Supplementary Materials

Combining Photoredox Catalysis and Hydrogen Atom Transfer for Dearomative Functionalization of Electron Rich Heteroarenes

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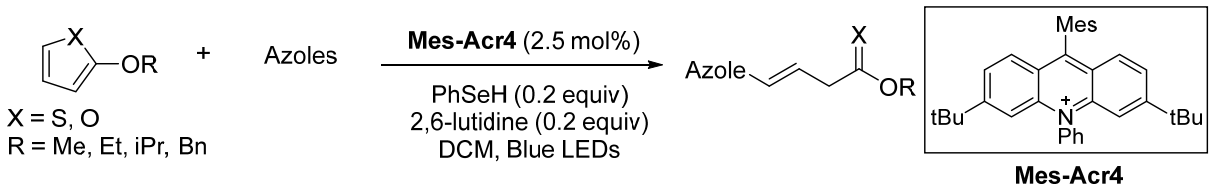
1. General Information

All commercially available reagents were purchased from Sigma Aldrich, Ark Pharm Inc., Matrix Chemical, Combi-Blocks, AKSci, Alfa Aesar, Acros, Ambeed or TCI America, and used as received unless otherwise noted. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with a fluorescence F254 indicator were used for thin-layer chromatography (TLC) analysis. **^{1}H** and **^{13}C NMR** spectra were recorded on Bruker Avance 500 MHz or Varian 400 MHz. Chemical shifts in **^{1}H NMR** spectra are reported in parts permillion (ppm) relative to residual chloroform (7.26 ppm) or dimethyl sulfoxide (2.50 ppm) as internal standards. ^{1}H NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, quint = quintet, sext = sextet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and hydrogen numbers based on integration intensities. **^{13}C NMR** chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) as internal standards. High-resolution mass spectrometry was performed in Analytical and Biological Mass Spectrometry Center. Both blue LED strip and 40 W Kessil Blue LEDs were purchased from Amazon. Cyclic voltammetry was performed at 25 °C on a CH Instrument CHI604xD electrochemical analyzer using a glassy carbon working electrode, a platinum wire counter electrode, and the Ag/AgCl reference electrode calibrated using ferrocene redox couple (4.8 V below vacuum). HPLC analyses with chiral stationary phase were carried out using a SHIMADZU HPLC system with SPD-20A detector. Samples are purified by flash column chromatography on Teledyne ISCO CombiFlash NextGen300+.

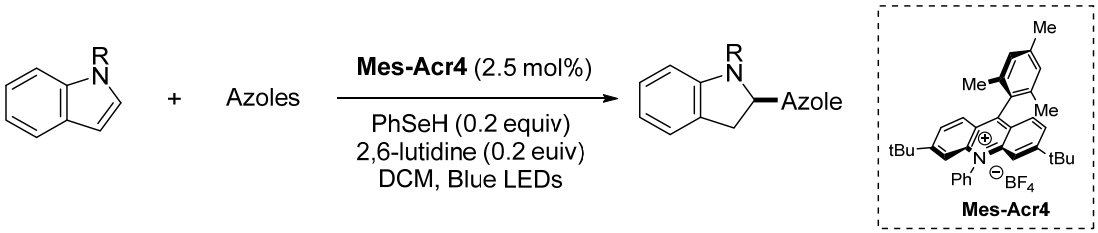
2. General Procedures and Optimization of Reaction Conditions

2.1 General procedure A (3-34)



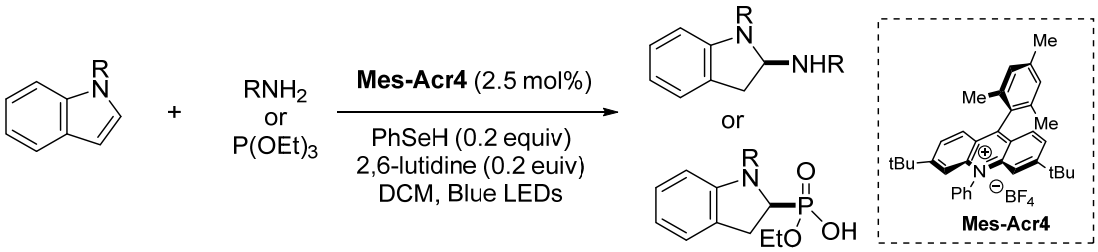
To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added nucleophiles (0.2 mmol), arenes (0.3 mmol), PhSeH (0.04 mmol), **Mes-Acr-4** (0.005 mmol), 2,6-lutidine (0.04 mmol) as the base, will be added. The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed dichloromethane (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs, cooling by the electronic fan (Figure S1). After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate or DCM/ethyl acetate in the indicated ratio.

2.2 General procedure B (36-73)



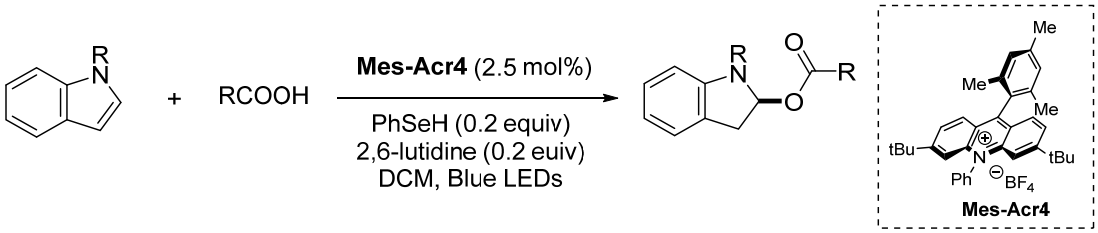
To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added azoles (0.24 mmol), indole (0.2 mmol), PhSeH (0.04 mmol), **Mes-Acr-4** (0.005 mmol), 2,6-lutidine (0.04 mmol) as the base, will be added. The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed dichloromethane (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs, cooling by the electronic fan (Figure S1). After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate or DCM/ethyl acetate in the indicated ratio.

2.3 General procedure C (74-71, 88-91)



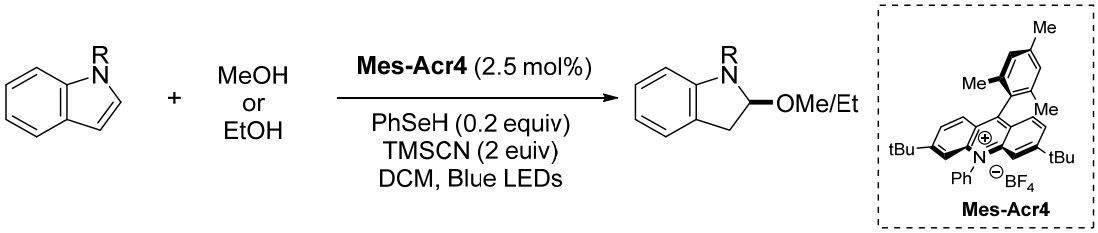
To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added amine or $P(OEt)_3$ (0.4 mmol), indole (0.2 mmol), PhSeH (0.04 mmol), **Mes-Acr-4** (0.005 mmol), 2,6-lutidine (0.04 mmol) as the base, will be added. The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed dichloromethane (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs, cooling by the electronic fan (Figure S1). After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate or DCM/ethyl acetate in the indicated ratio.

2.4 General procedure D (78-87)



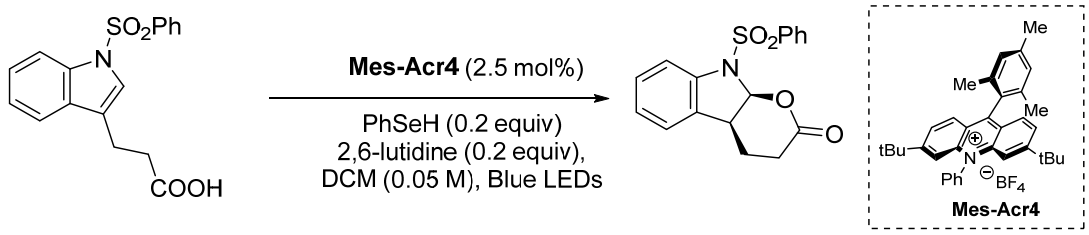
To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added carboxylic acids (0.6 mmol) or acetic acid (5.0 equiv), indole (0.2 mmol), PhSeH (0.04 mmol), **Mes-Acr-4** (0.005 mmol), 2,6-lutidine (0.04 mmol) as the base, will be added. The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed dichloromethane (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs, cooling by the electronic fan (Figure S1). After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate or DCM/ethyl acetate in the indicated ratio.

2.5 General procedure E (85-87)



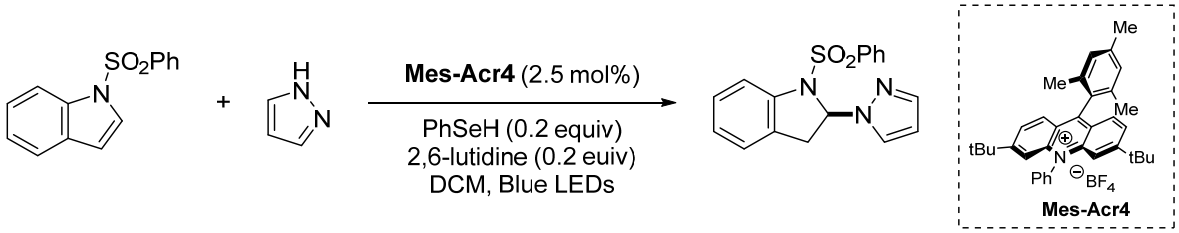
To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added indole (0.2 mmol), PhSeH (0.04 mmol), **Mes-Acr-4** (0.005 mmol), TMSCN (0.4 mmol). The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed MeOH or EtOH (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs for 48 hours, cooling by the electronic fan (Figure S1). After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate or DCM/ethyl acetate in the indicated ratio.

2.6 Intramolecular reaction



To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added indole acid (0.2 mmol), PhSeH (0.04 mmol), **Mes-Acr-4** (0.005 mmol), 2,6-lutidine (0.04 mmol). The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed DCM (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs for 48 hours, cooling by the electronic fan (Figure S1). After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate or DCM/ethyl acetate in the indicated ratio.

2.7 Large scale synthesis 36

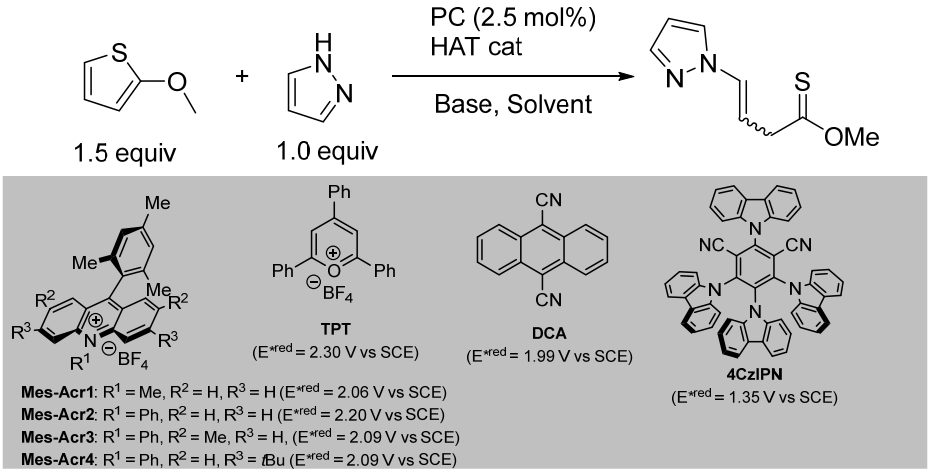


To an oven-dried 20 mL-Schlenk tube equipped with a stir bar, was added pyrazole (349 mg, 5.13 mmol) (5.0 equiv), indole (1.1 g, 4.28 mmmol), PhSeH (91 uL, 0.86 mmol), **Mes-Acr-4** (61 mg, 0.11 mmol), 2,6-lutidine (66 uL, 0.11 mmol) as the base, will be added. The tube was evacuated and back-filled with N_2 for three times, then sealed with rubber stopper and parafilm. Subsequently, the degassed dichloromethane (4 mL) was added. The reaction was irradiated by the two 40 W Kessil Blue LEDs, cooling by the electronic fan. After the completion of reactions, the resulted solution was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate (5:1) in the indicated ratio.

Figure S1. Reaction setup

2.8 reaction conditions optimization

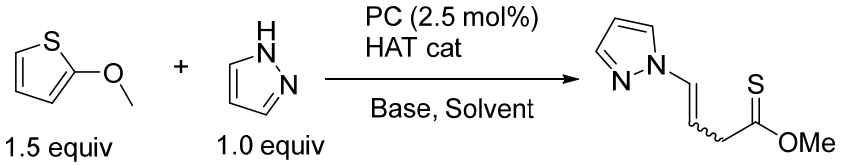
Table S1. Optimization of different photocatalyst.



PC (2.5 mol%)	Base (0.2 equiv)	HAT cat (0.2 equiv)	Solvent	Con (M)	Yield	Z/E
Mes-Acr2	2,6-lutidine	PhSeH	DCM	**0.05**	**42**	**1:1**
Mes-Acr4	2,6-lutidine	PhSeH	DCM	**0.05**	**81**	**1:1**
Mes-Acr3	2,6-lutidine	PhSeH	DCM	**0.05**	**58**	**1:1**

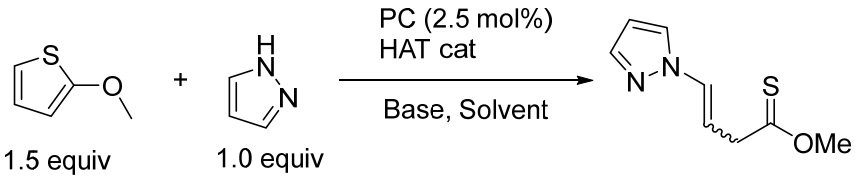
Mes-Acr1	2,6-lutidine	PhSeH	DCM	**0.05**	**50**	**1:1**
4CzIPN	2,6-lutidine	PhSeH	DCM	**0.05**	**trace**	**-**
DCA	2,6-lutidine	PhSeH	DCM	**0.05**	**trace**	**-**
TPT	2,6-lutidine	PhSeH	DCM	**0.05**	**trace**	**-**

Table S2. Optimization of HAT agents



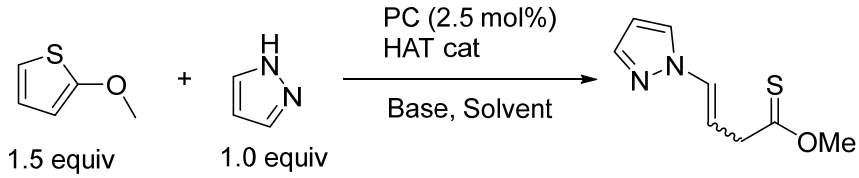
PC (2.5 mol%)	Base (0.2 equiv)	HAT cat (0.2 equiv)	Solvent	Con (M)	Yield	E/Z
Mes-Acr4	2,6-lutidine	PhSeH	DCM	0.05	81	1:1
Mes-Acr4	2,6-lutidine	Ph_3SiSH	DCM	0.05	60	2:1
Mes-Acr4	2,6-lutidine	iPr_3SiSH	DCM	0.05	57	1.2:1
Mes-Acr4	2,6-lutidine	PhSH	DCM	0.05	56	2.7:1
Mes-Acr4	2,6-lutidine	TRIPSH	DCM	0.05	54	1:1
Mes-Acr4	2,6-lutidine	4-NO_2PhSH	DCM	0.05	38	6.6:1
Mes-Acr4	2,6-lutidine	4-MeOPhSH	DCM	0.05	63	1:1
Mes-Acr4	2,6-lutidine	Cysteine	DCM	0.05	55	1.6:1
Mes-Acr4	2,6-lutidine	3,6-diCl-1,2-PhSH	DCM	0.05	53	1.2:1
Mes-Acr4	2,6-lutidine	2-NH_2PhSe	DCM	0.05	33	2.9:1
Mes-Acr4	2,6-lutidine	$SHCH_2COOMe$	DCM	0.05	56	2.7:1
Mes-Acr4	2,6-lutidine	Adman-SH	DCM	0.05	63	1:1
Mes-Acr4	2,6-lutidine	PhCOSH	DCM	0.05	56	2.1:1

Table S3. Optimization of Solvent.



PC (2.5 mol%)	Base (0.2 equiv)	HAT cat (0.2 equiv)	Solvent	Con (M)	Yield
Mes-Acr4	2,6-lutidine	PhSeH	DCE	0.05	63
Mes-Acr4	2,6-lutidine	PhSeH	DMF	0.05	trace
Mes-Acr4	2,6-lutidine	PhSeH	ACN	0.05	16
Mes-Acr4	2,6-lutidine	PhSeH	$PhCF_3$	0.05	57

Table S4. Optimization of concentration and control studies.



PC (2.5 mol%)	Base (0.2 equiv)	HAT cat (0.2 eq)	Solvent	Con (M)	Yield	E/Z
Mes-Acr4	2,6-lutidine	PhSeH	DCM	0.05	81	1:1
Mes-Acr4	2,6-lutidine	PhSeH	DCM	0.1	60	3:1
Mes-Acr4	2,6-lutidine	PhSeH	DCM	0.2	30	2:1
Mes-Acr4	none	PhSeH	DCM	0.05	68	1:1.4
Mes-Acr4	2,6-lutidine	none	DCM	0.05	23	1:1
Mes-Acr4	2,6-lutidine	PhSeH	DCM	0.05	trace	No light
Mes-Acr4	2,6-lutidine	PhSeH	DCM	0.05	trace	No PC

3. Measurement of redox potential

Procedure for measurement of the redox potential:

Voltammetric measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer using a standard three electrodes setup in dry and degassed MeCN (10 mL), with ferrocene as an internal reference ($E^0_{1/2}$ = + 0.40 V vs SCE) and nBu$_4$NPF$_6$ as the electrolyte (0.10 mmol). Cyclic voltammograms were recorded at a scan rate of 0.2 V/s.

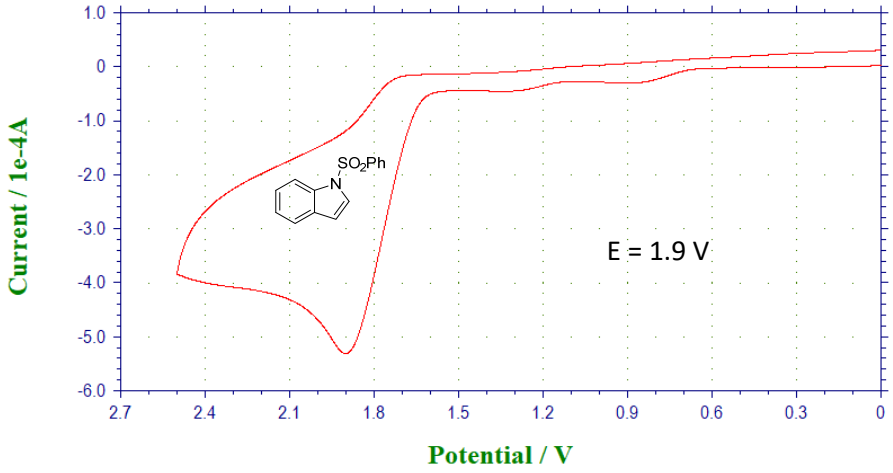


Figure S2. Redox potential of indole.

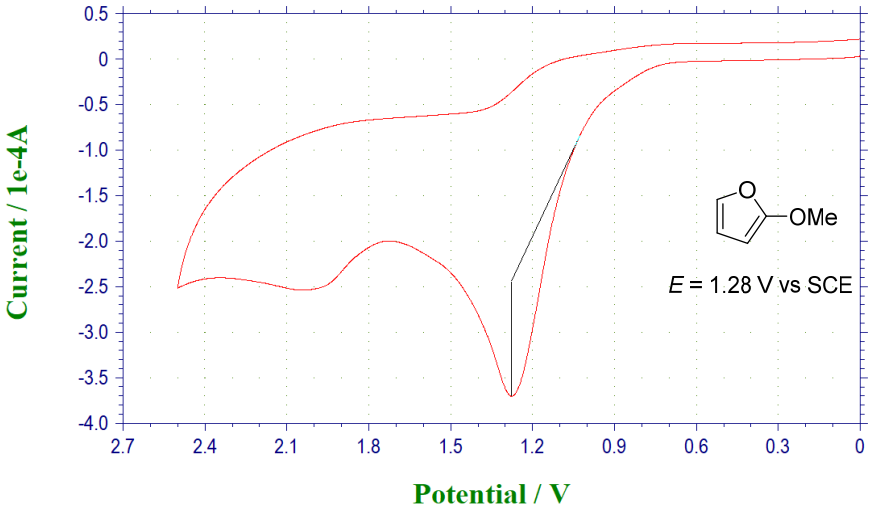


Figure S3. Redox potential of furan.

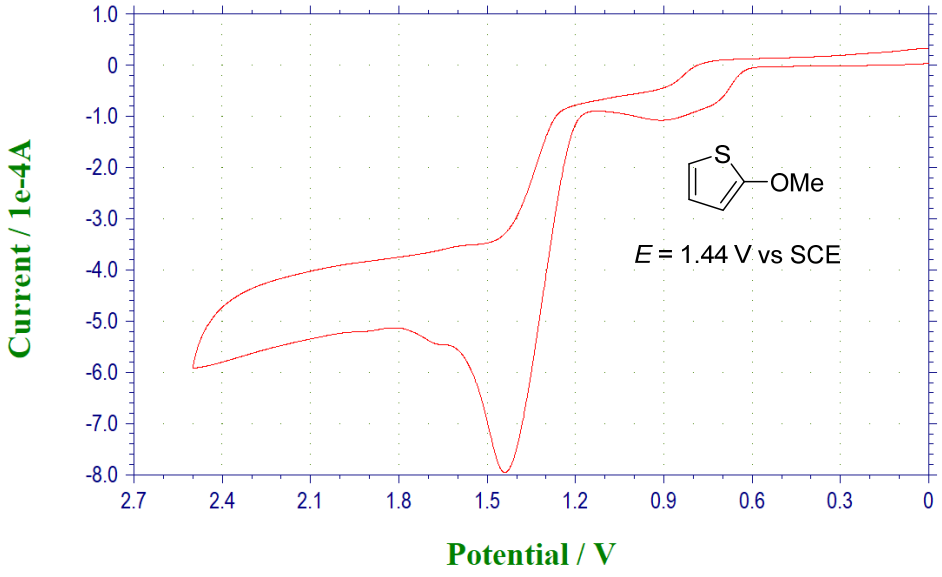


Figure S4. Redox potential of 2-methoxylthiophene.

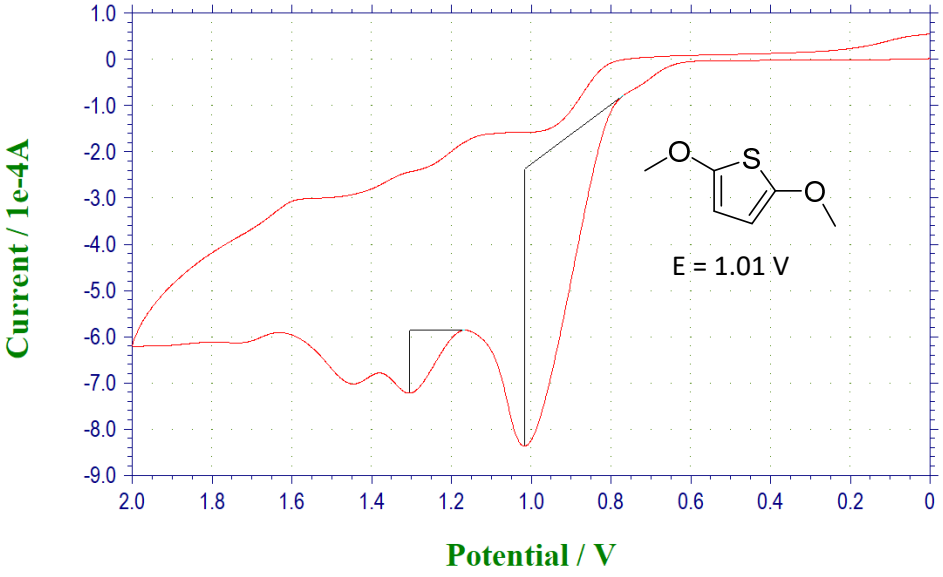
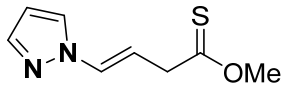


Figure S5. Redox potential of 2,5-dimethoxylthiophene.

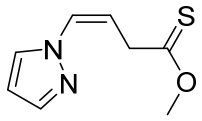
4. Compounds Characterization Data



***O*-methyl (*E*)-4-(1*H*-pyrazol-1-yl)but-3-enethioate (3)**: The title compound was prepared according to the general procedure A. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes/ethyl acetate (2:1) to furnish the pure compound as a yellow oil in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 6.94 (dt, *J* = 14.1, 1.4 Hz, 1H), 6.34 (t, *J* = 2.1 Hz, 1H), 6.25 (dt, *J* = 14.1, 7.6 Hz, 1H), 4.10 (s, 3H), 3.59 (dd, *J* = 7.6, 1.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.61, 140.85, 129.41, 127.56, 111.38, 107.00, 59.29, 46.68.

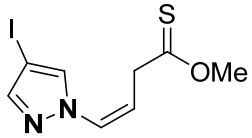


***O*-methyl (*Z*)-4-(1*H*-pyrazol-1-yl)but-3-enethioate (3)**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 1.8 Hz, 1H), 7.56 (d, J = 2.6 Hz, 1H), 6.85 (dt, J = 9.4, 1.9 Hz, 1H), 6.33 (t, J = 2.1 Hz, 1H), 5.61 (dt, J = 9.4, 7.1 Hz, 1H), 4.12 (s, 3H), 4.09 (dd, J = 7.1, 1.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.55, 140.95, 130.53, 126.56, 113.79, 106.46, 59.32, 44.10.

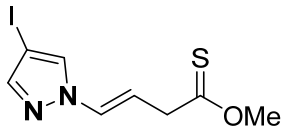
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_{10}N_2OS$: 183.0587, found 183.0585.



***O*-methyl (*Z*)-4-(4-iodo-1*H*-pyrazol-1-yl)but-3-enethioate (4)**: The title compound was prepared according to the general procedure A. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes/ethyl acetate (2:1) to furnish the pure compound as a yellow oil in 76% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.611 (s, 1H), 7.607 (s, 1H), 6.792 (dd, *J* = 9.3, 2.0 Hz, 1H), 5.647 (dt, *J* = 9.5, 7.2 Hz, 1H), 4.114 (s, 3H), 4.008 (dd, *J* = 7.2, 1.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.35, 145.80, 134.67, 125.97, 115.21, 59.36, 43.90, 29.55.

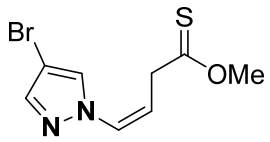


***O*-methyl (*E*)-4-(4-iodo-1*H*-pyrazol-1-yl)but-3-enethioate (4)**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.58 (s, 1H), 6.88 (d, *J* = 14.1 Hz, 1H), 6.23 (dt, *J* = 14.1, 7.6 Hz, 2H), 4.10 (s, 5H), 3.57 (dd, *J* = 7.5, 1.4 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.09, 145.64, 131.78, 128.80, 112.51, 59.29, 46.31, 29.70.

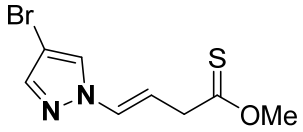
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_9IN_2OS$: 308.9553, found 308.9552.



***O*-methyl (*Z*)-4-(4-bromo-1*H*-pyrazol-1-yl)but-3-enethioate (5):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.57 (s, 1H), 6.77 (dt, *J* = 9.4, 1.9 Hz, 1H), 5.66 (dt, *J* = 9.3, 7.2 Hz, 1H), 4.11 (s, 3H), 4.00 (dd, *J* = 7.2, 1.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.82, 141.37, 130.31, 126.16, 115.21, 59.39, 43.84, 29.85.

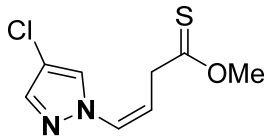


***O*-methyl (*E*)-4-(4-bromo-1*H*-pyrazol-1-yl)but-3-enethioate (5):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.54 (s, 1H), 6.97 – 6.71 (m, 1H), 6.22 (dt, *J* = 14.6, 7.6 Hz, 1H), 4.10 (s, 3H), 3.57 (dd, *J* = 7.6, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.23, 141.38, 129.16, 127.54, 112.53, 59.46, 46.43, 29.85.

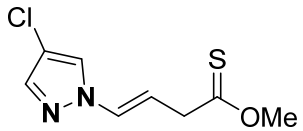
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_9BrN_2OS$: 260.9692, found 260.9690.



***O*-methyl (*Z*)-4-(4-chloro-1*H*-pyrazol-1-yl)but-3-enethioate (6):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.53 (s, 1H), 6.74 (d, *J* = 9.3 Hz, 1H), 5.66 (dt, *J* = 9.3, 7.2 Hz, 1H), 4.11 (s, 3H), 4.00 (dd, *J* = 7.2, 1.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.84, 139.31, 128.10, 126.26, 115.11, 59.39, 43.83, 33.28.

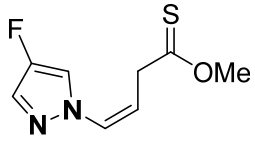


***O*-methyl (*E*)-4-(4-chloro-1*H*-pyrazol-1-yl)but-3-enethioate (6):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.51 (s, 1H), 6.84 (d, *J* = 14.2 Hz, 1H), 6.20 (dt, *J* = 14.1, 7.6 Hz, 1H), 4.10 (s, 4H), 3.56 (dd, *J* = 7.6, 1.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.25, 139.33, 129.31, 125.28, 112.40, 59.45, 46.43, 31.07.

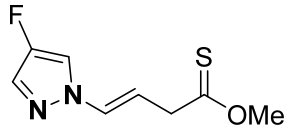
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_9ClN_2OS$: 217.0197, found 217.0194.



***O*-methyl (*Z*)-4-(4-fluoro-1*H*-pyrazol-1-yl)but-3-enethioate (7):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 4.7 Hz, 1H), 7.47 (d, *J* = 3.8 Hz, 1H), 6.69 (dt, *J* = 9.4, 1.9 Hz, 1H), 5.63 (dt, *J* = 9.4, 7.2 Hz, 1H), 4.11 (s, 3H), 3.99 (dd, *J* = 7.2, 1.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.95, 150.26 (d, *J* = 248.2 Hz), 128.38 (d, *J* = 13.8 Hz), 126.74, 116.17 (d, *J* = 27.9 Hz), 114.49, 59.36, 43.79.

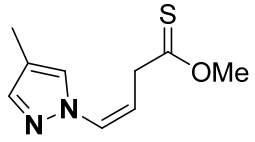


***O*-methyl (*E*)-4-(4-fluoro-1*H*-pyrazol-1-yl)but-3-enethioate (7):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 4.7 Hz, 1H), 7.44 (d, *J* = 4.1 Hz, 1H), 6.81 (dd, *J* = 14.3, 1.3 Hz, 1H), 6.11 (dt, *J* = 14.2, 7.5 Hz, 1H), 4.10 (s, 3H), 3.56 (dd, *J* = 7.5, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.40, 150.67 (d, *J* = 249.2 Hz), 130.05, 128.38 (d, *J* = 13.8 Hz), 113.17 (d, *J* = 28.1 Hz), 111.52, 59.44, 46.43.

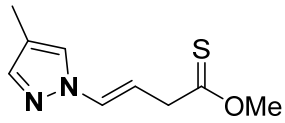
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_9ClN_2OS$: 217.0197, found 217.0194.



***O*-methyl (*Z*)-4-(4-methyl-1*H*-pyrazol-1-yl)but-3-enethioate (8)**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.32 (t, *J* = 0.9 Hz, 1H), 6.76 (dt, *J* = 9.4, 1.8 Hz, 1H), 5.51 (dt, *J* = 9.4, 7.1 Hz, 1H), 4.11 (s, 3H), 4.06 (dd, *J* = 7.2, 1.8 Hz, 2H), 2.12 – 1.91 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 221.73, 141.70, 129.06, 126.61, 112.48, 59.29, 44.11, 31.06, 8.86.

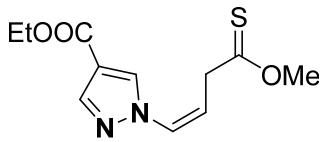


***O*-methyl (*E*)-4-(4-methyl-1*H*-pyrazol-1-yl)but-3-enethioate (8)**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.38 – 7.36 (m, 2H), 6.87 (d, *J* = 14.2 Hz, 1H), 6.11 (dt, *J* = 14.2, 7.6 Hz, 2H), 4.09 (s, 6H), 3.56 (dd, *J* = 7.5, 1.4 Hz, 4H), 2.08 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 221.03, 141.69, 129.74, 126.09, 110.16, 59.40, 46.85, 29.84, 8.98.

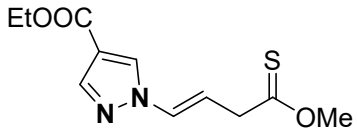
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_{12}N_2OS$: 197.0743, found 197.0743.



Ethyl (*Z*)-1-(4-methoxy-4-thioxobut-1-en-1-yl)-1*H*-pyrazole-4-carboxylate (9):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 14.3 Hz, 2H), 6.80 (dt, *J* = 9.4, 1.9 Hz, 1H), 5.77 (dt, *J* = 9.4, 7.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 3H), 4.03 (dd, *J* = 7.1, 1.9 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.62, 162.77, 142.01, 133.47, 125.88, 116.80, 115.83, 60.51, 59.33, 43.79, 14.47.

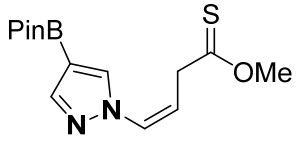


Ethyl (*E*)-1-(4-methoxy-4-thioxobut-1-en-1-yl)-1*H*-pyrazole-4-carboxylate (9):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.97 (s, 1H), 6.89 (dt, *J* = 14.0, 1.5 Hz, 1H), 6.39 (dt, *J* = 14.1, 7.5 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 3H), 3.59 (dd, *J* = 7.6, 1.4 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.88, 162.73, 142.13, 130.77, 128.79, 116.40, 114.58, 60.54, 59.45, 46.45, 14.48.

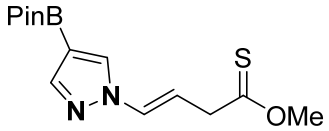
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{11}H_{14}N_2O_3S$: 255.0798, found 255.0797.



***O*-methyl (*Z*)-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (10):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.79 (s, 1H), 6.83 (d, *J* = 9.3 Hz, 1H), 5.89 – 5.51 (m, 1H), 4.11 (s, 3H), 4.09 (dd, *J* = 6.9, 2.0 Hz, 3H), 1.32 (s, 14H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.62, 137.39, 126.09, 114.84, 83.65, 59.30, 44.02, 24.93.

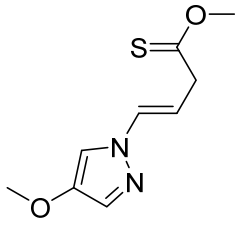


***O*-methyl (*E*)-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (10):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.84 (s, 1H), 6.92 (d, *J* = 14.1 Hz, 1H), 6.30 (dt, *J* = 14.5, 7.6 Hz, 1H), 4.09 (s, 3H), 3.66 – 3.50 (m, 2H), 1.32 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.51, 146.68, 134.64, 129.07, 112.72, 83.66, 59.42, 46.77, 24.93.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{14}H_{21}BN_2O_3S$: 309.1439, found 309.1439.

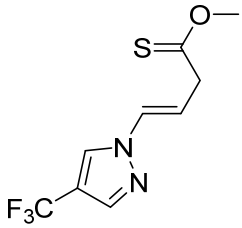


***O*-methyl (*E*)-4-(4-methoxy-1*H*-pyrazol-1-yl)but-3-enethioate (11):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.27 (s, 1H), 6.82 (dt, *J* = 14.2, 1.4 Hz, 2H), 6.00 (dt, *J* = 14.3, 7.5 Hz, 2H), 4.10 (s, 5H), 3.76 (s, 5H), 3.55 (dd, *J* = 7.5, 1.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.96, 148.12, 130.37, 129.33, 110.79, 109.41, 59.38, 58.88, 46.63.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_{12}N_2O_2S$: 213.0692, found 213.0692.

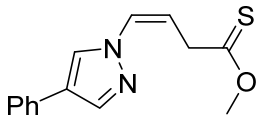


***O*-methyl (*E*)-4-(4-(trifluoromethyl)-1*H*-pyrazol-1-yl)but-3-enethioate (12):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (s, 1H), 6.90 (dt, 1H), 6.39 (dt, J = 14.1, 7.6 Hz, 1H), 4.11 (s, 3H), 3.59 (dd, J = 7.6, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.62, 137.97 (q, *J* = 2.7 Hz), 128.54, 126.80 (d, *J* = 3.9 Hz), 125.05 – 118.32 (m), 115.03, 114.76, 59.34, 46.18.

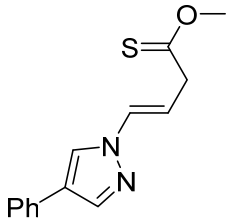
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_9F_3N_2OS$: 251.0460, found 251.0460.



***O*-methyl (*E*)-4-(4-phenyl-1*H*-pyrazol-1-yl)but-3-enethioate (13):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.82 (s, 1H), 7.48 (d, J = 6.5 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 2H), 7.25 (s, 1H), 6.86 (t, J = 7.2 Hz, 1H), 5.64 (t, *J* = 7.3 Hz, 1H), 4.44 – 3.98 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.38, 138.66, 131.90, 129.05, 127.04, 126.96, 126.49, 125.82, 123.69, 113.99, 59.38, 44.04.

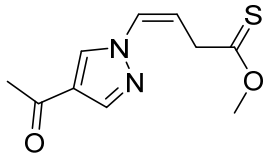


***O*-methyl (*Z*)-4-(4-phenyl-1H-pyrazol-1-yl)but-3-enethioate (13):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.82 (s, 1H), 7.49 (s, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.18 (m, 1H), 6.94 (dt, *J* = 14.4, 4.0 Hz, 1H), 6.26 (dt, *J* = 13.6, 6.7 Hz, 1H), 4.10 (dd, *J* = 5.2, 2.6 Hz, 3H), 3.60 (d, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.66, 138.67, 131.90, 129.48, 129.05, 127.00, 125.79, 124.41, 123.99, 111.60, 59.46, 46.71.

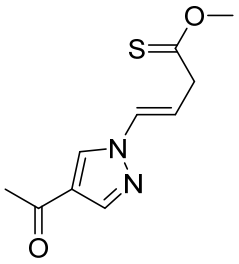
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{14}H_{14}N_2OS$: 259.0900, found 259.0898.



***O*-methyl (*Z*)-4-(4-acetyl-1*H*-pyrazol-1-yl)but-3-enethioate (14):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.98 (s, 1H), 6.81 (dt, *J* = 9.3, 1.9 Hz, 1H), 5.78 (dt, *J* = 9.4, 7.2 Hz, 1H), 4.10 (s, 3H), 4.01 (dd, *J* = 7.3, 1.8 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.38, 191.84, 141.25, 132.55, 125.82, 124.37, 117.20, 59.29, 43.73, 28.06.

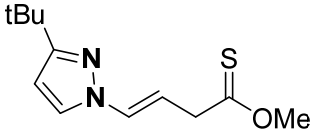


***O*-methyl (*E*)-4-(4-acetyl-1*H*-pyrazol-1-yl)but-3-enethioate (14)**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (s, 1H), 6.90 (dt, *J* = 14.0, 1.4 Hz, 1H), 6.42 (dt, *J* = 14.0, 7.6 Hz, 1H), 4.10 (s, 3H), 3.59 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.65, 191.78, 141.35, 129.75, 128.56, 124.92, 115.05, 59.35, 46.28, 28.01.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{10}H_{12}N_2O_2S$: 225.0692, found 225.0691.

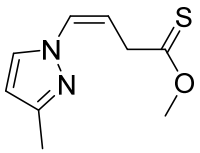


***O*-methyl (*E*)-4-(3-(tert-butyl)-1*H*-pyrazol-1-yl)but-3-enethioate (15):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 28.4, 2.5 Hz, 1H), 6.99 – 6.63 (m, 1H), 6.18 (dd, *J* = 11.8, 2.5 Hz, 1H), 6.15 – 5.41 (m, 1H), 4.10 (d, *J* = 8.6 Hz, 3H), 4.39 – 3.36 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 221.70 (d, *J* = 134.7 Hz), 163.68, 130.34 (d, *J* = 92.2 Hz), 127.15 (d, *J* = 152.3 Hz), 110.88 (d, *J* = 240.8 Hz), 103.39 (d, *J* = 113.0 Hz), 59.29 (d, *J* = 21.9 Hz), 45.66 (d, *J* = 336.4 Hz), 32.69 – 29.52 (m), 30.51 (d, *J* = 6.8 Hz).

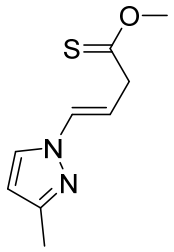
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{12}H_{18}N_2OS$: 239.1213, found 239.1211.



***O*-methyl (*Z*)-4-(3-methyl-1*H*-pyrazol-1-yl)but-3-enethioate (16):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.4 Hz, 1H), 6.76 (dt, *J* = 9.4, 1.8 Hz, 1H), 6.10 (d, *J* = 2.3 Hz, 1H), 5.50 (dt, *J* = 9.4, 7.1 Hz, 1H), 4.11 (s, 3H), 4.07 (dd, *J* = 7.2, 1.8 Hz, 2H), 2.30 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.61, 150.25, 131.05, 126.46, 112.32, 106.23, 59.12, 44.08, 13.68.

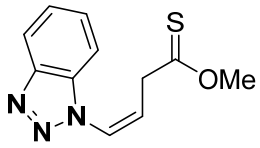


***O*-methyl (*E*)-4-(3-methyl-1*H*-pyrazol-1-yl)but-3-enethioate (16):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 2.4 Hz, 1H), 6.84 (dt, *J* = 14.1, 1.4 Hz, 1H), 6.16 (dt, *J* = 14.1, 7.6 Hz, 1H), 6.11 (d, *J* = 2.3 Hz, 1H), 4.09 (s, 3H), 3.56 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.85, 150.45, 129.25, 128.50, 110.07, 106.89, 59.24, 46.83, 13.63.

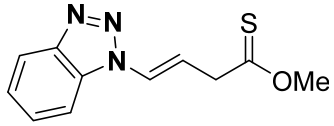
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_{12}N_2OS$: 197.0743, found 197.0743.



***O*-methyl (*Z*)-4-(1*H*-benzo[d][1,2,3]triazol-1-yl)but-3-enethioate (17):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.49 (m, 2H), 7.42 (ddd, *J* = 8.2, 4.9, 3.1 Hz, 1H), 7.16 (dt, *J* = 9.1, 2.0 Hz, 1H), 6.21 (dt, *J* = 9.1, 7.0 Hz, 1H), 4.11 (s, 3H), 4.08 (dd, *J* = 6.9, 1.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.48, 145.30, 132.85, 128.27, 124.66, 120.99, 120.59, 120.30, 109.58, 59.34, 44.28.

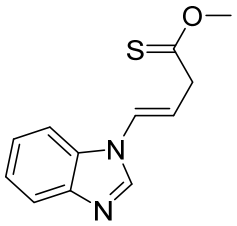


***O*-methyl (*E*)-4-(1*H*-benzo[d][1,2,3]triazol-1-yl)but-3-enethioate (17):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.56 (ddd, *J* = 8.3, 6.8, 0.9 Hz, 1H), 7.50 – 7.36 (m, 2H), 6.71 (dt, *J* = 14.7, 7.5 Hz, 1H), 4.15 (s, 2H), 3.73 (dd, *J* = 7.6, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.87, 146.41, 131.61, 128.45, 125.53, 124.70, 120.50, 116.55, 110.39, 59.54, 46.92.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{11}H_{11}N_3OS$: 234.0496, found 234.0493.

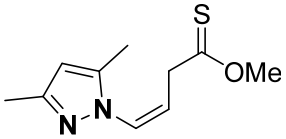


***O*-methyl (*E*)-4-(1*H*-benzo[d]imidazol-1-yl)but-3-enethioate (18):**

1H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.95 – 7.82 (m, 1H), 7.74 – 7.56 (m, 1H), 7.49 – 7.34 (m, 2H), 7.05 (dt, *J* = 14.3, 1.4 Hz, 1H), 6.44 (dt, *J* = 14.6, 7.5 Hz, 1H), 4.15 (s, 3H), 3.69 (dd, *J* = 7.5, 1.3 Hz, 2H).

13C NMR (126 MHz, $CDCl_3$) δ 218.46, 140.13, 133.67, 124.99, 124.45, 123.68, 119.35, 118.62, 117.50, 111.09, 59.43, 46.42.

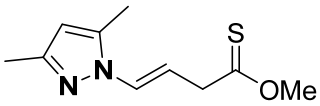
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{12}H_{12}N_2OS$: 233.0743, found 233.0743



***O*-methyl (*Z*)-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)but-3-enethioate (19):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (d, *J* = 9.3 Hz, 1H), 5.83 (s, 1H), 5.58 (dt, *J* = 9.3, 6.8 Hz, 1H), 4.16 (dd, *J* = 6.8, 1.8 Hz, 3H), 4.10 (s, 4H), 2.23 (d, *J* = 4.1 Hz, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 222.77, 149.35, 140.01, 123.11, 114.09, 105.90, 59.16, 44.11, 13.86, 11.31.

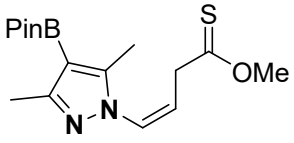


***O*-methyl (*E*)-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)but-3-enethioate (19):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 13.7, 1.6 Hz, 1H), 6.29 (dt, *J* = 14.4, 7.6 Hz, 1H), 5.84 (s, 1H), 4.08 (s, 3H), 3.58 (d, *J* = 7.7 Hz, 2H), 2.26 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 221.25, 149.98, 139.11, 125.97, 110.92, 106.77, 59.41, 47.59, 13.77, 11.11.

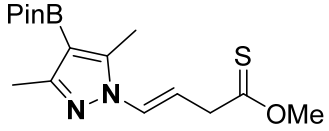
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{10}H_{14}N_2OS$: 211.0900, found 211.0897.



***O*-methyl (*Z*)-4-(3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (20):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (d, *J* = 9.3 Hz, 1H), 5.64 (dt, *J* = 9.3, 6.8 Hz, 1H), 4.11 (dd, *J* = 7.1, 2.1 Hz, 2H), 4.09 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H), 1.29 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 222.47, 155.95, 148.25, 123.20, 115.73, 82.77, 59.13, 44.12, 25.02, 14.33, 11.50.

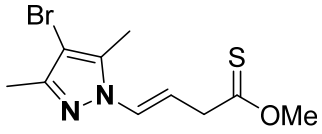


***O*-methyl (E)-4-(3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (20):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 – 6.66 (m, 1H), 6.34 (dt, *J* = 13.7, 7.7 Hz, 1H), 4.07 (s, 3H), 3.58 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.28 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.98, 156.56, 147.08, 125.53, 111.97, 82.65, 59.29, 47.54, 24.89, 14.14, 11.10.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{25}BN_2O_3S$: 337.1752, found 337.1750.

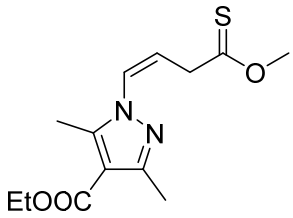


***O*-methyl (*E*)-4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)but-3-enethioate (21):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (dt, *J* = 13.7, 1.3 Hz, 1H), 6.33 (dt, *J* = 13.7, 7.7 Hz, 1H), 4.09 (s, 3H), 3.58 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.28 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.77, 148.39, 137.05, 126.20, 112.32, 96.24, 59.45, 47.24, 12.58, 10.46.

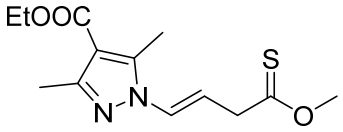
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{10}H_{13}BrN_2OS$: 289.0005, found 289.0003.



Ethyl (*Z*)-1-(4-methoxy-4-thioxobut-1-en-1-yl)-3,5-dimethyl-1*H*-pyrazole-4-carboxylate (22):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (dt, *J* = 9.1, 1.8 Hz, 1H), 5.84 (dt, *J* = 9.1, 6.9 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 3H), 4.01 (dd, *J* = 6.9, 1.8 Hz, 2H), 2.51 (s, 3H), 2.43 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.47, 164.56, 151.62, 144.75, 123.02, 119.13, 110.25, 59.91, 59.20, 44.01, 14.63, 14.53, 11.38.

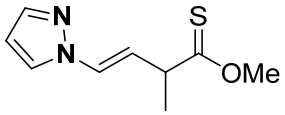


Ethyl (*E*)-1-(4-methoxy-4-thioxobut-1-en-1-yl)-3,5-dimethyl-1*H*-pyrazole-4-carboxylate (22):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dt, *J* = 13.7, 1.4 Hz, 1H), 6.47 (dt, *J* = 13.7, 7.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 3H), 3.61 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.56 (s, 3H), 2.44 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.28, 164.29, 152.11, 143.42, 125.02, 114.77, 110.85, 59.77, 59.31, 47.16, 14.47, 14.35, 10.85.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{13}H_{18}BrN_2O_3S$: 283.1111, found 283.1109.

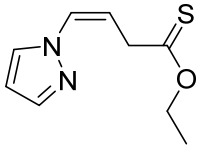


***O*-methyl (*E*)-2-methyl-4-(1*H*-pyrazol-1-yl)but-3-enethioate (23):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.8 Hz, 1H), 7.56 (dd, *J* = 2.5, 0.7 Hz, 1H), 6.93 (dd, *J* = 14.2, 1.0 Hz, 1H), 6.33 (dd, *J* = 2.5, 1.8 Hz, 1H), 6.20 (dd, *J* = 14.2, 8.6 Hz, 1H), 4.09 (s, 3H), 3.76 – 3.53 (m, 1H), 1.45 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 225.56, 140.92, 127.90, 127.70, 118.23, 107.10, 59.33, 50.88, 20.74.

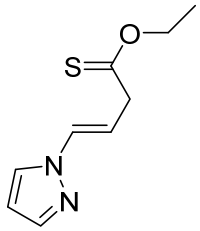
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_{12}N_2OS$: 197.0743, found 197.0741.



***O*-ethyl (*Z*)-4-(1*H*-pyrazol-1-yl)but-3-enethioate (24):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.8 Hz, 1H), 7.58 (dd, *J* = 2.4, 0.7 Hz, 1H), 6.85 (dt, *J* = 9.4, 1.9 Hz, 1H), 6.33 (dd, *J* = 2.5, 1.8 Hz, 1H), 5.63 (dt, *J* = 9.4, 7.1 Hz, 1H), 4.54 (t, *J* = 7.1 Hz, 2H), 4.04 (dd, *J* = 7.1, 1.8 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.58, 140.73, 130.31, 126.42, 113.81, 106.28, 68.53, 44.32, 13.57.

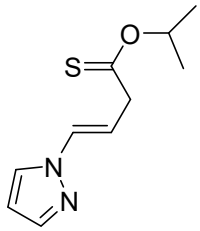


***O*-ethyl (*E*)-4-(1*H*-pyrazol-1-yl)but-3-enethioate (24):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 6.92 (dt, *J* = 14.1, 1.5 Hz, 1H), 6.32 (t, *J* = 2.1 Hz, 1H), 6.23 (dt, *J* = 14.1, 7.6 Hz, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 3.54 (dd, *J* = 7.6, 1.4 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.97, 140.81, 129.34, 127.54, 111.53, 106.98, 68.74, 47.07, 13.60.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_{12}N_2OS$: 197.0743, found 197.0743.

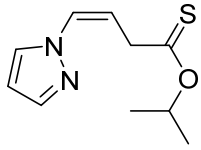


***O*-isopropyl (*E*)-4-(1*H*-pyrazol-1-yl)but-3-enethioate (25):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 1.7 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 6.94 (dt, *J* = 14.1, 1.5 Hz, 1H), 6.34 (t, *J* = 2.1 Hz, 1H), 6.23 (dt, *J* = 14.0, 7.5 Hz, 1H), 5.63 (p, *J* = 6.2 Hz, 1H), 3.51 (dd, *J* = 7.5, 1.4 Hz, 2H), 1.36 (d, *J* = 6.3 Hz, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.31, 140.89, 129.39, 127.62, 111.75, 107.09, 76.04, 47.68, 21.15.

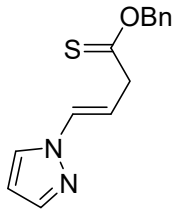
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{10}H_{14}N_2OS$: 211.0900, found 211.0899.



***O*-isopropyl (*Z*)-4-(1*H*-pyrazol-1-yl)but-3-enethioate (25):**

1H NMR (500 MHz, CDCl3) δ 7.62 (d, *J* = 1.8 Hz, 2H), 7.59 (d, *J* = 2.5 Hz, 2H), 6.85 (dt, *J* = 9.4, 1.9 Hz, 2H), 6.33 (t, *J* = 2.1 Hz, 2H), 5.67 (p, *J* = 6.2 Hz, 2H), 5.62 (dt, *J* = 9.4, 7.1 Hz, 2H), 3.97 (dd, *J* = 7.1, 1.9 Hz, 4H), 1.36 (d, *J* = 6.2 Hz, 12H).

13C NMR (126 MHz, CDCl3) δ 219.87, 140.85, 130.44, 126.56, 113.98, 106.43, 75.84, 45.00, 21.16.

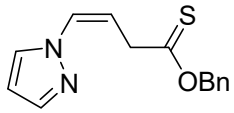


***O*-benzyl (E)-4-(1H-pyrazol-1-yl)but-3-enethioate (26):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.57 (dd, *J* = 2.4, 0.7 Hz, 1H), 7.47 – 7.33 (m, 5H), 6.95 (dt, *J* = 14.2, 1.4 Hz, 1H), 6.34 (dd, *J* = 2.5, 1.8 Hz, 1H), 6.27 (dt, J = 14.1, 7.6 Hz, 1H), 5.51 (s, 2H), 3.61 (dd, J = 7.6, 1.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 219.56, 140.82, 134.82, 129.50, 128.66, 128.62, 128.50, 127.49, 111.42, 106.98, 74.20, 46.88.

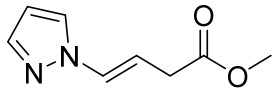
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{14}H_{14}N_2OS$: 259.0900, found 259.0898.



***O*-benzyl (Z)-4-(1H-pyrazol-1-yl)but-3-enethioate (26):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 1.8 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.43 – 7.33 (m, 5H), 6.85 (dt, J = 9.4, 1.8 Hz, 1H), 6.32 (t, J = 2.2 Hz, 1H), 5.64 (dt, J = 9.4, 7.1 Hz, 1H), 5.52 (s, 2H), 4.11 (dd, J = 7.1, 1.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.25, 140.77, 134.93, 130.33, 128.62, 128.54, 128.42, 126.47, 113.54, 106.29, 74.05, 44.26.

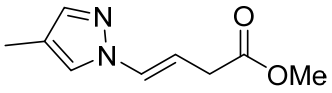


Methyl (E)-4-(1H-pyrazol-1-yl)but-3-enoate (27): The title compound was prepared according to the general procedure D. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes/ethyl acetate (2:1) to furnish the pure compound as a yellow oil in 76% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 14.2 Hz, 1H), 6.34 (t, *J* = 2.1 Hz, 1H), 6.15 (dt, *J* = 14.2, 7.5 Hz, 1H), 3.72 (s, 3H), 3.21 (dd, *J* = 7.5, 1.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.68, 140.97, 130.08, 127.60, 109.11, 107.18, 52.23, 35.00.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_{10}N_2O_2$: 167.0815, found 167.0814.

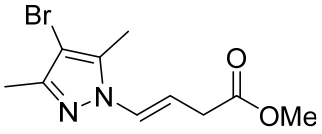


Methyl (E)-4-(4-methyl-1H-pyrazol-1-yl)but-3-enoate (28):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 13.5 Hz, 3H), 6.93 – 6.76 (m, 1H), 6.00 (dt, *J* = 14.6, 7.5 Hz, 1H), 3.70 (s, 4H), 3.17 (dd, *J* = 7.5, 1.5 Hz, 3H), 2.07 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.74, 141.63, 130.22, 125.96, 117.82, 107.69, 52.12, 34.98, 8.92.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_9H_{12}N_2O_2$: 181.0972, found 181.0971.

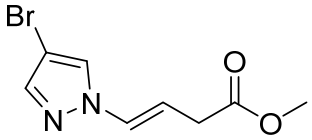


methyl (E)-4-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)but-3-enoate (29):

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, *J* = 13.8 Hz, 1H), 6.25 (dt, *J* = 13.7, 7.6 Hz, 2H), 3.71 (s, 5H), 3.19 (dd, *J* = 7.6, 1.4 Hz, 3H), 2.27 (s, 5H), 2.24 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.62, 148.40, 136.98, 126.67, 110.15, 96.25, 52.19, 35.27, 12.55, 10.41.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{10}H_{13}BrN_2O_2$: 273.0233, found 273.0231.

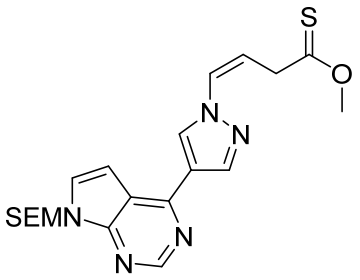


4-bromo-1-(5-methoxy-2,3-dihydrofuran-2-yl)-1H-pyrazole (30):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.53 (s, 1H), 6.89 (dt, *J* = 14.3, 1.5 Hz, 1H), 6.11 (dt, *J* = 14.2, 7.5 Hz, 1H), 3.72 (s, 3H), 3.20 (dd, *J* = 7.5, 1.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.23, 141.24, 129.57, 127.35, 110.00, 95.19, 52.15, 34.62.

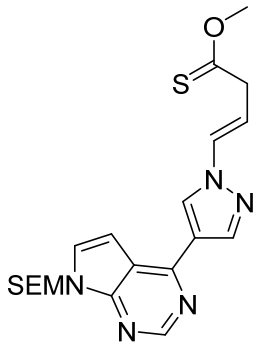
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_8H_9BrN_2O_2$: 244.9920, found 244.9920.



***O*-methyl (Z)-4-(4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-d]pyrimidin-4-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (31):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.38 (s, 1H), 8.37 (s, 1H), 7.40 (d, *J* = 3.7 Hz, 1H), 6.93 (dt, *J* = 9.4, 1.8 Hz, 1H), 6.80 (d, *J* = 3.8 Hz, 1H), 5.77 (dt, *J* = 9.3, 7.3 Hz, 1H), 5.67 (s, 2H), 4.14 (s, 3H), 4.16 – 4.10 (m, 2H), 3.61 – 3.48 (m, 2H), 1.05 – 0.69 (m, 2H), -0.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.82, 152.23, 151.90, 150.53, 140.59, 130.73, 128.47, 126.24, 122.15, 115.71, 114.34, 100.74, 72.80, 66.59, 59.24, 43.95, 17.74, -1.46.

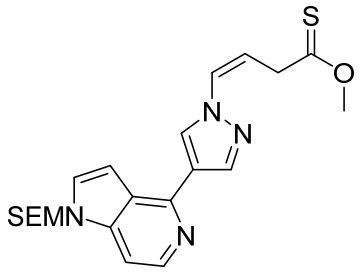


***O*-methyl (*E*)-4-(4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-d]pyrimidin-4-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (31):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.39 (s, 1H), 8.33 (s, 1H), 7.40 (d, J = 3.7 Hz, 1H), 7.01 (dt, *J* = 14.2, 1.5 Hz, 1H), 6.79 (d, *J* = 3.7 Hz, 1H), 6.43 (dt, *J* = 14.1, 7.6 Hz, 1H), 5.67 (s, 2H), 4.12 (s, 3H), 3.63 (dd, *J* = 7.6, 1.4 Hz, 2H), 3.60 – 3.42 (m, 2H), 1.06 – 0.77 (m, 2H), -0.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.02, 152.25, 151.88, 150.47, 140.58, 129.04, 128.49, 127.84, 122.81, 114.31, 113.47, 100.74, 72.80, 66.59, 59.31, 46.51, 17.74, -1.46.

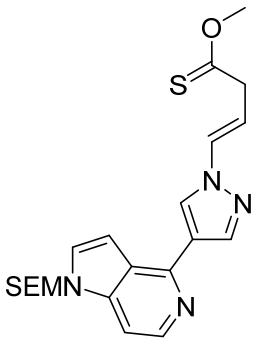
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{20}H_{27}N_5O_2SSi$: 430.1728, found 430.1727.



***O*-methyl (*Z*)-4-(4-(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrolo[3,2-c]pyridin-4-yl)-1*H*-pyrazol-1-yl)but-3-enethioate (32):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 5.0 Hz, 1H), 8.12 (s, 1H), 8.10 (s, 1H), 7.41 (d, *J* = 3.6 Hz, 1H), 7.19 (d, *J* = 5.0 Hz, 1H), 6.93 (dt, *J* = 9.4, 1.8 Hz, 1H), 6.72 (d, *J* = 3.7 Hz, 1H), 5.72 (d, *J* = 13.0 Hz, 3H), 4.14 (s, 2H), 4.13 (dd, *J* = 7.3, 1.8 Hz, 2H), 3.77 – 3.36 (m, 2H), 1.04 – 0.69 (m, 2H), -0.06 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 222.40, 150.33, 144.96, 141.24, 133.80, 130.33, 129.51, 127.83, 122.34, 118.91, 116.34, 115.22, 101.74, 74.46, 67.68, 60.72, 45.43, 19.22, -0.00.

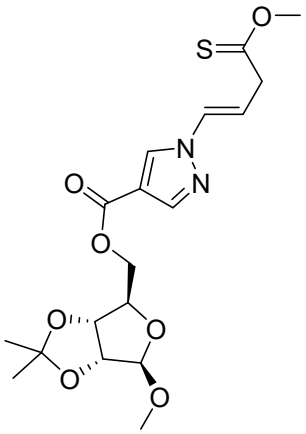


_O_-methyl (_E_)-4-(4-(1-((2-(trimethylsilyl)ethoxy)methyl)-1_H_-pyrrolo[3,2-c]pyridin-4-yl)-1_H_-pyrazol-1-yl)but-3-enethioate (32):

1H NMR (500 MHz, CDCl3) δ 8.32 (d, *J* = 5.0 Hz, 1H), 8.09 (s, 1H), 8.06 (s, 1H), 7.41 (d, *J* = 3.6 Hz, 1H), 7.18 (s, 1H), 7.01 (d, *J* = 14.1 Hz, 1H), 6.71 (d, *J* = 3.6 Hz, 1H), 6.37 (dt, *J* = 14.6, 7.5 Hz, 1H), 5.70 (s, 2H), 4.12 (s, 3H), 3.63 (d, *J* = 7.5 Hz, 2H), 3.56 (t, *J* = 8.2 Hz, 2H), 0.92 (t, *J* = 8.2 Hz, 2H), -0.07 (s, 9H).

13C NMR (126 MHz, CDCl3) δ 221.71, 150.33, 144.96, 141.30, 133.79, 130.63, 129.51, 127.37, 123.04, 118.90, 115.23, 113.99, 101.73, 74.46, 67.67, 60.79, 48.00, 19.22, 0.00.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{21}H_{28}N_4O_2SSi$: 429.1775, found 429.1775.

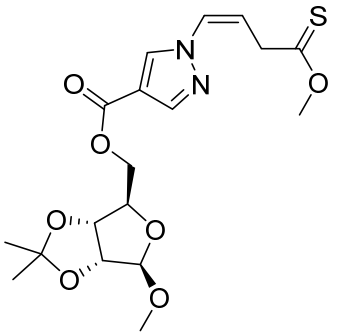


((3a_R_,4_R_,6_R_,6a_R_)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl 1-((_E_)-4-methoxy-4-thioxobut-1-en-1-yl)-1_H_-pyrazole-4-carboxylate (33):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 0.6 Hz, 1H), 8.00 (s, 1H), 6.90 (dt, *J* = 14.1, 1.5 Hz, 1H), 6.41 (dt, *J* = 14.0, 7.6 Hz, 1H), 5.00 (s, 1H), 4.72 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.63 (d, *J* = 5.9 Hz, 1H), 4.47 (td, *J* = 6.8, 1.1 Hz, 1H), 4.28 (dd, *J* = 6.8, 0.7 Hz, 2H), 4.10 (s, 3H), 3.59 (dd, *J* = 7.6, 1.4 Hz, 2H), 3.32 (s, 3H), 1.49 (d, *J* = 0.7 Hz, 4H), 1.33 (d, *J* = 0.7 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 219.63, 162.03, 142.14, 130.86, 128.60, 115.52, 114.81, 112.63, 109.51, 85.30, 84.36, 81.91, 64.62, 59.31, 54.94, 46.30, 26.47, 25.03.

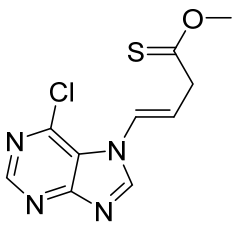
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{24}N_2O_7S$: 413.1377, found 413.1377.



((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl 1-((*Z*)-4-methoxy-4-thioxobut-1-en-1-yl)-1*H*-pyrazole-4-carboxylate (33):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.03 (s, 1H), 6.81 (dt, *J* = 9.2, 1.9 Hz, 1H), 5.79 (dt, *J* = 9.4, 7.2 Hz, 1H), 5.01 (s, 1H), 4.77 – 4.68 (m, 1H), 4.63 (d, *J* = 5.9 Hz, 1H), 4.47 (d, *J* = 1.1 Hz, 1H), 4.29 (dd, *J* = 6.7, 1.9 Hz, 2H), 4.12 (s, 3H), 4.04 (dd, *J* = 7.2, 1.8 Hz, 2H), 3.33 (s, 3H), 1.50 (d, *J* = 0.7 Hz, 3H), 1.39 – 1.19 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.40, 162.08, 142.05, 133.58, 125.73, 117.06, 114.99, 112.62, 109.52, 85.32, 84.37, 81.91, 64.60, 59.21, 54.93, 43.69, 26.47, 25.02.

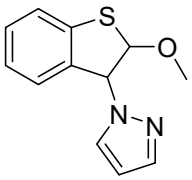


***O*-methyl (*E*)-4-(6-chloro-7*H*-purin-7-yl)but-3-enethioate (34):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.32 (s, 1H), 7.12 (dt, *J* = 14.4, 1.4 Hz, 1H), 6.74 (dt, *J* = 14.4, 7.5 Hz, 1H), 4.14 (s, 3H), 3.68 (dd, *J* = 7.5, 1.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 219.17, 152.56, 151.53, 150.75, 142.55, 132.03, 122.02, 118.09, 59.38, 46.57.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{10}H_9ClN_4OS$: 269.0258, found 269.0258.

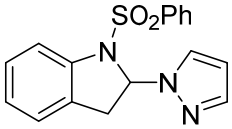


1-(2-methoxy-2,3-dihydrobenzo[b]thiophen-3-yl)-1H-pyrazole (35):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.12 (td, *J* = 7.4, 1.5 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 2.3 Hz, 1H), 6.25 (d, *J* = 5.0 Hz, 1H), 5.33 (d, *J* = 4.8 Hz, 1H), 3.27 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.51, 137.24, 136.47, 130.92, 129.46, 125.36, 124.99, 123.90, 106.24, 91.96, 72.19, 57.15.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{12}H_{12}N_2OS$: 233.0743, found 233.0743.

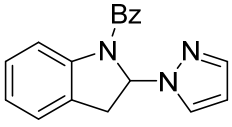


1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (36):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.5 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.33 (m, 3H), 7.32 – 7.22 (m, 2H), 7.15 – 7.11 (m, 1H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.46 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.11 (t, *J* = 2.1 Hz, 1H), 3.42 (dd, *J* = 16.9, 2.2 Hz, 1H), 3.33 (dd, *J* = 16.9, 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.70, 140.48, 138.69, 133.40, 129.39, 129.24, 129.19, 128.21, 126.85, 125.10, 124.72, 114.95, 106.28, 75.61, 36.00.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{15}N_3O_2S$: 181.0972, found 181.0971.

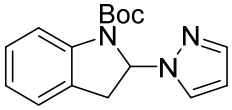


(2-(1*H*-pyrazol-1-yl)indolin-1-yl)(phenyl)methanone (37):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.07 (m, 8H), 7.07 – 6.82 (m, 2H), 6.67 – 6.41 (m, 1H), 6.05 (d, *J* = 2.3 Hz, 1H), 3.58 (dd, *J* = 16.7, 8.4 Hz, 1H), 3.26 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.62, 140.27, 135.57, 130.88, 129.52, 128.70, 128.38, 127.69, 127.10, 125.16, 124.75, 116.63, 105.91, 75.02, 36.49.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{15}N_3O$: 290.1288, found 290.1285.

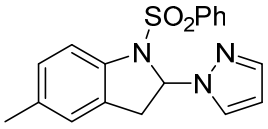


***tert*-butyl 2-(1*H*-pyrazol-1-yl)indoline-1-carboxylate (38):**

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.20 (td, *J* = 7.7, 1.3 Hz, 1H), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H), 6.62 (dd, *J* = 9.5, 2.1 Hz, 1H), 6.23 (t, *J* = 2.1 Hz, 1H), 3.69 (dd, *J* = 17.1, 9.4 Hz, 1H), 3.21 (d, *J* = 17.1 Hz, 1H), 1.39 (s, 10H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 151.12, 142.37, 139.76, 129.91, 129.07, 127.20, 124.50, 122.79, 114.05, 104.67, 81.04, 72.89, 33.58, 27.80.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{19}N_3O_2$: 286.1550, found 286.1550.

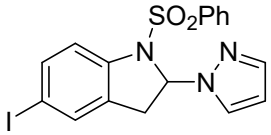


5-methyl-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (39):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 2.7 Hz, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.54 – 7.43 (m, 2H), 7.37 (q, J = 7.6 Hz, 3H), 7.08 – 6.86 (m, 2H), 6.51 (d, J = 8.9 Hz, 1H), 6.21 (d, J = 2.4 Hz, 1H), 3.47 (d, J = 16.8 Hz, 1H), 3.34 (dd, J = 16.8, 8.8 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.64, 138.55, 138.06, 134.62, 133.35, 129.65, 129.16, 129.14, 128.76, 126.85, 125.73, 115.01, 106.24, 75.81, 35.87, 21.08.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{17}N_3O_2S$: 340.1114, found 340.1113.

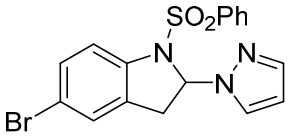


5-iodo-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (40):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.55 – 7.48 (m, 5H), 7.45 (s, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.21 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 8.9 Hz, 1H), 6.22 (s, 1H), 3.52 (d, J = 17.0 Hz, 1H), 3.43 (dd, J = 17.2, 8.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.96, 140.36, 138.35, 137.02, 133.90, 133.56, 131.87, 129.54, 129.24, 126.71, 116.43, 106.32, 87.82, 75.29, 35.38.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}IN_3O_2S$: 451.9924, found 451.9922.

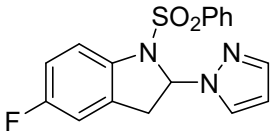


5-bromo-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (41):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.46 (d, J = 8.0 Hz, 3H), 7.38 (s, 1H), 7.35 – 7.13 (m, 5H), 6.47 (d, J = 8.9 Hz, 1H), 6.15 (s, 1H), 3.47 (d, J = 17.1 Hz, 1H), 3.35 (dd, J = 17.3, 8.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.00, 139.72, 138.43, 133.62, 131.75, 131.14, 129.58, 129.31, 128.20, 126.79, 117.47, 116.13, 106.40, 75.57, 35.57.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}BrN_3O_2S$: 404.0063, found 404.0061.

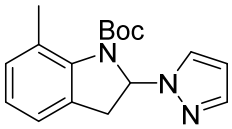


5-fluoro-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (42):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.55 (t, *J* = 8.3 Hz, 3H), 7.49 – 7.22 (m, 4H), 7.00 – 6.77 (m, 2H), 6.53 (d, *J* = 8.9 Hz, 1H), 6.24 (s, 1H), 3.54 (d, *J* = 17.1 Hz, 1H), 3.35 (dd, *J* = 17.3, 9.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.34, 159.41, 140.91, 138.29, 136.50, 133.61, 131.87 (d, *J* = 8.8 Hz), 129.45, 129.31, 126.86, 116.30 (d, *J* = 8.6 Hz), 114.84 (d, *J* = 23.5 Hz), 112.53 (d, *J* = 24.7 Hz), 76.01, 35.73.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}FN_3O_2S$: 344.0864, found 344.0861.

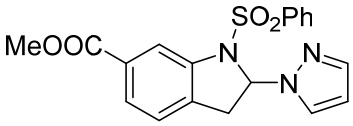


***tert*-butyl 7-methyl-2-(1*H*-pyrazol-1-yl)indoline-1-carboxylate (43):**

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.12 (dd, *J* = 6.3, 2.5 Hz, 1H), 7.07 – 6.92 (m, 2H), 6.67 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.24 (t, *J* = 2.1 Hz, 1H), 3.78 (dd, *J* = 16.7, 8.3 Hz, 1H), 3.32 (d, *J* = 16.8 Hz, 1H), 2.18 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 152.24, 139.99, 139.48, 131.88, 129.65, 128.78, 126.67, 124.51, 121.75, 105.40, 81.45, 75.63, 35.71, 27.82, 19.83.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{21}N_3O_2$: 300.1707, found 300.1705.

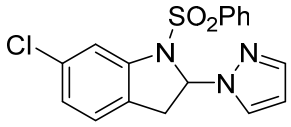


methyl 1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline-6-carboxylate (44):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 3.2 Hz, 1H), 7.68 (dd, *J* = 7.9, 3.1 Hz, 1H), 7.56 (d, *J* = 3.2 Hz, 1H), 7.50 – 7.36 (m, 3H), 7.33 (d, *J* = 3.0 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.18 – 7.01 (m, 1H), 6.51 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.11 (t, *J* = 2.6 Hz, 1H), 3.80 (d, *J* = 2.6 Hz, 3H), 3.48 (d, *J* = 17.3 Hz, 1H), 3.43 – 3.31 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.58, 141.00, 140.90, 138.53, 134.72, 133.59, 130.57, 129.61, 129.28, 126.84, 126.37, 124.91, 115.28, 106.36, 75.58, 52.39, 35.99.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{17}N_3O_4S$: 384.1013, found 384.1010.

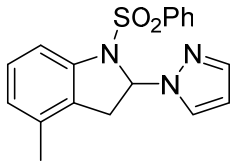


6-chloro-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (45):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 3H), 7.44 (d, *J* = 3.8 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 1H), 6.21 (s, 1H), 3.74 – 3.04 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.65, 141.01, 138.50, 133.90, 133.64, 129.56, 129.32, 127.79, 126.77, 125.79, 124.59, 114.99, 106.37, 75.88, 35.53.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}ClN_3O_2S$: 360.0568, found 360.0566.

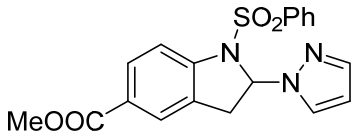


4-methyl-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (46):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.32 (m, 2H), 7.32 – 7.19 (m, 3H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.49 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.12 (t, *J* = 2.1 Hz, 1H), 3.34 (dd, *J* = 16.9, 2.4 Hz, 1H), 3.25 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.71, 140.16, 138.66, 134.75, 133.36, 129.26, 129.16, 128.33, 127.92, 126.87, 125.72, 112.20, 106.19, 75.56, 35.19, 18.80.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{17}N_3O_2S$: 340.1114, found 340.1111.

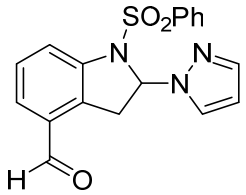


methyl 1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline-5-carboxylate (47):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.79 (d, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 2.5 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.37 – 7.31 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 6.56 (t, *J* = 5.8 Hz, 1H), 6.12 (t, *J* = 2.1 Hz, 1H), 3.78 (s, 3H), 3.48 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.54, 144.47, 141.07, 138.61, 133.61, 130.58, 129.74, 129.34, 129.23, 126.74, 126.52, 126.20, 113.40, 106.33, 75.69, 52.15, 35.63.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{17}N_3O_4S$: 384.1013, found 384.1012.

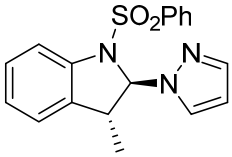


1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline-4-carbaldehyde (48):

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.52 (dd, *J* = 14.4, 7.7 Hz, 4H), 7.48 – 7.41 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.23 (d, *J* = 2.8 Hz, 1H), 4.02 (d, *J* = 18.7 Hz, 1H), 3.76 (dd, *J* = 18.8, 9.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.11, 142.19, 141.26, 138.64, 133.67, 132.58, 130.47, 129.94, 129.33, 129.03, 128.34, 126.81, 119.39, 106.28, 75.94, 36.12.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{15}N_3O_3S$: 354.0907, found 354.0905.

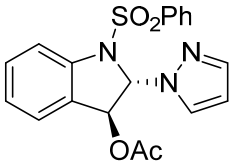


***trans*-3-methyl-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indoline (49):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 17.0, 8.0 Hz, 3H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 17.0, 9.3 Hz, 3H), 7.45 (dd, *J* = 11.4, 5.4 Hz, 1H), 7.37 – 7.18 (m, 3H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.27 (t, *J* = 2.0 Hz, 1H), 3.81 (p, *J* = 7.6 Hz, 1H), 1.07 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.77, 139.61, 138.74, 133.67, 133.29, 129.12, 128.41, 128.32, 126.92, 124.59, 123.84, 113.88, 106.15, 79.70, 41.31, 10.53.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{17}N_3O_2S$: 340.1114, found 340.1113.

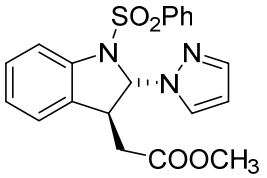


***trans*-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indolin-3-yl acetate (50):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 3H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.25 (q, *J* = 9.8, 8.6 Hz, 6H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.01 (dt, *J* = 7.6, 3.7 Hz, 1H), 6.58 (dd, *J* = 7.6, 2.6 Hz, 1H), 6.12 (d, *J* = 7.6 Hz, 1H), 6.03 (s, 1H), 1.64 (d, *J* = 2.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.45, 140.65, 140.38, 138.02, 133.59, 130.68, 130.05, 129.21, 127.06, 126.72, 125.39, 124.72, 114.19, 106.00, 76.16, 72.68, 19.96.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{17}N_3O_4S$: 384.1013, found 384.1012.

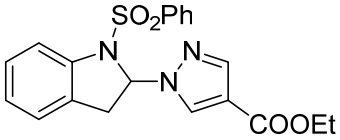


methyl 2-1-(phenylsulfonyl)-2-(1*H*-pyrazol-1-yl)indolin-3-yl)acetate (51):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.31 (m, 5H), 7.30 – 7.12 (m, 6H), 6.98 (q, *J* = 8.6, 7.9 Hz, 2H), 6.78 – 6.51 (m, 1H), 6.03 (s, 1H), 4.30 – 3.82 (m, 1H), 3.53 (d, *J* = 2.4 Hz, 3H), 2.61 (dd, *J* = 17.5, 5.8 Hz, 1H), 2.25 – 1.95 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.38, 140.95, 140.78, 138.85, 133.28, 131.11, 130.26, 129.08, 128.76, 126.85, 124.32, 123.37, 113.71, 105.74, 77.94, 52.05, 42.53, 31.36.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{20}H_{19}N_3O_4S$: 398.1169, found 398.1168.

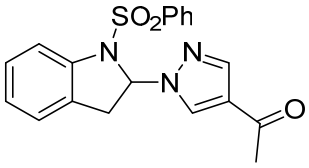


Ethyl 1-(1-(phenylsulfonyl)indolin-2-yl)-1H-pyrazole-4-carboxylate (52):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 0.6 Hz, 1H), 7.84 (d, *J* = 0.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.43 – 7.35 (m, 2H), 7.32 – 7.25 (m, 1H), 7.17 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.48 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.27 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.71 – 3.23 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.79, 142.10, 140.37, 138.26, 133.73, 132.17, 129.35, 128.98, 128.54, 126.87, 125.25, 125.23, 115.76, 115.49, 76.18, 60.42, 36.14, 14.52.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{17}N_3O_4S$: 384.1013, found 384.1012.

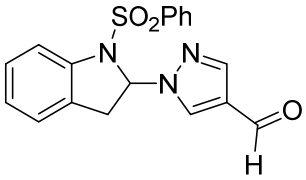


1-(1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazol-4-yl)ethan-1-one (53):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.71 (s, 1H), 7.61 – 7.50 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.32 – 7.22 (m, 2H), 7.20 – 7.11 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.97 (td, *J* = 7.5, 0.9 Hz, 1H), 6.36 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.46 – 3.18 (m, 2H), 2.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.94, 141.21, 140.27, 138.12, 133.77, 131.41, 129.35, 128.95, 128.54, 126.81, 125.31, 125.26, 124.47, 115.52, 76.23, 36.04, 28.06.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{17}N_3O_3S$: 368.1063, found 368.1061.

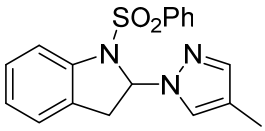


1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazole-4-carbaldehyde (54):

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.08 (s, 1H), 7.77 (s, 1H), 7.57 – 7.50 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.19 – 7.09 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.37 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.35 (dd, *J* = 17.2, 2.1 Hz, 1H), 3.27 (dd, *J* = 17.1, 8.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 184.02, 141.11, 140.21, 138.05, 133.87, 132.89, 129.42, 128.88, 128.61, 126.83, 125.41, 125.31, 124.54, 115.56, 76.36, 36.06.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{15}N_3O_3S$: 354.0907, found 354.0905.

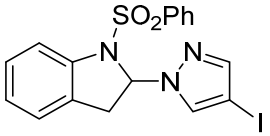


2-(4-methyl-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (55):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.44 – 7.32 (m, 3H), 7.25 – 7.20 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.11 – 7.02 (m, 1H), 6.47 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.73 – 3.21 (m, 2H), 1.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.18, 140.59, 138.80, 133.36, 129.51, 129.14, 128.25, 127.67, 126.92, 125.15, 124.73, 116.98, 115.06, 75.67, 35.96, 8.92.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{17}N_3O_2S$: 340.1114, found 340.1114.

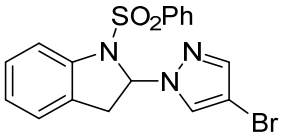


2-(4-iodo-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (56):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.35 (m, 5H), 7.30 – 7.20 (m, 3H), 7.18 – 7.08 (m, 1H), 7.03 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 6.35 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.37 – 3.12 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.33, 140.35, 138.33, 133.61, 133.28, 129.23, 128.99, 128.40, 126.73, 125.18, 124.95, 115.09, 75.95, 57.57, 35.89.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}IN_3O_2S$: 451.9924, found 451.9922.

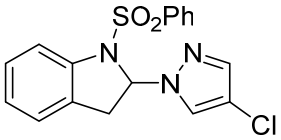


2-(4-bromo-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (57):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 3H), 7.48 – 7.38 (m, 2H), 7.32 – 7.23 (m, 2H), 7.21 – 7.11 (m, 1H), 7.06 (dd, *J* = 7.2, 1.4 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.35 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.36 (dd, *J* = 17.1, 2.2 Hz, 1H), 3.28 (dd, *J* = 17.1, 8.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.91, 140.32, 138.31, 133.62, 129.24, 129.04, 129.02, 128.40, 126.76, 125.17, 125.00, 115.19, 94.25, 76.17, 35.79.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}BrN_3O_2S$: 404.0063, found 404.0062.

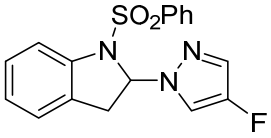


2-(4-chloro-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (58):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.38 (m, 5H), 7.38 – 7.23 (m, 3H), 7.22 – 7.14 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.35 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.39 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.29 (dd, *J* = 17.0, 8.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.34, 138.88, 138.36, 133.64, 129.27, 129.08, 128.44, 126.87, 126.80, 125.18, 125.04, 115.27, 111.06, 76.27, 35.76.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}ClN_3O_2S$: 360.0568, found 360.0566.

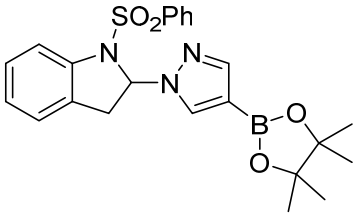


2-(4-fluoro-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (59):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.46 – 7.34 (m, 3H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.20 – 7.09 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.27 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.36 (dd, *J* = 17.1, 2.1 Hz, 1H), 3.23 (dd, *J* = 17.0, 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.90, 148.93, 140.34, 138.43, 133.59, 129.25, 128.35, 127.69 (d, *J* = 14.1 Hz), 126.82, 125.12, 125.01, 115.36, 114.88 (d, *J* = 28.0 Hz), 76.59, 35.48.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{14}FN_3O_2S$: 344.0864, found 344.0863.

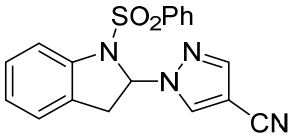


1-(phenylsulfonyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazol-1-yl)indoline (60):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.62 (s, 1H), 7.52 – 7.48 (m, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.16 (dd, *J* = 8.1, 6.8 Hz, 1H), 7.06 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 6.45 (t, *J* = 5.5 Hz, 1H), 3.32 (d, *J* = 5.5 Hz, 2H), 1.20 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.47, 140.57, 138.52, 135.59, 133.44, 129.19, 129.15, 128.33, 126.87, 125.22, 124.89, 115.24, 83.49, 75.69, 36.40, 24.98, 24.94, 24.92, 24.82.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{23}H_{26}BN_3O_4S$: 452.1810, found 452.1809.

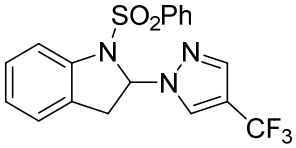


1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazole-4-carbonitrile (61):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.62 (s, 1H), 7.40 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.29 – 7.19 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.17 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.22 – 2.98 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.08, 139.95, 138.18, 137.71, 134.25, 134.03, 129.48, 128.68, 126.76, 125.52, 125.29, 115.52, 113.07, 92.99, 76.42, 35.91.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{14}N_4O_2S$: 351.0910, found 351.0909.

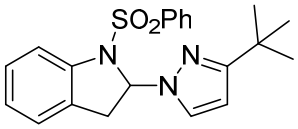


1-(phenylsulfonyl)-2-(4-(trifluoromethyl)-1*H*-pyrazol-1-yl)indoline (62):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.58 – 7.35 (m, 5H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.15 (q, *J* = 7.5, 6.4 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.02 – 6.87 (m, 1H), 6.57 – 6.06 (m, 1H), 3.52 – 3.14 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.33, 138.29, 137.98 (d, *J* = 2.7 Hz), 133.79, 129.37, 128.89, 128.59, 128.40 (d, *J* = 3.7 Hz), 126.76, 125.25 (d, *J* = 4.8 Hz), 122.41 (q, *J* = 266.2 Hz), 115.35, 114.30 (q, *J* = 38.1 Hz), 76.21, 36.06.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{14}F_3N_3O_2S$: 394.0832, found 394.0831.

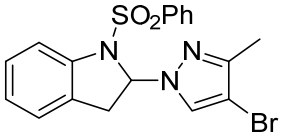


2-(3-(*tert*-butyl)-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (63):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.50 (dd, *J* = 9.8, 7.5 Hz, 2H), 7.42 (t, *J* = 2.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.54 (dt, *J* = 8.6, 2.1 Hz, 1H), 6.01 (t, *J* = 2.0 Hz, 1H), 3.46 (d, *J* = 16.8 Hz, 1H), 3.38 (dd, *J* = 17.0, 8.7 Hz, 1H), 1.24 (d, *J* = 1.8 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.76, 140.70, 138.87, 133.30, 129.69, 129.13, 128.61, 128.03, 126.90, 125.18, 124.52, 115.00, 102.69, 75.91, 36.45, 32.27, 30.62.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{21}H_{23}N_3O_2S$: 382.1583, found 392.1582.

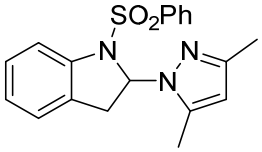


2-(4-bromo-3-methyl-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (64):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dtd, *J* = 54.0, 11.1, 9.9, 5.3 Hz, 5H), 7.43 (dt, *J* = 8.3, 5.0 Hz, 2H), 7.32 (q, *J* = 9.9 Hz, 1H), 7.29 – 7.19 (m, 1H), 7.14 (td, *J* = 7.5, 3.0 Hz, 1H), 6.52 (dd, *J* = 66.8, 8.9 Hz, 1H), 3.98 – 3.10 (m, 2H), 2.32 (dd, *J* = 148.6, 3.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.38, 140.71 (d, *J* = 45.1 Hz), 139.58 (d, *J* = 210.1 Hz), 138.08 (d, *J* = 72.2 Hz), 133.44 (d, *J* = 21.1 Hz), 129.13 (d, *J* = 7.3 Hz), 128.98 (d, *J* = 16.3 Hz), 128.26 (d, *J* = 20.5 Hz), 126.69 (d, *J* = 25.7 Hz), 124.79 (d, *J* = 14.5 Hz), 124.78 (d, *J* = 119.9 Hz), 114.60 (d, *J* = 146.3 Hz), 94.78 (d, *J* = 63.7 Hz), 74.63 (d, *J* = 385.2 Hz), 36.16 (d, *J* = 52.5 Hz), 10.94 (d, *J* = 276.0 Hz).

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{18}H_{16}BrN_3O_2S$: 418.0219, found 418.0217.

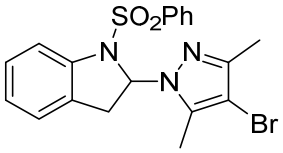


2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (65):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.46 (dd, *J* = 7.8, 6.4 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.16 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.48 (dd, *J* = 9.8, 3.1 Hz, 1H), 5.70 (s, 1H), 3.52 (dd, *J* = 16.8, 9.8 Hz, 1H), 3.34 (dd, *J* = 16.8, 3.1 Hz, 1H), 2.36 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.15, 141.13, 140.12, 139.09, 132.99, 129.05, 128.81, 127.87, 126.83, 124.81, 123.73, 113.76, 106.06, 72.20, 36.45, 13.68, 11.10.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{19}N_3O_2S$: 354.1271, found 354.1269.

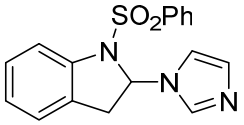


2-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(phenylsulfonyl)indoline (66):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 20.8, 7.9 Hz, 4H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.39 (dd, *J* = 9.7, 2.8 Hz, 1H), 3.46 (dd, *J* = 16.9, 9.8 Hz, 1H), 3.22 (dd, *J* = 16.9, 2.9 Hz, 1H), 2.25 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.57, 141.16, 138.83, 138.03, 133.15, 128.79, 128.76, 128.07, 126.61, 124.82, 123.90, 113.72, 95.66, 73.07, 36.29, 12.40, 10.43.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{18}BrN_3O_2S$: 432.0376, found 432.0375.

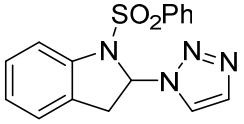


2-(1*H*-imidazol-1-yl)-1-(phenylsulfonyl)indoline (67):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.16 (dd, *J* = 9.3, 6.4 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.59 (s, 1H), 6.37 (d, *J* = 8.9 Hz, 1H), 3.47 (dd, *J* = 17.2, 9.0 Hz, 1H), 3.02 (d, *J* = 17.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.11, 138.52, 136.10, 133.57, 130.44, 129.33, 128.74, 127.97, 126.69, 125.26, 124.68, 116.01, 114.58, 71.69, 37.18.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{15}N_3O_2S$: 181.0972, found 181.0970.

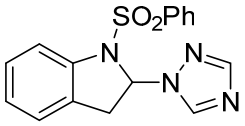


1-(phenylsulfonyl)-2-(1*H*-1,2,3-triazol-1-yl)indoline (68):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.1 Hz, 1H), 7.66 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 8.7, 1.7 Hz, 1H), 3.66 – 3.59 (m, 1H), 3.43 (dd, *J* = 17.2, 8.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.07, 137.90, 134.27, 133.95, 129.52, 129.00, 128.72, 126.91, 125.60, 125.45, 122.57, 116.04, 74.97, 36.23.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{15}N_4O_2S$: 327.0910, found 327.0908.

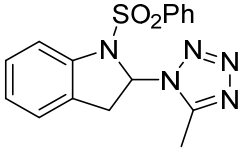


1-(phenylsulfonyl)-2-(1*H*-1,2,4-triazol-1-yl)indoline (69):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.70 (s, 1H), 7.57 – 7.46 (m, 2H), 7.45 – 7.37 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.45 (dd, *J* = 8.1, 2.7 Hz, 1H), 3.48 – 3.13 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.53, 143.13, 140.06, 138.07, 133.75, 129.35, 128.70, 128.48, 126.67, 125.18, 125.14, 115.25, 73.91, 35.74.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{15}N_4O_2S$: 327.0910, found 327.0910.



2-(5-methyl-1*H*-tetrazol-1-yl)-1-(phenylsulfonyl)indoline (70):

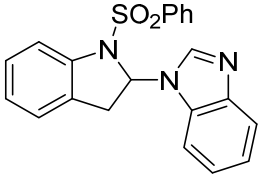
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 21.4, 7.9 Hz, 3H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 9.1 Hz, 1H), 3.60 (dd, *J* = 17.3, 9.2 Hz, 1H), 3.34 (d, *J* = 17.1 Hz, 1H), 2.36 (d, *J* = 2.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.66, 140.60, 138.20, 133.70, 129.28, 128.64, 128.06, 126.89, 125.12, 124.95, 115.00, 76.29, 36.11, 10.97.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.51 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 8.9 Hz, 1H), 3.54 (dd, *J* = 17.3, 9.2 Hz, 1H), 3.34 (d, *J* = 17.2 Hz, 1H), 2.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.59, 139.90, 137.46, 134.12, 129.53, 128.76, 128.36, 126.67, 125.51, 125.02, 115.46, 72.25, 36.49, 9.36.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{15}N_5O_2S$: 342.1019, found 342.1018.

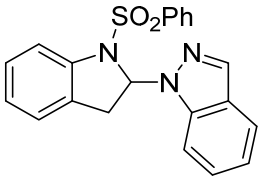


1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-benzo[d]imidazole (71):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 3H), 7.21 – 7.11 (m, 2H), 7.02 (dt, *J* = 23.5, 7.6 Hz, 4H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.66 (dd, *J* = 10.1, 2.7 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 3.62 (dd, *J* = 17.4, 9.9 Hz, 1H), 3.19 (dd, *J* = 17.4, 2.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.30, 142.36, 140.75, 138.15, 133.34, 131.27, 128.99, 128.94, 127.82, 126.20, 125.17, 124.65, 123.49, 122.74, 120.67, 114.05, 110.86, 71.61, 35.78.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{21}H_{17}N_3O_2S$: 376.1114, found 376.1112.

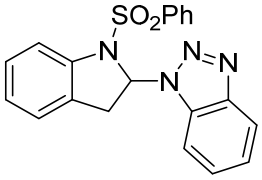


1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-indazole (72):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (dt, *J* = 16.7, 8.9 Hz, 4H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.26 (qd, *J* = 13.2, 11.4, 8.1 Hz, 4H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.58 (d, *J* = 17.0 Hz, 1H), 3.49 (dd, *J* = 17.2, 8.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.25, 140.69, 138.08, 133.60, 129.27, 129.12, 128.46, 126.84, 126.62, 125.43, 125.16, 122.16, 122.06, 121.67, 120.67, 117.86, 115.49, 77.35, 37.06.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{21}H_{17}N_3O_2S$: 376.1114, found 376.1114.

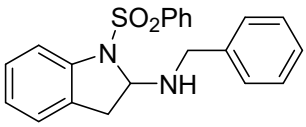


1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (73):

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 6.3, 3.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.42 (q, *J* = 8.0 Hz, 2H), 7.37 – 7.19 (m, 8H), 7.17 (dd, *J* = 6.5, 3.2 Hz, 1H), 3.73 (dd, *J* = 17.3, 9.6 Hz, 1H), 3.51 (dd, *J* = 17.4, 2.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.48, 140.71, 137.82, 133.48, 131.20, 129.04, 128.81, 128.75, 127.92, 126.53, 125.11, 125.07, 124.26, 120.04, 115.12, 110.51, 74.16, 35.97.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{20}H_{16}N_4O_2S$: 377.1067, found 377.1065.

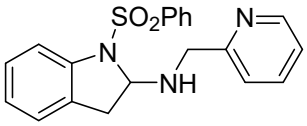


***N*-benzyl-1-(phenylsulfonyl)indolin-2-amine (74):**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.47 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.19 (m, 6H), 7.16 (tq, *J* = 6.3, 2.1, 1.6 Hz, 2H), 7.02 – 6.80 (m, 2H), 5.24 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.86 (q, *J* = 13.3 Hz, 2H), 2.85 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.67 (dd, *J* = 16.9, 2.5 Hz, 1H), 2.30 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.56, 139.92, 138.67, 133.09, 131.31, 129.11, 128.48, 128.39, 128.03, 127.10, 126.91, 125.09, 124.80, 117.33, 78.49, 47.53, 35.21.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{21}H_{20}N_2O_2S$: 365.1318, found 365.1317.

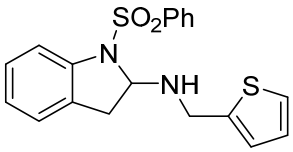


1-(phenylsulfonyl)-*N*-(pyridin-2-ylmethyl)indolin-2-amine (75):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.64 – 7.47 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.08 (m, 1H), 7.04 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.95 (dt, *J* = 14.6, 7.3 Hz, 2H), 5.28 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.33 – 3.69 (m, 2H), 2.82 (dd, *J* = 16.9, 8.4 Hz, 2H), 2.68 (dd, *J* = 17.0, 2.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.97, 149.23, 140.33, 138.61, 136.37, 132.96, 131.45, 128.98, 127.88, 126.78, 125.00, 124.80, 122.40, 121.89, 117.55, 78.33, 48.98, 35.33.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{20}H_{19}N_3O_2S$: 366.1271, found 366.1270.

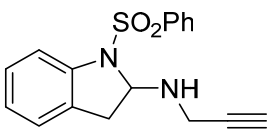


1-(phenylsulfonyl)-*N*-(thiophen-2-ylmethyl)indolin-2-amine (76):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.80 (m, 3H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.40 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.25 (d, *J* = 6.9 Hz, 2H), 7.21 – 7.01 (m, 2H), 5.50 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.41 (d, *J* = 14.1 Hz, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 3.11 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.94 (dd, *J* = 17.0, 2.3 Hz, 1H), 2.68 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.59, 140.40, 138.56, 133.14, 131.39, 129.13, 128.08, 126.91, 126.78, 125.25, 125.12, 124.97, 124.58, 117.65, 78.00, 42.88, 35.36.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{18}N_2O_2S_2$: 371.0882, found 371.0881.

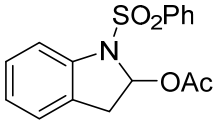


1-(phenylsulfonyl)-*N*-(prop-2-yn-1-yl)indolin-2-amine (77):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 2.2 Hz, 3H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.51 – 7.41 (m, 1H), 7.25 (d, *J* = 7.0 Hz, 2H), 5.42 (d, *J* = 8.3 Hz, 1H), 4.10 – 3.65 (m, 2H), 3.07 (dd, *J* = 17.0, 8.4 Hz, 1H), 2.90 (dd, *J* = 17.0, 2.2 Hz, 1H), 2.46 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.27, 138.45, 133.23, 131.25, 129.17, 128.17, 126.93, 125.17, 125.13, 117.81, 86.19, 81.74, 71.35, 35.37, 33.46.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{16}N_2O_2S$: 313.1005, found 313.1003.

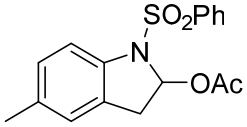


1-(phenylsulfonyl)indolin-2-yl acetate (78):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.70 – 7.56 (m, 2H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.35 – 7.23 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.12 – 7.01 (m, 1H), 6.86 (dd, *J* = 7.0, 1.2 Hz, 1H), 3.34 (dd, *J* = 17.5, 7.0 Hz, 1H), 2.94 (d, *J* = 17.5 Hz, 1H), 2.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.76, 140.62, 139.26, 133.55, 129.30, 128.53, 128.24, 127.17, 125.31, 124.29, 114.49, 85.81, 36.98, 21.11.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{15}NO_4S$: 318.0795, found 318.0794.

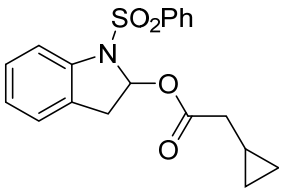


5-methyl-1-(phenylsulfonyl)indolin-2-yl acetate (79):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 3H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.76 (s, 1H), 6.59 (d, *J* = 6.8 Hz, 1H), 3.04 (dd, *J* = 17.5, 6.9 Hz, 1H), 2.65 (d, *J* = 17.5 Hz, 1H), 2.09 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.81, 139.17, 138.26, 134.18, 133.46, 129.27, 128.73, 127.15, 126.82, 125.95, 114.45, 86.05, 36.96, 21.13, 21.02.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{17}NO_4S$: 332.0951, found 332.0949.

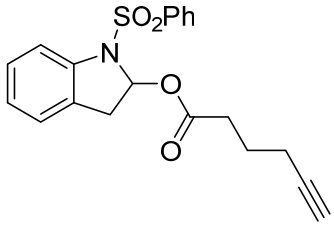


1-(phenylsulfonyl)indolin-2-yl 2-cyclopropylacetate (80):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.57 (m, 2H), 7.36 (td, *J* = 7.8, 4.9 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.65 (dd, *J* = 7.0, 1.3 Hz, 1H), 3.13 (dd, *J* = 17.6, 7.1 Hz, 1H), 2.71 (d, *J* = 17.5 Hz, 1H), 1.95 (qd, *J* = 16.0, 7.1 Hz, 2H), 0.80 (tdd, *J* = 10.3, 9.1, 5.1 Hz, 1H), 0.33 (dd, *J* = 8.1, 1.6 Hz, 2H), -0.07 (dd, *J* = 8.8, 4.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.06, 140.65, 139.26, 133.53, 129.30, 128.57, 128.21, 127.17, 125.30, 124.26, 114.50, 85.69, 39.31, 37.09, 6.64, 4.47, 4.43.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{19}NO_4S$: 358.1108, found 358.1107.

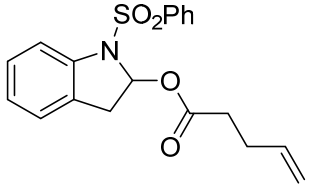


1-(phenylsulfonyl)indolin-2-yl hex-5-ynoate (81):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 7.97 (m, 2H), 7.87 – 7.74 (m, 2H), 7.69 (t, *J* = 7.7 Hz, 2H), 7.55 – 7.40 (m, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 3.53 (dd, *J* = 17.6, 7.1 Hz, 1H), 3.12 (d, *J* = 17.5 Hz, 1H), 2.60 (td, *J* = 7.4, 4.2 Hz, 2H), 2.46 (td, *J* = 6.9, 2.6 Hz, 2H), 2.18 (t, *J* = 2.7 Hz, 1H), 2.03 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.89, 140.58, 139.18, 133.58, 129.33, 128.46, 128.24, 127.15, 125.31, 124.28, 114.44, 85.69, 83.21, 69.43, 36.99, 32.92, 23.32, 17.86.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{20}H_{19}NO_4S$: 370.1108, found 370.1106.

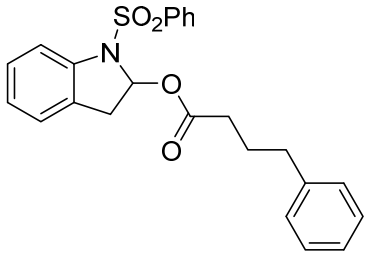


1-(phenylsulfonyl)indolin-2-yl pent-4-enoate (82):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.12 – 6.99 (m, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 6.9 Hz, 1H), 5.81 – 5.46 (m, 1H), 4.96 – 4.59 (m, 2H), 3.11 (dd, *J* = 17.5, 7.0 Hz, 1H), 2.68 (d, *J* = 17.5 Hz, 1H), 2.13 (t, *J* = 3.6 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.86, 140.61, 139.21, 136.39, 133.55, 129.31, 128.52, 128.23, 127.15, 125.30, 124.28, 115.89, 114.48, 85.76, 37.04, 33.52, 28.62.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{19}H_{19}NO_4S$: 357.1035, found 357.1033.

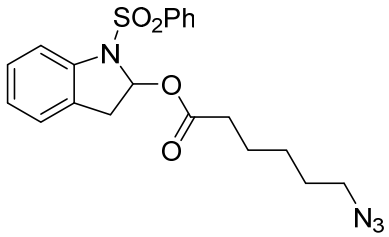


1-(phenylsulfonyl)indolin-2-yl 4-phenylbutanoate (83):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.86 (m, 2H), 7.77 – 7.58 (m, 2H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.36 (dt, *J* = 14.5, 7.6 Hz, 3H), 7.32 – 7.27 (m, 1H), 7.25 (dd, *J* = 7.8, 2.3 Hz, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.95 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.42 (dd, *J* = 17.5, 7.0 Hz, 1H), 2.98 (d, *J* = 17.5 Hz, 1H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.34 (hept, *J* = 7.9, 7.4 Hz, 2H), 2.02 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.26, 141.31, 140.62, 139.24, 133.51, 129.28, 128.65, 128.54, 128.50, 128.23, 127.13, 126.14, 125.31, 124.26, 114.46, 85.67, 37.01, 35.09, 33.58, 26.27.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{24}H_{23}NO_4S$: 422.1421, found 422.1420.

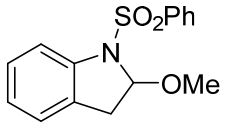


1-(phenylsulfonyl)indolin-2-yl 6-azidohexanoate (84):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.45 – 7.33 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.09 – 6.98 (m, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.11 (dd, *J* = 17.6, 7.1 Hz, 1H), 3.05 (t, *J* = 6.9 Hz, 2H), 2.68 (d, *J* = 17.5 Hz, 1H), 2.24 – 1.92 (m, 2H), 1.40 (dp, *J* = 20.0, 7.3 Hz, 4H), 1.29 – 1.13 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.24, 140.59, 139.18, 133.56, 129.32, 128.49, 128.25, 127.13, 125.31, 124.31, 114.51, 85.64, 51.29, 37.01, 34.10, 28.60, 26.20, 24.22.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{20}H_{22}N_4O_4S$: 415.1435, found 415.1433.

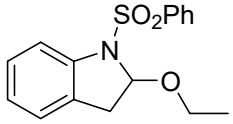


2-methoxy-1-(phenylsulfonyl)indoline (85):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.64 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.43 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.25 – 7.17 (m, 1H), 7.12 – 6.96 (m, 2H), 5.50 (dd, *J* = 4.9, 2.2 Hz, 1H), 3.51 (s, 3H), 2.90 – 2.64 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.28, 138.91, 133.21, 131.62, 129.09, 127.87, 126.95, 125.20, 125.13, 117.69, 93.50, 55.22, 36.48.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{15}H_{15}NO_3S$: 290.0845, found 290.0843.

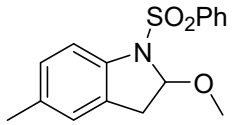


2-ethoxy-1-(phenylsulfonyl)indoline (86):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.95 (dt, *J* = 14.8, 7.4 Hz, 2H), 5.50 (dd, *J* = 4.9, 2.5 Hz, 1H), 3.87 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.58 (dq, *J* = 9.8, 6.9 Hz, 1H), 2.66 (d, *J* = 4.1 Hz, 2H), 1.09 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.33, 138.97, 133.15, 131.76, 129.05, 127.78, 126.93, 125.16, 125.09, 117.62, 92.19, 63.31, 36.71, 14.93.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{17}NO_3S$: 304.1002, found 304.1001.

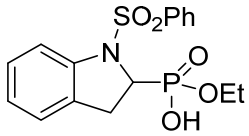


2-methoxy-5-methyl-1-(phenylsulfonyl)indoline (87):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.89 (s, 1H), 5.45 (dd, *J* = 5.4, 1.6 Hz, 1H), 3.51 (s, 3H), 3.04 – 2.53 (m, 2H), 2.27 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.90, 137.86, 135.10, 133.13, 131.84, 129.08, 128.50, 126.97, 125.78, 117.71, 93.71, 55.24, 36.53, 21.16.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{17}NO_3S$: 304.1002, found 304.1002.

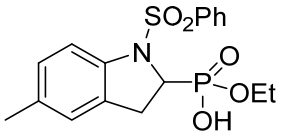


ethyl hydrogen (1-(phenylsulfonyl)indolin-2-yl)phosphonate (88):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.06 (dt, *J* = 14.7, 7.4 Hz, 2H), 5.59 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.25 – 3.83 (m, 1H), 3.68 (dq, *J* = 8.8, 7.0 Hz, 1H), 2.76 (d, *J* = 4.9 Hz, 2H), 1.19 (dd, *J* = 8.0, 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.32, 138.94, 133.16, 131.77, 129.06, 127.80, 126.93, 125.17, 125.12, 117.66, 92.20, 63.34, 36.72, 14.94.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{18}NO_5PS$: 368.0716, found 368.0715.

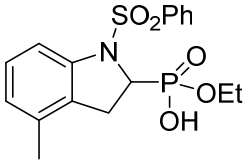


ethyl hydrogen (5-methyl-1-(phenylsulfonyl)indolin-2-yl)phosphonate (89):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.59 (m, 2H), 7.56 – 7.43 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.02 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.88 (s, 1H), 5.55 (dd, *J* = 5.2, 1.8 Hz, 1H), 3.97 (dq, *J* = 9.8, 7.1 Hz, 1H), 3.67 (dq, *J* = 9.7, 7.0 Hz, 1H), 2.84 – 2.59 (m, 2H), 2.27 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H).

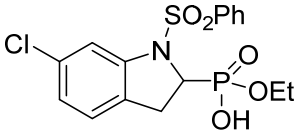
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.95, 137.93, 134.97, 133.07, 132.00, 129.03, 128.40, 126.95, 125.81, 117.64, 92.39, 63.28, 36.72, 21.16, 14.94.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{20}NO_5PS$: 382.0873, found 382.0873.



ethyl hydrogen (4-methyl-1-(phenylsulfonyl)indolin-2-yl)phosphonate (90):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.48 (m, 2H), 7.44 – 7.36 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.53 (dd, *J* = 6.1, 1.2 Hz, 1H), 3.87 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.58 (dq, *J* = 9.7, 7.0 Hz, 1H), 2.80 – 2.44 (m, 2H), 2.01 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.98, 139.02, 134.62, 133.10, 130.36, 129.01, 127.83, 126.98, 126.06, 114.79, 92.00, 63.33, 35.60, 18.80, 14.97.
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{20}NO_5PS$: 382.0873, found 382.0871.

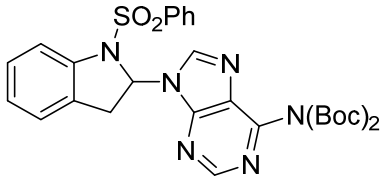


ethyl hydrogen (6-chloro-1-(phenylsulfonyl)indolin-2-yl)phosphonate (91):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.65 (m, 2H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.07 – 6.82 (m, 2H), 5.60 (dd, *J* = 4.8, 2.5 Hz, 1H), 3.94 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.65 (dq, *J* = 9.7, 7.0 Hz, 1H), 2.96 – 2.60 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.61, 138.89, 133.50, 133.43, 130.21, 129.26, 126.96, 125.90, 125.12, 117.83, 92.69, 63.48, 36.33, 14.92.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{16}H_{17}ClNO_5PS$: 402.0326, found 402.0325.

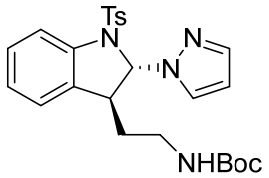


***tert*-butyl (*tert*-butoxycarbonyl)(9-(1-(phenylsulfonyl)indolin-2-yl)-9*H*-purin-6-yl)carbamate (92):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.08 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 – 7.06 (m, 2H), 6.83 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.53 (dd, *J* = 17.3, 9.0 Hz, 1H), 3.28 (dd, *J* = 17.3, 2.5 Hz, 1H), 1.46 (s, 20H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.39, 152.33, 150.63, 150.60, 142.39, 140.46, 137.51, 134.07, 129.54, 128.99, 128.92, 128.33, 126.97, 125.57, 125.54, 115.76, 83.98, 70.80, 37.25, 27.93.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{29}H_{32}N_6O_6S$: 593.2177, found 593.2176.

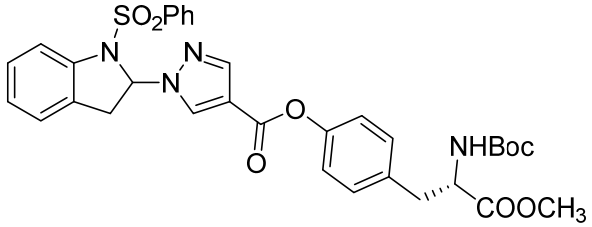


***tert*-butyl (2-(-2-(1*H*-pyrazol-1-yl)-1-tosylindolin-3-yl)ethyl)carbamate (93):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 19.8, 8.0 Hz, 3H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.32 – 7.24 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.26 (d, *J* = 2.2 Hz, 1H), 4.90 (s, 0H), 3.73 (p, *J* = 4.4 Hz, 1H), 3.30 (dt, *J* = 14.5, 7.2 Hz, 1H), 3.19 (dt, *J* = 13.8, 6.5 Hz, 1H), 2.48 (s, 3H), 1.60 (s, 9H), 1.27 (ddt, *J* = 15.7, 11.8, 6.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.26, 144.50 (d, *J* = 78.9 Hz), 140.78 (d, *J* = 9.7 Hz), 139.86, 135.96, 132.61, 129.71, 129.16, 128.42, 126.95, 124.32, 123.69, 113.83, 106.10, 79.12 (d, *J* = 87.2 Hz), 60.49, 43.95, 38.89, 28.53, 27.56, 21.61.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{29}H_{32}N_6O_6S$: 593.2177, found 593.2176.

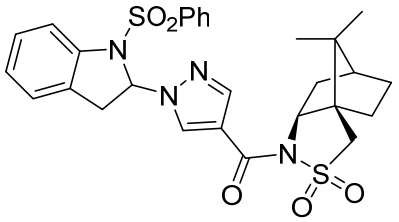


4-((*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl 1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazole-4-carboxylate (94):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.15 (s, 1H), 7.81 (dd, *J* = 22.5, 8.0 Hz, 3H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.52 – 7.41 (m, 1H), 7.40 – 7.17 (m, 6H), 6.90 – 6.62 (m, 1H), 5.19 (d, *J* = 8.3 Hz, 1H), 4.75 (d, *J* = 7.2 Hz, 1H), 3.88 (d, *J* = 1.8 Hz, 3H), 3.67 (d, *J* = 17.0 Hz, 1H), 3.58 (dd, *J* = 17.2, 8.7 Hz, 1H), 3.26 (dq, *J* = 14.1, 8.0 Hz, 2H), 1.59 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.33, 160.91, 155.19, 149.50, 142.58, 140.27, 138.07, 133.82, 133.76, 132.88, 130.40, 129.40, 128.92, 128.61, 126.87, 125.37, 125.29, 121.86, 115.62, 114.68, 80.12, 54.46, 52.39, 37.80, 36.14, 28.40.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{33}H_{34}N_4O_8S$: 647.2170, found 647.2168.

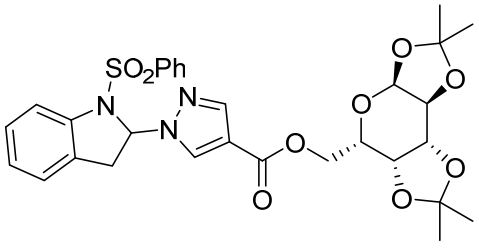


((3a*R*,6*S*,7a*S*)-8,8-dimethyl-2,2-dioxidotetrahydro-3*H*-3a,6-methanobenzo[c]isothiazol-1(4*H*)-yl)(1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazol-4-yl)methanone (95):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 13.7 Hz, 1H), 7.85 (d, *J* = 23.3 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H), 7.39 (dt, *J* = 21.7, 7.9 Hz, 2H), 7.27 (dt, *J* = 11.2, 7.8 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.07 (t, *J* = 6.9 Hz, 1H), 6.96 (td, *J* = 7.5, 3.5 Hz, 1H), 6.44 (ddd, *J* = 13.8, 8.7, 2.4 Hz, 1H), 4.02 (ddd, *J* = 7.5, 4.6, 2.6 Hz, 1H), 3.63 – 3.13 (m, 4H), 2.10 – 1.73 (m, 5H), 1.38 – 1.31 (m, 1H), 1.28 (q, *J* = 3.8, 2.8 Hz, 1H), 1.15 (d, *J* = 21.1 Hz, 3H), 0.89 (d, *J* = 7.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.38 (d, *J* = 10.7 Hz), 142.85 (d, *J* = 26.1 Hz), 140.38 (d, *J* = 15.4 Hz), 138.42 (d, *J* = 4.6 Hz), 133.59 (d, *J* = 53.8 Hz), 133.51, 129.22 (d, *J* = 8.3 Hz), 128.73 (d, *J* = 45.0 Hz), 128.24 (d, *J* = 5.8 Hz), 126.79 (d, *J* = 10.6 Hz), 125.00 (d, *J* = 8.2 Hz), 124.66 (d, *J* = 19.4 Hz), 117.06 (d, *J* = 2.4 Hz), 114.61 (d, *J* = 28.3 Hz), 75.81 (d, *J* = 11.9 Hz), 65.95 (d, *J* = 15.3 Hz), 53.56 (d, *J* = 12.7 Hz), 48.14 (d, *J* = 3.6 Hz), 47.81, 45.01 (d, *J* = 4.6 Hz), 38.47 (d, *J* = 5.3 Hz), 35.93 (d, *J* = 44.7 Hz), 33.08 (d, *J* = 5.7 Hz), 26.53, 21.14 (d, *J* = 17.1 Hz), 19.92 (d, *J* = 2.3 Hz).

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{28}H_{30}N_4O_5S_2$: 567.1730, found 567.1728.

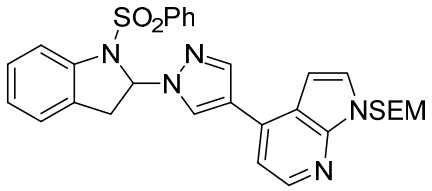


((3a*S*,5*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazole-4-carboxylate (96):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (t, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 5.6 Hz, 1H), 7.61 – 7.44 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.20 – 7.11 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.35 (dt, *J* = 5.6, 2.5 Hz, 1H), 5.42 (d, *J* = 4.8 Hz, 1H), 4.51 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.42 – 4.12 (m, 4H), 4.01 (dd, *J* = 5.1, 2.6 Hz, 1H), 3.30 (d, *J* = 5.7 Hz, 2H), 1.38 (d, *J* = 8.3 Hz, 3H), 1.34 (s, 3H), 1.22 (s, 3H), 1.20 (d, *J* = 4.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.49, 142.22 (d, *J* = 2.7 Hz), 139.31 (d, *J* = 270.3 Hz), 133.71, 132.43 (d, *J* = 20.1 Hz), 129.34, 128.68 (dd, *J* = 42.1, 2.7 Hz), 126.81 (d, *J* = 3.0 Hz), 125.20 (d, *J* = 3.8 Hz), 125.18 (d, *J* = 18.0 Hz), 115.39, 115.22 (d, *J* = 11.5 Hz), 109.36 (d, *J* = 103.6 Hz), 96.40, 76.13 (d, *J* = 7.2 Hz), 71.16, 70.71 (d, *J* = 21.5 Hz), 66.18 (d, *J* = 8.4 Hz), 63.43, 36.74, 36.16 (d, *J* = 6.3 Hz), 26.17 (d, *J* = 1.9 Hz), 26.08, 25.11, 24.58.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{30}H_{33}N_3O_9S$: 612.2010, found 612.2009.

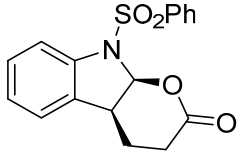


4-(1-(1-(phenylsulfonyl)indolin-2-yl)-1*H*-pyrazol-4-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrolo[2,3-*b*]pyridine (97):

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 4.9 Hz, 1H), 8.06 (s, 1H), 7.83 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 3.7 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.12 (m, 3H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.66 – 6.48 (m, 2H), 5.62 (s, 2H), 3.55 (d, *J* = 17.0 Hz, 1H), 3.50 – 3.34 (m, 3H), 0.84 (t, *J* = 8.2 Hz, 2H), -0.14 (d, *J* = 1.7 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.99, 143.60, 140.52, 139.63, 138.63, 137.23, 136.27, 133.57, 132.73, 129.26, 128.45, 128.10, 126.83, 125.22, 124.96, 120.99, 117.59, 115.07, 113.91, 100.51, 76.01, 73.13, 66.33, 35.92, 17.90, -1.30.

HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{30}H_{33}N_5O_3SSi$: 572.2146, found 572.2144.



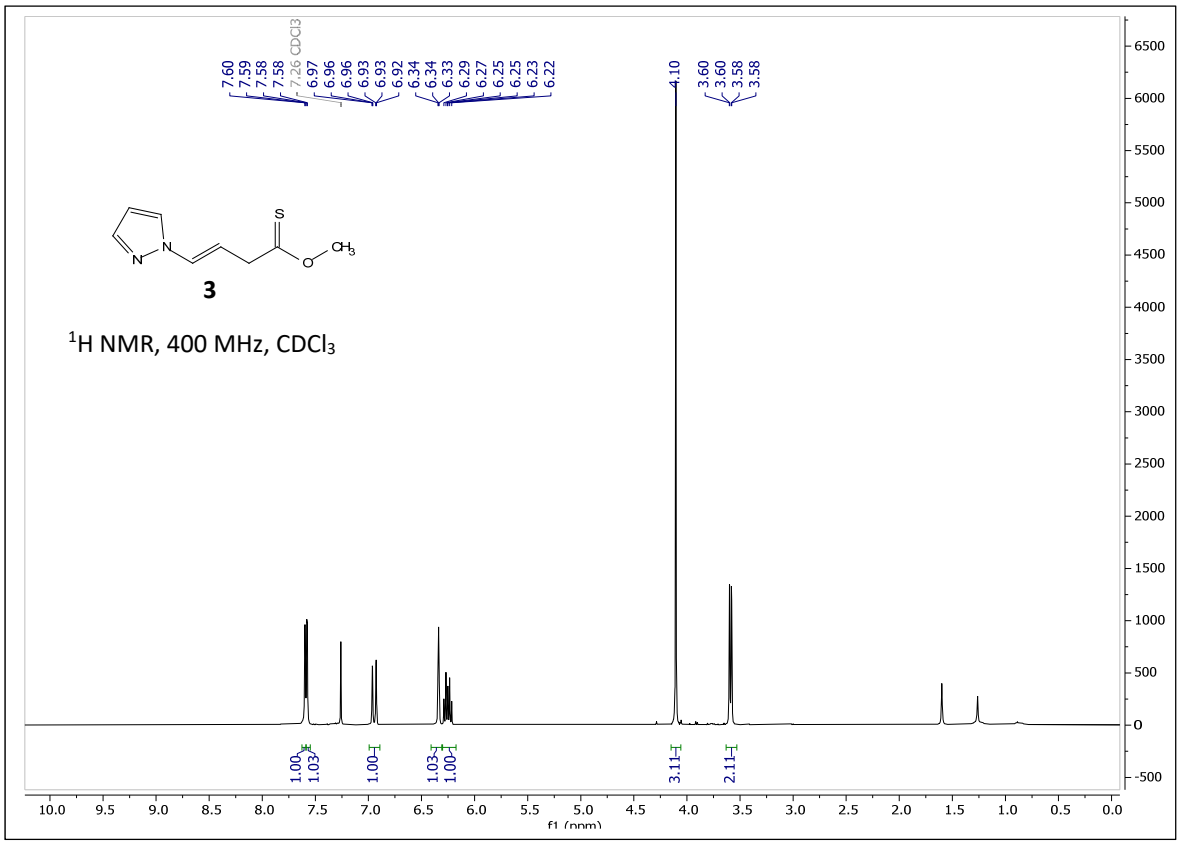
***trans*-9-(phenylsulfonyl)-4,4a,9,9a-tetrahydropyrano[2,3-*b*]indol-2(3*H*)-one (99):**

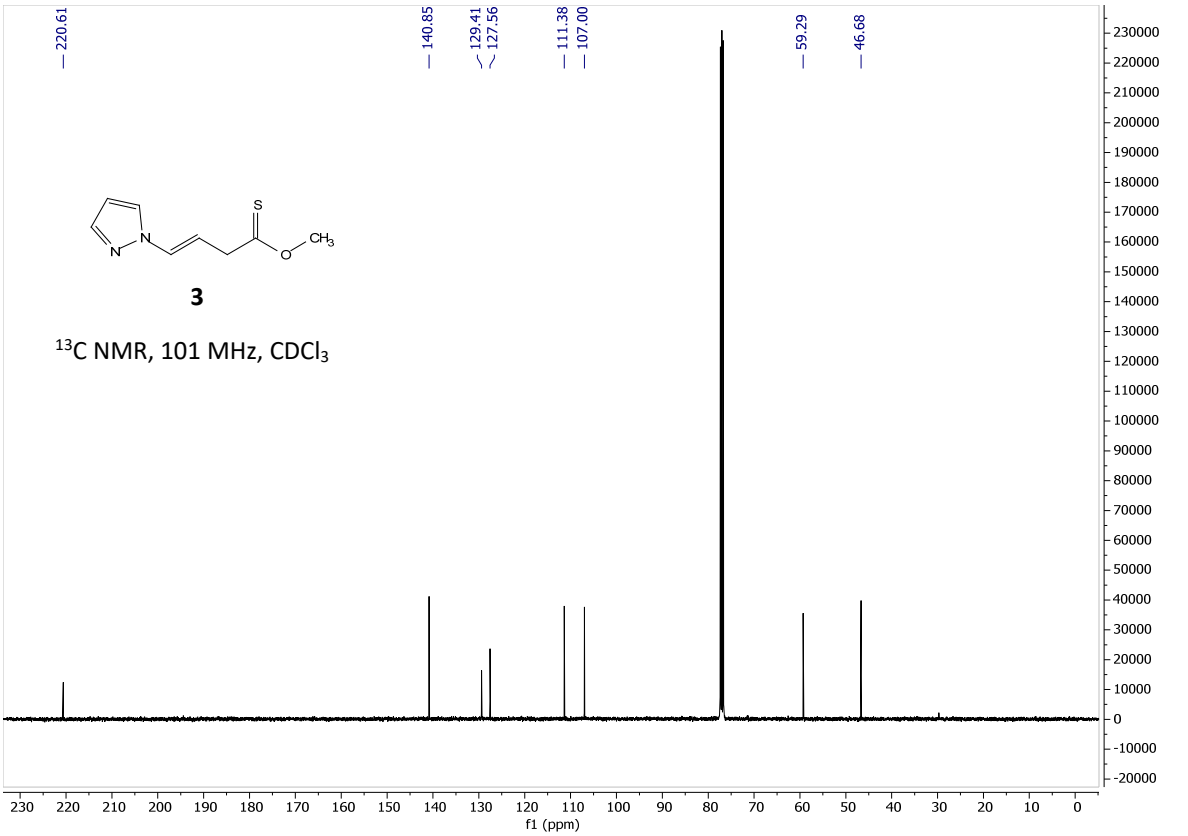
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 7.85 (m, 2H), 7.59 – 7.50 (m, 1H), 7.47 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.19 (q, *J* = 7.9, 7.4 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 3.72 (d, *J* = 6.0 Hz, 1H), 2.63 – 2.24 (m, 2H), 2.21 – 2.07 (m, 2H).

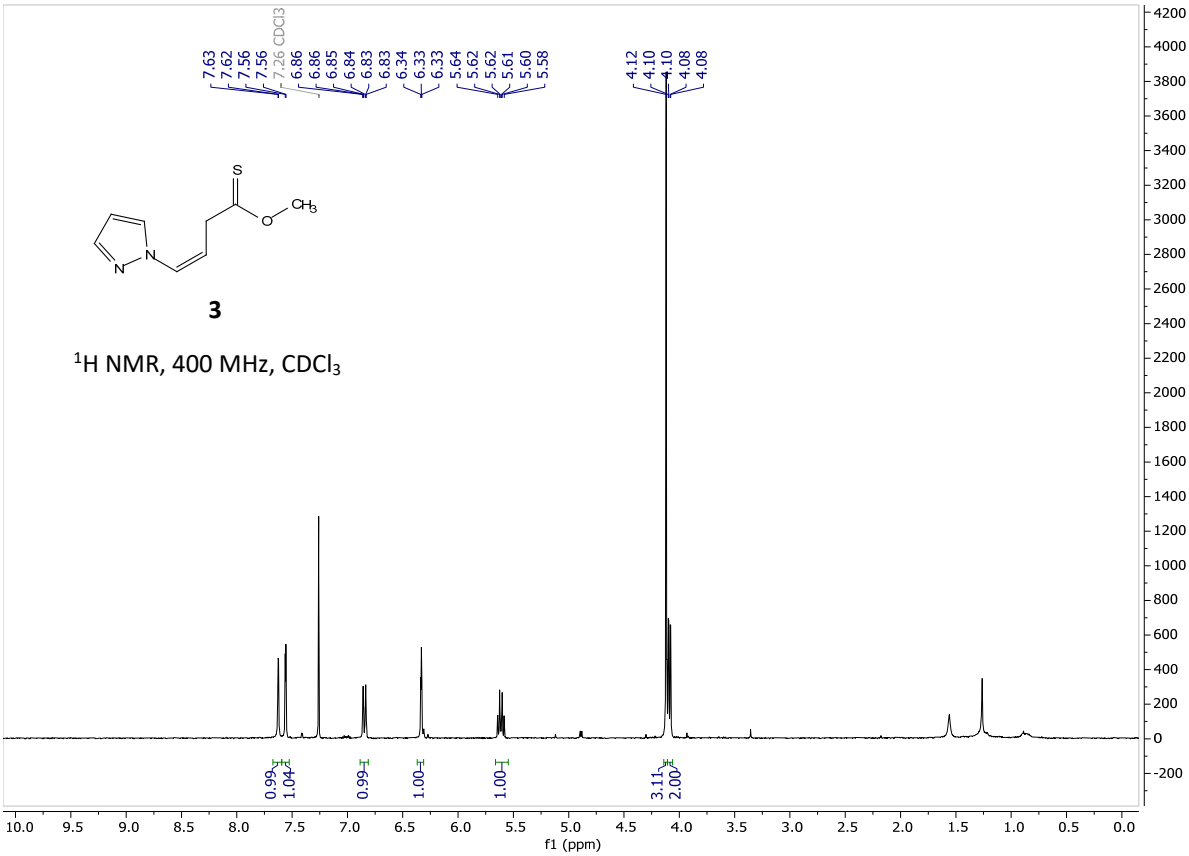
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.99, 140.68, 139.04, 133.74, 129.54, 129.31, 129.11, 127.96, 124.39, 123.96, 113.77, 91.55, 38.18, 26.97, 21.06.

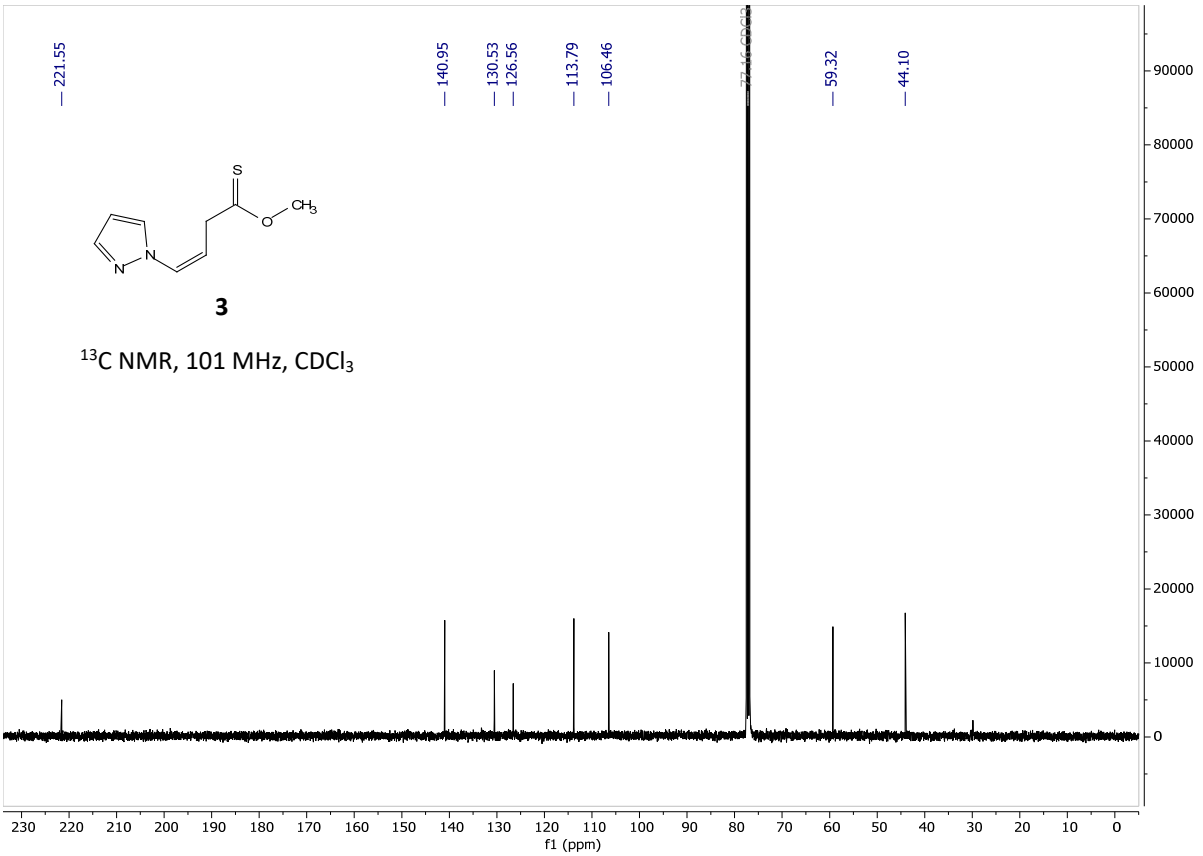
HRMS (ESI) m/z $[M + H]^+$ calculated for $C_{17}H_{15}NO_4S$: 330.0795 found 330.0793.

5. Spectral Data



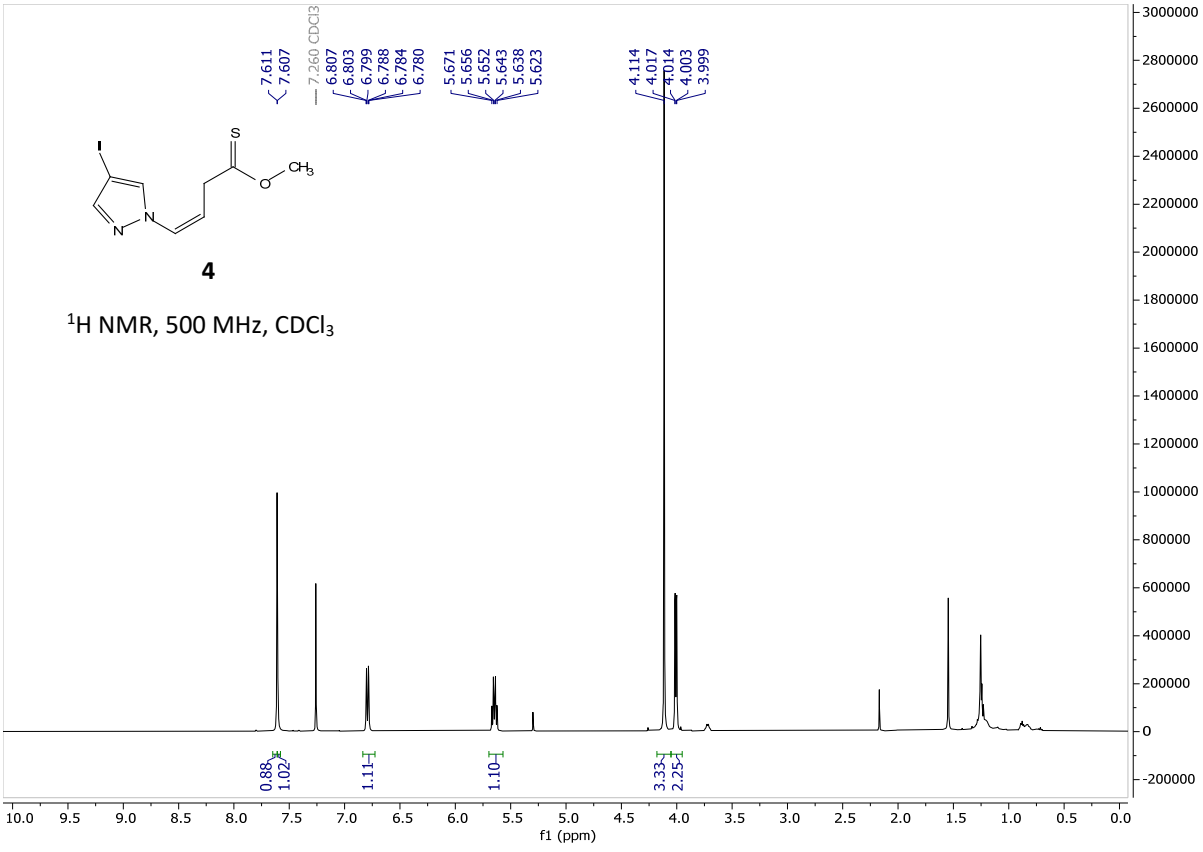

220.61
140.85
129.41
127.56
111.38
107.00
59.29
46.68
S
N
N
O
CH3
3
13C NMR, 101 MHz, CDCl3
f1 (ppm)


7.63
7.62
7.56
7.56
7.26 CDCl3
6.86
6.86
6.85
6.84
6.83
6.83
6.34
6.33
6.33
5.64
5.62
5.62
5.61
5.60
5.58
4.12
4.10
4.10
4.08
4.08
S
N
N
O
CH3
3
1H NMR, 400 MHz, CDCl3
0.99
1.04
0.99
1.00
1.00
3.11
2.00
f1 (ppm)



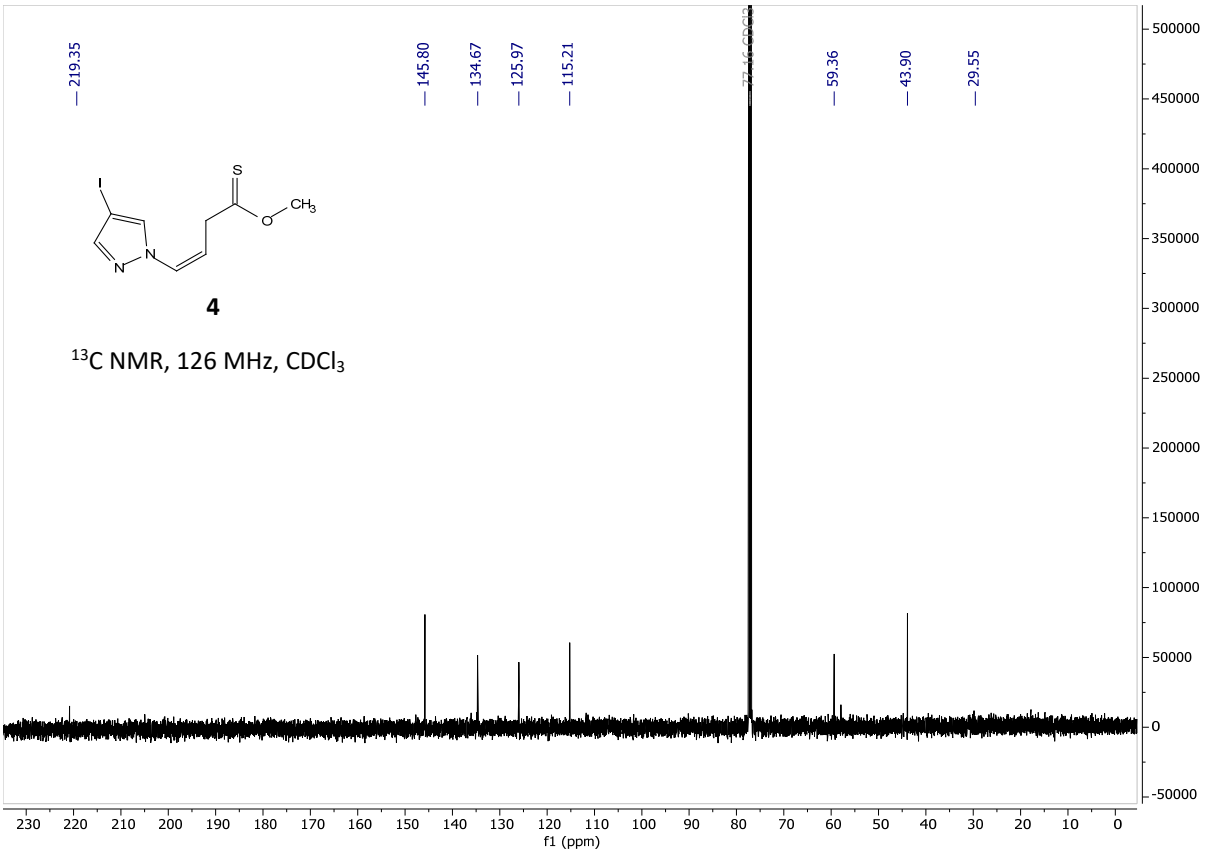
3

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



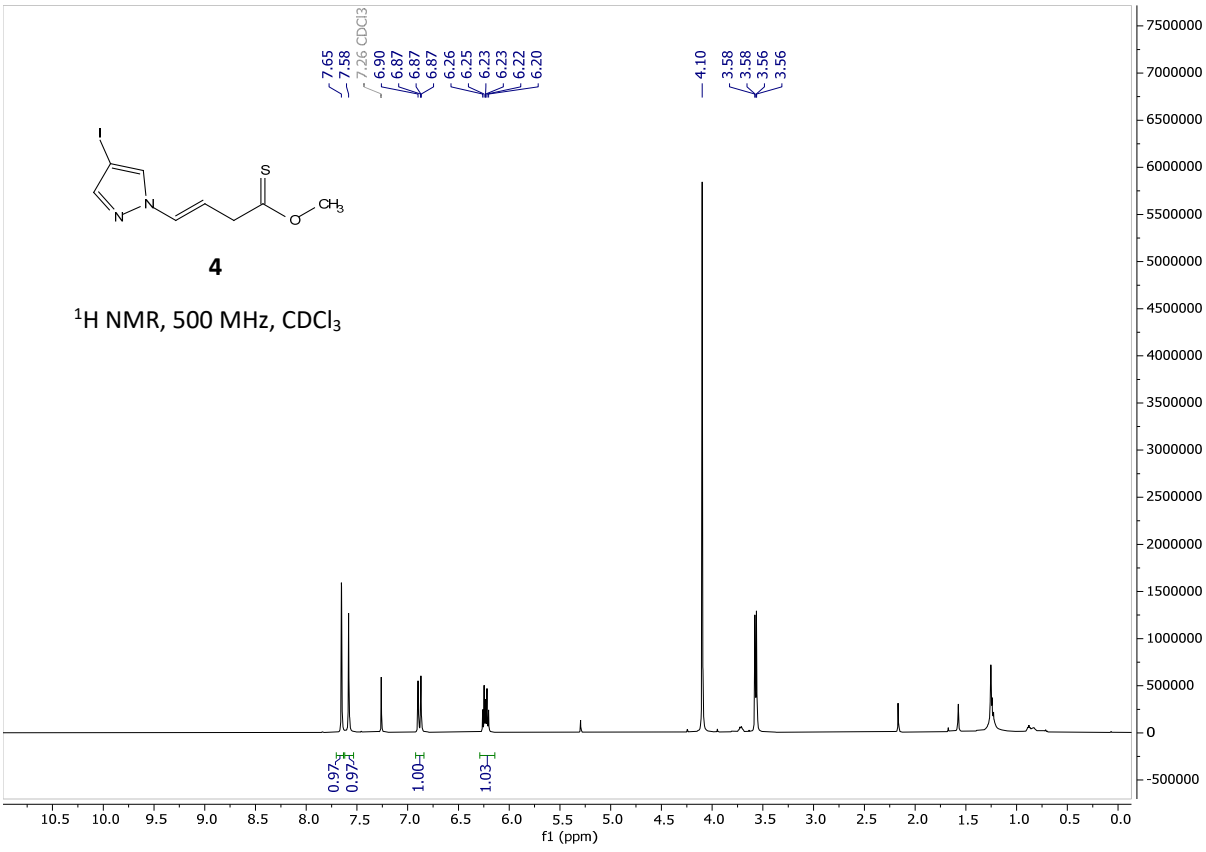
4

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



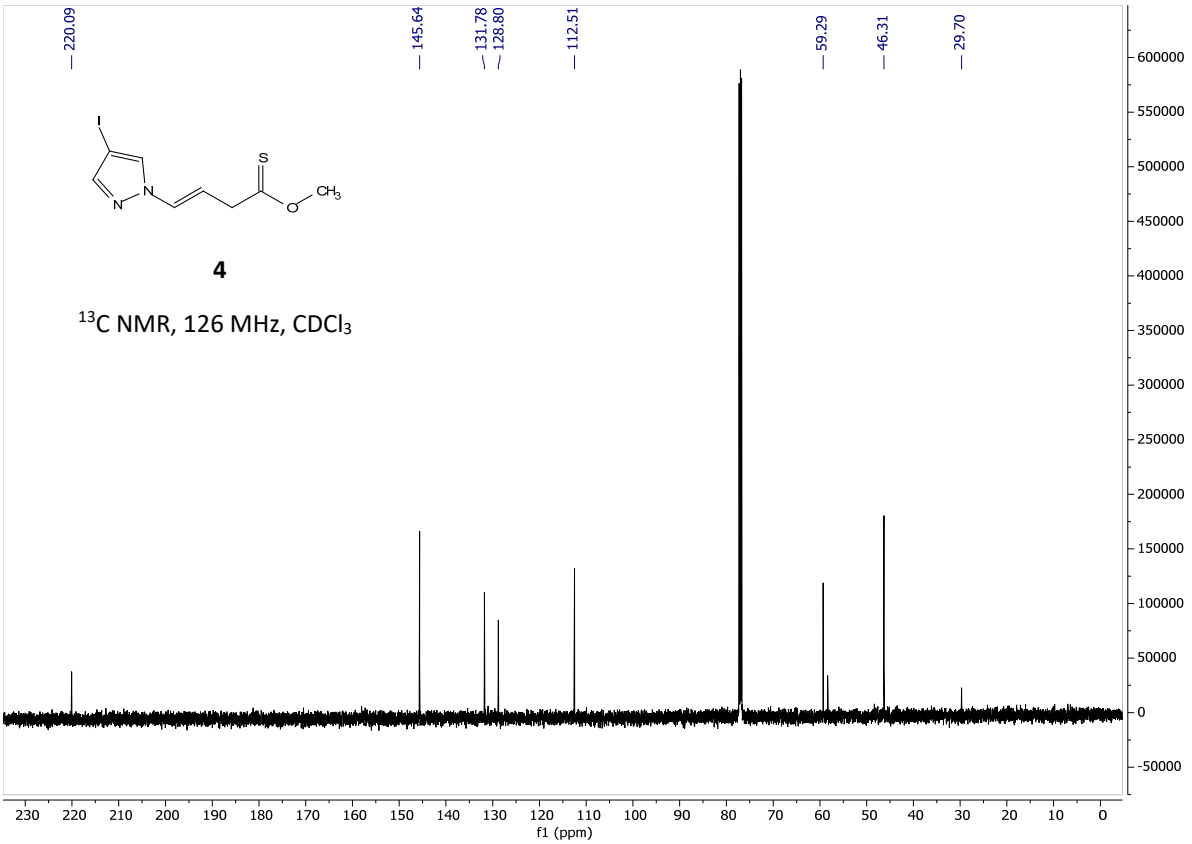
4

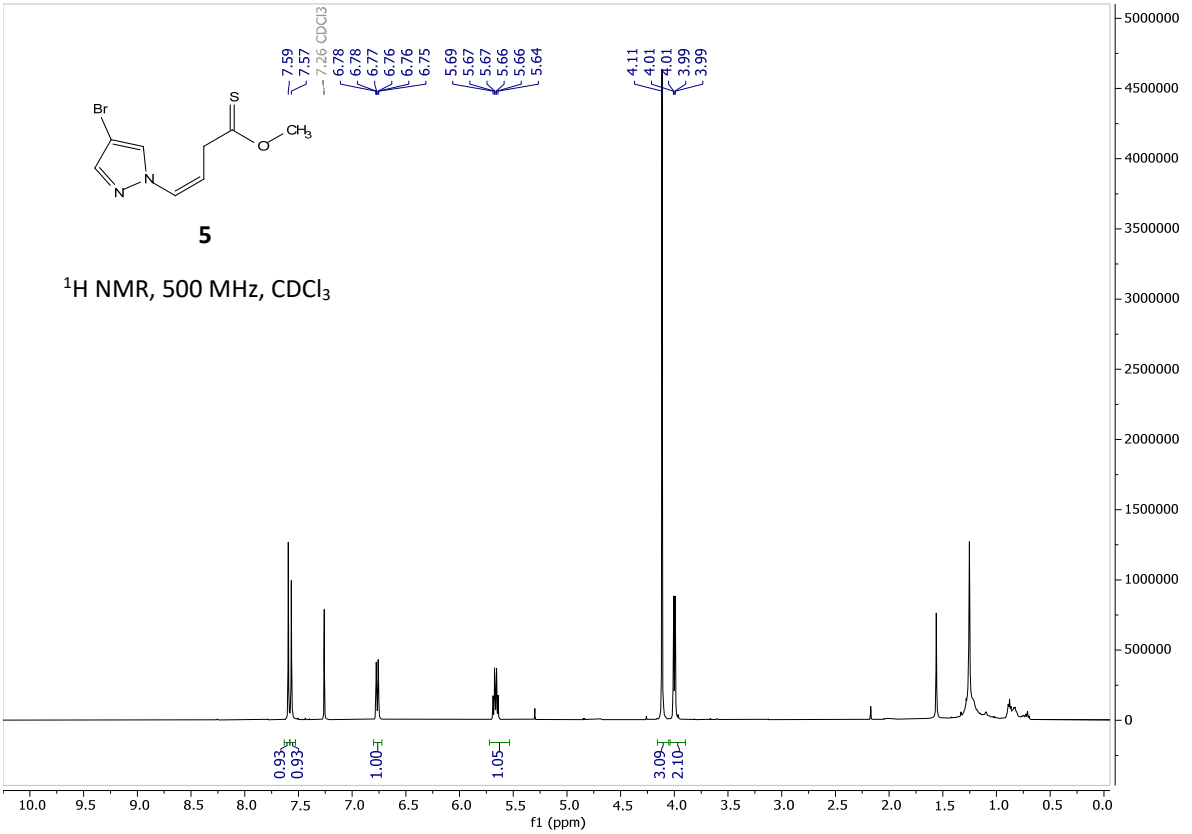
^{13}C NMR, 126 MHz, $CDCl_3$

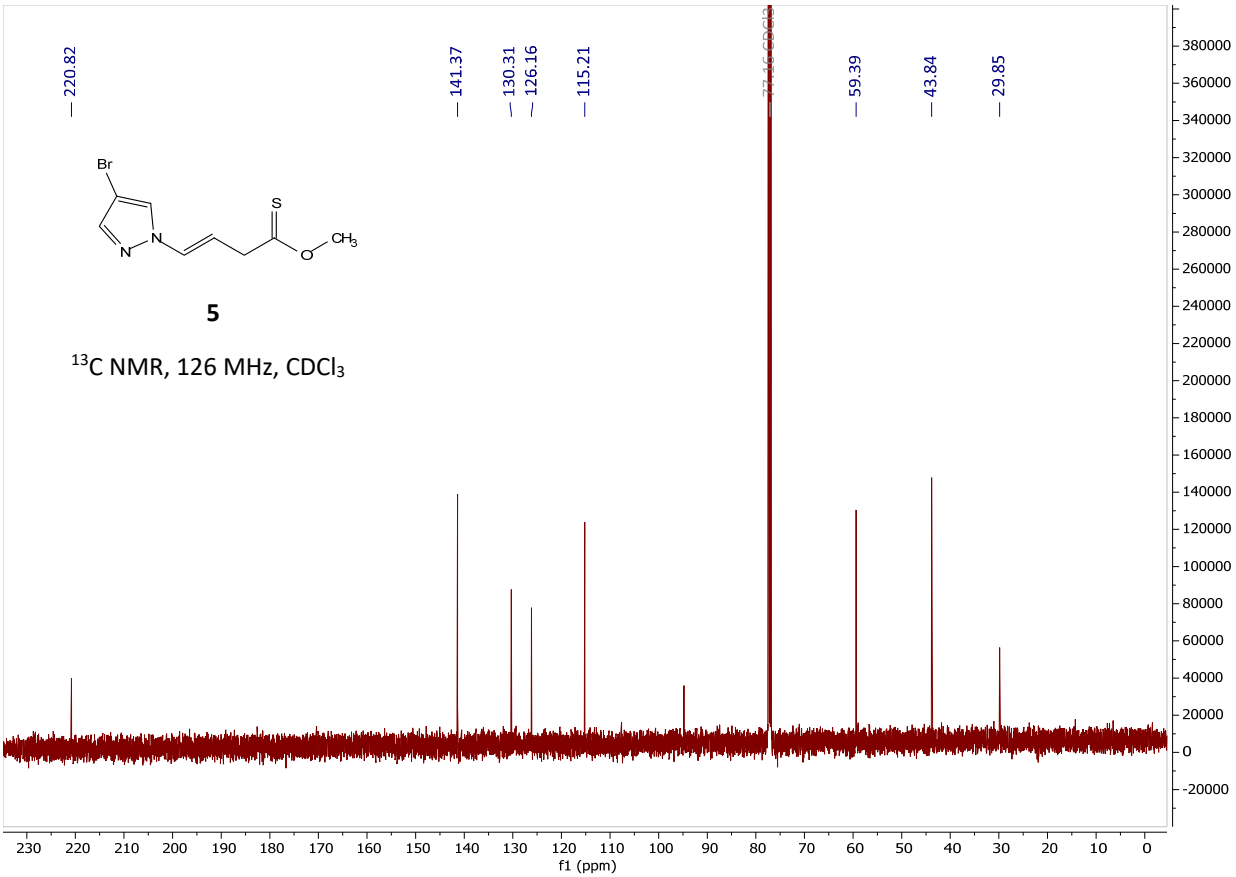


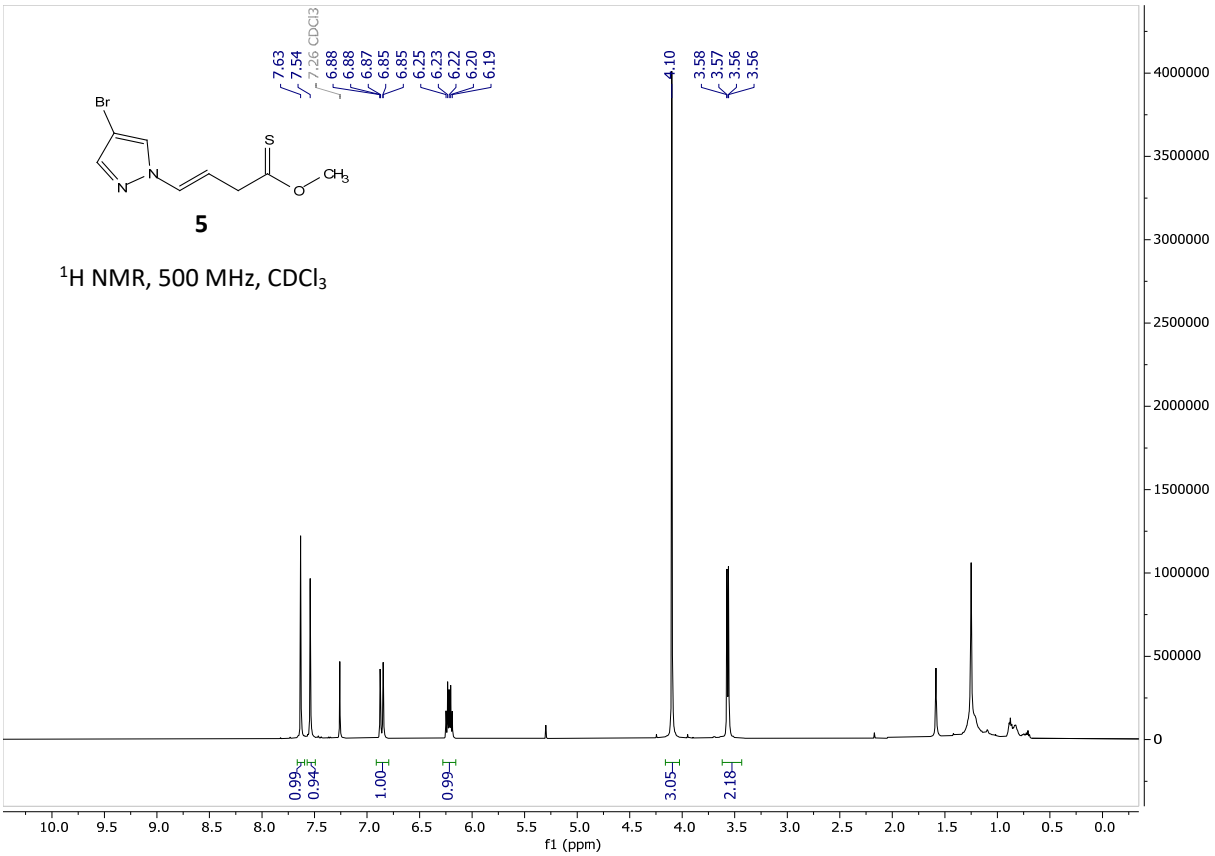
4

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


220.09
145.64
131.78
128.80
112.51
59.29
46.31
29.70
I
S
N
N
O
CH3
4
13C NMR, 126 MHz, CDCl3
f1 (ppm)

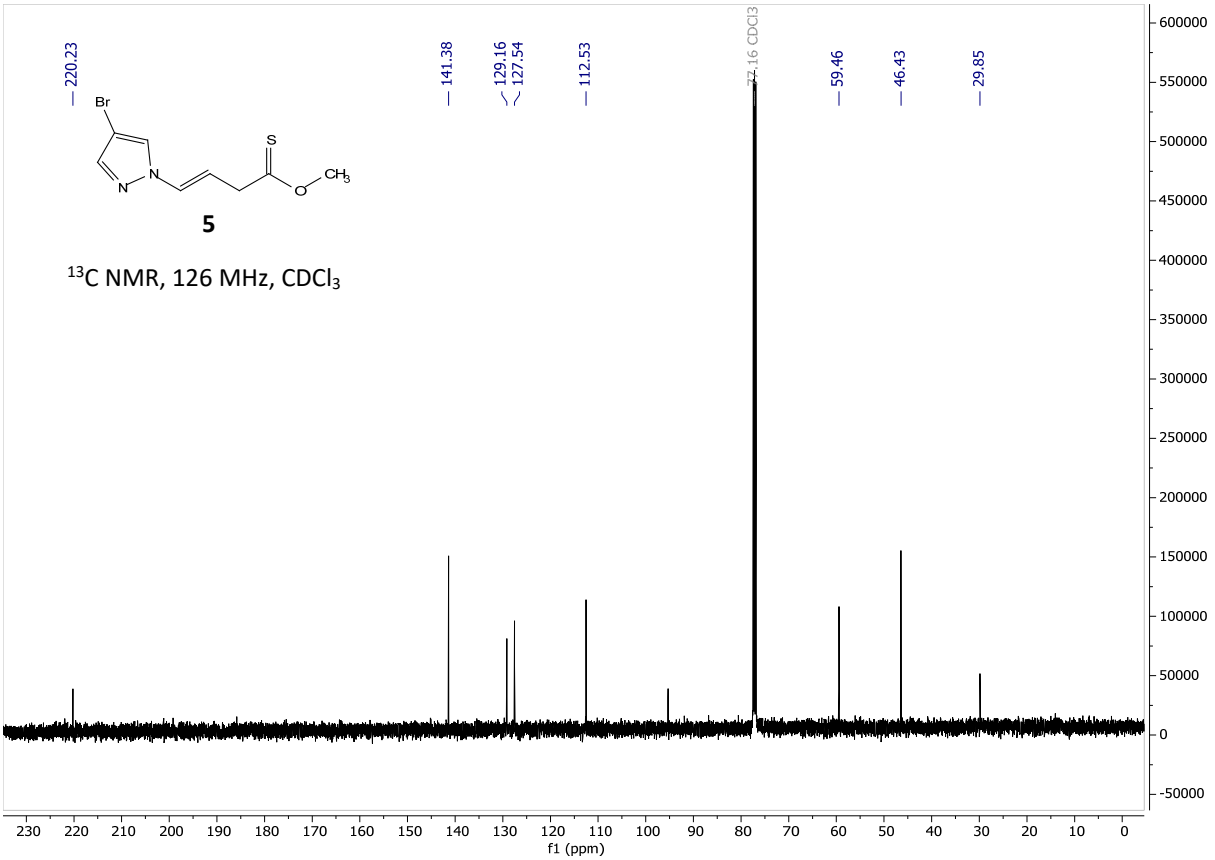

7.59
7.57
7.26 CDCl3
6.78
6.78
6.77
6.76
6.76
6.75
5.69
5.67
5.67
5.66
5.66
5.64
4.11
4.01
4.01
3.99
3.99
Br
S
N
N
O
CH3
5
1H NMR, 500 MHz, CDCl3
0.93
0.93
1.00
1.05
3.09
2.10
f1 (ppm)


220.82
141.37
130.31
126.16
115.21
59.39
43.84
29.85
Br
S
N
N
O
CH3
5
13C NMR, 126 MHz, CDCl3
f1 (ppm)



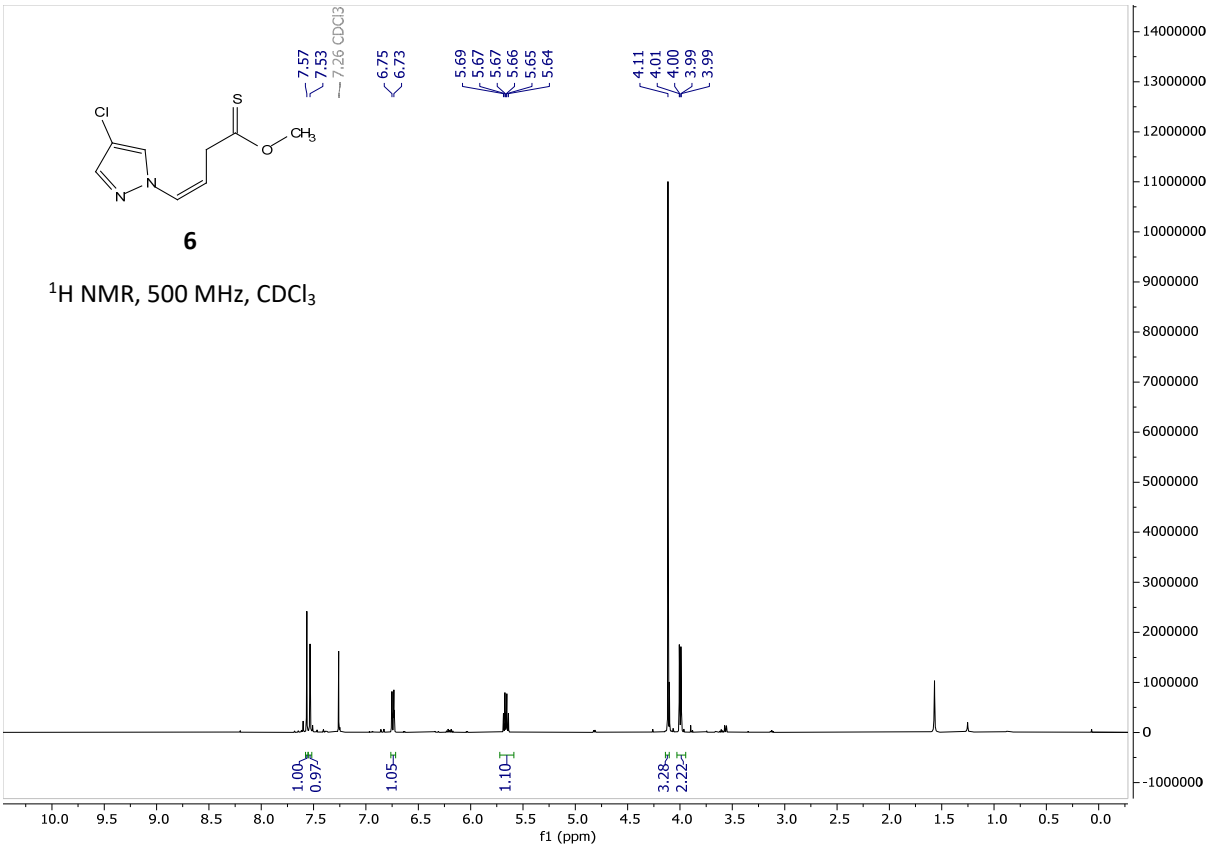
5

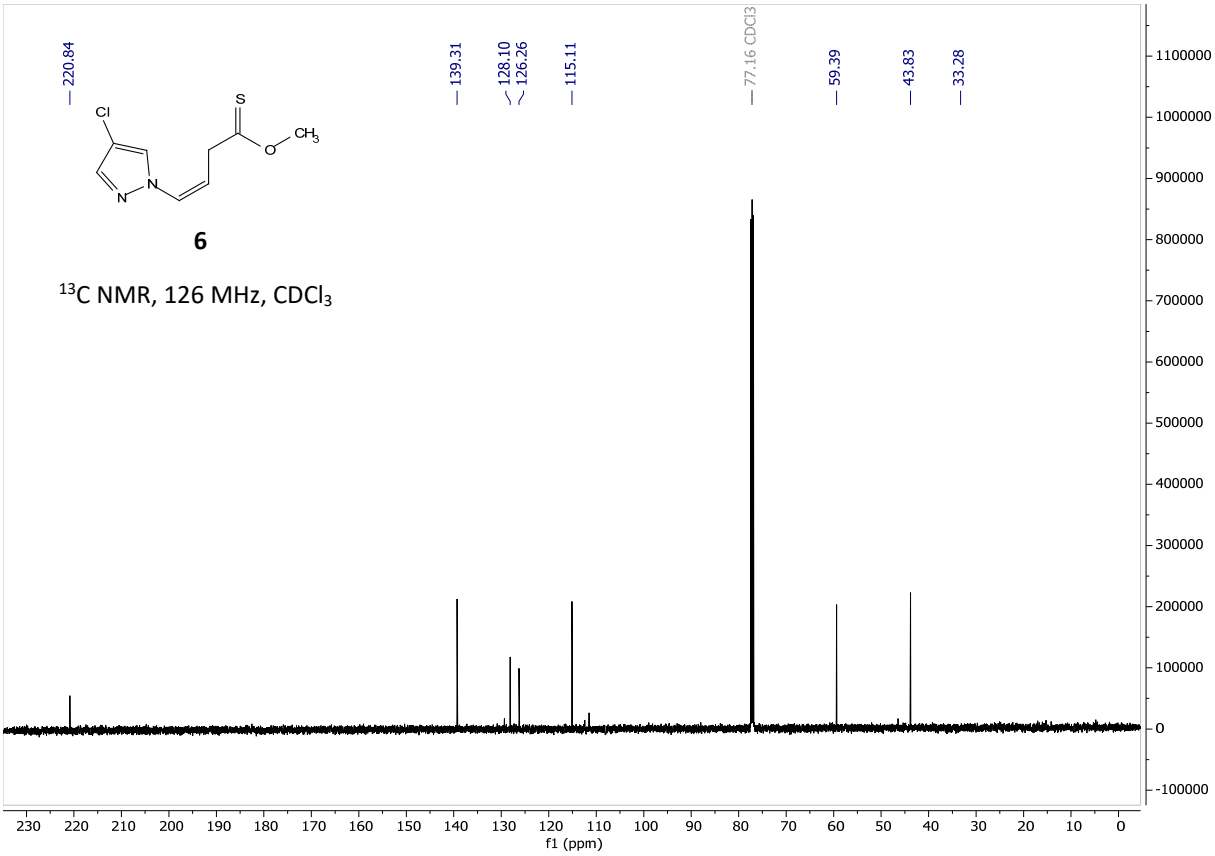
^{1}H NMR, 500 MHz, $CDCl_3$

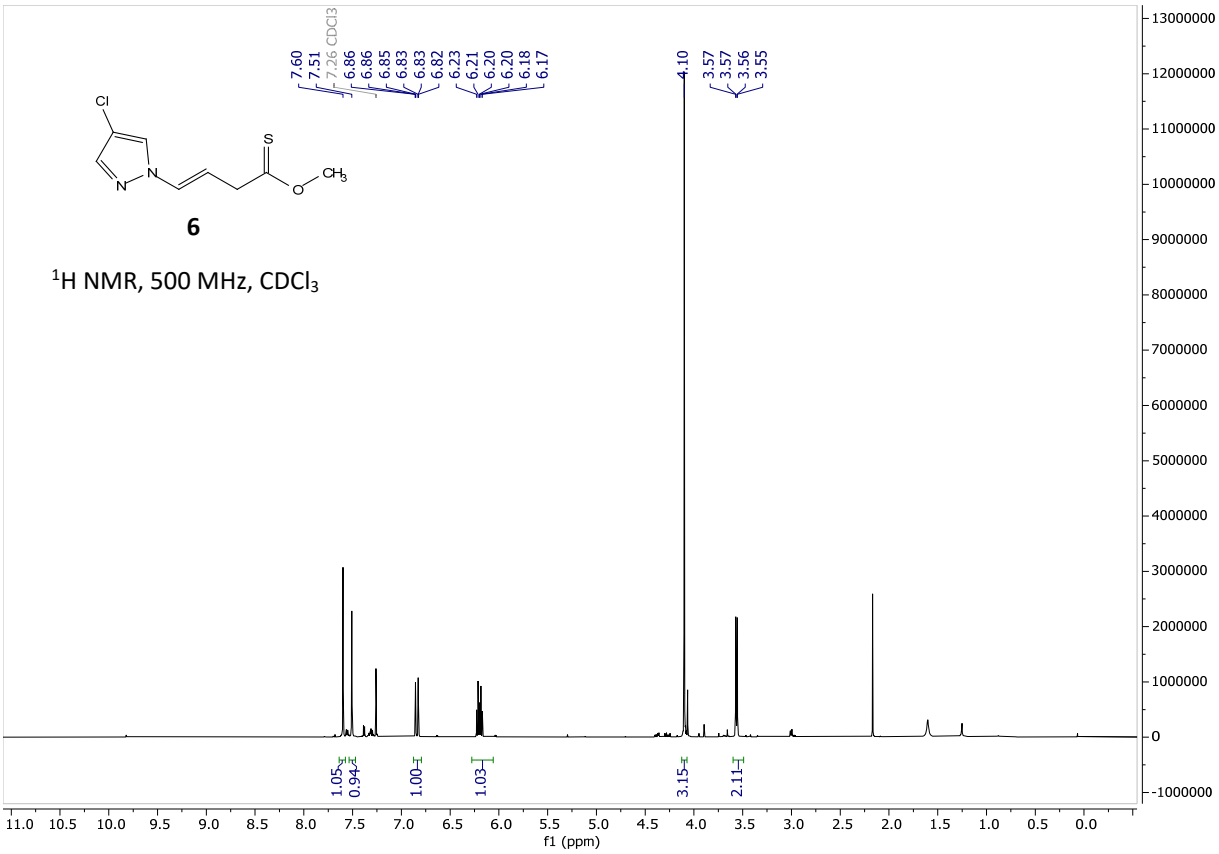


5

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

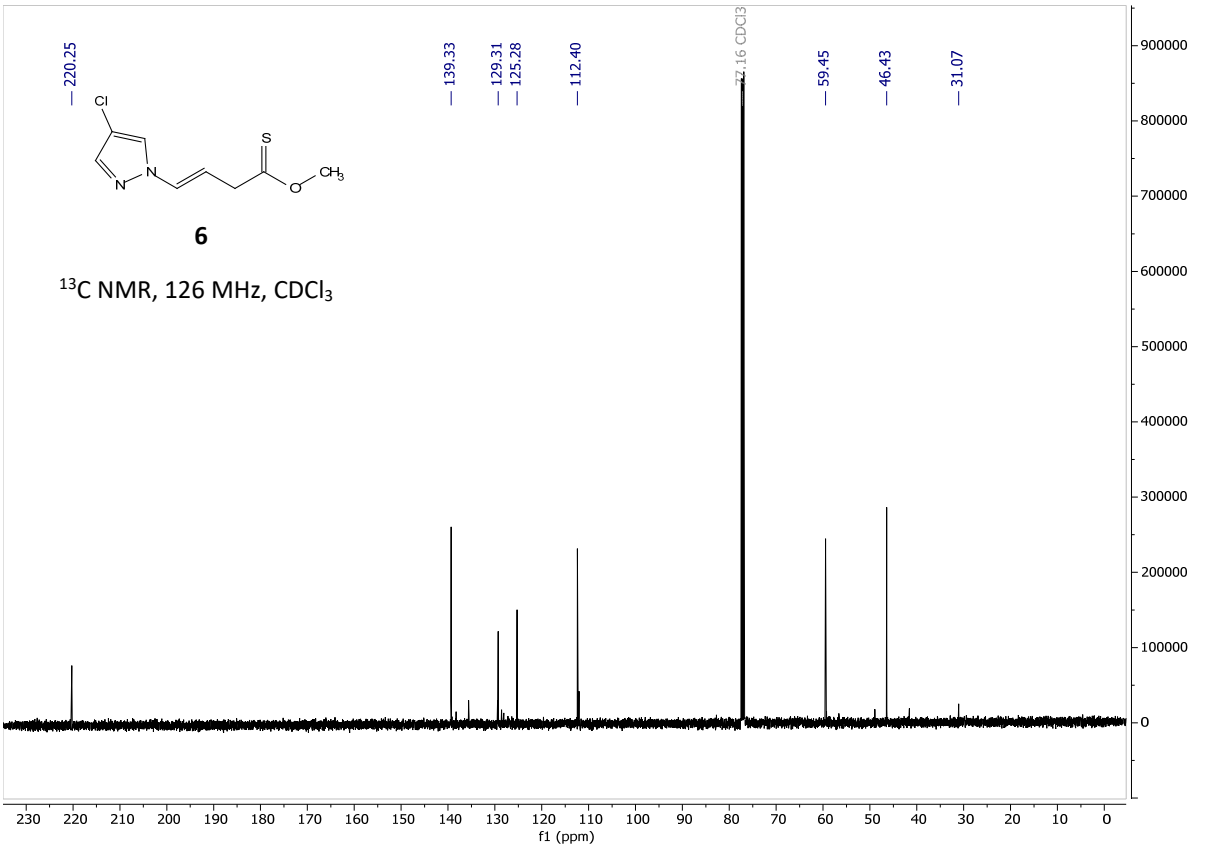

7.57
7.53
7.26 CDCl3
6.75
6.73
5.69
5.67
5.67
5.66
5.65
5.64
4.11
4.01
4.00
3.99
3.99
Cl
S
O
CH3
N
N
6
1H NMR, 500 MHz, CDCl3
1.00
0.97
1.05
1.10
3.28
2.22
f1 (ppm)


220.84
139.31
128.10
126.26
115.11
77.16 CDCl3
59.39
43.83
33.28
Cl
S
O
CH3
N
N
6
13C NMR, 126 MHz, CDCl3
f1 (ppm)



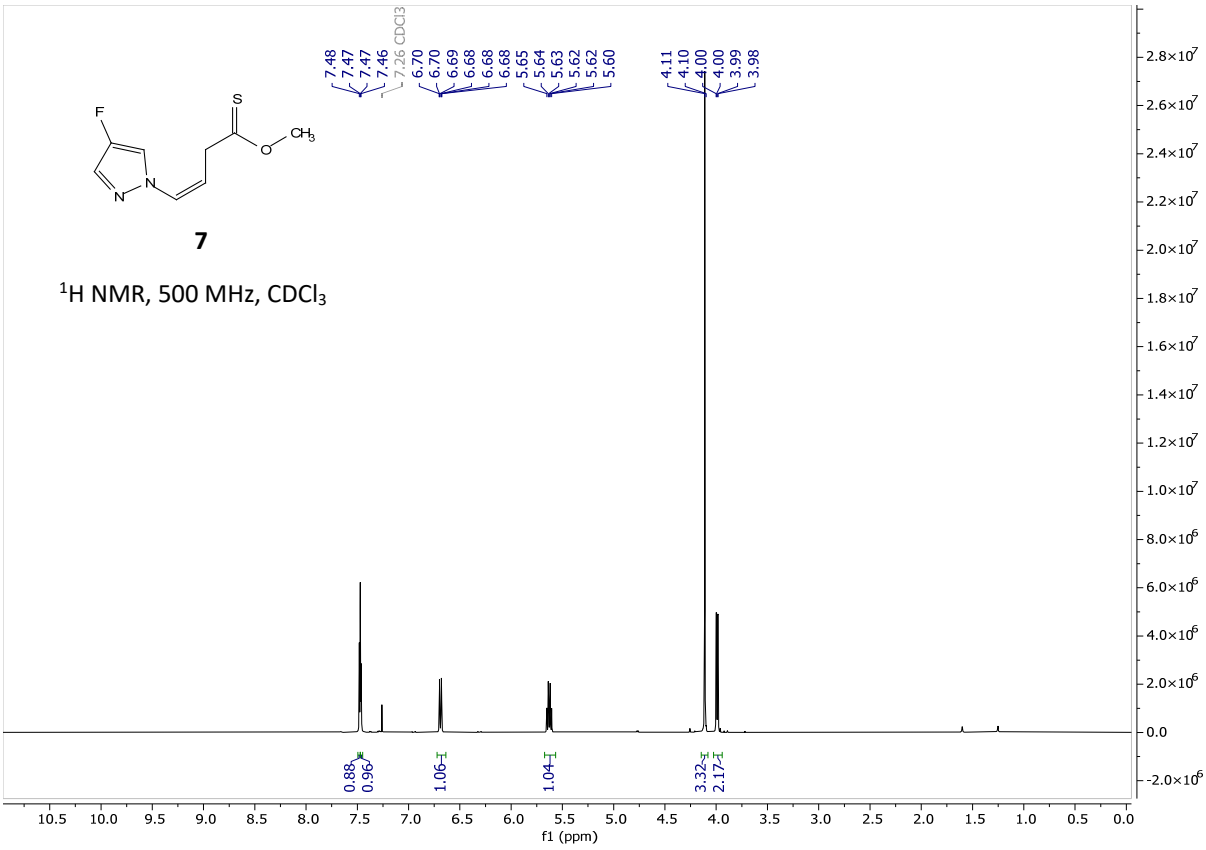
6

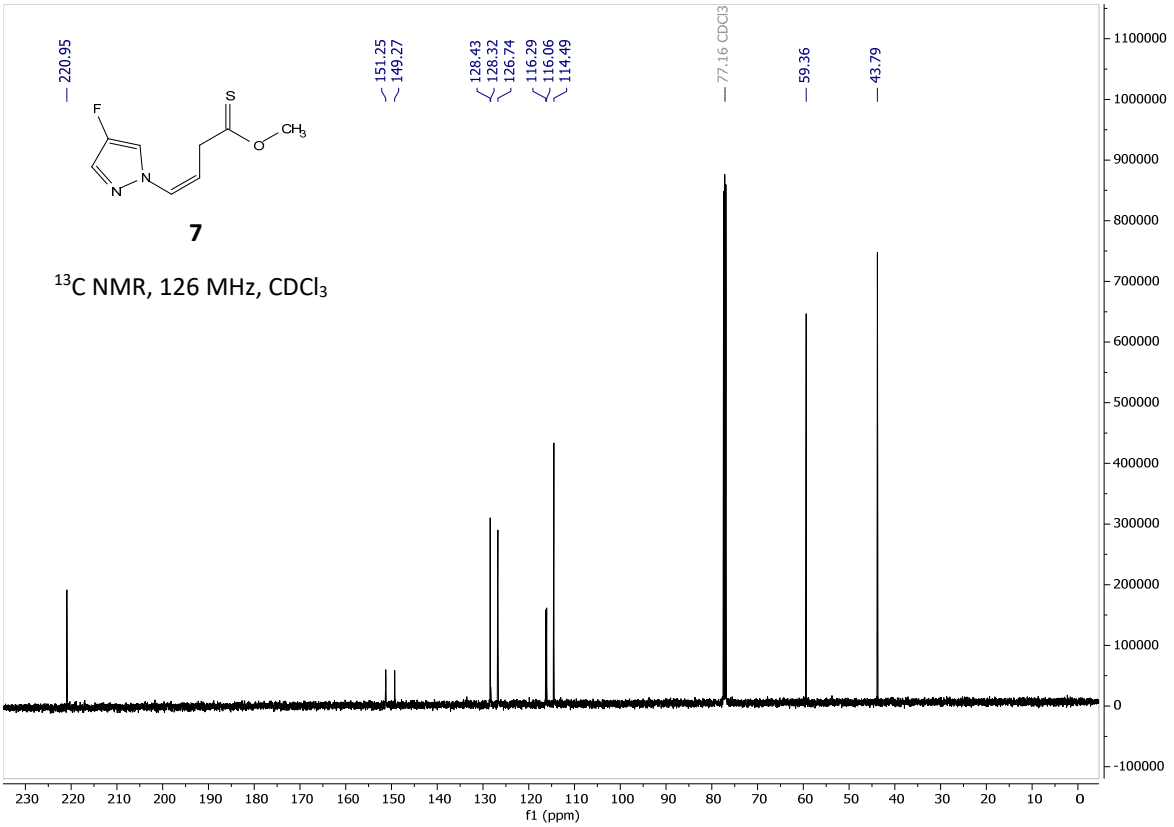
^{1}H NMR, 500 MHz, $CDCl_3$

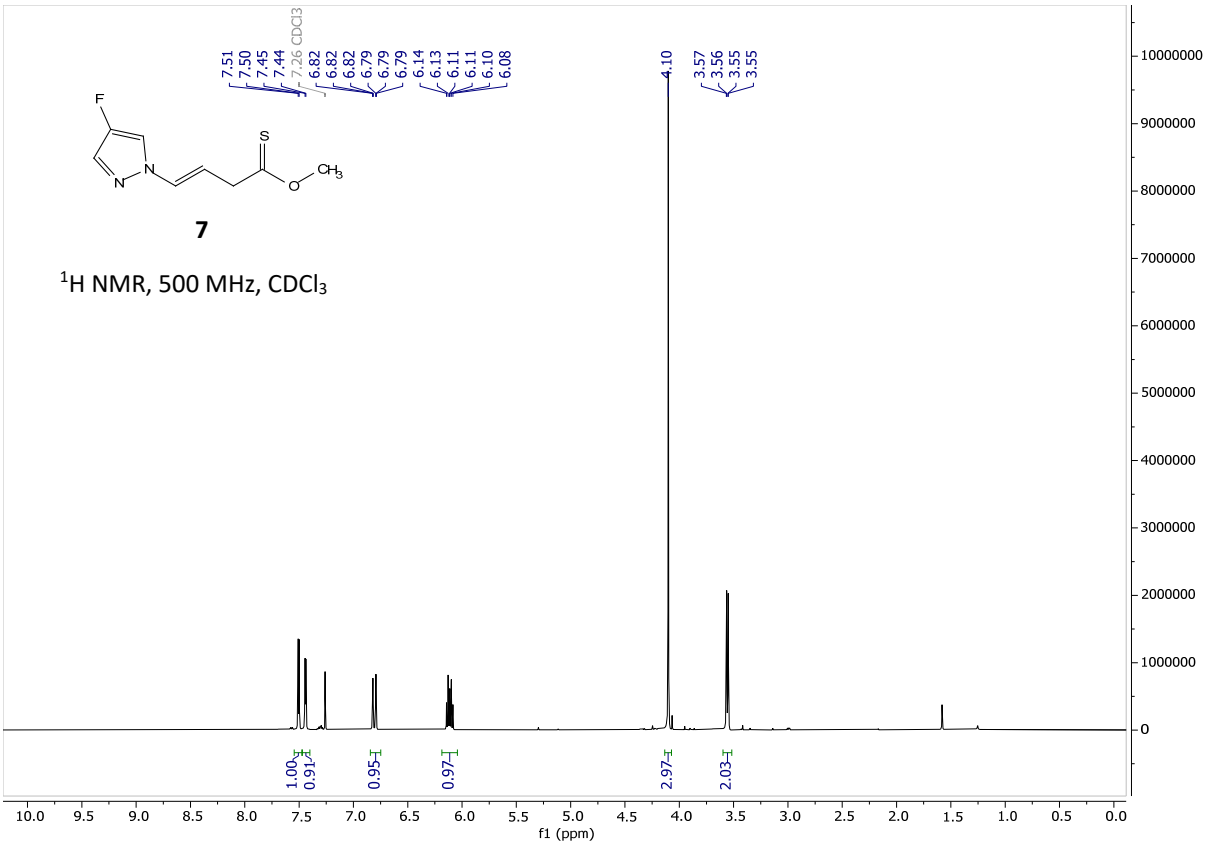


6

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

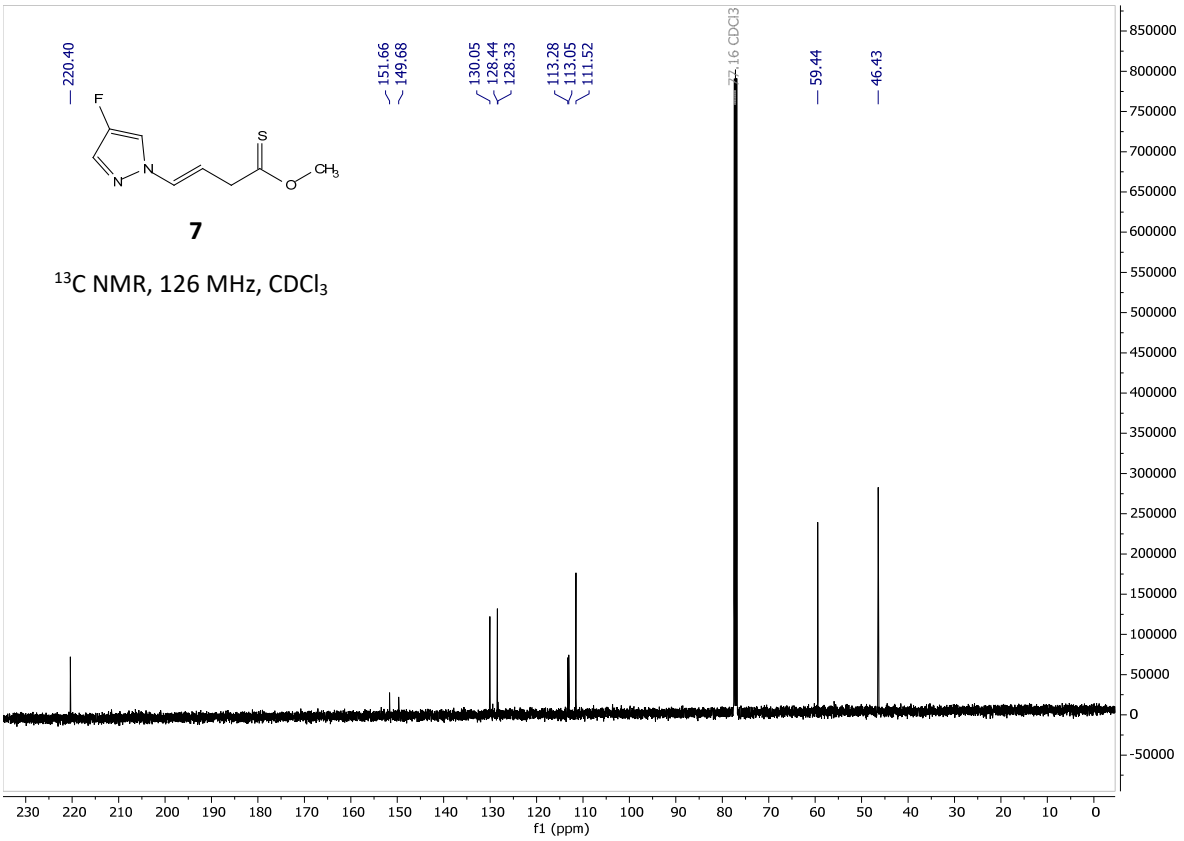

7.48
7.47
7.47
7.46
7.26 CDCl3
6.70
6.70
6.69
6.68
6.68
6.68
5.65
5.64
5.63
5.62
5.62
5.60
4.11
4.10
4.00
4.00
3.99
3.98
F
S
O
CH3
N
N
7
1H NMR, 500 MHz, CDCl3
0.88
0.96
1.06
1.04
3.32
2.17
f1 (ppm)


220.95
151.25
149.27
128.43
128.32
126.74
116.29
116.06
114.49
77.16 CDCl3
59.36
43.79
F
S
O
CH3
N
N
7
13C NMR, 126 MHz, CDCl3
f1 (ppm)



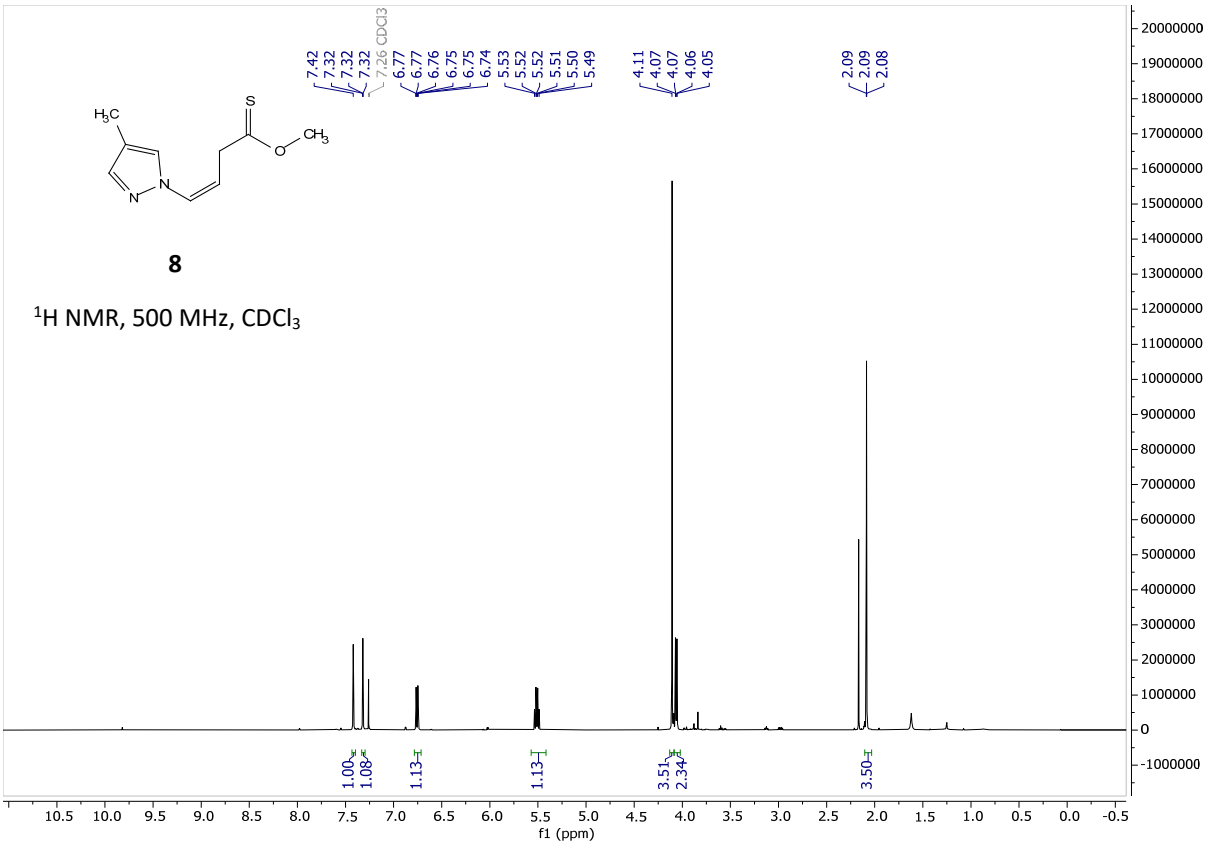
7

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



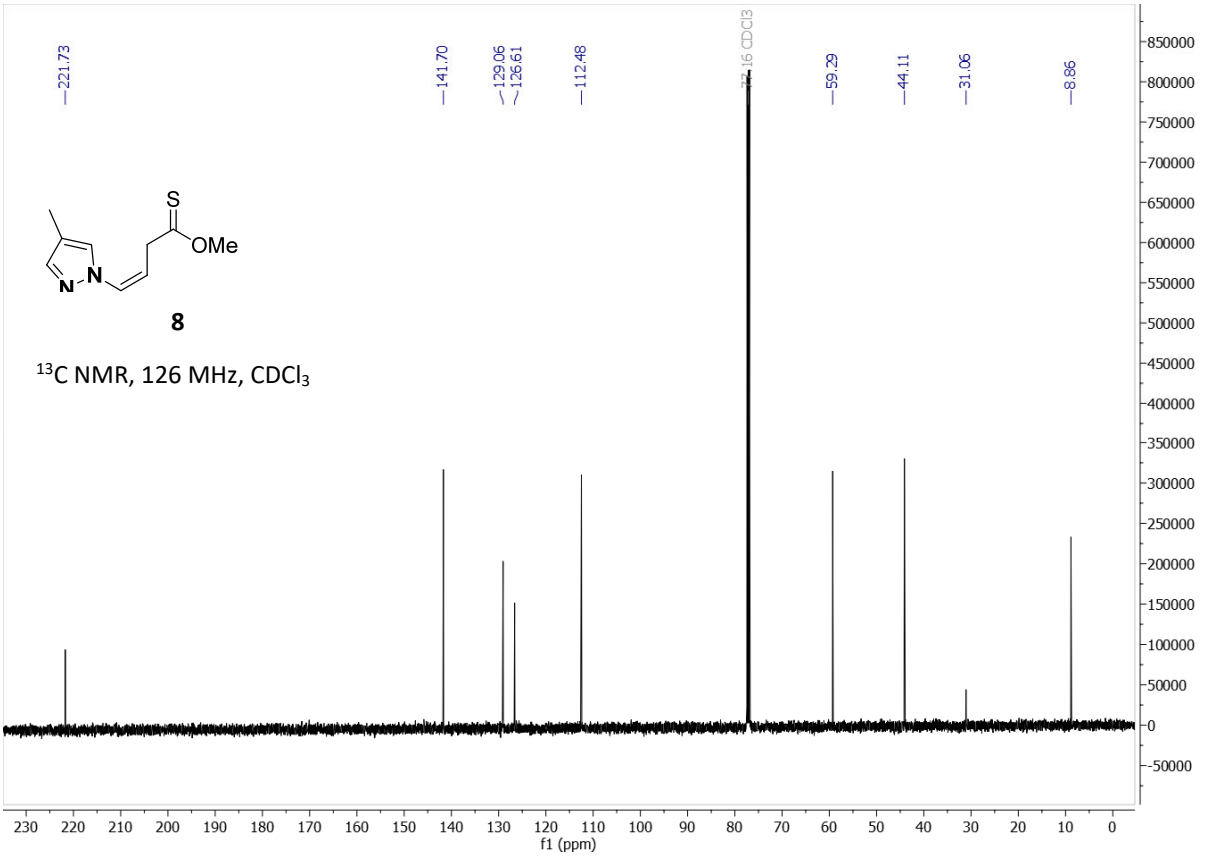
7

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



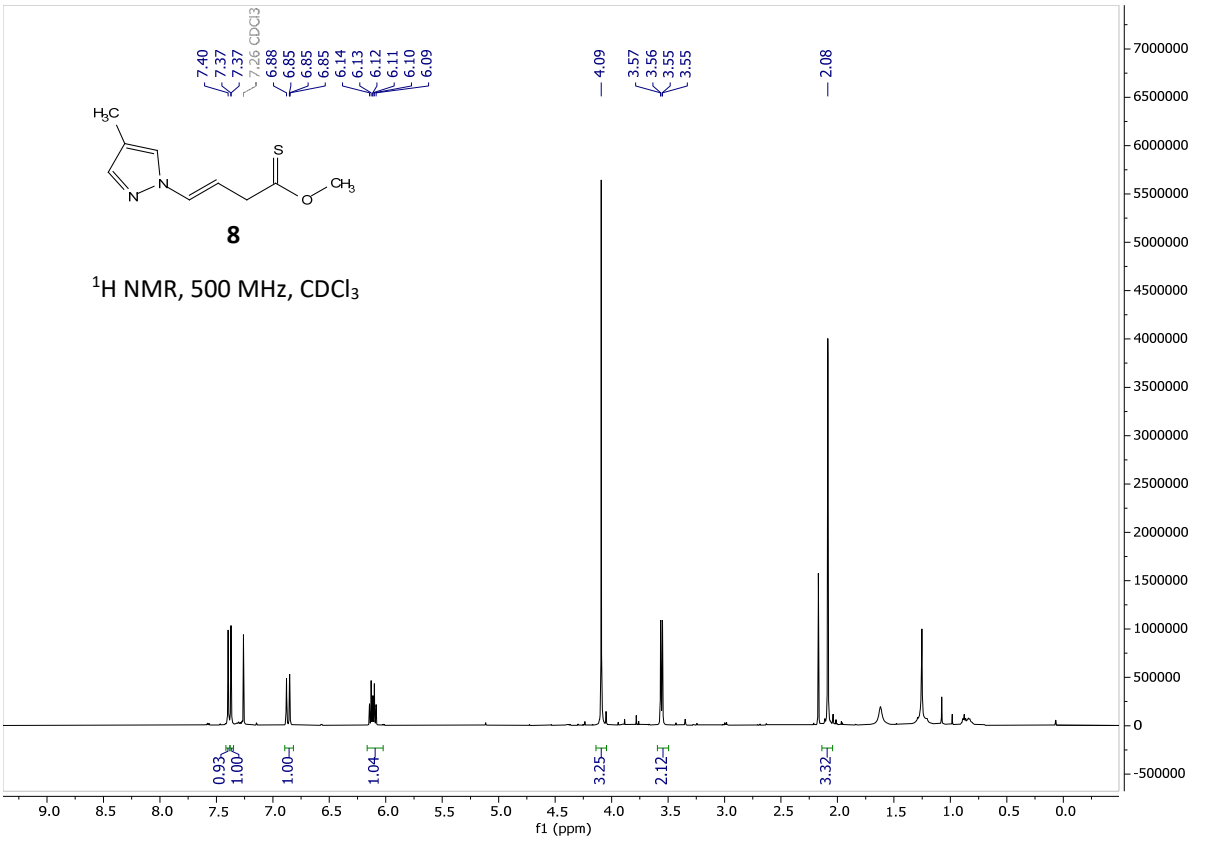
8

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



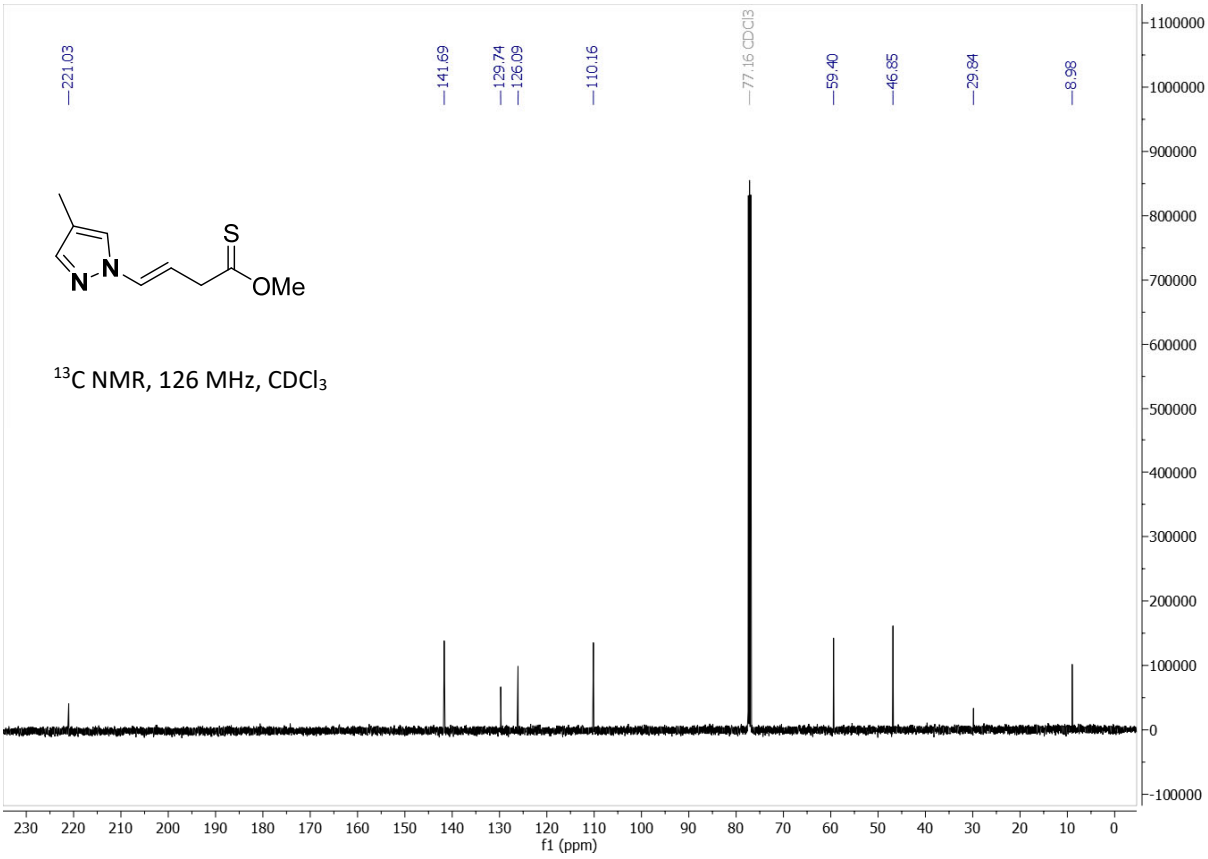
8

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

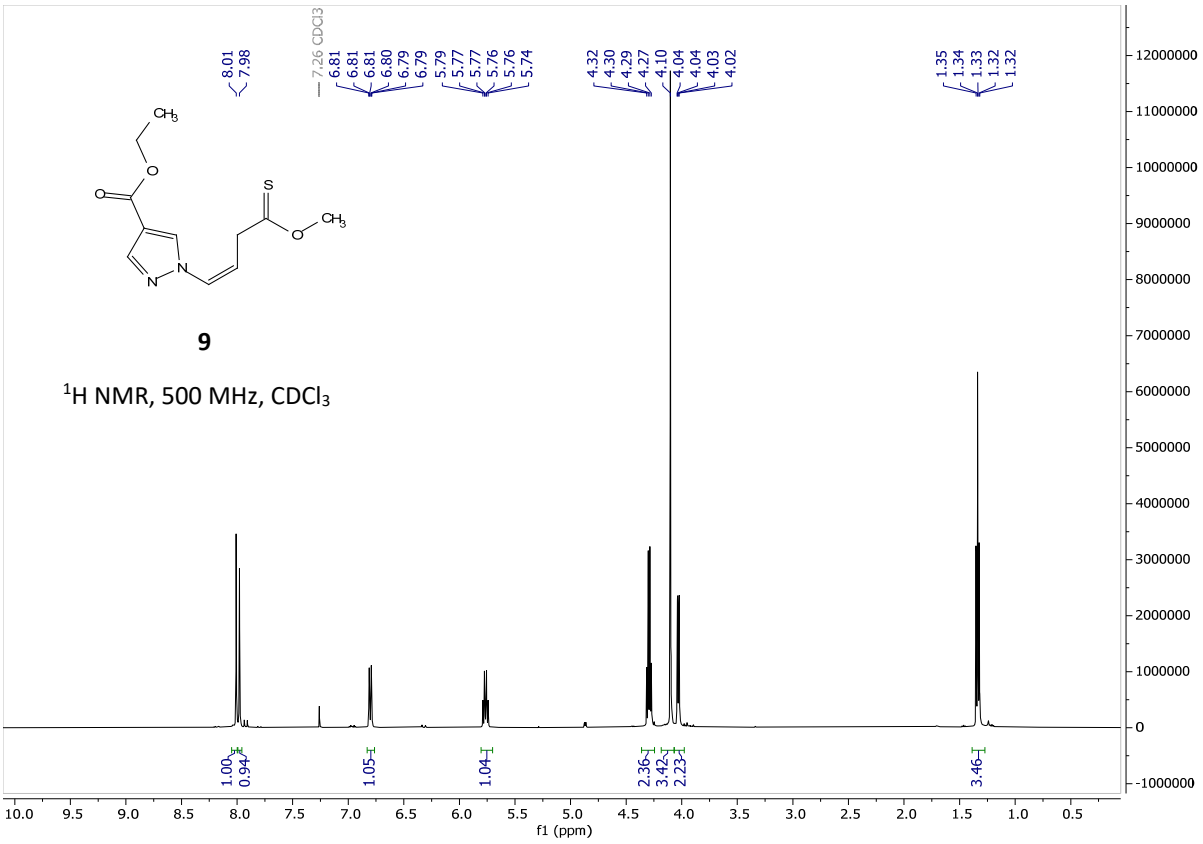


8

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

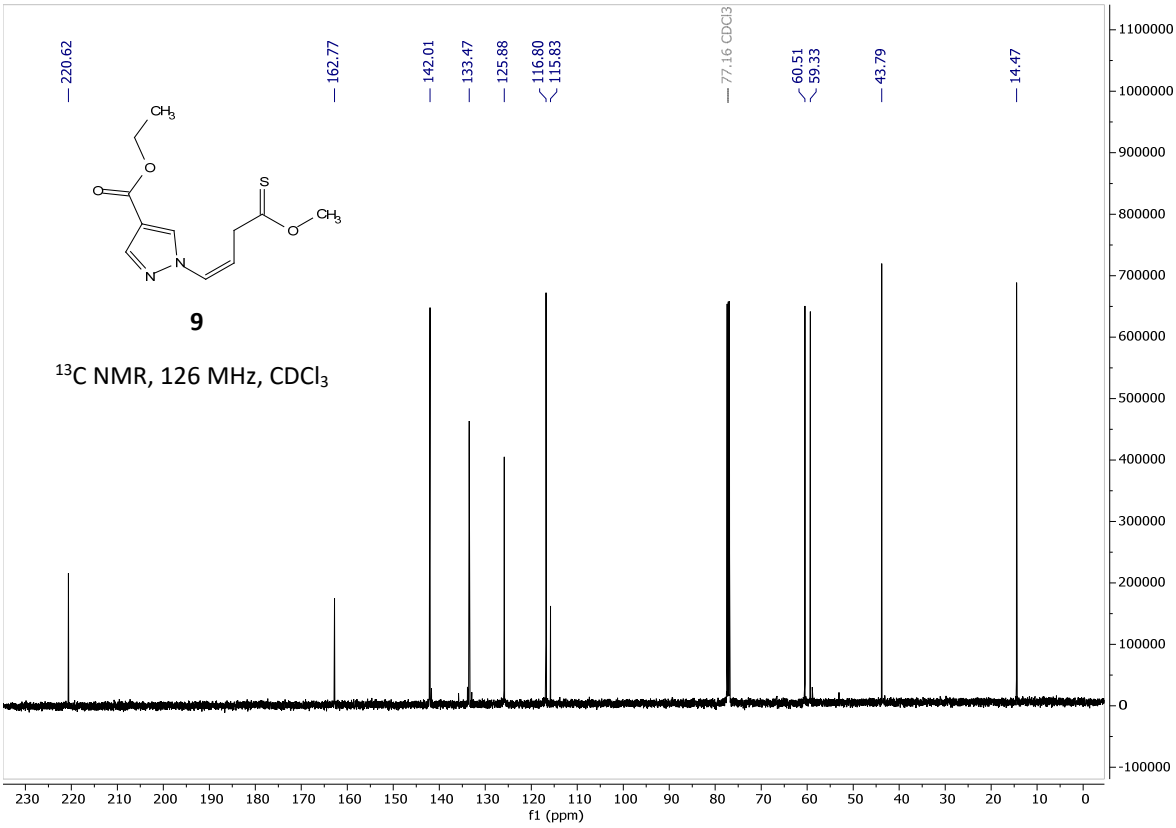


^{13}C NMR, 126 MHz, $CDCl_3$



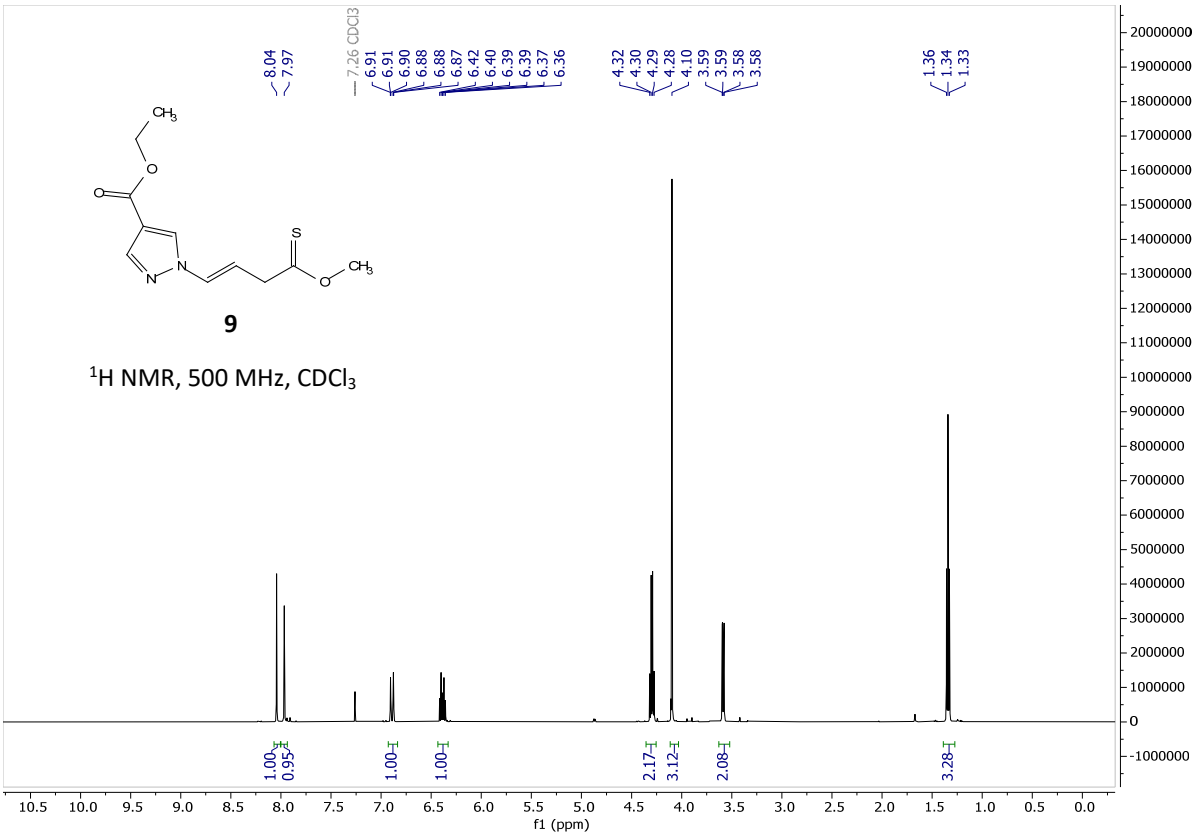
9

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



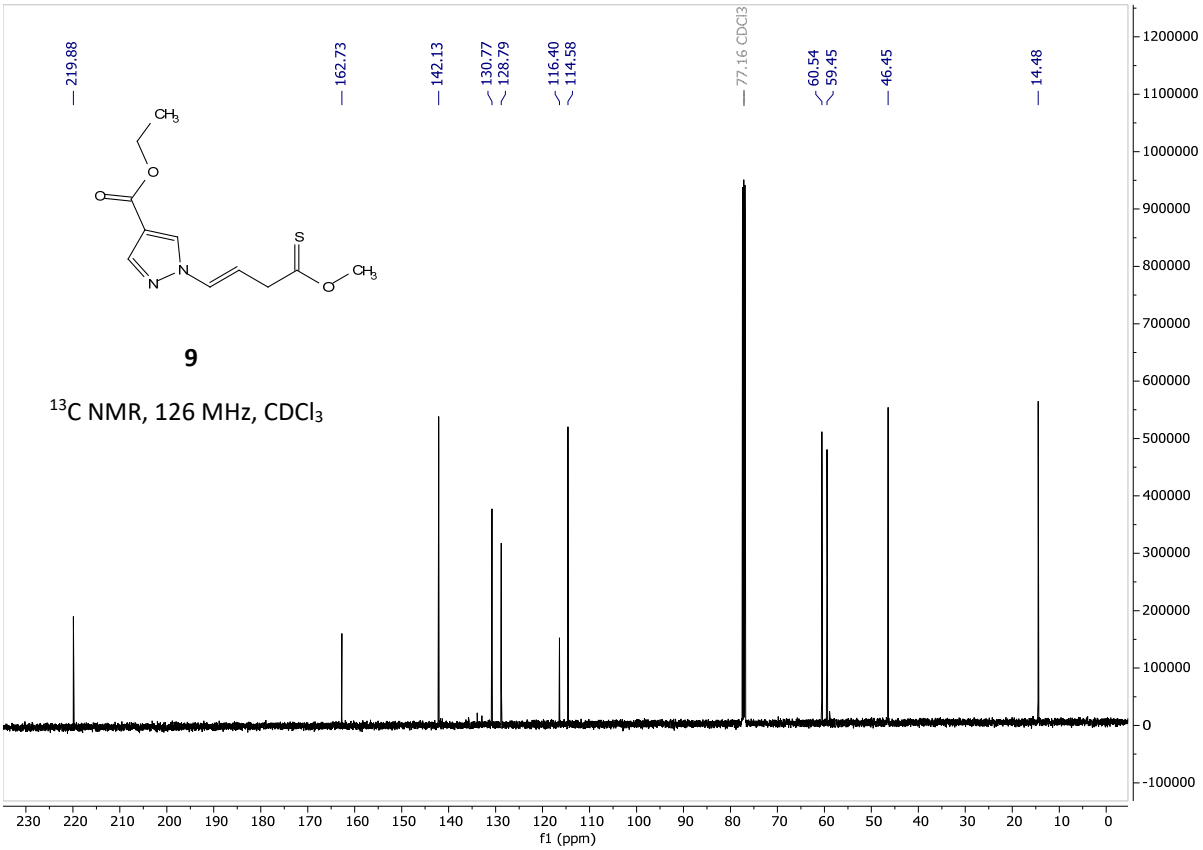
9

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



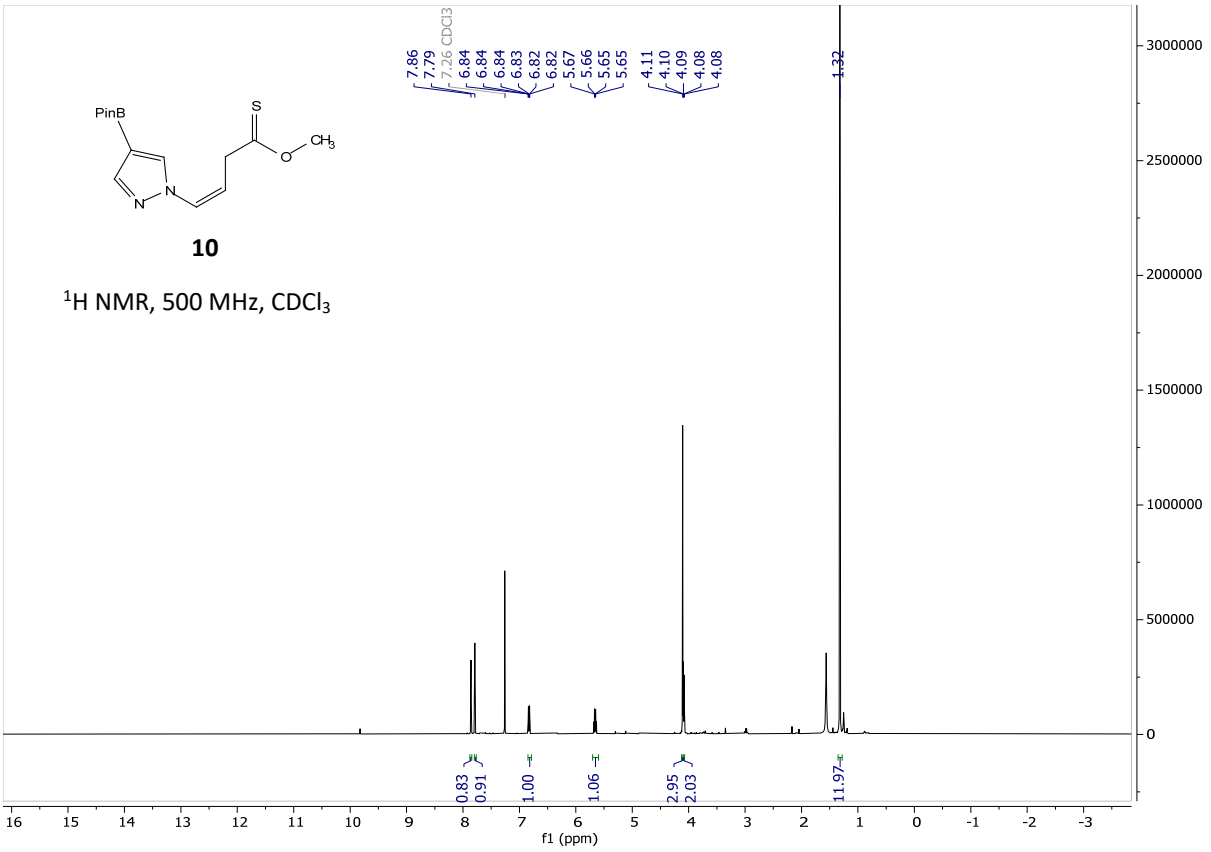
9

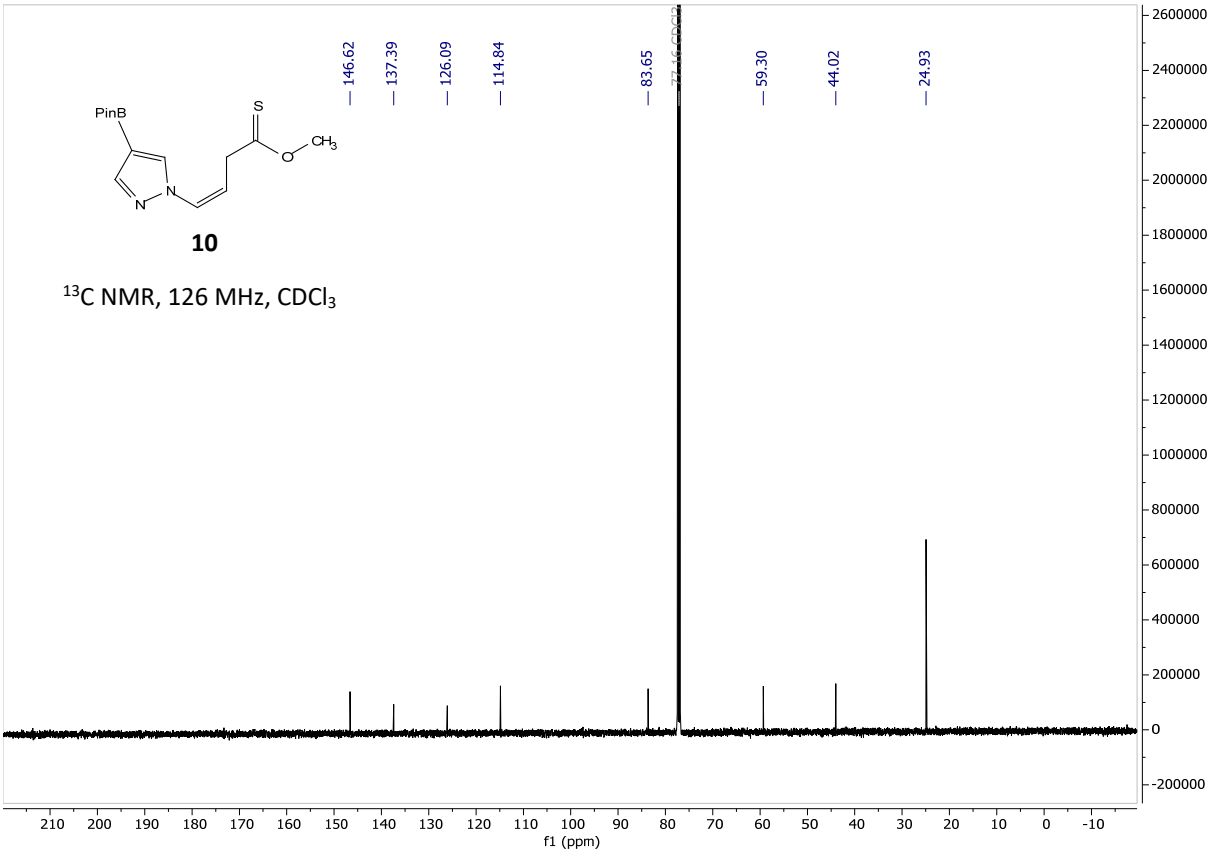
^{1}H NMR, 500 MHz, $CDCl_3$

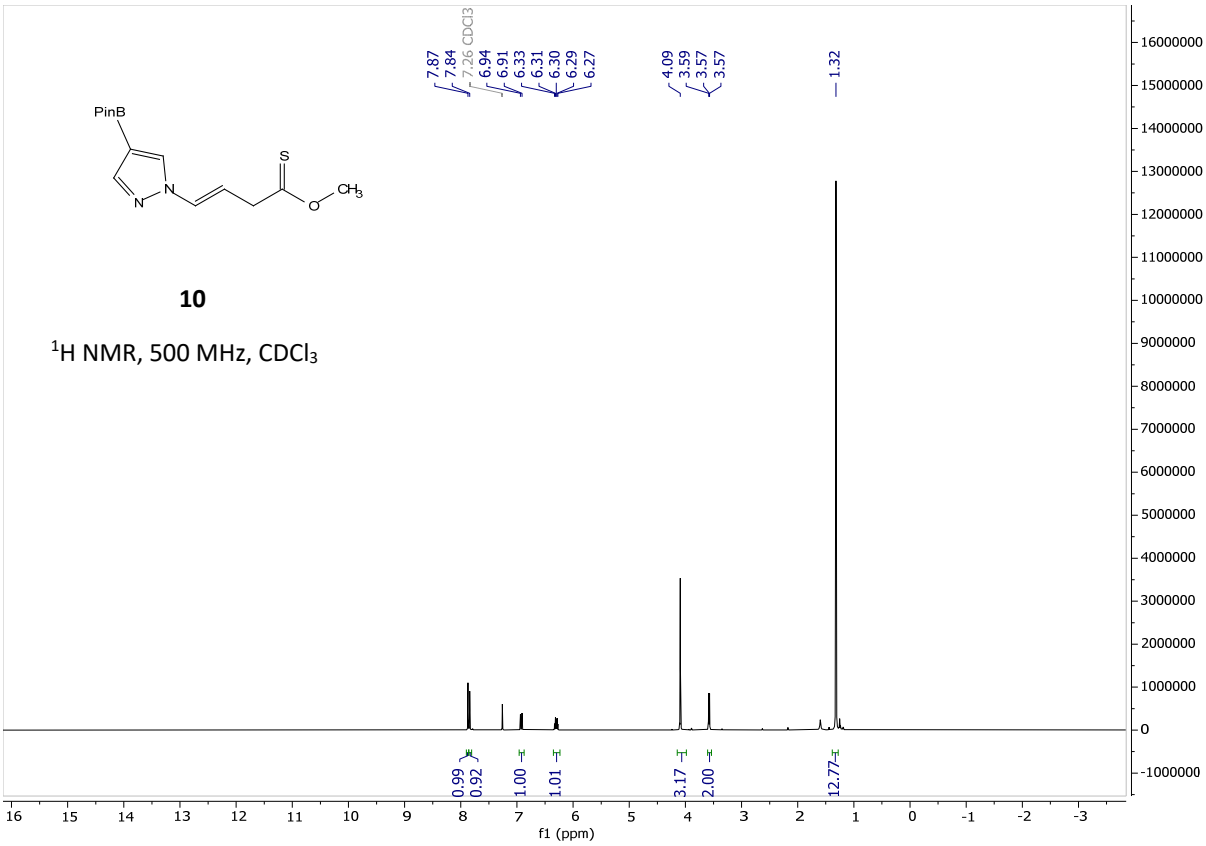


9

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

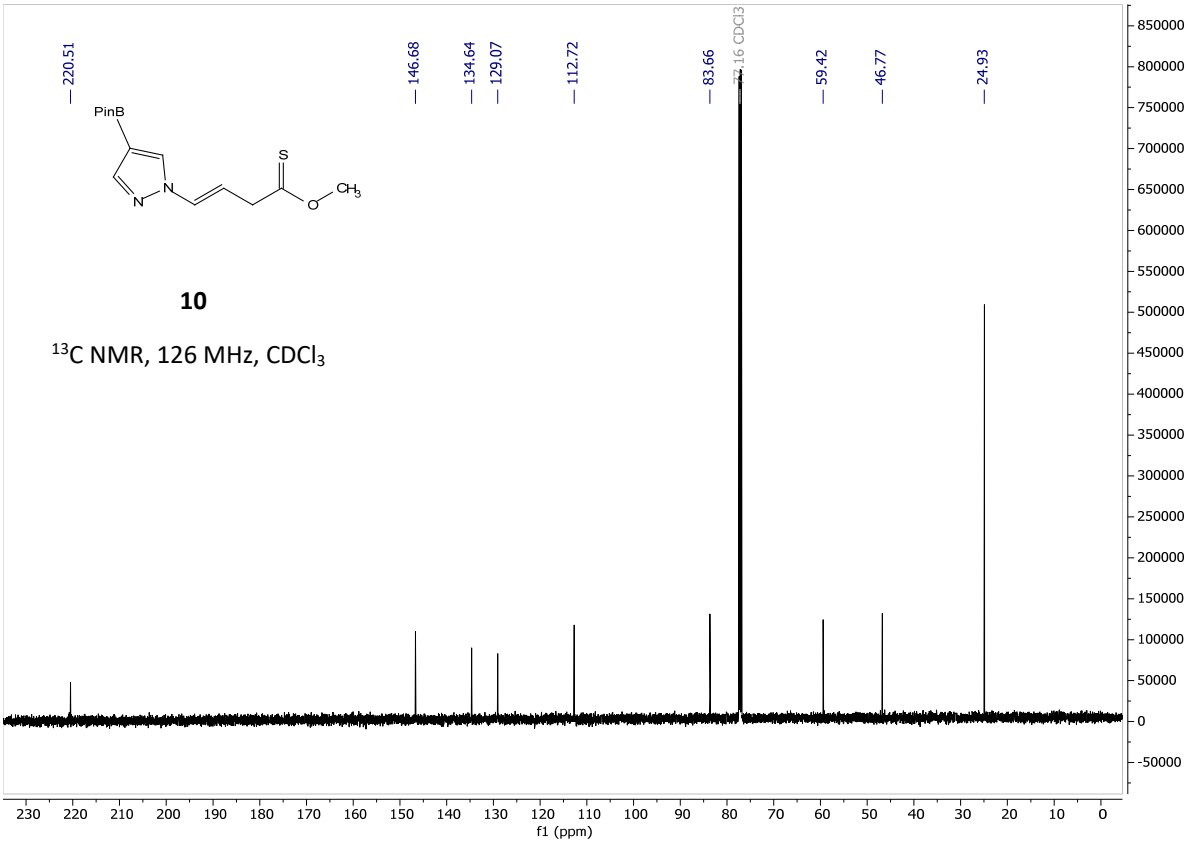

PinB
S
O
CH3
N
N
10
1H NMR, 500 MHz, CDCl3
7.86
7.79
7.26 CDCl3
6.84
6.84
6.84
6.83
6.82
6.82
5.67
5.66
5.65
5.65
4.11
4.10
4.09
4.08
4.08
1.32
0.83
0.91
1.00
1.06
2.95
2.03
11.97
f1 (ppm)


PinB
S
O
CH3
N
N
10
13C NMR, 126 MHz, CDCl3
146.62
137.39
126.09
114.84
83.65
77.46 CDCl3
59.30
44.02
24.93
f1 (ppm)



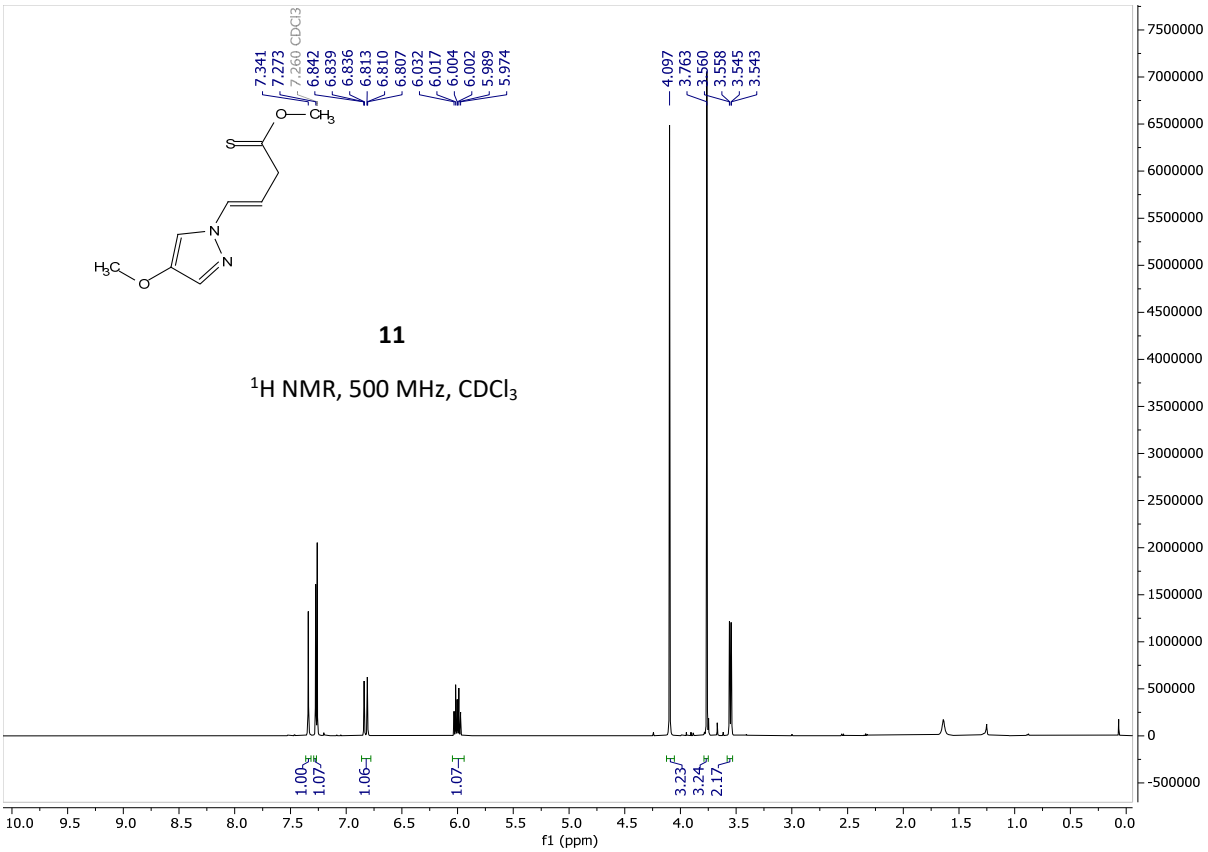
10

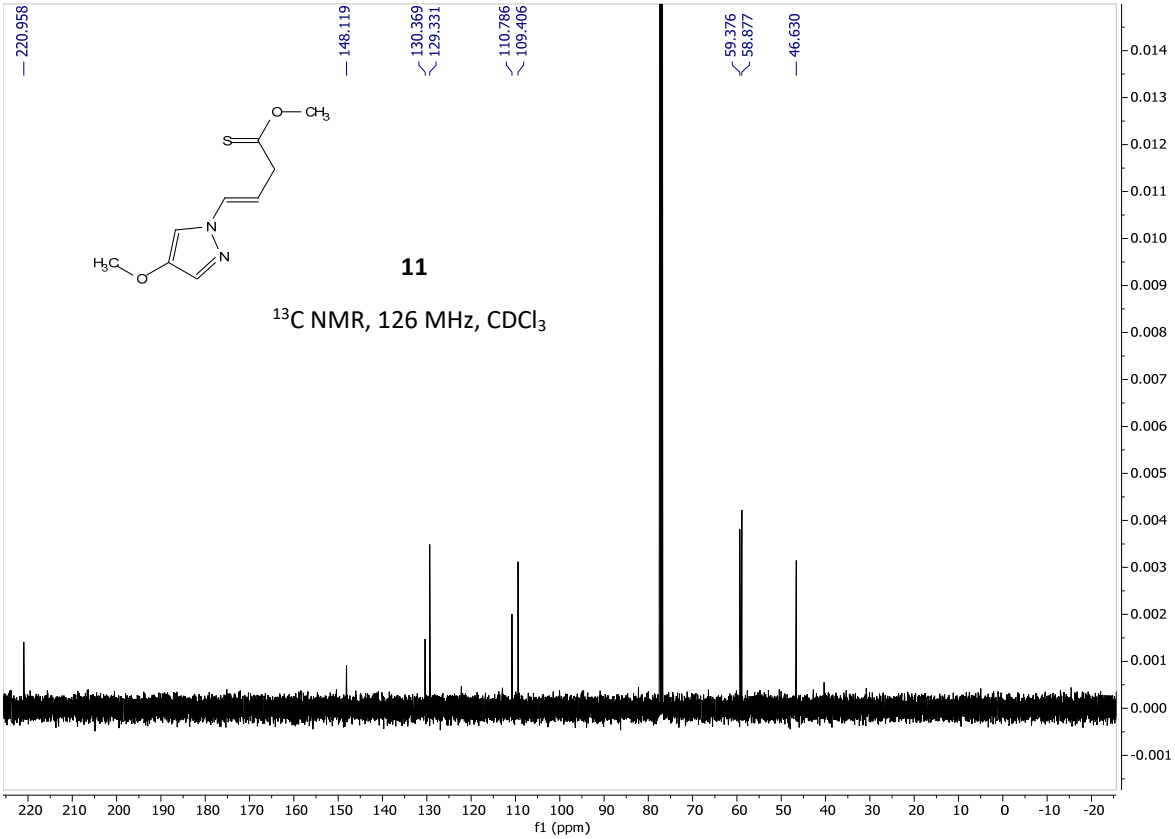
^{1}H NMR, 500 MHz, $CDCl_3$

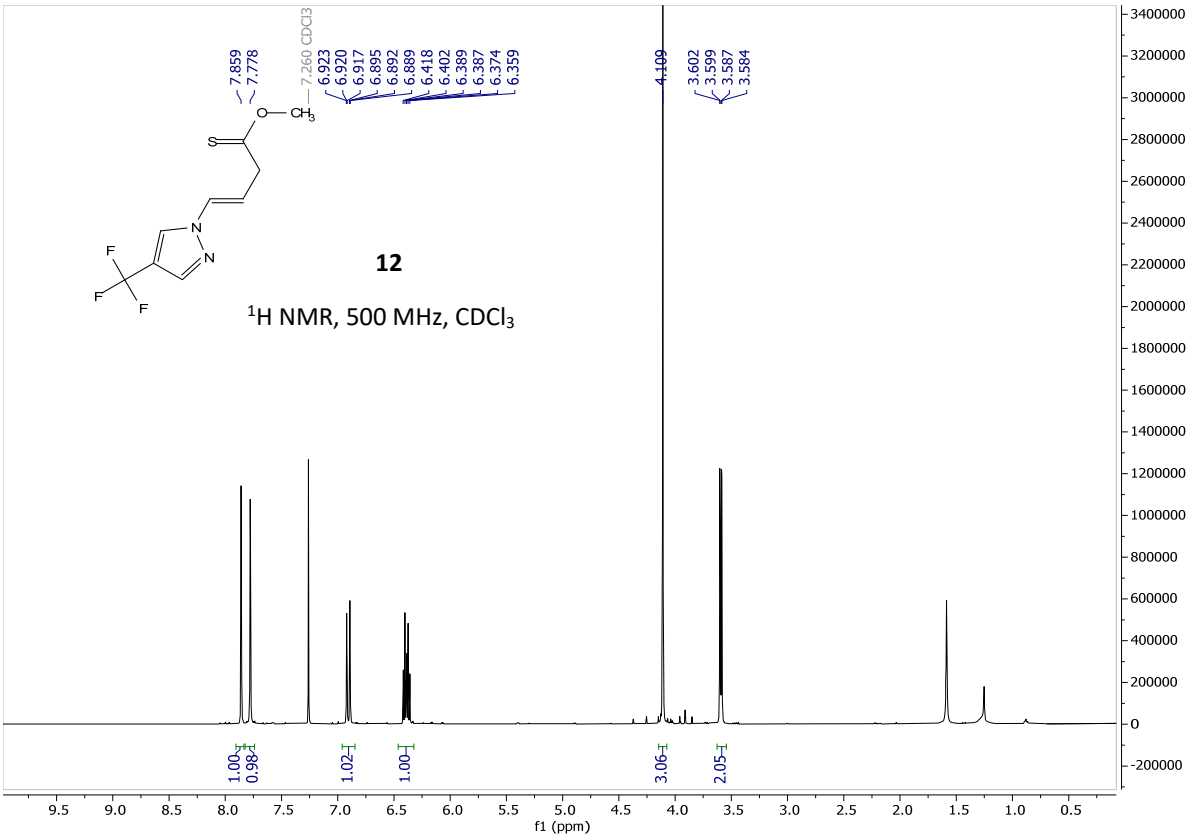


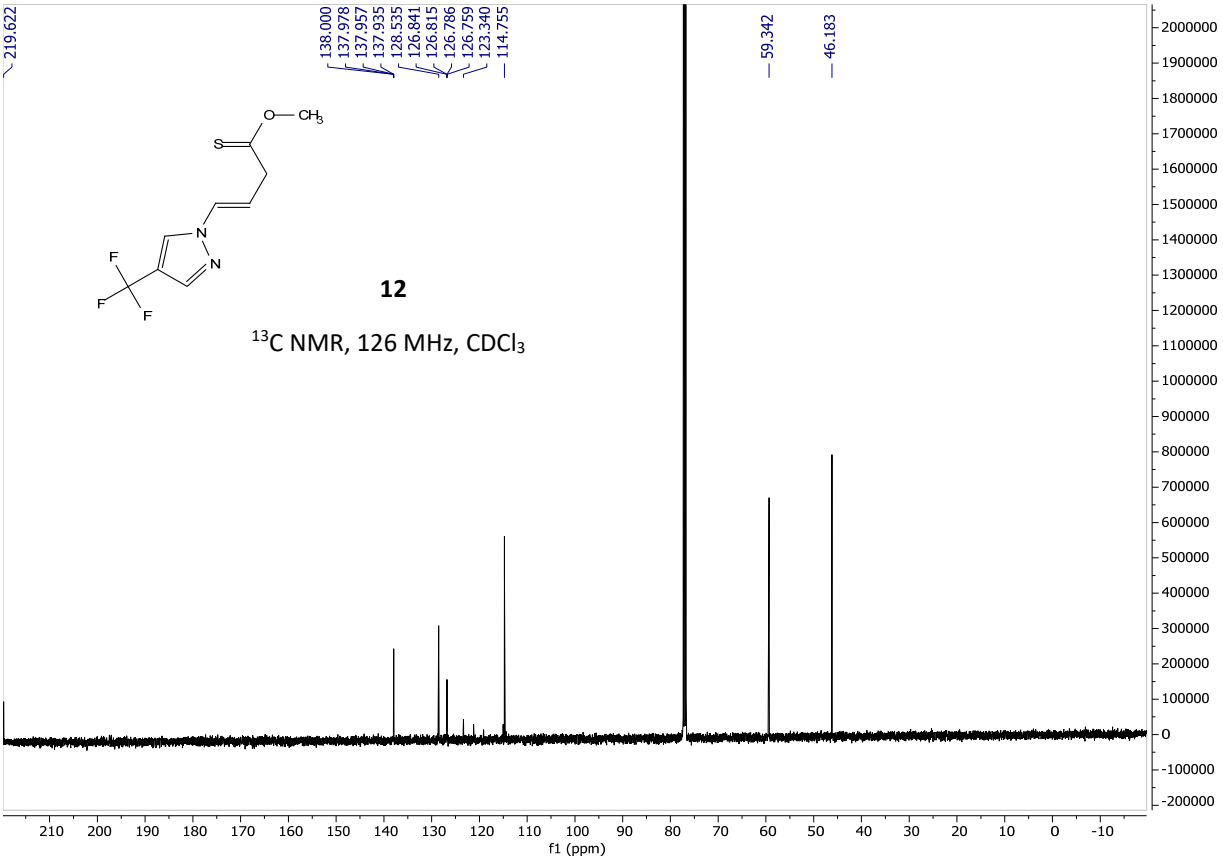
10

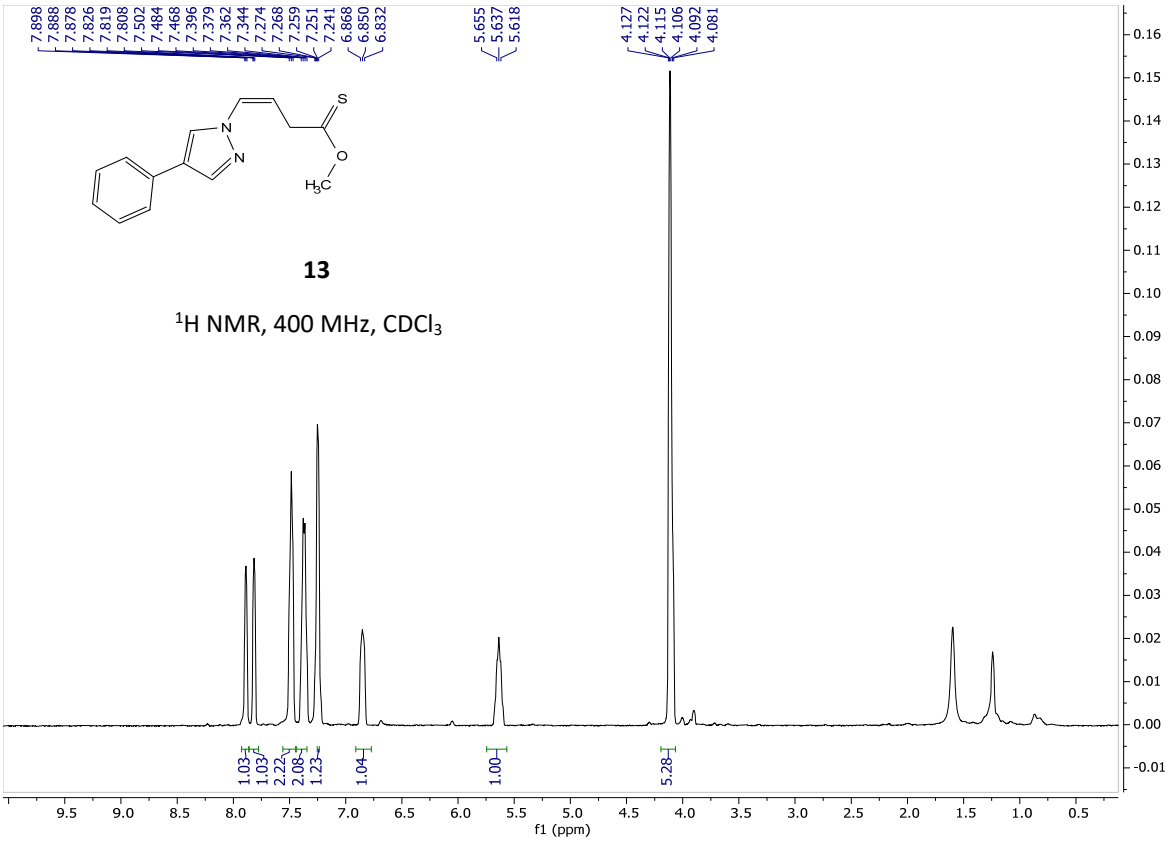
^{13}C NMR, 126 MHz, $CDCl_3$


7.341
7.273
7.260 CDCl3
6.842
6.839
6.836
6.813
6.810
6.807
6.032
6.017
6.004
6.002
5.989
5.974
4.097
3.763
3.560
3.558
3.545
3.543
O—CH3
S
N
N
H3C
O
11
1H NMR, 500 MHz, CDCl3
1.00
1.07
1.06
1.07
3.23
3.24
2.17
f1 (ppm)


220.958
148.119
130.369
129.331
110.786
109.406
59.376
58.877
46.630
O—CH3
S
N
N
H3C
O
11
13C NMR, 126 MHz, CDCl3
f1 (ppm)

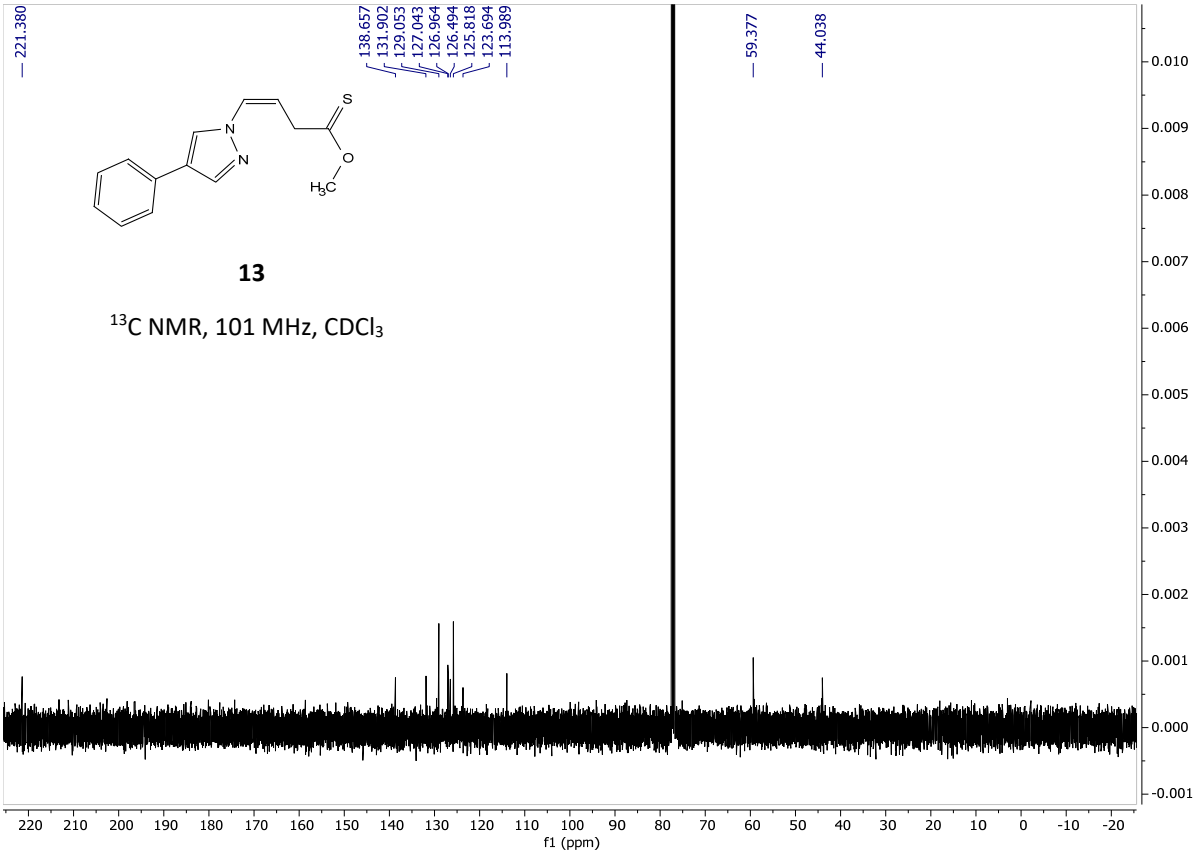

7.859
7.778
7.260 CDCl3
6.923
6.920
6.917
6.895
6.892
6.889
6.418
6.402
6.389
6.387
6.374
6.359
4.109
3.602
3.599
3.587
3.584
O—CH3
S
N
N
F
F
F
12
1H NMR, 500 MHz, CDCl3
1.00
0.98
1.02
1.00
3.06
2.05
f1 (ppm)


219.622
138.000
137.978
137.957
137.935
128.535
126.841
126.815
126.786
126.759
123.340
114.755
59.342
46.183
O—CH3
S
N
N
F
F
F
12
13C NMR, 126 MHz, CDCl3
f1 (ppm)



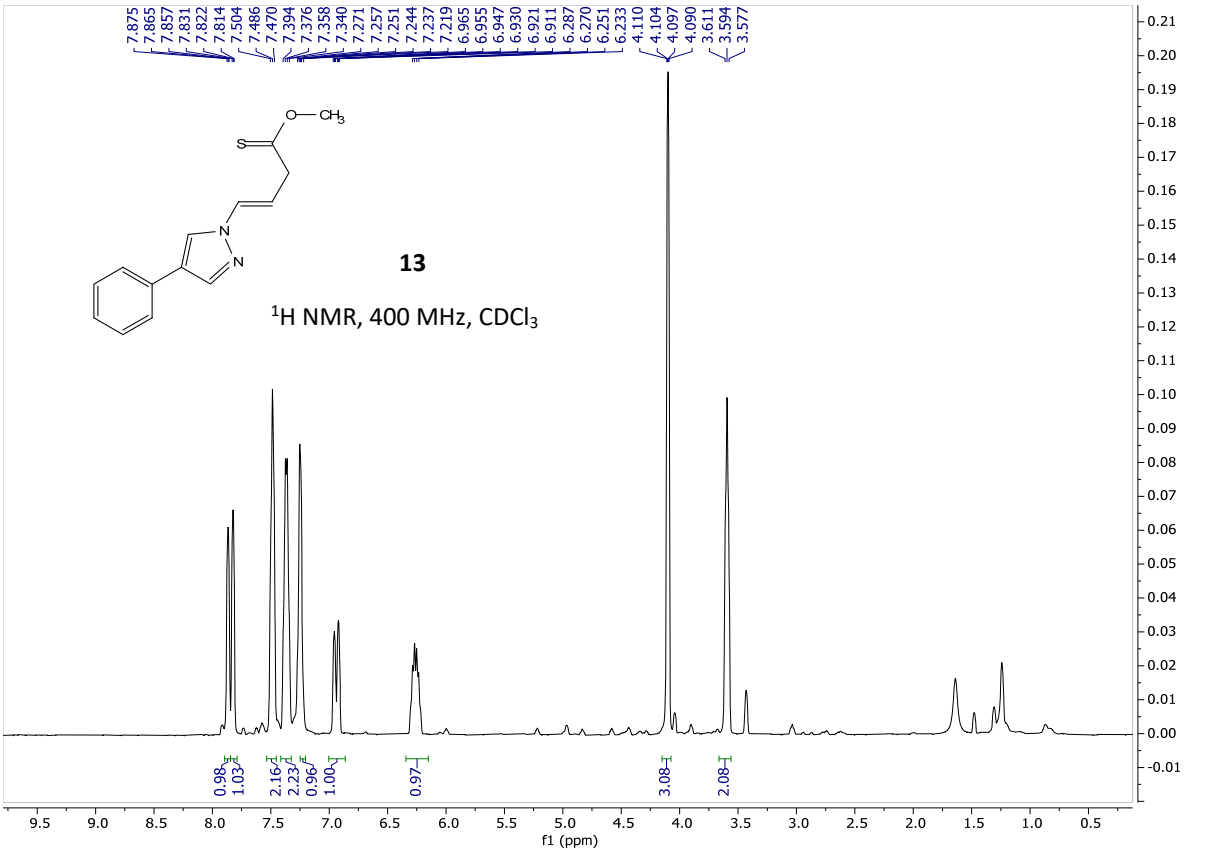
13

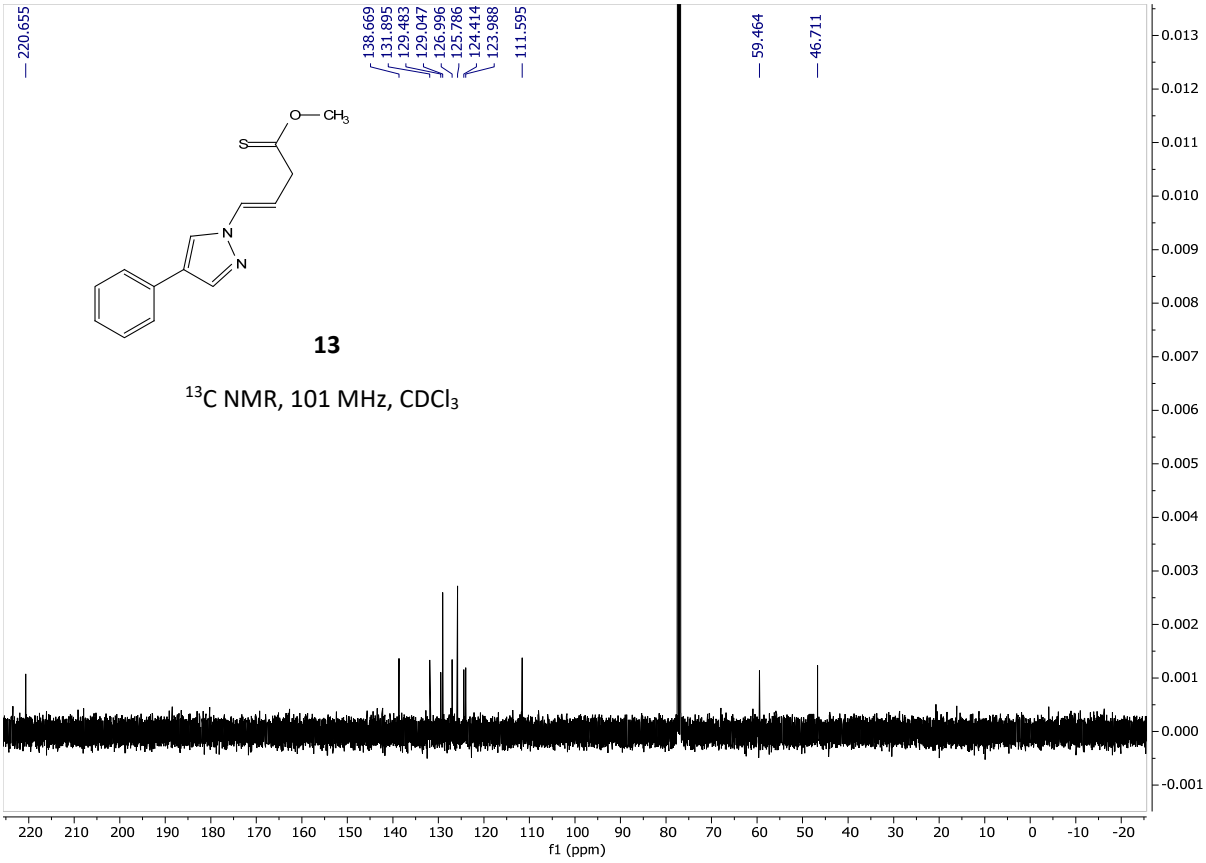
^{1}H NMR, 400 MHz, $CDCl_3$

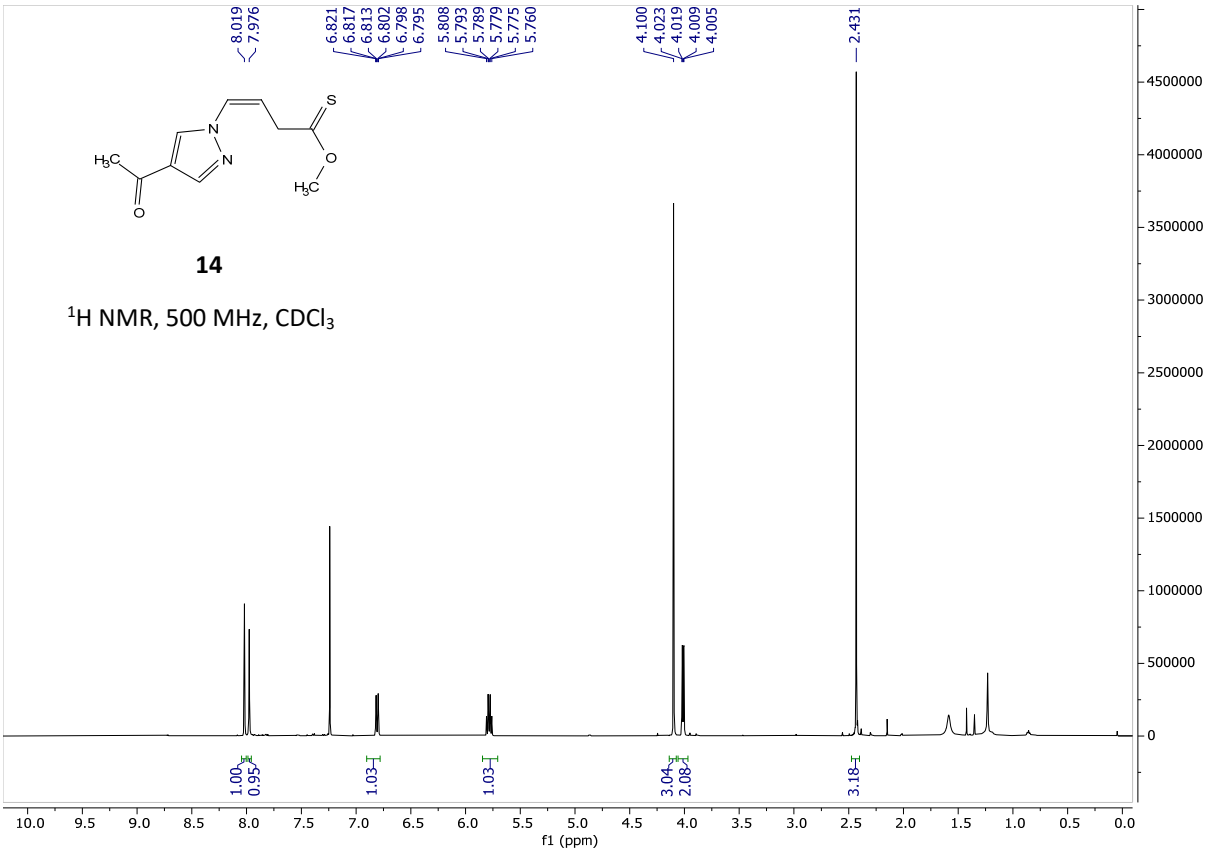


13

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

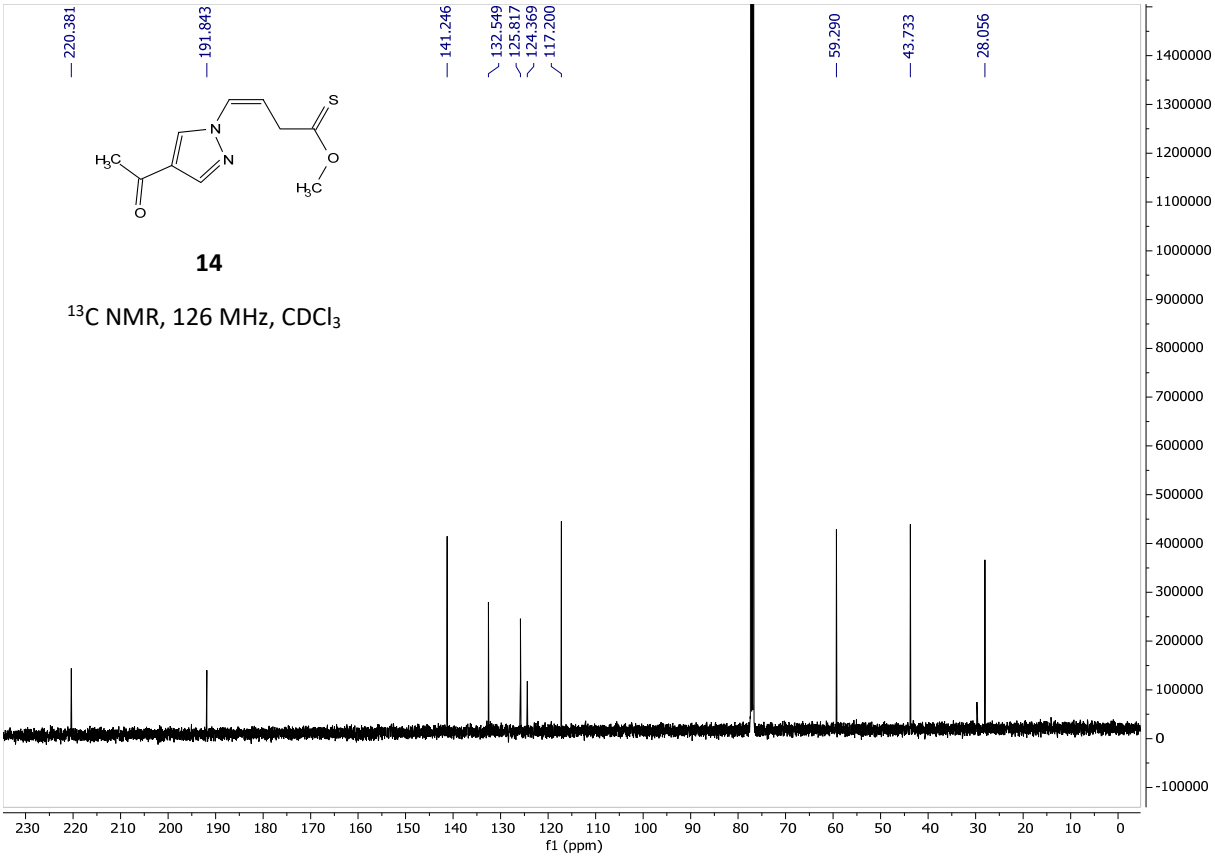

7.875
7.865
7.857
7.831
7.822
7.814
7.504
7.486
7.470
7.394
7.376
7.358
7.340
7.271
7.257
7.251
7.244
7.237
7.219
6.965
6.955
6.947
6.930
6.921
6.911
6.287
6.270
6.251
6.233
4.110
4.104
4.097
4.090
3.611
3.594
3.577
O—CH3
S
N
N
13
1H NMR, 400 MHz, CDCl3
0.98
1.03
2.16
2.23
0.96
1.00
0.97
3.08
2.08
f1 (ppm)


220.655
138.669
131.895
129.483
129.047
126.996
125.786
124.414
123.988
111.595
59.464
46.711
O—CH3
S
N
N
13
13C NMR, 101 MHz, CDCl3
f1 (ppm)



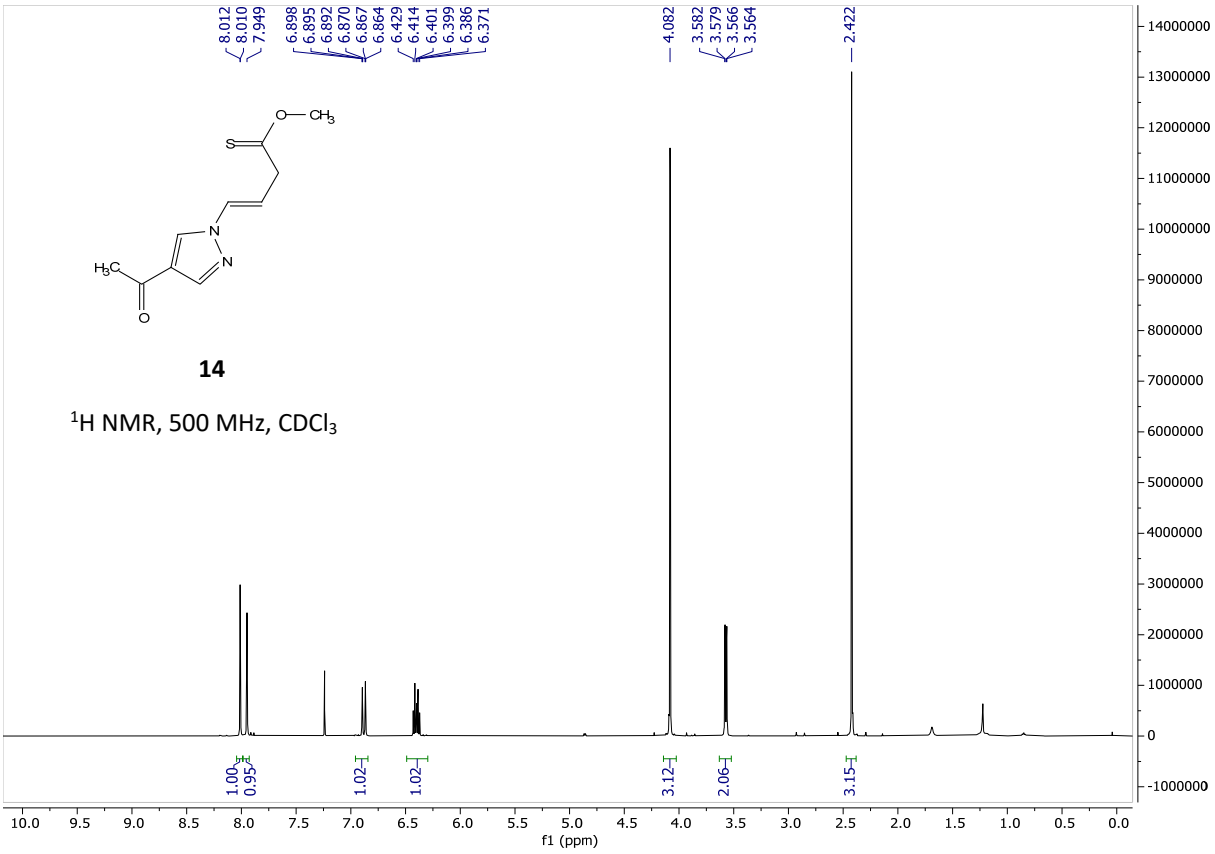
14

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



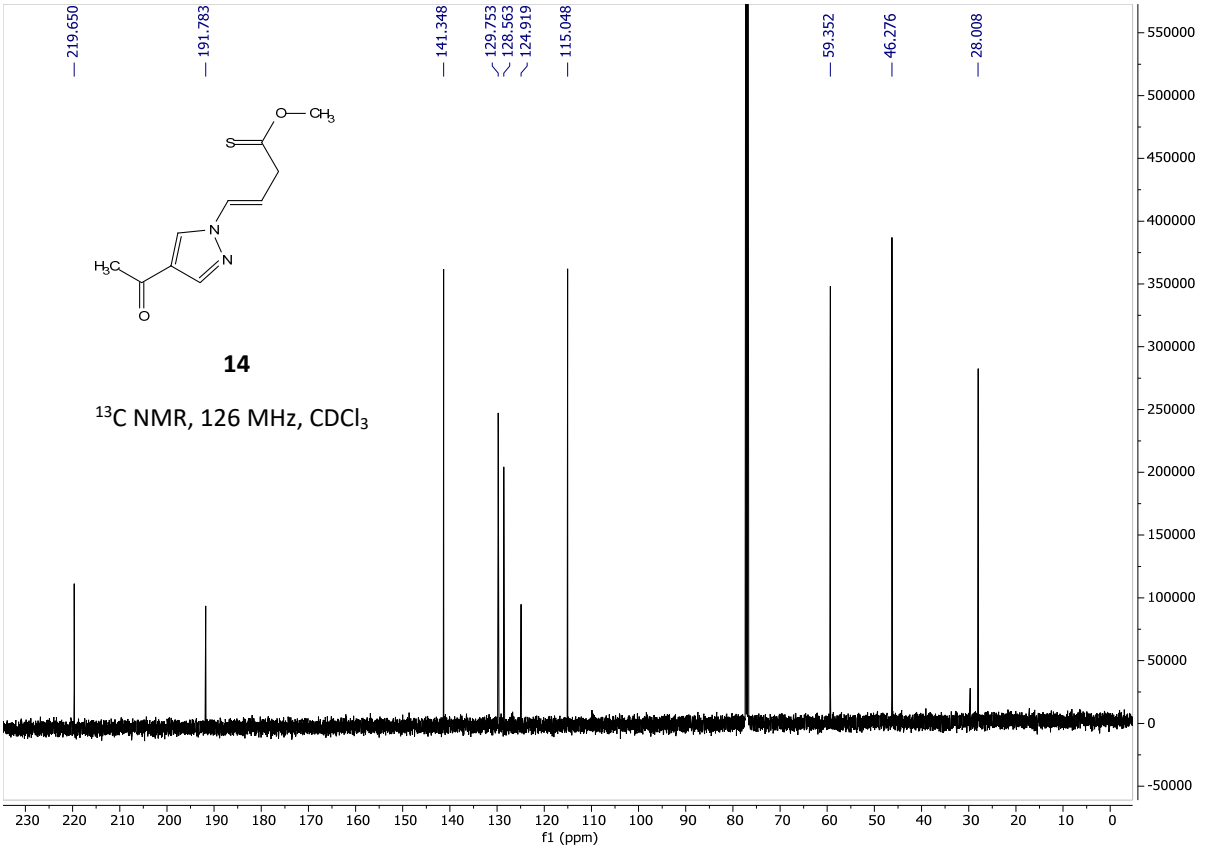
14

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



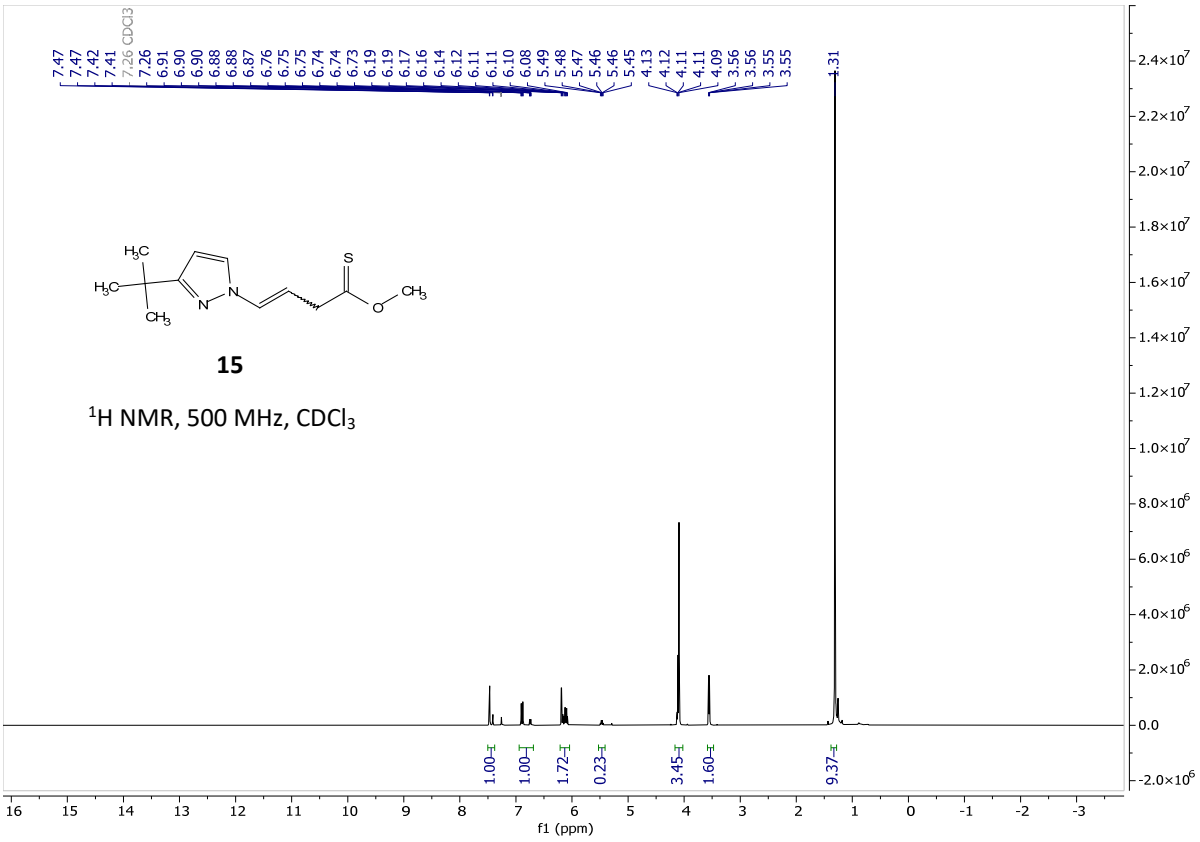
14

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



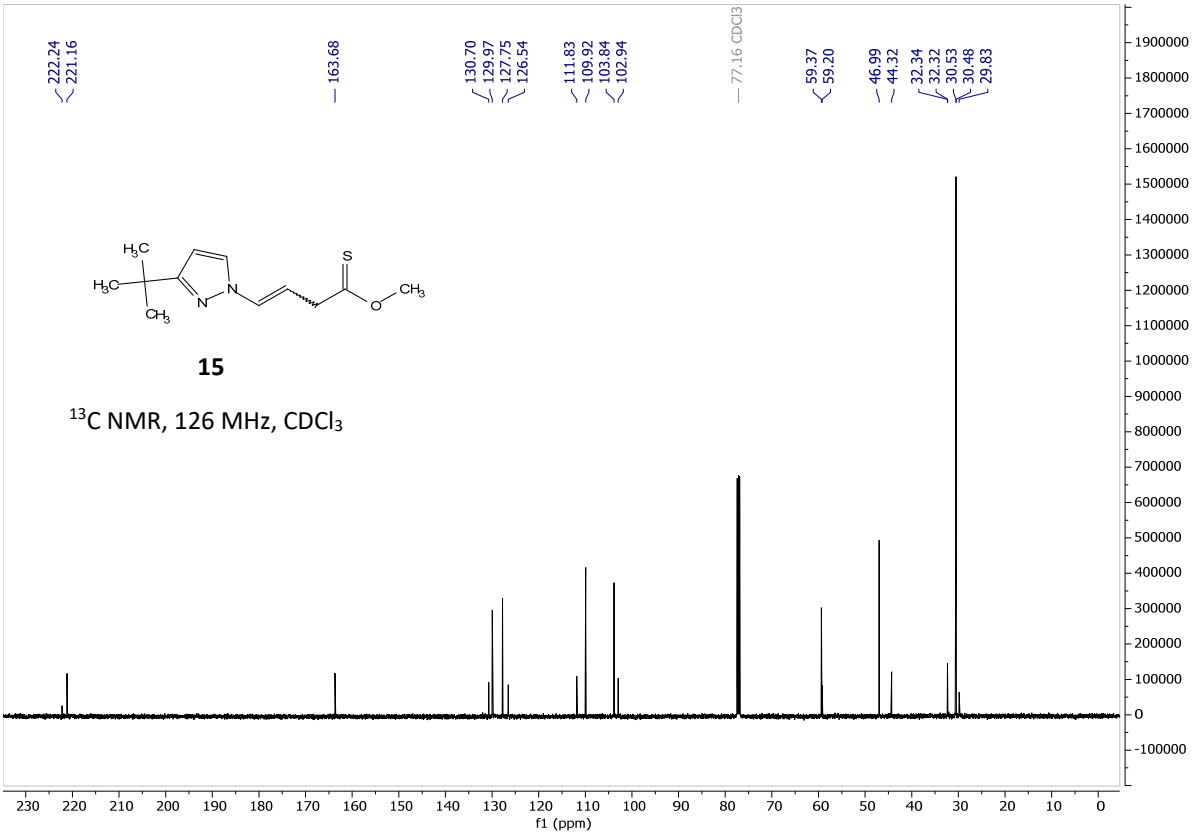
14

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



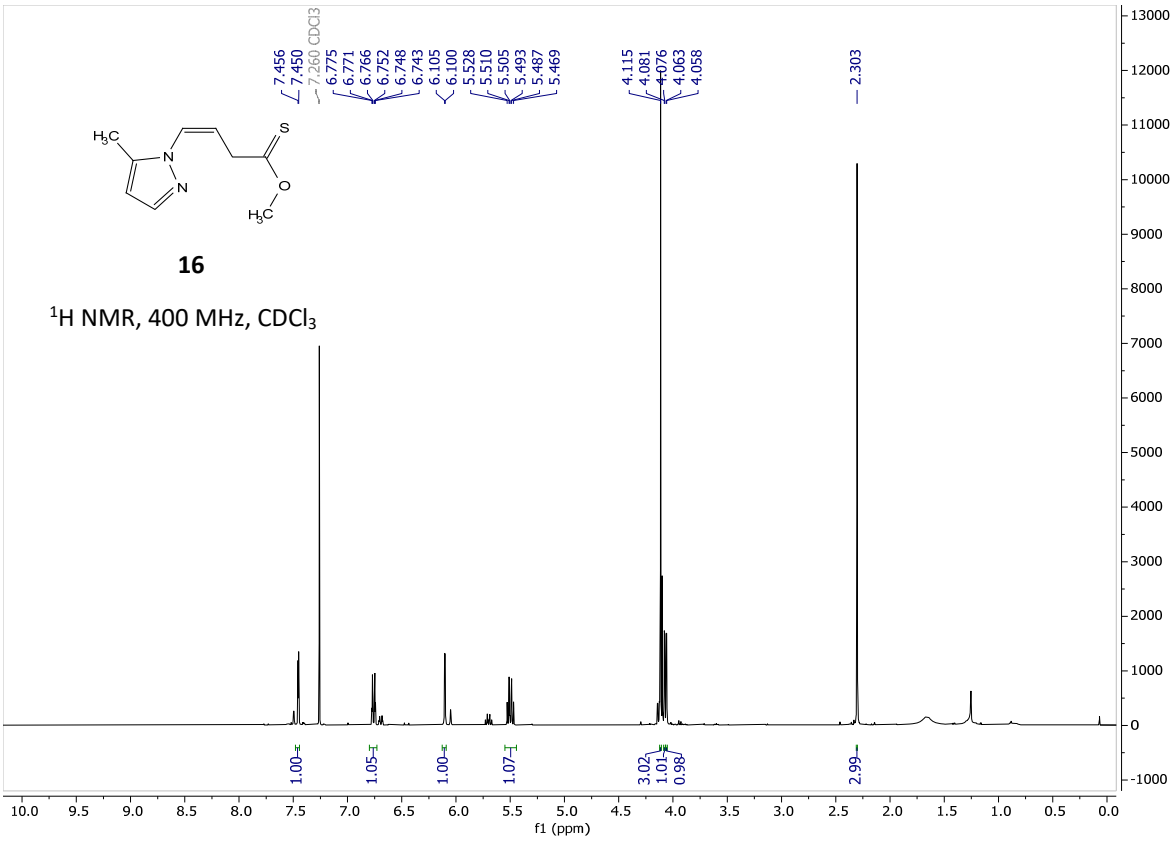
15

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



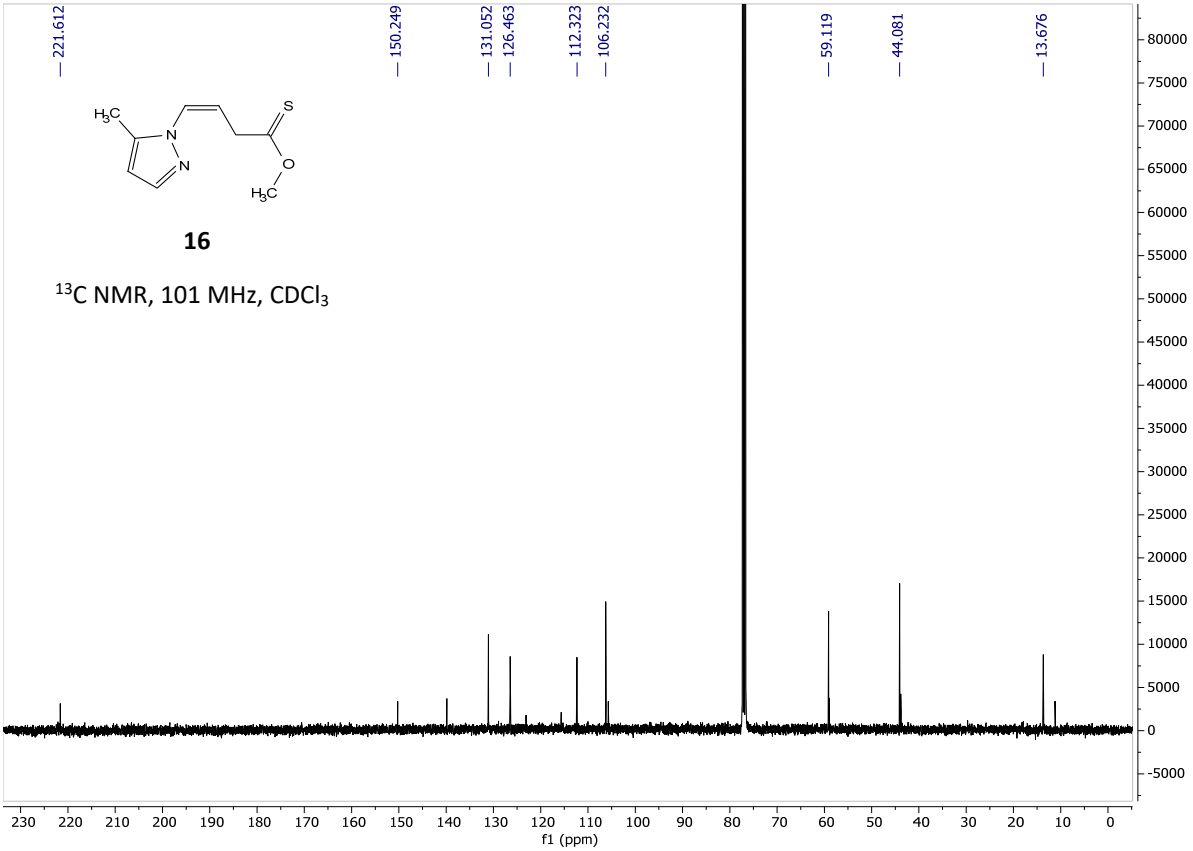
15

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



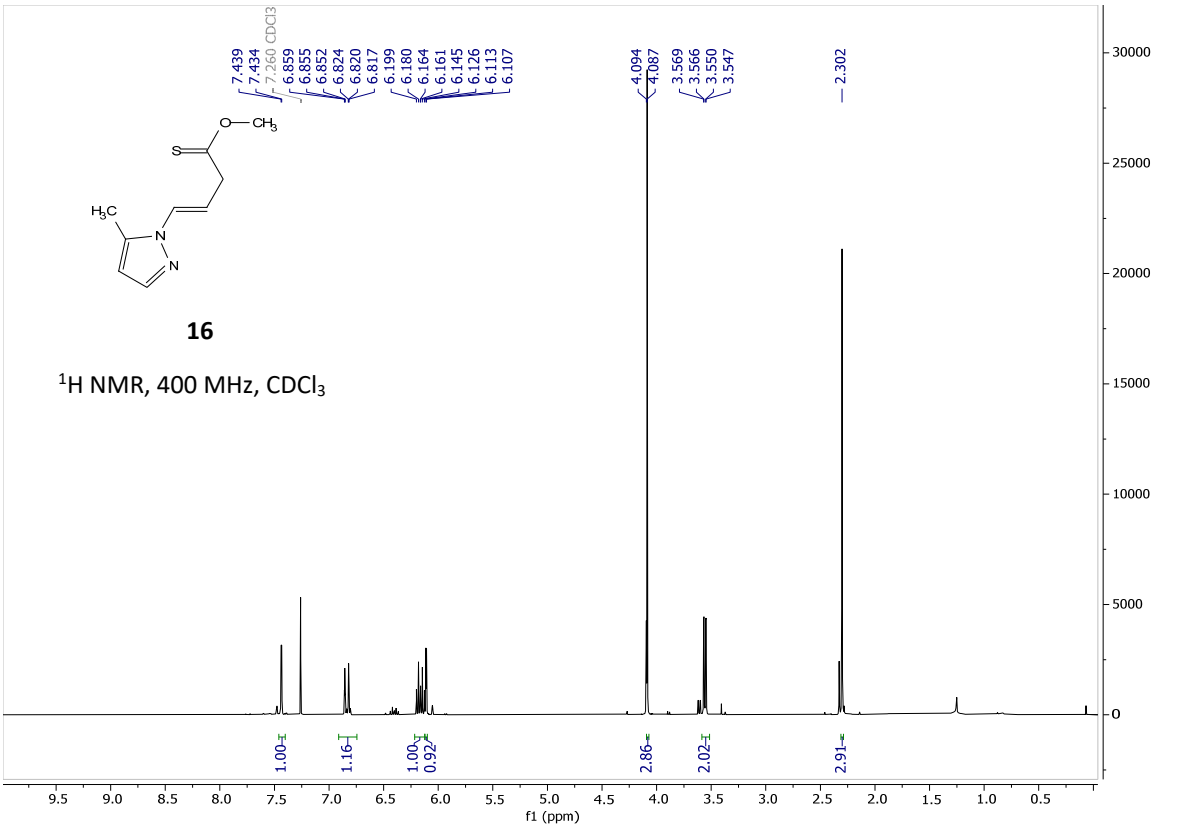
16

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



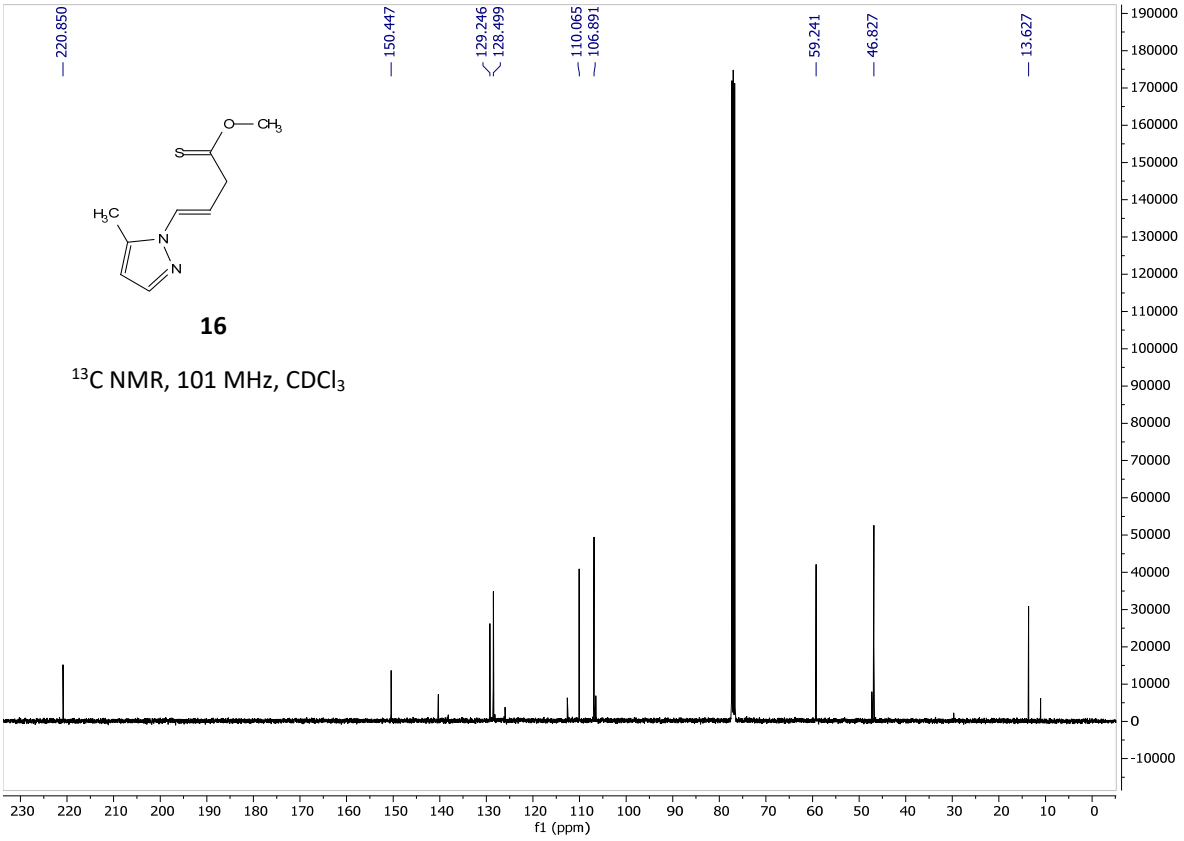
16

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



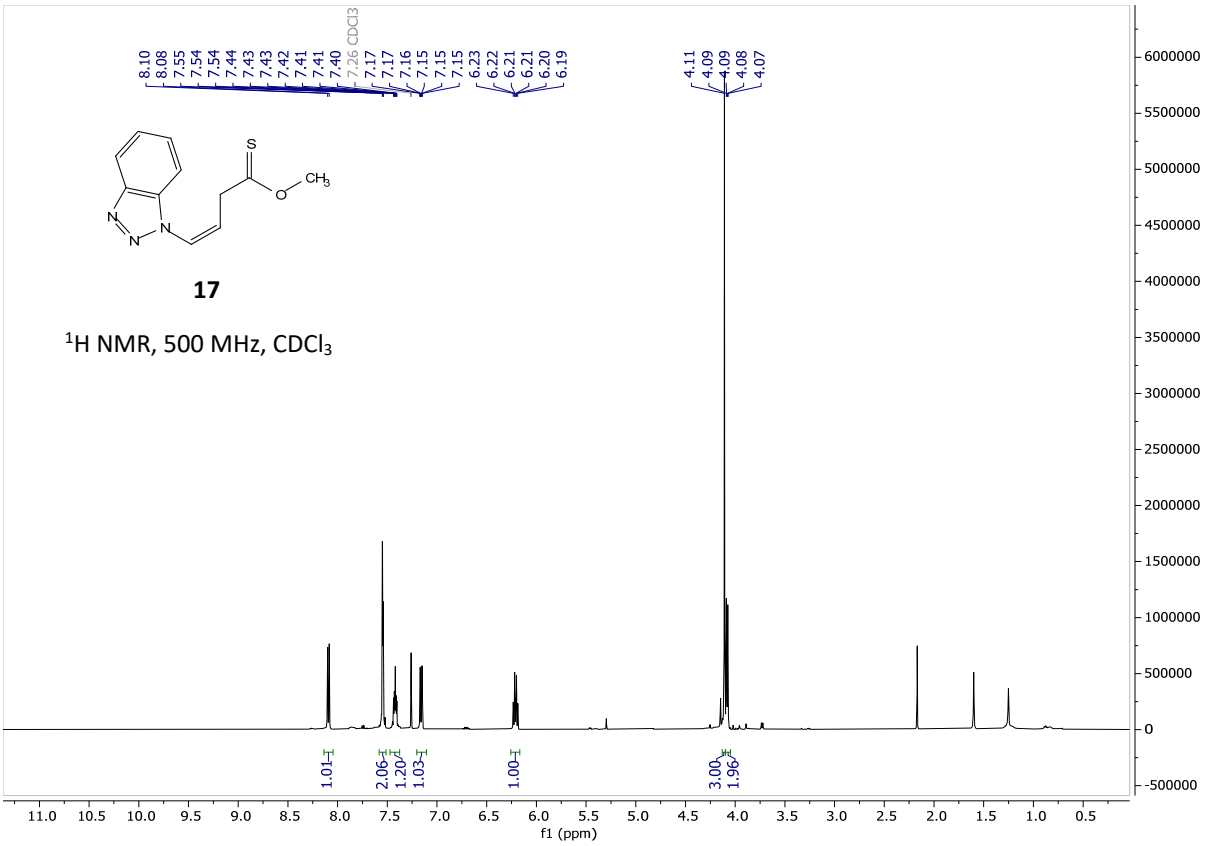
16

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



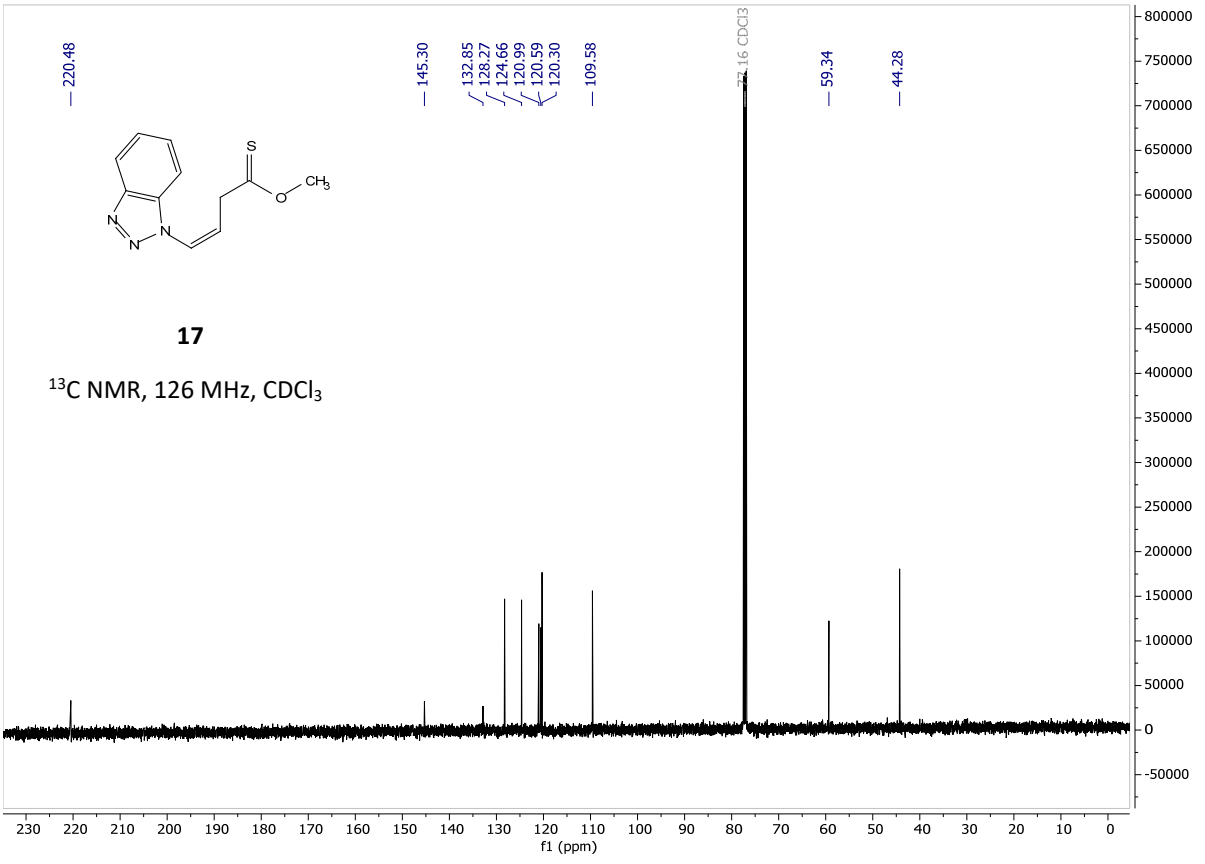
16

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



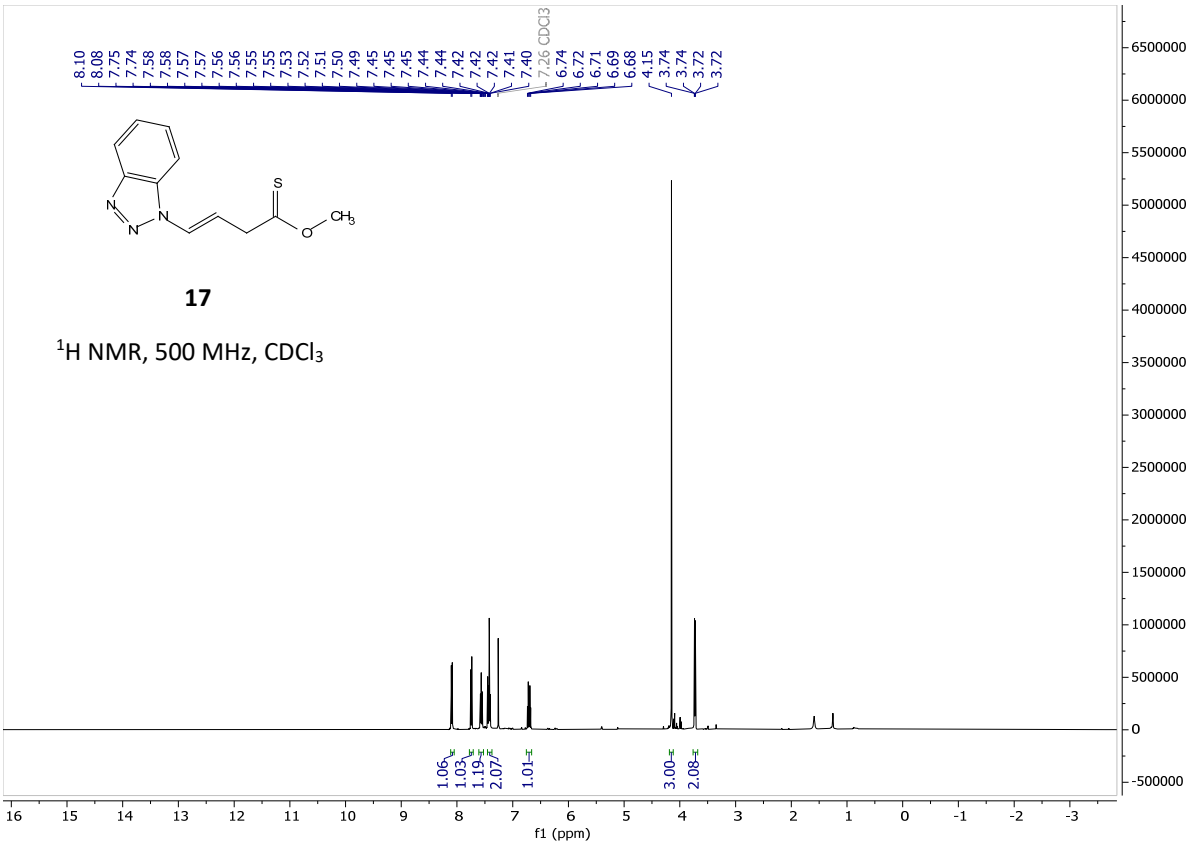
17

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



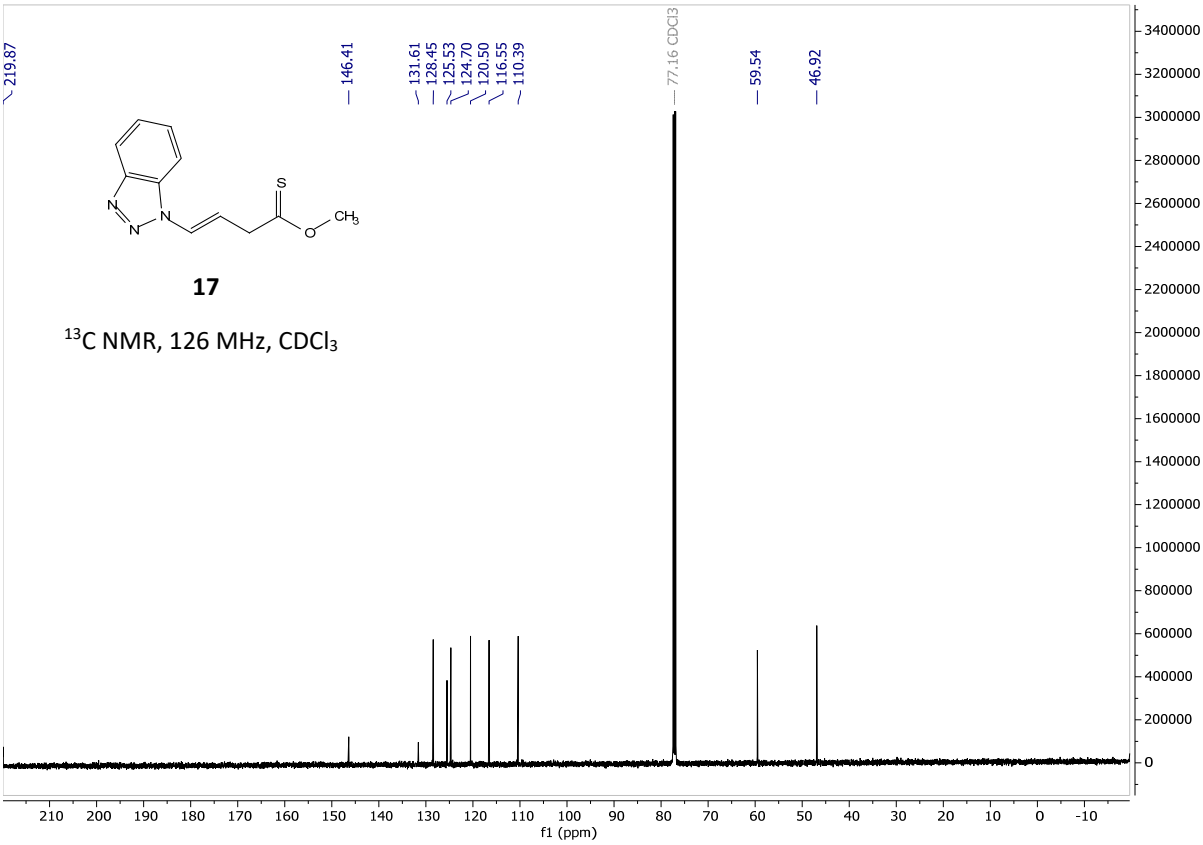
17

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



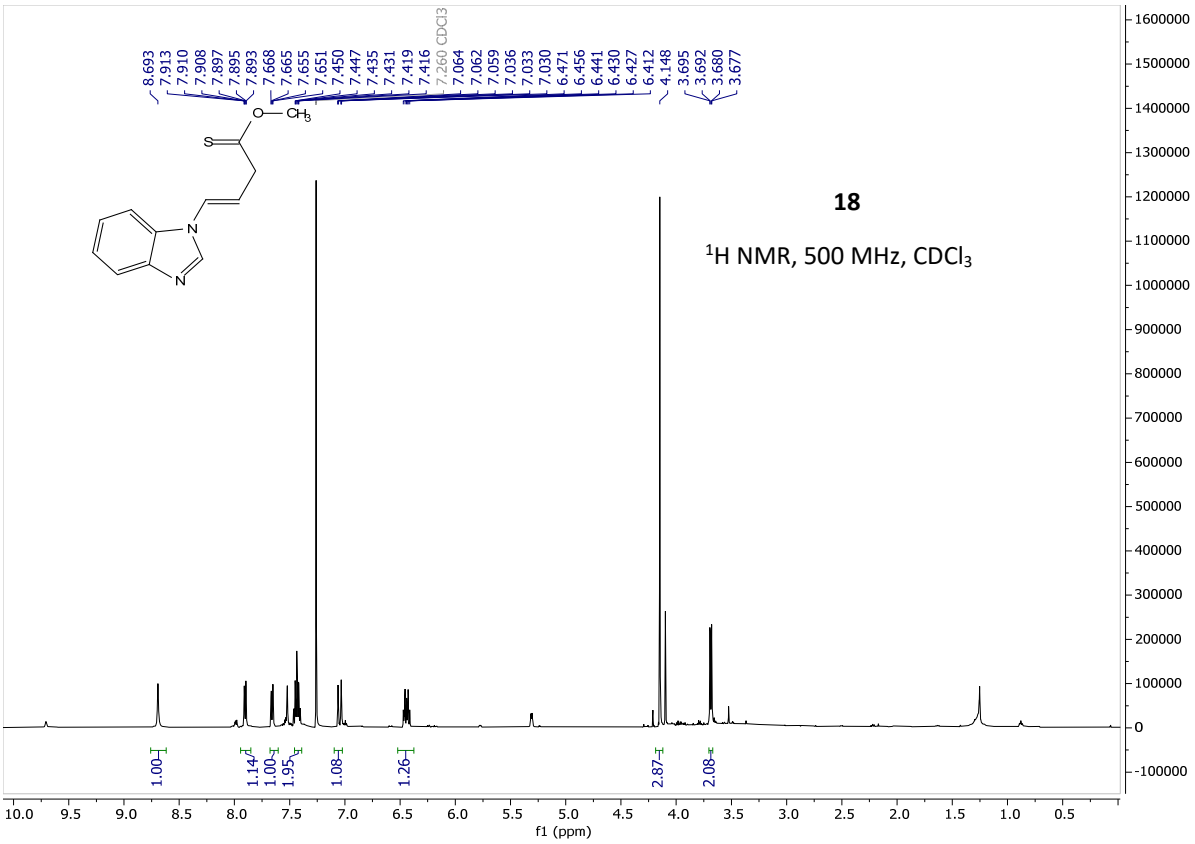
17

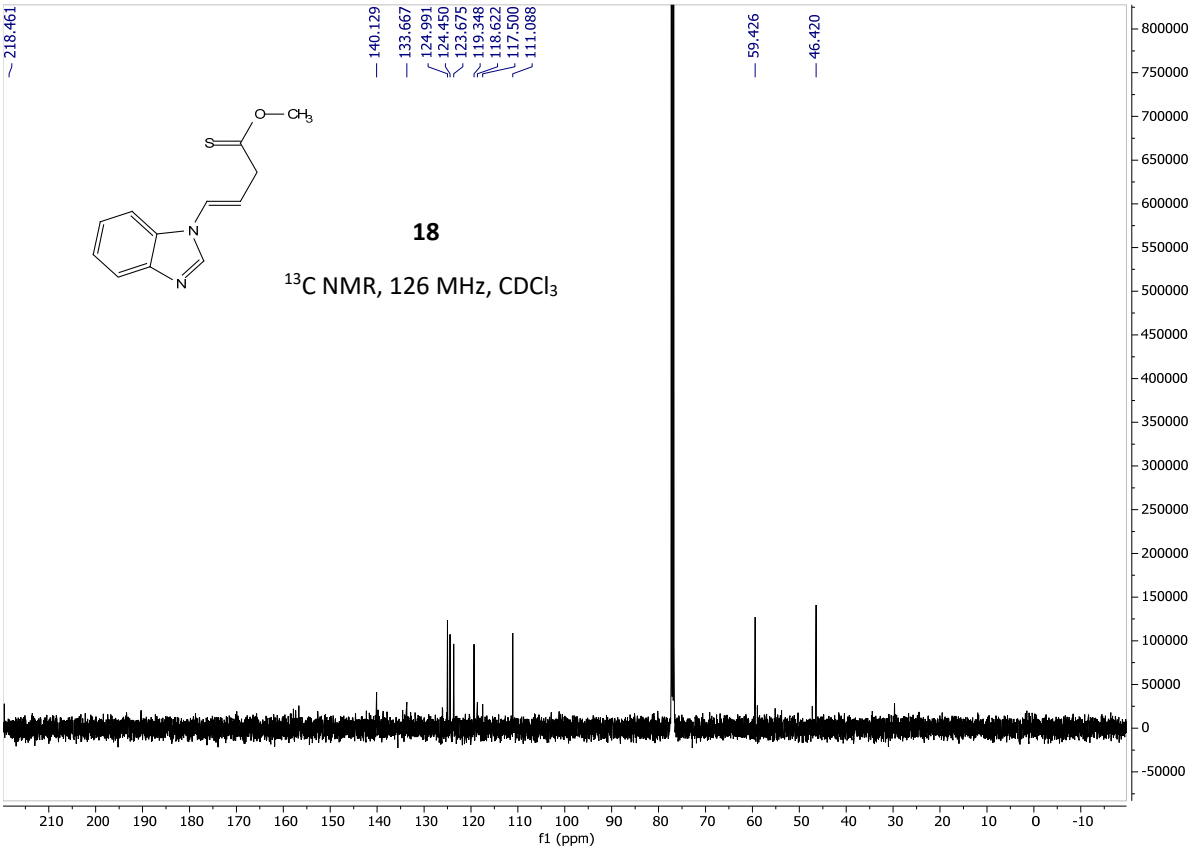
^{1}H NMR, 500 MHz, $CDCl_3$

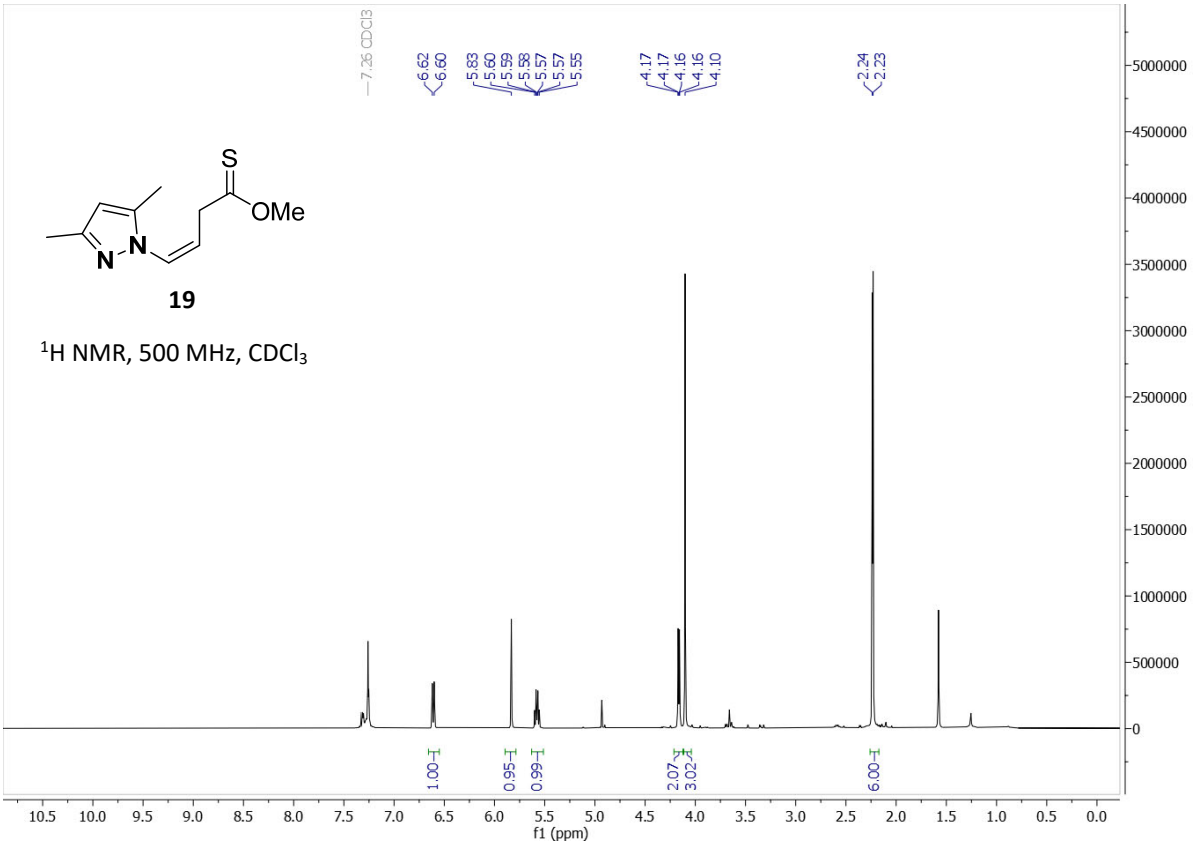


17

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

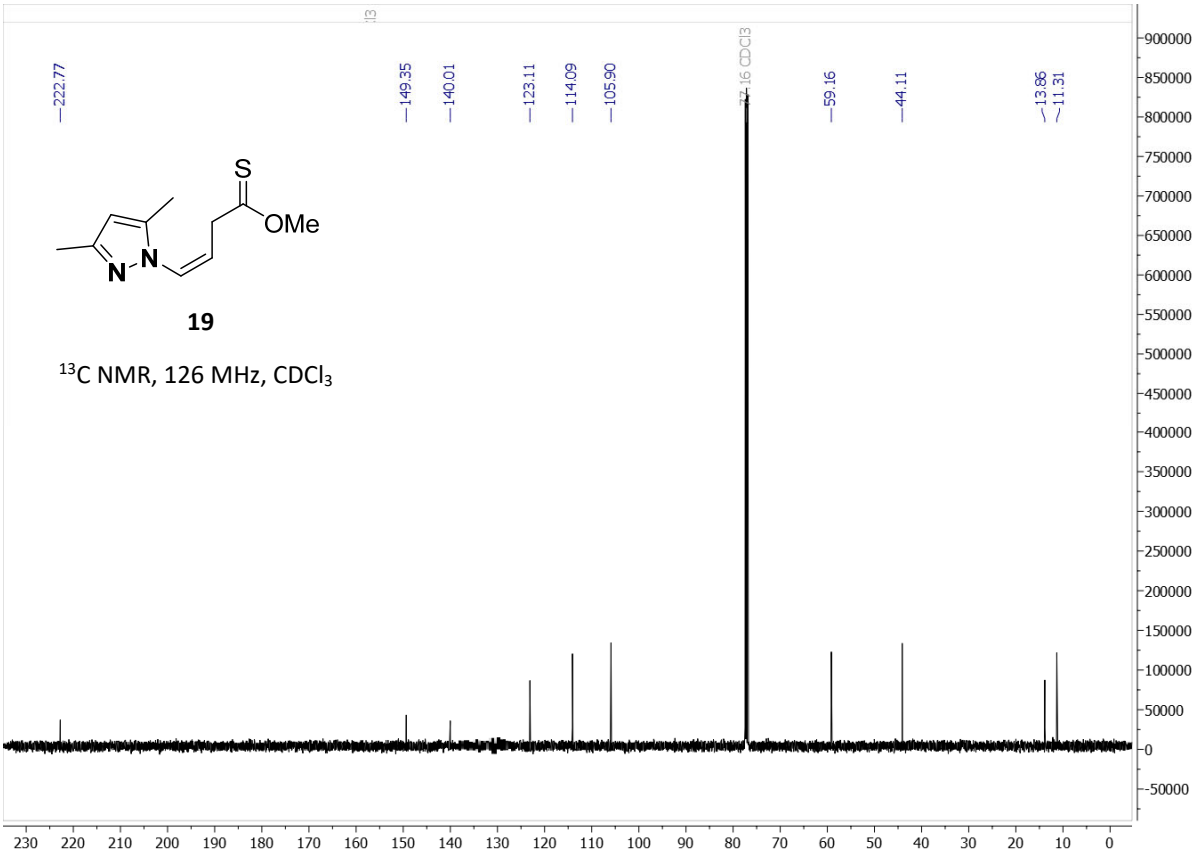

8.693
7.913
7.910
7.908
7.897
7.895
7.893
7.668
7.665
7.655
7.651
7.450
7.447
7.435
7.431
7.419
7.416
7.260 CDCl3
7.064
7.062
7.059
7.036
7.033
7.030
6.471
6.456
6.441
6.430
6.427
6.412
4.148
3.695
3.692
3.680
3.677
O—CH3
S
N
N
18
1H NMR, 500 MHz, CDCl3
1.00
1.14
1.00
1.95
1.08
1.26
2.87
2.08
f1 (ppm)


218.461
140.129
133.667
124.991
124.450
123.675
119.348
118.622
117.500
111.088
59.426
46.420
O—CH3
S
N
N
18
13C NMR, 126 MHz, CDCl3
f1 (ppm)



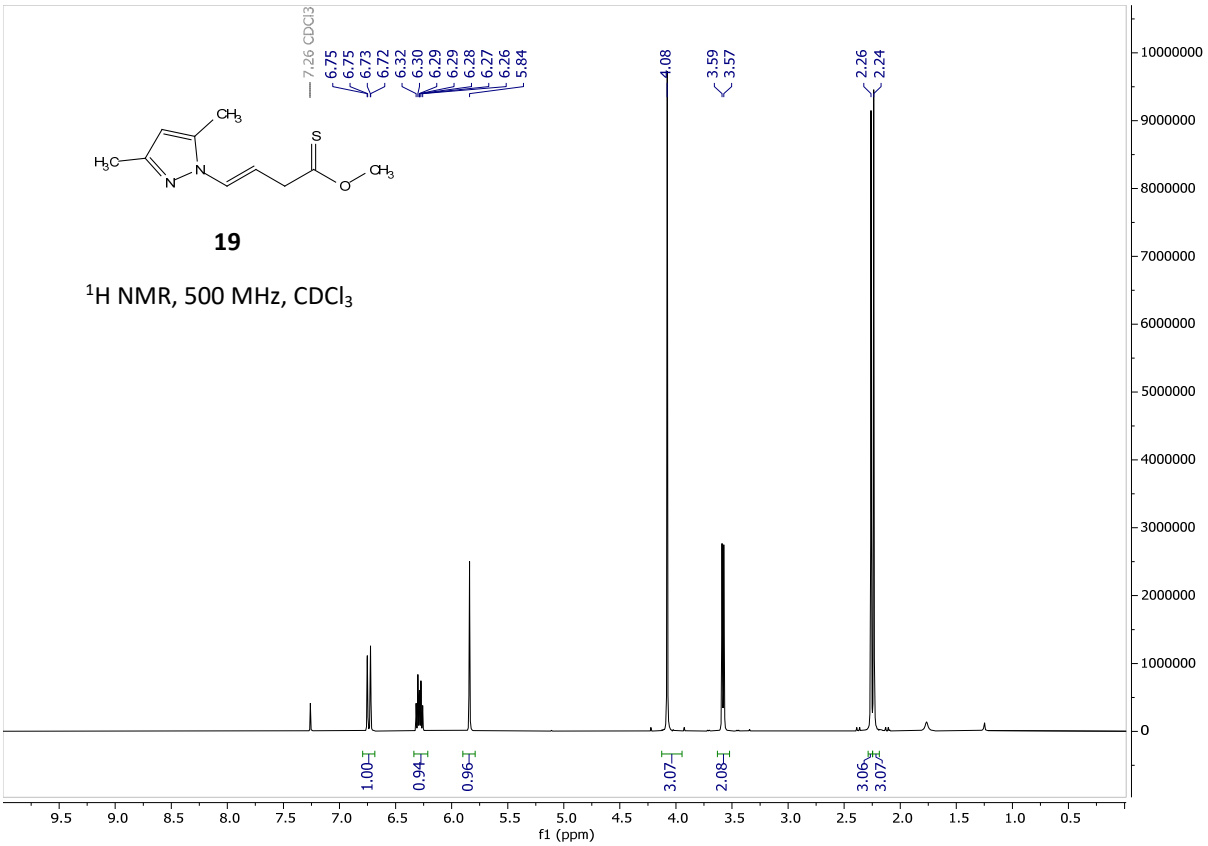
19

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



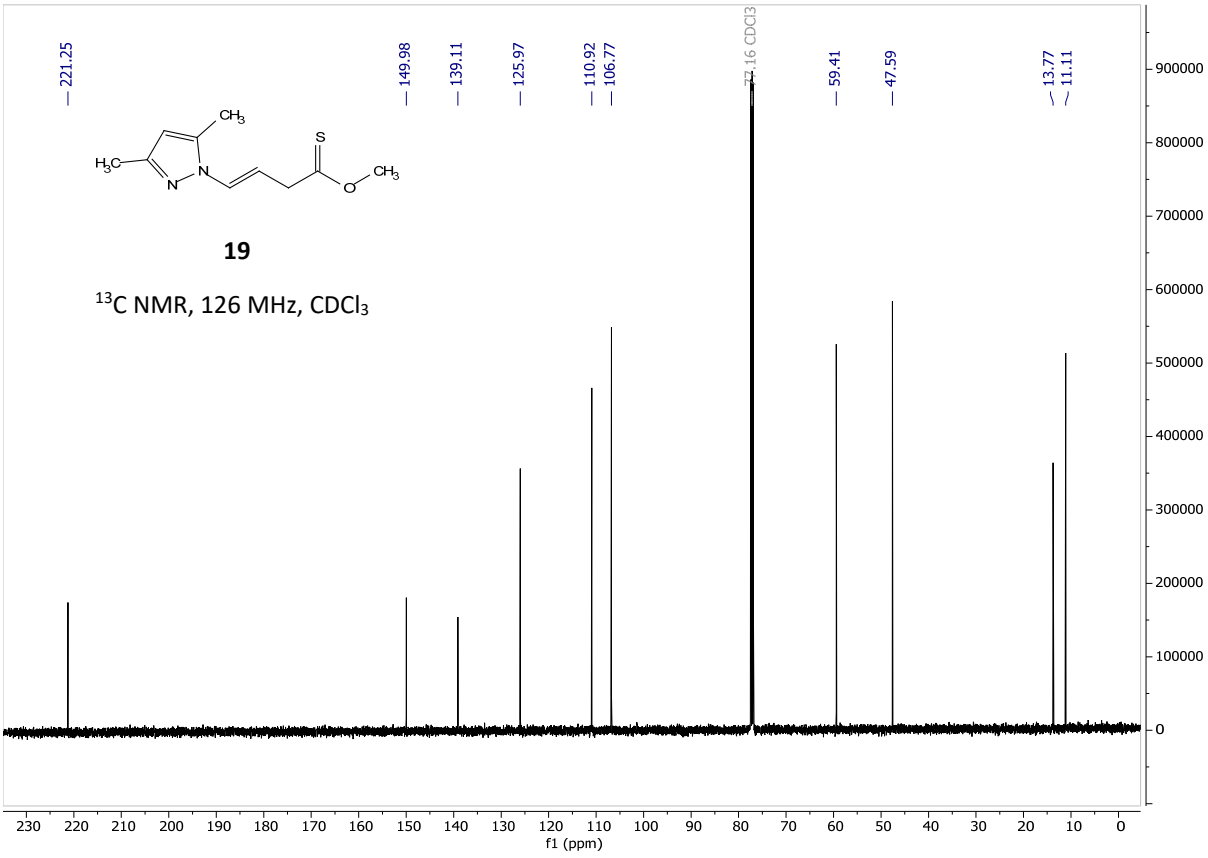
19

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



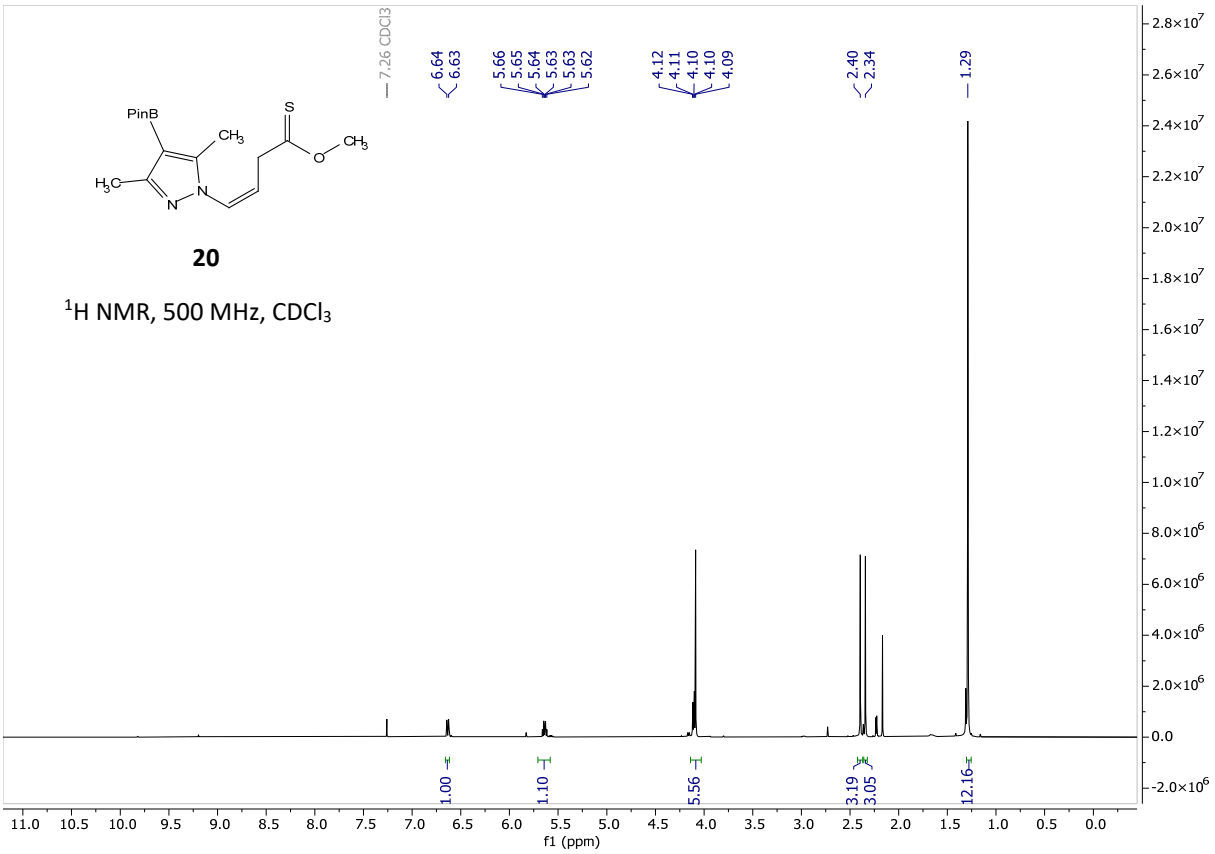
19

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



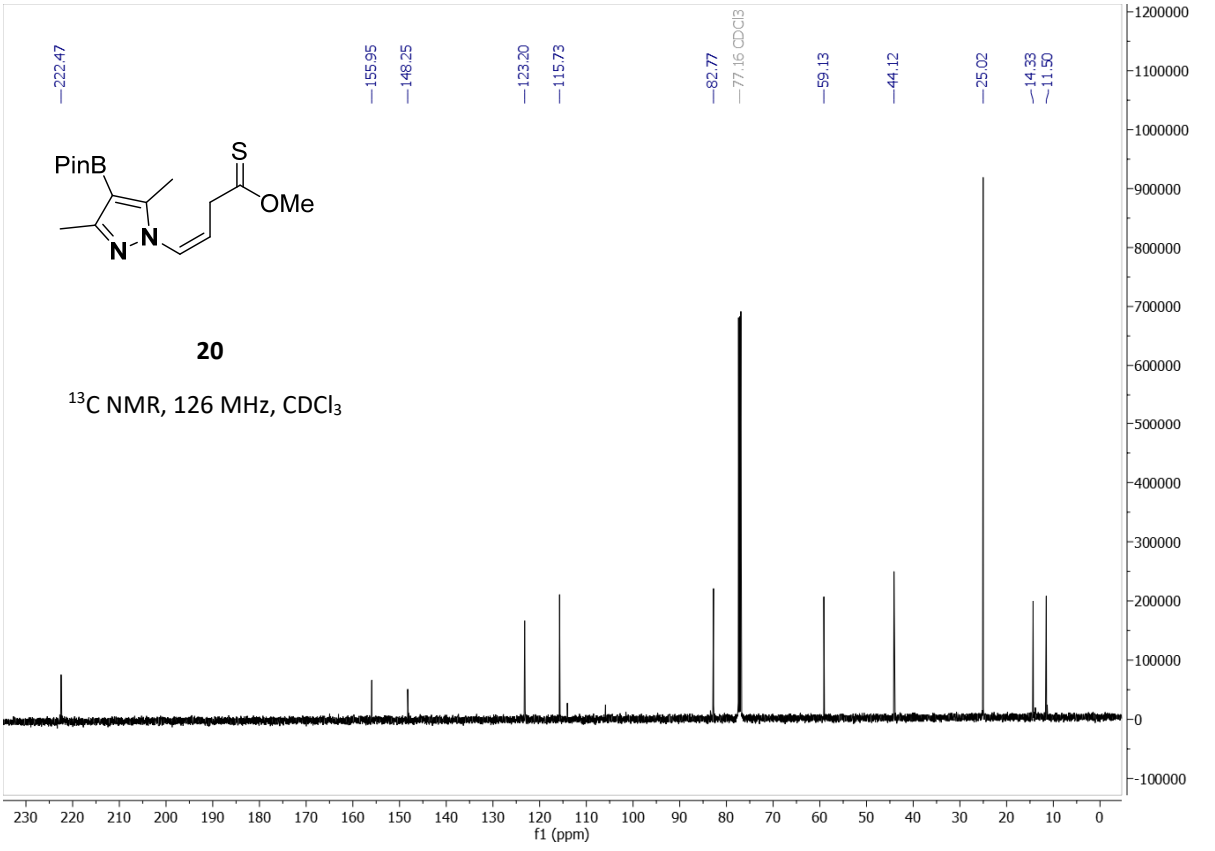
19

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



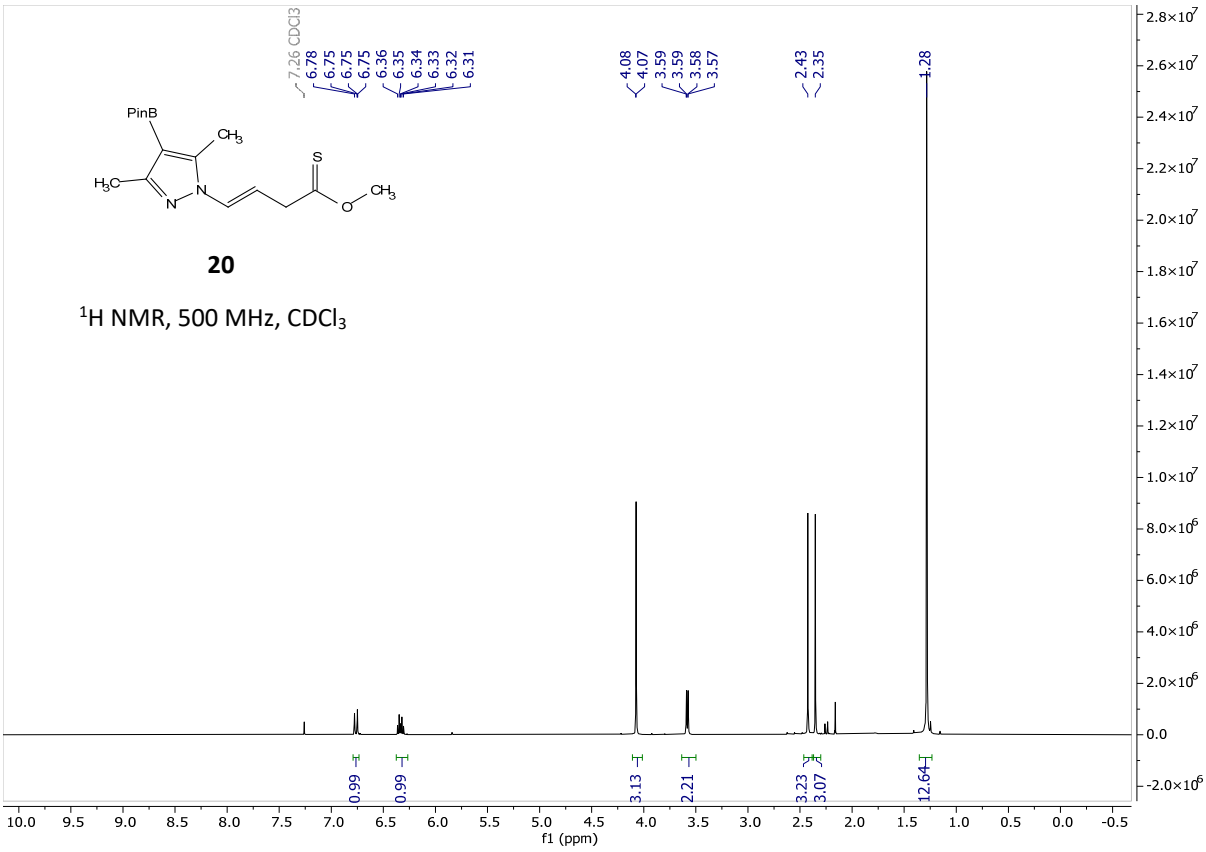
20

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



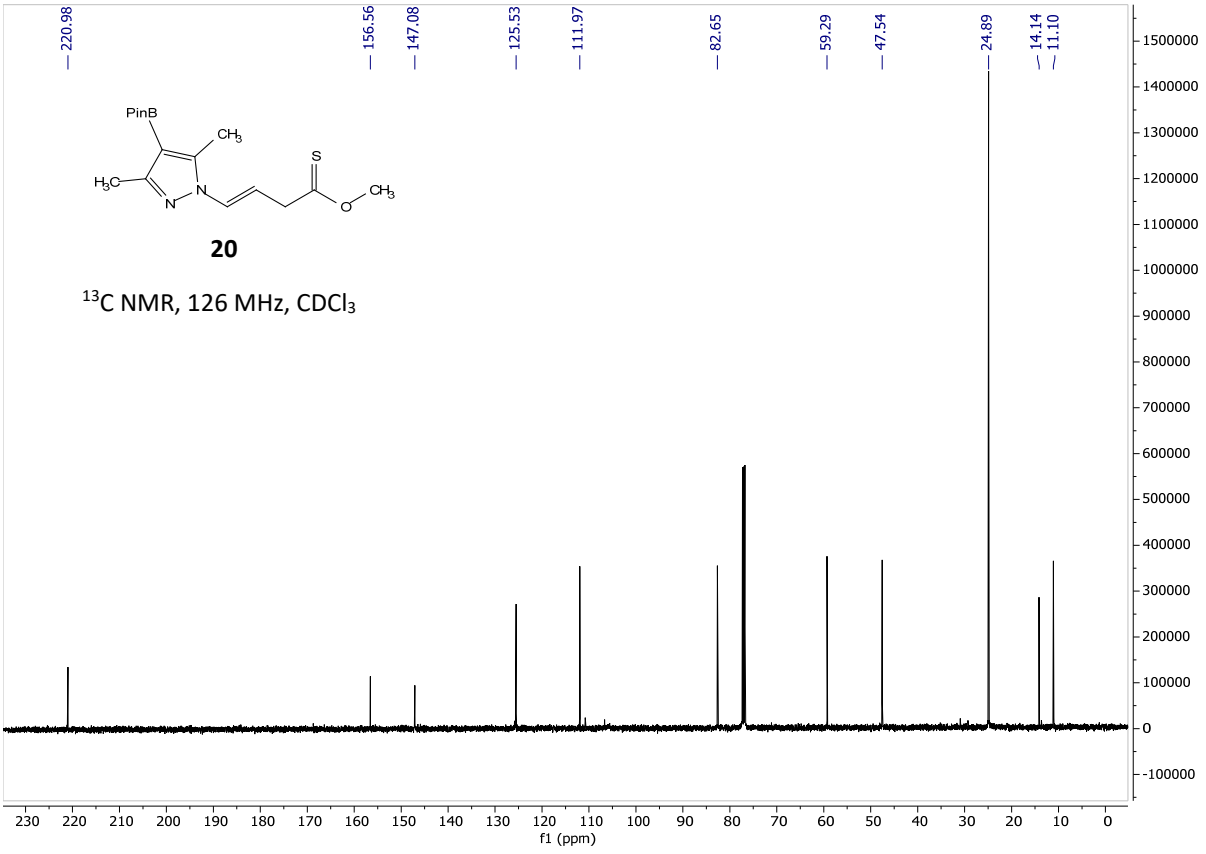
20

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



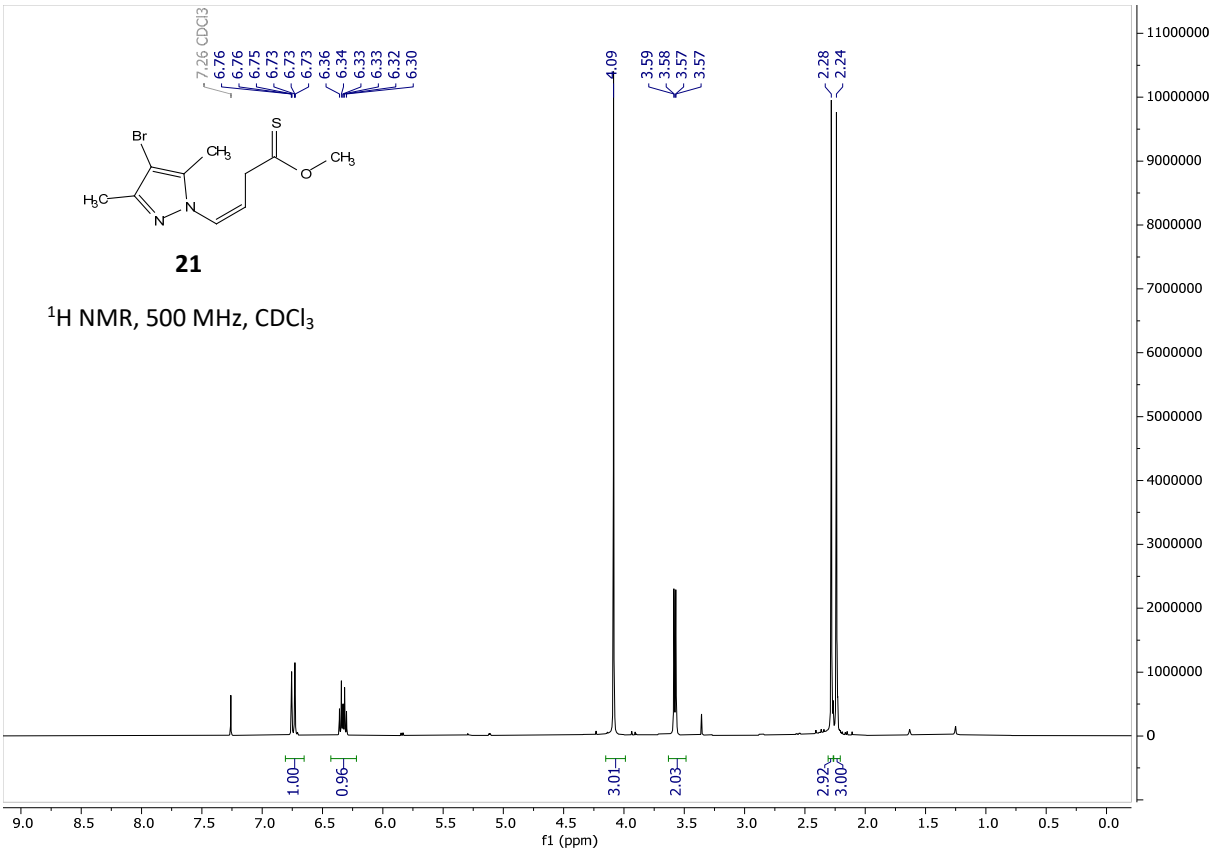
20

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



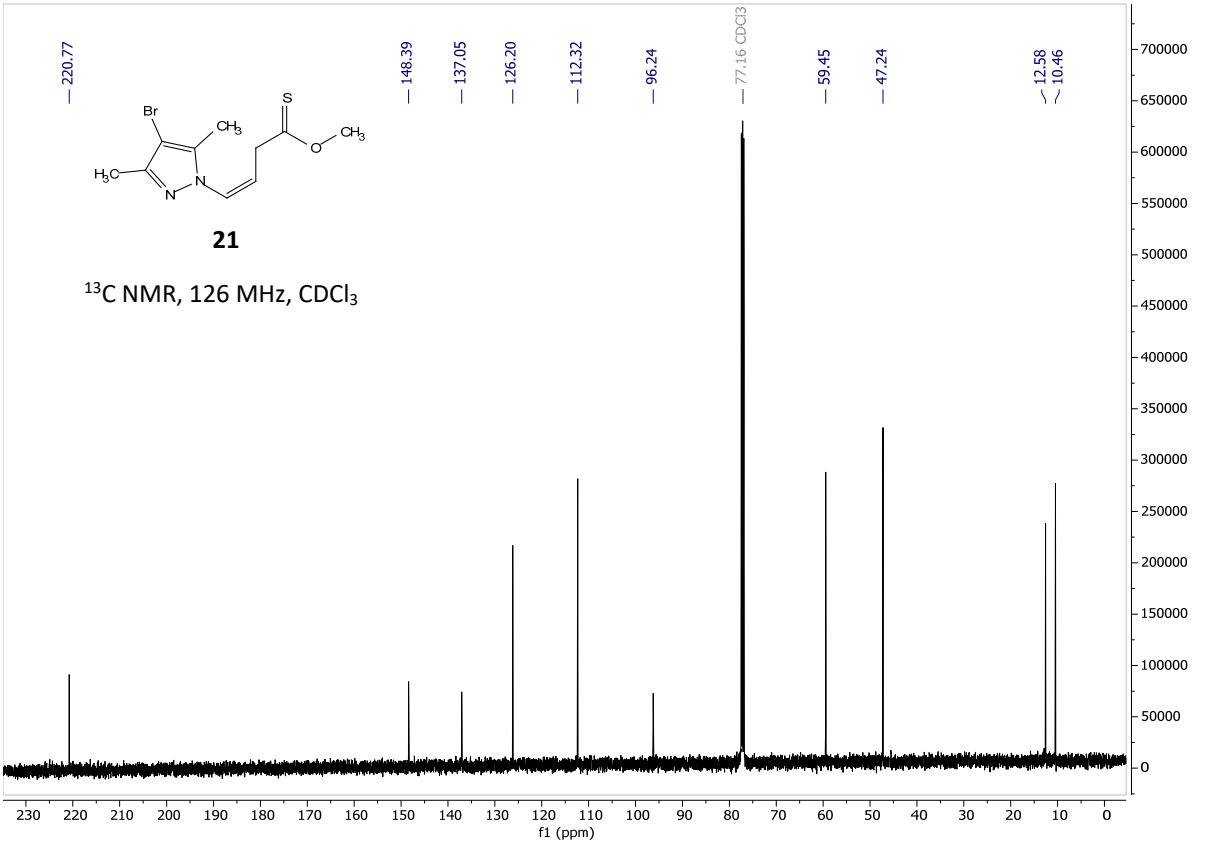
20

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



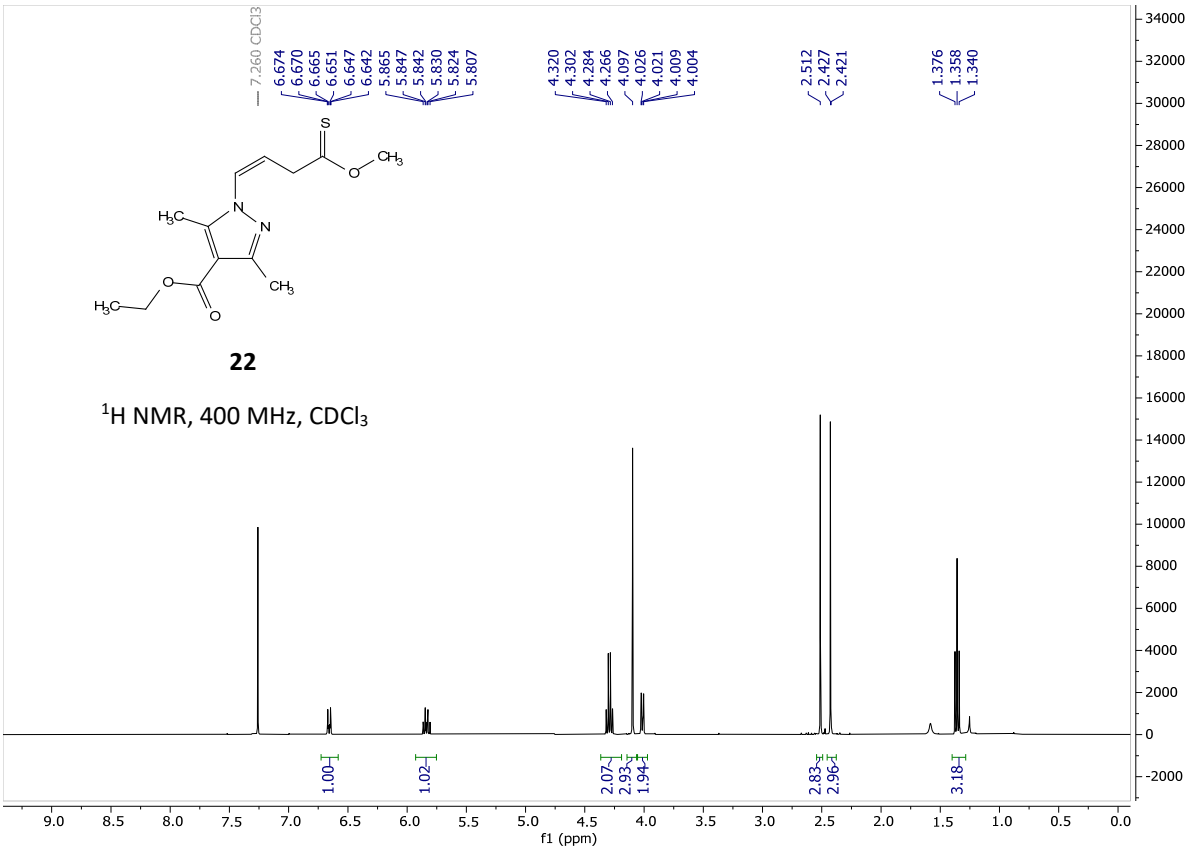
21

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



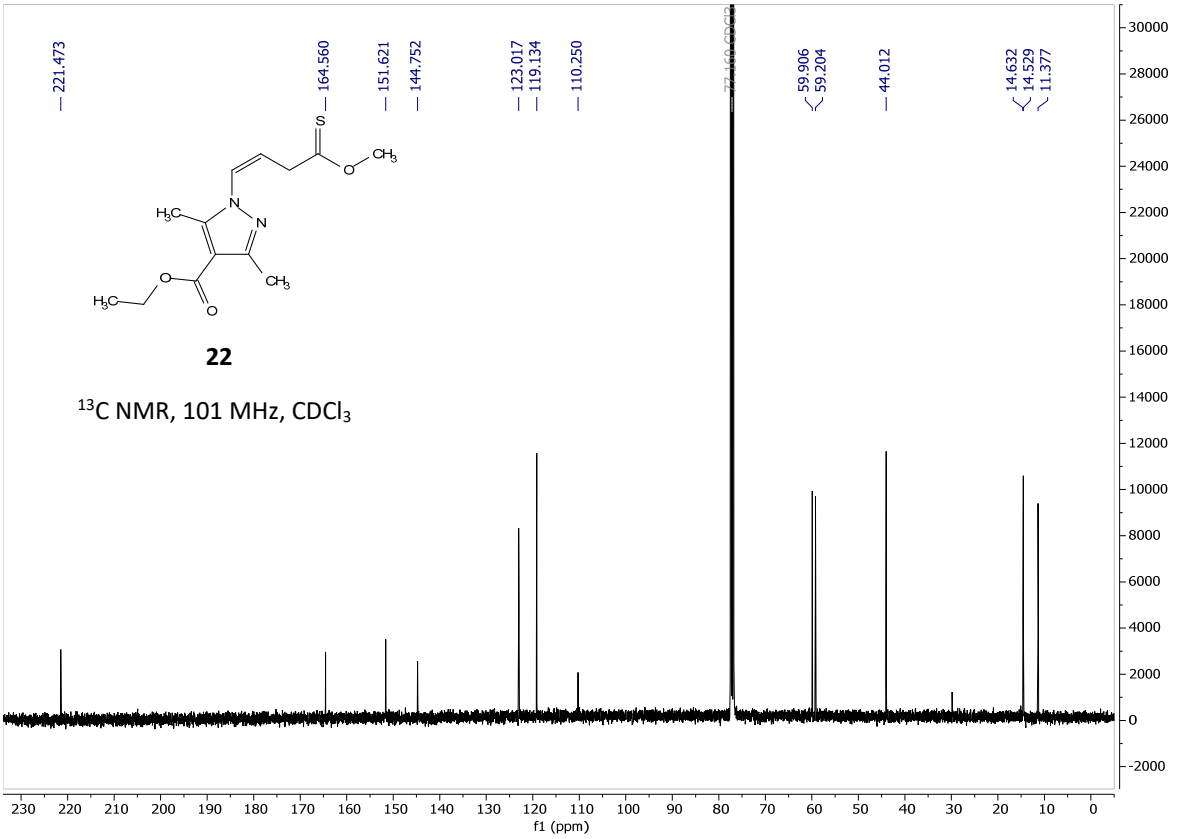
21

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



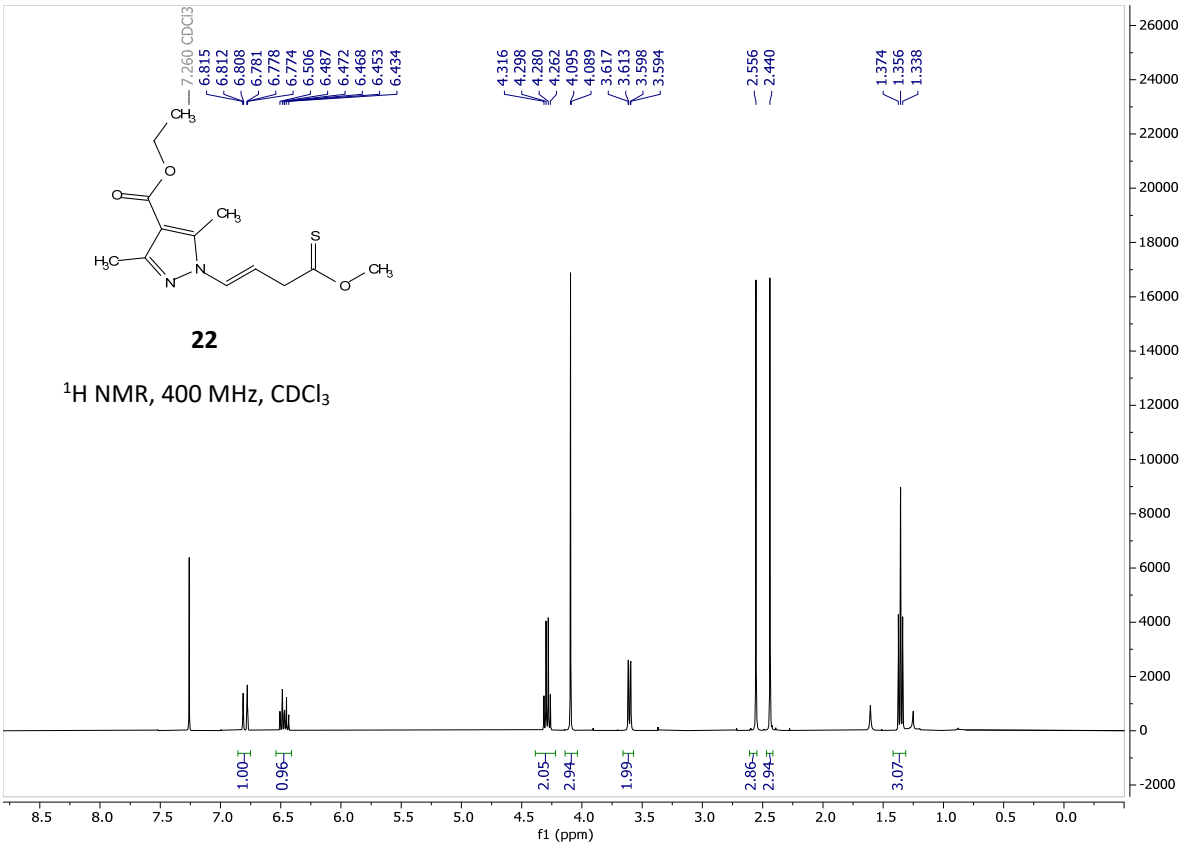
22

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



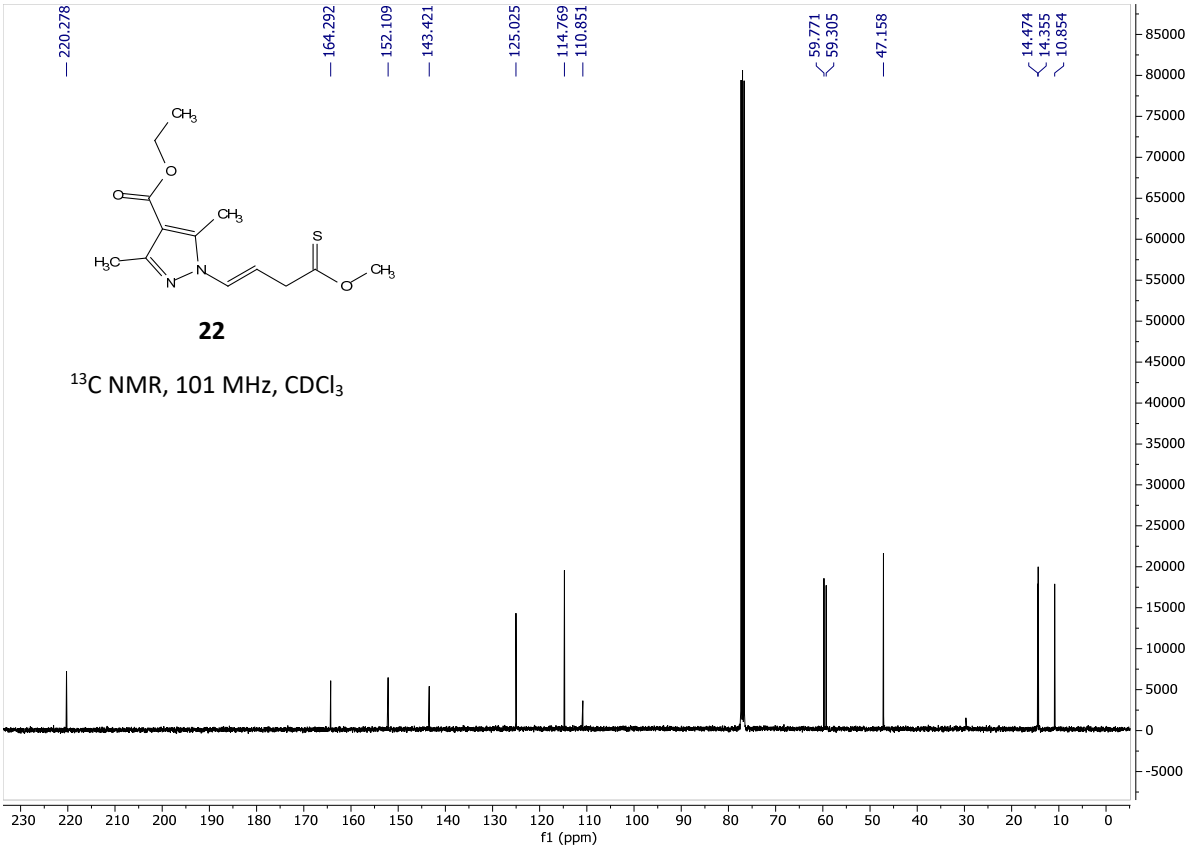
22

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



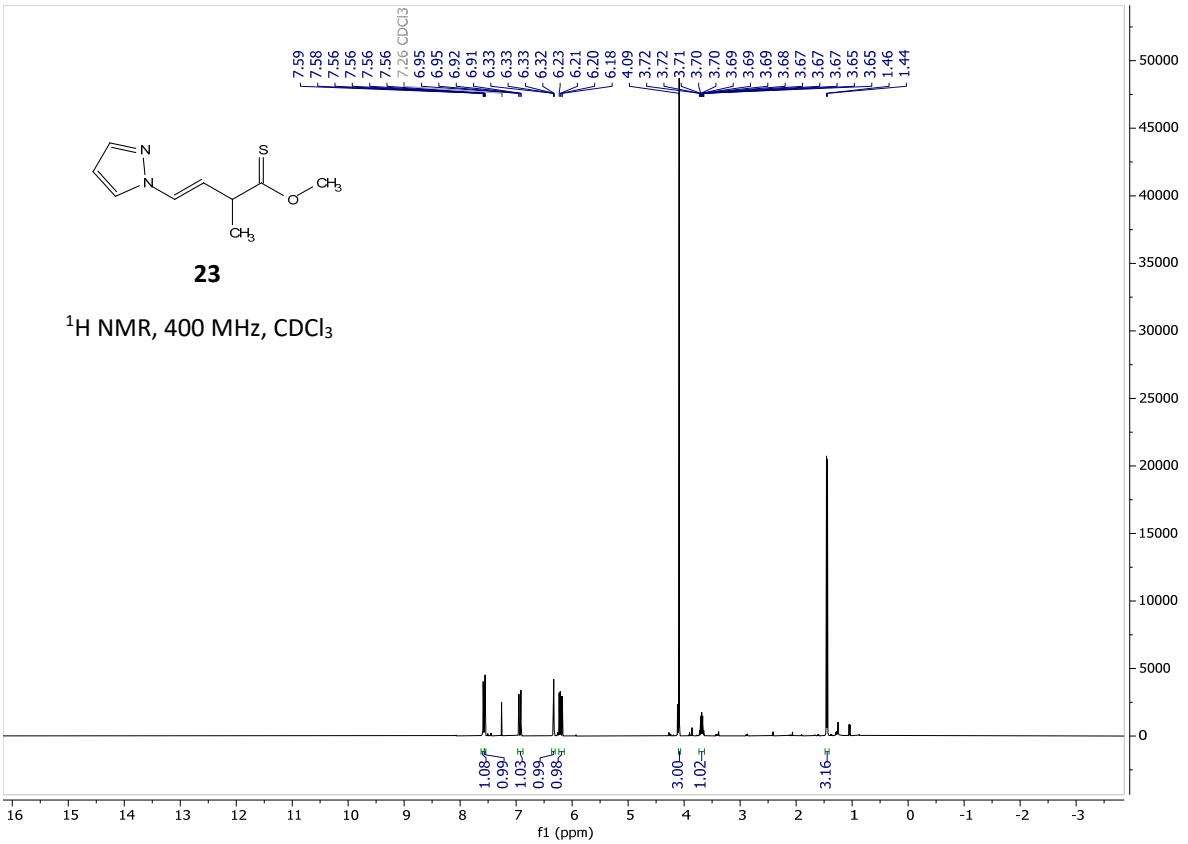
22

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



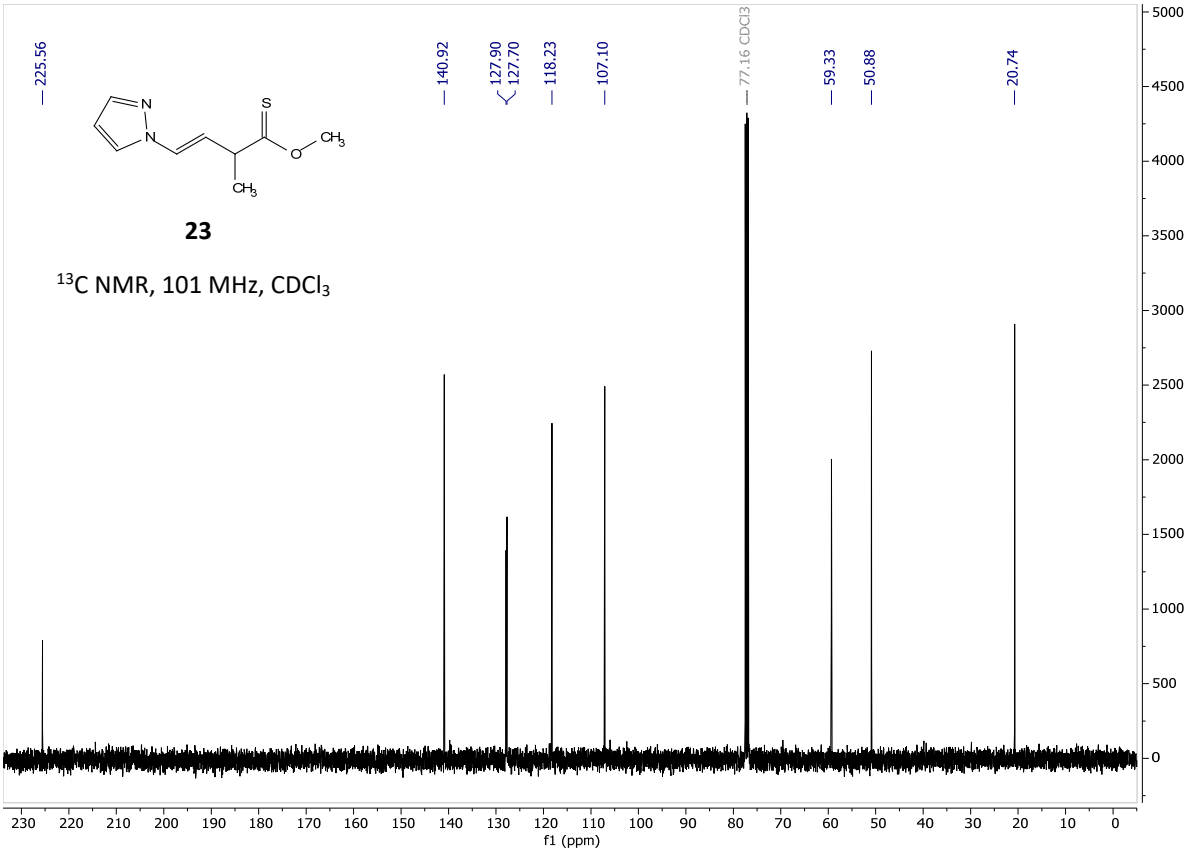
22

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



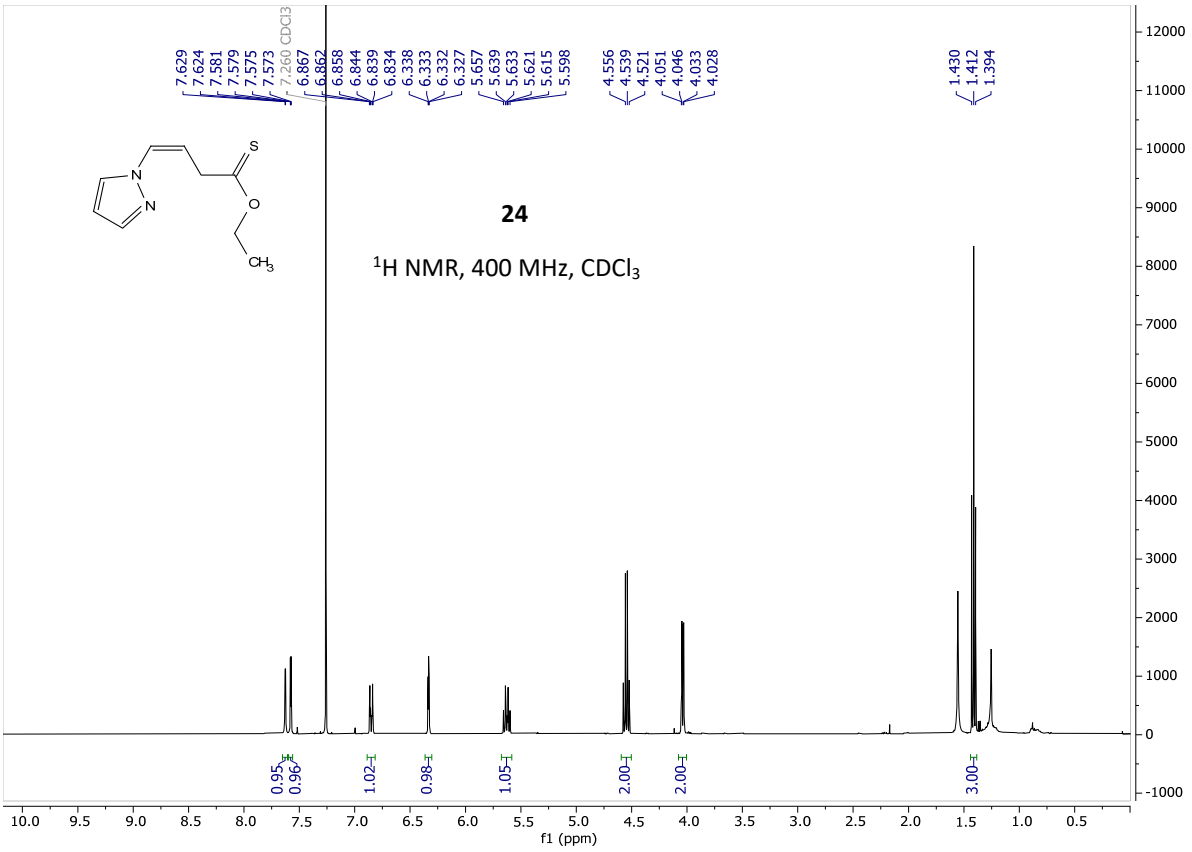
23

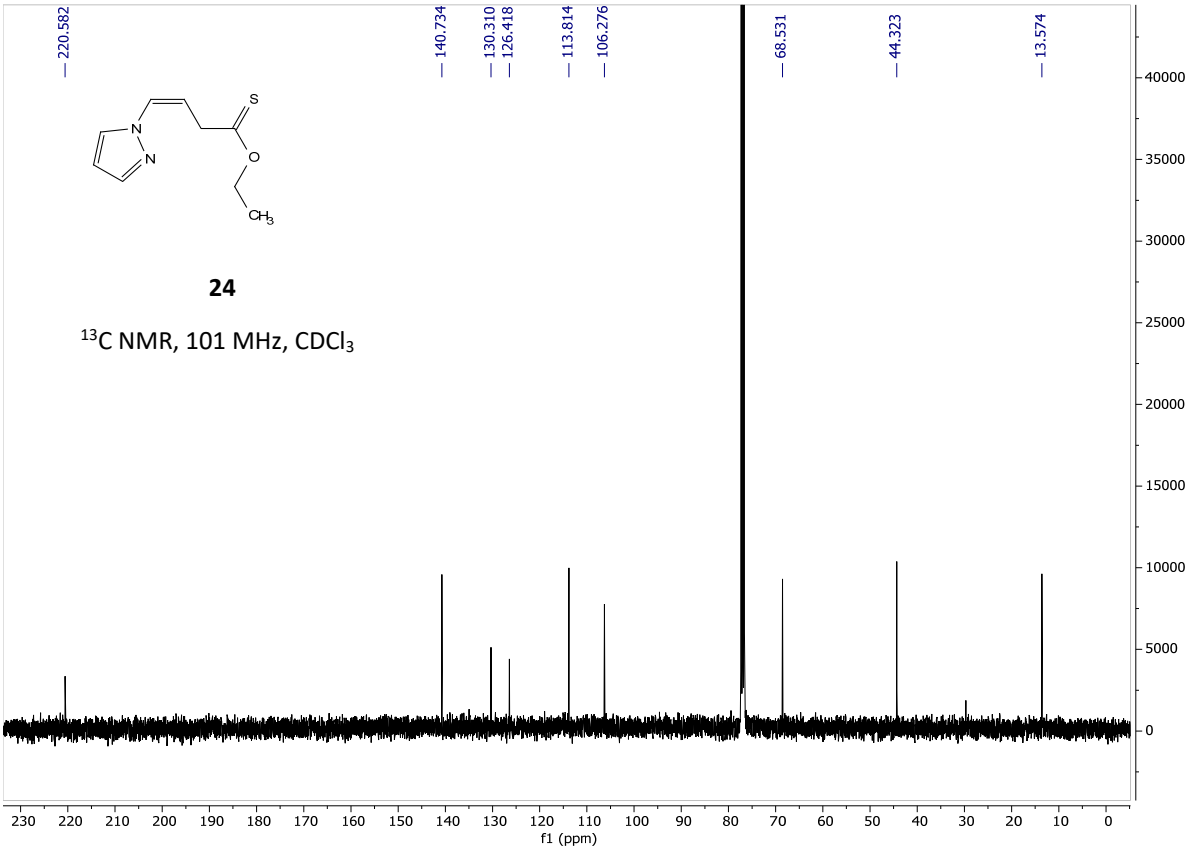
^{1}H NMR, 400 MHz, $CDCl_3$

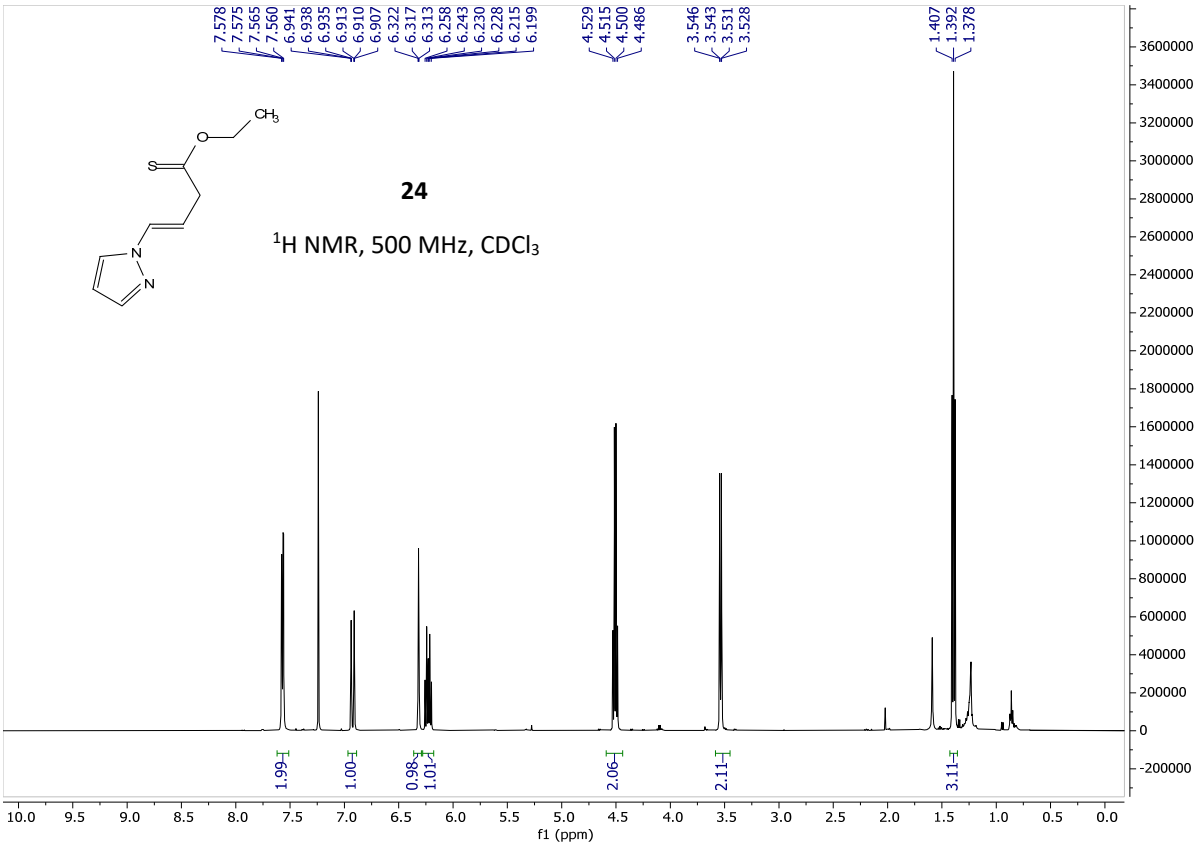


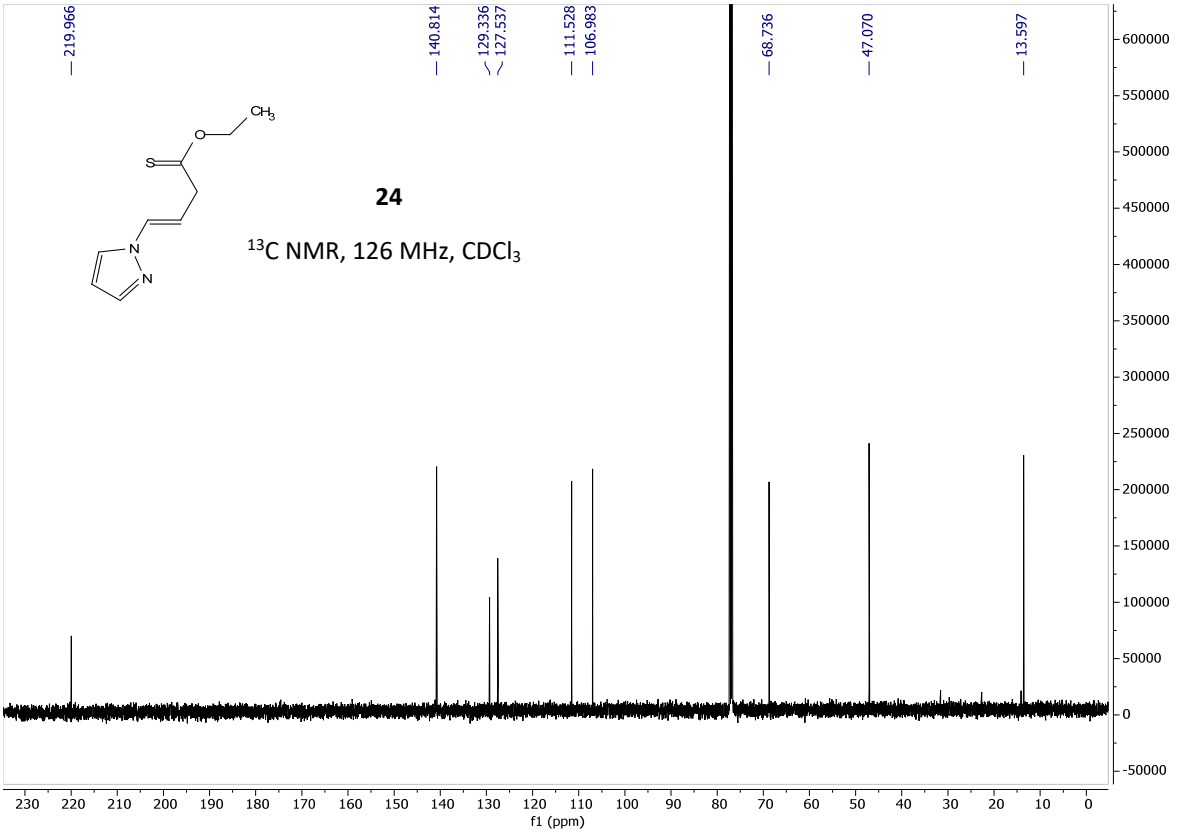
23

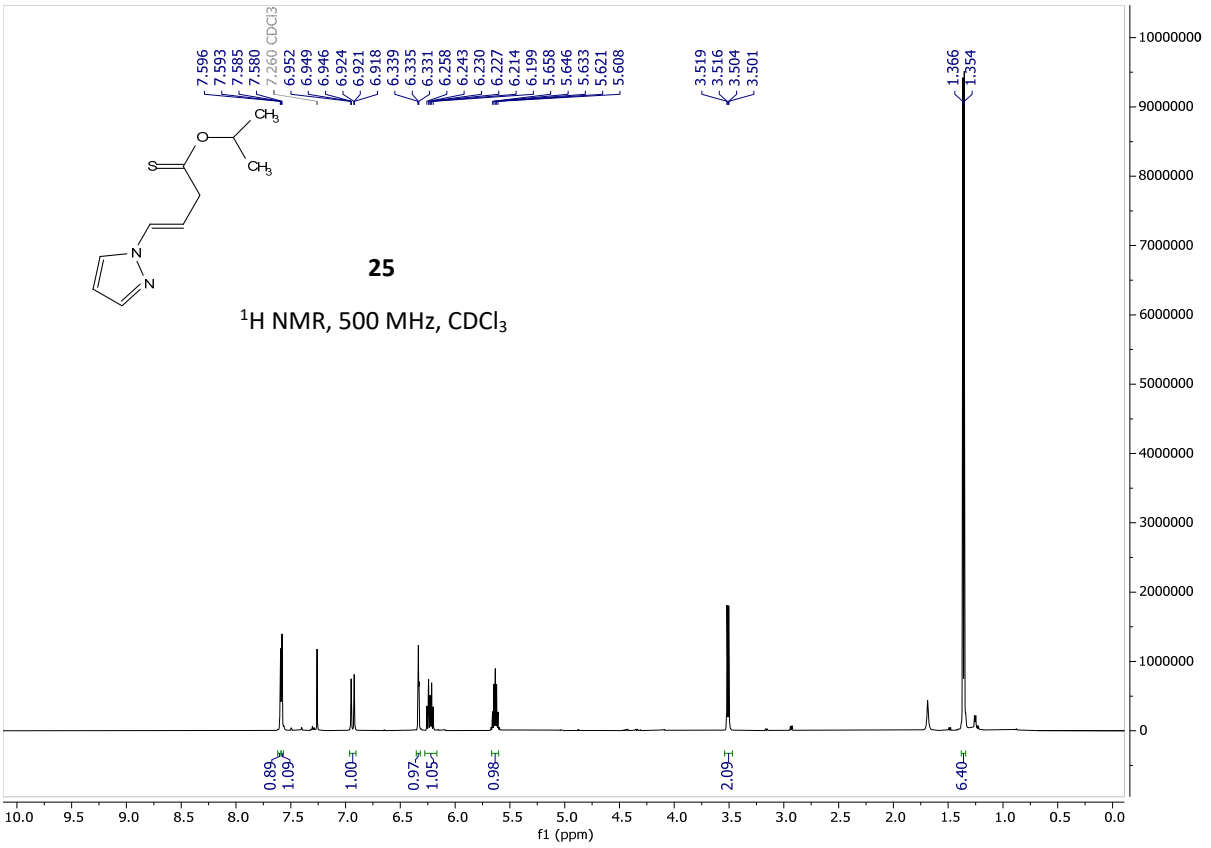
^{13}C NMR, 101 MHz, $CDCl_3$

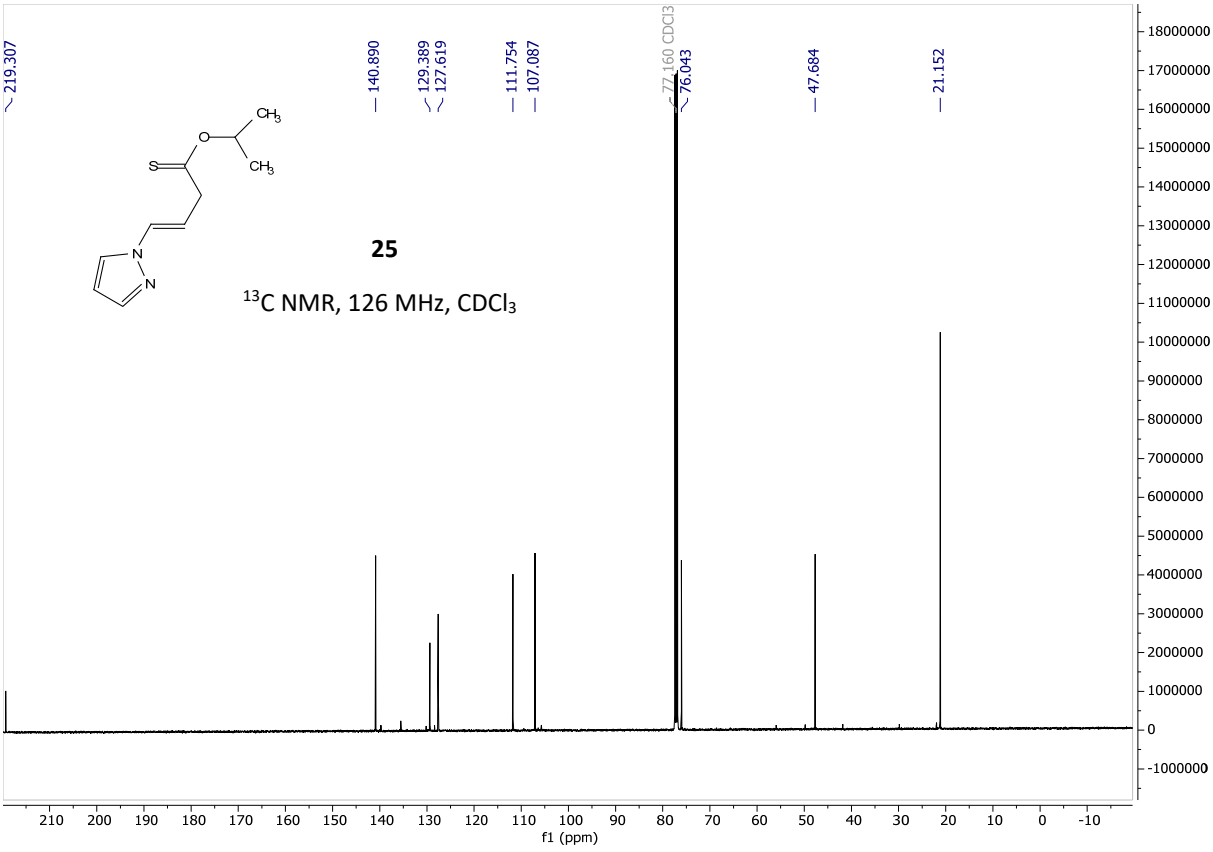

7.629
7.624
7.581
7.579
7.575
7.573
7.260 CDCl3
6.867
6.862
6.858
6.844
6.839
6.834
6.338
6.333
6.332
6.327
5.657
5.639
5.633
5.621
5.615
5.598
4.556
4.539
4.521
4.051
4.046
4.033
4.028
1.430
1.412
1.394
S
N
N
O
CH3
24
1H NMR, 400 MHz, CDCl3
0.95
0.96
1.02
0.98
1.05
2.00
2.00
3.00
f1 (ppm)

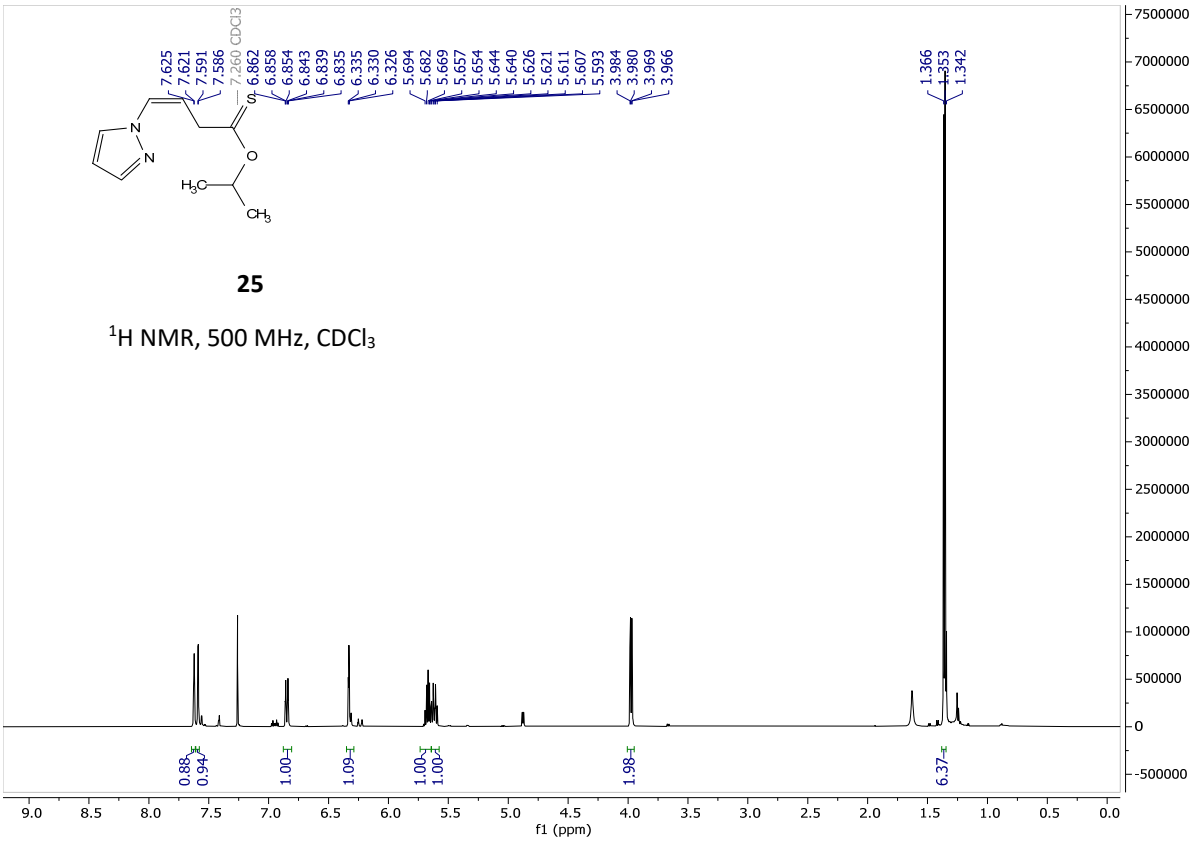

220.582
140.734
130.310
126.418
113.814
106.276
68.531
44.323
13.574
S
N
N
O
CH3
24
13C NMR, 101 MHz, CDCl3
f1 (ppm)


7.578
7.575
7.565
7.560
6.941
6.938
6.935
6.913
6.910
6.907
6.322
6.317
6.313
6.258
6.243
6.230
6.228
6.215
6.199
4.529
4.515
4.500
4.486
3.546
3.543
3.531
3.528
1.407
1.392
1.378
24
1H NMR, 500 MHz, CDCl3
1.99
1.00
0.98
1.01
2.06
2.11
3.11
f1 (ppm)


219.966
140.814
129.336
127.537
111.528
106.983
68.736
47.070
13.597
24
13C NMR, 126 MHz, CDCl3
f1 (ppm)

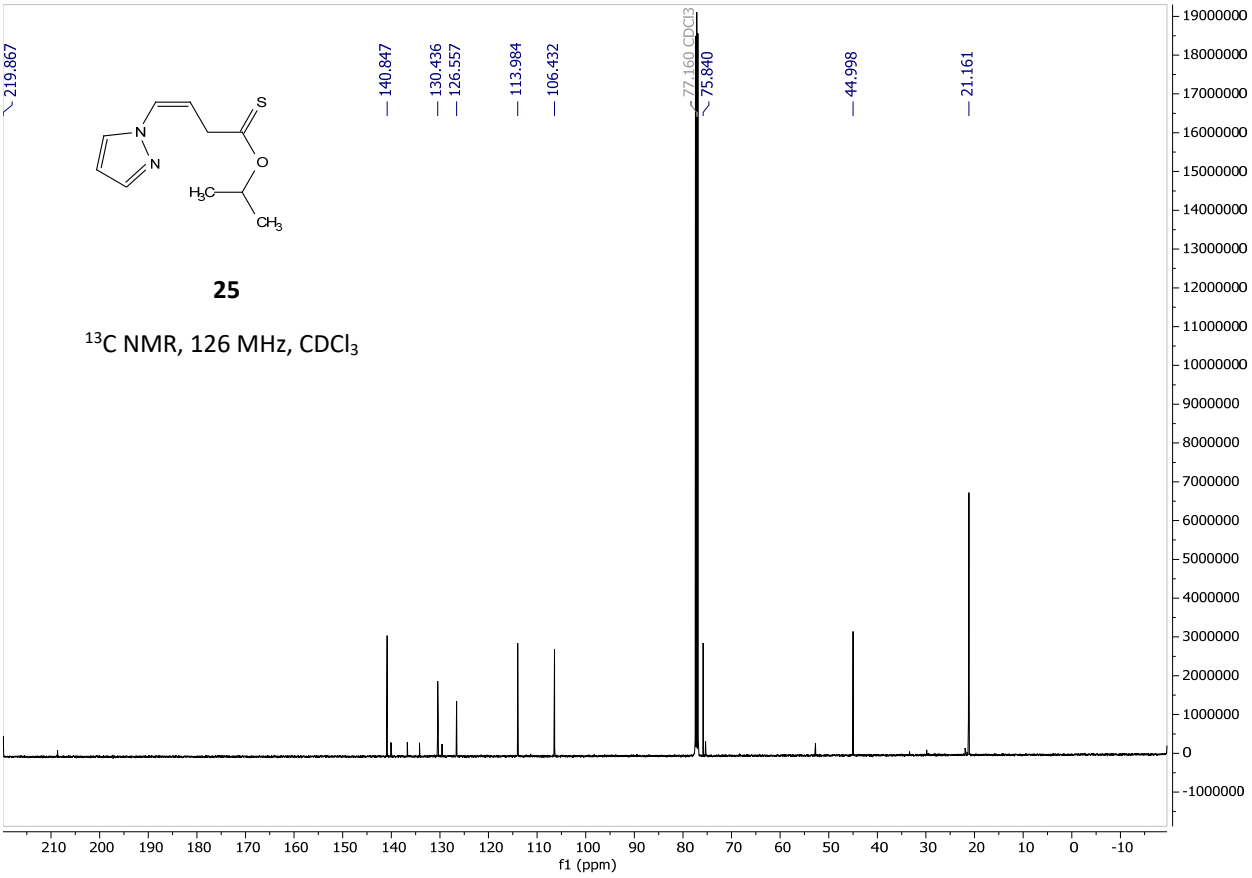

7.596
7.593
7.585
7.580
7.260 CDCl3
6.952
6.949
6.946
6.924
6.921
6.918
6.339
6.335
6.331
6.258
6.243
6.230
6.227
6.214
6.199
5.658
5.646
5.633
5.621
5.608
3.519
3.516
3.504
3.501
1.366
1.354
25
1H NMR, 500 MHz, CDCl3
0.89
1.09
1.00
0.97
1.05
0.98
2.09
6.40
f1 (ppm)


219.307
140.890
129.389
127.619
111.754
107.087
77.160 CDCl3
76.043
47.684
21.152
25
13C NMR, 126 MHz, CDCl3
f1 (ppm)



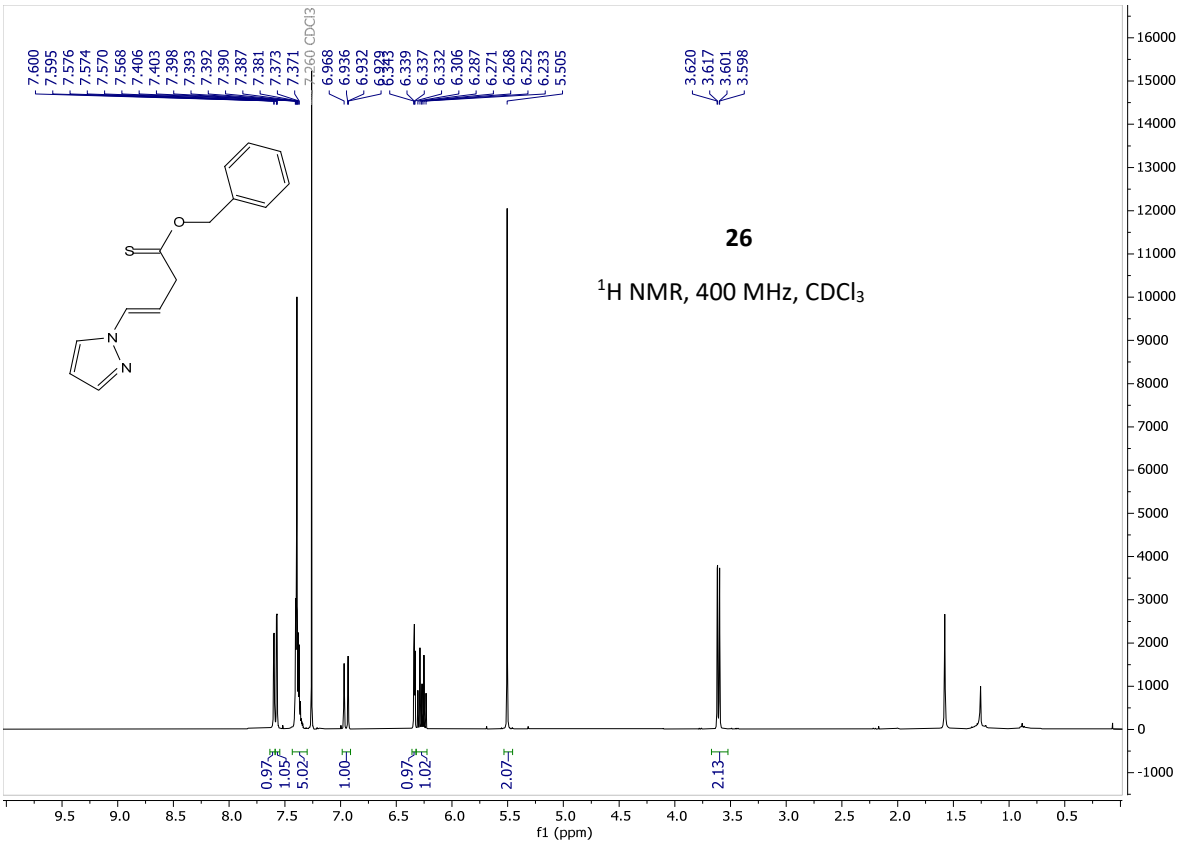
25

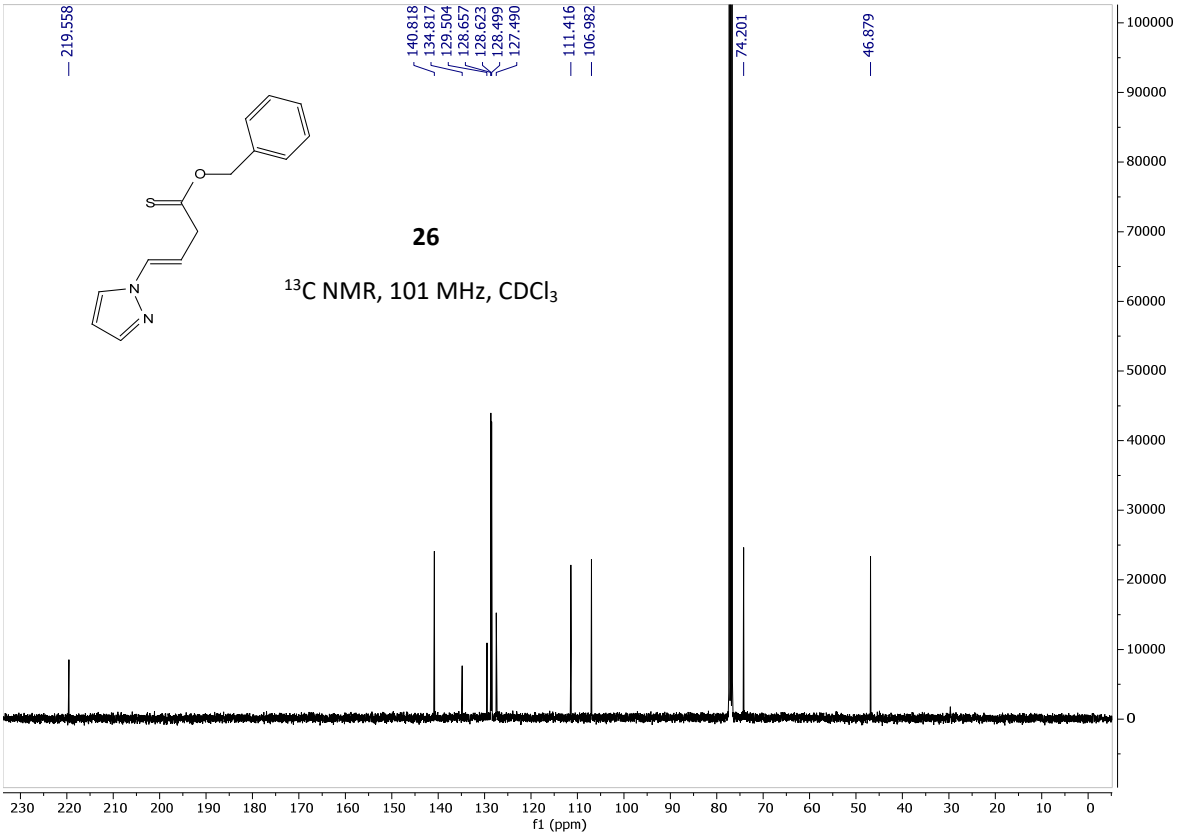
^{1}H NMR, 500 MHz, $CDCl_3$

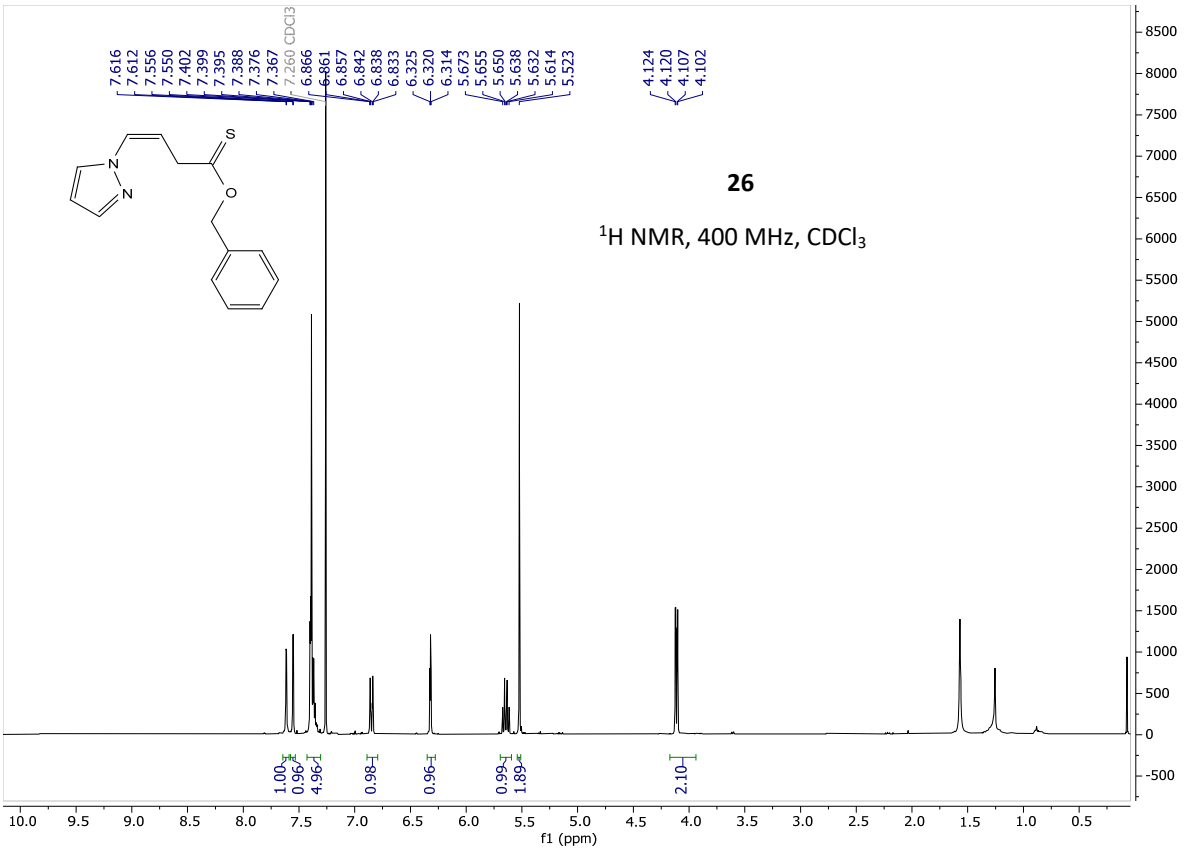


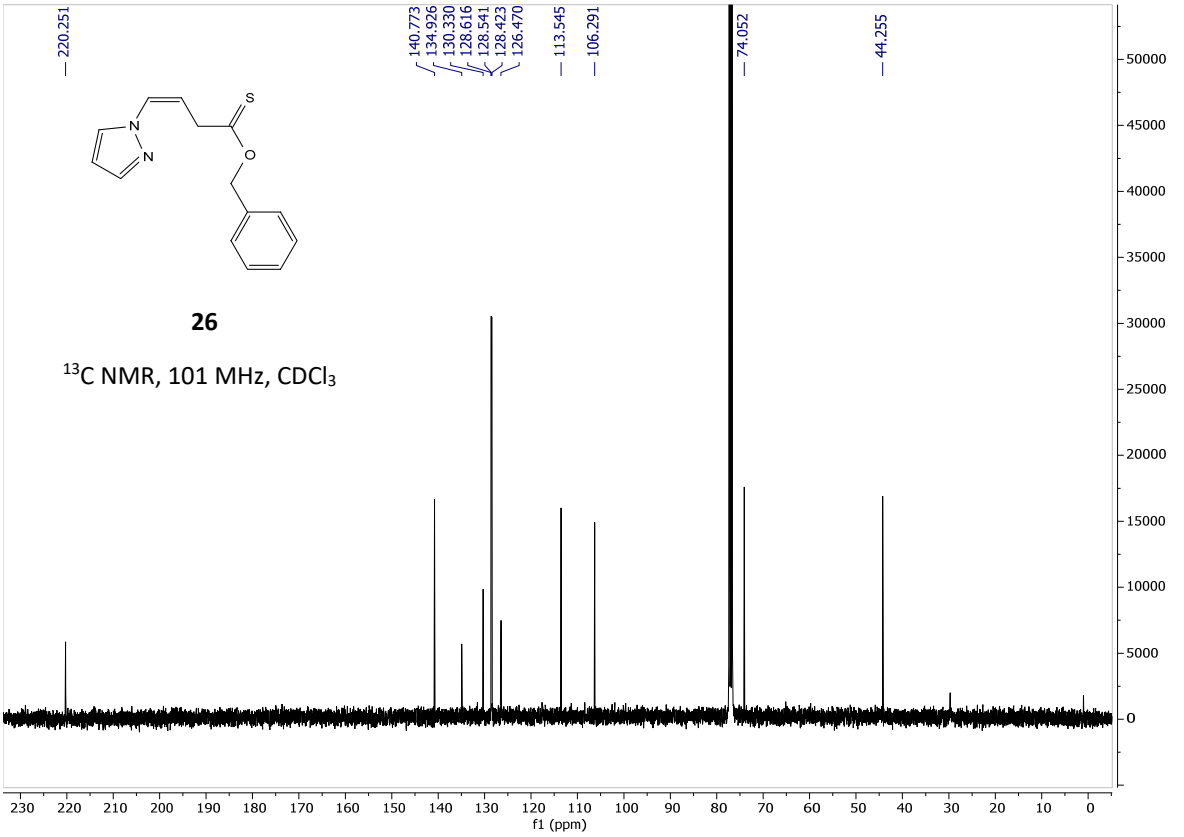
25

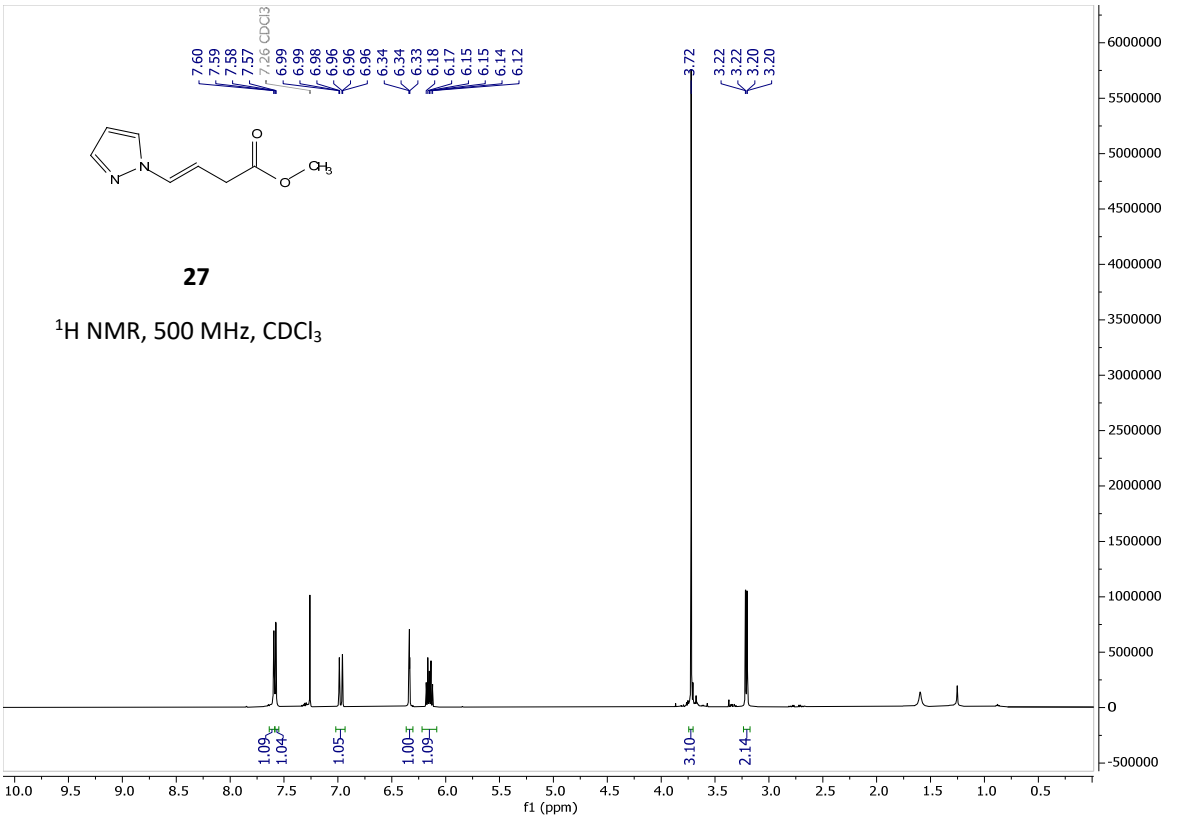
^{13}C NMR, 126 MHz, $CDCl_3$


7.600
7.595
7.576
7.574
7.570
7.568
7.406
7.403
7.398
7.393
7.392
7.390
7.387
7.381
7.373
7.371
7.260 CDCl3
6.968
6.936
6.932
6.339
6.337
6.332
6.306
6.287
6.271
6.268
6.252
6.233
5.505
3.620
3.617
3.601
3.598
26
1H NMR, 400 MHz, CDCl3
0.97
1.05
5.02
1.00
0.97
1.02
2.07
2.13
f1 (ppm)


219.558
140.818
134.817
129.504
128.657
128.623
128.499
127.490
111.416
106.982
74.201
46.879
26
13C NMR, 101 MHz, CDCl3
f1 (ppm)

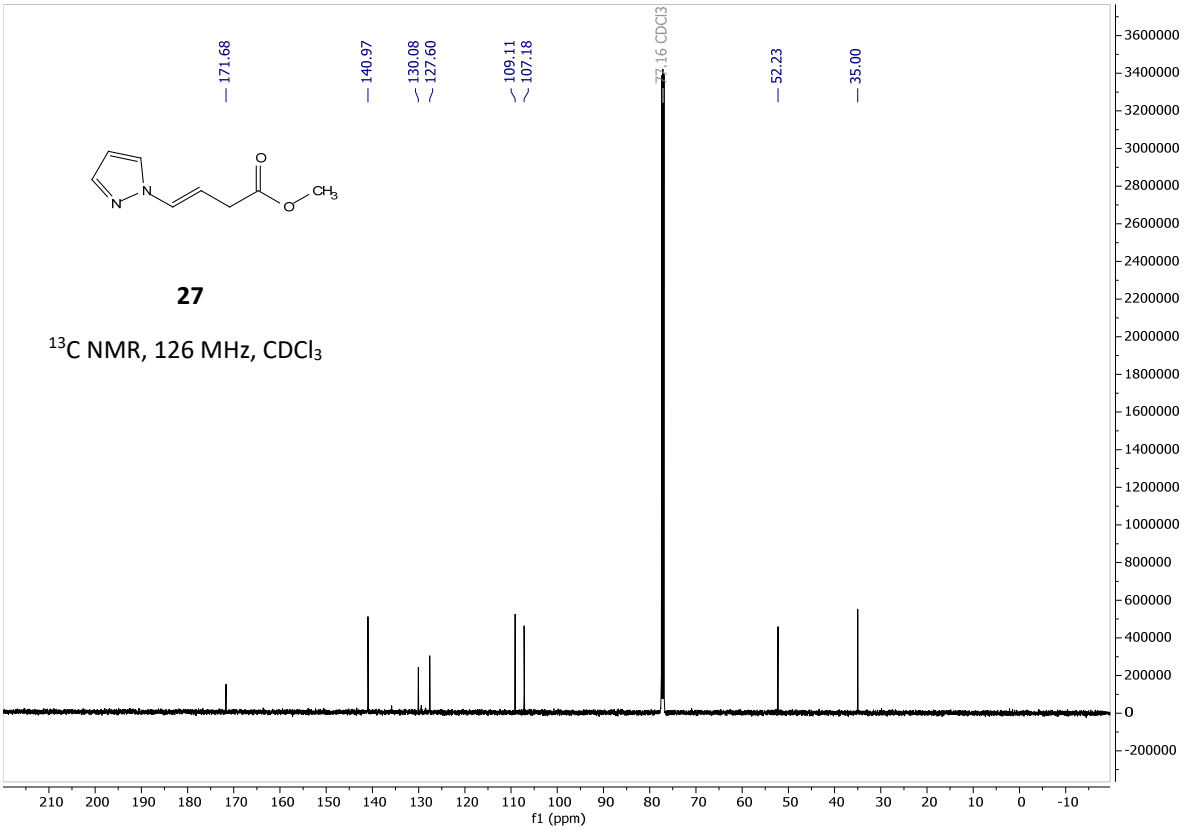

7.616
7.612
7.556
7.550
7.402
7.399
7.395
7.388
7.376
7.367
7.260 CDCl3
6.866
6.861
6.857
6.842
6.838
6.833
6.325
6.320
6.314
5.673
5.655
5.650
5.638
5.632
5.614
5.523
4.124
4.120
4.107
4.102
S
N
N
O
26
1H NMR, 400 MHz, CDCl3
1.00
0.96
4.96
0.98
0.96
0.99
1.89
2.10
f1 (ppm)


220.251
140.773
134.926
130.330
128.616
128.541
128.423
126.470
113.545
106.291
74.052
44.255
S
N
N
O
26
13C NMR, 101 MHz, CDCl3
f1 (ppm)



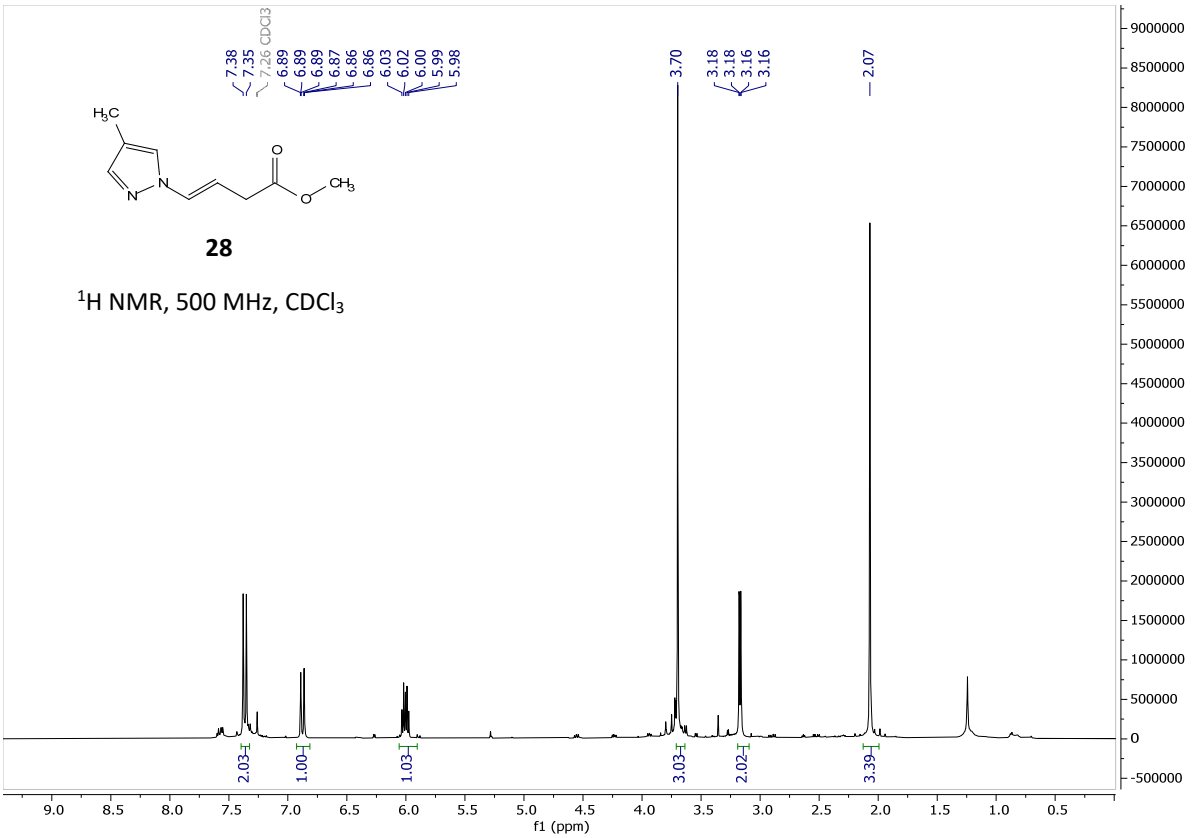
27

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



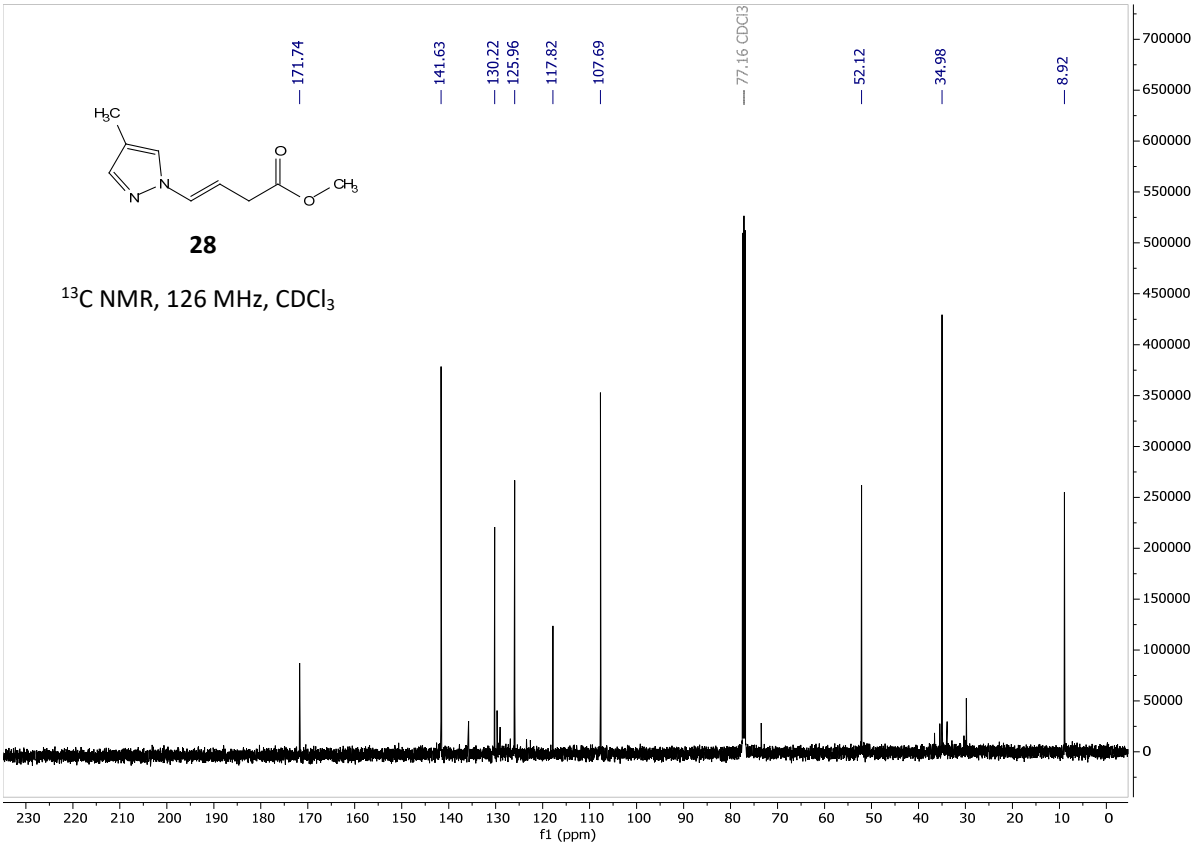
27

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



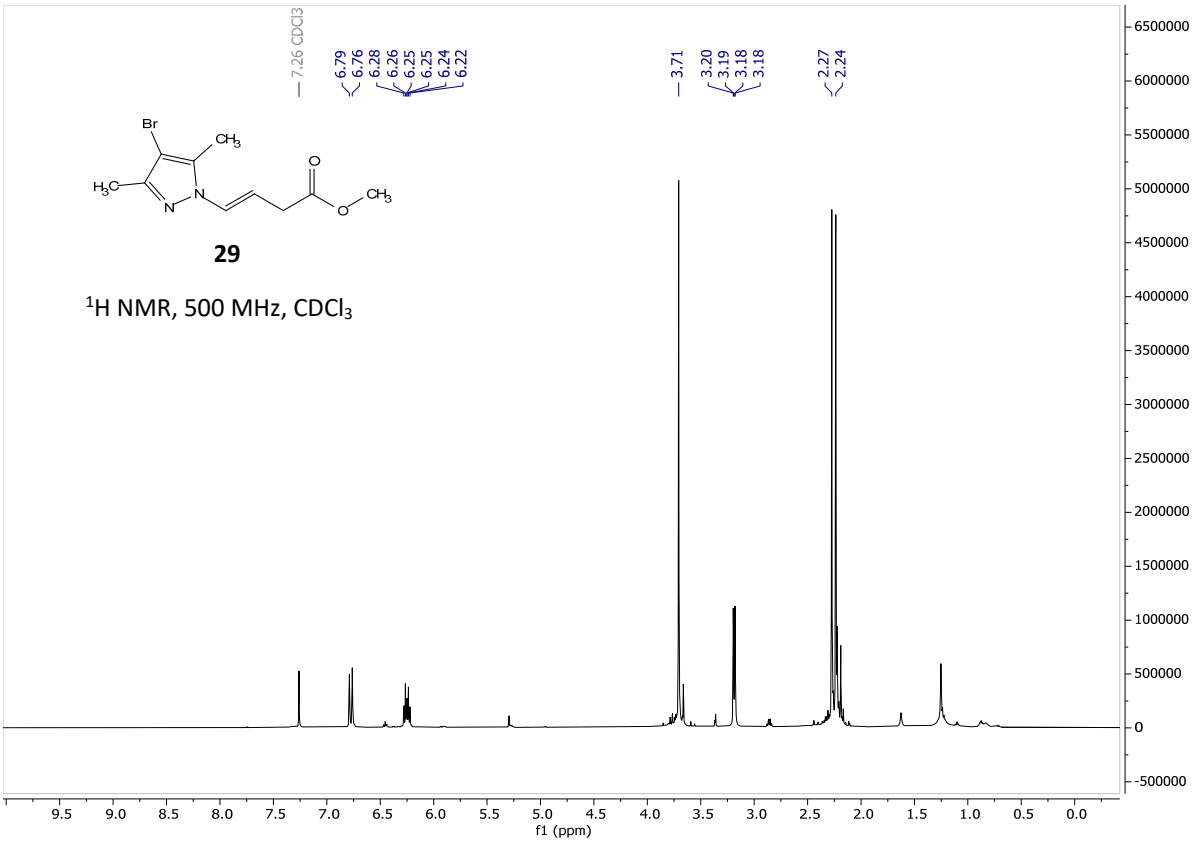
28

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



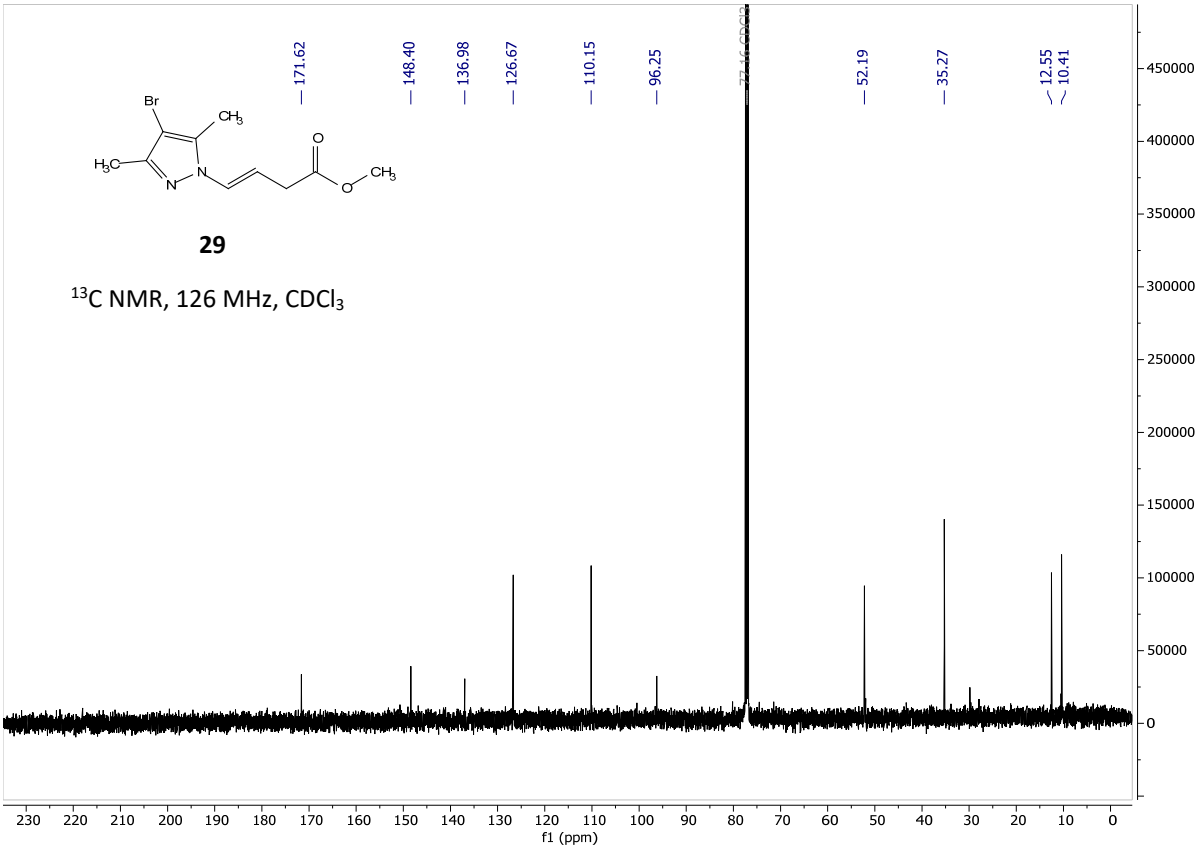
28

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



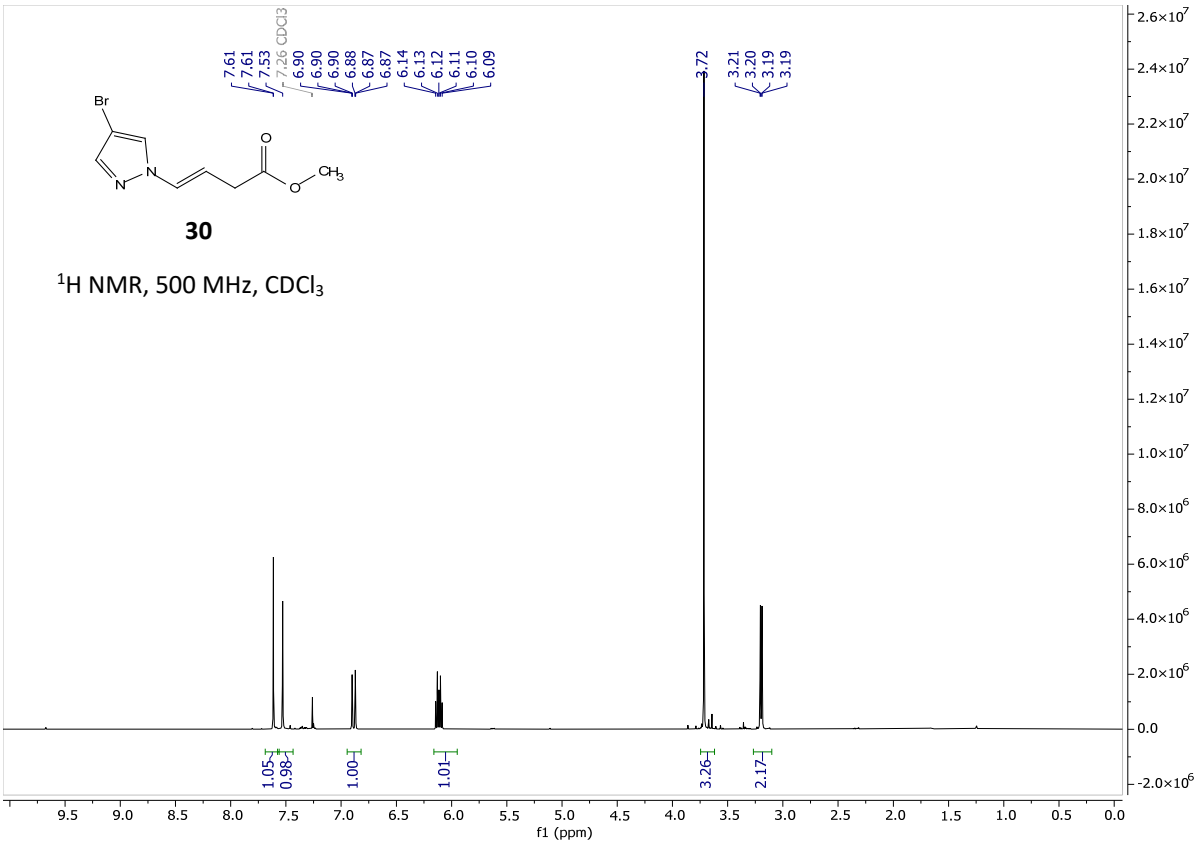
29

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



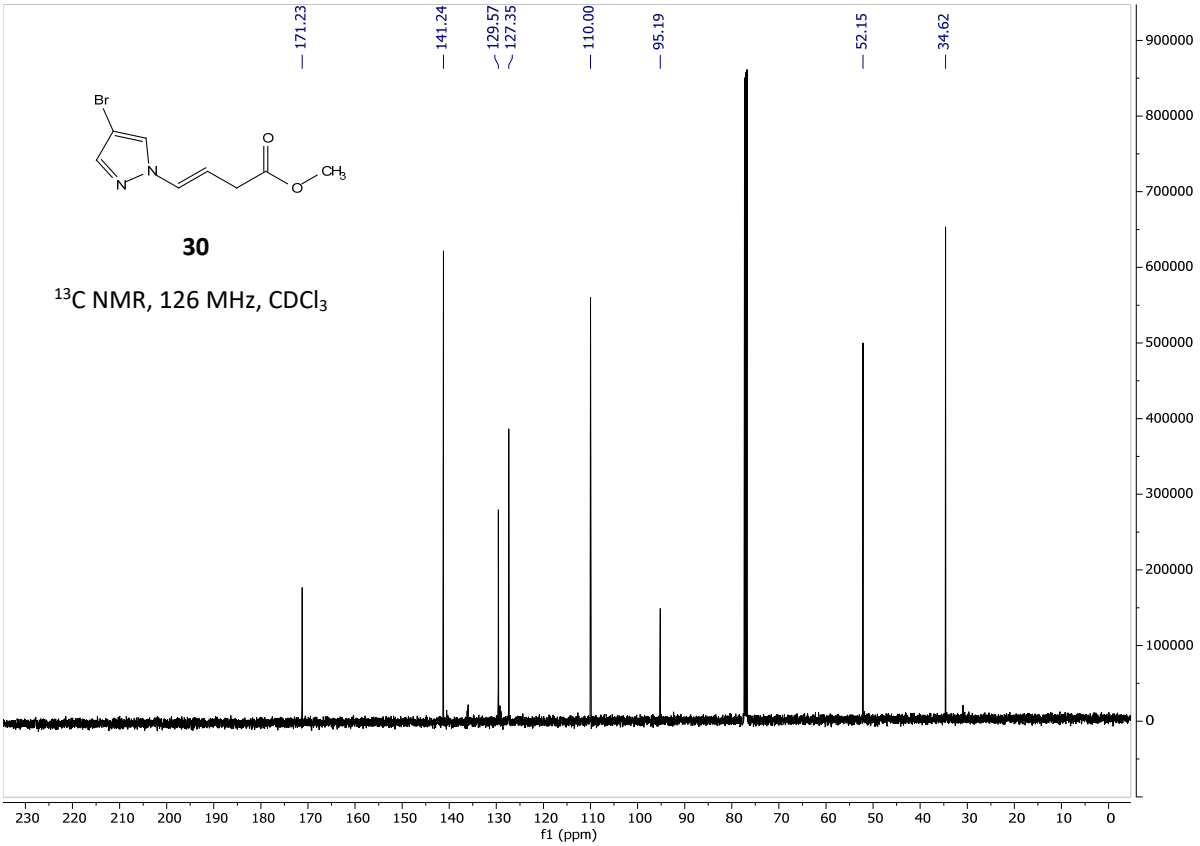
29

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



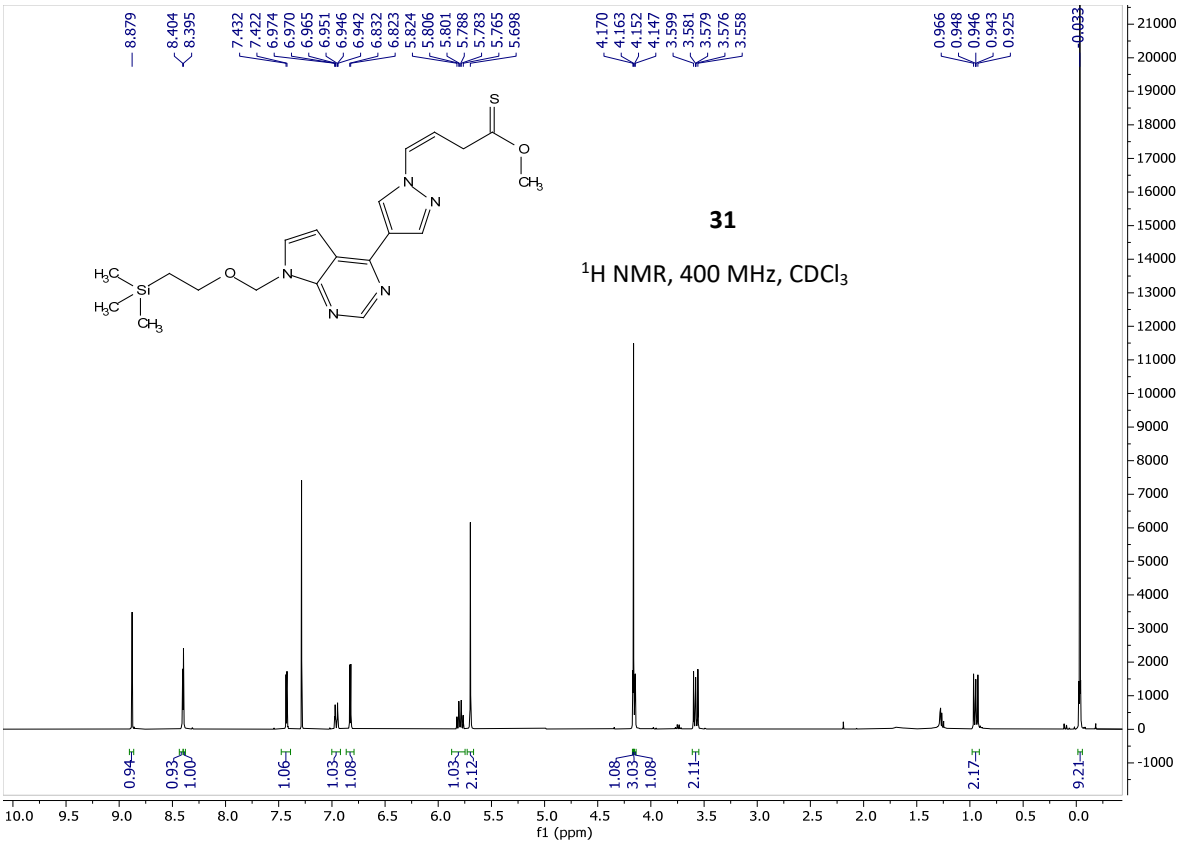
30

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



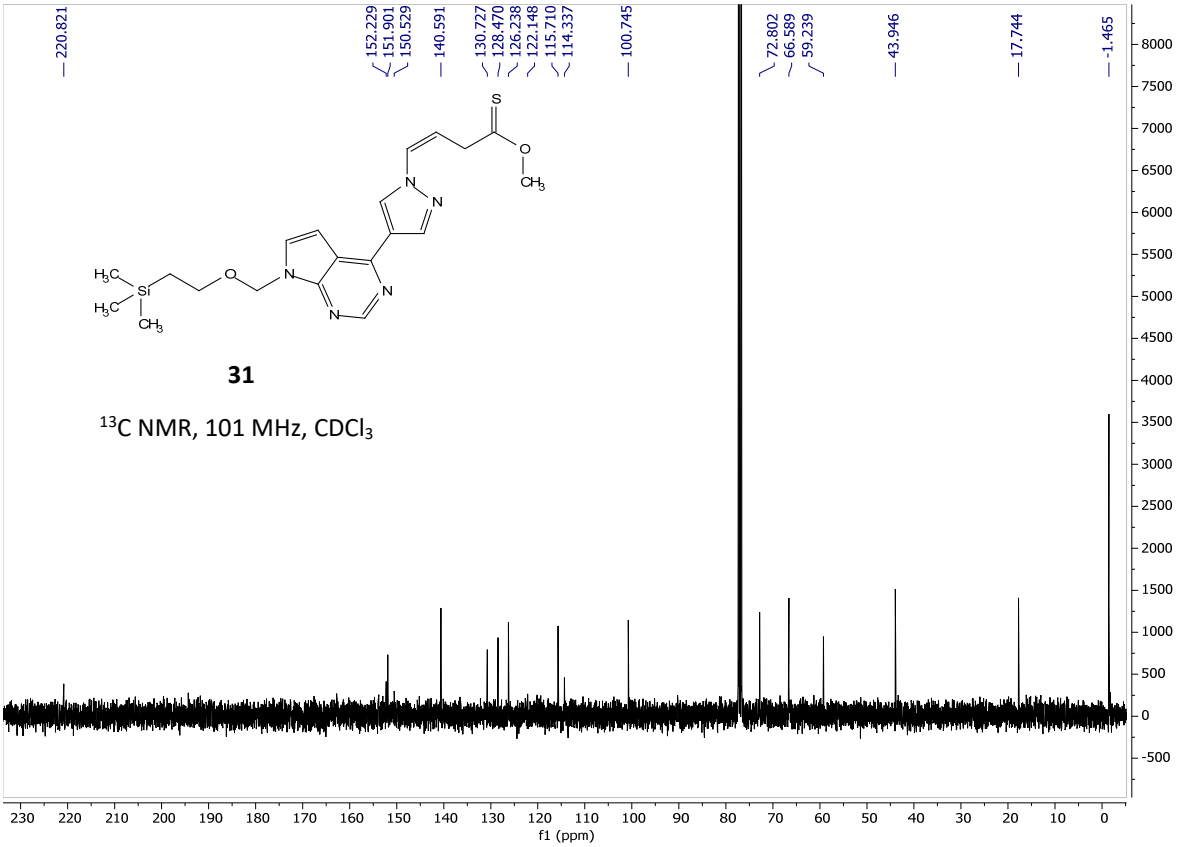
30

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



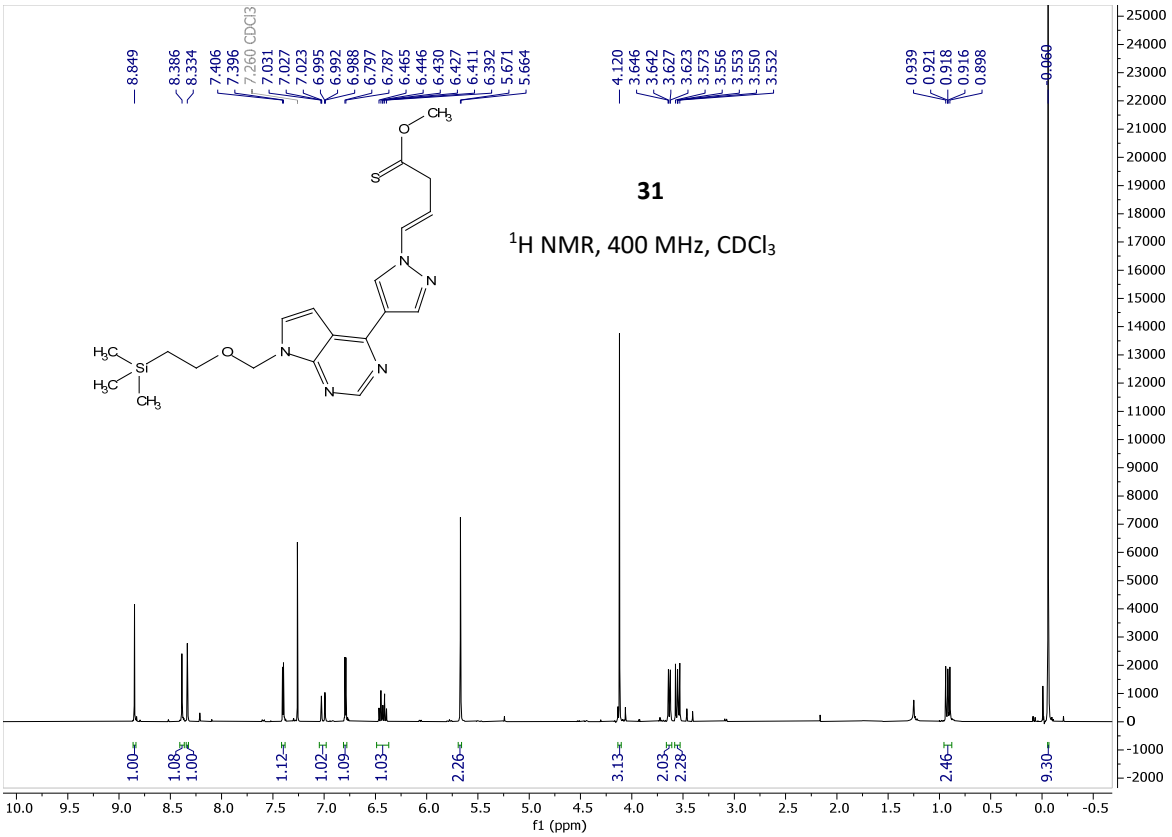
31

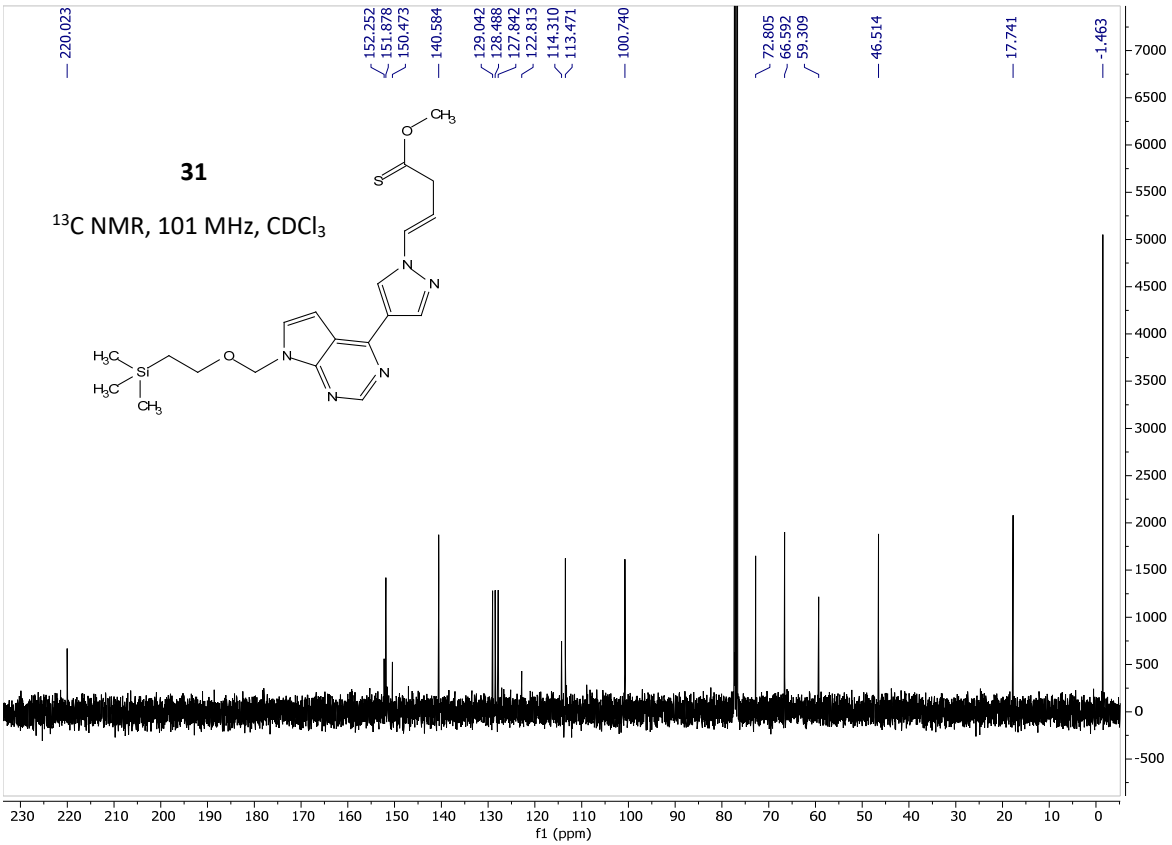
^{1}H NMR, 400 MHz, $CDCl_3$

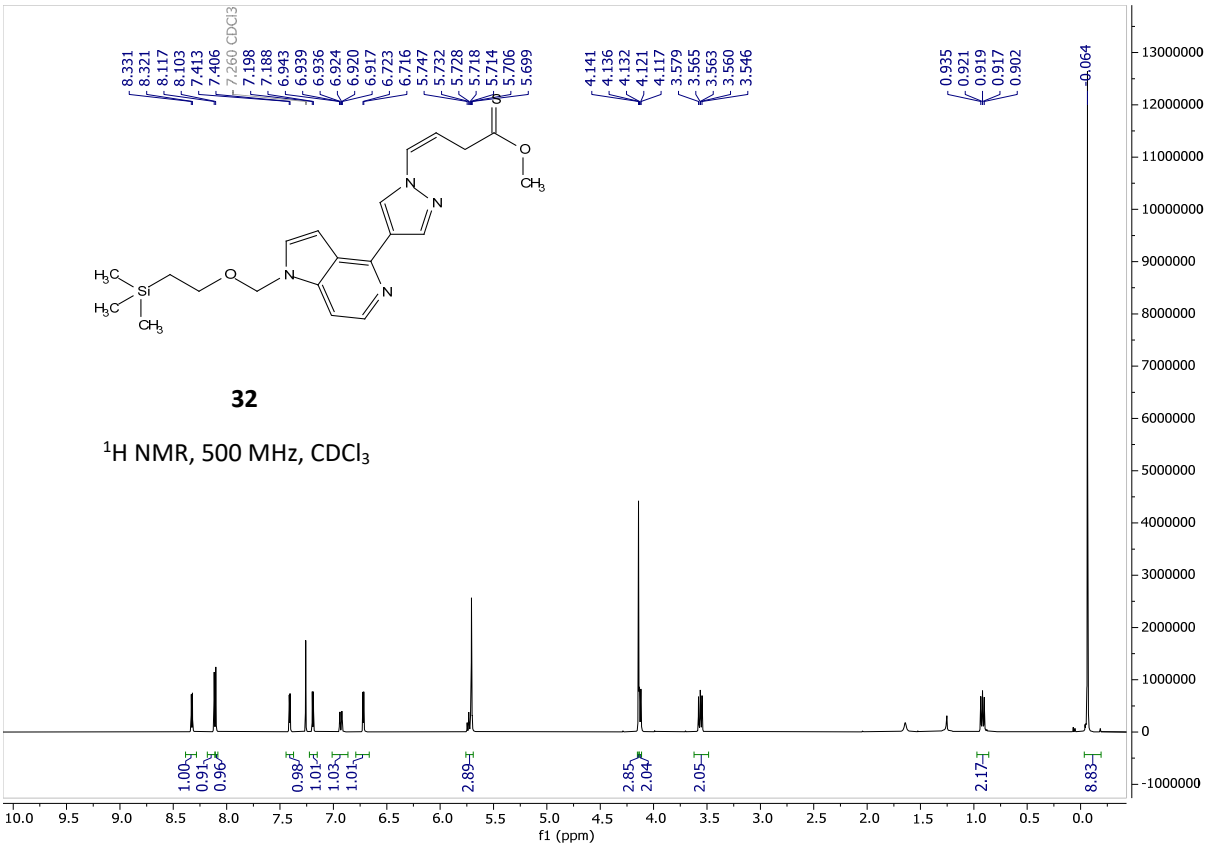


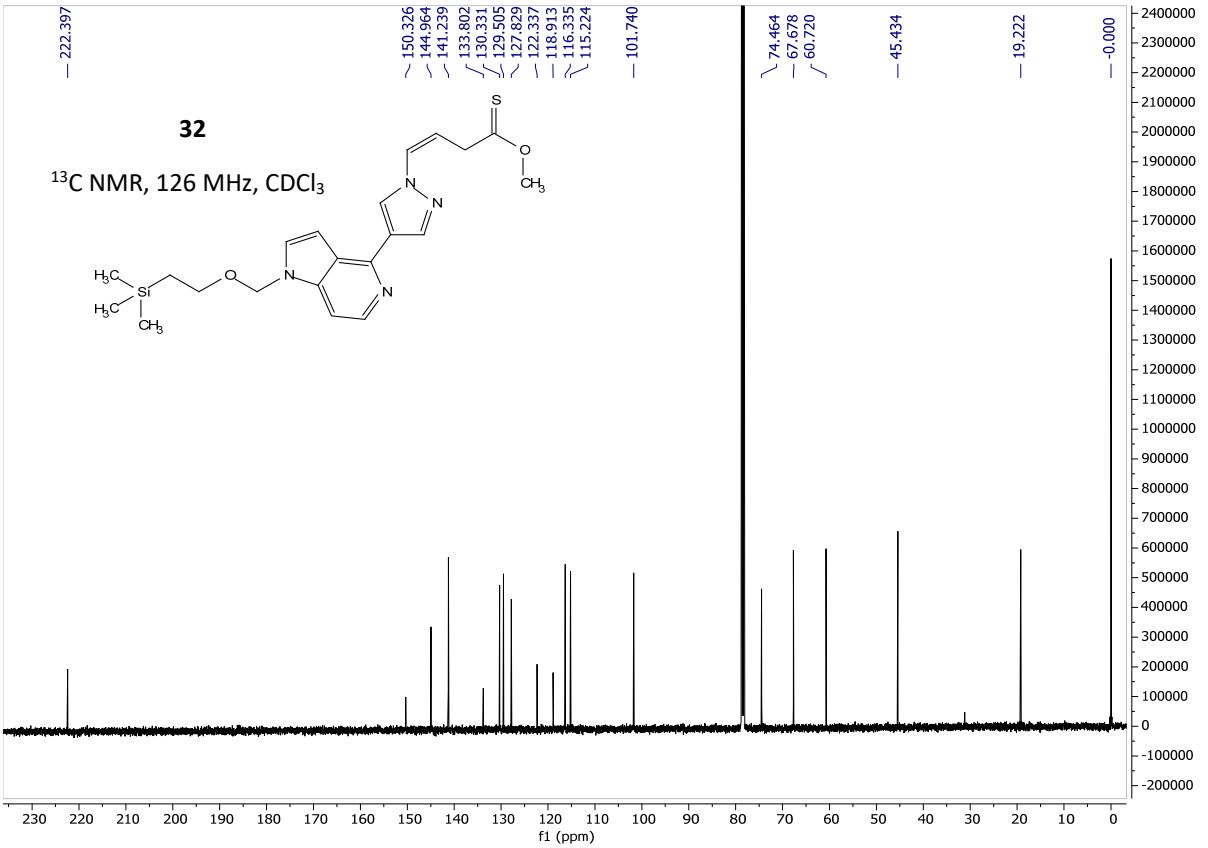
31

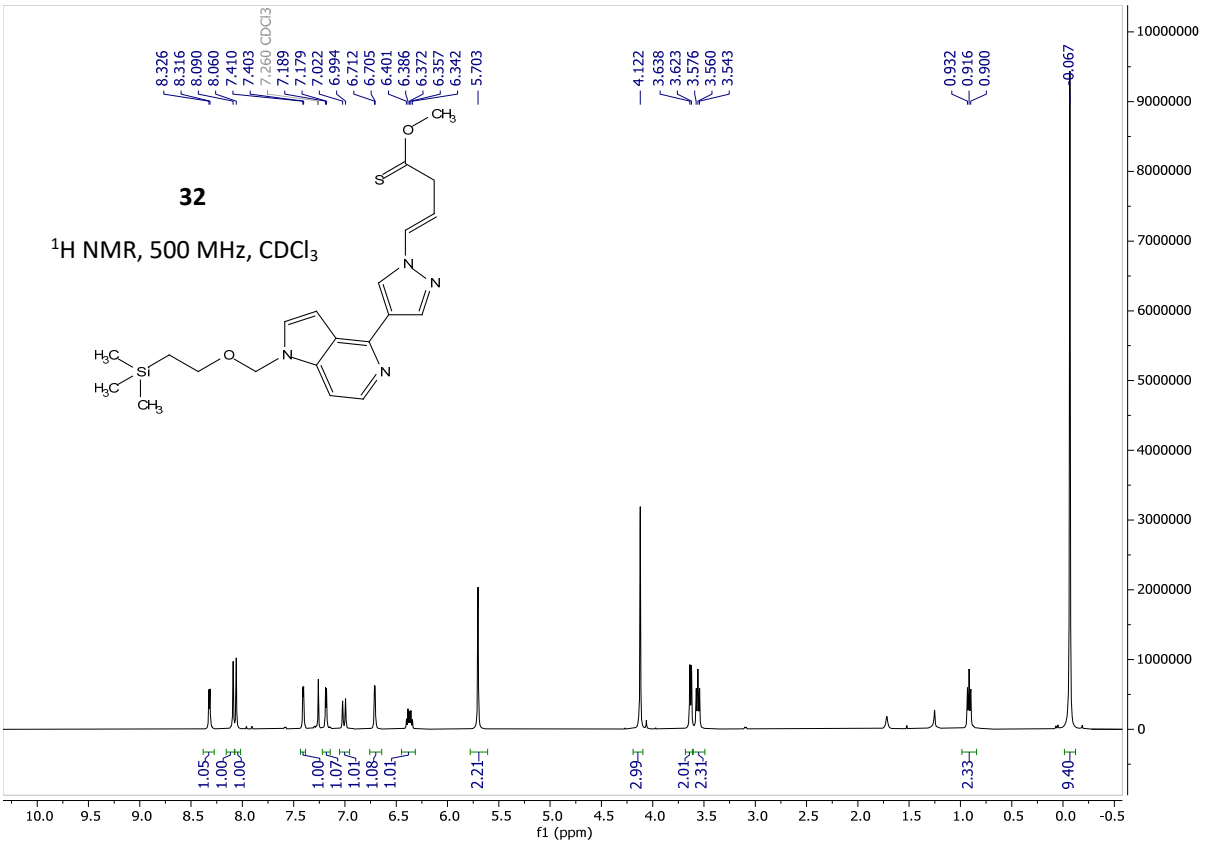
^{13}C NMR, 101 MHz, $CDCl_3$

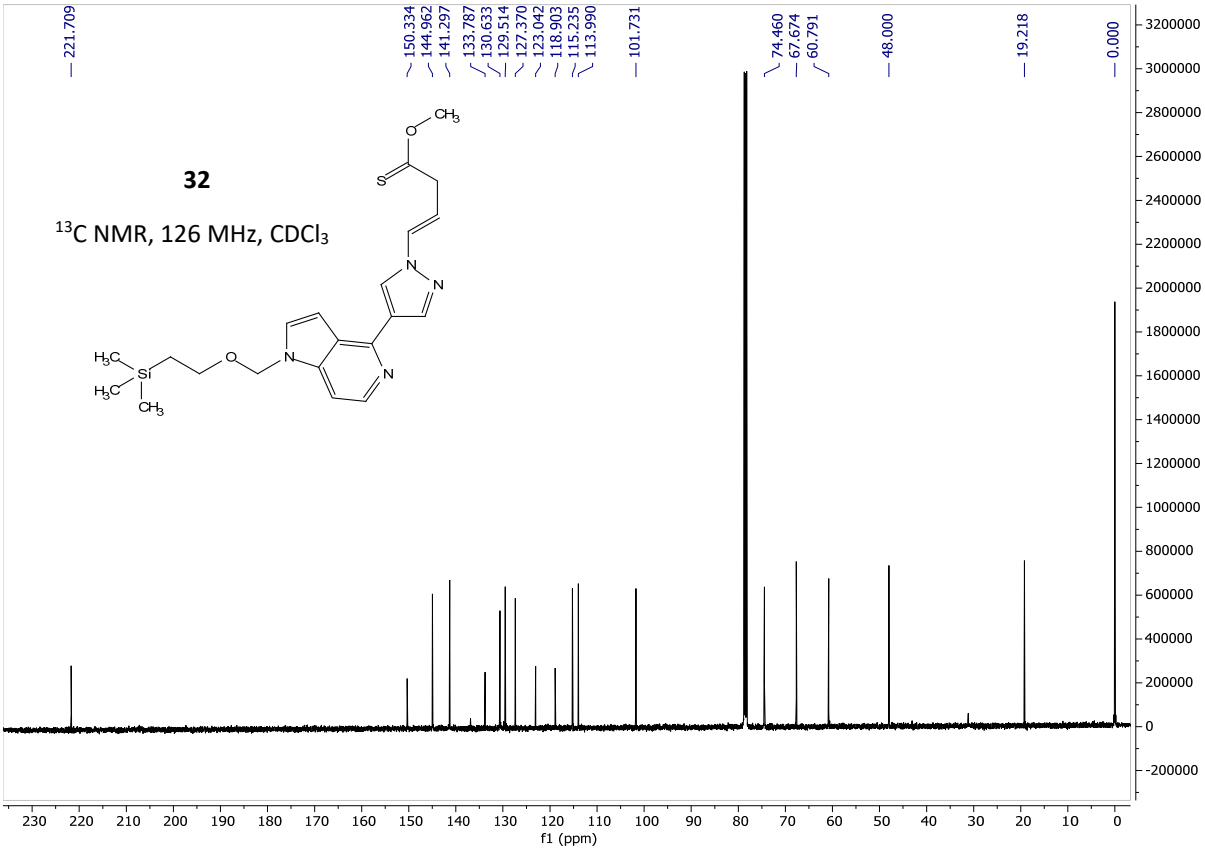

31
^{1}H NMR, 400 MHz, $CDCl_3$
8.849
8.386
8.334
7.406
7.396
7.260 CDCl3
7.031
7.027
7.023
6.995
6.992
6.988
6.797
6.787
6.465
6.446
6.430
6.427
6.411
6.392
5.671
5.664
4.120
3.646
3.642
3.627
3.623
3.573
3.556
3.553
3.550
3.532
0.939
0.921
0.918
0.916
0.898
0.060
1.00
1.08
1.00
1.12
1.02
1.09
1.03
2.26
3.13
2.03
2.28
2.46
9.30
f1 (ppm)

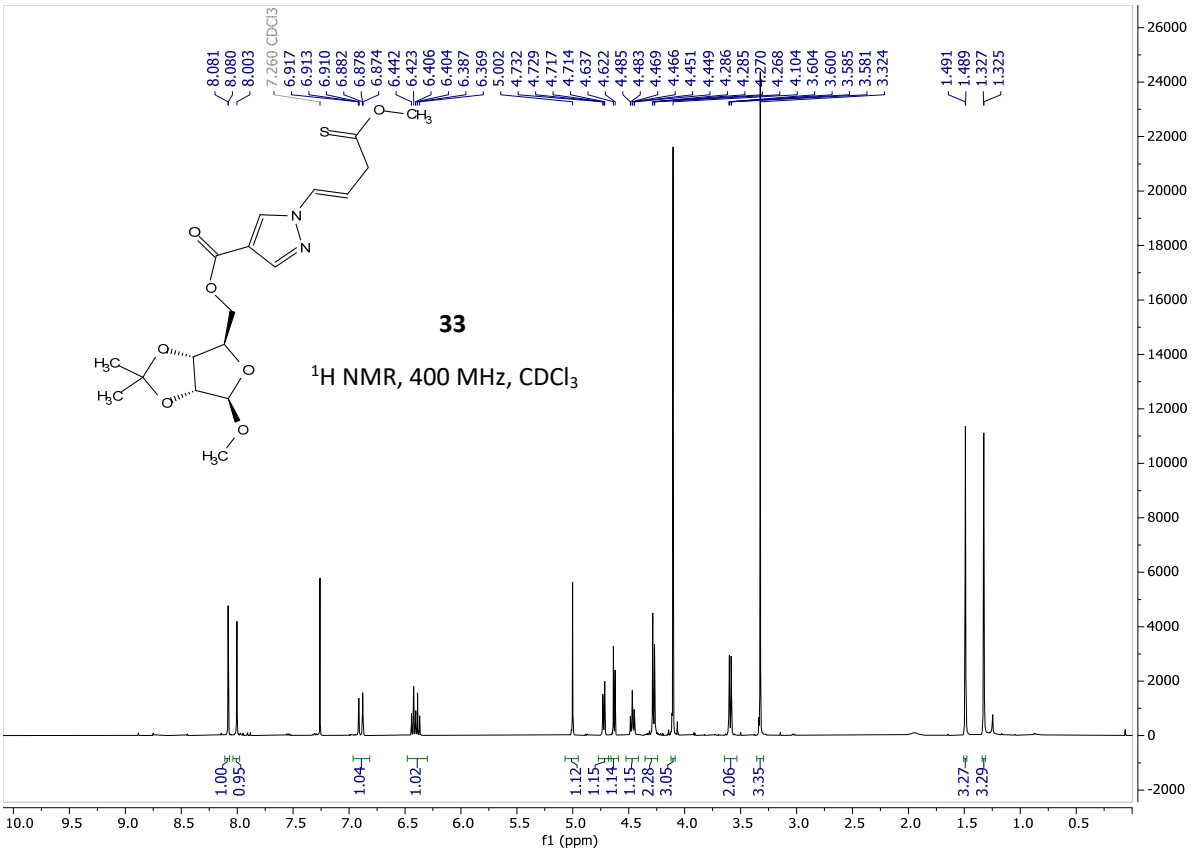

31
^{13}C NMR, 101 MHz, $CDCl_3$
220.023
152.252
151.878
150.473
140.584
129.042
128.488
127.842
122.813
114.310
113.471
100.740
72.805
66.592
59.309
46.514
17.741
-1.463
f1 (ppm)

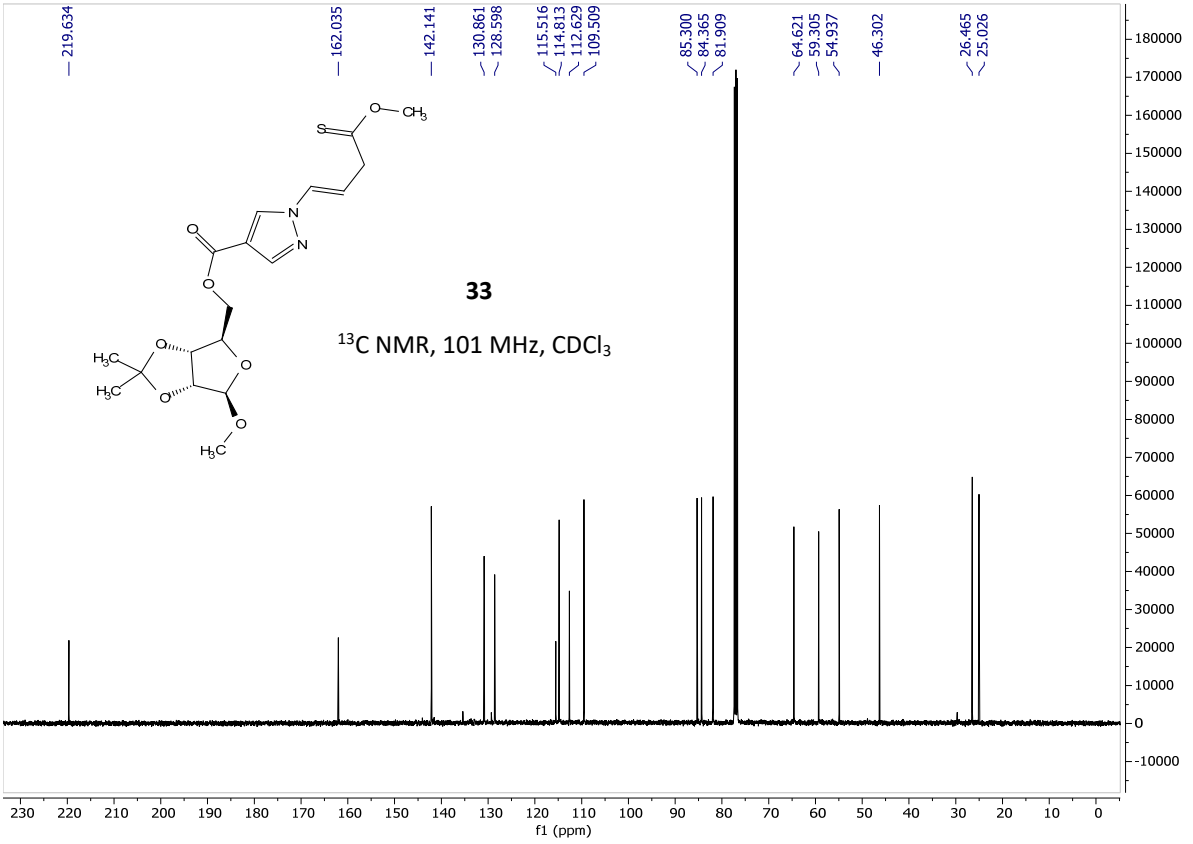

8.331
8.321
8.117
8.103
7.413
7.406
7.260 CDCl3
7.198
7.188
6.943
6.939
6.936
6.924
6.920
6.917
6.723
6.716
5.747
5.732
5.728
5.718
5.714
5.706
5.699
4.141
4.136
4.132
4.121
4.117
3.579
3.565
3.563
3.560
3.546
0.935
0.921
0.919
0.917
0.902
0.064
32
1H NMR, 500 MHz, CDCl3
1.00
0.91
0.96
0.98
1.01
1.03
1.01
2.89
2.85
2.04
2.05
2.17
8.83
f1 (ppm)

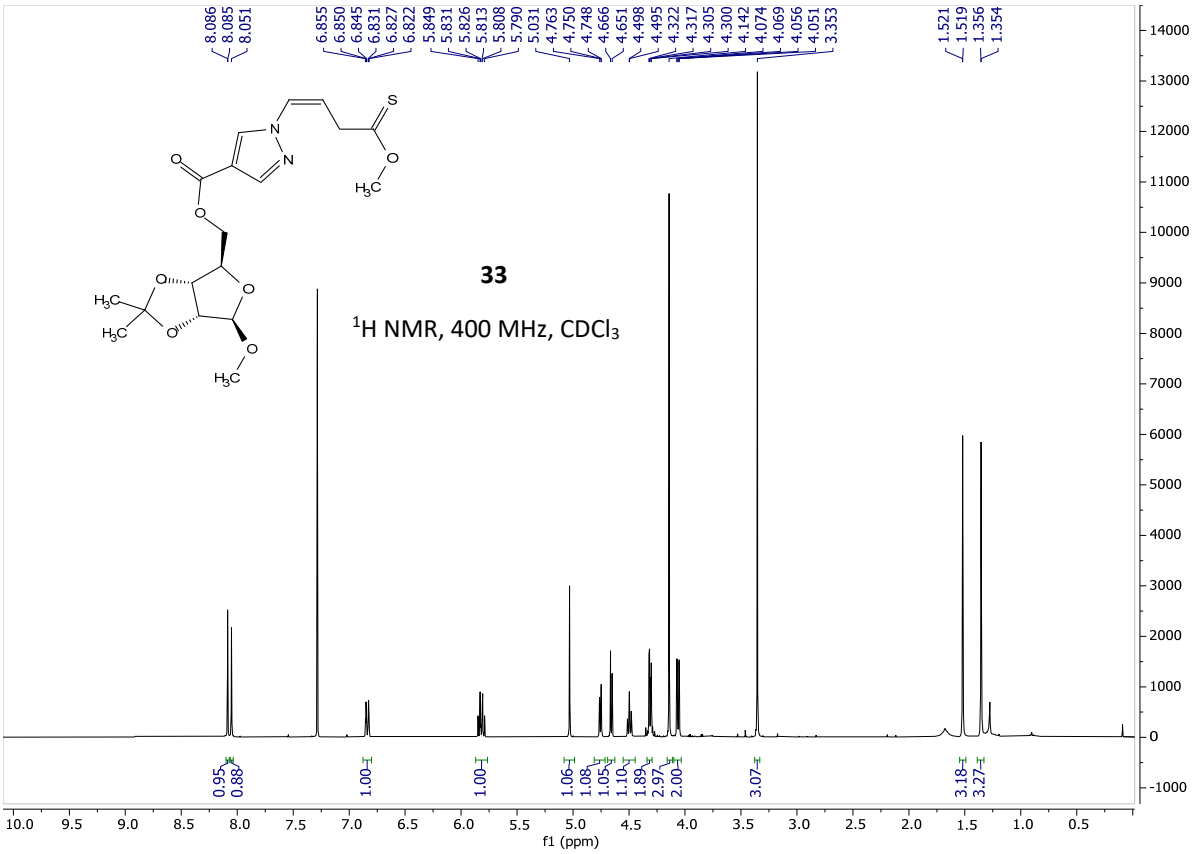

222.397
150.326
144.964
141.239
133.802
130.331
129.505
127.829
122.337
118.913
116.335
115.224
101.740
74.464
67.678
60.720
45.434
19.222
-0.000
32
13C NMR, 126 MHz, CDCl3
f1 (ppm)

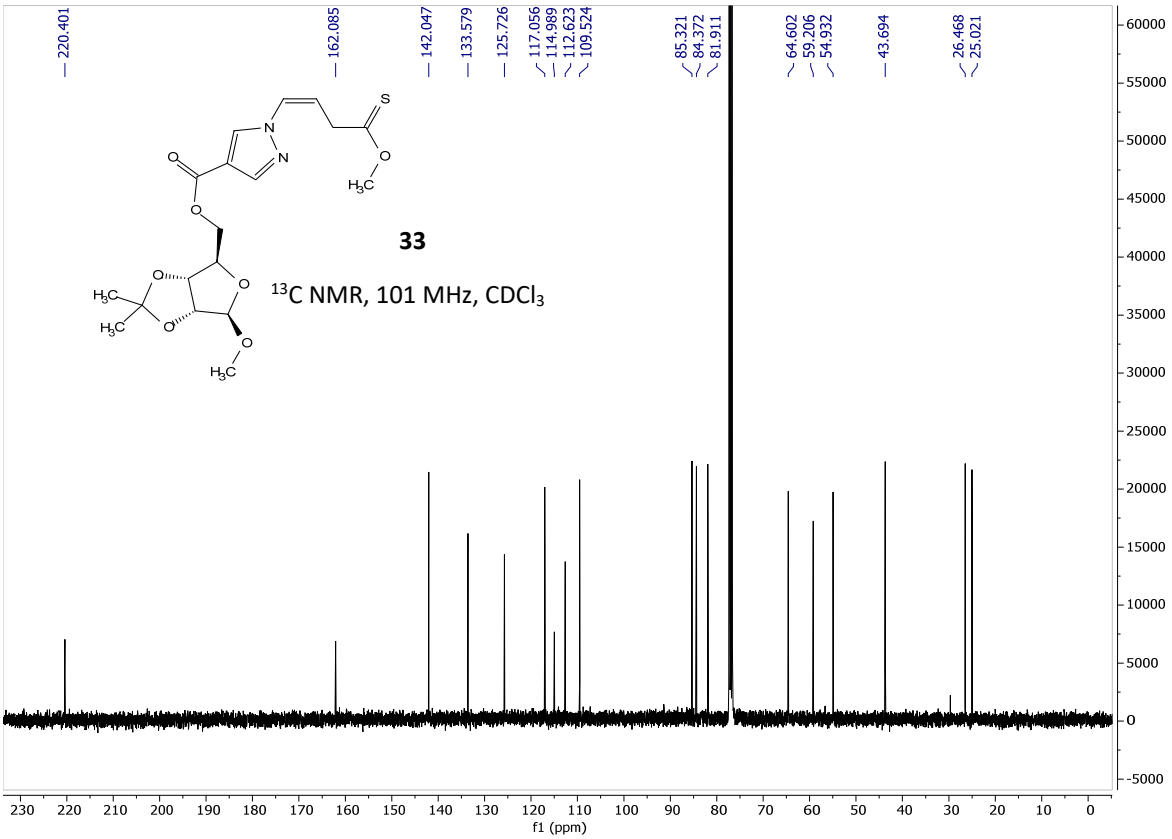

8.326
8.316
8.090
8.060
7.410
7.403
7.260 CDCl3
7.189
7.179
7.022
6.994
6.712
6.705
6.401
6.386
6.372
6.357
6.342
5.703
4.122
3.638
3.623
3.576
3.560
3.543
0.932
0.916
0.900
0.067
32
1H NMR, 500 MHz, CDCl3
1.05
1.00
1.00
1.00
1.07
1.01
1.08
1.01
2.21
2.99
2.01
2.31
2.33
9.40
f1 (ppm)

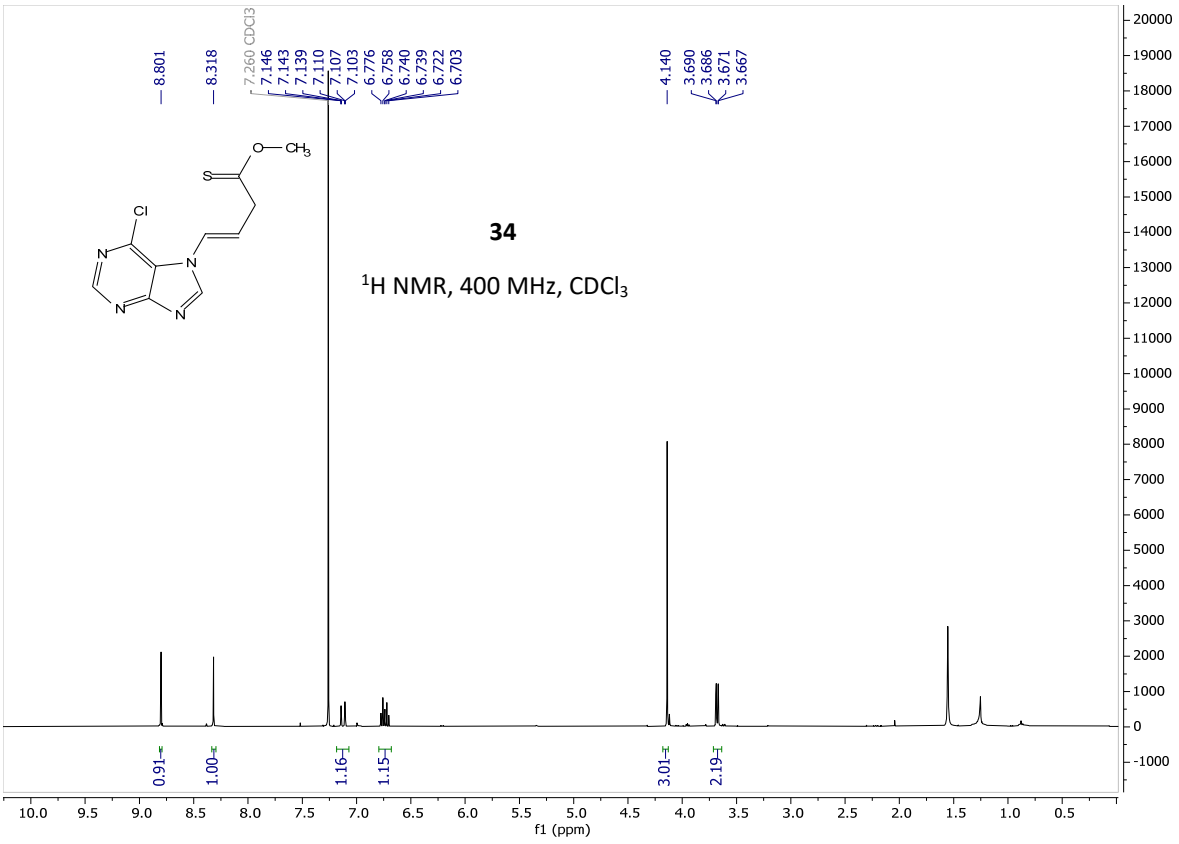

221.709
150.334
144.962
141.297
133.787
130.633
129.514
127.370
123.042
118.903
115.235
113.990
101.731
74.460
67.674
60.791
48.000
19.218
0.000
32
13C NMR, 126 MHz, CDCl3
f1 (ppm)

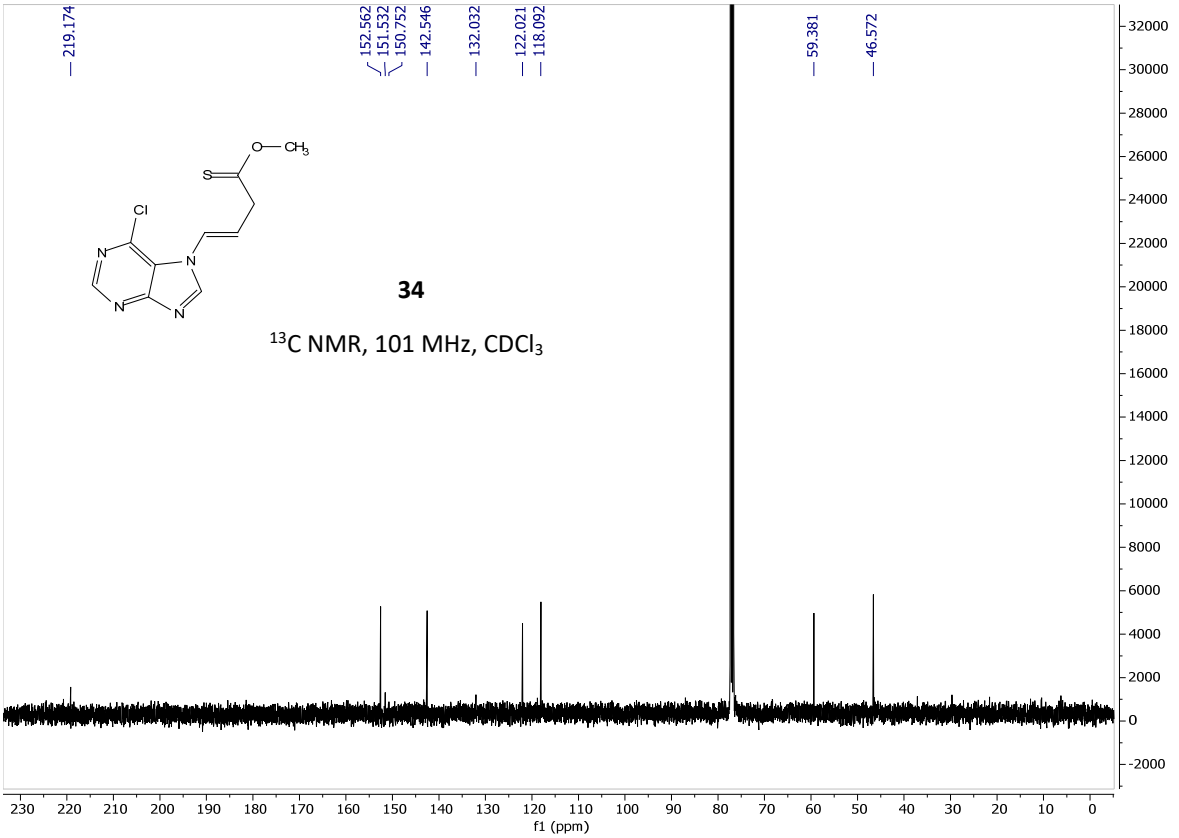

8.081
8.080
8.003
7.260 CDCl3
6.917
6.913
6.910
6.882
6.878
6.874
6.442
6.423
6.406
6.404
6.387
6.369
5.002
4.732
4.729
4.717
4.714
4.637
4.622
4.485
4.483
4.469
4.466
4.451
4.449
4.286
4.285
4.270
4.268
4.104
3.604
3.600
3.585
3.581
3.324
1.491
1.489
1.327
1.325
33
1H NMR, 400 MHz, CDCl3
1.00
0.95
1.04
1.02
1.12
1.15
1.14
1.15
2.28
3.05
2.06
3.35
3.27
3.29
f1 (ppm)

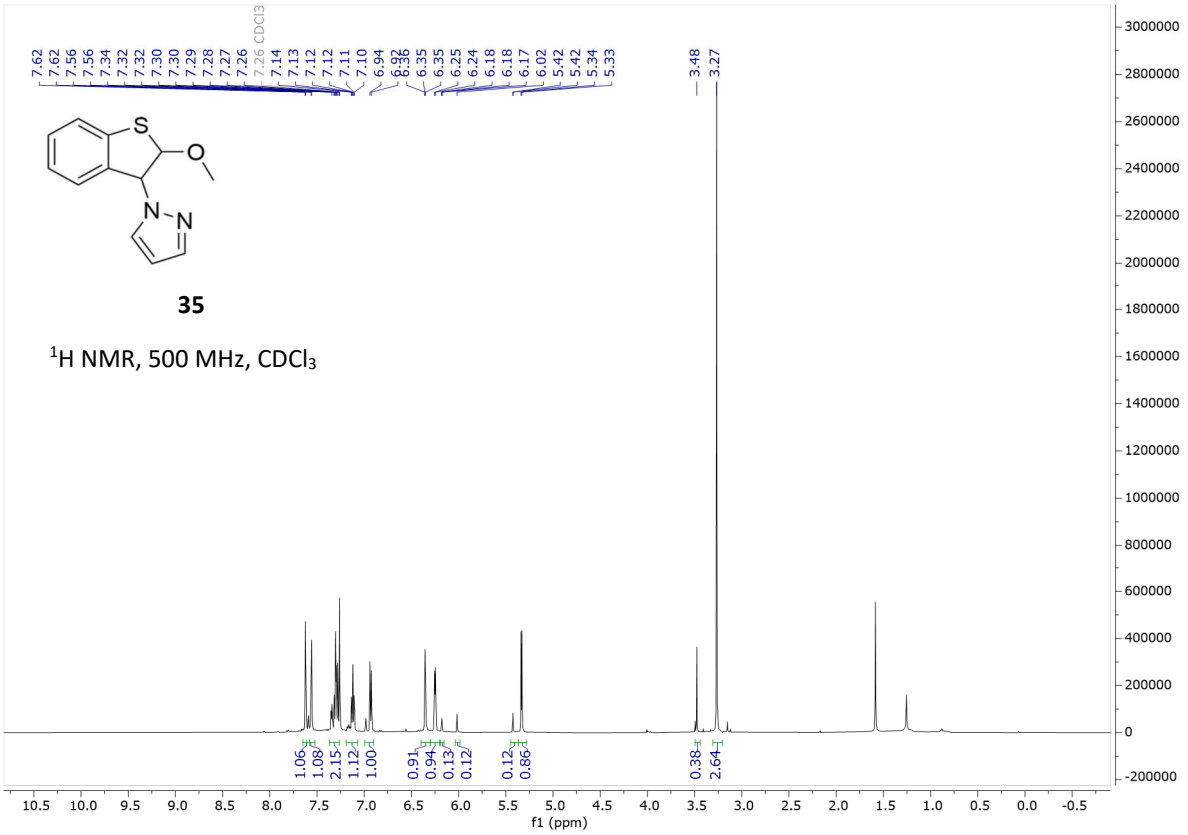

219.634
162.035
142.141
130.861
128.598
115.516
114.813
112.629
109.509
85.300
84.365
81.909
64.621
59.305
54.937
46.302
26.465
25.026
33
13C NMR, 101 MHz, CDCl3
f1 (ppm)


33
^{1}H NMR, 400 MHz, $CDCl_3$
f1 (ppm)


33
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)

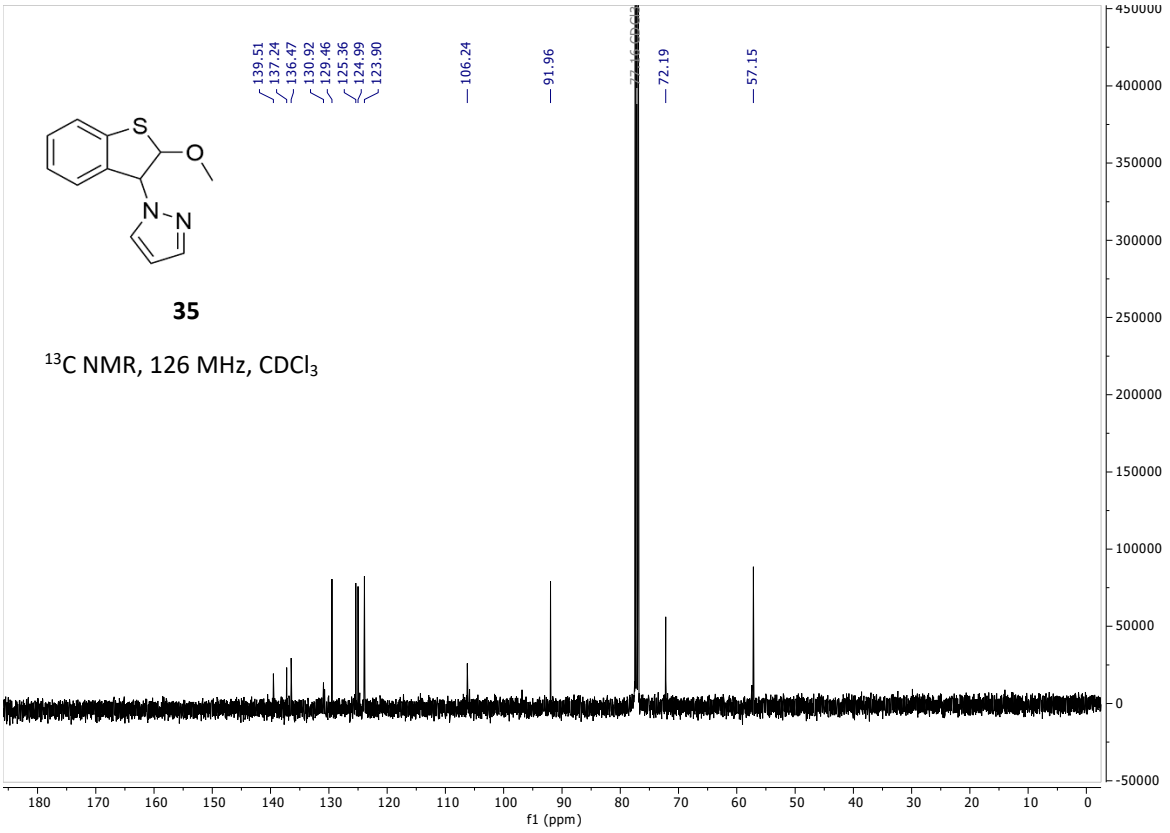

8.801
8.318
7.260 CDCl3
7.146
7.143
7.139
7.110
7.107
7.103
6.776
6.758
6.740
6.739
6.722
6.703
4.140
3.690
3.686
3.671
3.667
O—CH3
S
Cl
N
N
N
N
34
1H NMR, 400 MHz, CDCl3
0.91
1.00
1.16
1.15
3.01
2.19
f1 (ppm)


219.174
152.562
151.532
150.752
142.546
132.032
122.021
118.092
59.381
46.572
O—CH3
S
Cl
N
N
N
N
34
13C NMR, 101 MHz, CDCl3
f1 (ppm)



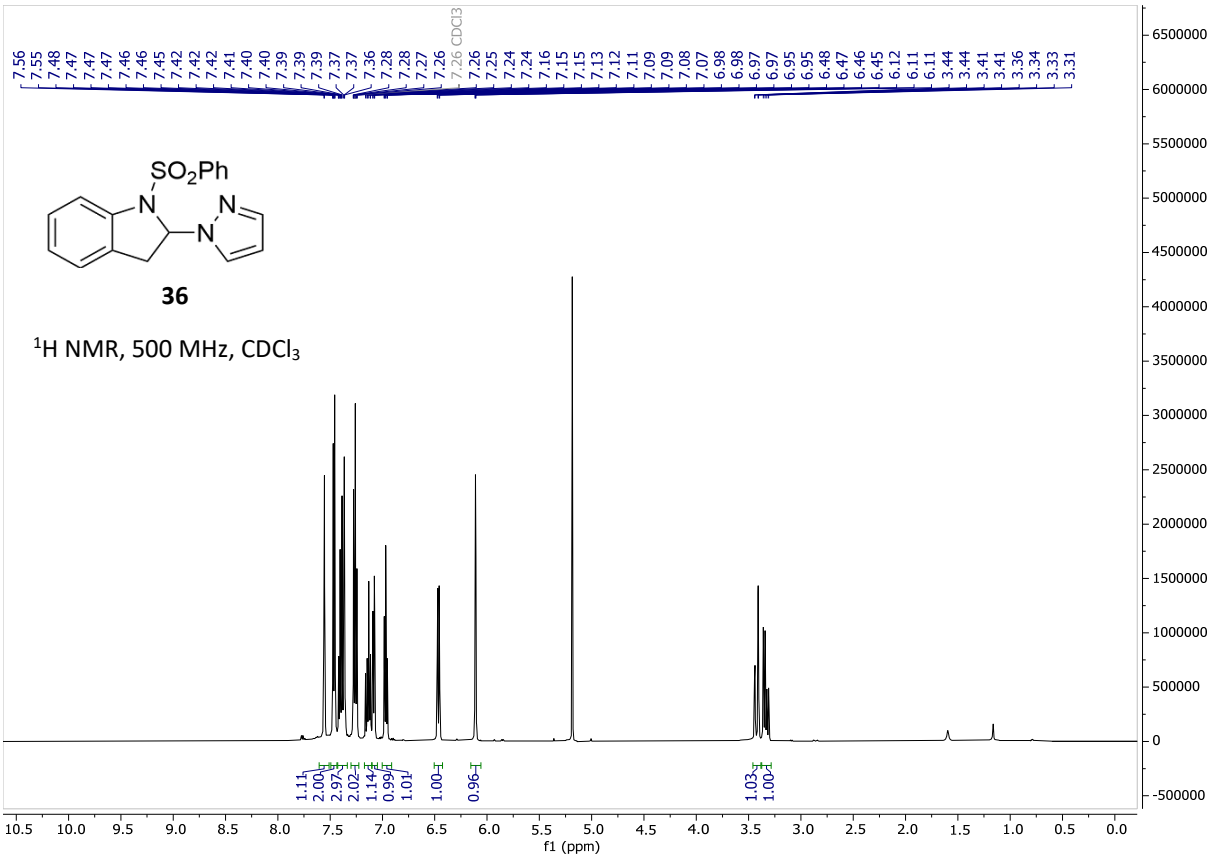
35

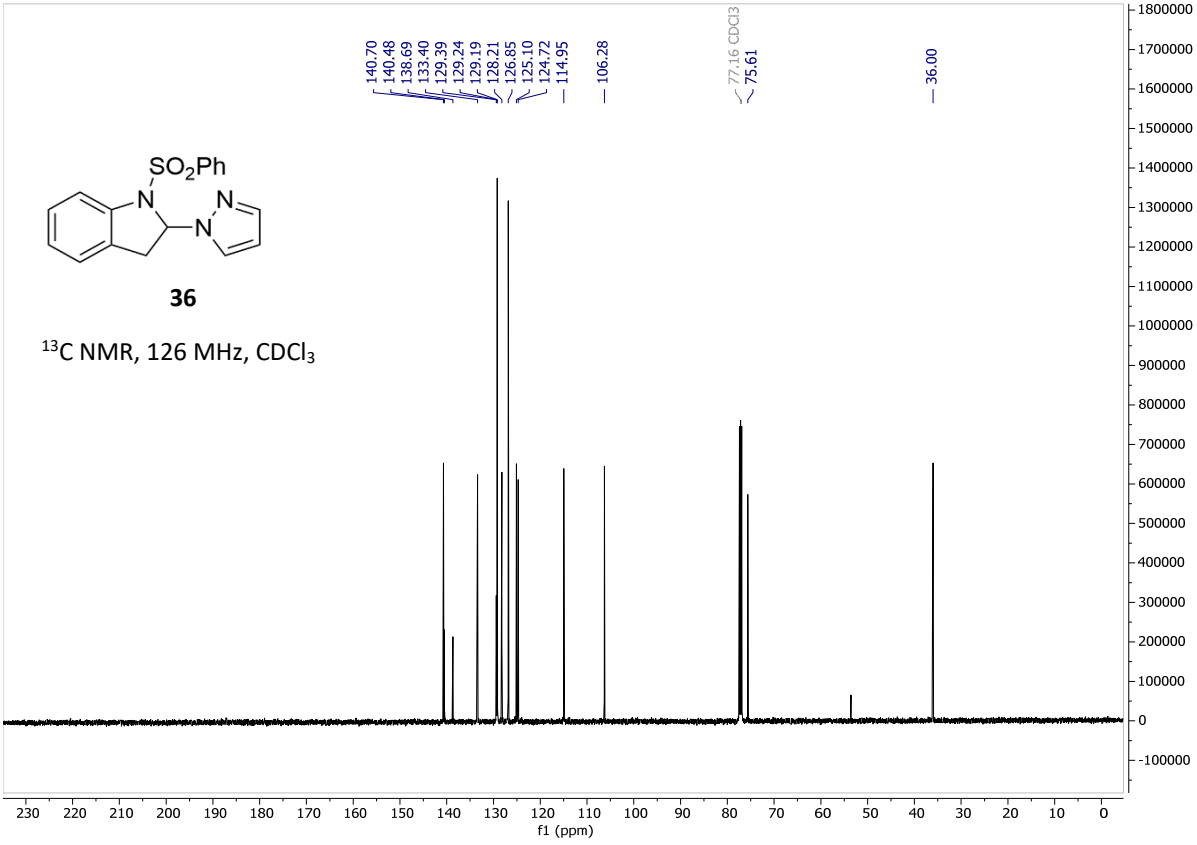
^{1}H NMR, 500 MHz, $CDCl_3$

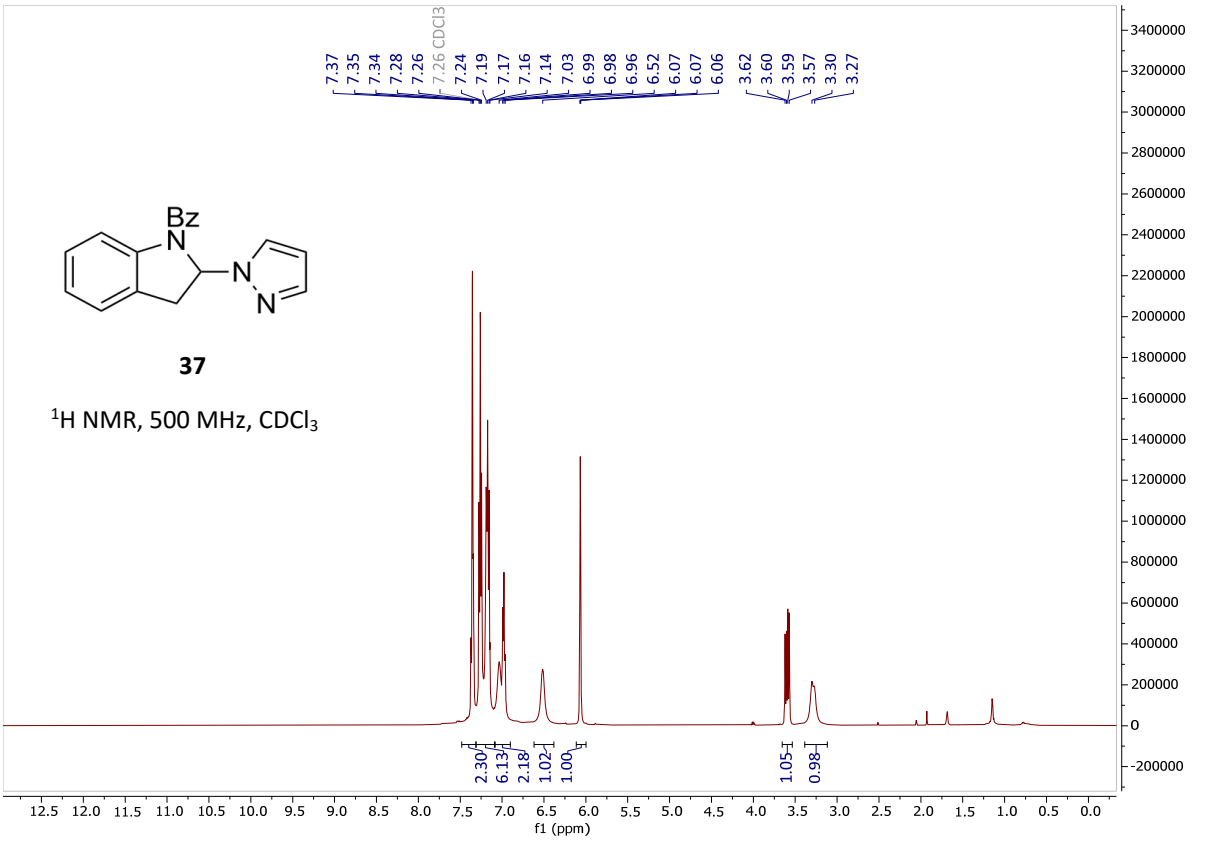


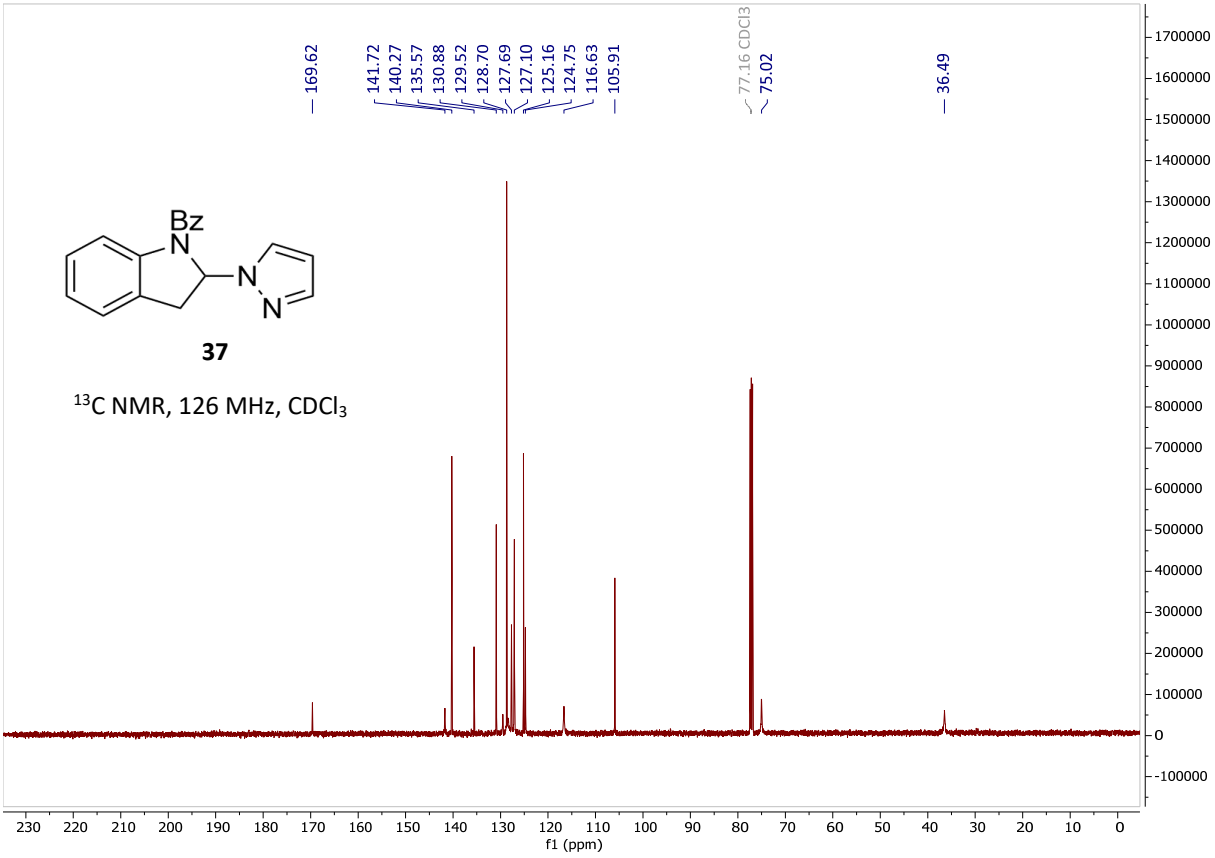
35

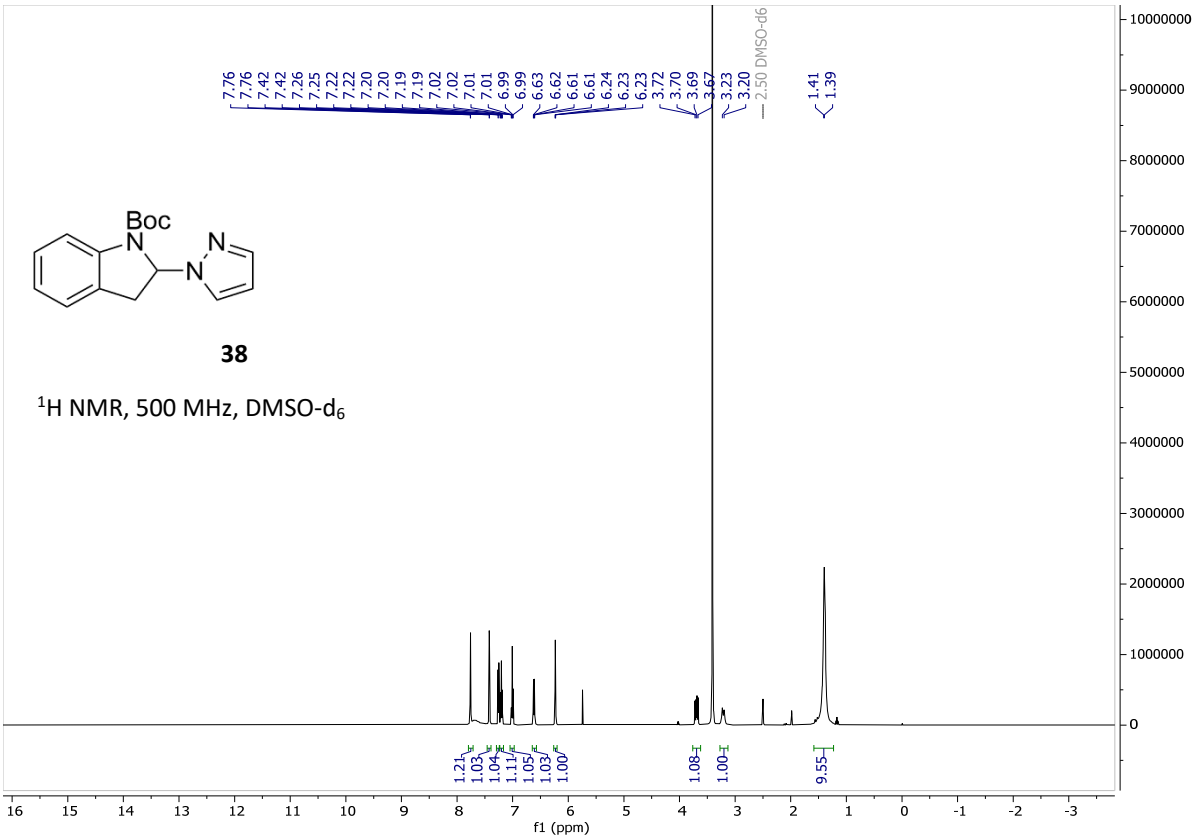
^{13}C NMR, 126 MHz, $CDCl_3$


7.56 7.55 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.39 7.37 7.37 7.36 7.28 7.28 7.27 7.26 7.26 CDCl3 7.26 7.25 7.24 7.24 7.16 7.15 7.15 7.13 7.12 7.11 7.09 7.09 7.08 7.07 6.98 6.98 6.97 6.97 6.95 6.95 6.48 6.47 6.46 6.45 6.12 6.11 6.11 3.44 3.44 3.41 3.41 3.36 3.34 3.33 3.31
SO2Ph
N
N
N
36
1H NMR, 500 MHz, CDCl3
1.11 2.00 2.97 2.02 1.14 0.99 1.01 1.00 0.96 1.03 1.00
f1 (ppm)


140.70 140.48 138.69 133.40 129.39 129.24 129.19 128.21 126.85 125.10 124.72 114.95 106.28 77.16 CDCl3 75.61 36.00
SO2Ph
N
N
N
36
13C NMR, 126 MHz, CDCl3
f1 (ppm)

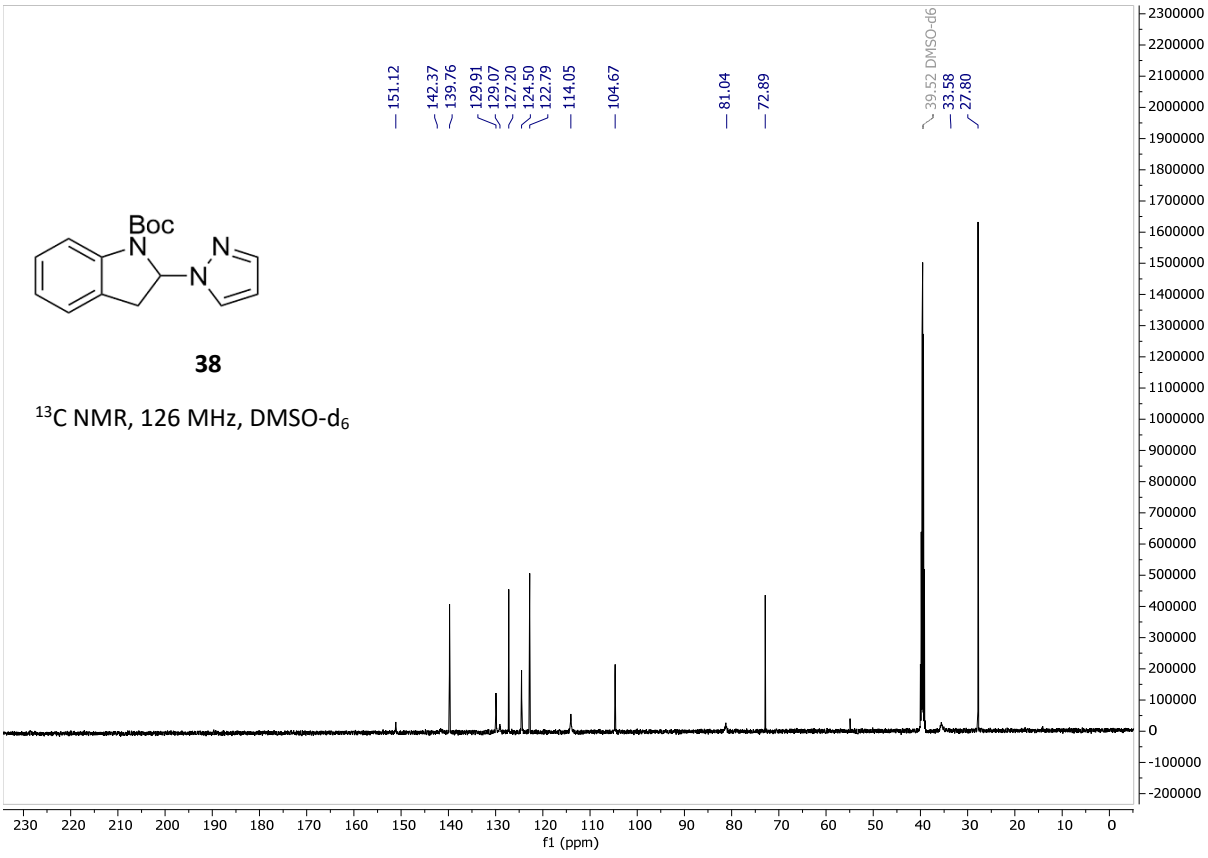

7.37
7.35
7.34
7.28
7.26
7.26 CDCl3
7.24
7.19
7.17
7.16
7.14
7.03
6.99
6.98
6.96
6.52
6.07
6.07
6.06
3.62
3.60
3.59
3.57
3.30
3.27
Bz
N
N
N
37
1H NMR, 500 MHz, CDCl3
2.30
6.13
2.18
1.02
1.00
1.05
0.98
f1 (ppm)


169.62
141.72
140.27
135.57
130.88
129.52
128.70
127.69
127.10
125.16
124.75
116.63
105.91
77.16 CDCl3
75.02
36.49
Bz
N
N
N
37
13C NMR, 126 MHz, CDCl3
f1 (ppm)



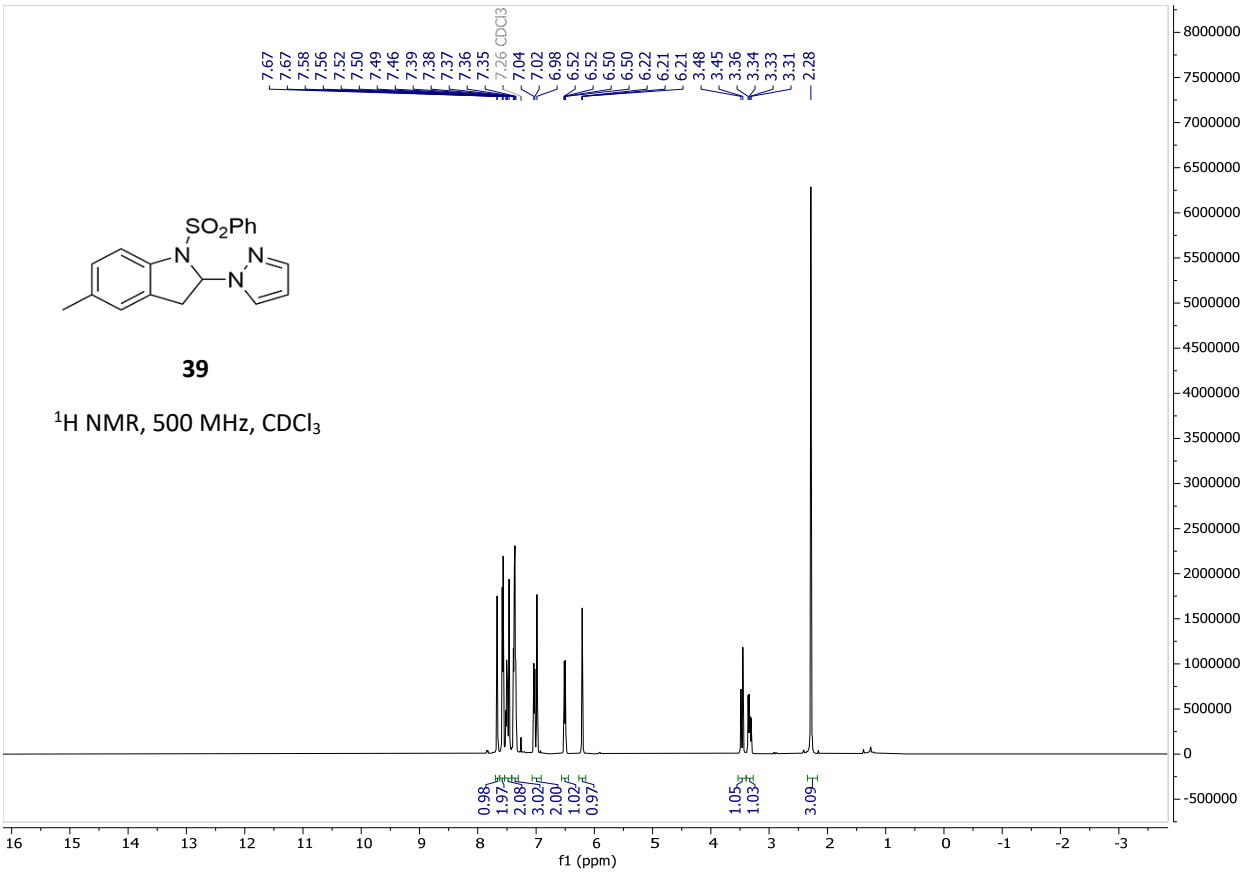
38

^{1}H NMR, 500 MHz, DMSO-d_6



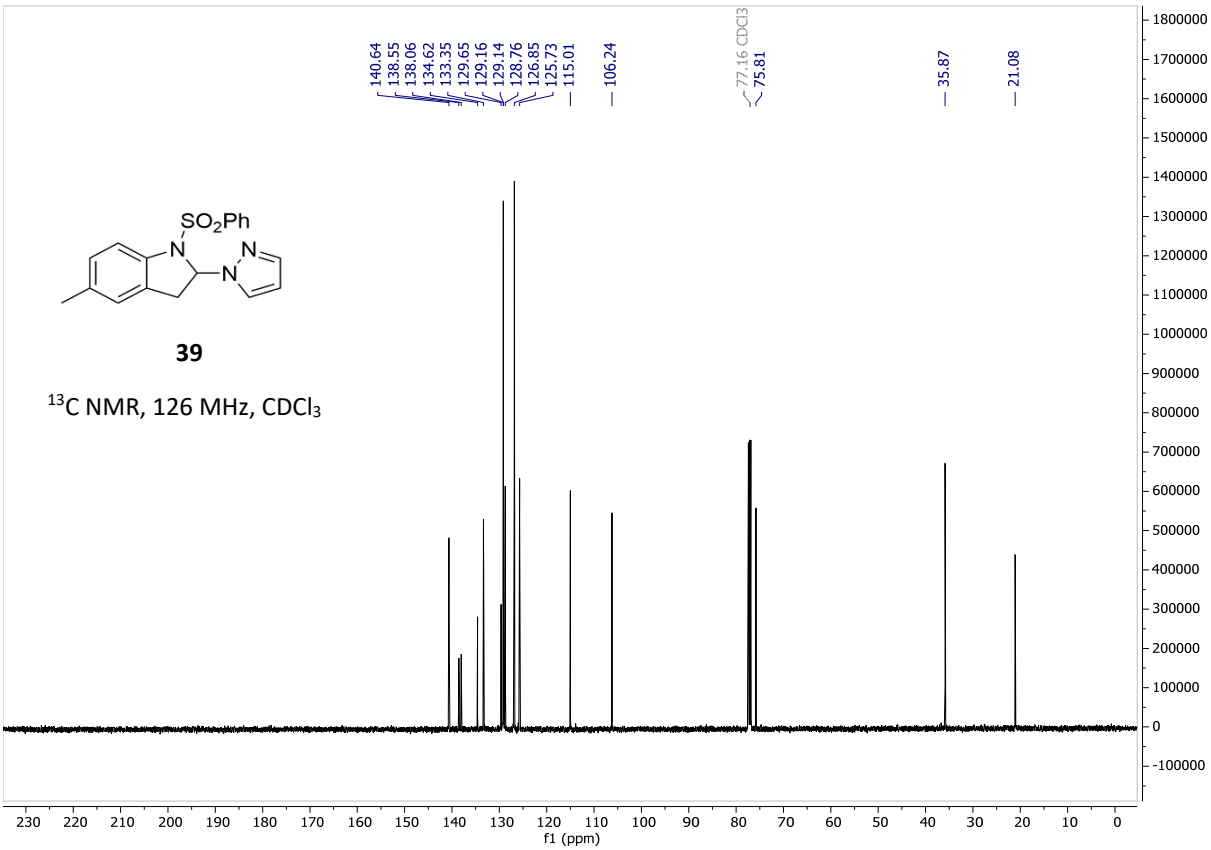
38

^{13}C NMR, 126 MHz, DMSO-d_6



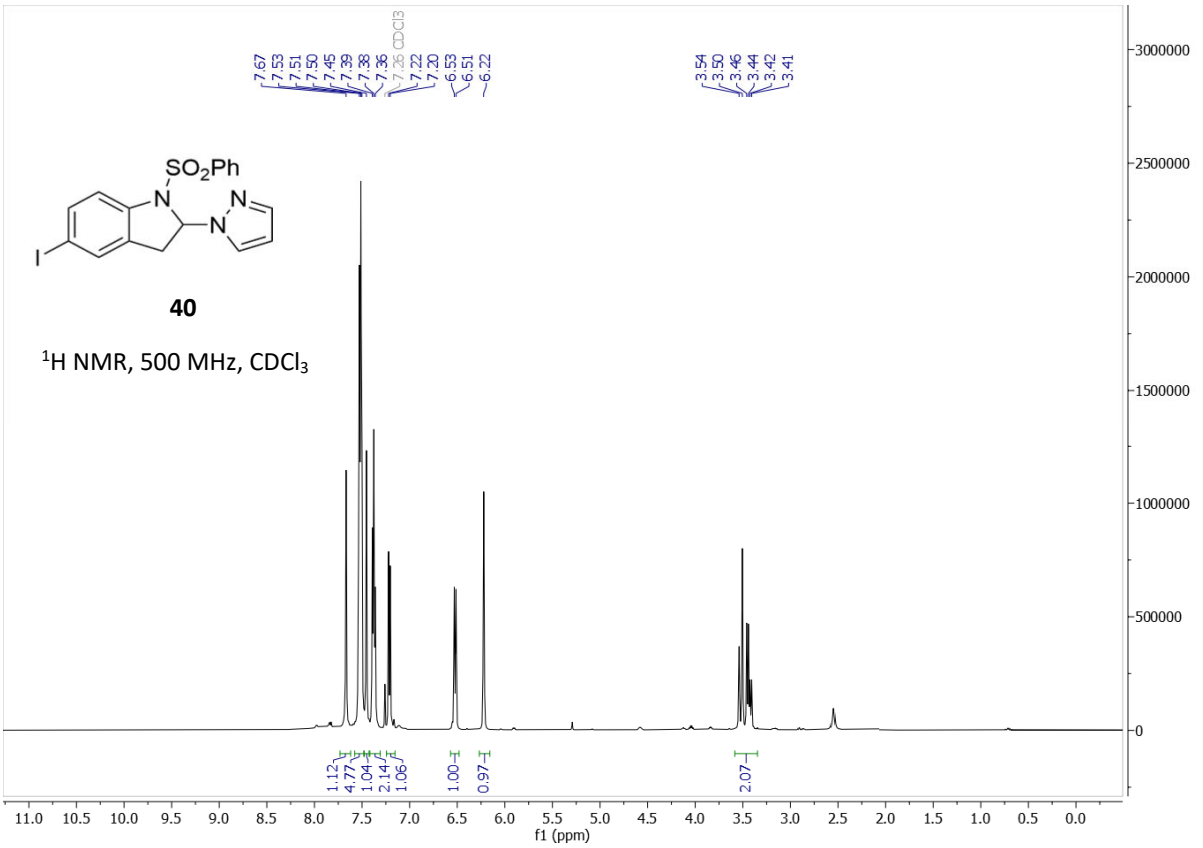
39

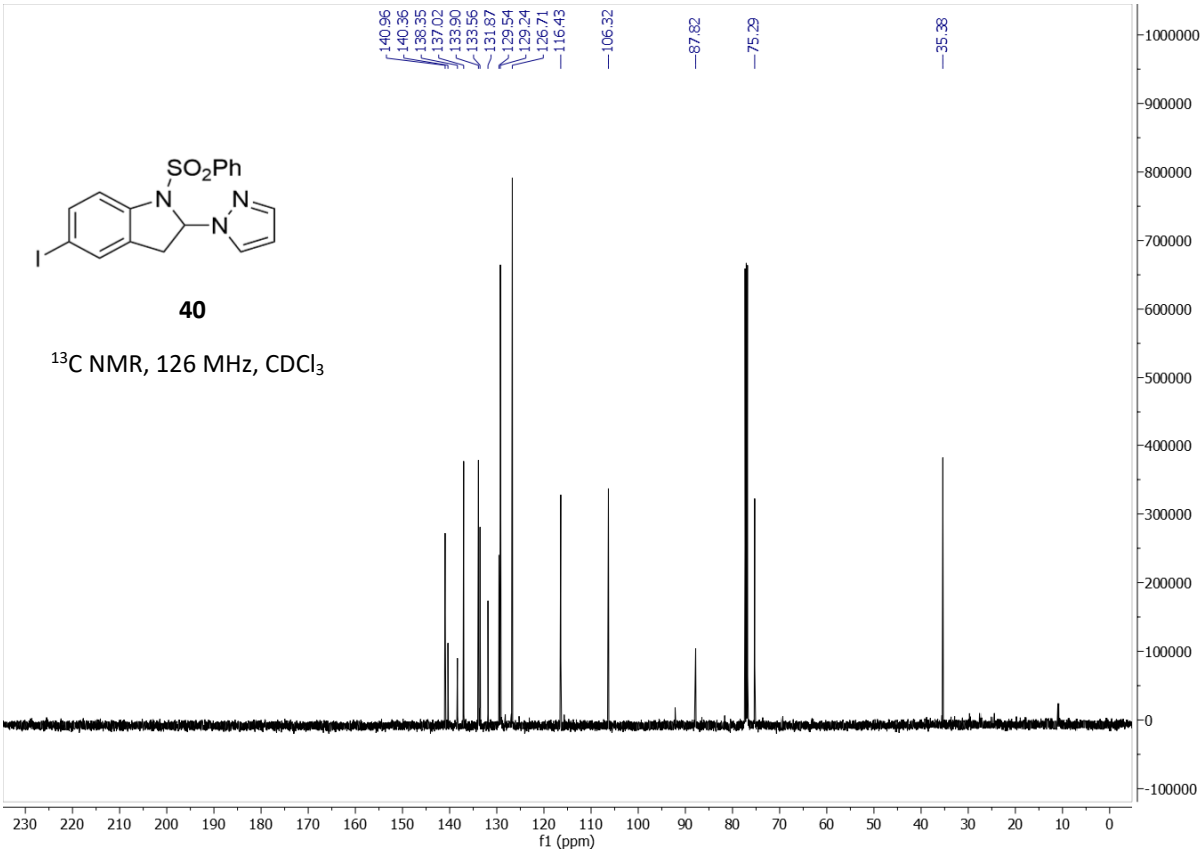
^{1}H NMR, 500 MHz, $CDCl_3$

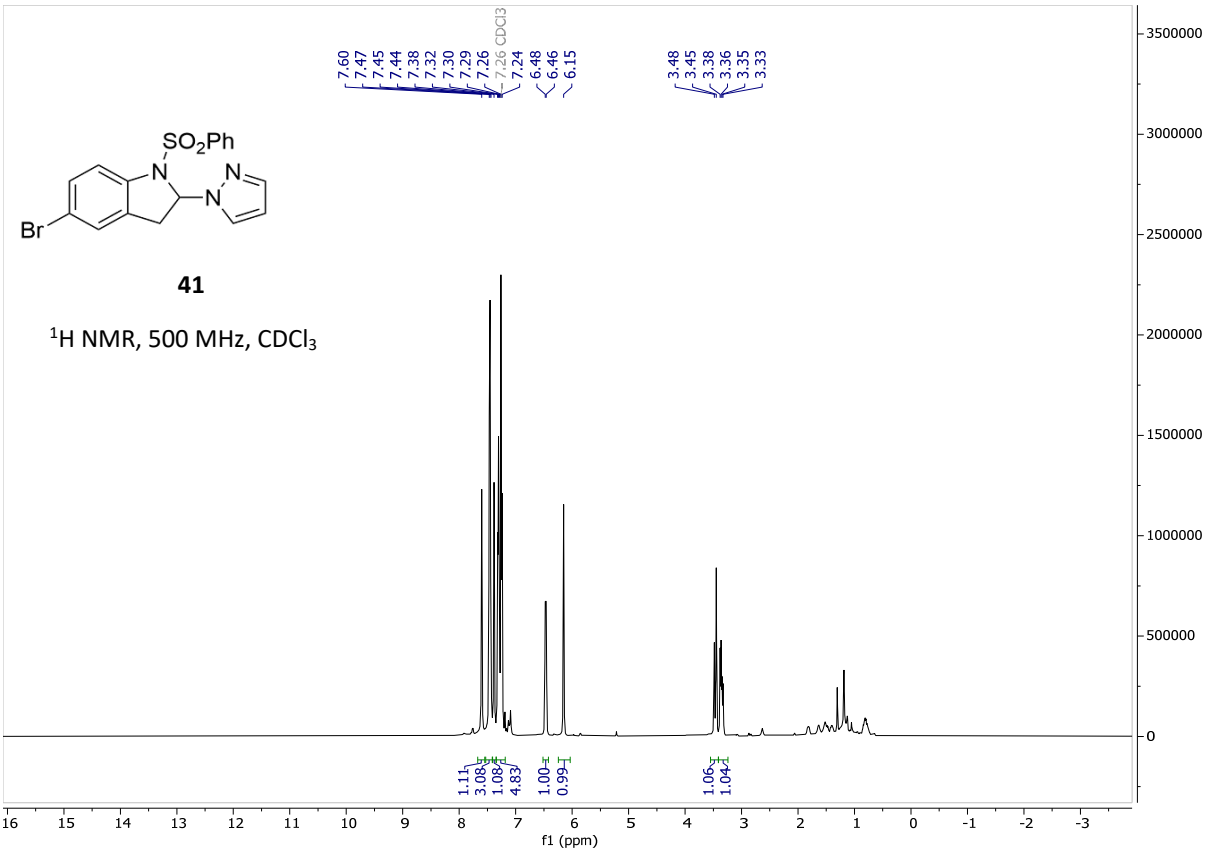


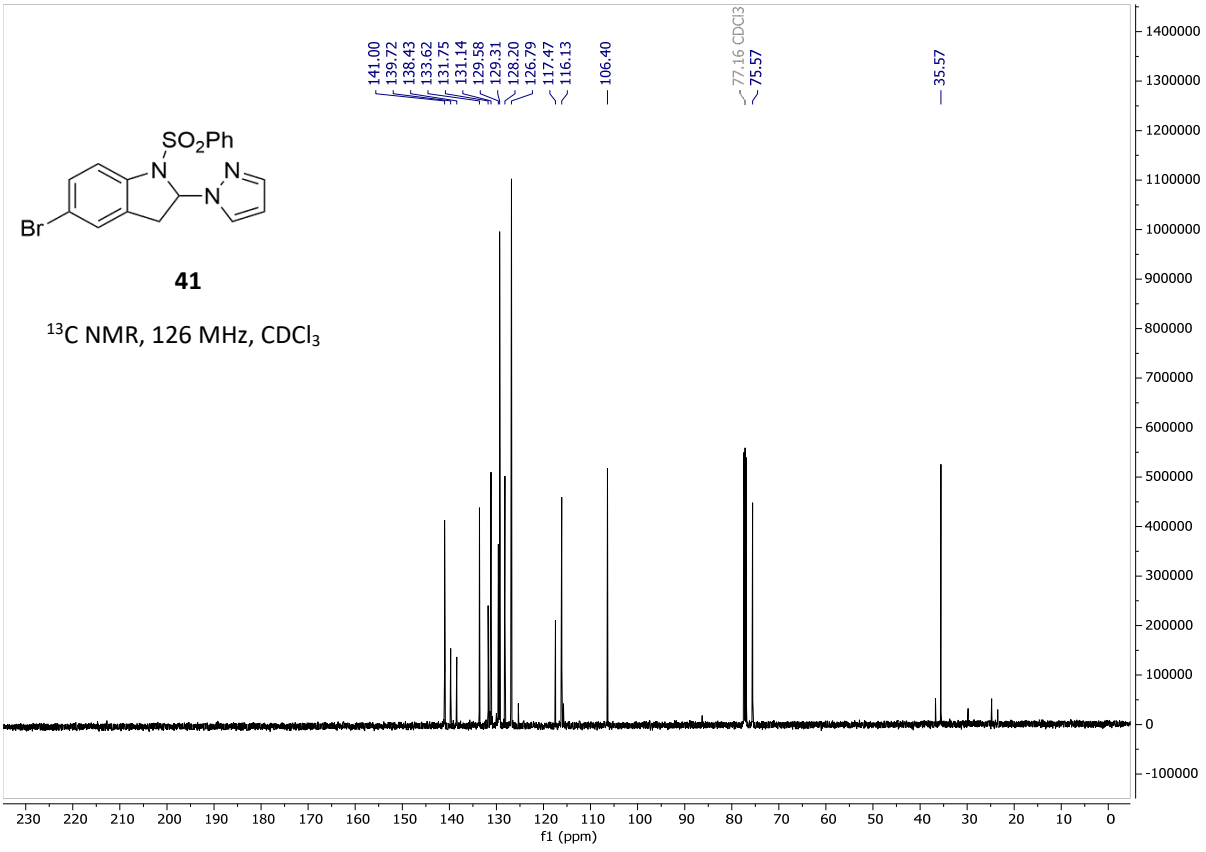
39

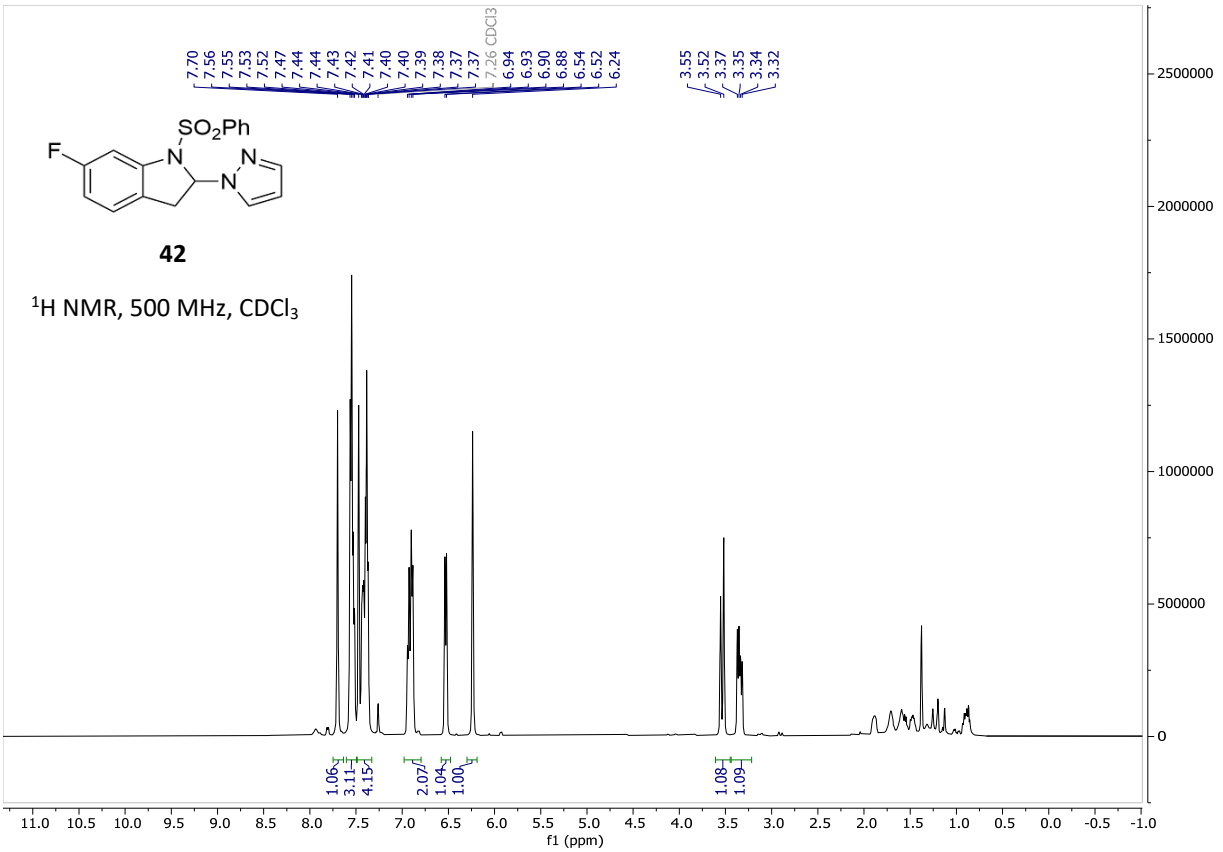
^{13}C NMR, 126 MHz, $CDCl_3$

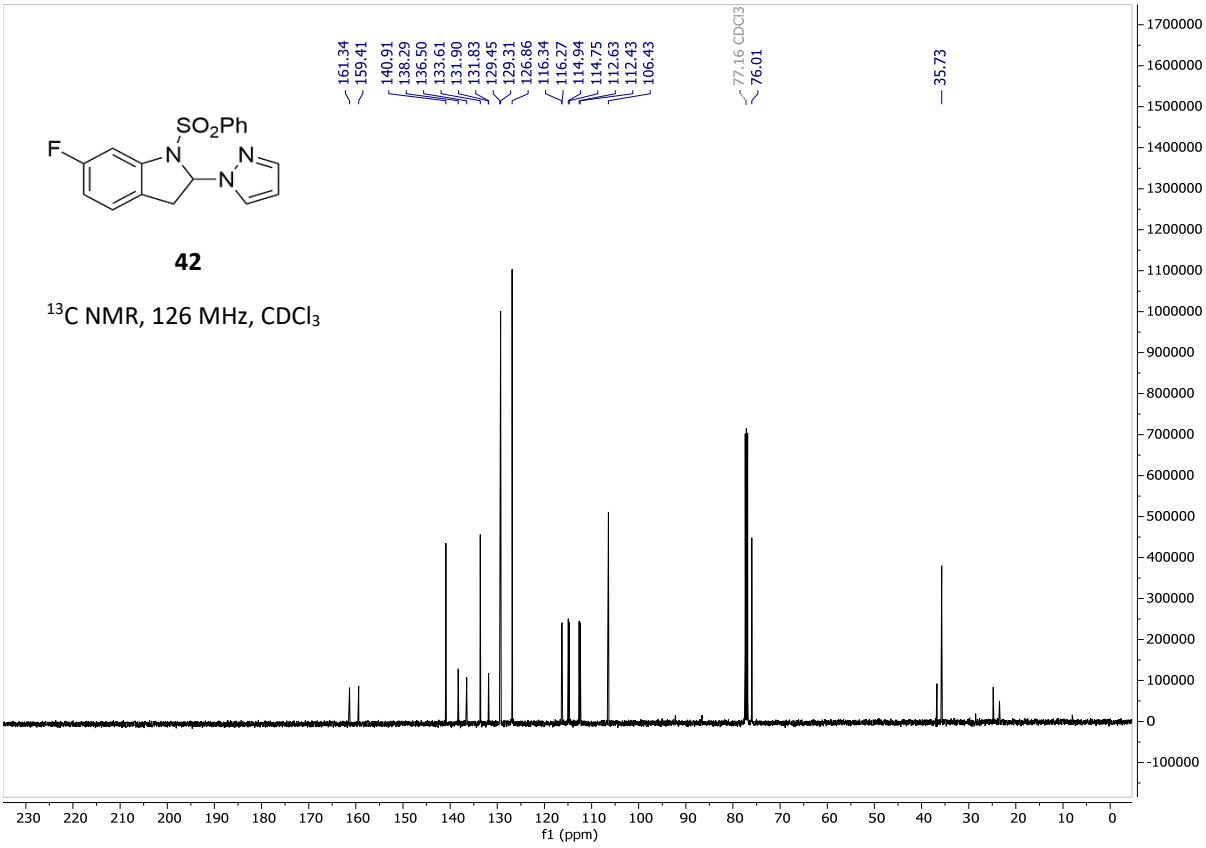

7.67
7.53
7.51
7.50
7.45
7.39
7.38
7.36
7.26 CDCl3
7.22
7.20
6.53
6.51
6.22
3.54
3.50
3.46
3.44
3.42
3.41
SO2Ph
N
N
N
I
40
1H NMR, 500 MHz, CDCl3
1.12
4.77
1.04
2.14
1.06
1.00
0.97
2.07
f1 (ppm)

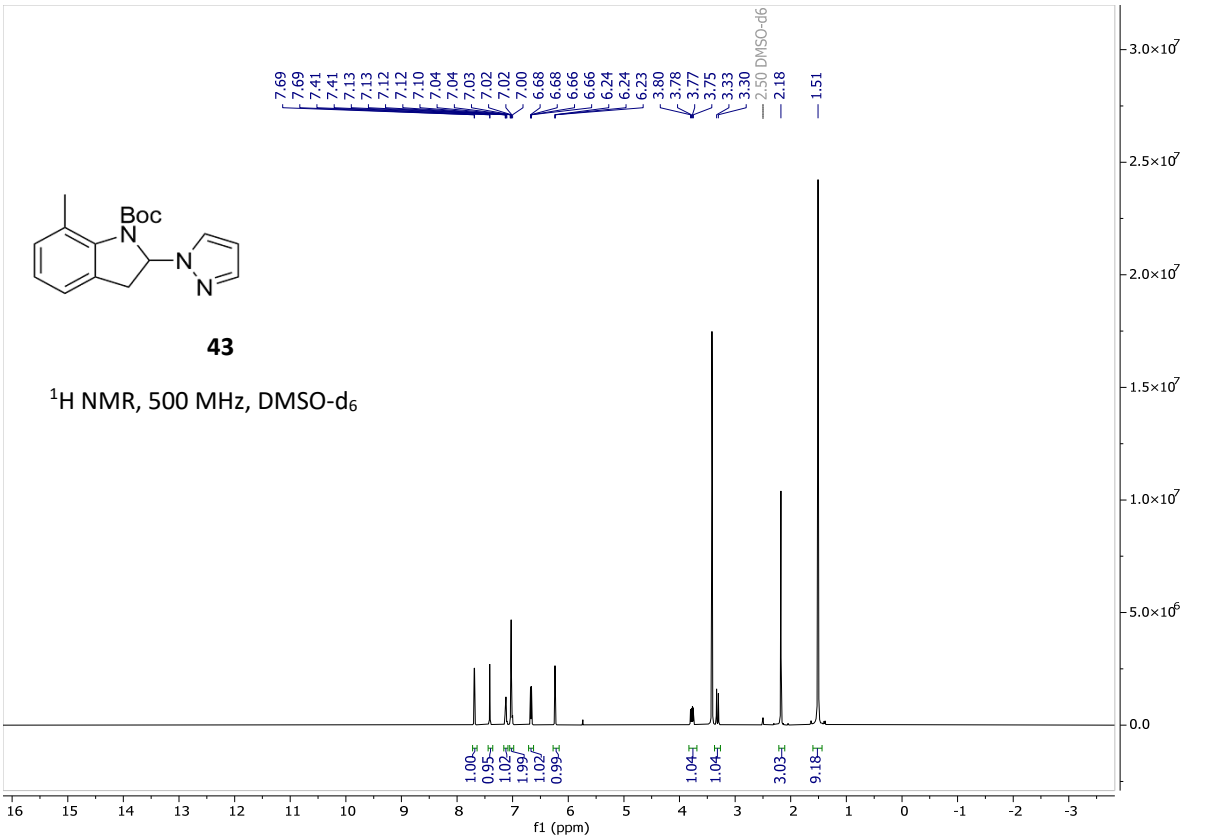

140.96
140.36
138.35
137.02
133.90
133.56
131.87
129.54
129.24
126.71
116.43
106.32
87.82
75.29
35.38
SO2Ph
N
N
N
I
40
13C NMR, 126 MHz, CDCl3
f1 (ppm)

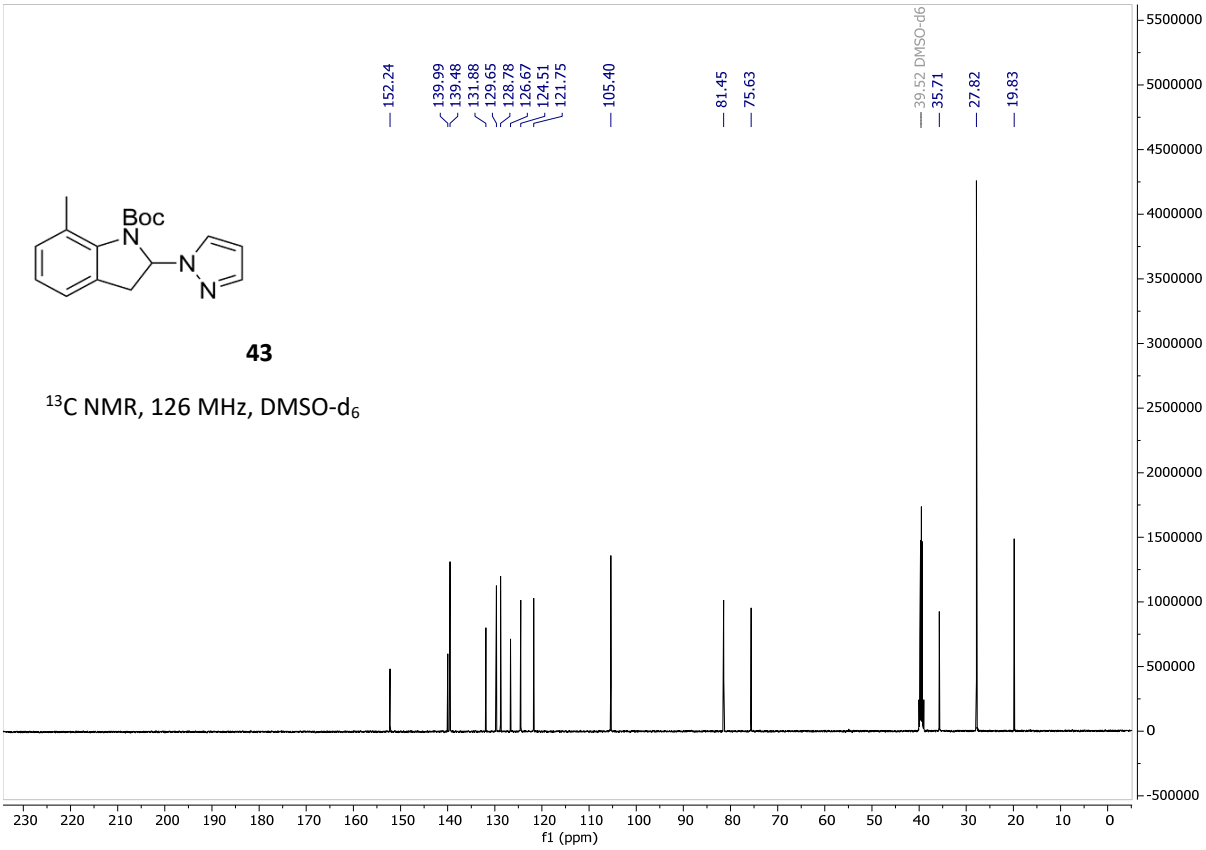

7.60
7.47
7.45
7.44
7.38
7.32
7.30
7.29
7.26
7.26 CDCl3
7.24
6.48
6.46
6.15
3.48
3.45
3.38
3.36
3.35
3.33
SO2Ph
N
N
N
Br
41
1H NMR, 500 MHz, CDCl3
1.11
3.08
1.08
4.83
1.00
0.99
1.06
1.04
f1 (ppm)

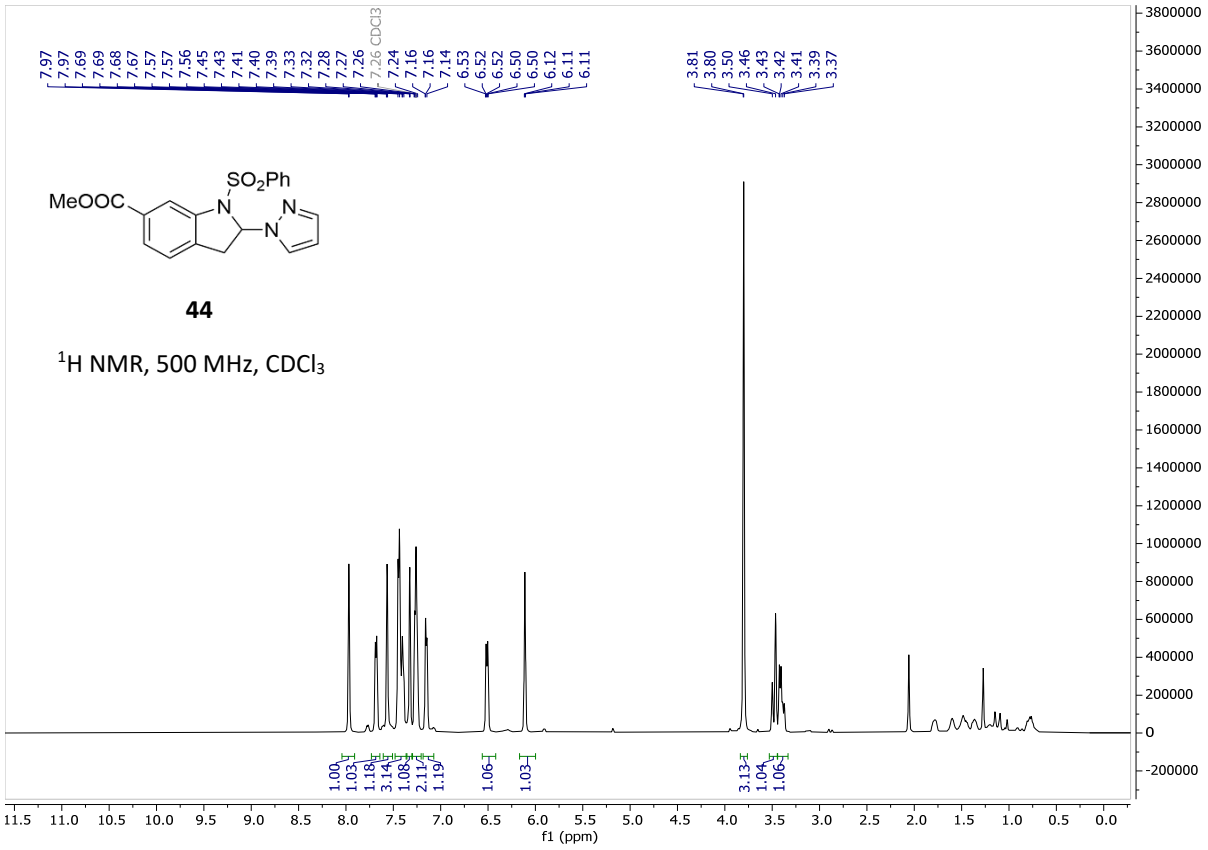

141.00
139.72
138.43
133.62
131.75
131.14
129.58
129.31
128.20
126.79
117.47
116.13
106.40
77.16 CDCl3
75.57
35.57
SO2Ph
N
N
N
Br
41
13C NMR, 126 MHz, CDCl3
f1 (ppm)

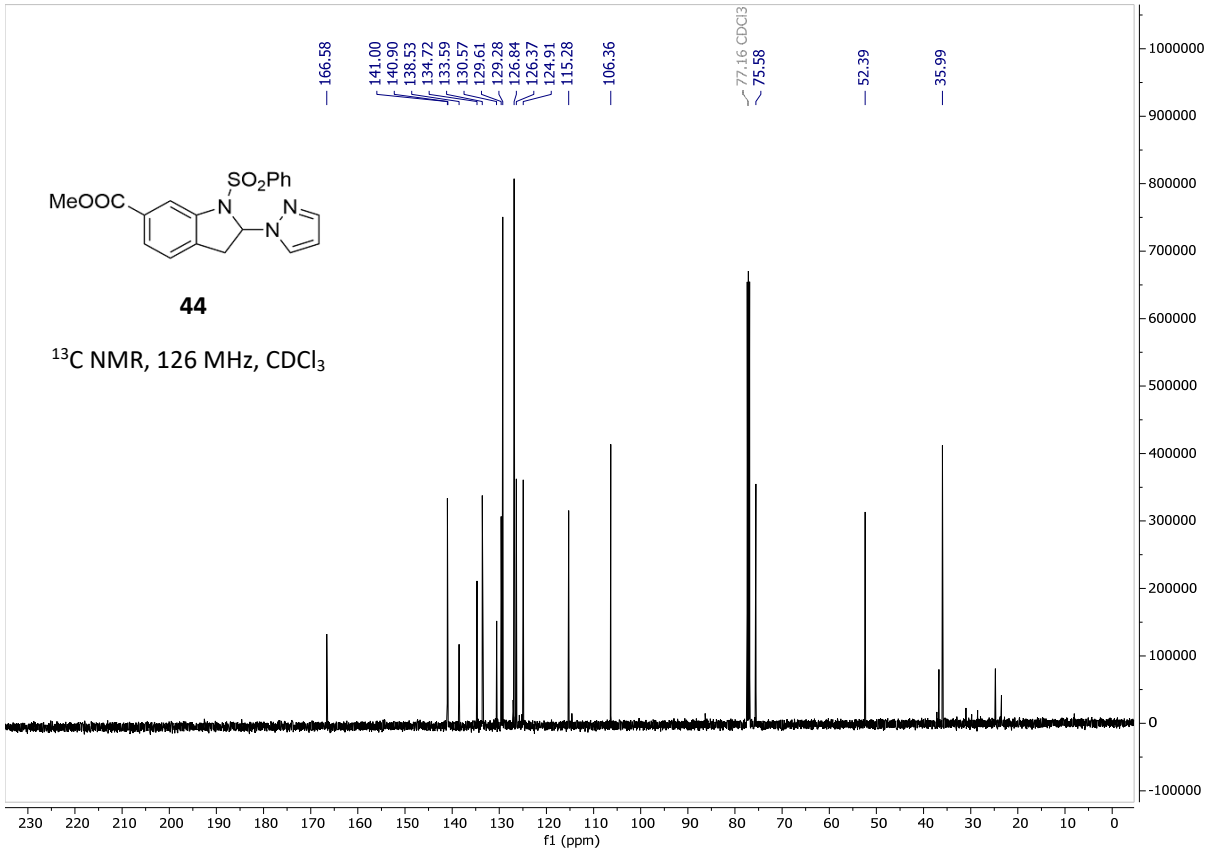

7.70
7.56
7.55
7.53
7.52
7.47
7.44
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.26 CDCl3
6.94
6.93
6.90
6.88
6.54
6.52
6.24
3.55
3.52
3.37
3.35
3.34
3.32
SO2Ph
F
N
N
N
42
1H NMR, 500 MHz, CDCl3
1.06
3.11
4.15
2.07
1.04
1.00
1.08
1.09
2500000
2000000
1500000
1000000
500000
0
11.0 10.5 10.0 9.5 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
f1 (ppm)

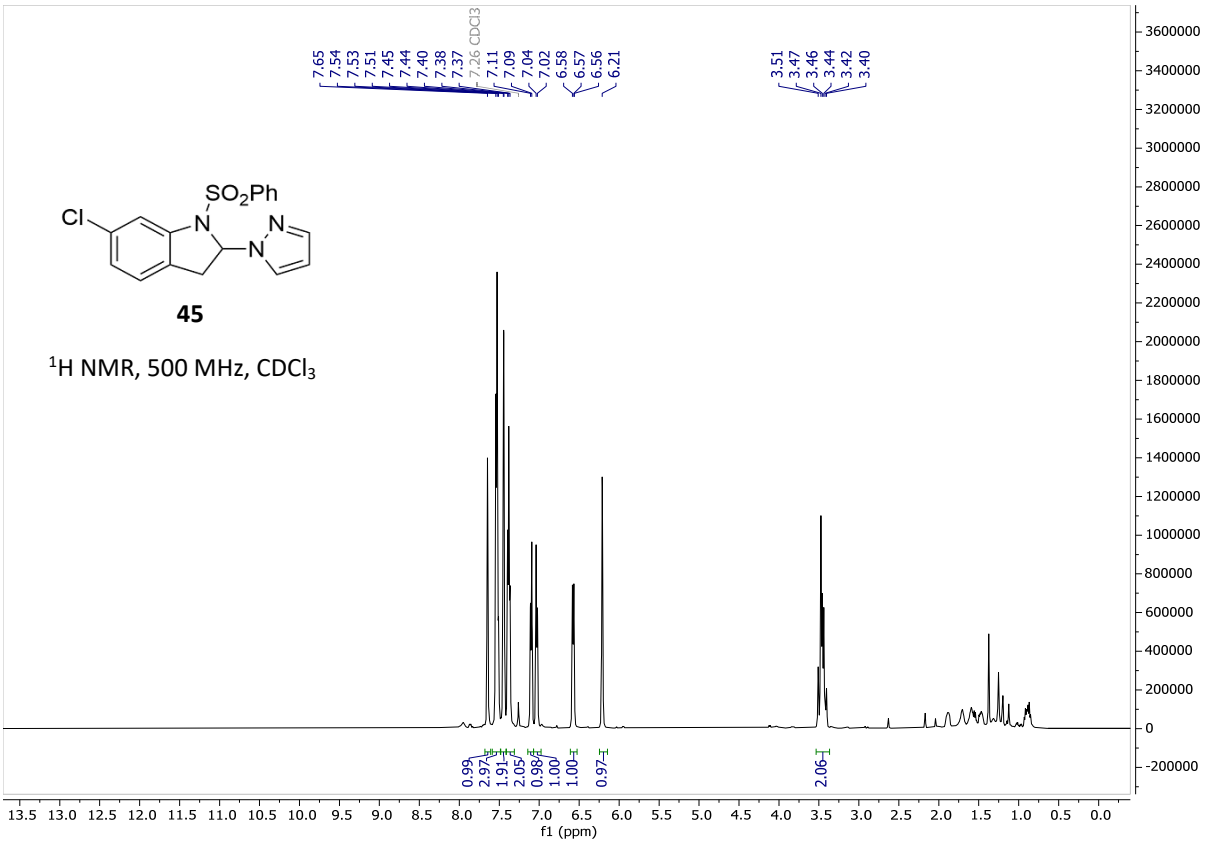

161.34
159.41
140.91
138.29
136.50
133.61
131.90
131.83
129.45
129.31
126.86
116.34
116.27
114.94
114.75
112.63
112.43
106.43
77.16 CDCl3
76.01
35.73
SO2Ph
F
N
N
N
42
13C NMR, 126 MHz, CDCl3
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

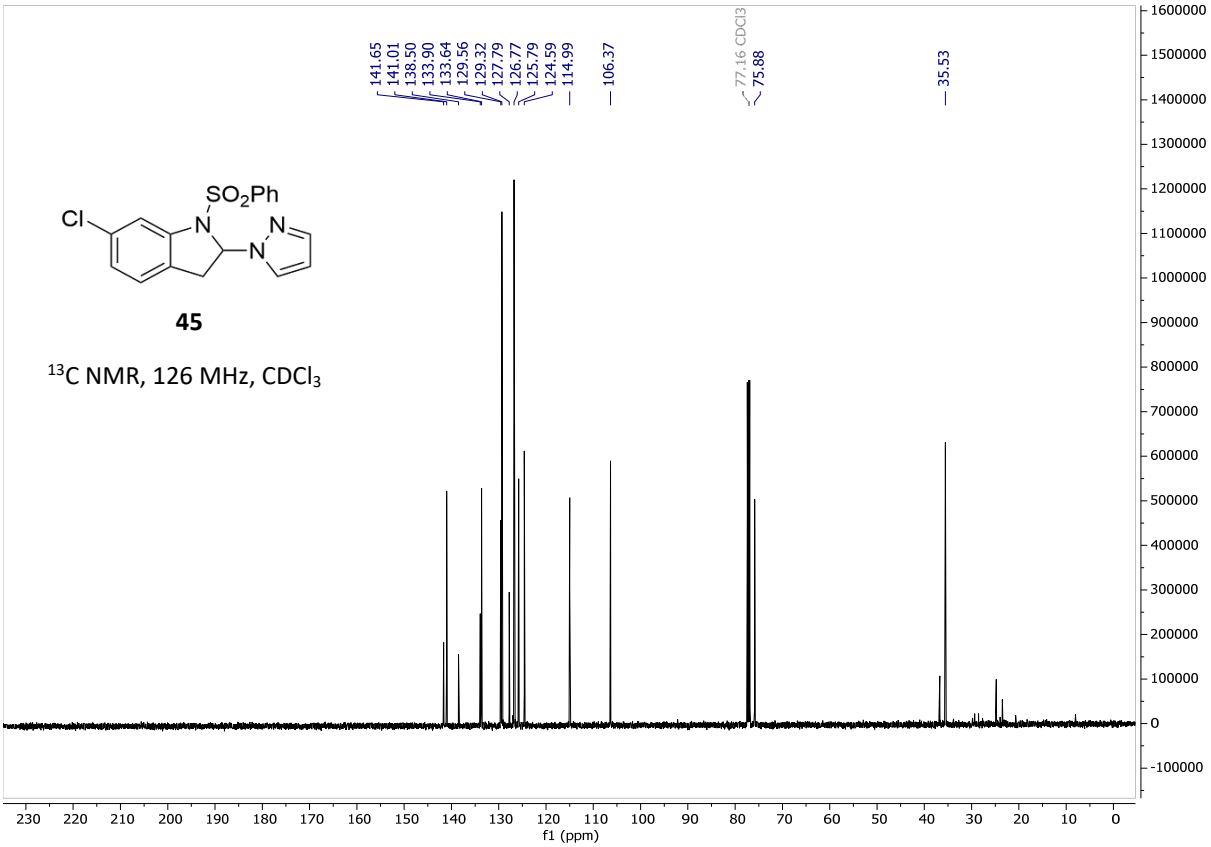

Boc
N
N
N
43
1H NMR, 500 MHz, DMSO-d6
7.69
7.69
7.41
7.41
7.13
7.13
7.12
7.12
7.10
7.04
7.04
7.03
7.02
7.02
7.00
6.68
6.68
6.66
6.66
6.24
6.23
3.80
3.78
3.77
3.75
3.33
3.30
2.50 DMSO-d6
2.18
1.51
1.00
0.95
1.02
1.99
1.02
0.99
1.04
1.04
3.03
9.18
f1 (ppm)

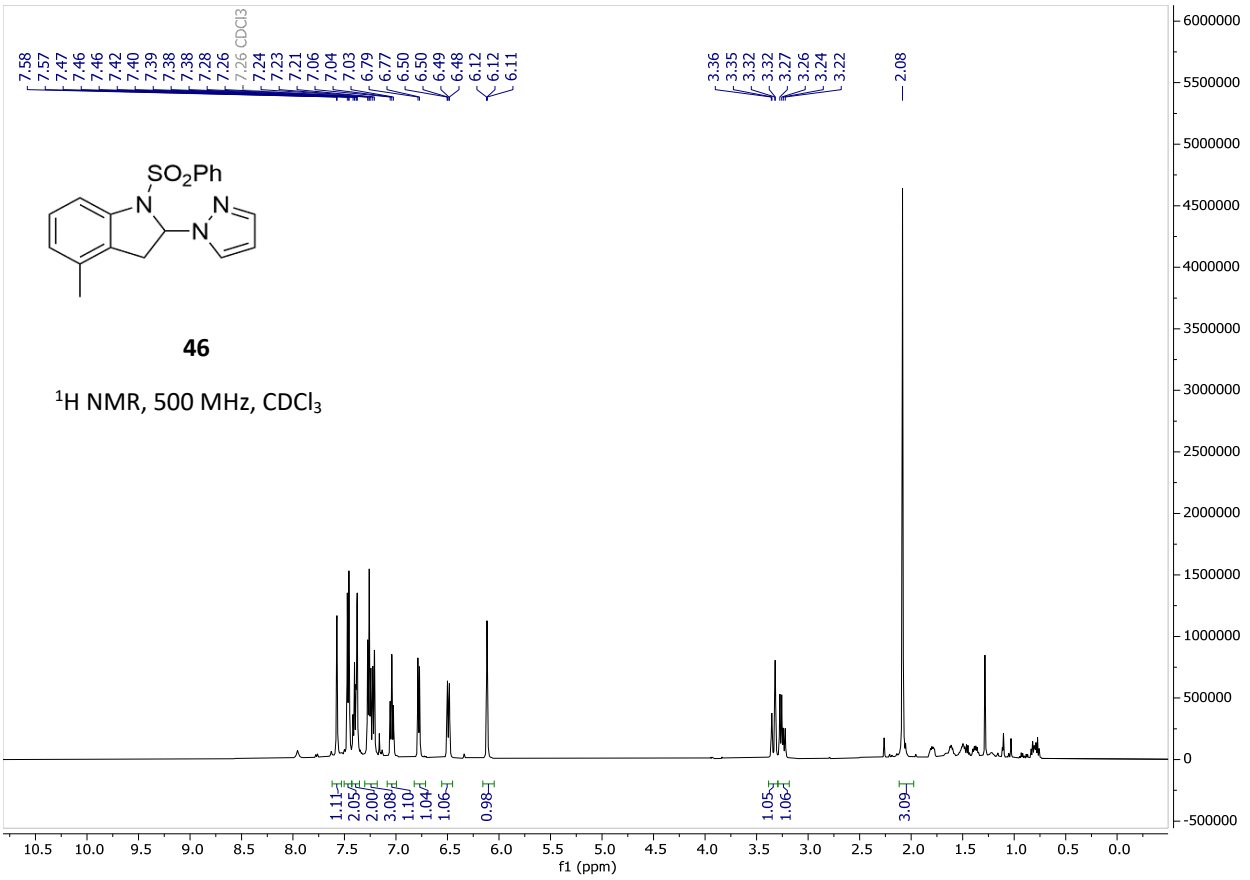

Boc
N
N
N
43
13C NMR, 126 MHz, DMSO-d6
152.24
139.99
139.48
131.88
129.65
128.78
126.67
124.51
121.75
105.40
81.45
75.63
39.52 DMSO-d6
35.71
27.82
19.83
f1 (ppm)


7.97
7.97
7.69
7.69
7.68
7.67
7.57
7.57
7.56
7.45
7.43
7.41
7.40
7.39
7.33
7.32
7.28
7.27
7.26
7.26 CDCl3
7.24
7.16
7.16
7.14
6.53
6.52
6.52
6.50
6.50
6.12
6.11
6.11
3.81
3.80
3.50
3.46
3.43
3.42
3.41
3.39
3.37
SO2Ph
MeOOC
N
N
N
44
1H NMR, 500 MHz, CDCl3
1.00
1.03
1.18
3.14
1.08
2.11
1.19
1.06
1.03
3.13
1.04
1.06
f1 (ppm)


166.58
141.00
140.90
138.53
134.72
133.59
130.57
129.61
129.28
126.84
126.37
124.91
115.28
106.36
77.16 CDCl3
75.58
52.39
35.99
SO2Ph
MeOOC
N
N
N
44
13C NMR, 126 MHz, CDCl3
f1 (ppm)

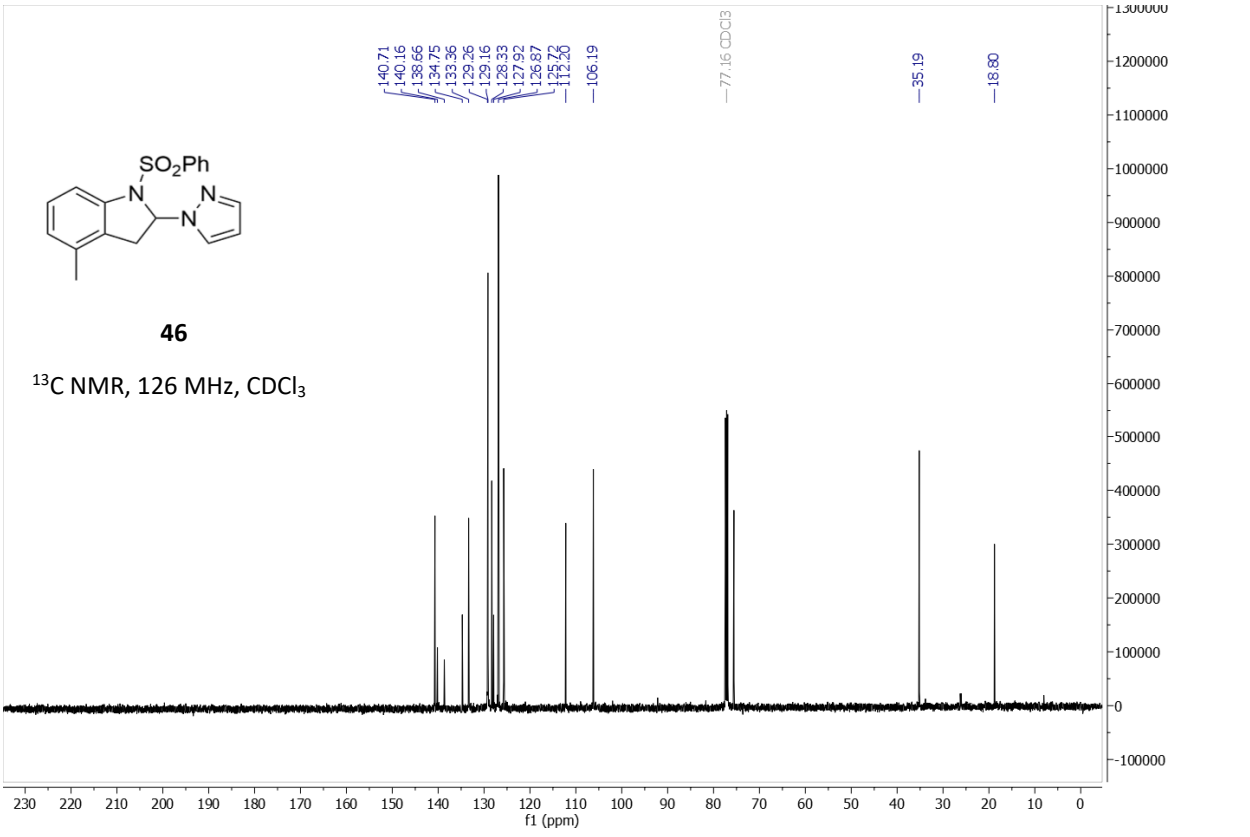

7.65
7.54
7.53
7.51
7.45
7.44
7.40
7.38
7.37
7.26 CDCl3
7.11
7.09
7.04
7.02
6.58
6.57
6.56
6.21
3.51
3.47
3.46
3.44
3.42
3.40
SO2Ph
Cl
N
N
N
45
1H NMR, 500 MHz, CDCl3
0.99
2.97
1.91
2.05
0.98
1.00
1.00
0.97
2.06
f1 (ppm)


141.65
141.01
138.50
133.90
133.64
129.56
129.32
127.79
126.77
125.79
124.59
114.99
106.37
77.16 CDCl3
75.88
35.53
SO2Ph
Cl
N
N
N
45
13C NMR, 126 MHz, CDCl3
f1 (ppm)



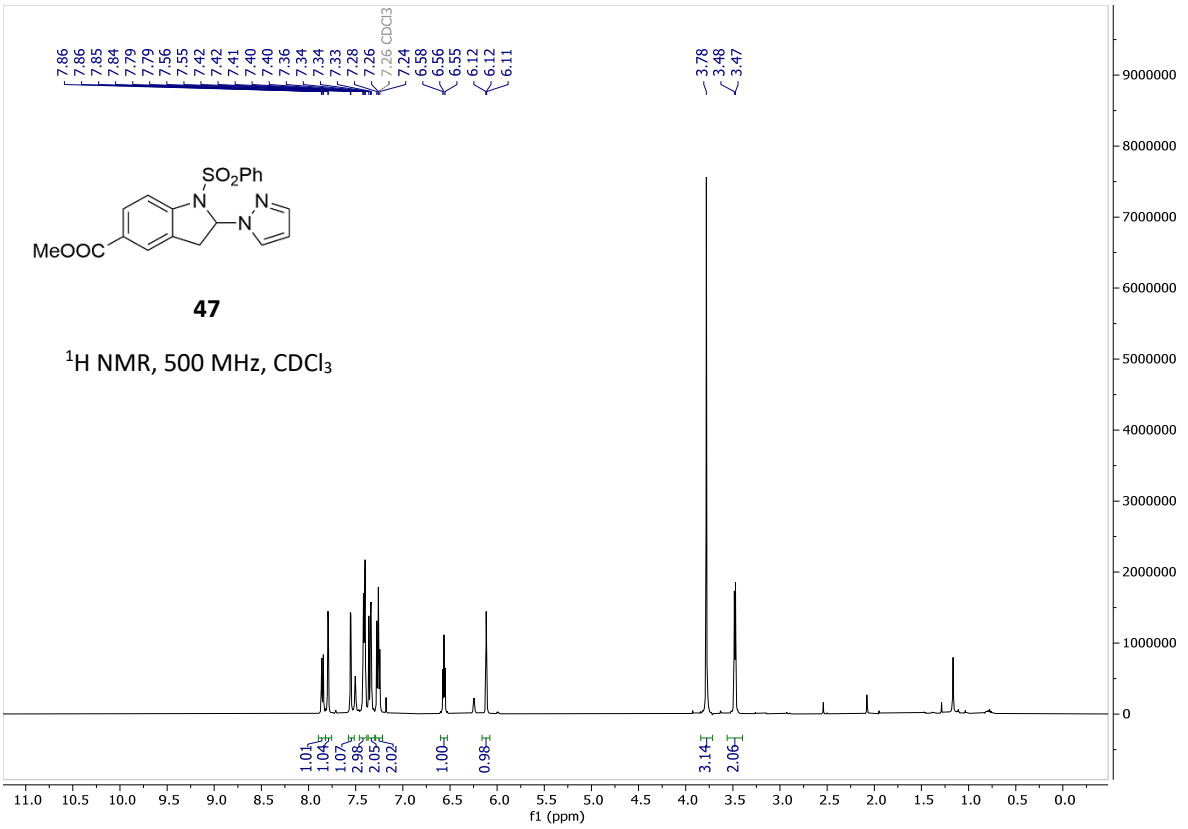
46

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



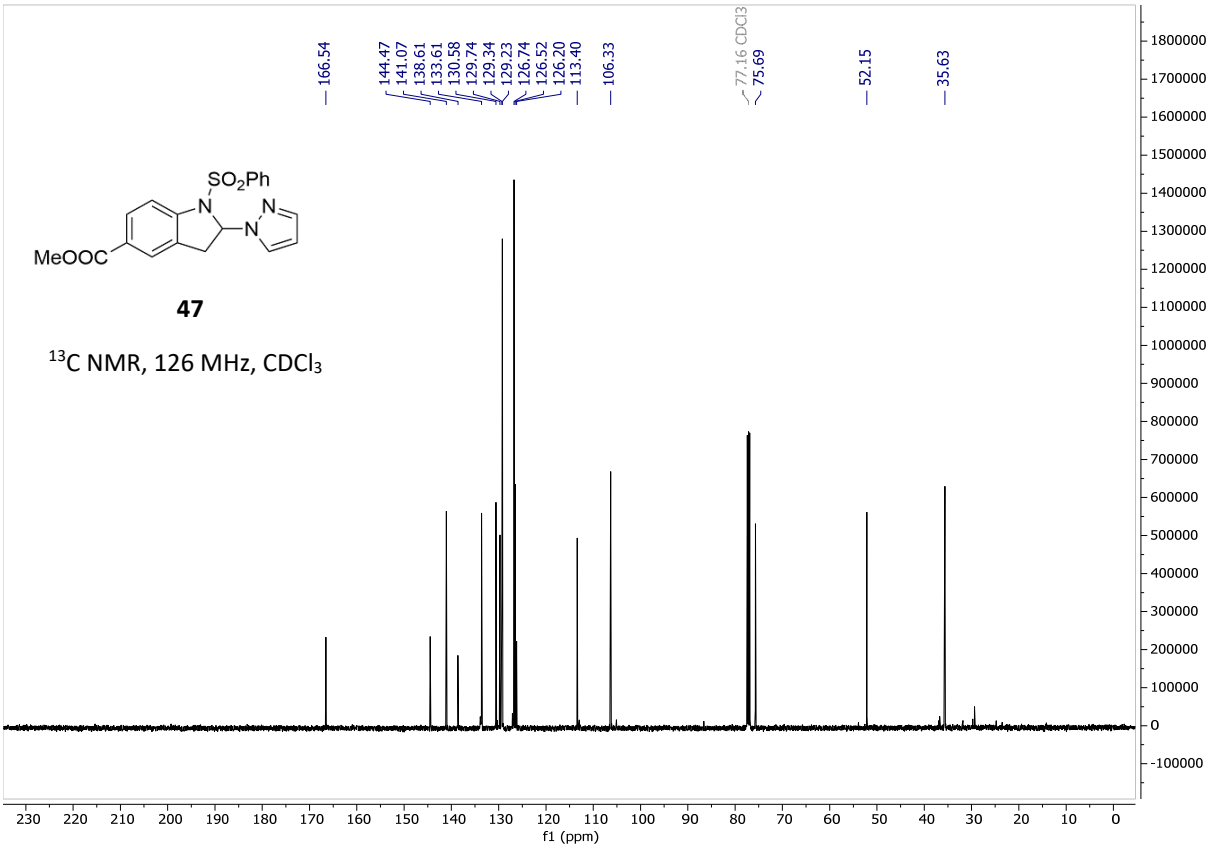
46

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



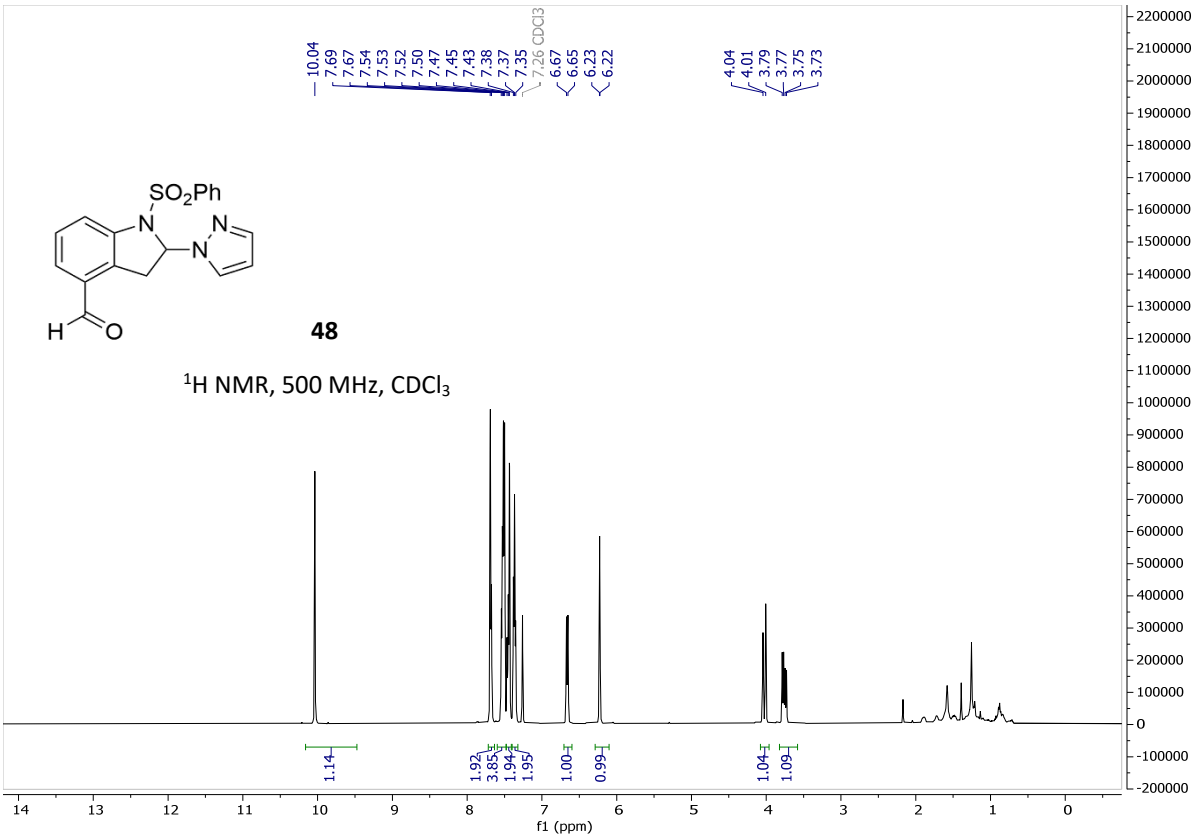
47

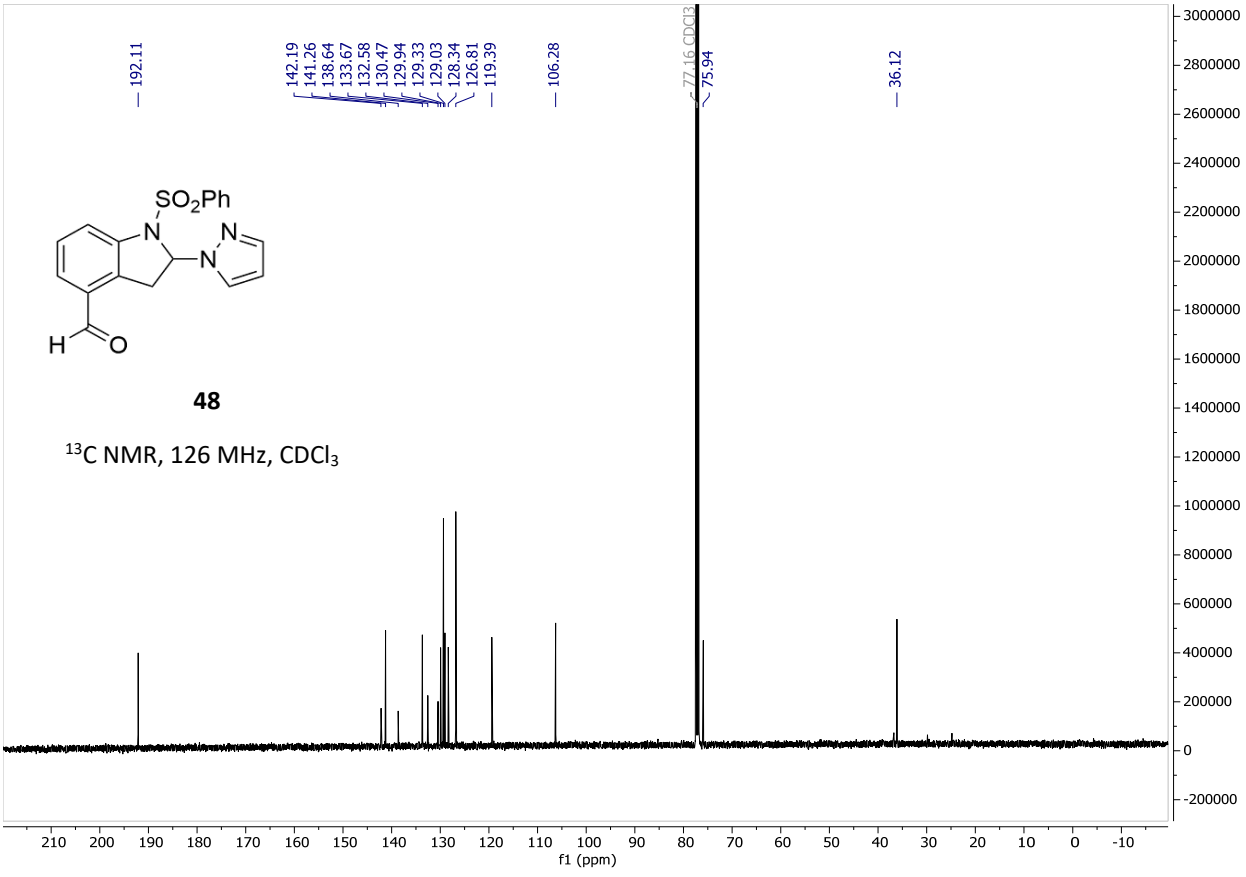
^{1}H NMR, 500 MHz, $CDCl_3$

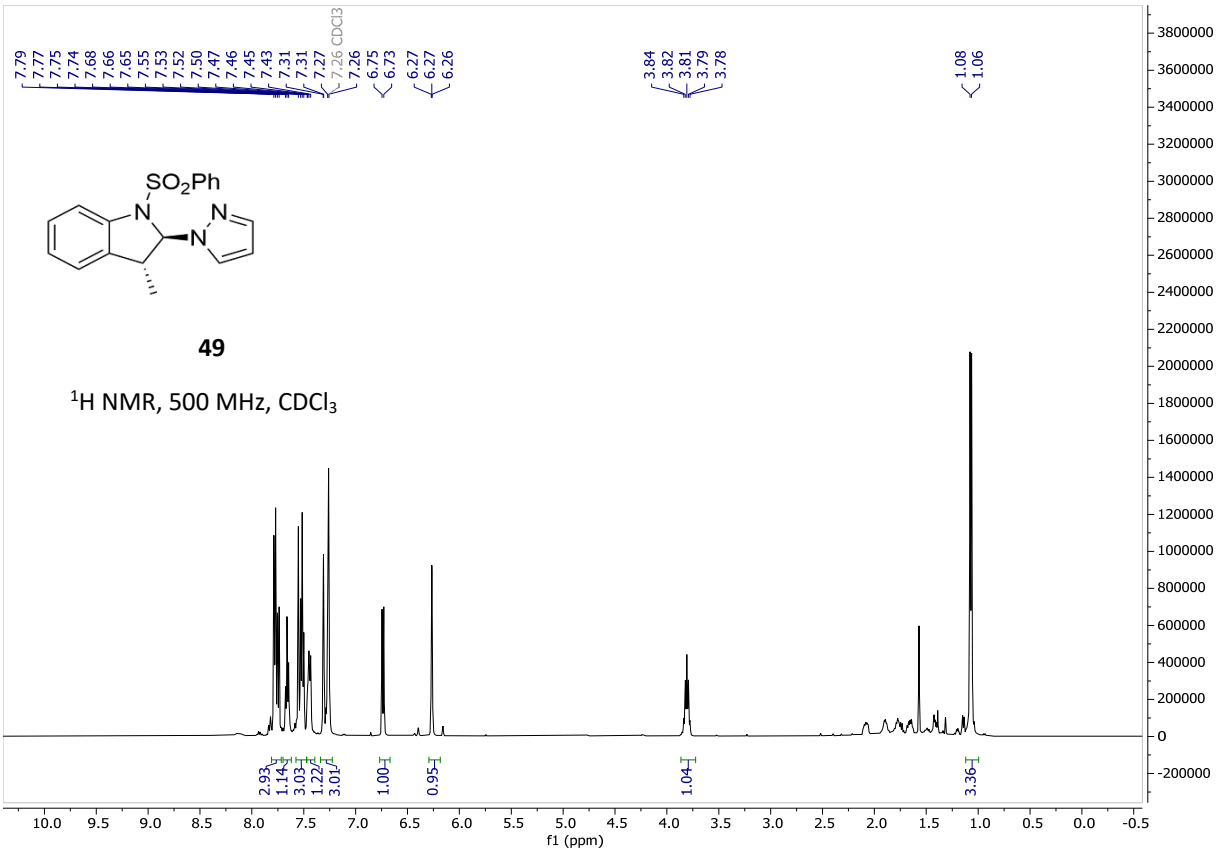


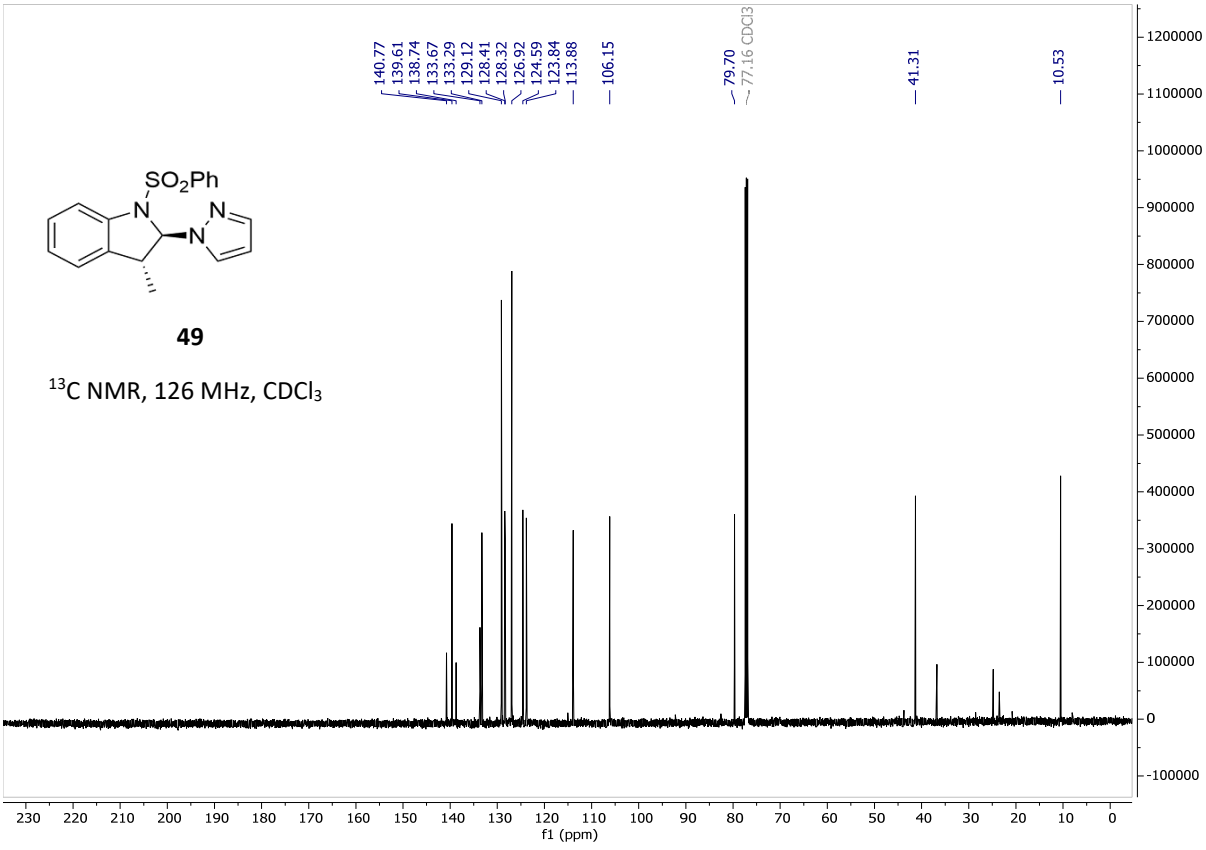
47

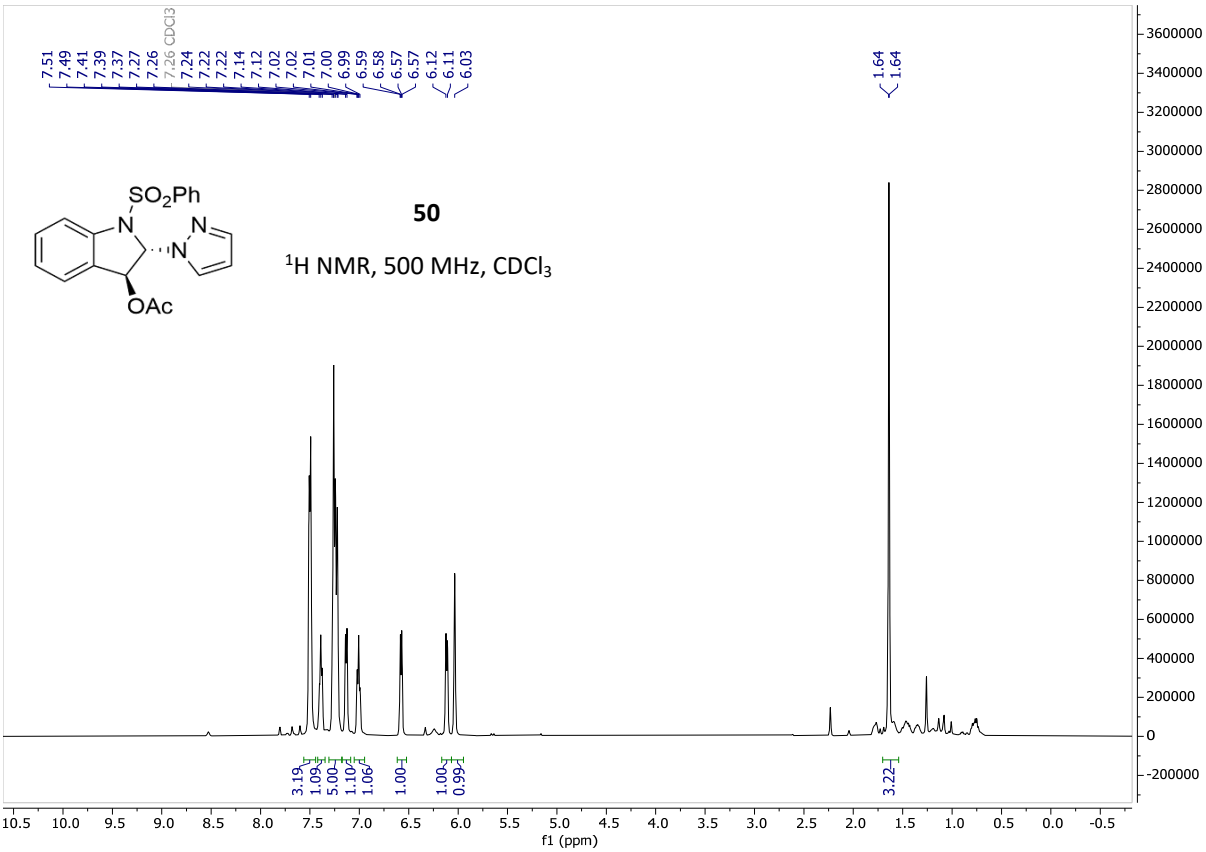
^{13}C NMR, 126 MHz, $CDCl_3$

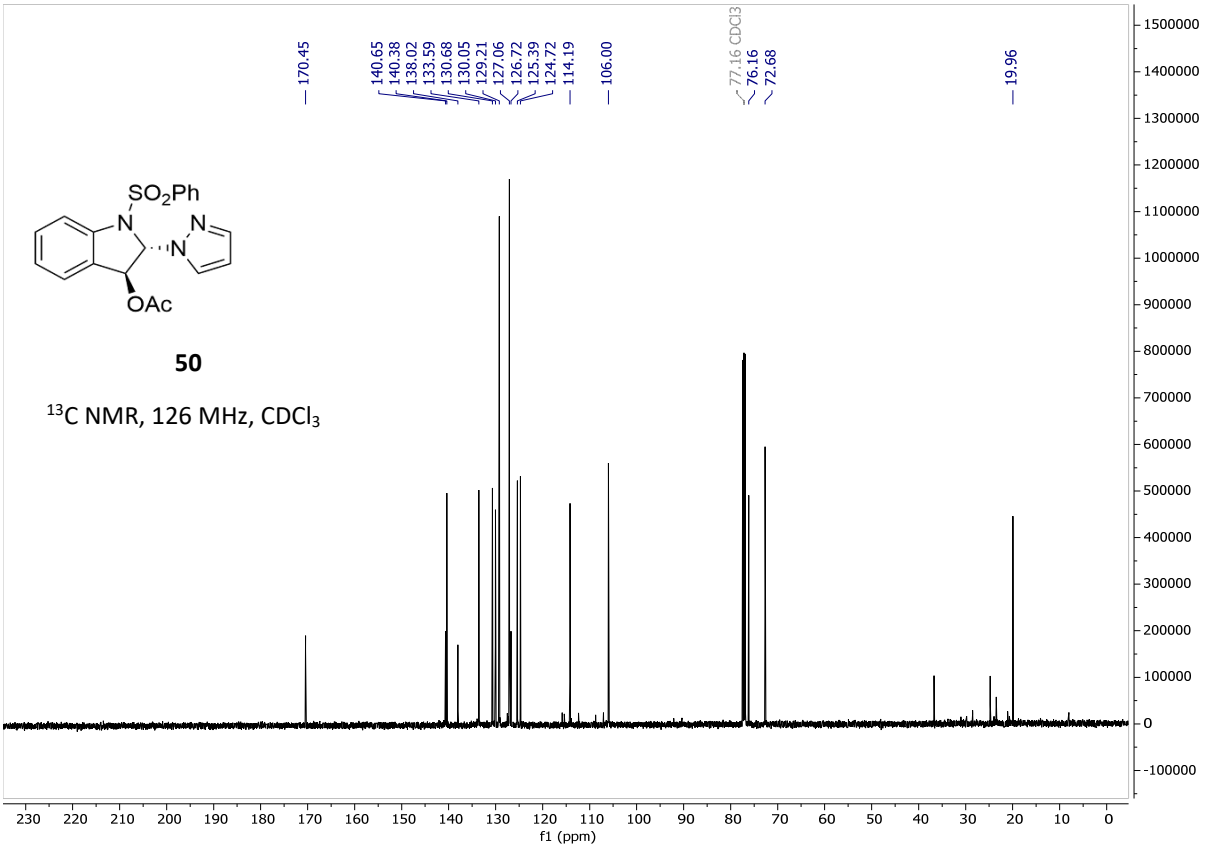

10.04
7.69
7.67
7.54
7.53
7.52
7.50
7.47
7.45
7.43
7.38
7.37
7.35
7.26 CDCl3
6.67
6.65
6.23
6.22
4.04
4.01
3.79
3.77
3.75
3.73
SO2Ph
N
N
N
H
O
48
1H NMR, 500 MHz, CDCl3
1.14
1.92
3.85
1.94
1.95
1.00
0.99
1.04
1.09
f1 (ppm)

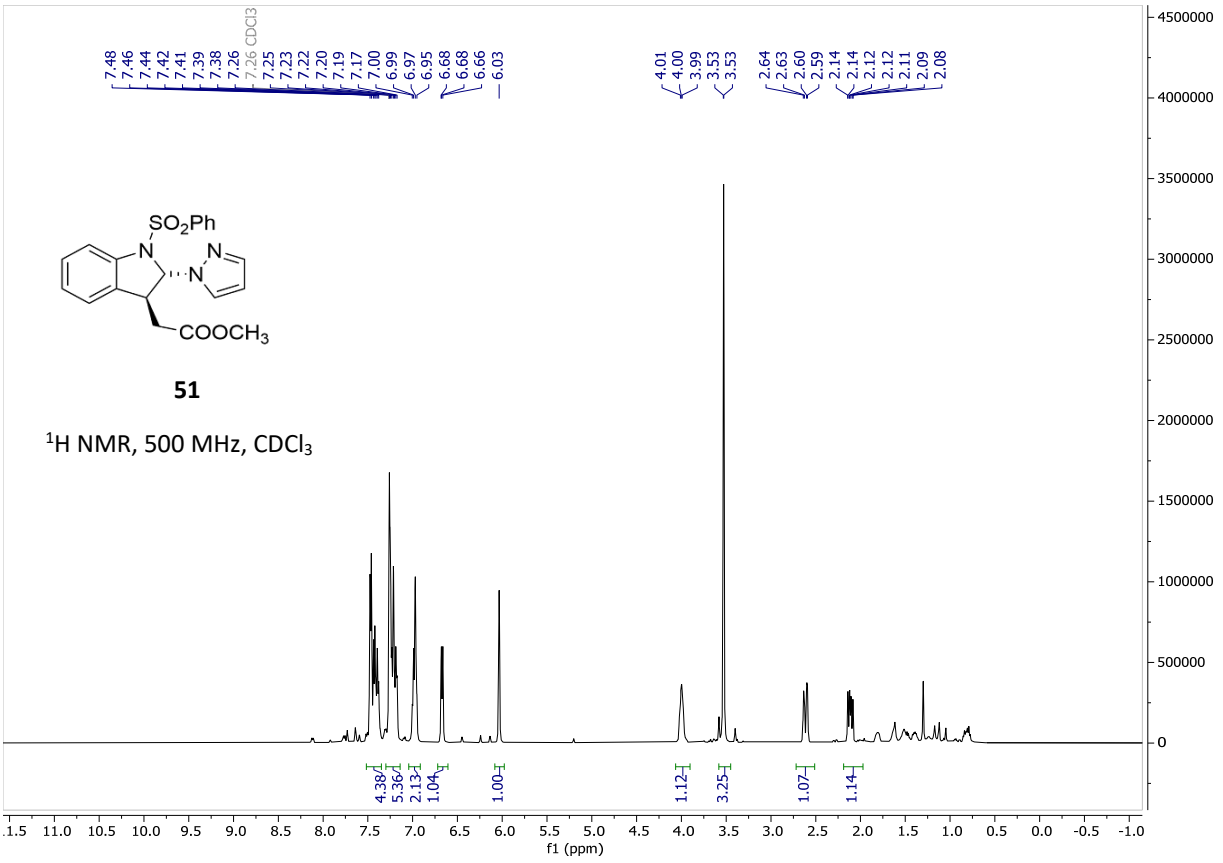

192.11
142.19
141.26
138.64
133.67
132.58
130.47
129.94
129.33
129.03
128.34
126.81
119.39
106.28
77.16 CDCl3
75.94
36.12
SO2Ph
N
N
N
H
O
48
13C NMR, 126 MHz, CDCl3
f1 (ppm)


7.79
7.77
7.75
7.74
7.68
7.66
7.65
7.55
7.53
7.52
7.50
7.47
7.46
7.45
7.43
7.31
7.31
7.27
7.26 CDCl3
7.26
6.75
6.73
6.27
6.27
6.26
3.84
3.82
3.81
3.79
3.78
1.08
1.06
SO2Ph
N
N
N
49
1H NMR, 500 MHz, CDCl3
2.93
1.14
3.03
1.22
3.01
1.00
0.95
1.04
3.36
f1 (ppm)


140.77
139.61
138.74
133.67
133.29
129.12
128.41
128.32
126.92
124.59
123.84
113.88
106.15
79.70
77.16 CDCl3
41.31
10.53
SO2Ph
N
N
N
49
13C NMR, 126 MHz, CDCl3
f1 (ppm)

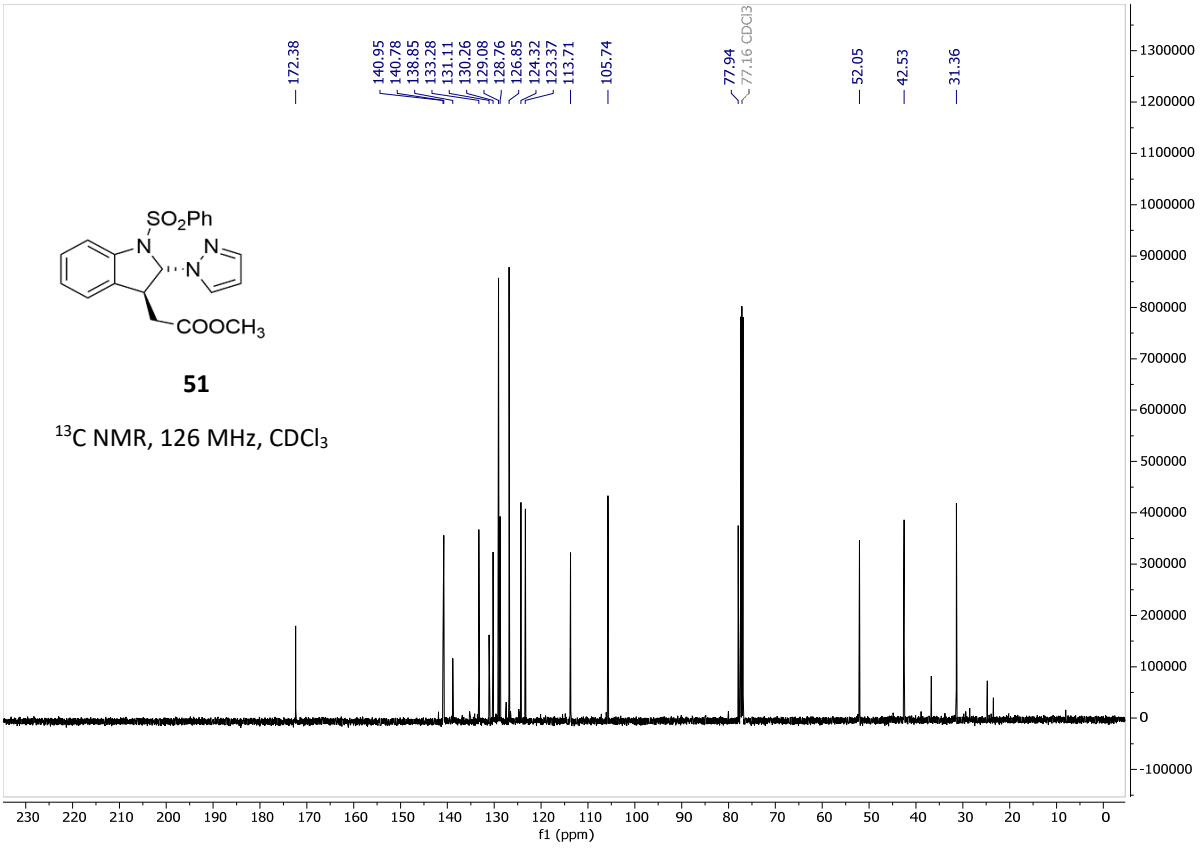

7.51
7.49
7.41
7.39
7.37
7.27
7.26
7.26 CDCl3
7.24
7.22
7.22
7.14
7.12
7.02
7.02
7.01
7.00
6.99
6.59
6.58
6.57
6.57
6.12
6.11
6.03
1.64
1.64
SO2Ph
N
N
N
OAc
50
1H NMR, 500 MHz, CDCl3
3.19
1.09
5.00
1.10
1.06
1.00
1.00
0.99
3.22
f1 (ppm)


170.45
140.65
140.38
138.02
133.59
130.68
130.05
129.21
127.06
126.72
125.39
124.72
114.19
106.00
77.16 CDCl3
76.16
72.68
19.96
SO2Ph
N
N
N
OAc
50
13C NMR, 126 MHz, CDCl3
f1 (ppm)



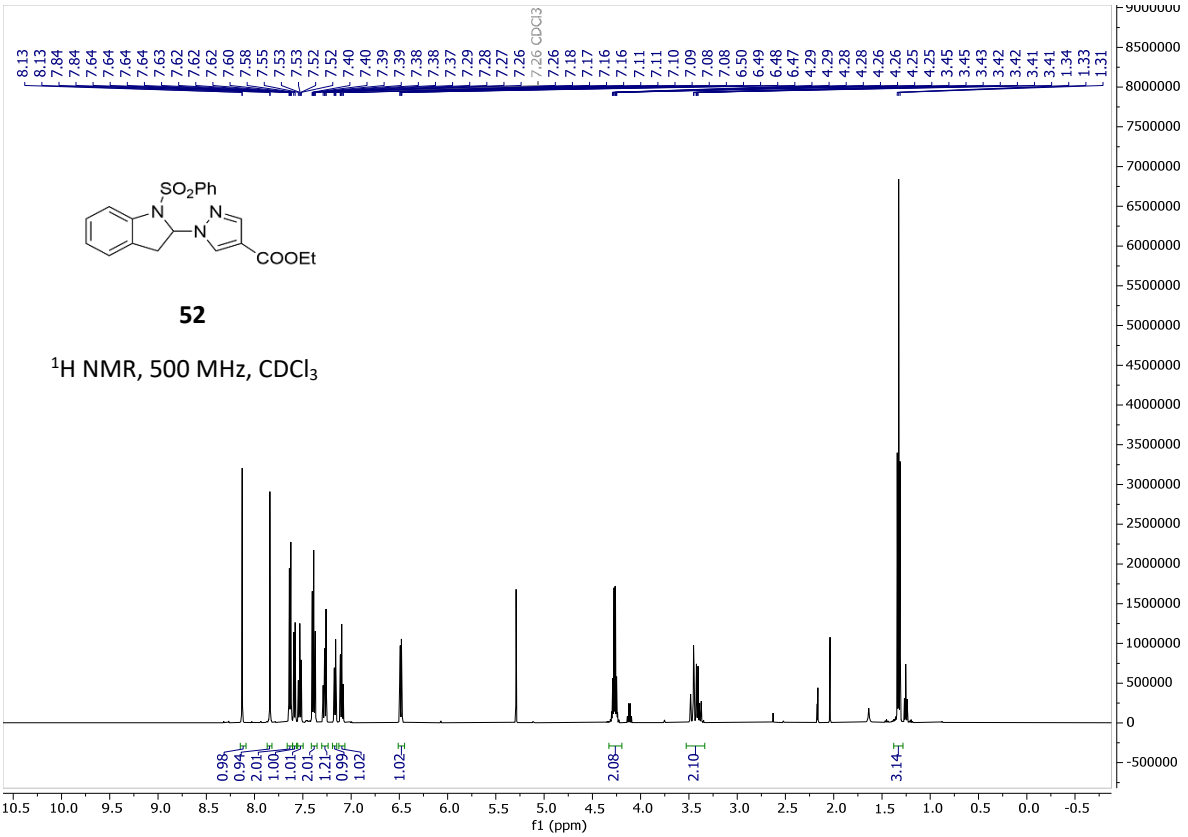
51

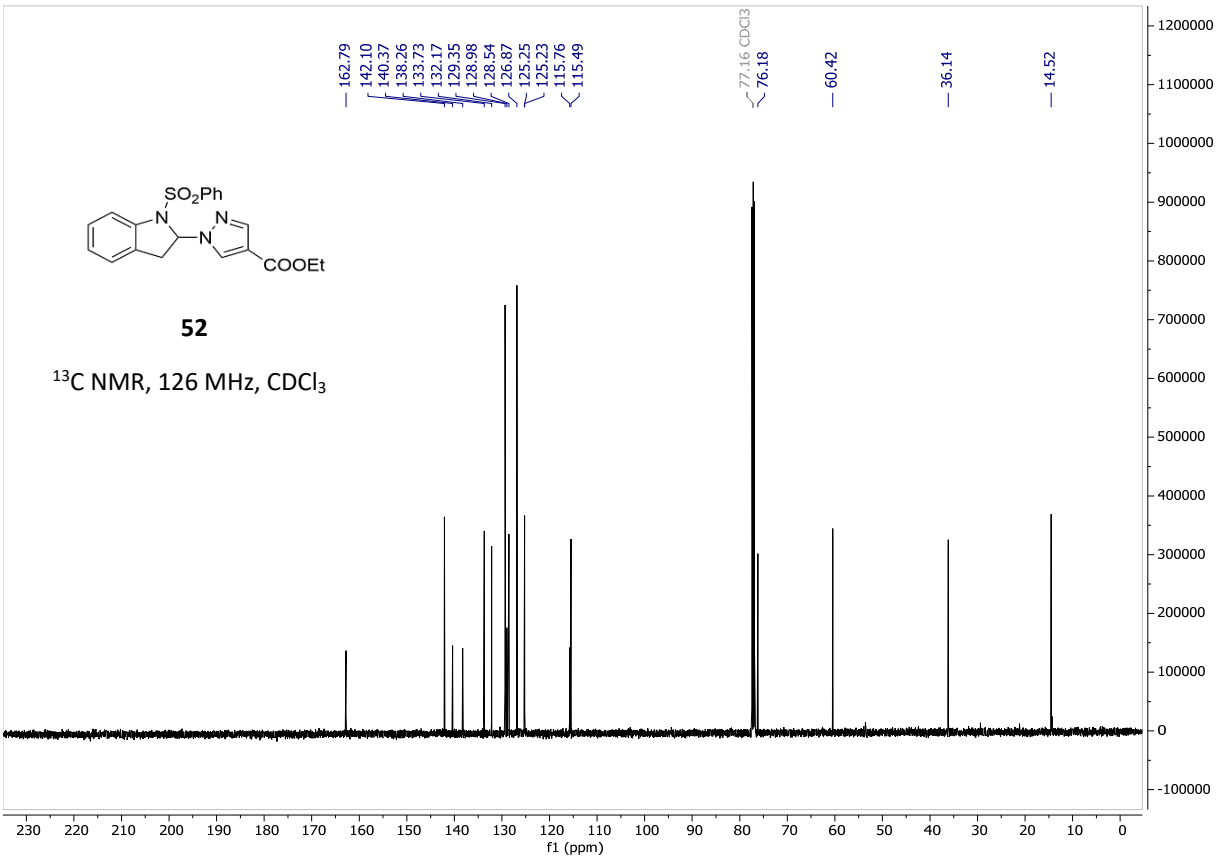
^{1}H NMR, 500 MHz, $CDCl_3$

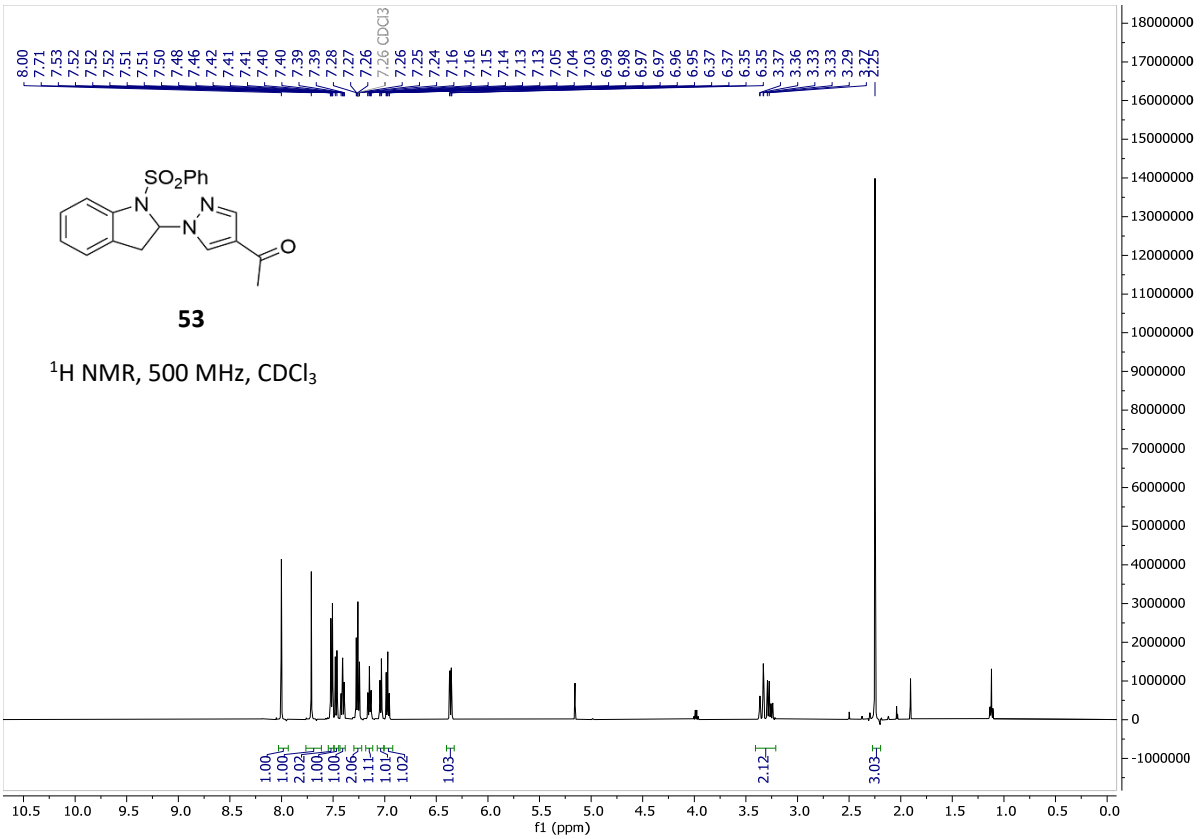


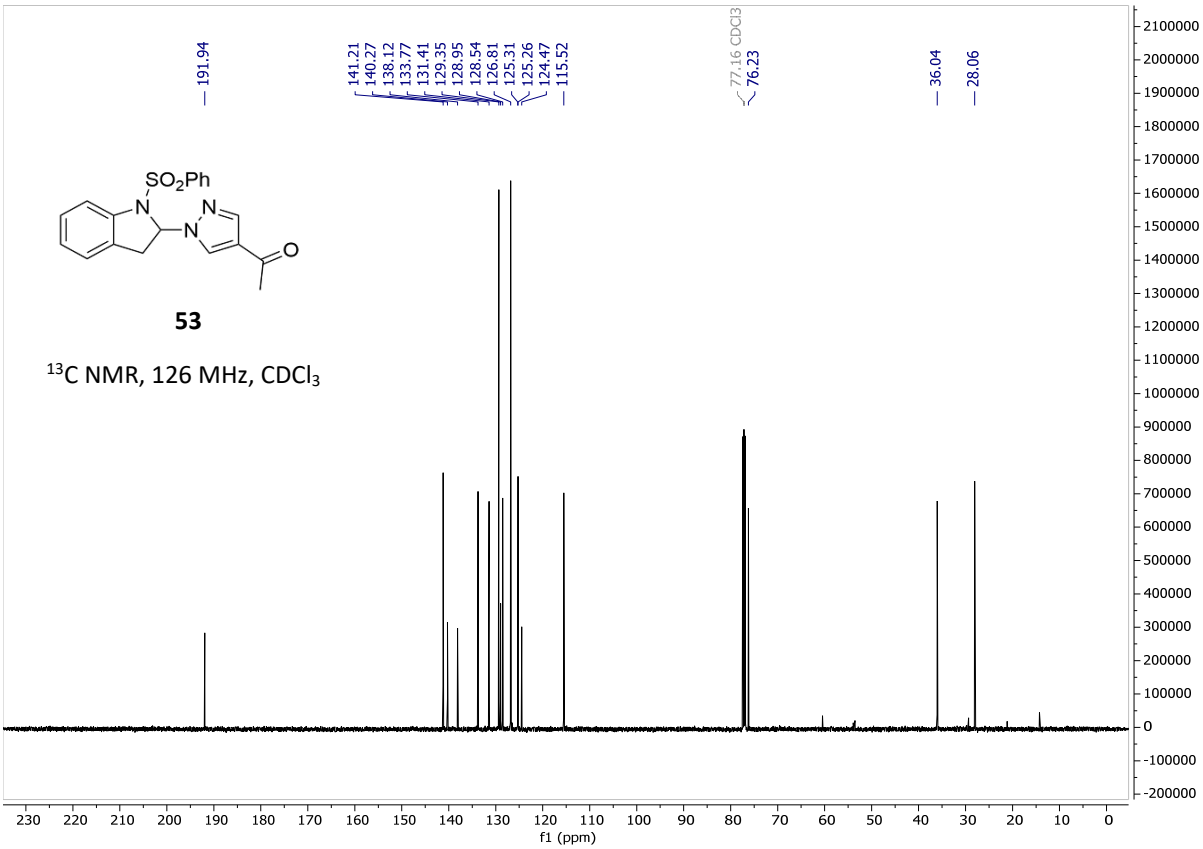
51

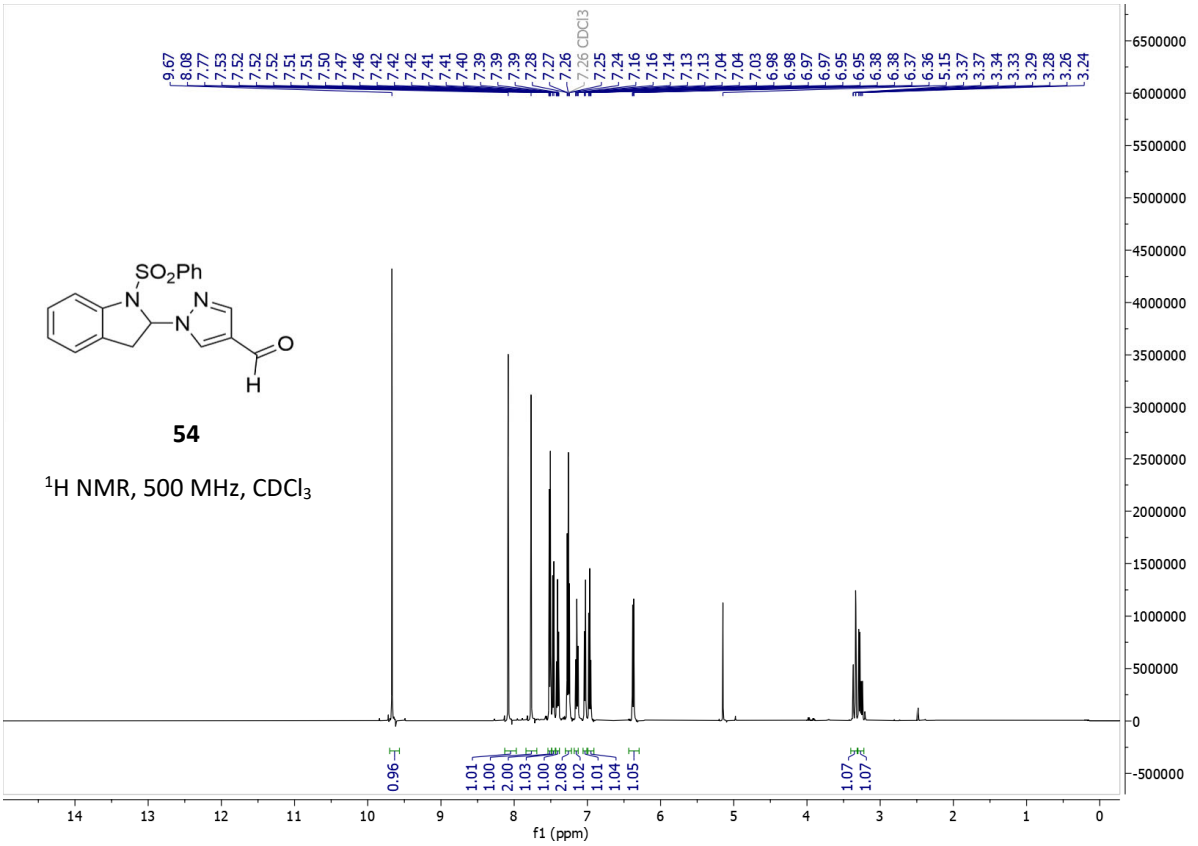
^{13}C NMR, 126 MHz, $CDCl_3$


SO2Ph
N
N
N
COOEt
52
1H NMR, 500 MHz, CDCl3
f1 (ppm)


SO2Ph
N
N
N
COOEt
52
13C NMR, 126 MHz, CDCl3
f1 (ppm)

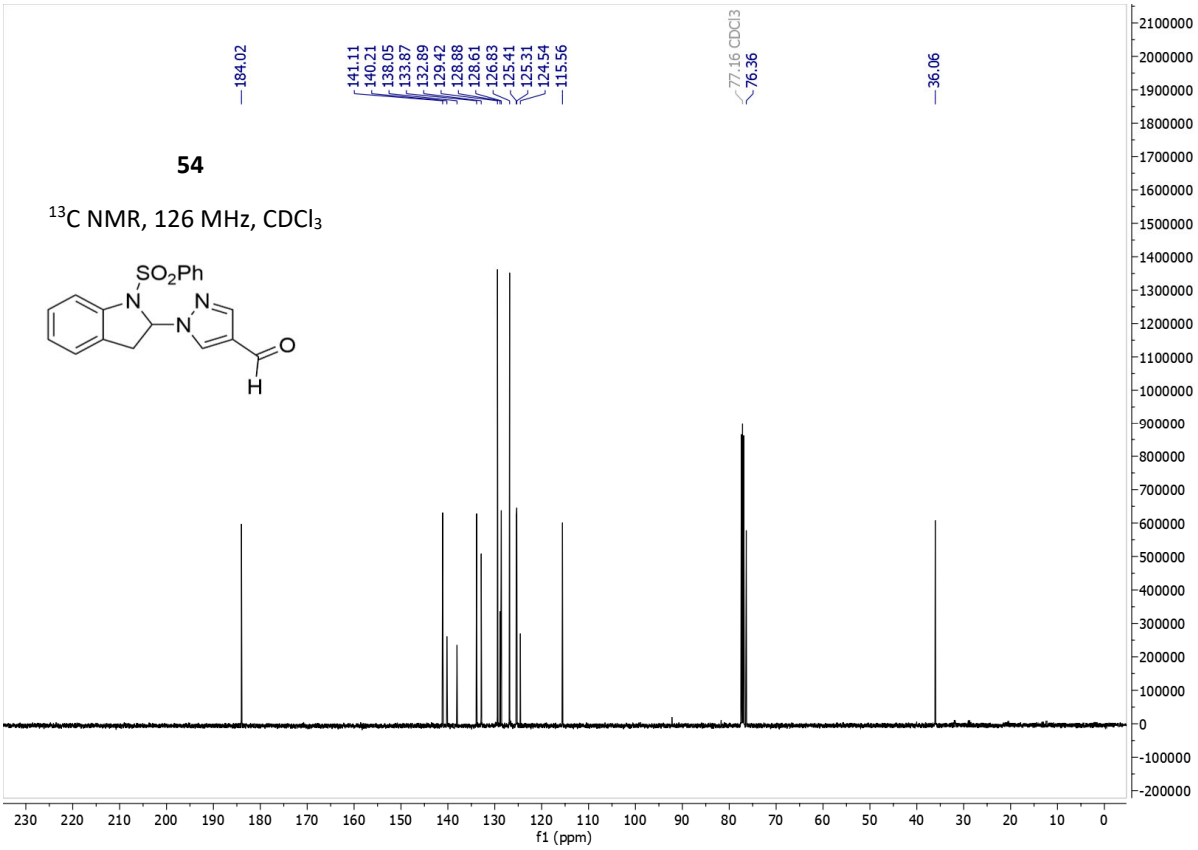

8.00 7.71 7.53 7.52 7.52 7.52 7.51 7.51 7.50 7.48 7.46 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.28 7.27 7.26 7.26 CDCl3 7.26 7.25 7.24 7.16 7.16 7.15 7.14 7.13 7.13 7.05 7.04 7.03 6.99 6.98 6.97 6.97 6.96 6.95 6.37 6.37 6.35 6.35 3.37 3.36 3.33 3.33 3.29 3.27 2.25
SO2Ph
N
N
N
O
53
1H NMR, 500 MHz, CDCl3
1.00 1.00 2.02 1.00 1.00 2.06 1.11 1.01 1.02 1.03 2.12 3.03
f1 (ppm)


191.94
141.21 140.27 138.12 133.77 131.41 129.35 128.95 128.54 126.81 125.31 125.26 124.47 115.52
77.16 CDCl3
76.23
36.04
28.06
SO2Ph
N
N
N
O
53
13C NMR, 126 MHz, CDCl3
f1 (ppm)



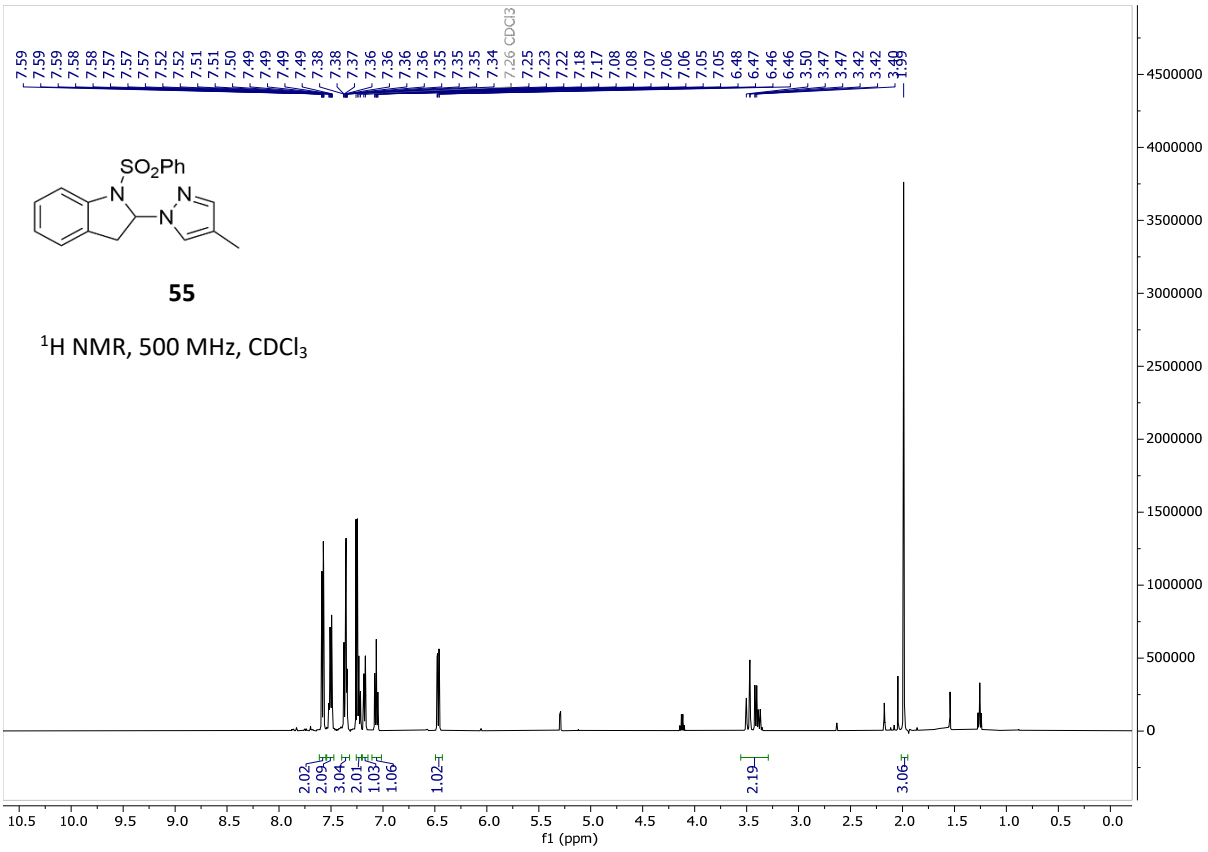
54

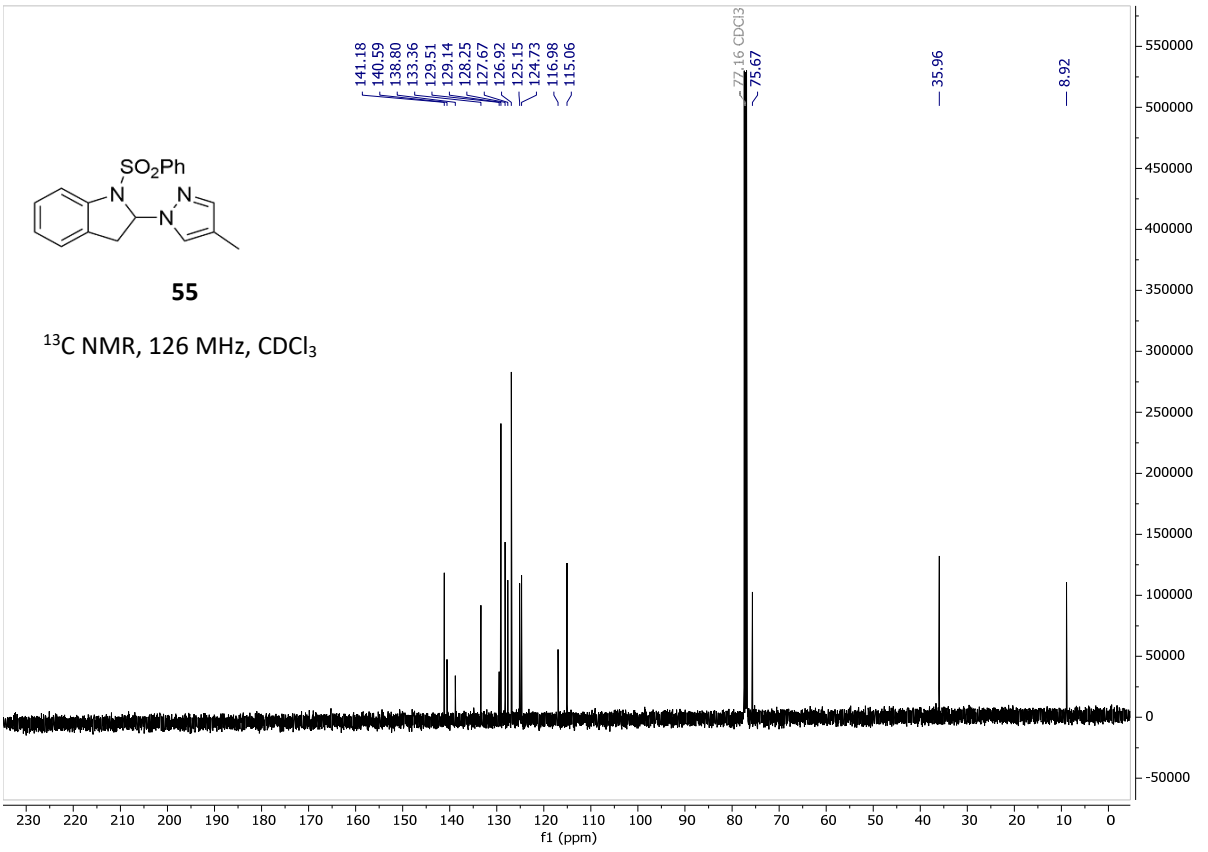
^{1}H NMR, 500 MHz, $CDCl_3$

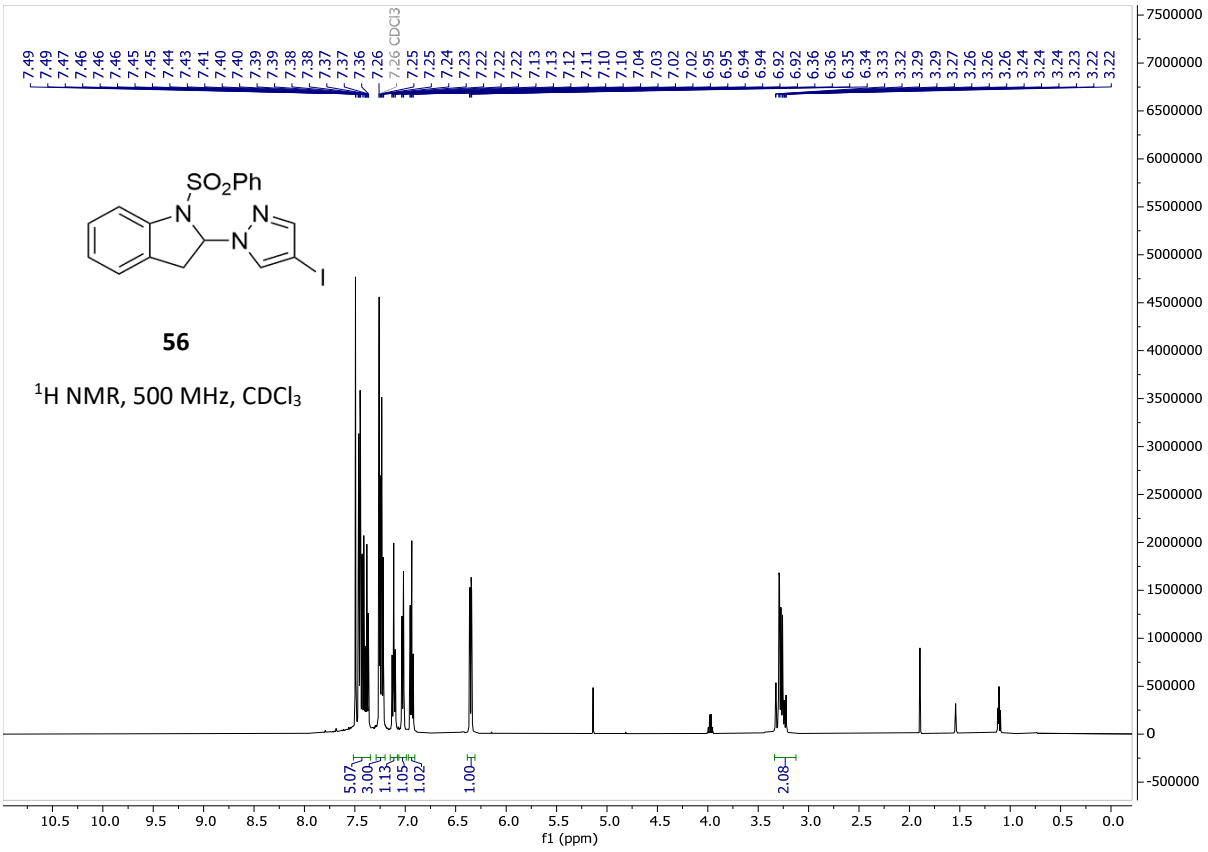


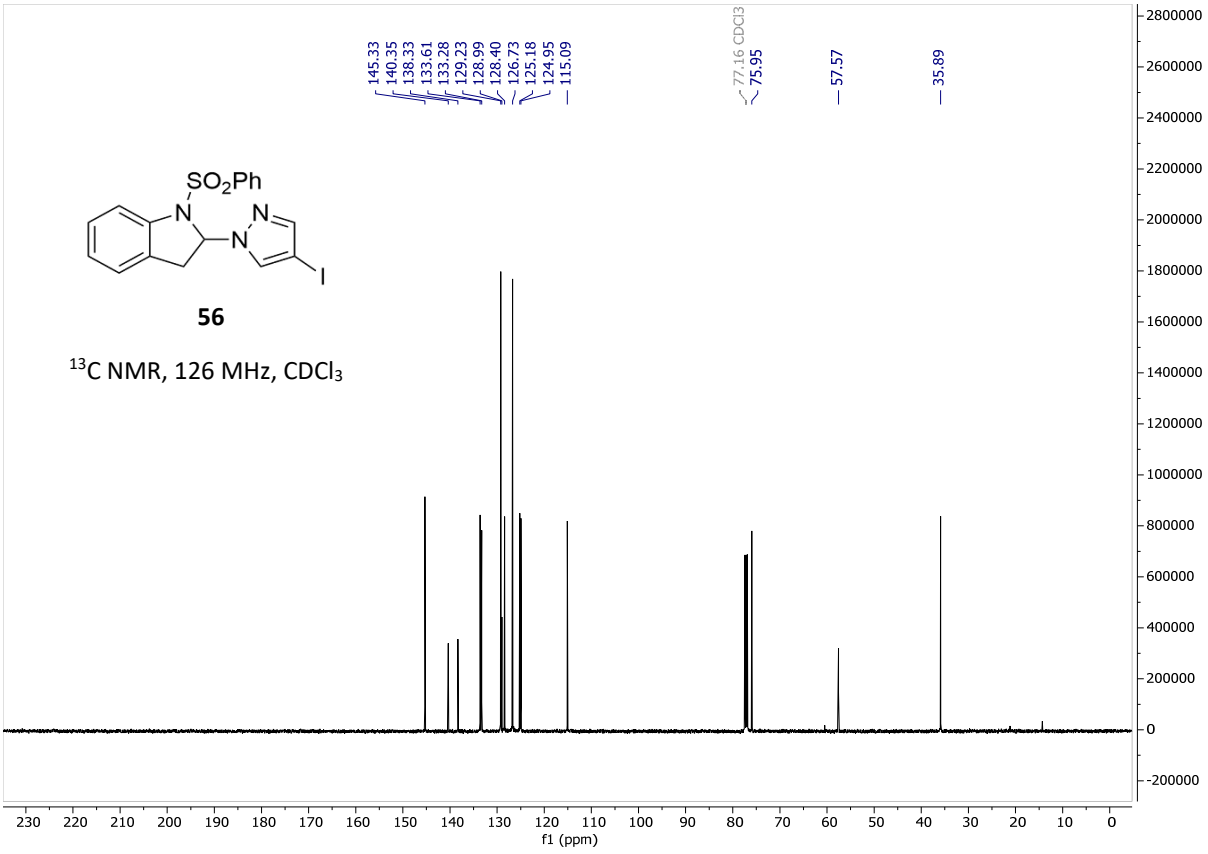
54

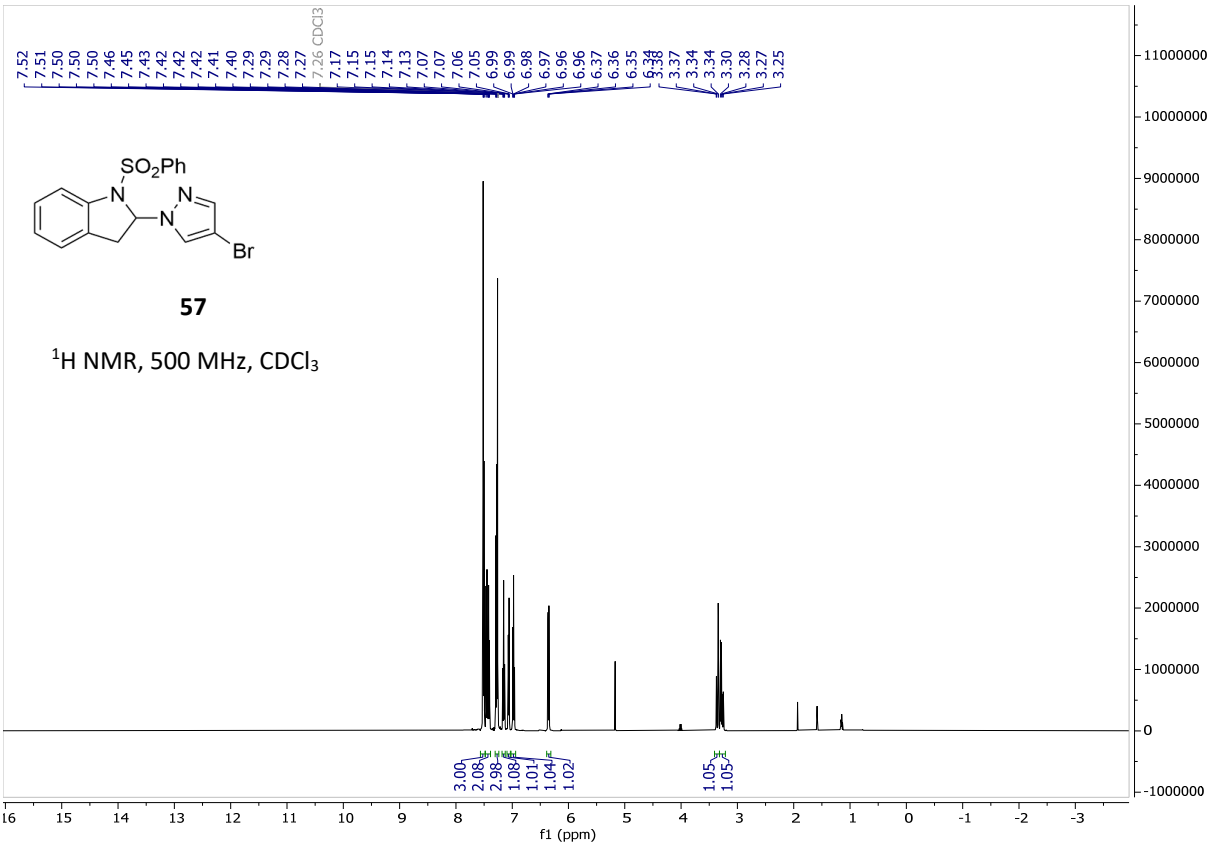
^{13}C NMR, 126 MHz, $CDCl_3$

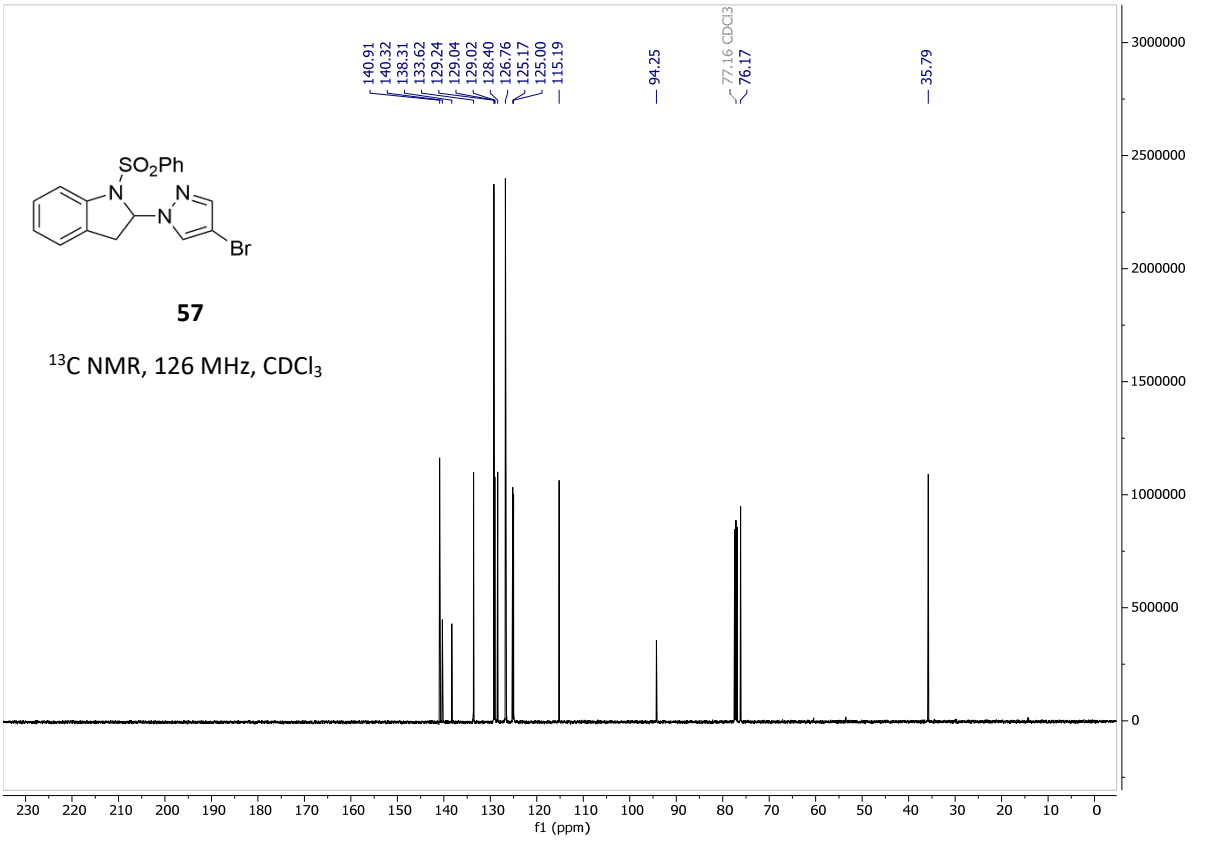

7.59 7.59 7.59 7.58 7.58 7.57 7.57 7.57 7.52 7.51 7.51 7.50 7.49 7.49 7.49 7.38 7.38 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.26 CDCl3 7.25 7.23 7.22 7.18 7.17 7.08 7.08 7.07 7.06 7.06 7.05 7.05 6.48 6.47 6.46 6.46 3.50 3.47 3.47 3.42 3.42 3.40 3.39 1.99
SO2Ph
N
N
N
55
1H NMR, 500 MHz, CDCl3
2.02 2.09 3.04 2.01 1.03 1.06 1.02 2.19 3.06
f1 (ppm)

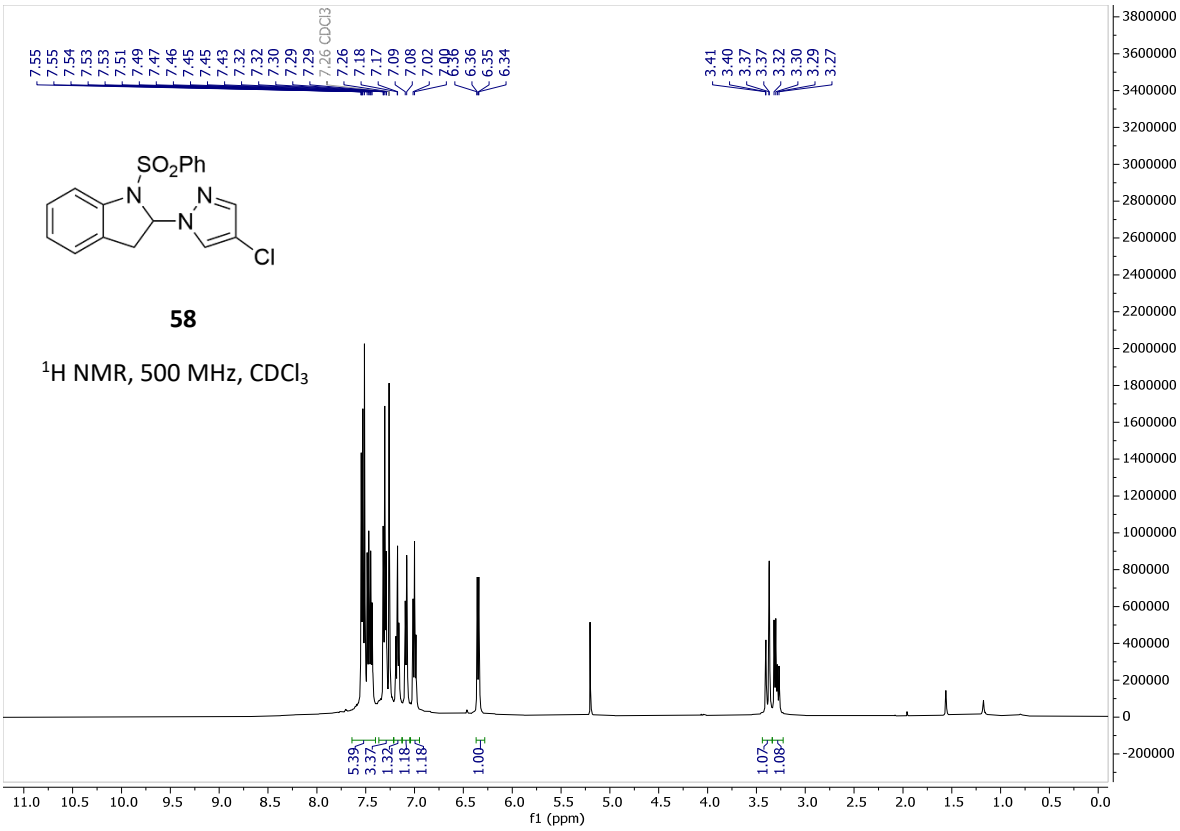

141.18 140.59 138.80 133.36 129.51 129.14 128.25 127.67 126.92 125.15 124.73 116.98 115.06
77.16 CDCl3
75.67
35.96
8.92
SO2Ph
N
N
N
55
13C NMR, 126 MHz, CDCl3
f1 (ppm)

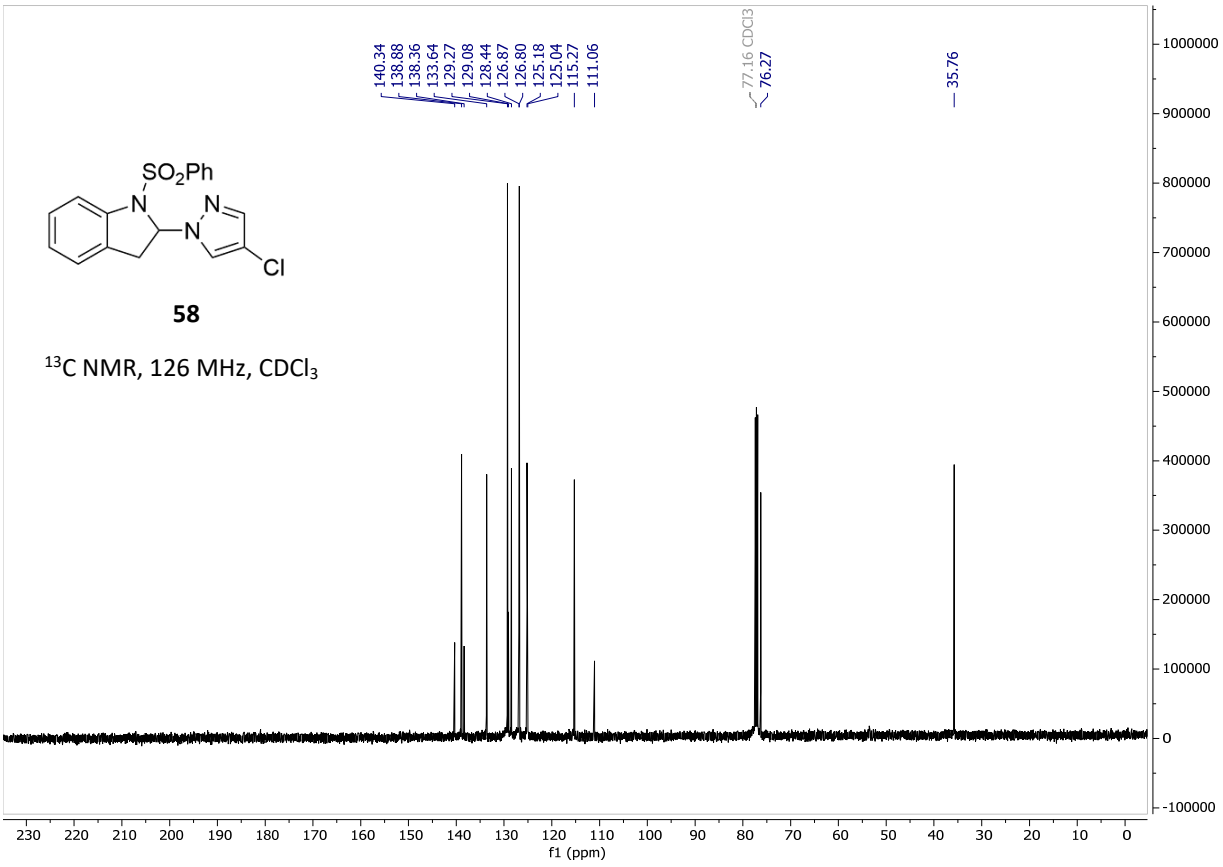

SO2Ph
N
N
N
I
56
1H NMR, 500 MHz, CDCl3
f1 (ppm)

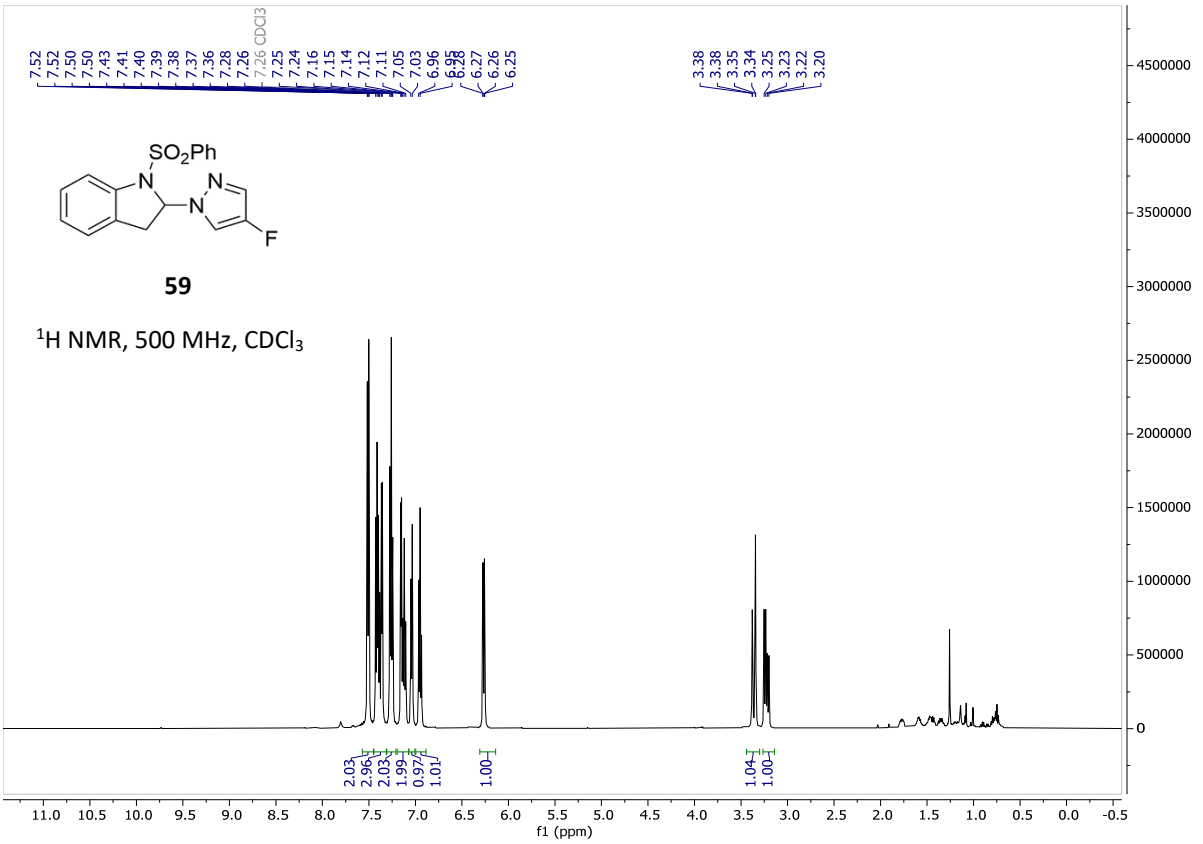

SO2Ph
N
N
N
I
56
13C NMR, 126 MHz, CDCl3
f1 (ppm)

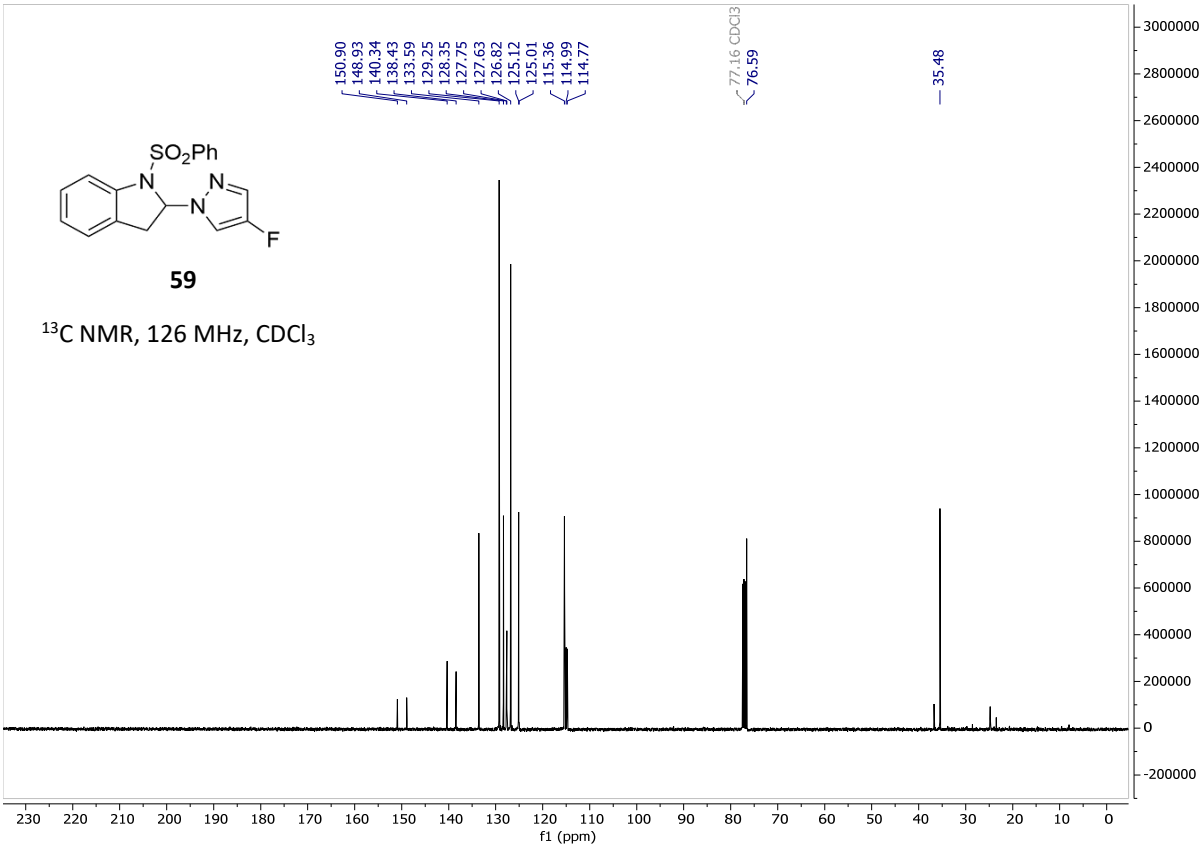

7.52
7.51
7.50
7.50
7.50
7.46
7.45
7.43
7.42
7.42
7.42
7.41
7.40
7.29
7.29
7.28
7.27
7.26 CDCl3
7.17
7.15
7.15
7.14
7.13
7.07
7.07
7.06
7.05
6.99
6.99
6.98
6.97
6.96
6.96
6.96
6.37
6.36
6.35
6.34
6.34
3.38
3.37
3.34
3.34
3.30
3.28
3.27
3.25
SO2Ph
N
N
N
Br
57
1H NMR, 500 MHz, CDCl3
3.00
2.08
2.98
1.08
1.01
1.04
1.02
1.05
1.05
f1 (ppm)

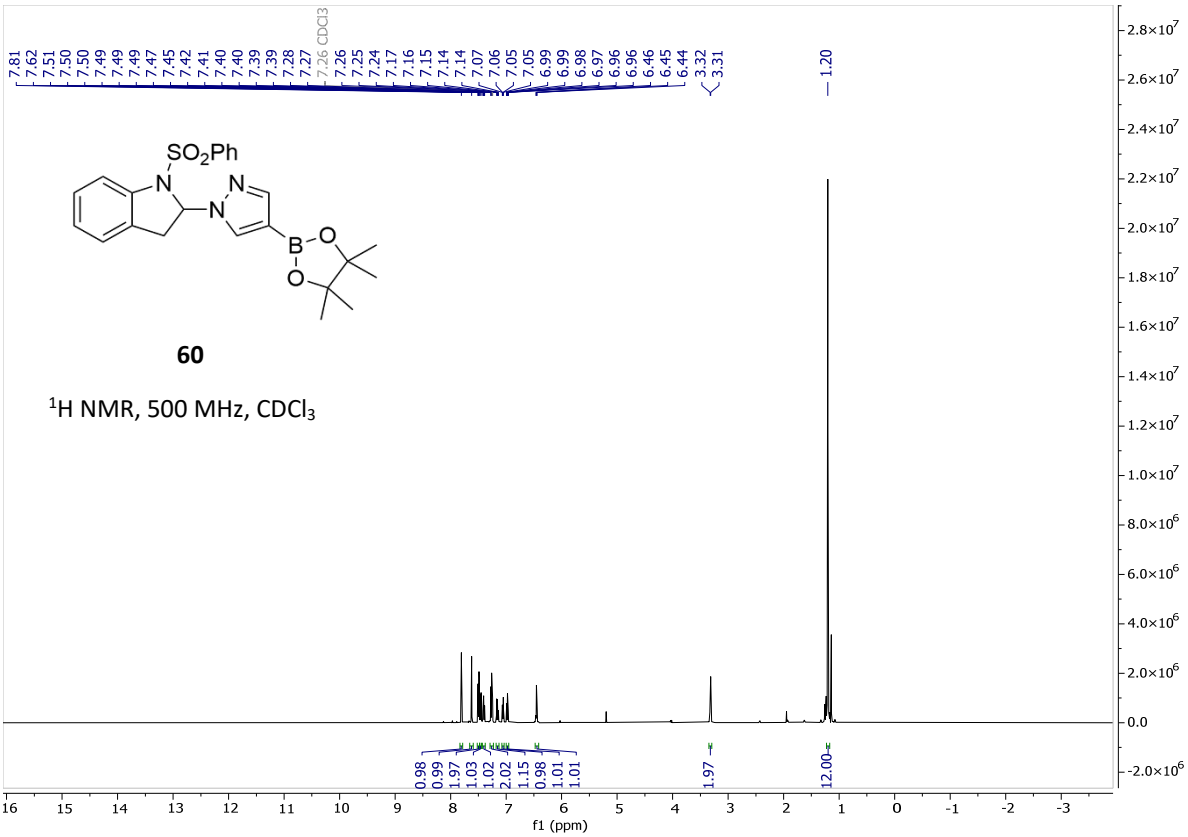

140.91
140.32
138.31
133.62
129.24
129.04
129.02
128.40
126.76
125.17
125.00
115.19
94.25
77.16 CDCl3
76.17
35.79
SO2Ph
N
N
N
Br
57
13C NMR, 126 MHz, CDCl3
f1 (ppm)


7.55
7.55
7.54
7.53
7.53
7.51
7.49
7.47
7.46
7.45
7.45
7.43
7.32
7.32
7.30
7.29
7.29
7.26 CDCl3
7.26
7.18
7.17
7.09
7.08
7.02
6.38
6.36
6.35
6.34
3.41
3.40
3.37
3.37
3.32
3.30
3.29
3.27
SO2Ph
N
N
N
Cl
58
1H NMR, 500 MHz, CDCl3
5.39
3.37
1.32
1.18
1.18
1.00
1.07
1.08
f1 (ppm)


140.34
138.88
138.36
133.64
129.27
129.08
128.44
126.87
126.80
125.18
125.04
115.27
111.06
77.16 CDCl3
76.27
35.76
SO2Ph
N
N
N
Cl
58
13C NMR, 126 MHz, CDCl3
f1 (ppm)

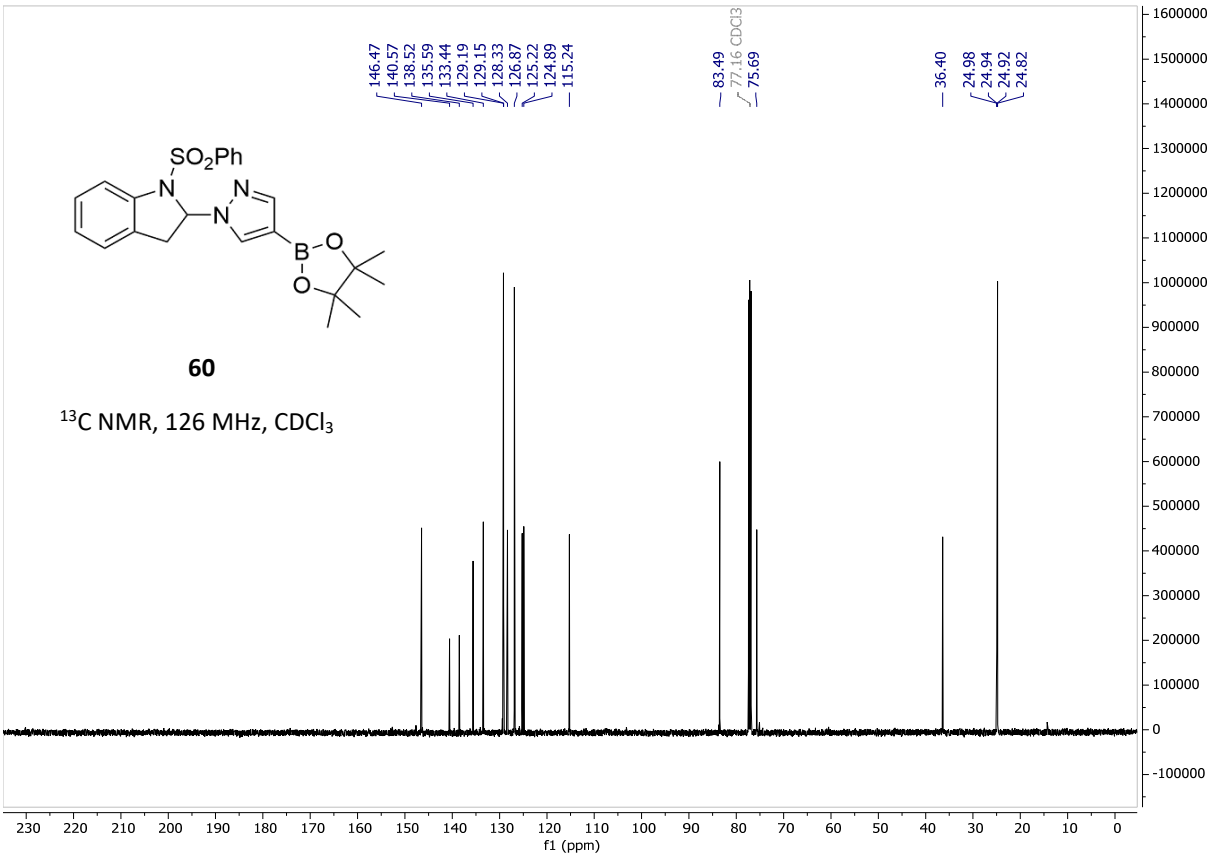

7.52
7.52
7.50
7.50
7.43
7.41
7.40
7.39
7.38
7.37
7.36
7.28
7.26
7.26 CDCl3
7.25
7.24
7.16
7.15
7.14
7.12
7.11
7.05
7.03
6.96
6.95
6.28
6.27
6.26
6.25
3.38
3.38
3.35
3.34
3.25
3.23
3.22
3.20
SO2Ph
N
N
N
F
59
1H NMR, 500 MHz, CDCl3
2.03
2.96
2.03
1.99
0.97
1.01
1.00
1.04
1.00
f1 (ppm)


150.90
148.93
140.34
138.43
133.59
129.25
128.35
127.75
127.63
126.82
125.12
125.01
115.36
114.99
114.77
77.16 CDCl3
76.59
35.48
SO2Ph
N
N
N
F
59
13C NMR, 126 MHz, CDCl3
f1 (ppm)



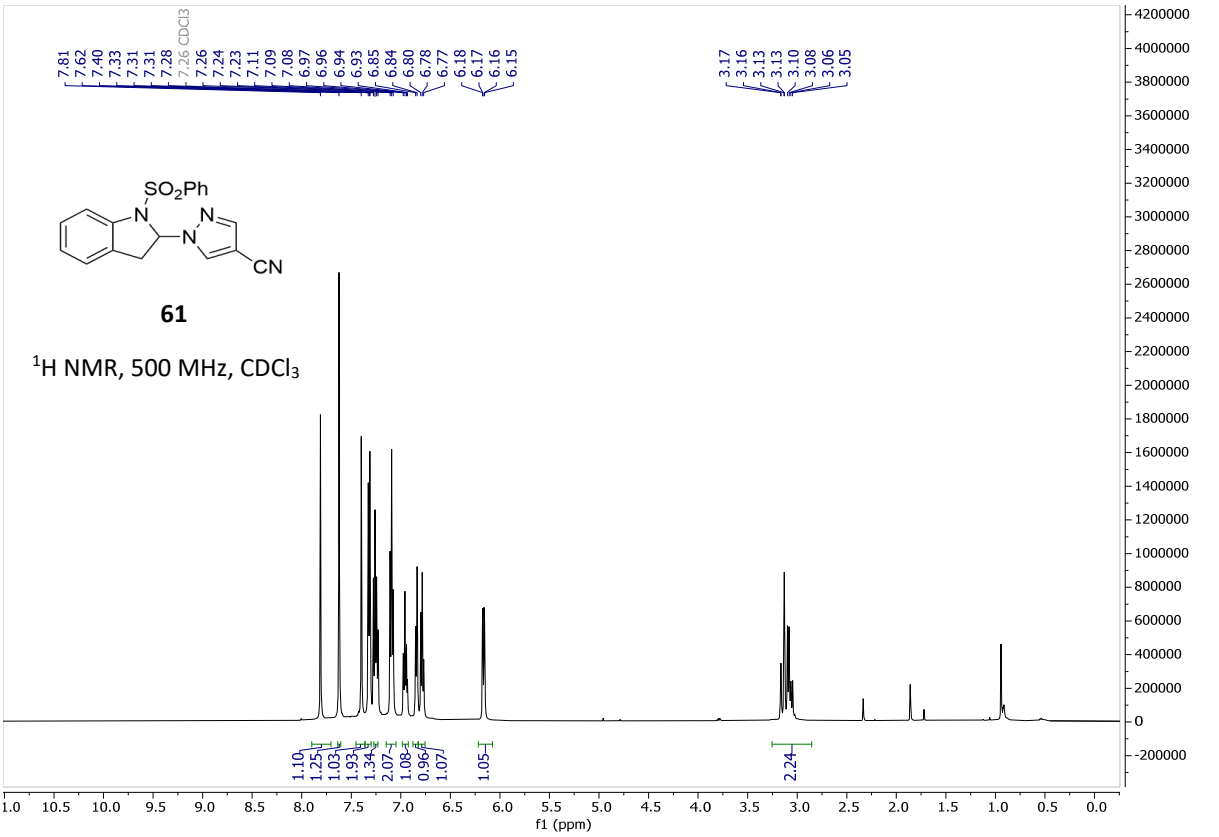
60

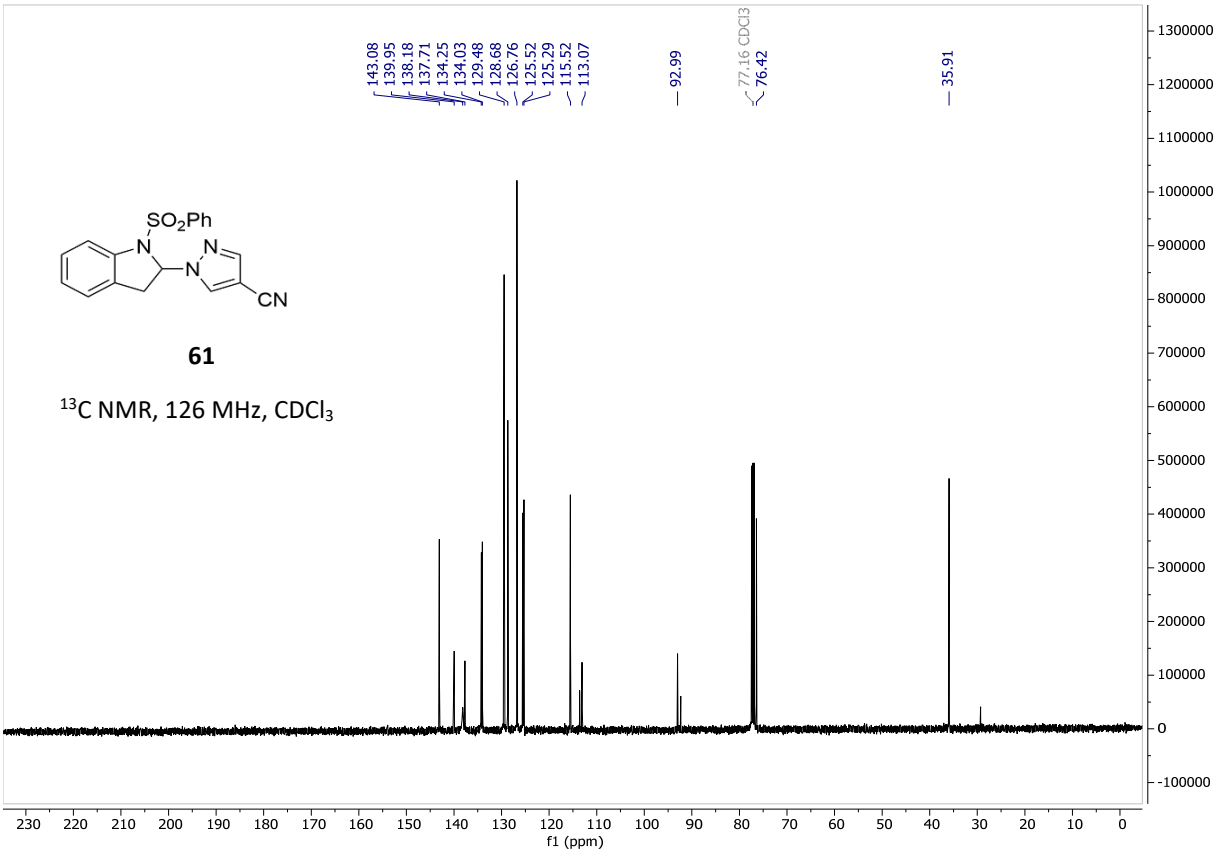
^{1}H NMR, 500 MHz, $CDCl_3$

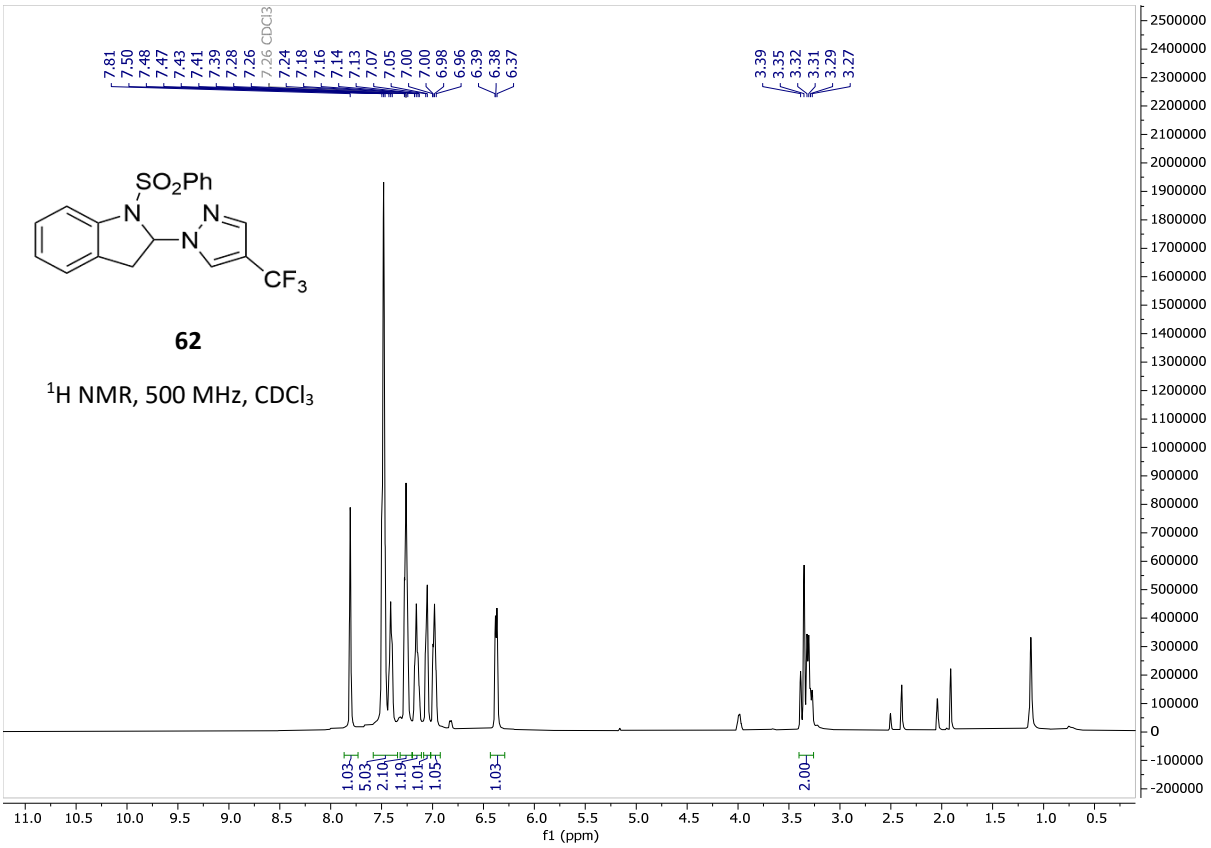


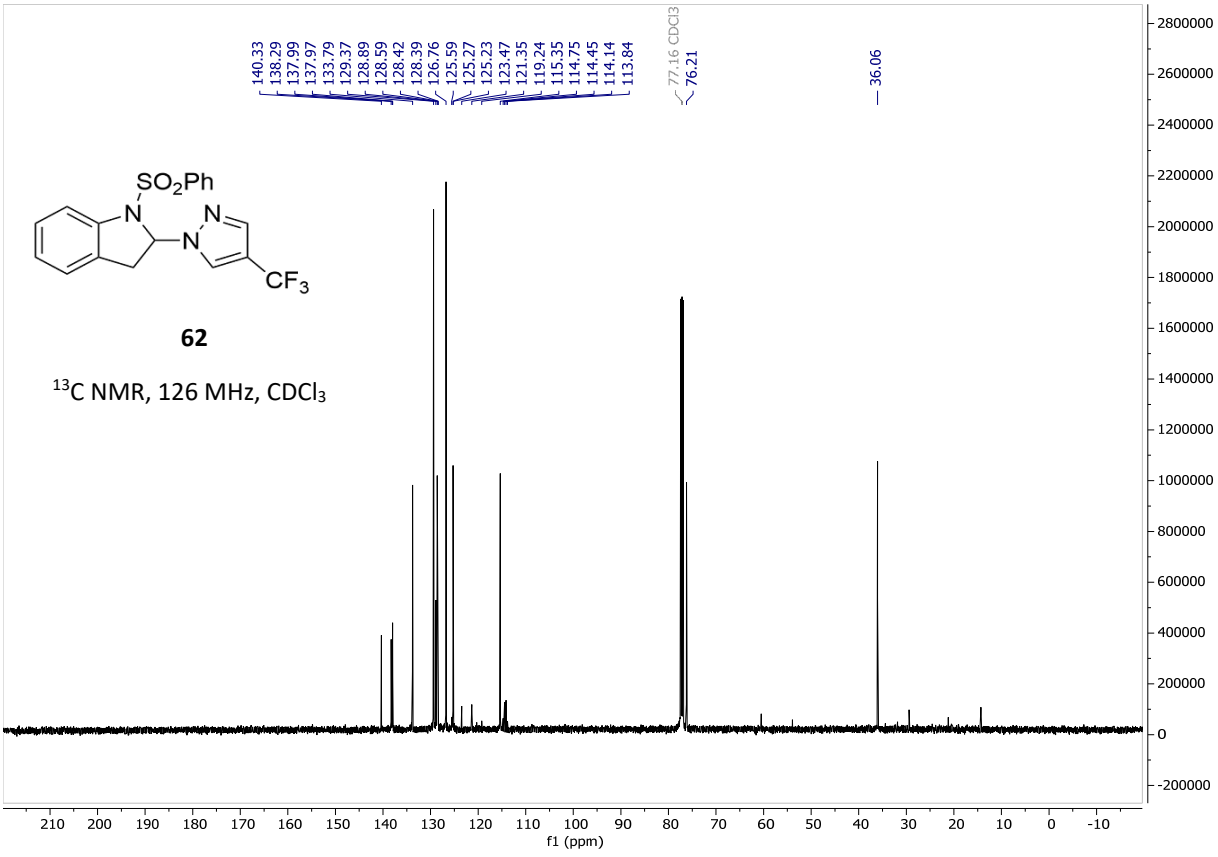
60

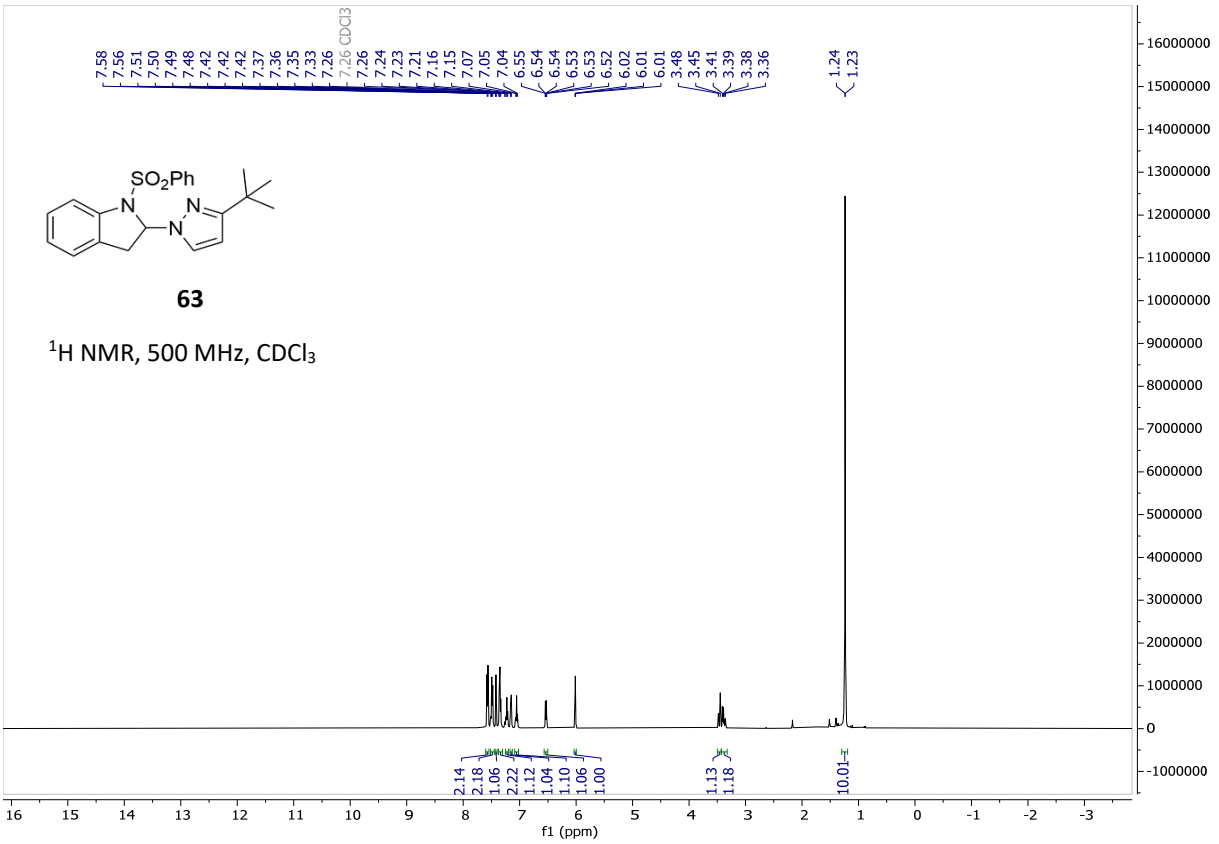
^{13}C NMR, 126 MHz, $CDCl_3$

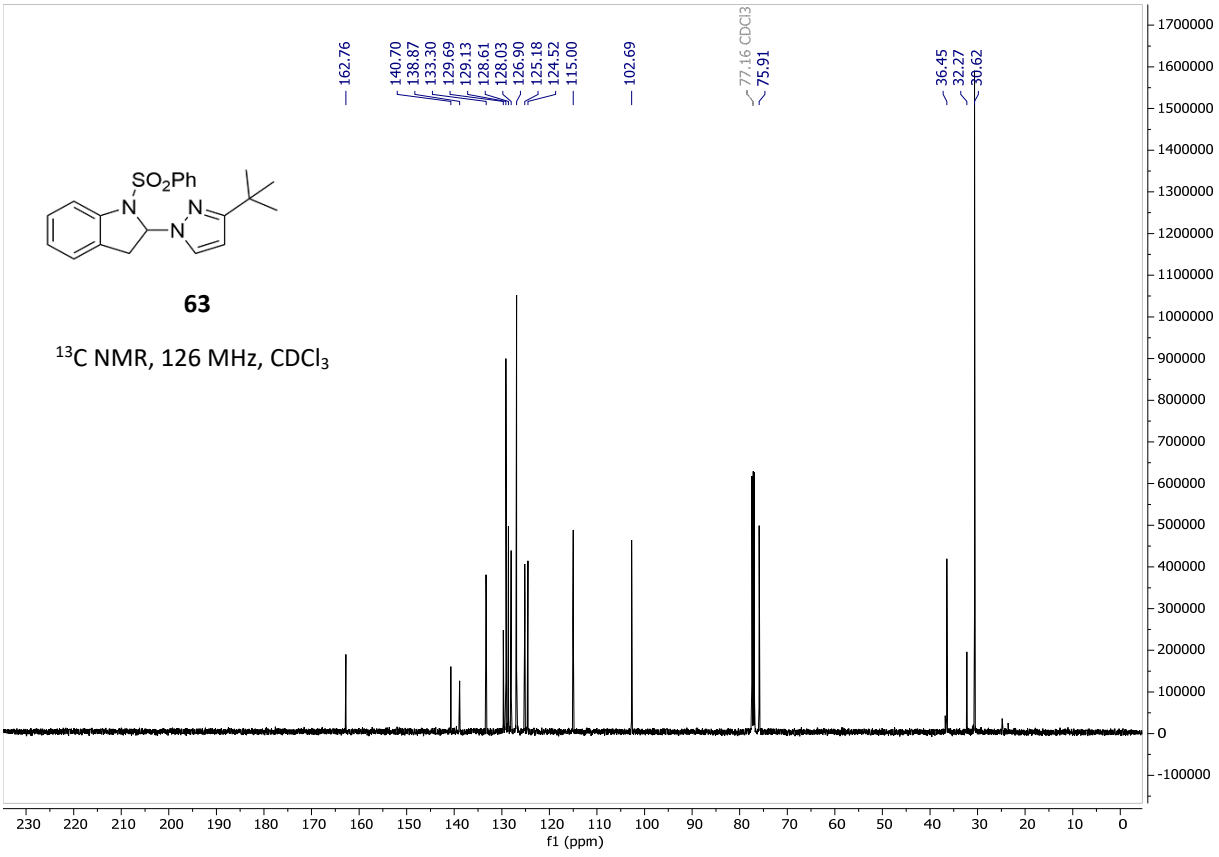

7.81
7.62
7.40
7.33
7.31
7.31
7.28
7.26 CDCl3
7.26
7.24
7.23
7.11
7.09
7.08
6.97
6.96
6.94
6.93
6.85
6.84
6.80
6.78
6.77
6.18
6.17
6.16
6.15
3.17
3.16
3.13
3.13
3.10
3.08
3.06
3.05
SO2Ph
N
N
N
CN
61
1H NMR, 500 MHz, CDCl3
1.10
1.25
1.03
1.93
1.34
2.07
1.08
0.96
1.07
1.05
2.24
f1 (ppm)

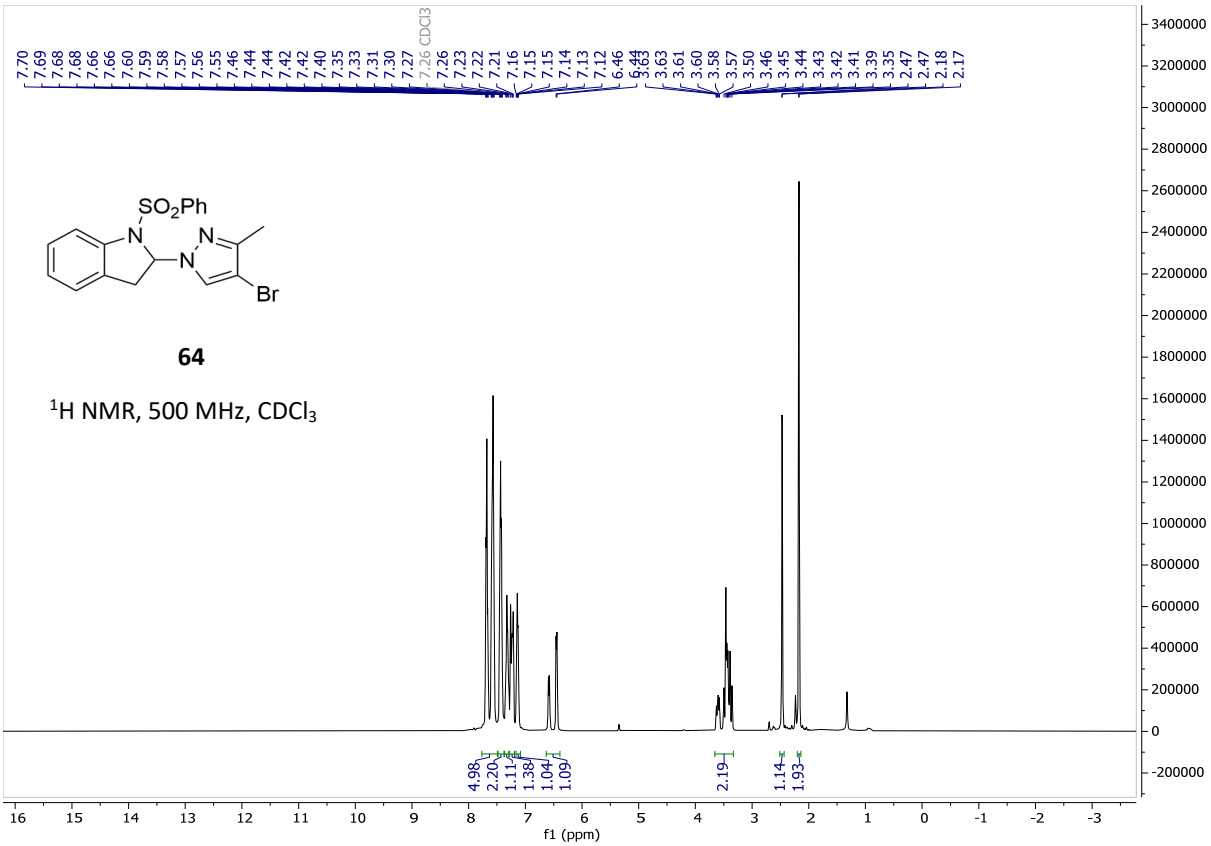

143.08
139.95
138.18
137.71
134.25
134.03
129.48
128.68
126.76
125.52
125.29
115.52
113.07
92.99
77.16 CDCl3
76.42
35.91
SO2Ph
N
N
N
CN
61
13C NMR, 126 MHz, CDCl3
f1 (ppm)

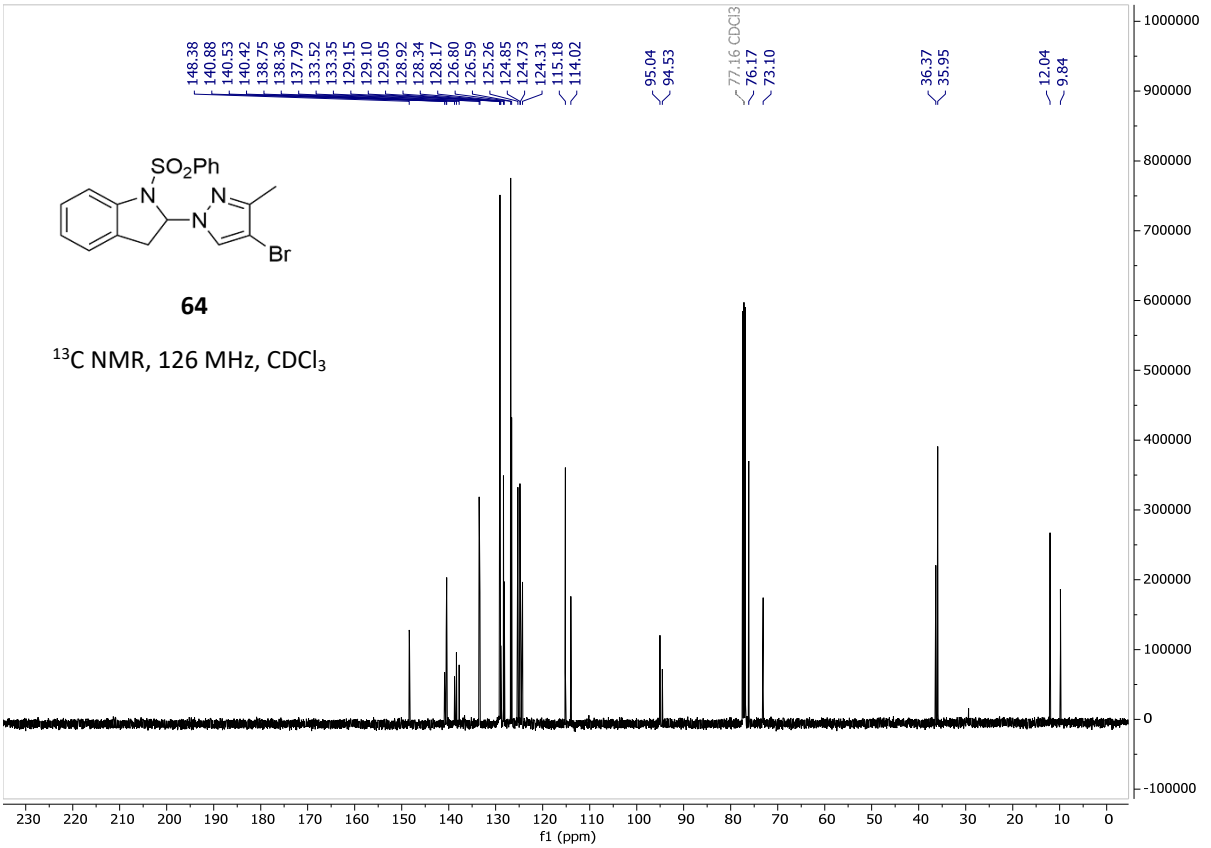

7.81
7.50
7.48
7.47
7.43
7.41
7.39
7.28
7.26
7.26 CDCl3
7.24
7.18
7.16
7.14
7.13
7.07
7.05
7.00
7.00
6.98
6.96
6.39
6.38
6.37
3.39
3.35
3.32
3.31
3.29
3.27
SO2Ph
N
N
N
CF3
62
1H NMR, 500 MHz, CDCl3
1.03
5.03
2.10
1.19
1.01
1.05
1.03
2.00
f1 (ppm)

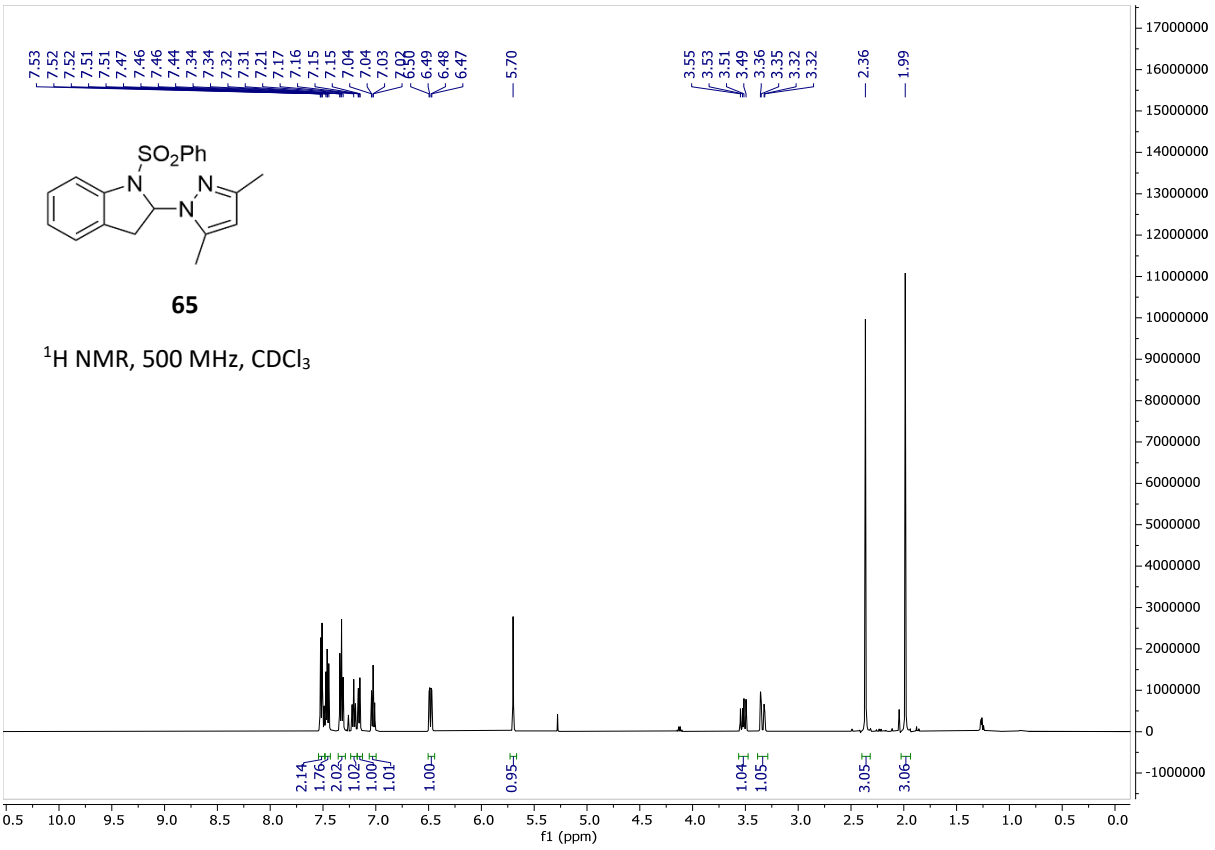

140.33
138.29
137.99
137.97
133.79
129.37
128.89
128.59
128.42
128.39
126.76
125.59
125.27
125.23
123.47
121.35
119.24
115.35
114.75
114.45
114.14
113.84
77.16 CDCl3
76.21
36.06
SO2Ph
N
N
N
CF3
62
13C NMR, 126 MHz, CDCl3
f1 (ppm)

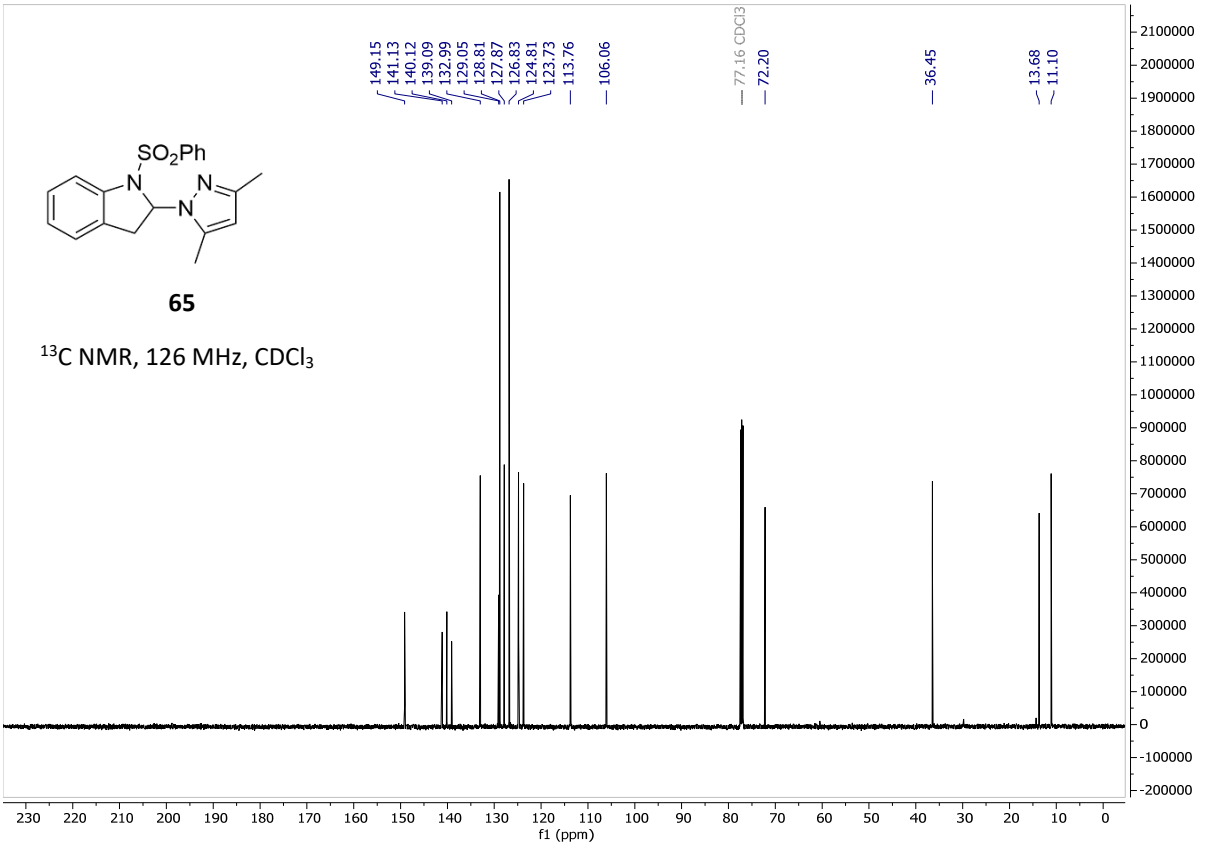

7.58 7.56 7.51 7.50 7.49 7.48 7.42 7.42 7.42 7.37 7.36 7.35 7.33 7.26 CDCl3 7.26 7.24 7.23 7.21 7.16 7.15 7.07 7.05 7.04 6.55 6.54 6.54 6.53 6.53 6.52 6.02 6.01 6.01 3.48 3.45 3.41 3.39 3.38 3.36 1.24 1.23
SO2Ph
N
N
N
63
1H NMR, 500 MHz, CDCl3
2.14 2.18 1.06 2.22 1.12 1.04 1.10 1.06 1.00 1.13 1.18 10.01
f1 (ppm)

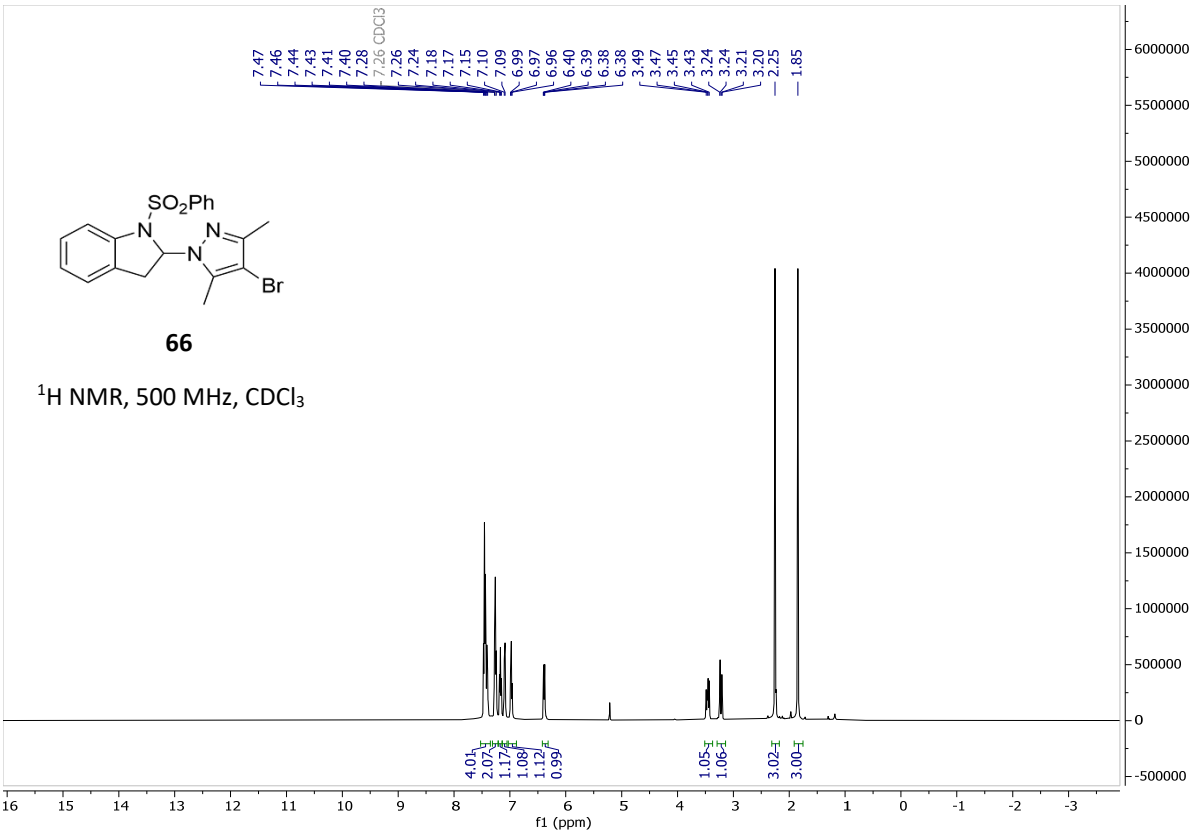

162.76 140.70 138.87 133.30 129.69 129.13 128.61 128.03 126.90 125.18 124.52 115.00 102.69 77.16 CDCl3 75.91 36.45 32.27 30.62
SO2Ph
N
N
N
63
13C NMR, 126 MHz, CDCl3
f1 (ppm)


7.70 7.69 7.68 7.68 7.66 7.66 7.60 7.59 7.58 7.57 7.56 7.55 7.46 7.44 7.44 7.42 7.42 7.40 7.35 7.33 7.31 7.30 7.27 7.26 CDCl3 7.26 7.23 7.22 7.21 7.16 7.15 7.15 7.14 7.13 7.12 6.46 6.44 3.63 3.63 3.61 3.60 3.58 3.57 3.50 3.46 3.45 3.44 3.43 3.42 3.41 3.39 3.35 2.47 2.47 2.18 2.17
SO2Ph
N
N
N
Br
64
1H NMR, 500 MHz, CDCl3
4.98 2.20 1.11 1.38 1.04 1.09 2.19 1.14 1.93
f1 (ppm)


148.38 140.88 140.53 140.42 138.75 138.36 137.79 133.52 133.35 129.15 129.10 129.05 128.92 128.34 128.17 126.80 126.59 125.26 124.85 124.73 124.31 115.18 114.02 95.04 94.53 77.16 CDCl3 76.17 73.10 36.37 35.95 12.04 9.84
SO2Ph
N
N
N
Br
64
13C NMR, 126 MHz, CDCl3
f1 (ppm)

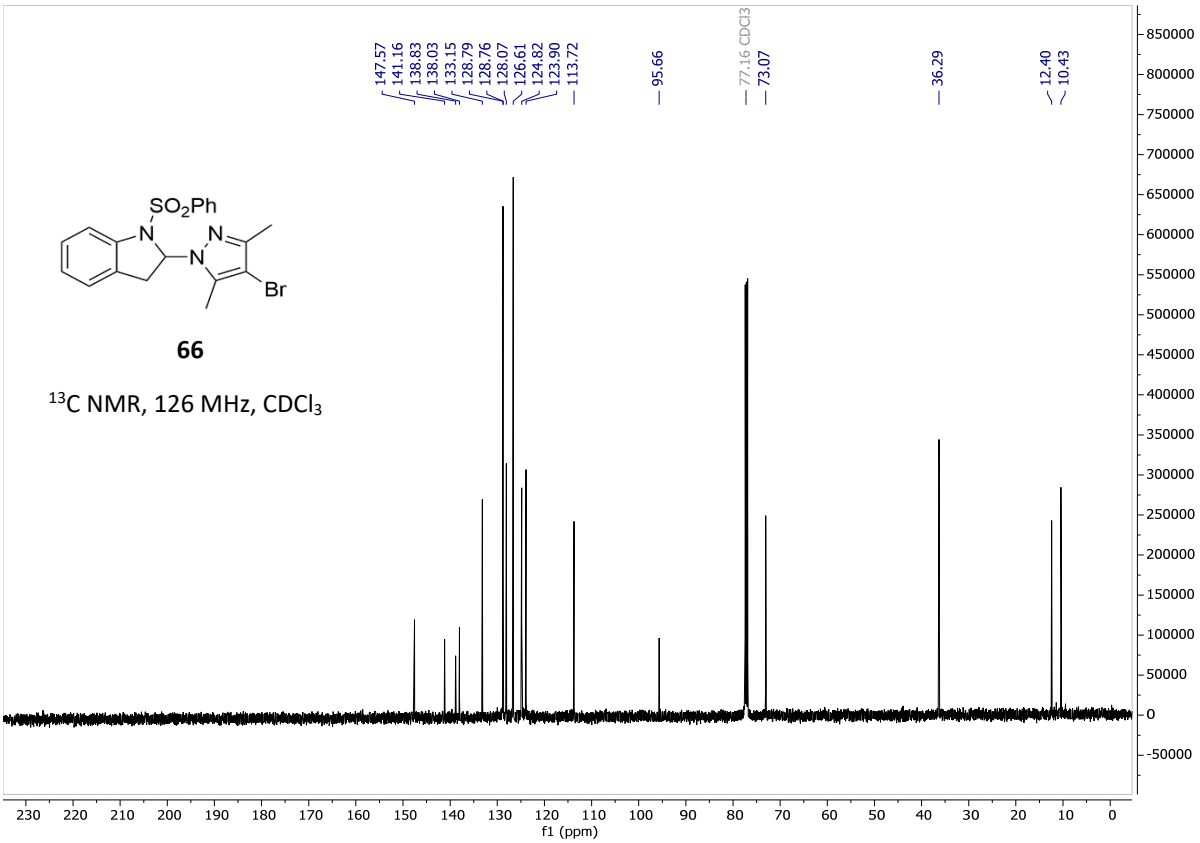

7.53
7.52
7.52
7.51
7.51
7.47
7.46
7.46
7.44
7.34
7.34
7.32
7.31
7.21
7.17
7.16
7.15
7.15
7.04
7.04
7.03
7.02
6.50
6.49
6.48
6.47
5.70
3.55
3.53
3.51
3.49
3.36
3.35
3.32
3.32
2.36
1.99
SO2Ph
N
N
N
65
1H NMR, 500 MHz, CDCl3
2.14
1.76
2.02
1.02
1.00
1.01
1.00
0.95
1.04
1.05
3.05
3.06
f1 (ppm)


149.15
141.13
140.12
139.09
132.99
129.05
128.81
127.87
126.83
124.81
123.73
113.76
106.06
77.16 CDCl3
72.20
36.45
13.68
11.10
SO2Ph
N
N
N
65
13C NMR, 126 MHz, CDCl3
f1 (ppm)



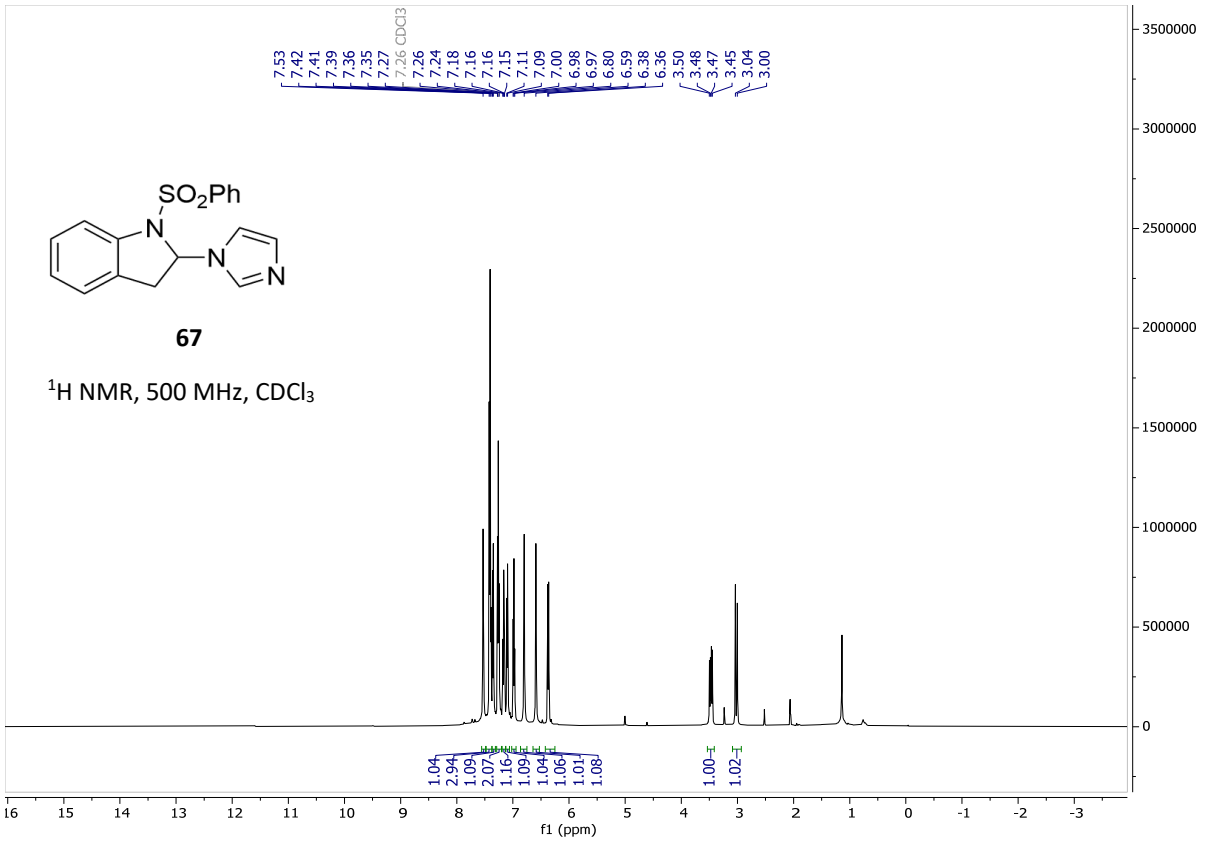
66

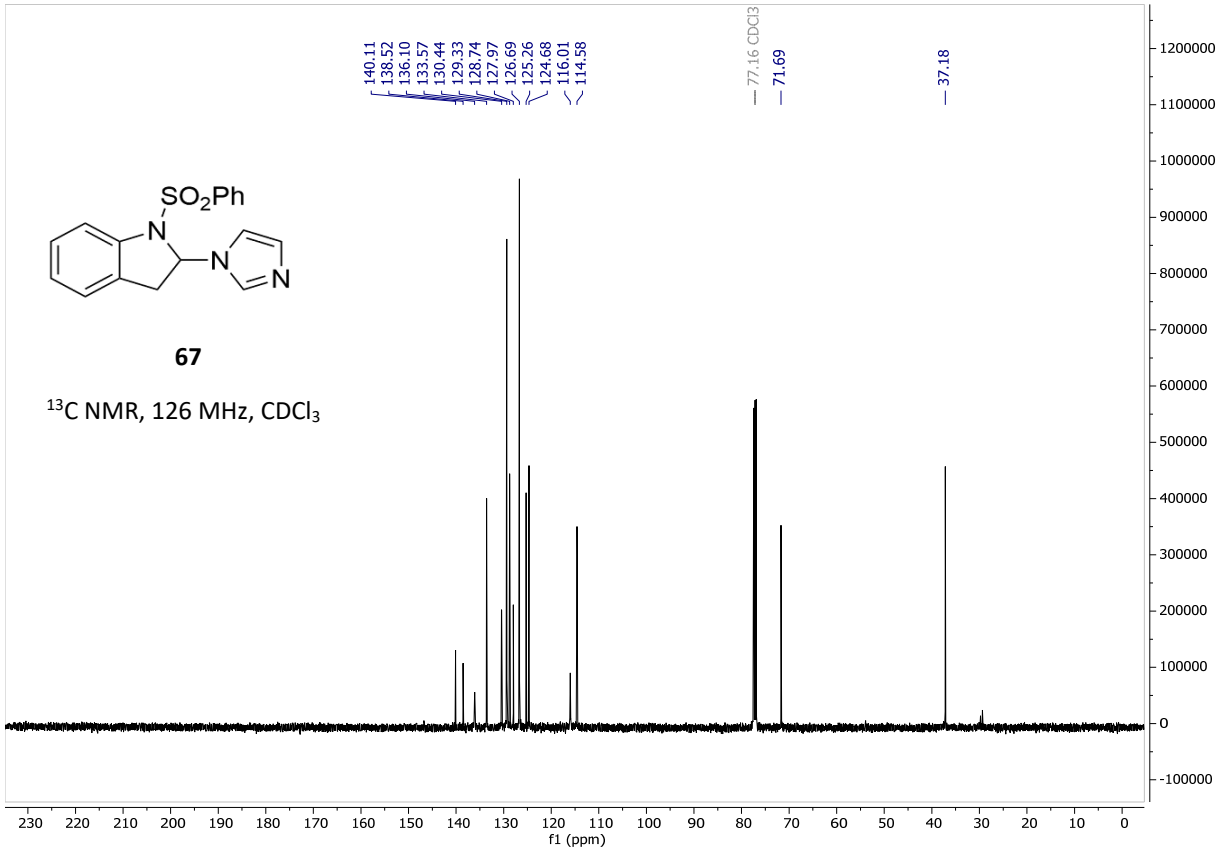
^{1}H NMR, 500 MHz, $CDCl_3$

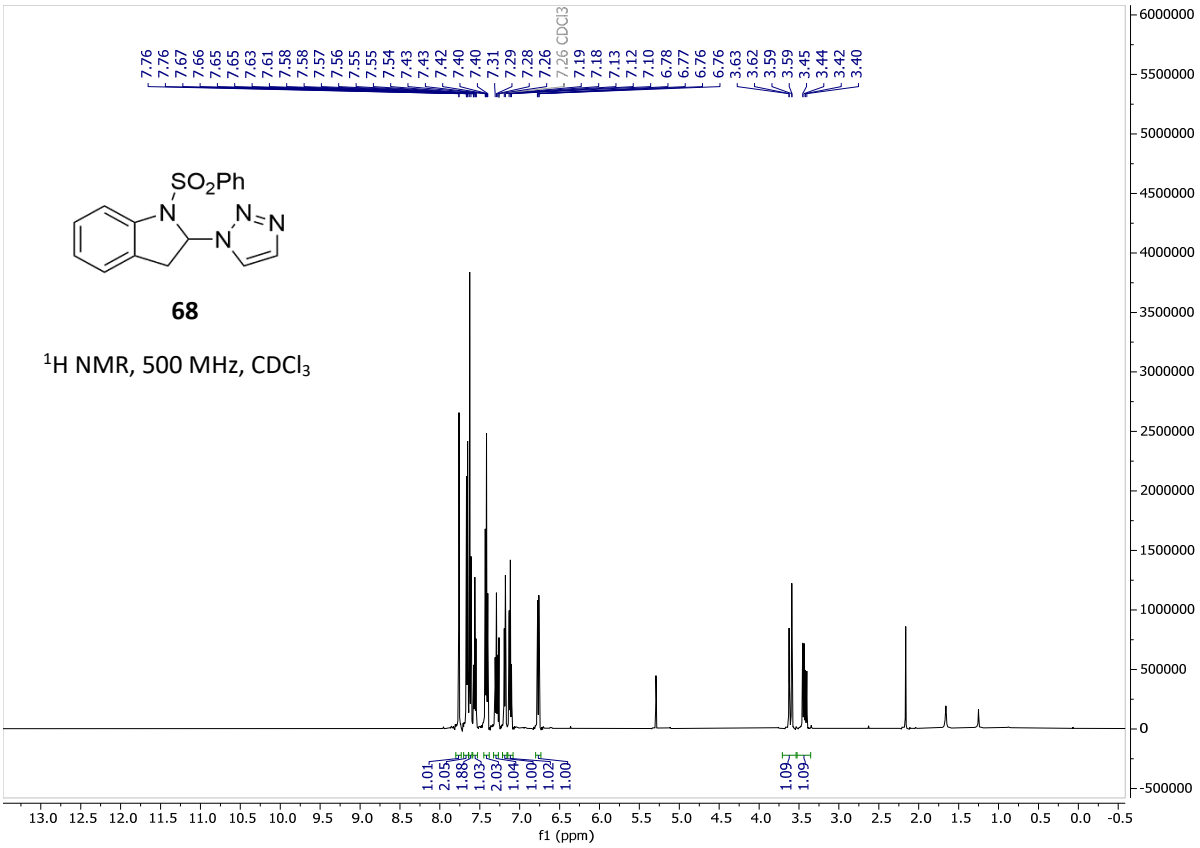


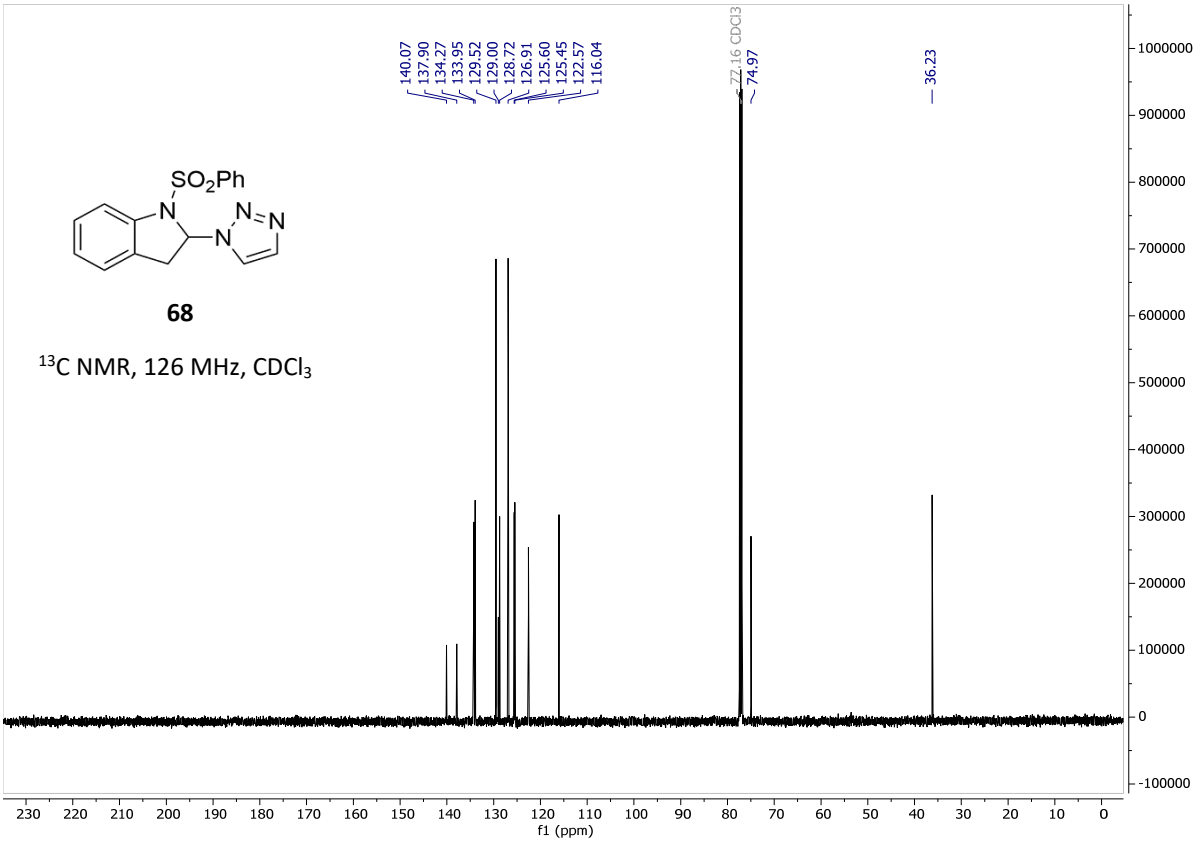
66

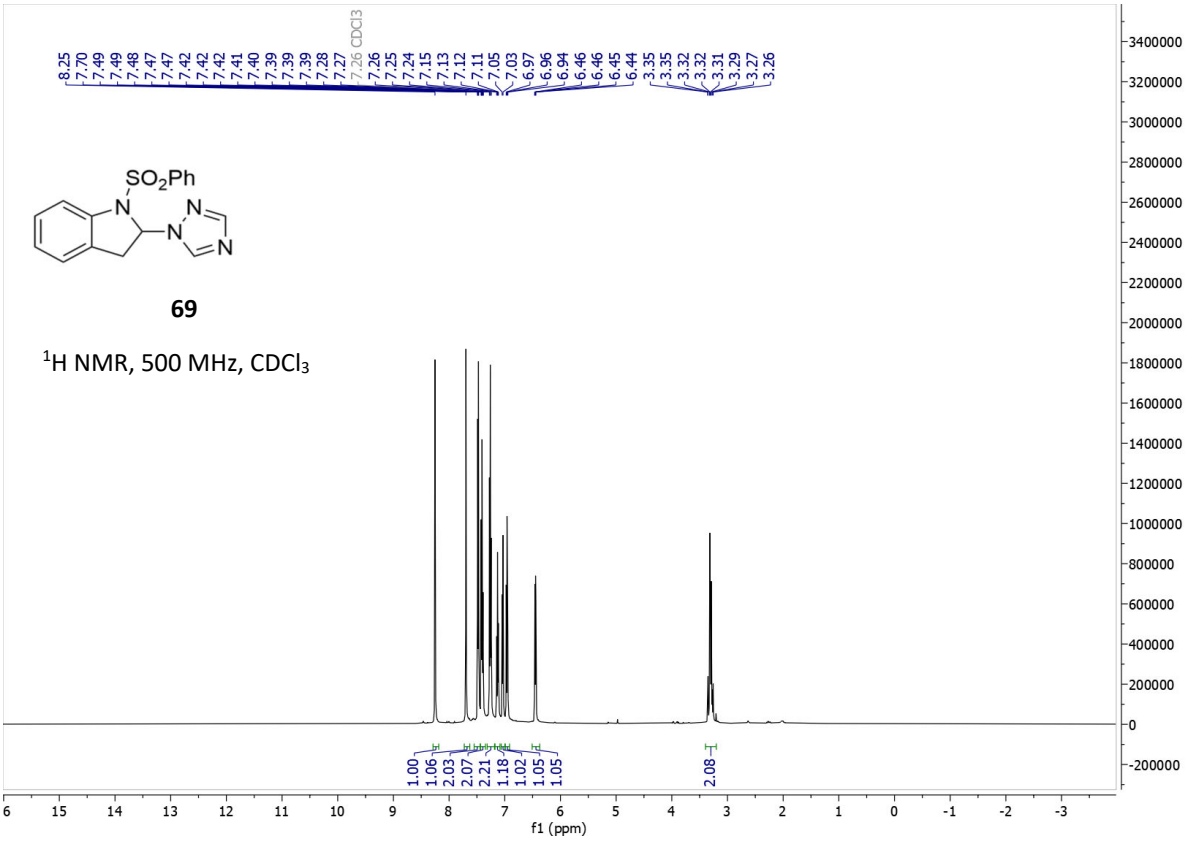
^{13}C NMR, 126 MHz, $CDCl_3$

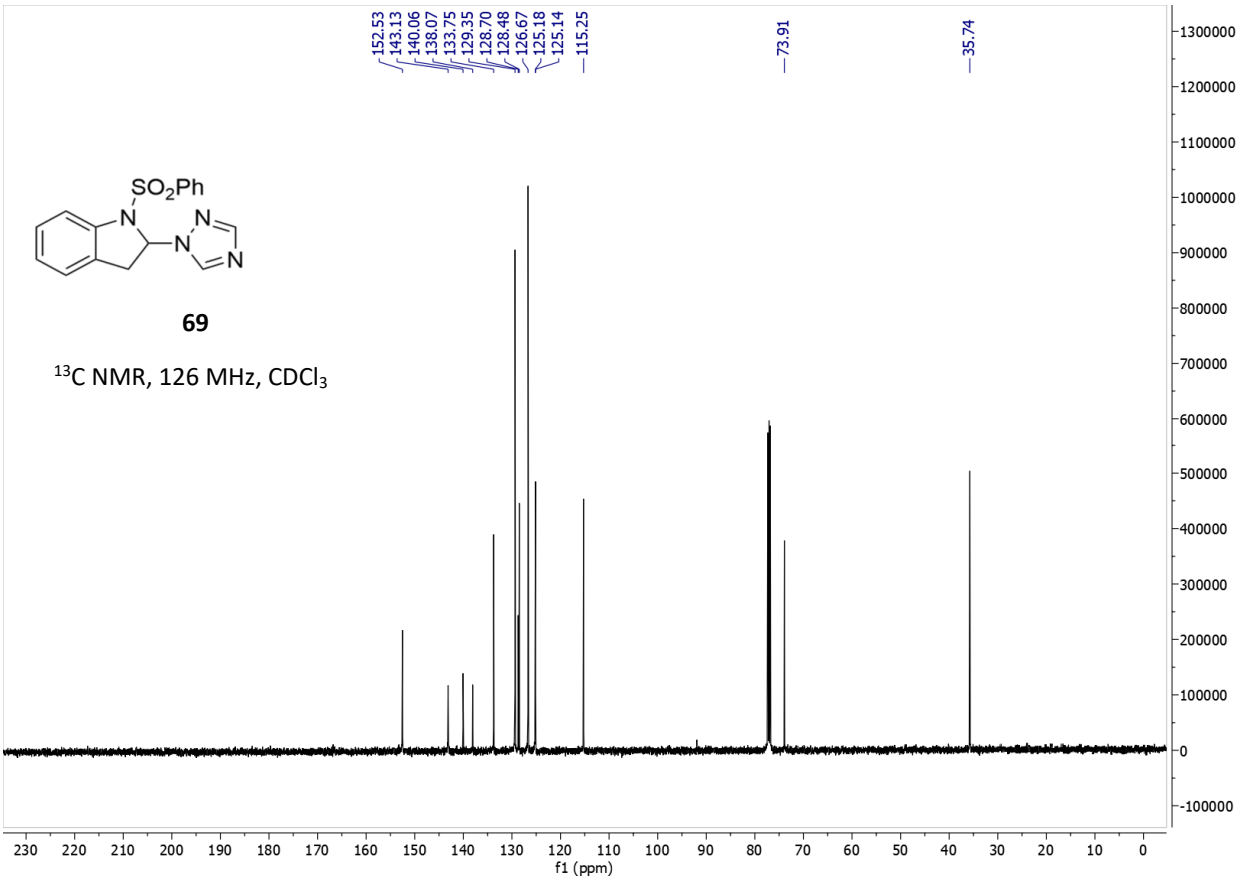

7.53
7.42
7.41
7.39
7.36
7.35
7.27
7.26 CDCl3
7.26
7.24
7.18
7.16
7.16
7.15
7.11
7.09
7.00
6.98
6.97
6.80
6.59
6.38
6.36
3.50
3.48
3.47
3.45
3.04
3.00
SO2Ph
N
N
N
67
1H NMR, 500 MHz, CDCl3
1.04
2.94
1.09
2.07
1.16
1.09
1.04
1.06
1.01
1.08
1.00
1.02
f1 (ppm)

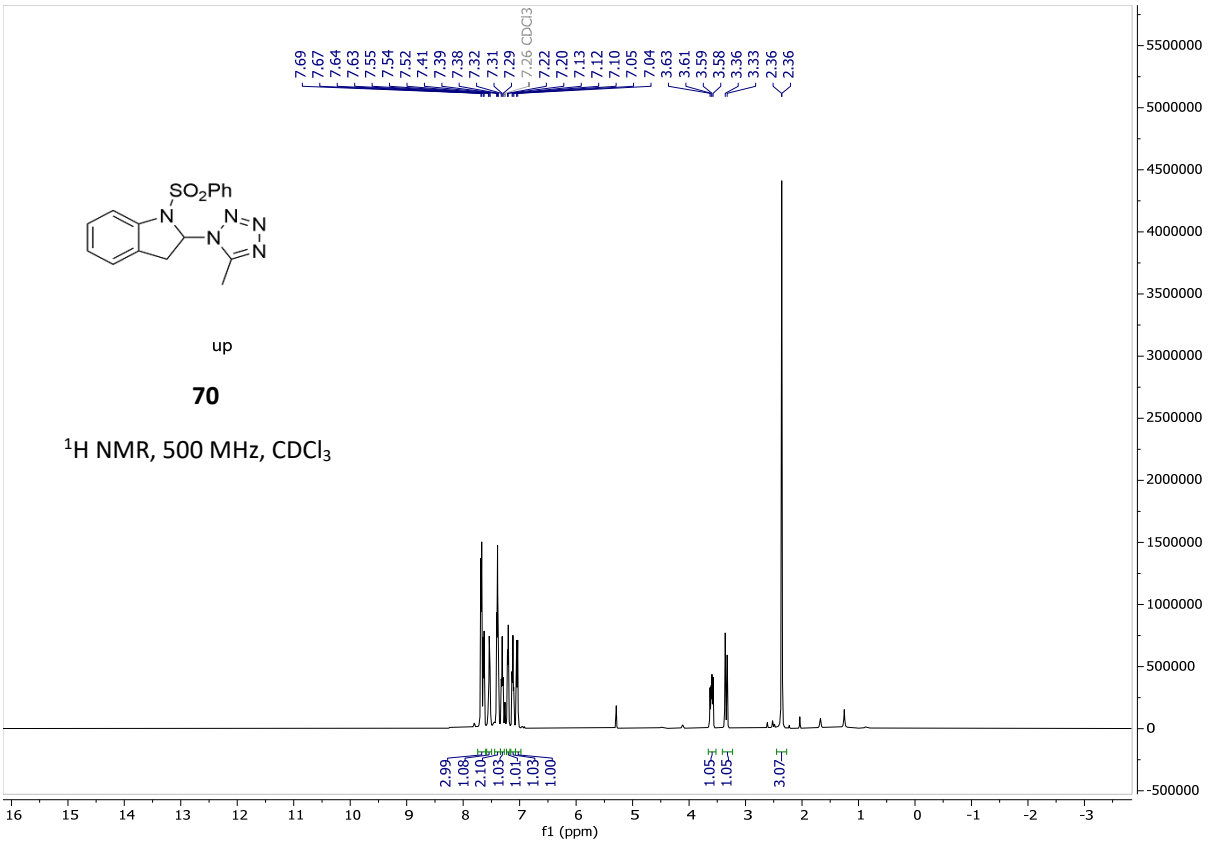

140.11
138.52
136.10
133.57
130.44
129.33
128.74
127.97
126.69
125.26
124.68
116.01
114.58
77.16 CDCl3
71.69
37.18
SO2Ph
N
N
N
67
13C NMR, 126 MHz, CDCl3
f1 (ppm)

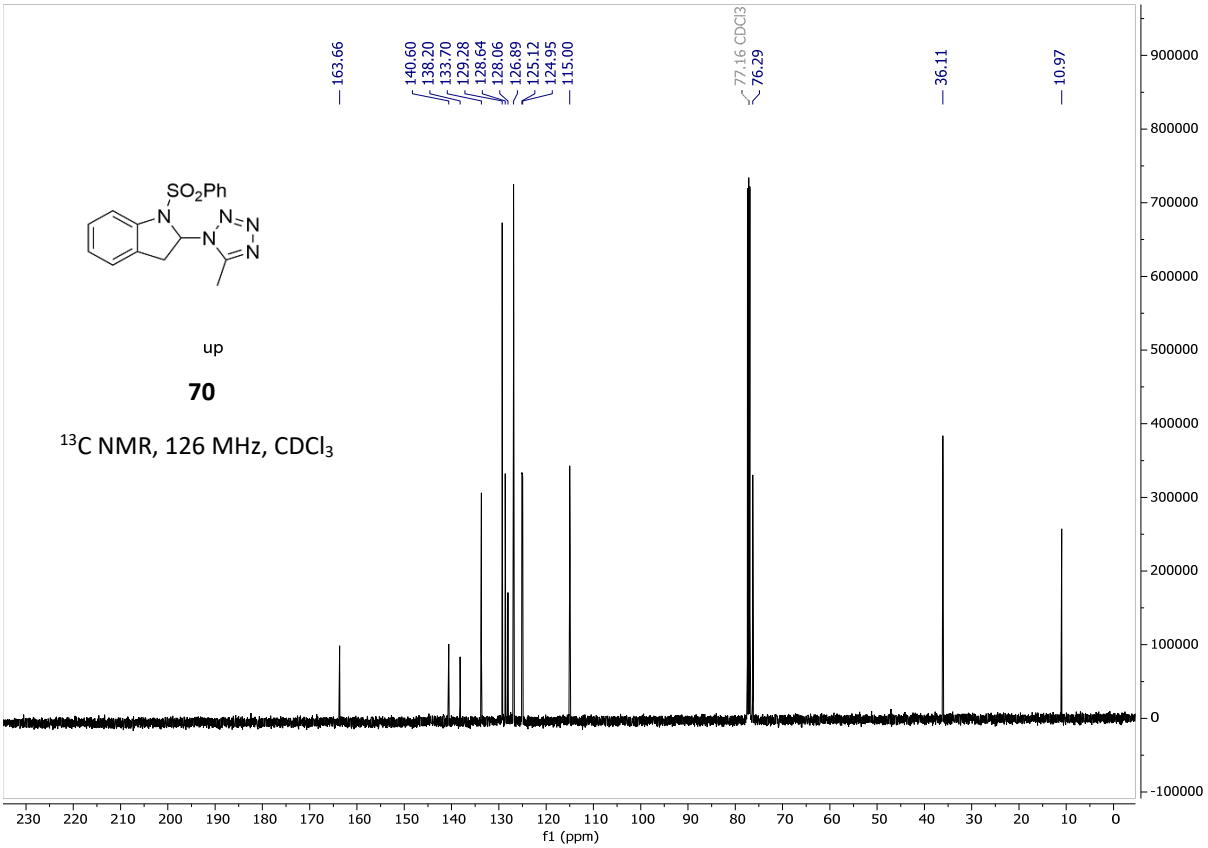

7.76 7.76 7.67 7.66 7.65 7.65 7.63 7.61 7.58 7.58 7.57 7.56 7.55 7.55 7.54 7.43 7.43 7.42 7.40 7.40 7.31 7.29 7.28 7.26 CDCl3 7.19 7.18 7.13 7.12 7.10 6.78 6.77 6.76 6.76 3.63 3.62 3.59 3.59 3.45 3.44 3.42 3.40
SO2Ph
N
N
N
N
68
1H NMR, 500 MHz, CDCl3
1.01 2.05 1.88 1.03 2.03 1.04 1.00 1.02 1.00 1.09 1.09
f1 (ppm)

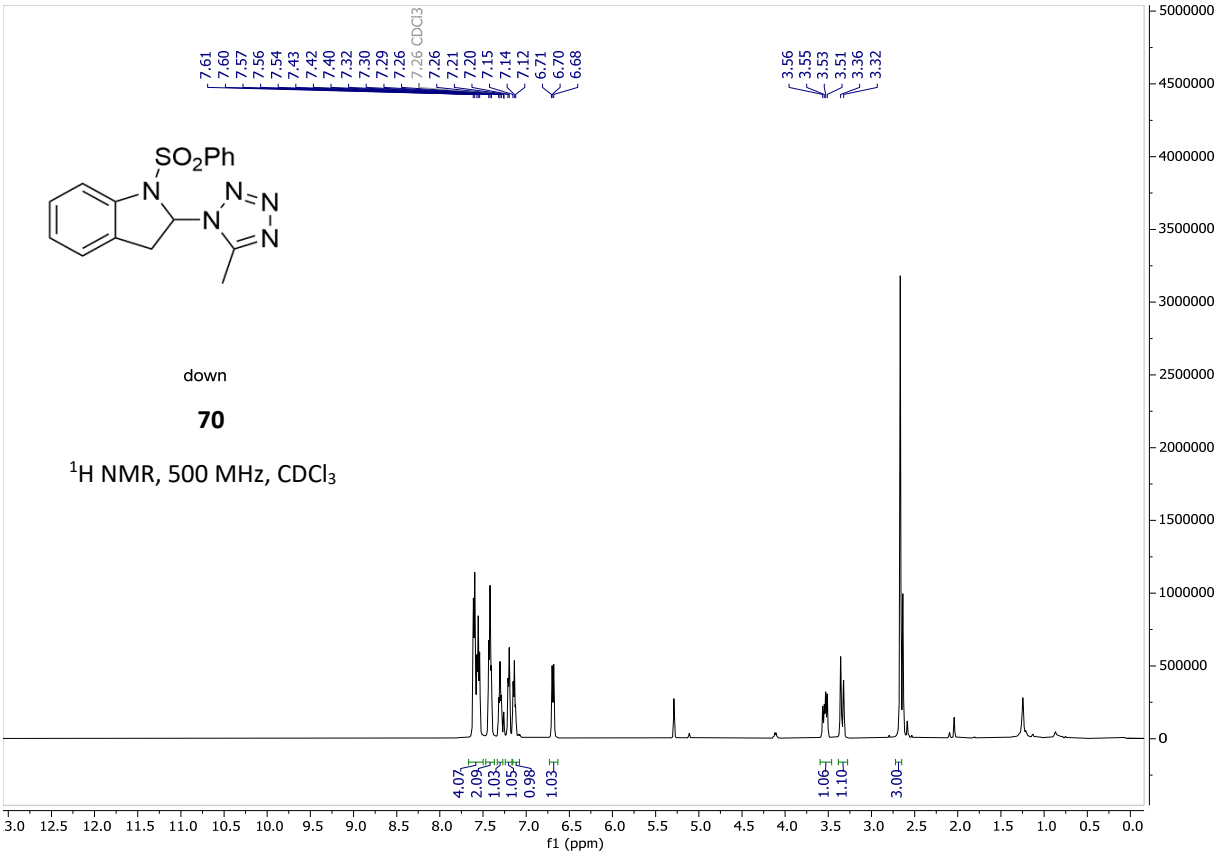

140.07 137.90 134.27 133.95 129.52 129.00 128.72 126.91 125.60 125.45 122.57 116.04 77.16 CDCl3 74.97 36.23
SO2Ph
N
N
N
N
68
13C NMR, 126 MHz, CDCl3
f1 (ppm)


8.25
7.70
7.49
7.49
7.48
7.47
7.47
7.42
7.42
7.42
7.41
7.40
7.39
7.39
7.39
7.28
7.27
7.26 CDCl3
7.26
7.25
7.24
7.15
7.13
7.12
7.11
7.05
7.03
6.97
6.96
6.94
6.46
6.46
6.45
6.44
3.35
3.35
3.32
3.32
3.31
3.29
3.27
3.26
SO2Ph
N
N
N
N
69
1H NMR, 500 MHz, CDCl3
1.00
1.06
2.03
2.07
2.21
1.18
1.02
1.05
1.05
2.08
f1 (ppm)


152.53
143.13
140.06
138.07
133.75
129.35
128.70
128.48
126.67
125.18
125.14
115.25
73.91
35.74
SO2Ph
N
N
N
N
69
13C NMR, 126 MHz, CDCl3
f1 (ppm)


7.69
7.67
7.64
7.63
7.55
7.54
7.52
7.41
7.39
7.38
7.32
7.31
7.29
7.26 CDCl3
7.22
7.20
7.13
7.12
7.10
7.05
7.04
3.63
3.61
3.59
3.58
3.36
3.33
2.36
2.36
SO2Ph
N
N
N
N
N
up
70
1H NMR, 500 MHz, CDCl3
2.99
1.08
2.10
1.03
1.01
1.03
1.00
1.05
1.05
3.07
f1 (ppm)

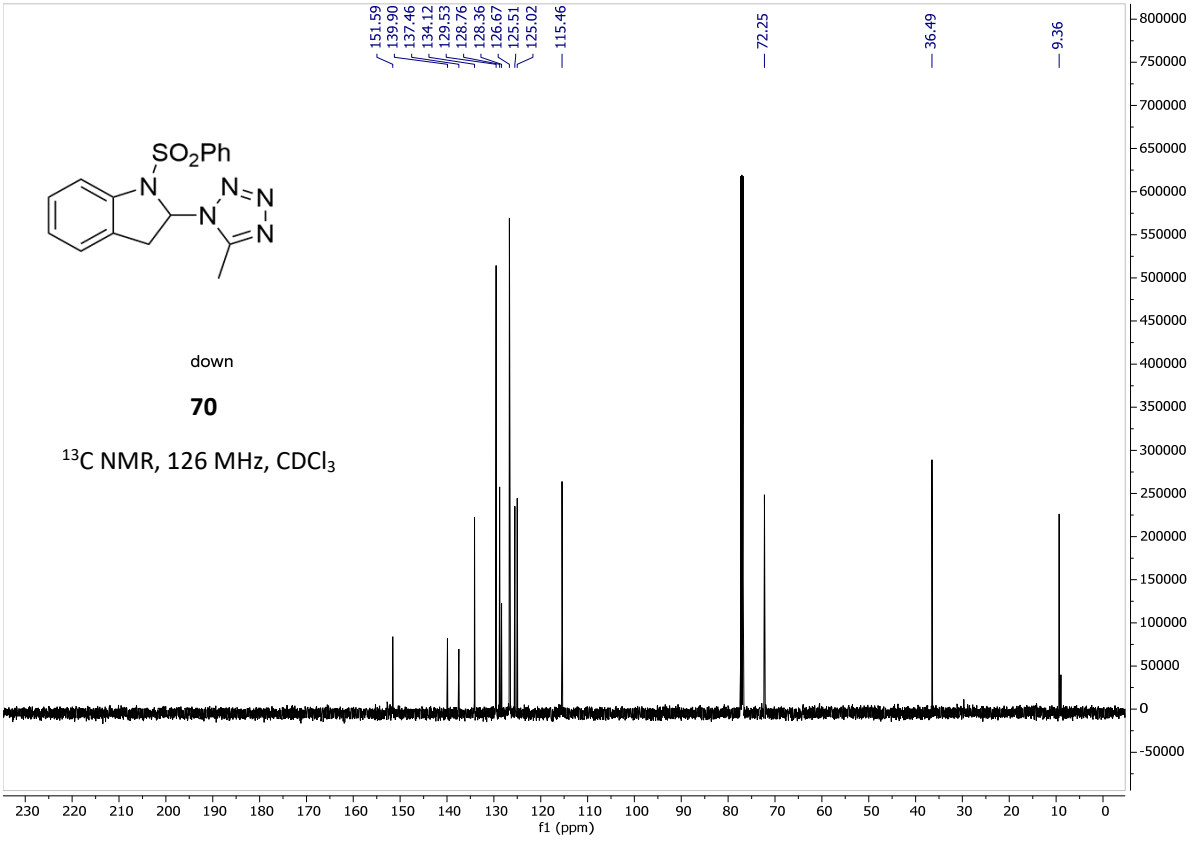

163.66
140.60
138.20
133.70
129.28
128.64
128.06
126.89
125.12
124.95
115.00
77.16 CDCl3
76.29
36.11
10.97
SO2Ph
N
N
N
N
N
up
70
13C NMR, 126 MHz, CDCl3
f1 (ppm)



down

70

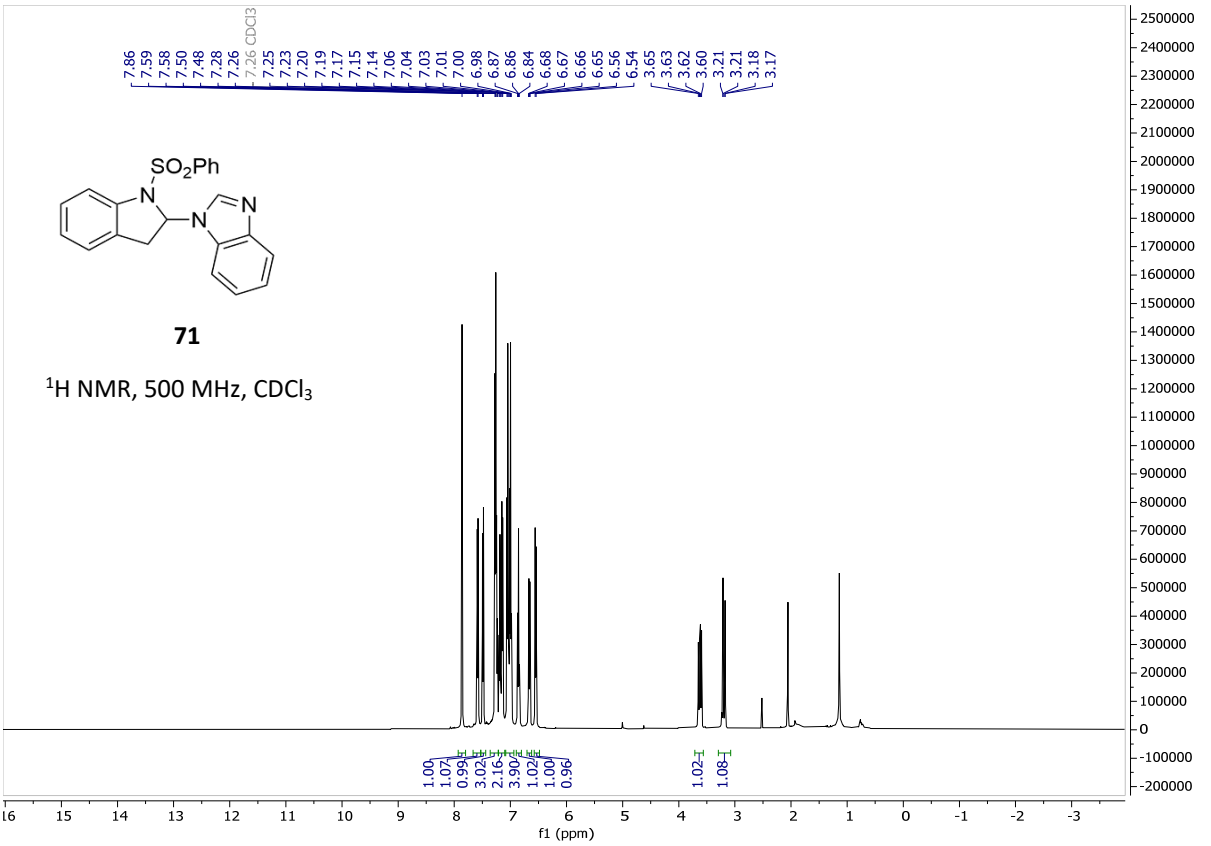
^{1}H NMR, 500 MHz, $CDCl_3$



down

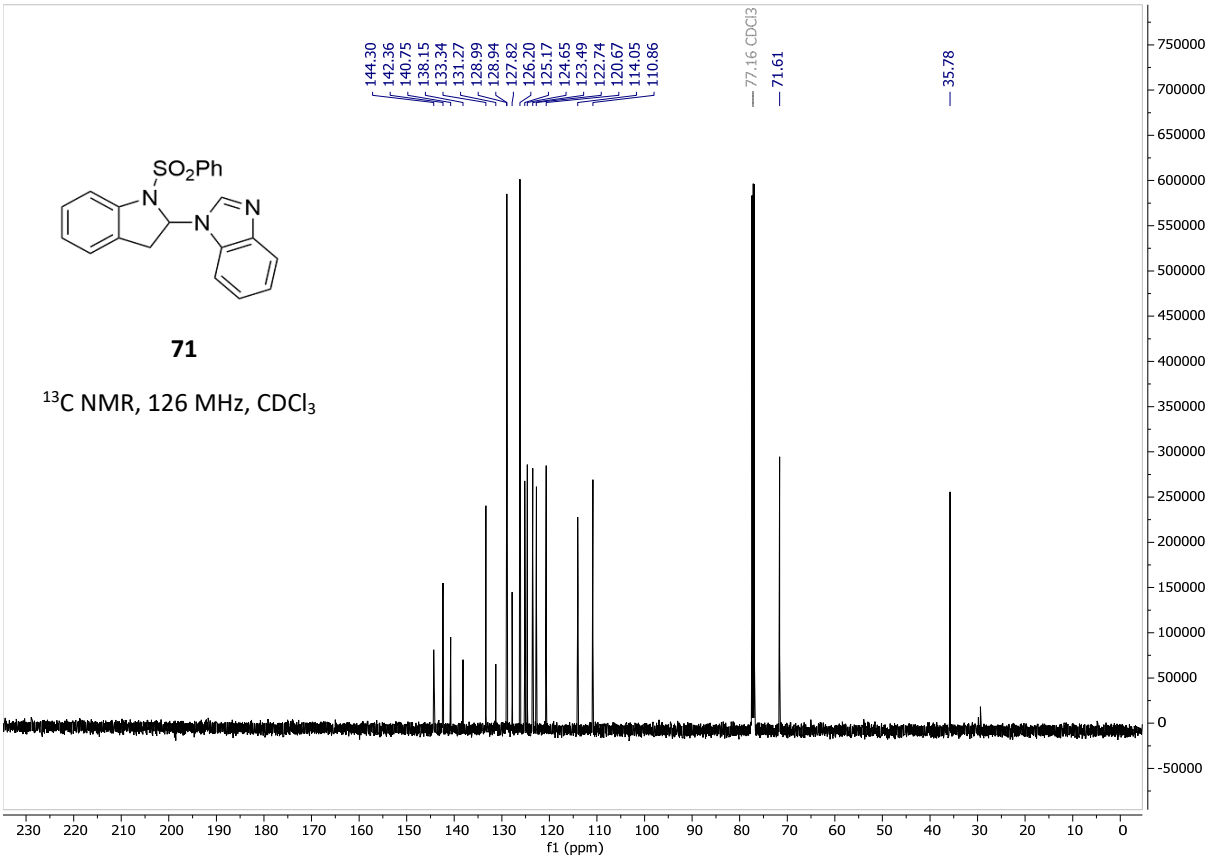
70

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



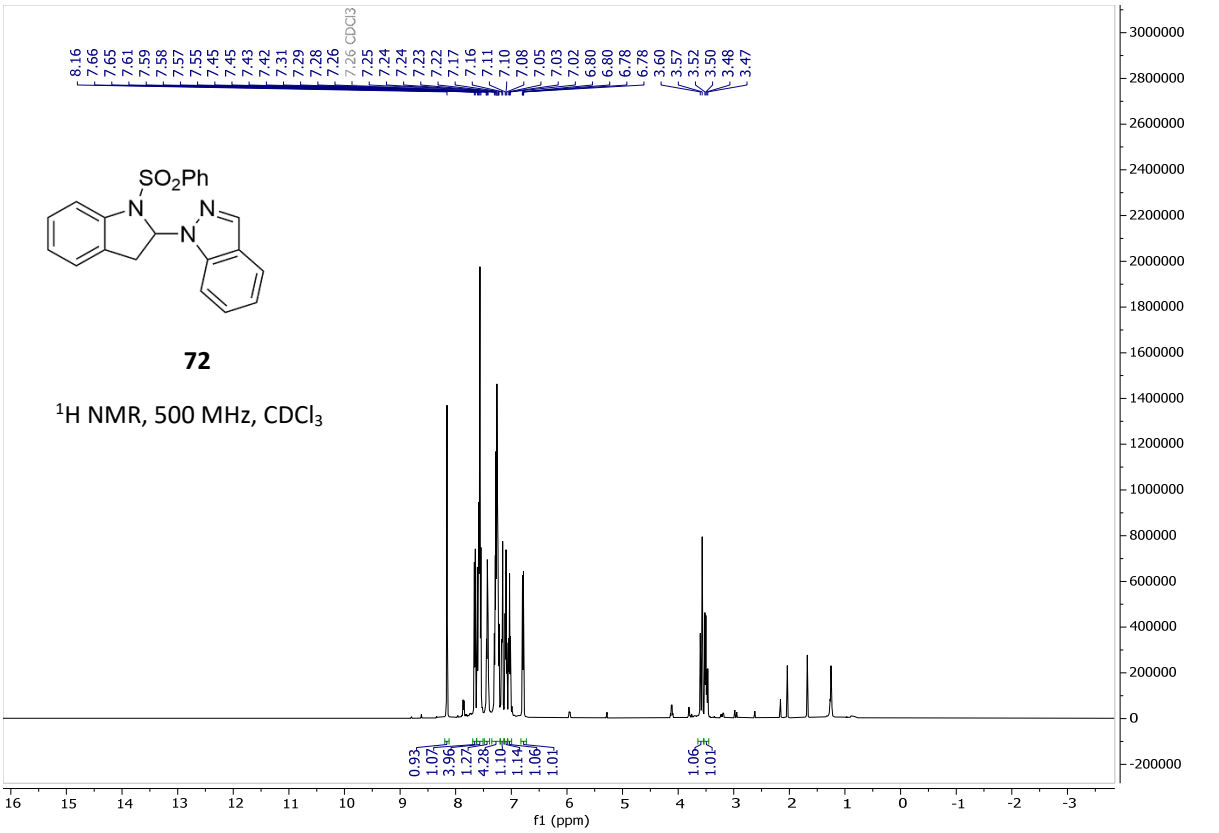
71

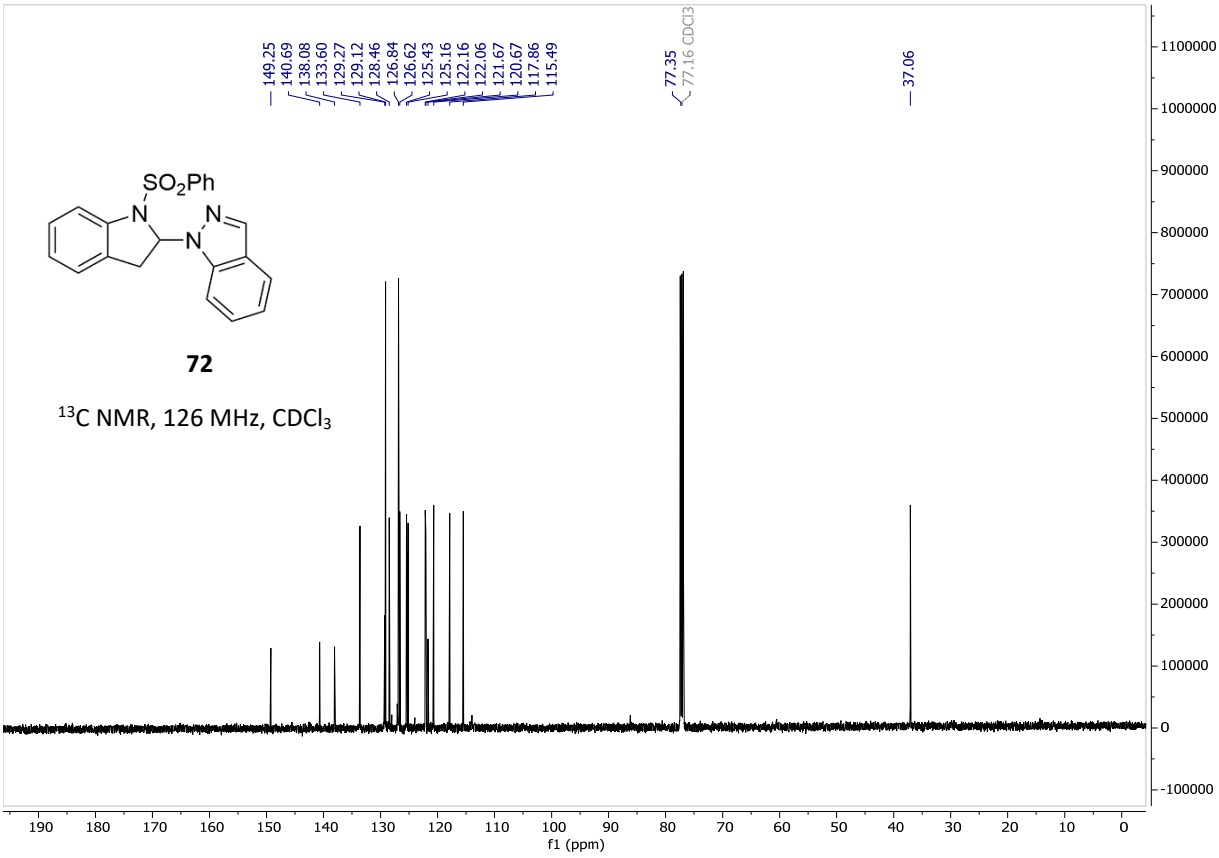
^{1}H NMR, 500 MHz, $CDCl_3$

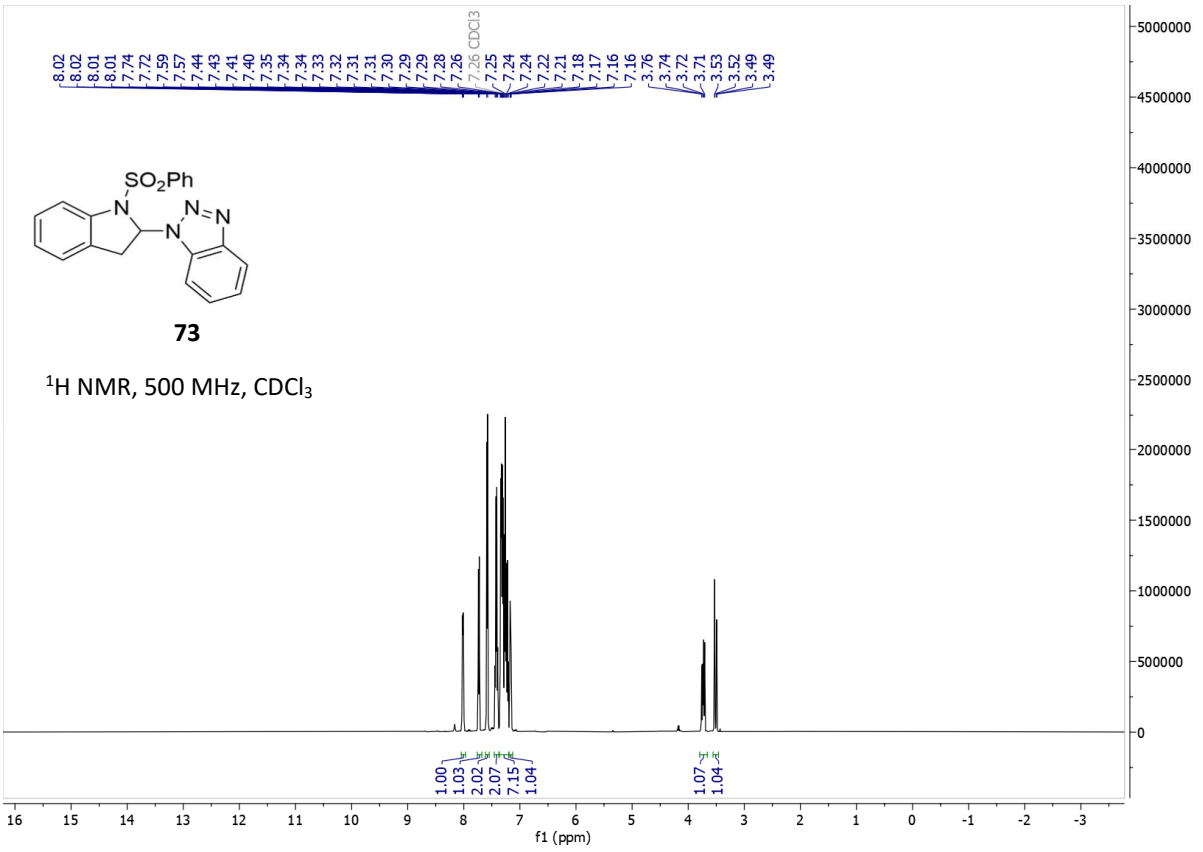


71

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

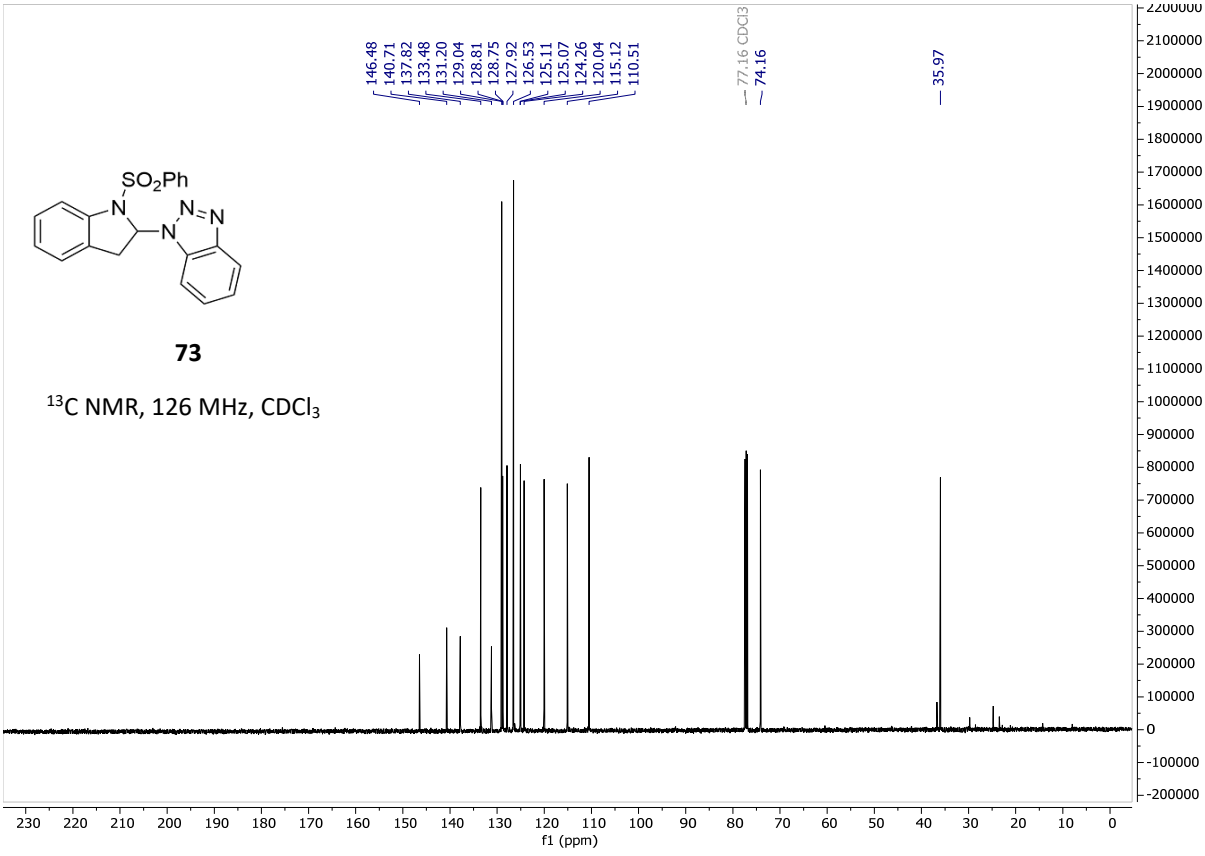

8.16
7.66
7.65
7.61
7.59
7.58
7.57
7.55
7.45
7.45
7.43
7.42
7.31
7.29
7.28
7.26
7.26 CDCl3
7.25
7.24
7.24
7.23
7.22
7.17
7.16
7.11
7.10
7.08
7.05
7.03
7.02
6.80
6.80
6.78
6.78
3.60
3.57
3.52
3.50
3.48
3.47
SO2Ph
N
N
N
72
1H NMR, 500 MHz, CDCl3
0.93
1.07
3.96
1.27
4.28
1.10
1.14
1.06
1.01
1.06
1.01
f1 (ppm)


149.25
140.69
138.08
133.60
129.27
129.12
128.46
126.84
126.62
125.43
125.16
122.16
122.06
121.67
120.67
117.86
115.49
77.35
77.16 CDCl3
37.06
SO2Ph
N
N
N
72
13C NMR, 126 MHz, CDCl3
f1 (ppm)



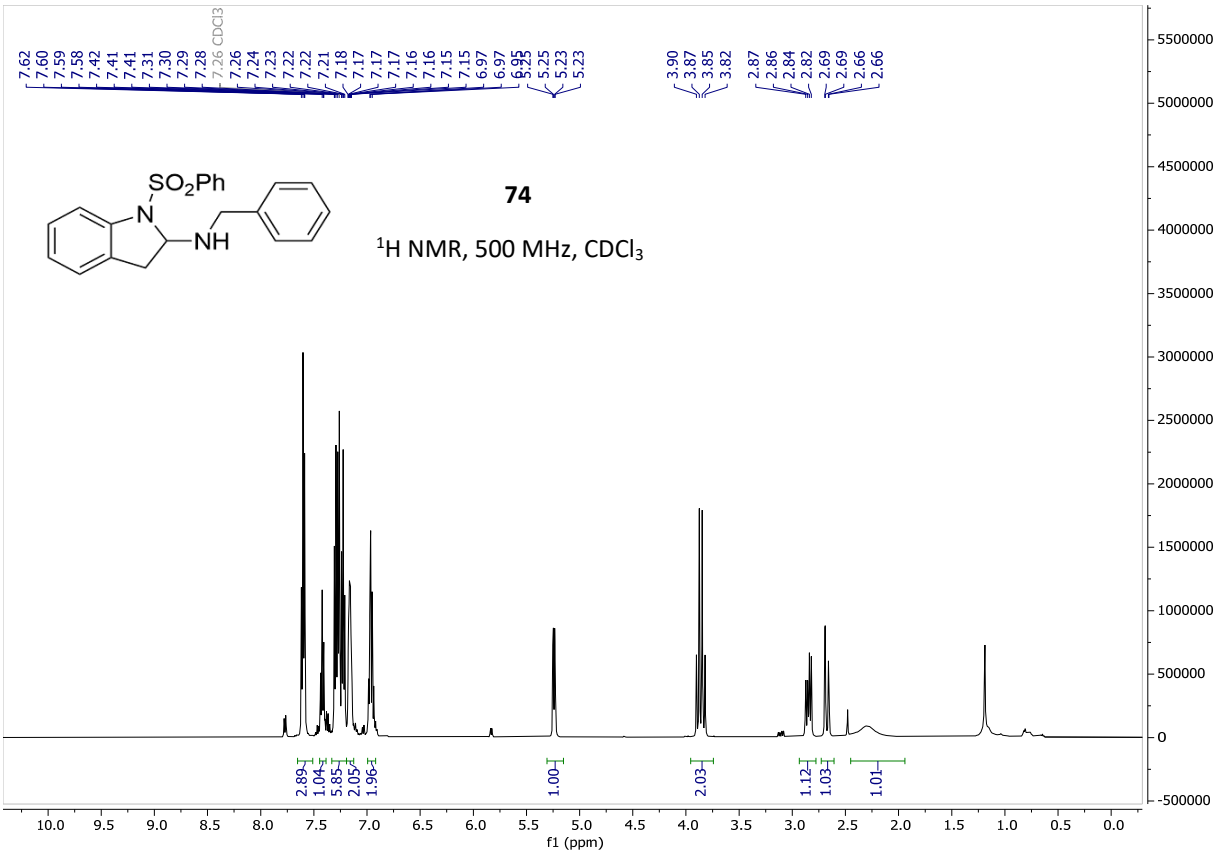
73

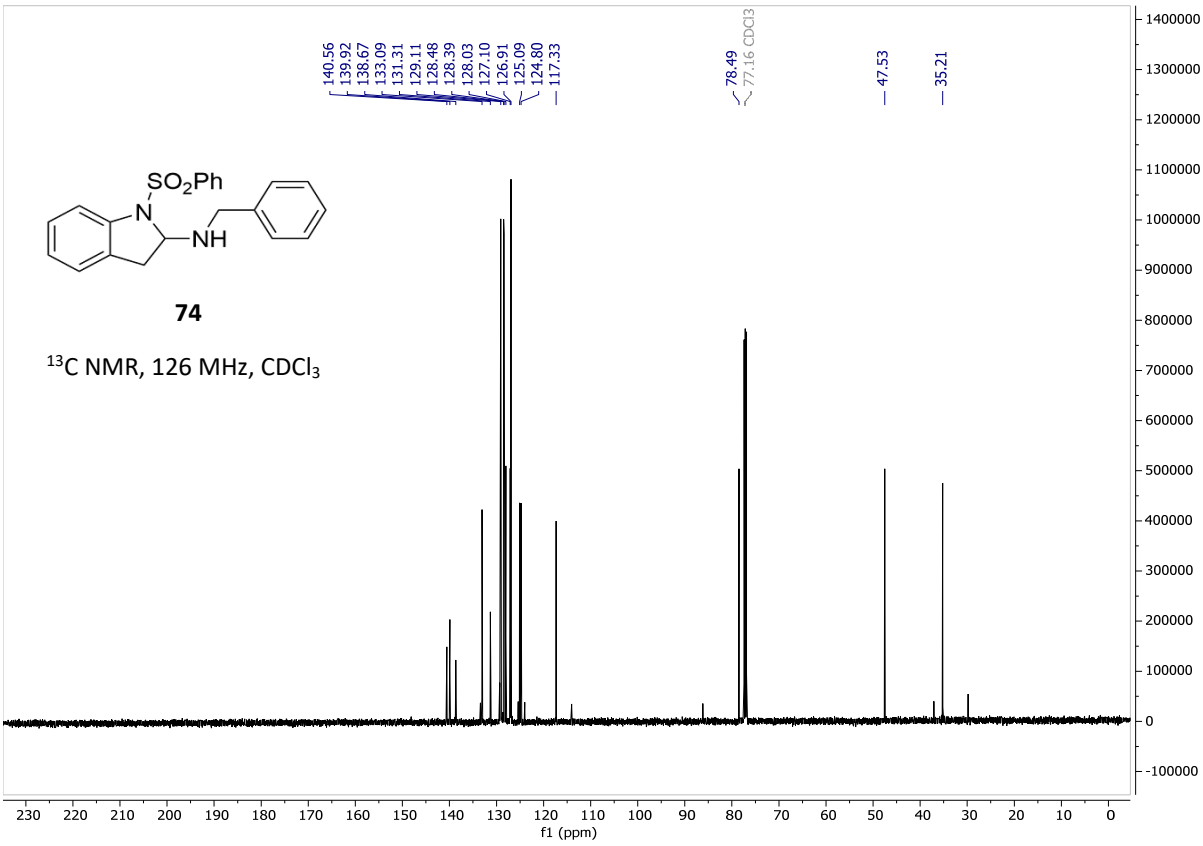
^{1}H NMR, 500 MHz, $CDCl_3$

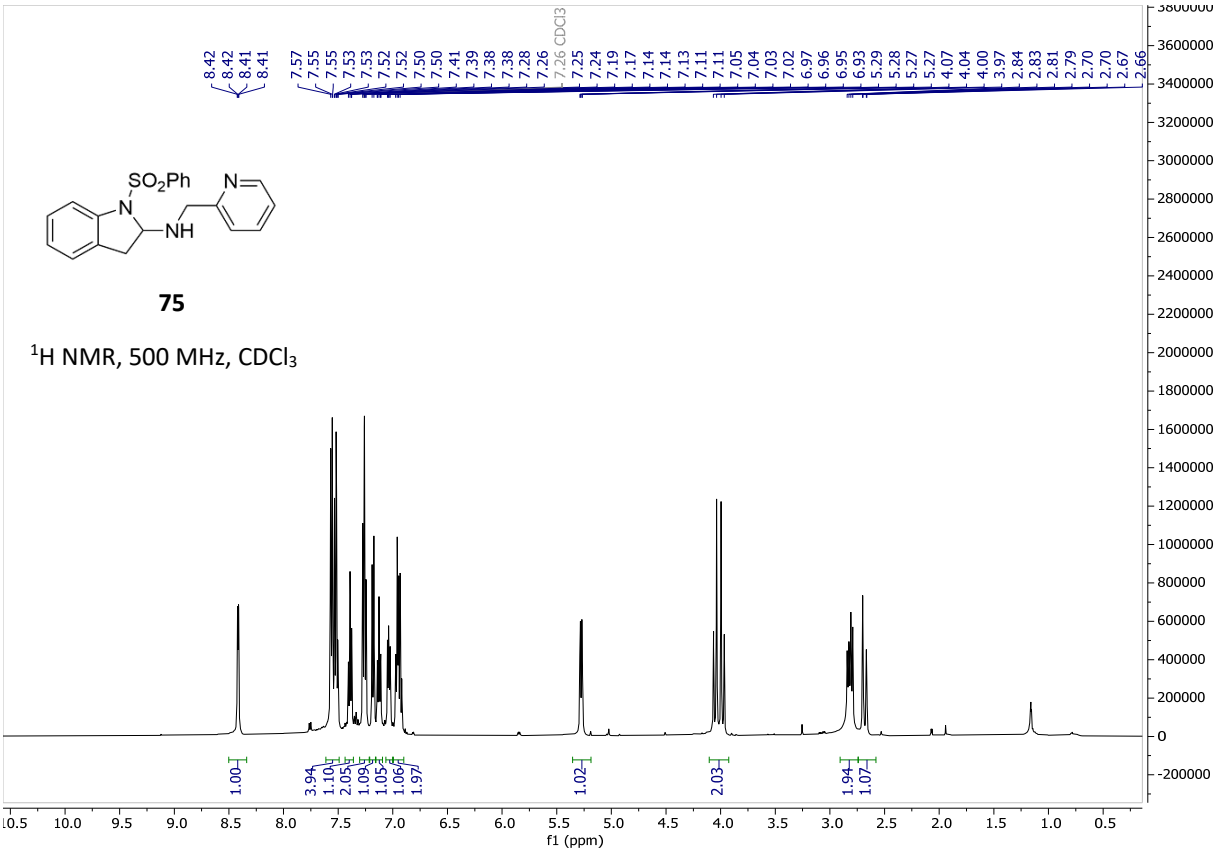


73

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

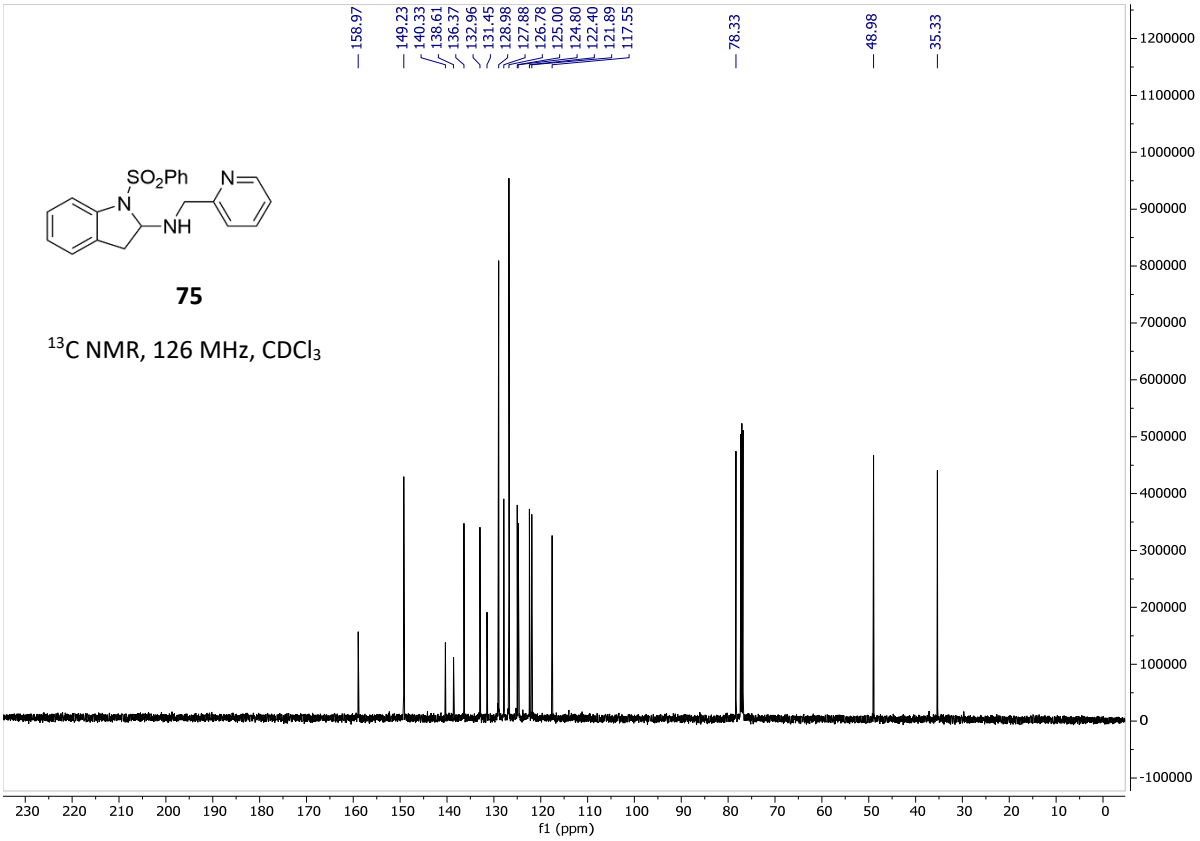

7.62
7.60
7.59
7.58
7.42
7.41
7.41
7.31
7.30
7.29
7.28
7.26 CDCl3
7.26
7.24
7.23
7.22
7.22
7.21
7.18
7.17
7.17
7.17
7.16
7.16
7.15
7.15
6.97
6.97
6.95
5.25
5.23
5.23
3.90
3.87
3.85
3.82
2.87
2.86
2.84
2.82
2.69
2.69
2.66
2.66
SO2Ph
N
NH
74
1H NMR, 500 MHz, CDCl3
2.89
1.04
5.85
2.05
1.96
1.00
2.03
1.12
1.03
1.01
f1 (ppm)


140.56
139.92
138.67
133.09
131.31
129.11
128.48
128.39
128.03
127.10
126.91
125.09
124.80
117.33
78.49
77.16 CDCl3
47.53
35.21
SO2Ph
N
NH
74
13C NMR, 126 MHz, CDCl3
f1 (ppm)



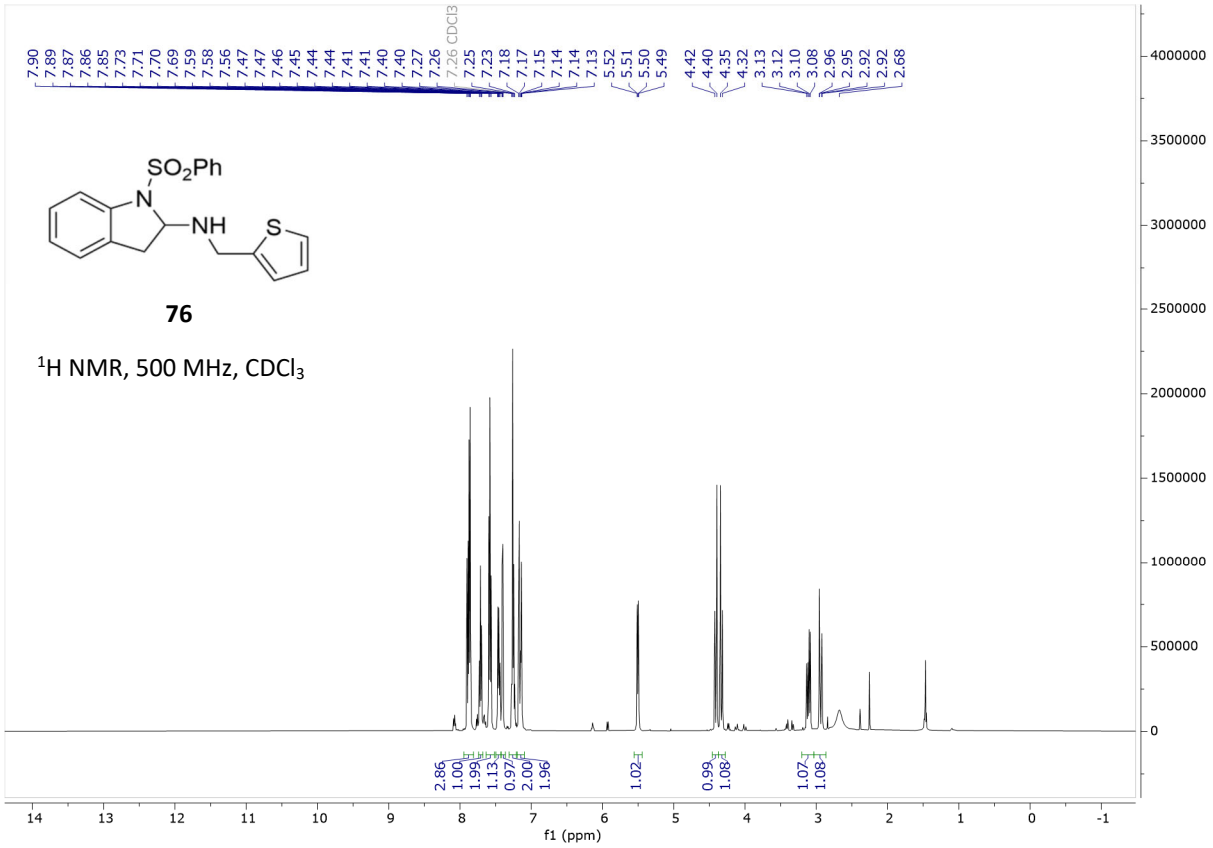
75

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



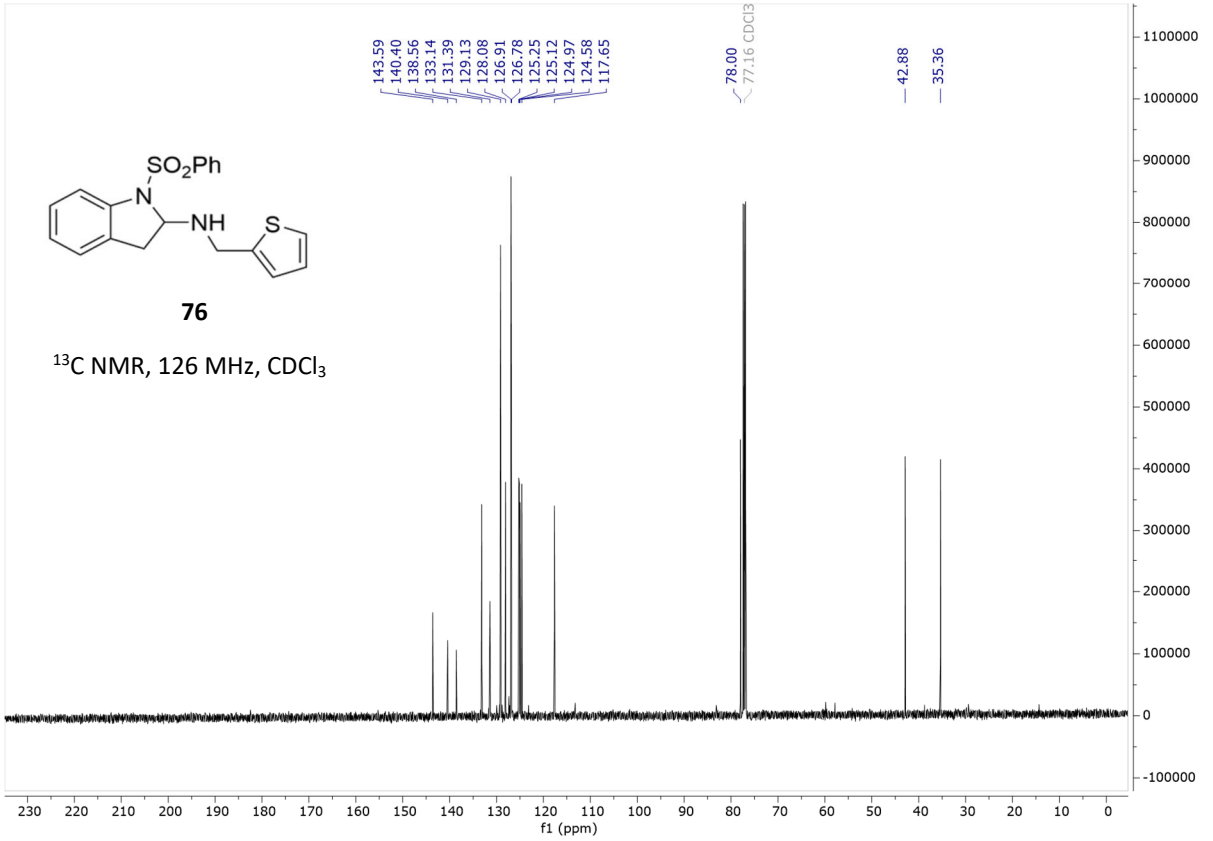
75

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



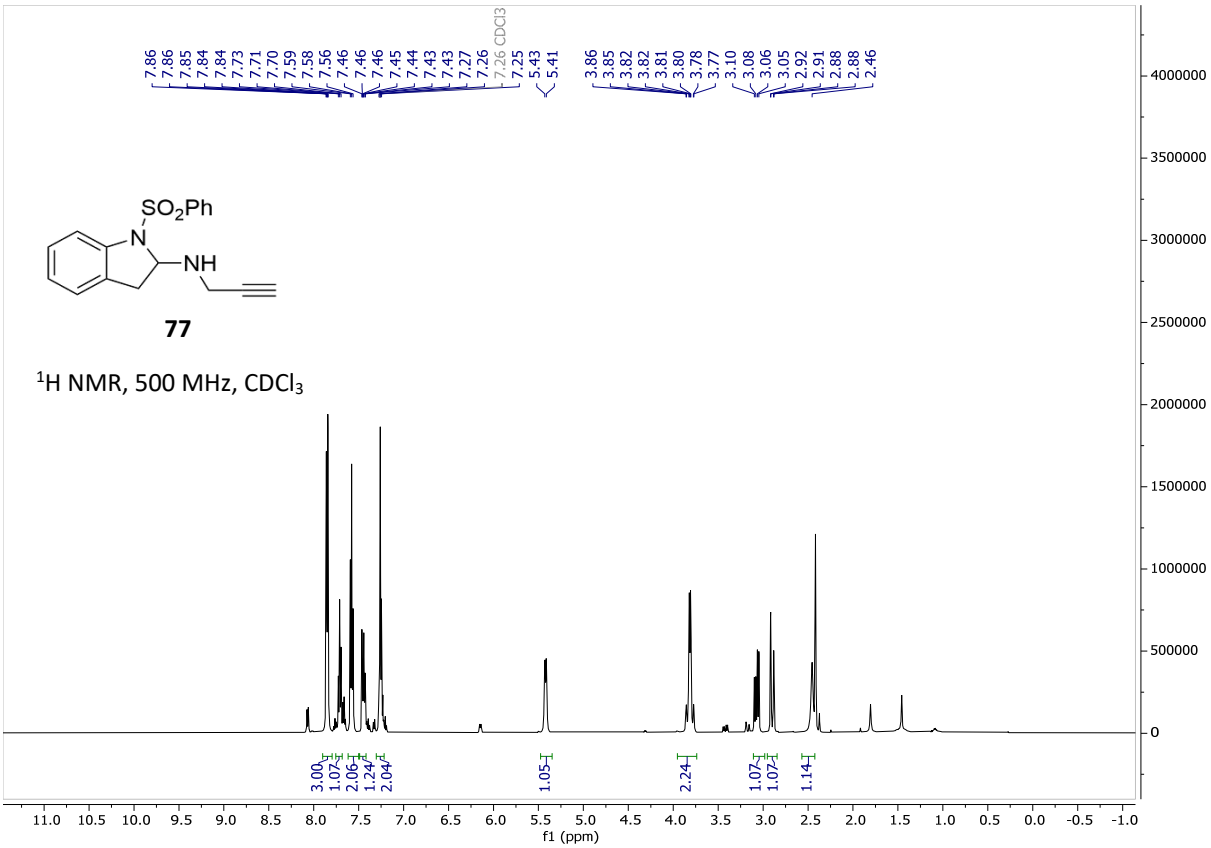
76

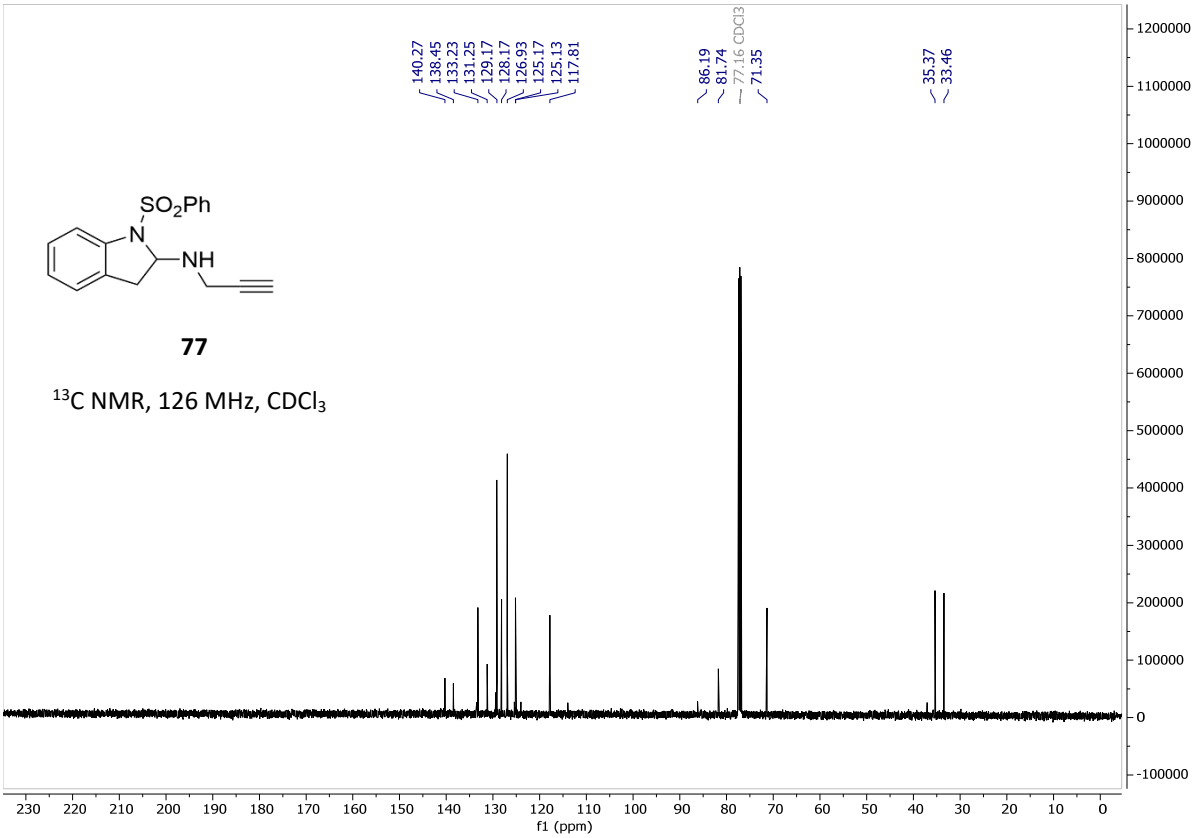
^{1}H NMR, 500 MHz, $CDCl_3$



76

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


7.86
7.86
7.85
7.84
7.84
7.73
7.71
7.70
7.59
7.58
7.56
7.46
7.46
7.46
7.45
7.44
7.43
7.43
7.27
7.26
7.26 CDCl3
7.25
5.43
5.41
3.86
3.85
3.82
3.82
3.81
3.80
3.78
3.77
3.10
3.08
3.06
3.05
2.92
2.91
2.88
2.88
2.46
SO2Ph
N
NH
77
1H NMR, 500 MHz, CDCl3
3.00
1.07
2.06
1.24
2.04
1.05
2.24
1.07
1.07
1.14
f1 (ppm)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138.45
133.23
131.25
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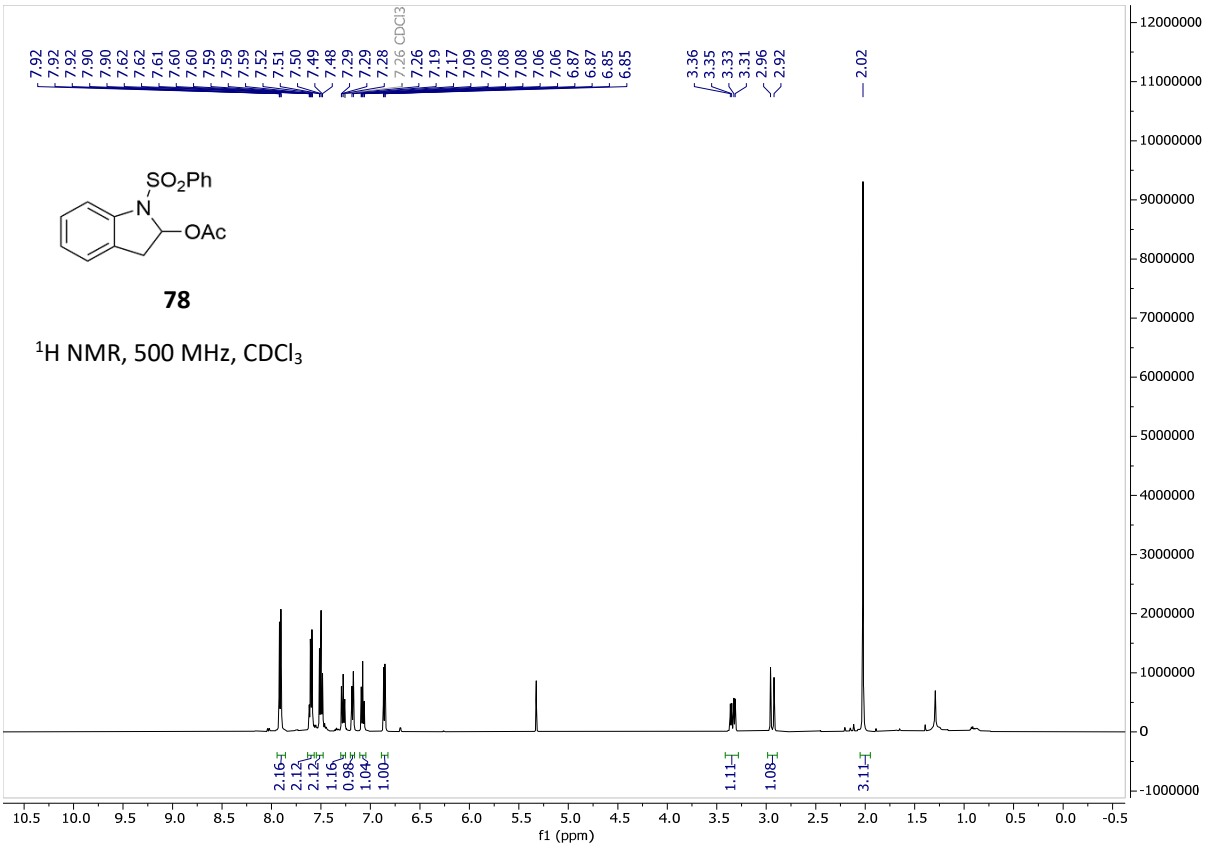
128.17
126.93
125.17
125.13
117.81
86.19
81.74
77.16 CDCl3
71.35
35.37
33.46
SO2Ph
N
NH
77
13C NMR, 126 MHz, CDCl3
f1 (ppm)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7.90
7.90
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7.61
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7.59
7.59
7.52
7.51
7.50
7.49
7.48
7.29
7.29
7.28
7.26 CDCl3
7.26
7.19
7.17
7.09
7.09
7.08
7.08
7.06
7.06
6.87
6.87
6.85
6.85
3.36
3.35
3.33
3.31
2.96
2.92
2.02
SO2Ph
N
OAc
78
1H NMR, 500 MHz, CDCl3
2.16
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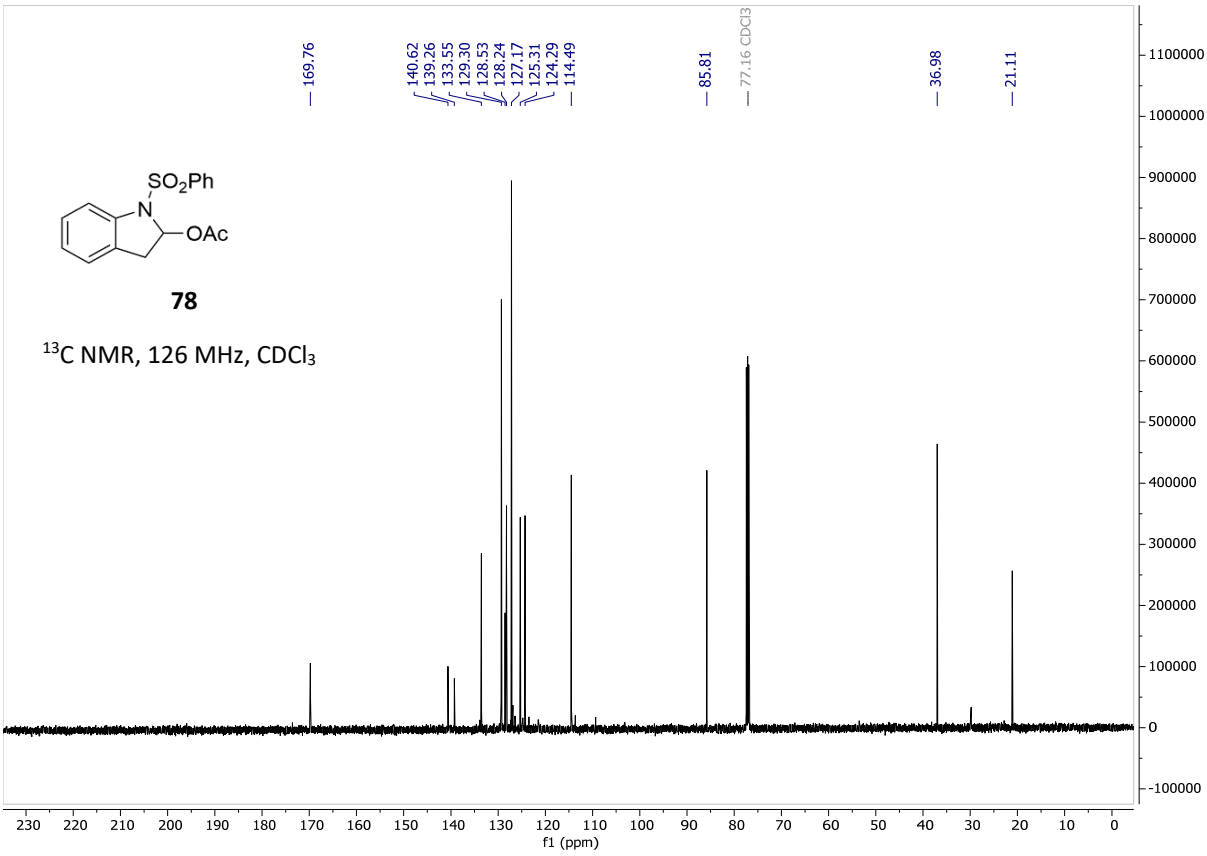
2.12
1.16
0.98
1.04
1.00
1.11
1.08
3.11
f1 (ppm)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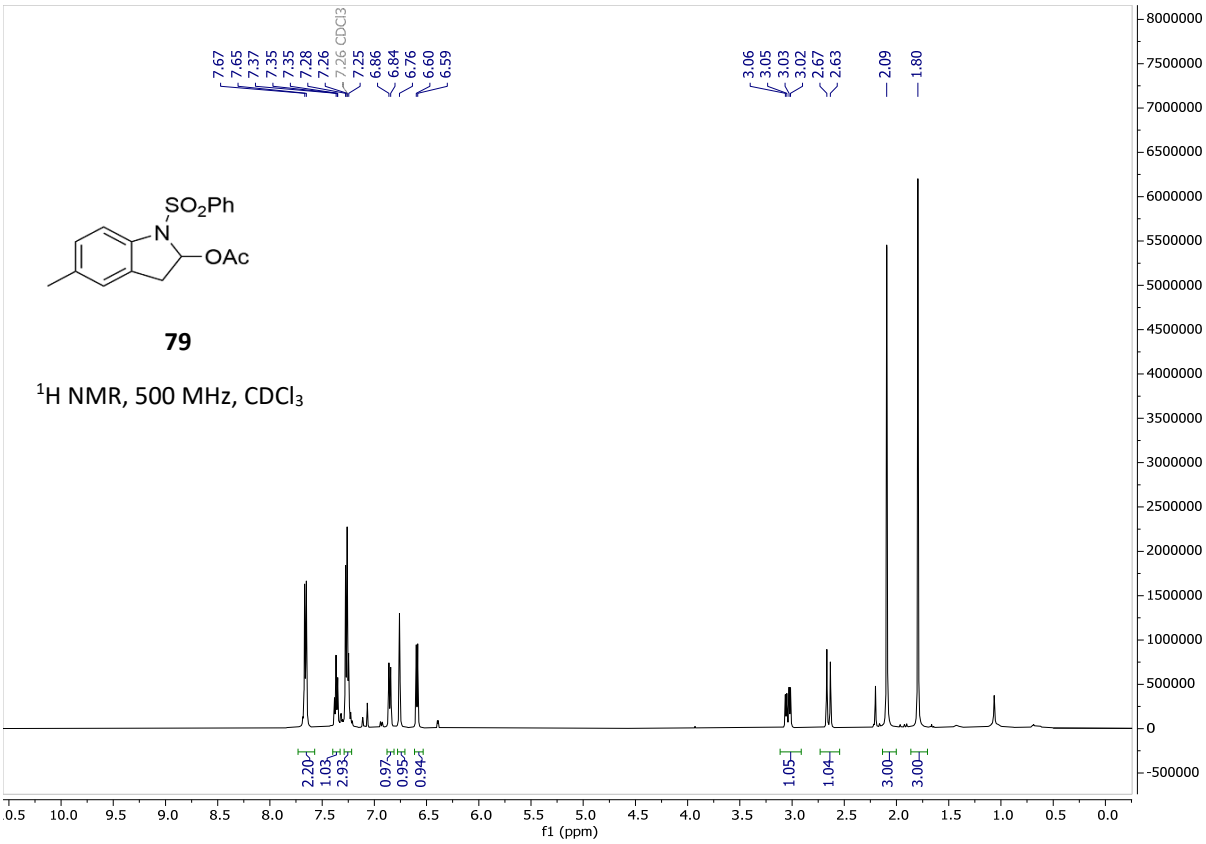
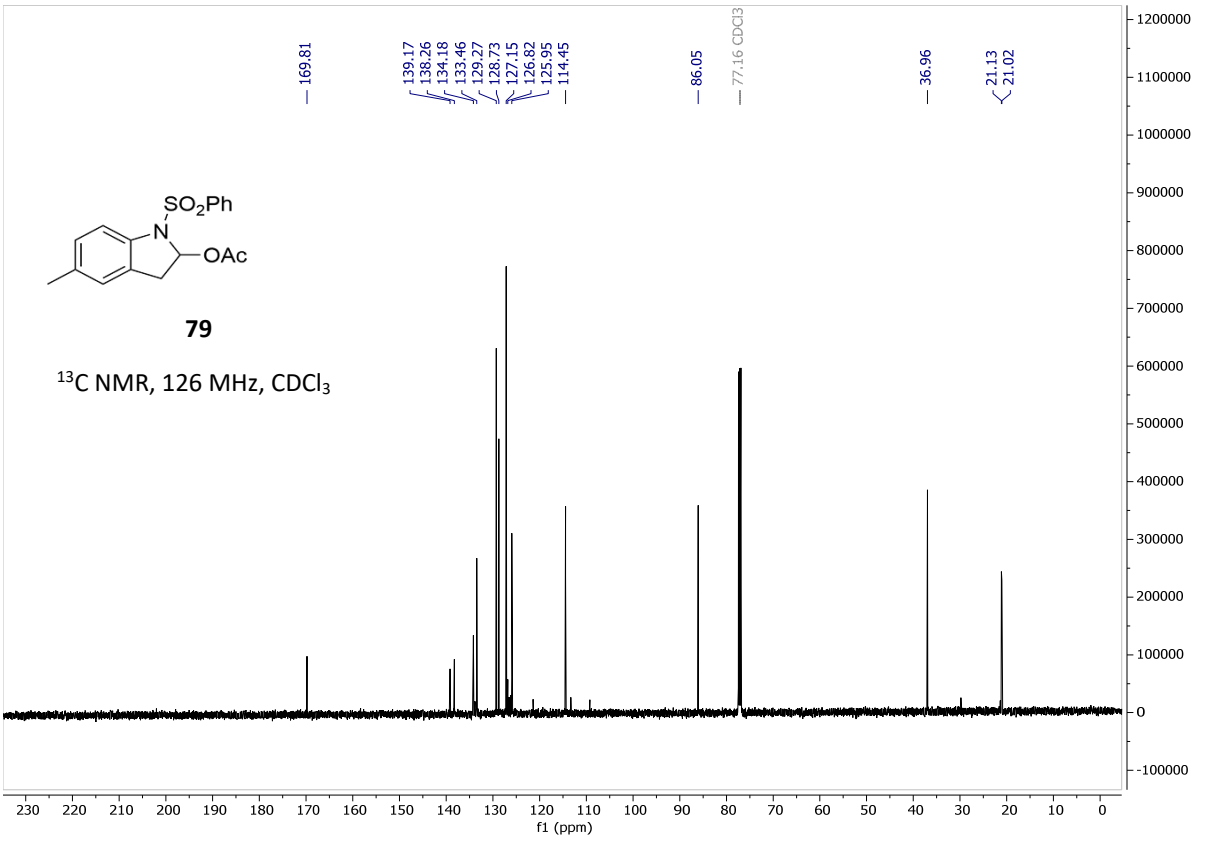
128.53
128.24
127.17
125.31
124.29
114.49
85.81
77.16 CDCl3
36.98
21.11
SO2Ph
N
OAc
78
13C NMR, 126 MHz, CDCl3
f1 (ppm)



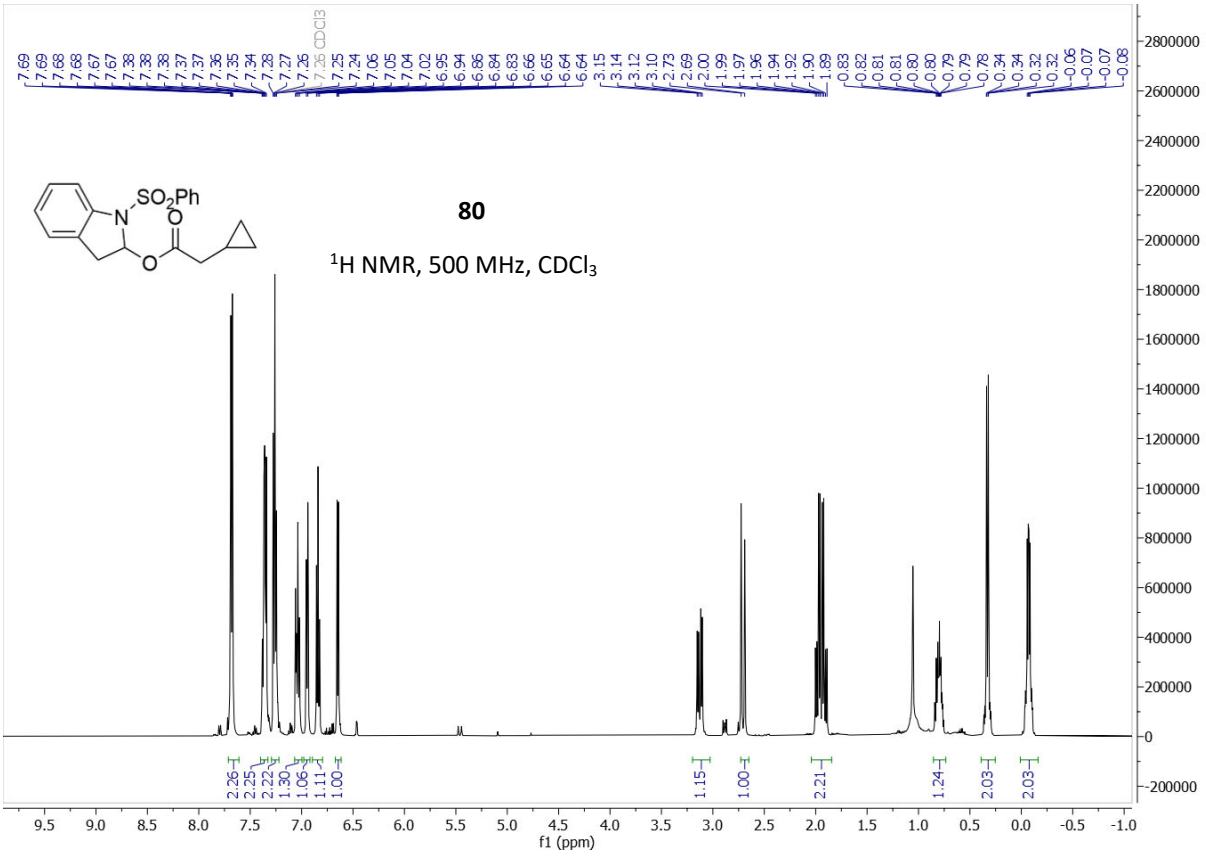
79

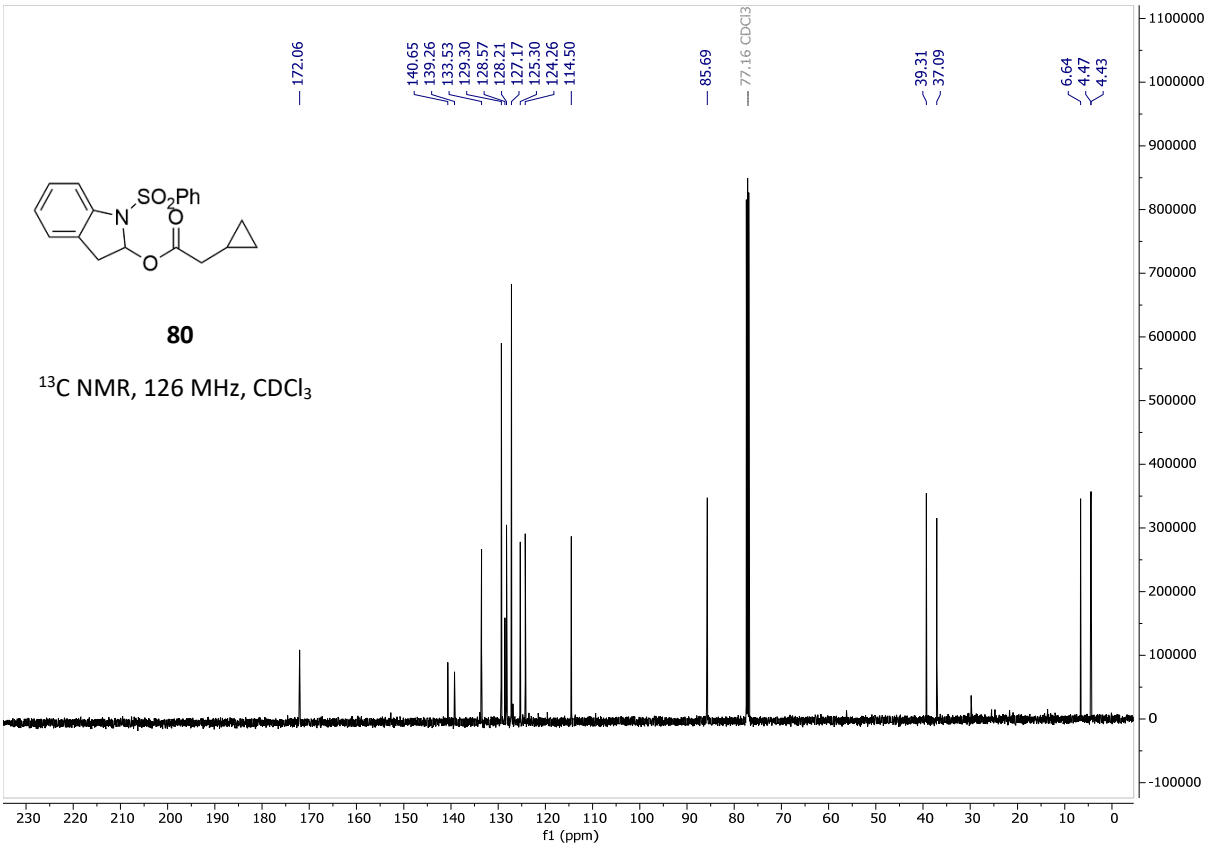
^{1}H NMR, 500 MHz, $CDCl_3$

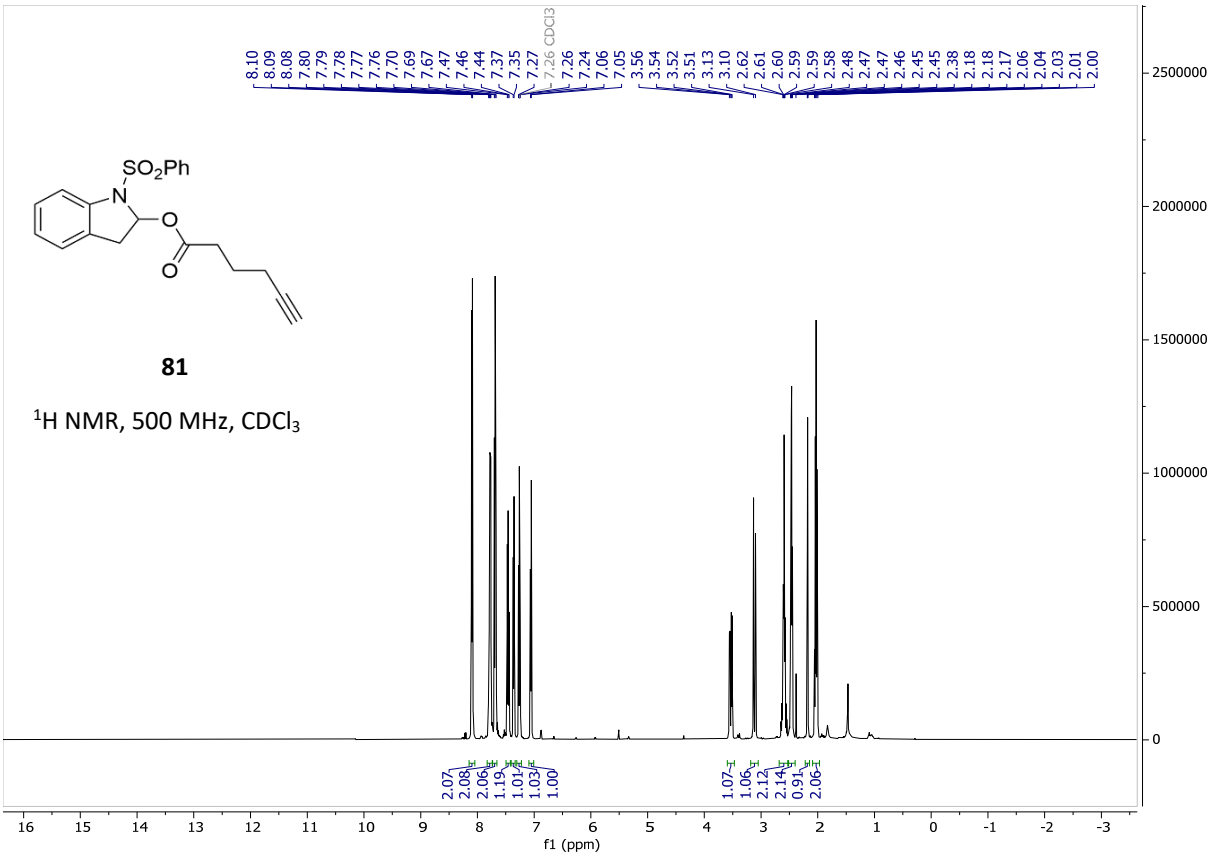


79

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


80
^{1}H NMR, 500 MHz, $CDCl_3$
f1 (ppm)


80
^{13}C NMR, 126 MHz, $CDCl_3$
f1 (ppm)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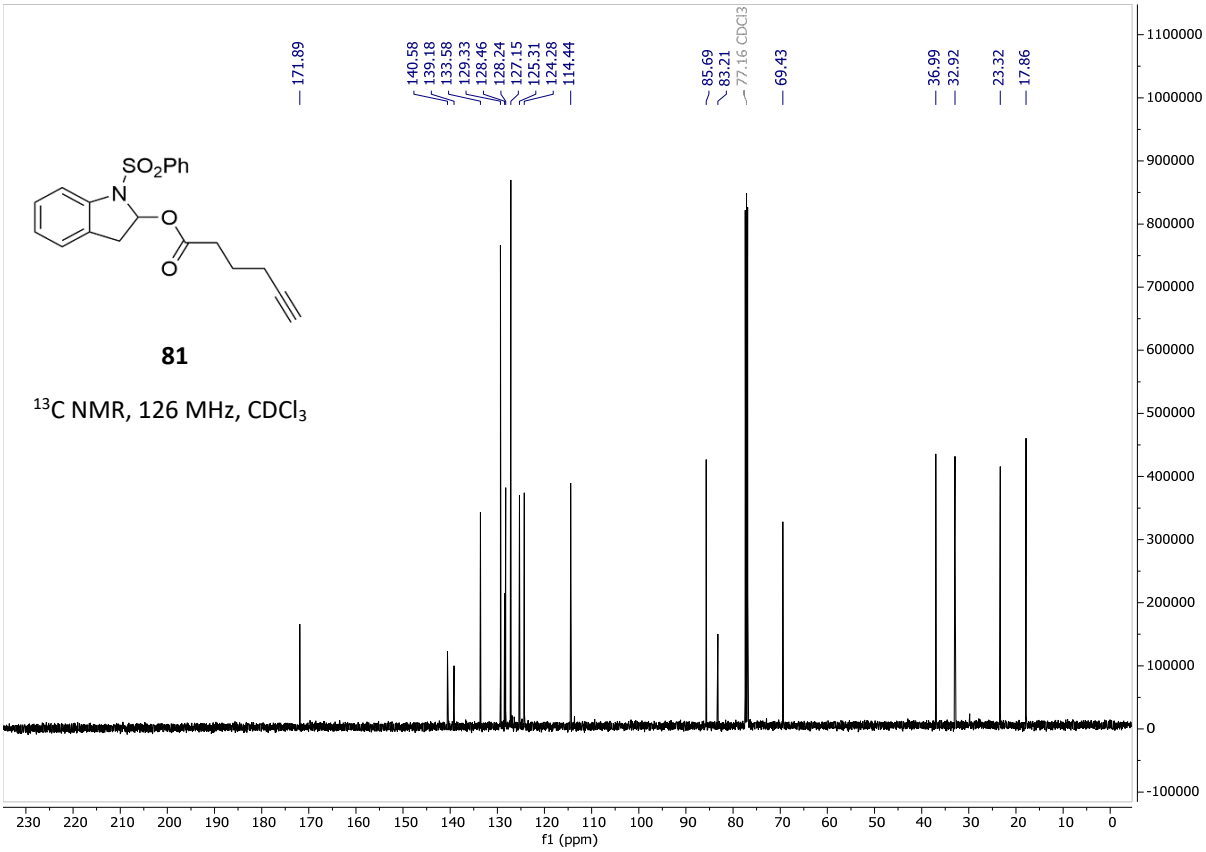
N
O
O
81
1H NMR, 500 MHz, CDCl3
f1 (ppm)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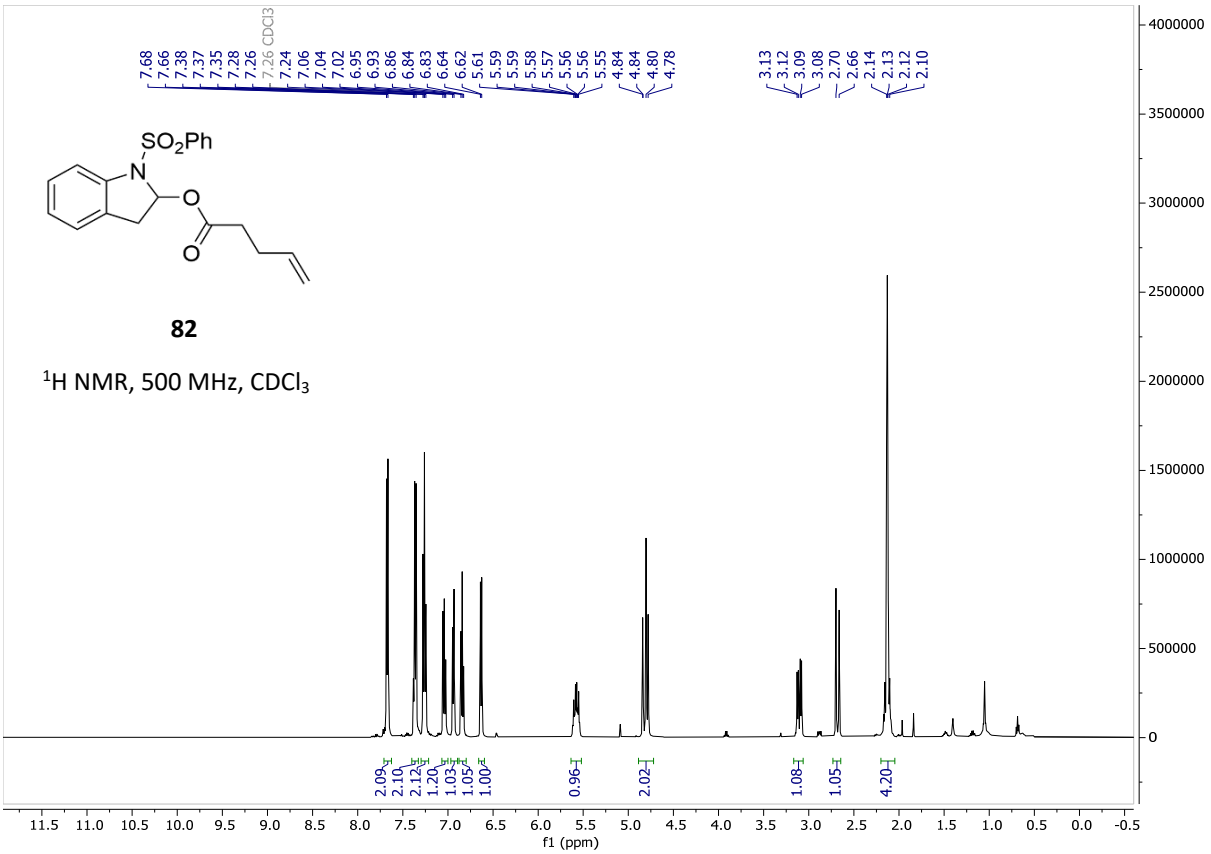
N
O
O
81
13C NMR, 126 MHz, CDCl3
f1 (ppm)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7.26
7.26 CDCl3
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6.84
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6.62
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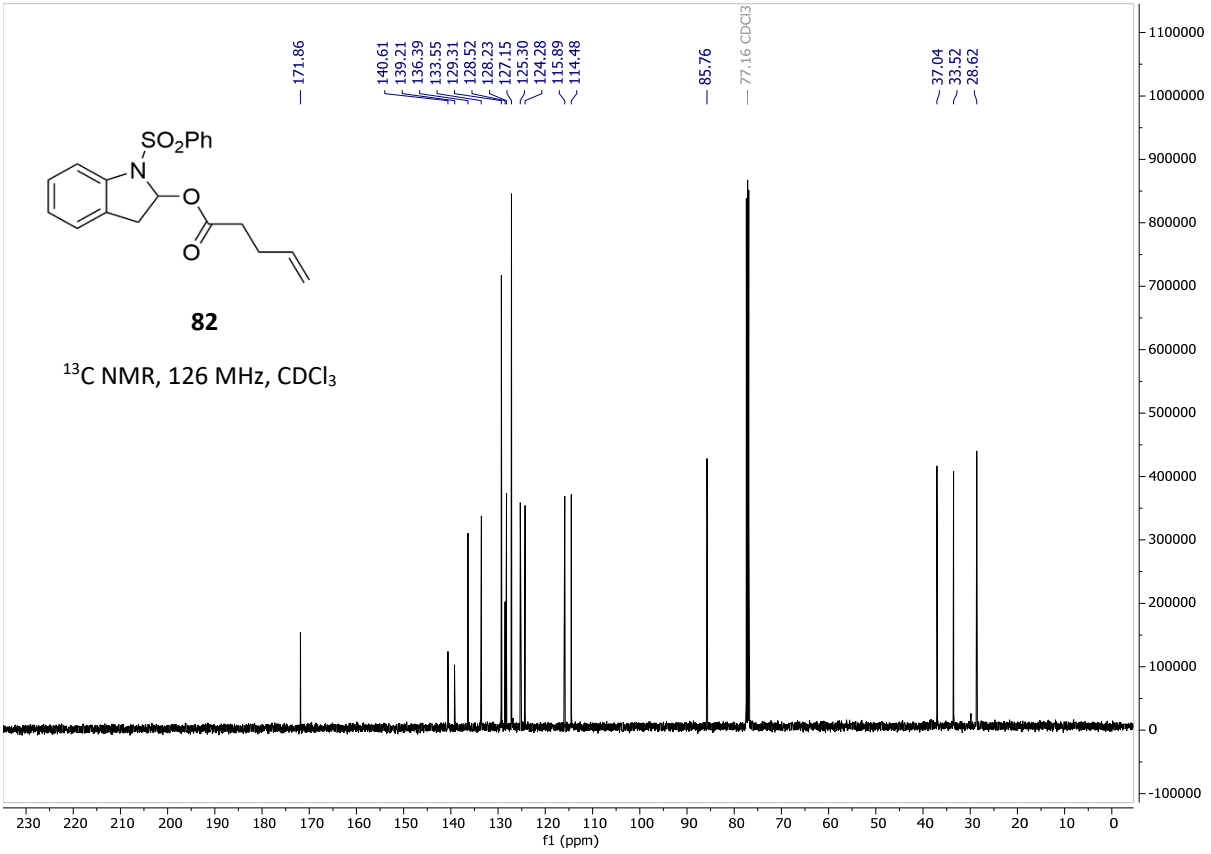
5.57
5.56
5.56
5.55
4.84
4.84
4.80
4.78
3.13
3.12
3.09
3.08
2.70
2.66
2.14
2.13
2.12
2.10
SO2Ph
N
O
O
82
1H NMR, 500 MHz, CDCl3
2.09
2.10
2.12
1.20
1.03
1.05
1.00
0.96
2.02
1.08
1.05
4.20
f1 (ppm)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129.31
128.52
128.23
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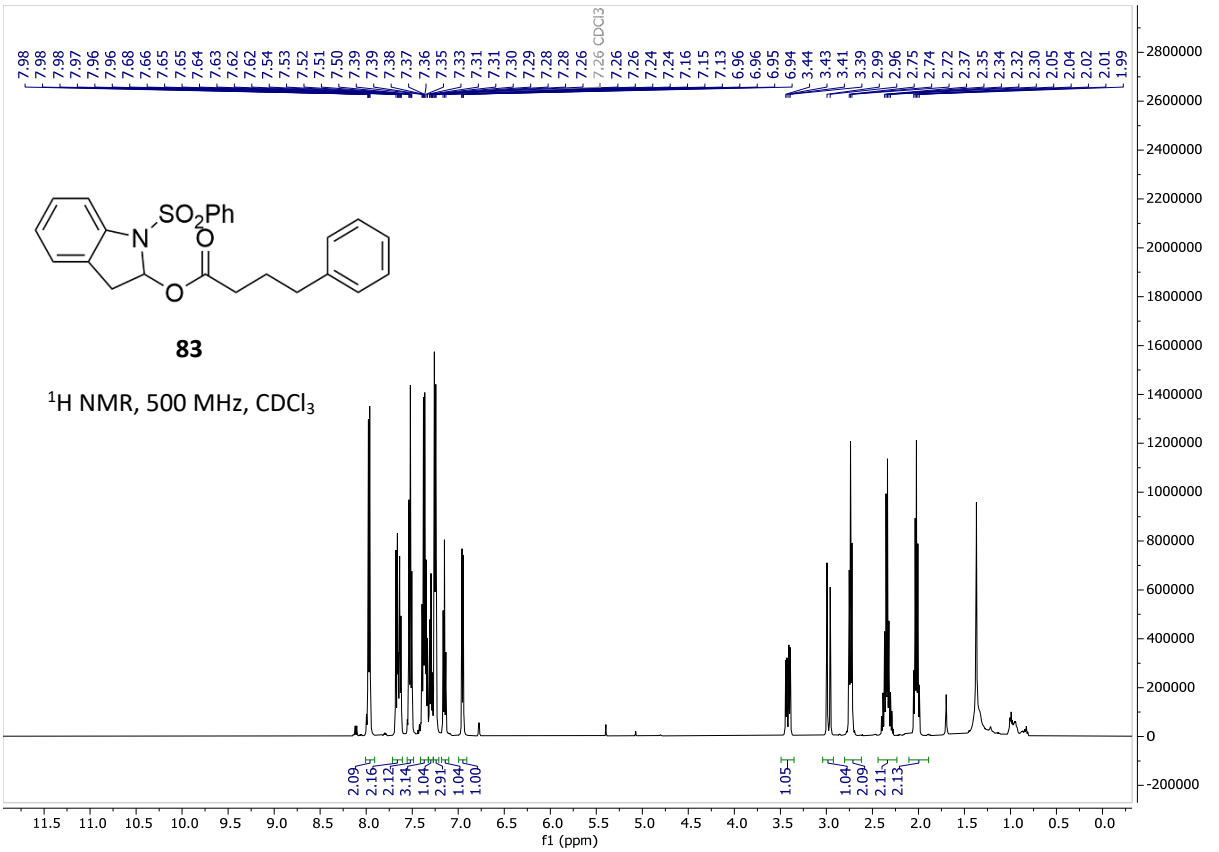
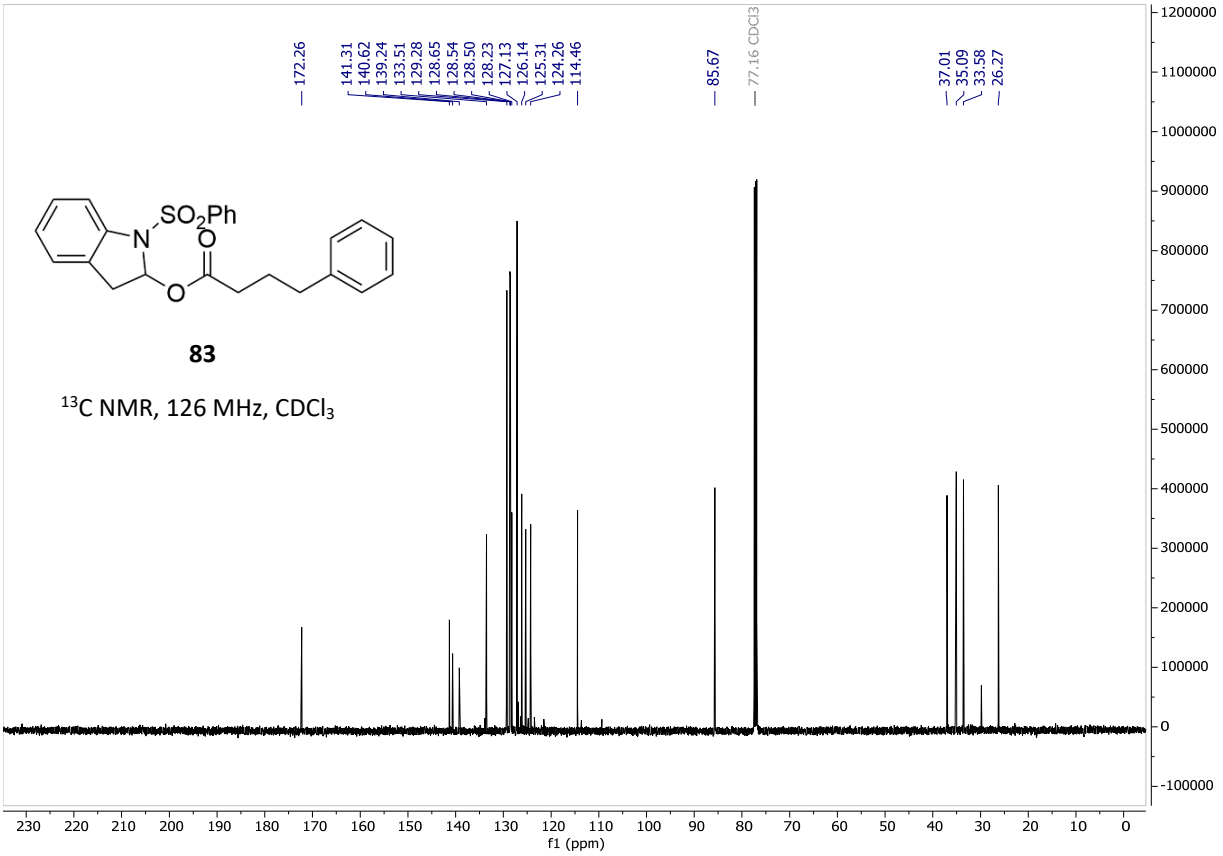
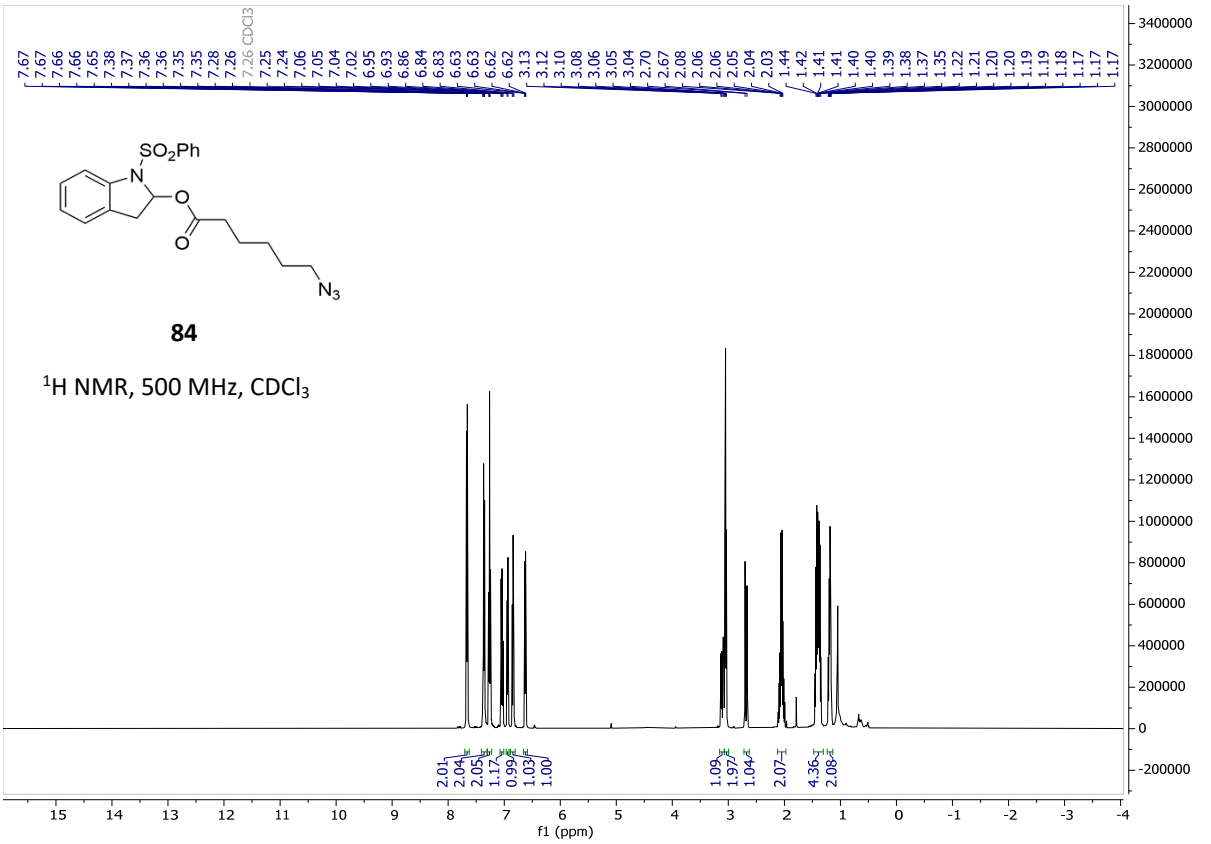
125.30
124.28
115.89
114.48
85.76
77.16 CDCl3
37.04
33.52
28.62
SO2Ph
N
O
O
82
13C NMR, 126 MHz, CDCl3
f1 (ppm)

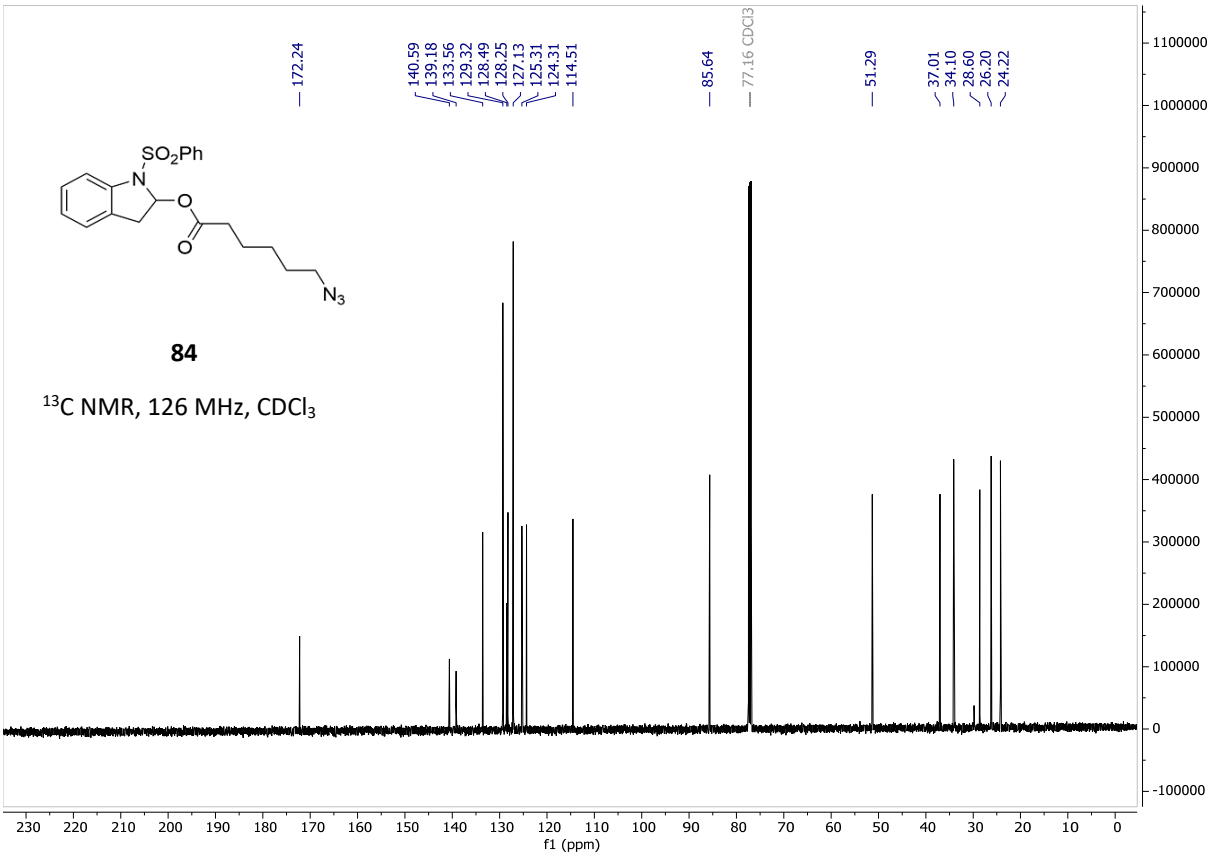

SO2Ph
N
O
O
83
1H NMR, 500 MHz, CDCl3
f1 (ppm)


SO2Ph
N
O
O
83
13C NMR, 126 MHz, CDCl3
f1 (ppm)



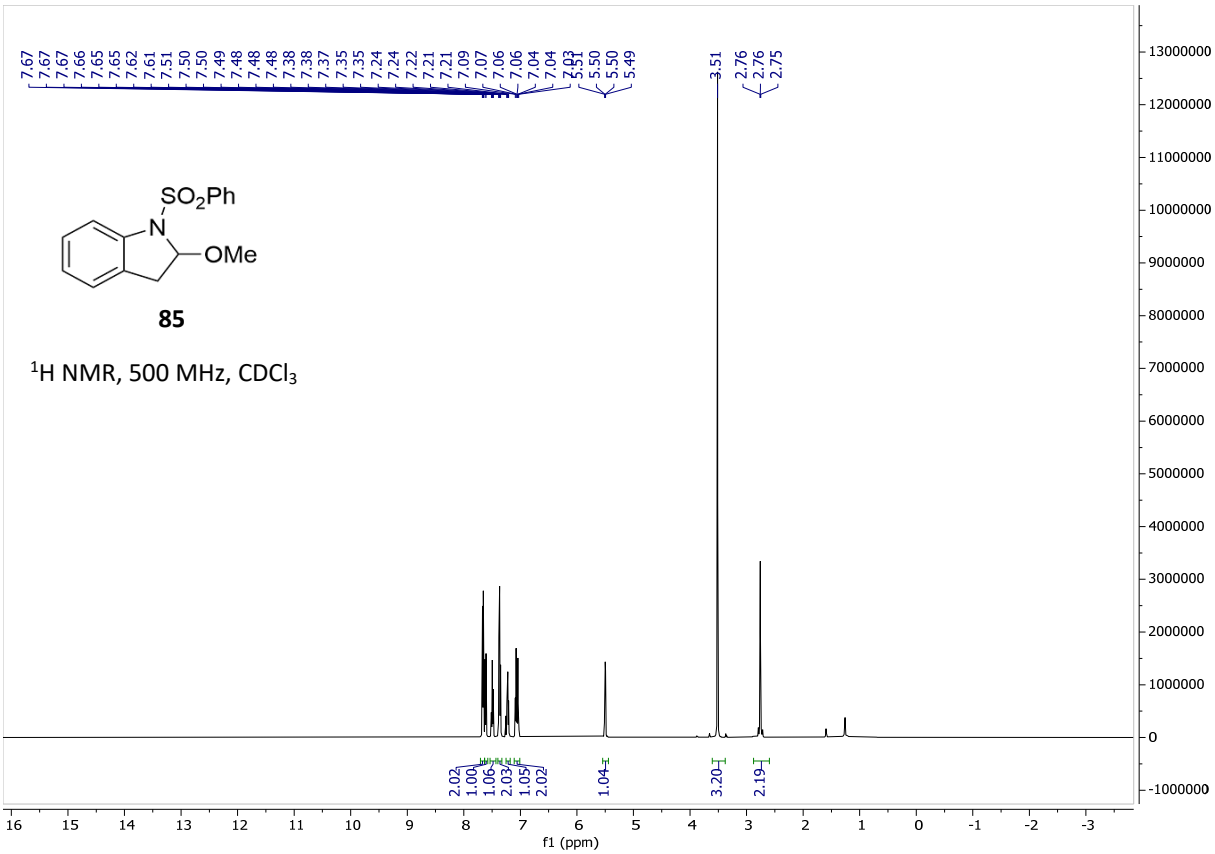
84

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



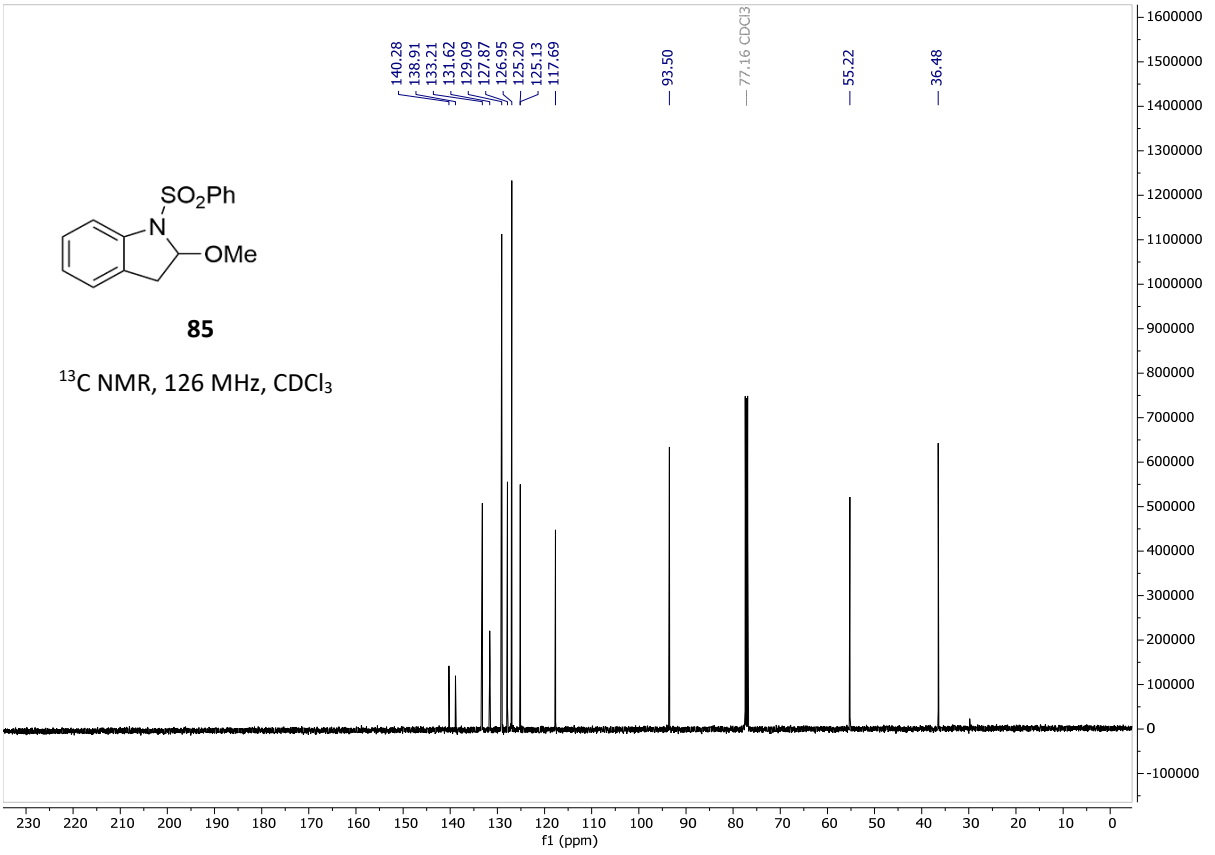
84

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



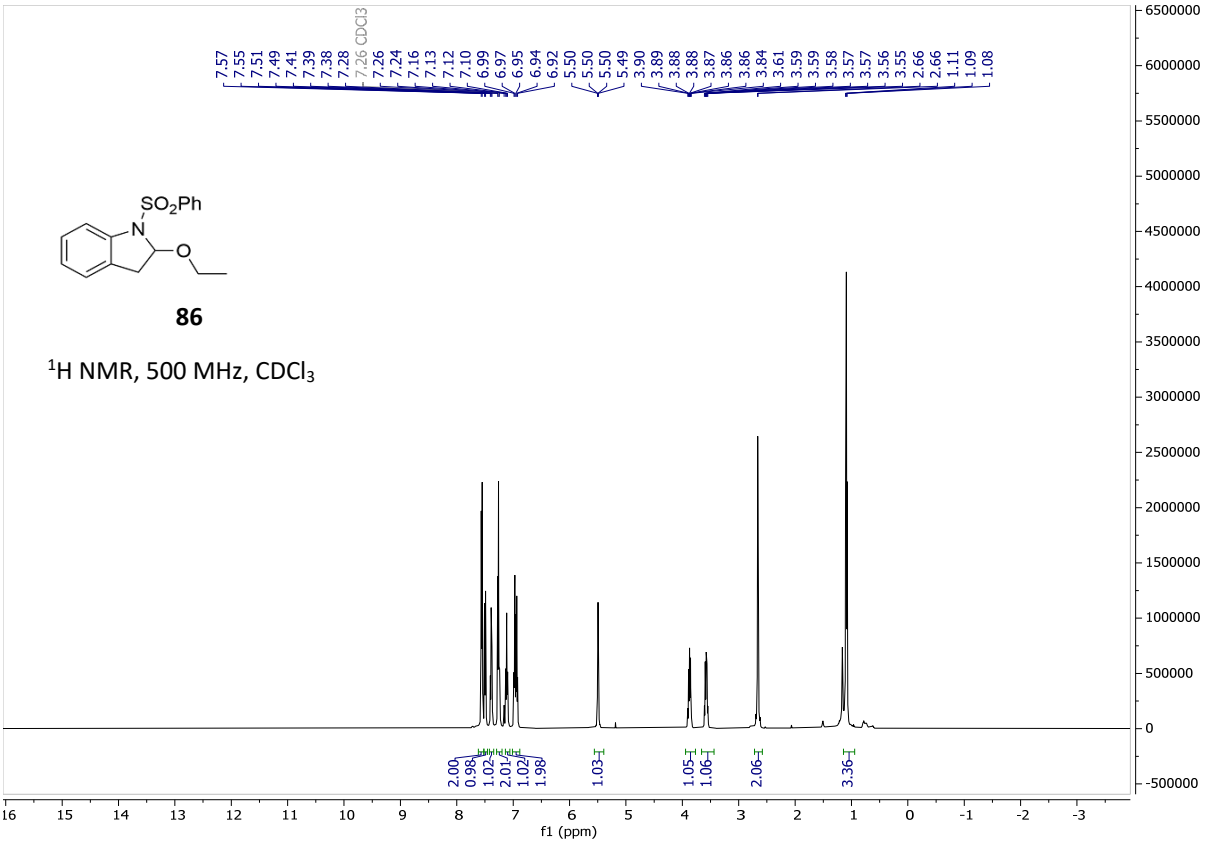
85

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



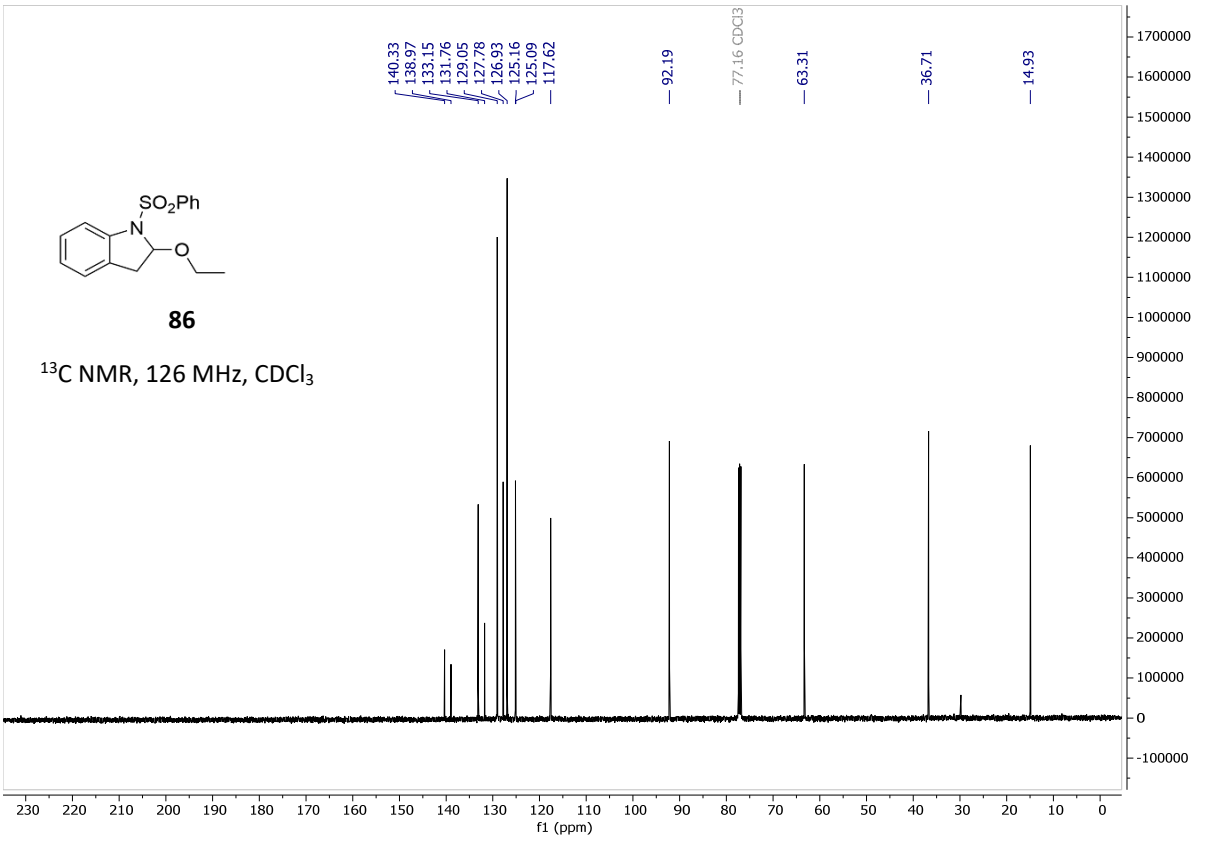
85

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



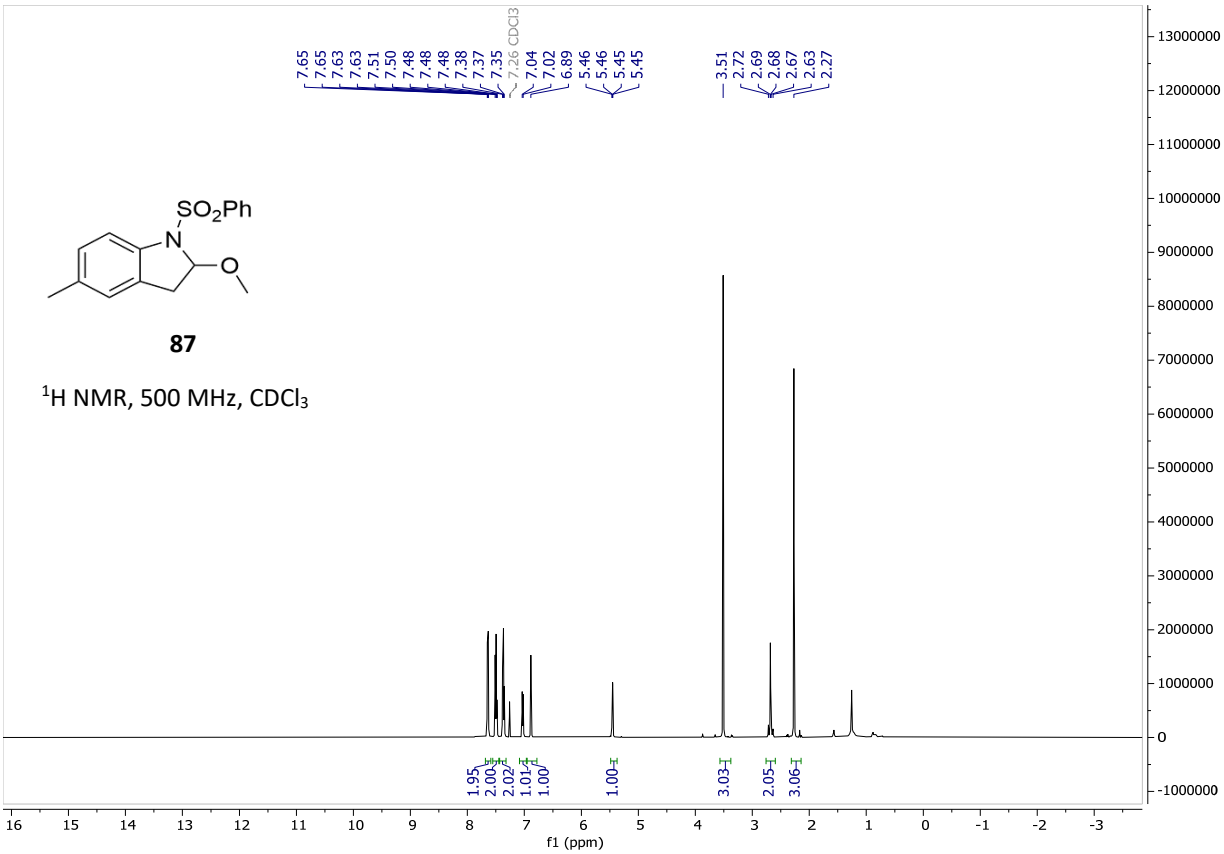
86

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



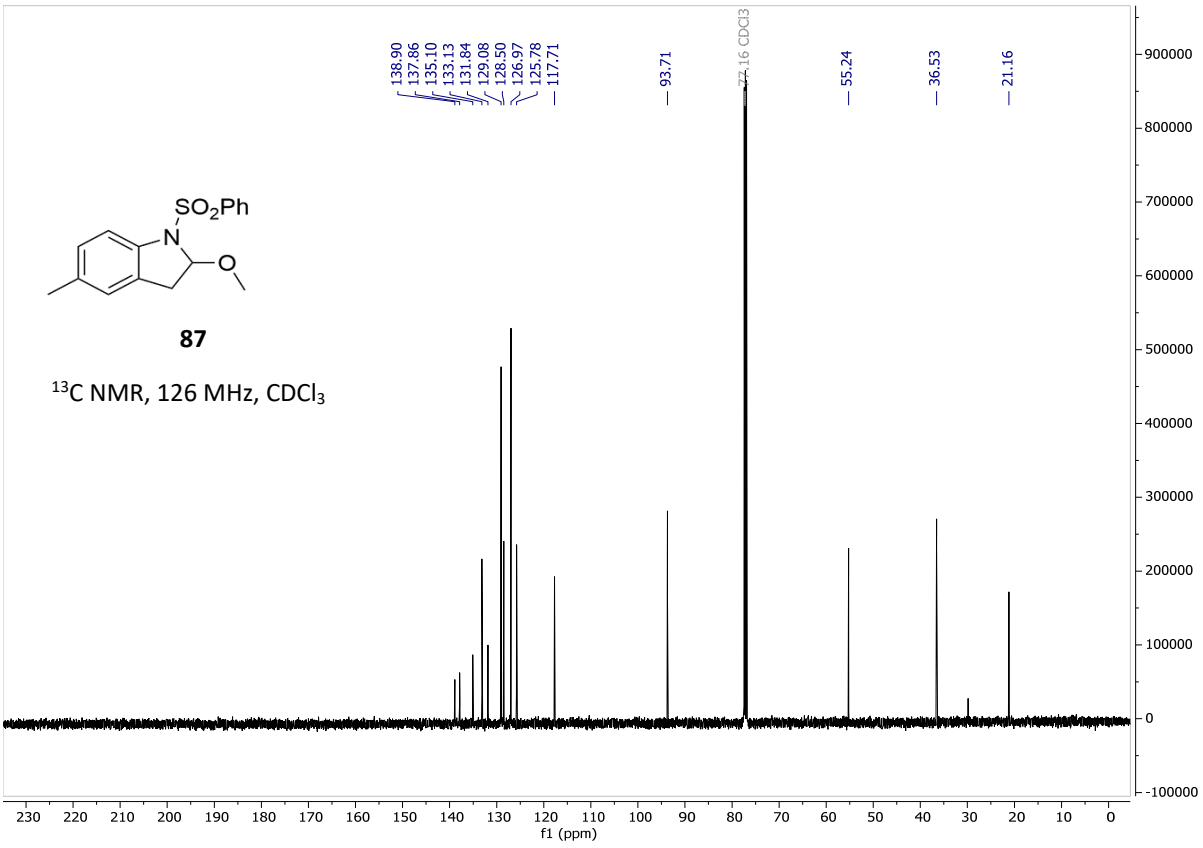
86

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



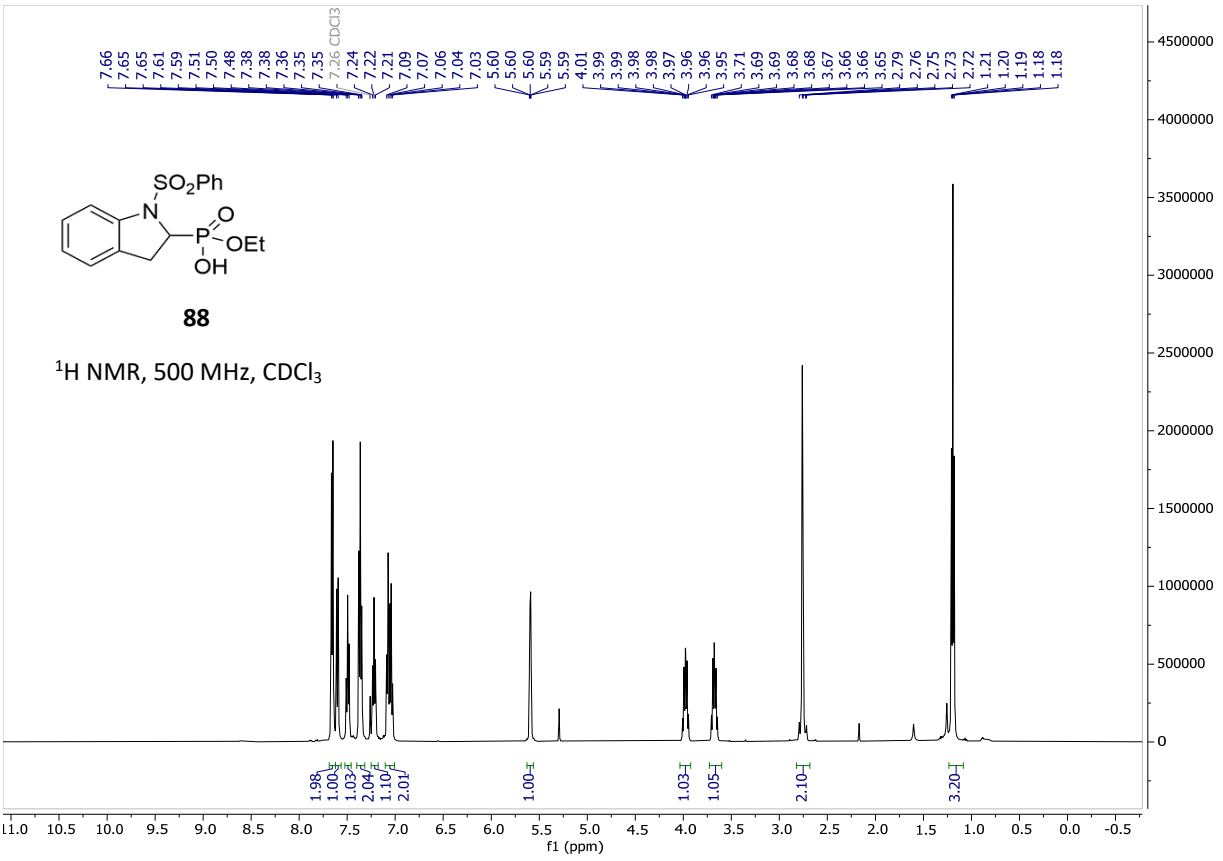
87

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



87

^{13}C NMR, 126 MHz, $CDCl_3$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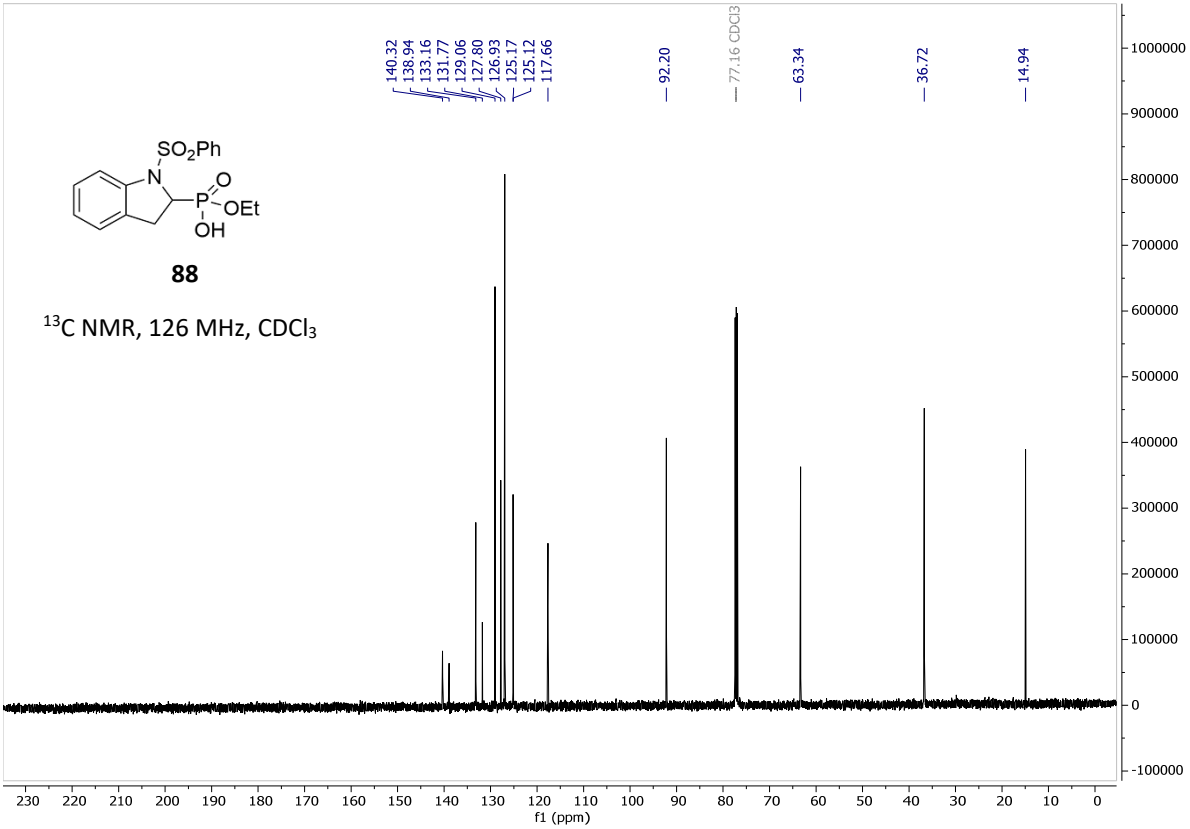
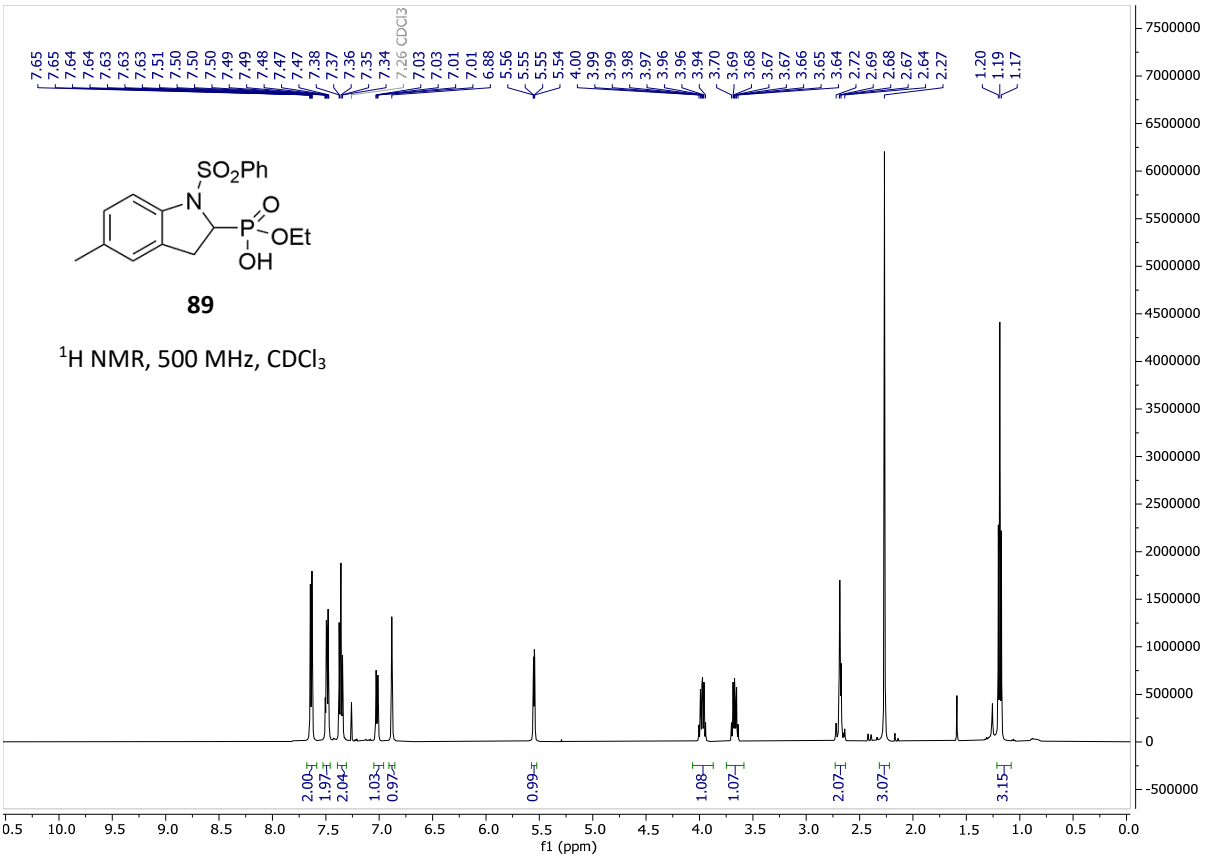
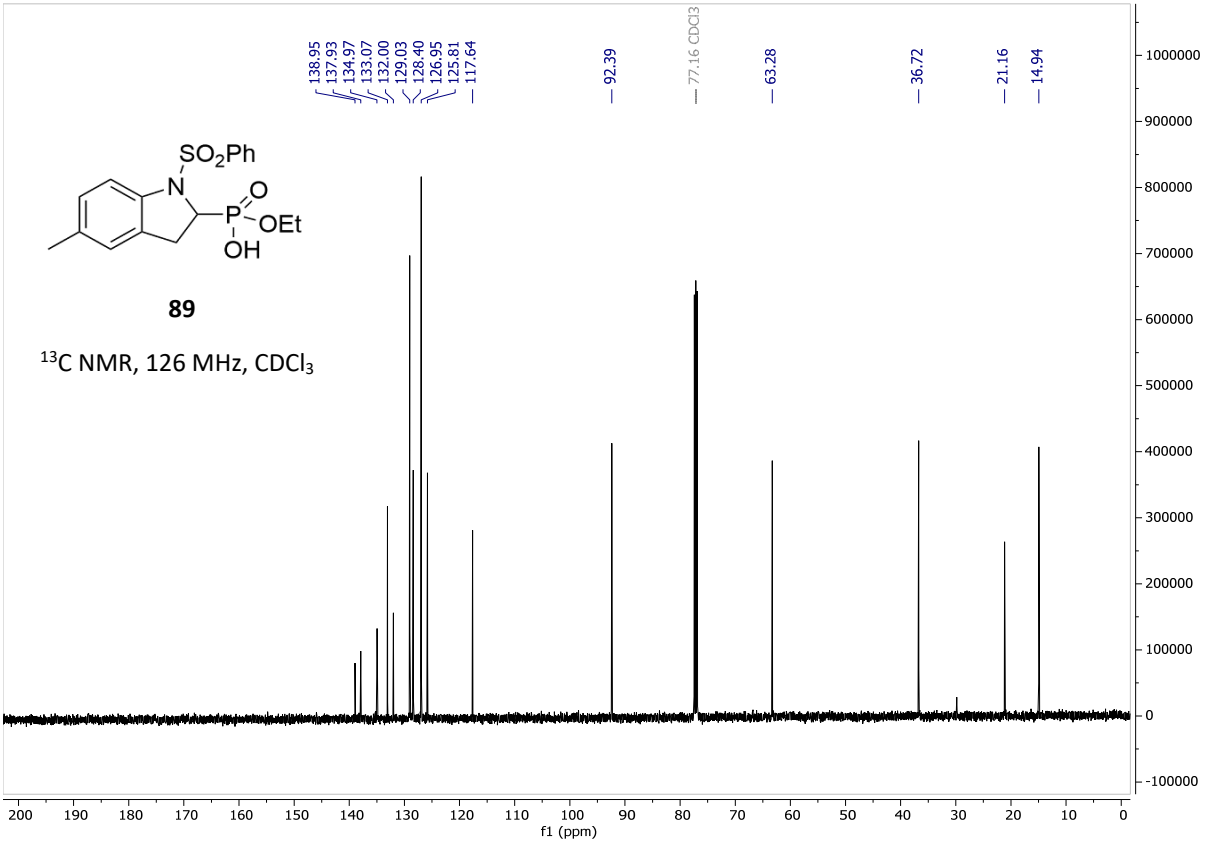
SO2Ph
N
P
O
OEt
OH
88
1H NMR, 500 MHz, CDCl3
1.98 1.00 1.03 2.04 1.10 2.01 1.00 1.03 1.05 2.10 3.20
f1 (ppm)


140.32 138.94 133.16 131.77 129.06 127.80 126.93 125.17 125.12 117.66 92.20 77.16 CDCl3 63.34 36.72 14.94
SO2Ph
N
P
O
OEt
OH
88
13C NMR, 126 MHz, CDCl3
f1 (ppm)


7.65 7.65 7.64 7.64 7.63 7.63 7.63 7.51 7.50 7.50 7.50 7.49 7.49 7.48 7.47 7.47 7.38 7.37 7.36 7.35 7.34 7.26 CDCl3 7.03 7.03 7.01 7.01 6.88 5.56 5.55 5.55 5.54 4.00 3.99 3.99 3.98 3.97 3.96 3.96 3.94 3.70 3.69 3.68 3.67 3.67 3.66 3.65 3.64 2.72 2.69 2.68 2.67 2.64 2.27 1.20 1.19 1.17
SO2Ph
N
P
O
OEt
OH
89
1H NMR, 500 MHz, CDCl3
2.00 1.97 2.04 1.03 0.97 0.99 1.08 1.07 2.07 3.07 3.15
f1 (ppm)


138.95 137.93 134.97 133.07 132.00 129.03 128.40 126.95 125.81 117.64 92.39 77.16 CDCl3 63.28 36.72 21.16 14.94
SO2Ph
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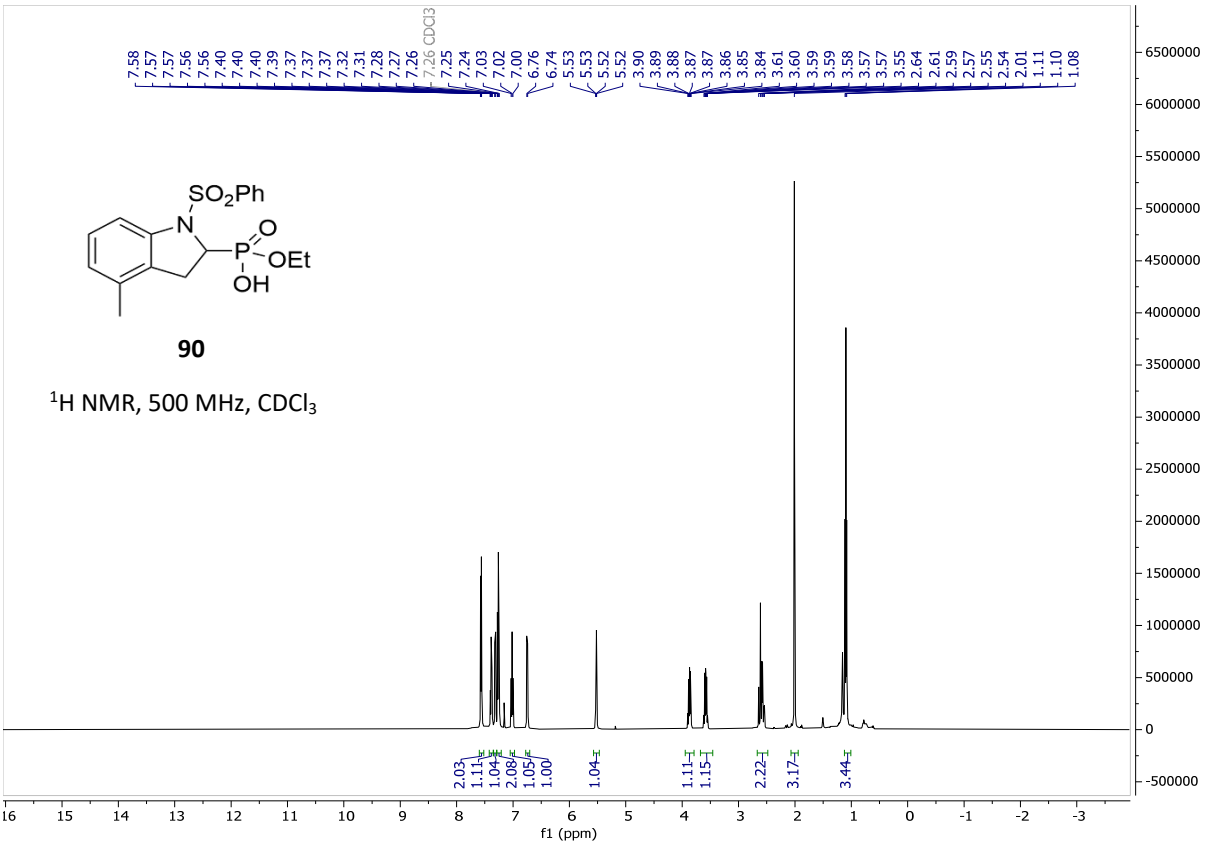
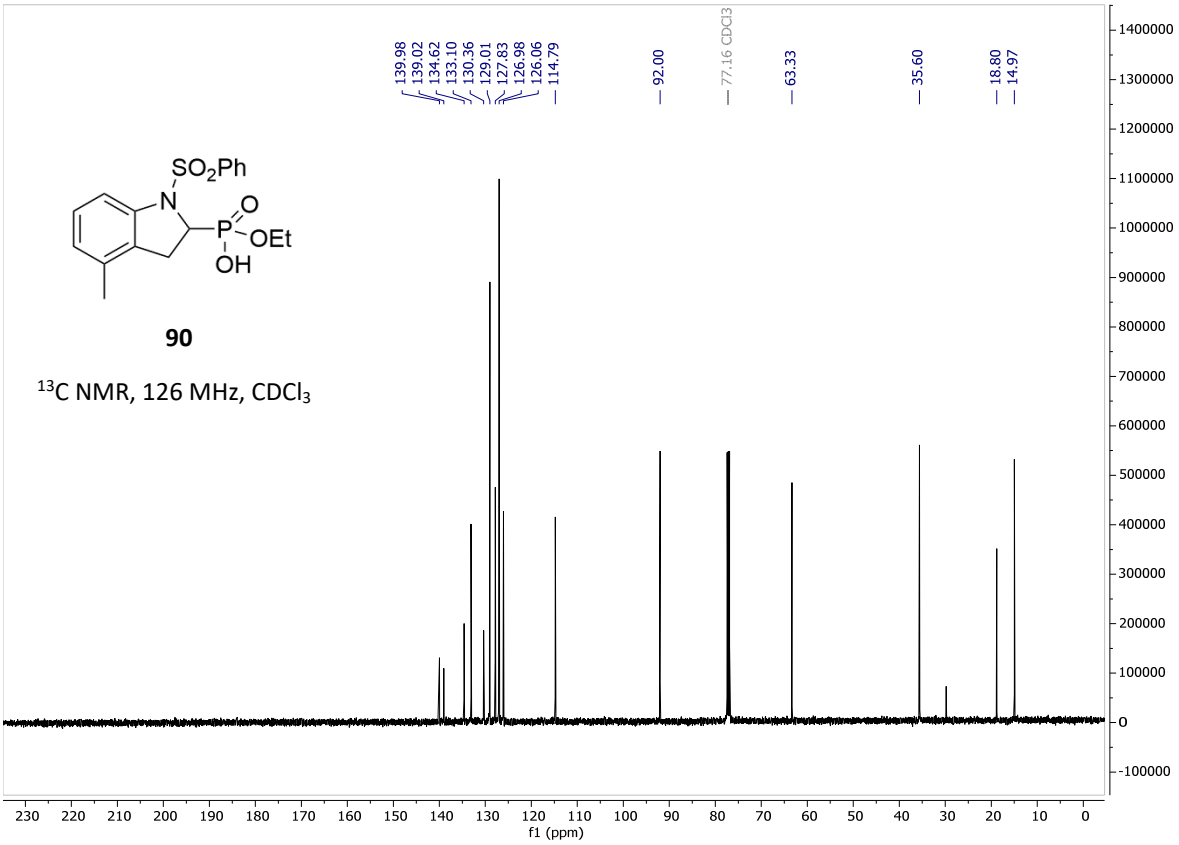
O
OEt
OH
89
13C NMR, 126 MHz, CDCl3
f1 (ppm)



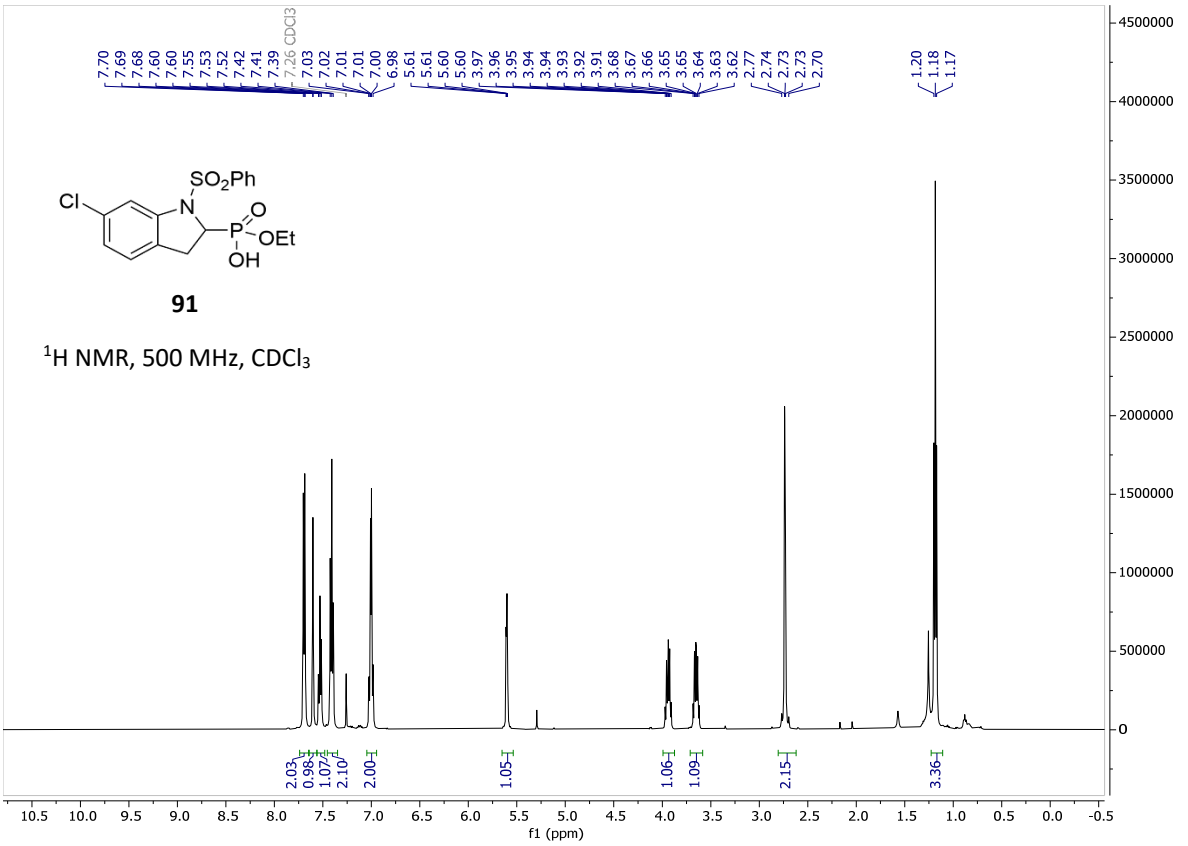
90

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



90

^{13}C NMR, 126 MHz, $CDCl_3$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7.60
7.55
7.53
7.52
7.42
7.41
7.39
7.26 CDCl3
7.03
7.02
7.01
7.01
7.00
6.98
5.61
5.61
5.60
5.60
3.97
3.96
3.95
3.94
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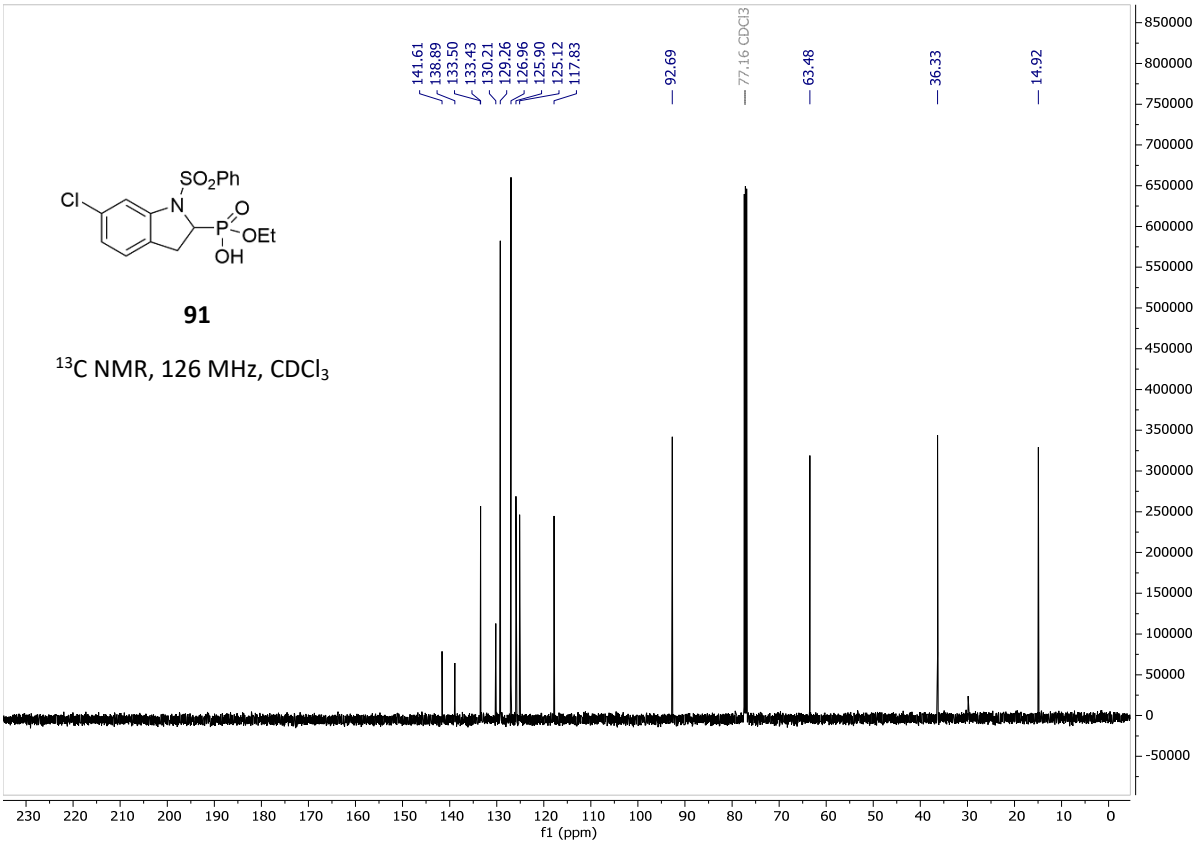
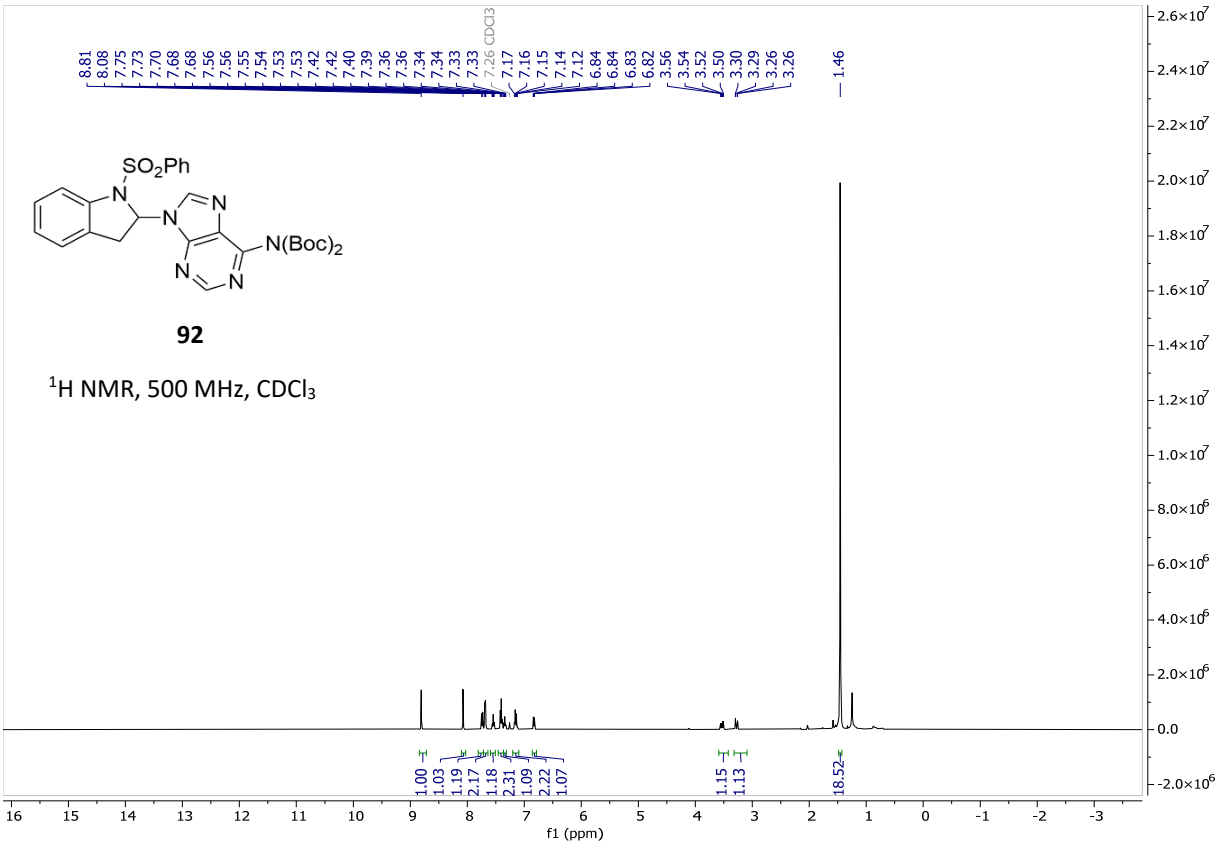
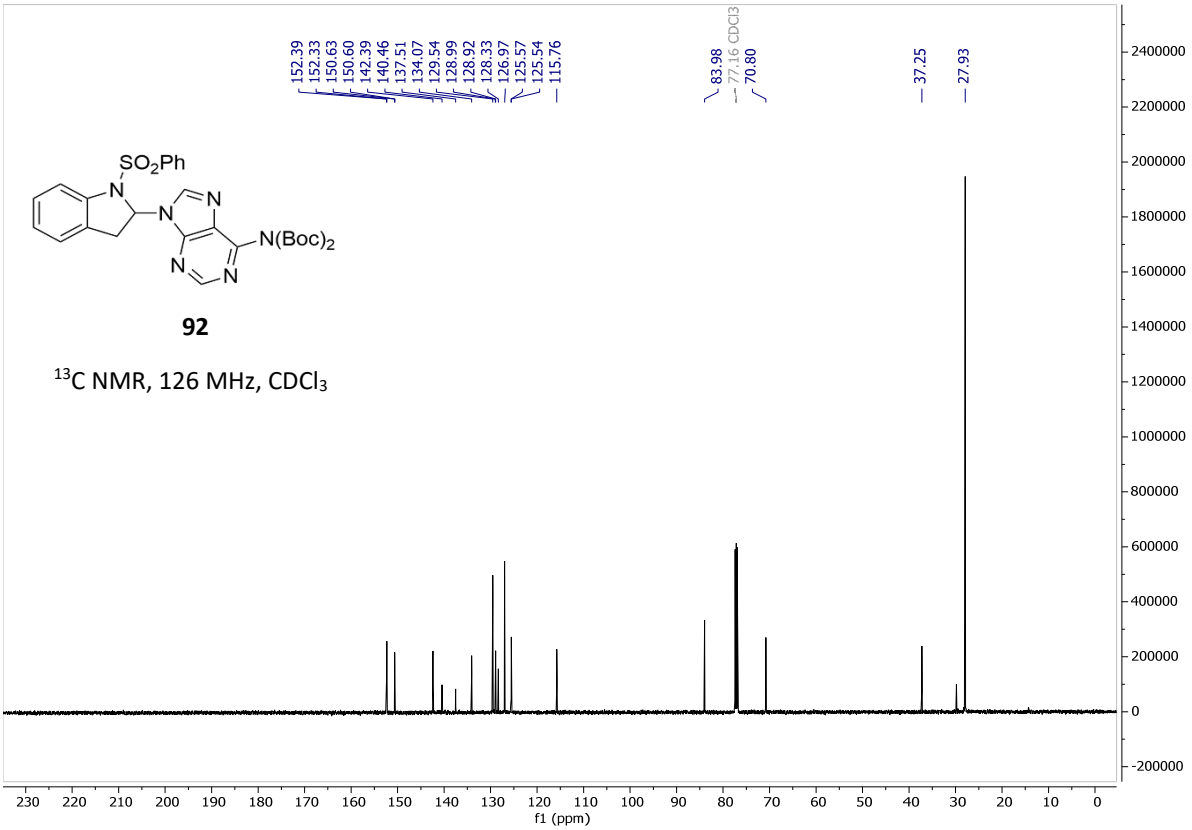
3.93
3.92
3.91
3.68
3.67
3.66
3.65
3.65
3.64
3.63
3.62
2.77
2.74
2.73
2.73
2.70
1.20
1.18
1.17
SO2Ph
Cl
N
P
O
OEt
OH
91
1H NMR, 500 MHz, CDCl3
2.03
0.98
1.07
2.10
2.00
1.05
1.06
1.09
2.15
3.36
f1 (ppm)


141.61
138.89
133.50
133.43
130.21
129.26
126.96
125.90
125.12
117.83
92.69
77.16 CDCl3
63.48
36.33
14.92
SO2Ph
Cl
N
P
O
OEt
OH
91
13C NMR, 126 MHz, CDCl3
f1 (ppm)



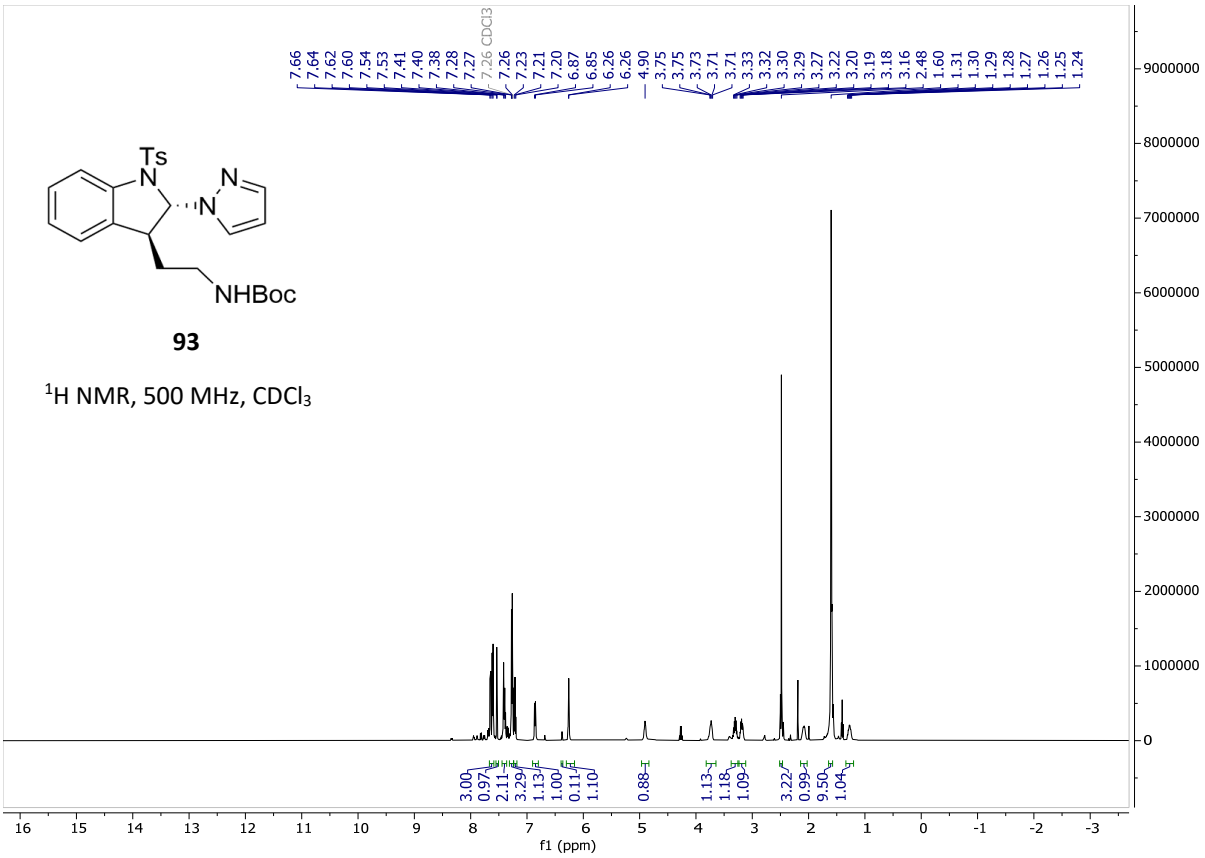
92

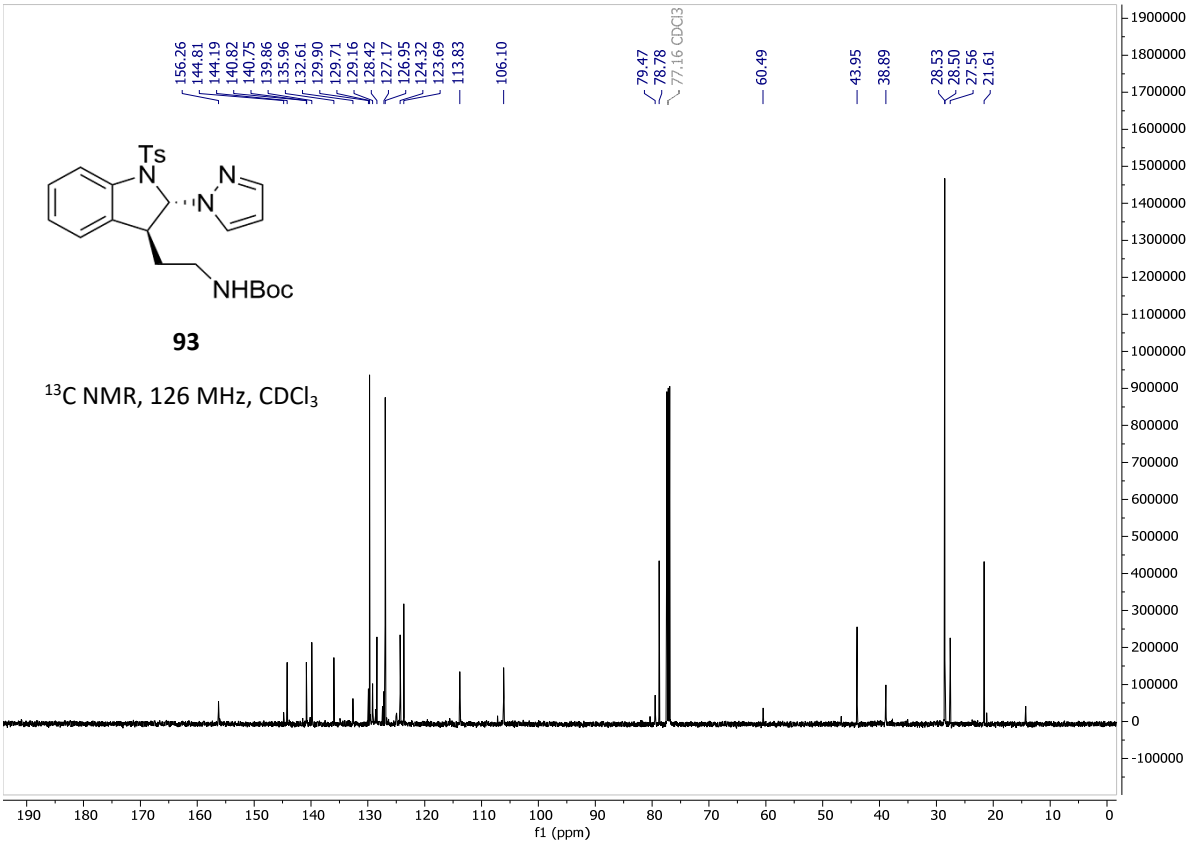
^{1}H NMR, 500 MHz, $CDCl_3$

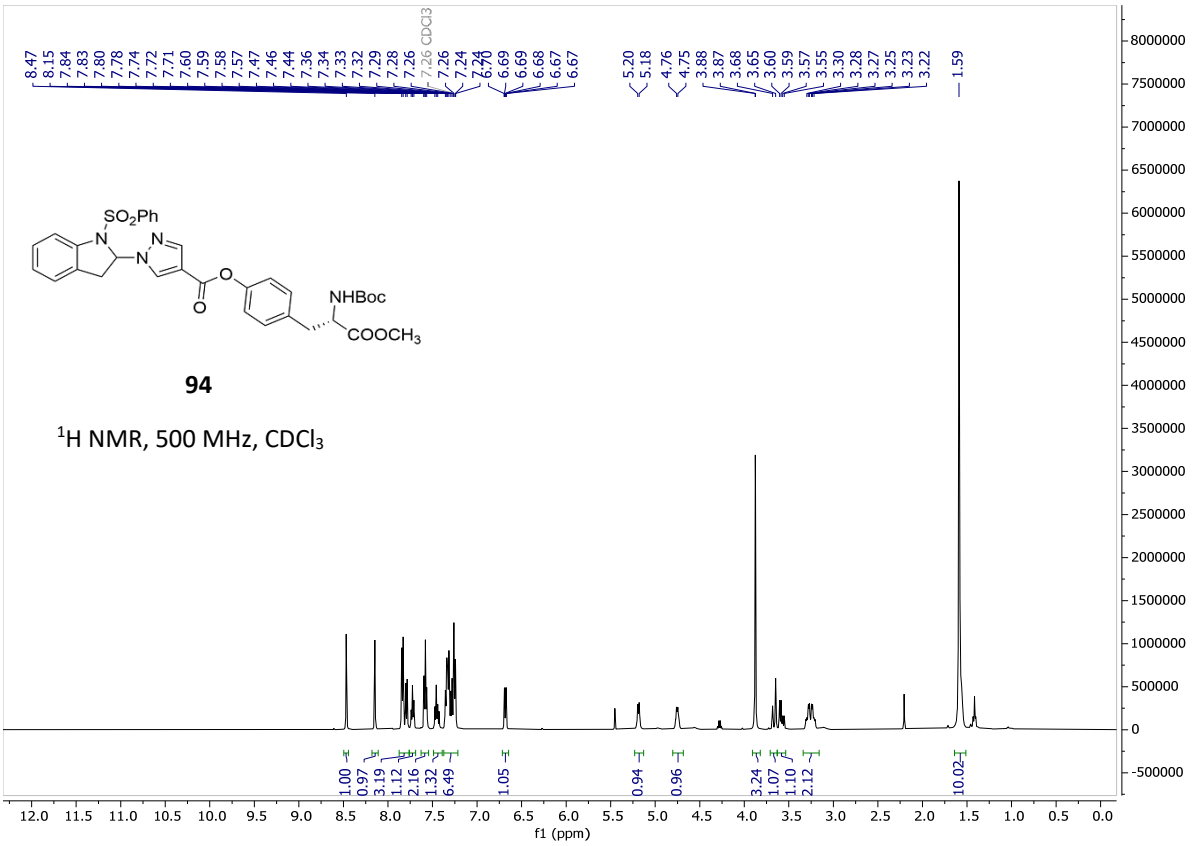


92

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


Ts
N
N
NHBoc
93
1H NMR, 500 MHz, CDCl3
f1 (ppm)


Ts
N
N
NHBoc
93
13C NMR, 126 MHz, CDCl3
f1 (ppm)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7.46
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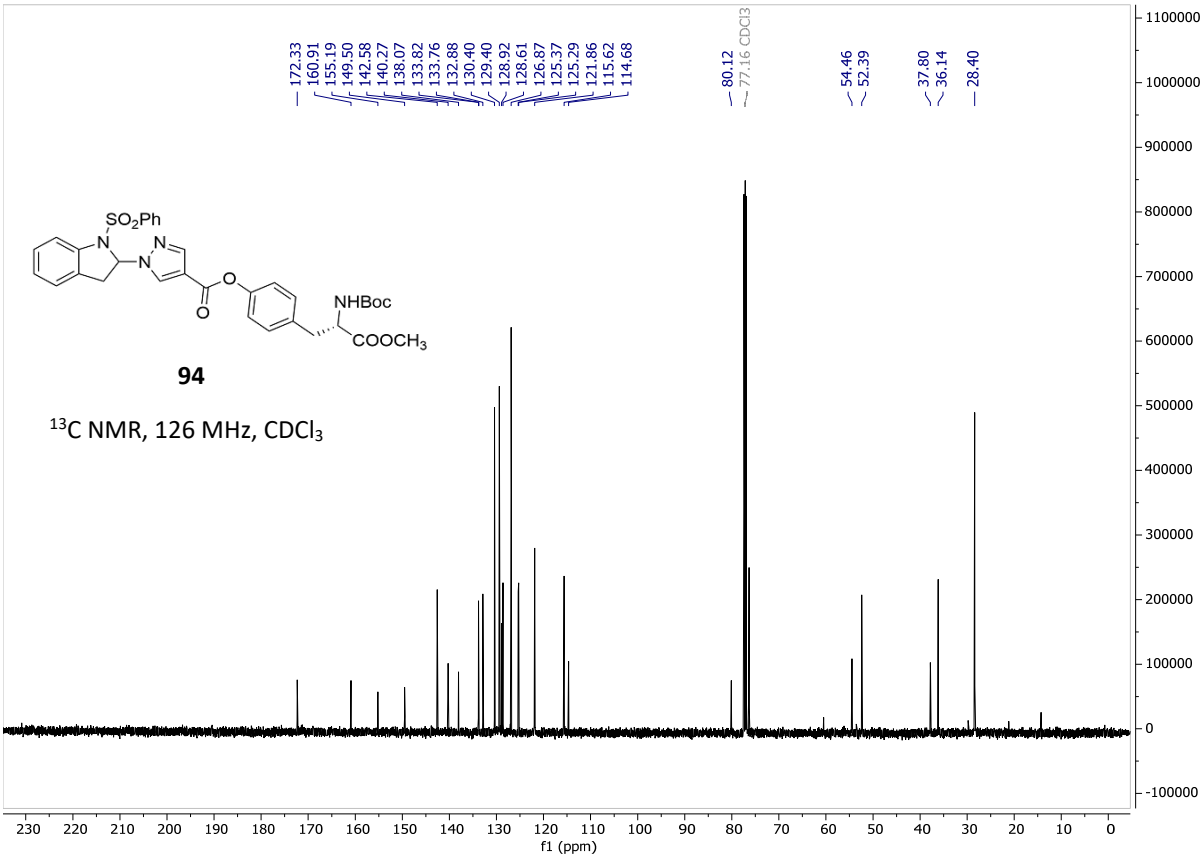
7.36
7.34
7.33
7.32
7.29
7.28
7.26
7.26 CDCl3
7.26
7.24
7.24
6.70
6.69
6.69
6.68
6.67
6.67
5.20
5.18
4.76
4.75
3.88
3.87
3.68
3.65
3.60
3.59
3.57
3.55
3.30
3.28
3.27
3.25
3.23
3.22
1.59
SO2Ph
N
N
N
O
O
NHBoc
COOCH3
94
1H NMR, 500 MHz, CDCl3
1.00
0.97
3.19
1.12
2.16
1.32
6.49
1.05
0.94
0.96
3.24
1.07
1.10
2.12
10.02
f1 (ppm)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133.82
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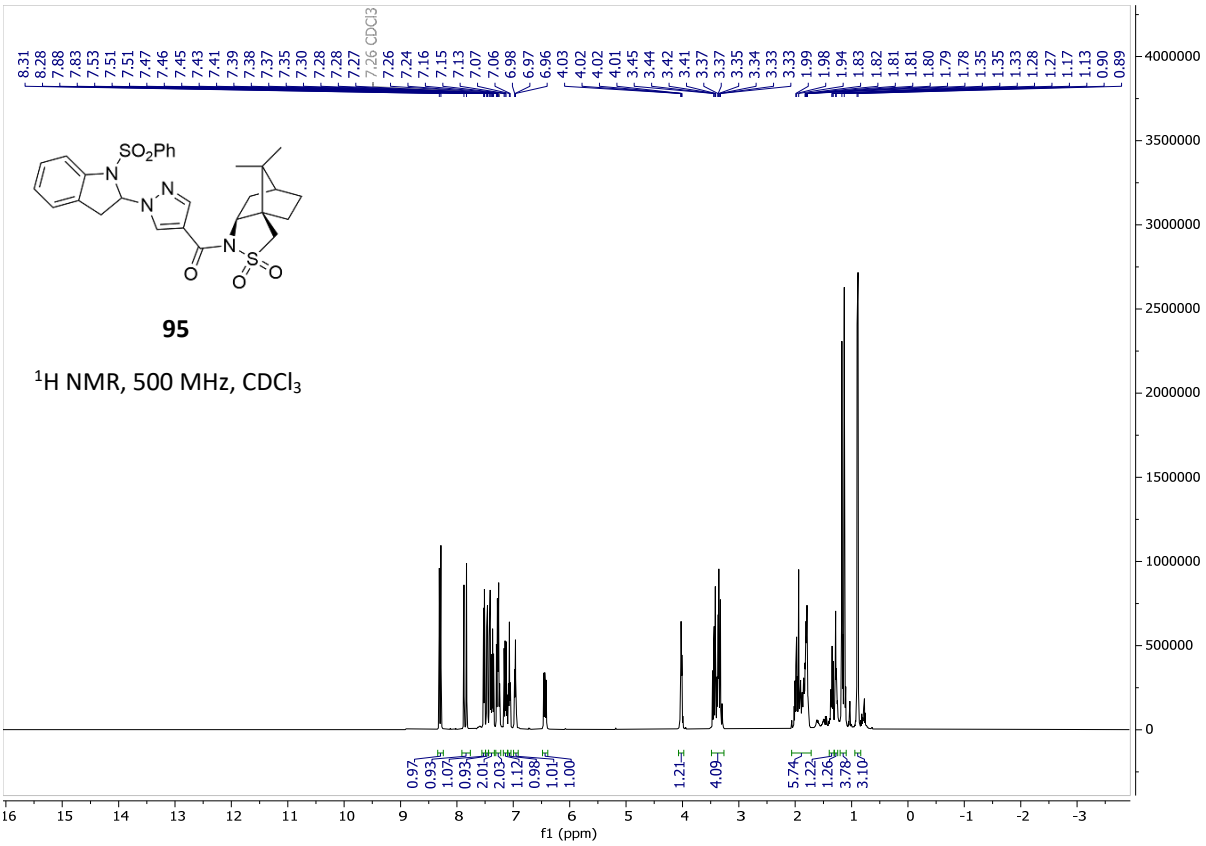
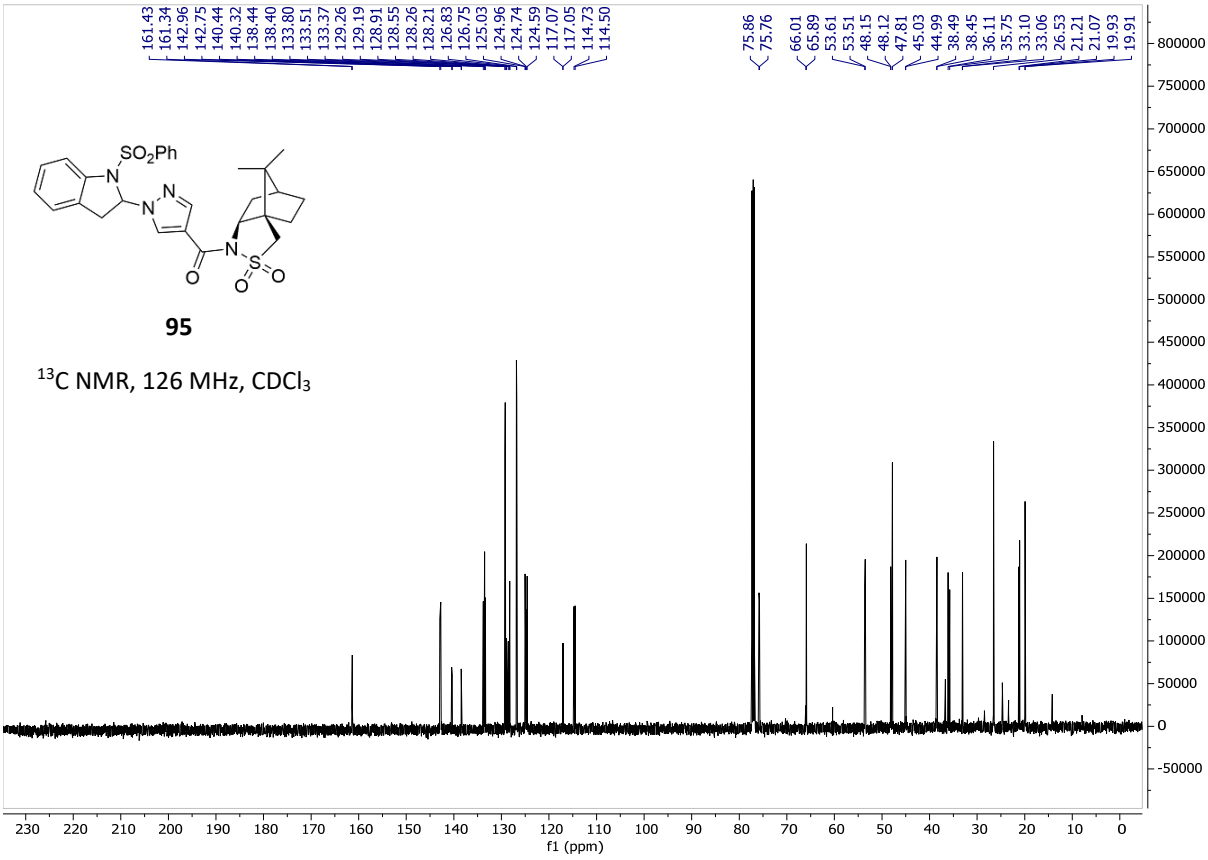
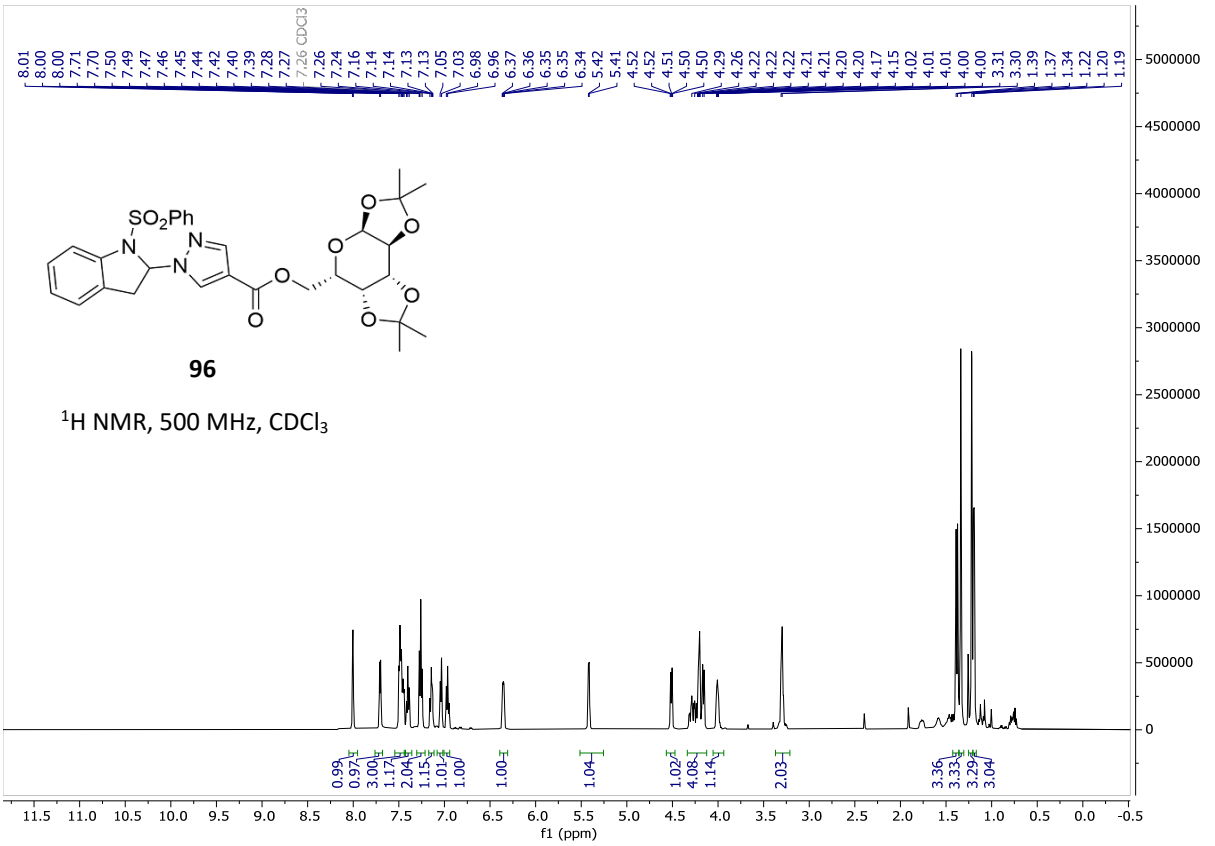
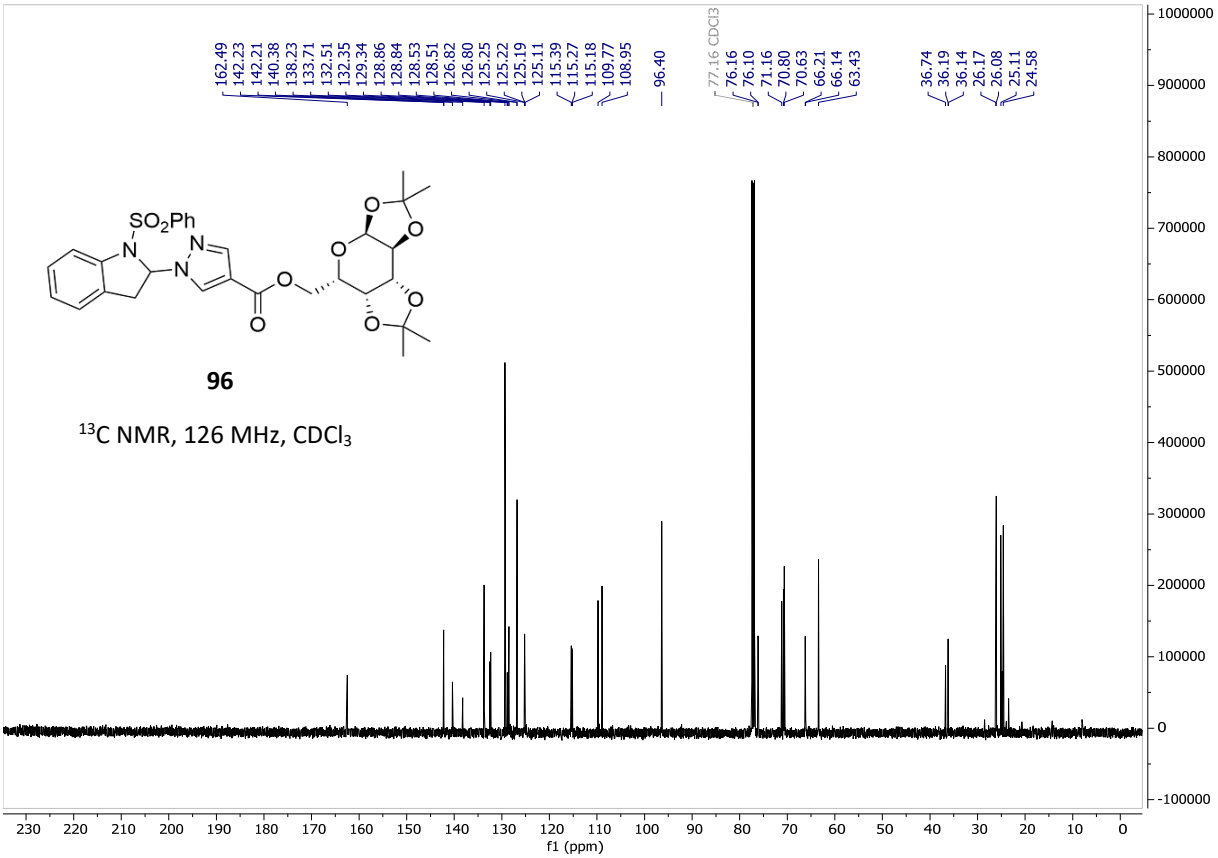
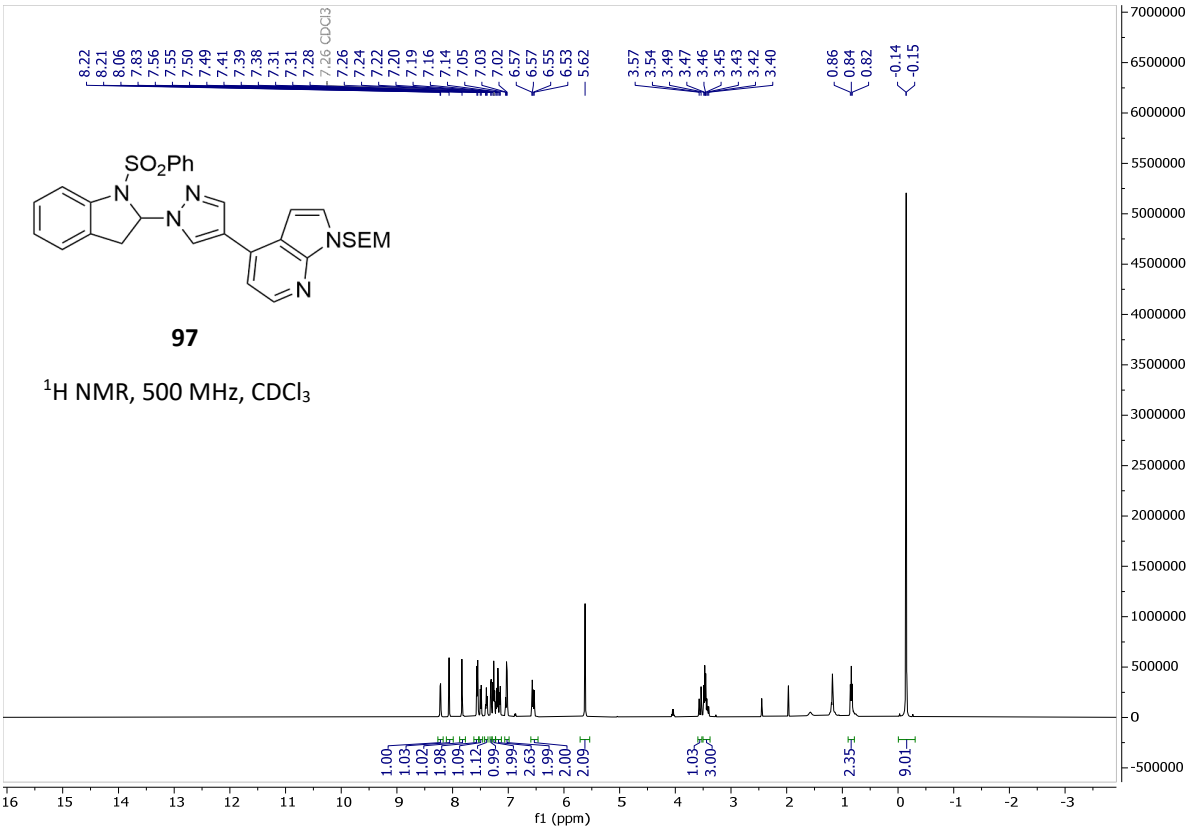
128.92
128.61
126.87
125.37
125.29
121.86
115.62
114.68
80.12
77.16 CDCl3
54.46
52.39
37.80
36.14
28.40
SO2Ph
N
N
N
O
O
NHBoc
COOCH3
94
13C NMR, 126 MHz, CDCl3
f1 (ppm)


SO2Ph
95
1H NMR, 500 MHz, CDCl3
f1 (ppm)


SO2Ph
95
13C NMR, 126 MHz, CDCl3
f1 (ppm)

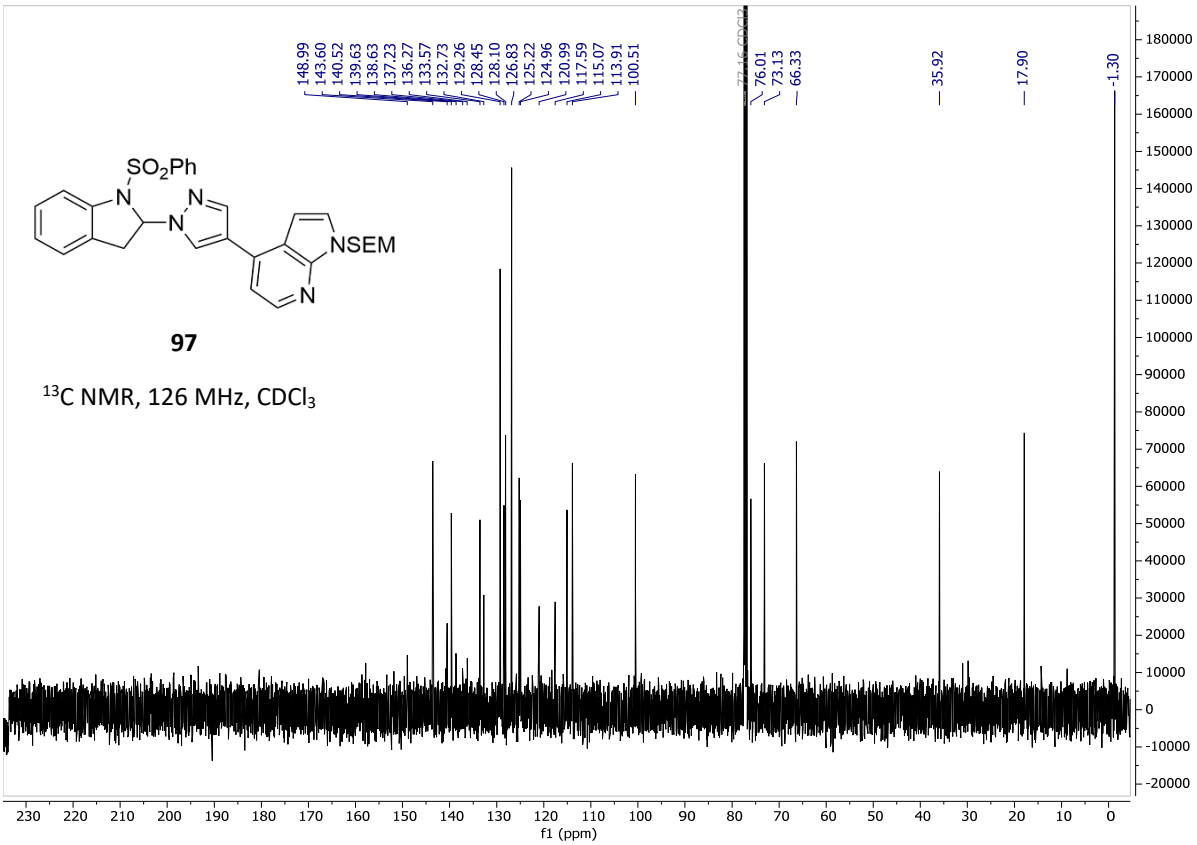

SO2Ph
96
1H NMR, 500 MHz, CDCl3
f1 (ppm)


SO2Ph
96
13C NMR, 126 MHz, CDCl3
f1 (ppm)



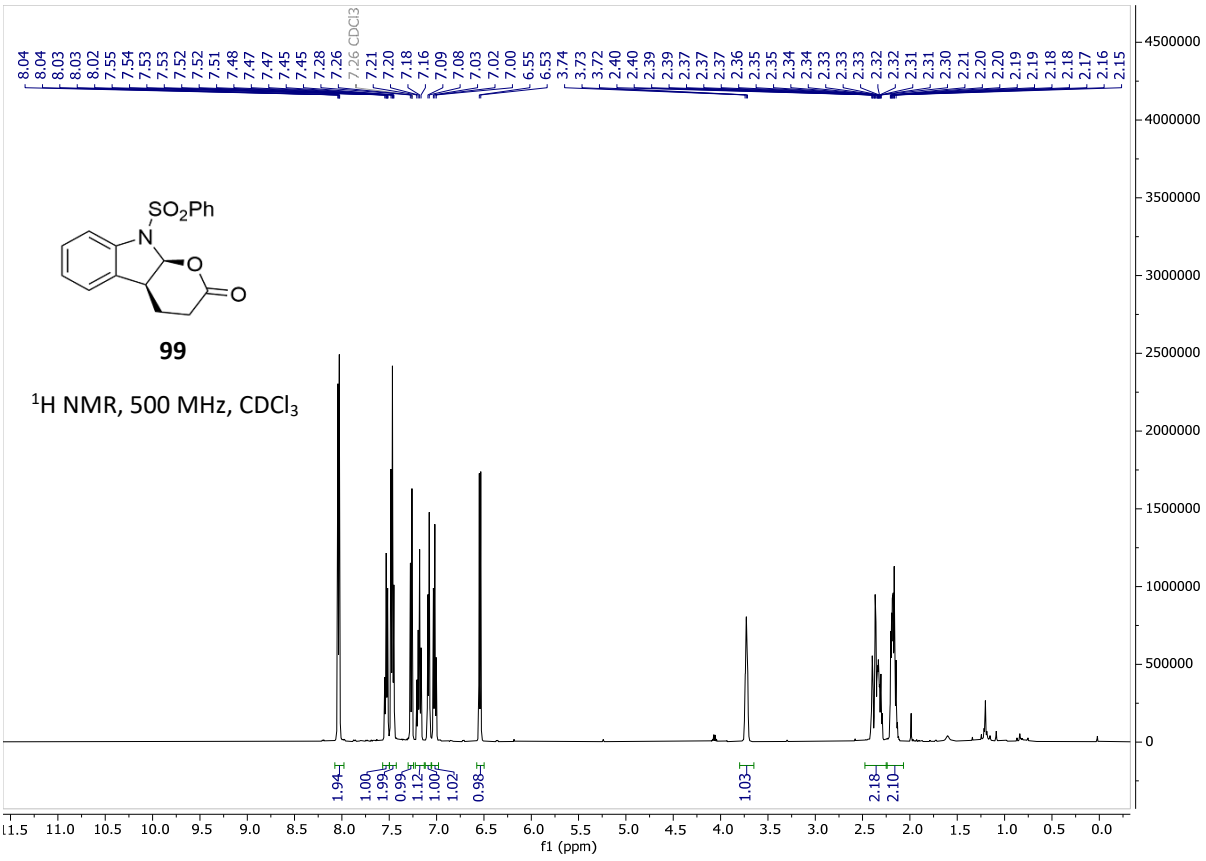
97

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



97

^{13}C NMR, 126 MHz, $CDCl_3$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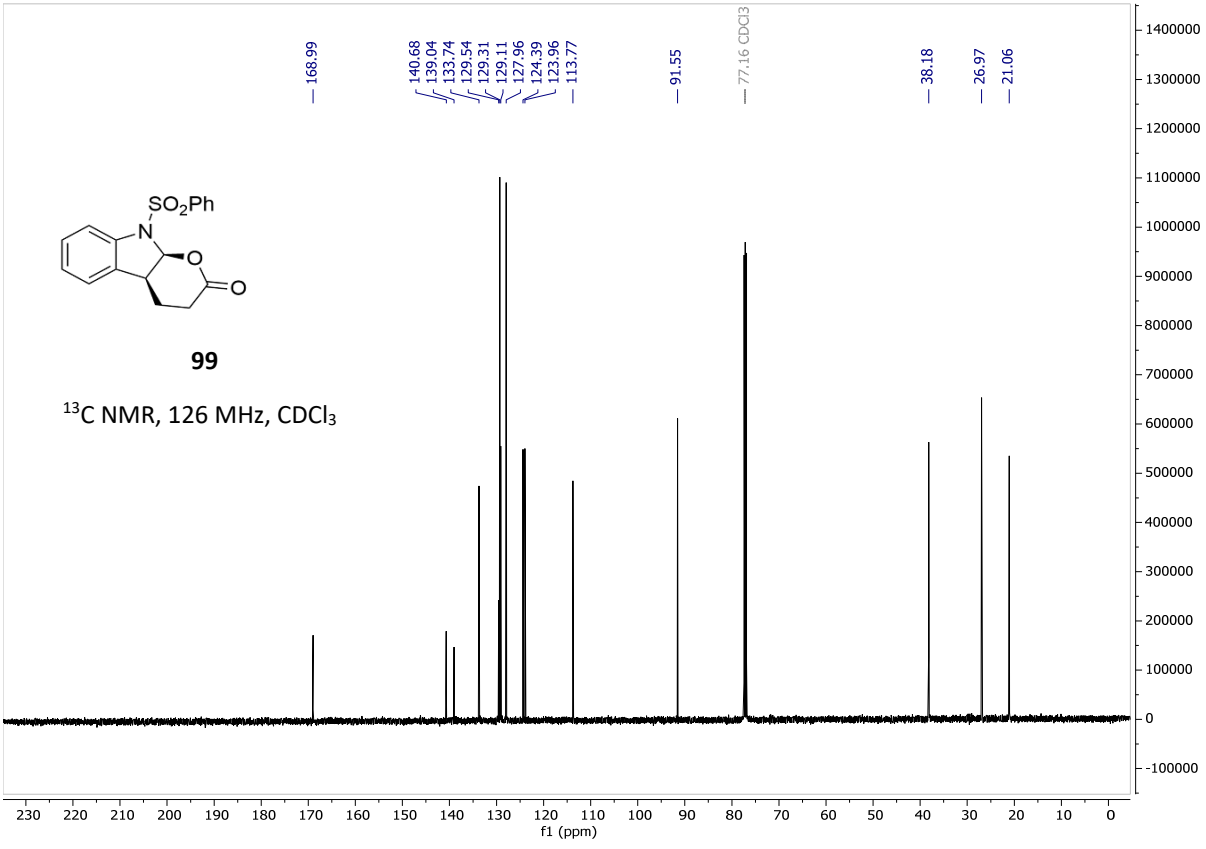
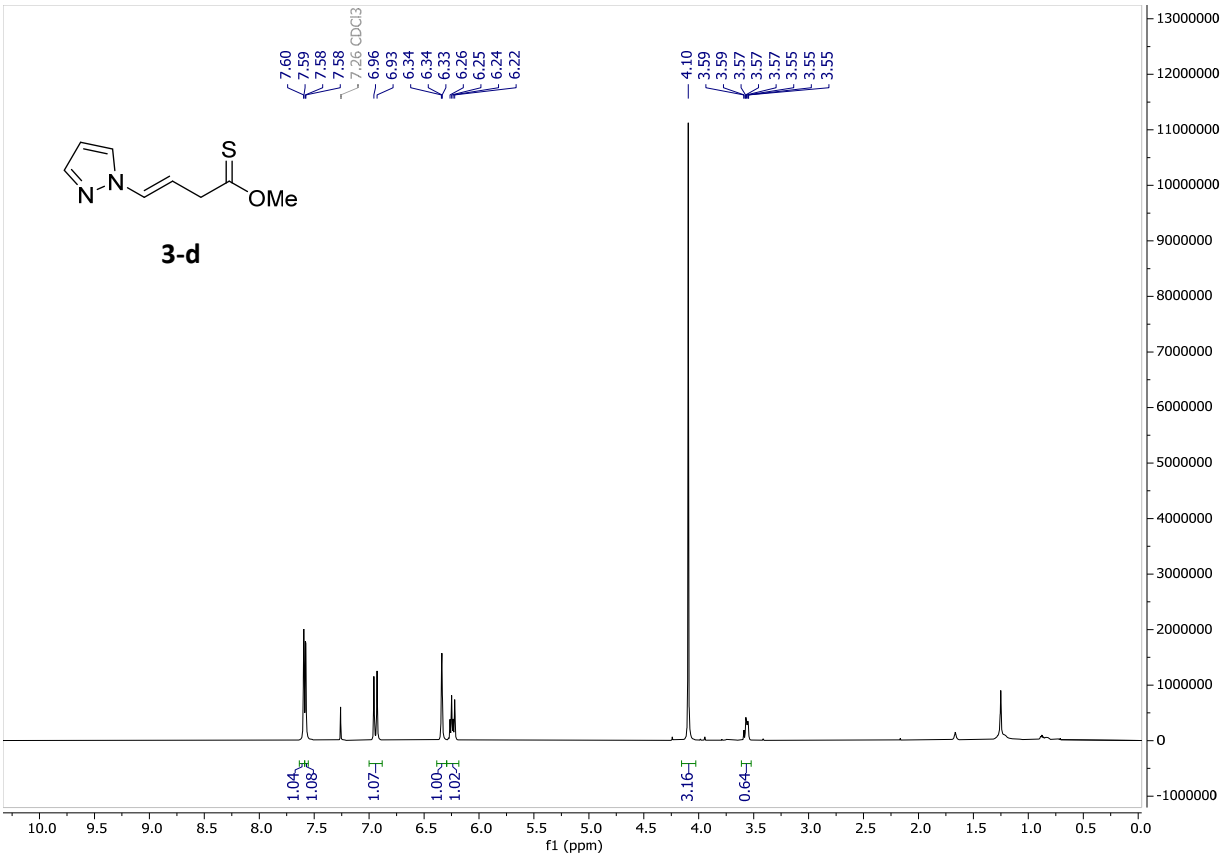
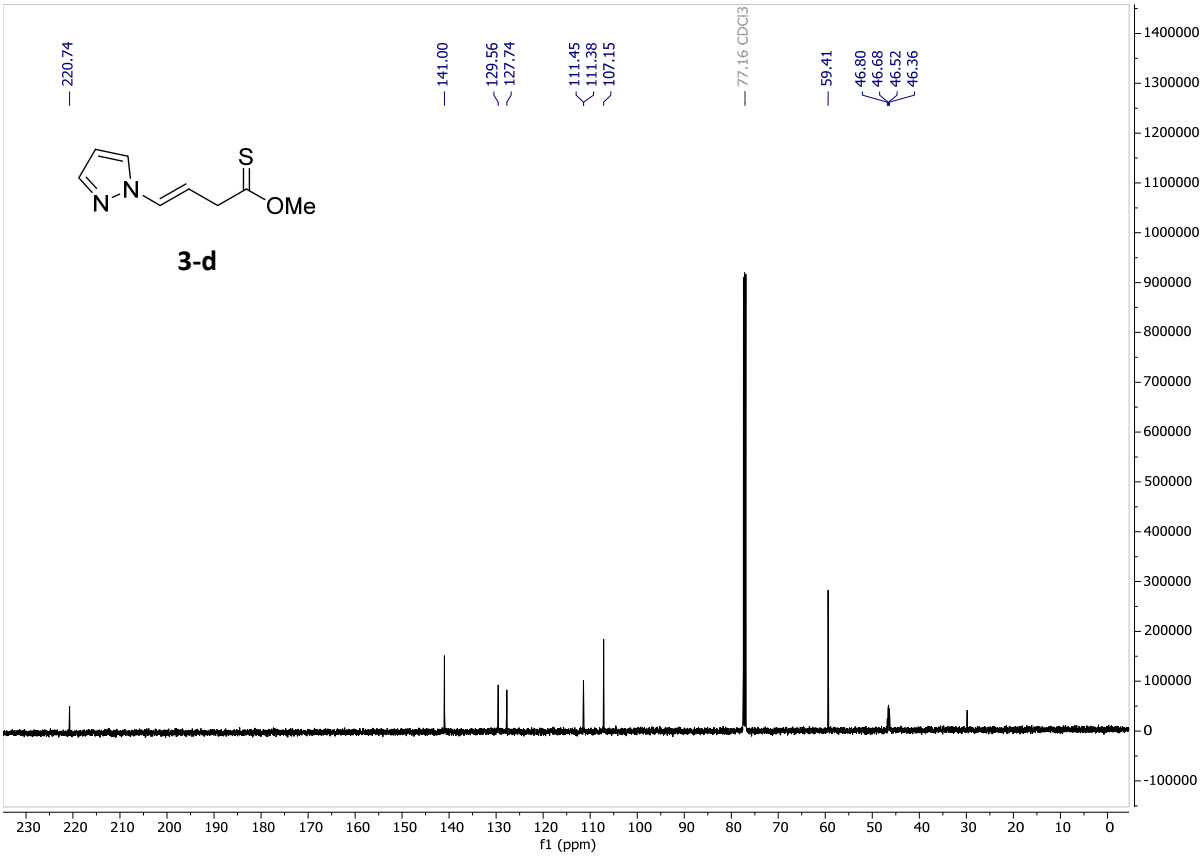
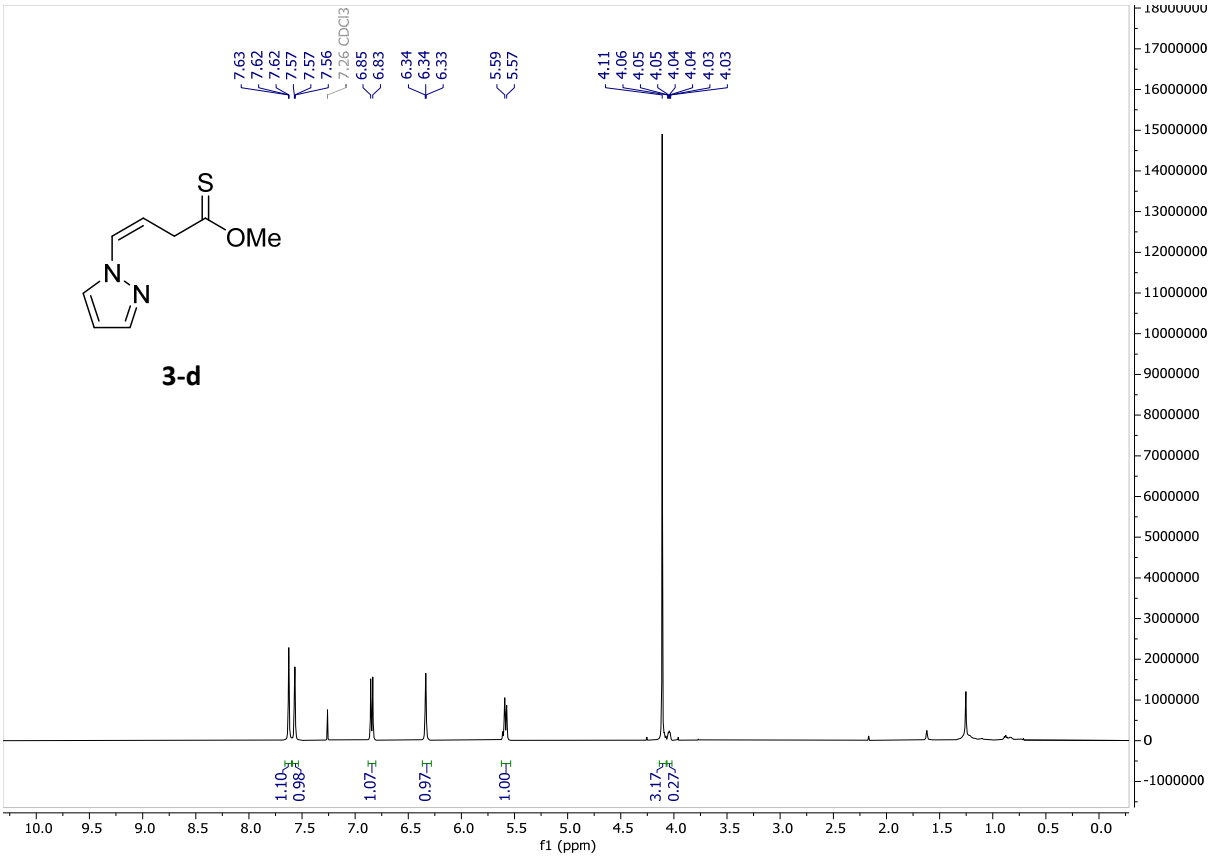
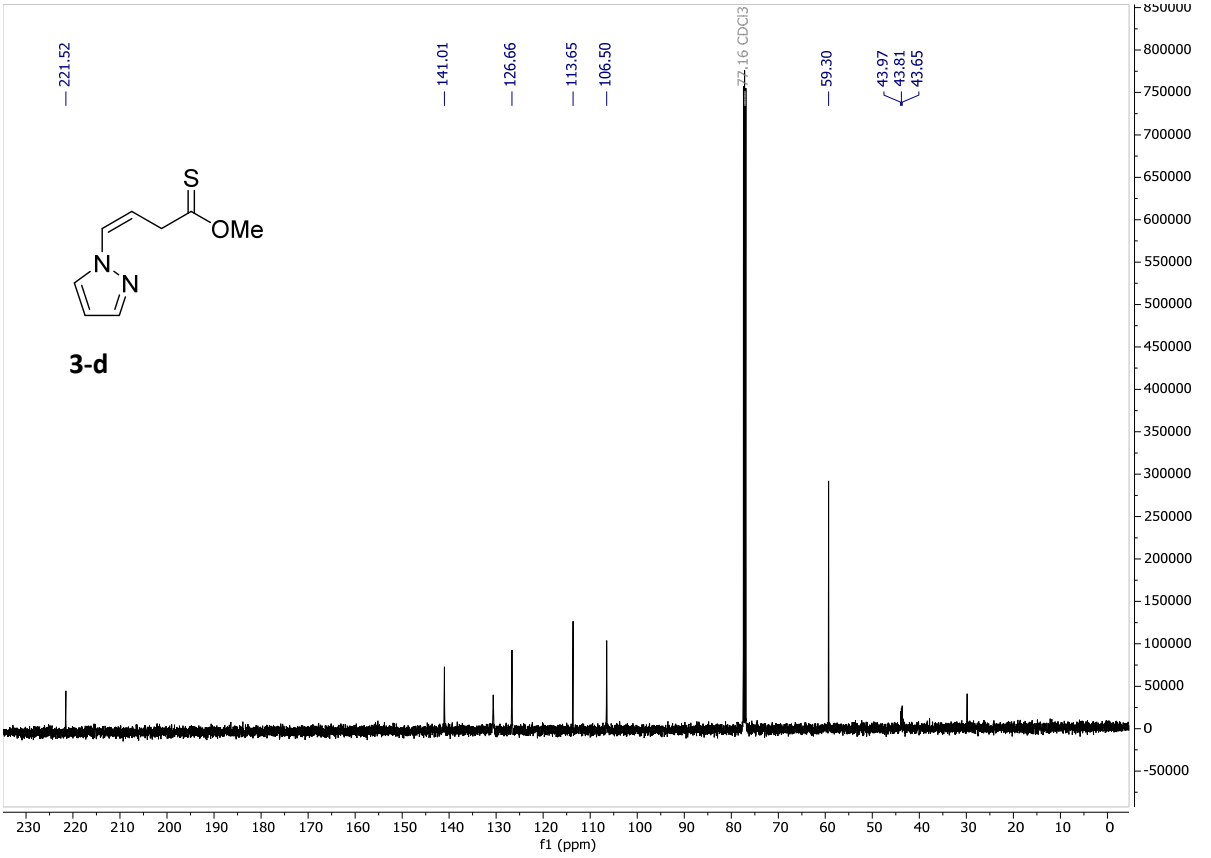
N
O
O
99
1H NMR, 500 MHz, CDCl3
f1 (ppm)


SO2Ph
N
O
O
99
13C NMR, 126 MHz, CDCl3
168.99
140.68
139.04
133.74
129.54
129.31
129.11
127.96
124.39
123.96
113.77
91.55
77.16 CDCl3
38.18
26.97
21.06
f1 (ppm)


7.60
7.59
7.58
7.58
7.26 CDCl3
6.96
6.93
6.34
6.34
6.33
6.26
6.25
6.24
6.22
4.10
3.59
3.59
3.57
3.57
3.57
3.55
3.55
3.55
S
N
N
OMe
3-d
1.04
1.08
1.07
1.00
1.02
3.16
0.64
f1 (ppm)


220.74
141.00
129.56
127.74
111.45
111.38
107.15
77.16 CDCl3
59.41
46.80
46.68
46.52
46.36
S
N
N
OMe
3-d
f1 (ppm)


7.63
7.62
7.62
7.57
7.57
7.56
7.26 CDCl3
6.85
6.83
6.34
6.34
6.33
5.59
5.57
4.11
4.06
4.05
4.05
4.04
4.04
4.03
4.03
S
OMe
N
N
3-d
1.10
0.98
1.07
0.97
1.00
3.17
0.27
f1 (ppm)


221.52
141.01
126.66
113.65
106.50
77.16 CDCl3
59.30
43.97
43.81
43.65
S
OMe
N
N
3-d
f1 (ppm)

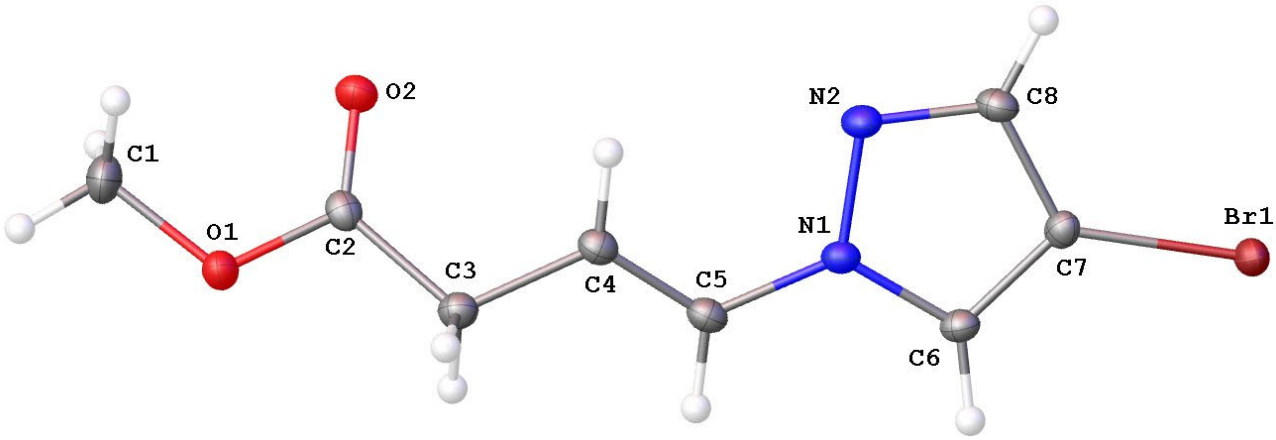
6. Single crystal X-ray diffraction data of 30

Table S5 Crystal data and structure refinement for mo_220822Peng_0ma.

Identification code	mo_220822Peng_0ma
Empirical formula	$C_8H_9BrN_2O_2$
Formula weight	245.08
Temperature/K	100
Crystal system	orthorhombic
Space group	Pccn
a/Å	13.2630(13)
b/Å	24.954(2)
c/Å	5.6399(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1866.6(3)
Z	8
ρ_{calc}g/cm^3	1.744
μ/mm^{-1}	4.372
F(000)	976.0
Crystal size/mm^3	0.4 × 0.2 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.264 to 52.766
Index ranges	$-16 \leq h \leq 15$, $-31 \leq k \leq 31$, $-7 \leq l \leq 6$
Reflections collected	11450
Independent reflections	1899 [R_{int} = 0.0190, R_{sigma} = 0.0128]

Data/restraints/parameters	1899/0/119
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0185, wR_2 = 0.0462
Final R indexes [all data]	R_1 = 0.0213, wR_2 = 0.0473
Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.23

Molecular structure. There are 8 molecules per unit cell, 1 molecule per asymmetric unit. The thermal displacement ellipsoids are at a 50% probability level.



Unit cell and packing. View almost along axis c:

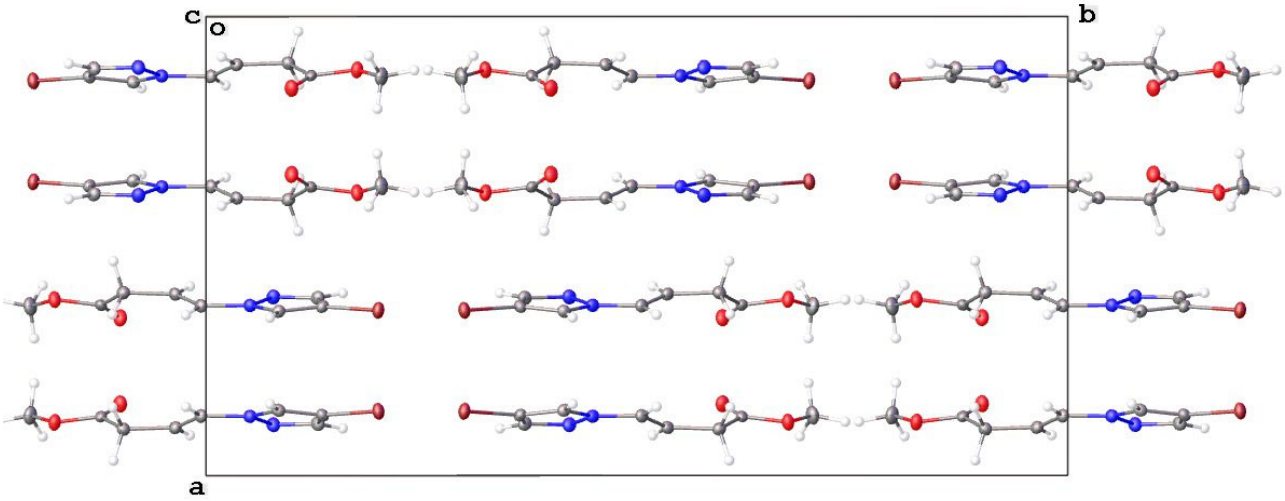


Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for mo_220822Peng_0ma. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3598.4(2)	7001.0(2)	-1184.7(3)	17.81(7)
O1	3838.3(9)	3244.7(5)	5371(2)	18.6(2)
O2	3437.3(8)	4006.0(5)	7275(2)	19.7(3)
N1	3707.8(9)	5511.8(6)	1510(2)	14.4(3)
N2	3891.7(10)	5782.8(6)	3556(2)	16.3(3)
C4	3953.1(11)	4643.0(6)	3285(3)	15.3(3)
C3	3985.8(12)	4041.9(6)	3180(3)	15.7(3)
C6	3576.9(11)	5844.0(7)	-372(3)	14.4(3)
C7	3682.3(11)	6353.9(6)	503(3)	14.3(3)
C5	3699.6(11)	4942.5(7)	1461(3)	15.6(3)
C2	3712.9(11)	3781.5(7)	5508(3)	14.4(3)
C8	3872.1(12)	6297.8(7)	2930(3)	16.3(3)
C1	3687.8(13)	2962.1(7)	7582(3)	23.3(4)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo_220822Peng_0ma. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	25.59(11)	12.92(10)	14.92(11)	0.28(6)	-0.75(6)	1.71(6)
O1	25.8(6)	13.8(6)	16.3(6)	0.2(5)	2.7(5)	-1.4(5)
O2	26.1(6)	16.9(6)	16.2(6)	-2.5(5)	3.5(5)	0.7(5)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo_220822Peng_0ma. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	16.2(6)	15.4(7)	11.7(6)	-1.9(5)	-0.6(5)	0.0(5)
N2	20.0(6)	17.1(7)	11.8(6)	-1.9(5)	-2.9(5)	0.5(5)
C4	15.3(7)	15.2(8)	15.5(8)	-2.3(6)	-0.6(6)	-1.1(6)
C3	16.2(7)	16.6(8)	14.3(8)	-0.9(7)	0.5(6)	0.8(6)
C6	15.3(7)	16.7(8)	11.3(7)	-1.1(6)	-1.1(6)	1.0(6)
C7	14.8(7)	14.1(8)	14.0(7)	1.3(6)	0.7(6)	2.5(6)
C5	16.6(7)	14.8(8)	15.2(8)	-3.4(6)	-0.3(6)	-0.5(6)
C2	12.0(7)	13.3(8)	17.9(8)	-0.3(7)	-2.3(6)	-1.2(6)
C8	17.8(7)	17.0(8)	14.3(8)	-4.1(7)	-1.8(6)	1.2(6)
C1	31.3(10)	16.4(9)	22.2(10)	5.2(7)	1.3(7)	-2.5(7)

Table S8 Bond Lengths for mo_220822Peng_0ma.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C7	1.8778(16)	N2	C8	1.333(2)
O1	C2	1.3519(19)	C4	C3	1.502(2)
O1	C1	1.446(2)	C4	C5	1.315(2)
O2	C2	1.200(2)	C3	C2	1.509(2)
N1	N2	1.3597(18)	C6	C7	1.372(2)
N1	C6	1.358(2)	C7	C8	1.399(2)
N1	C5	1.421(2)			

Table S9 Bond Angles for mo_220822Peng_0ma.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	114.65(13)	C6	C7	Br1	127.53(13)
N2	N1	C5	121.00(13)	C6	C7	C8	106.11(15)
C6	N1	N2	112.50(13)	C8	C7	Br1	126.36(13)
C6	N1	C5	126.46(14)	C4	C5	N1	123.44(15)
C8	N2	N1	104.56(13)	O1	C2	C3	110.35(14)
C5	C4	C3	122.98(15)	O2	C2	O1	123.17(16)
C4	C3	C2	112.90(14)	O2	C2	C3	126.47(15)
N1	C6	C7	105.79(14)	N2	C8	C7	111.05(15)

Table S10 Torsion Angles for mo_220822Peng_0ma.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C7	C8	N2	-179.38(11)	C6	N1	N2	C8	0.16(17)
N1	N2	C8	C7	-0.30(18)	C6	N1	C5	C4	171.33(15)
N1	C6	C7	Br1	179.49(10)	C6	C7	C8	N2	0.33(18)
N1	C6	C7	C8	-0.21(16)	C5	N1	N2	C8	178.12(13)
N2	N1	C6	C7	0.04(17)	C5	N1	C6	C7	-177.78(13)
N2	N1	C5	C4	-6.3(2)	C5	C4	C3	C2	-147.55(15)
C4	C3	C2	O1	-174.75(12)	C1	O1	C2	O2	-4.5(2)
C4	C3	C2	O2	4.1(2)	C1	O1	C2	C3	174.43(12)
C3	C4	C5	N1	-177.21(14)					

Table S11 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_220822Peng_0ma.

Atom	*x*	*y*	*z*	U(eq)
H4	4123.15	4814.67	4733.85	18
H3B	4672.79	3927.27	2717.42	19
H3A	3512.87	3916.29	1941.22	19
H6	3440.66	5743.99	-1965.36	17
H5	3500.64	4769.14	36.01	19
H8	3973.65	6588.3	3992.5	20
H1A	3828.1	2580.13	7350.71	35
H1B	2988.51	3007.98	8105.37	35
H1C	4144.83	3106.83	8788.03	35

Experimental

The single crystal XRD of $C_8H_9BrN_2O_2$ [mo_220822Peng_0ma] was studied on a 'Bruker Kappa APEX-II' diffractometer. The crystal was kept at 100.0 K during data collection. Using the Olex2 [1] environment, the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [mo_220822Peng_0ma]

Crystal Data for $C_8H_9BrN_2O_2$ (M =245.08 g/mol): orthorhombic, space group Pccn (no. 56), a = 13.2630(13) Å, b = 24.954(2) Å, c = 5.6399(5) Å, V = 1866.6(3) Å^3, Z = 8, T = 100 K, μ(MoKα) = 4.372 mm^{-1}, *Dcalc* = 1.744 g/cm^3, 11450 reflections measured (3.264° ≤ 2Θ ≤ 52.766°), 1899 unique (R_{int} = 0.0190, R_{sigma} = 0.0128) which were used in all calculations. The final R_1 was 0.0185 (I > 2σ(I)) and wR_2 was 0.0473 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C3(H3B,H3A)
2.b Aromatic/amide H refined with riding coordinates:
 C4(H4), C6(H6), C5(H5), C8(H8)
2.c Idealised Me refined as rotating group:
 C1(H1A,H1B,H1C)
```

References:

APEX2 (data collection)

Bruker (2007). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

SAINT (integration and reduction)

Bruker (2007). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

SADABS (absorption correction)

Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.

SHELXTL (structure solution and refinement)

Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

PLATON

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

OLEX2

Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann H. (2008), *J. Appl. Cryst.* **42**, 339-341.