

## **ELECTRONIC SUPPLEMENTARY INFORMATION**

### **Cobalt-catalyzed Reductive C-H Alkylation of Indoles using Carboxylic Acids and Molecular Hydrogen**

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## 1. GENERAL INFORMATION

All reagents were obtained commercially from various chemical companies and were used without further purification. Phosphine ligand **L2** was synthetized according previously described methodology.<sup>[1]</sup> All hydrogenation experiments were carried out in 300 mL autoclave or 100 mL autoclave in the case of kinetic studies (PARR Instrument Company). In order to avoid unspecific reductions, all catalytic reactions were carried out in 8 mL glass vials, which were set in an alloy plate and placed inside the autoclave. In the case of kinetic studies a 100 mL glass inlet was used. GC conversion and yields were determined by GC-FID, HP 6890 with FID detector, column HP530 m x 250 mm x 0.25 µm. Mass spectra were recorded on a GC-MS Agilent 5973 Network equipped with a mass selective detector. All the products were isolated by silica gel column chromatography using as eluent (*n*-heptane / AcOEt) mixtures. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker AV 300 or Bruker AV 400 spectrometer. All chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and coupling constants ( $J$ ) in herzs (Hz). All chemical shifts are reported relative to CDCl<sub>3</sub> (deuterated chloroform) peaks ( $\delta$  7.26 for <sup>1</sup>H NMR and  $\delta$  77.16 for <sup>13</sup>C NMR) or CD<sub>3</sub>OD (deuterated methanol) peaks ( $\delta$  4.87 and 3.31 for <sup>1</sup>H NMR and  $\delta$  49.00 for <sup>13</sup>C NMR). All measurements were carried out at room temperature unless otherwise stated. HRMS measurements of the all isolated products were performed using the electrospray ionization technique in UPLC (ultra-pressure) equipment.

## 2. ADDITIONAL EXPERIMENTAL PROCEDURES

### General experimental procedure for the reductive C-H alkylation of 2-methyl-1*H*-indole (**1a**) with acetic acid

**(2a):** A 8 mL glass vial containing a stirring bar was sequentially charged with 2-methyl-1*H*-indole **1a** (67.0 mg, 0.5 mmol), Co(acac)<sub>3</sub> (3.6 mg, 0.01 mmol, 2 mol%), Triphos **L1** (12.5 mg, 0.02 mmol, 4 mol%, 2 eq to Co), Al(OTf)<sub>3</sub> (11.9 mg, 0.025 mmol, 5 mol%, 2.5 eq to Co), *n*-hexadecane (50.0 mg) as an internal standard, MCPE (2.0 mL) as solvent and acetic acid **2a** (50.3  $\mu$ L, 0.875 mmol, 1.75 eq). Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 30 bar of hydrogen, then pressurized to 30 bar and placed into an aluminium block, which was preheated at 160 °C. After 18 h, the autoclave was cooled in an ice bath, and the remaining gas was carefully released. Finally, the reaction mixture was diluted with ethyl acetate and analysed by GC.

**General experimental procedure for the reductive C-H alkylation of indoles with carboxylic acids:** A 8 mL glass vial containing a stirring bar was sequentially charged with the indole substrate (0.5 mmol), Co(acac)<sub>3</sub> (2-6 mol%), Triphos **L1** (4-12 mol%, 2 eq to Co), Al(OTf)<sub>3</sub> (5-15 mol%, 2.5 eq to Co), MCPE (2.0 mL) as solvent and the carboxylic acid (0.875-1.75 mmol, 1.75-3.5 eq). Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 30-60 bar of hydrogen, then pressurized to 30 bar and placed into an aluminium block, which was preheated at 120-160 °C. After 18-48 h, the autoclave was cooled in an ice bath, and the remaining gas was carefully released. Finally, the reaction mixture was diluted with ethyl acetate and purified by silica gel column chromatography (*n*-heptane / ethyl acetate mixtures) obtaining the desired C3-substituted indole derivatives.

**General experimental procedure for the kinetic studies:** A 100 mL glass inlet containing a stirring bar was sequentially charged with the 2-methyl-1*H*-indole **1a** (402.0 mg, 3.0 mmol), Co(acac)<sub>3</sub> (21.6 mg, 0.06 mmol, 2 mol%), Triphos **L1** (75.0 mg, 0.12 mmol, 4 mol%, 2 eq to Co), Al(OTf)<sub>3</sub> (71.4 mg, 0.15 mmol, 5 mol%, 2.5 eq to Co), *n*-hexadecane (250.0 mg) as an internal standard, MCPE (12.0 mL) as solvent and acetic acid **2a** or phenylacetic acid **2p** (5.25 mmol, 1.75 eq). Afterwards, the reaction inlet was then placed into a 100 mL autoclave. Once sealed, the autoclave was purged three times with 30 bar of hydrogen, then pressurized to 30 bar and placed into an aluminium block, which was preheated at 140 or 160 °C. Periodically, aliquots of 200  $\mu$ L were taken at different times of reaction, diluted with ethyl acetate and analysed by GC.

**Experimental procedure for the synthesis of 5-aminophenyl-2-methyl-1*H*-indole (**S9**) through Buchwald-Hartwig amination<sup>[2]</sup>:** A 50 mL Schlenk containing a stirring bar was sequentially charged under argon with bromobenzene **S7** (268.0  $\mu$ L, 2.5 mmol), 5-amino-2-methyl-1*H*-indole **S8** (448.8 mg, 3.0 mmol, 1.2 eq), Pd<sub>2</sub>(dba)<sub>3</sub> (22.8 mg, 0.025 mmol, 1 mol%, 2 mol% Pd), XPhos (96.3 mg, 0.2 mmol, 8 mol%), K<sub>2</sub>CO<sub>3</sub> (691.3 mg, 5.0 mmol, 2 eq), and dry 1,4-dioxane (15 mL) as solvent. Afterwards, the Schlenk was sealed and set in an oil bath at 100 °C during 16 h. When the reaction was complete, the crude reaction mixture was allowed to reach room temperature, passed to a funnel extraction, and 20 mL of distilled water were added. The aqueous phase was extracted three times with 20 mL of dichloromethane. The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered under gravity. The solvent was removed under reduced pressure. Finally, reaction mixture was purified by silica gel column chromatography (*n*-heptane / ethyl acetate mixtures) obtaining 5-aminophenyl-2-methyl-1*H*-indole **S9** in 56% yield.

**General experimental procedure for the synthesis of indole derivatives (**S11** and **S12**) through Suzuki-Miyaura cross coupling reactions<sup>[3]</sup>:** A 250 mL Schlenk containing a stirring bar was sequentially charged under argon with 5-bromo-2-methyl-1*H*-indole **S10** (552.8 mg, 2.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (116.0 mg, 0.1 mmol, 4 mol%) and dry toluene (50 mL) as solvent. Then, a solution of boronic acid (3.75 mmol, 1.5 eq) in dry ethanol (15 mL) was added to the reaction followed by saturated 25 mL aqueous NaHCO<sub>3</sub>. Afterwards, the Schlenk was sealed and set in an oil bath at reflux during 20 h. When the reaction was complete, the crude reaction mixture was allowed to reach room temperature and the solvent was evaporated. Next, 20 mL of distilled water and 30 mL of ethyl acetate were added to the crude and passed to a funnel extraction. The aqueous phase was extracted three times with 30 mL of ethyl acetate. The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered under gravity. The solvent was removed under reduced pressure. Finally, reaction mixture was purified by silica gel column chromatography (*n*-heptane / ethyl acetate mixtures) obtaining the corresponding indole derivative **S11** or **S12** in 43% or 70% yield, respectively.

**Experimental procedure for the synthesis of (*E*)-2-methyl-3-styryl-1*H*-indole (**3p'**)<sup>[4]</sup>:** A 100 mL Schlenk containing a stirring bar was sequentially charged with 2-methyl-1*H*-indole **1a** (804.0 mg, 6.0 mmol), FeCl<sub>3</sub>·6H<sub>2</sub>O (48.7 mg, 0.18 mmol, 3 mol%), ethanol (780.0 μL, 13.2 mmol, 2.2 eq) as additive and dichloromethane (36 mL) as solvent. Then, phenylacetaldehyde **S13** (735.0 μL, 6.6 mmol, 1.1 eq) was added to the reaction mixture. Afterwards, the Schlenk was sealed and set under agitation at room temperature during 3 h. When the reaction was complete, the solvent was removed under reduced pressure. Finally, reaction mixture was purified by silica gel column chromatography (*n*-heptane / ethyl acetate mixtures) obtaining the corresponding product **3p'** in 70% yield.

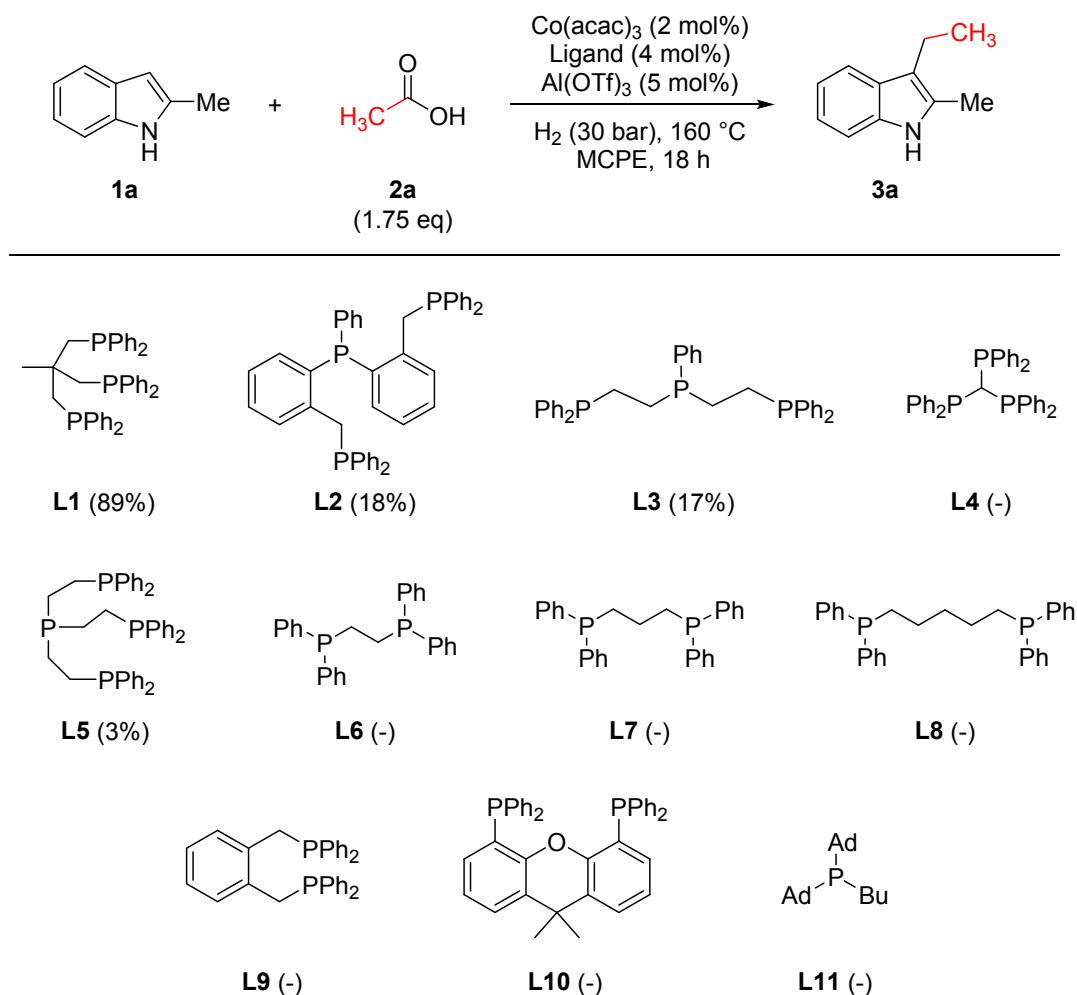
### 3. ADDITIONAL TABLES

**Table S1.** Study of the solvent effect in the cobalt-catalyzed reductive C-H alkylation of 2-methyl-1*H*-indole **1a** with acetic acid **2a** and molecular hydrogen

Entry <sup>[a]</sup>	Solvent	Conv. (%)	<b>3a</b> (%) <sup>[b]</sup>
1	THF	>99	70
2	THF:H <sub>2</sub> O (10:1)	48	7
3	1,4-dioxane	>99	72
4	Ethylenglycol diethyl ether	>99	74
5	Tetrahydropirane	>99	81
<b>6</b>	<b>MCPE</b>	<b>&gt;99</b>	<b>83</b>
7	2-Me-THF	>99	78
8	<i>n</i> -Bu <sub>2</sub> O	>99	65
9	Toluene	>99	76
10	DMF	2	-
11	MCPE:H <sub>2</sub> O (10:1)	13	2

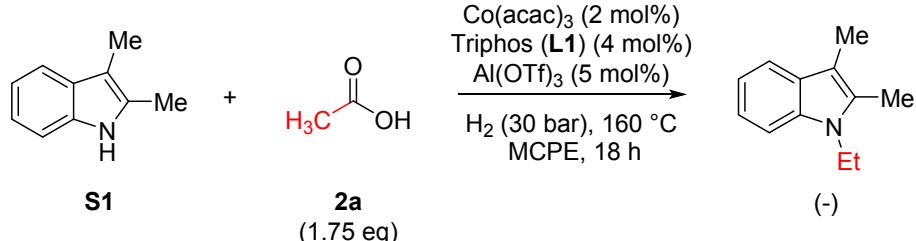
[a] Standard reaction conditions: 2-methyl-1*H*-indole **1a** (67.0 mg, 0.5 mmol), Co(acac)<sub>3</sub> (7.2 mg, 0.02 mmol, 4 mol%), Triphos (**L1**) (25.0 mg, 0.04 mmol, 8 mol%, 2 eq to Co), Al(OTf)<sub>3</sub> (23.8 mg, 0.05 mmol, 10 mol%, 2.5 eq to Co), solvent (2 mL), acetic acid **2a** (50.3 µL, 0.875 mmol, 1.75 eq) and H<sub>2</sub> (30 bar) at 160 °C during 18 h. [b] Conversions of **1a** and yields of product **3a** were calculated by GC using hexadecane as internal standard.

#### 4. ADDITIONAL SCHEMES

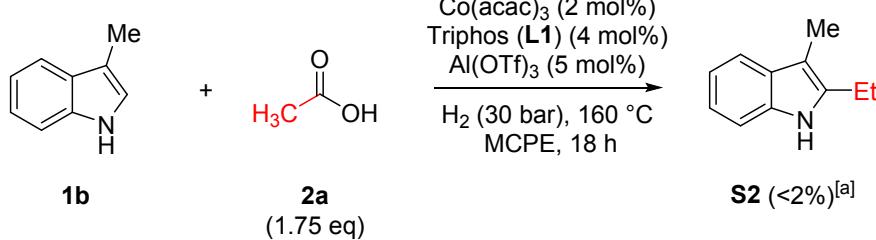


**Scheme S1.** Influence of the ligand in the formation of product **3a** by the cobalt-catalyzed reductive C-H alkylation of 2-methyl-1*H*-indole **1a** with acetic acid **2a**. Standard reaction conditions: 2-methyl-1*H*-indole **1a** (67.0 mg, 0.5 mmol),  $\text{Co}(\text{acac})_3$  (3.6 mg, 0.01 mmol, 2 mol%), ligand (0.02 mmol, 4 mol%, 2 eq to Co),  $\text{Al}(\text{OTf})_3$  (11.9 mg, 0.025 mmol, 5 mol%, 2.5 eq to Co), MCPE (2 mL), acetic acid **2a** (50.3  $\mu\text{L}$ , 0.875 mmol, 1.75 eq) and  $\text{H}_2$  (30 bar) at 160 °C during 18 h. In parentheses is shown the yield of product **3a** calculated by GC using hexadecane as internal standard.

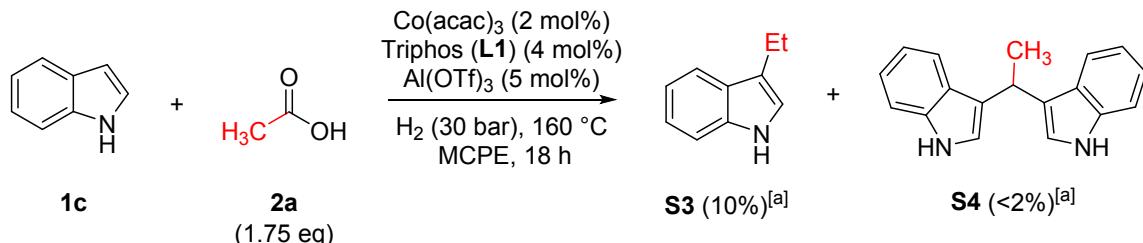
(A)



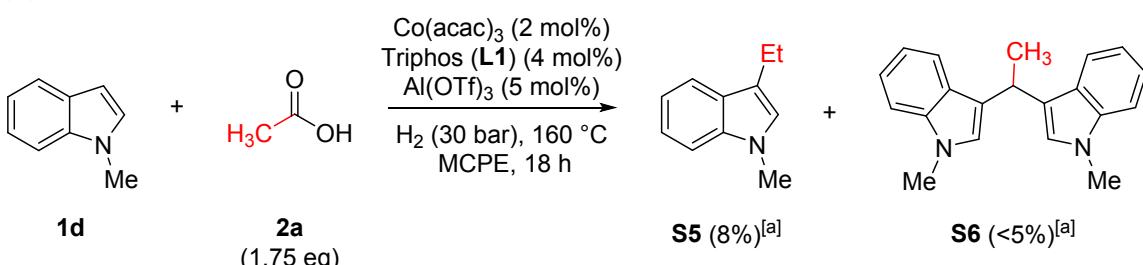
(B)



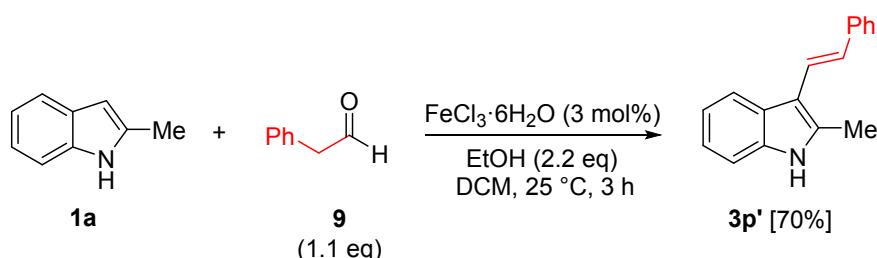
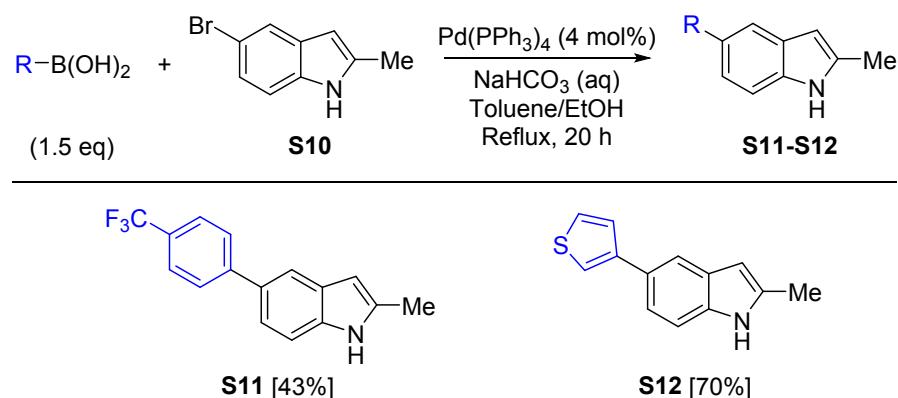
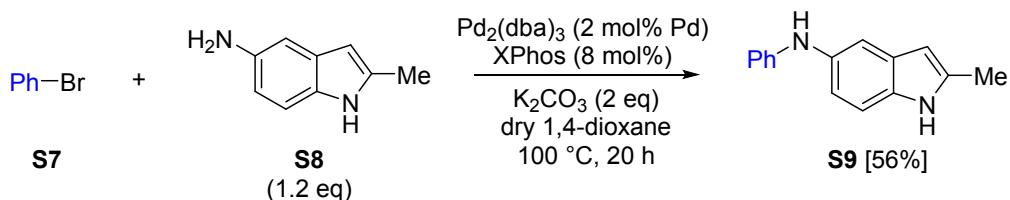
(C)

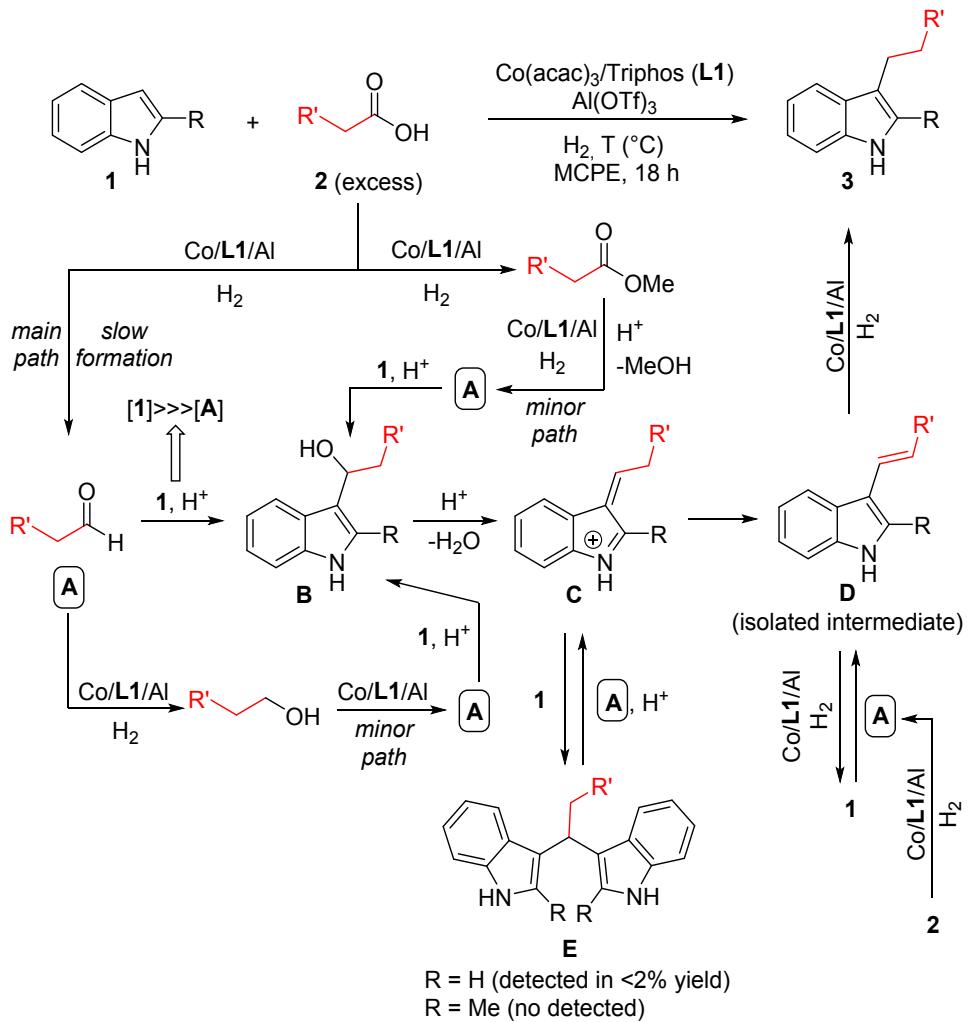


(D)



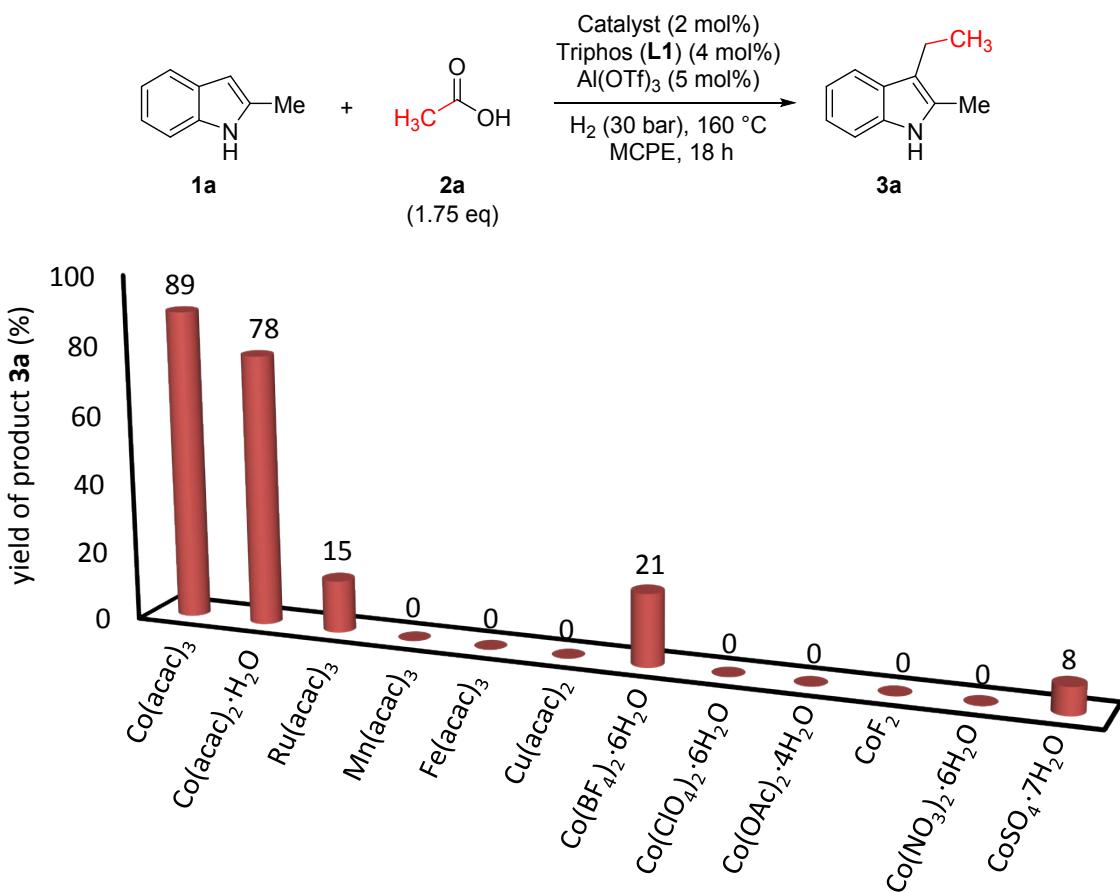
**Scheme S2.** Catalytic studies for the cobalt-catalyzed reductive C-H alkylation of 2,3-dimethyl-1*H*-indole (**S1**) (eq. A), 3-methyl-1*H*-indole (**1b**) (eq. B), 1*H*-indole (**1c**) and 1-methylindole (**1d**) (eq. D) with acetic acid **2a**. Standard reaction conditions: indole derivative (0.5 mmol),  $\text{Co}(\text{acac})_3$  (3.6 mg, 0.01 mmol, 2 mol%), Triphos (**L1**) (12.5 mg, 0.02 mmol, 4 mol%, 2 eq to Co),  $\text{Al}(\text{OTf})_3$  (11.9 mg, 0.025 mmol, 5 mol%, 2.5 eq to Co), MCPE (2 mL), acetic acid **2a** (50.3  $\mu\text{L}$ , 0.875 mmol, 1.75 eq) and  $\text{H}_2$  (30 bar) at 160 °C during 18 h. [a] The yield of product **S2**, **S3**, **S4**, **S5** and **S6** was calculated by GC using hexadecane as internal standard.



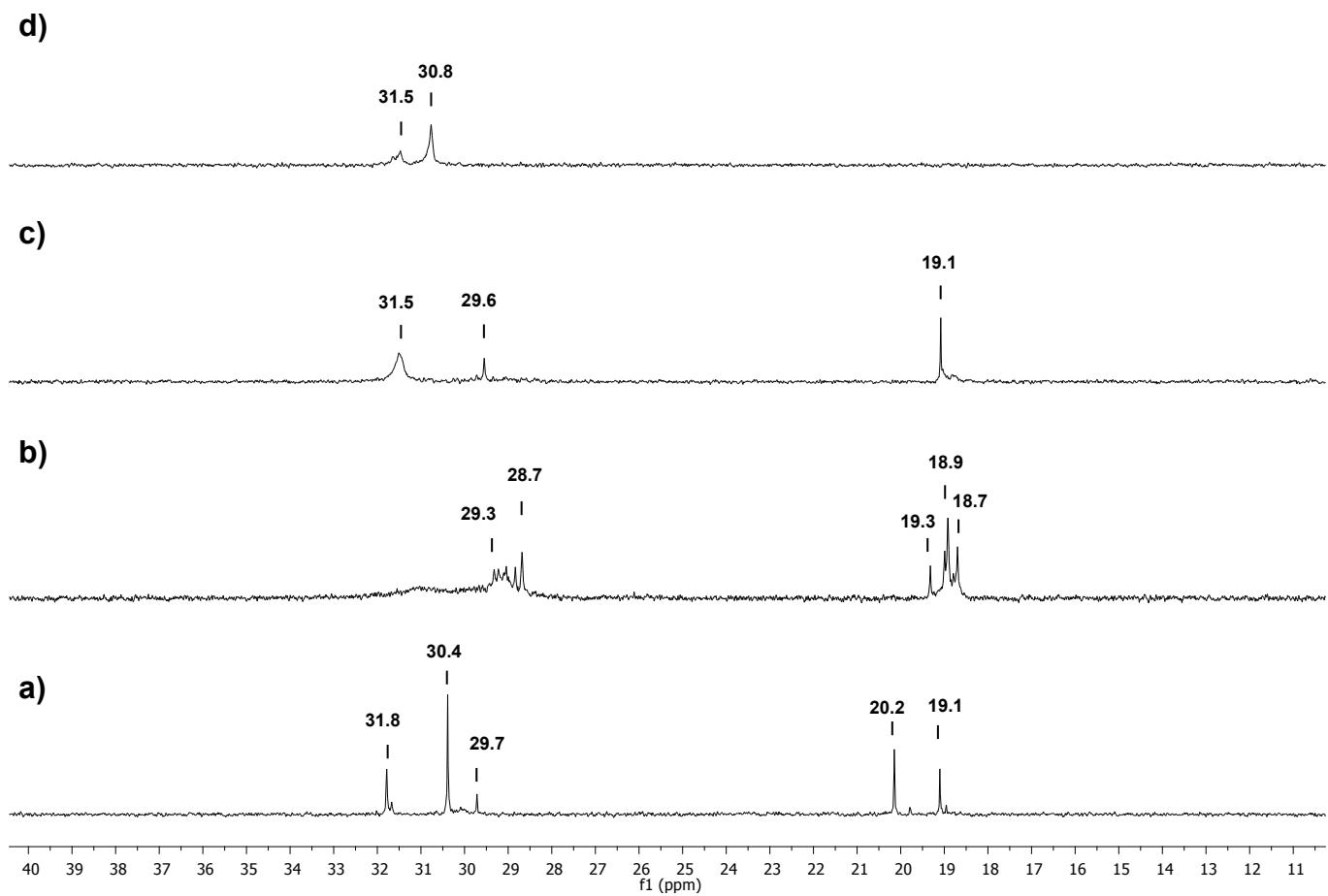


**Scheme S6.** Possible reaction mechanism for the  $[\text{Co}/\text{L1}/\text{Al}(\text{OTf})_3]$ -catalyzed reductive alkylation of indoles with carboxylic acids. Extended version that contains the minor pathways that are involved in the general process.

## 5. ADDITIONAL FIGURES

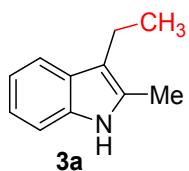


**Figure S1.** Influence of the metal precatalyst in the formation of product **3a** by the reductive C-H alkylation of 2-methyl-1*H*-indole **1a** with acetic acid **2a**. Standard reaction conditions: 2-methyl-1*H*-indole **1a** (67.0 mg, 0.5 mmol), metal precatalyst (0.01 mmol, 2 mol%), Triphos (**L1**) (12.5 mg, 0.02 mmol, 4 mol%, 2 eq to M), Al(O Tf)<sub>3</sub> (11.9 mg, 0.025 mmol, 5 mol%, 2.5 eq to M), MCPE (2 mL), acetic acid **2a** (50.3 µL, 0.875 mmol, 1.75 eq) and H<sub>2</sub> (30 bar) at 160 °C during 18 h. Yields of product **3a** were calculated by GC using hexadecane as internal standard.

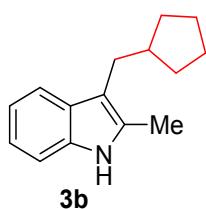


**Figure S2.**  $^{31}\text{P}\{\text{H}\}$  NMR (122 MHz,  $\text{CD}_3\text{OD}$ ) of: a) Standard reaction mixture:  $[\text{Co}(\text{acac})_3$  (7.2 mg, 0.02 mmol, 4 mol%), Triphos (**L1**) (25.0 mg, 0.04 mmol, 8 mol%, 2 eq to Co),  $\text{Al}(\text{OTf})_3$  (23.8 mg, 0.05 mmol, 10 mol%, 2.5 eq to Co), 2-methyl-1*H*-indole **1a** (67.0 mg, 0.5 mmol) and acetic acid **2a** (50.3  $\mu\text{L}$ , 0.875 mmol, 1.75 eq) in MCPE (2mL), at 160 °C, under  $\text{H}_2$  (30 bar) during 18 h] after evaporation of MCPE; b) Standard reaction mixture without 2-methyl-1*H*-indole **1a** after evaporation of MCPE; c) Standard reaction mixture without 2-methyl-1*H*-indole **1a** and acetic acid **2a** after evaporation of MCPE; d) Standard reaction mixture without 2-methyl-1*H*-indole **1a**, acetic acid **2a** and  $\text{Al}(\text{OTf})_3$  after evaporation of MCPE.

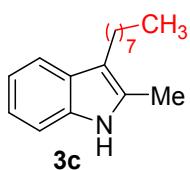
## 6. CHARACTERIZATION DATA OF THE ISOLATED PRODUCTS



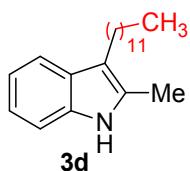
**3-ethyl-2-methyl-1*H*-indole (3a).**<sup>[5]</sup> Isolated yield: 80%. GC-MS (m/z, M<sup>+</sup> 159), major peaks found: 159 (35%), 144 (100%), 128 (5%), 115 (10%), 77 (8%). (The NMR spectrum is consistent with the reported data). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.60-7.34 (m, NH+1H), 7.13-7.09 (m, 1H), 7.04-7.00 (m, 1H), 7.00-6.95 (m, 1H), 2.61 (q, J = 7.6, 2H), 2.21 (s, 3H), 1.13 (t, J = 7.6, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.38, 130.23, 128.60, 120.91, 119.08, 118.20, 114.08, 110.26, 17.50, 15.56, 11.64. HRMS (ESI) [M+Na<sup>+</sup>; calculated for C<sub>11</sub>H<sub>13</sub>N: 159.1042] found m/z 159.1043.



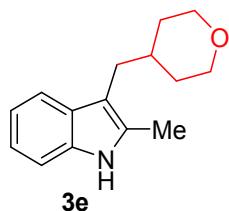
**3-(cyclopentylmethyl)-2-methyl-1*H*-indole (3b).** Isolated yield: 80%. GC-MS (m/z, M<sup>+</sup> 213), major peaks found: 213 (18%), 144 (100%), 128 (4%), 115 (5%), 77 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.48-7.40 (m, 2H), 7.12-7.07 (m, 1H), 7.04-6.94 (m, 2H), 2.58 (d, J = 7.3, 2H), 2.21 (s, 3H), 2.16-2.03 (m, 1H), 1.64-1.50 (m, 4H), 1.47-1.35 (m, 2H), 1.22-1.15 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.28, 130.96, 129.20, 120.77, 118.96, 118.43, 112.19, 110.20, 41.90, 32.75, 29.99, 24.98, 11.90. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>15</sub>H<sub>19</sub>N: 213.1512] found m/z 213.1514.



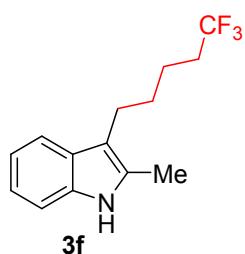
**2-methyl-3-octyl-1*H*-indole (3c).** Isolated yield: 67%. GC-MS (m/z, M<sup>+</sup> 243), major peaks found: 243 (20%), 144 (100%), 130 (5%), 115 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.50 (bs, NH), 7.44-7.39 (m, 1H), 7.16-7.10 (m, 1H), 7.04-7.00 (m, 1H), 7.00-6.94 (m, 1H), 2.58 (t, J = 7.4, 2H), 2.23 (s, 3H), 1.52 (quint, J = 7.1, 2H), 1.18 (bs, 10H), 0.84-0.74 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.33, 130.67, 128.93, 120.81, 119.00, 118.27, 112.57, 110.22, 32.08, 30.94, 29.80, 29.72, 29.52, 24.27, 22.83, 14.26, 11.75. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>25</sub>N: 243.1982] found m/z 243.1988.



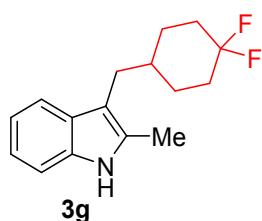
**2-methyl-3-dodecyl-1*H*-indole (3d).** Isolated yield: 74%. GC-MS (m/z, M<sup>+</sup> 299), major peaks found: 299 (15%), 144 (100%), 130 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.47 (bs, NH), 7.43-7.38 (m, 1H), 7.12-7.07 (m, 1H), 7.04-6.99 (m, 1H), 6.99-6.93 (m, 1H), 2.57 (t, J = 8.2, 2H), 2.20 (s, 3H), 1.58-1.45 (m, 2H), 1.17 (bs, 18H), 0.80 (t, J = 7.4, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.34, 130.67, 128.92, 120.78, 118.98, 118.26, 112.51, 110.24, 32.08, 30.94, 29.86, 29.80, 29.77, 29.52, 24.27, 22.85, 14.27, 11.69. HRMS (ESI) [M+Na<sup>+</sup>; calculated for C<sub>21</sub>H<sub>33</sub>N: 299.2607] found m/z 299.2607.



**2-methyl-3-((tetrahydro-2*H*-pyran-4-yl)methyl)-1*H*-indole (3e).** Isolated yield: 59%. GC-MS (m/z, M<sup>+</sup> 229), major peaks found: 229 (18%), 144 (100%), 115 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.79 (bs, NH), 7.42-7.36 (m, 1H), 7.16-7.10 (m, 1H), 7.06-6.95 (m, 2H), 3.86 (dd, J = 11.0, 3.8, 2H), 3.22 (td, J = 11.9, 2.1, 2H), 2.53 (d, J = 7.1, 2H), 2.23 (s, 3H), 1.83-1.65 (m, 1H), 1.51 (dd, J = 13.0, 1.9, 2H), 1.37-1.21 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.32, 131.64, 129.10, 120.88, 119.05, 118.22, 110.28, 109.87, 68.20, 36.70, 33.43, 31.64, 11.90. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>15</sub>H<sub>19</sub>ON: 229.1461] found m/z 229.1464.

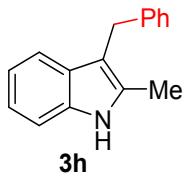


**2-methyl-3-(5,5,5-trifluoropentyl)-1*H*-indole (3f).** Isolated yield: 74%. GC-MS (m/z, M<sup>+</sup> 255), major peaks found: 255 (35%), 144 (100%), 128 (5%), 115 (7%), 77 (7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.67 (bs, NH), 7.50-7.45 (m, 1H), 7.27-7.23 (m, 1H), 7.15-7.04 (m, 2H), 2.72 (t, J = 7.1, 2H), 2.34 (s, 3H), 2.15-2.00 (m, 2H), 1.74-1.67 (m, 2H), 1.66-1.58 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.38, 131.03, 128.69, 127.39 (q, *J*<sup>1</sup><sub>C-F</sub> = 276.4, CF<sub>3</sub>), 121.07, 119.22, 118.07, 111.46, 110.35, 33.81 (q, *J*<sup>2</sup><sub>C-F</sub> = 28.3), 29.85, 23.87, 21.84 (q, *J*<sup>3</sup><sub>C-F</sub> = 2.8), 11.74. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ: -65.89 (t, J = 11.0, 3F). HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>14</sub>H<sub>16</sub>NF<sub>3</sub>: 255.1229] found m/z 255.1229.

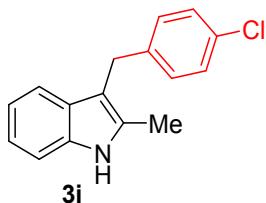


**3-((4,4-difluorocyclohexyl)methyl)-2-methyl-1*H*-indole (3g).** Isolated yield: 70%. GC-MS (m/z, M<sup>+</sup> 263), major peaks found: 263 (18%), 144 (100%), 115 (5%), 77 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.73 (bs, NH), 7.49 (dd, J =

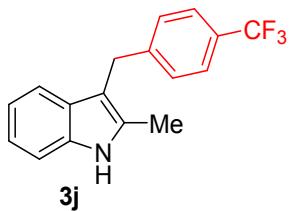
6.6, 1.9, 1H), 7.30-7.25 (m, 1H), 7.18-7.06 (m, 2H), 2.64 (d,  $J$  = 6.9, 2H), 2.37 (s, 3H), 2.14-2.01 (m, 2H), 1.86-1.74 (m, 3H), 1.73-1.58 (m, 2H), 1.45-1.34 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 135.32, 131.53, 129.04, 124.14 (dd,  $J^1_{\text{C}-\text{F}} = 241.8, 239.4$ ), 121.06, 119.21, 118.25, 110.47, 110.32, 37.56 (d,  $J^4_{\text{C}-\text{F}} = 1.0$ ), 33.70 (dd,  $J^2_{\text{C}-\text{F}} = 25.3, 22.3$ ), 30.67 (d,  $J^5_{\text{C}-\text{F}} = 2.8$ ), 29.31 (d,  $J^3_{\text{C}-\text{F}} = 9.7$ ), 11.96.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -90.96 (d,  $J$  = 234.5, 1F), -99.93-(-103.26) (m, 1F). HRMS (ESI) [M $^+$ ; calculated for  $\text{C}_{16}\text{H}_{19}\text{NF}_2$ : 263.1480] found m/z 263.1477.



**3-benzyl-2-methyl-1H-indole (3h).**<sup>[6]</sup> Isolated yield: 75%. GC-MS (m/z, M $^+$  221), major peaks found: 221 (95%), 206 (40%), 178 (15%), 144 (100%), 128 (5%), 115 (8%), 102 (10%), 77 (8%). (The NMR spectrum is consistent with the reported data).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.59 (bs, NH), 7.31 (d,  $J$  = 7.8, 1H), 7.18-7.11 (m, 5H), 7.10-7.04 (m, 1H), 7.01 (td,  $J$  = 7.5, 1.3, 1H), 6.94 (td,  $J$  = 7.5, 1.2, 1H), 3.97 (s, 2H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.77, 135.38, 131.76, 129.00, 128.40, 128.38, 125.78, 121.10, 119.36, 118.49, 110.65, 110.26, 30.22, 11.90. HRMS (ESI) [M $^+$ ; calculated for  $\text{C}_{16}\text{H}_{15}\text{N}$ : 221.1199] found m/z 221.1200.

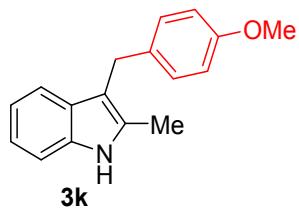


**3-(4-chlorobenzyl)-2-methyl-1H-indole (3i).** Isolated yield: 64%. GC-MS (m/z, M $^+$  255), major peaks found: 257 (25%), 255 (75%), 242 (10%), 240 (30%), 204 (10%), 144 (100%), 108 (18%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.59 (bs, NH), 7.24 (d,  $J$  = 7.8, 1H), 7.17-7.12 (m, 1H), 7.11-7.06 (m, 2H), 7.05-6.98 (m, 3H), 6.97-6.90 (m, 1H), 3.91 (s, 2H), 2.22 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.21, 135.37, 131.85, 131.42, 129.69, 128.77, 128.45, 121.24, 119.47, 118.32, 110.36, 110.10, 29.57, 11.83. HRMS (ESI) [M $^+$ ; calculated for  $\text{C}_{16}\text{H}_{14}\text{NCl}$  ( $^{37}\text{Cl}$ ): 257.0779] found m/z 257.0795 and [M $^+$ ; calculated for  $\text{C}_{16}\text{H}_{14}\text{NCl}$  ( $^{35}\text{Cl}$ ): 255.0809] found m/z 255.0814.

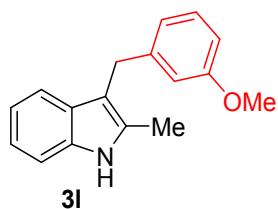


**2-methyl-3-(4-(trifluoromethyl)benzyl)-1H-indole (3j).**<sup>[7]</sup> Isolated yield: 49%. GC-MS (m/z, M $^+$  289), major peaks found: 289 (100%), 274 (35%), 144 (100%), 102 (7%). (The NMR spectrum is consistent with the reported data).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.79 (bs, NH), 7.52 (d,  $J$  = 8.1, 2H), 7.40 (d,  $J$  = 7.6, 1H), 7.37-7.28 (m, 3H), 7.21-7.14 (m, 1H), 7.09 (ddd,  $J$  = 8.1, 7.1, 1.1, 1H), 4.15 (s, 2H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 145.90, 135.41, 132.04, 128.73, 128.61, 127.93, 125.33 (q,  $J$  = 3.8), 124.53 (q,  $J^1_{\text{C}-\text{F}} = 271.8, \text{CF}_3$ ), 121.37, 119.58, 118.24, 110.43,

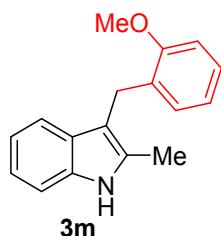
109.63, 30.07, 11.83.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -61.73 (s, 3F). HRMS (ESI) [ $M^+$ ; calculated for  $\text{C}_{17}\text{H}_{14}\text{NF}_3$ : 289.1072] found m/z 289.1066.



**3-(3-methoxybenzyl)-2-methyl-1H-indole (3k).**<sup>[6]</sup> Isolated yield: 46%. GC-MS (m/z,  $M^+$  251), major peaks found: 251 (100%), 236 (40%), 220 (8%), 206 (8%), 192 (8%), 144 (95%), 130 (7%). (The NMR spectrum is consistent with the reported data).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.68 (s, 1H), 7.32-7.27 (m, 1H), 7.18-7.13 (m, 1H), 7.06-7.01 (m, 2H), 7.01-6.97 (m, 1H), 6.96-6.90 (m, 1H), 6.71-6.65 (m, 2H), 3.91 (s, 2H), 3.65 (s, 3H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 157.72, 135.39, 133.89, 131.61, 129.22, 128.96, 121.04, 119.29, 118.47, 113.79, 110.97, 110.24, 55.34, 29.30, 11.88. HRMS (ESI) [ $M^+$ ; calculated for  $\text{C}_{17}\text{H}_{17}\text{ON}$ : 251.1304] found m/z 251.1310.

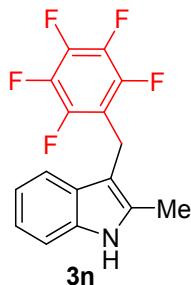


**3-(3-methoxybenzyl)-2-methyl-1H-indole (3l).**<sup>[6]</sup> Isolated yield: 68%. GC-MS (m/z,  $M^+$  251), major peaks found: 251 (100%), 236 (40%), 220 (8%), 206 (8%), 192 (8%), 144 (95%), 130 (7%). (The NMR spectrum is consistent with the reported data).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.53 (bs, NH), 7.30 (d,  $J$  = 8.3, 1H), 7.12-7.07 (m, 1H), 7.04 (t,  $J$  = 7.9, 1H), 7.01-6.95 (m, 1H), 6.95-6.89 (m, 1H), 6.74-6.66 (m, 2H), 6.59 (dd,  $J$  = 8.0, 2.4, 1H), 3.92 (s, 2H), 3.61 (s, 3H), 2.19 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.68, 143.53, 135.35, 131.79, 129.33, 128.94, 121.03, 120.89, 119.31, 118.40, 114.40, 110.80, 110.37, 110.26, 55.16, 30.20, 11.78. HRMS (ESI) [ $M+\text{Na}^+$ ; calculated for  $\text{C}_{17}\text{H}_{17}\text{ON}$ : 251.1304] found m/z 251.1309.

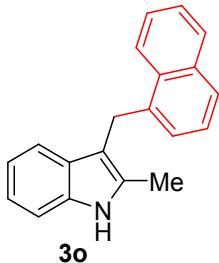


**3-(2-methoxybenzyl)-2-methyl-1H-indole (3m).**<sup>[6]</sup> Isolated yield: 47%. GC-MS (m/z,  $M^+$  251), major peaks found: 251 (100%), 236 (50%), 220 (20%), 144 (85%), 130 (48%). (The NMR spectrum is consistent with the reported data).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.74 (bs, NH), 7.33 (d,  $J$  = 7.8, 1H), 7.16 (d,  $J$  = 8.5, 1H), 7.09-7.04 (m, 1H), 7.03-6.99 (m, 1H), 6.96 (dd,  $J$  = 7.8, 1.2, 1H), 6.94-6.88 (m, 1H), 6.77 (d,  $J$  = 8.5, 1H), 6.69 (d,  $J$  = 7.4, 1H), 3.94 (s, 2H), 3.79 (s, 3H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 157.31, 135.41, 132.13, 129.78, 129.39, 129.28, 126.84, 120.88,

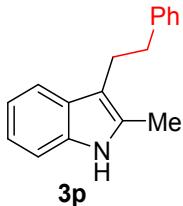
120.40, 119.14, 118.67, 110.18, 109.92, 109.78, 55.36, 23.87, 11.83. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>17</sub>ON: 251.1305] found m/z 251.1323.



**2-methyl-3-((perfluorophenyl)methyl)-1H-indole (3n).** Isolated yield: 35%. GC-MS (m/z, M<sup>+</sup>: 311), major peaks found: 311 (100%), 296 (25%), 276 (10%), 219 (10%), 144 (95%), 120 (10%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.63 (bs, NH), 7.47-7.37 (m, 1H), 7.15-7.11 (m, 1H), 7.06-7.01 (m, 1H), 7.01-6.96 (m, 1H), 3.96 (s, 2H), 2.36 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 147.35-143.17 (m), 141.95-137.56 (m), 139.71-135.53 (m), 135.12, 132.34, 127.97, 121.49, 119.78, 117.79 (t, J<sub>C-F</sub> = 3.2), 115.30-114.29 (m), 110.39, 107.34, 17.48, 11.76 (t, J<sub>C-F</sub> = 2.6). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): -142.36 (dd, J = 22.5, 8.0, 2F), -157.75 (t, J = 20.9, 1F), -162.42 (td, J = 22.2, 7.9, 2F). HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>16</sub>H<sub>10</sub>NF<sub>5</sub>: 311.0728] found m/z 311.0727.

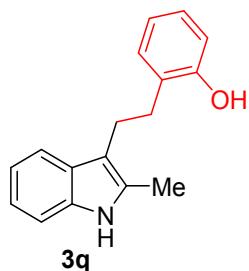


**2-methyl-3-(naphthalen-1-ylmethyl)-1H-indole (3o).**<sup>[7]</sup> Isolated yield: 73%. GC-MS (m/z, M<sup>+</sup>: 271), major peaks found: 271 (100%), 256 (50%), 207 (10%), 144 (100%), 127 (18%). (The NMR spectrum is consistent with the reported data). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.38-8.30 (m, 1H), 8.00-7.94 (m, 1H), 7.79 (d, J = 8.2, 1H), 7.72 (bs, NH), 7.67-7.55 (m, 2H), 7.43 (d, J = 7.8, 1H), 7.40-7.31 (m, 2H), 7.27-7.15 (m, 2H), 7.14-7.07 (m, 1H), 4.60 (s, 2H), 2.32 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 136.73, 135.43, 133.78, 132.33, 132.30, 129.27, 128.83, 126.61, 125.95, 125.75, 125.60, 125.56, 123.68, 121.11, 119.37, 118.56, 110.32, 109.22, 27.15, 11.85. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>20</sub>H<sub>17</sub>N: 271.1355] found m/z 271.1356.

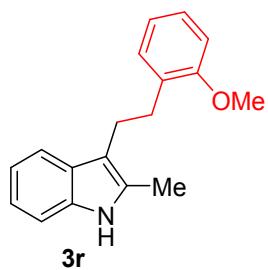


**2-methyl-3-phenethyl-1H-indole (3p).**<sup>[8]</sup> Isolated yield: 78%. GC-MS (m/z, M<sup>+</sup>: 235), major peaks found: 235 (15%), 144 (100%), 115 (5%), 91 (7%). (The NMR spectrum is consistent with the reported data). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.46-7.41 (m, 1H), 7.36 (bs, NH), 7.17-7.06 (m, 4H), 7.05-6.95 (m, 4H), 2.90-2.83 (m, 2H), 2.82-2.74 (m, 2H), 1.93 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.56, 135.33, 131.34, 128.74, 128.62, 128.29, 125.82, 120.90, 119.13,

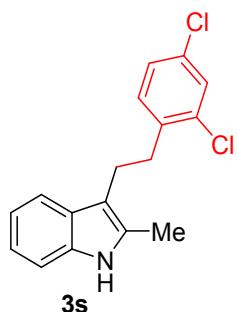
118.01, 111.10, 110.32, 37.05, 26.65, 11.31. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>17</sub>N: 235.1355] found m/z 235.1358.



**2-(2-methyl-1*H*-indol-3-yl)ethylphenol (3q).** Isolated yield: 70%. GC-MS (m/z, M<sup>+</sup> 251), major peaks found: 251 (15%), 207 (5%), 144 (100%), 115 (5%), 77 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.58 (bs, NH), 7.49 (dd, J = 6.2, 2.7, 1H), 7.17 (dd, J = 6.4, 2.4, 1H), 7.08-6.94 (m, 4H), 6.76 (td, J = 7.4, 1.2, 1H), 6.61 (dd, J = 8.4, 1.1, 1H), 4.50 (bs, OH), 2.96-2.87 (m, 2H), 2.86-2.79 (m, 2H), 1.97 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 135.43, 131.83, 131.69, 130.76, 128.25, 127.41, 126.21, 121.25, 120.93, 119.42, 117.96, 115.56, 110.90, 110.42, 31.51, 25.00, 11.21. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>17</sub>ON: 251.1304] found m/z 251.1307.

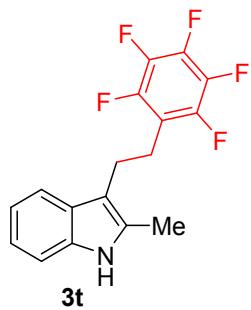


**3-(2-methoxyphenethyl)-2-methyl-1*H*-indole (3r).** Isolated yield: 55%. GC-MS (m/z, M<sup>+</sup> 265), major peaks found: 265 (15%), 144 (100%), 115 (5%), 91 (7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.35 (dd, J = 6.7, 1.9, 1H), 7.25 (bs, NH), 7.09 (dd, J = 6.7, 1.6, 1H), 7.02-6.96 (m, 1H), 6.89 (dd, J = 7.0, 1.4, 1H), 6.84 (dd, J = 6.7, 1.2, 1H), 6.78 (dd, J = 7.3, 1.7, 1H), 6.73 (d, J = 8.1, 1H), 6.66-6.60 (m, 1H), 3.64 (s, 3H), 2.78 (dd, J = 11.7, 4.3, 2H), 2.71 (dd, J = 11.2, 4.9, 2H), 1.98 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 158.98, 137.06, 132.50, 131.91, 131.22, 128.06, 121.43, 121.25, 121.02, 119.16, 118.55, 111.75, 111.25, 111.11, 55.67, 32.96, 25.81, 11.05. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>18</sub>H<sub>19</sub>ON: 265.1461] found m/z 265.1462.

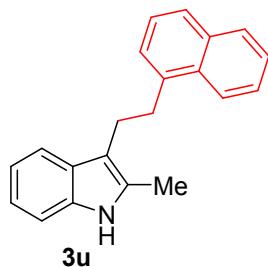


**3-(2,4-dichlorophenethyl)-2-methyl-1*H*-indole (3s).** Isolated yield: 72%. GC-MS (m/z, M<sup>+</sup> 304), major peaks found: 304 (5%), 303 (6%), 159 (5%), 144 (100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.58 (bs, NH), 7.49-7.43 (m, 1H),

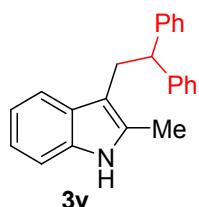
7.29 (d,  $J = 2.2$ , 1H), 7.20-7.15 (m, 1H), 7.08-7.00 (m, 1H), 7.03-7.00 (m, 1H), 6.98 (dd,  $J = 8.2$ , 2.2, 1H), 6.82 (d,  $J = 8.2$ , 1H), 2.89 (s, 4H), 2.06 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.44, 135.37, 134.65, 132.29, 131.82, 131.54, 129.18, 128.59, 126.88, 121.11, 119.32, 117.98, 110.68, 110.34, 34.42, 24.38, 11.42. HRMS (ESI) [M $^+$ ; calculated for  $\text{C}_{17}\text{H}_{15}\text{NCl}_2$  ( $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ): 303.0576] found m/z 303.0573 and [M $^+$ ; calculated for  $\text{C}_{17}\text{H}_{15}\text{NCl}$  ( $^{37}\text{Cl}$ ,  $^{35}\text{Cl}$ ): 305.0546] found m/z 305.0547.



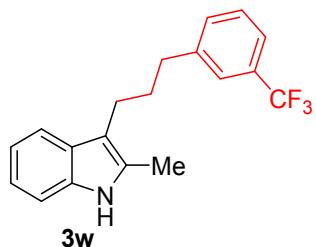
**2-methyl-3-(2-(perfluorophenyl)ethyl)-1H-indole (3t).** Isolated yield: 42%. GC-MS (m/z, M $^+$  325), major peaks found: 325 (20%), 181 (10%), 144 (100%), 115 (5%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.64 (bs, NH), 7.40 (dd,  $J = 6.3$ , 2.1, 1H), 7.19-7.15 (m, 1H), 7.07-7.02 (m, 1H), 7.02-6.99 (m, 1H), 2.87 (s, 4H), 2.23 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 135.30, 131.36, 128.41, 121.28, 119.49, 117.64, 110.38, 110.23, 106.02, 24.18, 23.66, 11.43. Aromatic C-F signals were not well observed.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ): -144.29 (dd,  $J = 22.6$ , 8.4, 2F), -157.68 (t,  $J = 20.9$ , 1F), -162.67 (td,  $J = 21.8$ , 7.9, 2F). HRMS (ESI) [M $^+$ ; calculated for  $\text{C}_{17}\text{H}_{12}\text{NF}_5$ : 325.0884] found m/z 325.0883.



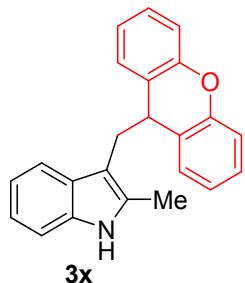
**2-methyl-3-(2-(naphthalen-1-yl)ethyl)-1H-indole (3u).** Isolated yield: 64%. GC-MS (m/z, M $^+$  285), major peaks found: 285 (15%), 144 (100%), 115 (7%), 77 (4%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06-8.00 (m, 1H), 7.81-7.75 (m, 1H), 7.63 (d,  $J = 8.2$ , 1H), 7.56-7.50 (m, 1H), 7.47-7.36 (m, 3H), 7.29-7.23 (m, 1H), 7.18-7.11 (m, 2H), 7.10-7.03 (m, 2H), 3.28 (dd,  $J = 8.9$ , 6.5, 2H), 3.03 (dd,  $J = 9.0$ , 6.5, 2H), 1.88 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.57, 135.38, 133.94, 132.04, 128.87, 128.67, 126.65, 126.35, 125.82, 125.67, 125.49, 123.89, 121.00, 119.26, 118.03, 110.38, 34.13, 25.72, 11.34. HRMS (ESI) [M $^+$ ; calculated for  $\text{C}_{21}\text{H}_{19}\text{N}$ : 285.1512] found m/z 285.1510.



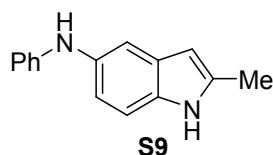
**3-(2,2-diphenylethyl)-2-methyl-1*H*-indole (3v).** Isolated yield: 70%. GC-MS (m/z, M<sup>+</sup> 311), major peaks found: 311 (5%), 165 (7%), 144 (100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.38-7.32 (m, 1H), 7.23 (bs, NH), 7.16-7.00 (m, 11H), 7.00-6.91 (m, 2H), 4.18 (t, J = 7.5, 1H), 3.27 (d, J = 7.6, 2H), 1.58 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 145.19, 135.32, 132.19, 128.81, 128.32, 128.23, 126.12, 120.85, 119.12, 118.00, 110.28, 109.59, 51.63, 31.44, 11.07. HRMS (ESI) [M+Na<sup>+</sup>; calculated for C<sub>23</sub>H<sub>21</sub>N: 311.1668] found m/z 311.1666.



**2-methyl-3-(3-(trifluoromethyl)phenyl)propyl-1*H*-indole (3w).** Isolated yield: 72%. GC-MS (m/z, M<sup>+</sup> 317), major peaks found: 317 (25%), 157 (5%), 144 (100%), 130 (7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.62 (bs, NH), 7.41-7.30 (m, 4H), 7.29-7.25 (m, 1H), 7.20-7.15 (m, 1H), 7.06-6.95 (m, 2H), 2.69-2.65 (m, 2H), 2.65-2.60 (m, 2H), 2.24 (s, 3H), 1.97-1.85 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 143.56, 135.41, 131.94, 130.98, 130.84, 128.82, 128.75, 128.01 (q, J<sup>1</sup><sub>C-F</sub> = 272.0, CF<sub>3</sub>), 125.21 (q, J<sup>3</sup><sub>C-F</sub> = 3.5), 122.66 (q, J<sup>3</sup><sub>C-F</sub> = 3.8), 121.05 (s), 119.21, 118.17, 111.59, 110.32, 35.53, 31.98, 23.82, 11.79. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ: -62.09 (s, 3F). HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>19</sub>H<sub>18</sub>NF<sub>3</sub>: 317.1385] found m/z 317.1390.

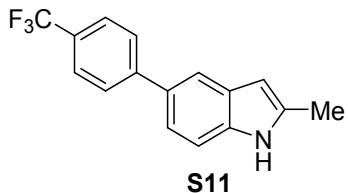


**3-((9*H*-xanthan-9-yl)methyl)-2-methyl-1*H*-indole (3x).** Isolated yield: 55%. GC-MS (m/z, M<sup>+</sup> 325), major peaks found: 325 (5%), 207 (5%), 181 (25%), 144 (100%), 115 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.40 (bs, NH), 7.34-7.29 (m, 1H), 7.14-7.08 (m, 2H), 7.05 (dd, J = 5.2, 1.6, 1H), 7.00 (td, J = 7.1, 1.3, 2H), 6.97-6.93 (m, 2H), 6.84 (td, J = 7.3, 1.3, 2H), 6.77 (dd, J = 7.6, 1.7, 2H), 4.03 (t, J = 7.1, 1H), 2.86 (d, J = 7.1, 2H), 1.43 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 152.34, 135.23, 133.25, 129.05, 128.73, 127.57, 125.92, 122.96, 120.98, 119.27, 117.82, 116.16, 110.31, 108.34, 40.65, 36.21, 10.67. HRMS (ESI) [M+H<sup>+</sup>; calculated for C<sub>23</sub>H<sub>19</sub>ON: 326.1539] found 326.1541.

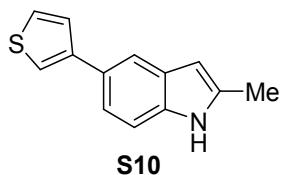


**5-aminophenyl-2-methyl-1*H*-indole (S9).** Isolated yield: 56%. GC-MS (m/z, M<sup>+</sup> 222), major peaks found: 222 (100%), 206 (20%), 180 (5%), 103 (10%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.81 (bs, NH), 7.32 (d, J = 2.0, 1H), 7.24-7.18

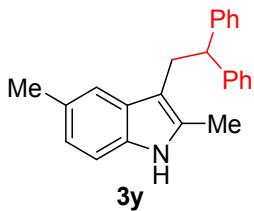
(m, 3H), 6.98-6.93 (m, 3H), 6.82 (tt,  $J = 7.4, 1.0, 1\text{H}$ ), 6.25-6.08 (m, 1H), 6.00 (bs, NH), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 146.33, 136.15, 134.81, 133.17, 129.91, 129.35, 119.28, 117.28, 115.52, 112.84, 110.89, 100.44, 13.90. HRMS (ESI) [ $\text{M}^+$ ; calculated for  $\text{C}_{15}\text{H}_{14}\text{N}_2$ : 222.1151] found m/z 222.1148.



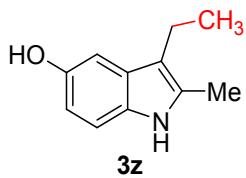
**2-methyl-5-(4-(trifluoromethyl)phenyl)-1H-indole (S11).** Isolated yield: 43%. GC-MS (m/z,  $\text{M}^+$  275), major peaks found: 275 (100%), 256 (5%), 204 (7%), 137 (8%), 127 (8%), 112 (5%), 102 (5%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.91 (bs, NH), 7.77-7.72 (m, 3H), 7.68 (d,  $J = 8.3, 2\text{H}$ ), 7.37-7.36 (m, 2H), 6.30 (s, 1H), 2.48 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 146.35, 136.35, 136.12, 131.74, 129.79, 128.29 (q,  $J^2_{\text{C}-\text{F}} = 32.2$ ), 127.53, 125.64 (q,  $J^3_{\text{C}-\text{F}} = 3.8$ ), 124.68 (q,  $J^1_{\text{C}-\text{F}} = 271.9$ ), 120.75, 118.63, 110.75, 101.04, 13.93.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -61.74 (s, 3F). HRMS (ESI) [ $\text{M}^+$ ; calculated for  $\text{C}_{16}\text{H}_{12}\text{NF}_3$ : 275.0916] found m/z 213.0912.



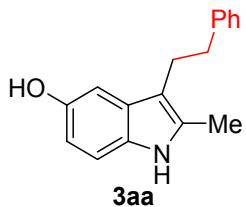
**2-methyl-5-(thiophen-3-yl)-1H-indole (S12).**<sup>[3]</sup> Isolated yield: 70%. GC-MS (m/z,  $\text{M}^+$  213), major peaks found: 213 (100%), 184 (5%), 167 (7%), 106 (5%). (The NMR spectrum is consistent with the reported data).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.65 (bs, NH+1H), 7.34 (d,  $J = 4.3, 1\text{H}$ ), 7.31-7.24 (m, 3H), 7.15 (d,  $J = 8.4, 1\text{H}$ ), 6.14 (s, 1H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.90, 135.95, 135.53, 129.58, 128.03, 126.93, 125.80, 120.29, 118.69, 117.58, 110.54, 100.79, 13.87. HRMS (ESI) [ $\text{M}^+$ ; calculated for  $\text{C}_{13}\text{H}_{11}\text{NS}$ : 213.0606] found m/z 213.0606.



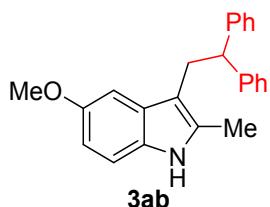
**3-(2,2-diphenylethyl)-2,5-dimethyl-1H-indole (3y).** Isolated yield: 67%. GC-MS (m/z,  $\text{M}^+$  325), major peaks found: 325 (5%), 158 (100%), 143 (7%), 115 (5%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.35 (bs, NH), 7.16-7.12 (m, 4H), 7.11-7.06 (m, 6H), 7.02 (d,  $J = 8.2, 2\text{H}$ ), 6.84 (dd,  $J = 8.2, 1.7, 1\text{H}$ ), 4.18 (t,  $J = 7.5, 1\text{H}$ ), 3.27 (d,  $J = 7.5, 2\text{H}$ ), 2.34 (s, 3H), 1.59 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 145.33, 133.66, 132.34, 129.11, 128.41, 128.26, 128.22, 126.10, 122.32, 117.85, 109.88, 109.22, 51.59, 31.45, 21.67, 11.11. HRMS (ESI) [ $\text{M}^+$ ; calculated for  $\text{C}_{24}\text{H}_{23}\text{N}$ : 325.1825] found m/z 325.1828.



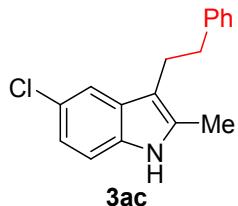
**3-ethyl-2-methyl-1H-indol-5-ol (3z).**<sup>[9]</sup> Isolated yield: 73%. GC-MS (m/z, M<sup>+</sup> 175), major peaks found: 175 (35%), 160 (100%), 146 (5%), 131 (7%), 117 (4%). (The NMR spectrum is consistent with the reported data). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 7.02 (dd, J = 8.5, 0.5, 1H), 6.81 (d, J = 2.0, 1H), 6.55 (dd, J = 8.5, 2.4, 1H), 2.59 (q, J = 7.5, 2H), 2.27 (s, 3H), 1.15 (t, J = 7.5, 3H). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ: 150.61, 132.50, 132.00, 130.34, 113.25, 111.50, 110.55, 103.18, 18.28, 15.85, 11.29. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>11</sub>H<sub>13</sub>ON: 175.0991] found m/z 175.0992.



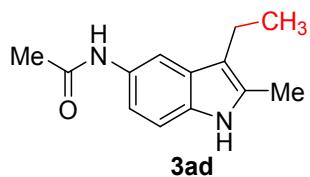
**2-methyl-3-phenethyl-1H-indol-5-ol (3aa).** Isolated yield: 74%. GC-MS (m/z, M<sup>+</sup> 251), major peaks found: 251 (10%), 160 (100%), 91 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.21-7.14 (m, 2H), 7.11 (dt, J = 5.7, 2.4, 1H), 7.05-7.01 (m, 3H), 6.86 (d, J = 2.3, 1H), 6.57 (dd, J = 8.5, 2.3, 1H), 2.94-2.73 (m, 4H), 1.97 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 150.77, 143.83, 133.76, 132.02, 130.52, 129.68, 129.07, 126.58, 111.57, 110.60, 110.40, 103.10, 37.91, 27.82, 11.14. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>17</sub>ON: 251.1304] found m/z 251.1309.



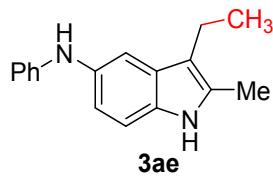
**3-(2,2-diphenylethyl)-5-methoxy-2-methyl-1H-indole (3ab).** Isolated yield: 67%. GC-MS (m/z, M<sup>+</sup> 341), major peaks found: 341 (5%), 174 (100%), 159 (10%), 131 (8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.29 (bs, NH), 7.17-7.03 (m, 10H), 6.96 (d, J = 8.6, 1H), 6.74 (d, J = 2.2, 1H), 6.65 (dd, J = 8.6, 2.4, 1H), 4.15 (t, J = 7.5, 1H), 3.69 (s, 3H), 3.26 (d, J = 7.5, 2H), 1.63 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 153.87, 145.28, 133.15, 130.44, 129.34, 128.37, 128.26, 126.15, 110.84, 110.33, 109.64, 100.60, 56.10, 51.61, 31.50, 11.22. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>24</sub>H<sub>23</sub>ON: 341.1774] found m/z 341.1775.



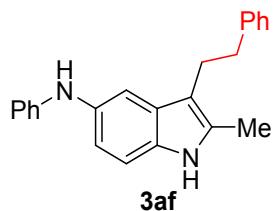
**5-chloro-2-methyl-3-phenethyl-1*H*-indole (3ac).** Isolated yield: 56%. GC-MS (m/z, M<sup>+</sup> 269), major peaks found: 271 (3%), 269 (9%), 180 (33%), 178 (100%), 143 (9%), 115 (6%), 91 (7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.68 (bs, NH), 7.46 (d, J = 1.9, 1H), 7.27-7.25 (m, 1H), 7.25-7.21 (m, 2H), 7.20-7.15 (m, 2H), 7.14-7.12 (m, 1H), 7.07 (dd, J = 8.5, 2.0, 1H), 2.99-2.91 (m, 2H), 2.91-2.84 (m, 2H), 2.07 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.23, 133.68, 133.09, 129.87, 128.78, 128.34, 125.94, 124.89, 121.08, 117.59, 111.20, 111.13, 36.95, 26.56, 11.46. HRMS (ESI) [M-H<sup>-</sup>; calculated for C<sub>17</sub>H<sub>16</sub>NCI (<sup>37</sup>Cl): 268.0898] found 268.0903 and [M-H<sup>-</sup>; calculated for C<sub>17</sub>H<sub>16</sub>NCI (<sup>35</sup>Cl): 270.0874] found 270.0881.



**N-(3-ethyl-2-methyl-1*H*-indol-5-yl)acetamide (3ad).** Isolated yield: 38%. GC-MS (m/z, M<sup>+</sup> 216), major peaks found: 216 (60%), 201 (100%), 173 (15%), 159 (50%), 130 (10%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.06 (bs, NH), 7.79 (s, 1H), 7.66 (bs, NH), 7.48-7.32 (m, 1H), 7.25 (s, 1H), 2.79 (q, J = 7.6, 2H), 2.46 (s, 3H), 2.30 (s, 3H), 1.32 (t, J = 7.6, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 168.69, 132.93, 131.53, 129.76, 128.67, 115.37, 114.14, 110.79, 110.32, 24.51, 17.41, 15.49, 11.65. HRMS (ESI) [M+Na<sup>+</sup>; calculated for C<sub>13</sub>H<sub>16</sub>ON<sub>2</sub>: 216.1257] found m/z 216.1254.

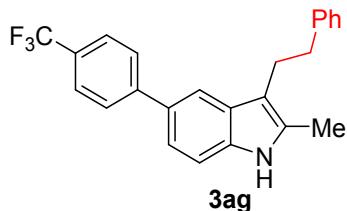


**5-aminophenyl-3-ethyl-2-methyl-1*H*-indole (3ae).** Isolated yield: 55%. GC-MS (m/z, M<sup>+</sup> 250), major peaks found: 250 (80%), 235 (100%), 220 (8%), 117 (15%), 92 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.62 (bs, NH), 7.34 (d, J = 2.0, 1H), 7.26-7.21 (m, 2H), 7.20-7.19 (m, 1H), 6.99-6.91 (m, 3H), 6.81 (tt, J = 7.5, 1.1, 1H), 5.63 (bs, NH), 2.68 (q, J = 7.5, 2H), 2.37 (s, 3H), 1.22 (t, J = 7.5, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 146.89, 134.27, 132.38, 131.29, 129.35, 129.29, 118.74, 117.44, 114.93, 113.97, 111.82, 110.83, 17.48, 15.53, 11.69. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>: 250.1464] found m/z 250.1469.

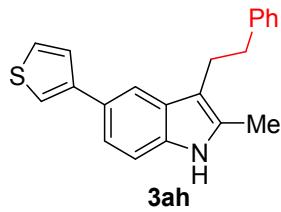


**5-aminophenyl-2-methyl-3-phenethyl-1*H*-indole (3af).** Isolated yield: 72%. GC-MS (m/z, M<sup>+</sup> 326), major peaks found: 326 (25%), 235 (100%), 207 (5%), 117 (5%), 91 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.47 (bs, NH), 7.21 (d, J = 2.1, 1H), 7.18-7.06 (m, 6H), 7.05-7.00 (m, 2H), 6.88-6.79 (m, 3H), 6.74-6.67 (m, 1H), 5.50 (bs, NH), 2.87-2.80 (m, 2H), 2.80-2.74 (m, 2H), 1.98 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 146.80, 142.48, 134.37, 132.37, 132.33,

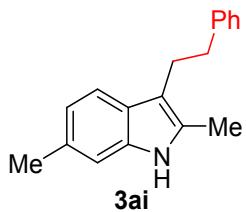
129.39, 129.36, 128.77, 128.31, 125.84, 118.81, 117.36, 114.97, 111.55, 111.11, 110.86, 37.04, 26.68, 11.47. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>: 326.1779] found m/z 326.1784.



**2-methyl-3-phenethyl-5-(4-(trifluoromethyl)phenyl)-1H-indole (3ag).** Isolated yield: 70%. GC-MS (m/z, M<sup>+</sup> 379), major peaks found: 379 (10%), 288 (100%), 207 (5%), 91 (10%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.78-7.73 (m, NH+2H), 7.72-7.67 (m, 3H), 7.38-7.35 (m, 2H), 7.28-7.26 (m, 1H), 7.26-7.24 (m, 1H), 7.23-7.19 (m, 1H), 7.18-7.12 (m, 2H), 3.08-3.00 (m, 2H), 2.98-2.90 (m, 2H), 2.14 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 146.51, 142.38, 135.33, 132.59, 131.27, 129.32, 128.84, 128.35, 128.28 (d,  $J^2_{C-F} = 32.3$ ), 127.61, 125.95, 125.64 (q,  $\beta^3_{C-F} = 3.8$ ), 124.69 (q,  $J^1_{C-F} = 271.7$ ), 120.66, 116.96, 111.81, 110.70, 37.14, 26.57, 11.52. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ: -61.73 (s, 3F). HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>24</sub>H<sub>20</sub>NF<sub>3</sub>: 379.1542] found m/z 379.1540.

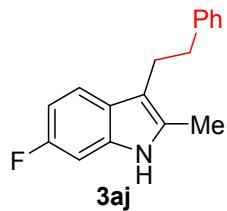


**2-methyl-3-phenethyl-5-(thiophen-3-yl)-1H-indole (3ah).** Isolated yield: 68%. GC-MS (m/z, M<sup>+</sup> 317), major peaks found: 317(15%), 226 (100%), 207 (8%), 91 (8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.59 (d,  $J = 1.3$ , 1H), 7.49 (bs, NH), 7.35 (dd,  $J = 4.4, 2.0$ , 1H), 7.30-7.24 (m, 3H), 7.19-7.08 (m, 4H), 7.06-7.01 (m, 2H), 2.94-2.86 (m, 2H), 2.86-2.77 (m, 2H), 1.96 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 144.08, 142.46, 134.76, 129.09, 128.81, 128.31, 127.57, 127.04, 125.88, 125.82, 120.24, 118.72, 115.95, 110.51, 37.08, 26.58, 11.44. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>21</sub>H<sub>19</sub>NS: 317.1233] found m/z 317.1239.

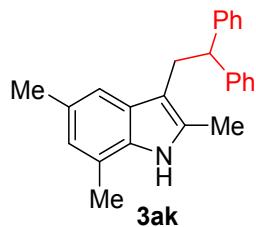


**2,6-dimethyl-3-phenethyl-1H-indole (3ai).** Isolated yield: 80%. GC-MS (m/z, M<sup>+</sup> 249), major peaks found: 249 (18%), 158 (100%), 143 (6%), 115 (6%), 91 (8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.32 (d,  $J = 7.9$ , 1H), 7.24 (bs, NH), 7.15-7.10 (m, 2H), 7.10-7.05 (m, 1H), 7.05-7.00 (m, 2H), 6.88-6.80 (m, 2H), 2.88-2.81 (m, 2H), 2.81-2.74 (m, 2H), 2.35 (s, 3H), 1.91 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.63, 135.80, 130.54, 130.52, 128.75, 128.28, 126.47,

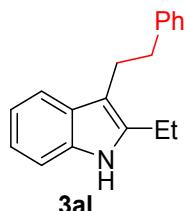
125.78, 120.75, 117.70, 110.90, 110.47, 37.08, 26.73, 21.81, 11.28. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>18</sub>H<sub>19</sub>N: 249.1512] found m/z 249.1517.



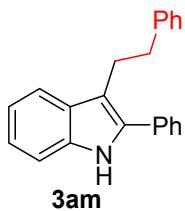
**6-fluoro-2-methyl-3-phenethyl-1H-indole (3aj).** Isolated yield: 70%. GC-MS (m/z, M<sup>+</sup> 253), major peaks found: 253 (15%), 162 (100%), 91 (7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.40 (bs, NH), 7.27 (dd, J = 8.5, 5.3, 1H), 7.18-7.06 (m, 3H), 7.03-6.98 (m, 2H), 6.81-6.70 (m, 2H), 2.88-2.80 (m, 2H), 2.80-2.72 (m, 2H), 1.93 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 159.46 (d, J<sup>1</sup><sub>C-F</sub> = 235.7), 142.36, 135.15 (d, J<sup>3</sup><sub>C-F</sub> = 12.4), 131.59 (d, J<sup>4</sup><sub>C-F</sub> = 3.6), 128.74, 128.33, 125.90, 125.21, 118.50 (d, J<sup>3</sup><sub>C-F</sub> = 9.9), 111.07, 107.48 (d, J<sup>2</sup><sub>C-F</sub> = 24.2), 96.86 (d, J<sup>2</sup><sub>C-F</sub> = 26.0), 36.99, 26.56, 11.32. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ: -122.34-(-122.46) (m, 1F). HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>16</sub>NF: 253.1261] found m/z 253.1265.



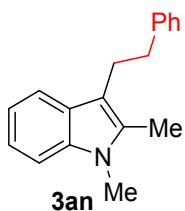
**3-(2,2-diphenylethyl)-2,5,7-trimethyl-1H-indole (3ak).** Isolated yield: 63%. GC-MS (m/z, M<sup>+</sup> 339), major peaks found: 339 (5%), 281 (5%), 253 (4%), 207 (8%), 172 (100%), 157 (8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.28 (bs, NH), 7.15 (dt, J = 7.0, 1.5, 2H), 7.13-7.10 (m, 5H), 7.09-7.06 (m, 3H), 7.01 (s, 1H), 6.67 (s, 1H), 4.19 (t, J = 7.5, 1H), 3.26 (d, J = 7.5 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 1.60 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 145.38, 133.15, 131.98, 128.67, 128.50, 128.42, 128.21, 126.08, 123.28, 118.96, 115.56, 109.74, 51.62, 31.63, 21.61, 16.66, 11.16. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>25</sub>H<sub>25</sub>N: 339.1981] found m/z 339.1990.



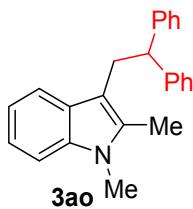
**2-ethyl-3-phenethyl-1H-indole (3al).** Isolated yield: 79%. GC-MS (m/z, M<sup>+</sup> 249), major peaks found: 249 (15%), 158 (100%), 143 (20%), 91 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.64 (bs, NH), 7.49-7.43 (m, 1H), 7.19-7.10 (m, 4H), 7.08-6.99 (m, 4H), 2.95-2.86 (m, 2H), 2.85-2.77 (m, 2H), 2.44 (q, J = 7.6, 2H), 1.02 (t, J = 7.6, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.61, 137.05, 135.38, 128.69, 128.62, 128.33, 125.84, 120.98, 119.14, 118.23, 110.44, 37.33, 26.66, 19.24, 14.20. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>18</sub>H<sub>19</sub>N: 249.1512] found m/z 249.1519.



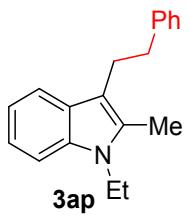
**3-phenethyl-2-phenyl-1H-indole (3am).** Isolated yield: 76%. GC-MS (m/z, M<sup>+</sup> 297), major peaks found: 297 (10%), 206 (100%), 178 (10%), 91 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.88 (bs, NH), 7.58 (d, J = 8.2, 1H), 7.37-7.23 (m, 6H), 7.20-7.05 (m, 7H), 3.09 (dd, J = 10.4, 6.1, 2H), 2.94 (dd, J = 9.9, 5.9, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.35, 136.02, 134.67, 133.29, 129.17, 128.90, 128.60, 128.46, 128.06, 127.71, 126.01, 122.38, 119.72, 119.26, 112.90, 110.99, 37.17, 26.96. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>22</sub>H<sub>19</sub>N: 297.1512] found m/z 297.1519.



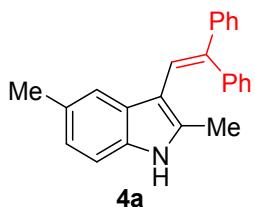
**1,2-dimethyl-3-phenethyl-1H-indole (3an).**<sup>[10]</sup> Isolated yield: 68%. GC-MS (m/z, M<sup>+</sup> 249), major peaks found: 249 (15%), 158 (100%), 143 (12%), 115 (5%), 91 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.46 (d, J = 7.5, 1H), 7.19-7.12 (m, 3H), 7.11-7.03 (m, 4H), 7.02-6.96 (m, 1H), 3.48 (s, 3H), 3.01-2.86 (m, 2H), 2.83-2.75 (m, 2H), 2.02 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.64, 136.69, 133.19, 128.72, 128.32, 127.65, 125.83, 120.55, 118.74, 117.96, 110.54, 108.65, 37.50, 29.52, 27.05, 9.98. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>18</sub>H<sub>19</sub>N: 249.1512] found m/z 249.1530.



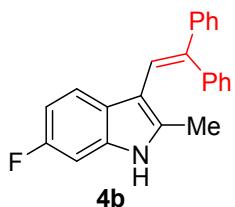
**3-(2,2-diphenylethyl)-1,2-dimethyl-1H-indole (3ao).** Isolated yield: 59%. GC-MS (m/z, M<sup>+</sup> 325), major peaks found: 325 (5%), 281 (5%), 253 (5%), 207 (8%), 158 (100%), 143 (8%), 115 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.38 (d, J = 7.7, 1H), 7.18-7.11 (m, 5H), 7.10-7.04 (m, 7H), 6.96 (td, J = 7.4, 6.9, 1.2, 1H), 4.18 (t, J = 7.5, 1H), 3.43 (s, 3H), 3.33 (d, J = 7.5, 2H), 1.65 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 145.20, 136.68, 134.05, 128.30, 128.15, 127.81, 126.03, 120.35, 118.61, 117.91, 108.90, 108.50, 51.90, 31.74, 29.47, 9.58. HRMS (ESI) [M+H<sup>+</sup>; calculated for C<sub>24</sub>H<sub>23</sub>N: 326.1903] found 326.1906.



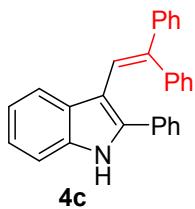
**1-ethyl-2-methyl-3-phenethyl-1H-indole (3ap).** Isolated yield: 49%. GC-MS ( $m/z$ ,  $M^+$  263), major peaks found: 263 (10%), 172 (100%), 144 (11%), 115 (5%), 91 (5%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $^1\text{H}$  NMR (300 MHz, Chloroform- $d$ )  $\delta$  7.48 (d,  $J$  = 7.3, 1H), 7.20-7.12 (m, 3H), 7.12-7.06 (m, 2H), 7.05-6.97 (m, 3H), 3.97 (q,  $J$  = 7.2, 2H), 2.95-2.87 (m, 2H), 2.83-2.75 (m, 2H), 1.98 (s, 3H), 1.18 (t,  $J$  = 7.2, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.63, 135.58, 132.48, 128.78, 128.26, 127.85, 125.79, 120.48, 118.66, 118.05, 110.60, 108.71, 37.77, 37.41, 27.03, 15.45, 9.73. HRMS (ESI) [ $M^+$ ; calculated for  $\text{C}_{19}\text{H}_{21}\text{N}$ : 263.1669] found  $m/z$  263.1674.



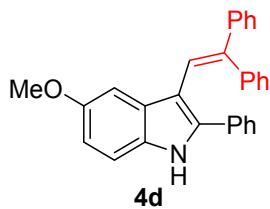
**3-(2,2-diphenylvinyl)-2,5-dimethyl-1H-indole (4a).** Isolated yield: 70%. GC-MS ( $m/z$ ,  $M^+$  323), major peaks found: 323 (100%), 308 (10%), 293 (8%), 246 (6%), 231 (10%), 217 (9%), 146 (6%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.37 (bs, NH), 7.32-7.26 (m, 2H), 7.26-7.17 (m, 3H), 7.13-7.03 (m, 5H), 6.95-6.86 (m, 2H), 6.81-6.76 (m, 2H), 2.18 (s, 3H), 1.78 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 144.53, 141.86, 140.80, 133.60, 133.51, 130.92, 128.78, 128.35, 128.25, 128.17, 127.11, 126.65, 122.71, 121.55, 119.51, 110.97, 109.72, 21.48, 12.85. HRMS (ESI) [ $M^+$ ; calculated for  $\text{C}_{24}\text{H}_{21}\text{N}$ : 323.1668] found  $m/z$  323.1665.



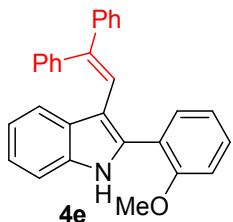
**3-(2,2-diphenylvinyl)-6-fluoro-2-methyl-1H-indole (4b).** Isolated yield: 88%. GC-MS ( $m/z$ ,  $M^+$  327), major peaks found: 327 (100%), 312 (20%), 250 (8%), 235 (18%), 148 (8%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.70 (bs, NH), 7.46-7.31 (m, 5H), 7.25-7.15 (m, 5H), 7.03-6.94 (m, 2H), 6.89 (dd,  $J$  = 9.5, 2.3, 1H), 6.69 (ddd,  $J$  = 9.7, 8.8, 2.3, 1H), 2.00 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.52 (d,  $J^1_{\text{C}-\text{F}}$  = 236.7), 144.33, 141.55, 135.17 (d,  $J^3_{\text{C}-\text{F}}$  = 12.4), 133.78 (d,  $J^4_{\text{C}-\text{F}}$  = 3.2), 130.81, 128.41, 128.25, 128.22, 127.32, 126.92, 125.05, 124.36, 120.89, 120.22 (d,  $J^3_{\text{C}-\text{F}}$  = 9.9), 111.44, 107.99 (d,  $J^2_{\text{C}-\text{F}}$  = 23.8), 96.68 (d,  $J^2_{\text{C}-\text{F}}$  = 26.1), 12.82.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -121.15(-122.53) (m, 1F). HRMS (ESI) [ $M^+$ ; calculated for  $\text{C}_{23}\text{H}_{18}\text{NF}$ : 327.1417] found  $m/z$  327.1425.



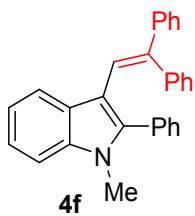
**3-(2,2-diphenylvinyl)-2-phenyl-1*H*-indole (4c).**<sup>[11]</sup> Isolated yield: 80%. GC-MS (m/z, M<sup>+</sup> 371), major peaks found: 371 (100%), 294 (15%), 204 (8%), 146 (10%). (The NMR spectrum is consistent with the reported data). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.88 (bs, NH), 7.42 (dd, J = 8.1, 1.3, 2H), 7.31-7.15 (m, 8H), 7.11 (d, J = 8.1, 1H), 7.08-7.02 (m, 2H), 7.00-6.84 (m, 6H), 6.77-6.68 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 144.15, 142.62, 141.16, 136.74, 135.97, 132.85, 130.57, 128.87, 128.49, 128.16, 127.94, 127.90, 127.79, 127.27, 127.21, 126.88, 122.39, 121.58, 120.98, 119.94, 112.32, 110.65. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>28</sub>H<sub>21</sub>N: 371.1668] found m/z 371.1681.



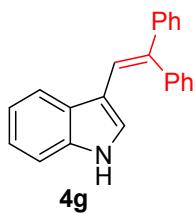
**3-(2,2-diphenylvinyl)-5-methoxy-2-phenyl-1*H*-indole (4d).** Isolated yield: 68%. GC-MS (m/z, M<sup>+</sup> 401), major peaks found: 401 (5%), 167 (100%), 152 (10%), 69 (12%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.68 (dd, J = 8.3, 1.3, 2H), 7.51-7.44 (m, 4H), 7.43-7.38 (m, 4H), 7.37-7.32 (m, 3H), 7.26-7.18 (m, 4H), 7.08 (bs, NH), 6.80 (dd, J = 8.7, 2.5, 1H), 6.43 (d, J = 2.4, 1H), 3.56 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 154.00, 144.35, 141.57, 141.54, 137.97, 132.90, 131.04, 130.62, 128.93, 128.61, 128.18, 128.14, 127.95, 127.82, 127.22, 127.09, 127.02, 122.12, 113.18, 112.22, 111.42, 102.35, 55.64. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>29</sub>H<sub>23</sub>ON: 401.1774] found m/z 401.1769.



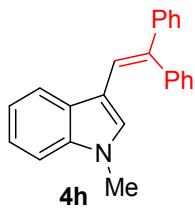
**3-(2,2-diphenylvinyl)-2-(2-methoxyphenyl)-1*H*-indole (4e).** Isolated yield: 63%. GC-MS (m/z, M<sup>+</sup> 401), major peaks found: 401 (100%), 386 (5%), 341 (5%), 309 (7%), 281 (9%), 253 (5%), 207 (15%), 165 (5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 9.18 (bs, NH), 7.98 (dd, J = 7.6, 1.6, 1H), 7.65-7.60 (m, 2H), 7.58-7.51 (m, 4H), 7.51-7.46 (m, 1H), 7.40-7.34 (m, 3H), 7.33-7.27 (m, 5H), 7.21 (td, J = 7.5, 1.1, 1H), 7.15 (d, J = 8.3, 1H), 7.11-7.05 (m, 1H), 4.06 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 156.44, 144.39, 142.02, 141.26, 135.57, 134.13, 131.91, 130.47, 129.09, 128.49, 128.12, 127.87, 127.14, 126.60, 126.49, 122.28, 122.09, 121.28, 121.24, 120.60, 119.45, 112.74, 111.56, 110.49, 55.84. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>29</sub>H<sub>23</sub>ON: 401.1774] found m/z 401.1768.



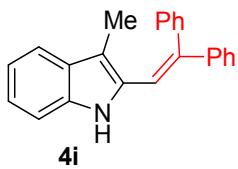
**3-(2,2-diphenylvinyl)-2-phenyl-1H-indole (4f).** Isolated yield: 70%. GC-MS (m/z, M<sup>+</sup> 385), major peaks found: 385 (100%), 369 (8%), 307 (10%), 291 (15%), 218 (7%), 193 (6%), 146 (7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.28-7.11 (m, 12H), 7.06 (dd, J = 6.9, 1.1, 1H), 6.97 (s, 4H), 6.90 (d, J = 8.0, 1H), 6.81-6.77 (m, 1H), 6.76 (s, 1H), 3.47 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 144.55, 141.55, 141.17, 140.45, 137.58, 131.77, 130.75, 130.70, 128.41, 128.38, 128.02, 127.87, 126.96, 126.58, 126.14, 121.86, 121.71, 120.87, 119.76, 112.55, 109.27, 31.22. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>29</sub>H<sub>23</sub>N: 385.1825] found m/z 385.1832.



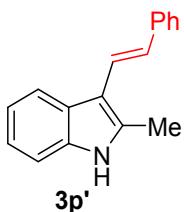
**3-(2,2-diphenylvinyl)-1H-indole (4g).** Isolated yield: 58%. GC-MS (m/z, M<sup>+</sup> 295), major peaks found: 295 (100%), 280 (5%), 217 (15%), 189 (5%), 146 (6%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.68-7.59 (m, NH+1H), 7.36-7.30 (m, 2H), 7.30-7.25 (m, 3H), 7.25-7.22 (m, 3H), 7.21-7.18 (m, 2H), 7.17-7.12 (m, 1H), 7.12-7.09 (m, 1H), 7.08 (d, J = 2.2, 1H), 7.06-7.01 (m, 1H), 6.03 (d, J = 2.4, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.98, 142.06, 138.28, 135.19, 130.17, 129.26, 128.36, 127.74, 127.33, 126.85, 126.80, 123.31, 122.50, 120.16, 118.70, 118.59, 113.98, 111.16. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>22</sub>H<sub>17</sub>N: 295.1355] found m/z 295.1357.



**3-(2,2-diphenylvinyl)-1-methyl-1H-indole (4h).** Isolated yield: 67%. GC-MS (m/z, M<sup>+</sup> 309), major peaks found: 309 (100%), 293 (12%), 231 (5%), 217 (6%), 146 (6%), 217 (9%), 146 (6%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.64 (dt, J = 7.7, 1.0, 1H), 7.39-7.34 (m, 1H), 7.34-7.28 (m, 4H), 7.26-7.20 (m, 5H), 7.20-7.14 (m, 1H), 7.14-7.09 (m, 3H), 7.05 (ddd, J = 8.1, 4.8, 3.4, 1H), 5.90 (s, 1H), 3.42 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 143.09, 142.20, 137.32, 136.21, 130.17, 129.33, 128.45, 128.34, 127.97, 127.35, 126.70, 126.67, 122.11, 119.79, 118.79, 118.61, 112.58, 109.34, 32.97. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>23</sub>H<sub>19</sub>N: 309.1512] found m/z 309.1521.



**2-(2,2-diphenylvinyl)-3-methyl-1*H*-indole (**4i**).** Isolated yield: 54%. GC-MS (m/z, M<sup>+</sup> 309), major peaks found: 309 (100%), 294 (20%), 217 (18%), 146 (10%), 73 (8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.41-7.35 (m, NH+3H), 7.30-7.23 (m, 5H), 7.23-7.20 (m, 1H), 7.20-7.14 (m, 1H), 7.04 (s, 1H), 7.00-6.87 (m, 3H), 6.78 (dd, J = 6.9, 1.3, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 142.56, 140.29, 138.12, 135.95, 131.87, 130.48, 129.36, 128.47, 128.38, 128.32, 127.49, 127.16, 123.05, 119.31, 118.83, 116.00, 114.23, 110.46, 9.07. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>23</sub>H<sub>19</sub>N: 309.1512] found m/z 309.1518.



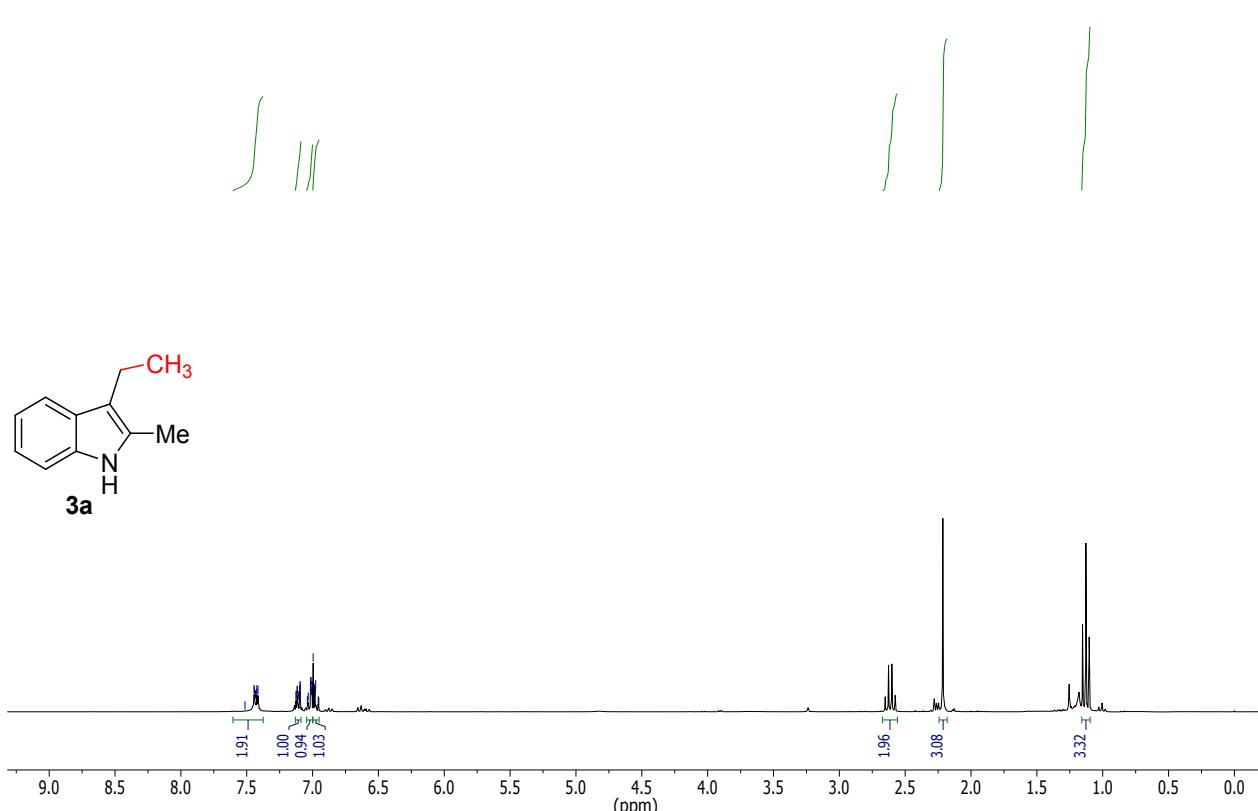
**(E)-2-methyl-3-styryl-1*H*-indole (**3p'**).<sup>[4]</sup>** Isolated yield: 72%. GC-MS (m/z, M<sup>+</sup> 233), major peaks found: 233 (100%), 218 (45%), 189 (7%), 154 (5%), 130 (7%), 109 (10%). (The NMR spectrum is consistent with the reported data). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.86 (dd, J = 5.7, 2.1, 1H), 7.60 (bs, NH), 7.45-7.40 (m, 2H), 7.26 (t, J = 7.6, 2H), 7.18 (d, J = 16.5, 1H), 7.14-7.05 (m, 4H), 7.00 (d, J = 16.5, 1H), 2.33 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 139.10, 135.60, 134.77, 128.75, 126.62, 126.54, 125.76, 125.26, 121.83, 121.76, 120.50, 119.77, 111.02, 110.72, 12.41. HRMS (ESI) [M<sup>+</sup>; calculated for C<sub>17</sub>H<sub>15</sub>N: 233.1199] found m/z 233.1198.

## 7. REFERENCES

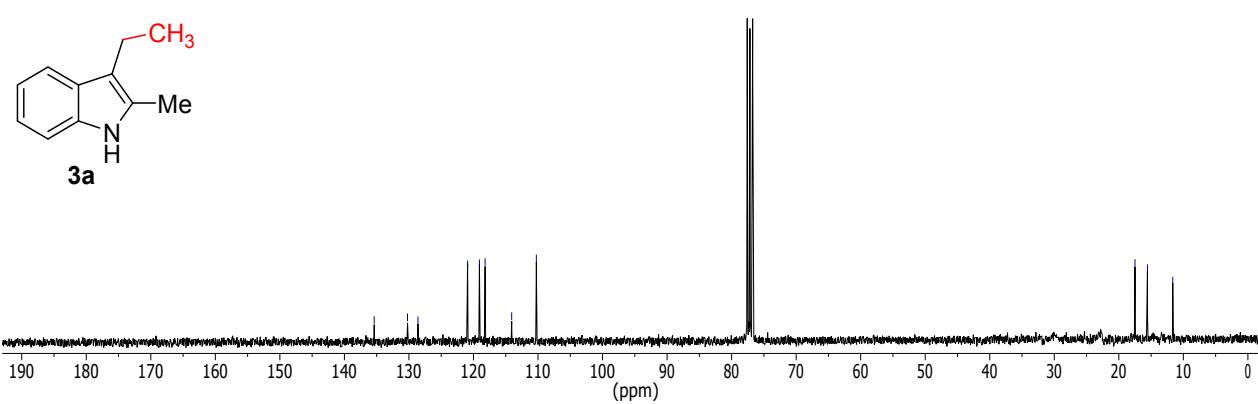
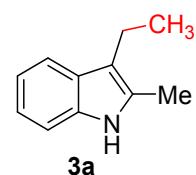
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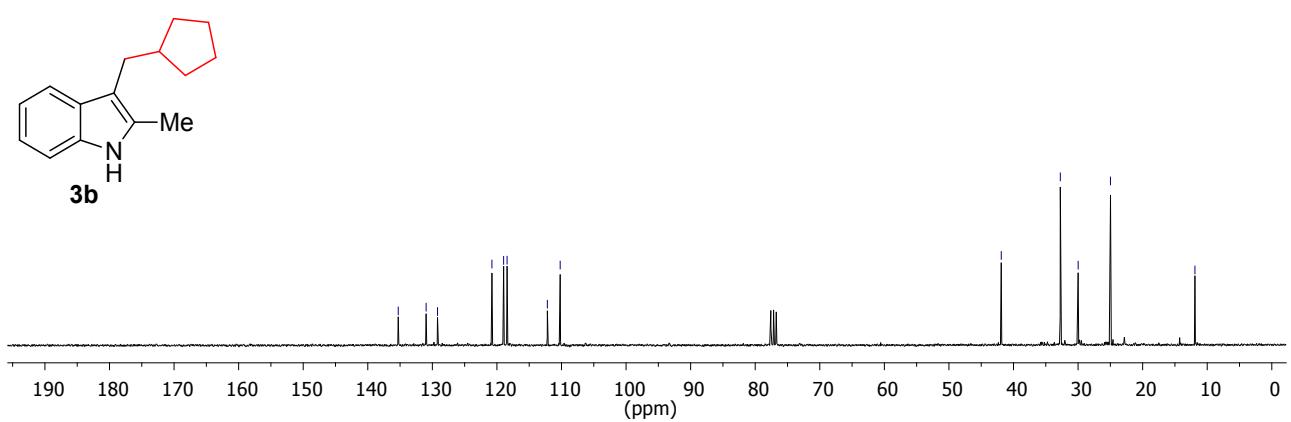
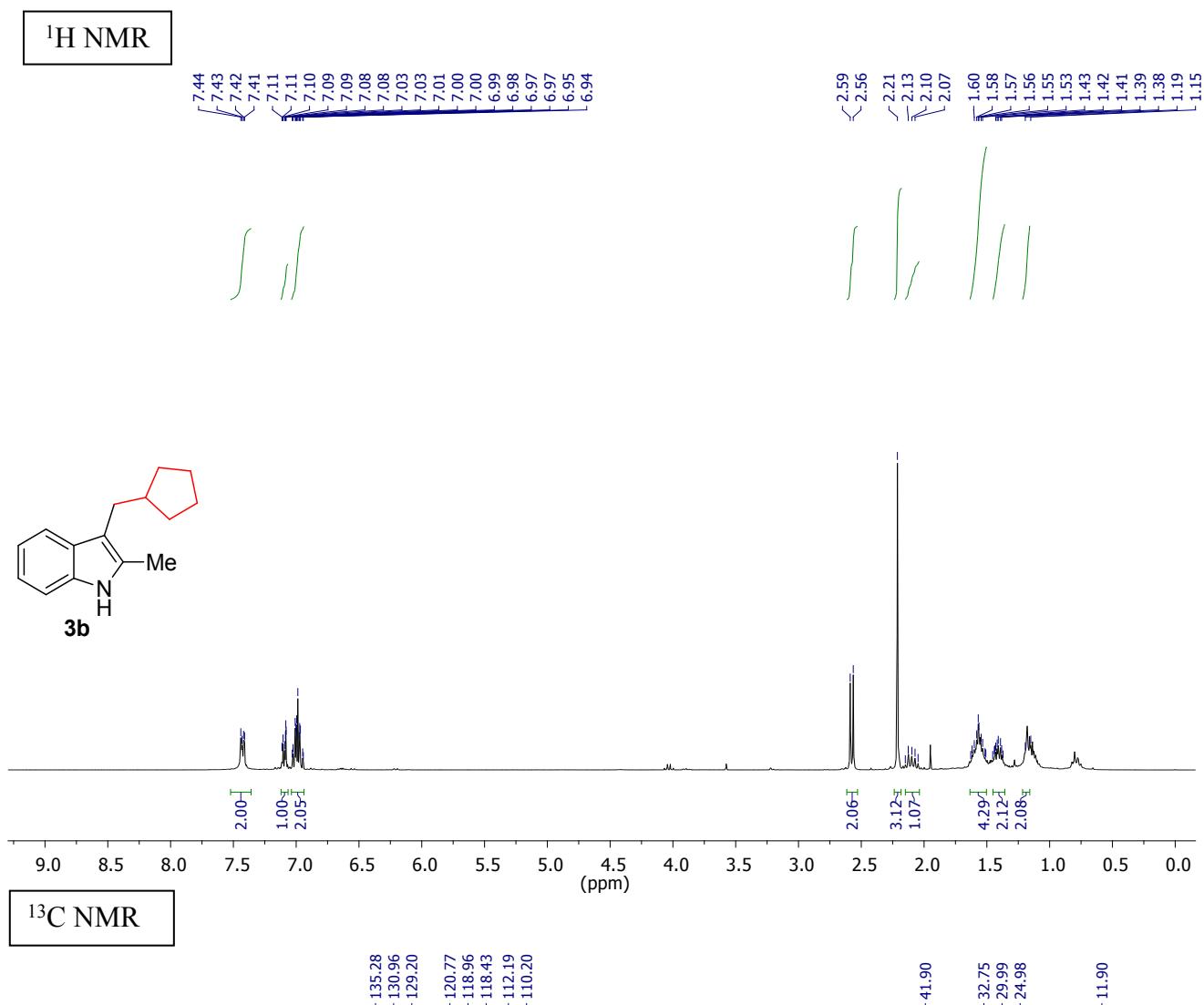
## 8. NMR SPECTRA OF THE ISOLATED PRODUCTS

<sup>1</sup>H NMR

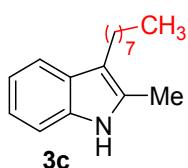


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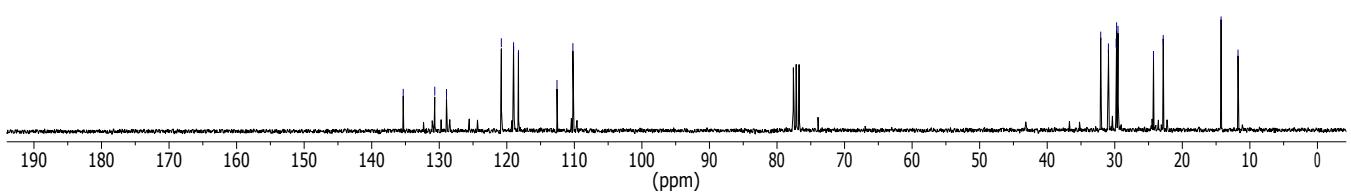
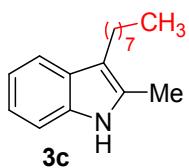
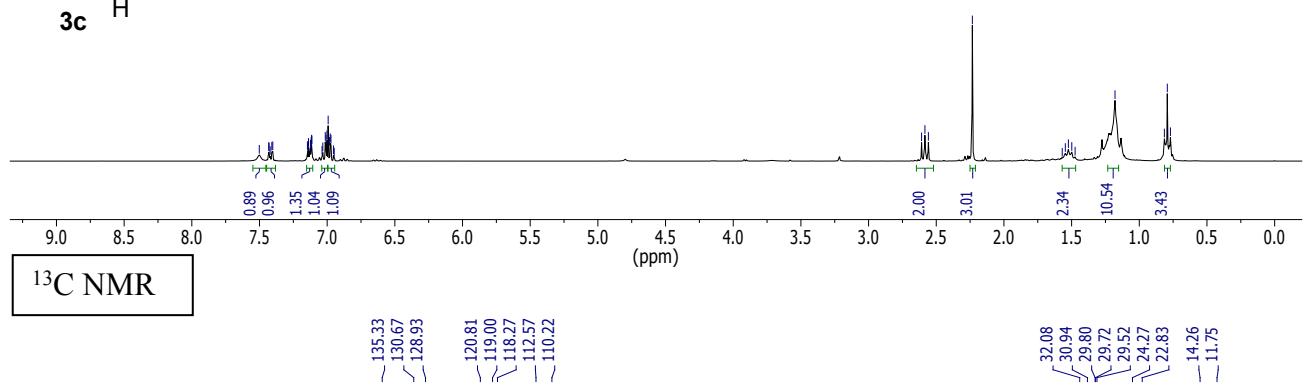




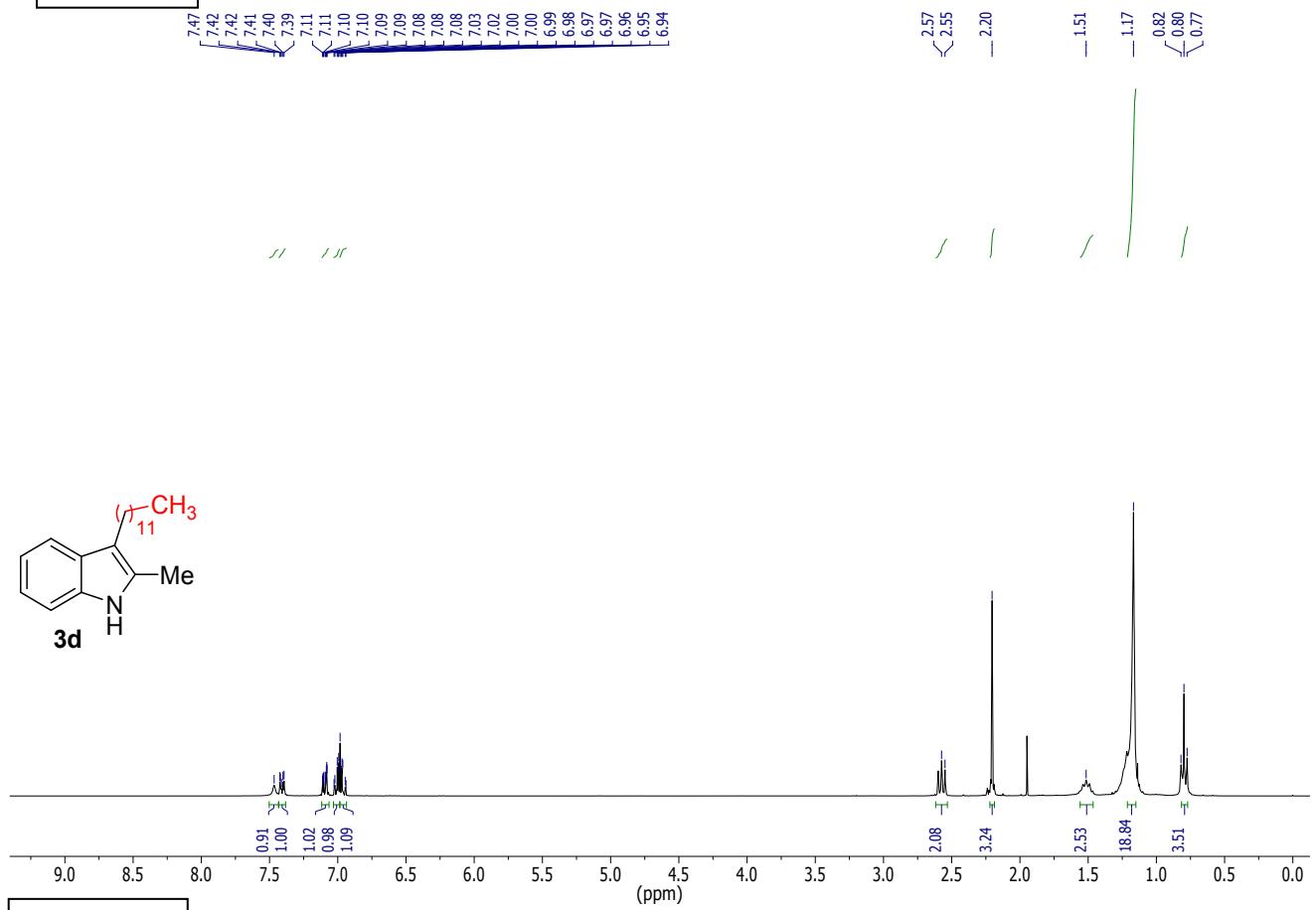
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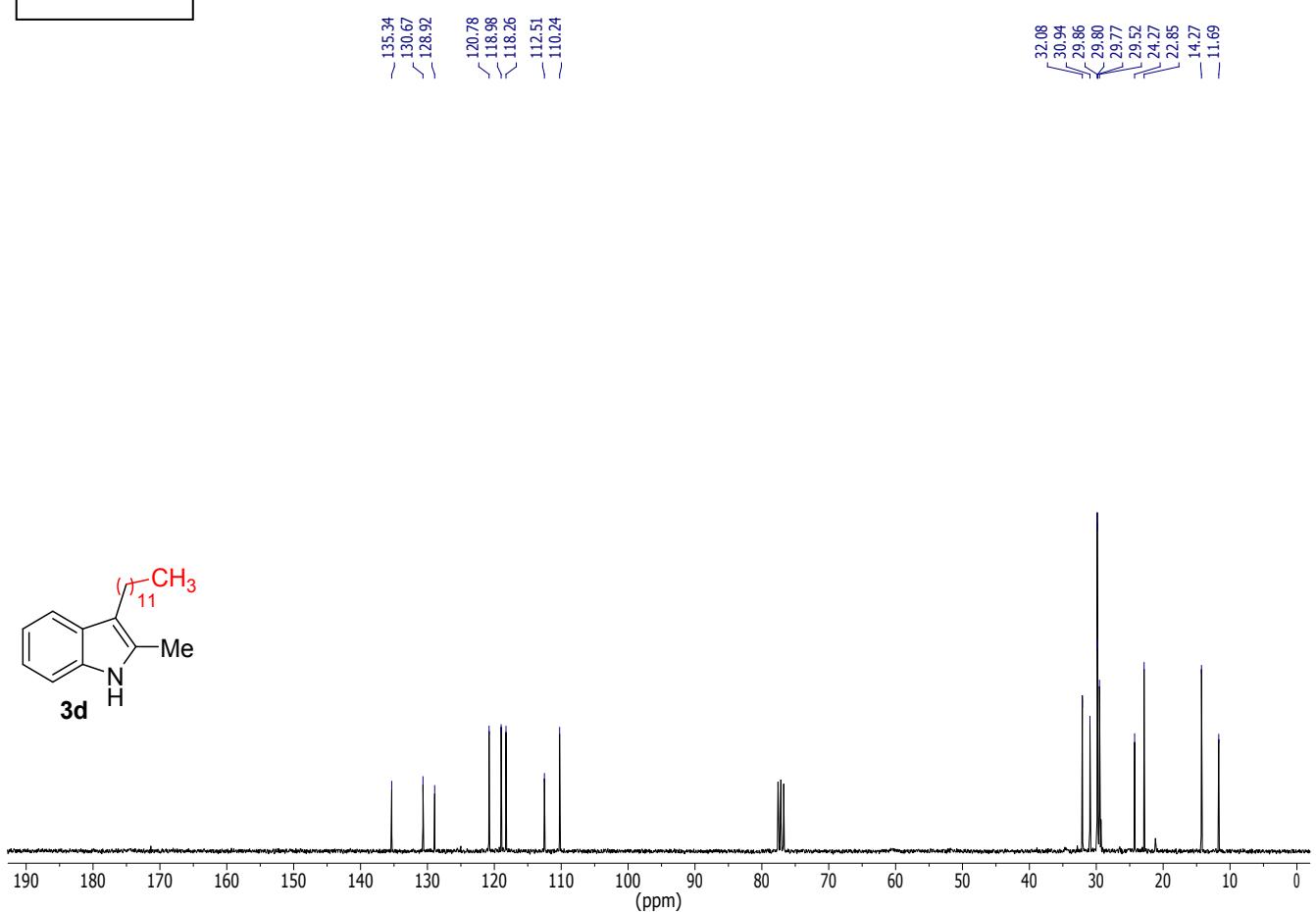
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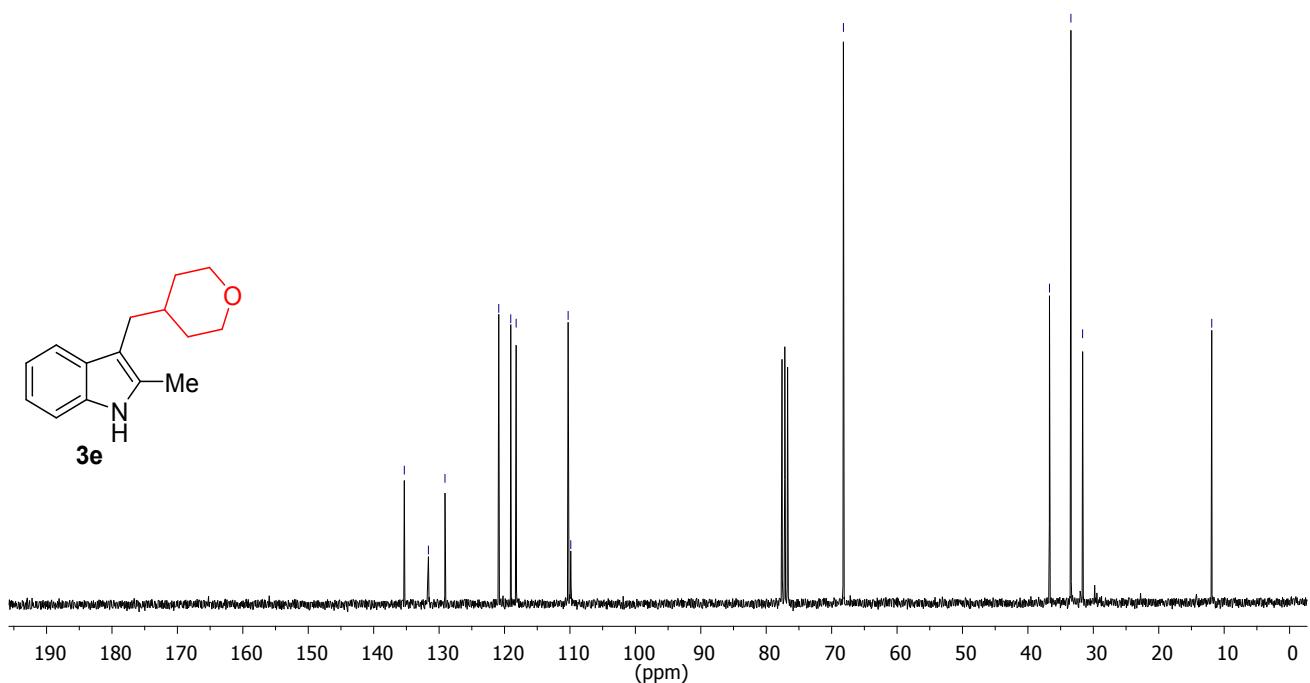
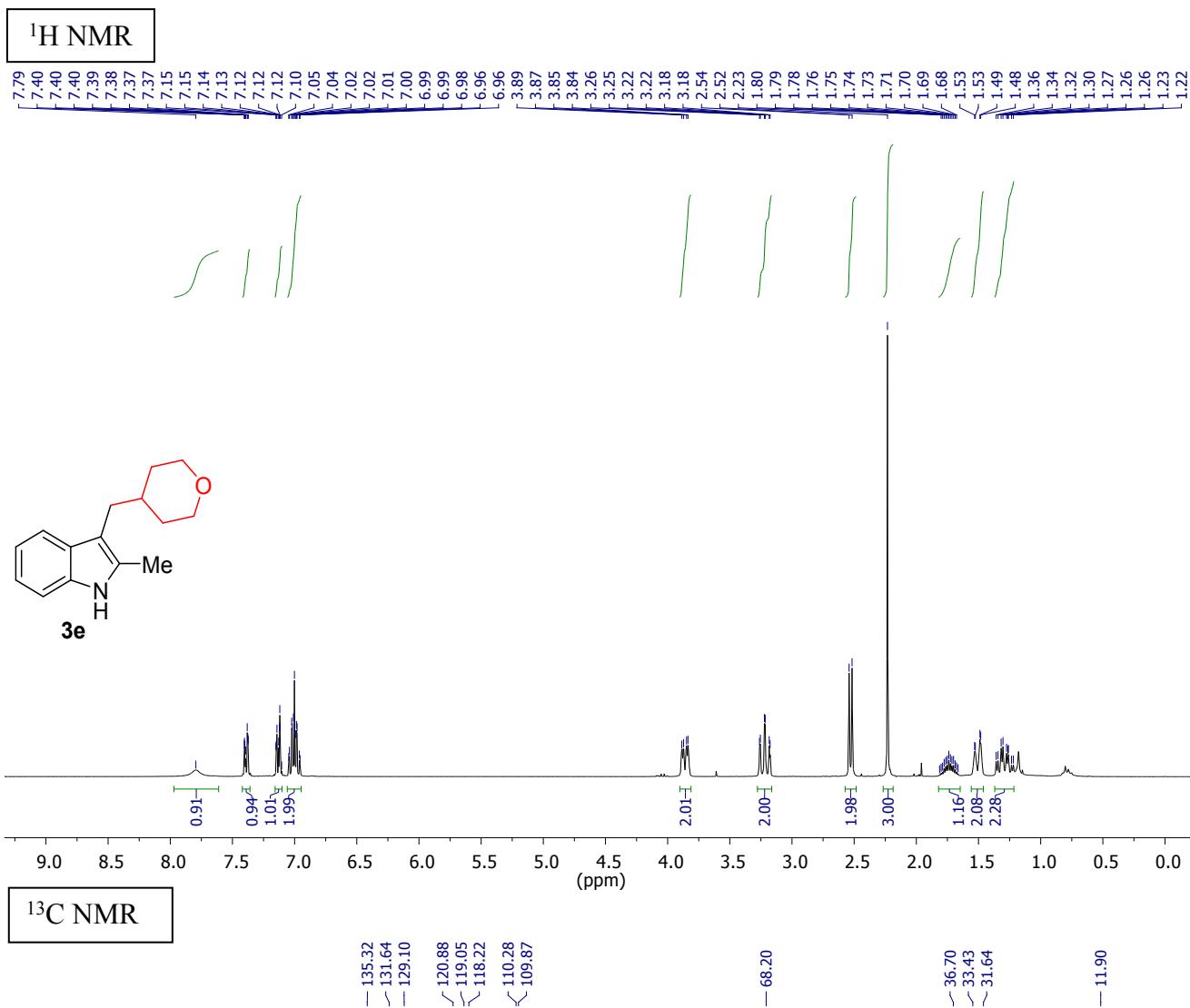


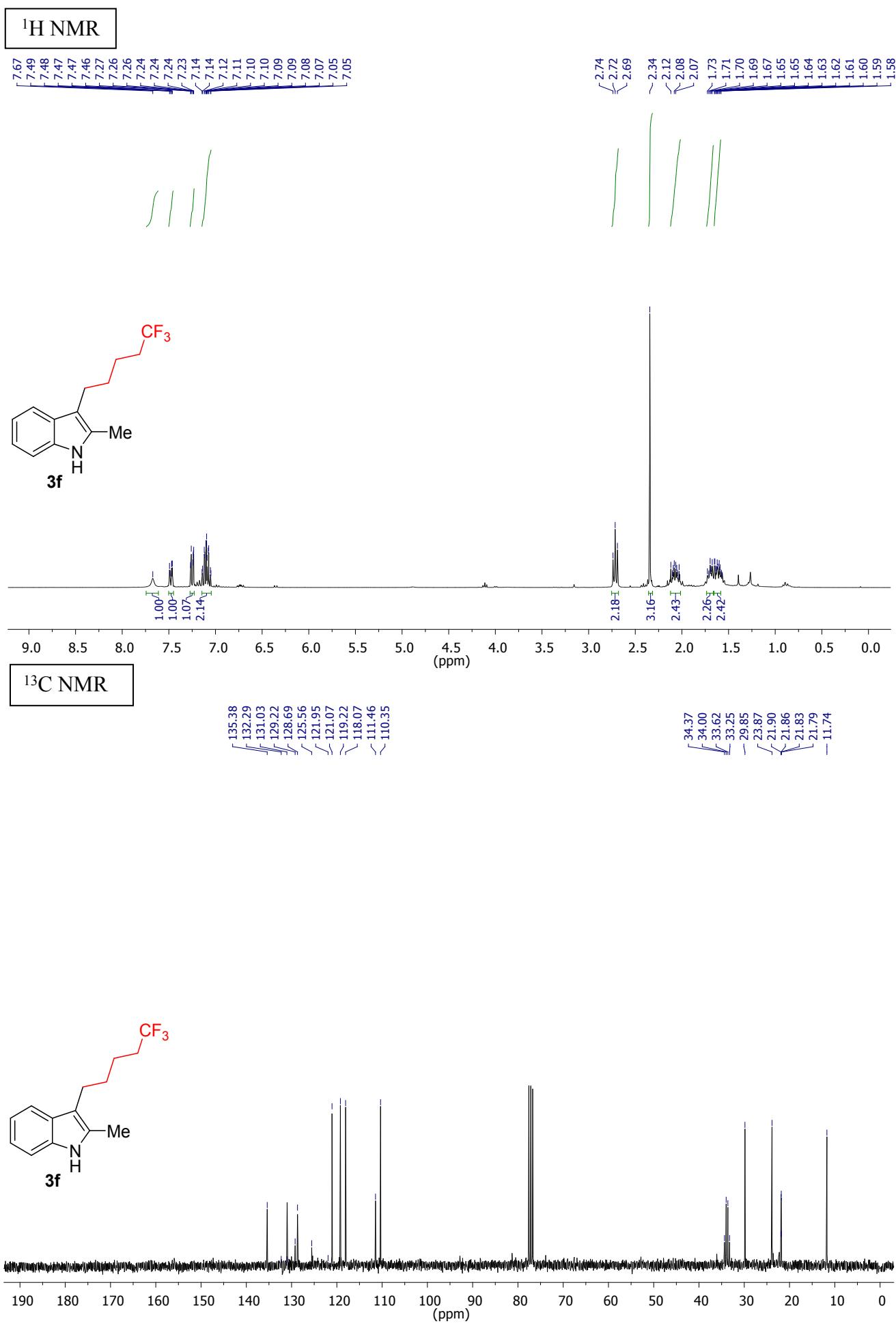
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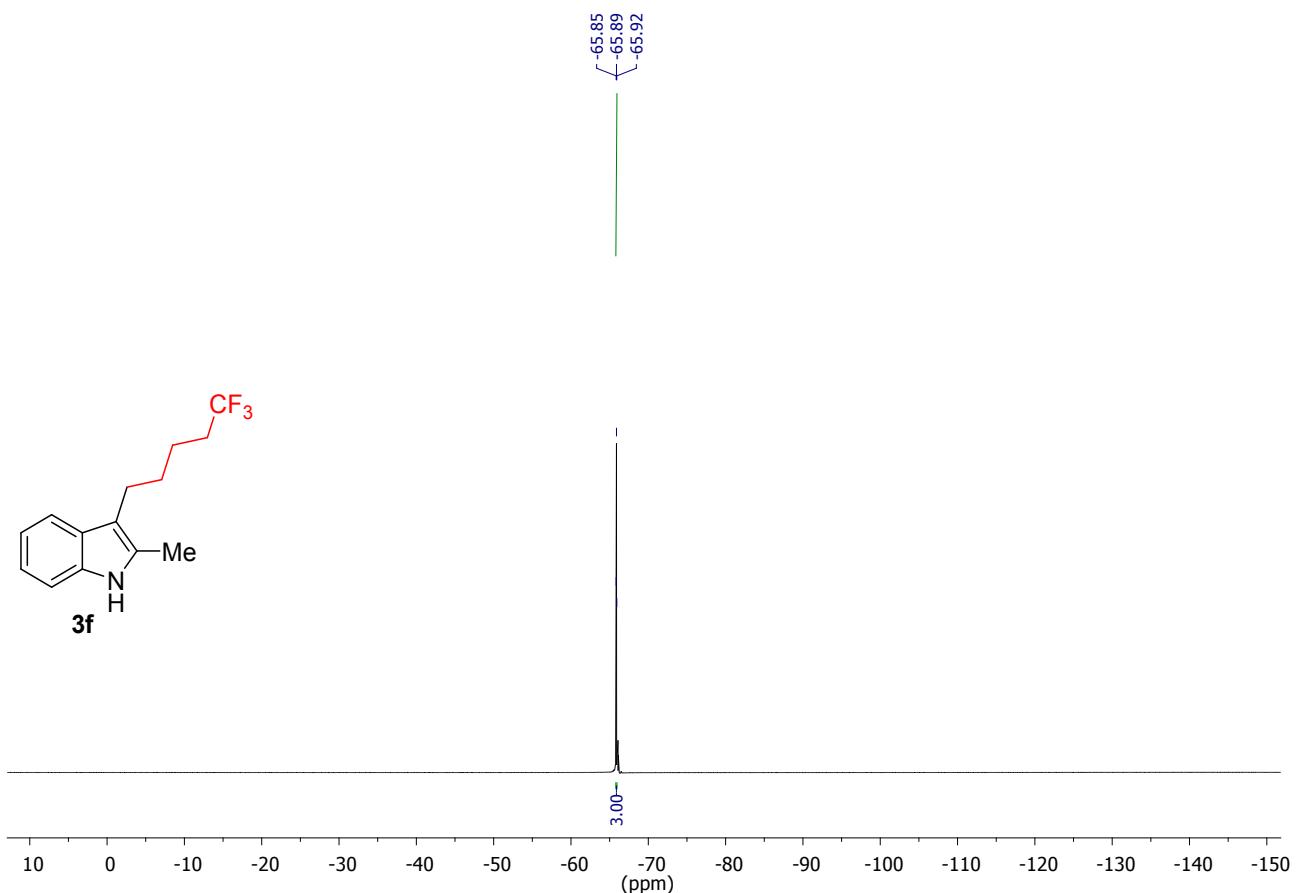
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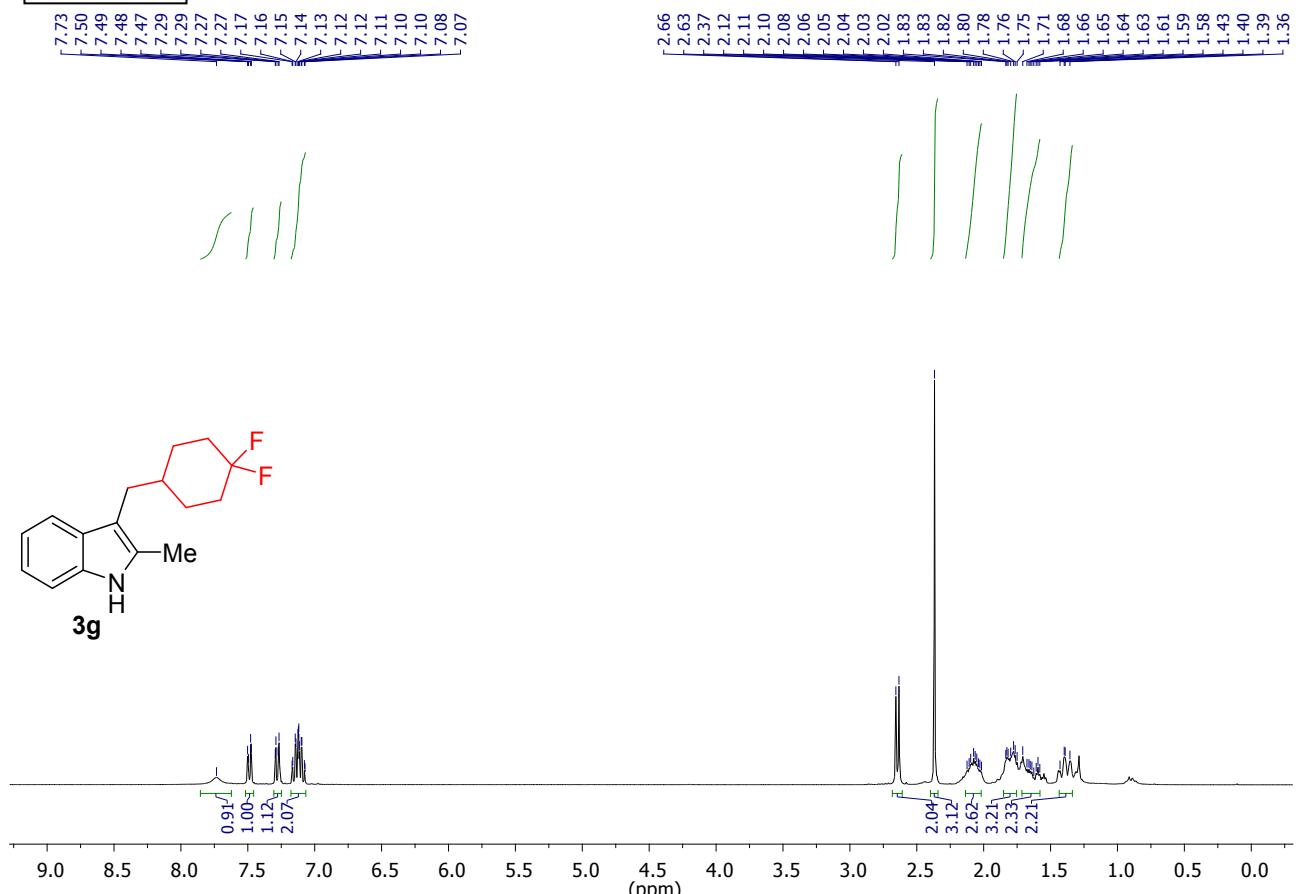




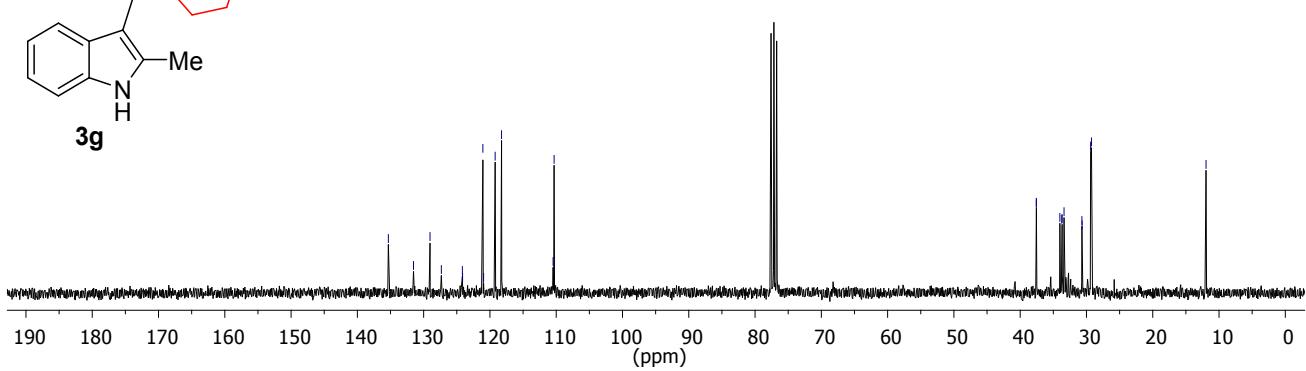
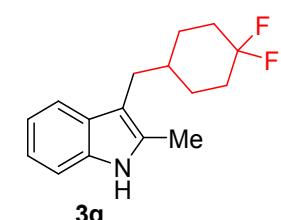
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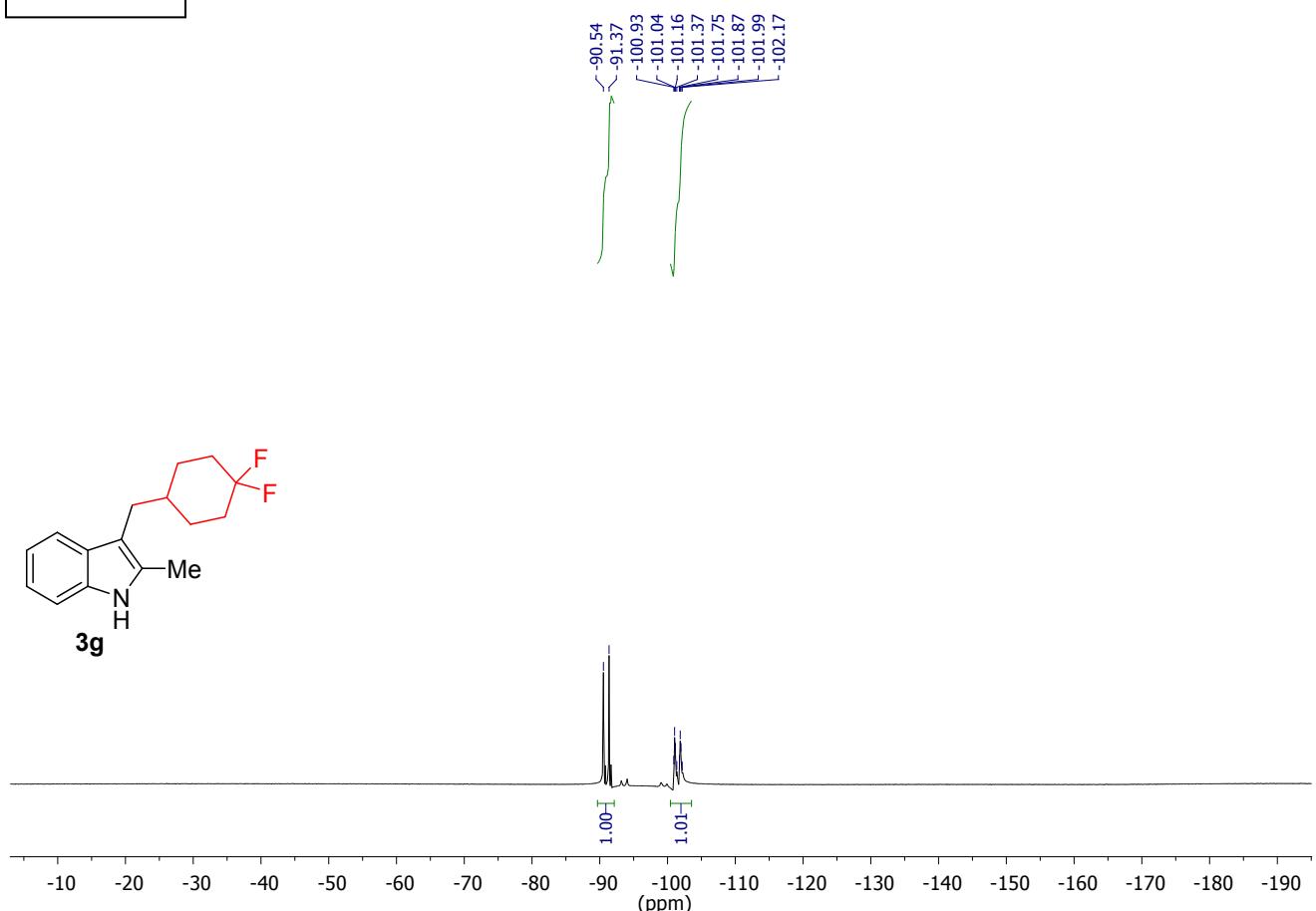
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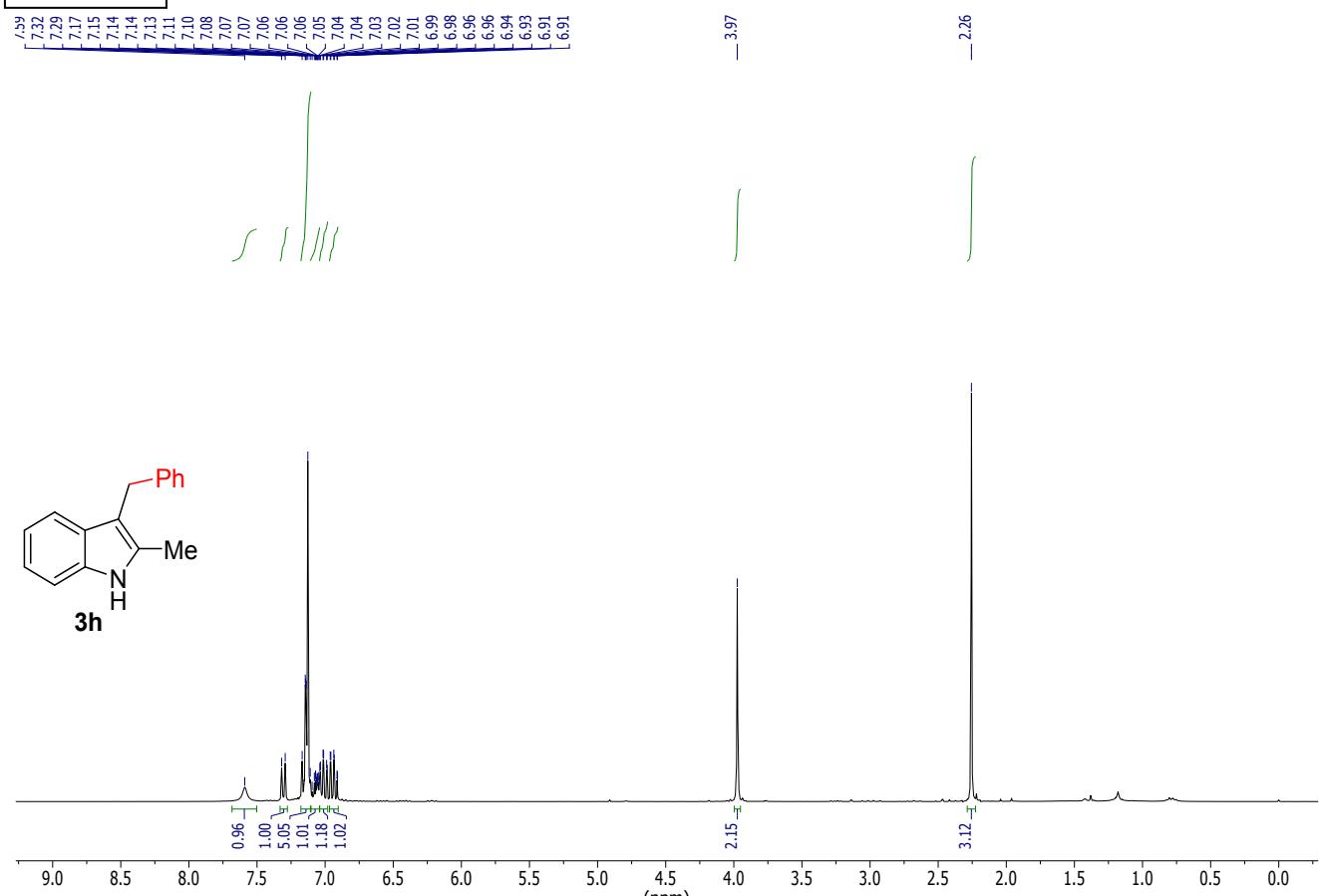
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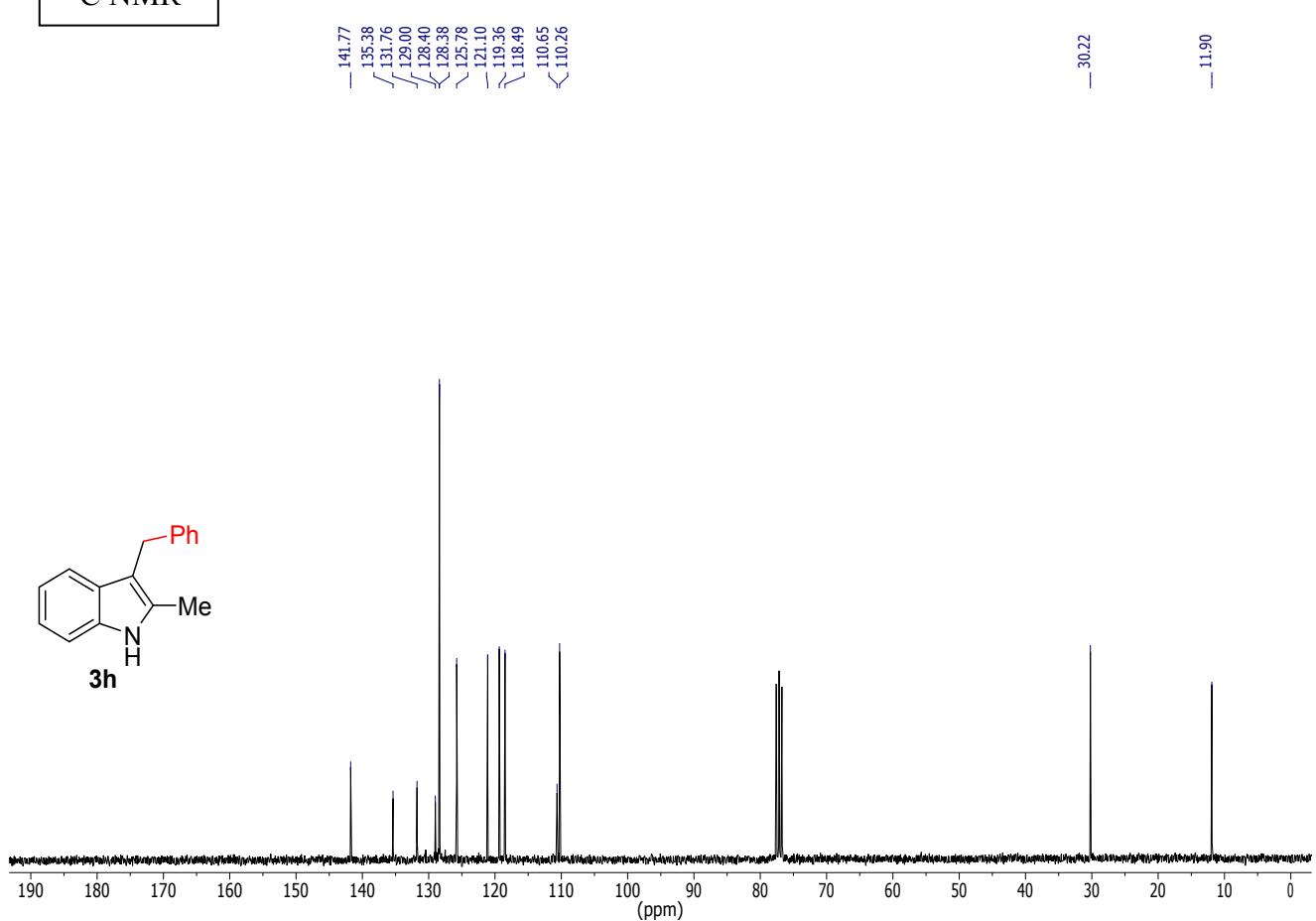
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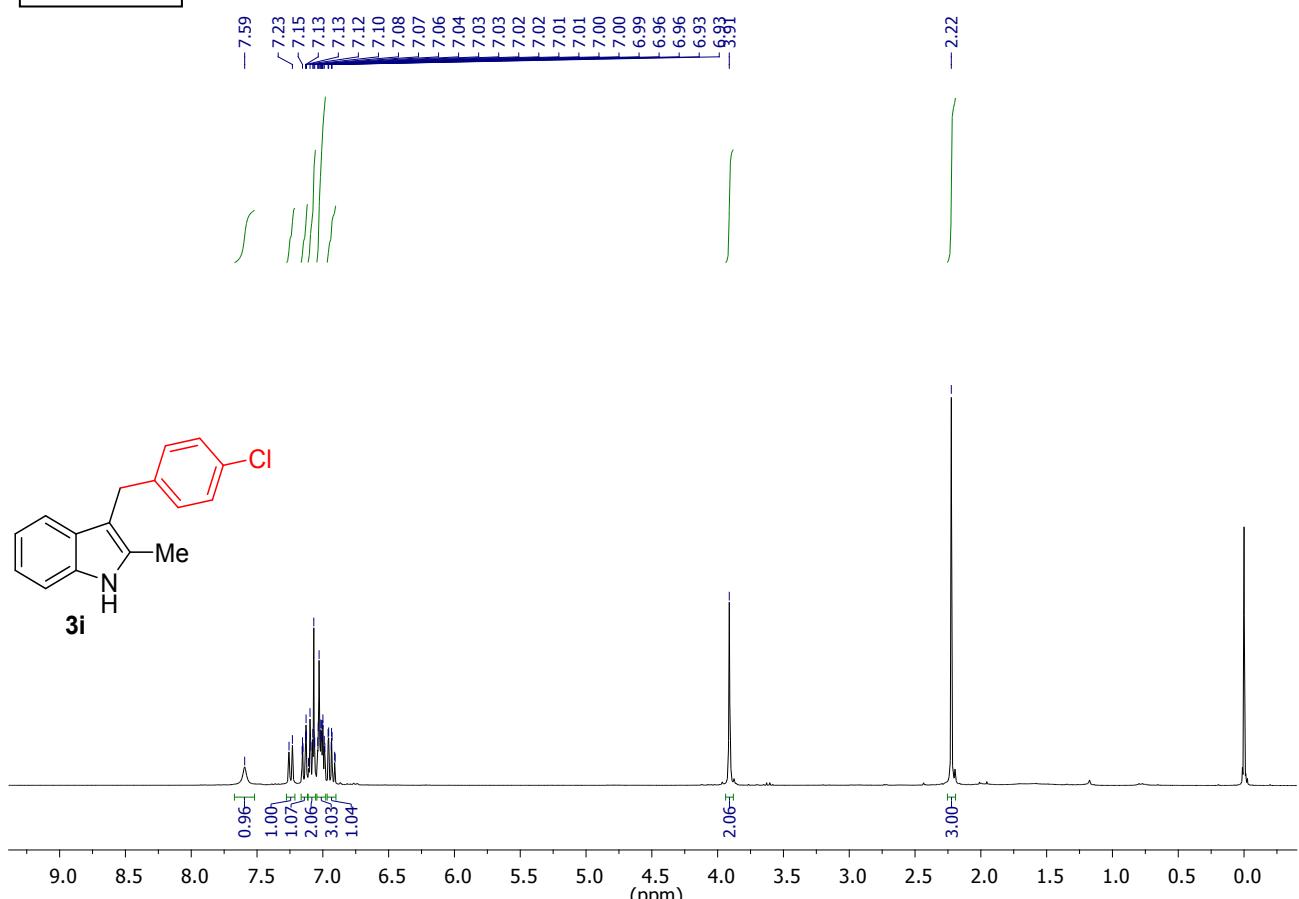
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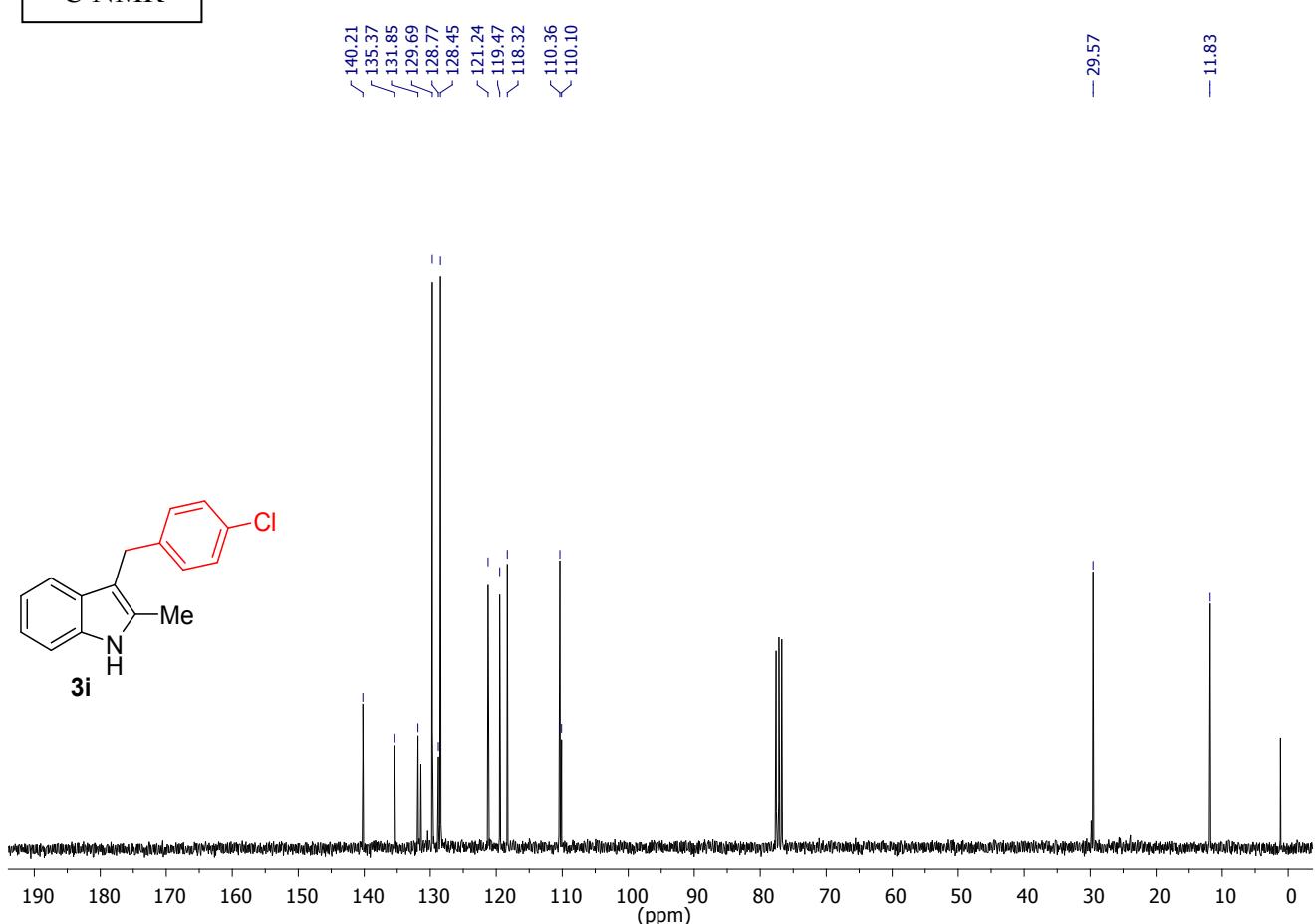
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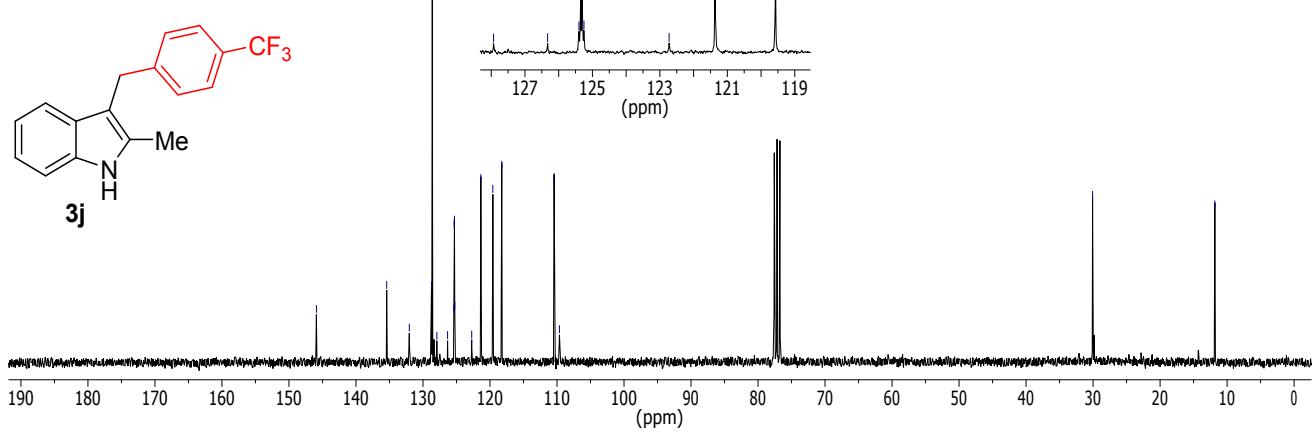
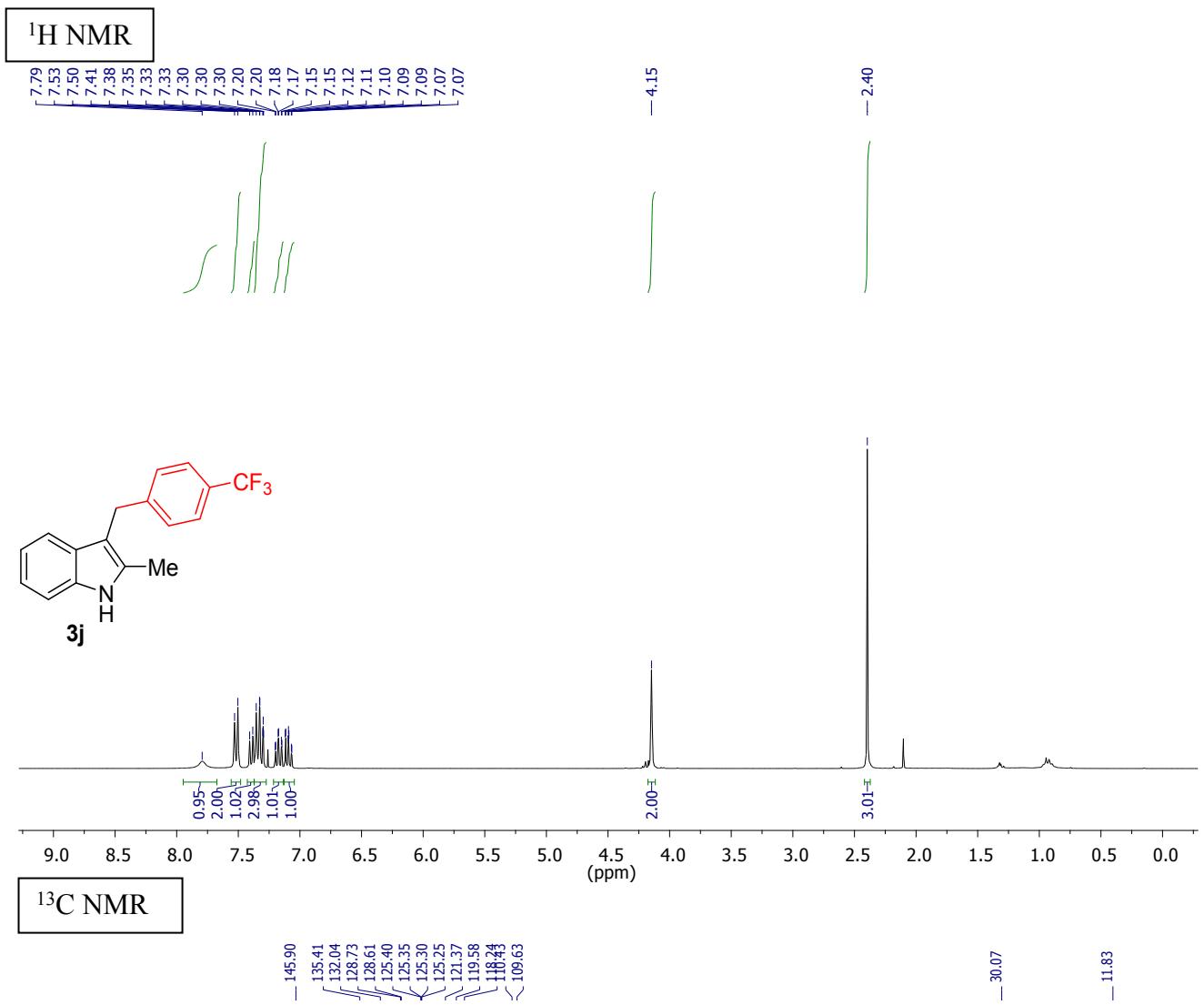


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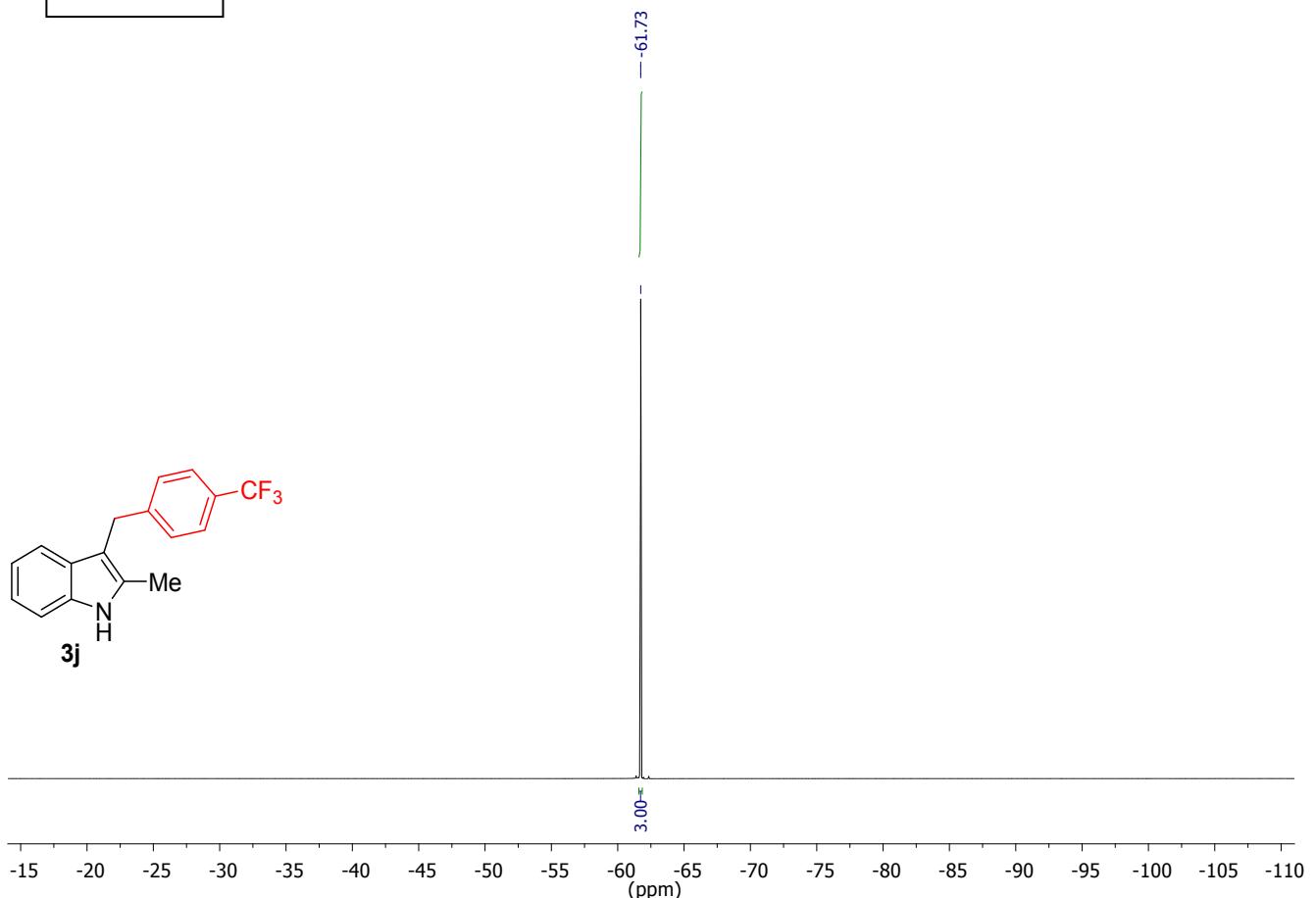


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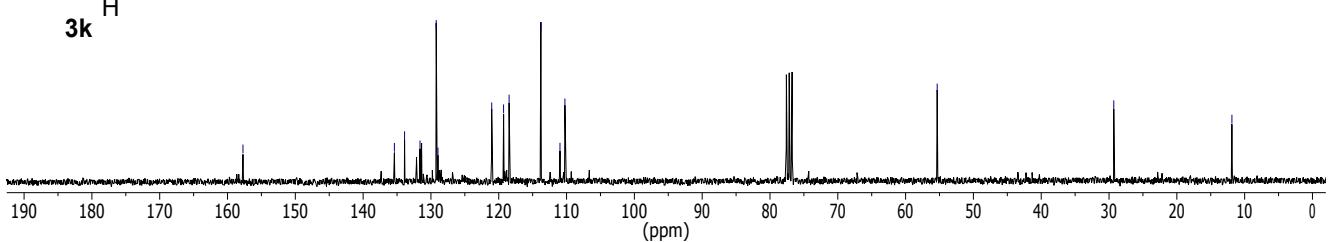
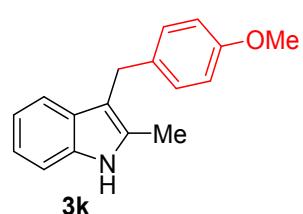
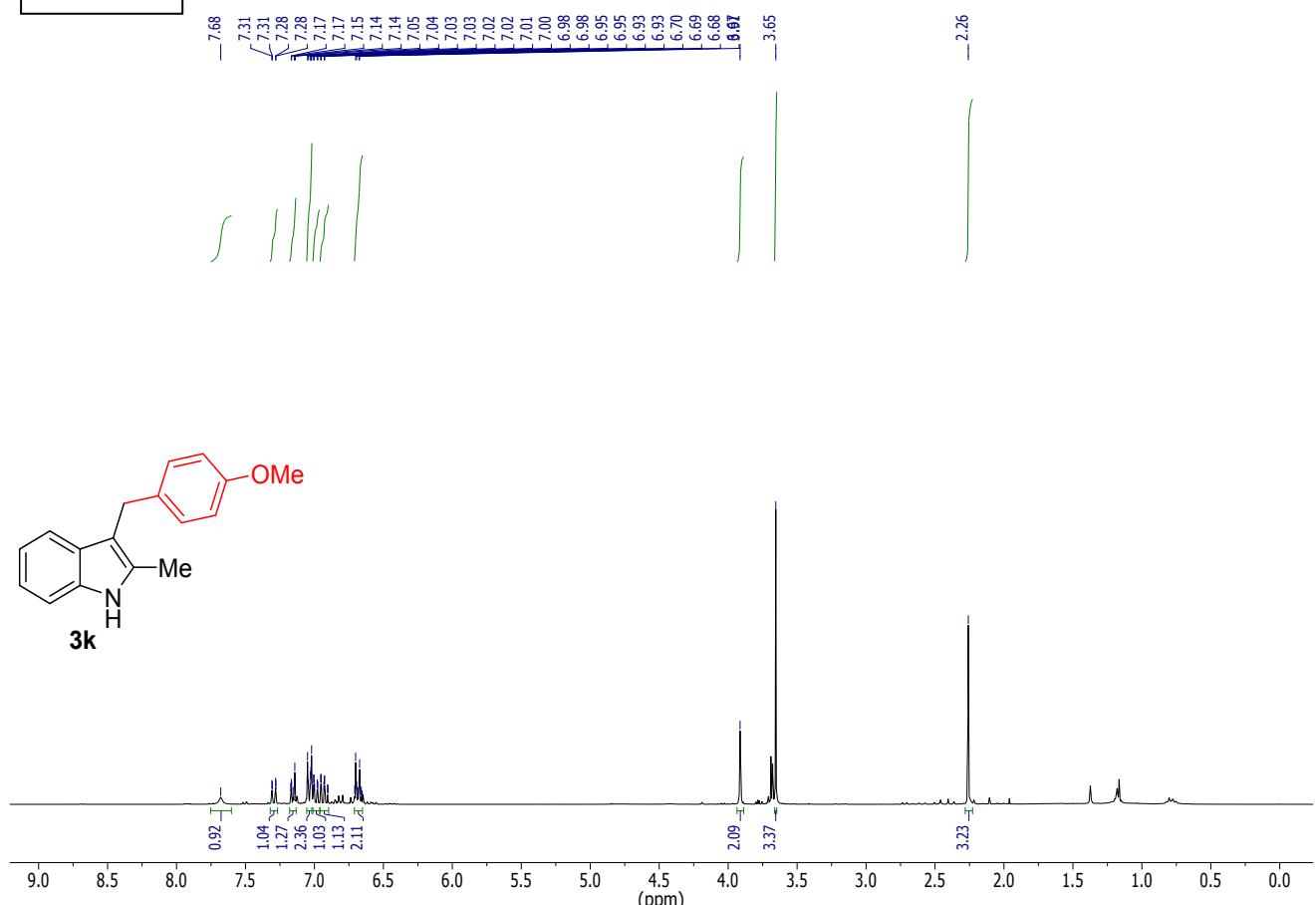




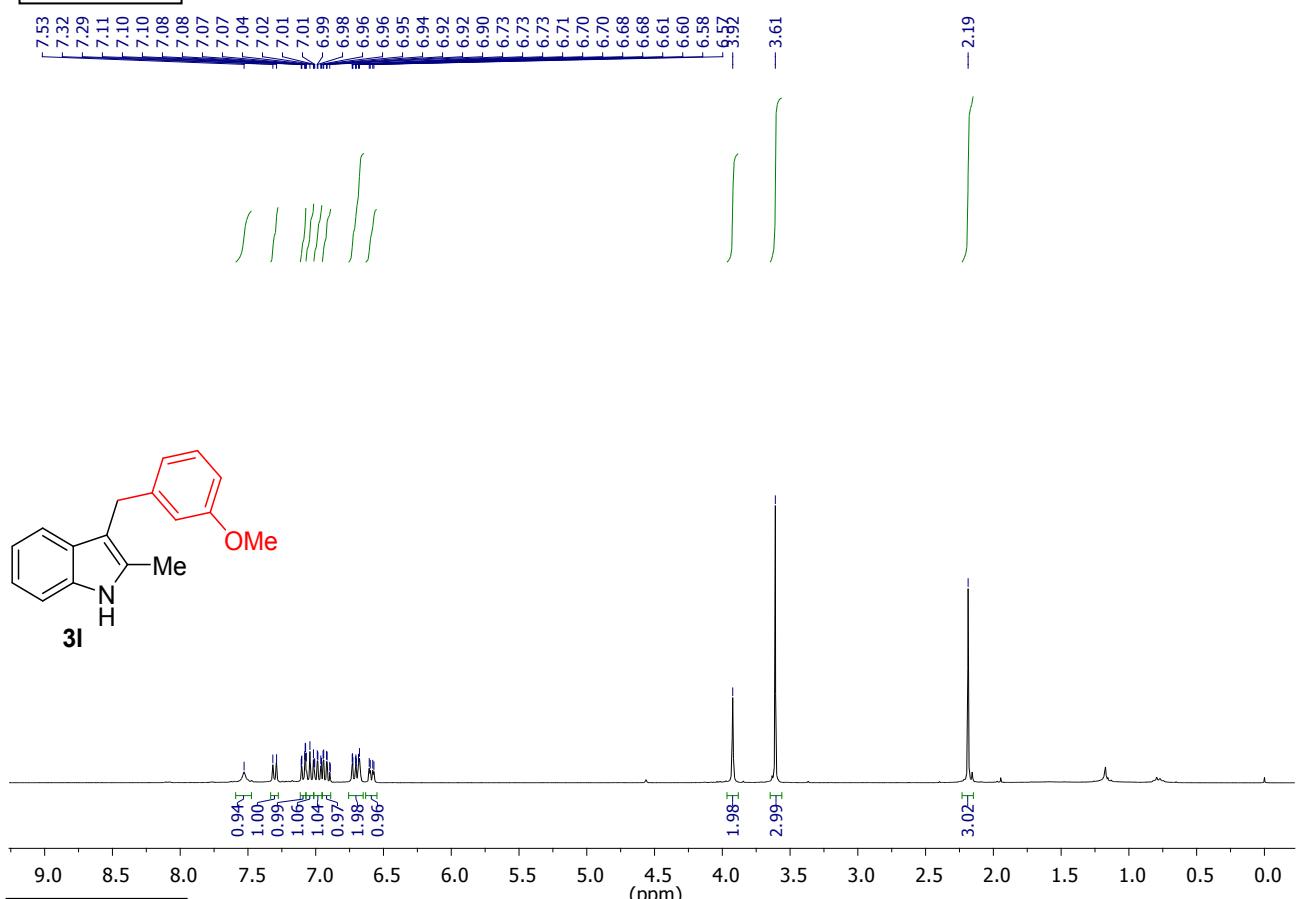
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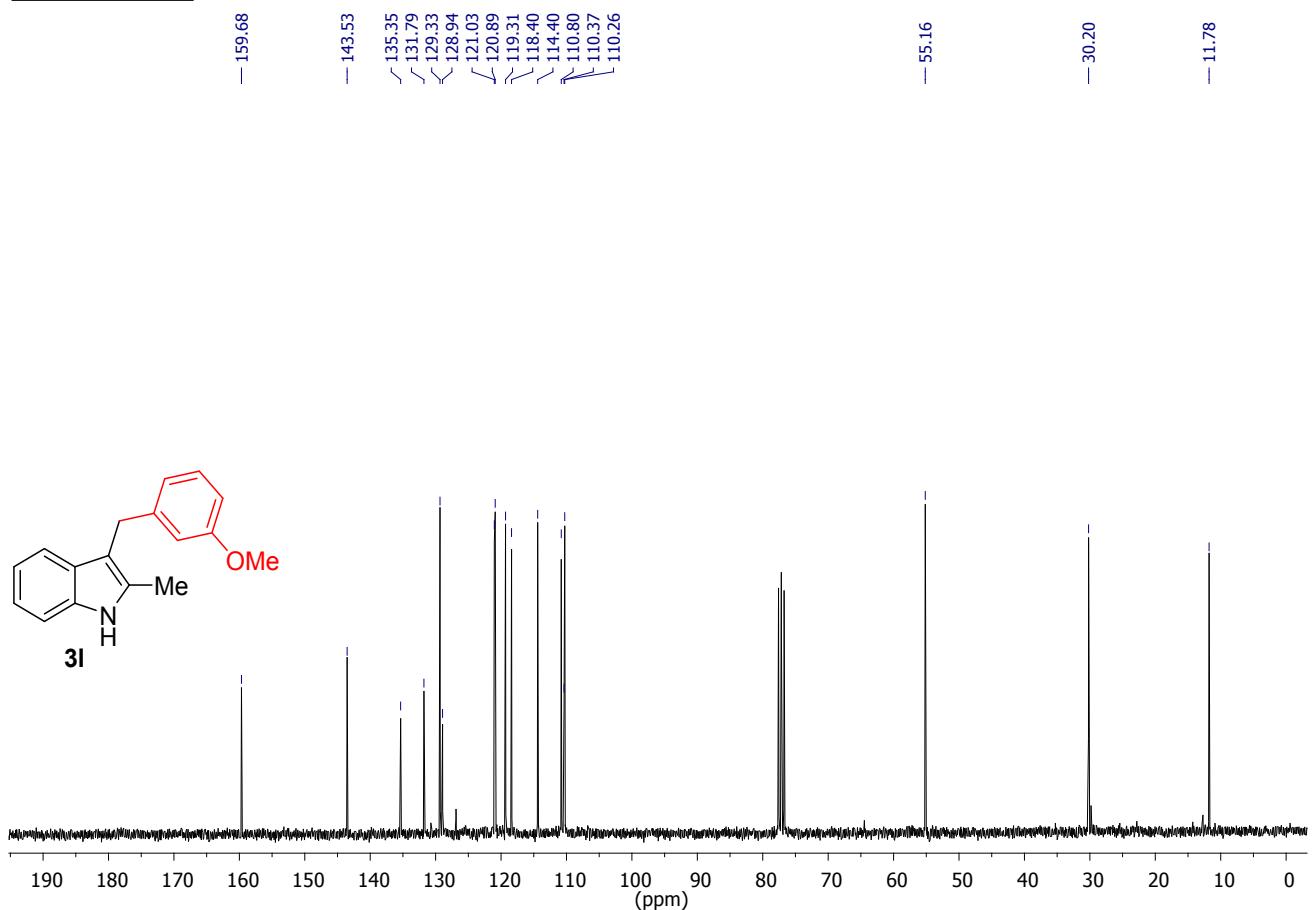
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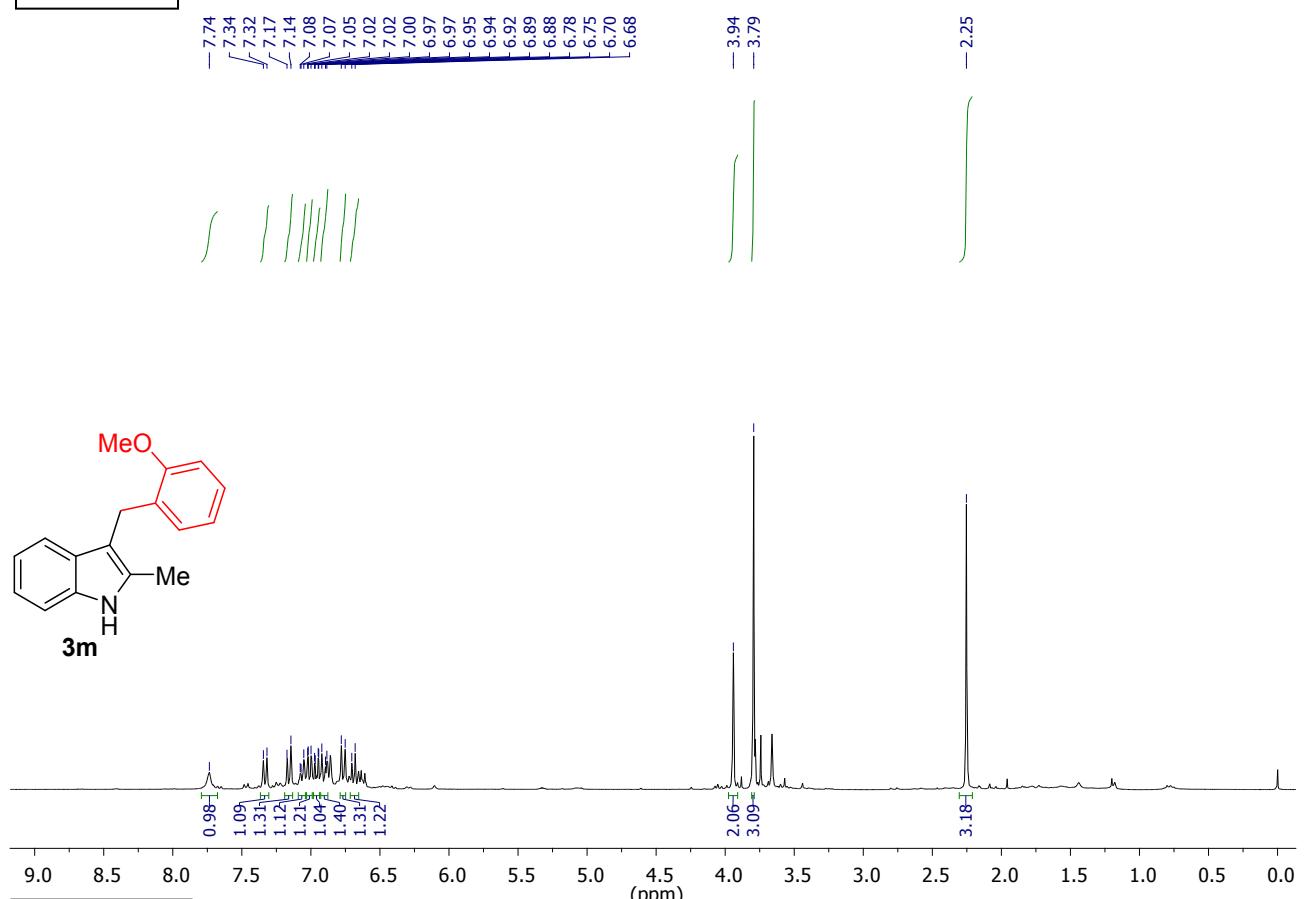
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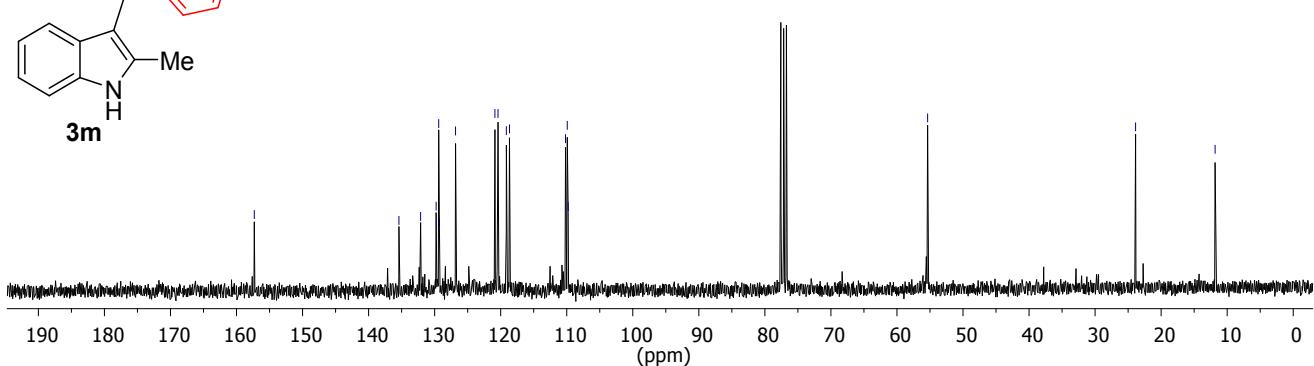
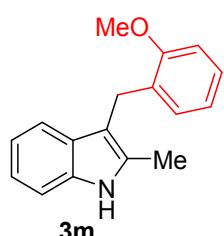
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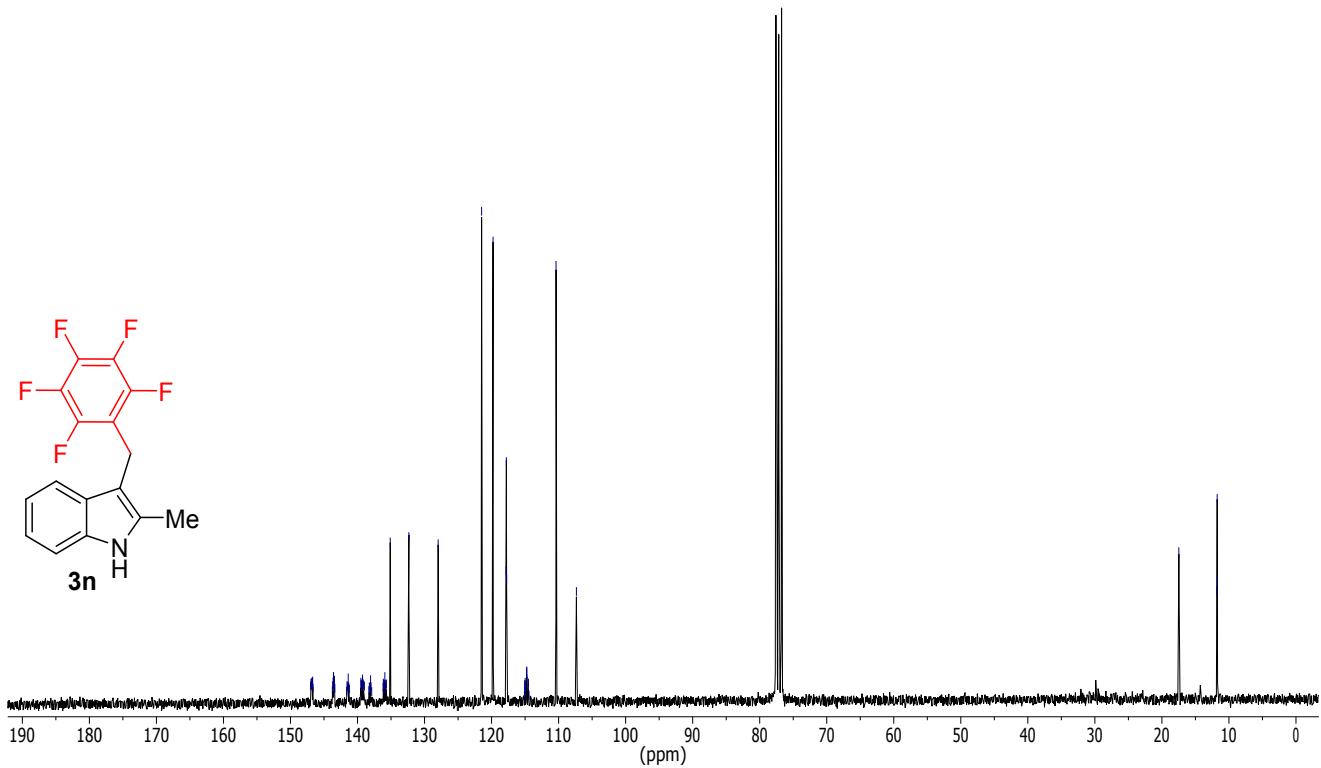
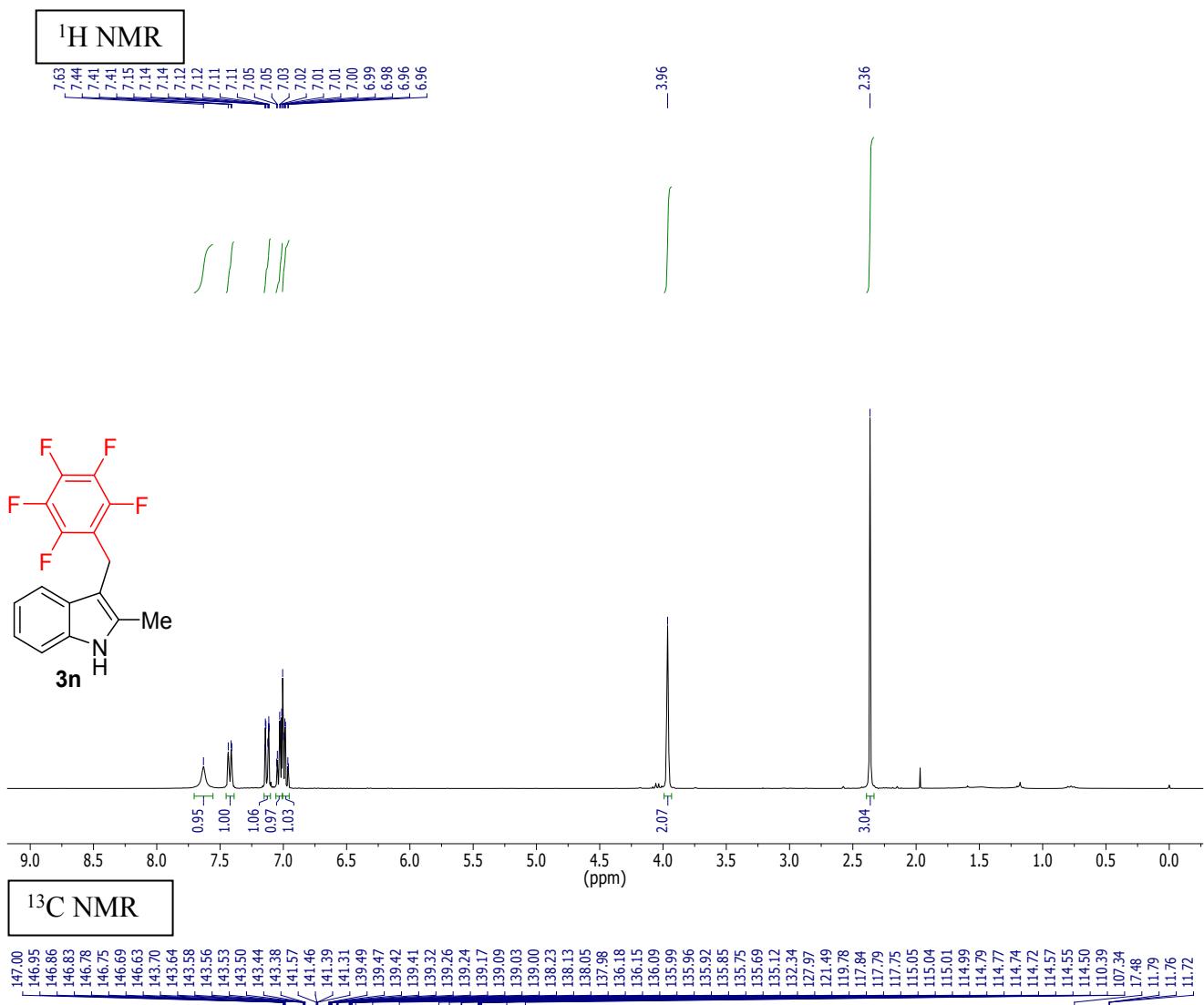


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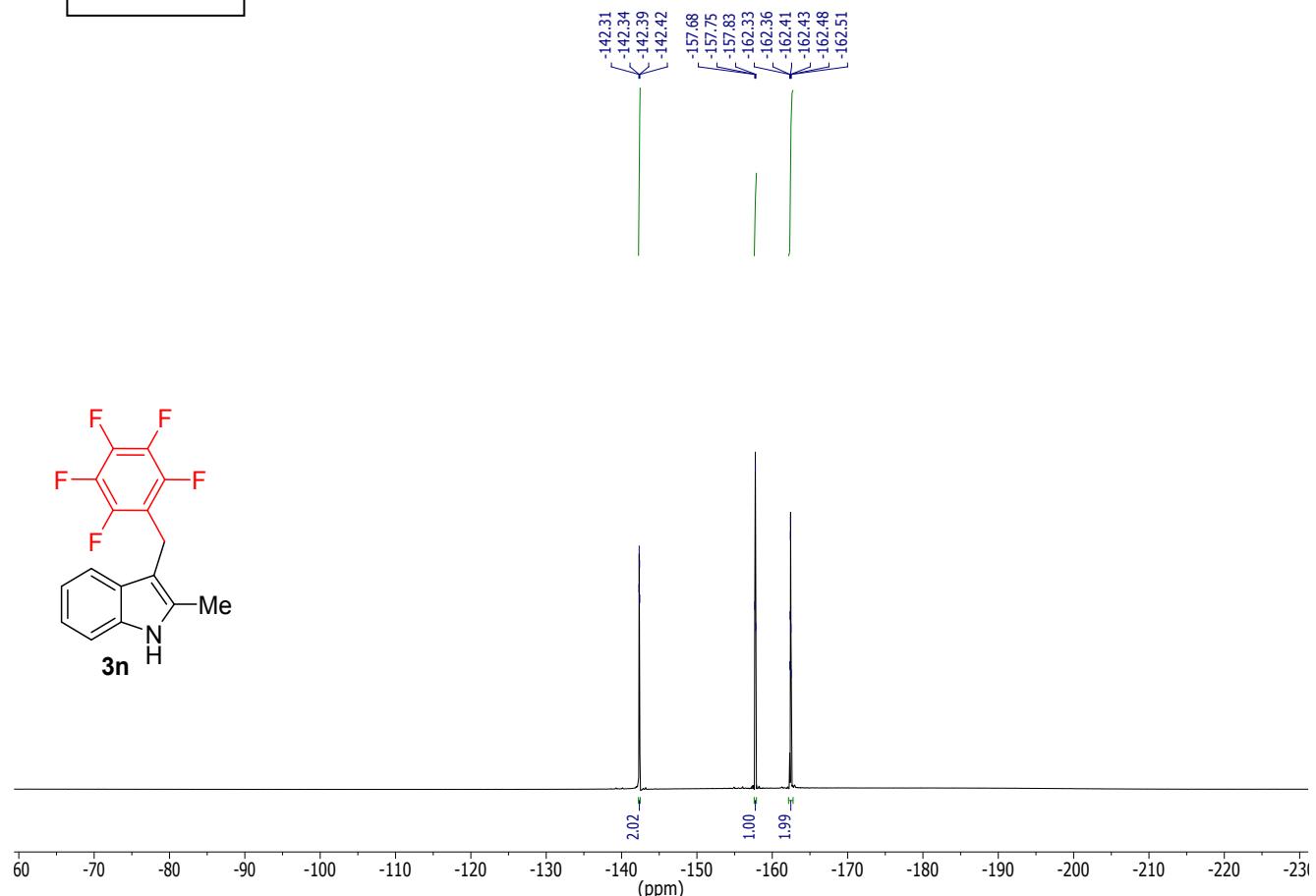


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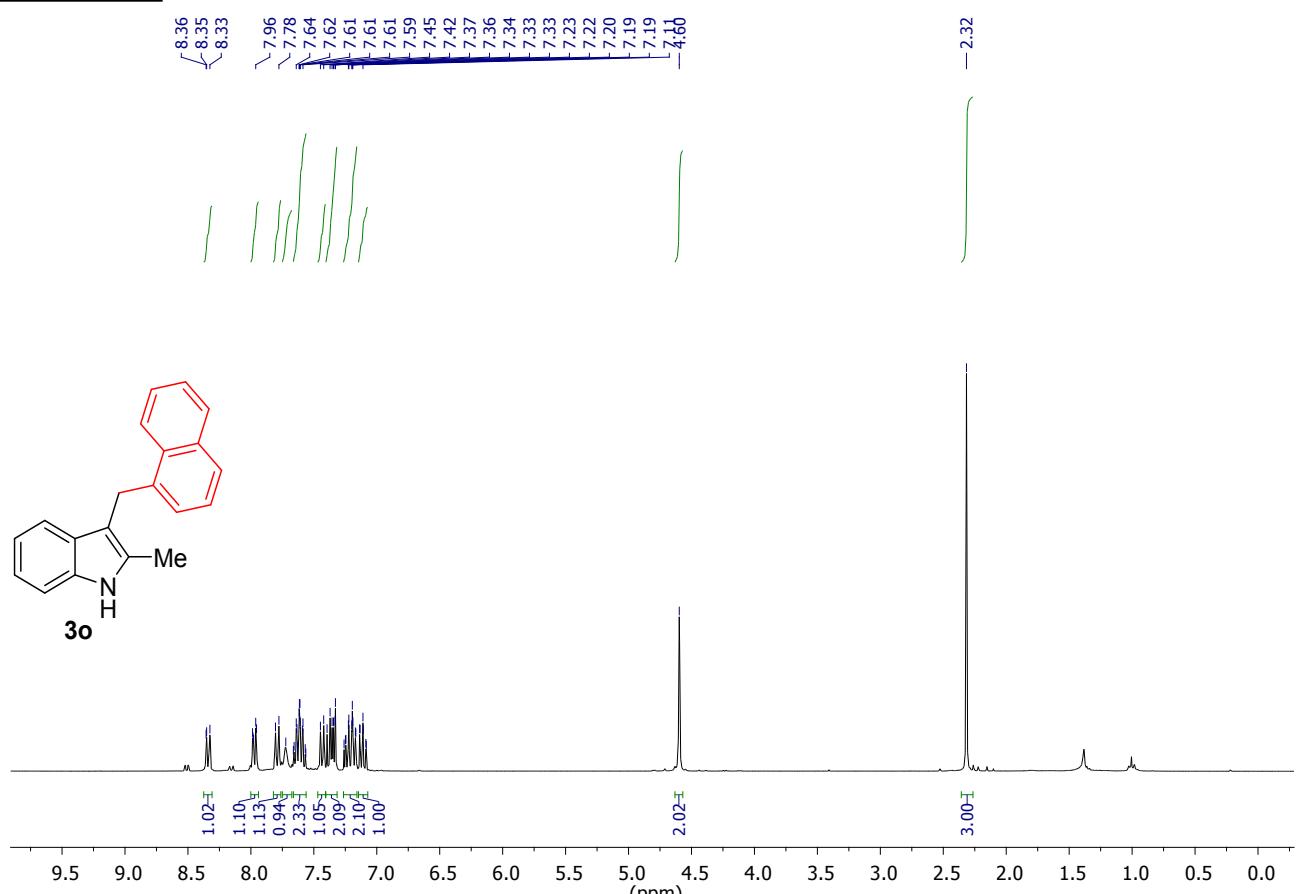




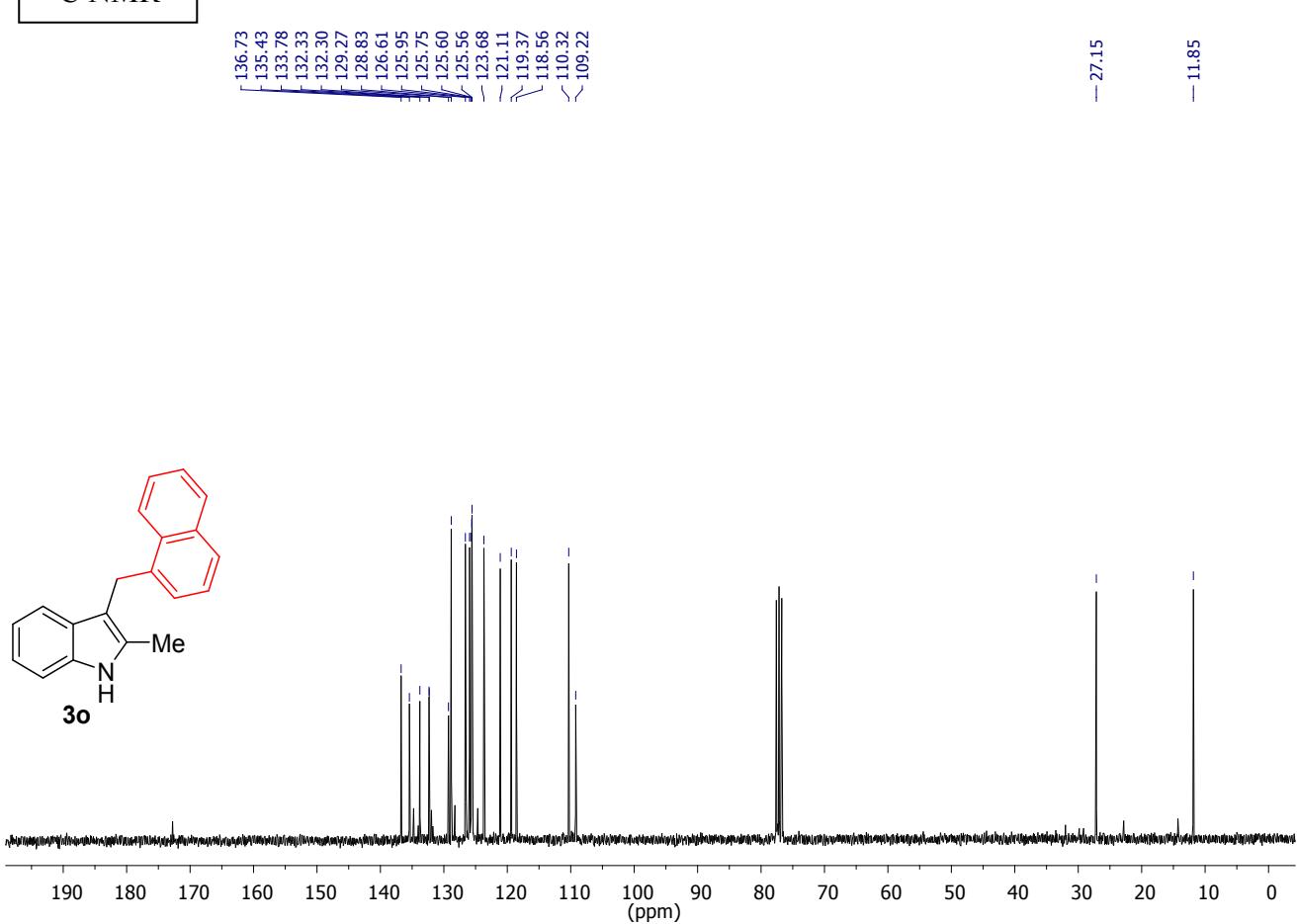
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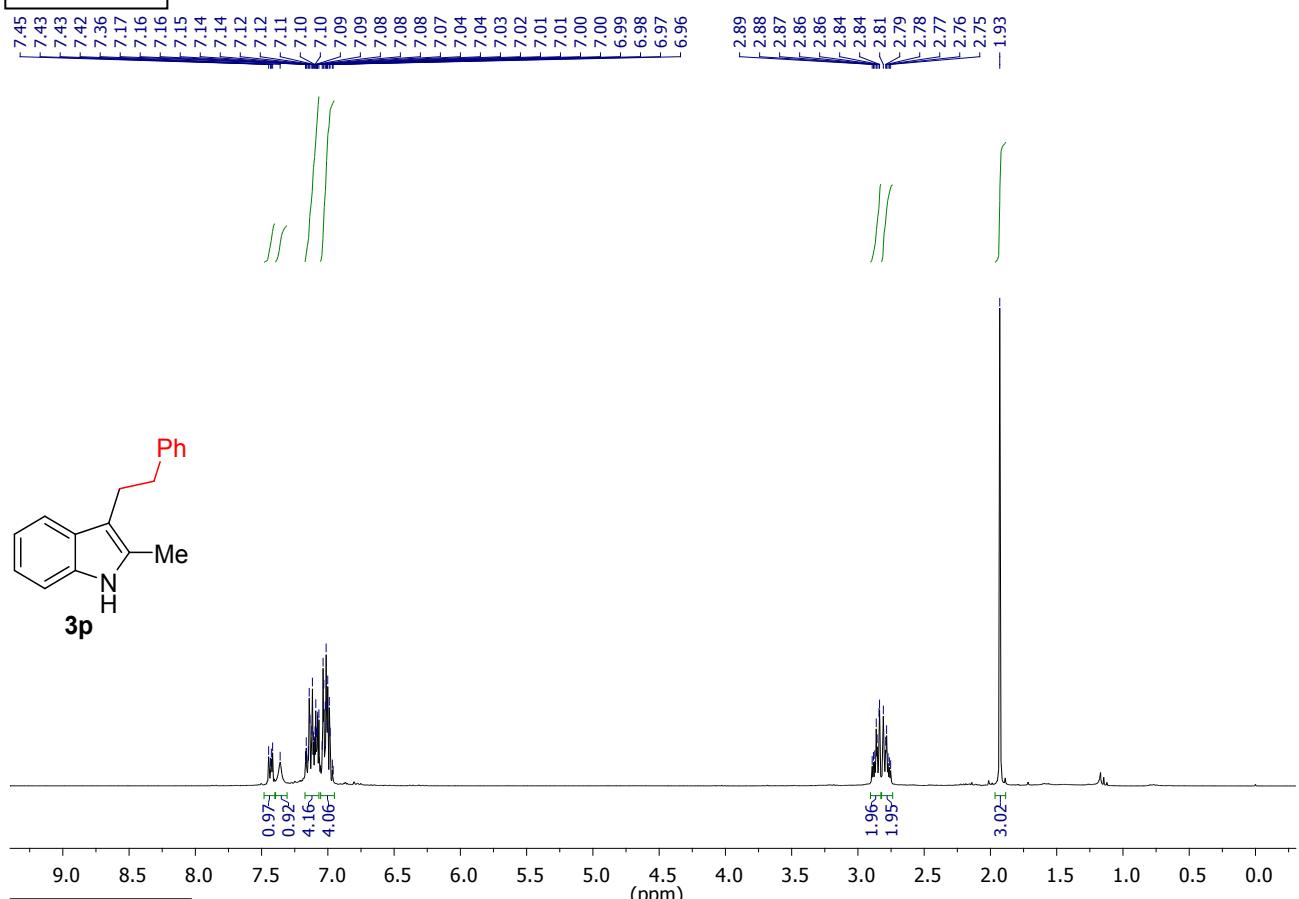
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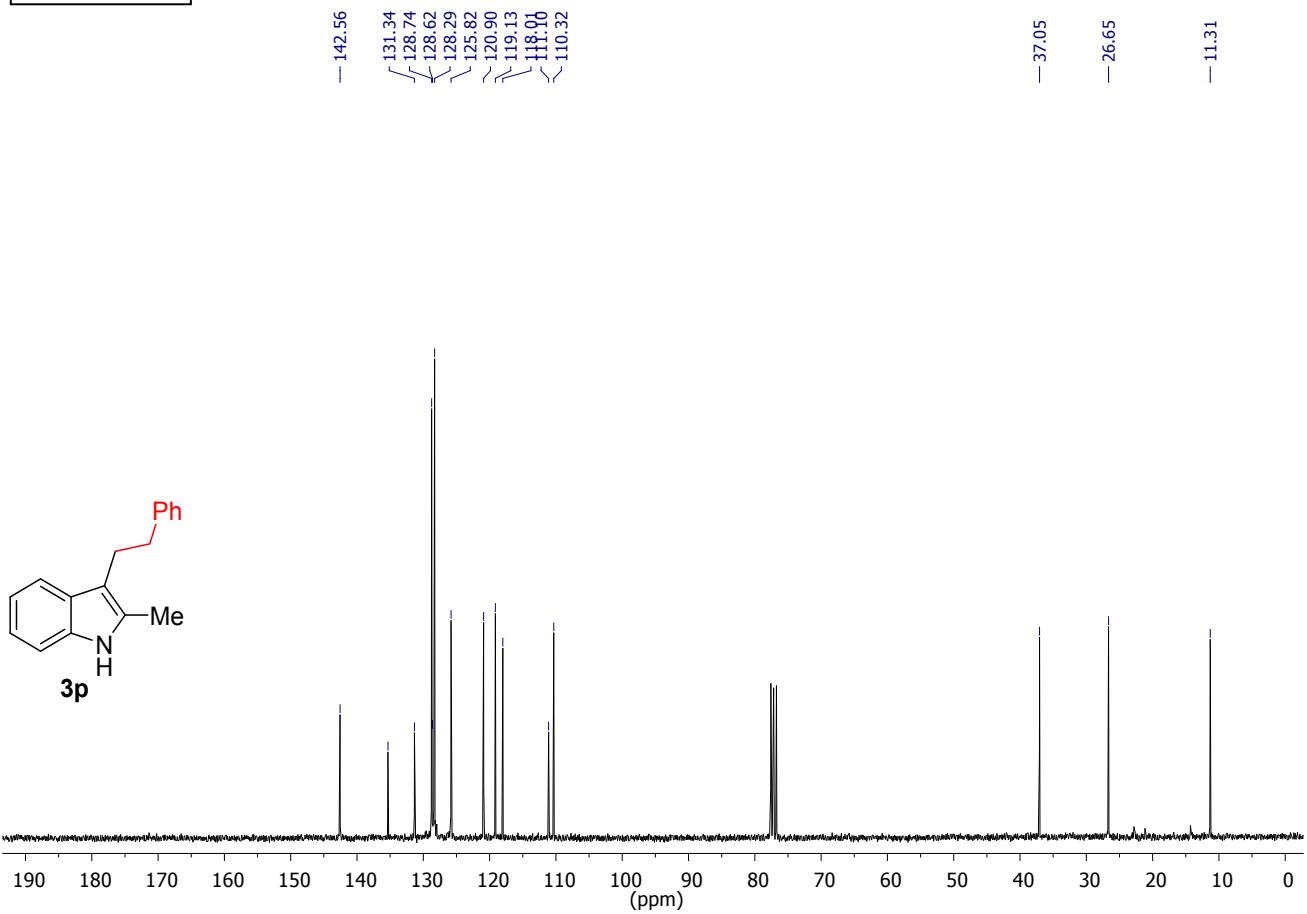
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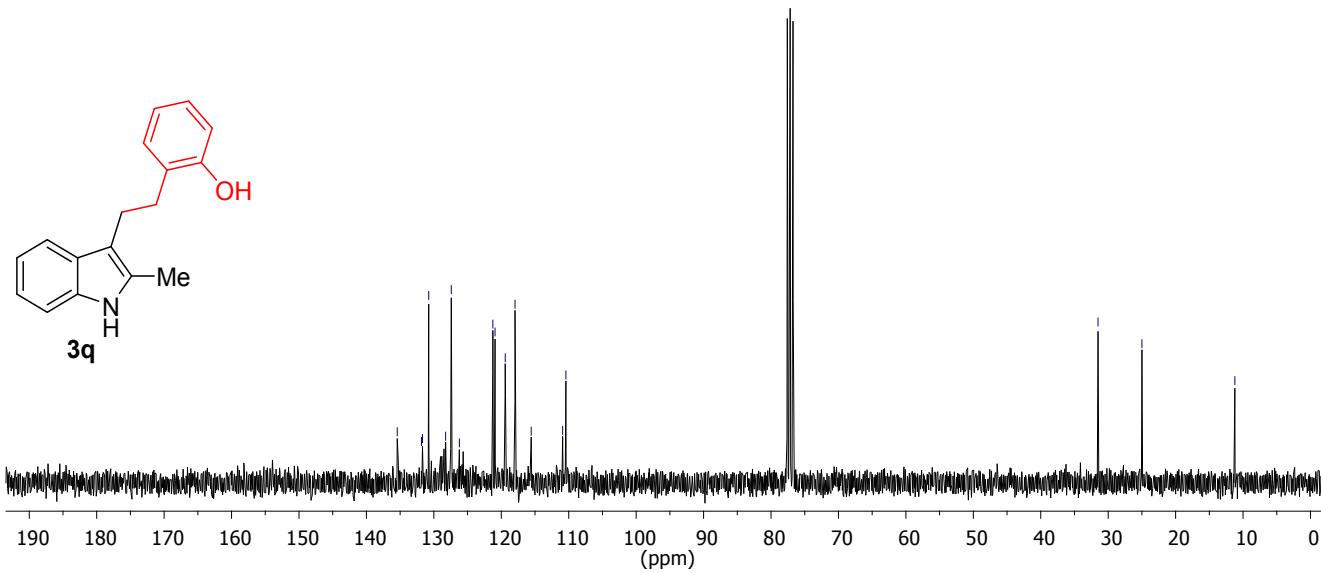
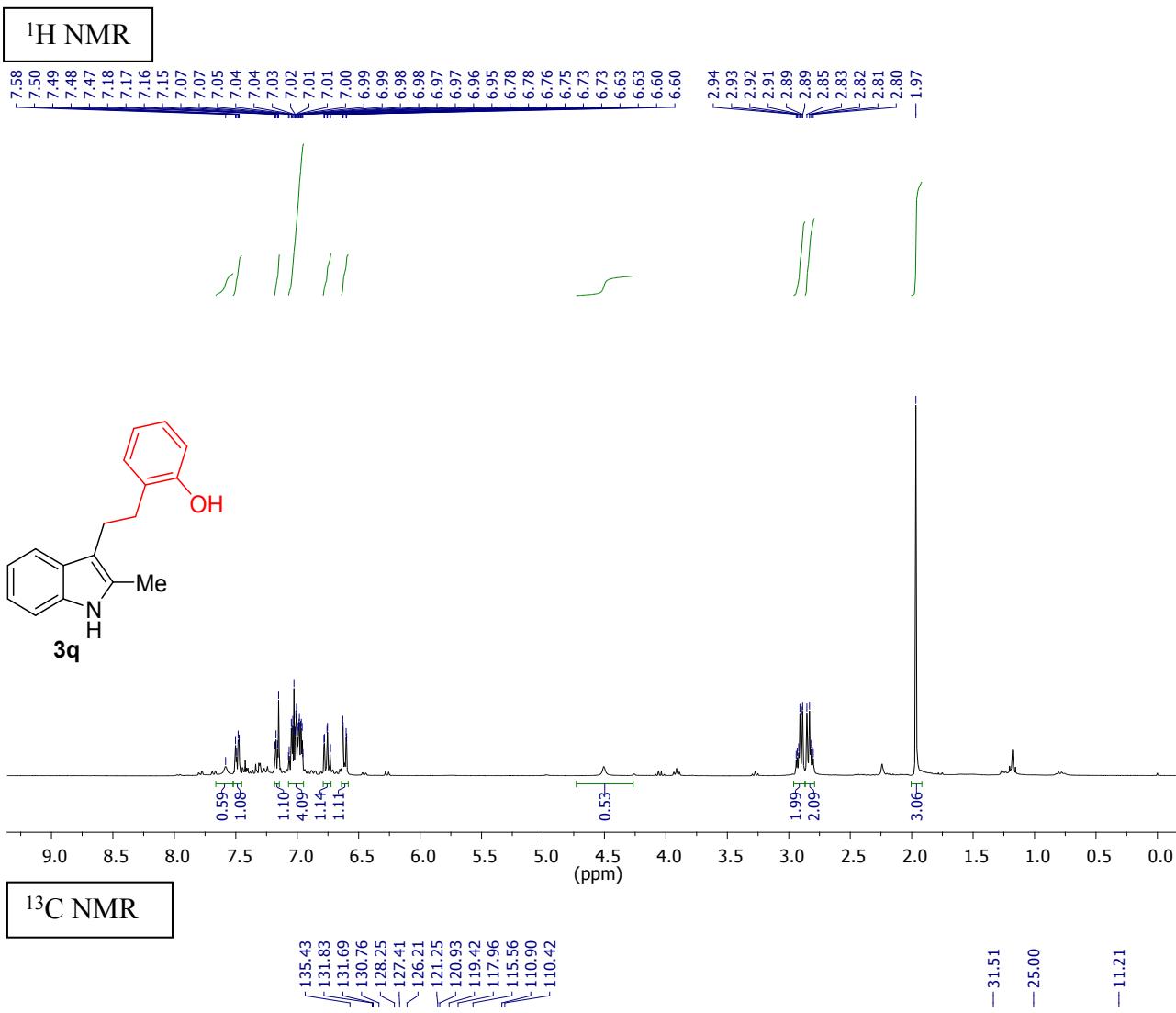


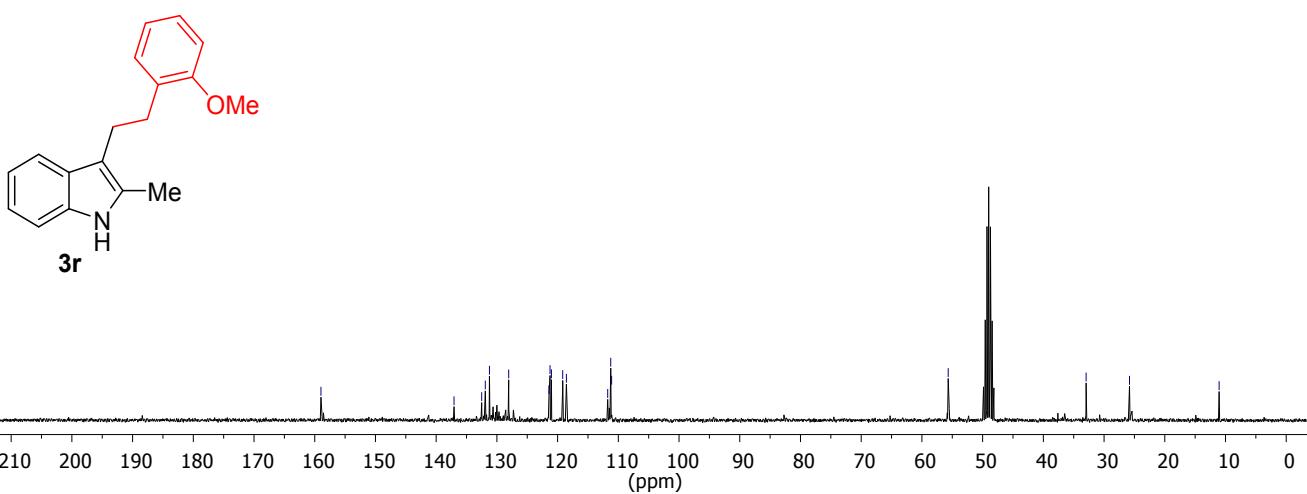
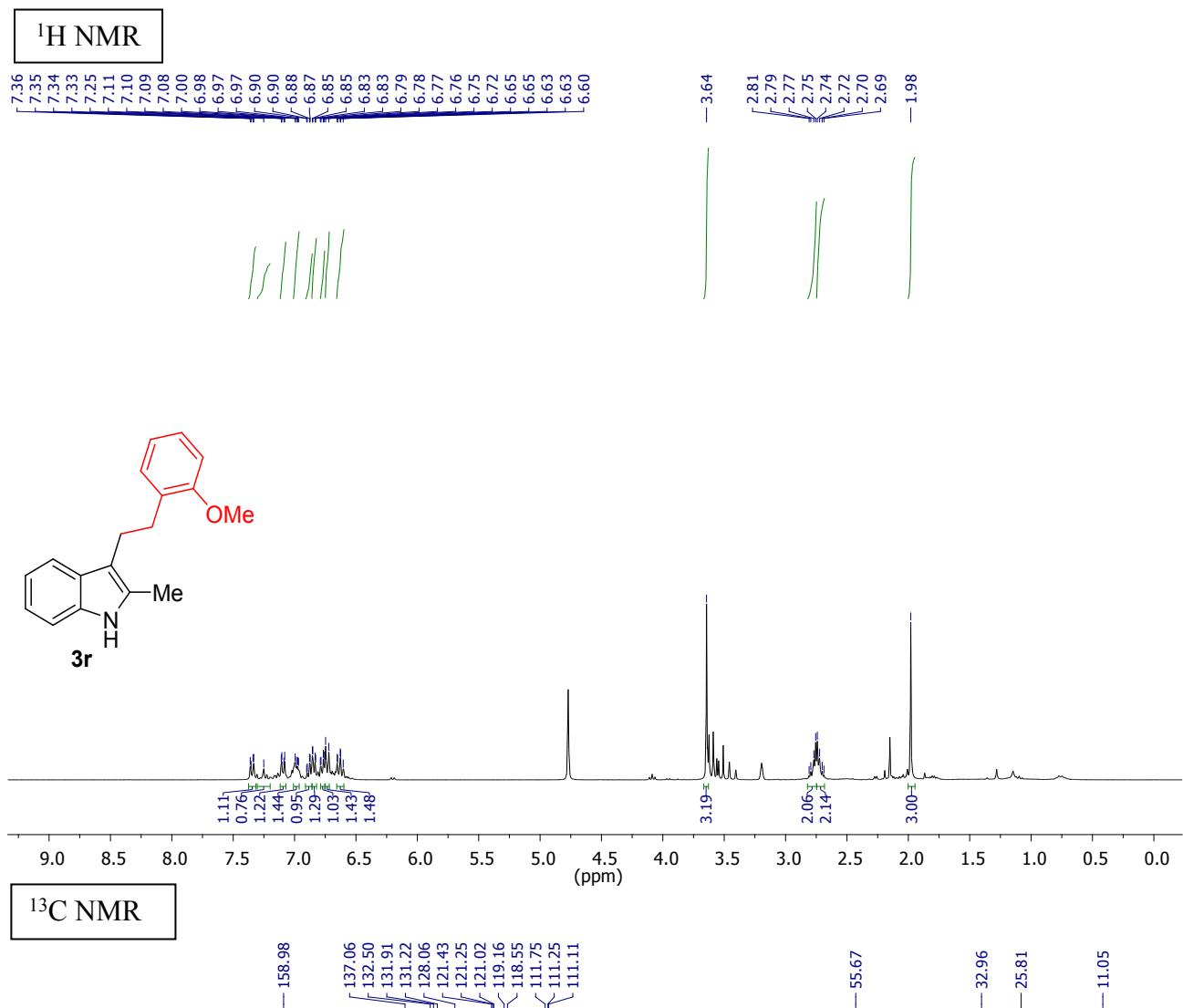
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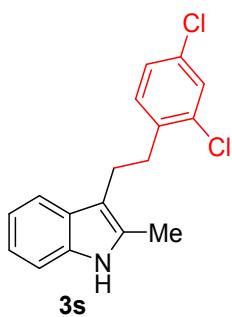


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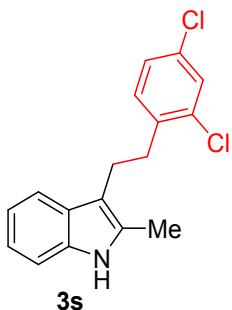
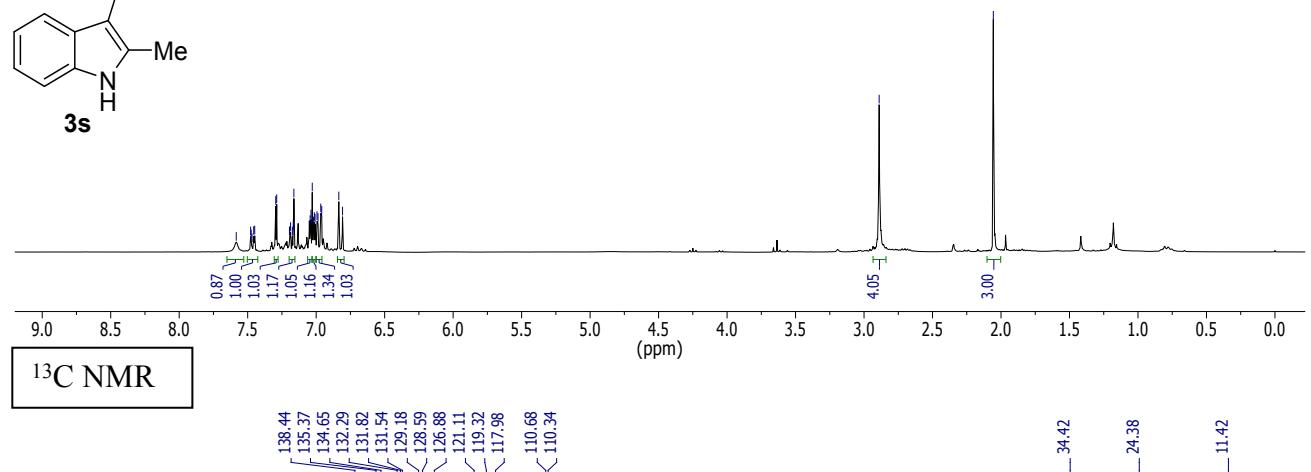




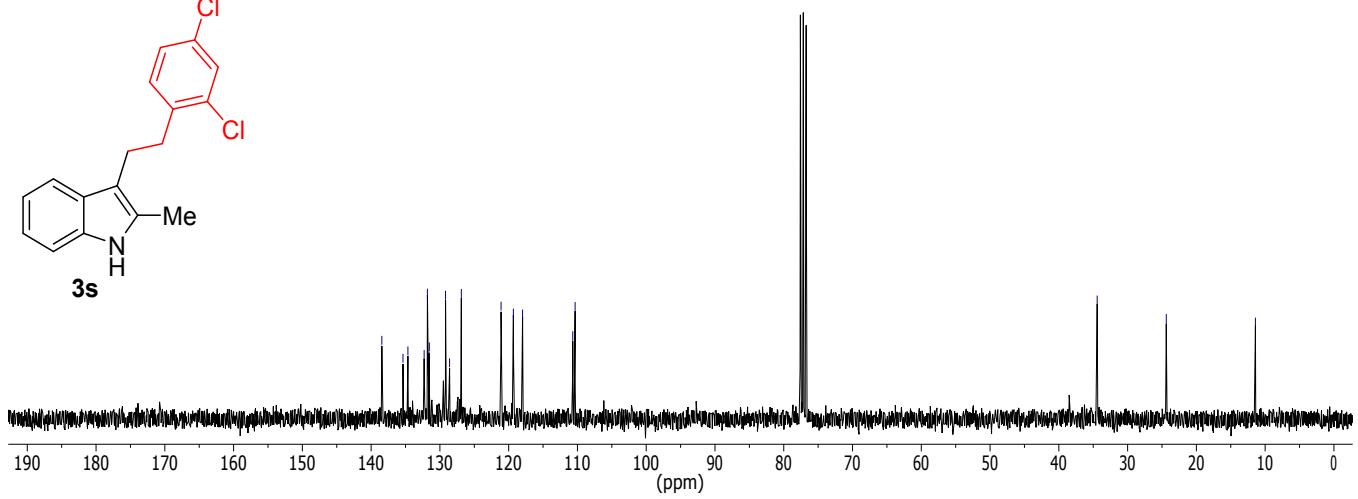




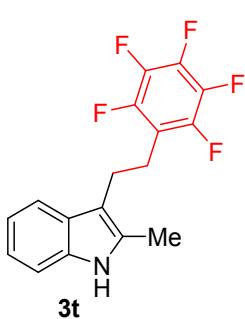
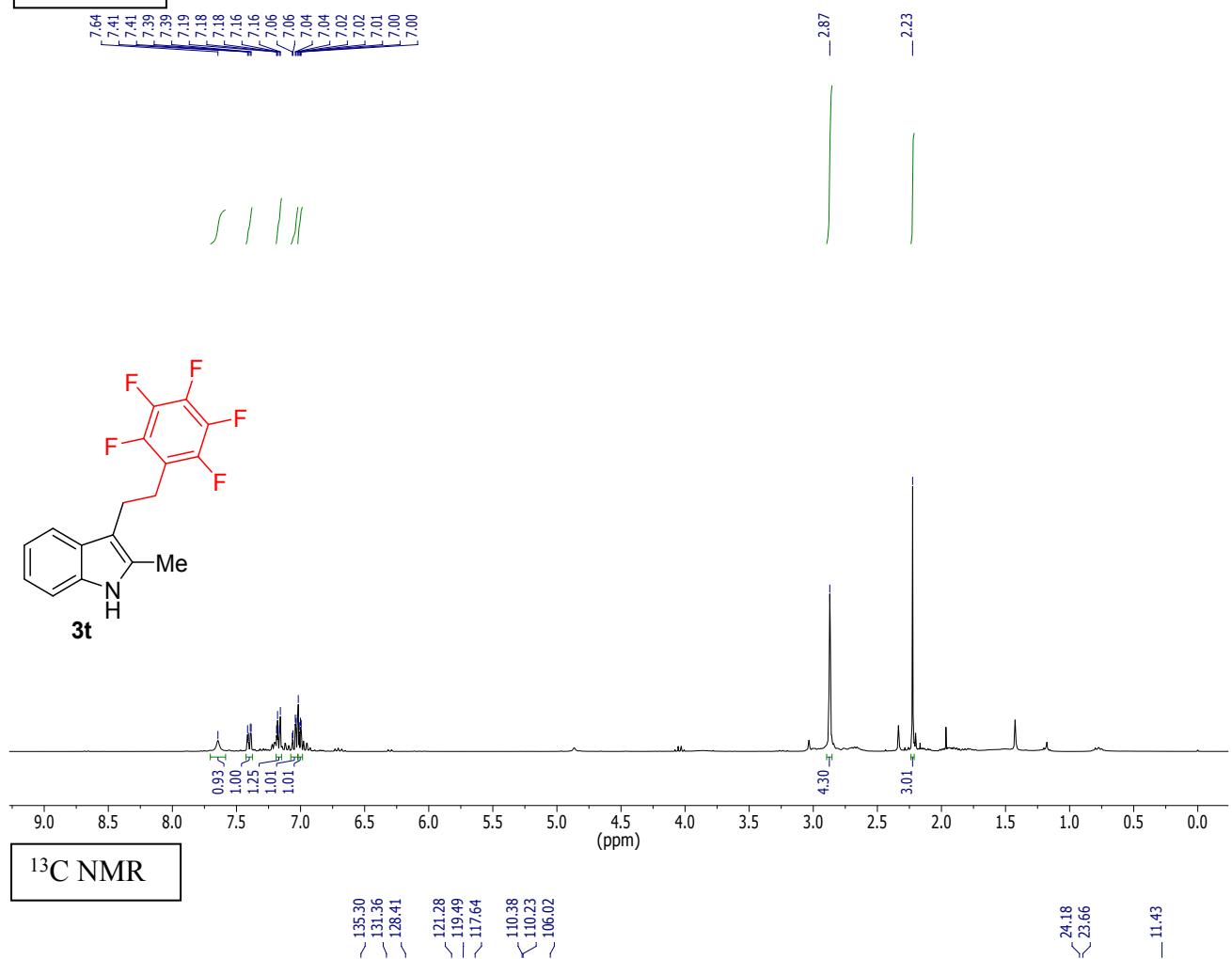
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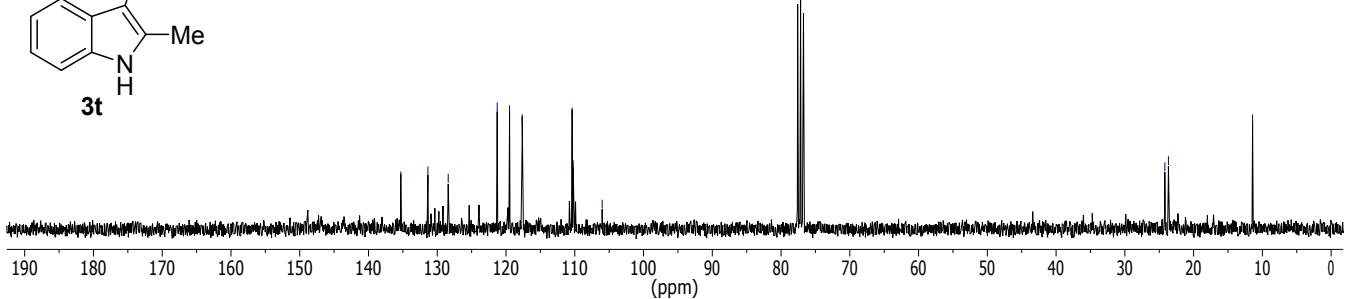
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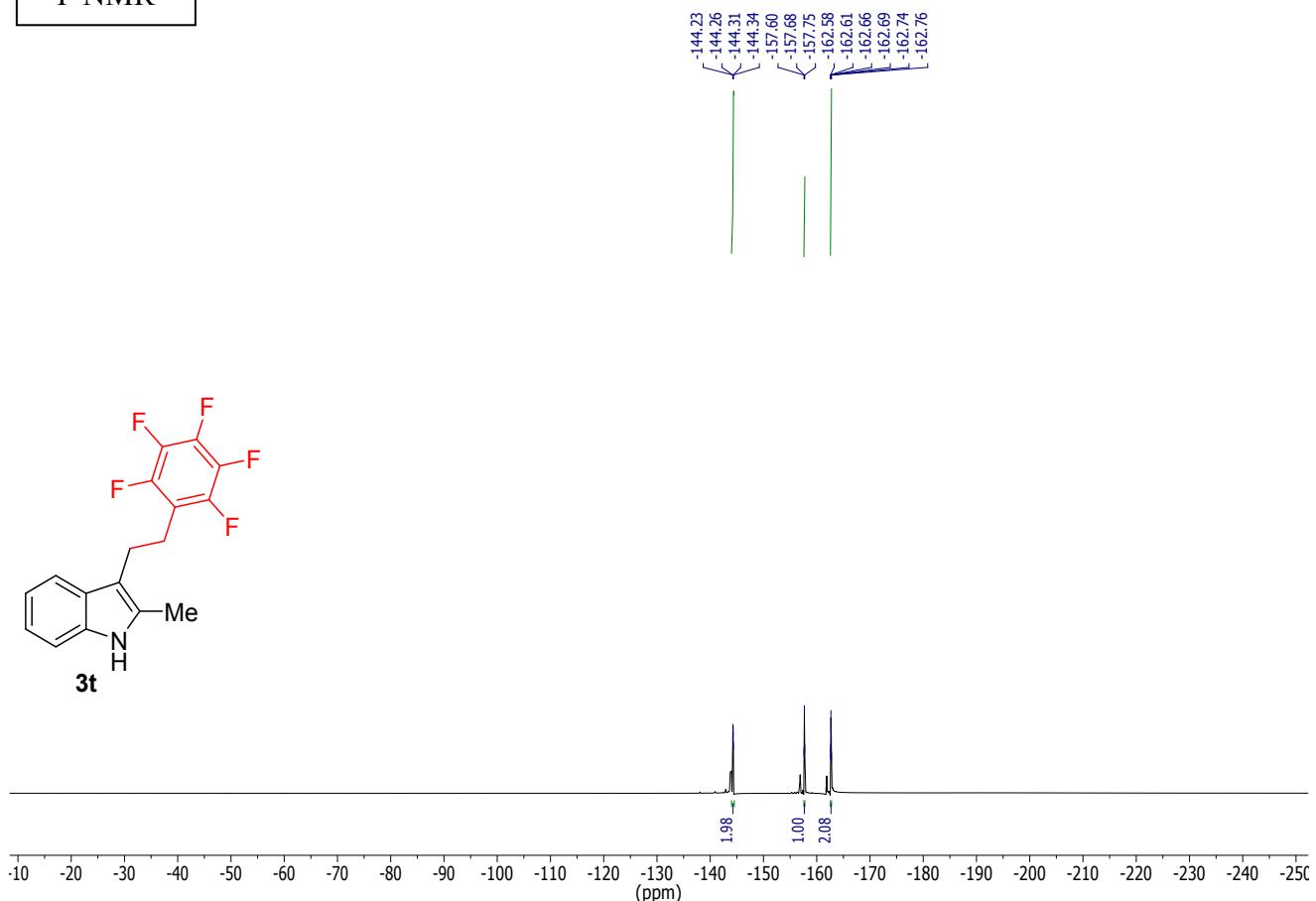
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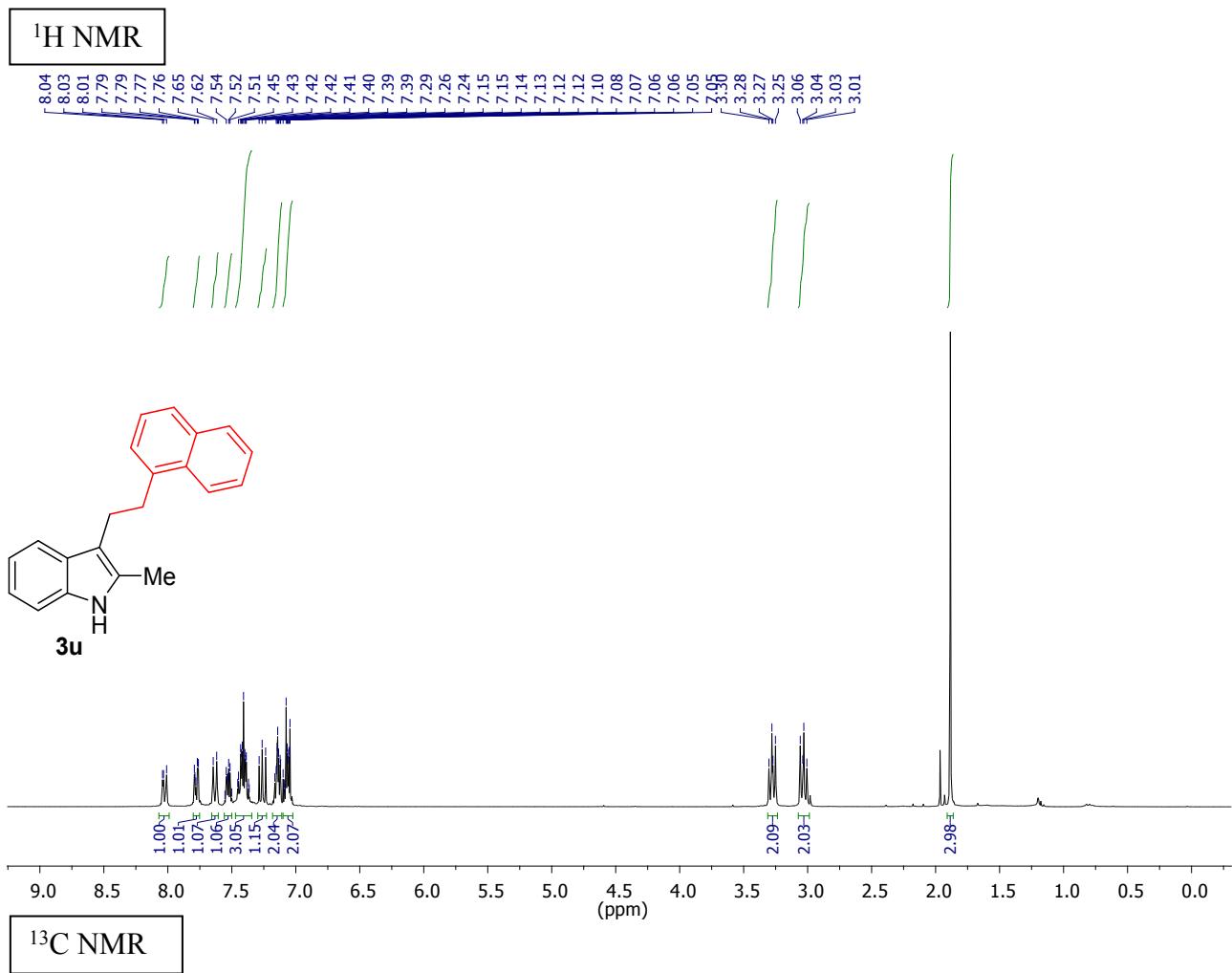


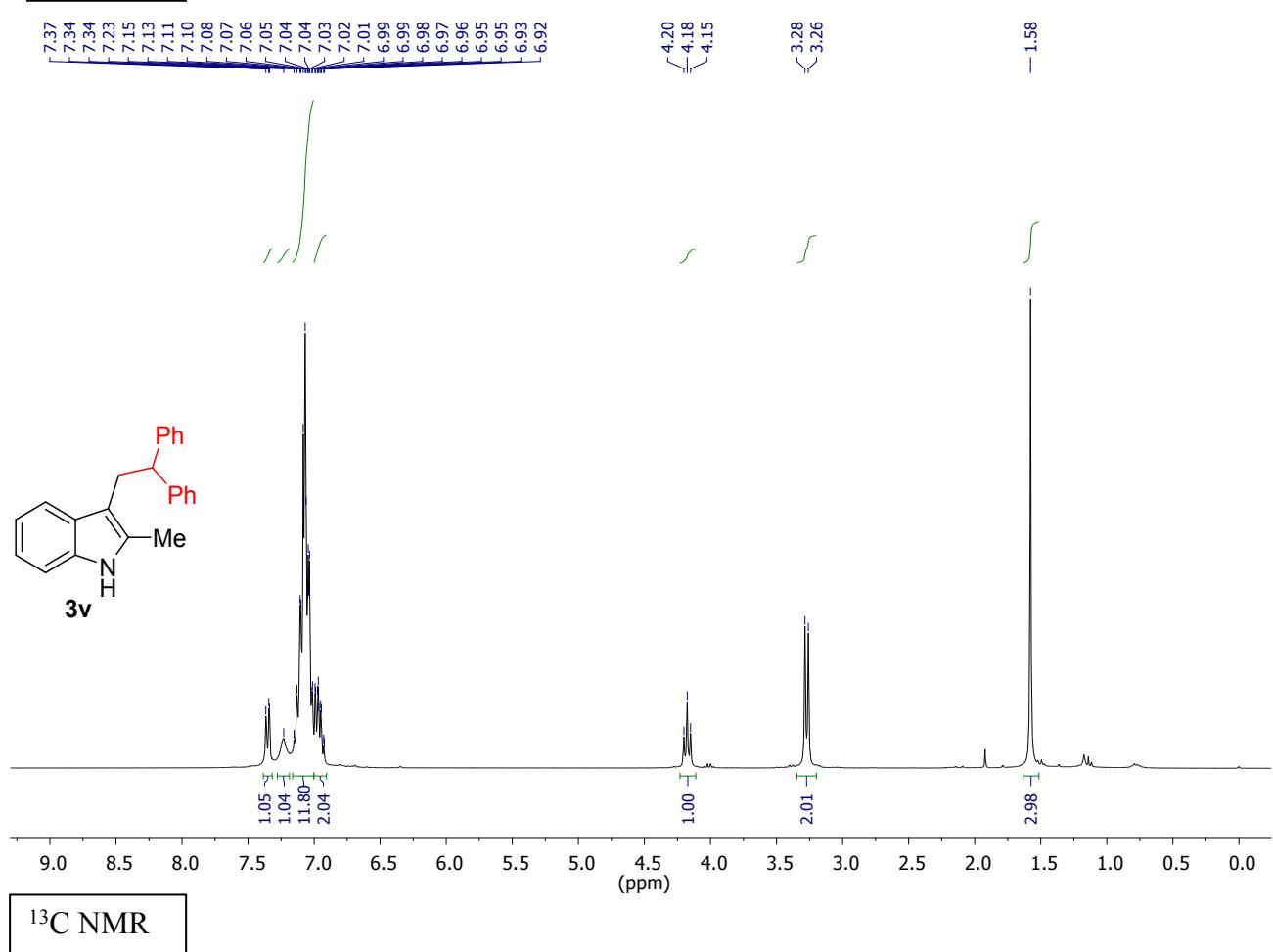
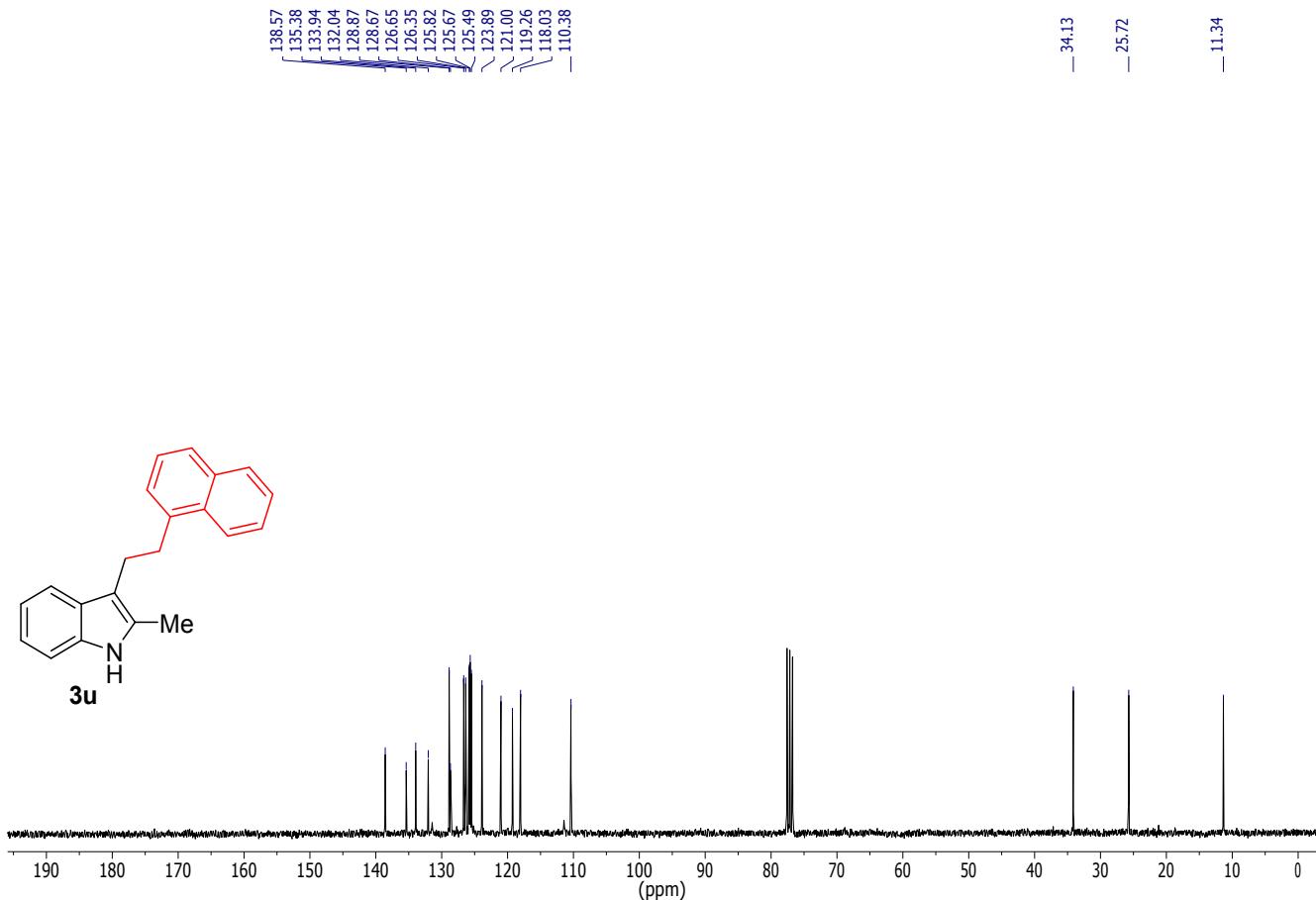
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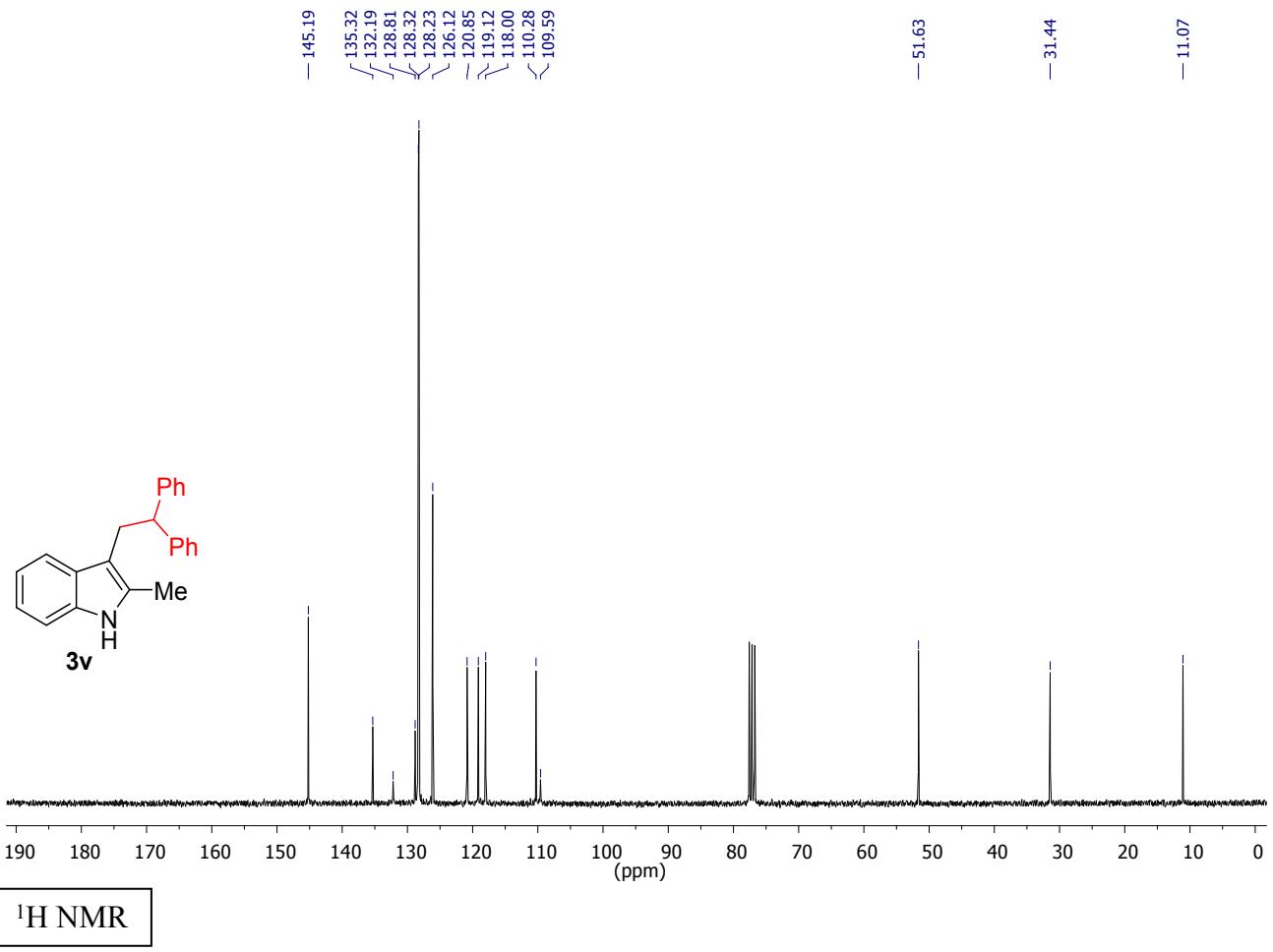


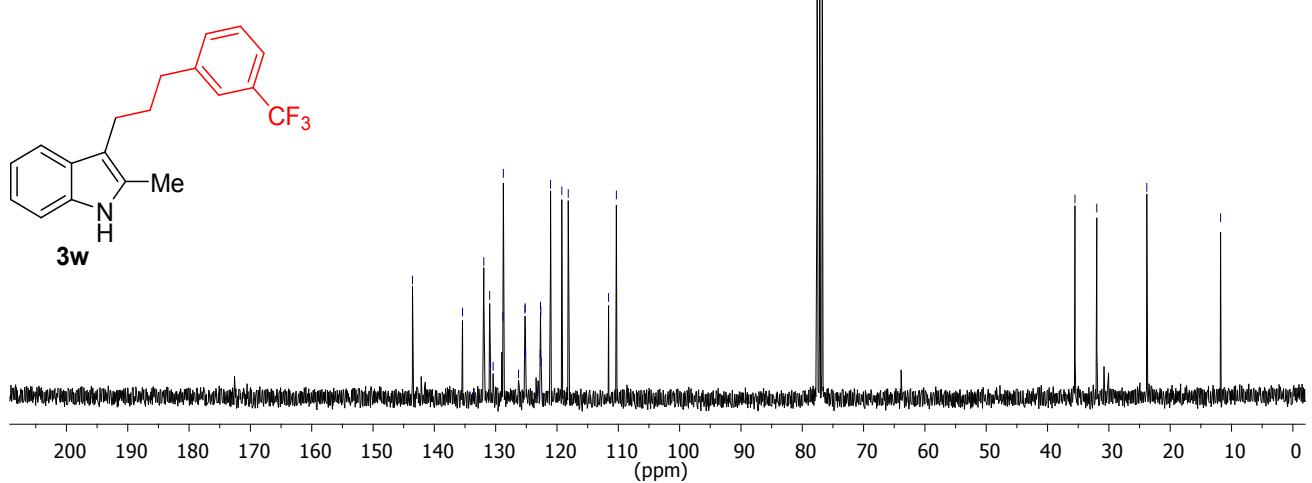
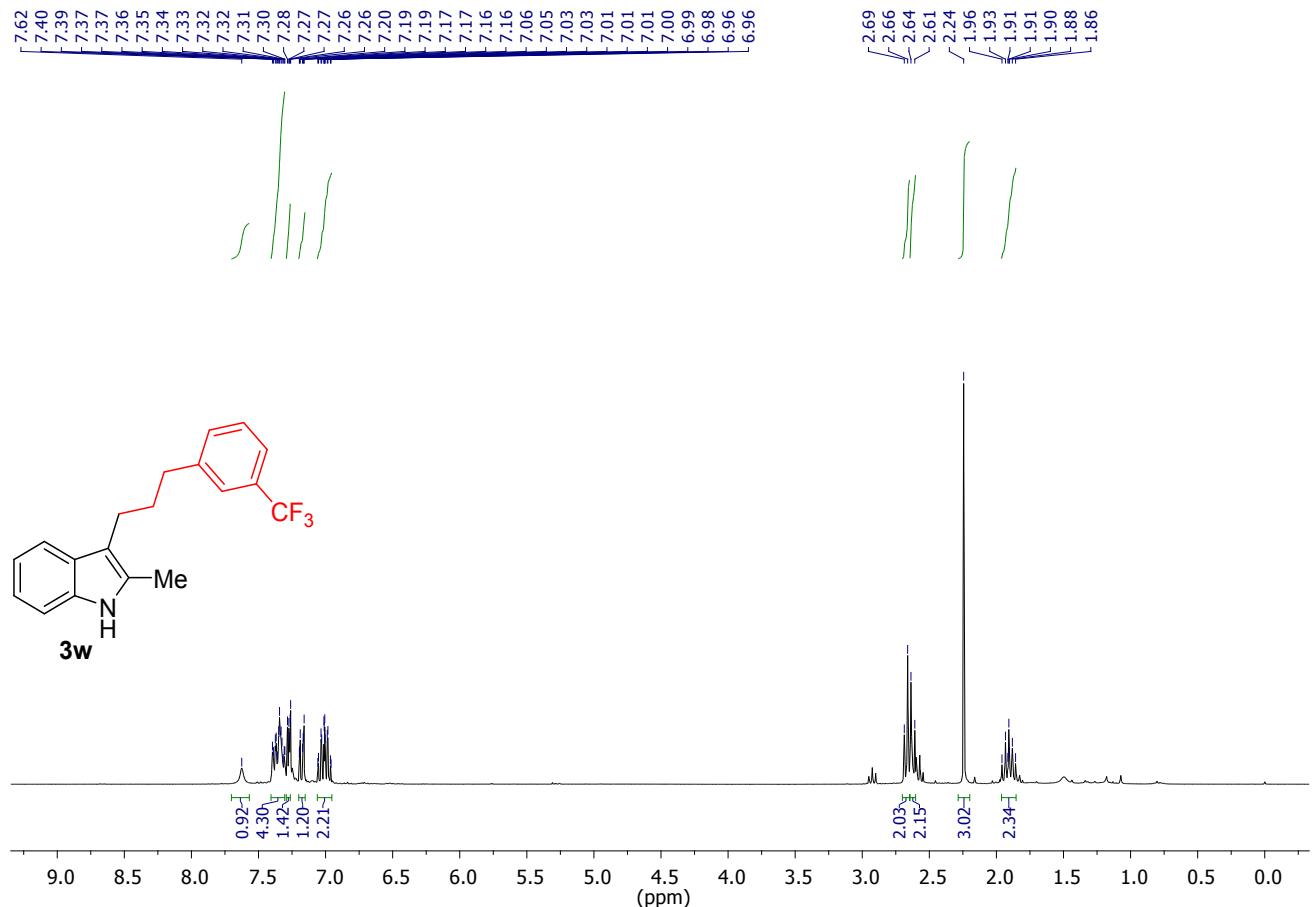
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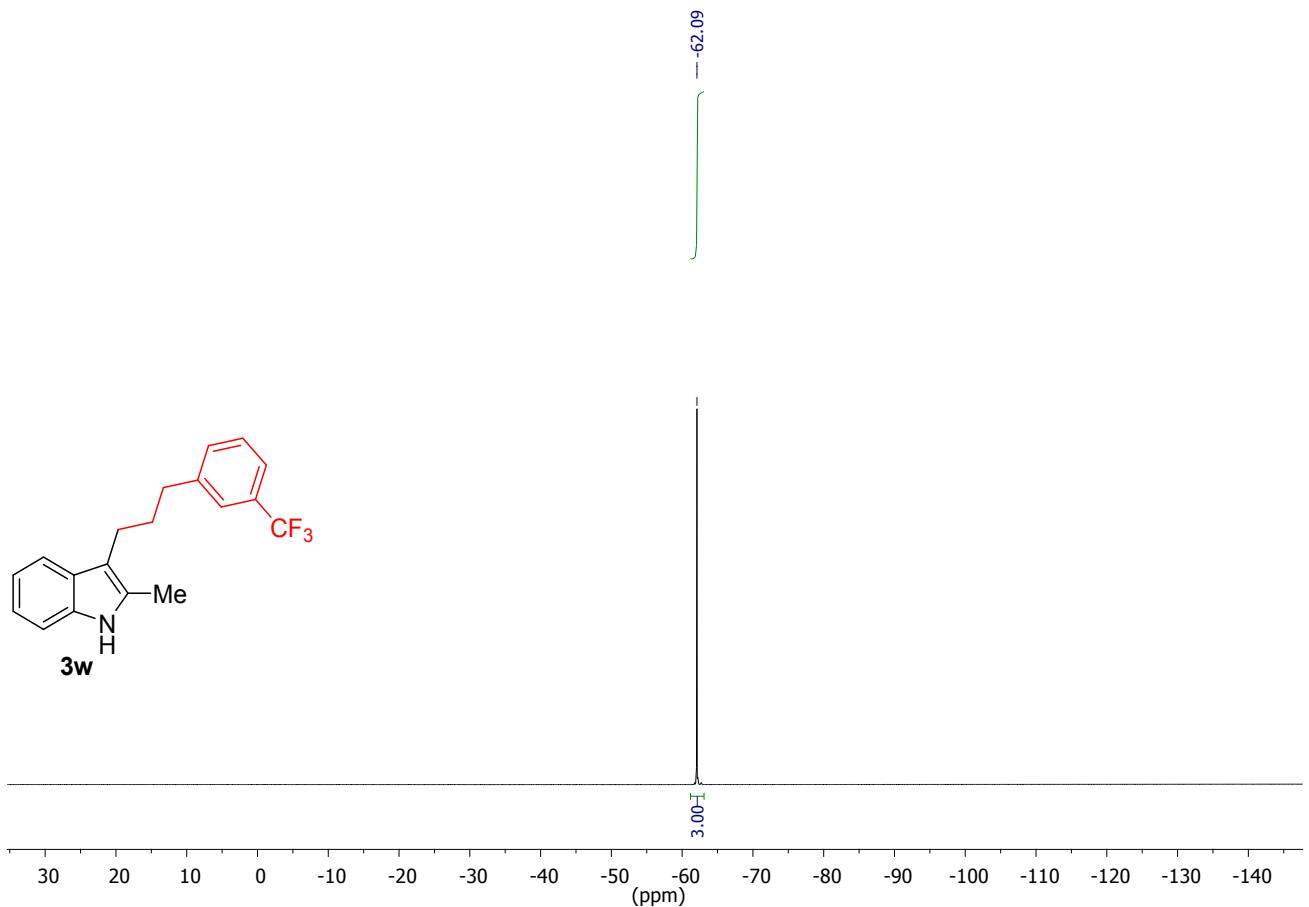




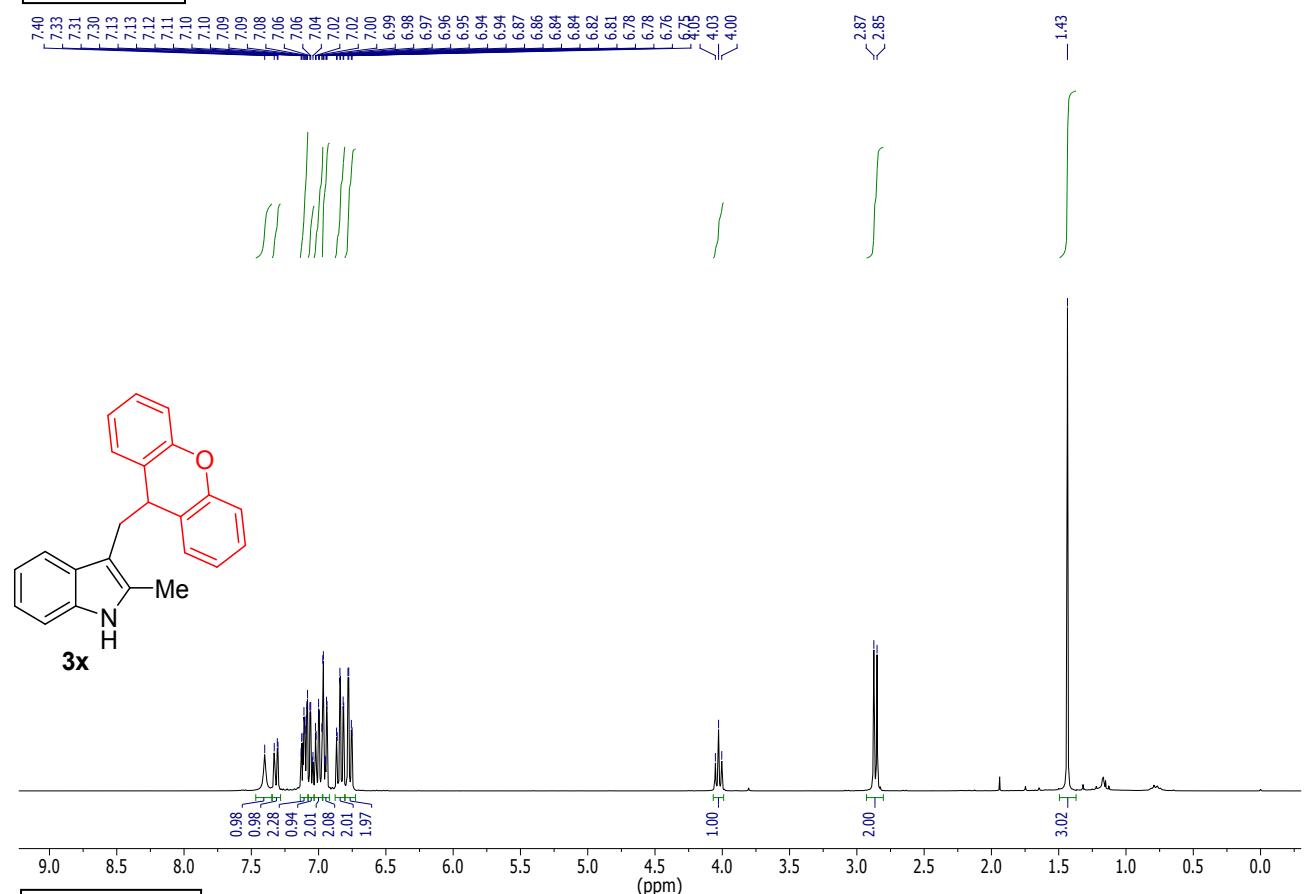




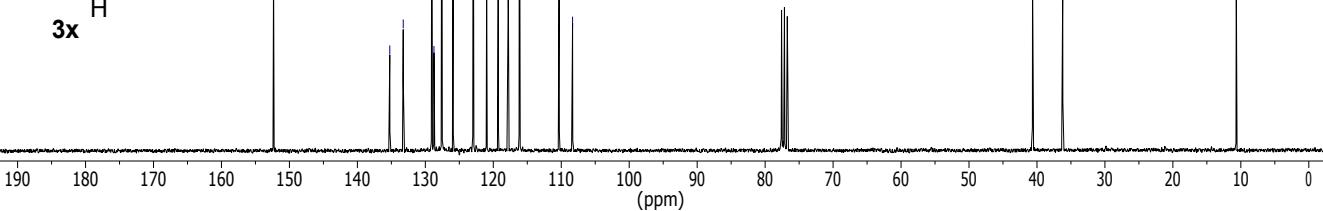
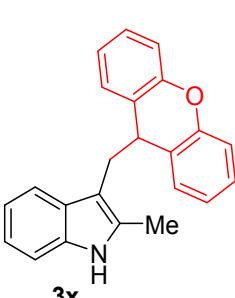
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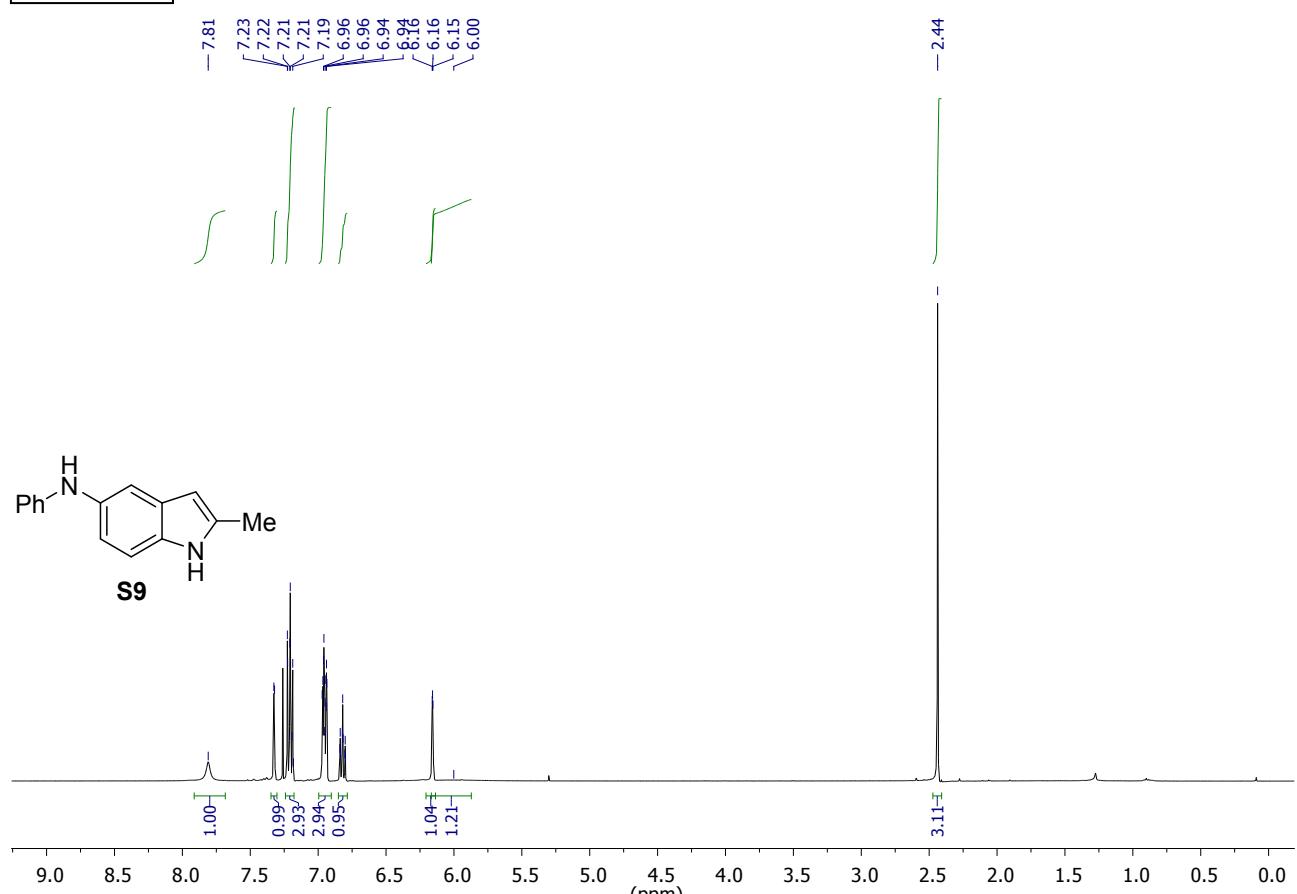
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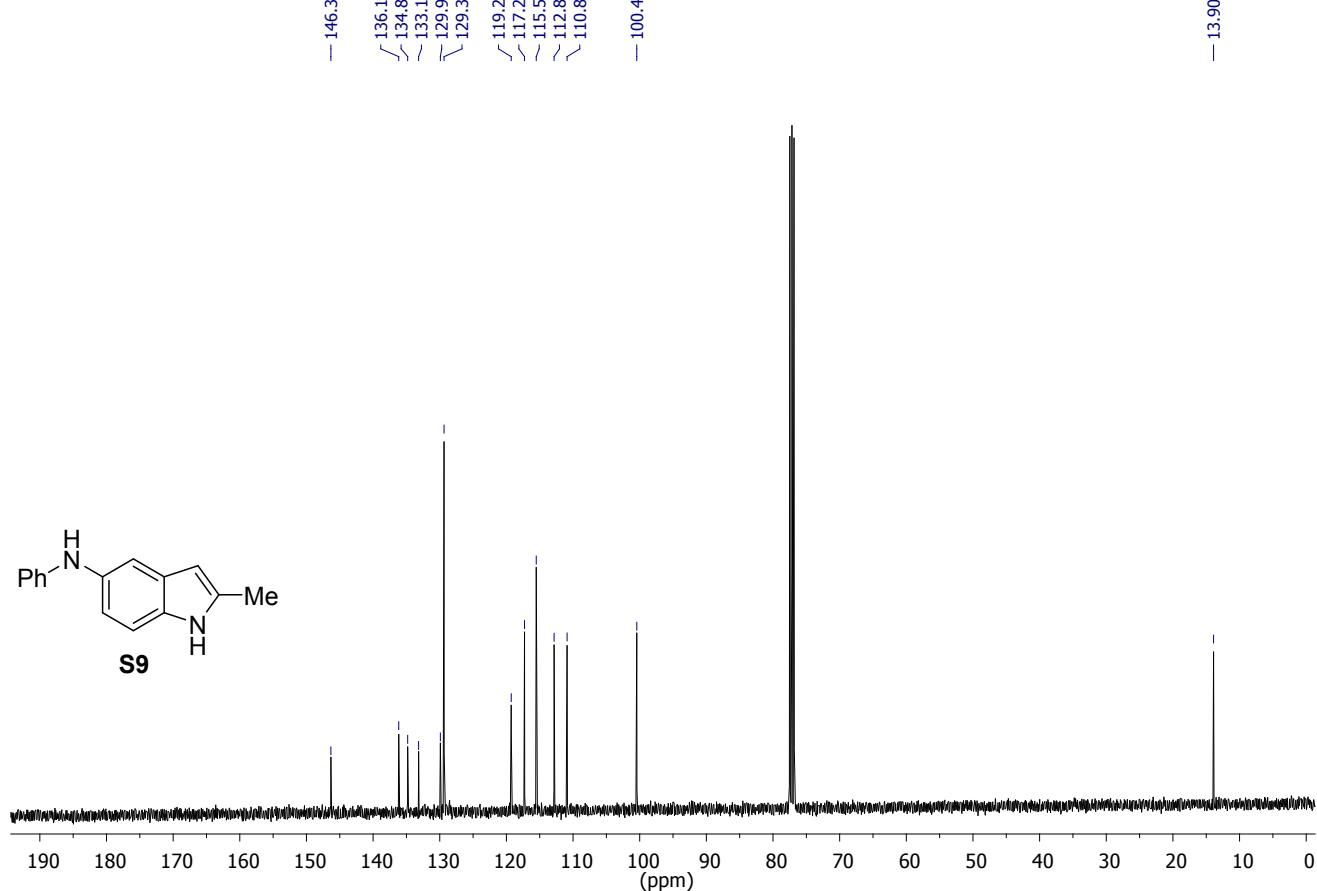
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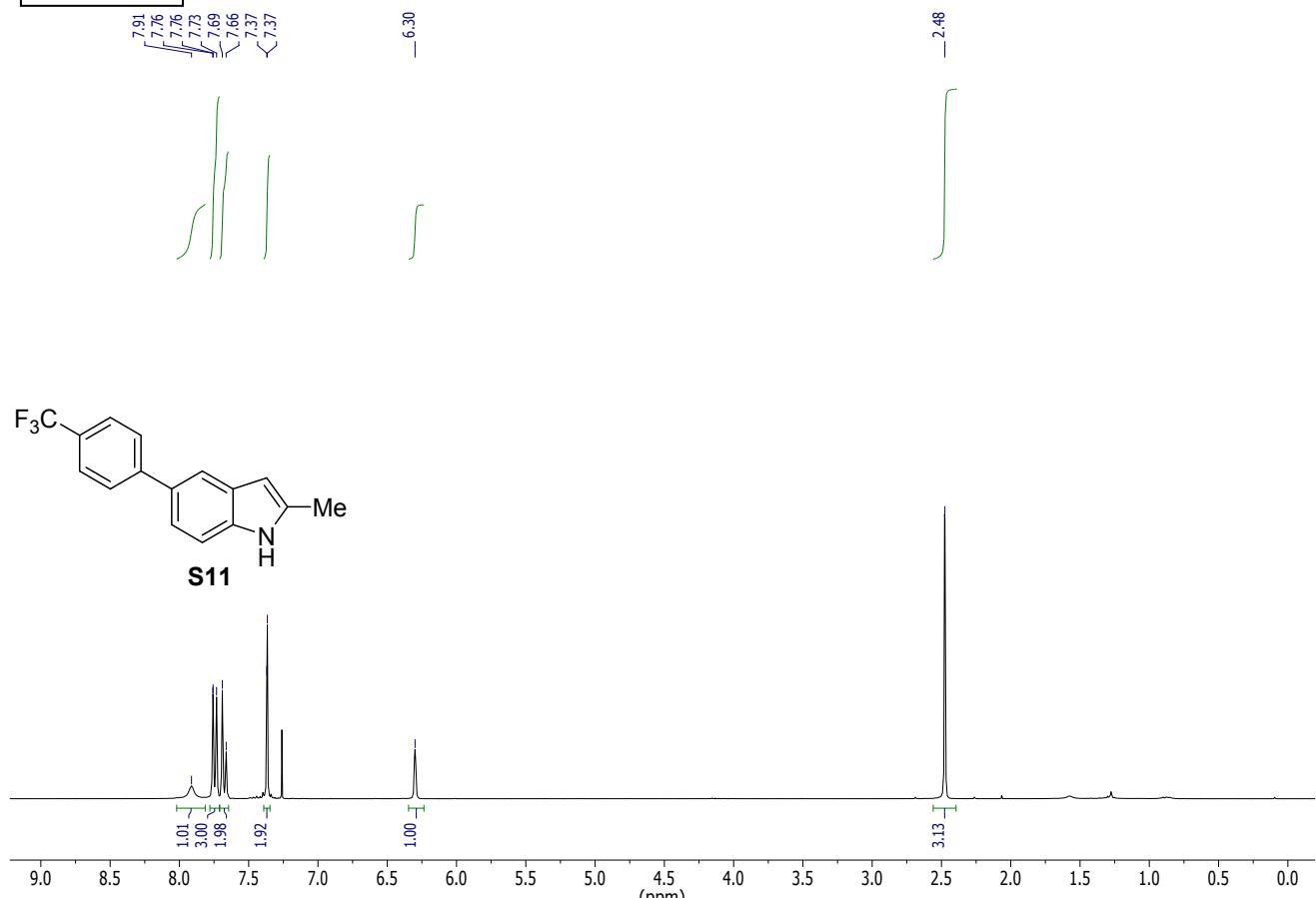
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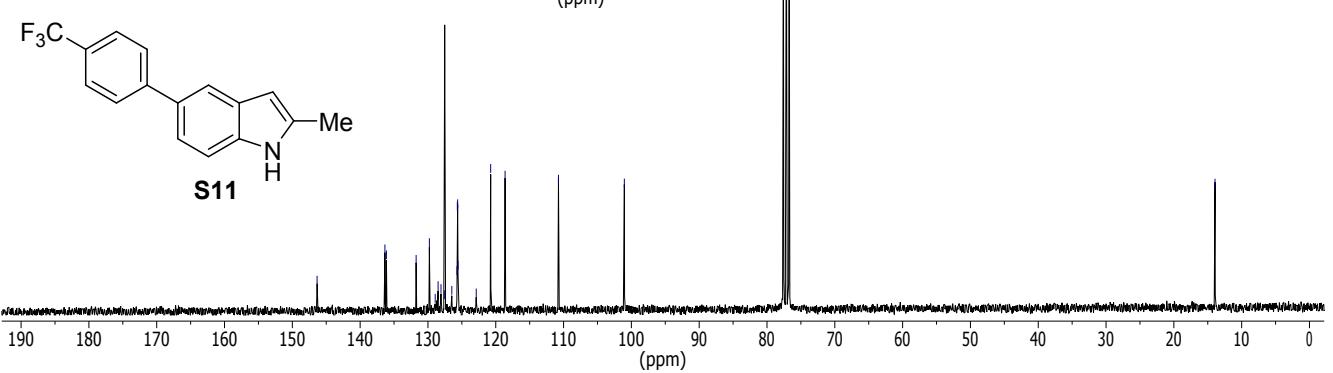
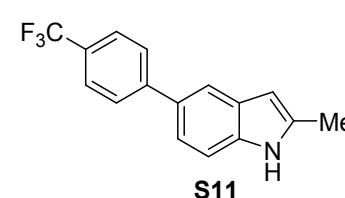
<sup>13</sup>C NMR



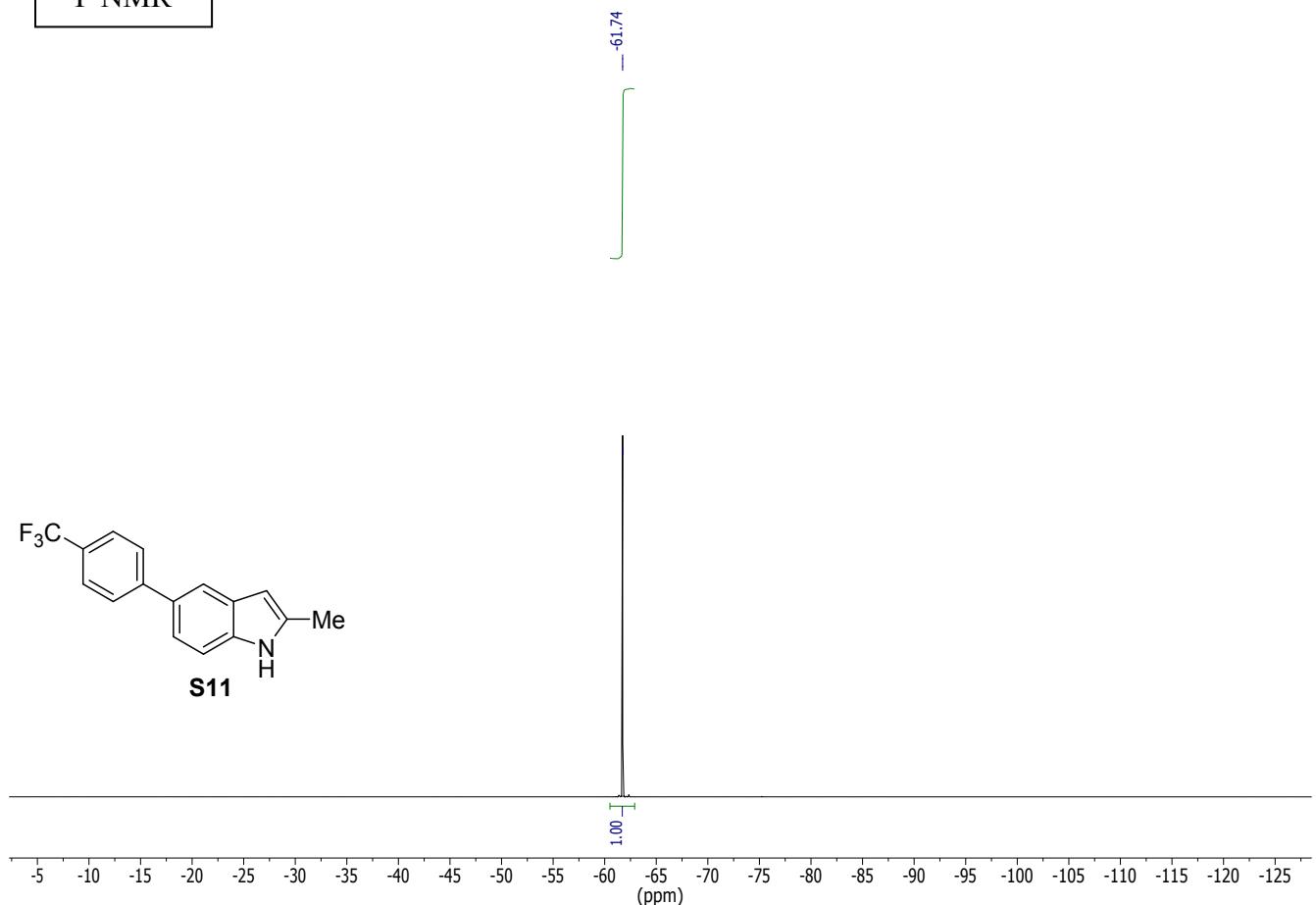
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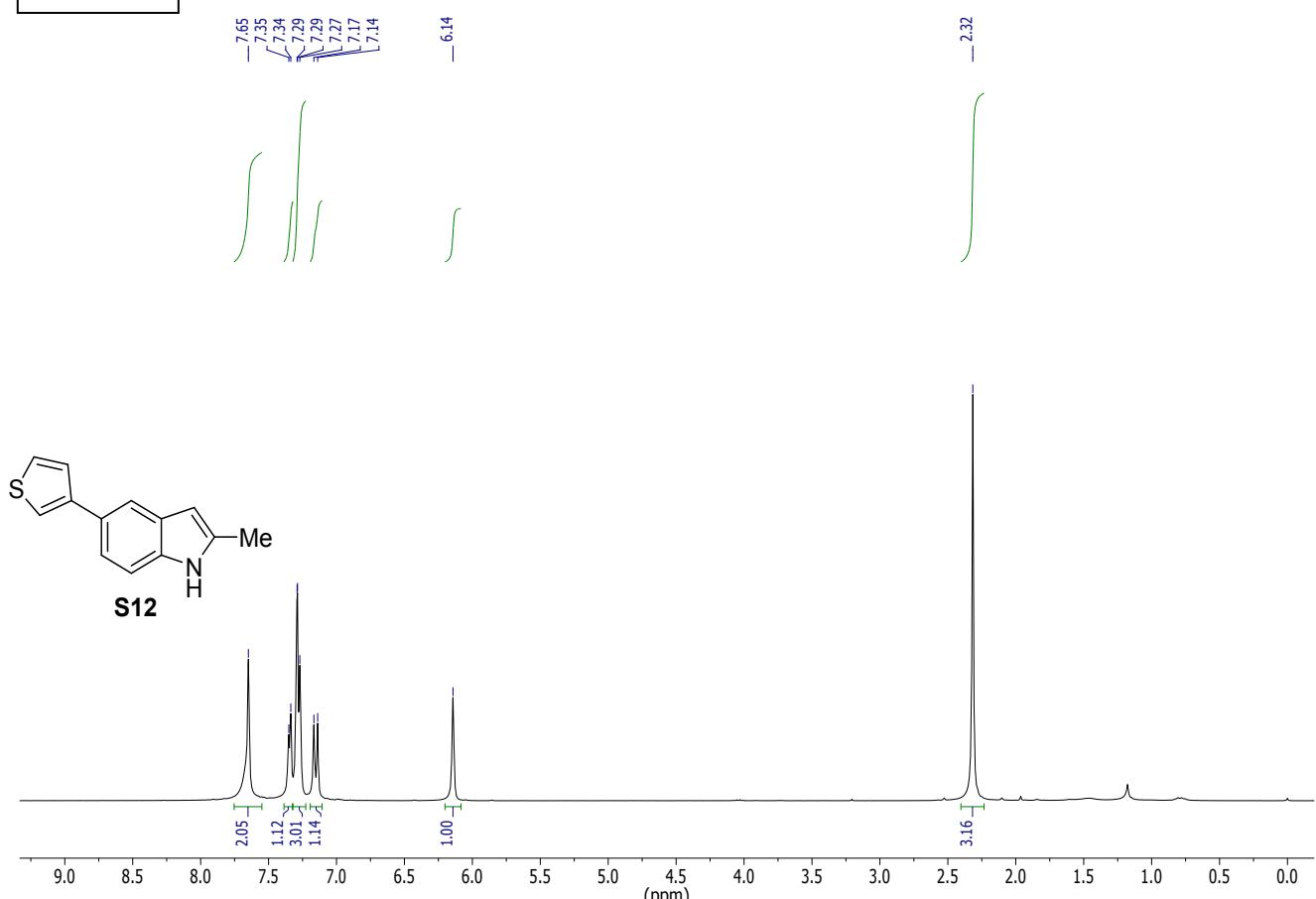
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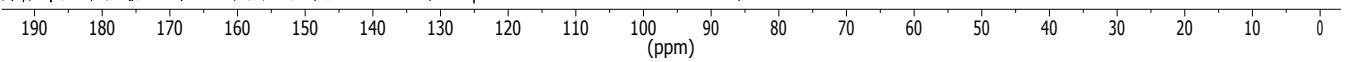
<sup>19</sup>F NMR



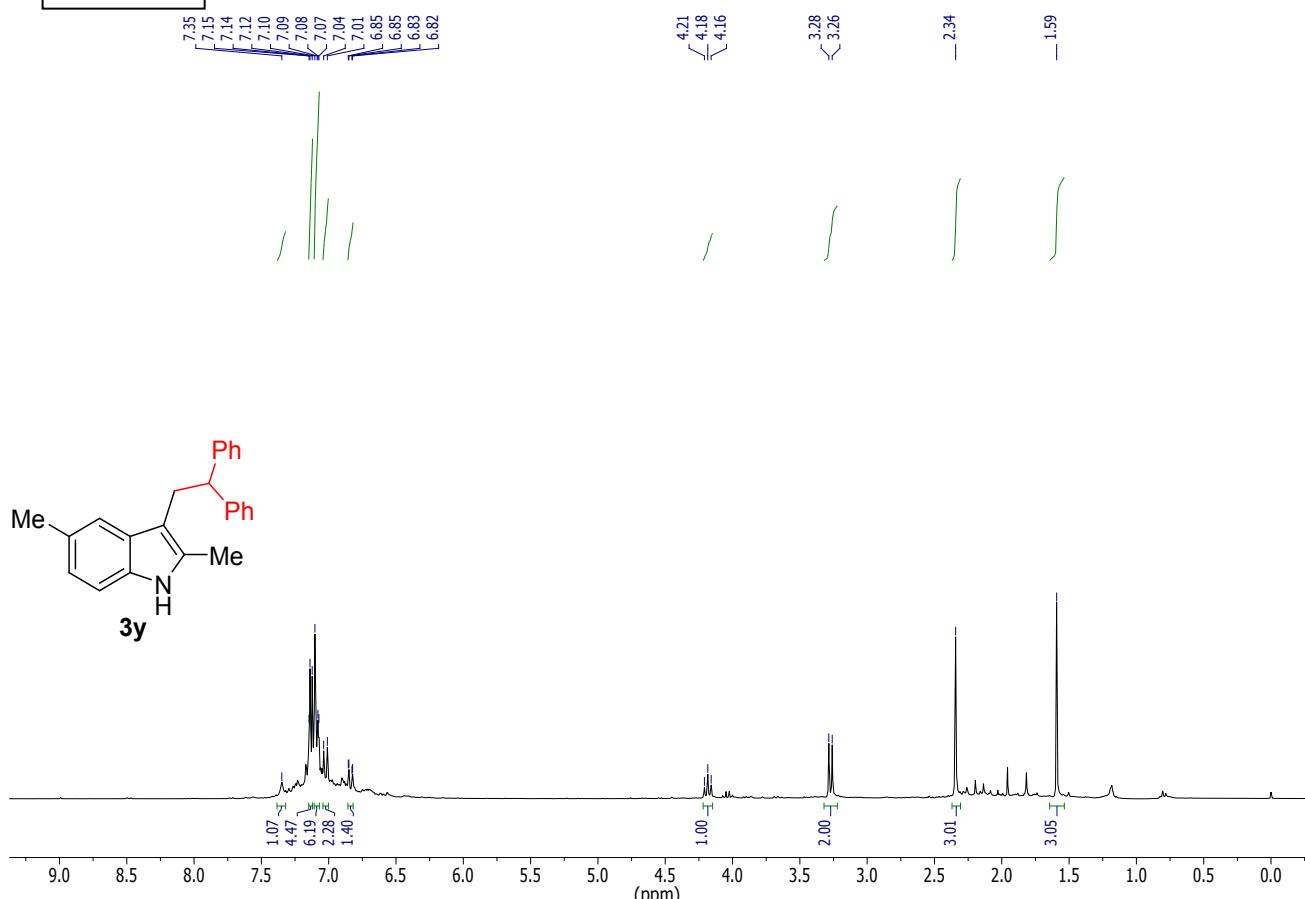
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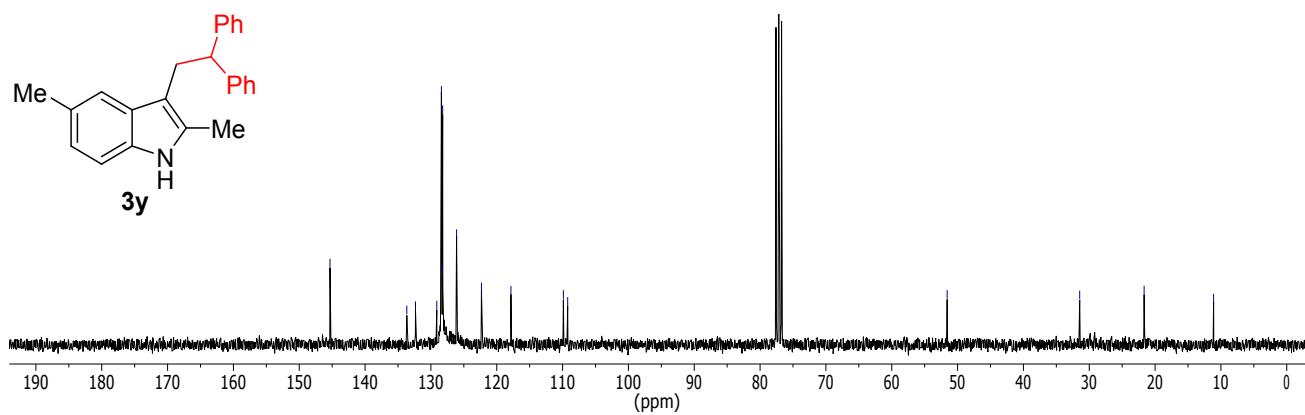
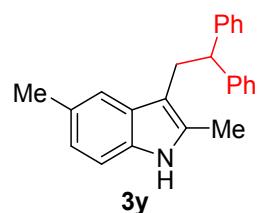
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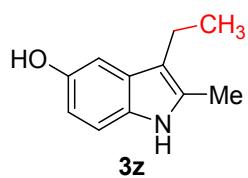
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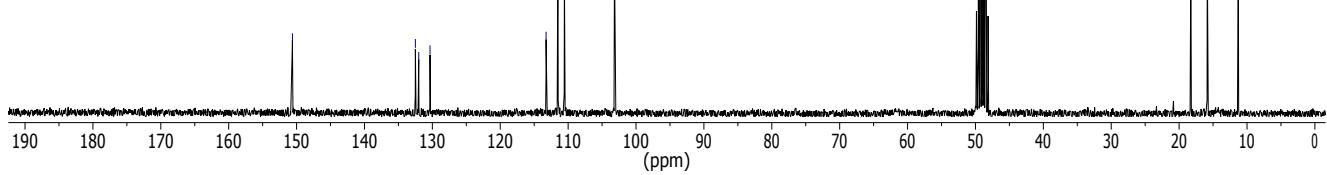
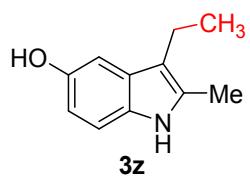
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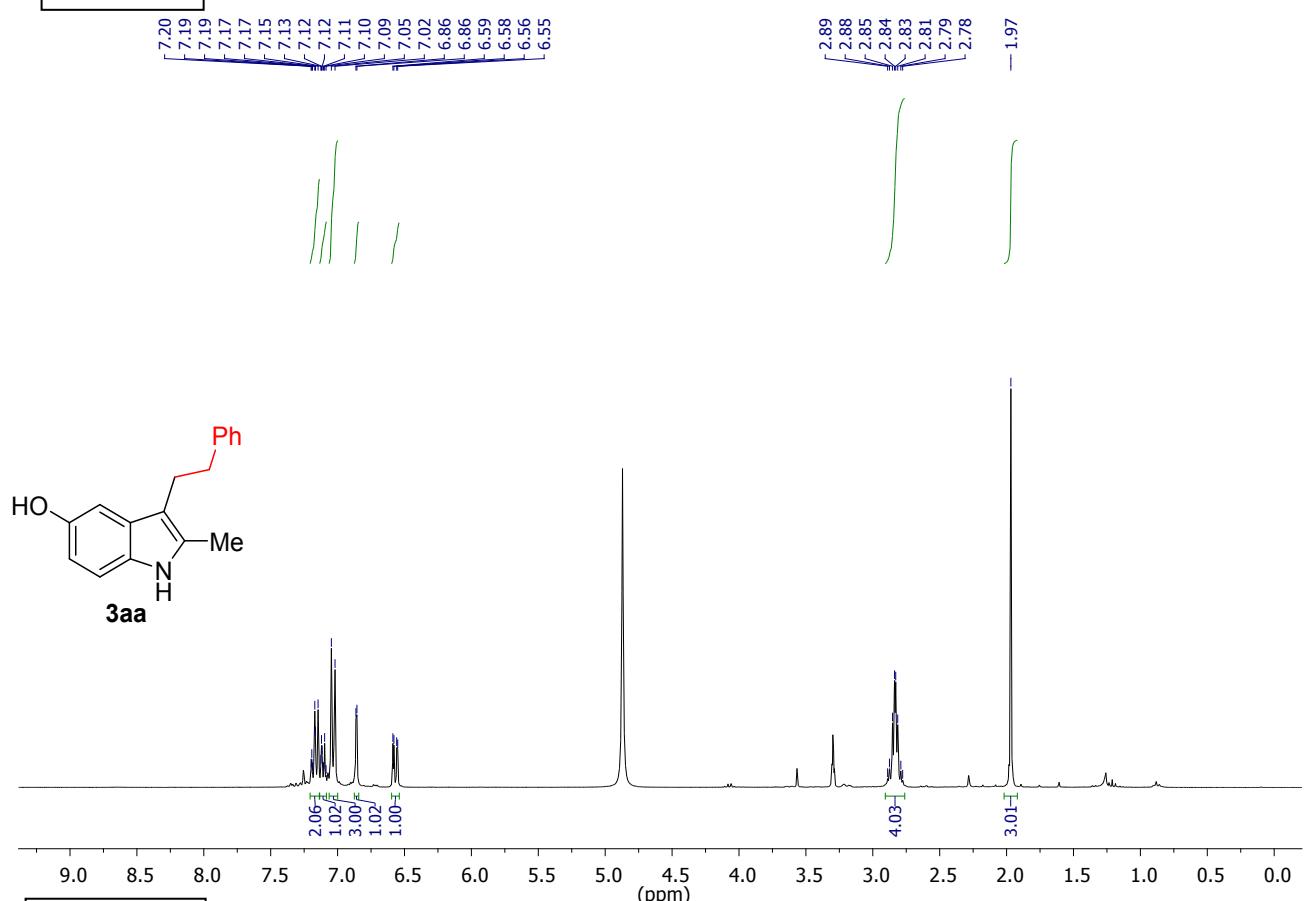
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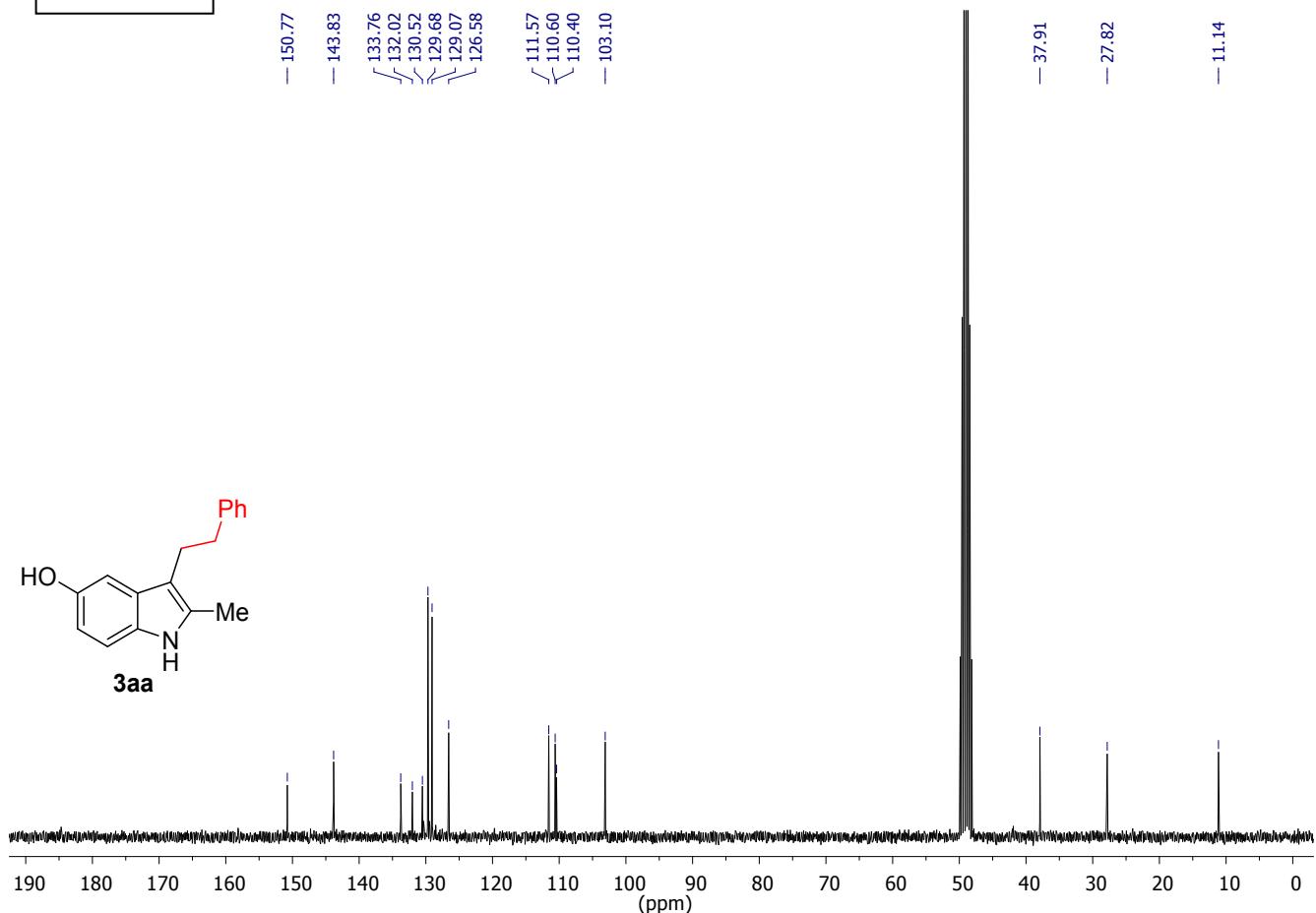
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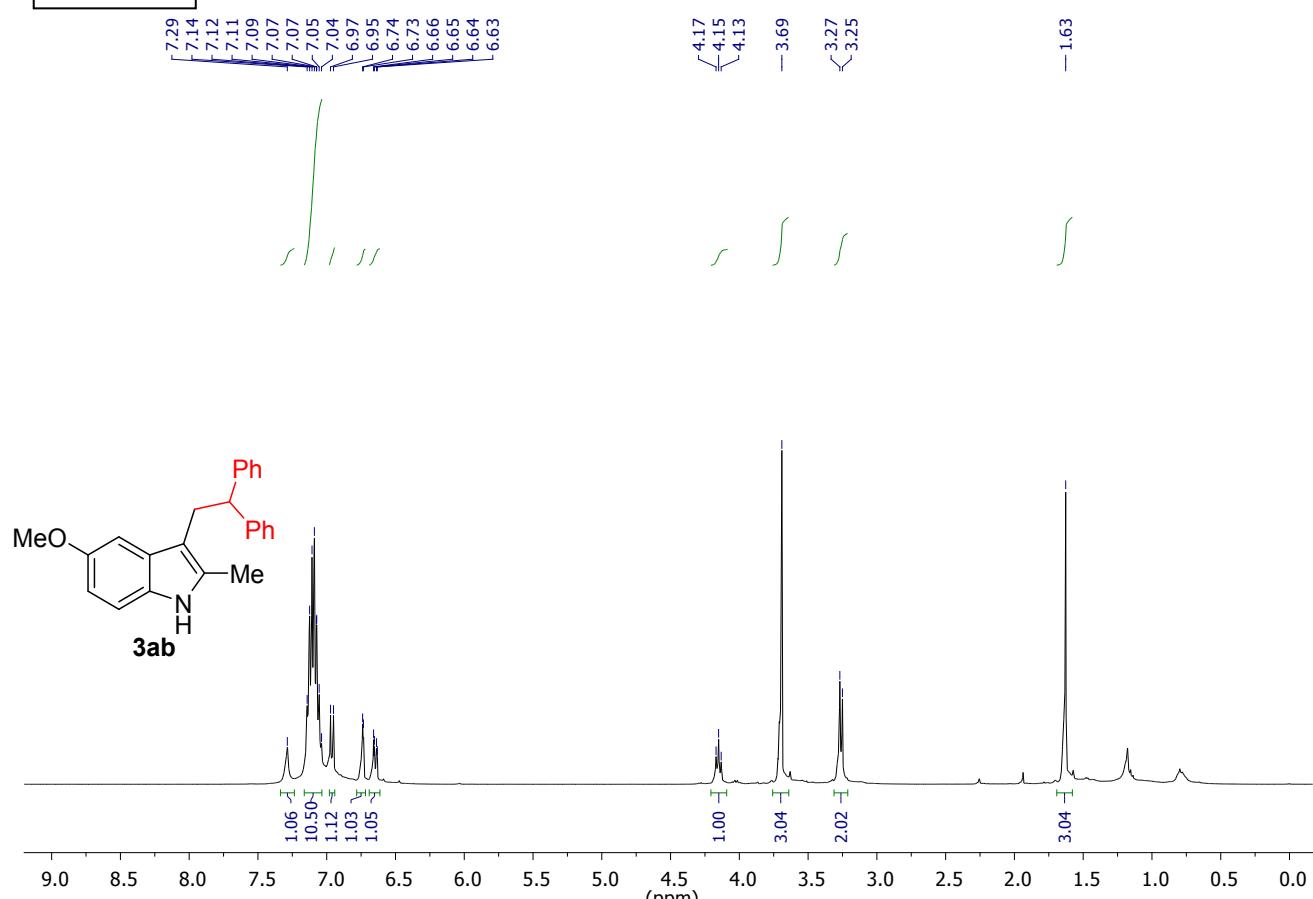
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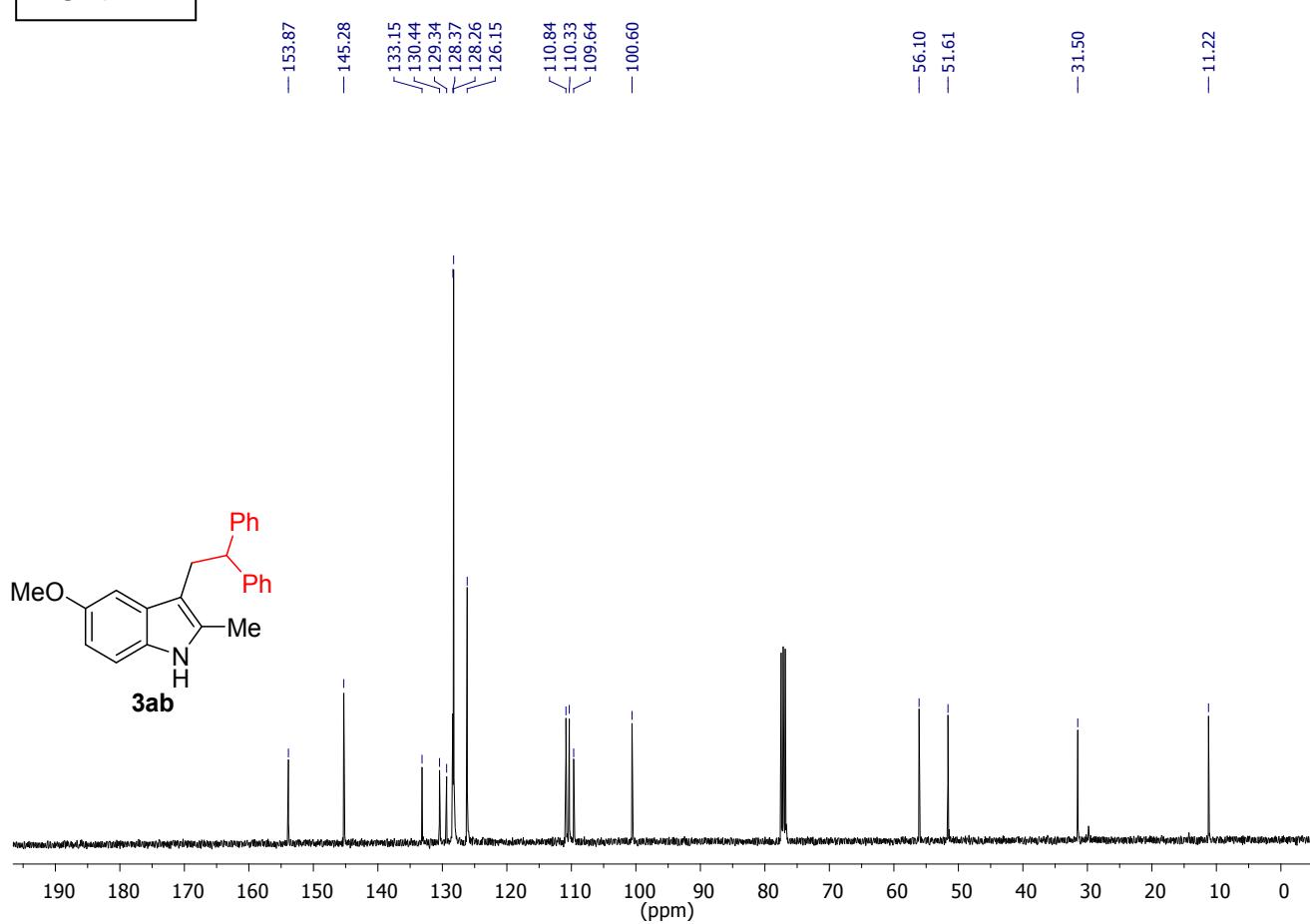
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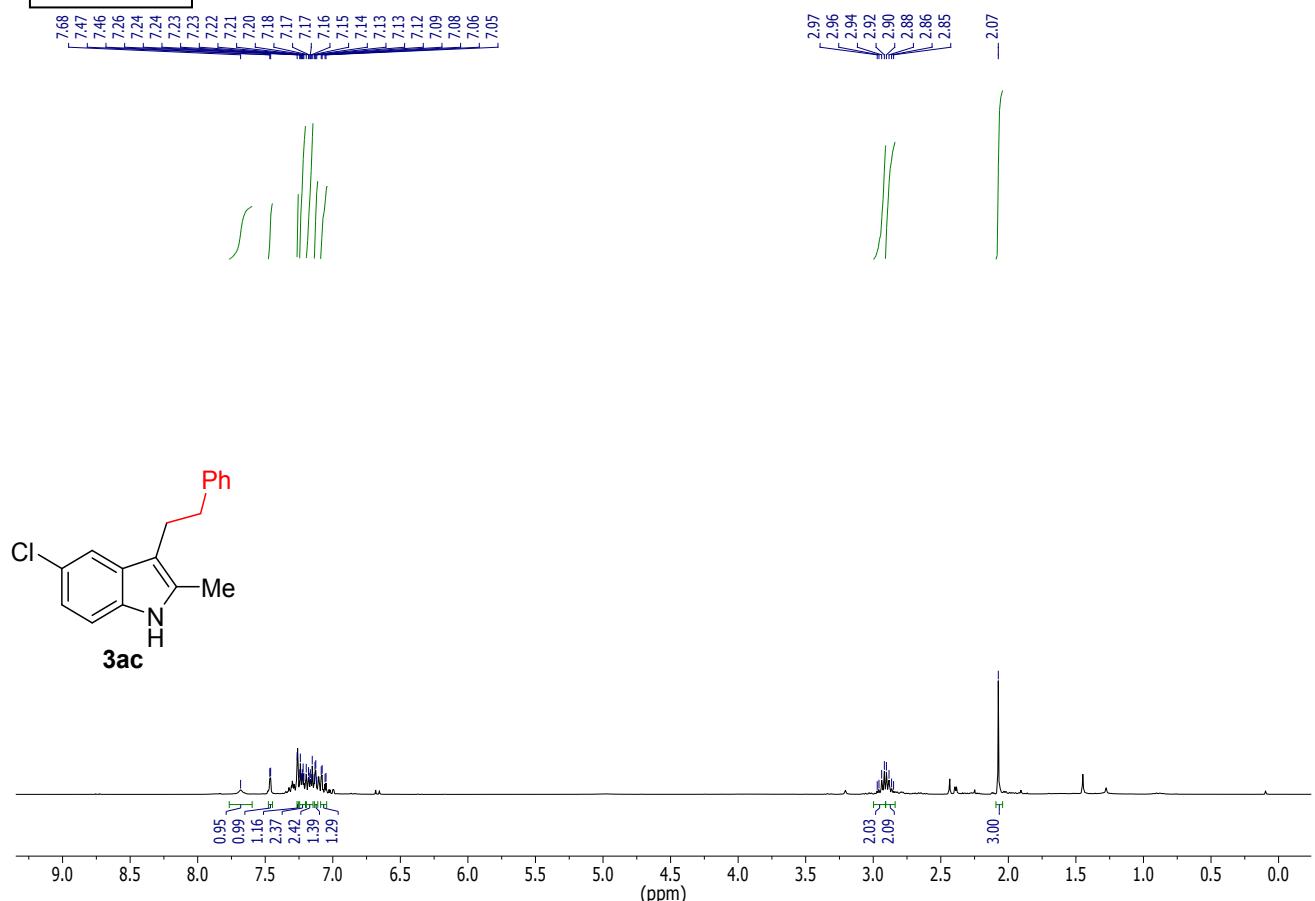
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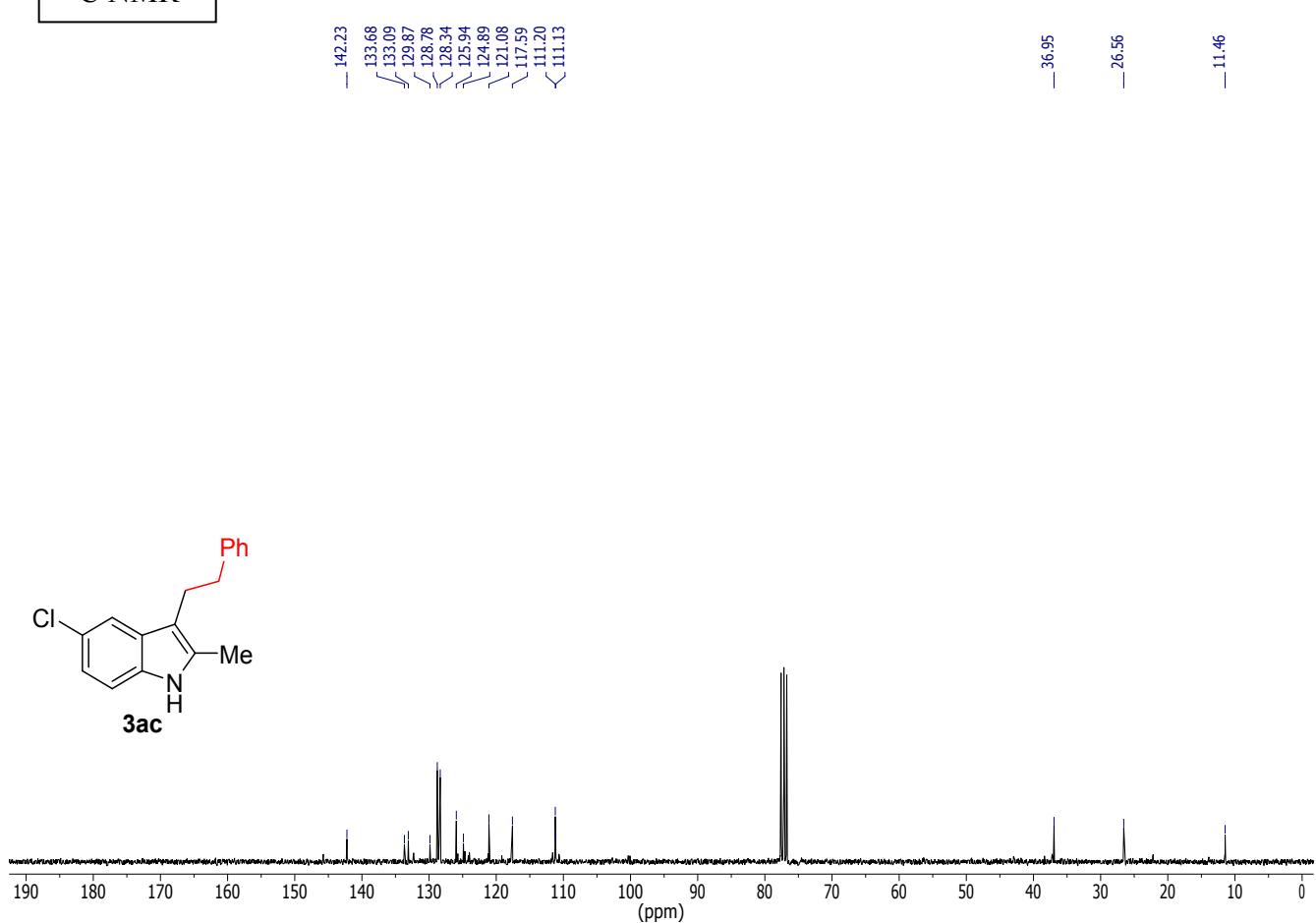
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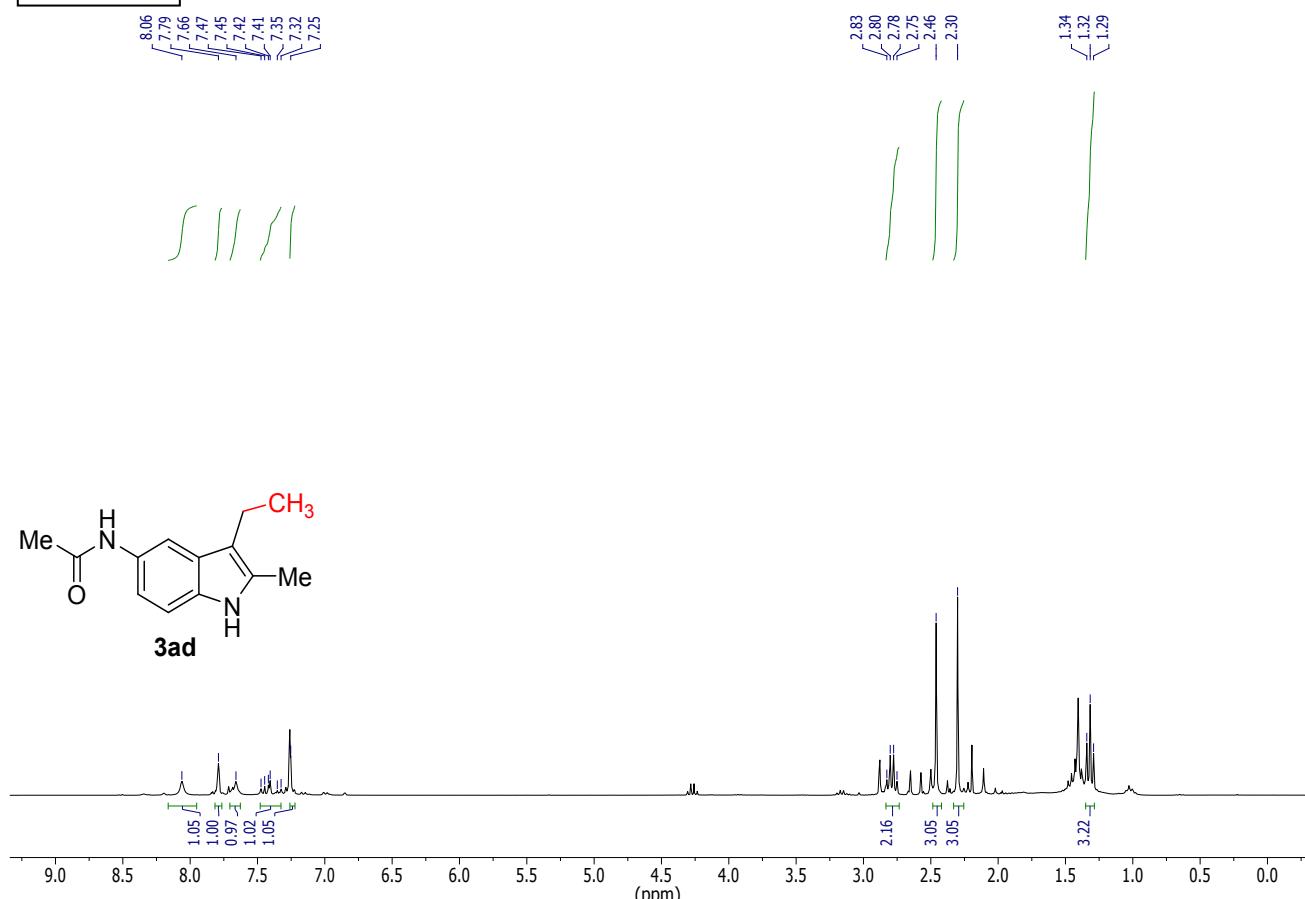
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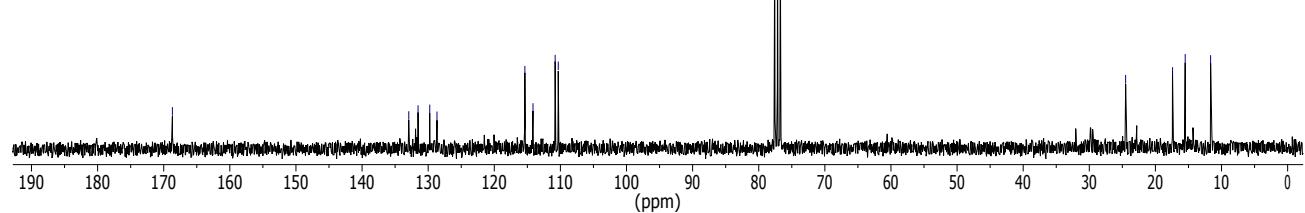
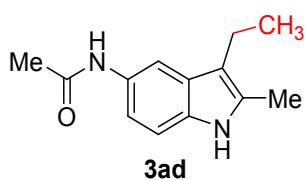
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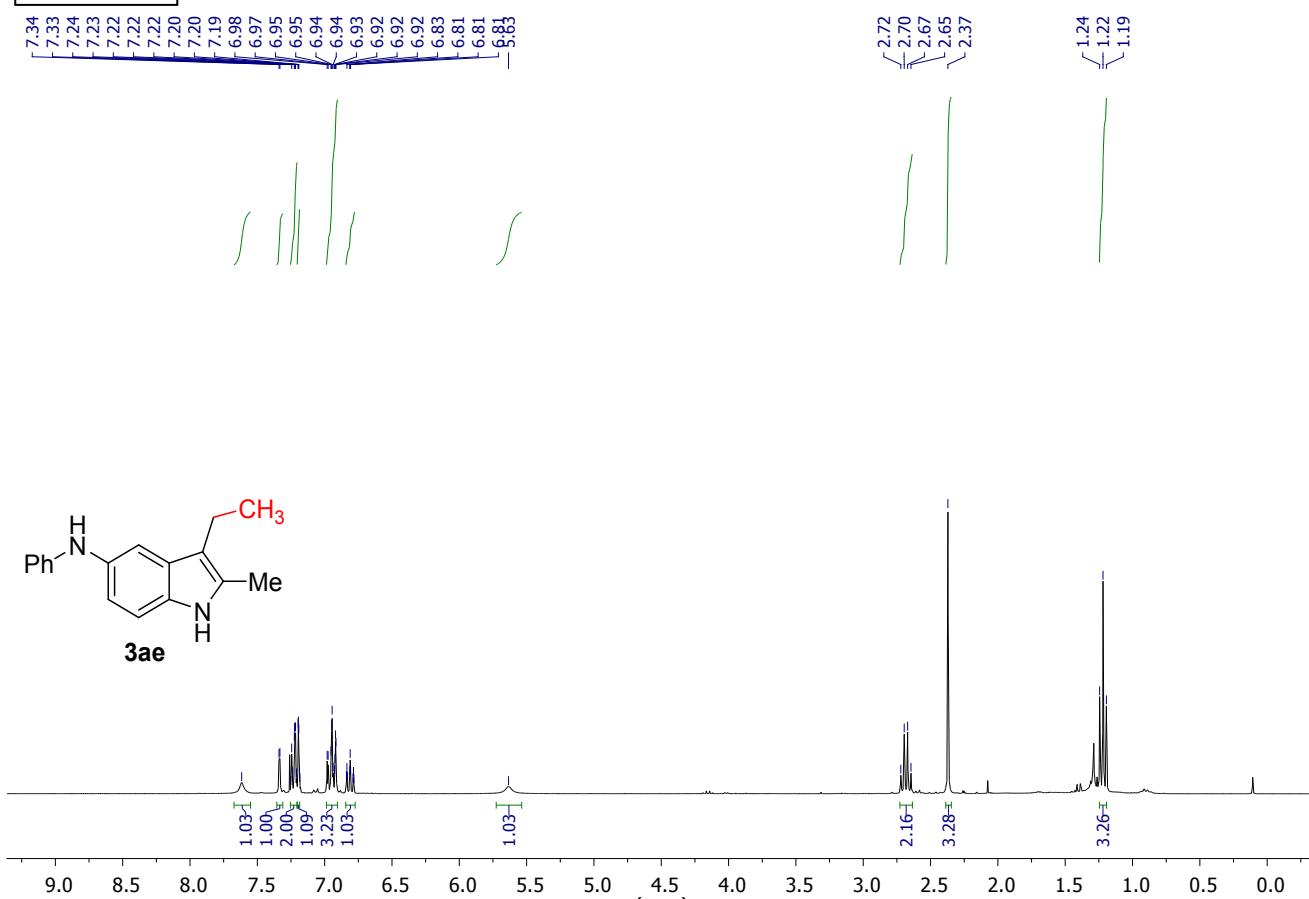
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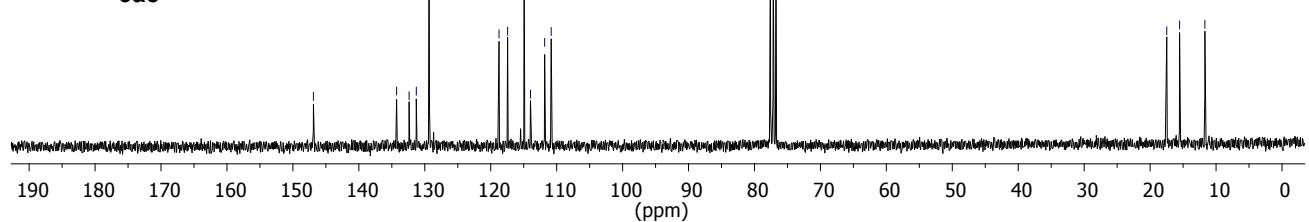
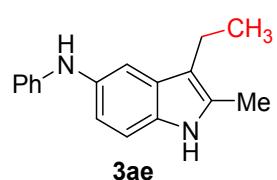
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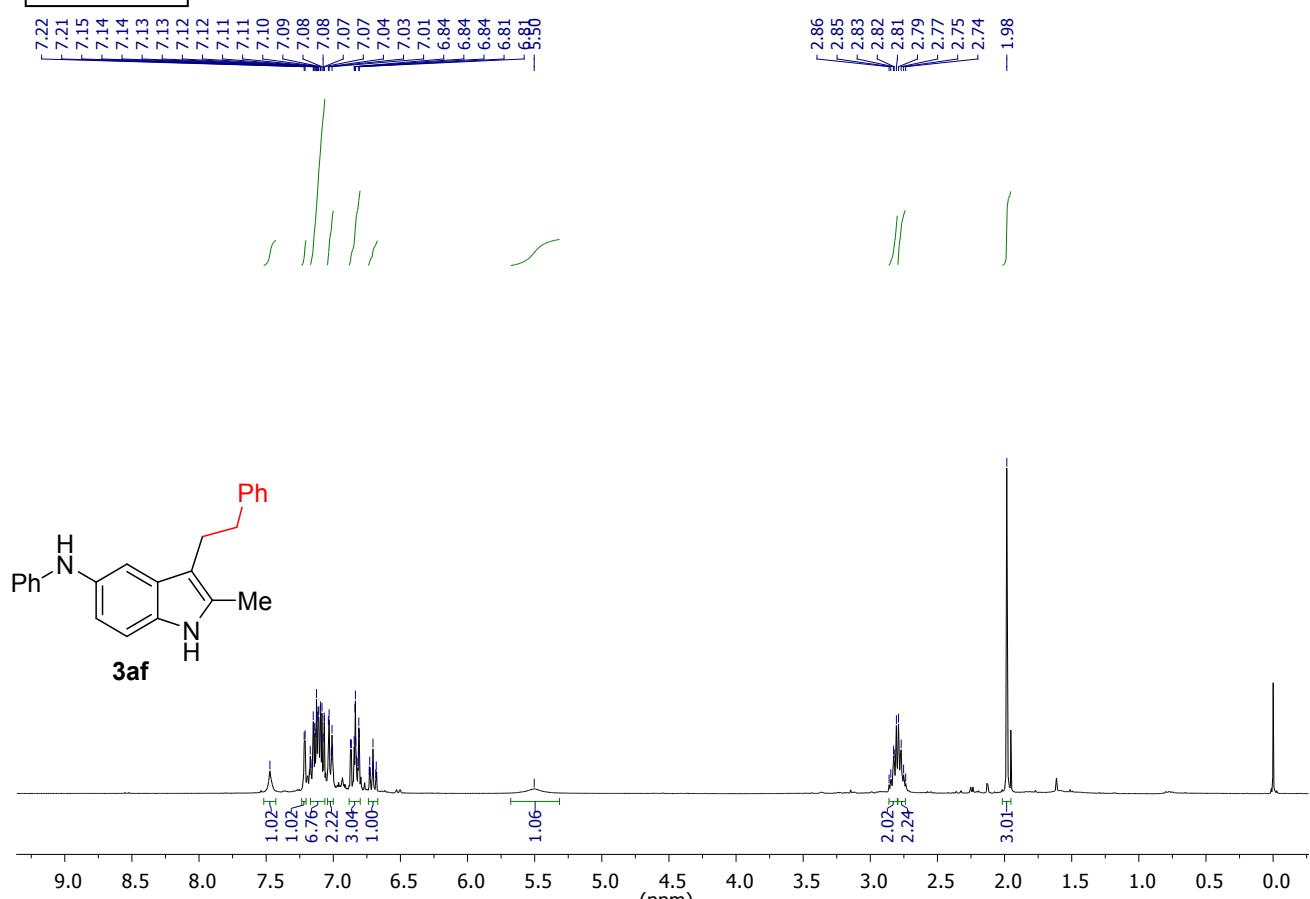
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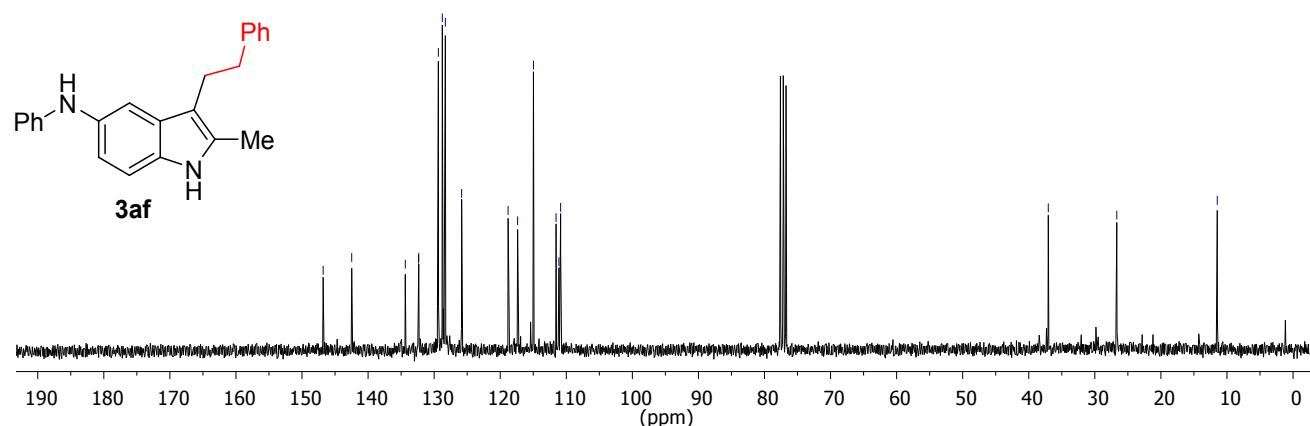
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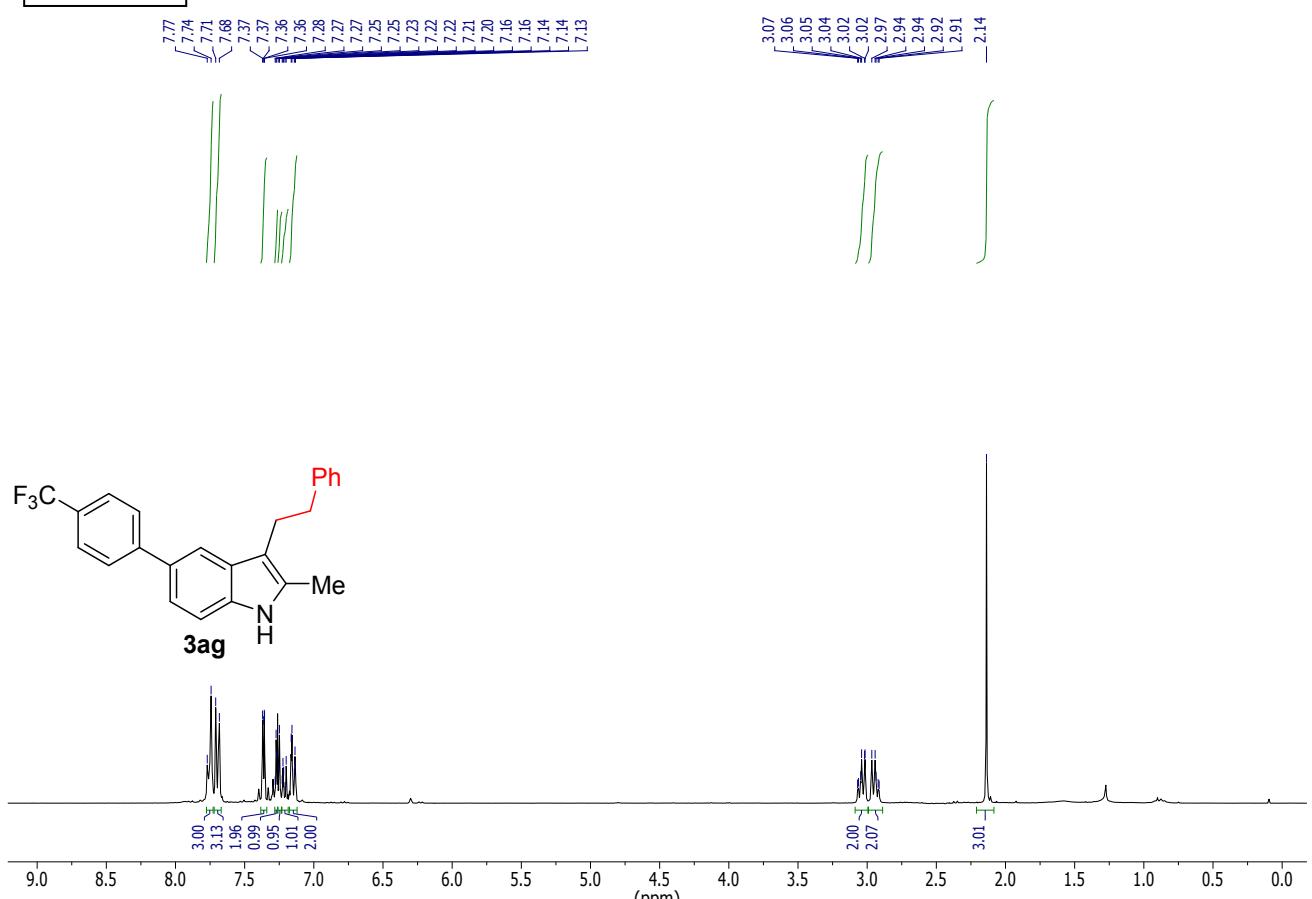
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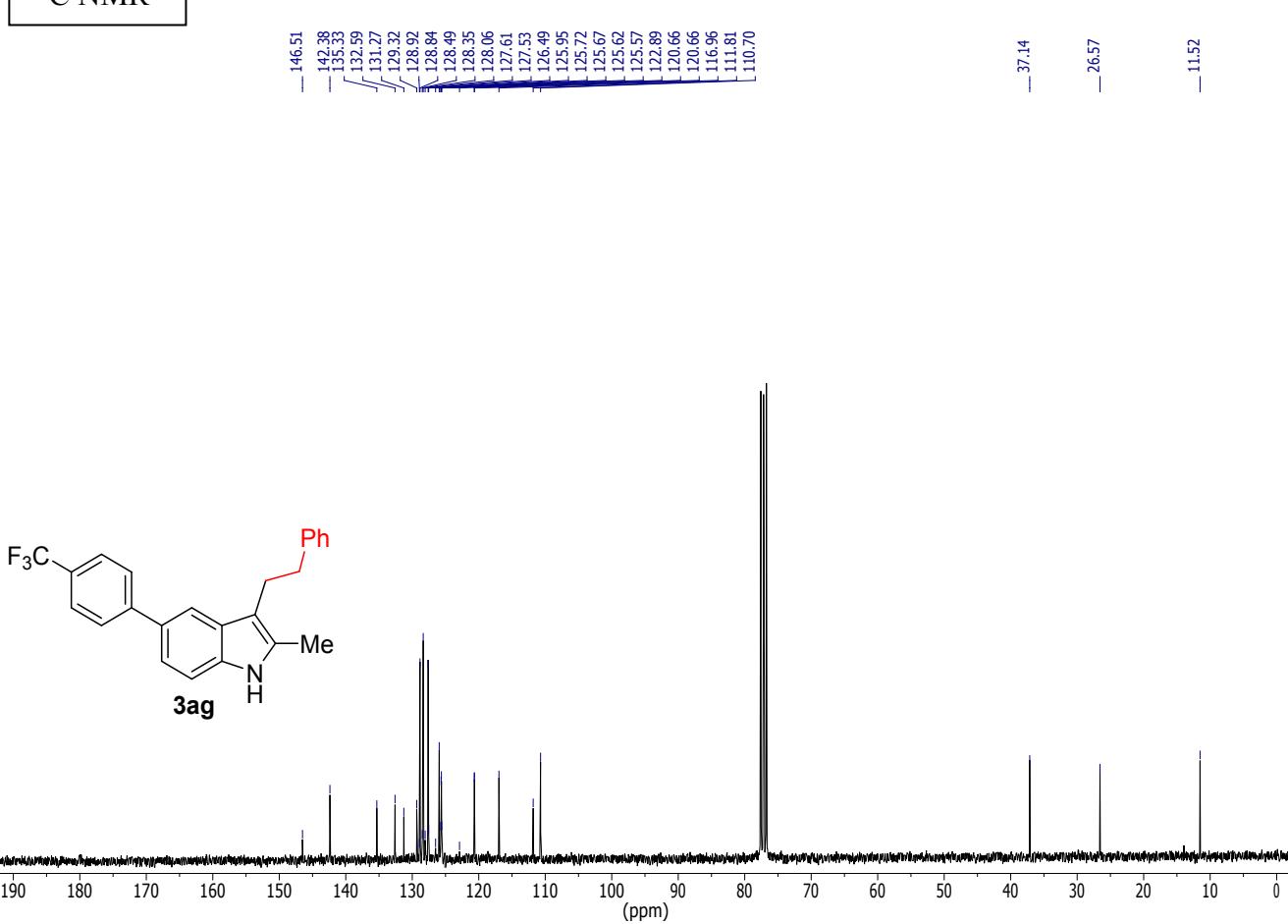
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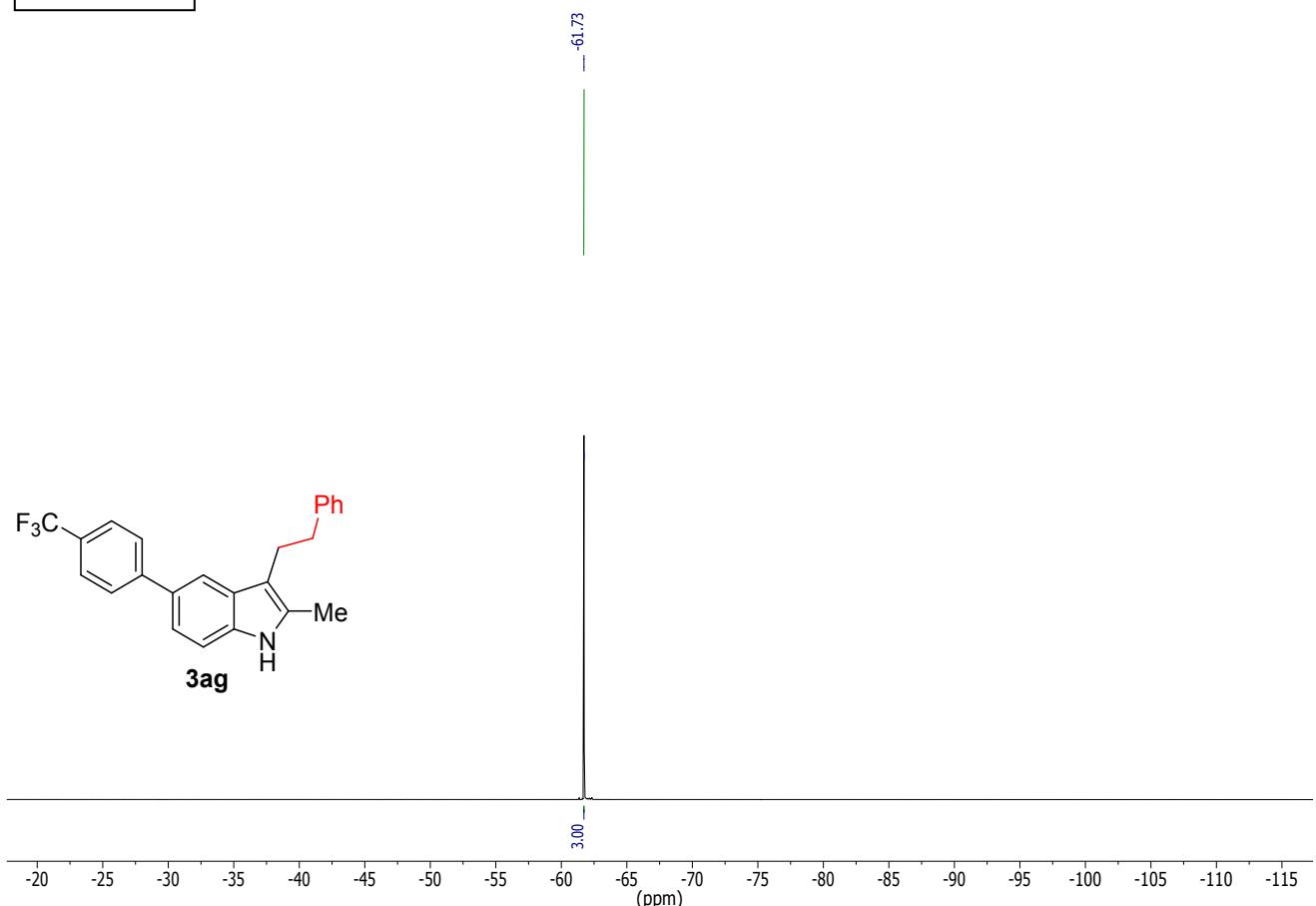
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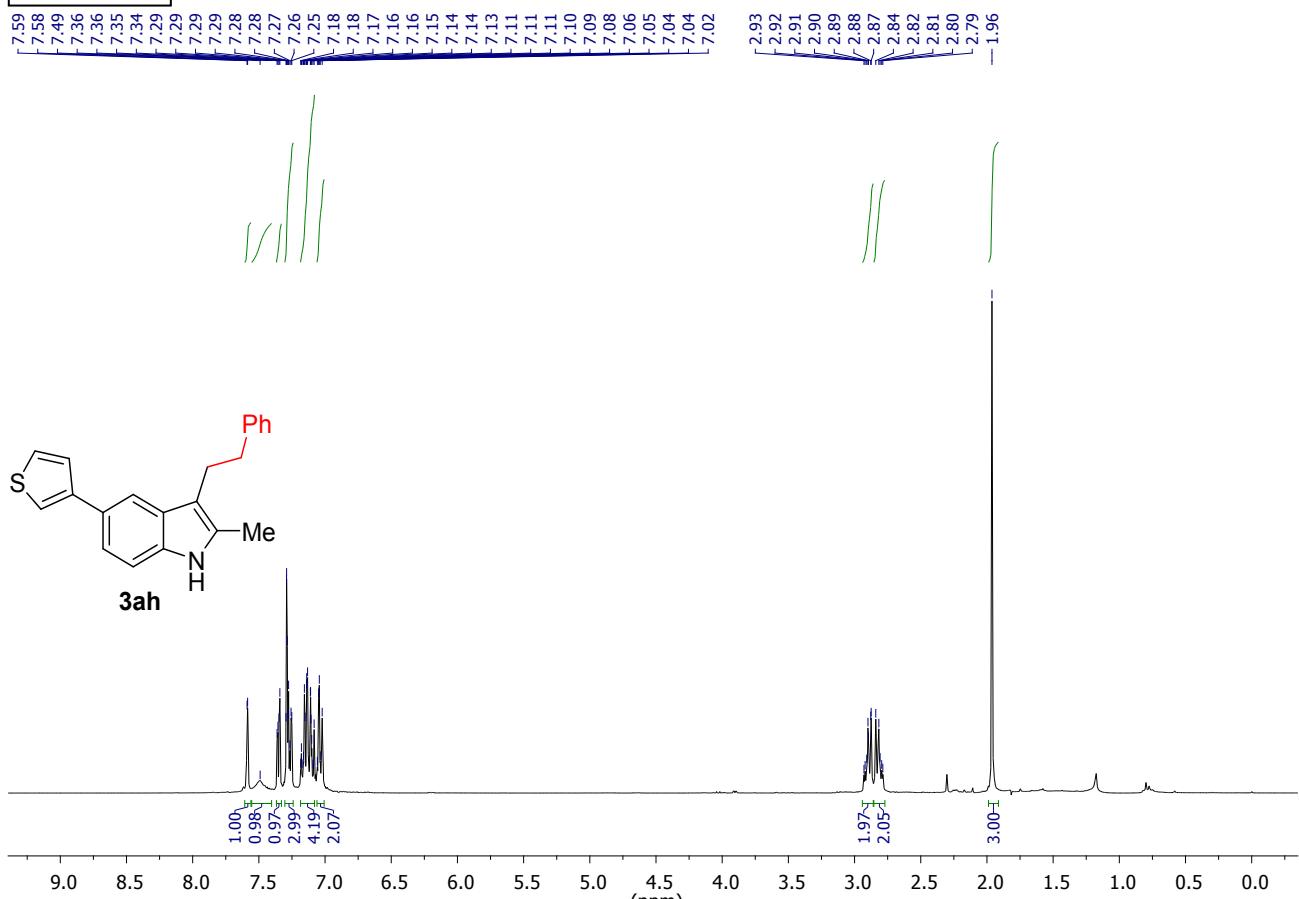
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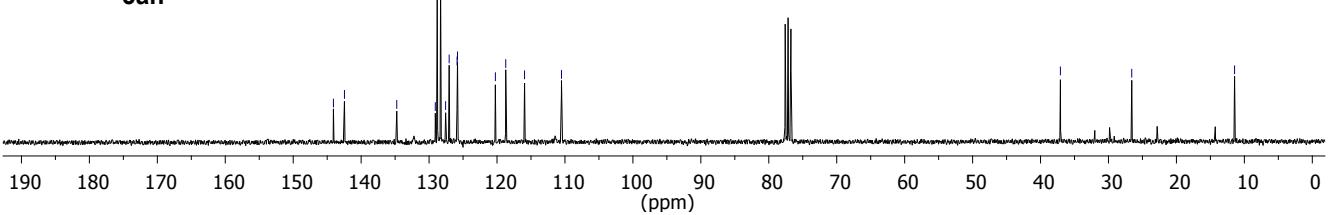
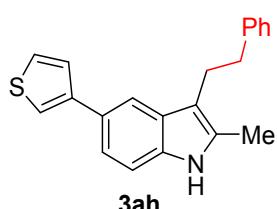
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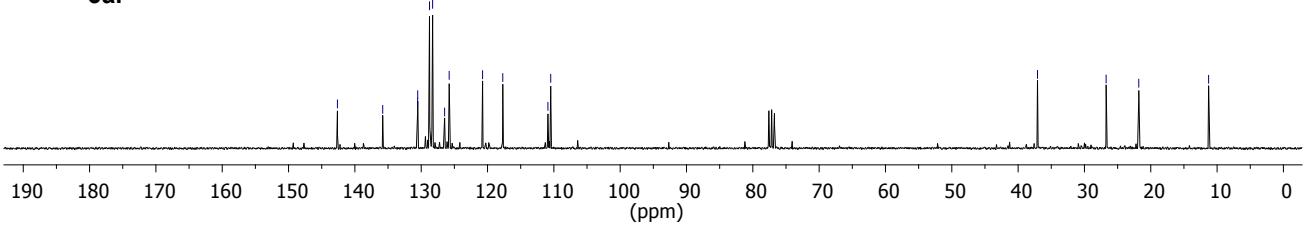
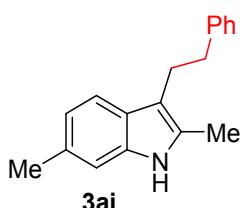
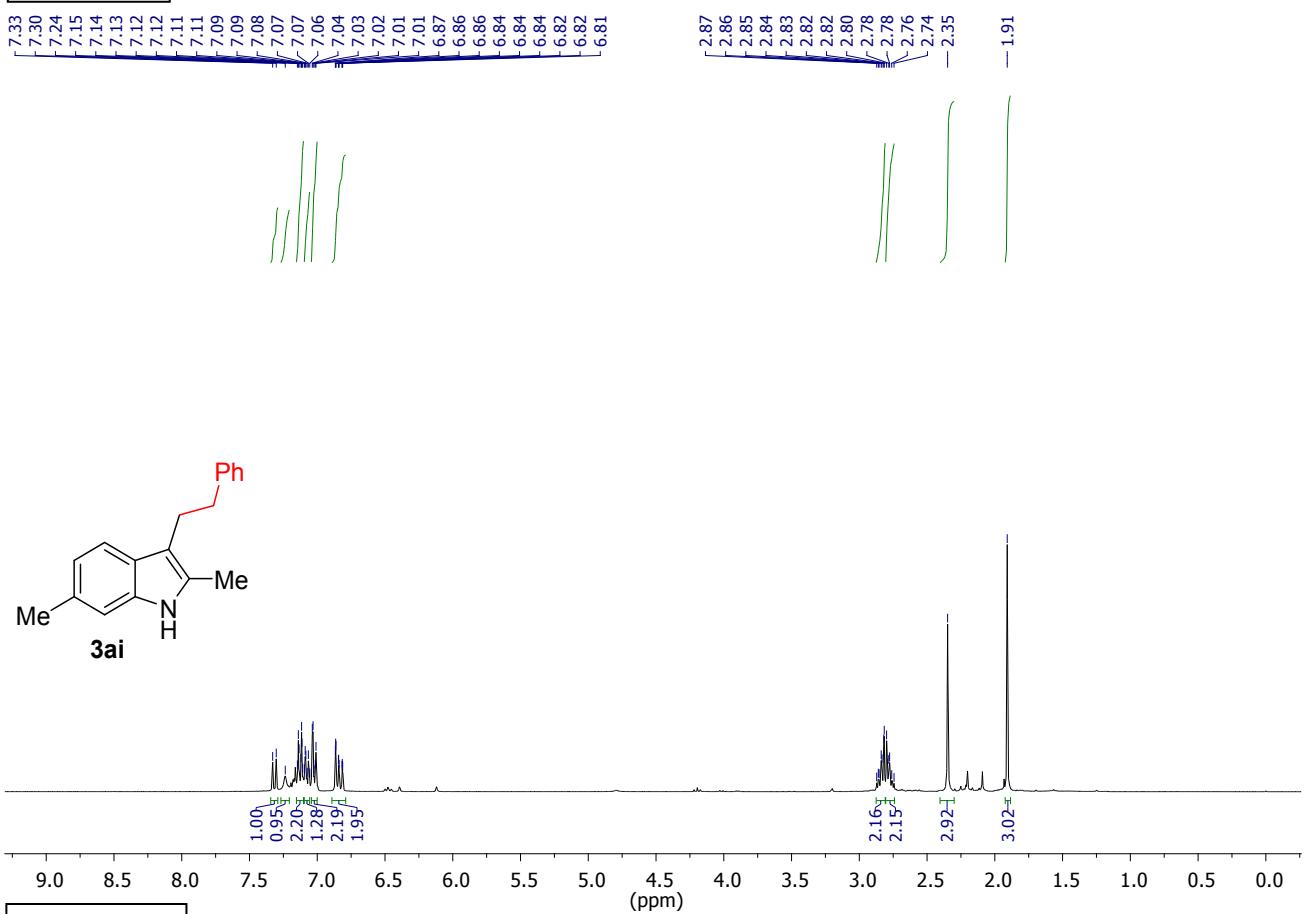
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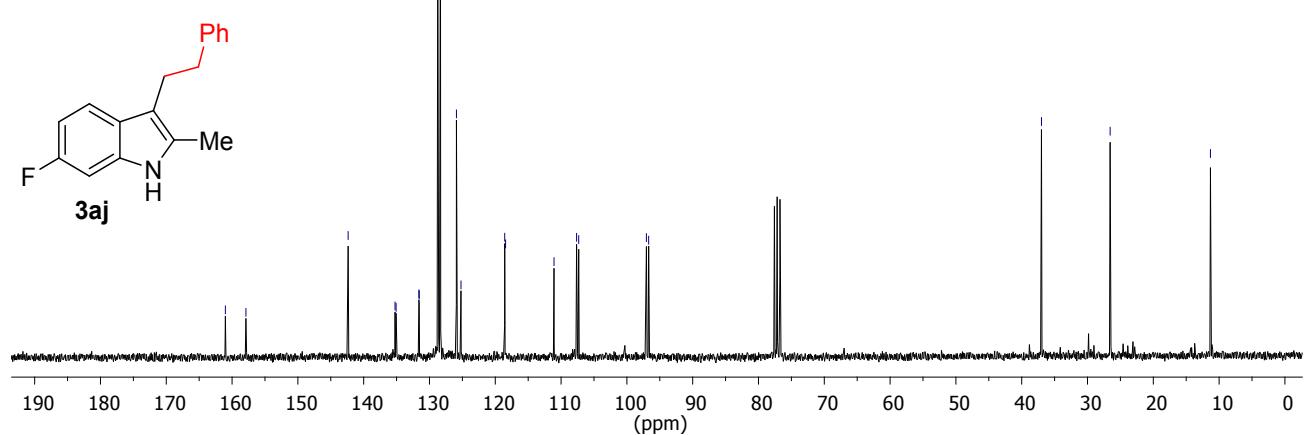
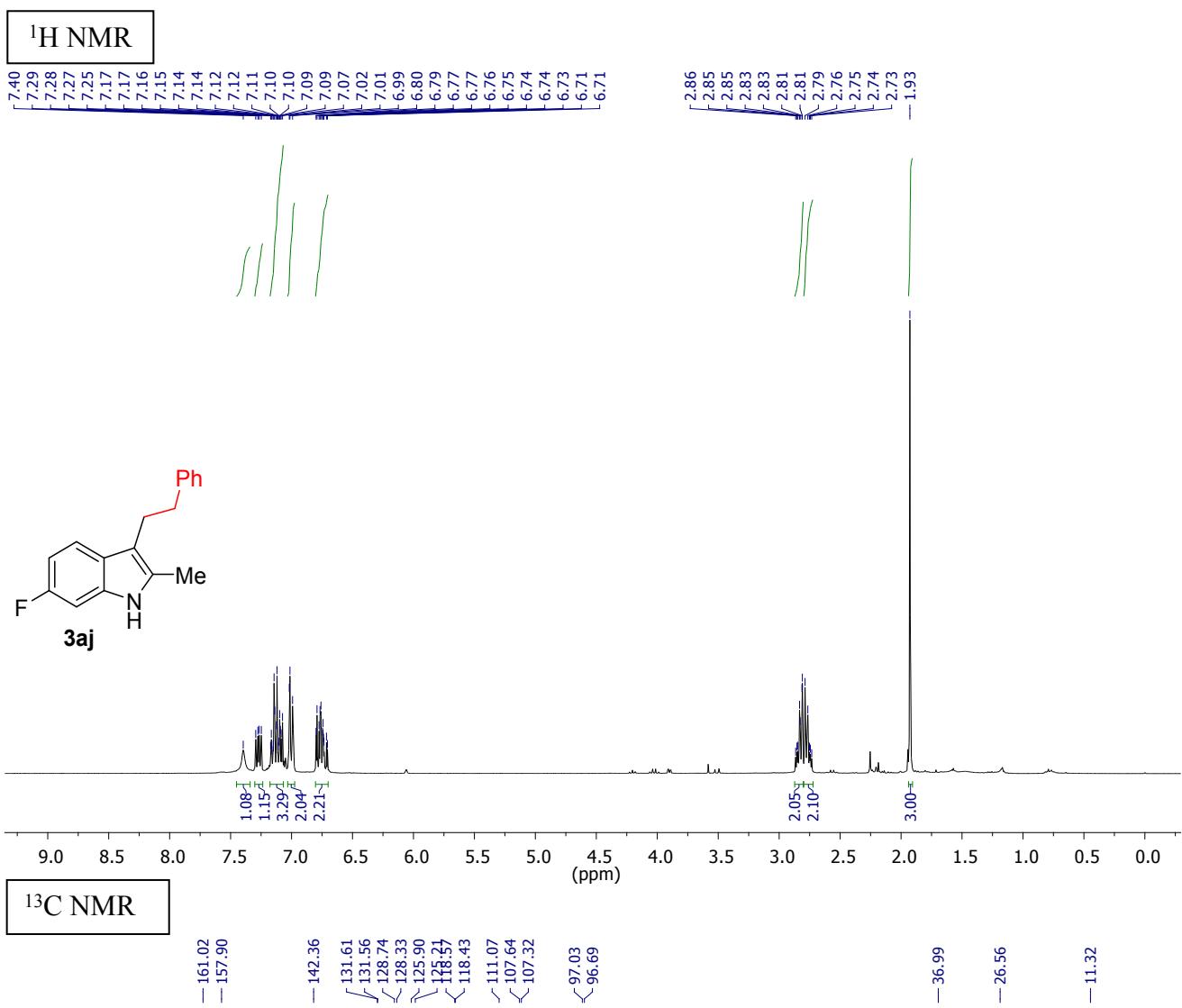


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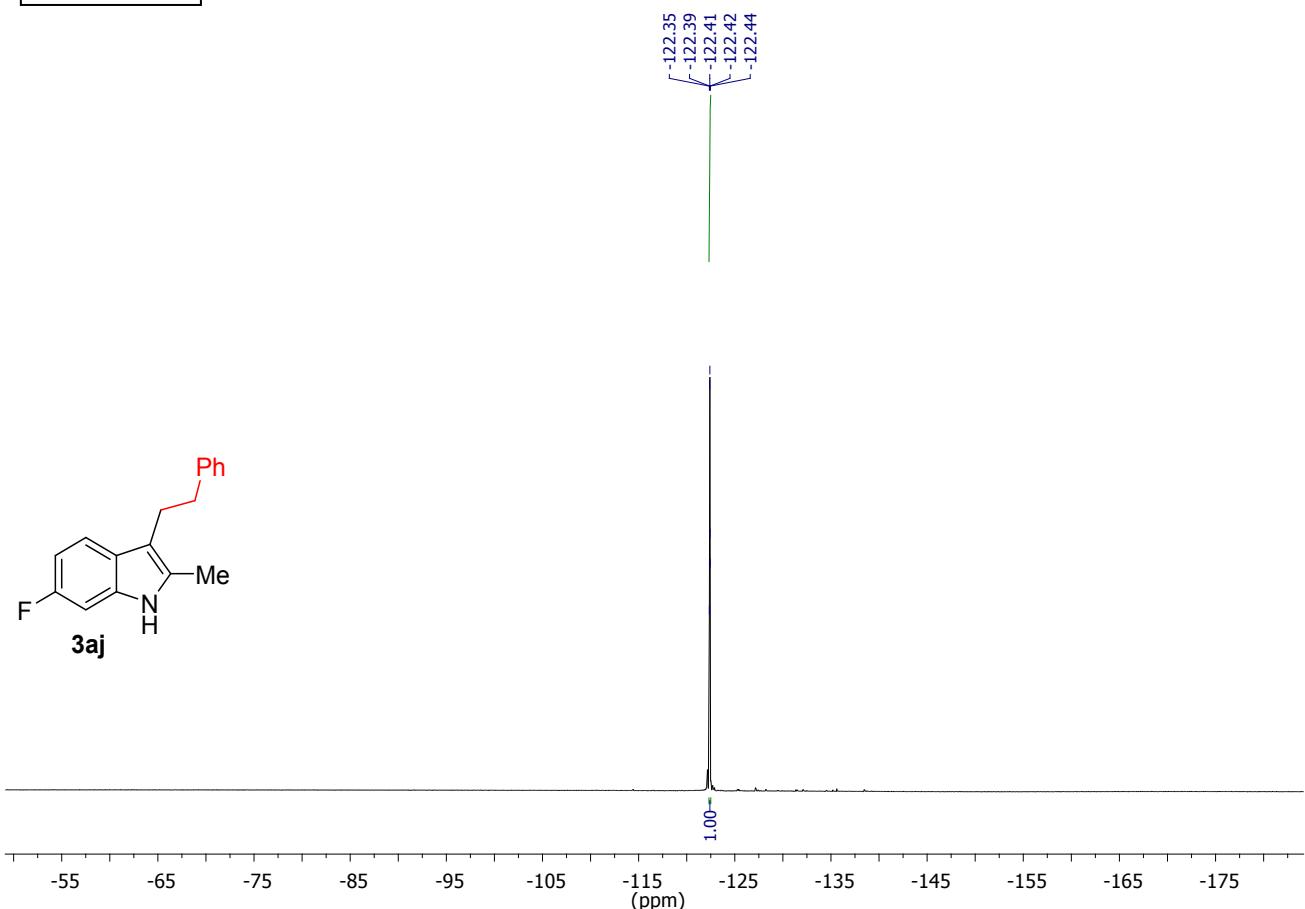


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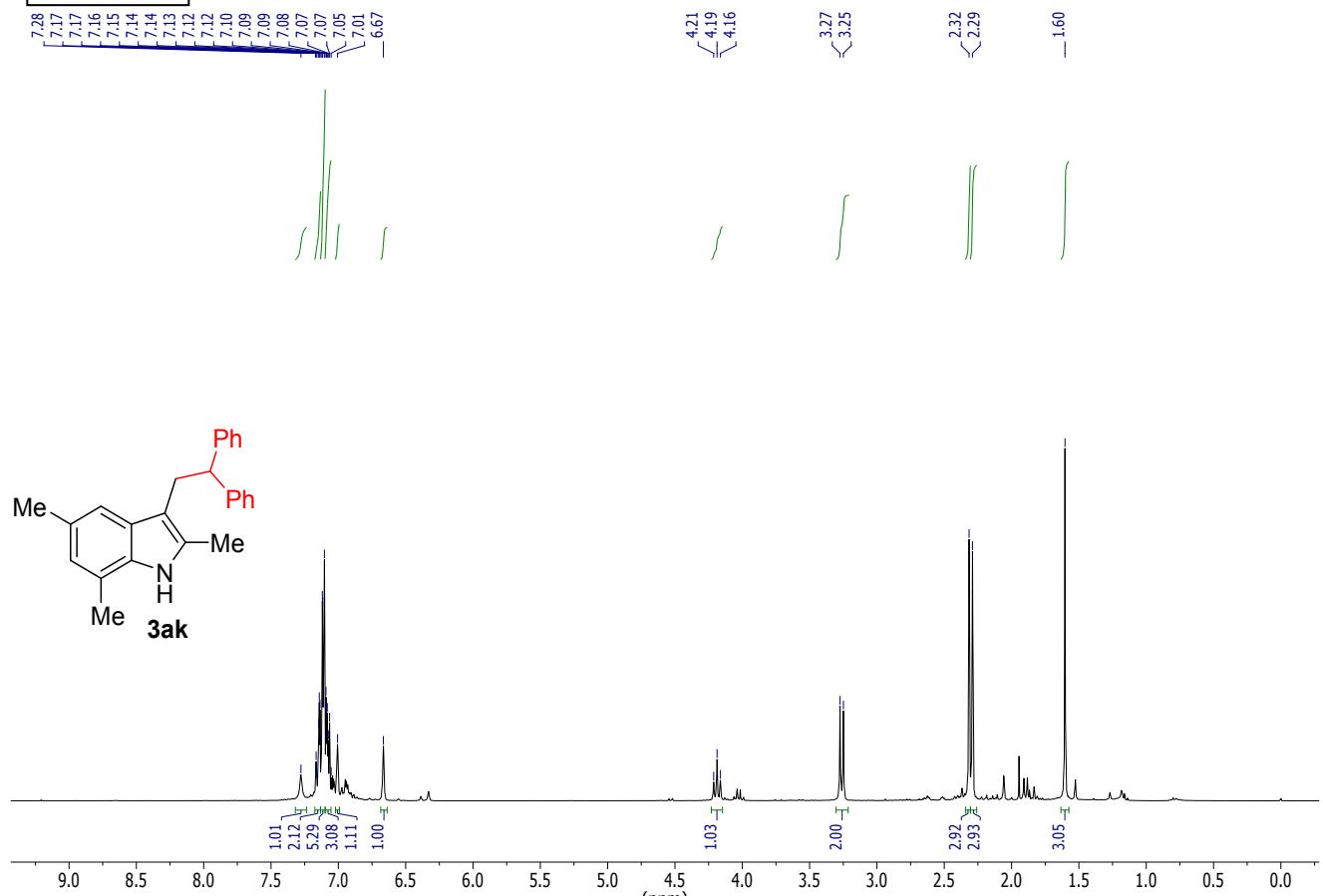




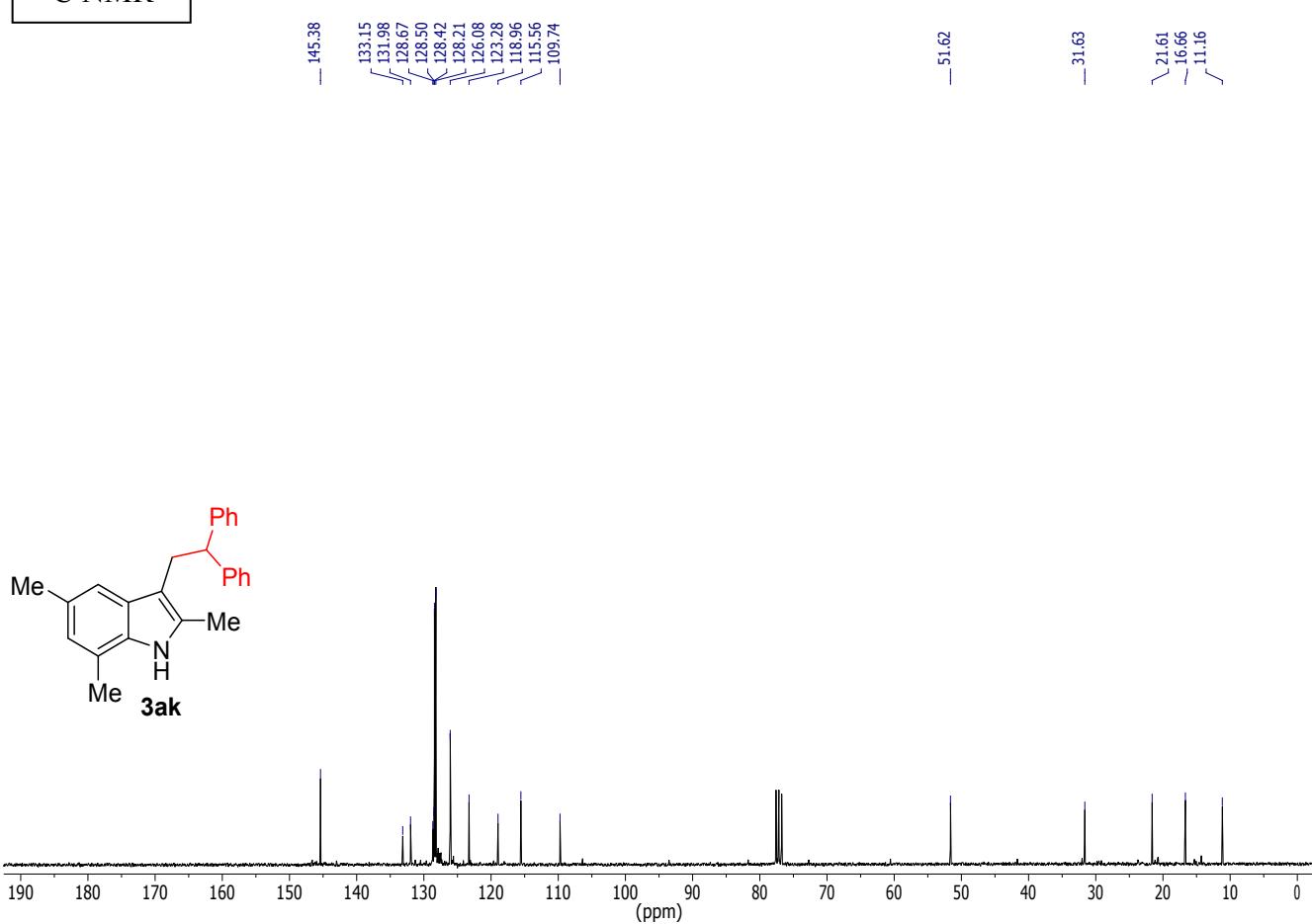
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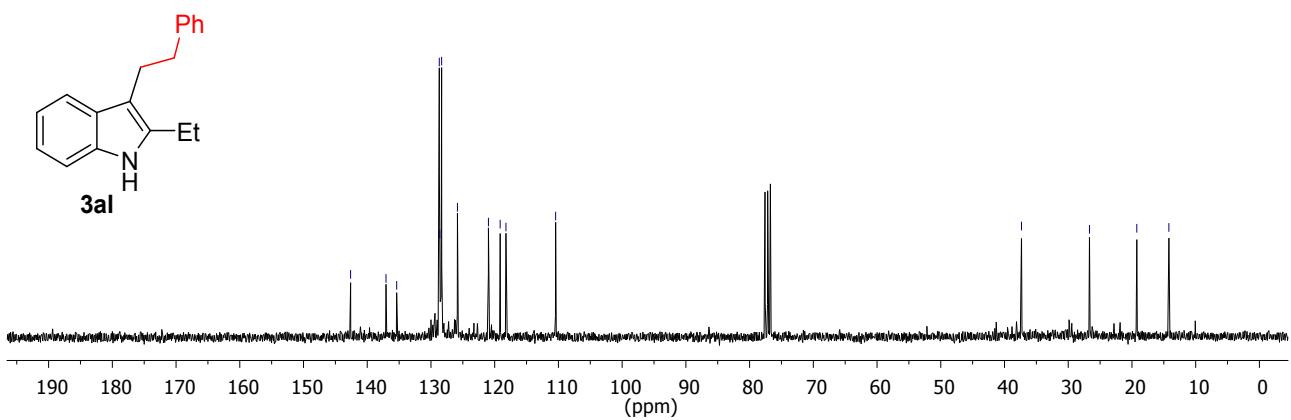
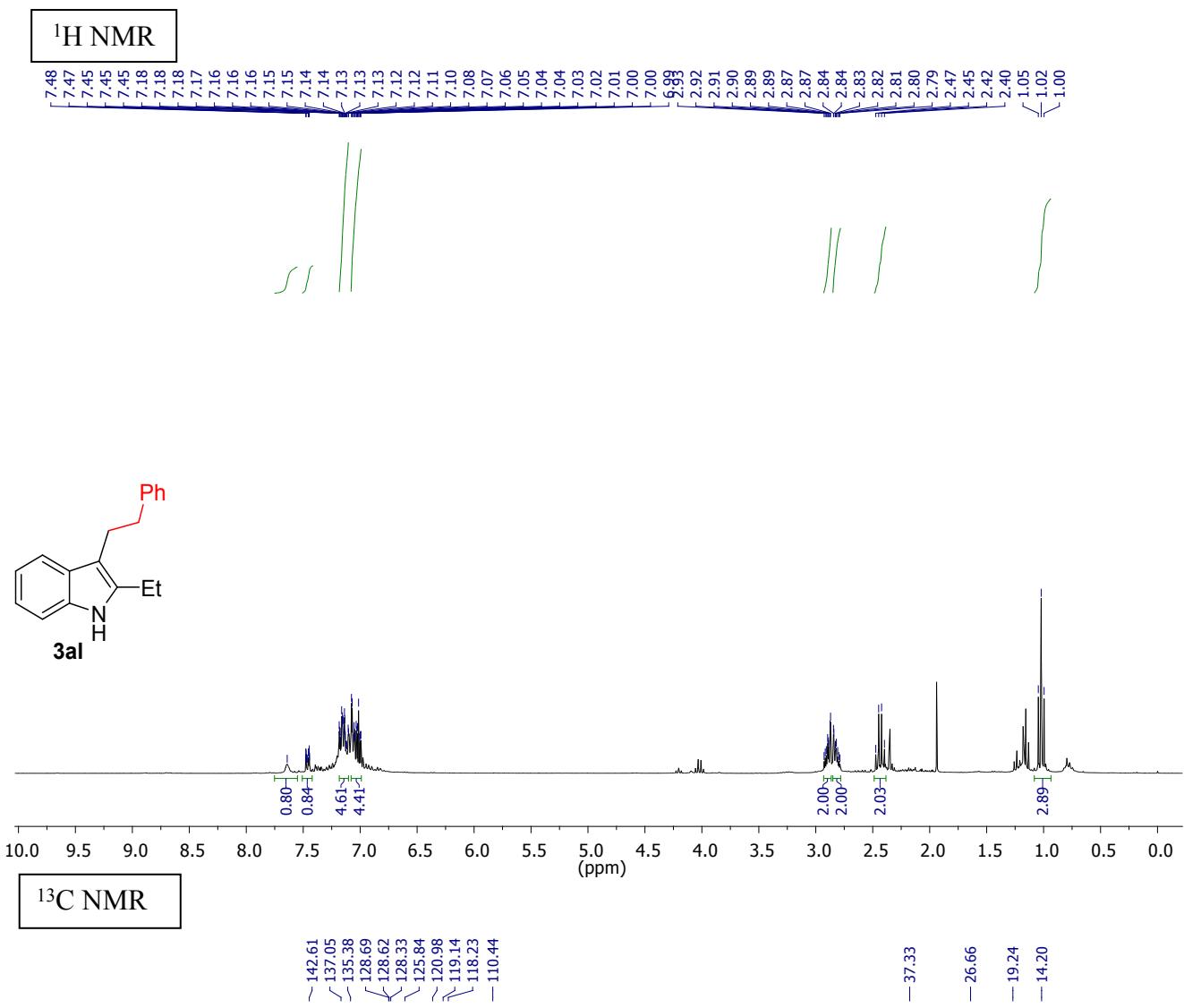


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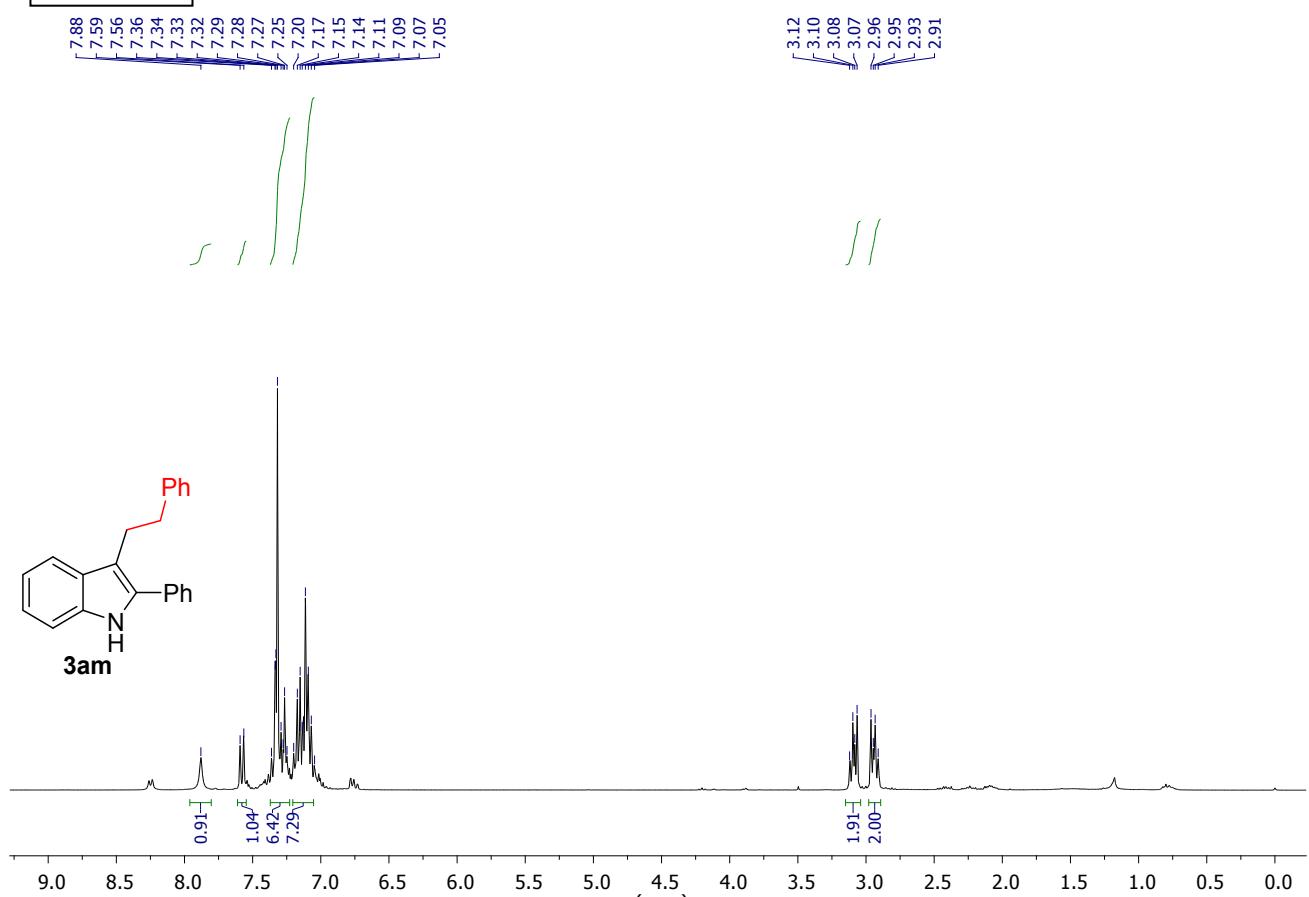


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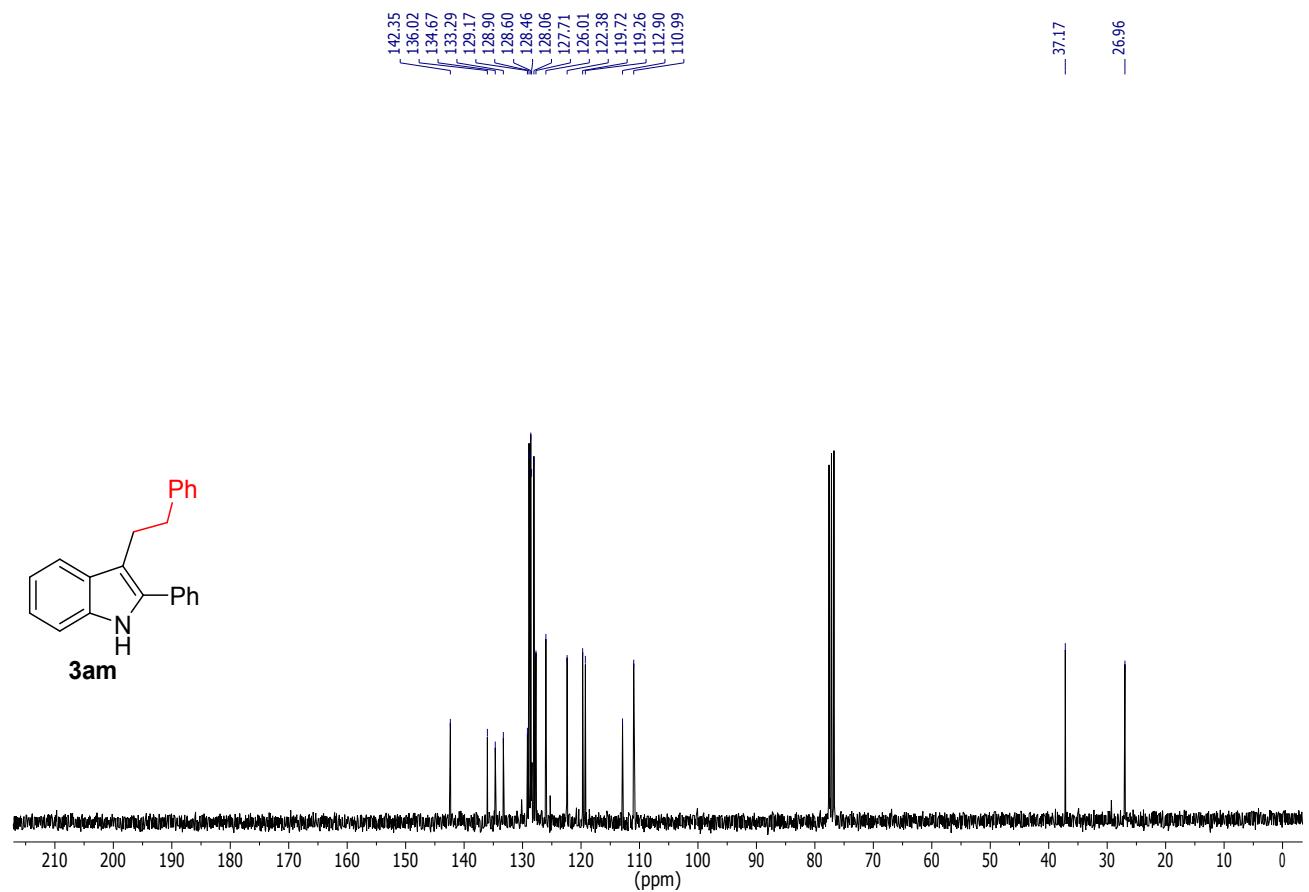




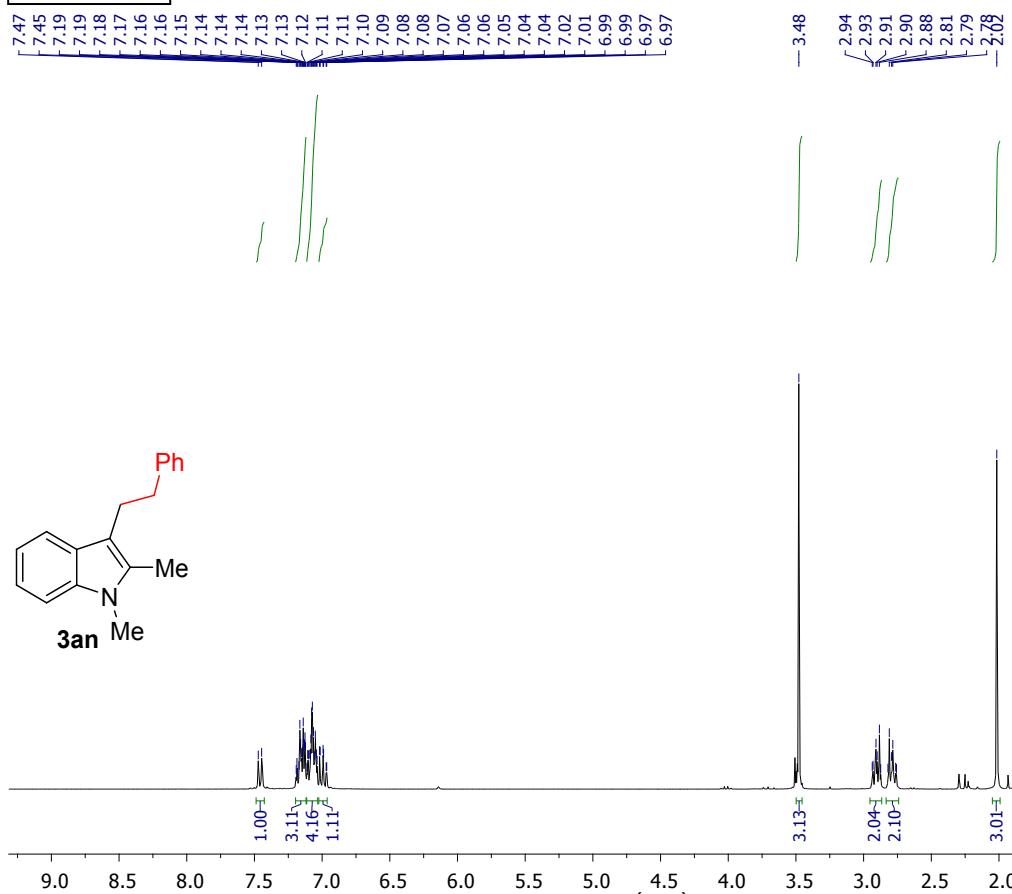
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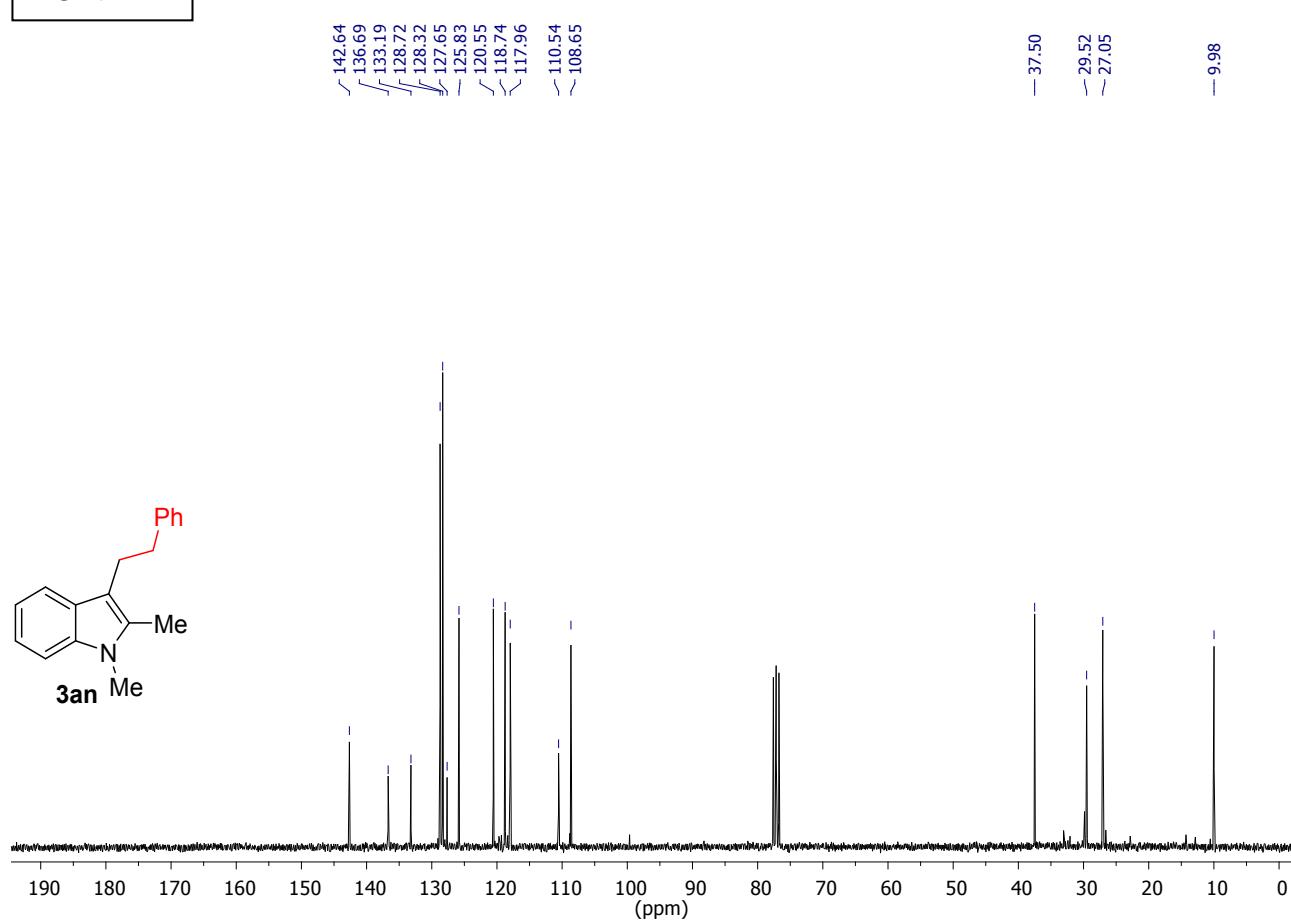
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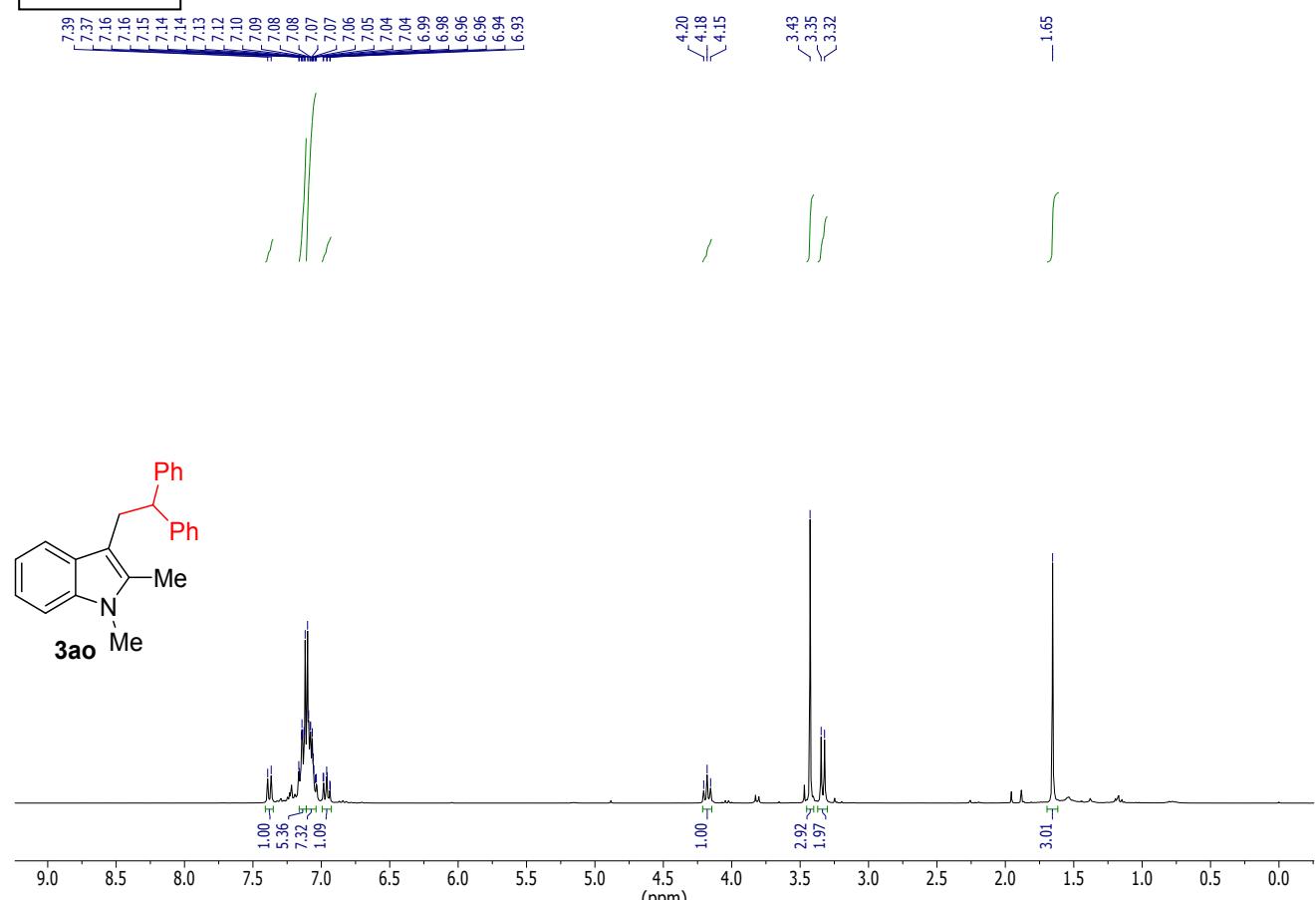
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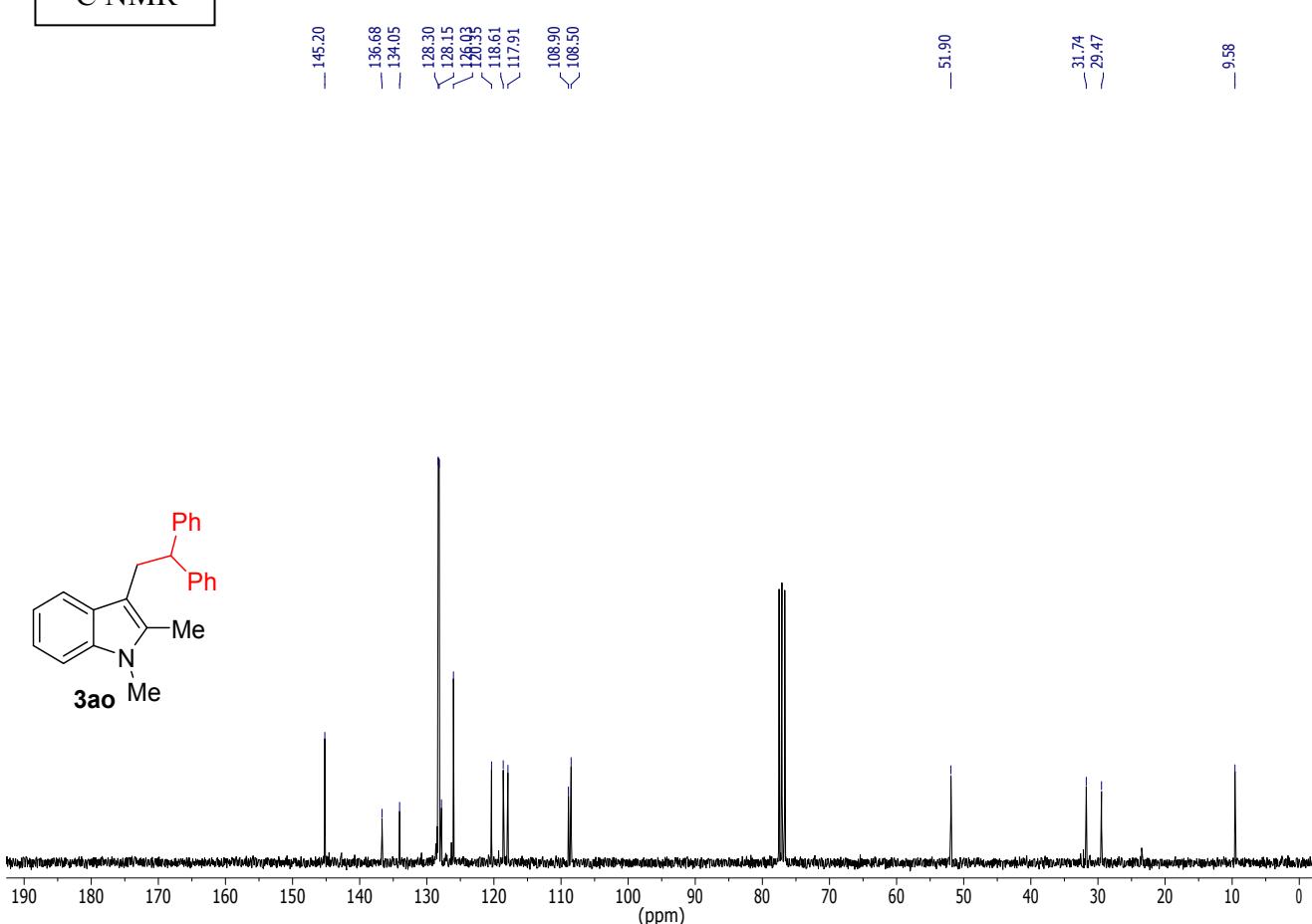
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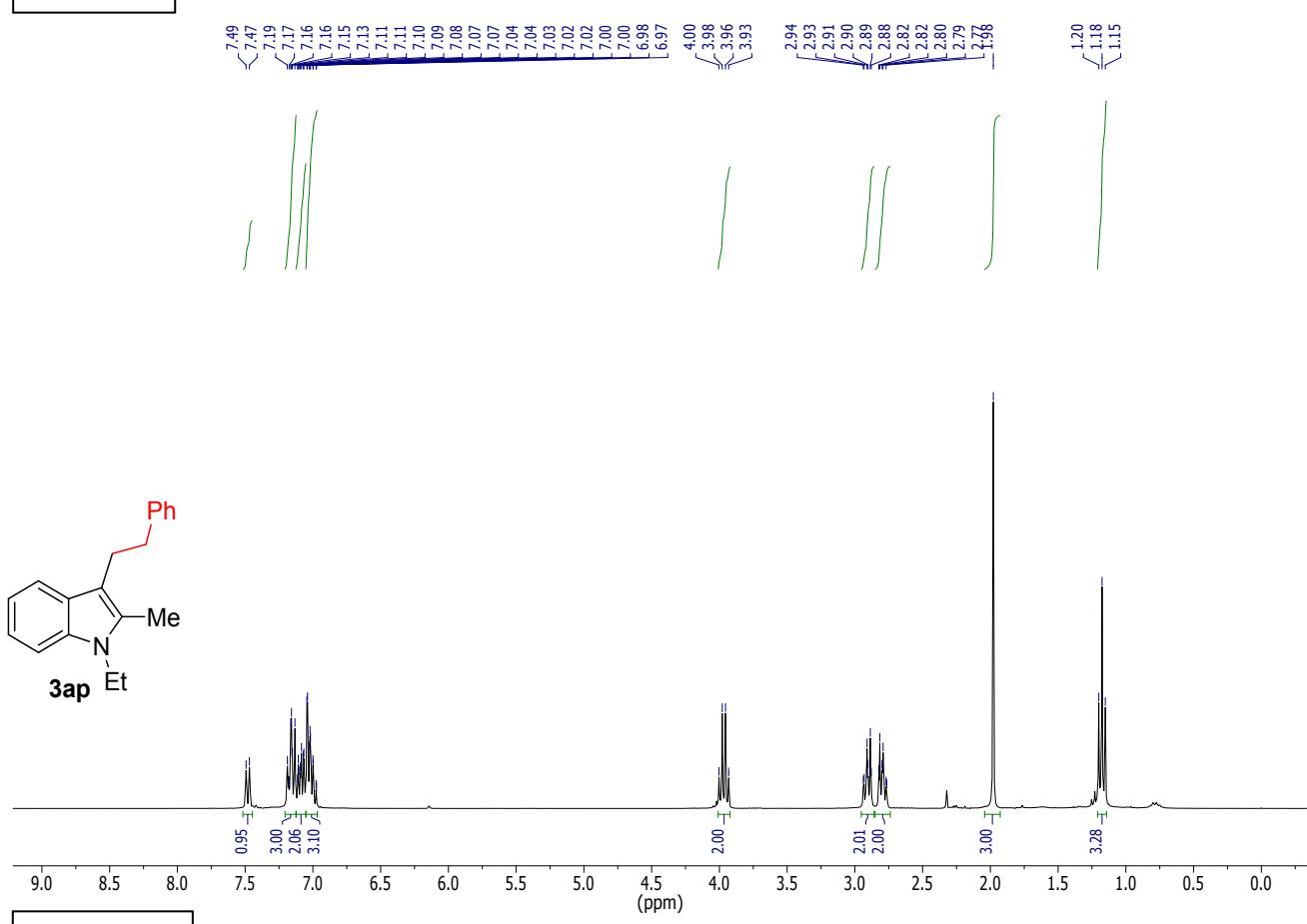
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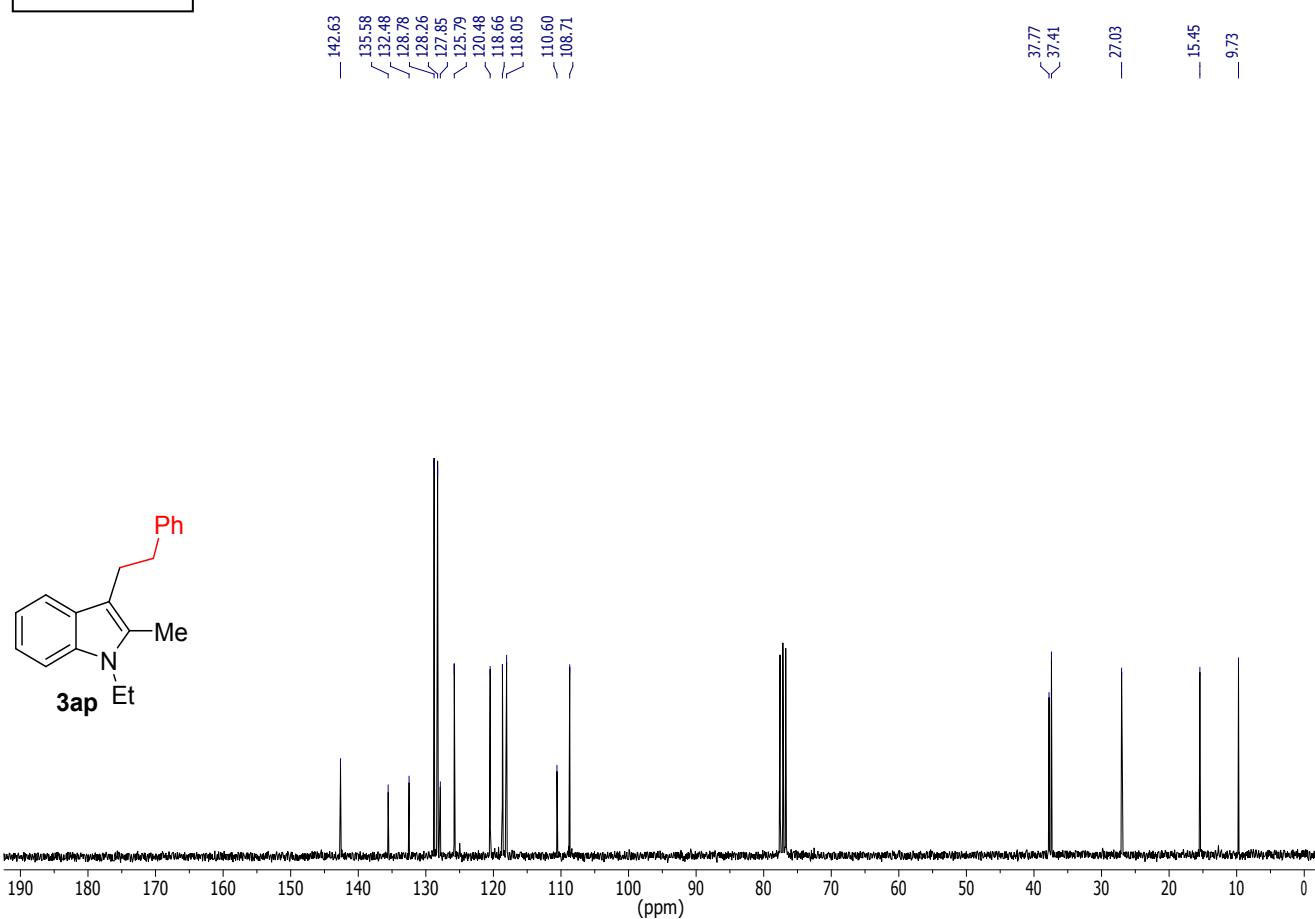
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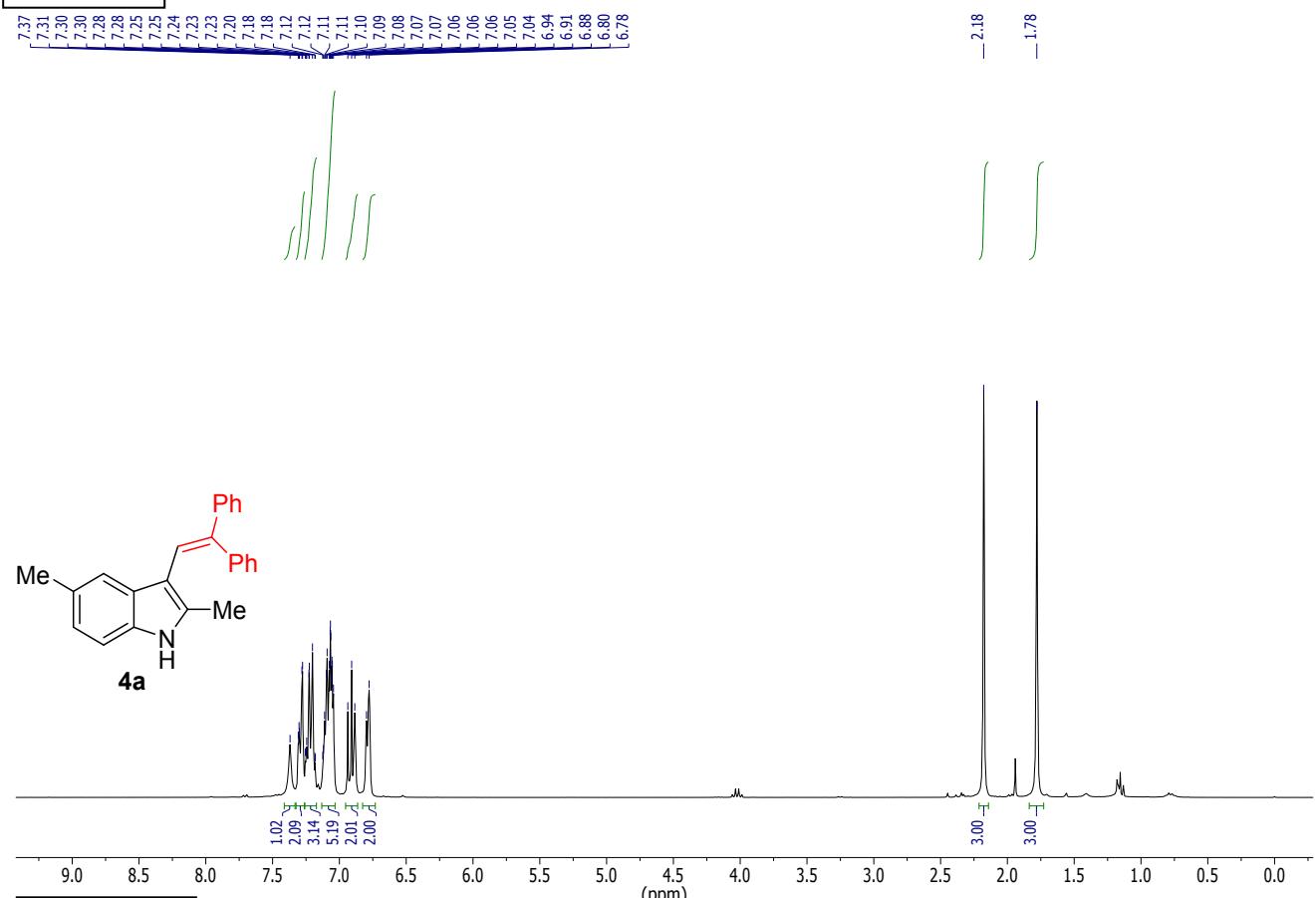
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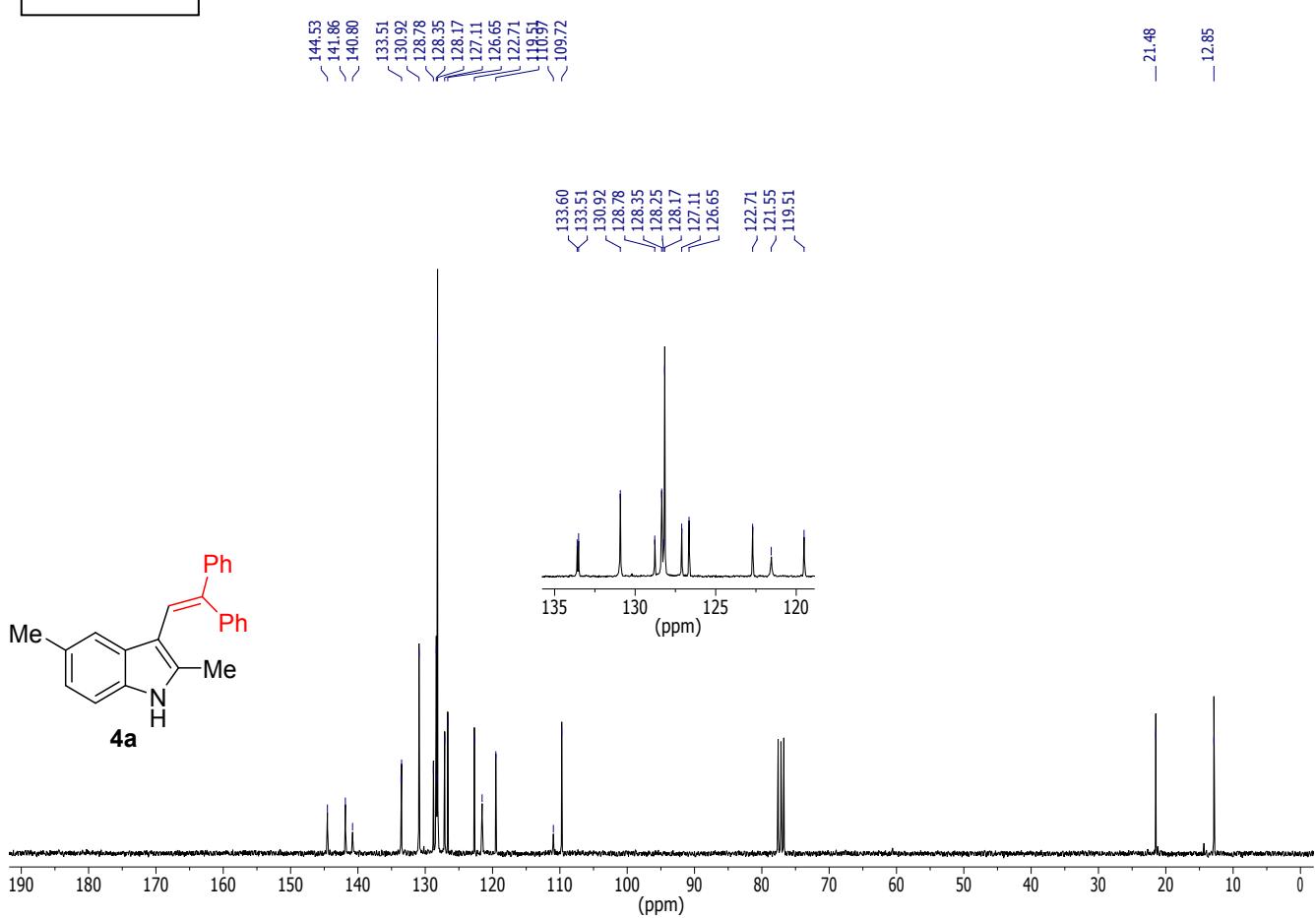
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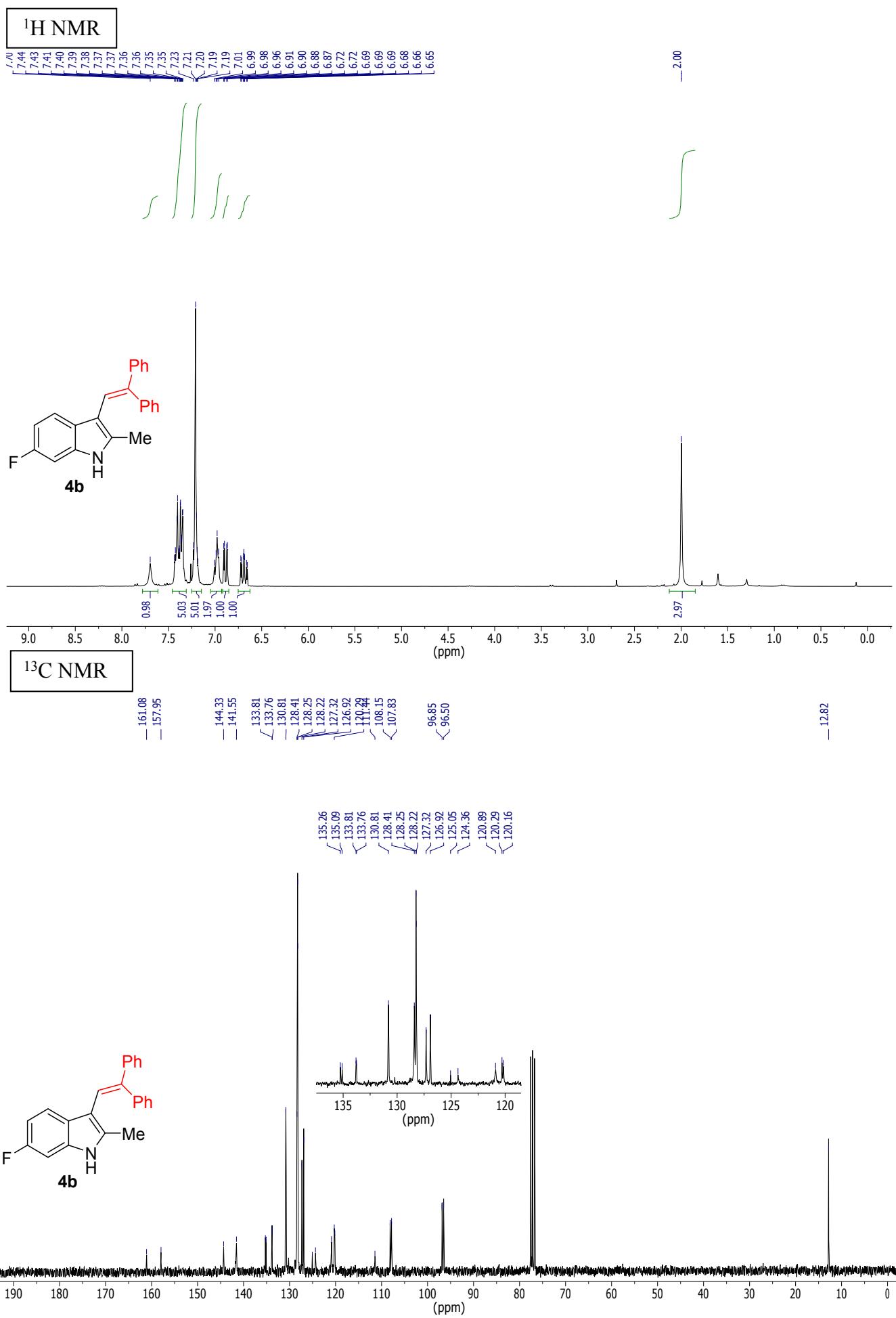


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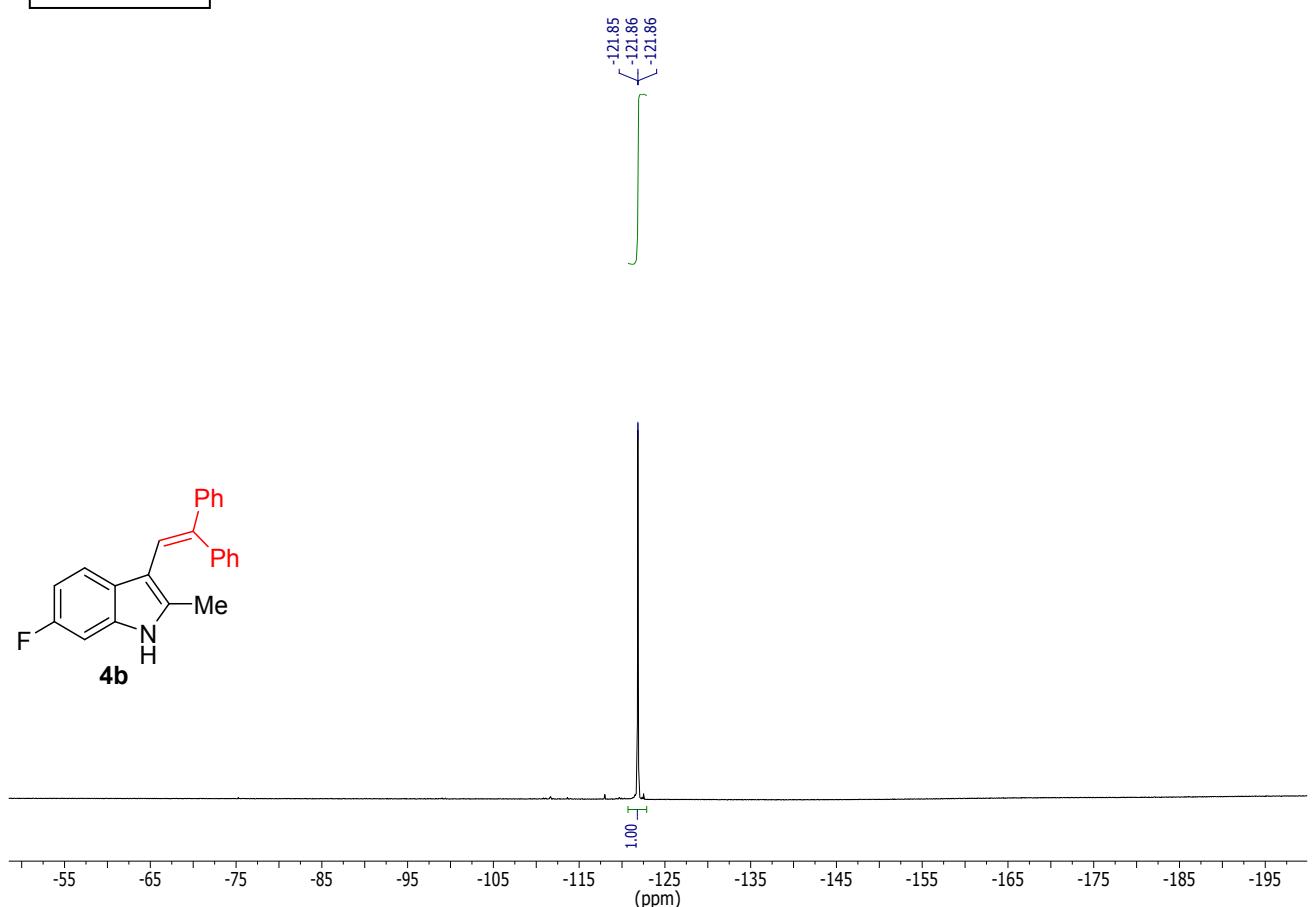


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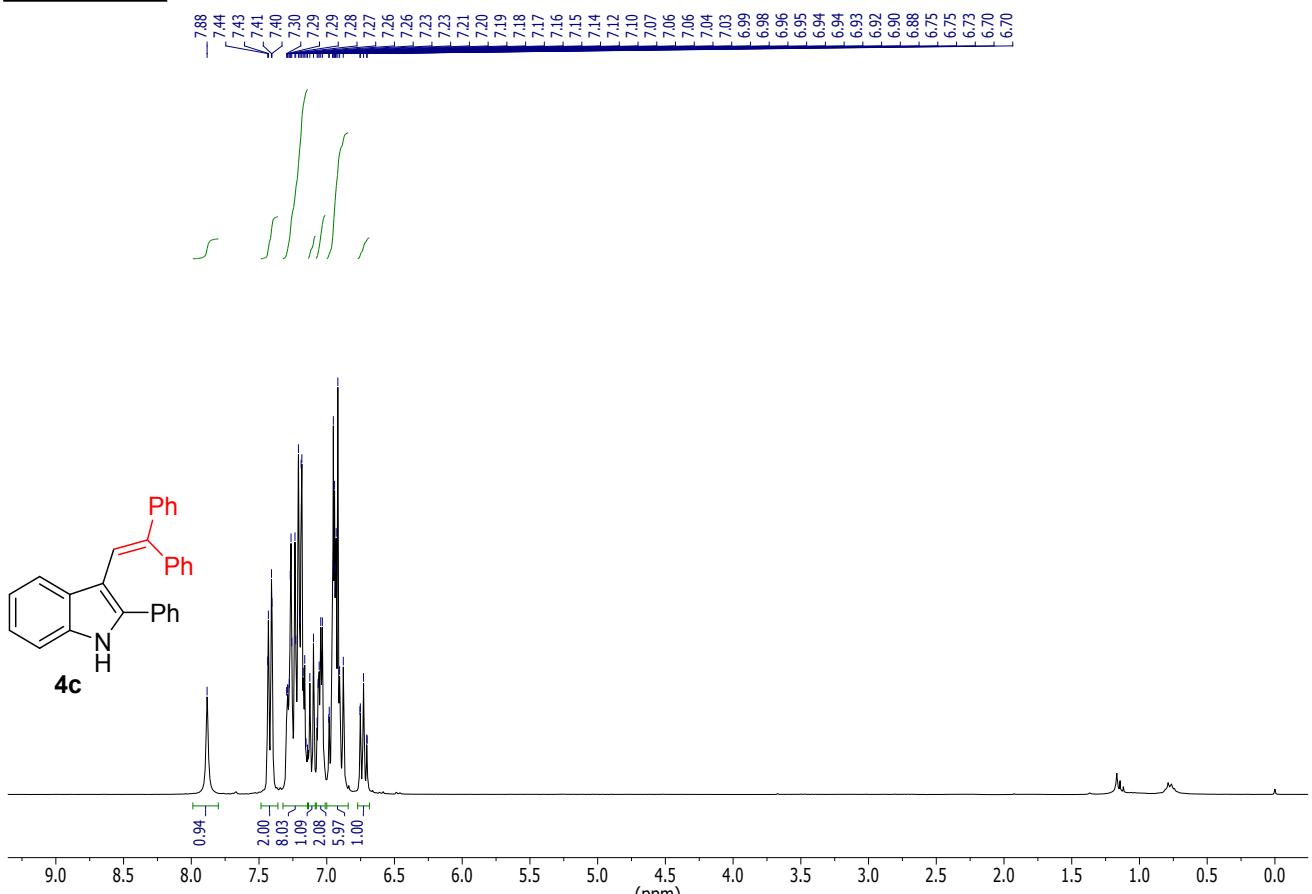




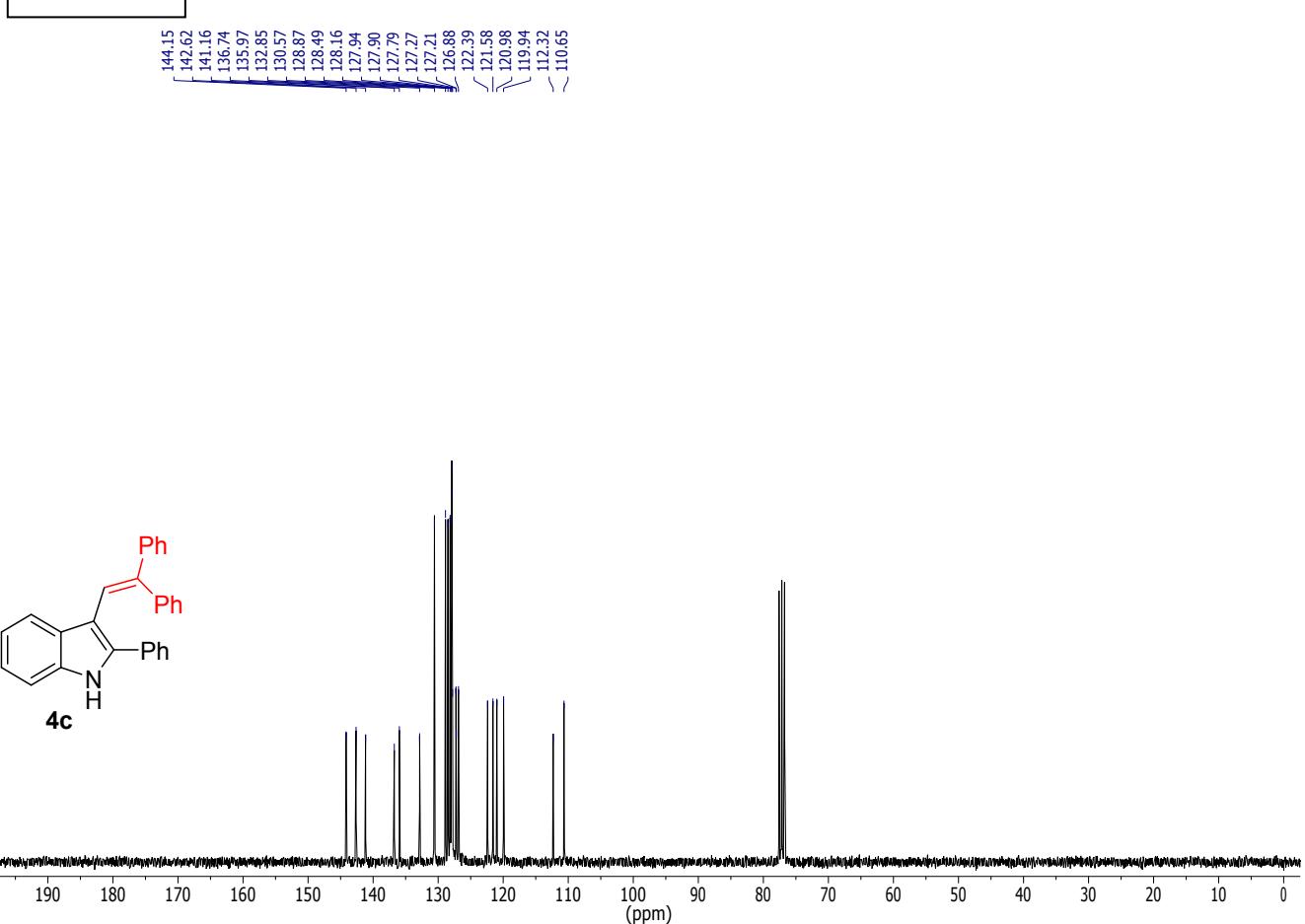
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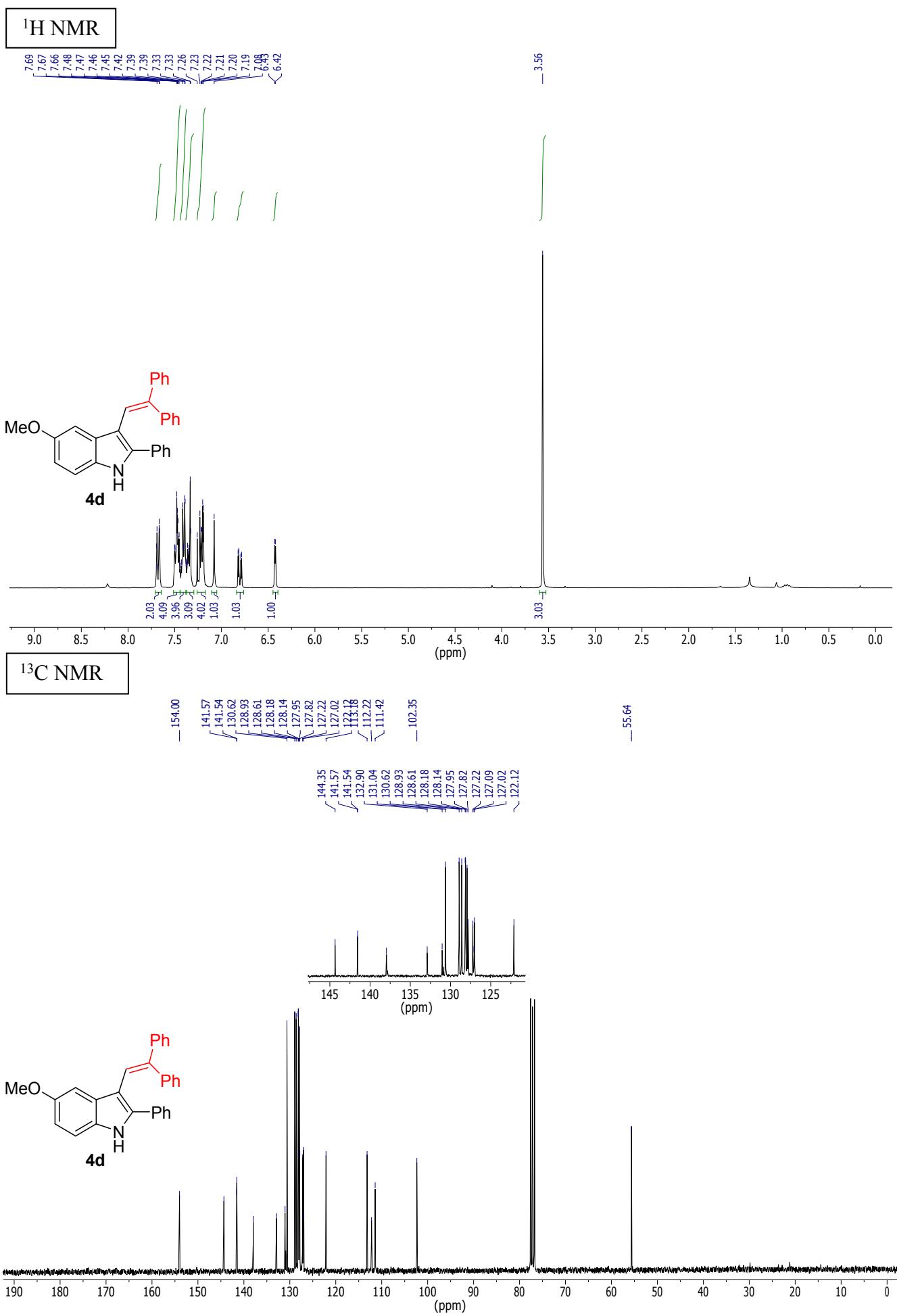


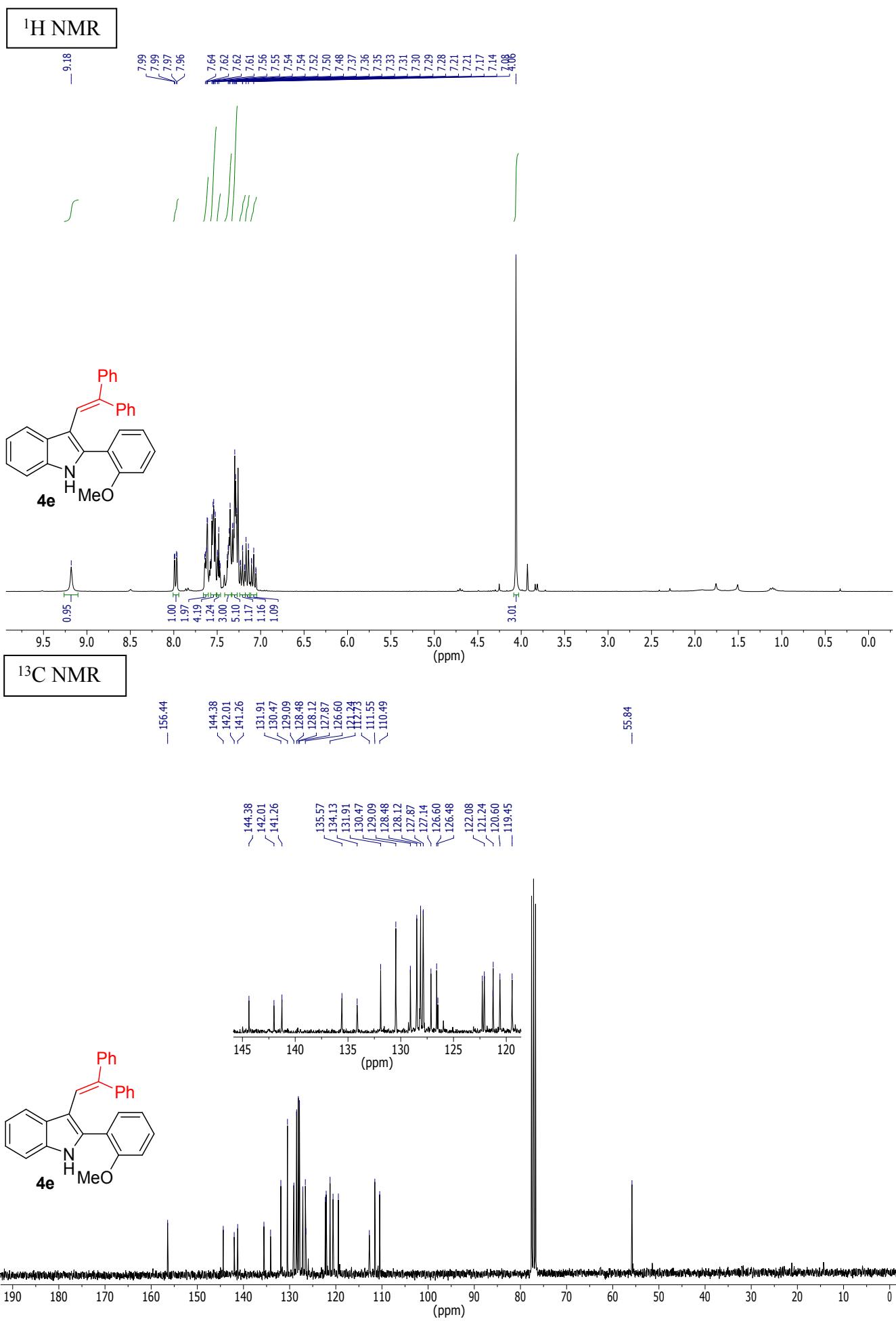
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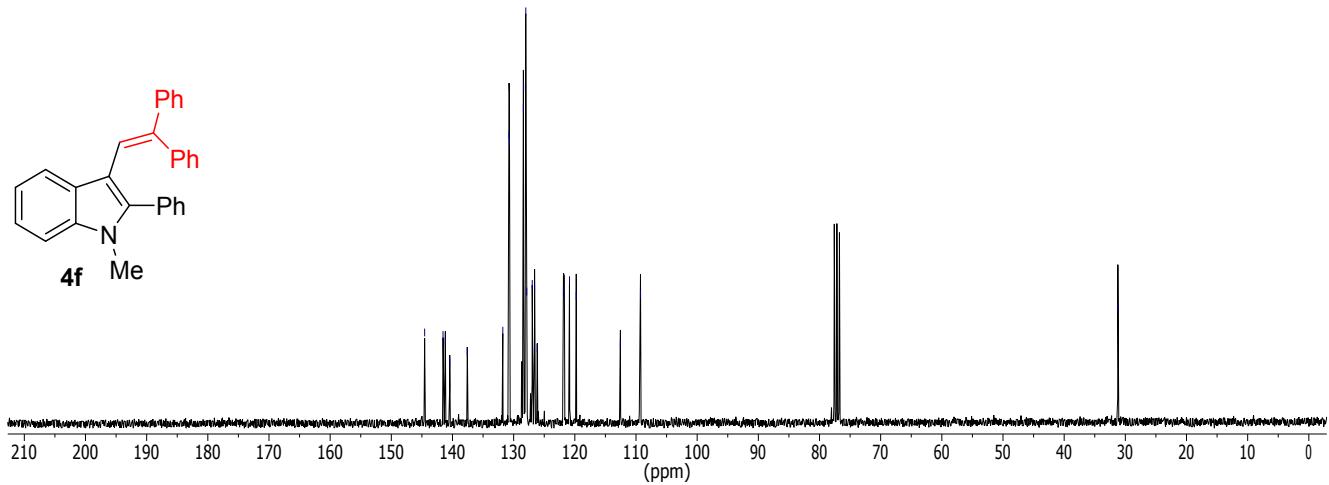
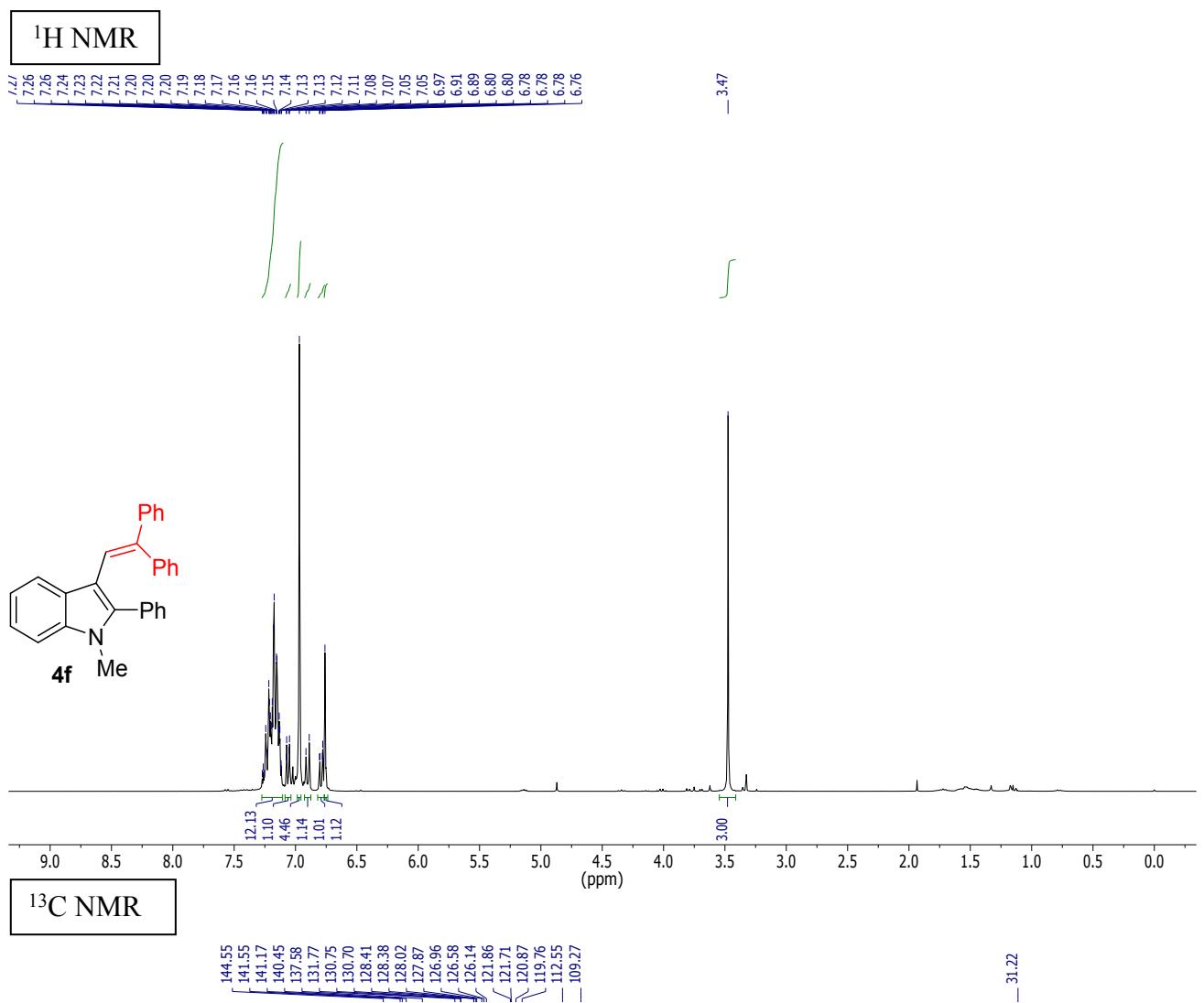


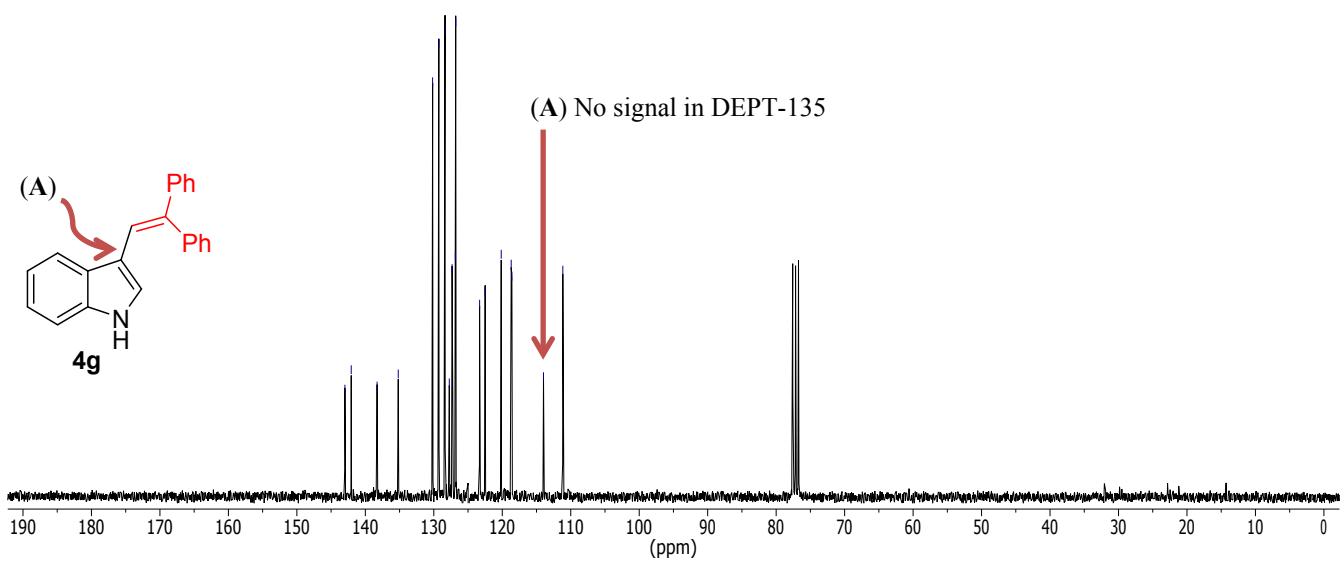
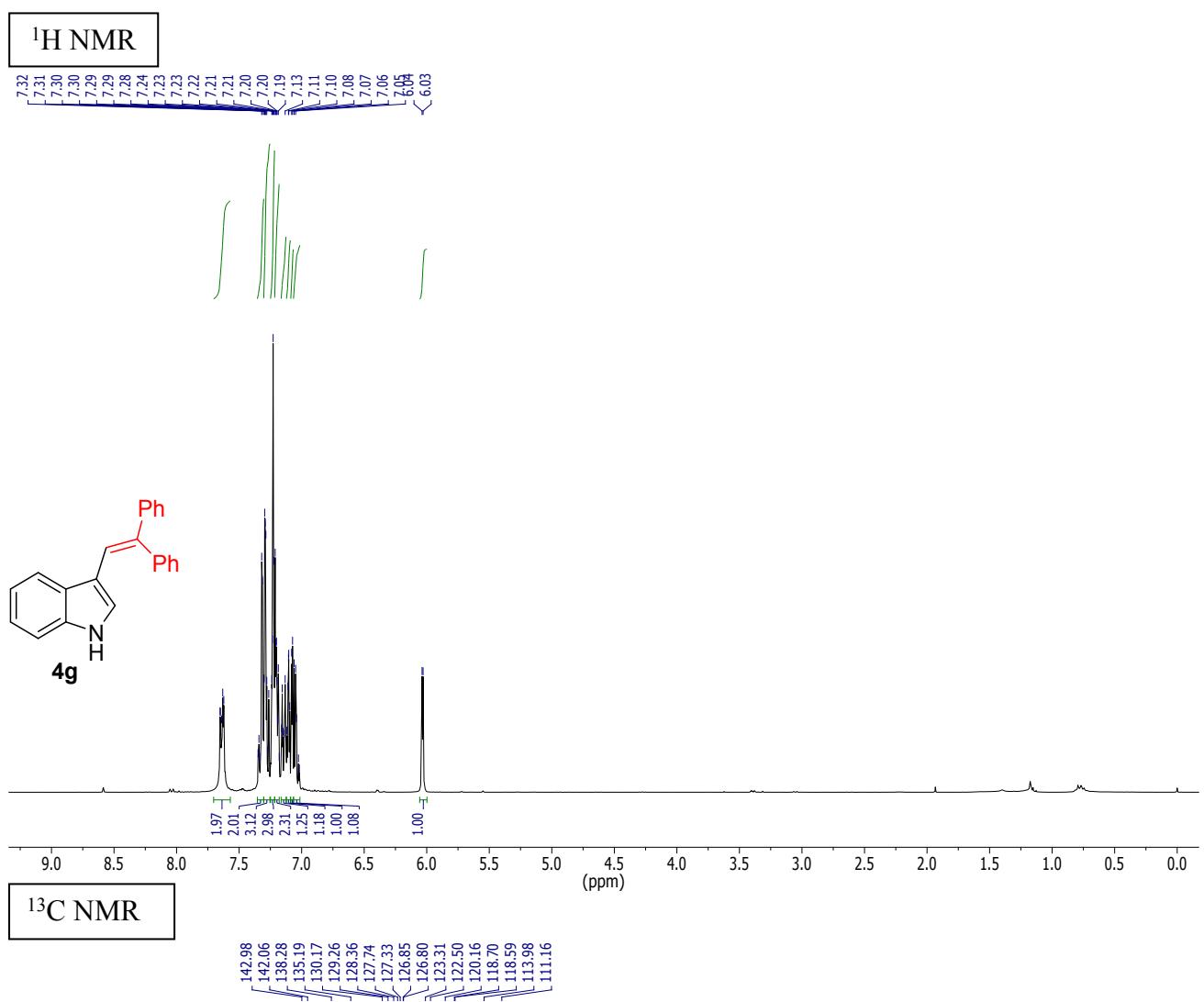
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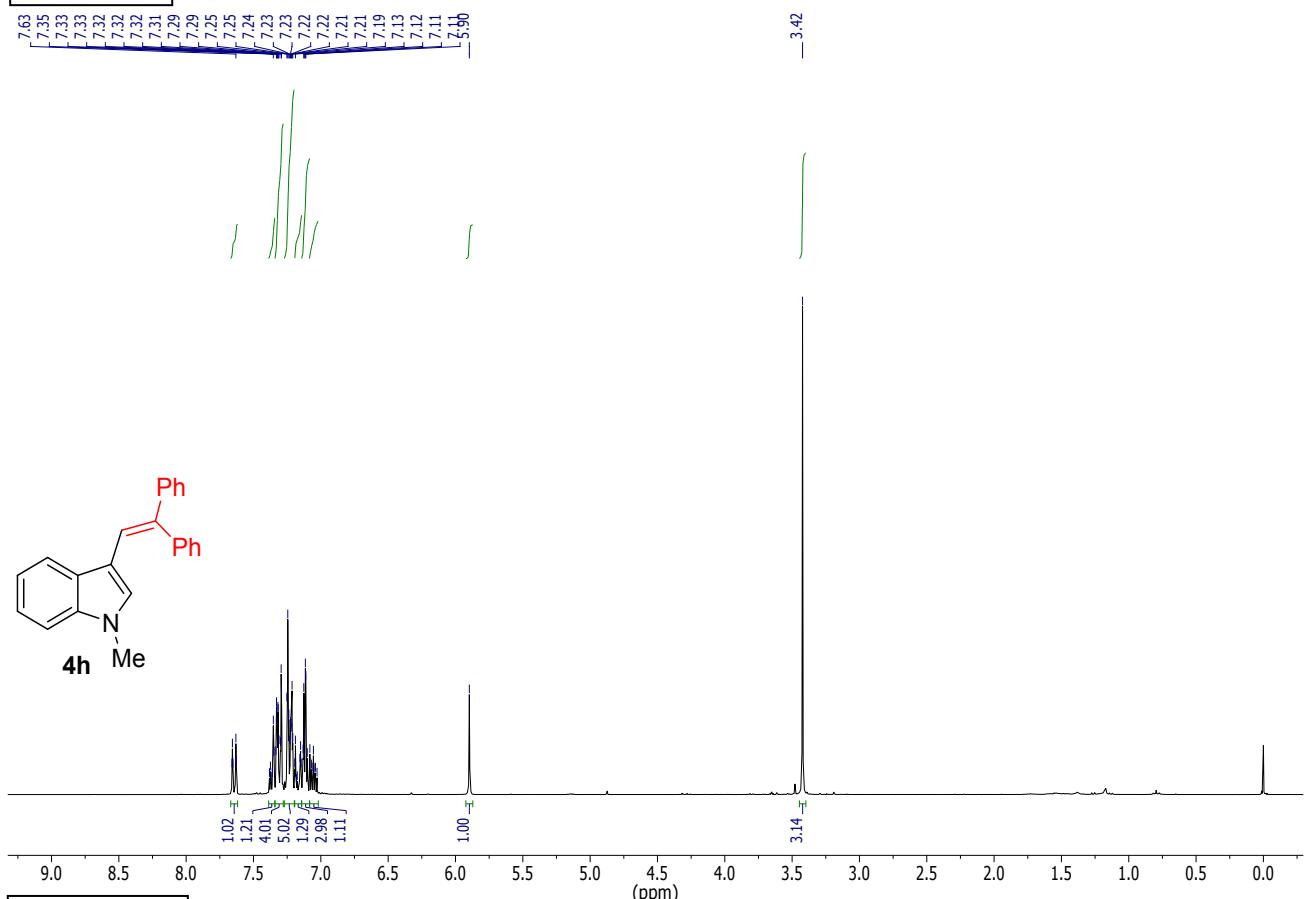








<sup>1</sup>H NMR



<sup>13</sup>C NMR



(A) No signal in DEPT-135

