Supporting Information

Photocatalytic Transition-Metal-Free Direct 3-Alkylation of 2-Aryl-2*H*-Indazoles in Dimethyl Carbonate†

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† Dedicated to the 100th anniversary of Chemistry at Nankai University

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1. General information

N, N-Dimethylethanolamine (DABCO) was purchased from Tansoole, Shanghai, China. Other reagents were purchased from Bidepharm.com. Unless otherwise stated, all commercially available reagents were directly used without further purification. All solvents were purified by standard methods prior to use. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 100-200 mesh of silica gel purchased from Tansoole, Shanghai, China. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 MHz in $CDCl_3$ at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Bruker compact Qq TOF MS/MS system with the ESI technique.

Photochemical reaction was carried out under visible light irradiation by a blue LED at 35 ºC. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system (See Figure A). Eight 10W blue LEDs were equipped in this Photo reactor. The blue LED's energy peak wavelength is 455 nm, peak width at half-height is 22.9 nm, lirradiance@10 W is 172.29 mW/cm^2. The reaction vessel is borosilicate glass test tube and no filters were applied.

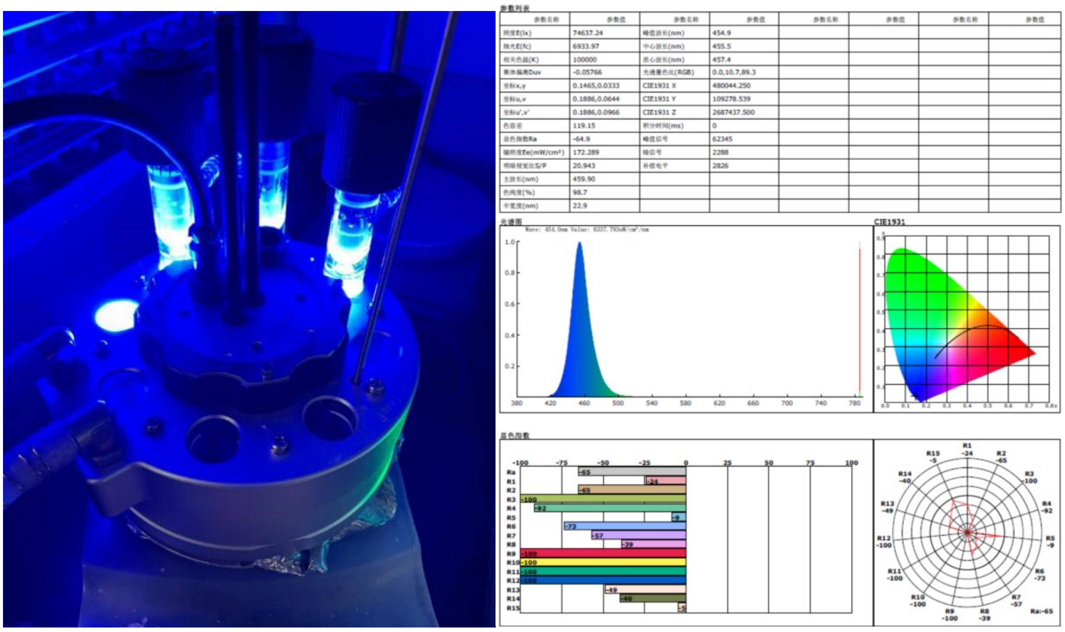


Figure A. The reaction apparatus and spectrum of blue LED

The UV-Vis spectra of 2-phenyl-2*H*-indazole **1a** and alkyl NHPI ester **2a** were showed in Figure B. It is obvious that the reactants **1a** and **2a** do not absorb light around 455 nm, suggesting that photocatalyst play a crucial role in this reaction.

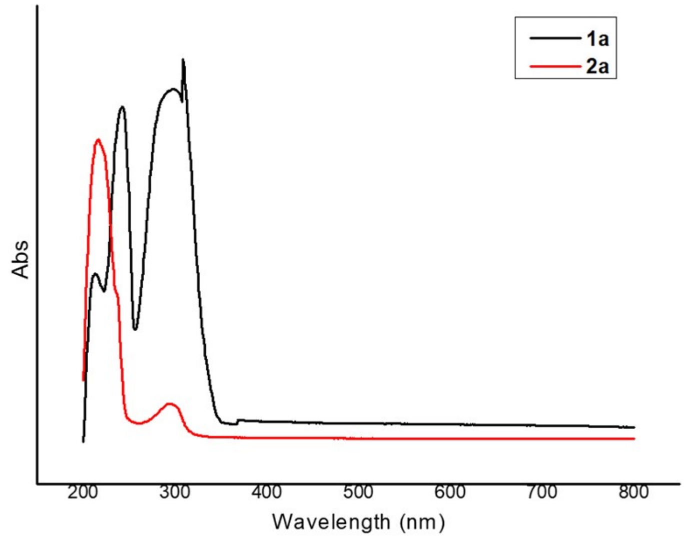
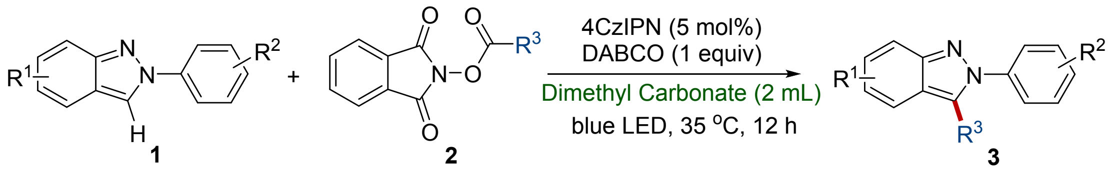


Figure B. The UV-Vis spectra of the substrates **1a** and **2a**

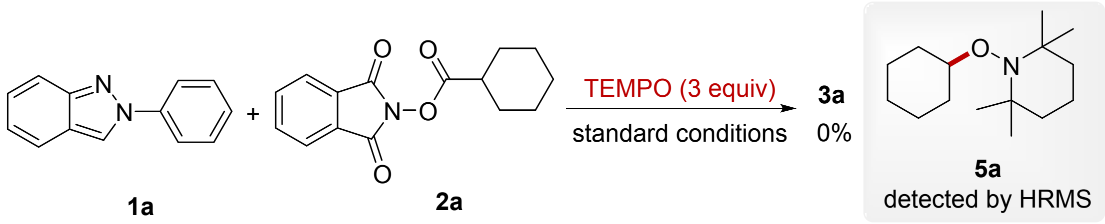
2. Experimental procedures

2.1 General experimental procedures for 3-alkylated 2*H*-indazoles

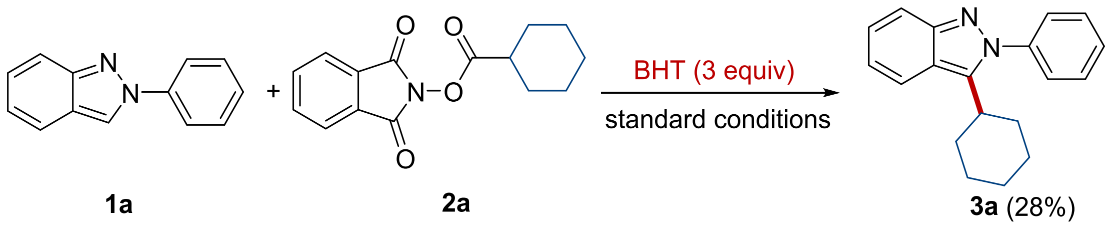


In a 10 mL reaction vial with a stirring bar, 2-phenyl-2*H*-indazole **1** (0.2 mmol), alkyl NHPI esters **2** (2.0 equiv.), and 4CzIPN (5 mol%) were added. The vial was then evacuated and backfilled three times with N_2, followed by adding dimethyl carbonate (2 mL) and DABCO (1.0 equiv.). The mixture was stirred at 35 °C with 10 W blue LED irradiation for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to afford the desired product **3**.

2.2 Control experiments



Control experiments with TEMPO: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2*H*-indazole **1** (0.2 mmol), alkyl NHPI esters **2** (2.0 equiv.), 4CzIPN (5 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv.) were added. The vial was then evacuated and backfilled three times with N_2, followed by adding dimethyl carbonate (2 mL) and DABCO (1.0 equiv.). The mixture was stirred at 35 °C with 10 W blue LED irradiation for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. No target product **3a** was generated, while the formation of TEMPO trapped cyclohexyl adduct **5a** was found by HRMS. It indicated that a radical pathway should be involved in this photocatalytic reaction and an alkyl radical was formed.



Control experiments with BHT: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2*H*-indazole **1** (0.2 mmol), alkyl NHPI esters **2** (2.0 equiv.), 4CzIPN (5 mol%) and 2,6-di-*tert*-butyl-4-methyl phenol (BHT, 3.0 equiv) were added. The vial was then evacuated and backfilled three times with N_2, followed by adding dimethyl carbonate (2 mL) and DABCO (1.0 equiv.). The mixture was stirred at 35 °C with 10 W blue LED irradiation for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to afford the desired product **3a** in 28% yield.

2.3 Procedure for emission quenching experiment

Stern-Volmer fluorescence quenching experiments were conducted via adding the appropriate amount of DABCO to a freshly prepared solution of 4CzIPN (1×10^{-4} M) in dry MeCN in a screw-top quartz cuvette at room temperature. After degassing with a stream of N_2 for 10 minutes, the sample was irradiated at 380 nm and the fluorescence was measured from 400 nm to 800 nm.

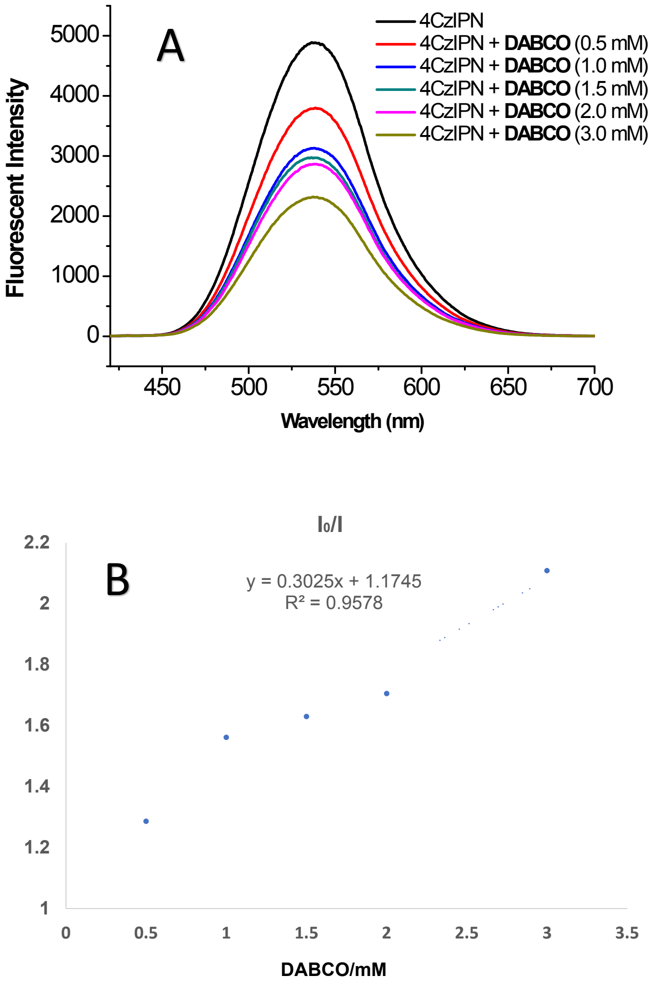


Figure S1. (A) The emission spectra of 1×10^{-4} M solution of 4CzIPN with various concentrations of **1a**. (B) The linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after adding the various concentration of DABCO, respectively) and the concentration of DABCO.

2.4 Procedure for cyclic voltammetry experiment

Cyclic voltammetry analysis of 2H-indazole **1a**, NHPI ester **2a** and DABCO were conducted by a potentiostat (CH instrument, 660E) with a three-electrode system (Reference electrode: SCE, working electrode: Glassy carbon, counter electrode: Pt wire). 0.1 M Bu_4NPF_6 in CH_3CN was used as a supporting electrolyte. The Pt disk was polished by using an alumina suspension (*d* = 50 nm) before each CV experiment.

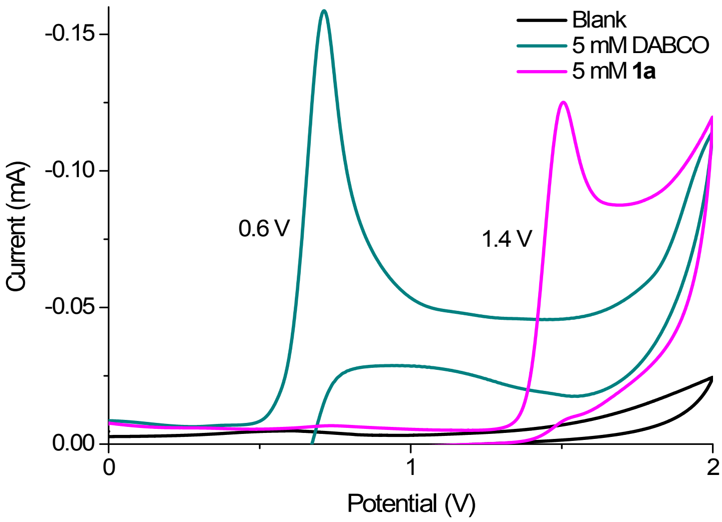


Figure S2. CV of DABCO (5 mM in CH_3CN), **1a** (5 mM in CH_3CN) and blank (only 0.1 M Bu_4NPF_6) under nitrogen atmosphere at room temperature. The scan rate was 0.10 V/s.

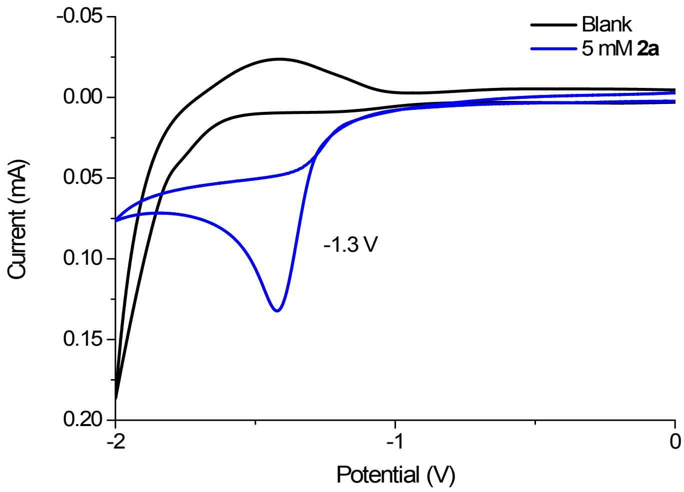


Figure S3. CV of **2a** (5 mM in CH_3CN) and blank (only 0.1 M Bu_4NPF_6) under nitrogen atmosphere at room temperature. The scan rate was 0.10 V/s.

3. Procedure and Results of Sensitivity Assessment

General Procedure:

The influence of parameter variations as shown in Table S1 on the reaction was investigated. Only one parameter, such as concentration, water level, oxygen level, light intensity, base dosage and catalyst dosage, was deliberately changed per experiment while maintaining the others at the standard level. Each experiment was carried out twice at the same time in order to reduce the error.

Table S1. Preparation of sensitivity assessment.

#	Experiment	Preparation
1	High *c*	1.6 mL DMC
2	Low *c*	2.4 mL DMC
3	High H_2O	2.0 mL DMC + 20 μL H_2O
4	High O_2	Under air
5	Low *I*	9W Blue LED
6	High base	2 eq DABCO
7	Low base	0.5 eq DABCO
8	High catalyst	10% 4CzIPN
9	Low catalyst	1% 4CzIPN
10	Control	Standard procedure

Results:

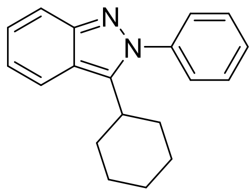
Deviation% = (Average Y. - Standard Y.) / Standard Y.

Table S2. Results of sensitivity assessment.

#	Experiment	Yield 1 / %	Yield 2 / %	Average Y. / %	Deviation / %
1	High *c*	50	59	55	-37.5%
2	Low *c*	87	85	86	-2.3%
3	High H_2O	26	28	27	69.3%
4	High O_2	0	0	0	-100%
5	Low *I*	82	88	85	-3.4%
6	High base	83	86	85	-3.4%
7	Low base	63	71	67	-23.9%
8	High catalyst	83	82	83	-5.7%
9	Low catalyst	89	92	91	3.4%
10	Control	87	89	88	-

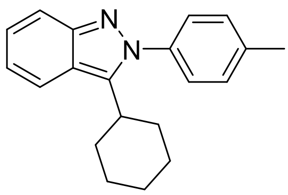
4. Characterization of compounds

3-cyclohexyl-2-phenyl-2H-indazole ***(3a)***[1]



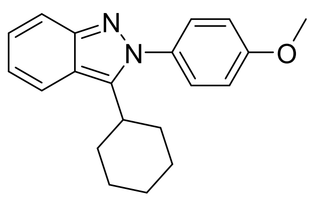
48.6 mg, 88%; White solid, m.p. 110-111 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.56-7.47 (m, 5H), 7.31-7.28 (m, 1H), 7.06-7.03 (m, 1H), 3.00-2.95 (m, 1H), 2.03-1.75 (m, 7H), 1.37-1.25 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 141.3, 140.3, 129.3, 129.1, 126.6, 126.4, 121.4, 120.6, 119.6, 118.0, 37.4, 32.7, 26.7, 26.0. HRMS Calcd for $C_{19}H_{21}N_2$ $[M + H]^+$: m/z 277.1699, Found: 277.1710.

*3-cyclohexyl-2-(p-tolyl)-2H-indazole (**3b**)*



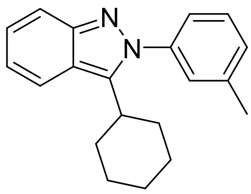
38.9 mg, 67%; White solid, m.p. 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.37-7.26 (m, 5H), 7.06-7.01 (m, 1H), 3.01-2.92 (m, 1H), 2.47 (s, 3H), 2.03-1.74 (m, 7H), 1.38-1.20 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.9, 141.2, 139.1, 137.8, 129.8, 126.3, 121.3, 120.5, 119.6, 117.9, 37.4, 32.7, 26.7, 26.0, 21.4. HRMS Calcd for $C_{20}H_{23}N_2$ $[M + H]^+$: m/z 291.1856, Found: 291.1851,.

*3-cyclohexyl-2-(4-methoxyphenyl)-2H-indazole (**3c**)*



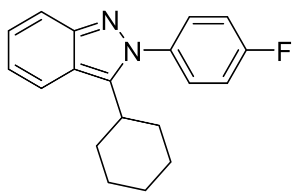
52.0 mg, 85%; White solid, m.p. 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 5.6 Hz, 1H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.39 (d, *J* = 5.6 Hz, 2H), 7.29 (t, *J* = 4.4 Hz, 1H), 7.05-7.02 (m, 3H), 3.90 (s, 3H), 2.97-2.91 (m, 1H), 2.01-1.75 (m, 7H), 1.39-1.23 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 148.8, 141.4, 133.3, 127.7, 126.3, 121.3, 120.5, 119.5, 117.9, 114.4, 55.7, 37.4, 32.7, 26.7, 26.0. HRMS Calcd for $C_{20}H_{23}N_2O$ $[M + H]^+$: m/z 307.1805, Found: 307.1811.

*3-cyclohexyl-2-(m-tolyl)-2H-indazole (**3d**)*



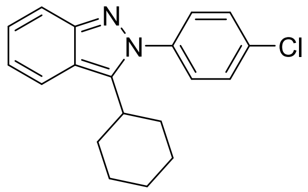
30.8 mg, 53%; White solid, m.p. 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33-7.26 (m, 3H), 7.25-7.22 (m, 1H), 7.06-7.02 (m, 1H), 3.03-2.94 (m, 1H), 2.46 (s, 3H), 2.04-1.75 (m, 7H), 1.38-1.21 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.9, 141.2, 140.2, 139.5, 129.9, 128.9, 127.3, 126.4, 123.4, 121.4, 120.6, 119.6, 118.0, 37.4, 32.7, 26.7, 26.0, 21.5. HRMS Calcd for $C_{20}H_{23}N_2$ $[M + H]^+$: m/z 291.1856, Found: 291.1886.

*3-cyclohexyl-2-(4-fluorophenyl)-2H-indazole (**3e**)*



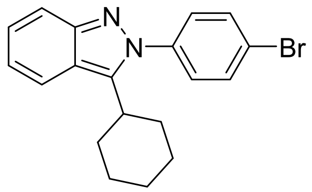
48.2 mg, 82%; White solid, m.p. 71-72 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.47-7.44 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 3.6 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 2.94-2.88 (m, 1H), 2.01-1.76 (m, 7H), 1.37-1.25 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8 (d, *J* = 247.5 Hz), 149.0, 141.5, 136.4 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 9.0 Hz), 126.6, 121.3, 120.8, 119.6, 117.9, 116.3 (d, *J* = 22.5 Hz), 37.5, 32.7, 26.7, 26.0. ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.8. HRMS Calcd for $C_{19}H_{20}FN_2$ $[M + H]^+$: m/z 295.1605, Found: 295.1612.

*2-(4-chlorophenyl)-3-cyclohexyl-2H-indazole (**3f**)*



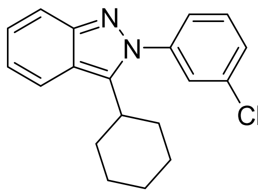
55.2 mg, 89%; White solid, m.p. 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.54-7.50 (m, 2H), 7.44-7.40 (m, 2H), 7.32-7.27 (m, 1H), 7.07-7.02 (m, 1H), 2.97-2.89 (m, 1H), 2.05-1.76 (m, 7H), 1.38-1.21 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.3, 141.2, 140.0, 129.39, 129.37, 127.8, 126.5, 126.2, 120.03, 119.98, 119.5, 37.3, 32.7, 26.6, 25.9. HRMS Calcd for $C_{19}H_{20}ClN_2$ [M + H]$^+$: m/z 311.1310, Found: 311.1342.

*2-(4-bromophenyl)-3-cyclohexyl-2H-indazole (**3g**)*



48.3 mg, 68%; White solid, m.p. 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.70-7.65 (m, 3H), 7.38-7.34 (m, 2H), 7.32-7.27 (m, 1H), 7.07-7.02 (m, 1H), 2.98-2.89 (m, 1H), 2.04-1.76 (m, 7H), 1.38-1.20 (m, 3H) ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 141.3, 139.3, 132.5, 128.1, 126.7, 123.1, 121.4, 120.9, 119.7, 117.9, 37.5, 32.7, 26.7, 26.0. HRMS Calcd for $C_{19}H_{20}BrN_2$ [M + H]$^+$: m/z 355.0804, Found: 355.0808.

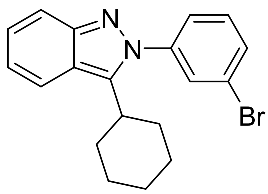
*2-(3-chlorophenyl)-3-cyclohexyl-2H-indazole (**3h**)*



56.4 mg, 91%; White solid, m.p. 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.54-7.45 (m, 3H), 7.38-7.35 (m, 1H), 7.32-7.28 (m, 1H), 7.07-7.03 (m, 1H), 3.00-2.92 (m, 1H), 2.05-1.76 (m, 7H), 1.43-1.23 (m, 3H).

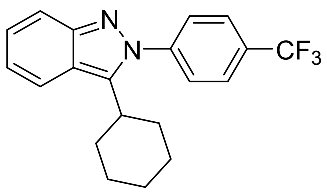
^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 141.4, 141.3, 135.1, 130.2, 129.4, 127.0, 126.8, 124.7, 121.4, 121.0, 119.7, 118.0, 37.5, 32.7, 26.9, 26.0. HRMS Calcd for $C_{19}H_{20}ClN_2$ $[M + H]^+$: m/z 311.1310, Found: 311.1317.

*2-(3-bromophenyl)-3-cyclohexyl-2H-indazole (**3i**)*



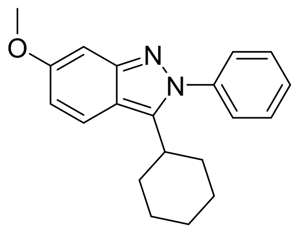
51.0 mg, 72%; White solid, m.p. 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.70-7.62 (m, 3H), 7.44-7.39 (m, 2H), 7.32-7.28 (m, 1H), 7.07-7.03 (m, 1H), 3.00-2.91 (m, 1H), 2.04-1.76 (m, 7H), 1.42-1.24 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 141.4, 141.3, 135.1, 130.2, 129.4, 127.0, 126.8, 124.7, 121.4, 121.0, 119.7, 118.0, 37.5, 32.7, 26.7, 26.0. HRMS Calcd for $C_{19}H_{20}BrN_2$ $[M + H]^+$: m/z 355.0804, Found: 355.0819.

*3-cyclohexyl-2-(4-(trifluoromethyl)phenyl)-2H-indazole (**3j**)*



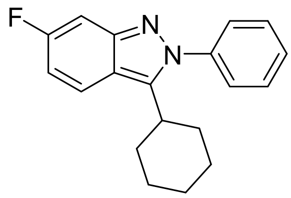
60.5 mg, 88%; White solid, m.p. 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 1H), 7.08-7.04 (m, 1H), 3.01-2.92 (m, 1H), 2.07-1.77 (m, 7H), 1.43-1.23 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.4, 143.2, 141.4, 131.1 (q, *J* = 33.0 Hz), 127.0, 126.9, 126.6 (q, *J* = 3.0 Hz), 123.9 (q, *J* = 270 Hz), 121.4, 121.1, 119.9, 118.0, 37.5, 32.8, 26.7, 25.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.5. HRMS Calcd for $C_{20}H_{20}F_3N_2$ $[M + H]^+$: m/z 345.1573, Found: 345.1564.

*3-cyclohexyl-6-methoxy-2-phenyl-2H-indazole (**3m**)*



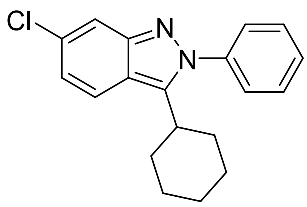
42.2 mg, 69%; White solid, m.p. 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1H), 7.56-7.49 (m, 3H), 7.47-7.44 (m, 2H), 7.04-7.00 (m, 2H), 3.89 (s, 3H), 2.98-2.89 (m, 1H), 1.97-1.83 (m, 7H), 1.34-1.25 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.1, 145.9, 140.5, 139.9, 129.2, 128.9, 126.5, 121.2, 119.4, 119.2, 97.9, 55.7, 37.2, 32.4, 26.7, 26.0. HRMS Calcd for $C_{20}H_{23}N_2O$ $[M + H]^+$: m/z 307.1805, Found: 307.1823.

*3-cyclohexyl-6-fluoro-2-phenyl-2H-indazole (**3n**)*



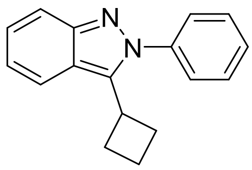
35.3 mg, 60%; Oily liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (q, J = 4.8 Hz, 1H), 7.56-7.52 (m, 3H), 7.46 (d, J = 7.2 Hz, 2H), 7.42 (dd, J = 1.8, 9.6 Hz, 1H), 7.12-7.08 (m, 1H), 2.96-2.91 (m, 1H), 1.92-1.74 (m, 7H), 1.35-1.24 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4 (d, J = 237.0 Hz), 146.4, 141.4 (d, J = 9.0 Hz), 140.2, 129.4, 129.3, 126.5, 119.9 (d, J = 10.5 Hz), 118.6 (d, J = 10.5 Hz), 118.0 (d, J = 28.5 Hz), 103.8 (d, J = 24.0 Hz), 37.2, 32.5, 26.7, 25.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ -121.0. HRMS Calcd for $C_{19}H_{20}FN_2$ $[M + H]^+$: m/z 295.1605, Found: 295.1615.

*6-chloro-3-cyclohexyl-2-phenyl-2H-indazole (**3o**)*



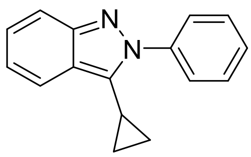
32.2 mg, 52%; White solid, m.p. 134-135°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.82 (m, 1H), 7.65-7.62 (m, 1H), 7.58-7.52 (m, 3H), 7.47-7.44 (m, 2H), 7.22 (dd, J = 2.0, 9.2 Hz, 1H), 2.98-2.89 (m, 1H), 1.94-1.83 (m, 7H), 1.41-1.25 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.1, 141.4, 138.8, 135.1, 129.5, 127.8, 126.7, 121.3, 120.9, 119.7, 117.9, 37.5, 32.7, 26.7, 25.9. HRMS Calcd for $C_{19}H_{20}ClN_2$ $[M + H]^+$: m/z 311.1310, Found: 311.1324.

*3-cyclobutyl-2-phenyl-2H-indazole (**3p**)*



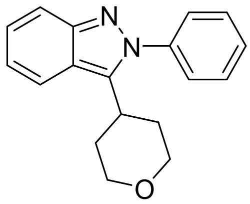
28.3 mg, 57%; White solid, m.p. 62-63 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.54-7.47 (m, 5H), 7.32-7.29 (m, 1H), 7.09-7.06 (m, 1H), 3.98-3.91 (m, 1H), 2.63-2.55 (m, 2H), 2.36-2.30 (m, 2H), 2.08-1.95 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 140.4, 139.4, 129.2, 128.9, 126.5, 126.3, 121.0, 120.6, 118.0, 33.1, 29.3, 19.1. HRMS Calcd for $C_{17}H_{17}N_2$ $[M + H]^+$: m/z 249.1386, Found: 249.1234.

*3-cyclopropyl-2-phenyl-2H-indazole (**3q**)*



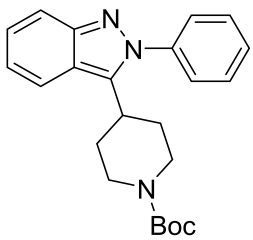
35.1 mg, 75%; White solid, m.p. 72-73 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.68 (m, 4H), 7.55-7.52 (m, 2H), 7.48-7.45 (m, 1H), 7.30-7.27 (m, 1H), 7.06-7.03 (m, 1H), 2.18-2.13 (m, 1H), 1.04-1.01 (m, 2H), 0.94-0.91 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.7, 140.6, 136.8, 129.1, 128.6, 126.6, 125.9, 121.2, 121.0, 120.4, 118.0, 7.71, 7.22. HRMS Calcd for $C_{16}H_{15}N_2$ $[M + H]^+$: m/z 235.1230, Found: 235.1242.

*2-phenyl-3-(tetrahydro-2H-pyran-4-yl)-2H-indazole (**3r**)*[2]



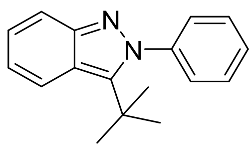
36.1 mg, 65%; White solid, m.p. 134-135 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.58-7.52 (m, 3H), 7.48-7.46 (m, 2H), 7.32 (t, *J* = 6.6 Hz, 1H), 7.10-7.07 (m, 1H), 4.08 (dd, *J* = 4.2, 12.0 Hz, 2H), 3.43-3.38 (m, 2H), 3.26-3.21 (m, 1H), 2.42-2.34 (m, 2H), 1.78 (dd, *J* = 1.8, 13.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 140.1, 139.0, 129.44, 129.38, 126.6, 126.5, 121.2, 120.9, 119.7, 118.1, 68.2, 34.7, 32.2. HRMS Calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$: m/z 279.1492, Found: 279.1496.

*tert-butyl 4-(2-phenyl-2H-indazol-3-yl)piperidine-1-carboxylate (**3s**)*



49.0 mg, 65%; White solid, m.p. 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.56-7.55 (m, 3H), 7.48-7.46 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 4.32-4.13 (m, 2H), 3.11 (t, *J* = 12.4 Hz, 1H), 2.67 (t, *J* = 10.8 Hz, 2H), 2.21-2.13 (m, 2H), 1.86 (d, *J* = 12.4 Hz, 2H), 1.50 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 149.0, 140.1, 139.0, 129.5, 129.4, 126.6, 126.5, 121.2, 120.8, 119.7, 118.1, 79.9, 35.7, 31.5, 28.6. HRMS Calcd for $C_{23}H_{28}N_3O_2$ $[M + H]^+$: m/z 378.2176, Found:378.2174.

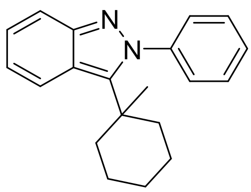
*3-(tert-butyl)-2-phenyl-2H-indazole (**3t**)*[2]



28.0 mg, 56%; White solid, m.p. 143-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J*

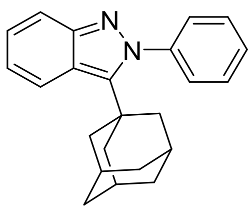
= 9.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.51-7.46 (m, 3H), 7.44-7.42 (m, 2H), 7.30-7.27 (m, 1H), 7.06-7.03 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 144.6, 143.1, 129.5, 128.6, 128.2, 126.1, 122.8, 120.9, 119.8, 118.0, 34.9, 32.0. HRMS Calcd for $C_{17}H_{19}N_2$ $[M + H]^+$: m/z 251.1543, Found: 251.1553.

*3-(1-methylcyclohexyl)-2-phenyl-2H-indazole (**3u**)*



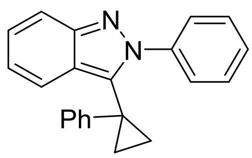
34.2 mg, 59%; White solid, m.p. 115-116 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.52-7.44 (m, 5H), 7.29-7.26 (m, 1H), 7.06-7.03 (m, 1H), 2.23-2.22 (m, 2H), 1.50-1.33 (m, 11H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.9, 143.5, 143.2, 129.5, 128.7, 127.6, 126.0, 122.9, 121.1, 120.0, 118.1, 39.4, 38.6, 29.8, 26.0, 23.0. HRMS Calcd for $C_{20}H_{23}N_2$ $[M + H]^+$: m/z 291.1856, Found: 291.1868.

*3-((3r,5r,7r)-adamantan-1-yl)-2-phenyl-2H-indazole (**3v**)*



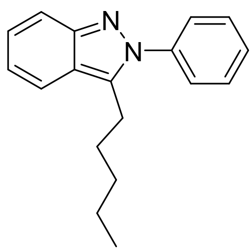
48.5 mg, 74%; White solid, m.p. 188-189°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.51-7.45 (m, 3H), 7.43-7.41 (m, 2H), 7.28-7.27 (m, 1H), 7.04-7.02 (m, 1H), 2.14-2.13 (m, 6H), 1.99 (s, 3H), 1.69 (q, J = 12 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.7, 144.8, 143.5, 129.5, 128.5, 128.3, 126.0, 123.1, 120.6, 119.6, 118.0, 42.7, 37.9, 36.6, 28.7. HRMS Calcd for $C_{23}H_{25}N_2$ $[M + H]^+$: m/z 329.2012, Found: 329.2008.

*2-phenyl-3-(1-phenylcyclopropyl)-2H-indazole (**3w**)*



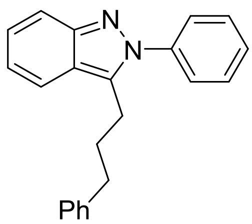
46.0 mg, 74%; White solid, m.p. 110-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2H), 7.49-7.47 (m, 2H), 7.42-7.37 (m, 4H), 7.30-7.28 (m, 2H), 7.23-7.19 (m, 1H), 7.18-7.14 (m, 1H), 7.02-6.99 (m, 2H), 1.46-1.43 (m, 2H), 1.31-1.28 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.7, 144.3, 140.6, 137.5, 128.9, 128.8, 128.5, 126.9, 126.0, 125.7, 125.2, 123.1, 122.0, 120.6, 118.2, 20.1, 19.1. HRMS Calcd for $C_{22}H_{19}N_2$ [M + H]$^+$: m/z 311.1543, Found: 311.1571.

*3-pentyl-2-phenyl-2H-indazole(**3x**)*[3]



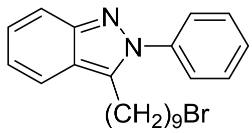
44.9 mg, 85%; White solid, m.p. 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.66 (m, 2H), 7.56-7.47 (m, 5H), 7.34-7.29 (m, 1H), 7.10-7.05 (m, 1H), 3.03 (t, *J* = 7.6 Hz, 2H), 1.67-1.61 (m, 2H), 1.27-1.23 (m, 4H), 0.84-0.80 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 140.3, 137.1, 129.3, 129.0, 126.8, 126.3, 121.2, 121.0, 120.4, 117.7, 31.6, 29.2, 25.4, 22.3, 14.0. HRMS Calcd for $C_{18}H_{21}N_2$ [M + H]$^+$: m/z 265.1699, Found: 265.1714.

*2-phenyl-3-(3-phenylpropyl)-2H-indazole (**3y**)*



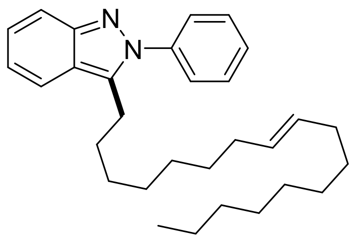
35.6 mg, 57%; White solid, m.p. 166-167 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.52-7.47 (m, 5H), 7.34-7.31 (m, 1H), 7.25 (t, *J* = 5.4 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.09-7.06 (m, 3H), 3.07 (t, *J* = 7.8 Hz, 2H), 2.60 (t, J = 7.8 Hz, 2H), 2.02-1.96 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 141.2, 140.1, 136.4, 129.3, 129.0, 128.5, 128.4, 126.8, 126.2, 126.1, 121.3, 121.2, 120.2, 117.8, 35.5, 30.8, 24.9. HRMS Calcd for $C_{22}H_{21}N_2$ $[M + H]^+$: m/z 313.1699, Found: 313.1702.

*3-(9-bromononyl)-2-phenyl-2H-indazole (**3z**)*



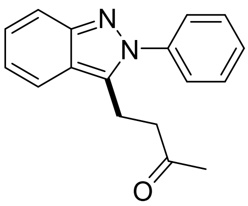
48.5 mg, 61%; Oily liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.56-7.49 (m, 5H), 7.33-7.31 (m, 1H), 7.09-7.07 (m, 1H), 3.39 (t, J = 6.6 Hz, 2H), 3.04 (t, J = 7.8 Hz, 2H), 1.84-1.79 (m, 2H), 1.66-1.61 (m, 2H), 1.39-1.35 (m, 2H), 1.26-1.21 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 140.3, 137.0, 129.3, 129.0, 126.8, 126.3, 121.2, 121.0, 120.3, 117.8, 34.1, 32.9, 29.5, 29.32, 29.27, 29.1, 28.8, 28.2, 25.4. HRMS Calcd for $C_{22}H_{28}BrN_2$ $[M + H]^+$: m/z 399.1430, Found: 399.1434.

*(E)-3-(heptadec-8-en-1-yl)-2-phenyl-2H-indazole (**4a**)*



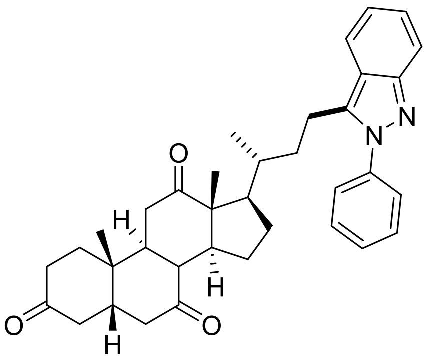
50.7 mg, 59%; oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.56-7.48 (m, 5H), 7.32 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 5.39-5.28 (m, 2H), 3.03 (t, J = 8.0 Hz, 2H), 2.03-1.96 (m, 4H), 1.69-1.61 (m, 2H), 1.27-1.23 (m, 20H), 0.88 (t, J = 6.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.7, 140.2, 137.0, 130.1, 129.8, 129.3, 129.0, 126.7, 126.3, 121.2, 121.0, 120.3, 117.7, 32.0, 29.9, 29.8, 29.6, 29.5, 29.43, 29.36, 29.13, 29.11, 27.3, 27.2, 25.4, 22.8, 14.2. HRMS Calcd for $C_{30}H_{43}N_2$ $[M + H]^+$: m/z 431.3421, Found:431.3419.

*4-(2-phenyl-2H-indazol-3-yl)butan-2-one (**4b**)*



23.7 mg, 45%; White solid, m.p. 109-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.57-7.49 (m, 5H), 7.34-7.30 (m, 1H), 7.11-7.07 (m, 1H), 3.36-3.32 (m, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.5, 148.8, 140.0, 135.0, 129.5, 129.3, 126.9, 126.2, 121.5, 121.0, 120.0, 117.9, 42.6, 30.0, 19.4. HRMS Calcd for $C_{17}H_{17}N_2O$ $[M + H]^+$: m/z 265.1335, Found: 265.1329.

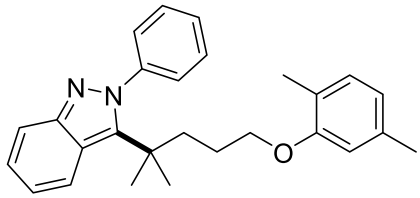
*(5S,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-5-(2-phenyl-2H-indazol-3-yl)pentan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (**4c**)*



47.4 mg, 43%; White solid, m.p. 240-241 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.56-7.49 (m, 5H), 7.32 (t, *J* = 6.6 Hz, 1H), 7.09-7.06 (m, 1H), 3.15-3.10 (m, 1H), 2.99-2.94 (m, 1H), 2.92-2.87 (m, 1H), 2.86-2.79 (m, 2H), 2.34-2.19 (m, 6H), 2.13-2.08 (m, 2H), 2.03-1.93 (m, 3H), 1.83-1.77 (m, 3H), 1.62-1.57 (m, 1H), 1.50-1.44 (m, 1H), 1.38 (s, 3H), 1.24-1.16 (m, 2H), 1.12-1.06 (m, 1H), 0.99 (s, 3H), 0.83 (d, *J* = 6.60 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.0, 209.1, 208.8, 148.8, 140.1, 137.1, 129.3, 129.1, 126.8, 126.3, 121.09, 121.05, 120.2, 117.8, 56.9, 51.8, 49.1, 46.9, 45.7, 45.3, 45.1, 42.9, 38.7, 36.6, 36.1, 35.9, 35.4, 35.3, 27.7, 25.2, 22.4, 22.0, 18.8, 11.9. HRMS Calcd for $C_{36}H_{43}N_2O_3$ $[M + H]^+$: m/z

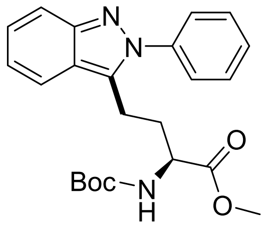
551.3268, Found: 551.3263.

3-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)-2-phenyl-2H-indazole ***(4d)***



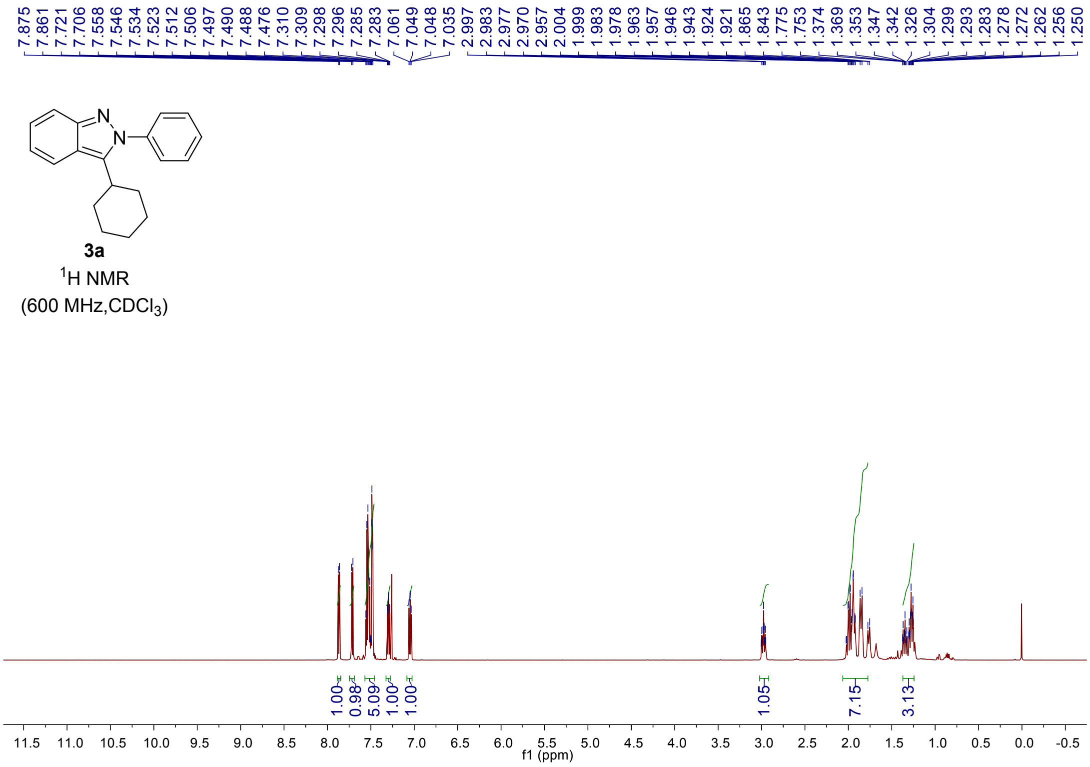
32.6 mg, 41%; White solid, m.p. 240-241 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.52-7.43 (m, 5H), 7.32-7.27 (m, 1H), 7.08-7.04 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 3.82 (t, *J* = 6.0 Hz, 2H), 2.28 (s, 3H), 2.14 (s, 3H), 1.98-1.94 (m, 2H), 1.67-1.60 (m, 2H), 1.43 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.0, 148.7, 143.1, 142.9, 136.6, 130.5, 129.6, 128.7, 128.0, 126.2, 123.6, 122.5, 121.2, 120.9, 120.5, 118.1, 112.0, 40.8, 38.2, 30.3, 25.5, 21.5, 16.0. HRMS Calcd for $C_{27}H_{31}N_2O$ $[M + H]^+$: m/z 399.2431, Found: 399.2464.

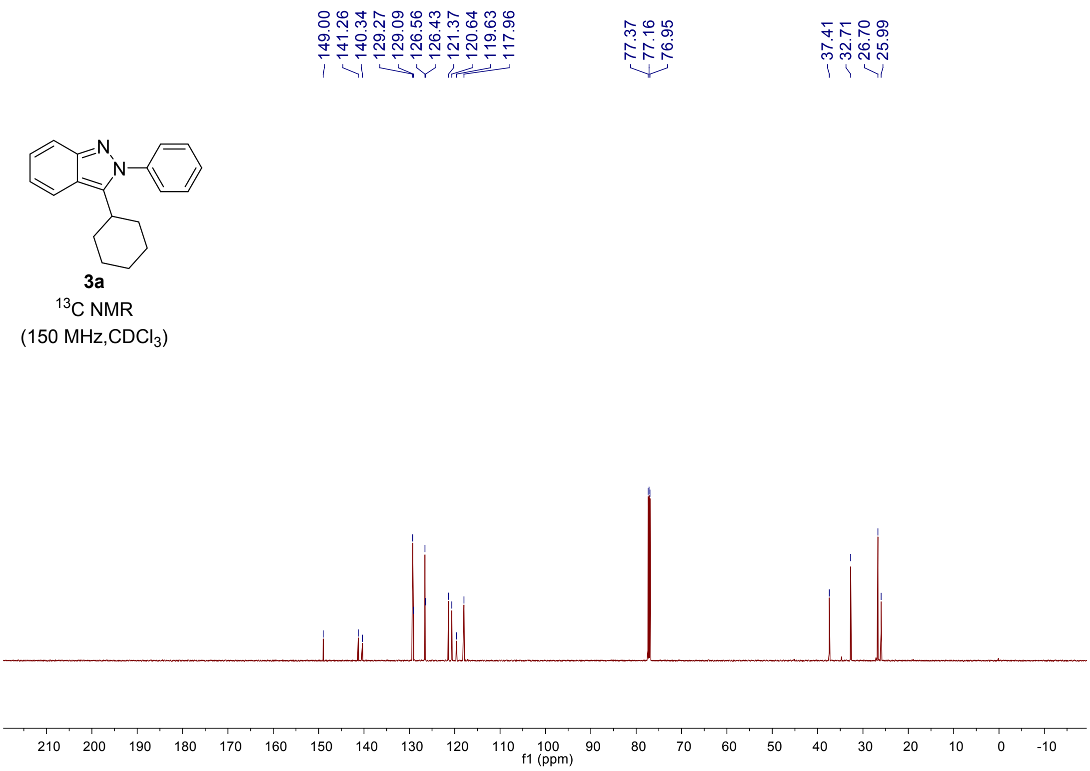
(S)-2-((tert-butoxycarbonyl)amino)-4-(2-phenyl-2H-indazol-3-yl)butanoate ***(4e)***

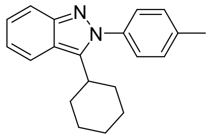


36.8 mg, 45%; White solid, m.p. 238-239°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.56-7.51 (m, 5H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 5.00-4.99 (m, 1H), 4.31-4.30 (m, 1H), 3.58 (s, 3H), 3.18-3.03 (m, 2H), 2.26-2.22 (m, 1H), 2.01-1.95 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 155.3, 148.8, 139.9, 134.8, 129.4, 129.2, 126.9, 126.3, 121.5, 121.2, 119.9, 117.9, 80.2, 53.1, 52.5, 32.2, 28.4, 21.4. HRMS Calcd for $C_{23}H_{28}N_3O_4$ $[M + H]^+$: m/z 410.2074, Found: 410.2069.

5. NMR copies of products



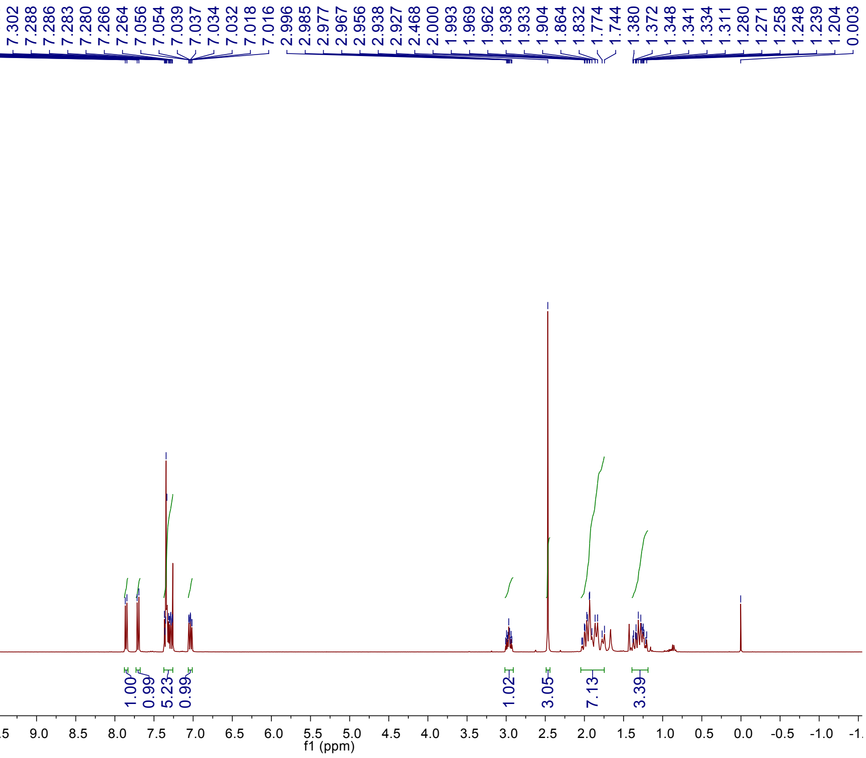


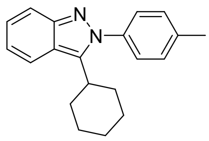


3b

^{1}H NMR

(400 MHz,$CDCl_3$)

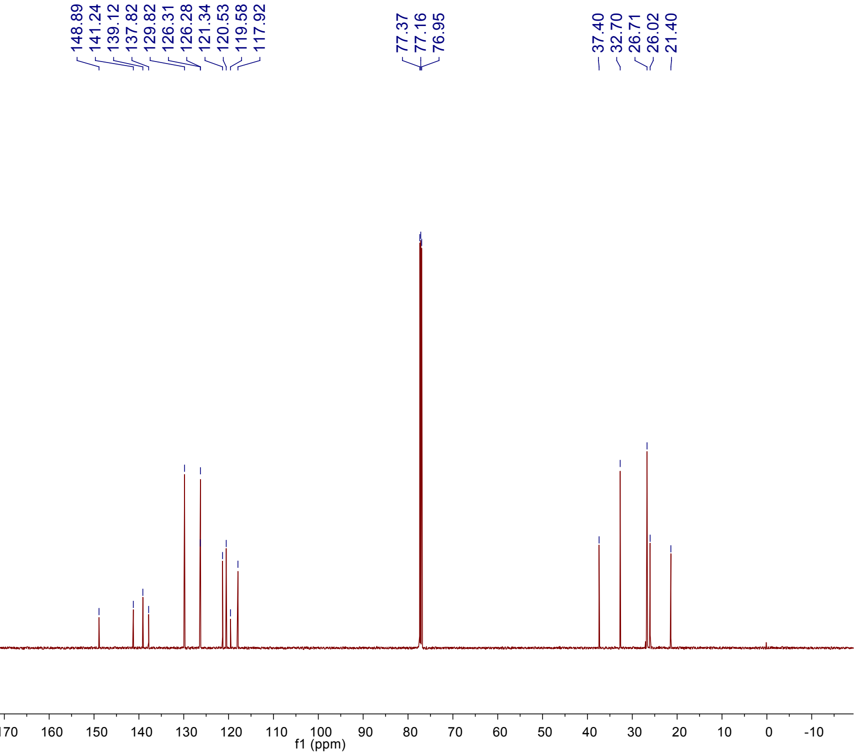


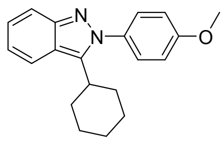


3b

^{13}C NMR

(150 MHz,$CDCl_3$)

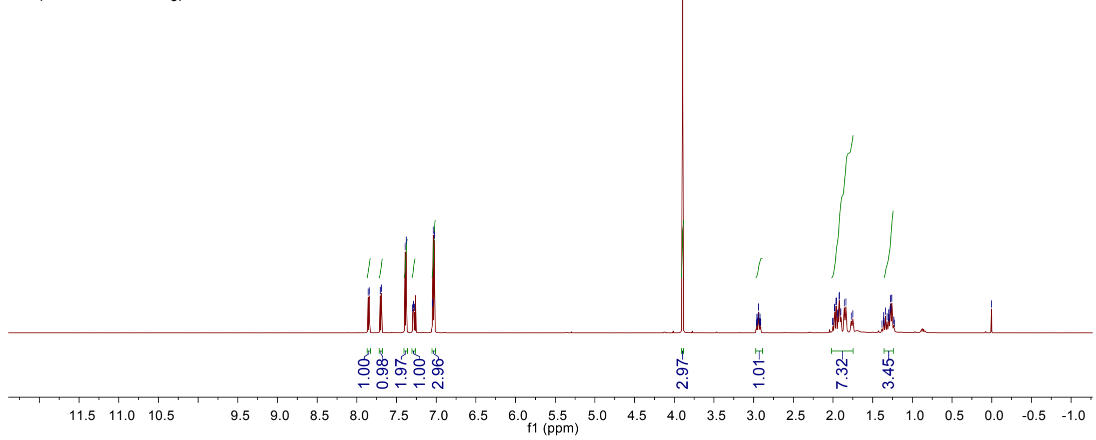


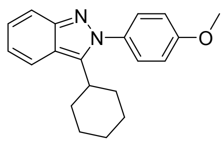


3c

^{1}H NMR

(400 MHz, $CDCl_3$)

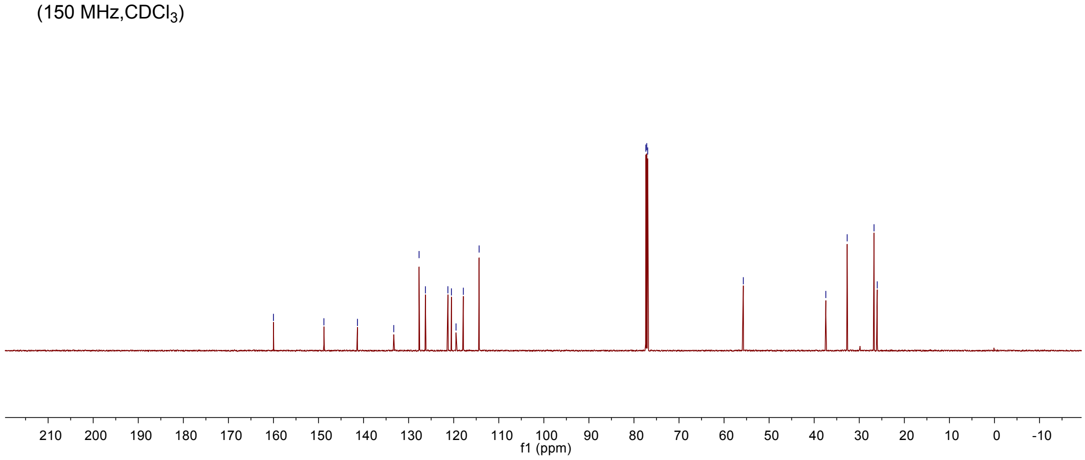


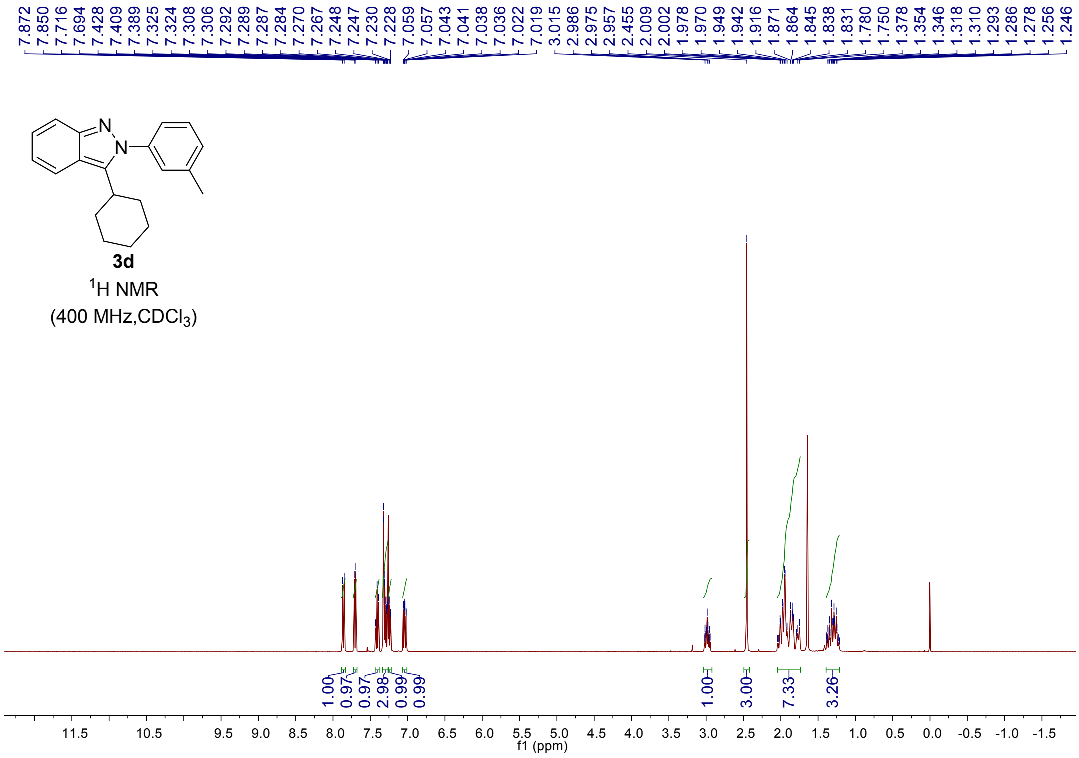


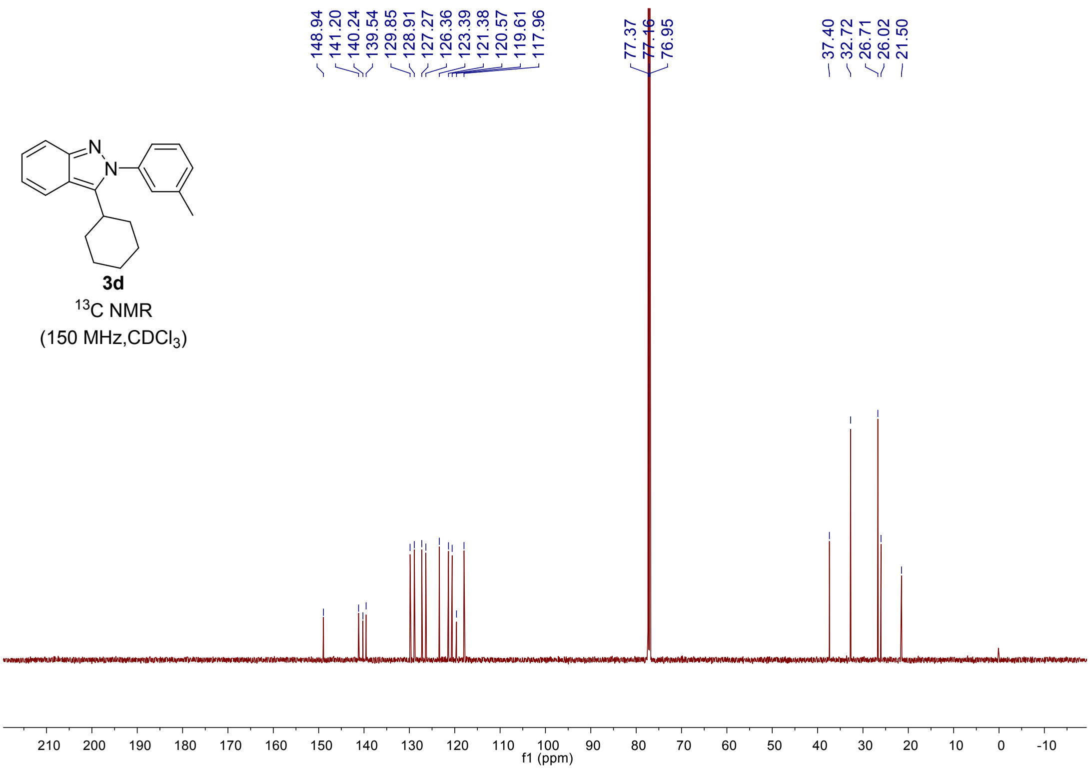
3c

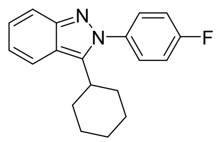
^{13}C NMR

(150 MHz, $CDCl_3$)




7.872
7.850
7.716
7.694
7.428
7.409
7.389
7.325
7.324
7.308
7.306
7.292
7.289
7.287
7.284
7.270
7.267
7.248
7.247
7.230
7.228
7.059
7.057
7.043
7.041
7.038
7.036
7.022
7.019
3.015
2.986
2.975
2.957
2.455
2.009
2.002
1.978
1.970
1.949
1.942
1.916
1.871
1.864
1.845
1.838
1.831
1.780
1.750
1.378
1.354
1.346
1.318
1.310
1.293
1.286
1.278
1.256
1.246
N
N
3d
^{1}H NMR
(400 MHz,CDCl$_3$)
1.00
0.97
0.97
2.98
0.99
0.99
1.00
3.00
7.33
3.26
f1 (ppm)

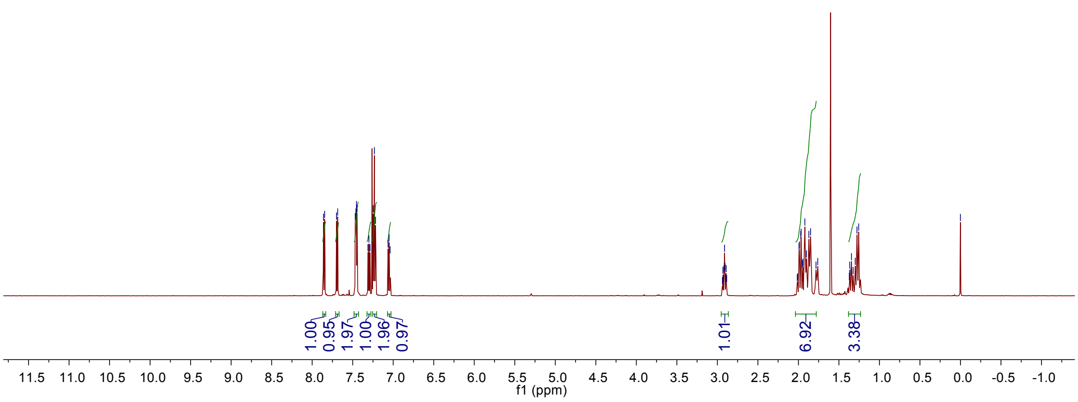

148.94
141.20
140.24
139.54
129.85
128.91
127.27
126.36
123.39
121.38
120.57
119.61
117.96
77.37
77.16
76.95
37.40
32.72
26.71
26.02
21.50
N
N
3d
^{13}C NMR
(150 MHz,CDCl$_3$)
f1 (ppm)

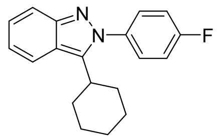


3e

^{1}H NMR

(600 MHz, $CDCl_3$)

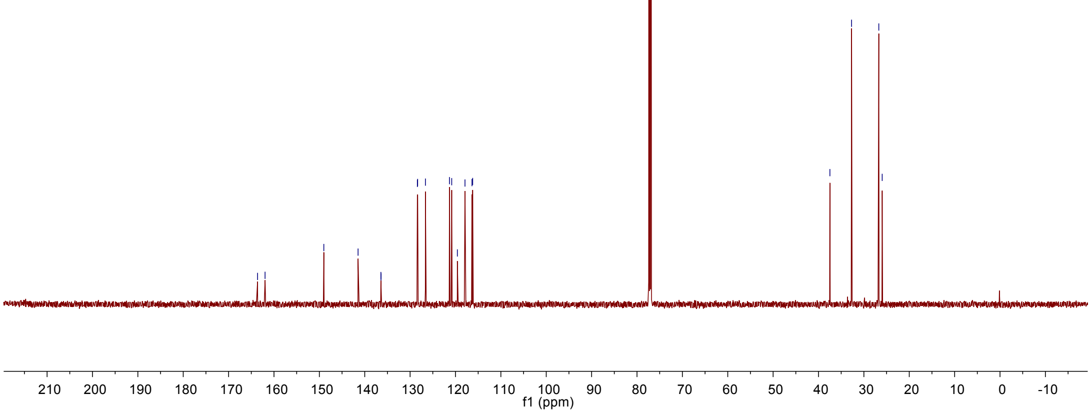


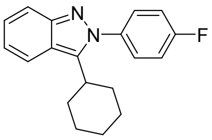


3e

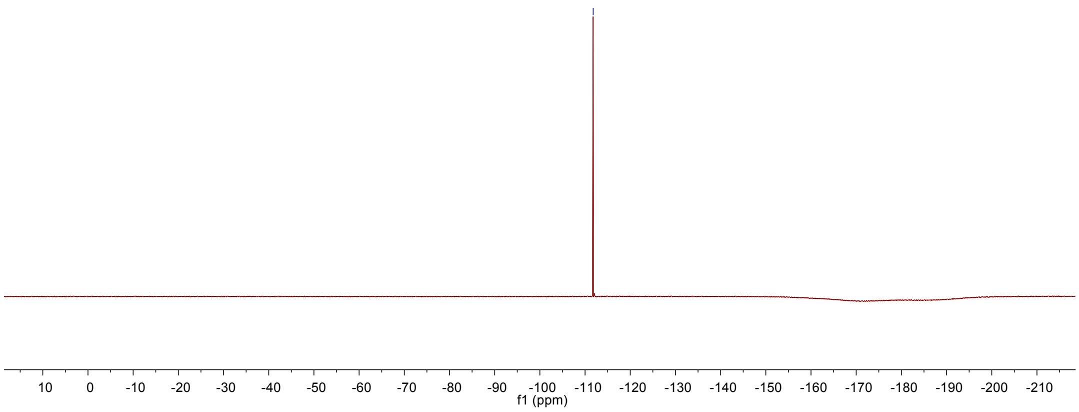
^{13}C NMR

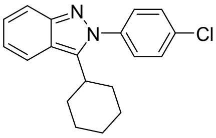
(150 MHz, $CDCl_3$)



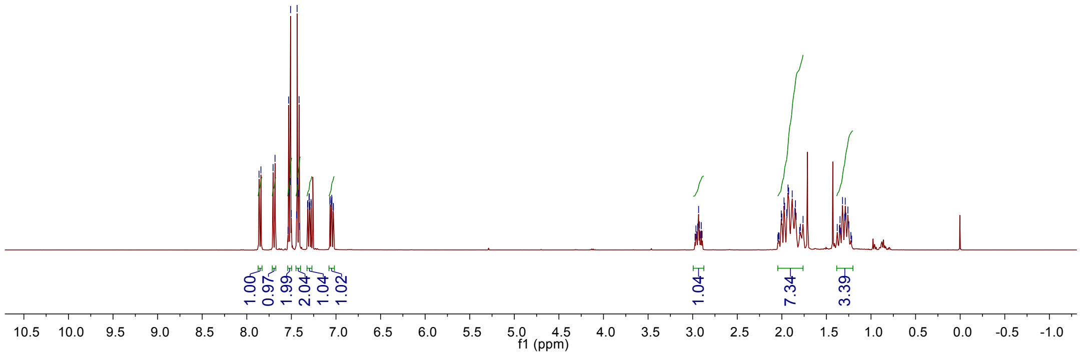


3e
^{19}F NMR
(564 MHz, $CDCl_3$)

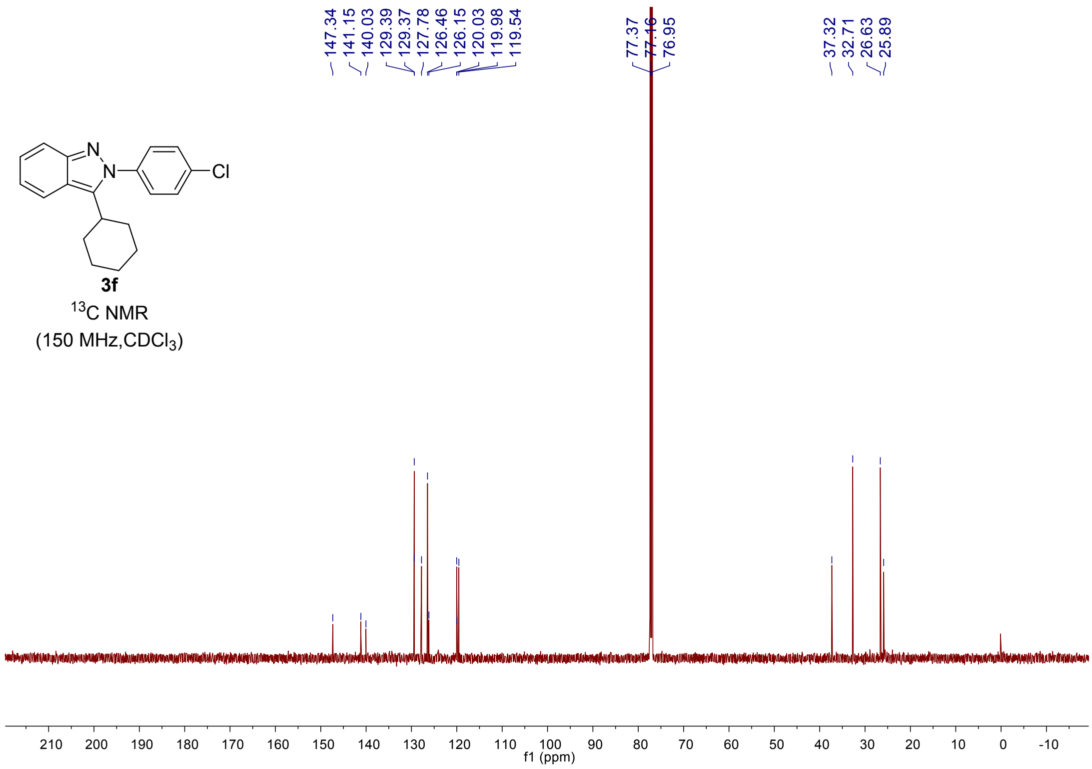




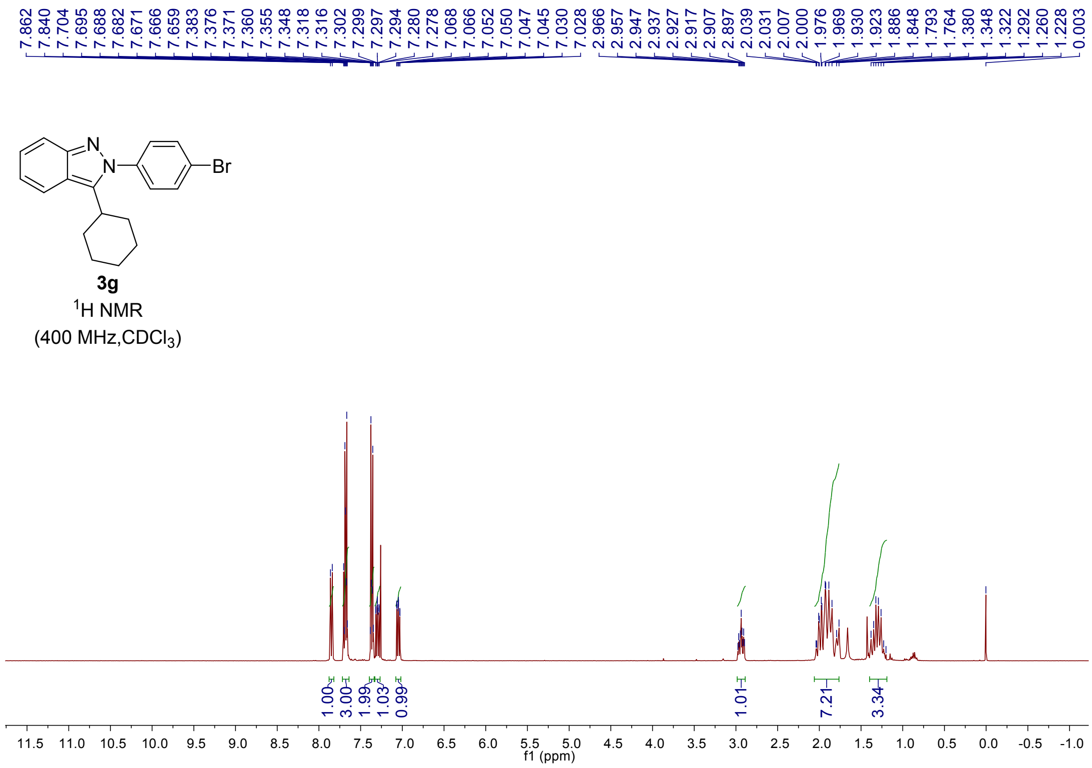
3f
^{1}H NMR
(400 MHz, $CDCl_3$)

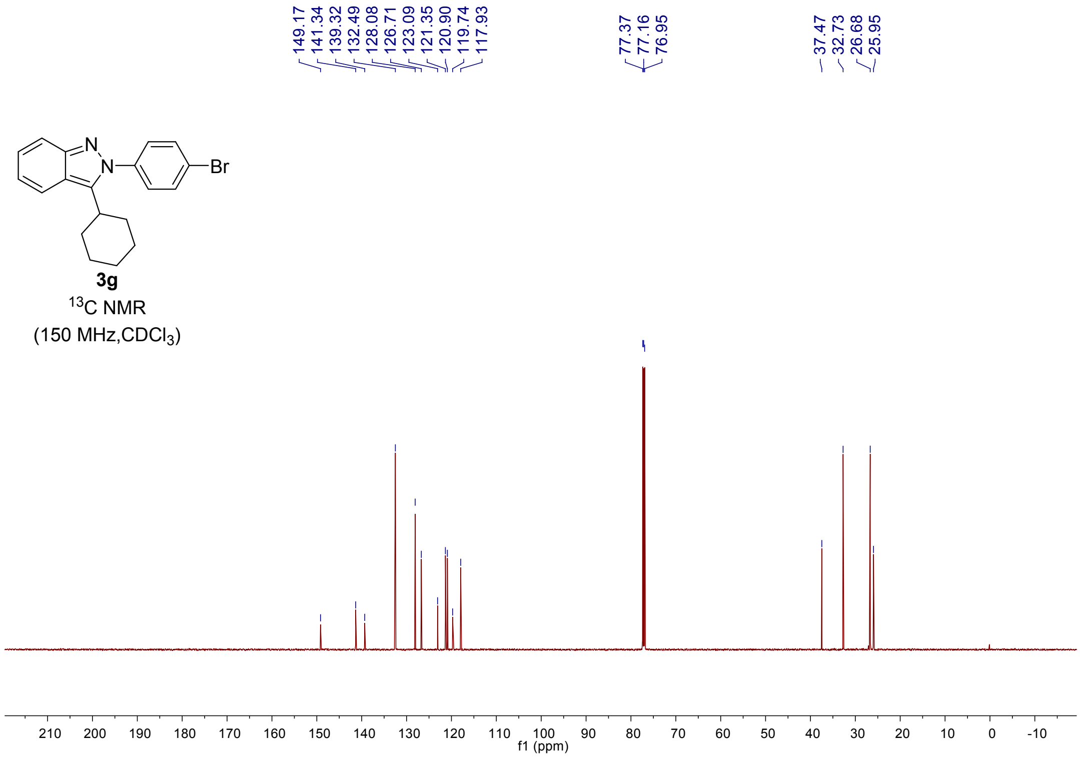


3f
^{13}C NMR
(150 MHz, $CDCl_3$)



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

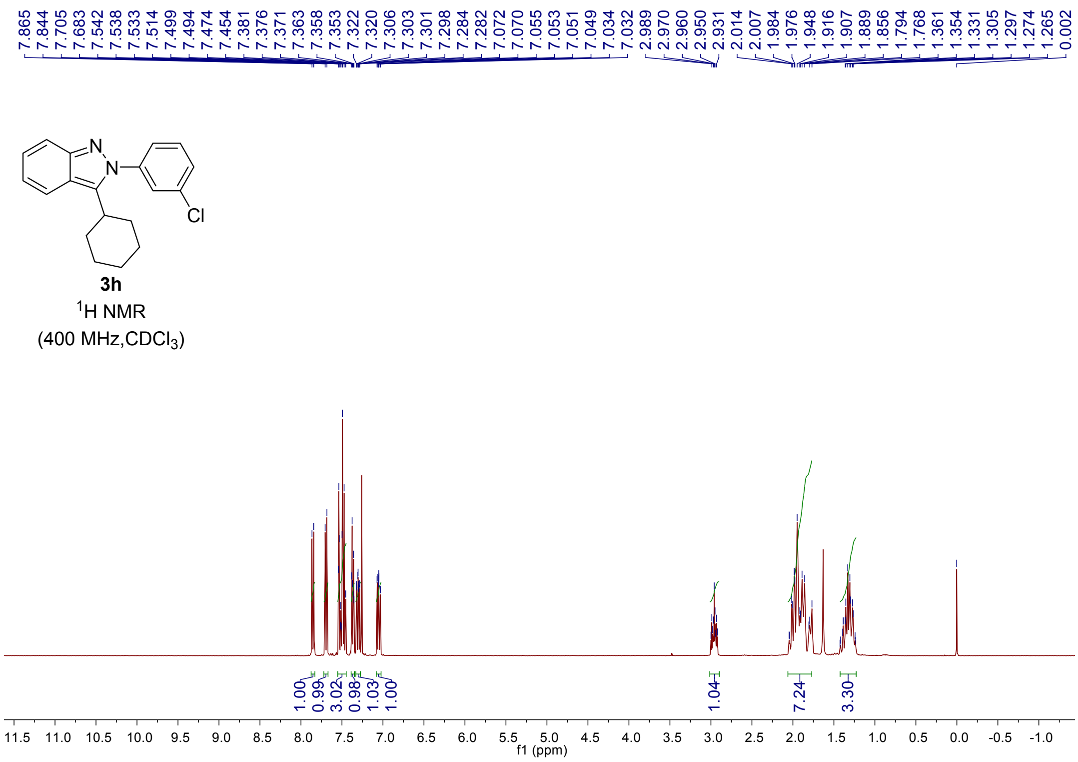




3g

^{13}C NMR

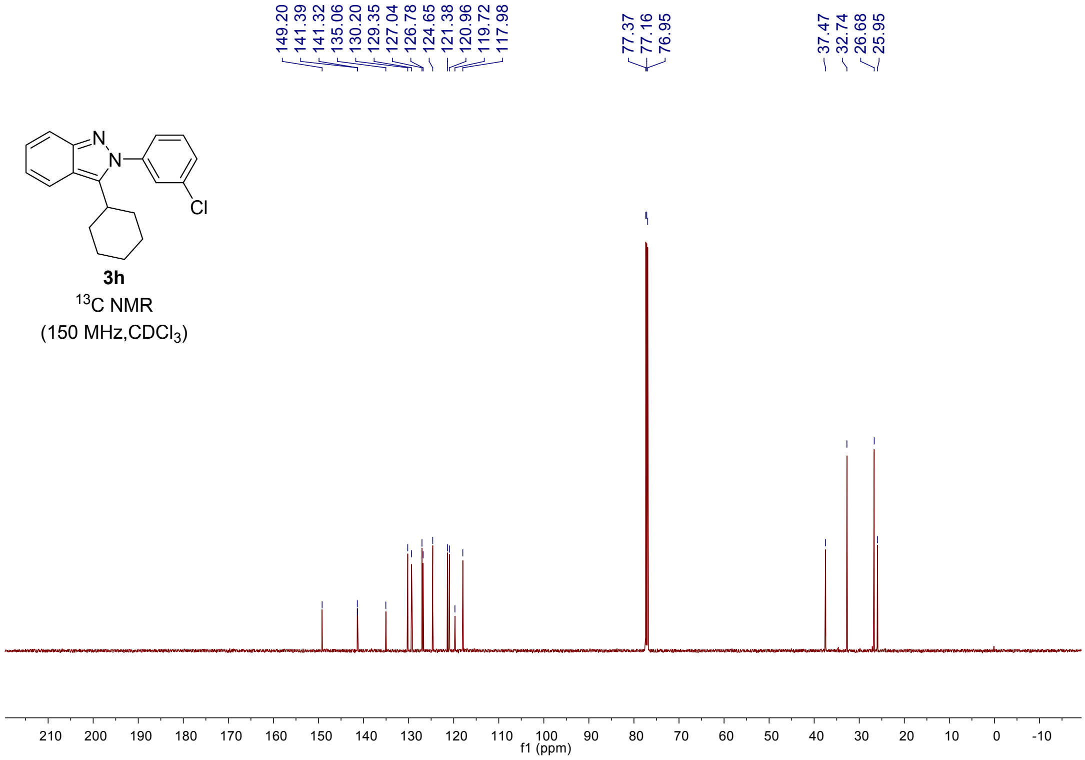
(150 MHz, $CDCl_3$)

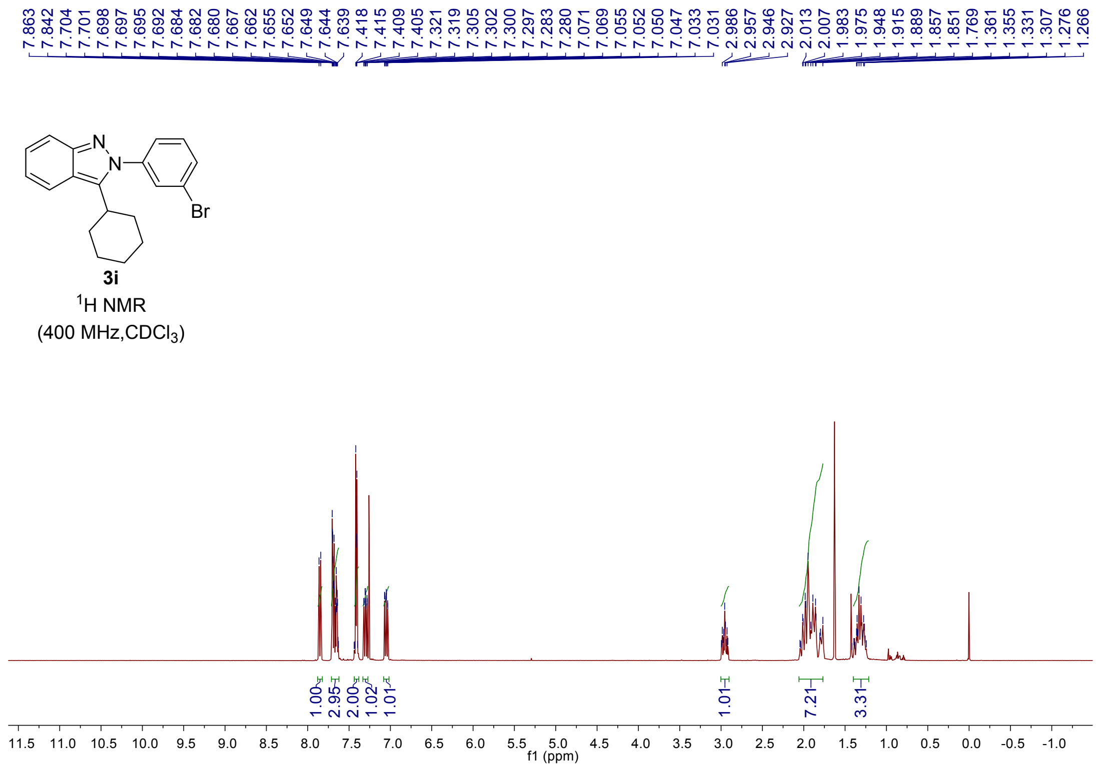


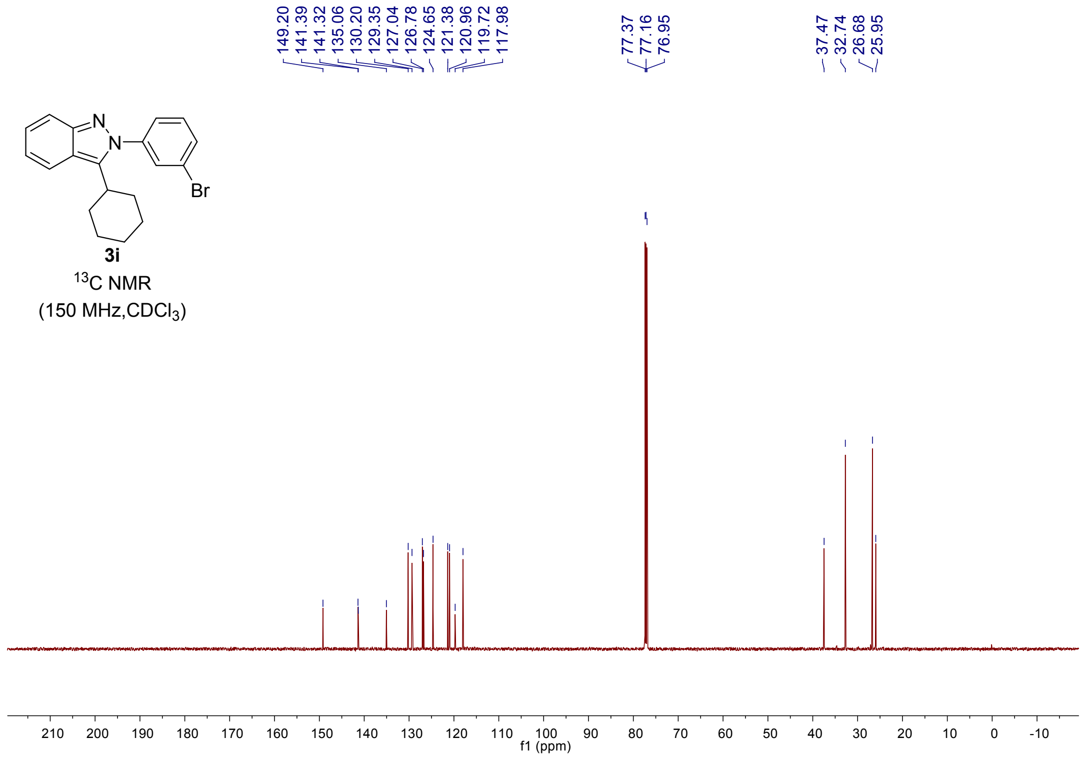
3h

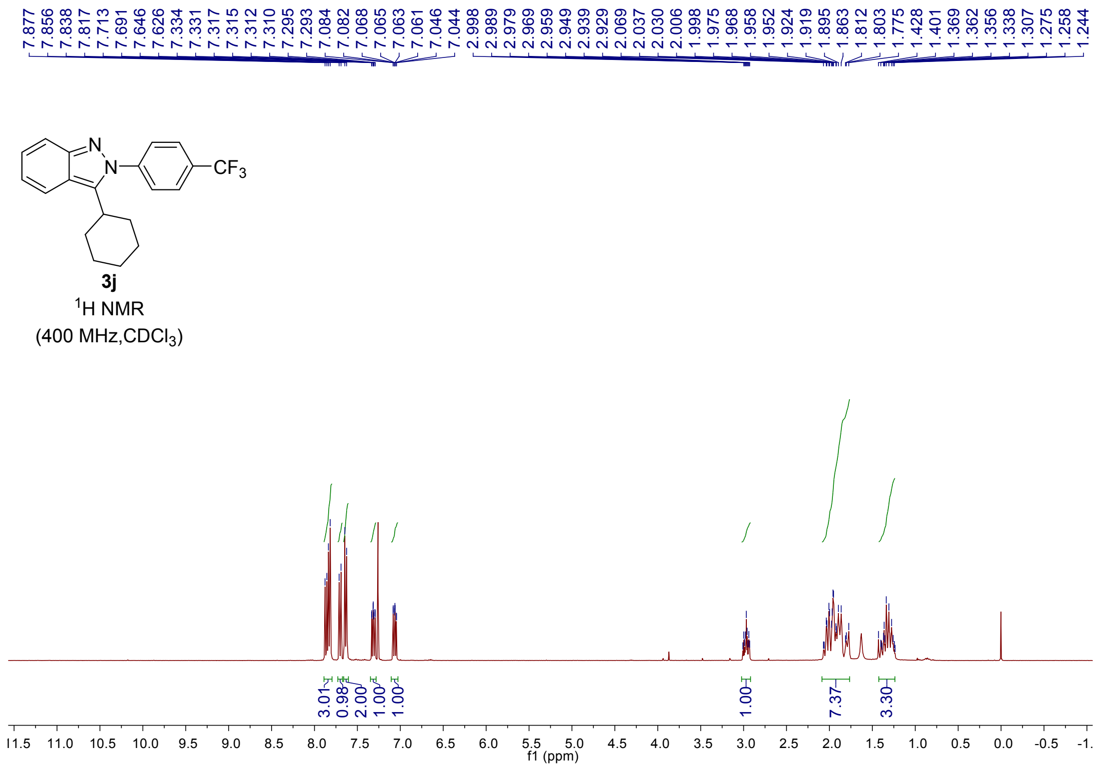
^{1}H NMR

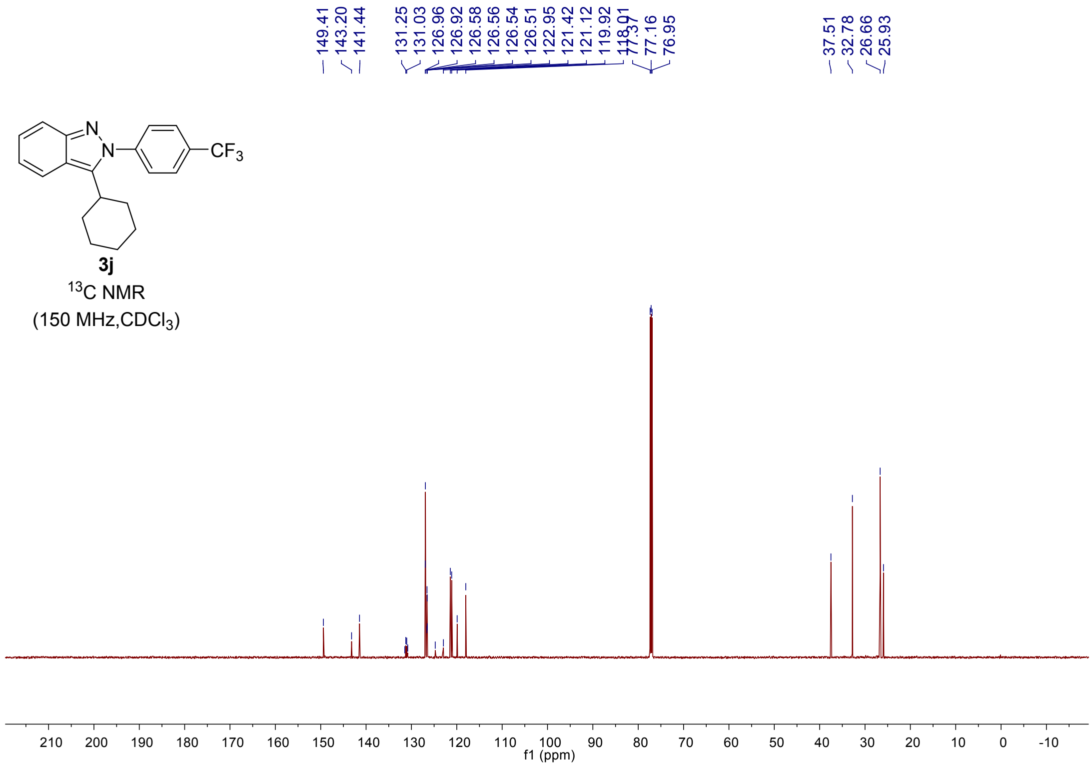
(400 MHz, $CDCl_3$)

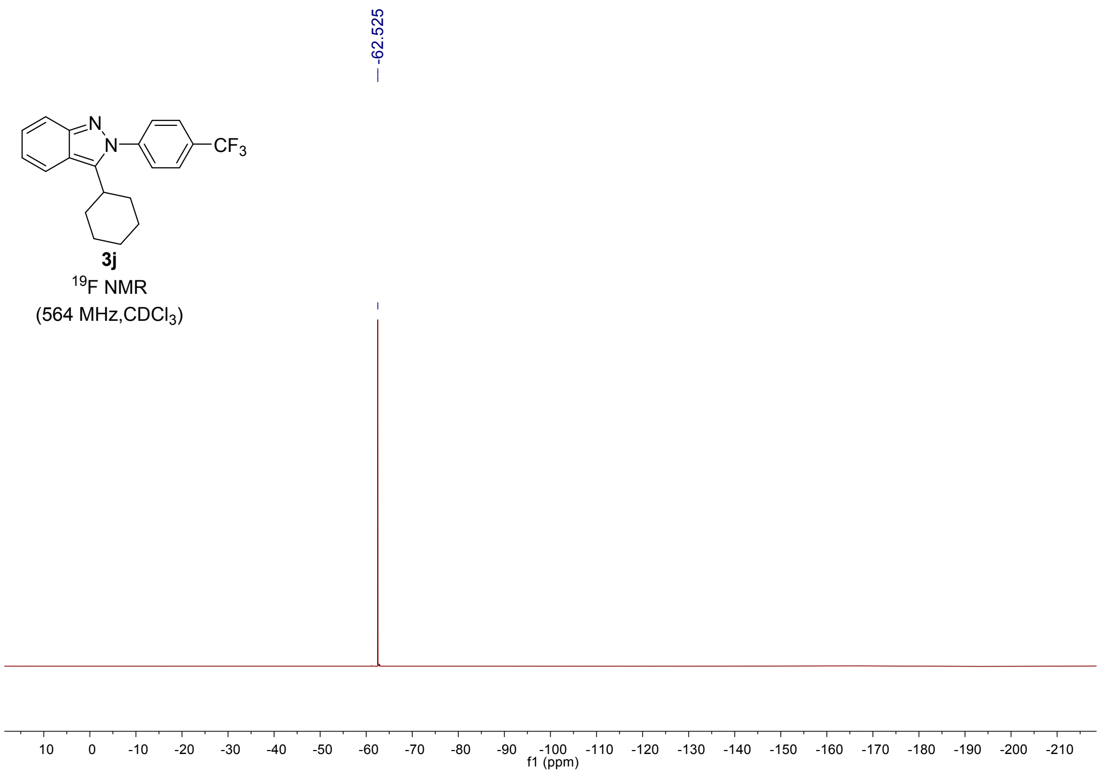

149.20
141.39
141.32
135.06
130.20
129.35
127.04
126.78
124.65
121.38
120.96
119.72
117.98
77.37
77.16
76.95
37.47
32.74
26.68
25.95
N
N
Cl
3h
^{13}C NMR
(150 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

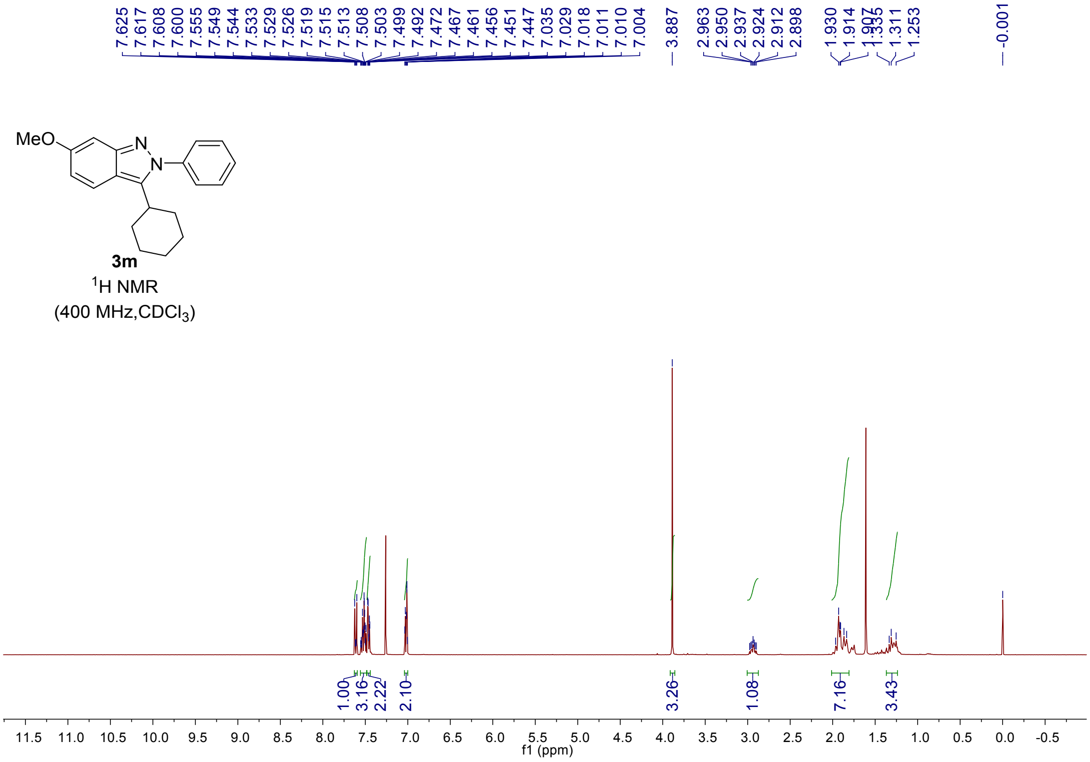

7.863
7.842
7.704
7.701
7.698
7.697
7.695
7.692
7.684
7.682
7.680
7.667
7.662
7.655
7.652
7.649
7.644
7.639
7.418
7.415
7.409
7.405
7.321
7.319
7.305
7.302
7.300
7.297
7.283
7.280
7.071
7.069
7.055
7.052
7.050
7.047
7.033
7.031
2.986
2.957
2.946
2.927
2.013
2.007
1.983
1.975
1.948
1.915
1.889
1.857
1.851
1.769
1.361
1.355
1.331
1.307
1.276
1.266
N
N
Br
3i
^{1}H NMR
(400 MHz, $CDCl_3$)
1.00
2.95
2.00
1.02
1.01
1.01
7.21
3.31
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

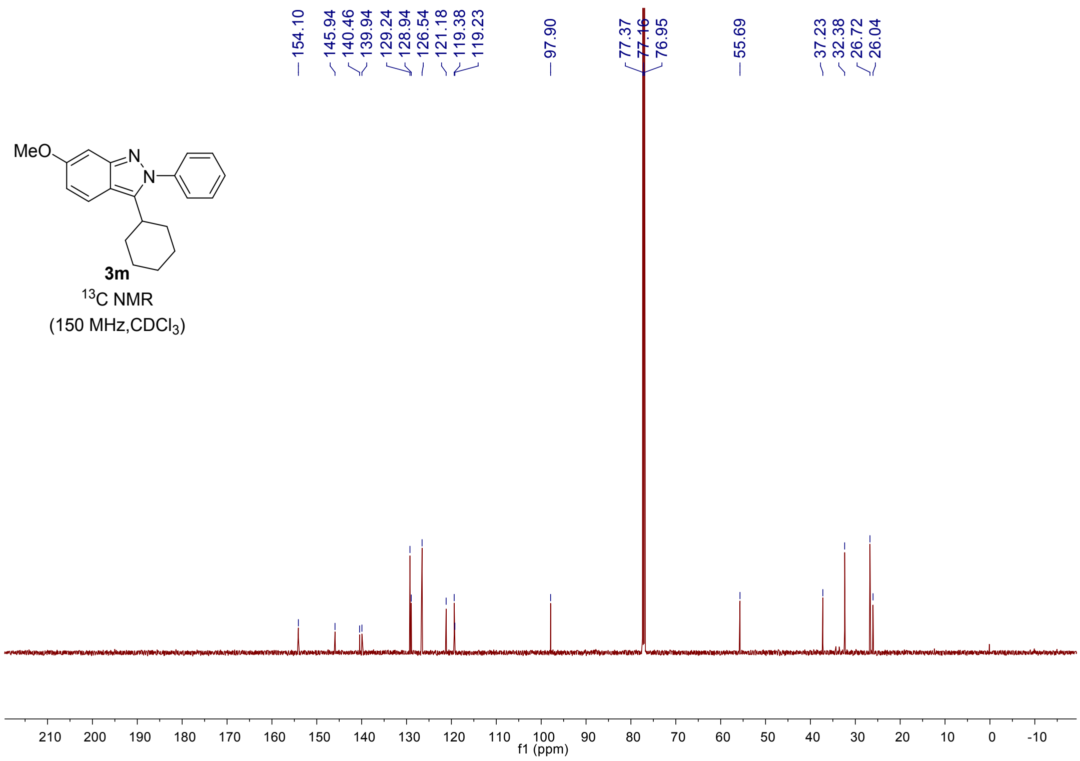

149.20
141.39
141.32
135.06
130.20
129.35
127.04
126.78
124.65
121.38
120.96
119.72
117.98
77.37
77.16
76.95
37.47
32.74
26.68
25.95
Br
3i
^{13}C NMR
(150 MHz,CDCl$_3$)
f1 (ppm)

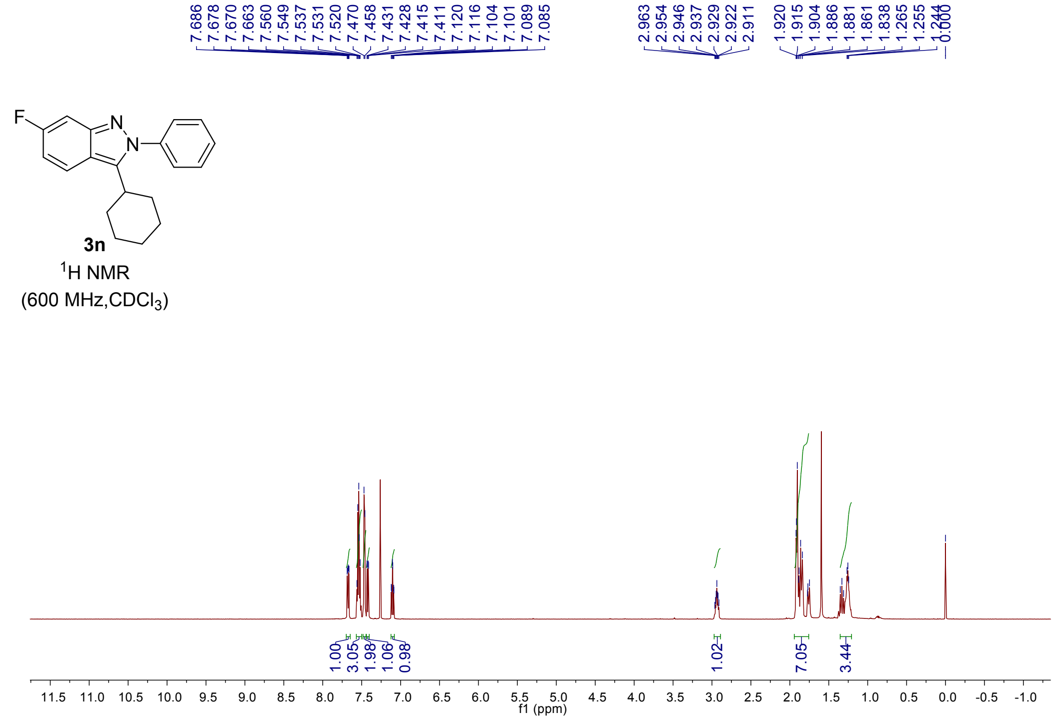

7.877
7.856
7.838
7.817
7.713
7.691
7.646
7.626
7.334
7.331
7.317
7.315
7.312
7.310
7.295
7.293
7.084
7.082
7.068
7.065
7.063
7.061
7.046
7.044
2.998
2.989
2.979
2.969
2.959
2.949
2.939
2.929
2.069
2.037
2.030
2.006
1.998
1.975
1.968
1.958
1.952
1.924
1.919
1.895
1.863
1.812
1.803
1.775
1.428
1.401
1.369
1.362
1.356
1.338
1.307
1.275
1.258
1.244
CF$_3$
3j
^{1}H NMR
(400 MHz,CDCl$_3$)
3.01
0.98
2.00
1.00
1.00
1.00
7.37
3.30
f1 (ppm)

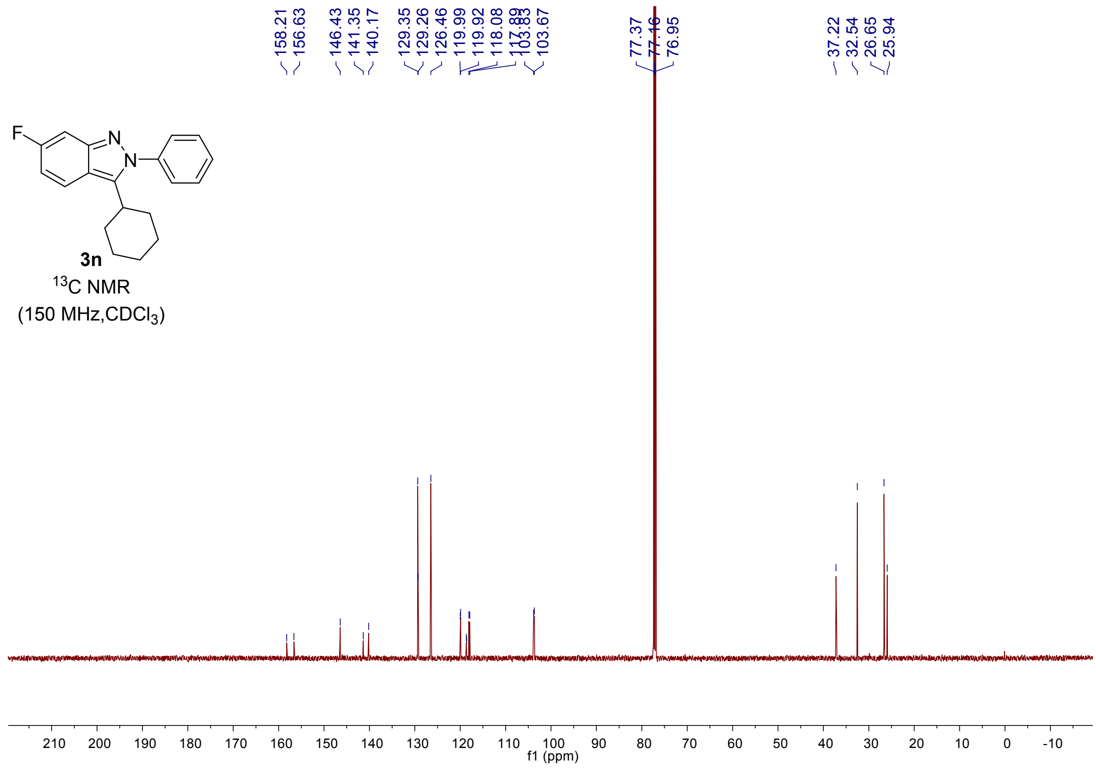

149.41
143.20
141.44
131.25
131.03
126.96
126.92
126.58
126.56
126.54
126.51
122.95
121.42
121.12
119.92
118.01
77.37
77.16
76.95
37.51
32.78
26.66
25.93
N
N
CF_3
3j
^{13}C NMR
(150 MHz,$CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

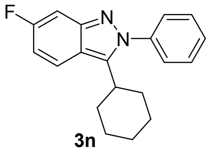

-62.525
N
N
CF_3
3j
^{19}F NMR
(564 MHz,$CDCl_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.625
7.617
7.608
7.600
7.555
7.549
7.544
7.533
7.529
7.526
7.519
7.515
7.513
7.508
7.503
7.499
7.492
7.472
7.467
7.461
7.456
7.451
7.447
7.035
7.029
7.018
7.011
7.010
7.004
3.887
2.963
2.950
2.937
2.924
2.912
2.898
1.930
1.914
1.907
1.335
1.311
1.253
-0.001
MeO
N
N
3m
^{1}H NMR
(400 MHz,CDCl$_3$)
1.00
3.16
2.22
2.10
3.26
1.08
7.16
3.43
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

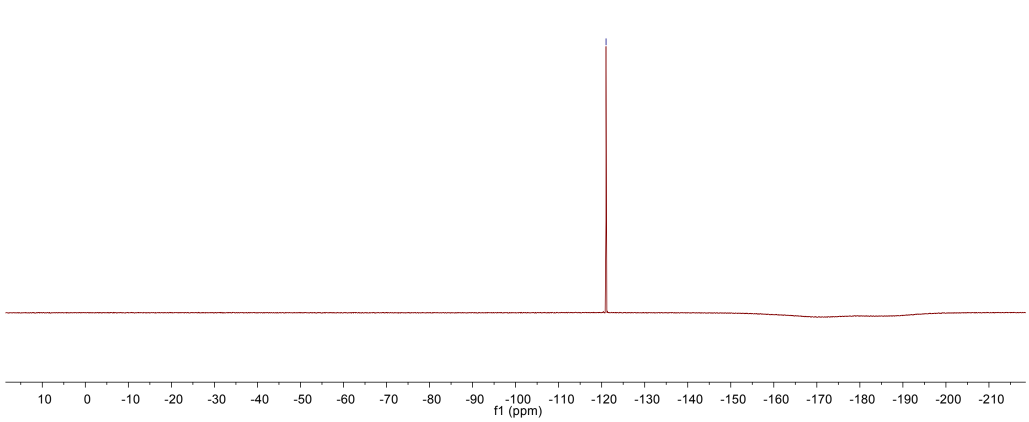

154.10
145.94
140.46
139.94
129.24
128.94
126.54
121.18
119.38
119.23
97.90
77.37
77.16
76.95
55.69
37.23
32.38
26.72
26.04
MeO
N
N
3m
^{13}C NMR
(150 MHz,CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

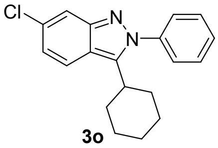

7.686 7.678 7.670 7.663 7.560 7.549 7.537 7.531 7.520 7.470 7.458 7.431 7.428 7.415 7.411 7.120 7.116 7.104 7.101 7.089 7.085
2.963 2.954 2.946 2.937 2.929 2.922 2.911
1.920 1.915 1.904 1.886 1.881 1.861 1.838 1.265 1.255 1.244 0.000
F
N
N
3n
1H NMR
(600 MHz,CDCl3)
1.00 3.05 1.98 1.06 0.98
1.02
7.05
3.44
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.21 156.63 146.43 141.35 140.17 129.35 129.26 126.46 119.99 119.92 118.08 117.89 103.83 103.67
77.37 77.16 76.95
37.22 32.54 26.65 25.94
F
N
N
3n
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

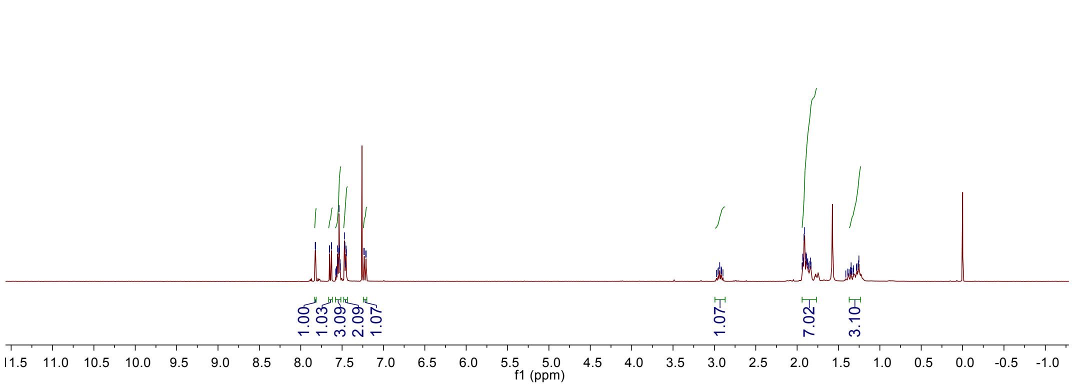


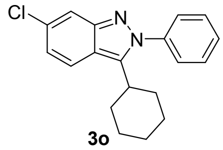
3n
^{19}F NMR
(564 MHz, $CDCl_3$)





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

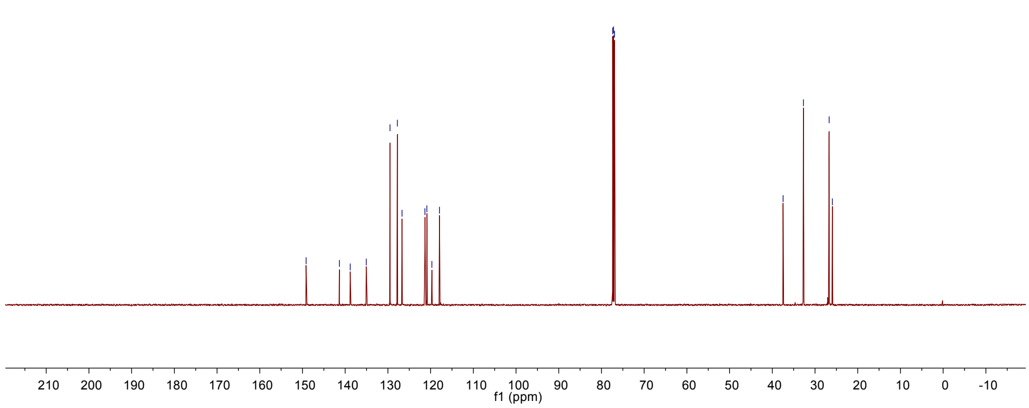


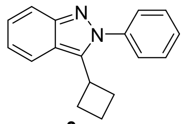


3o

^{13}C NMR

(150 MHz, $CDCl_3$)

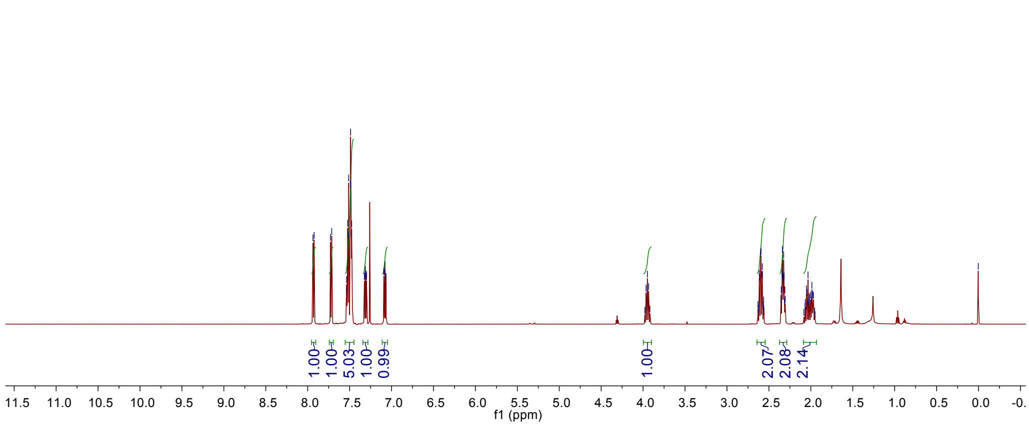


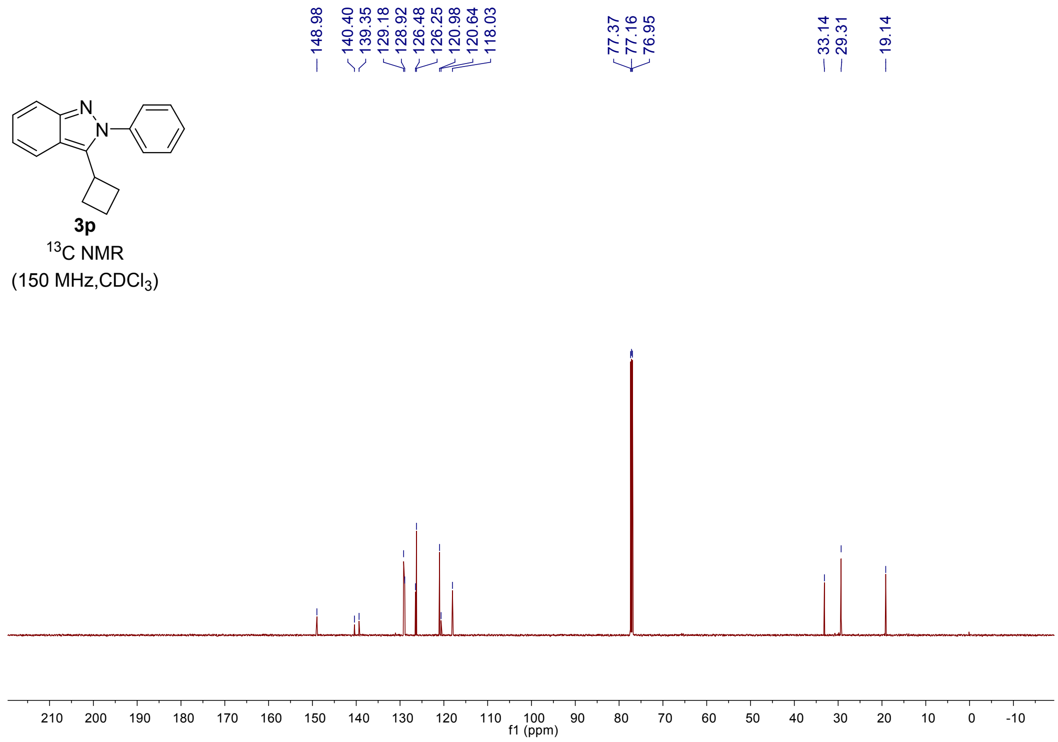


3p

^{1}H NMR

(600 MHz, $CDCl_3$)

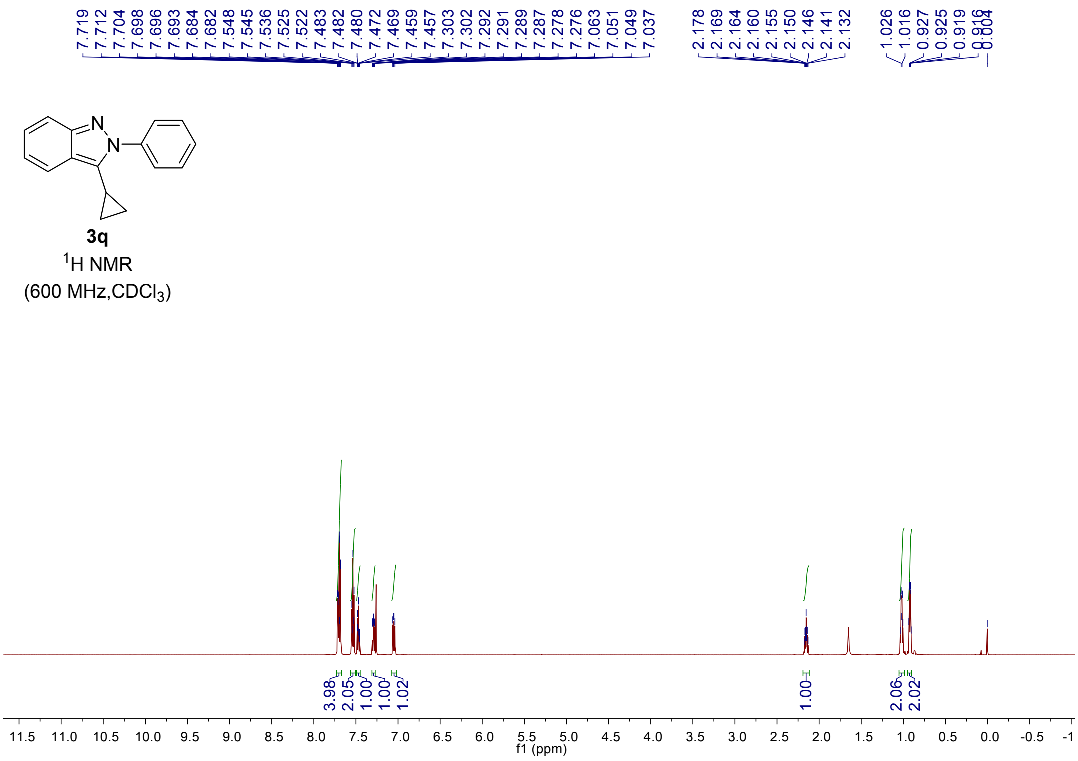




3p

^{13}C NMR

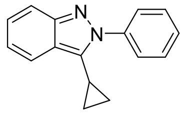
(150 MHz,$CDCl_3$)



3q

^{1}H NMR

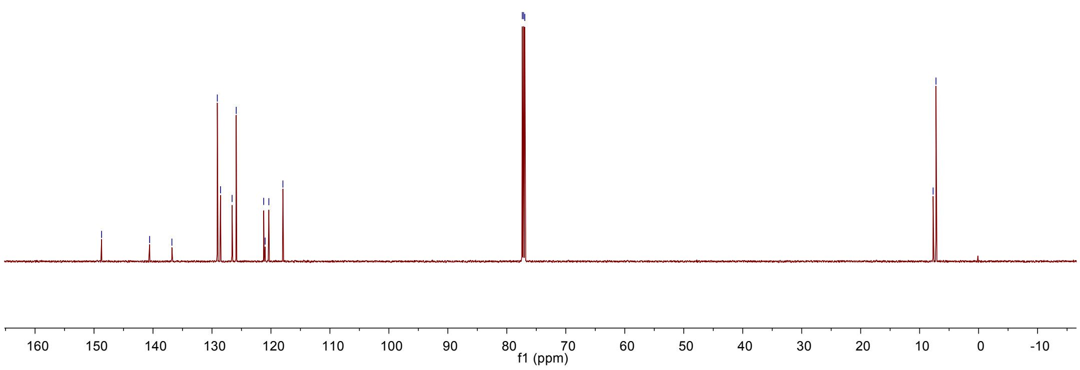
(600 MHz,$CDCl_3$)

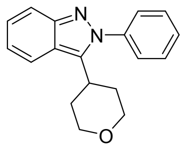


3q

^{13}C NMR

(150 MHz, $CDCl_3$)

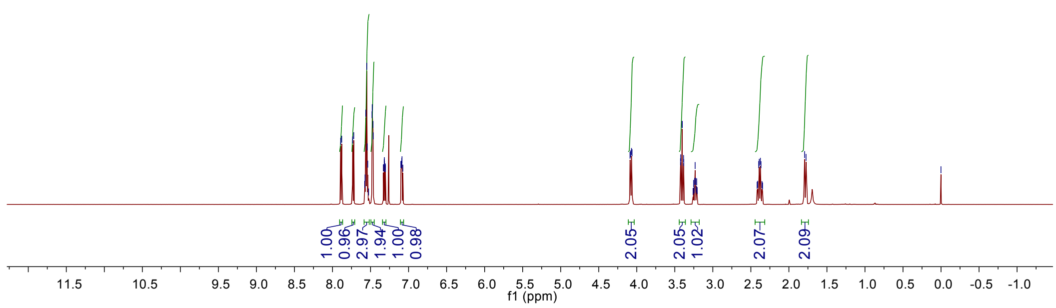


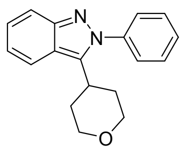


3r

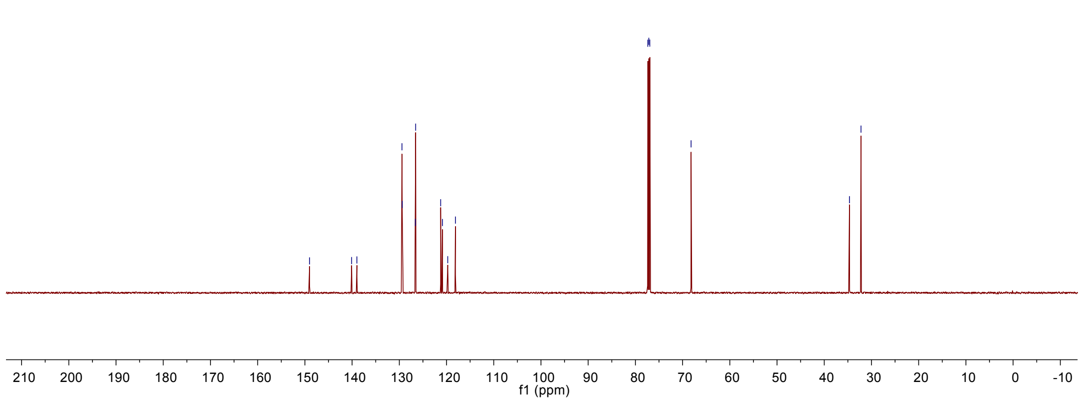
^{1}H NMR

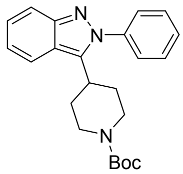
(600 MHz, $CDCl_3$)



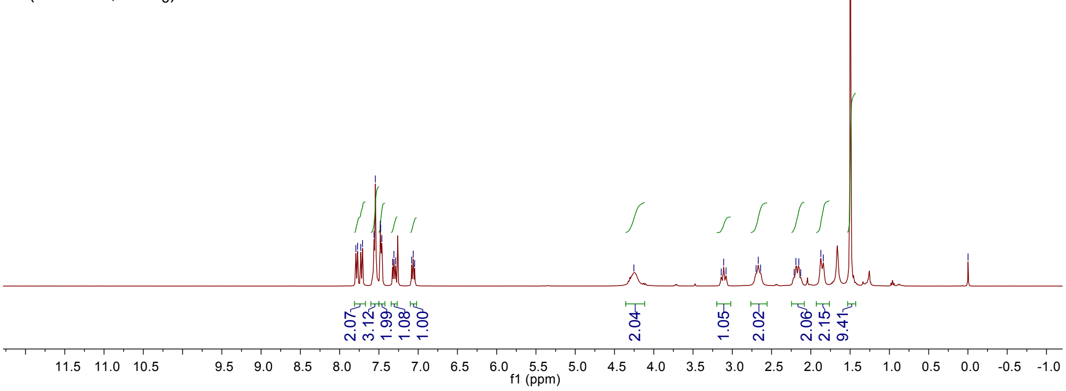


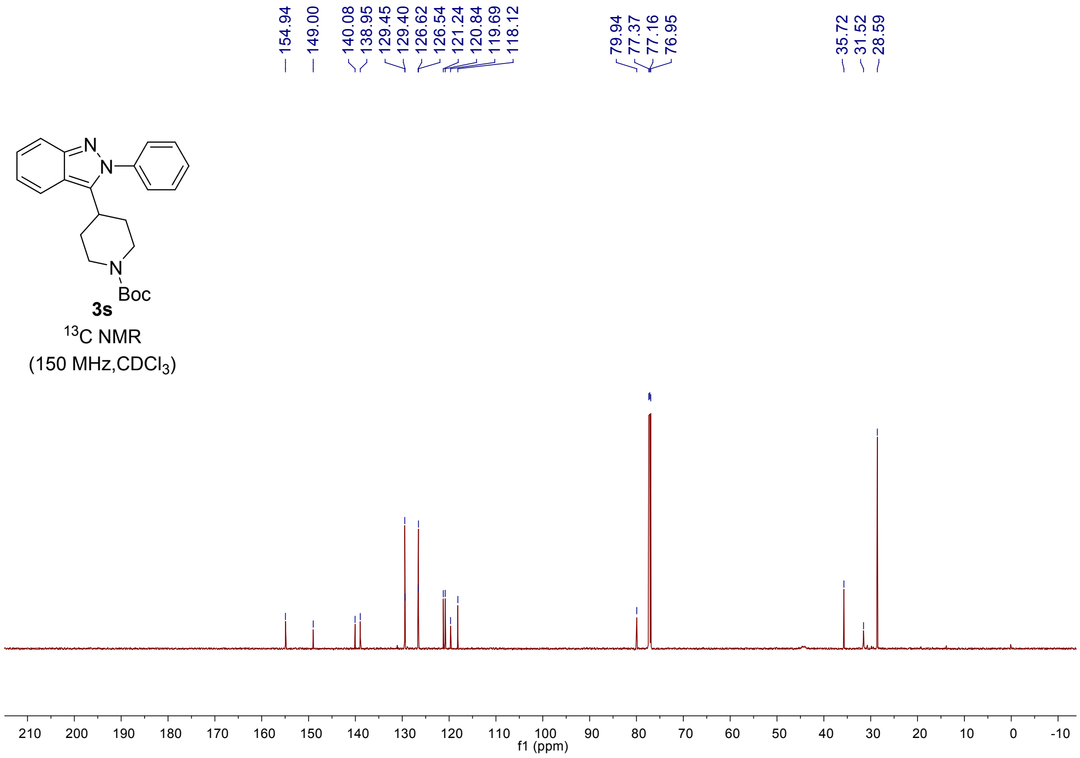
3r
^{13}C NMR
(150 MHz, $CDCl_3$)





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

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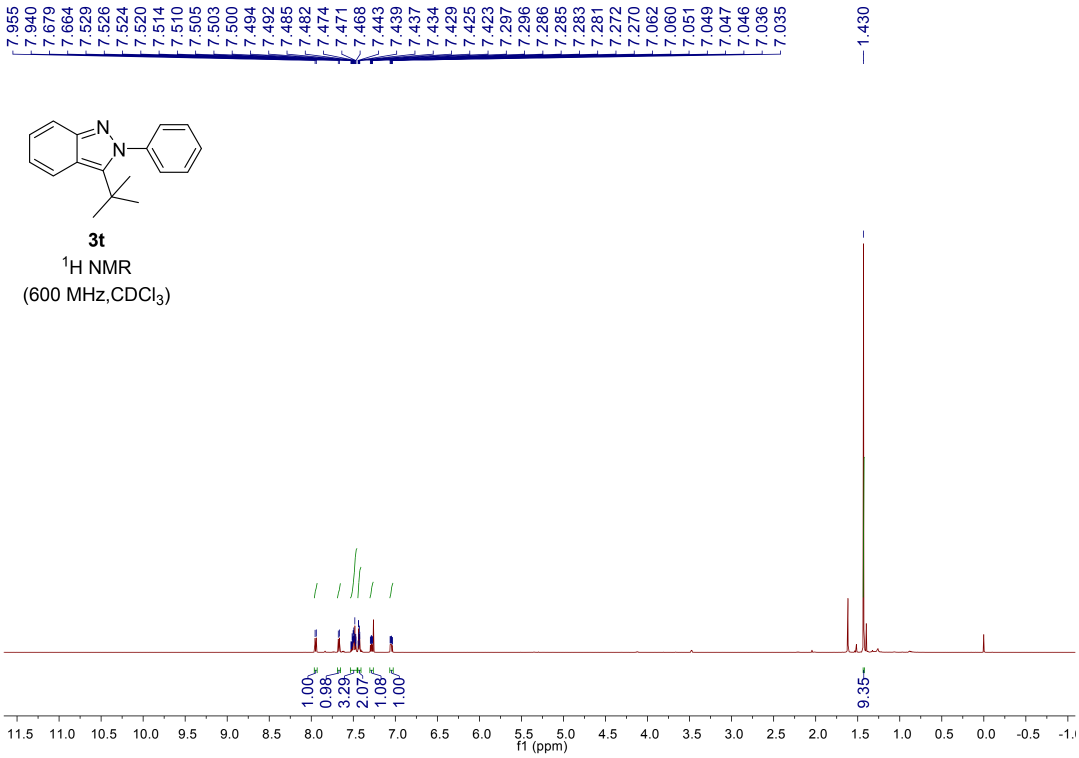
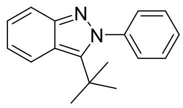
138.95
129.45
129.40
126.62
126.54
121.24
120.84
119.69
118.12
79.94
77.37
77.16
76.95
35.72
31.52
28.59
N
N
N
Boc
3s
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

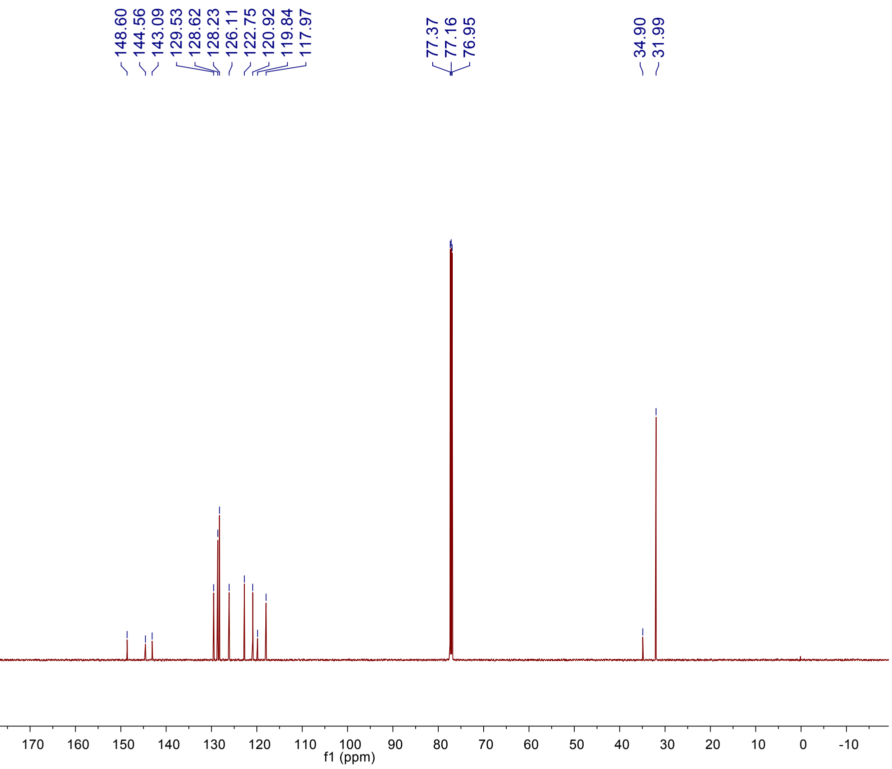

7.955
7.940
7.679
7.664
7.529
7.526
7.524
7.520
7.514
7.510
7.505
7.503
7.500
7.494
7.492
7.485
7.482
7.474
7.471
7.468
7.443
7.439
7.437
7.434
7.429
7.425
7.423
7.297
7.296
7.286
7.285
7.283
7.281
7.272
7.270
7.062
7.060
7.051
7.049
7.047
7.046
7.036
7.035
1.430
N
N
3t
1H NMR
(600 MHz,CDCl3)
1.00
0.98
3.29
2.07
1.08
1.00
9.35
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

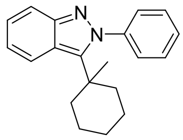


3t

^{13}C NMR

(150 MHz,$CDCl_3$)

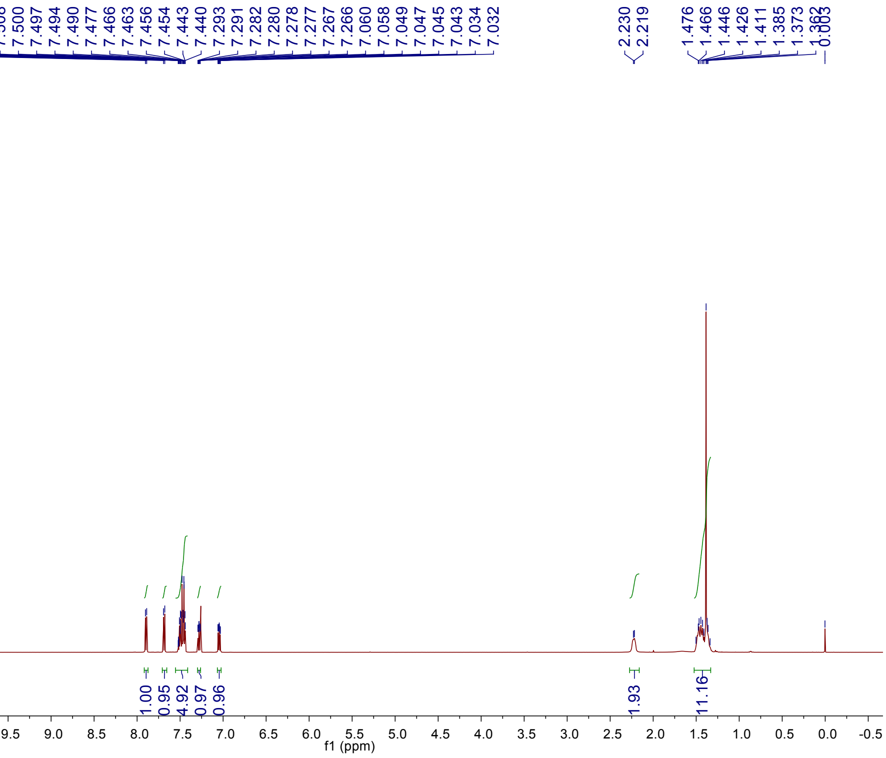


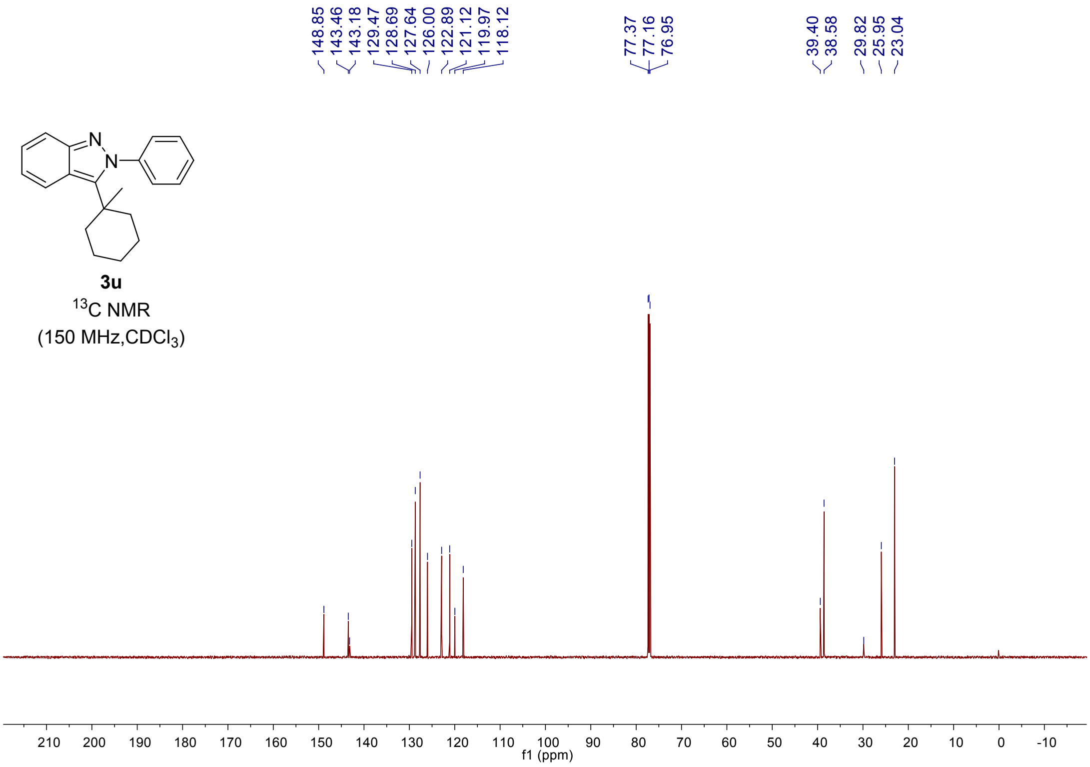


3u

^{1}H NMR

(600 MHz,$CDCl_3$)

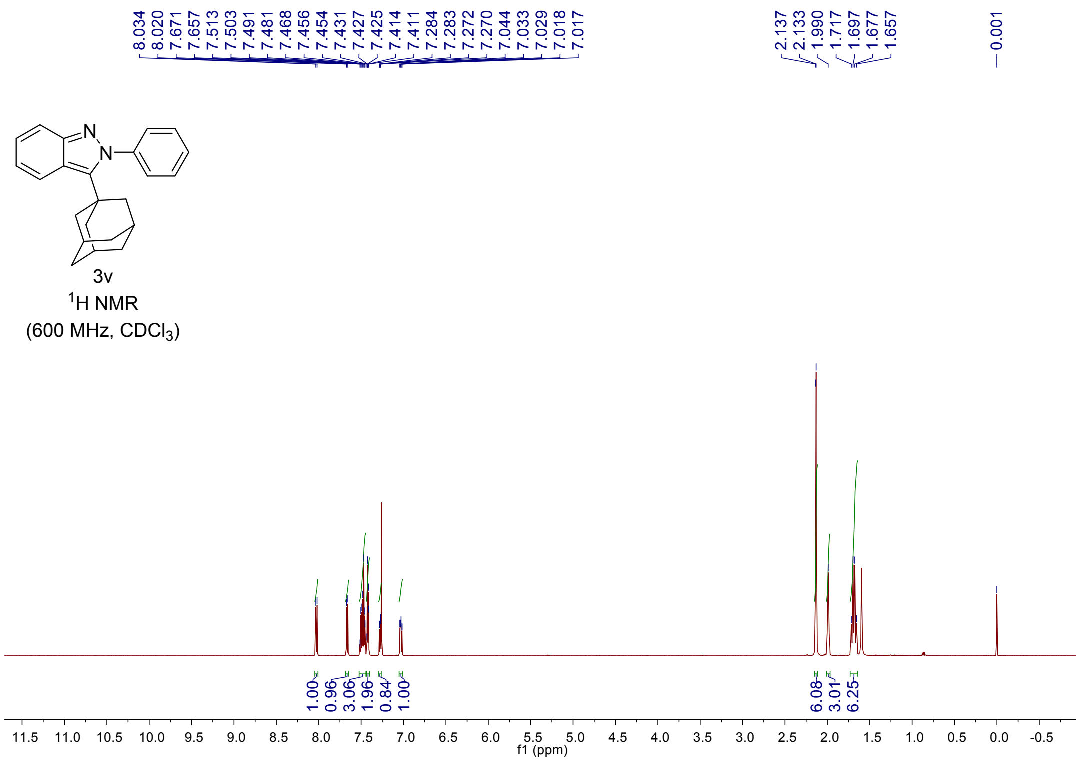




3u

^{13}C NMR

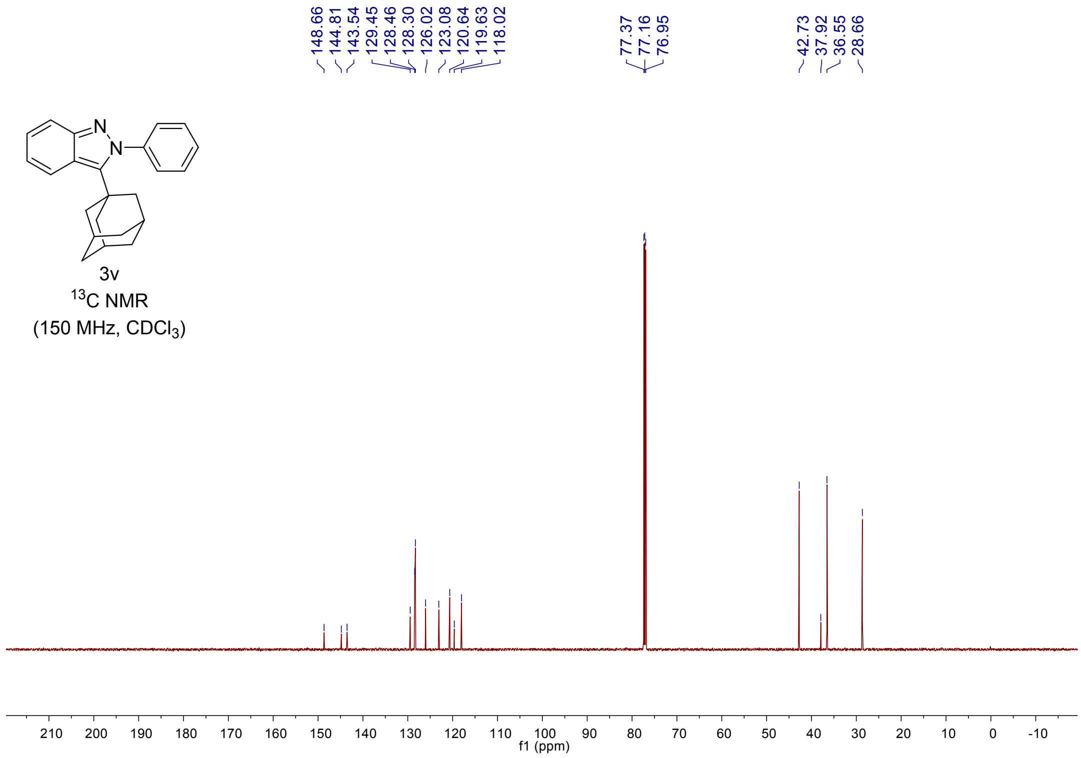
(150 MHz, $CDCl_3$)

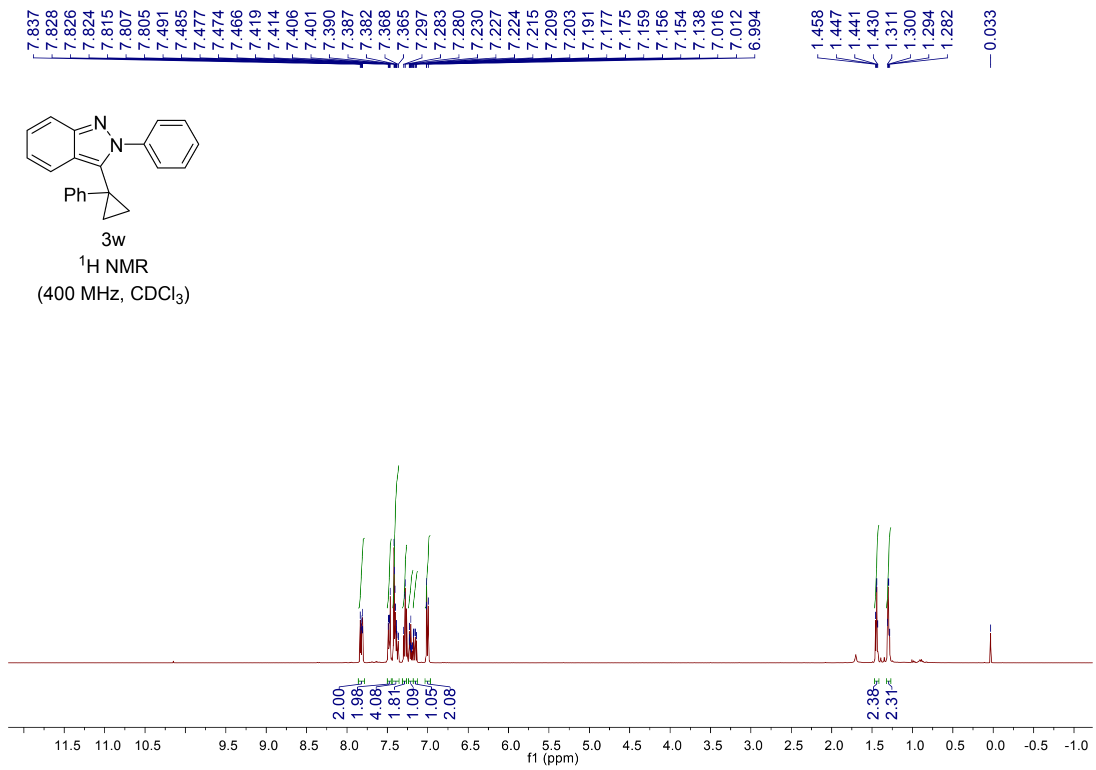


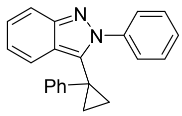
3v

^{1}H NMR

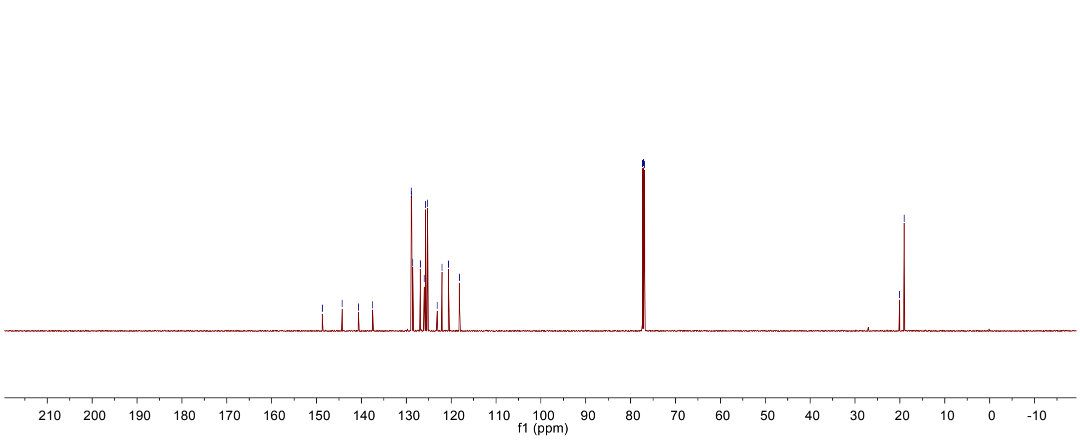
(600 MHz, $CDCl_3$)

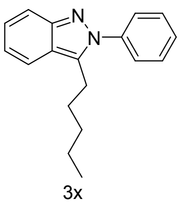

148.66
144.81
143.54
129.45
128.46
128.30
126.02
123.08
120.64
119.63
118.02
77.37
77.16
76.95
42.73
37.92
36.55
28.66
3v
13C NMR
(150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.837
7.828
7.826
7.824
7.815
7.807
7.805
7.491
7.485
7.477
7.474
7.466
7.419
7.414
7.406
7.401
7.390
7.387
7.382
7.368
7.365
7.297
7.283
7.280
7.230
7.227
7.224
7.215
7.209
7.203
7.191
7.177
7.175
7.159
7.156
7.154
7.138
7.016
7.012
6.994
1.458
1.447
1.441
1.430
1.311
1.300
1.294
1.282
-0.033
Ph
3w
1H NMR
(400 MHz, CDCl3)
2.00
1.98
4.08
1.81
1.09
1.05
2.08
2.38
2.31
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

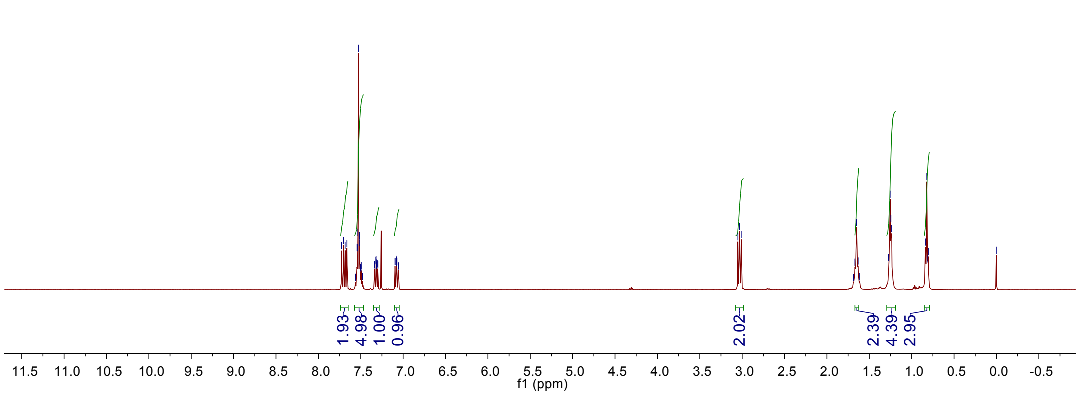


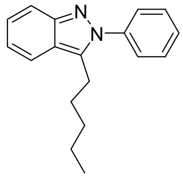
3w
^{13}C NMR
(150 MHz, $CDCl_3$)



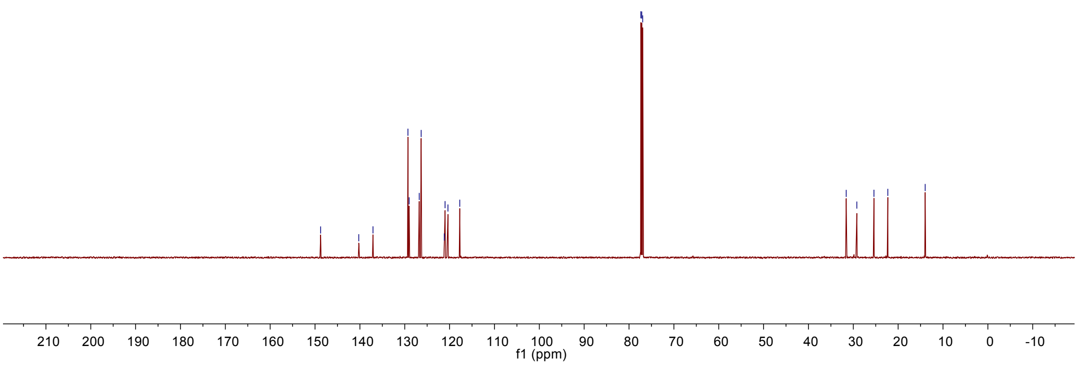


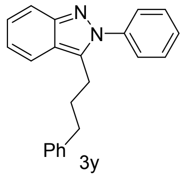
3x
^{1}H NMR
(400 MHz, $CDCl_3$)



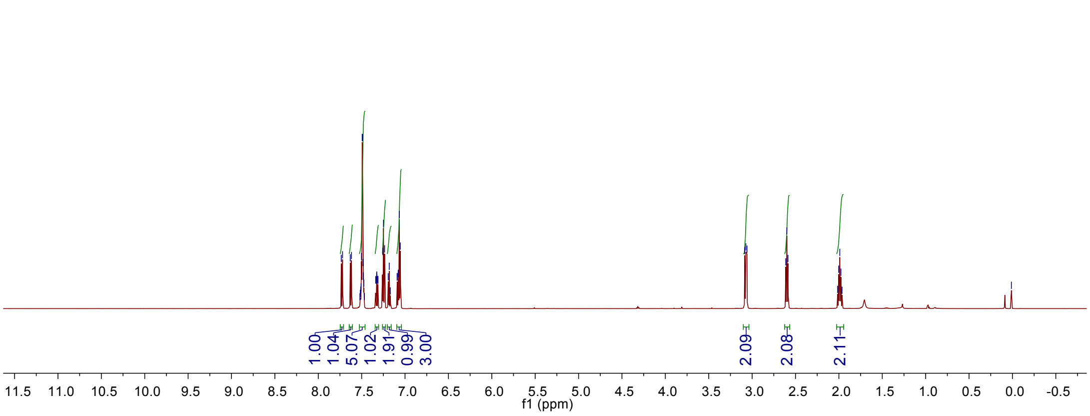


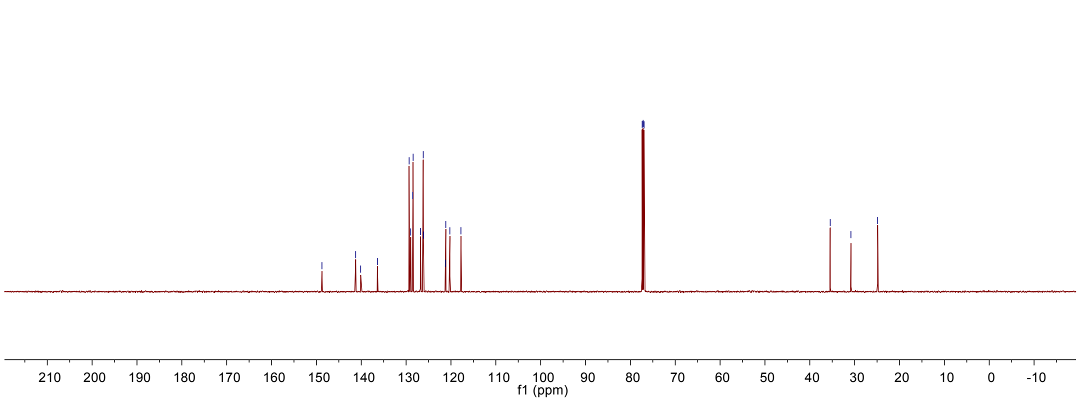
3x
^{13}C NMR
(150 MHz, $CDCl_3$)

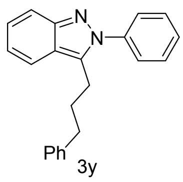




3y
^{1}H NMR
(600 MHz, $CDCl_3$)



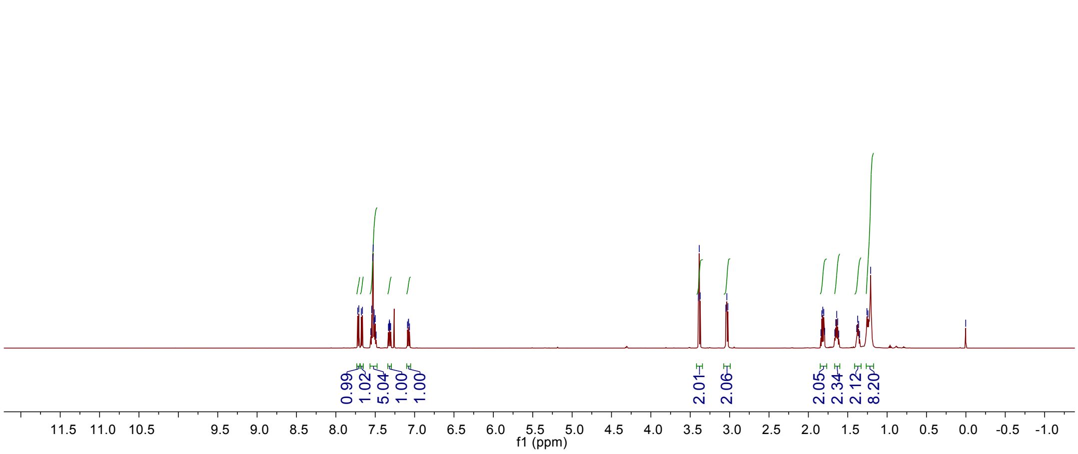


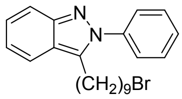


Ph 3y

^{13}C NMR

(150 MHz, $CDCl_3$)

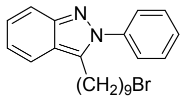




3z

^{1}H NMR

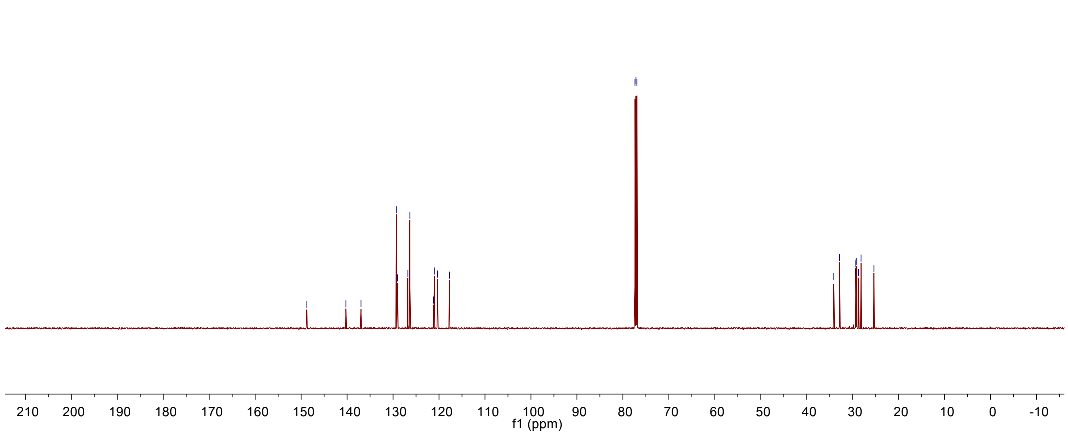
(600 MHz, $CDCl_3$)

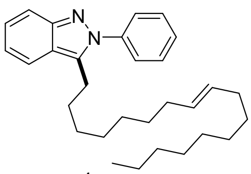


3z

^{13}C NMR

(150 MHz, $CDCl_3$)

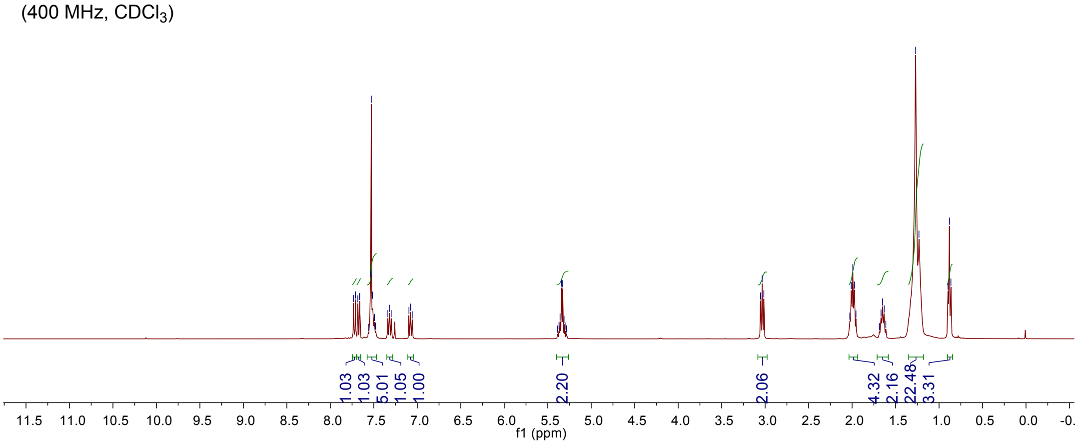


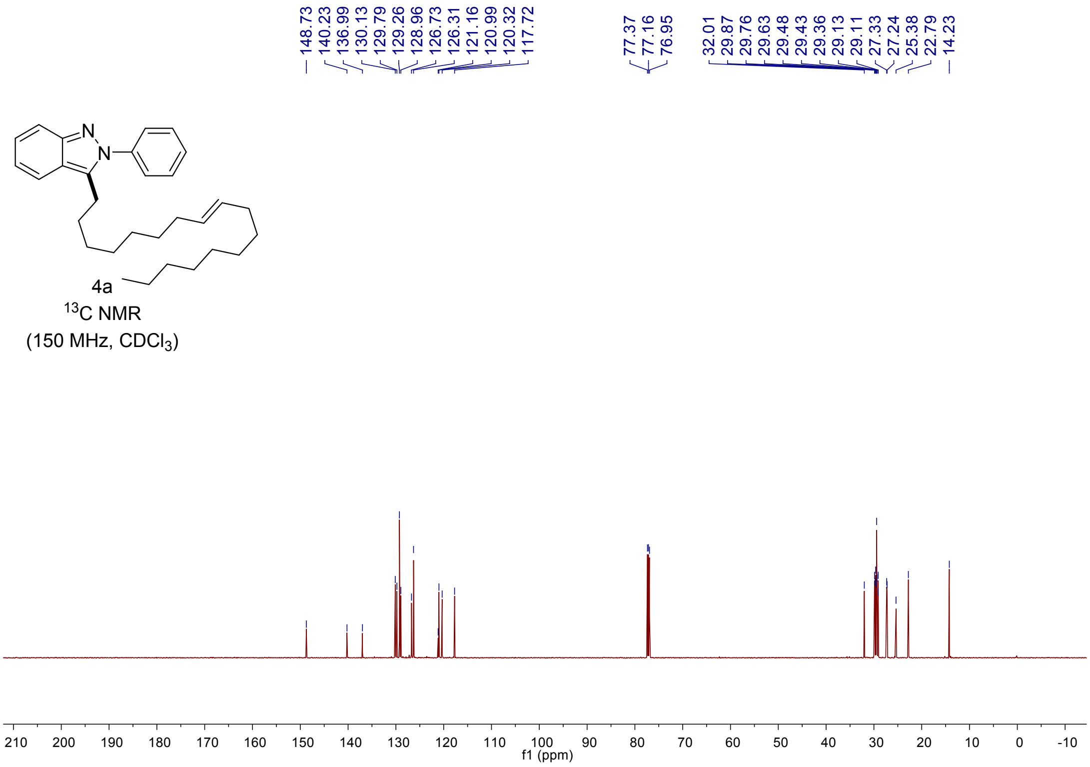


4a

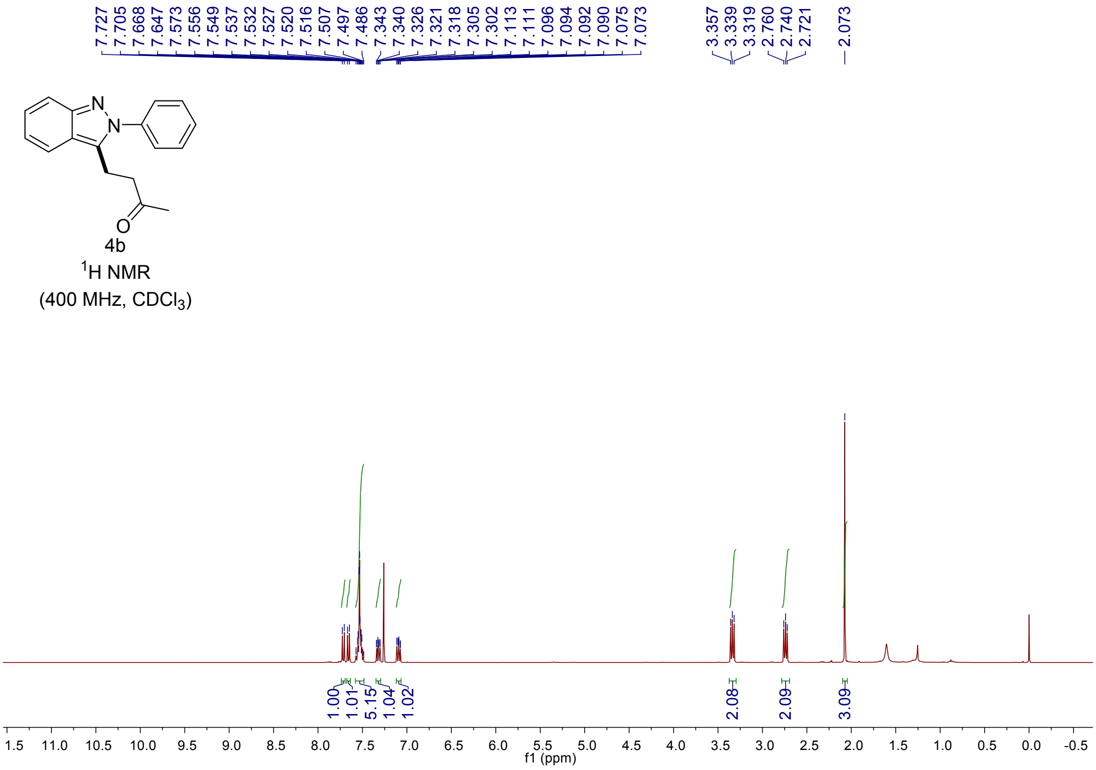
^{1}H NMR

(400 MHz, $CDCl_3$)

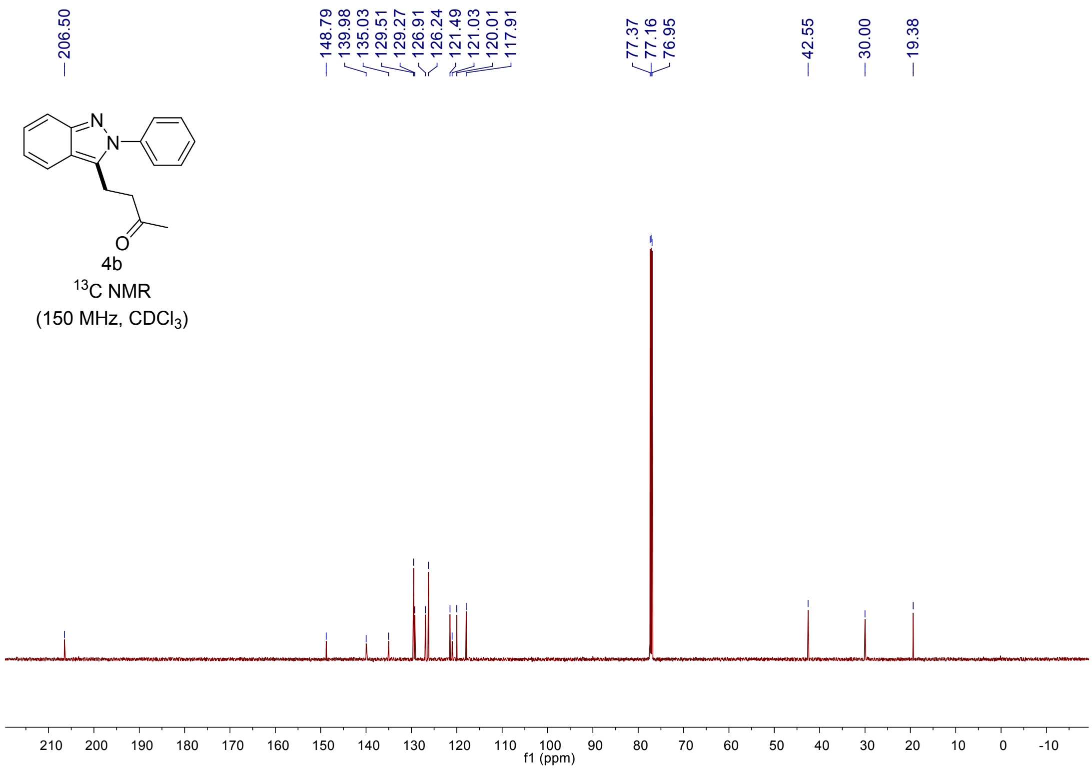


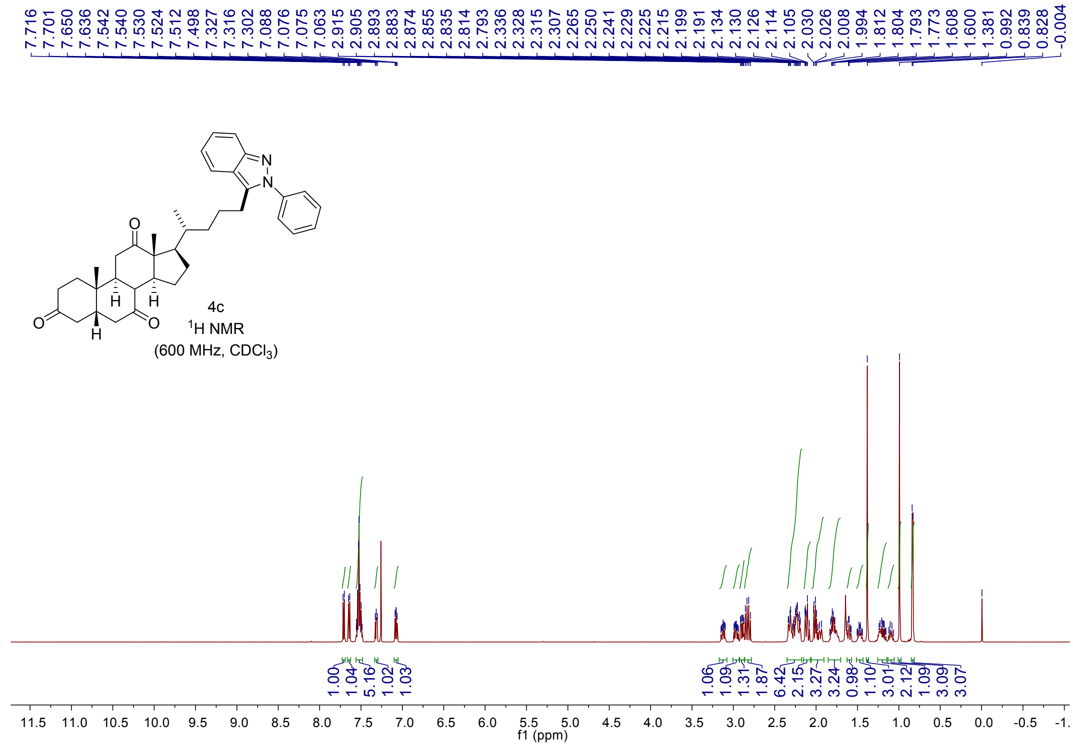


4a
^{13}C NMR
(150 MHz, $CDCl_3$)



4b
^{1}H NMR
(400 MHz, $CDCl_3$)


206.50
148.79
139.98
135.03
129.51
129.27
126.91
126.24
121.49
121.03
120.01
117.91
77.37
77.16
76.95
42.55
30.00
19.38
4b
13C NMR
(150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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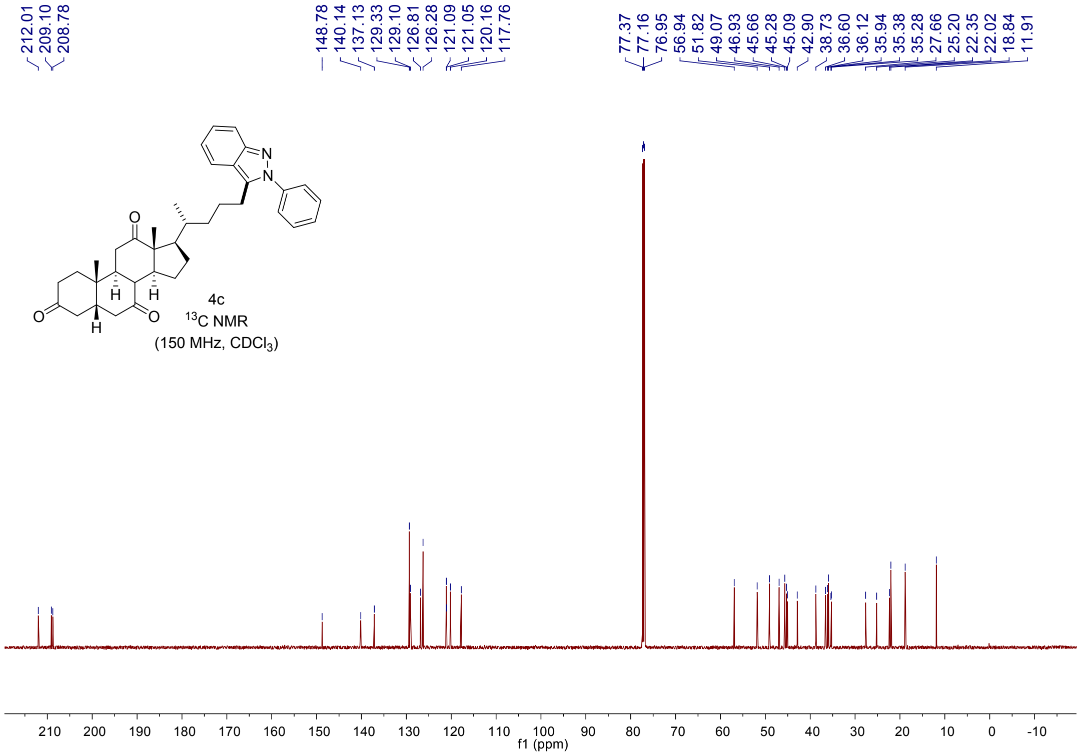
7.540
7.530
7.524
7.512
7.498
7.327
7.316
7.302
7.088
7.076
7.075
7.063
2.915
2.905
2.893
2.883
2.874
2.855
2.835
2.814
2.793
2.336
2.328
2.315
2.307
2.265
2.250
2.241
2.229
2.225
2.215
2.199
2.191
2.134
2.130
2.126
2.114
2.105
2.030
2.026
2.008
1.994
1.812
1.804
1.793
1.773
1.608
1.600
1.381
0.992
0.839
0.828
-0.004
4c
1H NMR
(600 MHz, CDCl3)
1.00
1.04
5.16
1.02
1.03
1.06
1.09
1.31
1.87
6.42
2.15
3.27
3.24
0.98
1.10
3.01
2.12
1.09
3.09
3.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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209.10
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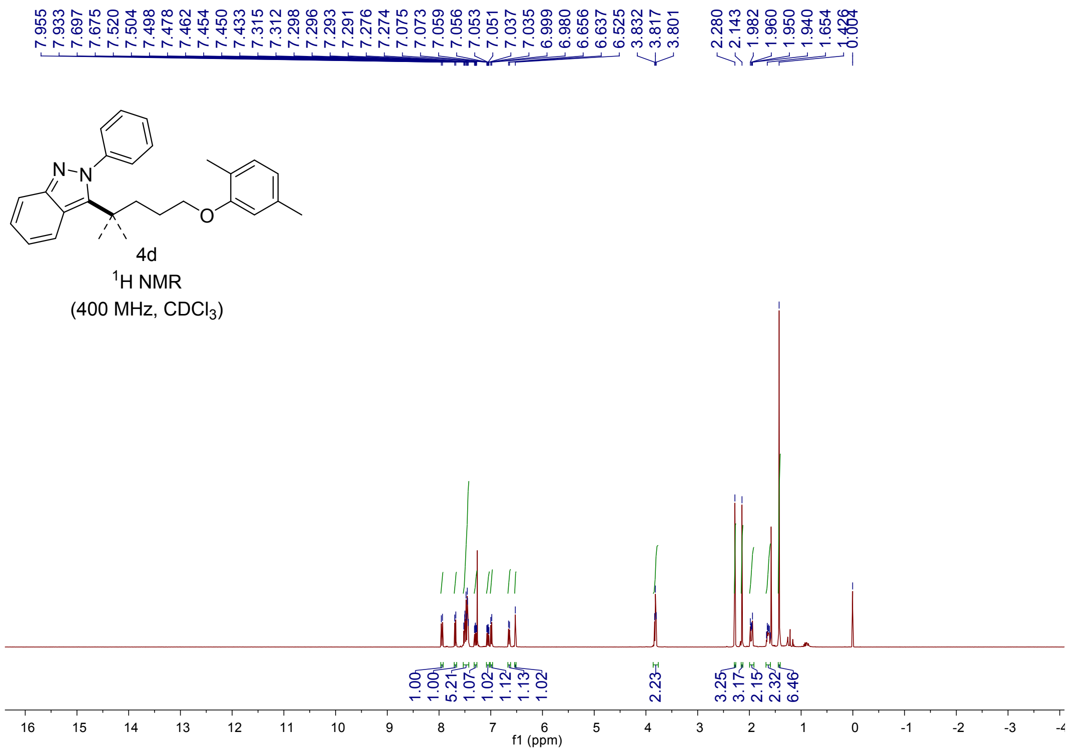
148.78
140.14
137.13
129.33
129.10
126.81
126.28
121.09
121.05
120.16
117.76
77.37
77.16
76.95
56.94
51.82
49.07
46.93
45.66
45.28
45.09
42.90
38.73
36.60
36.12
35.94
35.38
35.28
27.66
25.20
22.35
22.02
18.84
11.91
4c
^{13}C NMR
(150 MHz, CDCl$_3$)
f1 (ppm)


7.955
7.933
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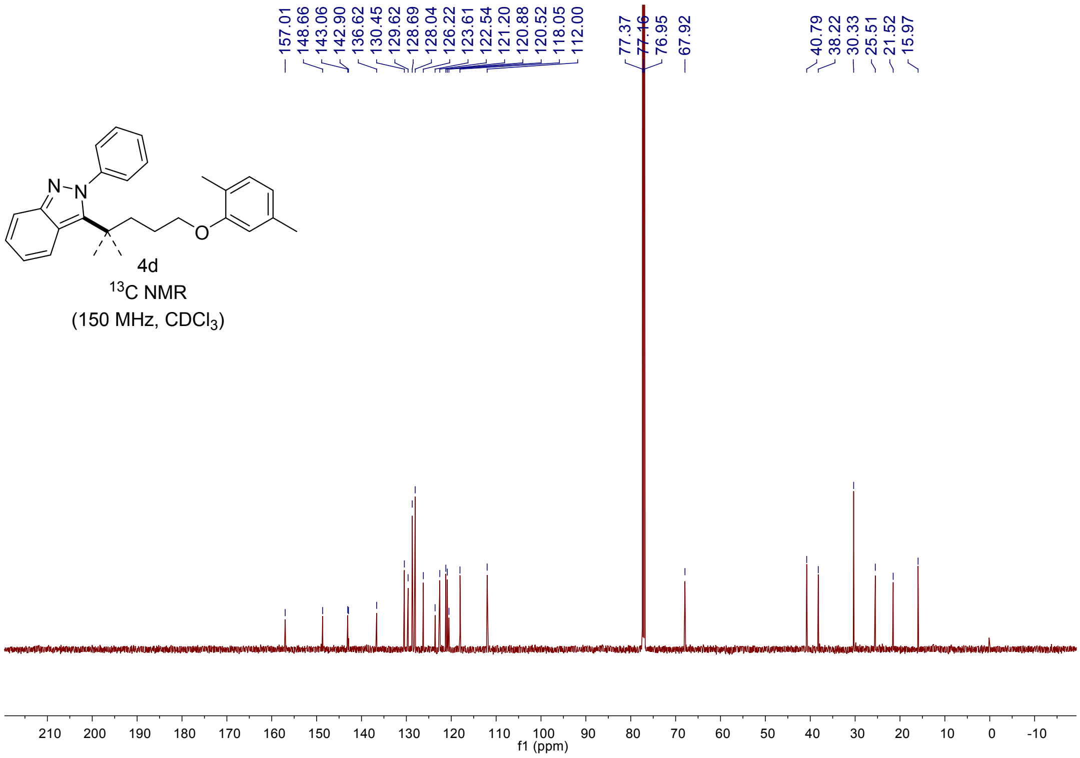
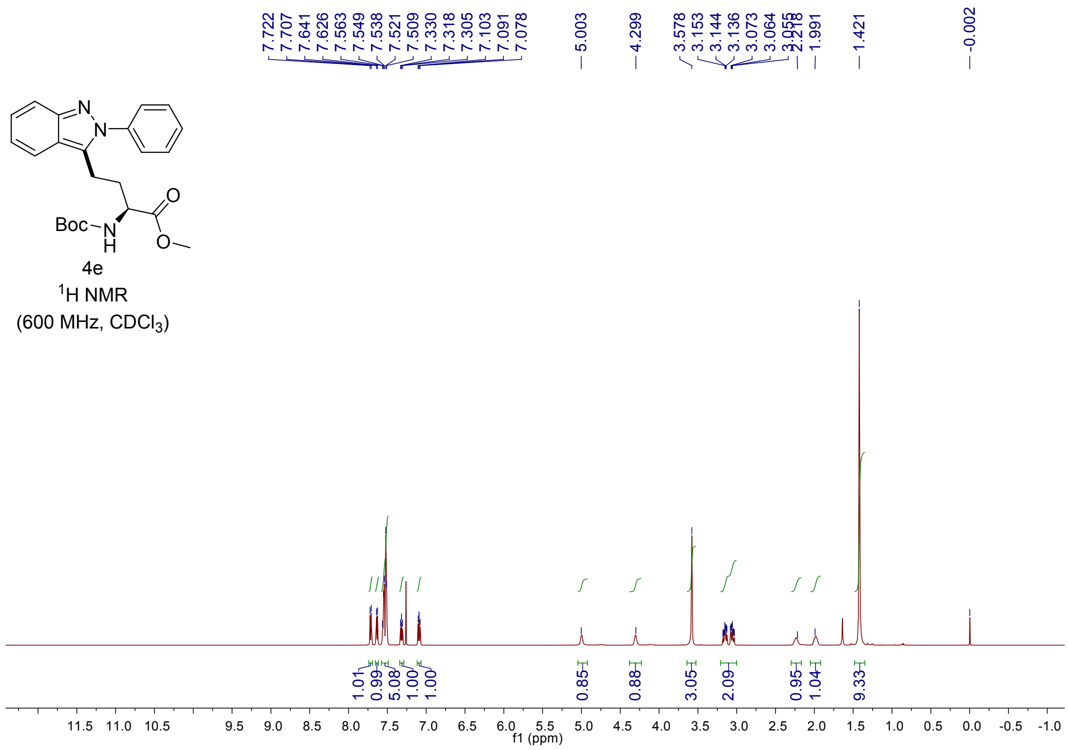
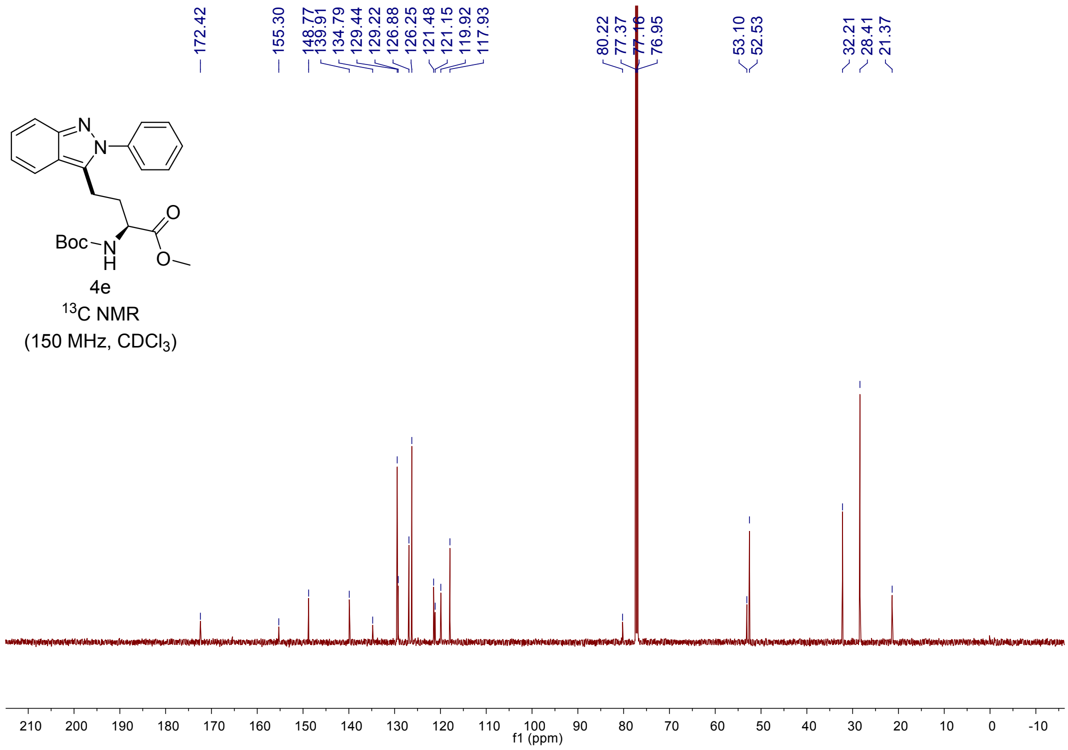
7.675
7.520
7.504
7.498
7.478
7.462
7.454
7.450
7.433
7.315
7.312
7.298
7.296
7.293
7.291
7.276
7.274
7.075
7.073
7.059
7.056
7.053
7.051
7.037
7.035
6.999
6.980
6.656
6.637
6.525
3.832
3.817
3.801
2.280
2.143
1.982
1.960
1.950
1.940
1.654
1.426
0.004
4d
^{1}H NMR
(400 MHz, CDCl$_3$)
1.00
1.00
5.21
1.07
1.02
1.12
1.13
1.02
2.23
3.25
3.17
2.15
2.32
6.46
f1 (ppm)


4d
^{13}C NMR
(150 MHz, $CDCl_3$)


4e
^{1}H NMR
(600 MHz, $CDCl_3$)



6. References

1. J. R. Hummel and J. A. Ellman, Cobalt(III)-Catalyzed Synthesis of Indazoles and Furans by C–H Bond Functionalization/Addition/Cyclization Cascades, *J. Am. Chem. Soc.*, 2015, **137**, 490-498.
2. L. Liu, P. Jiang, Y. Liu, H. Du and J. Tan, Direct radical alkylation and acylation of 2H-indazoles using substituted Hantzsch esters as radical reservoirs, *Organic Chemistry Frontiers*, 2020, **7**, 2278-2283.
3. Z. Long, Y. Yang and J. You, Rh(III)-Catalyzed [4 + 1]-Annulation of Azoxy Compounds with Alkynes: A Regioselective Approach to 2H-Indazoles, *Org. Lett.*, 2017, **19**, 2781-2784.