Supporting information for

Nucleophile-Assisted Cyclization of β-Propargylamino Acrylic Compounds Catalyzed by Gold(I): A Rapid Construction of Multisubstituted Tetrahydropyridines and their Fused Derivatives

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General information

All reagents and solvents were purchased from Sigma-Aldrich (Merck, KGaA, Darmstadt, Germany) and used without further purification. Solvents (DCM, THF) were dried prior to use (PureSolv PS-Micro, Innovative Technologies). The reactions carried out under an argon atmosphere were done in oven-dried glassware using Schlenk line techniques with magnetic stirring and dried solvents. TLC analyses were performed using Merck TLC Silica gel F_{254} TLC plates or Merck TLC Silica gel 60 RP-18 F_{254} and visualized by UV (254 nm) in combination with staining (using the solution of $Ce(SO_4)_2 \cdot 4H_2O$ (2 g), $H_3[P(Mo_3O_{10})_4]$ (4 g), conc. H_2SO_4 (10 mL) and H_2O (200 mL) with subsequent heating). Column chromatography was carried out on Merck Silica gel 60 (0.040–0.063 mm) and Merck LiChroPrep RP-18 (25–40 μm). ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with Varian VNMR S500 or Jeol JNM-ECZ600R instruments. The chemical shifts were recorded as δ values in parts per million (ppm) reported relative to TMS and referenced to the residual solvent peaks; the chemical shifts in ^{19}F spectra were indirectly referenced to an trifluoroacetic acid external standard (−76.87 ppm); the chemical shifts in ^{31}P spectra were indirectly referenced to an 85% phosphoric acid external standard (0.00 ppm). Coupling constants (*J*) are given in Hz. HR-MS data were recorded on a QTOF mass spectrometer using the electrospray ionization. Melting points were determined on Stuart SMP30 apparatus without correction.

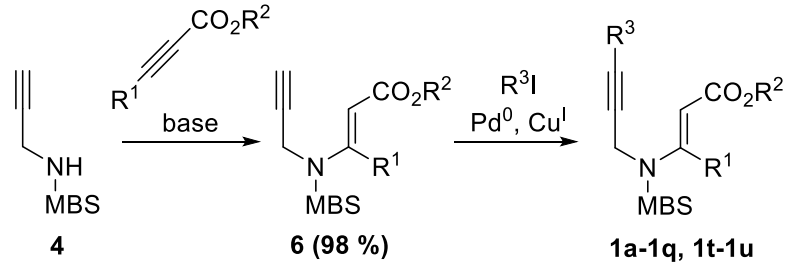
Synthetic procedures and characterizations

Preparation of (TFP)AuCl

(TFP)AuCl was prepared according to the published procedure.[1] Tetrahydrothiophene (0.38 mL, 4.2 mmol) was added dropwise to a solution of $HAuCl_4 \cdot 3H_2O$ (788 mg, 2 mmol) in a mixture of water (1.4 mL) and ethanol (6.6 mL), and the reaction mixture was stirred for 30 min at room temperature. The precipitate [chloro(tetrahydrothiophene)gold(I)] was filtered off, washed with ethanol and dried (611 mg). Dry (tht)AuCl was dissolved in DCM (10 mL) and trifurylphosphine (441 mg, 1.9 mmol) was added. The mixture was stirred at room temperature for 1 hour. The solvent was evaporated, the resultant powder was dissolved in a minimum amount of DCM and precipitated by hexane. The precipitate was filtered off, washed with hexane and dried. Grey powder, 86% overall yield (796 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.81–7.79 (m, 3H), 7.19–7.17 (m, 3H), 6.58–6.55 (m, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 150.0 (d, *J* = 6.7 Hz), 141.1 (d, *J* = 99.6 Hz), 125.3 (d, *J* = 26.6 Hz), 111.6 (d, *J* = 9.8 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$): δ −29.82.

Preparation of propargylamino acrylates 1a–1q and 1t–1u

Table 1. Overview of propargylamino acrylates **1a–1q, 1t and 1u**



Cpd	R^1	R^2	R^3	Overall Yield [%]
1a	H	Me	Ph	57
1b	H	Me	*p*-MeC_6H_4	63
1c	H	Me	*p*-$MeOC_6H_4$	56
1d	H	Me	*m*-$MeOC_6H_4$	72
1e	H	Me	1-Naphthyl	64
1f	H	Me	Bifenyl-4-yl	59
1g	H	Me	*p*-FC_6H_4	33
1h	H	Me	*p*-ClC_6H_4	68
1i	H	Me	*p*-BrC_6H_4	58
1j	H	Me	3,4-diClC_6H_4	68
1k	H	Me	*o*-$NO_2C_6H_4$	63
1l	H	Me	*m*-$NO_2C_6H_4$	72
1m	H	Me	*p*-$NO_2C_6H_4$	66
1n	H	Me	2-thienyl	58
1o	Me	Et	Ph	75
1p	Ph	Me	Ph	61
1q	CO_2Me	Me	Ph	69
1t	H	Me	(*E*)-oct-1-en-1-yl	52
1u	H	Me	(*E*)-2-phenylethen-1-yl	36

***N*-(prop-2-yn-1-yl)-4-methoxybenzenesulfonamide (4)**: 4-Methoxysulfonylchloride (9.68 g, 46.84 mmol) and TEA (7.4 mL, 52.695 mmol) were added to a solution of propargyl amine (3 mL, 46.84 mmol) in dry DCM (60 mL) in an oven-dried flask under argon atmosphere at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred for 30 minutes and then quenched with 50 mL of 5% HCl. The mixture was extracted with DCM (2 × 60 mL). The combined organic phases were dried over Na_2SO_4, and the inorganic residues were filtered off. The solution was evaporated to dryness

to give a white crystalline solid, 99% yield (10.5 g). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84–7.79 (m, AA′ BB′, 2H), 7.00–6.95 (m, AA′ BB′, 2H), 4.73 (bs, 1H), 3.87 (s, 3H), 3.83–3.80 (m, 2H), 2.10 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.1, 131.0, 129.5, 114.2, 78.0, 72.9, 55.6, 32.8.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]acrylate (6a): Methyl propiolate (0.441 mL, 4.96 mmol) followed by TEA (1.9 mL, 13.5 mmol, portionwise) were added to a solution of compound **4** (1.0106 g, 4.51 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature until TLC analysis indicated that the reaction was complete (3 h). The mixture was diluted with EtOAc (10 mL) and washed with 20 mL of a saturated NH_4Cl solution. The water phase was then extracted with EtOAc (2 × 30 mL), and the combined organic layers were dried over Na_2SO_4. The inorganic residues were filtered off, the solution was evaporated to dryness, and the residue was purified by chromatography on a column of silica gel (70 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a yellow crystalline solid, 85% yield (1.186 g). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 14.0 Hz, 1H), 7.85–7.75 (m, AA′ BB′, 2H), 7.03–6.96 (m, AA′ BB′, 2H), 5.31 (d, *J* = 14.0 Hz, 1H), 4.33 (d, *J* = 2.5 Hz, 2H), 3.88 (s, 3H), 3.74 (s, 3H); 2.08 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 163.9, 140.5, 129.8, 129.4, 114.6, 99.6, 75.0, 74.1, 55.7, 51.5, 35.3.

Ethyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]but-2-enoate (6o): Ethyl but-2-ynoate (0.406 mL, 3.48 mmol) followed by DABCO (39 mg, 0.348 mmol) were added to a solution of compound **4** (392 mg, 1.74 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere at room temperature. The reaction mixture was heated at reflux overnight. The mixture was then evaporated with 2 g of silica gel, and the residue purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a yellowish oil, 98% yield (575 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84–7.77 (m, AA′ BB′, 2H), 7.01–6.95 (m, AA′ BB′, 2H), 5.81 (s, 1H), 4.36 (d, *J* = 2.5 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.32 (s, 3H), 2.31 (t, *J* = 2.5 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 166.2, 163.4, 152.7, 130.3, 129.9, 114.2, 114.0, 77.7, 73.9, 60.1, 55.6, 38.6, 18.0, 14.2.

Methyl (*E*)-3-[(*N*-(4-methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]-3-phenylacrylate (6p): Methyl 3-phenylpropiolate (1.31 mL, 8.879 mmol) followed by DABCO (100 mg, 0.888 mmol) were added to a solution of compound **4** (1.000 g, 4.44 mmol) in dry THF (15 mL) in an oven-dried flask under argon atmosphere. The reaction was heated up at reflux overnight. The mixture was then evaporated with 5 g of silica gel, and the residue purified by chromatography on a column of silica gel (70 g), eluting with a hexane/EtOAc mixture (7:3) to obtain a yellowish oil, 90% yield (1.55 g). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$):

δ 7.66–7.60 (m, AA′ BB′, 2H), 7.59–7.54 (m, 2H), 7.45–7.37 (m, 1H), 7.36–7.29 (m, 2H), 6.91–6.84 (m, AA′ BB′, 2H), 6.19 (s, 1H), 4.60 (d, *J* = 2.5 Hz, 2H), 3.87 (s, 3H), 3.65 (s, 3H), 2.31 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 164.1, 163.1, 151.5, 137.5, 131.5, 130.4, 130.0, 128.4, 128.4, 116.4, 113.7, 78.4, 73.9, 55.6, 51.6, 41.2.

Dimethyl 2-[(*N*-4-(methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]maleate (6q). Dimethyl acetylenedicarboxylate (0.273 mL, 2.220 mmol) followed by TEA (0.928 mL, 6.66 mmol) were added to a solution of compound **4** (500 mg, 2.220 mmol) in dry DCM (10 mL) in an oven-dried flask under argon atmosphere. The reaction mixture was stirred overnight and quenched with a saturated NH_4Cl solution (10 mL). The mixture was extracted with DCM (2 × 50 mL), the combined organic phases were dried over Na_2SO_4, and the solution evaporated to dryness. The residue was purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (6:4); milky oil, 98% yield (360 mg) as a mixture of *trans* and *cis* isomers. All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94–7.88 (m, AA′ BB′, 2H), 7.81–7.75 (m, AA′ BB′, 2H), 7.01–6.98 (m, AA′ BB′, 2H), 6.98–6.95 (m, 3H), 5.82 (s, 1H), 4.33 (d, *J* = 2.5 Hz, 2H), 4.33 (d, *J* = 2.4 Hz, 2H), 3.93 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.72 (s, 3H), 2.26 (t, *J* = 2.4 Hz, 1H), 2.19 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 165.3, 164.0, 163.9, 144.4, 130.5, 130.1, 129.3, 129.0, 114.3, 114.0, 107.9, 75.6, 75.1, 74.3, 55.7, 53.3, 53.1, 52.2, 51.9, 39.3, 39.0.

General procedure for Sonogashira coupling: Preparation of substituted propargylamino acrylates 1a–1q:

Aryl iodide (1.21 mmol), $(PPh_3)_2PdCl_2$ (0.055 mmol) and CuI (0.11 mmol) were added to a solution of enyne **6** (1.1 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere. TEA (1.53 mL; 11.0 mmol) was then added portionwise at room temperature. The reaction mixture was stirred overnight, diluted with EtOAc (20 mL) and washed with a saturated NH_4Cl solution (20 mL). The water phase was then extracted with EtOAc (2 × 20 mL), the combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The solution was evaporated to dryness, and the residue was purified by chromatography on a column of silica gel (30–50 g), eluting with the mobile phases specified below to afford the corresponding acrylate **1**.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]acrylate (1a): Elution with hexane/EtOAc (7:3), light yellow solid, 68% yield (288 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 14.0 Hz, 1H), 7.87–7.82 (m, AA′ BB′, 2H), 7.33–7.22 (m, 3H), 7.13–7.09 (m, 2H), 6.97–6.92 (m, AA′ BB′, 2H), 5.39 (d, *J* = 14.0 Hz, 1H), 4.55 (s, 2H), 3.77 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.8, 140.8, 131.6, 129.8, 129.6, 128.7, 128.1, 121.7, 114.5, 99.7, 85.7, 80.2, 55.6, 51.4, 36.2.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(4-methylphenylprop-2-yn-1-yl)amino]acrylate (1b): Elution with hexane/EtOAc (7:3), yellow amorphous solid, 75% yield (330 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 14.0 Hz, 1H), 7.84–7.77 (m, AA′BB′, 2H), 7.12–6.95 (m, 4H), 6.95–6.89 (m, AA′BB′, 2H), 5.38 (d, *J* = 14.0 Hz, 1H), 4.54 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.8, 140.9, 138.9, 131.5, 129.8, 129.7, 128.9, 118.6, 114.5, 99.6, 85.9, 79.5, 55.6, 51.4, 36.2, 21.4.

Methyl (*E*)-3-[*N*-(4-methoxyphenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1c): Elution with hexane/EtOAc (9:1–8:2), light yellow amorphous solid, 66% yield (302 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 13.9 Hz, 1H), 7.85–7.73 (m, AA′BB′, 2H), 7.08–7.01 (m, AA′BB′, 2H), 6.96–6.91 (m, AA′BB′, 2H), 6.78–6.66 (m, AA′BB′, 2H), 5.38 (d, *J* = 13.9 Hz, 1H), 4.53 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.4, 163.7, 159.9, 140.9, 133.1, 129.8, 129.7, 114.5, 113.8, 113.7, 99.6, 85.7, 78.9, 55.6, 55.3, 51.4, 36.3.

Methyl (*E*)-3-[*N*-(3-methoxyphenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1d): Elution with hexane/EtOAc (8:2), yellowish oil, 86% yield (393 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 14.0 Hz, 1H), 7.86–7.71 (m, AA′BB′, 2H), 7.19–7.06 (m, 1H), 6.99–6.89 (m, AA′BB′, 2H), 6.88–6.78 (m, 1H), 6.73–6.64 (m, 1H), 6.62–6.58 (m, 1H), 5.37 (d, *J* = 14.0 Hz, 1H), 4.55 (s, 2H), 3.78 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.8, 159.1, 140.8, 129.9, 129.6, 129.2, 124.1, 122.7, 116.7, 115.0, 114.5, 99.7, 85.6, 80.0, 55.6, 55.2, 51.5, 36.1.

Methyl (*E,Z*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-naphthyl-prop-2-yn-1-yl)amino] acrylate (1e): Elution with hexane/EtOAc (8:2), light brown amorphous solid, isolated as mixture of isomers (*E*:Z = 95:5), 76% yield (364 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 14.0 Hz, 1H), 7.88–7.73 (m, 5H), 7.53–7.41 (m, 2H), 7.38–7.31 (m, 2H), 6.82–6.80 (m, AA′BB′, 2H), 5.51 (d, *J* = 14.0 Hz, 1H), 4.72 (s, 2H), 3.76 (s, 3H), 3.53 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.7, 140.9, 132.9, 130.8, 129.8, 129.8, 129.6, 129.5, 129.2, 128.2, 126.8, 126.4, 125.8, 124.9, 119.4, 114.6, 99.8, 85.0, 84.1, 55.4, 51.5, 36.4.

Methyl (*E*)-3-(*N*-[3-(1,1'-biphenyl-4-yl)prop-2-yn-1-yl]-*N*-[4-methoxyphenylsulfonyl]amino) acrylate (1f): Elution with hexane/EtOAc (8:2), yellowish solid, 70% yield (355 mg), m.p. 133.8 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.10 (d, *J* = 14.0 Hz, 1H), 7.90–7.81 (m, AA′BB′, 2H), 7.58–7.54 (m, 2H), 7.51–7.42 (m, 4H), 7.40–7.35 (m, 1H), 7.21–7.15 (m, 2H), 7.00–6.92 (m, AA′BB′, 2H), 5.41 (d, *J* = 14.0 Hz, 1H), 4.58 (s, 2H), 3.77 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.8, 141.5, 140.9, 140.1, 132.1, 129.9, 129.6, 128.9, 127.8, 127.0, 126.8, 120.6, 114.6, 99.7, 85.6,

80.9, 55.6, 51.5, 36.3; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1370, found 462.1366.

Methyl (*E*)-3-[*N*-(4-fluorophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1g): Elution with hexane/EtOAc (8:2); 39% yield (173 mg); m.p. 126.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 14.0 Hz, 1H), 7.86–7.80 (m, AA′BB′, 2H), 7.13–7.07 (m, AA′BB′, 2H), 6.98–6.91 (m, 4H), 5.37 (d, *J* = 14.0 Hz, 1H), 4.53 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.8, 162.7 (d, *J* = 250.4 Hz), 140.8, 133.6 (d, *J* = 8.6 Hz), 129.8, 129.7, 117.8 (d, *J* = 4.4 Hz), 115.5 (d, *J* = 22.3 Hz), 114.5, 99.7, 84.7, 80.1 (d, *J* = 1.7 Hz), 55.6, 51.5, 36.1; **^{19}F NMR** (470 MHz, acetone-d_6): −111.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{19}FNO_5S^+$ $[M+H]^+$ 404.0963, found 404.0966.

Methyl (*E*)-3-[*N*-(4-chlorophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1h): Elution with hexane/EtOAc (8:2), yellowish amorphous solid, 81% yield (374 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 13.9 Hz, 1H), 7.85–7.77 (m, AA′BB′, 2H), 7.24–7.18 (m, AA′BB′, 2H), 7.07–7.01 (m, AA′BB′, 2H), 6.95–6.89 (m, AA′BB′, 2H), 5.35 (d, *J* = 13.9 Hz, 1H), 4.52 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.9, 140.9, 134.9, 132.9, 129.9, 129.7, 128.6, 120.2, 114.6, 99.8, 84.7, 81.4, 55.7, 51.6, 36.2.

Methyl (*E*)-3-[*N*-(4-bromophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1i): Elution with hexane/EtOAc (9:1), light yellow amorphous solid, 69% yield (352 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 14.0 Hz, 1H), 7.83–7.80 (m, AA′BB′, 2H), 7.40–7.36 (m, AA′BB′, 2H), 6.99–6.61 (m, 4H), 5.35 (d, *J* = 14.0 Hz, 1H), 4.52 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H). **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 163.8, 140.8, 133.0, 131.4, 129.8, 129.6, 123.0, 120.6, 114.5, 99.7, 84.6, 81.5, 55.6, 51.5, 36.1.

Methyl (*E*)-3-[*N*-(3,4-dichlorophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino] acrylate (1j): Elution with hexane/EtOAc (85:15), yellow amorphous solid, 81% yield (405 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 14.0 Hz, 1H), 7.84–7.79 (m, AA′BB′, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.99–6.94 (m, 3H), 5.33 (d, *J* = 14.0 Hz, 1H), 4.53 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 163.9, 140.7, 133.3, 133.2, 132.4, 130.7, 130.3, 129.9, 129.5, 121.6, 114.6, 99.7, 83.4, 82.4, 55.7, 51.5, 36.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{18}Cl_2NO_5S^+$ $[M+H]^+$ 454.0277, found 454.0277.

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[3-(2-nitrophenyl)prop-2-yn-1-yl]amino]acrylate (1k): Elution with hexane/EtOAc (6:4), green slime, 75% yield (355 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 14.0 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.81–7.79 (m, AA′BB′, 2H), 7.54–7.39 (m, 2H), 7.30–7.21 (m, 1H), 6.91–6.90 (m, AA′BB′, 2H), 5.40 (d, *J* = 14.0 Hz, 1H), 4.62 (s, 2H), 3.76 (s, 3H), 3.74 (s, 3H); **^{13}C NMR**

(125.7 MHz, $CDCl_3$): δ 167.3, 163.9, 140.7, 135.0, 132.8, 129.9, 129.5, 129.3, 124.6, 117.2, 114.6, 100.0, 88.5, 81.0, 55.7, 51.6, 36.3.

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[3-(3-nitrophenyl)prop-2-yn-1-yl]amino]acrylate (1*l*): Elution with hexane/EtOAc (8:2), yellow solid, 85% yield (402 mg), m. p. 101.9 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.18–8.13 (m, 1H), 8.10 (d, *J* = 14.0 Hz, 1H), 7.89–7.86 (m, 1H), 7.86–7.83 (m, AA′BB′, 2H), 7.48–7.43 (m, 2H), 7.01–6.97 (m, AA′BB′, 2H), 5.35 (d, *J* = 14.0 Hz, 1H), 4.58 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.1, 164.0, 147.9, 140.7, 137.2, 129.9, 129.5, 129.3, 126.4, 123.44, 123.39, 114.6, 99.7, 83.2, 83.1, 55.7, 51.5, 35.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{19}N_2O_7S^+$ $[M+H]^+$ 431.0908, found 431.0909.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(4-nitrophenylprop-2-yn-1-yl)amino]acrylate (1m): Elution with hexane/EtOAc (8:2), light yellow solid, 79% yield (374 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.14–8.04 (m, 3H), 7.83–7.81 (m, AA′BB′, 2H), 7.26–7.25 (m, AA′BB′, 2H), 6.95–6.94 (m, AA′BB′, 2H), 5.33 (d, *J* = 14.0 Hz, 1H), 4.57 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.1, 163.9, 147.4, 140.7, 132.4, 129.9, 129.5, 128.4, 123.4, 114.6, 99.7, 85.7, 83.7, 55.7, 51.6, 36.0.

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[3-(thiophen-2-yl)prop-2-yn-1-yl]amino]acrylate (1n): Elution with hexane/EtOAc (8:2), orange amorphous solid, 69% yield (297 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 14.0 Hz, 1H), 7.83–7.81 (m, AA′BB′, 2H), 7.21 (dd, *J* = 5.1 Hz, *J* = 1.1 Hz, 1H), 6.99–6.88 (m, 3H), 6.90 (dd, *J* = 5.1 Hz, *J* = 3.7 Hz, 1H), 5.34 (d, *J* = 14.0 Hz, 1H), 4.56 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 163.8, 140.8, 132.7, 129.8, 129.4, 127.6, 126.8, 121.5, 114.6, 99.6, 84.2, 79.0, 55.6, 51.4, 36.2.

Ethyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]but-2-enoate (1o): Elution with hexane/EtOAc (8:2), brown oil, 77% yield (350 mg). All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.89–7.82 (m, AA′BB′, 2H), 7.37–7.22 (m, 5H), 6.96–6.90 (m, AA′BB′, 2H), 5.90 (d, *J* = 1.0 Hz, 1H), 4.60 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.42 (d, *J* = 1.0 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 166.3, 163.3, 153.1, 131.6, 130.6, 130.0, 128.7, 128.3, 122.1, 114.2, 114.1, 85.7, 83.1, 60.1, 55.6, 39.7, 18.3, 14.2.

Methyl 3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]-3-phenylacrylate (1p): Elution with hexane/EtOAc 8:2, light yellow oil, 68% yield (345 mg) as a mixture of *cis*- and *trans*-isomers. All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.89–7.83 (m, AA′BB′, 2H), 7.69–7.59 (m, 4H), 7.52–7.46 (m, 2H), 7.44–7.23 (m, 12H), 7.07–7.00 (m, 2H), 6.99–6.92 (m, 2H), 6.89–6.81 (m, 4H), 6.23 (s, 1H), 6.15 (s, 1H), 4.82 (s, 2H), 4.49 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.68 (s, 3H), 3.60 (s, 3H), 3.54 (s, 3H);

^{13}C NMR (125.7 MHz, $CDCl_3$): δ 166.0, 164.3, 163.4, 162.9, 152.3, 137.5, 134.0, 131.7, 131.5, 131.0, 130.3, 130.2, 130.0, 129.8, 129.5, 129.3, 128.6, 128.5, 128.4, 128.3, 128.32, 128.27, 128.21, 128.0, 127.9, 122.2, 116.7, 114.2, 114.0, 113.7, 85.8, 85.5, 83.9, 83.3, 55.62, 55.55, 51.6, 51.3, 42.1, 39.9.

Dimethyl 2-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1yl)amino]maleate (1q): Elution with hexane/EtOAc (7:3), yellow oil, 55% yield (268 mg) as a mixture of *cis*- and *trans*-isomers. All spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97–7.93 (m, AA′BB′, 2H), 7.85–7.81 (m, AA′BB′, 2H), 7.33–7.24 (m, 6H), 7.16–7.12 (m, 4H), 7.01 (s, 1H), 6.99–6.96 (m, AA′BB′, 2H), 6.93–6.89 (m, AA′BB′, 2H), 5.92 (s, 1H), 4.59 (s, 2H), 4.54 (s, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 165.4, 164.0, 163.8, 145.0, 131.6, 131.6, 130.5, 130.2, 129.3, 129.1, 128.7, 128.5, 128.2, 128.1, 121.7, 114.3, 113.9, 107.3, 86.9, 86.4, 80.8, 55.6, 55.5, 53.3, 53.1, 52.2, 51.9, 40.3, 40.1.

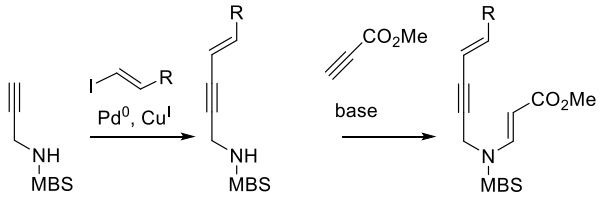
Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-((*E*)-undec-4-en-2-yn-1yl)amino]acrylate (1t): 1-Iodo-oct-2-ene (0.286 mL, 1.65 mmol), $(PPh_3)_2PdCl_2$ (39 mg, 0.055 mmol) and CuI (21 mg, 0.11 mmol) were added to a solution of enyne **6a** (340.3 mg, 1.1 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere. TEA (1.53 mL; 11.0 mmol) was then added portionwise at room temperature. The reaction mixture was stirred overnight, diluted with EtOAc (20 mL) and washed with a saturated NH_4Cl solution (20 mL). The water phase was then extracted with EtOAc (2 × 20 mL), the combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The solution was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (40 g), eluting with a hexane/EtOAc mixture (8:2); brownish oil, 62% yield (426 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (d, J = 14.0 Hz, 1H), 7.83–7.77 (m, AA′BB′, 2H), 7.01–6.94 (m, AA′BB′, 2H), 5.88 (dt, J = 15.9 Hz, J = 7.0 Hz, 1H), 5.30 (d, J = 14.0 Hz, 1H), 5.19 (dt, J = 15.9 Hz, J = 1.8 Hz, 1H), 4.41 (d, J = 2.0 Hz, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 2.05 – 1.99 (m, 2H), 1.38–1.22 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.7, 146.4, 140.8, 129.8, 129.7, 114.5, 108.1, 99.5, 84.6, 78.5, 55.6, 51.4, 36.2, 33.0, 31.6, 28.7, 28.5, 22.5, 14.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{30}NO_5S^+$ $[M+H]^+$ 420.1839, found 420.1838.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-((*E*)-5-phenylpent-4-en-2-yn-1-yl)amino]acrylate (1u): 1-Bromo-2-phenylethylene (0.212 mL, 1.21 mmol), $(PPh_3)_2PdCl_2$ (39 mg, 0.055 mmol) and CuI (21 mg, 0.11 mmol) were added to a solution of enyne **6a** (340.3 mg, 1.1 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere. TEA (1.53 mL; 11.0 mmol) was then added portionwise at room temperature. The reaction mixture was stirred overnight, diluted with EtOAc (20 mL) and washed with a saturated NH_4Cl solution (20 mL). The water phase was then extracted with EtOAc (2 × 20 mL), the combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The solution was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (70 g), eluting with a hexane/EtOAc mixture (8:2); yellow amorphous solid, 43% yield (195 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 14.0 Hz, 1H), 7.86–7.82 (m, AA′BB′, 2H), 7.38–7.27 (m, 5H), 7.04–6.98 (m, AA′BB′, 2H), 6.60 (d, *J* = 16.3 Hz, 1H), 5.86 (dt, *J* = 16.3 Hz, *J* = 2.1 Hz, 1H), 5.34 (d, *J* = 14.0 Hz, 1H), 4.50 (d, *J* = 2.1 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.3, 163.8, 142.5, 140.8, 135.7, 129.9, 129.7, 129.0, 128.7, 126.2, 114.5, 106.6, 99.7, 84.9, 82.3, 55.6, 51.5, 36.3; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{22}NO_5S^+$ $[M+H]^+$ 412.1213, found 412.1213.

Preparation of propargylamino acrylates 1r and 1s

Table 2. Overview of propargylamino acrylates **1r** and **1s**.



Cpd	R	Overall Yield [%]
1r	H	52
1s	CH_3	45

***N*-(pent-4-en-2-yn-1-yl)-4-methoxybenzenesulfonamide (11r)**: $(PPh_3)_2PdCl_2$ (779 mg, 1.11 mmol), CuI (423 mg, 2.22 mmol) and vinyl bromide (55.5 mL of 1M THF solution, 55.5 mmol) were added to a solution of sulfonamide **4** (5 g, 22.2 mmol) in dry DMF (50 mL) in an oven-dried flask under argon atmosphere. TEA (31 mL, 222 mmol) was then added portionwise at room temperature. The reaction mixture was stirred until TLC analysis indicated that the reaction was complete (1 hour). The mixture was diluted with EtOAc (50 mL) and washed with a saturated NH_4Cl solution (50 mL). The water phase was then extracted with EtOAc (2 × 50 mL), the combined organic layers washed with brine (20 mL) and dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the residue was purified by chromatography on a column of silica gel (150 g), eluting with a hexane/EtOAc mixture (75:25); yellow amorphous solid, 54% yield (3 g);**^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86–7.81 (m, AA′BB′, 2H), 7.01–6.95 (m, AA′BB′, 2H), 5.56 (ddt, *J* = 17.6 Hz, *J* = 10.9 Hz, *J* = 1.9 Hz, 1H), 5.43 (dd, *J* = 17.6 Hz, *J* = 2.0 Hz, 1H), 5.40 (dd, *J* = 10.9 Hz, *J* = 2.0 Hz, 1H), 4.73 (bs, 1H), 3.95 (d, *J* = 3.3 Hz, 2H), 3.87 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.1, 131.2, 129.6, 127.7, 116.2, 114.2, 83.9, 83.3, 55.6, 33.6; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{12}H_{14}NO_3S^+$ $[M+H]^+$ 252.0689, found 252.0694.

(*E,Z*)-*N*-(hex-4-en-2-yn-1-yl)-4-methoxybenzenesulfonamide (11s): $(PPh_3)_2PdCl_2$ (78 mg, 0.11 mmol), CuI (42 mg, 0.22 mmol) and propenyl bromide (0.475 mL, 5.55 mmol) were added to a solution of sulfonamide **4** (0.50 g, 2.22 mmol) in dry THF (15 mL) in an oven-dried flask under argon

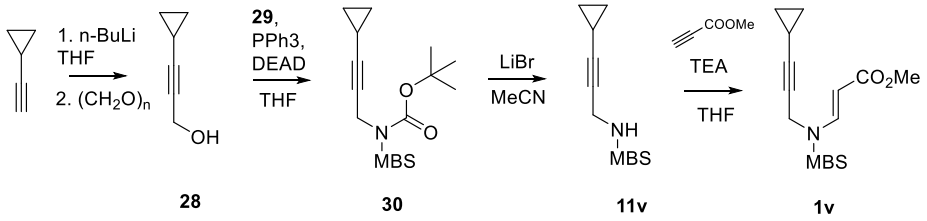
atmosphere. TEA (3.4 mL, 22.2 mmol) was then added portionwise at room temperature. The reaction mixture was stirred until TLC analysis indicated that the reaction was complete (4 hours). The mixture was diluted with EtOAc (20 mL) and washed with a saturated NH_4Cl solution (20 mL). The water phase was then extracted with EtOAc (2 × 20 mL), the combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the residue was purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (7:3); yellow amorphous solid, 50% yield (295 mg); isolated as a mixture of *E*/*Z*-isomers (a:b = 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86–7.81 (m, mixture of isomers a+b, 4H), 7.00–6.96 (m, mixture of isomers a+b, 4H), 5.92 (dq, *J* = 16.0 Hz, *J* = 6.9 Hz, overlap, isomer a, 1H), 5.94–5.88 (m, isomer b, 1H), 5.29–5.24 (m, mixture of isomers a+b, 2H), 4.72 (t, *J* = 6.1 Hz, isomer b, 1H), 4.67 (t, *J* = 6.1 Hz, isomer a, 1H), 3.99 (dd, *J* = 6.1 Hz, *J* = 2.0 Hz, isomer b, 2H), 3.92 (dd, *J* = 6.1 Hz, *J* = 2.0 Hz, isomer a, 2H), 3.87 (s, isomer a, 3H), 3.86 (s, isomer b, 3H), 1.72 (dd, *J* = 6.9 Hz, *J* = 1.9 Hz, isomer a, 3H), 1.70 (dd, *J* = 6.9 Hz, *J* = 1.4 Hz, isomer b, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.05, 163.03, 140.6, 139.3, 131.3, 131.2, 129.6, 129.5, 114.17, 114.15, 109.7, 109.0, 87.7, 83.5, 81.40, 81.37, 55.58, 55.56, 33.8, 33.7, 18.5, 15.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{13}H_{16}NO_3S^+$ $[M+H]^+$ 266.0846, found 266.0855; *m/z* calcd. for $C_{13}H_{15}NO_3SNa^+$ $[M+Na]^+$ 288.0665, found 288.0671.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(pent-4-en-2-yn-1-yl)amino]acrylate (1r): Methyl propiolate (0.670 mL, 7.53 mmol) followed by TEA (3.2 mL, 22.6 mmol, portionwise) were added to a solution of compound **11r** (1.89 g, 7.53 mmol) in dry THF (40 mL) in an oven-dried flask under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature until TLC analysis indicated that the reaction was complete (3 h). The mixture was diluted with EtOAc (30 mL) and washed with 30 mL of a saturated NH_4Cl solution. The water phase was then extracted with EtOAc (2 × 30 mL), and the combined organic layers were dried over Na_2SO_4. Inorganic residues were filtered off, the solution evaporated to dryness, and the residue purified by chromatography on a column of silica gel (100 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a yellow amorphous solid, 97% yield (2.45 g); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 13.9 Hz, 1H), 7.82–7.77 (m, AA′ BB′, 2H), 7.01–6.96 (m, AA′ BB′, 2H), 5.52 (ddt, *J* = 17.0 Hz, *J* = 11.5 Hz, *J* = 1.9 Hz, 1H), 5.41 (dd, overlap, *J* = 11.5 Hz, *J* = 2.3 Hz, 1H), 5.38 (dd, overlap, *J* = 17.0 Hz, *J* = 2.3 Hz, 1H), 5.29 (d, *J* = 14.0 Hz, 1H), 4.43 (d, *J* = 1.9 Hz, 2H), 3.86 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 163.8, 140.7, 129.8, 129.5, 128.1, 115.9, 114.5, 99.6, 84.2, 80.9, 55.7, 51.4, 36.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{16}H_{18}NO_5S^+$ $[M+H]^+$ 336.0900, found 336.0902.

Methyl (*E*)-3-[*N*-((*E*,*Z*)-hex-4-en-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1s): Methyl propiolate (0.091 mL, 1.02 mmol) followed by TEA (0.43 mL, 3.06 mmol, portionwise) were added to a solution of compound **11s** (270 mg, 1.02 mmol) in dry THF (5 mL) in an oven-dried flask under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature until TLC analysis indicated that the reaction was complete (12 h). The mixture was diluted with EtOAc

(10 mL) and washed with 10 mL of a saturated NH_4Cl solution. The water phase was then extracted with EtOAc (2 × 10 mL), and the combined organic layers were dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the residue was purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a yellow oil, 91% yield (323 mg); isolated as a mixture of *E*,*Z*-isomers (a:b = 3:1); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 13.9 Hz, overlap, isomer b, 1H), 8.01 (d, *J* = 13.9 Hz, overlap, isomer a, 1H), 7.81–7.75 (m, isomers a+b, 4H), 7.00–6.94 (m, isomers a+b, 4H), 5.93–5.82 (m, overlap, isomer b, 1H), 5.88 (dq, *J* = 15.7 Hz, *J* = 6.8 Hz, overlap, isomer a, 1H), 5.33 (d, *J* = 13.9, isomer b, 1H), 5.29 (d, *J* = 13.9 Hz, isomer a, 1H), 5.23–5.18 (m, isomers a+b, 1H), 4.47 (d, *J* = 2.0 Hz, isomer b, 2H), 4.39 (d, *J* = 2.0 Hz, isomer a, 2H), 3.86 (s, isomer b, 3H), 3.84 (s, isomer a, 3H), 3.72 (d, *J* = 1.1 Hz, 6H), 1.70 (dd, *J* = 6.8 Hz, *J* = 1.4 Hz, isomer a, 3H), 1.61 (dd, *J* = 6.8 Hz, *J* = 1.3 Hz, isomer b, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 167.28, 167.27, 163.74, 163.72, 141.0, 140.8, 140.7, 139.8, 129.73, 129.67, 114.44, 114.42, 109.4, 108.7, 99.50, 99.47, 84.6, 84.4, 82.5, 78.4, 55.64, 55.62, 51.4, 36.3, 36.2, 29.6, 18.4, 15.8; **HR MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{17}H_{20}NO_5Sa^+$ $[M+H]^+$ 350.1057, found 350.1066; *m/z* calcd. for $C_{17}H_{19}NO_5SNa^+$ $[M+Na]^+$ 372.0876, found 372.0876.

Preparation of the propargylamino acrylate 1v



Scheme 1. Synthesis of **1v**

3-Cyclopropylprop-2-yn-1-ol (28) was prepared according to a literature procedure.[3] n-BuLi (3.4 mL of 2.5M solution, 8.4 mmol) was added dropwise at −78 °C to a solution of cyclopropylacetylene (677 µl, 8 mmol) in dry THF (16 mL). The mixture was stirred for 30 minutes, then paraformaldehyde (432.4 mg, 14.4 mmol) was added in one portion. The resultant mixture was allowed to warm to room temperature overnight. The mixture was then quenched with a saturated NH_4Cl solution (20 mL), extracted with EtOAc (2 × 15 mL), and the combined organic layers were dried over Na_2SO_4. Inorganic residues were filtered off, and the solution was evaporated to dryness to obtain a light yellow oil, 90% yield (629 mg); all data were in agreement with those reported in literature: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.23 (dd, *J* = 2.0 Hz, *J* = 0.7 Hz, 2H), 2.05 (d, *J* = 0.7 Hz, 1H), 1.31–1.24 (m, 1H), 0.82–0.75 (m, 2H), 0.73–0.67 (m, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 89.7, 73.6, 51.4, 8.2, −0.6.

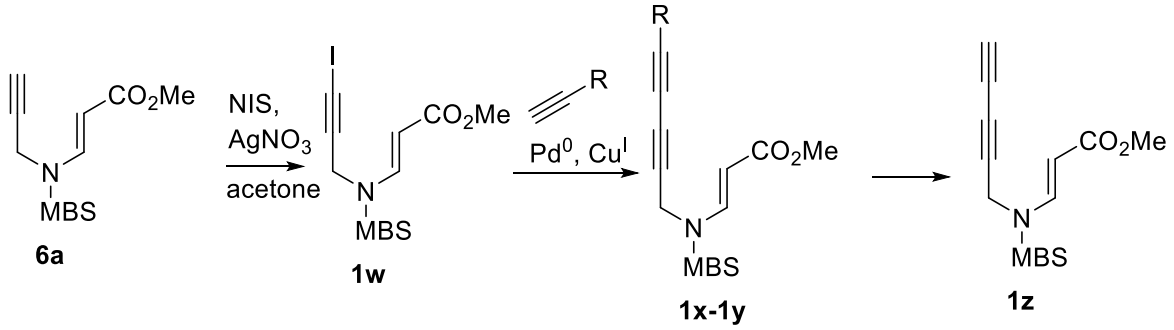
***Tert*-butyl *N*-(4-methoxyphenylsulfonyl)carbamate (29)** was prepared according to a literature procedure.[4] DMAP (171 mg, 1.4 mmol), di-*tert*-butyl dicarbonate (1.68 g, 7.7 mmol) and TEA (1.17 mL, 8.4 mmol) were successively added to a solution of 4-methoxyphenylsulfonamide (1.31 g, 7 mmol) in dry DCM (15 mL) under argon atmosphere. The reaction mixture was stirred at room temperature overnight, then quenched with 5% HCl (15 mL). The resultant mixture was extracted with EtOAc (2 × 10 mL), the combined organic layers were washed with a saturated solution of $NaHCO_3$ (10 mL) and brine (10 mL), and dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the crude product purified by chromatography on a column of silica gel (90 g), eluting with a hexane/EtOAc mixture (6:4); white solid, 95% yield (1.9 g); all data were in agreement with those reported in literature: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98–7.93 (m, AA′ BB′, 2H), 7.32 (s, 1H), 7.03–6.99 (m, AA′ BB′, 2H), 3.90 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.7, 149.1, 130.5, 130.3, 114.0, 84.0, 55.7, 27.9.

***Tert*-butyl *N*-(3-cyclopropylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)carbamate (30)**: A solution of imide **29** (747.2 mg, 2.6 mmol) in dry THF (5 mL) and triphenylphosphine (682 mg, 2.6 mmol) were successively added to a solution of propargyl alcohol **28** (250 mg, 2.6 mmol) in dry THF (5 mL) in an oven-dried flask under argon atmosphere. The reaction mixture was cooled down to 0 °C and the solution of DEAD in toluene was subsequently added dropwise (1.3 ml, 2.6 mmol). After 30 min, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, inorganic residues were filtered off, the solution was evaporated to dryness, and the crude product was purified by chromatography on a column of silica gel (70 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a yellowish amorphous solid; 77% yield (730 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03–7.93 (m, AA′ BB′, 2H), 7.01–6.93 (m, AA′ BB′, 2H), 4.56 (d, J = 1.9 Hz, 2H), 3.90 (s, 3H), 1.37 (s, 9H), 1.27–1.22 (m, 1H), 0.80–0.75 (m, 2H), 0.68–0.63 (m, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.4, 150.4, 131.3, 130.6, 113.6, 87.5, 84.5, 70.6, 55.7, 36.5, 27.9, 8.0, −0.6; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{18}H_{23}NO_5SNa^+$ $[M+Na]^+$ 388.1189, found 388.1192.

***N*-(3-cyclopropylprop-2-yn-1-yl)-4-methoxybenzenesulfonamide (11v)**: Dried lithium bromide (1 g, 11.52 mmol) was added in one portion to a solution of carbamate **30** (350 mg, 0.96 mmol) in dry acetonitrile (10 mL) in an oven-dried flask under argon atmosphere. The reaction mixture was stirred at 65 °C overnight. After cooling the mixture down, the solvent was evaporated to dryness, and the crude product purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a white solid; 92% yield (235 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, AA′ BB′, 2H), 7.01–6.97 (m, AA′ BB′, 2H), 4.47 (t, J = 6.0 Hz, 1H), 3.89 (s, 3H), 3.78 (dd, J = 6.0 Hz, J = 2.0 Hz, 2H), 1.08–0.97 (m, 1H), 0.73–0.64 (m, 2H), 0.48–0.39 (m, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.1, 131.4, 129.6, 114.1, 88.5, 69.5, 55.6, 33.4, 7.9, −0.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{13}H_{16}NO_3S^+$ $[M+H]^+$ 266.0846, found 266.0851.

Methyl (*E*)-3-[*N*-(3-cyclopropylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1v): Methyl propiolate (0.071 mL, 1.19 mmol) followed by TEA (0.45 mL, 3.23 mmol, portionwise) were added to a solution of compound **11v** (286 mg, 1.08 mmol) in dry THF (8 mL) in an oven-dried flask under argon atmosphere. The reaction mixture was stirred overnight, then diluted with EtOAc (10 mL) and washed with a saturated NH_4Cl solution (5 mL). The water phase was then extracted with EtOAc (2 × 10 mL), and the combined organic extracts were dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (8:2) to obtain a yellow oil, 16% yield (60 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 13.9 Hz, 1H), 7.79–7.75 (m, AA′ BB′, 2H), 7.01–6.97 (m, AA′ BB′, 2H), 5.28 (d, *J* = 13.9 Hz, 1H), 4.26 (d, *J* = 2.0 Hz, 2H), 3.88 (s, 3H), 3.74 (s, 3H), 1.02–0.94 (m, 1H), 0.66–0.59 (m, 2H), 0.40–0.34 (m, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.4, 163.7, 140.8, 129.8, 129.7, 114.4, 99.4, 89.6, 66.4, 55.7, 51.4, 35.9, 8.0, −0.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{17}H_{20}NO_5S^+$ $[M+H]^+$ 350.1057, found 350.1055.

Preparation of the propargylamino acrylates 1w–1z



Scheme 2. Overview of the synthesis of **1w–1z**

Methyl (*E*)-3-[*N*-(3-iodoprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1w): *N*-iodosuccinimide (270 mg, 1.2 mmol) and silver nitrate (17 mg, 0.1 mmol) were added to a solution of enyne **6a** (309 mg, 1 mmol) in acetone p.a. (10 mL) at room temperature. The reaction mixture was stirred until TLC analysis indicated that the reaction was complete (1.5 hour). The mixture was then poured onto ice, extracted with diethyl ether (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the residue was recrystallized from hot hexane; pink solid, m.p. 124–125 °C; 97% yield (423 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 14.0 Hz, 1H), 7.83–7.72 (m, AA′ BB′, 2H), 7.10–6.92 (m, AA′ BB′, 2H), 5.26 (d, *J* = 14.0 Hz, 1H), 4.44 (s, 2H), 3.90 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 163.9, 140.6, 129.8, 129.6, 129.2, 114.6, 99.7, 85.0, 55.7, 51.5, 37.0; **HR MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{14}H_{15}INO_5SNa^+$ $[M+H]^+$ 435.9710, found 435.9119.

Methyl (*E*)-3-[*N*-(5-cyclopropylpenta-2,4-diyn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (1x): Iodoenyne **1w** (435.2 mg, 1 mmol), $(PPh_3)_2PdCl_2$ (35 mg, 0.05 mmol) and CuI (19 mg, 0.1 mmol) were added to a solution of cyclopropylacetylene (93 μL, 1.1 mmol) in THF (10 mL) in an oven-dried flask under argon atmosphere. TEA (1.4 mL, 10 mmol) was then added to the solution dropwise. The reaction mixture was stirred at room temperature overnight, then quenched with saturated solution of NH_4Cl (10 mL), extracted with EtOAc (2 × 15 mL), and the combined organic layers were dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the crude product was purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (8:2); pale yellow oil, 38% yield (142 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 14.0 Hz, 1H), 7.81–7.75 (m, AA′ BB′, 2H), 7.04–6.96 (m, AA′ BB′, 2H), 5.25 (d, *J* = 14.0 Hz, 1H), 4.35 (s, 2H), 3.89 (s, 3H), 3.74 (s, 3H), 1.32–1.20 (m, 1H), 0.92–0.68 (m, 4H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.1, 163.9, 140.6, 129.7, 129.3, 114.6, 99.7, 84.4, 71.1, 66.0, 59.3, 55.7, 51.4, 36.0, 8.8, −0.2; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{19}H_{20}NO_5S^+$ $[M+H]^+$ 374.1057, found 374.1060.

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[5-(triethylsilyl)penta-2,4-diyn-1-yl]amino]acrylate (1y): Iodoenyne **1w** (435.2 mg, 1 mmol), $(PPh_3)_2PdCl_2$ (35 mg, 0.05 mmol) and CuI (19 mg, 0.1 mmol) were added to a solution of TES-acetylene (197 μL, 1.1 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere. TEA (1.4 mL, 10 mmol) was then added to the solution dropwise. The reaction mixture was stirred at room temperature overnight, then quenched with a saturated solution of NH_4Cl (10 mL), extracted with EtOAc (2 × 15 mL), and the combined organic layers were dried over Na_2SO_4. Inorganic residues were filtered off, the solution was evaporated to dryness, and the crude product was purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (8:2); yellowish amorphous solid, 31% yield (140 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 14.1 Hz, 1H), 7.84–7.77 (m, AA′ BB′, 2H), 7.04–6.99 (m, AA′ BB′, 2H), 5.26 (d, *J* = 14.1 Hz, 1H), 4.39 (s, 2H), 3.88 (s, 3H), 3.75 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.1, 164.0, 140.6, 129.8, 129.6, 114.7, 99.8, 87.5, 85.7, 70.8, 68.2, 55.7, 51.5, 35.9, 7.3, 4.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{30}NO_5SSi^+$ $[M+H]^+$ 448.1609, found 448.1606.

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(penta-2,4-diyn-1-yl)amino]acrylate (1z): K_2CO_3 (43 mg, 0.313 mmol) was added to a solution of compound **1y** (140 mg, 0.313 mmol) in MeOH p.a. (5 mL). The reaction mixture was stirred at room temperature until TLC analysis indicated that the reaction was complete (30 min). The reaction mixture was diluted with H_2O (10 mL) and then extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, inorganic residues were filtered off, and the solvent was evaporated to give a product, which was used without further purification. White amorphous solid, 80% yield (81.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 14.0 Hz, 1H), 7.81–7.78 (m, AA′ BB′, 2H), 7.05–7.00 (m, AA′ BB′, 2H), 5.25 (d, *J* = 14.0 Hz, 1H), 4.38 (d, *J* = 1.0 Hz, 2H), 3.89 (s, 3H), 3.75 (s, 3H), 2.07 (t, *J* = 1.0 Hz, 1H); **^{13}C NMR** (125.7 MHz,

$CDCl_3$): δ 167.0, 164.1, 140.5, 129.8, 129.62, 129.1, 114.7, 99.8, 69.9, 68.1, 67.7, 66.8, 55.7, 51.5, 35.7; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{16}H_{16}NO_5S^+$ $[M+H]^+$ 334.0744, found 334.0752.

Procedure for synthesis of tetrahydropyridines 3 and dihydropyridines 2o, 2p and 2w.

Silver tetrafluoroborate (7.8 mg, 0.04 mmol) was weighed into an oven-dried flask under argon atmosphere. Dry benzene (2 mL), (TFP)AuCl (9.3 mg, 0.02 mmol) and dry methanol (49 μL, 1.2 mmol) were added subsequently to form a white opalescent suspension. The solution of the appropriate propargylamino acrylate **1** (0.4 mmol) in dry benzene (3 ml) was cannulated into the reaction flask, and the mixture was stirred at room temperature, while monitoring by TLC and/or NMR analysis (ca 1–12 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate, the solvent of combined filtrate was evaporated to the dryness, and the residue was purified by chromatography on a column of silica gel (50–60 g) to afford tetrahydropyridine **3**.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (3a): Elution with hexane/EtOAc (8:2); white solid, m. p. 87–88 °C; 95% yield (159 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.84–7.80 (m, AA′BB′, 2H), 7.41–7.24 (m, 5H), 7.16–7.12 (m, AA′BB′, 2H), 6.23 (dd, *J* = 4.1 Hz, *J* = 2.8 Hz, 1H), 5.73 (d, *J* = 2.0 Hz, 1H), 4.06–4.03 (m, 1H), 3.96 (dd, *J* = 17.6, *J* = 4.1 Hz, 1H), 3.92 (s, 3H), 3.74 (dt, *J* = 17.6 Hz, *J* = 2.8 Hz, 1H), 3.60 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.4, 164.2, 140.6, 131.9, 131.3, 130.7, 129.2, 128.3, 126.2, 122.1, 115.0, 84.9, 56.1, 56.1, 52.6, 49.6, 42.1; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{23}NO_6SNa^+$ $[M+Na]^+$ 440.1138, found 440.1146.).

Methyl 2-methoxy-1-(4-methylphenylsulfonyl)-4-(4-methylphenyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3b): Elution with hexane/EtOAc (9:1–8:2); light yellow amorphous solid; 87% yield (150 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.85–7.78 (m, AA′BB′, 2H), 7.31–7.24 (m, AA′BB′, 2H), 7.18–7.09 (m, 4H), 6.19 (dd, *J* = 4.1 Hz, *J* = 2.7 Hz, 1H), 5.71 (d, *J* = 1.9 Hz, 1H), 4.03–4.00 (m, 1H), 3.94 (dd, overlap, *J* = 17.8 Hz, *J* = 4.1 Hz, 1H), 3.92 (s, overlap, 3H), 3.73 (dt, *J* = 17.8 Hz, *J* = 2.7 Hz, 1H), 3.59 (s, 3H), 3.39 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.5, 164.1, 137.9, 137.8, 131.9, 131.0, 130.7, 129.9, 126.1, 121.1, 115.0, 84.9, 56.12, 56.07, 52.6, 49.6, 42.0, 21.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{25}NO_6SNa^+$ $[M+Na]^+$ 454.1295, found 454.1296.

Methyl 2-methoxy-4-(4-methoxyphenyl)-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3c): Elution with hexane/EtOAc (8:2); white amorphous solid; 79% yield (141 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.85–7.78 (m, AA′BB′, 2H), 7.35–7.27 (m, AA′BB′, 2H), 7.17–7.10 (m, AA′BB′, 2H), 6.92–6.85 (m, AA′BB′, 2H), 6.12 (dd, *J* = 4.1 Hz, *J* = 2.8 Hz, 1H), 5.71 (d, *J* = 1.9 Hz, 1H), 4.02–3.98 (m, 1H), 3.98 (dd, overlap, *J* = 17.5 Hz, *J* = 4.1 Hz), 3.92 (s, overlap, 3H), 3.79 (s, 3H), 3.72 (dt, *J* = 17.5 Hz, *J* = 2.8 Hz, 1H), 3.60 (s, 3H), 3.39 (s, 3H); **^{13}C**

NMR (125.7 MHz, acetone-d_6): δ 170.5, 164.1, 160.2, 133.0, 132.0, 130.66, 130.65, 127.3, 120.2, 115.0, 114.6, 85.0, 56.12, 56.07, 55.5, 52.6, 49.6, 42.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{25}NO_7SNa^+$ $[M+Na]^+$ 470.1244, found 470.1257.

Methyl 2-methoxy-4-(3-methoxyphenyl)-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3d): Elution with hexane/EtOAc (8:2); light yellow amorphous solid, 77% yield (138 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.85–7.79 (m, AA′ BB′, 2H), 7.27–7.21 (m, 1H), 7.18–7.11 (m, AA′ BB′, 2H), 6.98–6.81 (m, 3H), 6.25 (dd, J = 4.1 Hz, J = 2.8 Hz, 1H), 5.72 (d, J = 1.9 Hz, 1H), 4.05–4.02 (m, 1H), 3.99–3.93 (m, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 3.74 (dt, J = 18.0 Hz, J = 2.8 Hz, 1H), 3.61 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.5, 164.2, 160.8, 142.1, 131.9, 131.2, 130.7, 130.2, 122.3, 118.5, 115.0, 113.7, 112.0, 84.9, 56.1, 56.1, 55.4, 52.6, 49.6, 42.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{25}NO_7SNa^+$ $[M+Na]^+$ 470.1244, found 470.1250.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-naphthyl-1,2,3,6-tetrahydropyridine-3-carboxylate (3e): Elution with hexane/EtOAc (8:2); light yellow oil, 78% yield (146 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 8.15–8.09 (m, 1H), 7.94–7.82 (m, 4H), 7.53–7.43 (m, 3H), 7.38–7.34 (m, 1H), 7.22–7.16 (m, AA′ BB′, 2H), 5.93 (dd, J = 3.8 Hz, J = 2.6 Hz, 1H), 5.78 (d, J = 1.8 Hz, 1H), 4.06 (dd, J = 17.4 Hz, J = 3.8 Hz, 1H), 3.95 (s, 3H), 3.91–3.88 (m, 1H), 3.82 (dt, J = 17.4 Hz, J = 2.6 Hz, 1H), 3.55 (s, 3H), 3.54 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.2, 164.2, 139.7, 134.7, 132.2, 131.9, 131.6, 130.7, 129.1, 128.6, 127.2, 126.8, 126.6, 126.1, 126.0, 125.6, 115.0, 84.9, 56.4, 56.1, 52.4, 52.2, 41.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{25}H_{25}NO_6SNa^+$ $[M+Na]^+$ 490.1295, found 490.1295.

Methyl 4-biphenyl-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3f): Elution with hexane/EtOAc (8:2); yellow amorphous solid, 94% yield (186 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.87–7.79 (m, AA′ BB′, 2H), 7.70–7.60 (m, 4H), 7.52–7.42 (m, 4H), 7.40–7.33 (m, 1H), 7.19–7.11 (m, AA′ BB′, 2H), 6.32 (dd, J = 4.0 Hz, J = 2.7 Hz, 1H), 5.76 (d, J = 2.0 Hz, 1H), 4.12 – 4.10 (m, 1H), 3.99 (dd, J = 17.7 Hz, J = 4.0 Hz, 1H), 3.92 (s, 3H), 3.77 (dt, J = 17.7 Hz, J = 2.7 Hz, 1H), 3.62 (s, 3H), 3.41 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.5, 164.2, 141.1, 140.8, 139.6, 131.9, 130.8, 130.7, 129.7, 128.2, 127.7, 127.5, 126.7, 122.1, 115.0, 84.9, 56.13, 56.12, 52.7, 49.4, 42.1; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{27}H_{27}NO_6SNa^+$ $[M+Na]^+$ 516.1451, found 516.1462.

Methyl 4-(4-fluorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3g): Elution with hexane/EtOAc (9:1–85:15); colorless oil, 44% yield (77 mg); **^{1}H NMR (**500 MHz, acetone-d_6): δ 7.83–7.80 (m, AA′ BB′, 2H), 7.45–7.41 (m, 2H), 7.16–7.07 (m, 4H), 6.20 (dd, J = 4.1 Hz, J = 2.8 Hz, 1H), 5.73 (d, J = 2.0 Hz, 1H), 4.04–4.02 (m, 1H), 3.97–3.92 (m, 1H), 3.92 (s, 3H), 3.73 (dt, J = 17.8 Hz, J = 2.6 Hz, 1H), 3.60 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.3, 164.2, 163.1 (d, J = 244.7 Hz), 137.1 (d, J = 3.4 Hz), 131.9, 130.7, 130.4, 128.3 (d, J = 8.0 Hz), 122.23, 115.9 (d, J = 21.6 Hz), 115.0, 84.9, 56.14, 56.11, 52.7, 49.7, 42.0; **^{19}F NMR**

(470 MHz, acetone-d_6): −112.1; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{22}FNO_6SNa^+$ $[M+Na]^+$ 458.1044, found 458.1052.

Methyl 4-(4-chlorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3h): Elution with hexan/EtOAc (85:15–8:2); yellowish oil, 86% yield (156 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.81–7.76 (m, AA′BB′, 2H), 7.30–7.20 (m, 4H), 7.00–6.95 (m, AA′BB′, 2H), 6.09 (dd, *J* = 3.9 Hz, *J* = 2.8 Hz, 1H), 5.78 (d, *J* = 1.8 Hz, 1H), 3.90–3.88 (m, 2H), 3.87 (s, 3H), 3.82 (dt, *J* = 17.6 Hz, *J* = 2.8 Hz, 1H), 3.61 (s, 3H), 3.47 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 169.7, 163.1, 137.9, 133.5, 130.7, 129.8, 129.8, 128.6, 126.8, 121.6, 114.1, 83.6, 56.2, 55.6, 52.5, 49.4, 41.1; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{22}ClNO_6SNa^+$ $[M+Na]^+$ 474.0748, found 474.0757.

Methyl 4-(4-bromophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3i): Elution with hexane/EtOAc (8:2); yellowish oil, 90% yield (179 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.81–7.76 (m, AA′BB′, 2H), 7.46–7.41 (m, AA′BB′, 2H), 7.19–7.14 (m, AA′BB′, 2H), 7.00–6.95 (m, AA′BB′, 2H), 6.10 (dd, *J* = 4.0 Hz, *J* = 2.8 Hz, 1H), 5.78 (d, *J* = 1.9 Hz, 1H), 3.92–3.86 (m, 2H), 3.87 (s, 3H), 3.84–3.78 (m, 1H), 3.61 (s, 3H), 3.47 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 169.7, 163.1, 138.4, 131.6, 130.7, 129.9, 129.8, 127.2, 121.70, 121.68, 114.1, 83.6, 56.2, 55.6, 52.5, 49.3, 41.1; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{22}BrNO_6SNa^+$ $[M+Na]^+$ 518.0243, found 518.0245.

Methyl 4-(3,4-dichlorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3j): Elution with hexane/EtOAc (8:2); pale yellow oil, 27% yield (52 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.85–7.79 (m, AA′BB′, 2H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.39 (dd, *J* = 8.5 Hz, *J* = 2.2 Hz, 1H), 7.19–7.10 (m, AA′BB′, 2H), 6.35 (dd, *J* = 4.1 Hz, *J* = 2.8 Hz, 1H), 5.77 (d, *J* = 2.0 Hz, 1H), 4.13–4.07 (m, 1H), 3.99–3.94 (m, 1H), 3.92 (s, 3H), 3.78–3.72 (m, 1H), 3.61 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.1, 164.2, 141.5, 132.8, 131.8, 131.4, 131.3, 130.7, 129.6, 128.4, 126.4, 124.4, 115.0, 84.8, 56.2, 56.1, 52.7, 49.2, 42.1; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{21}Cl_2NO_6SNa^+$ $[M+Na]^+$ 508.0359, found 508.0359.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(4-nitrophenyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3m): Elution with hexane/EtOAc (8:2–7:3); light yellow amorphous solid, 23% yield (43 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.20–8.14 (m, AA′BB′, 2H), 7.81–7.75 (m, AA′BB′, 2H), 7.48–7.41 (m, AA′BB′, 2H), 7.01–6.94 (m, AA′BB′, 2H), 6.26 (dd, *J* = 4.0 Hz, *J* = 2.8 Hz, 1H), 5.82 (d, *J* = 2.0 Hz, 1H), 3.98–3.90 (m, 2H), 3.87 (s, 3H), 3.88–3.83 (m, 1H), 3.62 (s, 3H), 3.47 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 169.3, 163.2, 147.1, 145.9, 130.5, 129.8, 129.6, 126.3, 124.9, 123.8, 114.1, 83.4, 56.2, 55.6, 52.6, 49.3, 41.2; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{22}N_2O_8SNa^+$ $[M+Na]^+$ 485.0989, found 485.0995.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(thiophen-2-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3n): Elution with hexane/EtOAc (9:1); yellow oil, 62% yield (105 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.81–7.76 (m, AA′BB′, 2H), 7.14 (dd, *J* = 5.1 Hz, *J* = 1.1 Hz, 1H), 7.00–6.89 (m, 4H),

6.16 (dd, *J* = 4.1 Hz, *J* = 2.8 Hz, 1H), 5.74 (d, *J* = 1.9 Hz, 1H), 3.92–3.87 (m, 2H), 3.86 (s, 3H), 3.81 (dt, *J* = 17.8 Hz, *J* = 2.8 Hz, 1H), 3.65 (s, 3H), 3.46 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 169.7, 163.1, 143.5, 130.6, 129.8, 127.3, 125.1, 124.2, 122.7, 119.4, 114.1, 83.5, 56.2, 55.6, 52.6, 49.8, 40.8; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{19}H_{21}NO_6SNa^+$ $[M+Na]^+$ 446.0702, found 446.0703.

Ethyl 1-(4-methoxyphenylsulfonyl)-2-methyl-4-phenyl-1,6-dihydropyridine-3-carboxylate (2o): Elution with hexane/EtOAc 7:3; yellowish oil; 51% yield (93 mg); all data were in agreement with those reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72–7.62 (m, AA′BB′, 2H), 7.20–7.09 (m, 3H), 6.81–6.74 (m, 4H), 5.44 (t, *J* = 4.8 Hz, 1H), 4.40 (d, *J* = 4.8 Hz, 2H), 3.82 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 2.50 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 166.8, 163.1, 143.6, 138.7, 137.4, 131.1, 129.2, 127.9, 127.3, 126.3, 124.6, 117.5, 114.0, 60.6, 55.4, 45.8, 20.4, 13.3.

Methyl 1-(4-methoxyphenylsulfonyl)-2,4-diphenyl-1,6-dihydropyridine-3-carboxylate (2p): Elution with hexane/EtOAc 9:1; yellow amorphous solid; 67% yield (124 mg); all data were in agreement with those reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64–7.53 (m, 4 H), 7.42–7.33 (m, 3H), 7.25–7.14 (m, 3H), 6.92–6.81 (m, 4H), 5.49 (t, *J* = 4.7 Hz, 1H), 4.66 (d, *J* = 4.7 Hz, 2H), 3.81 (s, 3H), 3.22 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.1, 163.2, 141.8, 137.6, 137.6, 135.7, 131.3, 130.2, 129.6, 129.6, 127.8, 127.8, 127.7, 127.6, 127.6, 125.7, 119.0, 114.2, 113.9, 55.6, 51.8, 46.6.

Dimethyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-2,3-dicarboxylate (3q): Elution with hexane/EtOAc (8:2); colorless oil, 44% yield (84 mg); **^{1}H NMR** (500 MHz, CD_3OD): δ 7.98–7.92 (m, AA′BB′, 2H), 7.36–7.23 (m, 5H), 7.12–7.07 (m, AA′BB′, 2H), 6.28 (t, *J* = 3.7 Hz, 1H), 4.04 (td, *J* = 3.7 Hz, *J* = 1.3 Hz, 2H), 3.92 (t, *J* = 1.3 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.52 (s, 3H), 3.46 (s, 3H), 3.33 – 3.30 (m, 1H); **^{13}C NMR** (125.7 MHz, CD_3OD): δ 171.2, 169.4, 164.9, 139.3, 132.2, 131.8, 131.3, 129.7, 129.0, 126.3, 122.3, 115.0, 90.6, 56.3, 55.8, 53.44, 53.38, 53.0, 46.1; **HR MS** (TOF-ESI$^+$): *m/*z calcd. for $C_{23}H_{25}NO_8SNa^+$ $[M+Na]^+$ 498.1193, found 498.1198.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridine-3-carboxylate (3r):

Silver tetrafluoroborate (296 mg, 1.52 mmol) was weighed into an oven-dried flask under argon atmosphere. Dry benzene (10 mL), (TFP)AuCl (353 mg, 0.76 mmol) and dry methanol (1.8 mL, 45.6 mmol) were added subsequently to form a white opalescent suspension. A solution of the propargylamino acrylate **1r** (5.1 g, 15.2 mmol) in dry benzene (10 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by TLC monitoring (ca 12 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to the dryness, and the residue was purified by chromatography on a column of silica gel (150 g), eluting with a hexane/EtOAc mixture (8:2–7:3); white crystalline solid, m. p. 91–92 °C, 37% (2.075 g); **^{1}H**

NMR (500 MHz, acetone-d_6): δ 7.80–7.77 (m, AA′BB′, 2H), 7.14–7.11 (m, AA′BB′, 2H), 6.41 (dd, J = 17.6 Hz, J = 10.9 Hz, 1H), 5.90 (t, J = 3.4 Hz, 1H), 5.63 (d, J = 1.9 Hz, 1H), 5.10 (d, J = 17.6, 1H), 5.00 (d, J = 10.9 Hz, 1H), 3.91 (s, 3H), 3.91–3.86 (m, 1H), 3.76–3.73 (m, 1H), 3.68–3.62 (m, 1H), 3.64 (s, 3H), 3.34 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 169.4, 163.3, 137.7, 131.1, 129.8, 129.5, 124.8, 114.1, 111.6, 83.8, 55.3, 55.2, 51.7, 46.0, 40.8; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{17}H_{21}NO_6SNa^+$ $[M+Na]^+$ 390.0982, found 390.0987.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(prop-1-en-1-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3s): Elution with hexane/EtOAc (98:2–9:1); white oil, 45% yield (69 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.81–7.76 (m, AA′BB′, 2H), 7.13–7.09 (m, AA′BB′, 2H), 6.09 (d, J = 15.7, 1H), 5.72 (t, J = 3.6 Hz, 1H), 5.62–5.54 (m, 2H), 3.91 (s, 3H), 3.87–3.81 (m, 1H), 3.70–3.68 (m, 1H), 3.65–3.59 (m, 1H), 3.64 (s, 3H), 3.33 (s, 3H), 1.71 (d, J = 6.7, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 169.6, 163.3, 132.3, 131.2, 129.8, 129.1, 123.4, 121.7, 114.1, 83.9, 55.3, 55.2, 51.8, 46.7, 40.8, 17.4; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{18}H_{23}NO_6SNa^+$ $[M+Na]^+$ 404.1138, found 404.1140.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(oct-1-en-1-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3t): Elution with hexane/EtOAc (9:1); light yellow oil, 52% yield (94 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.81–7.76 (m, AA′BB′, 2H), 7.14–7.09 (m, AA′BB′, 2H), 6.08 (d, J = 15.4 Hz, 1H), 5.73 (dd, J = 4.2 Hz, J = 2.9 Hz, 1H), 5.60 (d, overlap, J = 2.0 Hz, 1H), 5.58 (dt, overlap, J = 15.4 Hz, J = 6.9, 1H), 3.91 (s, 3H), 3.83 (dd, J = 17.8 Hz, J = 4.1 Hz, 1H), 3.72–3.69 (m, 1H), 3.66–3.60 (m, overlap, 1H), 3.63 (s, 3H), 3.34 (s, 3H), 2.12–2.04 (m, 2H), 1.41–1.25 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.3, 164.0, 131.9, 131.8, 130.5, 129.9, 129.7, 122.6, 114.8, 84.6, 56.0, 55.9, 52.4, 47.5, 41.5, 33.2, 32.3, 29.9, 29.3, 23.1, 14.2; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{23}H_{33}NO_6SNa^+$ $[M+Na]^+$ 474.1921, found 474.1924.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(2-phenylethen-1-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3u): Elution with hexane/EtOAc (8:2–7:3); colorless oil, 95% yield (169 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.83–7.77 (m, AA′BB′, 2H), 7.50–7.45 (m, 2H), 7.35–7.29 (m, 2H), 7.25–7.20 (m, 1H), 7.15–7.11 (m, AA′BB′, 2H), 6.94 (d, J = 16.4 Hz, 1H), 6.55 (d, J = 16.4 Hz, 1H), 6.04 (t, J = 3.6 Hz, 1H), 5.69 (d, J = 1.9 Hz, 1H), 3.96 (dd, overlap, J = 18.5 Hz, J = 4.2 Hz, 1H), 3.95–3.93 (m, 1H), 3.92 (s, 3H), 3.72 (dt, J = 18.5 Hz, J = 2.7 Hz, 1H), 3.66 (s, 3H), 3.37 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.3, 164.1, 138.1, 131.9, 130.61, 130.59, 130.3, 129.4, 128.3, 127.7, 127.2, 125.8, 115.0, 84.7, 56.11, 56.05, 52.7, 47.3, 42.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{23}H_{25}NO_6SNa^+$ $[M+Na]^+$ 466.1295, found 466.1303.

Methyl 4-cyclopropyl-2-methoxy-1-(4-methoxyphenylsulfonyl)- 1,2,3,6-tetrahydropyridine-3-carboxylate (3v): Elution with hexane/EtOAc (8:2); pale white oil, 36% yield (55 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.81–7.75 (m, AA′BB′, 2H), 7.13–7.08 (m, AA′BB′, 2H), 5.57 (d, J = 1.8 Hz, 1H), 5.51–5.47 (m, 1H), 3.91 (s, 3H), 3.71–3.66 (m, 1H), 3.68 (s, 3H), 3.52–3.44 (m, 1H), 3.37–3.35 (m,

1H), 3.33 (s, 3H), 1.43–1.40 (m, 1H), 0.67–0.56 (m, 2H), 0.54–0.22 (m, 1H), 0.30–0.22 (m, 1H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.8, 164.0, 133.0, 132.0, 130.6, 117.6, 114.9, 84.5, 56.1, 55.8, 52.5, 50.7, 41.4, 17.0, 5.5, 5.4; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{18}H_{23}NO_6SNa^+$ $[M+Na]^+$ 404.1138, found 404.1142.

Methyl 4-iodo-1-(4-methoxyphenylsulfonyl)-1,6-dihydropyridine-3-carboxylate (2w): Not fully characterized due to the instability. Only the NMR of crude mixture was measured. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.79–7.75 (m, AA′ BB′, 2H), 7.07–7.03 (m, AA′ BB′, 2H), 6.11 (t, J = 4.7 Hz, 1H), 4.01 (d, J = 4.7 Hz, 2H), 3.91 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.2, 164.2, 164.0, 140.7, 137.5, 129.8, 128.3, 126.9, 114.9, 109.7, 83.6, 55.8, 51.7, 46.5.

Methyl 4-(cyclopropylethynyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (3x): Elution with hexane/EtOAc (9:1–85:15); light yellow oil, 16% yield (23 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.80–7.76 (m, AA′ BB′, 2H), 7.14–7.09 (m, AA′ BB′, 2H), 6.02 (dd, J = 4.4 Hz, J = 2.7 Hz, 1H), 5.56 (d, J = 1.7 Hz, 1H), 3.92 (s, 3H), 3.84–3.77 (m, 1H), 3.68 (s, 3H), 3.58 (dt, J = 18.3 Hz, J = 2.7 Hz, 1H), 3.41–3.37 (m, 1H), 3.34 (s, 3H), 1.37–1.30 (m, 1H), 0.84–0.79 (m, 2H), 0.63–0.58 (m, 2H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 169.8, 164.2, 131.8, 130.6, 129.7, 115.0, 93.7, 84.1, 75.8, 56.1, 56.0, 52.6, 51.5, 41.5, 31.7, 8.81, 8.80, 0.4; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{23}NO_6SNa^+$ $[M+Na]^+$ 428.1138, found 428.1146.

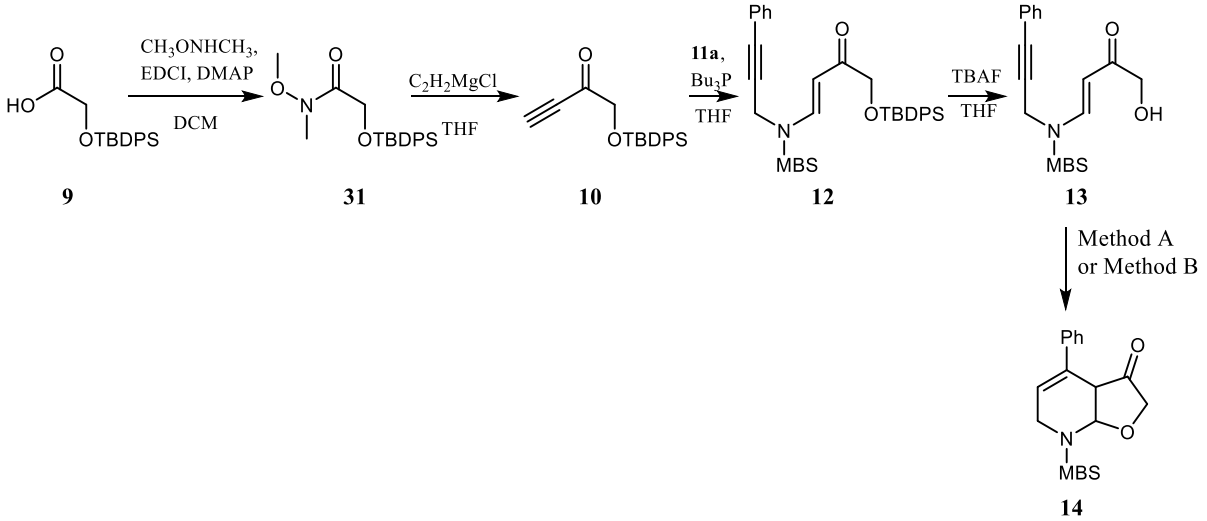
Methyl 2-ethoxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (7a):

Silver tetrafluoroborate (7.8 mg, 0.04 mmol) was weighed into an oven-dried flask under argon atmosphere. Dry benzene (2 mL), (TFP)AuCl (9.3 mg, 0.02 mmol) and ethanol (70 μL, 1.2 mmol) were added subsequently to form a white opalescent suspension. A solution of the propargylamino acrylate **1a** (154 mg, 0.4 mmol) in dry benzene (3 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by TLC monitoring (12 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to the dryness, and the residue was purified by chromatography on a column of silica gel (60 g), eluting with a hexane/EtOAc mixture (9:1–8:2); yellow amorphous solid, 92% yield (159 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.85–7.78 (m, AA′ BB′, 2H), 7.42–7.24 (m, 5H), 7.17–7.11 (m, AA′ BB′, 2H), 6.25 (dd, J = 4.1 Hz, J = 2.8 Hz, 1H), 5.82 (d, J = 1.9 Hz, 1H), 4.04–4.02 (m, 1H), 3.97 (dd, J = 17.6 Hz, J = 4.1 Hz, 1H), 3.92 (s, 3H), 3.76 (dt, J = 17.6 Hz, J = 2.8 Hz, 1H), 3.69–3.63 (m, 2H), 3.60 (s, 3H), 1.11 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 169.7, 163.3, 139.9, 131.2, 130.5, 129.9, 128.5, 127.5, 125.4, 121.3, 114.2, 82.6, 63.5, 55.3, 51.8, 49.0, 41.4, 14.4; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{25}NO_6SNa^+$ $[M+Na]^+$ 454.1295, found 454.1303.

Methyl 2-hydroxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (8a):

Silver tetrafluoroborate (7.8 mg, 0.04 mmol) was weighed into an oven-dried flask under argon atmosphere. Dry benzene or THF (2 ml), (TFP)AuCl (9.3 mg, 0.02 mmol) and distilled water (22 µl, 1.2 mmol) were added subsequently to form a white opalescent suspension. A solution of the propargylamino acrylate **1a** (154 mg, 0.4 mmol) in dry benzene or THF (3 ml) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material as shown by TLC monitoring (12 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad washed with ethyl acetate. The solvent was evaporated to the dryness, and the residue was purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (9:1–8:2); white amorphous solid, 7% yield (11 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.88–7.84 (m, AA′ BB′, 2H), 7.42–7.23 (m, 5H), 7.13–7.09 (m, AA′ BB′, 2H), 6.33–6.31 (m, 1H), 6.17–6.14 (m, 1H), 5.26 (d, J = 6.1 Hz, 1H), 4.08 (dd, J = 17.4 Hz, J = 4.2 Hz, 1H), 3.94–3.92 (m, 1H), 3.91 (s, 3H), 3.71 (dt, J = 17.4 Hz, J = 2.6 Hz, 1H), 3.62 (s, 3H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.4, 164.0, 140.8, 131.6, 130.94, 130.86, 129.2, 128.2, 126.2, 122.5, 114.8, 77.5, 56.1, 52.7, 52.5, 42.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{21}NO_6SNa^+$ $[M+Na]^+$ 426.0982, found 426.0982.

Procedure of synthesis of ortho-fused cycles 14, 18 and 22



Scheme 3. Overview of synthesis of **14**

2-((*Tert*-butyldiphenylsilyl)oxy)acetic acid (9): Glycolic acid (2.5 g, 32.85 mmol) was dissolved in pyridine (40 mL), and the solution was cooled down to 0 °C. *tert*-Butyldiphenylchlorosilane (11.2 g, 41 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 12 hours. Pyridine was evaporated, and the crude mixture was partitioned between water (100 mL) and

EtOAc (3 × 100 mL). The organic layer was washed with a 5% solution of HCl (100 mL) and brine (100 mL), dried over Na_2SO_4 and evaporated to dryness. White oily compound; 95% yield (9.8 g). All spectral data were in agreement with those reported in the literature.[5] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69–7.64 (m, 4H), 7.51–7.45 (m, 2H), 7.45–7.39 (m, 4H), 4.25 (s, 2H), 1.12 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 173.2, 135.4, 131.7, 130.3, 128.1, 61.9, 26.7, 19.1.

2-((*Tert*-butyldiphenylsilyl)oxy)-*N*-methoxy-*N*-methylacetamide (31): *N*-, *O*-dimethylhydroxylamine hydrochloride (2.56 g, 26.24 mmol) was added to a solution of acid **9** (5.5 g, 17.49 mmol) in dry DCM (20 mL) in an oven-dried flask under argon atmosphere. EDCI (5.03 g, 26.24 mmol) and DMAP (3.21 g, 26.24 mmol) were subsequently added to the solution. The reaction mixture was stirred at room temperature for 5 hours, then quenched with water (30 mL) and extracted with DCM (2 × 20 mL). The organic layers were washed with 5% HCl (20 mL) and brine (20 mL), and dried over Na_2SO_4. Inorganic residues were filtered off, and the solvent was evaporated to dryness. The crude product was purified by chromatography on a column of silica gel (100 g), eluting with a hexane/EtOAc mixture (9:1 – 85:15) to obtain amide **31**; white solid, m. p. 56–57 °C, 64% yield (4 g). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.77–7.71 (m, 4H), 7.47–7.40 (m, 6H), 4.44 (s, 2H), 3.45 (s, 3H), 3.15 (s, 3H), 1.12 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 171.8, 135.7, 133.2, 129.7, 127.7, 62.0, 61.2, 32.4, 26.7, 19.3; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{27}NO_3SiNa^+$ $[M+Na]^+$ 380.1652, found 380.1664.

1-((*Tert*-butyldiphenylsilyl)oxy)but-3-yn-2-one (10): Amide **31** (1.5 g, 4.195 mmol) was dissolved in dry THF (10 mL) in an oven-dried flask under argon atmosphere. The solution was cooled down to 0 °C, ethynyl magnesium chloride (28.5 mL, 0.5M solution in THF) was added dropwise, and the reaction mixture was stirred until TLC analysis indicated that the reaction was complete (2 hours). The reaction mixture was then quenched with a 1M solution of $NaHSO_4$ (15 mL) and extracted with EtOAc (2 × 20 mL). The combined organic layers were dried over Na_2SO_4, inorganic residues were filtered off, and the solution was evaporated to dryness. The crude product was purified by chromatography on a column of silica gel (80 g), eluting with a hexane/EtOAc mixture (9:1) to obtain ynone **10**; pale yellow oil, 95% yield (1.29 g); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71–7.69 (m, 4H), 7.47–7.41 (m, 6H), 4.37 (s, 2H), 3.28 (s, 1H), 1.13 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 185.3, 135.5, 132.5, 130.0, 127.9, 81.2, 79.6, 70.5, 26.6, 19.3; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{22}O_2SiNa^+$ $[M+Na]^+$ 345.1281, found 345.1290.

***N*-(3-phenylprop-2-yn-1-yl)-4-methoxybenzenesulfonamide (11a)**: $(PPh_3)_2PdCl_2$ (312 mg, 0.444 mmol), CuI (169 mg, 0.888 mmol) and iodobenzene (1.043 mL, 9.32 mmol) were added to a solution of sulfonamide **4** (2 g, 8.88 mmol) in dry THF (20 mL) in an oven-dried flask under argon atmosphere. TEA (12.4 mL, 88.8 mmol) was then added to the solution portionwise at room temperature. The reaction mixture was stirred for 1 hour, then diluted with EtOAc (20 mL) and washed with a

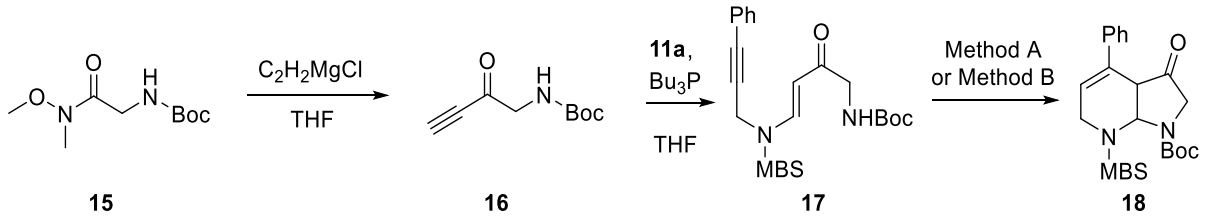
saturated solution of NH_4Cl (20 mL). The water phase was extracted with EtOAc (2 × 20 mL), the combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. Inorganic residues were filtered off, and the solvent evaporated to dryness. The crude product was purified by chromatography on a column of silica gel (80 g), eluting with a hexane/EtOAc mixture (7:3 – 6:4) to obtain sulfonamide **11a**; yellowish amorphous solid, 84% yield (2.248 g); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91–7.84 (m, AA′BB′, 2H), 7.34–7.22 (m, 3H), 7.20–7.14 (m, 2H), 6.98–6.91 (m, AA′BB′, 2H), 4.75 (t, *J* = 6.2 Hz, 1H), 4.08 (d, *J* = 6.2 Hz, 2H), 3.78 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 163.1, 131.6, 131.3, 129.6, 128.5, 128.1, 122.1, 114.2, 84.7, 83.3, 55.5, 33.7; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{16}H_{16}NO_3S^+$ $[M+H]^+$ 302.0846, found 302.0857.

***(E)*-1-((*tert*-butyldiphenylsilyl)oxy)-4-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]but-3-en-2-one (12)**: Sulfonamide **11a** (1.028 g, 3.41 mmol) was added to a solution of ynone **10** (1 g, 3.1 mmol) in dry THF (15 mL) in an oven-dried flask under argon atmosphere. Tributylphosphine (0.38 mL, 1.55 mmol) was then added to the solution portionwise, and the mixture was stirred at room temperature for 15 min. When complete conversion was confirmed by TLC analysis, the reaction mixture was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (9:1 – 85:15) to obtain ketone **12**; white solid, m. p. 91–92 °C, 56% yield (1.082 g); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 13.9 Hz, 1H), 7.88–7.82 (m, AA′BB′, 2H), 7.66–7.60 (m, 4H), 7.44–7.38 (m, 2H), 7.35–7.18 (m, 9H), 7.10–7.04 (m, 2H), 6.98–6.91 (m, AA′BB′, 2H), 6.36 (d, *J* = 13.9 Hz, 1H), 4.60 (s, 2H), 4.24 (s, 2H), 3.78 (s, 3H), 1.07 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 197.9, 163.8, 141.0, 135.5, 132.6, 131.6, 129.94, 129.89, 129.6, 128.6, 128.1, 127.8, 121.7, 114.6, 103.1, 85.6, 80.3, 69.2, 55.6, 36.3, 26.7, 19.2; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{36}H_{37}NO_5SiNa^+$ $[M+Na]^+$ 646.2054, found 646.2053.

***(E)*-1-hydroxy-4-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]but-3-en-2-one (13)**: TBAF (2 mL, 1M solution) was added dropwise to a solution of **12** (812 mg, 1.3 mmol) in THF (10 mL). The reaction mixture was stirred for 5 min, then quenched with H_2O (10 mL) and extracted with EtOAc (2 × 10 mL). The organic phase was washed with brine (10 mL), dried over Na_2SO_4, the solution was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (7:3) to obtain hydroxyketone **13**. Yellowish solid, m. p. 104.5–105.5 °C, 60% yield (300 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 14.0 Hz, 1H), 7.89–7.75 (m, AA′BB′, 2H), 7.36–7.20 (m, 3H), 7.15–7.06 (m, 2H), 7.01–6.92 (m, AA′BB′, 2H), 5.71 (d, *J* = 14.0 Hz, 1H), 4.58 (s, 2H), 4.37 (s, 2H), 3.77 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 196.5, 164.0, 140.7, 131.6, 129.9, 129.1, 128.9, 128.2, 121.4, 114.7, 103.2, 86.0, 79.9, 67.0, 55.6, 36.2; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{20}H_{20}NO_5S^+$ $[M+H]^+$ 386.1057, found 386.1066.

7-(4-Methoxyphenylsulfonyl)-4-phenyl-2,3,3a,6,7,7a-hexahydrofuro[2,3-*b*]pyridin-3-one (14): Method A: Silver tetrafluoroborate (4.6 mg, 0.023 mmol) was weighed into an oven-dried flask under

argon atmosphere. Dry benzene (1 mL), (TFP)AuCl (5.4 mg, 0.012 mmol) and methanol (28 µL, 0.7 mmol) were added subsequently to form a white opalescent suspension. A solution of the enynone **13** (90 mg, 0.4 mmol) in dry benzene (2 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by TLC monitoring (1.5 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to the dryness, and the residue was purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (7:3); white amorphous solid, 62% yield (56 mg). Method B: Silver tetrafluoroborate (4.6 mg, 0.023 mmol) was weighed into an oven-dried flask under argon atmosphere. Dry benzene (1 mL) and (TFP)AuCl (5.4 mg, 0.012 mmol) were added subsequently to form a white opalescent suspension. A solution of the enynone **13** (90 mg, 0.4 mmol) in dry benzene (2 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by TLC monitoring (1.5 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to the dryness, and the residue was purified by chromatography on a column of silica gel (30 g), eluting with a hexane/EtOAc mixture (7:3); white amorphous solid, 54% yield (49 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97–7.89 (m, AA′ BB′, 2H), 7.47–7.41 (m, 2H), 7.37–7.25 (m, 3H), 7.17–7.11 (m, AA′ BB′, 2H), 6.45 (d, *J* = 6.0 Hz, 1H), 6.33–6.26 (m, 1H), 4.24–4.17 (m, 1H), 4.07–4.03 (m, 1H), 4.00–3.98 (s, 1H), 3.97 (s, 1H), 3.92 (s, 3H), 3.63 (dt, *J* = 16.5 Hz, *J* = 2.6 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 208.4, 164.2, 138.9, 132.0, 131.5, 131.0, 128.9, 128.5, 127.4, 123.6, 115.0, 85.8, 70.6, 56.1, 48.0, 40.7; **HR-MS** (TOF-ESI$^+$): *m/*z calcd. for $C_{20}H_{20}NO_5S^+$ $[M+H]^+$ 385.0984, found 386.1060.



Scheme 4. Overview of synthesis of **18**

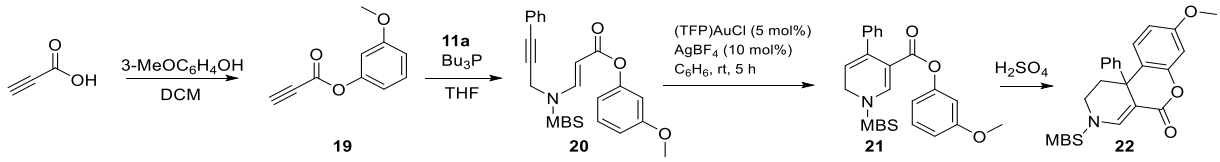
***tert*-butyl-(2-oxobut-3-yn-1-yl)carbamate (16)** was prepared according to the published procedure[6]: Amide **15** (1 g, 4.58 mmol) was dissolved in dry THF (10 mL) in an oven-dried flask under argon atmosphere. The solution was cooled down to −78 °C, ethynyl magnesium chloride (46 mL, 0.5M solution in THF) was added dropwise, and the reaction mixture was stirred at −78 °C for 1 hour and then at room temperature over night. The reaction mixture was then quenched with a 1M solution of $NaHSO_4$ (15 mL) and extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed with saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, inorganic

residues were filtered off, and the solution was evaporated to dryness. The crude product was purified by chromatography on a column of silica gel (80 g), eluting with a hexane/EtOAc mixture (9:1) to obtain carbamate **16**. White oil, 63% yield (530 mg); All spectral data were in agreement with those reported in the literature:[6] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.16 (bs, 1H), 4.16 (d, *J* = 5.5 Hz, 2H), 3.36 (s, 1H), 1.45 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 128.8, 155.4, 81.4, 80.3, 79.4, 52.2, 28.2

***tert*-butyl (*E*)-4-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]-2-oxobut-3-en-1-yl)carbamate (17):** Sulfonamide **11a** (905 mg, 3 mmol) was added to a solution of carbamate **16** (500 mg, 2.73 mmol) in dry THF (10 mL) in an oven-dried flask under argon atmosphere. Tributylphosphine (0.34 mL, 1.365 mmol) was then added to the solution portionwise, and the mixture was stirred at room temperature for 15 min. When complete conversion of carbamate was confirmed by TLC analysis, the reaction mixture was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (20 g), eluting with a hexane/EtOAc mixture (9:1) to obtain carbamate **17**; yellowish oil, 21% yield (279 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 13.9 Hz, 1H), 7.92–7.78 (m, AA′ BB′, 2H), 7.35–7.19 (m, 3H), 7.13–7.07 (m, 2H), 6.98–6.92 (m, AA′ BB′, 2H), 5.72 (d, *J* = 13.9 Hz, 1H), 5.39 (s, 1H), 4.57 (s, 2H), 4.15 (d, *J* = 4.7 Hz, 2H), 3.77 (s, 3H), 1.45 (s, 9H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 192.7, 163.9, 155.7, 140.6, 131.6, 129.9, 129.2, 128.8, 128.2, 121.5, 114.6, 104.8, 85.9, 79.92, 79.69, 55.62, 49.25, 36.21, 28.31; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{25}H_{28}N_2O_6SNa^+$ $[M+Na]^+$ 507.1560, found 507.1564.

***tert*-Butyl 7-(4-methoxyphenylsulfonyl)-3-oxo-4-phenyl-2,3,3a,6,7,7a-hexahydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate 18:** Method A: Silver tetrafluoroborate (3.2 mg, 0.017 mmol) was weighed into an oven-dried flask under an argon atmosphere. Dry benzene (2 mL), (TFP)AuCl (4 mg, 0.0083 mmol) and methanol (20 μL, 0.5 mmol) were added subsequently to form a white opalescent suspension. A solution of carbamate **17** (80 mg, 0.165 mmol) in dry benzene (2 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by NMR analysis of the crude reaction mixture (5 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to dryness, and the residue was purified by chromatography on a column of C18-silica gel (3 g), eluting with a water/MeOH mixture (7:3); white amorphous solid, 53% yield (42 mg). Method B: Silver tetrafluoroborate (3.2 mg, 0.017 mmol) was weighed into an oven-dried flask under an argon atmosphere. Dry benzene (2 mL) and (TFP)AuCl (4 mg, 0.0083 mmol) were added subsequently to form a white opalescent suspension. A solution of carbamate **17** (80 mg, 0.165 mmol) in dry benzene (2 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by NMR analysis of the crude reaction mixture (12 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to dryness, and the residue was purified by chromatography on a column of C18-silica gel (3 g), eluting with a water/MeOH

mixture (7:3); white amorphous solid, 48% yield (38 mg).**^{1}H NMR** (500 MHz, CD_3OD) δ 7.79–7.73 (m, AA′ BB′, 2H), 7.30–7.21 (m, 3H), 7.19–7.06 (m, 2H), 6.95–6.89 (m, 1H), 6.38–6.33 (m, 1H), 6.09–6.05 (m, 1H), 4.18–4.12 (m, 1H), 4.07 (d, *J* = 7.6 Hz, 1H), 4.00–3.91 (m, 1H), 3. 3.78 (ddd, *J* = 18.3 Hz, *J* = 3.3 Hz, *J* = 1.4 Hz, 1H), 3.73 (s, 3H), 3.69 (dd, *J* = 18.5 Hz, *J* = 0.8 Hz, 1H), 1.57 (s, 9H); **^{13}C NMR** (125.7 MHz, CD_3OD) δ 206.5,164.6, 155.8, 139.3, 134.9, 130.7, 129.9, 129.2, 129.1, 128.8, 127.2, 115.5, 82.8, 70.5, 56.1, 53.4, 50.4, 28.7, 28.3. **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{25}H_{28}N_2O_6SNa^+$ $[M+Na]^+$ 507.1560, found 507.1551.



Scheme 5. Overview of synthesis of **22**

3-methoxyphenyl propiolate (19) was prepared according to a literature procedure. The solution of 3-methoxyphenol (3.3 mL, 30.5 mmol) and propionic acid (2.354 g, 33.6. mmol) in DCM (30 mL) was cooled down to 0 °C, then solution of DCC (6.293 g, 30.5 mmol) and DMAP (373 mg, 3.05 mmol) dissolved in DCM was added dropwise, and the mixture was stirred for 4 hours. When complete conversion of starting materials was confirmed by TLC analysis, the precipitate was filtered off, and the solution was washed with brine (2 × 30 mL). The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (95:5) to obtain colourless oil; 51% yield (2.739 g). All spectral data were in agreement with those reported in the literature.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.2 Hz, 1H), 6.83 (ddd, *J* = 8.4, 2.4, 0.9 Hz, 1H), 6.76 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 1H), 6.71 (t, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 3.08 (s, 1H); **^{13}C NMR** (125.7 MHz, cdcl$_3$) δ 160.6, 150.8, 150.7, 130.0, 113.4, 112.4, 107.2, 76.7, 74.2, 55.5.

3-methoxyphenyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]acrylate (20): Sulfonamide **11a** (1000 mg, 3.32 mmol) was added to a solution of propiolate **19** (600 mg, 3.4 mmol) in dry THF (5 mL) in an oven-dried flask under argon atmosphere. Tributylphosphine (0.41 mL, 1.66 mmol) was then added to the solution portionwise, and the mixture was stirred at room temperature for 1 h. When complete conversion of propiolate was confirmed by TLC analysis, the reaction mixture was evaporated to dryness, and the residue purified by chromatography on a column of silica gel (50 g), eluting with a hexane/EtOAc mixture (7:3) to obtain acrylate **20**; white solid, m. p. 92–93 °C; 68% yield (1081 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 13.9 Hz, 1H), 7.91–7.84 (m, AA′ BB′, 2H), 7.35–7.25 (m, 5H), 7.18–7.13 (m, 2H), 7.01–6.95 (m, AA′ BB′, 2H), 6.79 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 6.75 (ddd, *J* = 8.1, 2.3, 0.9 Hz, 1H), 6.71 (t, *J* = 2.3

Hz, 1H), 5.55 (d, *J* = 13.9 Hz, 1H), 4.62 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 165.3, 163.9, 160.4, 151.7, 142.3, 131.7, 129.9, 129.7, 129.4, 128.8, 128.2, 121.6, 114.6, 113.9, 111.6, 107.7, 98.8, 85.8, 80.1, 55.6, 55.4, 36.3; **IR** (ATR): ν 3587, 3566, 2378, 2316, 1738, 1731, 1714, 1698, 1680, 1613, 1574, 1508, 1496, 1455, 1436, 1417, 1363, 1338, 1306, 1283, 1262, 1165, 1185, 1138, 1091, 1056, 1039, 1024, 970, 958, 936, 906, 874, 856, 839, 827, 818, 809, 768, 706, 691, 680, 673, 647, 628, 614 cm^{-1}; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{26}H_{24}NO_6S^+$ $[M+H]^+$ 478.1319, found 478.1316.

3-methoxyphenyl 1-(4-methoxyphenylsulfonyl)-4-phenyl-1,6-dihydropyridine-3-carboxylate (21): Silver tetrafluoroborate (7.8 mg, 0.04 mmol) was weighed into an oven-dried flask under an argon atmosphere. Dry benzene (2 mL) and (TFP)AuCl (9.3 mg, 0.02 mmol) were added subsequently to form a white opalescent suspension. A solution of the enyne **20** (191 mg, 0.4 mmol) in dry benzene (3 mL) was cannulated into the reaction flask, and the mixture was stirred at room temperature until complete consumption of the starting material, as shown by NMR analysis of the crude reaction mixture (1 h). After the full conversion, the reaction mixture was filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to dryness, and the compound was characterized without further purification; white amorphous solid, 97% yield (185 mg). **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.08 (s, 1H), 8.02–7.88 (m, AA′ BB′, 2H), 7.36–7.19 (m, 9H), 6.75 (ddd, *J* = 8.4 Hz, *J* = 2.3 Hz, *J* = 0.9 Hz, 1H), 6.51 (ddd, *J* = 8.1 Hz, *J* = 2.3 Hz, *J* = 0.9 Hz, 1H), 6.41 (t, *J* = 2.3 Hz, 1H), 5.60 (t, *J* = 4.7 Hz, 1H), 4.28 (d, *J* = 4.7 Hz, 2H), 3.96 (s, 3H), 3.74 (s, 3H). **^{13}C NMR** (125.7 MHz, Acetone-d_6) δ 165.2, 163.9, 161.3, 152.6, 140.5, 139.8, 136.7, 130.9, 130.3, 129.1, 128.8, 128.1, 127.7, 116.9, 115.9, 114.6, 112.2, 112.0, 108.3, 56.4, 55.7, 44.8. **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{26}H_{23}NO_6SNa^+$ $[M+Na]^+$ 500.1138, found 500.1139.

8-methoxy-3-(4-methoxyphenylsulfonyl)-10b-phenyl-1,2,3,10b-5H-chromeno[3,4-*c*]pyridin-5-one (22): Dihydropyridine **21** (50 mg, 0.105 mmol) was treated with conc. H_2SO_4 (500 μl) at −10 °C for 15 min. After the full conversion, iced water was added to the solution, and the mixture was subsequently extracted with ethyl acetate. The organic phase was dried over Na_2SO_4, inorganic residues were filtered off, and the solution was evaporated to dryness. The crude product was purified by chromatography on a column of silica gel (20 g), eluting with a hexane/EtOAc mixture (7:3) to obtain chromenopyridine **22**; white oil, 66% yield (33 mg). **^{1}H NMR** (600 MHz, Acetone-d_6) δ 8.24 (s, 1H), 7.89–7.83 (m, AA′ BB′, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.21–7.08 (m, 6H), 7.05 (d, *J* = 1.0 Hz, 1H), 6.80 (dd, *J* = 8.6 Hz, *J* =2.6 Hz, 1H), 6.51 (d, *J* = 2.6 Hz, 1H), 3.91 (s, 3H), 3.89–3.85 (m, 1H), 3.76 (s, 3H), 2.82 (dt, *J* = 13.4 Hz, *J* = 2.9 Hz, 1H), 2.71 (td, *J* = 13.4 Hz, *J* = 2.9 Hz, 1H), 1.98 (td, *J* = 13.4 Hz, *J* = 4.2 Hz, 1H); **^{13}C NMR** (151 MHz, Acetone-d_6) δ 164.3, 163.2, 160.3, 151.3, 144.8, 137.82, 129.7, 128.6, 128.4, 127.1, 127.0, 126.5, 120.7, 115.1, 110.7, 105.7, 102.5, 55.6, 55.1, 40.9, 40.0, 32.9; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{26}H_{24}NO_6S^+$ $[M+H]^+$ 478.1319, found 478.1322.

Procedure for synthesis of piperidines 23

The appropriate tetrahydropyridine **3** (77 mg, 0.18 mmol) was dissolved in dry methanol or ethyl acetate (5 mL) in an oven-dried two-necked flask. Then 10% Pd/C (10 mg, 0.009 mmol) was added to the solution, and the atmosphere above the solution was evacuated and changed to H_2. The reaction mixture was stirred under a hydrogen-filled balloon overnight, then filtered through a pad of Celite®, and the pad was washed with ethyl acetate. The solvent was evaporated to dryness, and the crude product was purified by chromatography on a column of silica gel (25 g) to afford piperidine **23**.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-phenylpiperidine-3-carboxylate (23a): Elution with hexane-EtOAc (8:2); white oil; 93% yield (72 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.91–7.82 (m, AA′BB′, 2H), 7.31–7.11 (m, 7H), 5.47 (d, J = 2.2 Hz, 1H), 3.93 (s, 3H), 3.66–3.59 (m, 1H), 3.47 (s, 3H), 3.41 (s, 3H), 3.33 (dt, J = 13.2 Hz, J = 4.0 Hz, 1H), 3.30–3.25 (m, 1H), 3.18 (td, J = 12.7 Hz, J = 3.1 Hz, 1H), 2.56 (dtd, J = 25.8. Hz, J = 12.9 Hz, J = 5.0 Hz, 1H), 1.78–1.70 (m, 1H); **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 169.5, 163.1, 142.5, 132.0, 129.7, 128.0, 127.5, 126.3, 113.5, 84.8, 55.2, 55.0, 50.8, 49.7, 40.3, 36.1, 24.3; **HR-MS** (TOF-ESI$^+$): *m/*z calcd. for $C_{21}H_{25}NO_6SNa^+$ $[M+Na]^+$ 422.1295, found 422.1299.

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(4-methylphenyl)piperidine-3-carboxylate (23b): Elution with hexane-EtOAc (8:2); white oil; 58% yield (45 mg); **^{1}H NMR** (500 MHz,): δ 7.86–7.82 (m, AA′BB′, 2H), 7.17–7.06 (m, 6H), 5.45 (d, J = 2.1 Hz, 1H), 3.93 (s, 3H), 3.65–3.57 (m, 1H), 3.48 (s, 3H), 3.39 (s, 3H), 3.28 (dt, J = 13.0 Hz, J = 4.1 Hz, 1H), 3.25–3.23 (m, 1H), 3.16 (td, J = 12.7 Hz, J = 3.1 Hz, 1H), 2.55 (dtd, J = 25.8. Hz, J = 12.9 Hz, J = 5.0 Hz, 1H), 2.27 (s, 3H), 1.73–1.66 (m, 1H); **^{13}C NMR** (125.7 MHz,): δ 170.4, 163.9, 140.2, 136.4, 132.8, 130.6, 129.5, 128.2, 114.9, 85.7, 56.1, 55.9, 51.6, 50.6, 41.1, 36.5, 25.2, 20.9; **HR MS** (TOF-ESI$^+$): *m/*z calcd. for $C_{22}H_{27}NO_6SNa^+$ $[M+Na]^+$ 456.1451, found 456.1460.

Methyl 4-biphenyl-2-methoxy-1-(4-methoxyphenylsulfonyl)piperidine-3-carboxylate (23f): Elution with hexane-EtOAc (9:1–85:15); white oil; 44% yield (34 mg); **^{1}H NMR** (500 MHz, acetone-d_6): δ 7.89–7.83 (m, AA′BB′, 2H), 7.67–7.62 (m, 2H), 7.61–7.55 (m, AA′BB′, 2H), 7.49–7.41 (m, 2H), 7.39–7.31 (m, 3H), 7.17–7.12 (m, AA′BB′, 2H), 5.51 (d, J = 2.2 Hz, 1H), 3.93 (s, 3H), 3.68–3.62 (m, 1H), 3.50 (s, 3H), 3.42 (s, 3H), 3.38 (dt, J = 13.0 Hz, J = 4.0 Hz, 1H), 3.35 – 3.32 (m, 1H), 3.20 (td, J = 12.7 Hz, J = 3.0 Hz, 1H), 2.60 (dtd, J = 25.8. Hz, J = 13.0 Hz, J = 5.0 Hz, 1H), 1.83–1.75 (m, 1H).δ **^{13}C NMR** (125.7 MHz, acetone-d_6): δ 170.4, 164.0, 142.6, 141.5, 139.8, 132.8, 130.6, 129.6, 128.9, 129.0, 127.5, 127.3, 114.9, 85.7, 56.1, 55.9, 51.7, 50.5, 41.1, 36.6, 25.2; **HR MS** (TOF-ESI$^+$): *m/*z calcd. for $C_{27}H_{29}NO_6SNa^+$ $[M+Na]^+$ 518.1608, found 518.1613.

Methyl 4-(4-fluorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)piperidine-3-carboxylate (23g): Elution with hexane-EtOAc (9:1–85:15); white oil; 34% yield (26 mg); **^{1}H NMR** (500 MHz,): δ ^{1}H NMR (500 MHz, acetone) δ 7.89–7.80 (m, AA′BB′, 2H), 7.32–7.27 (m, 2H), 7.19–7.10 (m, 2H), 7.10–6.98 (m, AA′BB′, 2H), 5.47 (d, J = 2.2 Hz, 1H), 3.93 (s, 3H), 3.66–3.59 (m, 1H), 3.49 (s, 3H),

3.40 (s, 3H), 3.33 (dt, J = 13.2 Hz, J = 4.1 Hz, 1H), 3.29–3.25 (m, 1H), 3.16 (td, J = 12.7 Hz, J = 3.0 Hz, 1H), 2.52 (dtd, J = 25.8. Hz, J = 12.9 Hz, J = 4.9 Hz, 1H), 1.78–1.69 (m, 1H). **^{13}C NMR** (125.7 MHz,): δ 170.3, 163.9, 162.2 (d, J = 242.7 Hz), 139.4, 132.7, 130.6, 130.2 (d, J = 7.7 Hz), 115.4 (d, J = 21.3 Hz), 114.9, 85.7, 56.1, 55.9, 51.7, 50.5, 41.0, 36.3, 25.3; **^{19}F NMR** (470 MHz, acetone-d_6): −119.2; **HR MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{21}H_{24}FNO_6SNa^+$ $[M+Na]^+$ 460.1200, found 460.1212.

Procedure of Diels-Alder cycloaddition for the synthesis of tetrahydroisoquinolines 25

Dimethyl acetylenedicarboxylate (246 µl, 2 mmol) was added in one portion to a solution of tetrahydropyridine **3r-3u** (0.5 mmol) in xylene (5 mL), and the reaction mixture was stirred under reflux (150 °C bath temperature) for 1 hour, while monitoring by TLC. When all the starting material consumed, the solvent was evaporated, and the crude product was purified by chromatography on a column of silica gel (60 g) to afford tetrahydroisoquinoline **25**.

Trimethyl 2-(4-methoxyphenylsulfonyl)-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (25r): Elution with hexane/EtOAc (7:3); yellowish solid, 62% yield (148 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.77–7.73 (m, AA′BB′, 2H), 7.04–6.99 (m, AA′BB′, 2H), 6.48 (t, J = 3.3 Hz, 1H), 4.18 (dd, J = 11.8 Hz, J = 3.3 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.17–3.05 (m, 3H), 2.88 (t, J = 11.8 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.4, 167.3, 165.6, 163.8, 135.1, 133.7, 132.0, 129.4, 128.7, 123.5, 119.2, 114.8, 108.4, 55.7, 52.5, 52.4, 51.6, 47.3, 33.7, 28.2; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{24}NO_9S^+$ $[M+H]^+$ 478.1167, found 478.1174.

Trimethyl 2-(4-methoxyphenylsulfonyl)-6-methyl-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (25s): Elution with hexane/EtOAc (8:2); yellow solid, 56% yield (138 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.82–7.75 (m, AA′BB′, 2H), 7.06–6.97 (m, AA′BB′, 2H), 6.30 (d, J = 3.6 Hz, 1H), 4.47 (dd, J = 11.8 Hz, J = 3.6 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.36–3.28 (m, 1H), 3.07–2.99 (m, 1H), 2.83 (t, J = 11.8 Hz, 1H), 1.14 (d, J = 7.1 Hz, 3H); **^{13}C NMR** (125.7. MHz, $CDCl_3$): δ 168.5, 166.4, 165.6, 163.8, 143.4, 135.4, 129.8, 129.4, 128.9, 127.5, 125.2, 123.0, 114.8, 108.1, 55.8, 52.3, 51.6, 48.8, 33.9, 33.3, 20.6; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{23}H_{26}NO_9S^+$ $[M+H]^+$ 492.1323, found 492.1327; *m/z* calcd. for $C_{23}H_{25}NO_9SNa^+$ $[M+Na]^+$ 514.1142, found 514.1146.

Trimethyl 6-hexyl-2-(4-methoxyphenylsulfonyl)-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (25t): Elution with hexane/EtOAc (8:2–7:3); yellowish oil, 52% yield (146 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.81–7.77 (m, AA′BB′, 2H), 7.04–6.99 (m, AA′BB′, 2H), 6.27 (dd, J = 3.6 Hz, J = 1.3 Hz, 1H), 4.50 (dd, J = 11.8 Hz, J = 3.6 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.41–3.35 (m, 1H), 3.03–2.95 (m, 1H), 2.82 (t, J = 11.8 Hz, 1H), 1.58–1.40 (m, 2H), 1.34–0.98 (m, 8H), 0.84 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 168.7, 166.1, 165.5, 163.7, 143.4, 135.1, 129.4, 128.9, 127.6, 124.2, 123.9, 114.7, 108.1, 60.4, 55.7, 52.4, 51.5, 49.0,

38.4, 33.9, 33.1, 31.5, 29.2, 25.1, 22.5, 14.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{28}H_{36}NO_9S^+$ $[M+H]^+$ 562.2106, found 562.2108.

Trimethyl 2-(4-methoxyphenylsulfonyl)-6-phenyl-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (25u): Elution with hexane/EtOAc (8:2–7:3); yellow amorphous solid, 71% yield (186 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.85–7.78 (m, AA′BB′, 2H), 7.28–7.19 (m, 3H), 7.07–7.00 (m, 4H), 6.37 (d, *J* = 3.7 Hz, 1H), 4.63 (dd, *J* = 11.6 Hz, *J* = 2.8 Hz, 1H)), 4.50 (dd, *J* = 6.8 Hz, *J* = 3.7 Hz, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.52 (s, 3H), 3.11–3.05 (m, 1H), 3.02 (t, *J* = 11.6 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.4, 166.8, 165.4, 163.9, 140.3, 139.1, 135.5, 129.9, 129.5, 128.82, 128.75, 128.2, 127.4, 123.7, 122.4, 114.8, 108.1, 55.8, 52.6, 52.1, 51.6, 49.0, 44.7, 34.0; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{28}H_{28}NO_9S^+$ $[M+H]^+$ 554.1479, found 554.1486; *m/z* calcd. for $C_{28}H_{27}NO_9SNa^+$ $[M+Na]^+$ 576.1299, found 576.1302.

Procedure for synthesis of isoquinoline derivatives 26r and 27r

Trimethyl 2-(4-methoxyphenylsulfonyl)-1,2-dihydroisoquinoline-4,7,8-tricarboxylate (26r): NBS (89 mg, 0.5 mmol) was added to the solution of tetrahydroisoquinoline **25r** (239 mg, 0.5 mmol) in carbon tetrachloride (8 mL), and the reaction mixture was stirred under reflux for 1 hour, then diluted with ethyl acetate (10 mL) and extracted with 5% solution of $NaHCO_3$ (2 × 10 mL). The organic phase was washed with brine (10 mL), dried with Na_2SO_4 and evaporated. The crude product was purified by chromatography on a column of silica gel (30 g) using a hexane/EtOAc mixture (75:25) to obtain dihydroisoquinoline **26r**. Yellowish amorphous solid; 75% yield (179 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.5 Hz, 1H), 8.17 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.82–7.79 (m, AA′BB′, 2H), 7.04–7.01 (m, AA′BB′, 2H), 4.58 (s, 2H), 3.95 (s, 3H), 3.88 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H). ; **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 168.4, 165.7, 165.1, 164.2, 139.6, 132.9, 132.4, 129.8, 129.72, 127.74, 126.5, 125.3, 124.2, 114.9, 108.1, 55.8, 52.9, 52.5, 51.7, 44.3; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{22}H_{22}NO_9S^+$ $[M+H]^+$ 476.1010, found 476.0986; calcd. for $C_{22}H_{21}NO_9SNa^+$ $[M+Na]^+$ 498.0829, found 498.0833.

Trimethyl isoquinoline-4,7,8-tricarboxylate (27r): Method A: NBS (120 mg, 0.678 mg) was added to a solution of dihydroisoquinoline **25r** (161 mg, 0,339 mmol) in carbon tetrachloride (6 mL), and the reaction mixture was stirred under reflux for 3 hours, then diluted with EtOAc (10 mL) and extracted with 5% solution of $NaHCO_3$ (2 × 10 mL). The organic phase was washed with brine (10 mL), dried with Na_2SO_4 and evaporated. The crude product was purified by chromatography on a column of silica gel (60 g) using a hexane/EtOAc mixture (7:3) to obtain isoquinoline **27r**. White amorphous solid, 68% yield (69 mg); Method B: NBS (108 mg, 0.6 mg) was added to a solution of tetrahydroisoquinoline **25r** (90 mg, 0,2 mmol) in carbon tetrachloride (5 mL), and the reaction mixture was stirred under reflux for 3 hours, then diluted with EtOAc (10 mL) and extracted with 5% solution of $NaHCO_3$ (2 × 10 mL). The

organic phase was washed with brine (10 mL), dried with Na_2SO_4 and evaporated. The crude product was purified by chromatography on a column of silica gel (300 g) using a hexane/EtOAc mixture (9:1–8:2) to obtain isoquinoline **27r**. White amorphous solid, 51% yield (29 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.43 (d, *J* = 0.9 Hz, 1H), 9.30 (s, 1H), 9.12 (dd, *J* = 9.1 Hz, *J* = 0.9 Hz, 1H), 8.34 (d, *J* = 9.1 Hz, 1H), 4.12 (s, 3H), 4.05 (s, 3H), 4.00 (s, 3H).; **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 167.9, 166.1, 165.1, 155.2, 148.6, 135.54, 135.46, 131.1, 126.8, 126.4, 124.5, 120.2, 53.3, 53.0, 52.6; **HR-MS** (TOF-ESI$^+$): *m/z* calcd. for $C_{15}H_{14}NO_6^+$ $[M+H]^+$ 304.0826, found 304.0824.

NOESY experiments on 3q, 14 and 23a

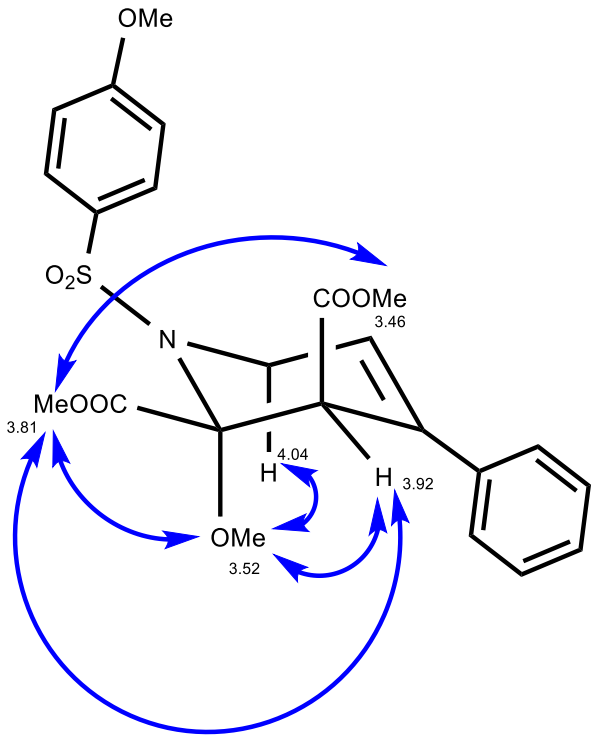
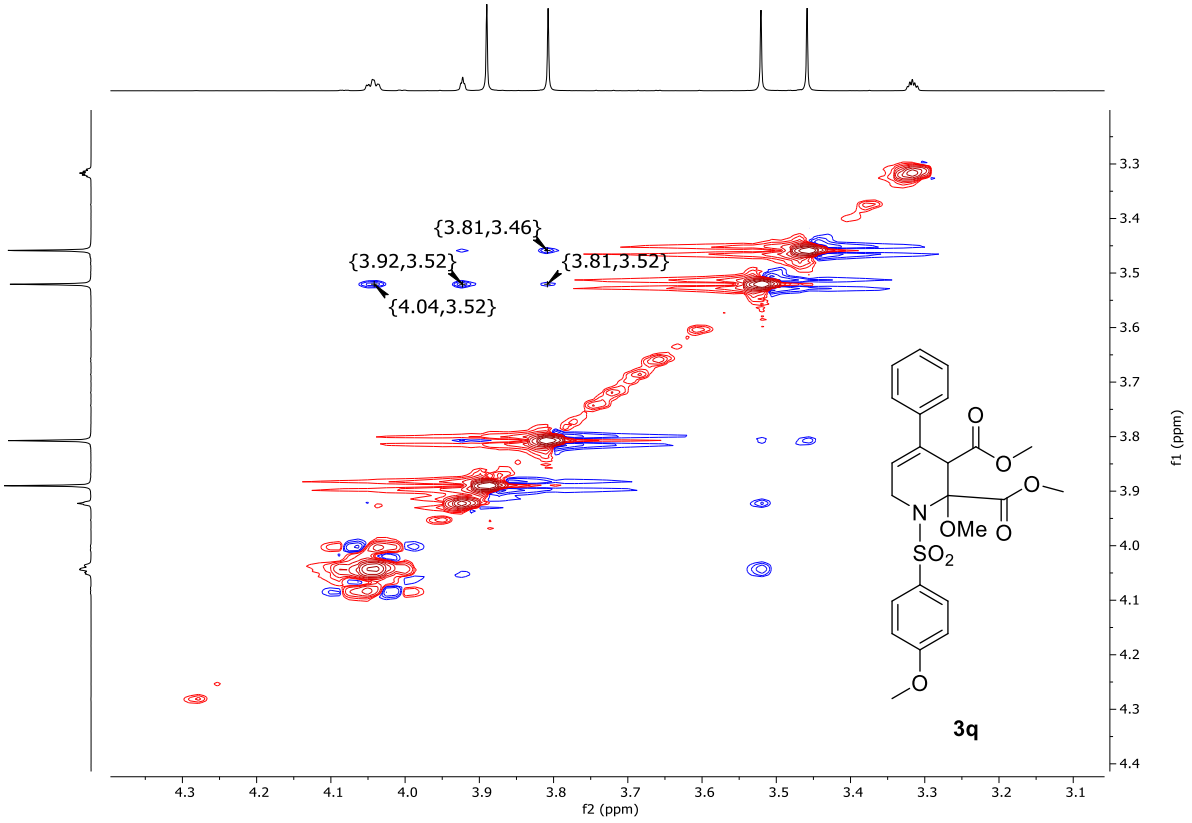


Figure 1: NOESY correlations on **3q**



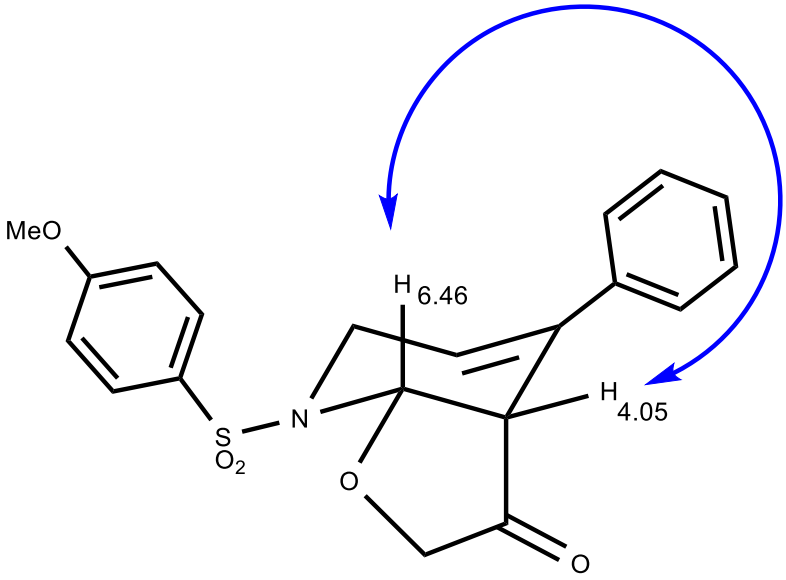
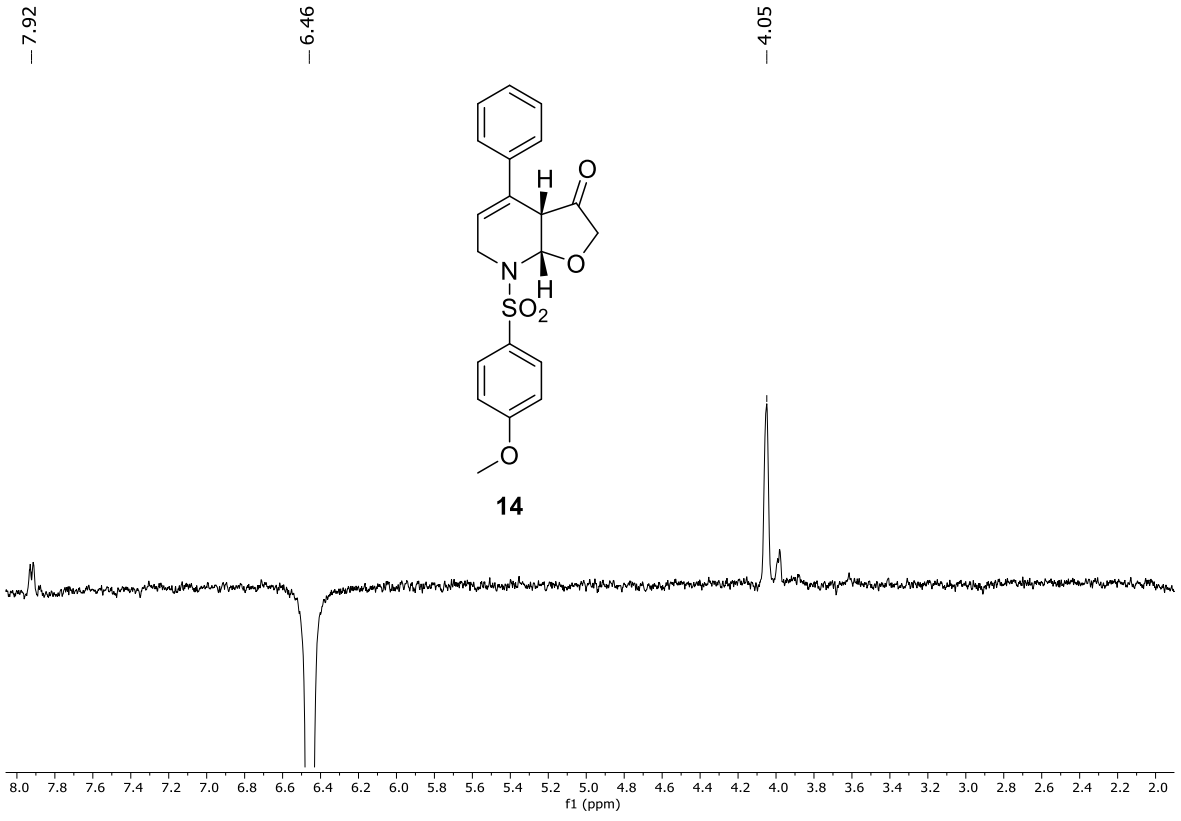


Figure 2: NOESY correlations on **14**



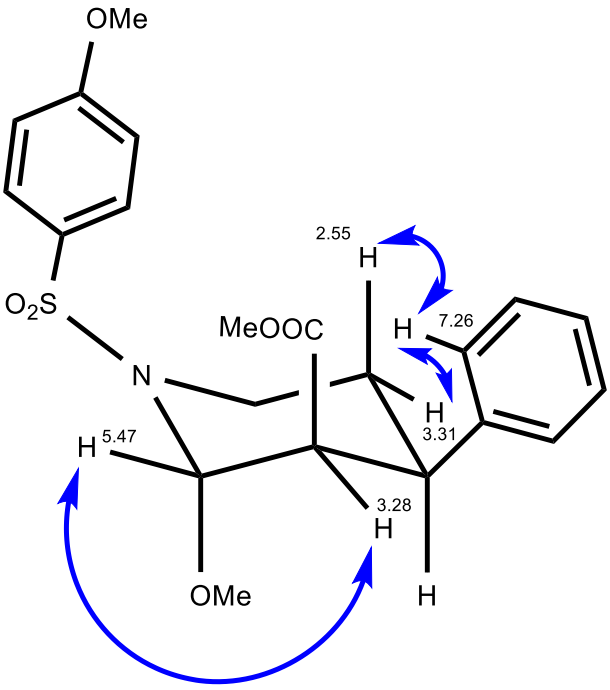
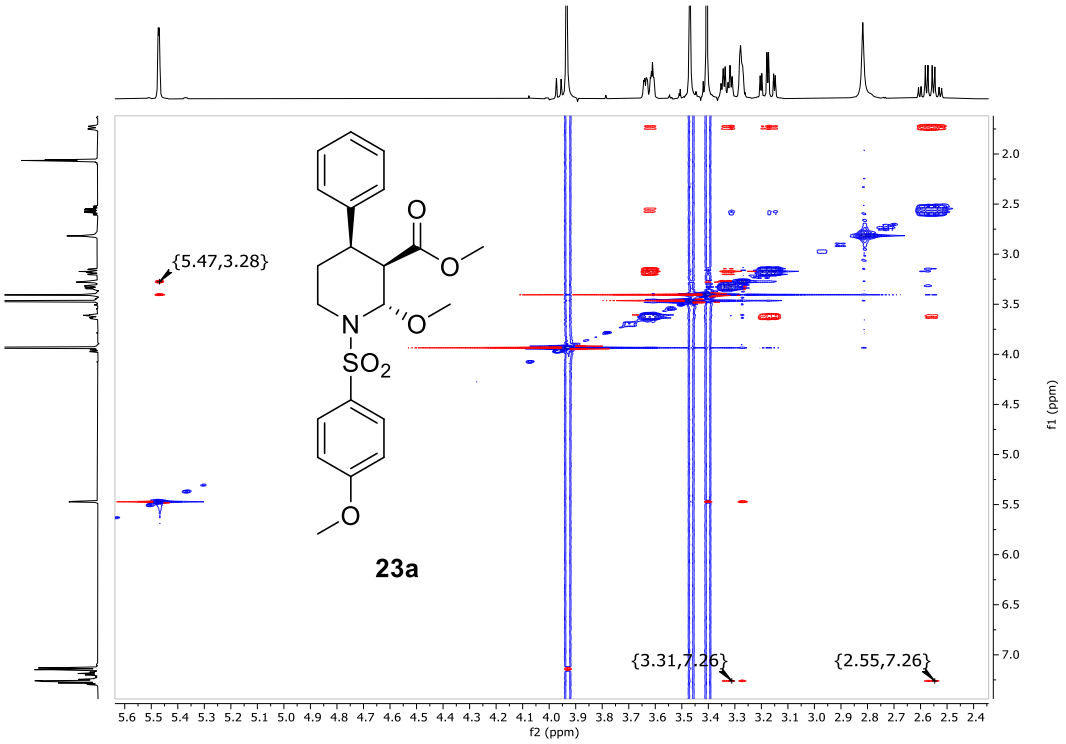


Figure 3: NOESY correlations on **23a**



X-ray crystallography of 3r

The X-ray data for the compound **3r** (colourless crystals by slow evaporation of a methanol solution) was collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K_α radiation; λ = 0.71073 Å) microfocus X-ray (IμS) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection. Obtained data were treated by XT-version 2014/5 and SHELXL-2017/1 software implemented in APEX3 v2016.9-0 (Bruker AXS) system.[8] $R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | \, | F_o | - | F_c | \, | / \sum | F_o |$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1976913. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

The frames for **3r** were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.921. The structure was solved and refined using the Bruker SHELXTL Software Package.

Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure uniformity of treatment of crystal, all hydrogens were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ (methyl). H atoms in methyl, and methine moieties were placed with C-H distances of 0.96 Å and 0.98 Å, 0.93Å for C-H within the vinylidenes or phenyl rings.

The molecular structure of **3r** was unambiguously confirmed by sc-XRD techniques. The compound **3r** crystallizes in the monoclinic space group $P2_1/n$. All the structural parameters, e.g. interatomic distances and angles found for this molecule are close to the appropriate values found for related 1-sulfonyl-1,2,3,6-tetrahydropyridin-3-ols and similar compounds.[9] Namely, the positions of the double bonds within the system between C3-C4 and C9-C10 atoms (see the caption of Fig. 3), the N1-S1 distance and the localization of the N1 atom above the pseudoplanar ring of the tetrahydropyridine moiety in an envelope-like conformation are typical. Another description comes from the mutual orientation of the central ring substituents, where the ester and sulfonyl substituents are *syn*-oriented together with the N1 atom, while the methoxy group is found bellow the plane defined by the heterocycle and the vinylidene group is coplanar. Surprisingly enough, molecules are held together in a layered array only by C-H…O weak interactions.

Table 3. Experimental details

Crystal data	
Chemical formula	$C_{17}H_{21}NO_6S$
M_r	367.41
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	12.909 (2), 9.8608 (13), 14.025 (3)
β (°)	96.066 (6)
V (Å^3)	1775.4 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.22
Crystal size (mm)	0.59 × 0.47 × 0.40
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.680, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	45702, 4079, 3520
R_{int}	0.041
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.086, 1.04
No. of reflections	4079
No. of parameters	230
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.40

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

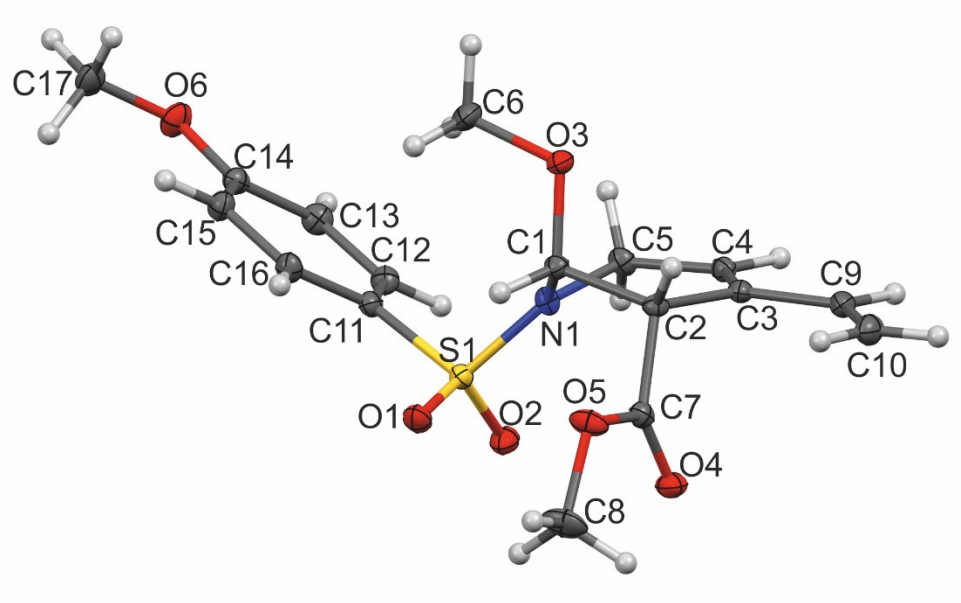


Figure 4. The molecular structure of **3r**, ORTEP diagram, 50% probability level. Selected interatomic distances [Å] and angles [°]: S1 O1 1.4345(10), S1 O2 1.4346(10), S1 N1 1.6246(11), N1 C1 1.4608(16), C1 O3 1.4079(15), C1 C2 1.5363(17), C2 C3 1.5131(17), C2 C7 1.5248(17), C3 C4 1.3341(18), C3 C9 1.4648(17), O3 C6 1.4342(16), C4 C5 1.4949(18), O4 C7 1.2008(16), O5 C7 1.3401(16), O5 C8 1.4521(17), O6 C14 1.3591(16), O6 C17 1.4316(18), C9 C10 1.331(2), O1 S1 O2 119.96(6), O1 S1 N1 106.24(6), C10 C9 C3 126.12(13).

Copies of NMR Spectra

Trifurylphosphine gold(I) chloride S43

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]acrylate (**1a**)..... S45

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(4-methylphenylprop-2-yn-1-yl)amino]acrylate (**1b**) S46

Methyl (*E*)-3-[*N*-(4-methoxyphenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1c**)..... S47

Methyl (*E*)-3-[*N*-(3-methoxyphenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1d**)..... S48

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-naphthalen-1-yl-prop-2-yn-1-yl)amino] acrylate (**1e**) .. S49

Methyl (*E*)-3-(*N*-[3-(1,1'-biphenyl-4-yl)prop-2-yn-1-yl]-*N*-[4-methoxyphenylsulfonyl]amino) acrylate (**1f**) S50

Methyl (*E*)-3-[*N*-(4-fluorophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1g**)..... S51

Methyl (*E*)-3-[*N*-(4-chlorophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1h**) S53

Methyl (*E*)-3-[*N*-(4-bromophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1i**) S54

Methyl (*E*)-3-[*N*-(3,4-dichlorophenylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino] acrylate (**1j**) .. S55

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[3-(2-nitrophenyl)prop-2-yn-1-yl]amino]acrylate (**1k**)..... S56

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[3-(3-nitrophenyl)prop-2-yn-1-yl]amino]acrylate (**1*l***)..... S57

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(4-nitrophenylprop-2-yn-1-yl)amino]acrylate (**1m**)..... S58

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[3-(thiophen-2-yl)prop-2-yn-1-yl]amino]acrylate (**1n**)..... S59

Ethyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]but-2-enoate (**1o**)..... S60

Methyl 3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]-3-phenylacrylate (**1p**) S61

Dimethyl 2-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1yl)amino]maleate (**1q**)..... S62

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(pent-4-en-2-yn-1-yl)amino]acrylate (**1r**)..... S63

Methyl (*E*)-3-[*N*-((*E,Z*)-hex-4-en-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1s**)..... S64

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-((*E*)-undec-4-en-2-yn-1yl)amino]acrylate (**1t**)..... S65

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-((*E*)-5-phenylpent-4-en-2-yn-1-yl)amino]acrylate (**1u**).... S66

Methyl (*E*)-3-[*N*-(3-cyclopropylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1v**)..... S67

Methyl (*E*)-3-[*N*-(3-iodoprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1w**)..... S68

Methyl (*E*)-3-[*N*-(5-cyclopropylpenta-2,4-diyn-1-yl)-*N*-(4-methoxyphenylsulfonyl)amino]acrylate (**1x**)... S69

Methyl (*E*)-3-[*N*-[4-methoxyphenylsulfonyl]-*N*-[5-(triethylsilyl)penta-2,4-diyn-1-yl]amino]acrylate (**1y**) . S70

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(penta-2,4-diyn-1-yl)amino]acrylate (**1z**)..... S71

Ethyl 1-(4-methoxyphenylsulfonyl)-2-methyl-4-phenyl-1,6-dihydropyridine-3-carboxylate (**2o**) S72

Methyl 1-(4-methoxyphenylsulfonyl)-2,4-diphenyl-1,6-dihydropyridine-3-carboxylate (**2p**)..... S73

Methyl 4-iodo-1-(4-methoxyphenylsulfonyl)-1,6-dihydropyridine-3-carboxylate (**2w**)..... S74

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (**3a**) S75

Methyl 2-methoxy-1-(4-methylphenylsulfonyl)-4-(4-methylphenyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3b**) S76

Methyl 2-methoxy-4-(4-methoxyphenyl)-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3c**) S77

Methyl 2-methoxy-4-(3-methoxyphenyl)-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3d**)..... S78

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-naftyl-1,2,3,6-tetrahydropyridine-3-carboxylate (**3e**) . S79

Methyl 4-bifenyl-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3f**) S80

Methyl 4-(4-fluorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3g**) S81

Methyl 4-(4-chlorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3h**) S83

Methyl 4-(4-bromophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3i**) S84

Methyl 4-(3,4-dichlorophenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3j**) S85

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(4-nitrophenyl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3m**) S86

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(thiophen-2-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3n**) S87

Dimethyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-2,3-dicarboxylate (**3q**) S88

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridine-3-carboxylate (**3r**) .. S89

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(prop-1-en-1-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3s**) S90

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(oct-1-en-1-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3t**) S91

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(2-phenylethen-1-yl)-1,2,3,6-tetrahydropyridine-3-carboxylate (**3u**) S92

Methyl 4-cyclopropyl-2-methoxy-1-(4-methoxyphenylsulfonyl)- 1,2,3,6-tetrahydropyridine-3-carboxylate (**3v**) S93

Methyl 4-(cyclopropylethynyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)- 1,2,3,6-tetrahydropyridine-3-carboxylate (**3x**) S94

Methyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]acrylate (**6a**) S95

Ethyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]but-2-enoate (**6o**) S96

Dimethyl 2-[(*N*-4-(methoxyphenylsulfonyl)-*N*-(prop-2-yn-1-yl)amino]maleate (**6q**) S97

Methyl 2-ethoxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (**7a**)... S98

Methyl 2-hydroxy-1-(4-methoxyphenylsulfonyl)-4-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (**8a**) S99

1-((*Tert*-butyldiphenylsilyl)oxy)but-3-yn-2-one (**10**) S100

N-(3-phenylprop-2-yn-1-yl)-4-methoxybenzenesulfonamide (**11a**) S101

N-(pent-4-en-2-yn-1-yl)-4-methoxybenzenesulfonamide (**11r**) S102

(*E,Z*)-*N*-(hex-4-en-2-yn-1-yl)-4-methoxybenzenesulfonamide (**11s**) S103

N-(3-cyclopropylprop-2-yn-1-yl)-4-methoxybenzenesulfonamide (**11v**) S104

(E)-1-((*tert*-butyldiphenylsilyl)oxy)-4-[*N*-(4-methoxybenzenesulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]but-3-en-2-one (**12**) S105

(E)-1-hydroxy-4-[*N*-(4-methoxybenzenesulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]but-3-en-2-one (**13**) S106

7-(4-Methoxyphenylsulfonyl)4-phenyl-2,3,3a,6,7,7a-hexahydrofuro[2,3-b]pyridin-3-one (**14**) S107

tert-Butyl (*E*)-4-[N-(4-methoxyphenylsulfonyl)-N-(3-phenylprop-2-yn-1-yl)amino]-2-oxobut-3-en-1-yl) carbamate (**17**) S108

tert-Butyl 7-(4-methoxyphenylsulfonyl)-3-oxo-4-phenyl-2,3,3a,6,7,7a-hexahydro-1*H*-pyrrolo[2,3-b]pyridine-1-carboxylate (**18**)..... S109

3-Methoxyphenyl (*E*)-3-[*N*-(4-methoxyphenylsulfonyl)-*N*-(3-phenylprop-2-yn-1-yl)amino]acrylate (**20**) S110

3-Methoxyphenyl 1-(4-methoxyphenylsulfonyl)-4-phenyl-1,6-dihydropyridine3-carboxylate (**21**) S111

8-Methoxy-3-(4-methoxyphenylsulfonyl)-10b-phenyl-1,2,3,10b-5*H*-chromeno[3,4-c]pyridin-5-one (**22**) S112

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-phenylpiperidine-3-carboxylate (**23a**)..... S113

Methyl 2-methoxy-1-(4-methoxyphenylsulfonyl)-4-(4-methylphenyl)piperidine-3-carboxylate (**23b**) S114

Methyl 4-biphenyl-2-methoxy-1-(4-methoxyphenylsulfonyl)piperidine-3-carboxylate (**23f**) S115

Methyl 4-(4-fluorphenyl)-2-methoxy-1-(4-methoxyphenylsulfonyl)piperidine-3-carboxylate (**23g**)..... S116

Trimethyl 2-(4-methoxyphenylsulfonyl)-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (**25r**)..... S118

Trimethyl 2-(4-methoxyphenylsulfonyl)-6-methyl-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (**25s**) S119

Trimethyl 6-hexyl-2-(4-methoxyphenylsulfonyl)-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (**25t**) S120

Trimethyl 2-(4-methoxyphenylsulfonyl)-6-phenyl-1,2,6,8a-tetrahydroisoquinoline-4,7,8-tricarboxylate (**25u**) S121

Trimethyl 2-(4-methoxyphenylsulfonyl)-1,2-dihydroisoquinoline-4,7,8-tricarboxylate (**26r**) S122

Trimethyl isoquinoline-4,7,8-tricarboxylate (**27r**) S123

Tert-butyl *N*-(3-cyclopropylprop-2-yn-1-yl)-*N*-(4-methoxyphenylsulfonyl)carbamate (**30**) S124

2-((*Tert*-butyldiphenylsilyl)oxy)-*N*-methoxy-*N*-methylacetamide (**31**) S125

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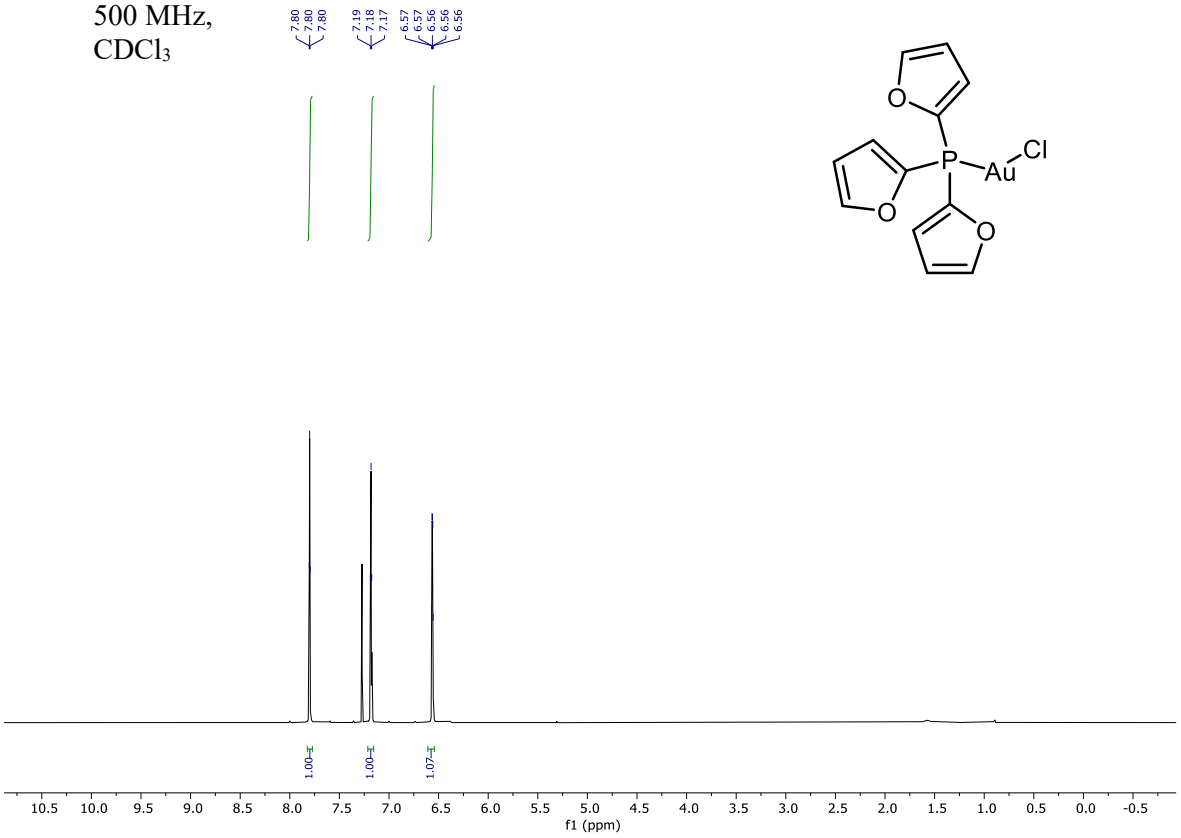

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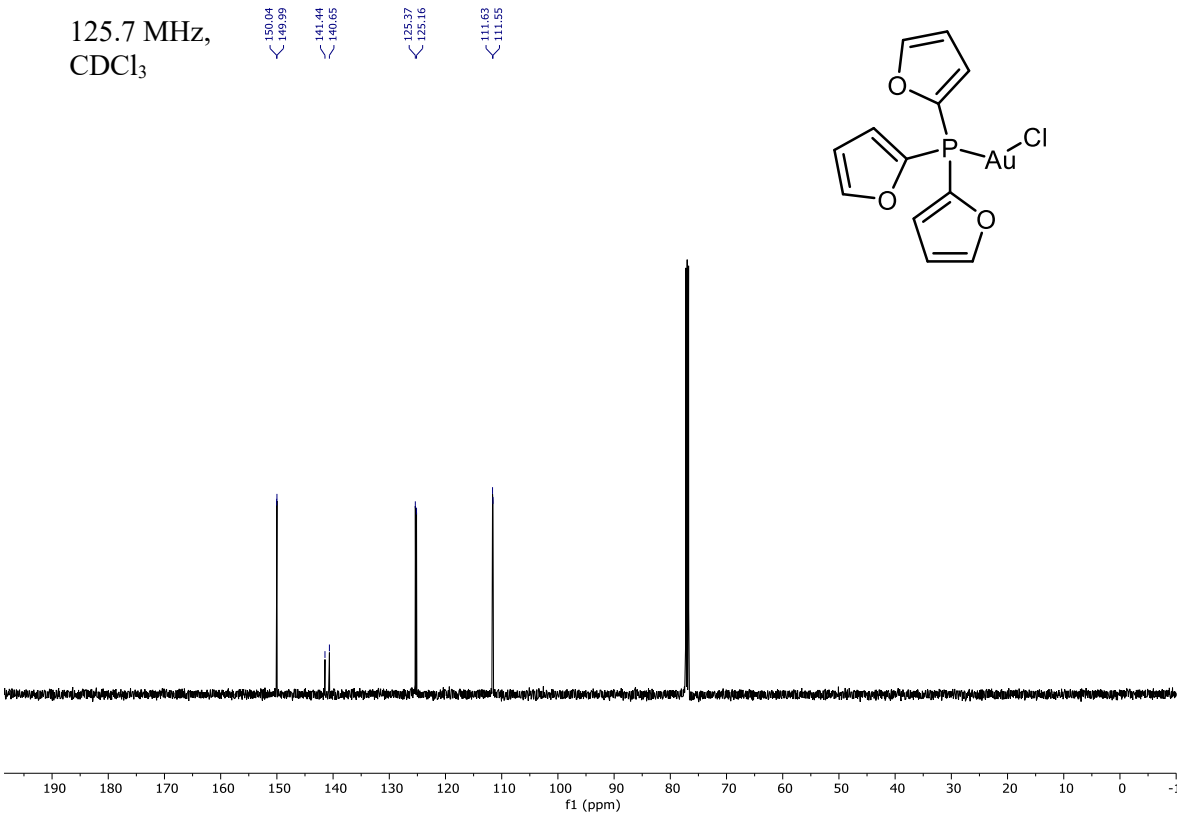

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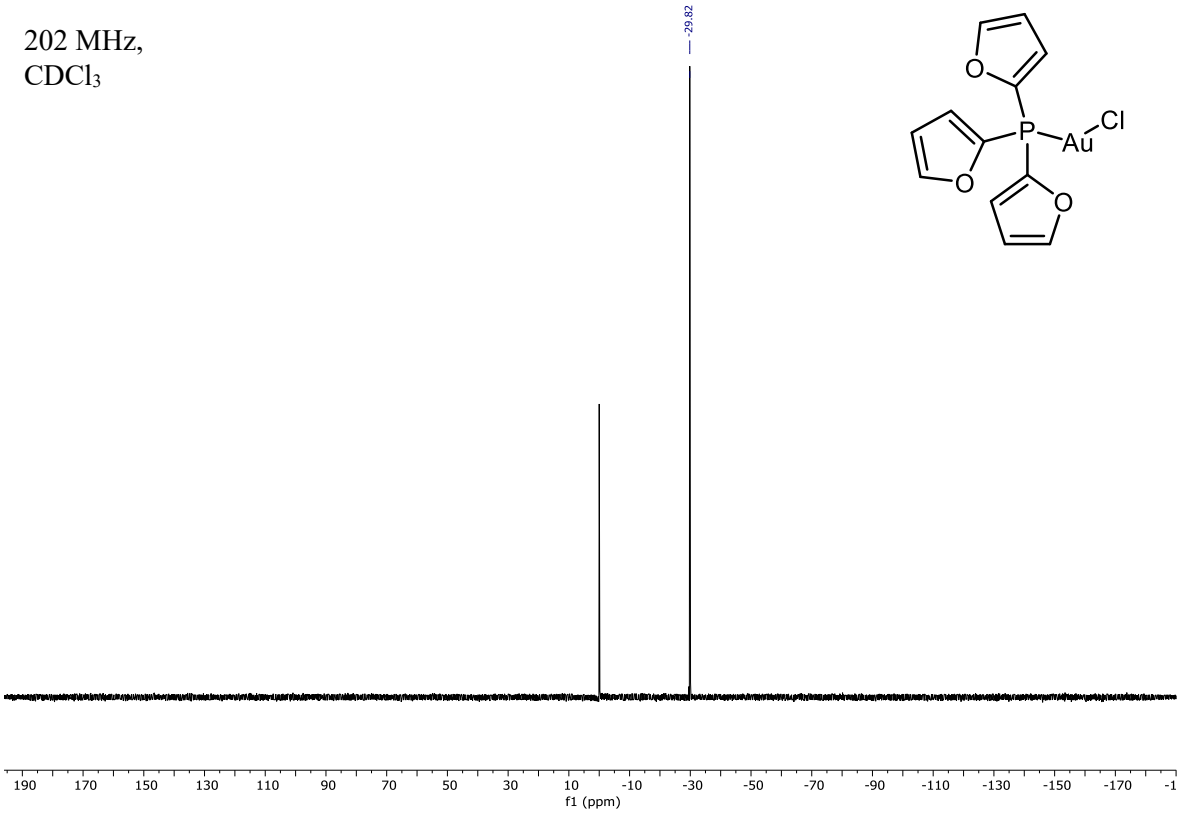

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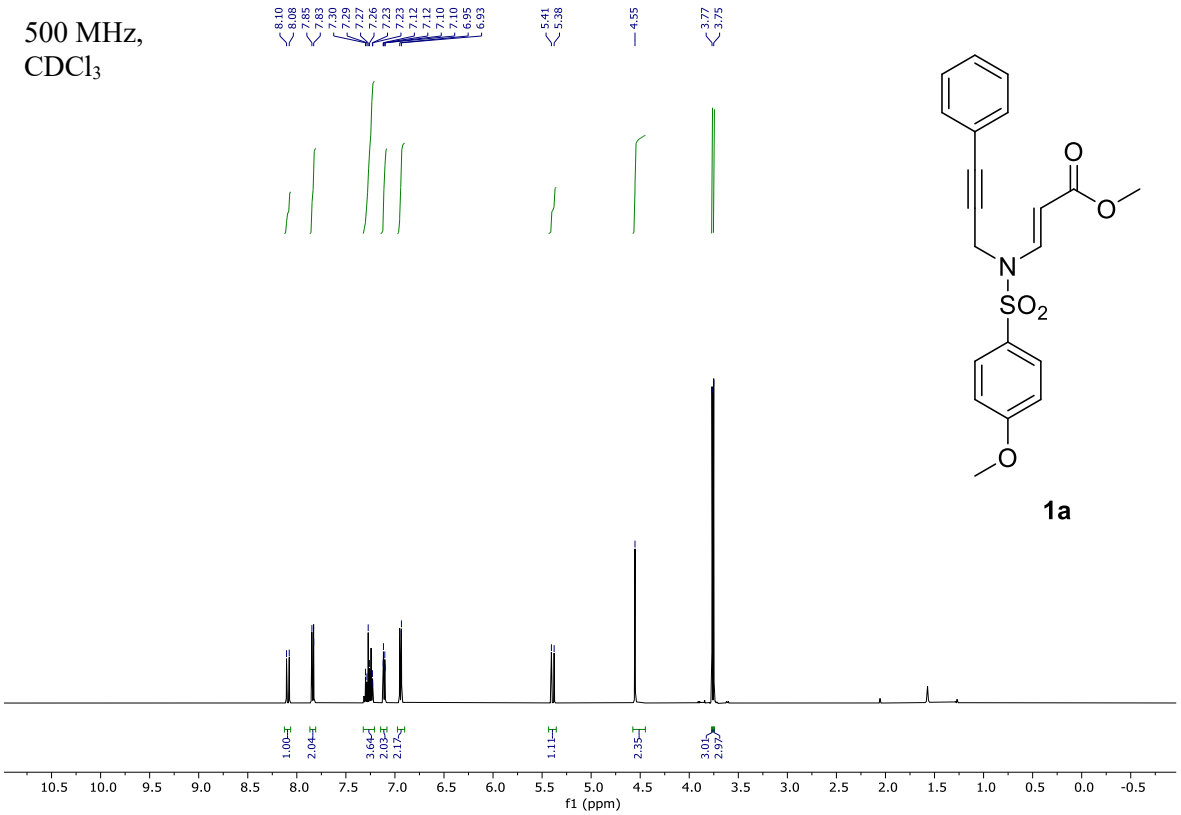

1a

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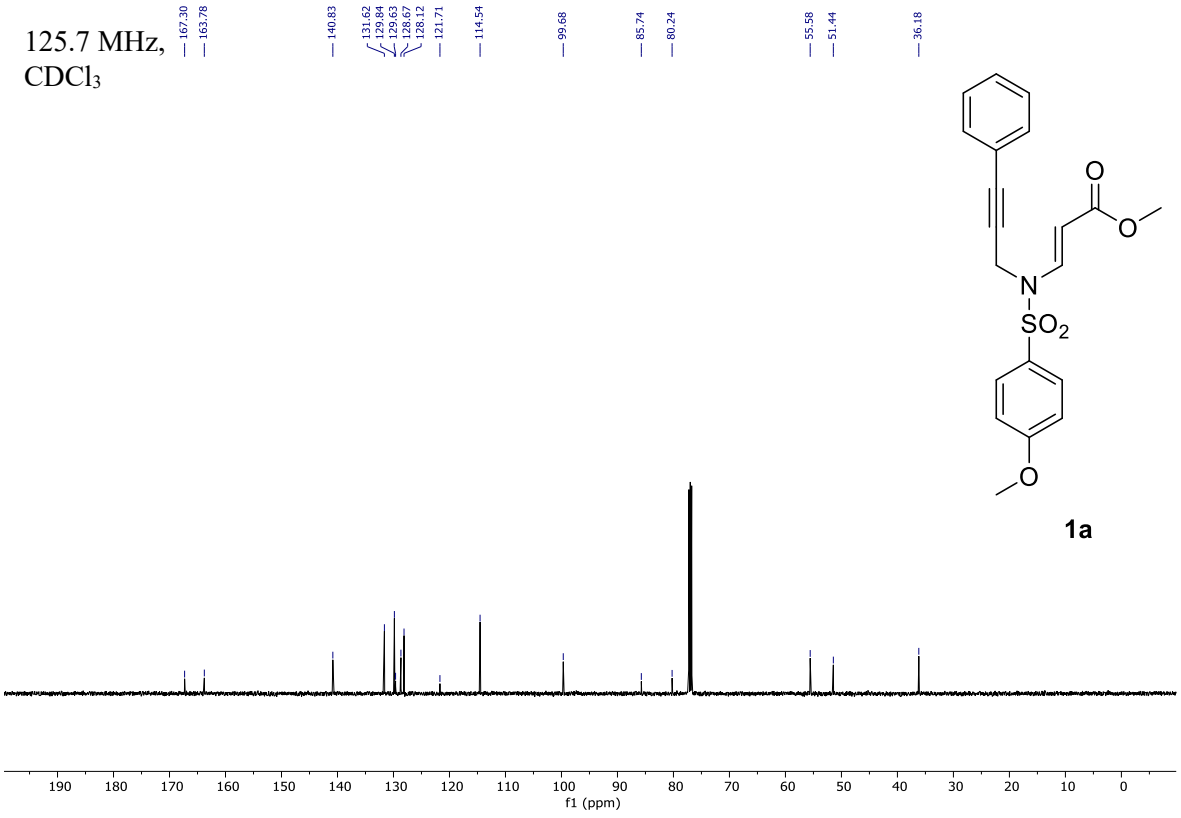

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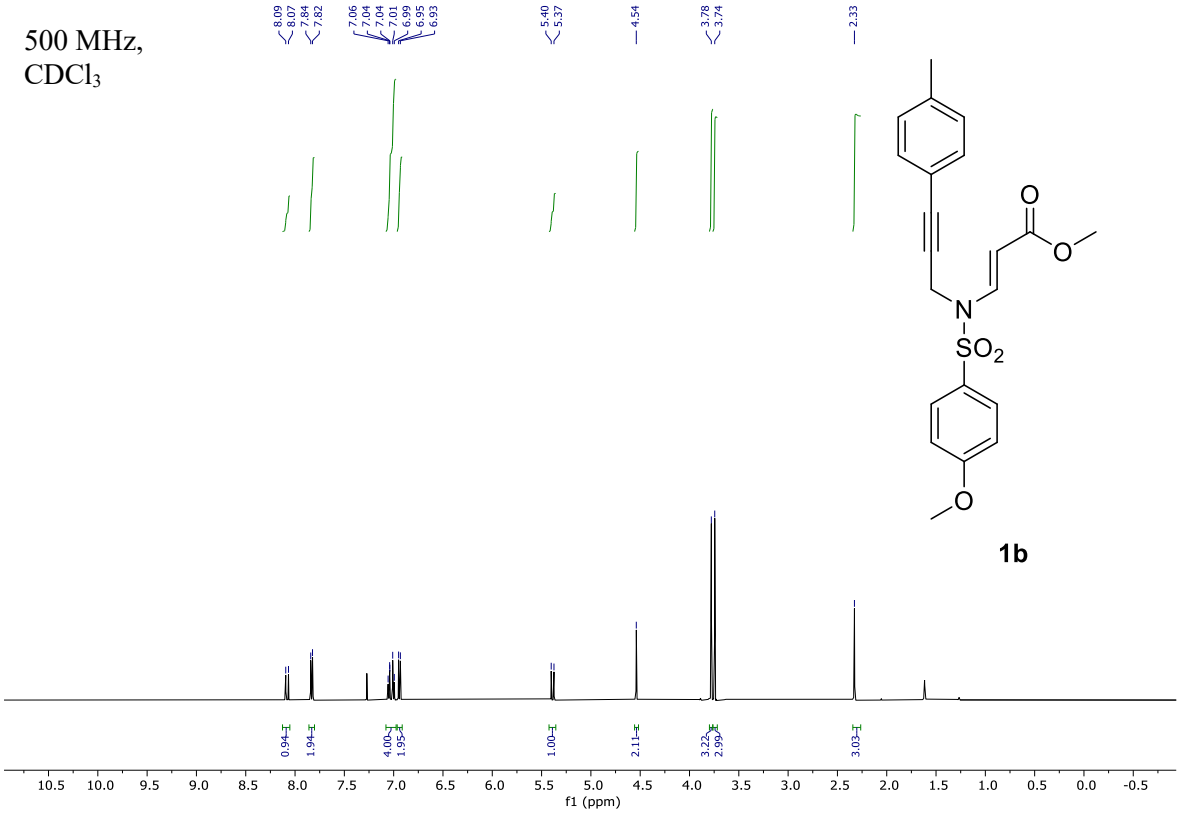

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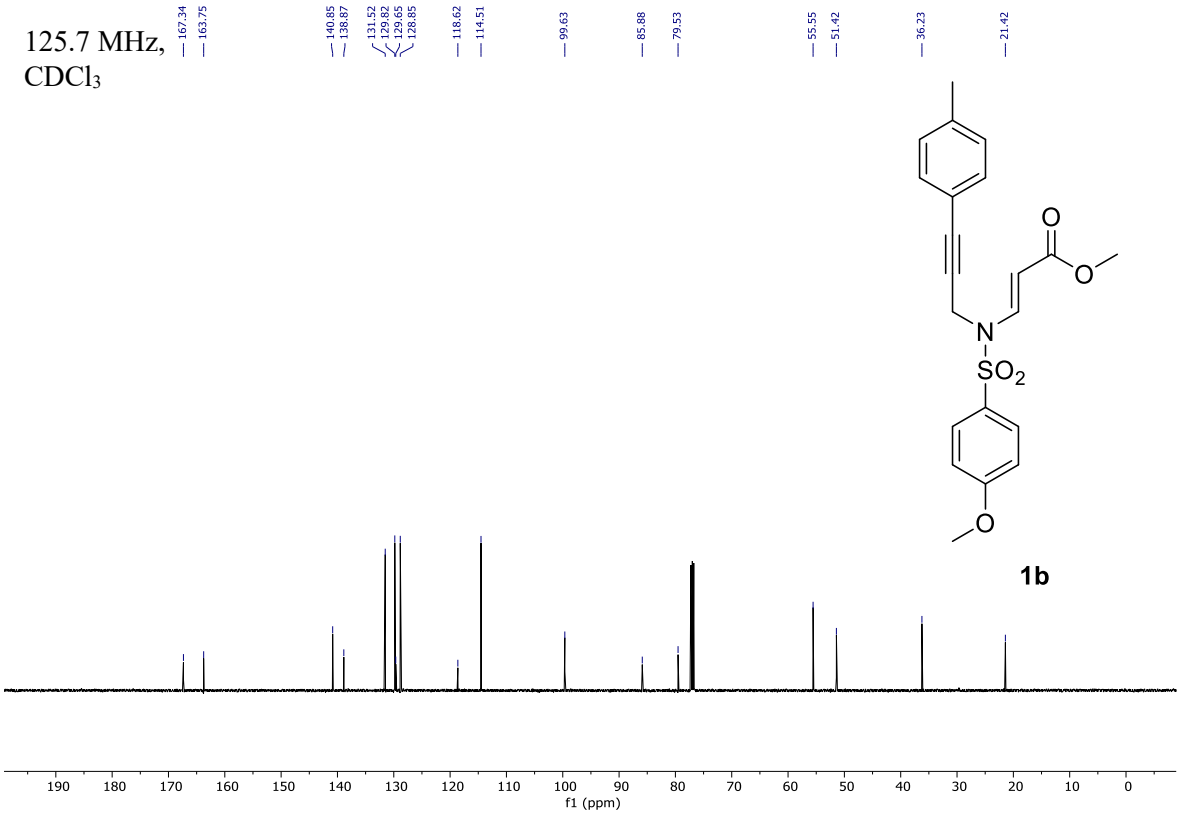

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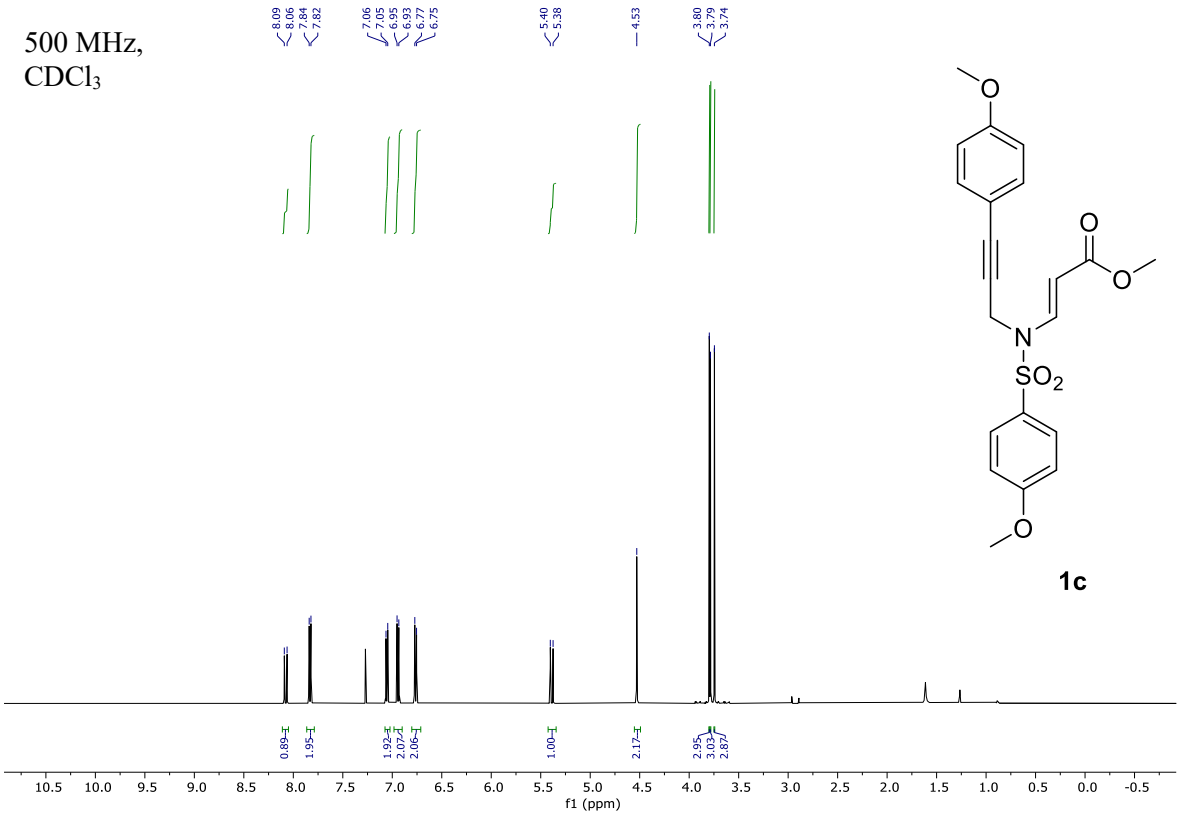

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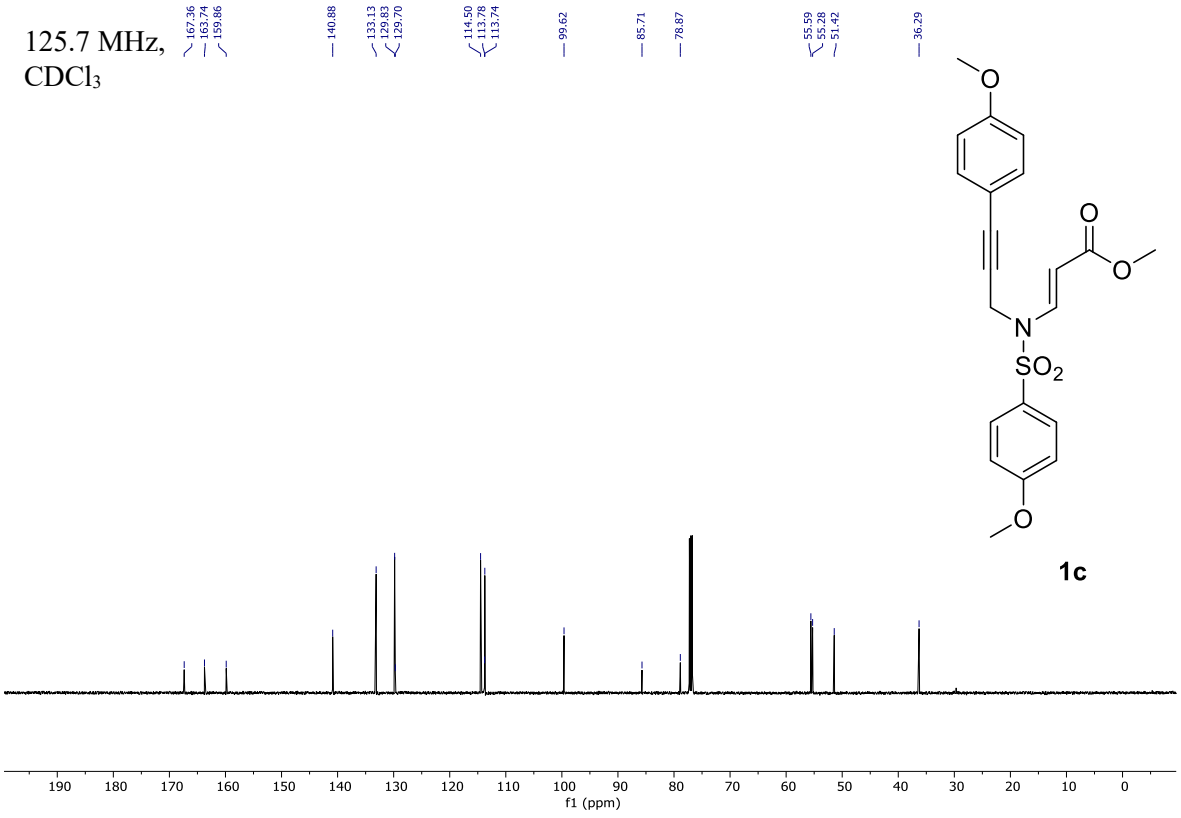

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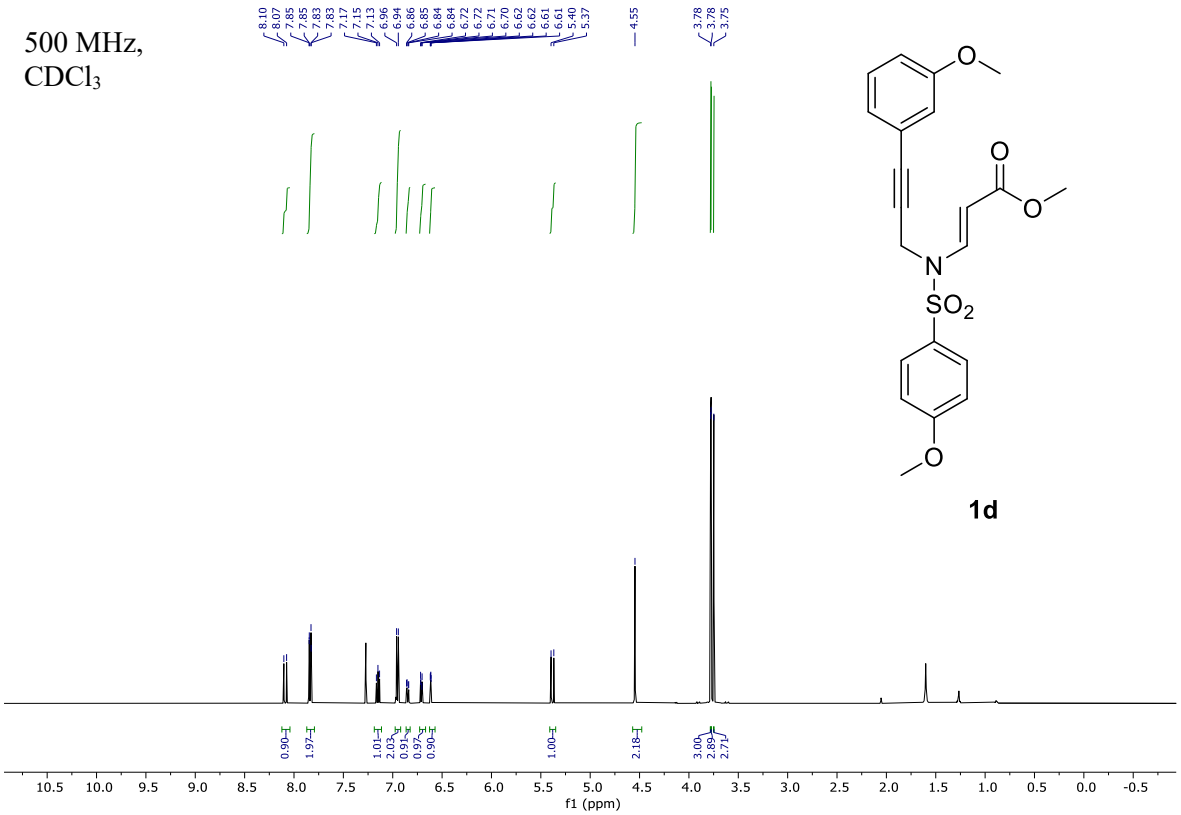

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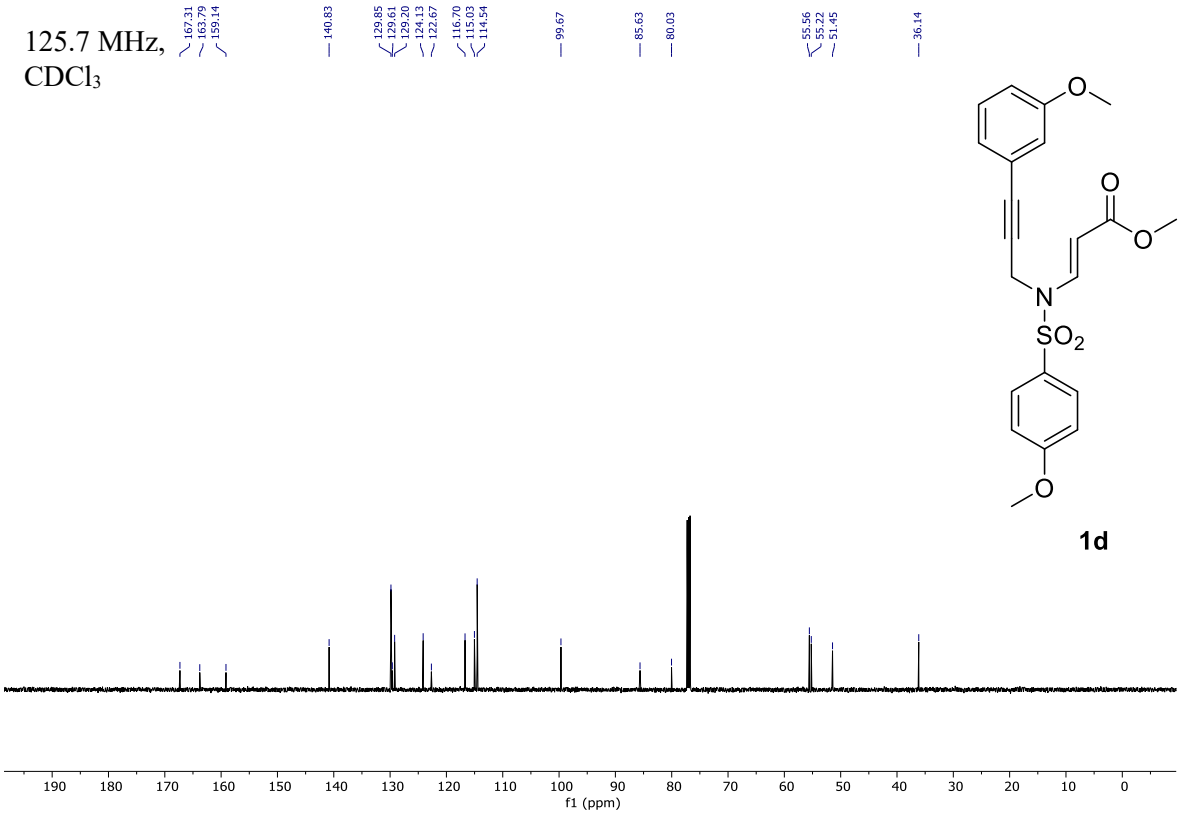

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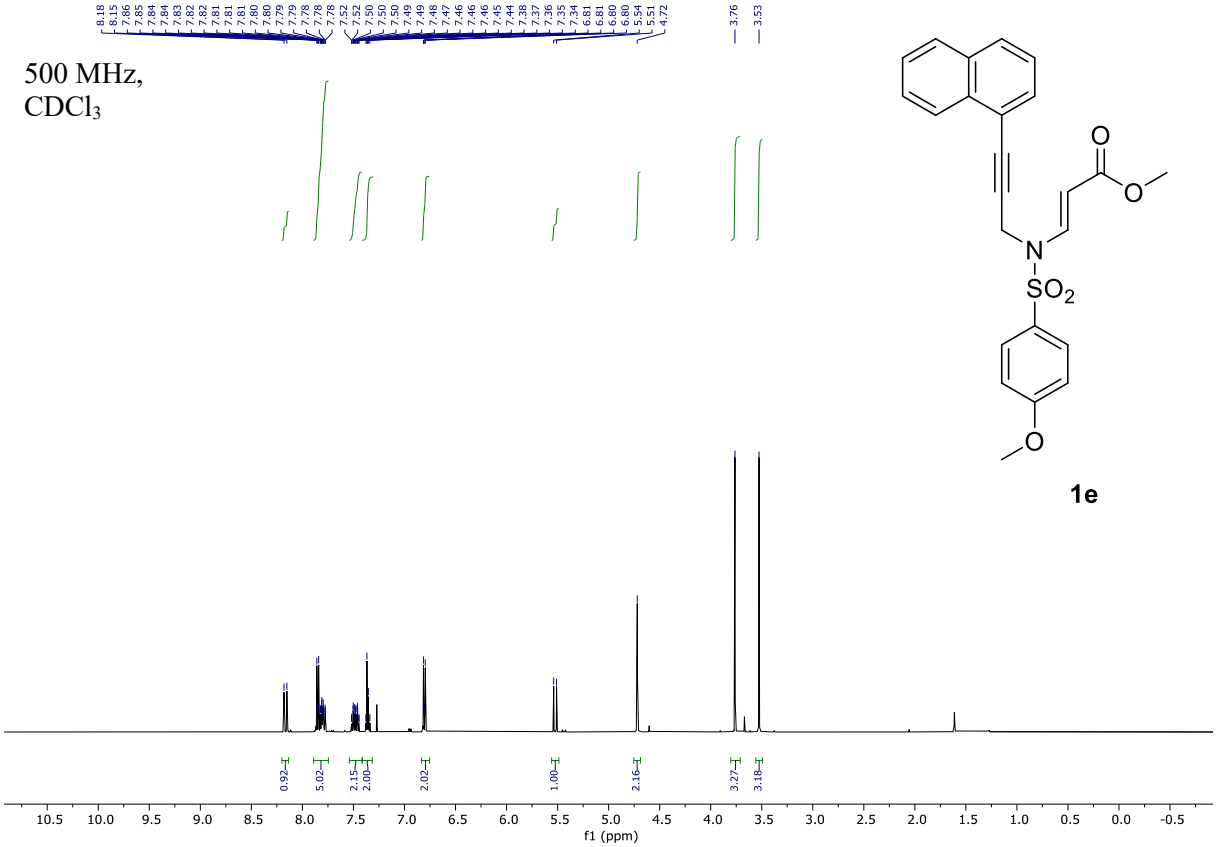

1e

125.7 MHz,
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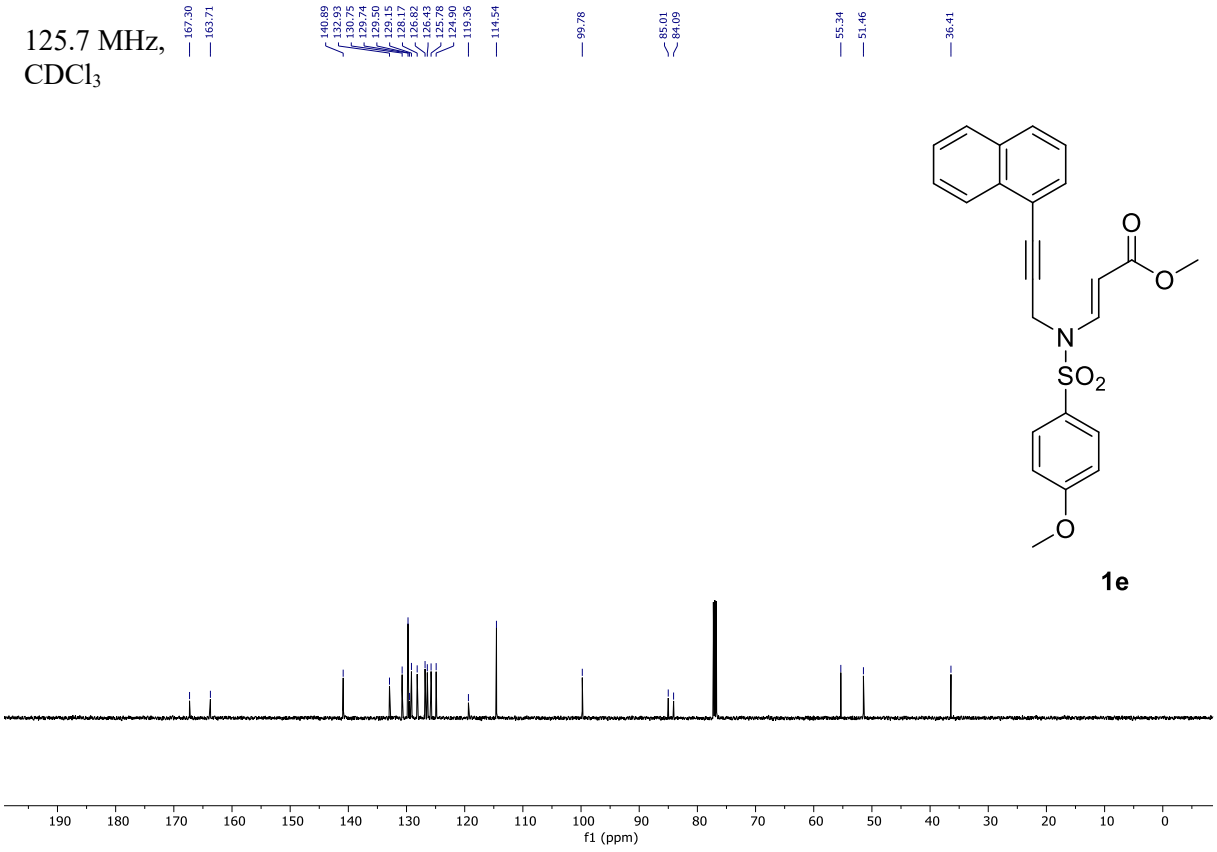

1e

500 MHz,
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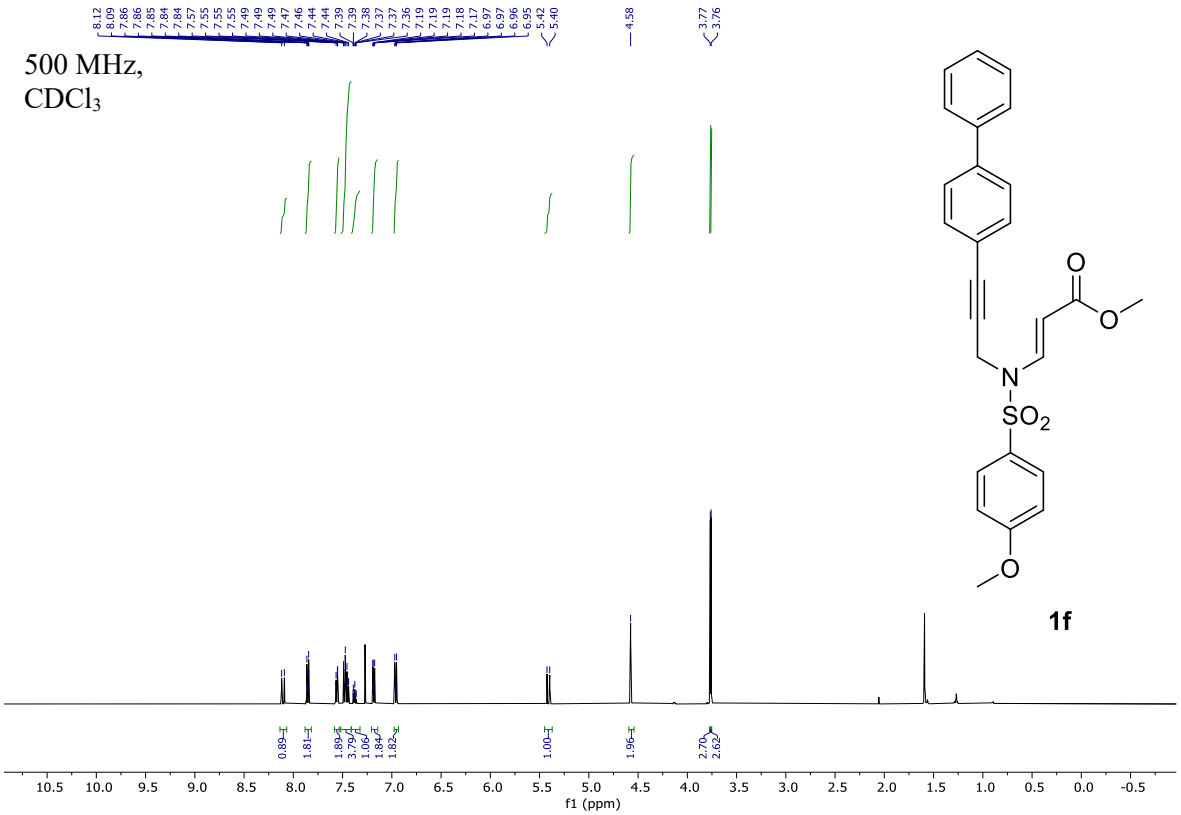
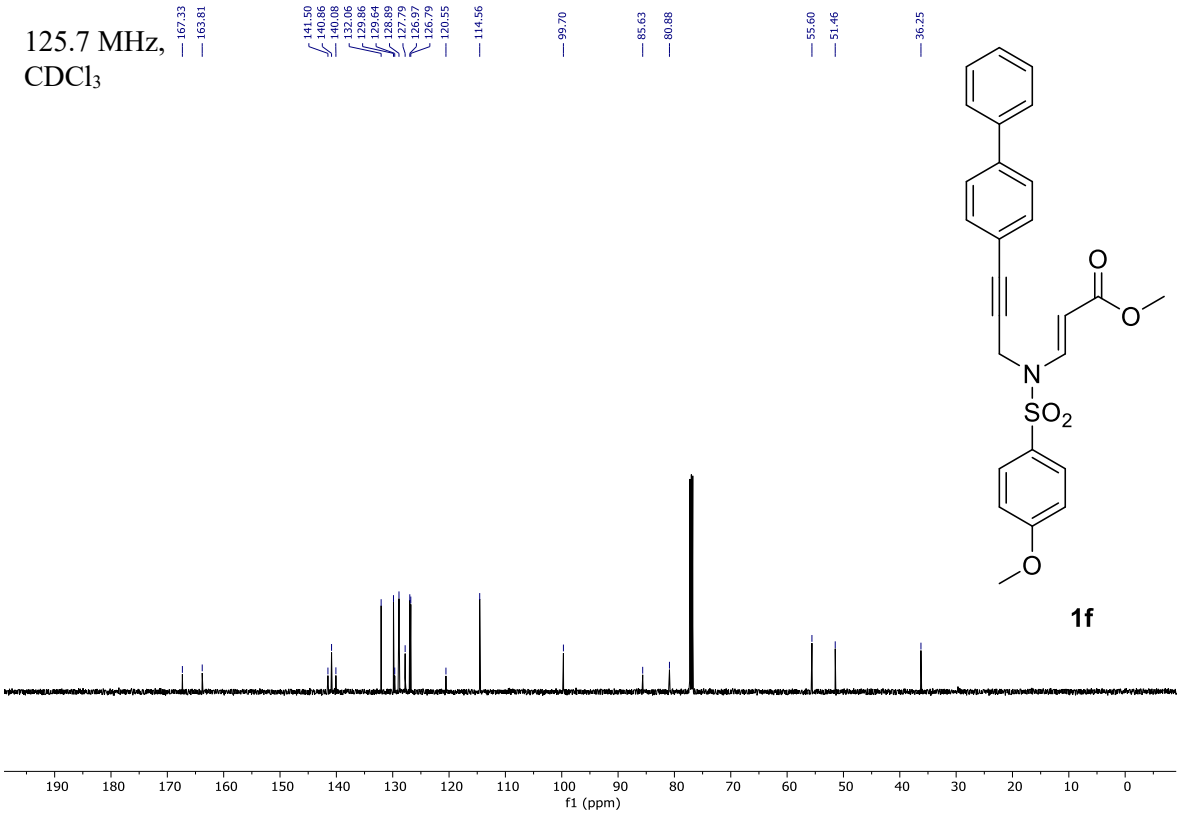


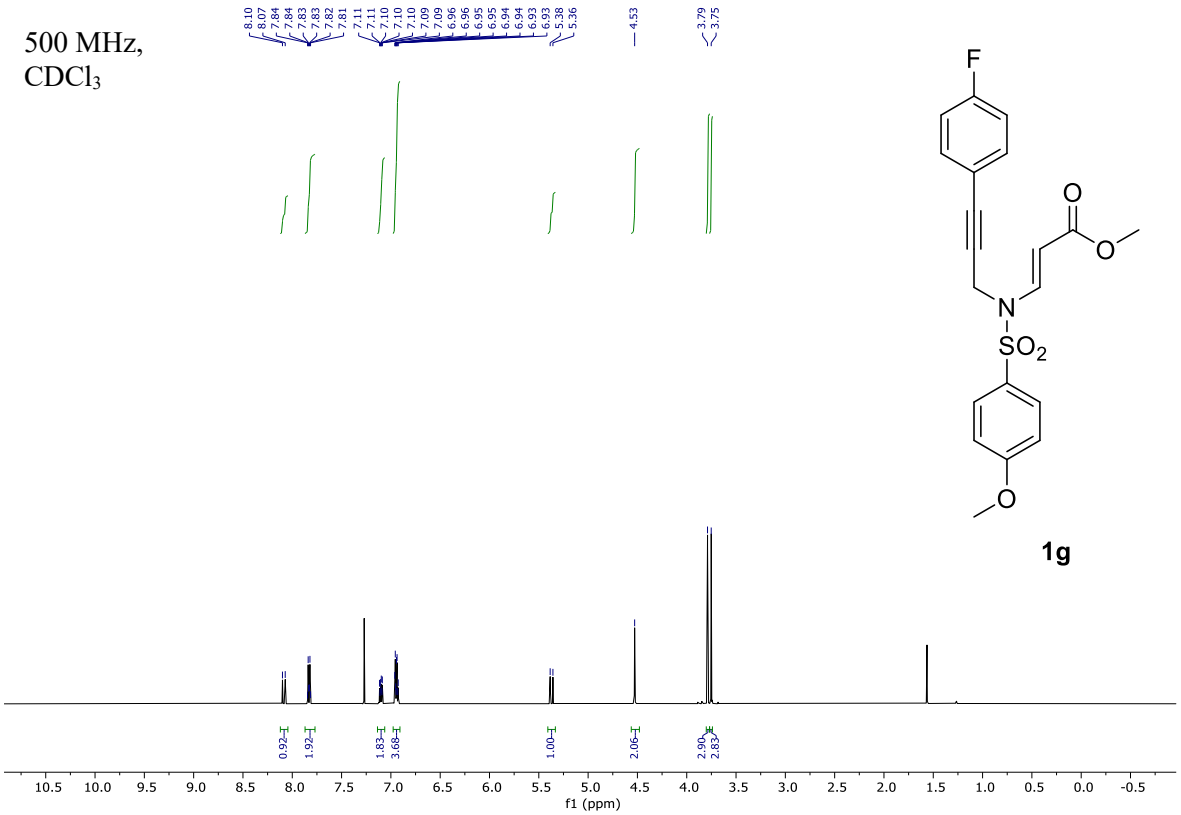
1f

125.7 MHz,
$CDCl_3$



1f

500 MHz,
$CDCl_3$



125.7 MHz,
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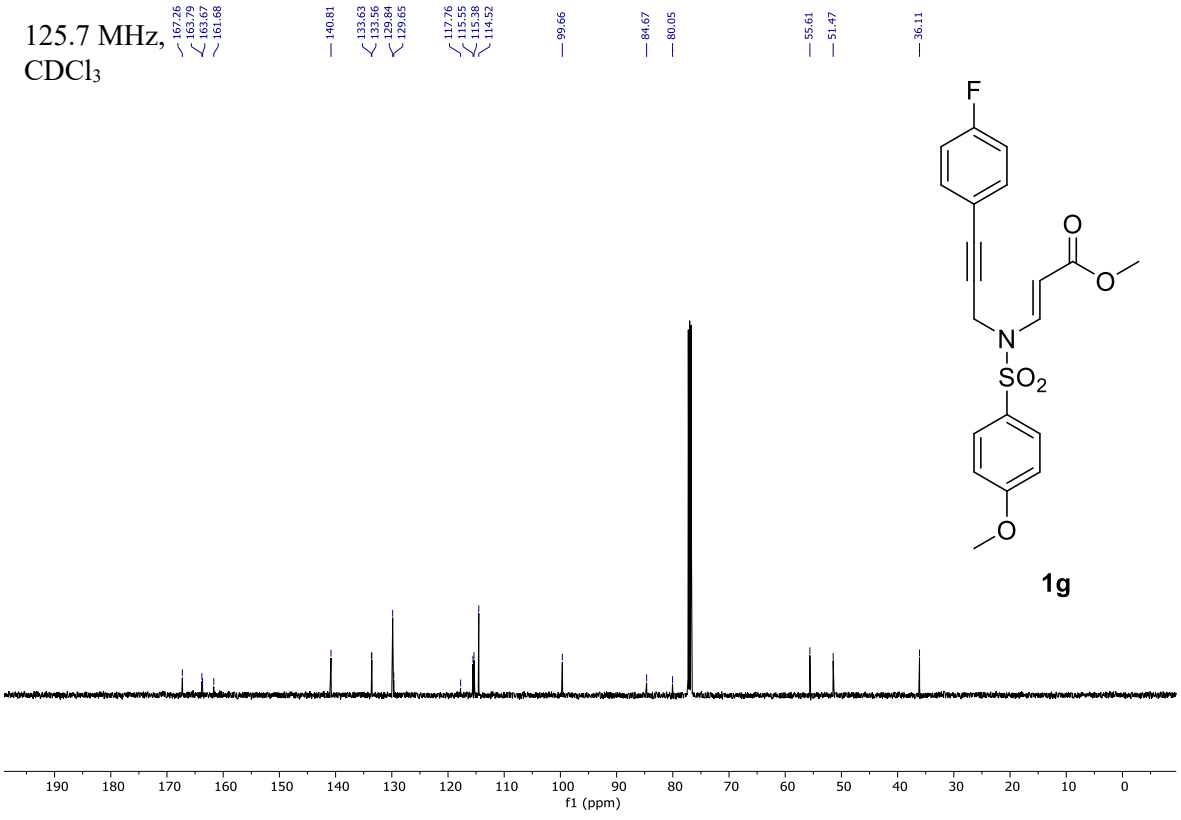
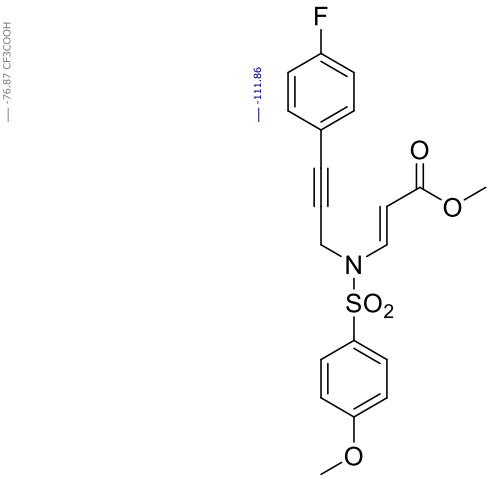
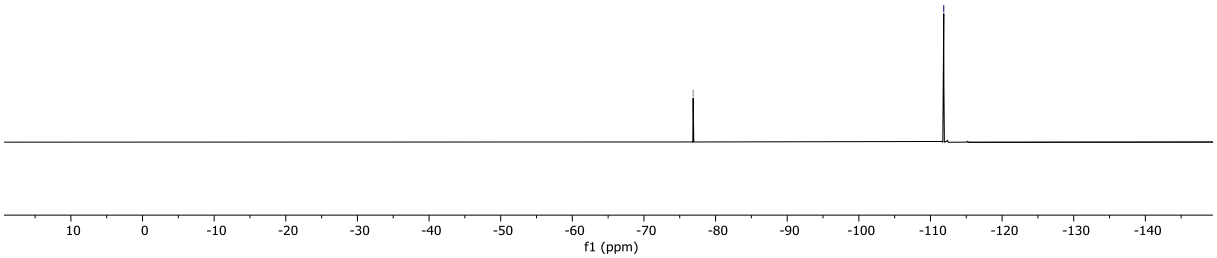


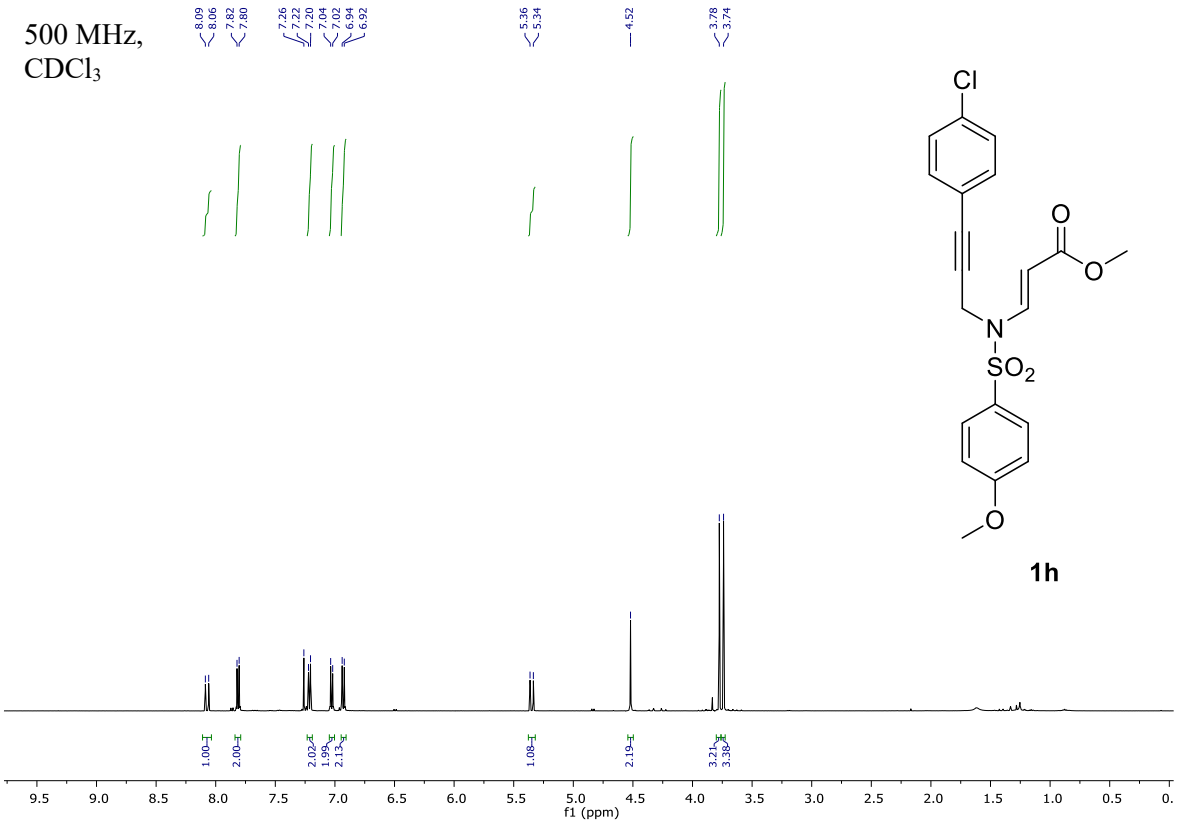
470 MHz,
Acetone-d_6



1g



500 MHz,
$CDCl_3$



125.7 MHz,
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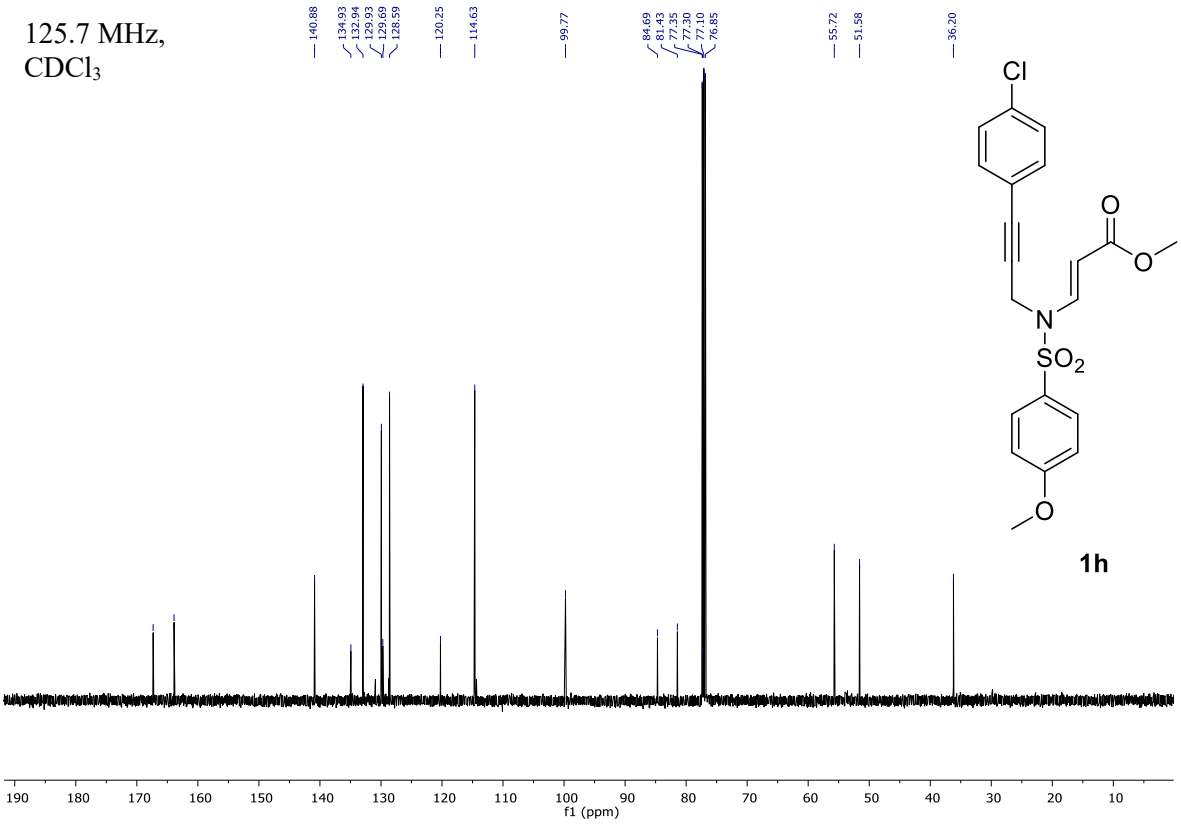
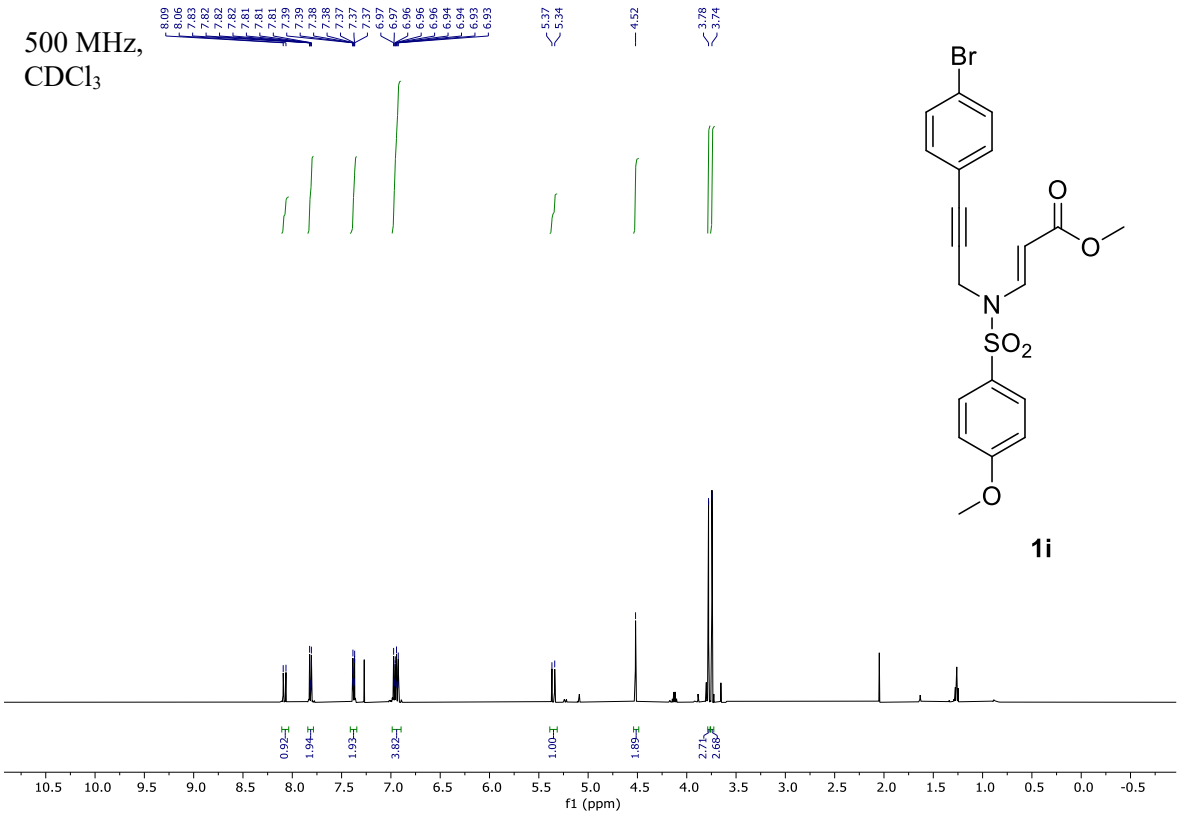
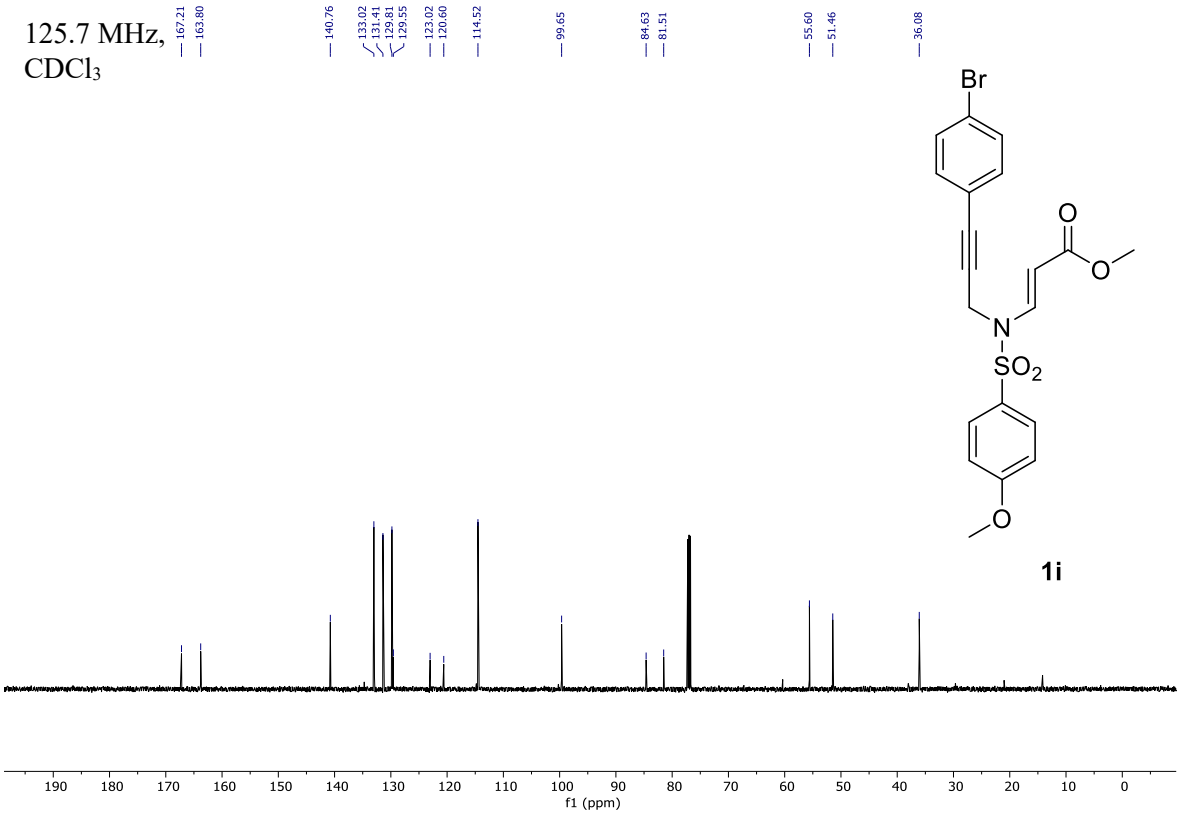


500 MHz, $CDCl_3$



125.7 MHz, $CDCl_3$



500 MHz,
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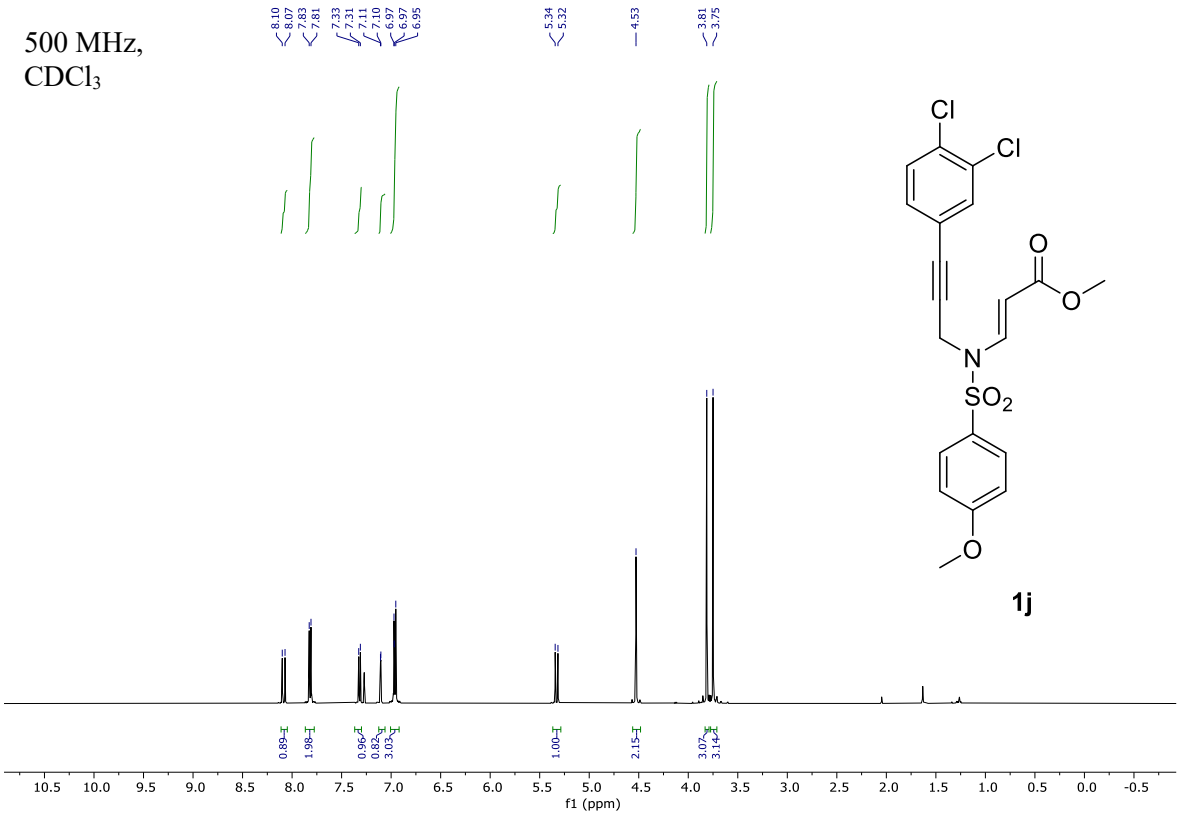
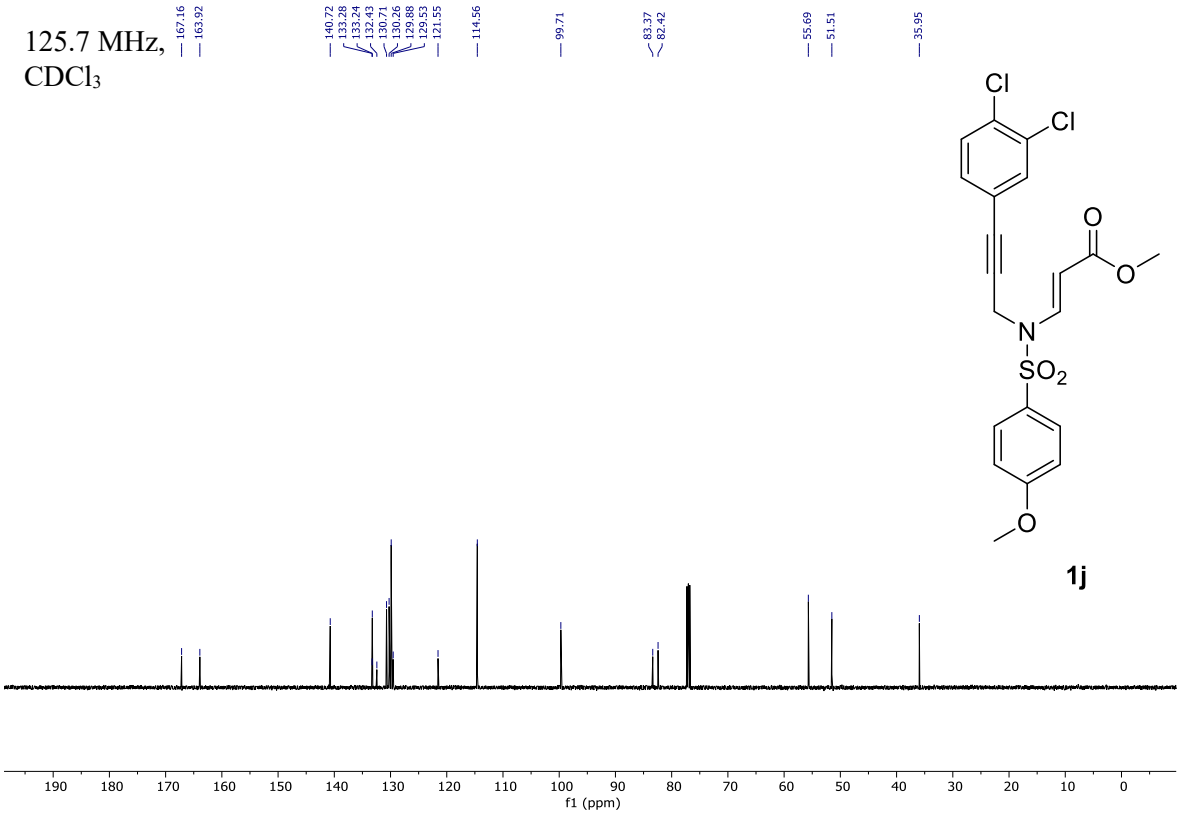


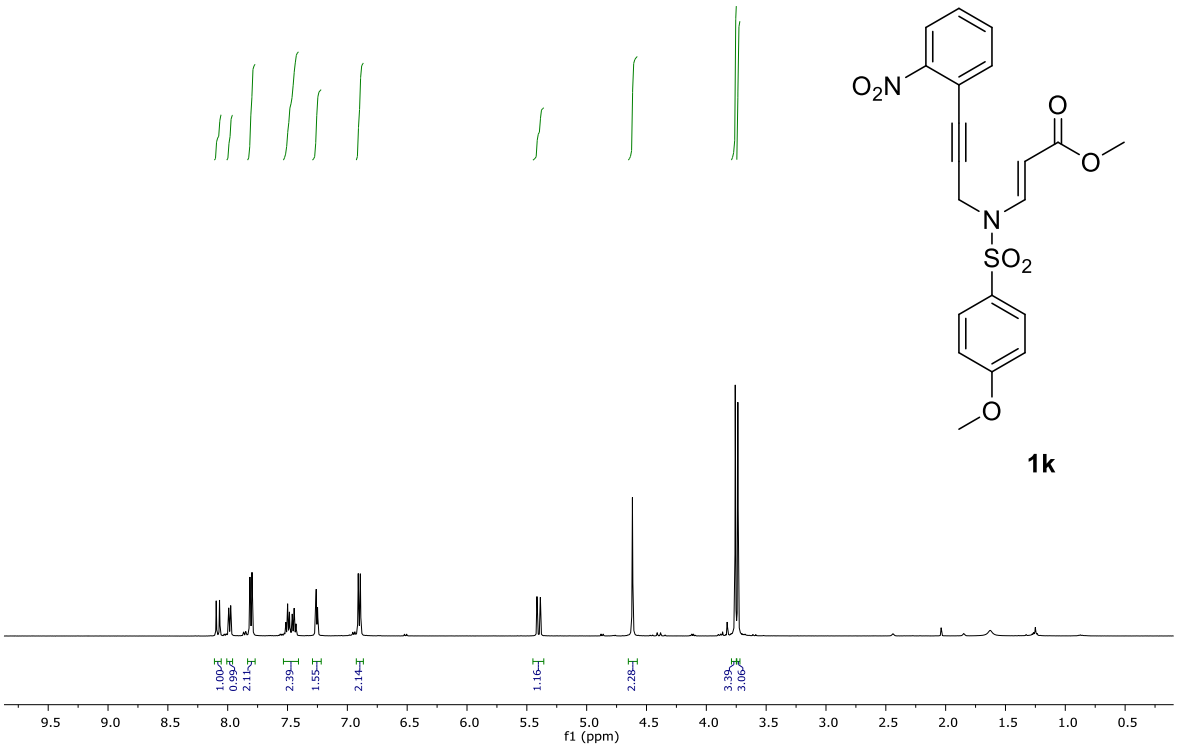
1j

125.7 MHz,
$CDCl_3$

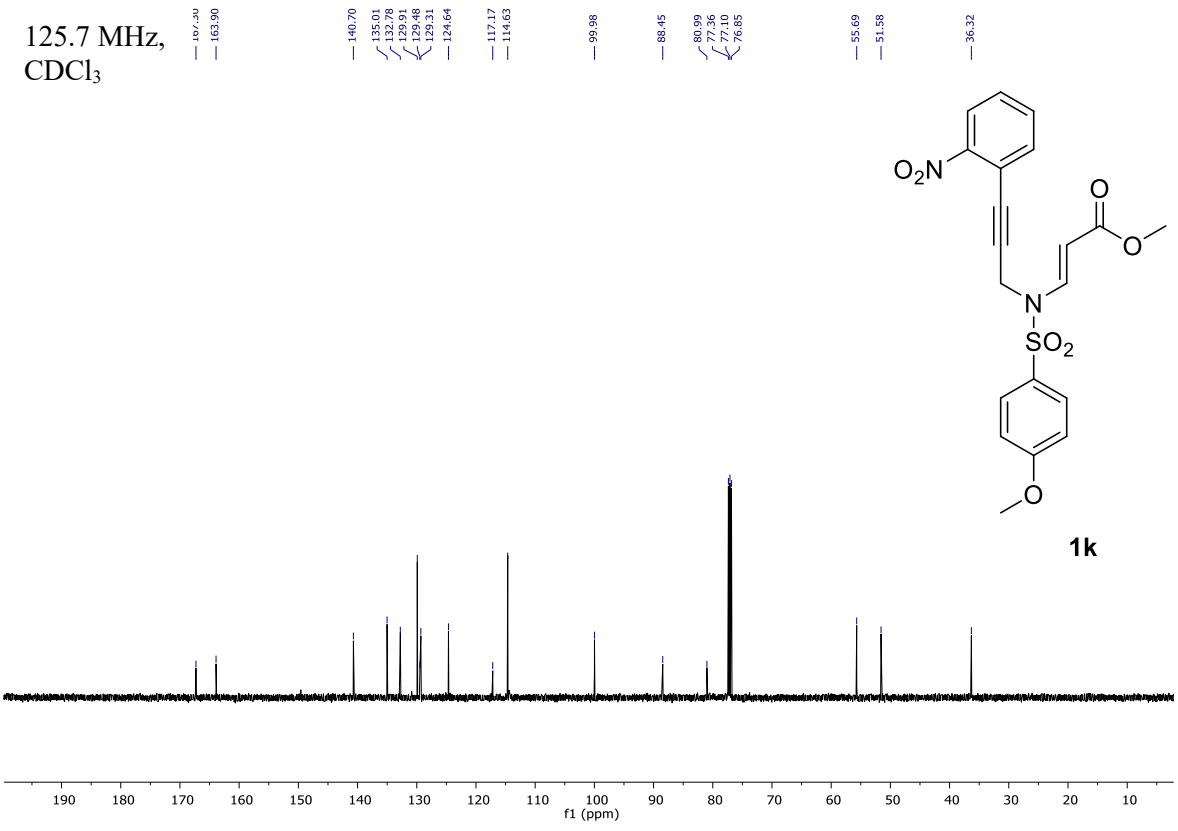


1j

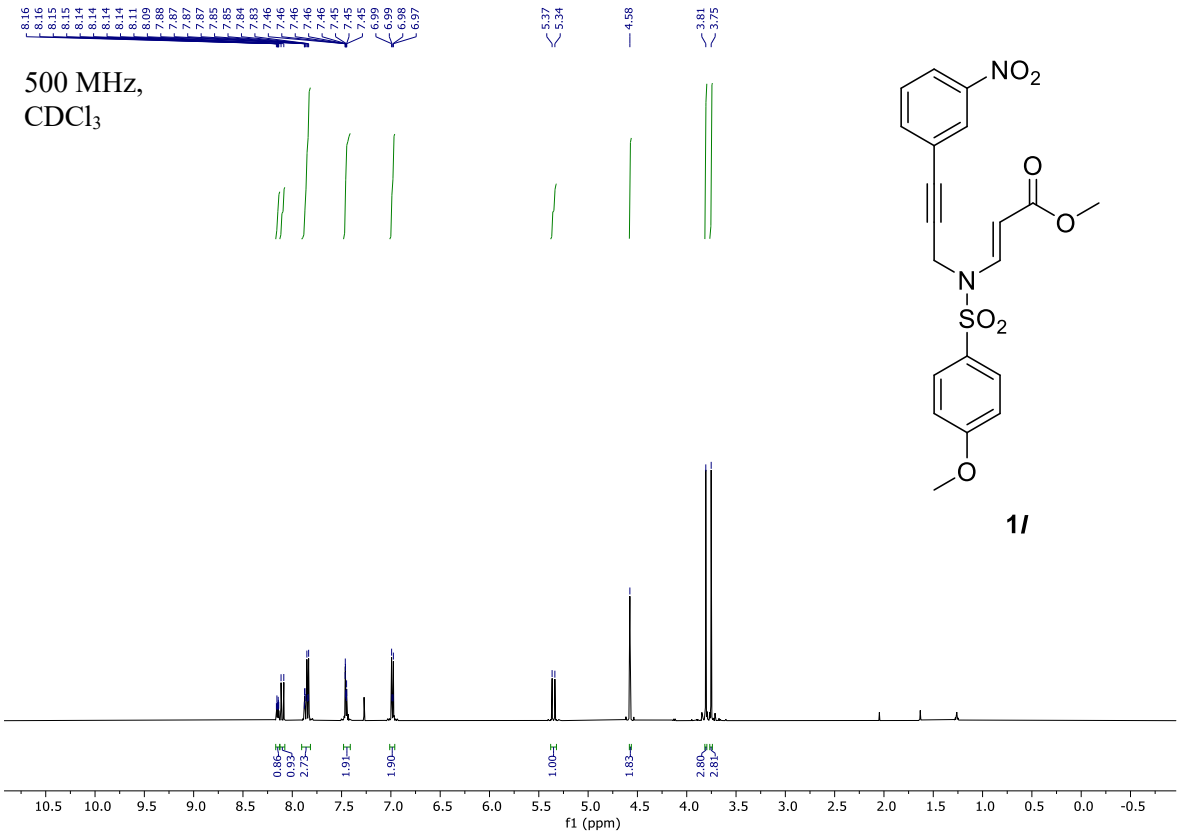
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

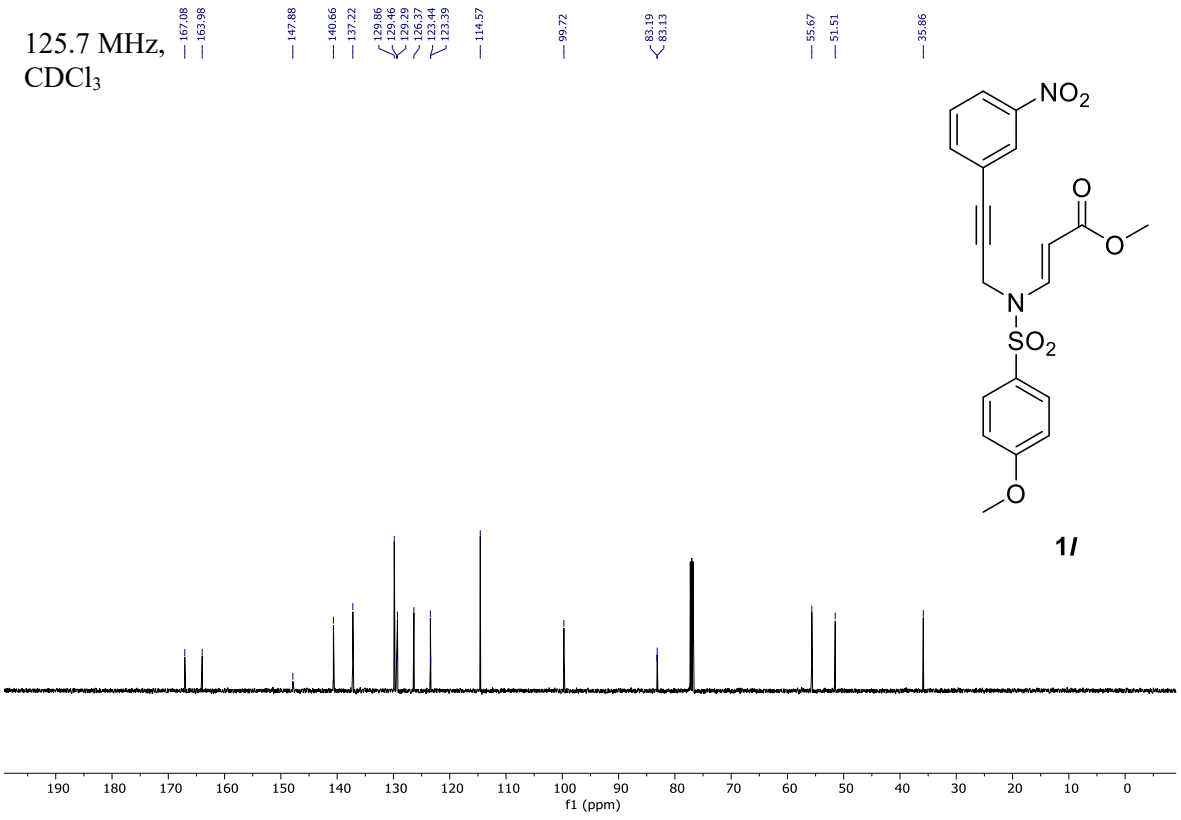


500 MHz,
$CDCl_3$



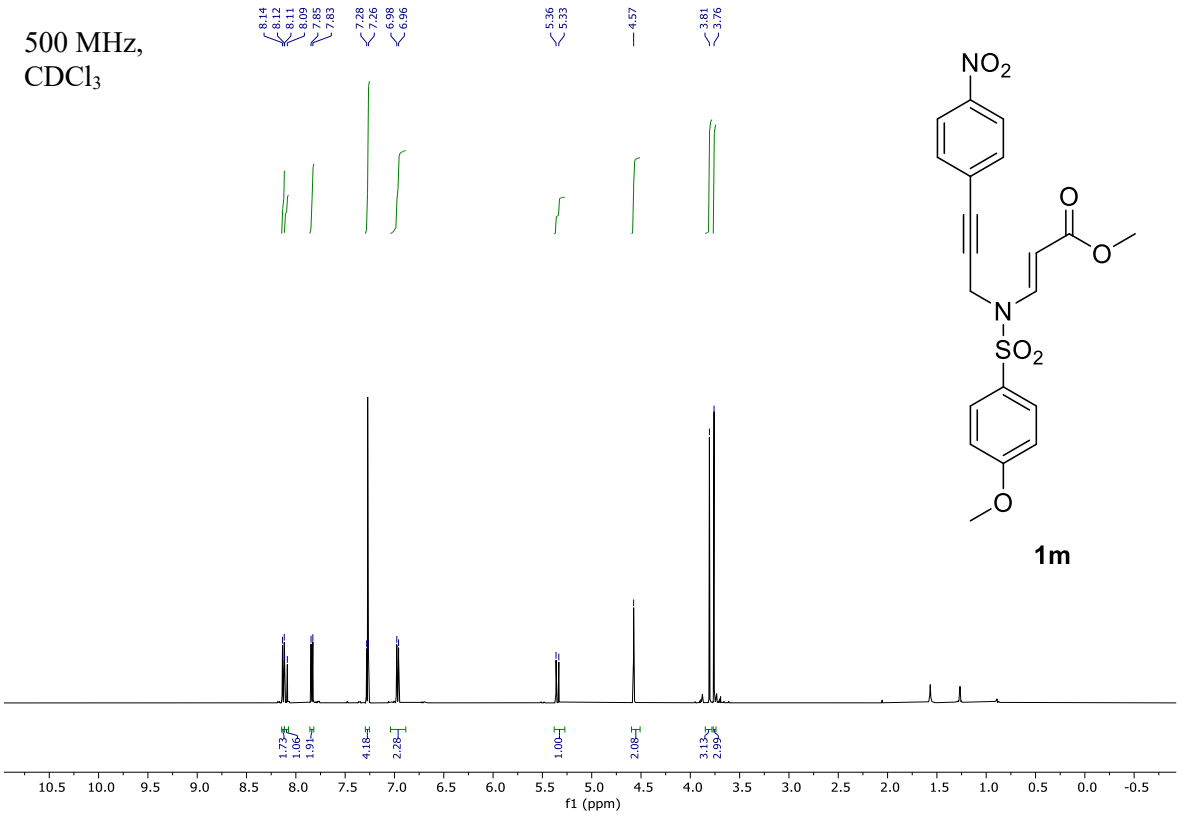
1*l*

125.7 MHz,
$CDCl_3$



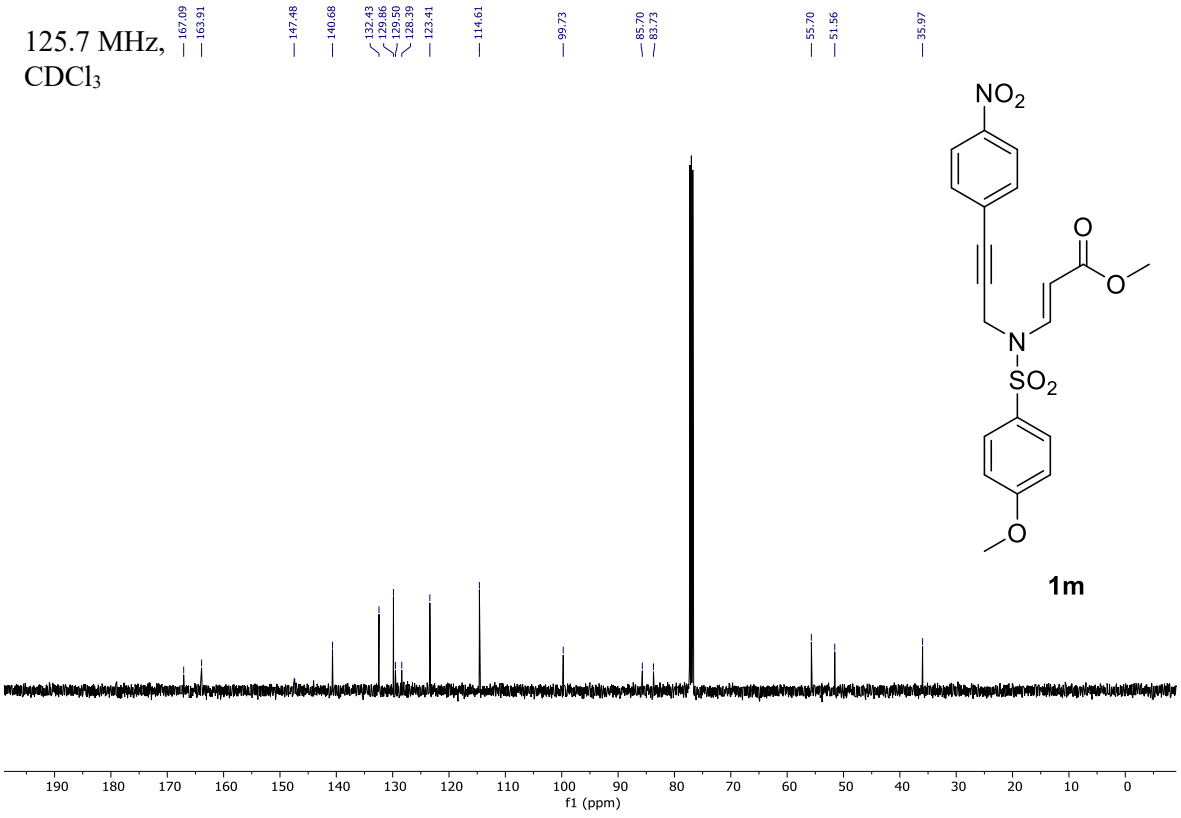
1*l*

500 MHz,
$CDCl_3$



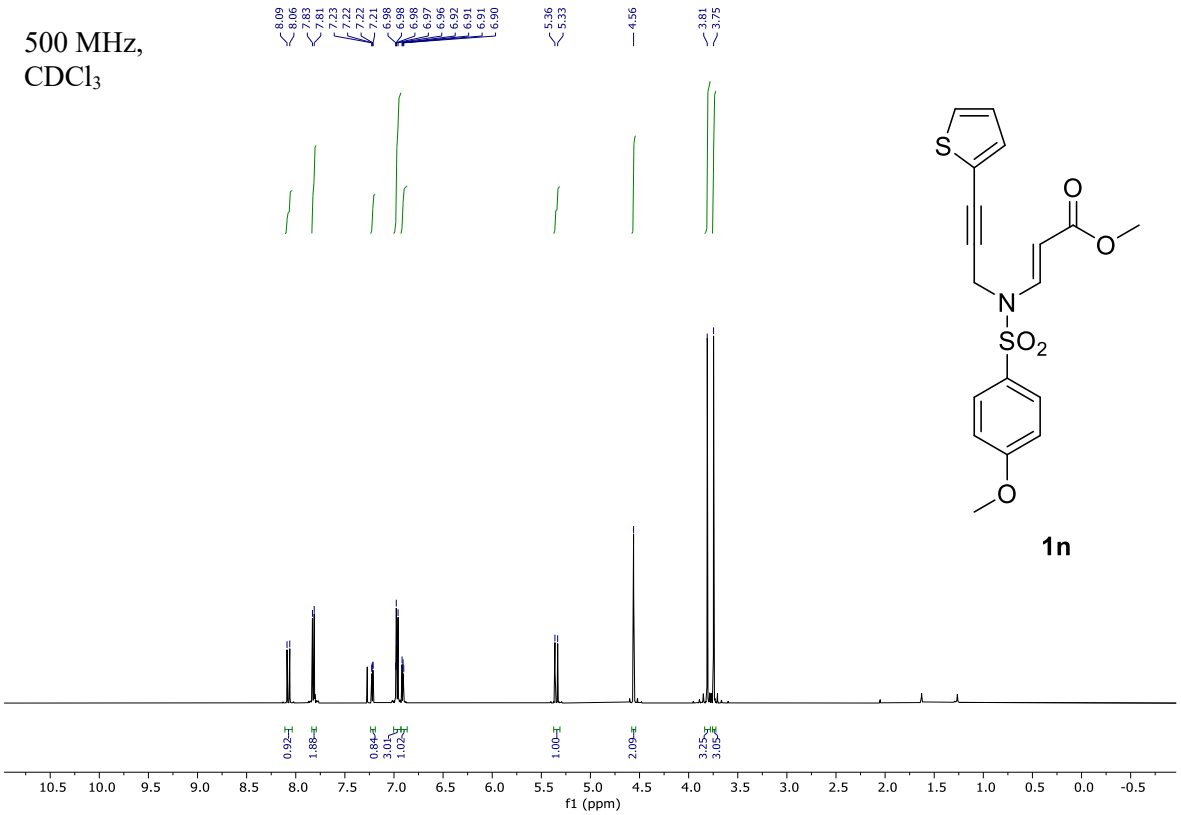
1m

125.7 MHz,
$CDCl_3$



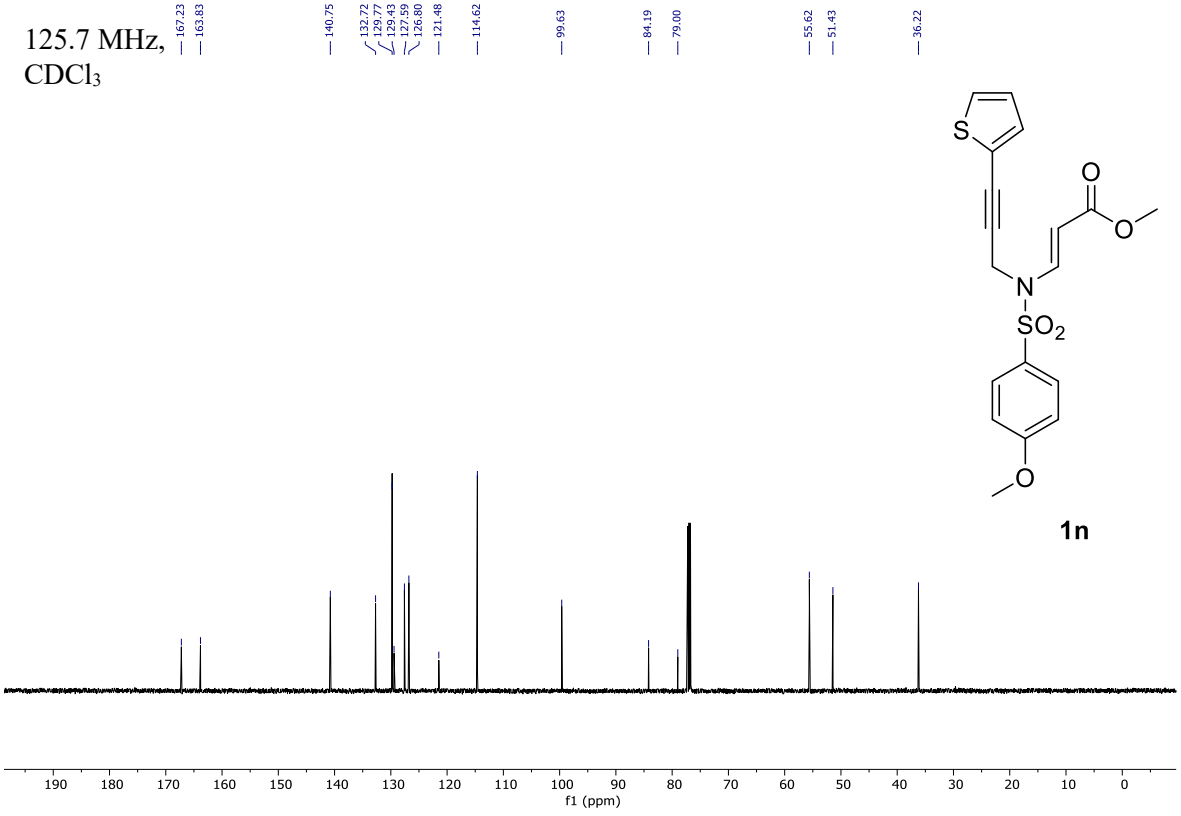
1m

500 MHz,
$CDCl_3$



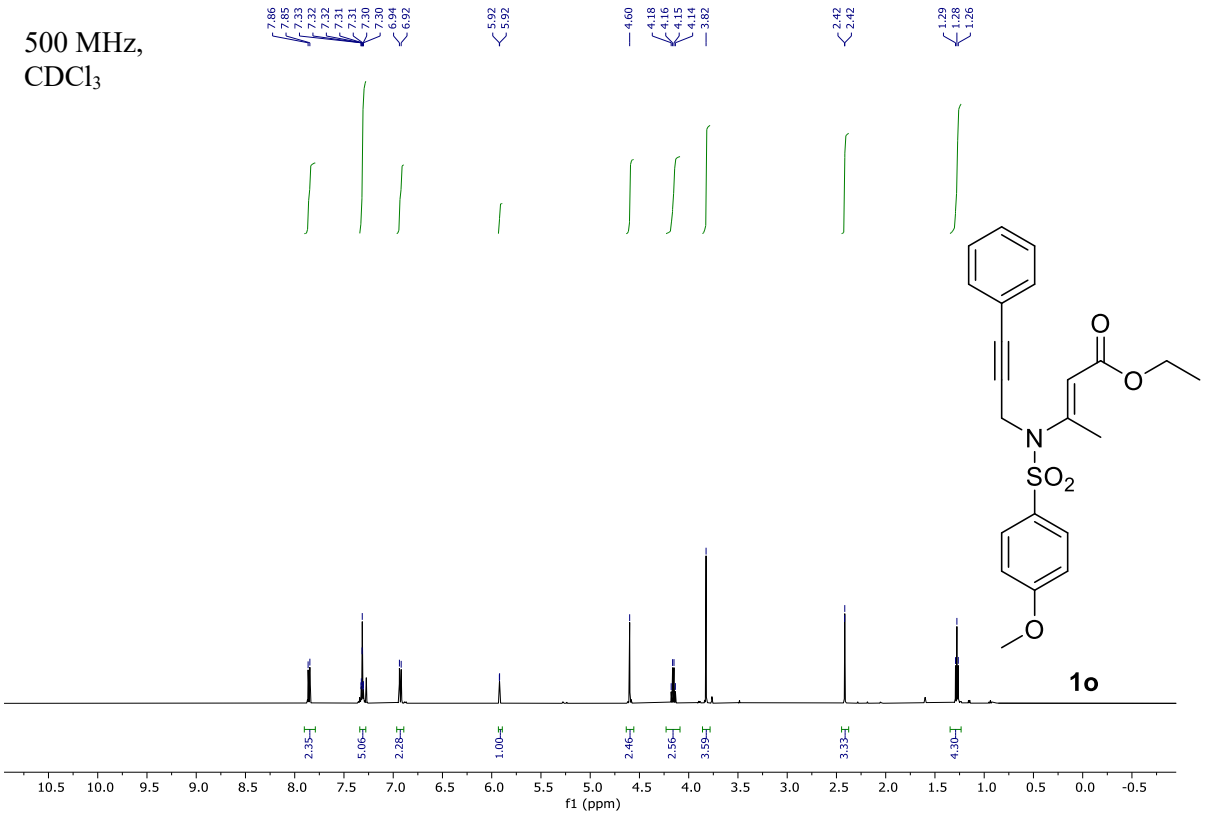
1n

125.7 MHz,
$CDCl_3$

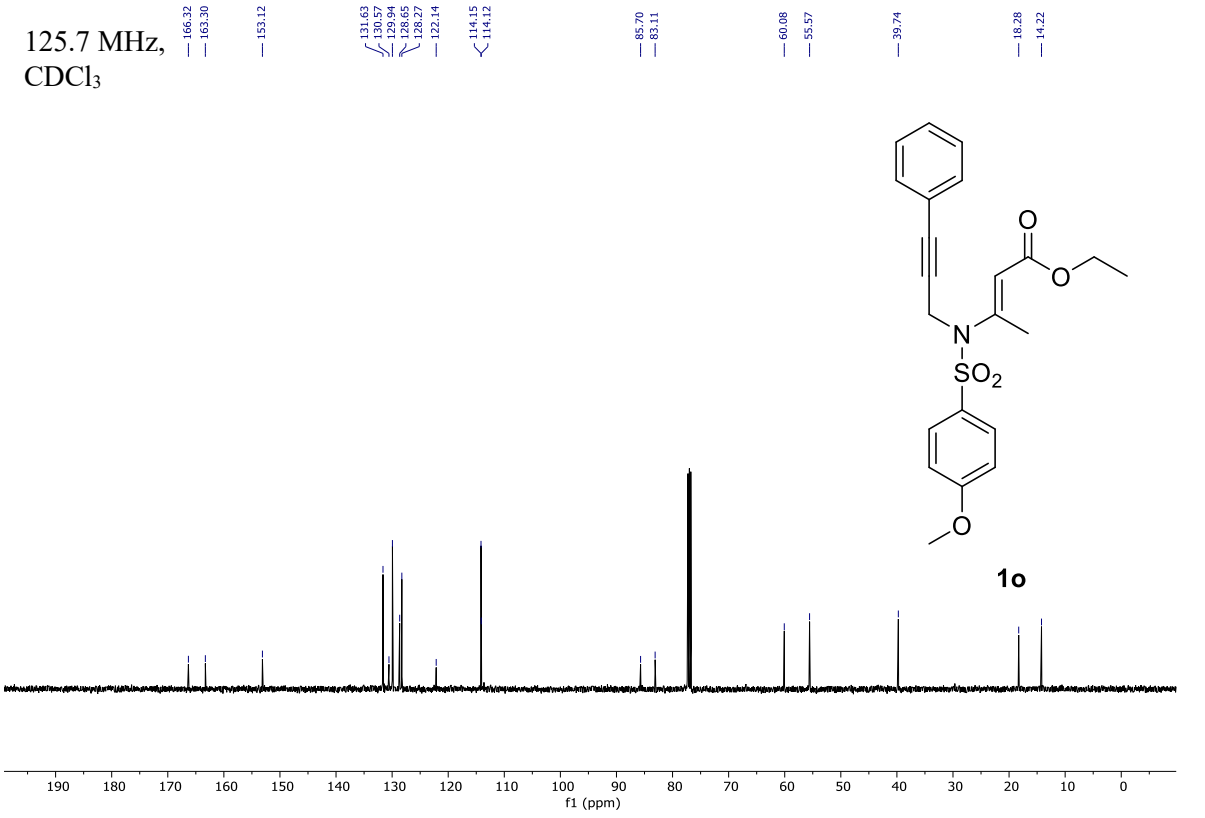


1n

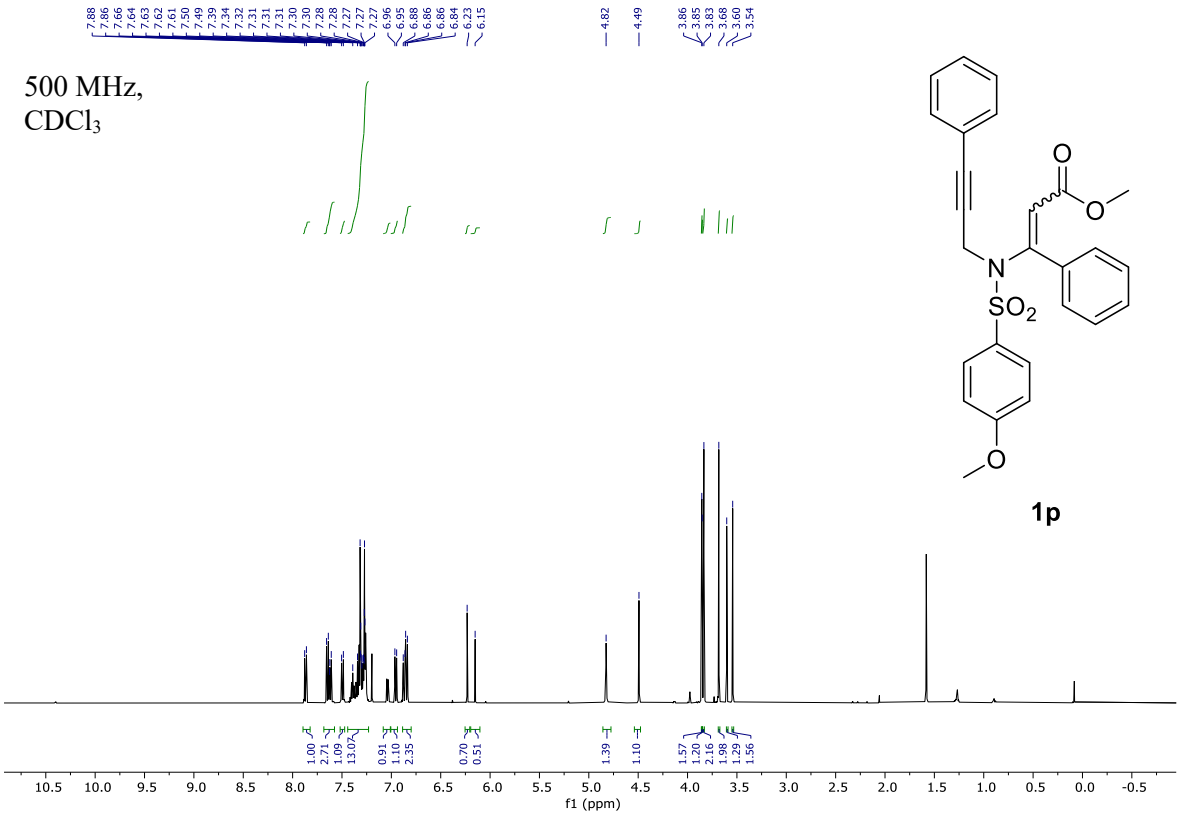
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

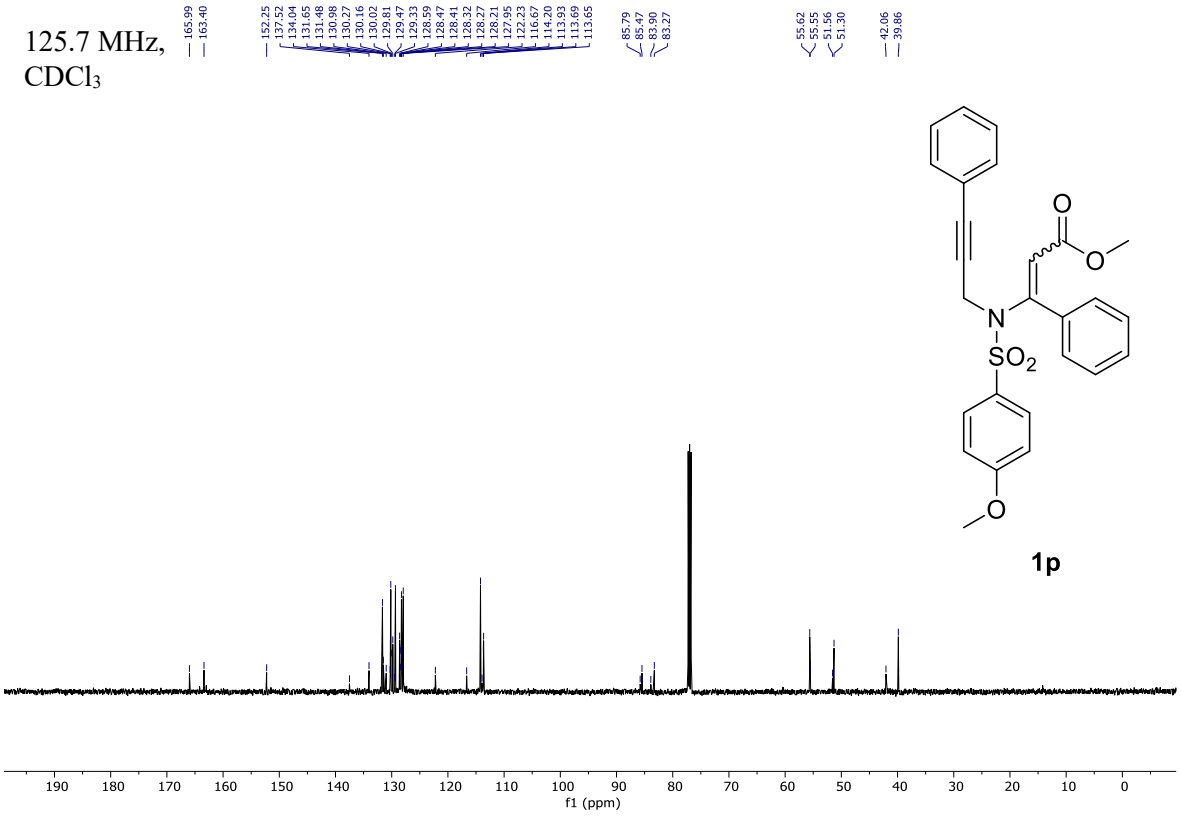


500 MHz,
$CDCl_3$



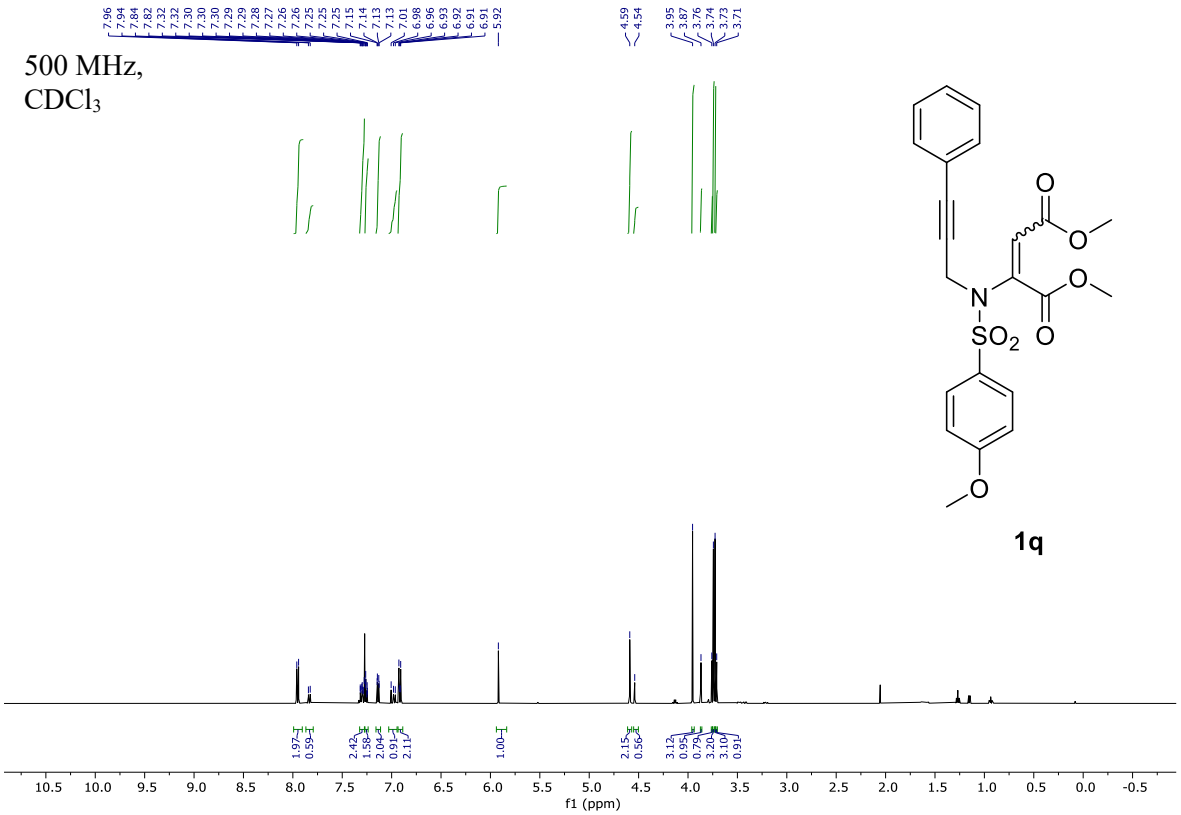
1p

125.7 MHz,
$CDCl_3$



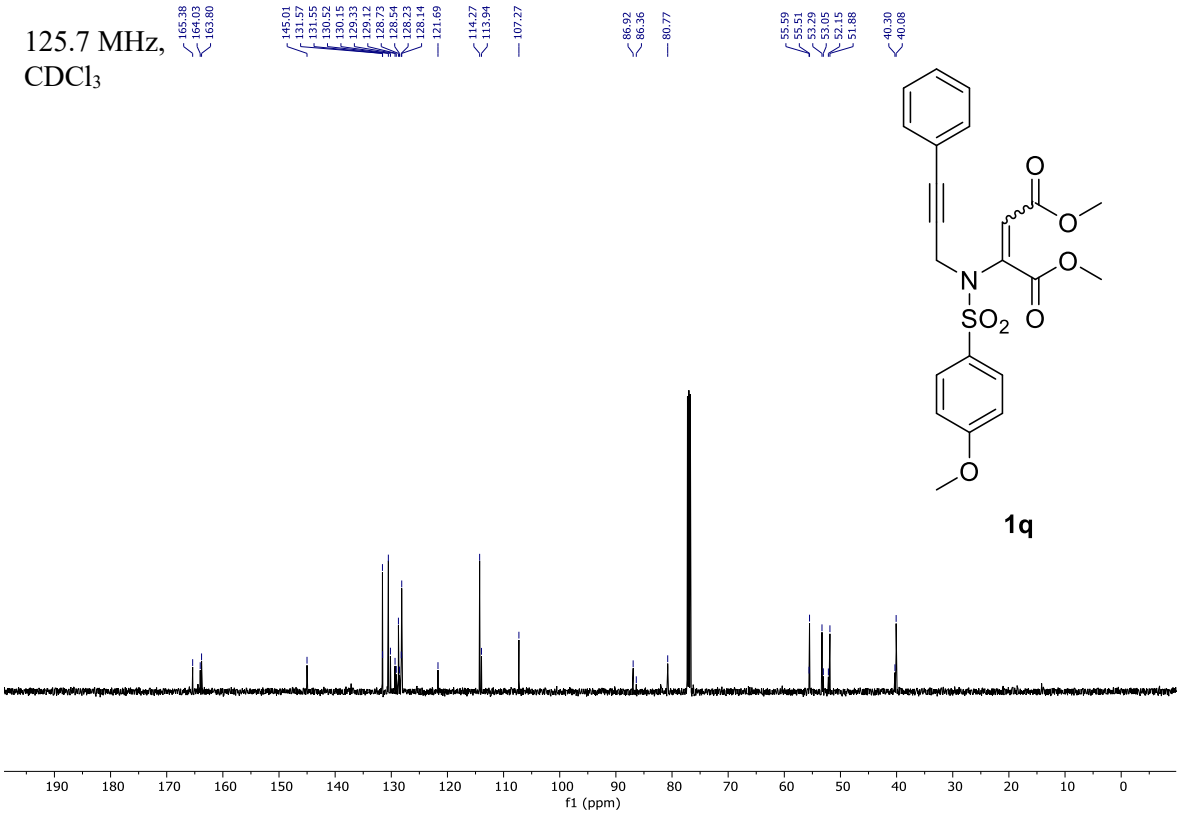
1p

500 MHz,
$CDCl_3$



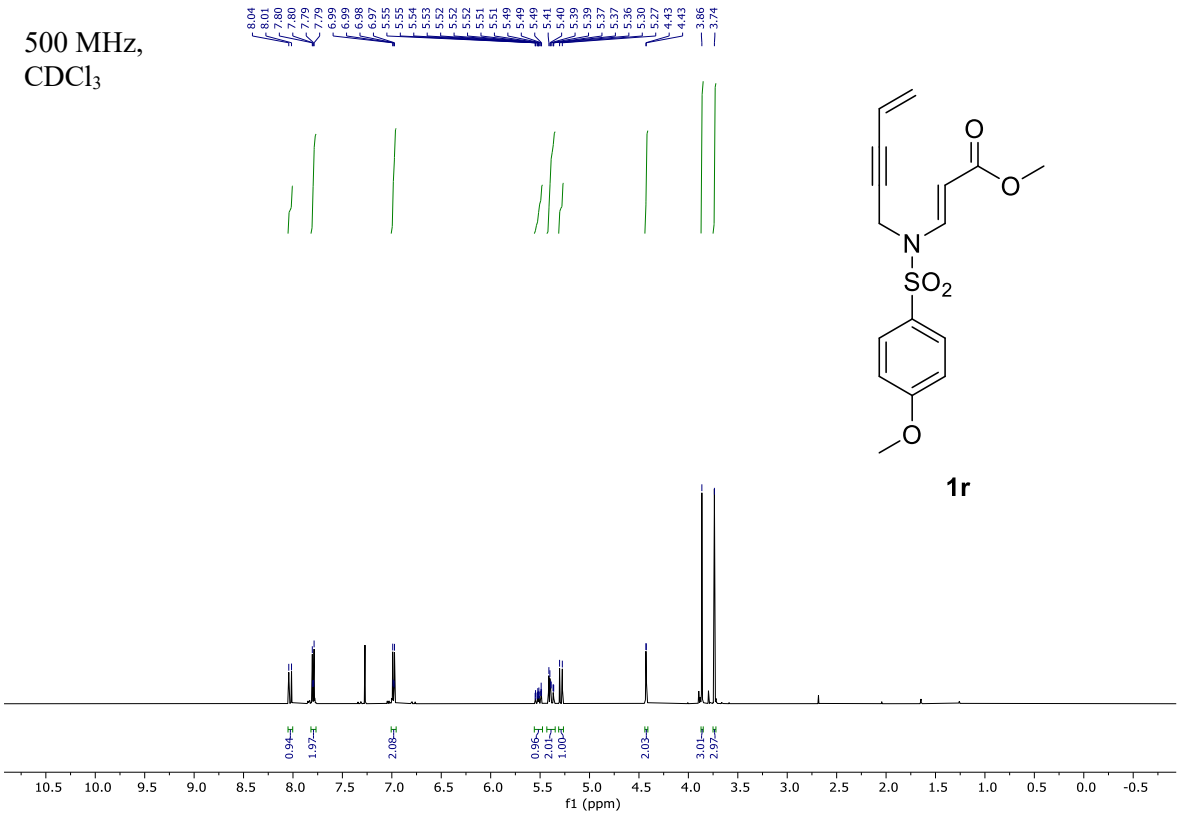
1q

125.7 MHz,
$CDCl_3$



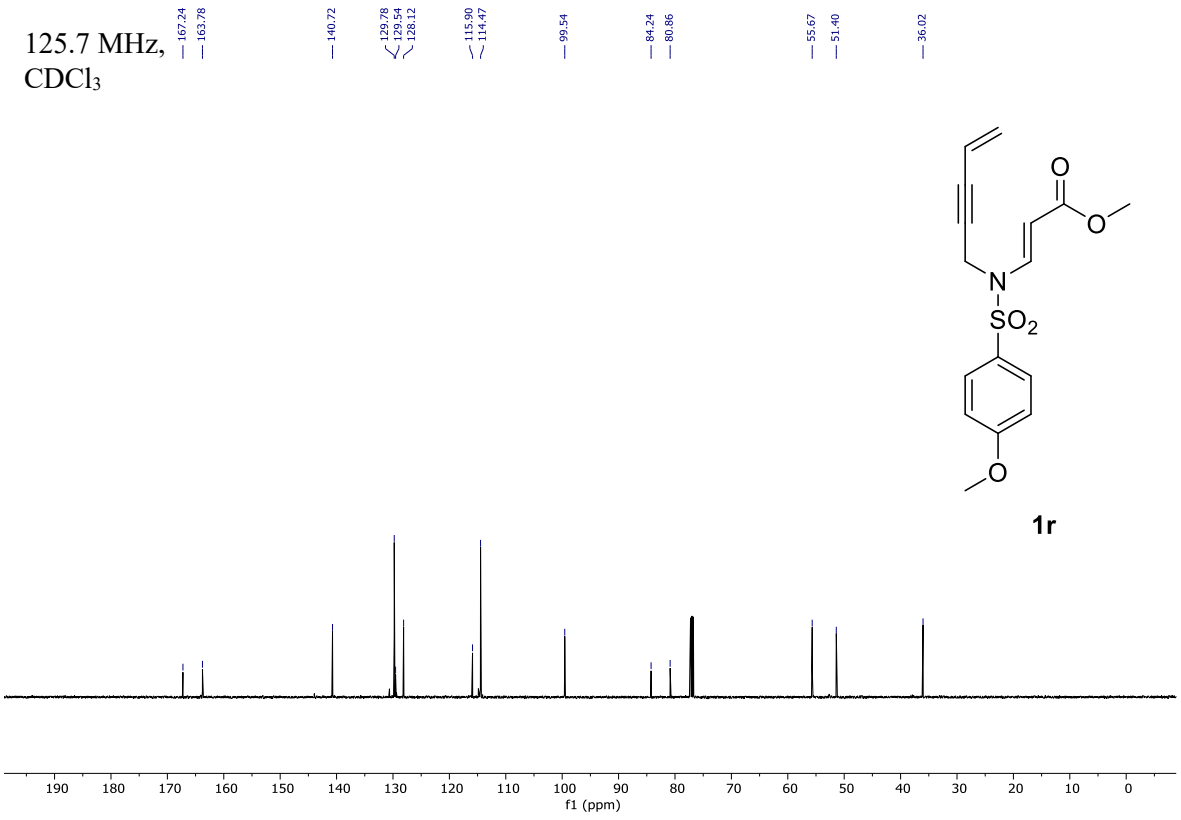
1q

500 MHz,
$CDCl_3$



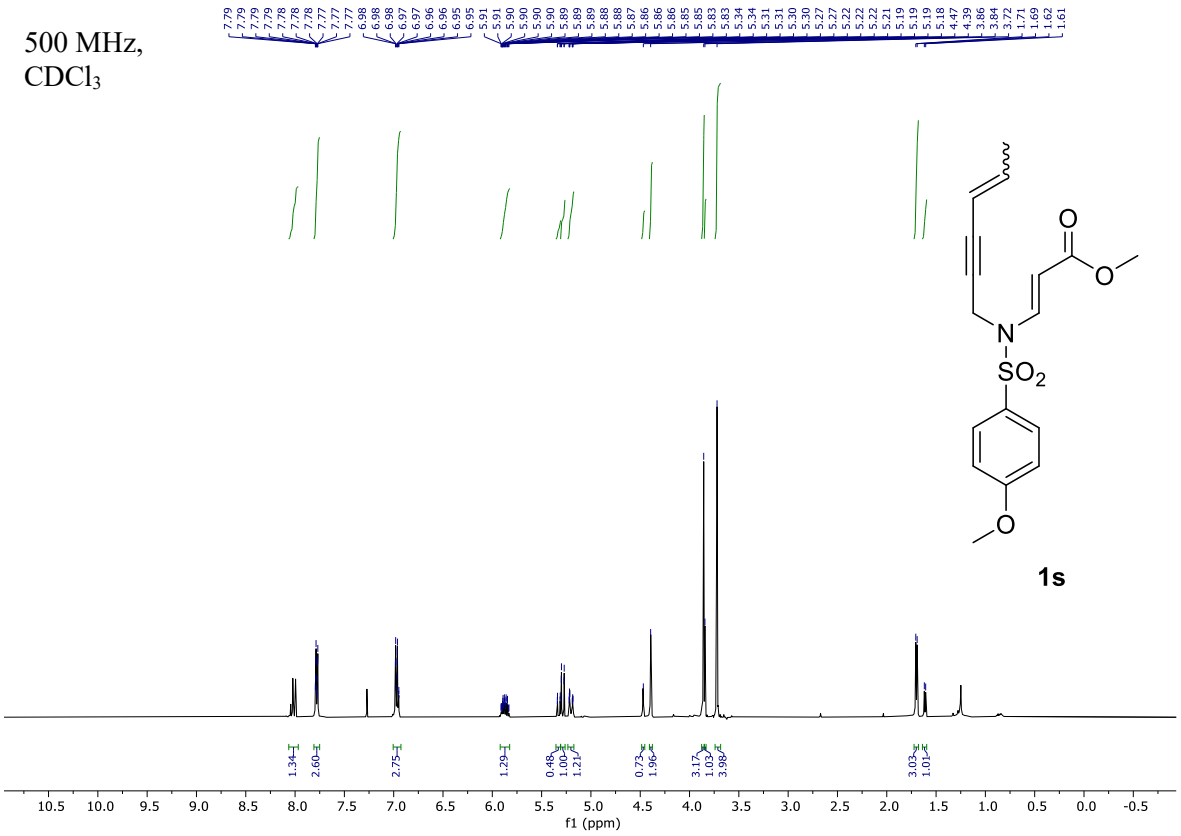
1r

125.7 MHz,
$CDCl_3$

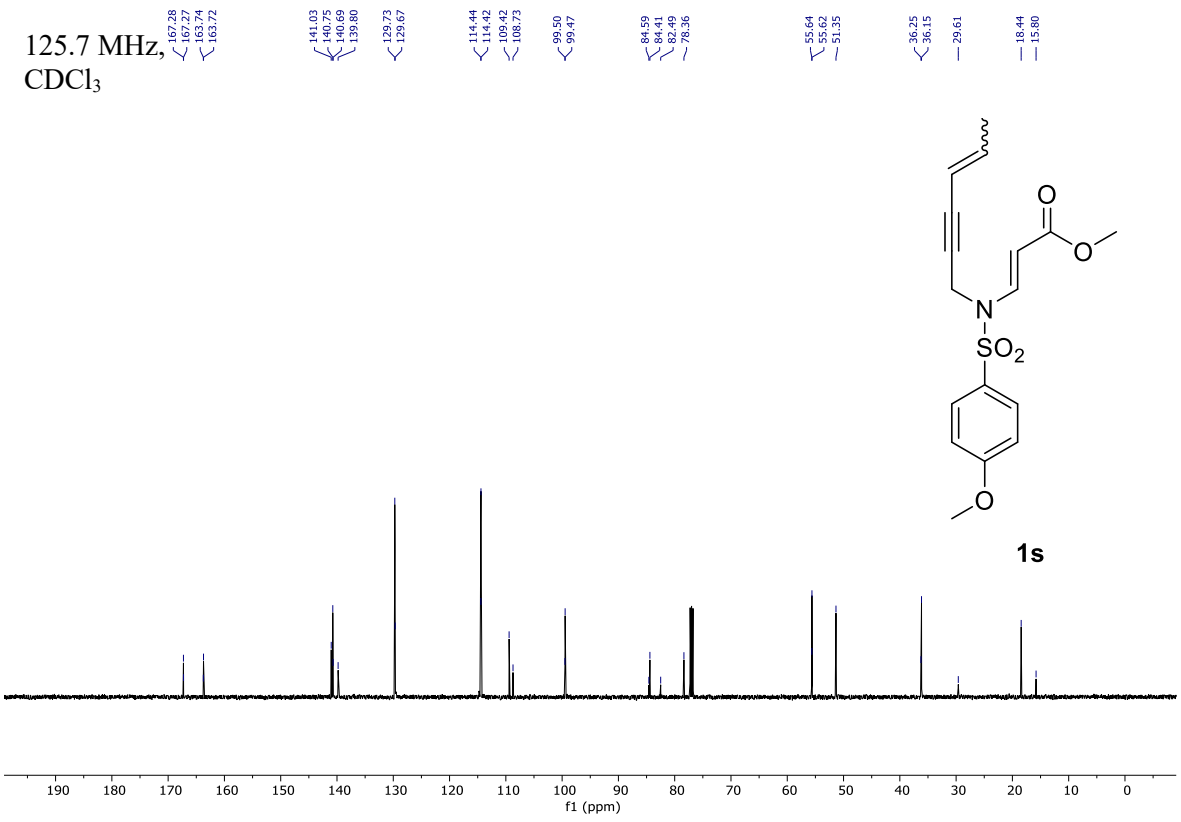


1r

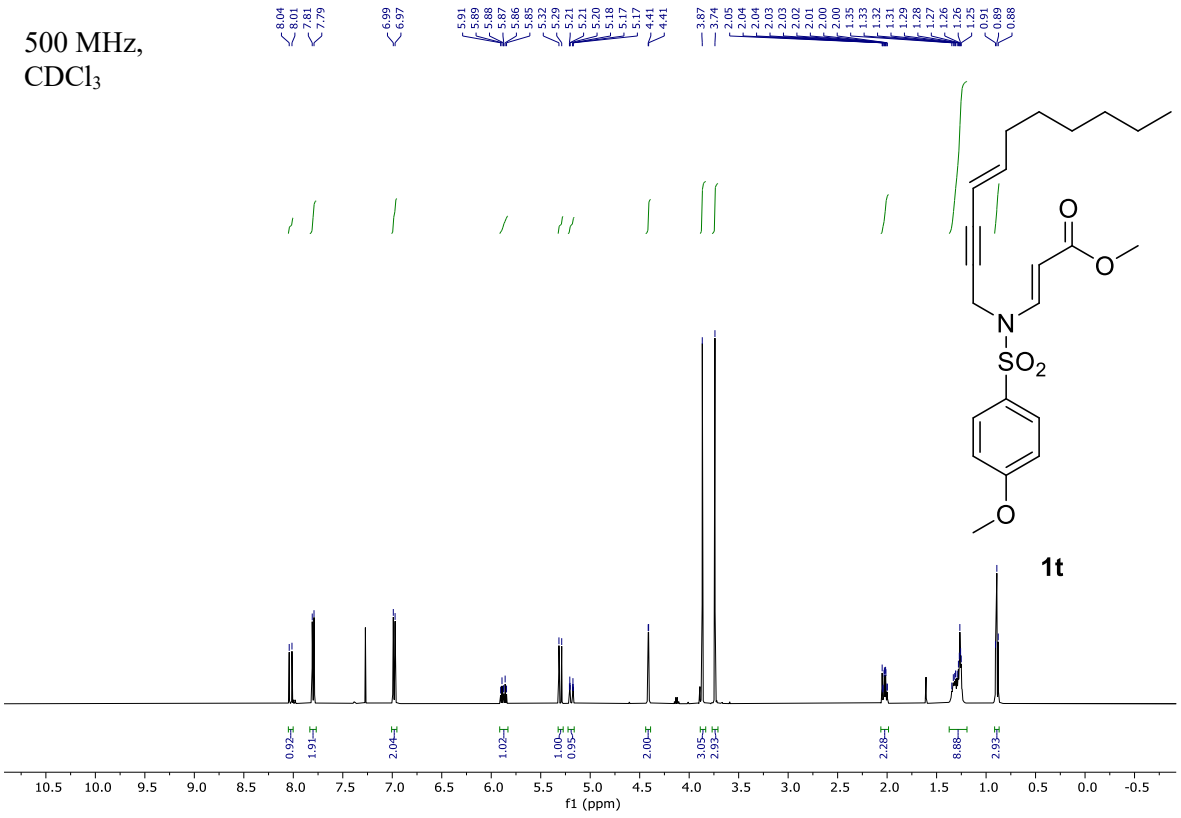
500 MHz,
$CDCl_3$



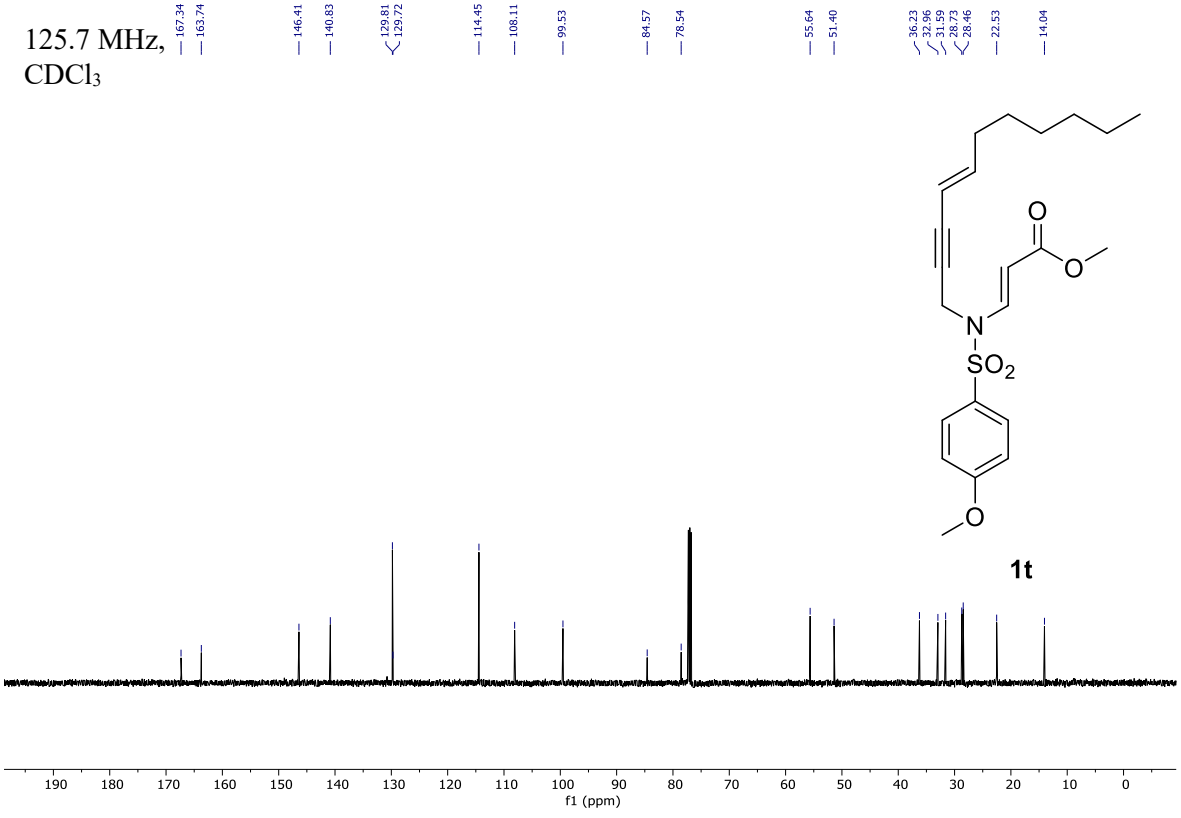
125.7 MHz,
$CDCl_3$



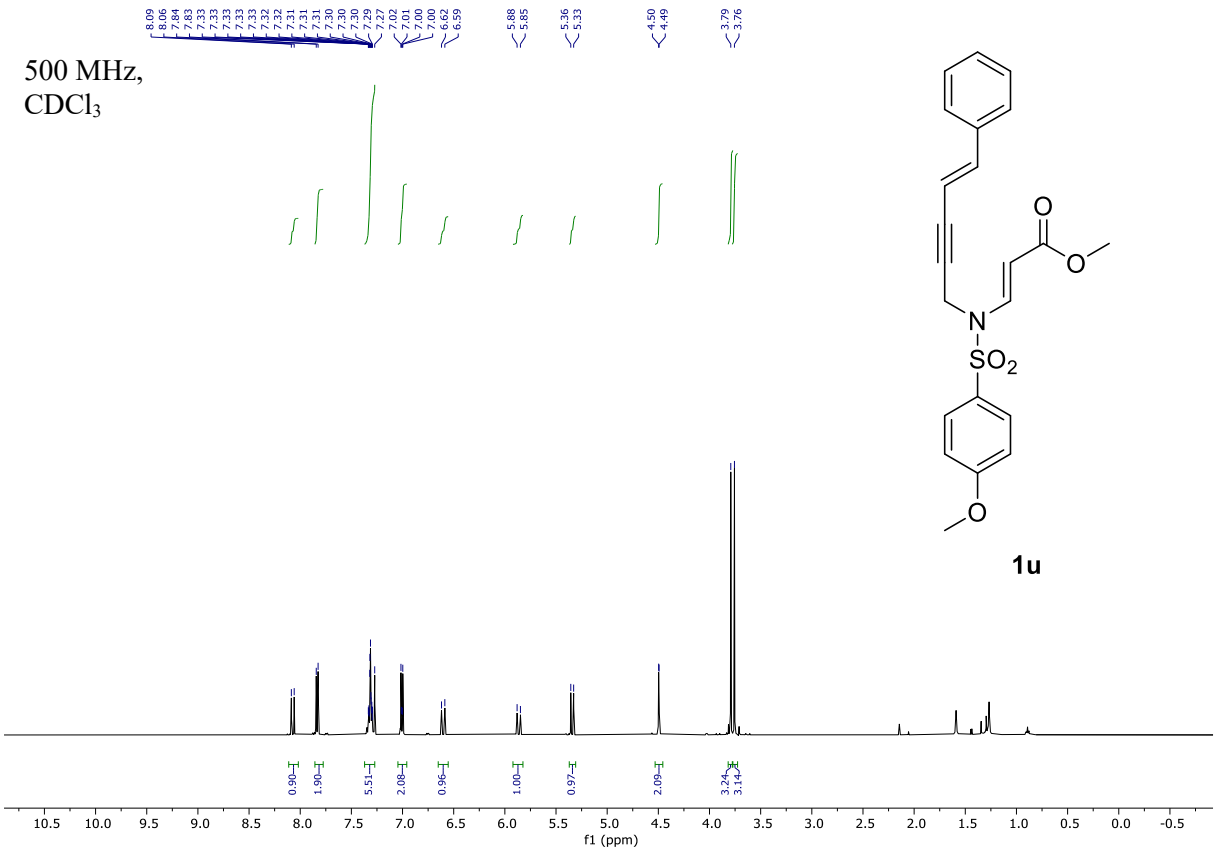
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

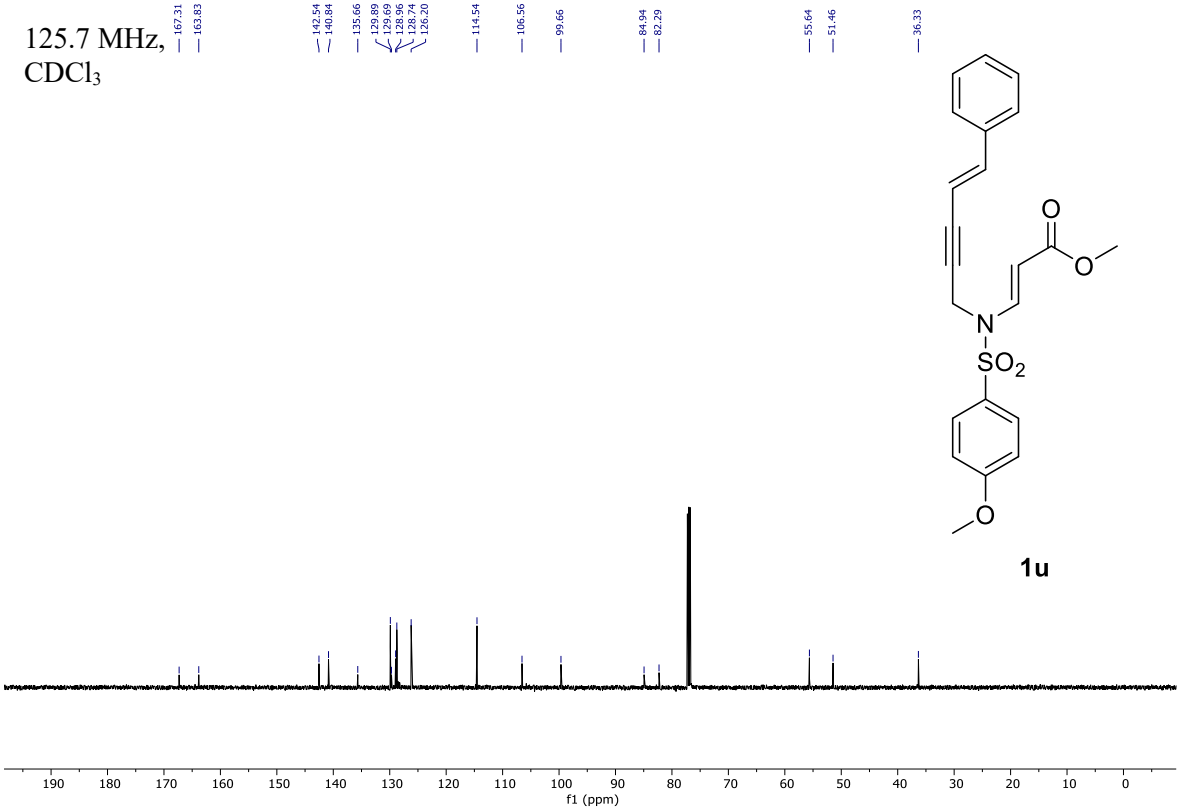


500 MHz,
$CDCl_3$



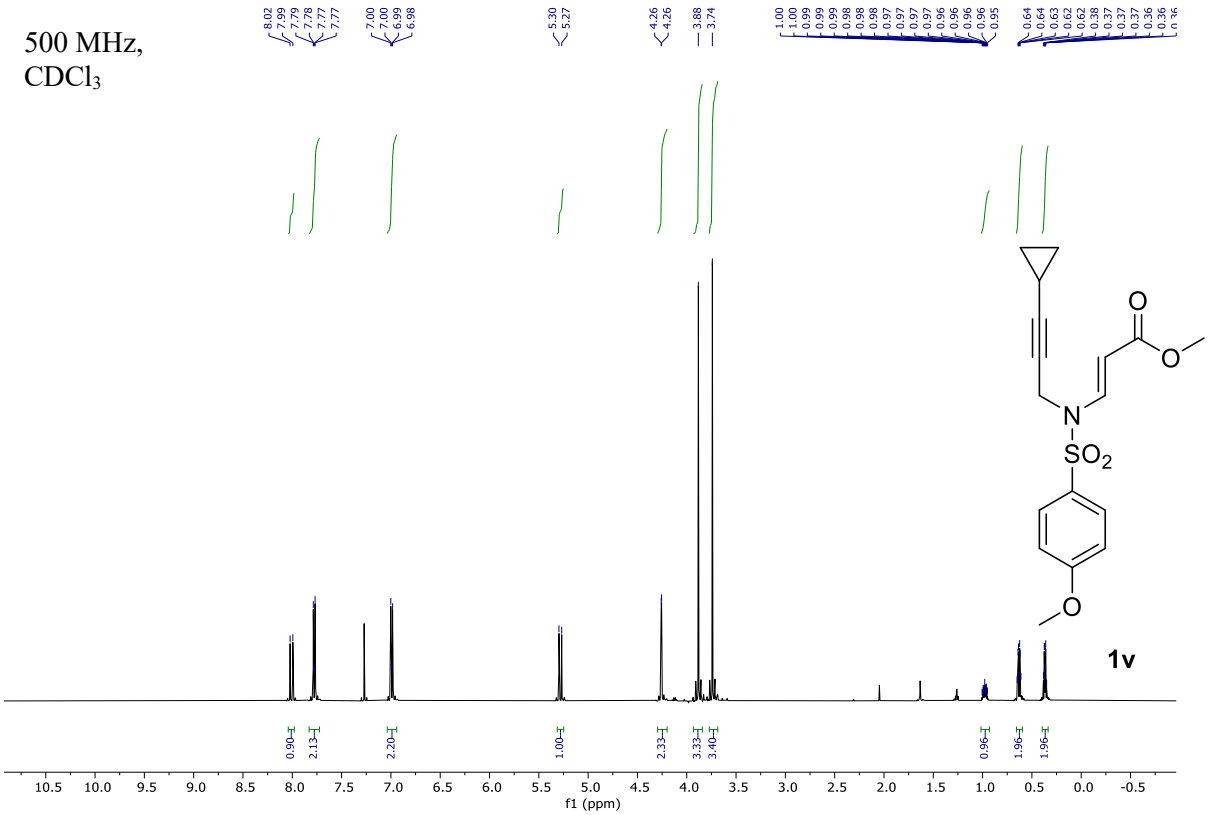
1u

125.7 MHz,
$CDCl_3$

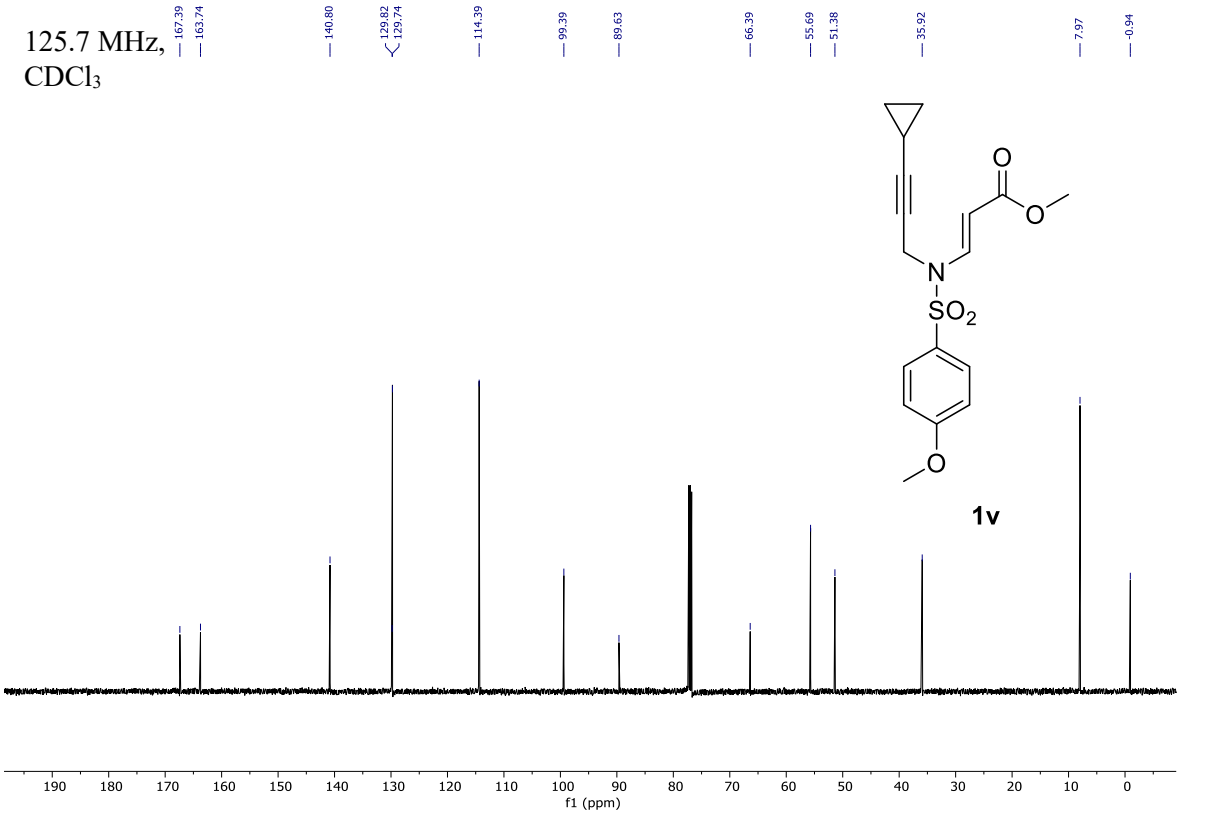


1u

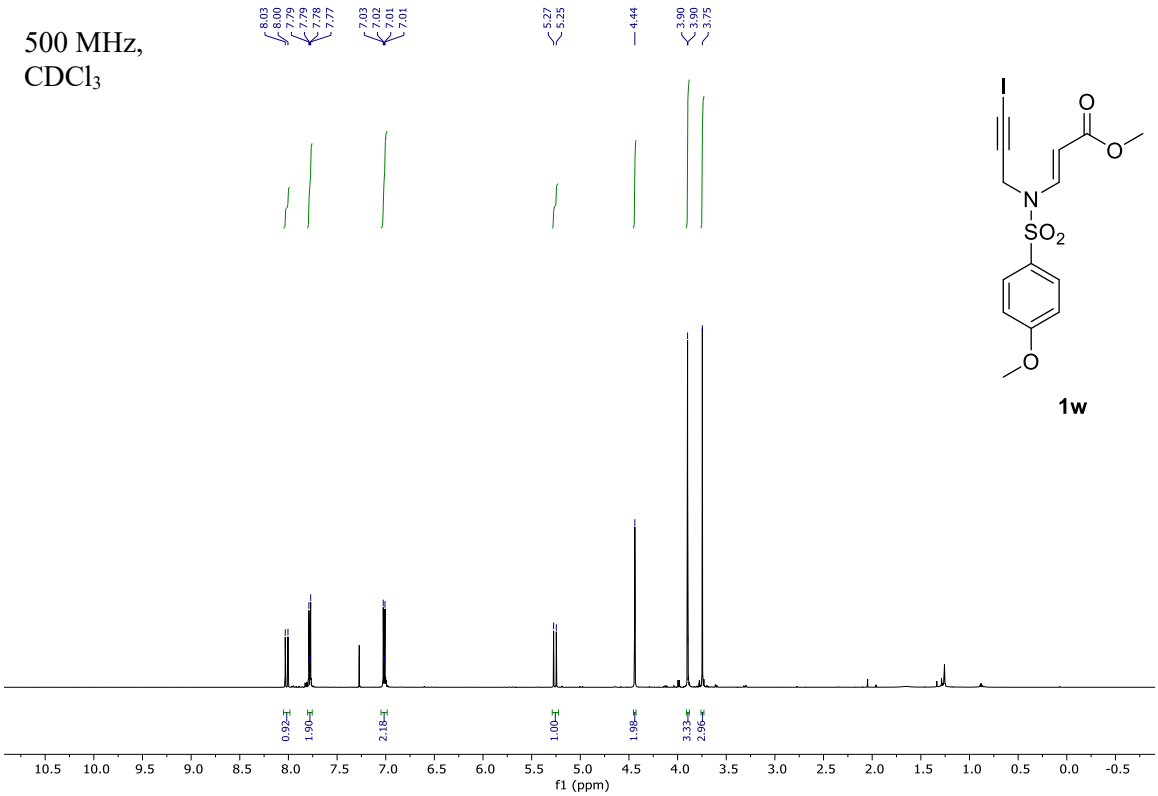
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

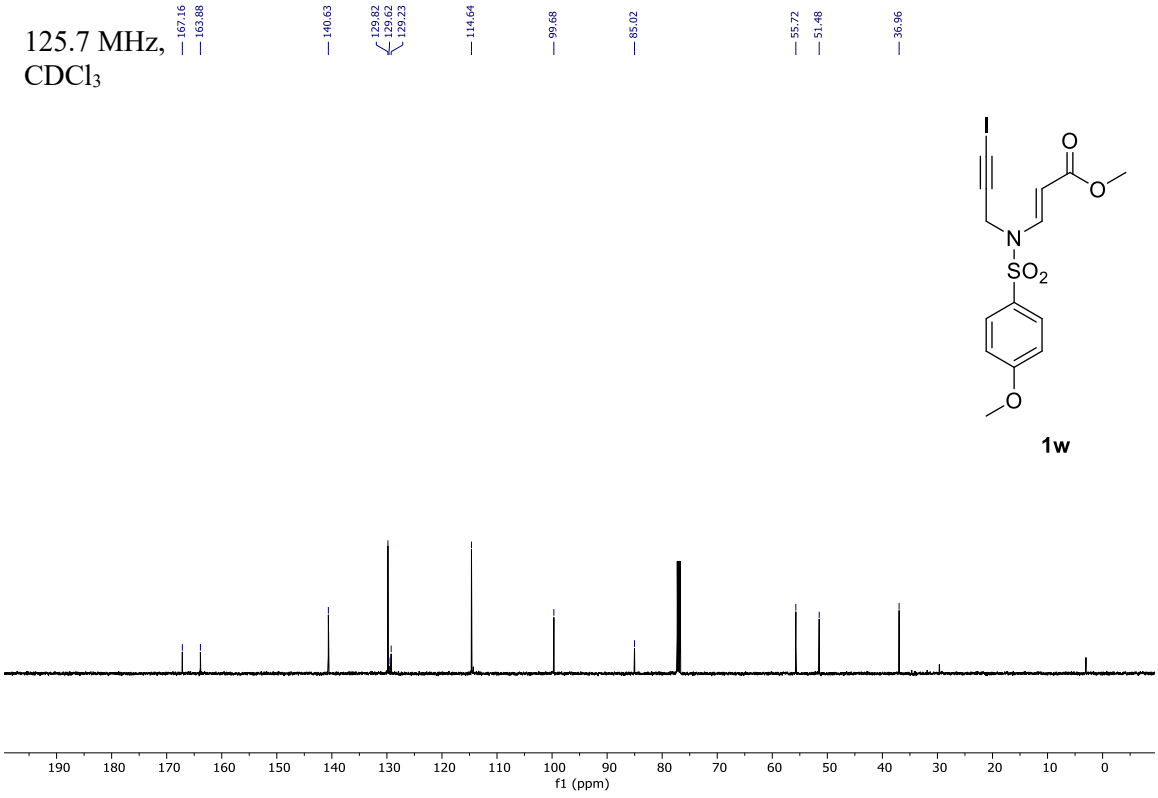


500 MHz,
$CDCl_3$



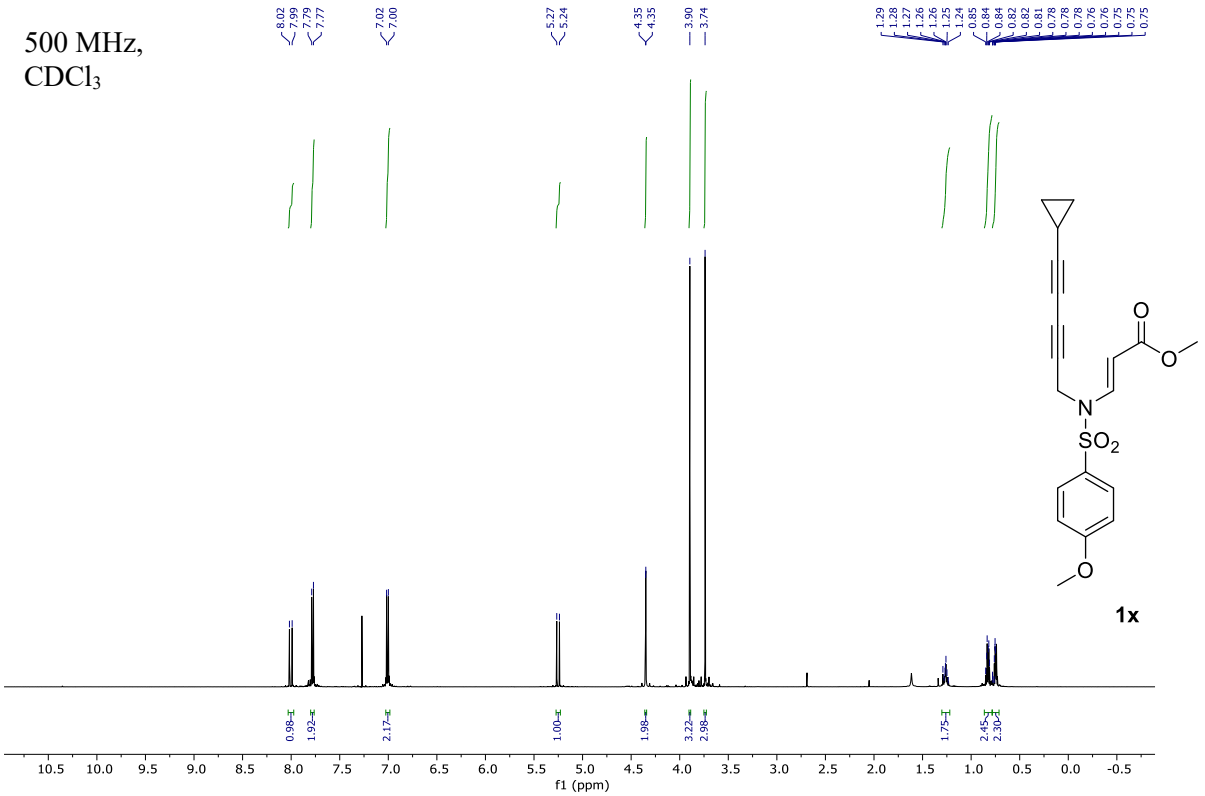
1w

125.7 MHz,
$CDCl_3$

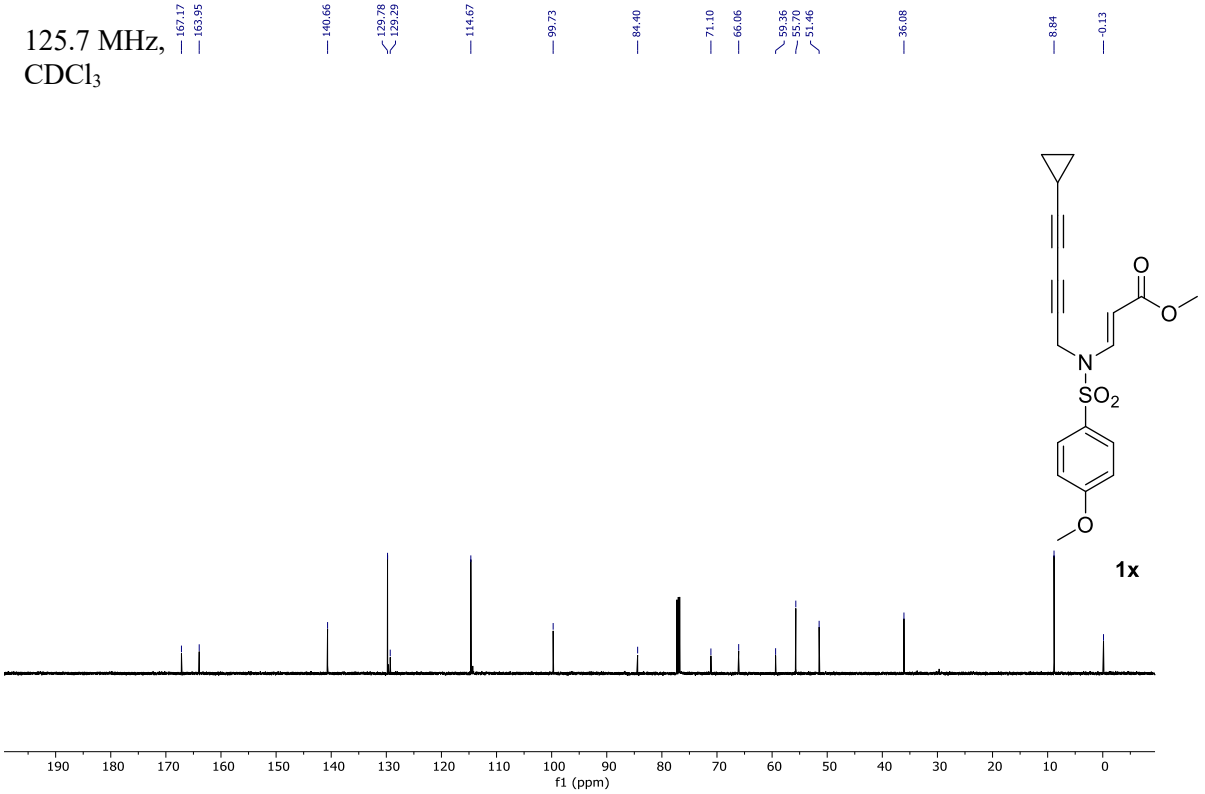


1w

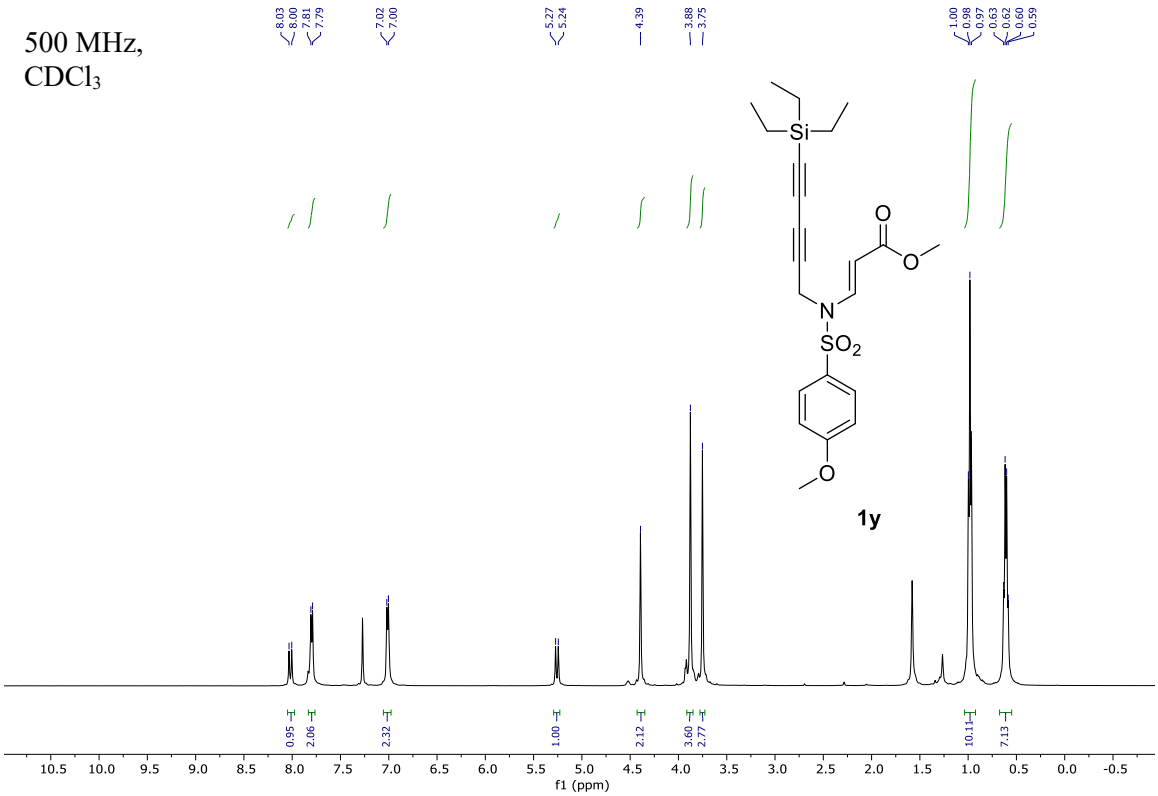
500 MHz,
$CDCl_3$



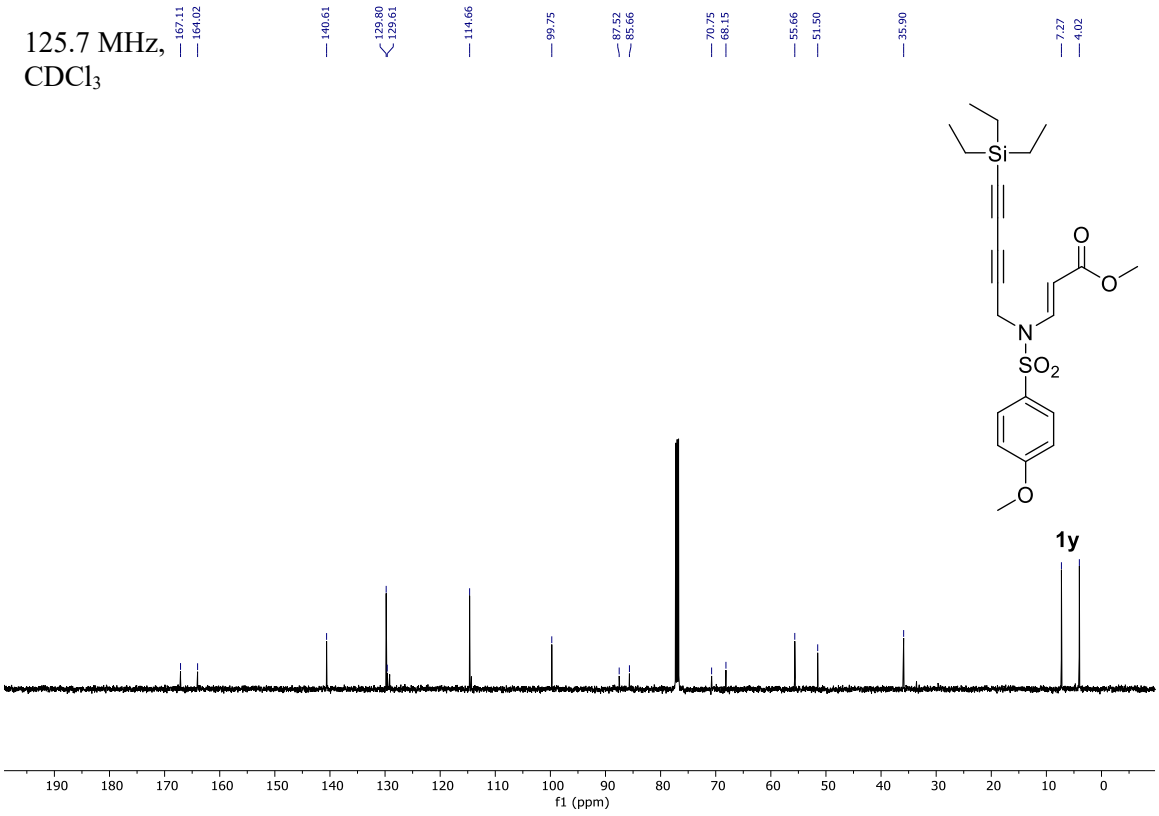
125.7 MHz,
$CDCl_3$



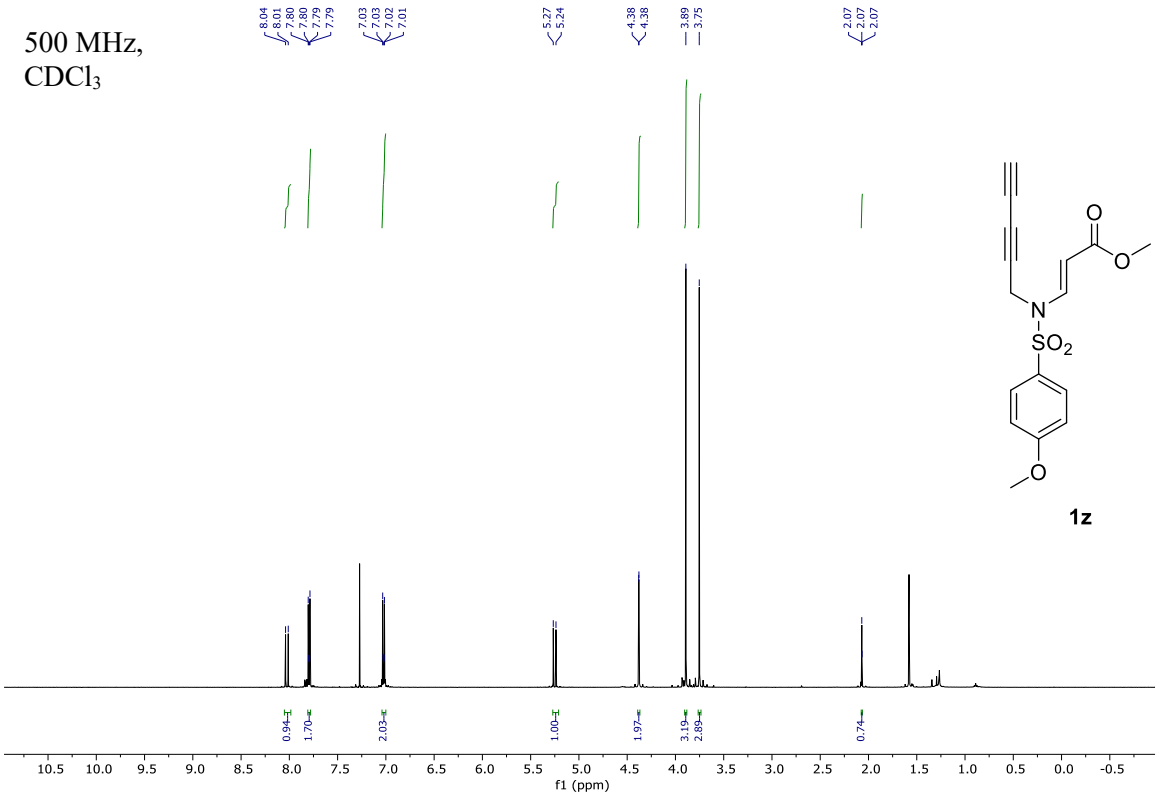
500 MHz,
$CDCl_3$



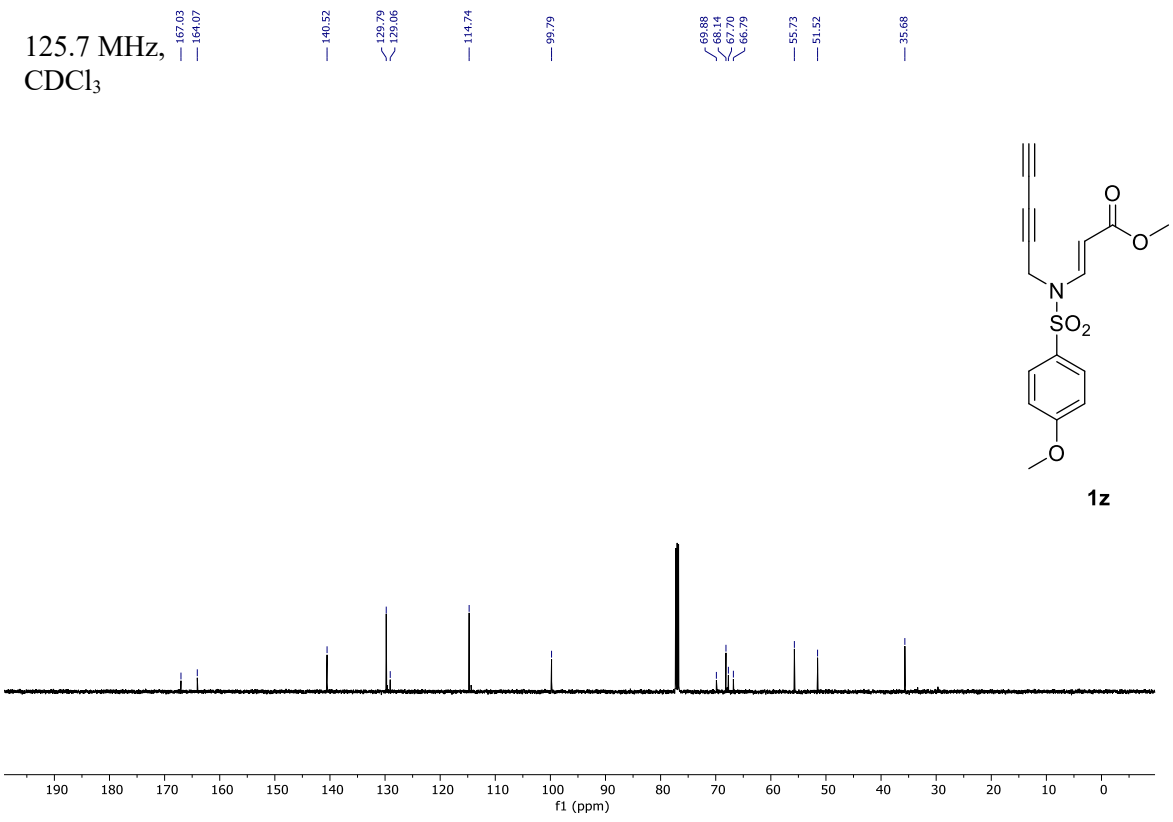
125.7 MHz,
$CDCl_3$



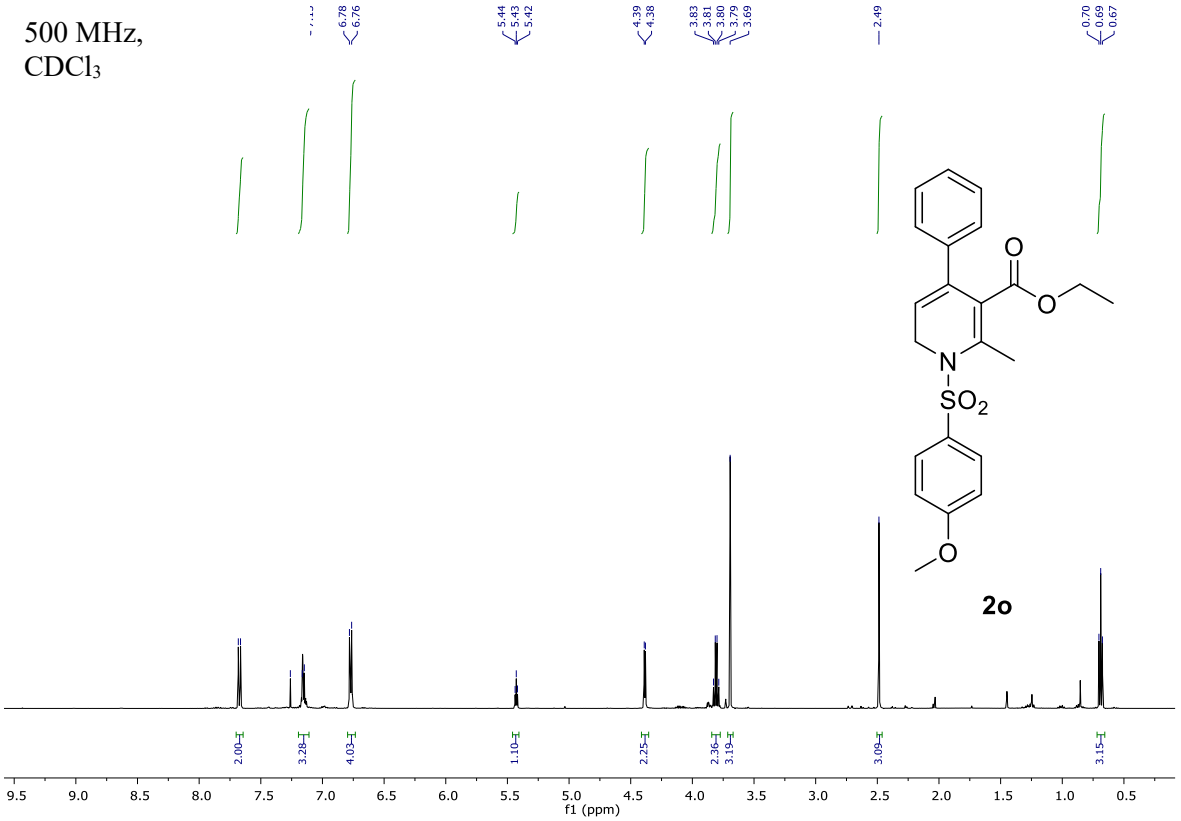
500 MHz,
$CDCl_3$



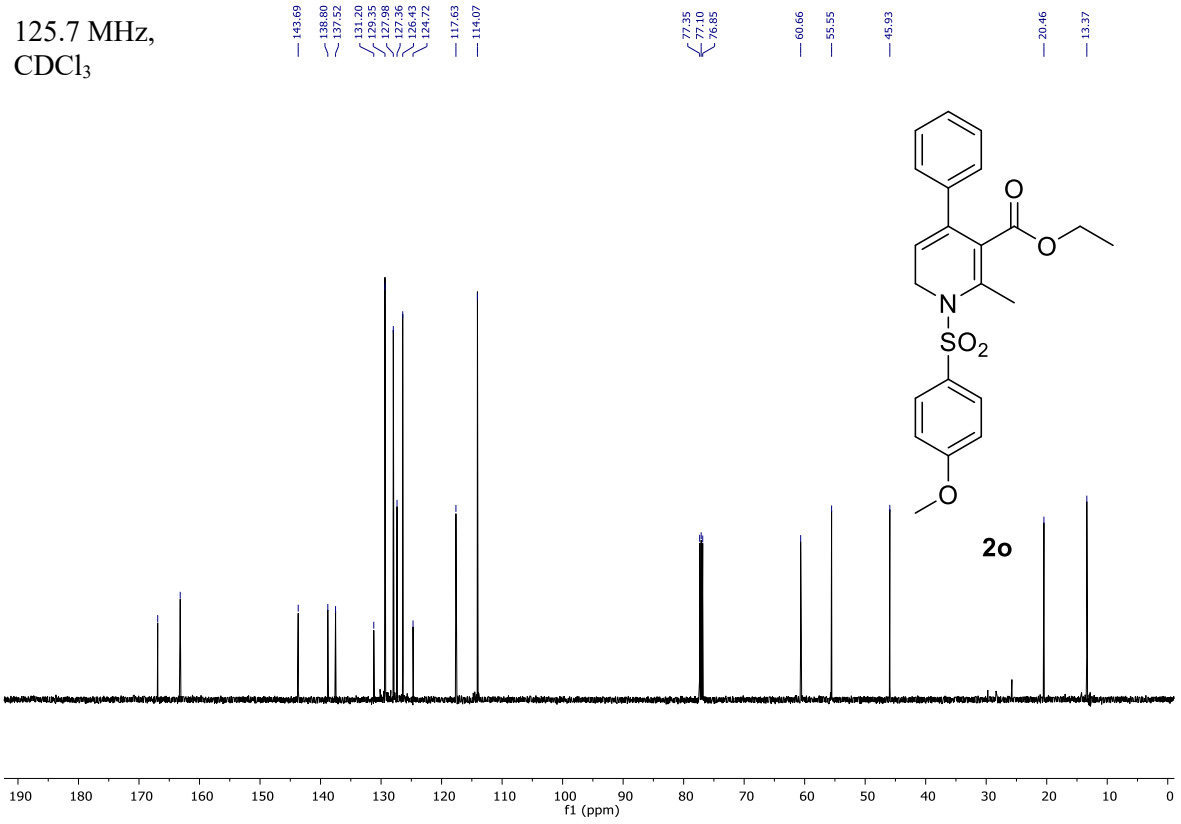
125.7 MHz,
$CDCl_3$



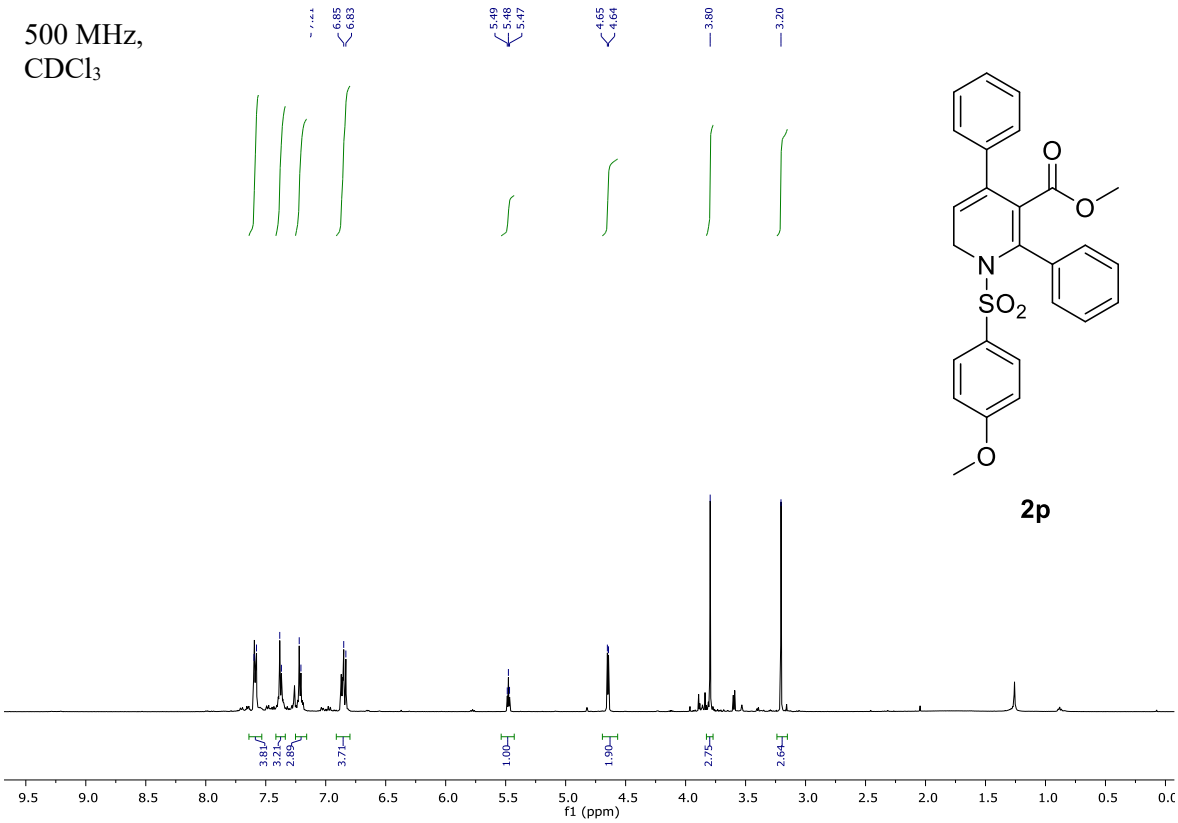
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

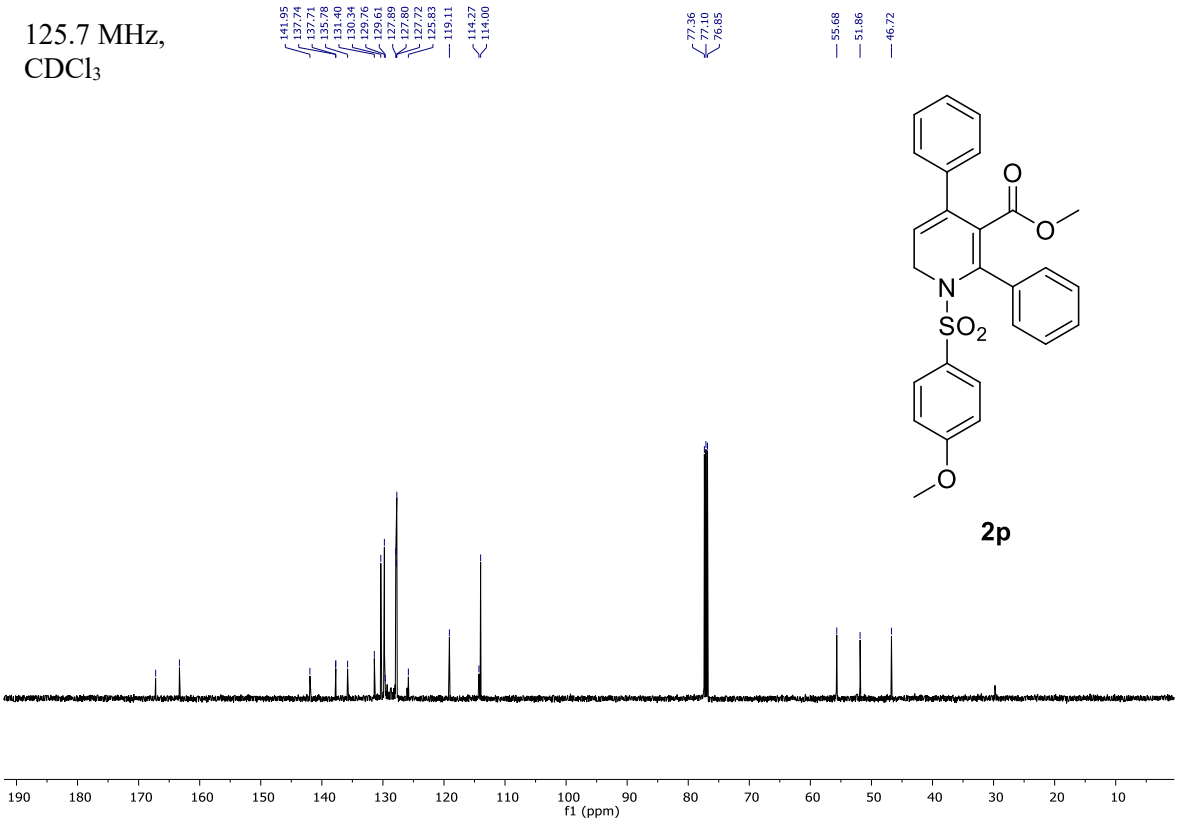


500 MHz,
$CDCl_3$



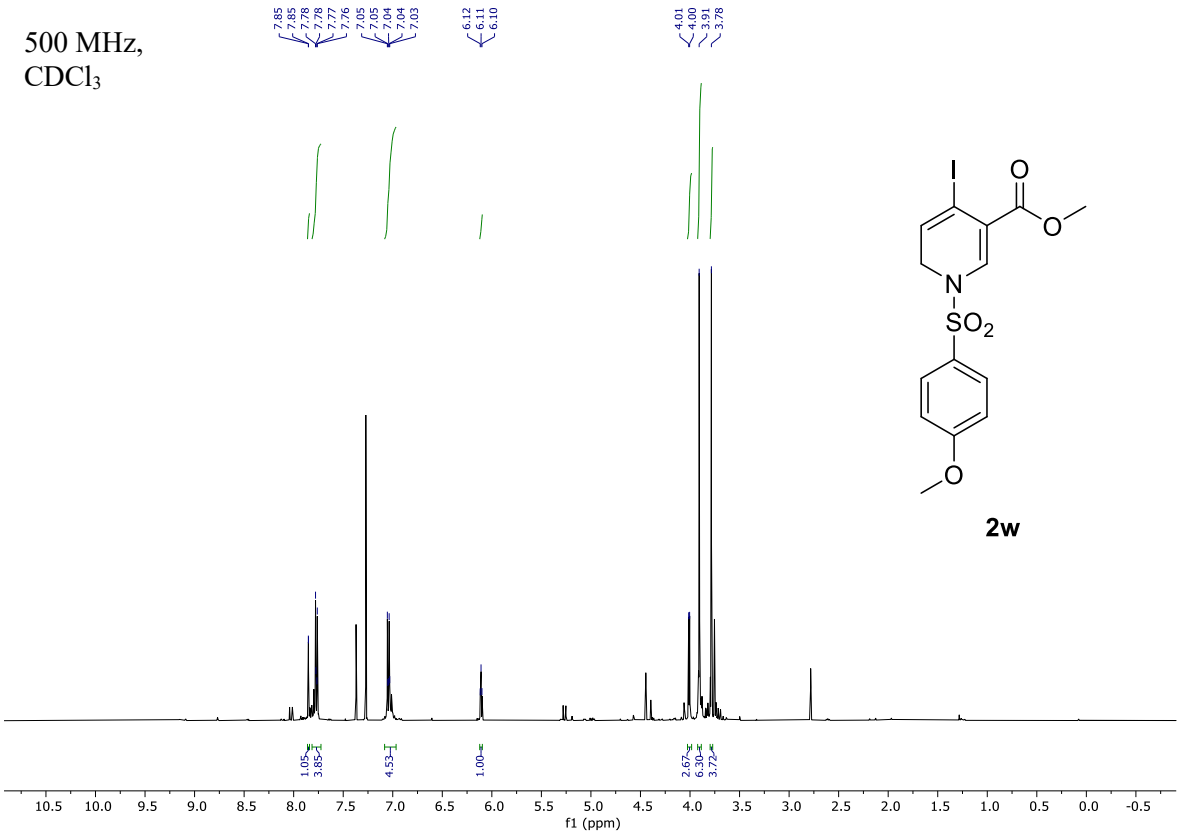
2p

125.7 MHz,
$CDCl_3$



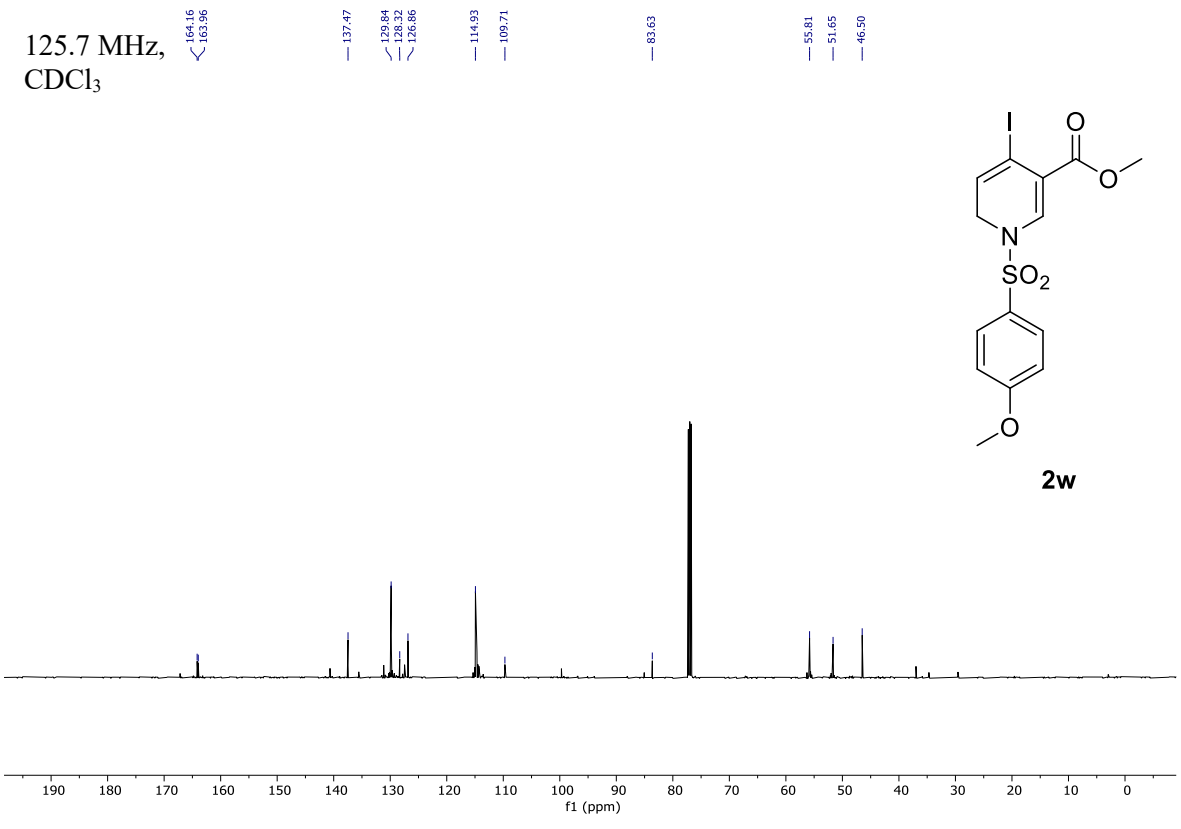
2p

500 MHz,
$CDCl_3$



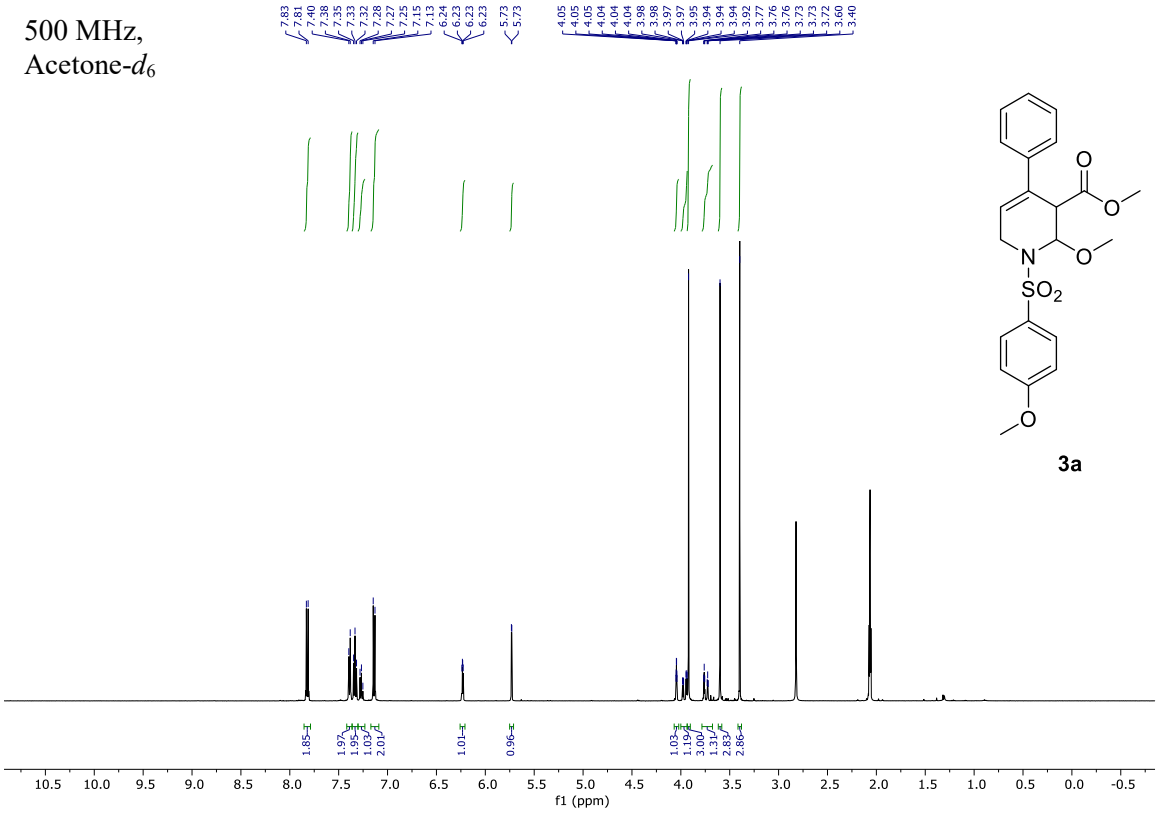
2w

125.7 MHz,
$CDCl_3$



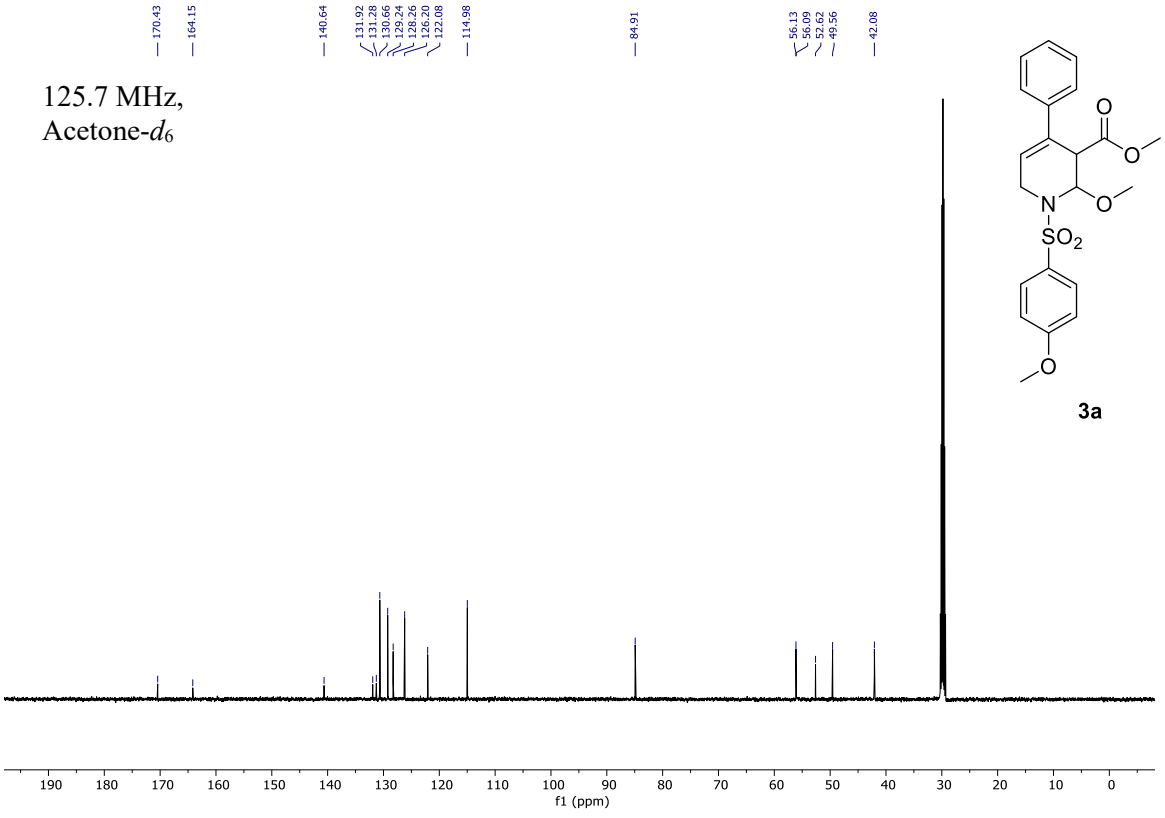
2w

500 MHz,
Acetone-d_6



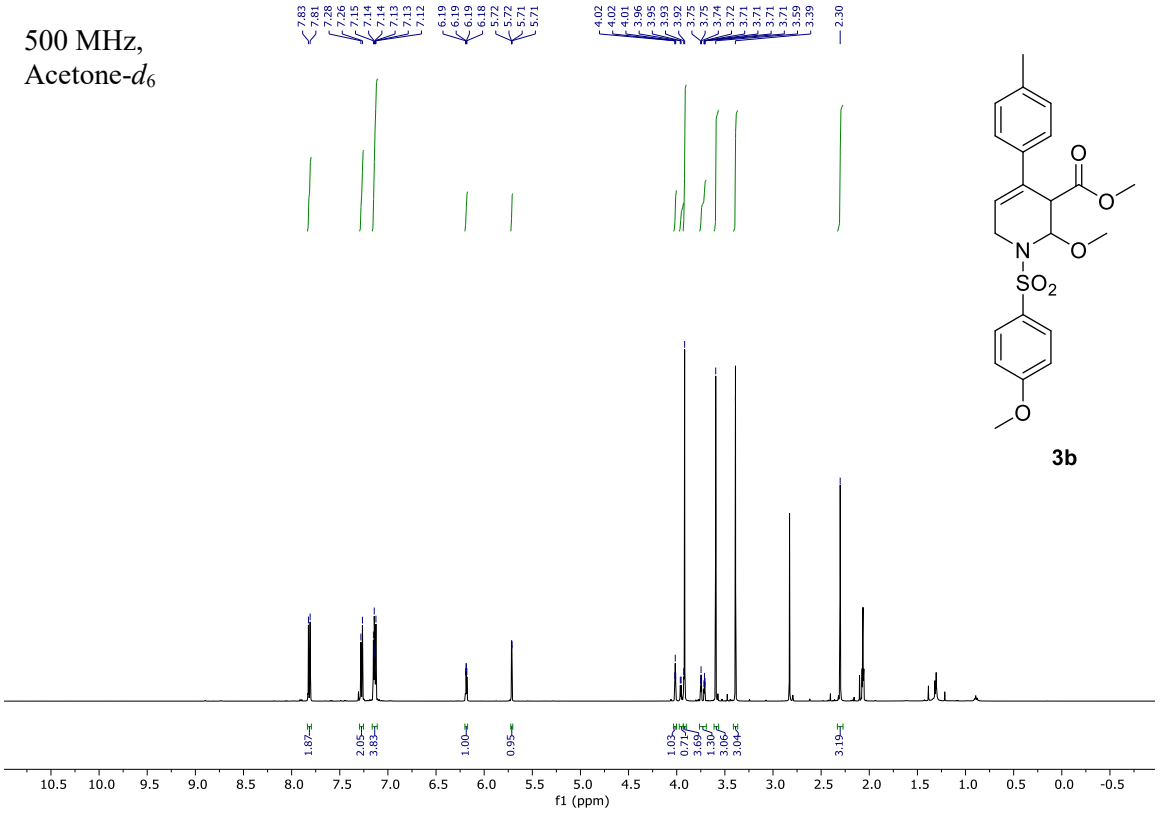
3a

125.7 MHz,
Acetone-d_6



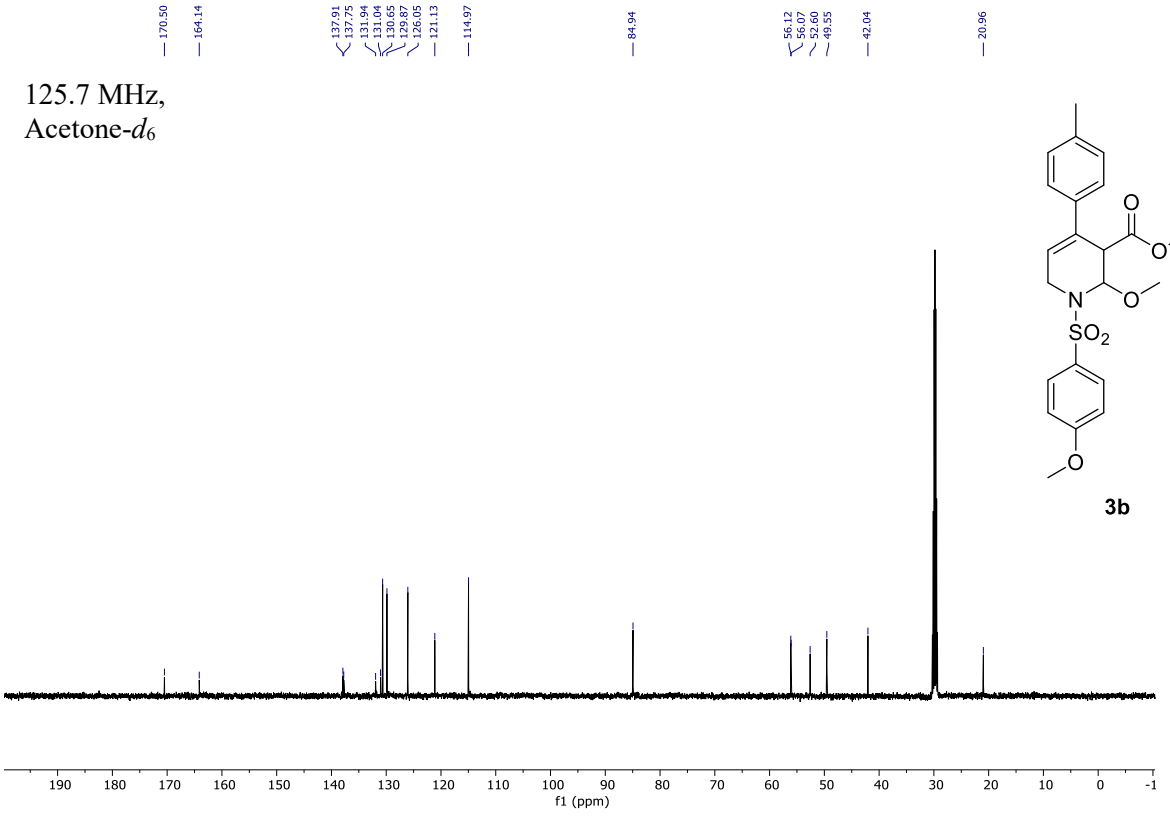
3a

500 MHz,
Acetone-d_6



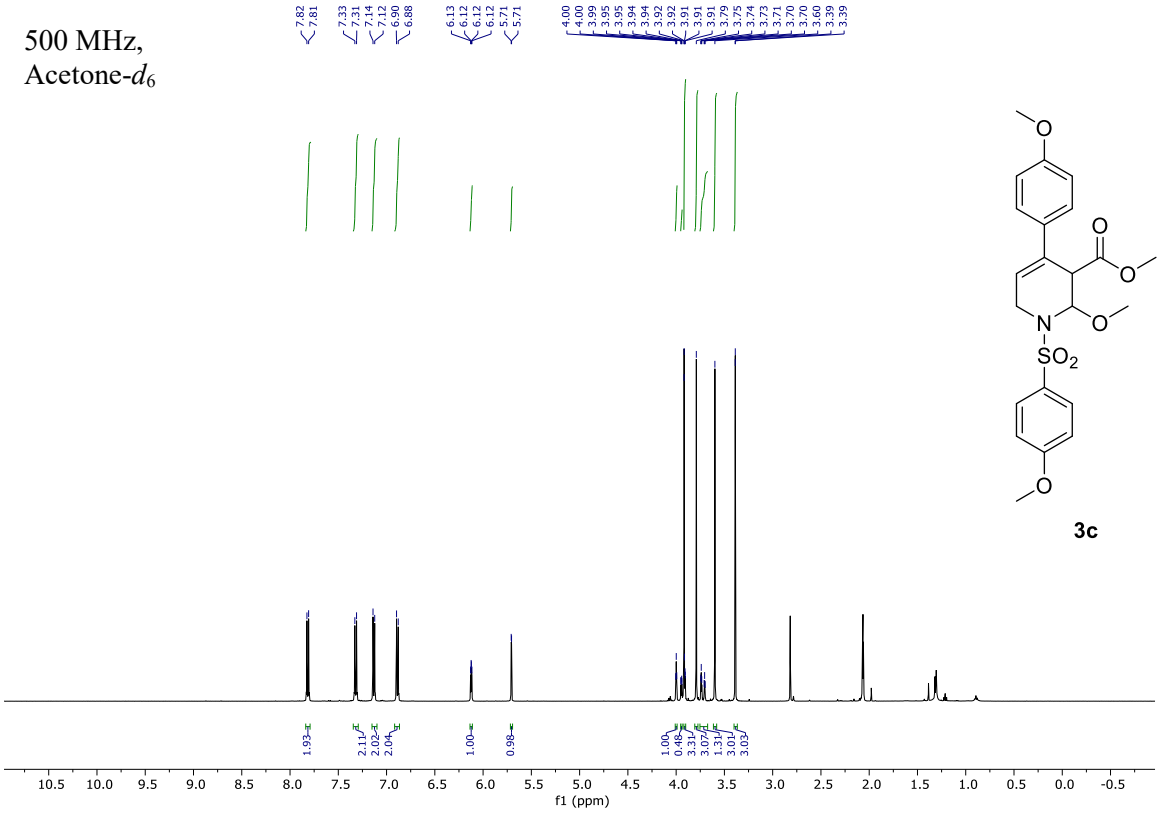
3b

125.7 MHz,
Acetone-d_6



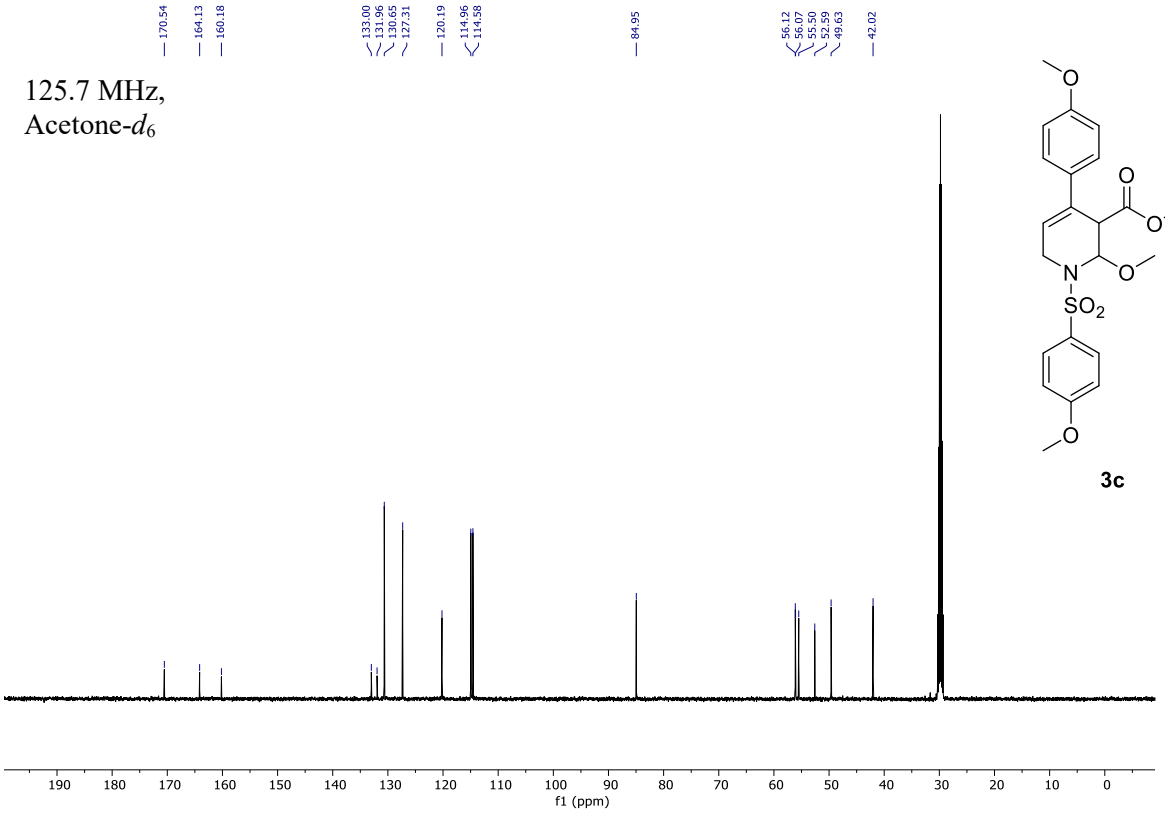
3b

500 MHz,
Acetone-d_6



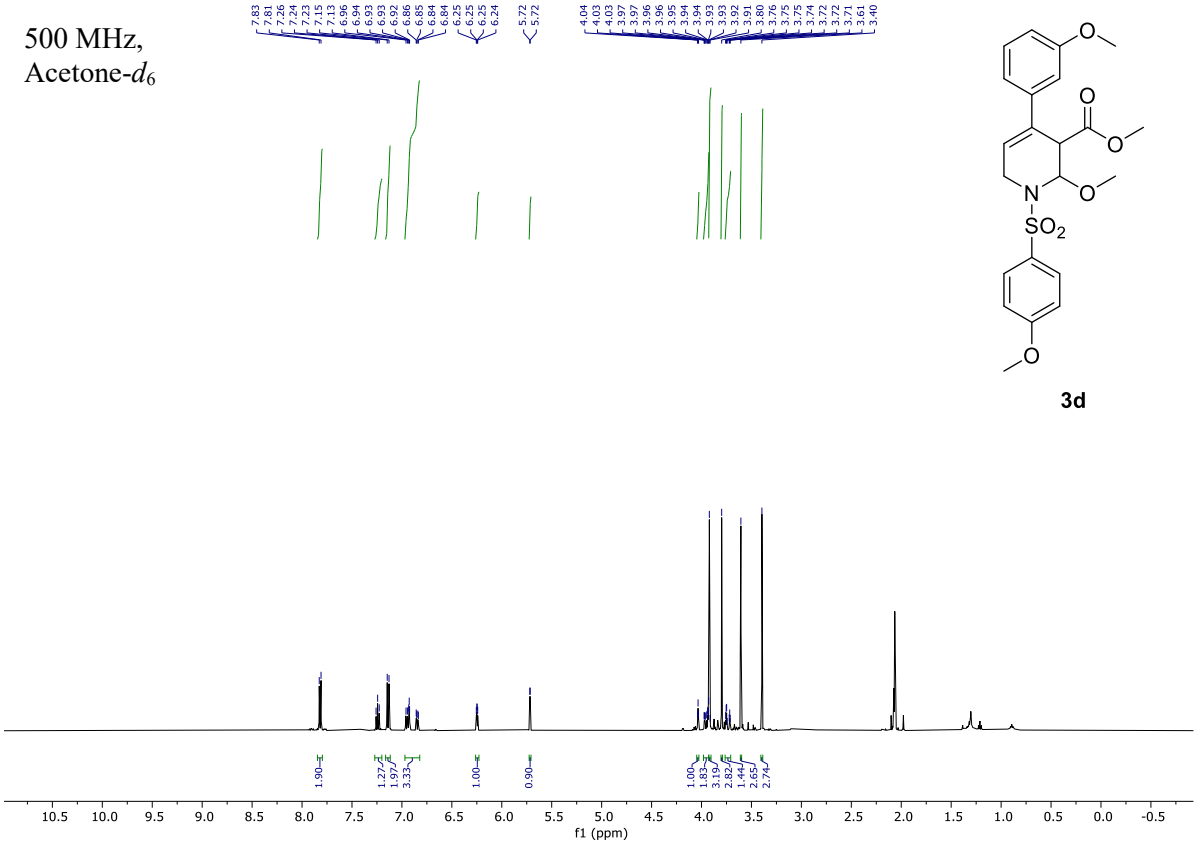
3c

125.7 MHz,
Acetone-d_6



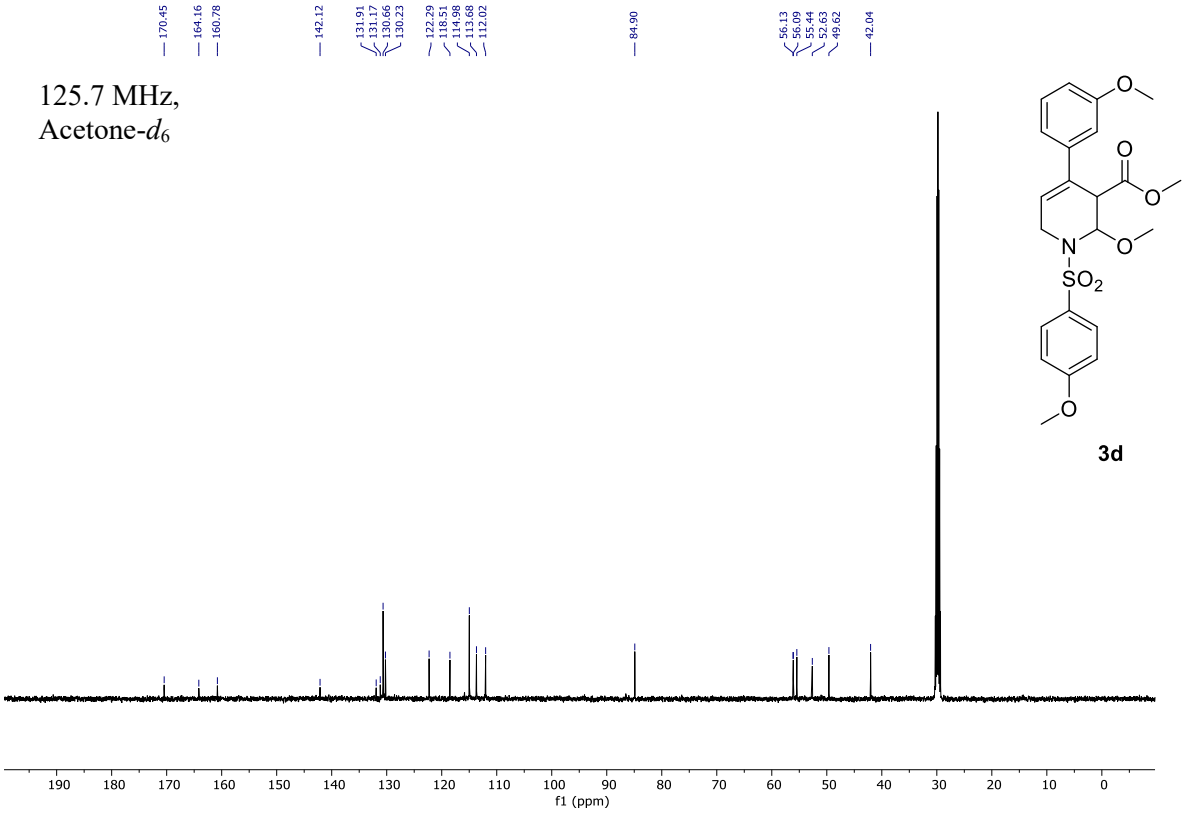
3c

500 MHz,
Acetone-d_6



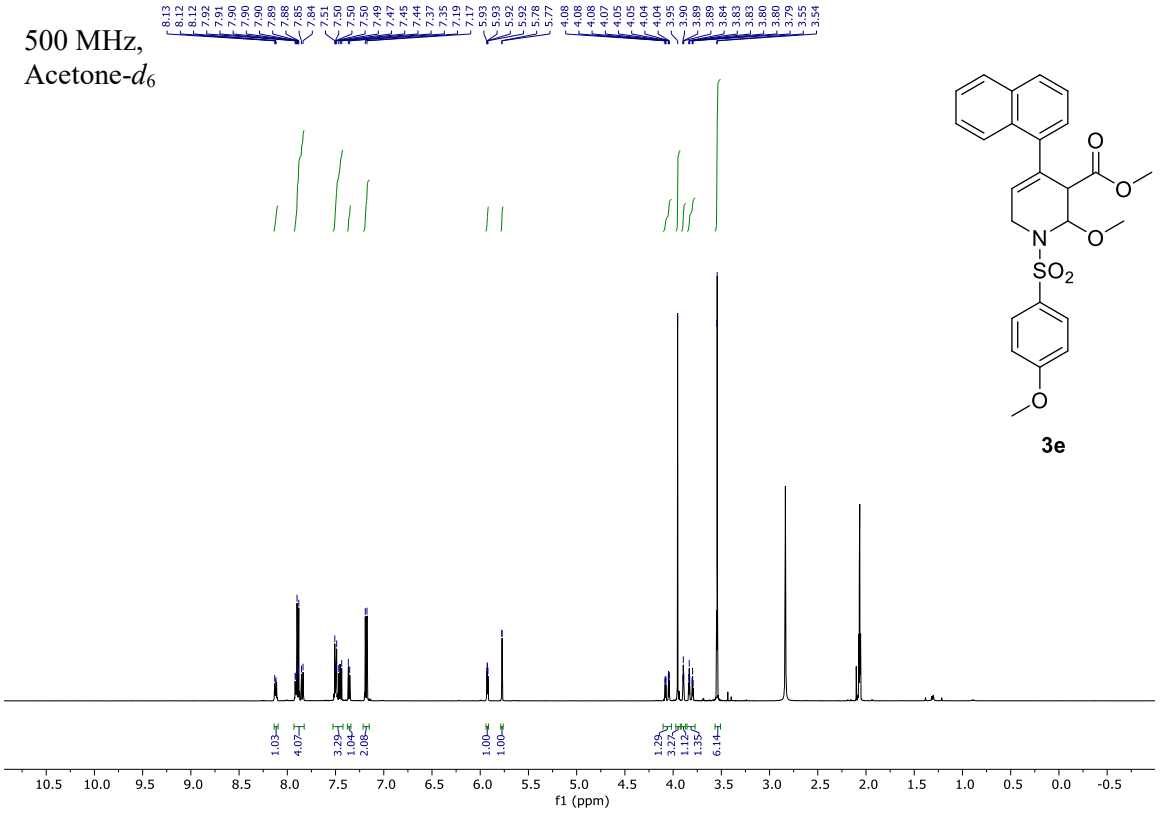
3d

125.7 MHz,
Acetone-d_6



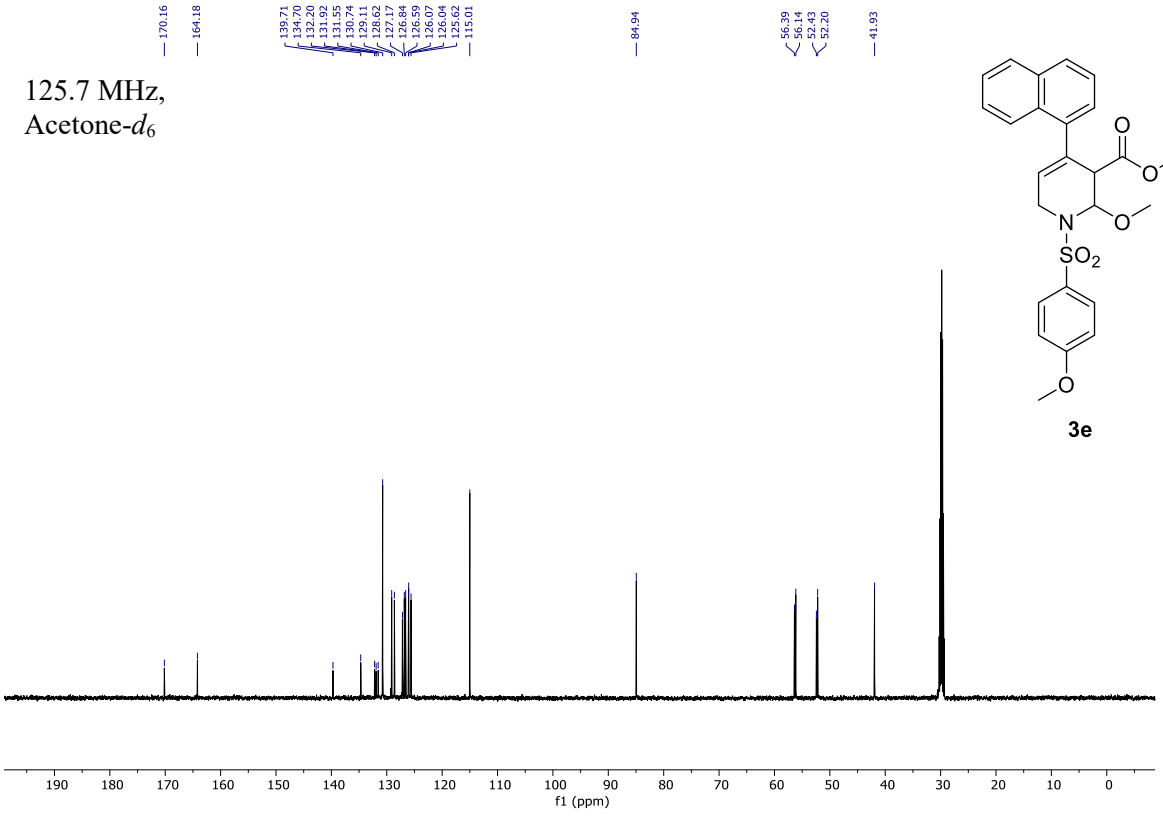
3d

500 MHz,
Acetone-d_6



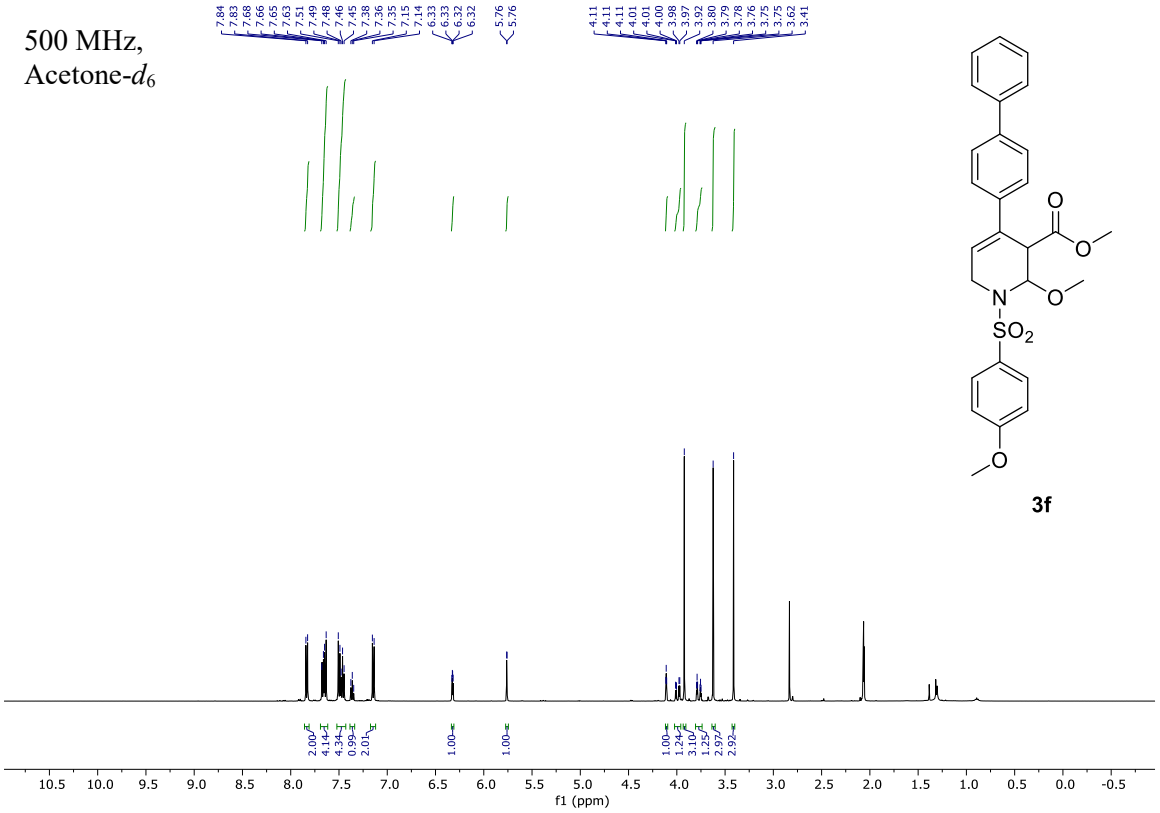
3e

125.7 MHz,
Acetone-d_6

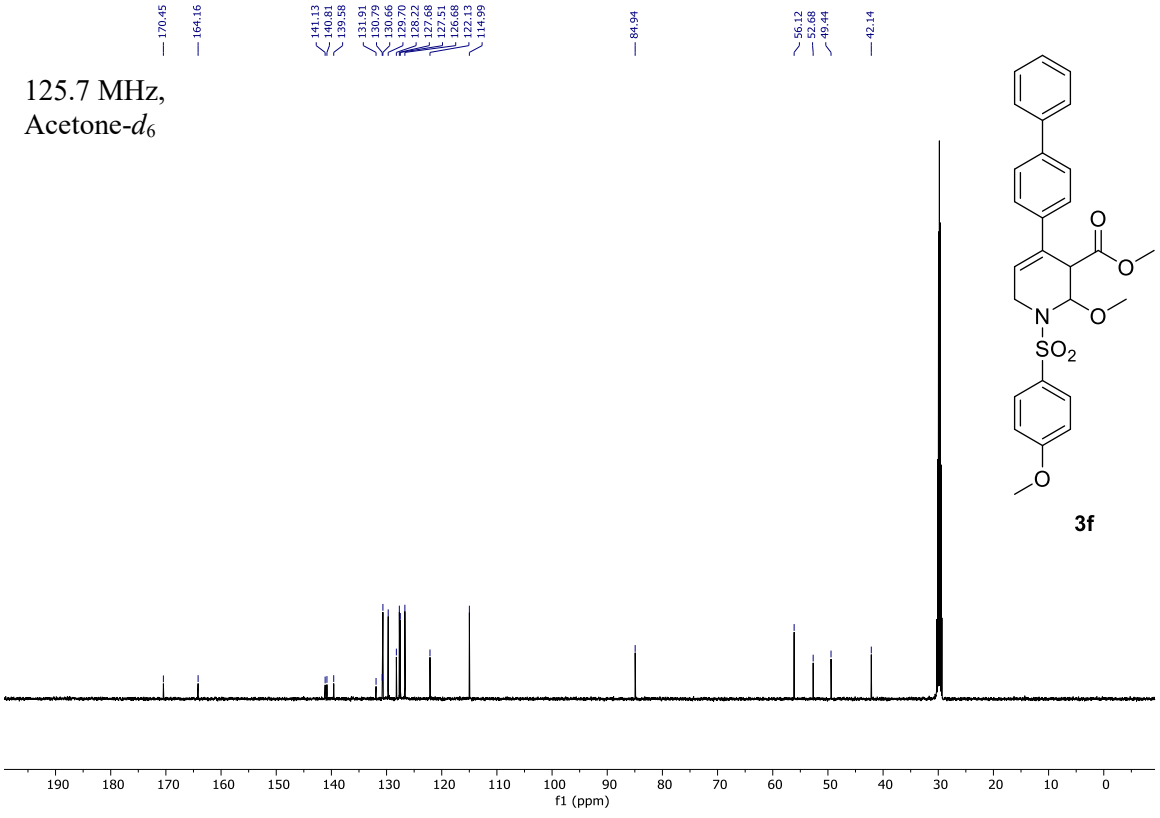


3e

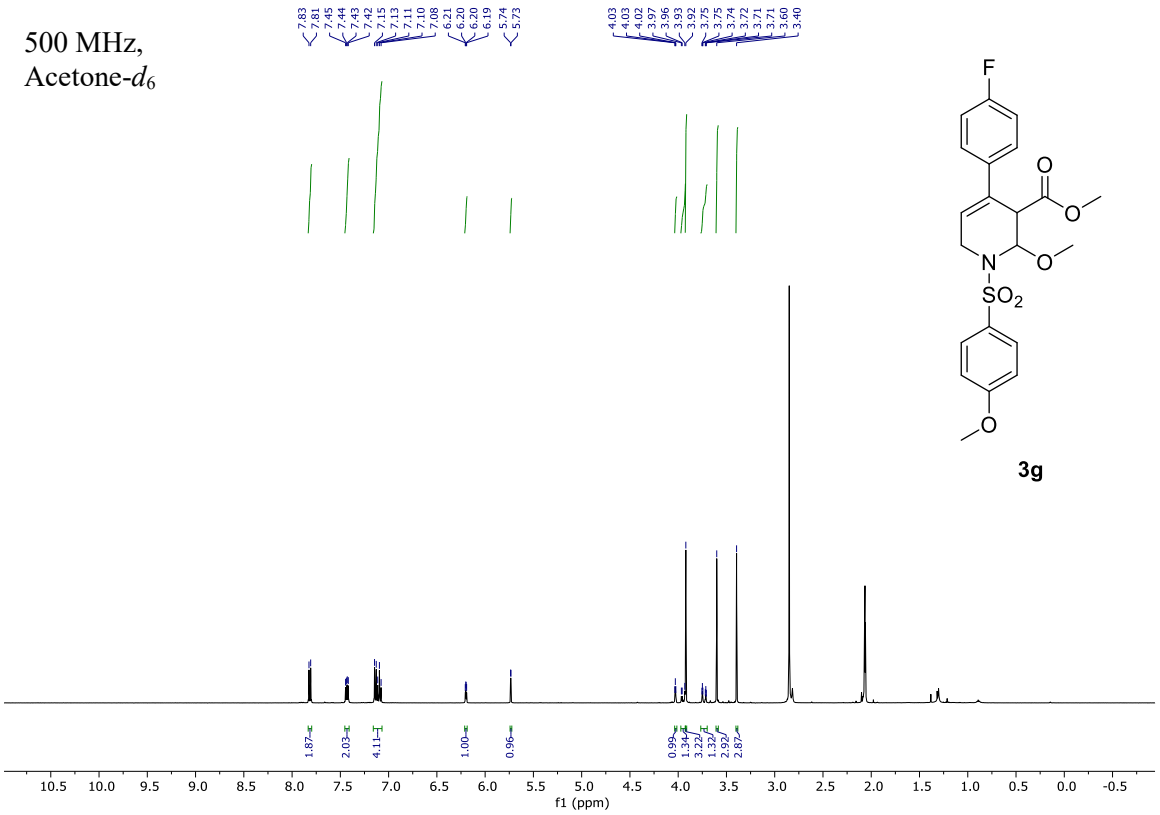
500 MHz,
Acetone-d_6



125.7 MHz,
Acetone-d_6

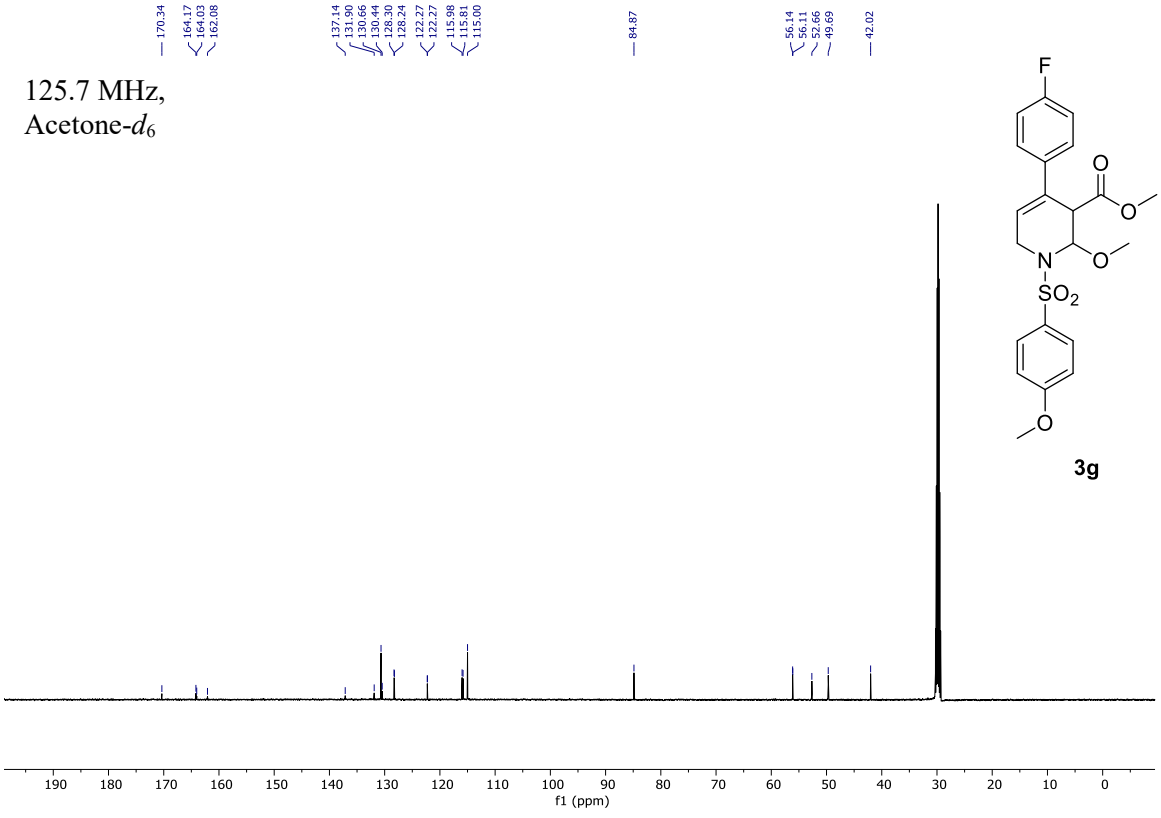


500 MHz,
Acetone-d_6



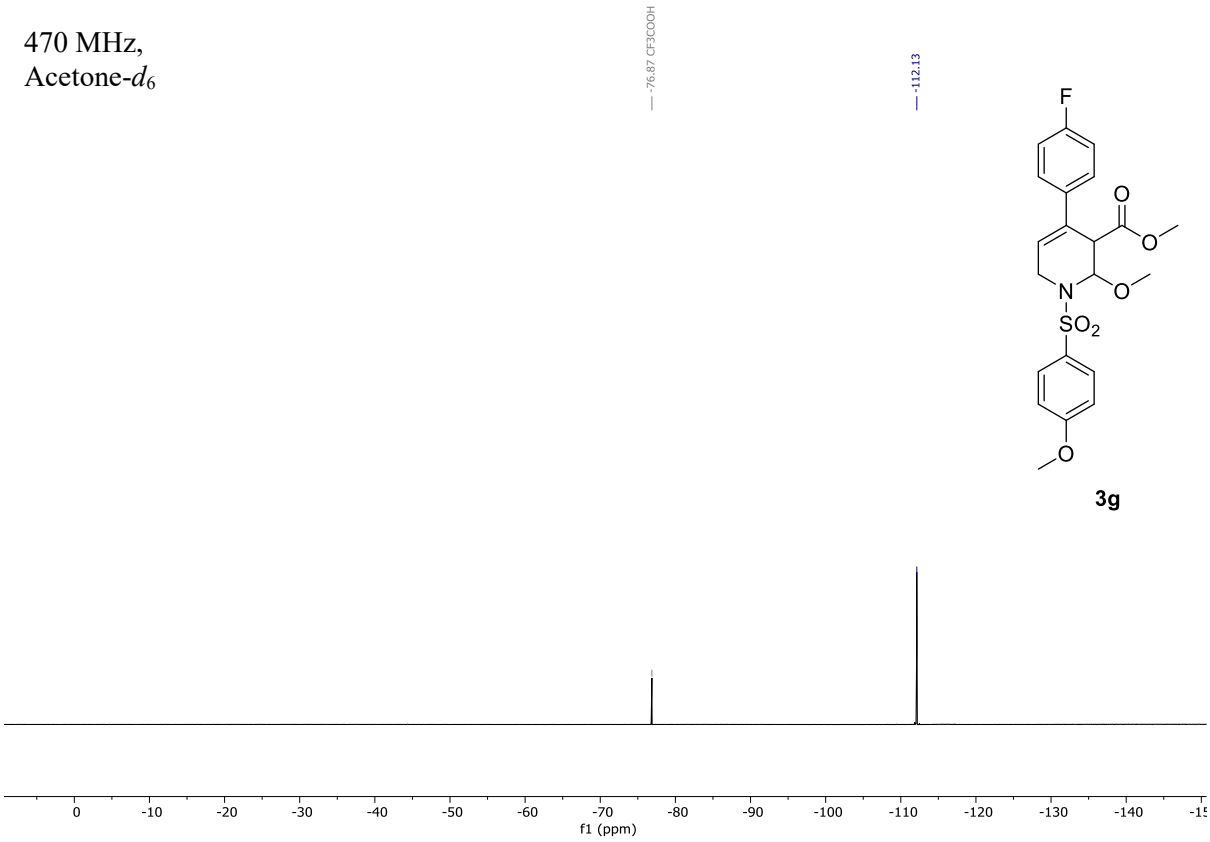
3g

125.7 MHz,
Acetone-d_6

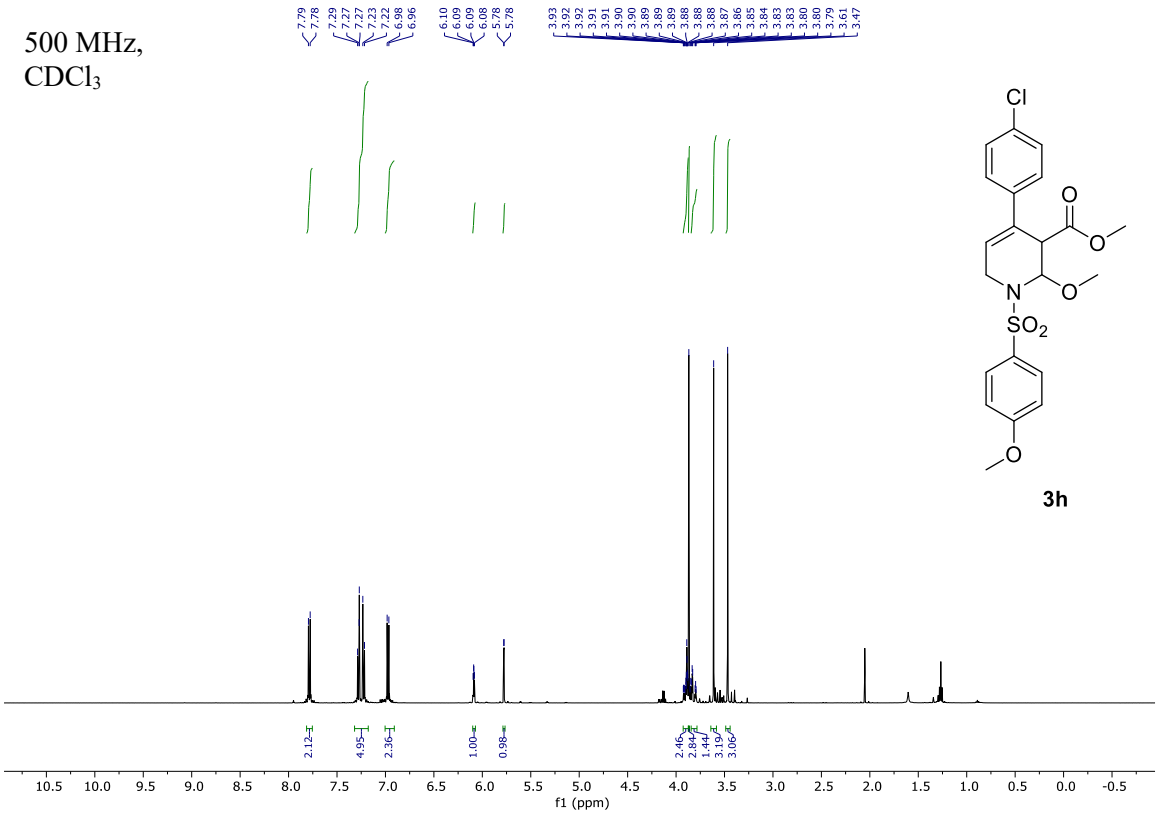


3g

470 MHz,
Acetone-d_6

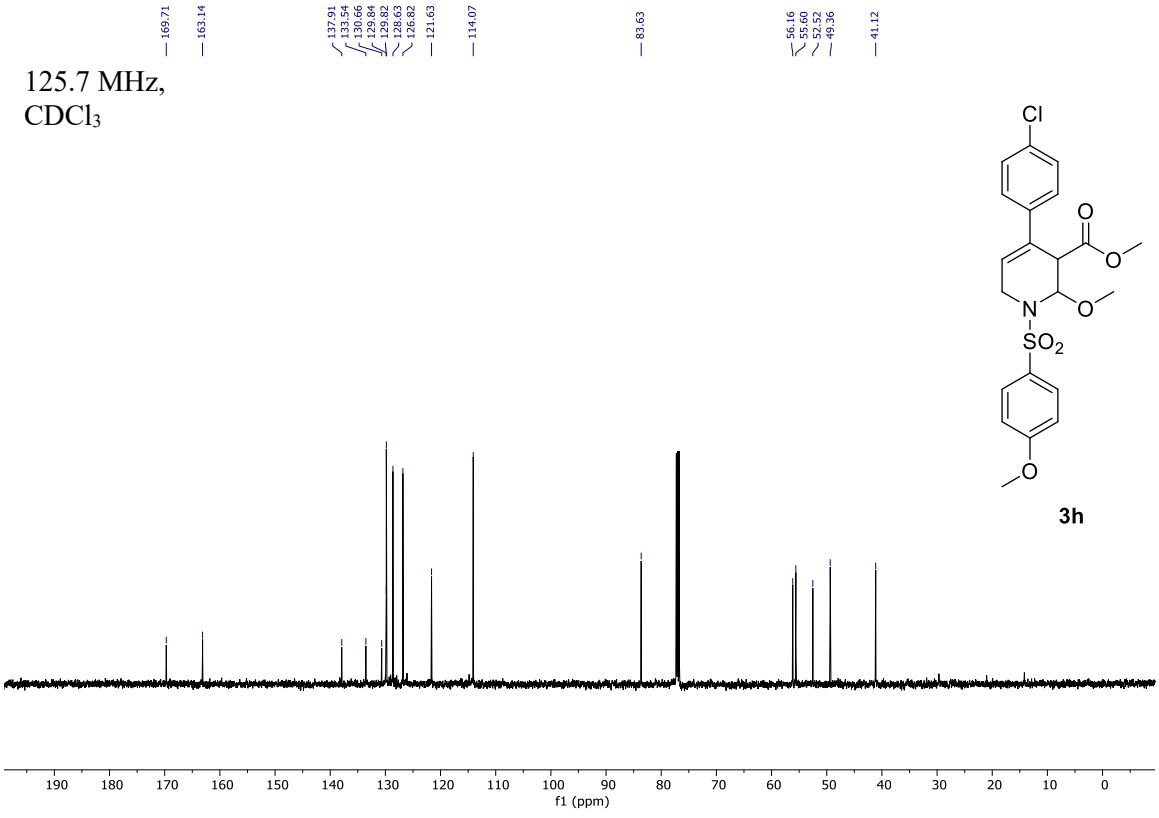


500 MHz,
$CDCl_3$



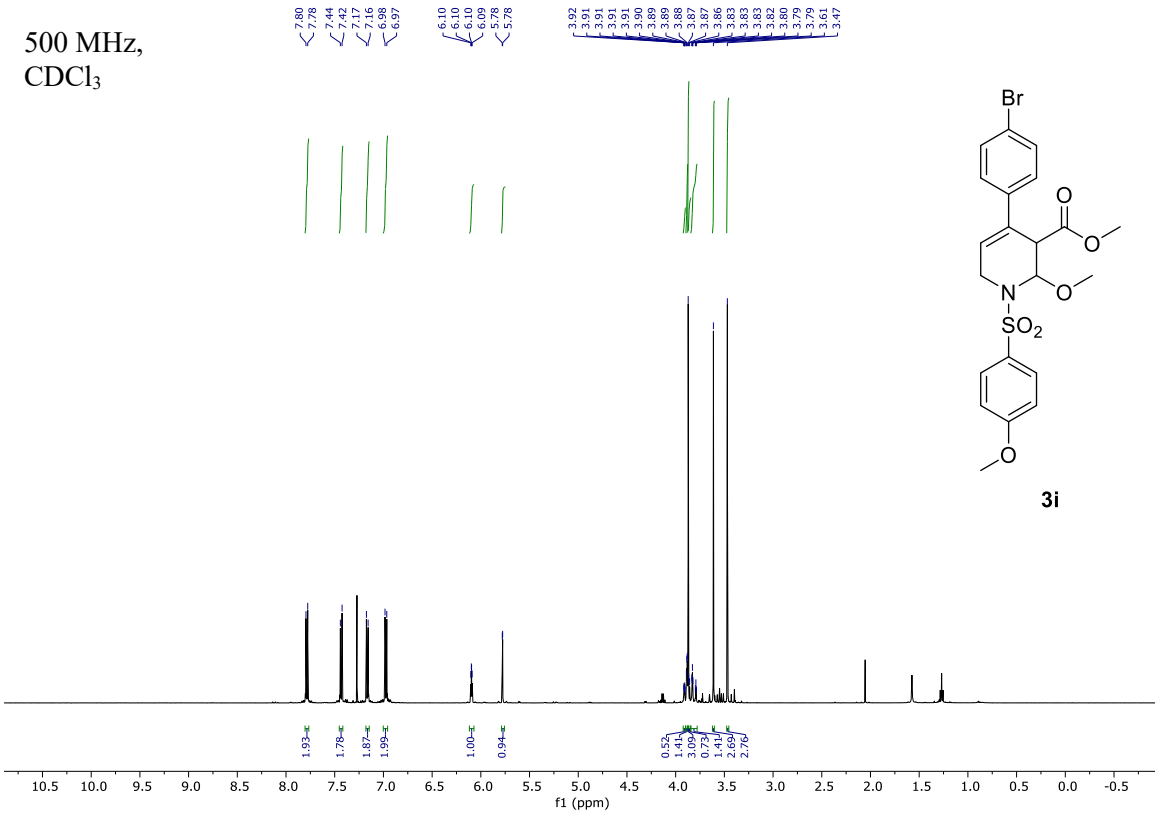
3h

125.7 MHz,
$CDCl_3$

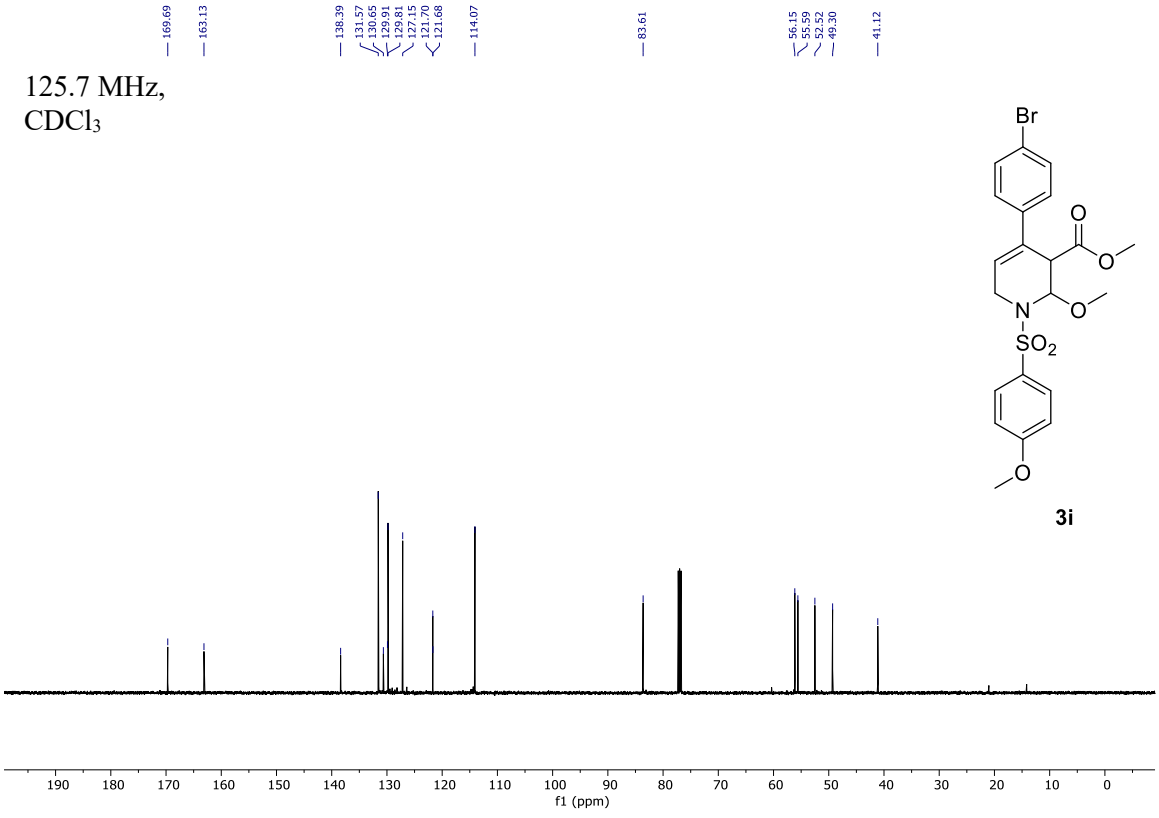


3h

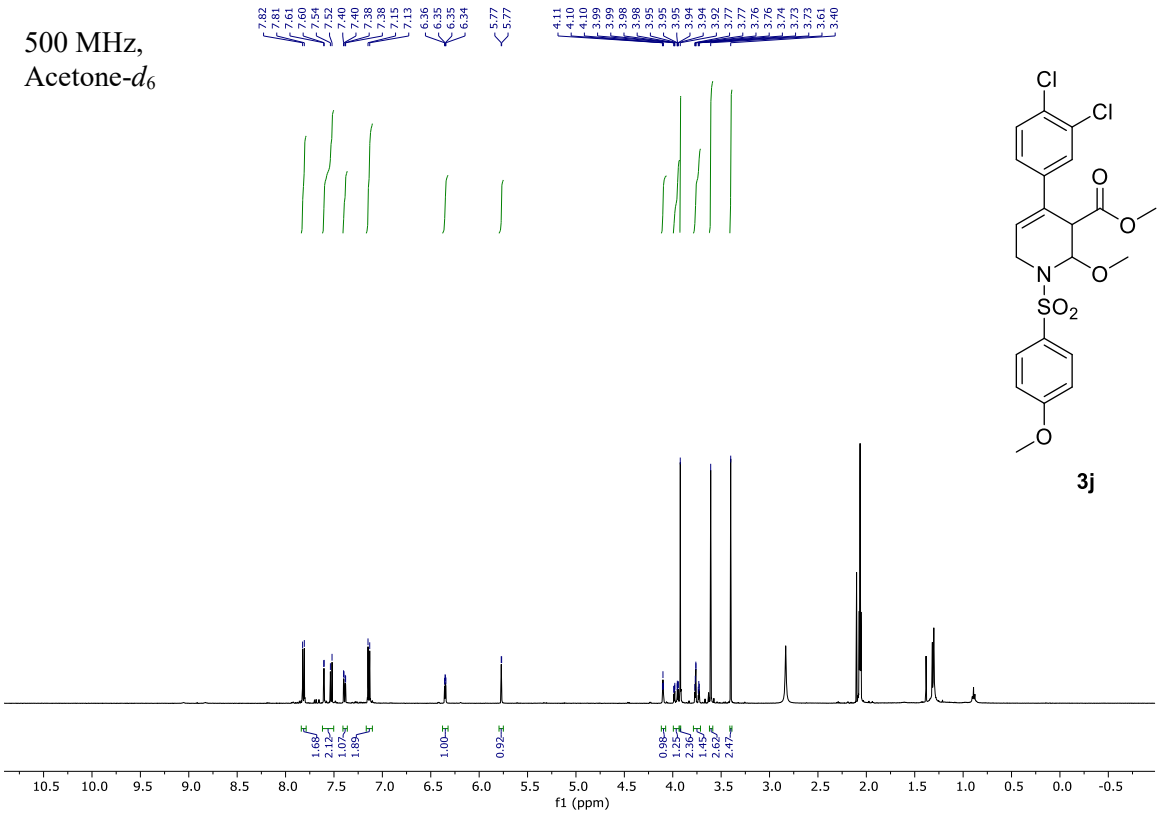
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

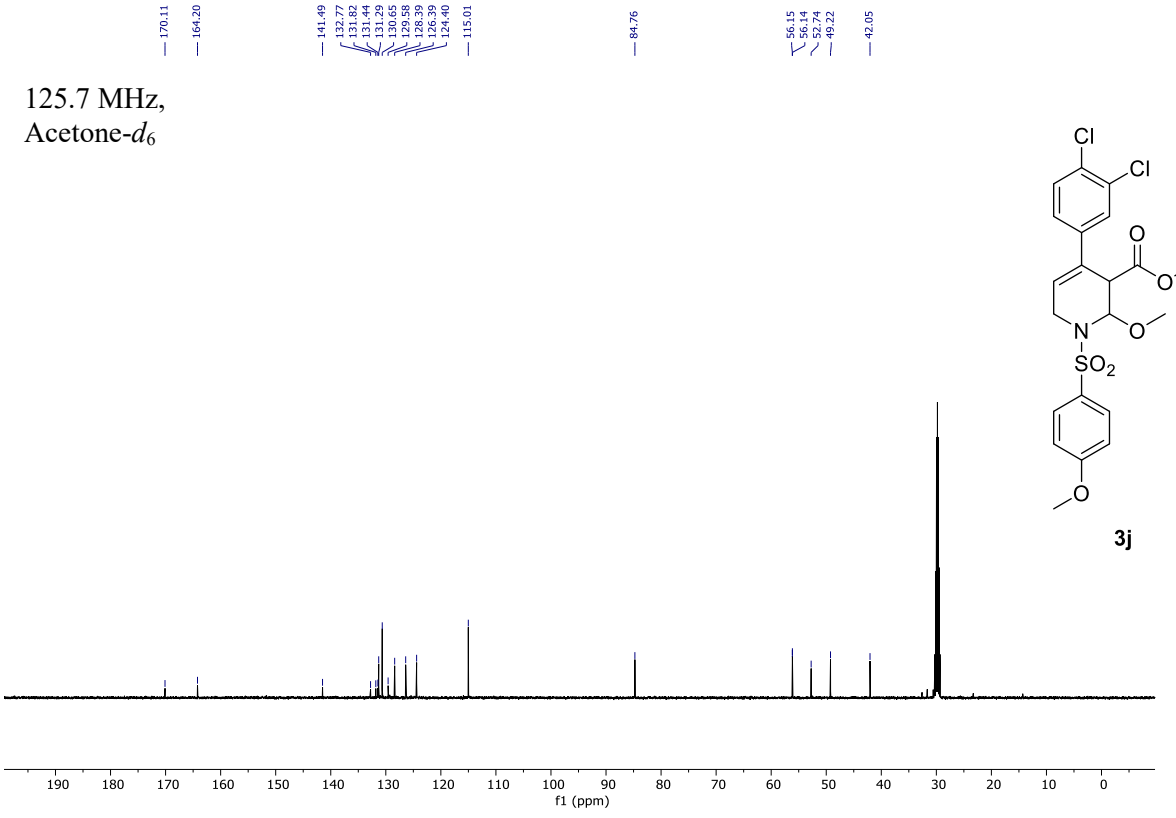


500 MHz,
Acetone-d_6



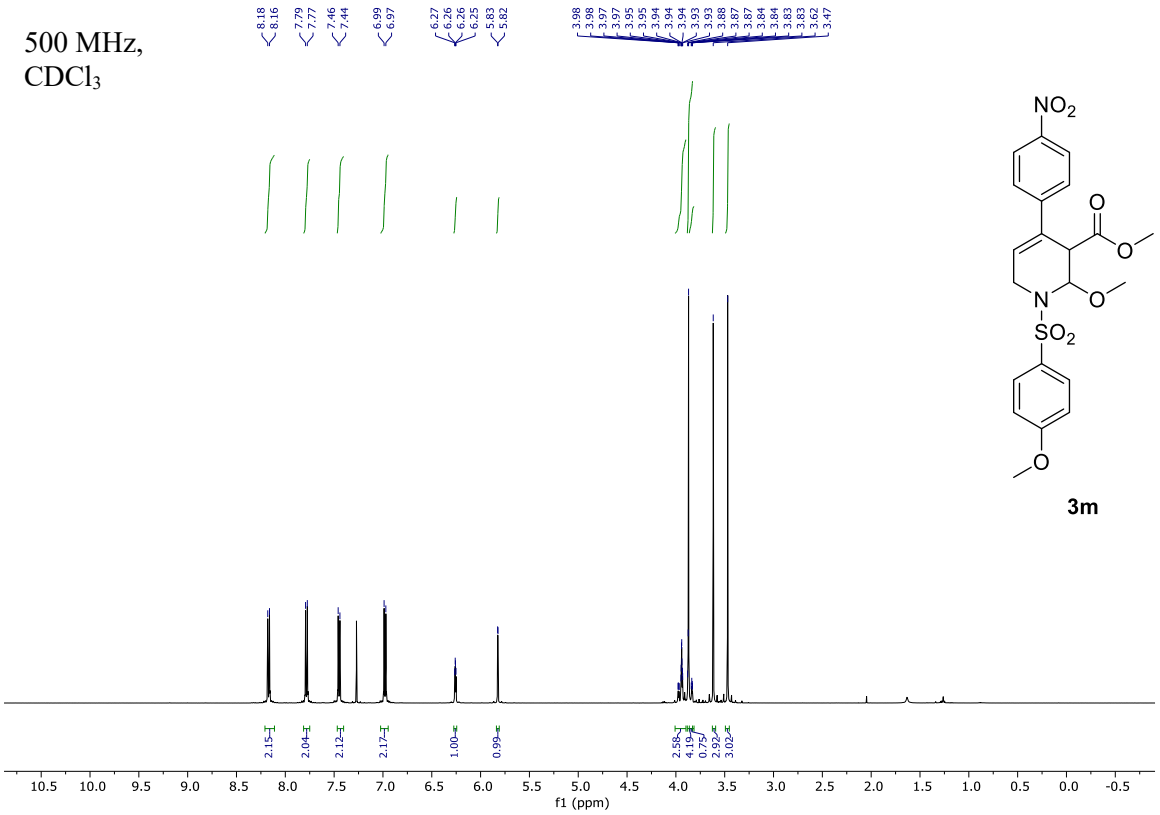
3j

125.7 MHz,
Acetone-d_6

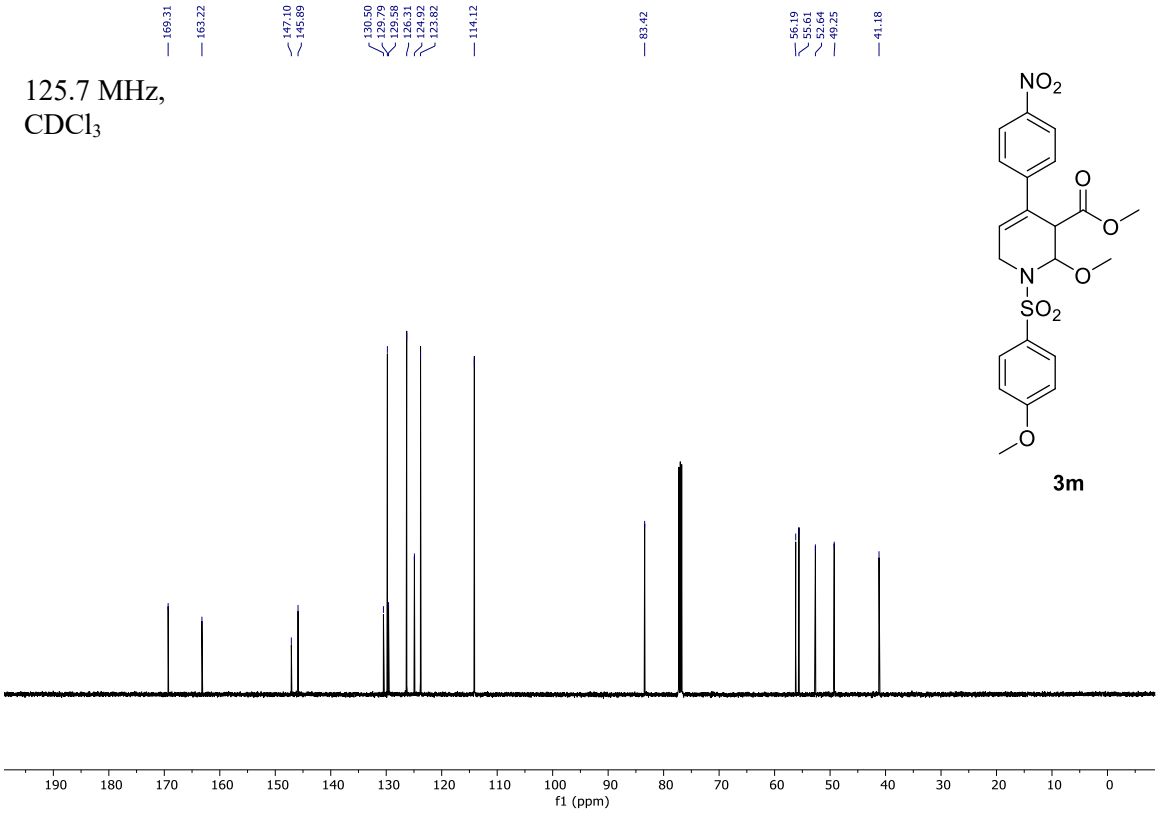


3j

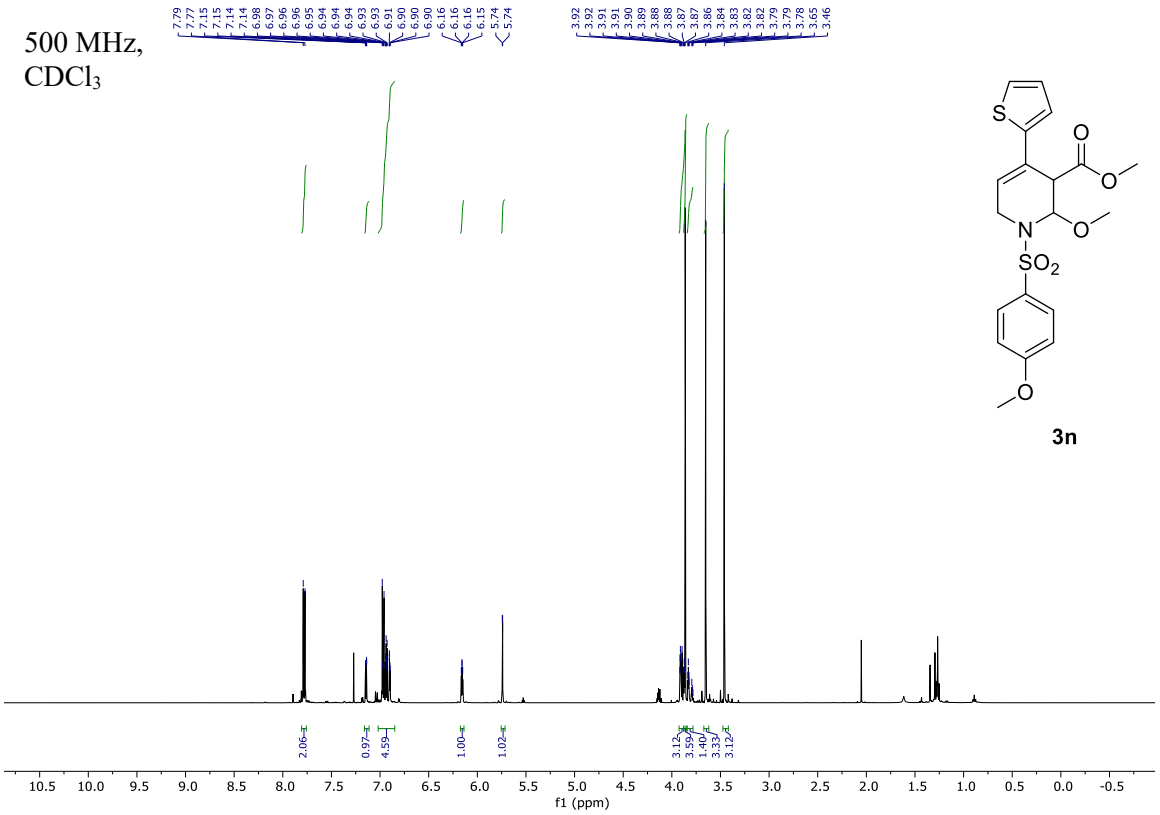
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

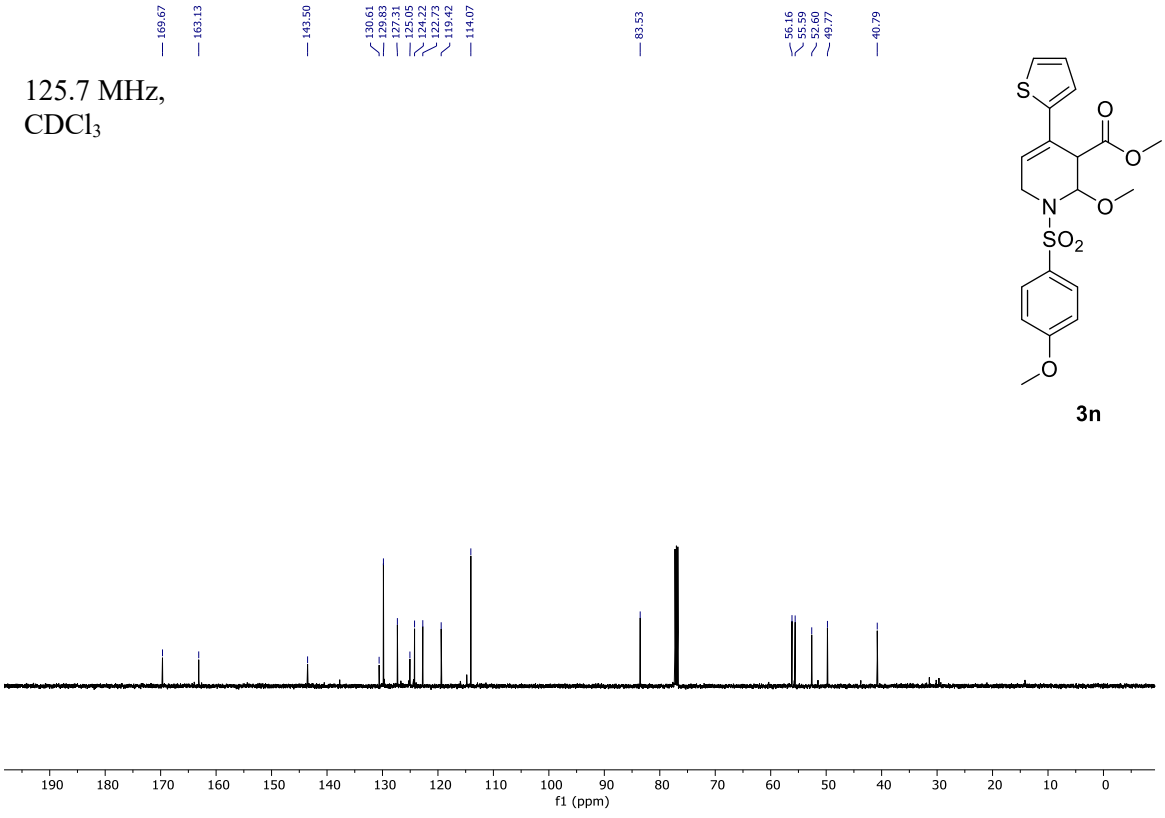


500 MHz,
$CDCl_3$



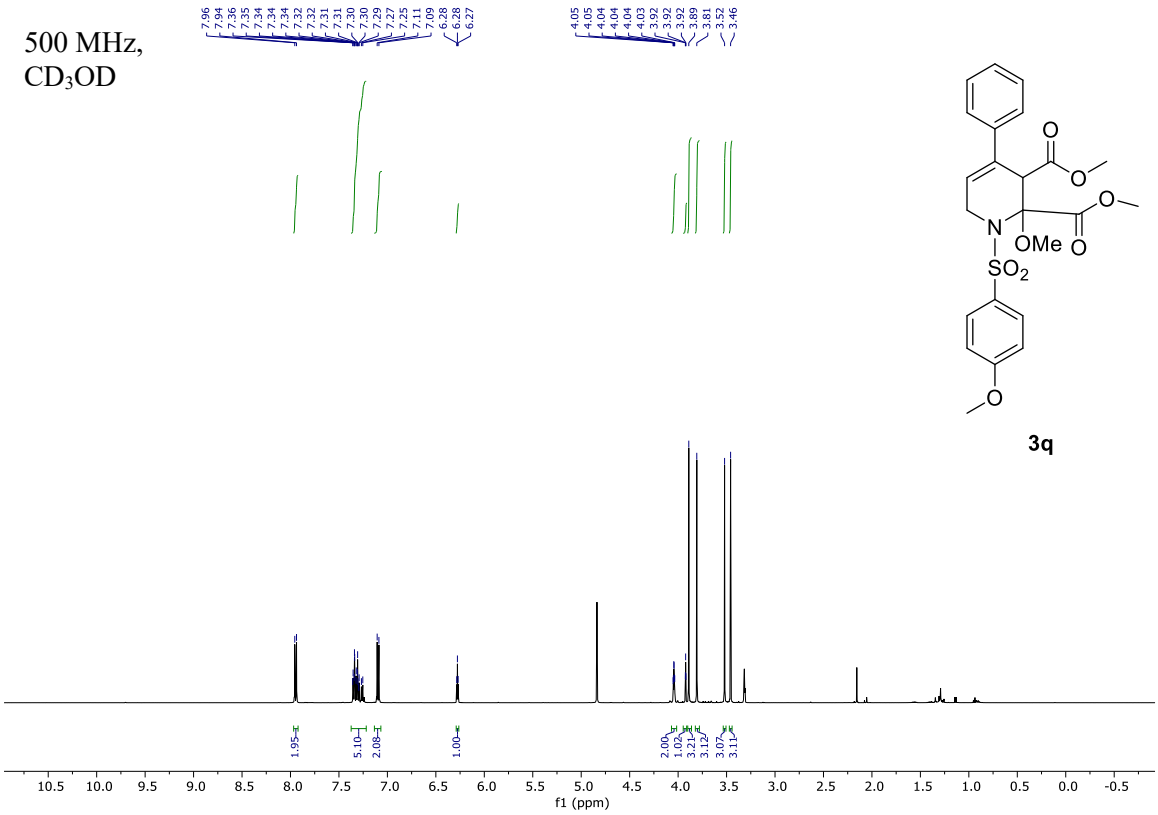
3n

125.7 MHz,
$CDCl_3$



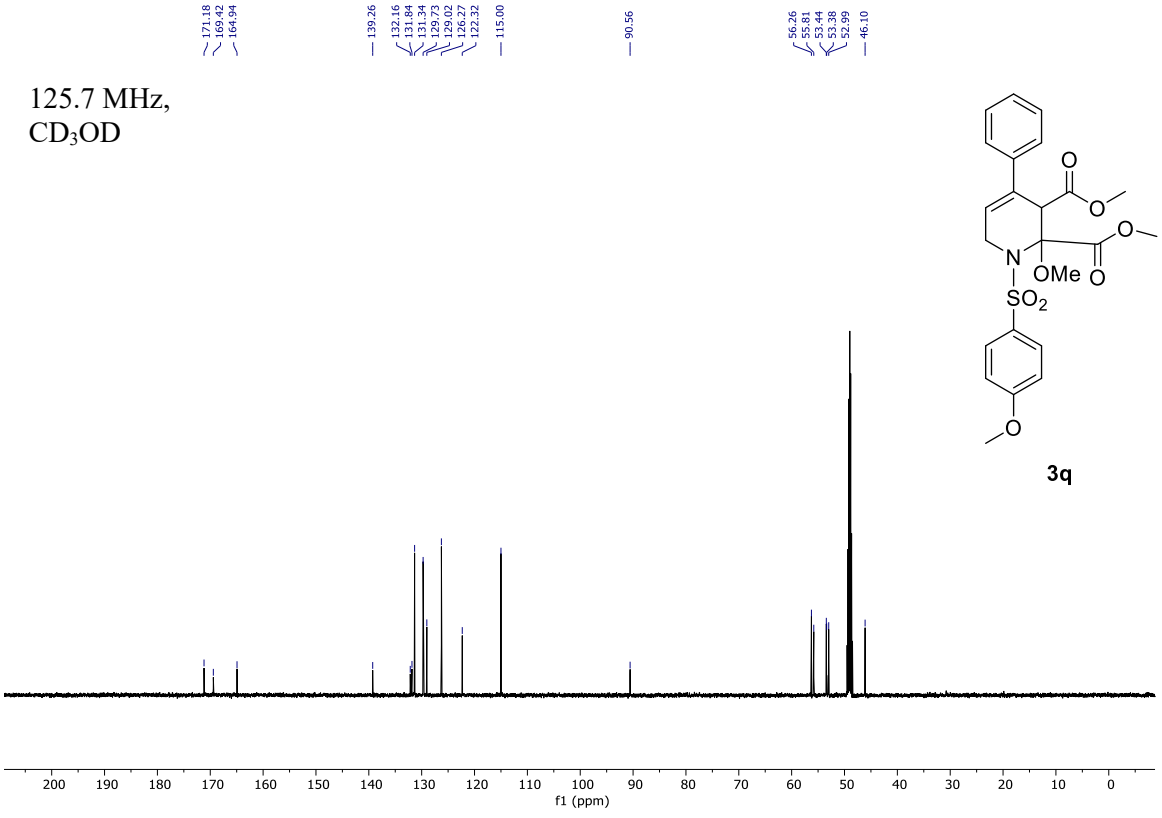
3n

500 MHz,
CD_3OD



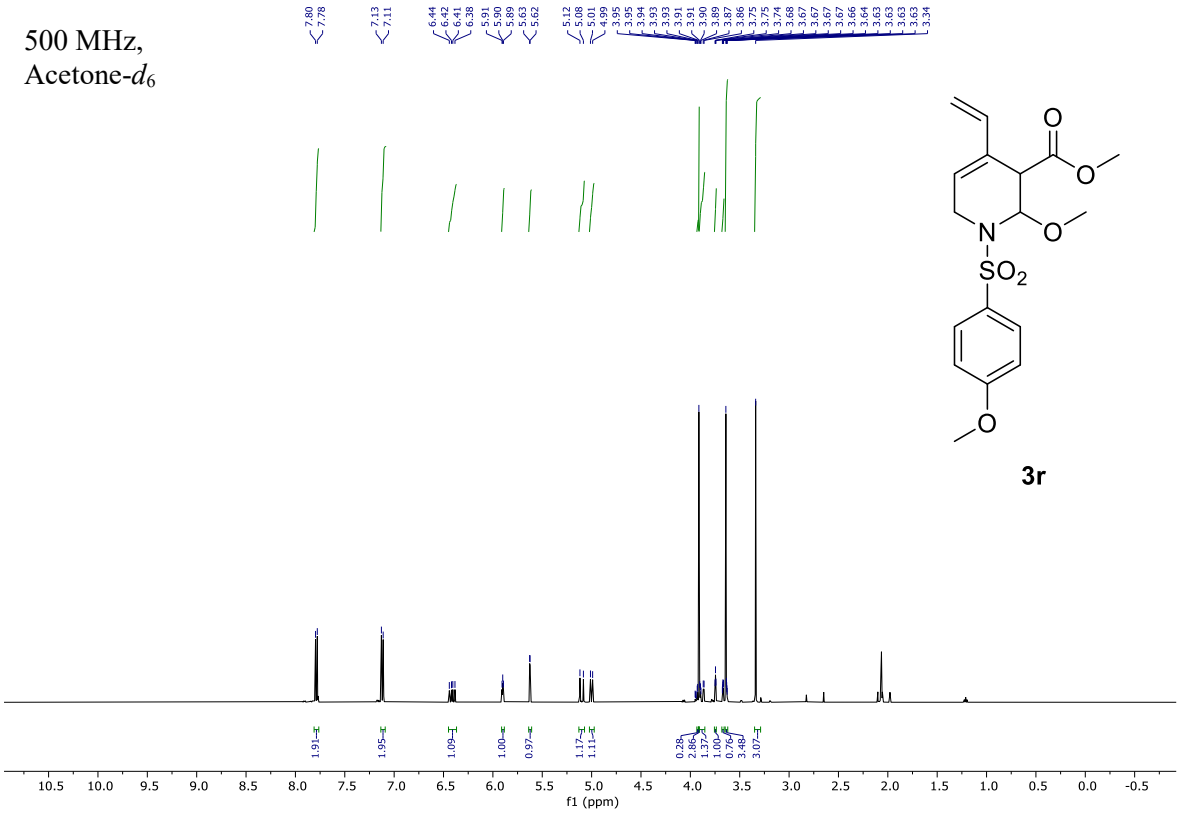
3q

125.7 MHz,
CD_3OD



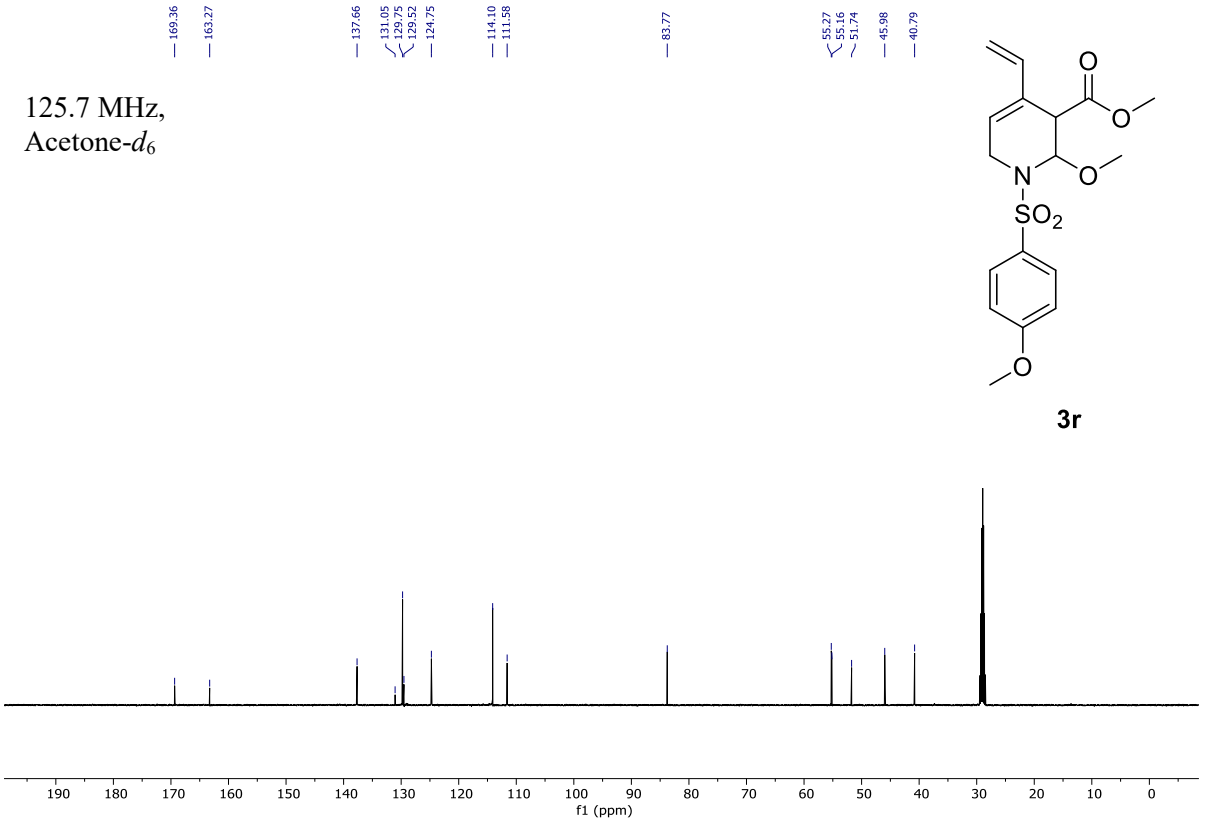
3q

500 MHz,
Acetone-d_6



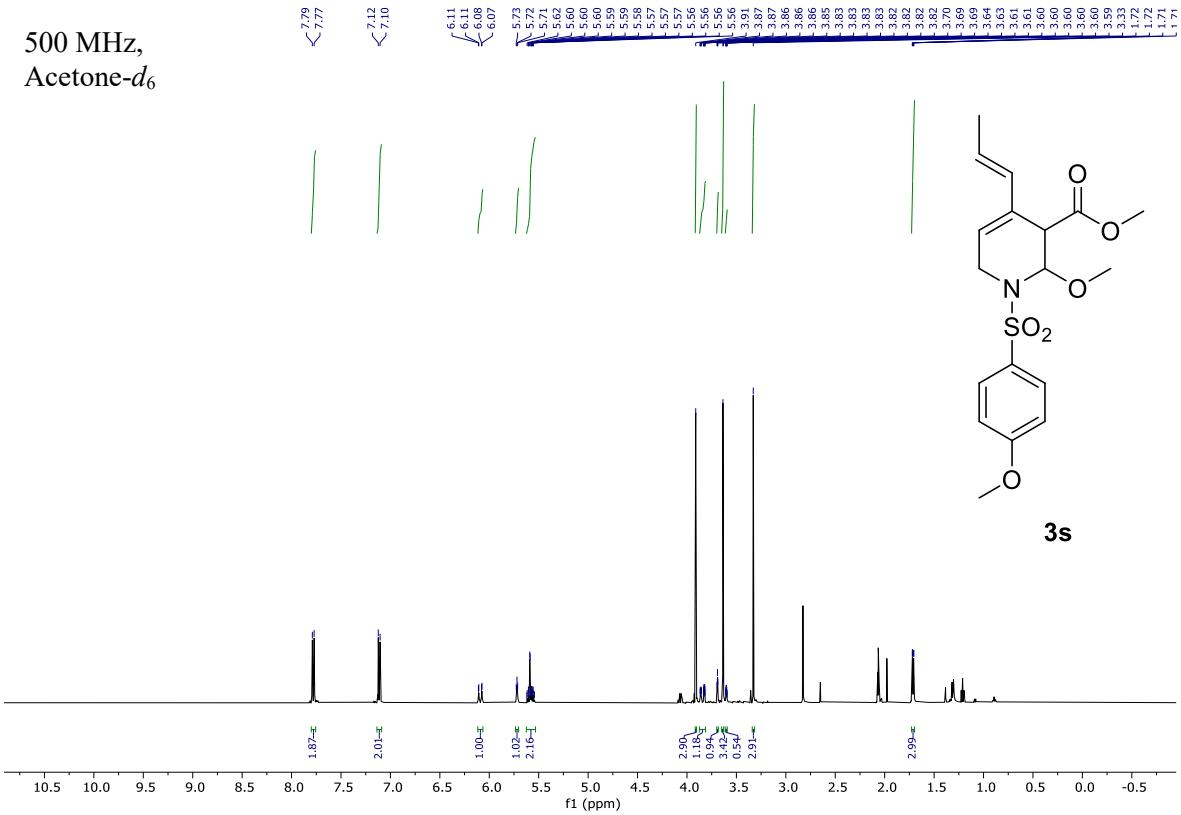
3r

125.7 MHz,
Acetone-d_6



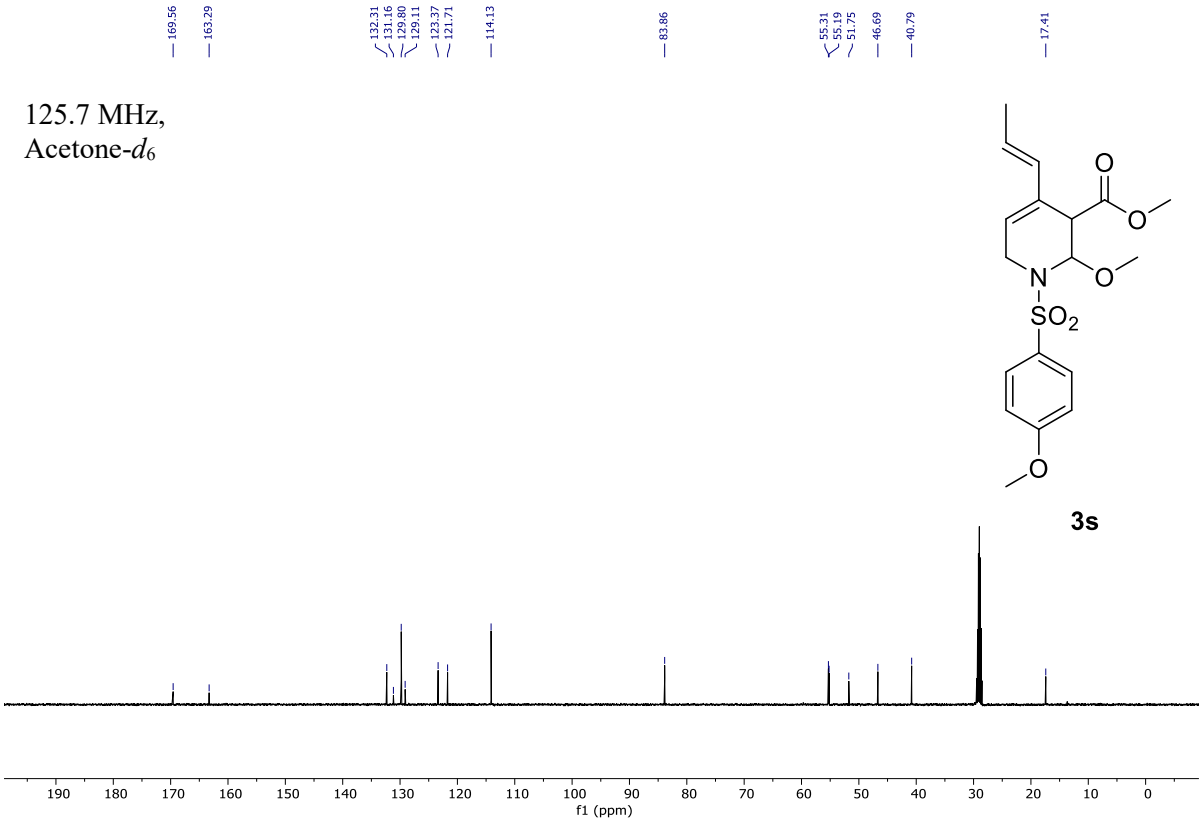
3r

500 MHz,
Acetone-d_6



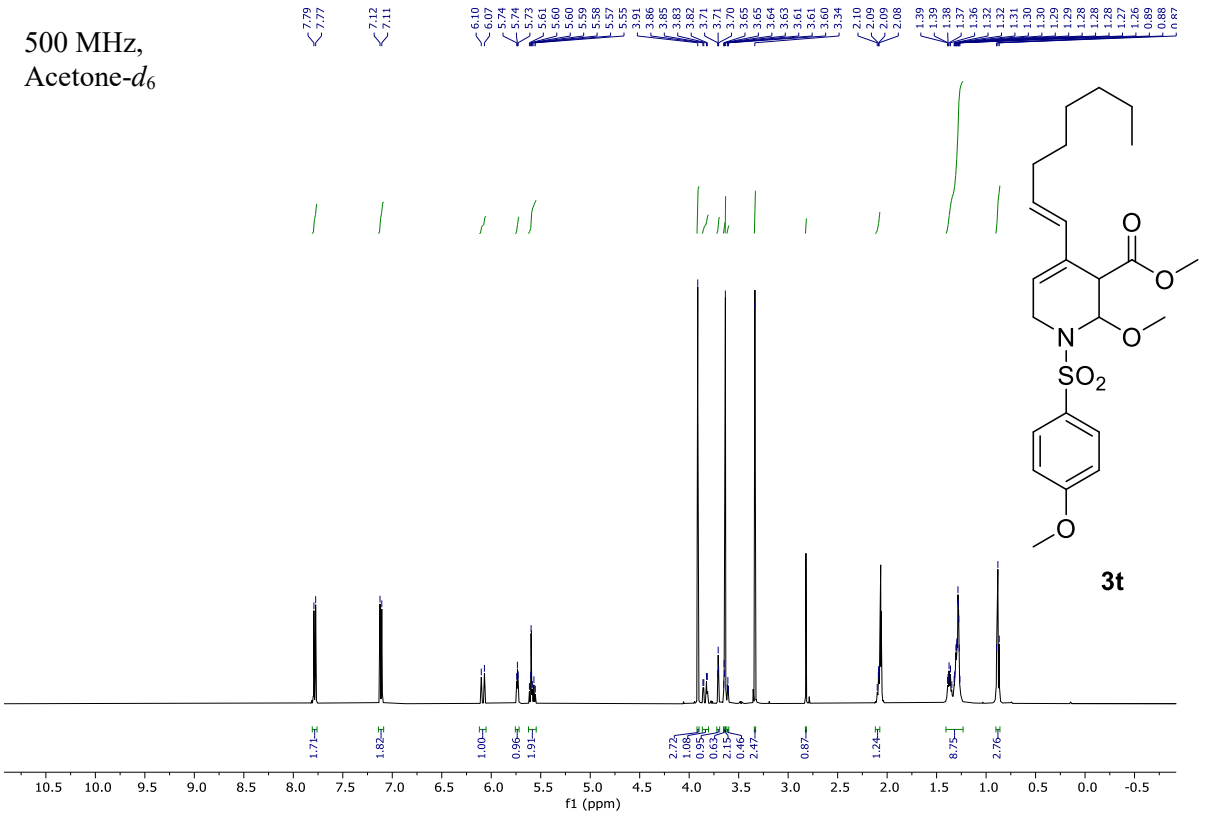
3s

125.7 MHz,
Acetone-d_6

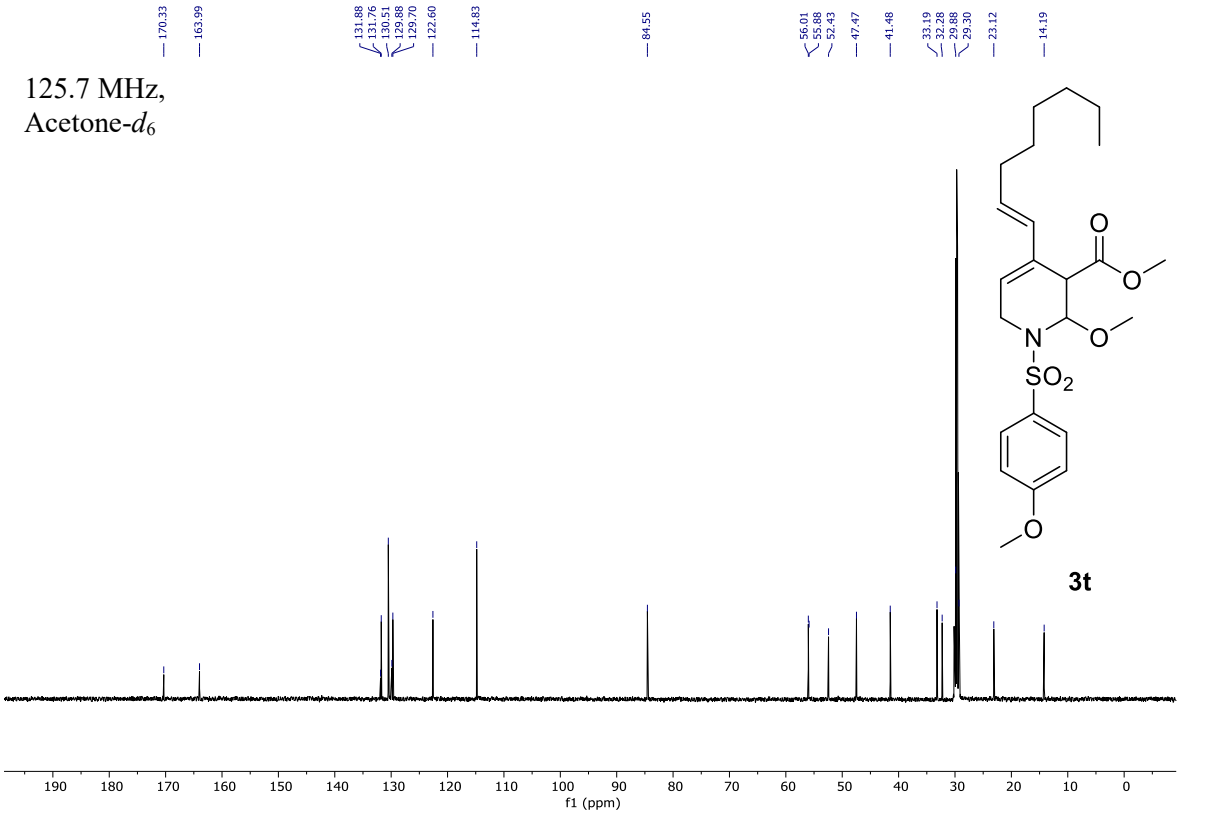


3s

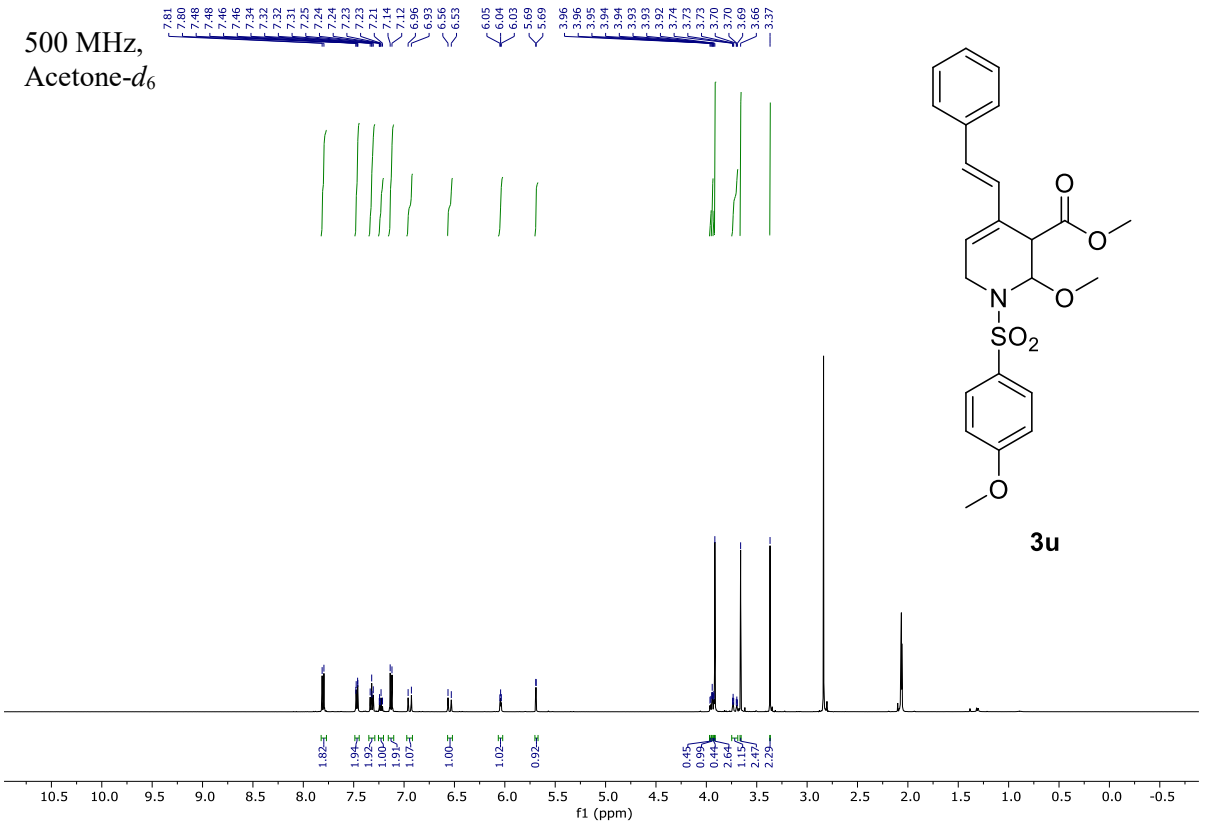
500 MHz,
Acetone-d_6



125.7 MHz,
Acetone-d_6

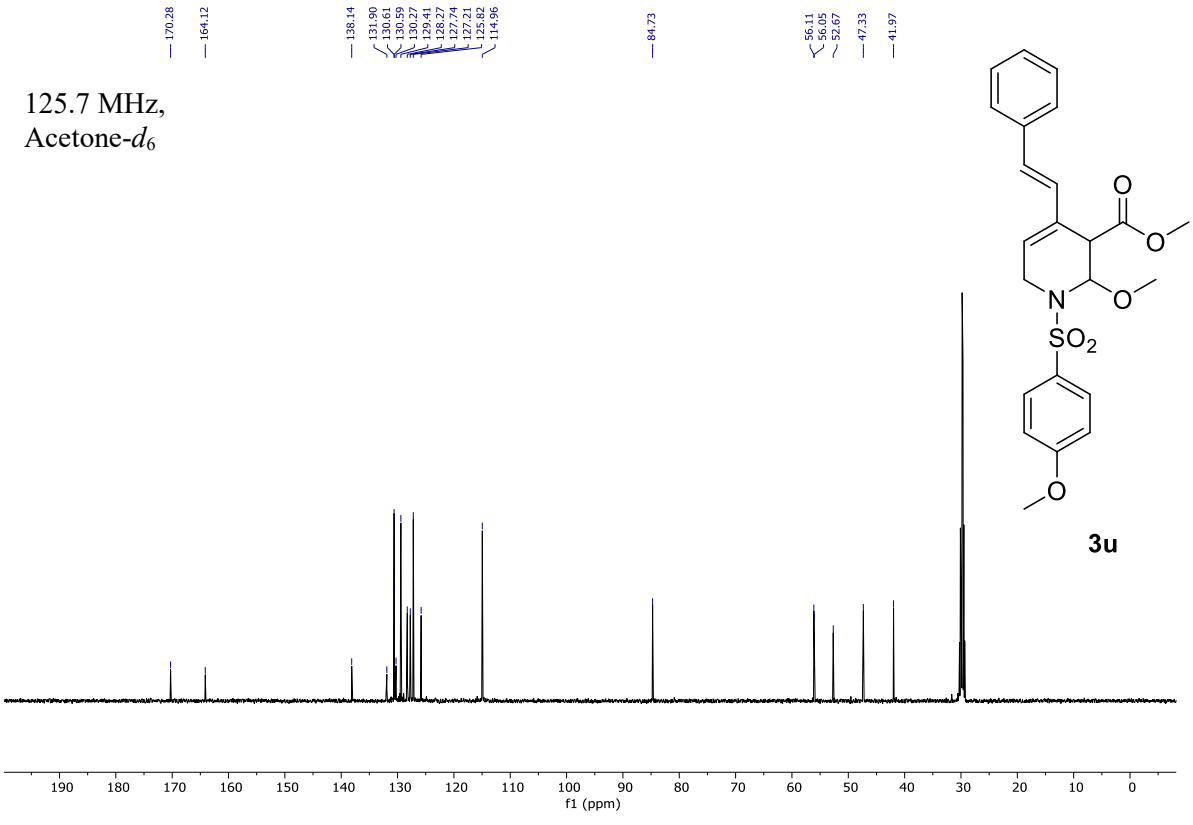


500 MHz,
Acetone-d_6



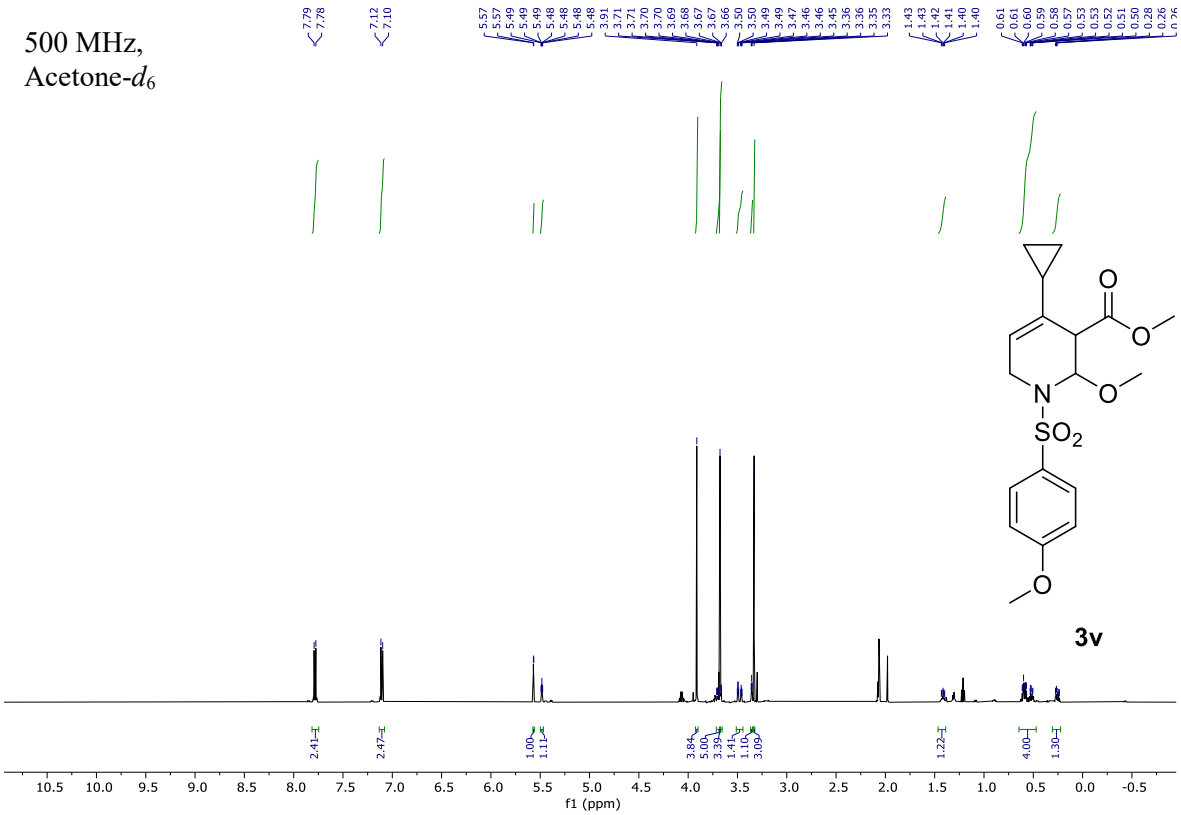
3u

125.7 MHz,
Acetone-d_6

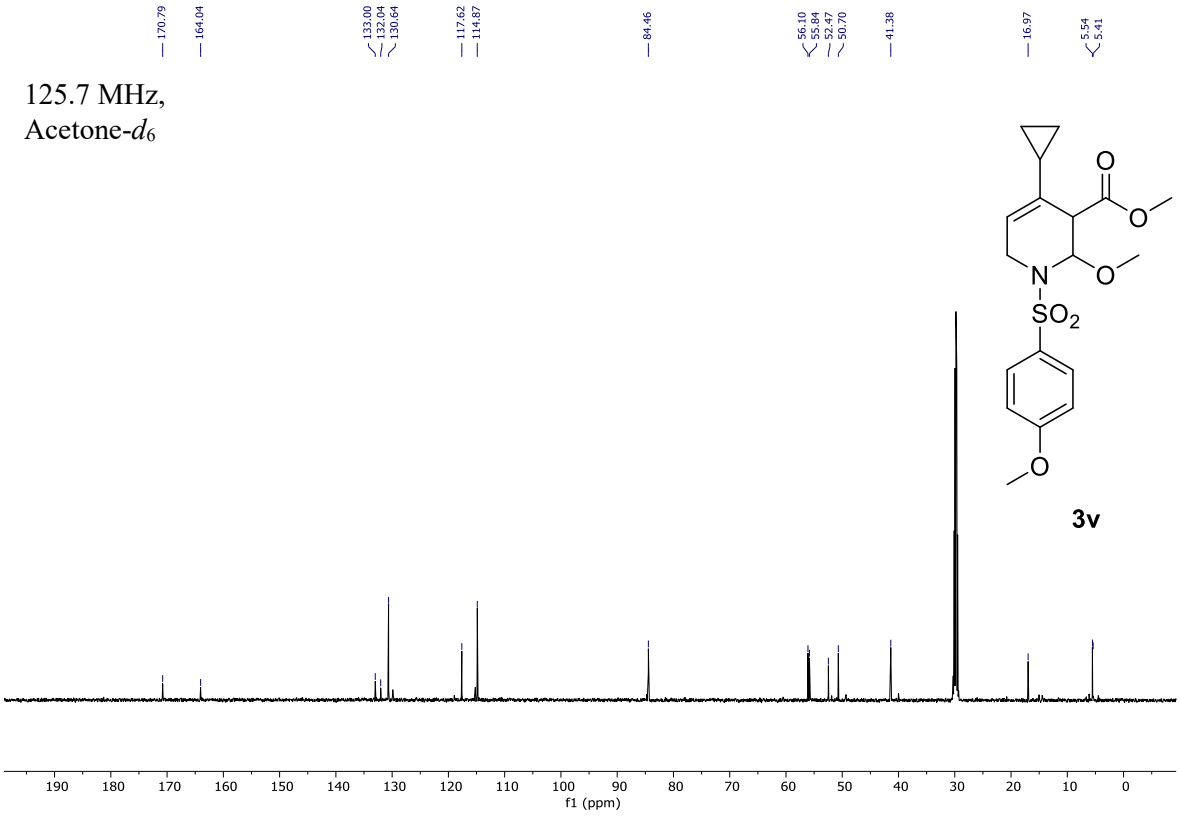


3u

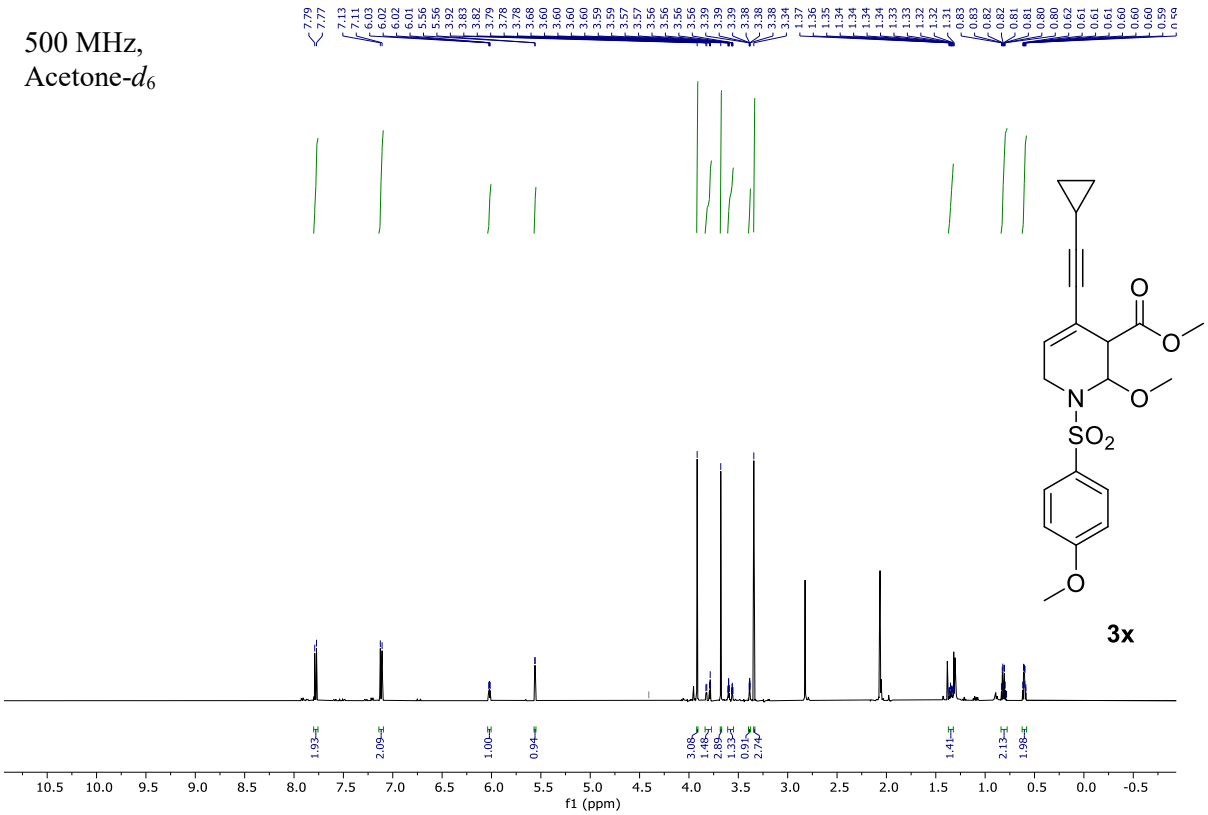
500 MHz,
Acetone-d_6



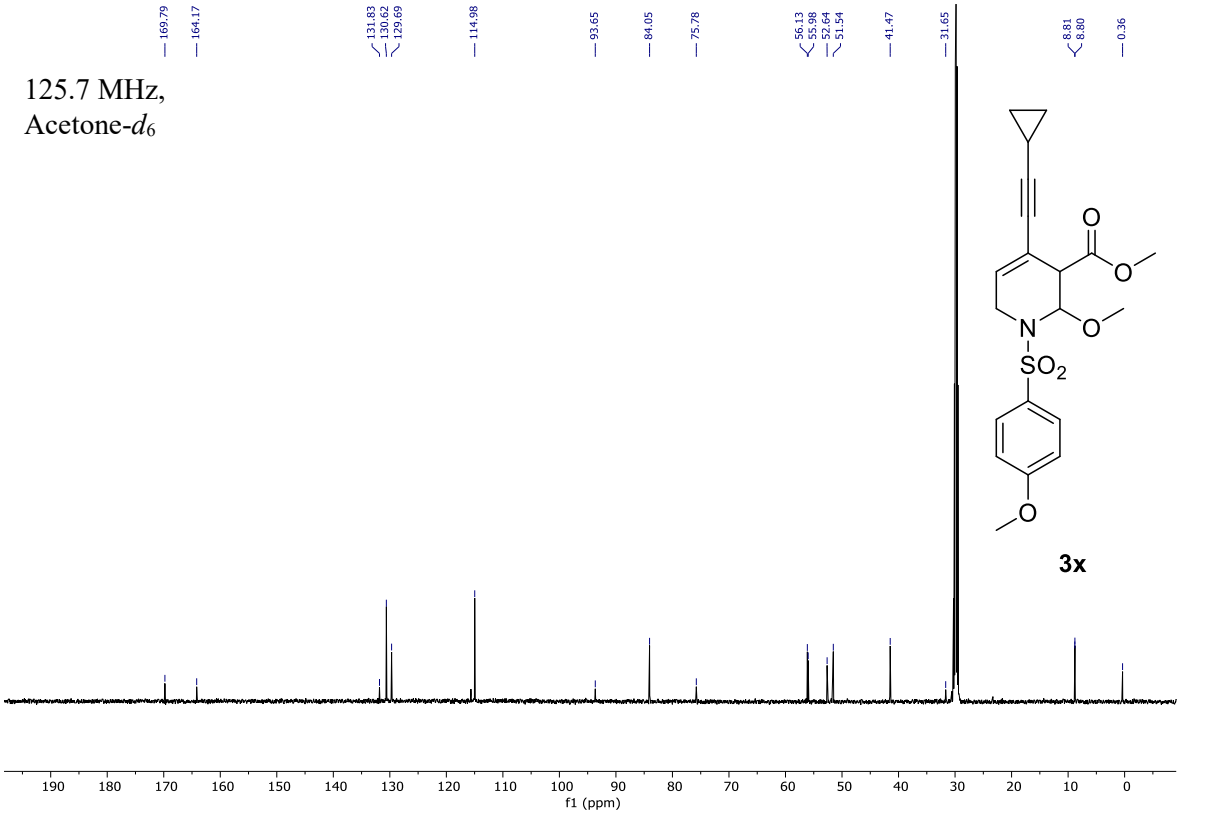
125.7 MHz,
Acetone-d_6



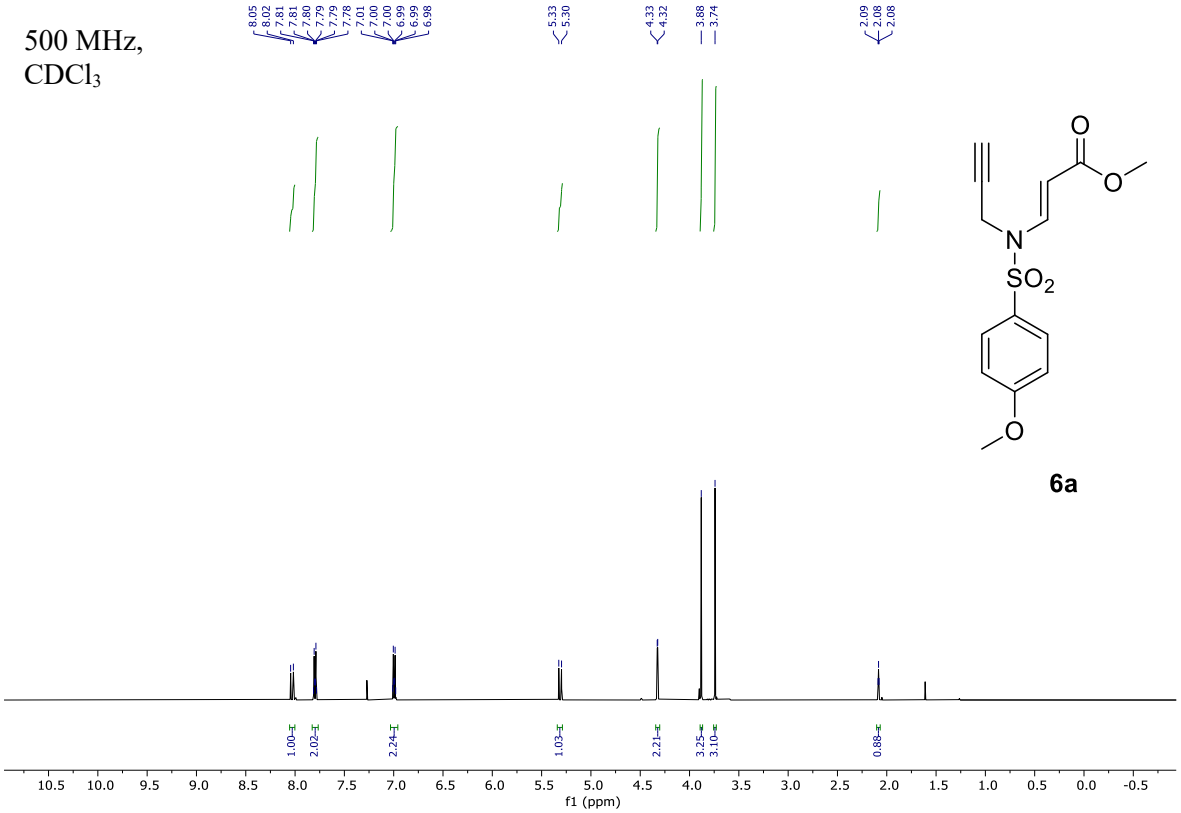
500 MHz,
Acetone-d_6



125.7 MHz,
Acetone-d_6

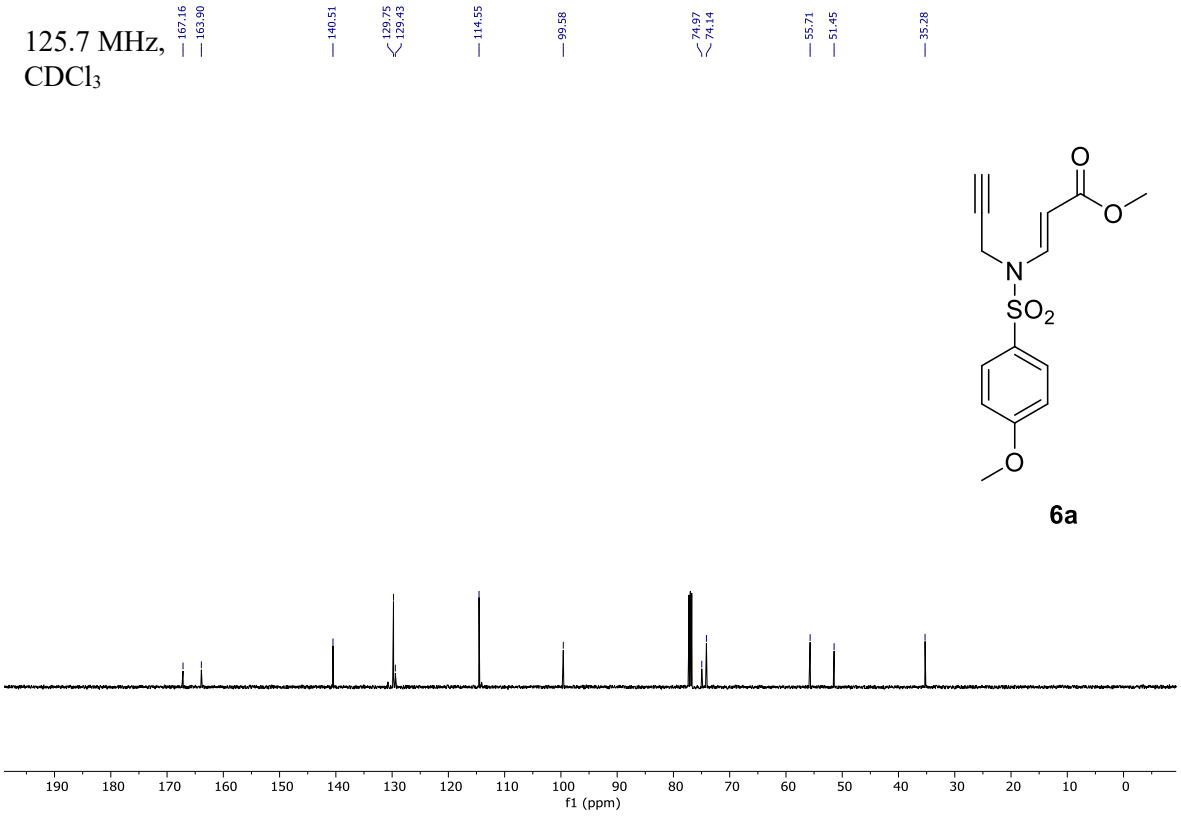


500 MHz,
$CDCl_3$



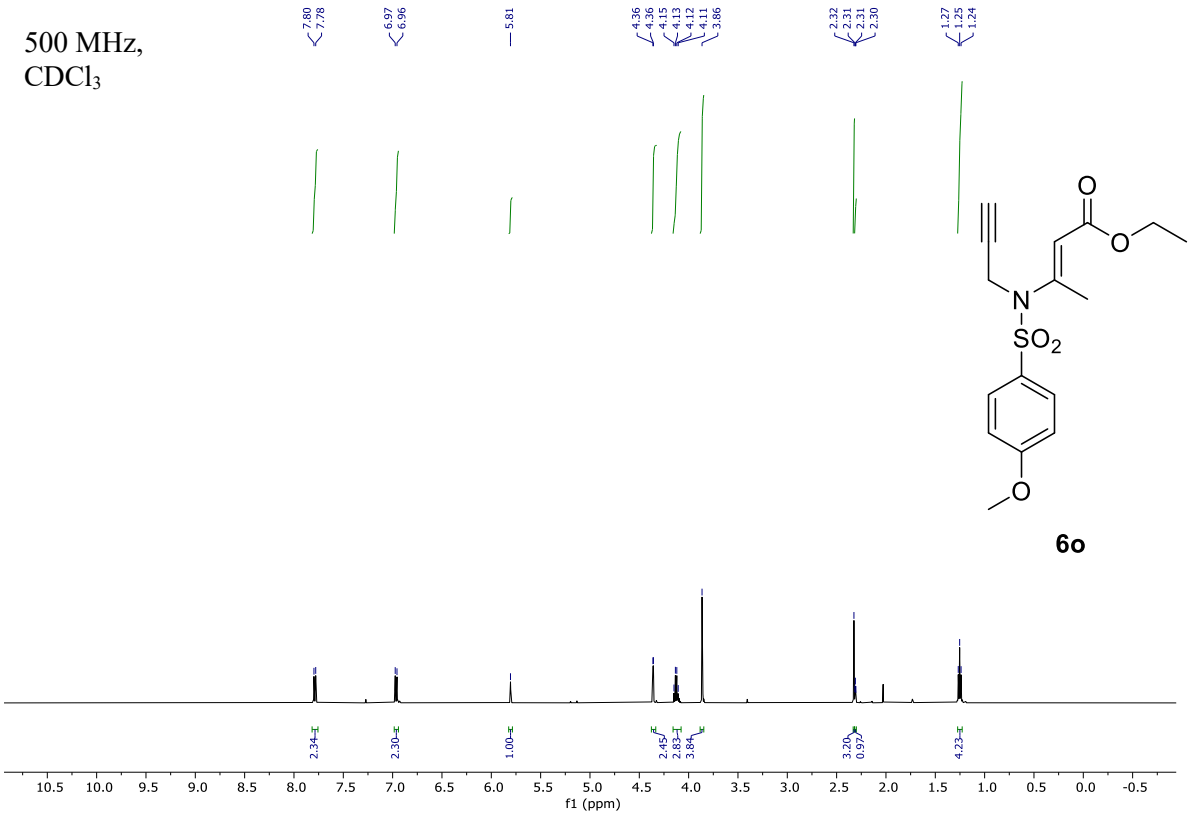
6a

125.7 MHz,
$CDCl_3$



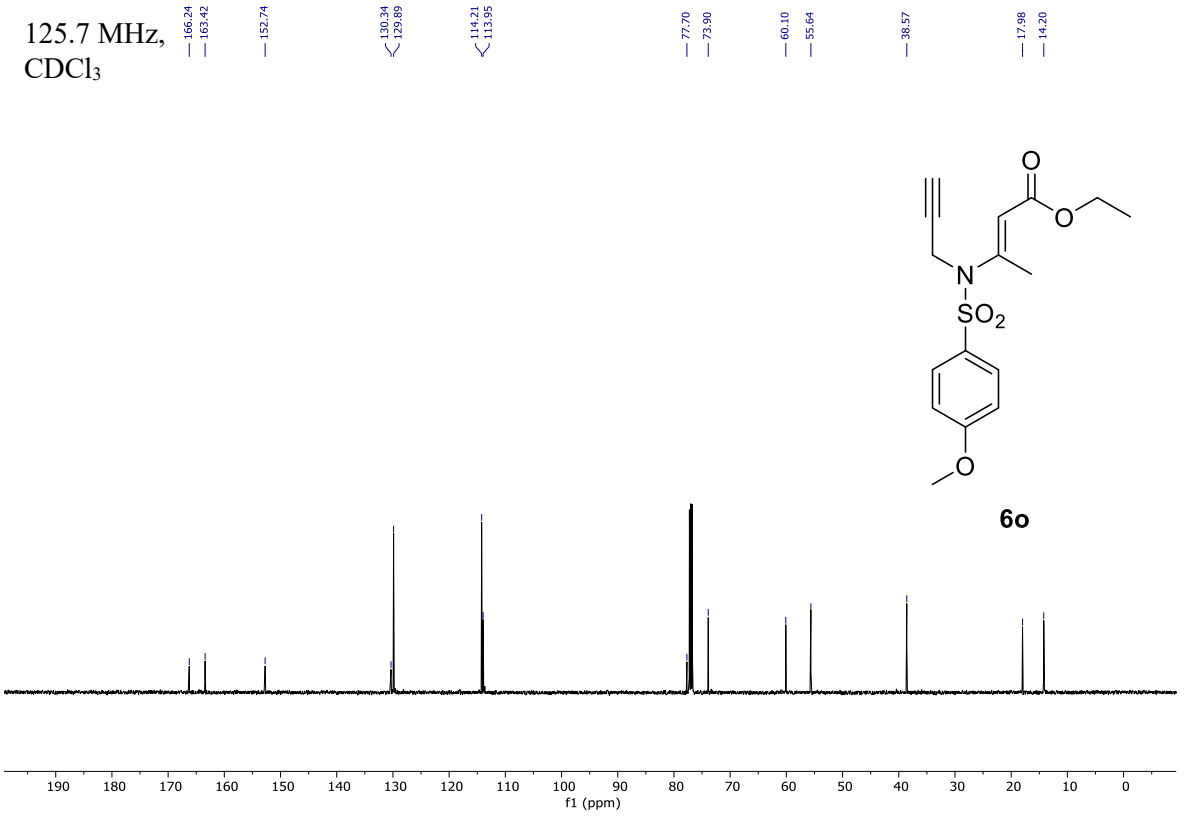
6a

500 MHz,
$CDCl_3$



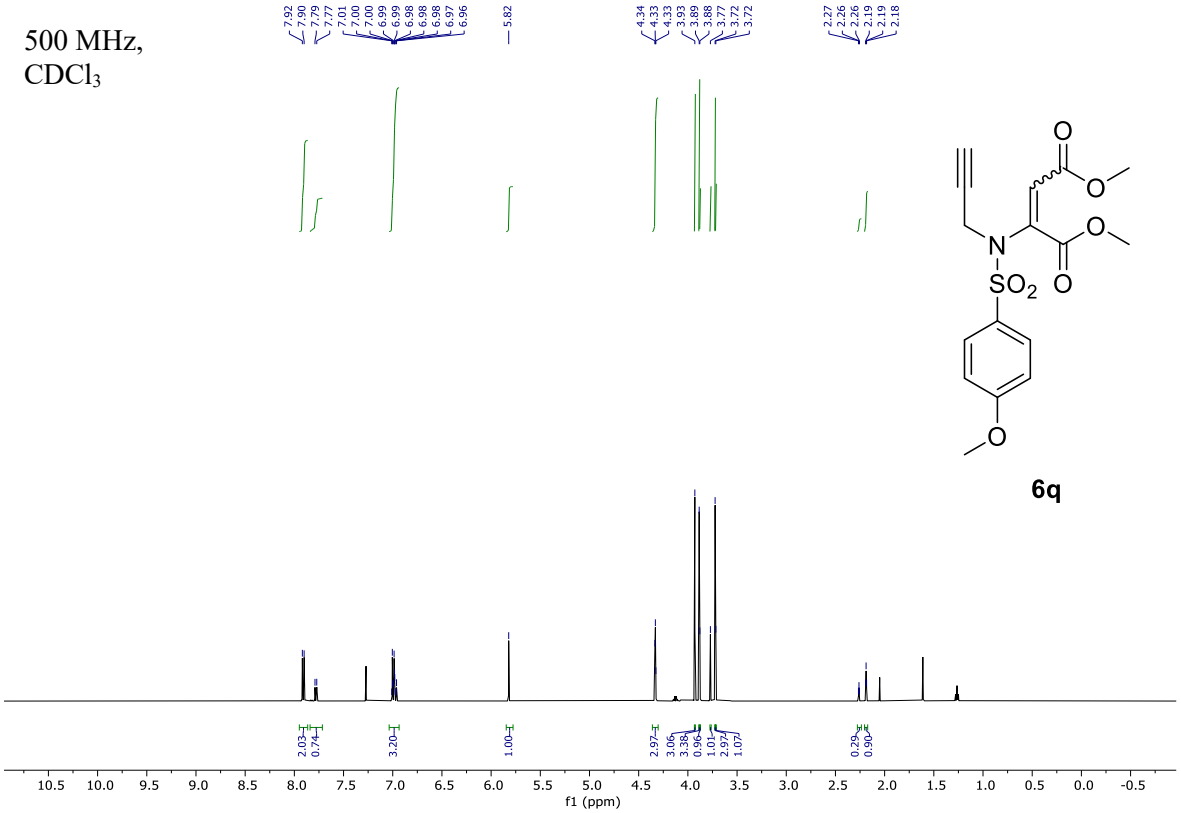
6o

125.7 MHz,
$CDCl_3$



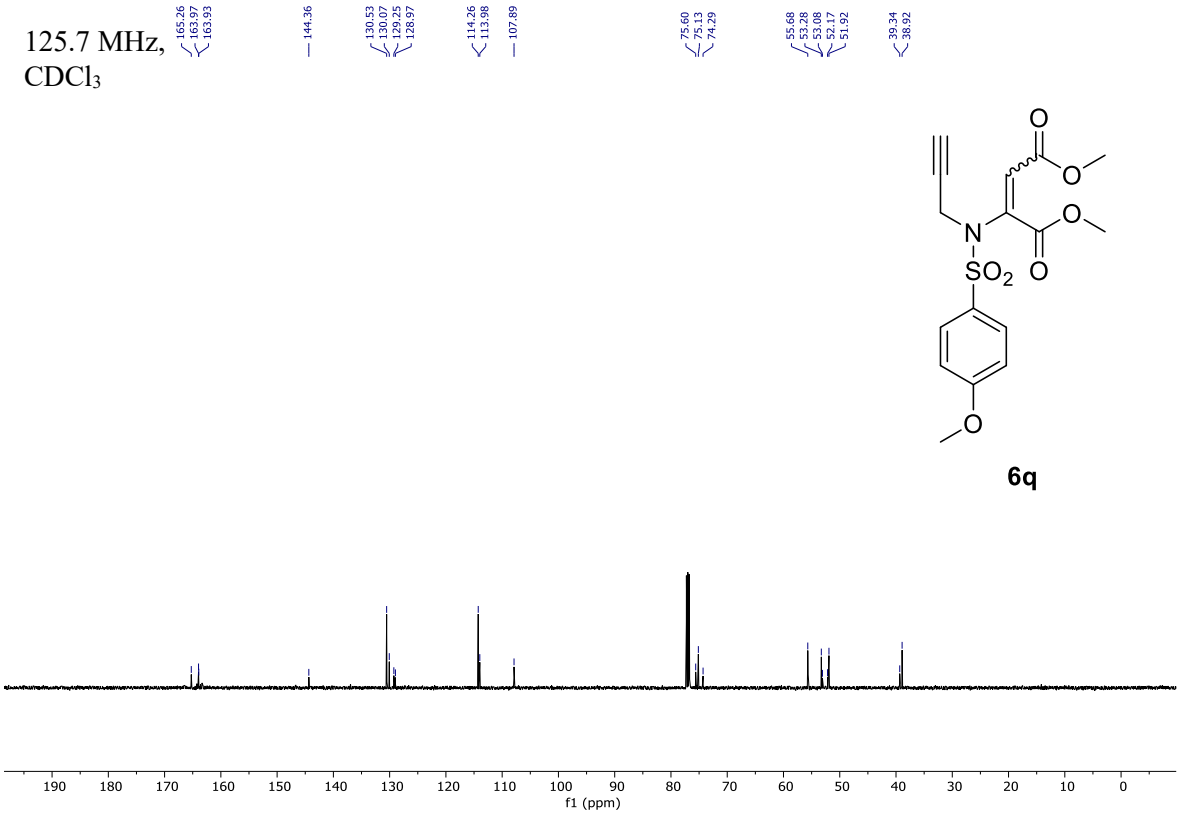
6o

500 MHz,
$CDCl_3$



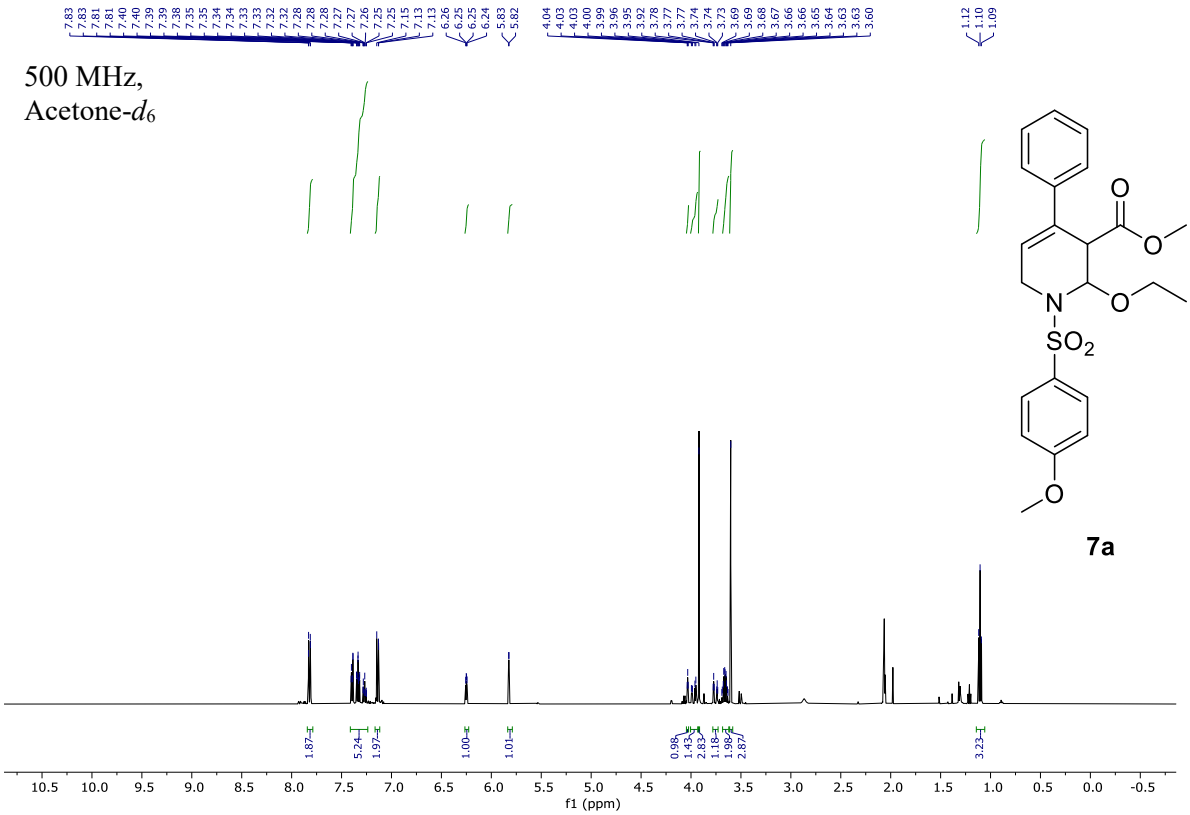
6q

125.7 MHz,
$CDCl_3$

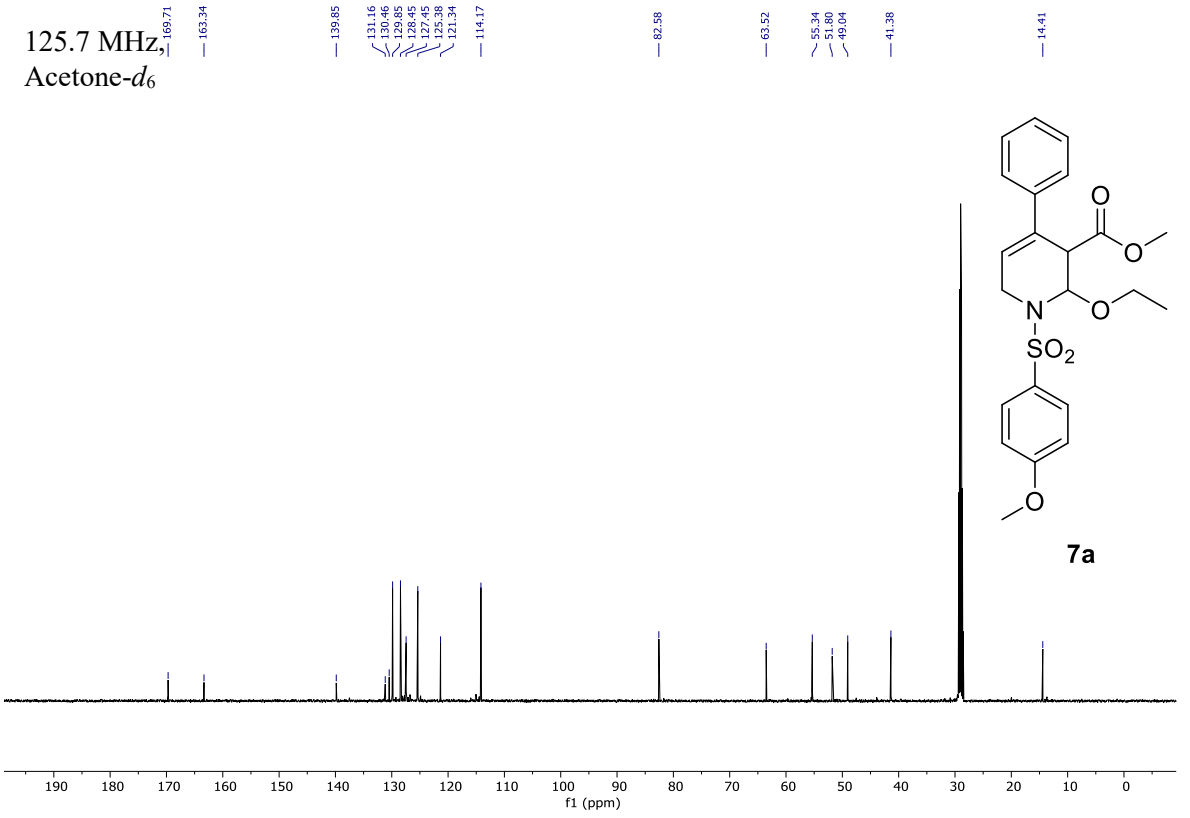


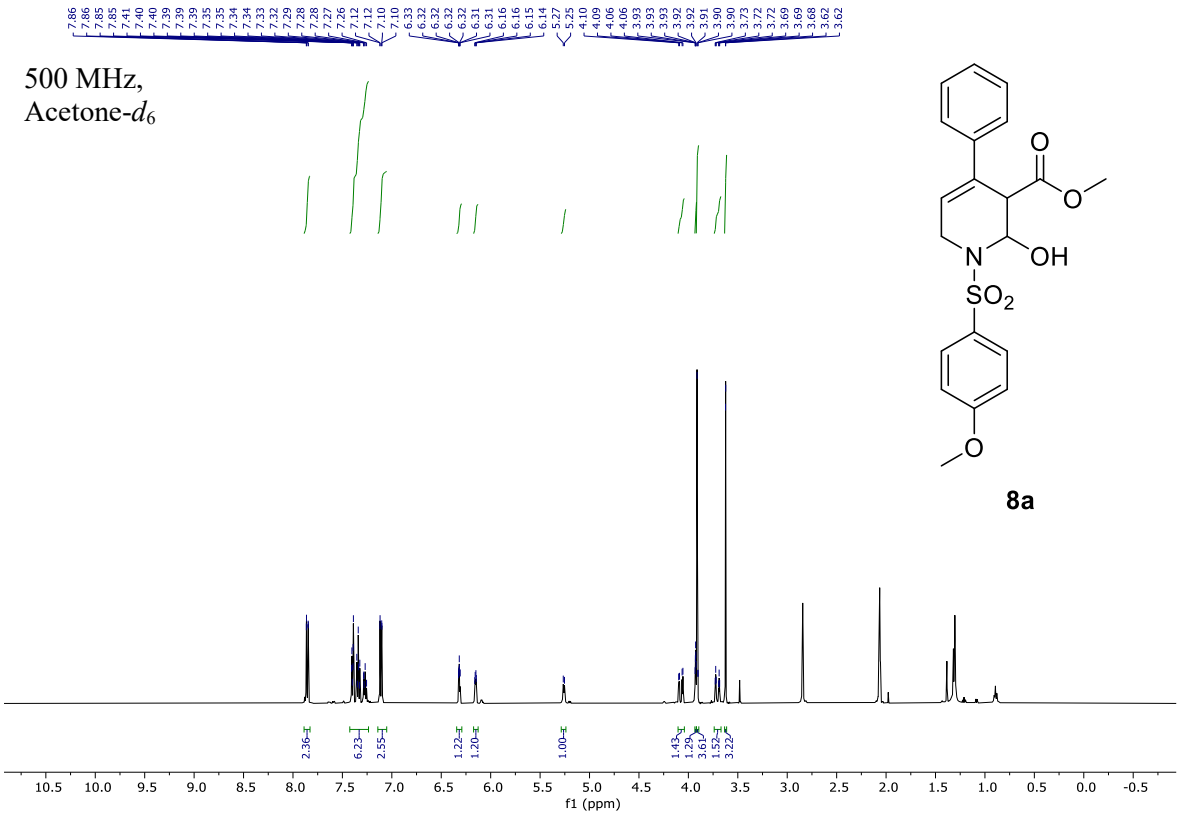
6q

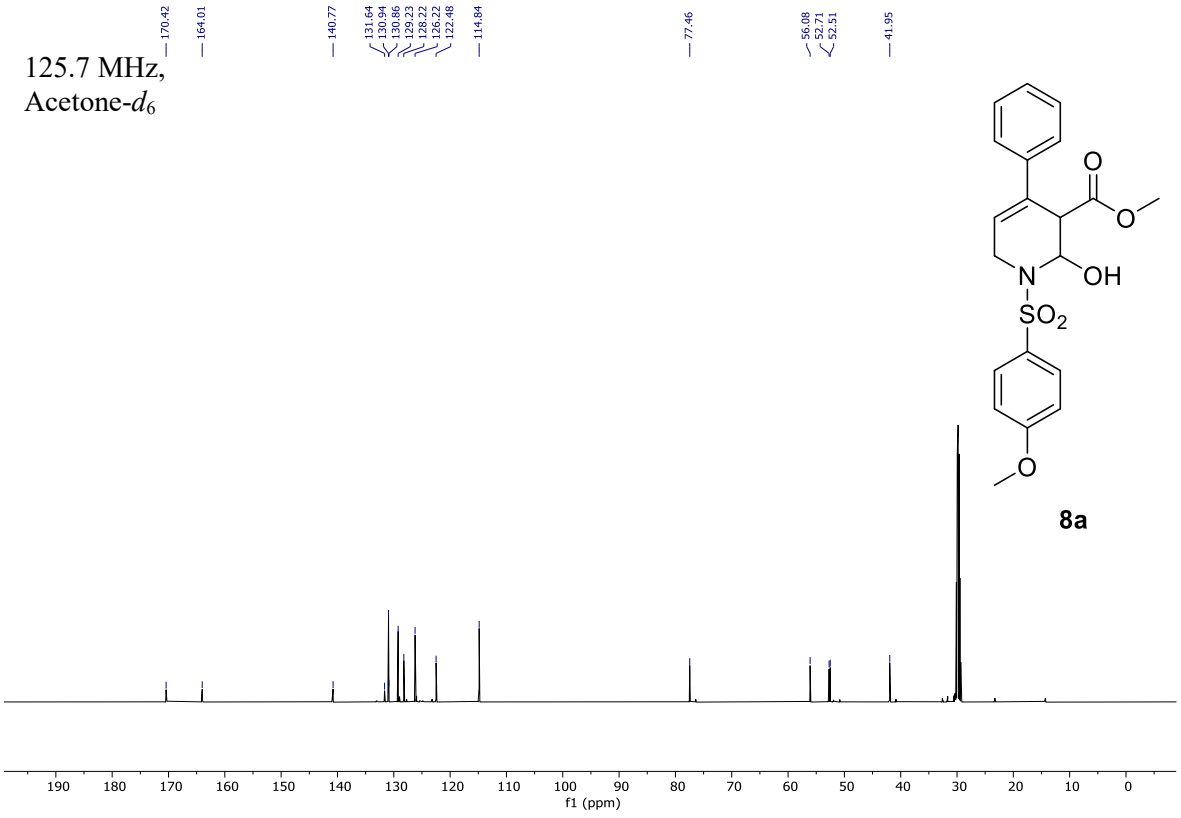
500 MHz,
Acetone-d_6



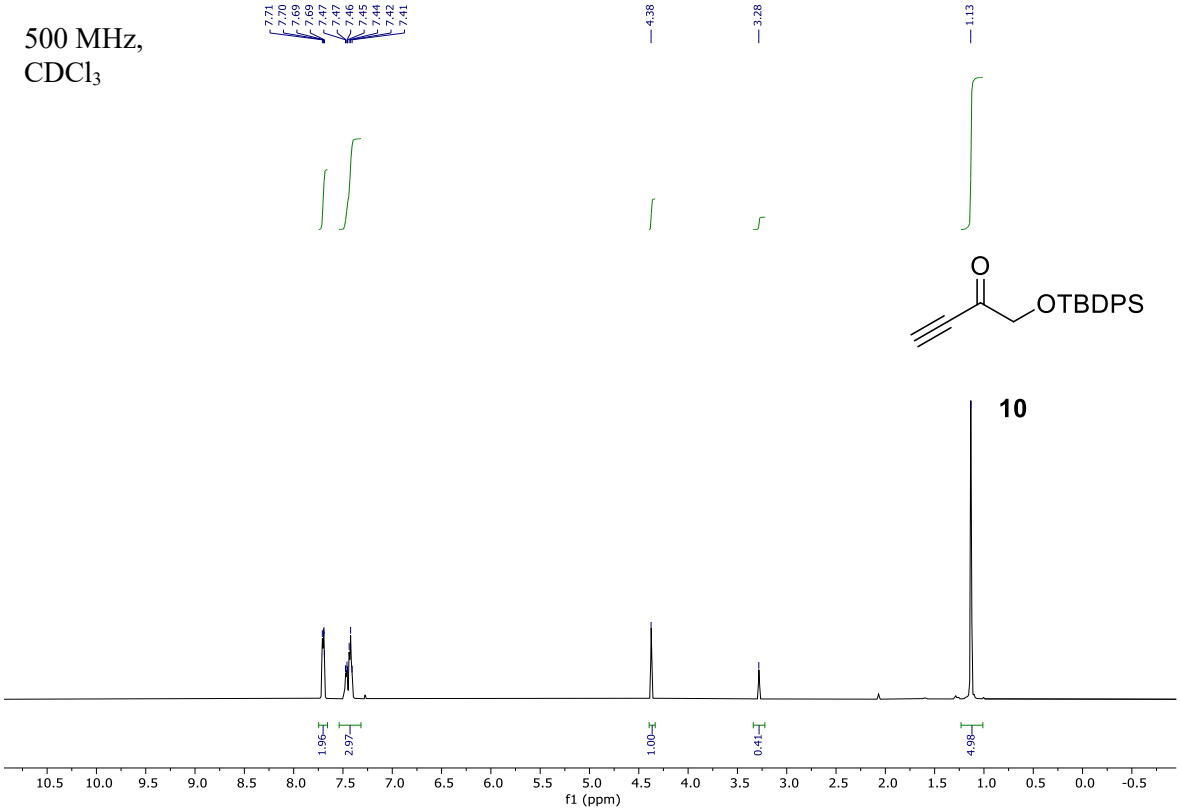
125.7 MHz,
Acetone-d_6




500 MHz,
Acetone-d_6
8a
f1 (ppm)


125.7 MHz,
Acetone-d_6
8a
f1 (ppm)

500 MHz,
$CDCl_3$



125.7 MHz,
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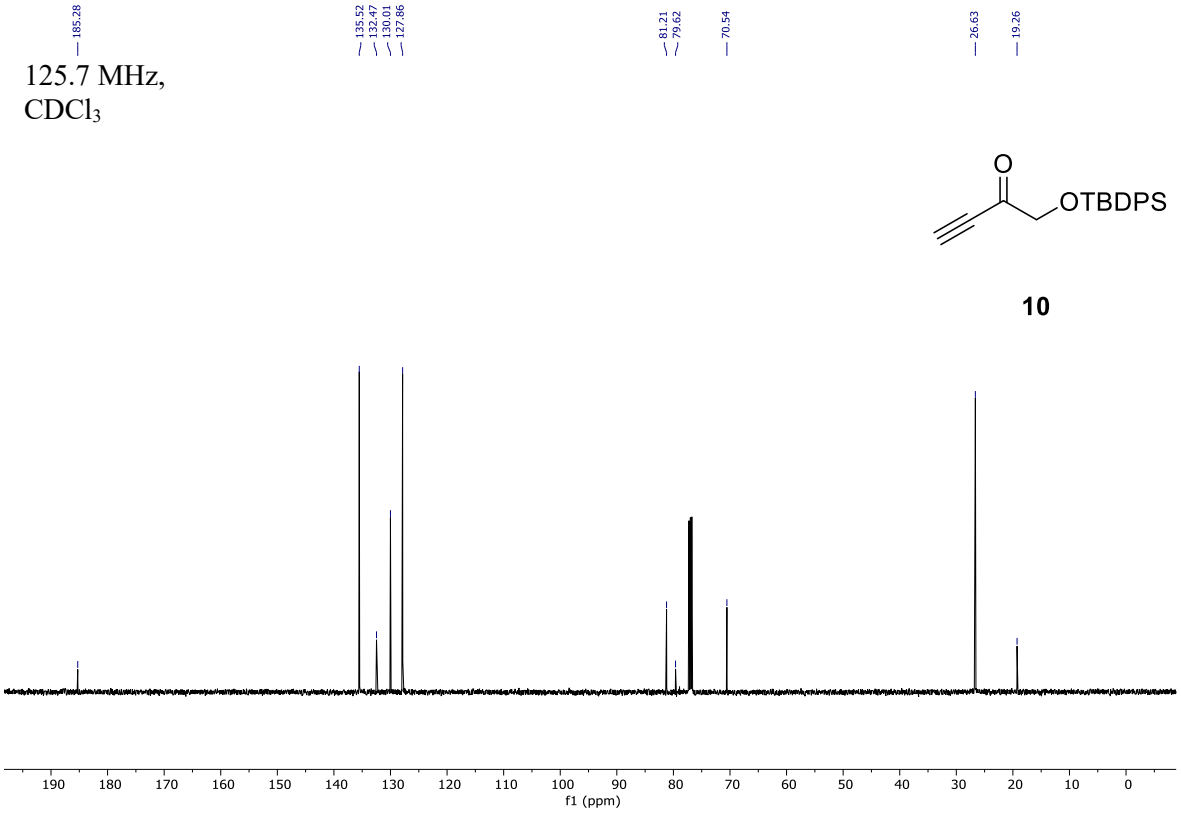
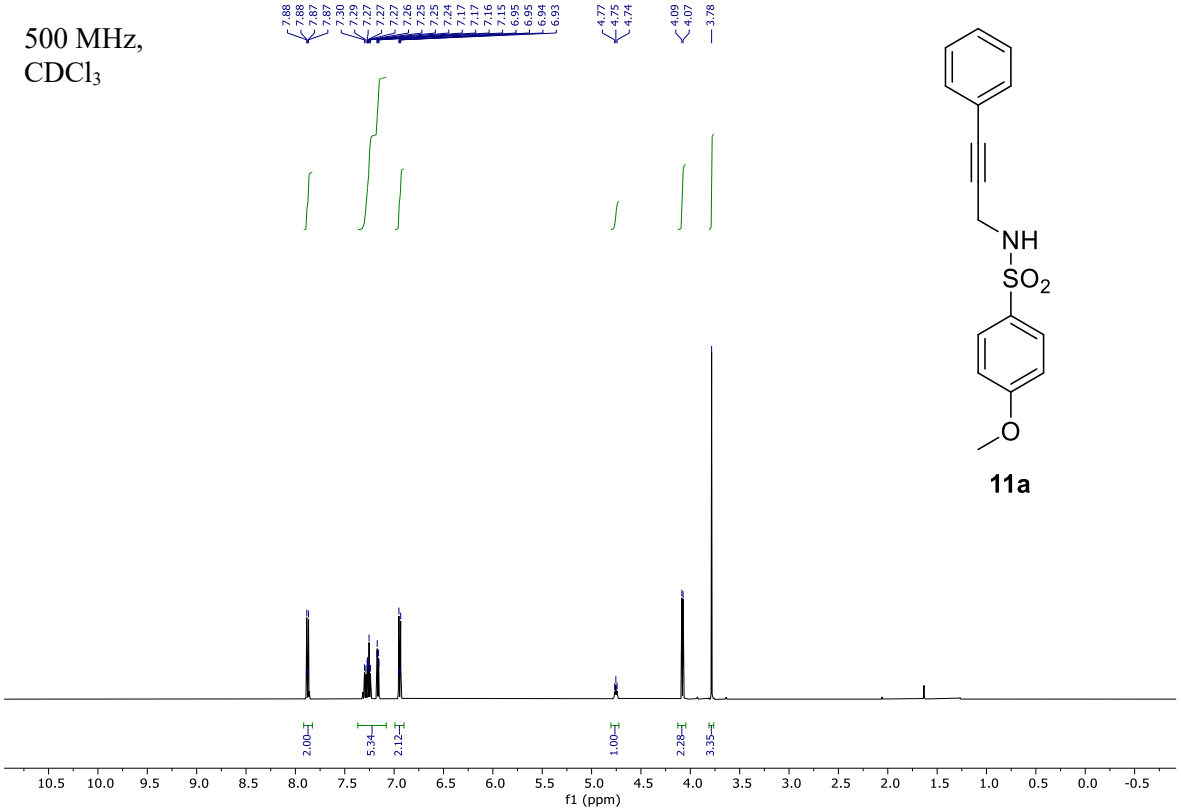
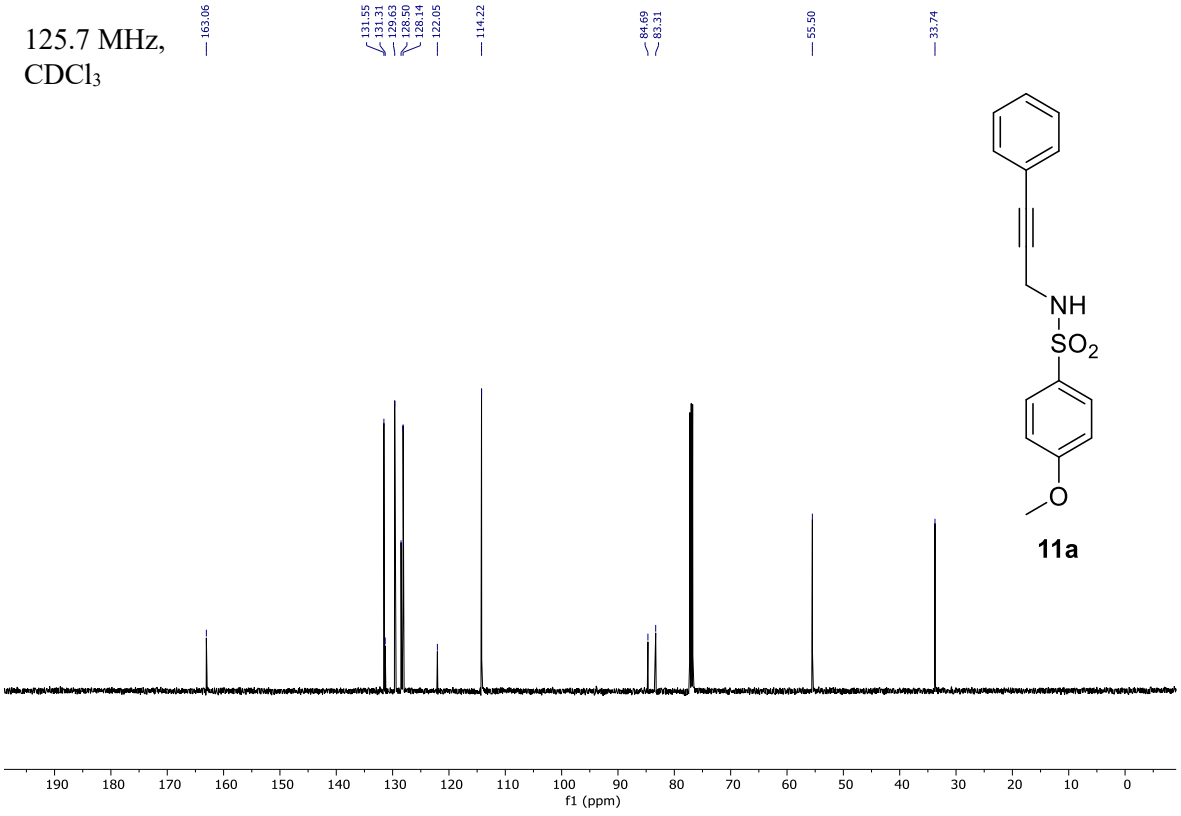


500 MHz,
$CDCl_3$



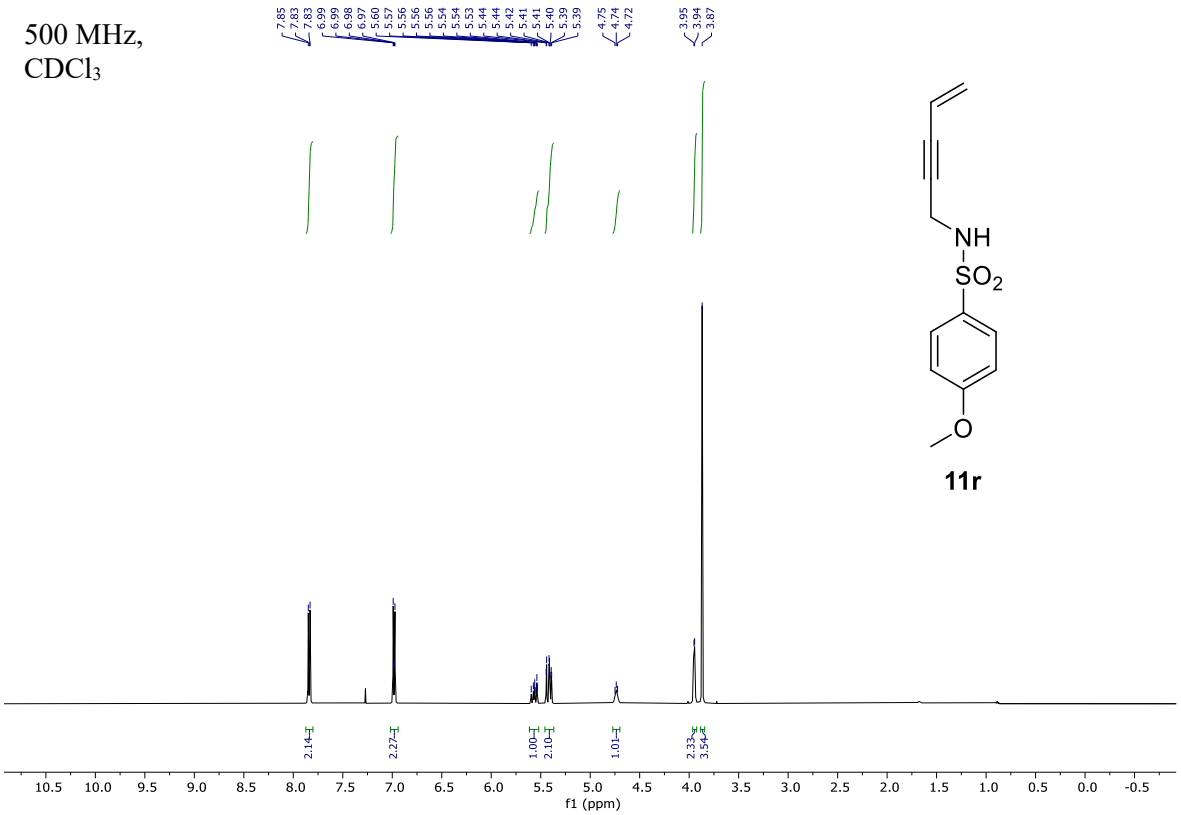
11a

125.7 MHz,
$CDCl_3$

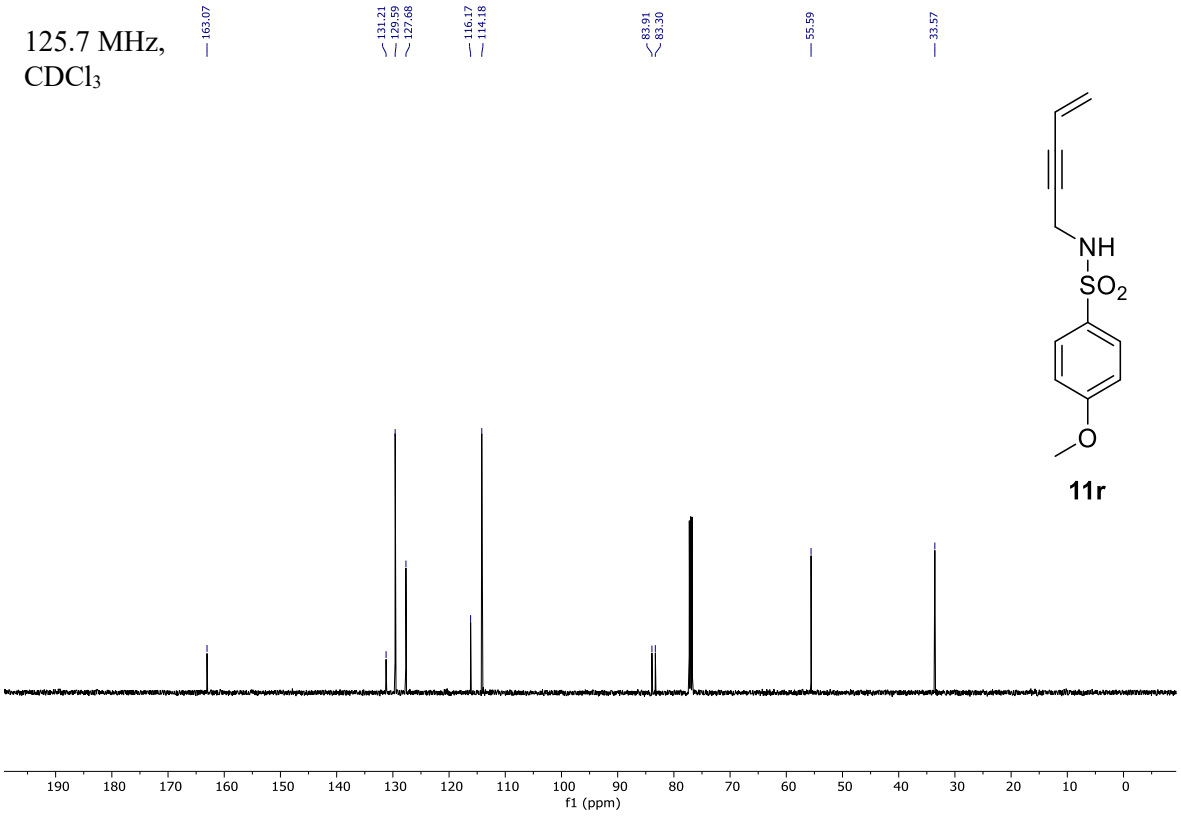


11a

500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$



500 MHz,
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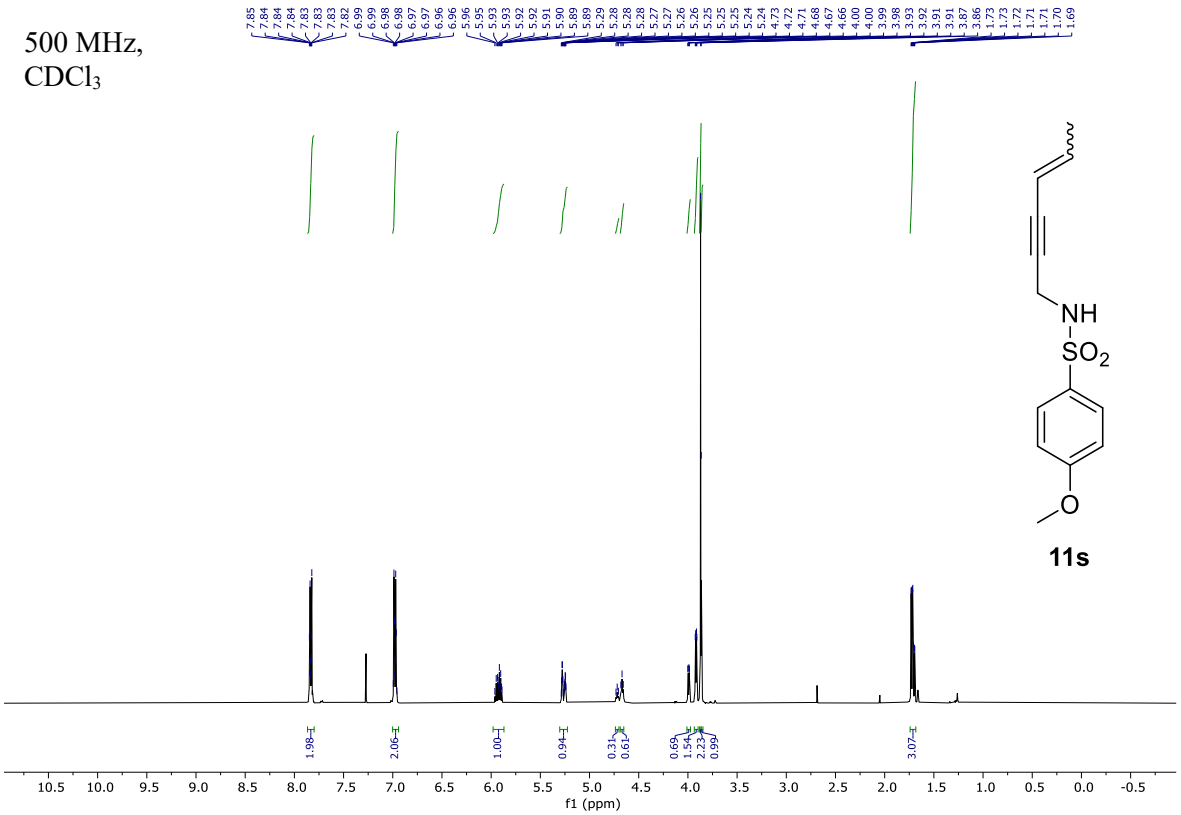
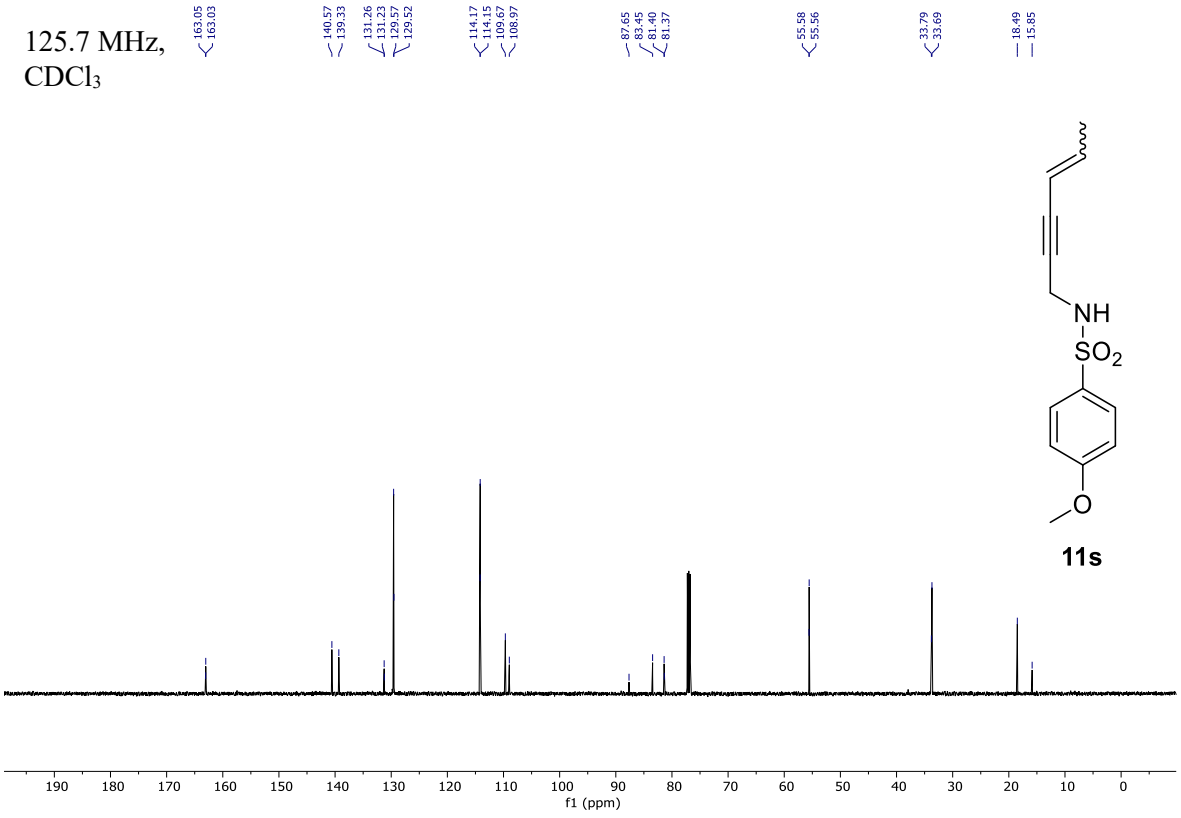
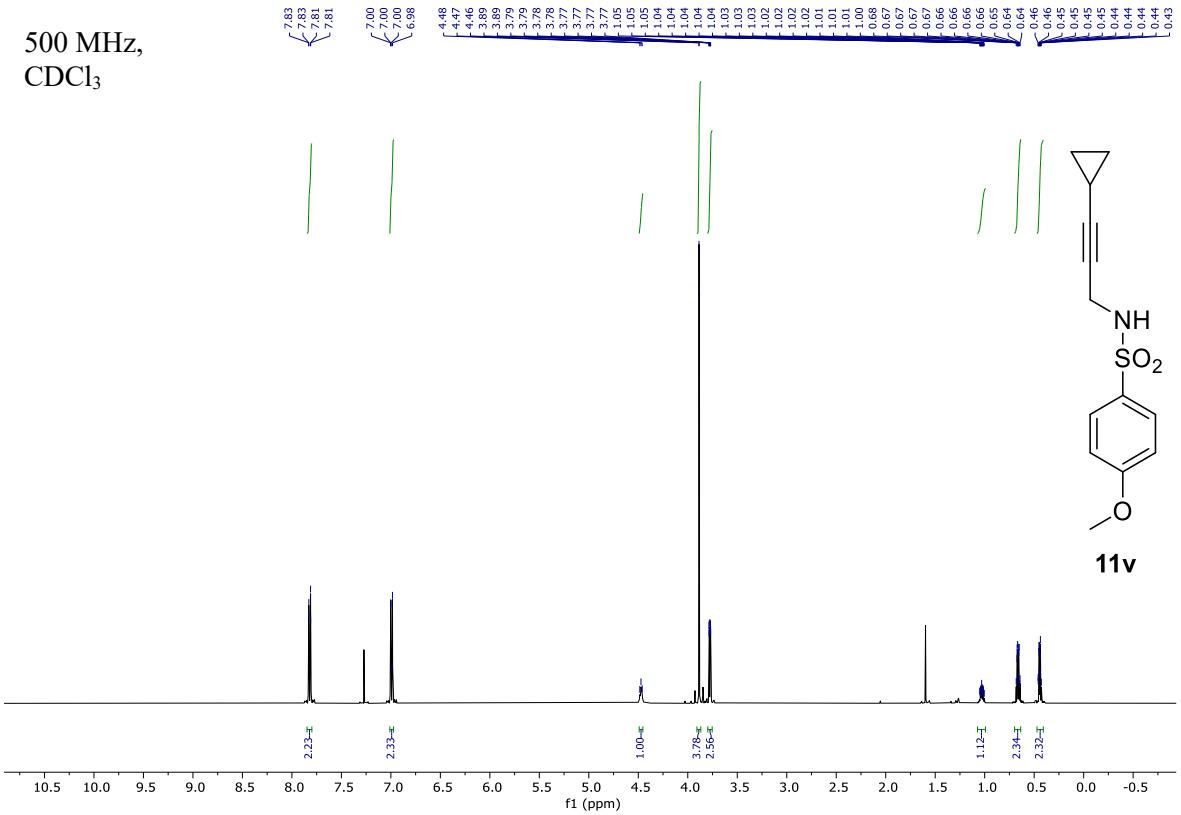


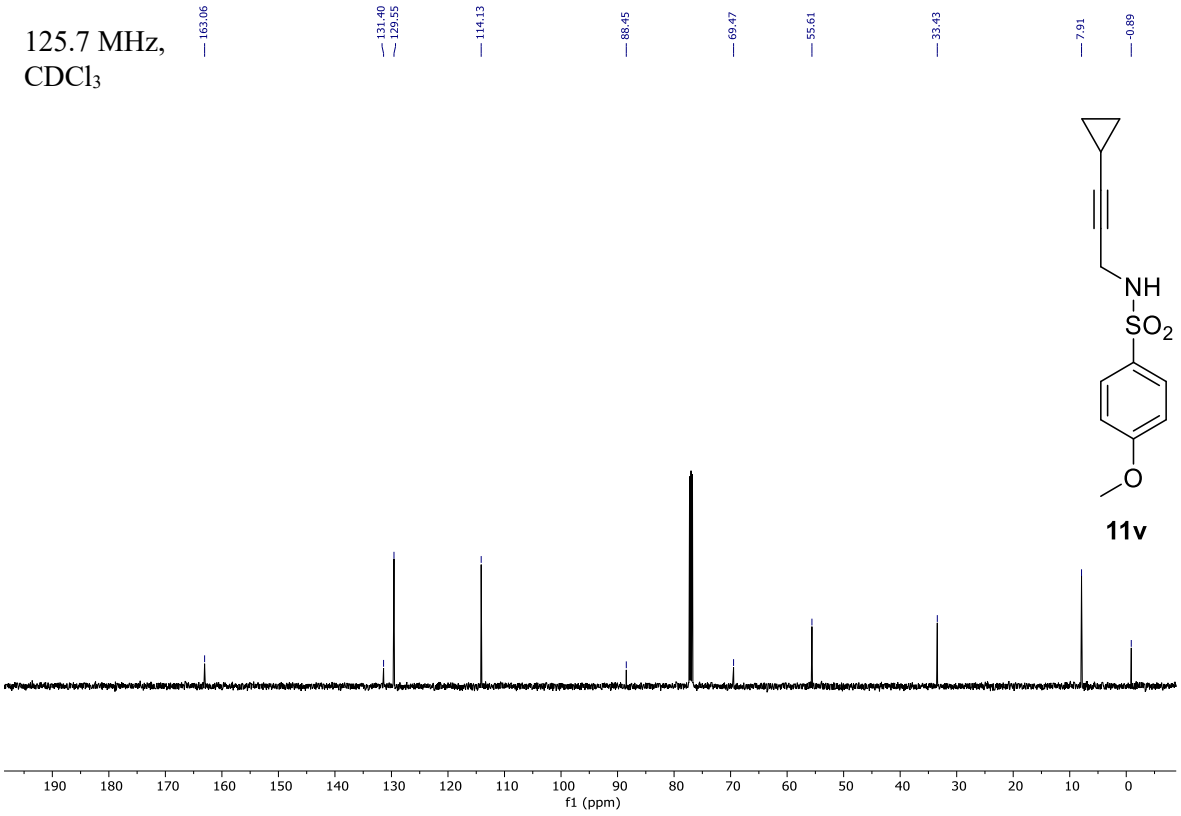
125.7 MHz,
$CDCl_3$



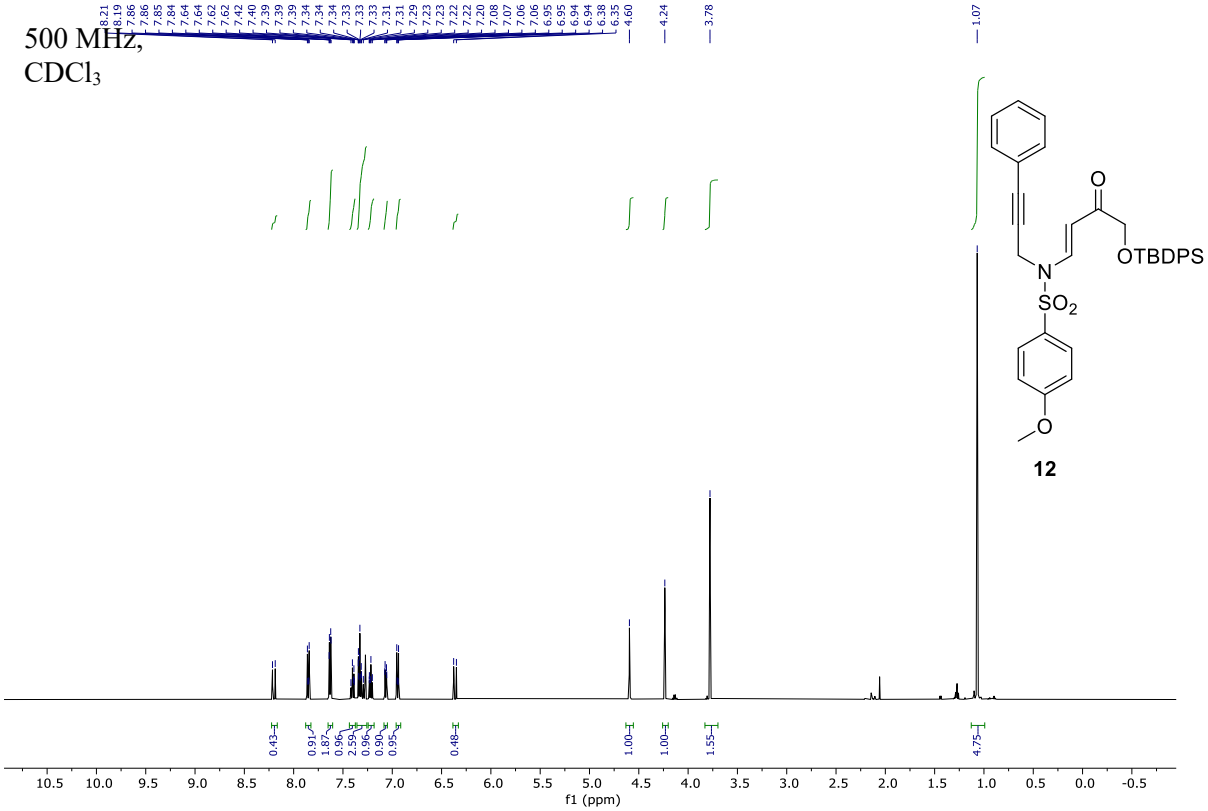
500 MHz,
$CDCl_3$



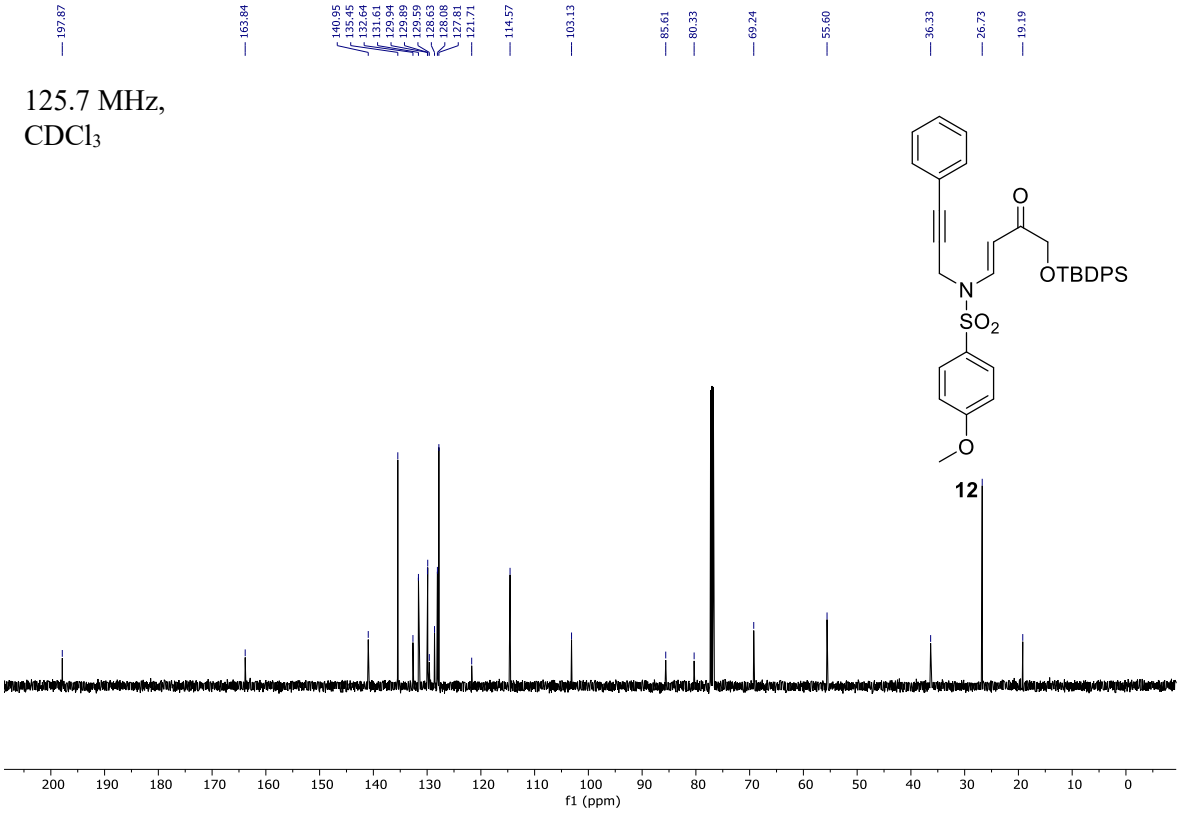
125.7 MHz,
$CDCl_3$



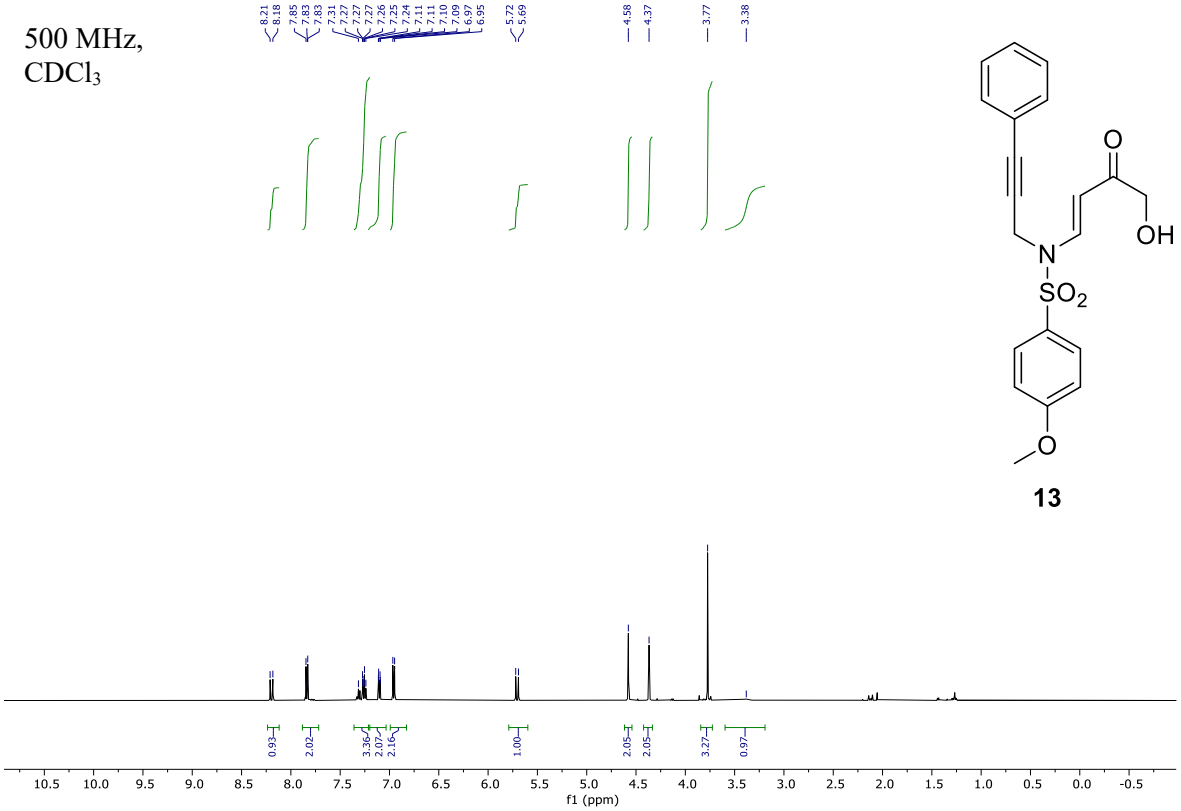
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

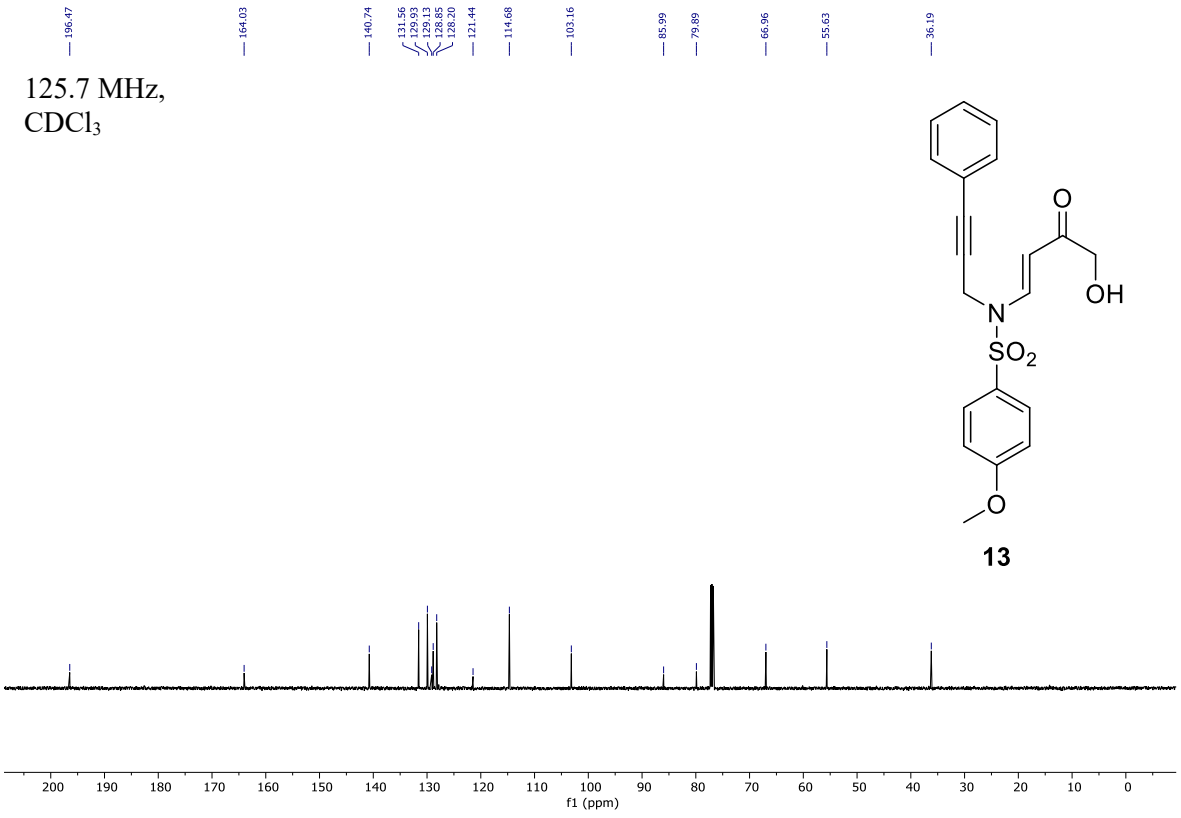


500 MHz,
$CDCl_3$



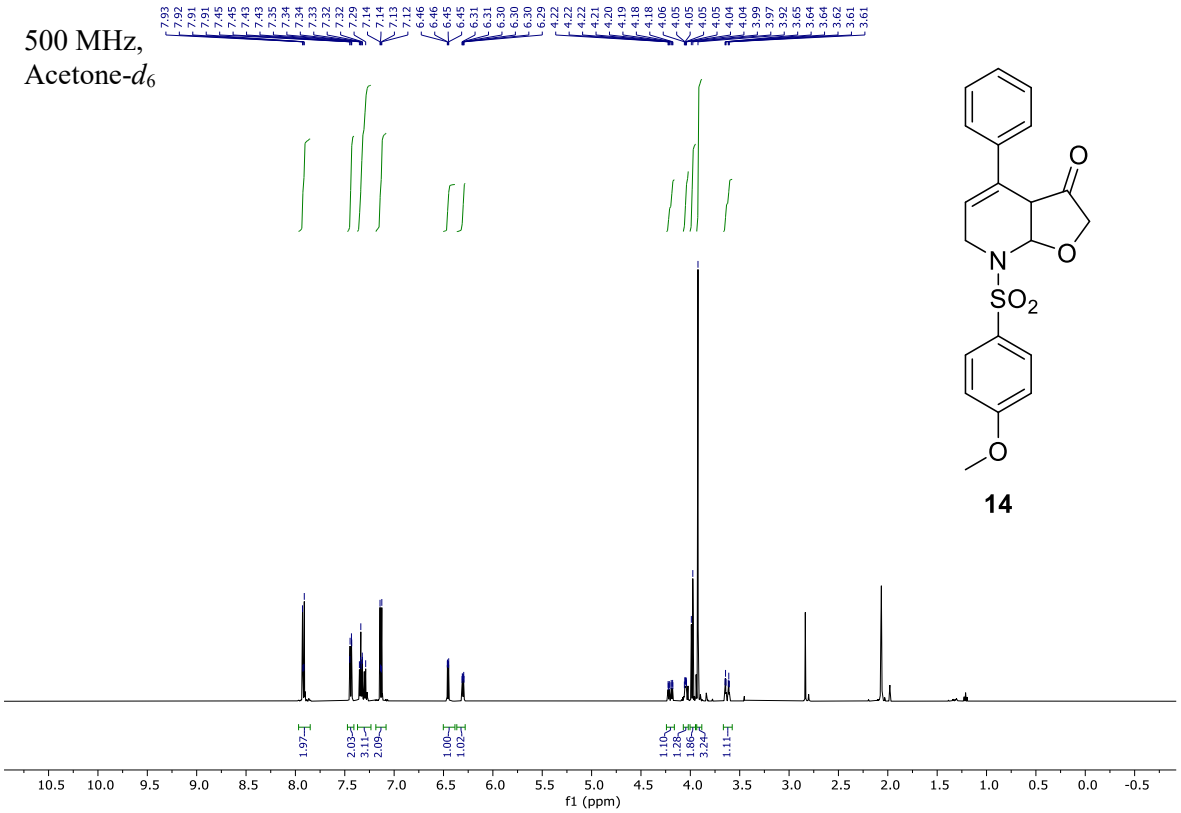
13

125.7 MHz,
$CDCl_3$



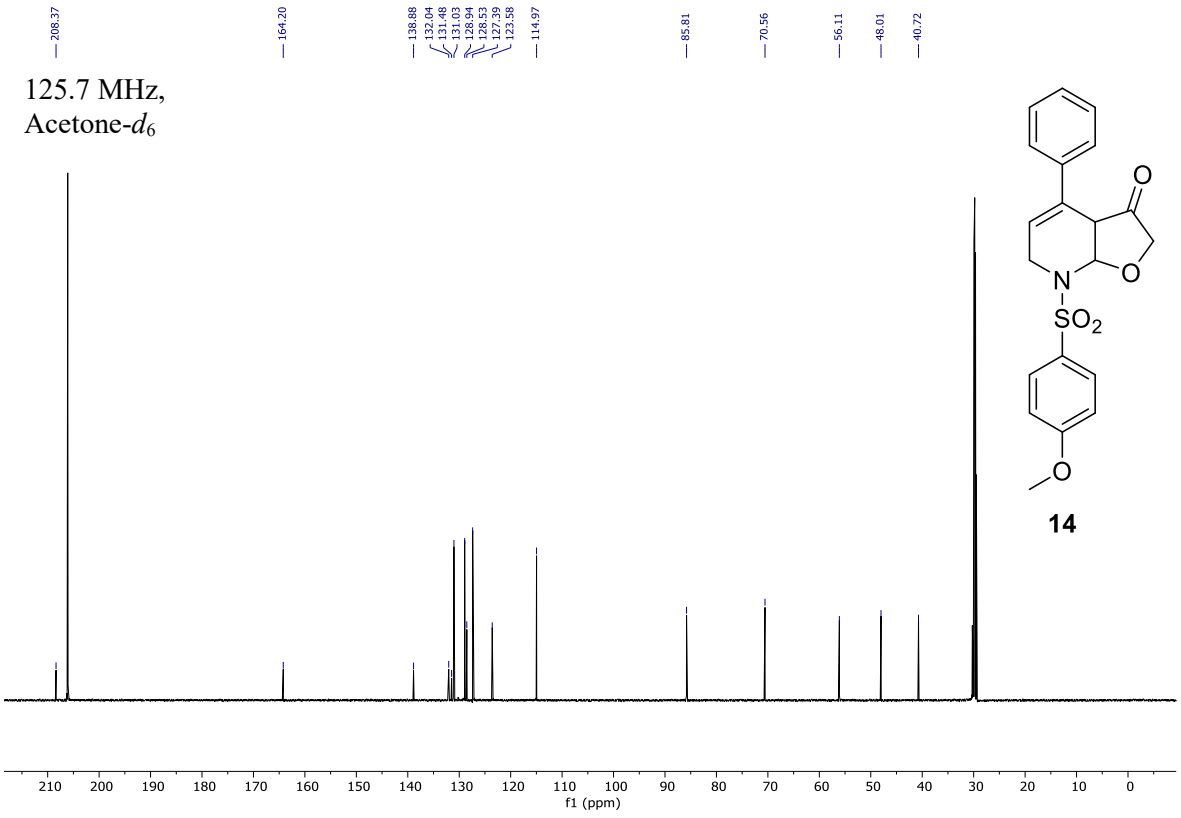
13

500 MHz,
Acetone-d_6



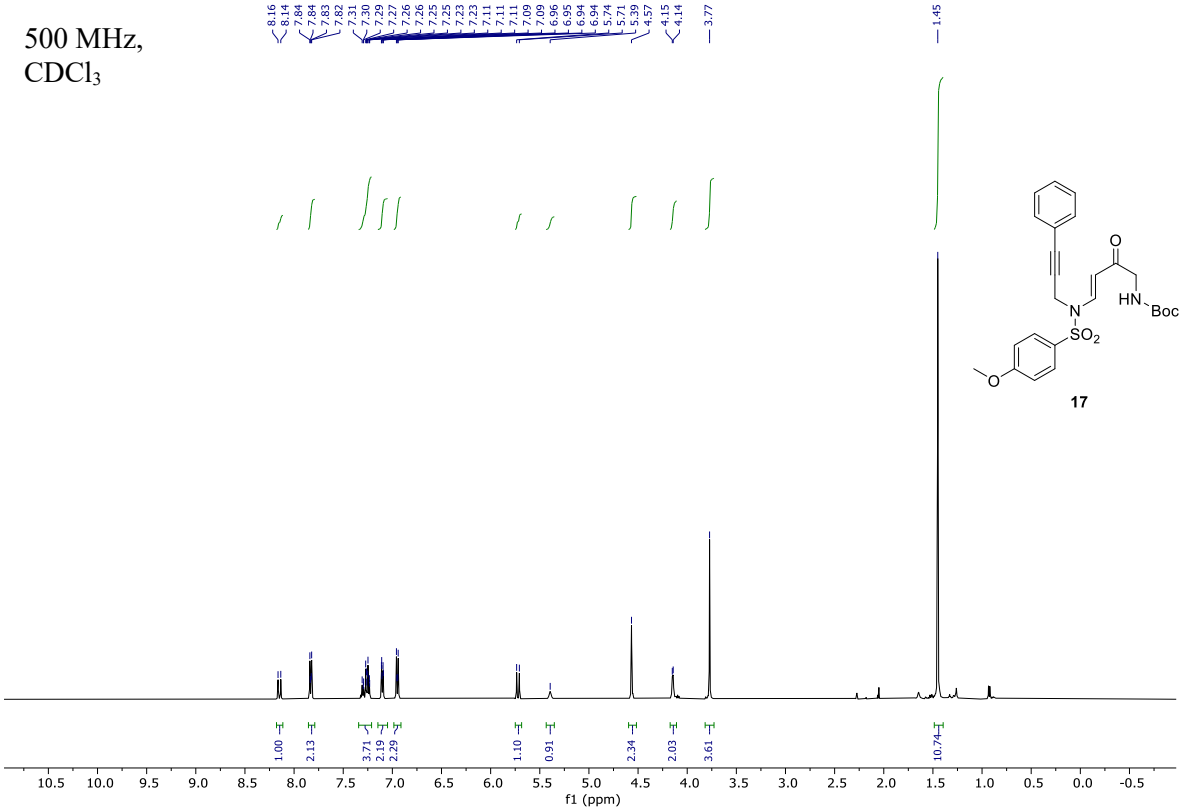
14

125.7 MHz,
Acetone-d_6

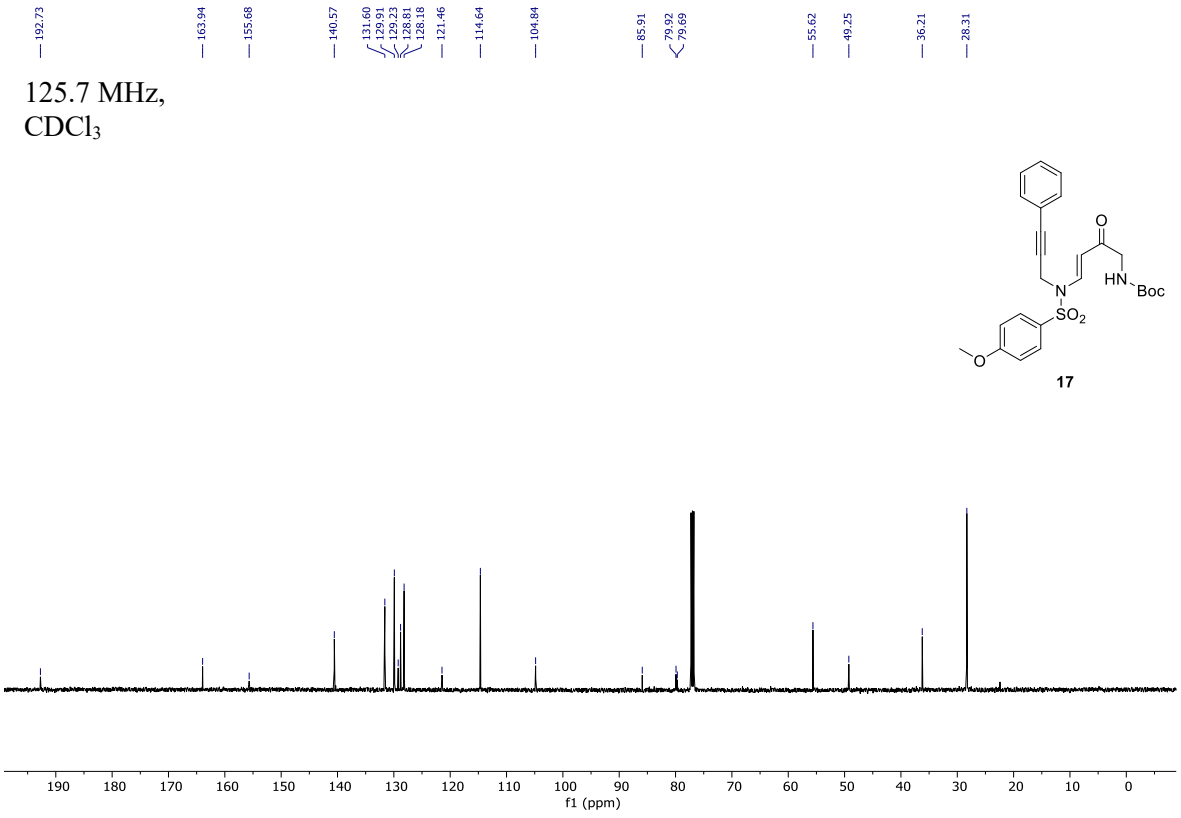


14

500 MHz,
$CDCl_3$

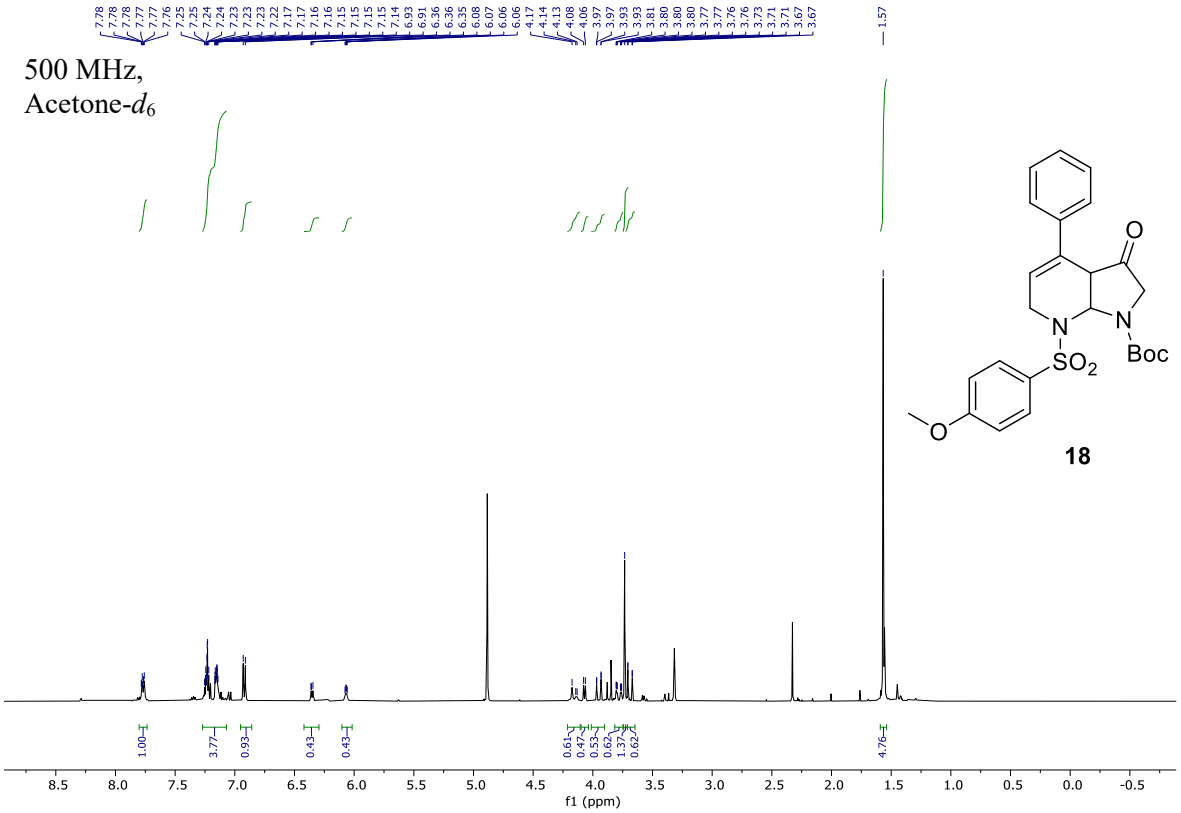


17



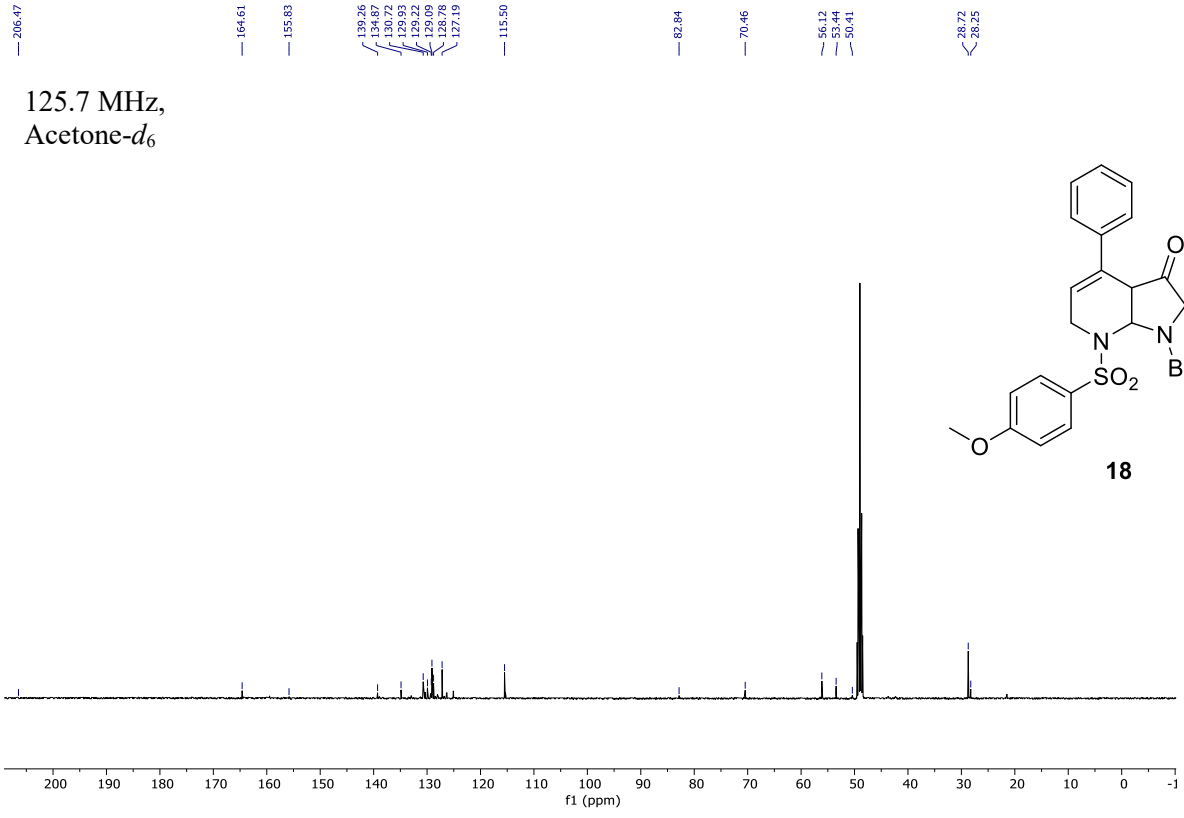
125.7 MHz,
$CDCl_3$

17



500 MHz,
Acetone-d_6

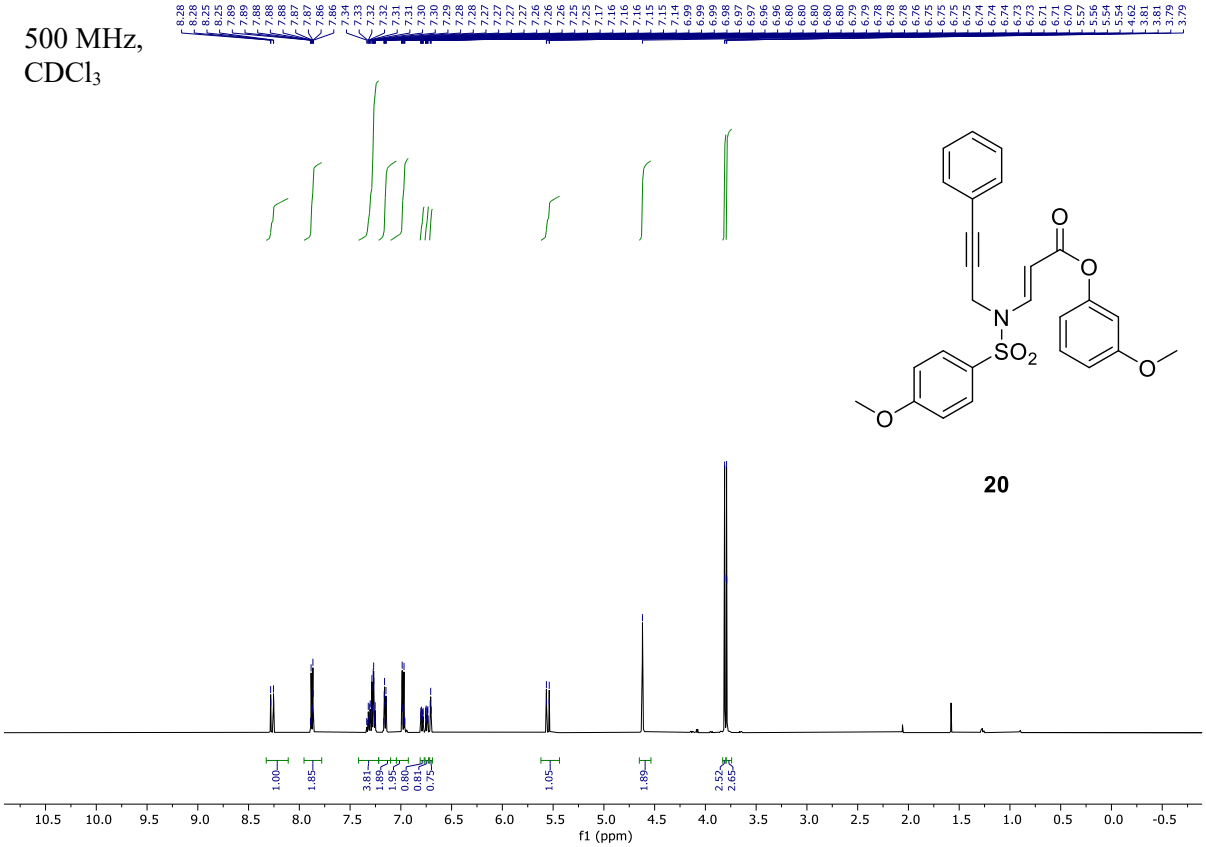
18



125.7 MHz,
Acetone-d_6

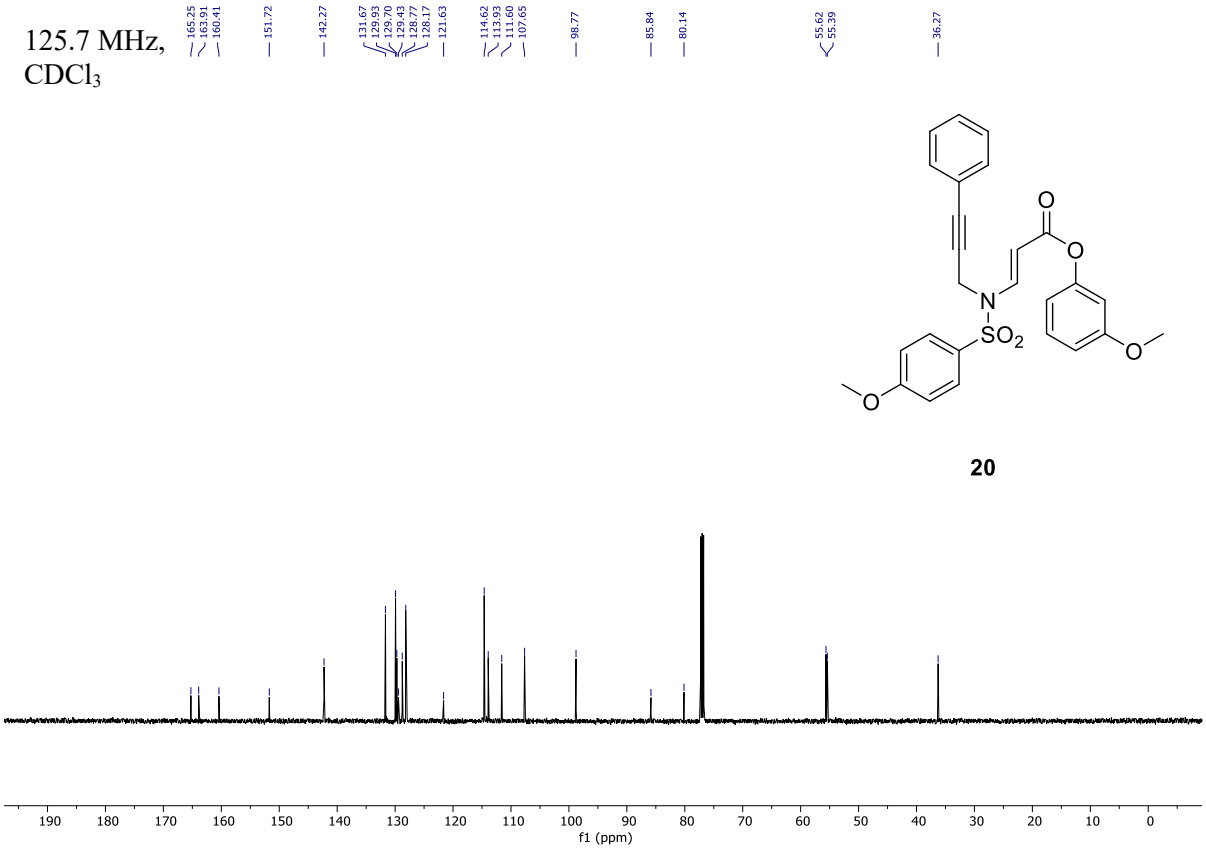
18

500 MHz,
$CDCl_3$



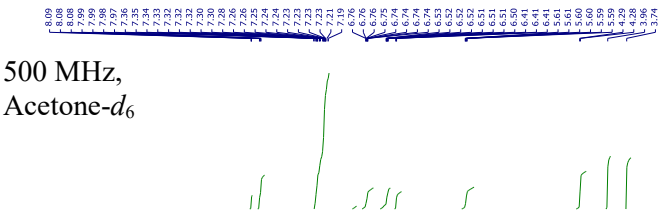
20

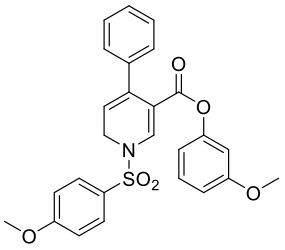
125.7 MHz,
$CDCl_3$



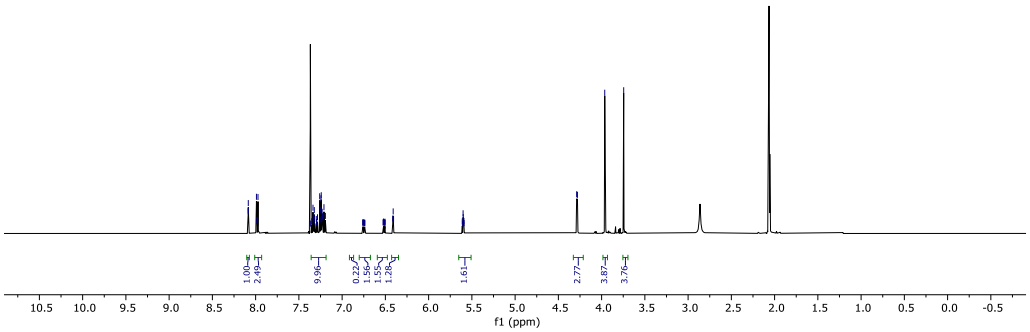
20

500 MHz,
Acetone-d_6

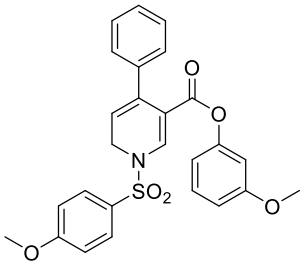




21

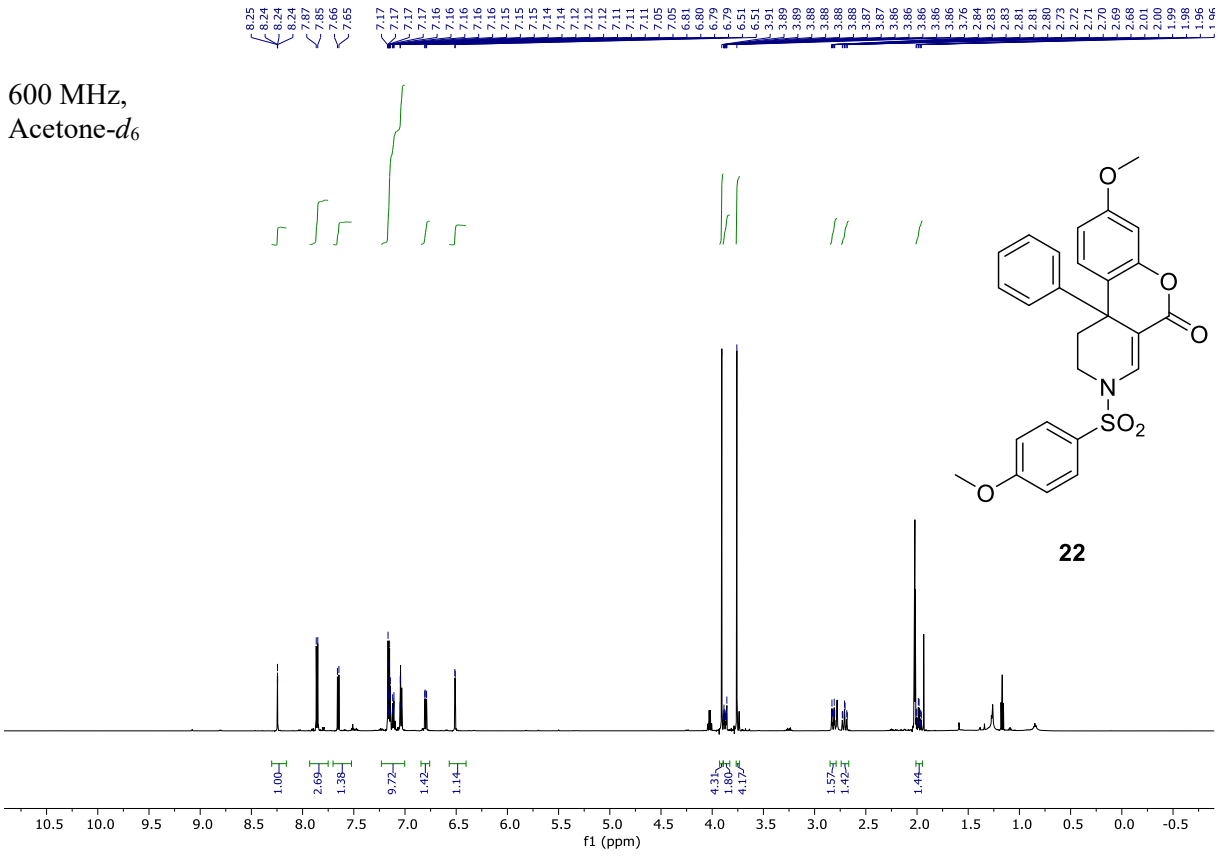


125.7 MHz,
Acetone-d_6



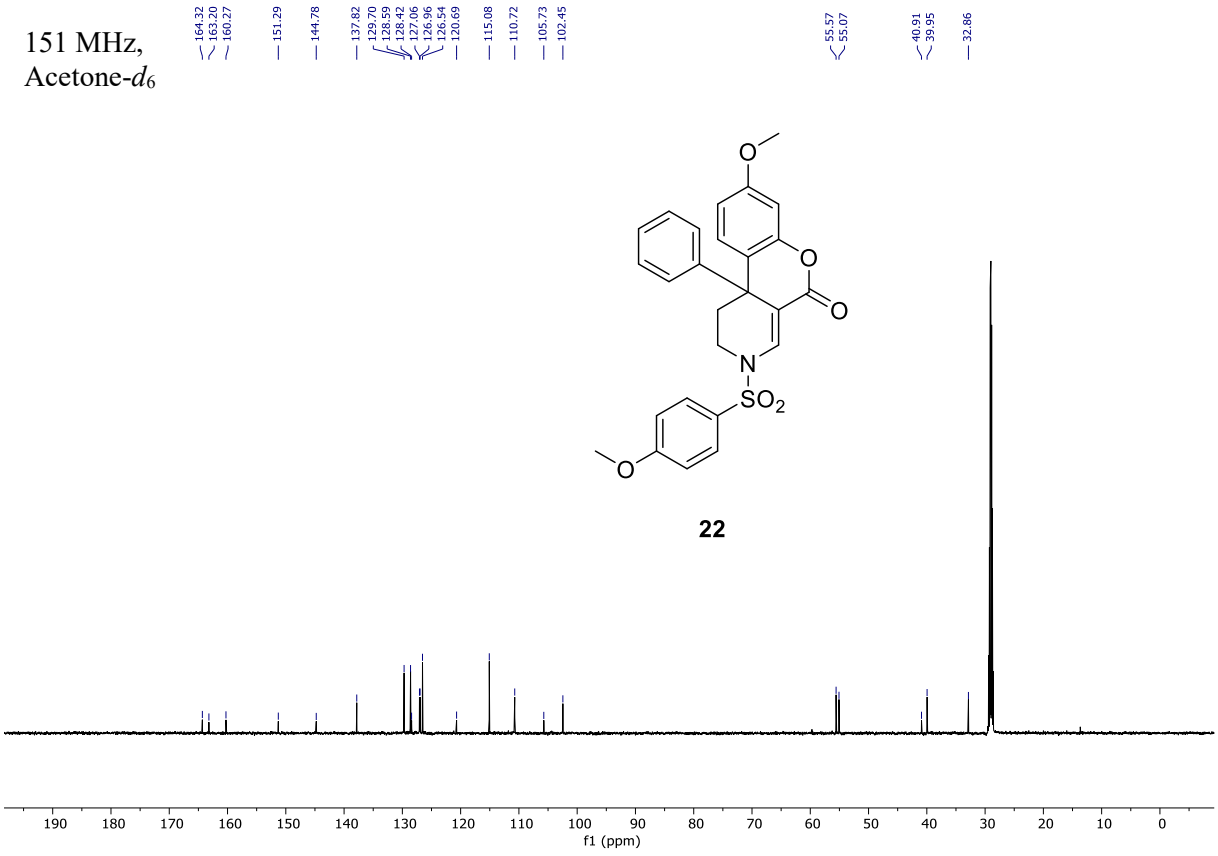
21

600 MHz,
Acetone-d_6



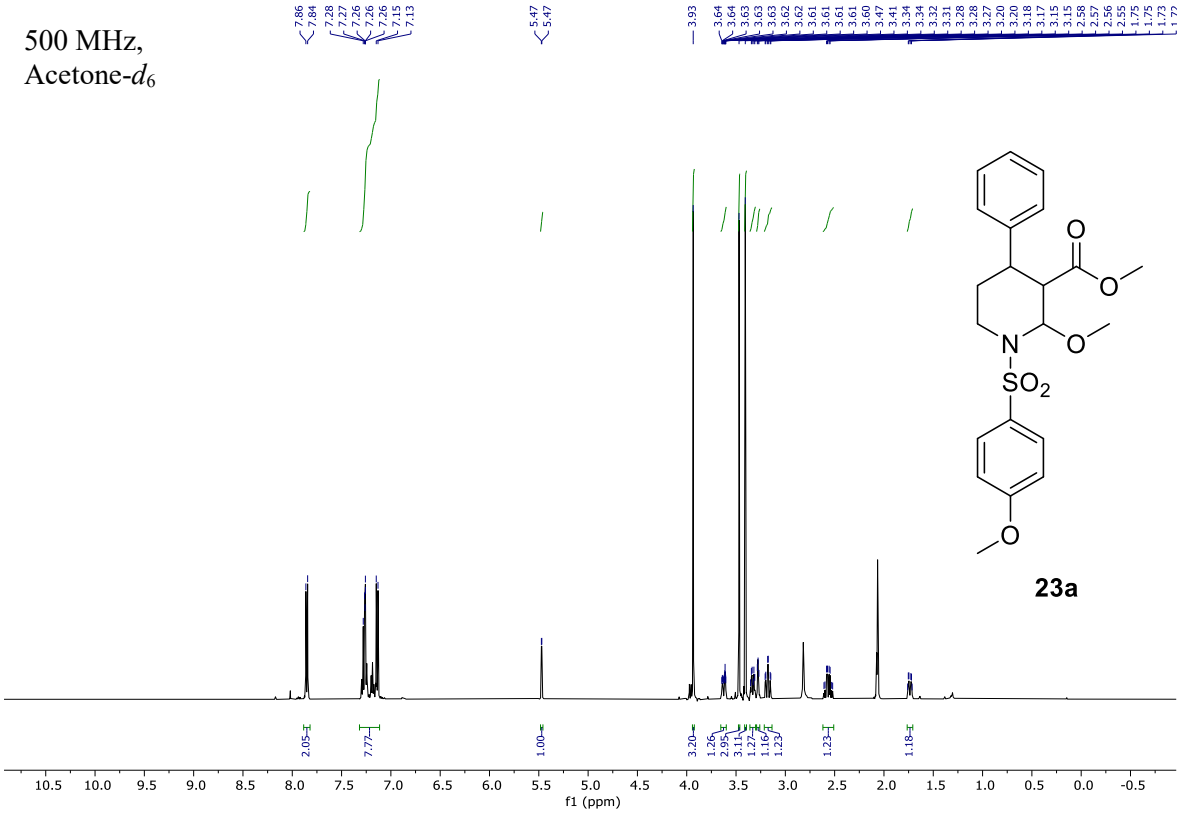
22

151 MHz,
Acetone-d_6

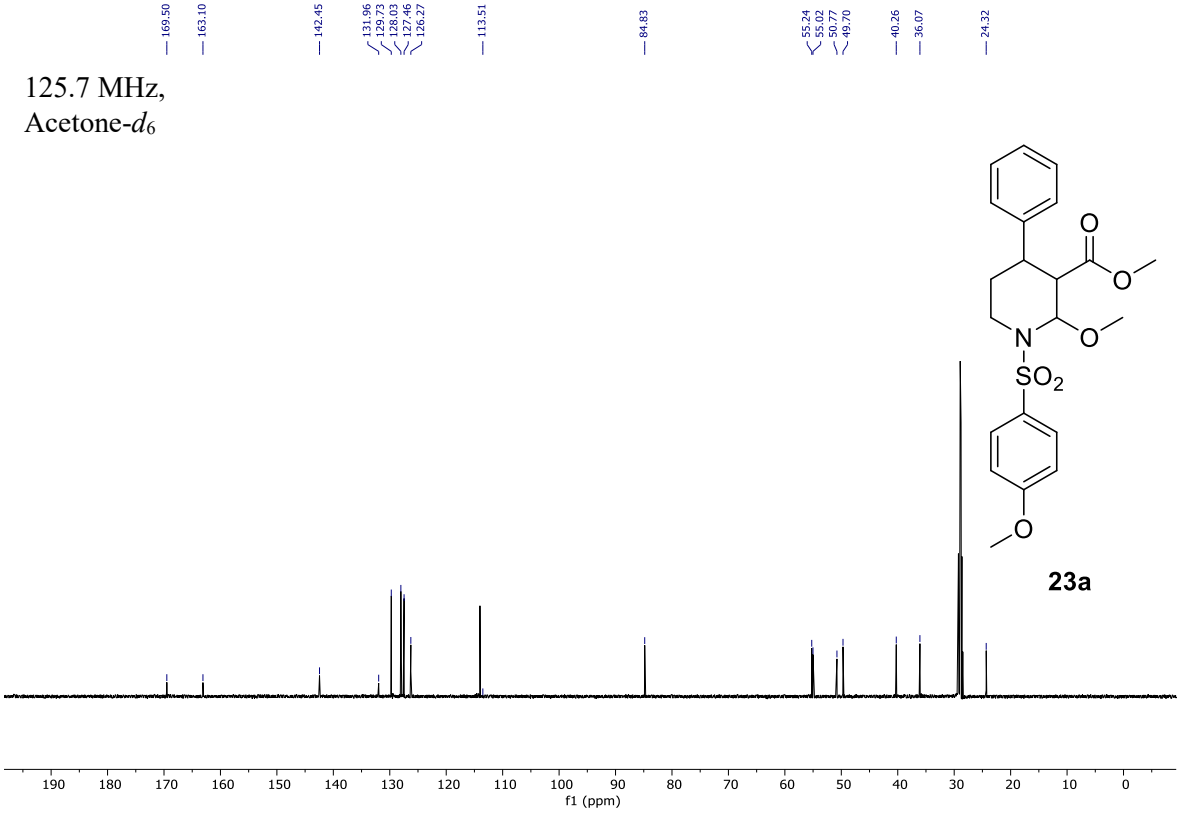


22

500 MHz,
Acetone-d_6



125.7 MHz,
Acetone-d_6



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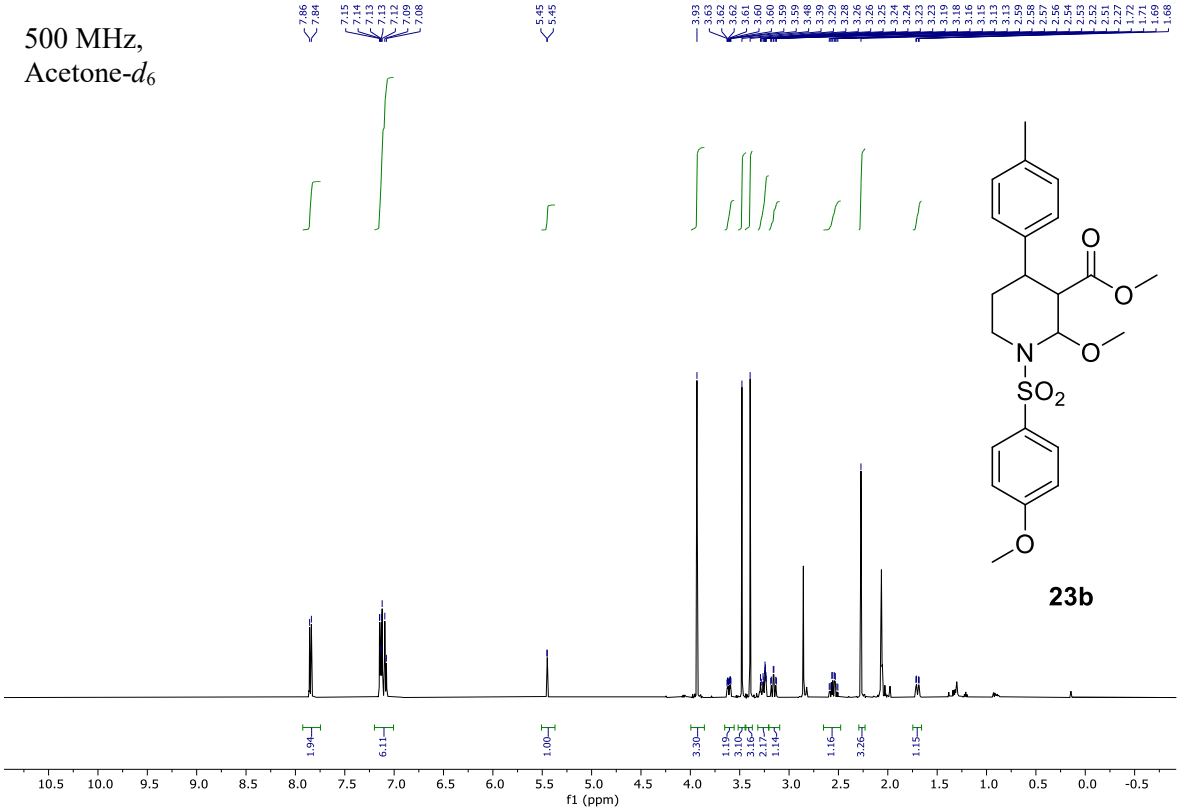
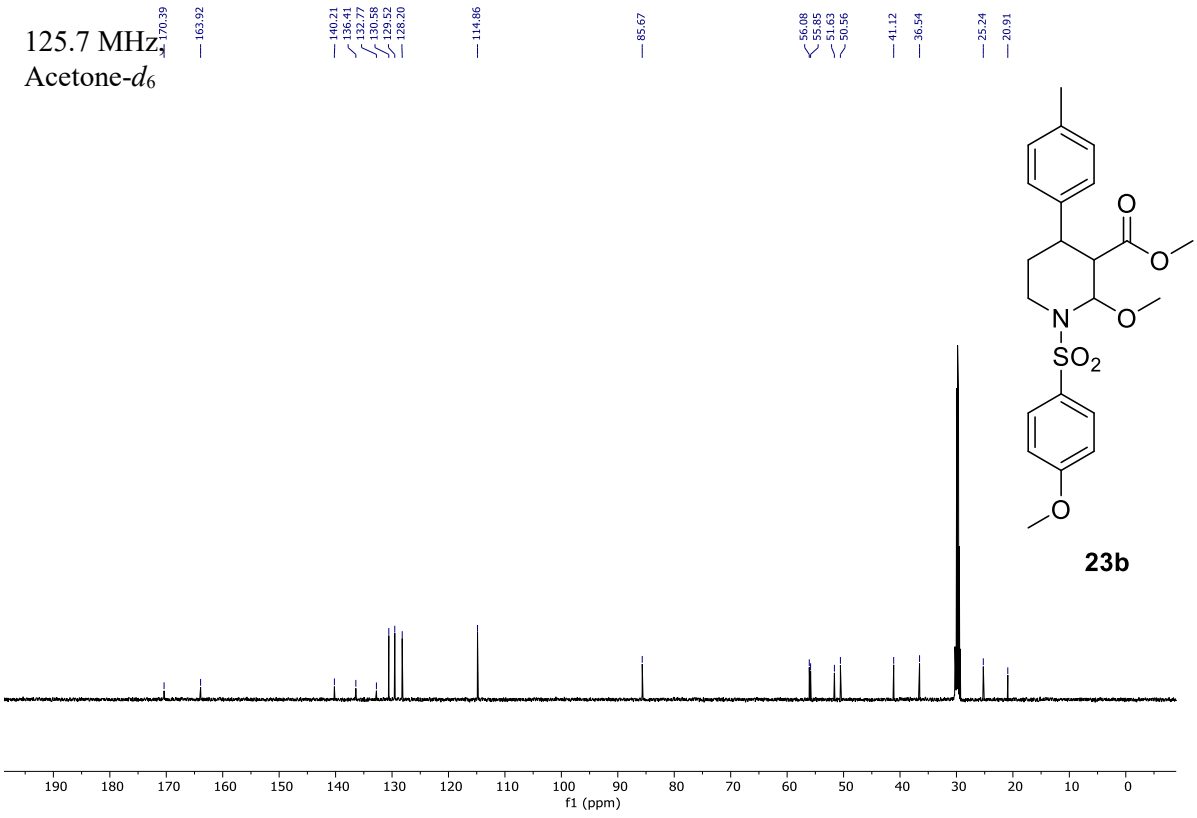
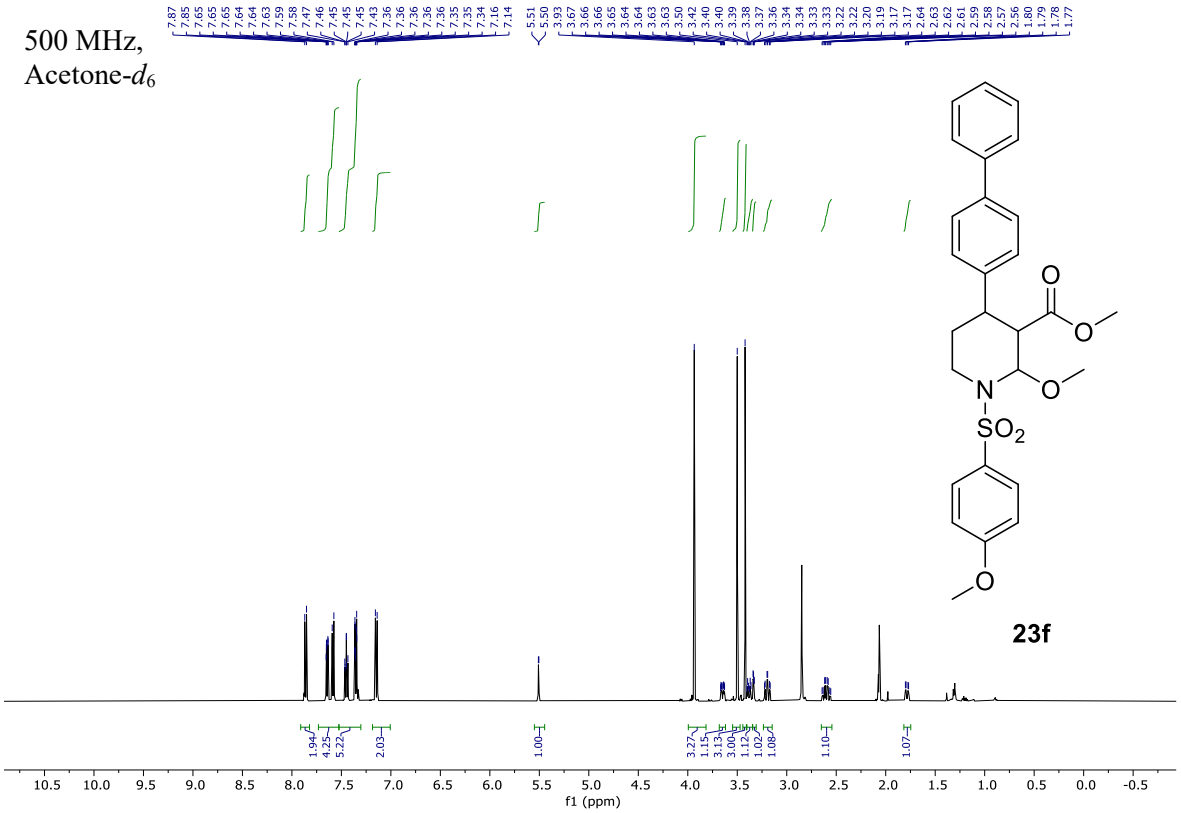
Acetone-d_6



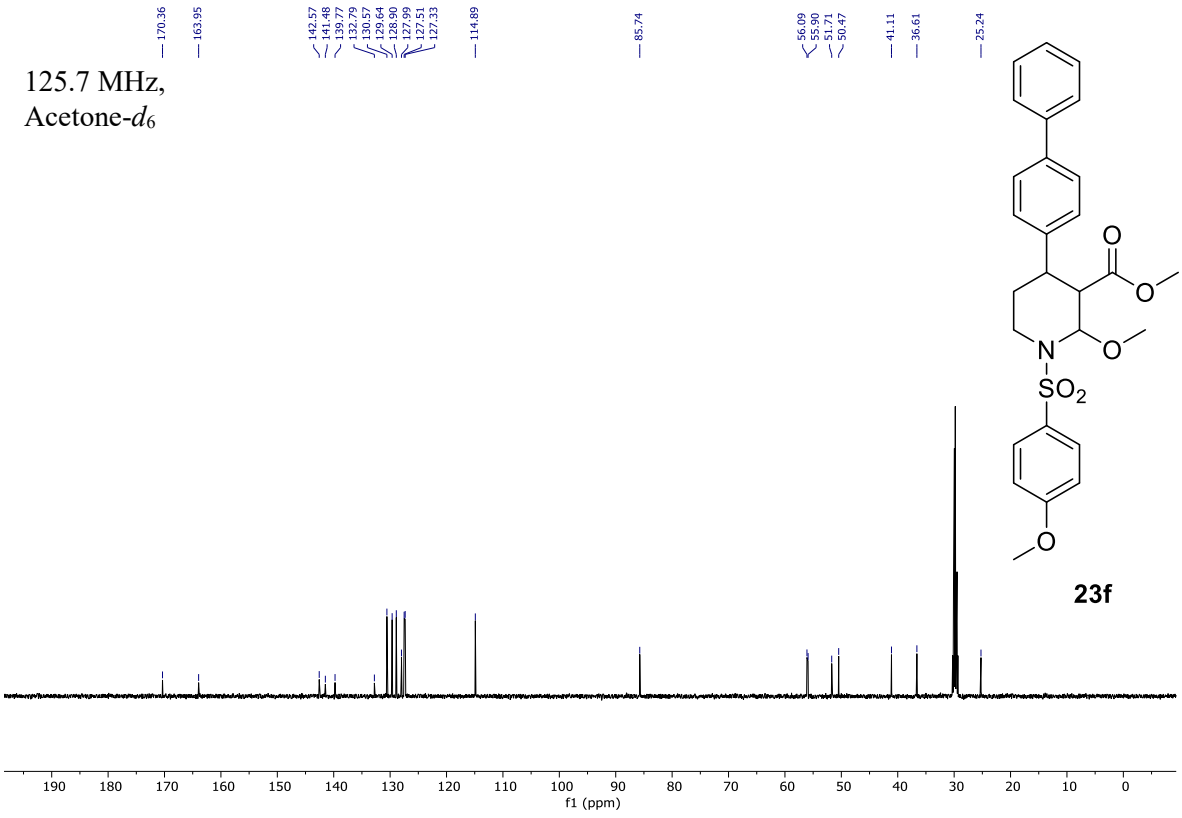
125.7 MHz,
Acetone-d_6



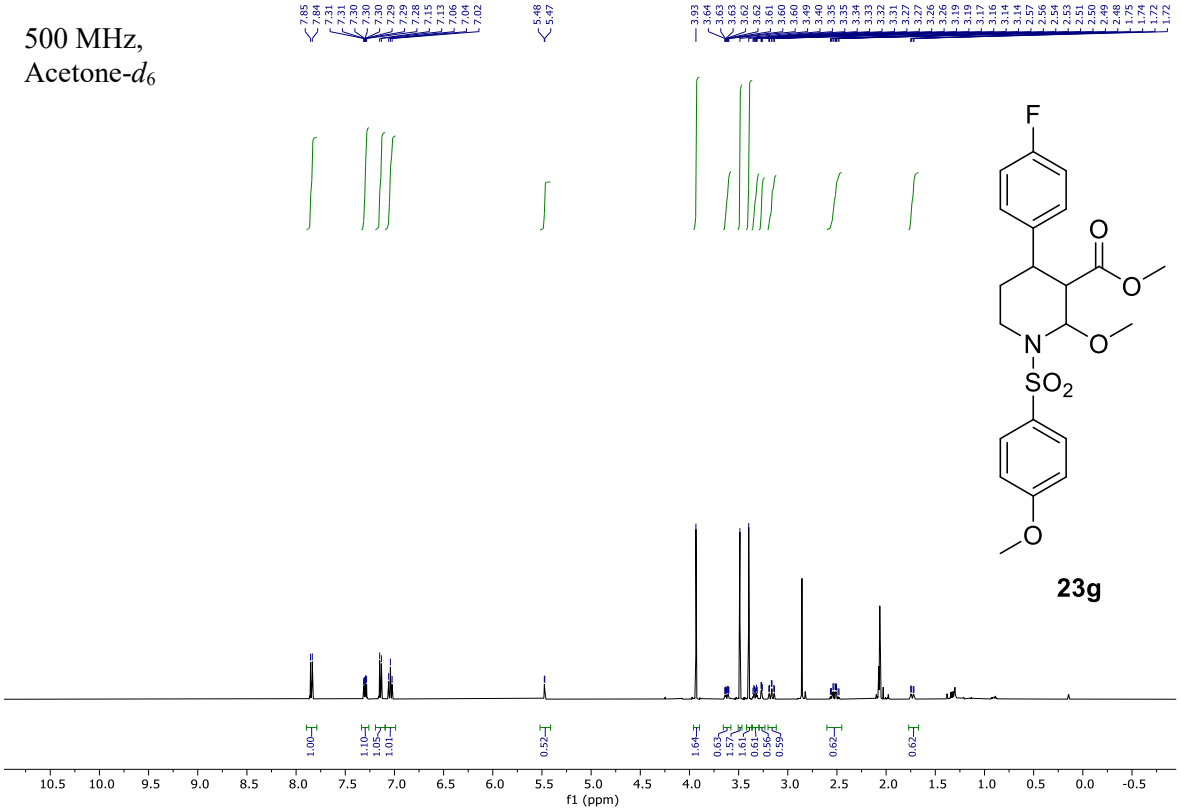
500 MHz,
Acetone-d_6



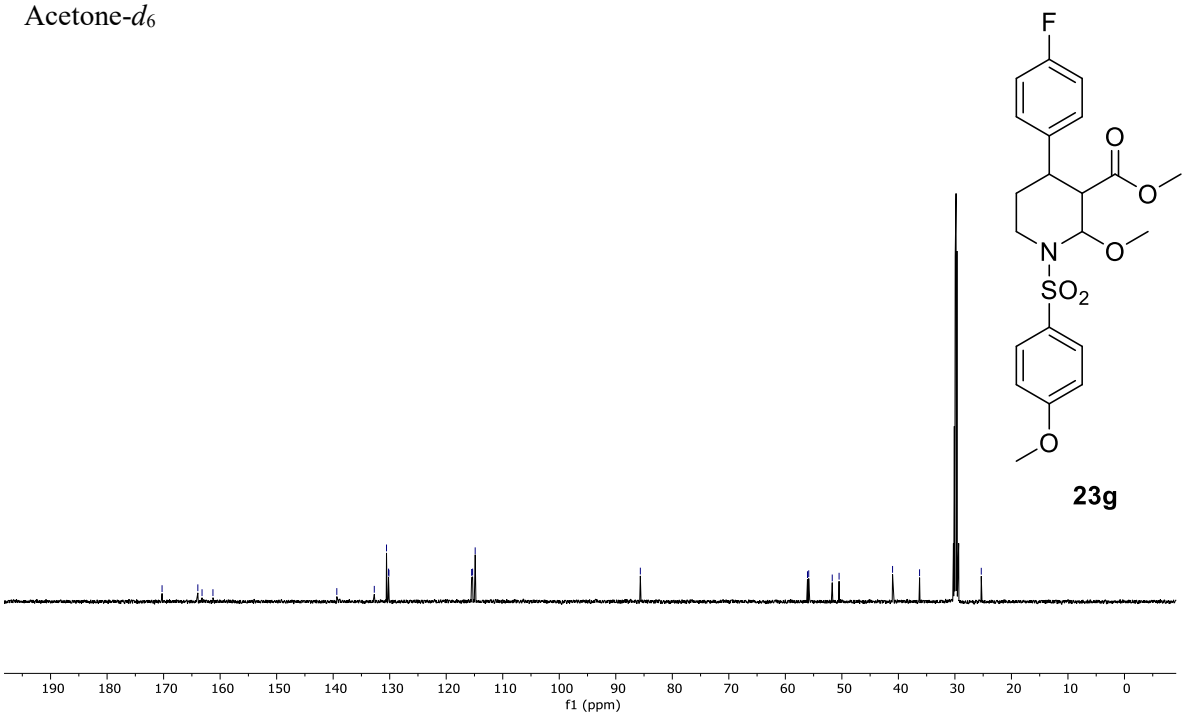
125.7 MHz,
Acetone-d_6



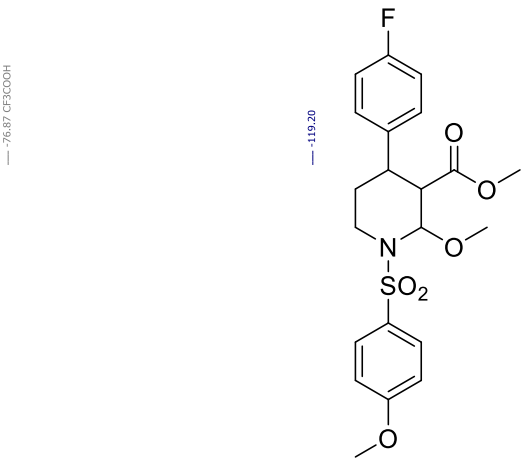
500 MHz,
Acetone-d_6



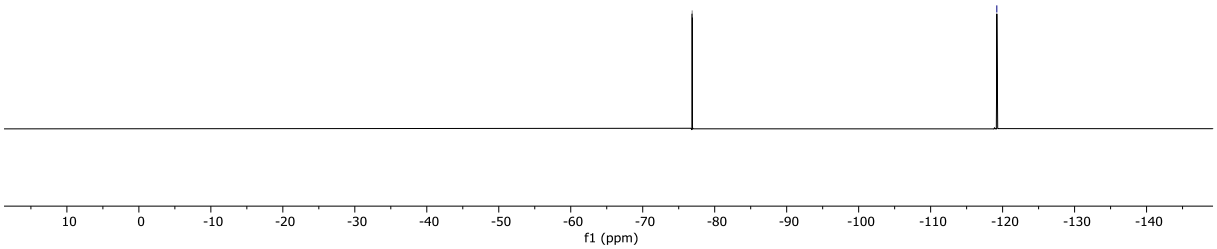
125.7 MHz,
Acetone-d_6



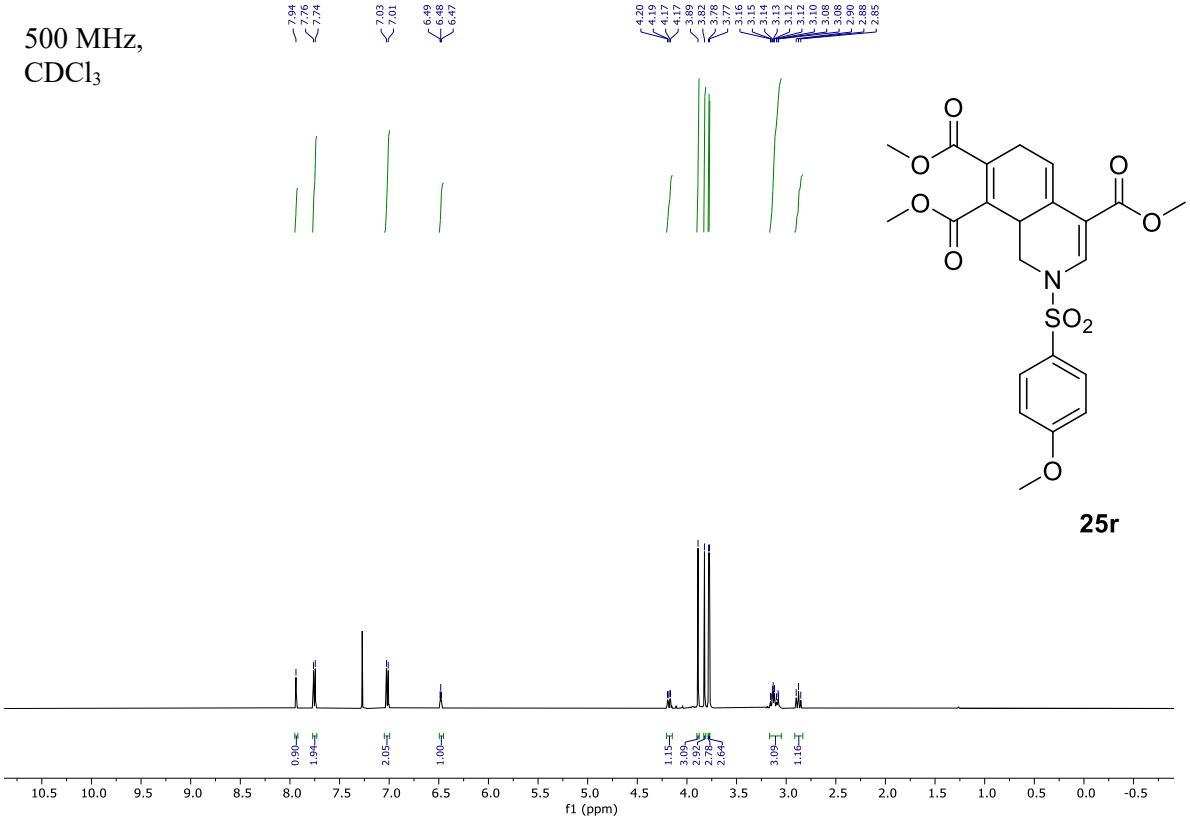
470 MHz,
Acetone-d_6



23g

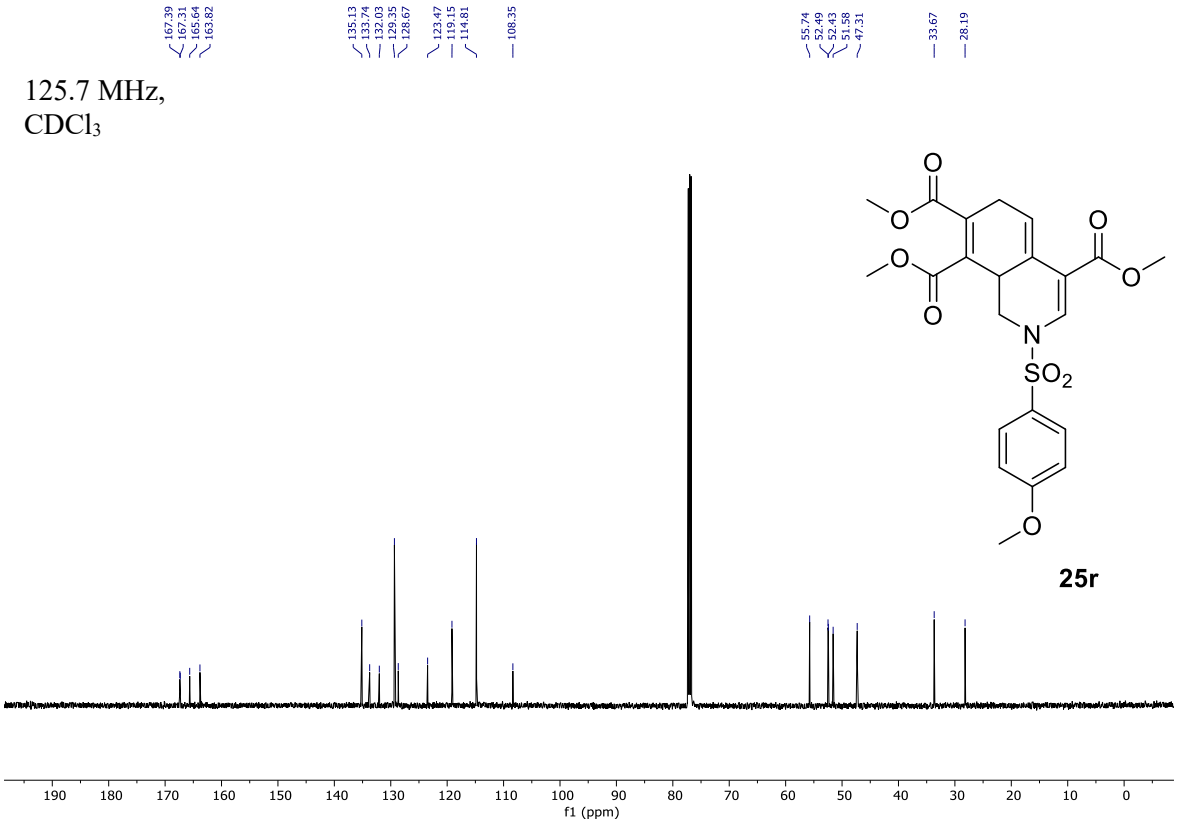


500 MHz,
$CDCl_3$



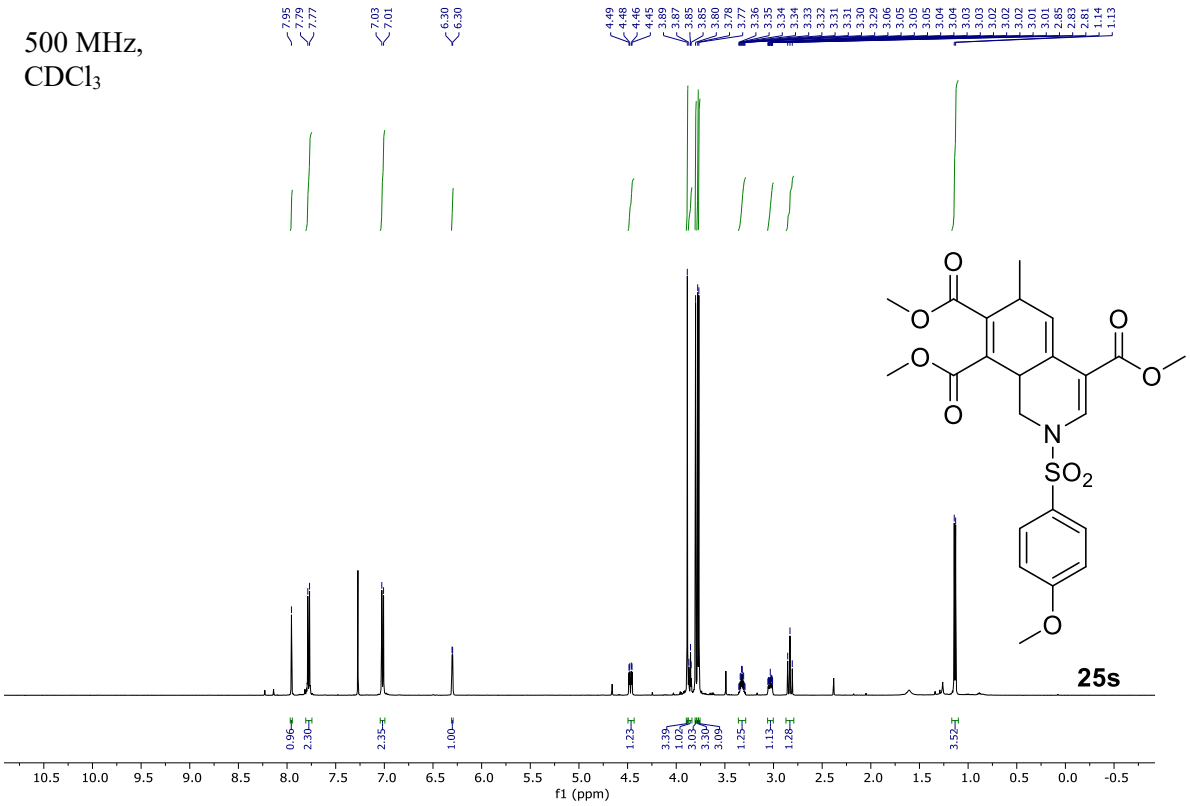
25r

125.7 MHz,
$CDCl_3$

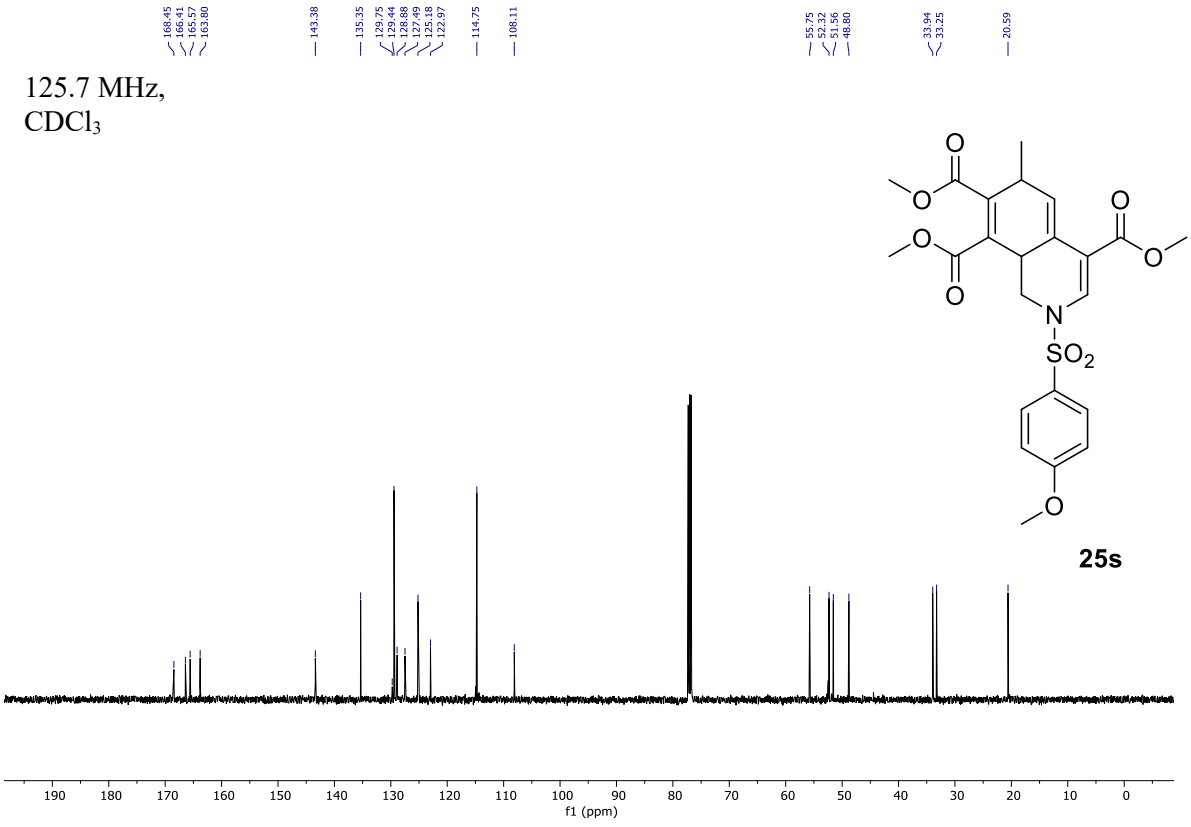


25r

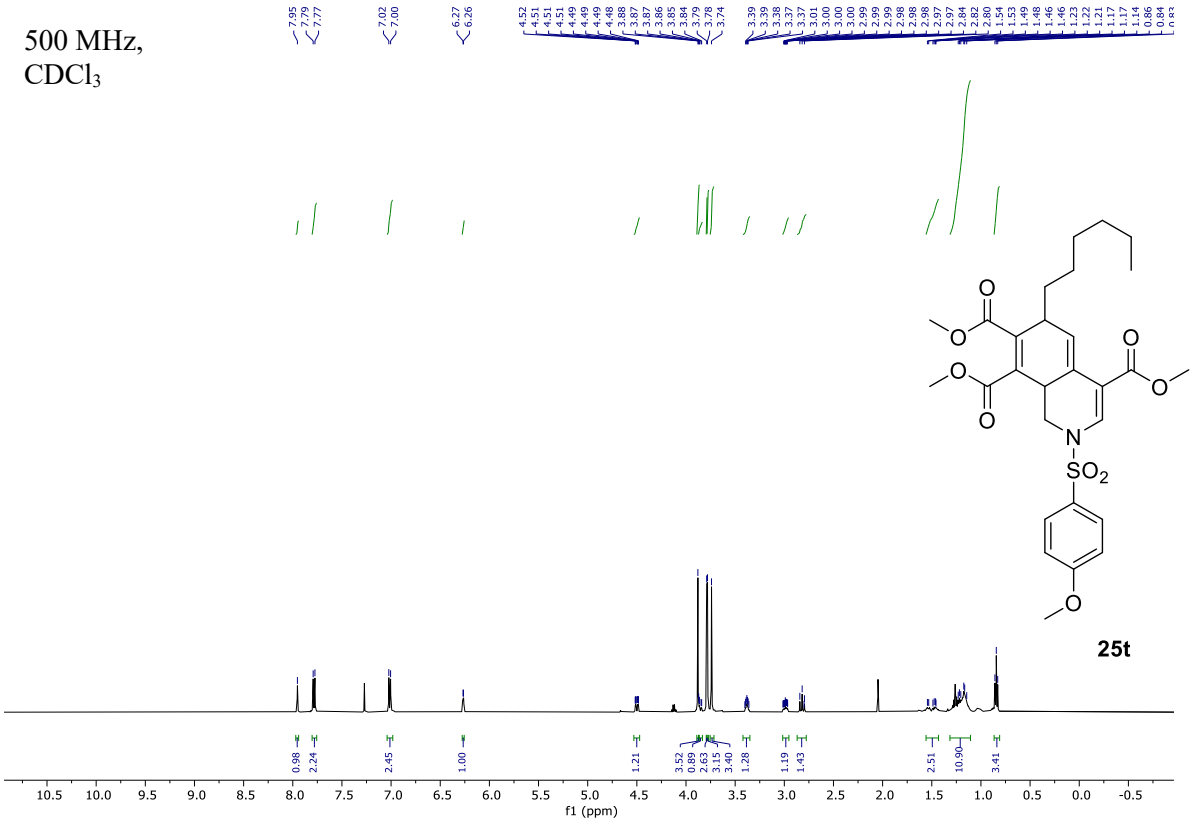
500 MHz,
$CDCl_3$



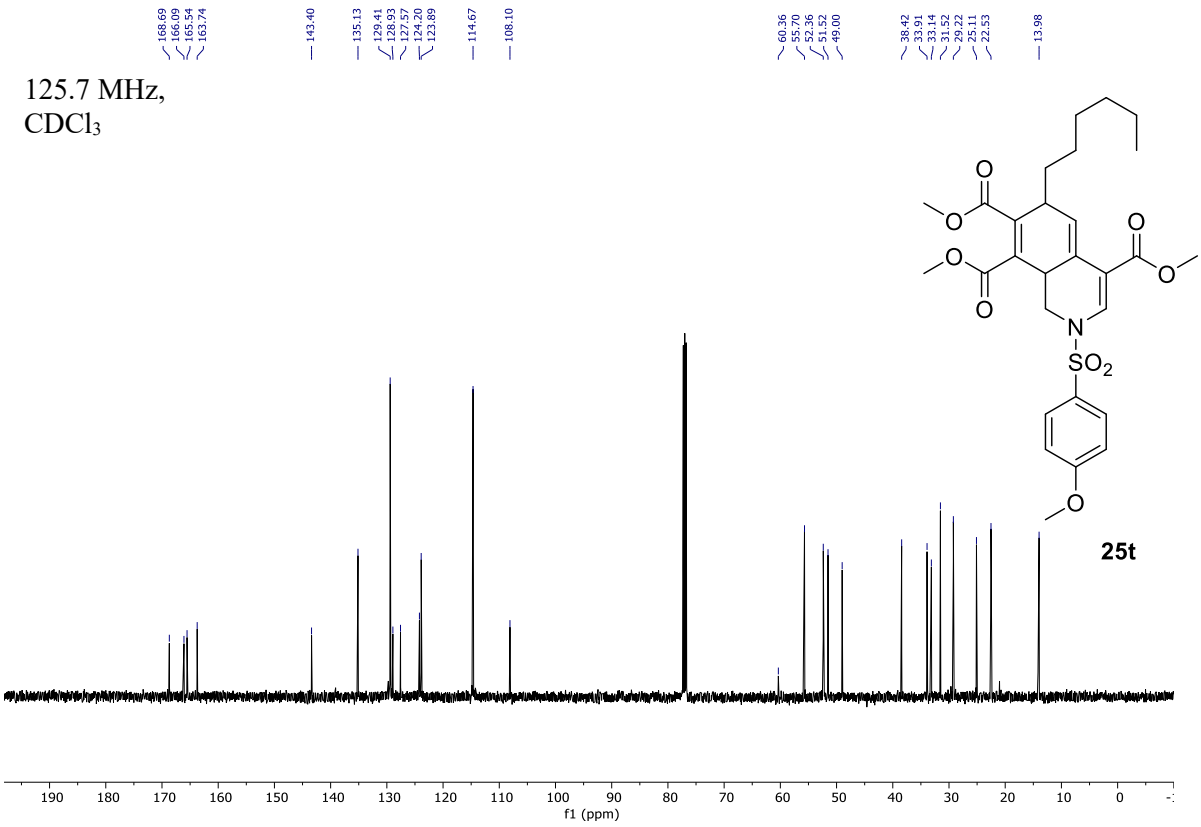
125.7 MHz,
$CDCl_3$



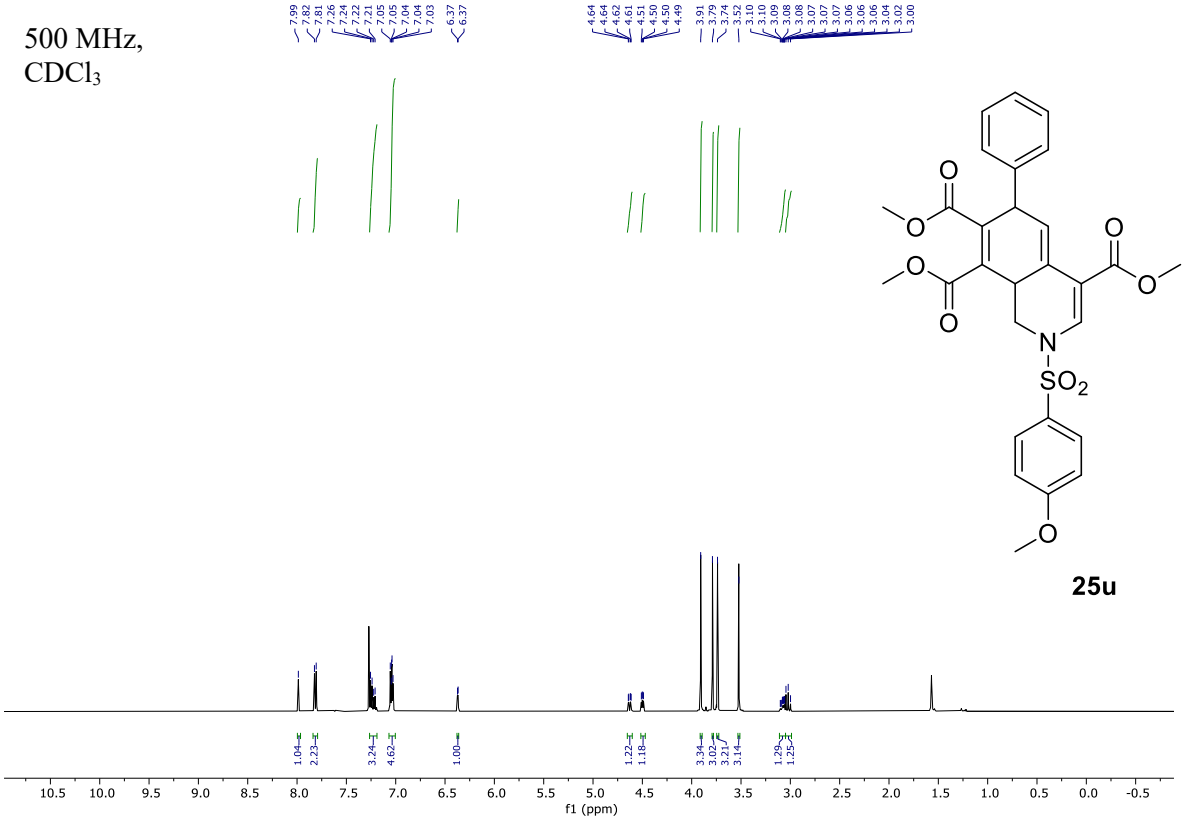
500 MHz,
$CDCl_3$



125.7 MHz,
$CDCl_3$

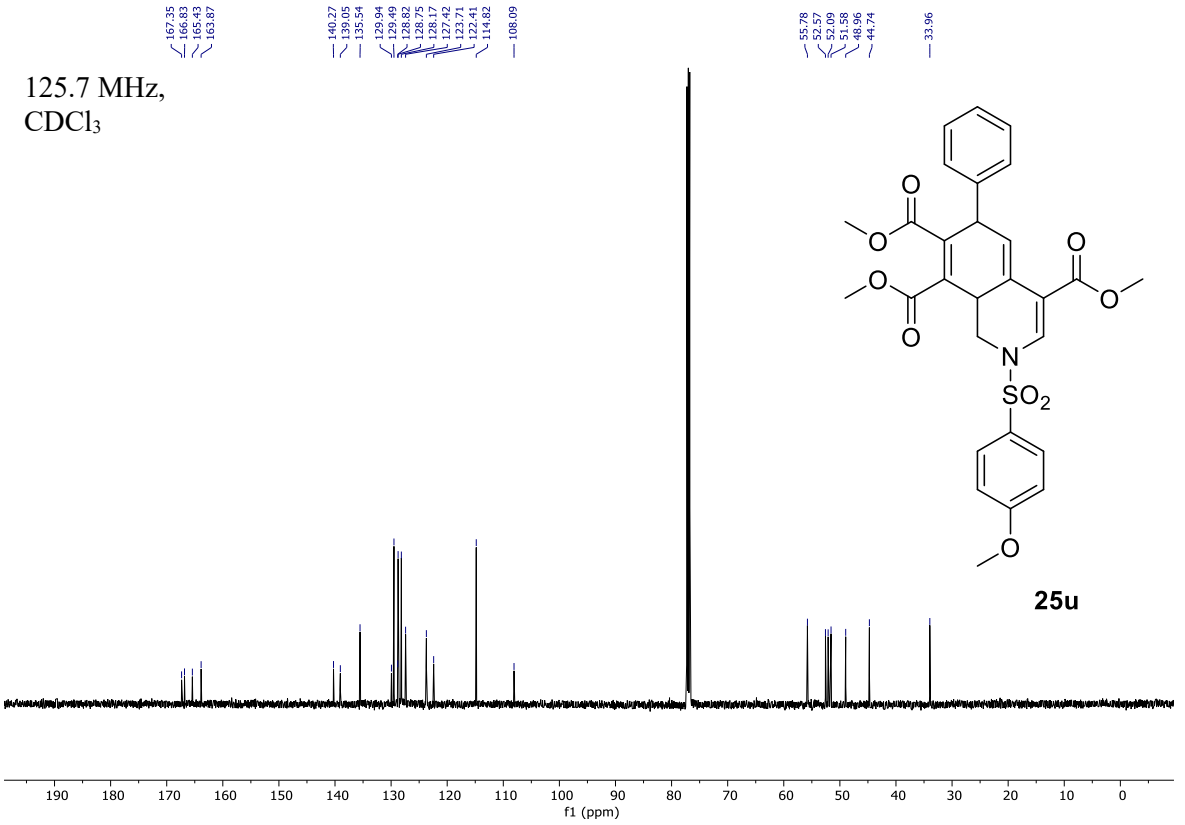


500 MHz,
$CDCl_3$



25u

125.7 MHz,
$CDCl_3$



25u

500 MHz,
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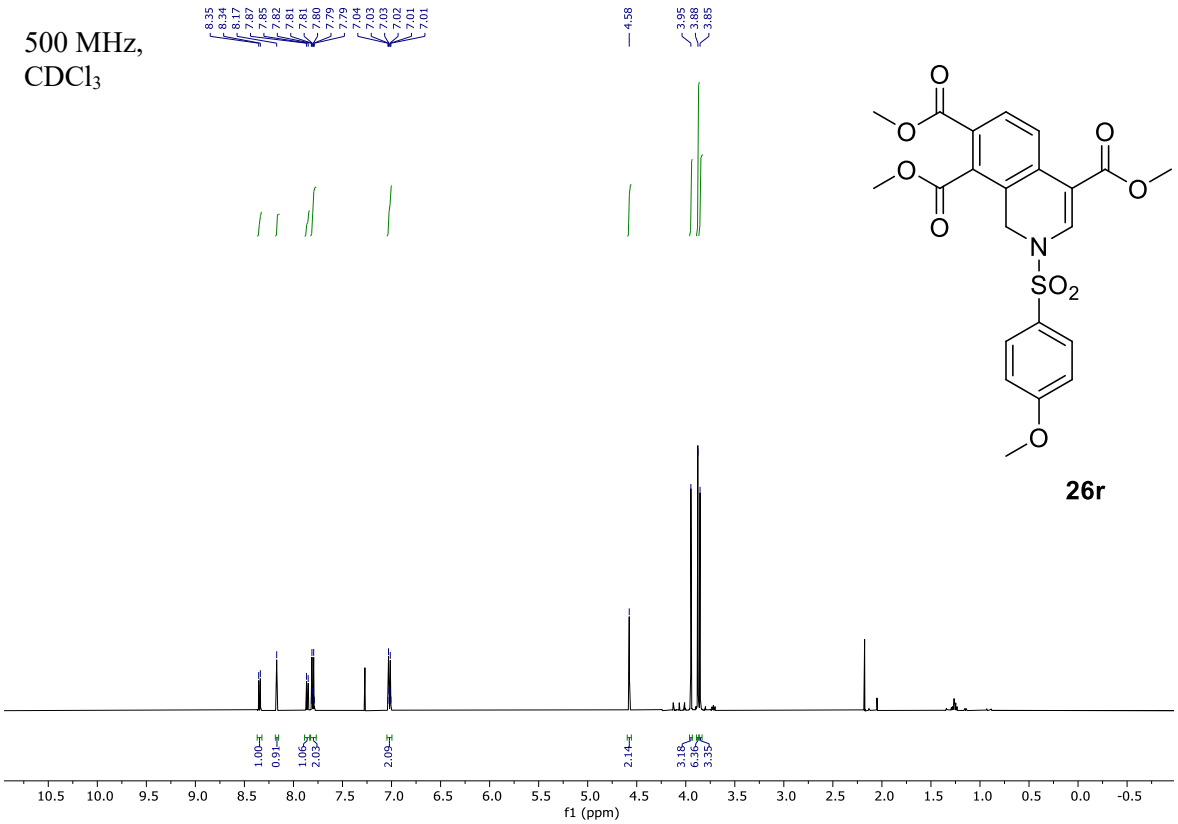

26r

125.7 MHz,
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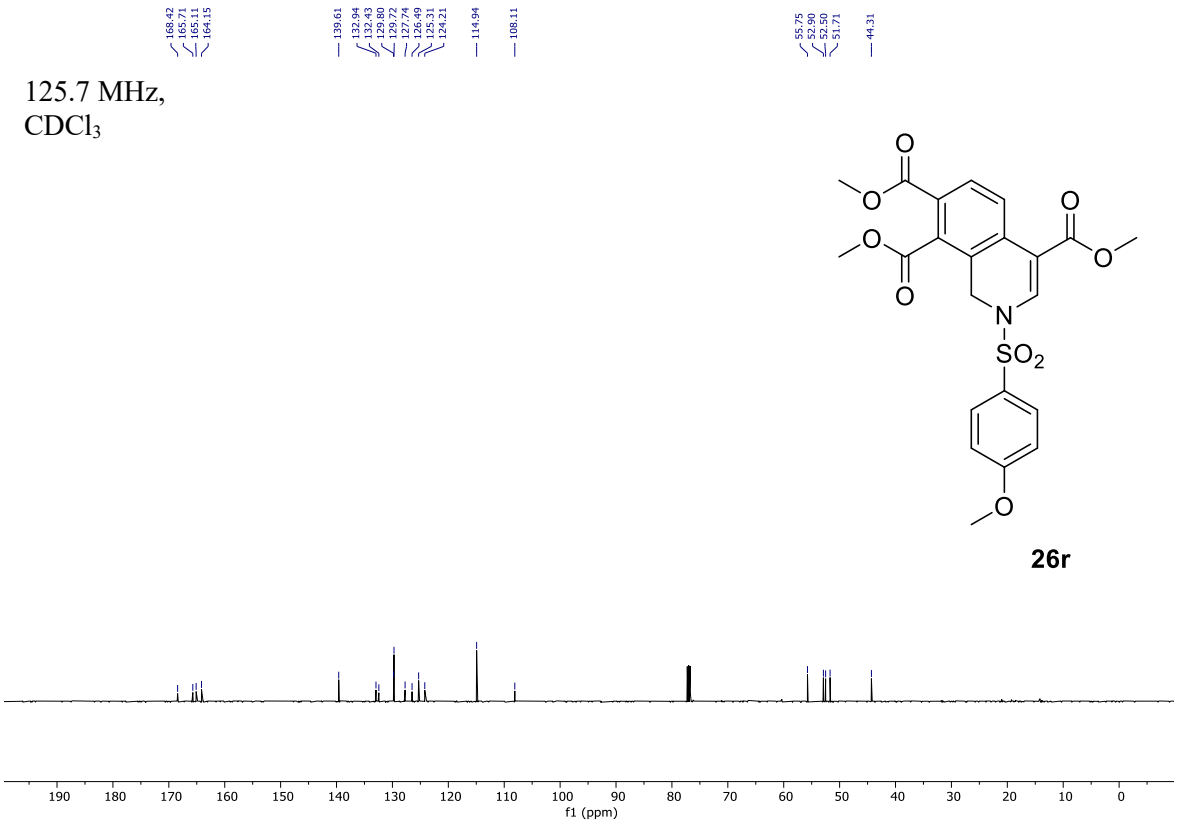
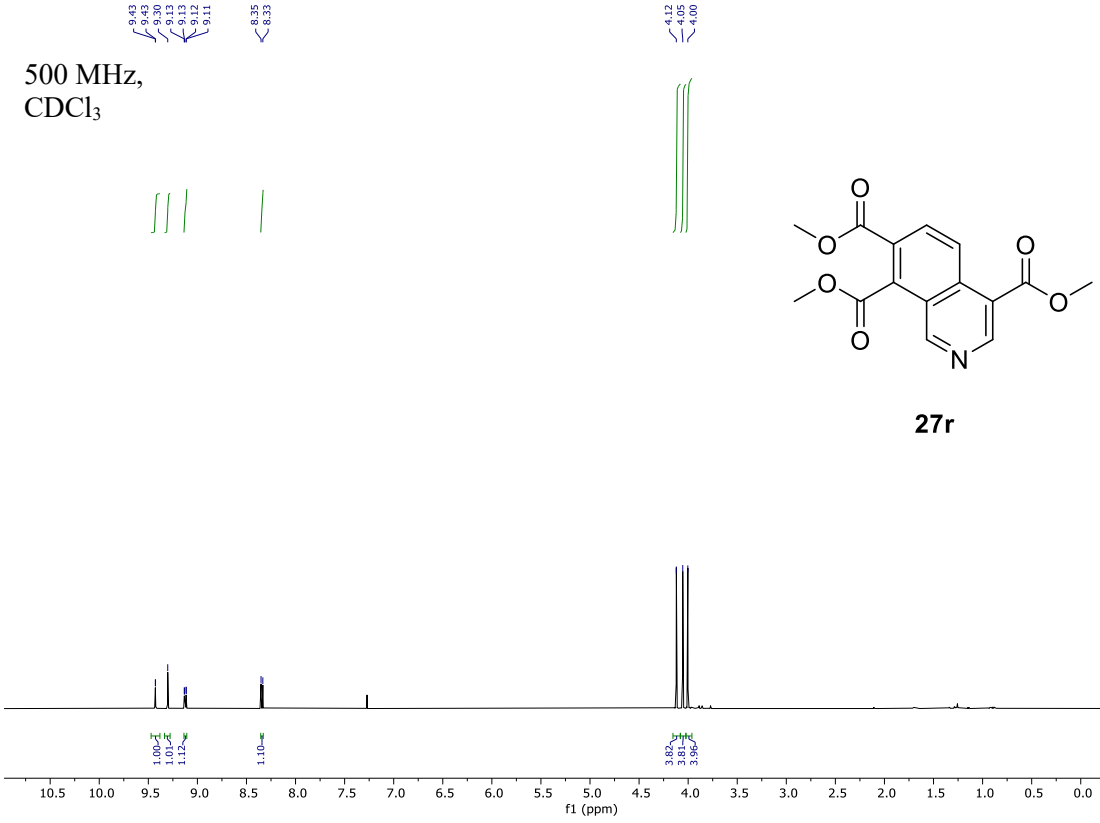


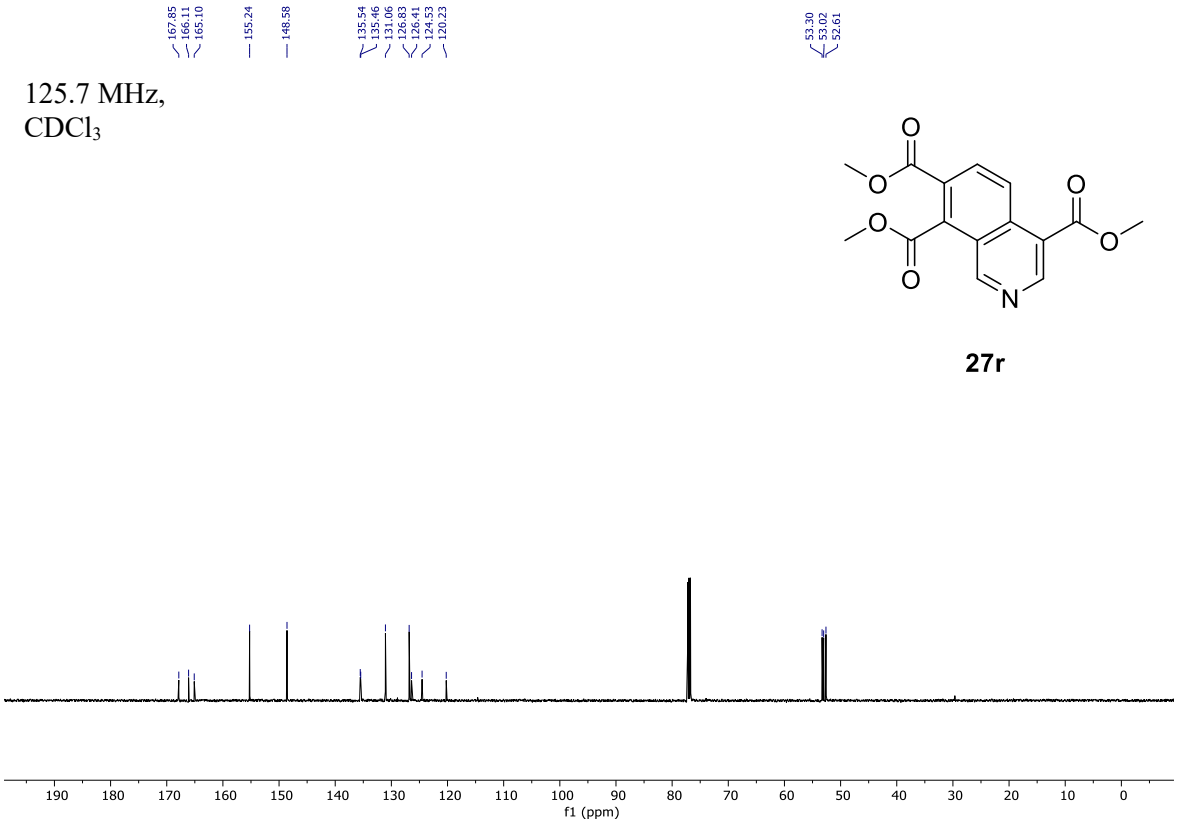
26r

500 MHz,
$CDCl_3$



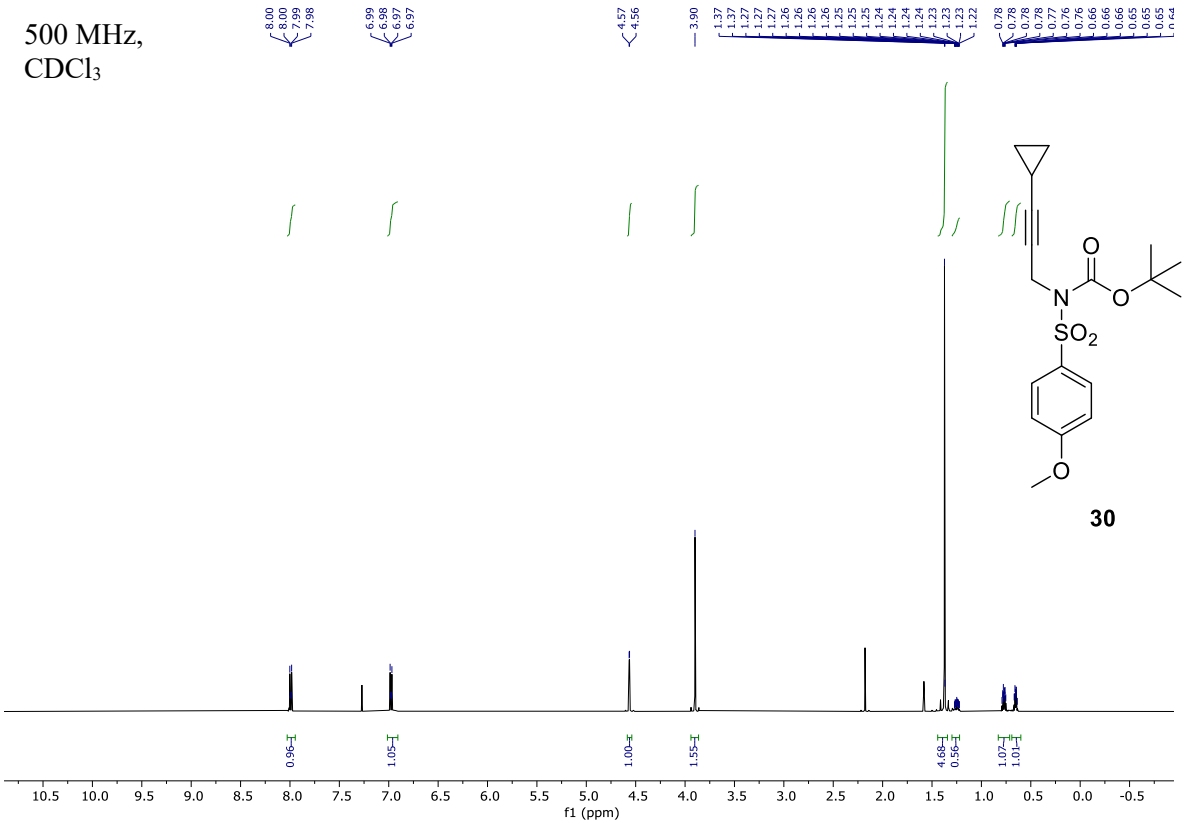
27r

125.7 MHz,
$CDCl_3$



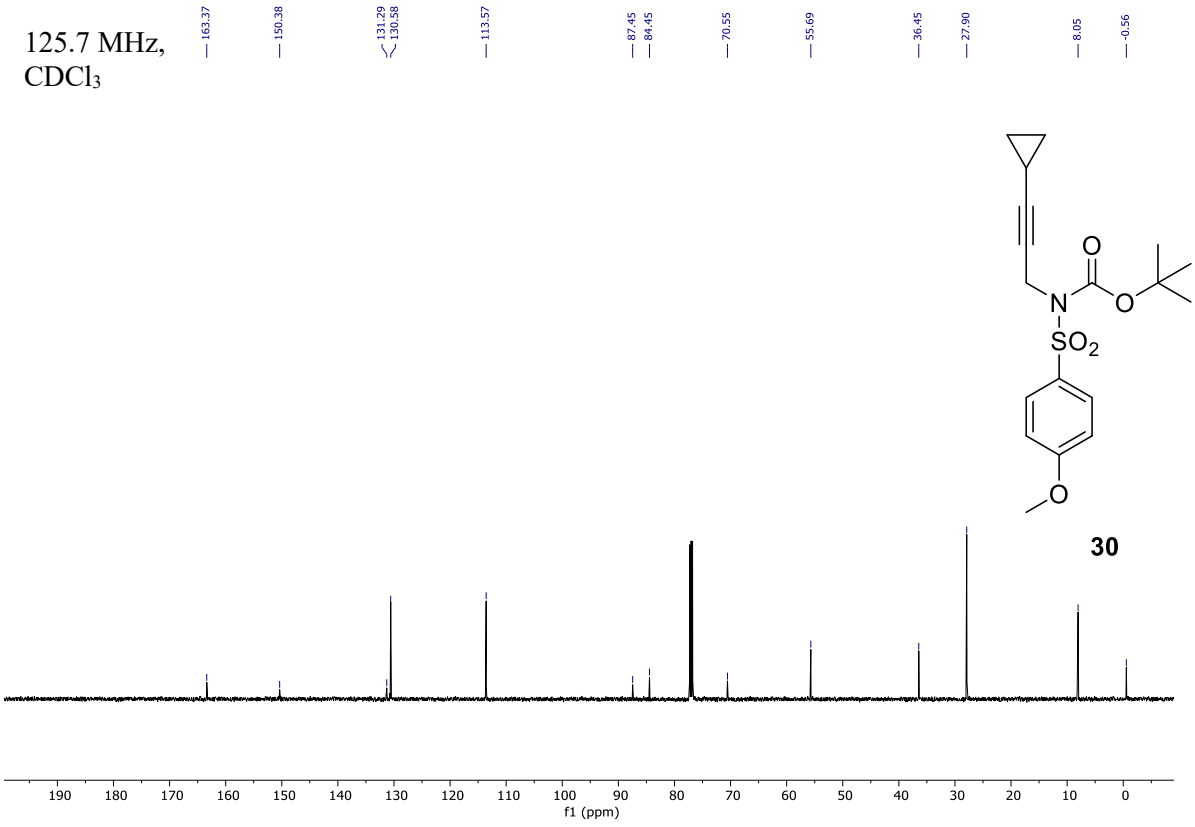
27r

500 MHz,
$CDCl_3$



30

125.7 MHz,
$CDCl_3$



30

500 MHz,
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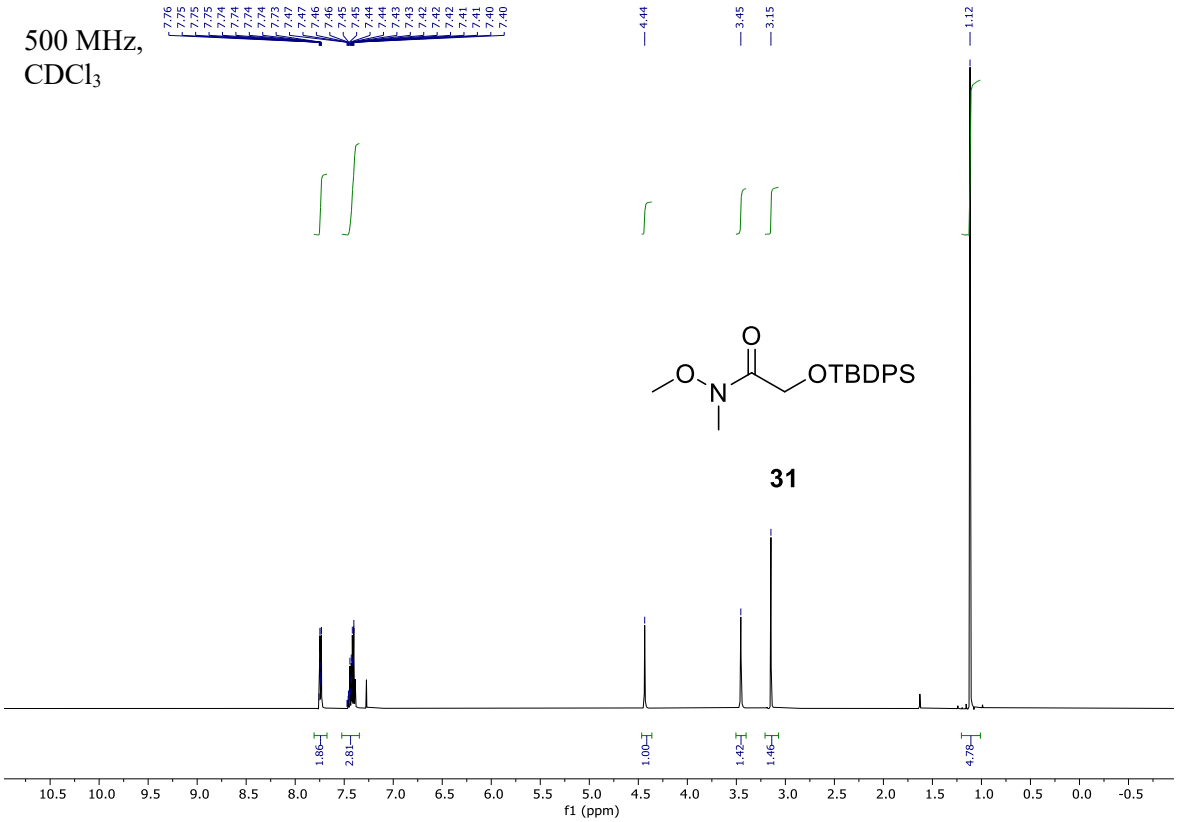
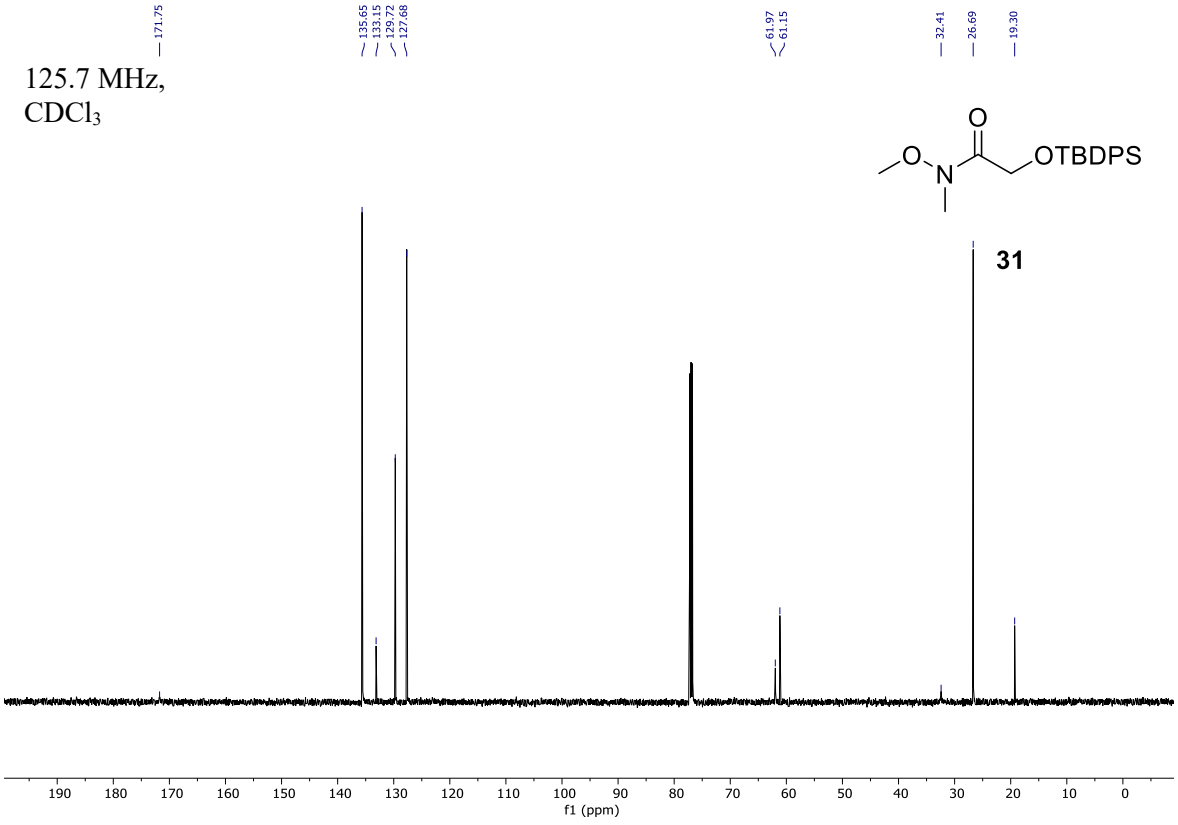


31

125.7 MHz,
$CDCl_3$



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