Electronic Supporting Information for

Base-promoted Conia-ene Cyclization of Propargyl Amides

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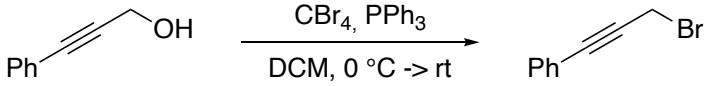
General Remarks

All chemicals those syntheses are not reported hereafter were purchased from commercial sources and used as received. Solvents were dried passing through alumina columns using an Inert® system and were stored under nitrogen. Chromatographic purifications were performed under gradient using a Combiflash® system and prepacked disposable silica cartridges or through isocratic flash chromatography using commercial 60 Å silica gel. All reactions that required heating were performed with the use of high-vacuum grade silicon oil. ^{1}H and ^{13}C NMR spectra were recorded at 300 K on a Bruker 400 MHz spectrometer using residual non-deuterated solvents as internal standards (7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C-NMR for $CDCl_3$). ^{19}F-NMR spectra were recorded in $CDCl_3$ at 298 K on a Jeol 600 spectrometer fitted with a BBFO probehead at 564 MHz. The terms m, s, d, t, q and quint represent multiplet, singlet, doublet, triplet, quadruplet and quintuplet respectively, and the term br means a broad signal. Reported assignments were based on decoupling, COSY, NOESY, HSQC and HMBC correlation experiments. Mass analyses were recorded on an Infusion Water Acquity Ultra Performance LC HO6UPS-823M instrument equipped with a SQ detector (Electrospray source).

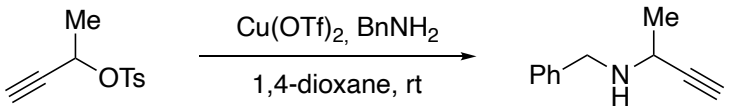
Synthesis of substrates

Synthesis of (3-bromoprop-1-yn-1-yl)benzene:



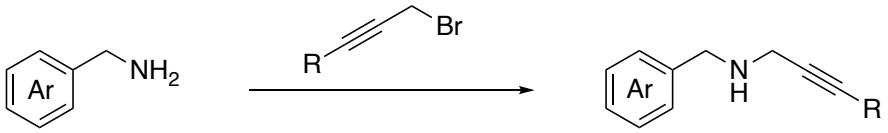
Following a reported procedure.[1] To a solution of alcohol derivative (1 eq) in dry DCM (0.25 M), CBr_4 (1.2 eq), PPh_3 (1.5 eq) were added under an inert atmosphere at 0 °C, and the mixture was stirred at room temperature for 2 h. The mixture was then poured into DCM, and the organic layer was washed with brine. The organic layer was then dried over anhydrous Na_2SO_4 and evaporated, and the purified product was obtained via flash chromatography by using hexane ethyl acetate as eluent.

Synthesis of N-benzylbut-3-yn-2-amine:



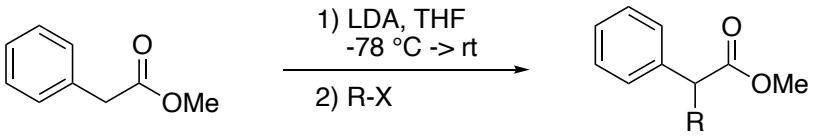
Following a reported procedure,[2] a solution of $Cu(OTf)_2$ (0.01 eq) in (0.013 M) 1,4-dioxane was cooled to 10 °C and treated with benzylamine (2 eq). After 15 min, a solution of the tosyl alcohol (1 eq) in 1,4-dioxane (0.87 M) was slowly added. The reaction mixture was warmed to room temperature, stirred for 3 h, and extracted with 1N HCl. The aqueous layer was neutralized with NaOH and then extracted with EtOAc. The organic extracts were dried (Na_2SO_4) and concentrated. The resulting greenish oil was purified by column chromatography on SiO_2 (hexanes/EtOAc 8:2).

Synthesis of secondary propargyl amines [GP-1]



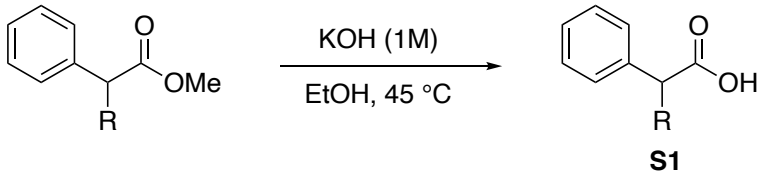
In a round bottom flask equipped with a magnetic stirring bar, the corresponding propargyl bromide (1 eq) was added at 0 °C to benzylamine (6 eq) and the resulting solution was stirred for 18 h at room temperature. After complete conversion as monitored by TLC, the mixture was quenched with a saturated $NaHCO_3$ solution and extracted with Et_2O (3 times). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude was finally purified by chromatography on silica gel (n-hexane/EtOAc gradient).

Synthesis of α-branched esters [GP-2]



To a solution of diisopropylamine (1.2 eq) in tetrahydrofuran (0.9 M) was added n-butyllithium (2.5 M in hexane, 4.8 mL) at −78 °C under N_2 atmosphere, and the mixture was stirred for 30 min. Then a solution of the corresponding methyl 2-phenyl acetate (1 eq) in tetrahydrofuran (0.6 M) was added dropwise, and the mixture was stirred for 20 min at the same temperature. After warming the reaction mixture to 0 °C, the corresponding alkyl halide (1.6 eq) was added slowly, and the mixture was stirred for 30 min. The reaction mixture was then quenched by adding 2 M hydrochloric acid solution and extracted with EtOAc for 3 times. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give a residue, which was purified by column chromatography (hexane/EtOAc gradient).

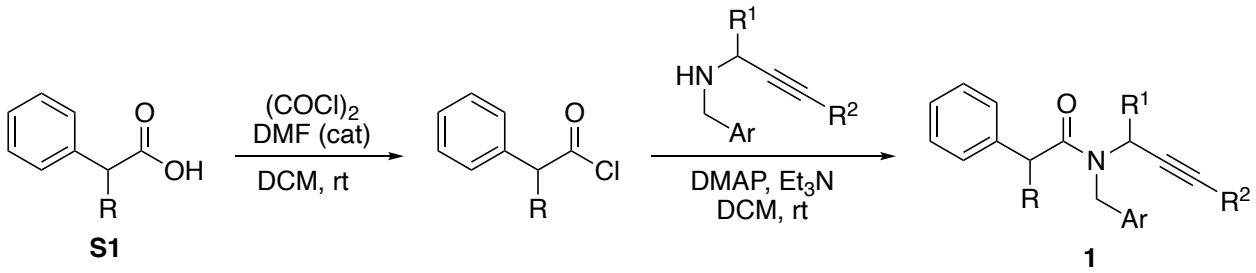
Synthesis of carboxylic acids [GP-3]:



S1

In a round bottom flask equipped with a stir bar were added the desired ester (1 eq), EtOH (0.15 M) and a 1 M solution of KOH (2.5 eq). The resulting mixture was stirred 18 h at 45 °C. After complete conversion as monitored by TLC, the mixture was concentrated under reduced pressure and acidified to pH = 1 with a 1 M HCl solution, extracted with EtOAc for 3 times. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give a residue, which was purified by column chromatography (hexane/EtOAc gradient).

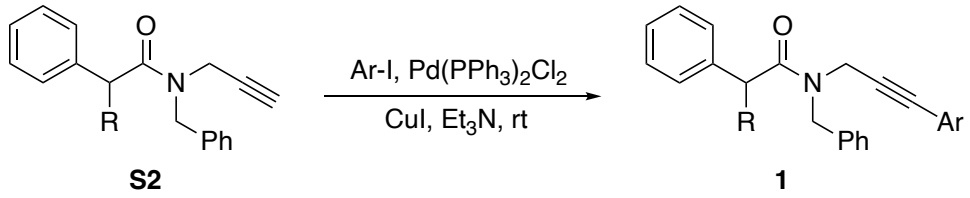
Synthesis of propargyl amides via acyl chloride [GP-4]



S1 **1**

In a 25 mL round bottom flask equipped with a magnetic stirring bar, the desired acid (1 eq) was dissolved in DCM (0.2 M) and a catalytic amount of DMF (2 drops) and oxalyl chloride (1.5 eq) were added. The solution was stirred for 2 h. Then, the mixture was concentrated under reduced pressure to afford the acyl chloride, that was added to a solution of DMAP (0.02 equiv.), TEA (1 equiv.) and secondary amine (1 equiv.) in DCM (0.25 M) at 0 °C. The mixture was stirred for 18 h at room temperature. After complete conversion as monitored by TLC, the solution was diluted with DCM and washed with a saturated NH_4Cl solution followed by a saturated $NaHCO_3$. The aqueous layers were extracted with DCM (3 times), and the combined organic phase was finally washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and the crude was purified by chromatography on silica gel (n-hexane/EtOAc gradient).

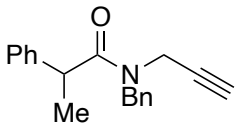
Synthesis of propargyl amides via Sonogashira cross-coupling [GP-5]:



S2 **1**

In a Schlenk-type flask equipped with a stirring magnetic bar were added propargil amide, (1.2 eq.), $Pd(PPh_3)_4$ (0.05 eq), CuI (0.1 eq., TEA (14 eq) and the desired iodobenzene (1 eq) and the solution was stirred at room temperature for 18 h. After complete conversion as monitored by TLC, the mixture extracted with Et_2O, washed with H_2O and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude was then purified by chromatography on silica gel (n-hexane/EtOAc gradient).

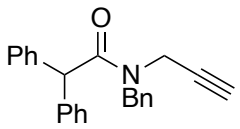
N-benzyl-2-phenyl-N-(prop-2-yn-1-yl)propenamide



Propargyl amide **1a** was prepared following **GP-4**. After purification, product resulted as a yellow oil (563 mg, 77%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.14 (m, 10HrotA, 10HrotB), 5.10 (d, J = 14.9 Hz, 1HrotB), 4.65 (d, J = 16.7 Hz, 1HrotA), 4.49 (d, J = 16.7 Hz, 1HrotA), 4.43 – 4.30 (m, 1HrotA, 1HrotB), 4.15 – 3.97 (m, 1HrotA, 2HrotB), 3.91 (q, J = 6.8 Hz, 1HrotA), 3.60 (dd, J = 18.6, 2.5 Hz, 1HrotB), 2.28 (t, J = 2.4 Hz, 1HrotB), 2.18 (t, J = 2.5 Hz, 1HrotA), 1.54 (d, J = 6.8 Hz, 3HrotB), 1.49 (d, J = 6.8 Hz, 3HrotA). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.73 (Cq), 173.66 (Cq), 141.6 (2Cq), 137.0 (Cq), 136.3 (Cq), 129.1 (4CH), 128.9 (2CH), 128.6 (2CH), 128.2 (2CH), 127.8 (CH), 127.5 (CH), 127.34 (2CH), 127.30 (2CH), 127.11 (CH), 127.06 (CH), 126.8 (2CH), 78.9 (Cq), 78.5 (Cq), 72.8 (CH), 72.0 (CH), 49.9 (CH_2), 48.5 (CH_2), 43.7 (CH), 43.4 (CH), 36.1 (CH_2), 34.5 (CH_2), 21.0 ($2CH_3$). **ESI-MS** calcd for $C_{19}H_{19}NNaO^+$ $[M+Na]^+$ 300.14, found 300.28.

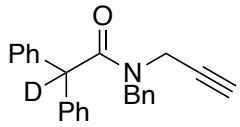
N-benzyl-2,2-diphenyl-N-(prop-2-yn-1-yl)acetamide



Propargyl amide **1b** was prepared following **GP-4**. After purification, product resulted as a yellow oil (425 mg, 51%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.20 (m, 15HrotA, 15HrotB), 5.47 (s, 1HrotB), 5.20 (s, 1HrotA), 4.79 (s, 2HrotB), 4.66 (s, 2HrotA), 4.34 (d, *J* = 2.5 Hz, 2HrotA), 3.90 (d, *J* = 2.4 Hz, 2HrotB), 2.39 (s, 1HrotB), 2.24 (t, *J* = 2.5 Hz, 1HrotA). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0 (Cq), 171.9 (Cq) , 139.2 (2Cq), 139.1 (2Cq), 136.9 (Cq), 136.5 (Cq), 129.1 (2CH), 129.03 (4CH), 128.89 (4CH), 128.68 (4CH), 128.67 (2CH), 128.6 (4CH) , 128.4 (2CH), 127.9 (CH), 127.6 (CH), 127.3 (2CH), 127.2 (2CH), 126.5 (2CH), 78.7 (2Cq), 72.9 (CH), 72.1 (CH), 55.0 (CH), 54.7 (CH), 50.3 (CH_2), 48.9 (CH_2), 36.5 (CH_2), 35.2 (CH_2). **ESI-MS** calcd for $C_{24}H_{21}NNaO^+$ $[M+Na]^+$ 362.15, found 362.30.

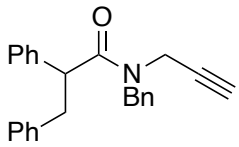
N*-benzyl-2,2-diphenyl-*N*-(prop-2-yn-1-yl)acetamide-*d



Propargyl amide **d-1b** was prepared following **GP-4**, starting from the deuterated diphenyl acetic acid. After purification, product resulted as a yellow oil (525 mg, 63 %). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.20 (m, 15HrotA, 15HrotB), 4.79 (s, 2HrotB), 4.66 (s, 2HrotA), 4.34 (d, *J* = 2.5 Hz, 2HrotA), 3.90 (d, *J* = 2.4 Hz, 2HrotB), 2.39 (s, 1HrotB), 2.24 (t, *J* = 2.5 Hz, 1HrotA). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0 (Cq), 171.9 (Cq) , 139.2 (2Cq), 139.1 (2Cq), 136.9 (Cq), 136.5 (Cq), 129.1 (2CH), 129.03 (4CH), 128.89 (4CH), 128.68 (4CH), 128.67 (2CH), 128.6 (4CH) , 128.4 (2CH), 127.9 (CH), 127.6 (CH), 127.3 (2CH), 127.2 (2CH), 126.5 (2CH), 78.7 (2Cq), 72.9 (CH), 72.1 (CH), 55.0 (CH), 54.5 (q, *J* = 20.1 Hz, CH), 50.3 (CH_2), 48.9 (CH_2), 36.5 (CH_2), 35.2 (CH_2). **ESI-MS** calcd for $C_{24}H_{21}DNNaO^+$ $[M+Na]^+$ 363.15, found 363.22.

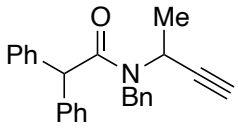
N-benzyl-2,3-diphenyl-N-(prop-2-yn-1-yl)propanamide



Propargyl amide **1c** was prepared following **GP-4**. After purification, product resulted as a white oil (686 mg, 78%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.15 (m, 11HrotA, 14HrotB), 7.10 (m, 2HrotA, 1HrotB), 6.86 (m, 2HrotA), 4.84 (d, J = 14.9 Hz, 1HrotB), 4.69 – 4.50 (m, 1HrotA,1HrotB), 4.44 – 4.32 (m, 2HrotA), 4.23 (dd, J = 8.2, 6.5 Hz, 1HrotB), 4.09 – 3.79 (m, 2HrotA, 1HrotB), 3.74 – 3.46 (m, 2HrotB, 1HrotA), 3.07 (dd, J = 13.6, 6.5 Hz, 1HrotB), 2.97 (dd, J = 13.3, 5.8 Hz,1HrotA), 2.22 (t, J = 2.5 Hz, 1HrotB), 2.16 (t, J = 2.5 Hz, 1HrotA). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6 (Cq), 172.5 (Cq), 139.8 (Cq) , 139.7 (Cq), 139.3 (Cq), 139.1 (Cq), 136.8(Cq), 136.1 (Cq), 129.4 (2CH), 129.3 (2CH), 128.9 (2CH), 128.83 (4CH), 128.82 (2CH), 128.5 (2CH), 128.3 (2CH), 128.2 (2CH), 128.11 (2CH), 128.10 (2CH), 128.0 (2CH), 127.6 (CH), 127.4 (CH), 127.31 (CH), 127.27 (CH), 126.6 (2CH), 126.24 (CH), 126.20 (CH), 78.7 (Cq), 78.5 (Cq), 72.7 (CH), 71.8 (CH), 51.6 (CH_2), 51.2 (CH_2), 49.8 (CH), 48.8 (CH), 41.7(CH_2), 41.4 (CH_2), 36.2 (CH_2), 34.8(CH_2). **ESI- MS** calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$ 376.17, found 376.07.

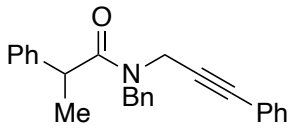
N-benzyl-N-(but-3-yn-2-yl)-2,2-diphenylacetamide



Propargyl amide **1d** was prepared following **GP-4**. After purification, product resulted as a white oil (424 mg, 80%).

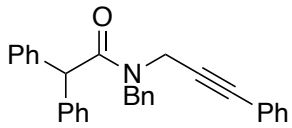
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.09 (m, 16H), 7.09 – 6.92 (m, 2H), 5.81 (qd, J = 7.0, 2.4 Hz, 1H), 4.94 (s, 1H), 4.68 (d, J = 17.8 Hz, 1H), 4.49 (d, J = 17.8 Hz, 1H), 2.22 (d, J = 2.4 Hz, 1H), 1.38 (d, J = 6.9 Hz, 3H**). ^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2 (Cq), 139.2 (Cq), 138.8 (Cq), 138.7 (Cq), 128.92 (2CH), 128.85 (2CH), 128.81 (2CH), 128.7 (2CH), 128.4 (2CH), 127.5 (CH), 127.2 (CH), 127.0 (CH), 126.2 (2CH), 82.9 (Cq), 72.4 (CH), 55.3 (CH), 47.5 (CH_2), 42.8 (CH), 20.4 (CH_3). **ESI-MS** calcd for $C_{25}H_{24}NO^+$ $[M+Na]^+$ 354.19, found 354.33.

N-benzyl-2-phenyl-N-(3-phenylprop-2-yn-1-yl)propanamide



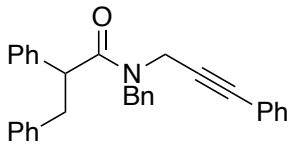
Propargyl amide **1e** was prepared following **GP-5**. After purification, product resulted as a yellow oil (196.5 mg, 91%). Two rotamers in equimolar ratio are observed due to the dynamic amide group.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.24 (m, 28H), 7.21 – 7.12 (m, 2H), 5.10 (d, J = 14.9 Hz, 1H), 4.75 (d, J = 16.8 Hz, 1H), 4.61 (dd, J = 21.3, 16.6 Hz, 3H), 4.40 (d, J = 17.4 Hz, 1H), 4.29 (d, J = 18.6 Hz, 1H), 4.18 (q, J = 6.8 Hz, 1H), 4.03 – 3.84 (m, 2H), 1.61 (d, J = 6.8 Hz, 3H), 1.55 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.80 (Cq), 173.78 (Cq), 141.7 (2Cq), 137.2 (Cq), 136.6 (Cq), 131.78 (2CH), 131.76 (2CH), 129.1 (4CH), 128.9 (2CH), 128.64 (CH), 128.62 (2CH), 128.4 (2CH), 128.32 (CH), 128.30 (2CH), 128.28 (2CH), 127.7 (CH), 127.5 (CH), 127.40 (2CH), 127.38 (2CH), 127.09 (CH), 127.05 (CH), 126.8 (2CH), 122.9 (Cq), 122.4 (Cq), 84.4 (2Cq), 83.9 (Cq), 83.8 (Cq), 50.1 (CH_2), 48.8 (CH_2), 43.7 (CH), 43.5 (CH), 37.1 (CH_2), 35.5 (CH_2), 21.1 ($2CH_3$). **ESI-MS** calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$ 376.17, found 376.57.

N-benzyl-2,2-diphenyl-N-(3-phenylprop-2-yn-1-yl)acetamide



Propargyl amide **1f** was prepared following **GP-4**. After purification, product resulted as a viscous yellow oil (724 mg, 87%). Two rotamers are observed due to the dynamic amide group.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.22 (m, 20HrotA, 20HrotB), 5.56 (s, 1HrotB), 5.21 (s, 1HrotA), 4.84 (s, 2HrotB), 4.71 (s, 2HrotA), 4.58 (s, 2HrotA), 4.14 (s, 1HrotB). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.04 (Cq), 172.02 (Cq), 139.22 (2Cq), 139.21 (2Cq) 137.1 (Cq), 136.8 (Cq), 131.8 (2CH), 131.7 (2CH), 129.07 (4CH), 129.06 (2CH), 129.00 (4CH), 128.72 (CH), 128.67 (4CH), 128.66 (2CH), 128.62 (4CH), 128.5 (2CH), 128.4 (2CH), 128.34 (CH), 128.28 (2CH), 127.8 (CH), 127.6 (CH), 127.21 (2CH), 127.19 (2CH), 126.6 (2CH), 122.8 (Cq), 122.3 (Cq), 84.7 (Cq), 84.2 (Cq), 84.0 (Cq), 83.9 (Cq), 55.0 (CH), 54.8 (CH), 50.5 (CH_2), 49.2 (CH_2), 37.5 (CH_2), 36.2 (CH_2). **ESI-MS** calcd for $C_{30}H_{25}NNaO^+$ $[M+Na]^+$ 483.18, found 483.32.

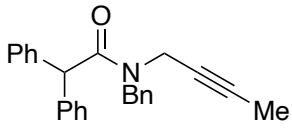
N-benzyl-2,3-diphenyl-N-(3-phenylprop-2-yn-1-yl)propenamide



Propargyl amide **1g** was prepared following **GP-5**. After purification, product resulted as a yellow oil (245 mg, 91%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 6.87 (m, 40H), 4.81 – 4.69 (m, 2H), 4.65 (d, J = 17.0 Hz, 1H), 4.56 (d, J = 17.4 Hz, 1H), 4.44 (d, J = 17.0 Hz, 1H), 4.37 (dd, J = 8.6, 6.1 Hz, 1H), 4.30 (d, J = 17.4 Hz, 1H), 4.14 (d, J = 18.7 Hz, 1H), 4.03 (dd, J = 8.7, 5.7 Hz, 1H), 3.87 (d, J = 18.6 Hz, 1H), 3.61 (m, 2H), 3.07 (dd, J = 13.6, 6.1 Hz, 1H), 2.98 (dd, J = 13.4, 5.7 Hz, 1H**). ^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7 (Cq), 172.6 (Cq), 139.8 (2Cq), 139.4 (Cq), 139.3 (Cq), 137.0 (Cq), 136.4 (Cq), 131.8 (2CH), 131.7 (2CH), 129.4 (2CH), 129.2 (2CH), 128.9 (4CH), 128.8 (2CH), 128.6 (CH), 128.5 (2CH), 128.31 (2CH), 128.29 (2CH), 128.27 (3CH), 128.22 (2CH), 128.1 (4CH), 128.0 (2CH), 127.5 (CH), 127.34 (CH), 127.30 (CH), 127.26 (CH), 126.6 (2CH), 126.23 (CH), 126.15 (CH), 122.8 (Cq), 122.3 (Cq), 84.5 (Cq), 84.3 (Cq), 83.9 (Cq), 83.8 (Cq), 51.6 (CH), 51.2 (CH), 50.0 (CH_2), 49.2 (CH_2), 41.7 (CH_2), 41.5 (CH_2), 37.3 (CH_2), 35.8 (CH_2). **ESI-MS** calcd for $C_{31}H_{27}NNaO^+$ $[M+Na]^+$ 452.20, found 452.02.

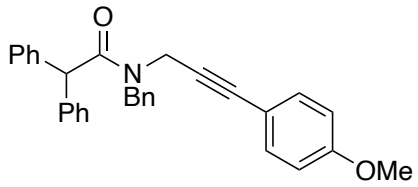
N-benzyl-N-(but-2-yn-1-yl)-2,2-diphenylacetamide



Propargyl amide **1h** was prepared following **GP-4**. After purification, product resulted as a white solide (680 mg, 77%). Two rotamers are observed due to the dynamic amide group.

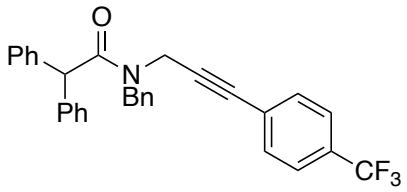
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.17 (m, 15HrotA, 15HrotB), 5.47 (s, 1HrotA), 5.15 (s, 1HrotB), 4.74 (s, 2HrotB), 4.63 (s, 2HrotA), 4.28 (s, 2HrotB), 3.83 (s, 2HrotA), 1.86 (s, 3HrotA), 1.80 (s, 3HrotB). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0 (Cq), 171.9 (Cq), 139.4 (2Cq), 139.3 (2Cq), 137.3 (Cq), 137.0 (Cq), 129.1 (4CH), 129.01 (4CH), 129.00 (2CH), 128.61 (4CH), 128.58 (6CH), 128.4 (2CH), 127.7 (CH), 127.5 (CH) , 127.1 (4CH), 126.5 (2CH), 80.7 (Cq), 79.9 (Cq), 74.1 (Cq), 73.9 (Cq), 54.8 (CH), 54.8 (CH), 50.2 (CH_2), 48.9 (CH_2), 37.0 (CH_2), 35.8 (CH_2), 3.6 ($2CH_3$). **ESI-MS** calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$ 376.17, found 376.32.

N-benzyl-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2,2-diphenylacetamide



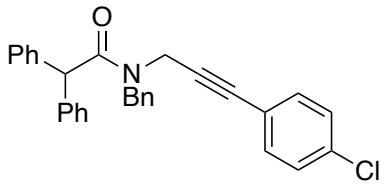
Propargyl amide **1i** was prepared following **GP-5**. After purification, product resulted as a viscous red oil (240 mg, 90%). Two rotamers in equimolar ratio are observed due to the dynamic amide group. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 6.99 (m, 34H), 6.86 (dd, J = 19.9, 8.8 Hz, 4H), 5.56 (s, 1H), 5.19 (s, 1H), 4.82 (s, 2H), 4.70 (s, 2H), 4.55 (s, 2H), 4.11 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1 (Cq), 172.0 (Cq), 159.9 (Cq), 159.6 (Cq), 139.31 (2Cq), 139.28 (2Cq), 137.2 (Cq), 136.9 (Cq), 133.22 (2CH), 133.19 (2CH), 129.1 (4CH), 129.04 (2CH), 129.02 (4CH), 128.7 (4CH), 128.64 (2CH), 128.62 (4CH), 128.5 (2CH), 127.8 (CH), 127.6 (CH), 127.19 (2CH), 127.18 (2CH), 126.6 (2CH), 114.9 (Cq), 114.3 (Cq), 114.1 (2CH), 113.9 (2CH), 84.6 (Cq), 83.9 (Cq), 82.7 (Cq), 82.5 (Cq), 55.4 (CH_3), 55.3 (CH_3), 55.0 (CH), 54.8 (CH), 50.5 (CH_2), 49.2 (CH_2), 37.6 (CH_2), 36.3 (CH_2). **ESI-MS** calcd for $C_{31}H_{28}NO_2^+$ $[M+H]^+$ 446.21, found 446.36.

N-benzyl-2,2-diphenyl-N-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)acetamide



Propargyl amide **1j** was prepared following **GP-5**. After purification, product resulted as a viscous red oil (243 mg, 84%). Two rotamers are observed due to the dynamic amide group.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.12 (m, 19HrotA, 19HrotB), 5.49 (s, 1HrotB), 5.19 (s, 1HrotA), 4.81 (s, 2HrotA), 4.68 (s, 2HrotA), 4.55 (s, 2HrotA), 4.15 (s, 2HrotB**). ^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1 (Cq), 172.0 (Cq), 139.1 (4Cq), 136.9 (Cq), 136.6 (Cq), 132.0 (2CH), 131.9 (2CH), 130.47 (q, J=32.84, Cq), 130.09 (q, J=32.73, Cq), 129.1 (2CH), 129.02 (4CH), 128.96 (4CH), 128.71 (4CH), 128.69 (2CH), 128.65 (4CH), 128.5 (2CH), 127.9 (CH), 127.7 (CH), 127.3 (2CH), 127.3 (2CH),126.55 (q, J=1.46, Cq), 126.51 (2CH), 126.00 (q, J=1.46, Cq), 125.36 (q, J = 3.8 Hz, 2CH), 125.22 (q, J = 3.8 Hz, 2CH), 123.89 (q, J=271.5, Cq), 123.83 (q, J=271.5, Cq), 86.9 (Cq), 86.5 (Cq), 83.3 (Cq), 82.5 (Cq), 55.1 (CH), 54.8 (CH), 50.7 (CH_2), 49.3 (CH_2), 37.5 (CH_2), 36.2 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.74 (s, 3F, rotA), -62.78 (s, 3F, rotB). **ESI-MS** calcd for $C_{31}H_{25}F_3NO^+$ $[M+H]^+$ 484.19, found 484.32.

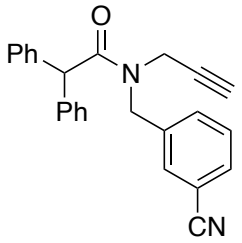
***N*-benzyl-*N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-2,2-diphenylacetamide**



Propargyl amide **1k** was prepared following **GP-5**. After purification, product resulted as a viscous red oil (228 mg, 84%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.16 (m, 19HrotA, 19HrotB), 5.52 (s, 1HrotB), 5.20 (s, 1HrotA), 4.82 (s, 2HrotB), 4.69 (s, 2HrotA), 4.55 (s, 2HrotA), 4.14 (s, 2HrotB). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.03 (Cq), 171.98 (Cq), 139.2 (2Cq), 139.1 (2Cq), 137.0 (Cq), 136.7 (Cq), 134.8 (Cq), 134.4 (Cq), 133.0 (2CH), 132.9 (2CH), 129.06 (2CH), 129.04 (4CH), 128.97 (4CH), 128.78 (2CH), 128.69 (4CH), 128.66 (2CH), 128.63 (6CH), 128.5 (2CH), 127.9 (CH), 127.6 (CH), 127.24 (2CH), 127.22 (2CH), 126.5 (2CH), 121.2 (Cq), 120.7 (Cq), 85.3 (Cq), 84.9 (Cq), 83.5 (Cq), 82.8 (Cq), 55.0 (CH), 54.8 (CH), 50.6 (CH_2), 49.3 (CH_2), 37.5 (CH_2), 36.2 (CH_2). **ESI-MS** calcd for $C_{30}H_{24}ClNNaO^+$ $[M+Na]^+$ 472.14, found 472.28.

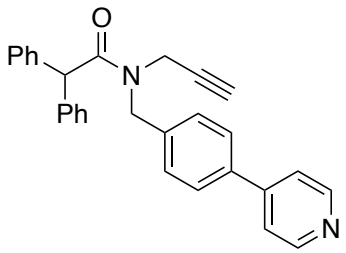
***N*-(3-cyanobenzyl)-2,2-diphenyl-*N*-(prop-2-yn-1-yl)acetamide**



Propargyl amide **1l** was prepared following **GP-5**. After purification, product resulted as white solid (335 mg, 92%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.19 (m, 14HrotA, 14HrotB), 5.45 (s, 1HrotA), 5.12 (s, 1HrotB), 4.75 (s, 2HrotA), 4.70 (s, 2HrotB), 4.28 (d, J = 2.5 Hz, 2HrotB), 3.93 (d, J = 2.5 Hz, 2HrotA), 2.42 (t, J = 2.4 Hz, 1HrotA), 2.25 (t, J = 2.5 Hz, 1HrotB). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2 (Cq), 138.7 (2Cq), 132.6 (Cq), 131.5 (CH), 130.3 (CH), 129.8 (CH), 129.5 (CH), 129.0 (4CH), 128.8 (4CH), 127.5 (2CH), 118.6 (Cq), 112.7 (CH), 78.2 (Cq), 73.7 (Cq), 54.9 (CH), 49.0 (CH_2), 37.4 (CH_2). **ESI-MS** calcd for $C_{25}H_{20}N_2NaO^+$ $[M+Na]^+$ 387.15, found 387.23.

2,2-diphenyl-*N*-(prop-2-yn-1-yl)-*N*-(4-(pyridin-4-yl)benzyl)acetamide

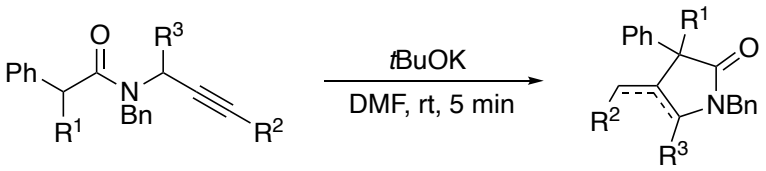


Propargyl amide **1l** was prepared following **GP-5**. After purification, product resulted as a white solid (354 mg, 85%). Two rotamers are observed due to the dynamic amide group.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 13.9, 6.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 15.1, 6.2 Hz, 2H), 7.40 – 7.19 (m, 12H), 5.44 (s, 1HrotB), 5.16 (s, 1HrotA), 4.80 (s, 1HrotB), 4.70 (s, 1HrotA), 4.33 (d, *J* = 2.5 Hz, 1HrotA), 3.92 (d, *J* = 2.5 Hz, 1HrotB), 2.39 (t, *J* = 2.4 Hz, 1HrotB), 2.23 (t, *J* = 2.5 Hz, 1HrotA). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0 (Cq), 150.4 (CH), 147.9 (Cq), 139.0 (Cq), 138.1 (Cq), 137.6 (Cq), 129.1 (2CH), 129.0 (2CH), 128.7 (4CH), 127.6 (4CH), 127.3 (4CH), 121.5 (2CH), 78.5 (Cq), 73.2 (CH), 55.0 (CH), 50.1 (CH), 36.8 (CH). **ESI-MS** calcd for $C_{29}H_{24}N_2NaO^+$ $[M+Na]^+$ 439.18, found 439.22.

Characterization of products

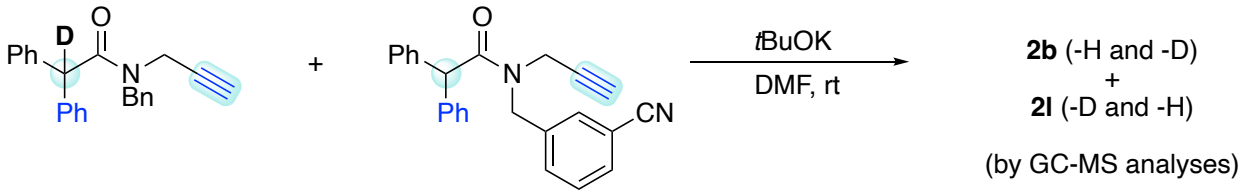
Base-promoted *Conia-ene* cyclization reaction [GP-6 a,b,c] :



1 **2**

The desired propargylic amide (1 eq) and DMF (0.20 M) were sequentially added to a Schlenk tube equipped with a magnetic stirring bar under air. The resulting mixture was stirred at room temperature for 10 minutes prior to the addition of *t*BuOK (0.3 eq[a], 1 eq[b], 3 eq[c]). After complete conversion as monitored by TLC, a saturated NH_4Cl solution was added. The mixture was extracted with EtOAc (3 x 15 mL), the organic layers separated and dried over Na_2SO_4. The solution was concentrated under reduced pressure and the crude purified by chromatography on silica gel (n-hexane/EtOAc gradient).

Double-tagging experiment:

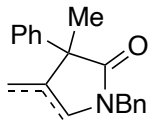


d-1b (0.1 mmol) **1l** (0.1 mmol)

The d- amide **1b** (0.1 mmol, 1 eq) and amide **1l** (0.1 mmol, 1 eq.) in DMF (0.20 M) were sequentially added to a Schlenk tube equipped with a magnetic stirring bar under air. The resulting mixture was stirred at room temperature for 10 minutes prior to the addition of *t*BuOK (0.6 eq) and the mixture was then analyzed by TLC, collecting 50 µL samples at regular intervals for GC-MS analyses. The conversion of **1l** was significantly faster than that of **1b**, likely because of a significant primary kinetic isotope effect. The reaction required a longer time for the full consumption of the two starting materials (90 minutes), and significant decomposition was observed by TLC analyses. According to GC-MS analyses, both protio **2b** and deuteron **2l** (both as their corresponding *endo*/*exo* mixtures)

were detected together with the expected deutero-**2b** and protio-**2l**. This result is consistent with the formation of products through a multi-molecular mechanism, in agreement with the proposed chain scenario presented in the main manuscript.

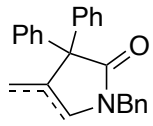
1-benzyl-3,4-dimethyl-3-phenyl-1,3-dihydro-2H-pyrrol-2-one - 1-benzyl-3-methyl-4-methylene-3- phenylpyrrolidin-2-one



Product **2a** was prepared following **GP-6[a]** from correspondent propargyl amide **1a** (79.1 mg, 0.28 mmol). After purification, products resulted as viscous white oil (66.4 mg, 84%, *exo:endo*=40:60)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.7 Hz, 2Hexo), 7.39 – 7.23 (m, 8Hexo, 10Hendo), 7.20 (d, J = 7.3 Hz, 2Hexo), 6.14 (s, 1Hendo), 5.22 (s, 1Hexo), 5.13 (s, 1Hexo), 4.79 – 4.45 (m, 2Hexo, 2Hendo), 4.13 – 3.76 (m, 2Hexo), 1.69 (s, 3Hexo), 1.64 (s, 3Hendo), 1.61 (s, 3Hendo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.2 (Cq), 176.2 (Cq), 147.4 (Cq), 142.2 (Cq), 139.1 (Cq), 137.1 (Cq), 136.1 (Cq), 128.83 (2CH), 128.79 (2CH), 128.76 (2CH) 128.5 (2CH), 128.1 (2CH), 127.8 (2CH), 127.71 (CH), 127.69 (CH), 127.1 (CH), 127.0 (CH), 126.5 (2CH), 126.4 (2CH), 125.8 (Cq), 124.7 (CH), 110.1 (CH_2), 55.8 (Cq), 52.9 (Cq), 50.3 (CH_2), 46.5 (CH_2), 45.6 (CH_2), 24.1 (CH_3), 19.7 (CH_3), 10.6 (CH_3). **ESI-MS** calcd for $C_{19}H_{19}NNaO^+$ $[M+Na]^+$ 300.14, found 300.27.

1-benzyl-4-methyl-3,3-diphenyl-1,3-dihydro-2H-pyrrol-2-one - 1-benzyl-4-methylene-3,3-diphenylpyrrolidin-2-one

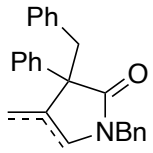


Product **2b** was prepared following **GP-6[a]** from correspondent propargyl amide **1b** (81.6 mg, 0.20 mmol). After purification, products resulted as viscous white oil (73.4 mg, 90%, *exo:endo*=81:19)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.13 (m, 15Hexo, 15Hendo), 6.22 (d, J = 1.7 Hz, 1Hendo), 5.36 (t, J = 1.8 Hz, 1Hexo), 4.85 (t, J = 2.1 Hz, 1Hexo), 4.69 (s, 2Hendo), 4.61 (s, 2Hexo), 3.94 (t, J = 2.0 Hz, 2Hexo), 1.71 (d, J = 1.6 Hz, 3Hendo**). ^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2 (Cq), 174.7

(Cq), 146.6 (Cq), 141.2 (Cq), 140.2 (Cq), 136.8 (Cq), 136.0 (Cq), 129.8 (4CH), 129.0 (2CH), 128.9 (2CH), 128.8 (4CH), 128.7 (2CH), 128.5 (2CH), 128.3 (4CH), 128.0 (4CH), 127.83 (2CH), 127.76 (CH), 127.68 (CH), 127.2 (2CH), 127.2 (2CH), 126.0 (CH), 123.2 (Cq), 113.9 (CH_2), 66.6 (Cq), 63.7 (Cq), 50.5 (CH_2), 46.7 (CH_2), 45.8 (CH_2), 12.1 (CH_3). **ESI- MS** calcd for $C_{24}H_{21}NNaO^+$ $[M+Na]^+$ 362.17, found 362.29.

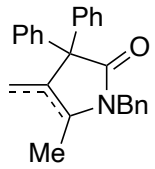
1,3-dibenzyl-4-methyl-3-phenyl-1,3-dihydro-2H-pyrrol-2-one - 1,3-dibenzyl-4-methylene-3-phenylpyrrolidin-2-one



Product **2c** was prepared following **GP-6[a]** from correspondent propargyl amide **1c** (72.3 mg, 0.20 mmol). After purification, products resulted as viscous white oil (64.6 mg, 90%, *exo:endo*=35:65)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2Hendo), 7.45 – 7.16 (m, 13Hexo, 11Hendo), 6.95 – 6.87 (m, 2Hexo), 6.73 (dd, *J* = 7.3, 2.2 Hz, 2Hendo), 5.88 (q, *J* = 1.7 Hz, 1Hendo), 5.32 (t, *J* = 2.1 Hz, 1Hexo), 5.18 (t, *J* = 2.5 Hz, 1Hexo), 4.59 (d, *J* = 15.3 Hz, 1Hendo), 4.46 – 4.11 (m, 2Hexo, 1Hendo), 3.81 (d, *J* = 12.7 Hz, 1Hexo), 3.71 (d, *J* = 12.9 Hz, 1Hexo, 1Hendo), 3.30 (d, *J* = 12.7 Hz, 1Hendo), 3.23 (d, *J* = 12.7 Hz, 1Hexo), 3.16 (dt, *J* = 14.1, 2.3 Hz, 1Hexo), 1.75 (d, *J* = 1.7 Hz, 3Hendo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5 (Cq), 174.9 (Cq), 145.1 (Cq), 142.5 (Cq), 139.2 (Cq), 136.9 (Cq), 136.33 (Cq), 136.31 (Cq), 135.7 (Cq), 130.9 (2CH), 130.1 (2CH), 128.9 (2CH), 128.62 (2CH), 128.60 (2CH), 128.57 (2CH), 128.1 (2CH), 128.0 (4CH), 127.6 (2CH), 127.5 (CH), 127.4 (2CH), 127.2 (CH), 127.1 (CH), 126.71 (4CH), 126.7 (CH), 126.3 (CH), 122.0 (Cq), 112.2 (CH_2), 62.0 (Cq), 59.2 (Cq), 50.6 (CH_2), 46.4 (CH_2), 45.2 (CH_2), 43.6 (CH_2), 38.6 (CH_2), 11.6 (CH_3). **ESI- MS** calcd for $C_{24}H_{21}NNaO^+$ $[M+Na]^+$ 353.18, found 353.33.

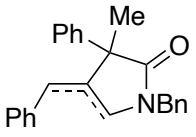
1-benzyl-4,5-dimethyl-3,3-diphenyl-1,3-dihydro-2H-pyrrol-2-one - 1-benzyl-5-methyl-4-methylene-3,3- diphenylpyrrolidin-2-one



Product **2d** was prepared following **GP-6**[b] from correspondent propargyl amide **1d** (71.4 mg, 0.20 mmol). After purification, products resulted as viscous white oil (32.2 mg, 45%, *exo:endo*=69:31)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.13 (m, 13Hexo, 15Hendo), 7.09 – 7.02 (m, 2Hexo), 5.34 (d, J = 1.9 Hz, 1HA), 5.18 (d, J = 15.0 Hz, 1Hexo), 4.82 (d, J = 2.2 Hz, 1Hendo), 4.74 (s, 2Hendo), 4.13 – 3.95 (m, 2Hexo), 1.87 (d, J = 1.3 Hz, 3Hendo), 1.63 (d, J = 1.2 Hz, 3Hendo), 1.28 (d, J = 6.4 Hz, 3Hexo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.7 (Cq), 174.6 (Cq), 152.6 (Cq), 142.3 (Cq), 141.4 (Cq), 140.8 (2Cq), 138.0 (Cq), 136.1 (Cq), 133.4 (Cq), 129.2 (2CH), 128.84 (2CH), 128.76 (4CH), 128.72 (2CH), 128.68 (2CH), 128.4 (4CH), 128.2 (2CH), 128.1 (2CH), 127.9 (2CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 127.1 (2CH) , 127.0 (CH), 126.9 (2CH), 116.2 (Cq), 113.4 (CH_2), 66.0 (Cq), 63.4 (Cq), 55.2 (CH), 44.2 (CH_2), 43.8 (CH_2), 18.5 (CH_3), 10.6 (CH_3), 10.2 (CH_3). **ESI-MS** calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$ 376.17, found 376.31.

(Z)-1-benzyl-4-benzylidene-3-methyl-3-phenylpyrrolidin-2-one - 1,4-dibenzyl-3-methyl-3-phenyl-1,3- dihydro-2H-pyrrol-2-one

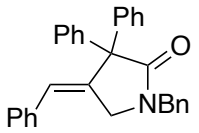


Product **2e** was prepared following **GP-6**[b] from correspondent propargyl amide **1e** (71.9 mg, 0.20 mmol). After purification, products resulted as viscous white oil (43.8 mg, 61%, *exo:endo*=43:57)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.04 (m, 15Hexo, 15Hendo), 6.46 (t, J = 2.4 Hz, 1Hexo), 5.86 (t, J = 2.0 Hz, 1Hendo), 4.77 – 4.52 (m, 2Hexo, 2Hendo), 4.35 – 4.21 (m, 2Hexo), 3.31 – 3.16 (m,

2Hendo), 1.84 (s, 3Hexo), 1.67 (s, 3Hendo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.3 (Cq), 176.0 (Cq), 142.9 (Cq), 140.3 (Cq), 139.0 (Cq), 138.1 (Cq), 137.0 (Cq), 136.13 (Cq), 136.06 (Cq), 130.5 (Cq), 129.2 (2CH), 128.9 (2CH), 128.84 (2CH), 128.78 (2CH), 128.64 (2CH), 128.57 (2CH), 128.45 (2CH), 128.3 (2CH), 128.0 (2CH), 127.7 (CH), 127.63 (CH), 127.59 (2CH), 127.34 (CH), 127.28 (CH), 127.1 (CH), 126.6 (2CH), 126.5 (2CH), 126.4 (CH), 126.1 (CH), 125.6 (CH), 55.9 (Cq), 53.7 (Cq), 49.8 (CH_2), 46.6 (CH_2), 45.7 (CH_2), 32.2 (CH_2), 24.4 (CH_3), 20.2 (CH_3). **ESI-MS** calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$ 376.17, found 376.22.

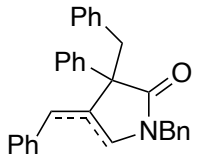
(Z)-1-benzyl-4-benzylidene-3,3-diphenylpyrrolidin-2-one



Product **2f** was prepared following **GP-6^a** from correspondent propargyl amide **1f** (103.4 mg, 0.25 mmol). After purification, products resulted as viscous white oil (96.1 mg, 93%, trace of *endo* and *E*-isomers)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.03 (m, 24H), 6.15 (t, J = 2.3 Hz, 1H), 4.65 (s, 2H), 4.27 (d, J = 2.3 Hz, 2H). **^{13}C NMR (**101 MHz, $CDCl_3$) δ 174.6 (Cq), 141.5 (2Cq), 139.5 (Cq), 136.0 , 135.7 (Cq), 129.23 (CH), 129.16 (4CH), 128.8 (2CH) , 128.6 (2CH), 128.4 (2CH), 128.3 (4CH), 127.8 (2CH), 127.6 (CH), 127.5 (CH), 127.3 (2CH), 64.5 (Cq), 49.8 (CH_2), 46.7 (CH_2). **ESI-MS** calcd for $C_{30}H_{26}NO^+$ $[M+H]^+$ 416.20, found 416.35.

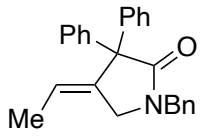
(Z)-1,3-dibenzyl-4-benzylidene-3-phenylpyrrolidin-2-one - 1,3,4-tribenzyl-3-phenyl-1,3-dihydro-2H- pyrrol-2-one



Product **2g** was prepared following **GP-6[b]** from correspondent propargyl amide **1g** (89 mg, 0.20 mmol). After purification, products resulted as viscous white oil (55.5 mg, 62%, *exo:endo*=87:13)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 6.60 (m, 20Hexo, 20Hendo), 6.46 (t, J = 2.6 Hz, 1Hexo), 5.48 (t, J = 2.1 Hz, 1Hendo), 4.73 – 4.47 (m, 1Hexo, 1Hendo), 4.42 – 4.27 (m, 1Hexo, 1Hendo), 4.03 (dd, J = 14.8, 2.5 Hz, 1Hexo), 3.96 (d, J = 12.5 Hz, 1Hexo), 3.85 (d, J = 12.8 Hz, 1Hendo), 3.57 (dd, J = 17.0, 2.2 Hz, 1Hendo), 3.50 – 3.35 (m, 2Hexo, 1Hendo), 3.21 (dd, J = 17.0, 2.1 Hz, 1Hendo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.9 (Cq), 174.8 (Cq), 143.0 (Cq), 139.2 (Cq), 138.8 (Cq), 137.5 (Cq), 136.9 (Cq), 136.3 (Cq), 136.22 (Cq), 136.16 (Cq), 135.7 (Cq), 130.8 (2CH), 130.1 (2CH), 129.3 (2CH), 129.1 (2CH), 128.69 (4CH), 128.66 (2CH), 128.52 (2CH), 128.46 (2CH), 128.20 (2CH), 128.18 (2CH), 128.12 (2CH), 127.9 (2CH), 127.6 (Cq), 127.53 (CH), 127.50 (CH), 127.482 (CH), 127.476 (CH), 127.36 (2CH), 127.33 (3CH), 127.25 (CH), 127.24 (CH), 126.89 (CH), 126.81 (CH), 126.7 (2CH), 126.5 (CH), 61.6 (Cq), 60.1 (Cq), 50.6 (CH_2), 46.5 (CH_2), 45.4 (CH_2), 44.0 (CH_2), 38.7 (CH_2), 32.7 (CH_2). **ESI-MS** calcd for $C_{31}H_{27}NNaO^+$ $[M+Na]^+$ 452.20, found 451.97.

(Z)1-benzyl-4-ethylidene-3,3-diphenylpyrrolidin-2-one

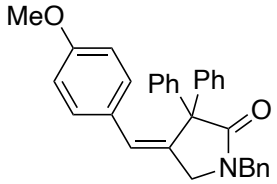


Product **2h** was prepared following **GP-6[b]** from correspondent propargyl amide **1h** (73 mg, 0.20 mmol). After purification, products resulted as viscous white oil (48 mg, 66%, *E-/Z-* = 84:16)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 13HZ, 13HE), 7.21 – 7.12 (m, 2HZ, 2HE), 5.68 (qt, J = 7.2, 1.8 Hz, 1HZ), 5.26 – 5.19 (m, 1HE), 4.61 (s, 2HE), 4.55 (s, 2HZ), 3.93 – 3.90 (m, 2HE), 3.88

(t, J = 1.9 Hz, 2HZ), 1.63 (dt, J = 7.0, 1.3 Hz, 3HE), 1.14 (dt, J = 7.3, 1.8 Hz, 3HZ). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6 (Cq), 175.2 (Cq), 142.3 (2Cq),140.0 (2Cq), 137.7 (Cq), 136.8 (Cq), 136.3 (Cq), 136.2 (Cq), 129.1 (4CH), 129.0 (4CH), 128.8 (2CH), 128.7 (2CH), 128.2 (4CH), 128.13 (4CH), 128.09 (2CH), 127.9 (2CH), 127.62 (CH), 127.59 (CH), 127.1 (2CH), 126.9 (2CH), 124.0 (CH), 123.4 (CH), 63.3 (Cq), 62.5 (Cq), 51.0 (CH_2), 47.9 (CH_2), 46.80 (CH_2), 46.75 (CH_2), 13.9 (CH_3), 13.7 (CH_3). **ESI-MS** calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$ 376.17, found 376.52.

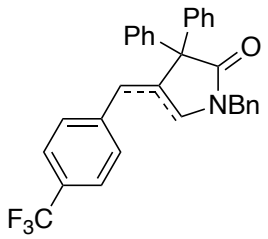
(E/Z)-1-benzyl-4-(4-methoxybenzylidene)-3,3-diphenylpyrrolidin-2-one



Product **2i** was prepared following **GP-6^c** from correspondent propargyl amide **1i** (90.8 mg, 0.20 mmol). After purification, products resulted as viscous white oil (46.6 mg, 51%, *E-/Z-* = 40:60)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.20 (m, 15HE, 15HZ), 7.12 – 7.01 (m, 2HZ), 6.92 – 6.84 (m, 2HZ), 6.77 – 6.73 (m, 2HE), 6.72 (t, J = 2.0 HZ, 1HE), 6.64 – 6.28 (m, 2HE), 6.09 (t, J = 2.4 Hz, 1HZ), 4.66 (s, 2HZ), 4.58 (s, 2HE), 4.26 (d, J = 2.3 Hz, 2HZ), 4.10 (d, J = 1.8 Hz, 2HE), 3.81 (s, 3HZ), 3.67 (s, 3HE). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5 (Cq), 174.7 (Cq), 158.9 (Cq), 158.4 (Cq), 141.7 (2Cq), 138.4 (2Cq), 137.2 (Cq), 136.5 (Cq), 136.2 (Cq), 136.1 (Cq), 130.2 (2CH), 129.8 (2CH), 129.5 (4CH), 129.2 (4CH), 128.79 (2CH), 128.77 (2CH), 128.66 (CH), 128.5 (Cq), 128.3 (4CH), 128.2 (CH), 127.99 (2CH), 127.96 (4CH), 127.8 (2CH), 127.63 (CH), 127.61 (CH), 127.2 (4CH), 127.1 (Cq), 114.0 (2CH), 112.6 (2CH), 64.4 (Cq), 63.3 (Cq), 55.3 (CH_3), 55.1 (CH_3), 52.5 (CH_2), 49.8 (CH_2), 46.7 (2CH_2). **ESI-MS** calcd for $C_{31}H_{27}NNaO_2^+$ $[M+Na]^+$ 468.19, found 468.14.

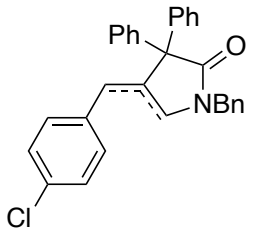
(Z)-1-benzyl-3,3-diphenyl-4-(4-(trifluoromethyl)benzylidene)pyrrolidin-2-one - 1-benzyl-3,3-diphenyl- 4-(4-(trifluoromethyl)benzyl)-1,3-dihydro-2H-pyrrol-2-one



Product **2j** was prepared following **GP-6**[b] from correspondent propargyl amide **1j** (99.6 mg, 0.20 mmol). After purification, products resulted as viscous white oil (50.9 mg, 51%, *exo:endo* = 35:65)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2Hexo), 7.47 (d, J = 8.0 Hz, 2Hendo,), 7.41 – 7.06 (m, 17Hendo, 17Hexo), 6.18 (t, J = 2.5 Hz, 1Hexo), 5.80 (t, J = 2.0 Hz, 1Hendo), 4.64 (s, 2Hexo), 4.63 (s, 2Hendo), 4.24 (d, J = 2.3 Hz, 2Hexo), 3.38 (d, J = 1.9 Hz, 2Hendo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2 (Cq), 174.3 (Cq), 142.4 (Cq), 142.08 (q, J = 1.3 Hz, Cq), 141.1 (2Cq), 139.8 (2Cq), 139.09 (q, J = 1.4 Hz, Cq), 136.6 (Cq), 135.8 (Cq), 129.5 (2CH), 129.36 (q, J=32.2 Hz, Cq), 129.1 (4CH), 128.9 (2CH), 128.8 (2CH), 128.76 (q, J=16.1, Cq), 128.7 (4CH), 128.64 (4CH), 128.61 (2CH), 128.5 (4CH), 128.0 (CH), 127.8 (CH), 127.75 (CH), 127.73 (CH), 127.55 (2CH), 127.50 (2CH), 127.3 (Cq), 125.51 (q, J = 3.6 Hz, 2CH), 125.37 (q, J = 4.0 Hz, 2CH), 124.21 (q, J=271.5 Hz, Cq), 123.99 (q, J=271.5 Hz, Cq), 66.6 (Cq), 64.6 (Cq), 49.6 (CH_2), 46.8 (CH_2), 45.9 (CH_2), 32.8 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.34 (s, 3Fendo)), -62.53 (s, 3Fexo). **ESI-MS** calcd for $C_{31}H_{24}F_3NNaO^+$ $[M+Na]^+$ 506.17, found 506.29.

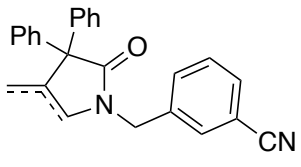
(Z)-1-benzyl-4-(4-chlorobenzylidene)-3,3-diphenylpyrrolidin-2-one - 1-benzyl-4-(4-chlorobenzyl)-3,3- diphenyl-1,3-dihydro-2H-pyrrol-2-one



Product **2k** was prepared following **GP-6[b]** from correspondent propargyl amide **1k** (111 mg, 0.25 mmol). After purification, products resulted as viscous white oil (74.4 mg, 67 %, *exo:endo* = 44:56)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.25 (m, 13Hexo, 14Hendo), 7.25 – 7.14 (m, 6Hexo), 7.10 – 6.97 (m, 5Hendo), 6.13 (s, 1Hexo), 5.81 (s, 1Hendo), 4.67 (s, 2Hexo), 4.66 (s, 2Hendo), 4.25 (d, J = 2.3 Hz, 2Hexo), 3.31 (d, J = 2.0 Hz, 2Hendo). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2 (Cq), 174.4 (Cq), 141.3 (2Cq), 140.4 (Cq), 140.0 (2Cq), 136.7 (Cq), 136.3 (Cq), 136.0 (Cq), 134.2 (Cq), 133.3 (Cq), 132.2 (Cq), 130.6 (2CH), 129.7 (2CH), 129.1 (4CH), 128.9 (2CH), 128.82 (2CH), 128.77 (2CH), 128.72 (4CH), 128.68 (4CH), 128.62 (2CH), 128.4 (4CH), 128.1 (CH), 128.0 (Cq), 127.8 (2CH), 127.7 (2CH), 127.6 (CH), 127.51 (2CH), 127.50 (2CH) 127.4 (2CH), 66.6 (Cq), 64.5 (Cq), 49.6 (CH_2), 46.7 (CH_2), 45.9 (CH_2), 32.4 (CH_2). **ESI-MS** calcd for $C_{30}H_{24}ClNNaO^+$ $[M+Na]^+$ 472.14, found 471.93.

3-((4-methylene-2-oxo-3,3-diphenylpyrrolidin-1-yl)methyl)benzonitrile - 3-((4-methyl-2-oxo-3,3-diphenyl-2,3-dihydro-1*H*-pyrrol-1-yl)methyl)benzonitrile

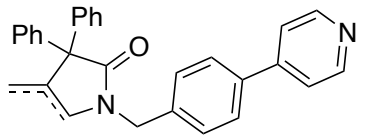


Product **2l** was prepared following **GP-6[a]** from correspondent propargyl amide **1l** (72.8 mg, 0.2 mmol). After purification, products resulted as viscous white oil (63.1 mg, 87%, *exo:endo* = 80:20)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.42 (m, 2H_{exo}, 1H_{endo}), 7.38 – 7.27 (m, 11H_{exo}, 12H_{endo}), 7.20 (d, *J* = 6.7 Hz, 1H_{exo}, 1H_{endo}), 6.22 (d, *J* = 1.7 Hz, 1H_{endo}), 5.40 (s, 1H_{exo}), 4.86 (s, 1H_{exo}), 4.70 (s,

$2H_{endo}$), 4.61 (s, $2H_{exo}$), 3.94 (s, $2H_{exo}$), 1.72 (d, J = 1.7 Hz, $3H_{endo}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1 (Cq), 146.1 (Cq), 140.6 (2Cq), 137.8 (Cq), 132.1 (CH), 131.5 (CH), 131.1 (CH), 129.7 (CH), 128.9 (4CH), 128.4 (4CH), 127.5 (2CH), 125.5 (Cq), 114.3 (CH), 112.9 (Cq), 63.6 (Cq), 50.6 (CH_2), 45.9 (CH_2). **ESI-MS** calcd for $C_{25}H_{20}N_2NaO^+$ $[M+Na]^+$ 387.15, found 387.19.

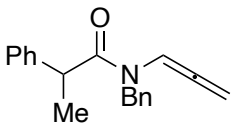
4-methylene-3,3-diphenyl-1-(4-(pyridin-4-yl)benzyl)pyrrolidin-2-one - 4-methyl-3,3-diphenyl-1-(4-(pyridin-4-yl)benzyl)-1,3-dihydro-2*H*-pyrrol-2-one



Product **2m** was prepared following **GP-6^a** from correspondent propargyl amide **1m** (83 mg, 0.2 mmol). After purification, products resulted as white solid (73.0 mg, 88%, *exo:endo* = 77:23)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 6.1 Hz, $2H_{exo}$, $2H_{endo}$), 7.66 – 7.43 (m, $4H_{exo}$, $4H_{endo}$), 7.40 – 7.18 (m, $12H_{exo}$, $12H_{endo}$), 6.25 (d, J = 1.7 Hz, $1H_{endo}$), 5.37 (s, $1H_{exo}$), 4.85 (s, $1H_{exo}$), 4.73 (s, $1H_{exo}$), 4.65 (s, $2H_{exo}$), 3.96 (s, $2H_{endo}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8 (Cq), 150.3 (2CH), 147.7 (Cq), 146.5 (Cq), 141.0 (2Cq), 137.5 (Cq), 137.2 (CH) 129.0 (4CH), 128.6 (2CH), 128.3 (4CH), 127.4 (2CH), 127.3 (2CH), 121.5 (2CH), 114.1 (CH), 63.6 (Cq), 50.6 (CH_2), 46.3 (CH_2). **ESI-MS** calcd for $C_{29}H_{24}N_2NaO^+$ $[M+Na]^+$ 439.18, found 439.21.

***N*-benzyl-2-phenyl-*N*-(propa-1,2-dien-1-yl)propanamide**



Product **1a'** was obtained as side product following **GP-6^b** and using KHMDS as base, from correspondent propargyl amide **1a** (55.4 mg, 0.2 mmol). After purification, products resulted as yellow oil (38.2 mg, 69%). Two rotamers in equimolar ratio are observed due to the dynamic amide group.

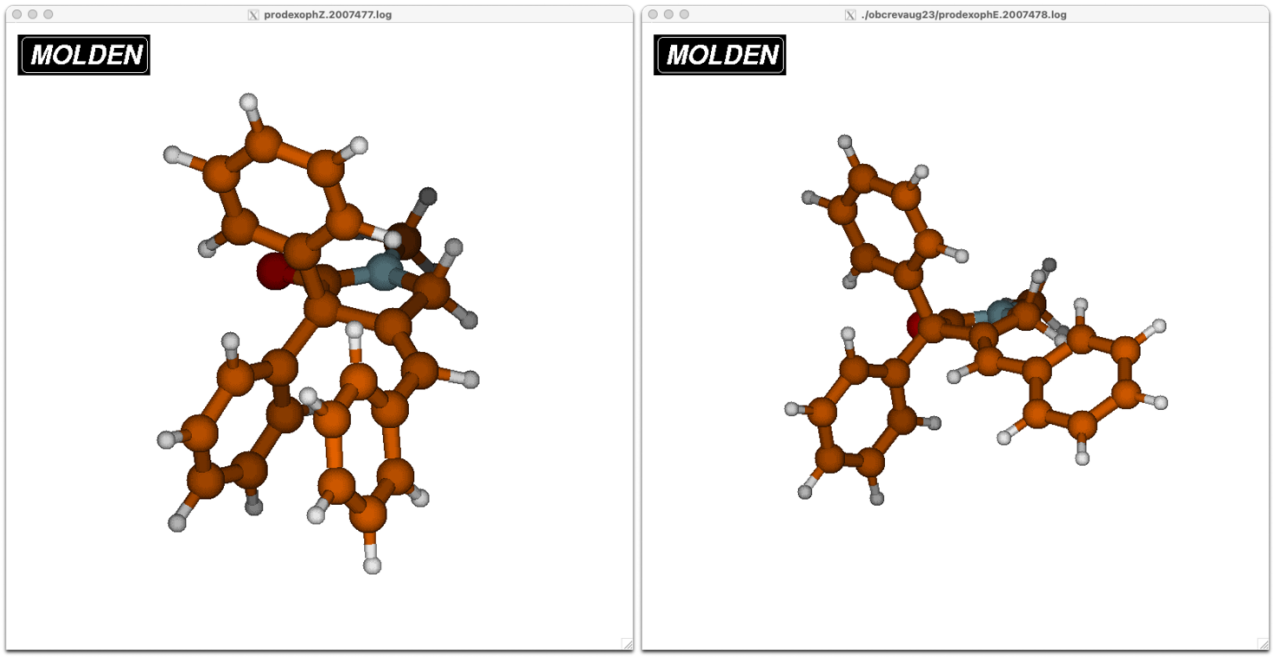
^{1}H NMR (400 MHz, CDCl3) δ 7.72 (t, *J* = 6.4 Hz, 1H), 7.38 – 7.07 (m, 20H), 6.77 (t, *J* = 6.2 Hz, 1H), 5.22 (d, *J* = 6.4 Hz, 2H), 5.17 (d, *J* = 6.2 Hz, 1H), 4.83 (d, *J* = 14.8 Hz, 1H), 4.63 (d, *J* = 14.8 Hz, 1H), 4.48 (d, *J* = 17.4 Hz, 1H), 4.04 (q, *J* = 6.8 Hz, 1H), 3.75 (q, *J* = 6.8 Hz, 1H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H). **ESI-MS** calcd for $C_{19}H_{19}NNaO^+$ $[M+Na]^+$ 300.14, found 300.21.

Computational details

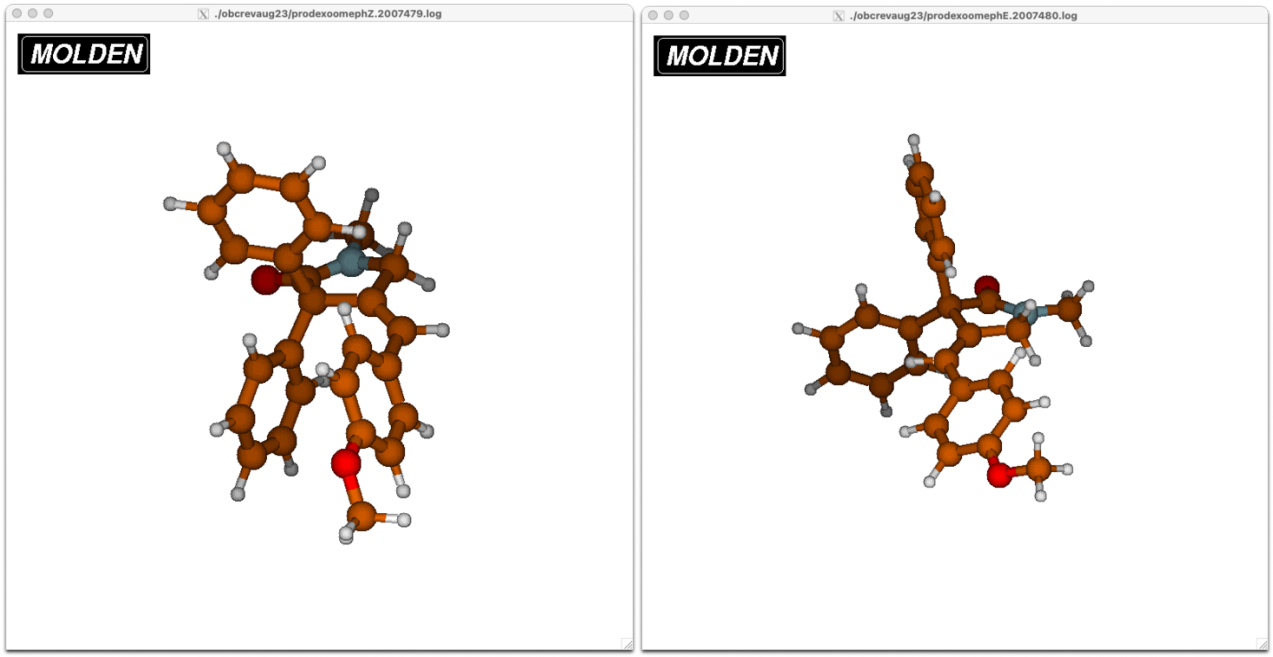
Calculations were performed at the DFT level using Gaussian16.[3] Optimization were performed without any constraint using the hybrid M06 functional described by Zhao and Truhlar[4] in combination with the the Def2-SVP basis set described by Weigend and Ahlrichs.[5] Solvated structures were modeled using DMF as implicit solvent through the use of the CPCM method introduced by Barone and Cossi.[6] Free re-optimization on all structures was then carried out using the Def2-TZVP basis set,[5] which provided a set of data comparable to those obtained using the lower end double-ζ peer. All values and geometries reported hereafter are those of the freely optimized solvated structures, calculated at the M06/Def2-TZVP level. All intermediates were characterized by the absence of any imaginary frequency in their Hessian matrix. All transition states were characterized by the presence of a single imaginary frequency in their Hessian matrix, which corresponds to the molecular vibration connecting the reactant with the product.

Comparison of the stability of *E*-/*Z*- products 2f and 2i

We modeled by DFT the two *E*- and *Z*- isomers of **2f**, chosen as representative example of the products in which such a mixture is formed. The experimentally favored *Z*- isomer was less stable than the *E*- one by 2.9 kcal/mol because the latter can benefit from a favorable π-stacking interaction between the aryl alfa to the carbonyl and that of the styryl arm. In both cases, the steric hindrance of the cyclic compound induce a tilt of the aryl ring of the stryryl arm, reducing the conjugation of the arene with the alkene unit (dihedral angle ca 35° for both isomers). The same energetic trend was observed for **2i** (*E*- isomer was favored by 3.6 kcal/mol). Moreover, an identical trend was observed for the four corresponding parent anionic intermediate **IV**, in which the *E*- isomer, regardless of the substitution of the aryl ring, results more stable (by 6.3-6.6 kcal/mol). 3D images of these structures follow hereafter.



Z-**2f** (left) and *E*-**2f** (right)



Z-**2i** (left) and *E*-**2i** (right)

Regarding the geometry of **TS**-*exo* (Scheme 2 of the main manuscript), the less stable *Z*- isomer becomes the most abundant product (*E*-/*Z*- ratios are 1:99 for **2e**, **2f**, **2g**, **2j** and **2k**; 16:84 for **2h**) because the corresponding vinyl carbanion **IV** has a less hindered face from which a substrate molecule could more easily approach.

Because no significant differences emerged comparing **2f** and **2i**, (for which the *E*-/*Z*- ratio is 60:40 instead), we suppose that the predominant formation of the more thermodynamically stable *E*- isomer in this case results from a secondary isomerization, which might be promoted by the acid used to quench the reaction mixture and that would become possible thanks to its very electron rich anethole arm. The presence of a secondary isomerization process might fit with the significantly lower yield of **2i** compared to that of **2f** (51% and 93%, respectively).

XYZ Coordinates

tBuOH
15
scf done: -233.605413

C	4.873289	-1.787637	-2.049047
O	3.607822	-1.700081	-1.389090
C	4.586073	-1.521393	-3.509732
C	5.812586	-0.738377	-1.485212
C	5.448978	-3.178198	-1.858588
H	3.750364	-1.858979	-0.449917
H	5.988480	-0.912826	-0.419585
H	6.779156	-0.764573	-1.994304
H	5.384249	0.259231	-1.605710
H	4.760372	-3.931188	-2.248559
H	6.404895	-3.280434	-2.378129
H	5.618914	-3.381961	-0.797201
H	5.506186	-1.570024	-4.095543
H	3.886717	-2.263334	-3.901830
H	4.146743	-0.529395	-3.637157

$tBuO^-$
14
scf done: -233.085224

C	4.788734	-1.783409	-2.009360
O	3.615101	-1.715670	-1.342560
C	4.602987	-1.523069	-3.516643
C	5.799890	-0.743887	-1.488830
C	5.442720	-3.170396	-1.864556
H	5.980259	-0.911580	-0.421727
H	6.765852	-0.775478	-2.009024
H	5.381119	0.261326	-1.604462
H	4.759186	-3.935185	-2.248385
H	6.397373	-3.263711	-2.397707
H	5.620006	-3.381075	-0.804459
H	5.537897	-1.578925	-4.088682
H	3.904516	-2.259080	-3.929038
H	4.169243	-0.528378	-3.665909

1a
37
scf done: -825.760337

C	2.310103	-0.535903	0.180295
C	3.613386	-0.665398	-0.610460
N	3.879041	-1.883564	-1.151581
C	2.973242	-3.018651	-1.085458
O	4.379870	0.274760	-0.720224
C	5.035781	-2.067437	-2.003414
H	4.719108	-2.352805	-3.010980
H	5.594342	-1.137753	-2.054802

H	5.680519	-2.854974	-1.606223
C	1.986847	-3.014055	-2.159233
H	3.578455	-3.927821	-1.143997
H	2.477742	-3.061066	-0.112856
C	1.178833	-2.975645	-3.043422
H	0.461055	-2.948273	-3.830767
C	2.456824	-1.093501	1.579293
C	1.820728	0.893474	0.157145
H	1.539761	-1.126007	-0.326375
C	1.322289	-1.560072	2.235763
C	1.401769	-2.047929	3.527741
C	2.622518	-2.077476	4.184419
C	3.757409	-1.616773	3.539749
C	3.675678	-1.128115	2.244731
H	0.366028	-1.536208	1.721137
H	0.508303	-2.409712	4.023140
H	2.687986	-2.461378	5.195593
H	4.715776	-1.637088	4.045427
H	4.571631	-0.764153	1.751989
C	0.950169	1.289773	-0.850472
C	0.497797	2.596850	-0.924450
C	0.913157	3.526861	0.014113
C	1.781596	3.140533	1.022838
C	2.231459	1.832862	1.093525
H	0.622644	0.560252	-1.586225
H	-0.184227	2.887740	-1.715067
H	0.558409	4.549598	-0.037512
H	2.110440	3.862559	1.761462
H	2.909443	1.538297	1.887654

1a-tBuO$^-$

51

scf done: -1058.847500

C	0.006799	0.064119	0.003420
C	0.002087	-0.000176	1.399241
C	1.241101	-0.058836	2.039242
C	2.427981	-0.036951	1.322664
C	2.409743	0.029728	-0.060758
C	1.188041	0.076381	-0.716865
C	-1.310282	-0.065034	2.121030
C	-1.299150	0.336853	3.540212
N	-0.753623	1.561717	3.868594
C	-0.392737	2.587041	2.907011
C	-0.801566	3.919493	3.332240
C	-1.119671	5.024220	3.673988
C	-1.935092	-1.426715	1.929855
C	-3.201001	-1.573646	1.374347
C	-3.767666	-2.828052	1.190370
C	-3.074158	-3.967477	1.558545
C	-1.806561	-3.841171	2.110597
C	-1.249955	-2.587684	2.289820

O	-1.788138	-0.343911	4.444461
C	-0.568621	1.879150	5.265956
O	-2.728939	1.648370	0.715657
C	-3.870835	2.281282	1.183638
C	-4.102021	2.021820	2.674778
C	-3.741516	3.788433	0.963192
C	-5.097902	1.793414	0.409653
H	-1.436299	2.392201	5.697538
H	-0.402584	0.963858	5.829971
H	0.300630	2.530529	5.378598
H	-0.884483	2.369170	1.951743
H	0.692291	2.595213	2.724474
H	-1.407227	6.005534	3.973059
H	-2.106276	0.814638	1.486677
H	-0.946947	0.122018	-0.511993
H	1.156799	0.130228	-1.799897
H	3.336684	0.044776	-0.622388
H	3.374085	-0.082569	1.851445
H	1.277540	-0.124117	3.123130
H	-3.735929	-0.681492	1.067396
H	-4.756197	-2.912947	0.751572
H	-3.513050	-4.948294	1.414017
H	-1.251681	-4.726318	2.403010
H	-0.258124	-2.497542	2.724399
H	-5.013769	2.516350	3.024549
H	-4.201991	0.949851	2.870145
H	-3.263516	2.395838	3.271929
H	-4.631097	4.332562	1.299740
H	-2.874949	4.174762	1.507243
H	-3.597141	3.994500	-0.101932
H	-6.010294	2.319968	0.710092
H	-4.945133	1.954984	-0.661609
H	-5.257002	0.723243	0.570296

I

36

scf done: -825.248643

C	2.017680	-0.313401	0.126602
C	3.142460	-0.558299	-0.882910
N	3.148631	-1.736126	-1.546624
C	2.289071	-2.892645	-1.268721
O	4.007977	0.287299	-1.065258
C	4.255425	-1.996658	-2.444145
H	3.956029	-2.764914	-3.157443
H	4.523357	-1.089260	-2.980869
H	5.136794	-2.355326	-1.903131
C	2.982962	-3.982392	-0.584141
H	1.422055	-2.561903	-0.695785
C	3.576633	-4.901613	-0.014741
C	2.295736	-1.045940	1.419275
C	1.779443	1.169100	0.307242

C	1.235221	-1.572500	2.147183
C	1.454164	-2.233001	3.344036
C	2.743561	-2.374645	3.832271
C	3.807595	-1.852592	3.115570
C	3.585064	-1.193876	1.917048
H	0.224661	-1.466840	1.763104
H	0.615343	-2.642370	3.895007
H	2.918469	-2.894759	4.766690
H	4.819545	-1.962682	3.487778
H	4.426193	-0.794994	1.358391
C	0.914015	1.817422	-0.566653
C	0.677625	3.177148	-0.458255
C	1.306174	3.912592	0.533689
C	2.169403	3.276504	1.410533
C	2.403274	1.915384	1.297774
H	0.417117	1.243397	-1.343409
H	-0.003606	3.662704	-1.147622
H	1.120399	4.976361	0.625603
H	2.664581	3.842897	2.191058
H	3.078899	1.428635	1.992596
H	1.089883	-0.718904	-0.287234
H	1.894909	-3.231046	-2.235794

II

36

scf done: -825.243029

C	2.305065	-0.478639	0.172483
C	3.592551	-0.632667	-0.632817
N	3.758595	-1.818484	-1.253898
C	2.894950	-2.956161	-1.066832
O	4.423739	0.272012	-0.674733
C	4.961764	-2.026714	-2.035509
H	4.711386	-2.621980	-2.915210
H	5.378800	-1.071895	-2.348718
H	5.717652	-2.568754	-1.457356
C	2.347273	-3.588721	-2.116252
H	2.800736	-3.317494	-0.047229
C	1.967398	-4.257946	-3.126191
H	1.004344	-4.113486	-3.611885
C	2.445319	-1.057883	1.563150
C	1.845958	0.958986	0.191218
C	1.297177	-1.458468	2.239577
C	1.368697	-1.967952	3.523541
C	2.597397	-2.087691	4.155801
C	3.746503	-1.694939	3.491898
C	3.670939	-1.183490	2.204533
H	0.334803	-1.366618	1.743893
H	0.462831	-2.277039	4.032523
H	2.657248	-2.488862	5.160751
H	4.711926	-1.786591	3.976442
H	4.578179	-0.874347	1.695263

C	0.902312	1.386692	-0.734634
C	0.472344	2.704139	-0.758439
C	0.983691	3.616109	0.149385
C	1.925007	3.200203	1.078744
C	2.350353	1.883141	1.099031
H	0.497777	0.673238	-1.446240
H	-0.267641	3.016642	-1.486480
H	0.647627	4.646480	0.136710
H	2.329715	3.907385	1.793989
H	3.085411	1.564865	1.830781
H	1.537782	-1.069497	-0.338300

III

36

scf done: -825.252699

C	0.440977	0.420761	0.160226
C	0.298850	-0.321408	1.351348
C	1.494237	-0.851800	1.876623
C	2.722113	-0.655406	1.271014
C	2.829564	0.079237	0.099341
C	1.667372	0.613524	-0.444534
C	-0.983023	-0.519808	2.008545
C	-2.177276	-0.505851	1.239018
N	-3.410416	-0.281402	1.929936
C	-3.472435	0.876333	2.804626
C	-3.257303	2.135669	2.090928
O	-2.248767	-0.668514	0.007723
C	-4.602484	-0.428474	1.126611
C	-3.067831	3.140798	1.462231
C	-1.006624	-0.796270	3.448481
C	-1.795164	-1.815628	4.002954
C	-1.842369	-2.047693	5.366353
C	-1.083030	-1.283801	6.241053
C	-0.277973	-0.280797	5.719511
C	-0.245888	-0.042911	4.357394
H	-2.743515	0.791355	3.614411
H	-4.456847	0.895836	3.284127
H	-4.561180	-1.358334	0.562989
H	-5.473809	-0.456444	1.785848
H	-4.743326	0.389617	0.404943
H	-2.900320	4.038853	0.913918
H	-2.385475	-2.435136	3.336599
H	-2.468211	-2.847073	5.750058
H	-1.114409	-1.469430	7.308407
H	0.321162	0.333630	6.383771
H	0.374806	0.761493	3.973871
H	1.450480	-1.443521	2.785112
H	3.608773	-1.094470	1.718222
H	3.790500	0.231482	-0.378148
H	1.719734	1.201823	-1.355794
H	-0.444747	0.853490	-0.288664

TS (1a-III)

51

scf done: -1058.847500

C	0.007178	0.063436	0.003540
C	0.002316	-0.000283	1.399403
C	1.241295	-0.058160	2.039535
C	2.428234	-0.036018	1.323047
C	2.410130	0.030157	-0.060392
C	1.188462	0.075976	-0.716643
C	-1.310148	-0.065273	2.120859
C	-1.299339	0.336468	3.540163
N	-0.754136	1.561424	3.868643
C	-0.393261	2.586807	2.907123
C	-0.802080	3.919246	3.332396
C	-1.120100	5.023978	3.674199
C	-1.934995	-1.426949	1.929594
C	-3.201793	-1.573756	1.376083
C	-3.768592	-2.828148	1.192427
C	-3.074327	-3.967676	1.558843
C	-1.805810	-3.841492	2.108813
C	-1.249090	-2.588026	2.287776
O	-1.788269	-0.344514	4.444254
C	-0.569012	1.878839	5.265998
O	-2.729191	1.647921	0.715635
C	-3.870771	2.281490	1.183396
C	-4.101996	2.022556	2.674643
C	-3.740889	3.788523	0.962426
C	-5.098053	1.793855	0.409629
H	-1.436261	2.392773	5.697369
H	-0.403922	0.963433	5.830093
H	0.300858	2.529397	5.378711
H	-0.884950	2.368931	1.951837
H	0.691780	2.594992	2.724622
H	-1.407600	6.005290	3.973333
H	-2.106314	0.814350	1.486655
H	-0.946567	0.120556	-0.511976
H	1.157279	0.129379	-1.799698
H	3.337121	0.045429	-0.621929
H	3.374285	-0.081030	1.851977
H	1.277721	-0.123082	3.123445
H	-3.737319	-0.681557	1.070324
H	-4.757840	-2.912946	0.755225
H	-3.513319	-4.948480	1.414533
H	-1.250343	-4.726729	2.399839
H	-0.256585	-2.497952	2.720835
H	-5.013668	2.517267	3.024353
H	-4.202020	0.950642	2.870299
H	-3.263422	2.396639	3.271652
H	-4.630335	4.333072	1.298646
H	-2.874267	4.174784	1.506430

H	-3.596316	3.994100	-0.102762
H	-6.010250	2.320748	0.710081
H	-4.945423	1.955166	-0.661695
H	-5.257428	0.723758	0.570503

TS (III-IV)

36

scf done: -825.230175

C	0.157072	0.463667	0.060921
C	0.164082	-0.076722	1.359999
C	1.427692	-0.352905	1.903835
C	2.595691	-0.117791	1.198283
C	2.558625	0.403929	-0.085571
C	1.321017	0.689378	-0.647274
C	-1.094313	-0.290136	2.056533
C	-2.214909	-0.812930	1.249970
N	-3.399975	-0.192918	1.542381
C	-3.366700	0.984558	2.374710
C	-2.066461	1.659868	2.218301
O	-2.153132	-1.709312	0.407729
C	-4.677627	-0.780628	1.255578
C	-1.470246	2.751284	2.136598
C	-1.137283	-0.662704	3.471384
C	-2.007757	-1.654096	3.955669
C	-2.091998	-1.962295	5.303118
C	-1.298361	-1.306338	6.230365
C	-0.426216	-0.323579	5.778298
C	-0.352469	-0.005813	4.436477
H	-3.548272	0.725937	3.431382
H	-4.179639	1.656379	2.071527
H	-4.527217	-1.681140	0.663611
H	-5.197717	-1.047129	2.185001
H	-5.317646	-0.091267	0.696611
H	-0.466724	3.124772	2.019847
H	-2.627903	-2.207124	3.255282
H	-2.778736	-2.736942	5.628410
H	-1.356968	-1.552890	7.283973
H	0.195737	0.214416	6.486480
H	0.308710	0.792374	4.116920
H	1.496506	-0.786885	2.894768
H	3.549246	-0.357986	1.657626
H	3.473526	0.587730	-0.636654
H	1.263190	1.103391	-1.648788
H	-0.796687	0.711578	-0.394247

IV

36

scf done: -825.262277

C	0.066296	0.300742	0.346065
N	0.529914	-0.213407	1.501764
C	1.882615	0.186238	1.827858

C	2.177290	1.318631	0.872792
C	1.205479	1.102283	-0.308274
C	-0.195702	-1.144581	2.315776
H	2.560464	-0.675124	1.703698
H	1.949940	0.504058	2.874416
C	1.787290	0.177149	-1.380799
C	0.730416	2.411768	-0.884311
O	-1.051727	0.116836	-0.109273
H	-1.172750	-1.323988	1.870038
H	0.343661	-2.094126	2.389820
H	-0.330960	-0.751941	3.327697
C	3.093128	2.266176	1.088900
H	3.102262	2.972232	0.234761
C	0.977283	-0.268222	-2.425745
C	1.477418	-1.096240	-3.413751
C	2.804320	-1.500961	-3.379444
C	3.618272	-1.066747	-2.349032
C	3.113115	-0.234881	-1.358859
H	-0.060429	0.045298	-2.456785
H	0.829180	-1.427296	-4.217537
H	3.198527	-2.149189	-4.153682
H	4.657730	-1.373465	-2.312023
H	3.755720	0.117431	-0.558569
C	1.340310	2.978747	-1.997520
C	0.965223	4.231121	-2.461666
C	-0.033654	4.941983	-1.820444
C	-0.646940	4.392086	-0.704113
C	-0.263608	3.146041	-0.241644
H	2.125349	2.433562	-2.510746
H	1.460077	4.651345	-3.330188
H	-0.332672	5.918299	-2.184131
H	-1.428395	4.939317	-0.188670
H	-0.742027	2.736366	0.642259

V

73

scf done: -1651.037875

C	2.642038	1.829908	0.202660
C	1.603074	0.924094	0.014992
C	0.298043	1.401090	0.003654
C	0.033592	2.752908	0.168784
C	1.075204	3.646179	0.347205
C	2.381765	3.179008	0.364011
C	1.841284	-0.560922	-0.132142
C	2.562457	-1.117835	1.074092
C	1.816603	-1.557076	2.162479
C	2.439809	-2.040022	3.300061
C	3.824066	-2.084826	3.367279
C	4.576113	-1.649064	2.288792
C	3.948952	-1.171969	1.149357
C	2.538657	-0.916095	-1.441952

O	3.073713	-0.069083	-2.140491
N	2.515877	-2.226694	-1.805983
C	3.133833	-2.641634	-3.047602
C	1.886092	-3.302070	-1.056791
C	2.841029	-4.139564	-0.341488
C	3.620591	-4.849271	0.229919
H	2.368330	-2.897550	-3.790091
H	3.747571	-1.835353	-3.438831
H	3.759821	-3.520812	-2.876053
H	1.327548	-3.923280	-1.766642
H	1.119518	-2.909903	-0.386235
H	4.313621	-5.473042	0.745595
H	0.842644	-1.025646	-0.176617
H	0.731570	-1.523268	2.104168
H	1.843395	-2.383414	4.137592
H	4.314606	-2.461844	4.257058
H	5.658661	-1.685977	2.331198
H	4.548959	-0.847299	0.304129
H	-0.515233	0.692417	-0.135844
H	-0.991382	3.106357	0.159498
H	0.872985	4.703153	0.477283
H	3.203228	3.872081	0.506708
H	3.666631	1.475242	0.224096
C	-1.291562	-2.129126	-0.983687
H	-1.757700	-3.110184	-0.772203
C	-1.163900	-1.961500	-2.301706
C	-0.537895	-0.751025	-2.951794
H	0.260999	-0.311273	-2.349522
H	-1.262122	0.055579	-3.158768
N	-0.005498	-1.257737	-4.198893
C	-0.508351	-2.453250	-4.561105
C	-1.536435	-2.879257	-3.496193
C	-1.459720	-4.342134	-3.143995
C	-2.907029	-2.527634	-4.086846
C	-0.304399	-5.093504	-3.339014
C	-3.766707	-1.624327	-3.475990
C	-5.008438	-1.337833	-4.025948
C	-5.411729	-1.951214	-5.198333
C	-4.563266	-2.857749	-5.817682
C	-3.326896	-3.141296	-5.266886
C	-0.224186	-6.410882	-2.915644
C	-1.301873	-7.009025	-2.283574
C	-2.459772	-6.275630	-2.082779
C	-2.535508	-4.960149	-2.510083
O	-0.215081	-3.059056	-5.581190
C	0.883048	-0.473056	-5.008167
H	1.202326	-1.063548	-5.865798
H	0.387442	0.435200	-5.366389
H	1.760219	-0.179467	-4.423257
H	-2.667883	-3.852262	-5.753495
H	-4.869270	-3.348973	-6.734696

H	-6.381974	-1.729084	-5.627609
H	-5.664242	-0.631570	-3.528931
H	-3.458900	-1.156340	-2.546917
H	-3.449671	-4.398102	-2.349529
H	-3.312039	-6.729300	-1.589250
H	-1.241471	-8.039950	-1.954445
H	0.687150	-6.973287	-3.086467
H	0.545526	-4.649243	-3.844837

TS-exo

73

scf done: -1651.027031

C	0.269685	0.610349	0.257371
C	0.161123	0.207540	1.585779
C	1.332449	0.033247	2.314236
C	2.571607	0.273170	1.741211
C	2.663906	0.687800	0.423524
C	1.505143	0.851475	-0.318577
C	-1.189298	-0.150126	2.170594
C	-1.301112	-0.133006	3.704771
C	-2.097749	-1.359669	4.073935
N	-1.981520	-2.221851	2.920079
C	-1.492827	-1.615665	1.821819
C	-0.885603	0.777344	4.575913
C	-2.327467	0.726168	1.658781
C	-2.182475	2.113247	1.669248
C	-3.230404	2.944198	1.322688
C	-4.458744	2.409097	0.958964
C	-4.619195	1.036160	0.946641
C	-3.562409	0.203126	1.291609
O	-1.345888	-2.133869	0.728932
C	-2.528111	-3.549151	2.926431
C	-2.297921	1.057249	7.064813
C	-3.514727	0.284414	6.757592
N	-4.366813	0.779535	5.781027
C	-4.026404	1.788480	4.798001
C	-4.906143	2.952620	4.826086
C	-5.642002	3.900034	4.820465
C	-1.360277	0.421211	8.017651
C	-0.921316	-0.895388	7.812958
C	0.003169	-1.494218	8.647922
C	0.540623	-0.798703	9.722009
C	0.134034	0.507729	9.936758
C	-0.794934	1.105598	9.099666
C	-2.476494	2.524890	7.271837
C	-1.490798	3.420403	6.851170
C	-1.607499	4.780879	7.078531
C	-2.715331	5.286018	7.743950
C	-3.699601	4.412751	8.177569
C	-3.579217	3.052546	7.941995
O	-3.799827	-0.792684	7.282623

C	-5.578864	0.057043	5.478166
H	-5.435126	-0.646655	4.645094
H	-5.905217	-0.506356	6.347900
H	-6.362627	0.762689	5.191262
H	-4.075971	1.340841	3.793106
H	-2.990518	2.099535	4.919813
H	-6.288727	4.746660	4.825197
H	-1.560729	0.900261	5.908677
H	-0.615737	3.029775	6.340462
H	-0.827621	5.452952	6.737014
H	-2.806903	6.350537	7.926591
H	-4.567246	4.792141	8.706544
H	-4.355492	2.378755	8.293144
H	-1.327544	-1.458225	6.981852
H	0.313203	-2.515938	8.454395
H	1.266434	-1.267197	10.376678
H	0.539395	1.072310	10.770001
H	-1.094221	2.129170	9.298096
H	-0.347782	1.630474	4.144125
H	-3.159369	-1.136006	4.274718
H	-1.705064	-1.860022	4.965317
H	-2.343308	-4.015509	1.960431
H	-2.065369	-4.152189	3.711664
H	-3.607442	-3.519700	3.109299
H	-0.629023	0.734916	-0.336675
H	1.562248	1.167195	-1.354203
H	3.632208	0.880374	-0.023922
H	3.470424	0.134824	2.331641
H	1.268564	-0.289333	3.346735
H	-1.232338	2.545069	1.965678
H	-3.090547	4.019224	1.340463
H	-5.281818	3.060461	0.689539
H	-5.570914	0.600884	0.663830
H	-3.719425	-0.870616	1.271596

VI

73

scf done: -1651.089885

C	1.322224	3.186287	1.579356
C	1.261608	2.314836	0.494733
C	1.040453	2.845761	-0.769562
C	0.874523	4.210916	-0.948319
C	0.924574	5.066544	0.137964
C	1.149672	4.547666	1.403988
C	1.552306	0.841497	0.694548
C	1.021336	0.328794	2.053750
N	2.008396	-0.358964	2.658237
C	3.267192	-0.369623	1.948265
C	3.042397	0.599936	0.830718
O	-0.106936	0.485016	2.478427
C	1.862947	-1.049268	3.908071

C	3.998853	1.180827	0.129942
C	0.904301	-0.053389	-0.360952
C	-0.478692	-0.008522	-0.535184
C	-1.102812	-0.817618	-1.465297
C	-0.357968	-1.694830	-2.240716
C	1.012916	-1.750745	-2.074182
C	1.639205	-0.935732	-1.141079
H	3.494654	-1.382523	1.586322
H	4.083470	-0.035825	2.603849
H	0.845000	-0.913763	4.270750
H	2.061106	-2.117817	3.784021
H	2.565211	-0.649123	4.647151
H	3.775722	1.892803	-0.657211
H	-1.066027	0.671921	0.070348
H	-2.178569	-0.763586	-1.587427
H	-0.847045	-2.328805	-2.971042
H	1.607406	-2.430579	-2.673665
H	2.716130	-0.984884	-1.030671
H	0.999666	2.185415	-1.629217
H	0.705006	4.604188	-1.944155
H	0.789620	6.133083	0.000701
H	1.192002	5.204181	2.266228
H	1.507481	2.800599	2.579704
H	5.043890	0.967210	0.326115
C	4.611986	1.932903	4.107987
H	3.536711	1.776653	3.885350
C	4.771473	2.242056	5.396853
C	6.105668	2.527402	6.044371
H	6.777728	3.073874	5.373237
H	6.637170	1.617036	6.368943
N	5.774648	3.332437	7.201410
C	4.461780	3.352179	7.502896
C	3.736726	2.404687	6.529641
C	2.442368	2.990973	6.024056
C	3.525186	1.106904	7.313744
C	2.365577	4.348695	5.718474
C	4.077513	-0.099690	6.904097
C	3.865368	-1.265357	7.627767
C	3.097845	-1.243356	8.778044
C	2.543469	-0.043835	9.201676
C	2.756536	1.115089	8.478162
C	1.217034	4.898607	5.179736
C	0.114504	4.096951	4.918764
C	0.180908	2.744597	5.200090
C	1.333488	2.200351	5.749464
O	3.956652	3.983555	8.417672
C	6.789058	3.975837	7.984637
H	6.320034	4.503923	8.813224
H	7.494300	3.239685	8.382952
H	7.351900	4.690852	7.377755
H	2.320901	2.049521	8.814438

H	1.939170	-0.012711	10.101495
H	2.930526	-2.153098	9.343147
H	4.304798	-2.195695	7.285158
H	4.669111	-0.121258	5.994209
H	1.367889	1.137039	5.963175
H	-0.663462	2.100174	4.983818
H	-0.784888	4.525473	4.491104
H	1.181386	5.960041	4.959285
H	3.225726	4.985286	5.901119

TS-endo

73

scf done: -1651.063889

C	0.047923	0.840139	-0.071833
C	0.093775	0.412286	1.250989
C	1.342570	0.220296	1.834937
C	2.506465	0.463031	1.126232
C	2.446473	0.888387	-0.192460
C	1.211305	1.071992	-0.789969
C	-1.166880	0.014308	1.977817
C	-1.427933	-1.491337	1.828384
C	-2.038552	-1.937022	3.129470
N	-1.608374	-0.925690	4.072369
C	-1.067217	0.171882	3.505923
C	-1.129448	-2.276309	0.799392
C	-1.832384	-1.076719	5.481451
O	-0.623584	1.133909	4.109154
C	-2.369510	0.861411	1.558055
C	-3.503444	0.302488	0.983537
C	-4.578141	1.097727	0.609680
C	-4.535118	2.466063	0.804787
C	-3.407482	3.036612	1.377869
C	-2.338812	2.242312	1.749876
O	0.063281	-2.666392	-3.365169
C	-0.410152	-3.479243	-2.580114
C	0.311010	-4.733463	-2.031712
C	-0.608643	-5.164353	-0.891256
C	-1.811307	-4.346710	-0.920042
N	-1.646809	-3.472967	-2.069352
C	1.706288	-4.435005	-1.527876
C	2.006537	-3.206611	-0.943778
C	3.254358	-2.964872	-0.394338
C	4.229342	-3.949396	-0.410467
C	3.942155	-5.177515	-0.981589
C	2.694016	-5.414518	-1.535111
C	0.297550	-5.718723	-3.199348
C	1.079848	-5.452098	-4.323238
C	1.065251	-6.295897	-5.417759
C	0.260672	-7.426495	-5.417750
C	-0.525628	-7.697292	-4.313403
C	-0.507725	-6.850005	-3.213678

C	-2.583035	-2.415259	-2.319079
C	-0.288650	-6.073143	0.035952
H	-2.770514	-4.870445	-0.922906
H	-1.615165	-3.485772	0.146929
H	-2.300834	-1.888741	-3.229703
H	-3.588875	-2.825541	-2.437180
H	-2.599014	-1.701614	-1.485280
H	0.656219	-6.604558	0.015786
H	1.705532	-4.567028	-4.333452
H	1.685986	-6.070524	-6.277639
H	0.249802	-8.090066	-6.274695
H	-1.160129	-8.576384	-4.299814
H	-1.122019	-7.078183	-2.350765
H	2.483978	-6.381316	-1.980403
H	4.693458	-5.958998	-0.999288
H	5.206474	-3.759727	0.018523
H	3.460437	-1.996417	0.048848
H	1.255854	-2.422620	-0.913232
H	-0.987570	-6.333840	0.824339
H	-0.660356	-1.721612	-0.027719
H	-1.681100	-2.926840	3.433277
H	-3.139166	-1.977967	3.103773
H	-1.458058	-0.195072	5.998696
H	-2.900353	-1.188869	5.691750
H	-1.315397	-1.961767	5.862472
H	-1.459713	2.692705	2.197465
H	-3.360793	4.108539	1.533832
H	-5.373036	3.087723	0.511200
H	-5.452294	0.639586	0.160780
H	-3.538628	-0.768379	0.815365
H	-0.914128	0.982719	-0.553638
H	1.148722	1.397429	-1.822218
H	3.357834	1.073845	-0.749137
H	3.467826	0.314242	1.605541
H	1.406994	-0.130741	2.859541

VII

36

scf done: -825.278642

C	0.119345	0.215754	0.291542
N	0.515532	-0.080897	1.528044
C	1.808153	0.464788	1.868570
C	2.204529	1.323326	0.839384
C	1.249388	1.069017	-0.342046
C	-0.174434	-0.984503	2.395778
H	1.964348	0.661568	2.924837
C	1.861164	0.177758	-1.414665
C	0.713347	2.380080	-0.872551
O	-0.909208	-0.158716	-0.274430
H	-1.103138	-1.301851	1.923336
H	0.446943	-1.862759	2.603986

H	-0.405121	-0.504582	3.352171
C	3.221727	2.237009	0.760617
H	3.396941	2.809809	-0.142144
C	1.142309	-0.105833	-2.575599
C	1.650371	-0.955613	-3.541487
C	2.892435	-1.548334	-3.365932
C	3.613890	-1.280007	-2.216655
C	3.103475	-0.423744	-1.250298
H	0.167018	0.345050	-2.717294
H	1.073117	-1.157571	-4.436963
H	3.292737	-2.214064	-4.122122
H	4.585738	-1.737224	-2.066488
H	3.677091	-0.206196	-0.357024
C	1.275826	3.020246	-1.971332
C	0.829927	4.268872	-2.376248
C	-0.193359	4.902112	-1.691471
C	-0.763467	4.275618	-0.593862
C	-0.311987	3.031294	-0.191283
H	2.080406	2.538654	-2.516505
H	1.287904	4.748750	-3.234054
H	-0.545162	5.876496	-2.010200
H	-1.564528	4.759982	-0.046738
H	-0.757053	2.557575	0.678603
H	3.902949	2.392218	1.591362

2a-*exo*

37

scf done: -825.815301

C	0.058537	0.280995	0.334955
N	0.515336	-0.219809	1.501681
C	1.862792	0.180151	1.837316
C	2.141591	1.275491	0.855128
C	1.204821	1.087824	-0.319559
C	-0.210941	-1.151296	2.318820
H	2.555586	-0.666812	1.727190
H	1.925048	0.525472	2.873936
C	1.797369	0.165040	-1.387037
C	0.738146	2.410939	-0.887799
O	-1.043516	0.091643	-0.138501
H	-1.190240	-1.319631	1.874950
H	0.322489	-2.103865	2.383858
H	-0.337748	-0.757877	3.330511
C	3.006350	2.256923	1.030996
H	3.142501	3.032994	0.285915
C	0.983344	-0.277609	-2.428605
C	1.485693	-1.099796	-3.419102
C	2.814161	-1.499004	-3.388630
C	3.630135	-1.065673	-2.360569
C	3.125186	-0.238495	-1.366766
H	-0.054844	0.033061	-2.456227
H	0.837118	-1.430429	-4.222196

H	3.208729	-2.143088	-4.165719
H	4.670587	-1.367522	-2.326673
H	3.781577	0.103427	-0.574874
C	1.332972	2.964695	-2.014183
C	0.956354	4.217825	-2.473197
C	-0.025220	4.935316	-1.813083
C	-0.620936	4.395591	-0.683295
C	-0.237735	3.148581	-0.223999
H	2.103905	2.412838	-2.541071
H	1.434665	4.632028	-3.353242
H	-0.325368	5.911890	-2.174467
H	-1.388413	4.949921	-0.155503
H	-0.703312	2.743483	0.668875
H	3.610650	2.318089	1.929144

2a-*endo*

37

scf done: -825.821992

C	0.201346	0.127609	0.309164
N	0.586758	-0.024279	1.603573
C	1.743679	0.728223	1.865108
C	2.189635	1.358815	0.784049
C	1.255739	1.034022	-0.368180
C	-0.105597	-0.825430	2.578000
H	2.144607	0.740146	2.869952
C	1.890047	0.176559	-1.452996
C	0.637118	2.323984	-0.875830
O	-0.771049	-0.371020	-0.215154
H	-0.969812	-1.277739	2.095200
H	0.541885	-1.615981	2.962692
H	-0.446086	-0.212399	3.414953
C	3.352672	2.267929	0.684117
C	1.250606	0.016822	-2.679475
C	1.772321	-0.824370	-3.645375
C	2.941483	-1.528514	-3.400739
C	3.576657	-1.389385	-2.179714
C	3.051957	-0.546259	-1.212146
H	0.332130	0.557963	-2.876932
H	1.261330	-0.932515	-4.595170
H	3.352320	-2.184667	-4.159065
H	4.487223	-1.939885	-1.973411
H	3.551500	-0.456917	-0.253762
C	1.298964	3.092656	-1.828947
C	0.794442	4.318004	-2.228118
C	-0.382310	4.800612	-1.678154
C	-1.044191	4.049700	-0.722336
C	-0.536718	2.823558	-0.323400
H	2.220973	2.725142	-2.267304
H	1.324956	4.898649	-2.973906
H	-0.780253	5.757926	-1.993393
H	-1.963975	4.417100	-0.282241

H	-1.069505	2.253141	0.429856
H	3.895946	2.302852	1.629560
H	4.050267	1.951817	-0.098062
H	3.043511	3.287421	0.433732

Z-2f

47

scf done: -1056.768731

C	-0.275633	3.091093	-0.118802
C	0.555528	2.352201	-0.957175
C	0.835748	2.860143	-2.216792
C	0.307127	4.075210	-2.626880
C	-0.515667	4.800199	-1.783691
C	-0.808443	4.300445	-0.523580
C	1.163335	1.067037	-0.420125
C	0.062810	0.220710	0.278179
N	0.532845	-0.187818	1.472155
C	1.850706	0.301026	1.793662
C	2.113672	1.331180	0.733796
O	-1.021321	-0.052007	-0.194266
C	-0.153918	-1.105091	2.338613
C	2.967316	2.331265	0.924125
C	1.746293	0.133799	-1.479167
C	0.954444	-0.282023	-2.548759
C	1.446471	-1.159442	-3.496867
C	2.739395	-1.650260	-3.392245
C	3.530640	-1.255736	-2.329415
C	3.036391	-0.372322	-1.380793
H	2.580740	-0.521303	1.766431
H	1.877910	0.728694	2.801430
H	-1.117400	-1.352062	1.897006
H	0.428443	-2.021848	2.466580
H	-0.313467	-0.657865	3.322901
C	3.361622	3.399623	-0.005876
H	-0.060340	0.087869	-2.633866
H	0.814840	-1.463879	-4.323435
H	3.124784	-2.337806	-4.135905
H	4.541507	-1.634163	-2.231687
H	3.672768	-0.071112	-0.555859
H	1.487734	2.313142	-2.887694
H	0.547636	4.456347	-3.612862
H	-0.929450	5.748763	-2.105277
H	-1.454229	4.855614	0.146859
H	-0.501605	2.717945	0.876137
H	3.428725	2.388061	1.910450
C	3.224765	4.730941	0.385084
C	3.599739	5.760553	-0.459110
C	4.147352	5.476949	-1.701434
C	4.311199	4.158346	-2.091386
C	3.918111	3.128974	-1.252277
H	2.805687	4.953813	1.361495

H	3.471784	6.789606	-0.143587
H	4.451296	6.282535	-2.359511
H	4.747223	3.927140	-3.056543
H	4.048147	2.099022	-1.566015

E-2f

47

scf done: -1056.771898

C	-0.171299	3.173181	-0.207859
C	0.785630	2.401022	-0.860376
C	1.437162	2.945987	-1.959078
C	1.134622	4.225060	-2.402018
C	0.171808	4.977311	-1.753353
C	-0.480419	4.446056	-0.650810
C	1.163505	1.045104	-0.303092
C	-0.058325	0.280521	0.253760
N	0.299468	-0.269846	1.431116
C	1.637054	0.059142	1.866098
C	2.043783	1.150777	0.926430
O	-1.136046	0.158690	-0.292577
C	-0.522641	-1.175585	2.184118
C	2.951680	2.101861	1.128723
C	1.774547	0.118490	-1.358755
C	1.008984	-0.251726	-2.463523
C	1.528762	-1.080285	-3.439642
C	2.826027	-1.560276	-3.330691
C	3.593154	-1.201775	-2.238291
C	3.071157	-0.367718	-1.259106
H	2.286828	-0.827147	1.802391
H	1.637677	0.387371	2.911805
H	-1.477345	-1.290126	1.674575
H	-0.040959	-2.153765	2.268025
H	-0.697197	-0.789816	3.191688
H	3.036790	2.869018	0.360510
H	-0.005499	0.119955	-2.551817
H	0.918200	-1.353093	-4.292699
H	3.234202	-2.209533	-4.096346
H	4.608458	-1.568588	-2.141481
H	3.691219	-0.088512	-0.414469
H	2.194313	2.367045	-2.476570
H	1.656605	4.632000	-3.260334
H	-0.069828	5.974459	-2.102137
H	-1.233930	5.027399	-0.132124
H	-0.679611	2.774412	0.664500
C	3.839550	2.282754	2.273348
C	4.304864	3.568417	2.559245
C	5.138234	3.804706	3.635879
C	5.542204	2.754108	4.445439
C	5.112592	1.468215	4.160381
C	4.272880	1.233223	3.085807
H	3.995956	4.391466	1.922818

H	5.479023	4.812588	3.842517
H	6.199641	2.935261	5.287536
H	5.441533	0.637658	4.774123
H	3.981578	0.214873	2.858046

Z-2i

51

scf done: -1171.277764

C	-0.363138	3.007176	-0.119448
C	0.491342	2.291902	-0.955131
C	0.765151	2.810584	-2.211529
C	0.211179	4.014925	-2.620043
C	-0.633284	4.717142	-1.779184
C	-0.922014	4.205136	-0.522860
C	1.133978	1.024195	-0.416513
C	0.055605	0.146234	0.276970
N	0.530639	-0.246299	1.474229
C	1.832475	0.281009	1.801261
C	2.069961	1.318001	0.742266
O	-1.017275	-0.159651	-0.201297
C	-0.132489	-1.183568	2.337532
C	2.889833	2.346135	0.937800
C	1.747564	0.109206	-1.473902
C	0.972797	-0.329770	-2.546717
C	1.494749	-1.191241	-3.493497
C	2.801598	-1.642595	-3.384353
C	3.576505	-1.224993	-2.318276
C	3.052050	-0.357707	-1.370941
H	2.585230	-0.520898	1.778376
H	1.842882	0.709547	2.809145
H	-1.084982	-1.461318	1.890385
H	0.477522	-2.081502	2.470378
H	-0.312221	-0.740709	3.320345
C	3.262792	3.420670	0.009103
H	-0.052570	0.008872	-2.635133
H	0.875770	-1.514173	-4.322638
H	3.210510	-2.317537	-4.127010
H	4.598066	-1.572578	-2.217035
H	3.675513	-0.037181	-0.543306
H	1.434044	2.282257	-2.880723
H	0.449009	4.405523	-3.603011
H	-1.066851	5.657337	-2.099339
H	-1.584938	4.742102	0.145711
H	-0.585199	2.625296	0.873038
H	3.335943	2.418178	1.930534
C	3.127496	4.747892	0.399827
C	3.468901	5.796675	-0.438705
C	3.992394	5.524386	-1.697818
C	4.162450	4.200775	-2.094061
C	3.797883	3.170692	-1.254540
H	2.729235	4.970118	1.385179

H	3.332180	6.814779	-0.098989
O	4.367049	6.466347	-2.589423
H	4.582911	4.001425	-3.073206
H	3.935617	2.146469	-1.583525
C	4.206415	7.819632	-2.234010
H	4.554173	8.407938	-3.080566
H	3.156911	8.061765	-2.038286
H	4.801385	8.077573	-1.352122

E-2i

51

scf done: -1171.281320

C	-0.187312	3.171872	-0.253815
C	0.781087	2.399237	-0.888868
C	1.474757	2.955801	-1.955405
C	1.201869	4.246373	-2.384510
C	0.227234	4.998818	-1.754067
C	-0.466849	4.456097	-0.683005
C	1.121655	1.028612	-0.343340
C	-0.131186	0.269840	0.148673
N	0.169976	-0.304806	1.330221
C	1.489699	0.004462	1.829518
C	1.950557	1.102836	0.923723
O	-1.186882	0.170173	-0.443799
C	-0.694650	-1.211800	2.032024
C	2.864714	2.035911	1.179645
C	1.761951	0.114037	-1.392014
C	1.037411	-0.225408	-2.533871
C	1.585352	-1.043634	-3.503308
C	2.870491	-1.543998	-3.350741
C	3.596941	-1.216342	-2.221410
C	3.046475	-0.392830	-1.248848
H	2.131532	-0.889244	1.786950
H	1.445104	0.321096	2.878306
H	-1.625756	-1.310224	1.477273
H	-0.226584	-2.195781	2.124928
H	-0.912214	-0.837833	3.035754
H	2.993038	2.811464	0.425511
H	0.032254	0.161731	-2.656475
H	1.006535	-1.292369	-4.385396
H	3.300870	-2.185079	-4.111132
H	4.602326	-1.599522	-2.090172
H	3.633972	-0.137857	-0.373898
H	2.241678	2.377011	-2.458486
H	1.756610	4.662151	-3.217712
H	0.008965	6.004933	-2.092384
H	-1.229972	5.037383	-0.178478
H	-0.728019	2.763883	0.594526
C	3.709155	2.188808	2.357890
C	4.213855	3.458371	2.664451
C	5.003923	3.674406	3.768492

C	5.337438	2.613825	4.609412
C	4.874278	1.338189	4.311071
C	4.073801	1.139391	3.197653
H	3.967021	4.292336	2.015236
H	5.383226	4.662432	4.002463
O	6.115471	2.916615	5.667912
H	5.138070	0.491005	4.930084
H	3.760174	0.127813	2.969644
C	6.480816	1.876501	6.545613
H	7.090417	2.327069	7.325859
H	5.602304	1.410449	7.002744
H	7.067272	1.106810	6.034196

Z-IVf

46

scf done: -1056.244077

C	-0.172332	3.153421	-0.189420
C	0.359759	2.235205	-1.093602
C	0.154375	2.464947	-2.447032
C	-0.541658	3.581792	-2.886046
C	-1.056100	4.489217	-1.977652
C	-0.869785	4.266588	-0.621739
C	1.097963	1.030072	-0.521987
C	0.028789	0.150703	0.196803
N	0.455372	-0.020943	1.453549
C	1.636408	0.722754	1.714328
C	2.044504	1.429143	0.622232
O	-0.993609	-0.299299	-0.303799
C	-0.228664	-0.789781	2.451198
C	3.104557	2.363466	0.622188
C	1.762812	0.092059	-1.528696
C	1.010636	-0.555109	-2.510256
C	1.599171	-1.443135	-3.393771
C	2.955347	-1.715765	-3.313509
C	3.711110	-1.093853	-2.335499
C	3.120378	-0.203515	-1.452448
H	2.029316	0.734397	2.720996
H	-1.110071	-1.244110	2.001891
H	0.420720	-1.577183	2.844003
H	-0.539321	-0.155310	3.286738
C	3.710573	3.162403	-0.371226
H	-0.055819	-0.377486	-2.564938
H	0.989822	-1.930380	-4.146702
H	3.416580	-2.411565	-4.004983
H	4.772313	-1.301032	-2.253967
H	3.723482	0.286061	-0.695711
H	0.559961	1.780149	-3.181788
H	-0.676313	3.741233	-3.949991
H	-1.597978	5.362783	-2.320968
H	-1.268537	4.965766	0.104631
H	-0.022828	2.993068	0.873972

H	3.522608	2.515101	1.619136
C	4.707513	4.104283	0.024183
C	5.342357	4.940510	-0.863850
C	5.043883	4.911741	-2.226873
C	4.090871	3.992189	-2.651231
C	3.451088	3.142376	-1.770198
H	4.963120	4.159866	1.079844
H	6.088281	5.636231	-0.489399
H	5.541472	5.572030	-2.926911
H	3.841709	3.926644	-3.707245
H	2.739964	2.434346	-2.171135

E-IVf

46

scf done: -1056.253580

C	-0.391067	2.974381	-0.158375
C	0.674064	2.365885	-0.817719
C	1.280332	3.059963	-1.858723
C	0.833160	4.317161	-2.233955
C	-0.231744	4.906530	-1.574301
C	-0.841820	4.228406	-0.530685
C	1.195656	1.033210	-0.318958
C	0.027058	0.147469	0.177971
N	0.296330	-0.153810	1.454268
C	1.481677	0.485544	1.924266
C	2.051370	1.247867	0.942994
O	-0.936913	-0.222430	-0.481198
C	-0.510879	-1.000265	2.282249
C	3.166007	2.098220	0.885176
C	1.895129	0.192359	-1.377270
C	1.293784	-0.002887	-2.620120
C	1.871665	-0.823691	-3.571536
C	3.064007	-1.477247	-3.298117
C	3.665402	-1.301245	-2.064830
C	3.086117	-0.474119	-1.112969
H	1.698262	0.396469	2.975849
H	-1.359786	-1.356390	1.701111
H	0.067174	-1.858343	2.637559
H	-0.879235	-0.453181	3.155172
H	3.318518	2.612684	-0.060825
H	0.355427	0.492827	-2.839946
H	1.386730	-0.956230	-4.532180
H	3.518698	-2.120195	-4.043024
H	4.595641	-1.809287	-1.836267
H	3.567437	-0.335147	-0.152097
H	2.116553	2.613462	-2.385291
H	1.323405	4.837900	-3.048834
H	-0.584213	5.887722	-1.870292
H	-1.674799	4.678506	-0.002592
H	-0.872198	2.460832	0.668584
C	4.134158	2.358121	1.880987

C	5.178142	3.290575	1.625668
C	6.147721	3.590386	2.551931
C	6.158250	2.978998	3.808376
C	5.161030	2.056027	4.085755
C	4.174935	1.748807	3.163317
H	5.197157	3.780854	0.655228
H	6.916934	4.314042	2.298023
H	6.921064	3.217264	4.539973
H	5.146834	1.556071	5.050326
H	3.438374	1.003355	3.429161

Z-IVi

50

scf done: -1170.746855

C	-0.410106	2.974331	-0.163751
C	0.177821	2.089748	-1.067257
C	-0.079659	2.278394	-2.418008
C	-0.880589	3.323606	-2.855549
C	-1.449758	4.198319	-1.947903
C	-1.212057	4.015371	-0.593919
C	1.032580	0.965178	-0.495322
C	0.070235	0.027739	0.297519
N	0.567991	-0.074804	1.532749
C	1.707352	0.756862	1.719388
C	1.996709	1.475322	0.590536
O	-0.936355	-0.515256	-0.144321
C	0.001991	-0.875889	2.576610
C	2.960310	2.496135	0.506465
C	1.722271	0.047497	-1.503345
C	0.980820	-0.672343	-2.441506
C	1.595334	-1.543789	-3.323862
C	2.968507	-1.726242	-3.285837
C	3.715206	-1.031310	-2.350920
C	3.098208	-0.157911	-1.468731
H	2.128668	0.841328	2.710909
H	-0.862692	-1.408021	2.183485
H	0.733630	-1.600674	2.945646
H	-0.313085	-0.252264	3.418944
C	3.446316	3.313059	-0.551025
H	-0.096180	-0.564158	-2.462360
H	0.993821	-2.088786	-4.042793
H	3.450293	-2.408596	-3.976722
H	4.789933	-1.167242	-2.303142
H	3.692692	0.391440	-0.746562
H	0.363534	1.617586	-3.153091
H	-1.054548	3.452628	-3.917946
H	-2.074059	5.015556	-2.289980
H	-1.652624	4.689242	0.132269
H	-0.221205	2.845311	0.897725
H	3.412936	2.725905	1.473096
C	4.337694	4.372335	-0.246223

C	4.859710	5.234351	-1.194019
C	4.518399	5.092306	-2.534510
C	3.661325	4.055192	-2.881726
C	3.150412	3.192040	-1.933842
H	4.621373	4.518679	0.793068
H	5.532534	6.020088	-0.870351
O	4.969567	5.892925	-3.554325
H	3.404514	3.924402	-3.929211
H	2.514473	2.389372	-2.278209
C	5.832357	6.939832	-3.211608
H	6.080950	7.464947	-4.133170
H	5.362298	7.648194	-2.518002
H	6.759837	6.574017	-2.753589

E-IVi

50

scf done: -1170.757684

C	-0.422065	2.990141	-0.228583
C	0.654750	2.371214	-0.858992
C	1.300899	3.062974	-1.877193
C	0.882438	4.328673	-2.257423
C	-0.193795	4.928585	-1.626385
C	-0.844687	4.252152	-0.606314
C	1.143122	1.030260	-0.351831
C	-0.049019	0.150365	0.097875
N	0.188313	-0.186340	1.370198
C	1.373001	0.422505	1.887051
C	1.961287	1.221182	0.938744
O	-1.002555	-0.191597	-0.593575
C	-0.638444	-1.056585	2.151743
C	3.067844	2.072933	0.936952
C	1.870895	0.190334	-1.392888
C	1.302911	-0.004318	-2.651460
C	1.909941	-0.817776	-3.591017
C	3.099194	-1.464831	-3.289737
C	3.667630	-1.289751	-2.040809
C	3.059282	-0.469502	-1.100987
H	1.537843	0.339910	2.948842
H	-1.476370	-1.390813	1.542267
H	-0.069092	-1.927497	2.490469
H	-1.023011	-0.538236	3.035363
H	3.252042	2.617616	0.014097
H	0.367430	0.486539	-2.893191
H	1.450674	-0.949301	-4.564356
H	3.576964	-2.101908	-4.025230
H	4.595054	-1.792803	-1.790552
H	3.514641	-0.329832	-0.127516
H	2.146822	2.608172	-2.380777
H	1.404060	4.847806	-3.053679
H	-0.523857	5.916368	-1.926341
H	-1.687382	4.710304	-0.100958

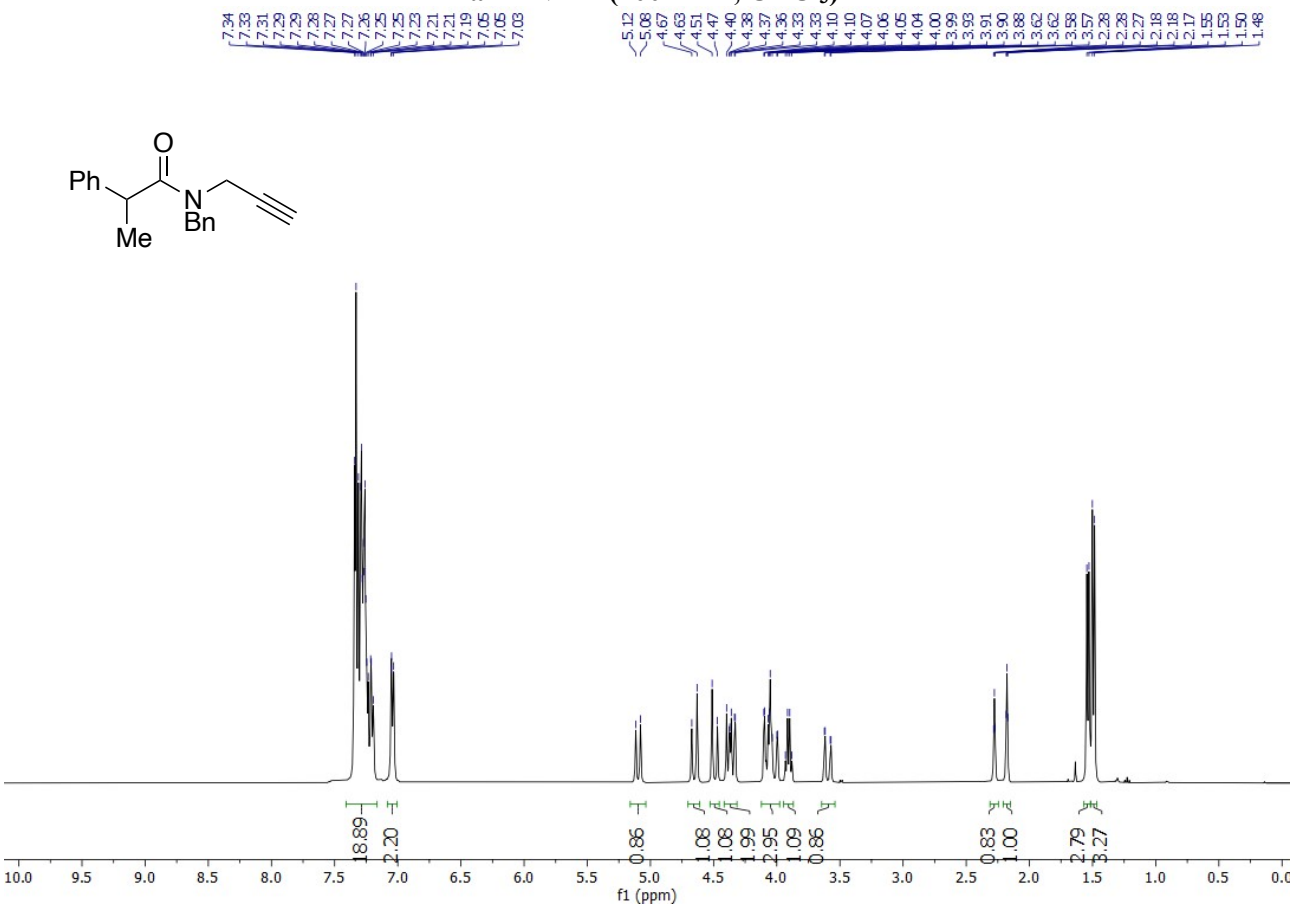
H	-0.933915	2.477505	0.580413
C	4.014886	2.290508	1.974884
C	5.061106	3.231478	1.784354
C	6.012008	3.492831	2.737576
C	5.993833	2.827113	3.966354
C	4.998804	1.894269	4.193750
C	4.031333	1.634077	3.224563
H	5.104698	3.764989	0.838244
H	6.795235	4.221926	2.553806
O	6.981612	3.164315	4.853105
H	4.953230	1.350527	5.130194
H	3.293114	0.876051	3.446057
C	6.989067	2.501980	6.086772
H	7.833806	2.891128	6.653659
H	6.068231	2.684653	6.654104
H	7.111832	1.418479	5.967905

Comprehensive Table in AU

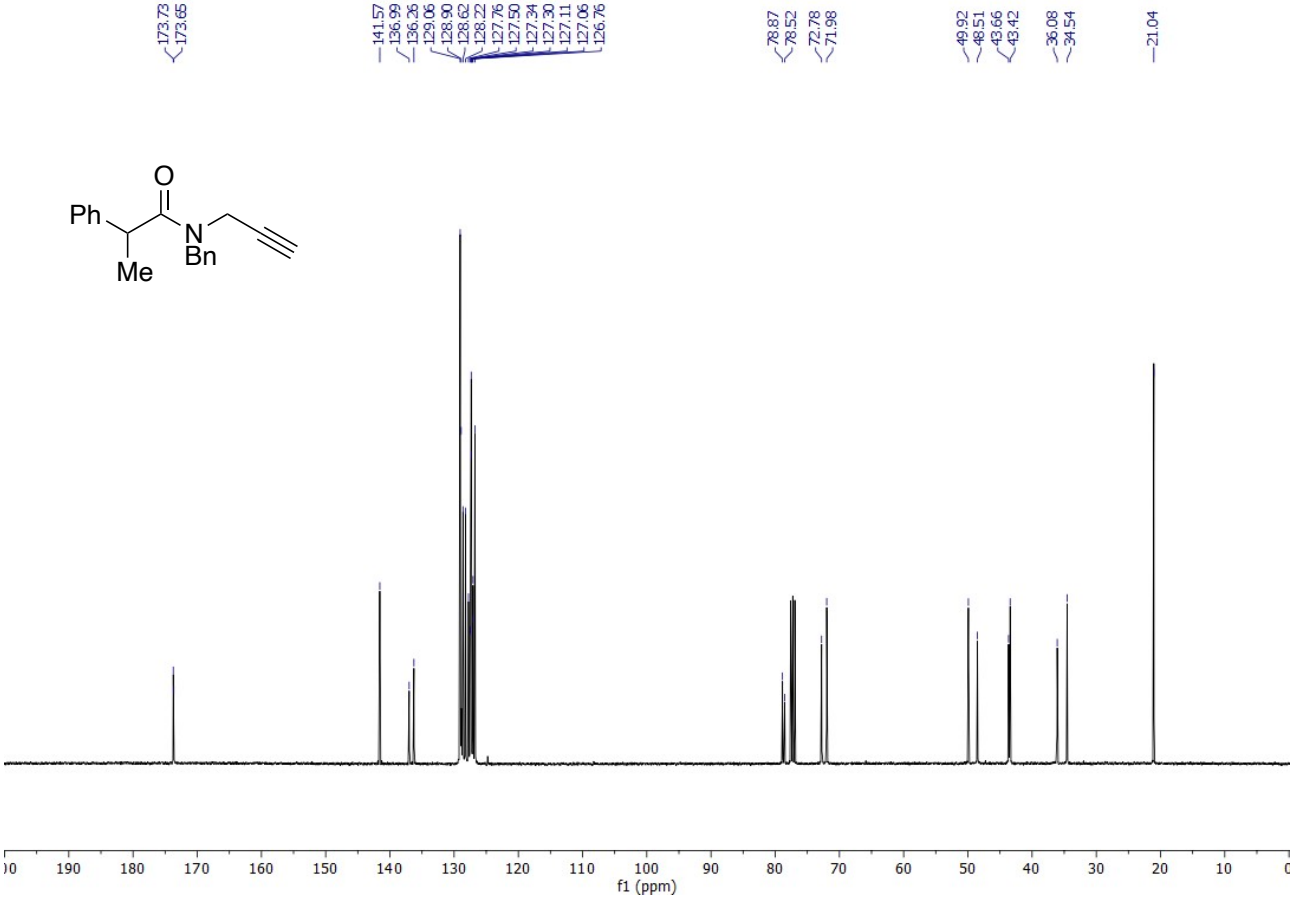
Values calcd. at the M06/Def2-TZVP level, CPCM = DMF

	H (Hartrees)	S (cal/K*mol)	Imag. freq. (cm^{-1})
tBuOH	-233.470360	76.586	
$tBuO^-$	-232.964403	75.059	
1a	-825.459031	143.368	
1a-$tBuO^-$	-1058.438539	178.598	
TS (1a-III)	-1058.428801	172.705	-1690.096
III	-824.966215	140.004	
I	-824.958868	140.154	
II	-824.956862	143.793	
TS (III-IV)	-824.944676	133.696	-523.7105
IV	-824.973039	132.66	
V	-1650.445840	229.232	
TS-*exo*	-1650.441330	229.879	-1328.6908
VI	-1650.496531	227.149	
TS-*endo*	-1650.476670	225.497	-1459.4579
VII	-824.991746	134.461	
2a-*exo*	-825.512131	133.761	
2a-*endo*	-825.519433	135.029	
			ΔG
Z-2f	-1056.384383	154.163	
E-2f	-1056.387415	157.53	-2.9064814
Z-2i	-1170.861147	166.692	
E-2i	-1170.864692	171.314	-3.6025723
Z-IVf	-1055.875216	155.8	
E-IVf	-1055.884689	157.674	-6.5031353
Z-IVi	-1170.345995	169.409	
E-IVi	-1170.356577	170.297	-6.905068

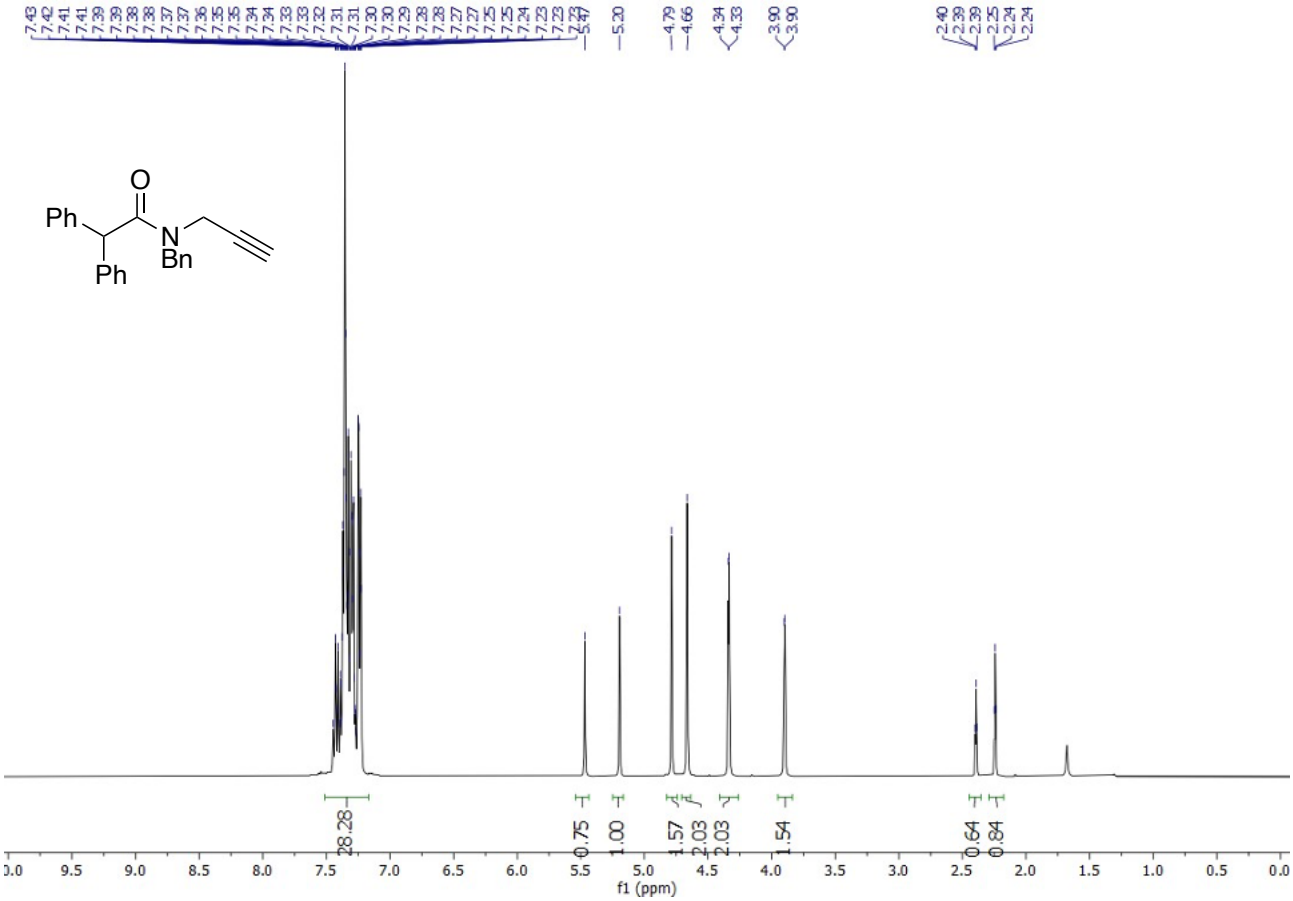
1a ^{1}H NMR (400 MHz, $CDCl_3$)



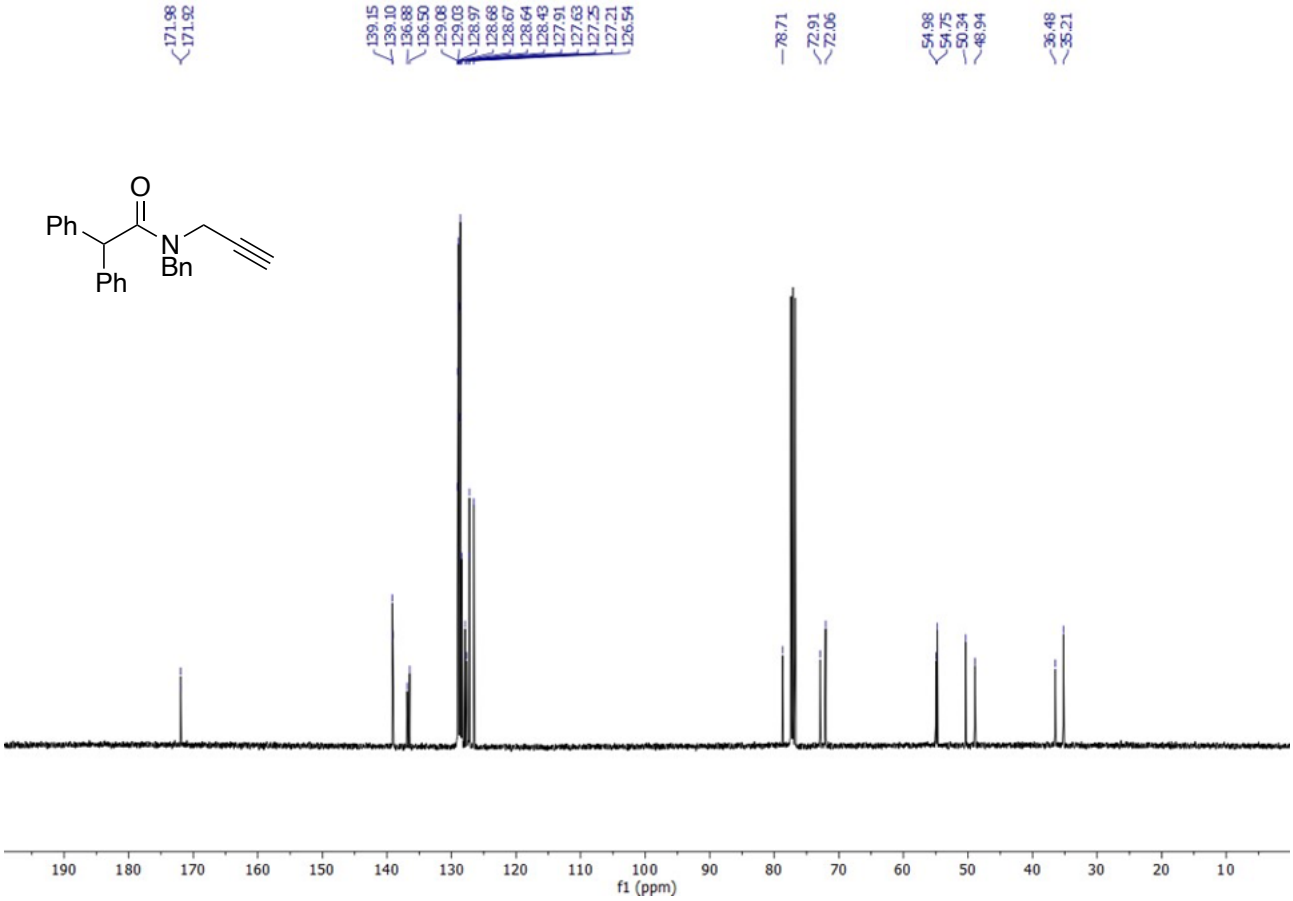
1a ^{13}C NMR (101 MHz, $CDCl_3$)



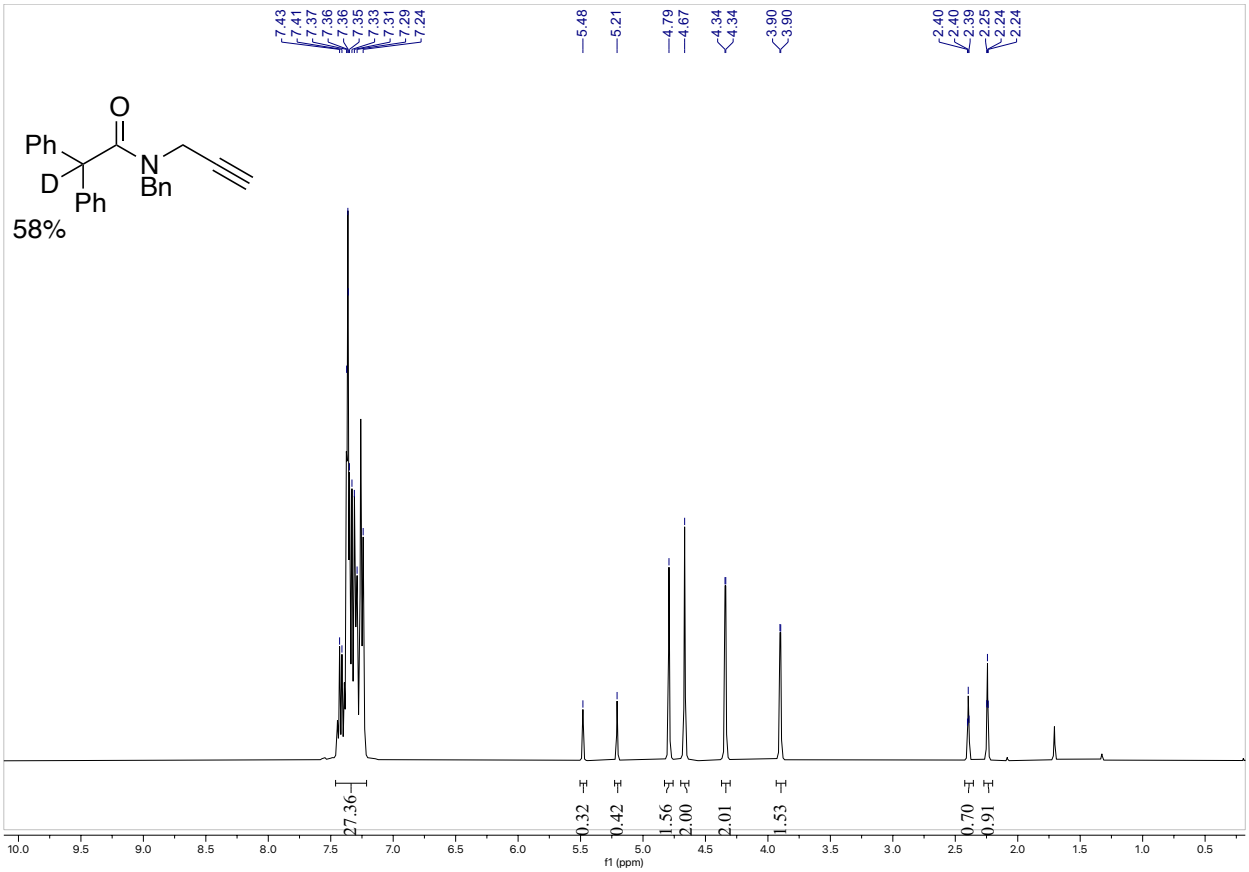
1b ^{1}H NMR (400 MHz, $CDCl_3$)



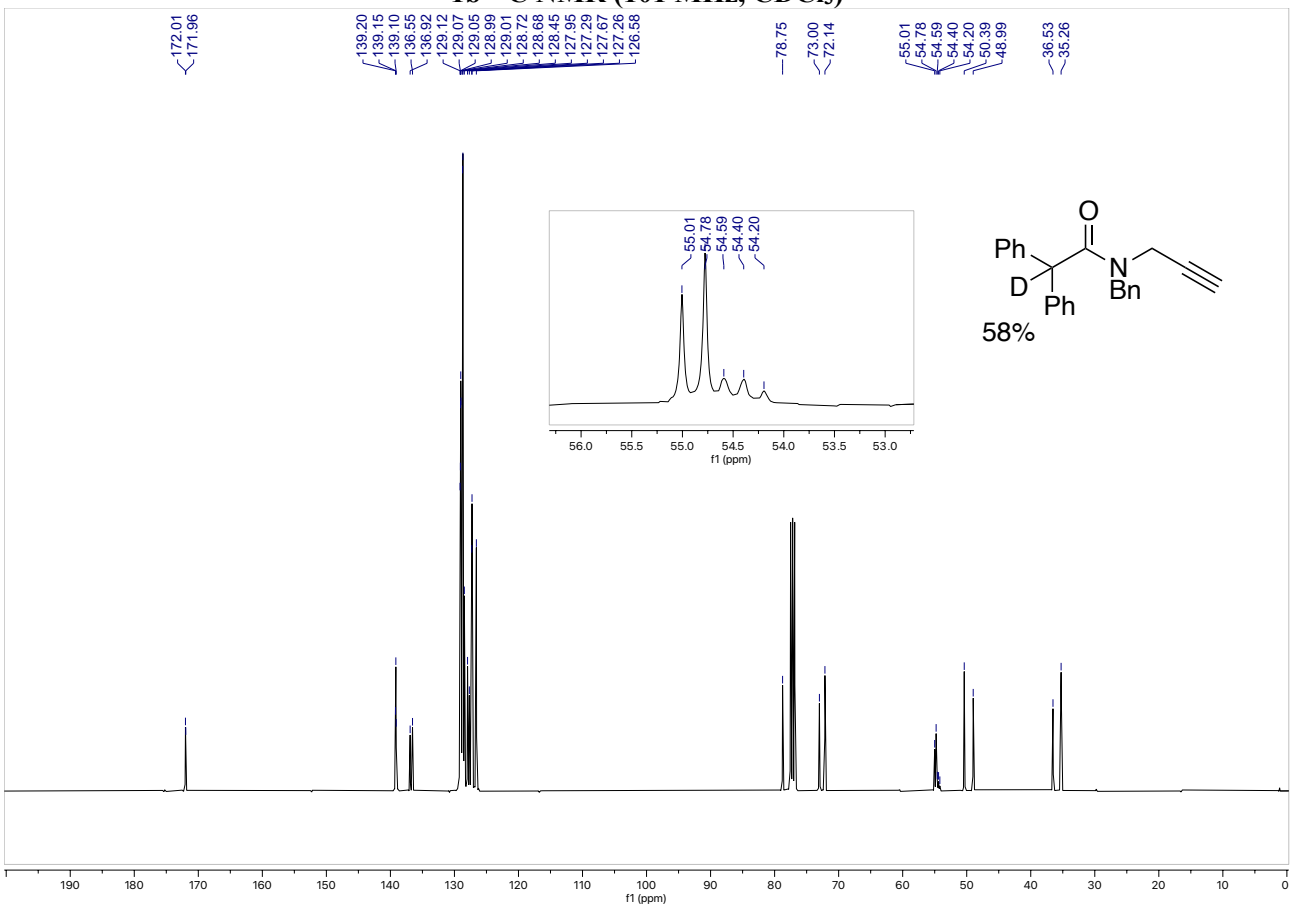
1b ^{13}C NMR (101 MHz, $CDCl_3$)



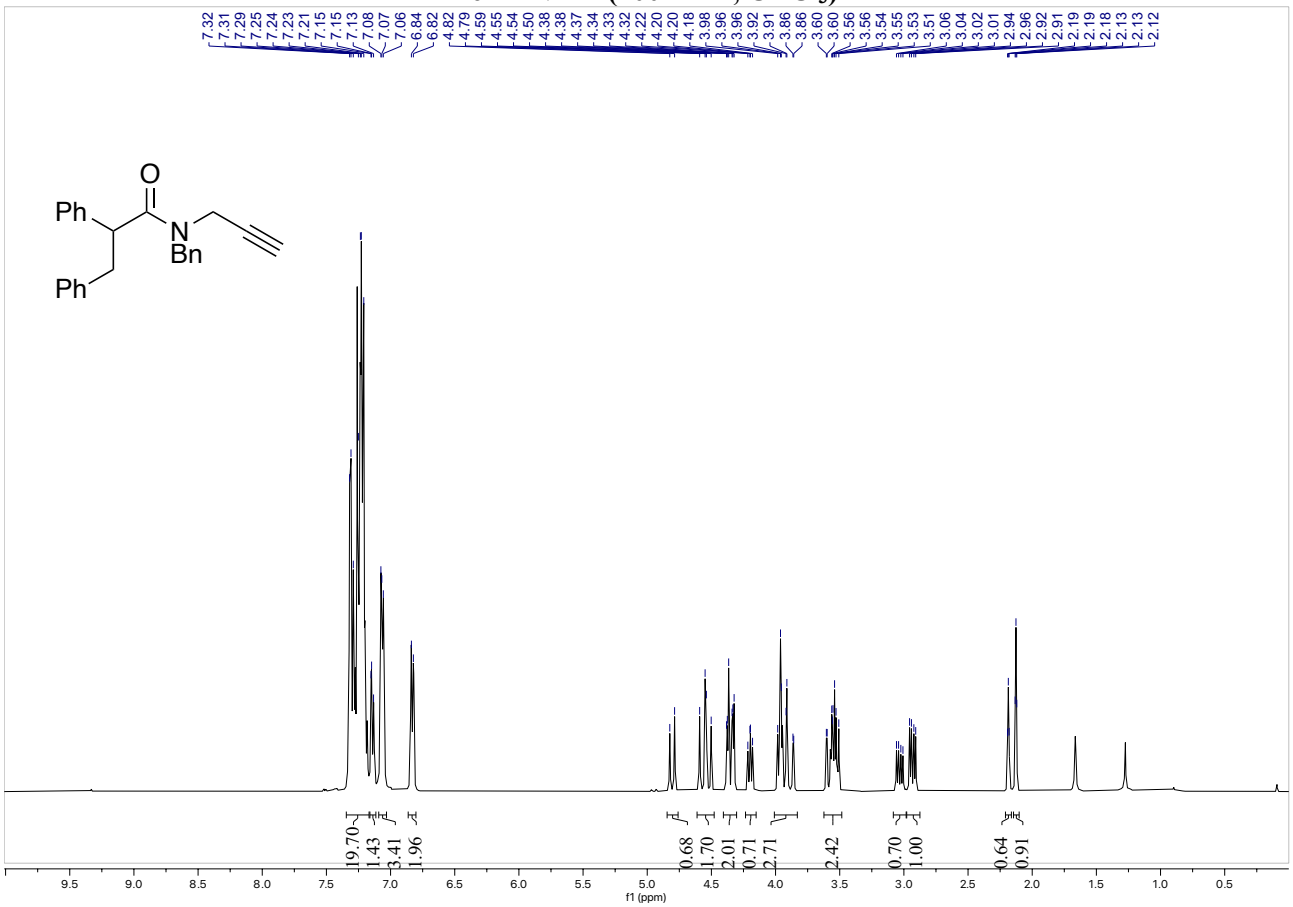
d-1b ^{1}H NMR (400 MHz, $CDCl_3$)



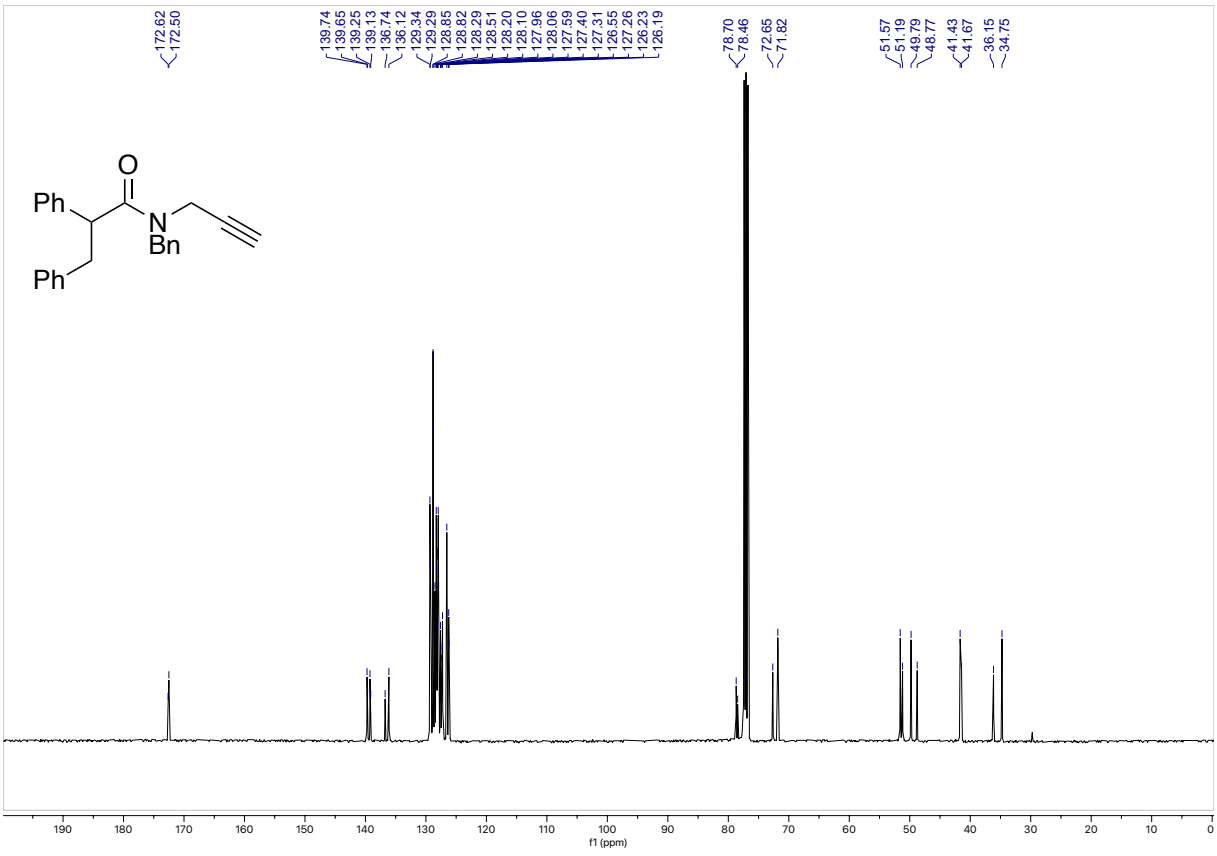
1b ^{13}C NMR (101 MHz, $CDCl_3$)



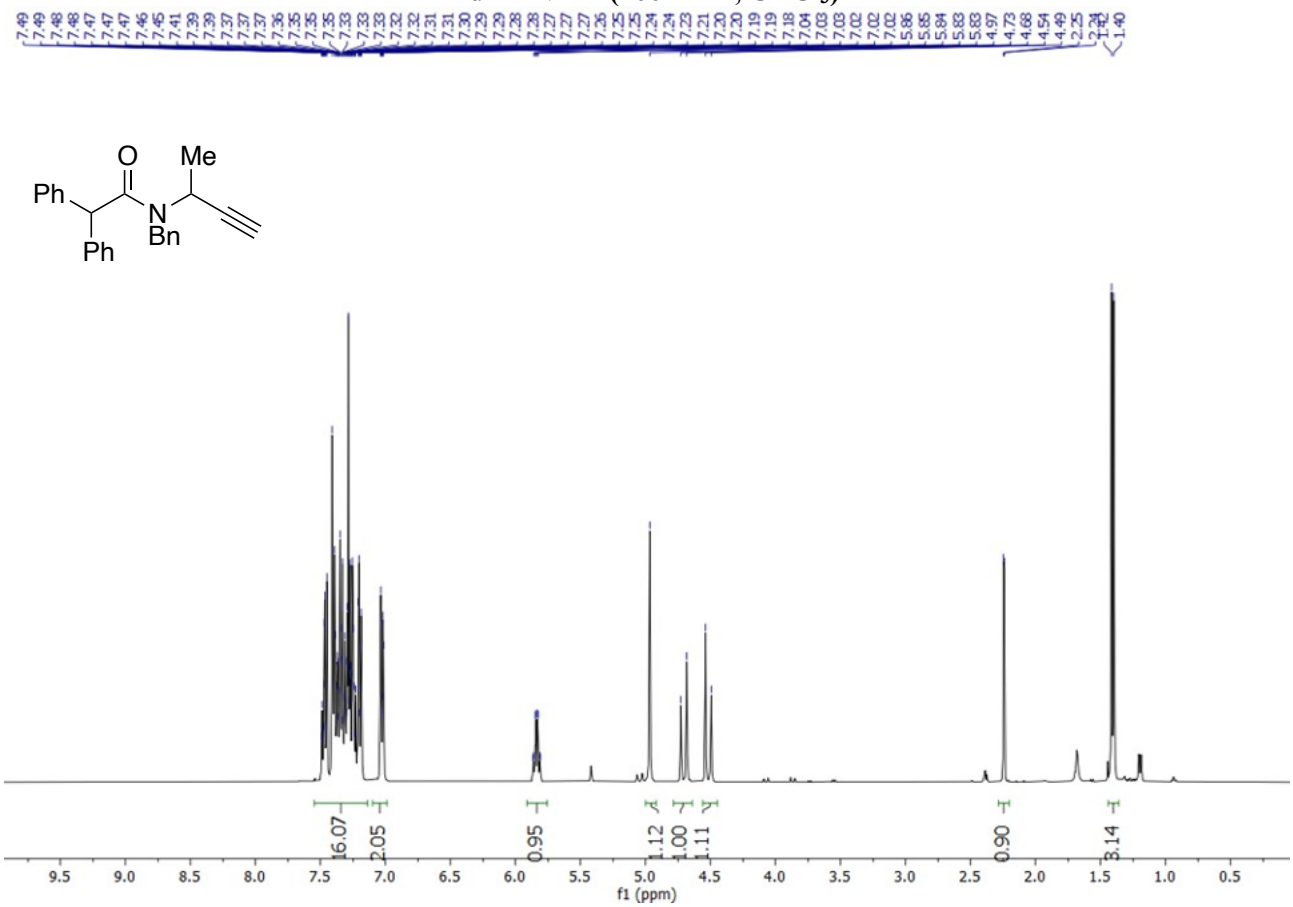
1c ^{1}H NMR (400 MHz, $CDCl_3$)



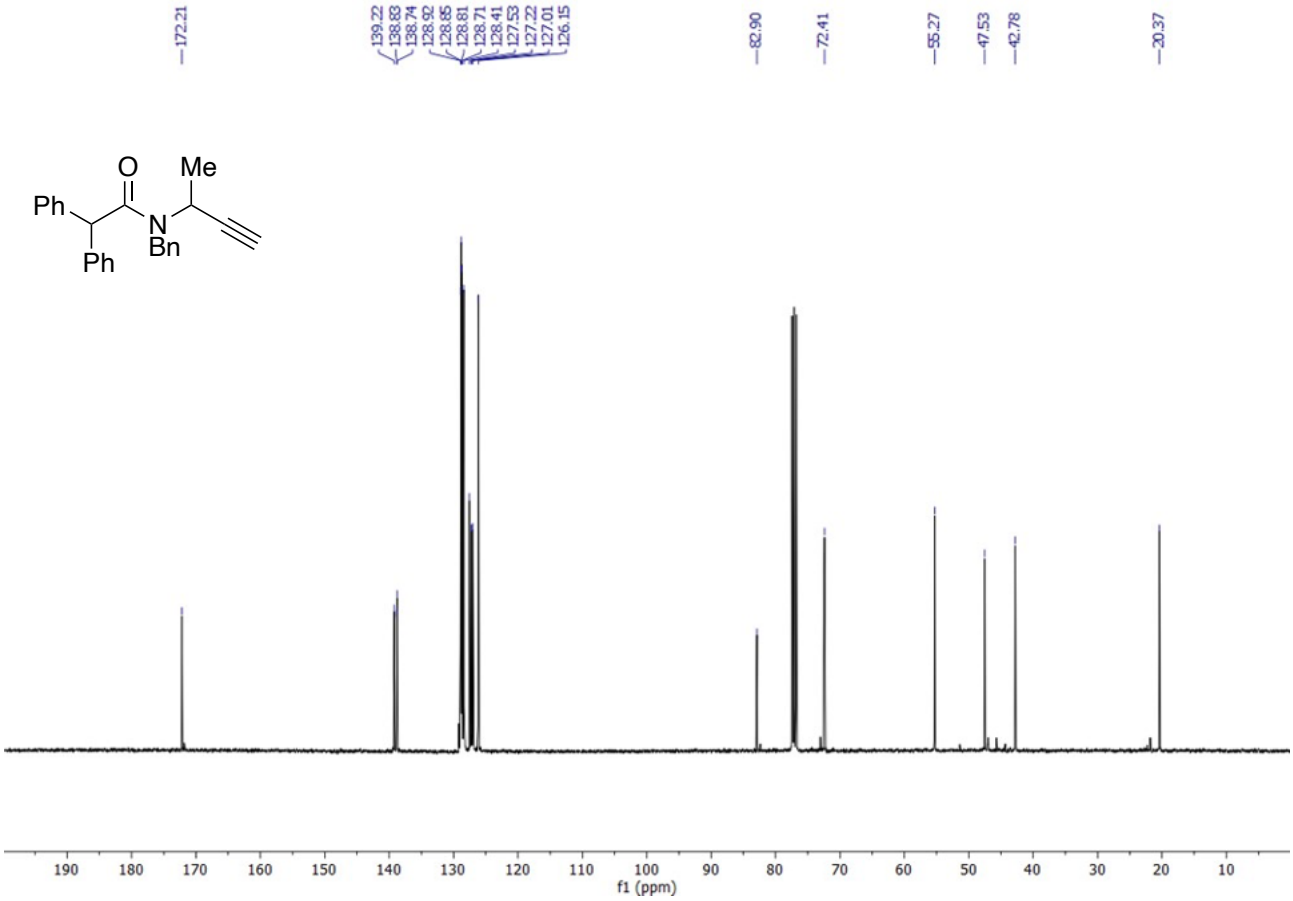
1c ^{13}C NMR (101 MHz, $CDCl_3$)



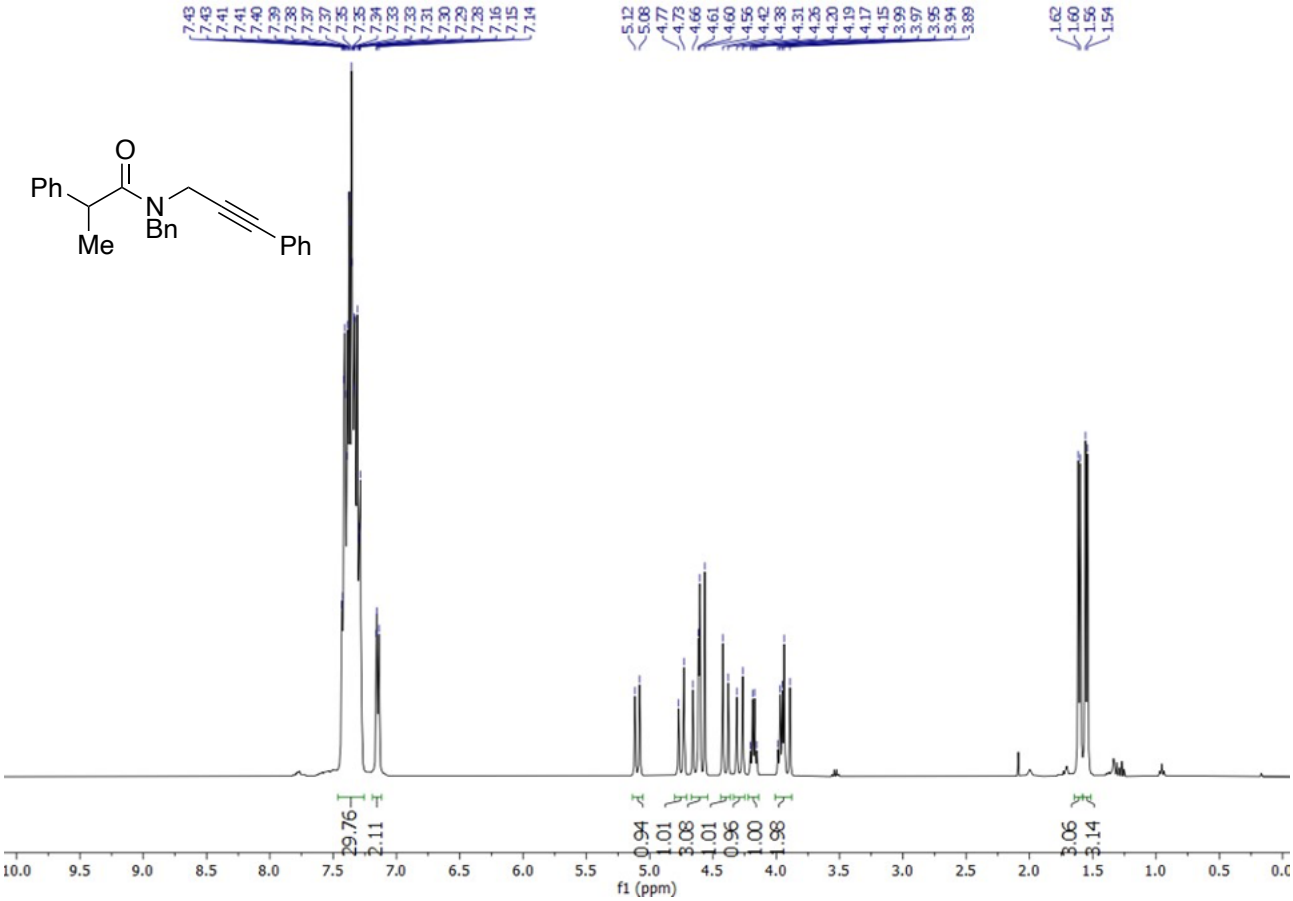
1d ^{1}H NMR (400 MHz, $CDCl_3$)



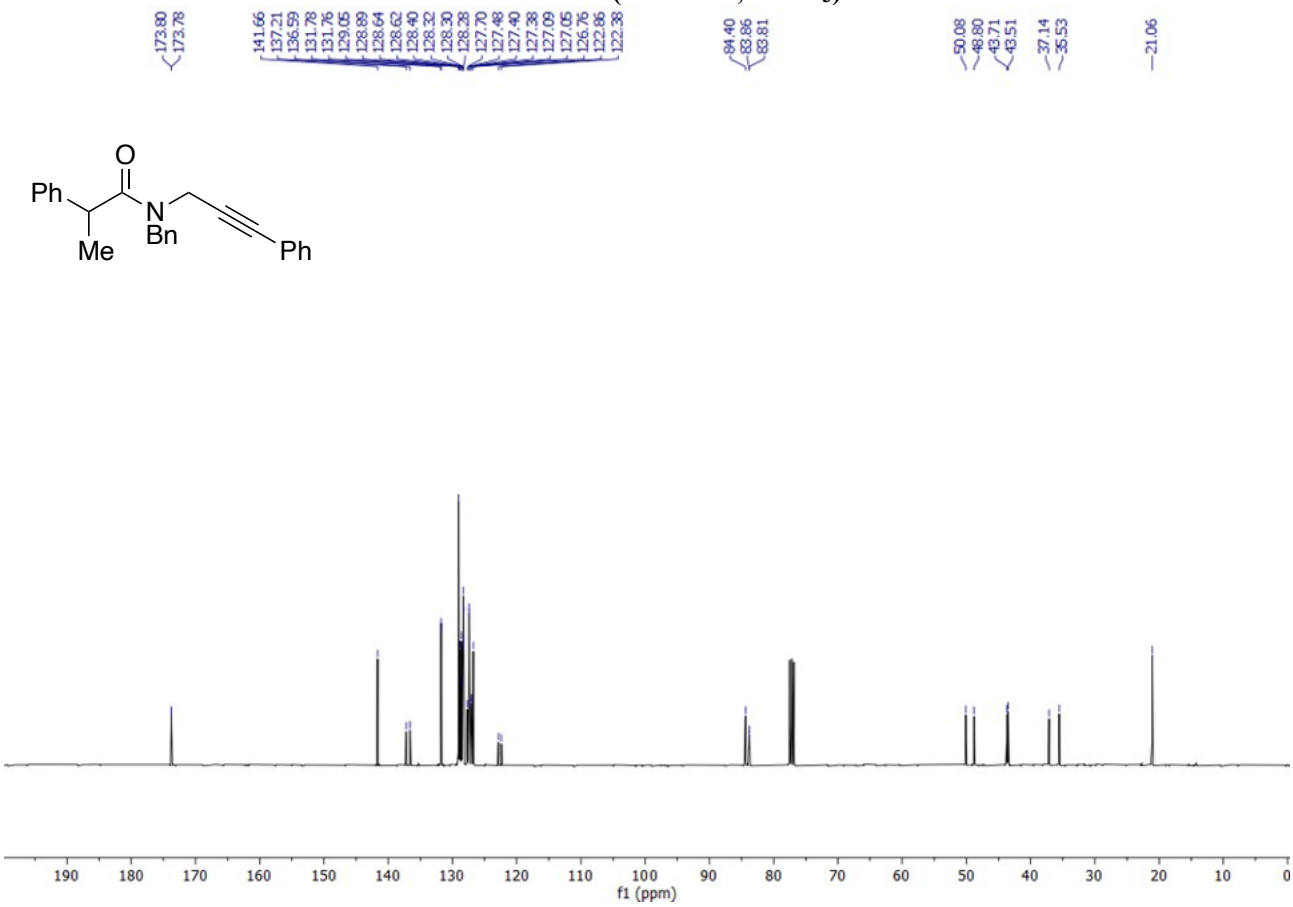
1d ^{13}C NMR (101 MHz, $CDCl_3$)



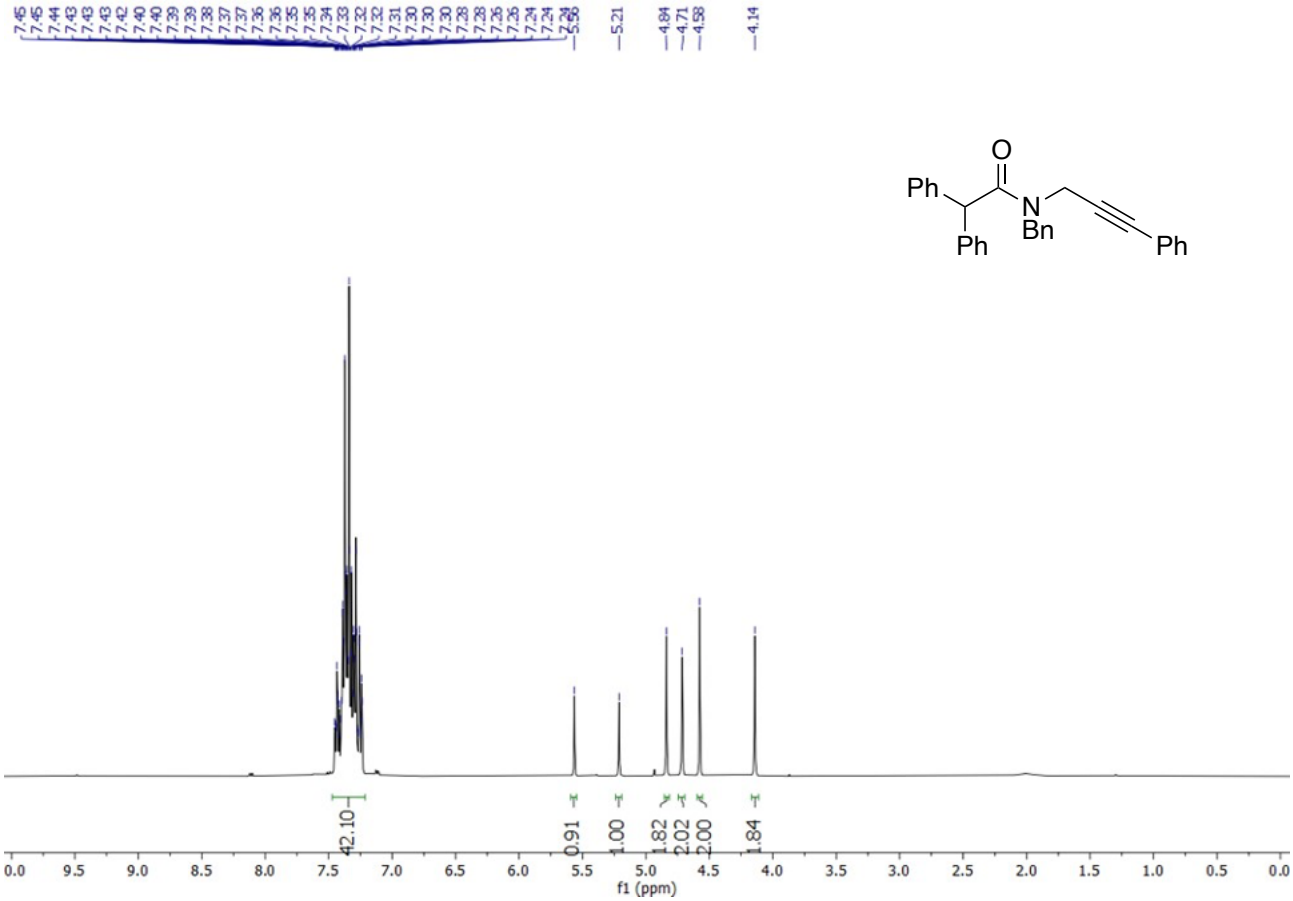
1e ^{1}H NMR (400 MHz, $CDCl_3$)



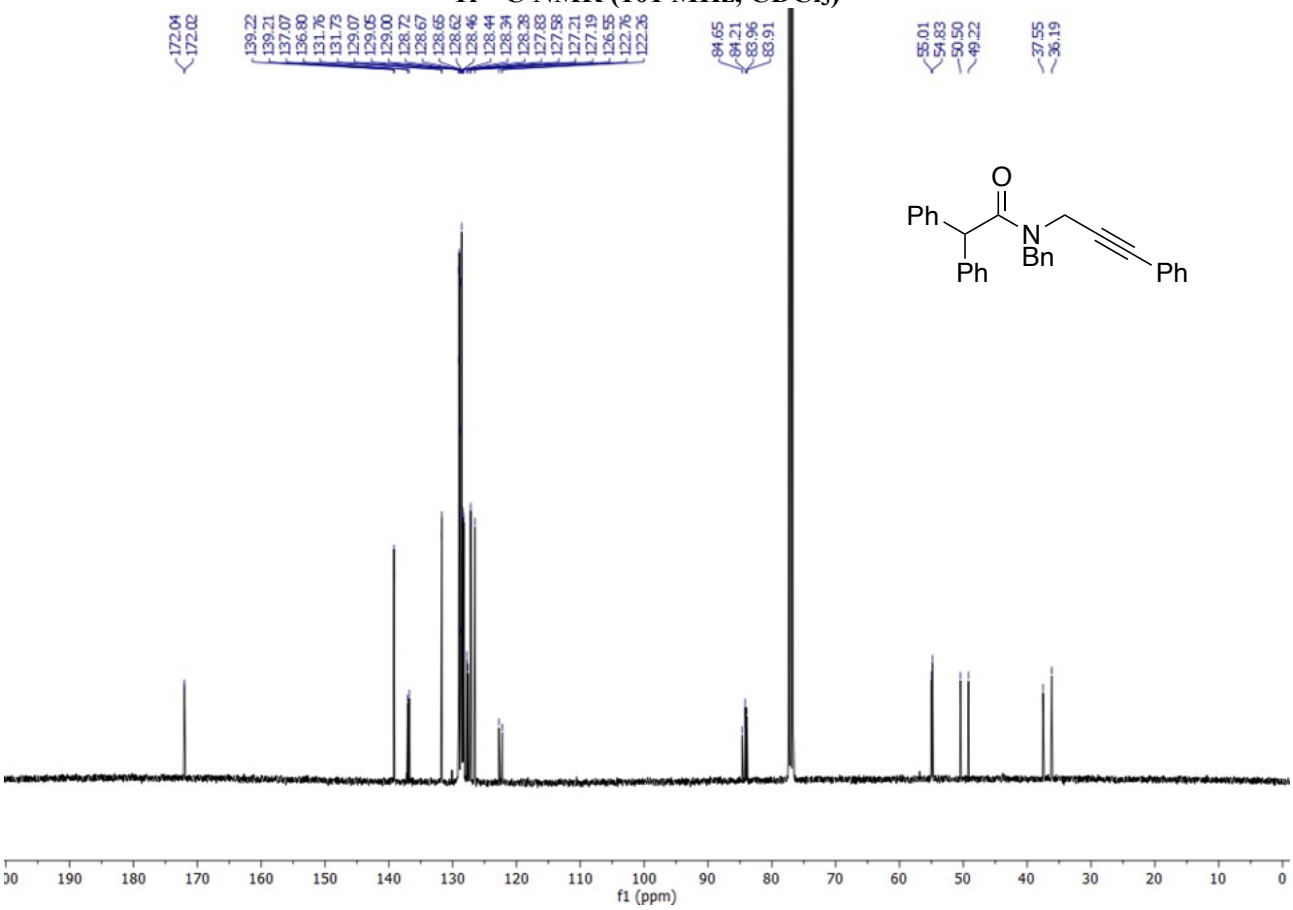
1e ^{13}C NMR (101 MHz, $CDCl_3$)



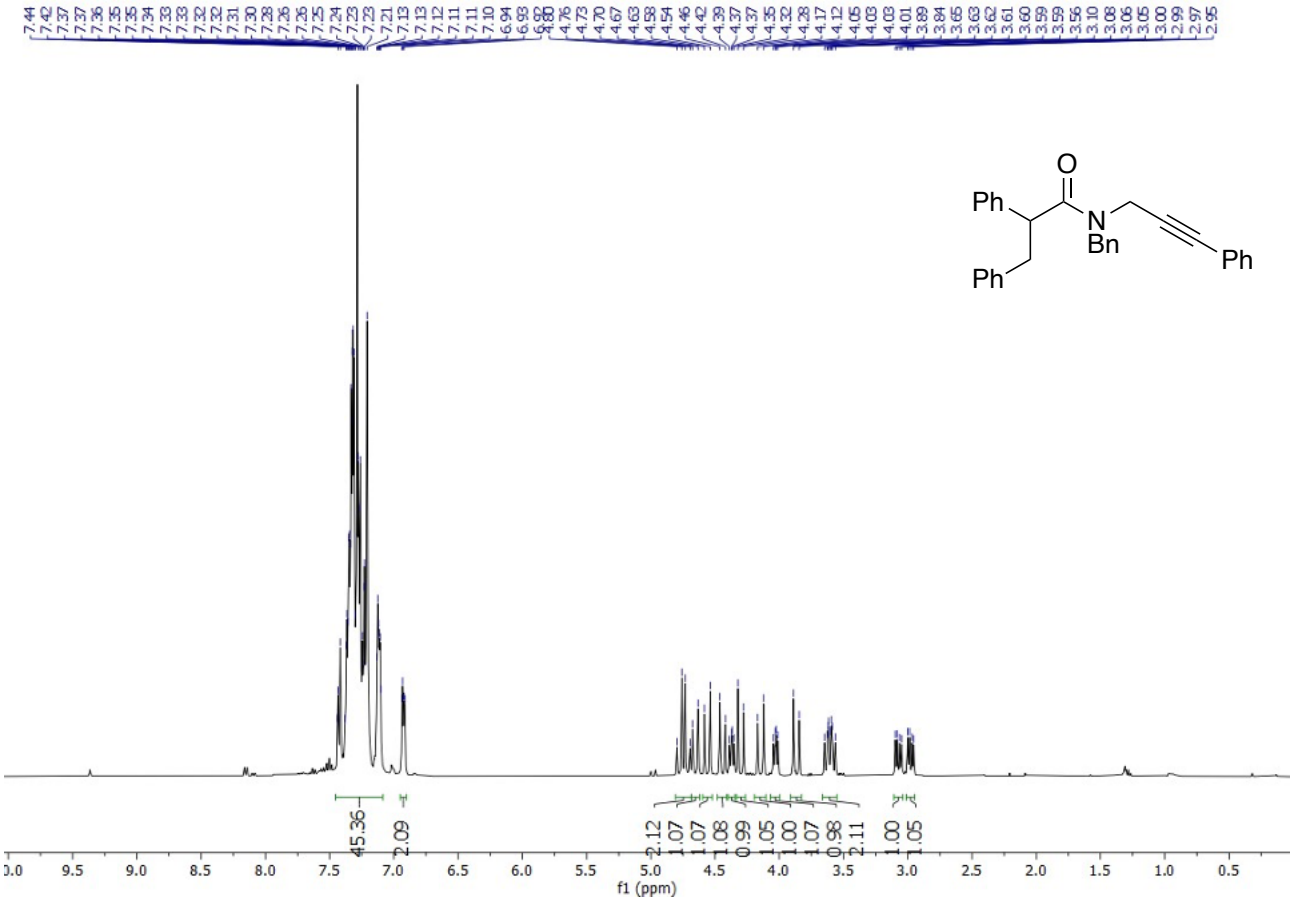
1f ^{1}H NMR (400 MHz, $CDCl_3$)



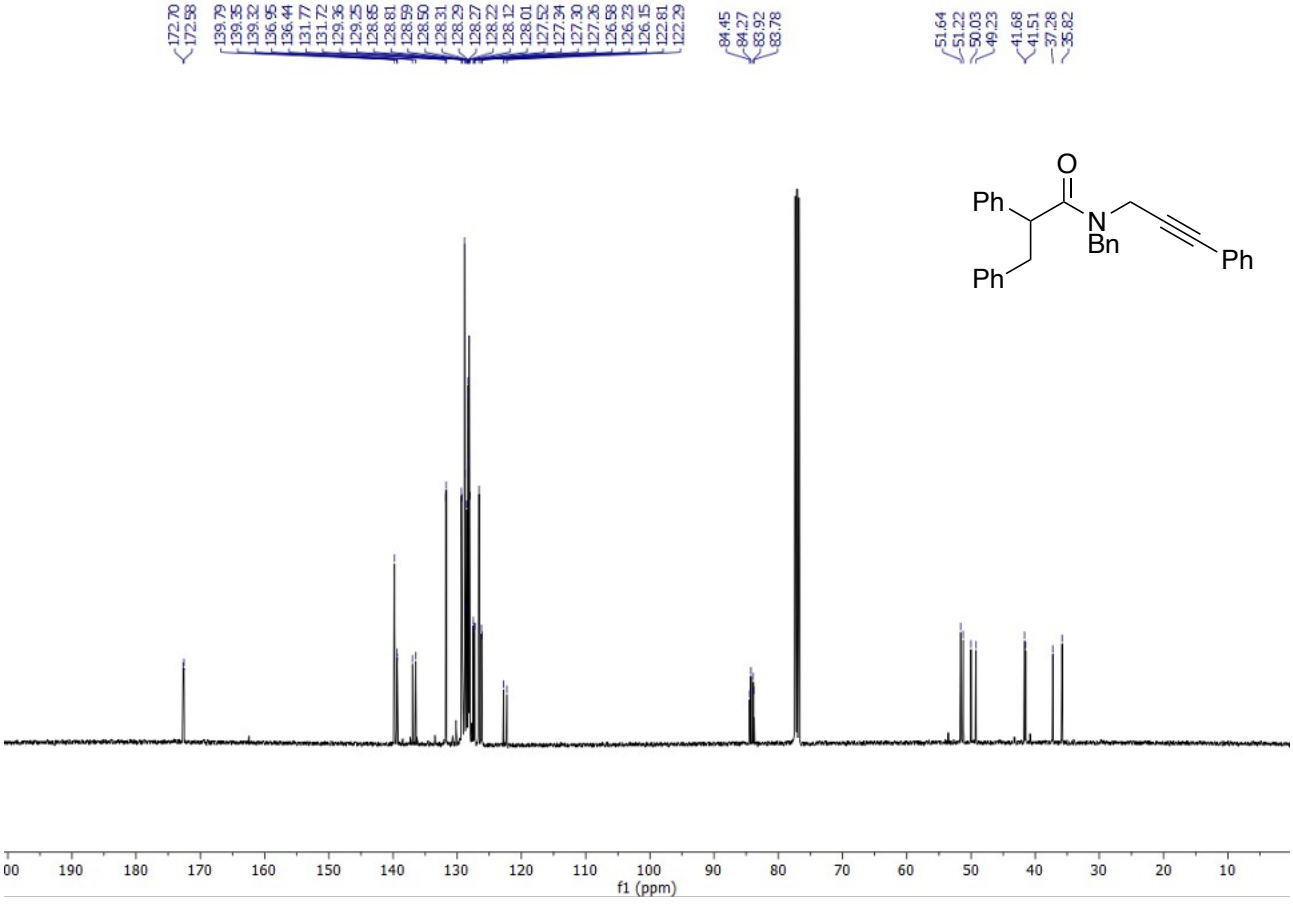
1f ^{13}C NMR (101 MHz, $CDCl_3$)



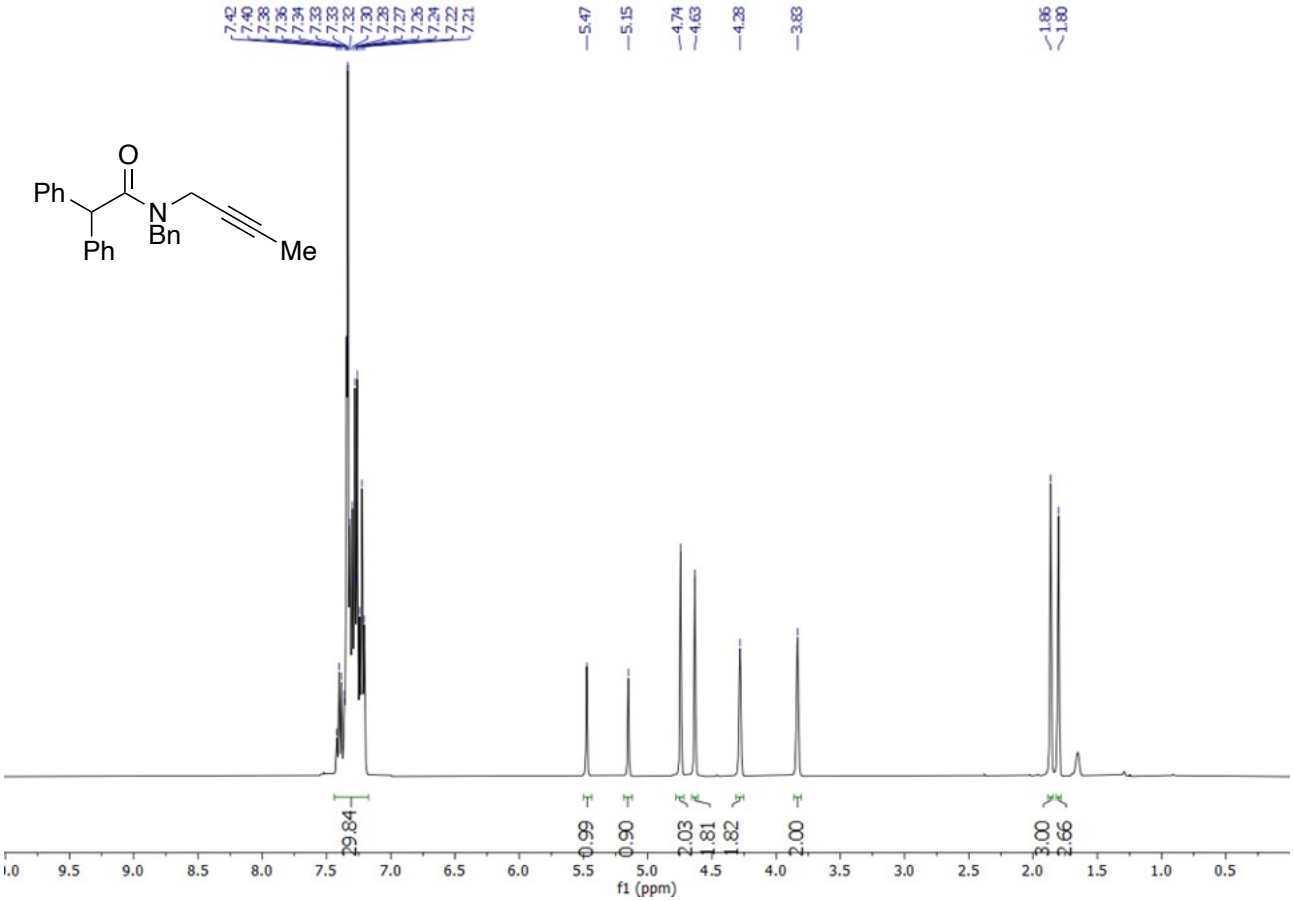
1g ^{1}H NMR (400 MHz, $CDCl_3$)



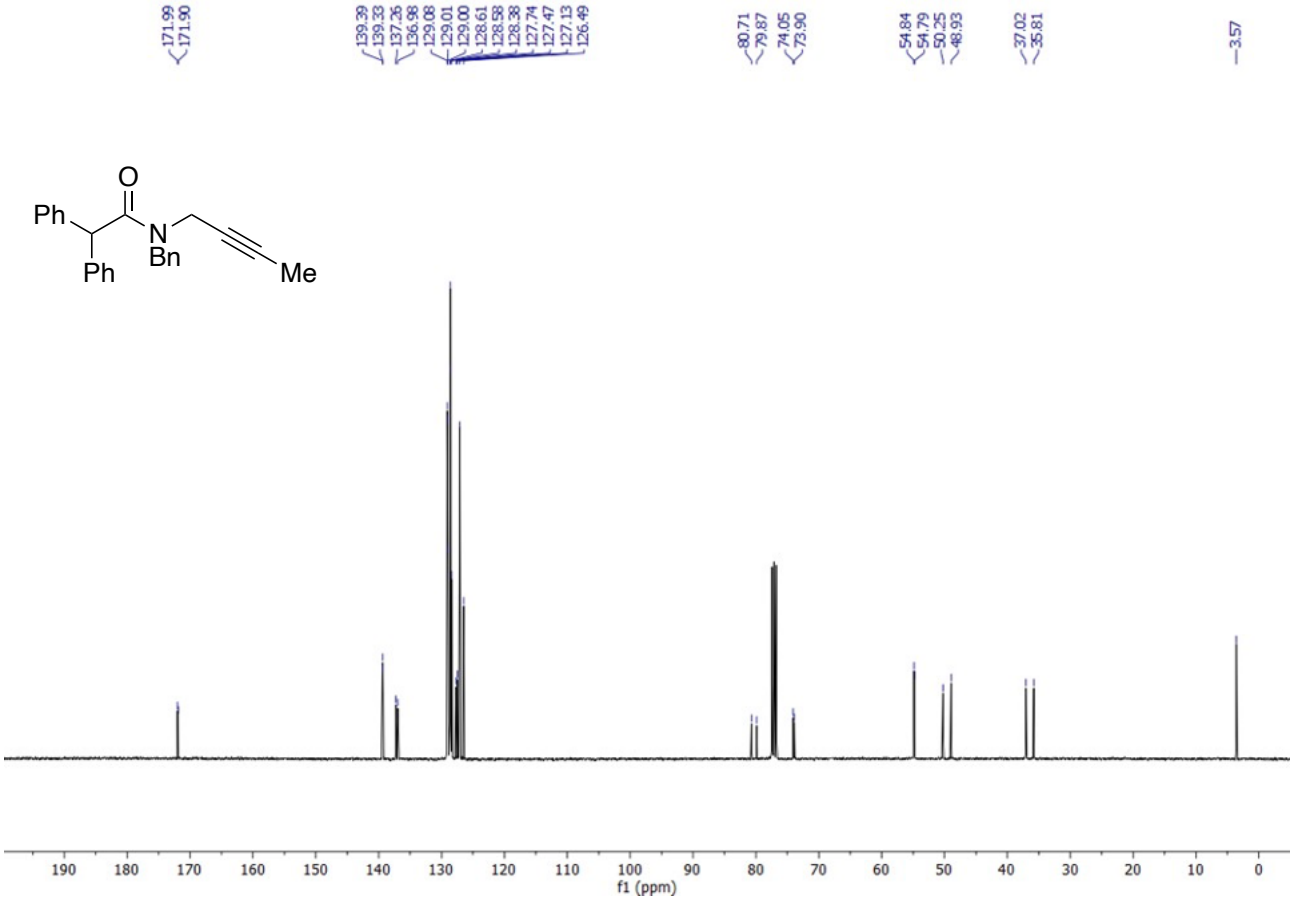
1g ^{13}C NMR (101 MHz, $CDCl_3$)



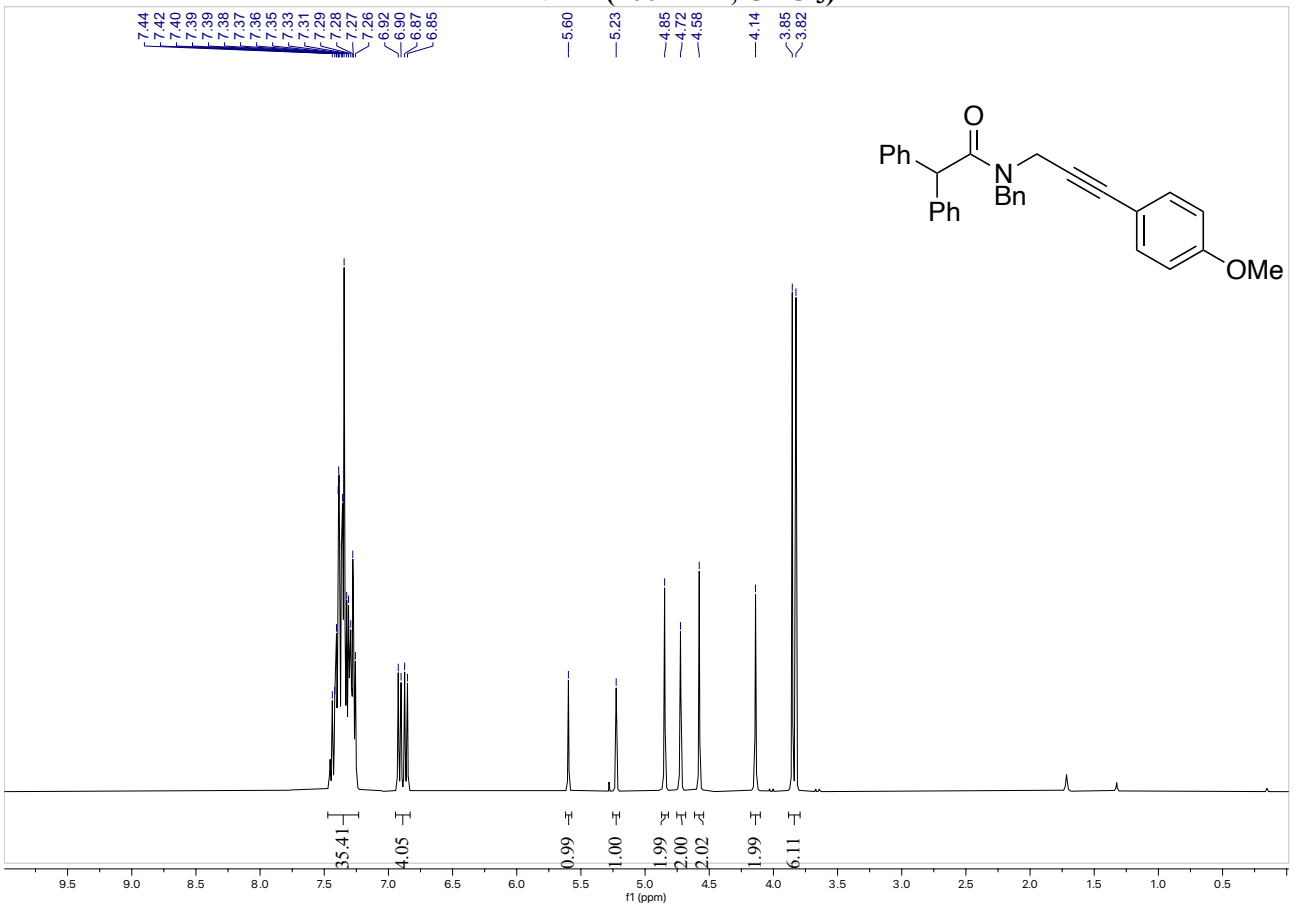
1h ^{1}H NMR (400 MHz, $CDCl_3$)



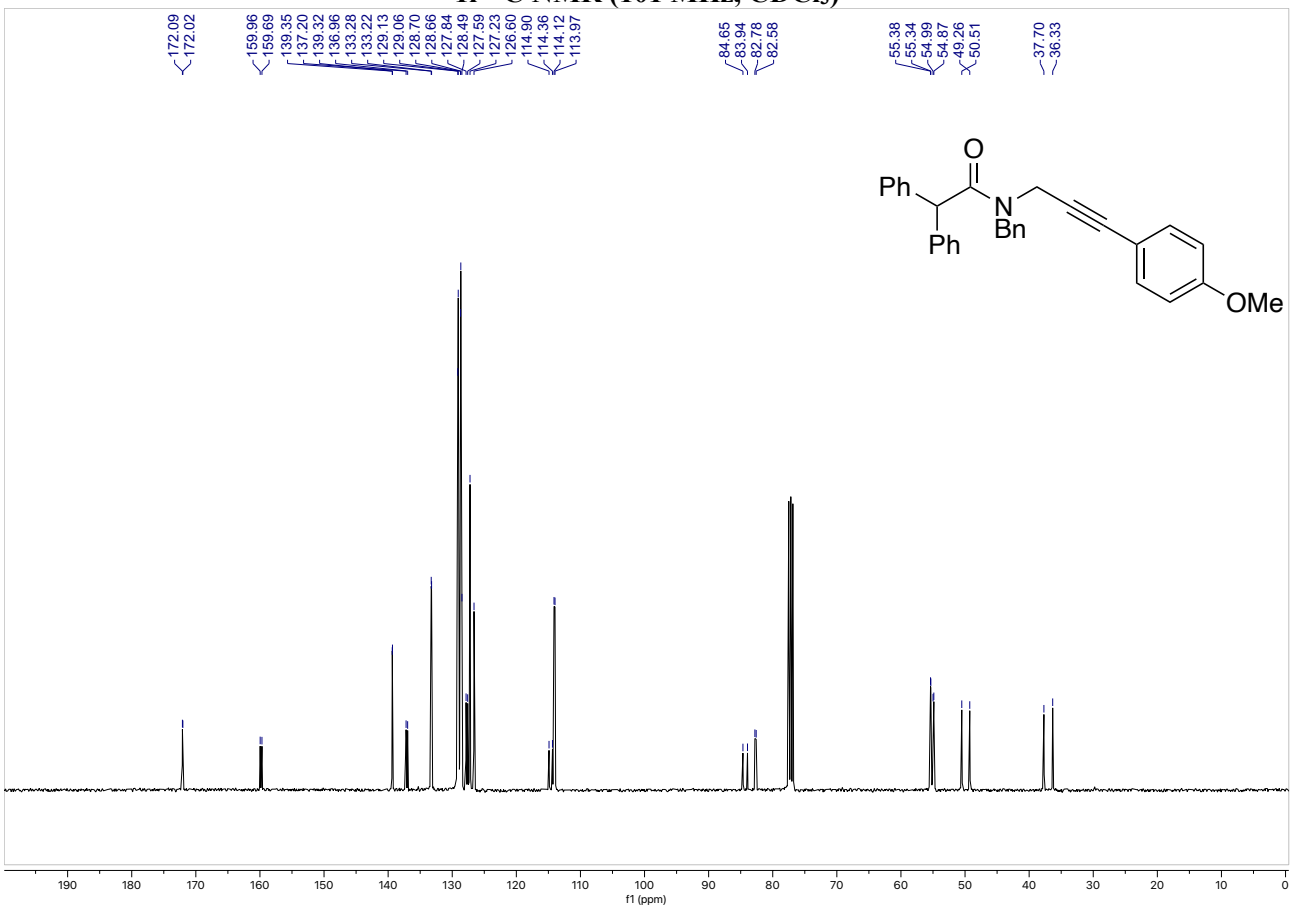
1h ^{13}C NMR (101 MHz, $CDCl_3$)



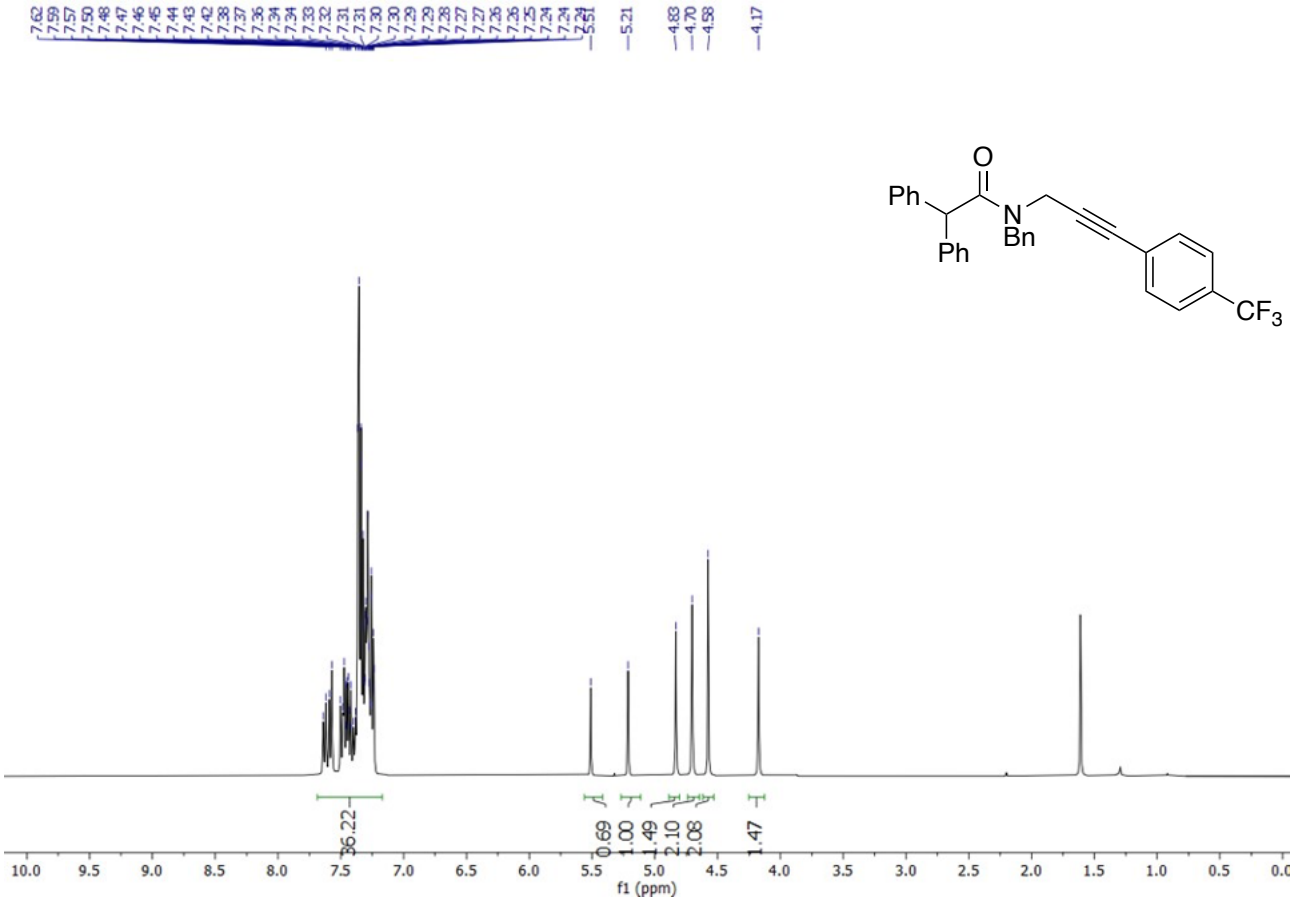
1i ^{1}H NMR (400 MHz, $CDCl_3$)



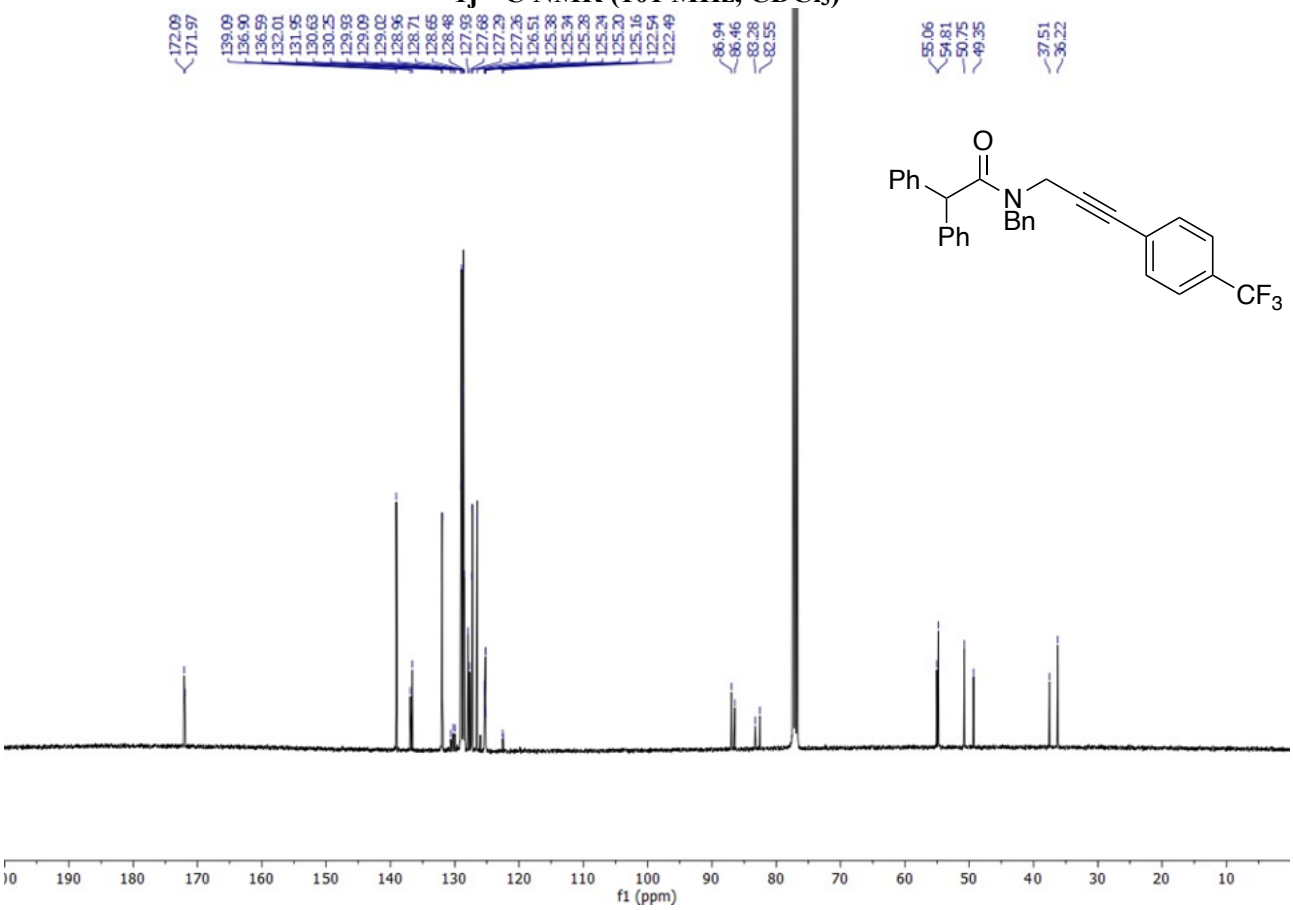
1i ^{13}C NMR (101 MHz, $CDCl_3$)



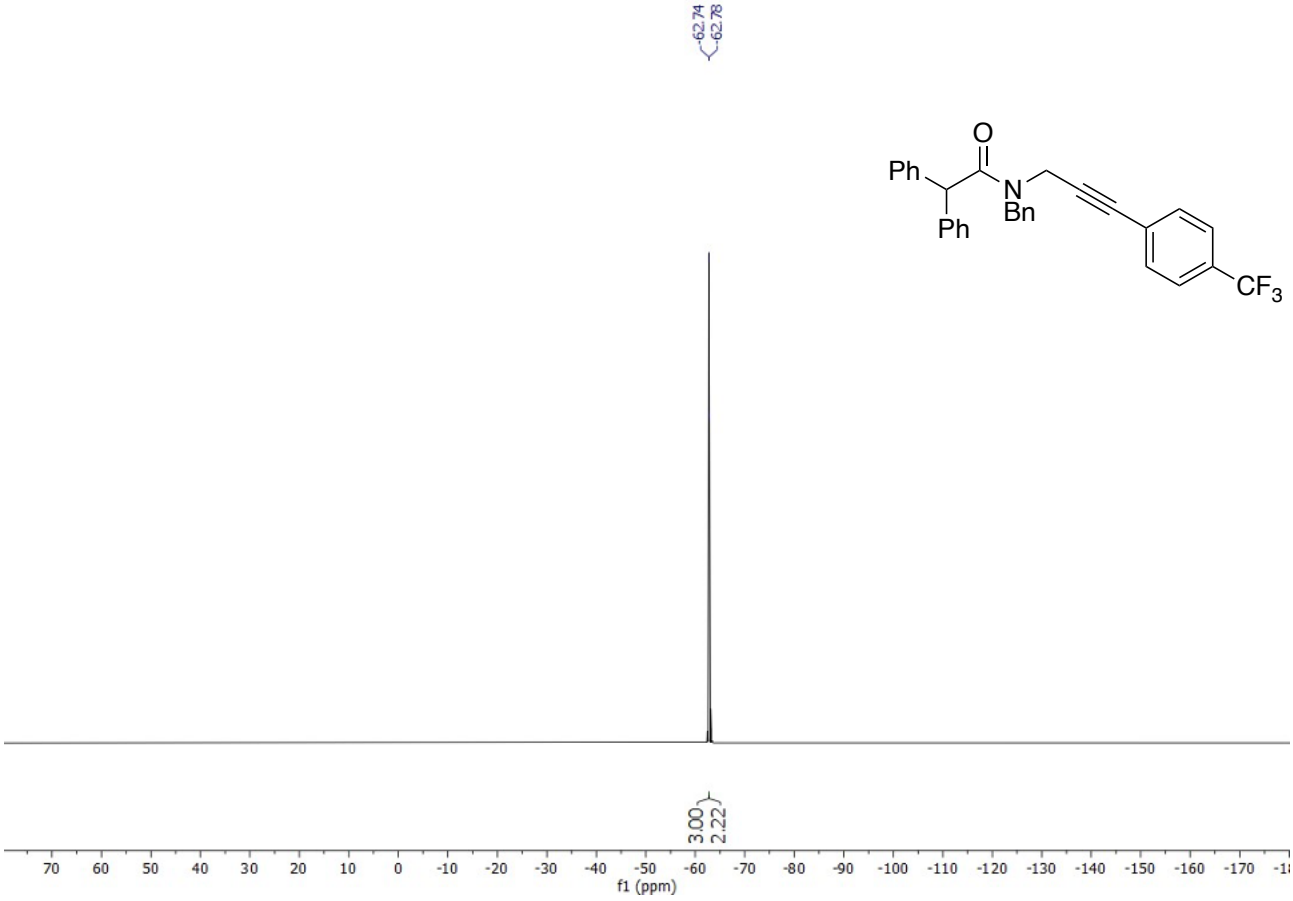
1j ^{1}H NMR (400 MHz, $CDCl_3$)



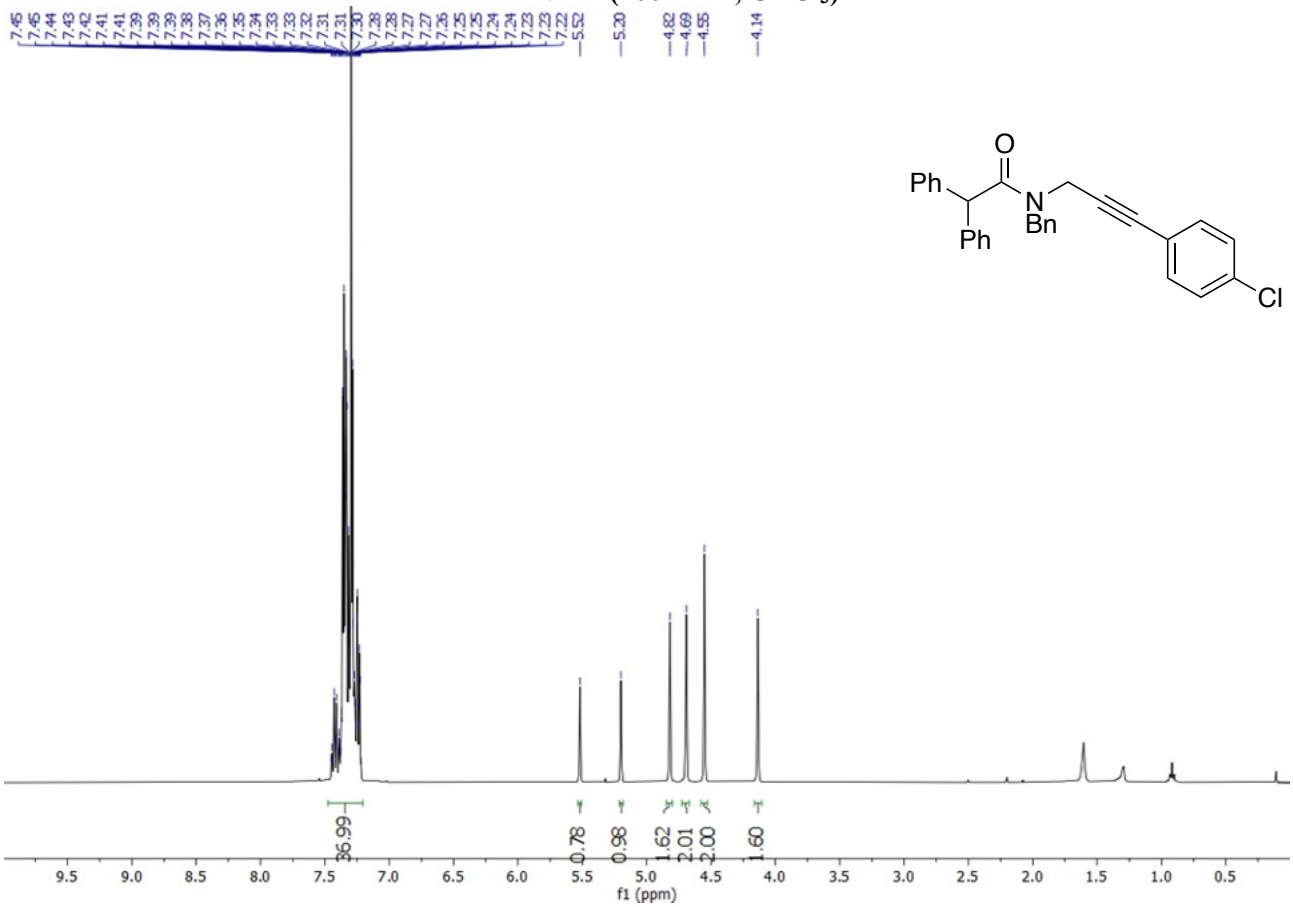
1j ^{13}C NMR (101 MHz, $CDCl_3$)



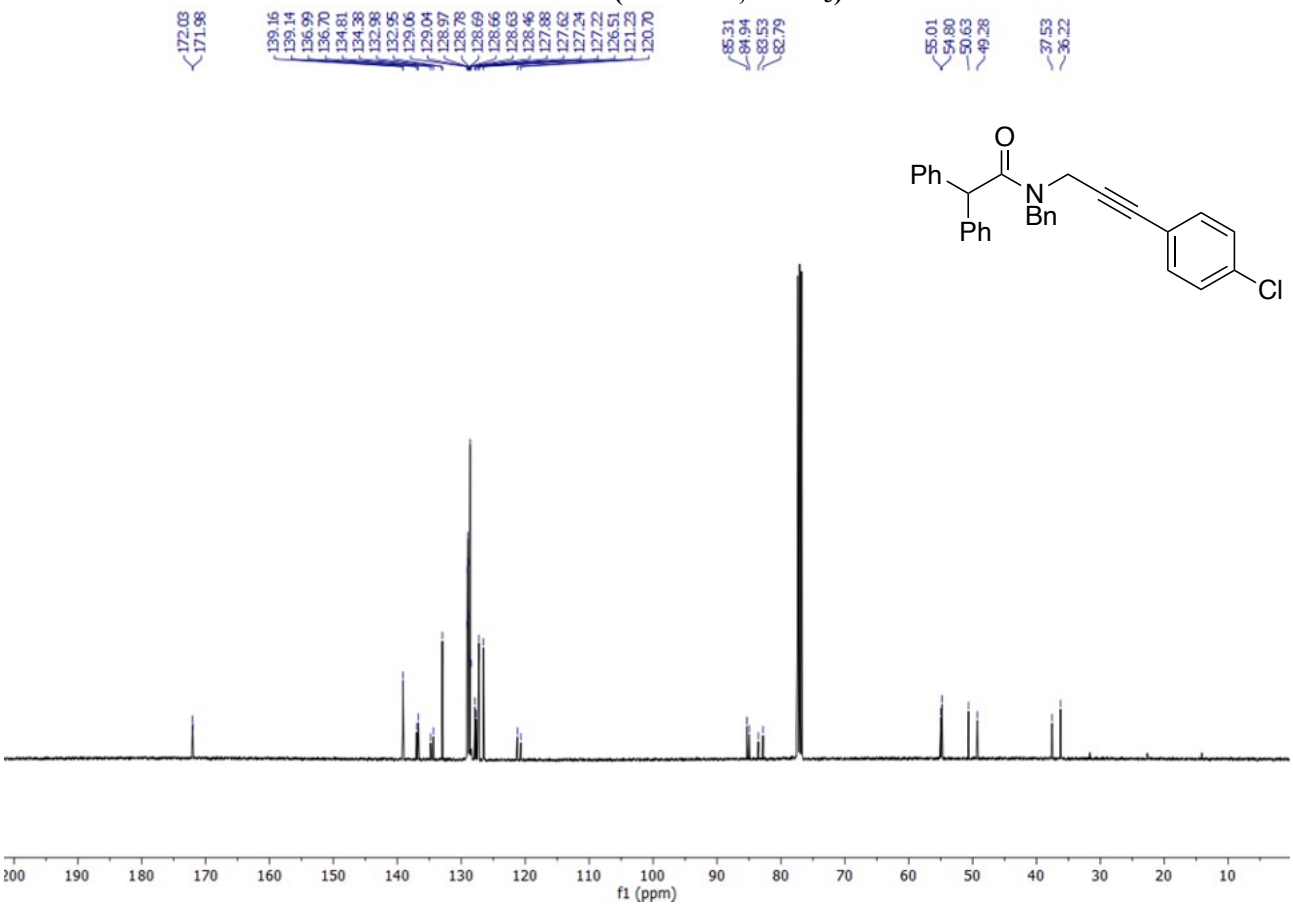
1j ^{19}F NMR (565 MHz, $CDCl_3$)



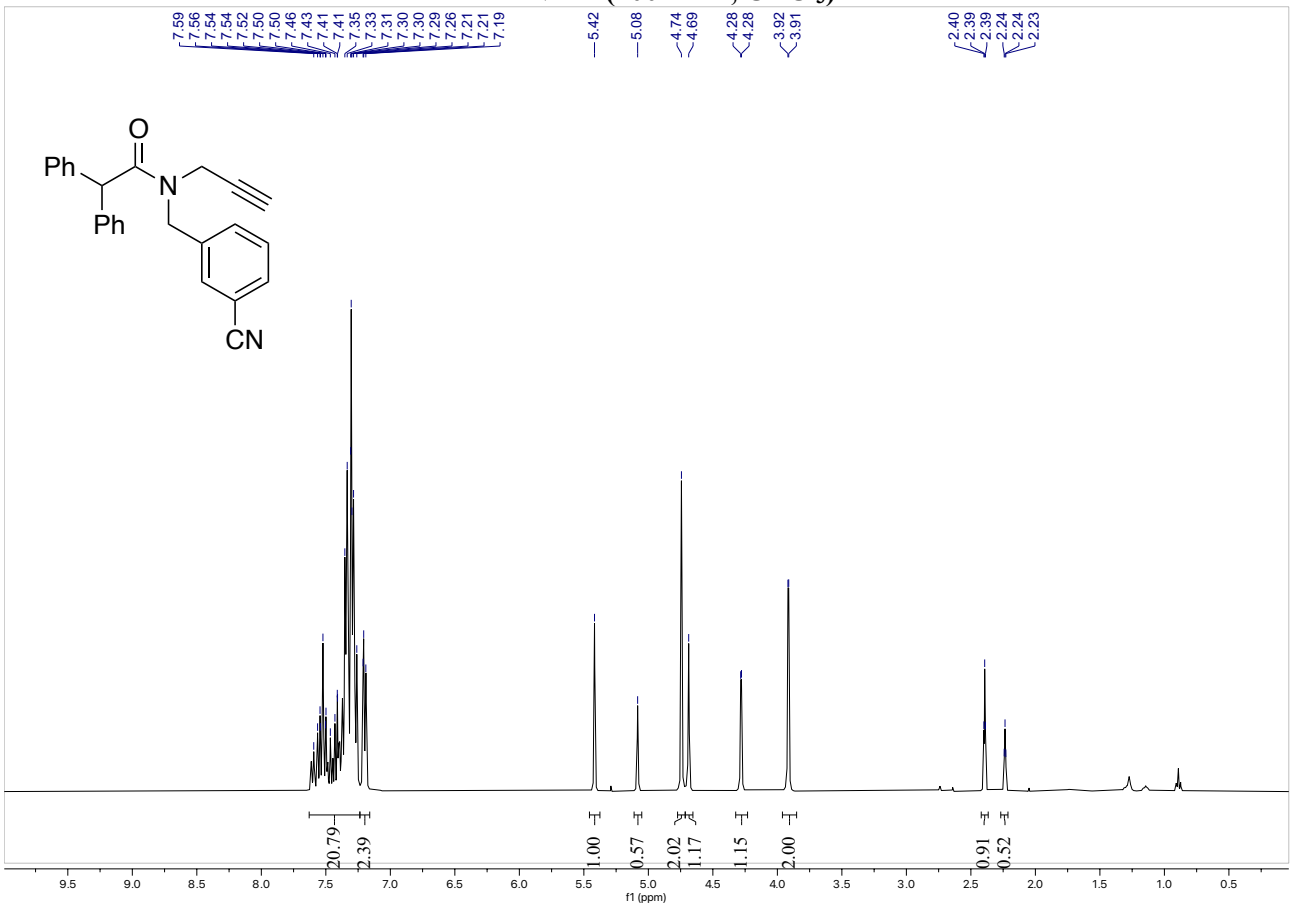
1k ^{1}H NMR (400 MHz, $CDCl_3$)



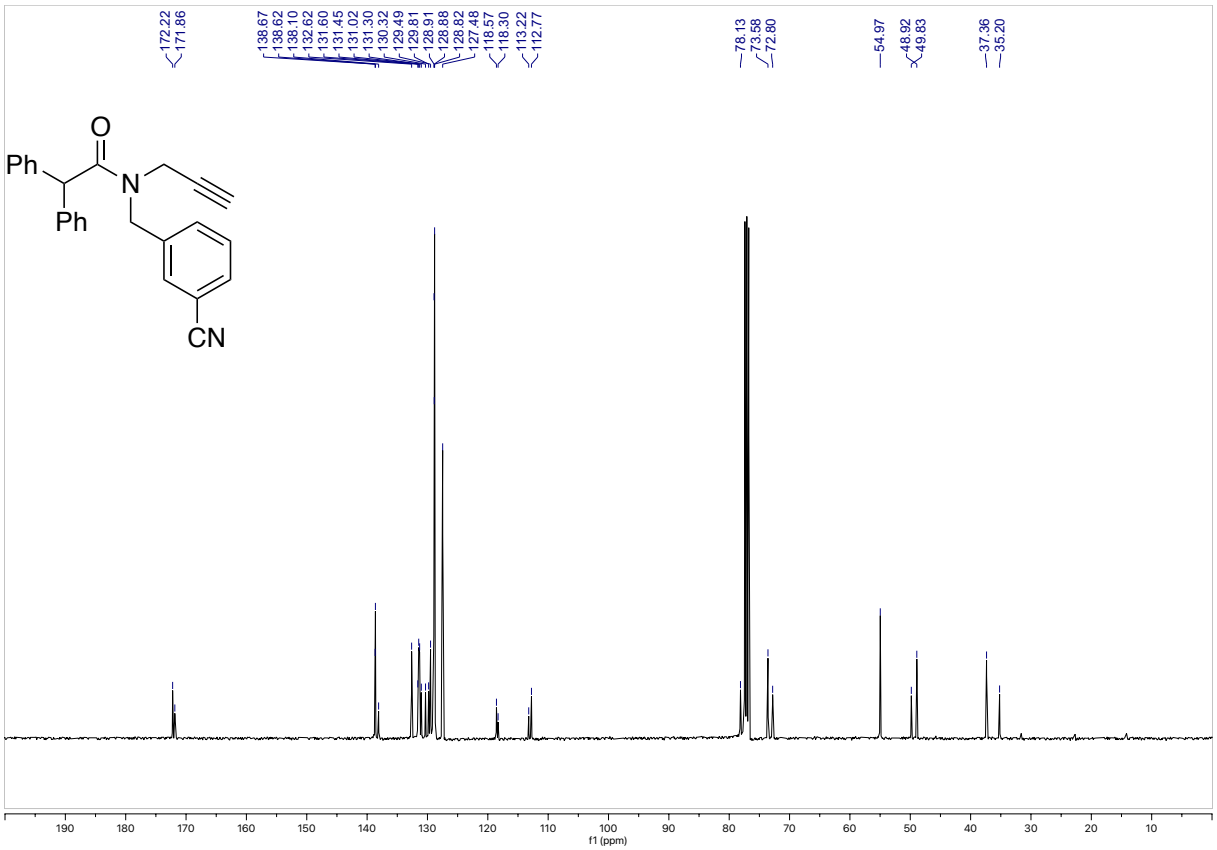
1k ^{13}C NMR (101 MHz, $CDCl_3$)



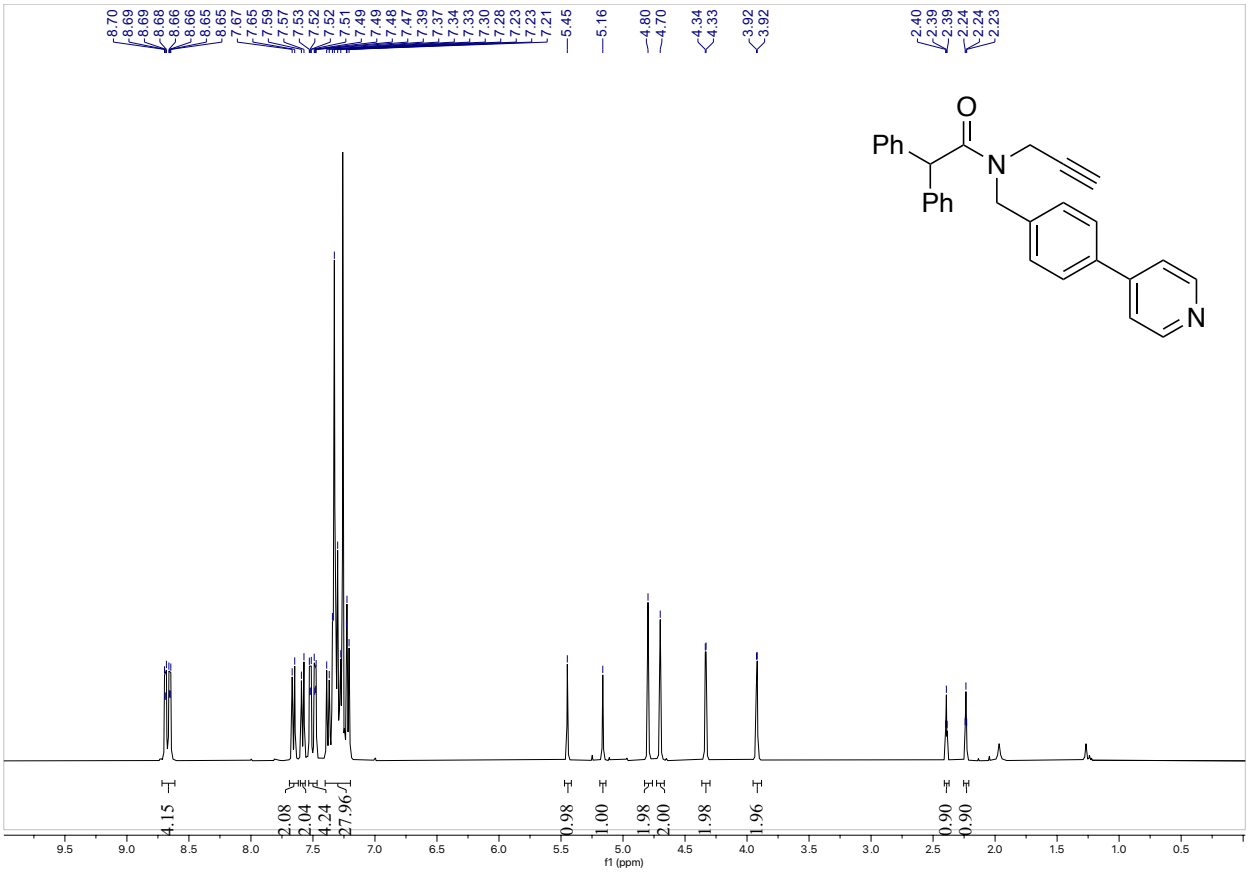
1l ^{1}H NMR (400 MHz, $CDCl_3$)



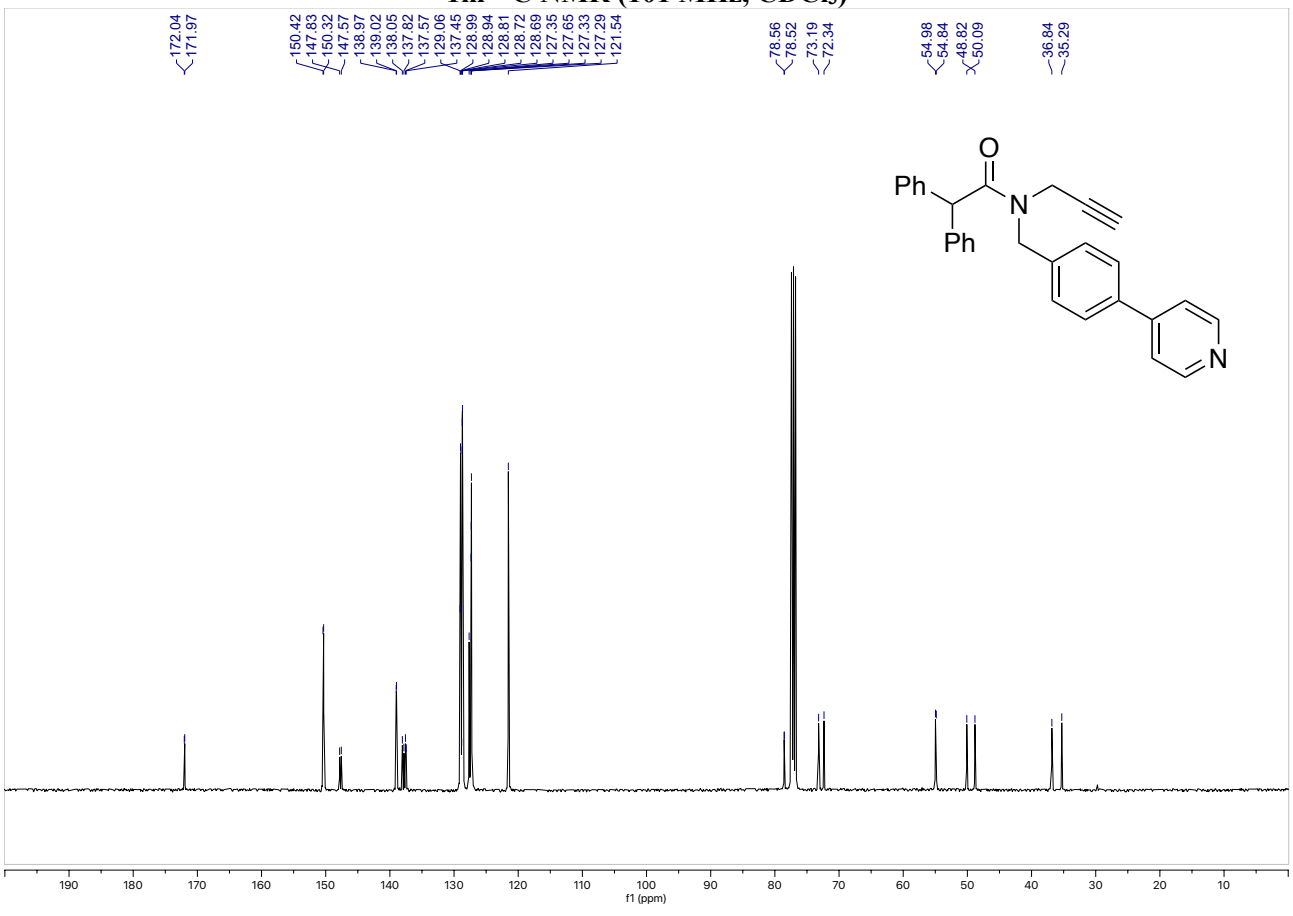
1l ^{13}C NMR (101 MHz, $CDCl_3$)



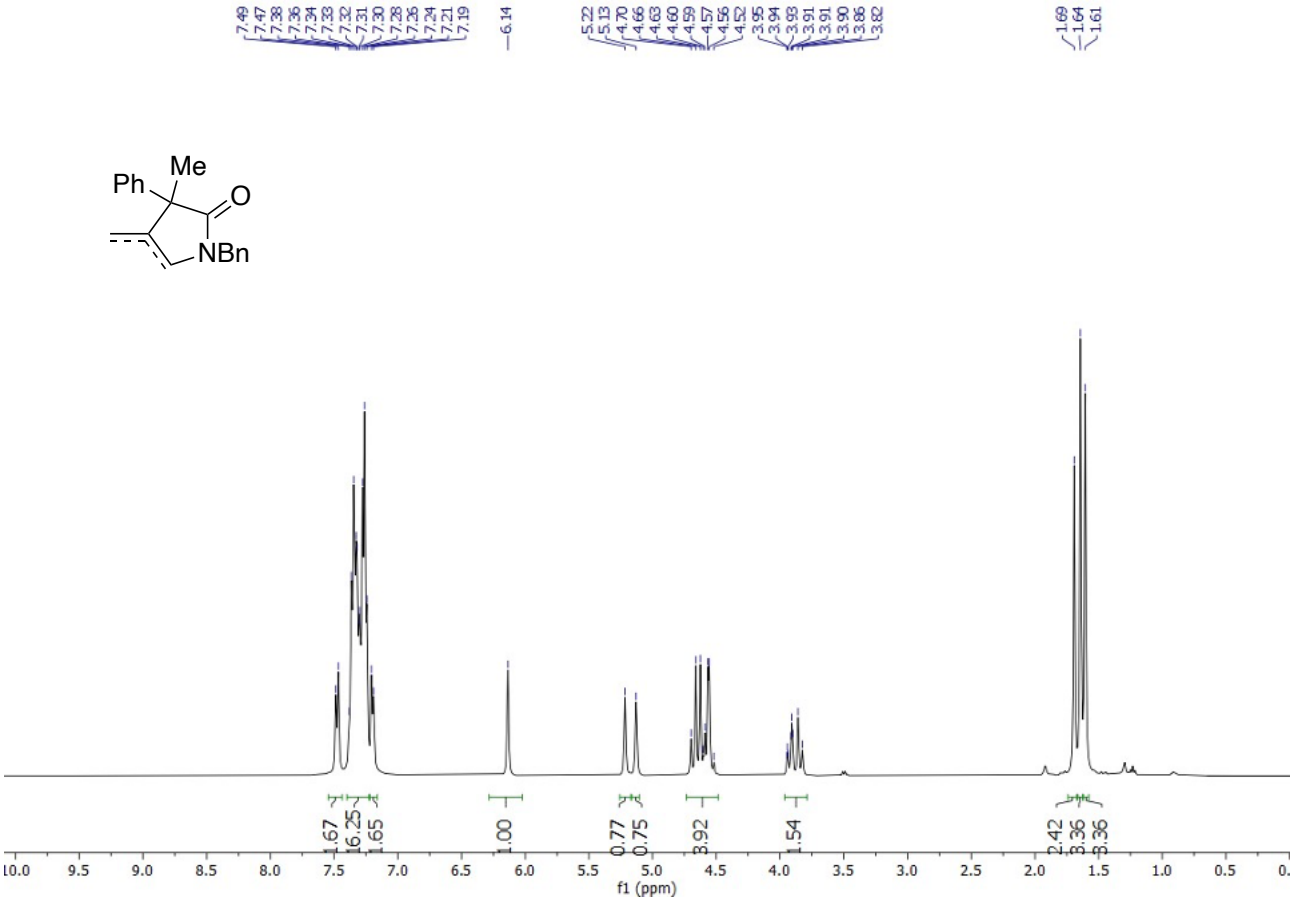
1m ^{1}H NMR (400 MHz, $CDCl_3$)



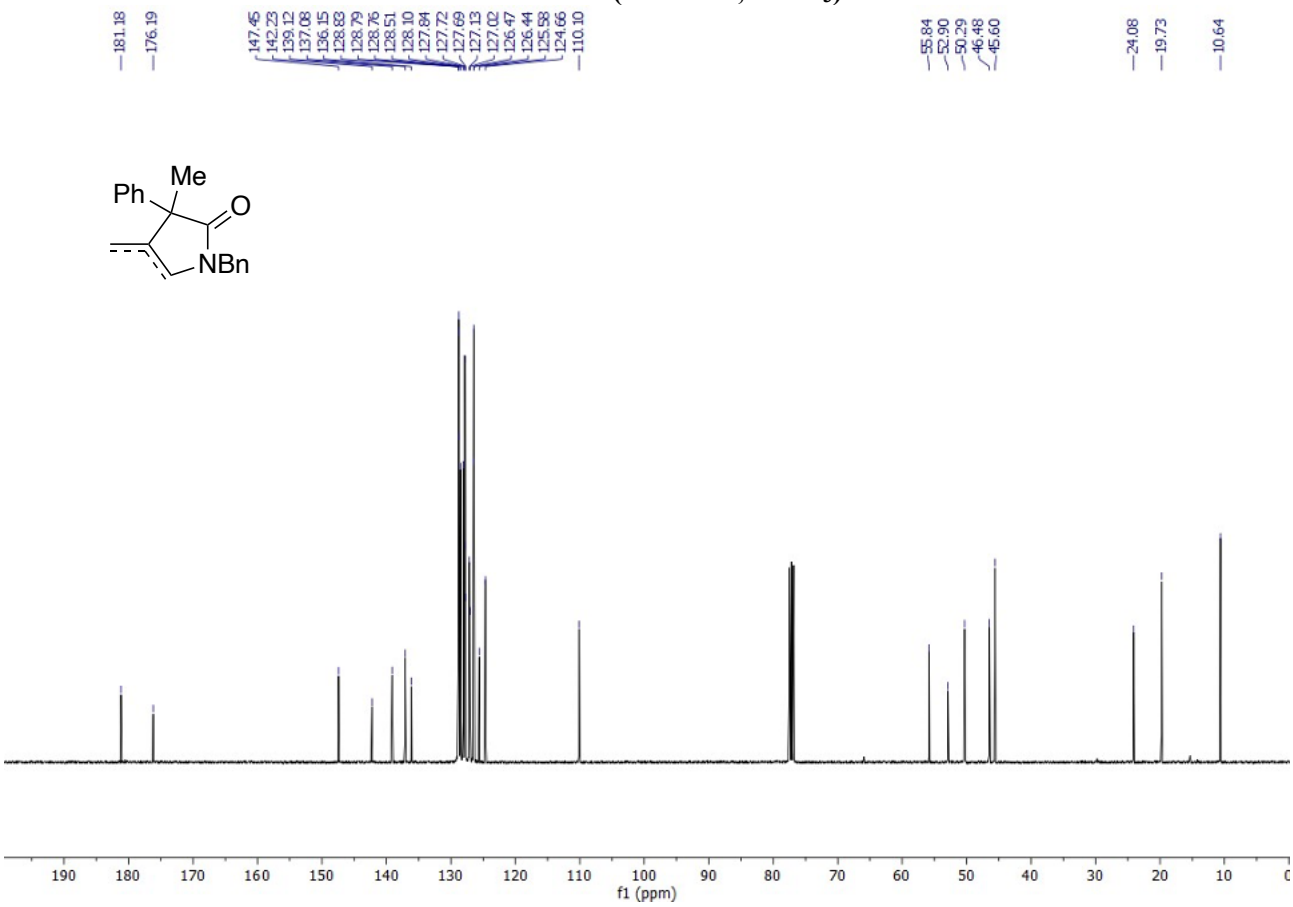
1m ^{13}C NMR (101 MHz, $CDCl_3$)



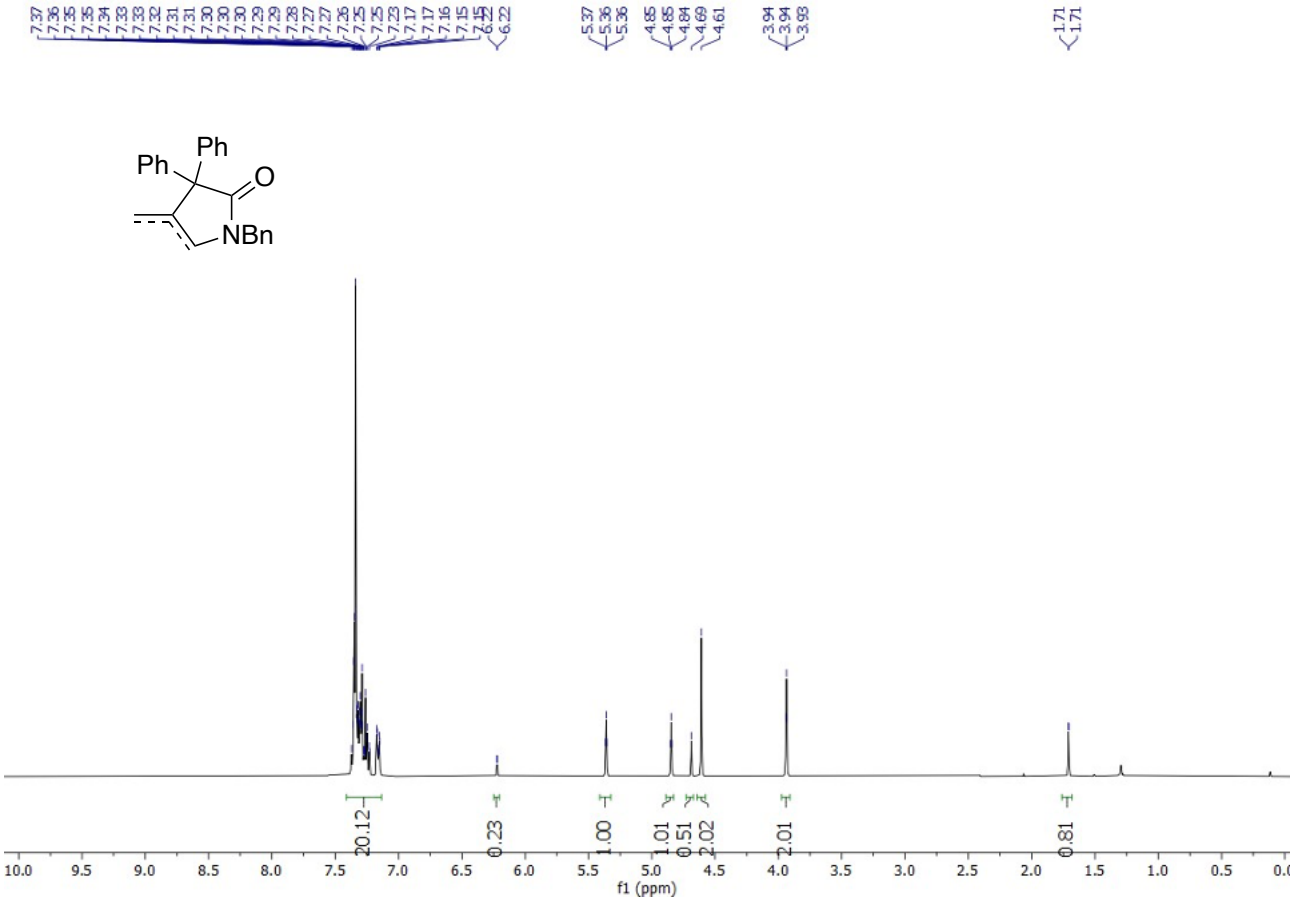
2a ^{1}H NMR (400 MHz, $CDCl_3$)



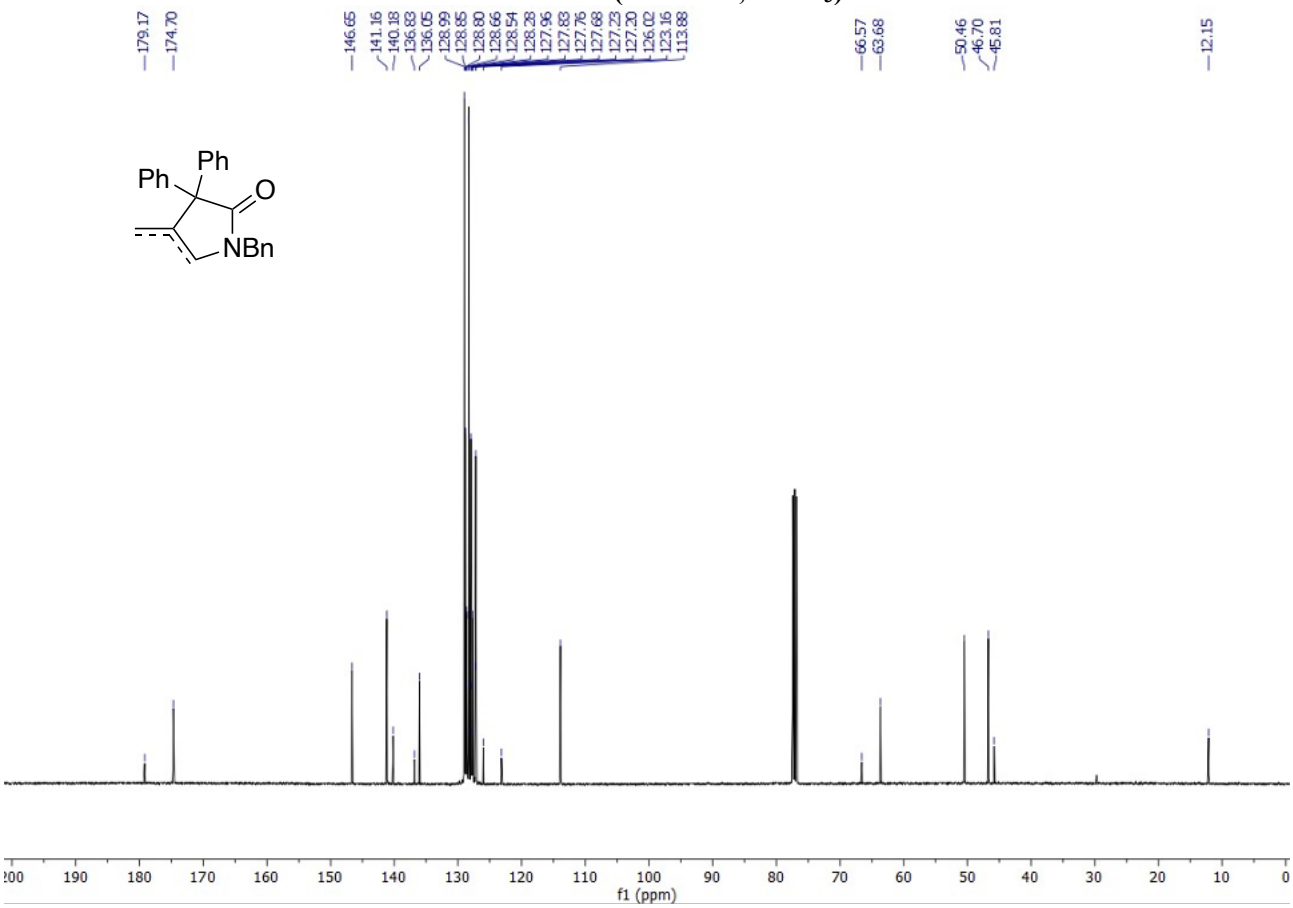
2a ^{13}C NMR (101 MHz, $CDCl_3$)



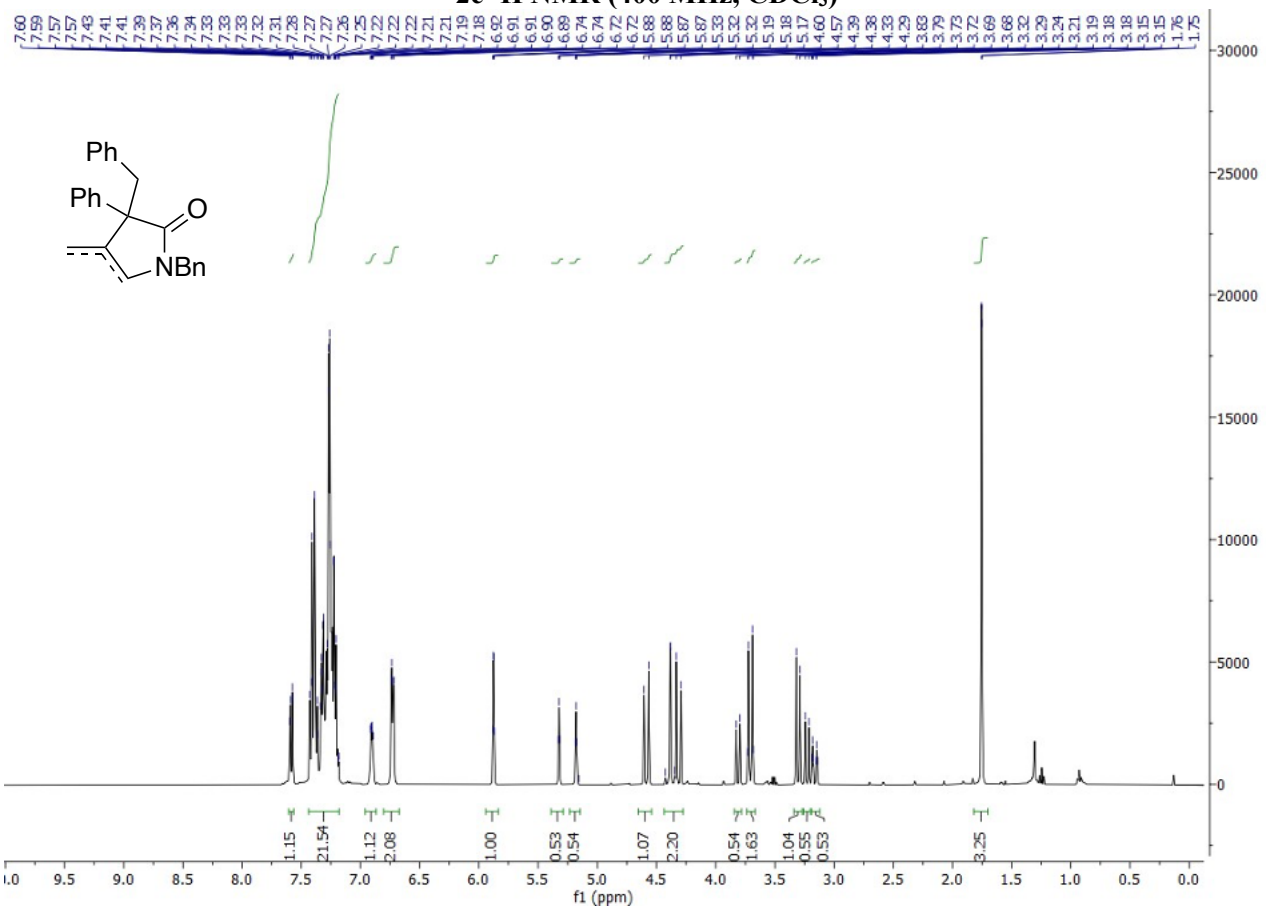
2b ^{1}H NMR (400 MHz, $CDCl_3$)



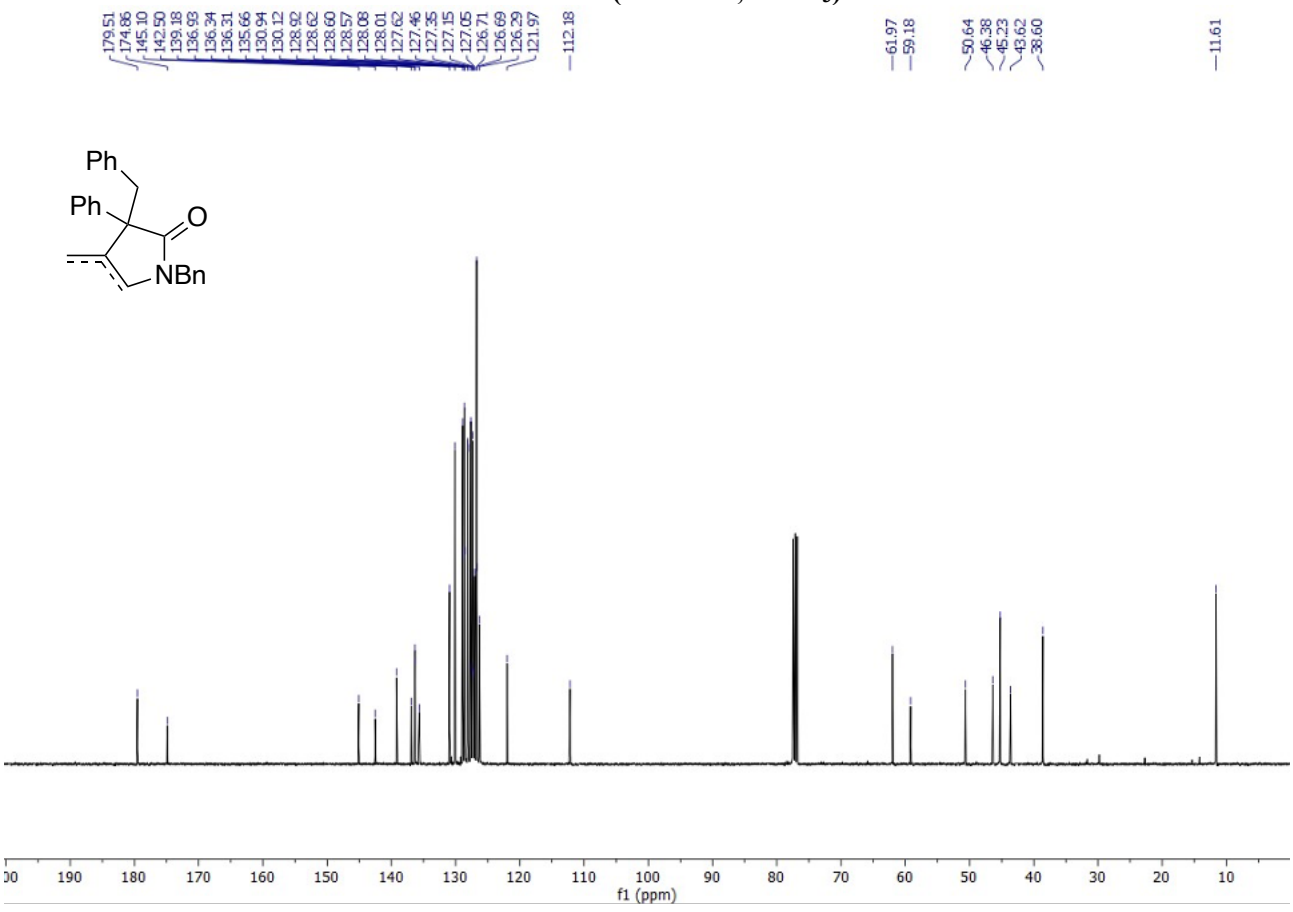
2b ^{13}C NMR (101 MHz, $CDCl_3$)



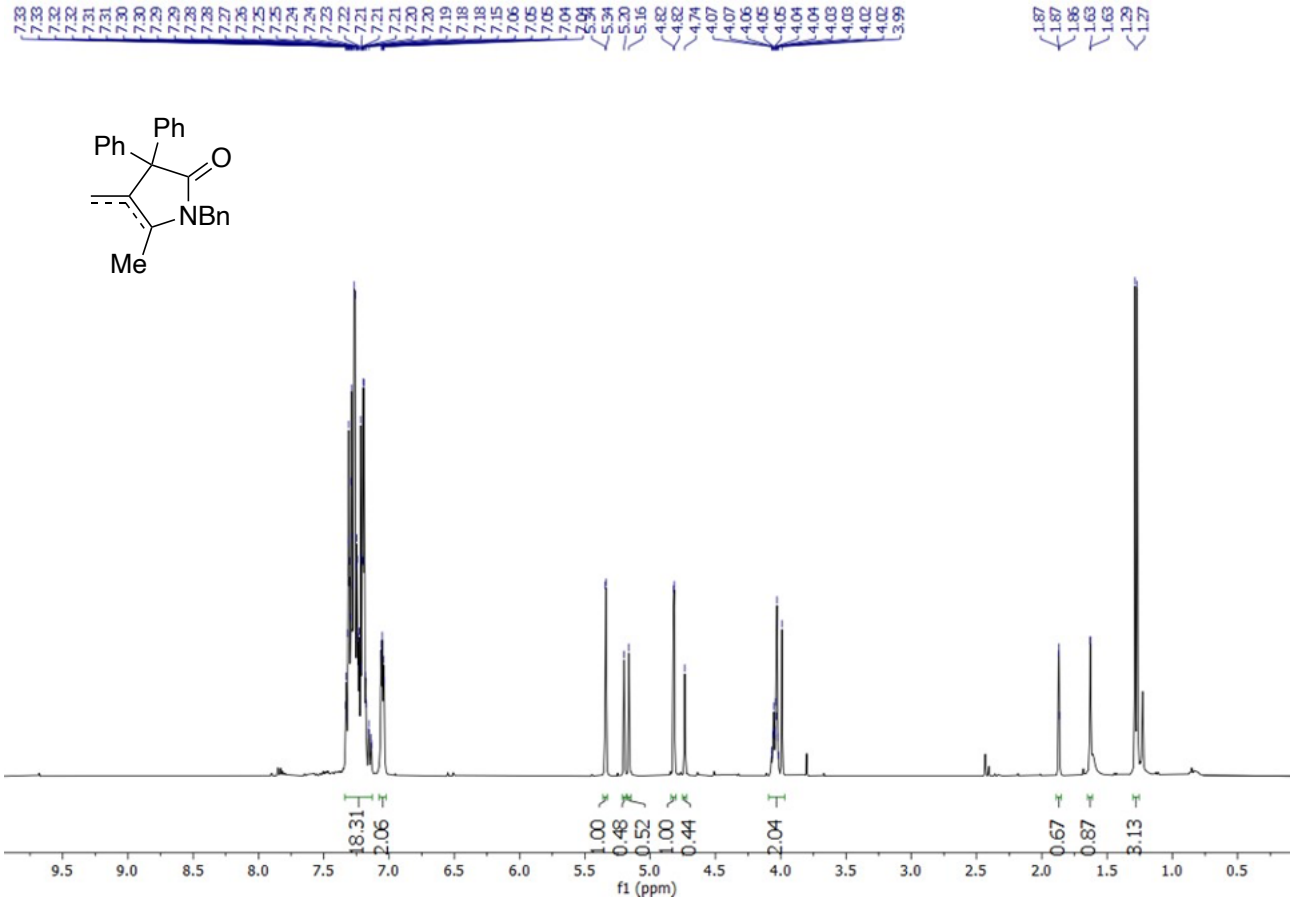
2c ^{1}H NMR (400 MHz, $CDCl_3$)



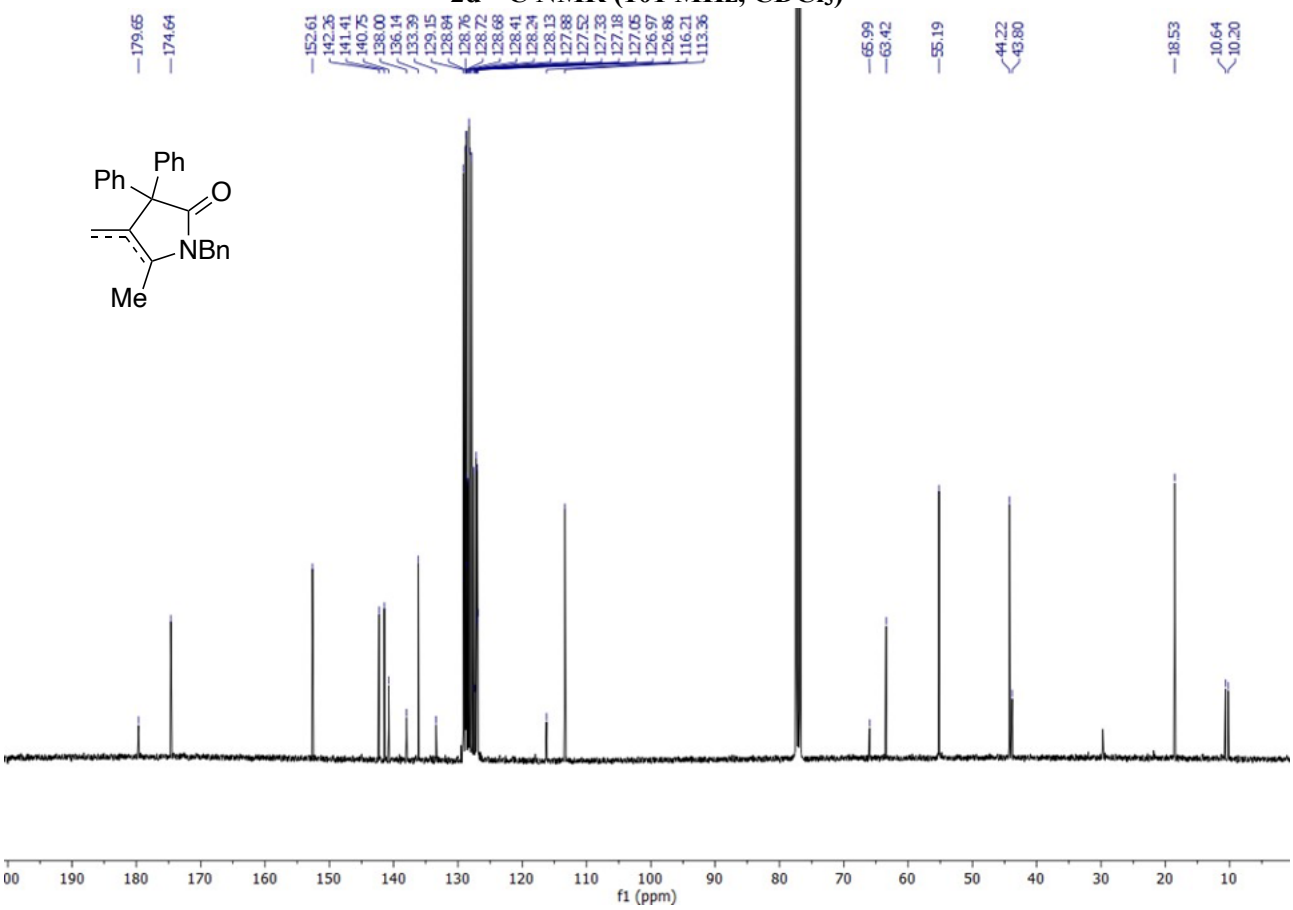
2c ^{13}C NMR (101 MHz, $CDCl_3$)



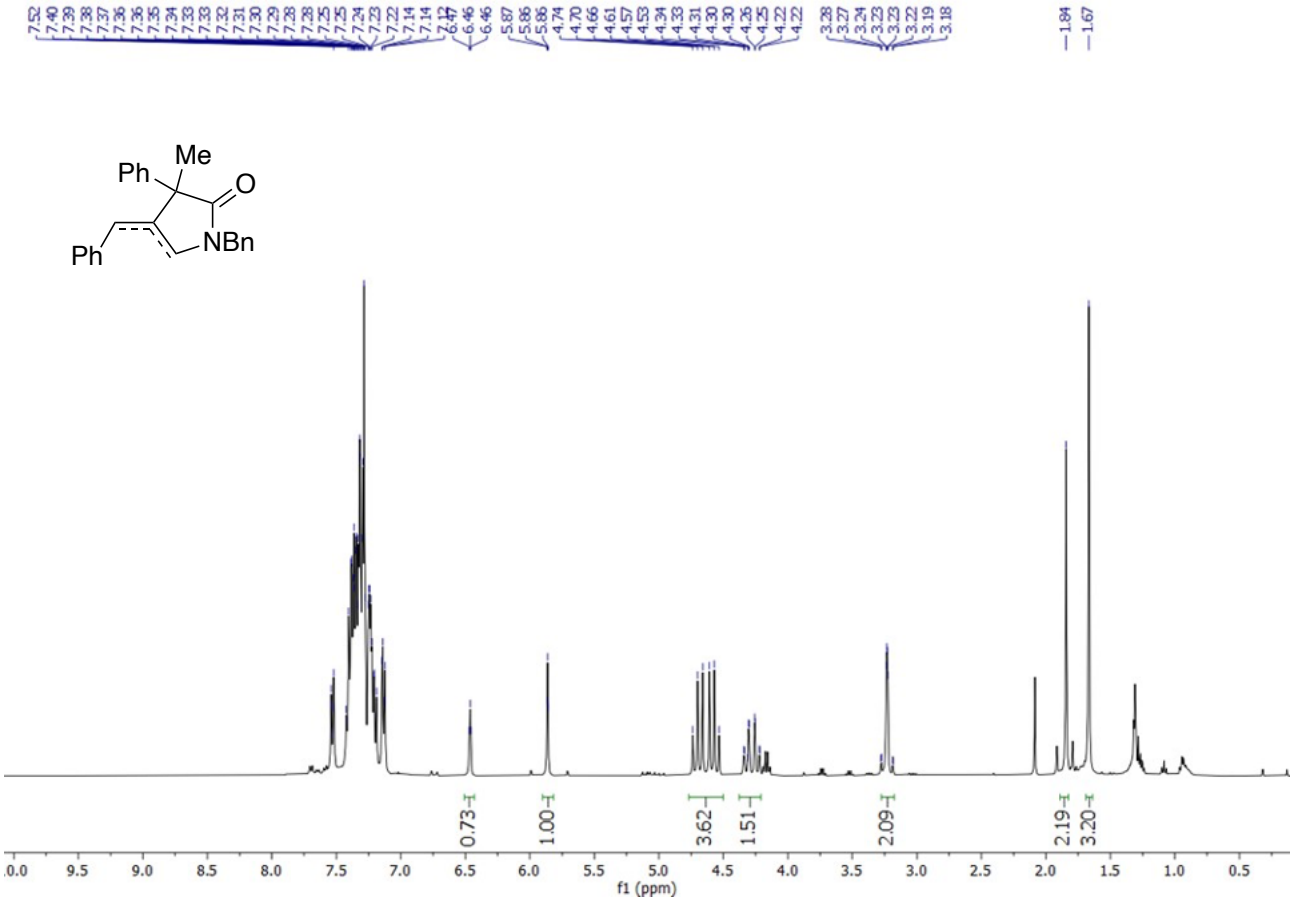
2d ^{1}H NMR (400 MHz, $CDCl_3$)



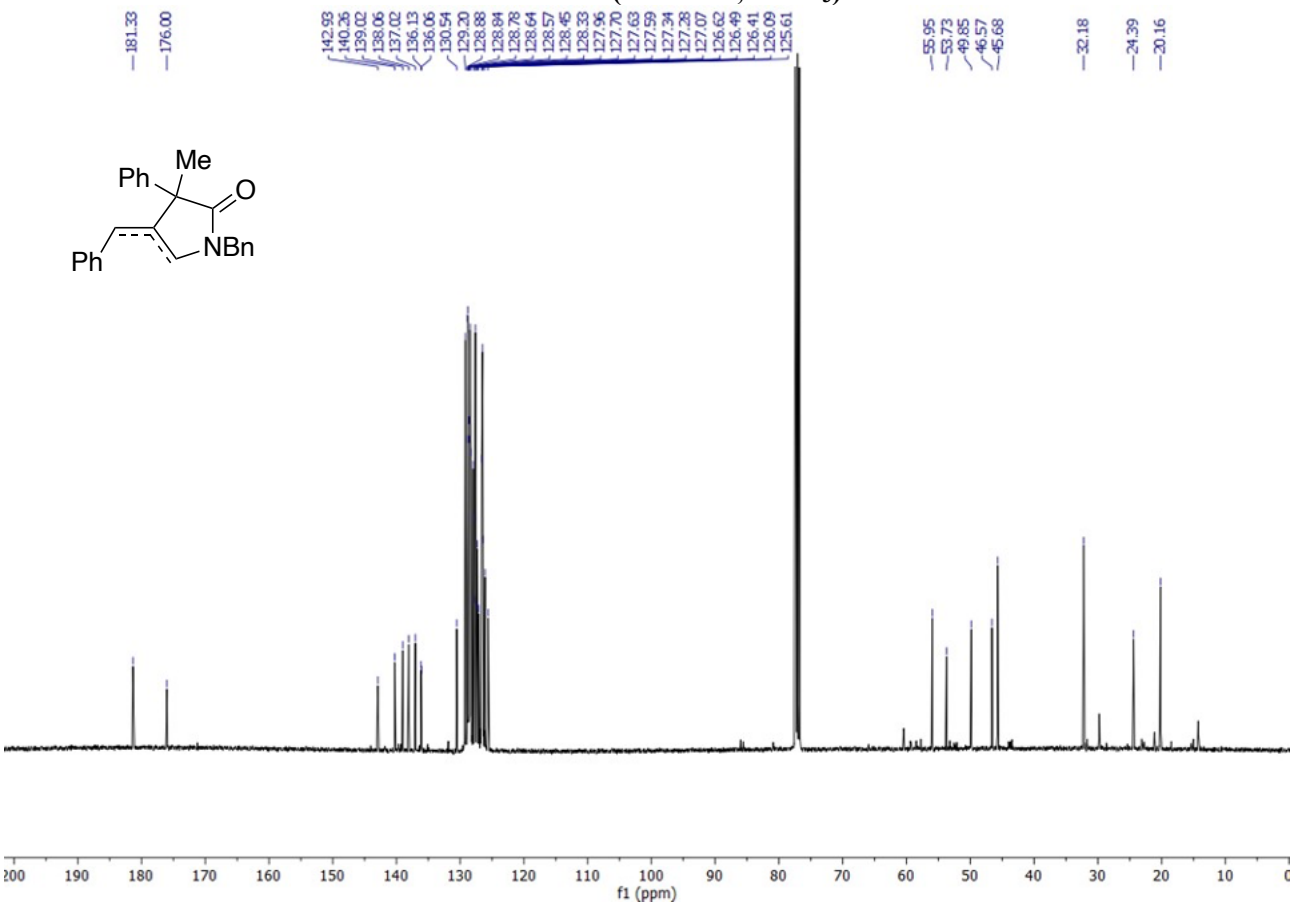
2d ^{13}C NMR (101 MHz, $CDCl_3$)



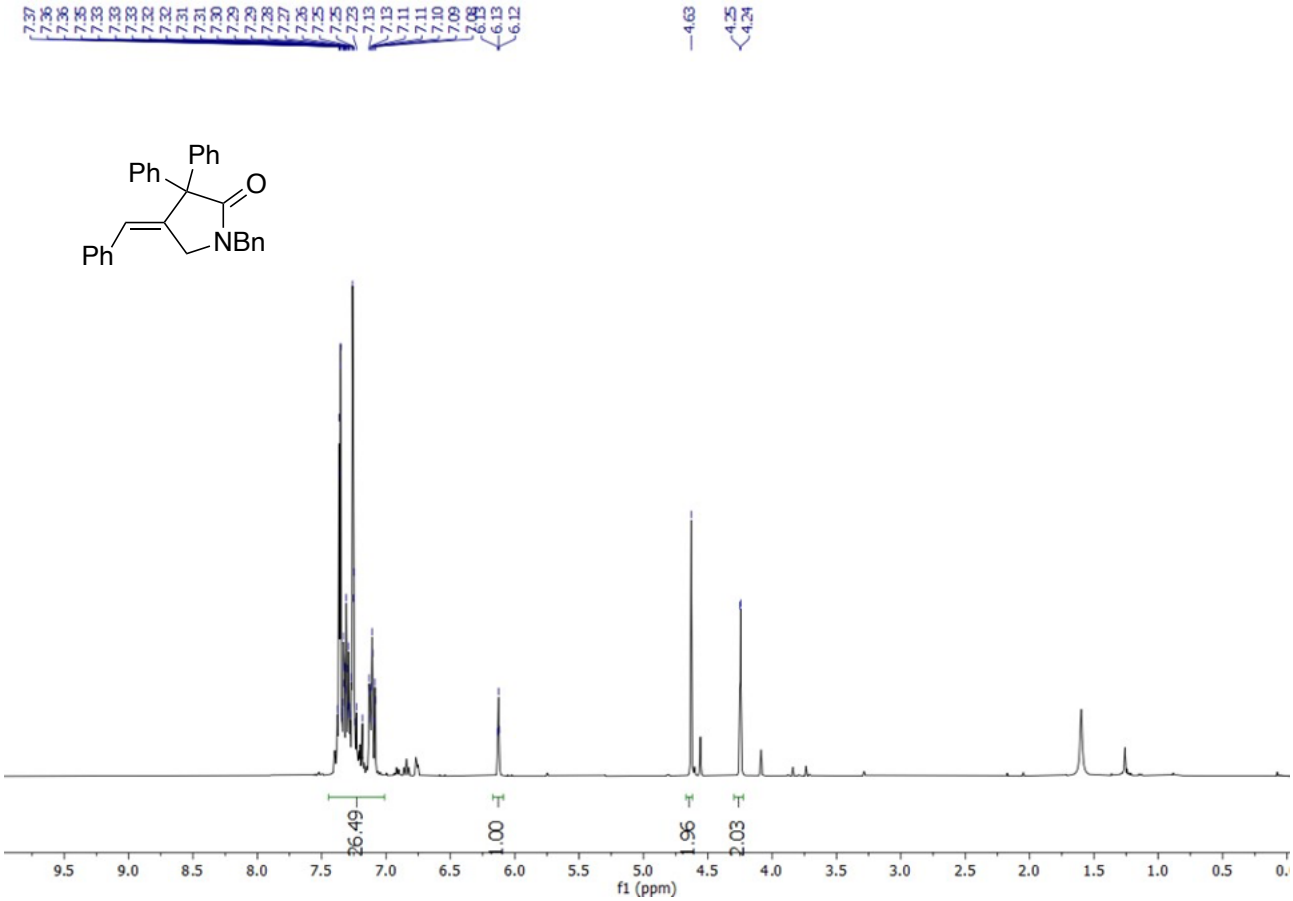
2e ^{1}H NMR (400 MHz, $CDCl_3$)



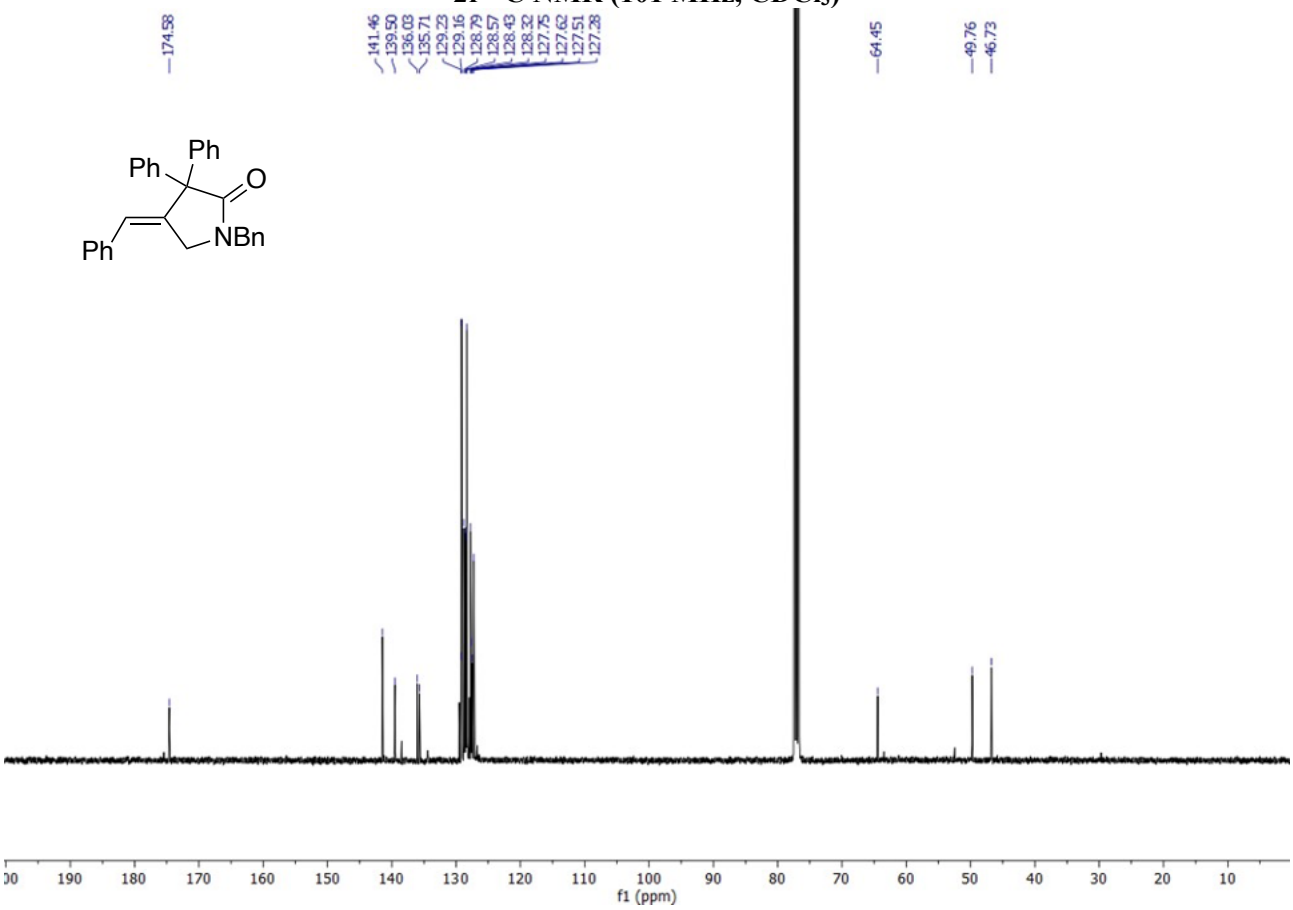
2e ^{13}C NMR (101 MHz, $CDCl_3$)



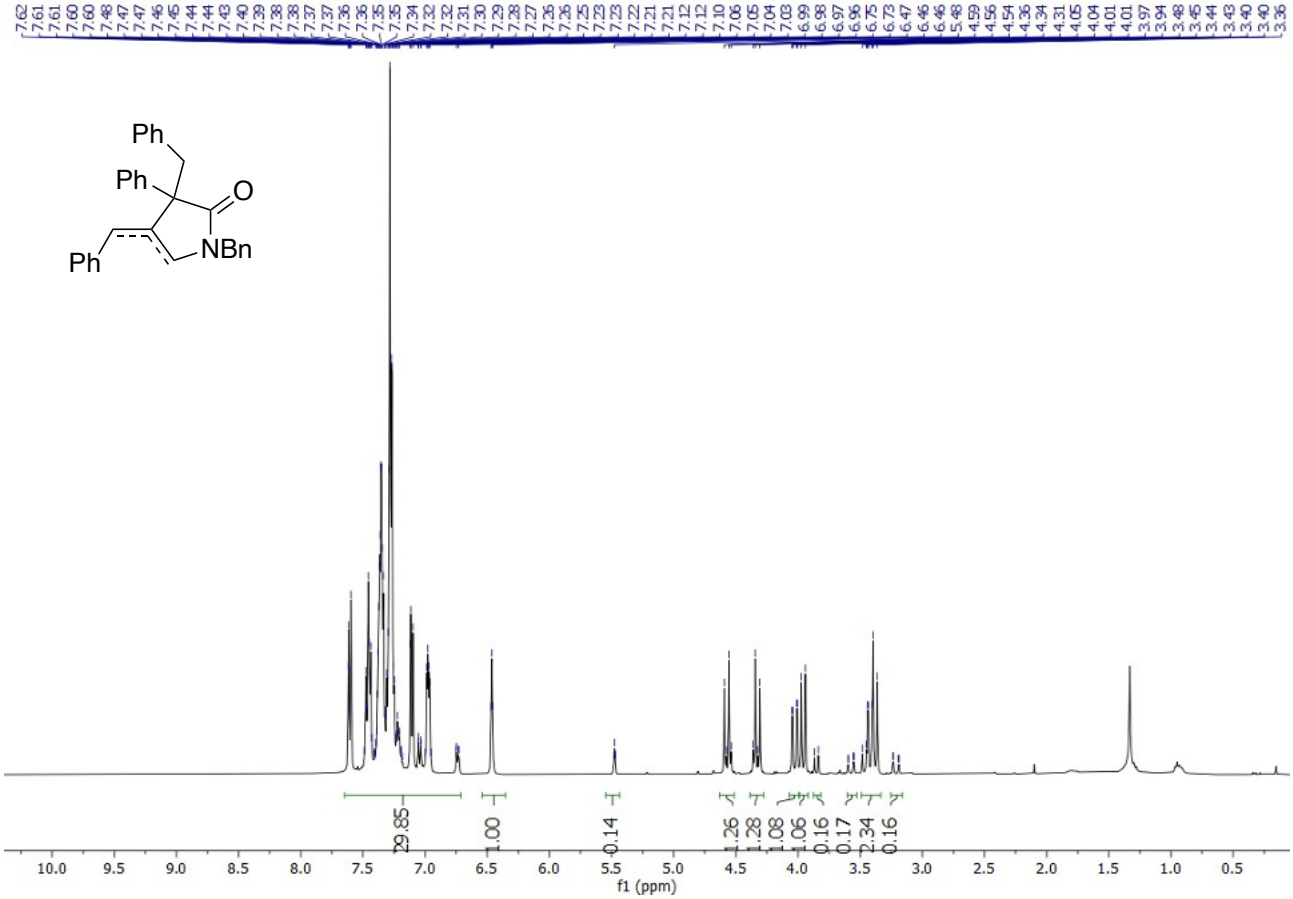
2f ^{1}H NMR (400 MHz, $CDCl_3$)



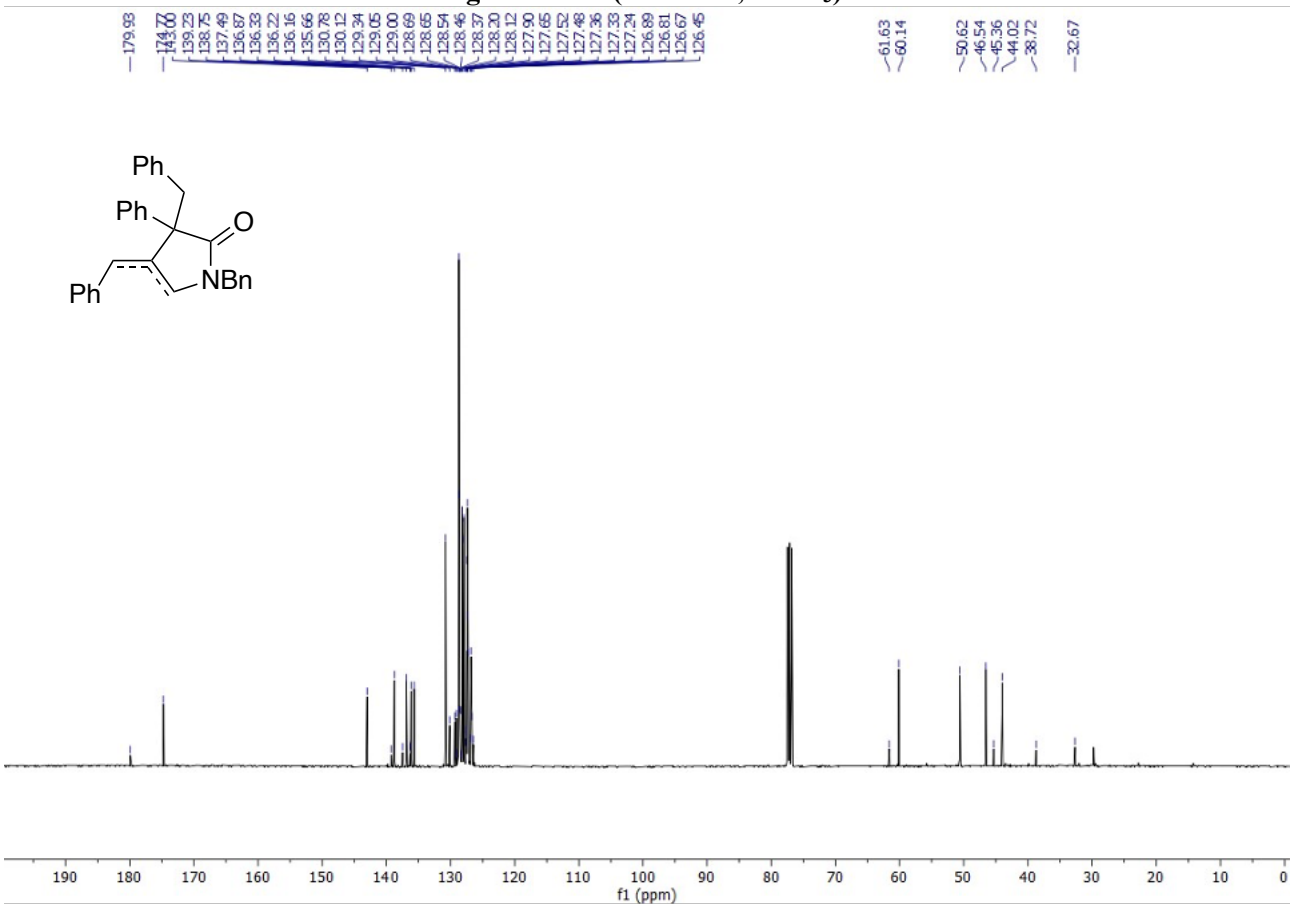
2f ^{13}C NMR (101 MHz, $CDCl_3$)



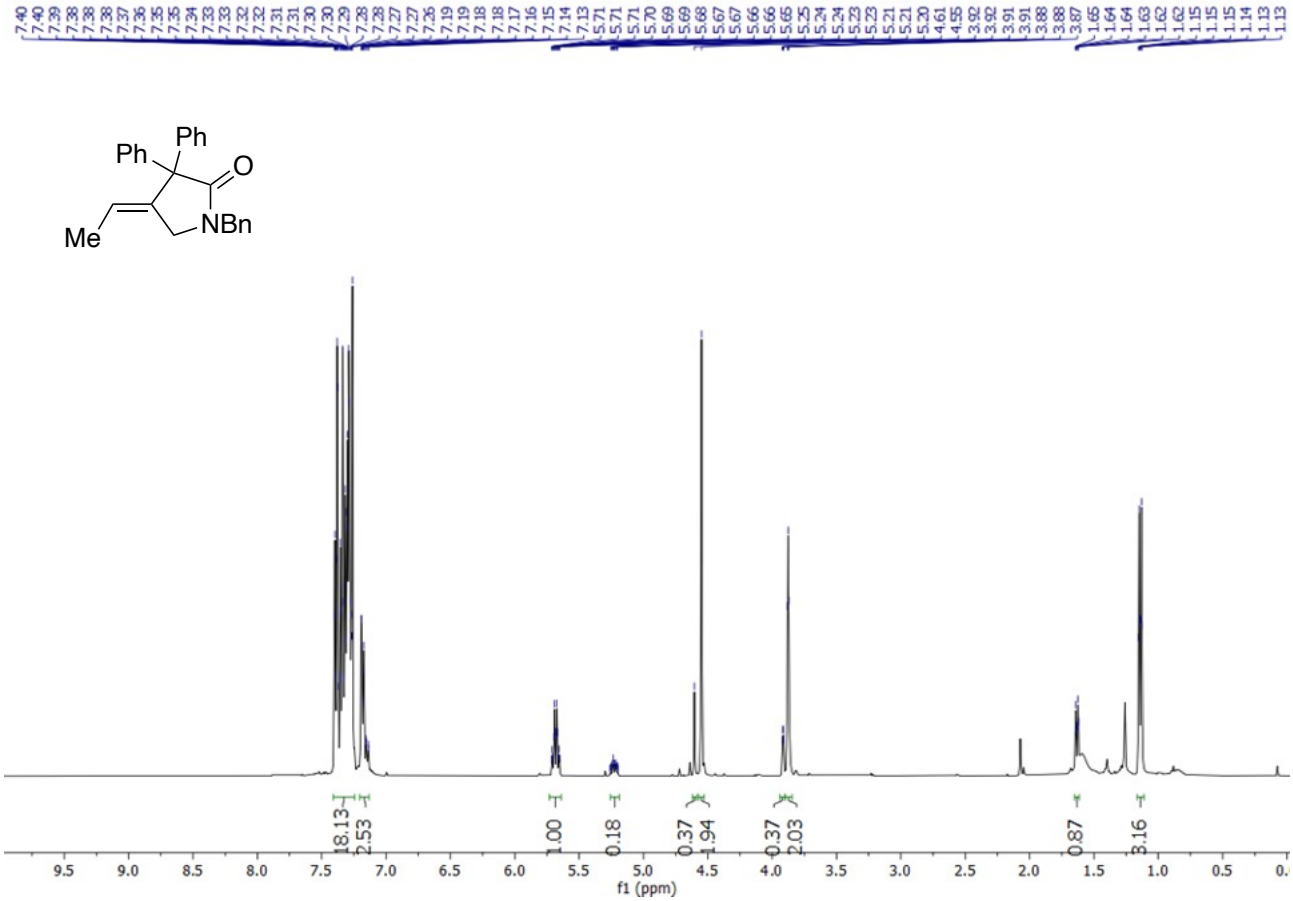
2g ^{1}H NMR (400 MHz, $CDCl_3$)



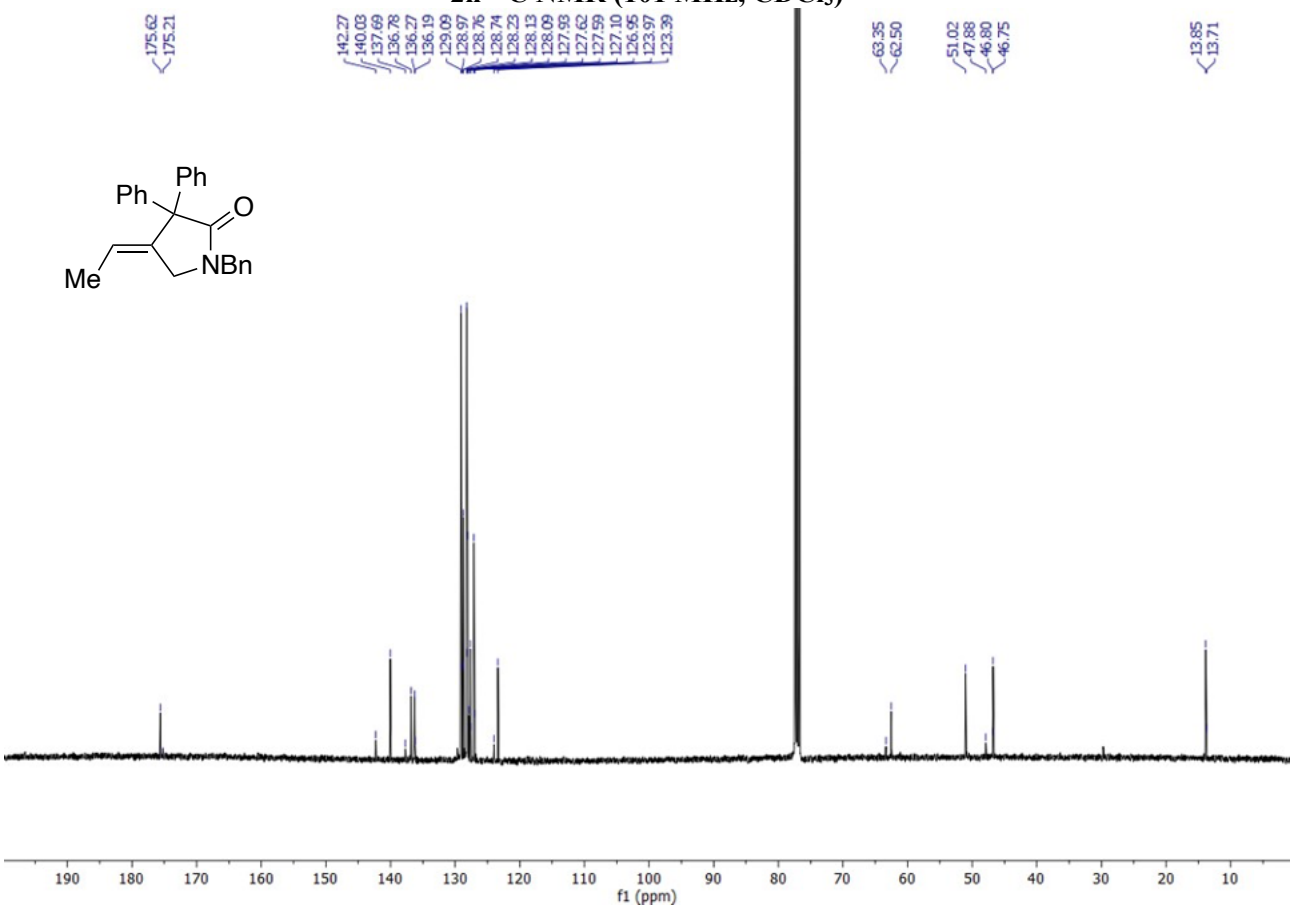
2g ^{13}C NMR (101 MHz, $CDCl_3$)



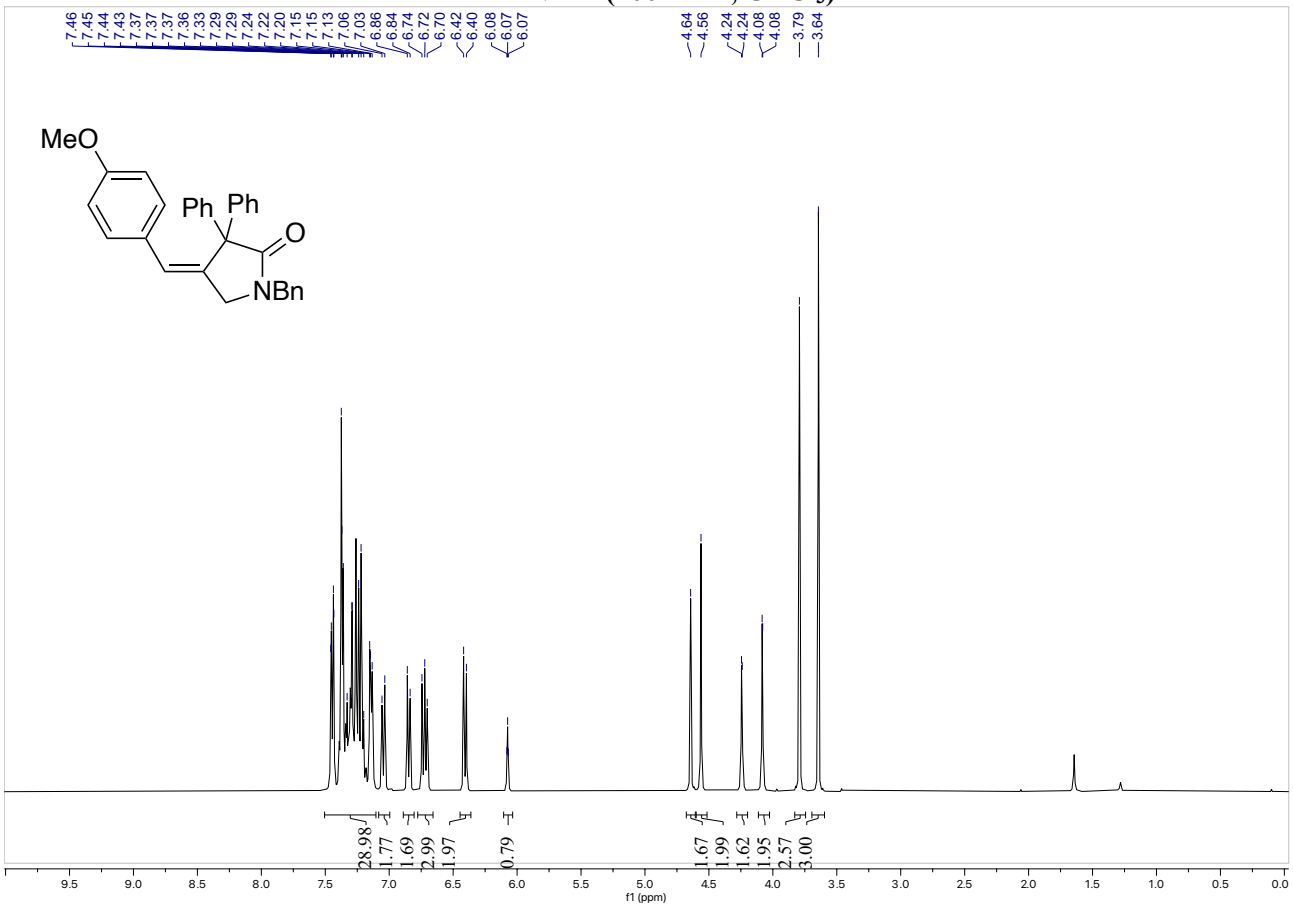
2h ^{1}H NMR (400 MHz, $CDCl_3$)



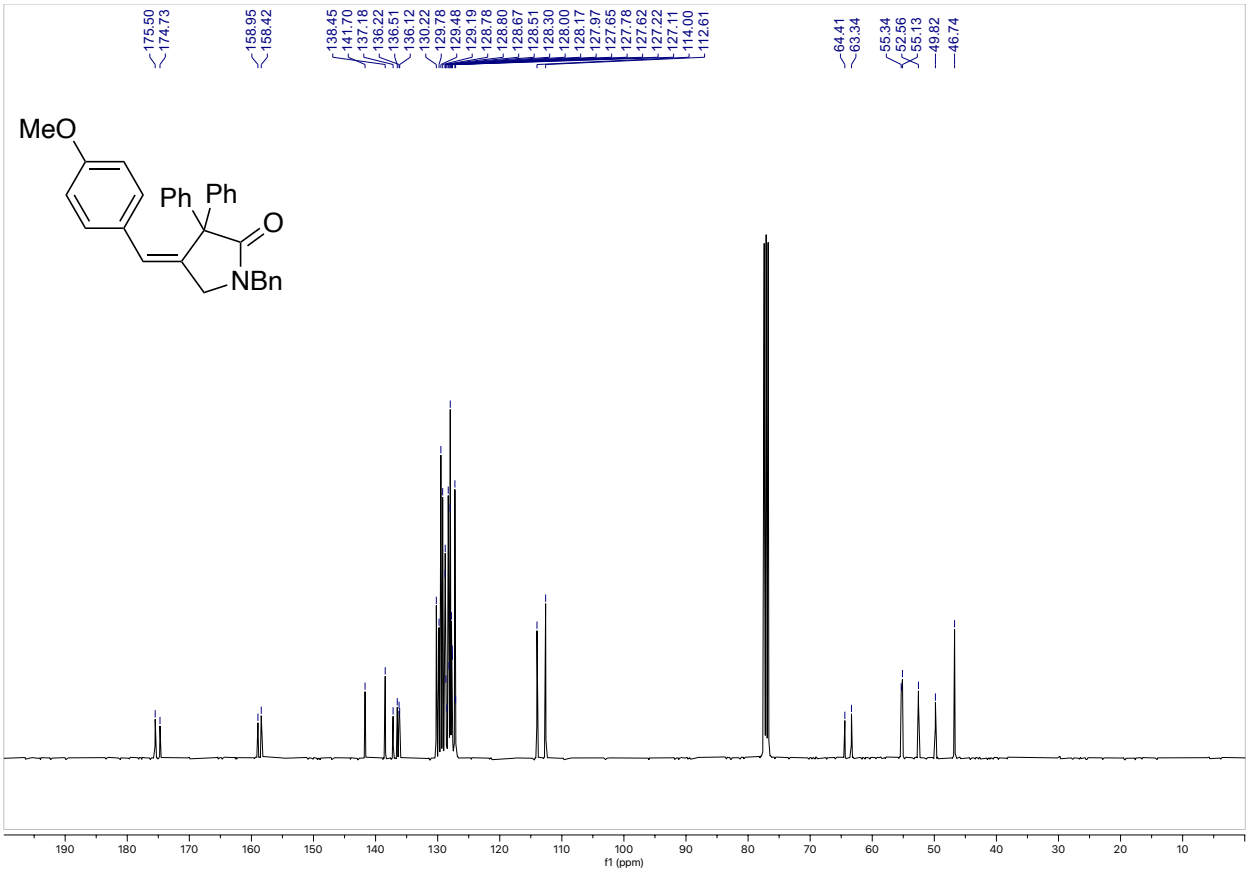
2h ^{13}C NMR (101 MHz, $CDCl_3$)



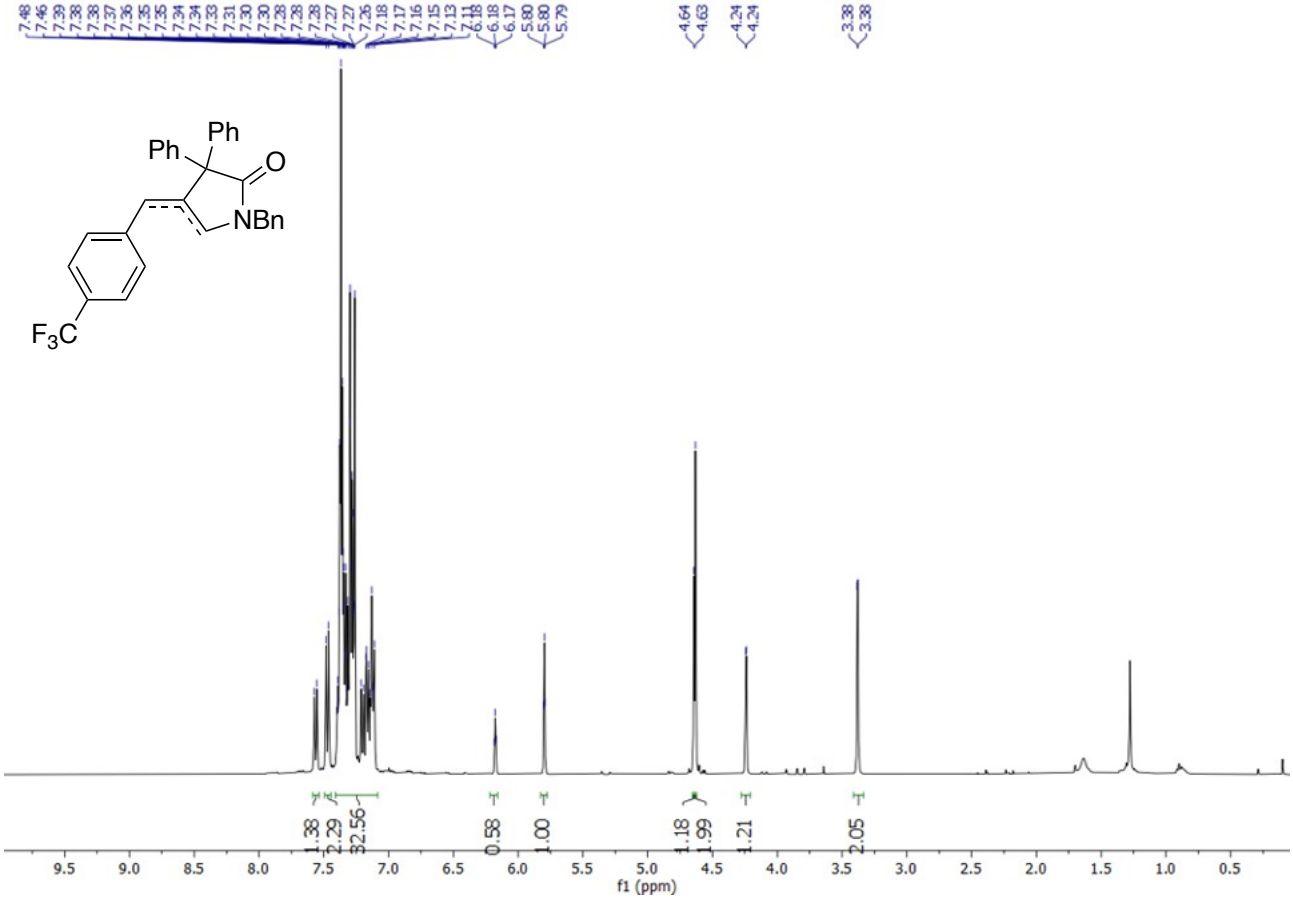
2i ^{1}H NMR (400 MHz, $CDCl_3$)



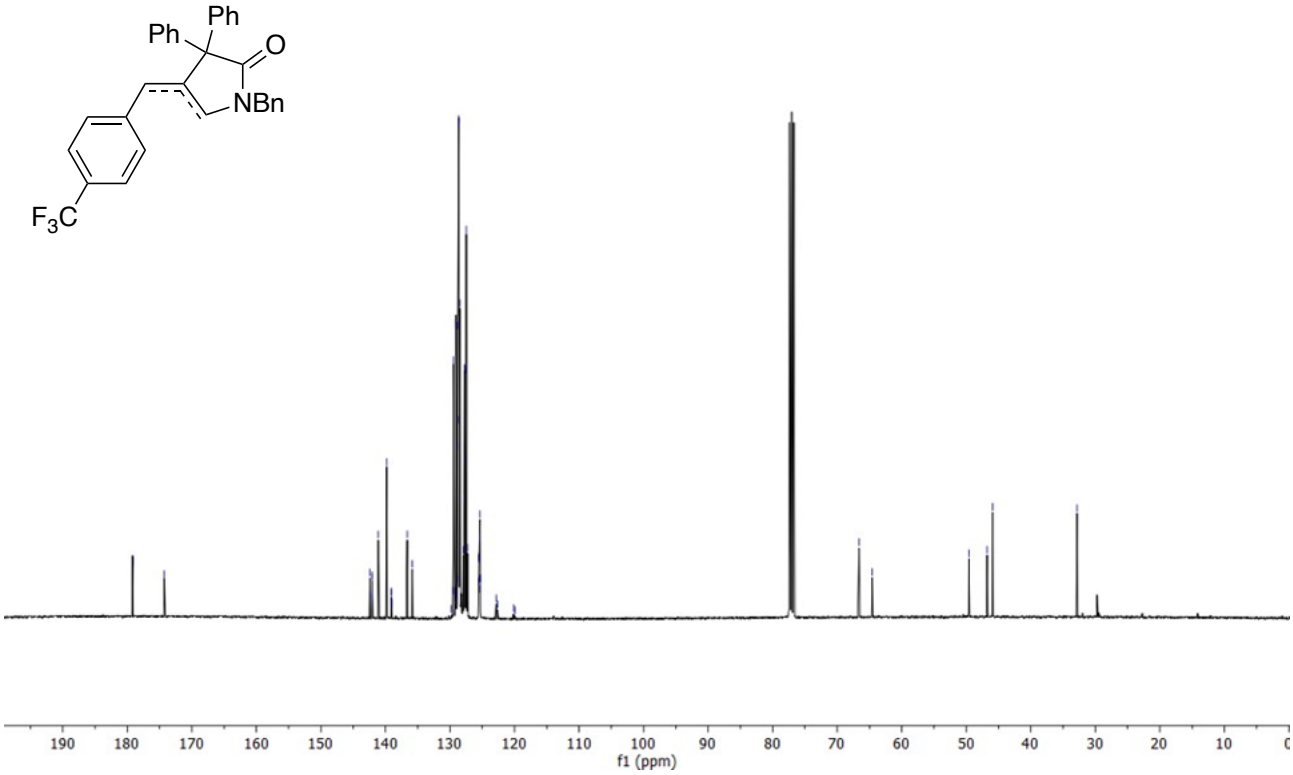
2i ^{13}C NMR (101 MHz, $CDCl_3$)



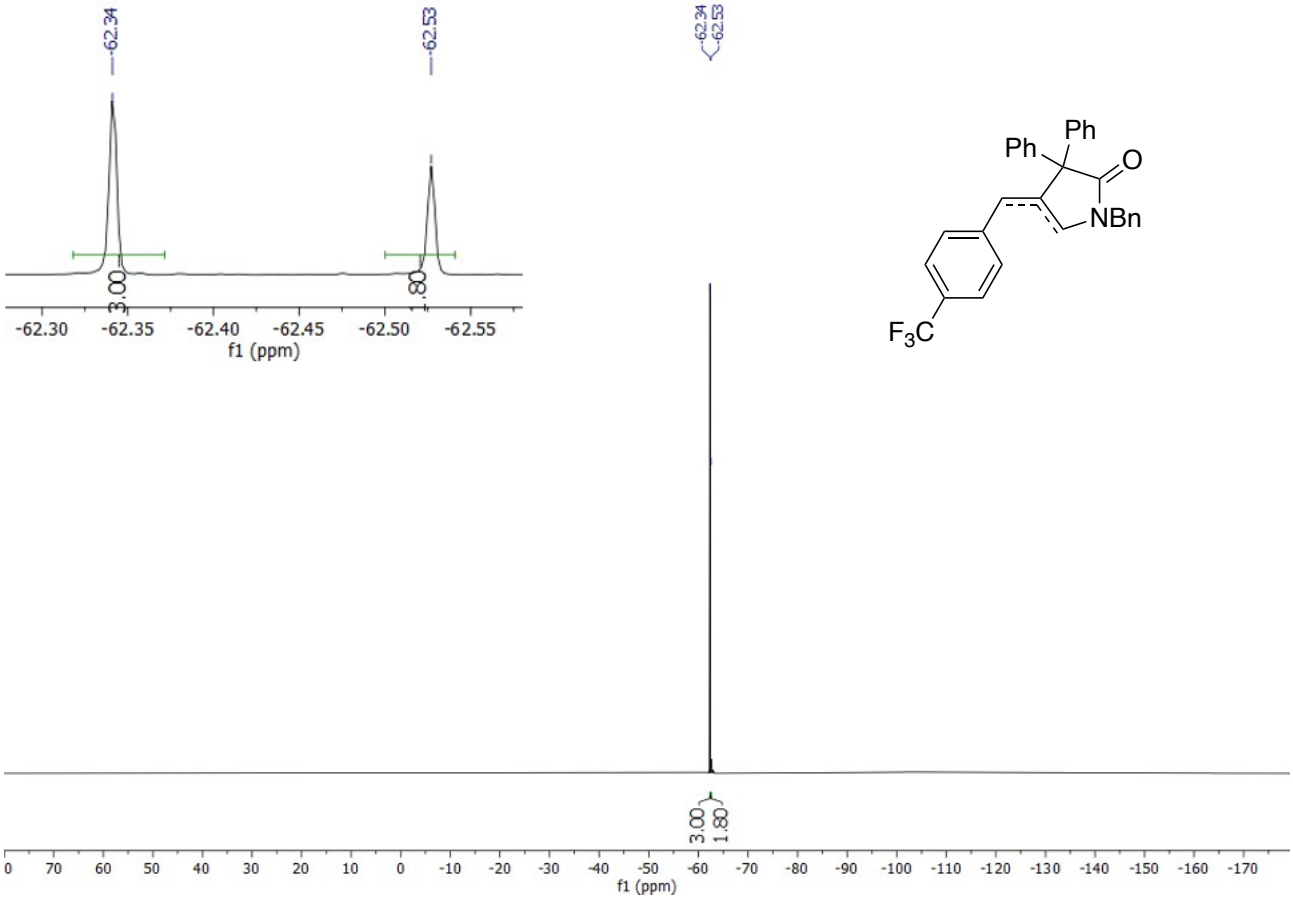
2j ^{1}H NMR (400 MHz, $CDCl_3$)



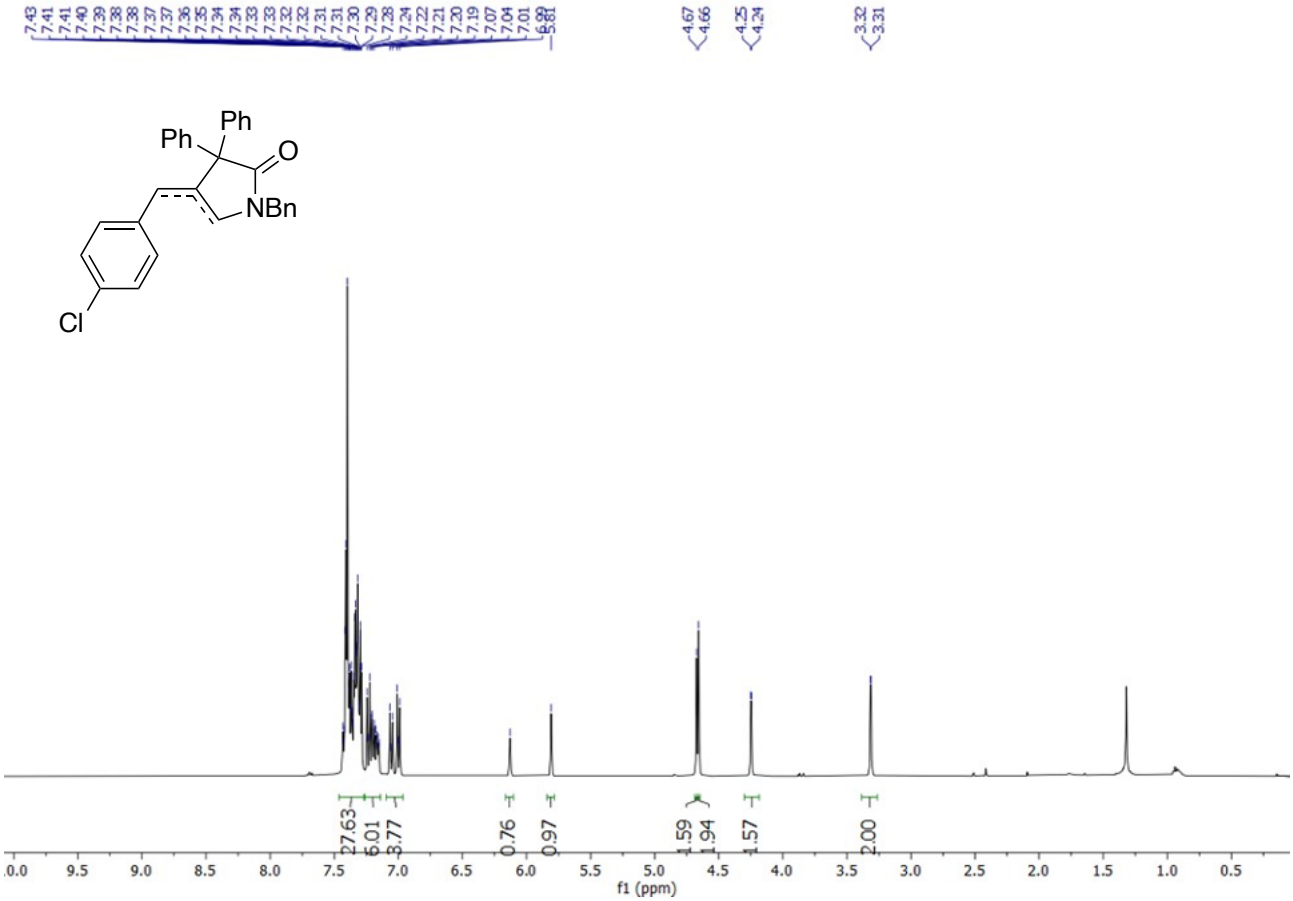
2j ^{13}C NMR (101 MHz, $CDCl_3$)



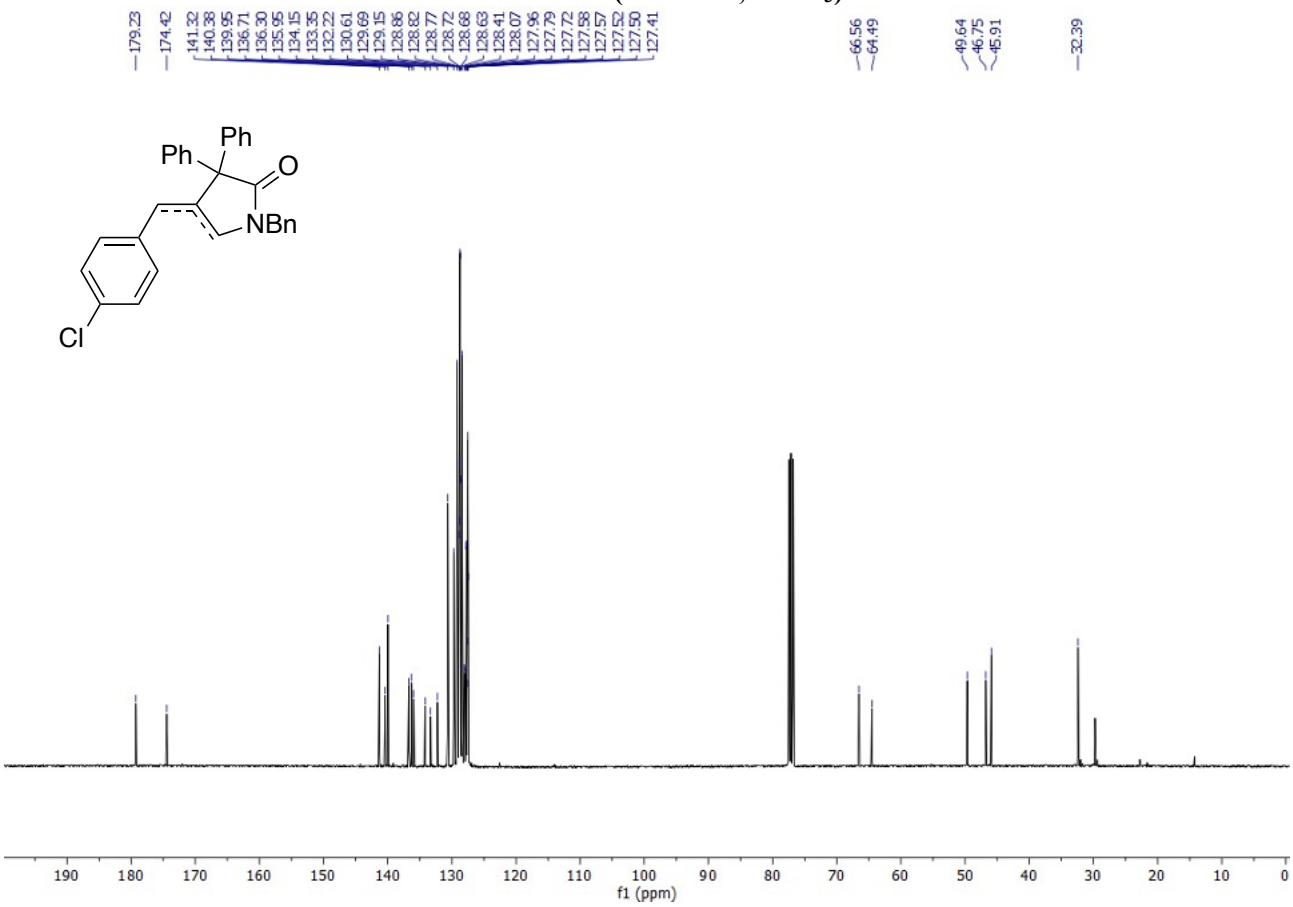
2j ^{19}F NMR (565 MHz, $CDCl_3$)



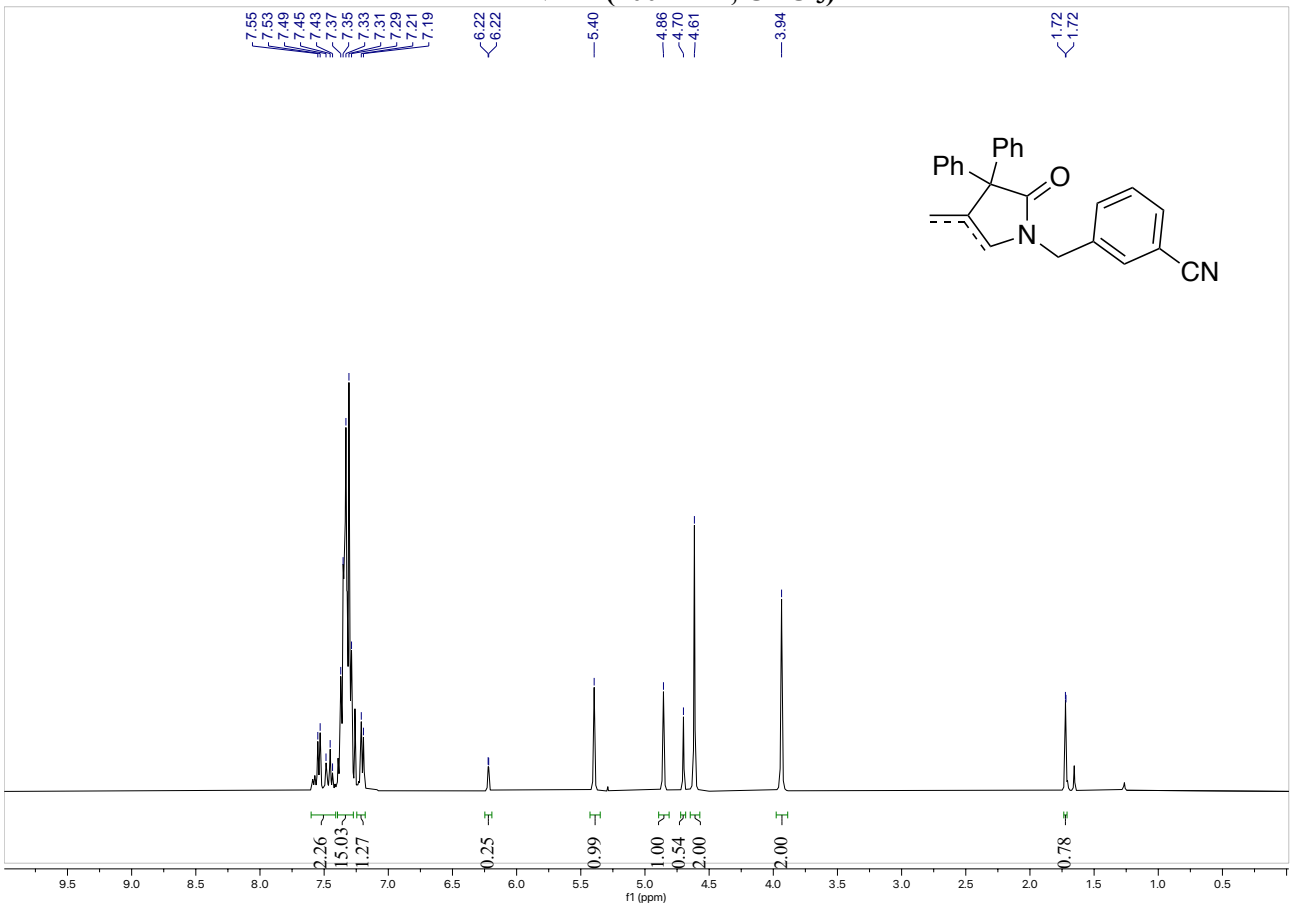
2k ^{1}H NMR (400 MHz, $CDCl_3$)



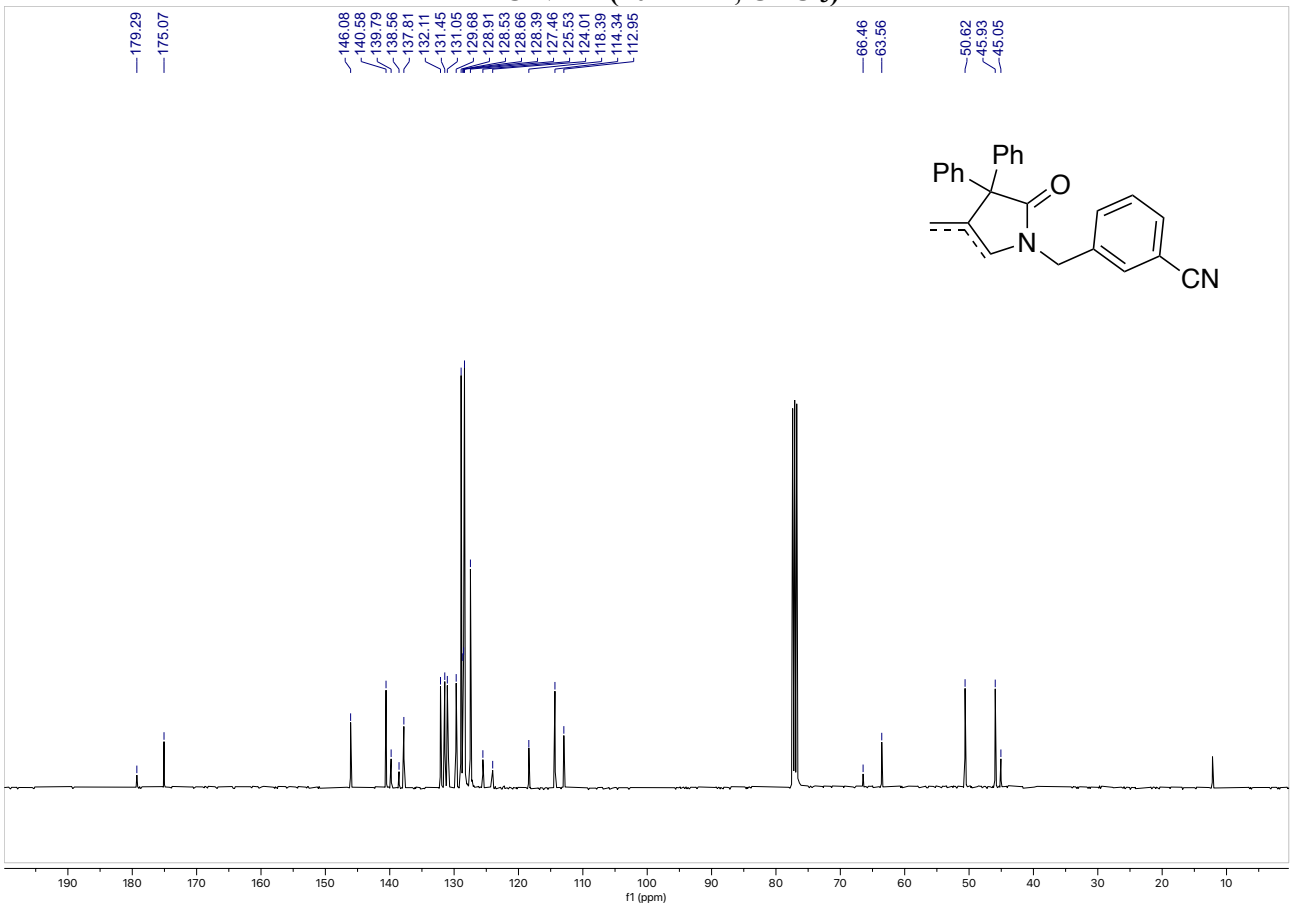
2k ^{13}C NMR (101 MHz, $CDCl_3$)



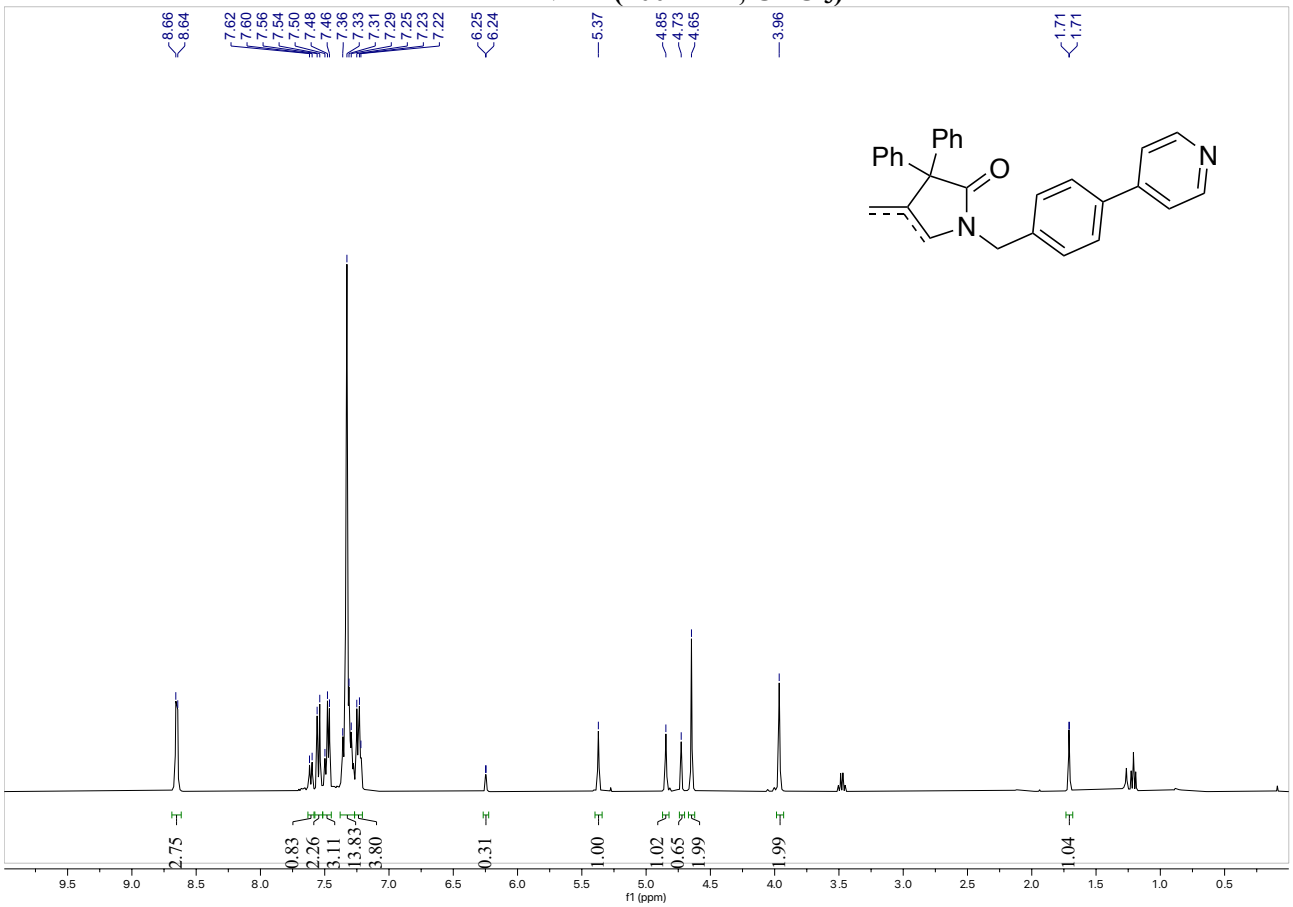
2l ^{1}H NMR (400 MHz, $CDCl_3$)



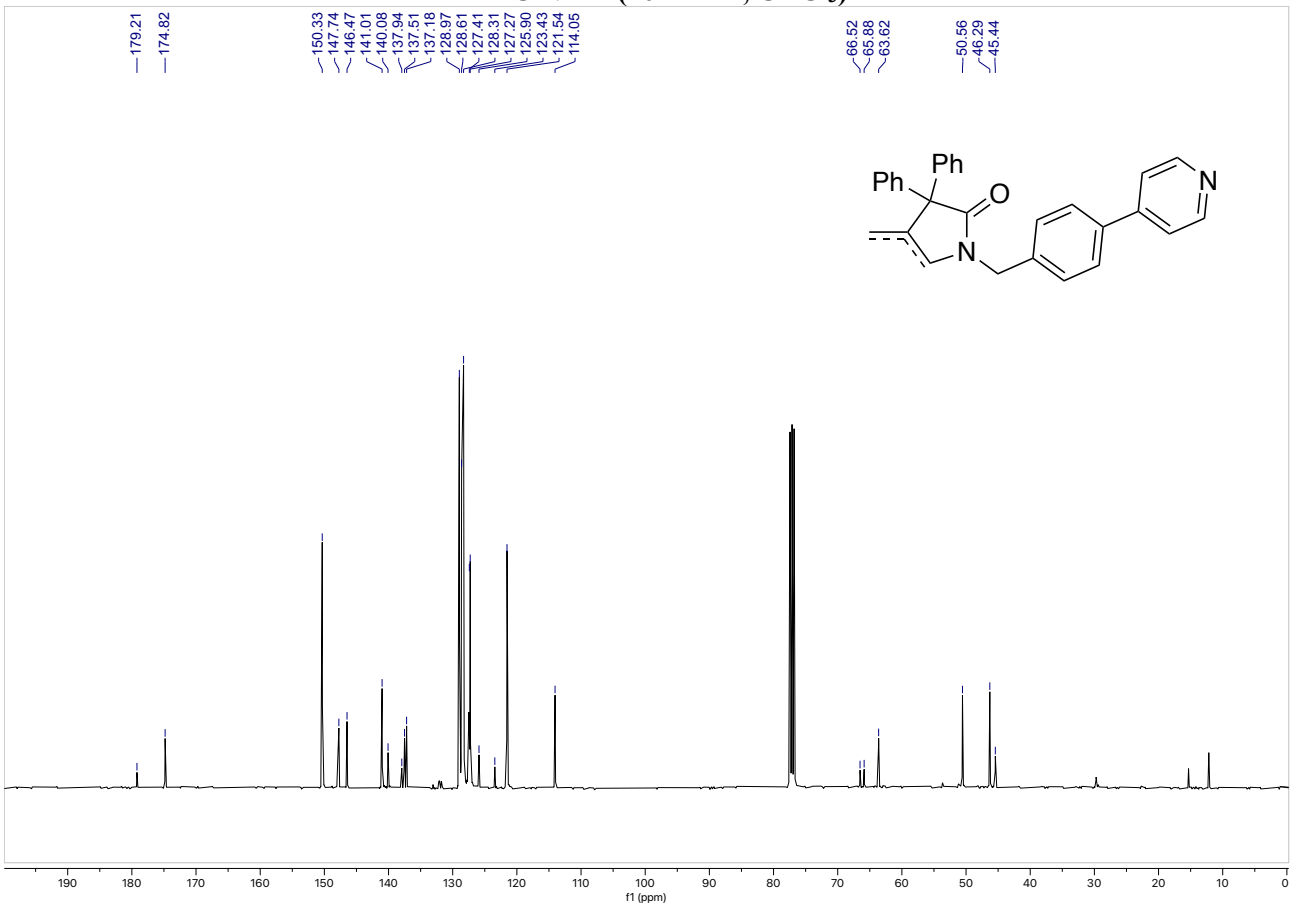
2l ^{13}C NMR (101 MHz, $CDCl_3$)



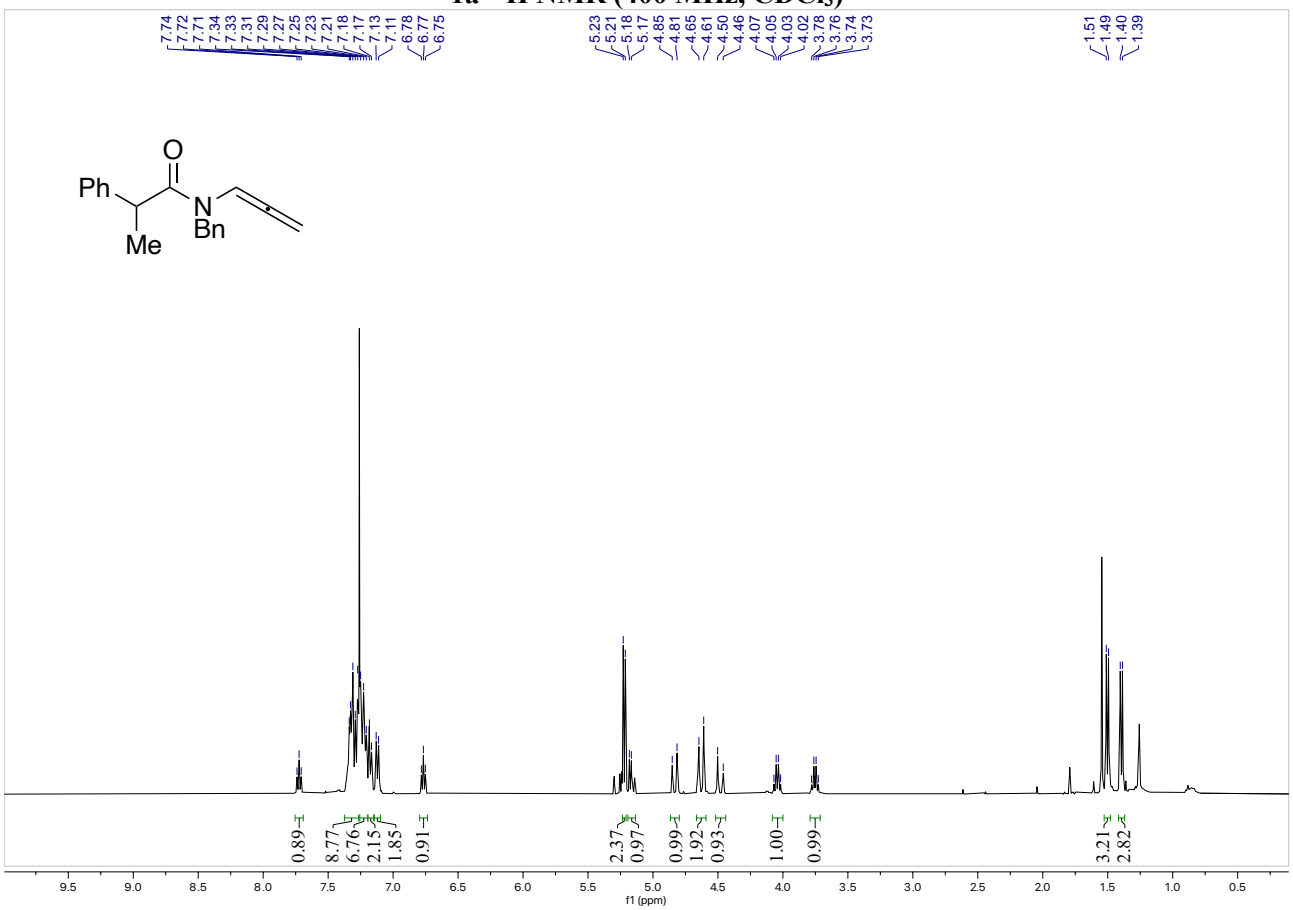
2m ^{1}H NMR (400 MHz, $CDCl_3$)



2m ^{13}C NMR (101 MHz, $CDCl_3$)



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



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