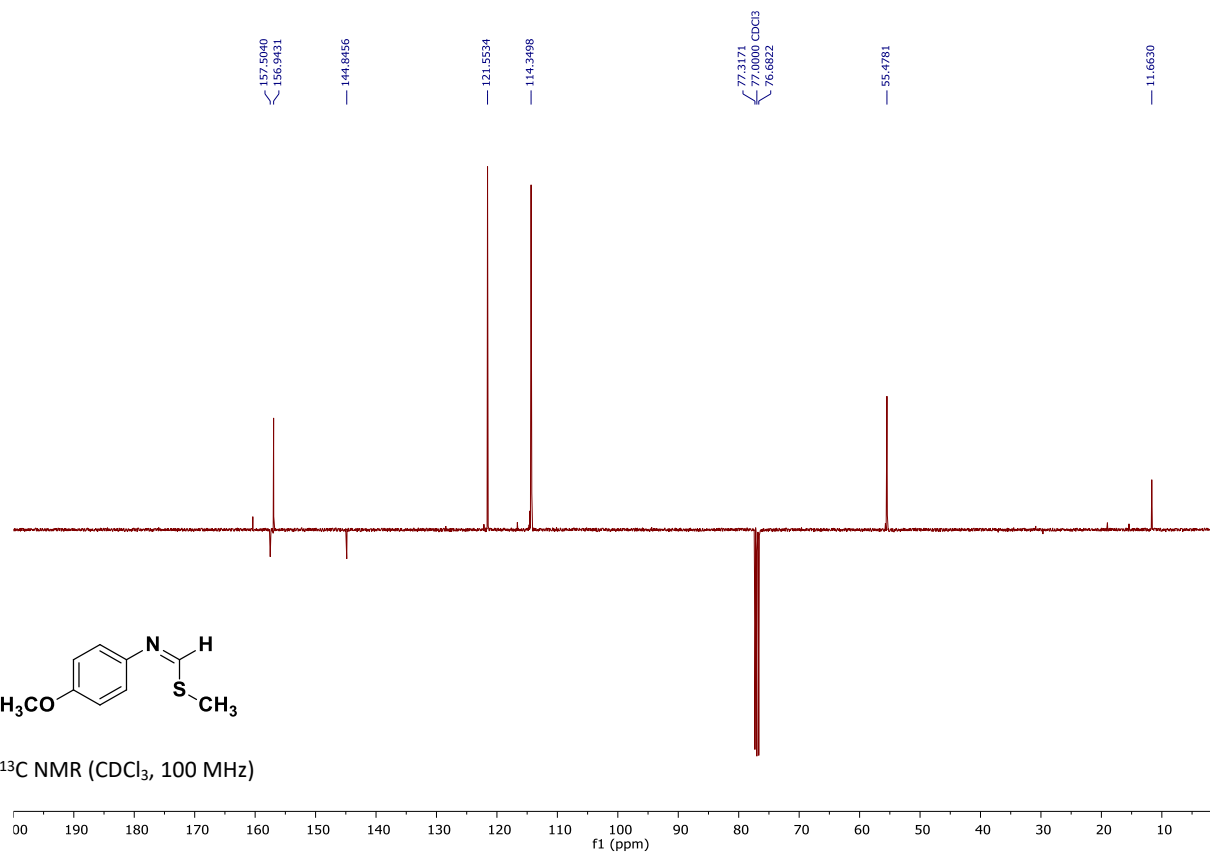
Methyl (4-methoxyphenyl)imidothioformate (33)



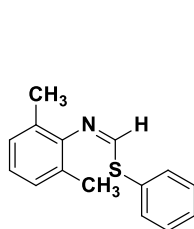
^1H NMR (CDCl_3 , 400 MHz)



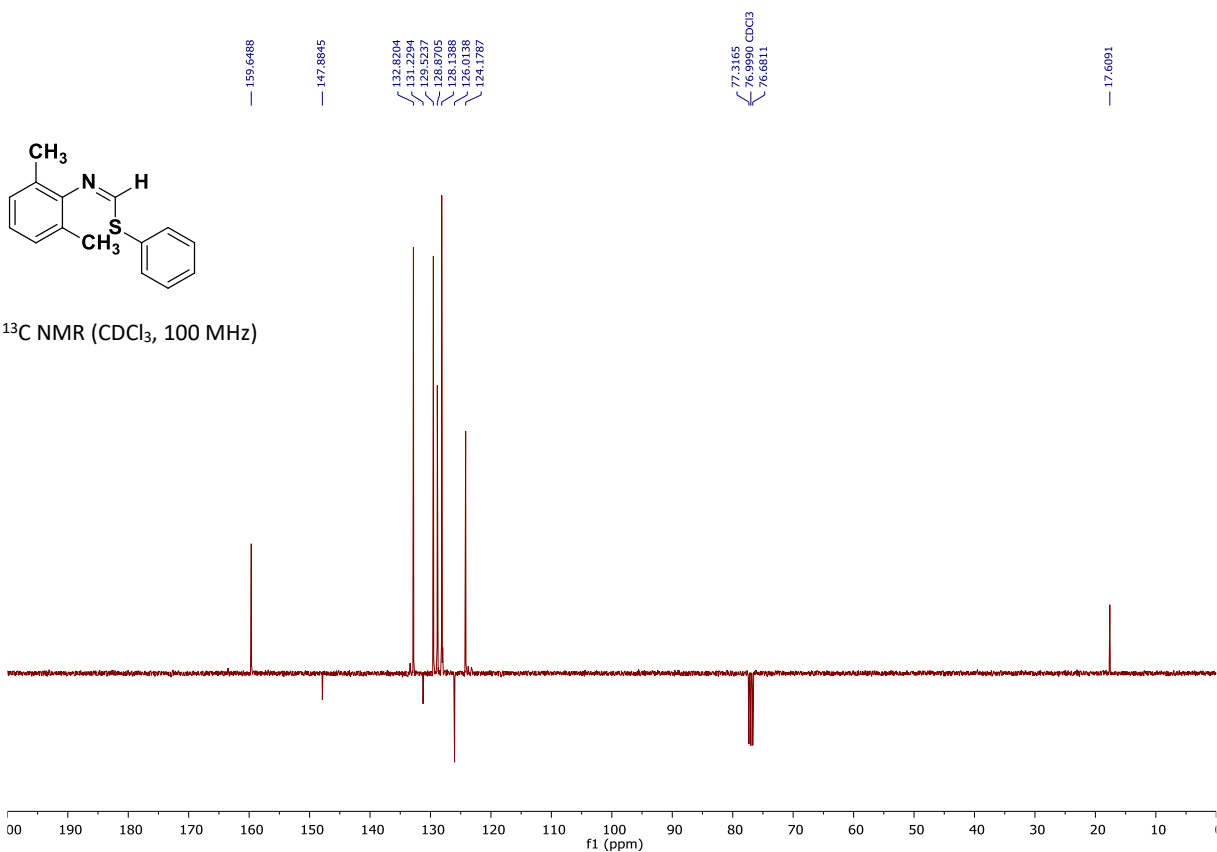
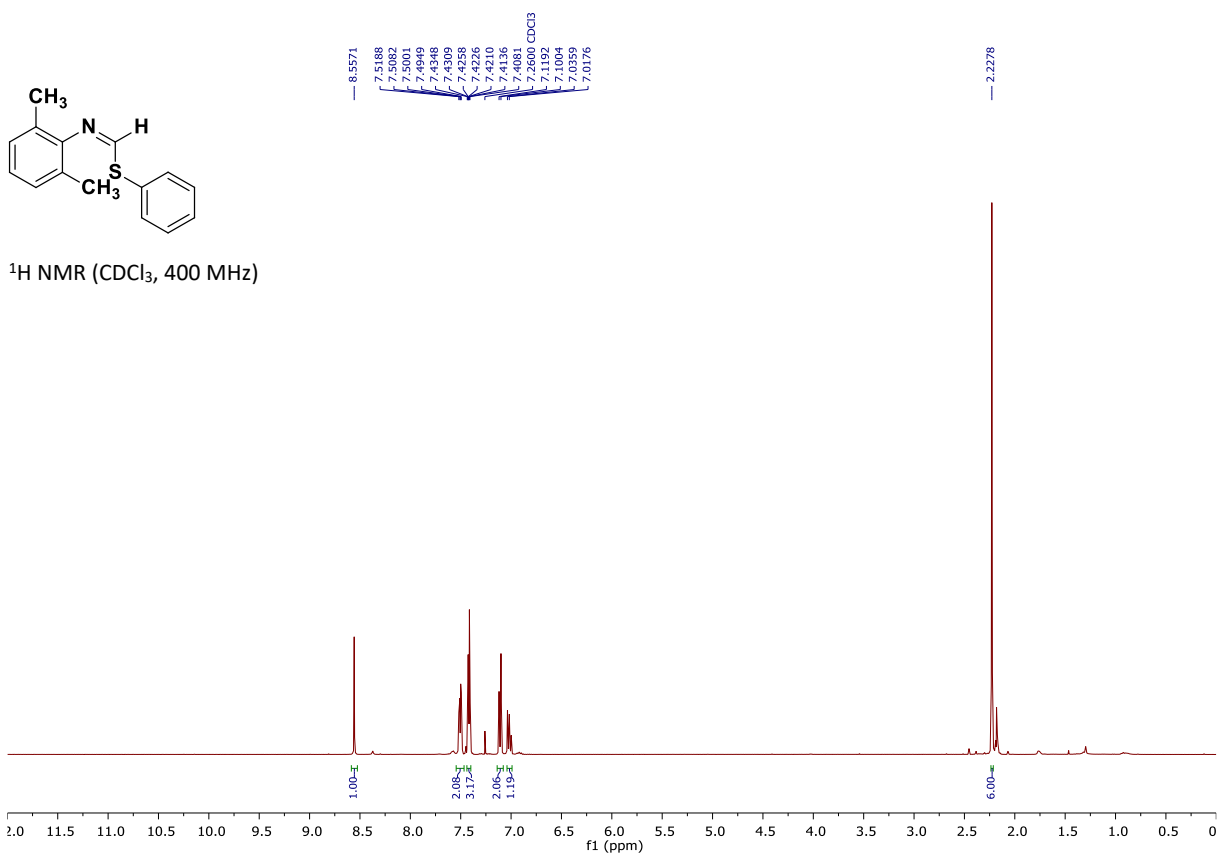
^{13}C NMR (CDCl_3 , 100 MHz)



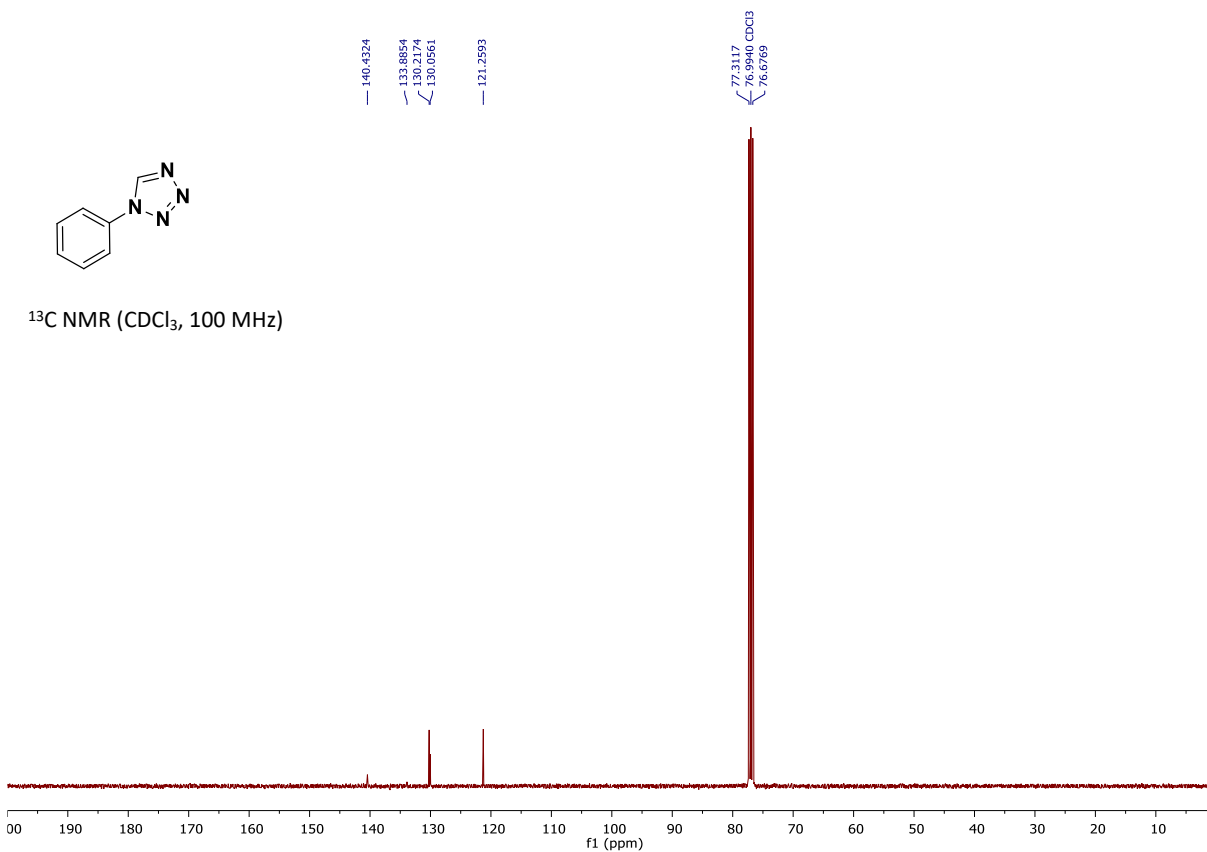
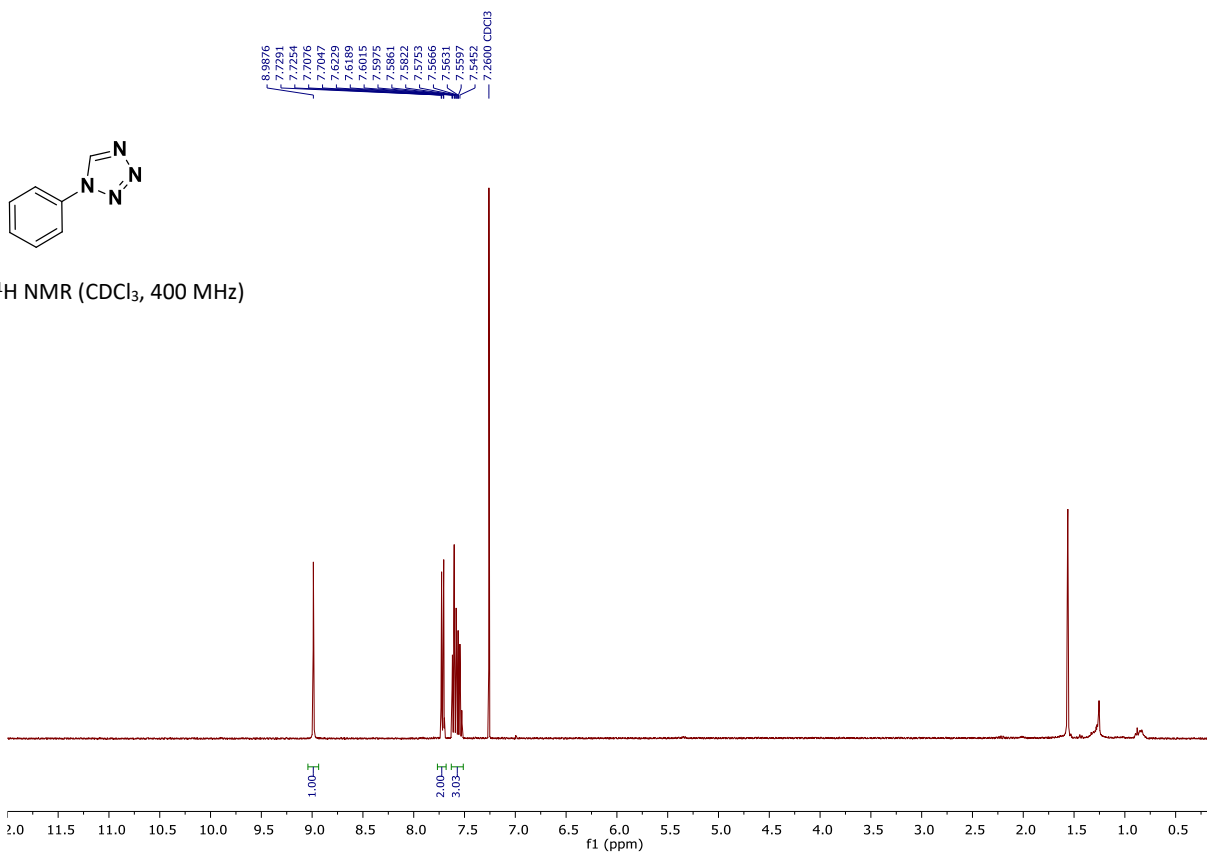
Phenyl (2,6-dimethylphenyl)imidothioformate (34)



¹H NMR (CDCl₃, 400 MHz)



1-Phenyl-1H-tetrazole (35)



5. References

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