Deoxygenative Alkynylation of Amides via C=O Bond Cleavage

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared according to the method reported previously.[1-2] Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving SmI_2 were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on JEOL spectrometers at 400 (^{1}H NMR) and 101 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.0 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5977C inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 45 °C. The injector temperature was 280 °C. The detector temperature was 280 °C. For runs with the initial oven temperature of 45 °C, temperature was increased with a 20 °C/min ramp after 45 °C hold for 2.5 min to a final temperature of 280 °C, then hold at 280 °C for 2 min (splitless mode of injection, total run time of 16.25 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds.

Experimental Procedures

General Procedure A for the Synthesis of Amides.[1] An oven-dried vial (20 mL) equipped with a stir bar was charged with amine (6.0 mmo1, 1.2 equiv), dimethylaminopyridine (typically, 0.005 equiv), triethylamine (typically, 1.5 equiv), and dichloromethane (typically, 10 mL). Acyl chloride (typically, 1.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 ℃, and the reaction mixture was stirred 12 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL), washed with 1 M HCl (20 mL), H_2O (20 mL), brine (20mL). Then the organic layer was dried by Na_2SO_4, filtrated and concentrated. The crude product was purified by recrystallization to give analytically pure product.

General Procedure B for the Synthesis of Amides.[2] An oven-dried flask (25 mL) equipped with a stir bar was charged with carboxylic acid (6.0 mmol, 1.0 equiv), DMF (typically, one drop), dichloromethane (typically, 0.50 M) and oxalyl chloride (typically, 9.0 mmol, 1.5 equiv) at 0 ℃, and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was dried and concentrated to get crude first-step product. Then an oven-dried flask (25 mL) equipped with a stir bar was charged with amine (6.0 mmo1, 1.2 equiv), dimethylaminopyridine (typically, 0.005 equiv), triethylamine (typically, 1.5 equiv), and dichloromethane (typically, 10 mL), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The crude first-step product (typically, 5.0 mmol, 1.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL). The reaction mixture washed with 1 M HCl (20 mL), H_2O (20 mL), brine (20mL). The crude product was purified by chromatography (ethyl acetate/hexane = 1/5 to 1/1) to give analytically pure product.

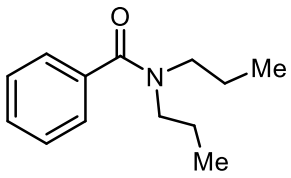
General Procedure for Deoxygenative Alkynylation of Amides. An oven-dried Schlenk tube equipped with a stir bar was charged with amides (neat, 1.0 equiv), alkynes (neat, 4.0 equiv), $AgBF_4$ (typically, 30 mol %), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The Schlenk tube was then transferred to the glovebox, samarium (typically, 2.0 equiv), and samarium diiodide (typically, 2.2 equiv, 0.1 M in THF) were added with vigorous stirring at room temperature. The Schlenk tube was then

transferred out of the glovebox and placed in a preheated oil bath at 70 °C, which was stirred for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature. The reaction mixture was added dichloromethane (10 mL) and washed with saturated $NaHCO_3$ solution (2×10 mL). The obtained solution was dried with anhydrous sodium sulfate, filtrated, concentrated to get crude product. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/ethyl acetate) afforded the title product. Caution: reactions involving high pressure must be carried out in a well-ventilated hood with appropriate pressure vessels, pressure relief equipment, and/or blast shields.

Representative Procedure for Deoxygenative Alkynylation of Amides. An oven-dried Schlenk tube equipped with a stir bar was charged with phenyl(pyrrolidin-1-yl)methanone (neat, 35.0 mg, 0.2 mmol, 1.0 equiv), phenylacetylene (neat, 81.7 mg, 0.8 mmol, 4.0 equiv), $AgBF_4$ (11.7 mg, 0.06 mmol, 0.3 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The Schlenk tube was then transferred to the glovebox, samarium (60.1 mg, 0.4 mmol, 2.0 equiv), and samarium diiodide (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) were added with vigorous stirring at room temperature. The Schlenk tube was then transferred out of the glovebox and placed in a preheated oil bath at 70 °C, which was stirred for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature. The reaction mixture was added dichloromethane (10 mL) and washed with saturated $NaHCO_3$ solution (2×10 mL). The obtained solution was dried with anhydrous sodium sulfate, filtrated, concentrated to get crude product. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/ethyl acetate) afforded the title product. Yield 80% (41.8 mg, 0.160 mmol). White Solid. Characterization data are included in the section below. Caution: reactions involving high pressure must be carried out in a well-ventilated hood with appropriate pressure vessels, pressure relief equipment, and/or blast shields.

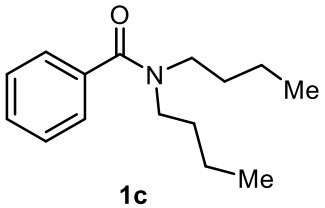
Characterization Data for Starting Materials

Note: All starting materials have been prepared according to the procedure A[1] or procedure B[2]. The yields have not been optimized.



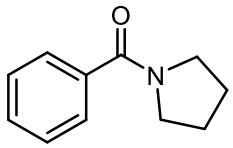
1b

***N,N*-Dipropylbenzamide (1b)**.[3] This compound was synthesized using procedure A. Yield 90% (0.923 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (s, 5H), 3.28 (d, *J* = 30.7 Hz, 4H), 1.58 (d, *J* = 18.9 Hz, 4H), 0.82 (d, *J* = 24.7 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.67, 137.17, 128.85, 128.19, 126.27, 50.49, 46.12, 21.73, 20.53, 11.27, 10.82.



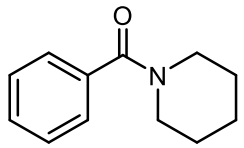
1c

***N,N*-Dibutylbenzamide (1c).**[4] This compound was synthesized using procedure A. Yield 88% (1.028 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (s, 5H), 3.32 (d, *J* = 31.0 Hz, 4H), 1.62-1.11 (m, 8H), 0.86 (d, *J* = 19.9 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.58, 137.24, 128.91, 128.23, 126.34, 48.64, 44.36, 30.68, 29.58, 20.21, 19.62, 13.85, 13.52.



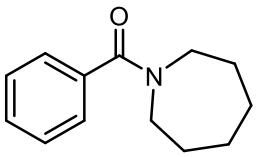
1d

Phenyl(pyrrolidin-1-yl)methanone (1d).[1] This compound was synthesized using procedure A. Yield 95% (0.832 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.40 (m, 2H), 7.29-7.27 (m, 3H), 3.53 (t, *J* = 7.0 Hz, 2H), 3.30 (t, *J* = 6.6 Hz, 2H), 1.87-1.80 (m, 2H), 1.77-1.70 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.16, 136.64, 129.27, 127.71, 126.55, 49.09, 45.68, 25.85, 23.91.



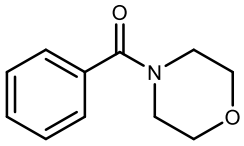
1e

Phenyl(piperidin-1-yl)methanone (1e).[4] This compound was synthesized using procedure A. Yield 87% (0.823 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (s, 5H), 3.43 (d, *J* = 37.9 Hz, 1H), 1.58 (s, 4H), 1.42 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.00, 136.13, 129.06, 128.09, 126.46, 48.45, 42.78, 26.21, 25.32, 24.25.



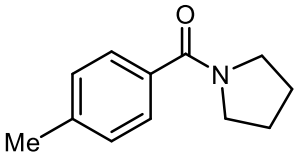
1f

Azepan-1-yl(phenyl)methanone (1f).[4] This compound was synthesized using procedure A. Yield 91% (0.925 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (s, 5H), 3.65 (t, *J* = 5.4 Hz, 2H), 3.34 (t, *J* = 5.4 Hz, 2H), 1.84-1.79 (m, 2H), 1.60-1.57 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.48, 137.18, 128.90, 128.23, 126.28, 49.61, 46.19, 29.36, 27.70, 27.12, 26.31.



1g

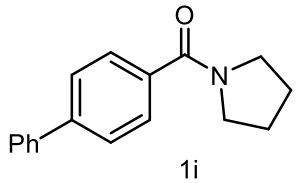
Morpholino(phenyl)methanone (1g).[4] This compound was synthesized using procedure A. Yield 85% (0.813 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (s, 5H), 3.75-3.42 (m, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.41, 135.19, 129.84, 128.51, 127.02, 66.83, 42.57.



1h

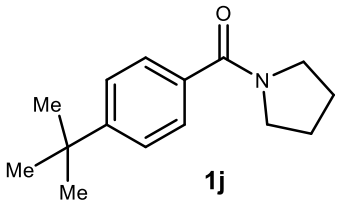
Pyrrolidin-1-yl(*p*-tolyl)methanone (1h).[4] This compound was synthesized using procedure A.

Yield 94% (0.890 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 3.41 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 1.96-1.89 (m, 2H), 1.87-1.80 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.71, 139.78, 134.18, 128.70, 127.10, 49.55, 46.09, 26.31, 24.35, 21.28.



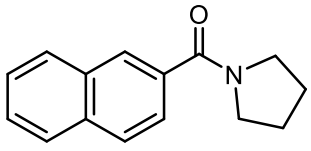
1i

[1,1'-Biphenyl]-4-yl(pyrrolidin-1-yl)methanone (1i).[4] This compound was synthesized using procedure B. Yield 83% (1.043 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 8.7 Hz, 6H), 7.47-7.35 (m, 3H), 3.58 (d, *J* = 17.3 Hz, 4H), 1.94 (d, *J* = 5.5 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.31, 142.44, 140.12, 135.73, 130.27, 128.70, 127.57, 126.97, 126.74, 49.53, 46.15, 26.29, 24.30.



1j

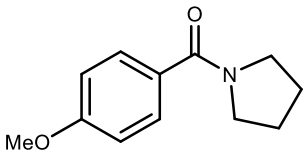
(4-(*tert*-Butyl)phenyl)(pyrrolidin-1-yl)methanone (1j).[1] This compound was synthesized using procedure B. Yield 86% (0.995 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46-7.43 (m, 2H), 7.40-7.37 (m, 2H), 3.54 (s, 4H), 1.90 (s, 4H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.76, 152.94, 134.16, 126.93, 125.04, 46.05, 34.72, 31.15, 26.56.



1k

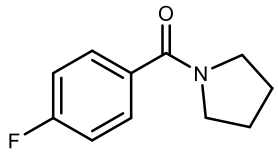
Naphthalen-2-yl(pyrrolidin-1-yl)methanone (1k).[4] This compound was synthesized using procedure B. Yield 75% (0.845 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88-7.81 (m, 3H), 7.50-7.44 (m, 4H), 3.80 (t, *J* = 7.1 Hz, 2H), 3.07 (t, *J* = 6.8 Hz, 2H), 1.97-1.90 (m, 2H), 1.78-

1.71 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.08, 135.21, 133.23, 130.38, 128.91, 128.15, 126.74, 126.05, 124.94, 124.56, 123.54, 48.32, 45.52, 25.67, 24.33.



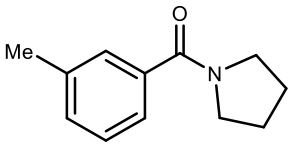
1l

(4-Methoxyphenyl)(pyrrolidin-1-yl)methanone (1l).[4] This compound was synthesized using procedure A. Yield 93% (0.954 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.43 (t, *J* = 6.1 Hz, 2H), 1.92-1.89 (m, 2H), 1.84-1.80 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.31, 160.64, 129.21, 129.01, 113.25, 55.17, 49.66, 46.19, 26.34, 24.29.



1m

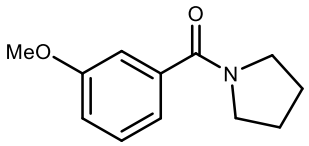
Pyrrolidin-1-yl(*p*-tolyl)methanone (1m).[4] This compound was synthesized using procedure A. Yield 93% (0.927 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53-7.50 (m, 2H), 7.05 (t, *J* = 2.1 Hz, 2H), 3.51 (d, *J* = 11.9 Hz, 4H), 1.90 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.56, 163.32 (d, J^F= 249.5 Hz), 133.11 (d, J^F = 3.3 Hz), 129.31 (d, J^F = 8.6 Hz), 115.12 (d, J^F = 21.7 Hz), 49.54, 46.18, 26.04, 24.26. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.37.



1n

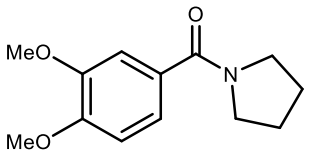
Pyrrolidin-1-yl(*m*-tolyl)methanone (1n).[5] This compound was synthesized using procedure A. Yield 93% (0.880 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (s, 1H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 3.65 (t, *J* = 7.0 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 1.97 (p, *J* = 6.6 Hz, 2H), 1.88 (q, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.75, 137.83,

136.97, 130.26, 127.86, 127.48, 123.78, 49.40, 45.91, 26.13, 24.25, 21.15.



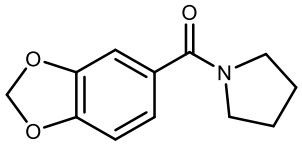
1o

(3-Methoxyphenyl)(pyrrolidin-1-yl)methanone (1o).[5] This compound was synthesized using procedure A. Yield 83% (0.852 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 4.00 (s, 3H), 3.83-3.80 (m, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.14 (p, *J* = 7.4, 6.8 Hz, 2H), 2.05 (p, *J* = 6.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.29, 159.21, 138.25, 129.13, 118.99, 115.52, 112.16, 55.12, 49.39, 45.95, 26.12, 24.22.



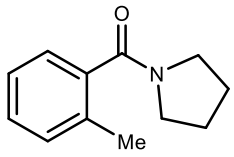
1p

(3,4-Dimethoxyphenyl)(pyrrolidin-1-yl)methanone (1p).[4] This compound was synthesized using procedure A. Yield 87% (1.023 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.06-7.03 (m, 2H), 6.77 (d, *J* = 2.1 Hz, 1H), 3.82 (s, 6H), 3.48 (d, *J* = 13.2 Hz, 4H), 1.83 (d, *J* = 5.7 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.13, 150.06, 148.36, 129.21, 120.03, 110.67, 109.91, 55.67, 49.65, 46.15, 26.23, 24.17.



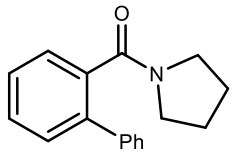
1q

Benzo[d][1,3]dioxol-5-yl(pyrrolidin-1-yl)methanone (1q).[4] This compound was synthesized using procedure B. Yield 82% (0.899 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.05-7.01 (m, 2H), 6.79 (d, *J* = 2.0 Hz, 1H), 5.98 (s, 2H), 3.52 (d, *J* = 12.8 Hz, 4H), 1.90 (s, 4H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.99, 148.75, 147.30, 130.84, 121.71, 108.04, 107.87, 101.29, 49.79, 46.30, 26.38, 24.38.



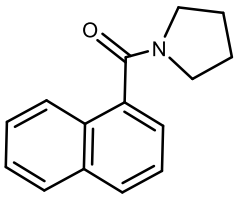
1r

Pyrrolidin-1-yl(*o*-tolyl)methanone (1r).[5] This compound was synthesized using procedure A. Yield 94% (0.890 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35-7.31 (m, 1H), 7.27 (d, *J* = 4.0 Hz, 3H), 3.73 (t, *J* = 7.0 Hz, 2H), 3.20 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 2.07-2.00 (m, 2H), 1.97-1.90 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.87, 137.72, 133.60, 130.29, 128.64, 125.76, 125.42, 48.26, 45.20, 25.90, 24.50, 18.84.



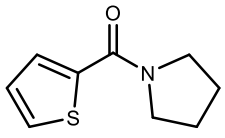
1s

[1,1'-Biphenyl]-2-yl(pyrrolidin-1-yl)methanone (1s).[6] This compound was synthesized using procedure B. Yield 81% (1.018 g). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 1.7Hz, 2H), 7.42-7.32 (m, 7H), 3.38 (s, 2H), 2.72 (s, 2H), 1.52 (d, *J* = 17.9 Hz, 4H). **^{13}C N MR (101 MHz, $CDCl_3$)** δ 169.66, 139.83, 138.16, 136.79, 129.35, 129.26, 128.40, 128.30, 127.61, 127.49, 127.03, 47.40, 45.24, 25.43, 24.11.



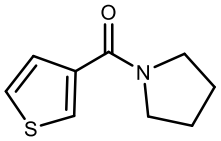
1t

Naphthalen-1-yl(pyrrolidin-1-yl)methanone (1t).[5] This compound was synthesized using procedure B. Yield 83% (0.935 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (s, 1H), 7.83 (t, *J* = 8.3 Hz, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.52-7.47 (m, 2H), δ 3.69 (t, *J* = 7.1 Hz, 1H), 3.45 (t, *J* = 6.7 Hz, 2H), 1.98-1.91(m, 2H), 1.86-1.80 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.58, 134.23, 133.57, 132.37, 128.31, 127.89, 127.56, 126.87, 126.79, 126.36, 124.23, 49.55, 46.14, 26.22, 24.29.



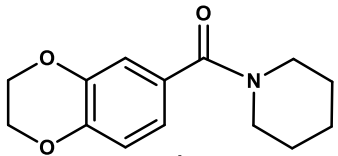
1u

Pyrrolidin-1-yl(thiophen-2-yl)methanone (1u).[4] This compound was synthesized using procedure A. Yield 87% (0.788 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 3.1 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.05-7.02 (m, 1H), 3.68 (d, *J* = 9.7 Hz, 4H), 1.93 (d, *J* = 4.1 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.70, 139.38, 129.44, 129.41, 126.96, 48.79, 47.20, 26.57, 23.92.



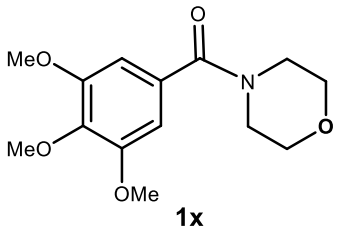
1v

Pyrrolidin-1-yl(thiophen-3-yl)methanone (1v).[7] This compound was synthesized using procedure B. Yield 83% (0.734 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 2.7 Hz, 1H), 7.11-7.09 (m, 1H), 7.03-7.01 (m, 2.8 Hz, 1H), 3.34 (s, 4H), 1.65 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.70, 137.80, 133.56, 127.82, 125.57, 49.52, 46.83, 26.66, 24.44.



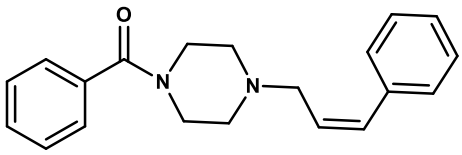
1w

Pyrrolidin-1-yl(thiophen-3-yl)methanone (1w).[1] This compound was synthesized using procedure B. Yield 91% (1.125 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.93 (d, *J* = 1.6 Hz, 1H), 6.90-6.84 (m, 2H), 4.26 (s, 4H), 3.52 (d, *J* = 45.8 Hz, 4H), 1.62 (d, *J* = 32.3 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.81, 144.61, 143.23, 129.54, 120.44, 117.11, 116.45, 64.41, 64.27, 29.67, 26.15, 24.60.



1x

Pyrrolidin-1-yl(thiophen-3-yl)methanone (1x).[1] This compound was synthesized using procedure A. Yield 81% (1.138 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.62 (s, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 3.70 (s, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.12, 153.29, 139.19, 130.57, 104.23, 66.82, 60.82, 56.18, 48.34.

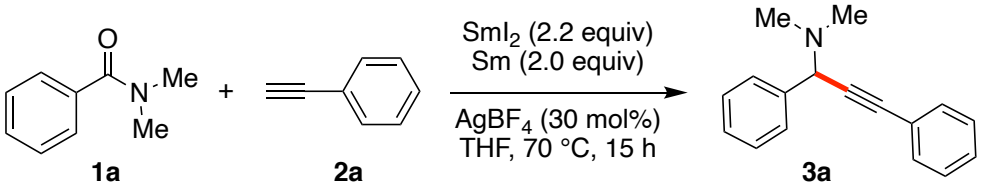


1y

(*Z*)-Phenyl(4-(3-phenylallyl)piperazin-1-yl)methanone (1y).[8] This compound was synthesized using procedure A. Yield 80% (1.226 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (d, *J* = 6.5 Hz, 2H), 7.39 (t, *J* = 1.6 Hz, 6H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.55 (d, *J* = 4.0 Hz, 1H), 6.30-6.23 (m, 1H), 3.74-3.69 (m, 4H), 3.40-3.33 (m, 2H), 2.90-2.77 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.43, 136.00, 134.67, 129.60, 128.98, 128.60, 128.43, 127.04, 126.80, 126.37, 122.35, 58.81, 58.81, 58.43, 52.99.

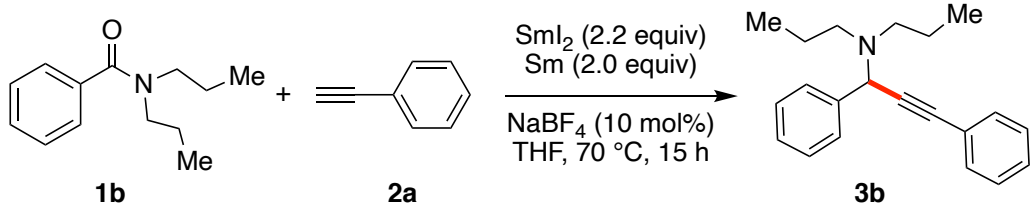
Characterization Data for Deoxygenative Alkynylation of Amides

(*R*)-*N,N*-Dimethyl-1,3-diphenylprop-2-yn-1-amine (Scheme 1, 3a)[9]



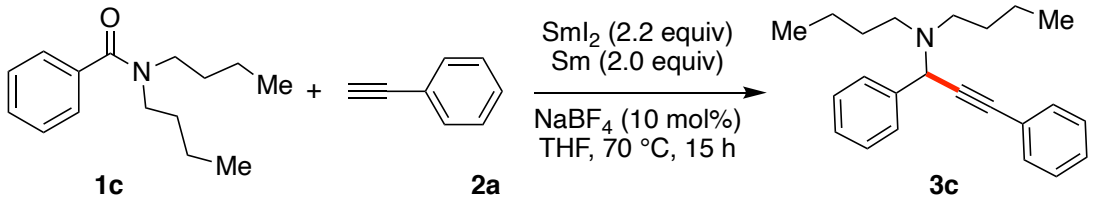
According to the general procedure, the reaction of *N,N*-dimethylbenzamide (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 56% yield (26.4 mg). Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.54-7.52 (m, 2H), 7.39-7.31 (m, 6H), 4.84 (s, 1H), 2.34 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.40, 131.81, 128.51, 128.31, 128.23, 128.21, 127.75, 123.07, 88.48, 84.54, 62.20, 41.54

(*R*)-1,3-Diphenyl-*N,N*-dipropylprop-2-yn-1-amine (Scheme 1, 3b)[10]



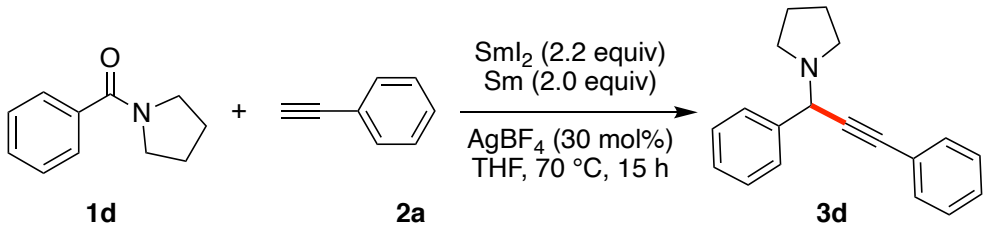
According to the general procedure, the reaction of *N,N*-dipropylbenzamide (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 65% yield (37.9 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.55-7.53 (m, 2H), 7.38-7.30 (m, 6H), 5.03 (s, 1H), 2.56-2.41 (m, 4H), 1.54-1.45 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.93, 131.81, 128.48, 128.39, 128.27, 127.91, 127.17, 123.43, 87.43, 86.11, 57.44, 52.86, 21.29, 11.87.

(*R*)-*N*-Butyl-*N*-(1,3-diphenylprop-2-yn-1-yl)butan-1-amine (Scheme 1, 3c)[11]



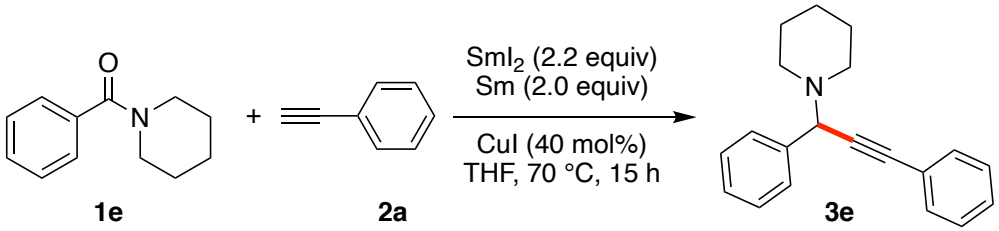
According to the general procedure, the reaction of *N,N*-dibutylbenzamide (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 58% yield (37.1 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 3.9 Hz, 2H), 7.38-7.29 (m, 6H), 5.05 (s, 1H), 2.52 (t, *J* = 6.8 Hz, 4H), 1.49-1.21 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.92, 131.81, 128.65, 128.40, 128.27, 127.92, 127.16, 123.45, 87.48, 86.08, 57.37, 50.55, 30.40, 20.46, 14.01.

(*R*)-1-(1,3-Diphenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3d)[9]



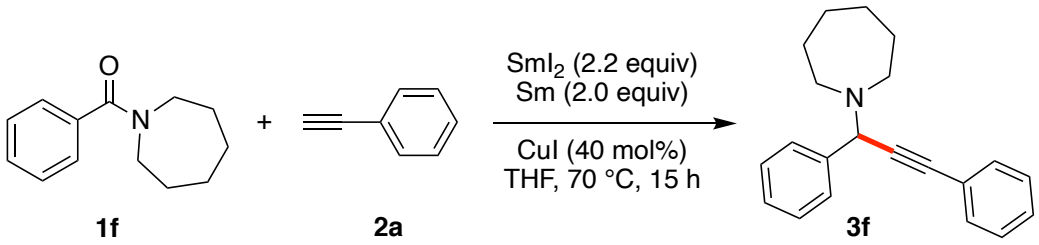
According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 80% yield (41.8 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 7.3 Hz, 2H), 7.52-7.49 (m, 2H), 7.40-7.29 (m, 6H), 4.91 (s, 1H), 2.72 (t, *J* = 6.7 Hz, 4H), 1.85-1.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.38, 131.75, 128.25, 128.23, 128.06, 127.55, 123.16, 86.90, 86.58, 59.08, 50.24, 23.44.

(*R*)-1-(1,3-Diphenylprop-2-yn-1-yl)piperidine (Scheme 1, 3e)[9]



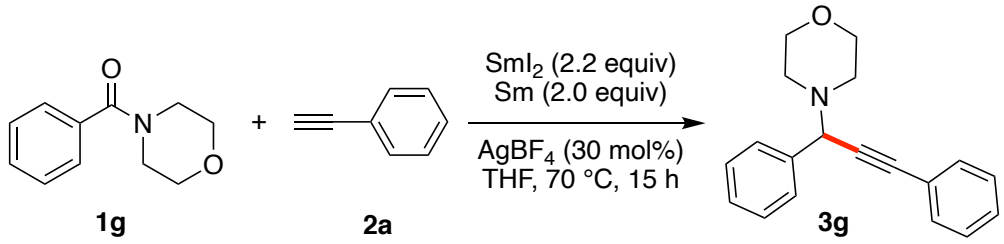
According to the general procedure, the reaction of phenyl(piperidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 58% yield (31.9 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.53-7.51 (m, 2H), 7.37-7.30 (m, 6H), 4.82 (s, 1H), 2.58 (s, 4H), 1.61 (d, *J* = 6.1 Hz, 4H), 1.46 (d, *J* = 6.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.37, 131.79, 128.57, 128.26, 128.06, 127.50, 123.25, 87.89, 85.91, 62.36, 50.66, 26.06, 24.35.

(*R*)-1-(1,3-Diphenylprop-2-yn-1-yl)azepane (Scheme 1, 3f)[12]



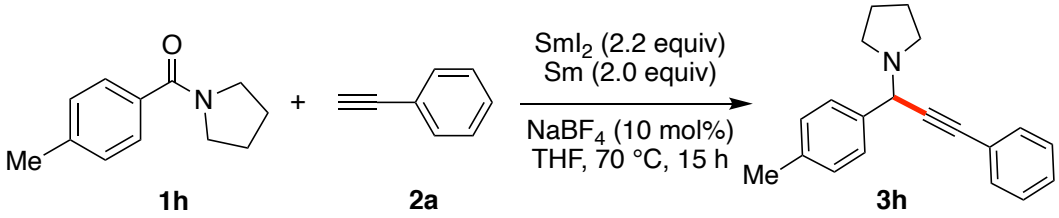
According to the general procedure, the reaction of azepan-1-yl(phenyl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 67% yield (38.8 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.54-7.51 (m, 2H), 7.39-7.30 (m, 6H). 4.94 (s, 1H), 2.75 (s, 4H), 1.62 (s, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.36, 131.80, 128.35, 128.27, 128.03, 127.39, 123.32, 87.19, 86.52, 62.66, 52.65, 28.73, 26.96.

(*R*)-4-(1,3-Diphenylprop-2-yn-1-yl)morpholine (Scheme 1, 3g)[9]



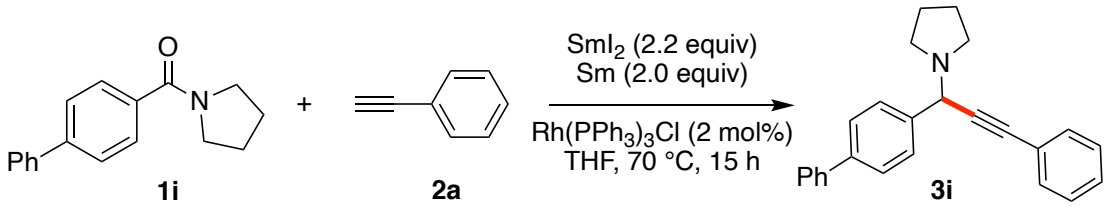
According to the general procedure, the reaction of morpholino(phenyl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 49% yield (27.2 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.54-7.51 (m, 2H), 7.40-7.31 (m, 6H), 4.80 (s, 1H), 3.79-3.70 (m, 4H), 2.65 (t, *J* = 4.8 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.69, 131.78, 128.58, 128.29, 128.22, 127.78, 122.91, 88.49, 84.94, 67.10, 62.01, 49.84.

(*R*)-1-(3-Phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3h)[13]



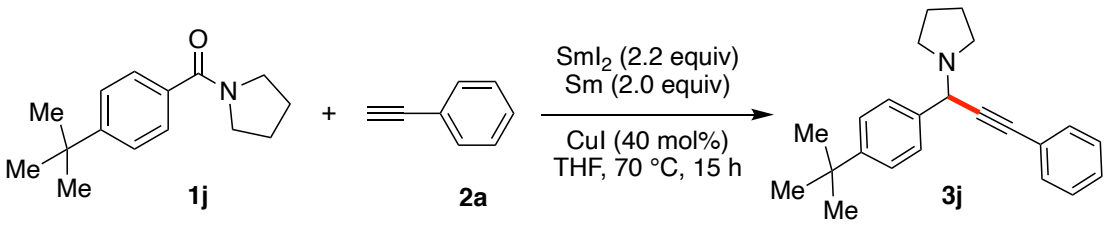
According to the general procedure, the reaction of pyrrolidin-1-yl(*p*-tolyl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 56% yield (30.8 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (t, *J* = 5.5 Hz, 4H), 7.33-7.27 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.87 (s, 1H), 2.71 (t, *J* = 4.5 Hz, 4H), 2.36 (s, 3H), 1.85-1.80 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.33, 136.15, 131.75, 129.61, 128.95, 128.22, 128.07, 123.16, 86.78, 86.66, 58.85, 50.27, 23.43, 21.10.

(*R*)-1-(1-([1,1'-Biphenyl]-4-yl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3i)[14]



According to the general procedure, the reaction of [1,1'-biphenyl]-4-yl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 38% yield (25.6 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 5.3 Hz, 4H), 7.53-7.50 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37-7.33 (m, 4H), 4.99 (s, 1H), 2.78 (s, 4H), 1.84 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.79, 140.70, 137.78, 131.82, 128.81, 128.75, 128.31, 127.29, 127.11, 87.30，86.77，58.80, 50.31, 23.51.

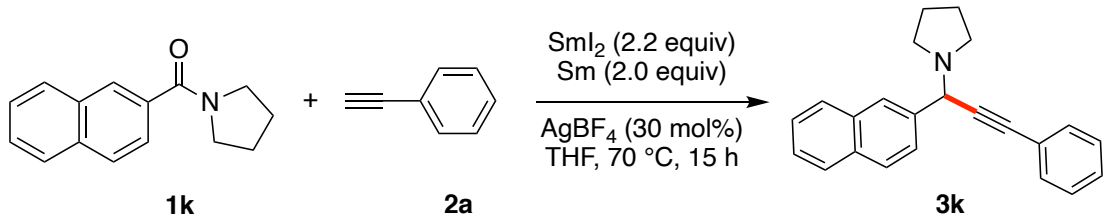
(*R*)-1-(1-(4-(*tert*-Butyl)phenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3j)[15]



According to the general procedure, the reaction of (4-(*tert*-butyl)phenyl)(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 56% yield (35.6 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.50-7.48 (m, 2H), 7.38 (d, *J* = 8.2 Hz,

2H), 7.32-7.31 (m, 3H), 4.89 (s, 1H), 2.73 (s, 4H), 1.86-1.77 (m, 4H), 1.32 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.63, 131.77, 128.24, 128.00, 127.24, 125.22, 123.12, 120.97, 86.92, 86.44, 58.77, 50.31, 34.50, 31.34, 23.45.

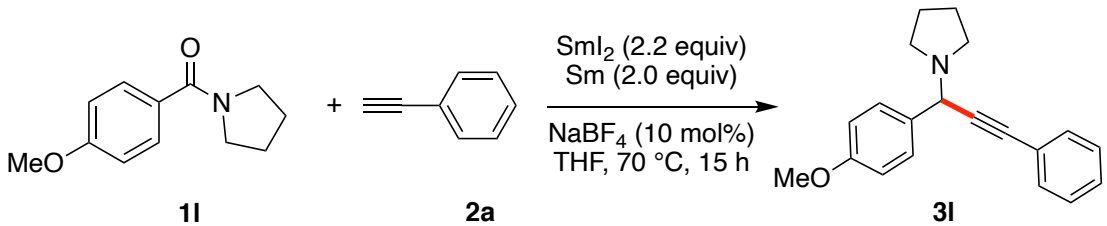
(*R*)-1-(1-(Naphthalen-2-yl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3k)[13]



1k **2a** **3k**

According to the general procedure, the reaction of naphthalen-2-yl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 51% yield (31.8 mg). Light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.58-7.46 (m, 6H), 7.35-7.33 (m, 2H), 5.60 (s, 1H), 2.85-2.80 (m, 2H), 2.73-2.67 (m, 2H), 1.82-1.75 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.25, 133.92, 131.78, 131.47, 128.45, 128.32, 128.25, 128.03, 125.94, 125.91, 125.56, 125.01, 124.41, 123.31, 87.37, 86.69, 56.60, 50.17, 23.66.

(*R*)-1-(1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3l)[13]

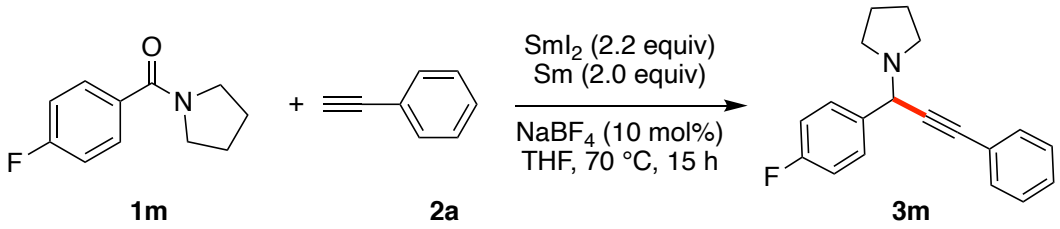


1l **2a** **3l**

According to the general procedure, the reaction of (4-methoxyphenyl)(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44

mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 71% yield (41.4 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54-7.48 (m, 4H), 7.32-7.31 (m, 3H), 6.92-6.88 (m, 2H), 4.86 (s, 1H), 3.81 (s, 3H), 2.71 (t, *J* = 6.4 Hz, 4H), 1.81 (t, *J* = 6.4 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.07, 131.75, 131.38, 129.42, 128.24, 128.08, 123.14, 113.58, 86.79, 86.71, 58.49, 55.25, 50.23, 23.43.

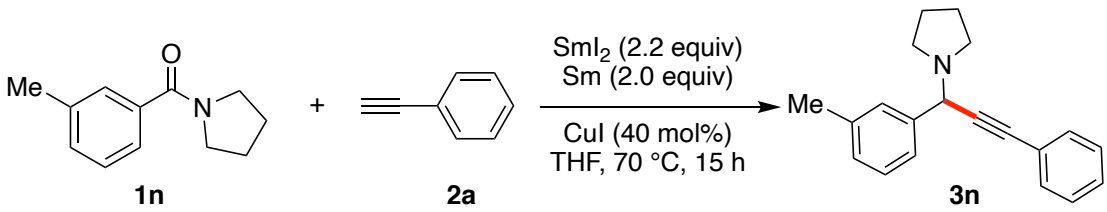
(*R*)-1-(1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3m)[13]



1m **2a** **3m**

According to the general procedure, the reaction of (4-fluorophenyl)(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 55% yield (30.7 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60-7.57 (m, 2H), 7.50-7.48 (m, 2H), 7.34-7.31 (m, 3H), 7.07-7.01 (m, 2H), 4.88 (s, 1H), 2.68 (d, *J* = 1.6 Hz, 4H), 1.84-1.77 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.21 (d, J^F = 245.8 Hz), 135.32, 131.76, 129.81 (d, J^F = 8.1 Hz), 128.28, 128.19, 123.01, 115.01 (d, J^F = 21.5 Hz), 87.15, 86.26, 58.30, 50.12, 23.45. **^{19}F NMR (376 MHz, CDCl3)** δ -114.95.

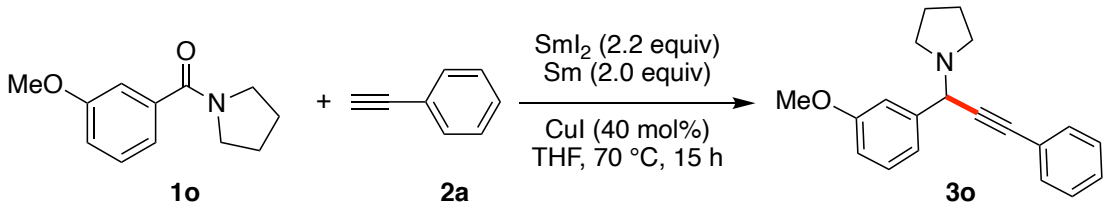
(*R*)-1-(3-Phenyl-1-(*m*-tolyl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3n)[13]



1n **2a** **3n**

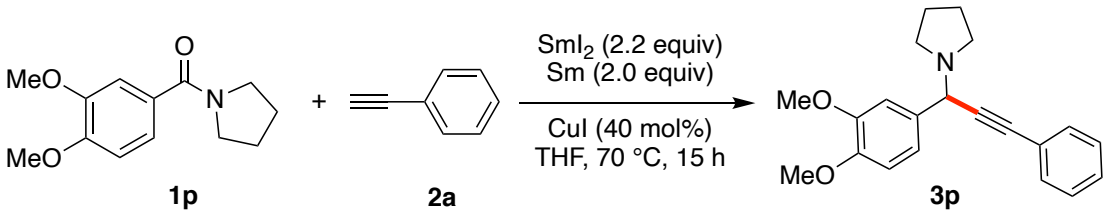
According to the general procedure, the reaction of pyrrolidin-1-yl(*m*-tolyl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 57% yield (31.4 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53-7.50 (m, 2H), 7.43 (d, *J* = 6.5 Hz, 2H), 7.35-7.33 (m, 2.0 Hz, 3H), 7.30-7.28 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 4.86 (s, 1H), 2.74 (s, 4H), 2.40 (s, 3H), 1.84 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.24, 137.92, 131.76, 128.97, 128.38, 128.23, 128.11, 128.05, 125.36, 123.22, 86.77, 86.73, 59.21, 50.38, 23.43, 21.45.

(*R*)-1-(1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3o)[14]



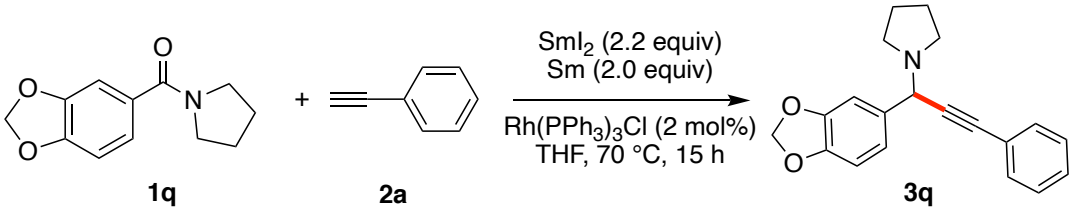
According to the general procedure, the reaction of (3-methoxyphenyl)(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 60% yield (35.0 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.47 (m, 2H), 7.32-7.28 (m, 4H), 7.20 (d, *J* = 4.6 Hz, 2H), 6.85-6.83 (m, 1H), 4.85 (s, 1H), 3.83 (s, 3H), 2.68 (s, 4H), 1.80 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.58, 141.02, 131.77, 129.19, 128.24, 128.09, 123.15, 120.68, 113.85, 113.07, 86.83, 86.57, 59.13, 55.27, 50.35, 23.47.

(*R*)-1-(1-(3,4-Dimethoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3p)[15]



According to the general procedure, the reaction of (3,4-dimethoxyphenyl)(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 64% yield (41.1 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56-7.53 (m, 2H), 7.39-7.37 (m, 3H), 7.33 (d, *J* = 1.6 Hz, 2H), 6.92-6.90 (m, 1H), 4.89 (s, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 2.79 (s, 4H), 1.89 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.84, 148.56, 135.99, 131.75, 129.32, 128.29, 120.43, 111.43, 110.58, 85.99, 85.29, 59.06, 55.98, 55.89, 50.48.

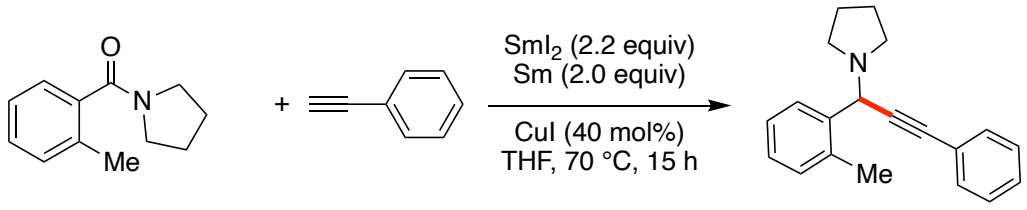
(*R*)-1-(1-(Benzo[d][1,3]dioxol-5-yl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3q)[16]



According to the general procedure, the reaction of benzo[d][1,3]dioxol-5-yl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 68% yield (41.5 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49-7.47 (m, 2H), 7.32-7.31 (m, 3H), 7.14 (d, *J* = 1.7 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 2H), 4.80 (s, 1H), 2.70 (t, *J* = 6.7 Hz, 4H), 1.84-1.77 (m, 4H). **^{13}C NMR (101 MHz,**

$CDCl_3$) δ 147.60, 147.03, 131.77, 128.26, 128.17, 123.01, 121.61, 108.81, 107.83, 101.04, 86.93, 86.43, 61.86, 58.80, 50.23, 23.44.

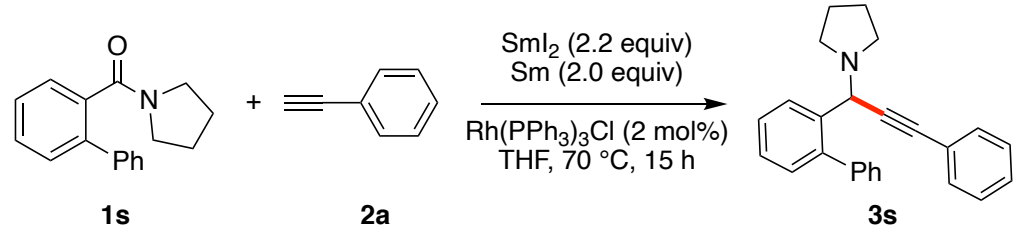
(*S*)-1-(3-Phenyl-1-(*o*-tolyl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3r)[17]



1r **2a** **3r**

According to the general procedure, the reaction of pyrrolidin-1-yl(*o*-tolyl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 43% yield (23.7 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (t, *J* = 4.5 Hz, 1H), 7.48 (d, *J* = 4.0 Hz, 2H), 7.32-7.30 (m, 3H), 7.21-7.18 (m, 3H), 5.02 (s, 1H), 2.73-2.63 (m, 4H), 2.47 (s, 3H), 1.77 (t, *J* = 6.3 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.64, 140.60, 131.78, 129.21, 128.27, 128.17, 127.68, 126.33, 125.56, 123.00, 86.28, 86.17, 54.43, 49.97, 29.68, 23.52.

(*R*)-1-(1-(3,4-Dimethoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3s)

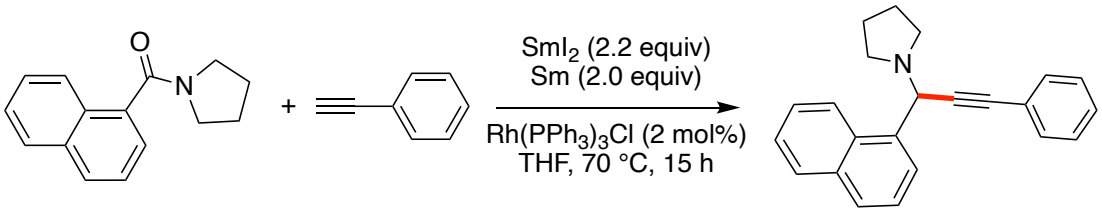


1s **2a** **3s**

According to the general procedure, the reaction of [1,1'-biphenyl]-2-yl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 46% yield

(31.0 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 6.6 Hz, 2H), 7.45-7.28 (m, 11H), 4.76 (s, 1H), 2.59 (s, 4H), 1.74 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.64, 141.01, 139.06, 137.50, 131.71, 129.73, 128.84, 128.18, 127.91, 127.32, 127.04, 124.11, 123.34, 87.90, 86.07, 55.61, 50.07, 23.38. **HRMS** calcd for $C_{25}H_{23}N$ (M^+) 337.1825, found 337.1832.

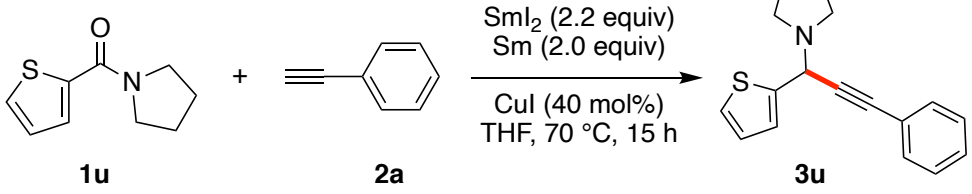
(*S*)-1-(1-(Naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3t)[17]



1t **2a** **3t**

According to the general procedure, the reaction of naphthalen-1-yl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 44% yield (27.4 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (s, 1H), 7.88-7.84 (m, 3H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.54-7.47 (m, 4H), 7.35-7.33 (m, 3H), 5.05 (s, 1H), 2.75 (s, 4H), 1.86-1.81 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.82, 133.18, 133.00, 131.82, 128.29, 128.18, 128.10, 128.02, 127.58, 126.94, 126.45, 125.99, 125.92, 123.12, 87.25, 86.46, 59.33, 50.44, 23.51.

(*S*)-1-(3-Phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3u)[18]

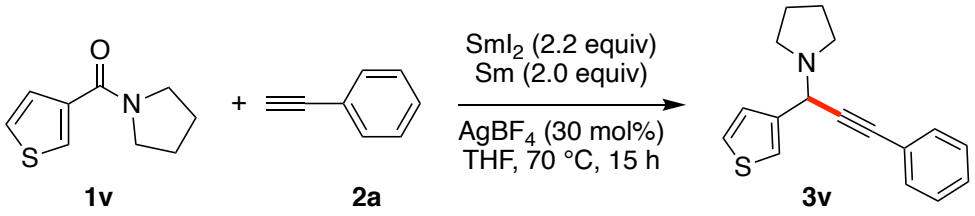


1u **2a** **3u**

According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-2-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 2.0 equiv), CuI (0.08

mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 95% yield (50.8 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55-7.52 (m, 2H), 7.37-7.29 (m, 4H), 7.25 (s, 1H), 7.01-6.98 (m, 1H), 5.23 (s, 1H), 2.80 (s, 4H), 1.86 (t, *J* = 6.6 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.13, 131.82, 128.27, 126.57, 126.19, 125.46, 125.26, 122.87, 86.39, 85.72, 54.33, 49.78, 23.59.

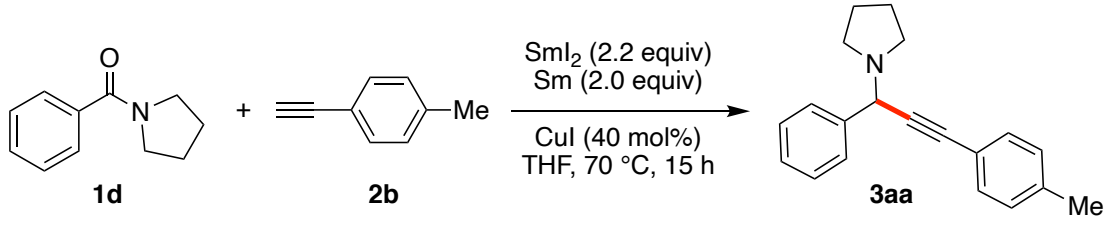
(*S*)-1-(3-Phenyl-1-(thiophen-3-yl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3v)



1v **2a** **3v**

According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), ethynylbenzene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 45% yield (24.1 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50-7.47 (m, 2H), 7.42-7.41 (m, 1H), 7.33-7.27 (m, 5H), 5.00 (s, 1H), 2.72 (d, *J* = 5.4 Hz, 4H), 1.85-1.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.68, 131.75, 128.23, 128.20, 127.98, 127.46, 125.61, 123.31, 86.80, 86.68, 56.16, 50.15, 23.54. **HRMS** calcd for $C_{17}H_{17}NS$ (M^+) 267.1076, found 267.1069.

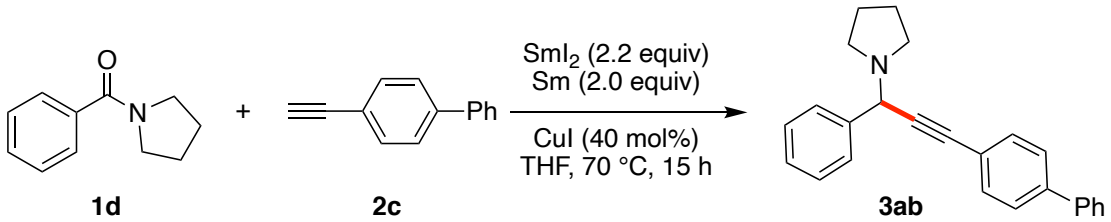
(*R*)-1-(1-Phenyl-3-(p-tolyl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3aa)[13]



1d **2b** **3aa**

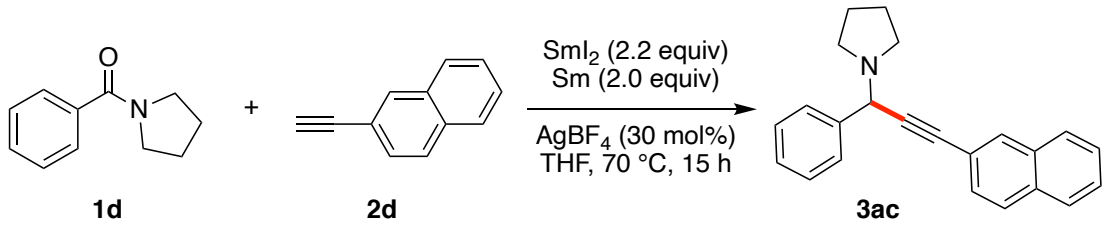
According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 41% yield (22.6 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.40-7.35 (m, 4H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.98 (s, 1H), 2.78 (s, 4H), 2.36 (s, 3H), 1.88-1.81 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.43, 133.20, 131.67, 128.46, 128.35, 127.89, 127.22, 119.72, 87.61, 87.54, 59.15, 50.32, 23.50, 21.46.

(*R*)-1-(3-([1,1'-Biphenyl]-4-yl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ab)[18]



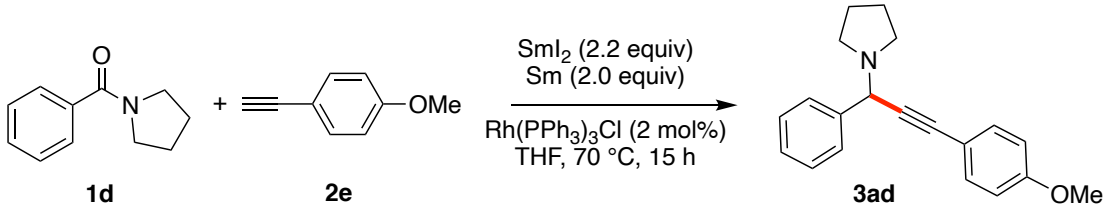
According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 4-ethynyl-1,1'-biphenyl (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 41% yield (27.7 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.60-7.57 (m, 6H), 7.47-7.43 (m, 3H), 7.41-7.37 (m, 3H), 5.03 (s, 1H), 2.81 (s, 4H), 1.86 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.14, 140.40, 140.29, 132.23, 128.86, 128.51, 128.43, 127.99, 127.66, 127.01, 120.69, 85.68, 84.44, 59.16, 50.33, 23.51.

(*R*)-1-(3-(Naphthalen-2-yl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ac)



According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 2-ethynylnaphthalene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 44% yield (27.4 mg). *New compound*. Yellow solid. **Mp** = 41-43 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 4H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.55-7.48 (m, 3H), 7.38 (d, *J* = 7.8 Hz, 2H), 4.97 (s, 1H), 2.77 (s, 4H), 1.85 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.05, 140.00, 139.14, 132.92, 131.58, 128.60, 128.40, 127.95, 127.75, 127.67, 126.64, 126.56, 120.17, 89.29, 88.42, 59.25, 50.39, 23.51. **HRMS** calcd for $C_{23}H_{21}N$ (M^+) 311.1669, found 311.1668.

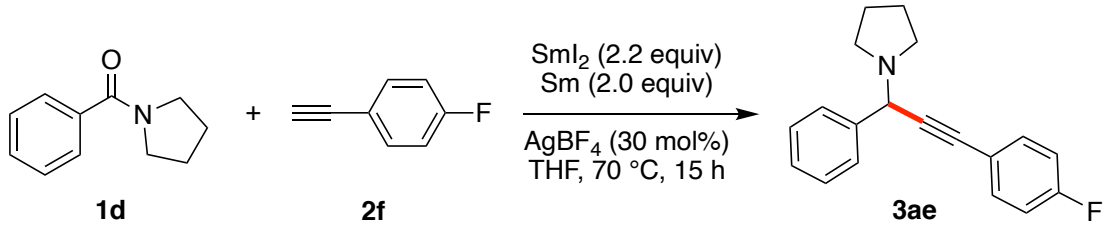
(*R*)-1-(3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ad)[13]



According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.8 mmol, 4.0 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 45% yield (26.2 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.48-7.42 (m, 3H), 7.39-7.36 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 4.96 (s, 1H), 3.82 (s, 3H),

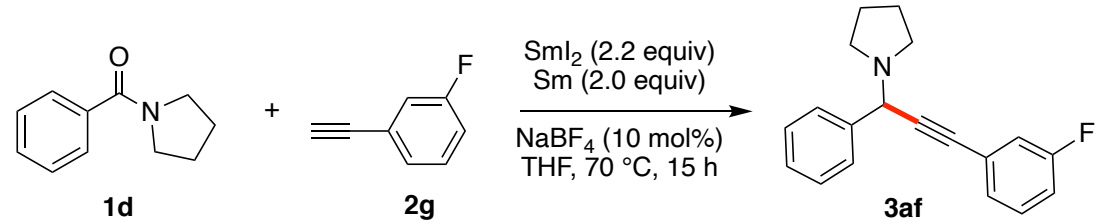
2.78 (s, 4H), 1.84 (t, J = 6.4 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.18, 134.01, 133.23, 128.52, 128.40, 128.04, 114.08, 113.91, 87.63, 87.48, 59.24, 55.29, 50.39, 23.50.

(*R*)-1-(3-(4-Fluorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ae)[13]



According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-4-fluorobenzene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 56% yield (31.3 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 6.4 Hz, 2H), 7.38-7.30 (m, 3H), 7.01 (t, J = 8.1 Hz, 2H), 4.86 (s, 1H), 2.69 (s, 4H), 1.81 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.38 (d, J^F = 249.0 Hz), 139.19, 133.62 (d, J^F = 8.3 Hz), 128.30, 128.26, 127.68, 119.19 (d, J^F = 3.3 Hz), 115.50 (d, J^F = 21.9 Hz), 86.27, 85.82, 59.13, 50.34, 23.42. **^{19}F NMR (101 MHz, $CDCl_3$)** δ -111.03.

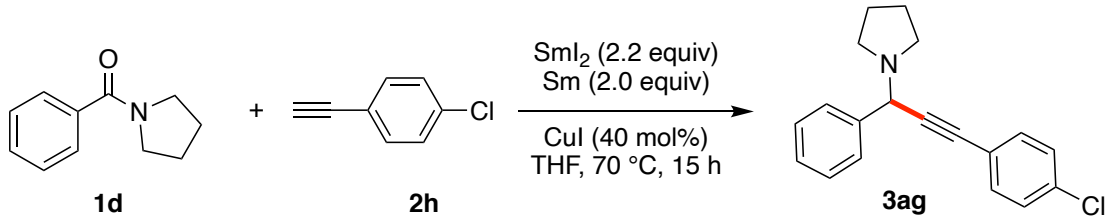
(*R*)-1-(3-(3-Fluorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3af)[19]



According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-3-fluorobenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl

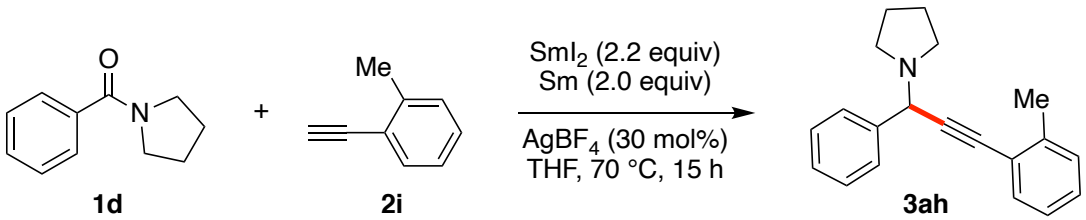
acetate = 10/1 to 1/1) the title compound in 52% yield (29.1 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.42-7.31 (m, 5H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 4.90 (s, 1H), 2.70 (s, 4H), 1.81 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.32 (d, J^F = 246.5 Hz), 138.33, 129.86 (d, J^F = 8.7 Hz), 128.38 (d, J^F = 2.4 Hz), 127.95, δ 127.68 (d, J^F = 3.1 Hz), 124.74 (d, J^F = 9.1 Hz), 118.60 (d, J^F = 22.6 Hz), 115.62 (d, J^F = 21.2 Hz), 87.17, 86.04, 59.00, 50.29, 23.44. **^{19}F NMR (101 MHz, $CDCl_3$)** δ -112.93.

(*R*)-1-(3-(4-Chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ag)[20]



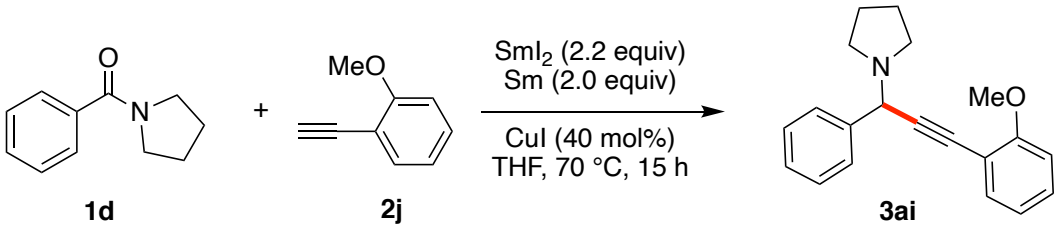
According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 1-chloro-4-ethynylbenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 50% yield (29.6 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.1 Hz, 2H), 7.42-7.35 (m, 4H), 7.32-7.28 (m, 3H), 4.89 (s, 1H), 2.70 (s, 4H), 1.85-1.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.78, 134.16, 133.00, 128.59, 128.34, 128.30, 127.80, 121.51, 87.46, 85.91, 59.12, 50.33, 23.42.

(*R*)-1-(1-Phenyl-3-(*o*-tolyl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ah)



According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methylbenzene (0.8 mmol, 4.0 equiv), $AgBF_4$ (0.06 mmol, 30 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 56% yield (30.8 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.43-7.30 (m, 5H), 7.21-7.18 (m, 1H), 5.08 (s, 1H), 2.81 (s, 4H), 2.52 (s, 3H), 1.87 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.10, 139.81, 133.16, 132.22, 129.44, 128.40, 128.32, 127.76, 125.53, 122.84, 86.70, 84.33, 59.18, 50.17, 23.52, 21.08. **HRMS** calcd for $C_{20}H_{21}N$ (M^+) 275.1669, found 275.1667.

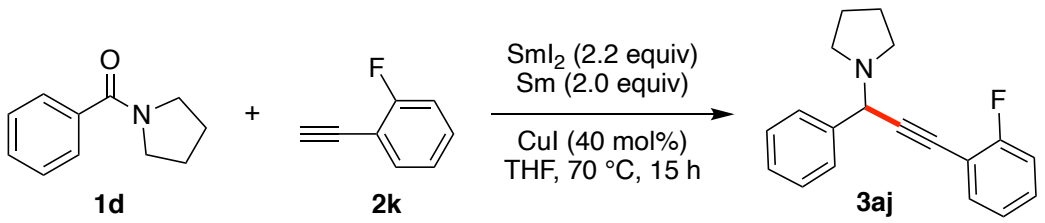
(*R*)-1-(3-(2-Methoxyphenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ai)



1d **2j** **3ai**

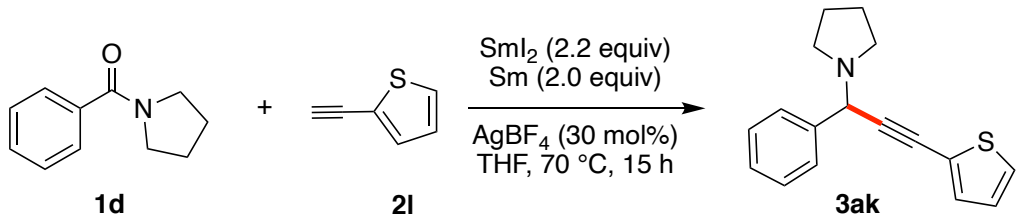
According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 50% yield (29.1 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 6.7 Hz, 2H), 7.46 (d, *J* = 5.8 Hz, 1H), 7.39-7.29 (m, 4H), 6.94-6.89 (m, 2H), 5.15 (s, 1H), 3.89 (s, 3H), 2.83 (s, 4H), 1.86 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.35, 139.17, 133.50, 129.81, 128.69, 128.34, 120.37, 112.00, 110.65, 87.21, 87.00, 60.38, 59.19, 55.75, 23.59. **HRMS** calcd for $C_{20}H_{21}NO$ (M^+) 291.1618, found 291.1623.

(*R*)-1-(3-(2-Fluorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (Scheme 1, 3aj)



According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-fluorobenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 41% yield (22.9 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.39-7.30 (m, 4H), 7.12-7.07 (m, 2H), 4.99 (s, 1H), 2.73 (d, J = 7.2 Hz, 4H), 1.85-1.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.95 (d, J^F = 250.3 Hz), 138.75, 133.57, 129.83 (d, J^F = 7.9 Hz), 128.33 (d, J^F = 4.2 Hz) 127.73, 123.86 (d, J^F = 3.9 Hz), 115.45 (d, J^F = 20.8 Hz), 111.62 (d, J^F = 15.1 Hz), 91.64, 80.81, 59.08, 50.09, 23.48. **^{19}F NMR (101 MHz, CDCl3)** δ -109.61. **HRMS** calcd for $C_{19}H_{18}FN$ (M^+) 279.1418, found 279.1420.

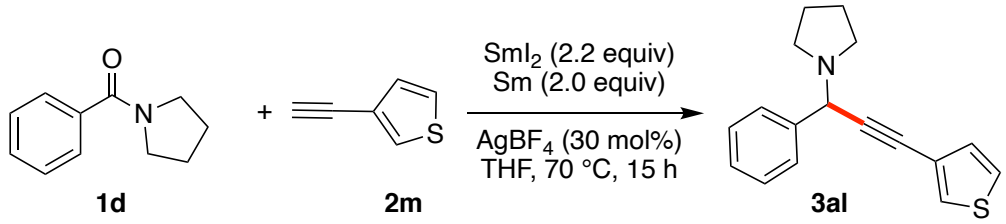
(*R*)-1-(1-Phenyl-3-(thiophen-2-yl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3ak)



According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 33% yield (17.6 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, J = 6.4 Hz, 2H), 7.38- 7.32 (m, 2H), 7.29 (d, J = 7.5 Hz, 1H), 7.23-7.21 (m, 2H), 6.97-6.94 (m,

1H), 4.93 (s, 1H), 2.71 (s, 4H), 1.80 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.95, 131.86, 128.57, 128.52, 128.22, 127.75, 126.43, 122.94, 89.27, 88.50, 61.51, 52.92, 22.68. **HRMS** calcd for $C_{17}H_{17}NS$ (M^+) 267.1076, found 267.1071.

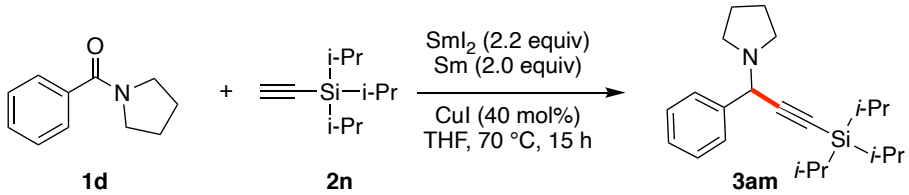
(*R*)-1-(1-Phenyl-3-(thiophen-3-yl)prop-2-yn-1-yl)pyrrolidine (Scheme 1, 3al)



1d **2m** **3al**

According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 41% yield (21.9 mg). *New compound*. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (d, J = 7.6 Hz, 2H), 7.17-7.05 (m, 5H), 6.94 (d, J = 5.0 Hz, 1H), 4.67 (s, 1H), 2.50 (s, 4H), 1.60 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.66, 132.00, 130.06, 128.37, 127.88, 126.92, 125.32, 122.87, 83.04, 81.77, 59.32, 50.34, 23.45. **HRMS** calcd for $C_{17}H_{17}NS$ (M^+) 267.1076, found 267.1077.

(*R*)-1-(1-Phenyl-3-(triisopropylsilyl)prop-2-yn-1-yl)pyrrolidine (Scheme 2, 3am)

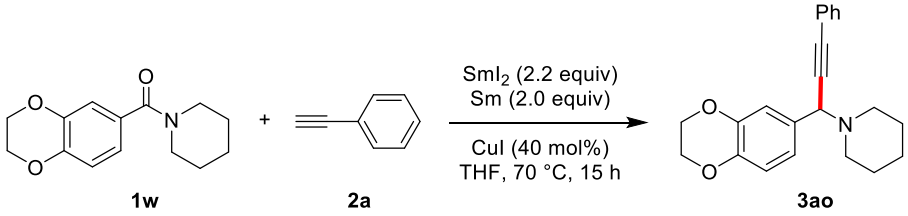


1d **2n** **3am**

According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1)the title compound in 95% yield

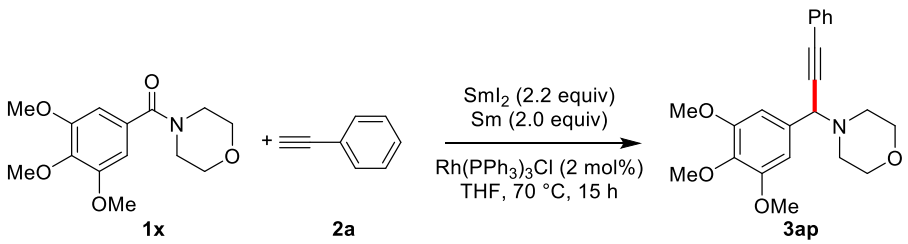
(64.9 mg). *New compound*. Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 4.85 (s, 1H), 2.69 (d, *J* = 21.8 Hz, 4H), 1.78 (s, 4H), 1.11 (s, 21H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.90, 128.33, 128.16, 127.53, 91.94, 88.45, 58.96, 49.68, 23.58, 18.67, 11.24. **HRMS** calcd for $C_{22}H_{35}NSi$ (M^+) 341.2533, found 341.2539.

(*S*)-1-(1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-3-phenylprop-2-yn-1-yl)piperidine (Scheme 2, 3ao)[21]



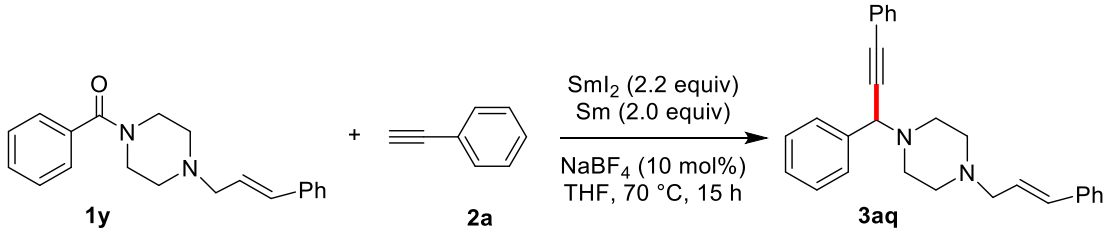
According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), CuI (0.08 mmol, 40 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 50% yield (33.3 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 4.2 Hz, 2H), 7.32 (d, *J* = 4.8 Hz, 3H), 7.17 (s, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.71 (s, 1H), 4.27 (s, 4H), 2.56 (s, 4H), 1.62-1.58 (m, 4H), δ 1.45 (d, *J* = 5.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.02, 142.88, 131.79, 128.22, 128.01, 126.97, 123.25, 121.57, 117.45, 116.70, 87.62, 86.05, 64.33, 61.72, 50.56, 31.18, 26.06, 24.38.

(*S*)-3-(3-Phenyl-1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-yl)-1,3-oxazinane (Scheme 2, 3ap)[22]



According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 37% yield (27.2 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.49 (m, 2H), 7.35-7.33 (m, 3H), 6.91 (s, 2H), 4.71 (s, 1H), 3.89 (s, 6H), 3.86 (s, 3H), 3.78-3.74 (d, *J* = 4.2 Hz, 4H), 2.65 (d, *J* = 14.1 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.01, 140.59, 137.39, 131.73, 128.36, 127.92, 122.82, 105.42, 88.52, 85.01, 67.13, 62.17, 60.85, 56.73, 56.14.

(*S*)-1-Cinnamyl-4-(1,3-diphenylprop-2-yn-1-yl)piperazine (Scheme 2, 3aq)[21]



According to the general procedure, the reaction of pyrrolidin-1-yl(thiophen-3-yl)methanone (0.2 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.8 mmol, 4.0 equiv), $NaBF_4$ (0.02 mmol, 10 mol %), Sm (0.4 mmol, 2.0 equiv), SmI_2 (4.4 mL, 0.1 M in THF, 0.44 mmol, 2.2 equiv) for 15 h at 70 °C, afforded after work-up and chromatography (hexane/ethyl acetate = 10/1 to 1/1) the title compound in 46% yield (36.1 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.52-7.50 (m, 2H), 7.38-7.34 (m, 5H), 7.32-7.30 (m, 6H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.36-6.29 (m, 1H), 4.84 (s, 1H), 3.28 (s, 2H), 2.77 (s, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.93, 136.49, 133.34, 131.85, 129.20, 128.70, 128.57, 128.52, 128.22, 128.18, 127.75, 126.43, 124.70, 122.93, 88.43, 84.95, 61.50, 60.62, 52.89, 48.54.

References

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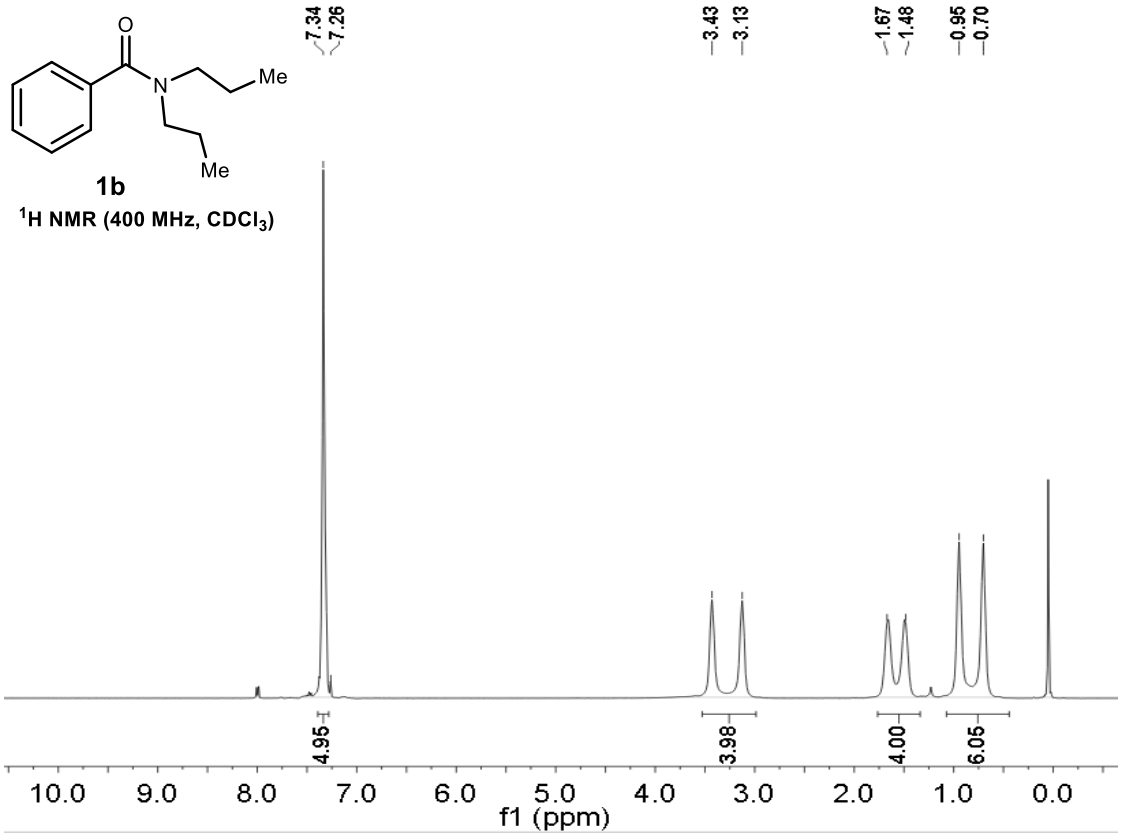
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7.26
3.43
3.13
1.67
1.48
0.95
0.70
Me
N
Me
O
1b
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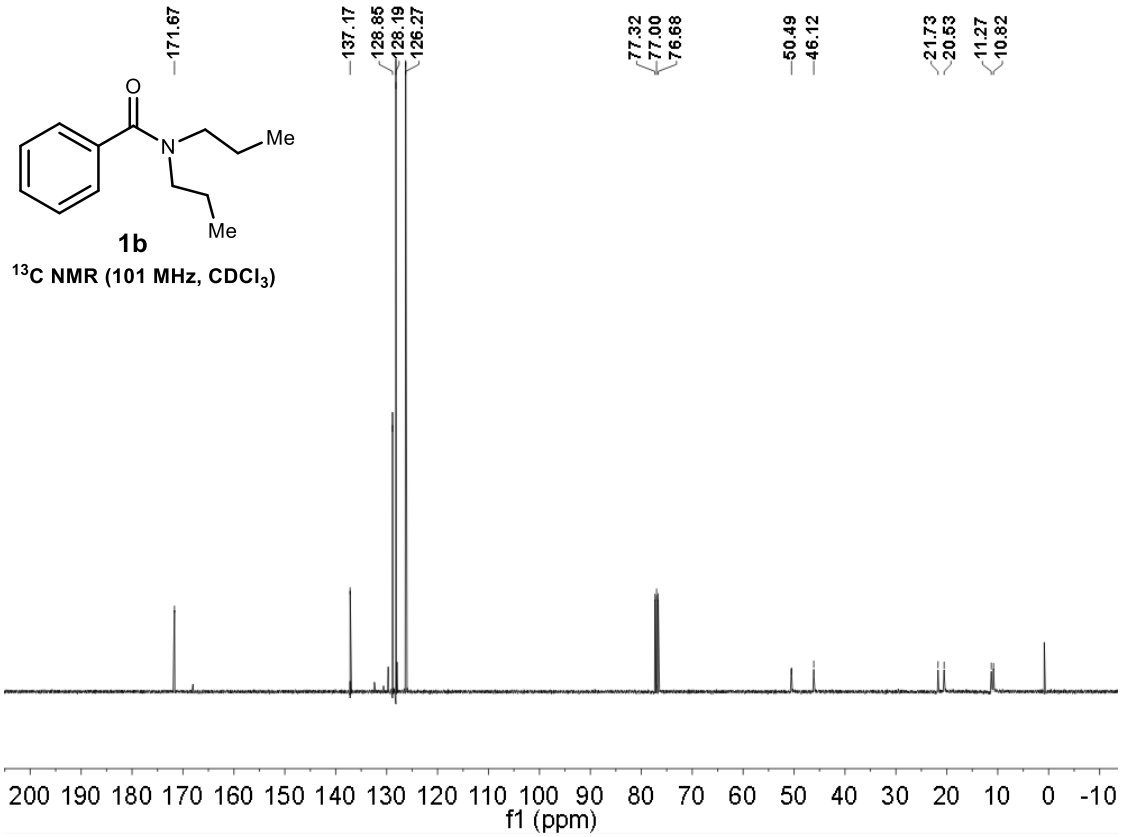
4.95
3.98
4.00
6.05
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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137.17
128.85
128.19
126.27
77.32
77.00
76.68
50.49
46.12
21.73
20.53
11.27
10.82
Me
N
Me
O
1b
^{13}C NMR (101 MHz, CDCl$_3$)
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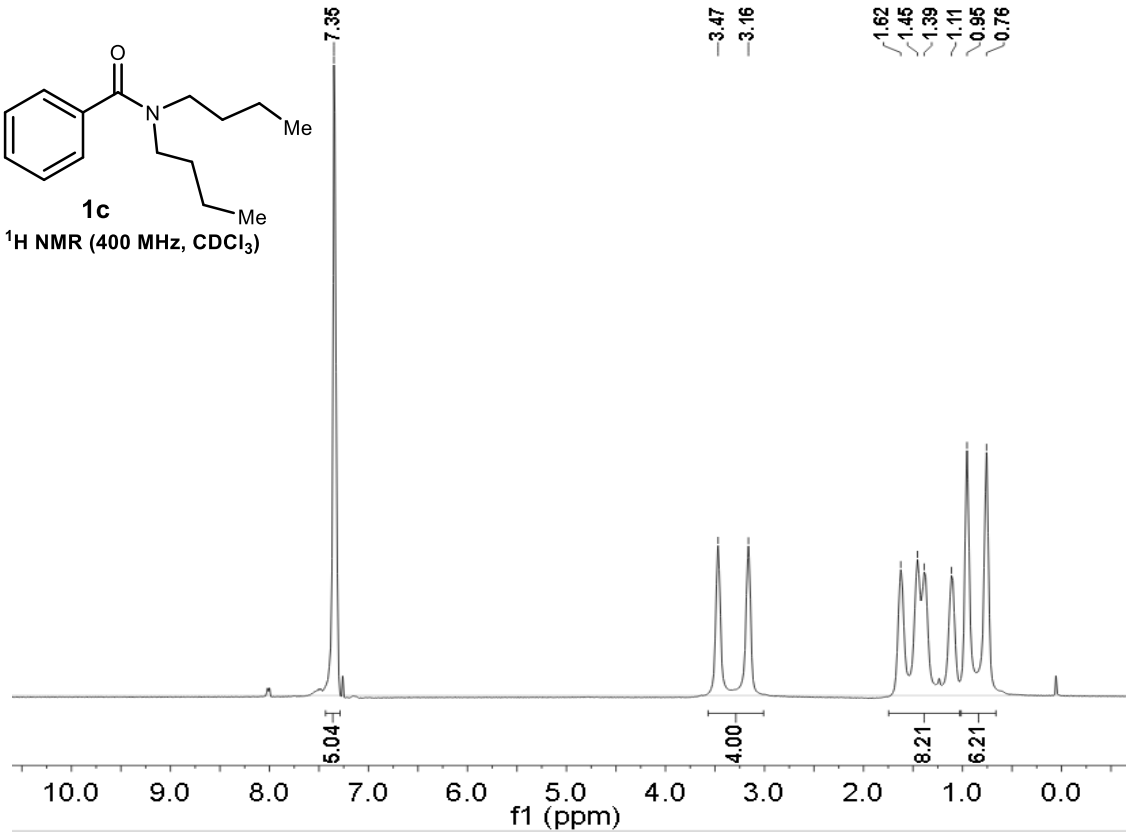
f1 (ppm)



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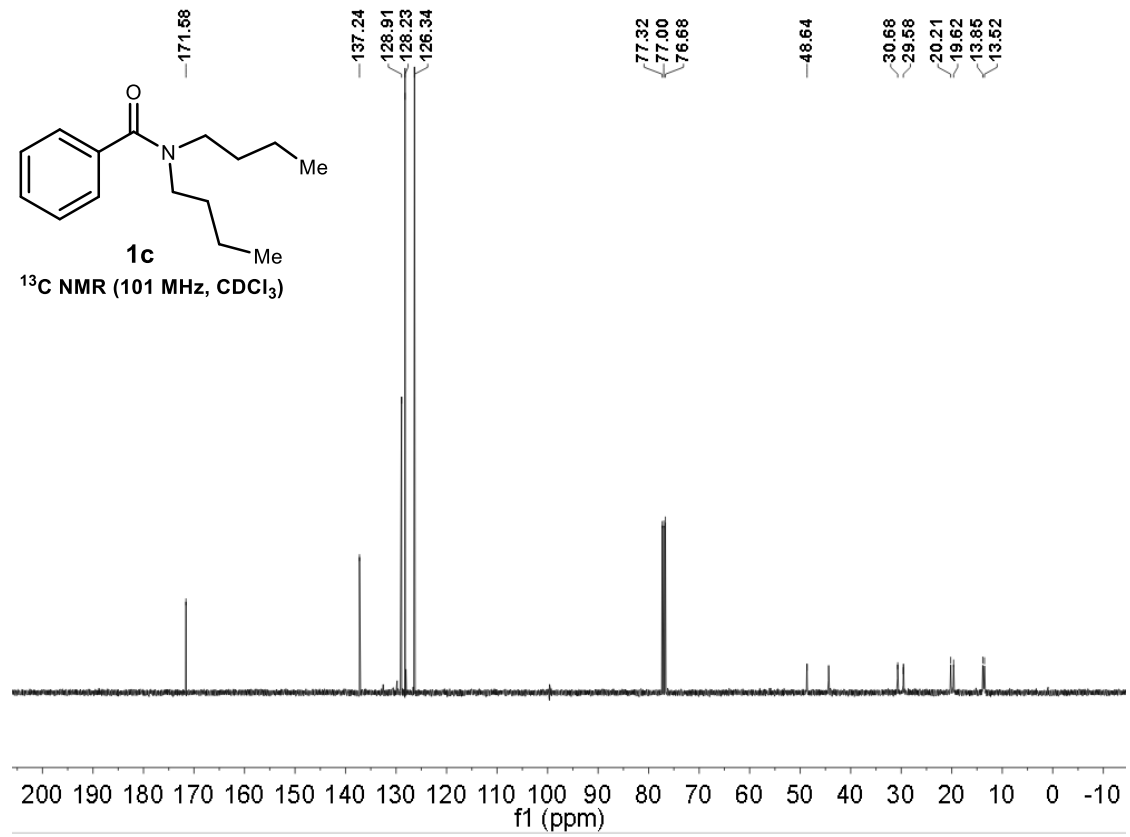

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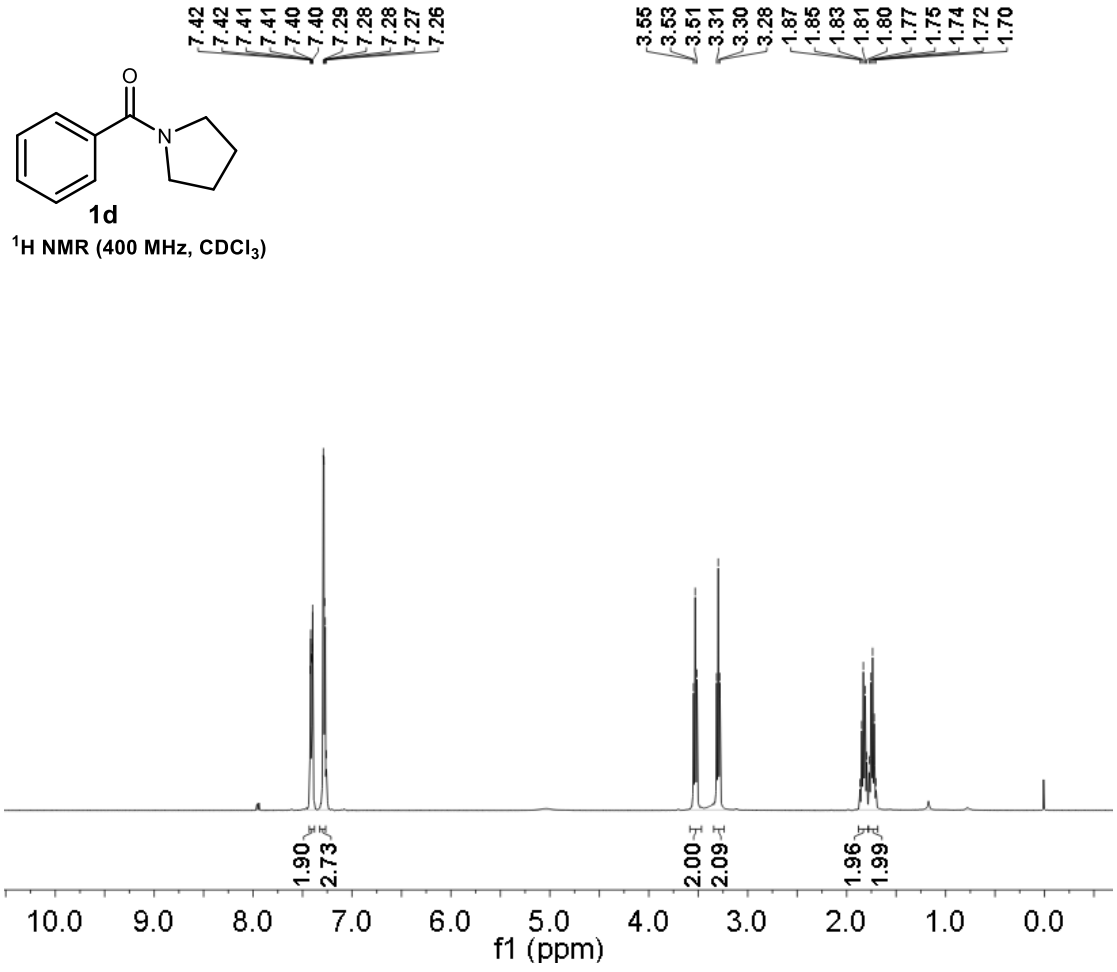
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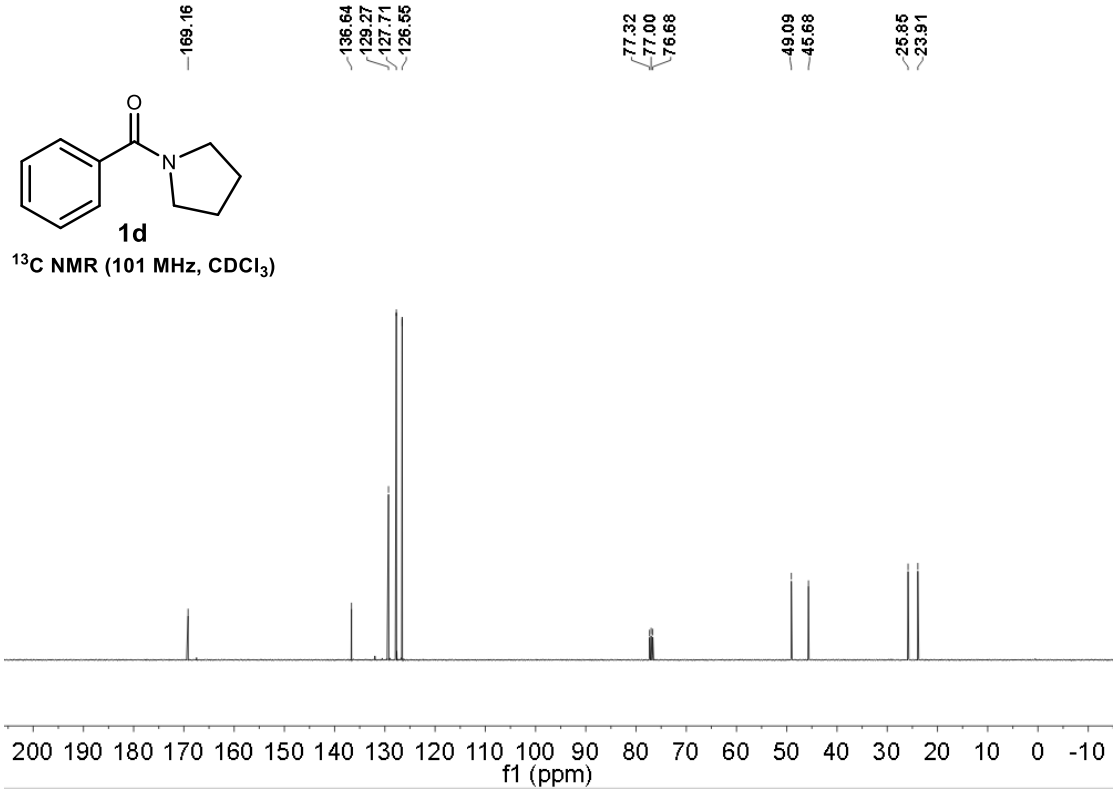
7.42
7.41
7.41
7.40
7.40
7.29
7.28
7.28
7.27
7.26
3.55
3.53
3.51
3.31
3.30
3.28
1.87
1.85
1.83
1.81
1.80
1.77
1.75
1.74
1.72
1.70
O
N
1d
1H NMR (400 MHz, CDCl3)
1.90
2.73
2.00
2.09
1.96
1.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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136.64
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127.71
126.55
77.32
77.00
76.68
49.09
45.68
25.85
23.91
O
N
1d
13C NMR (101 MHz, CDCl3)
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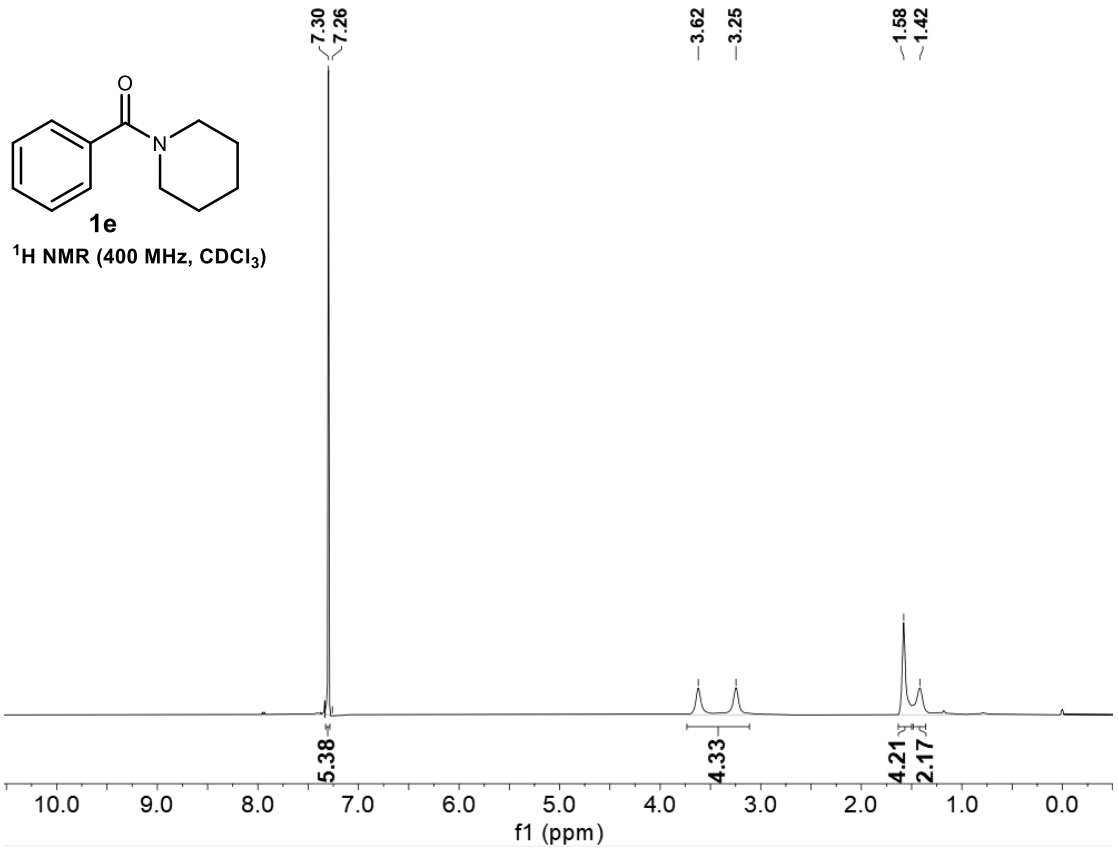
f1 (ppm)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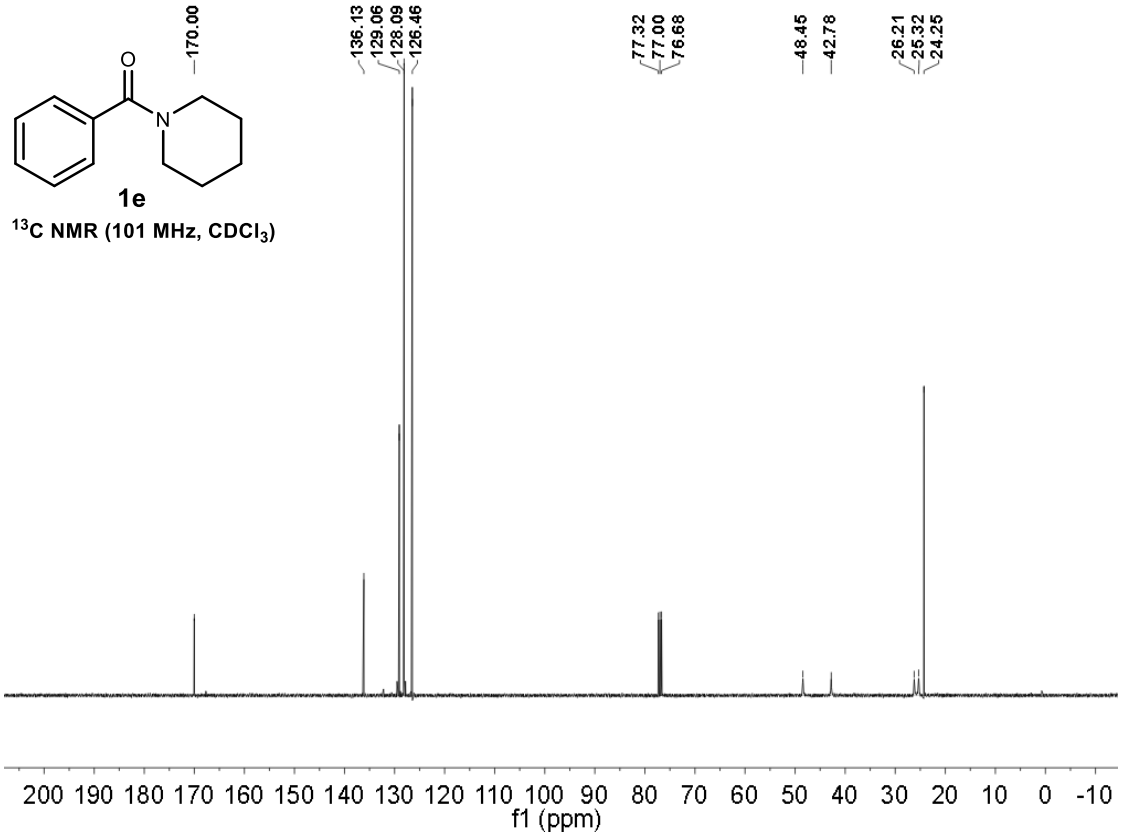
7.26
3.62
3.25
1.58
1.42
O
N
1e
^{1}H NMR (400 MHz, CDCl$_3$)
5.38
4.33
4.21
2.17
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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77.32
77.00
76.68
48.45
42.78
26.21
25.32
24.25
O
N
1e
^{13}C NMR (101 MHz, CDCl$_3$)
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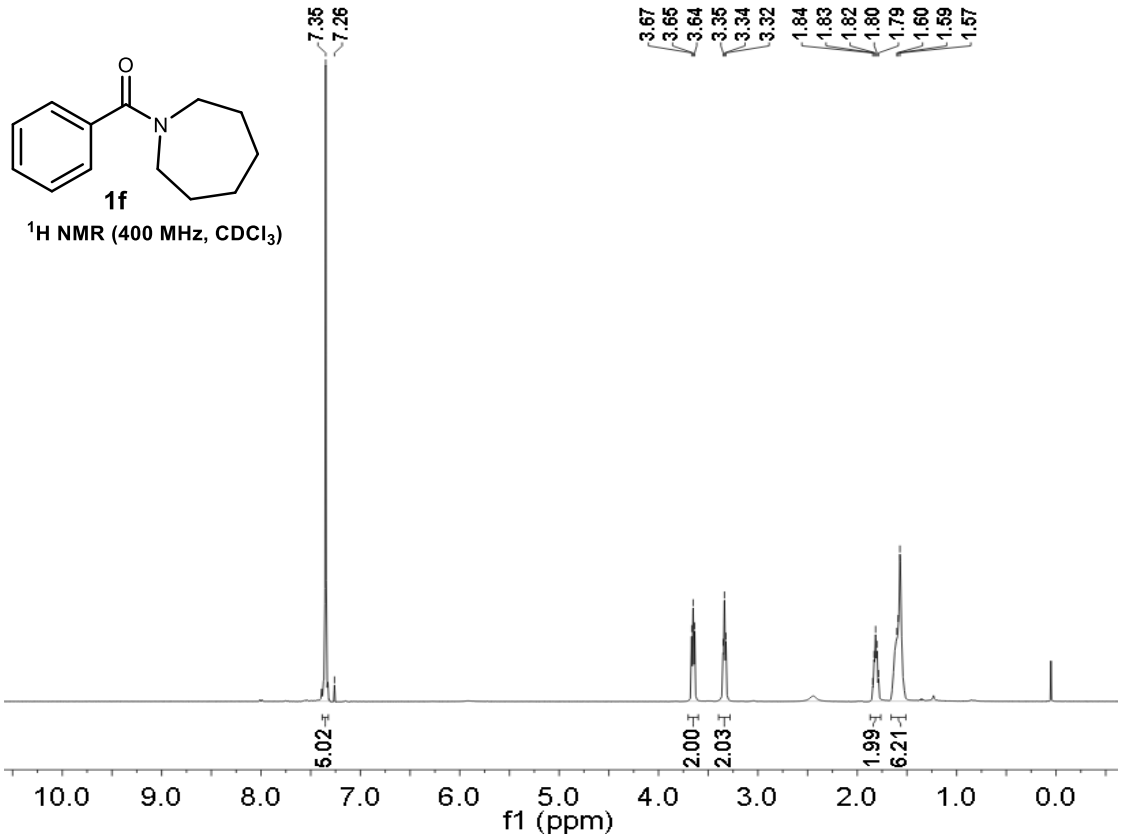
f1 (ppm)



1f

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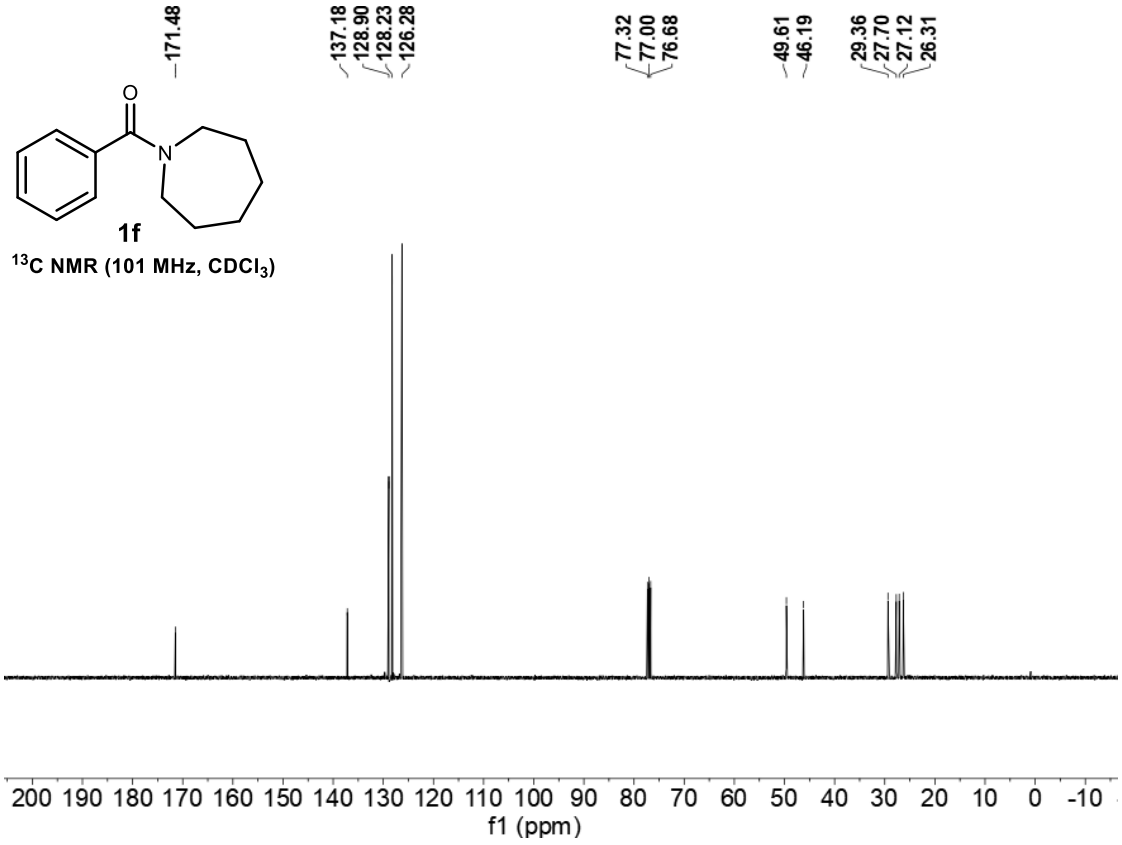

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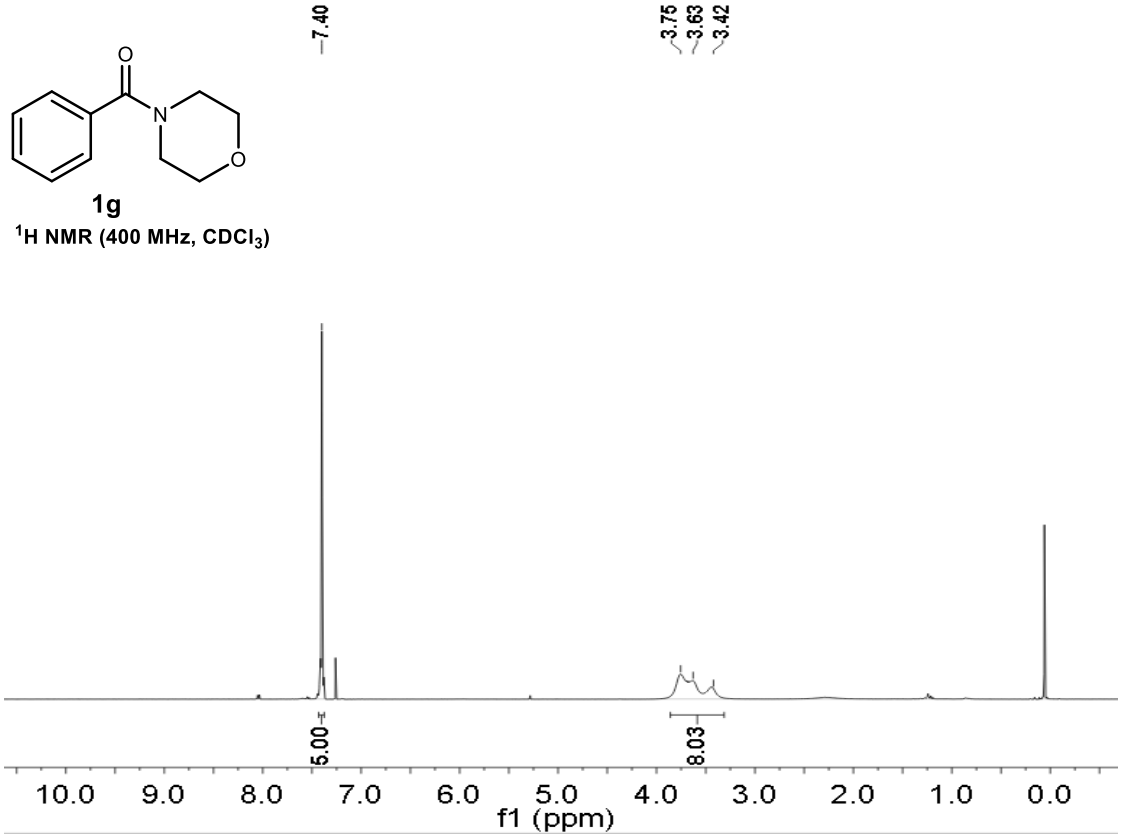

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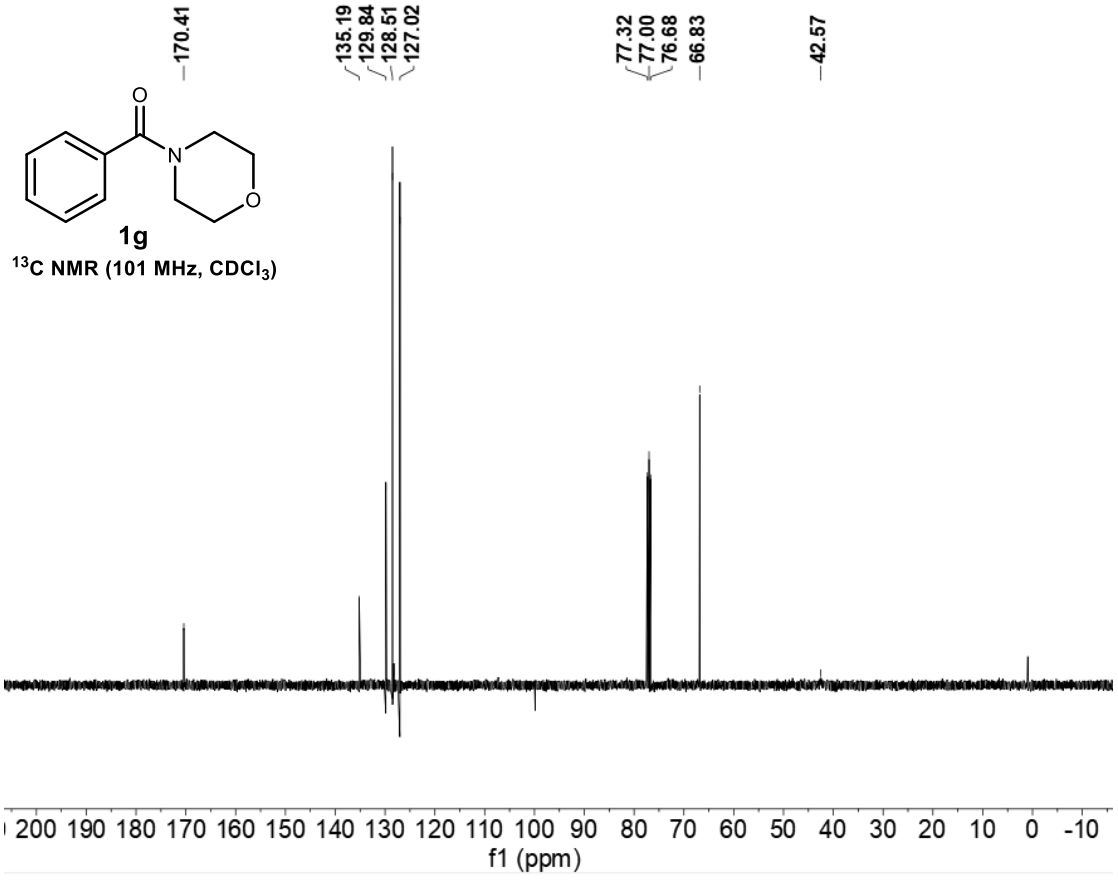

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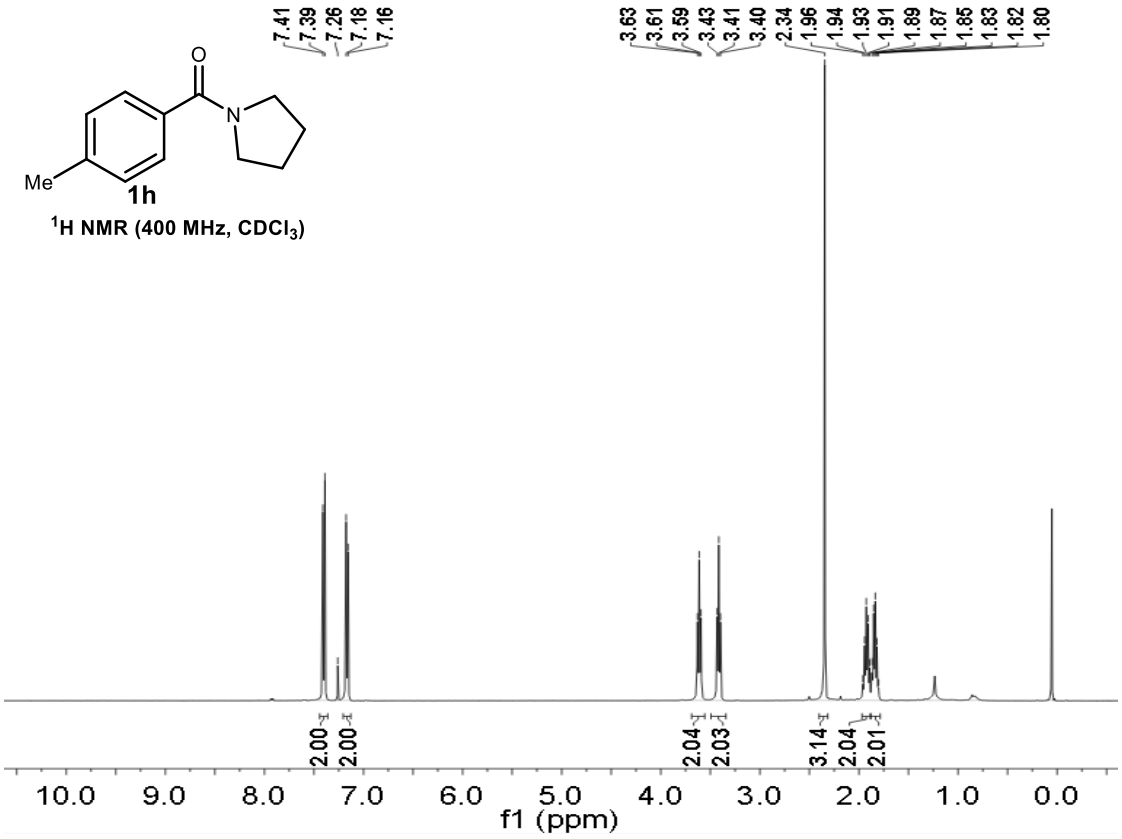
^{13}C NMR (101 MHz, $CDCl_3$)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7.16
3.63
3.61
3.59
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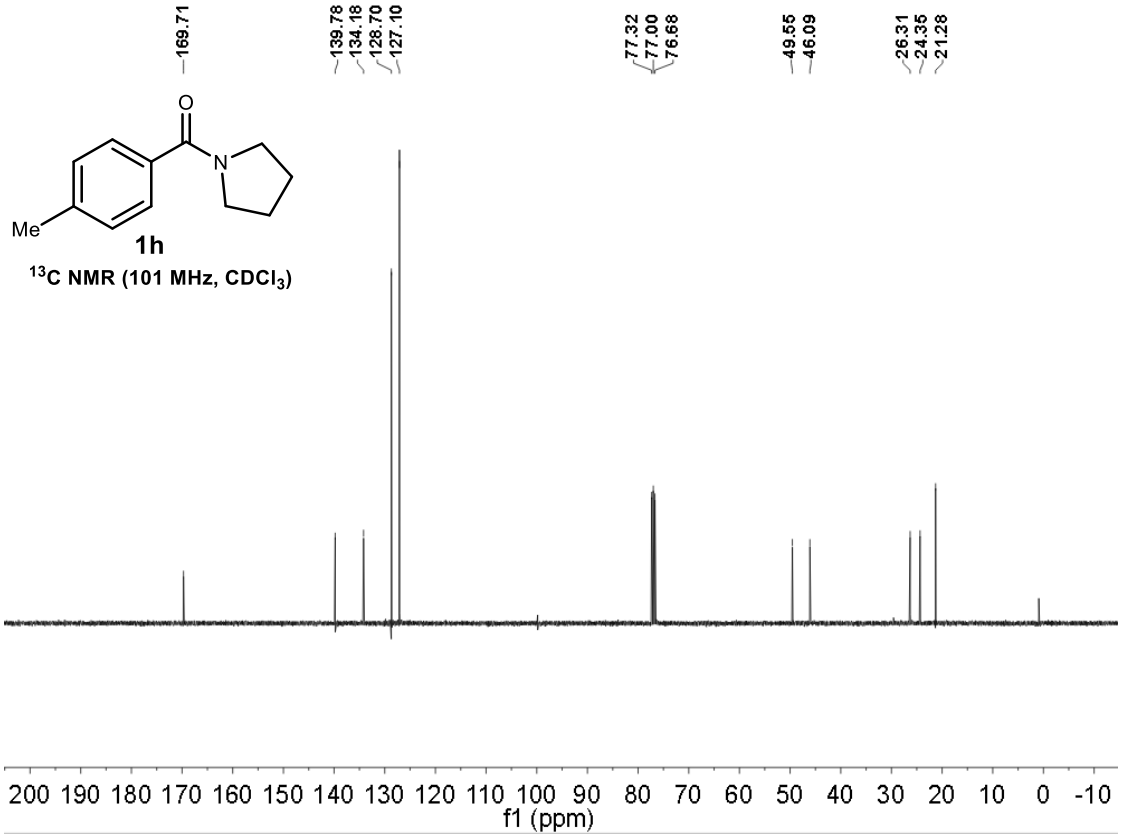
3.41
3.40
2.34
1.96
1.94
1.93
1.91
1.89
1.87
1.85
1.83
1.82
1.80
O
N
Me
1h
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.00
2.04
2.03
3.14
2.04
2.01
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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127.10
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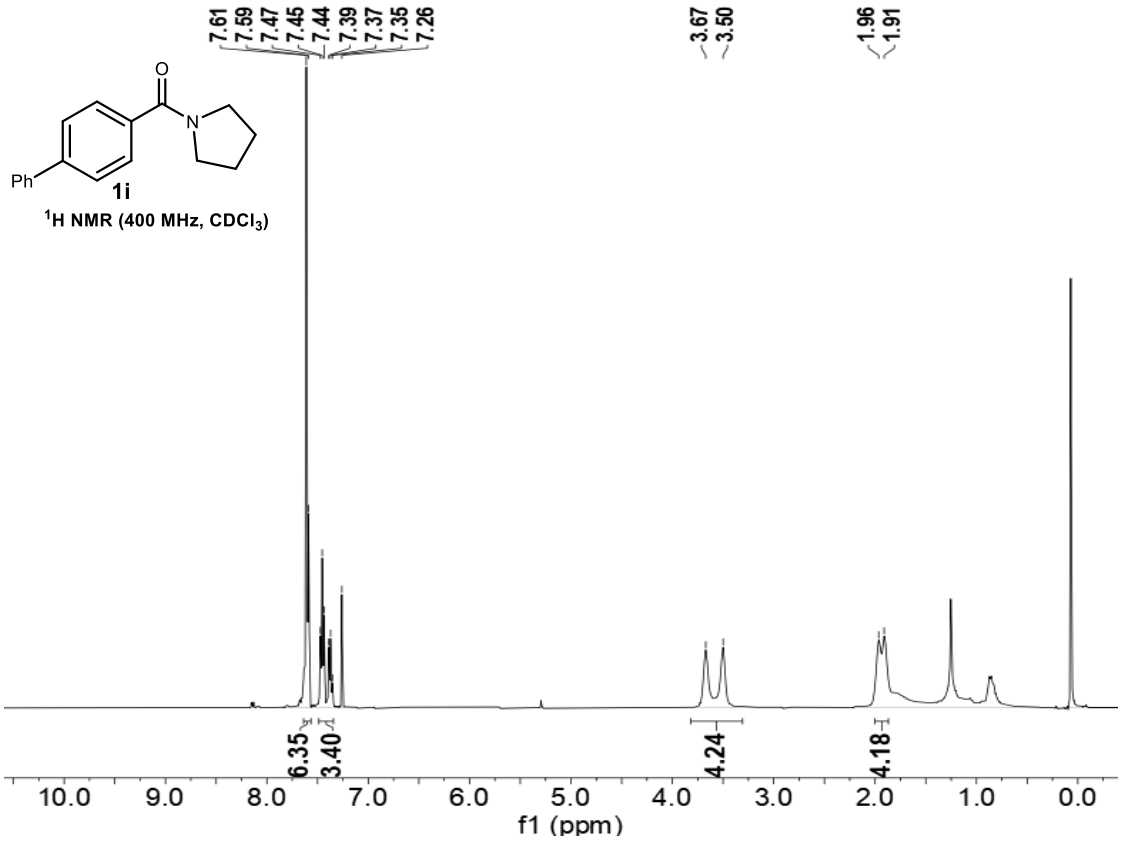
77.00
76.68
49.55
46.09
26.31
24.35
21.28
O
N
Me
1h
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.39
7.37
7.35
7.26
3.67
3.50
1.96
1.91
Ph
O
N
1i
^{1}H NMR (400 MHz, CDCl$_3$)
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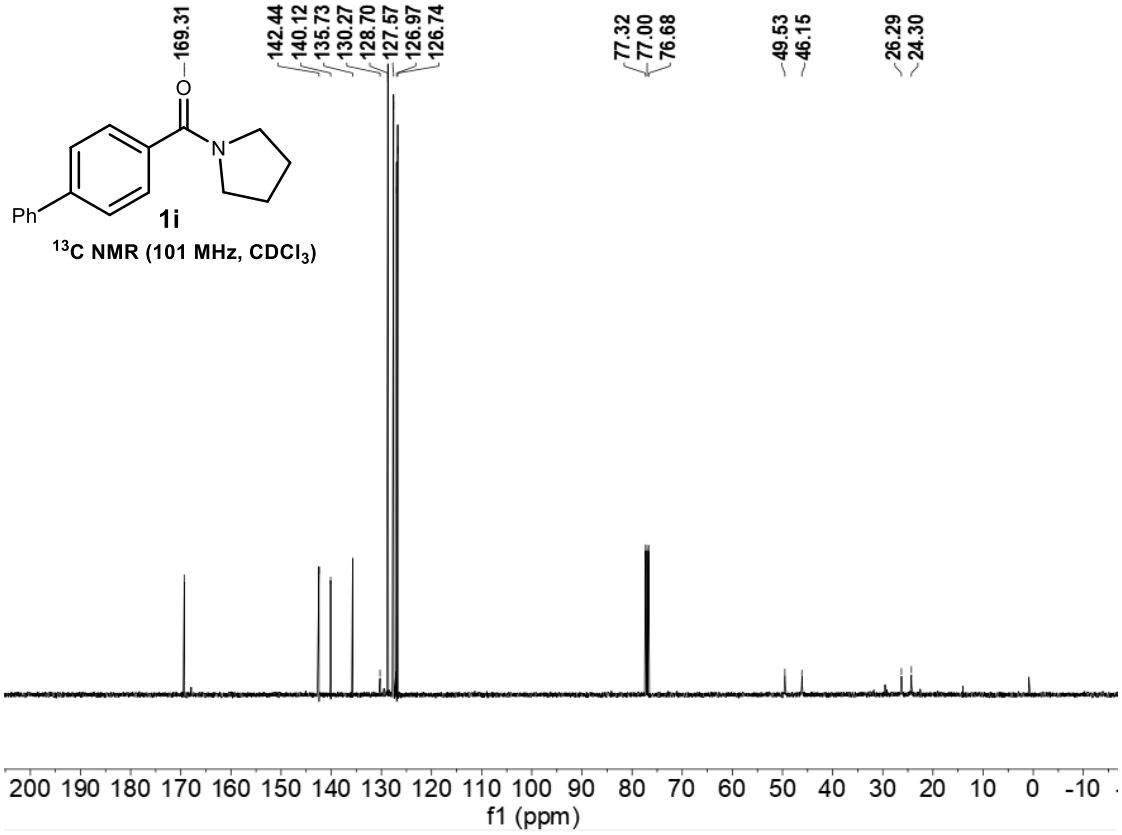
3.40
4.24
4.18
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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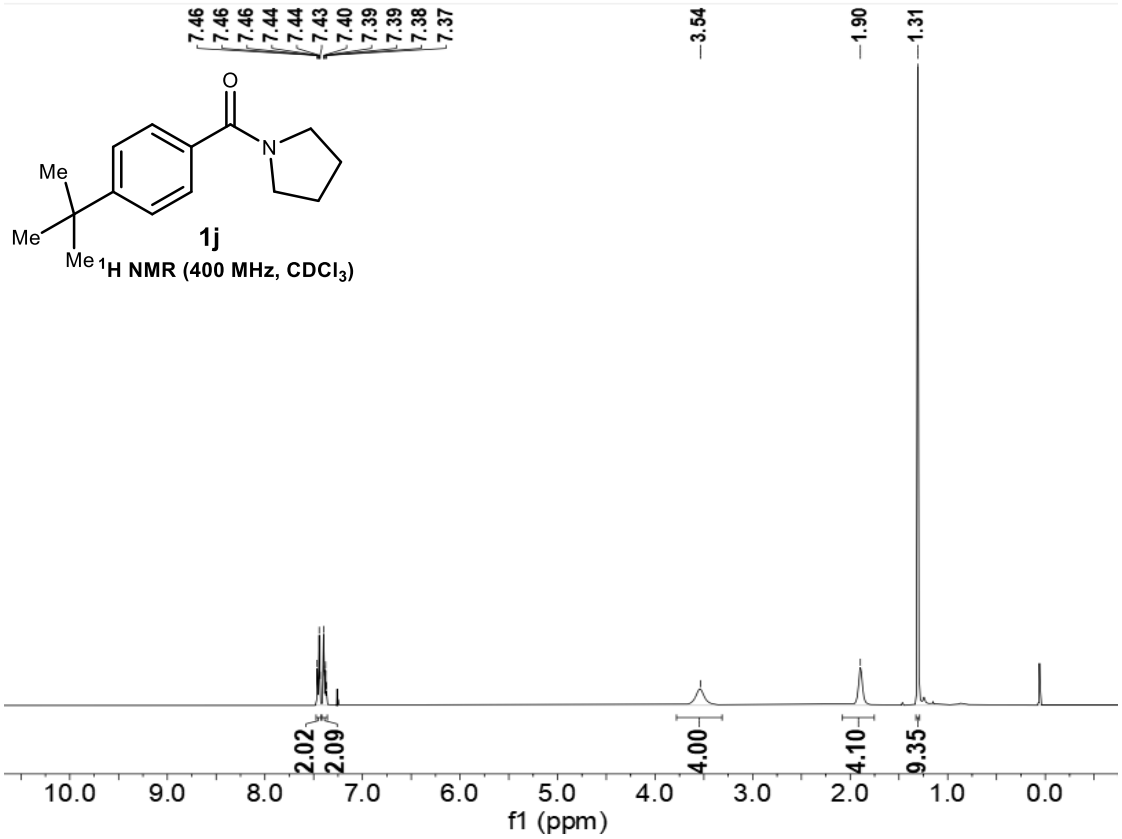
77.32
77.00
76.68
49.53
46.15
26.29
24.30
Ph
O
N
1i
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.46
7.46
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7.39
7.38
7.37
3.54
1.90
1.31
O
N
Me
Me
Me
1j
^{1}H NMR (400 MHz, CDCl$_3$)
2.02
2.09
4.00
4.10
9.35
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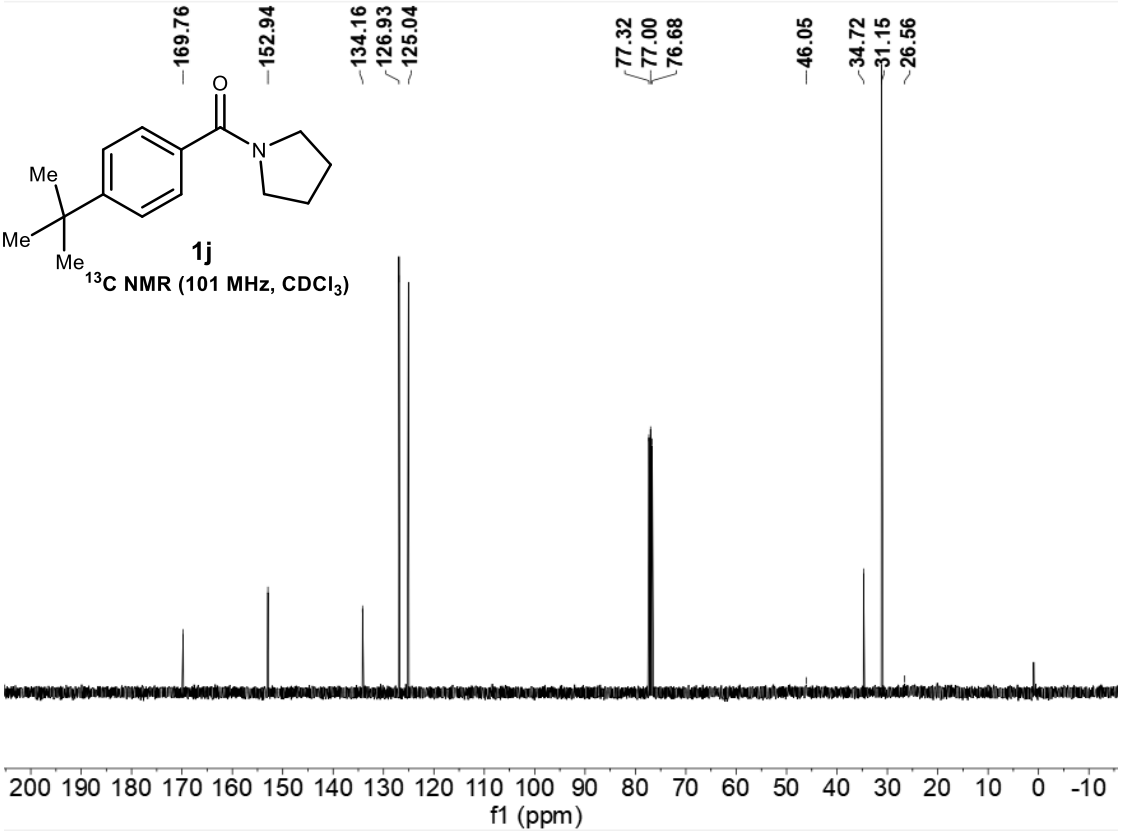
f1 (ppm)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76.68
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34.72
31.15
26.56
O
N
Me
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Me
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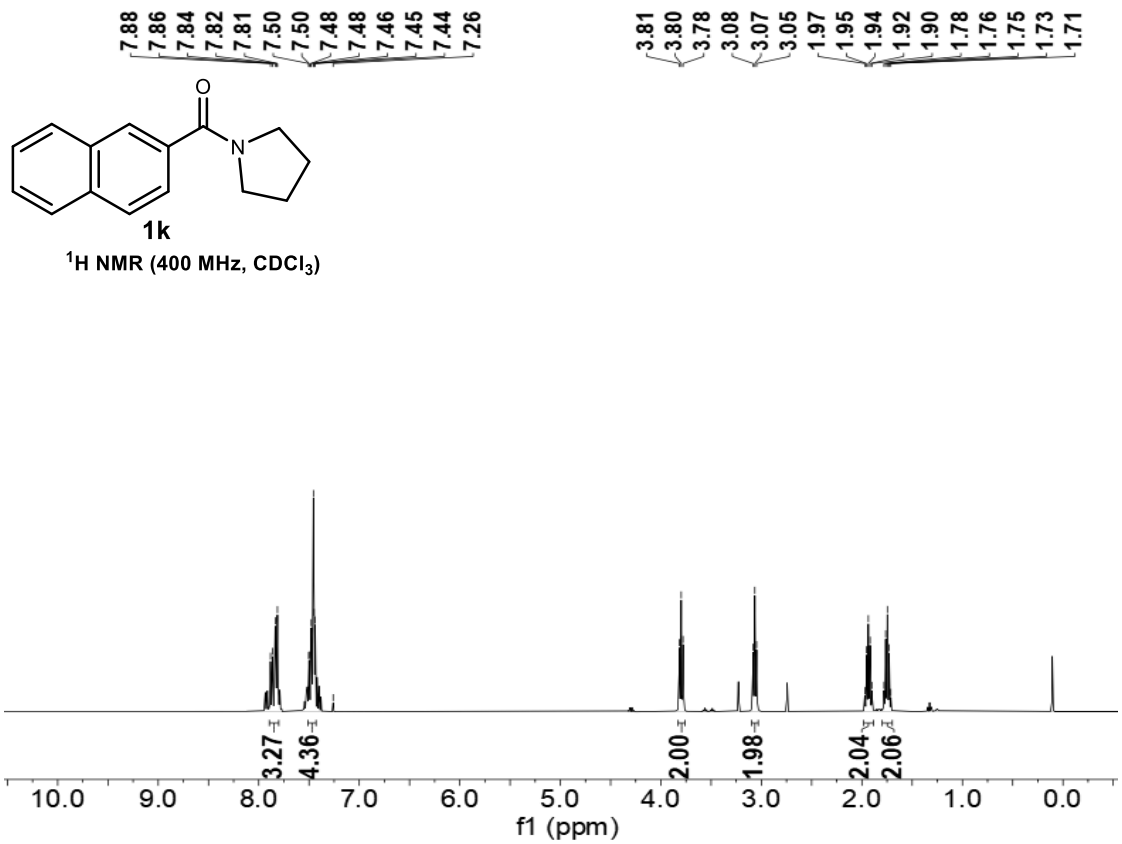
f1 (ppm)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7.48
7.48
7.46
7.45
7.44
7.26
3.81
3.80
3.78
3.08
3.07
3.05
1.97
1.95
1.94
1.92
1.90
1.78
1.76
1.75
1.73
1.71
O
N
1k
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3.27
4.36
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2.06
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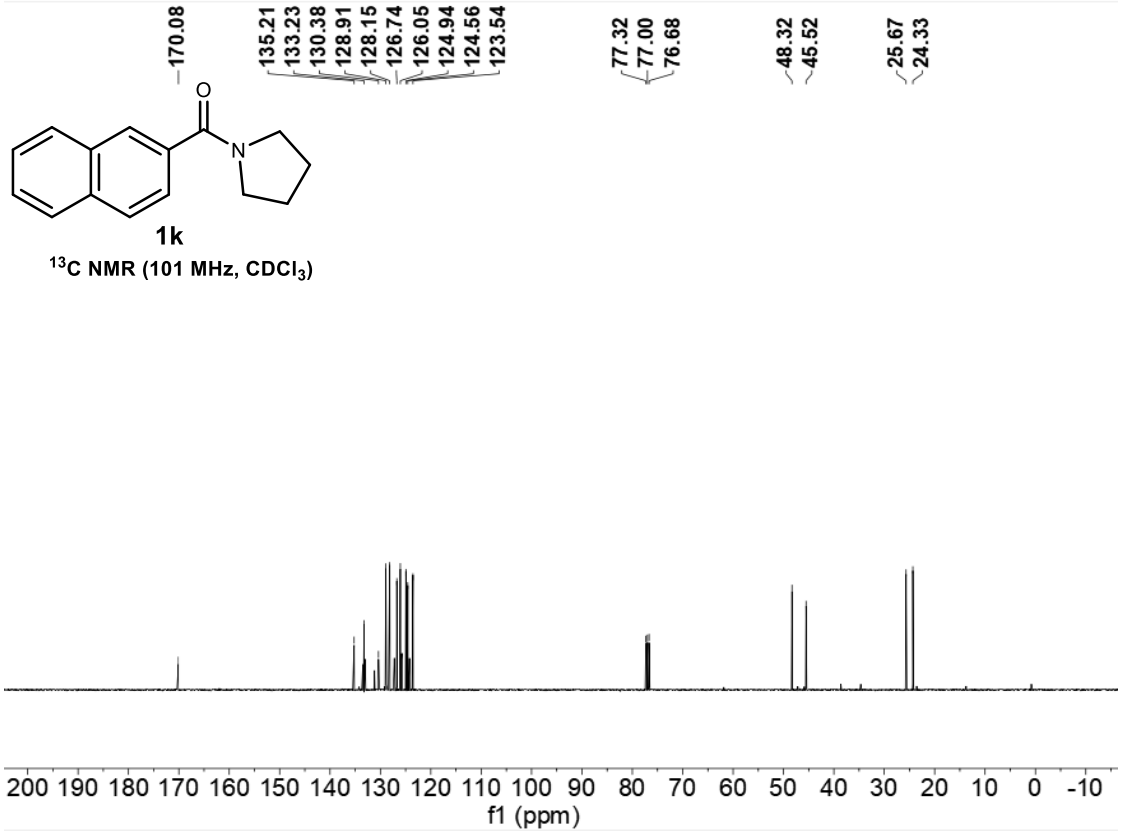
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77.00
76.68
48.32
45.52
25.67
24.33
O
N
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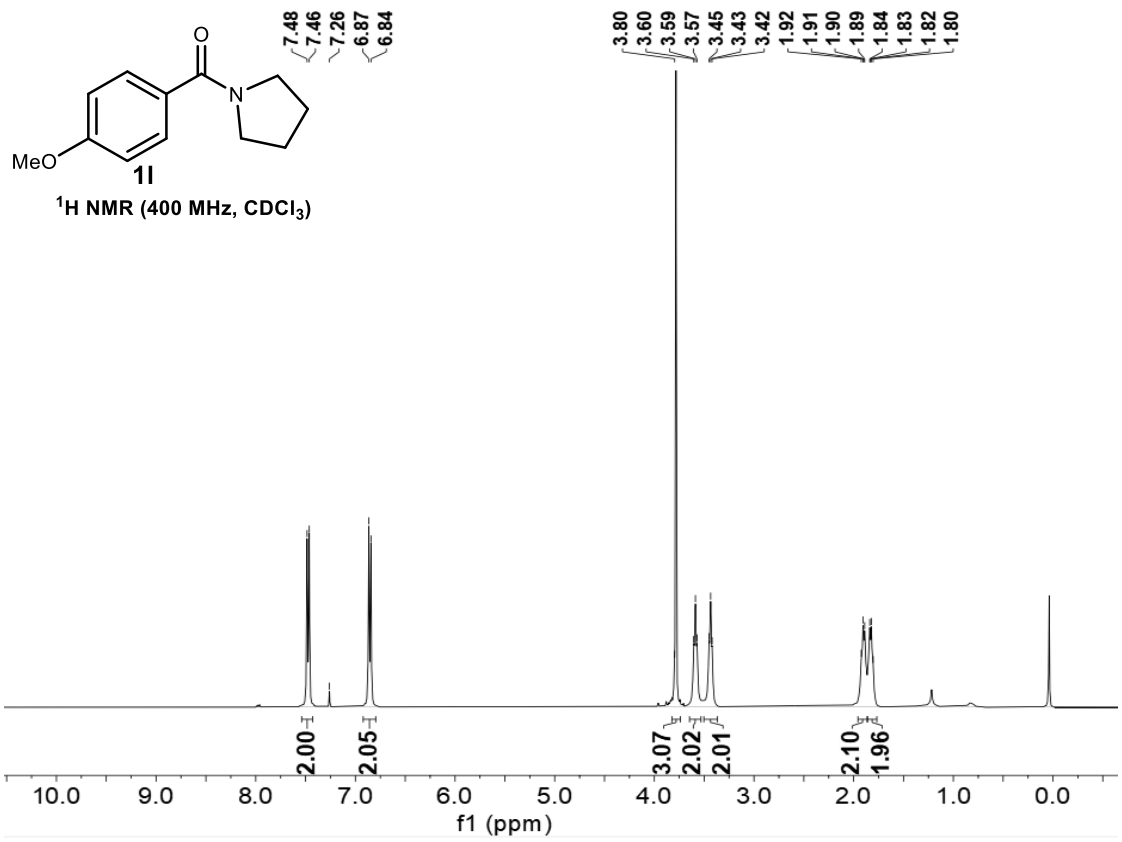
f1 (ppm)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3.45
3.43
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1.92
1.91
1.90
1.89
1.84
1.83
1.82
1.80
O
N
MeO
1l
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2.00
2.05
3.07
2.02
2.01
2.10
1.96
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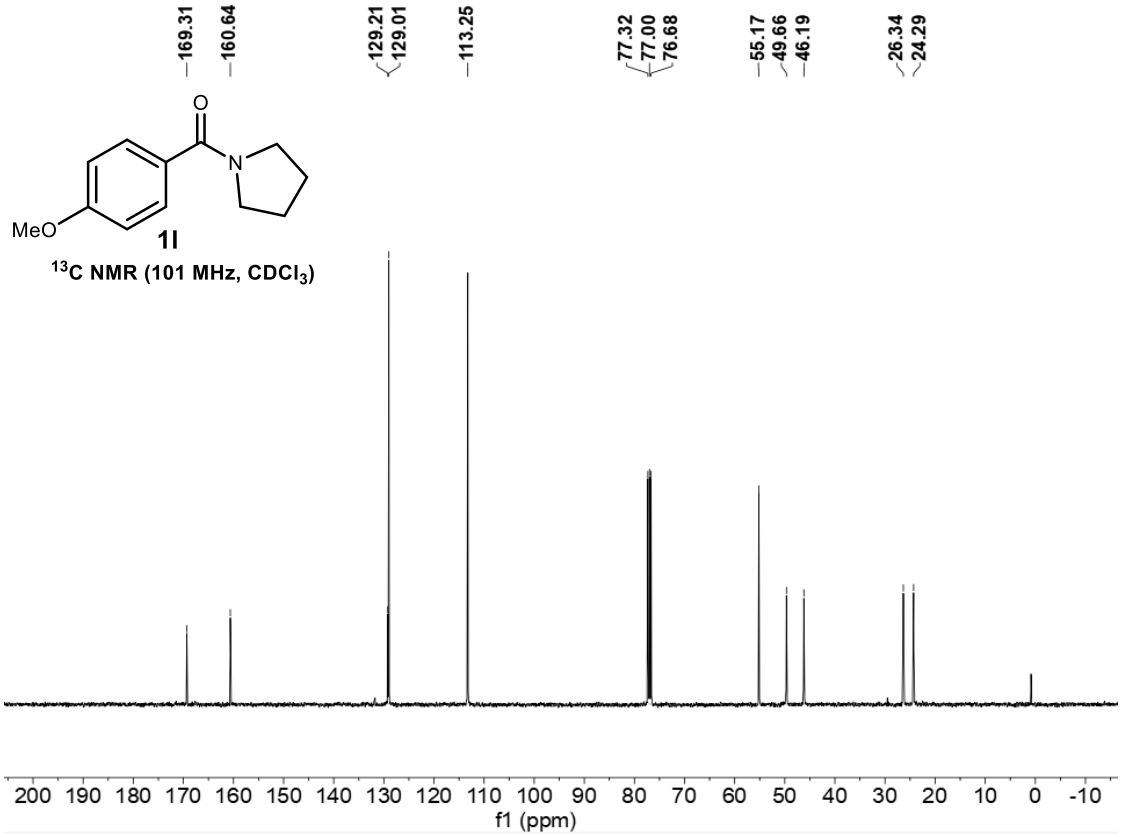
f1 (ppm)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24.29
O
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MeO
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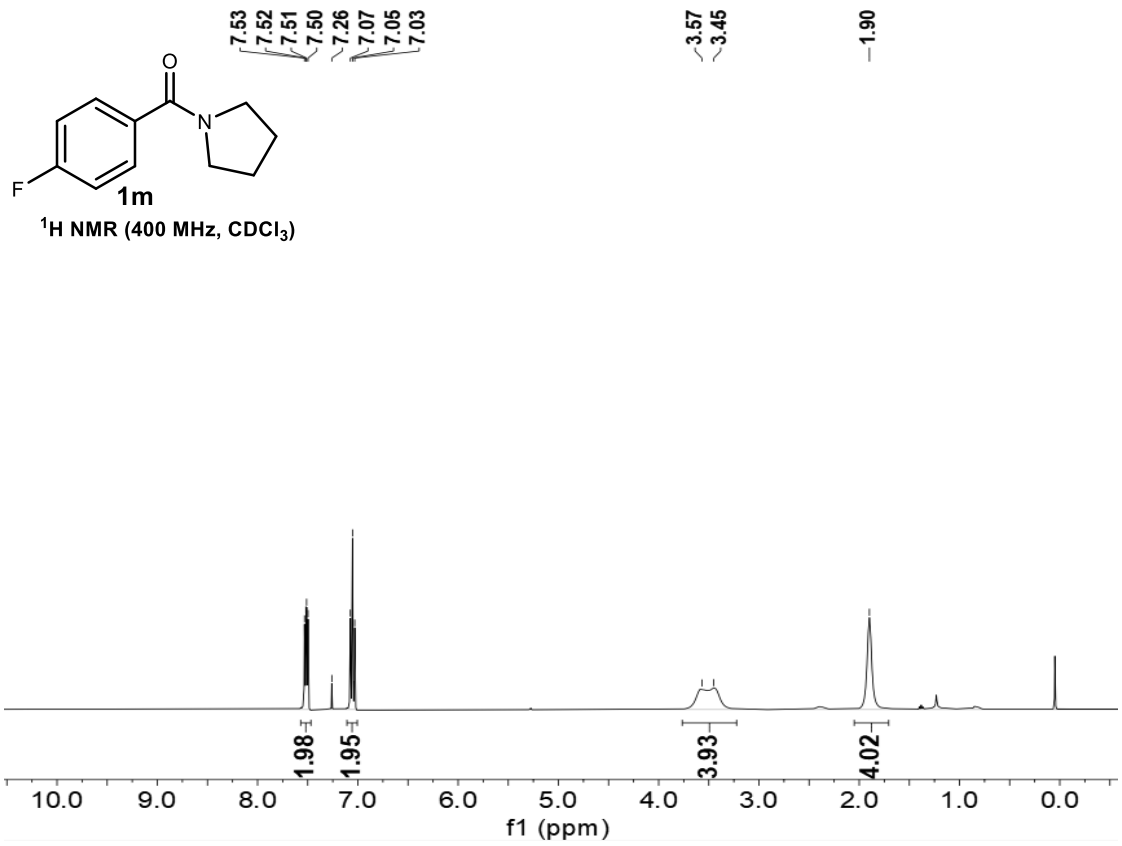
f1 (ppm)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7.07
7.05
7.03
3.57
3.45
1.90
O
N
F
1m
^{1}H NMR (400 MHz, CDCl$_3$)
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4.02
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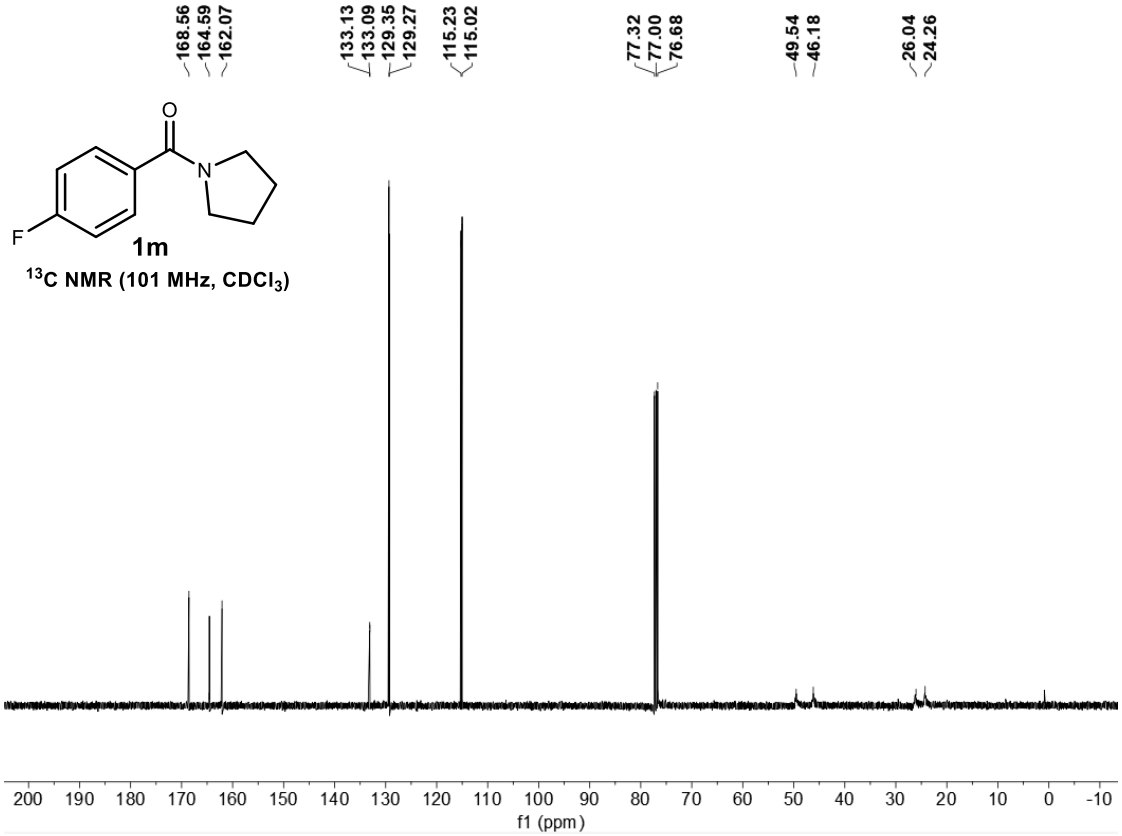
f1 (ppm)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49.54
46.18
26.04
24.26
O
N
F
1m
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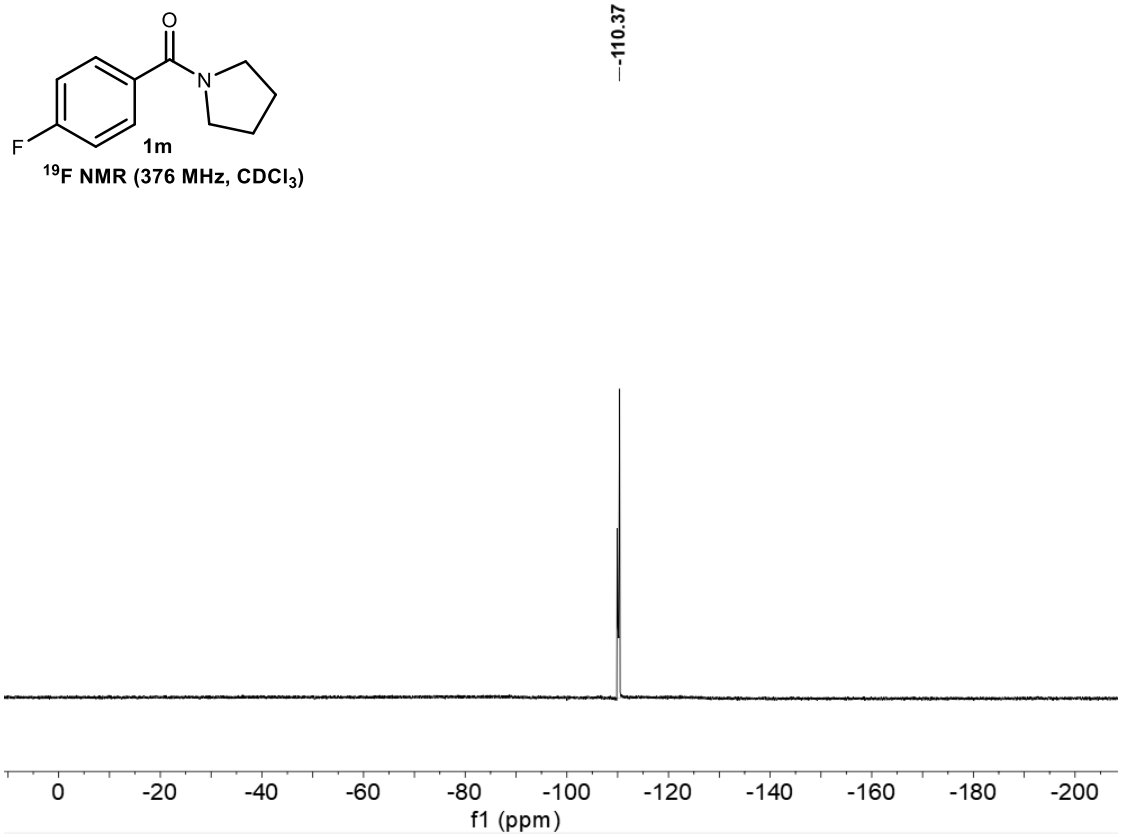
f1 (ppm)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F
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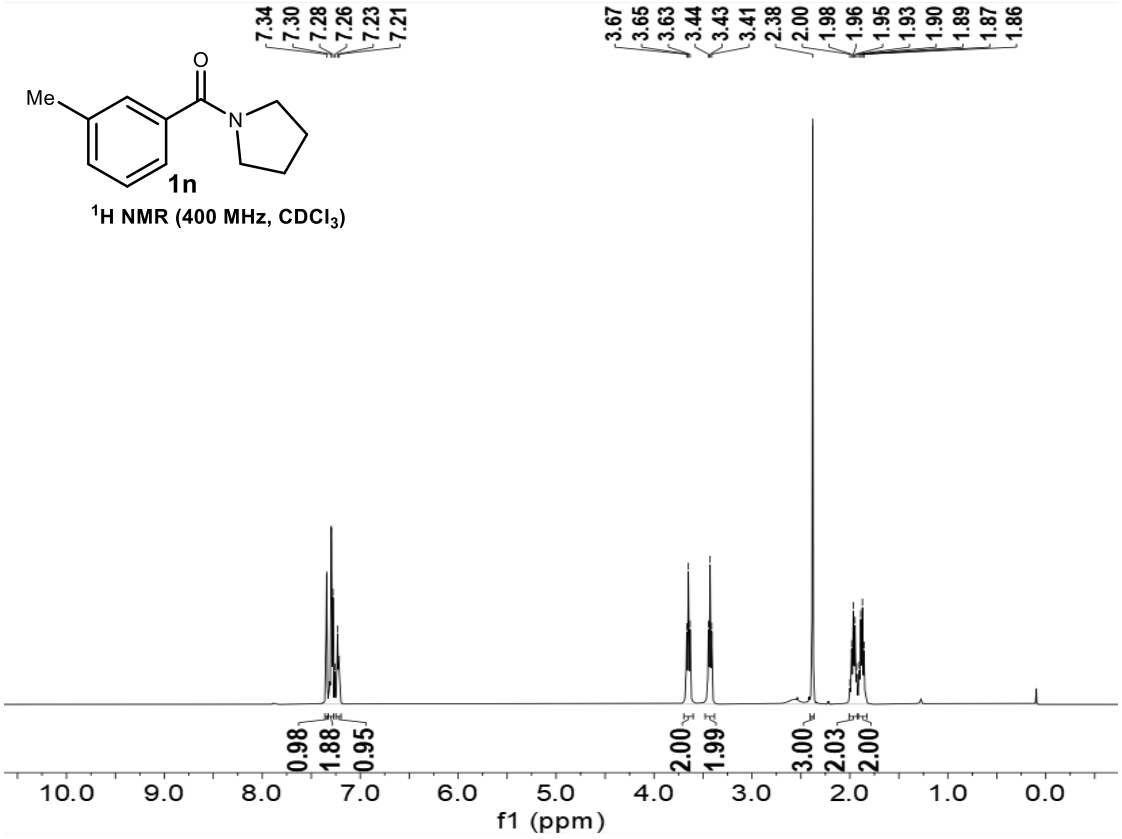
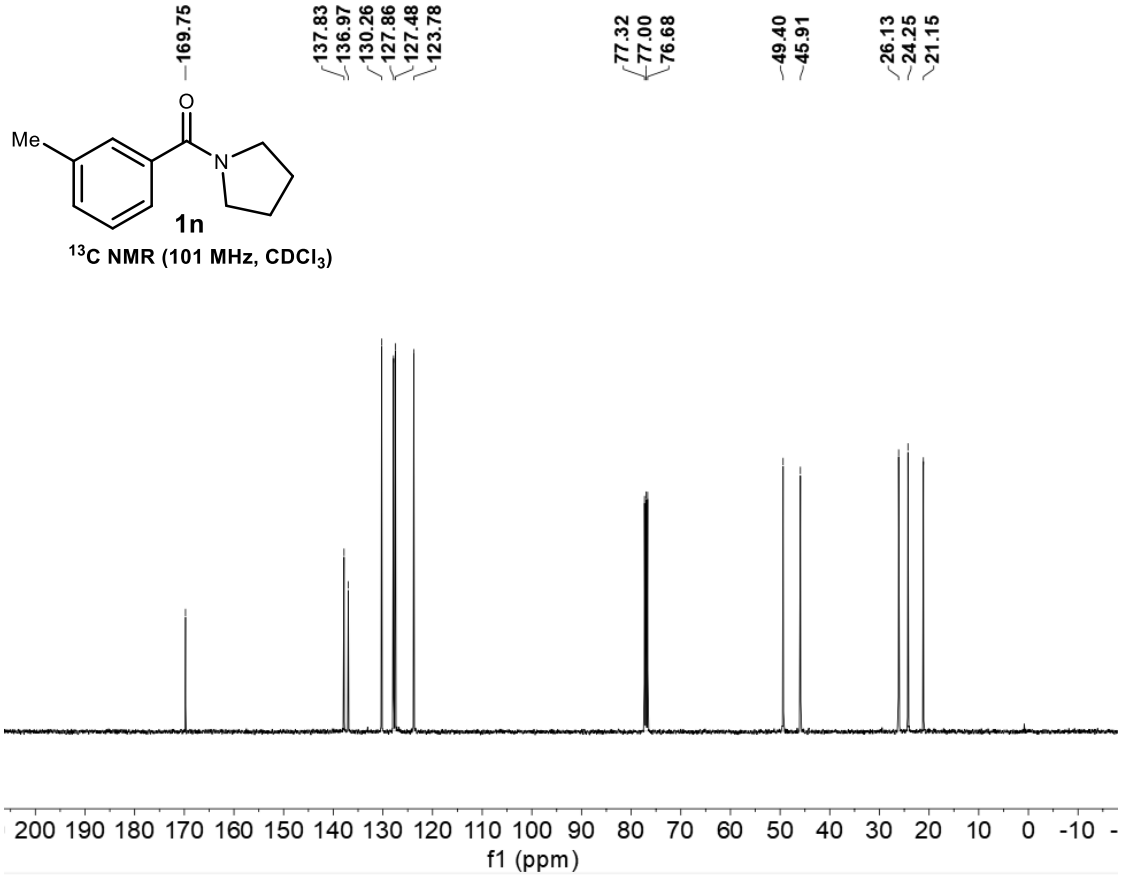
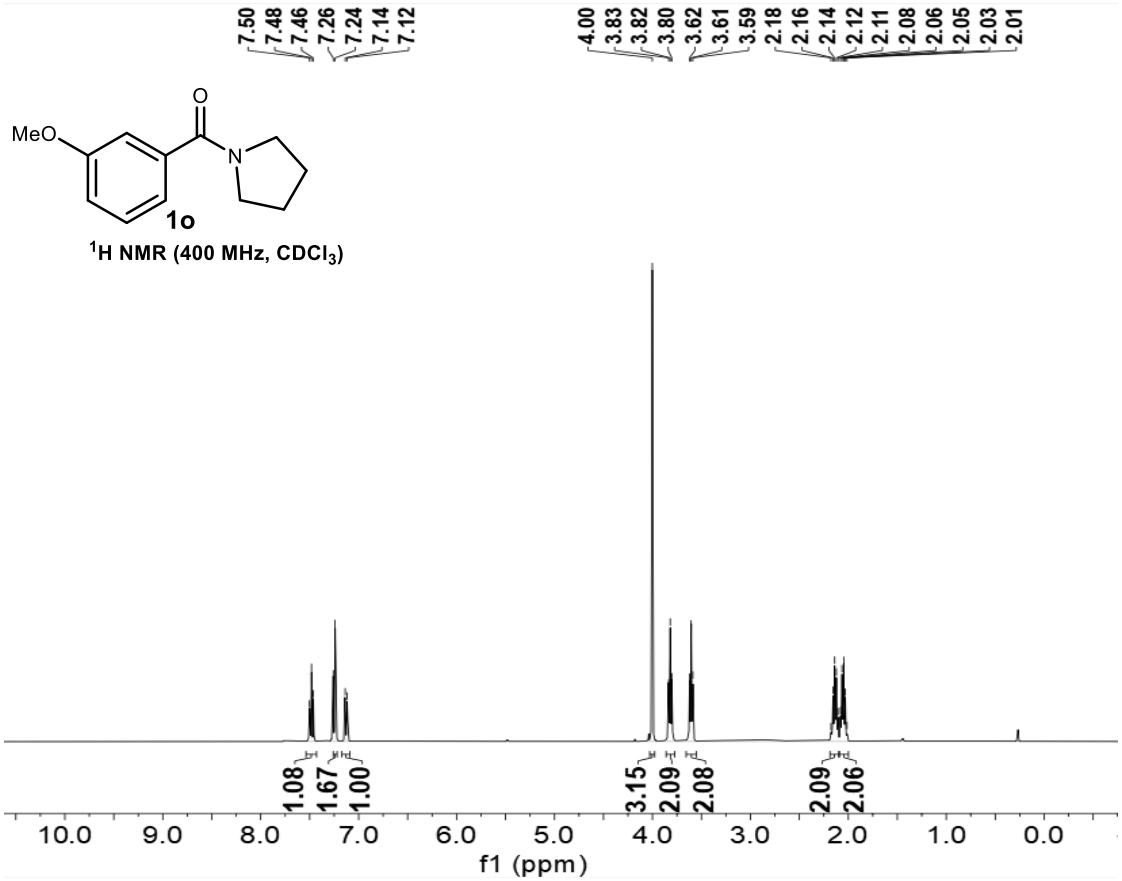
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

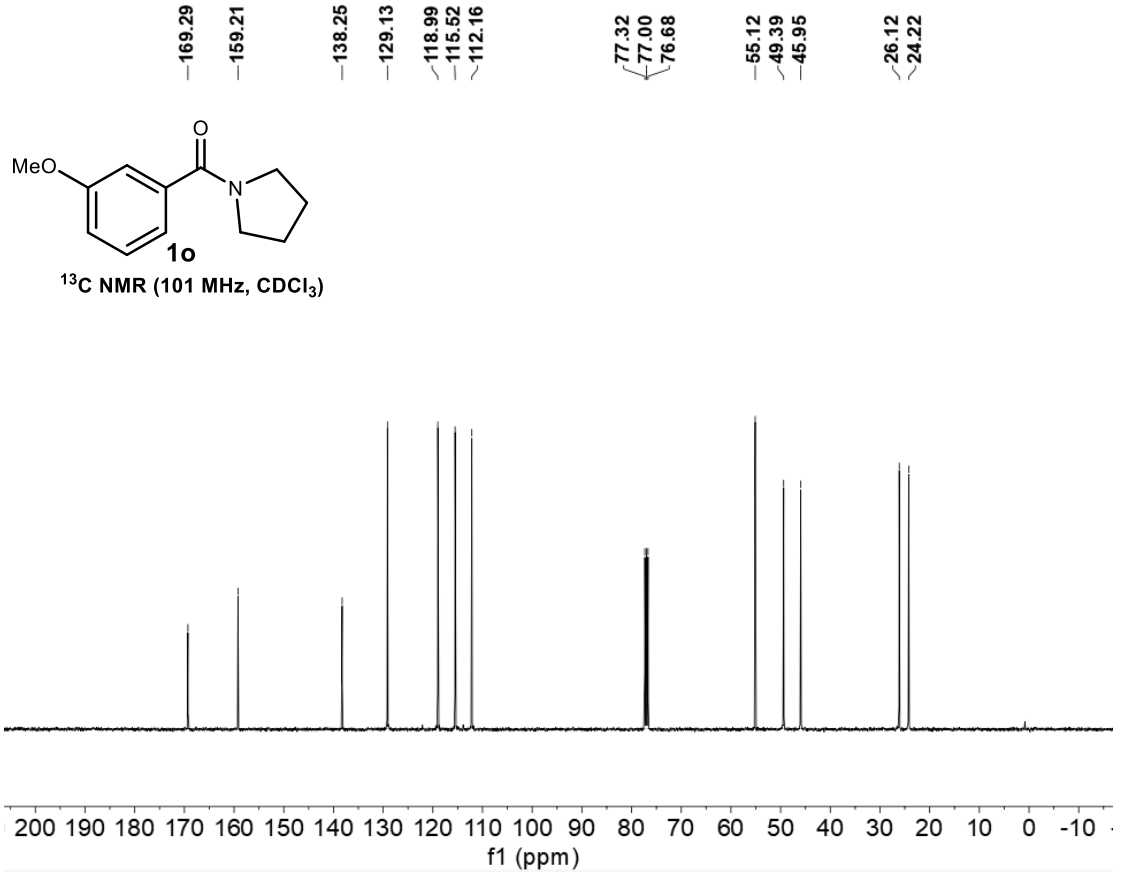


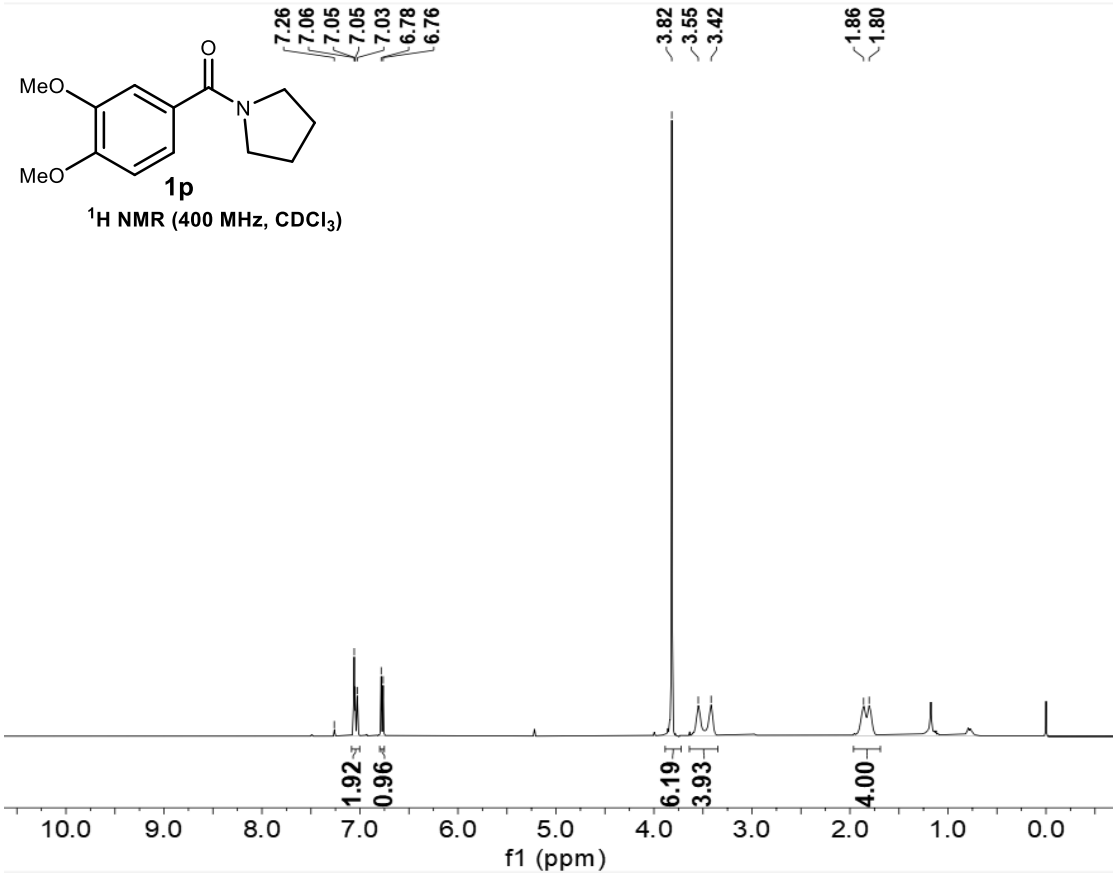
^{1}H NMR (400 MHz, $CDCl_3$)

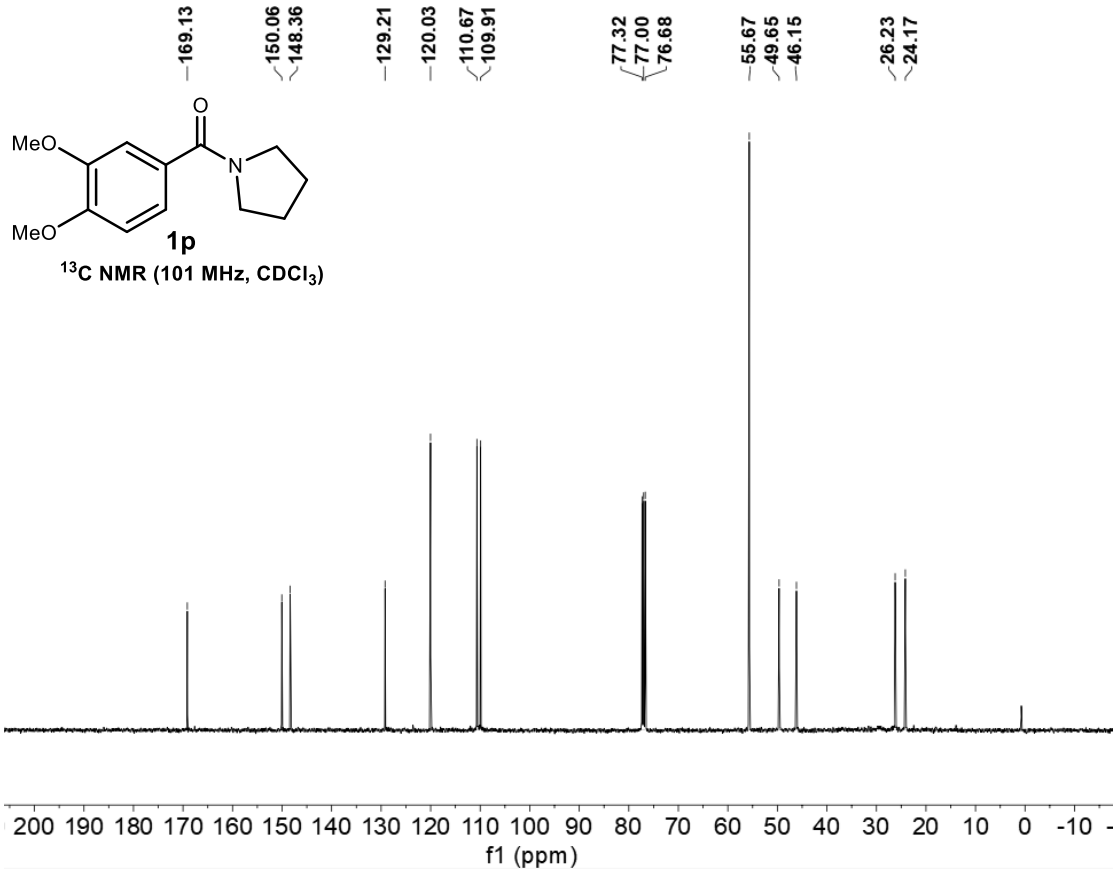


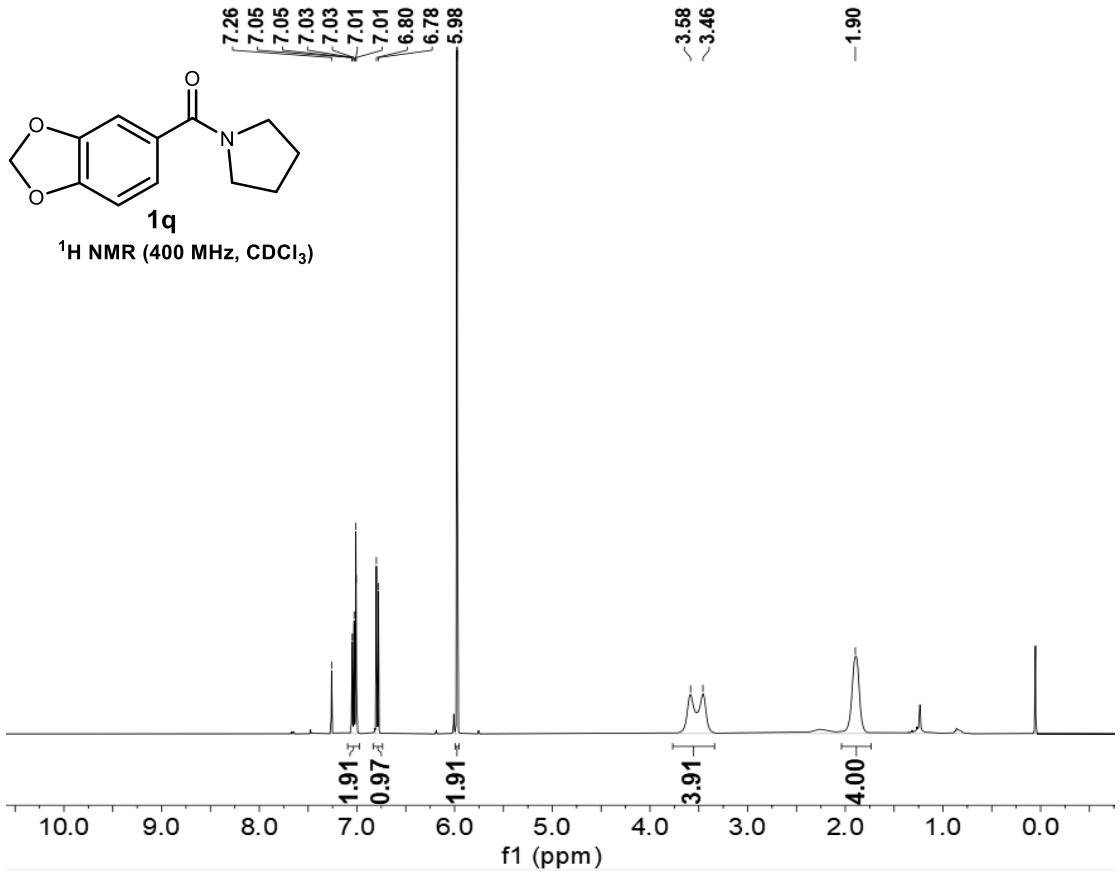
^{13}C NMR (101 MHz, $CDCl_3$)

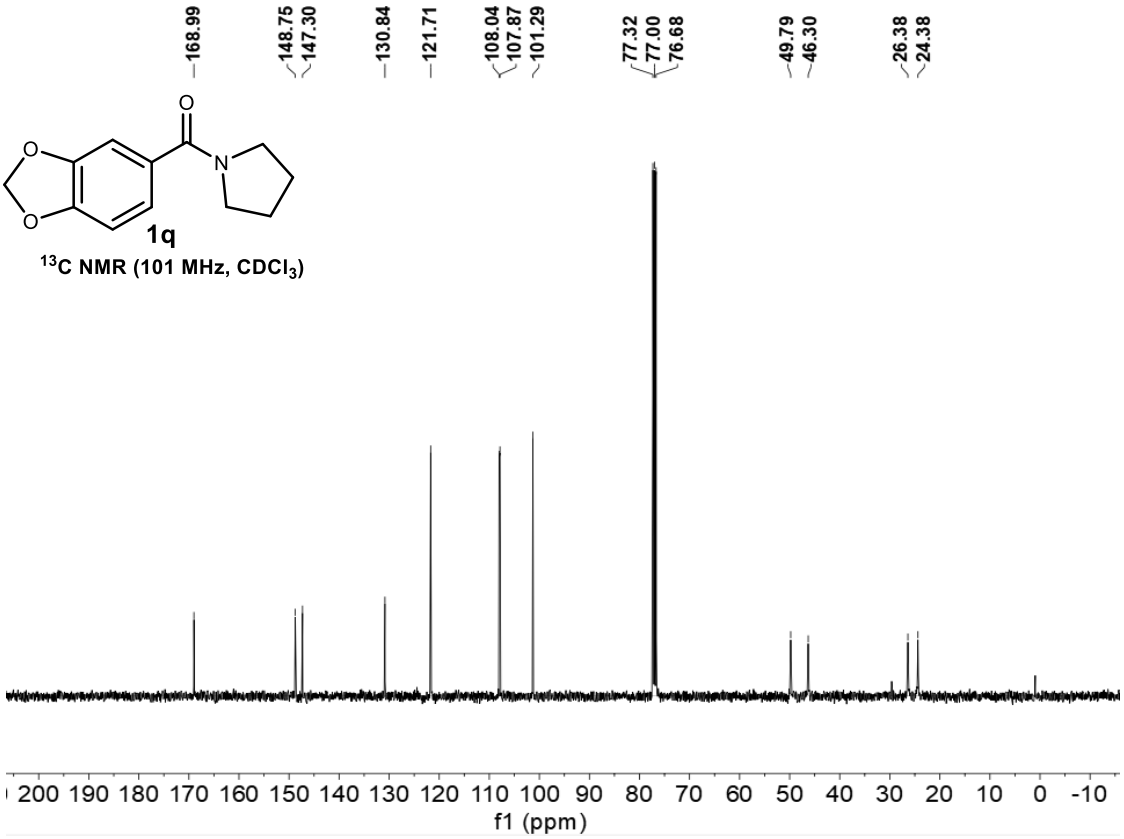

7.50
7.48
7.46
7.26
7.24
7.14
7.12
4.00
3.83
3.82
3.80
3.62
3.61
3.59
2.18
2.16
2.14
2.12
2.11
2.08
2.06
2.05
2.03
2.01
MeO
O
N
1o
1H NMR (400 MHz, CDCl3)
1.08
1.67
1.00
3.15
2.09
2.08
2.09
2.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

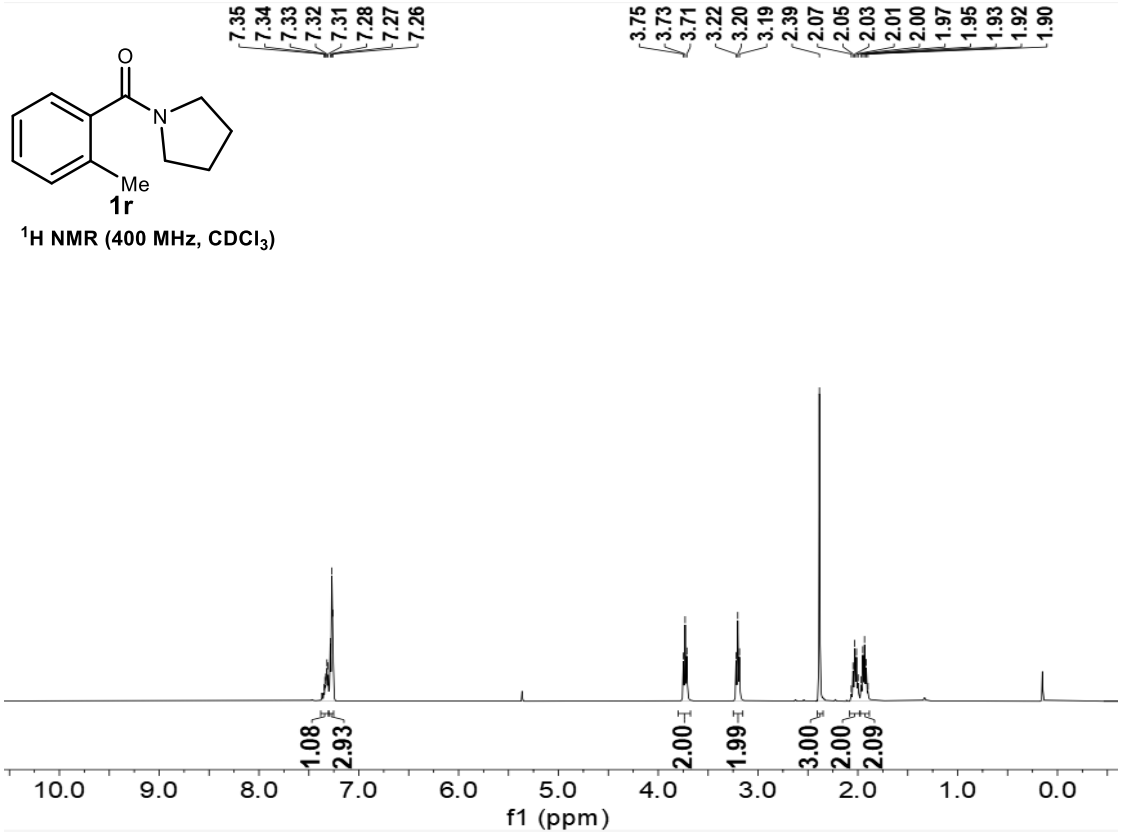

169.29
159.21
138.25
129.13
118.99
115.52
112.16
77.32
77.00
76.68
55.12
49.39
45.95
26.12
24.22
MeO
O
N
1o
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

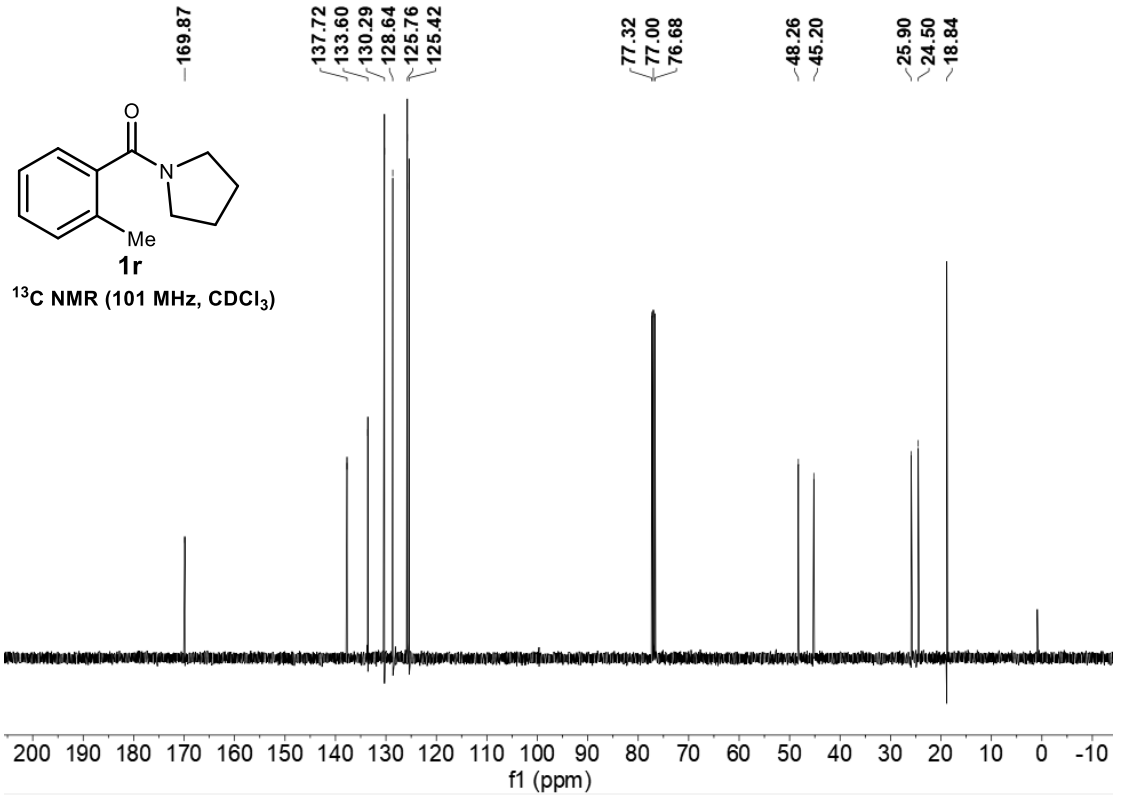

7.26
7.06
7.05
7.05
7.03
6.78
6.76
3.82
3.55
3.42
1.86
1.80
MeO
MeO
O
N
1p
^{1}H NMR (400 MHz, CDCl$_3$)
1.92
0.96
6.19
3.93
4.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

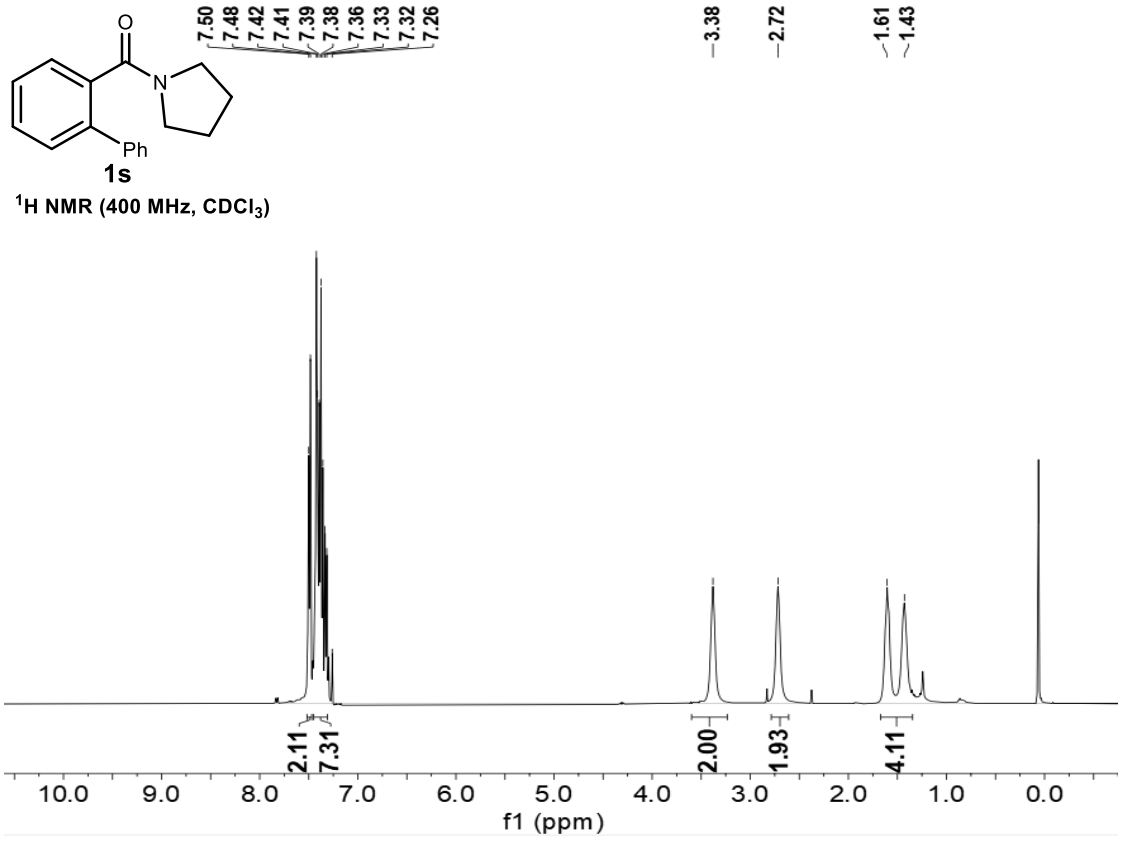

169.13
150.06
148.36
129.21
120.03
110.67
109.91
77.32
77.00
76.68
55.67
49.65
46.15
26.23
24.17
MeO
MeO
O
N
1p
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

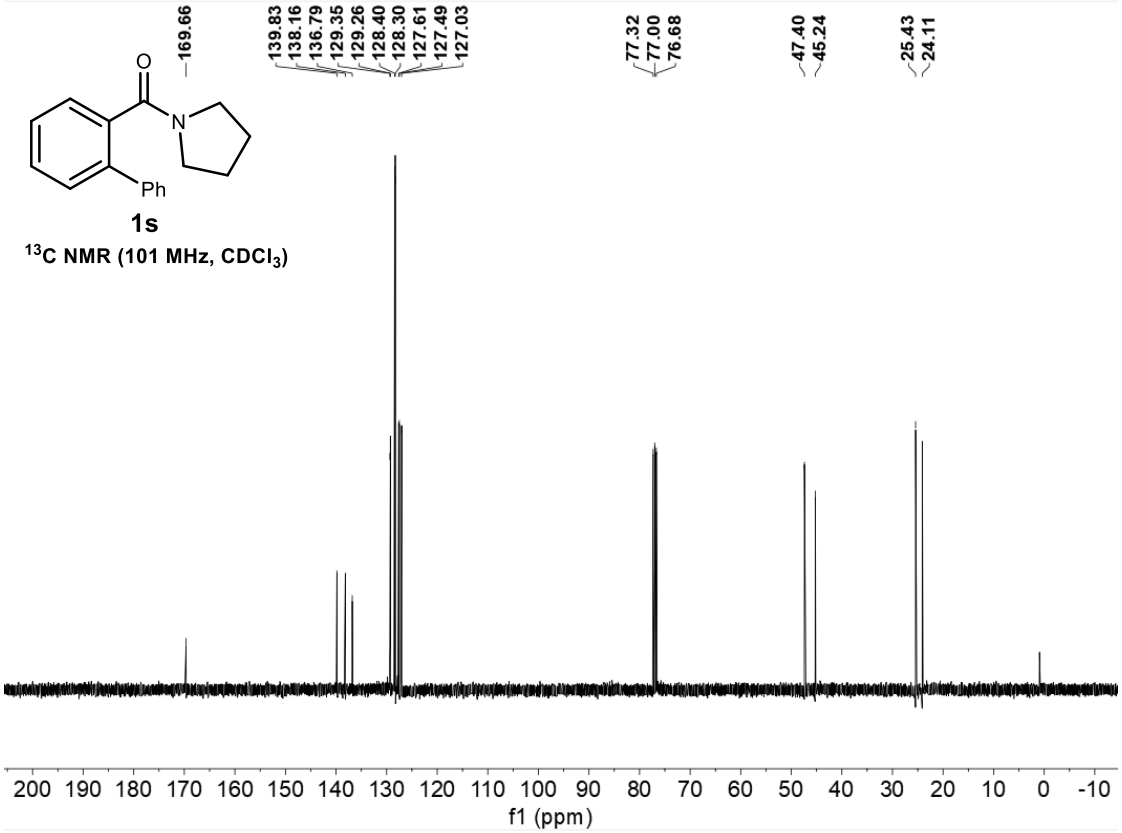

7.26
7.05
7.05
7.03
7.03
7.01
7.01
6.80
6.78
5.98
3.58
3.46
1.90
1q
1H NMR (400 MHz, CDCl3)
1.91
0.97
1.91
3.91
4.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

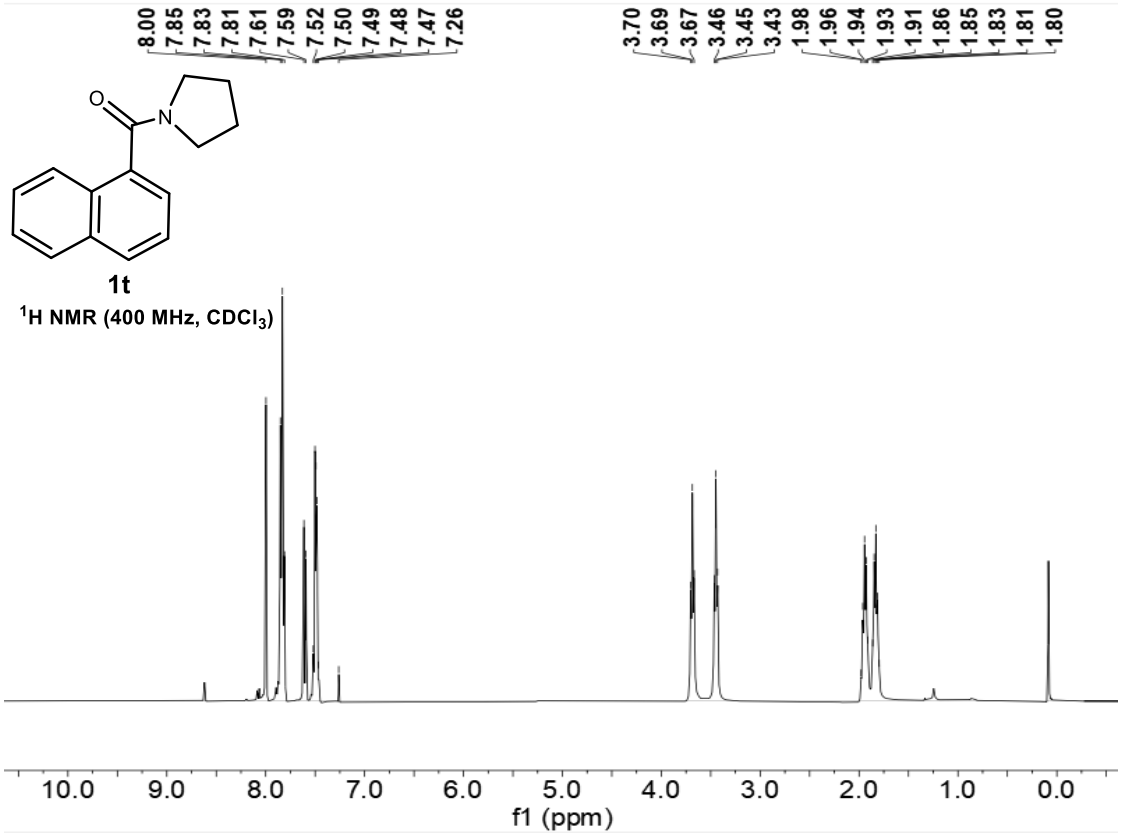

168.99
148.75
147.30
130.84
121.71
108.04
107.87
101.29
77.32
77.00
76.68
49.79
46.30
26.38
24.38
1q
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

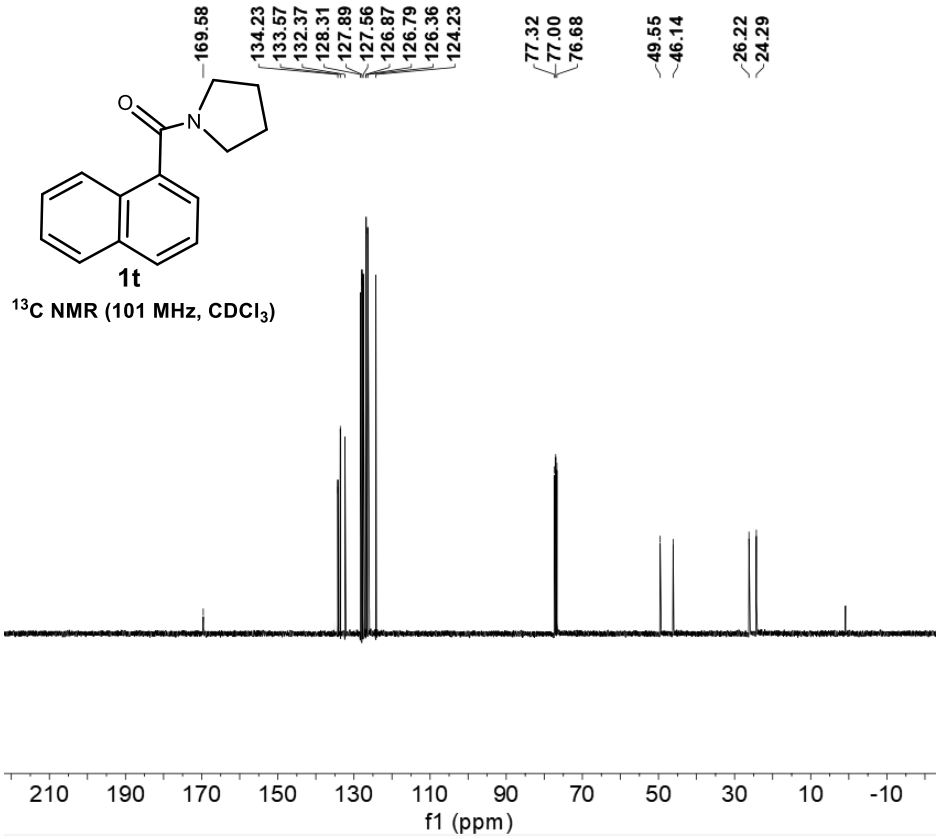

7.35
7.34
7.33
7.32
7.31
7.28
7.27
7.26
3.75
3.73
3.71
3.22
3.20
3.19
2.39
2.07
2.05
2.03
2.01
2.00
1.97
1.95
1.93
1.92
1.90
O
N
Me
1r
1H NMR (400 MHz, CDCl3)
1.08
2.93
2.00
1.99
3.00
2.00
2.09
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

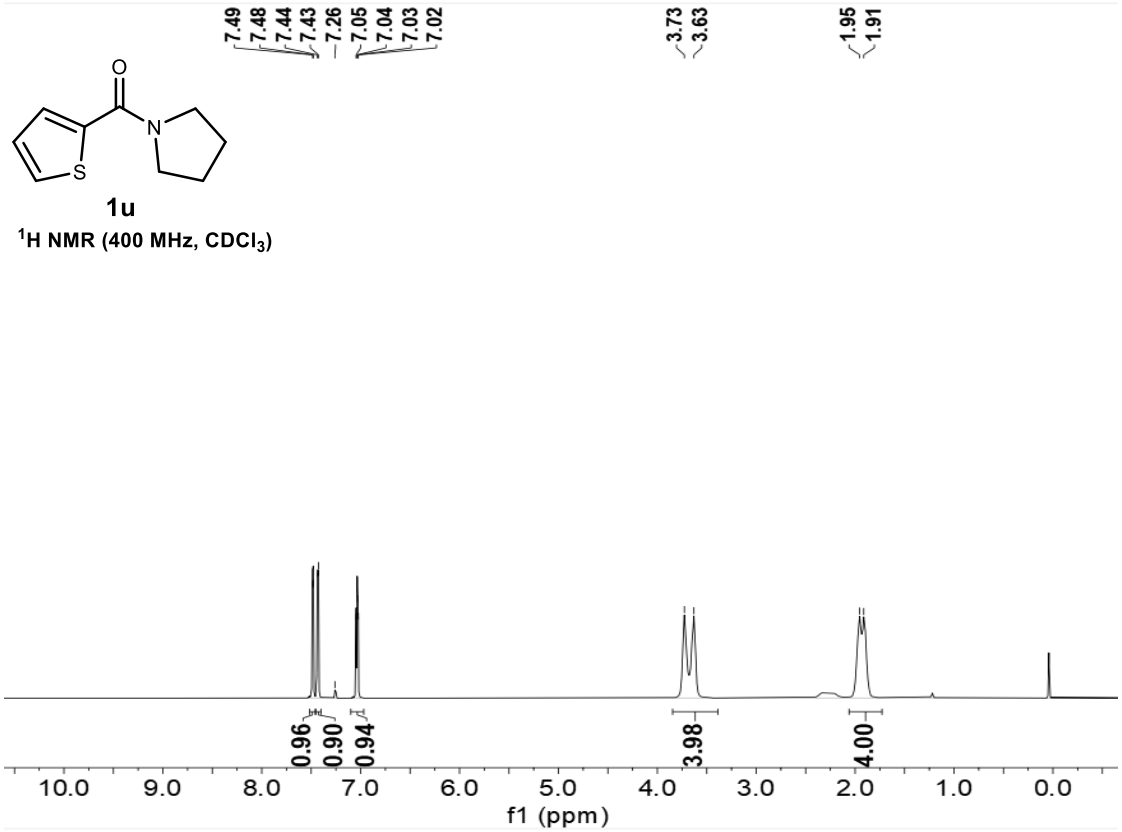

169.87
137.72
133.60
130.29
128.64
125.76
125.42
77.32
77.00
76.68
48.26
45.20
25.90
24.50
18.84
O
N
Me
1r
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.50
7.48
7.42
7.41
7.39
7.38
7.36
7.33
7.32
7.26
3.38
2.72
1.61
1.43
O
N
Ph
1s
^{1}H NMR (400 MHz, CDCl$_3$)
2.11
7.31
2.00
1.93
4.11
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


169.66
139.83
138.16
136.79
129.35
129.26
128.40
128.30
127.61
127.49
127.03
77.32
77.00
76.68
47.40
45.24
25.43
24.11
O
N
Ph
1s
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

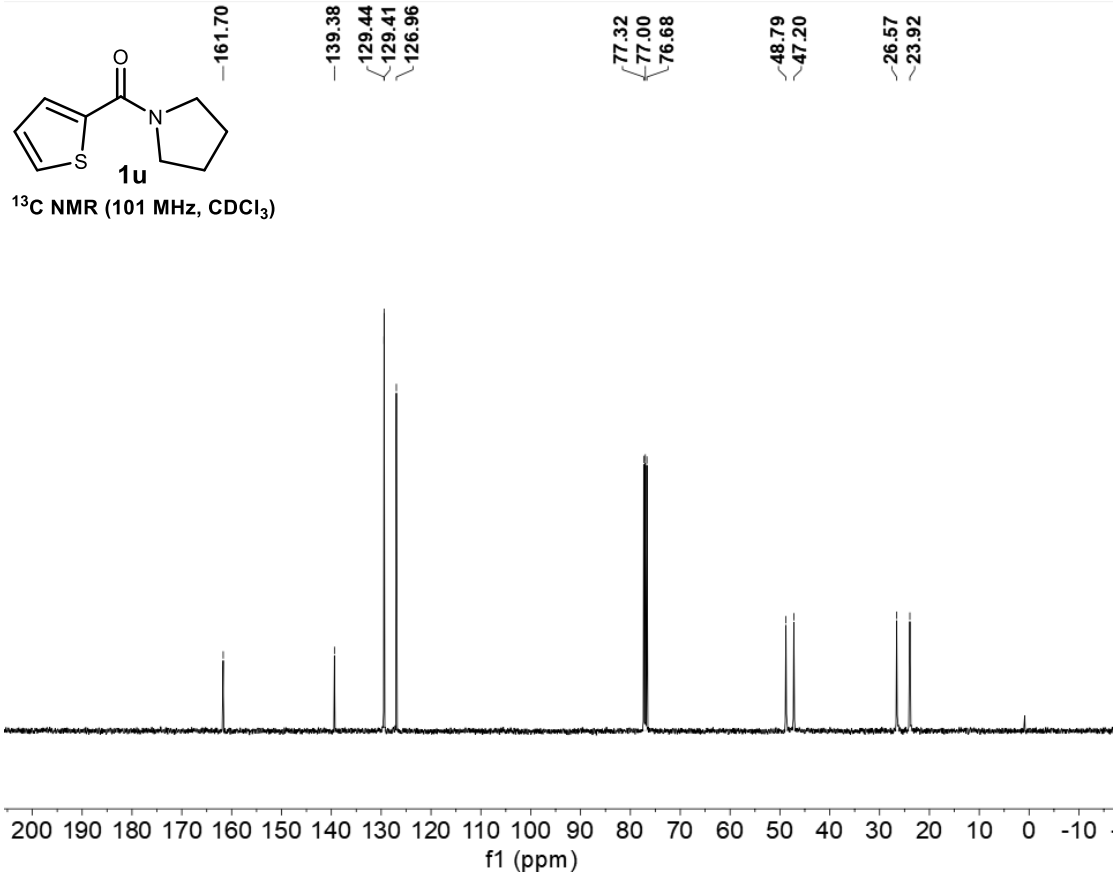

8.00
7.85
7.83
7.81
7.61
7.59
7.52
7.50
7.49
7.48
7.47
7.26
3.70
3.69
3.67
3.46
3.45
3.43
1.98
1.96
1.94
1.93
1.91
1.86
1.85
1.83
1.81
1.80
O
N
1t
^{1}H NMR (400 MHz, CDCl$_3$)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


169.58
134.23
133.57
132.37
128.31
127.89
127.56
126.87
126.79
126.36
124.23
77.32
77.00
76.68
49.55
46.14
26.22
24.29
O
N
1t
^{13}C NMR (101 MHz, CDCl$_3$)
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



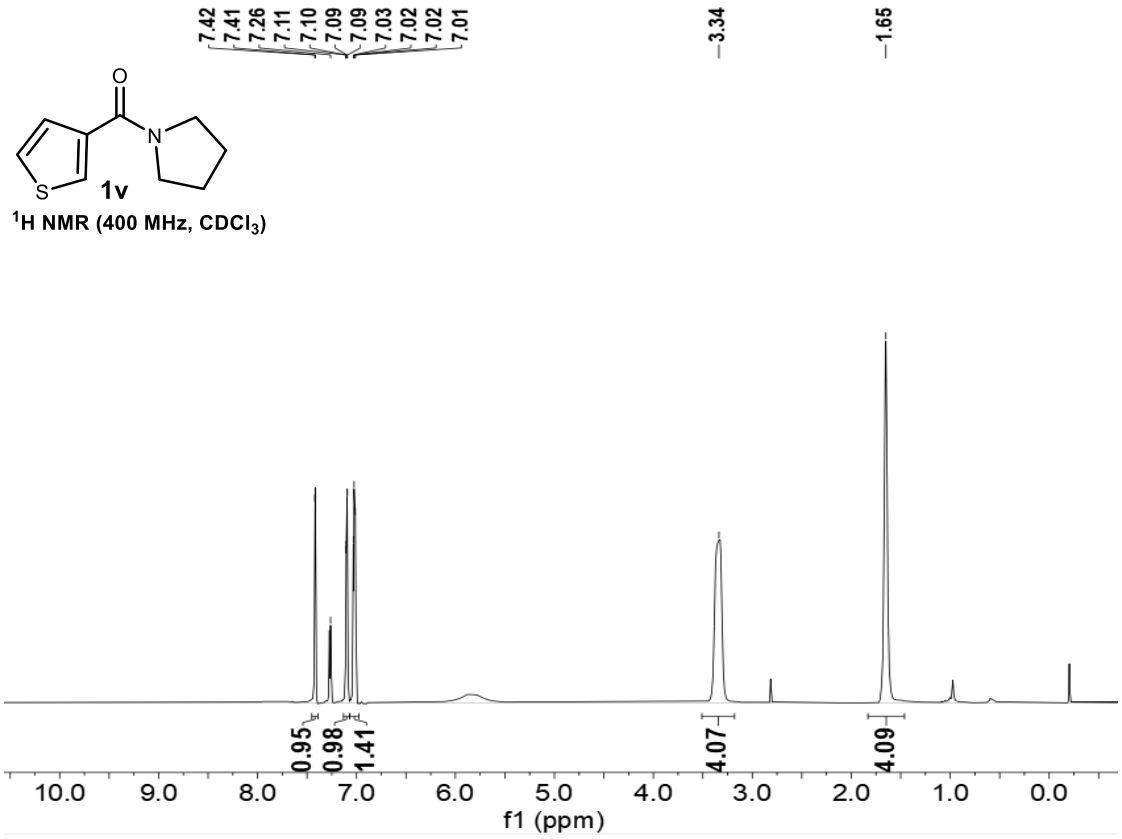
1u

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

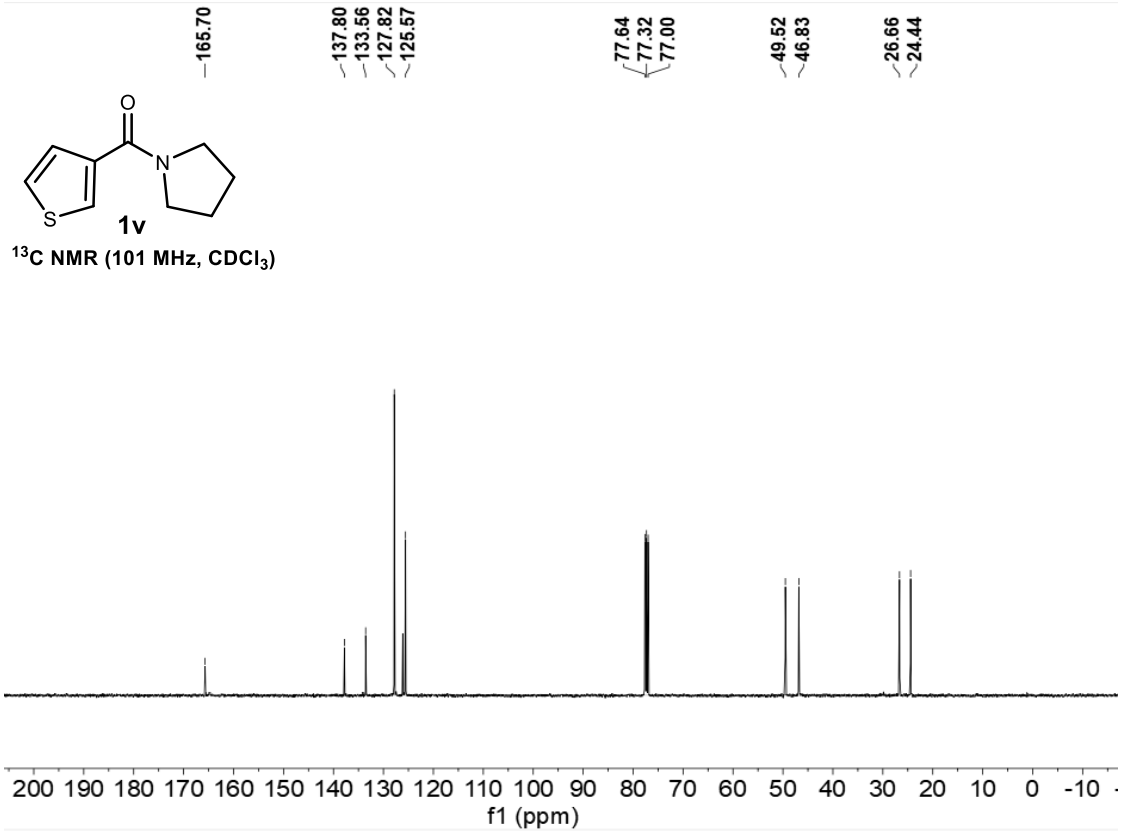


1u

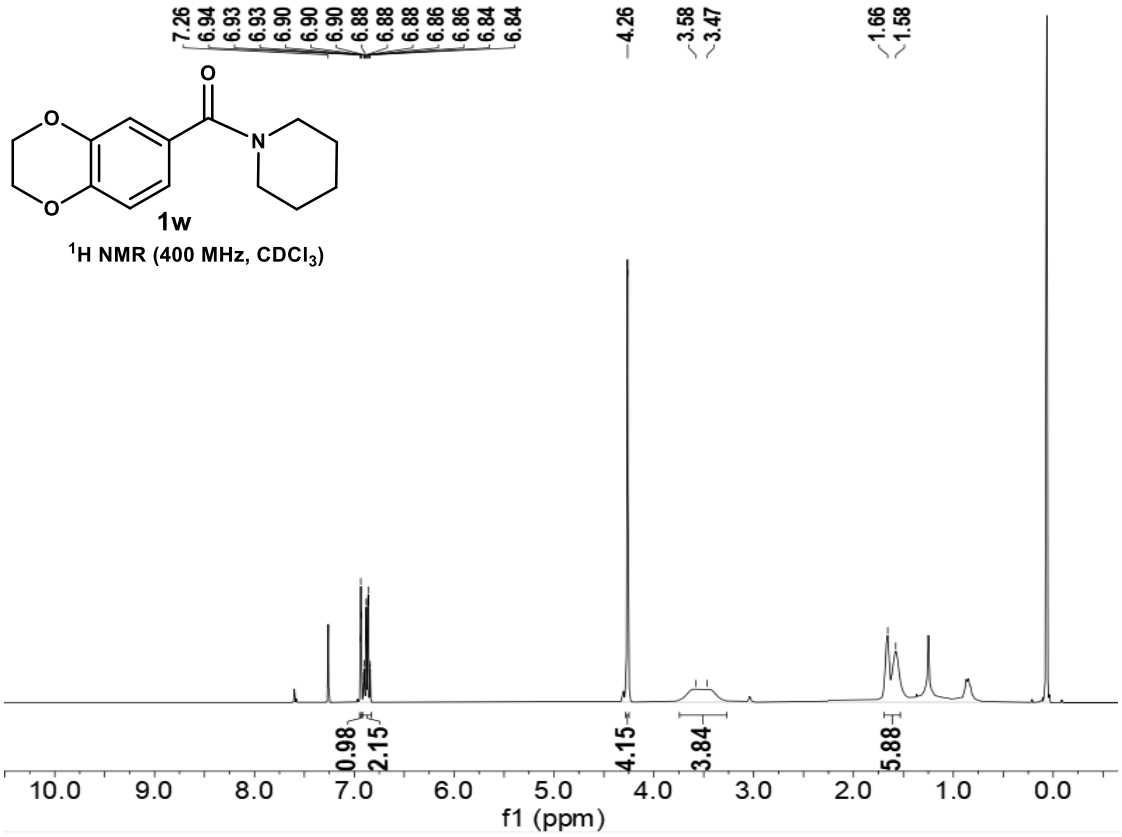
^{13}C NMR (101 MHz, $CDCl_3$)

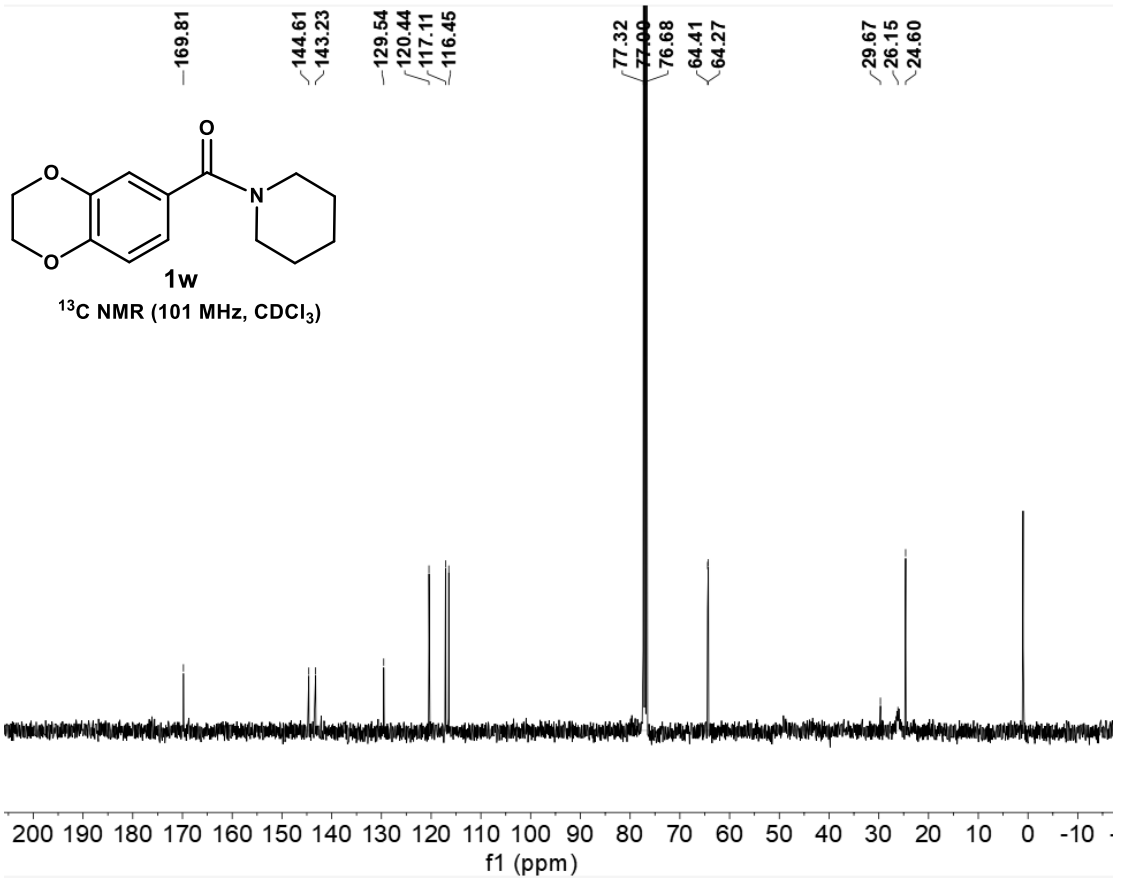


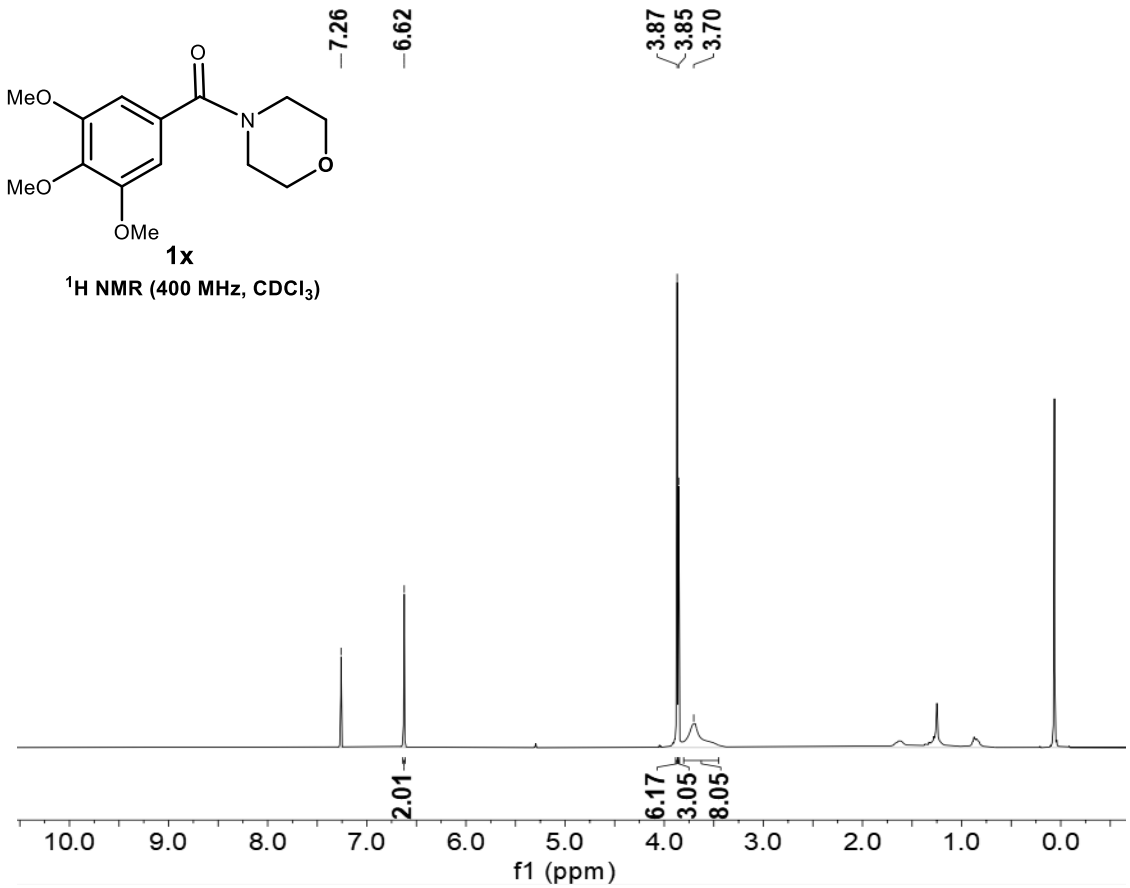
^{1}H NMR (400 MHz, $CDCl_3$)

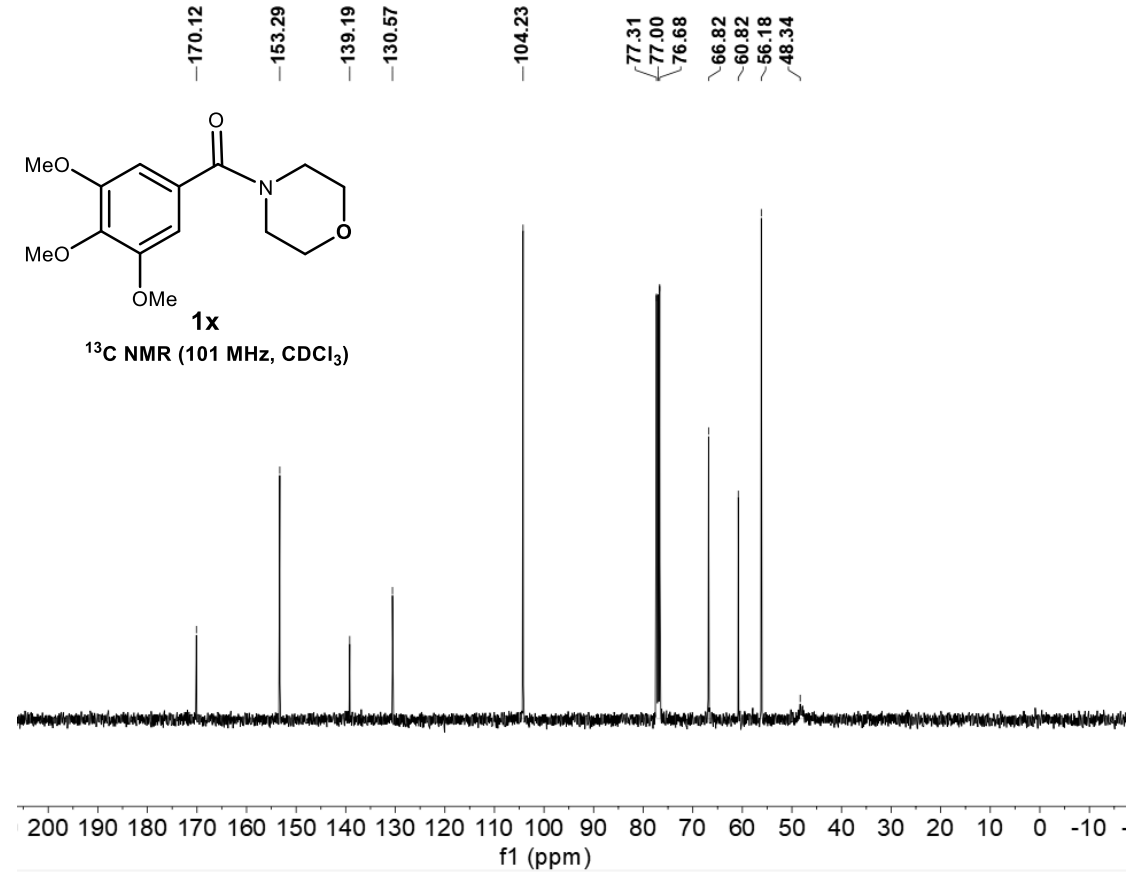


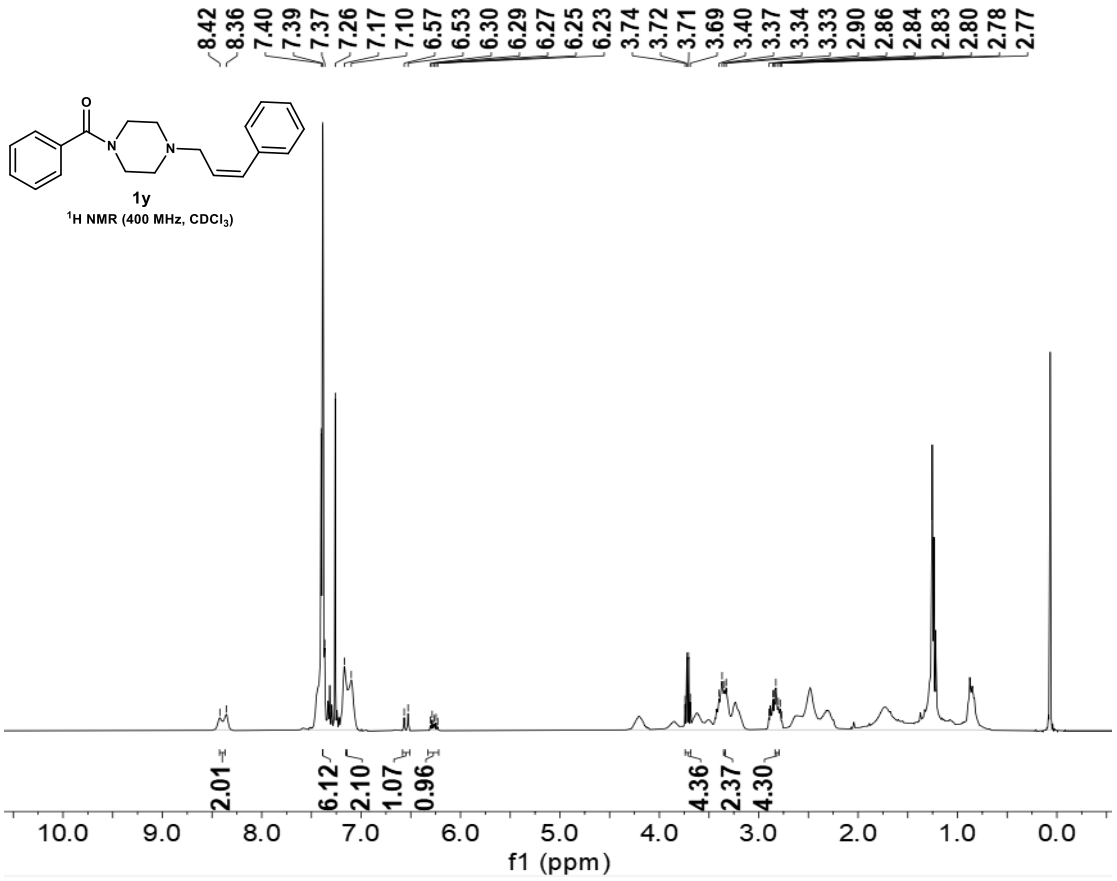
^{13}C NMR (101 MHz, $CDCl_3$)

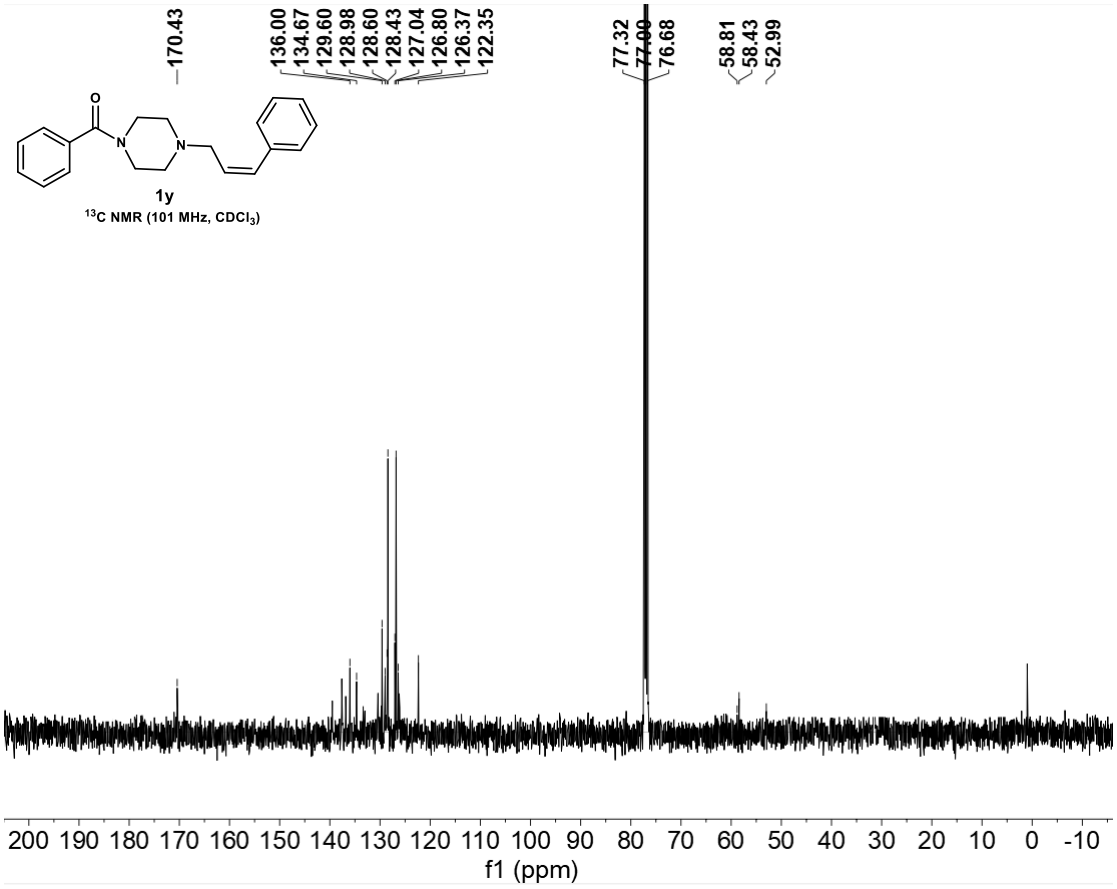

7.26
6.94
6.93
6.93
6.90
6.90
6.90
6.88
6.88
6.88
6.86
6.86
6.84
6.84
4.26
3.58
3.47
1.66
1.58
O
O
O
N
1w
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
2.15
4.15
3.84
5.88
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

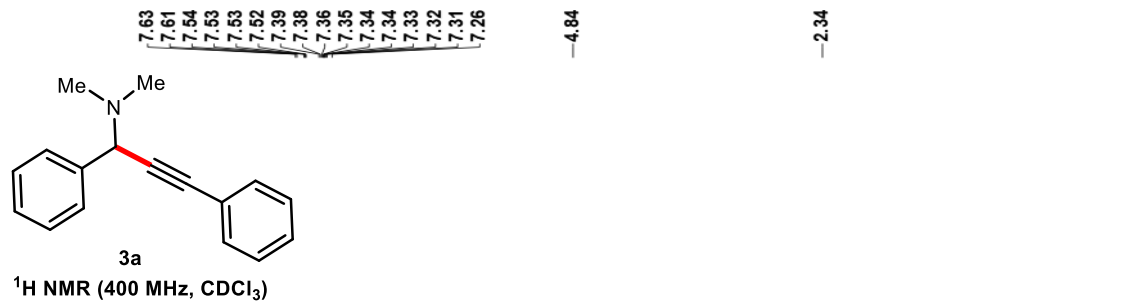

169.81
144.61
143.23
129.54
120.44
117.11
116.45
77.32
77.00
76.68
64.41
64.27
29.67
26.15
24.60
O
O
O
N
1w
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
6.62
3.87
3.85
3.70
MeO
MeO
OMe
O
N
O
1x
^{1}H NMR (400 MHz, CDCl$_3$)
2.01
6.17
3.05
8.05
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


170.12
153.29
139.19
130.57
104.23
77.31
77.00
76.68
66.82
60.82
56.18
48.34
MeO
MeO
OMe
O
N
O
1x
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

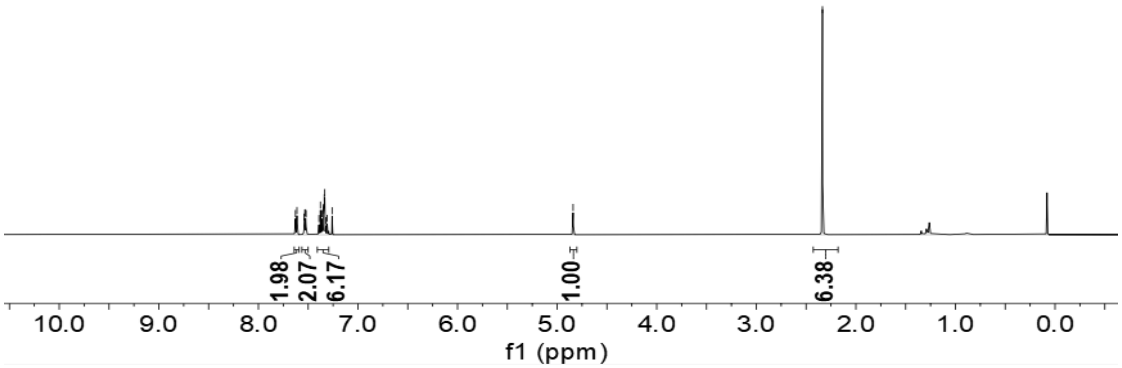

8.42
8.36
7.40
7.39
7.37
7.26
7.17
7.10
6.57
6.53
6.30
6.29
6.27
6.25
6.23
3.74
3.72
3.71
3.69
3.40
3.37
3.34
3.33
2.90
2.86
2.84
2.83
2.80
2.78
2.77
1y
1H NMR (400 MHz, CDCl3)
2.01
6.12
2.10
1.07
0.96
4.36
2.37
4.30
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

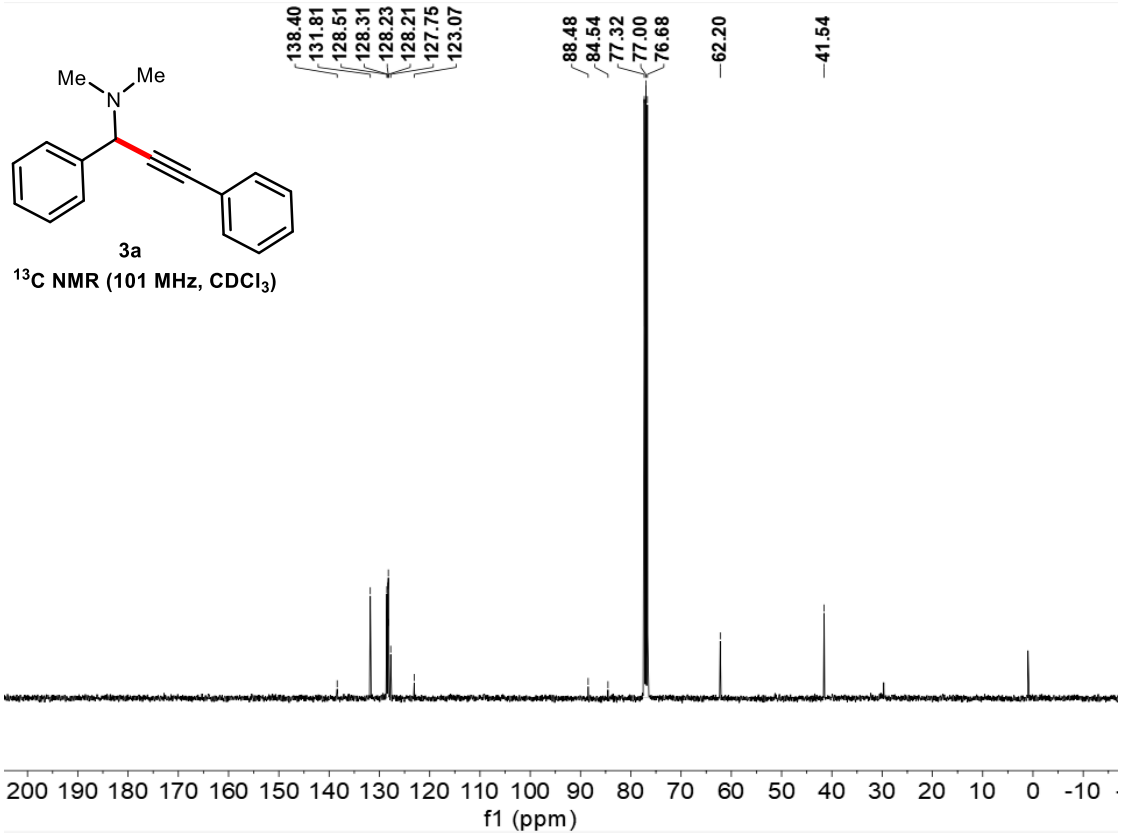

170.43
136.00
134.67
129.60
128.98
128.60
128.43
127.04
126.80
126.37
122.35
77.32
77.00
76.68
58.81
58.43
52.99
1y
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3a

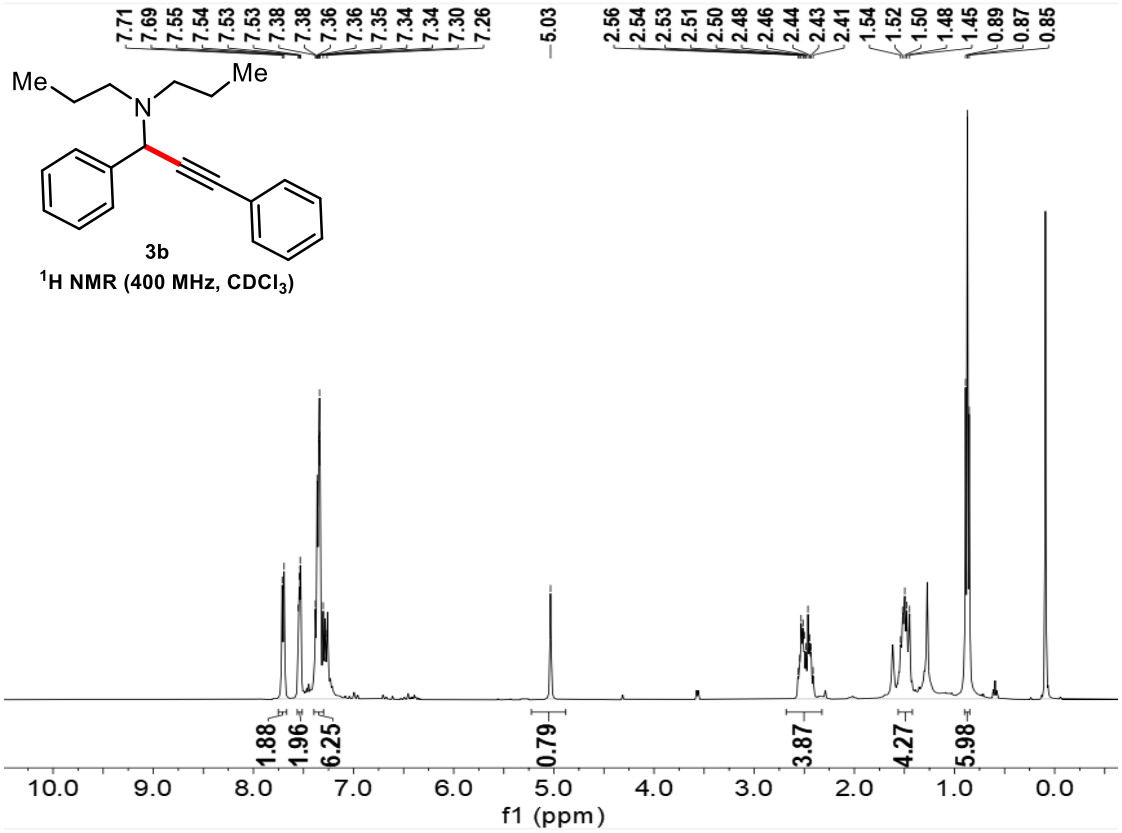
^{1}H NMR (400 MHz, $CDCl_3$)

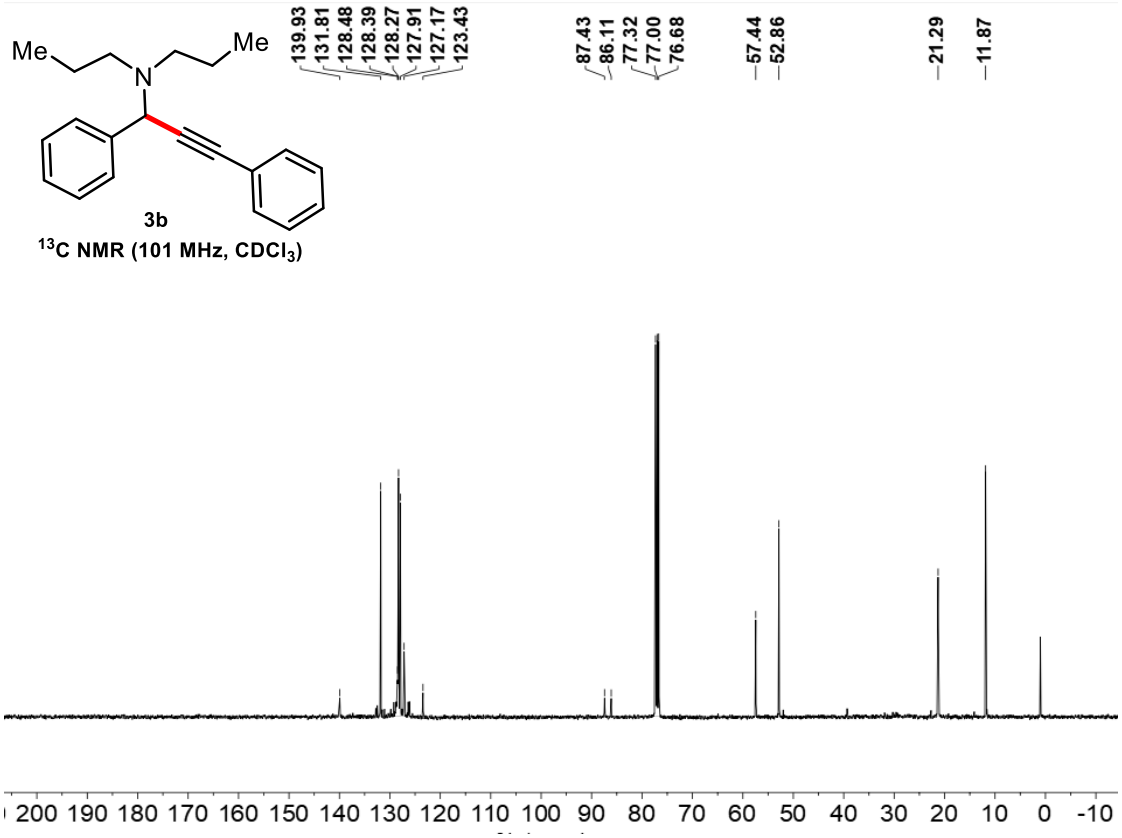


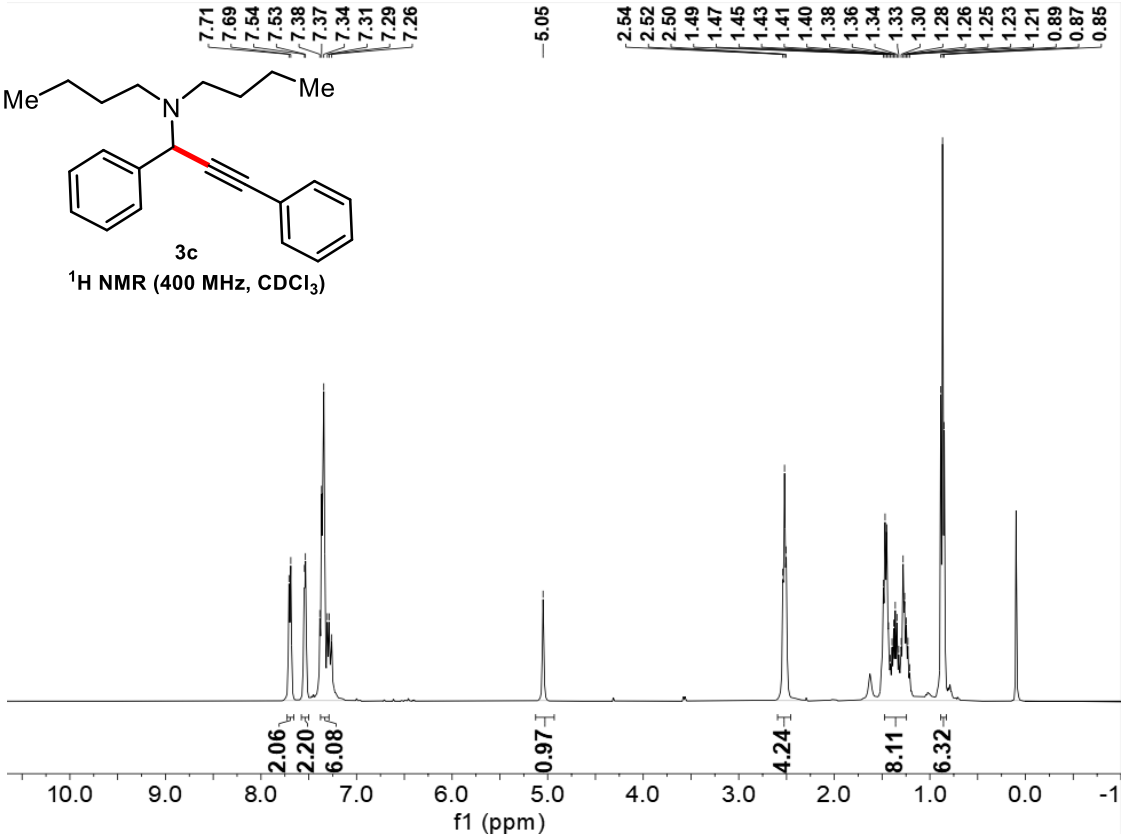


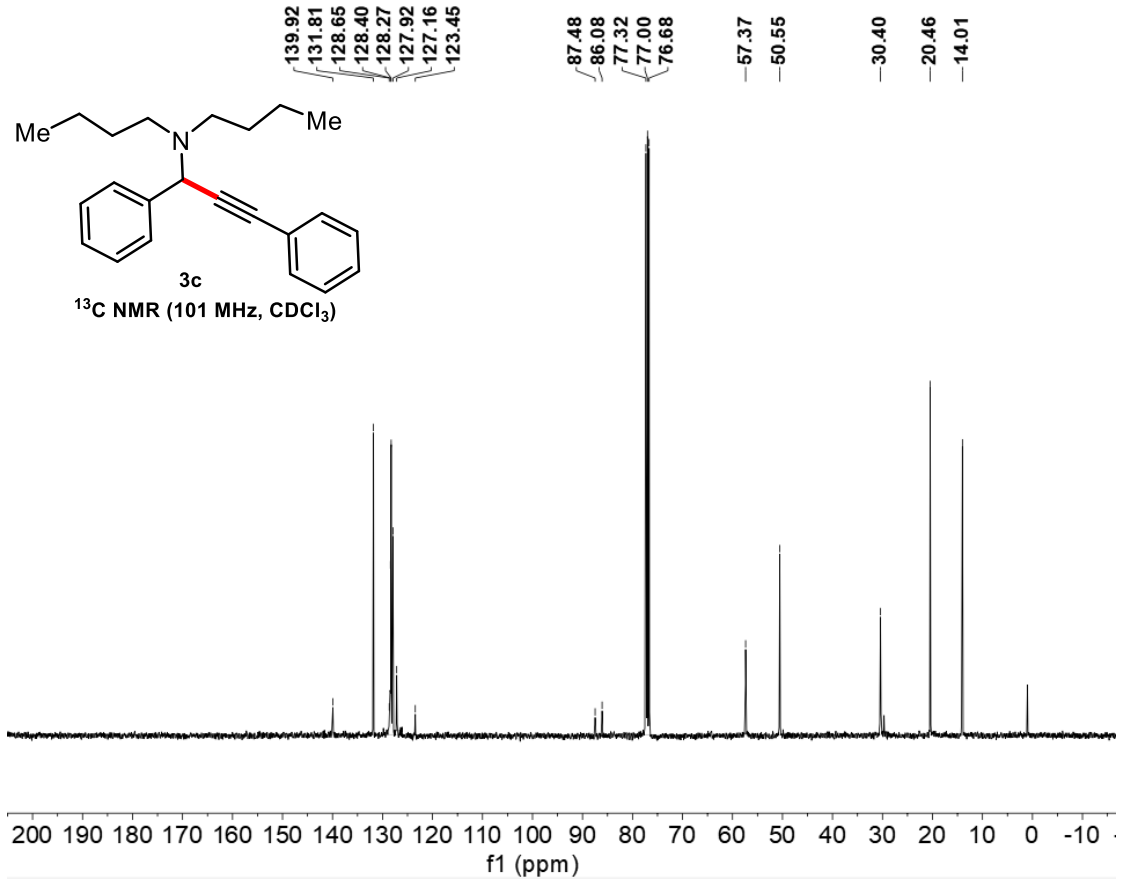
3a

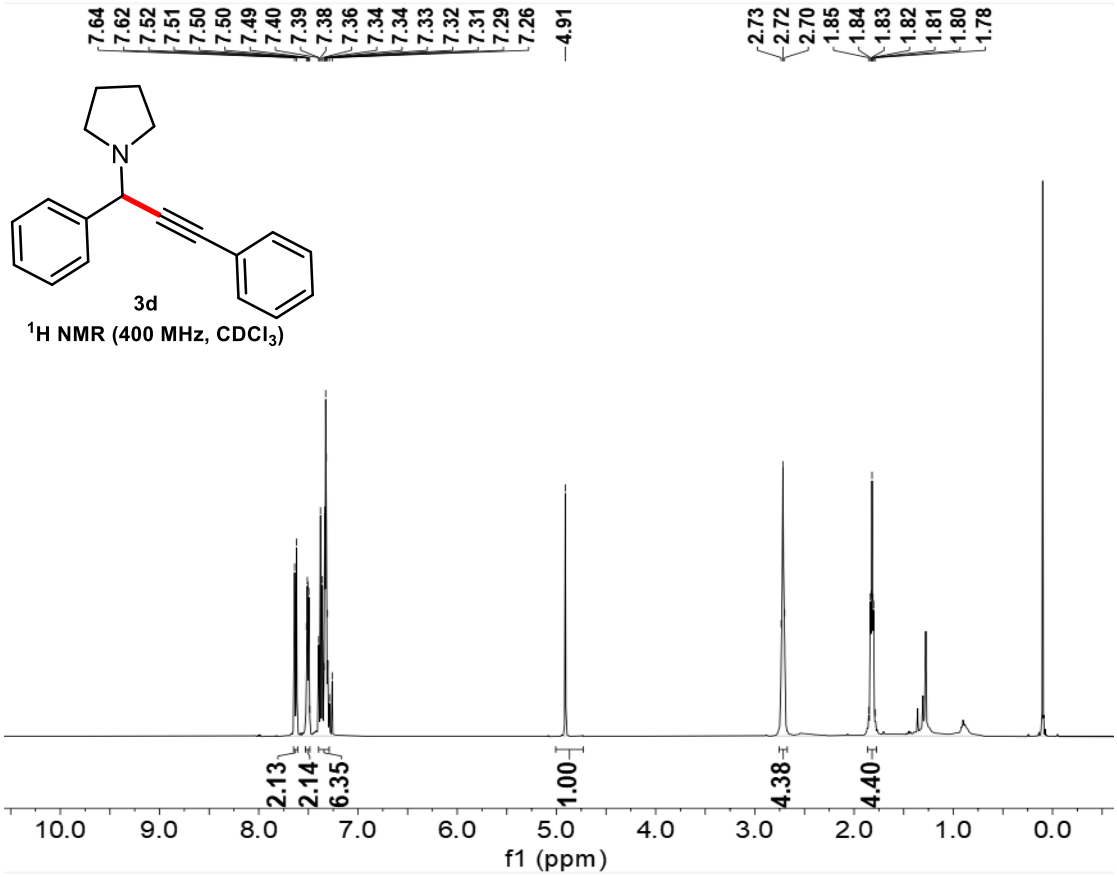
^{13}C NMR (101 MHz, $CDCl_3$)


7.71
7.69
7.55
7.54
7.53
7.53
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.30
7.26
5.03
2.56
2.54
2.53
2.51
2.50
2.48
2.46
2.44
2.43
2.41
1.54
1.52
1.50
1.48
1.45
0.89
0.87
0.85
Me
N
Me
3b
^{1}H NMR (400 MHz, CDCl$_3$)
1.88
1.96
6.25
0.79
3.87
4.27
5.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


139.93
131.81
128.48
128.39
128.27
127.91
127.17
123.43
87.43
86.11
77.32
77.00
76.68
57.44
52.86
21.29
11.87
Me
N
Me
3b
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.71
7.69
7.54
7.53
7.38
7.37
7.34
7.31
7.29
7.26
5.05
2.54
2.52
2.50
1.49
1.47
1.45
1.43
1.41
1.40
1.38
1.36
1.34
1.33
1.30
1.28
1.26
1.25
1.23
1.21
0.89
0.87
0.85
Me
N
Me
3c
^{1}H NMR (400 MHz, CDCl$_3$)
2.06
2.20
6.08
0.97
4.24
8.11
6.32
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
f1 (ppm)


139.92
131.81
128.65
128.40
128.27
127.92
127.16
123.45
87.48
86.08
77.32
77.00
76.68
57.37
50.55
30.40
20.46
14.01
Me
N
Me
3c
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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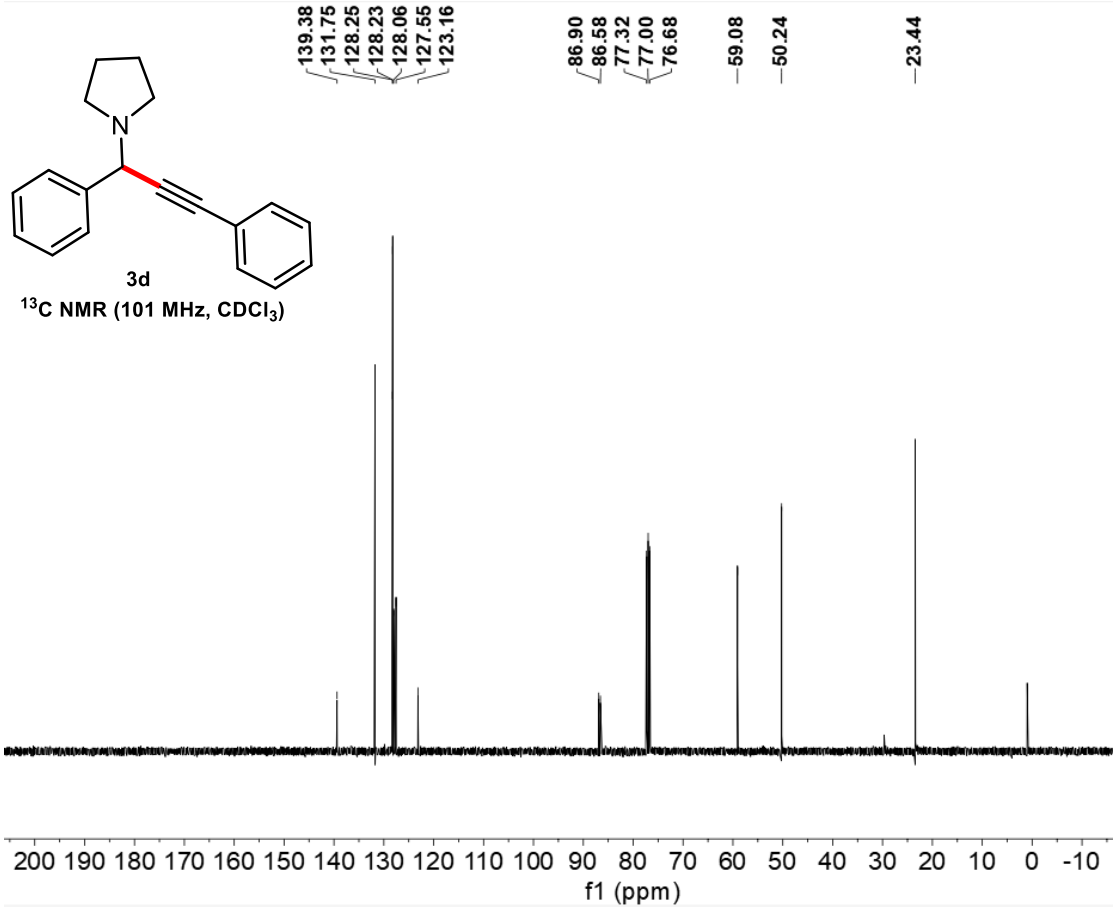
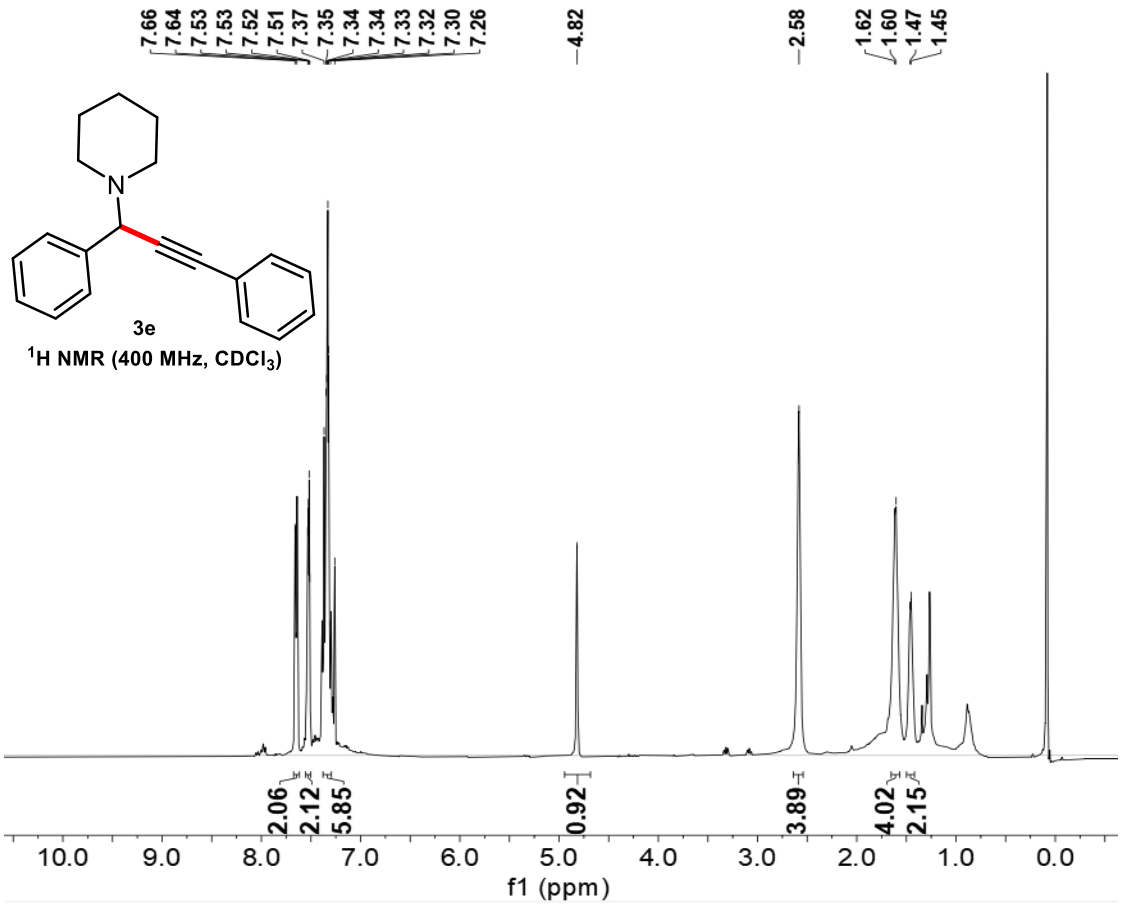
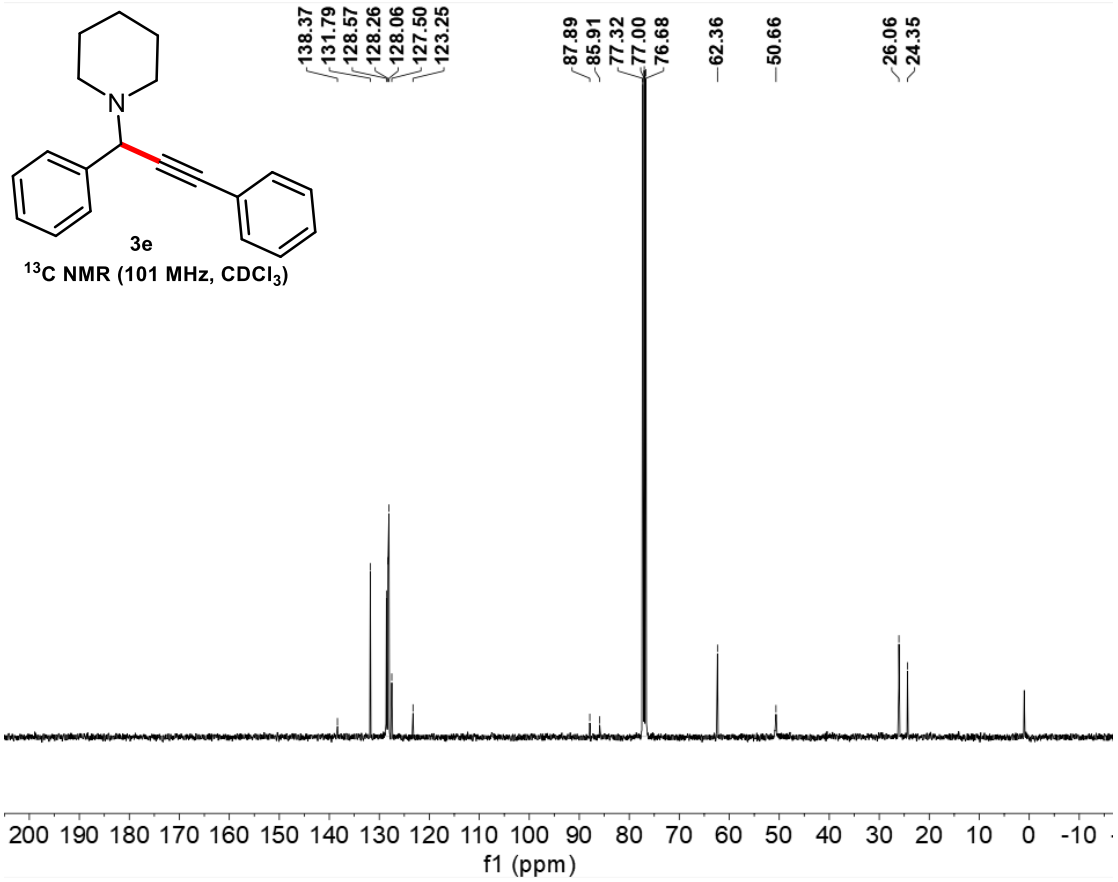
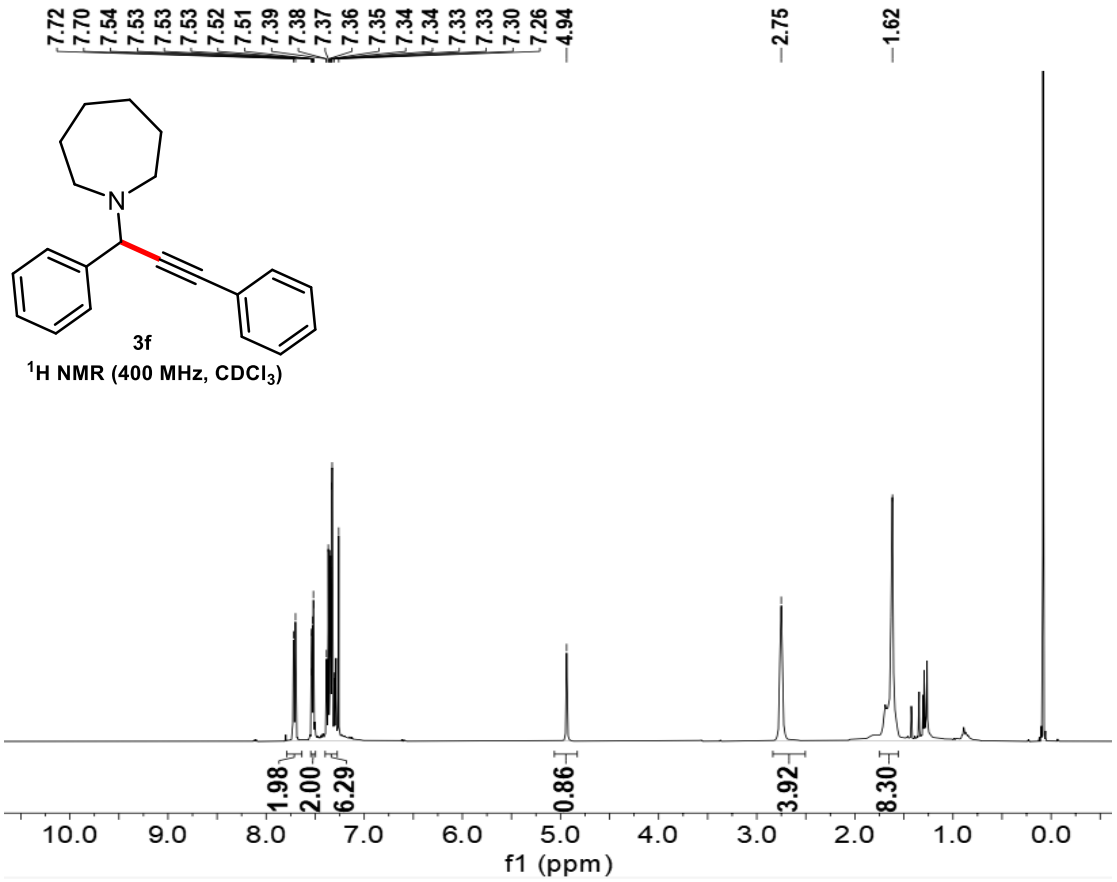
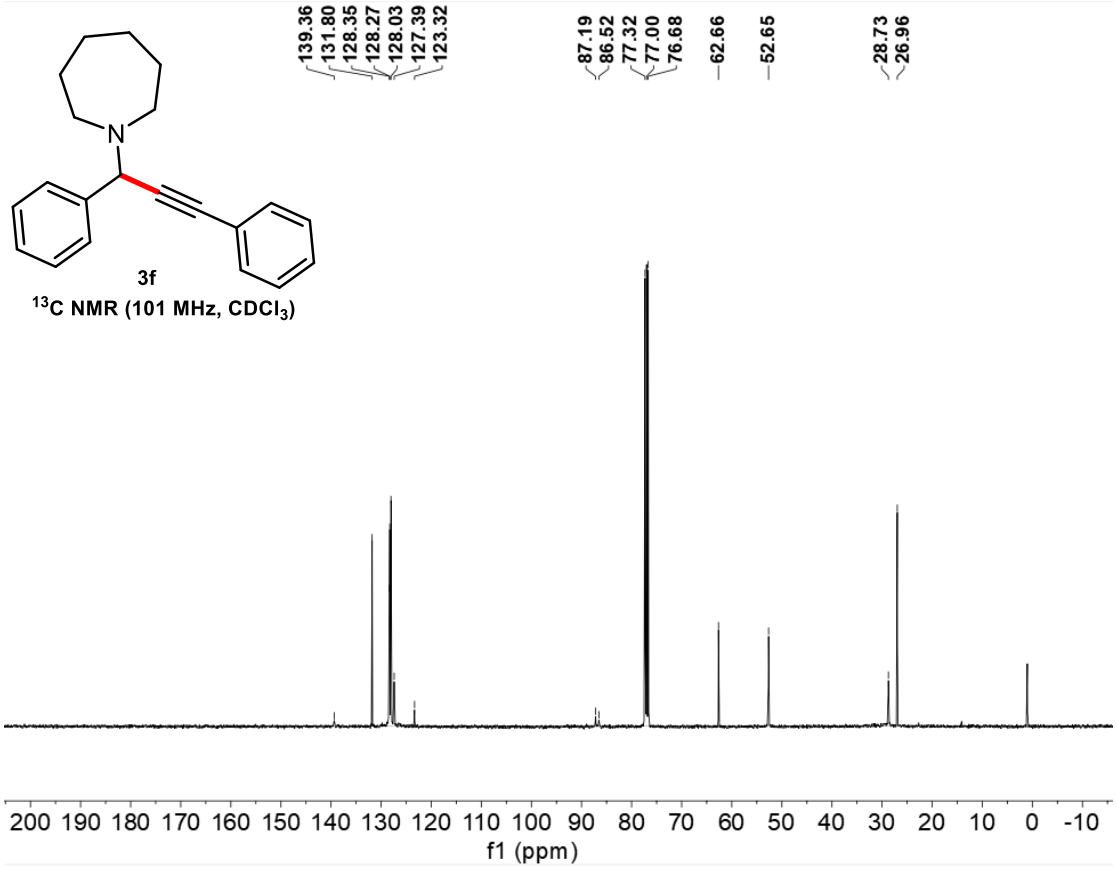
7.62
7.52
7.51
7.50
7.50
7.49
7.40
7.39
7.38
7.36
7.34
7.34
7.33
7.32
7.31
7.29
7.26
4.91
2.73
2.72
2.70
1.85
1.84
1.83
1.82
1.81
1.80
1.78
3d
^{1}H NMR (400 MHz, CDCl$_3$)
2.13
2.14
6.35
1.00
4.38
4.40
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

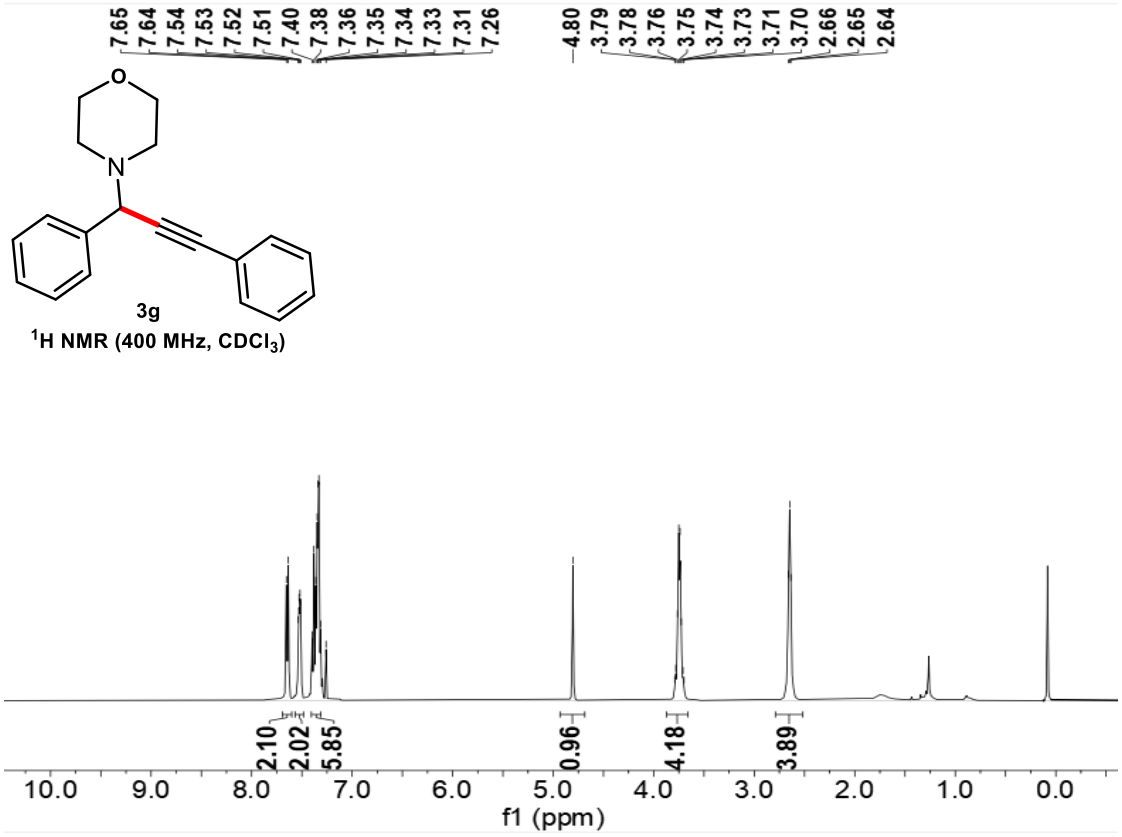

139.38
131.75
128.25
128.23
128.06
127.55
123.16
86.90
86.58
77.32
77.00
76.68
59.08
50.24
23.44
3d
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

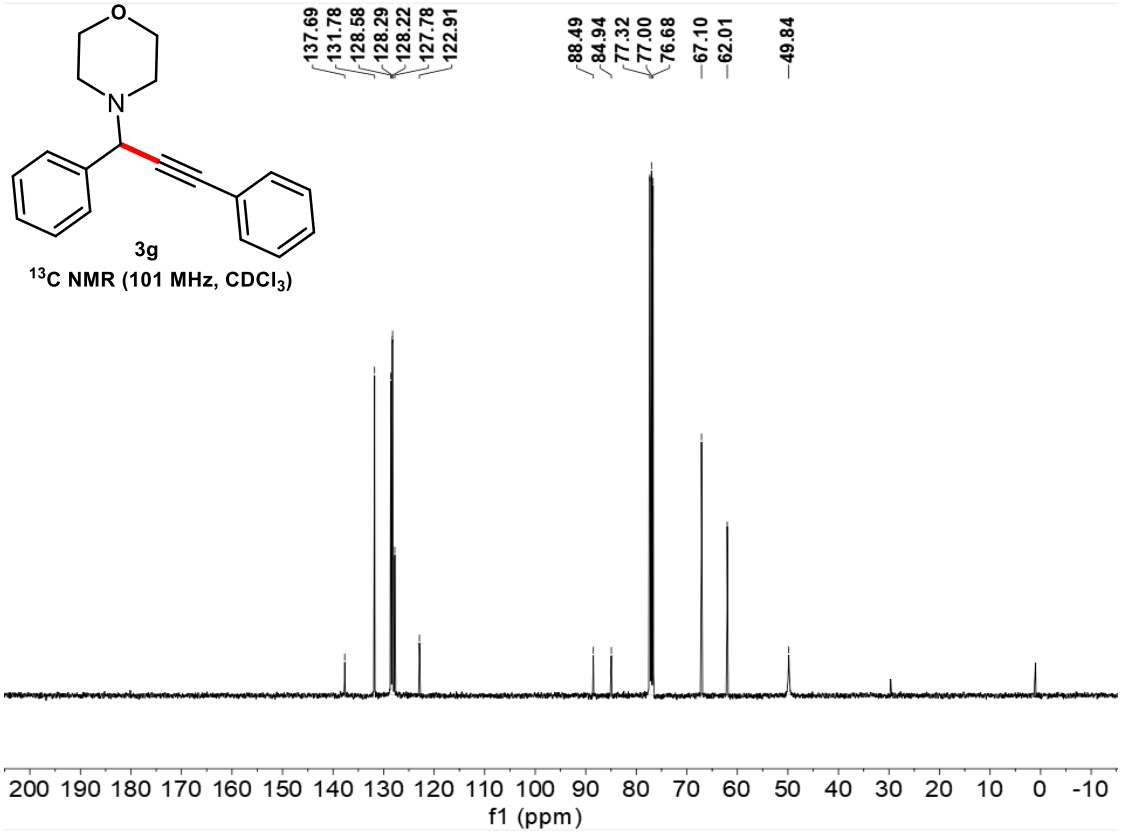

7.66
7.64
7.53
7.53
7.52
7.51
7.37
7.35
7.34
7.34
7.33
7.32
7.30
7.26
4.82
2.58
1.62
1.60
1.47
1.45
N
3e
^{1}H NMR (400 MHz, CDCl$_3$)
2.06
2.12
5.85
0.92
3.89
4.02
2.15
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

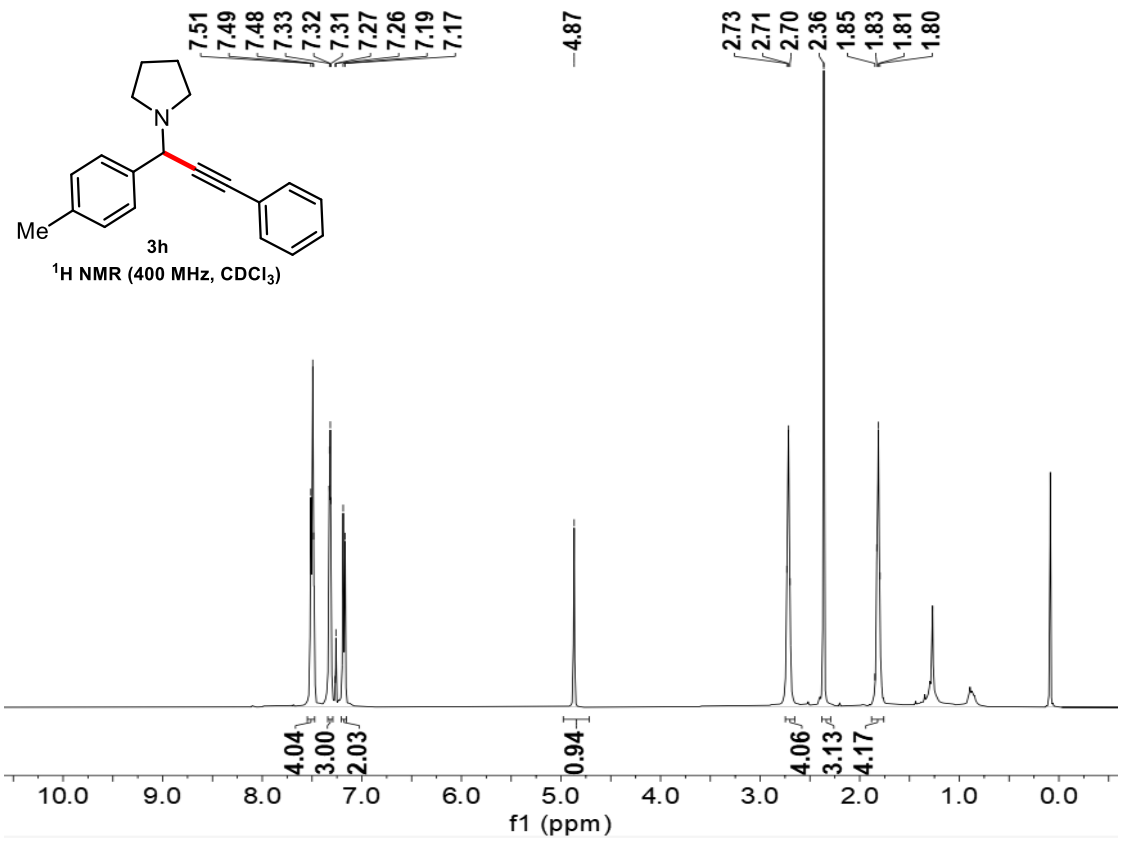

138.37
131.79
128.57
128.26
128.06
127.50
123.25
87.89
85.91
77.32
77.00
76.68
62.36
50.66
26.06
24.35
N
3e
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

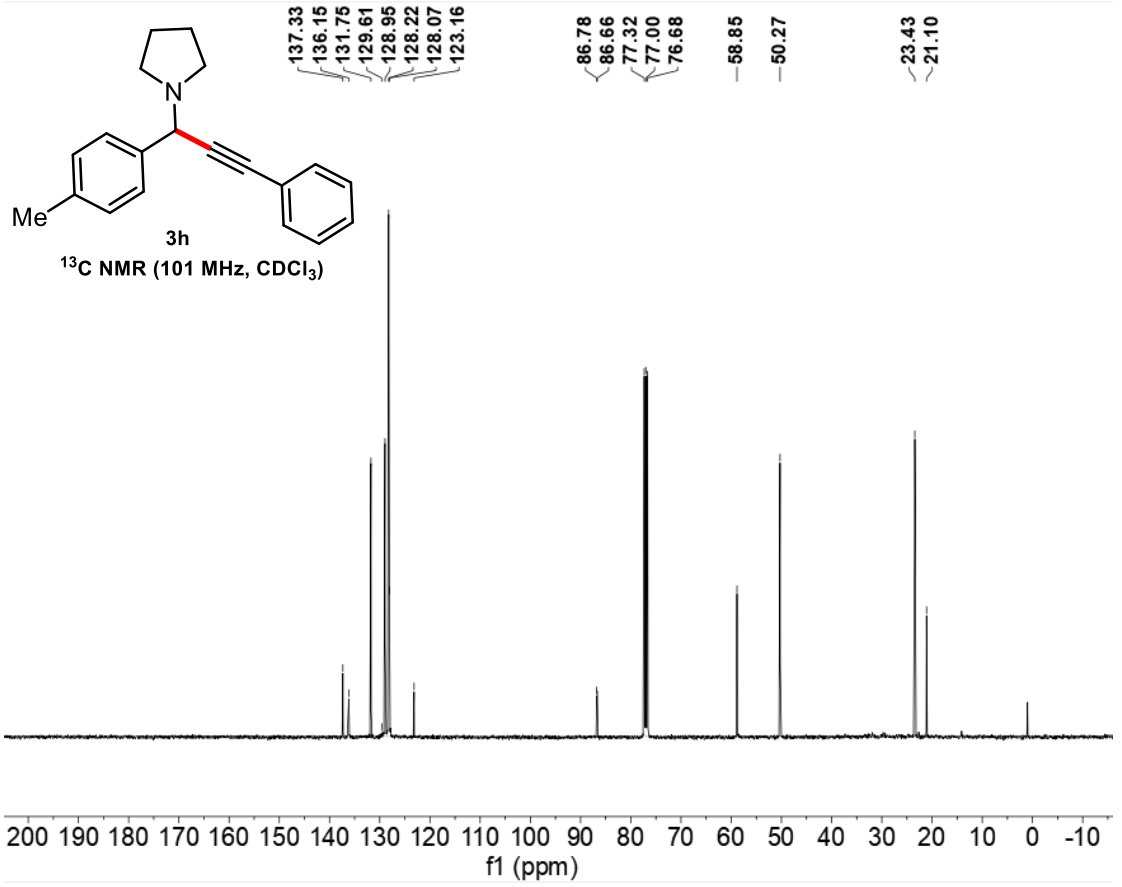

7.72
7.70
7.54
7.53
7.53
7.53
7.52
7.51
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.30
7.26
4.94
2.75
1.62
3f
^{1}H NMR (400 MHz, CDCl$_3$)
1.98
2.00
6.29
0.86
3.92
8.30
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

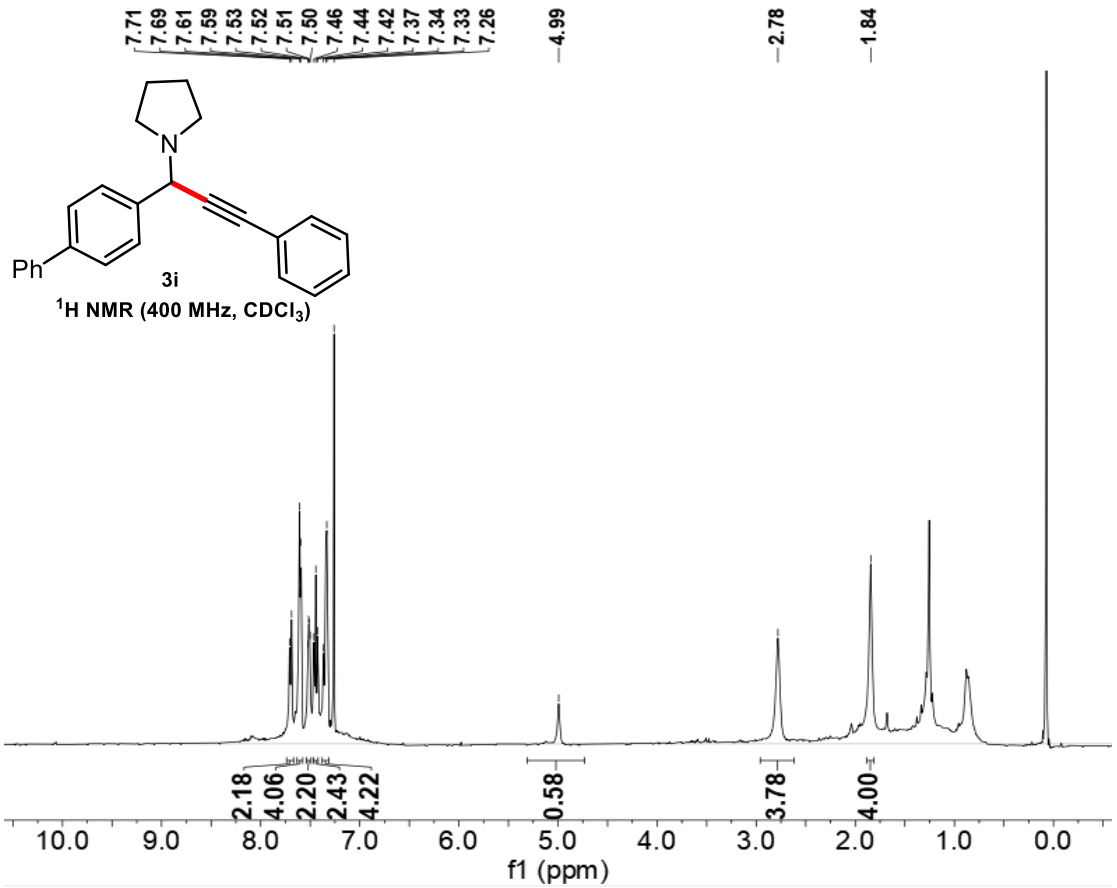

139.36
131.80
128.35
128.27
128.03
127.39
123.32
87.19
86.52
77.32
77.00
76.68
62.66
52.65
28.73
26.96
3f
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

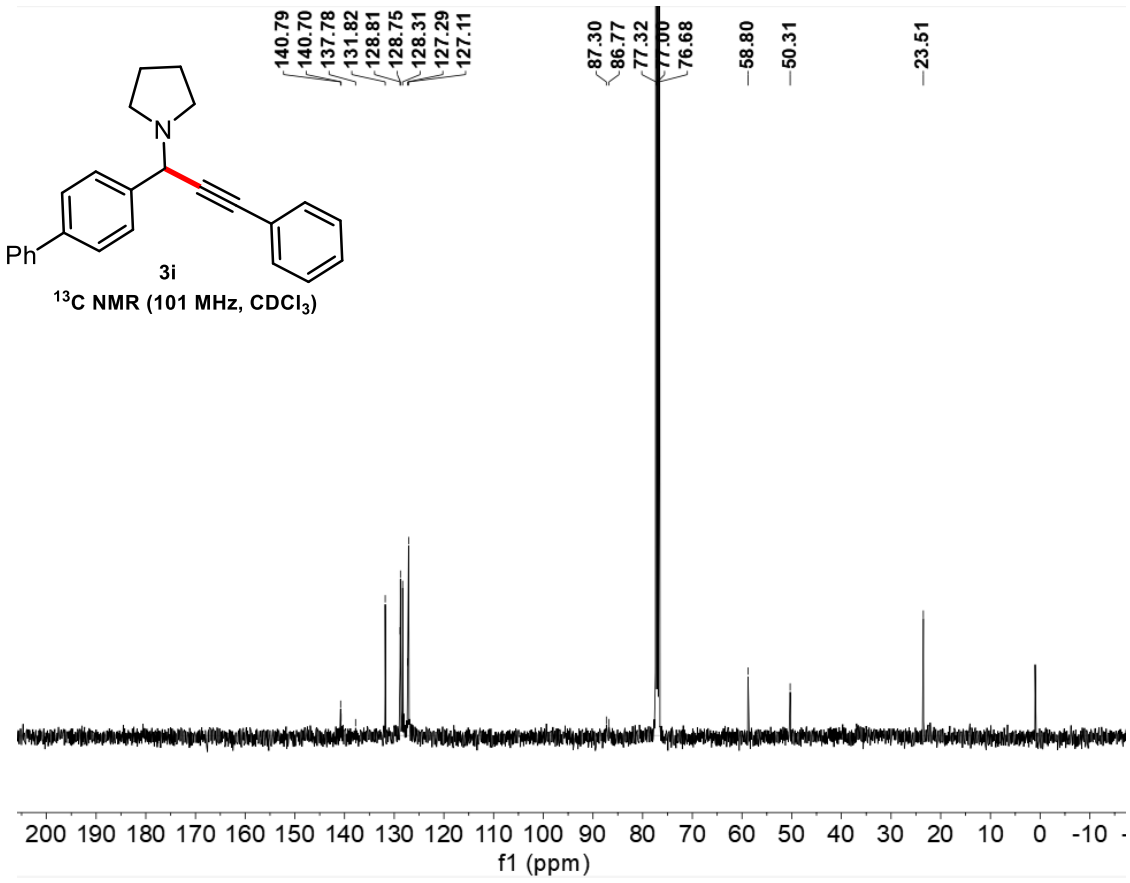

7.65
7.64
7.54
7.53
7.52
7.51
7.40
7.38
7.36
7.35
7.34
7.33
7.31
7.26
4.80
3.79
3.78
3.76
3.75
3.74
3.73
3.71
3.70
2.66
2.65
2.64
O
N
3g
^{1}H NMR (400 MHz, CDCl$_3$)
2.10
2.02
5.85
0.96
4.18
3.89
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

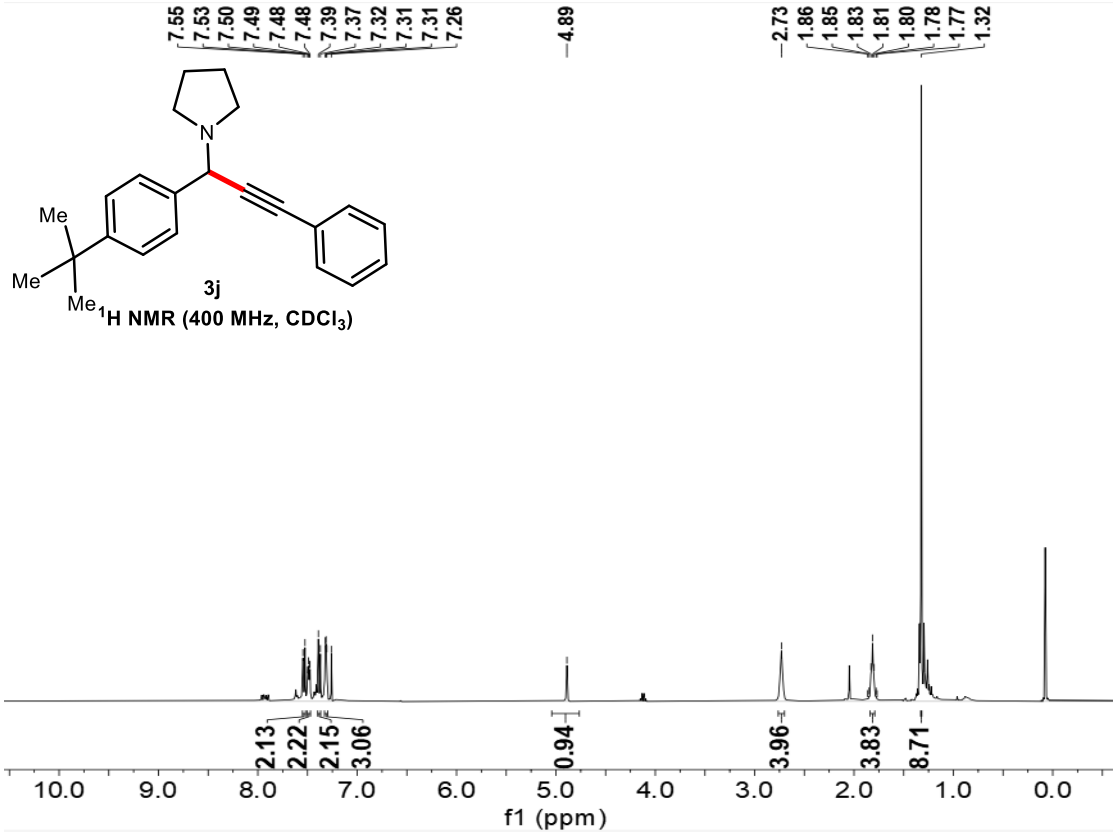

137.69
131.78
128.58
128.29
128.22
127.78
122.91
88.49
84.94
77.32
77.00
76.68
67.10
62.01
49.84
O
N
3g
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

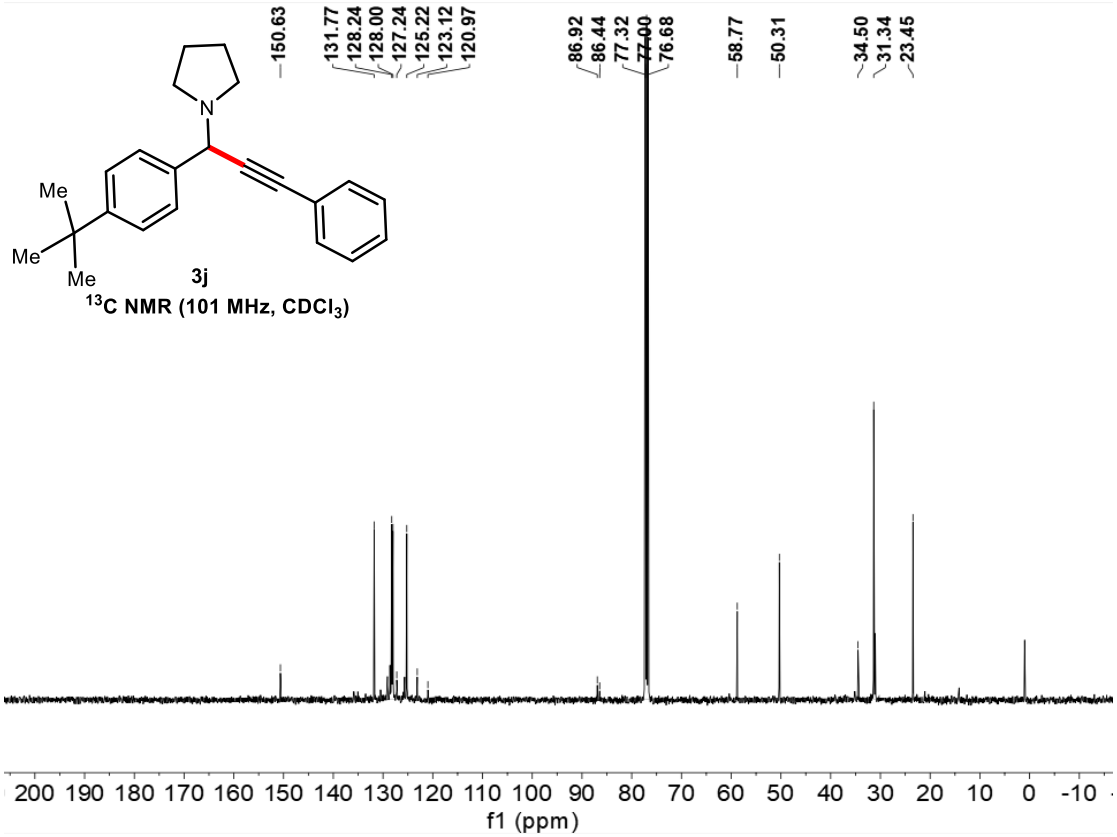

7.51
7.49
7.48
7.33
7.32
7.31
7.27
7.26
7.19
7.17
4.87
2.73
2.71
2.70
2.36
1.85
1.83
1.81
1.80
N
Me
3h
^{1}H NMR (400 MHz, CDCl$_3$)
4.04
3.00
2.03
0.94
4.06
3.13
4.17
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

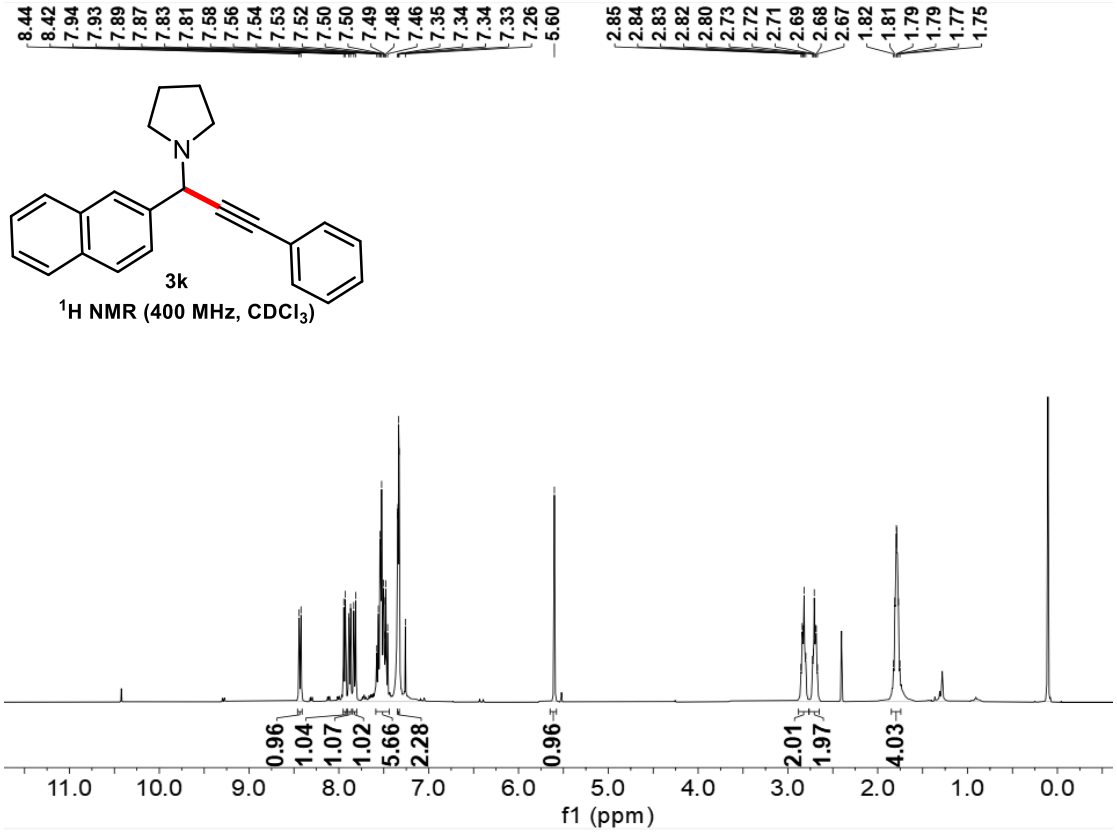

137.33
136.15
131.75
129.61
128.95
128.22
128.07
123.16
86.78
86.66
77.32
77.00
76.68
58.85
50.27
23.43
21.10
N
Me
3h
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

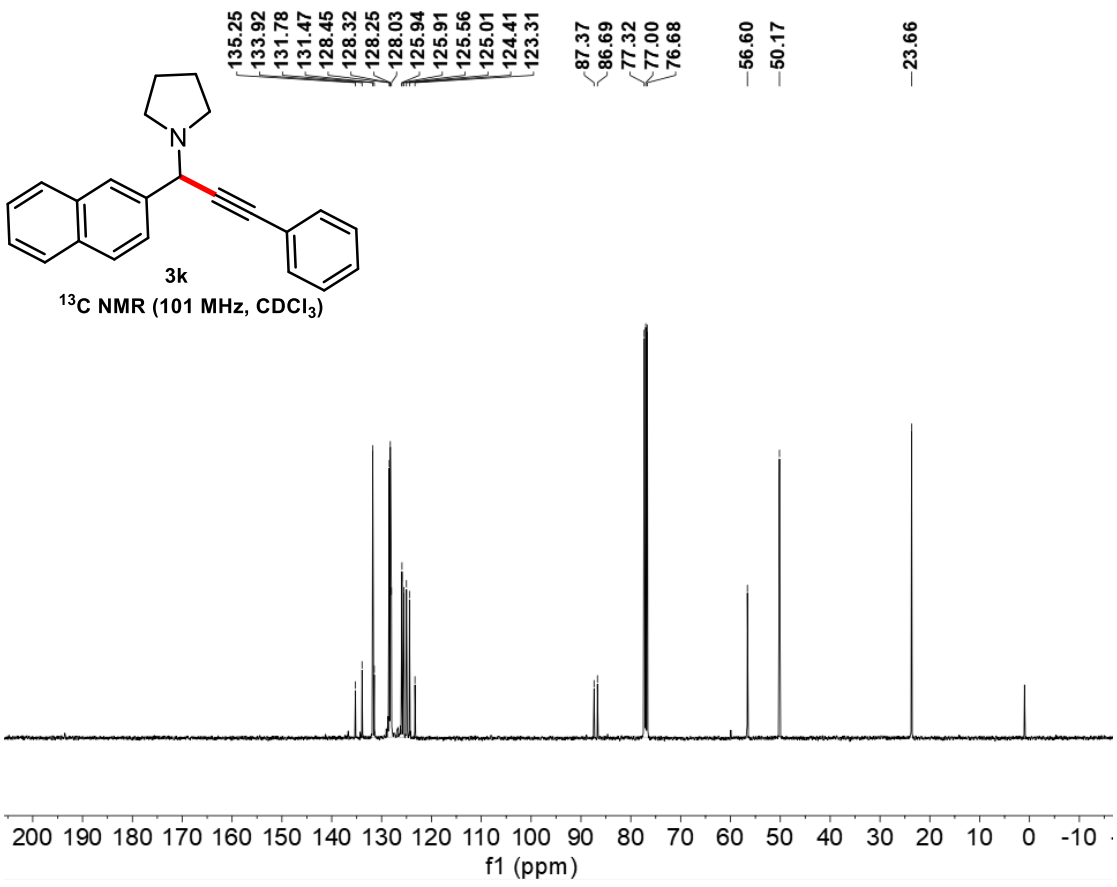

7.71
7.69
7.61
7.59
7.53
7.52
7.51
7.50
7.46
7.44
7.42
7.37
7.34
7.33
7.26
4.99
2.78
1.84
N
Ph
3i
^{1}H NMR (400 MHz, CDCl$_3$)
2.18
4.06
2.20
2.43
4.22
0.58
3.78
4.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

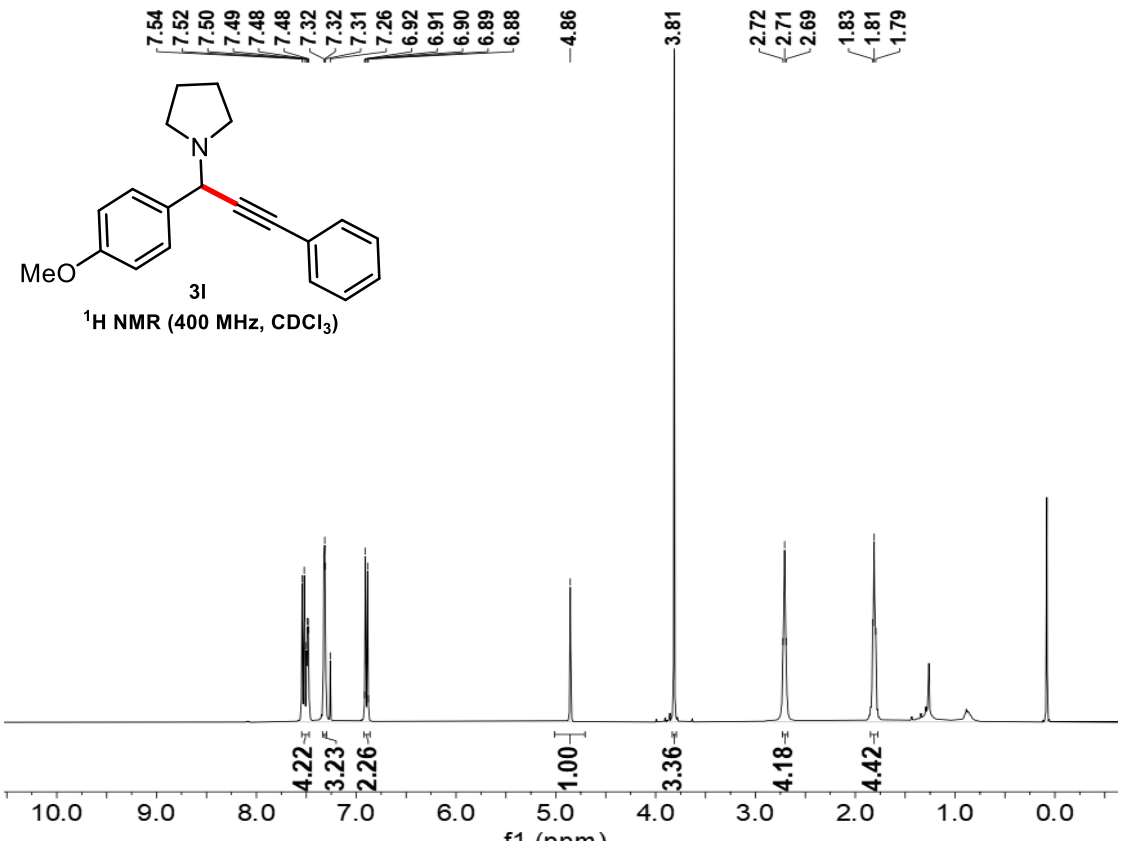

140.79
140.70
137.78
131.82
128.81
128.75
128.31
127.29
127.11
87.30
86.77
77.32
77.00
76.68
58.80
50.31
23.51
N
Ph
3i
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.55
7.53
7.50
7.49
7.48
7.48
7.39
7.37
7.32
7.31
7.31
7.26
4.89
2.73
1.86
1.85
1.83
1.81
1.80
1.78
1.77
1.32
N
Me
Me
Me
3j
^{1}H NMR (400 MHz, CDCl$_3$)
2.13
2.22
2.15
3.06
0.94
3.96
3.83
8.71
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


150.63
131.77
128.24
128.00
127.24
125.22
123.12
120.97
86.92
86.44
77.32
77.00
76.68
58.77
50.31
34.50
31.34
23.45
N
Me
Me
Me
3j
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

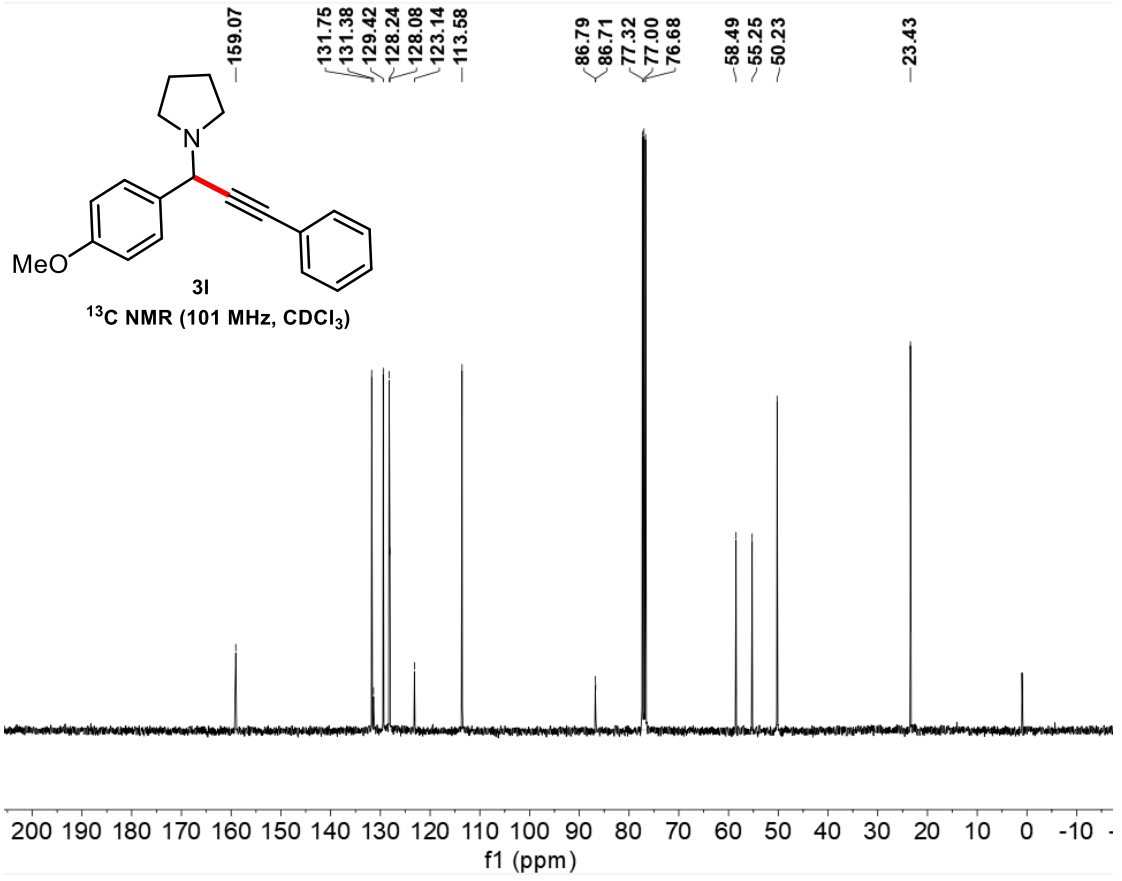

8.44
8.42
7.94
7.93
7.89
7.87
7.83
7.81
7.58
7.56
7.54
7.53
7.52
7.50
7.50
7.49
7.48
7.46
7.35
7.34
7.34
7.33
7.26
5.60
2.85
2.84
2.83
2.82
2.80
2.73
2.72
2.71
2.69
2.68
2.67
1.82
1.81
1.79
1.79
1.77
1.75
N
3k
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
1.04
1.07
1.02
5.66
2.28
0.96
2.01
1.97
4.03
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


135.25
133.92
131.78
131.47
128.45
128.32
128.25
128.03
125.94
125.91
125.56
125.01
124.41
123.31
87.37
86.69
77.32
77.00
76.68
56.60
50.17
23.66
N
3k
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



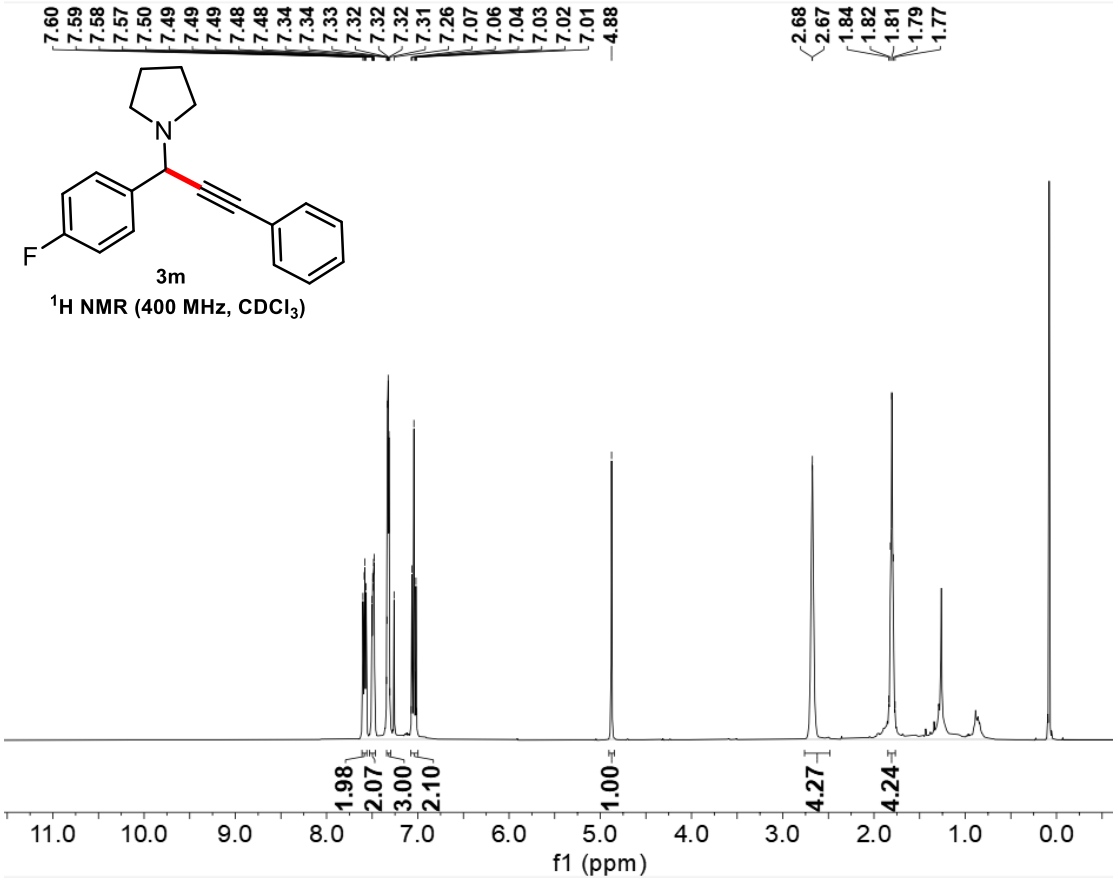
3l

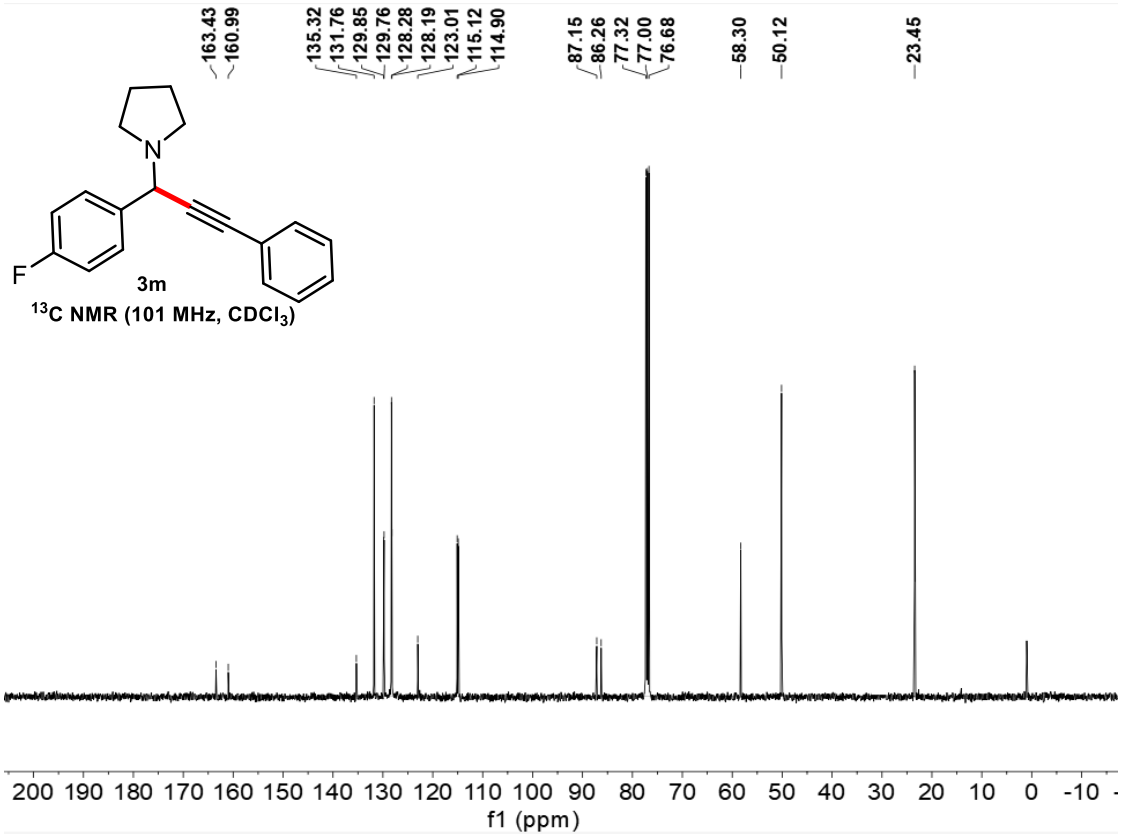
^{1}H NMR (400 MHz, $CDCl_3$)

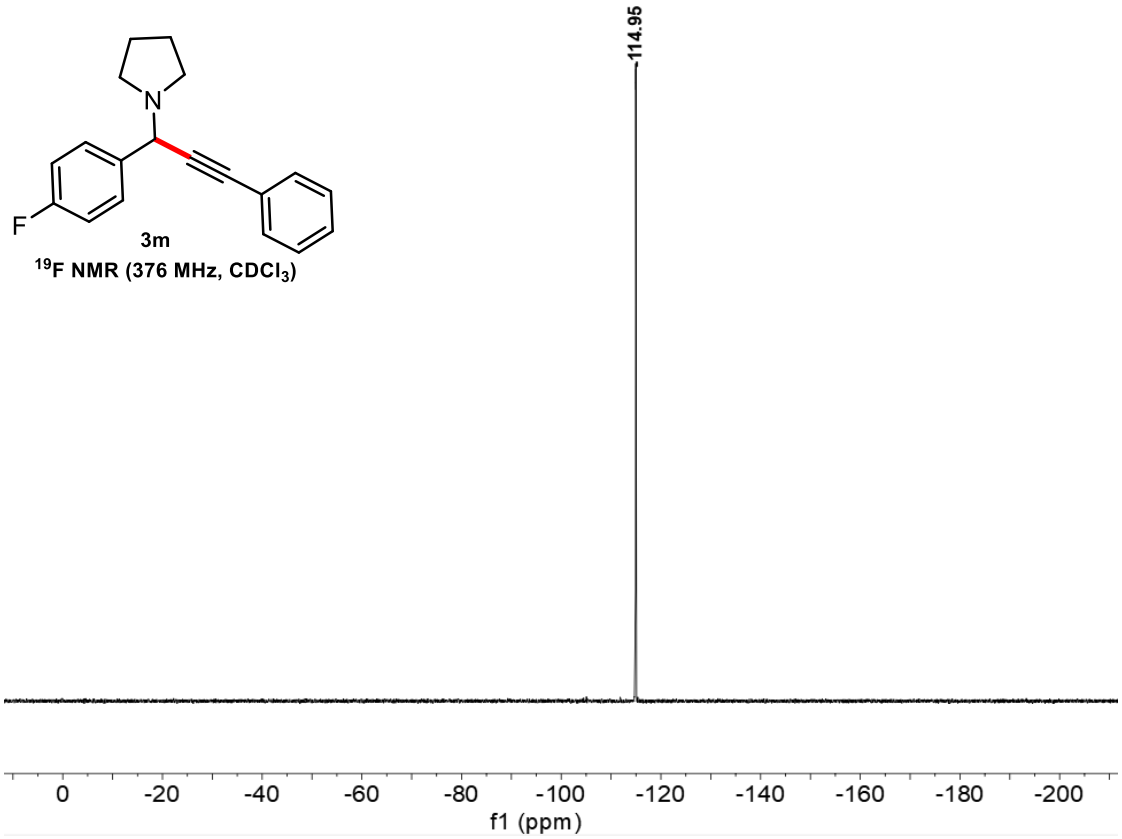


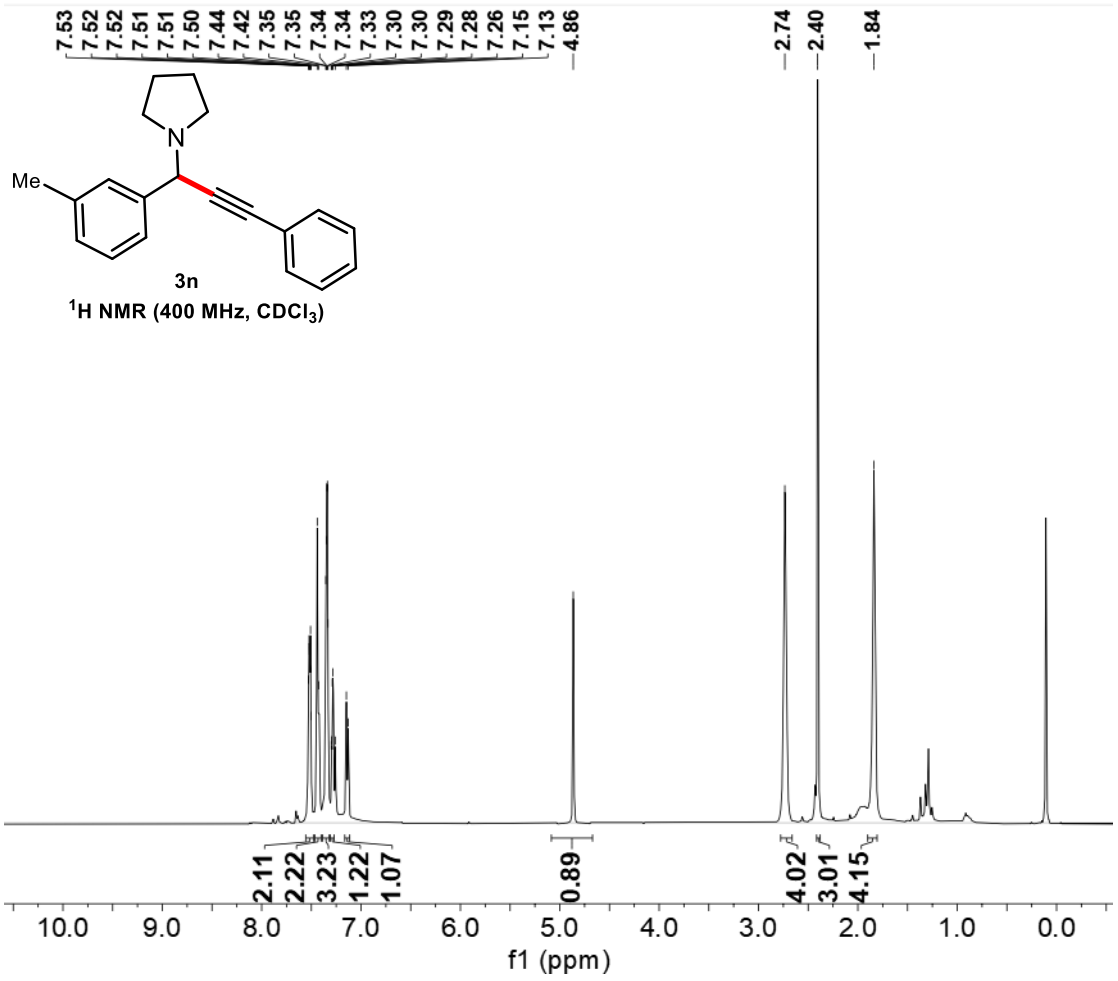
3l

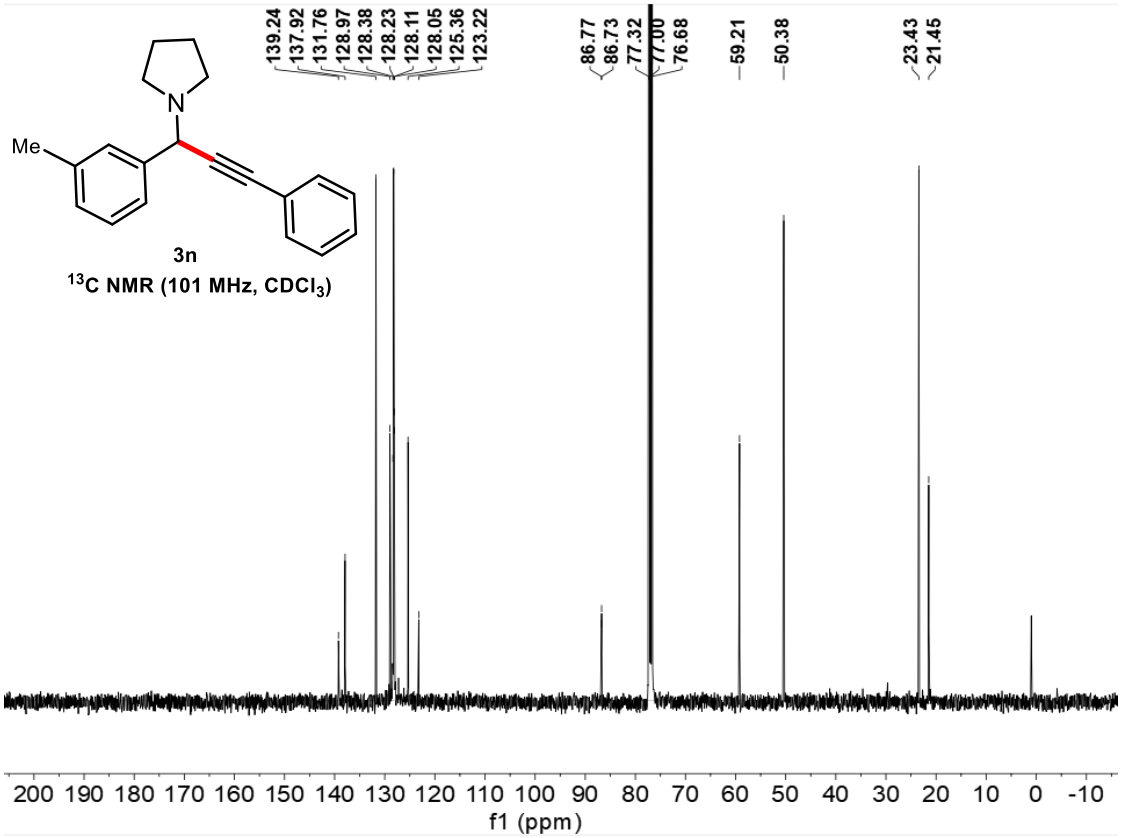
^{13}C NMR (101 MHz, $CDCl_3$)

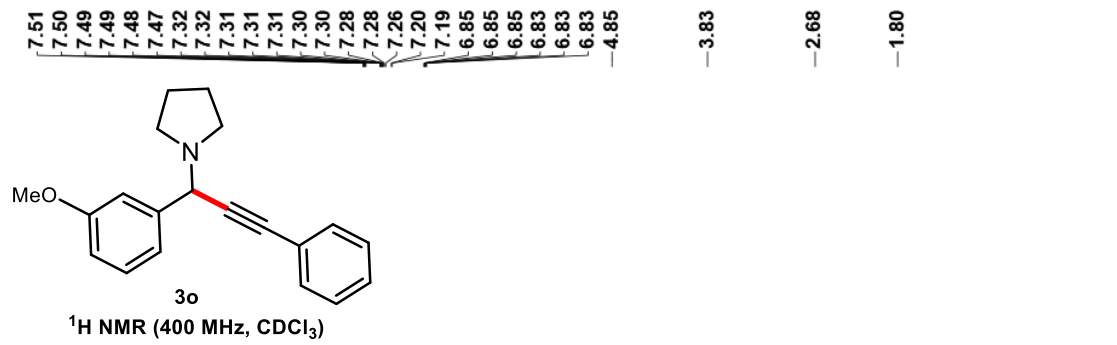

7.60
7.59
7.58
7.57
7.50
7.49
7.49
7.49
7.48
7.48
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.26
7.07
7.06
7.04
7.03
7.02
7.01
4.88
2.68
2.67
1.84
1.82
1.81
1.79
1.77
N
F
3m
^{1}H NMR (400 MHz, CDCl$_3$)
1.98
2.07
3.00
2.10
1.00
4.27
4.24
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


163.43
160.99
135.32
131.76
129.85
129.76
128.28
128.19
123.01
115.12
114.90
87.15
86.26
77.32
77.00
76.68
58.30
50.12
23.45
N
F
3m
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
F
3m
^{19}F NMR (376 MHz, CDCl$_3$)
114.95
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

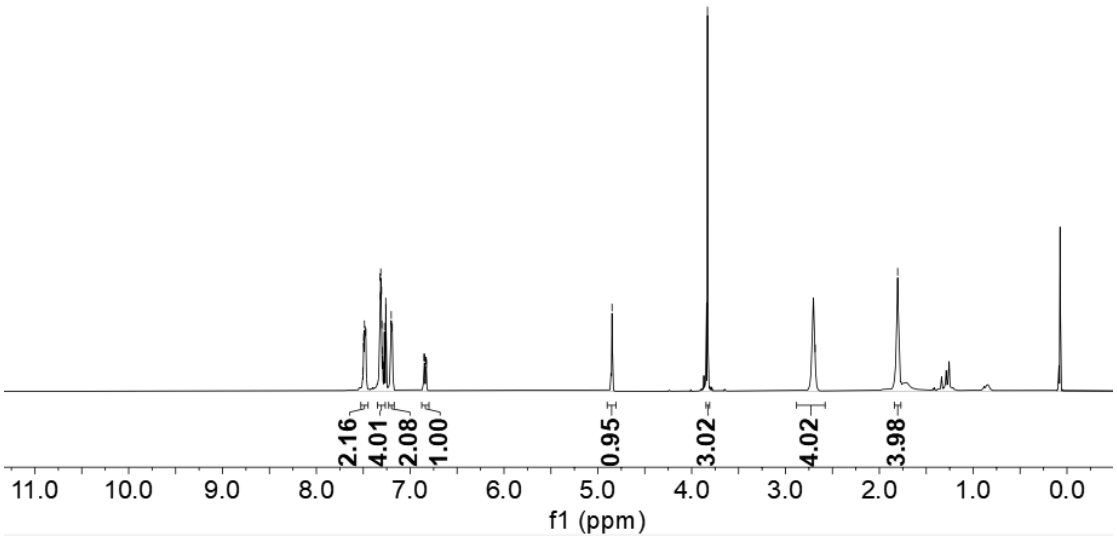

7.53
7.52
7.52
7.51
7.51
7.50
7.44
7.42
7.35
7.35
7.34
7.34
7.33
7.30
7.30
7.29
7.28
7.26
7.15
7.13
4.86
2.74
2.40
1.84
Me
N
3n
^{1}H NMR (400 MHz, CDCl$_3$)
2.11
2.22
3.23
1.22
1.07
0.89
4.02
3.01
4.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

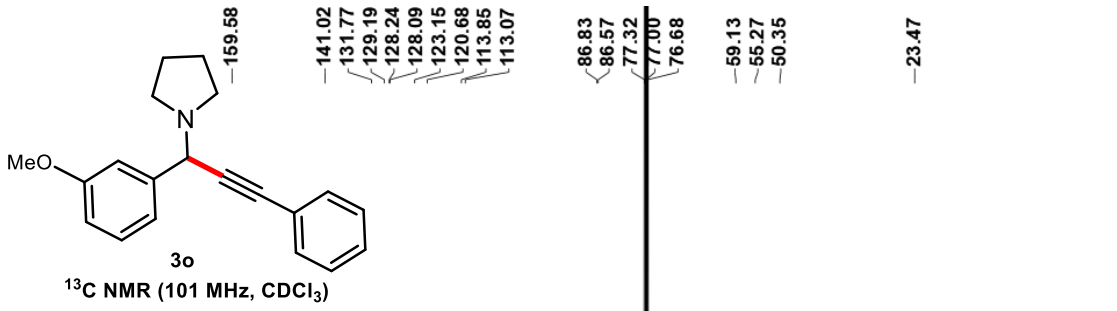

139.24
137.92
131.76
128.97
128.38
128.23
128.11
128.05
125.36
123.22
86.77
86.73
77.32
77.00
76.68
59.21
50.38
23.43
21.45
Me
N
3n
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3o

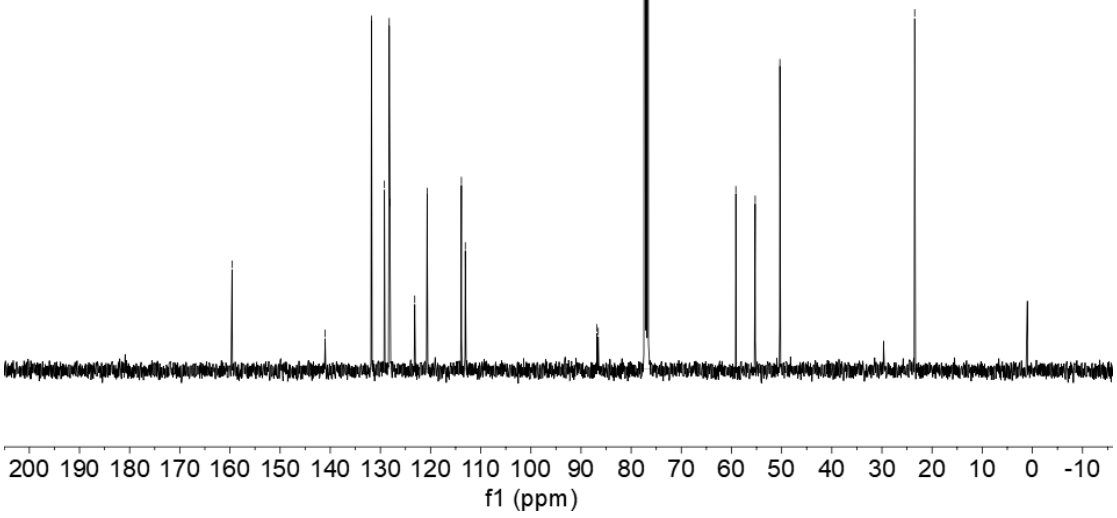
^{1}H NMR (400 MHz, $CDCl_3$)

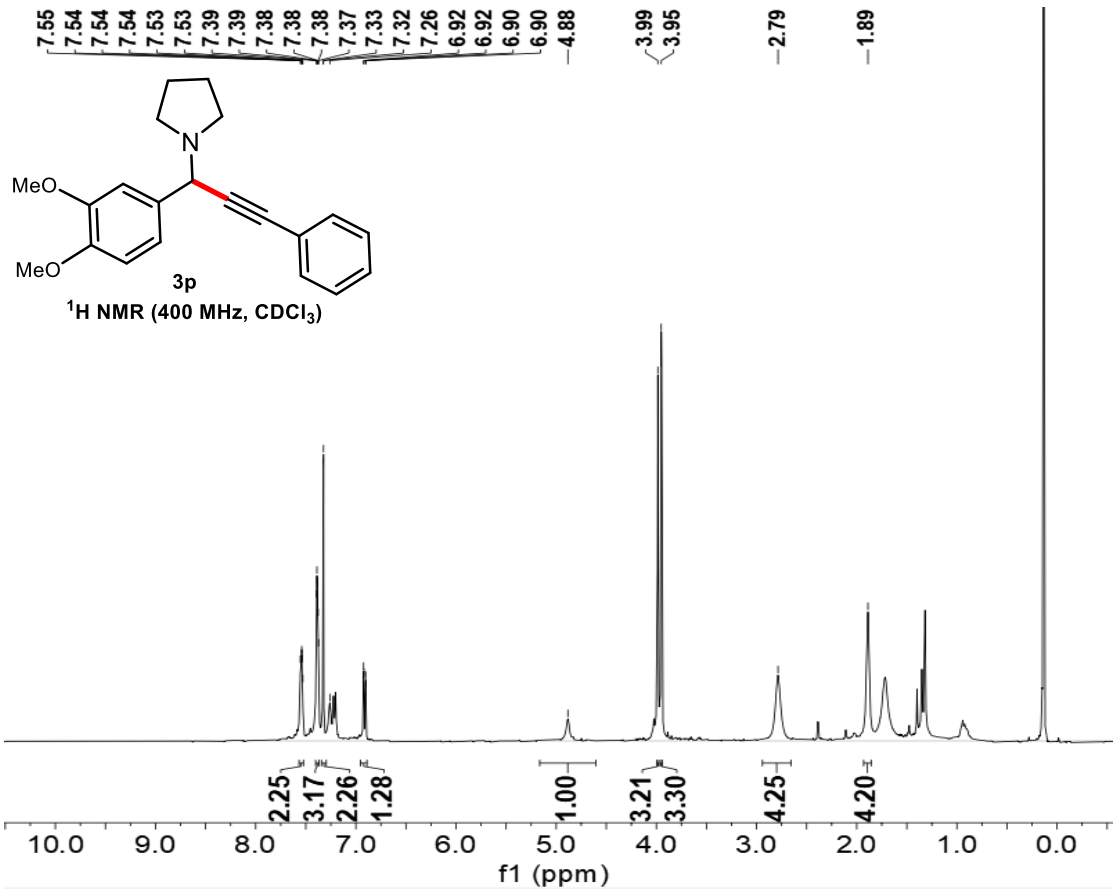


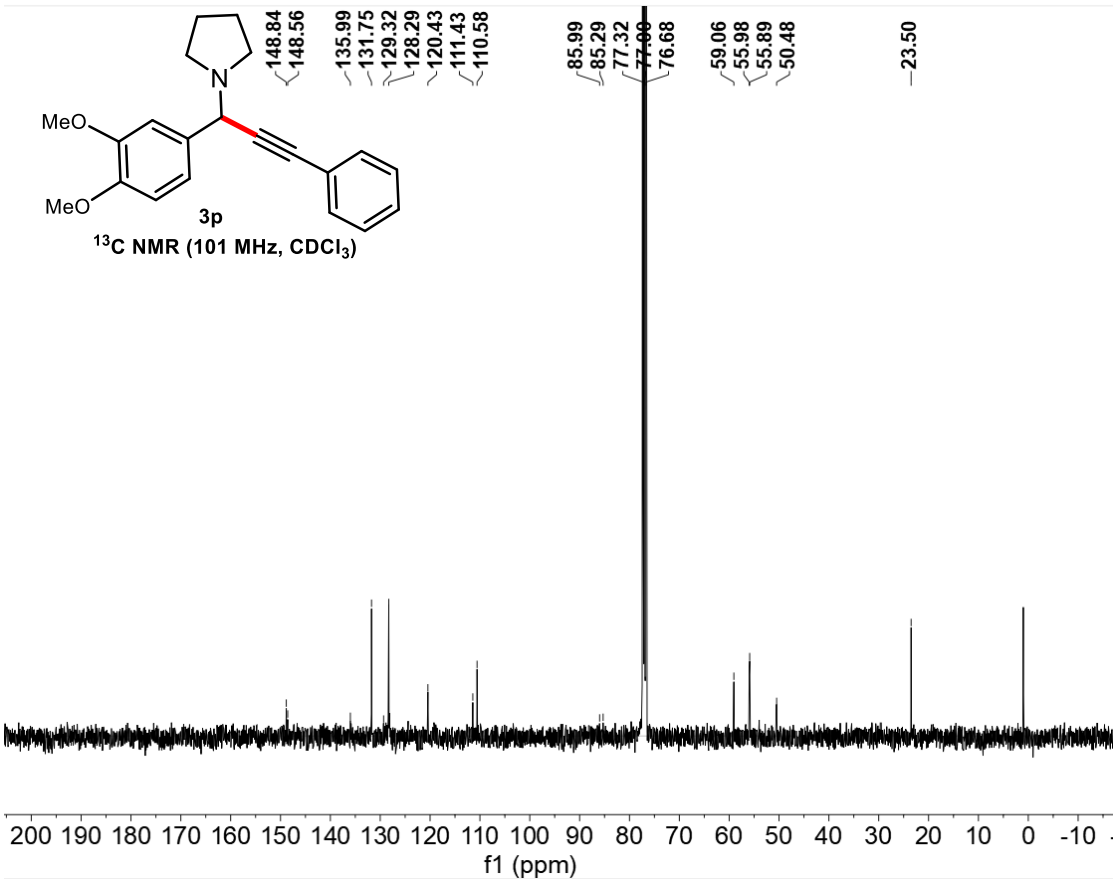


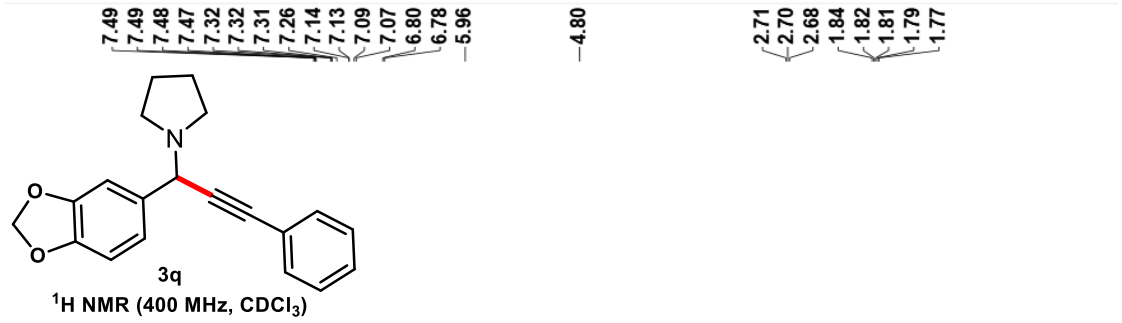
3o

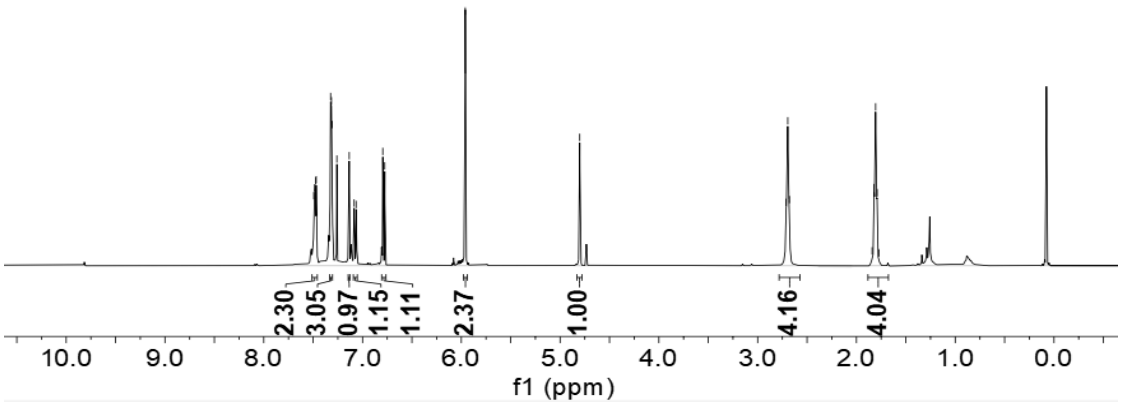
^{13}C NMR (101 MHz, $CDCl_3$)

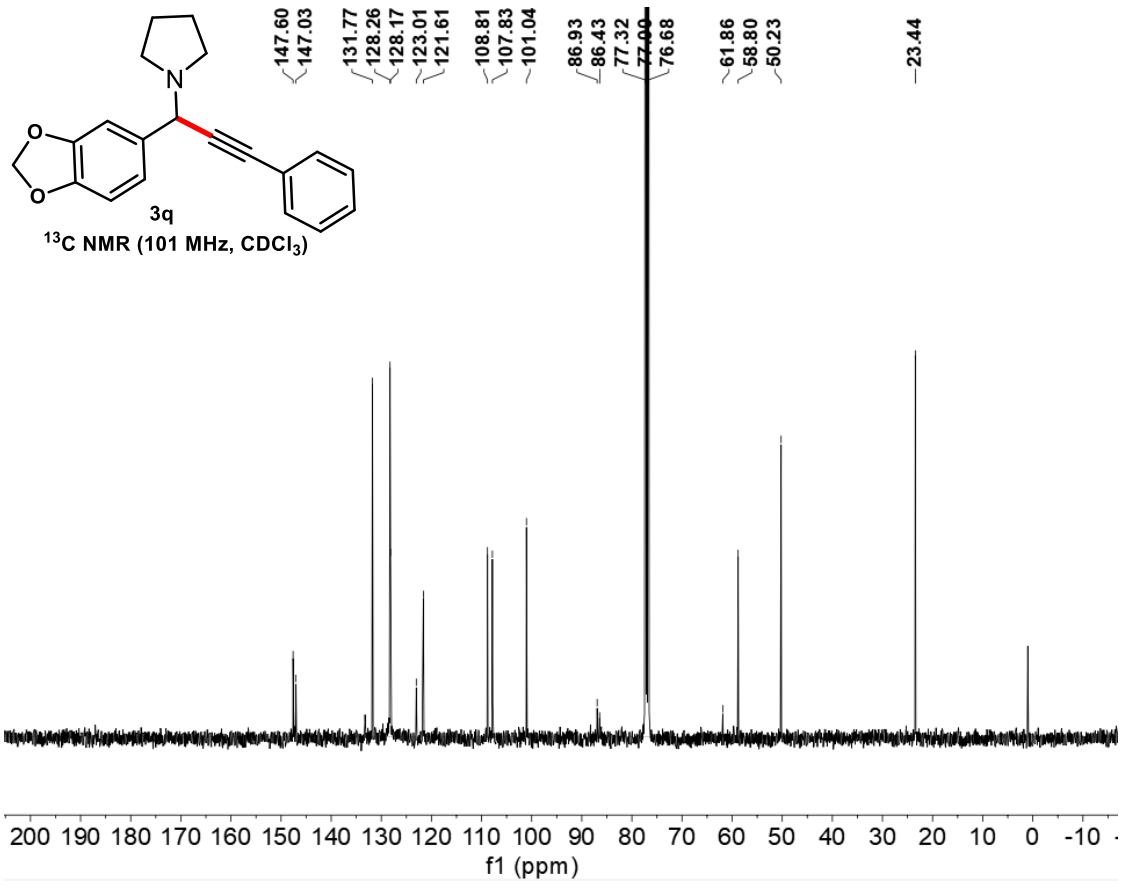


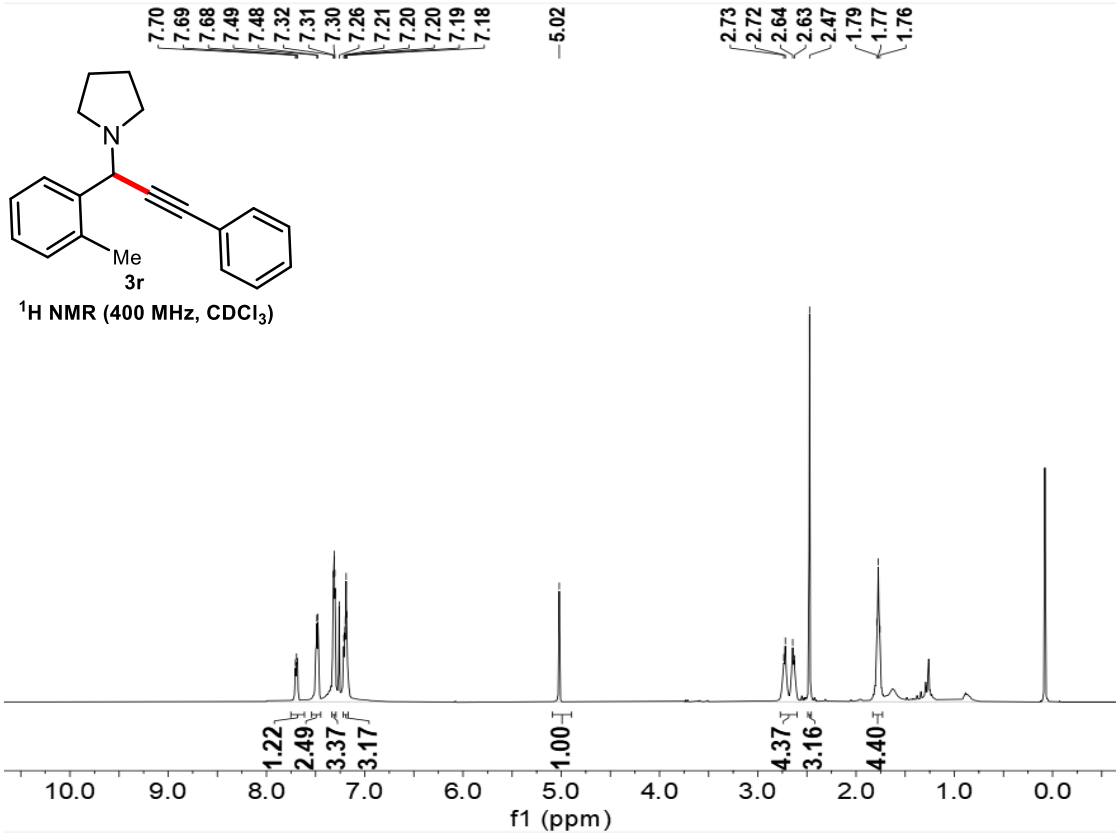

7.55
7.54
7.54
7.54
7.53
7.53
7.39
7.39
7.38
7.38
7.38
7.37
7.33
7.32
7.26
6.92
6.92
6.90
6.90
4.88
3.99
3.95
2.79
1.89
MeO
MeO
N
3p
^{1}H NMR (400 MHz, CDCl$_3$)
2.25
3.17
2.26
1.28
1.00
3.21
3.30
4.25
4.20
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

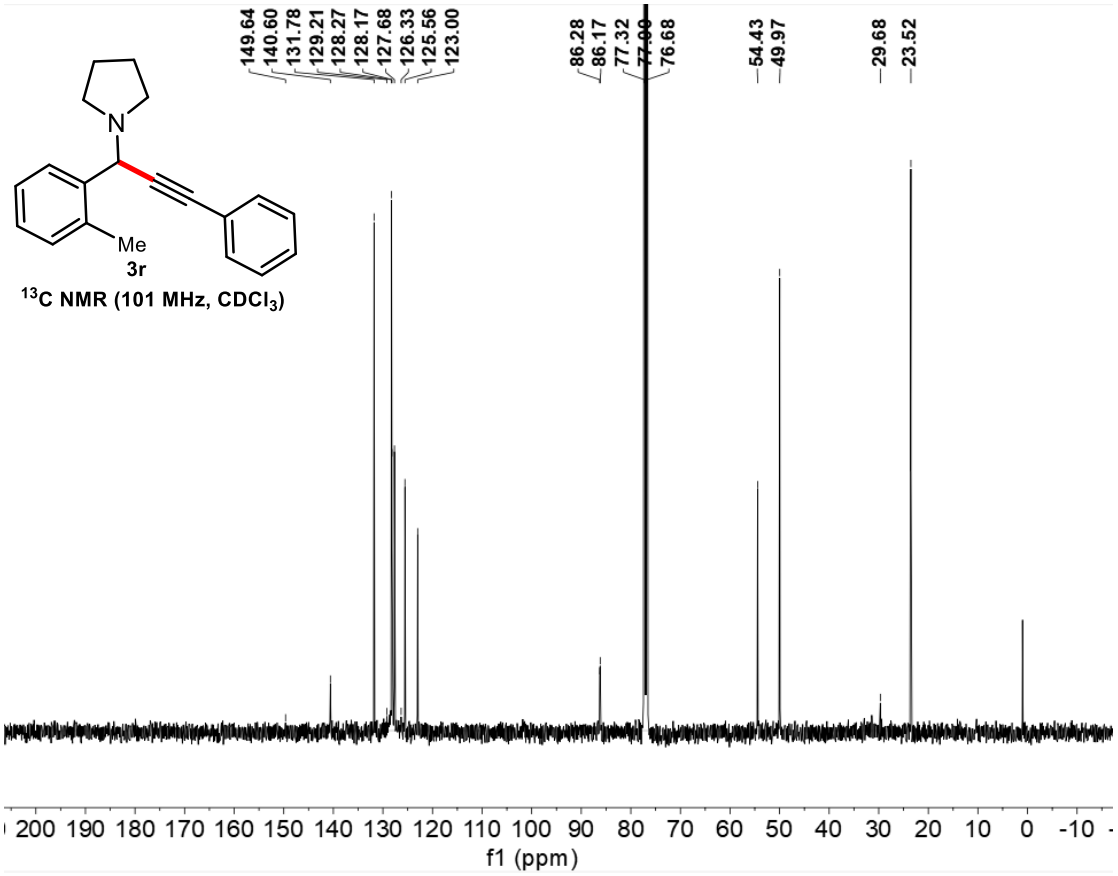

148.84
148.56
135.99
131.75
129.32
128.29
120.43
111.43
110.58
85.99
85.29
77.32
77.00
76.68
59.06
55.98
55.89
50.48
23.50
MeO
MeO
N
3p
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

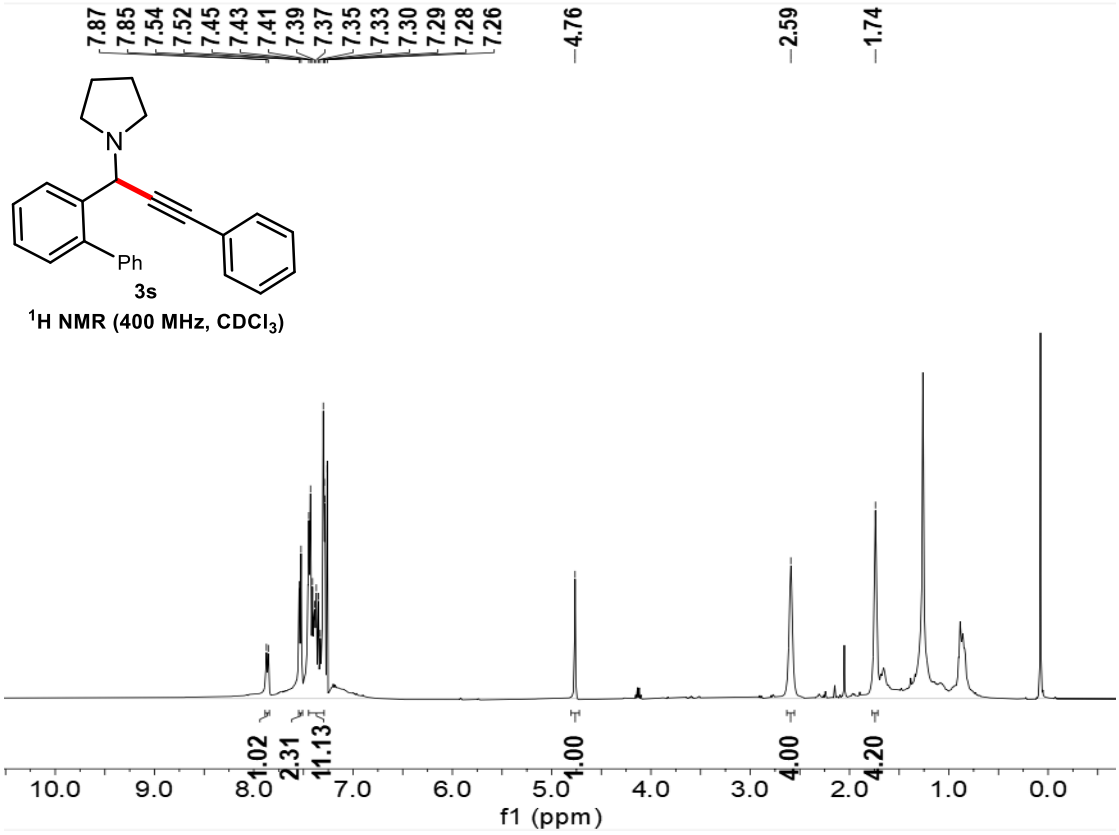

7.49
7.49
7.48
7.47
7.32
7.32
7.31
7.26
7.14
7.13
7.09
7.07
6.80
6.78
5.96
4.80
2.71
2.70
2.68
1.84
1.82
1.81
1.79
1.77
N
O
O
3q
^{1}H NMR (400 MHz, CDCl$_3$)

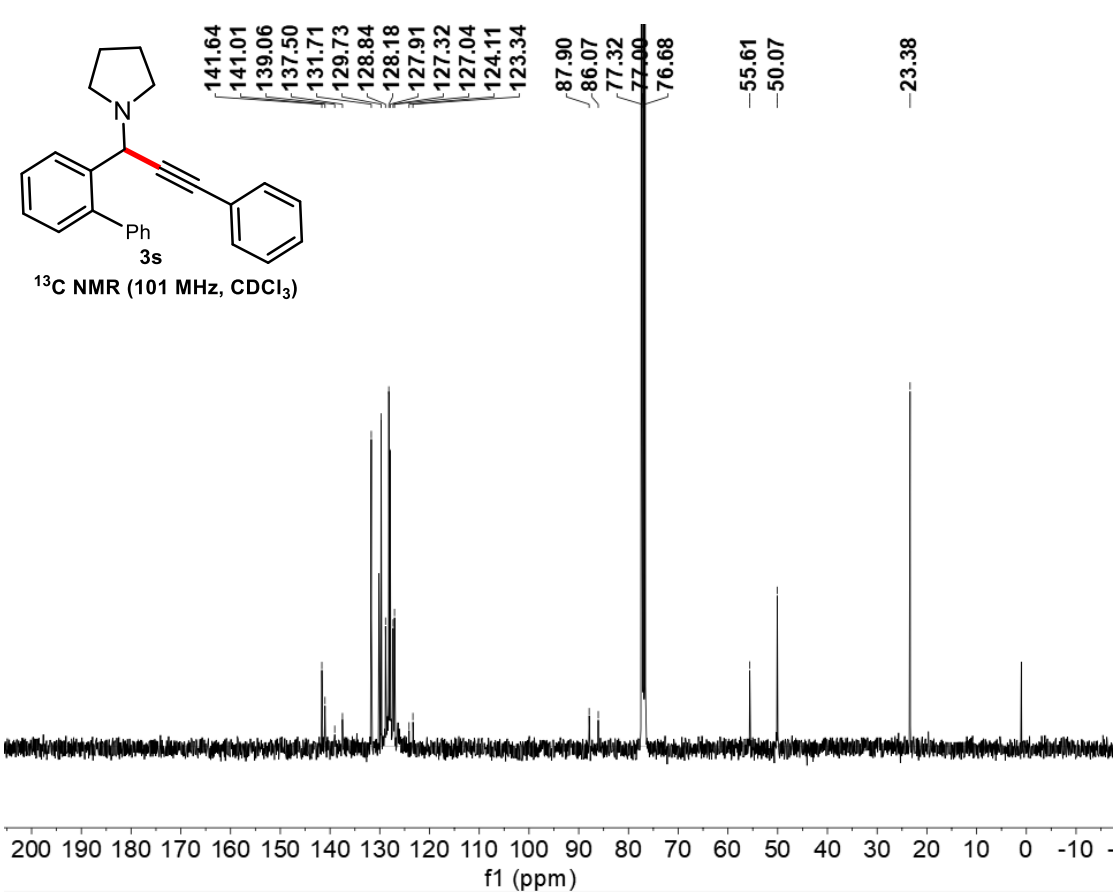

2.30
3.05
0.97
1.15
1.11
2.37
1.00
4.16
4.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

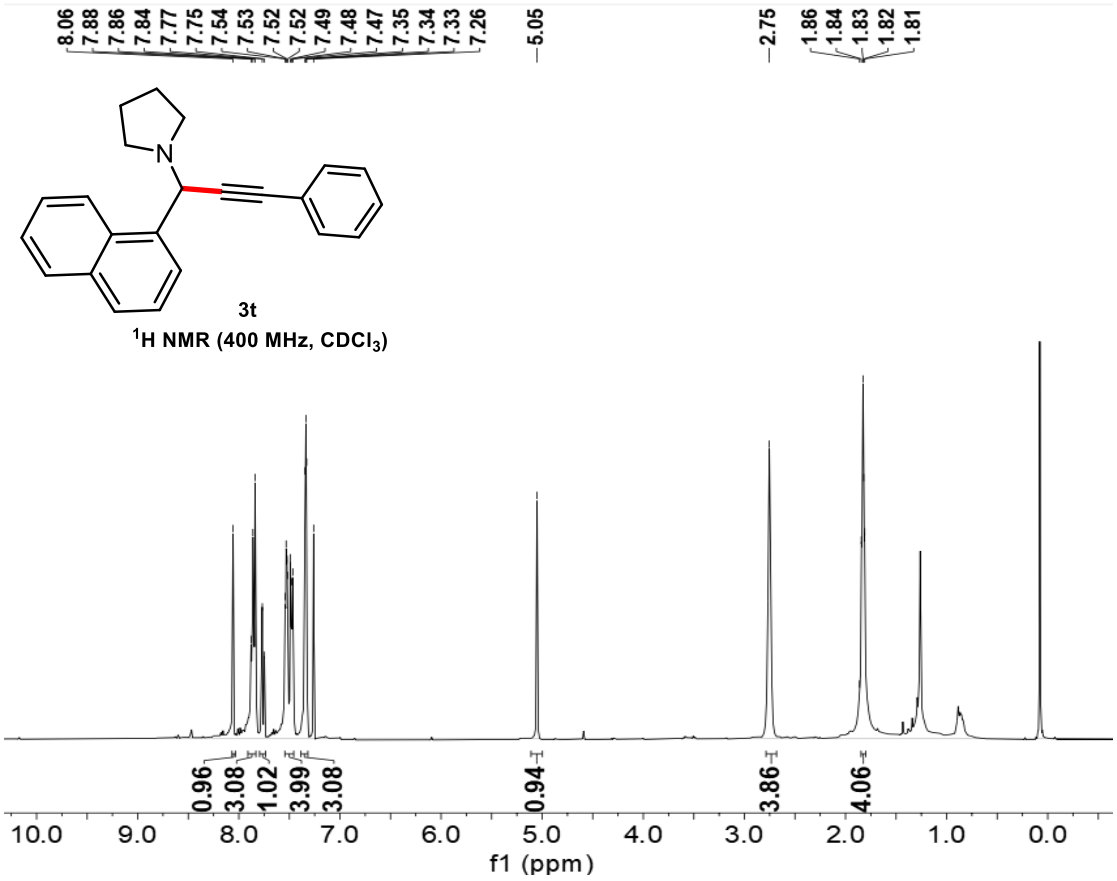

147.60
147.03
131.77
128.26
128.17
123.01
121.61
108.81
107.83
101.04
86.93
86.43
77.32
77.00
76.68
61.86
58.80
50.23
23.44
N
O
O
3q
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

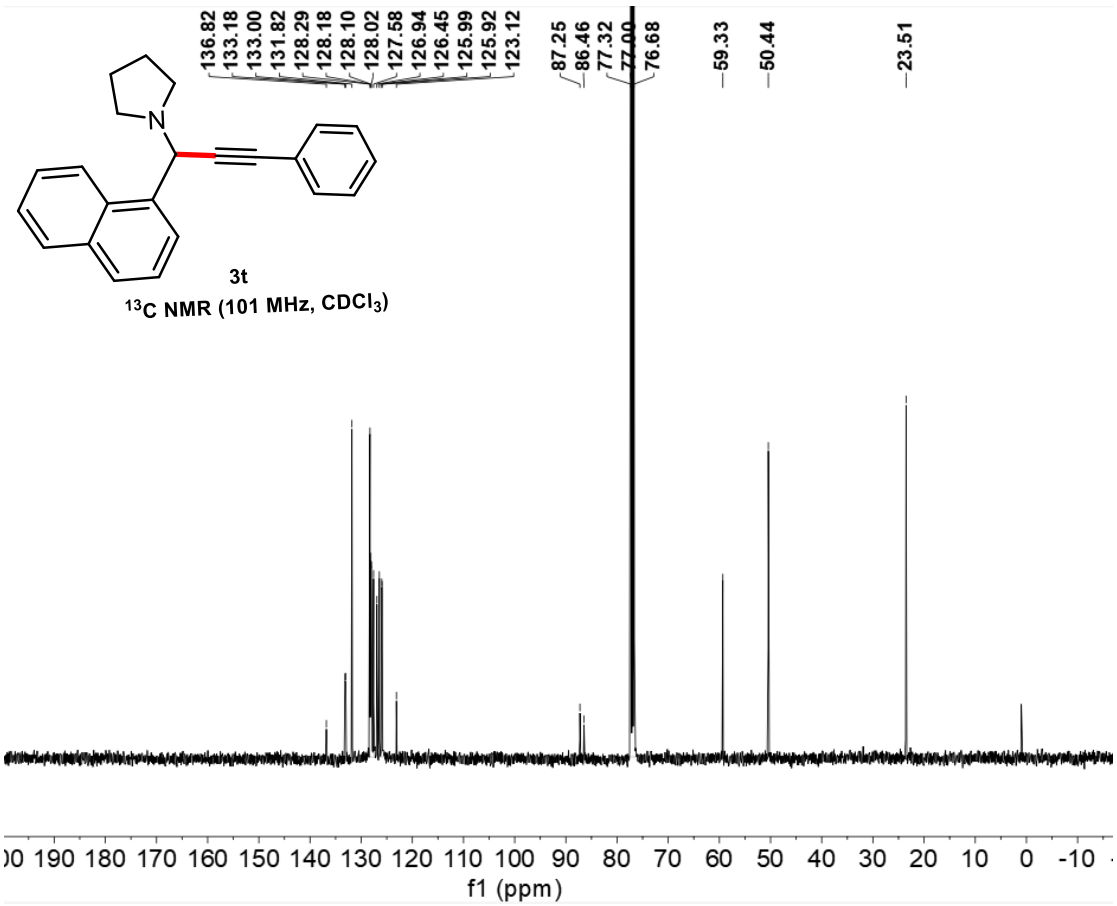

7.70
7.69
7.68
7.49
7.48
7.32
7.31
7.30
7.26
7.21
7.20
7.20
7.19
7.18
5.02
2.73
2.72
2.64
2.63
2.47
1.79
1.77
1.76
N
Me
3r
^{1}H NMR (400 MHz, CDCl$_3$)
1.22
2.49
3.37
3.17
1.00
4.37
3.16
4.40
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

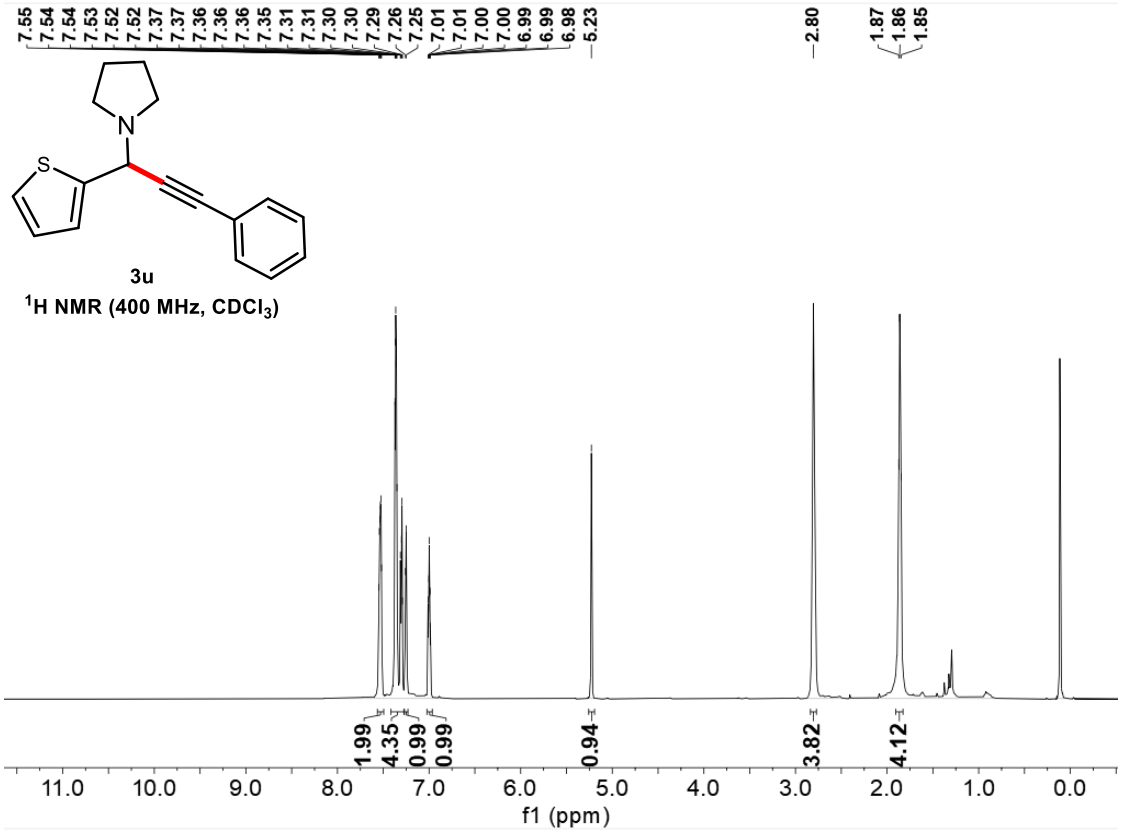

149.64
140.60
131.78
129.21
128.27
128.17
127.68
126.33
125.56
123.00
86.28
86.17
77.32
77.00
76.68
54.43
49.97
29.68
23.52
N
Me
3r
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

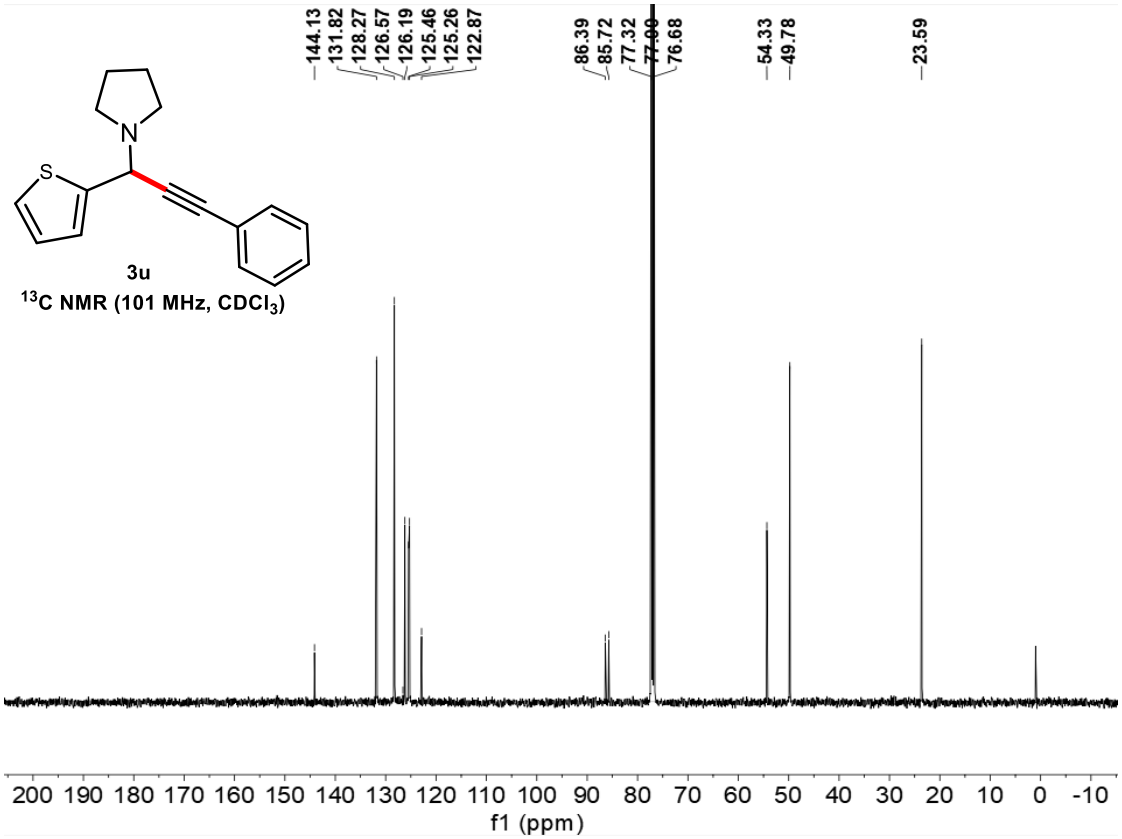

7.87
7.85
7.54
7.52
7.45
7.43
7.41
7.39
7.37
7.35
7.33
7.30
7.29
7.28
7.26
4.76
2.59
1.74
N
Ph
3s
^{1}H NMR (400 MHz, CDCl$_3$)
1.02
2.31
11.13
1.00
4.00
4.20
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

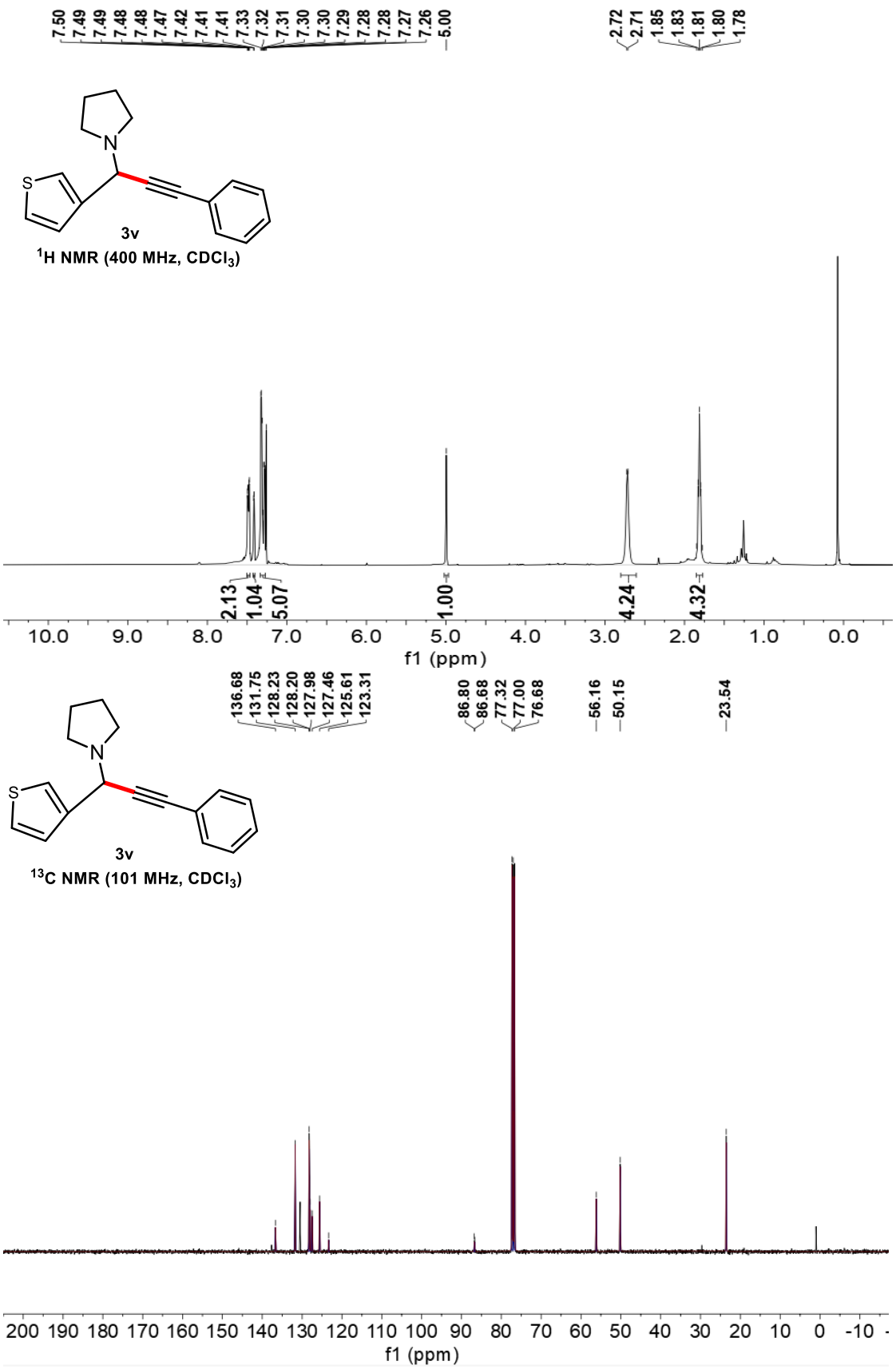

141.64
141.01
139.06
137.50
131.71
129.73
128.84
128.18
127.91
127.32
127.04
124.11
123.34
87.90
86.07
77.32
77.00
76.68
55.61
50.07
23.38
N
Ph
3s
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

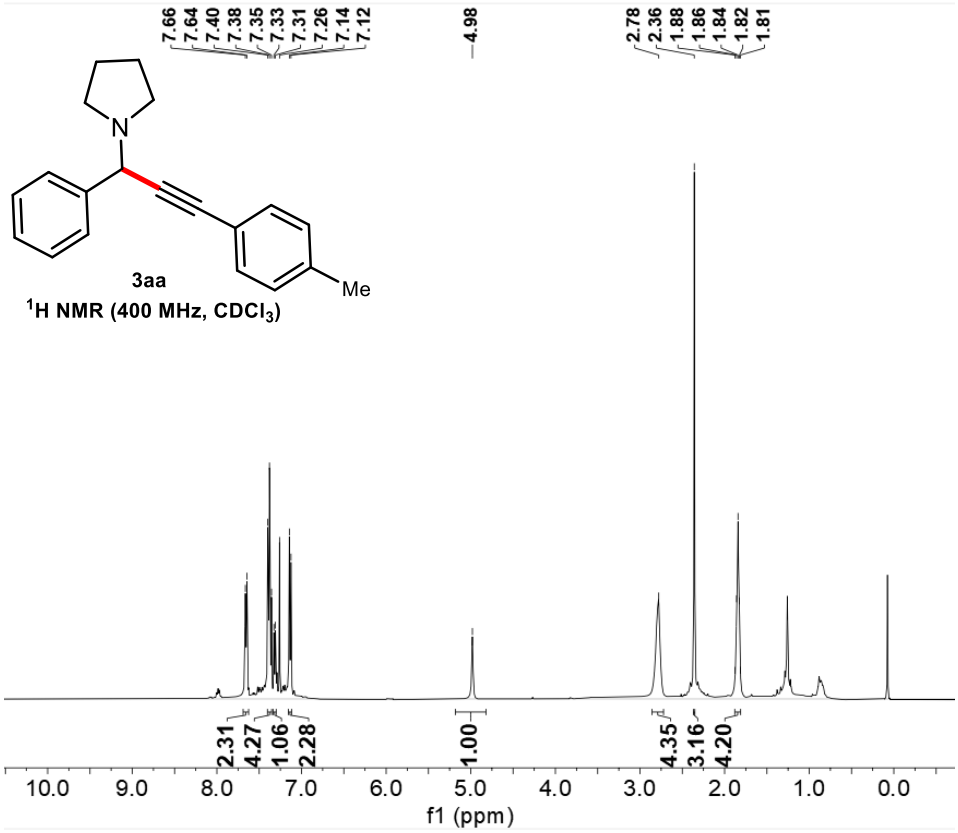

8.06
7.88
7.86
7.84
7.77
7.75
7.54
7.53
7.52
7.52
7.49
7.48
7.47
7.35
7.34
7.33
7.26
5.05
2.75
1.86
1.84
1.83
1.82
1.81
N
3t
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
3.08
1.02
3.99
3.08
0.94
3.86
4.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

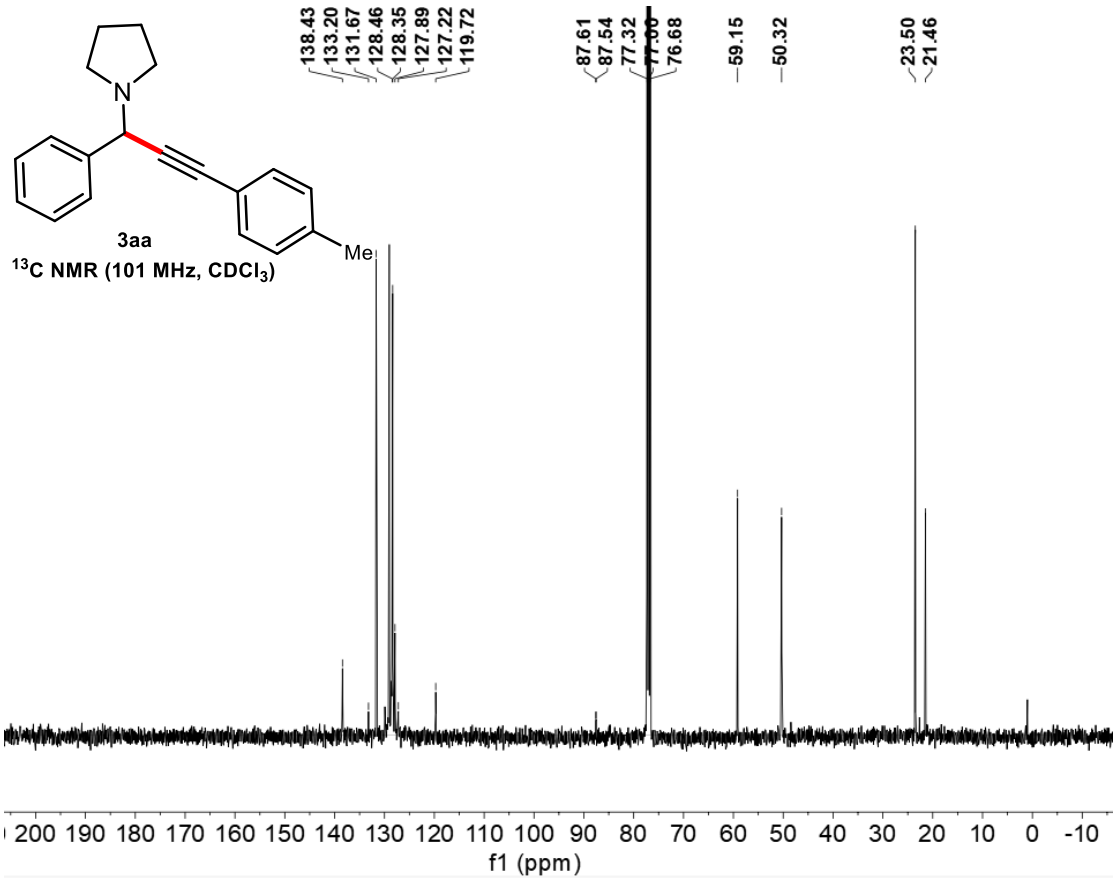

136.82
133.18
133.00
131.82
128.29
128.18
128.10
128.02
127.58
126.94
126.45
125.99
125.92
123.12
87.25
86.46
77.32
77.00
76.68
59.33
50.44
23.51
N
3t
^{13}C NMR (101 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

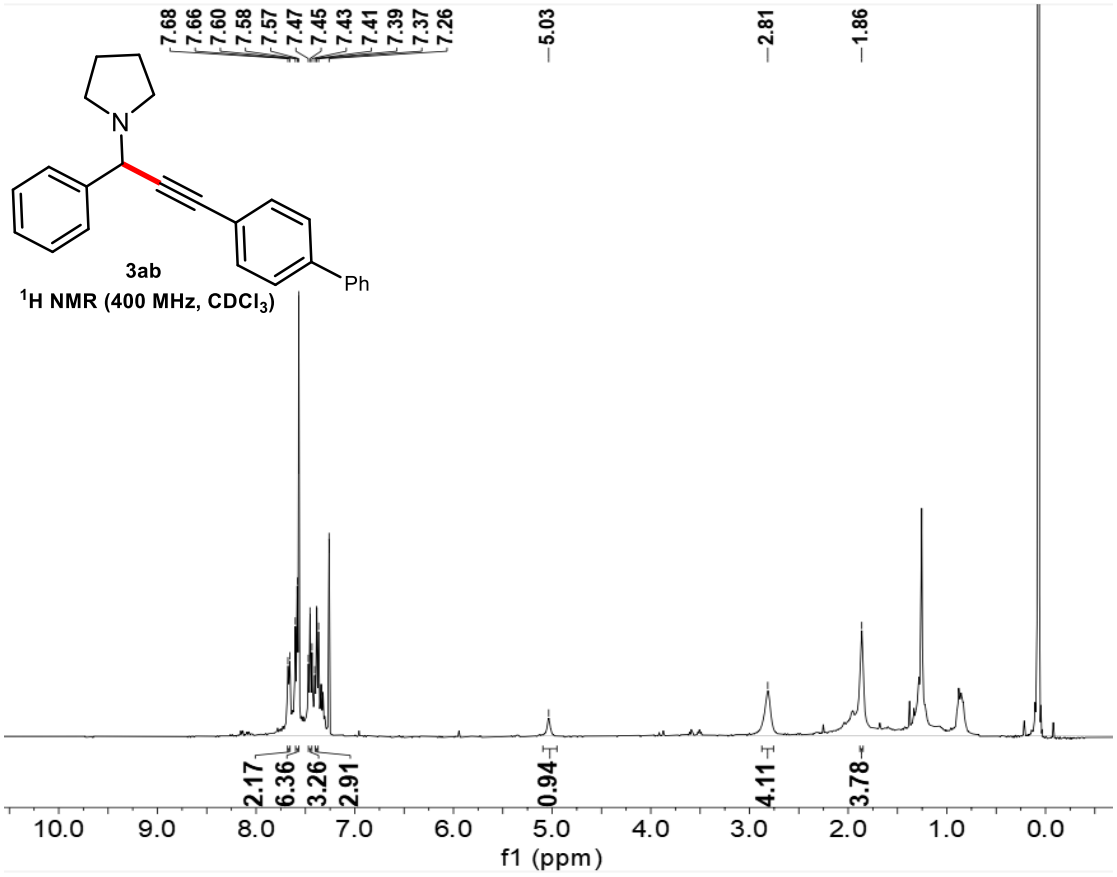

7.55
7.54
7.54
7.53
7.52
7.52
7.37
7.37
7.36
7.36
7.36
7.35
7.31
7.31
7.30
7.30
7.29
7.26
7.25
7.01
7.01
7.00
7.00
6.99
6.99
6.98
5.23
2.80
1.87
1.86
1.85
N
S
3u
^{1}H NMR (400 MHz, CDCl$_3$)
1.99
4.35
0.99
0.99
0.94
3.82
4.12
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

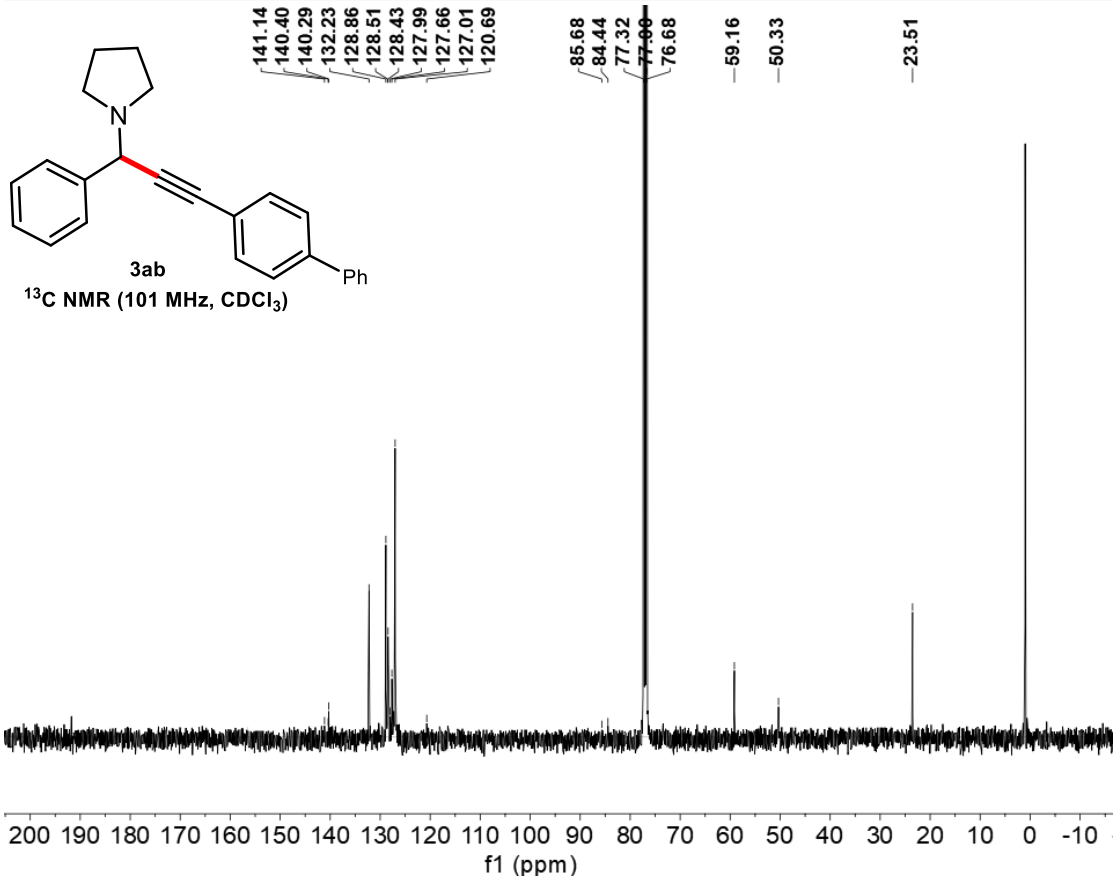

144.13
131.82
128.27
126.57
126.19
125.46
125.26
122.87
86.39
85.72
77.32
77.00
76.68
54.33
49.78
23.59
N
S
3u
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

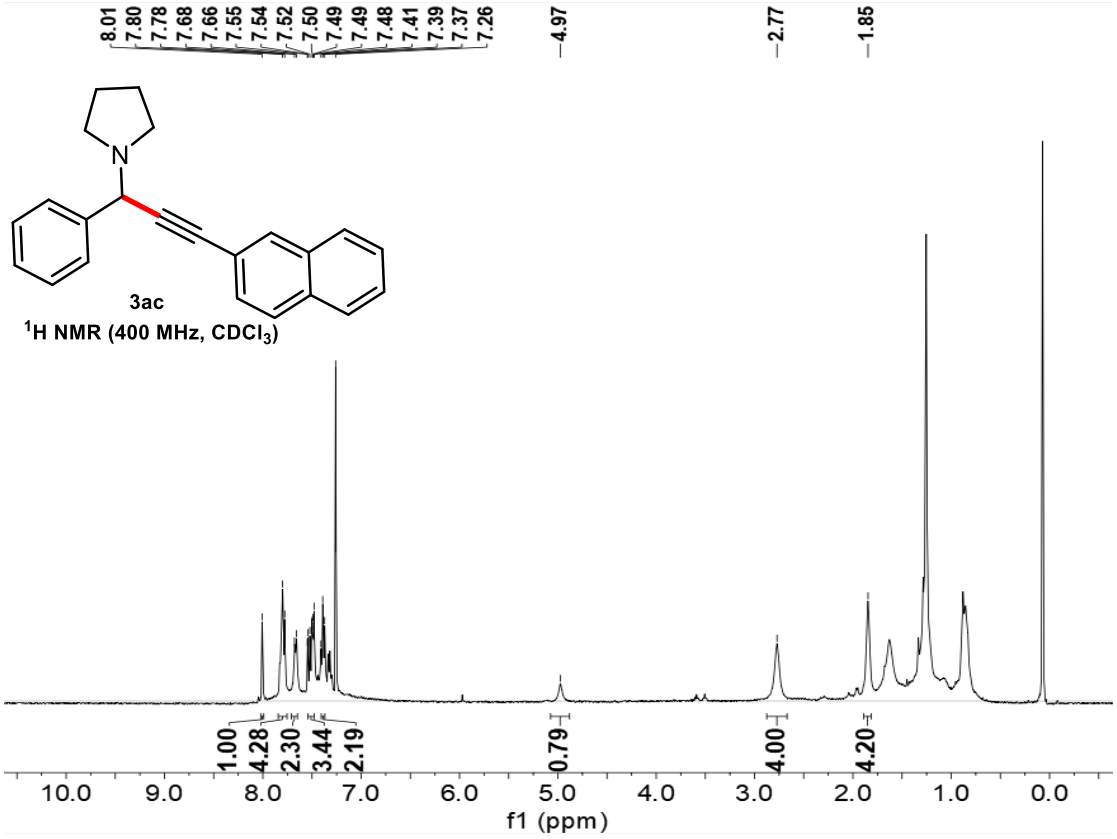

7.50
7.49
7.49
7.48
7.48
7.47
7.42
7.41
7.41
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
5.00
2.72
2.71
1.85
1.83
1.81
1.80
1.78
N
S
3v
^{1}H NMR (400 MHz, CDCl$_3$)
2.13
1.04
5.07
1.00
4.24
4.32
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
136.68
131.75
128.23
128.20
127.98
127.46
125.61
123.31
86.80
86.68
77.32
77.00
76.68
56.16
50.15
23.54
N
S
3v
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

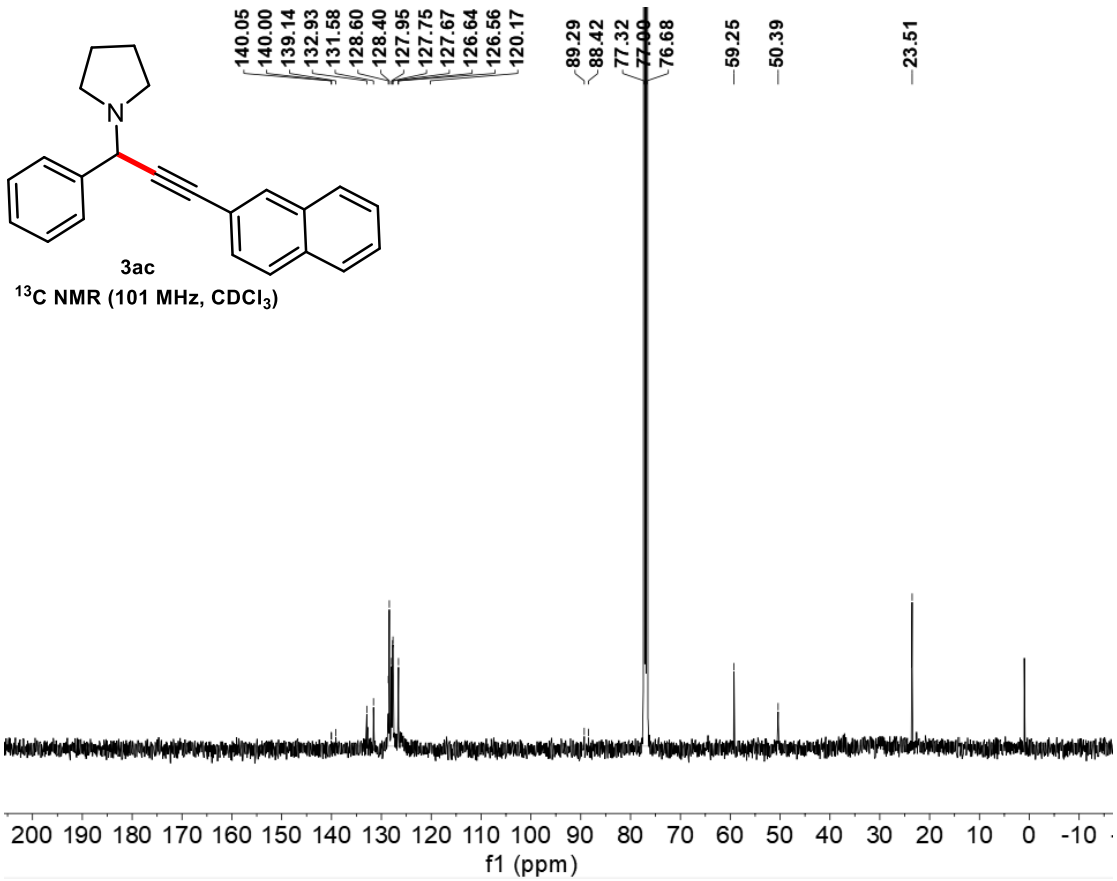

7.66
7.64
7.40
7.38
7.35
7.33
7.31
7.26
7.14
7.12
4.98
2.78
2.36
1.88
1.86
1.84
1.82
1.81
N
Me
3aa
^{1}H NMR (400 MHz, CDCl$_3$)
2.31
4.27
1.06
2.28
1.00
4.35
3.16
4.20
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

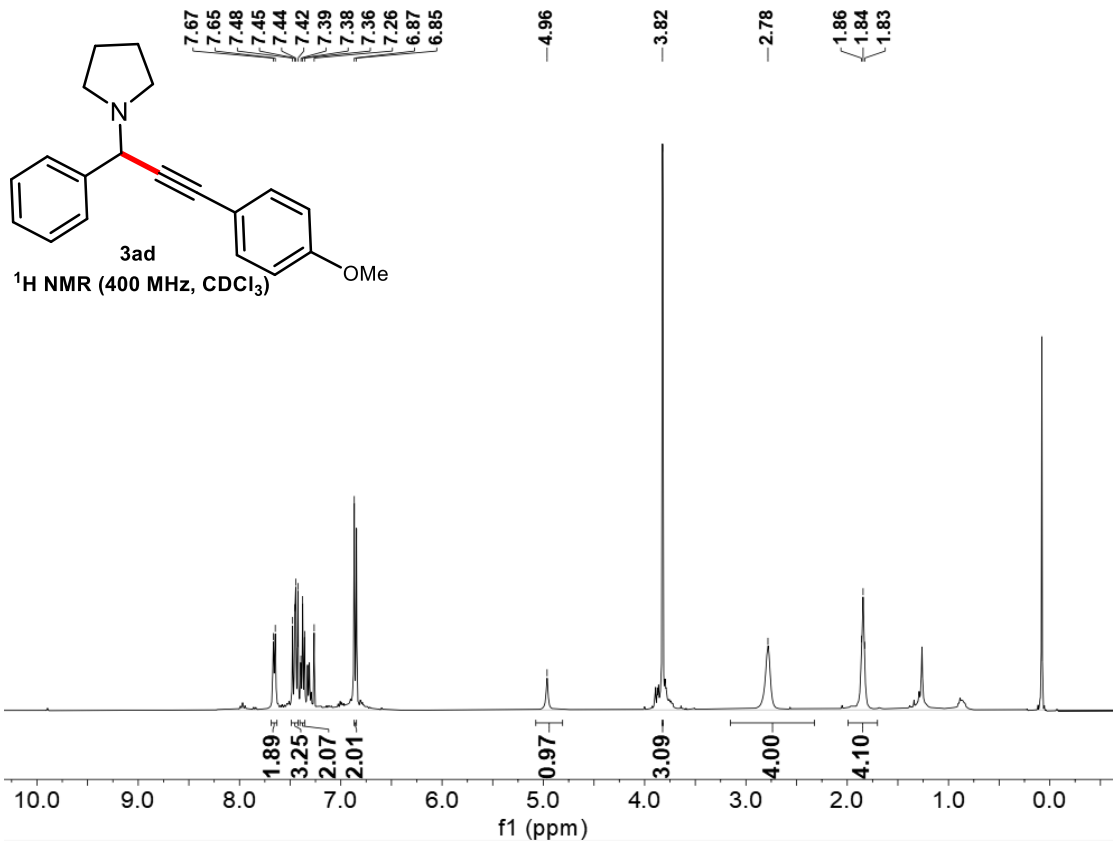

138.43
133.20
131.67
128.46
128.35
127.89
127.22
119.72
87.61
87.54
77.32
77.00
76.68
59.15
50.32
23.50
21.46
N
Me
3aa
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

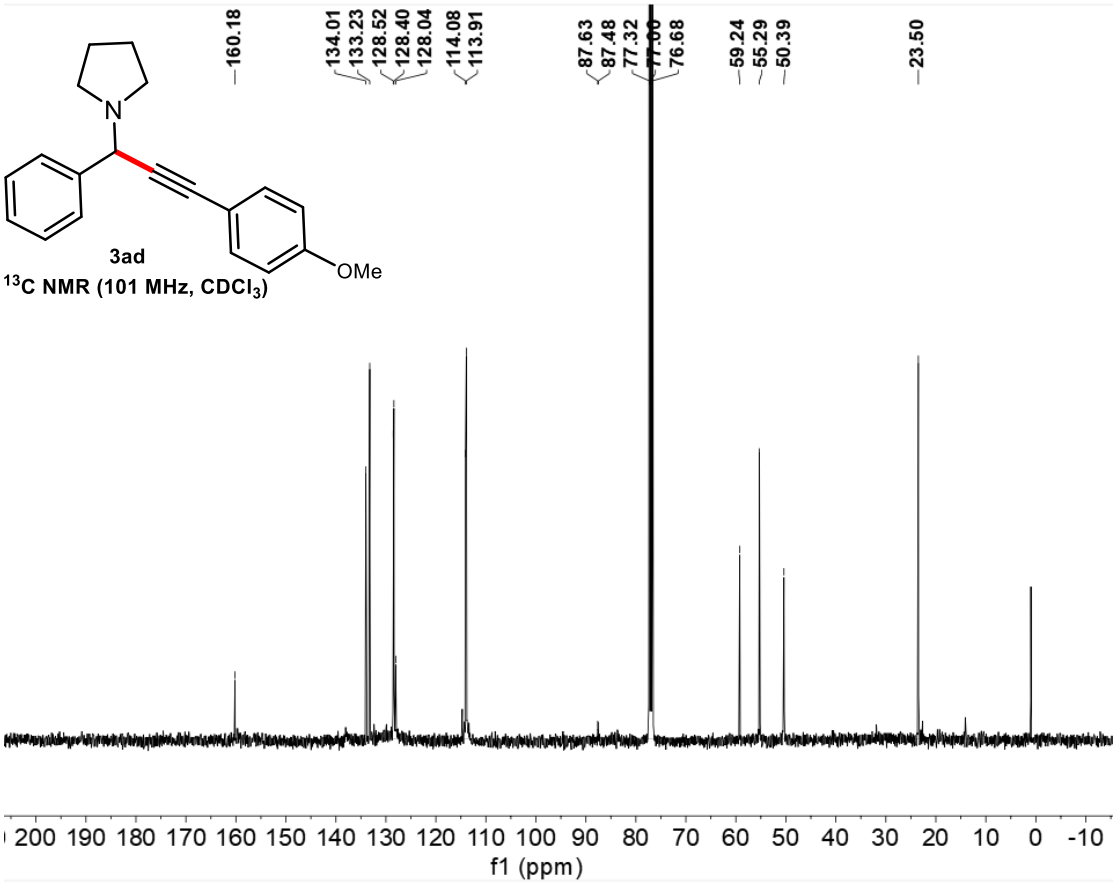

7.68
7.66
7.60
7.58
7.57
7.47
7.45
7.43
7.41
7.39
7.37
7.26
5.03
2.81
1.86
N
Ph
3ab
^{1}H NMR (400 MHz, CDCl$_3$)
2.17
6.36
3.26
2.91
0.94
4.11
3.78
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

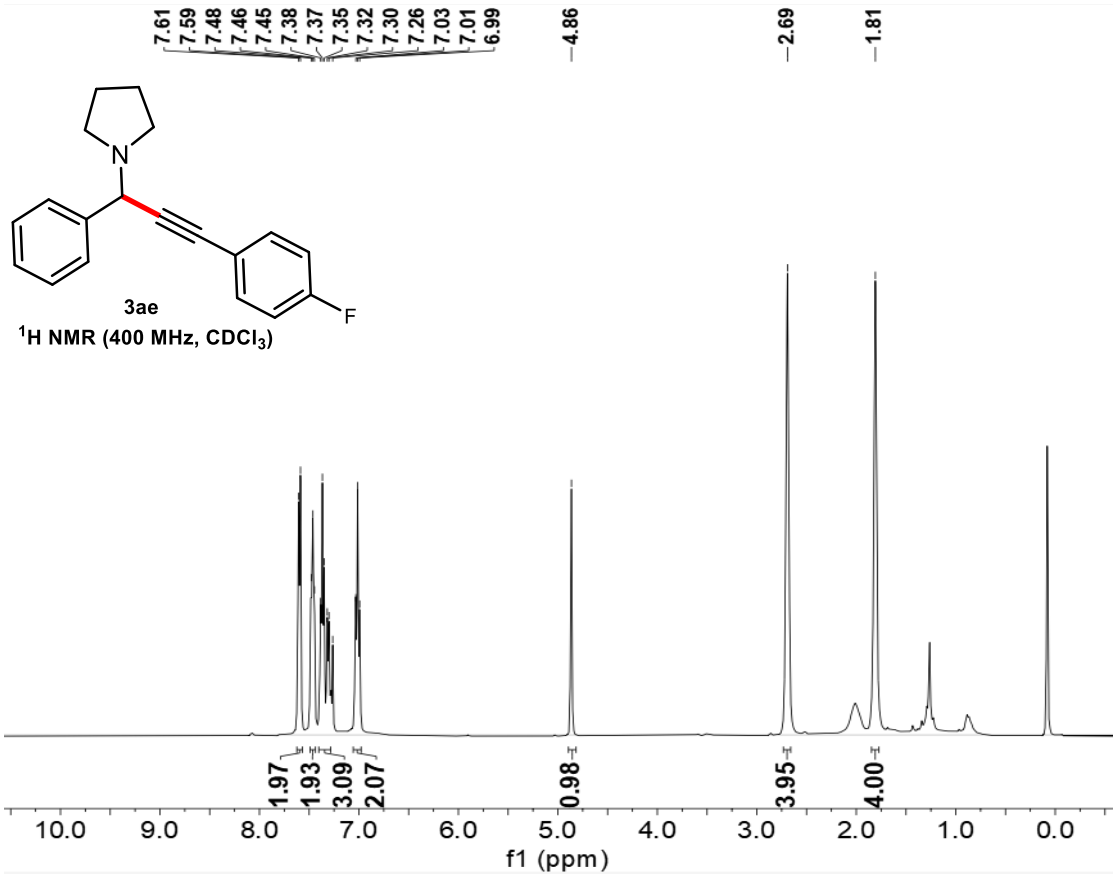

141.14
140.40
140.29
132.23
128.86
128.51
128.43
127.99
127.66
127.01
120.69
85.68
84.44
77.32
77.00
76.68
59.16
50.33
23.51
N
Ph
3ab
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

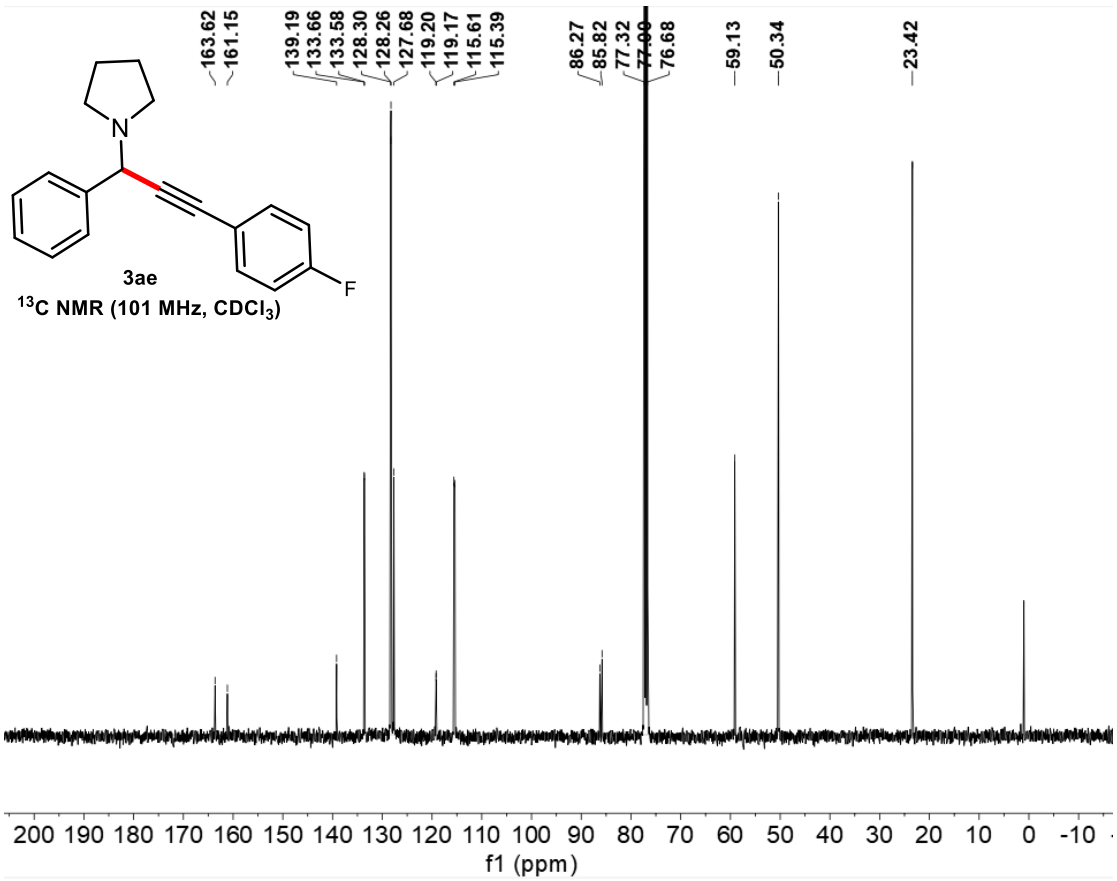

8.01
7.80
7.78
7.68
7.66
7.55
7.54
7.52
7.50
7.49
7.49
7.48
7.41
7.39
7.37
7.26
4.97
2.77
1.85
3ac
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
4.28
2.30
3.44
2.19
0.79
4.00
4.20
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

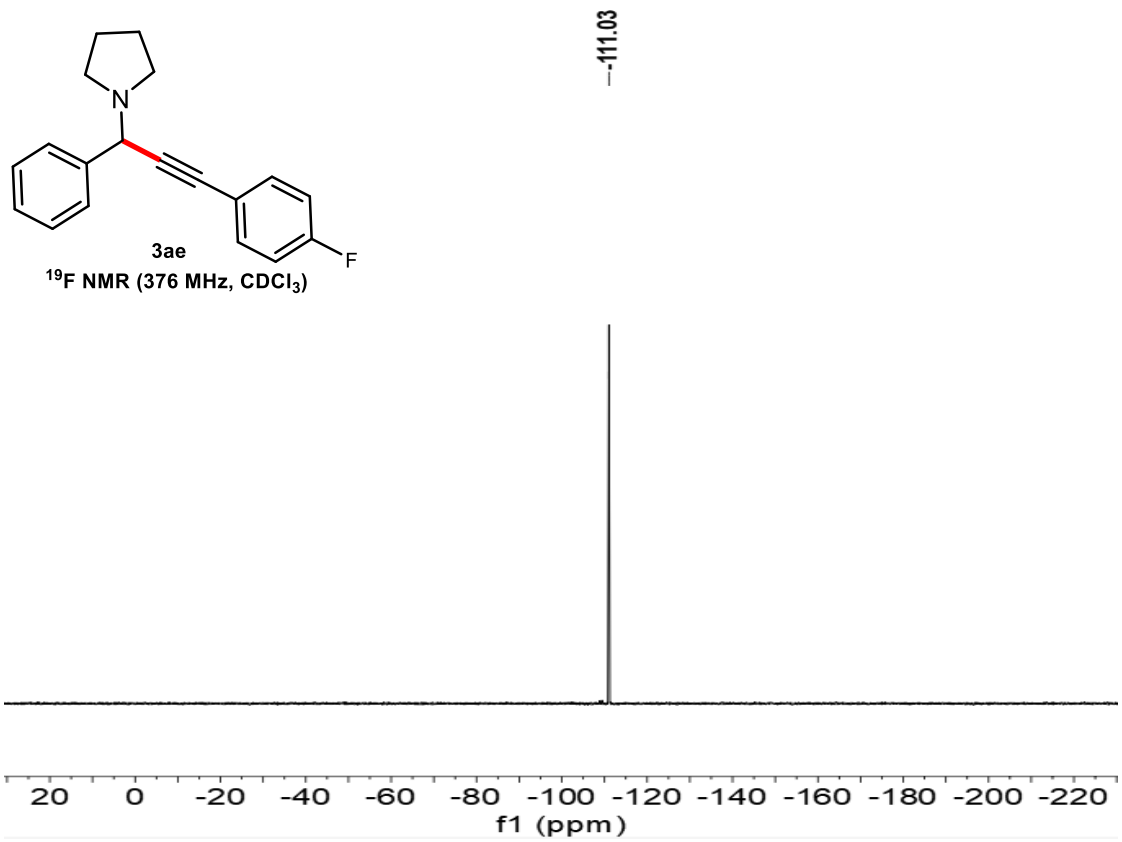

140.05
140.00
139.14
132.93
131.58
128.60
128.40
127.95
127.75
127.67
126.64
126.56
120.17
89.29
88.42
77.32
77.00
76.68
59.25
50.39
23.51
3ac
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.67
7.65
7.48
7.45
7.44
7.42
7.39
7.38
7.36
7.26
6.87
6.85
4.96
3.82
2.78
1.86
1.84
1.83
N
OMe
3ad
^{1}H NMR (400 MHz, CDCl$_3$)
1.89
3.25
2.07
2.01
0.97
3.09
4.00
4.10
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


160.18
134.01
133.23
128.52
128.40
128.04
114.08
113.91
87.63
87.48
77.32
77.00
76.68
59.24
55.29
50.39
23.50
N
OMe
3ad
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

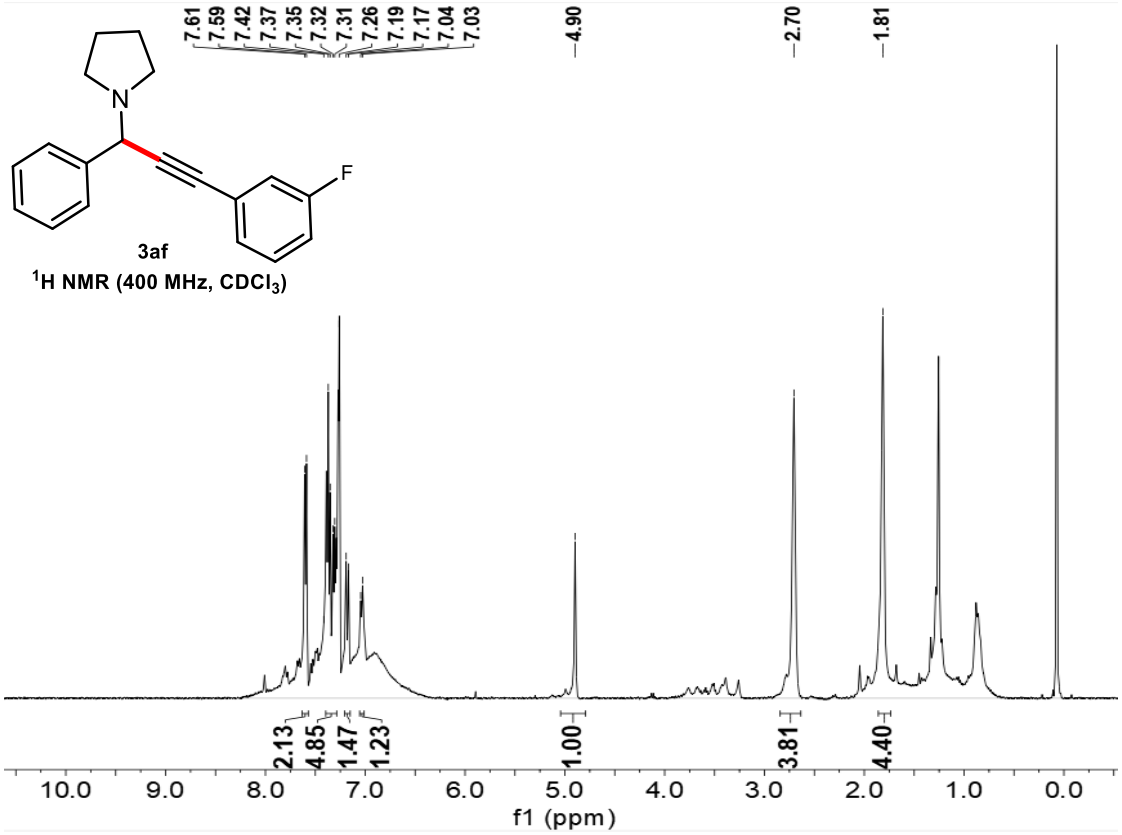

7.61
7.59
7.48
7.46
7.45
7.38
7.37
7.35
7.32
7.30
7.26
7.03
7.01
6.99
4.86
2.69
1.81
N
F
3ae
^{1}H NMR (400 MHz, CDCl$_3$)
1.97
1.93
3.09
2.07
0.98
3.95
4.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

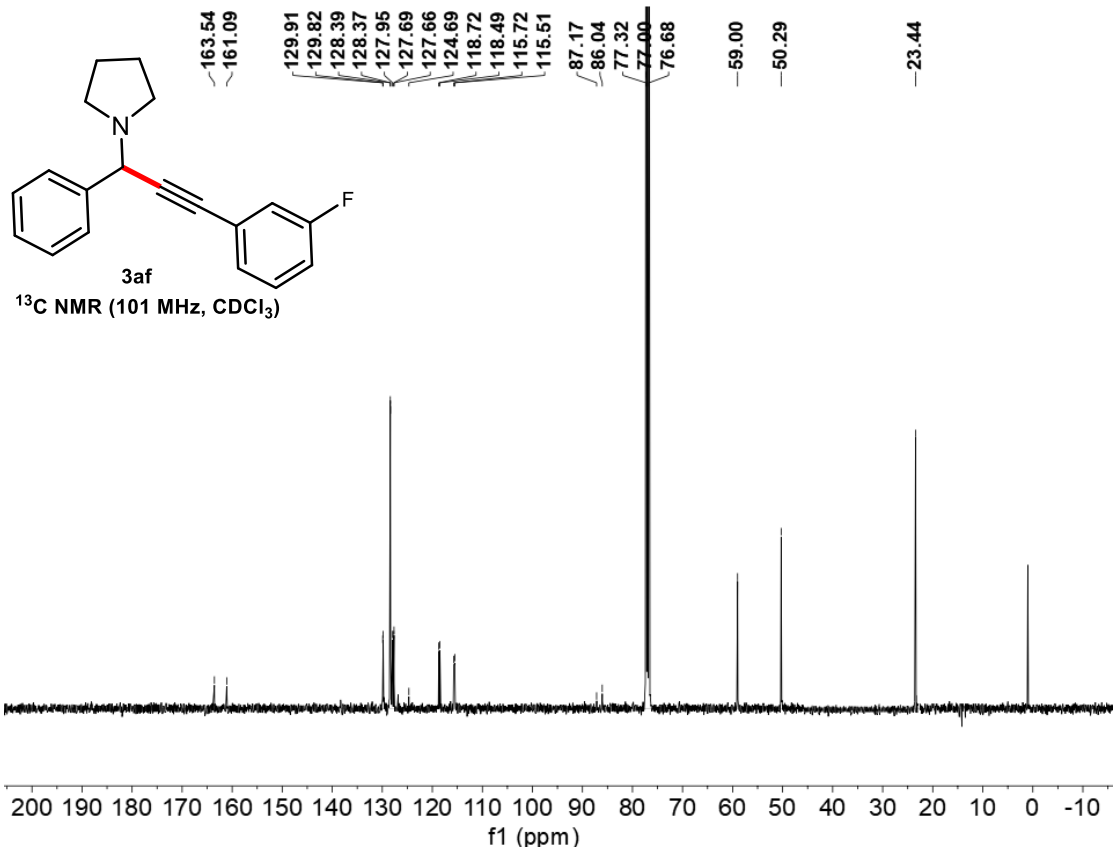

163.62
161.15
139.19
133.66
133.58
128.30
128.26
127.68
119.20
119.17
115.61
115.39
86.27
85.82
77.32
77.00
76.68
59.13
50.34
23.42
N
F
3ae
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

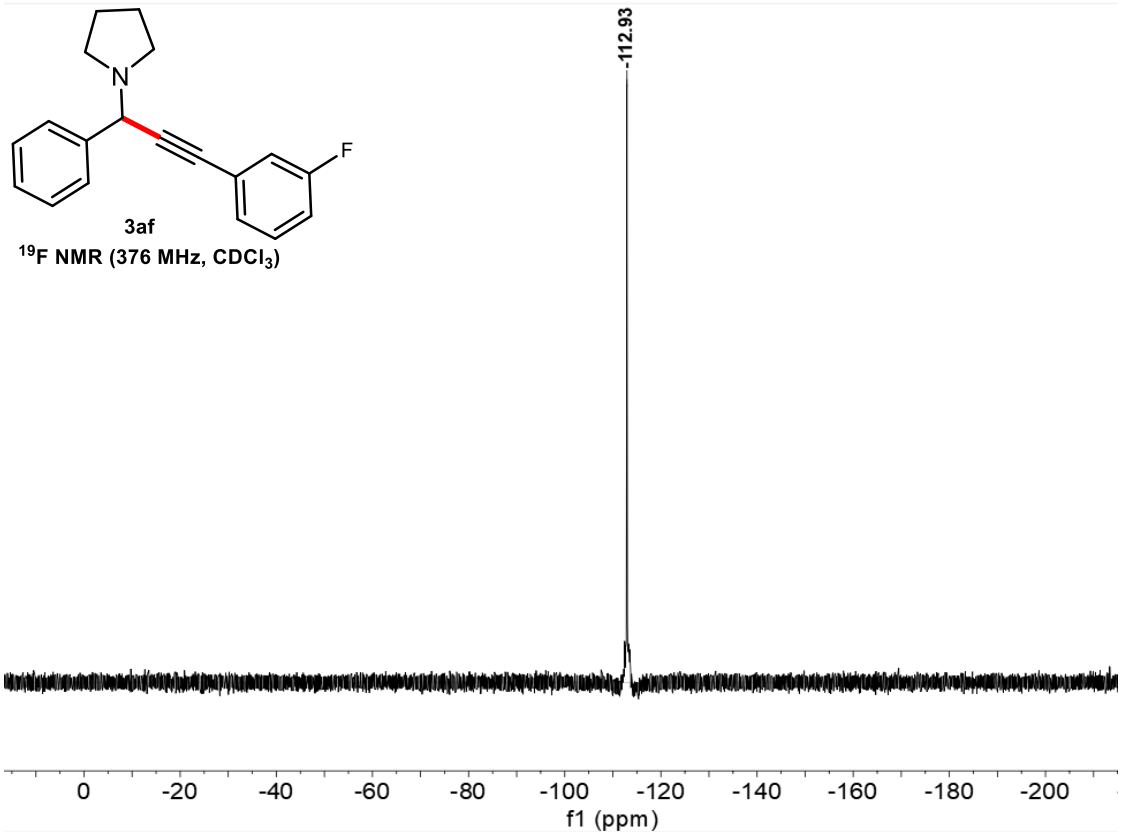


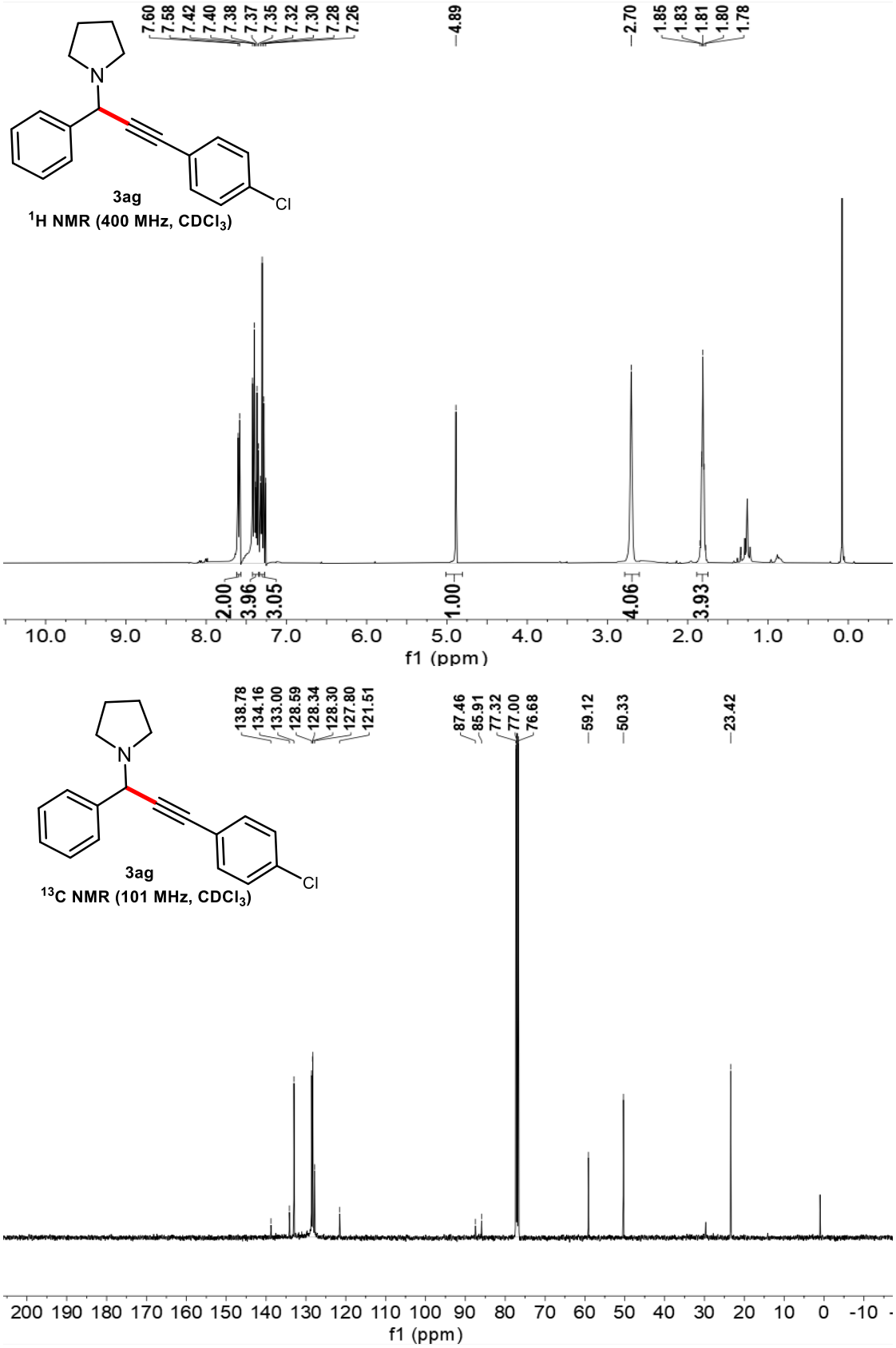
3ae

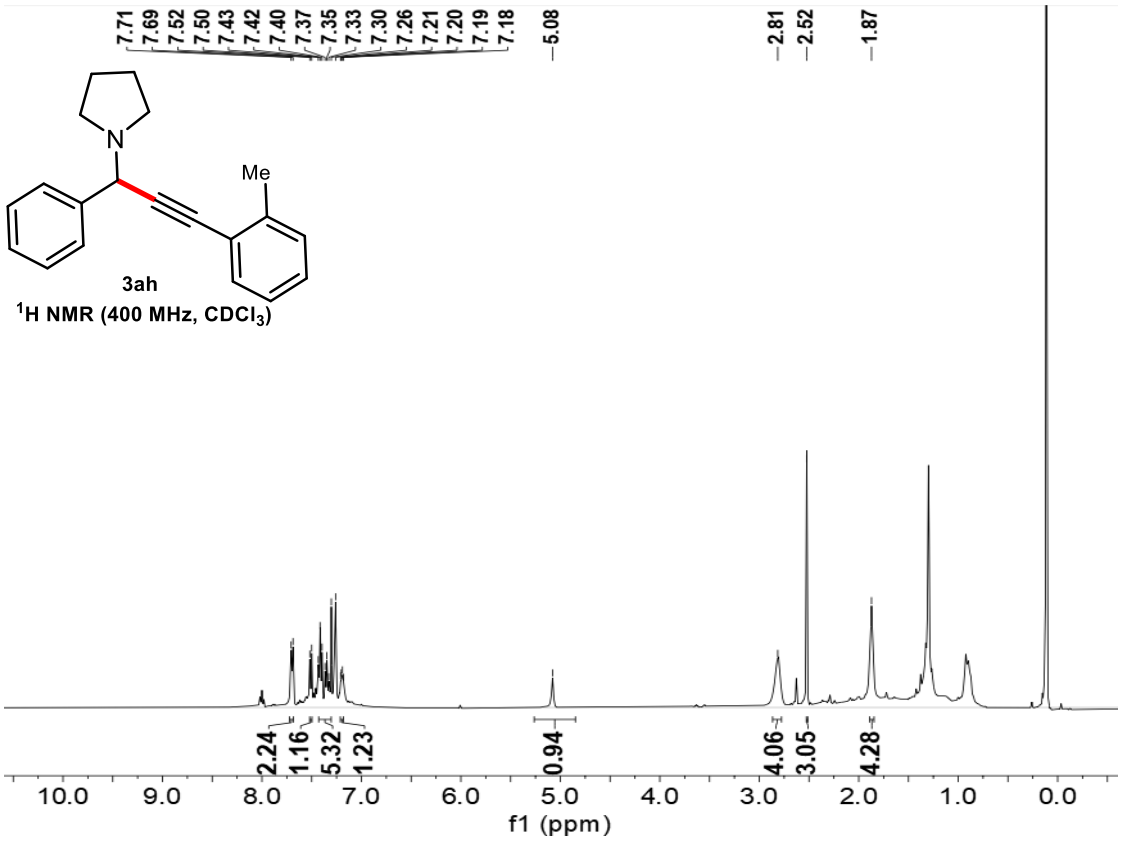
^{19}F NMR (376 MHz, $CDCl_3$)

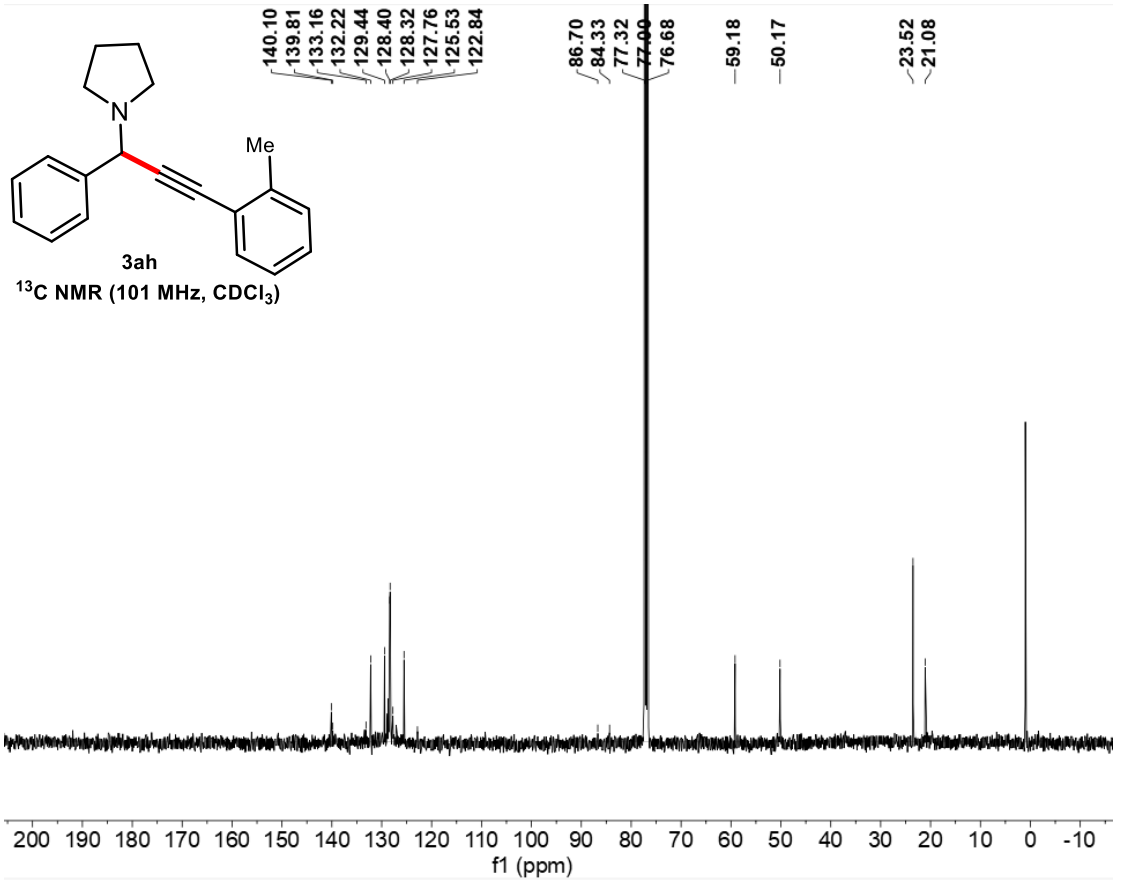

7.61
7.59
7.42
7.37
7.35
7.32
7.31
7.26
7.19
7.17
7.04
7.03
4.90
2.70
1.81
N
F
3af
^{1}H NMR (400 MHz, CDCl$_3$)
2.13
4.85
1.47
1.23
1.00
3.81
4.40
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

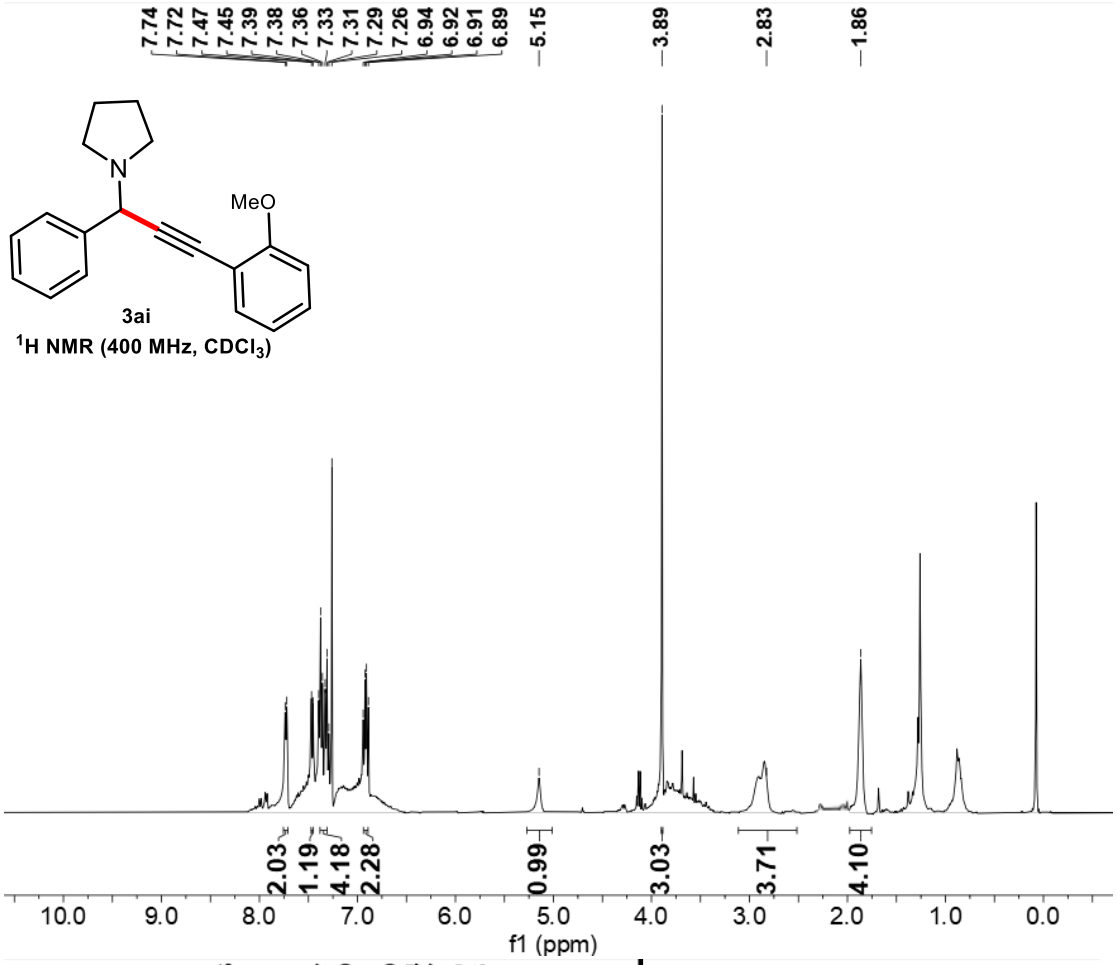

163.54
161.09
129.91
129.82
128.39
128.37
127.95
127.69
127.66
124.69
118.72
118.49
115.72
115.51
87.17
86.04
77.32
77.00
76.68
59.00
50.29
23.44
N
F
3af
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

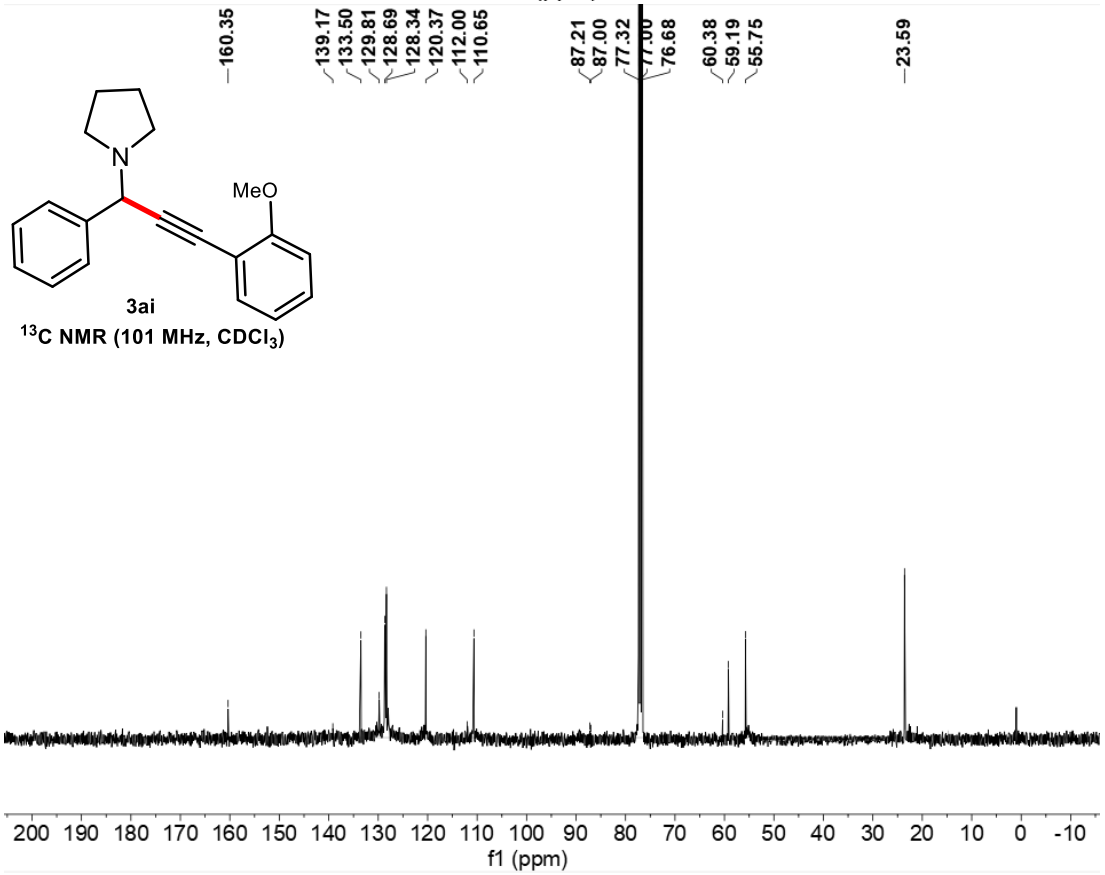

N
F
3af
^{19}F NMR (376 MHz, CDCl$_3$)
-112.93
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

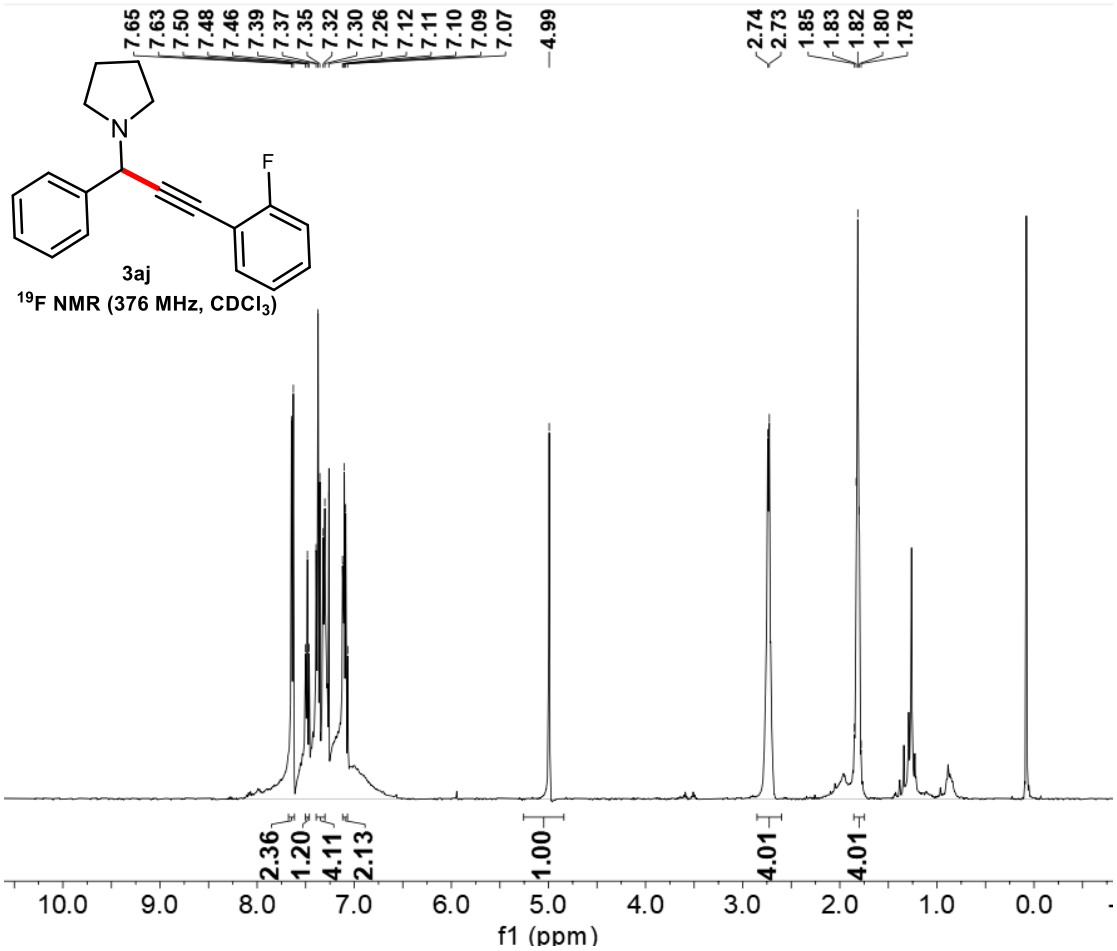

7.60
7.58
7.42
7.40
7.38
7.37
7.35
7.32
7.30
7.28
7.26
4.89
2.70
1.85
1.83
1.81
1.80
1.78
N
Cl
3ag
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
3.96
3.05
1.00
4.06
3.93
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
138.78
134.16
133.00
128.59
128.34
128.30
127.80
121.51
87.46
85.91
77.32
77.00
76.68
59.12
50.33
23.42
N
Cl
3ag
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

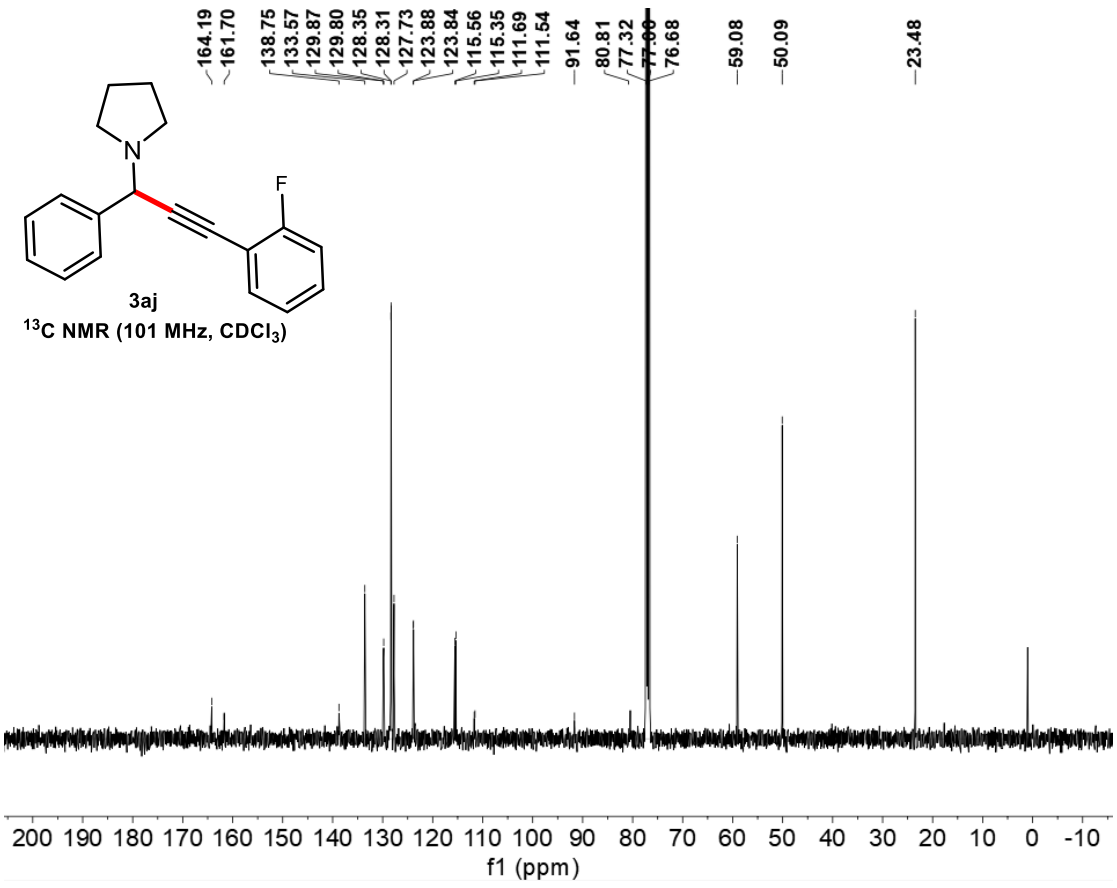

7.71
7.69
7.52
7.50
7.43
7.42
7.40
7.37
7.35
7.33
7.30
7.26
7.21
7.20
7.19
7.18
5.08
2.81
2.52
1.87
N
Me
3ah
^{1}H NMR (400 MHz, CDCl$_3$)
2.24
1.16
5.32
1.23
0.94
4.06
3.05
4.28
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

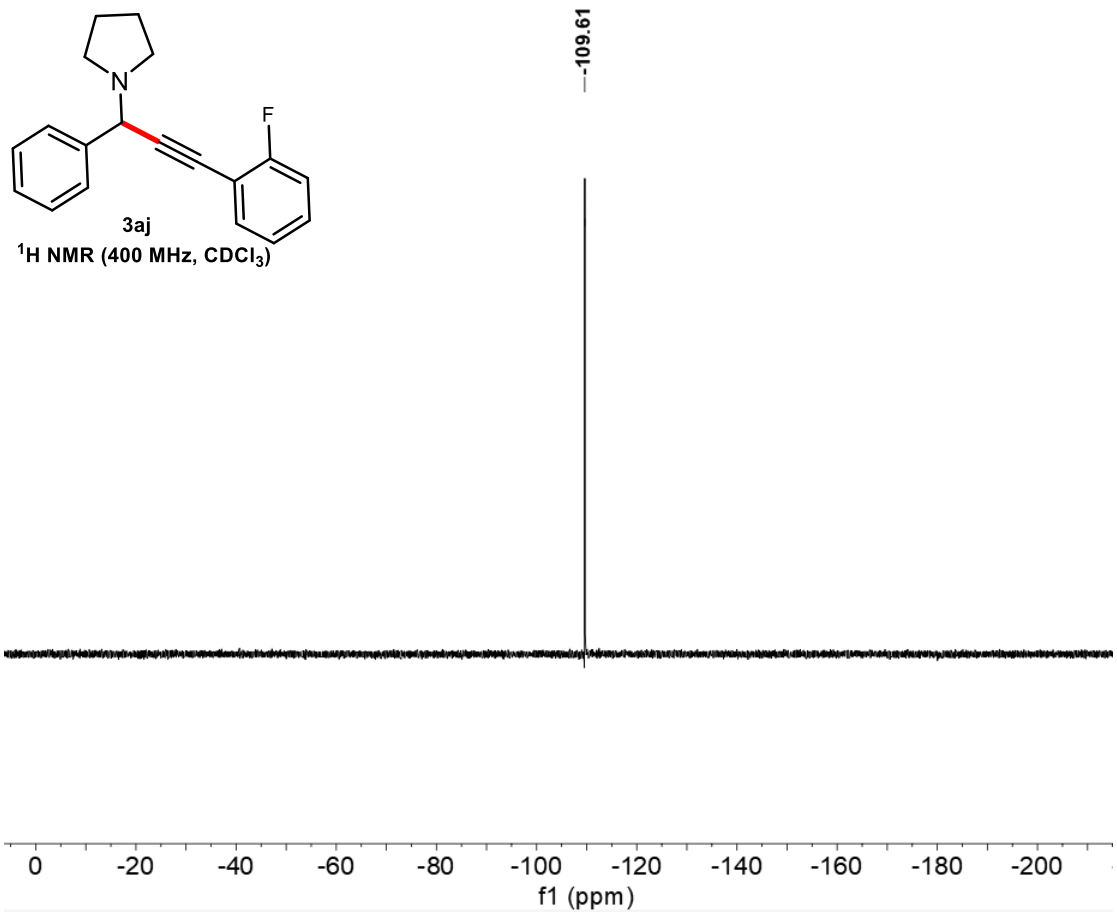

140.10
139.81
133.16
132.22
129.44
128.40
128.32
127.76
125.53
122.84
86.70
84.33
77.32
77.00
76.68
59.18
50.17
23.52
21.08
N
Me
3ah
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

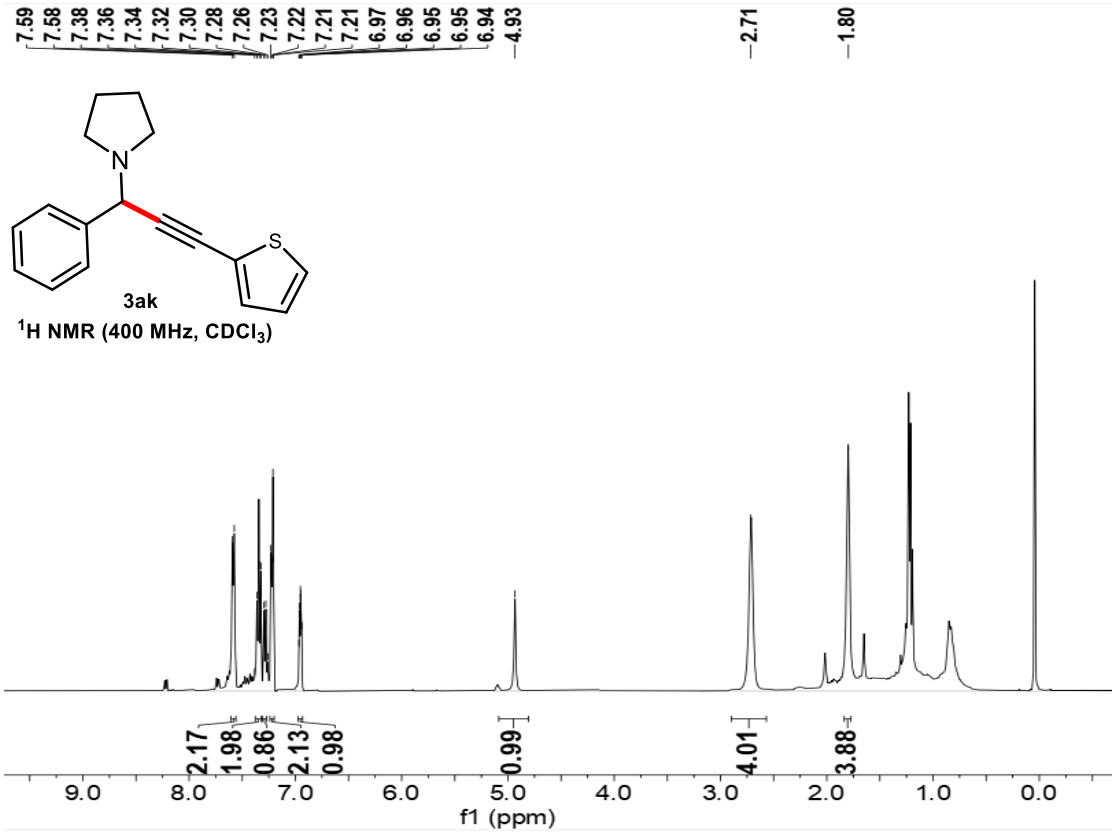

7.74
7.72
7.47
7.45
7.39
7.38
7.36
7.33
7.31
7.29
7.26
6.94
6.92
6.91
6.89
5.15
3.89
2.83
1.86
N
MeO
3ai
^{1}H NMR (400 MHz, CDCl$_3$)
2.03
1.19
4.18
2.28
0.99
3.03
3.71
4.10
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

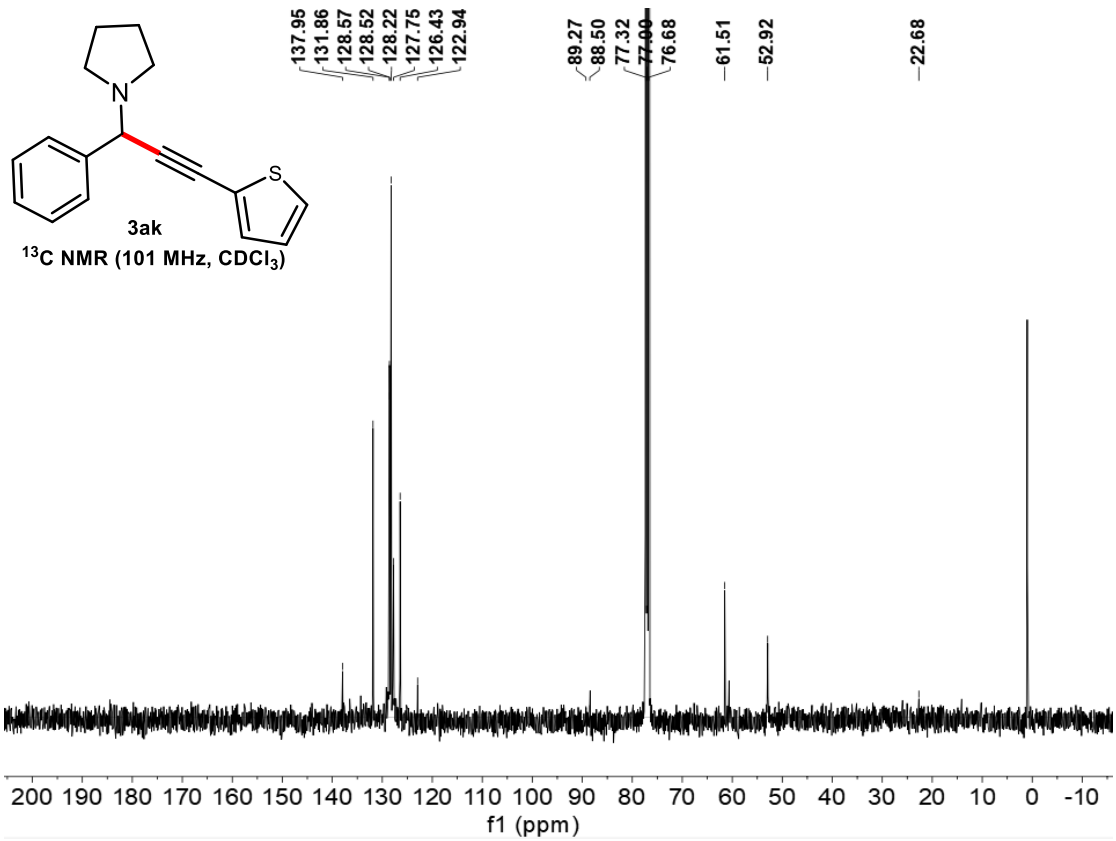

160.35
139.17
133.50
129.81
128.69
128.34
120.37
112.00
110.65
87.21
87.00
77.32
77.00
76.68
60.38
59.19
55.75
23.59
N
MeO
3ai
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

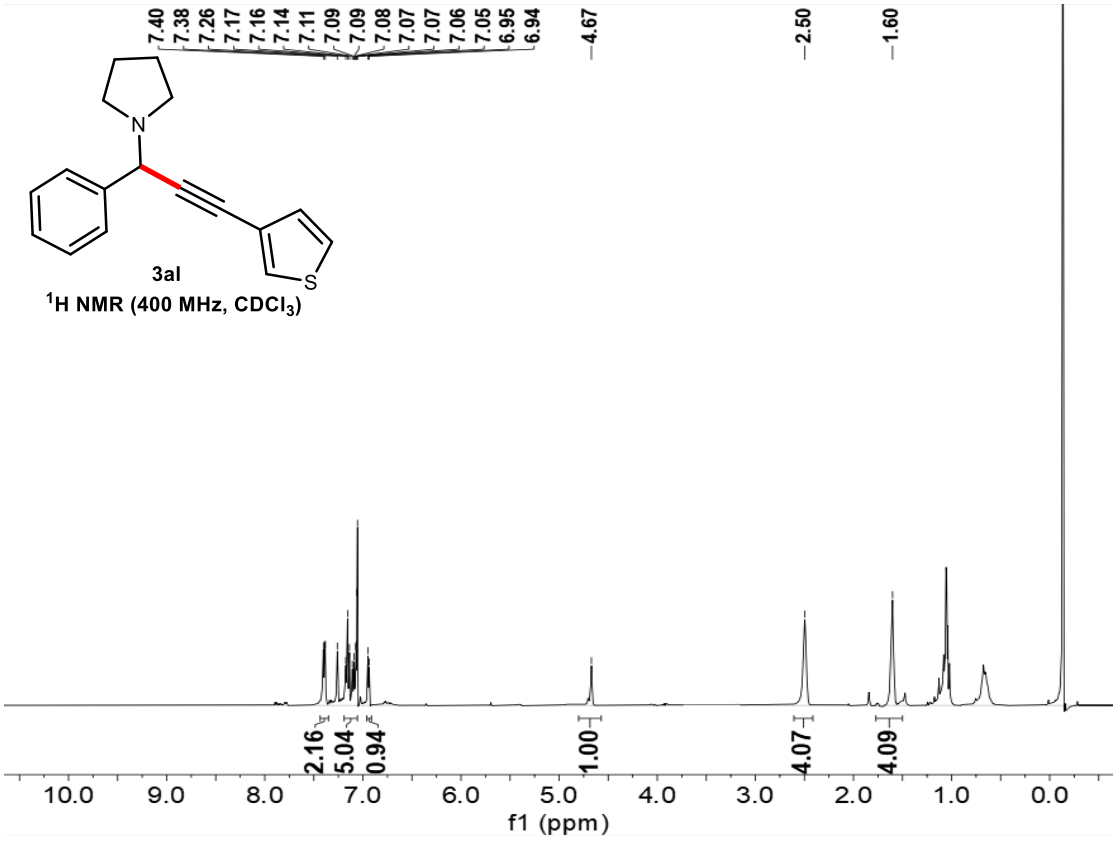

7.65
7.63
7.50
7.48
7.46
7.39
7.37
7.35
7.32
7.30
7.26
7.12
7.11
7.10
7.09
7.07
4.99
2.74
2.73
1.85
1.83
1.82
1.80
1.78
N
F
3aj
19F NMR (376 MHz, CDCl3)
2.36
1.20
4.11
2.13
1.00
4.01
4.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

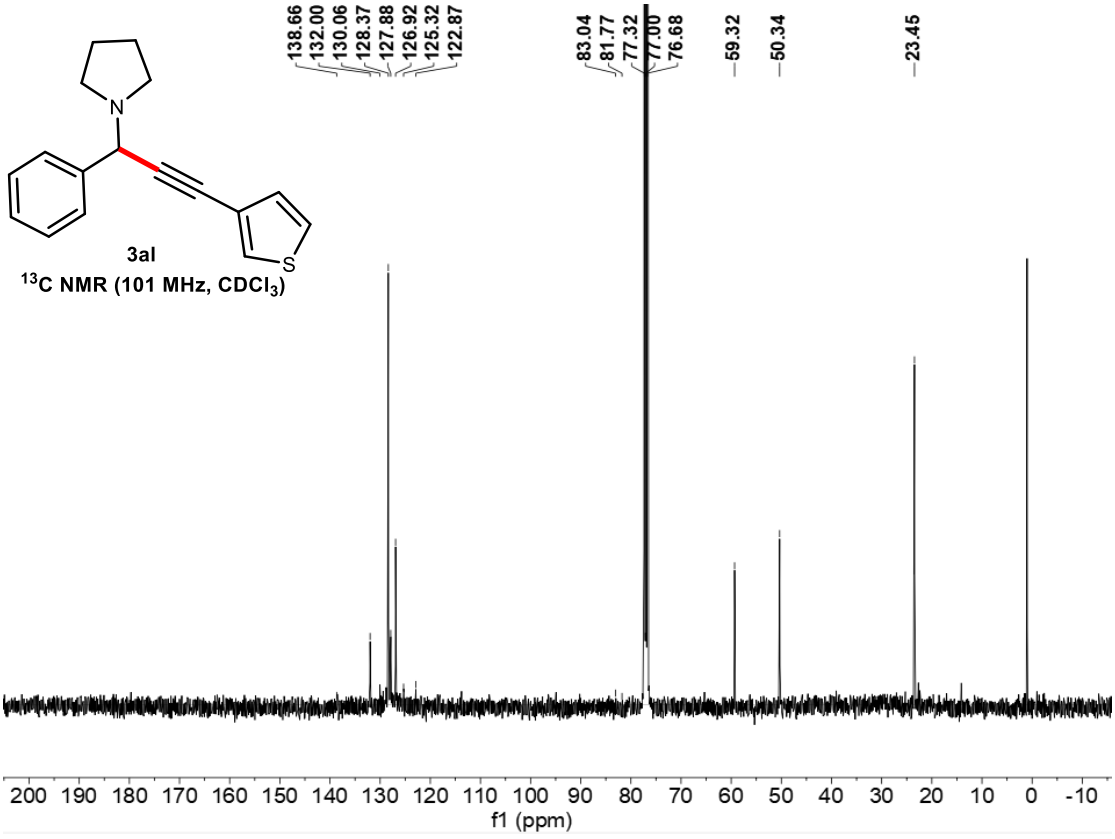

164.19
161.70
138.75
133.57
129.87
129.80
128.35
128.31
127.73
123.88
123.84
115.56
115.35
111.69
111.54
91.64
80.81
77.32
77.00
76.68
59.08
50.09
23.48
N
F
3aj
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

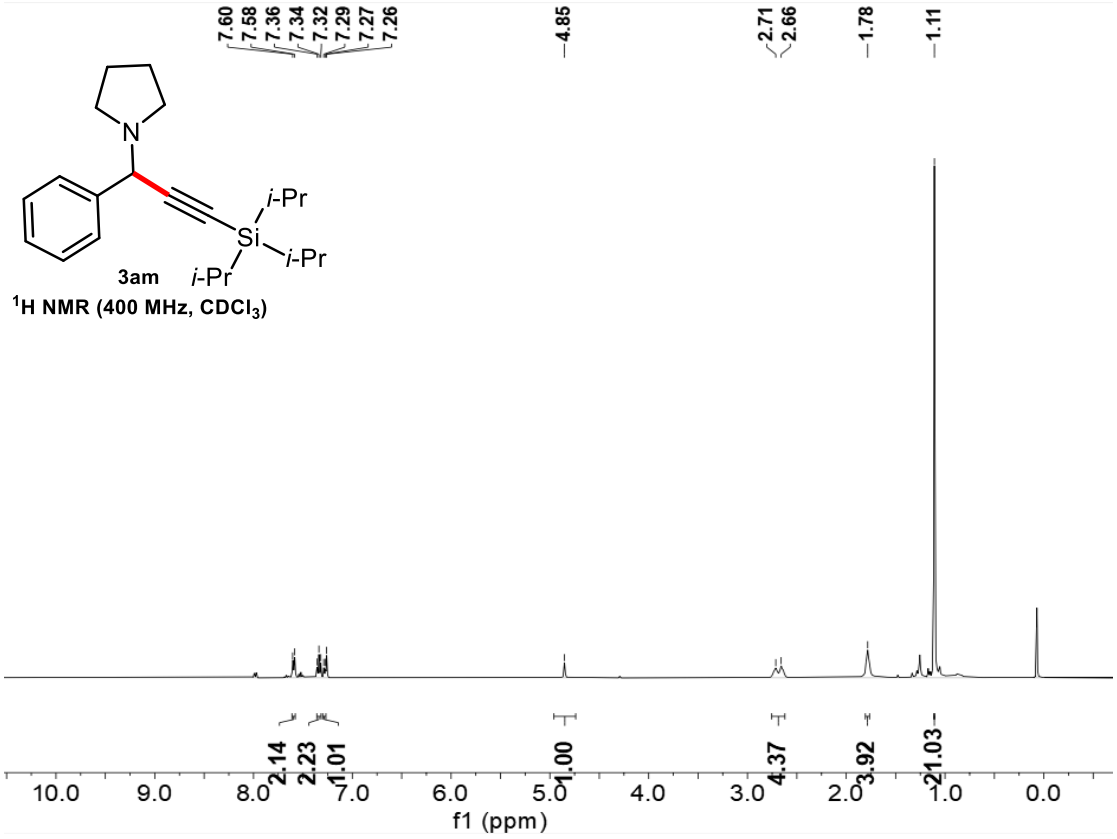

N
F
3aj
^{1}H NMR (400 MHz, CDCl$_3$)
-109.61
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.59
7.58
7.38
7.36
7.34
7.32
7.30
7.28
7.26
7.23
7.22
7.21
7.21
6.97
6.96
6.95
6.95
6.94
4.93
2.71
1.80
N
S
3ak
^{1}H NMR (400 MHz, CDCl$_3$)
2.17
1.98
0.86
2.13
0.98
0.99
4.01
3.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

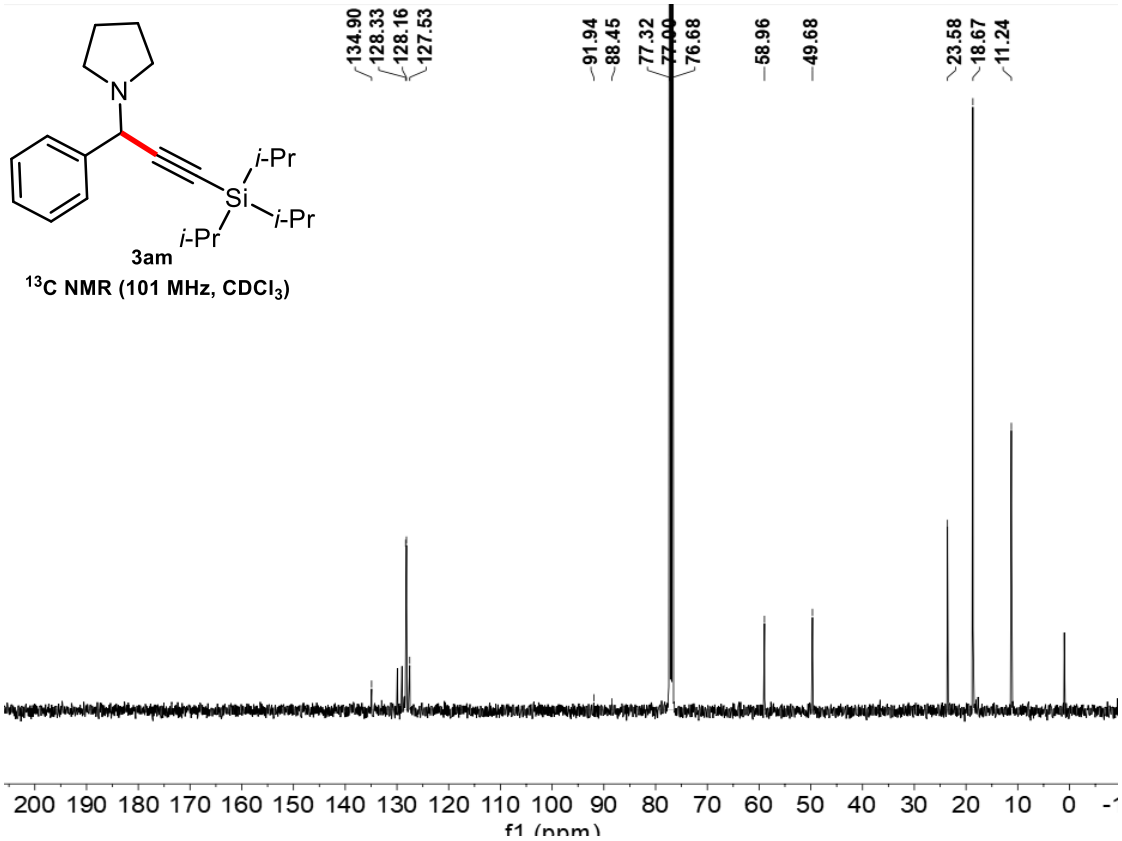

137.95
131.86
128.57
128.52
128.22
127.75
126.43
122.94
89.27
88.50
77.32
77.00
76.68
61.51
52.92
22.68
N
S
3ak
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.40
7.38
7.26
7.17
7.16
7.14
7.11
7.09
7.09
7.08
7.07
7.07
7.06
7.05
6.95
6.94
4.67
2.50
1.60
N
S
3al
^{1}H NMR (400 MHz, CDCl$_3$)
2.16
5.04
0.94
1.00
4.07
4.09
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

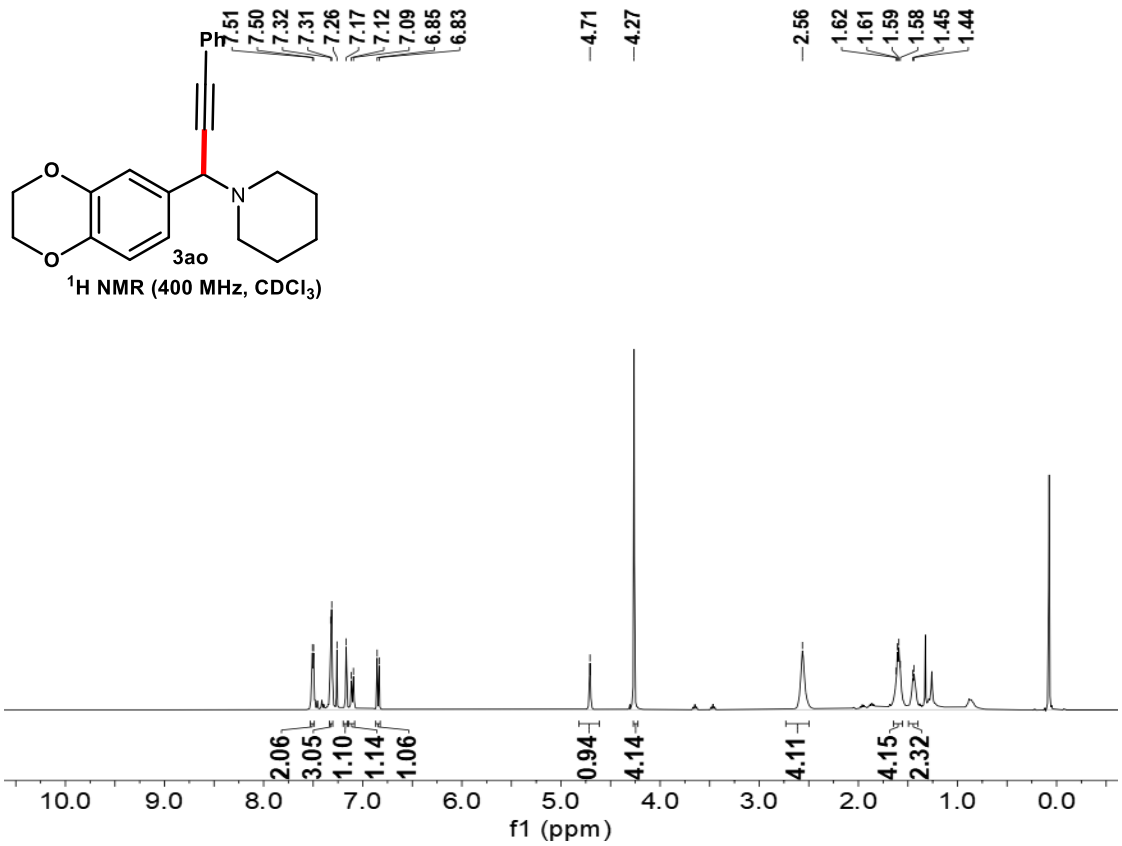

138.66
132.00
130.06
128.37
127.88
126.92
125.32
122.87
83.04
81.77
77.32
77.00
76.68
59.32
50.34
23.45
N
S
3al
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

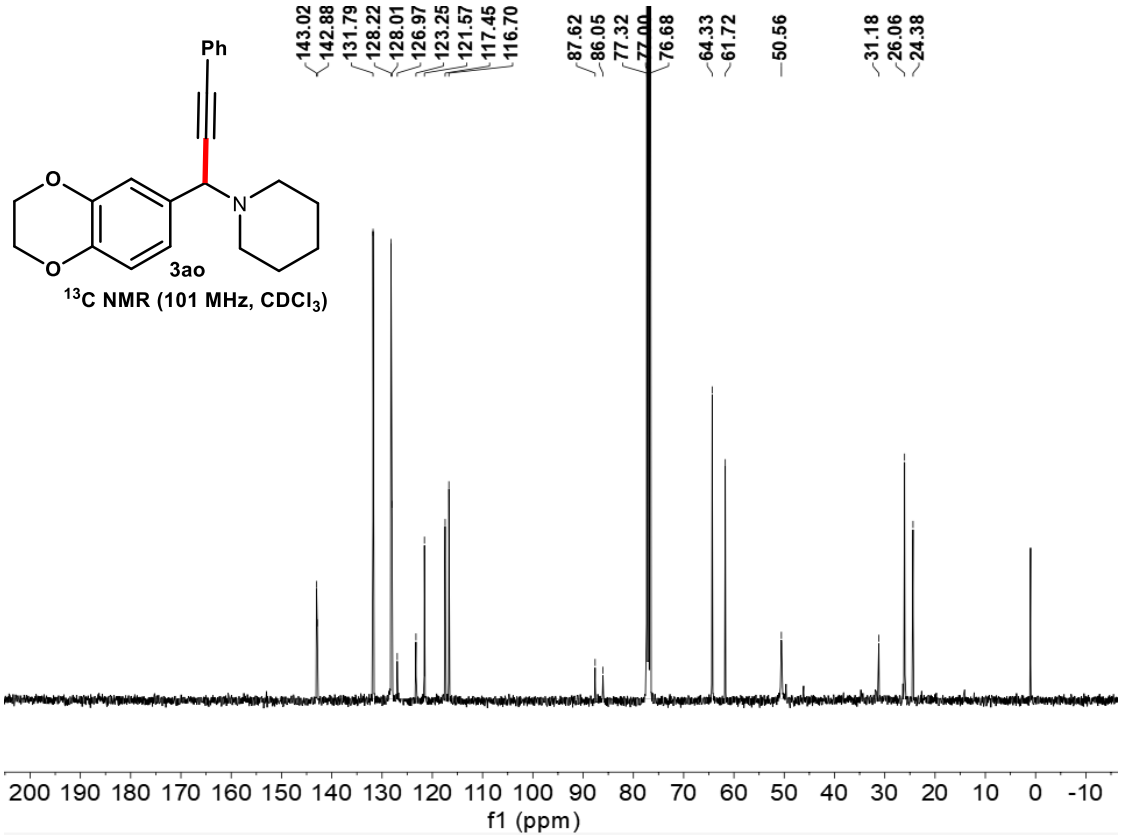


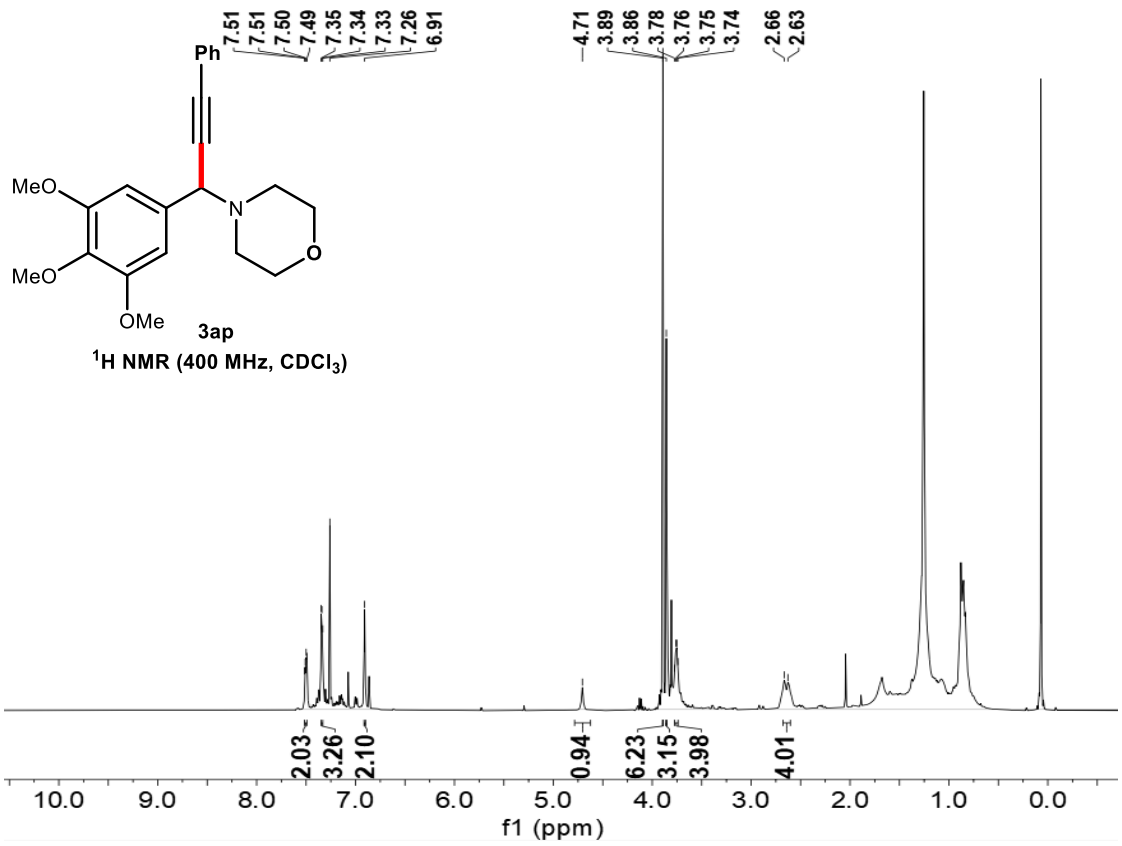
^{1}H NMR (400 MHz, $CDCl_3$)



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

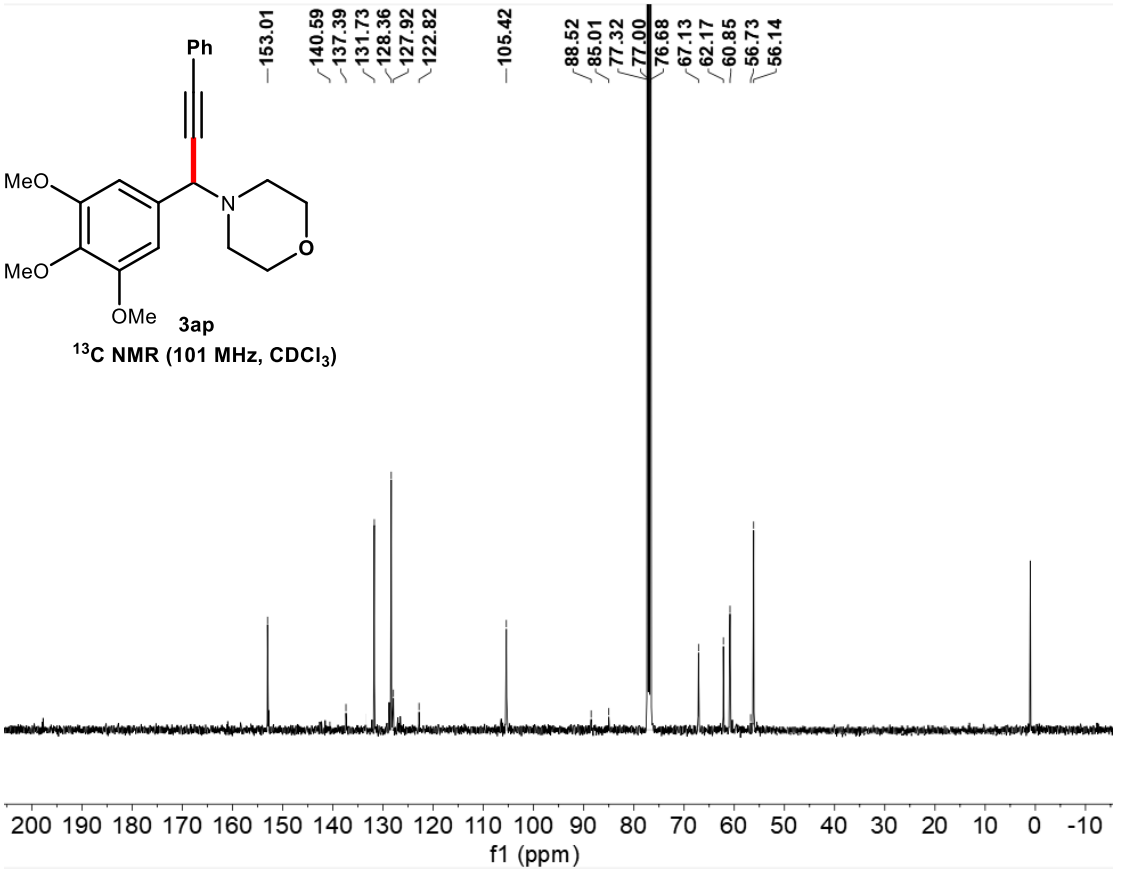

Ph
7.51
7.50
7.32
7.31
7.26
7.17
7.12
7.09
6.85
6.83
4.71
4.27
2.56
1.62
1.61
1.59
1.58
1.45
1.44
O
O
N
3ao
^{1}H NMR (400 MHz, CDCl$_3$)
2.06
3.05
1.10
1.14
1.06
0.94
4.14
4.11
4.15
2.32
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


Ph
143.02
142.88
131.79
128.22
128.01
126.97
123.25
121.57
117.45
116.70
87.62
86.05
77.32
77.00
76.68
64.33
61.72
50.56
31.18
26.06
24.38
O
O
N
3ao
^{13}C NMR (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



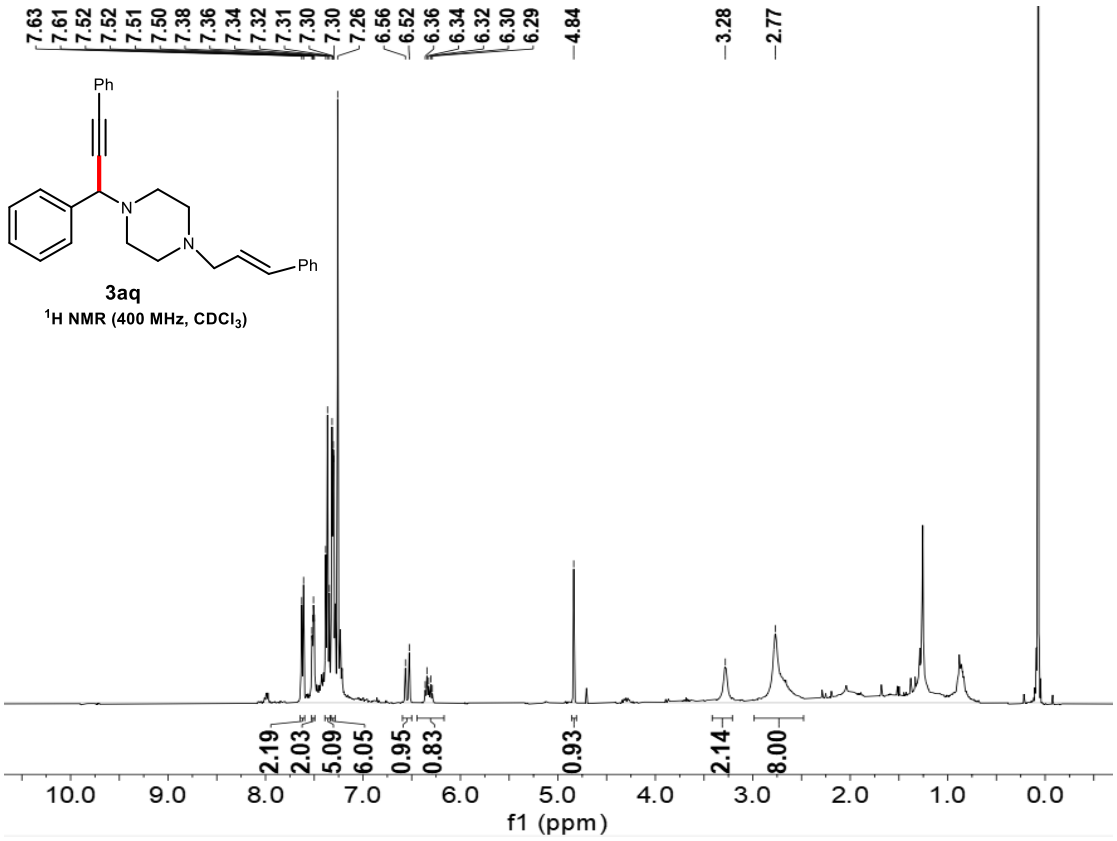
3ap

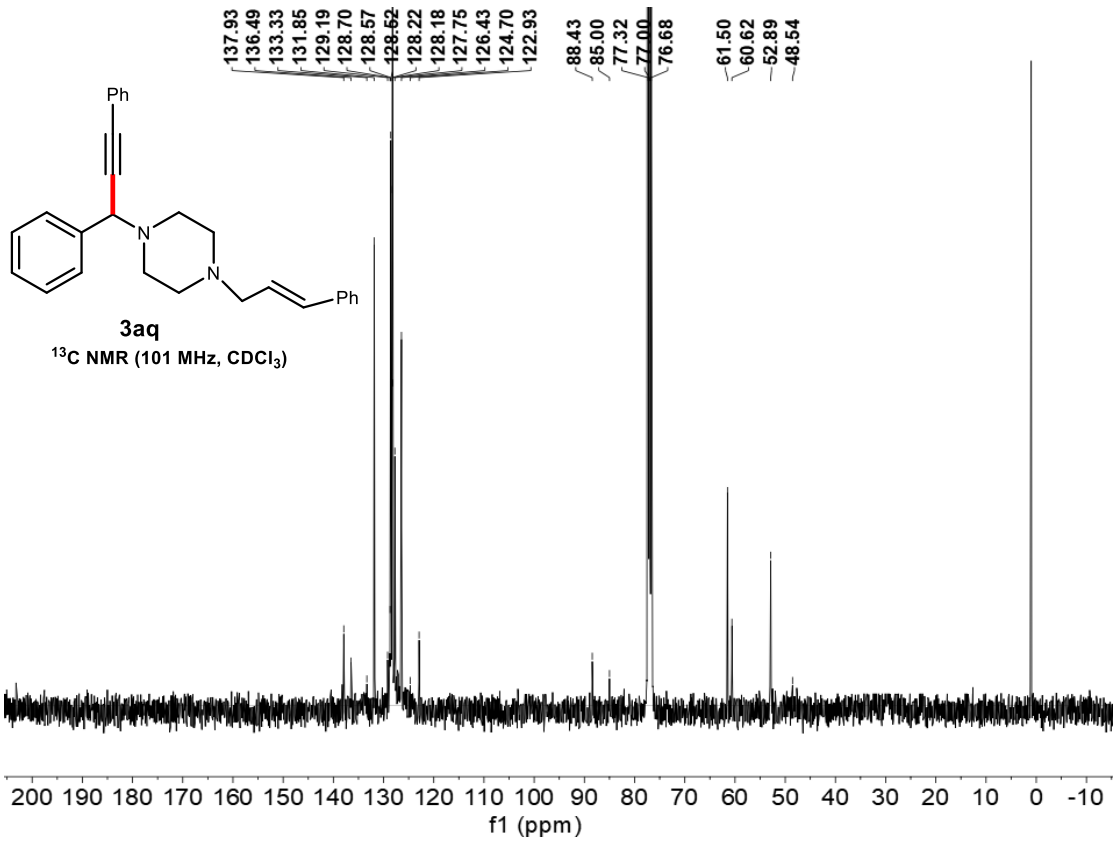
^{1}H NMR (400 MHz, $CDCl_3$)



3ap

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


7.63
7.61
7.52
7.52
7.51
7.50
7.38
7.36
7.34
7.32
7.31
7.30
7.30
7.26
6.56
6.52
6.36
6.34
6.32
6.30
6.29
4.84
3.28
2.77
Ph
N
N
Ph
3aq
1H NMR (400 MHz, CDCl3)
2.19
2.03
5.09
6.05
0.95
0.83
0.93
2.14
8.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


137.93
136.49
133.33
131.85
129.19
128.70
128.57
128.62
128.22
128.18
127.75
126.43
124.70
122.93
88.43
85.00
77.32
77.00
76.68
61.50
60.62
52.89
48.54
Ph
N
N
Ph
3aq
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)