Supporting Information

Photocatalytic Carbamoylation to Access Thiocarbonyl Amino Acid/Peptide Derivatives in Sustainable Solvent

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1. General Information

1.1 Materials and instruments

All commercially available reagents were used directly without further purification. All reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography using 200-300 mesh silica gel as the stationary phase. All the ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on JEOL 400M spectrometers. All NMR spectra were recorded in $CDCl_3$ at room temperature (26 ± 2 °C). Proton chemical shifts δ were given in ppm using TMS as the internal standard. High-resolution mass spectra (HRMS) were obtained with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique.

1.2 The spectrum of our lamp and the visible-light irradiation instrument

The photochemical reaction was carried out under visible light irradiation by a blue LED at room temperature. RLH-18CU 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 15 W blue LEDs were equipped in this Photo reactor. The blue LED's energy peak wavelength is 460 nm, the peak width at half-width is 20.6 nm, and lirradiance@15 W. The reaction vessel is a borosilicate glass tube 1.5 cm from the lamp, and no filter is applied.

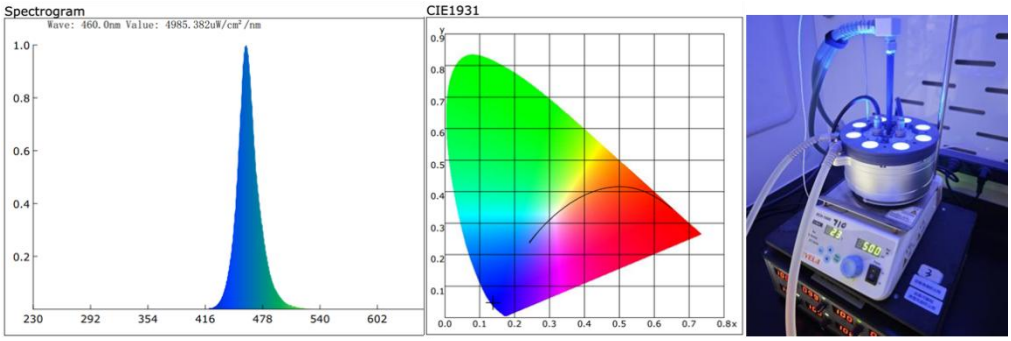
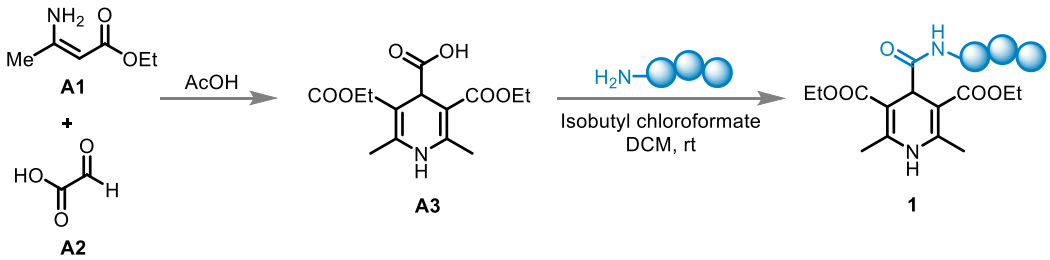


Figure S1 The spectrum of our lamp (blue LED) and the visible-light irradiation instrument.

2. Experimental procedures

2.1 General experimental procedure for preparation of substrates and target products

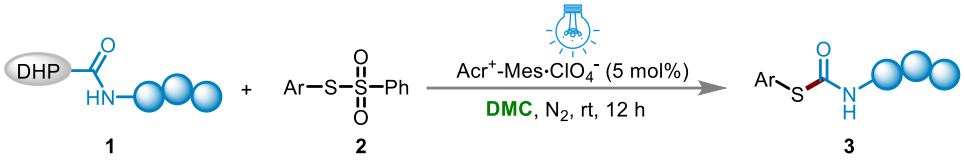


Scheme S1. General experimental procedures for substrates **1**.

Following a method described in the literature,[1] a solution of ethyl-3-aminocrotonate **A1** (10 mmol, 2.0 equiv.) in 10 mL of glacial acetic acid was mixed in a 50 mL flask. Then, 50% glyoxylic acid **A2** in water (5 mmol, 1 equiv) was added to the reaction system at 0 °C. The reaction mixture rapidly became yellow and a precipitate deposited. After the evolution of heat had ceased, the reaction mixture was left stirring overnight at room temperature. The solid was collected by filtration and washed with acetic acid and water. The solids were dried overnight under reduced pressure to obtain the **A3** as a white powder.

In a round-bottom flask, the **A3** (3 mmol, 1 equiv.) was suspended in DCM (0.2 M) followed by the addition of triethylamine (1.2 equiv. or 2 equiv. when amine hydrochloride salts are used). The resulting yellow solution was cooled down to 0 °C and isobutyl chloroformate (1.2 equiv.) was then added dropwise. After 10 minutes, the mixture was allowed to warm up to ambient temperature and stirred for 20 minutes. Next, the primary amine (1.2-1.5 equiv.) was added and the resulting solution stirred at ambient temperature overnight. After completion of the reaction (as judged by TLC, petroleum ether/EtOAc 1:1), the solution was diluted with DCM, washed with sat. $NaHCO_3$ and water. The organic layers were combined, dried (Na_2SO_4) and concentrated. The remaining residue was purified by flash column chromatography to give the desired products **1**.

2.2 Synthesis of the products 3a-3az



Scheme S2. Synthesis of the products **3a-3az**

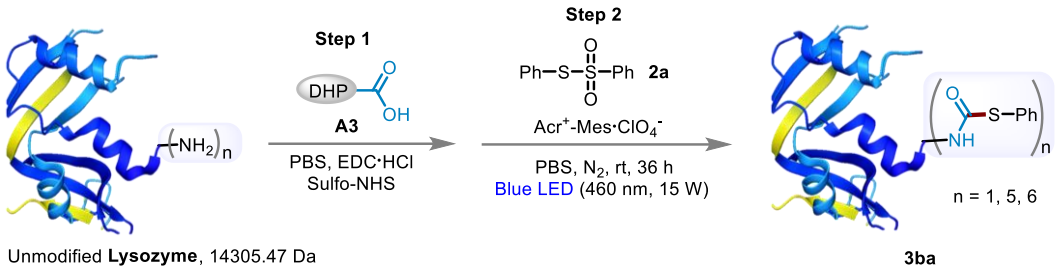
The mixture of **1** (0.3 mmol, 1.5 equiv.), **2** (0.2 mmol, 1 equiv.), Acr^+-$Mes{\cdot}ClO_4^-$ (0.01 mmol, 4.12 mg), and DMC (2.5 mL) were sequentially added into a 25 mL Schlenk tube. Then the reaction tube was exposed to the irradiation of a 15 W blue LED at room temperature in an N_2 atmosphere for 12 h. After the reaction, the solvent was evaporated under vacuum, and all the crude products were purified by flash column chromatography using petroleum ether (PE) and ethyl acetate (EA) as the eluent to afford the target products **3a-3az**. (**3k** and **3l** reaction for 24 h)

2.3 Applications in protein

ESI-MS was performed on a linear quadrupole ion trap detector mass spectrometer (LC/Q-TOF from Agilent).

Sequence of protein lysozyme:

KVFGRCELAAAMKRHGLDNYRGYSLGNWVCAAKFESNFNTQATNRNTDGSTDYGILQINSR
WWCNDGRTPGSRNLCNIPCSALLSSDITASVNCAKKIVSDGNGMNAWVAWRNRCKGTDVQA
WIRGCRL



Scheme S3. Applications in protein

A one-pot, two-step procedure was employed, obviating the need to isolate intermediates.

Step 1: In a 25 mL Schlenk tube, reagent **A3** (0.2 mmol, 100 equiv) was dispersed in 1 mL of PBS buffer and stirred at 0 °C. Subsequently, EDC·HCl (0.2 mmol, 100 equiv) and Sulfo-NHS (0.2 mmol, 100 equiv) were added to the reaction mixture, and stirring at 0 °C was maintained for 5 minutes. The protein (2 μmol, 1 equiv, dissolved in 5 mL PBS buffer) was then added dropwise to the reaction mixture at 0 °C. Upon completion of the addition, the reaction was allowed to proceed overnight at 4 °C. After completion, the reaction mixture was advanced directly to Step 2 without isolation of any intermediates.

Step 2: The activated protein from Step 1 was treated with **2a** (0.2 mmol, 100 equiv) and Acr^{+}-$Mes{\cdot}ClO_4^{-}$ (0.01 mmol, 20 equiv). The mixture was stirred under irradiation with a 15 W 460 nm blue LED under N_2 at room temperature for 36 h. The product (**3ba**) was characterized by high-resolution mass spectrometry. The results are illustrated in Figure S2 (n = 1: singly modified protein; n = 5: fivefold modified protein; n = 6: sixfold modified protein).

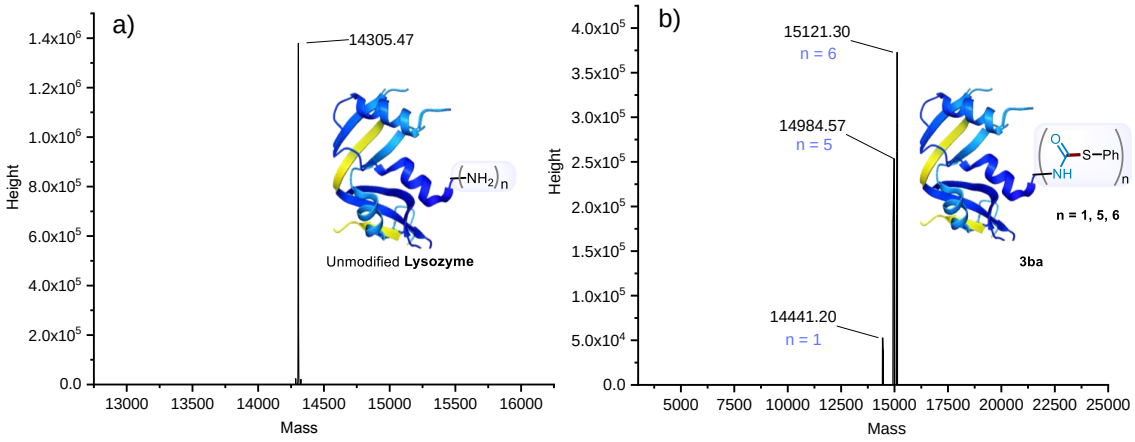


Figure S2. HRMS data analysis: a) Unmodified Lysozyme, b) The product of **3ba**

2.4 The gram-scale synthesis

Figure S3. The gram-scale synthesis of **3a**

The gram-scale synthesis of **3a**: **1a** (3 mmol, 1.5 equiv.), **2a** (2 mmol, 1 equiv.), Acr^{+}-Mes·ClO_4^{-} (5 mol%) and DMC (20 mL) were sequentially added into the reaction flask. and the reaction system was replaced with an N_2 atmosphere. The reaction system was reacted under blue LED (40 W, 456 nm) of Kessil PR160L irradiation for 23 h. The isolated yield of **3a** (82%, 0.81 g) was given.

2.5 Procedure for emission quenching experiments

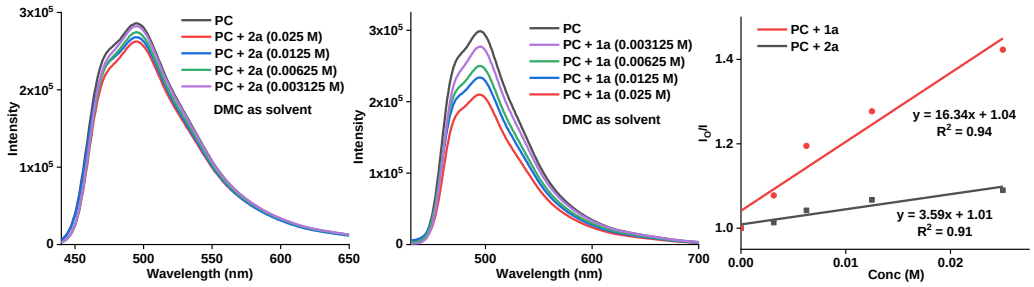


Figure S4. The Stern-Volmer fluorescence quenching of **1a** and **2a**.

Emission intensities were recorded using an F-4600 FL Spectrophotometer. First, the emission intensity of Acr^{+}-Mes·ClO_4^{-} solutions was observed at 500 nm. The solutions were irradiated at 494 nm (Maximum absorption wavelength of Acr^{+}-Mes·ClO_4^{-}) and fluorescence was measured from 400 nm to 750 nm. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of Acr^{+}-Mes·ClO_4^{-} with different concentrations of **1a** or **2a** in degassed anhydrous DMC in 10 mm path length quartz cuvette was collected. The emission spectra of a 5×10^{-5} M solution of Acr^{+}-Mes·ClO_4^{-} with various concentrations of **1a** or **2a** in degassed anhydrous DMC and the linear relationship between I_0/I and the increasing concentration of **1a** or **2a** (I_0 and I_n are the fluorescence intensities before and after increasing the concentration of **1a** or **2a**, respectively).

2.6 The cyclic voltammetry experiments

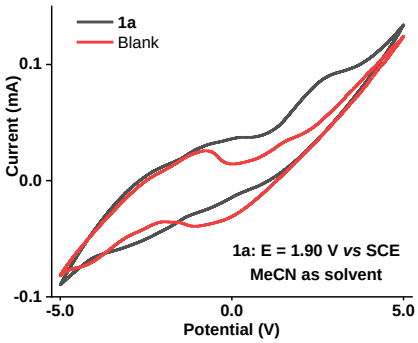


Figure S5. The cyclic voltammetry

Cyclic voltammetric investigations were performed on the CHI-660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) with the conventional three-electrode system. The electrodes are first polished with sandpaper in steps (3000 mesh - 2000 mesh - 1000 mesh); then with 1.0μm, 0.3μm, and 0.05μm alumina powder until the surface of the electrodes is mirror-like. Finally, the electrodes are washed with distilled water and ultrasonication. The solvent exhaust employs a nitrogen blast for 0.5 h. A glass carbon electrode was used as the working electrode; a saturated calomel electrode (SCE) and Pt column (Φ1 mm x 5 mm) were used as the reference electrode and counter electrode, respectively. The **1a** (0.06 M) were tested with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte, respectively. The scan direction was reversed, the starting point was 0 V (initial potential: 0 V), and the scan rate was 100 mV/s. The test temperature is room temperature. The measured oxidation potential was **1a** ($E^{ox}_{1/2}$ = 1.90 V *vs*. SCE).

2.7 HRMS data analysis

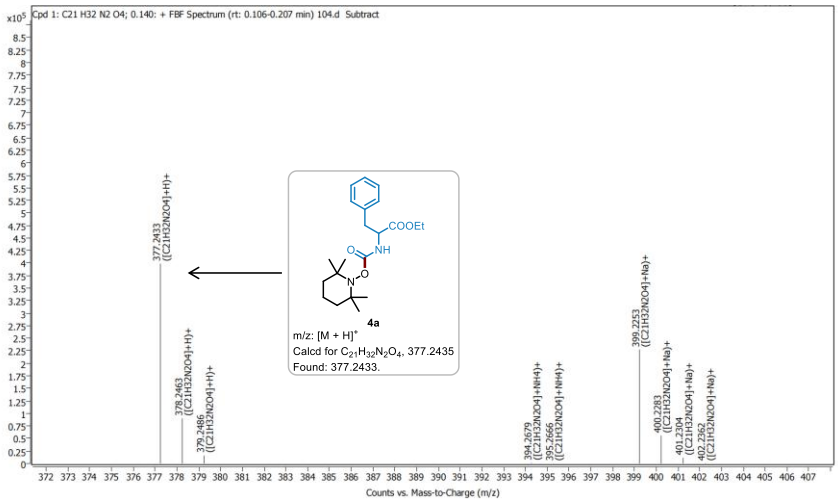


Figure S6a. HRMS data analysis of **4a**

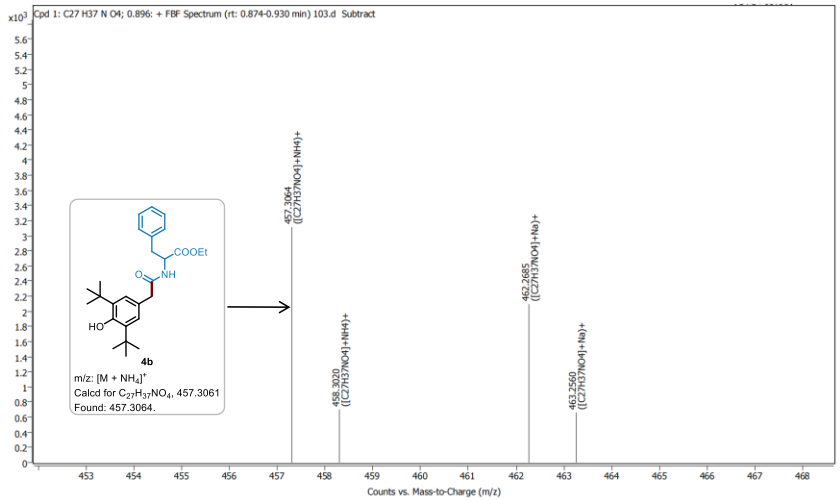


Figure S6b. HRMS data analysis of **4b**

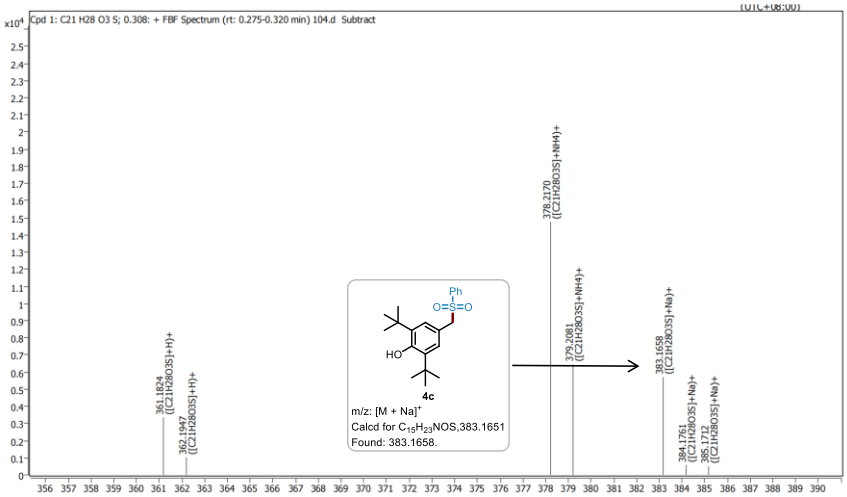
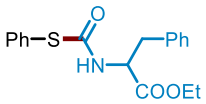


Figure S6c. HRMS data analysis of **4c**

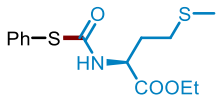
3. Characterization Data for Products

Ethyl ((phenylthio)carbonyl)phenylalaninate (3a)



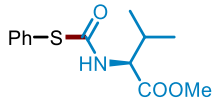
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3a**. White solid (64.5 mg, 98% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.50 (m, 2H), 7.42 – 7.36 (m, 3H), 7.27 – 7.24 (m, 3H), 7.02 – 7.00 (m, 2H), 5.82 (d, *J* = 7.3 Hz, 1H), 4.79 (q, *J* = 5.7 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.15 – 3.04 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 166.3, 135.7, 135.4, 130.1, 129.7, 129.4, 128.7, 128.0, 127.2, 61.8, 54.6, 37.9, 14.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}NO_3S$, 330.1158 , Found: 330.1159.

Ethyl ((phenylthio)carbonyl)-L-methioninate (3b)



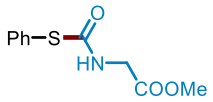
Purification by silica gel column chromatography (PE:EA, 10:1, v/v) to provide **3b**. Colorless oil (58.3 mg, 95% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.57 (m, 2H), 7.46 – 7.42 (m, 3H), 6.18 (d, *J* = 7.6 Hz, 1H), 4.68 – 4.63z (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.50 – 2.44 (m, 2H), 2.19 – 2.11 (m, 1H), 2.06 (s, 3H), 2.02 – 1.93 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 166.6, 135.7, 130.0, 129.6, 128.0, 62.0, 53.3, 31.7, 29.8, 15.6, 14.2. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{14}H_{19}NO_3S_2$, 336.0699, Found: 336.0691.

Methyl ((phenylthio)carbonyl)-L-valinate (3c)



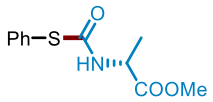
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3c**. Colorless oil (50.8 mg, 95% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.58 (m, 2H), 7.46 – 7.42 (m, 3H), 5.86 (d, *J* = 8.6 Hz, 1H), 4.50 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.73(s, 3H), 2.18 – 2.09 (m, 1H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.0, 166.7, 135.7, 130.0, 129.7, 128.2, 58.7, 52.5, 31.6, 19.0, 17.7. HRMS (ESI-TOF) *m/z*: [M + K]$^{+}$ Calcd for $C_{13}H_{17}NO_3S$, 306.0561, Found: 306.0564.

Methyl ((phenylthio)carbonyl)glycinate (3d)



Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3d**. White solid (43.3 mg, 96% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.58 (m, 2H), 7.46 – 7.42 (m, 3H), 5.91 (s, 1H), 4.05 (d, *J* = 5.3 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 167.1, 135.7, 130.1, 129.7, 130.0, 52.7, 42.6. HRMS (ESI-TOF) *m/z*: [M + K]$^{+}$ Calcd for $C_{10}H_{11}NO_3S$, 264.0091, Found: 264.0099.

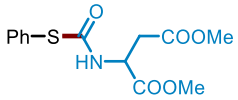
Methyl ((phenylthio)carbonyl)-D-alaninate (3e)



Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3e**. Colorless oil (39.7 mg, 83% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.55 (m, 2H), 7.45 – 7.41 (m, 3H), 6.04 (d, *J* = 7.3 Hz, 1H), 4.59 – 4.52 (m, 1H), 3.74 (s, 3H), 1.40 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

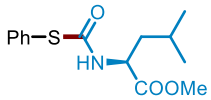
Chloroform-*d*) δ 173.0, 166.2, 135.7, 130.0, 129.6, 128.1, 52.8, 49.8, 18.7. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{11}H_{13}NO_3S$, 278.0248, Found: 278.0247.

Dimethyl ((phenylthio)carbonyl)aspartate (3f)



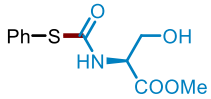
Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3f**. Colorless oil (47.6 mg, 80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.46 – 7.42 (m, 3H), 6.45 (d, *J* = 7.9 Hz, 1H), 4.81 – 4.77 (m, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 3.03 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.86 (dd, *J* = 17.4, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*)Unknown NMR (101 MHz, Chloroform-d) δ 171.3, 170.6, 166.8, 135.6, 130.0, 129.5, 127.8, 53.1, 52.2, 50.0, 36.1. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{13}H_{15}NO_5S$, 336.0303, Found: 336.0305.

Methyl ((phenylthio)carbonyl)-L-leucinate (3g)



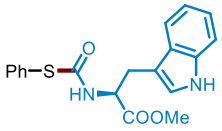
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3g**. White solid (54.0 mg, 96% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.45 – 7.41 (m, 3H), 5.77 (d, *J* = 8.3 Hz, 1H), 4.63 – 4.57 (m, 1H), 3.73 (s, 3H), 1.64 – 1.58 (m, 2H), 1.54 – 1.47 (m, 1H), 0.92 – 0.90 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 165.5, 134.7, 129.0, 128.7, 127.2, 51.7, 51.5, 40.9, 24.0, 21.9, 21.2. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{14}H_{19}NO_3S_2$, 320.0717, Found: 320.0710.

Methyl ((phenylthio)carbonyl)-L-serinate (3h)



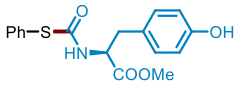
Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3h**. White solid (47.0 mg, 92% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.47 – 7.41 (m, 3H), 6.35 (d, *J* = 6.6 Hz, 1H), 4.63 – 4.60 (m, 1H), 4.01 – 3.90 (m, 2H), 3.78 (s, 3H), 2.15 (t, *J* = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 166.5, 134.7, 129.1, 128.7, 126.9, 62.1, 55.3, 52.2. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{13}NO_4S$, 278.0457, Found: 278.0456.

Methyl ((phenylthio)carbonyl)-L-tryptophanate (3i)



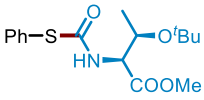
Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3i**. White solid (63.8 mg, 90% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.38 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 7.17 – 7.11 (m, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 5.92 (d, *J* = 7.6 Hz, 1H), 4.92 – 4.83 (m, 1H), 3.67(s, 3H), 3.37 – 3.20 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 166.5, 136.1, 135.6, 129.9, 129.5, 127.9, 127.5, 122.8, 122.4, 119.8, 118.7, 111.3, 109.4, 54.4, 52.6, 27.7. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{19}H_{18}NO_3S$, 393.0670, Found: 393.0672.

Methyl ((phenylthio)carbonyl)-L-tyrosinate (3j)



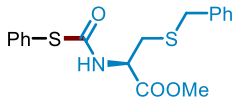
Purification by silica gel column chromatography (PE:EA, 7:1, v/v) to provide ***3j***. Colorless oil (51.7 mg, 78% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.43 – 7.34 (m, 3H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.67 – 6.65 (m, 2H), 5.88 (d, *J* = 7.7 Hz, 1H), 4.84 – 4.69 (m, 1H), 3.71 (s, 3H), 3.07 – 2.93 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 167.2, 155.3, 135.7, 130.31, 130.26, 129.8, 127.7, 126.7, 115.7, 54.8, 52.7, 37.0. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{17}H_{17}NO_4S$, 370.0510, Found: 370.0508.

Methyl O-(tert-butyl)-N-((phenylthio)carbonyl)-L-threoninate (3k)



Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3k**. White solid (44.2 mg, 68% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.44 – 7.41 (m, 3H), 6.15 (d, *J* = 9.5 Hz, 1H), 4.40 (d, *J* = 9.1 Hz, 1H), 4.18 – 4.13 (m, 1H), 3.70 (s, 3H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 166.4, 134.8, 128.9, 128.6, 127.4, 73.2, 66.4, 58.4, 51.5, 27.3, 20.3. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{16}H_{23}NO_4S$, 364.0979, Found: 364.0980.

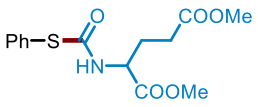
Methyl S-benzyl-N-((phenylthio)carbonyl)-L-cysteinate (3l)



Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3l**. White solid (46.9 mg, 65% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.58 (m, 2H), 7.47 – 7.43 (m, 3H), 7.33 – 7.30 (m, 2H), 7.28 – 7.25 (m, 3H), 6.20 (d, *J* = 7.4 Hz, 1H), 4.77 – 4.73 (m, 1H), 3.73 (s, 3H), 3.67 (s, 2H),

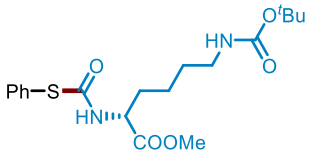
2.91 (dd, J = 14.1, 4.8 Hz, 1H), 2.81 (dd, J = 14.1, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 166.7, 137.5, 135.7, 130.1, 129.7, 129.0, 128.7, 127.9, 127.4, 53.4, 53.0, 36.7, 33.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}NO_3S_2$, 362.0879, Found: 362.0879.

Dimethyl ((phenylthio)carbonyl)glutamate (3m)



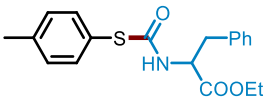
Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3m**. Colorless oil (42.4 mg, 68% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.45 – 7.42 (m, 3H), 6.15 (d, J = 7.6 Hz, 1H), 4.62 – 4.57 (m, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 2.41 – 2.32 (m, 2H), 2.24 – 2.17 (m, 1H), 2.01 – 1.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 171.8, 166.7, 135.6, 130.0, 129.6, 127.9, 53.3, 52.9, 52.1, 30.0, 27.5. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_5S$, 334.0720, Found: 334.0711.

Methyl N6-(tert-butoxycarbonyl)-N2-((phenylthio)carbonyl)-D-lysinat (3n)



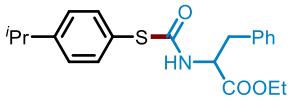
Purification by silica gel column chromatography (PE:EA, 10:1, v/v) to provide **3n**. White solid (67.4 mg, 85% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.45 – 7.43 (m, 3H), 6.06 (d, J = 7.5 Hz, 1H), 4.58 – 4.53 (m, 2H), 3.73 (s, 3H), 3.09 (d, J = 6.8 Hz, 2H), 1.89 – 1.81 (m, 1H), 1.72 – 1.64 (m, 1H), 1.45 (s, 11H), 1.35 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 165.5, 155.3, 134.7, 129.0, 128.7, 127.1, 78.4, 52.8, 51.8, 39.2, 31.2, 28.8, 27.6, 21.4. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{28}N_2O_5S$, 435.1351, Found: 435.1345.

Ethyl ((p-tolylthio)carbonyl)phenylalaninate (3o)



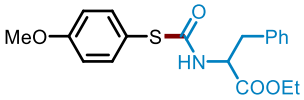
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3o**. White solid (58.4 mg, 85% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, J = 8.0 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.19 – 7.17 (m, 2H), 7.01 – 6.99 (m, 2H), 5.80 (d, J = 7.4 Hz, 1H), 4.81 – 4.76 (m, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.13 – 3.03 (m, 2H), 2.37 (s, 3H), 1.21 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.8, 139.5, 134.7, 134.5, 129.6, 128.4, 127.7, 126.2, 123.5, 60.8, 53.6, 36.9, 20.5, 13.2. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{21}NO_3S$, 382.0874, Found: 382.0876.

Ethyl (((4-isopropylphenyl)thio)carbonyl)phenylalaninate (3p)



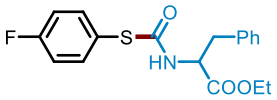
Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3p**. White solid (52.0 mg, 70% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.41 (m, 2H), 7.25 – 7.23 (m, 5H), 7.02 – 7.00 (m, 2H), 5.81 (d, *J* = 7.6 Hz, 1H), 4.82 – 4.77 (m, 1H), 4.13 (q, *J* = 7.2, 2H), 3.08 – 3.03 (m, 2H), 2.96 – 2.89 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 165.7, 150.1, 134.7, 134.5, 128.4, 127.6, 126.9, 126.2, 123.8, 60.7, 53.6, 36.9, 33.0, 22.9, 22.8, 13.2. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{21}H_{25}NO_3S$, 410.1187, Found: 410.1185.

Ethyl (((4-methoxyphenyl)thio)carbonyl)phenylalaninate (3q)



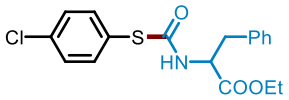
Purification by silica gel column chromatography (PE:EA, 10:1, v/v) to provide **3q**. White solid (54.0 mg, 75% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.41 (m, 2H), 7.24 (dd, *J* = 6.7, 3.7 Hz, 3H), 7.00 (s, 2H), 6.90 – 6.88 (m, 2H), 5.77 (d, *J* = 7.9 Hz, 1H), 4.79 – 4.77 (m, 1H), 4.13 (q, *J* = 8.0 2H), 3.83 (s, 3H), 3.08 (d, *J* = 1.2 Hz, 2H), 1.23 – 1.19 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 167.2, 161.1, 137.4, 135.4, 129.3, 128.6, 127.2, 118.6, 115.3, 61.7, 55.4, 54.4, 37.8, 14.1. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{21}NO_4S$, 398.0823, Found: 398.0822.

Ethyl (((4-fluorophenyl)thio)carbonyl)phenylalaninate (3r)



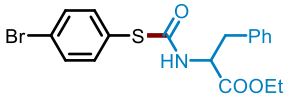
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3r**. White solid (42.0 mg, 61% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.46 (m, 2H), 7.30 – 7.25 (m, 4H), 7.10 – 7.01 (m, 4H), 5.79 (d, *J* = 7.7 Hz, 1H), 4.81 – 4.77 (m, 1H), 4.16 (q, *J* = 8.7 Hz, 2H), 3.16 – 3.07 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.2, 164.6 (d, *J* = 252.5 Hz), 161.7, 137.0, 136.9 (d, *J* = 8.08 Hz), 134.5, 128.5, 127.8, 126.4, 116.0 (d, *J* = 22.2 Hz), 115.8, 61.0, 53.8, 37.0, 13.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.96. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}FNO_3S$, 348.1064, Found: 348.1072.

Ethyl (((4-chlorophenyl)thio)carbonyl)phenylalaninate (3s)



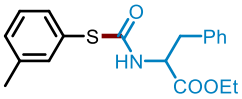
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3s**. White solid (56.0 mg, 77% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.39 (m, 2H), 7.35 – 7.32 (m, 2H), 7.27 – 7.24 (m, 3H), 7.02 (dd, *J* = 6.7, 2.9 Hz, 2H), 5.79 (d, *J* = 7.7 Hz, 1H), 4.87 – 4.66 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.10 (dd, *J* = 5.6, 2.1 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 165.5, 136.8, 136.4, 135.3, 129.8, 129.4, 128.7, 127.3, 126.5, 61.9, 54.7, 37.9, 14.2. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{18}H_{18}ClNO_3S$, 402.0328, Found: 402.0325.

Ethyl (((4-bromophenyl)thio)carbonyl)phenylalaninate (3t)



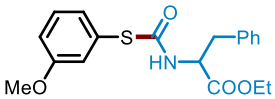
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3t**. White solid (70.0 mg, 86% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.25 (m, 3H), 7.07 – 6.99 (m, 2H), 5.80 (d, *J* = 7.6 Hz, 1H), 4.86 – 4.70 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.11 (dd, *J* = 5.6, 1.9 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 165.4, 137.0, 135.3, 132.7, 129.4, 128.7, 127.4, 127.1, 124.7, 61.9, 54.7, 37.9, 14.2. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{18}BrNO_3S$, 430.0083, Found: 430.0090.

Ethyl ((m-tolylthio)carbonyl)phenylalaninate (3u)



Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3u**. Colorless oil (59.4 mg, 80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 7.26 – 7.20 (m, 5H), 7.01 – 6.99 (m, 2H), 5.83 (d, *J* = 7.7 Hz, 1H), 4.80 – 4.76 (m, 1H), 4.13 (q, *J* = 7.3 Hz, 2H), 3.14 – 3.03 (m, 2H), 2.33 (s, 3H), 1.20 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.6, 138.7, 135.3, 134.5, 131.8, 130.0, 128.6, 128.5, 127.7, 126.8, 126.3, 60.8, 53.7, 36.9, 20.4, 13.2. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{19}H_{21}NO_3S$, 382.0874, Found: 382.0877.

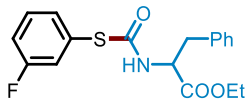
Ethyl (((3-methoxyphenyl)thio)carbonyl)phenylalaninate (3v)



Purification by silica gel column chromatography (PE:EA, 7:1, v/v) to provide **3v**. Colorless oil (57.5 mg, 80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*)δ 7.31 – 7.22 (m, 4H), 7.11 – 7.07 (m, 1H), 7.05 (d,

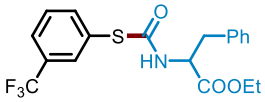
J = 2.0 Hz, 1H), 7.01 – 6.94 (m, 3H), 5.85 (d, *J* = 7.7 Hz, 1H), 4.78 (q, *J* = 5.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.14 – 3.03 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 165.3, 159.2, 134.5, 129.6, 128.4, 128.0, 127.7, 126.9, 126.3, 119.4, 115.6, 60.8, 54.6, 53.7, 36.9, 13.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}NO_4S$, 360.1264, Found: 360.1266.

Ethyl (((3-fluorophenyl)thio)carbonyl)phenylalaninate (3w)



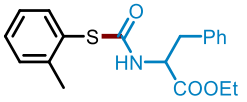
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3w**. White solid (66.0 mg, 95% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 1H), 7.29 – 7.23 (m, 5H), 7.14 – 7.09 (m, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 5.84 (d, *J* = 7.3 Hz, 1H), 4.82 – 4.78 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.17 – 3.07 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 164.2, 161.6 (d, *J* = 251.8 Hz), 134.3, 130.1 (d, *J* = 3.5 Hz), 129.7 (d, *J* = 8.7 Hz), 128.4, 127.7, 126.3, 125.14, 121.4 (d, *J* = 22.4 Hz), 116.1 (d, *J* = 20.9 Hz), 60.9, 53.8, 36.9, 13.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.85. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{18}FNO_3S$, 370.0884, Found: 370.0893.

Ethyl (((3-(trifluoromethyl)phenyl)thio)carbonyl)phenylalaninate (3x)



Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3x**. White solid (70.0 mg, 88% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.09 – 7.06 (m, 2H), 5.94 (d, *J* = 7.6 Hz, 1H), 4.84 – 4.78 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.19 – 3.08 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 163.8, 137.8, 134.4, 131.1 (q, *J* = 3.8 Hz), 130.8 (q, *J* = 32.6 Hz), 128.9, 128.5, 128.4, 127.8, 126.5, 125.5 (q, *J* = 3.8 Hz), 122.7 (q, *J* = 273.1 Hz), 61.1, 54.0, 37.1, 13.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.48. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{18}F_3NO_3S$, 436.0591, Found: 436.0605.

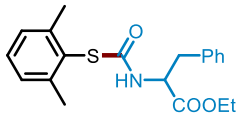
Ethyl ((o-tolylthio)carbonyl)phenylalaninate (3y)



Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3y**. Colorless oil (50.8 mg, 74% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.29 (m, 2H),

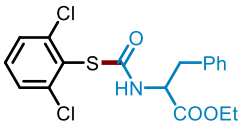
7.24 – 7.19 (m, 4H), 6.98 – 6.95 (m, 2H), 5.73 (d, J = 7.8 Hz, 1H), 4.79 – 4.74 (m, 1H), 4.13 (q, J = 7.0 Hz, 2H), 3.12 – 2.99 (m, 2H), 2.40 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.2, 142.2, 136.3, 134.5, 130.4, 130.0, 128.3, 127.8, 126.6, 126.29, 126.27, 60.8, 53.6, 36.9, 20.2, 13.3. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{21}NO_3S$, 382.0874, Found: 382.0877.

Ethyl (((2,6-dimethylphenyl)thio)carbonyl)phenylalaninate (3z)



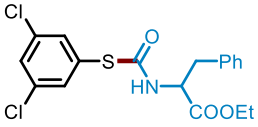
Purification by silica gel column chromatography (PE:EA, 20:1, v/v) to provide **3z**. White solid (67.9 mg, 95% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.14 (m, 6H), 6.93 – 6.89 (m, 2H), 5.61 (d, J = 10.5 H, 1H), 4.77 – 4.70 (m, 1H), 4.21 – 4.05 (m, 2H), 3.10 – 2.92 (m, 2H), 2.43 – 2.39 (m, 6H), 1.24 – 1.19 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 165.9, 144.0, 135.4, 130.6, 129.1, 128.9, 128.7, 127.4, 127.2, 61.7, 54.4, 37.8, 22.1, 14.2. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{20}H_{23}NO_3S$, 396.1030, Found: 396.1028.

Ethyl (((2,6-dichlorophenyl)thio)carbonyl)phenylalaninate (3aa)



Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3aa**. White solid (43.8 mg, 55% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.50 (m, 2H), 7.44 – 7.36 (m, 3H), 7.24 (d, J = 2.0 Hz, 1H), 7.02 – 7.00 (m, 2H), 5.81 (d, J = 7.7 Hz, 1H), 4.81 – 4.77 (m, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.15 – 3.04 (m, 2H), 1.22 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.4, 134.8, 134.5, 129.2, 128.8, 128.5, 127.8, 127.1, 126.4, 60.9, 53.8, 37.0, 13.3. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{18}H_{17}Cl_2NO_3S$, 435.9938, Found: 435.9947.

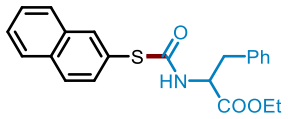
Ethyl (((3,5-dichlorophenyl)thio)carbonyl)phenylalaninate (3ab)



Purification by silica gel column chromatography (PE:EA, 20:1, v/v) to provide **3ab**. White solid (51.8 mg, 65% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.38 (m, 3H), 7.32 – 7.27 (m, 3H), 7.10 – 7.07 (m, 2H), 5.90 (d, J = 7.6 Hz, 1H), 4.83 – 4.78 (m, 1H), 4.19 (q, J = 7.5 Hz, 2H), 3.19 – 3.09 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 163.1, 134.4, 134.3, 132.3, 129.9, 128.9, 128.4, 127.8, 126.5, 61.1, 54.0, 37.0, 13.2. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for

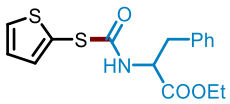
$C_{18}H_{17}ClNO_3S$, 420.0198, Found: 420.0196.

Ethyl ((naphthalen-2-ylthio)carbonyl)phenylalaninate (3ac)



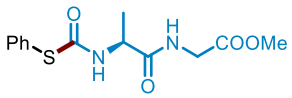
Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3ac**. White solid (66.8 mg, 88% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.7 Hz, 1H), 7.87 – 7.81(m, 3H), 7.59 – 7.51 (m, 3H), 7.16 – 7.08 (m, 3H), 6.94 (d, *J* = 6.8 Hz, 2H), 5.82 (d, *J* = 7.8 Hz, 1H), 4.82 – 4.77 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.12 – 3.02 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 166.4, 135.8, 135.2, 133.7, 133.5, 131.6, 129.4, 129.2, 128.5, 128.2, 127.9, 127.6, 127.2, 126.9, 125.2, 61.7, 54.6, 37.8, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{21}NO_3S$, 380.1315, Found: 380.1323.

Ethyl ((thiophen-2-ylthio)carbonyl)phenylalaninate (3ad)



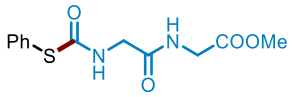
Purification by silica gel column chromatography (PE:EA, 1:1, v/v) to provide **3ad**. White solid (44.3 mg, 66% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.55 (m, 1H), 7.26 – 7.24 (m, 4H), 7.09 – 7.06 (m, 1H), 7.02 – 7.00 (m, 2H), 5.95 (d, *J* = 7.0 Hz, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.14 – 3.04 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 165.9, 137.9, 135.3, 133.4, 129.4, 128.7, 128.5, 127.3, 125.7, 61.9, 54.6, 37.8, 14.2. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{16}H_{17}NO_3S_2$, 374.0281, Found: 374.0277.

Methyl ((phenylthio)carbonyl)-L-alanylglycinate (3ae)



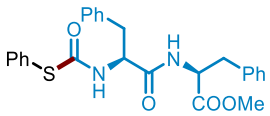
Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3ae**. White solid (52.7 mg, 89% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.45 – 7.33 (m, 3H), 6.88 (t, *J* = 5.5 Hz, 1H), 6.40 (d, *J* = 7.4 Hz, 1H), 4.64 – 4.44 (m, 1H), 3.99 – 3.82 (m, 2H), 3.75 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 170.1, 166.9, 135.7, 129.9, 129.5, 127.9, 52.5, 50.5, 41.2, 18.8. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{13}H_{16}N_2O_4S$, 335.0462, Found: 335.0469.

Methyl ((phenylthio)carbonyl)glycylglycinate (3af)



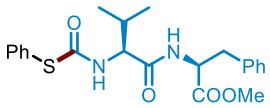
Purification by silica gel column chromatography (PE:EA, 1:2, v/v) to provide **3af**. White solid (50.2 mg, 89% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.55 (m, 2H), 7.50 – 7.41 (m, 3H), 6.64 (s, 1H), 6.30 (s, 1H), 4.00 (d, *J* = 5.2 Hz, 4H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 167.9, 167.1, 135.2, 129.6, 129.1, 127.3, 52.1, 43.79, 40.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{14}N_2O_4S$, 305.0566, Found: 305.0567.

Methyl ((phenylthio)carbonyl)-L-phenylalanyl-L-phenylalaninate (3ag)



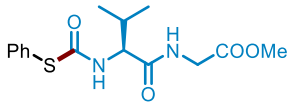
Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3ag**. White solid (53.7 mg, 58% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.36 (m, 5H), 7.25 – 7.23 (m, 6H), 7.09 – 7.06 (m, 2H), 6.97 – 6.94 (m, 2H), 6.14 (d, *J* = 7.7 Hz, 1H), 5.95 (d, *J* = 7.5 Hz, 1H), 4.74 (q, *J* = 7.6, 6.8 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 1H), 3.69(s, 3H), 3.08 – 2.93 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 169.6, 166.9, 135.9, 135.6, 135.5, 130.1, 129.8, 129.4, 129.3, 128.8, 128.7, 127.8, 127.3, 127.2, 55.7, 53.5, 52.5, 38.0, 37.9. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{26}H_{26}N_2O_4S$, 501.1245, Found: 504.1243.

Methyl ((phenylthio)carbonyl)-L-valyl-L-phenylalaninate (3ah)



Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3ah**. White solid (53.9 mg, 65% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.54 (m, 2H), 7.44 – 7.40 (m, 3H), 7.29 – 7.21 (m, 3H), 7.08 – 7.06 (m, 2H), 6.26 (d, *J* = 7.9 Hz, 1H), 6.01 (d, *J* = 8.6 Hz, 1H), 4.81 (q, *J* = 2.2 Hz, 1H), 4.19 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.70 (s, 3H), 3.13 – 3.02 (m, 2H), 2.04 – 1.96 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 170.1, 166.8, 135.6, 135.5, 130.0, 129.7, 129.3, 128.8, 128.2, 127.4, 59.9, 53.3, 52.5, 37.9, 31.4, 19.1, 17.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}N_2O_4S$, 415.1686, Found: 415.1685.

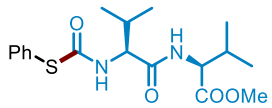
Methyl ((phenylthio)carbonyl)-L-valylglycinate (3ai)



Purification by silica gel column chromatography (PE:EA, 3:1, v/v) to provide **3ai**. White solid (33.1

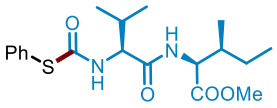
mg, 51% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.55 (m, 2H), 7.45 – 7.41 (m, 3H), 6.65 – 6.62 (m, 1H), 6.12 (d, *J* = 8.7 Hz, 1H), 4.32 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.02 (dd, *J* = 18.0, 5.6 Hz, 1H), 3.82 (d, *J* = 5.3 Hz, 1H), 3.75 (s, 3H), 2.12 – 2.04 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.91, 169.08, 166.2, 134.8, 129.1, 128.7, 127.2, 59.0, 51.6, 40.2, 30.7, 18.3, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{20}N_2O_4S$, 347.1036, Found: 347.1033.

Methyl ((phenylthio)carbonyl)-L-valyl-L-valinate (3aj)



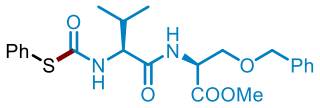
Purification by silica gel column chromatography (PE:EA, 7:1, v/v) to provide **3aj**. White solid (46.2 mg, 63% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.56 (m, 2H), 7.45 – 7.42 (m, 3H), 6.34 (d, *J* = 8.7 Hz, 1H), 6.06 (d, *J* = 8.6 Hz, 1H), 4.52 – 4.48 (m, 1H), 4.29 (q, *J* = 8.4, 6.4 Hz, 1H), 3.74 – 3.73 (m, 3H), 2.22 – 2.00 (m, 2H), 0.95 – 0.89 (m, 3H), 0.87 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 169.6, 166.1, 134.7, 129.1, 128.8, 127.3, 59.1, 56.4, 51.4, 30.6, 30.2, 18.3, 18.1, 17.0. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{26}N_2O_4S$, 367.1686, Found: 367.1690.

Methyl ((phenylthio)carbonyl)-L-valyl-L-isoleucinate (3ak)



Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3ak**. White solid (48.7 mg, 64% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.43 – 7.42 (m, 3H), 6.43 (d, *J* = 8.4 Hz, 1H), 6.10 (d, *J* = 8.4 Hz, 1H), 4.53 (dd, *J* = 8.3, 4.8 Hz, 1H), 4.32 – 4.28 (m, 1H), 3.73 (s, 3H), 2.10 – 2.01 (m, 1H), 1.91 – 1.85 (m, 1H), 1.44 – 1.35 (m, 1H), 1.22 – 1.11 (m, 1H), 0.94 – 0.88 (m, 9H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 169.5, 166.0, 134.7, 129.1, 128.8, 127.4, 56.0, 55.8, 51.4, 36.8, 30.6, 24.4, 18.3, 17.0, 14.6, 10.8. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{19}H_{28}N_2O_4S$, 381.1843, Found: 381.1852.

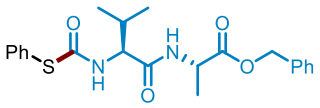
Methyl O-benzyl-N-(((phenylthio)carbonyl)-L-valyl)-L-serinate (3al)



Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3al**. White solid (71.1 mg, 80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.42 – 7.40 (m, 3H), 7.36 –

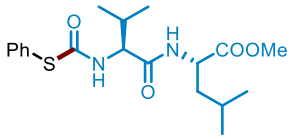
7.30 (m, 3H), 7.26 – 7.24 (m, 2H), 6.53 (d, *J* = 8.3 Hz, 1H), 6.12 (d, *J* = 8.4 Hz, 1H), 4.73 – 4.70 (m, 1H), 4.55 – 4.44 (m, 2H), 4.30 (dd, *J* = 8.5, 5.7 Hz, 1H), 3.90 (dd, *J* = 9.6, 2.9 Hz, 1H), 3.72 (s, 3H), 3.63 (dd, *J* = 9.5, 3.1 Hz, 1H), 2.12 – 2.04 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 169.4, 165.7, 136.4, 134.7, 129.0, 128.7, 127.7, 127.4, 127.2, 126.9, 72.5, 68.4, 58.8, 51.8, 51.7, 31.0, 18.2, 16.8. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{23}H_{28}N_2O_5S$, 467.1611, Found: 467.1614.

Benzyl ((phenylthio)carbonyl)-L-valyl-L-alaninate (3am)



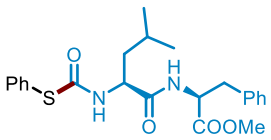
Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3am**. White solid (73.8 mg, 89% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.54 (m, 2H), 7.43 – 7.40 (m, 3H), 7.36 – 7.31 (m, 5H), 6.55 (d, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 5.15 (d, *J* = 15.4 Hz, 2H), 4.60 – 4.53 (m, 1H), 4.30 – 4.25 (m, 1H), 2.06 – 1.97 (m, 1H), 1.37 (t, *J* = 6.2 Hz, 3H), 0.91 (t, *J* = 6.0 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 169.2, 166.1, 134.7, 134.4, 129.1, 128.7, 127.8, 127.7, 127.4, 127.3, 66.1, 58.9, 47.4, 30.9, 18.2, 17.2, 17.0. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{22}H_{26}N_2O_4S$, 415.1686, Found: 415.1689.

Methyl ((phenylthio)carbonyl)-L-valyl-L-leucinate (3an)



Purification by silica gel column chromatography (PE:EA, 10:1, v/v) to provide **3an**. White solid (54.8 mg, 72% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.55 (m, 2H), 7.43 – 7.41 (m, 3H), 6.35 (d, *J* = 7.9 Hz, 1H), 6.10 (d, *J* = 8.5 Hz, 1H), 4.57 – 4.52 (m, 1H), 4.30 – 4.26 (m, 1H), 3.72 (s, 3H), 2.09 – 2.01 (m, 1H), 1.66 – 1.58 (m, 2H), 1.55 – 1.48 (m, 1H), 0.95 – 0.86 (m, 9H), 0.87 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 169.5, 166.1, 134.7, 129.1, 128.8, 127.3, 58.9, 51.5, 50.0, 40.2, 30.7, 24.0, 22.0, 21.0, 18.2, 17.0. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{19}H_{28}N_2O_4S$, 419.1401, Found: 419.1408.

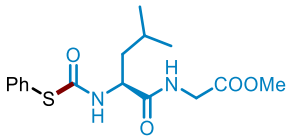
Methyl ((phenylthio)carbonyl)-L-leucyl-L-phenylalaninate (3ao)



Purification by silica gel column chromatography (PE:EA, 8:1, v/v) to provide **3ao**. White solid (60.8

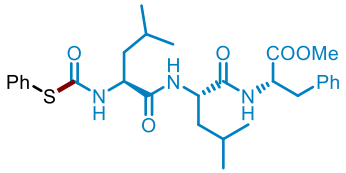
mg, 71% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 2H), 7.45 – 7.42 (m, 3H), 7.29 – 7.23 (m, 3H), 7.10 – 7.08 (m, 2H), 6.35 (d, *J* = 7.9 Hz, 1H), 5.80 (d, *J* = 8.2 Hz, 1H), 4.85 – 4.80 (m, 1H), 4.40 – 4.34 (m, 1H), 3.72 (s, 3H), 3.17 – 3.04 (m, 2H), 1.60 – 1.53 (m, 2H), 1.46 – 1.38 (m, 1H), 0.87 (d, *J* = 5.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 169.9, 165.7, 134.6, 134.6, 129.0, 128.7, 128.4, 127.8, 126.3, 123.4, 53.5, 52.4, 51.6, 40.2, 36.9, 23.8, 21.9, 21.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}N_2O_4S$, 429.1843, Found: 429.1843.

Methyl ((phenylthio)carbonyl)-L-leucylglycinate (3ap)



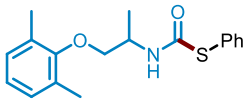
Purification by silica gel column chromatography (PE:EA, 3:1, v/v) to provide **3ap**. White solid (35.2 mg, 52% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 2H), 7.44 – 7.40 (m, 3H), 6.63 (t, *J* = 5.8 Hz, 1H), 6.01 (d, *J* = 8.2 Hz, 1H), 4.51 – 4.45 (m, 1H), 4.07 – 3.92 (m, 2H), 3.76 (s, 3H), 1.69 – 1.60 (m, 2H), 1.55 – 1.46 (m, 1H), 0.92 (d, *J* = 4.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 169.1, 166.1, 134.6, 129.0, 128.6, 127.0, 52.4, 51.58, 51.57, 40.3, 23.8, 22.0, 21.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{22}N_2O_4S$, 339.1373, Found: 339.1375.

Methyl ((phenylthio)carbonyl)-L-leucyl-L-leucyl-L-phenylalaninate (3aq)



Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3aq**. White solid (54.0 mg, 50% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.44 – 7.39 (m, 3H), 7.26 – 7.20 (m, 3H), 7.08 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 8.1 Hz, 1H), 4.84 – 4.79 (m, 1H), 4.45 – 4.37 (m, 2H), 3.70 (s, 3H), 3.12 – 3.01 (m, 2H), 1.64 – 1.45 (m, 4H), 0.89 – 0.81 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.8, 170.7, 166.0, 135.1, 134.7, 129.0, 128.7, 128.5, 127.8, 127.3, 126.4, 52.7, 52.6, 51.6, 51.0, 40.5, 40.4, 37.2, 24.0, 23.9, 22.2, 22.0, 21.6, 21.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{29}H_{39}N_3O_5S$, 564.2503, Found: 564.2500.

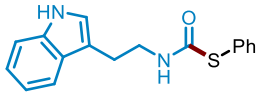
S-phenyl (1-(2,6-dimethylphenoxy)propan-2-yl)carbamothioate (3ar)



Purification by silica gel column chromatography (PE:EA,15:1, v/v) to provide **3ar**. White solid (49.8

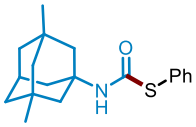
mg, 79% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.57 (m, 2H), 7.44 – 7.39 (m, 3H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.92 (dd, *J* = 8.4, 6.3 Hz, 1H), 5.82 (d, *J* = 7.7 Hz, 1H), 4.43 – 4.16 (m, 1H), 3.78 – 3.66 (m, 2H), 2.18 (s, 6H), 1.39 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 135.69, 135.68, 130.85, 130.84, 129.9, 129.7, 129.1, 124.3, 73.6, 47.9, 17.8, 16.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}NO_2S$, 316.1366, Found: 316.1368.

S-phenyl (2-(1H-indol-3-yl)ethyl)carbamothioate (3as)



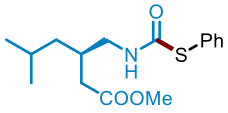
Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3as**. White solid (26.1 mg, 44% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.46 – 7.43 (m, 2H), 7.39 – 7.26 (m, 4H), 7.21 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 5.38 (s, 1H), 3.59 (q, *J* = 6.4 Hz, 2H), 2.95 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 136.4, 135.6, 129.7, 129.5, 128.6, 127.2, 122.4, 122.2, 119.7, 118.8, 112.4, 111.4, 41.6, 25.2. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{17}H_{16}N_2OS$, 335.0615, Found: 335.0617.

S-phenyl ((1S,3R)-3,5-dimethyladamantan-1-yl)carbamothioate (3at)



Purification by silica gel column chromatography (PE:EA, 25:1, v/v) to provide **3at**. White solid (54.3 mg, 86% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.51 (m, 2H), 7.41 – 7.38 (m, 3H), 5.12 (s, 1H), 2.14 – 2.11 (m, 1H), 1.77 (d, *J* = 3.1 Hz, 2H), 1.60 (s, 4H), 1.36 – 1.31 (m, 2H), 1.26 (dd, *J* = 12.1, 3.2 Hz, 2H), 1.16 – 1.08 (m, 2H), 0.82 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 135.5, 129.0, 130.0, 129.1, 55.8, 50.4, 47.6, 42.5, 40.3, 32.6, 30.2, 30.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{25}NOS$, 338.1549, Found: 338.1552.

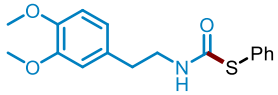
Methyl (R)-5-methyl-3-((((phenylthio)carbonyl)amino)methyl)hexanoate (3au)



Purification by silica gel column chromatography (PE:EA, 15:1, v/v) to provide **3au**. White solid (58.1 mg, 94% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (t, *J* = 4.1 Hz, 2 H), 7.44 – 7.41 (m, 3H), 5.63 (d, *J* = 7.5 Hz, 1H), 3.67 (s, 3H), 3.37 – 3.30 (m, 1H), 3.13 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.31 – 2.09 (m, 3H), 1.64 – 1.54 (m, 1H), 1.08 – 1.07 (m, 2H), 0.88 – 0.81 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 166.5, 135.7, 129.8, 129.6, 128.6, 51.9, 45.0, 41.5, 37.2, 33.3, 25.2, 22.8, 22.7.

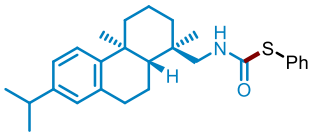
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}NO_3S$, 310.1471, Found: 310.1470.

S-phenyl (3,4-dimethoxyphenethyl)carbamothioate (3av)



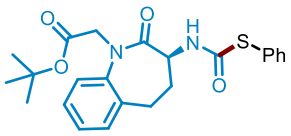
Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3av**. White solid (50.1 mg, 79% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 2H), 7.40 – 7.34 (m, 3H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.35(s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.49 (q, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 149.1, 147.8, 135.5, 130.8, 129.8, 129.5, 128.5, 120.6, 111.8, 111.4, 56.0, 55.9, 42.6, 35.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{19}NO_3S$, 340.0978, Found: 340.0977.

S-phenyl (((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamothioate (3aw)



Purification by silica gel column chromatography (PE:EA, 20:1, v/v) to provide **3aw**. White solid (59.9 mg, 71% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 3H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.88 (s, 1H), 5.22 (t, *J* = 5.7 Hz, 1H), 3.16 – 3.07 (m, 2H), 2.89 – 2.80 (m, 2H), 2.62 – 2.53 (m, 1H), 2.26 (d, *J* = 12.7 Hz, 1H), 1.69 – 1.60 (m, 4H), 1.25 (d, *J* = 6.9 Hz, 8H), 1.17 (s, 3H), 1.15 – 1.09 (m, 2H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 147.1, 145.8, 135.8, 134.7, 130.0, 129.7, 128.9, 126.9, 124.3, 123.9, 51.3, 44.9, 38.5, 37.7, 37.5, 36.0, 33.6, 30.1, 25.2, 24.2, 24.1, 18.8, 18.7, 18.6. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{27}H_{35}NOS$, 460.2071, Found: 460.2084.

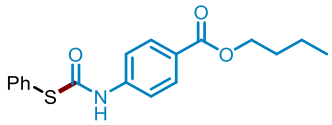
Tert-butyl(S)-2-(2-oxo-3-(((phenylthio)carbonyl)amino)-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)acetate (3ax)



Purification by silica gel column chromatography (PE:EA, 5:1, v/v) to provide **3ax**. White solid (80.2 mg, 94% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.42 – 7.36 (m, 3H), 7.29 – 7.24 (m, 1H), 7.22 – 7.15 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 6.8 Hz, 1H), 4.68 – 4.63 (m, 1H), 4.50 – 4.46 (m, 1H), 4.23 (d, *J* = 16.9 Hz, 1H), 3.33 – 3.28 (m, 1H), 2.71 – 2.65 (m, 1H), 2.57 (dd,

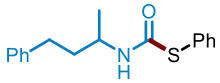
J = 13.4, 7.1 Hz, 1H), 1.96 – 1.92 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 166.6, 164.7, 139.4, 134.6, 128.8, 128.5, 127.3, 127.1, 126.5, 121.6, 81.4, 50.4, 50.1, 35.4, 27.12, 27.05. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{23}H_{26}N_2O_4S$, 465.1245, Found: 465.1246.

Butyl 4-(((phenylthio)carbonyl)amino)benzoate (3ay)



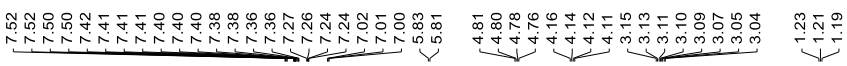
Purification by silica gel column chromatography (PE:EA, 18:1, v/v) to provide **3ay**. White solid (39.5 mg, 60% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.59 (m, 2H), 7.47 – 7.45 (m, 5H), 4.30 (t, *J* = 6.4 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.51 – 1.43 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 163.8, 140.7, 134.7, 130.0, 129.3, 128.7, 126.5, 125.3, 117.5, 64.0, 29.9, 18.4, 12.9. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{18}H_{19}NO_3S$, 368.0717, Found: 368.0719.

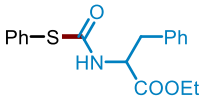
S-phenyl (4-phenylbutan-2-yl)carbamothioate (3az)



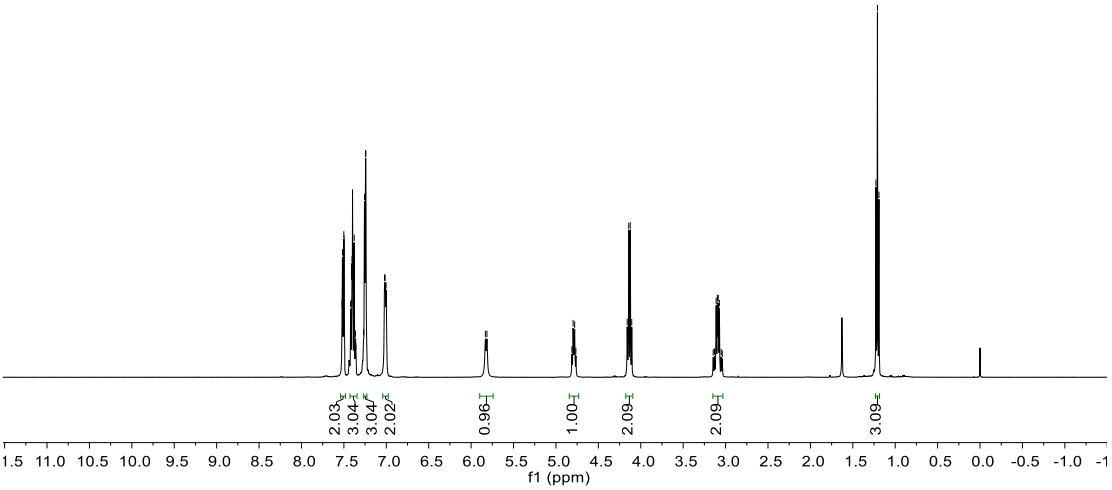
Purification by silica gel column chromatography (PE:EA, 1:3, v/v) to provide **3az**. White solid (50.2 mg, 88% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.44 – 7.41 (m, 3H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 5.16 (d, *J* = 8.3 Hz, 1H), 4.03 – 3.96 (m, 1H), 2.63 – 2.58 (m, 2H), 1.72 (q, *J* = 7.6 Hz, 2H), 1.16 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 141.5, 135.6, 129.7, 129.6, 128.8, 128.6, 128.4, 126.1, 47.7, 38.7, 32.5, 21.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{19}NOS$, :286.1260, Found: 286.1258.

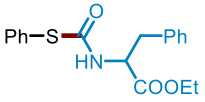
4. Copies of spectra of products



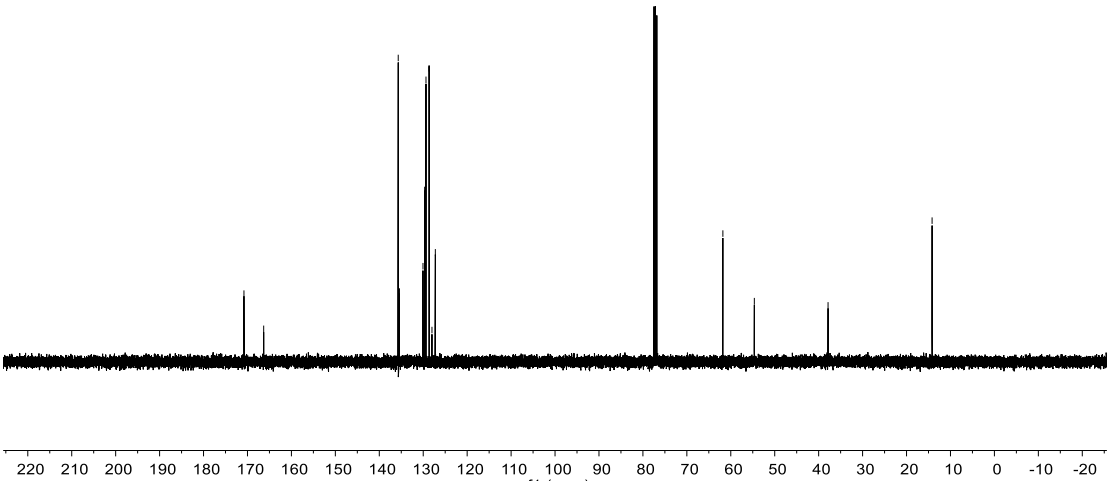


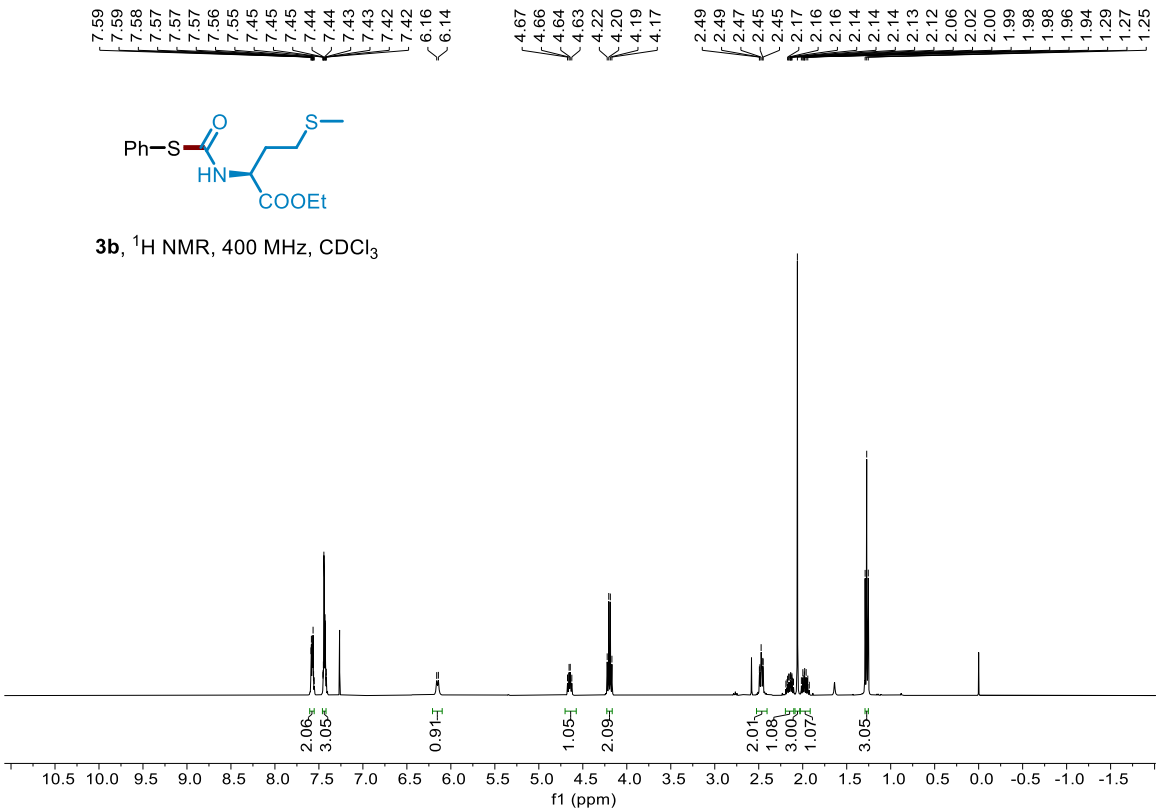
3a, ^{1}H NMR, 400 MHz, $CDCl_3$

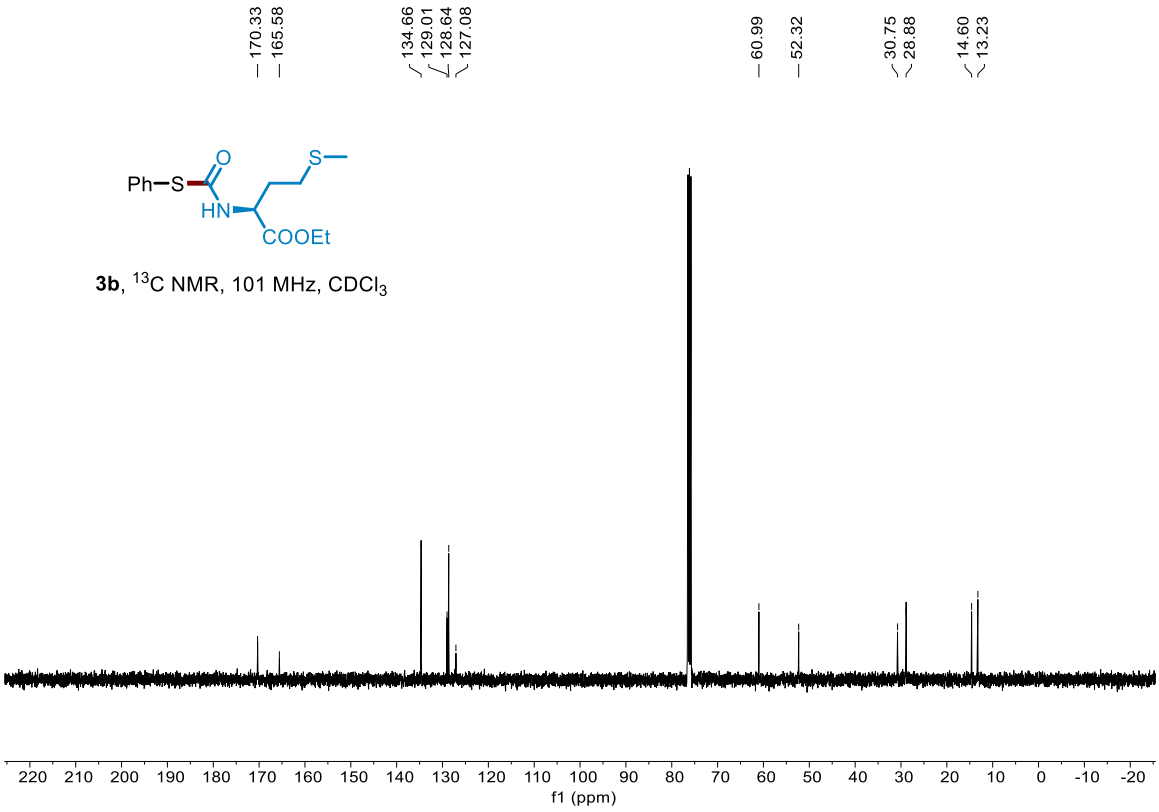


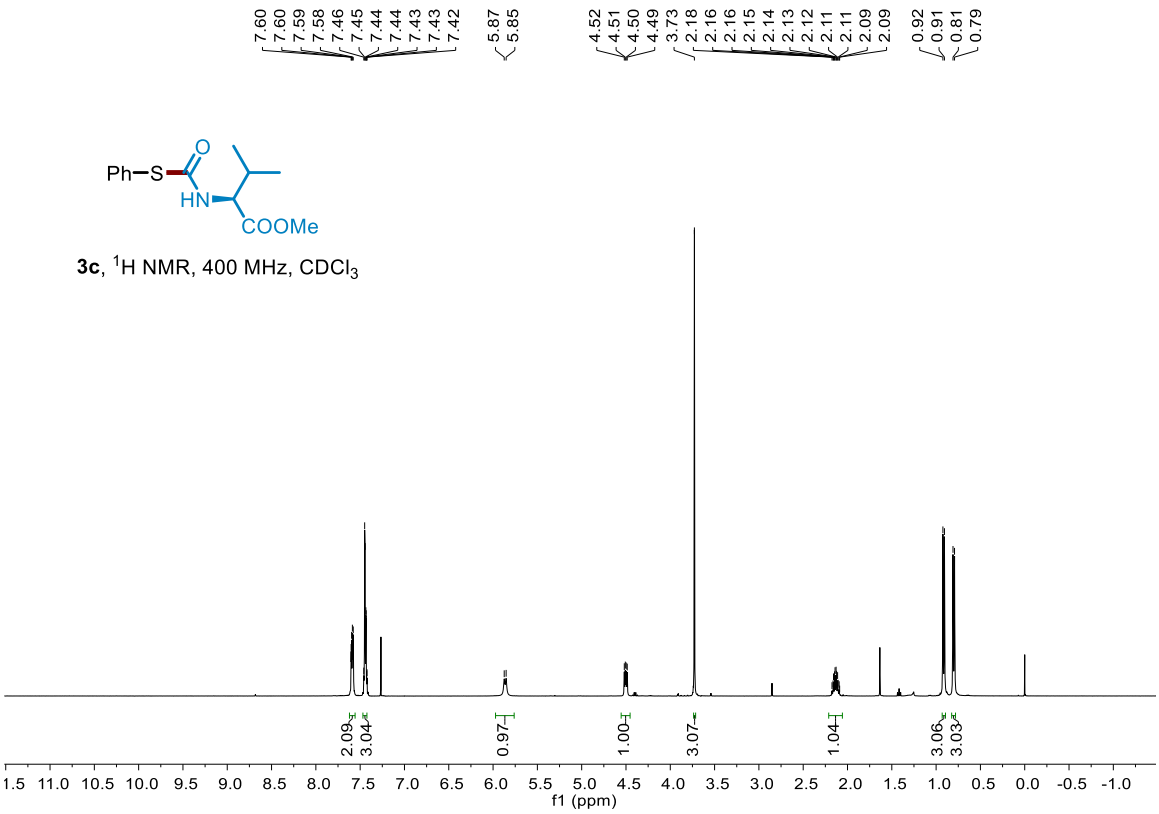


3a, ^{13}C NMR, 101 MHz, $CDCl_3$

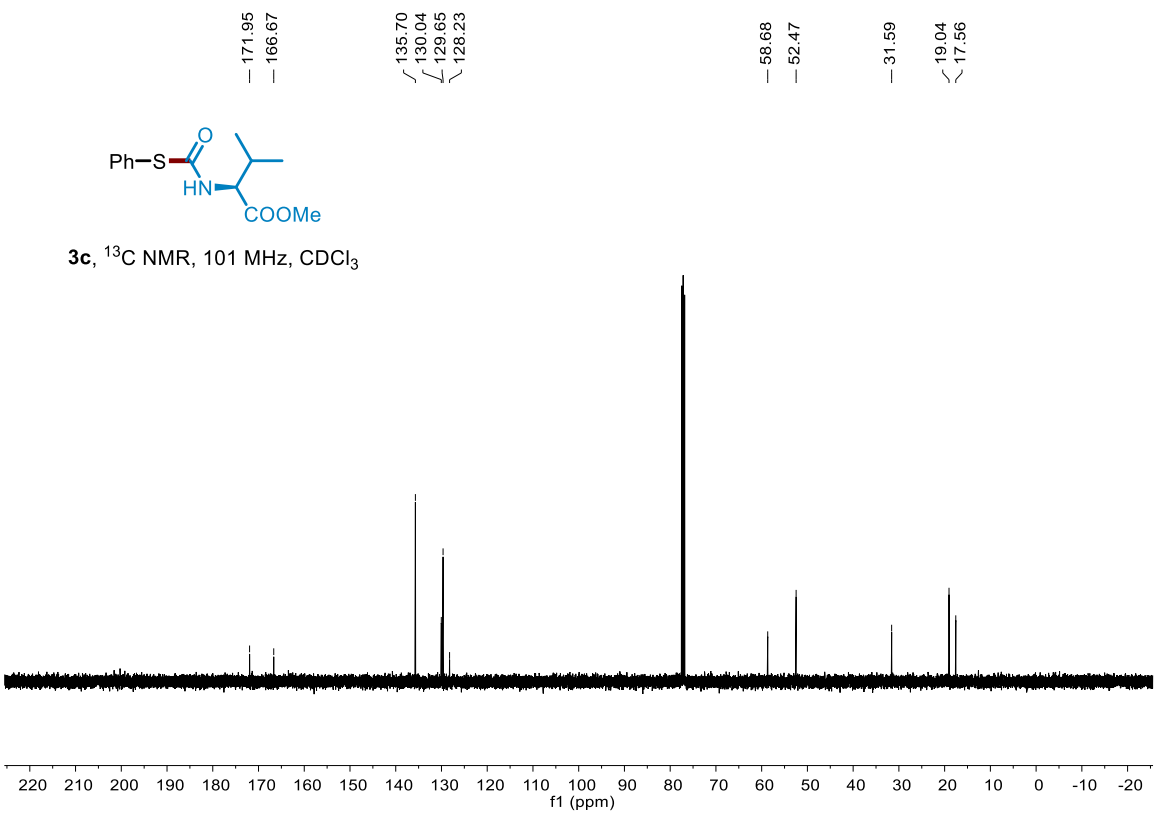



7.59 7.59 7.58 7.57 7.57 7.57 7.56 7.55 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 6.16 6.14
4.67 4.66 4.64 4.63 4.22 4.20 4.19 4.17
2.49 2.49 2.47 2.45 2.45 2.17 2.16 2.16 2.14 2.14 2.13 2.12 2.06 2.02 2.00 1.99 1.98 1.98 1.96 1.94 1.29 1.27 1.25
Ph–S
O
HN
S
COOEt
3b, 1H NMR, 400 MHz, CDCl3
2.06 3.05 0.91 1.05 2.09 2.01 1.08 3.00 1.07 3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

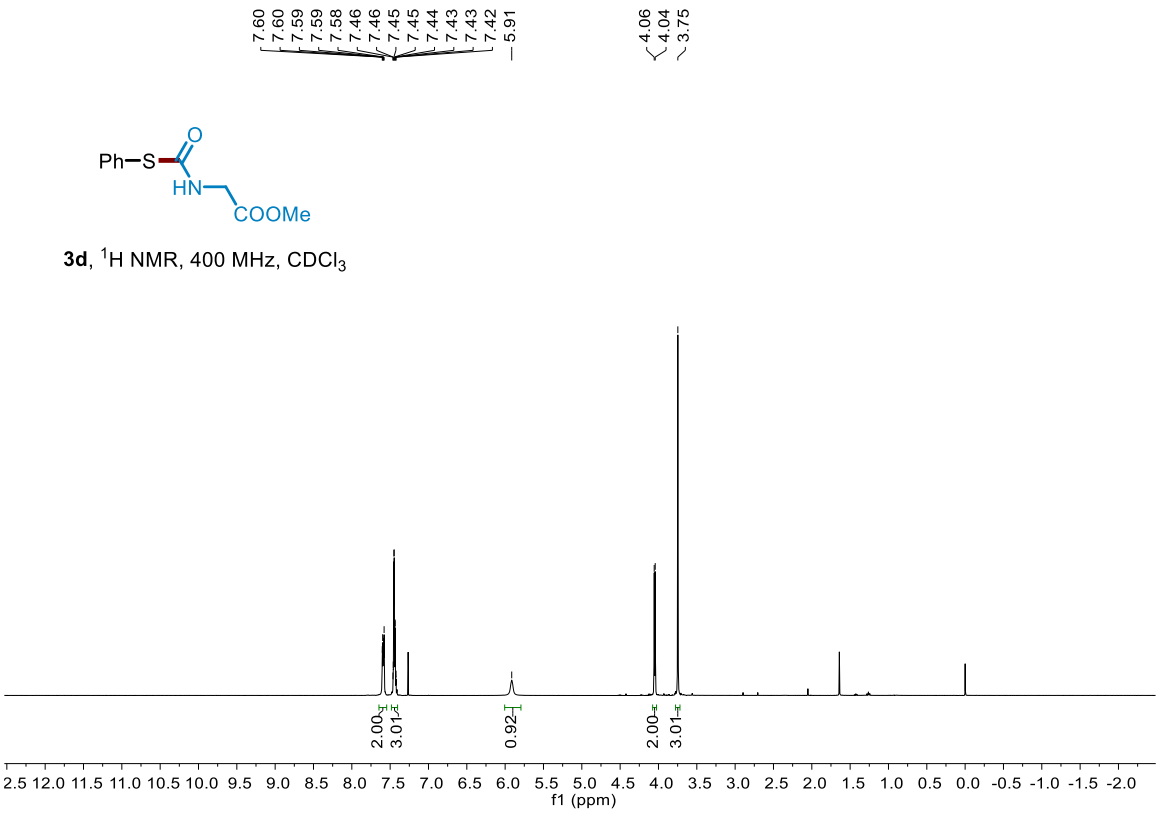

170.33 165.58
134.66 129.01 128.64 127.08
60.99 52.32 30.75 28.88 14.60 13.23
Ph–S
O
HN
S
COOEt
3b, 13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



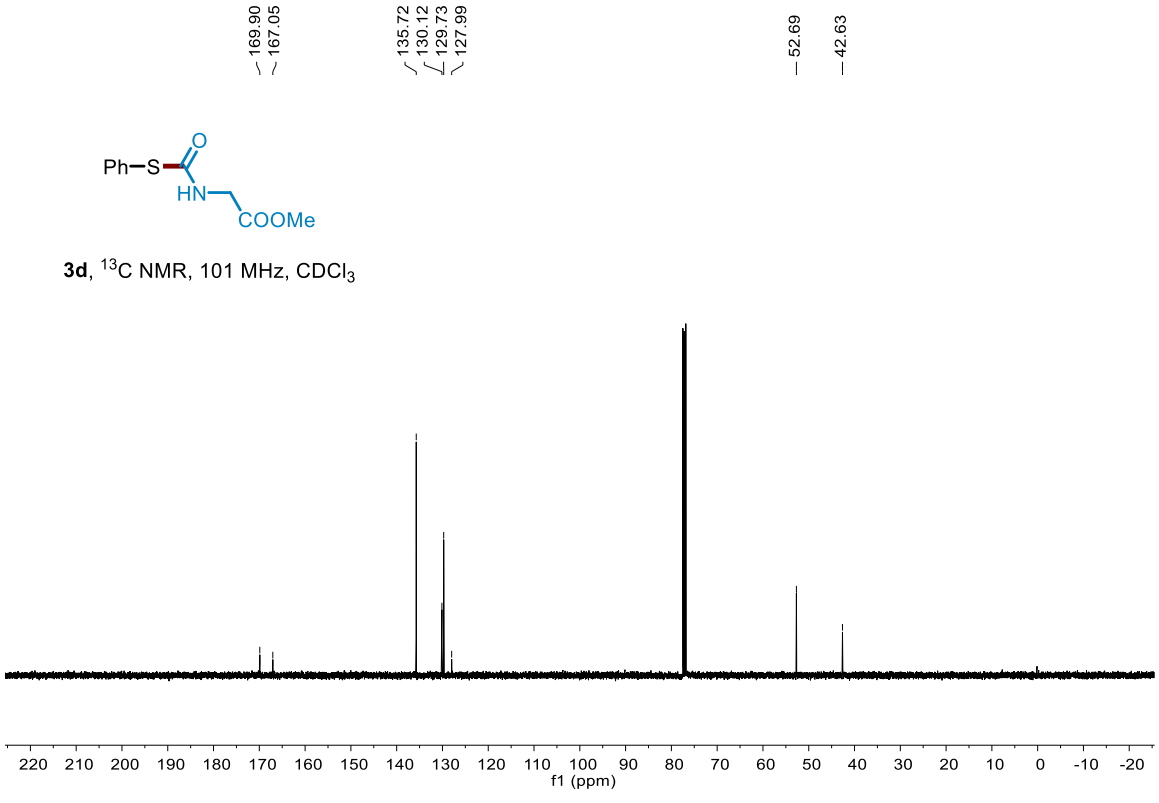
3c, ^{1}H NMR, 400 MHz, $CDCl_3$



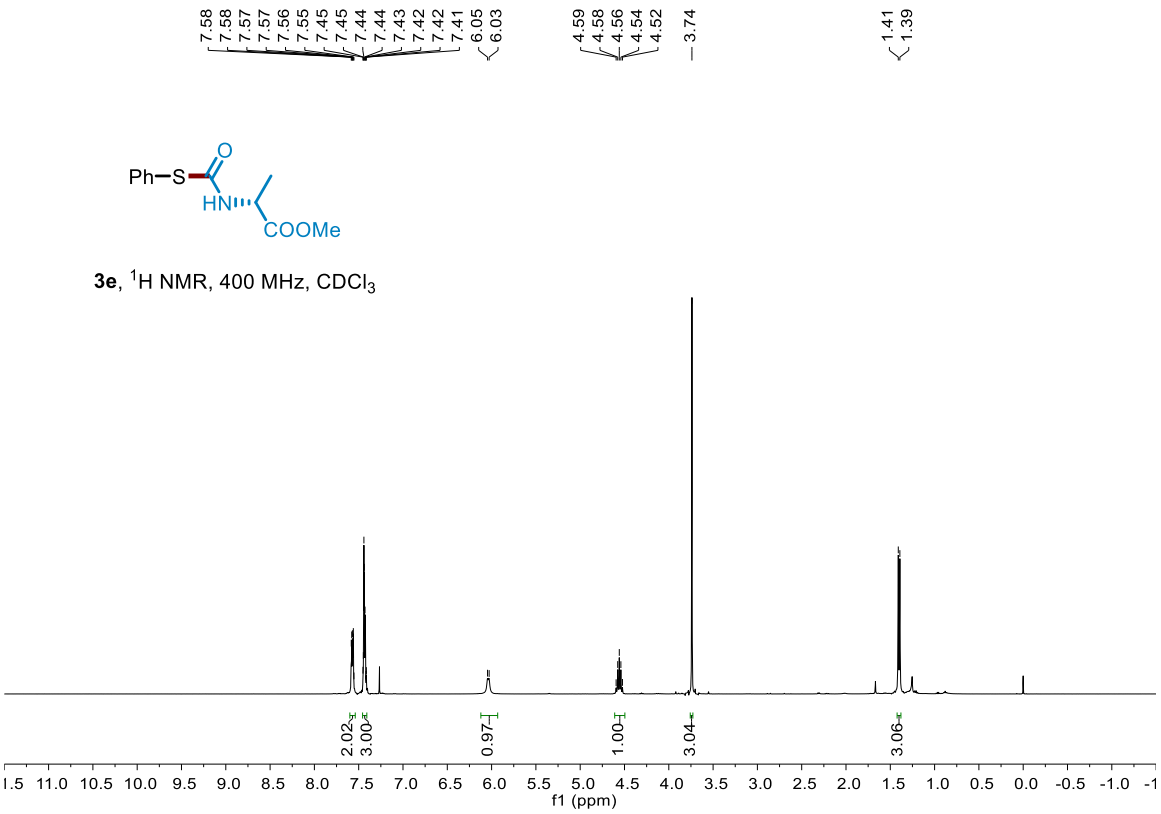
3c, ^{13}C NMR, 101 MHz, $CDCl_3$



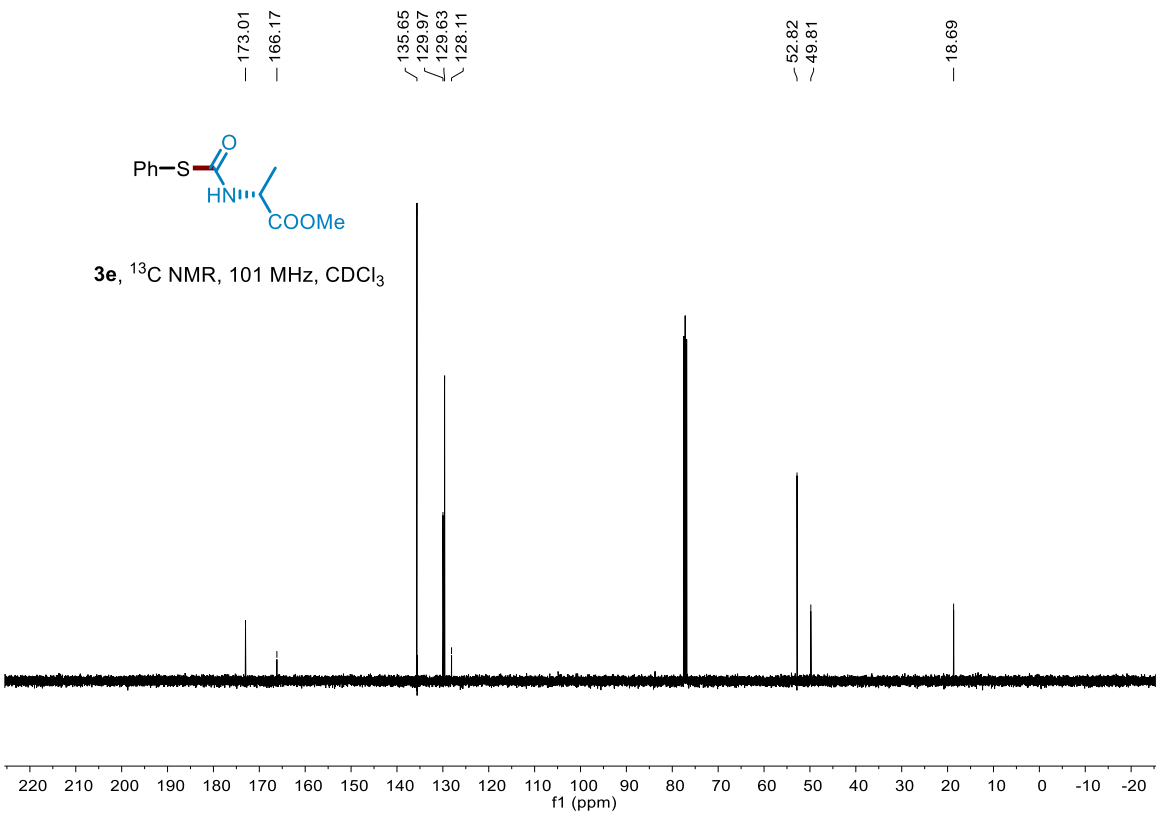
3d, ^{1}H NMR, 400 MHz, $CDCl_3$



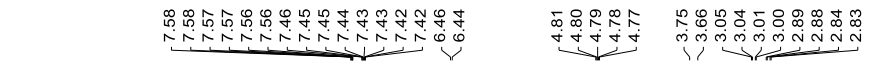
3d, ^{13}C NMR, 101 MHz, $CDCl_3$

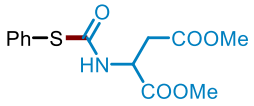


3e, ^{1}H NMR, 400 MHz, $CDCl_3$

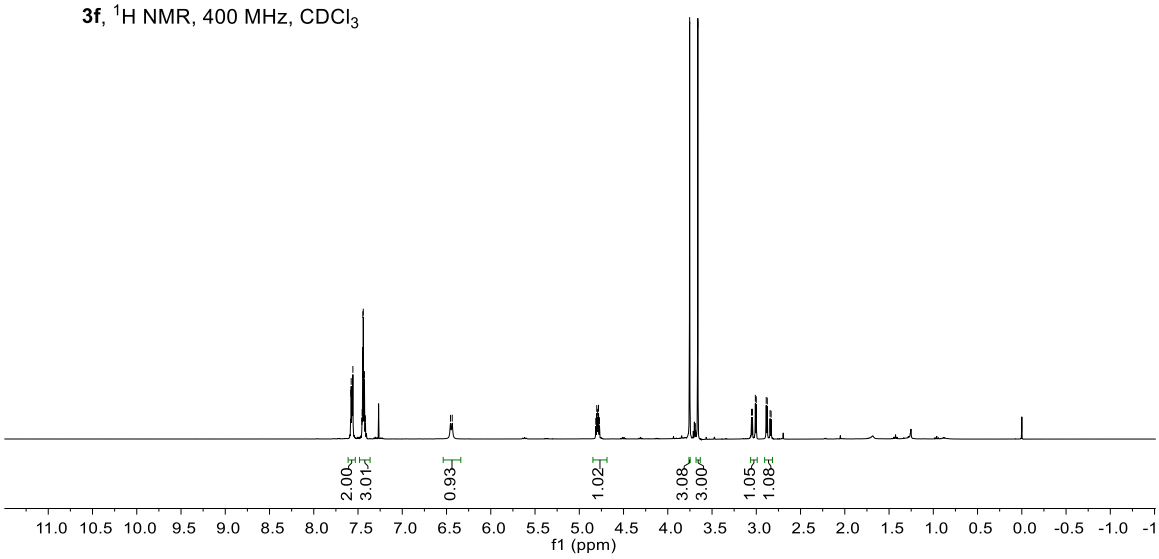


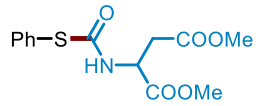
3e, ^{13}C NMR, 101 MHz, $CDCl_3$



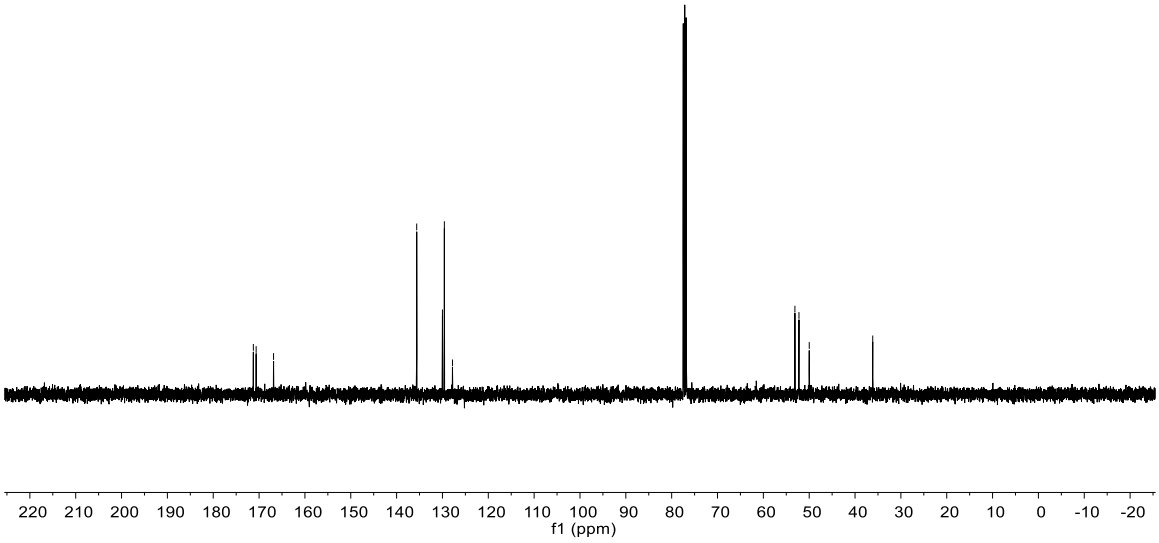


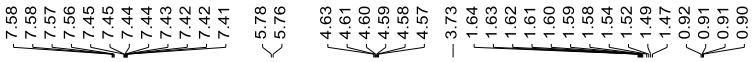
3f, ^{1}H NMR, 400 MHz, $CDCl_3$

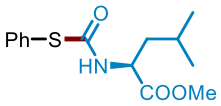




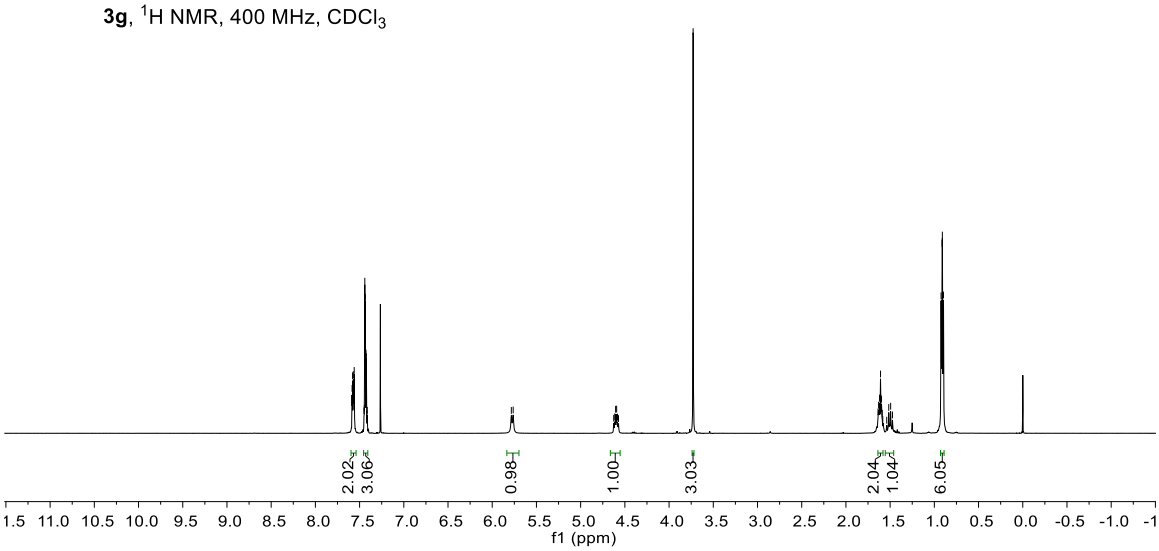
3f, ^{13}C NMR, 101 MHz, $CDCl_3$

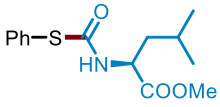




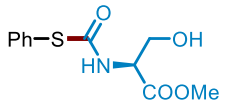


3g, ^{1}H NMR, 400 MHz, $CDCl_3$

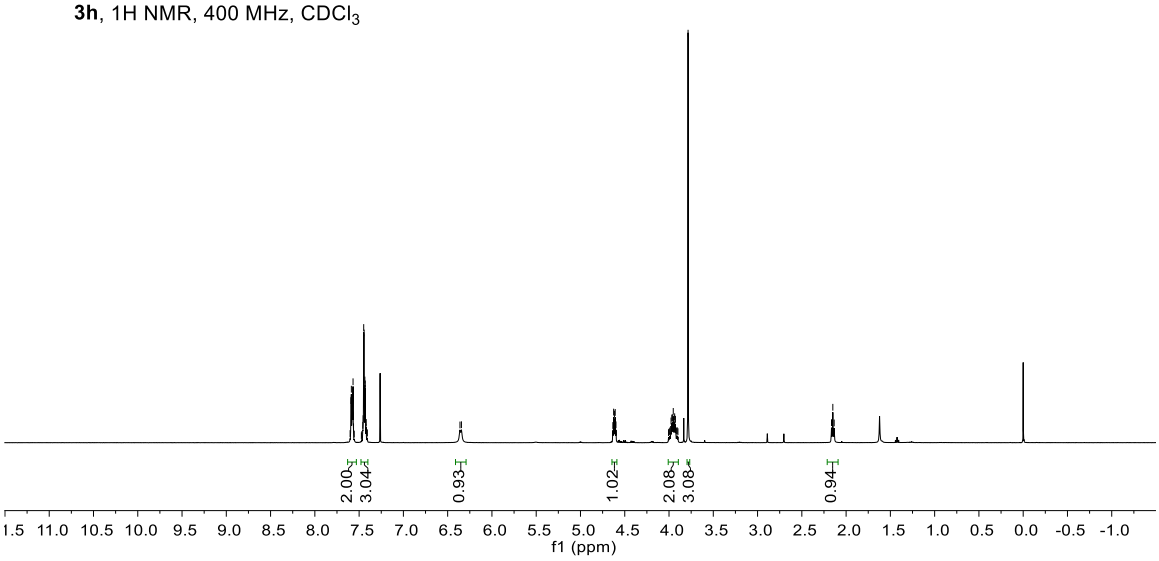


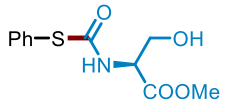


3g, ^{13}C NMR, 101 MHz, $CDCl_3$

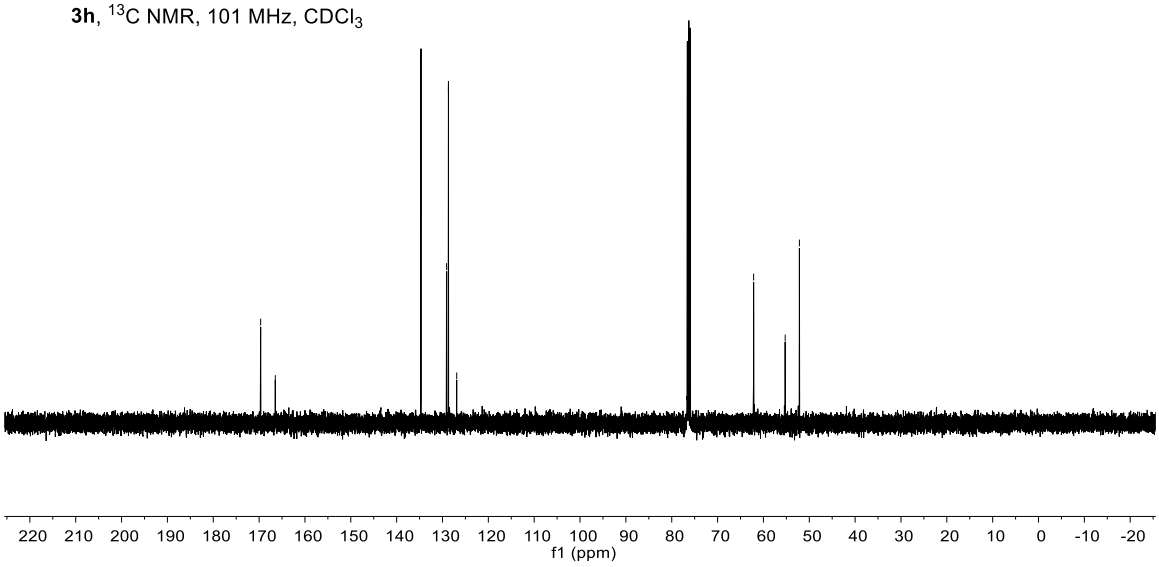


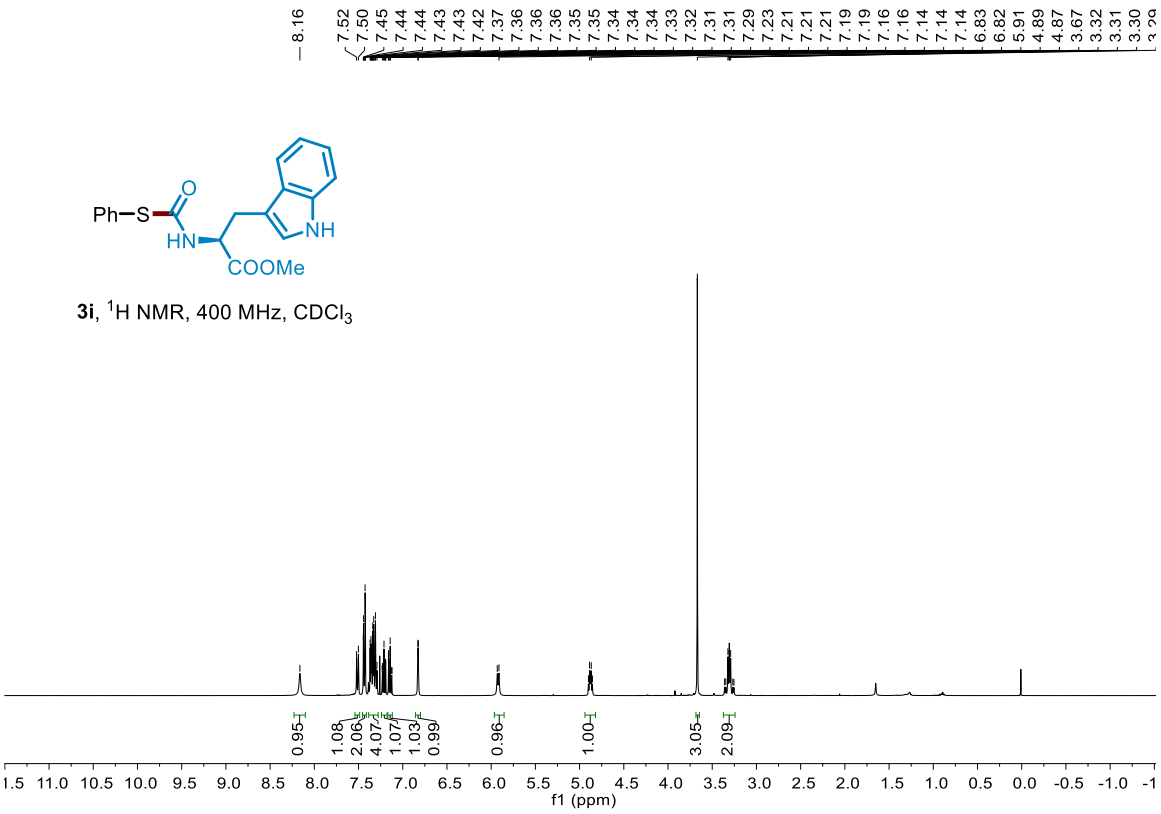
3h, 1H NMR, 400 MHz, $CDCl_3$



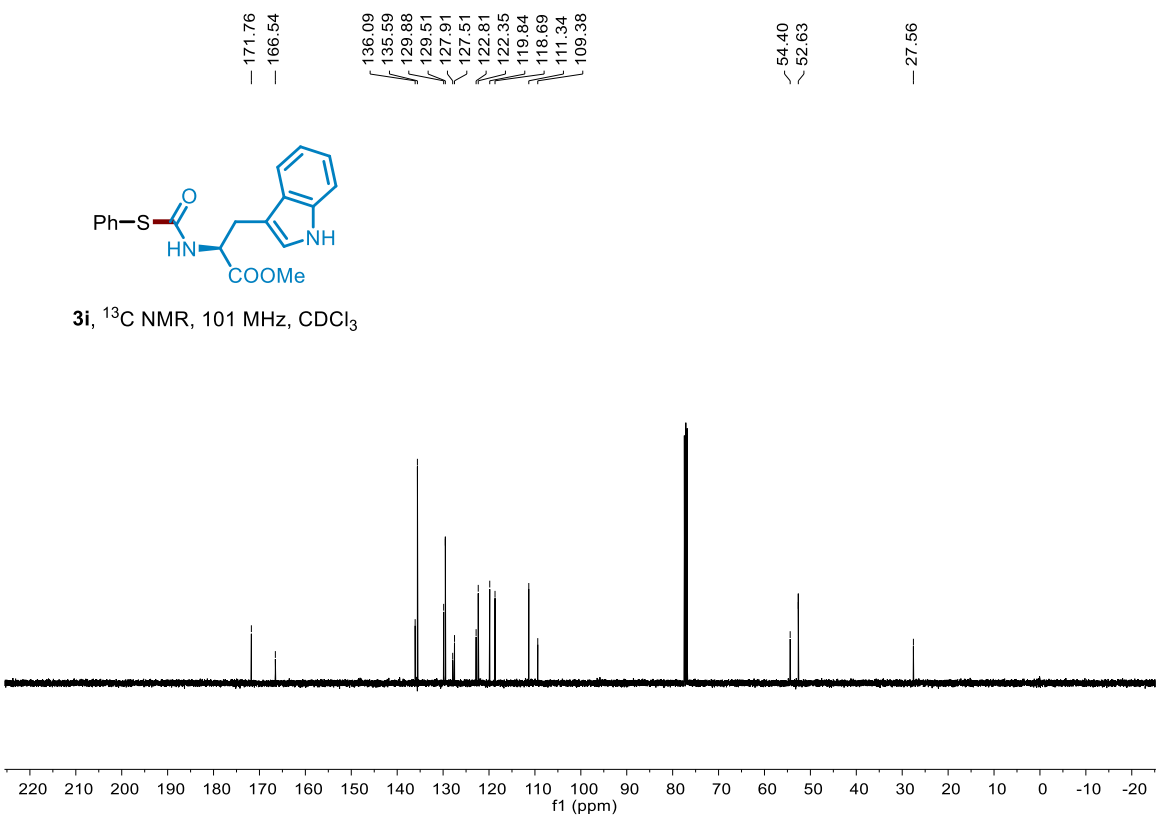


3h, ^{13}C NMR, 101 MHz, $CDCl_3$

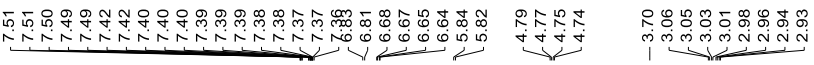


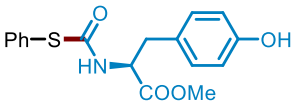


3i, ^{1}H NMR, 400 MHz, $CDCl_3$

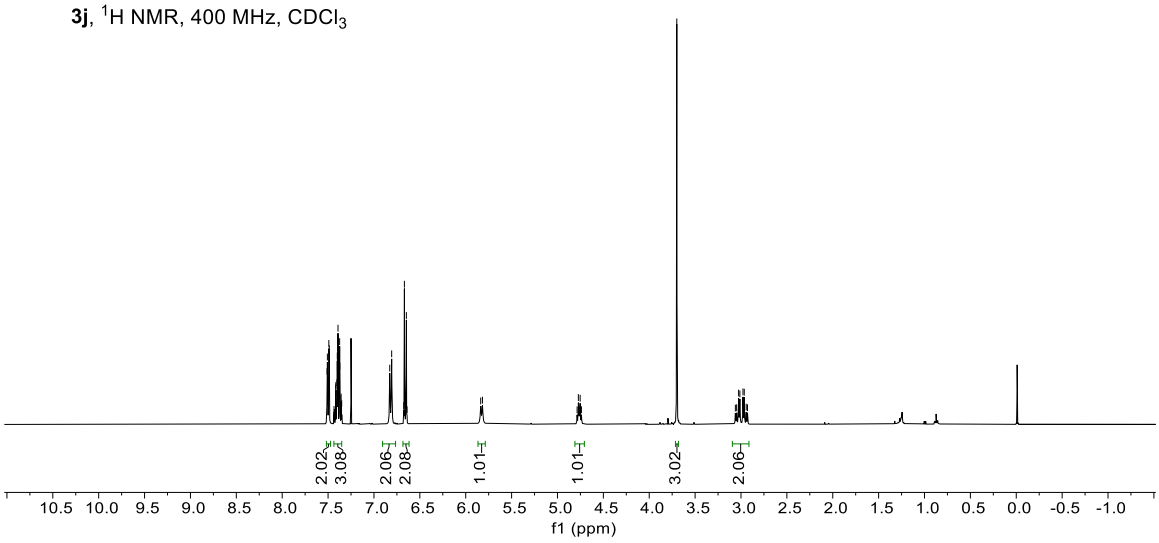


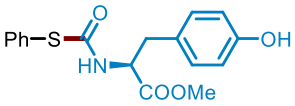
3i, ^{13}C NMR, 101 MHz, $CDCl_3$



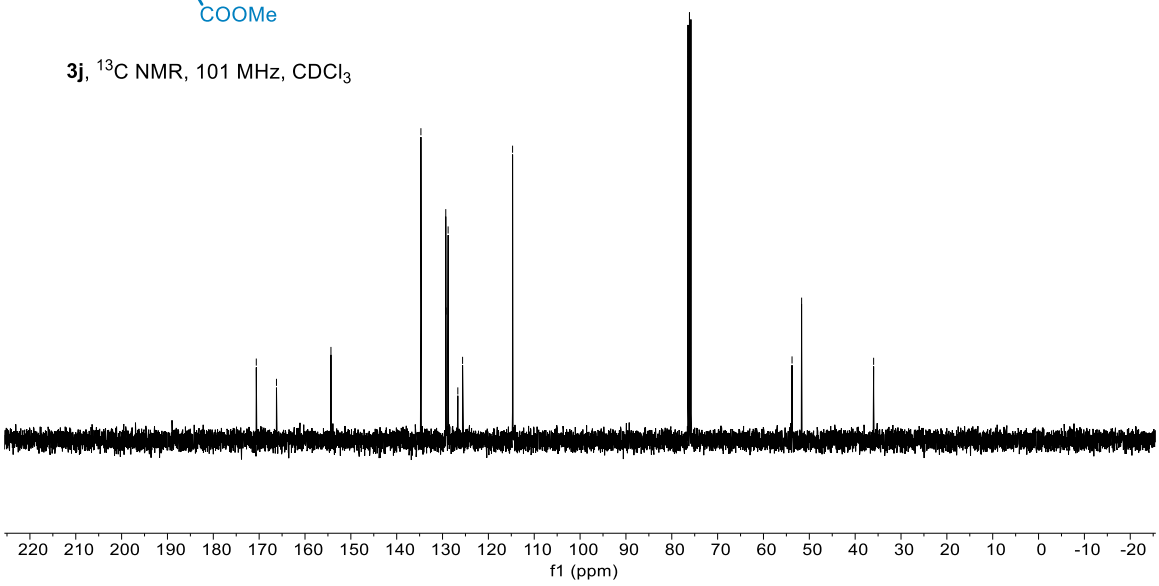


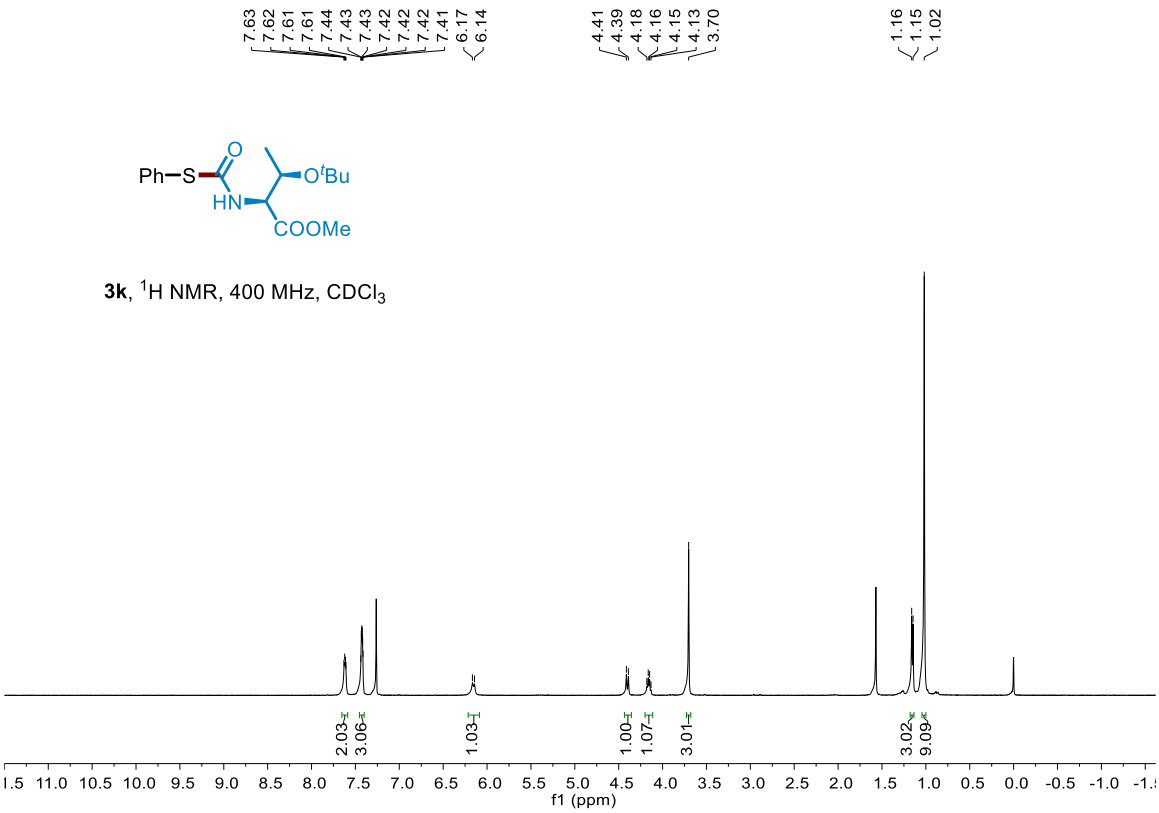
3j, ^{1}H NMR, 400 MHz, $CDCl_3$



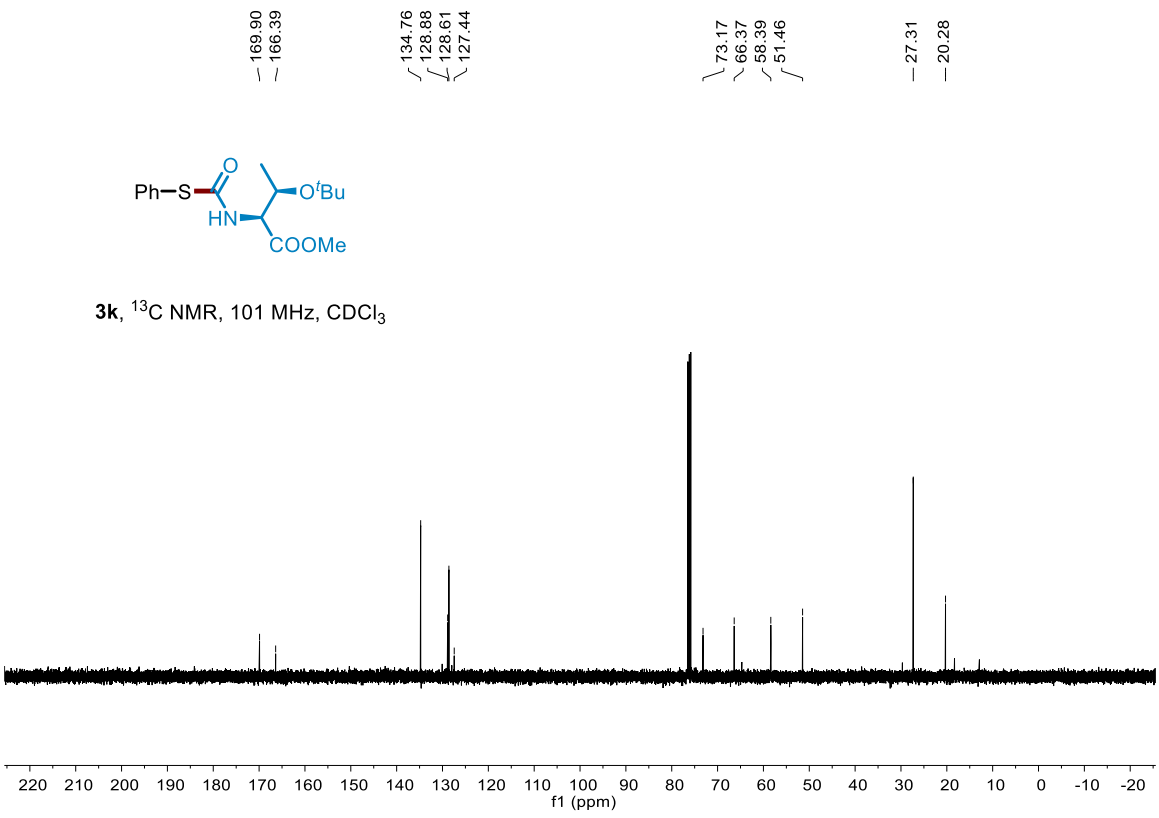


3j, ^{13}C NMR, 101 MHz, $CDCl_3$

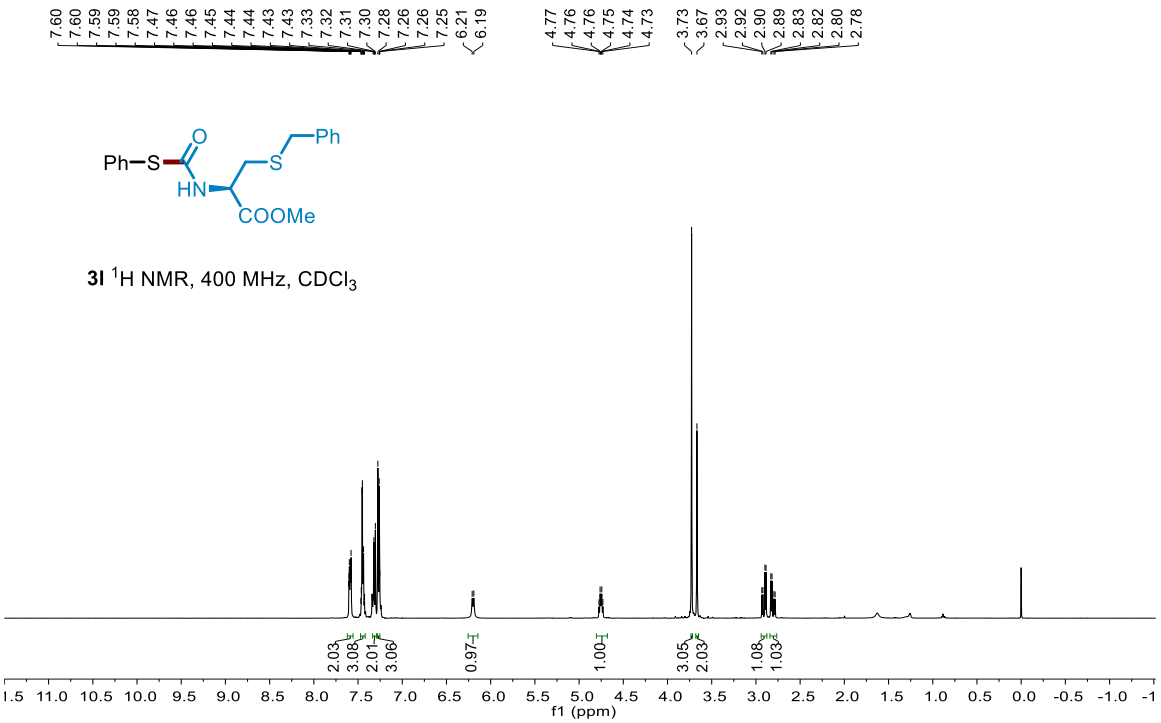




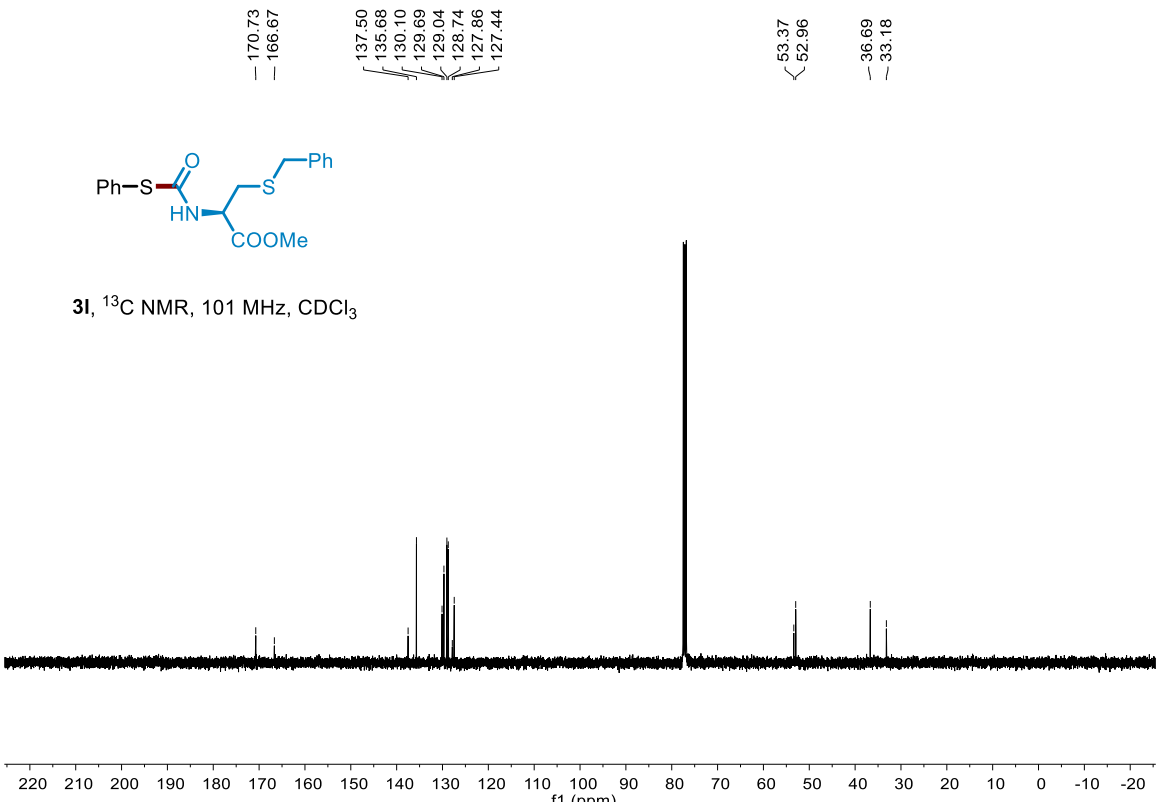
3k, ^{1}H NMR, 400 MHz, $CDCl_3$



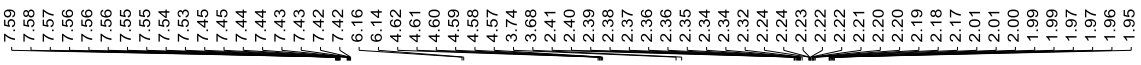
3k, ^{13}C NMR, 101 MHz, $CDCl_3$

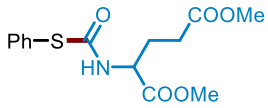


3l ^{1}H NMR, 400 MHz, $CDCl_3$

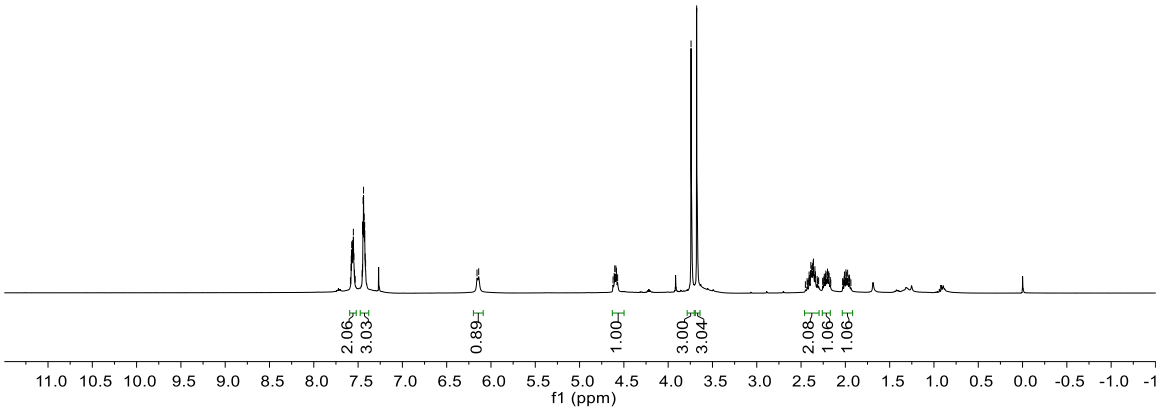


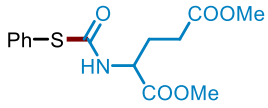
3l, ^{13}C NMR, 101 MHz, $CDCl_3$



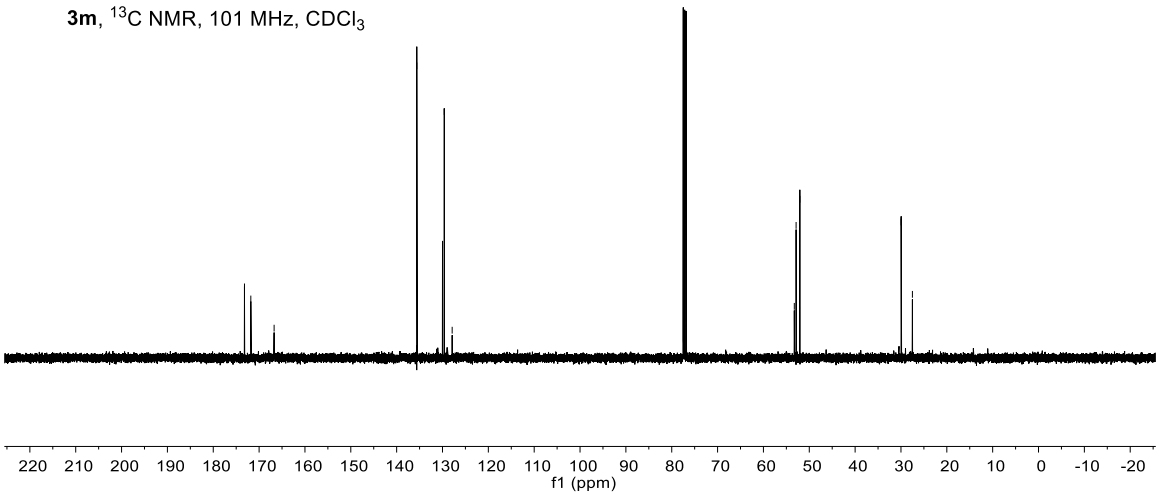


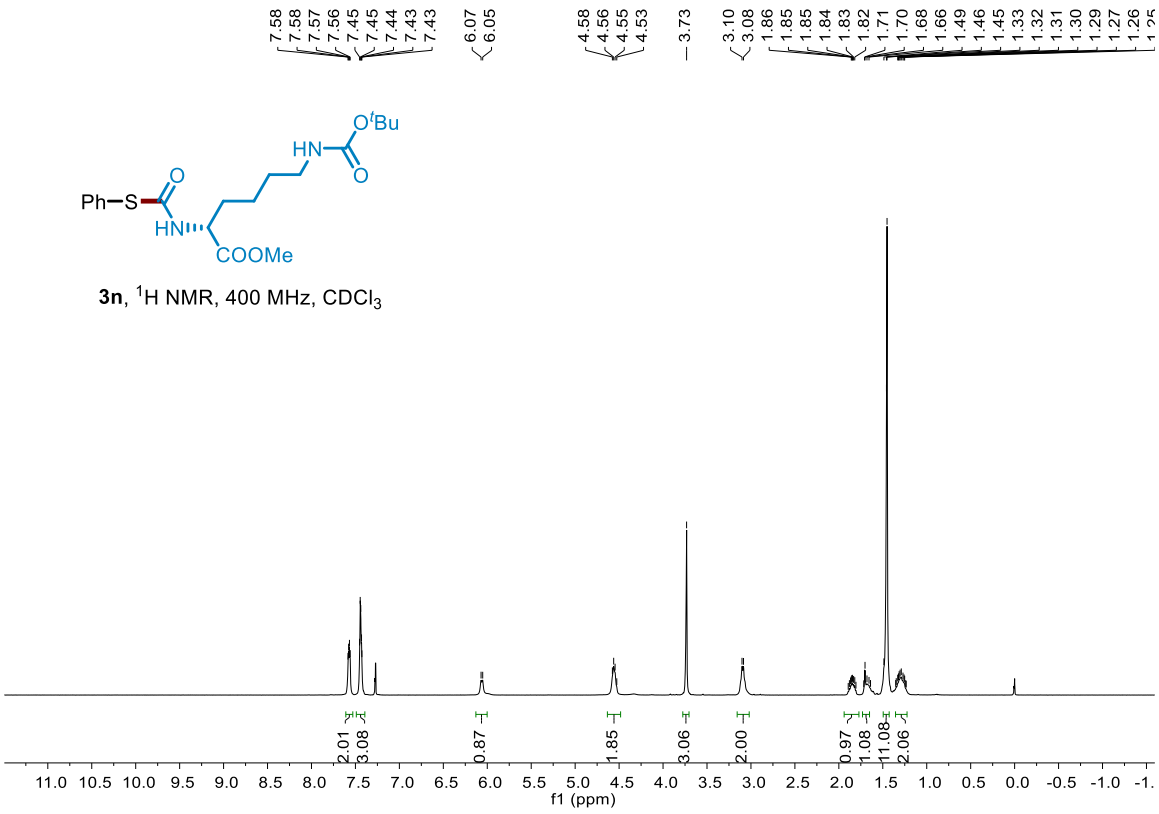
3m, ^{1}H NMR, 400 MHz, $CDCl_3$



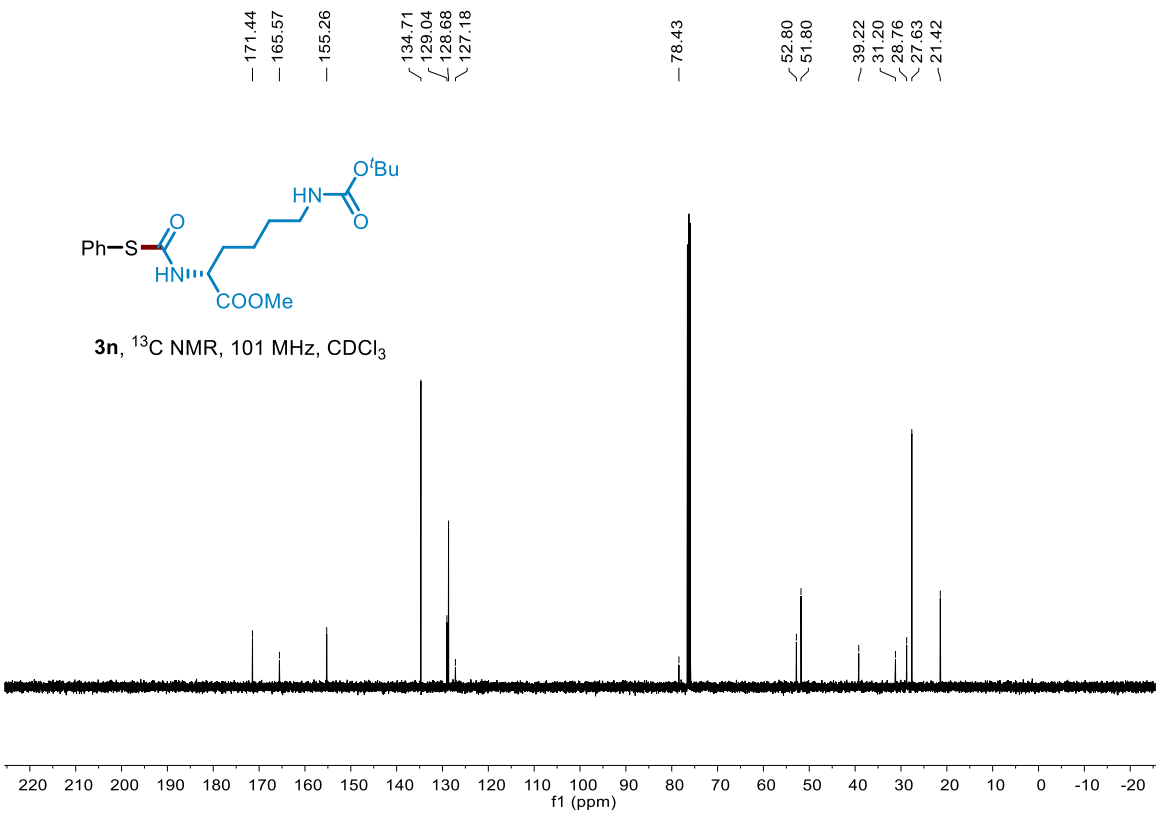


3m, ^{13}C NMR, 101 MHz, $CDCl_3$

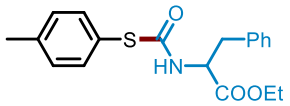




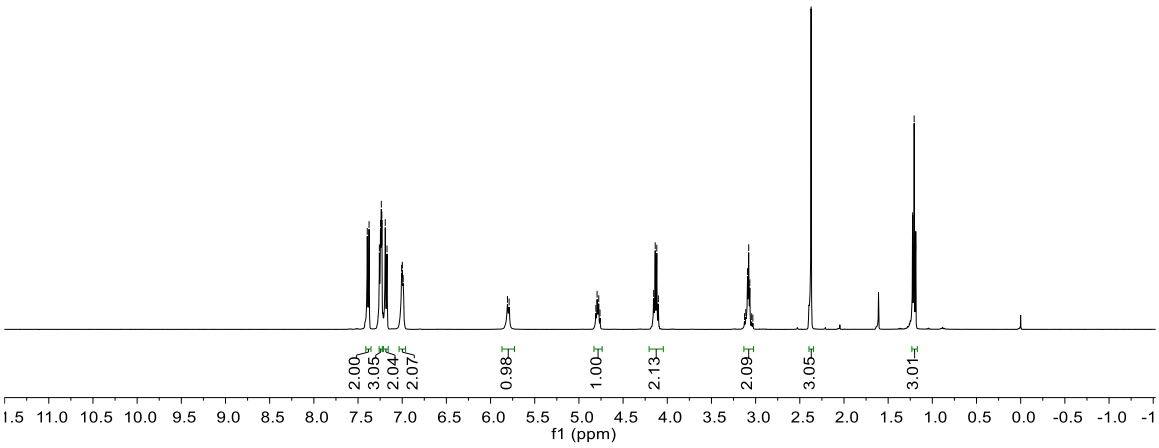
3n, ^{1}H NMR, 400 MHz, $CDCl_3$

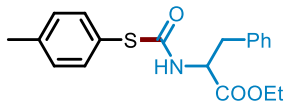


3n, ^{13}C NMR, 101 MHz, $CDCl_3$

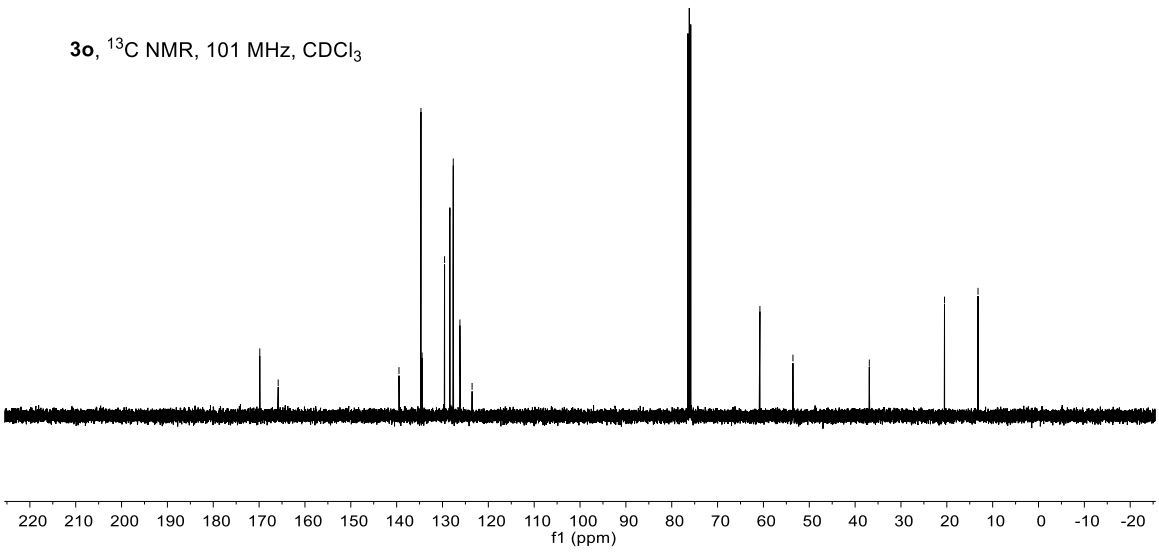


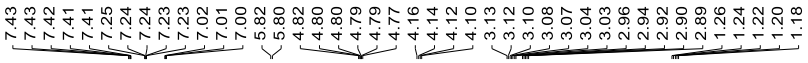
3o, ^{1}H NMR, 400 MHz, $CDCl_3$

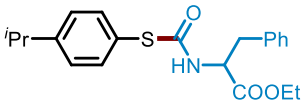




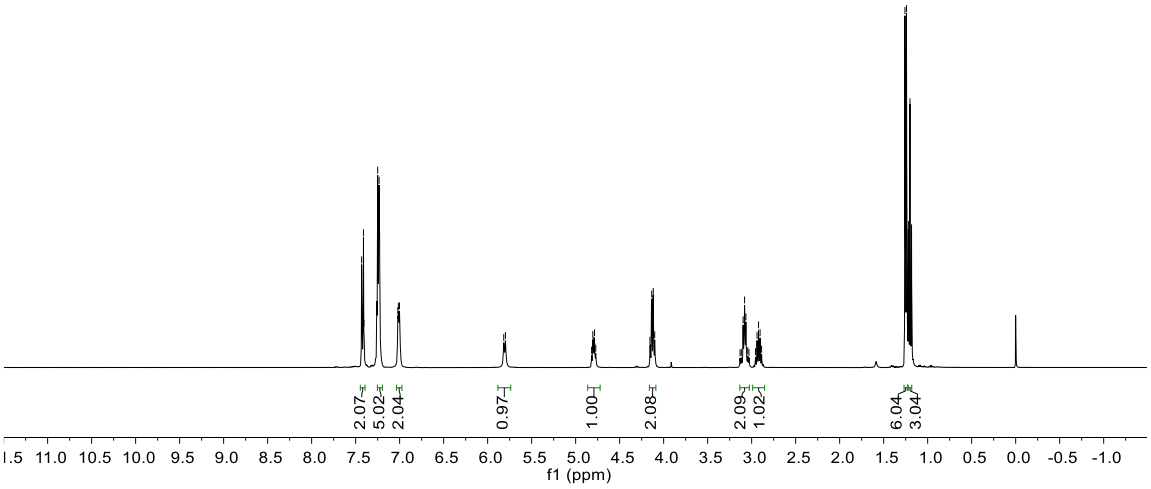
3o, ^{13}C NMR, 101 MHz, $CDCl_3$

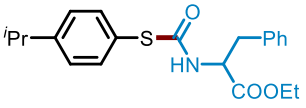




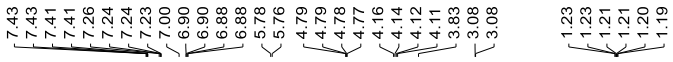


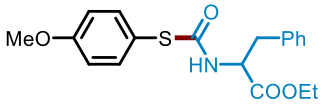
3p, ^{1}H NMR, 400 MHz, $CDCl_3$



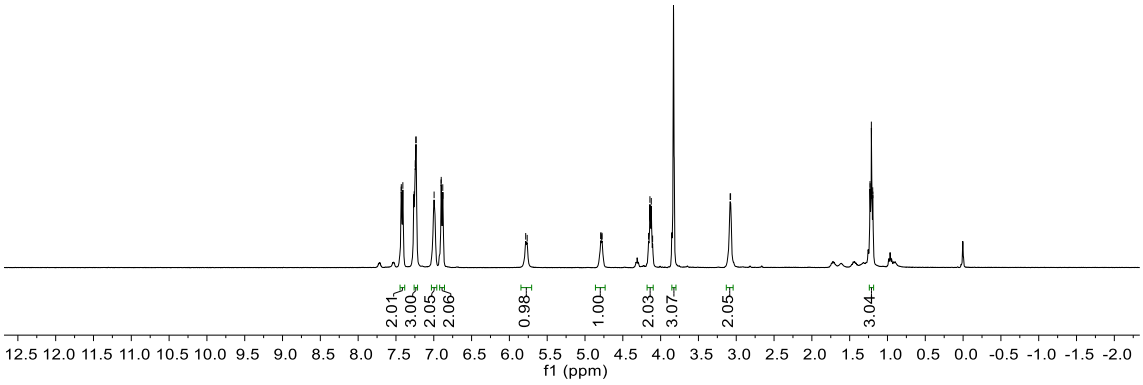


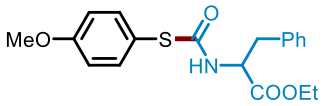
3p, ^{13}C NMR, 101 MHz, $CDCl_3$



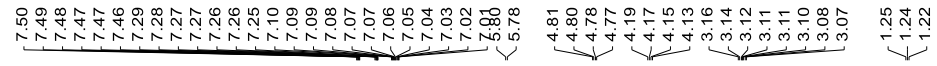


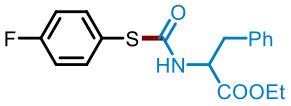
3q, ^{1}H NMR, 400 MHz, $CDCl_3$



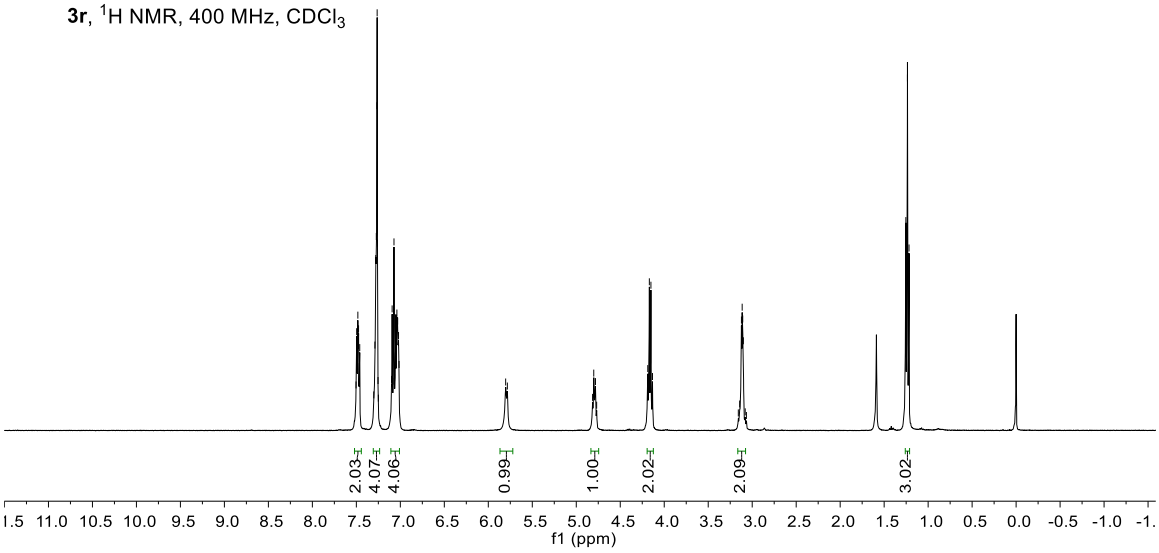


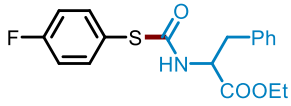
3q, ^{13}C NMR, 101 MHz, $CDCl_3$



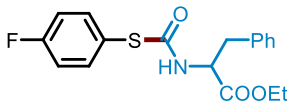


3r, ^{1}H NMR, 400 MHz, $CDCl_3$

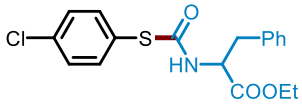




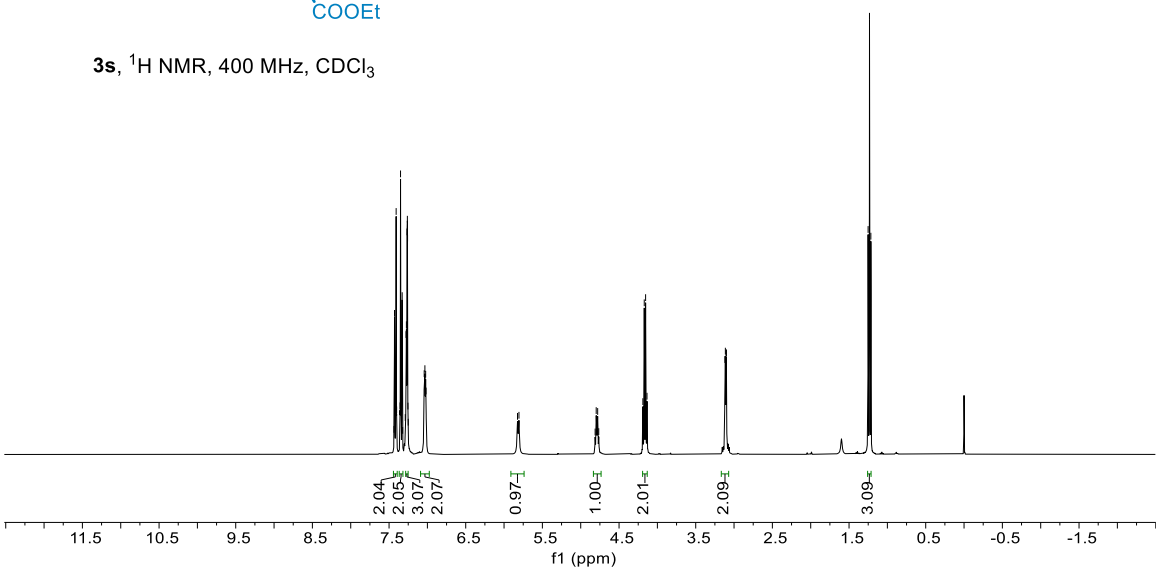
3r, ^{13}C NMR, 101 MHz, $CDCl_3$

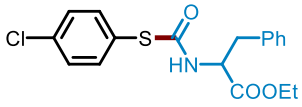


3r, ^{19}F NMR, 376 MHz, $CDCl_3$

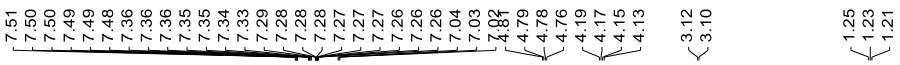


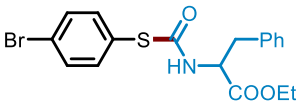
3s, ^{1}H NMR, 400 MHz, $CDCl_3$



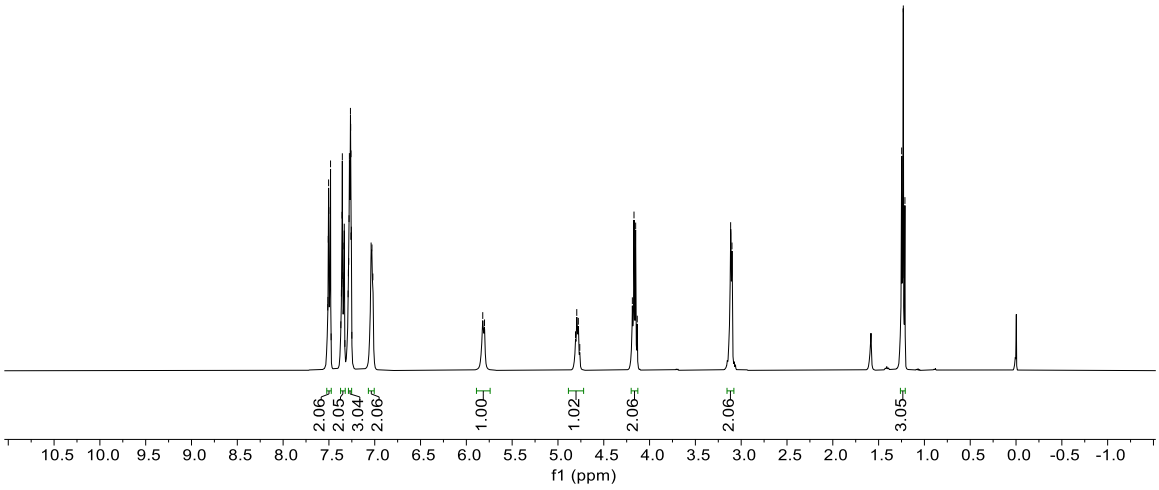


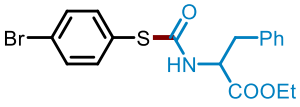
3s, ^{13}C NMR, 101 MHz, $CDCl_3$



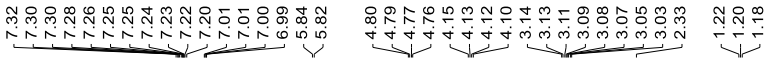


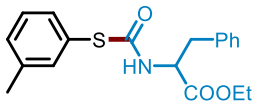
3t, ^{1}H NMR, 400 MHz, $CDCl_3$



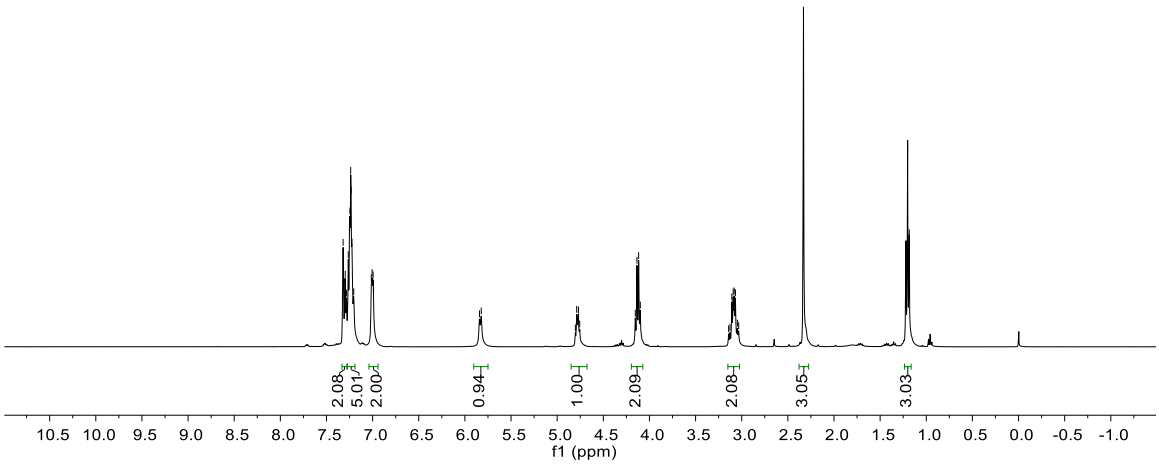


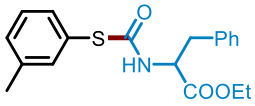
3t, ^{13}C NMR, 101 MHz, $CDCl_3$



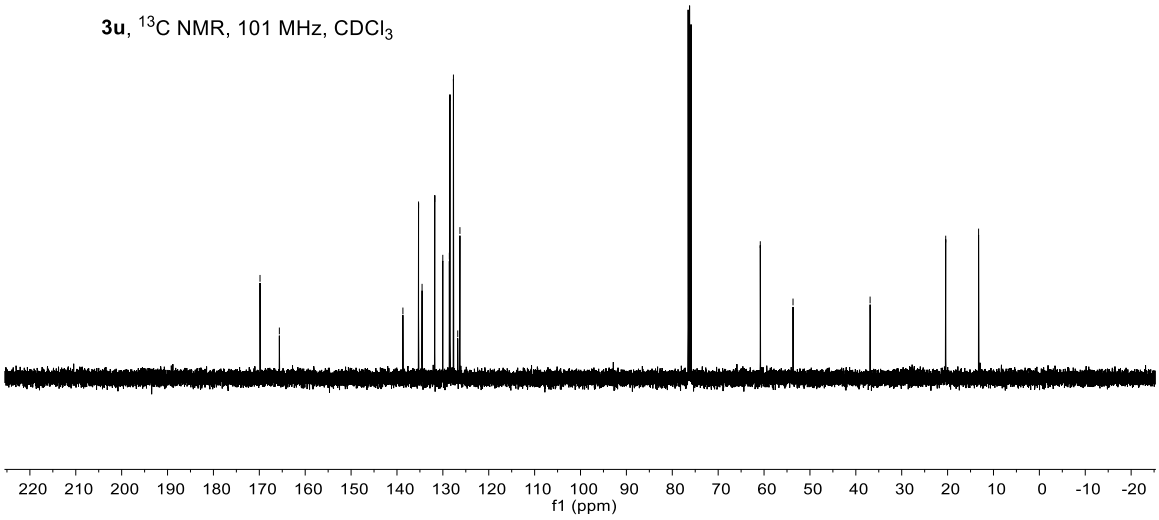


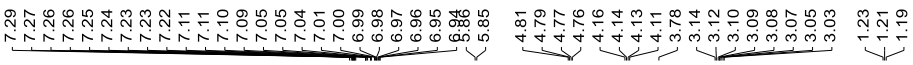
3u, ^{1}H NMR, 400 MHz, $CDCl_3$

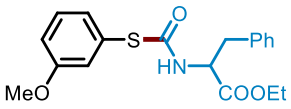




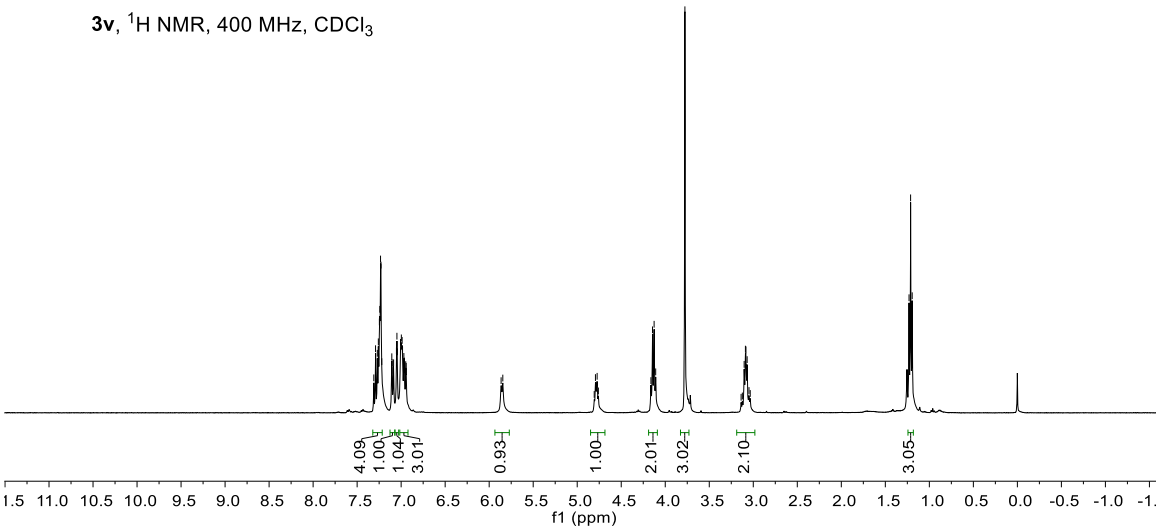
3u, ^{13}C NMR, 101 MHz, $CDCl_3$

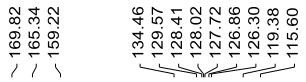


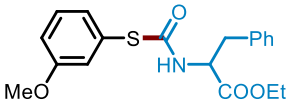




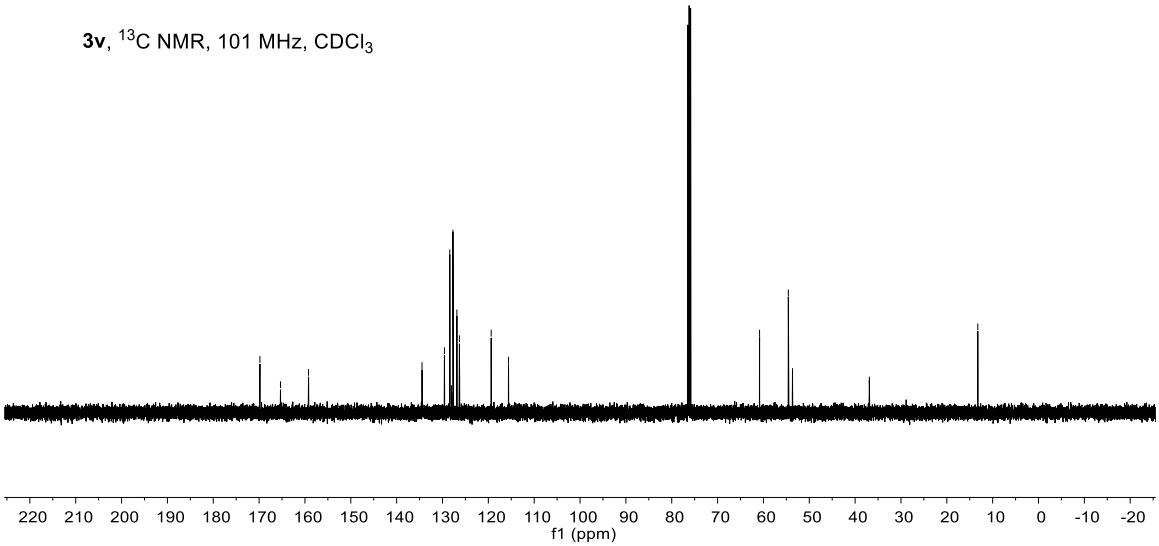
3v, ^{1}H NMR, 400 MHz, $CDCl_3$

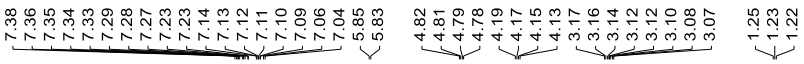


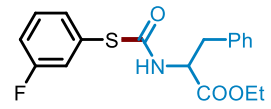




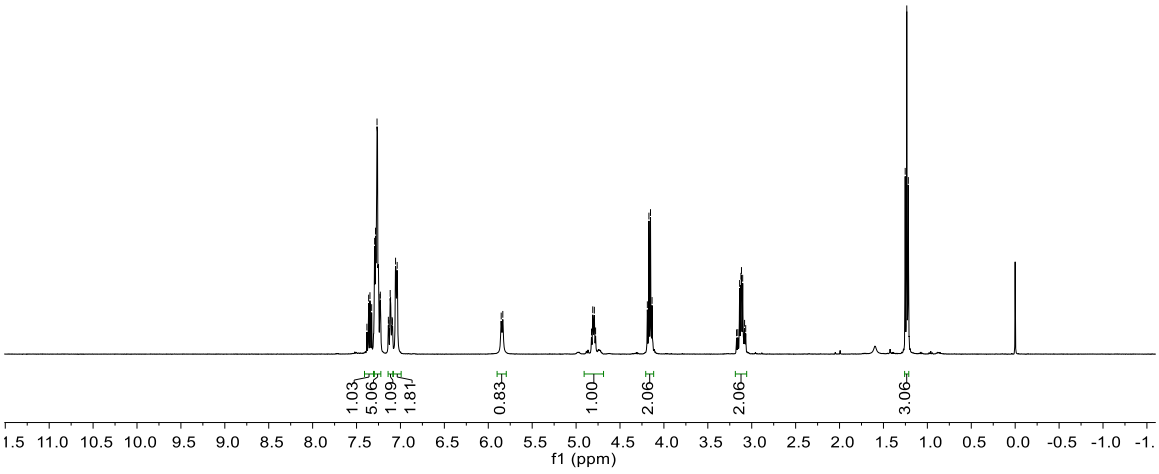
3v, ^{13}C NMR, 101 MHz, $CDCl_3$

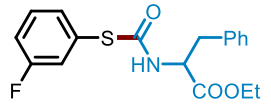




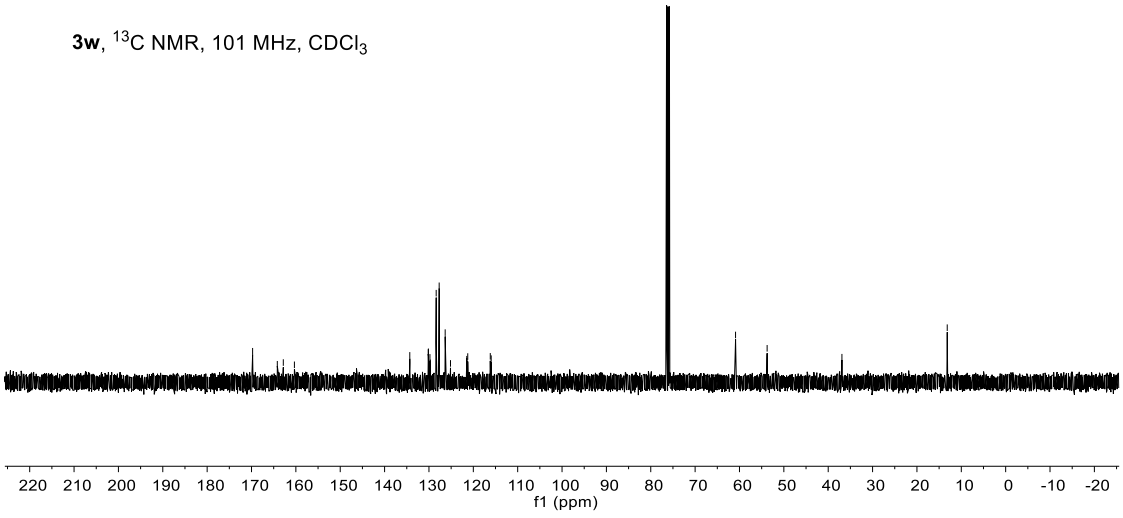


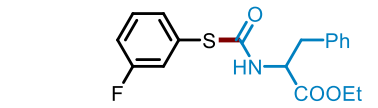
3w, ^{1}H NMR, 400 MHz, $CDCl_3$



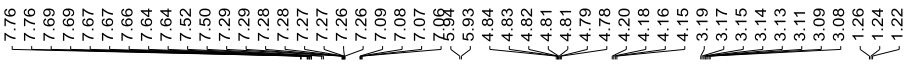


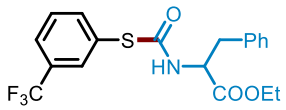
3w, ^{13}C NMR, 101 MHz, $CDCl_3$



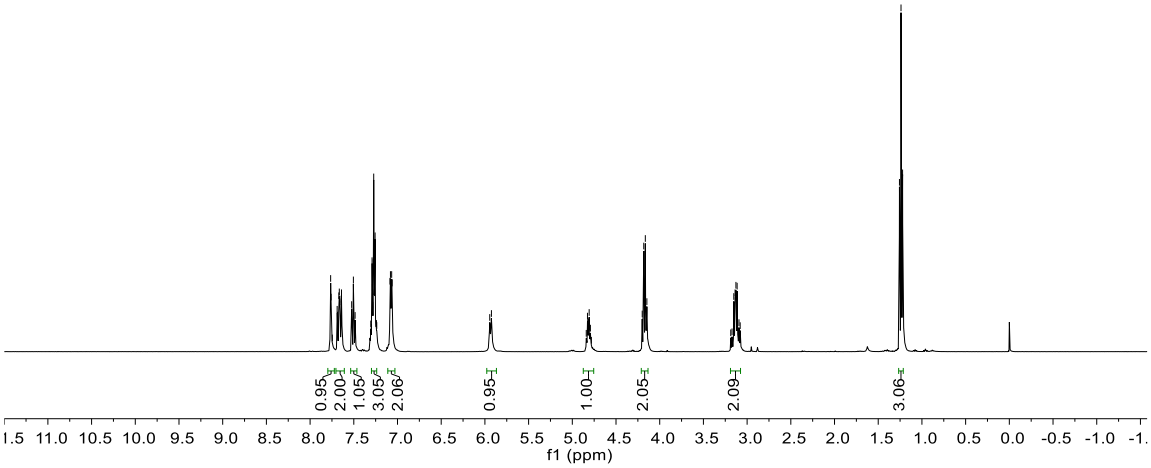


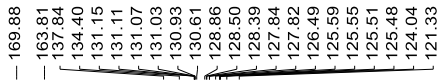
3w, ^{19}F NMR, 376 MHz, $CDCl_3$

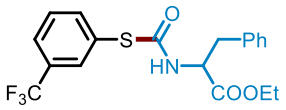




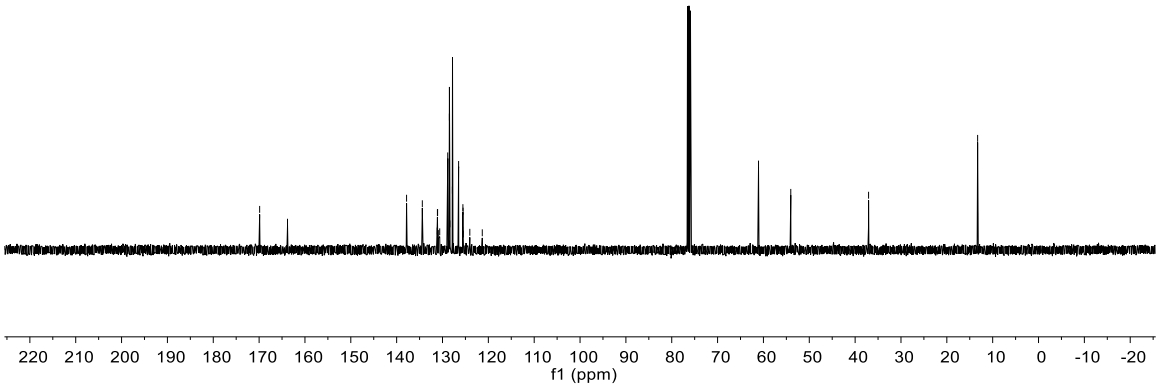
3x, ^{1}H NMR, 400 MHz, $CDCl_3$

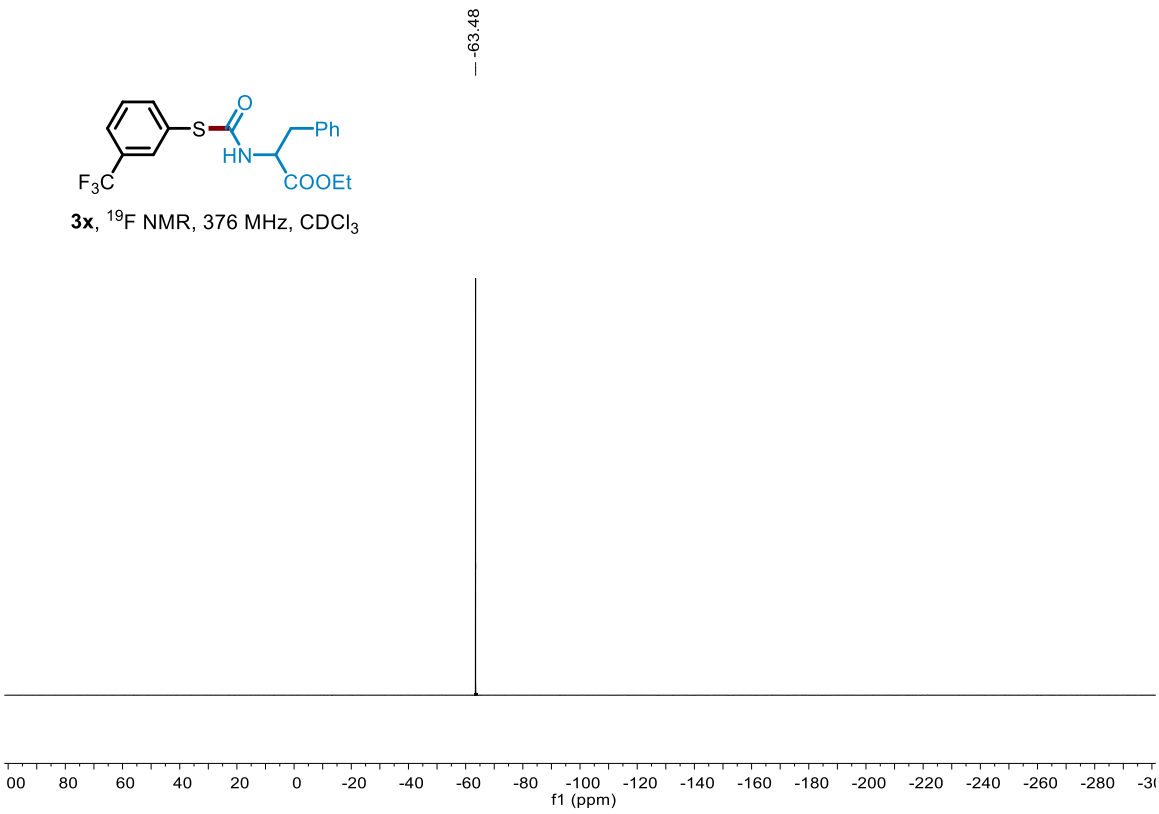




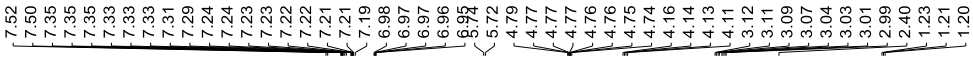


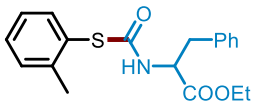
3x, ^{13}C NMR, 101 MHz, $CDCl_3$



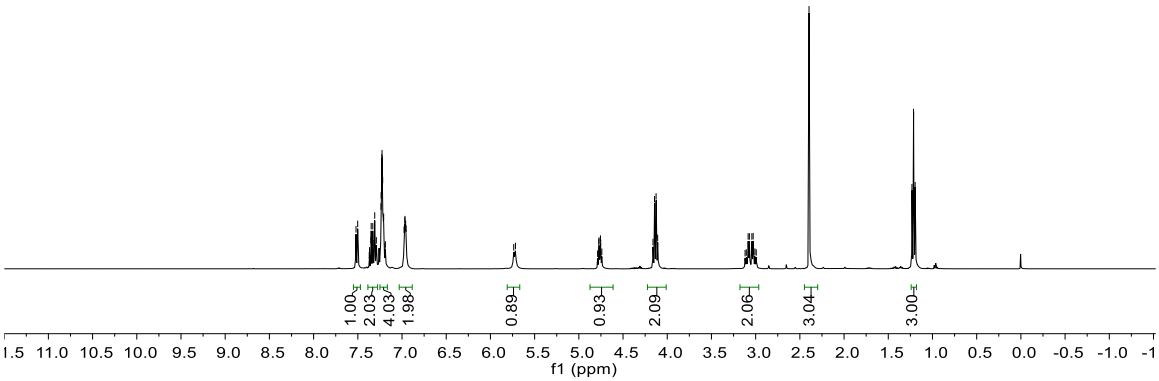


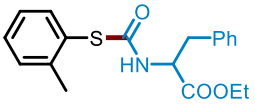
3x, ^{19}F NMR, 376 MHz, $CDCl_3$



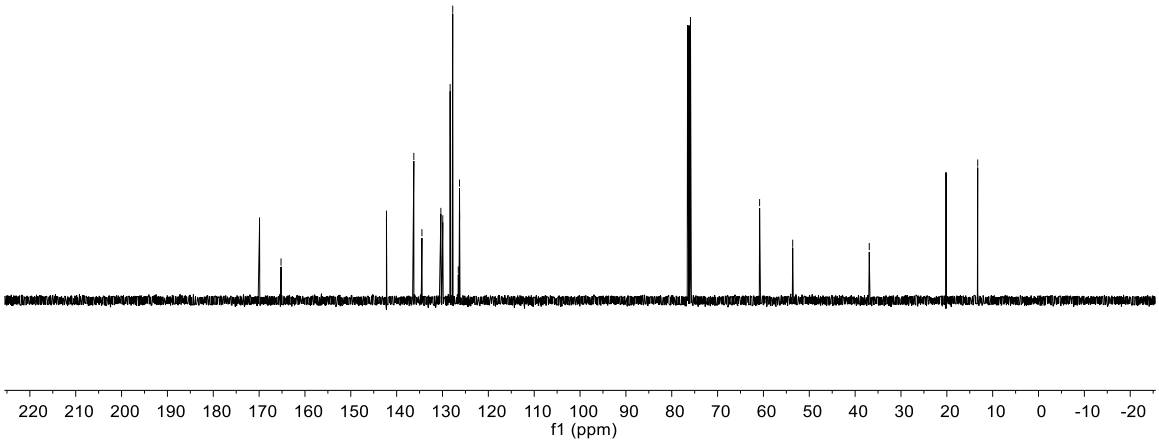


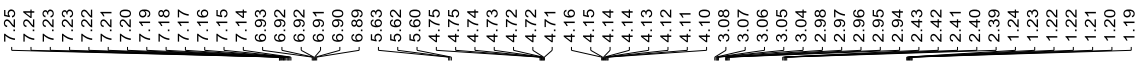
3y, ^{1}H NMR, 400 MHz, $CDCl_3$

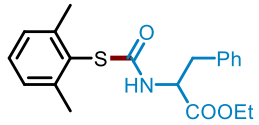




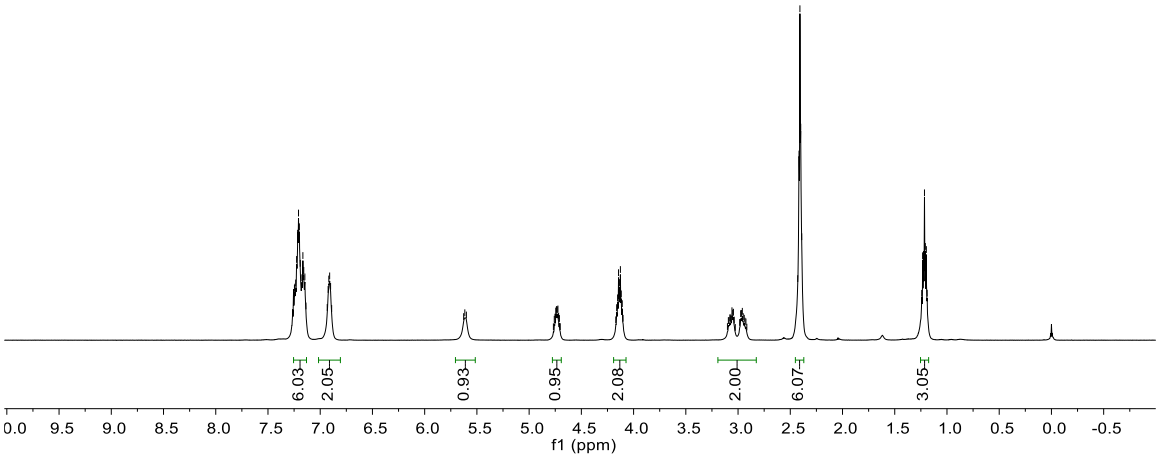
3y, ^{13}C NMR, 101 MHz, $CDCl_3$

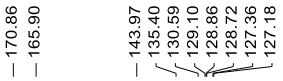


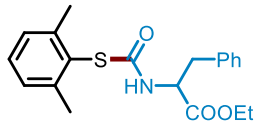




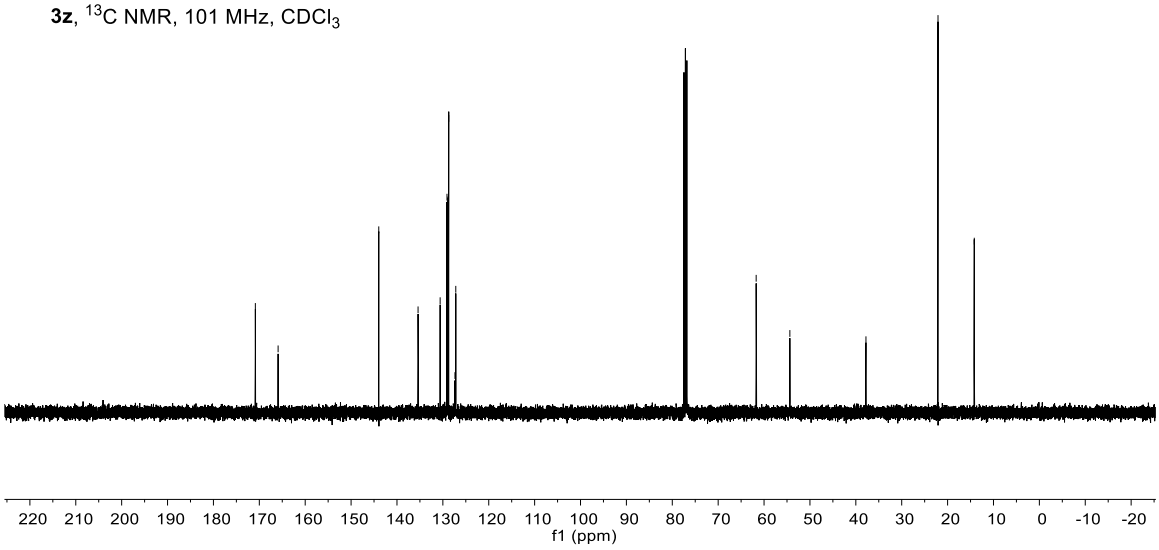
3z, ^{1}H NMR, 400 MHz, $CDCl_3$

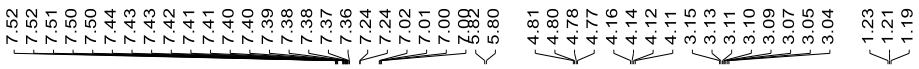


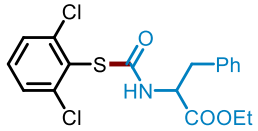




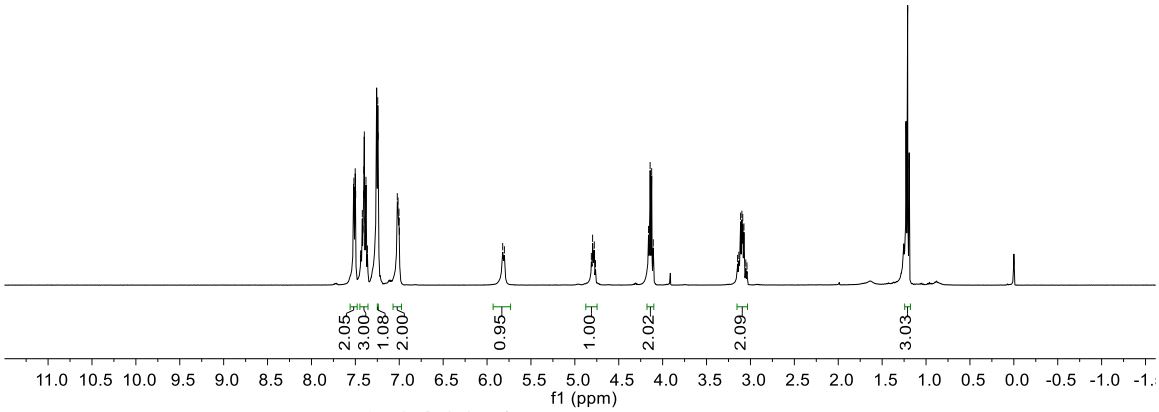
3z, ^{13}C NMR, 101 MHz, $CDCl_3$

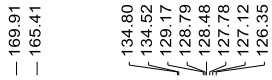


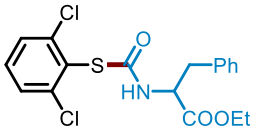




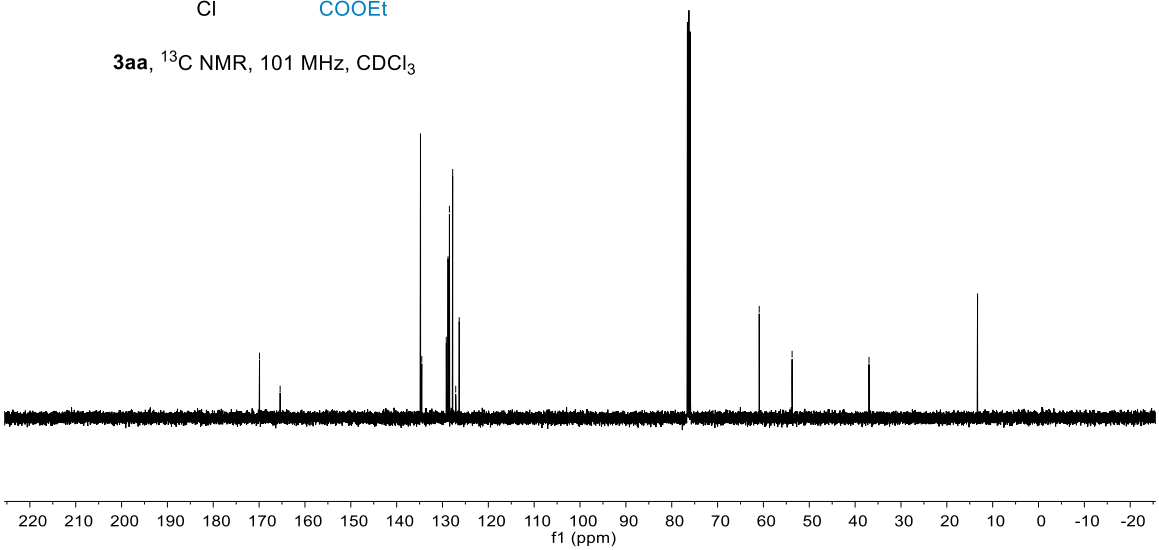
3aa, ^{1}H NMR, 400 MHz, $CDCl_3$

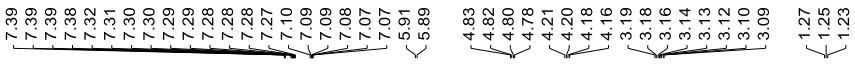


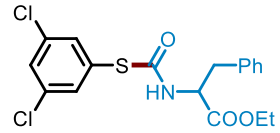




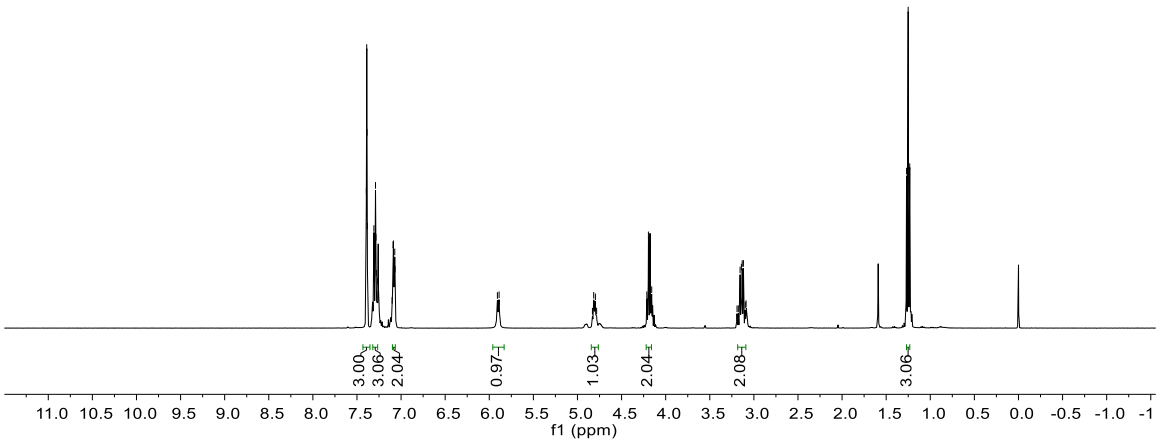
3aa, ^{13}C NMR, 101 MHz, $CDCl_3$

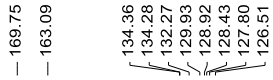


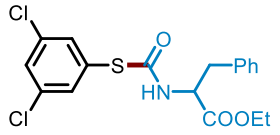




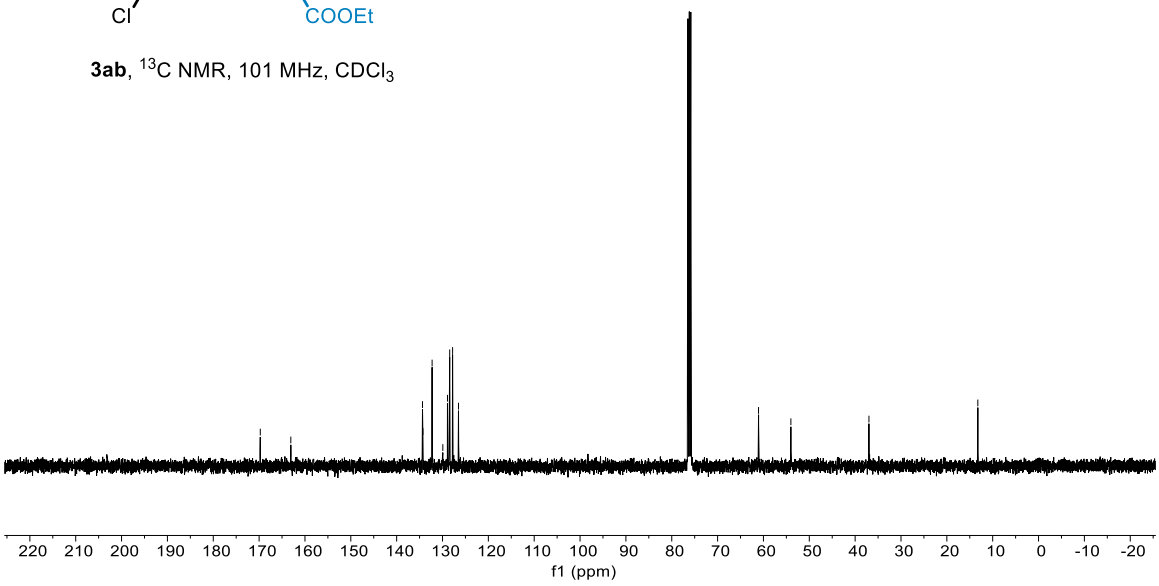
3ab, ^{1}H NMR, 400 MHz, $CDCl_3$

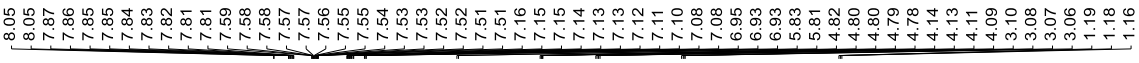


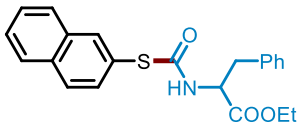




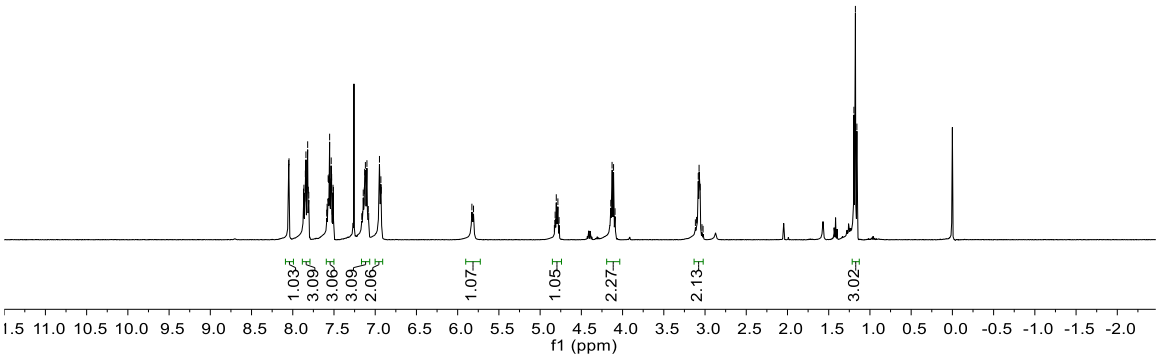
3ab, ^{13}C NMR, 101 MHz, $CDCl_3$

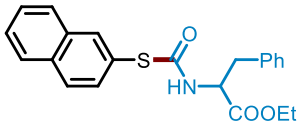




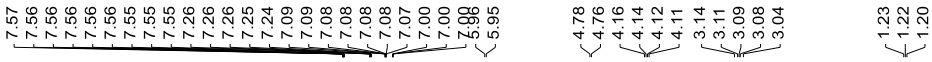


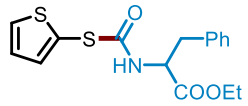
3ac, ^{1}H NMR, 400 MHz, $CDCl_3$



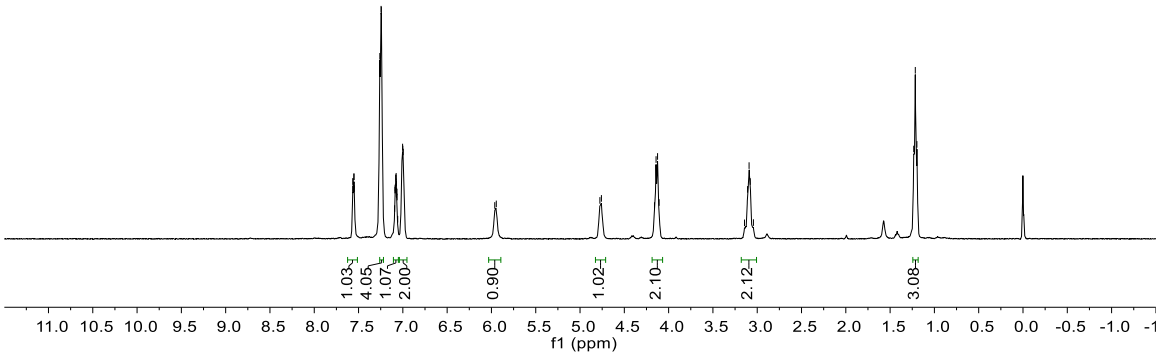


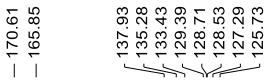
3ac, ^{13}C NMR, 101 MHz, $CDCl_3$

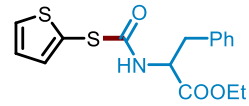




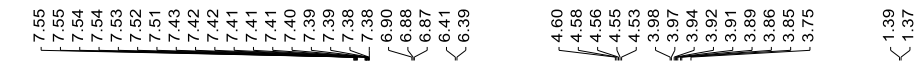
3ad, ^{1}H NMR, 400 MHz, $CDCl_3$

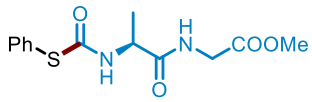




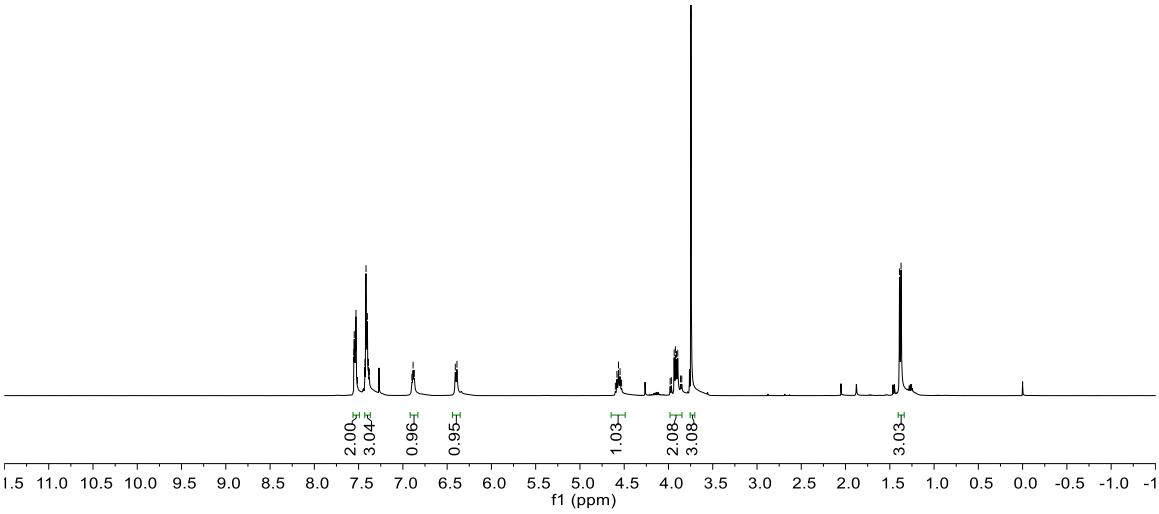


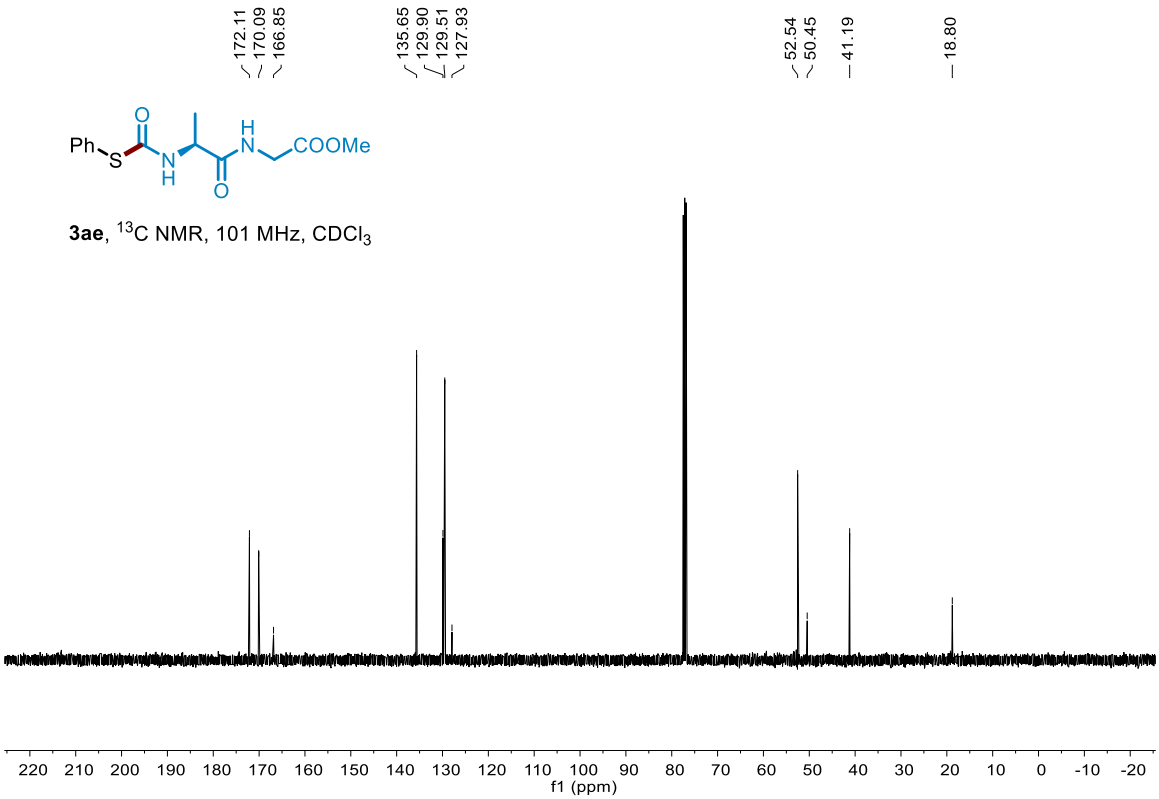
3ad, ^{13}C NMR, 101 MHz, $CDCl_3$



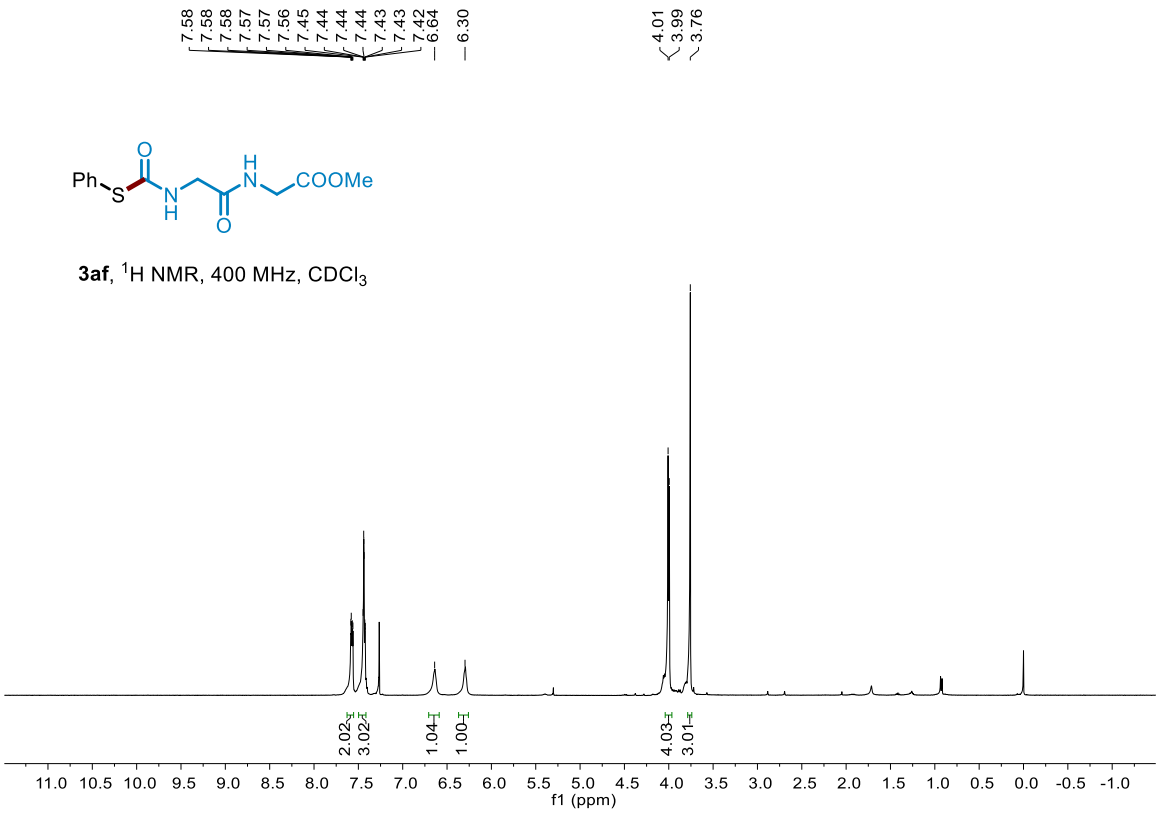


3ae, ^{1}H NMR, 400 MHz, $CDCl_3$

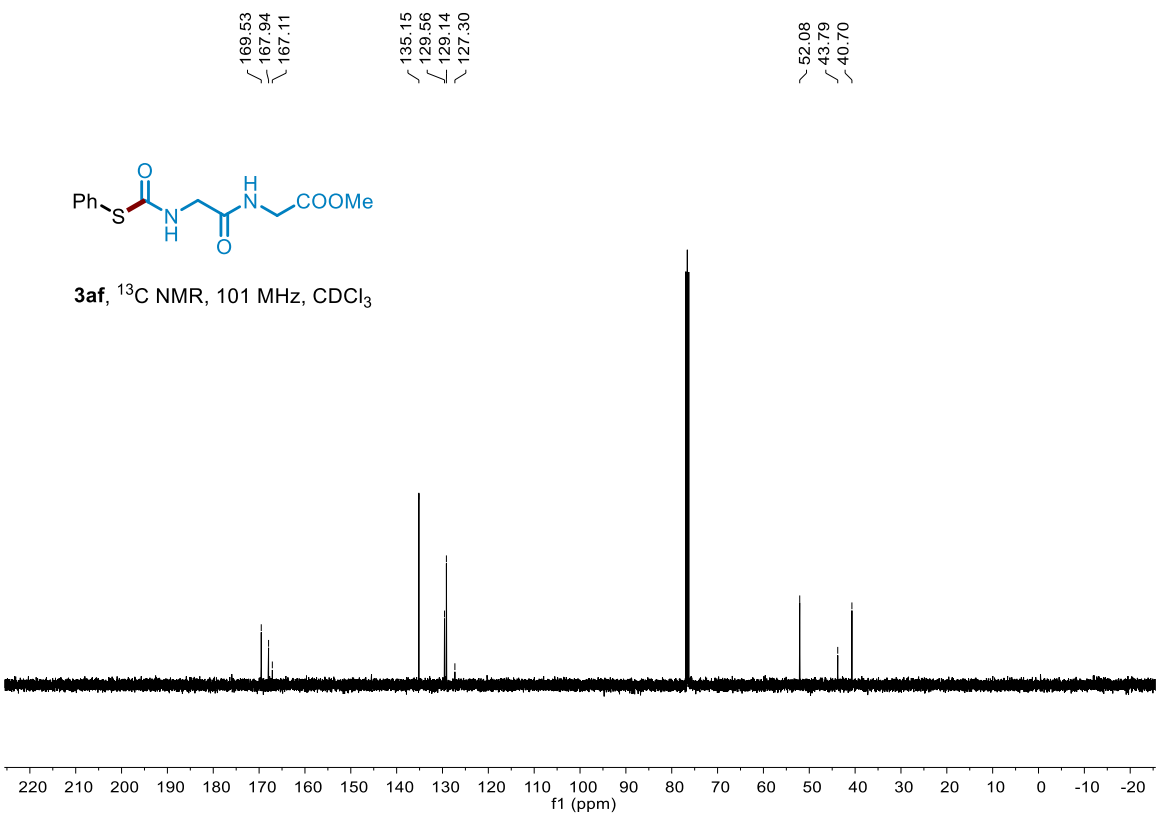




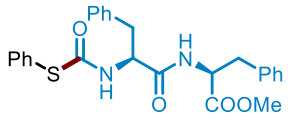
3ae, ^{13}C NMR, 101 MHz, $CDCl_3$



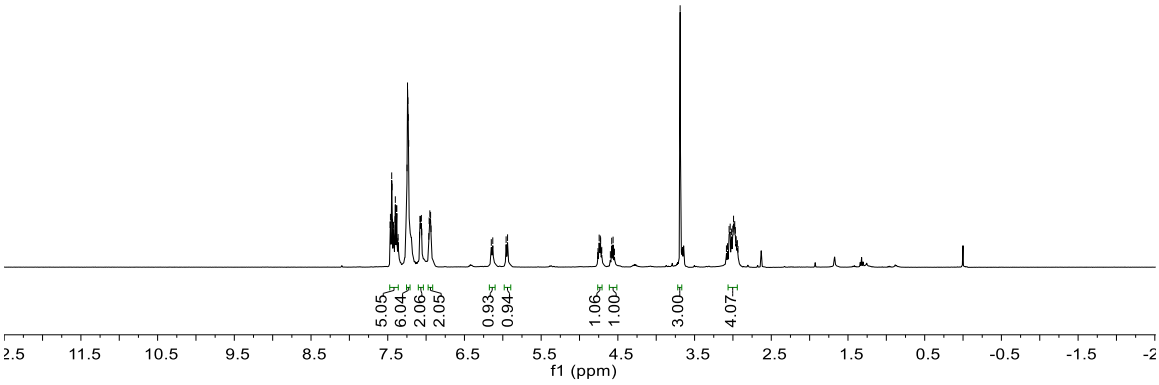
3af, ^{1}H NMR, 400 MHz, $CDCl_3$

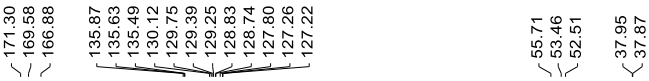


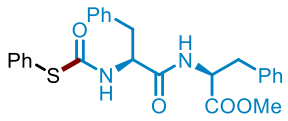
3af, ^{13}C NMR, 101 MHz, $CDCl_3$



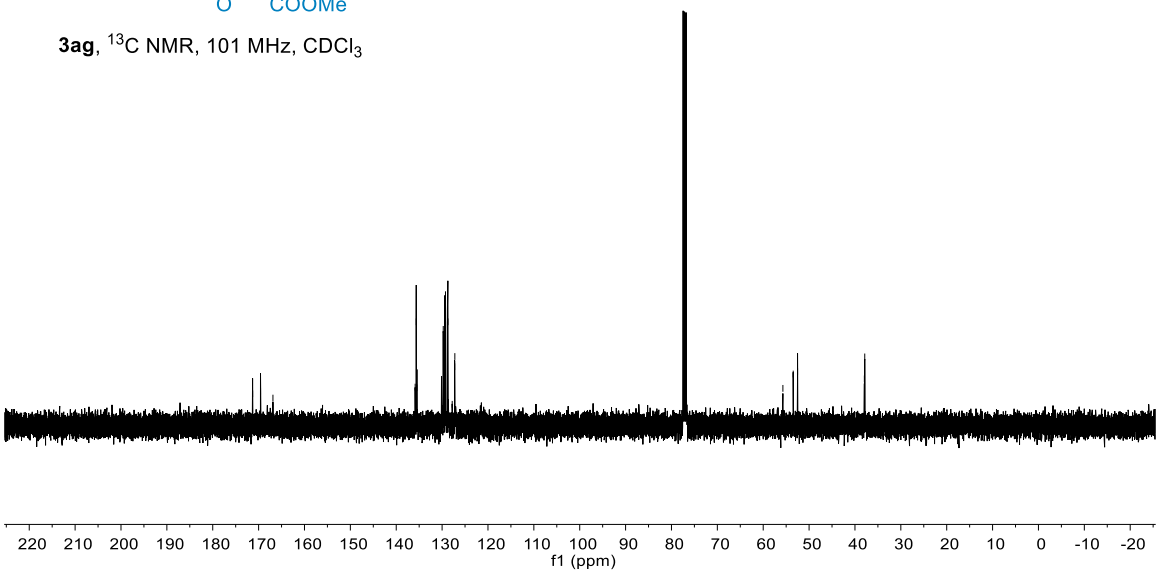
3ag, ^{1}H NMR, 400 MHz, $CDCl_3$

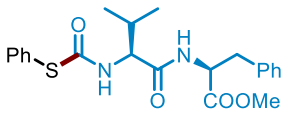




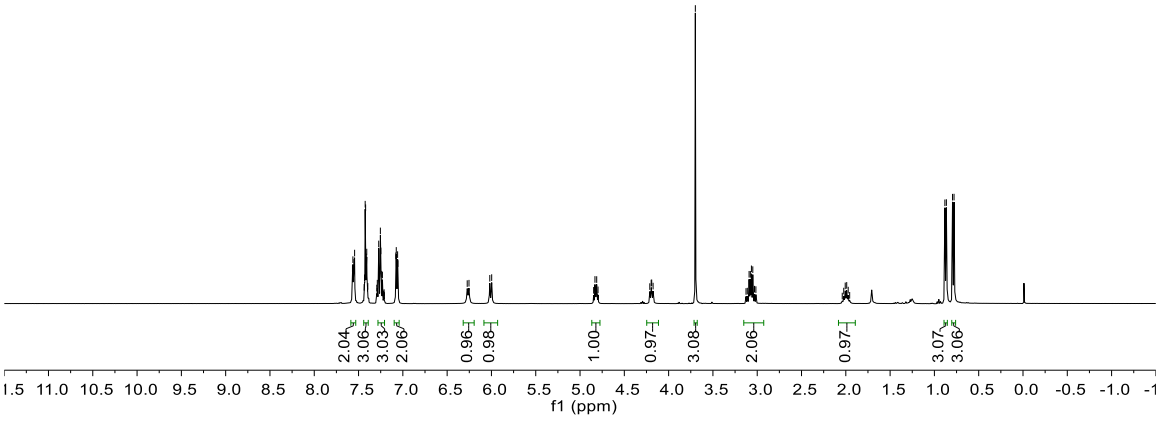


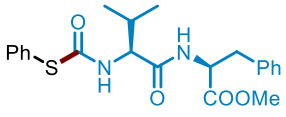
3ag, ^{13}C NMR, 101 MHz, $CDCl_3$



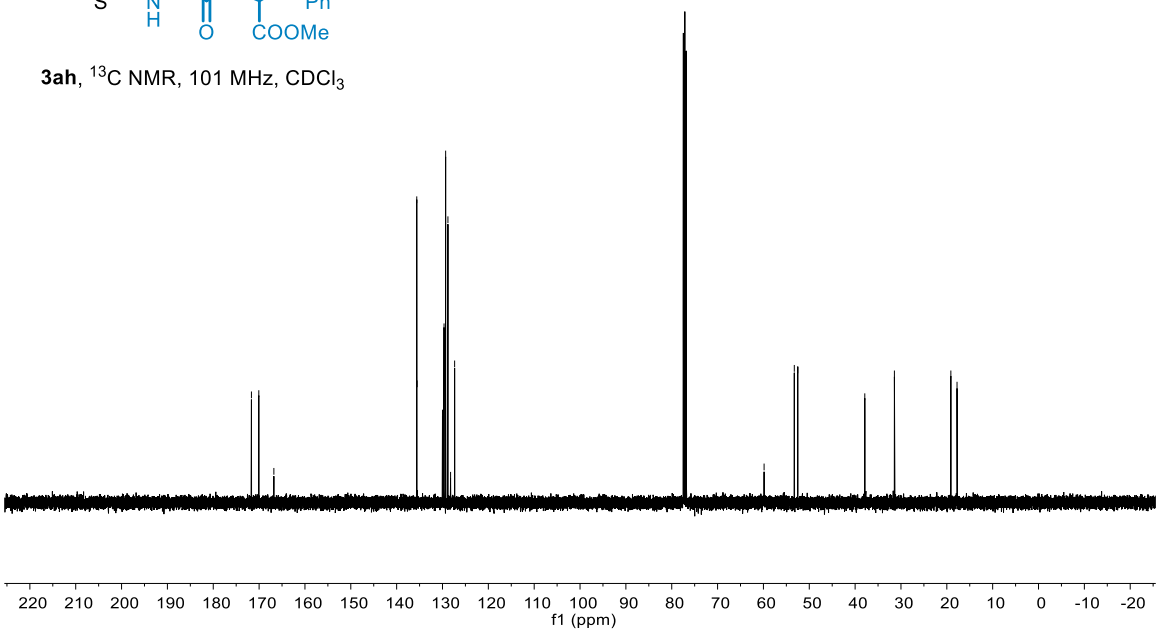


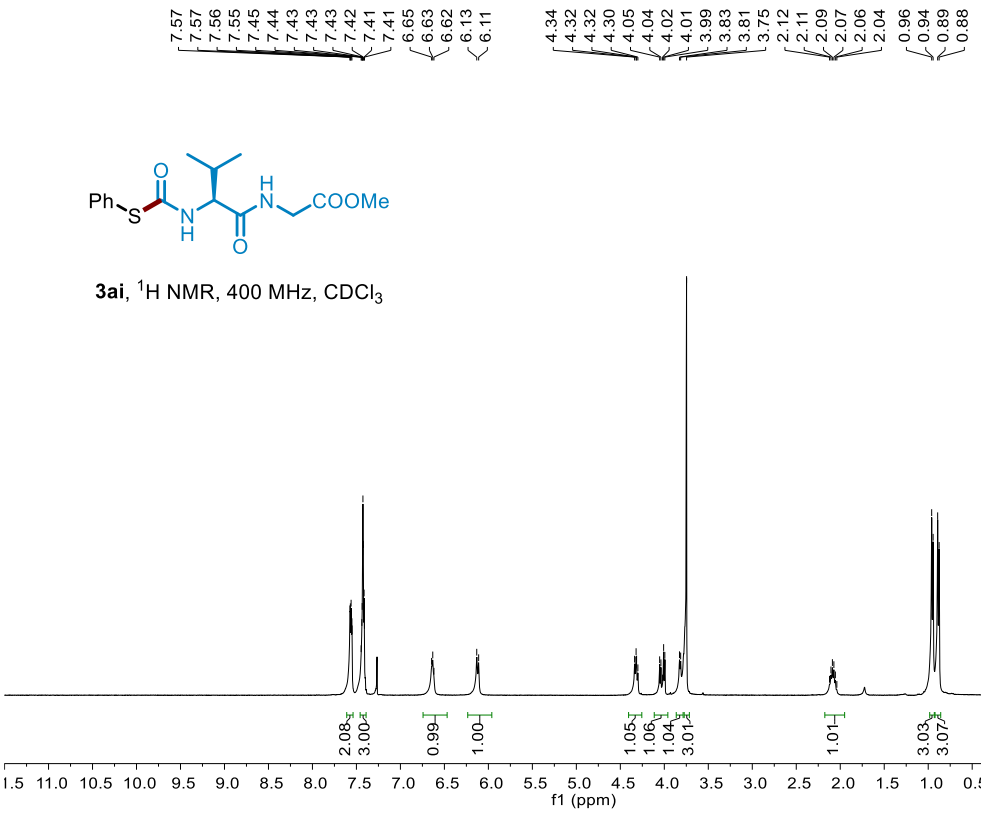
3ah, ^{1}H NMR, 400 MHz, $CDCl_3$



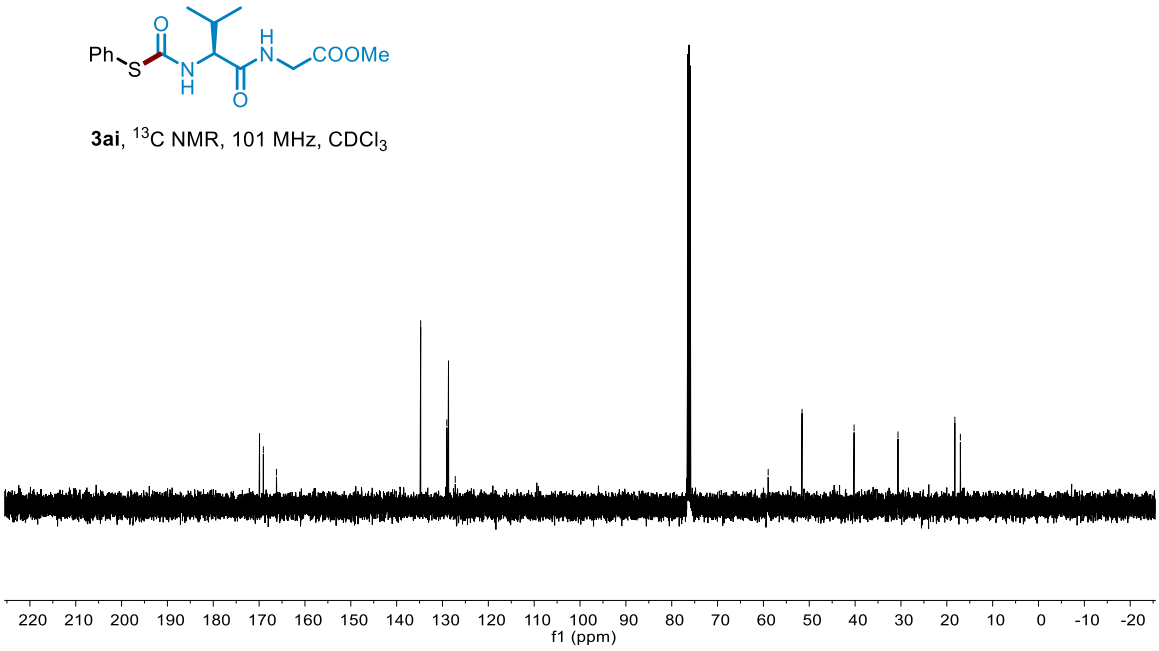


3ah, ^{13}C NMR, 101 MHz, $CDCl_3$

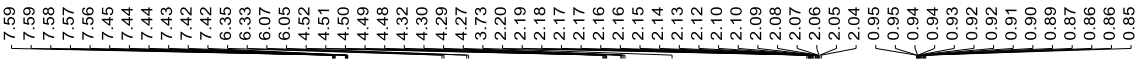


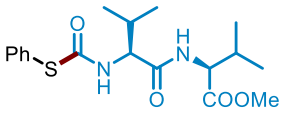


3ai, ^{1}H NMR, 400 MHz, $CDCl_3$

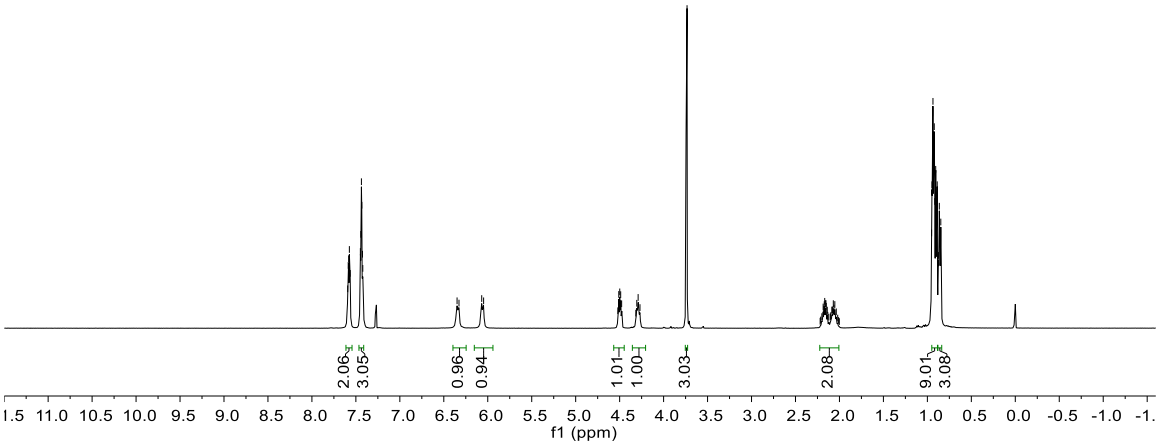


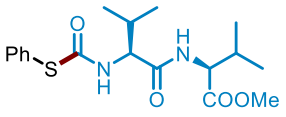
3ai, ^{13}C NMR, 101 MHz, $CDCl_3$



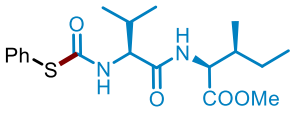


3aj, ^{1}H NMR, 400 MHz, $CDCl_3$

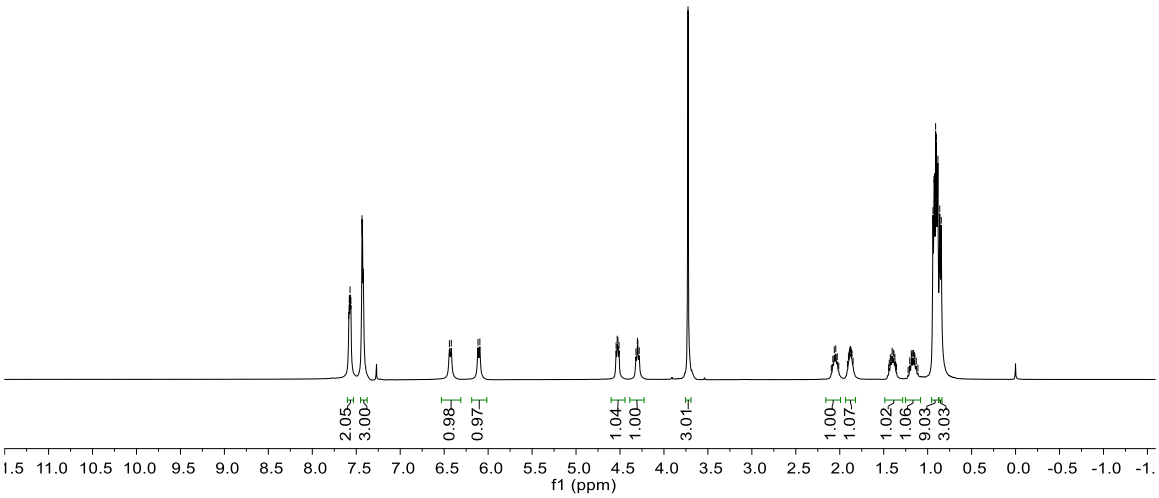


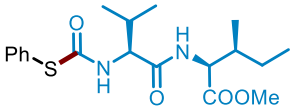


3aj, ^{13}C NMR, 101 MHz, $CDCl_3$

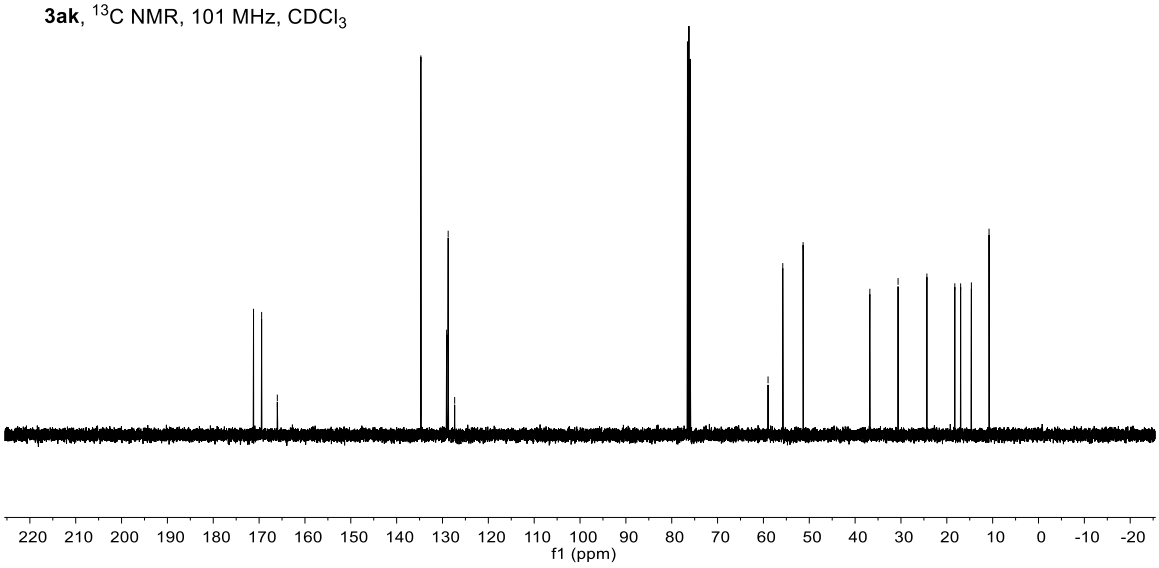


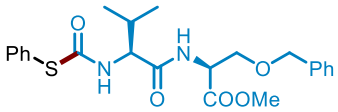
3ak, ^{1}H NMR, 400 MHz, $CDCl_3$



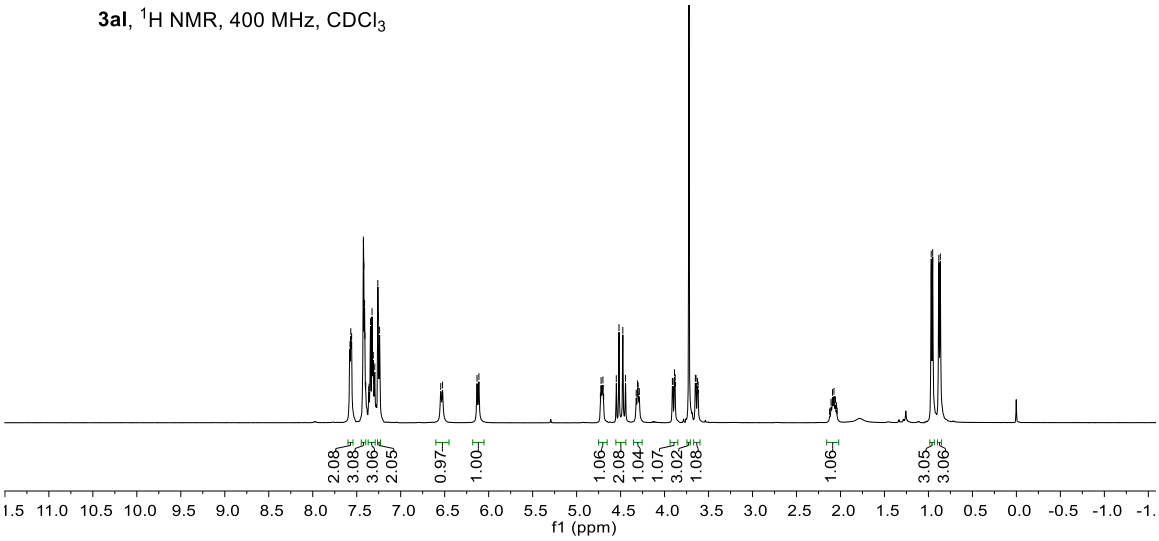


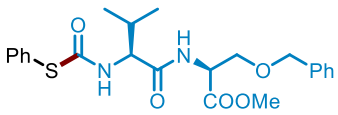
3ak, ^{13}C NMR, 101 MHz, $CDCl_3$



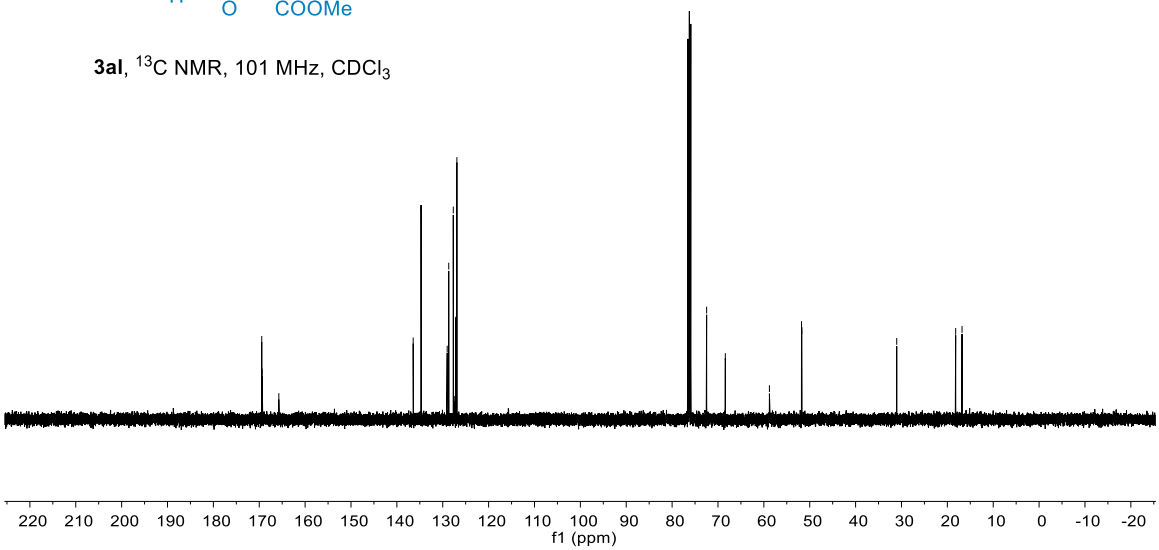


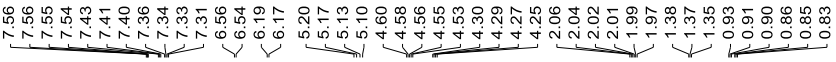
3al, ^{1}H NMR, 400 MHz, $CDCl_3$

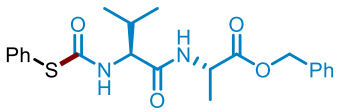




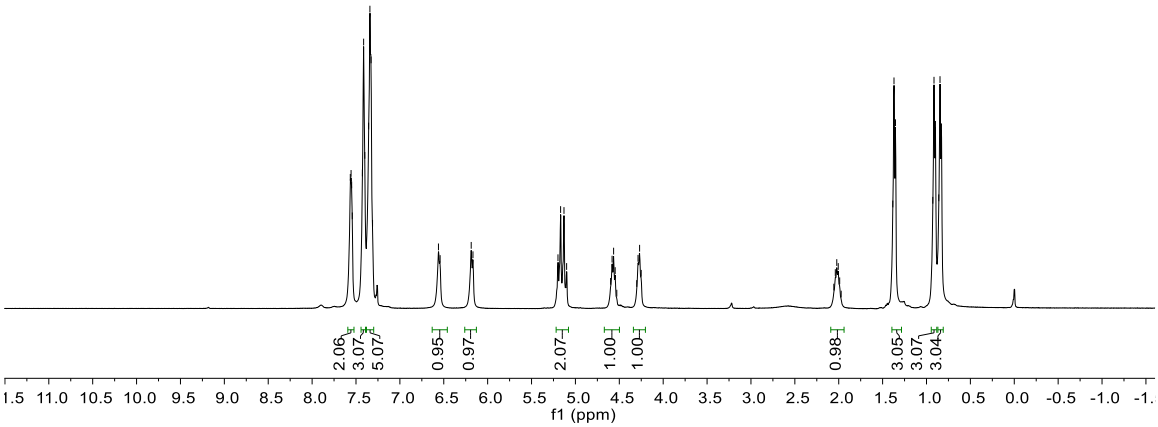
3al, ^{13}C NMR, 101 MHz, $CDCl_3$

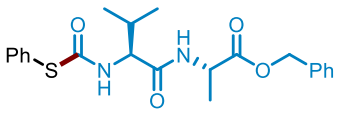




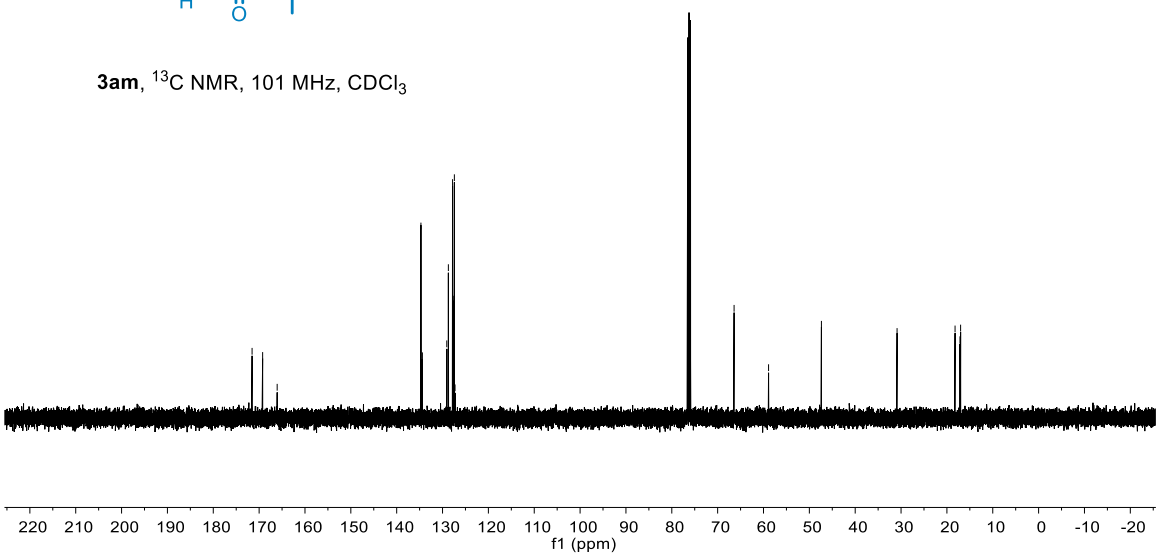


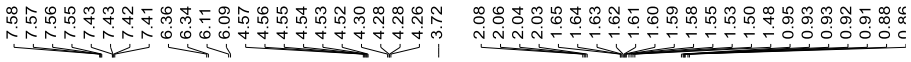
3am, ^{1}H NMR, 400 MHz, $CDCl_3$

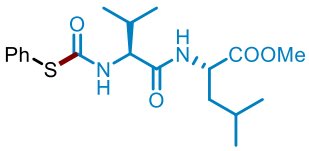




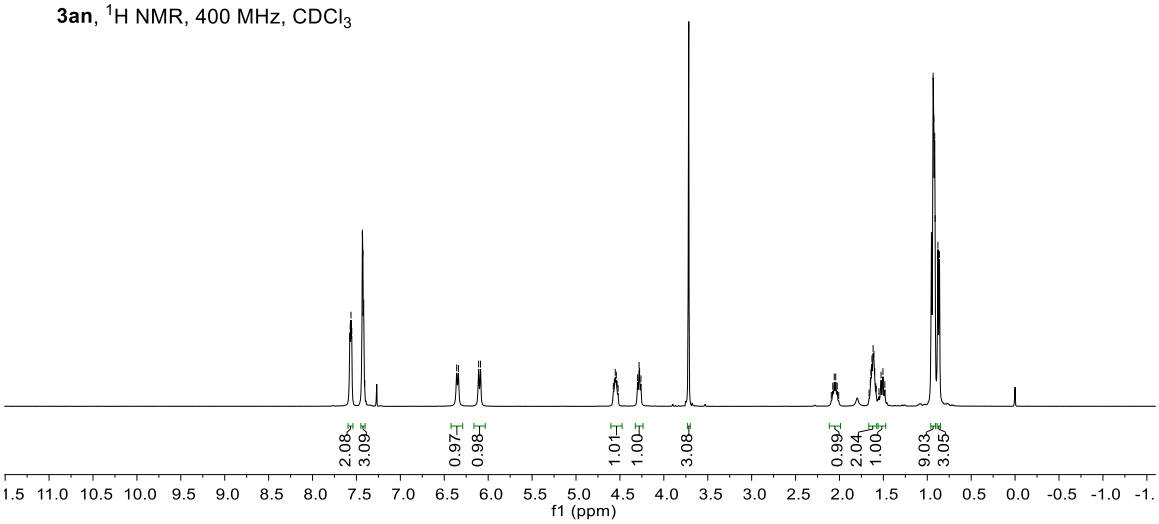
3am, ^{13}C NMR, 101 MHz, $CDCl_3$

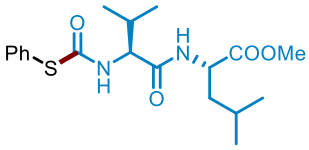




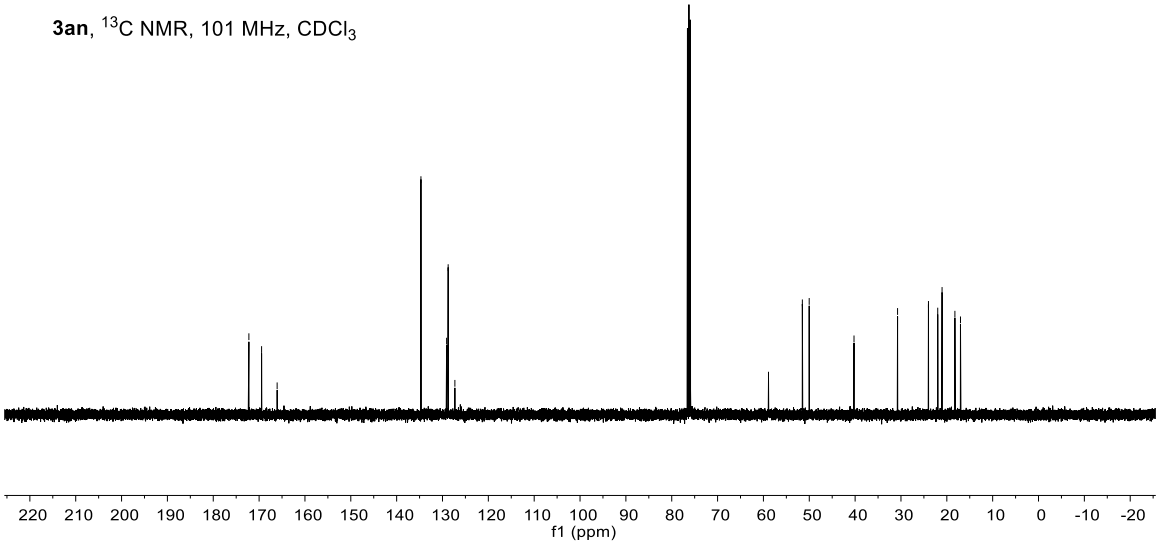


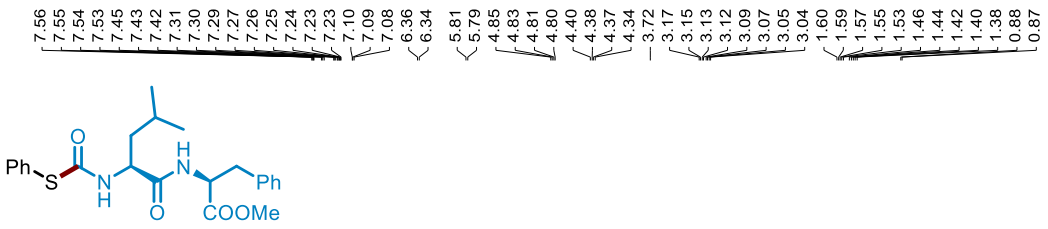
3an, ^{1}H NMR, 400 MHz, $CDCl_3$



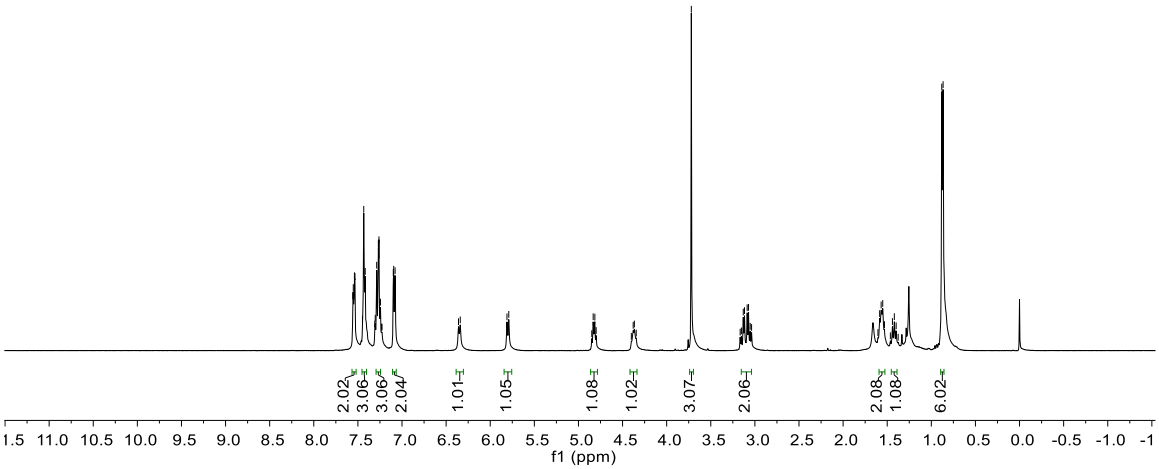


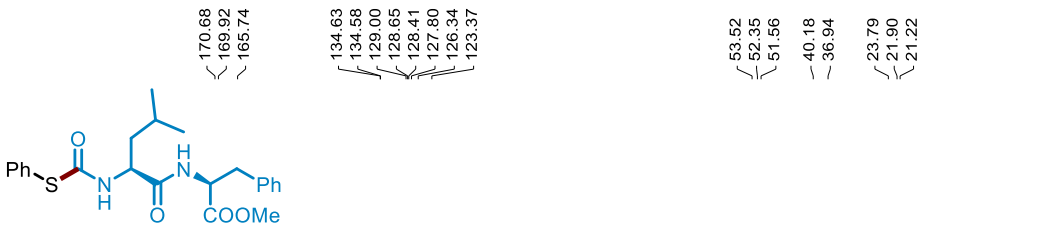
3an, ^{13}C NMR, 101 MHz, $CDCl_3$



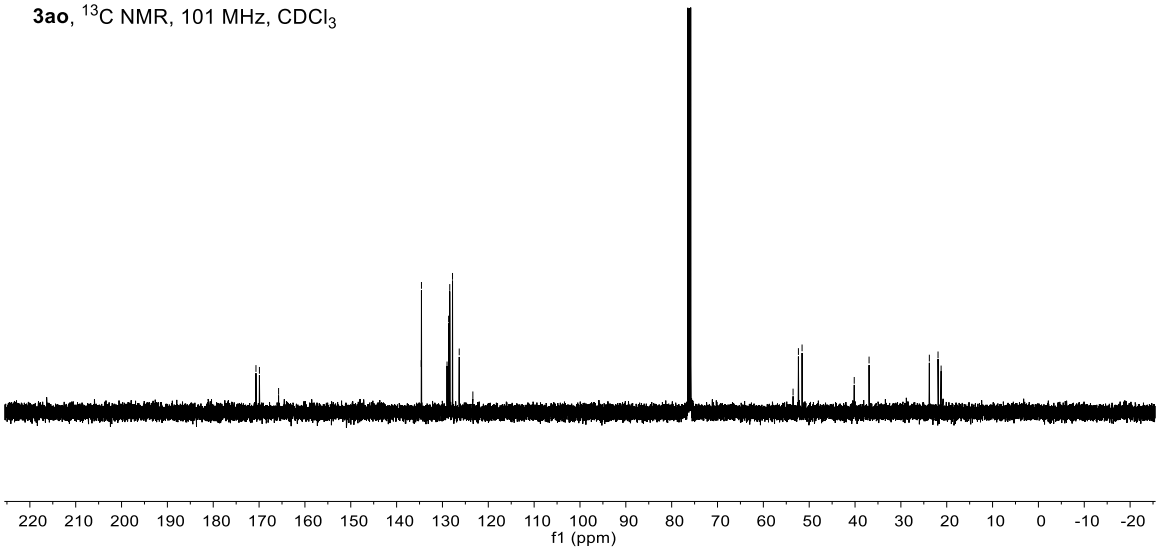


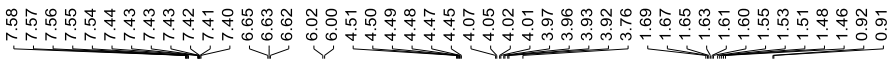
3ao, ^{1}H NMR, 400 MHz, $CDCl_3$

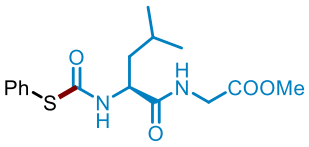




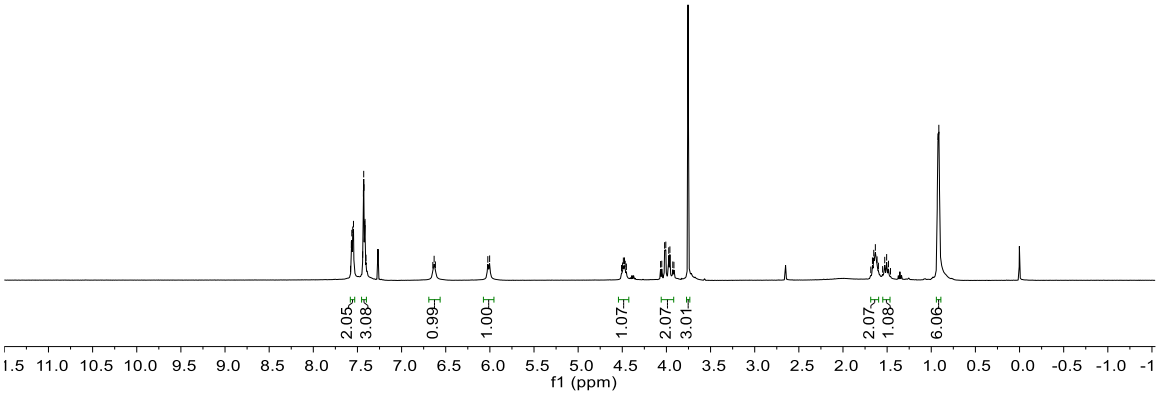
3ao, ^{13}C NMR, 101 MHz, $CDCl_3$

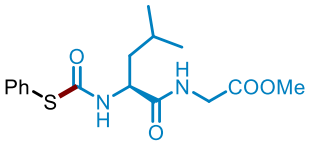




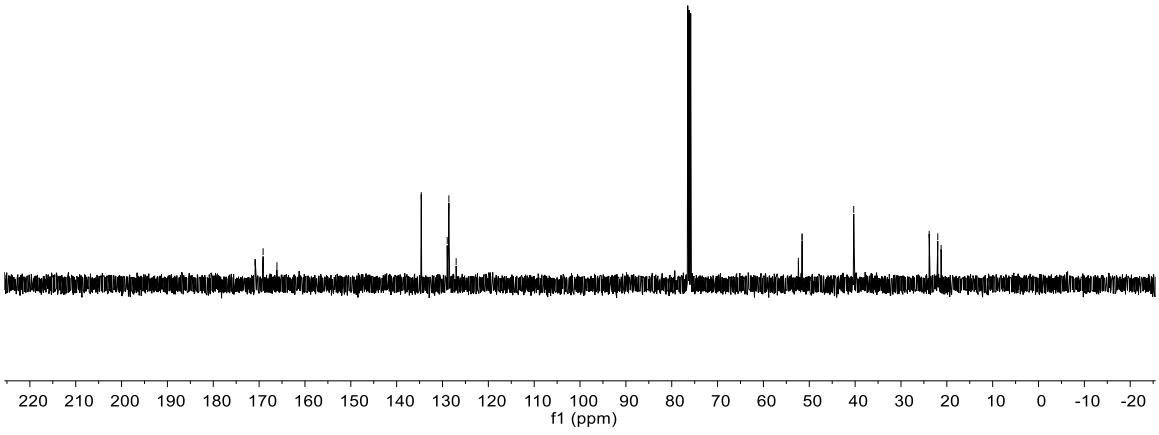


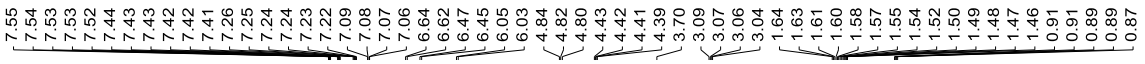
3ap, ^{1}H NMR, 400 MHz, $CDCl_3$

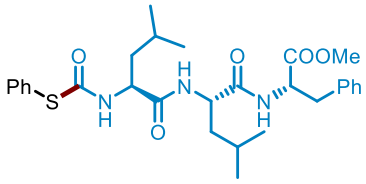




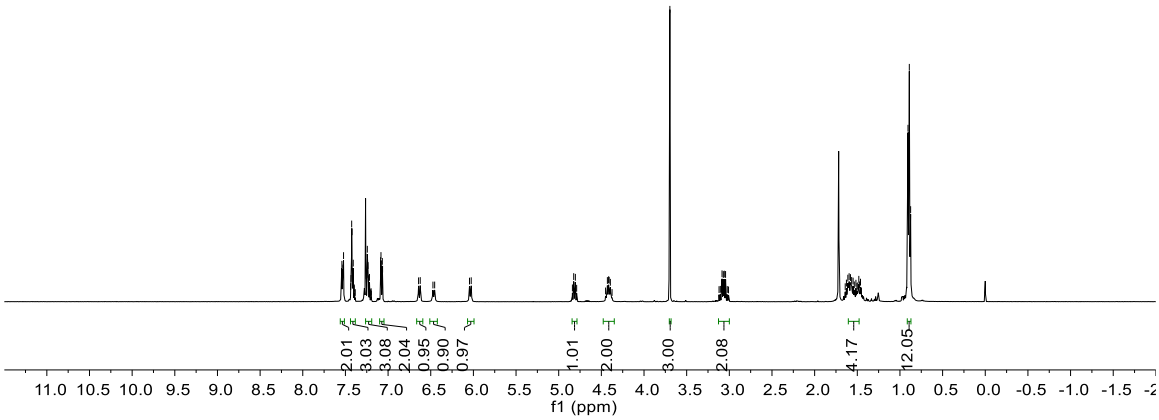
3ap, ^{13}C NMR, 101 MHz, $CDCl_3$

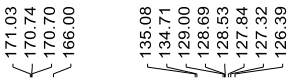


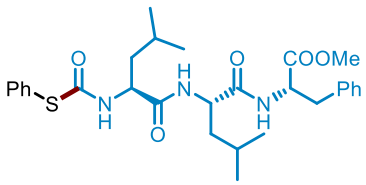




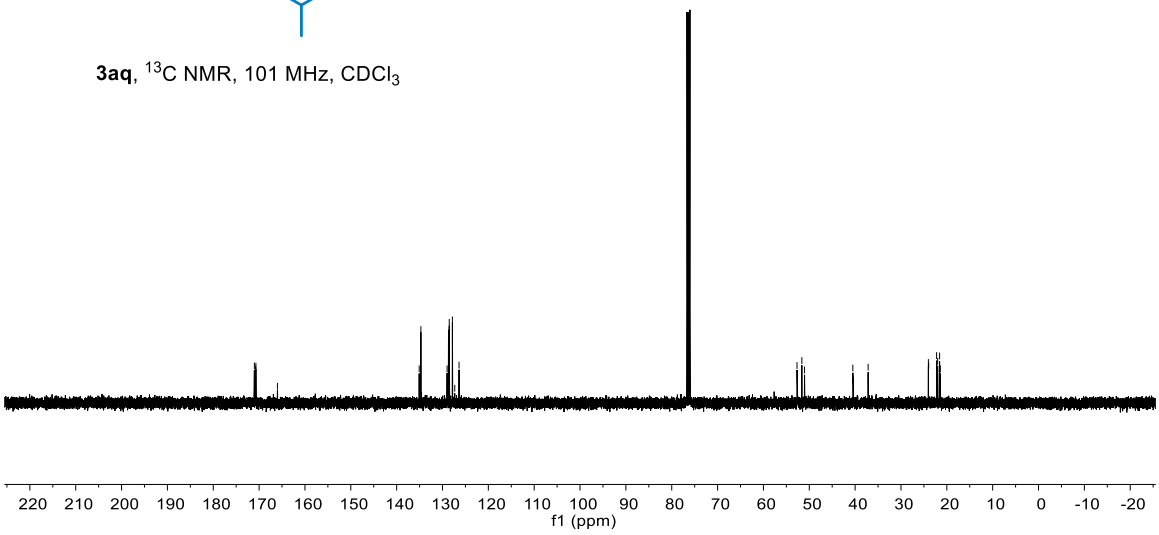
3aq, ^{1}H NMR, 400 MHz, $CDCl_3$

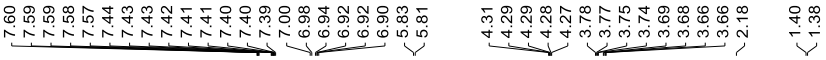


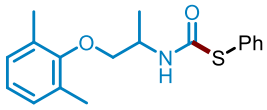




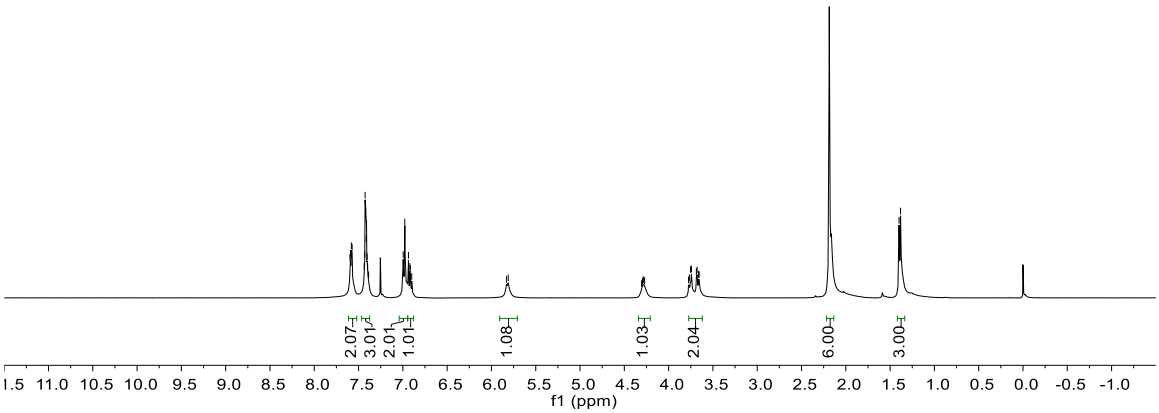
3aq, ^{13}C NMR, 101 MHz, $CDCl_3$

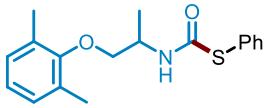




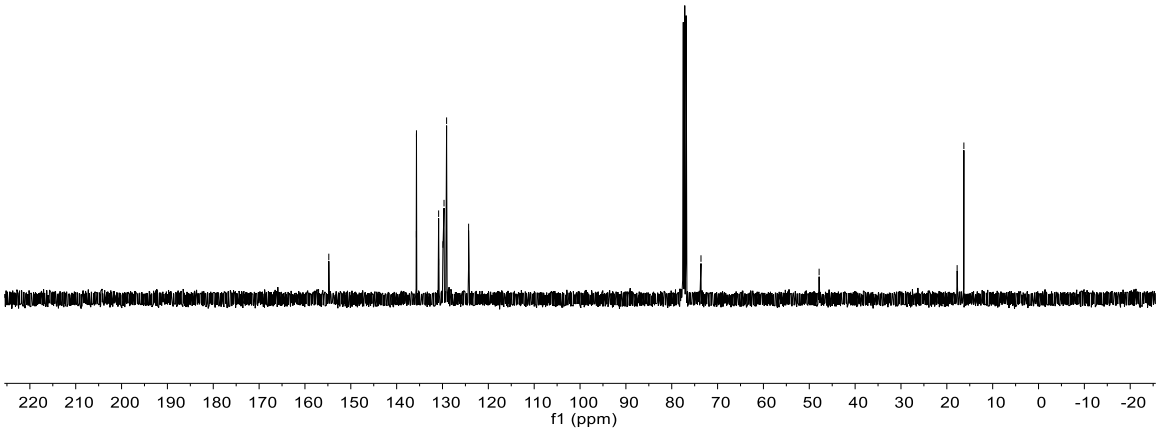


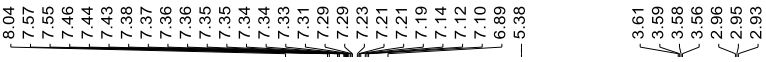
3ar, ^{1}H NMR, 400 MHz, $CDCl_3$

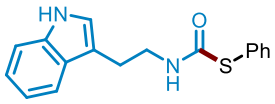




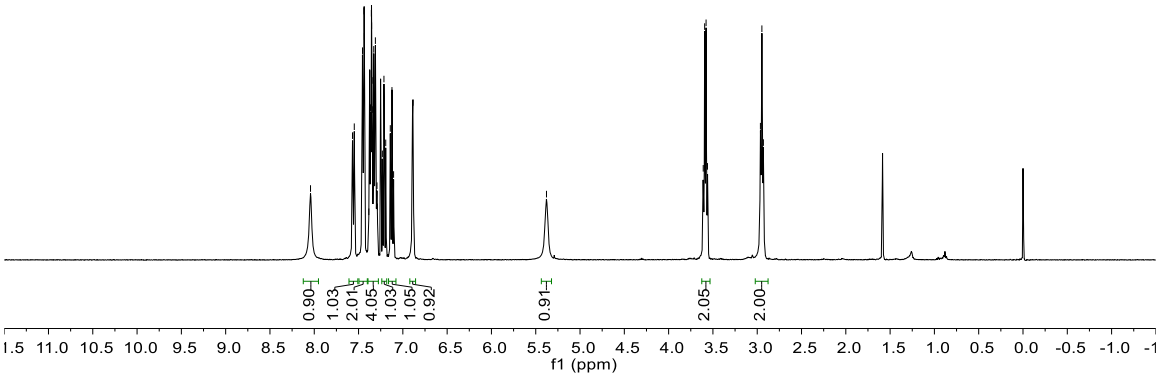
3ar, ^{13}C NMR, 101 MHz, $CDCl_3$

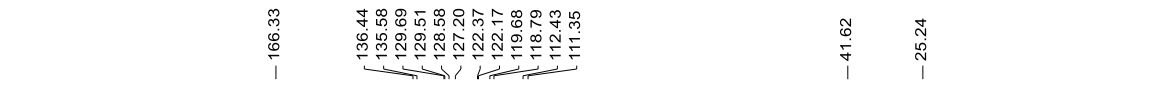


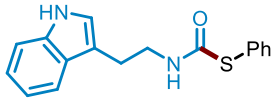




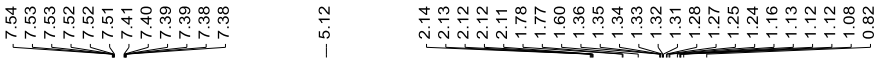
3as, ^{1}H NMR, 400 MHz, $CDCl_3$

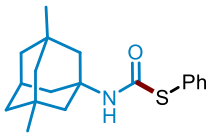




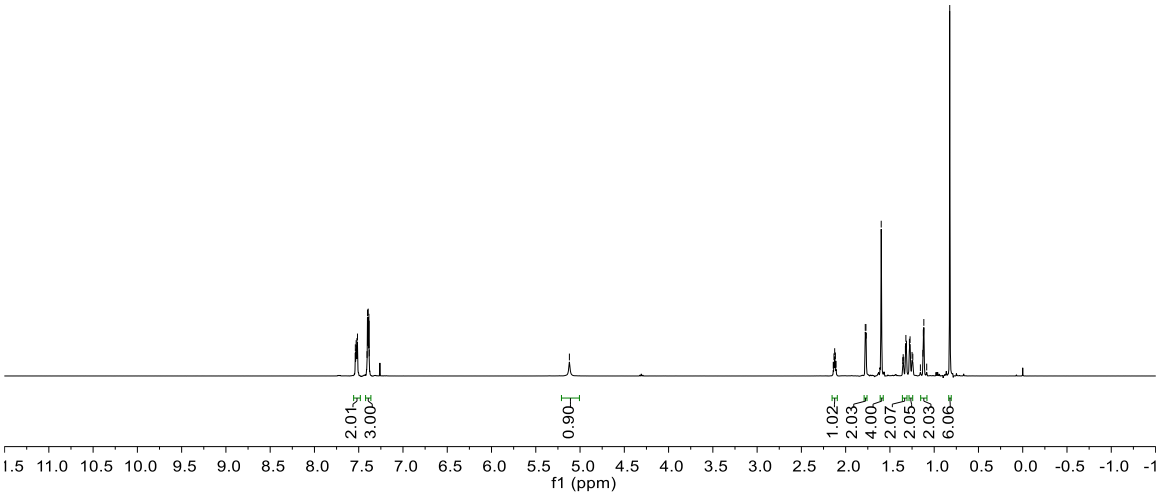


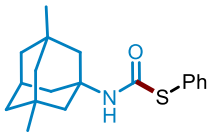
3as, ^{13}C NMR, 101 MHz, $CDCl_3$



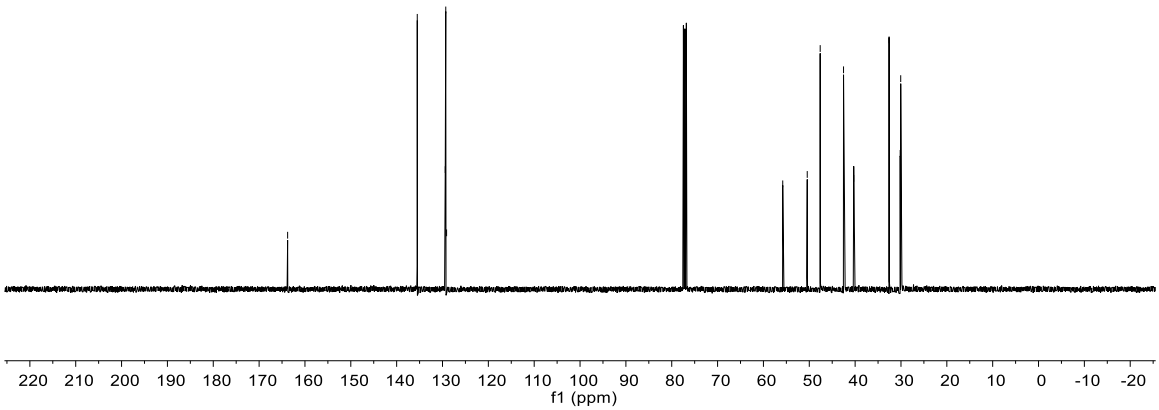


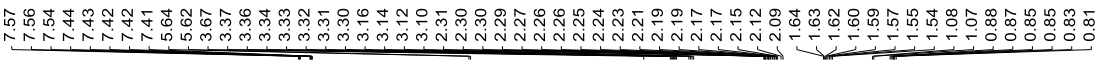
3at, ^{1}H NMR, 400 MHz, $CDCl_3$

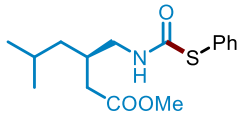




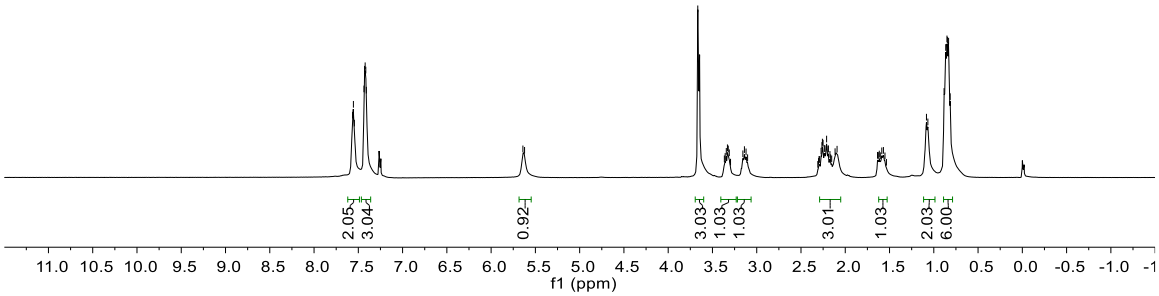
3at, ^{13}C NMR, 101 MHz, $CDCl_3$

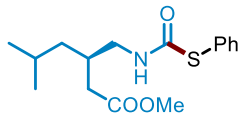




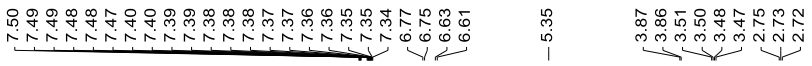


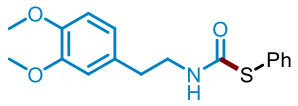
3au, ^{1}H NMR, 400 MHz, $CDCl_3$



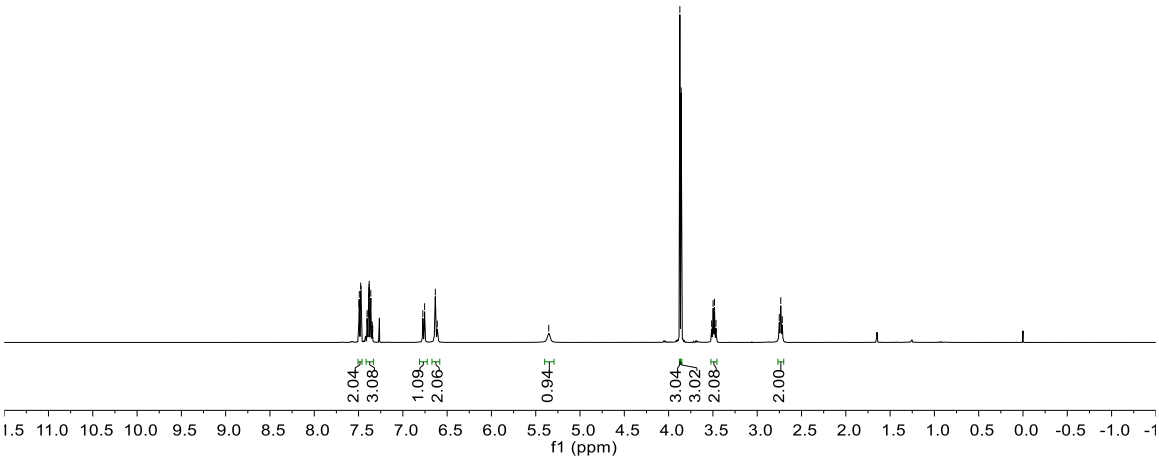


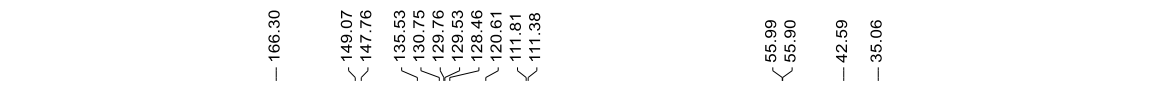
3au, ^{13}C NMR, 101 MHz, $CDCl_3$

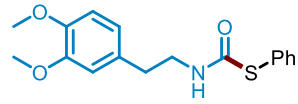




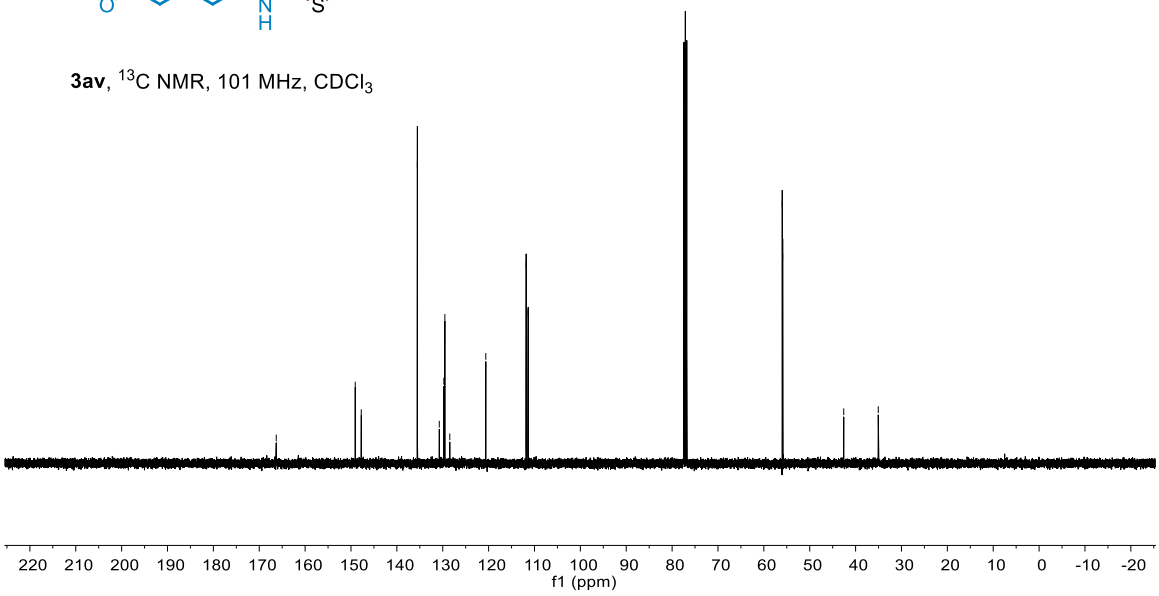
3av, ^{1}H NMR, 400 MHz, $CDCl_3$

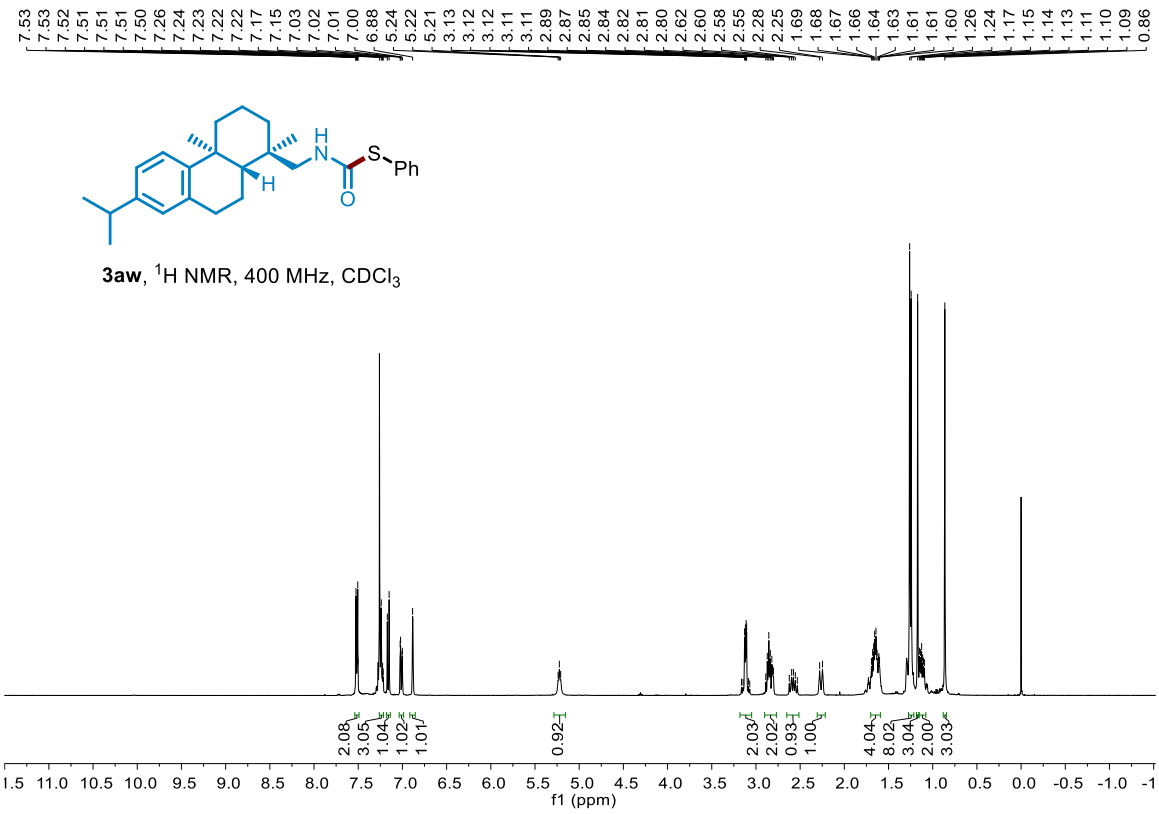




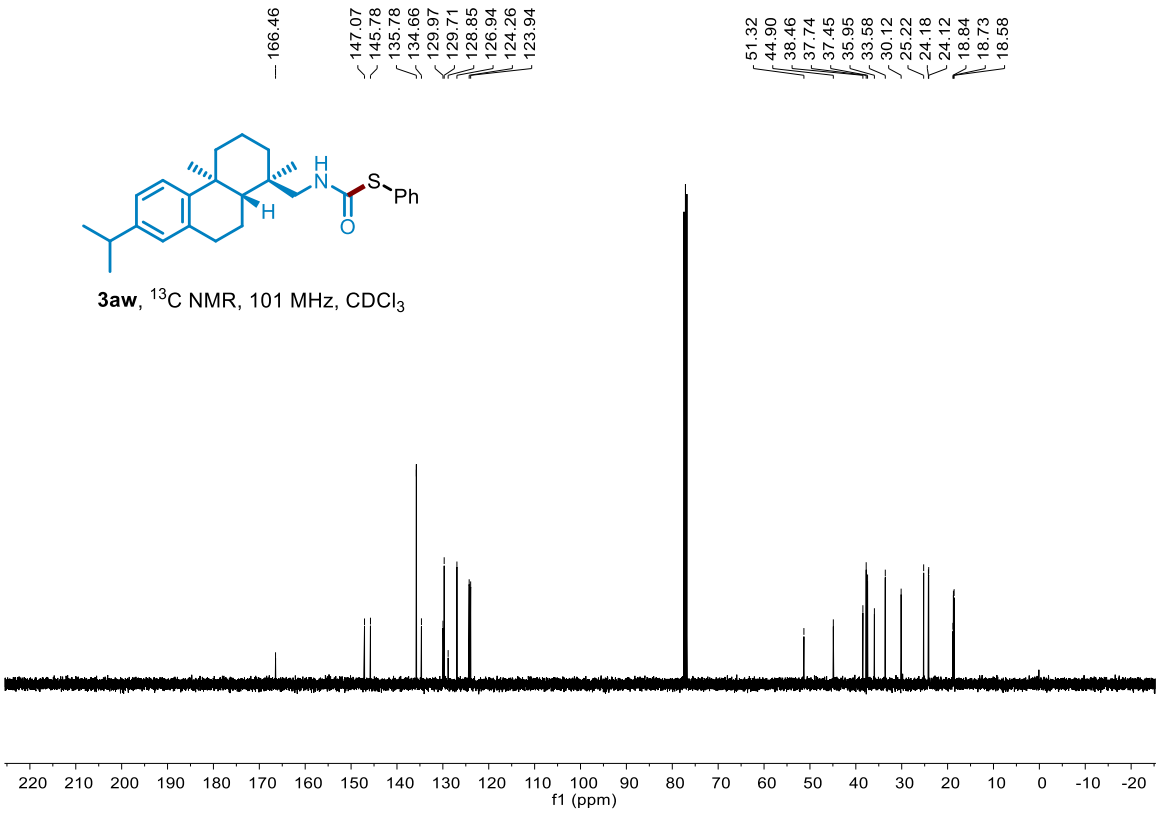


3av, ^{13}C NMR, 101 MHz, $CDCl_3$

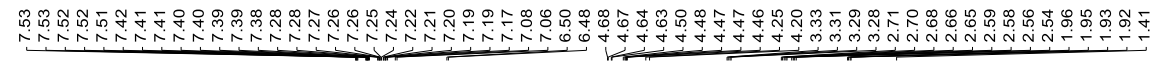


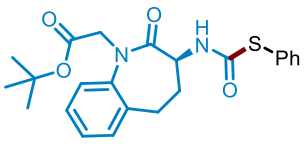


3aw, ^{1}H NMR, 400 MHz, $CDCl_3$

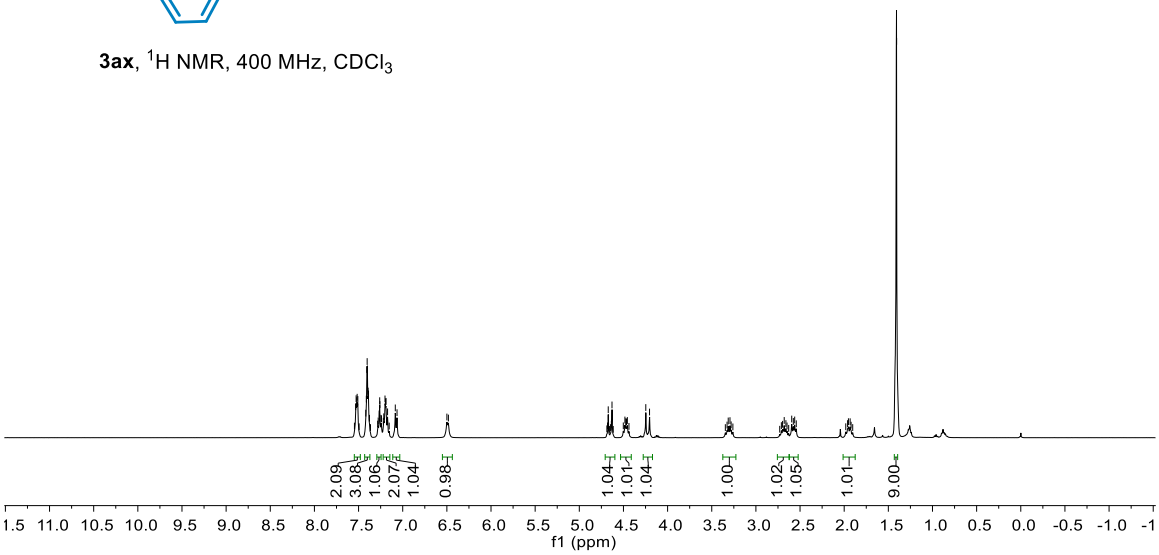


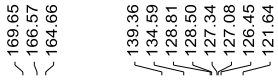
3aw, ^{13}C NMR, 101 MHz, $CDCl_3$

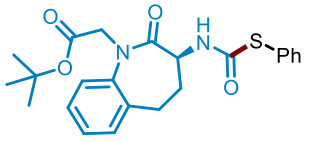




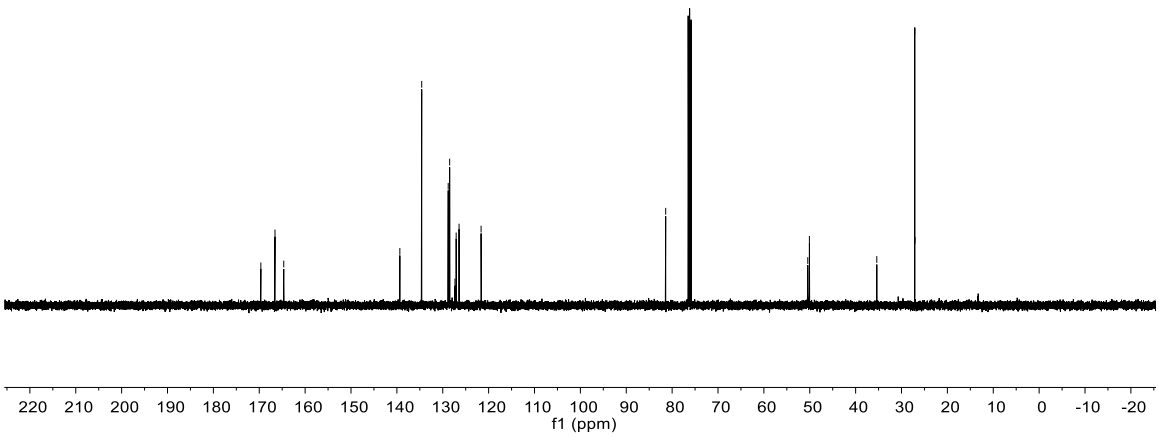
3ax, ^{1}H NMR, 400 MHz, $CDCl_3$

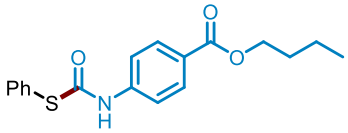




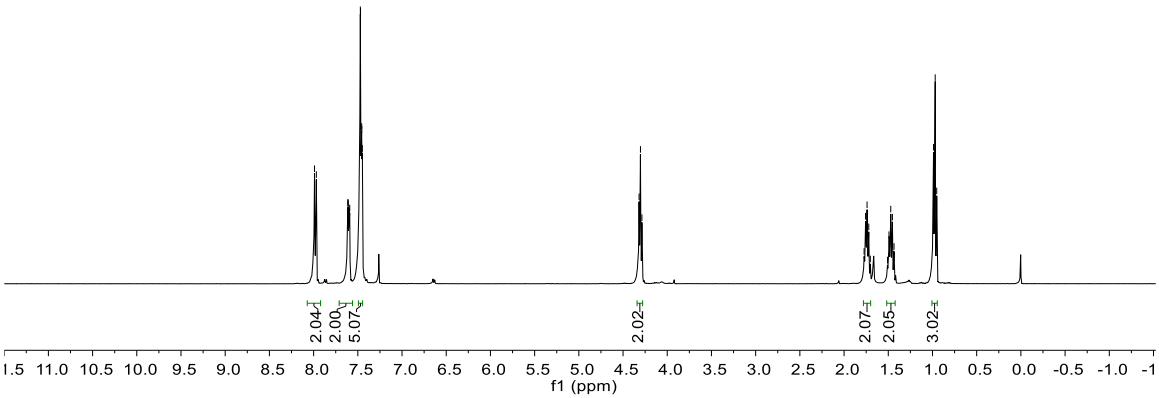


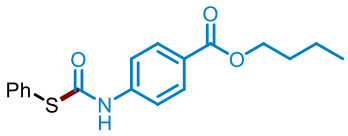
3ax, ^{13}C NMR, 101 MHz, $CDCl_3$



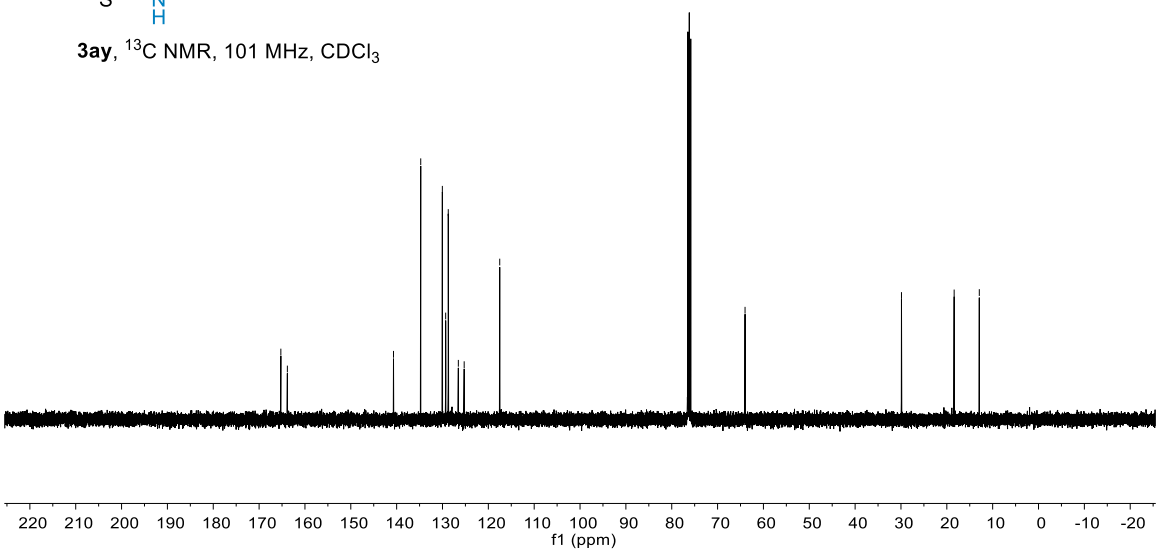


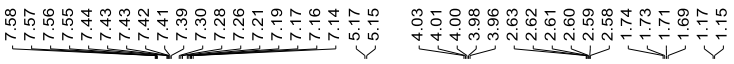
3ay, ^{1}H NMR, 400 MHz, $CDCl_3$

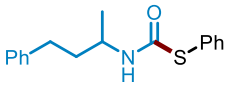




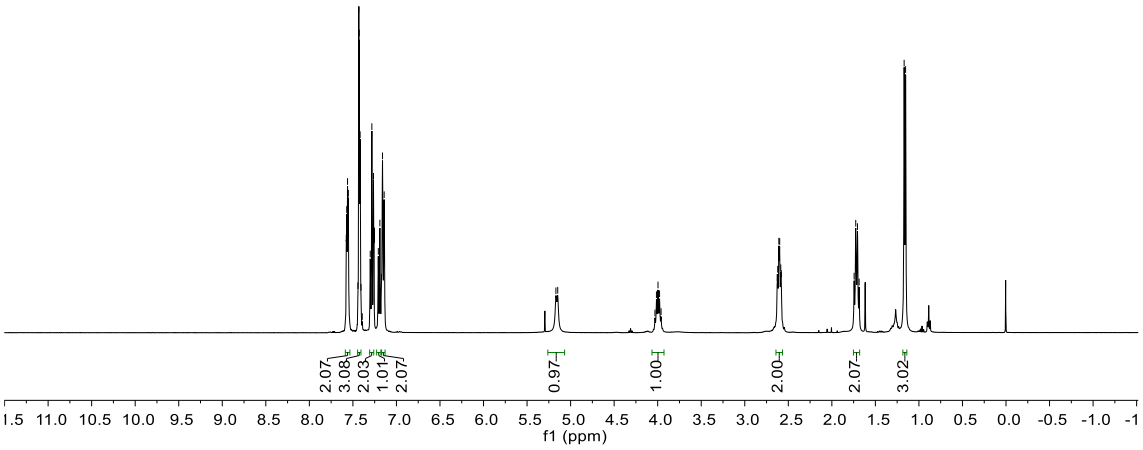
3ay, ^{13}C NMR, 101 MHz, $CDCl_3$

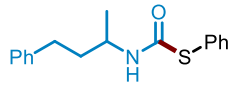




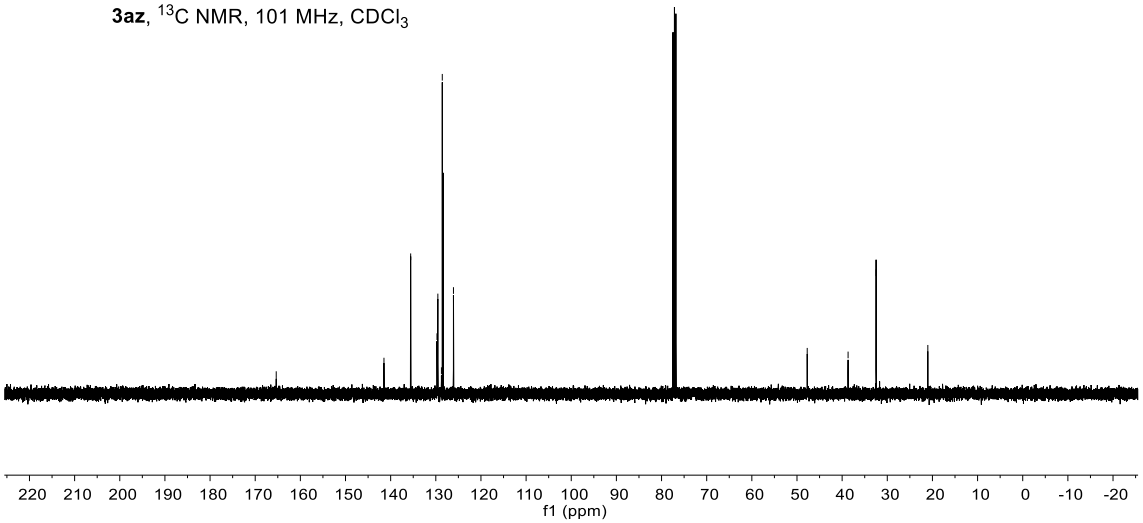


3az, ^{1}H NMR, 400 MHz, $CDCl_3$





3az, ^{13}C NMR, 101 MHz, $CDCl_3$



5. Reference

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(2) Hu, A.-M.; Tu, J.-L.Luo, M.-Q.; Yang, C.; Guo, L.; Xia, W.-J., *Org. Chem. Front.* **2023**, 4764-4773.