Base-mediated three-component system for the synthesis of *S*-substituted *N*-acyl ureas

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Supporting Information

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1. General Information

1.1 Reagent information

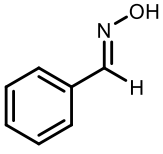
The thiourea CP used was purchased from Associated Chemical Enterprises (PTY) LTD. The sodium carbonate used was purchased from Sisco Research Laboratories Pvt. LTD. The rest of the solvents and commercially available reagents used were purchased from Sigma Aldrich and used as received. Synthesised substrates were prepared using the reported protocol, and the spectral data were matched to those reported in the literature.

1.1 General analytical information

The reaction crudes were further monitored using thin-layer chromatography (TLC) on aluminium-backed Merck silica gel 60 F254 plates using an ascending technique. The TLC plates were visualised using UV light at 254 nm. The synthesised compounds were purified using either gravity column chromatography on Merck silica gel 60 (230-400 mesh) or recrystallisation and characterised using NMR spectroscopy, FTIR, LC-MS and melting point (where applicable). The ^{1}H (7.26 ppm reference)

and ^{13}C (77.16 ppm reference) were recorded in $CDCl_3$ solutions using a 500 MHz magnet coupled to an Avance III HD 500 MHz Console and reported in ppm. NMR data is reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, coupling constant (Hz), and integration. For IR stretching frequencies, SHIMADZU IR Affinity-1s in cm^{-1} was used. For accurate mass analysis, the samples were dissolved in ultra purity lc methanol (Romil-UpS™,Microsep, South Africa). Analysis was performed using flow injection analysis (FIA); the flow rate was set to 0.4 ml/min, and the injection volume was 5 µl. Ultra-purity methanol spiked with 0.1 % formic acid (Fluka® Analytical, Sigma-Aldrich, South Africa) was used throughout the 1-minute run. Compound detection was performed using a Waters® Synapt G2 high-definition mass spectrometry (HDMS) system (Waters Inc., Milford, Massachusetts, USA). Samples were analysed using flow injection analysis (FIA). The system comprises of a Waters Acquity Ultra Performance Liquid Chromatography (UPLC®) system hyphenated to a quadrupole-time-of-flight (QTOF) instrument. The system was operated with MassLynxTM (version 4.1) software (Waters Inc., Milford, Massachusetts, USA) for data acquisition and processing. An internal lock mass control standard, 2 pg/µL solution leucine enkephalin (m/z 555.2693), was directly infused into the source through a secondary orthogonal electrospray ionisation (ESI) probe, allowing intermittent sampling. The internal control was used to compensate for instrumental drift, ensuring good mass accuracy. The source conditions were as follows: the capillary voltage for ESI was 2.6 kV for positive mode ionisation. The source temperature was set at 120 °C, the sampling cone voltage at 25 V, extraction cone voltage at 4.0 V and cone gas (nitrogen) flow at 10.0 L/Hr. The desolvation temperature was set at 350 °C with a gas (nitrogen) flow of 600.0 L/Hr. Mass spectral scans were collected every 0.3 seconds. The raw data was collected in the form of a centroid profile. Mass to charge ratios (m/z) between 50 and 1 200 Da were recorded. The melting points were determined using a Stuart SMP10 thermobaric hot-stage microscope. The reactions were heated using either a Carousel Stirring Hotplate (when pressure tubes were used) or an oil bath (when round-bottom flasks were used).

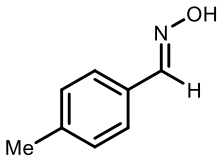
2. Synthesis of Phenyl Oxime Substrates



Benzaldehyde oxime (S1): To a 100 mL round-bottom flask equipped with a magnetic stirrer bar was added NaOH (2.5 g, 50.0 mmol, 2.5 equiv.) and dissolved in deionised water (30 mL). Hydroxylamine hydrochloride (8.7 g, 125 mmol, 5.0 equiv.) was added and stirred to dissolve. Benzaldehyde (2.5 mL, 25.0 mmol, 1 equiv.) was added dropwise, and the reaction was stirred overnight at room temperature. The reaction mixture was extracted with DCM (3 × 25 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting clear

oil (2.8 g, 92% yield) was used without further purification. The characterisation data is in agreement with the literature.[1]

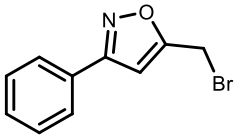
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.19 (s, 1H), 7.66 – 7.55 (m, 2H), 7.47 – 7.33 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150., 131.0, 129.8, 128.9, 128.7, 127.0.



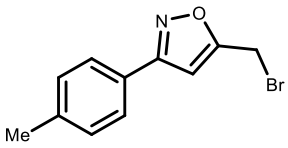
4-Methylbenzaldehyde oxime (S2): To a 100 mL round-bottom flask equipped with a magnetic stirrer bar was added NaOH (2.5 g, 50.0 mmol, 2.5 equiv.) and dissolved in deionised water (30 mL). Hydroxylamine hydrochloride (8.7 g, 125 mmol, 5.0 equiv.) was added and stirred to dissolve. 4-Methylbenzaldehyde (3.0 g, 25.0 mmol, 1 equiv.) was added dropwise, and the reaction was stirred overnight at room temperature. The reaction mixture was extracted with DCM (3 × 25 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting white solids (3.0 g, 89% yield) were used without further purification. The characterisation data is in agreement with the literature.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.14 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 140.4, 129.6, 129.3, 127.1, 21.5.

3. Synthesis of Phenyl Isoxazole Substrates



5-(Bromomethyl)-3-phenylisoxazole (S3): To a 100 mL round bottom flask equipped with a magnetic stirrer bar was added MeOH (30 mL), (diacetoxyiodo)benzene (1.9 g, 6 mmol, 1.2 equiv.), trifluoroacetic acid (8 µL, 0.1 mmol, 1 mol%) and propargyl bromide (0.5 mL, 6 mmol, 1.2 equiv.). The oxime (**S1**) (0.6 g, 5 mmol, 1 equiv.) dissolved in MeOH (5 mL) was added dropwise. The reaction was stirred overnight at room temperature. The reaction mixture was extracted with DCM (2 × 50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting white solids were recrystallised from EtOAc in *n*-hexanes under refrigeration to give the isoxazole as a white solid (0.9 g, 78%). The characterisation data is in agreement with the literature.[2]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.52 – 7.32 (m, 3H), 6.63 (s, 1H), 4.52 (s, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 162.9, 130.3, 129.1, 128.7, 126.9, 102.0, 18.7.



5-(Bromomethyl)-3-(*p*-tolyl)isoxazole (S4): To a 100 mL round bottom flask equipped with a magnetic stirrer bar was added MeOH (30 mL), (diacetoxyiodo)benzene (1.9 g, 6 mmol, 1.2 equiv.), trifluoroacetic acid (8

µL, 0.1 mmol, 1 mol%) and propargyl bromide (0.5 mL, 6 mmol, 1.2 equiv.). The oxime (**S2**) (0.7 g, 5 mmol, 1 equiv.) dissolved in MeOH (5 mL) was added dropwise. The reaction was stirred overnight at room temperature. The reaction mixture was extracted with DCM (2 × 50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting white solids were recrystallised from EtOAc in *n*-hexanes under refrigeration to give the isoxazole as a white solid (0.9 g, 72%). Characterisation data were consistent with the literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.60 (s, 1H), 4.50 (s, 2H), 2.40 (s, 3H).

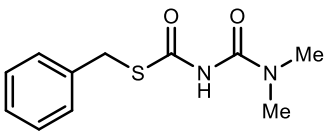
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 162.8, 140.5, 129., 127.60, 126.8, 125.8, 101.9, 21.5, 18.8.

4. Preparation of *S*-substituted *N*-acylureas from alkyl halides, thiourea and carbamoyl chlorides

4.1 General Procedure A

To a 50 mL pressure tube equipped with a magnetic stirrer bar was added thiourea (1.5 mmol, 1.5 equiv.), Na_2CO_3 (1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), carbamoyl chloride (1.0 mmol, 1 equiv.), and alkyl halide (1.5 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at 40 °C. The reaction mixture was filtered, quenched with deionised water (30 mL) and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure and purified *via* column chromatography on silica gel using 30% EtOAc in *n*-hexanes system to afford the products. *For iodoalkane starting materials, the combined EtOAc layers were further washed with 10% sodium thiosulfate solution.

Characterisation Data of S-substituted N-acylurea products Generated from Procedure A



***S*-benzyl-*(N,N*-dimethyl-carbonyl)carbamothioate (3a)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.22 g, 92% yield). For recrystallisation, chloroform:*n*-hexane (3:1) mixture was used, followed by refrigeration overnight.

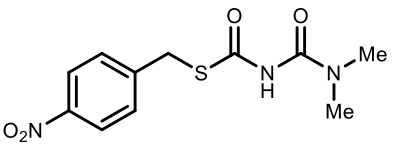
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 4.32 (s, 2H), 3.13 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 162.8, 137.5, 128.7, 128.6, 127.3, 37.4, 35.4, 34.8.

IR (film): ν_{max} 3654, 1578, 1372, 1218, 1052, 749, 709 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{11}H_{14}N_2O_2S$ [$(M+H^+)$] 239.08487, found 239.0894.

Melting point: 141 – 143 °C.



***S*-(4-nitrobenzyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3b)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 4-nitrobenzyl bromide (0.32 g, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.24 g, 84% yield).

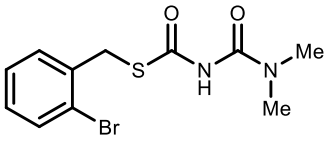
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 4.39 (s, 2H), 3.08 (s, 3H), 2.95 (s, 3H), 1.63 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 162.6, 147.3, 145.7, 129.5, 123.9, 37.4, 35.5, 33.9.

IR (film): ν_{max} 3739, 3293, 2962, 2922, 1738, 1584, 1509, 1464, 1429, 1378, 1344, 1258, 1235, 1206, 1092, 1012, 881, 795, 755, 738, 715 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{11}H_{13}N_3O_4S$ [$(M+Na^+)$] 305.0519, found 305.0747.

Melting point: 169 – 172 °C.



***S*-(2-bromobenzyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3c)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 2-bromobenzyl bromide (0.37 g, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.23 g, 74% yield).

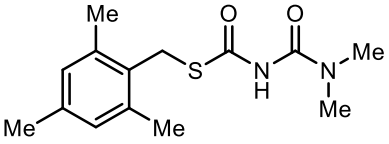
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.26 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.15 – 7.05 (m, 1H), 4.45 (s, 2H), 3.14 (s, 3H), 2.95 (s, 3H), 1.72 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 162.8, 137.0, 132.9, 130.8, 129.0, 127.8, 124.6, 37.5, 35.5, 35.2.

IR (film): ν_{max} 3745, 3671, 3305, 2922, 2361, 2161, 2030, 1967, 1578, 1538. 1435, 1372, 1258, 1218, 1092, 1023, 869, 795, 738 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{11}H_{13}BrN_2O_2S$ [$(M+H)^+$], 318.9851 found 318.9101.

Melting point: 112 – 113 °C.



***S*-(2,4,6-trimethylbenzyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3d)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 2,4,6-trimethylbenzyl chloride (0.32 g, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as an off-white solid (0.23 g, 81% yield).

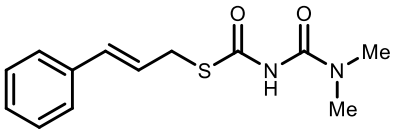
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.35 (s, 2H), 3.20 (s, 3H), 2.98 (s, 3H), 2.36 (s, 6H), 2.26 (s, 3H), 1.61 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 162.9, 137.6, 137.3, 129.2, 37.5, 35.5, 30.4, 21.0, 19.8.

IR (film): ν_{max} 3305, 2916, 1578, 1441, 1372, 1264, 1224, 1098, 1023, 846, 975, 749 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{14}H_{20}N_2O_2S$ [$(M+H^+)$] 281.1320, found 281.1153.

Melting point: 163 – 165 °C.



***S*-cinnamyl (*N,N*-dimethyl-carbonyl)carbamothioate (3e)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and cinnamyl bromide (0.22 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.21 g, 81% yield).

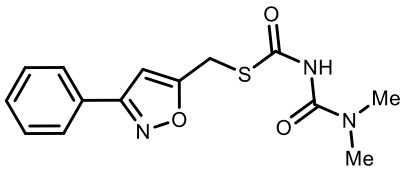
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 15.7 Hz, 1H), 6.39 – 6.23 (m, 1H), 3.88 (d, J = 7.2 Hz, 2H), 3.18 (s, 3H), 2.96 (s, 3H), 1.62 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 162.8, 136.7, 133.0, 128.7, 127.8, 126.5, 125.1, 37.5, 35.5, 33.4.

IR (film): ν_{max} 3293, 3110, 3025, 2962, 1578, 1452, 1418, 1349, 1298, 1258, 1223, 1195, 1092, 1017, 966, 869, 795, 743, 703 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{13}H_{16}N_2O_2S$ [$(M+H^+)$] 265.1005, found 265.1180.

Melting point: 127 – 129 °C.



***S*-((3-phenylisoxazol-5-yl)methyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3f)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N,N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 eqiv.), and 5-(bromomethyl)-3-phenylisoxazole (0.36 g, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.27 g, 88% yield).

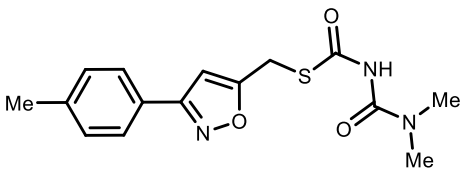
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.55 – 7.39 (m, 3H), 6.52 (s, 1H), 4.41 (s, 2H), 3.11 (s, 3H), 2.95 (s, 3H), 1.62 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 165.6, 162.8, 162.5, 130.1, 129.0, 126.9, 100.7, 37.5, 35.5, 25.4.

IR (film): ν_{max} 3677, 3642, 3614, 3305, 3248, 3116, 2922, 1738, 1590, 1538, 1464, 1441, 1372, 1264, 1218, 1098, 1029, 995, 949, 921, 875, 852, 795, 760 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{14}H_{15}N_3O_3S$ [$(M+H^+)$] 305.0907, found 305.0977.

Melting point: 141 – 143 °C.



***S*-((3-(*p*-tolyl)isoxazol-5-yl)methyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3g)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N,N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 5-(bromomethyl)-3-(p-tolyl)isoxazole (0.38 g, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.27 g, 86% yield).

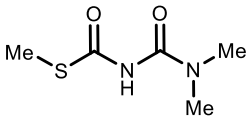
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 6.49 (s, 1H), 4.39 (s, 2H), 3.10 (s, 3H), 2.94 (s, 3H), 2.39 (s, 3H), 1.73 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 165.7, 162.7, 162.5, 140.3, 129.7, 126.8, 126.2, 100.7, 37.4, 35.5, 25.4, 21.5.

IR (film): ν_{max} 3311, 3248, 2916, 1590, 1544, 1429, 1373, 1218, 1098, 1058, 995, 955, 915, 875, 858, 812, 795, 755 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{14}H_{17}N_3O_3S$ [$(M+H^+)$] 320.1063, found 320.0928.

Melting point: 166 – 168 °C.



***S*-methyl (*N,N*-dimethyl-carbonyl)carbamothioate (3h)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and iodomethane (0.09 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.13 g, 81% yield).

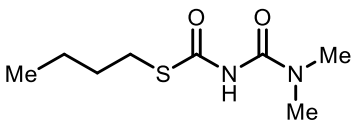
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.12 (s, 3H), 2.92 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 162.8, 37.3, 35.3, 13.5.

IR (film): ν_{max} 3768, 3637, 3305, 3116, 2928, 1738, 1584, 1458, 1372, 1258, 1224, 1098, 961, 869, 795, 755 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_5H_{10}N_2O_2S$ [$(M+H^+)$] 163.0536, found 163.0371.

Melting point: 142 – 143 °C.



***S*-butyl (*N,N*-dimethyl-carbonyl)carbamothioate (3i)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 1-bromobutane (0.16 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a yellow solid (0.18 g, 87% yield). Characterisation data were consistent with the literature.

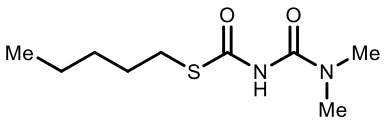
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.12 (s, 3H), 3.00 (t, J = 7.4 Hz, 2H), 2.94 (s, 3H), 1.71 – 1.60 (m, 2H), 1.47 – 1.34 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 162.9, 37.3, 35.4, 31.8, 30.5, 22.1, 13.7.

IR (film): ν_{max} 3311, 3248, 3168, 2956, 2928, 2865, 1687, 1584, 1441, 1372, 1264, 1212, 1092, 1035, 989, 921, 869, 795 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_8H_{16}N_2O_2S$ [$(M+H^+)$] 205.1005, found 205.0910.

Melting point: 69 – 71 °C.



***S*-pentyl (*N,N*-dimethyl-carbonyl)carbamothioate (3j)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N,N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 1-bromopentane (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a yellow solid (0.16 g, 74% yield).

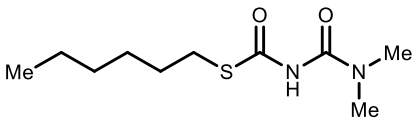
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (s, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.91 (s, 3H), 1.69 – 1.60 (m, 2H), 1.35 – 1.25 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 162.9, 37.2, 35.3, 31.1, 30.7, 29.4, 22.3, 14.0.

IR (film): ν_{max} 3311, 3173, 2945, 2928, 2859, 1578, 1447, 1367, 1264, 1206, 1092, 995, 869, 795, 760, 726 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_9H_{18}N_2O_2S$ [$(M+H^+)$] 219.1163, found 219.1029.

Melting point: 75 – 76 °C.



***S*-hexyl (*N,N*-dimethyl-carbonyl)carbamothioate (3k)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N,N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 1-iodohexane (0.22 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a yellow solid (0.21 g, 91% yield).

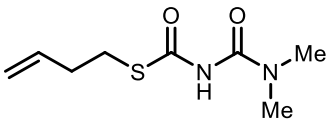
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.12 (s, 3H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.93 (s, 3H), 2.70 (s, 1H), 1.71 – 1.59 (m, 2H), 1.43 – 1.32 (m, 2H), 1.31 – 1.22 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 162.9, 37.3, 35.4, 34.9, 31.4, 30.8, 29.7, 28.6, 22.6, 14.0.

IR (film): ν_{max} 3322, 3253, 3173, 3122, 2922, 2853, 1687, 1590, 1532, 1465, 1378, 1264, 1218, 1092, 1018, 989, 955, 869, 789, 749 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{10}H_{20}N_2O_2S$ [$(M+H^+)$] 233.1320, found 233.1089.

Melting point: 59 – 61 °C.



***S*-(but-3-en-1-yl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3l)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 4-bromobut-1-ene (0.15 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a yellow solid (0.19 g, 93% yield).

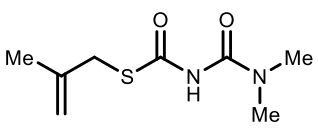
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.20 – 4.88 (m, 42H), 3.12 (s, 3H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.93 (s, 3H), 2.43 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.32 (s, 1H), 1.25 (d, *J* = 14.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 162.9, 136.4, 116., 37.38, 35.4, 34.0, 29.9.

IR (film): ν_{max} 3316, 3248, 3173, 3076, 2922, 2853, 1584, 1584, 1532, 1435, 1372, 1264, 1218, 1081, 989, 909, 875, 795, 755 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_8H_{14}N_2O_2S$ [$(M+H^+)$] 203.0854, found 203.0746.

Melting point: 42 – 43 °C.



***S*-(2-methylallyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3m)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 4-bromo-2-butene (0.10 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in

the general procedure A and purified by column chromatography to afford the title product as a clear solid (0.16 g, 77% yield).

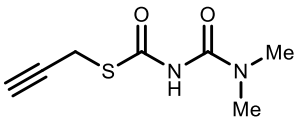
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (s, 1H), 4.87 (s, 1H), 3.73 (s, 2H), 3.13 (s, 3H), 2.94 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 162.8, 141.1, 114.1, 37.6, 37.4, 35.4, 21.3.

IR (film): ν_{max} 3305, 3236, 3168, 2933, 1572, 1441, 1372, 1264, 1218, 1098, 1052, 989, 903, 869, 795, 749 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_8H_{14}N_2O_2S$ [(M+Na^+)] 225.0673, found 225.0663.

Melting point: 83 – 85 °C.



***S*-(prop-2-yn-1-yl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3n)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N,N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and propargyl bromide (0.13 mL, 1.5 mmol, 1.5 equiv.) or propargyl chloride (0.11 g, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a clear solid (0.14 g, 77% yield (from bromide), 0.15 g, 79% yield (from chloride)).

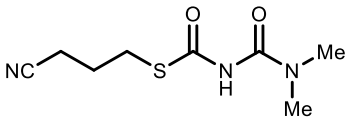
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 2H), 3.16 (s, 3H), 2.95 (s, 3H), 2.21 (s, 1H), 1.60 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 162.5, 79.4, 71.1, 37.4, 35.5, 19.2.

IR (film): ν_{max} 3653, 2361, 1590, 1378, 869, 789, 749 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_7H_{10}N_2O_2S$ [(M+H^+)] 187.0536, found 187.0598.

Melting point: 112 – 114 °C.



***S*-(3-cyanopropyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3o)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N,N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 4-bromobutanenitrile (0.15 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure

outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.19 g, 87% yield).

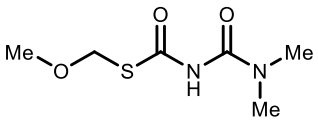
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.15 (d, *J* = 6.9 Hz, 2H), 3.13 (s, 3H), 2.95 (s, 3H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.08 (p, *J* = 6.9 Hz, 2H), 1.67 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 162.7, 119.0, 37.4, 35.5, 29.2, 25.8, 16.2.

IR (film): ν_{max} 3739, 3311, 3242, 3173, 2933, 2248, 1590, 1538, 1441, 1412, 1378, 1264, 1224, 1104, 1058, 989, 852, 789, 743, 709 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_8H_{13}N_3O_2S$ [$(M+H^+)$] 216.0801, found 216.0672.

Melting point: 102 – 104 °C.



***S*-(methoxymethyl)-(*N,N*-dimethyl-carbonyl)carbamothioate (3p)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and chloromethyl methyl ether (0.11 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.15 g, 80% yield).

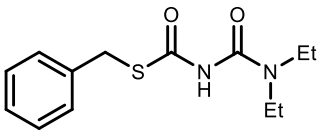
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 (s, 2H), 3.39 (s, 3H), 3.12 (s, 3H), 2.91 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 162.8, 74.0, 56.6, 37.4, 35.4.

IR (film): ν_{max} 3725, 3288, 3173, 2928, 2361, 2247, 1584, 1435, 1378, 1264, 1212, 1184, 1081, 1023, 943, 892, 789, 743 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_6H_{12}N_2O_3S$ [$(M+H^+)$] 193.0641, found 193.0463.

Melting point: 116 – 118 °C.



***S*-benzyl (*N,N*-diethyl-carbonyl)carbamothioate (3q)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-diethylcarbamoyl chloride (0.13 mL, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure

A and purified by column chromatography to afford the title product as a white solid (0.23 g, 85% yield).

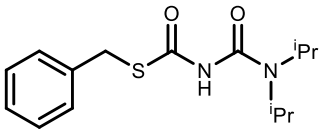
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 4.31 (s, 2H), 3.53 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 7.0 Hz, 2H), 1.13 (dt, *J* = 23.3, 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 162.0, 137.4, 128.7, 128.7, 127.4, 42.4, 40.6, 34.7, 14.4, 13.5.

IR (film): ν_{max} 3299, 2968, 2928, 1675, 1578, 1452, 1412, 1361, 1281, 1075, 949, 858, 789, 732, 703 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}N_2O_2S$ [$(M+H^+)$] 267.1162, found 267.0962.

Melting point: 104 – 106 °C.



***S*-benzyl (*N,N*-diisopropyl-carbonyl)carbamothioate (3r)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*, *N*-diisopropylcarbamoyl chloride (0.16 g, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.27 g, 91% yield).

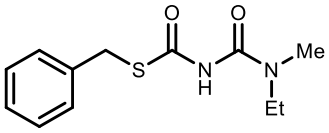
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 4.65 (s, 1H), 4.30 (s, 2H), 3.74 (s, 1H), 1.60 (s, 1H), 1.33 (d, J = 6.6 Hz, 6H), 1.17 (d, J = 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 161.8, 137.4, 128.8, 128.7, 127.4, 47.1, 44.9, 34.8, 21.2, 20.9.

IR (film): ν_{max} 3359, 3253, 2968, 1738, 1584, 1527, 1424, 1367, 1327, 1212, 1149, 1092, 1035, 789, 715 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{15}H_{22}N_2O_2S$ [$(M+H^+)$] 295.1465, found 295.1328.

Melting point: 119 – 121 °C.



***S*-benzyl (*N*-ethyl-*N*-methyl-carbonyl)carbamothioate (3s)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*-ethyl-*N*-methylcarbamoyl chloride (0.12 g, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5

equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.19 g, 75% yield).

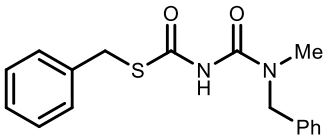
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 6.8, 4.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 4.32 (d, *J* = 9.8 Hz, 2H), 3.57 (q, *J* = 7.1 Hz, 1H), 3.39 (q, *J* = 7.1 Hz, 1H), 3.10 (s, 1H), 2.93 (s, 2H), 1.62 (s, 1H), 1.12 (dt, *J* = 25.1, 7.1 Hz, 3H) (mixture of rotamers).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 162.5, 137.5, 128.8, 128.7, 128.7, 127.4, 127.4, 44.6, 42.5, 34.9, 34.8, 33.0, 13.4, 12.6 (mixture of rotamers).

IR (film): ν_{max} 3694, 3614, 1578, 1532, 1424, 1389, 1298, 1258, 1201, 1081, 1018, 858, 789, 738, 709 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{12}H_{16}N_2O_2S$ [$(M+H^+)$] 253.1005, found 253.1191.

Melting point: 106 – 108 °C.



***S*-benzyl (*N*-benzyl-*N*-methyl-carbonyl)carbamothioate (3t)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*-benzyl-*N*-methylcarbamoyl chloride (0.18 g, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.27 g, 87% yield).

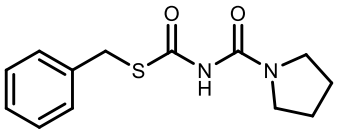
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 22.6, 12.9, 5.7 Hz, 6H), 7.20 (d, *J* = 8.0 Hz, 4H), 4.82 (s, 1H), 4.58 (s, 1H), 4.34 (s, 1H), 4.20 (s, 1H), 3.09 (s, 1H), 2.91 (s, 2H), 1.58 (s, 1H) (mixture of rotamers).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 163.0, 138.5, 138.2, 137.3, 128.9, 128.7, 128.7, 128.6, 127.8, 127.5, 127.3, 127.2, 127.2, 127.1, 53.4, 51.3, 35.3, 35.0, 34.8, 33.3 (mixture of rotamers).

IR (film): ν_{max} 3654, 3288, 3025, 1572, 1515, 1384, 1355, 1252, 1023, 961, 875, 795, 766, 720 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{17}H_{18}N_2O_2S$ [$(M+H^+)$] 315.1162, found 315.1263.

Melting point: 119 – 121 °C.



***S*-benzyl (pyrrolidine-1-carbonyl)carbamothioate (3u)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), 1-pyrolidinecarbonyl chloride (0.11 mL, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.23 g, 88% yield).

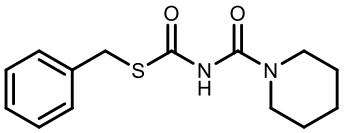
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 4.33 (s, 2H), 3.57 (t, *J* = 6.2 Hz, 2H), 3.43 (t, *J* = 6.3 Hz, 2H), 1.92 – 1.83 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 161.3, 137.8, 128.8, 128.7, 127.4, 47.3, 45.4, 34.8, 25.8, 25.1.

IR (film): ν_{max} 3711, 1578, 1401, 795, 709 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{13}H_{16}N_2O_2S$ [$(M+H^+)$] 265.1005, found 265.1128.

Melting point: 104 – 106 °C.



***S*-benzyl (piperidine-1-carbonyl)carbamothioate (3v)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), 1-piperidinecarbonyl chloride (0.13 mL, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.25 g, 89% yield).

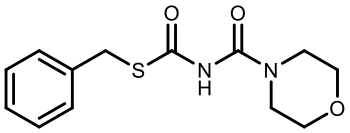
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 4.29 (s, 2H), 3.81 – 3.68 (m, 2H), 3.57 – 3.46 (m, 2H), 1.74 – 1.42 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 161.3, 137.6, 128.8, 128.7, 127.4, 46.2, 43.3, 34.9, 26.4, 26.0, 24.9.

IR (film): ν_{max} 3345, 3242, 3179, 3019, 2928, 2853, 1738, 1590, 1527, 1492, 1447, 1418, 1384, 1263, 1109, 1012, 915, 846, 778, 743, 720 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{14}H_{18}N_2O_2S$ [$(M+H^+)$] 279.1162, found 279.1017.

Melting point: 133 – 135 °C.



***S*-benzyl (morpholine-4-carbonyl)carbamothioate (3w)**: According to the general procedure A, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), 4-morpholinecarbonyl chloride (0.12 mL, 1.0 mmol, 1 equiv.), and benzyl bromide (0.18 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure A and purified by column chromatography to afford the title product as a white solid (0.23 g, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 4.28 (s, 2H), 3.77 (s, 2H), 3.67 (d, *J* = 3.6 Hz, 2H), 3.58 (d, *J* = 17.6 Hz, 4H), 1.66 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 137.1, 128.7, 128.7, 127.5, 67.0, 45.5, 42.7, 35.0.

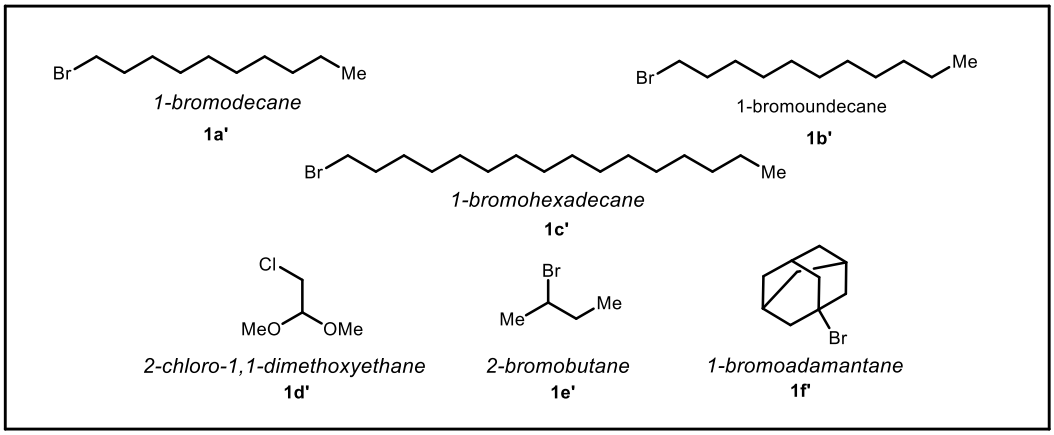
IR (film): ν_{max} 3751, 3648, 1578, 1527, 1418, 1246, 1109, 709 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{13}H_{16}N_2O_3S$ [$(M+H^+)$] 281.0954, found 281.0513.

Melting point: 112 – 113 °C.

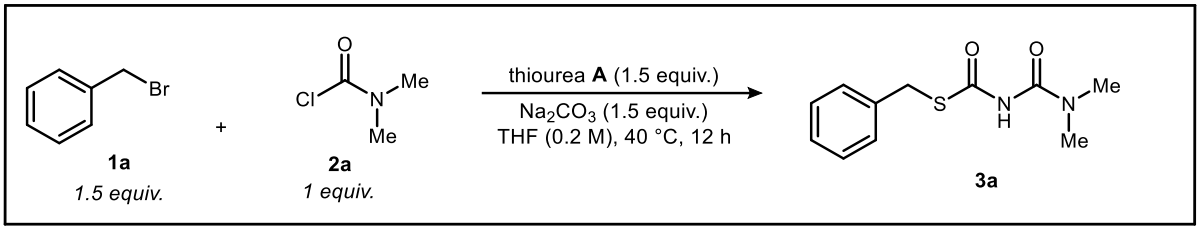
4.2 Failed Substrates

Figure S1. Substrates that failed to yield the desired products



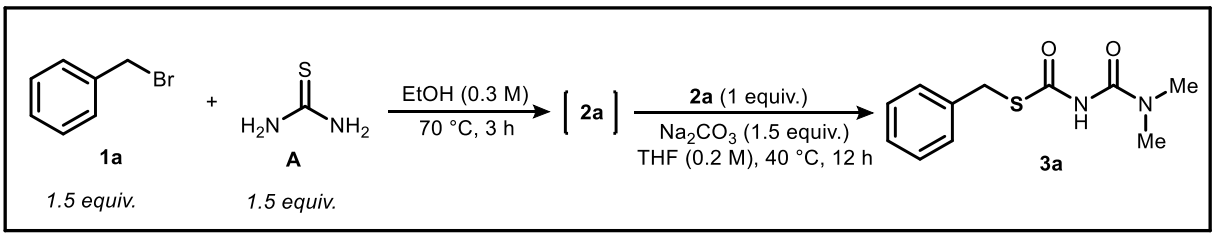
The limitation is presumably due to the inability of the long straight-chain bromo-alkanes to achieve the S_N2 reaction mechanism with thiourea at low temperatures in THF. A significant improvement was observed when 1-bromodecane **1a'** and 1-bromohexadecane **1b'** isothiouronium salts (Scheme 2b) were first prepared at 80 °C in EtOH. A similar fate is presumed for the 2-chloro-1,1-dimethoxyethane **1c'** secondary **1d'** and tertiary **1e'** alkane substrates.

4.3 General Procedure B



To a 250 mL pressure tube equipped with a magnetic stirrer bar was added thiourea **A** (2.3 g, 30 mmol, 1.5 equiv.), anhydrous Na_2CO_3 (3.2 g, 30 mmol, 1.5 equiv.), THF (100 mL, 0.2 M), carbamoyl chloride **2a** (1.8 mL, 20 mmol, 1 equiv.), and benzyl bromide **1a** (3.6 mL, 30 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at 40 °C. The reaction mixture was filtered and concentrated under reduced pressure. The resulting crude was dissolved in EtOAc (10 mL), quenched with deionised water (60 mL) and extracted with EtOAc (3 × 20 mL). The combined EtOAc layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure and purified by recrystallisation using EtOAc;*n*-hexanes (1:3) and refrigerated overnight, affording the title product as a white solid (4.2 g, 89% yield).

4.4 General Procedure C

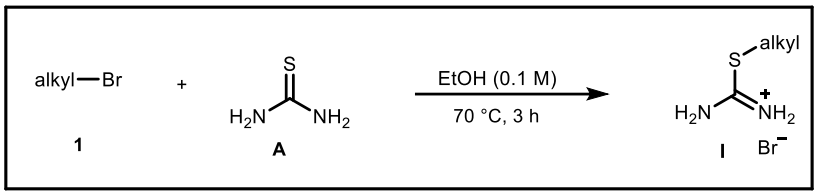


To a 50 mL pressure tube equipped with a magnetic stirrer, was added benzyl bromide **1a** (0.18 mL, 1.5 mmol, 1.5 equiv.), thiourea **A** (0.11 g, 1.5 mmol, 1.5 equiv.) and ethanol (3 mL, 0.5 M). The reaction mixture was stirred for 3 h (complete consumption of **1a** was observed *via* TLC analysis) at 70 °C resulting in [**2a**].[3] Anhydrous Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), and *N*,*N*-dimethylcarbamoyl chloride **2a** (0.09 mL, 1.0 mmol, 1 equiv.) were added. The reaction mixture was stirred for 12 h at 40 °C. The reaction mixture was quenched with deionised water (30 mL) and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure and purified *via* column chromatography on silica gel using 30% EtOAc in *n*-hexanes system to afford the title product as a white solid (0.22 g, 93% yield).

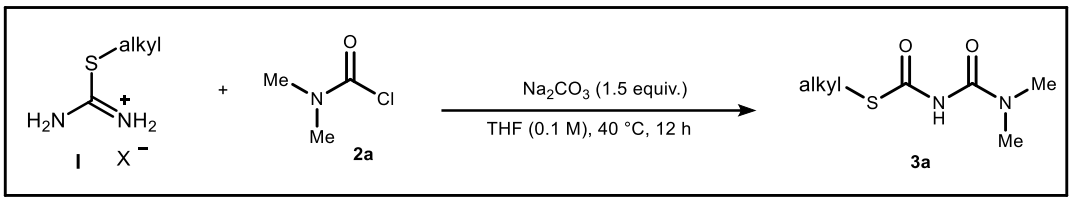
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 4.32 (s, 2H), 3.13 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 162.8, 137.5, 128.7, 128.6, 127.3, 37.4, 35.4, 34.8.

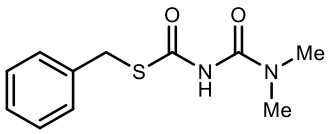
4.5 General Procedure D



To a 50 mL pressure tube equipped with a magnetic stirrer bar was added alkyl bromide **46** (10 mmol, 1 equiv.) thiourea **47** (0.76 g, 10 mmol, 1 equiv.) and ethanol (50 mL, 0.1 M). The reaction mixture was stirred for 3 h at 70 °C. The reaction mixture was concentrated, and the resulting solids were washed with cold Et_2O, affording the desired salts in quantitative yields as white solids and used without any further purification in the next step.[3]



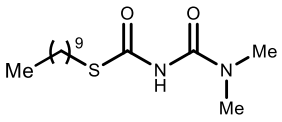
To a 50 mL pressure tube was added salt (1.5 mmol, 1.5 equiv.), anhydrous Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), and *N*,*N*-dimethylcarbamoyl chloride **2a** (0.09 mL, 1.0 mmol, 1 equiv.). The reaction mixture was stirred for 12 h at 40 °C. The reaction mixture was quenched with deionised water (30 mL) and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure and purified *via* column chromatography on silica gel using 30% EtOAc in *n*-hexanes system to afford the title products (No further optimisation was conducted. The reaction time, temperature and solvent used are identical to those reported in table S1 entry 1).



***S*-benzyl-*(N,N*-dimethyl-carbonyl)carbamothioate (3a)**: According to the general procedure D, 2-benzylisothiouronium chloride (0.30 g, 1.5 mmol, 1.5 equiv.) Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), and *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure D and purified by column chromatography to afford the title product as a white solid (0.20 g, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 4.32 (s, 2H), 3.13 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 162.8, 137.5, 128.7, 128.6, 127.3, 37.4, 35.4, 34.8.



***S*-decyl (*N,N*-dimethyl-carbonyl)carbamothioate (3x)**: According to the general procedure D, 2-decylisothiouronium bromide (0.45 g, 1.5 mmol, 1.5 equiv.) Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), and *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure D and purified by column chromatography to afford the title product as a white solid (0.26 g, 91% yield).

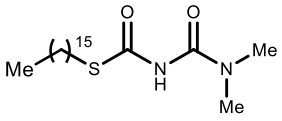
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.11 (s, 3H), 2.99 – 2.95 (m, 2H), 2.92 (s, 3H), 2.72 – 2.62 (m, 1H), 1.65 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.36 (dd, *J* = 15.6, 9.4 Hz, 3H), 1.24 (s, 12H), 0.86 (t, *J* = 6.9 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 162.9, 37.3, 35.4, 35.0, 31.9, 30.8, 29.8, 29.6, 29.6, 29.3, 29.3, 29.0, 22.7, 14.1.

IR (film): ν_{max} 3299, 3173, 2950, 2922, 2847, 2161, 1732, 1664, 1584, 1509, 1458, 1372, 1269, 1218, 1178, 1126, 1041, 983, 869, 795, 755, 726 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{14}H_{18}N_2O_2S$ [$(M+H^+)$] 289.1945, found 289.1526.

Melting point: 48 – 50 °C.



***S*-hexadecyl (*N,N*-dimethyl-carbonyl)carbamothioate (3y)**: According to the general procedure D, 2-hexadecylisothiouronium bromide (0.57 g, 1.5 mmol, 1.5 equiv.) Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), and *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure D and purified by column chromatography to afford the title product as a white solid (0.34 g, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.13 (s, 3H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.95 (s, 3H), 1.72 – 1.63 (m, 2H), 1.60 (s, 1H), 1.37 (s, 2H), 1.25 (s, 24H), 0.88 (t, *J* = 6.7 Hz, 3H).

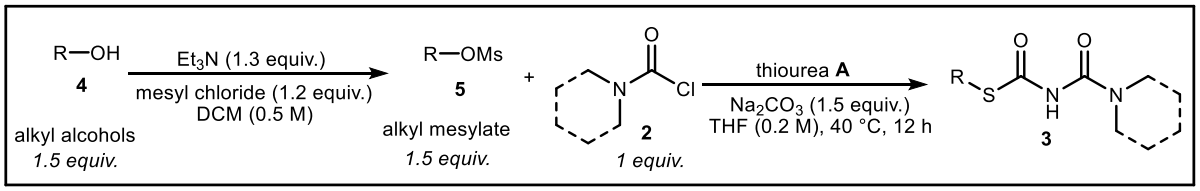
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 163.0, 37.3, 35.4, 32.0, 30.9, 29.8 (dd, *J* = 4.5, 2.4 Hz), 29.7, 29.6, 29.5, 29.3, 29.0, 22.8, 14.2.

IR (film): ν_{max} 3785, 3657, 3637, 3602, 3579, 3299, 2916, 2847, 2384, 1584, 1464, 1372, 1264, 1224, 875, 795, 760, 720 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{20}H_{40}N_2O_2S$ [$(M+H^+)$] 373.2883, found 373.2227.

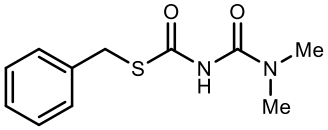
Melting point: 75 – 77 °C.

4.6 General Procedure E



To a 100 mL round-bottom flask was added alcohol **4** (1.5 mmol, 1.5 equiv.) and DCM (3 mL, 0.5 M), and the reaction mixture was cooled using an ice bath. Triethylamine (0.18 mL, 1.3 mmol, 1.3 equiv.) was added. The reaction mixture was stirred for 5 minutes, and methanesulfonyl chloride (0.09 mL, 1.2 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred for 4 h at room temperature, then quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 × 15 mL). The combined DCM layers were washed with deionised H_2O and brine sequentially, dried over anhydrous $MgSO_4$, concentrated under reduced pressure and used without further purification in the next step.[4]

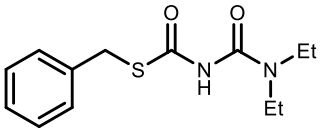
In the same round-bottom flask was added anhydrous Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), and carbamoyl chloride **2** (0.09 mL, 1.0 mmol, 1 equiv.). The reaction mixture was stirred for 12 h at 40 °C. The reaction mixture was filtered, quenched with deionised water (30 mL) and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure and purified *via* column chromatography on silica gel using a 30% EtOAc in *n*-hexanes system to afford the products.



***S*-benzyl-*(N,N*-dimethyl-carbonyl)carbamothioate (3a)**: According to the general procedure E, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and benzyl alcohol (0.15 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure E and purified by column chromatography to afford the title product as a white solid (0.18 g, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 4.32 (s, 2H), 3.13 (s, 3H), 2.95 (s, 3H).

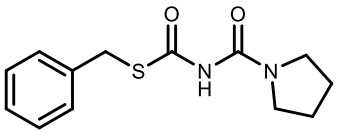
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 162.8, 137.5, 128.7, 128.6, 127.3, 37.4, 35.4, 34.8.



***S*-benzyl (*N,N*-diethyl-carbonyl)carbamothioate (3q)**: According to the general procedure E, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-diethylcarbamoyl chloride (0.13 mL, 1.0 mmol, 1 equiv.), and benzyl alcohol (0.15 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure E and purified by column chromatography to afford the title product as a white solid (0.20 g, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 4.31 (s, 2H), 3.53 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 7.0 Hz, 2H), 1.13 (dt, *J* = 23.3, 7.0 Hz, 6H).

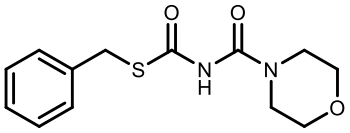
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 162.0, 137.4, 128.7, 128.7, 127.4, 42.4, 40.6, 34.7, 14.4, 13.5.



***S*-benzyl (pyrrolidine-1-carbonyl)carbamothioate (3u)**: According to the general procedure E, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), 1-pyrolidinecarbonyl chloride (0.11 mL, 1.0 mmol, 1 equiv.), and benzyl alcohol (0.15 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure E and purified by column chromatography to afford the title product as a white solid (0.17 g, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 4.33 (s, 2H), 3.57 (t, *J* = 6.2 Hz, 2H), 3.43 (t, *J* = 6.3 Hz, 2H), 1.92 – 1.83 (m, 4H).

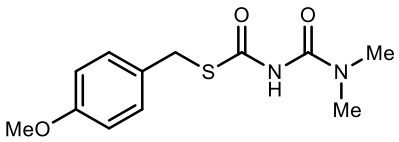
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 161.3, 137.8, 128.8, 128.7, 127.4, 47.3, 45.4, 34.8, 25.8, 25.1.



***S*-benzyl (morpholine-4-carbonyl)carbamothioate (3w)**: According to the general procedure E, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), 4-morpholinecarbonyl chloride (0.12 mL, 1.0 mmol, 1 equiv.), and benzyl alcohol (0.15 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure E and purified by column chromatography to afford the title product as a white solid (0.17 g, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 4.28 (s, 2H), 3.77 (s, 2H), 3.67 (d, *J* = 3.6 Hz, 2H), 3.58 (d, *J* = 17.6 Hz, 4H), 1.66 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 137.1, 128.7, 128.7, 127.5, 67.0, 45.5, 42.7, 35.0.



***S*-(4-methoxybenzyl)-*(N,N*-dimethyl-carbonyl)carbamothioate (3z)**: According to the general procedure E, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and 4-methoxybenzyl alcohol (0.19 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure E and purified by column chromatography to afford the title product as a white solid (0.19 g, 70% yield).

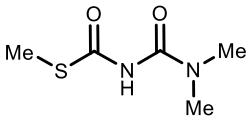
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 3H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.27 (s, 2H), 3.78 (s, 3H), 3.15 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 162.8, 159.0, 130.0, 129.3, 114.1, 55.4, 37.5, 35.5, 34.4.

IR (film): ν_{max} 3717, 3659, 3299, 3128, 2196, 1250, 1578, 1509, 1452, 1372, 1246, 1172, 1098, 1029, 926, 749 cm^{-1}.

HRMS (ESI): m/z calculated for $C_{12}H_{16}N_2O_3S$ [$(M+H^+)$] 269.0955, found 269.0658.

Melting point: 120 – 122 °C.



***S*-methyl (*N,N*-dimethyl-carbonyl)carbamothioate (3h)**: According to the general procedure E, thiourea (0.11 g, 1.5 mmol, 1.5 equiv.), Na_2CO_3 (0.16 g, 1.5 mmol, 1.5 equiv.), THF (5 mL, 0.2 M), *N*,*N*-dimethylcarbamoyl chloride (0.09 mL, 1.0 mmol, 1 equiv.), and methanol (0.06 mL, 1.5 mmol, 1.5 equiv.) were used. After 12 hours, the reaction was subjected to a workup procedure outlined in the general procedure E and purified by column chromatography to afford the title product as a white solid (0.10 g, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.1 (s, 3H), 2.9 (s, 3H), 2.3 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.60, 162.84, 37.39, 35.38, 13.56.

5. X-ray Crystallography Data

Table S2. Crystal data and structure refinement

Molecule name	*S*-benzyl-(N,N-dimethyl-carbonyl)carbamothioate (**3a**)
Empirical formula	$C_{11}H_{14}N_2O_2S$
Formula weight	238.30
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.8421(3)
b/Å	9.9787(5)
c/Å	10.4247(5)
α/°	90
β/°	101.544(2)
γ/°	90
Volume/Å^3	595.43(5)
Z	2
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	0.259
F(000)	252.0
Crystal size/mm^3	0.198 × 0.149 × 0.124
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.988 to 56.54
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	10468
Independent reflections	2678 [R_{int} = 0.0386, R_{sigma} = 0.0357]
Data/restraints/parameters	2678/205/149
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1028
Largest diff. peak/hole / e Å^{-3}	0.44/-0.37
Flack parameter	0.14(12)

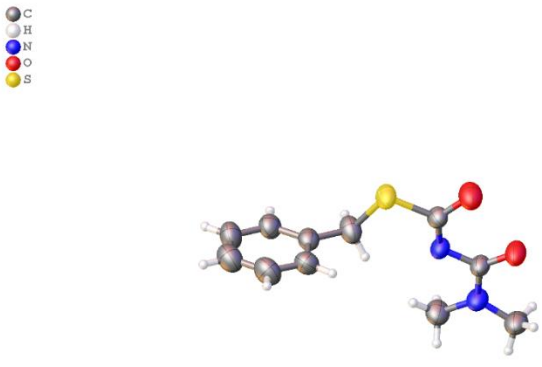


Figure S2. Solid state structure of *S*-benzyl-(N,N-dimethyl-carbonyl)carbamothioate (**3a**) with thermal ellipsoids at 50% probability level.

6. References

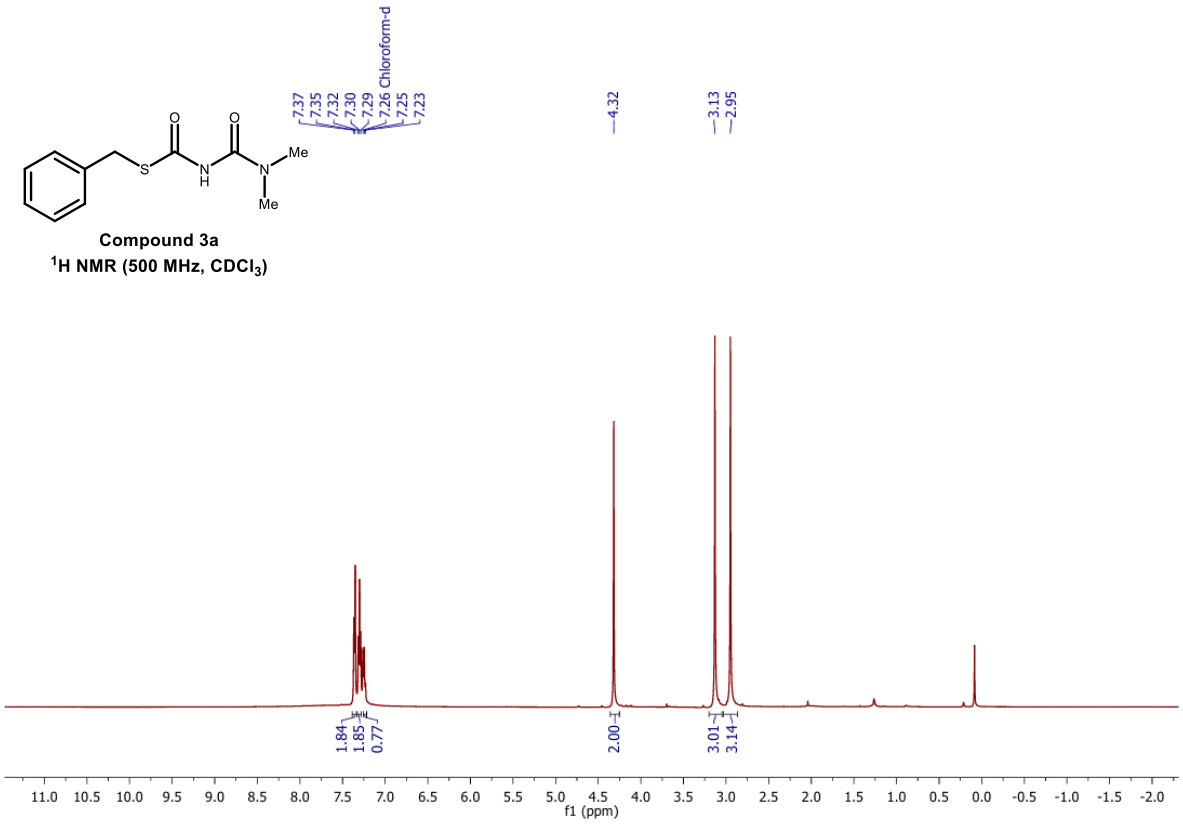
(1) S. Mohamadian, G. Aghapour. *Phosphorus Sulfur Silicon Relat. Elem.* 2024, **199** , 783-794.

(2) J. L. Mabasa, T. F. Mabasa, M. L. Nyathi, P. T. Moshapo, P. T. *Eur. J. Med. Chem. Rep.,* 2024, **10**, 100128-100139.

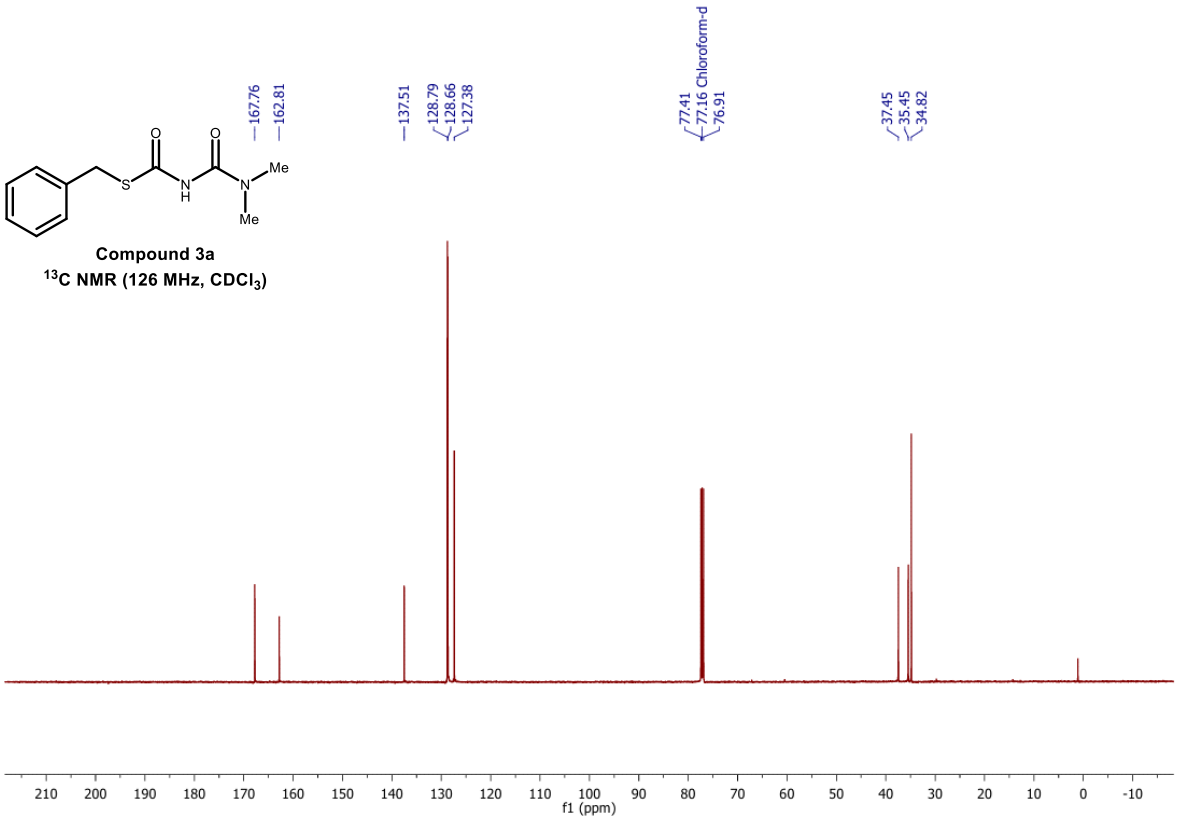
(3) J. J. Donleavy. *J. Am. Chem., Soc.,* 1936, **58**, 865-1066.

(4) A. L. Pace, F. Xu, W. Liu, M. N. Lavagnino, D. W. C. MacMillan. *J. Am. Chem. Soc.,* 2024, **146**, 32925-32932.

7. Spectral Data

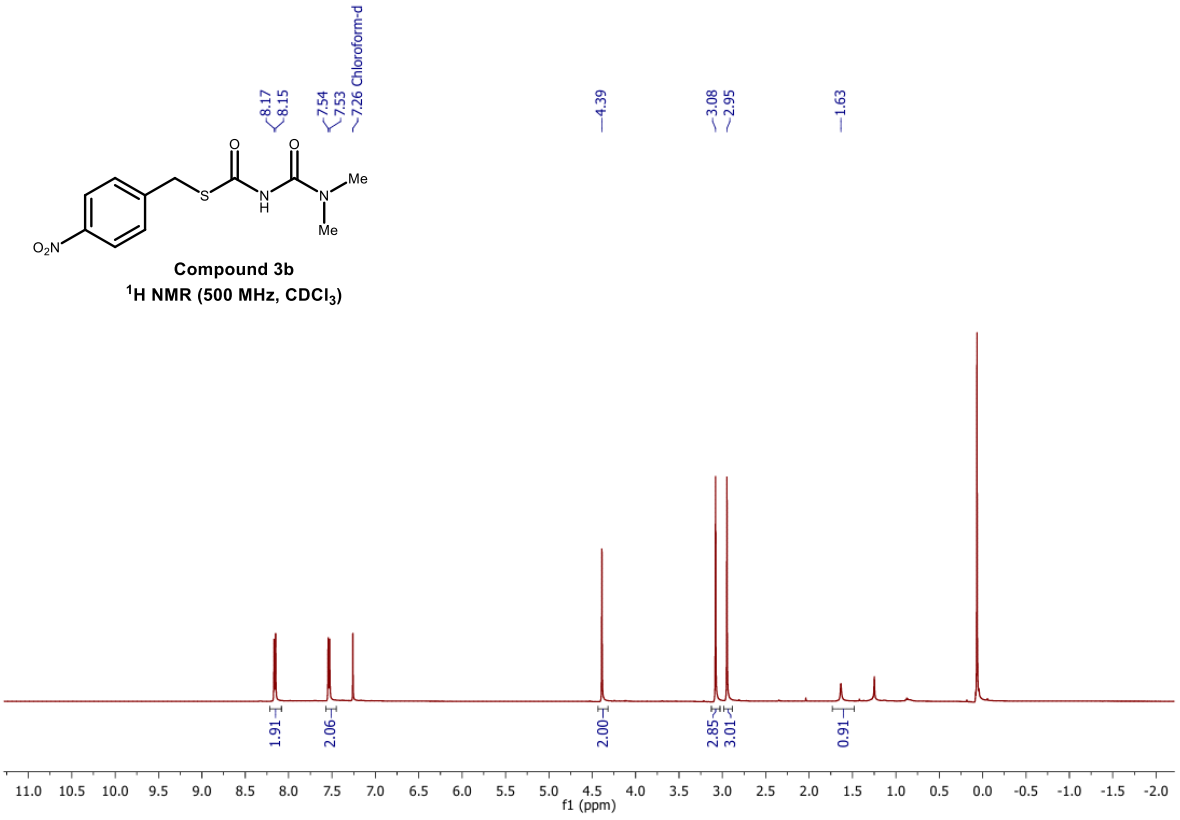


Compound 3a
^{1}H NMR (500 MHz, $CDCl_3$)



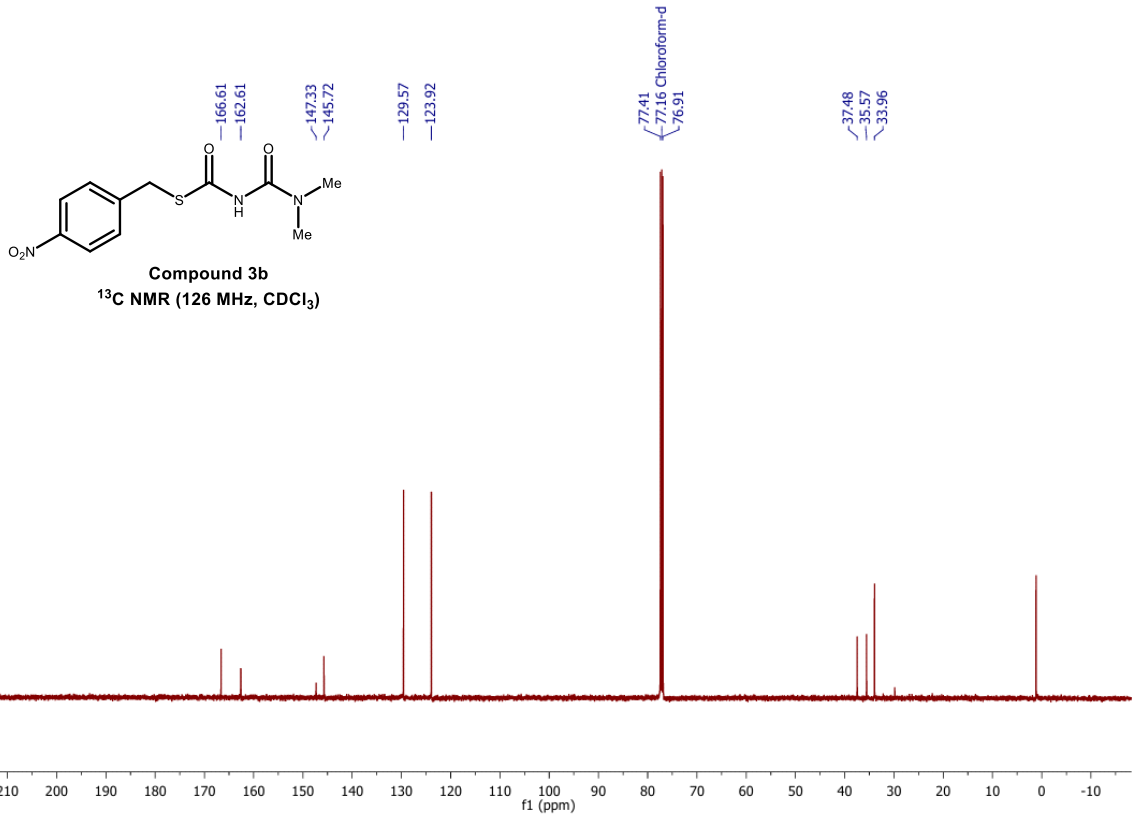
Compound 3a

^{13}C NMR (126 MHz, $CDCl_3$)



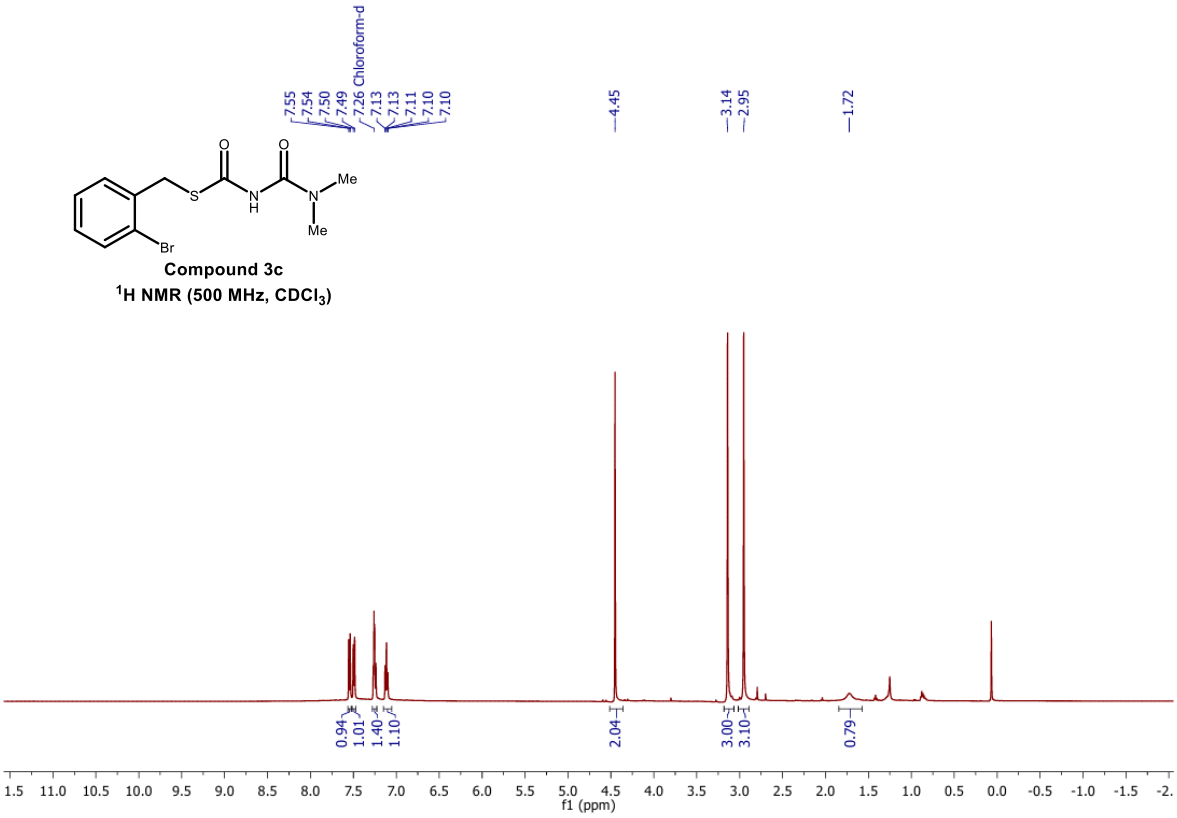
Compound 3b

^{1}H NMR (500 MHz, $CDCl_3$)



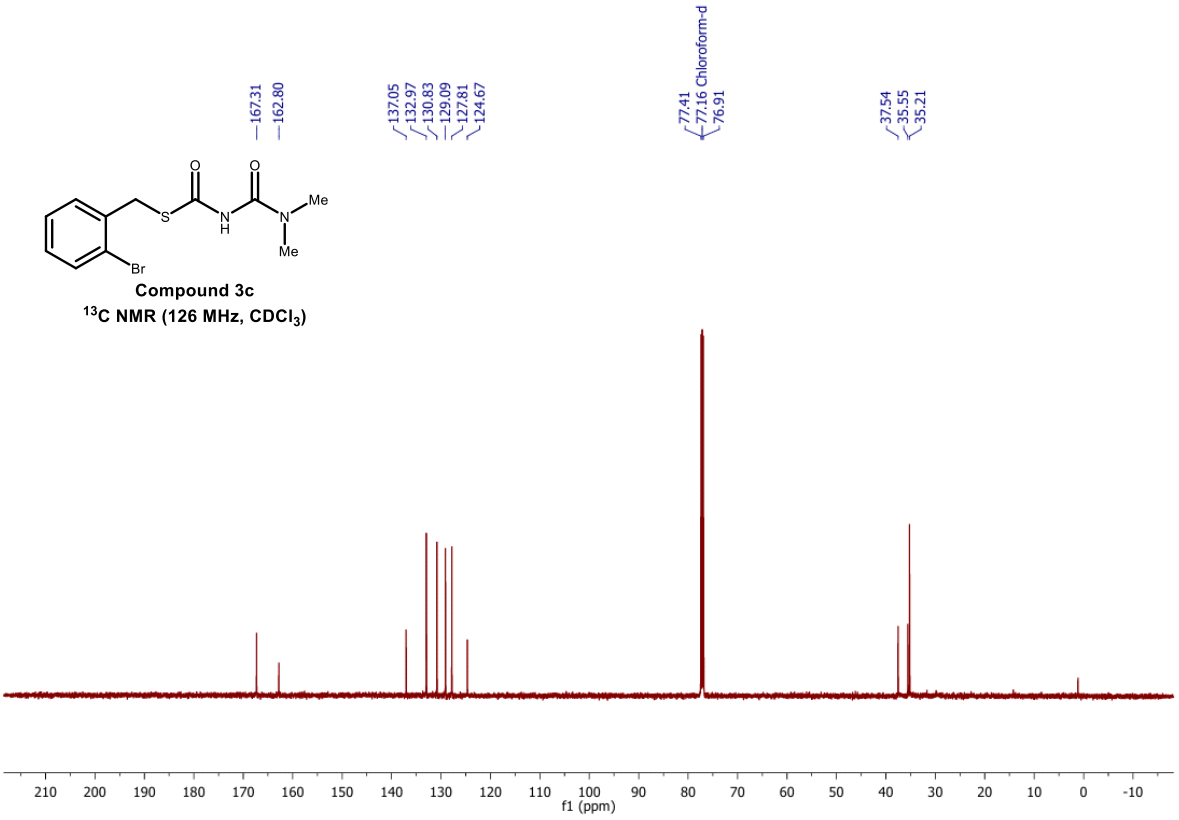
Compound 3b

^{13}C NMR (126 MHz, $CDCl_3$)



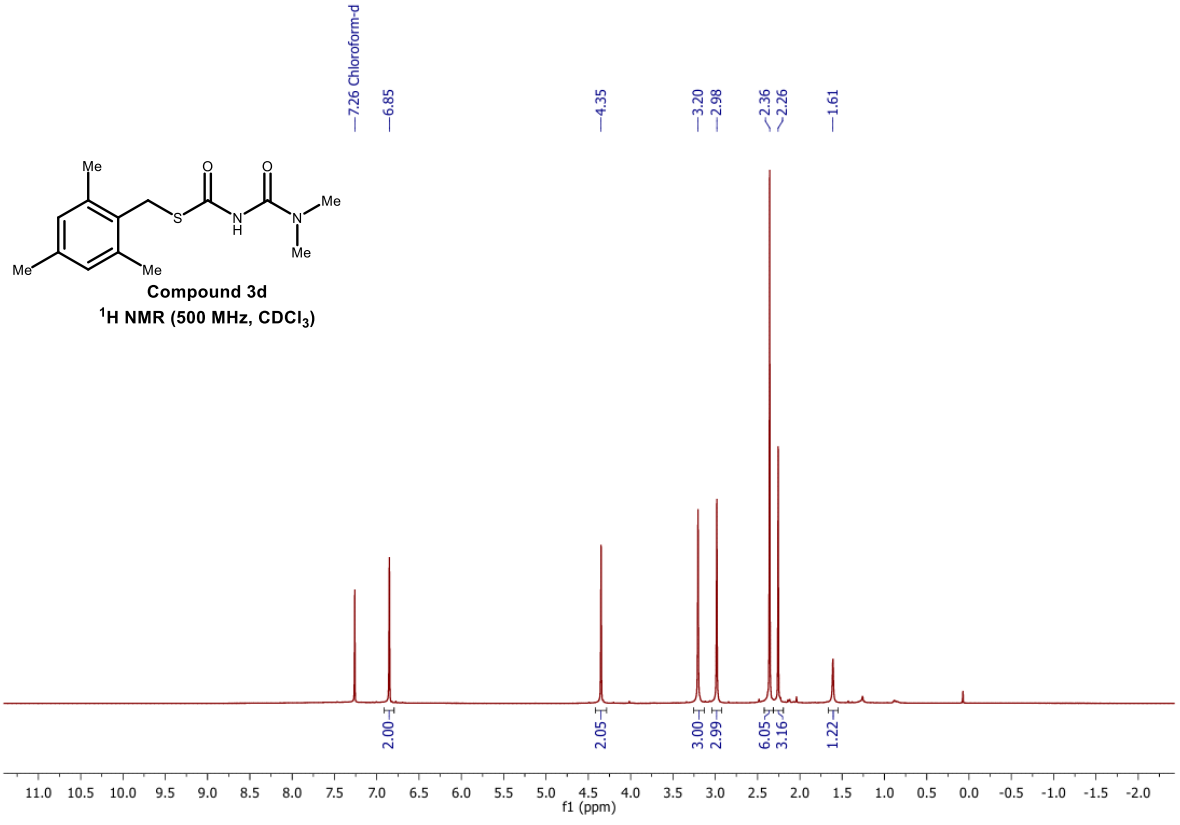
Compound 3c

^{1}H NMR (500 MHz, $CDCl_3$)



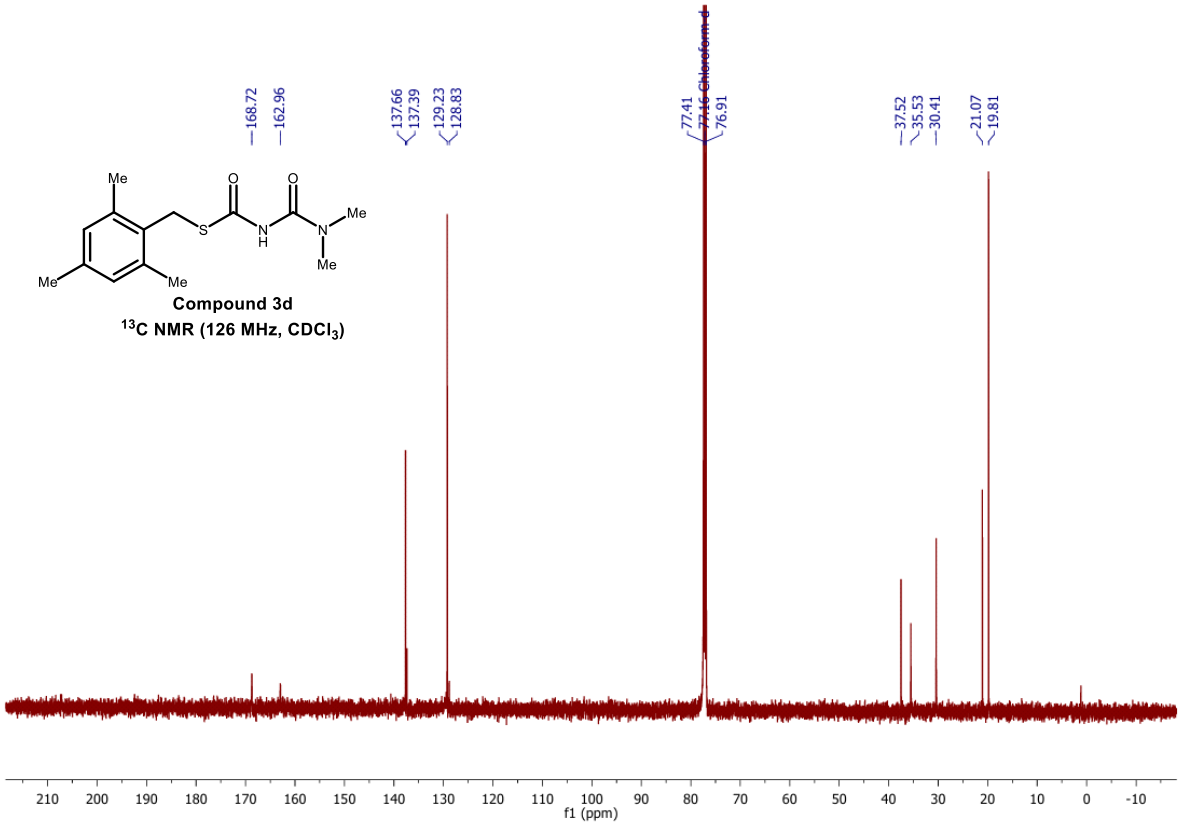
Compound 3c

^{13}C NMR (126 MHz, $CDCl_3$)



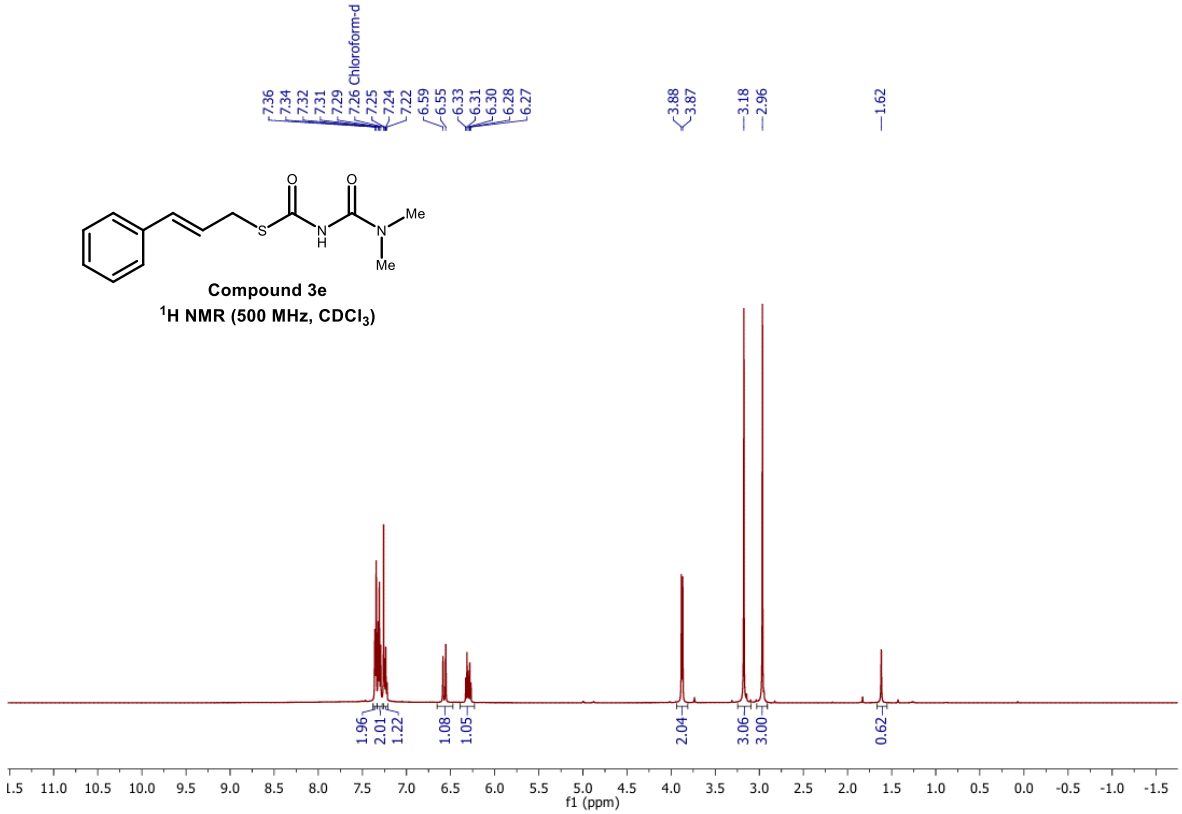
Compound 3d

^{1}H NMR (500 MHz, $CDCl_3$)



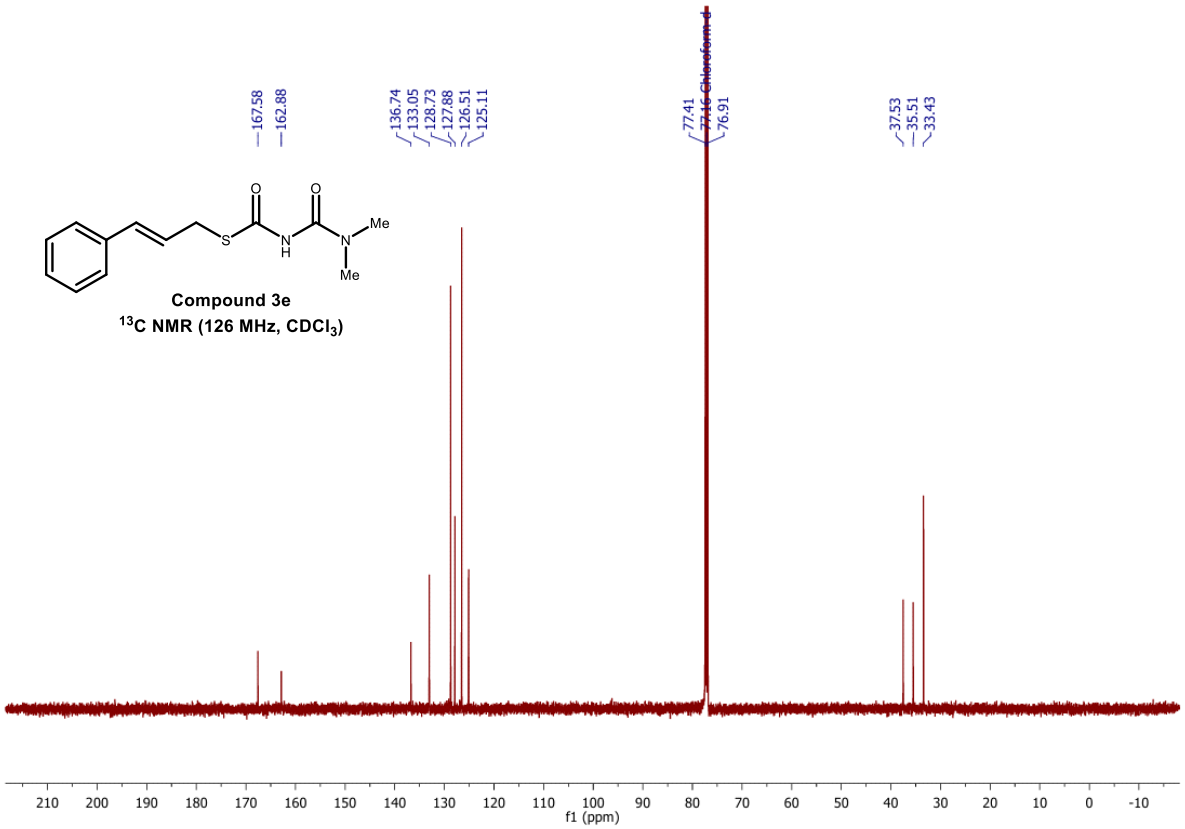
Compound 3d

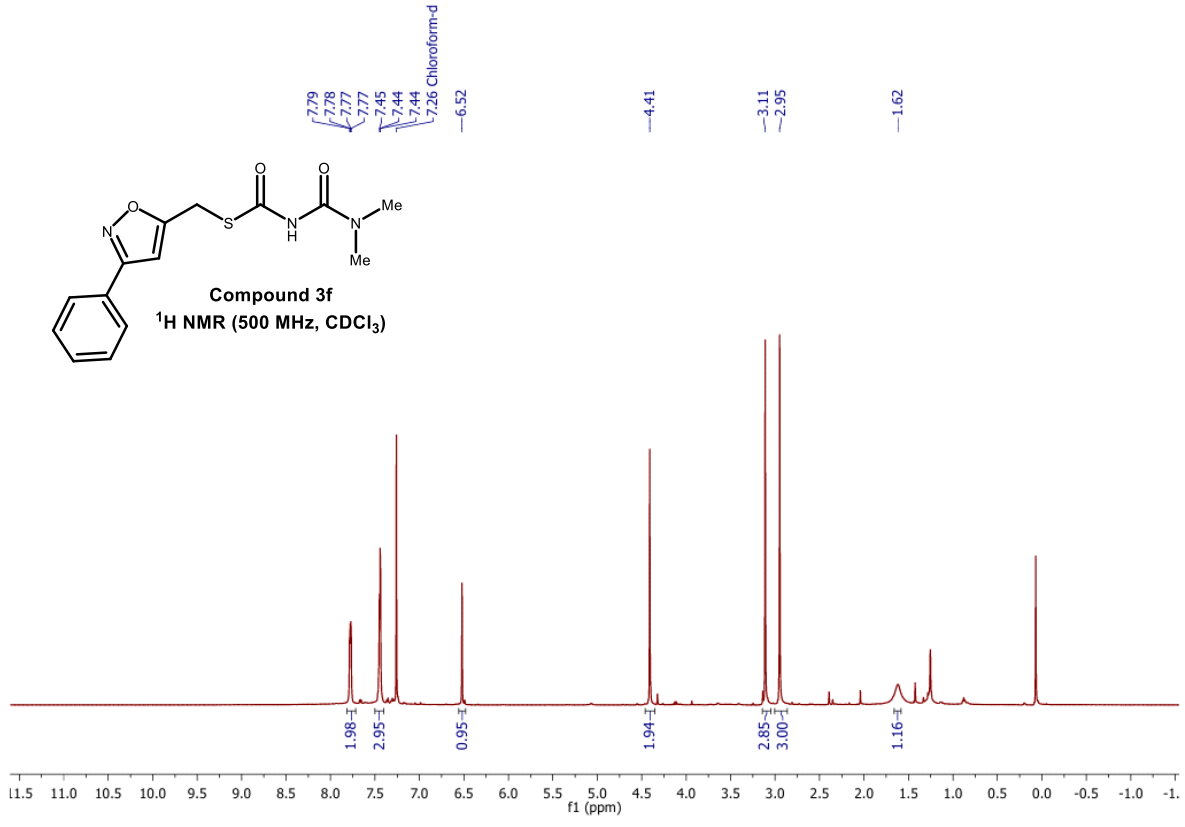
^{13}C NMR (126 MHz, $CDCl_3$)

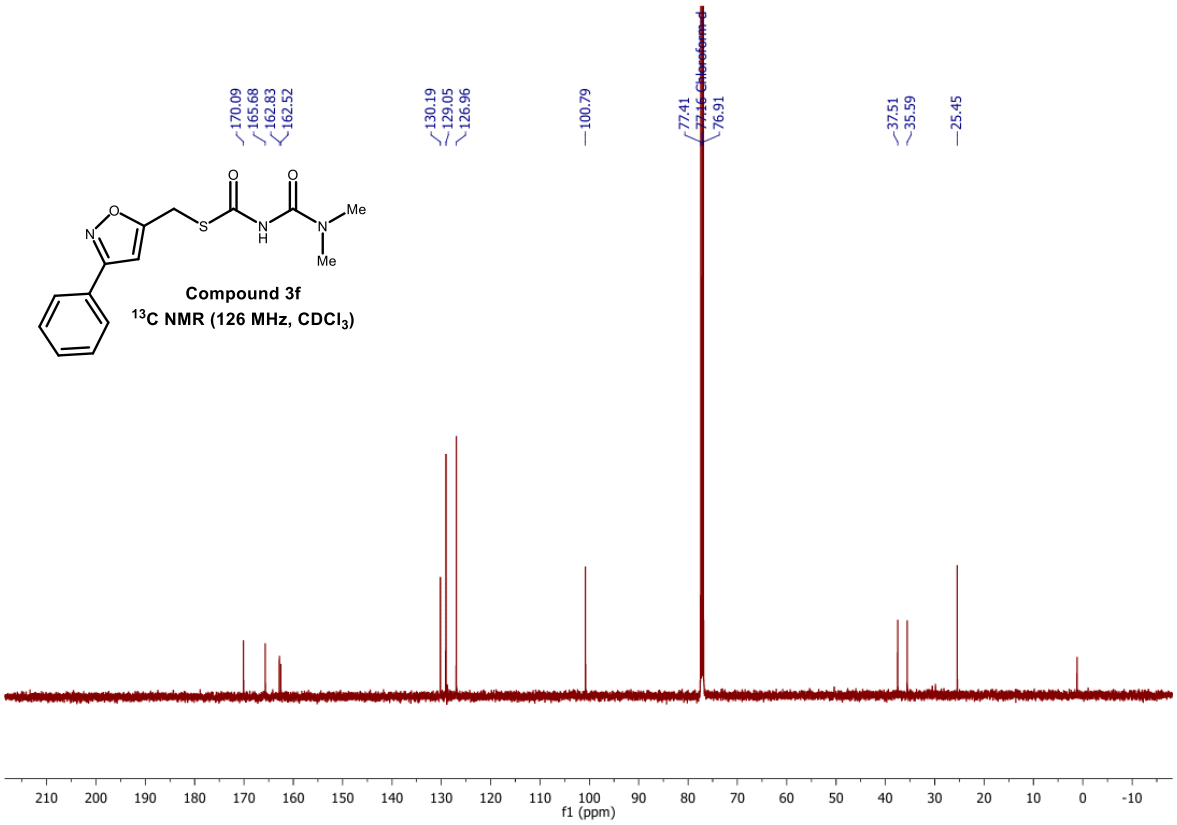


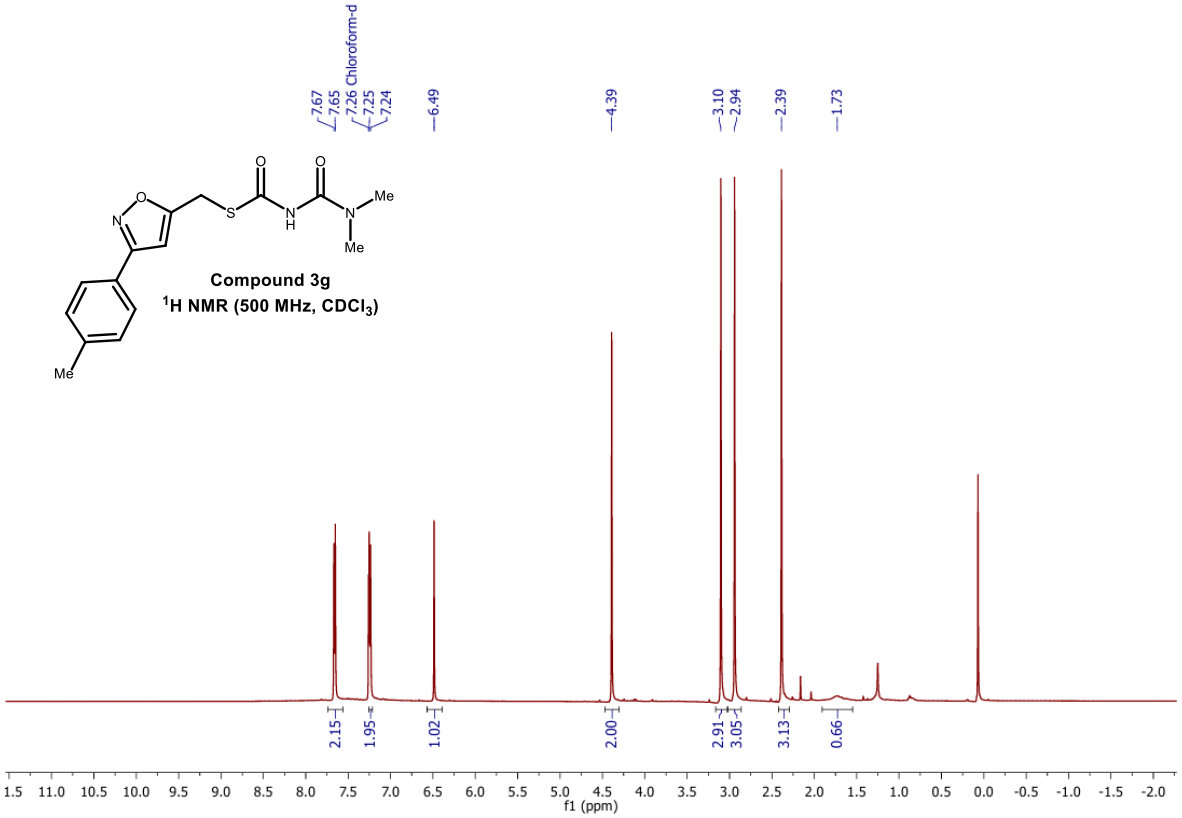
Compound 3e

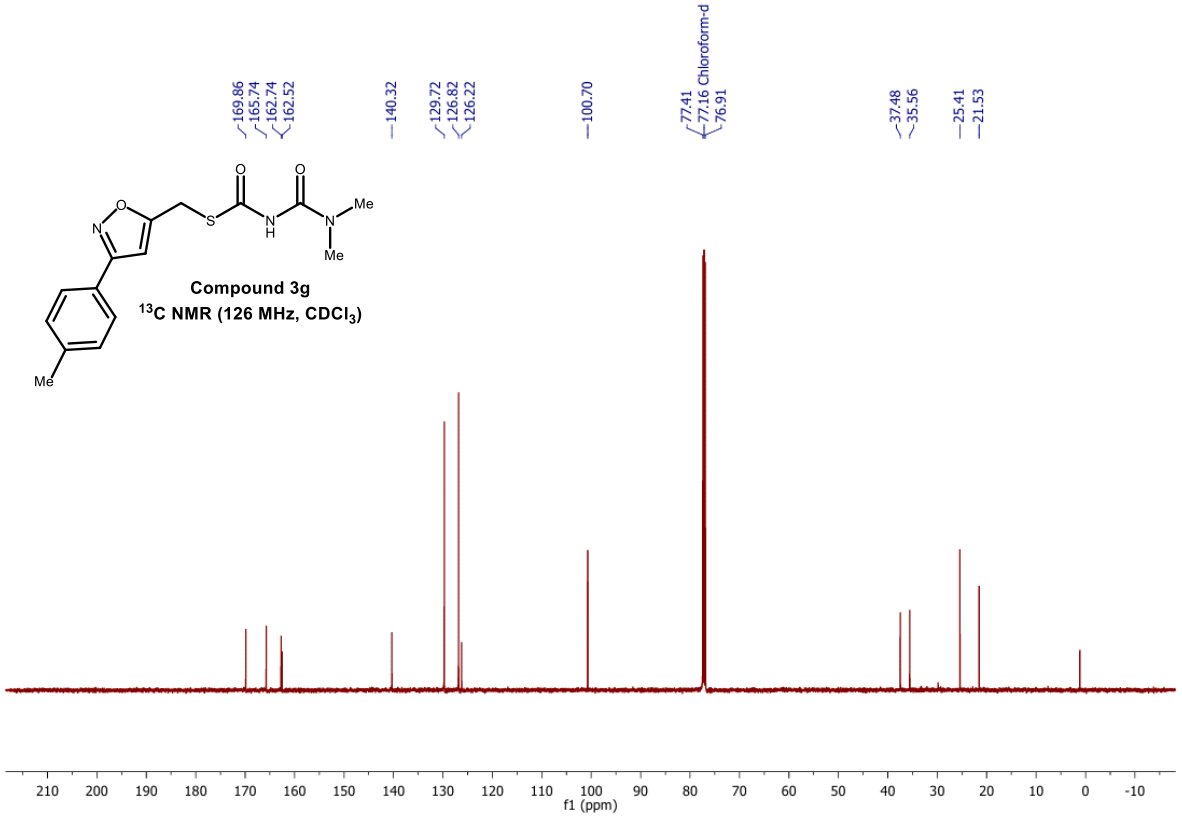
^{1}H NMR (500 MHz, $CDCl_3$)

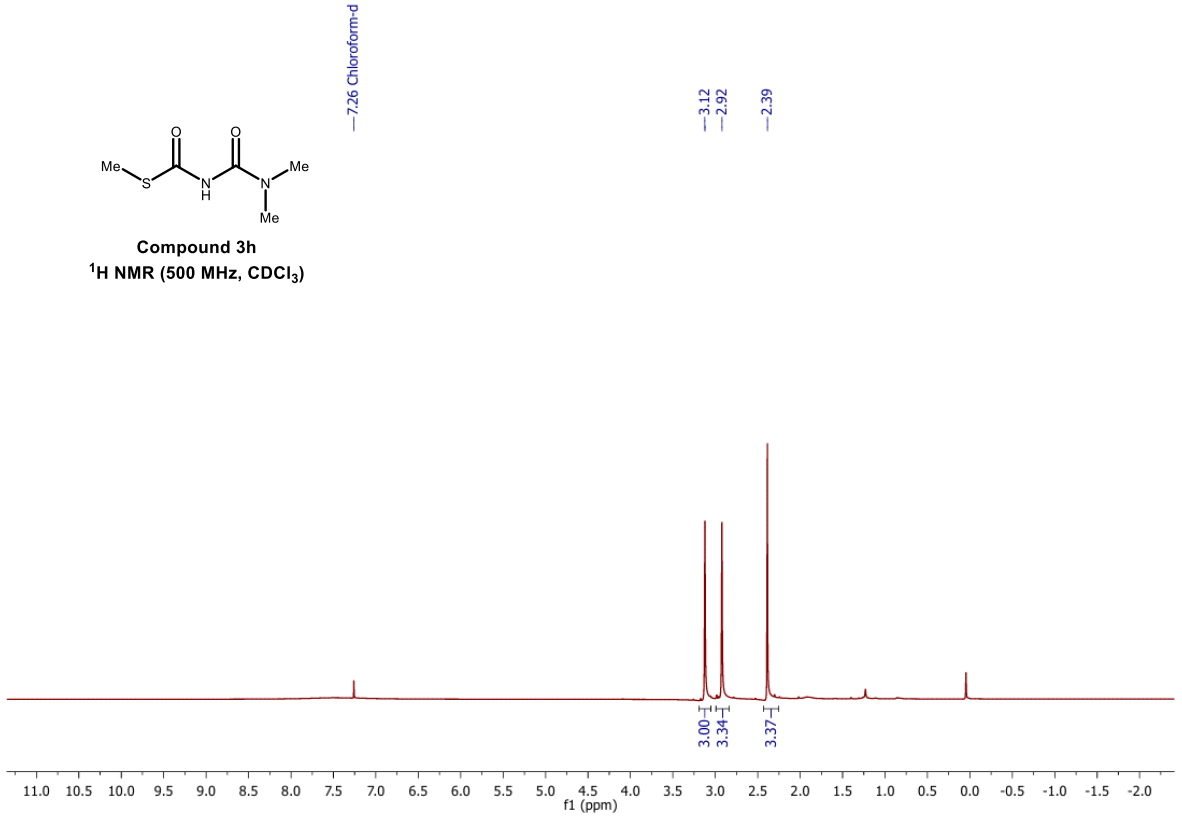

167.58
162.88
136.74
133.05
128.73
127.88
126.51
125.11
77.41
77.16 Chloroform-d
76.91
37.53
35.51
33.43
O
O
S
N
H
N
Me
Me
Compound 3e
13C NMR (126 MHz, CDCl3)
f1 (ppm)

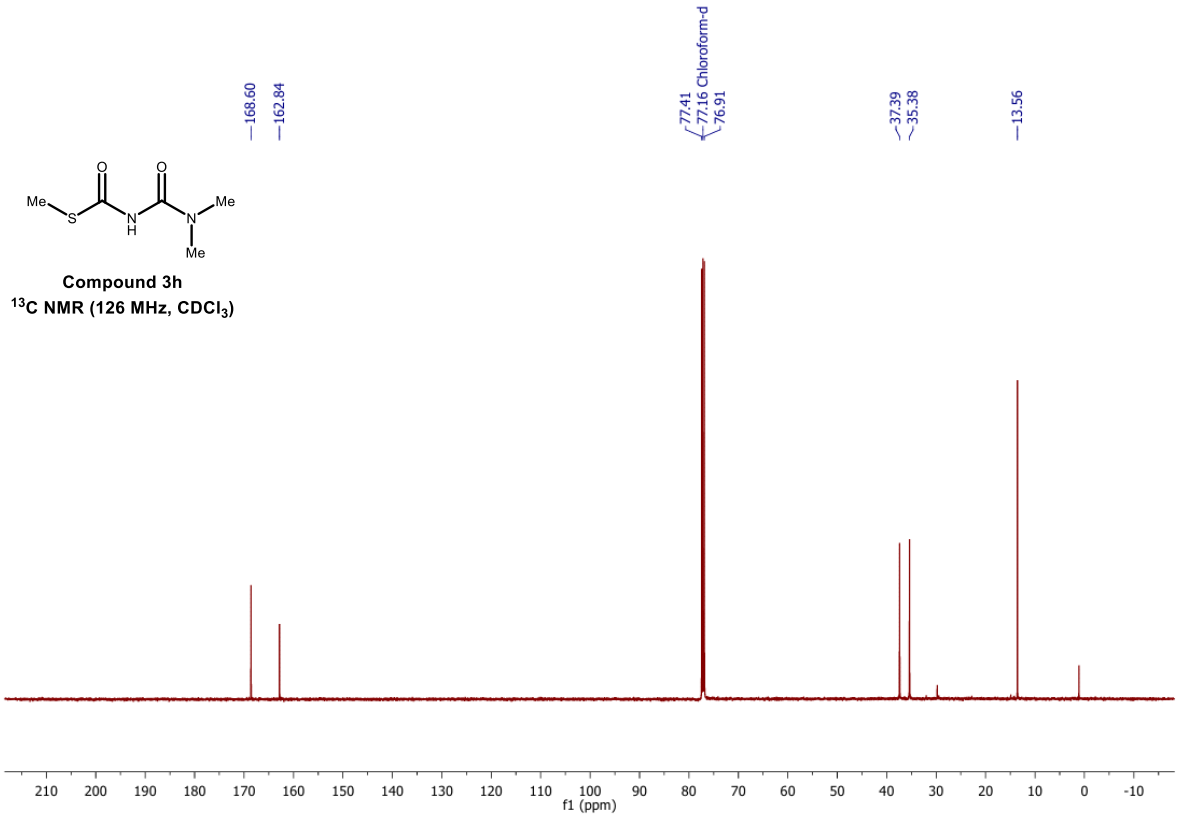

7.79
7.78
7.77
7.77
7.45
7.44
7.44
7.26 Chloroform-d
6.52
4.41
3.11
2.95
1.62
O
N
O
S
N
H
N
Me
Me
Compound 3f
1H NMR (500 MHz, CDCl3)
1.98
2.95
0.95
1.94
2.85
3.00
1.16
f1 (ppm)


170.09
165.68
162.83
162.52
130.19
129.05
126.96
100.79
77.41
77.16 Chloroform-d
76.91
37.51
35.59
25.45
Compound 3f
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.67
7.65
7.26 Chloroform-d
7.25
7.24
6.49
4.39
3.10
2.94
2.39
1.73
Compound 3g
1H NMR (500 MHz, CDCl3)
2.15
1.95
1.02
2.00
2.91
3.05
3.13
0.66
f1 (ppm)

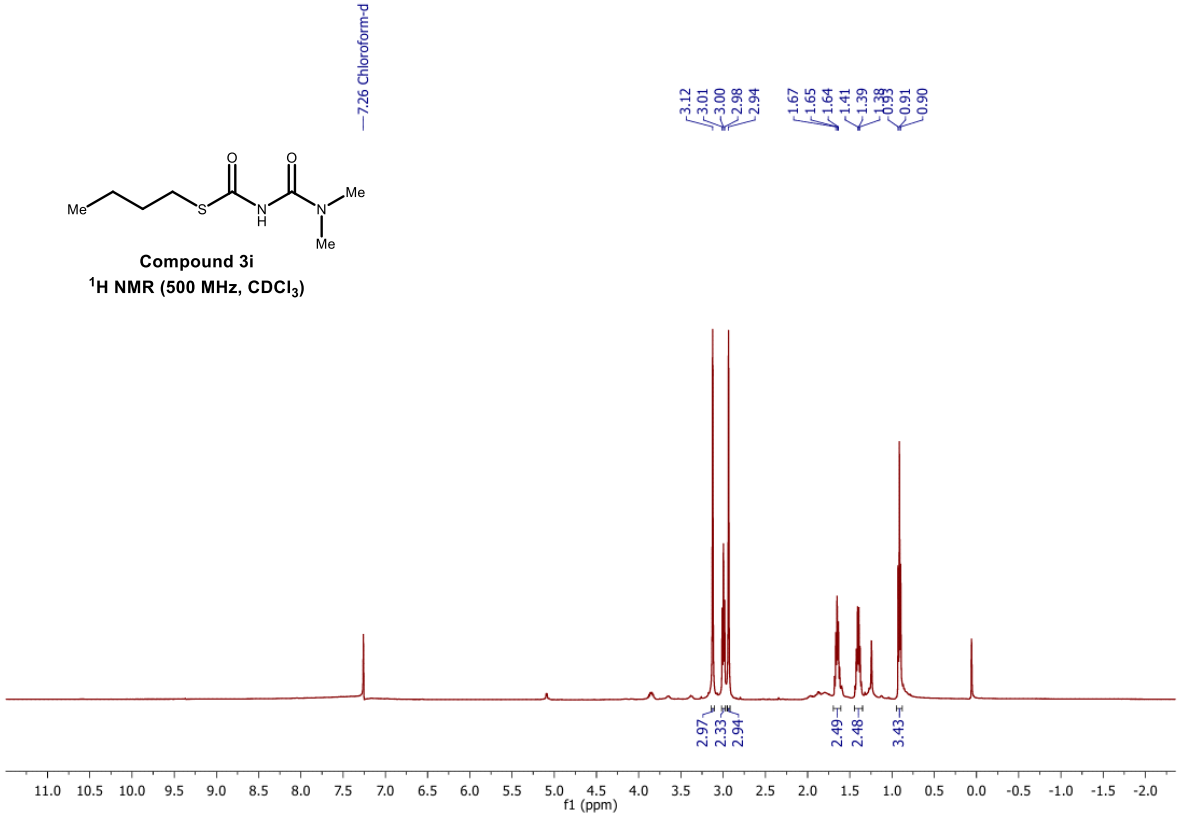

169.86
165.74
162.74
162.52
140.32
129.72
126.82
126.22
100.70
77.41
77.16 Chloroform-d
76.91
37.48
35.56
25.41
21.53
Me
Me
Me
Me
Compound 3g
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.26 Chloroform-d
3.12
2.92
2.39
Me
Me
Me
Compound 3h
1H NMR (500 MHz, CDCl3)
3.00
3.34
3.37
f1 (ppm)



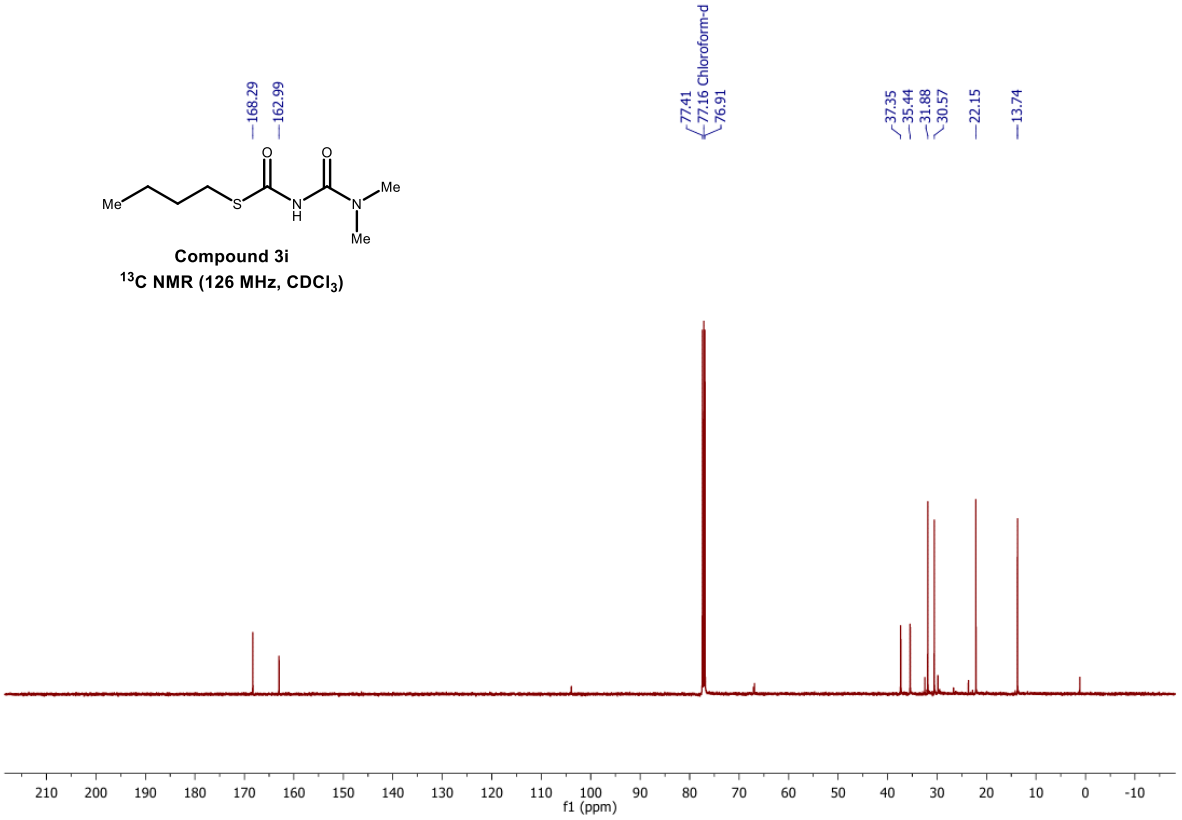
Compound 3h

^{13}C NMR (126 MHz, $CDCl_3$)



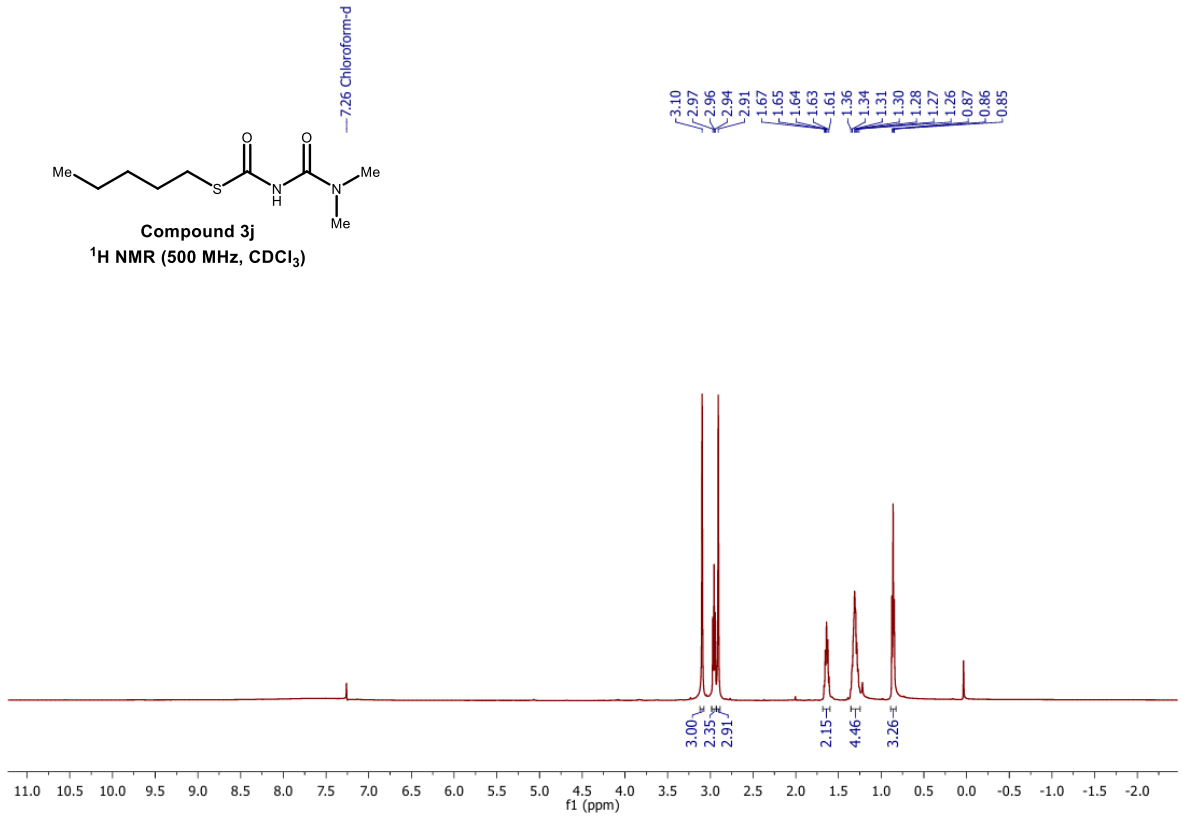
Compound 3i

^{1}H NMR (500 MHz, $CDCl_3$)



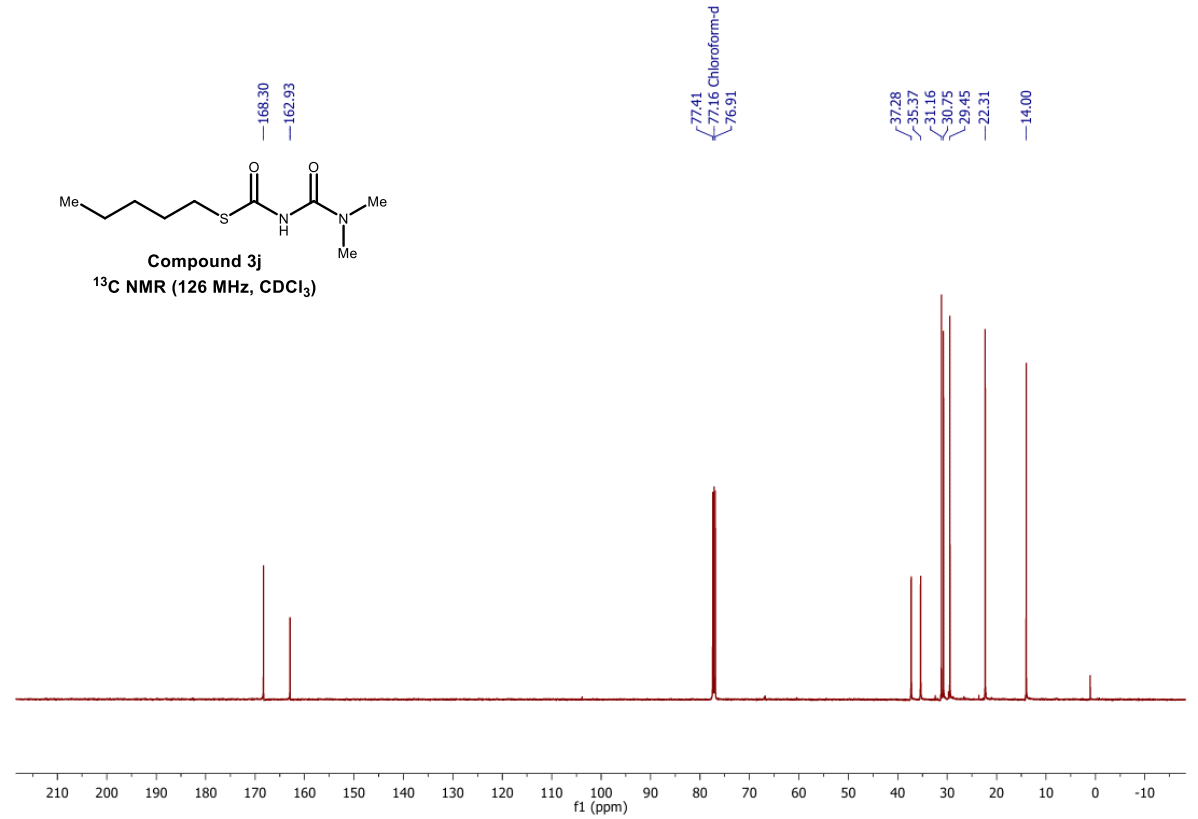
Compound 3i

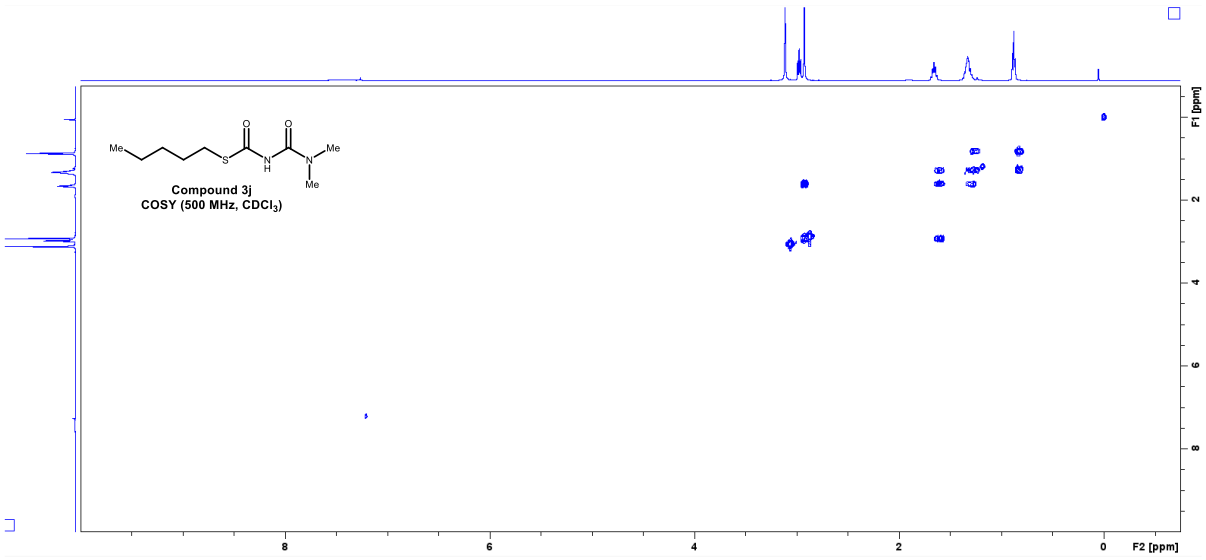
^{13}C NMR (126 MHz, $CDCl_3$)

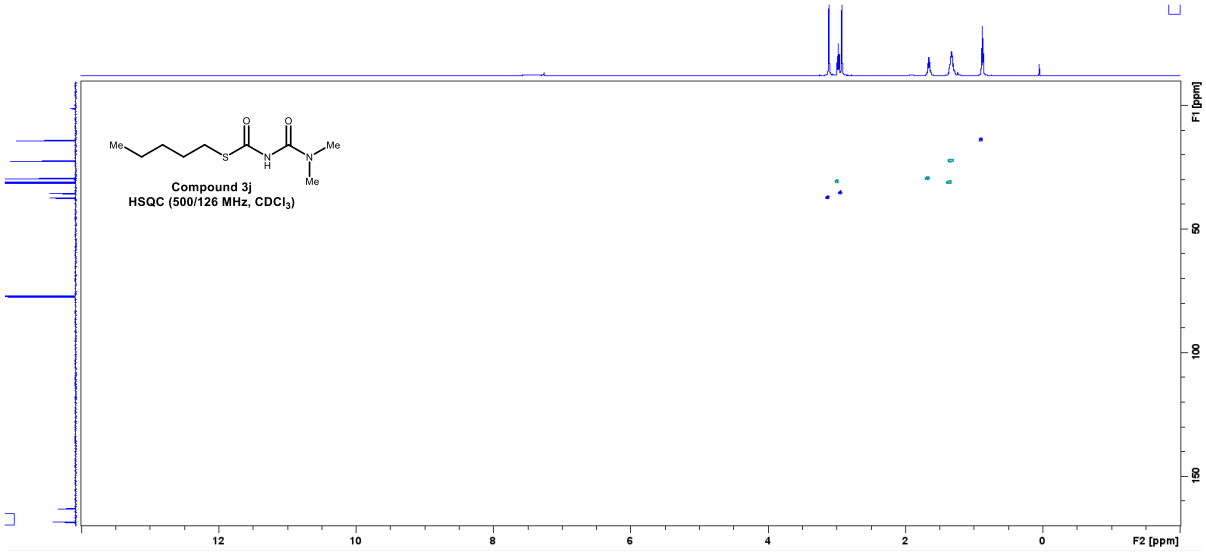


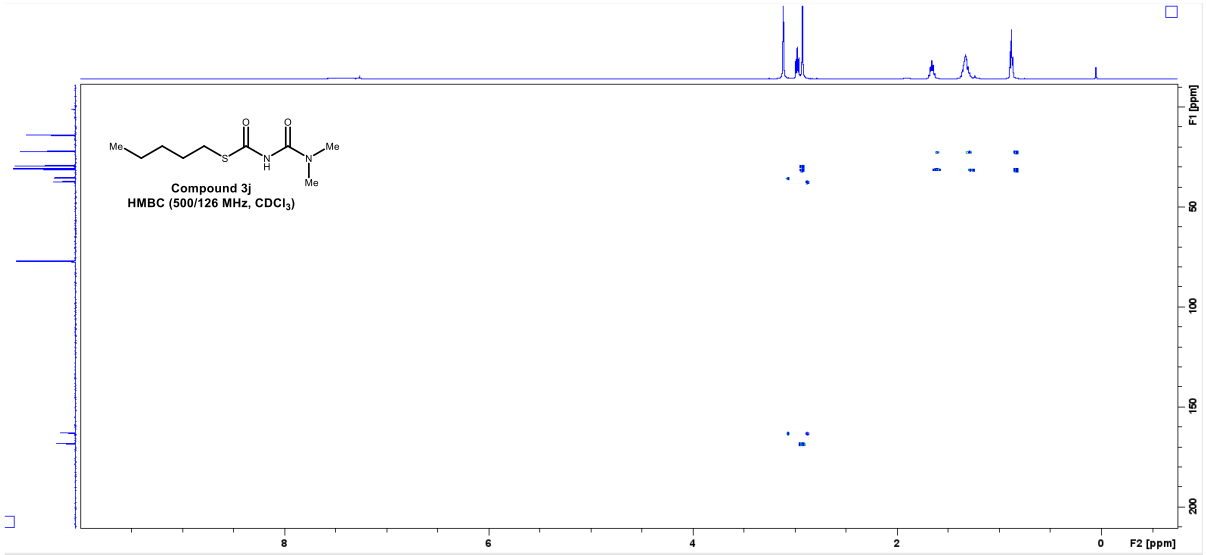
Compound 3j

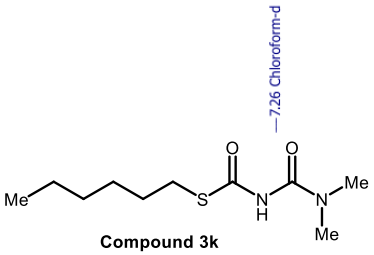
^{1}H NMR (500 MHz, $CDCl_3$)


168.30
162.93
77.41
77.16 Chloroform-d
76.91
37.28
35.37
31.16
30.75
29.45
22.31
14.00
Me
S
O
N
H
O
N
Me
Me
Compound 3j
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Me
S
O
N
H
O
N
Me
Me
Compound 3j
COSY (500 MHz, CDCl3)
F1 [ppm]
F2 [ppm]

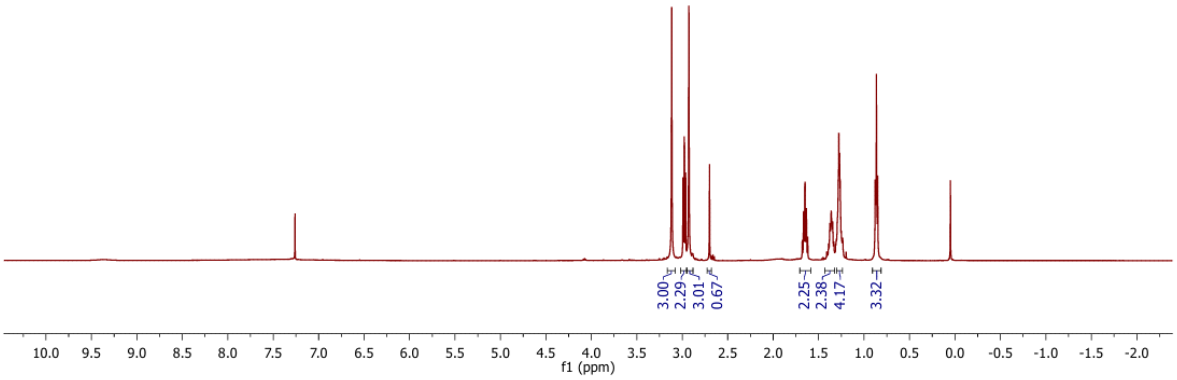

Me
S
O
N
H
O
N
Me
Me
Compound 3j
HSQC (500/126 MHz, CDCl3)
F1 [ppm]
50
100
150
12
10
8
6
4
2
0
F2 [ppm]

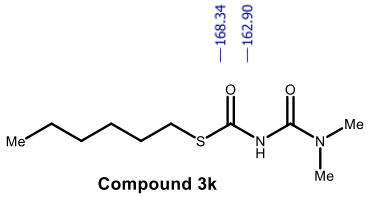

Me
S
O
N
H
O
N
Me
Me
Compound 3j
HMBC (500/126 MHz, CDCl3)
F1 [ppm]
50
100
150
200
8
6
4
2
0
F2 [ppm]



Compound 3k

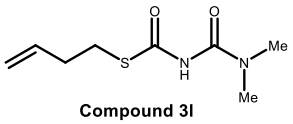
^{1}H NMR (500 MHz, $CDCl_3$)





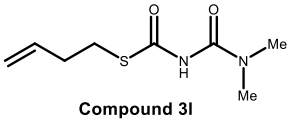
Compound 3k

^{13}C NMR (126 MHz, $CDCl_3$)



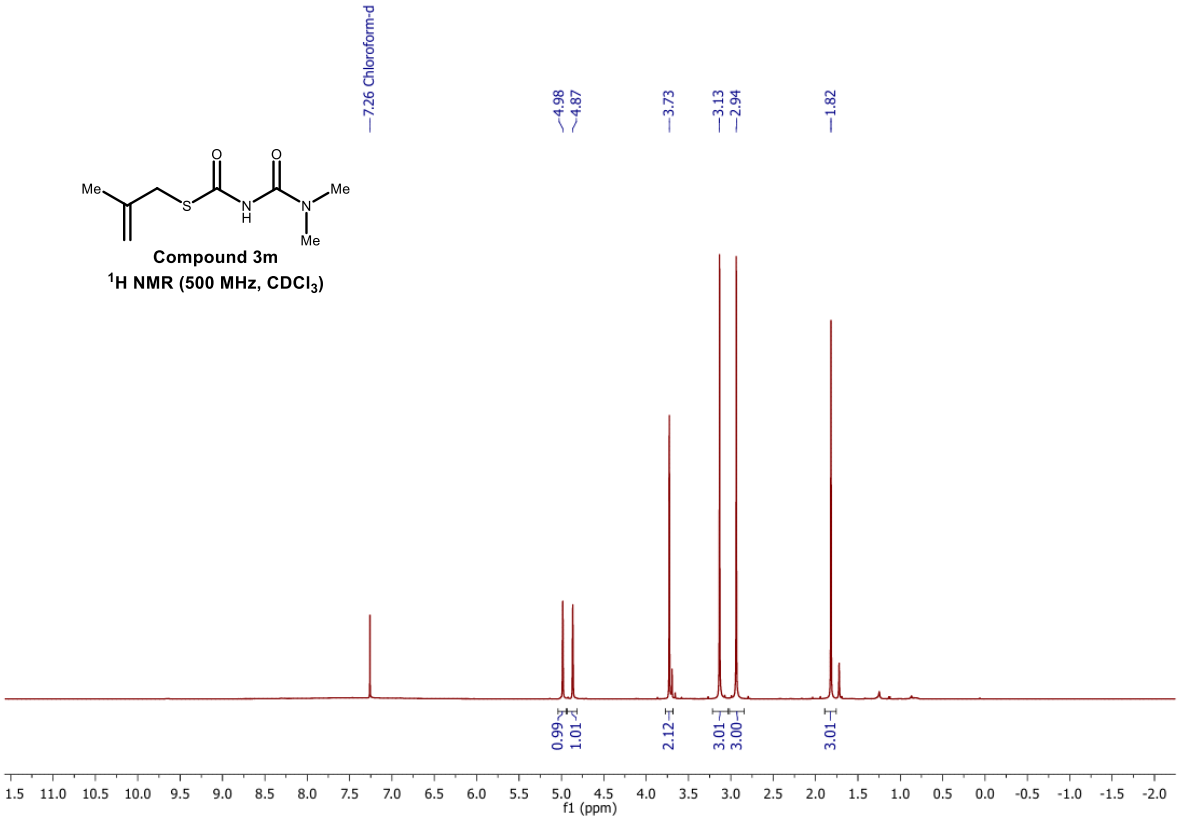
Compound 3l

^{1}H NMR (500 MHz, $CDCl_3$)



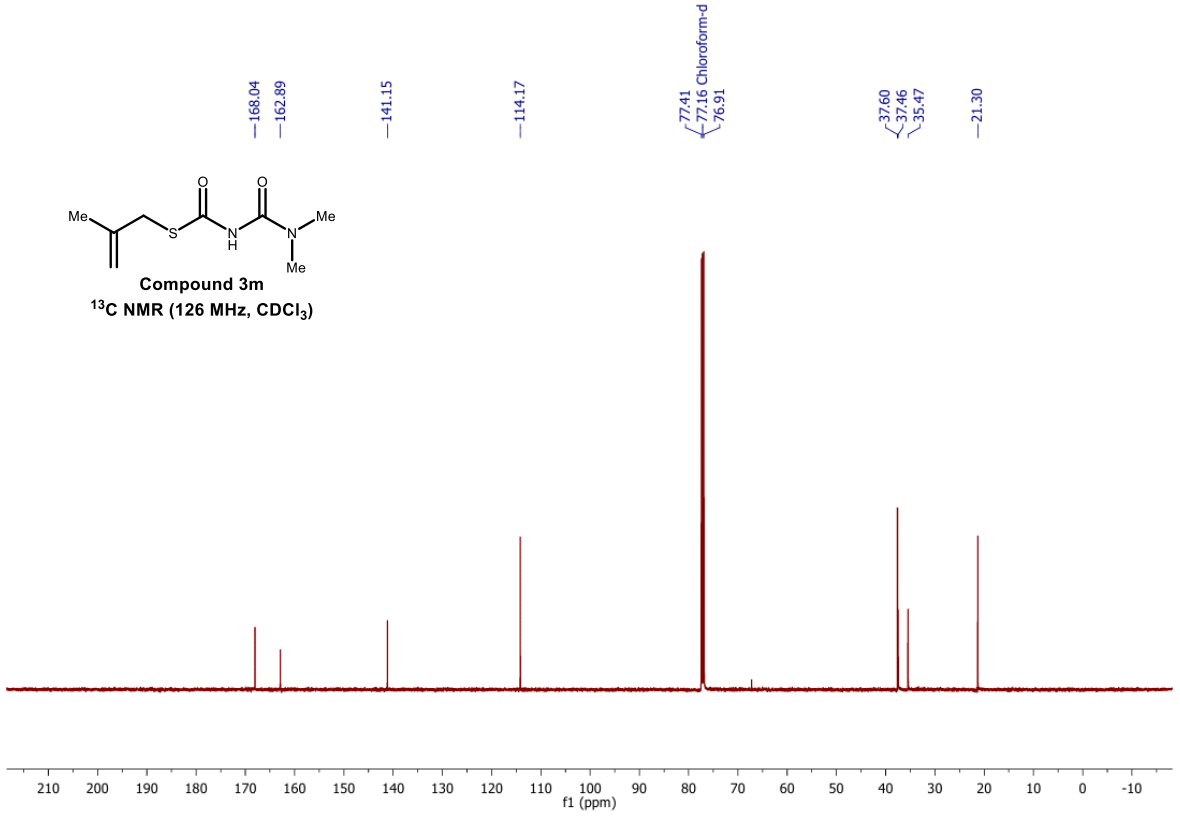
Compound 3l

^{13}C NMR (126 MHz, $CDCl_3$)



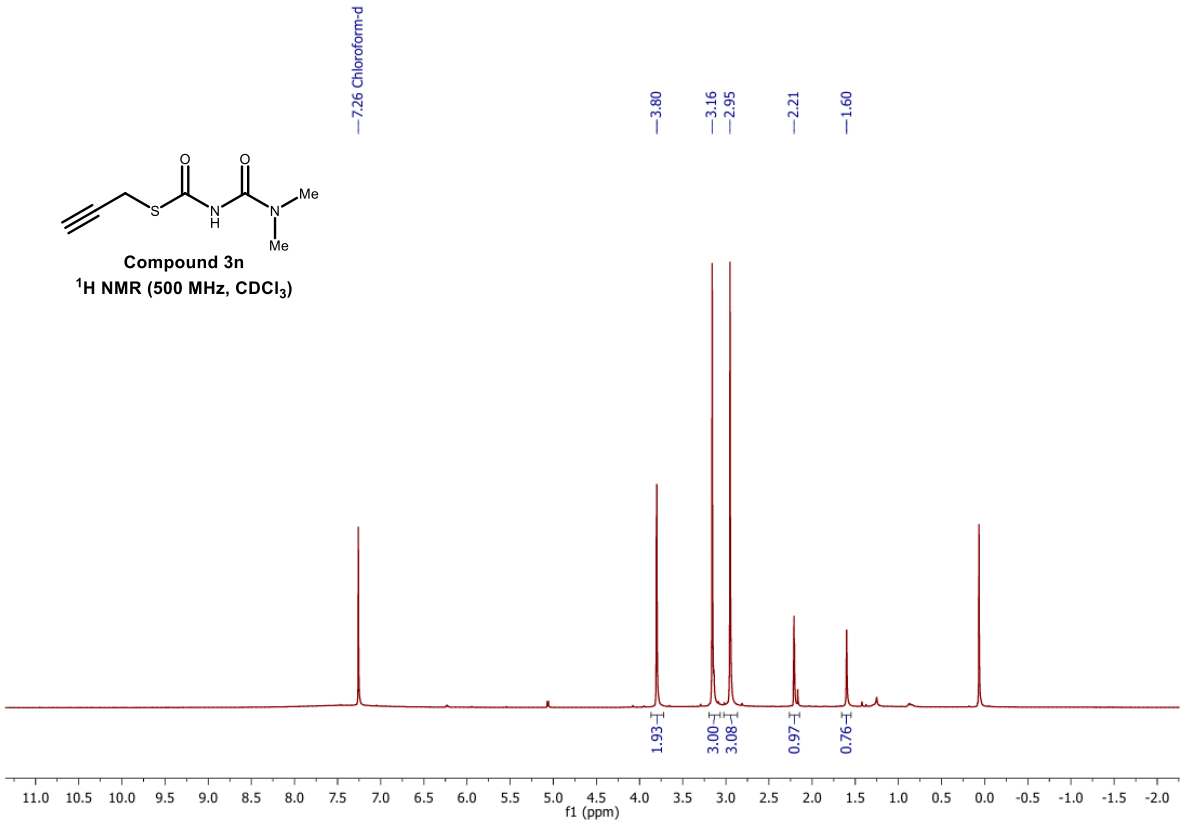
Compound 3m

^{1}H NMR (500 MHz, $CDCl_3$)



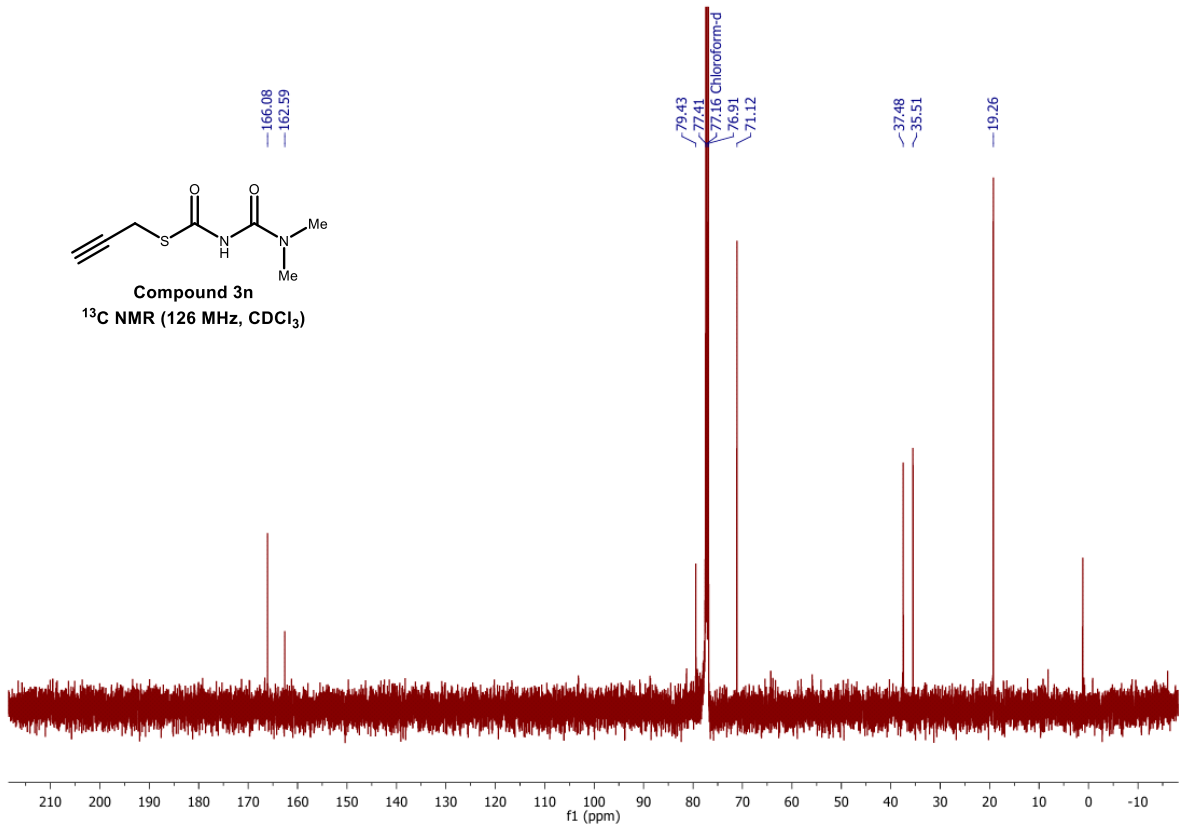
Compound 3m

^{13}C NMR (126 MHz, $CDCl_3$)



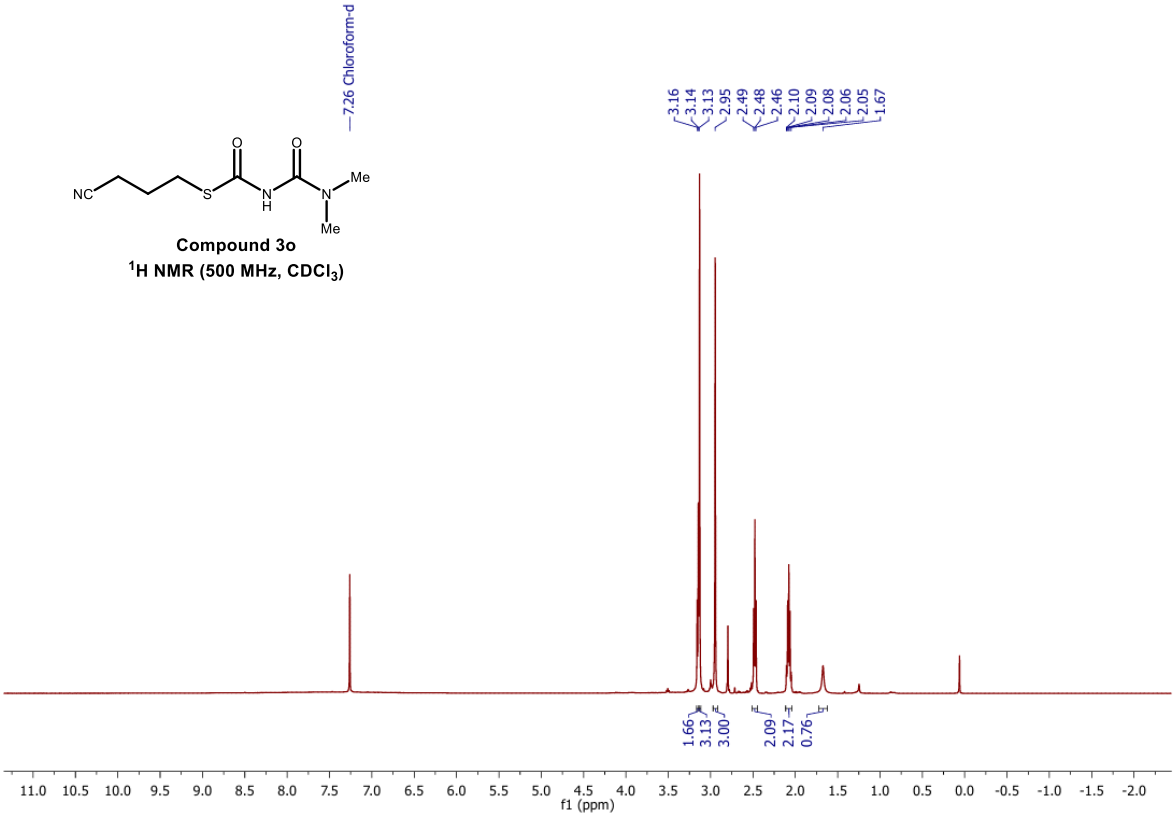
Compound 3n

^{1}H NMR (500 MHz, $CDCl_3$)



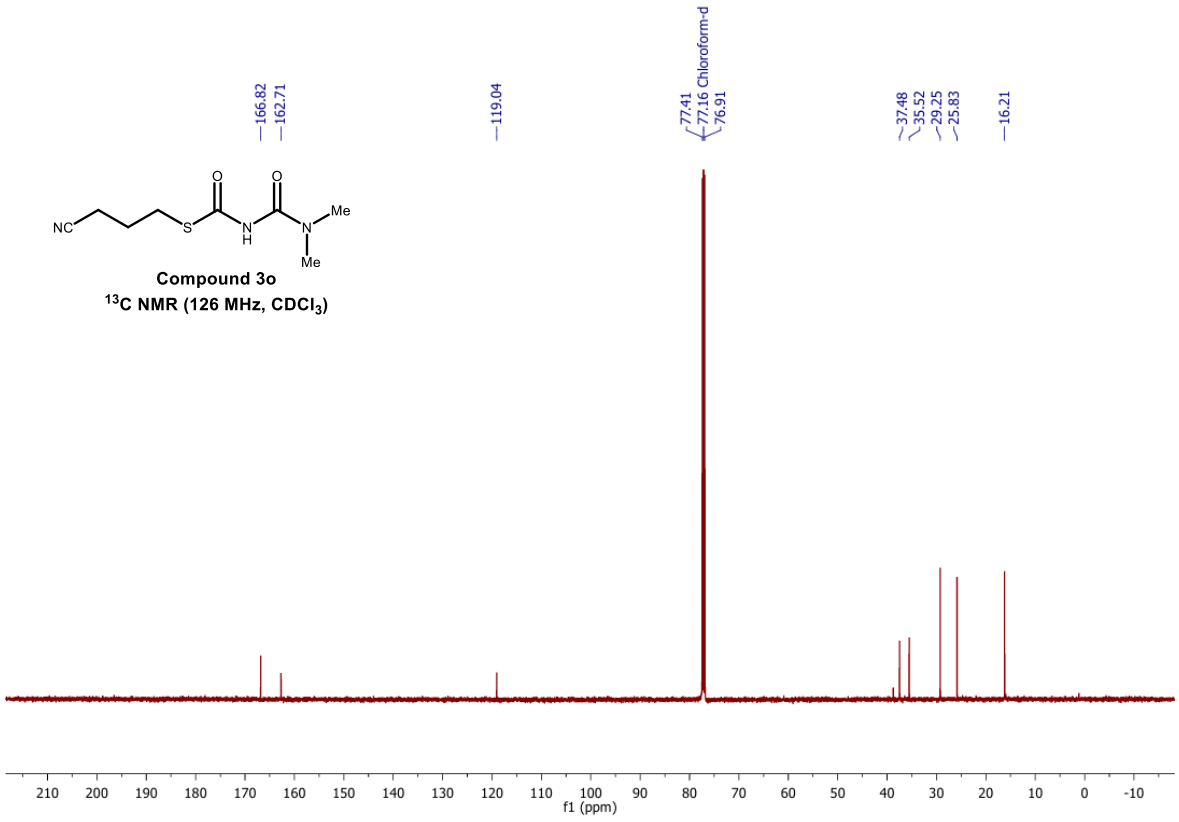
Compound 3n

^{13}C NMR (126 MHz, $CDCl_3$)



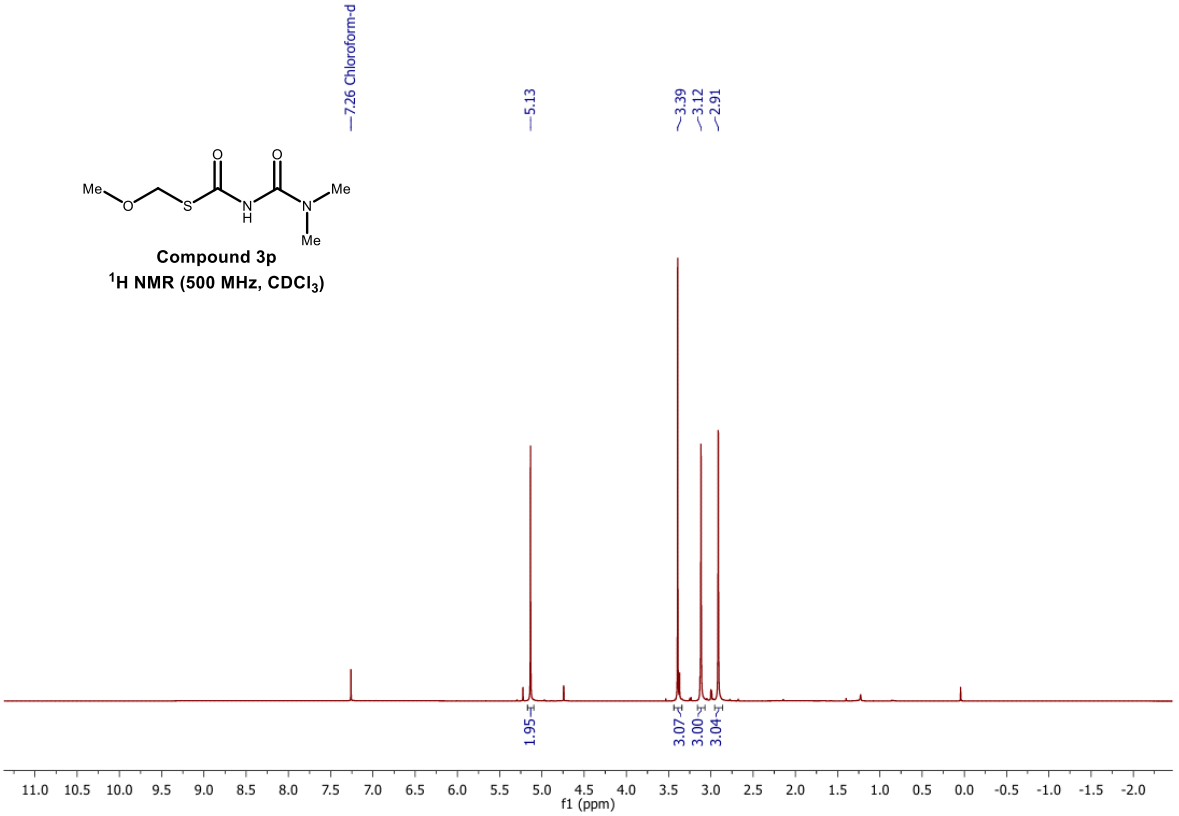
Compound 3o

^{1}H NMR (500 MHz, $CDCl_3$)



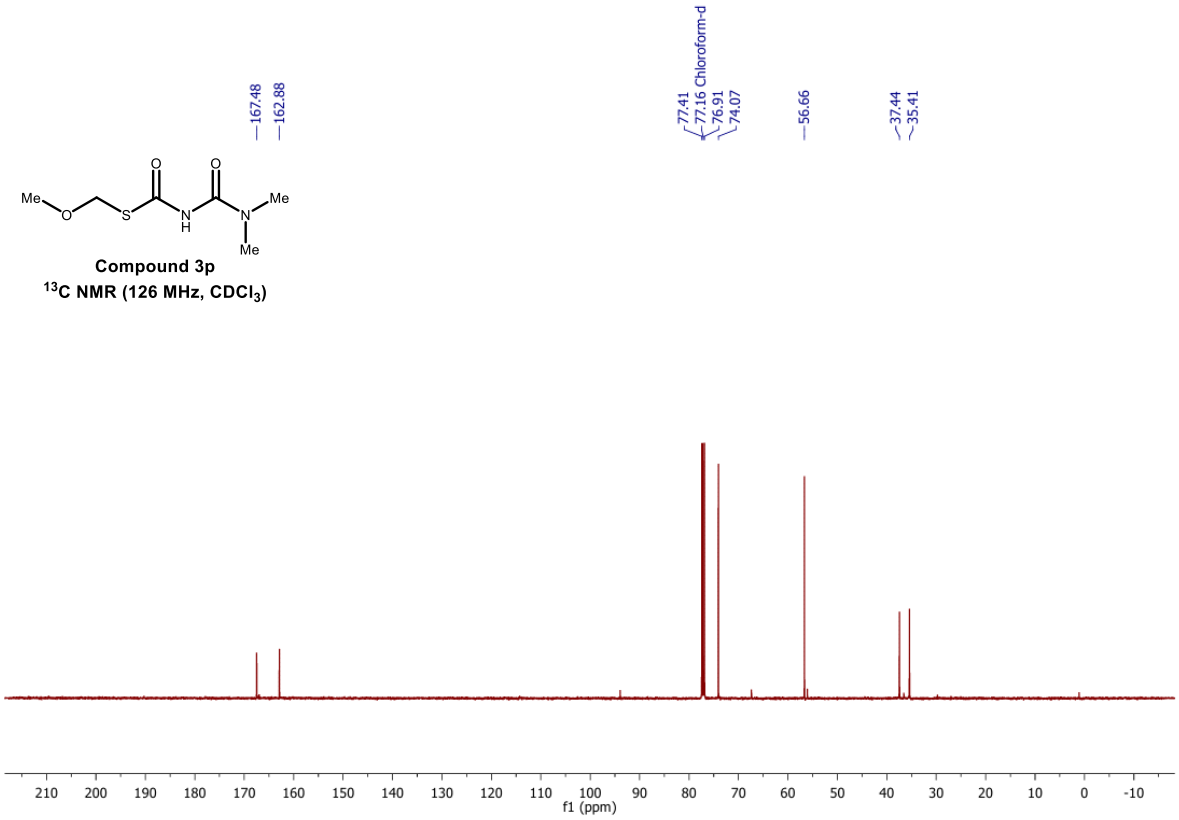
Compound 3o

^{13}C NMR (126 MHz, $CDCl_3$)



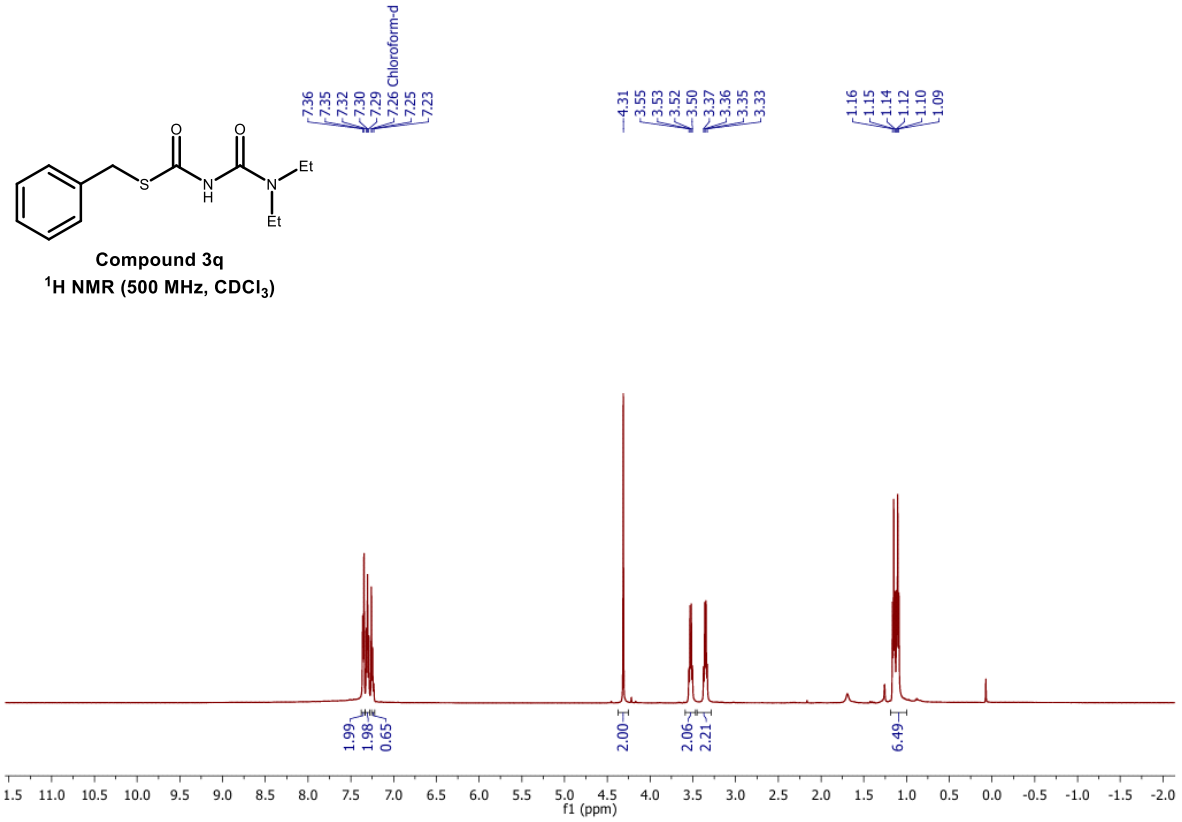
Compound 3p

^{1}H NMR (500 MHz, $CDCl_3$)

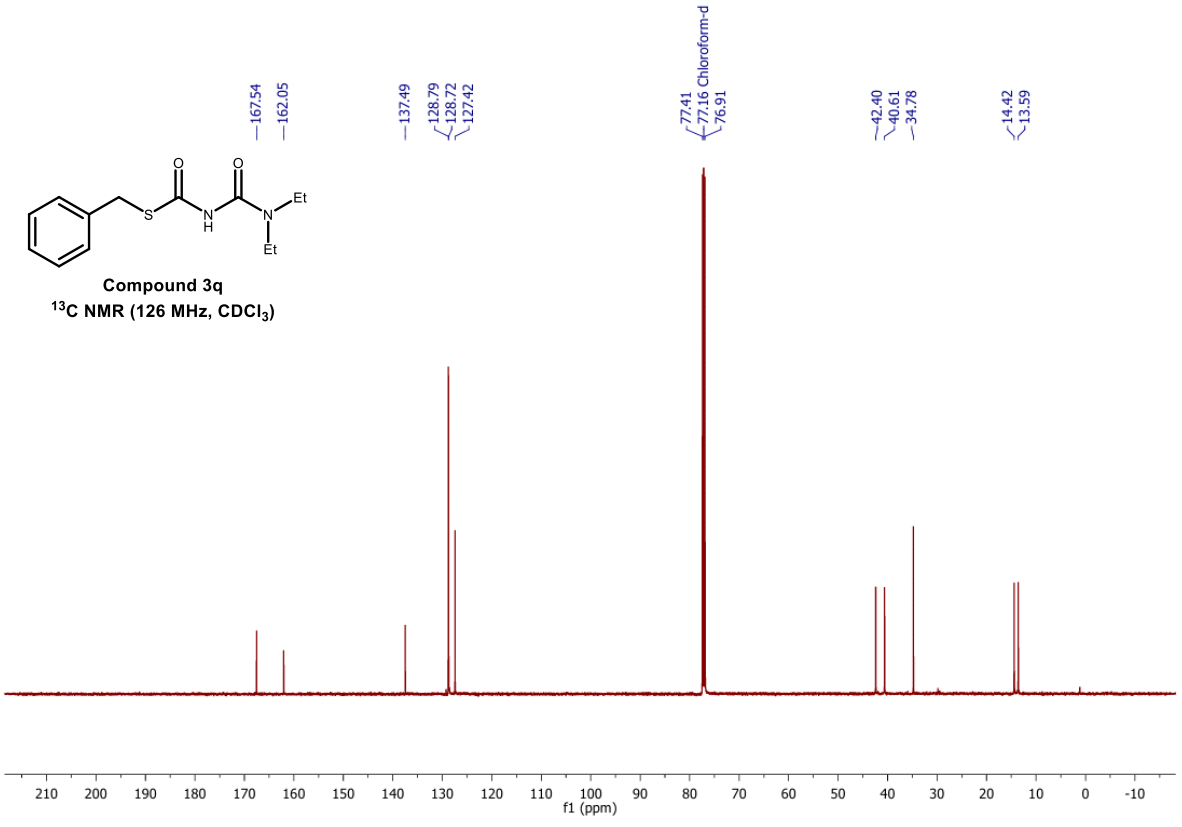


Compound 3p

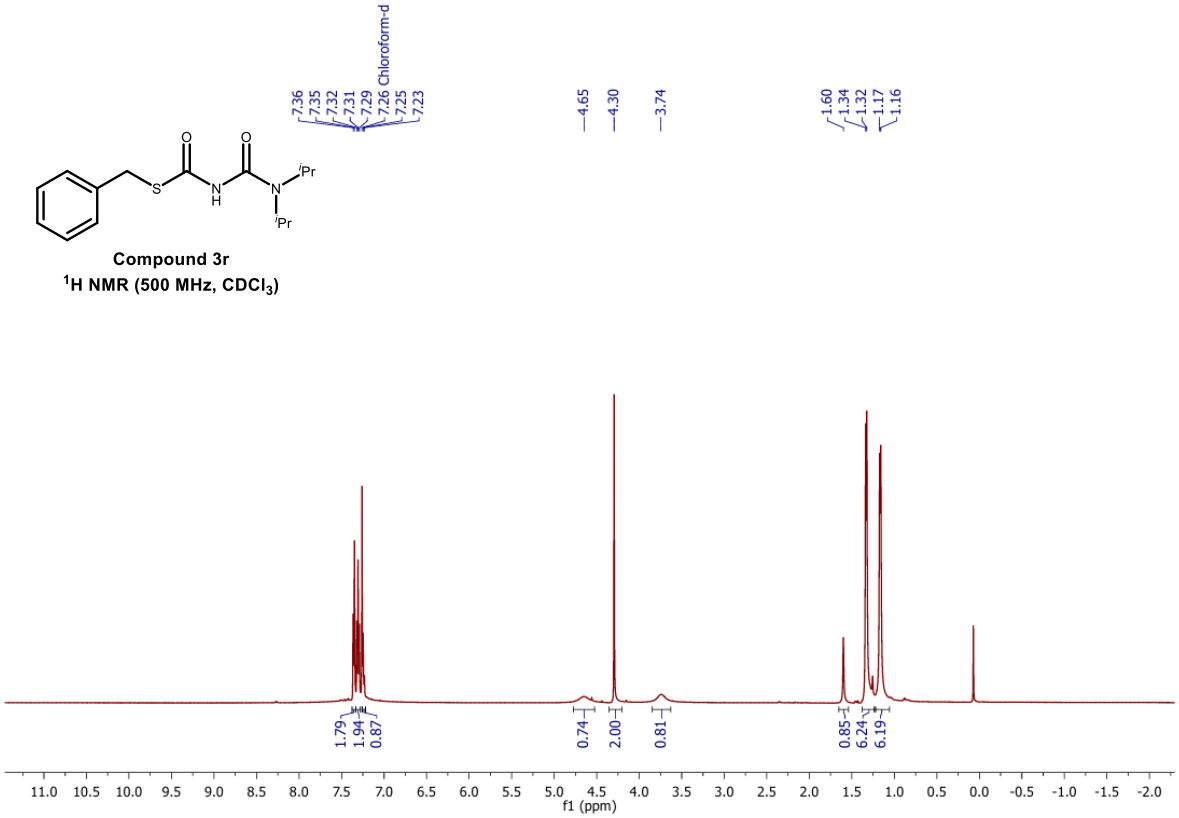
^{13}C NMR (126 MHz, $CDCl_3$)



Compound 3q
^{1}H NMR (500 MHz, $CDCl_3$)

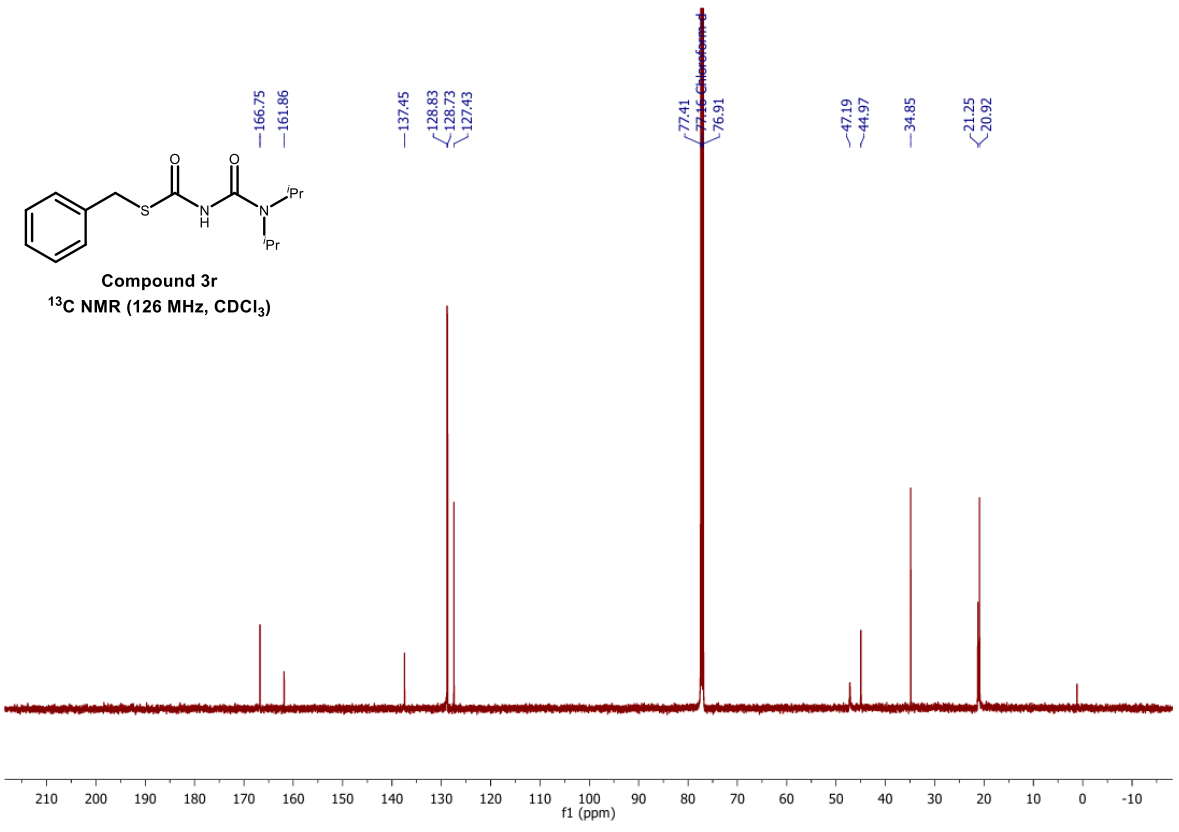


Compound 3q
^{13}C NMR (126 MHz, $CDCl_3$)



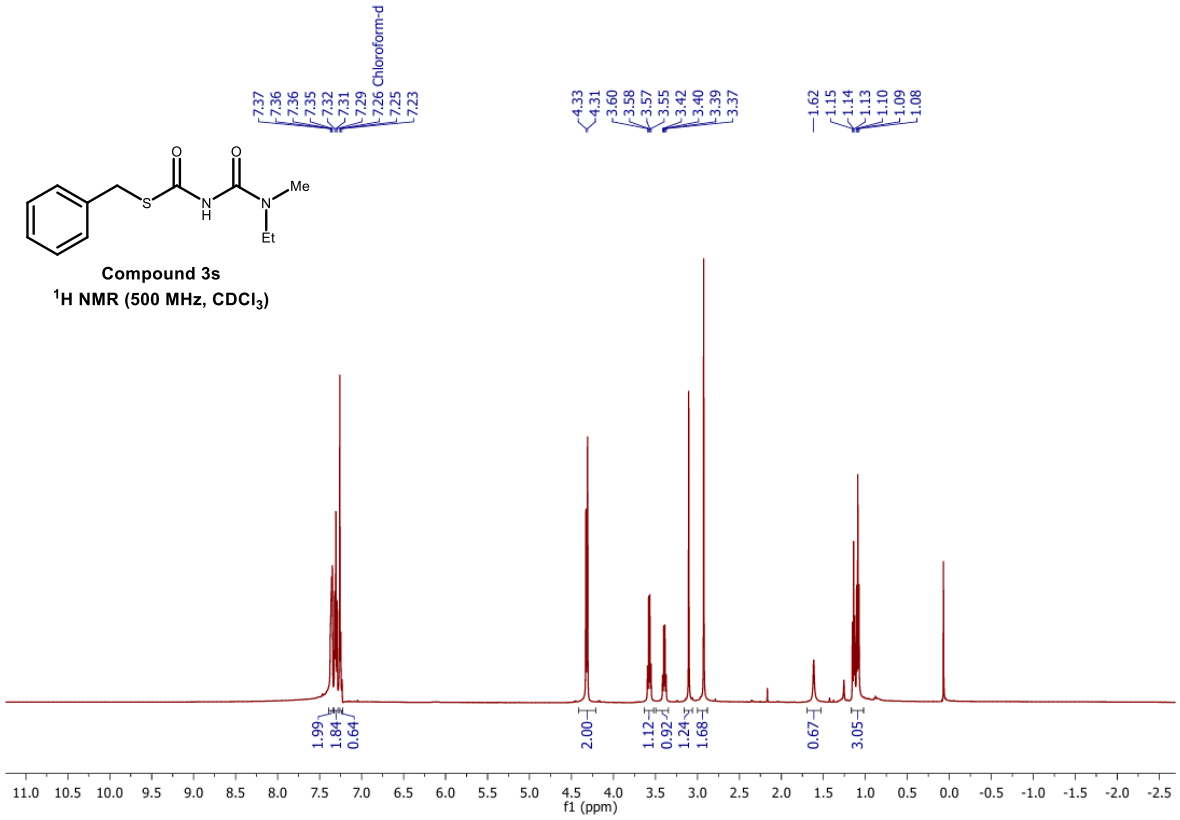
Compound 3r

^{1}H NMR (500 MHz, $CDCl_3$)



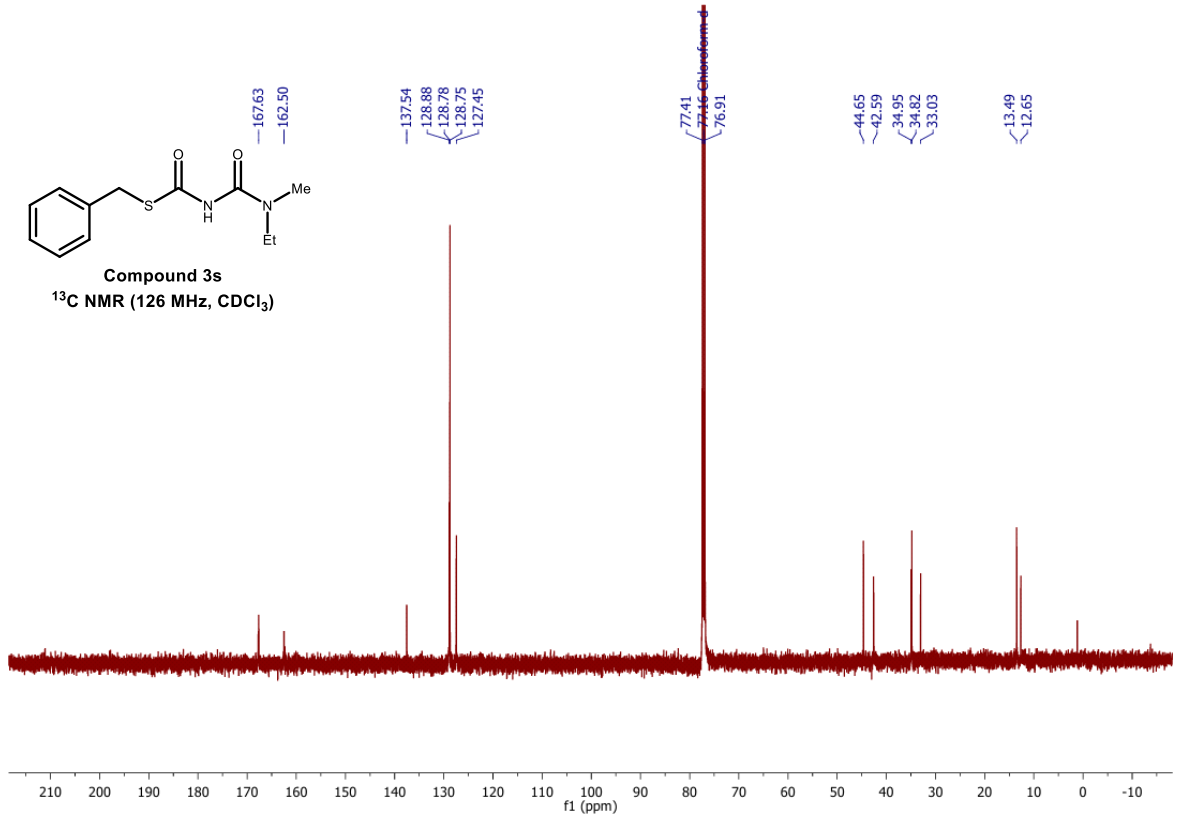
Compound 3r

^{13}C NMR (126 MHz, $CDCl_3$)



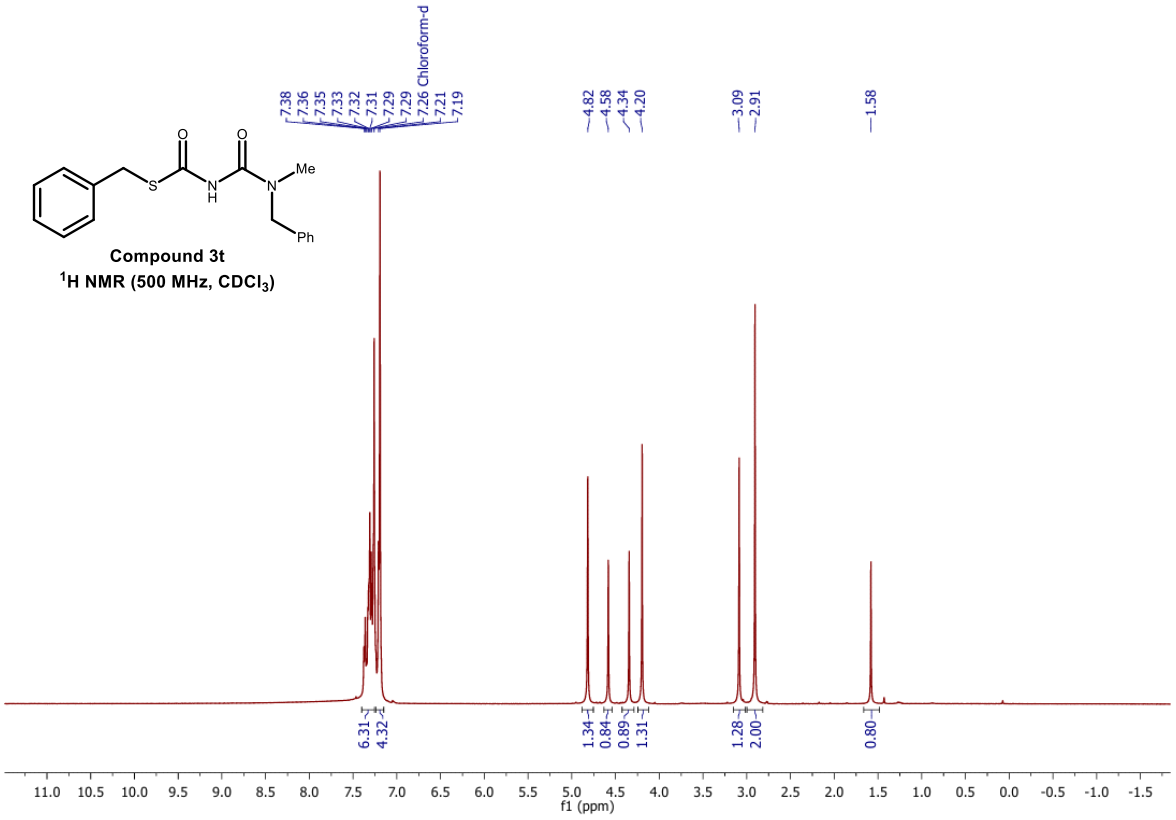
Compound 3s

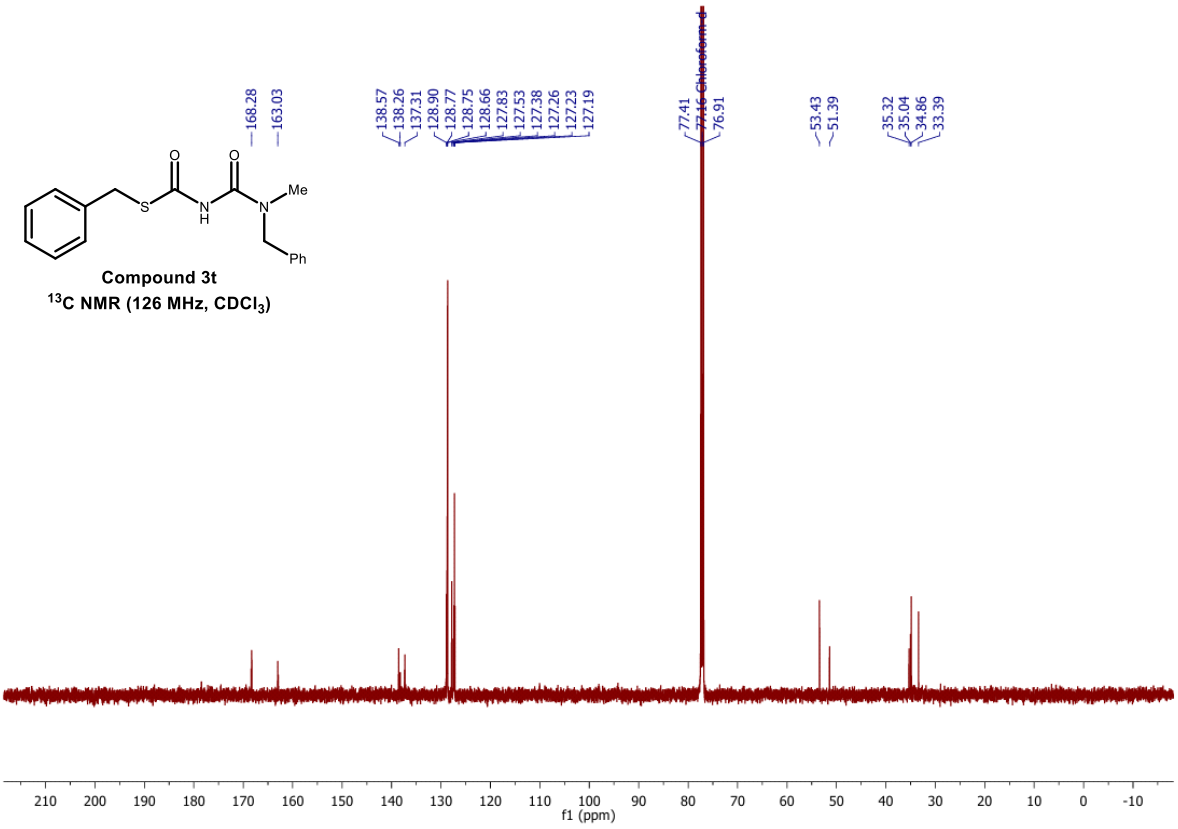
^{1}H NMR (500 MHz, $CDCl_3$)

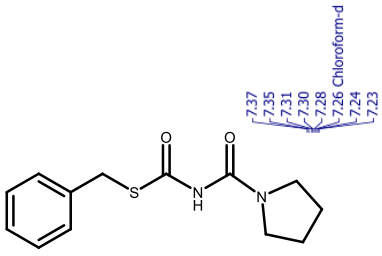


Compound 3s

^{13}C NMR (126 MHz, $CDCl_3$)

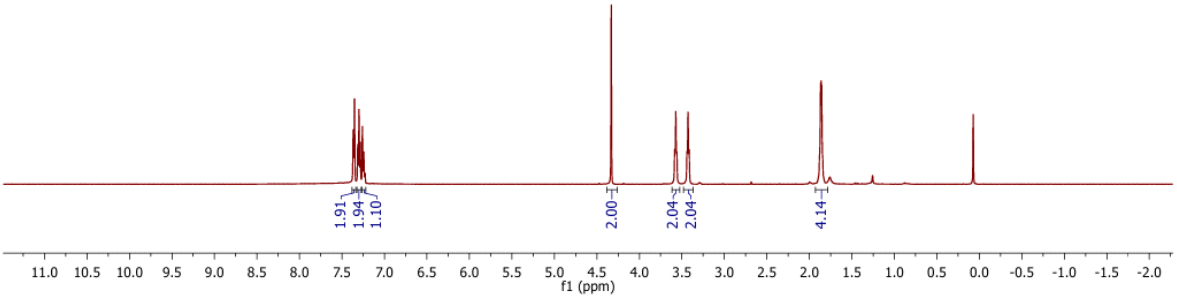

Compound 3t
^{1}H NMR (500 MHz, CDCl$_3$)
7.38
7.36
7.35
7.33
7.32
7.31
7.29
7.29
7.26 Chloroform-d
7.21
7.19
4.82
4.58
4.34
4.20
3.09
2.91
1.58
6.31
4.32
1.34
0.84
0.89
1.31
1.28
2.00
0.80
f1 (ppm)

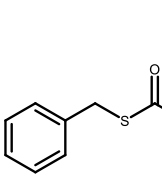

Compound 3t
^{13}C NMR (126 MHz, CDCl$_3$)
168.28
163.03
138.57
138.26
137.31
128.90
128.77
128.75
128.66
127.83
127.53
127.38
127.26
127.23
127.19
77.41
77.16 Chloroform-d
76.91
53.43
51.39
35.32
35.04
34.86
33.39
f1 (ppm)



Compound 3u

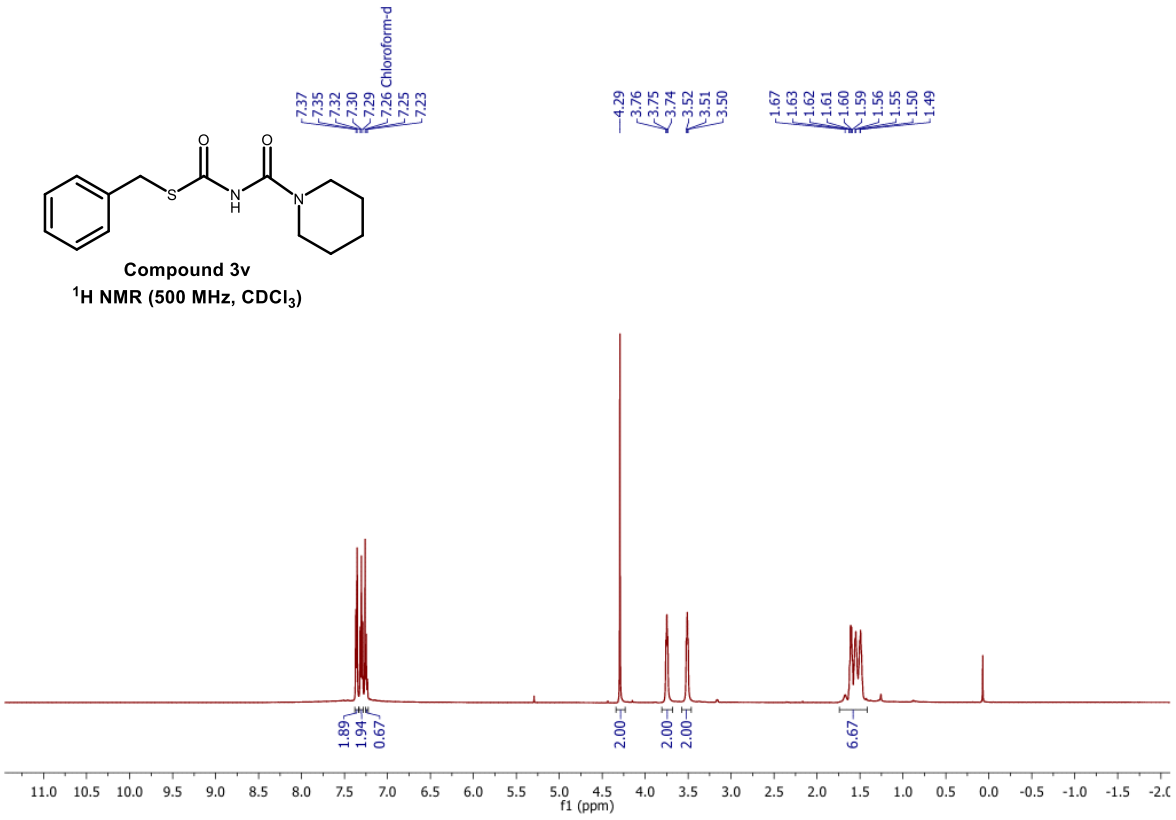
^{1}H NMR (500 MHz, $CDCl_3$)





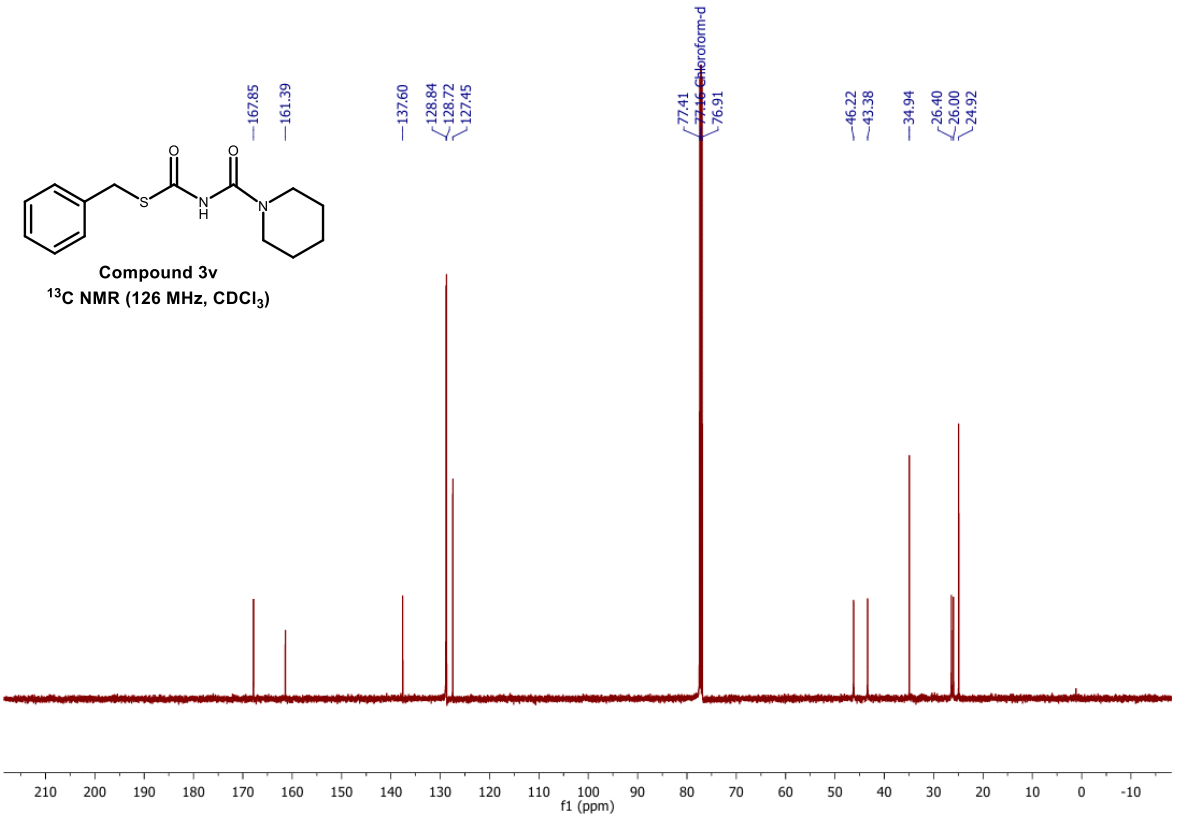
Compound 3u

^{13}C NMR (126 MHz, $CDCl_3$)



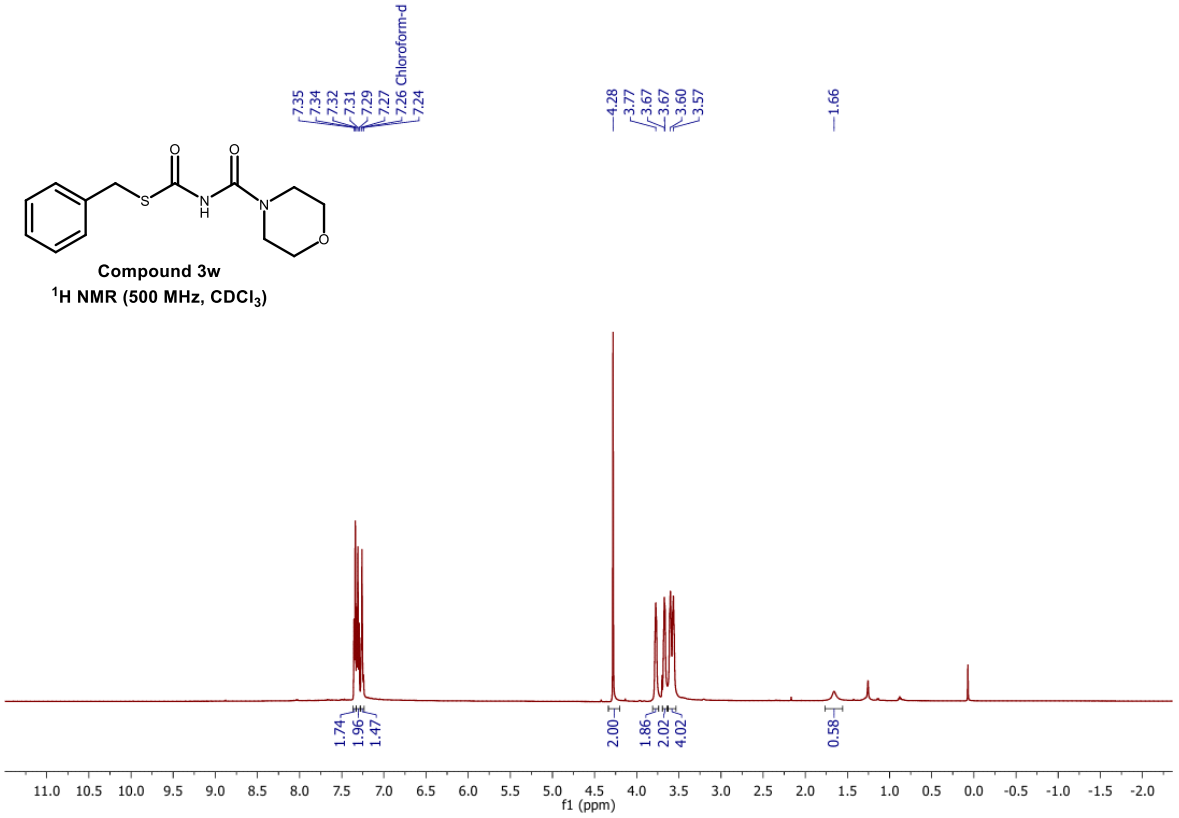
Compound 3v

^{1}H NMR (500 MHz, $CDCl_3$)



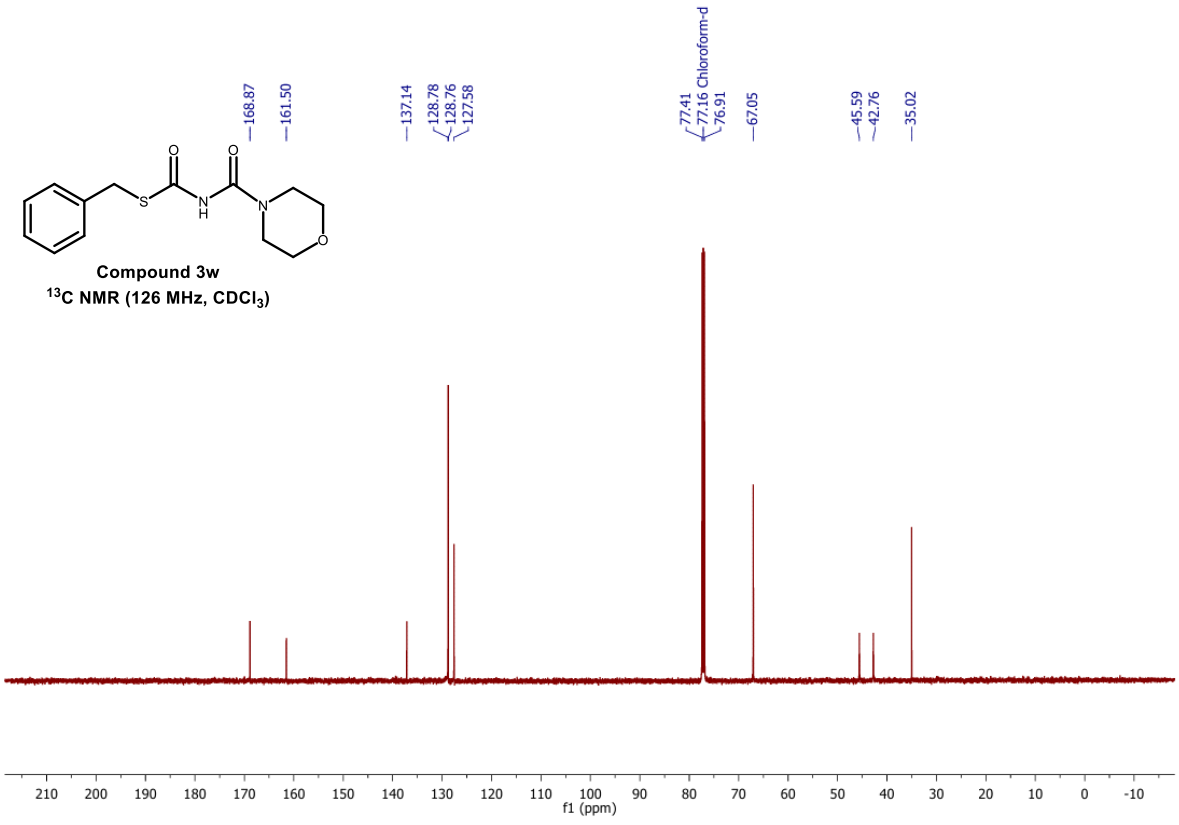
Compound 3v

^{13}C NMR (126 MHz, $CDCl_3$)



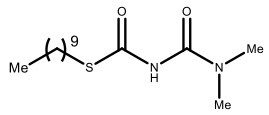
Compound 3w

^{1}H NMR (500 MHz, $CDCl_3$)



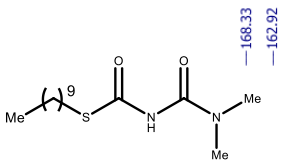
Compound 3w

^{13}C NMR (126 MHz, $CDCl_3$)



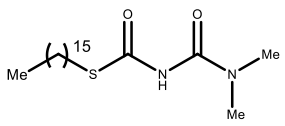
Compound 3x

^{1}H NMR (500 MHz, $CDCl_3$)



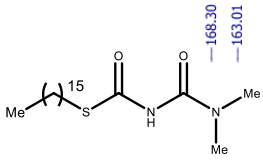
Compound 3x

^{13}C NMR (126 MHz, $CDCl_3$)



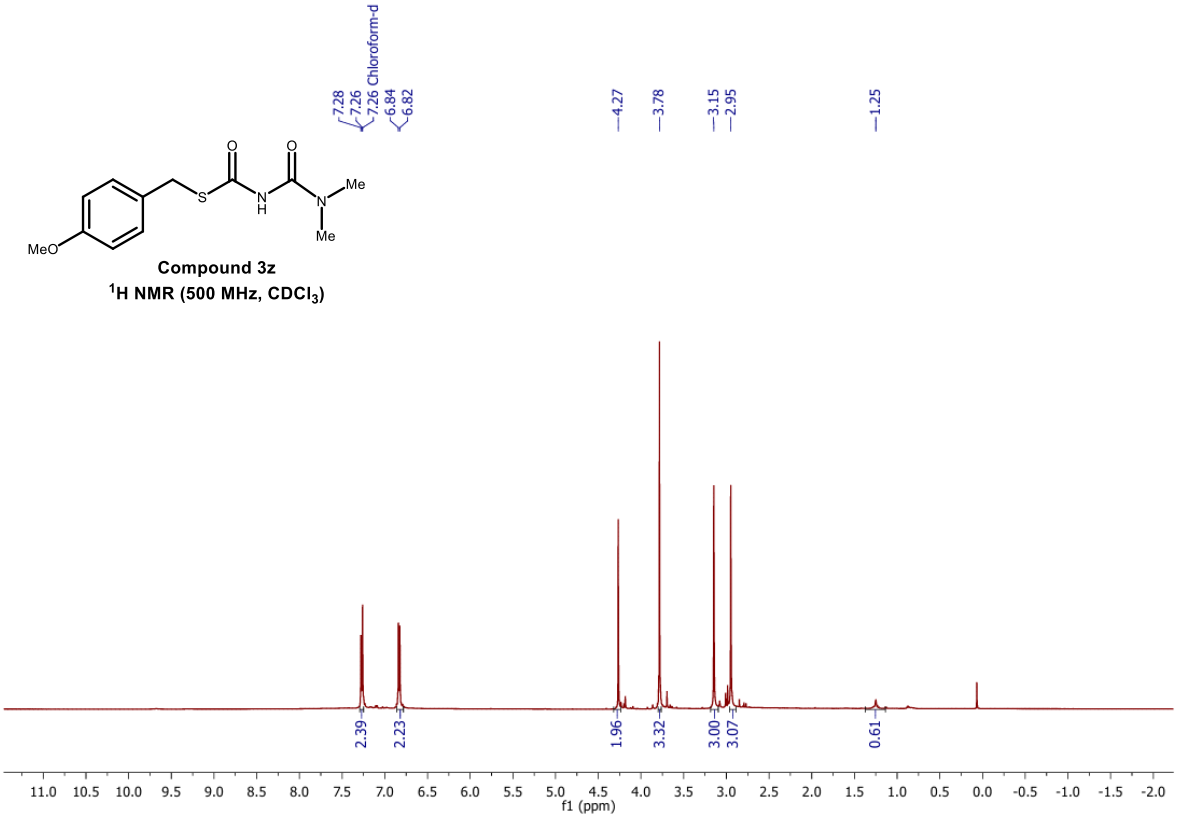
Compound 3y

^{1}H NMR (500 MHz, $CDCl_3$)



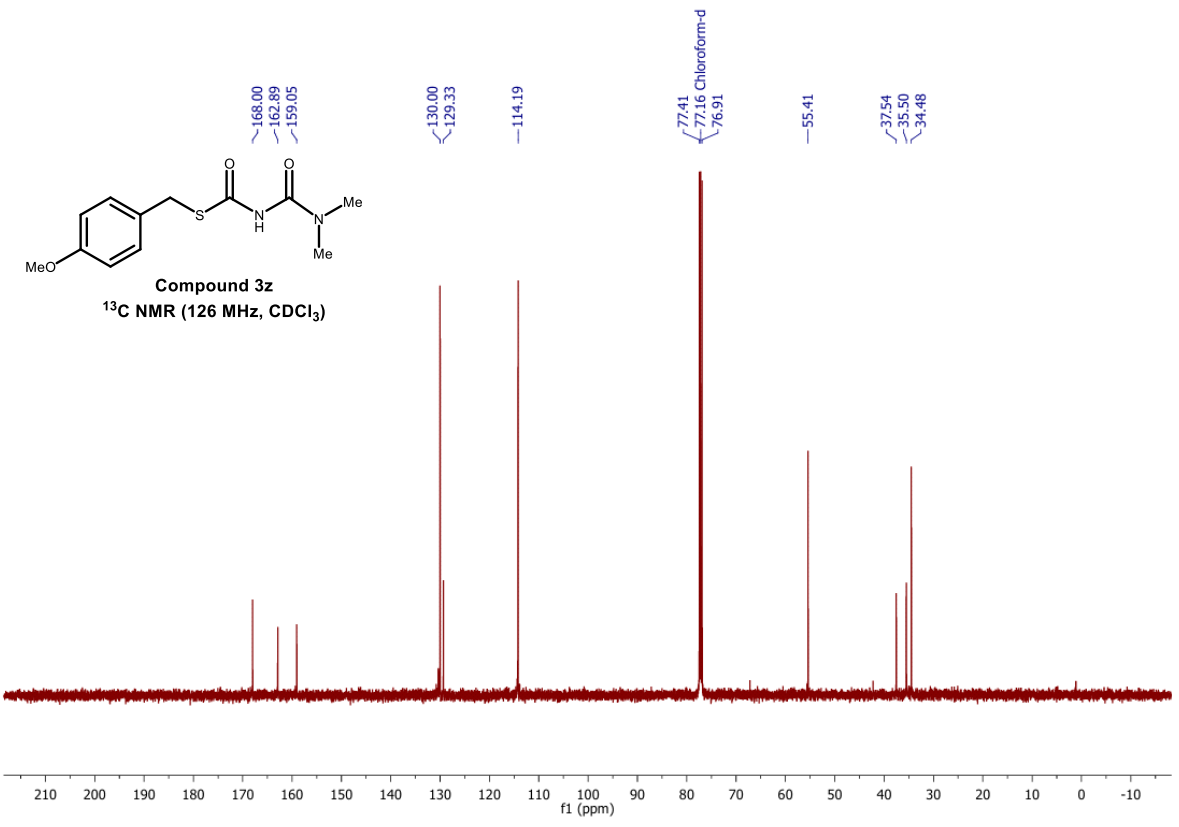
Compound 3y

^{13}C NMR (126 MHz, $CDCl_3$)



Compound 3z

^{1}H NMR (500 MHz, $CDCl_3$)



Compound 3z

^{13}C NMR (126 MHz, $CDCl_3$)