

## Supporting Information

### **Electrochemical C3 Acyloxylation Reactions of 2*H*-Indazoles with Carboxylic Acids via C(sp<sup>2</sup>)-O Coupling**

Xin Liu, Yibin Hu, Yuanbin She, Meichao Li\* and Zhenlu Shen\*

*College of Chemical Engineering, Zhejiang University of Technology, Hangzhou  
310032, PR China*

*E-mail address: limc@zjut.edu.cn; zhenlushen@zjut.edu.cn*

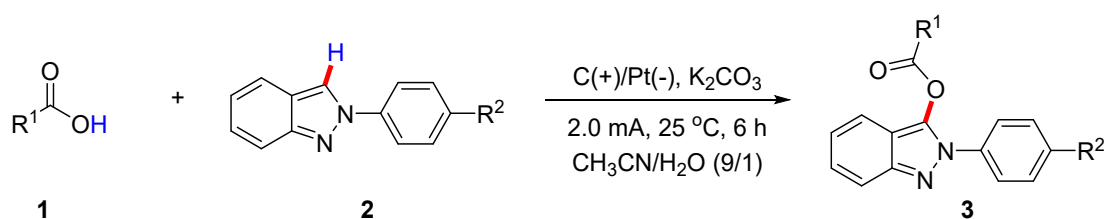
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## 1 General information

2*H*-indazoles were synthesized in our laboratory according to the literatures.<sup>1,2</sup> Unless specifically emphasized, chemicals and materials used in the experiments were purchased from suppliers and used directly without further purification. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (<sup>1</sup>H NMR) and 100 MHz (<sup>13</sup>C NMR) with CDCl<sub>3</sub> as the solvent using tetramethylsilane (TMS) as the internal standard. High resolution mass spectra (HRMS) were measured with an Agilent 6230 TOF instrument.

## 2 General procedure for electrochemical C3 acyloxylation of 2*H*-indazoles



Carboxylic acids (**1**, 0.2 mmol), 2*H*-indazoles (**2**, 0.4 mmol), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol) and CH<sub>3</sub>CN/H<sub>2</sub>O (10 mL, V/V = 9/1) were added to a 25 mL undivided three-necked flask with a stir bar. The three-necked flask was equipped with a carbon plate anode (2.25 cm<sup>2</sup>) and a platinum plate cathode (2.25 cm<sup>2</sup>). The reaction mixture was stirred and electrolyzed at a constant current of 2.0 mA at 25 °C for 6 h. After completion of the reaction, anhydrous sodium sulfate was added to the mixture to remove water. Then, the mixture was concentrated in vacuo and the residue was purified by column chromatography using petroleum ether/ethyl acetate as the eluent to afford a product.

## 3 Detail descriptions for products

### *2-Phenyl-2H-indazol-3-yl benzoate (3aa):*

White solid (48.8 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.19-8.17 (m, 2H), 7.77-

7.74 (m, 2H), 7.73-7.67 (m, 2H), 7.55-7.46 (m, 5H), 7.42-7.38 (m, 1H), 7.36-7.32 (m, 1H), 7.12-7.08 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.7, 148.0, 138.2, 136.8, 134.7, 130.7, 129.4, 129.0, 128.7, 127.4, 127.4, 124.4, 122.3, 119.3, 118.2, 111.9; HRMS m/z (ESI): calc. for C<sub>20</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 315.1128, found 315.1130.

***2-Phenyl-2H-indazol-3-yl 4-fluorobenzoate (3ba):***

White solid (41.5 mg, 63%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.22-8.18 (m, 2H), 7.74-7.70 (m, 3H), 7.54-7.47 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 8.6 Hz, 2H), 7.12-7.08 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.8 (*J* = 256.0 Hz), 161.8, 148.0, 138.1, 136.6, 133.5 (*J* = 9.0 Hz), 129.4, 128.8, 127.4, 124.4, 123.7 (*J* = 3.0 Hz), 122.5, 119.2, 118.3, 116.4 (*J* = 22.0 Hz), 111.9. HRMS m/z (ESI): calc. for C<sub>20</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 333.1034, found 333.1036.

***2-Phenyl-2H-indazol-3-yl 4-chlorobenzoate (3ca):***

White solid (45.2 mg, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.12-8.09 (m, 2H), 7.73-7.70 (m, 3H), 7.53-7.47 (m, 5H), 7.43-7.39 (m, 1H), 7.36-7.32 (m, 1H), 7.12-7.09 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.9, 148.0, 141.5, 138.1, 136.5, 132.1, 129.5, 129.5, 128.8, 127.5, 125.9, 124.4, 122.5, 119.2, 118.3, 111.9. HRMS m/z (ESI): calc. for C<sub>20</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 349.0738, found 349.0740.

***2-Phenyl-2H-indazol-3-yl 4-bromobenzoate (3da):***

White solid (51.6 mg, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.04-8.01 (m, 2H), 7.72-7.67 (m, 5H), 7.53-7.47 (m, 3H), 7.44-7.40 (m, 1H), 7.36-7.32 (m, 1H), 7.13-7.09 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.1, 148.1, 138.1, 136.5, 132.5, 132.1, 130.3, 129.5, 128.9, 127.5, 126.4, 124.4, 122.5, 119.2, 118.3, 111.9. HRMS m/z (ESI): calc. for C<sub>20</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 393.0233, found 393.0236.

***2-Phenyl-2H-indazol-3-yl 3-bromobenzoate (3ea):***

White solid (40.7 mg, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (t, *J* = 1.8 Hz, 1H),

8.11-8.08 (m, 1H), 7.82-7.80 (m, 1H), 7.74-7.70 (m, 3H), 7.53-7.47 (m, 3H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.13-7.09 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.5, 148.0, 138.1, 137.7, 136.4, 133.6, 130.6, 129.5, 129.4, 129.2, 128.9, 127.5, 124.5, 123.1, 122.6, 119.1, 118.3, 118.4. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{20}\text{H}_{14}\text{BrN}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 393.0233, found 393.0237.

***2-Phenyl-2H-indazol-3-yl 2-bromobenzoate (3fa):***

Light yellow solid (41.7 mg, 53%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95-7.92 (m, 1H), 7.77-7.70 (m, 4H), 7.59 (d,  $J = 8.6$  Hz, 1H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 3H), 7.37-7.32 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.9, 148.0, 138.1, 136.4, 135.1, 134.2, 132.2, 129.4, 129.3, 128.9, 127.6, 127.4, 124.7, 123.1, 122.5, 119.2, 118.3, 111.9. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{20}\text{H}_{14}\text{BrN}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 393.0233, found 393.0236.

***2-Phenyl-2H-indazol-3-yl 4-(tert-butyl)benzoate (3ga):***

White solid (46.0 mg, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12 (d,  $J = 8.5$  Hz, 2H), 7.78-7.76 (m, 2H), 7.71 (d,  $J = 8.9$  Hz, 1H), 7.57-7.47 (m, 5H), 7.44-7.39 (m, 1H), 7.35-7.31 (m, 1H), 7.11-7.07 (m, 1H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.7, 158.8, 148.1, 138.3, 137.0, 130.7, 129.4, 128.7, 127.4, 126.1, 124.7, 124.4, 122.3, 119.4, 118.2, 112.0, 35.5, 31.1. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 371.1754, found 371.1756.

***2-Phenyl-2H-indazol-3-yl 4-methylbenzoate (3ha):***

White solid (41.6 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07 (d,  $J = 8.2$  Hz, 2H), 7.76-7.73 (m, 2H), 7.70 (d,  $J = 8.9$  Hz, 1H), 7.53 (d,  $J = 8.5$  Hz, 1H), 7.50-7.45 (m, 2H), 7.42-7.38 (m, 1H), 7.35-7.31 (m, 3H), 7.11-7.07 (m, 1H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.8, 148.1, 145.9, 138.3, 137.0, 130.8, 129.8, 129.4, 128.7, 127.4, 124.7, 124.4, 122.3, 119.4, 118.3, 112.0, 22.0. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{21}\text{H}_{17}\text{N}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 329.1285, found 329.1286.

***2-Phenyl-2H-indazol-3-yl 3-methylbenzoate (3ia):***

White solid (37.2 mg, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* = 6.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.54-7.47 (m, 4H), 7.44-7.39 (m, 2H), 7.35-7.31 (m, 1H), 7.11-7.08 (m, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.0, 148.1, 139.0, 138.3, 137.0, 135.6, 131.3, 129.4, 129.0, 128.7, 127.9, 127.4, 127.4, 124.4, 122.3, 119.3, 118.3, 112.0, 21.4. HRMS *m/z* (ESI): calc. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 329.1285, found 329.1284.

***2-Phenyl-2H-indazol-3-yl 2-methylbenzoate (3ja):***

White solid (39.5 mg, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.15 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.55-7.47 (m, 4H), 7.44-7.40 (m, 1H), 7.36-7.32 (m, 3H), 7.12-7.09 (m, 1H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.9, 148.1, 142.6, 138.3, 137.0, 133.9, 132.4, 131.6, 129.4, 128.8, 127.4, 126.4, 126.4, 124.6, 122.3, 119.2, 118.3, 112.1, 22.0. HRMS *m/z* (ESI): calc. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 329.1285, found 329.1283.

***2-Phenyl-2H-indazol-3-yl 2,4,6-trimethoxybenzoate (3ka):***

White solid (45.3 mg, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.52-7.45 (m, 3H), 7.38-7.35 (m, 1H), 7.17-7.14 (m, 1H), 6.91 (s, 2H), 2.32 (s, 3H), 2.28 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.9, 148.0, 141.1, 138.1, 136.9, 136.4, 129.3, 129.0, 129.0, 127.8, 127.2, 125.3, 122.4, 118.9, 118.3, 111.8, 21.2, 20.1. HRMS *m/z* (ESI): calc. for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub> ([M+H<sup>+</sup>]) 405.1455, found 405.1458.

***2-Phenyl-2H-indazol-3-yl 1-naphthoate (3la):***

Light yellow solid (27.2 mg, 37%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.94 (d, *J* = 8.6 Hz, 1H), 8.50-8.48 (m, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.96-7.93 (m, 1H), 7.80-7.78 (m, 2H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.67-7.63 (m, 1H), 7.61-7.56 (m, 3H), 7.50-7.47 (m, 2H), 7.43-

7.34 (m, 2H), 7.15-7.11 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.9, 148.2, 138.4, 137.1, 135.7, 134.1, 132.3, 132.0, 129.5, 129.0, 129.0, 128.8, 127.4, 127.0, 125.6, 124.7, 124.6, 123.5, 122.4, 119.3, 118.4, 112.2. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{24}\text{H}_{17}\text{N}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 365.1285, found 365.1287.

***2-Phenyl-2H-indazol-3-yl [1,1'-biphenyl]-2-carboxylate (3ma):***

Light yellow liquid (42.1 mg, 54%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 7.7$  Hz, 1H), 7.68 (d,  $J = 9.1$  Hz, 1H), 7.63 (d,  $J = 7.8$  Hz, 3H), 7.53-7.43 (m, 5H), 7.39-7.35 (m, 4H), 7.33-7.29 (m, 3H), 7.09-7.05 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.9, 147.9, 144.1, 140.5, 138.2, 136.6, 132.9, 131.5, 130.7, 129.3, 128.7, 128.5, 128.3, 127.8, 127.7, 127.5, 127.2, 124.6, 122.1, 119.1, 118.1, 111.7. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{26}\text{H}_{19}\text{N}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 391.1441, found 391.1445.

***2-Phenyl-2H-indazol-3-yl 2-benzylbenzoate (3na):***

White solid (47.0 mg, 58%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.14 (d,  $J = 7.8$  Hz, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.66 (d,  $J = 7.2$  Hz, 2H), 7.60-7.56 (m, 1H), 7.48-7.38 (m, 4H), 7.37-7.29 (m, 3H), 7.28 (s, 1H), 7.24-7.21 (m, 2H), 7.12 (d,  $J = 7.0$  Hz, 2H), 7.08-7.04 (m, 1H), 4.44 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.9, 148.0, 144.5, 140.3, 138.2, 136.8, 133.9, 132.4, 131.8, 129.4, 129.0, 128.7, 128.6, 127.3, 126.9, 126.6, 126.3, 124.5, 122.2, 119.2, 118.2, 112.0, 39.8. HRMS  $m/z$  (ESI): calc. for  $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}_2$  ( $[\text{M}+\text{H}^+]$ ) 405.1598, found 405.1598.

***2-Phenyl-2H-indazol-3-yl 2-phenethylbenzoate (3oa):***

White solid (54.2 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 (d,  $J = 7.8$  Hz, 1H), 7.81-7.77 (m, 3H), 7.59 (d,  $J = 8.5$  Hz, 1H), 7.57-7.53 (m, 1H), 7.50 (t,  $J = 7.7$  Hz, 2H), 7.43-7.36 (m, 3H), 7.31-7.26 (m, 3H), 7.22-7.13 (m, 4H), 3.31-3.27 (m, 2H), 2.85-2.81 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.8, 148.0, 146.0, 141.5, 138.2, 136.9, 133.9, 131.9, 131.7, 129.3, 128.7, 128.6, 128.4, 127.3, 126.6, 126.0, 126.0, 124.5,

122.3, 119.0, 118.3, 112.1, 37.8, 37.0. HRMS m/z (ESI): calc. for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 419.1754, found 419.1758.

***2-Phenyl-2H-indazol-3-yl 2-benzoylbenzoate (3pa):***

Light yellow liquid (54.0 mg, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.91-7.88 (m, 2H), 7.87-7.84 (m, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 4H), 7.32-7.27 (m, 3H), 7.19-7.11 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.99-6.95 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.0, 167.4, 151.6, 146.7, 140.1, 137.4, 133.1, 132.6, 130.3, 130.3, 129.7, 128.6, 126.7, 126.3, 125.6, 125.4, 125.1, 125.0, 124.9, 122.1, 116.7, 101.2. HRMS m/z (ESI): calc. for C<sub>27</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> ([M+H<sup>+</sup>]) 419.1390, found 419.1397.

***2-Phenyl-2H-indazol-3-yl thiophene-3-carboxylate (3qa):***

White solid (25.8 mg, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.35 (d, *J* = 2.4 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.43-7.40 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.12-7.08 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.2, 148.0, 138.2, 136.6, 135.9, 130.5, 129.4, 128.7, 128.3, 127.4, 127.2, 124.4, 122.3, 119.3, 118.2, 111.9. HRMS m/z (ESI): calc. for C<sub>18</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>S ([M+H<sup>+</sup>]) 321.0692, found 321.0692.

***2-Phenyl-2H-indazol-3-yl 3-methylbenzofuran-2-carboxylate (3ra):***

White solid (28.0 mg, 38%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84-7.81 (m, 2H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.39-7.33 (m, 2H), 7.14-7.10 (m, 1H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.1, 155.2, 148.0, 138.4, 138.2, 136.1, 130.3, 129.4, 129.3, 128.8, 128.8, 127.4, 124.5, 123.8, 122.5, 121.6, 119.3, 118.3, 112.5, 112.0, 9.8. HRMS m/z (ESI): calc. for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> ([M+H<sup>+</sup>]) 369.1234, found 369.1237.



***2-Phenyl-2H-indazol-3-yl 1-phenylcyclopropane-1-carboxylate (3sa):***

Light yellow solid (38.4 mg, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66 (d, *J* = 8.8 Hz, 1H), 7.51-7.44 (m, 6H), 7.43-7.34 (m, 5H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 1.77-1.74 (m, 2H), 1.43-1.40 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.7, 147.8, 138.0, 137.8, 136.9, 130.7, 129.2, 128.5, 128.4, 128.0, 127.2, 124.3, 122.0, 119.3, 118.1, 111.5, 29.0, 18.2. HRMS *m/z* (ESI): calc. for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 355.1441, found 355.1442.

***2-Phenyl-2H-indazol-3-yl 3-phenylpropanoate (3ta):***

Light yellow solid (15.7 mg, 23%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66 (d, *J* = 9.0 Hz, 1H), 7.63-7.61 (m, 2H), 7.50-7.43 (m, 3H), 7.35-7.27 (m, 5H), 7.22-7.20 (m, 2H), 7.07-7.04 (m, 1H), 3.06-3.02 (m, 2H), 2.97-2.93 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.0, 147.9, 139.5, 138.1, 136.6, 129.4, 128.9, 128.8, 128.4, 127.4, 126.9, 124.5, 122.3, 119.0, 118.2, 111.8, 35.49, 30.68. HRMS *m/z* (ESI): calc. for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 343.1441, found 343.1443.

***2-(4-fluorophenyl)-2H-indazol-3-yl benzoate (3ab):***

White solid (36.6 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.18 (d, *J* = 7.3 Hz, 2H), 7.75-7.69 (m, 4H), 7.54 (t, *J* = 8.8 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 8.5 Hz, 2H), 7.12-7.09 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.7, 162.5 (d, *J* = 248.0 Hz), 148.1, 136.9, 134.9, 134.3 (d, *J* = 3.0 Hz), 130.7, 129.1, 127.5, 127.4, 126.3 (d, *J* = 8.0 Hz), 122.5, 119.2, 118.2, 116.4 (d, *J* = 23.0 Hz), 111.9. HRMS *m/z* (ESI): calc. for C<sub>20</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 333.1034, found 333.1036.

***2-(4-chlorophenyl)-2H-indazol-3-yl benzoate (3ac):***

White solid (36.3 mg, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.74-7.68 (m, 4H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.47-7.44 (m, 2H), 7.36-7.32 (m, 1H), 7.12-7.08 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.7, 148.2,

136.8, 135.0, 134.6, 130.8, 129.7, 129.2, 127.7, 127.4, 125.5, 122.6, 119.3, 118.3, 112.1. HRMS m/z (ESI): calc. for C<sub>20</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 349.0738, found 349.0737.

***2-(4-bromophenyl)-2H-indazol-3-yl benzoate (3ad):***

White solid (39.2 mg, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.74-7.64 (m, 4H), 7.62-7.54 (m, 4H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.36-7.32 (m, 1H), 7.12-7.08 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.7, 148.3, 137.3, 136.9, 135.0, 132.6, 130.8, 129.2, 127.7, 127.3, 125.8, 122.6, 119.3, 118.3, 112.1. HRMS m/z (ESI): calc. for C<sub>20</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 393.0233, found 393.0232.

***2-(p-tolyl)-2H-indazol-3-yl benzoate (3ae):***

White solid (42.0 mg, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.20-8.18 (m, 2H), 7.72-7.67 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.56-7.52 (m, 3H), 7.35-7.31 (m, 1H), 7.28-7.26 (m, 2H), 7.11-7.07 (m, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.8, 147.9, 138.8, 136.7, 135.8, 134.7, 130.8, 130.0, 129.1, 127.6, 127.3, 124.2, 122.2, 119.2, 118.2, 112.0, 21.3. HRMS m/z (ESI): calc. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> ([M+H<sup>+</sup>]) 329.1285, found 329.1285.

***2-(4-methoxyphenyl)-2H-indazol-3-yl benzoate (3af):***

White solid (45.5 mg, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.20 (d, *J* = 7.2 Hz, 2H), 7.73-7.65 (m, 4H), 7.58-7.54 (m, 3H), 7.37-7.33 (m, 1H), 7.13-7.10 (m, 1H), 7.02-6.98 (m, 2H), 3.85 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.8, 159.8, 147.8, 136.7, 134.7, 131.2, 130.8, 129.1, 127.6, 127.2, 125.8, 122.2, 119.2, 118.1, 114.5, 111.8, 55.6. HRMS m/z (ESI): calc. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> ([M+H<sup>+</sup>]) 345.1234, found 345.1237.

***ethyl 4-(3-(benzoyloxy)-2H-indazol-2-yl)benzoate (3ag):***

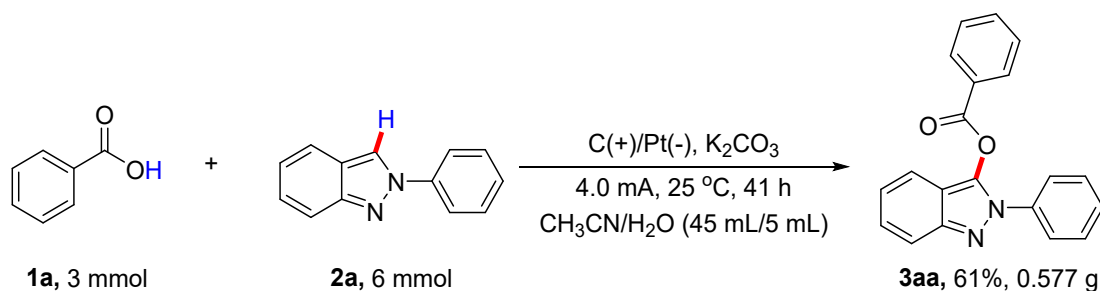
White solid (30.6 mg, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21-8.19 (m, 2H), 8.18-8.15 (m, 2H), 7.89-7.87 (m, 2H), 7.74-7.69 (m, 2H), 7.58-7.51 (m, 3H), 7.36-7.32 (m, 1H), 7.12-7.08 (m, 1H), 4.41-4.36 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>):  $\delta$  165.8, 162.6, 148.5, 141.8, 137.1, 135.0, 130.9, 130.8, 130.4, 129.2, 127.9, 127.3, 123.8, 122.8, 119.4, 118.4, 112.3, 61.5, 14.4. HRMS m/z (ESI): calc. for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> ([M+H<sup>+</sup>]) 387.1339, found 387.1338.

#### 4 Procedure for cyclic voltammetry

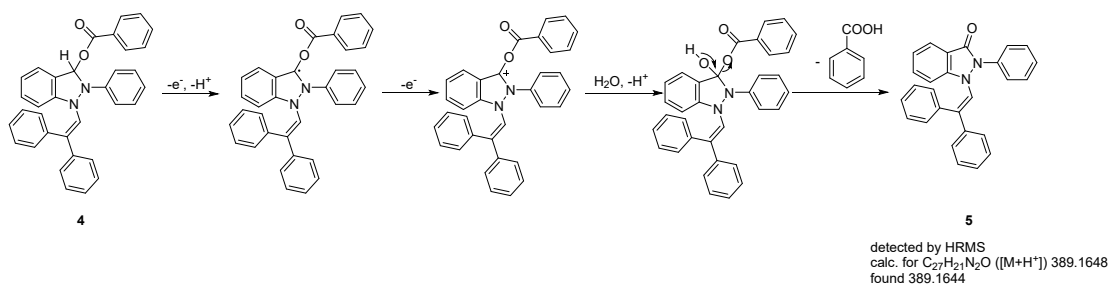
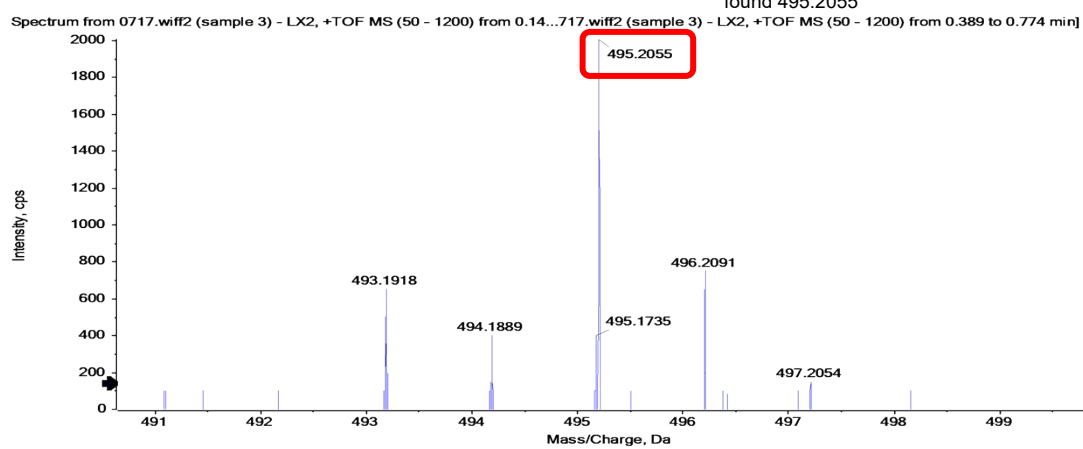
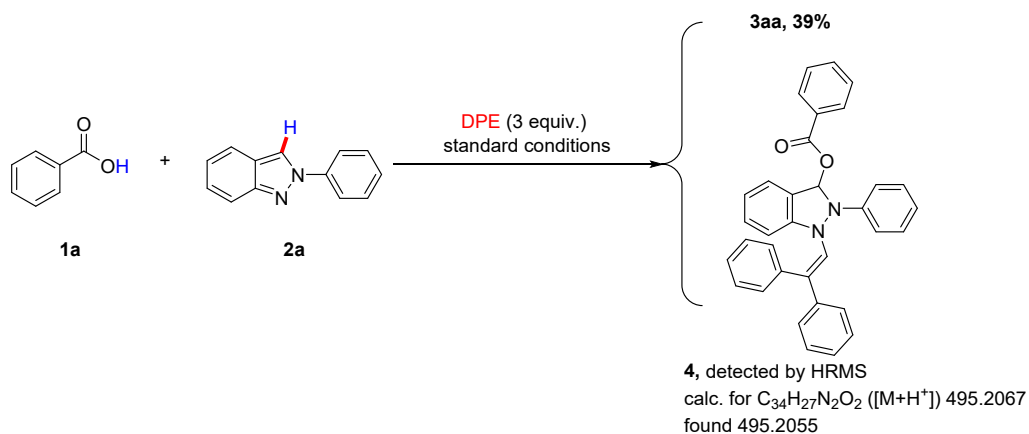
Cyclic voltammetry experiments were carried out in a 25 mL undivided cell at room temperature on a CHI600e workstation. The total amount of solvent was 10 mL, including 9 mL CH<sub>3</sub>CN and 1 mL H<sub>2</sub>O. The working electrode was an L-type glassy carbon (diameter, 3.0 mm) while the counter electrode was a platinum plate (2.25 cm<sup>2</sup>). In addition, an Ag/Ag<sup>+</sup> (0.1 mol/L AgNO<sub>3</sub> in CH<sub>3</sub>CN) was used as the reference electrode.

#### 5 Gram scale synthesis

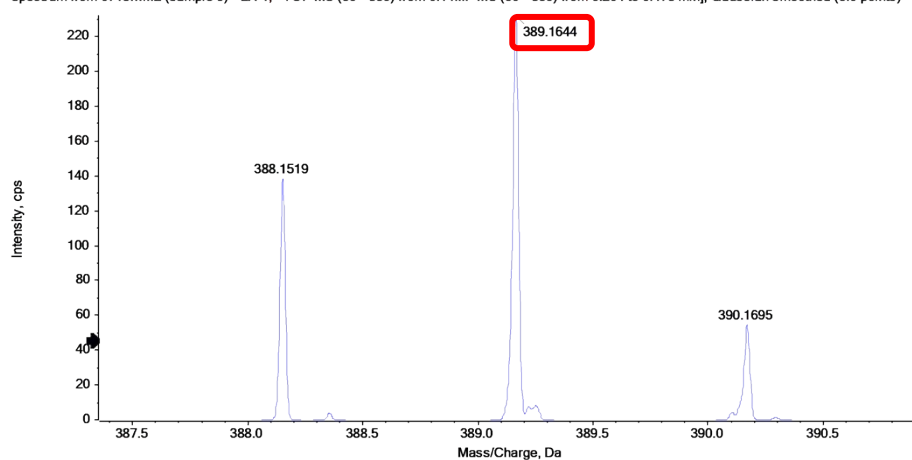


Benzoic acid (**1a**, 3 mmol), 2-phenyl-2H-indazole (**2a**, 6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol) and CH<sub>3</sub>CN/H<sub>2</sub>O (50 mL, V/V = 45/5) were added to a 50 mL undivided cell with a stir bar. The cell was equipped with a carbon plate anode (4.5 cm<sup>2</sup>) and a platinum plate cathode (4.5 cm<sup>2</sup>). The reaction mixture was stirred and electrolyzed at a constant current of 4.0 mA at 25 °C for 41 h. After completion of the reaction, anhydrous sodium sulfate was added to the mixture to remove water. Then, the mixture was concentrated in vacuo and the residue was purified by column chromatography using petroleum ether/ethyl acetate as the eluent to afford a product.

## 6 HRMS of DPE-trapped compound 4 and its corresponding oxidation product 5



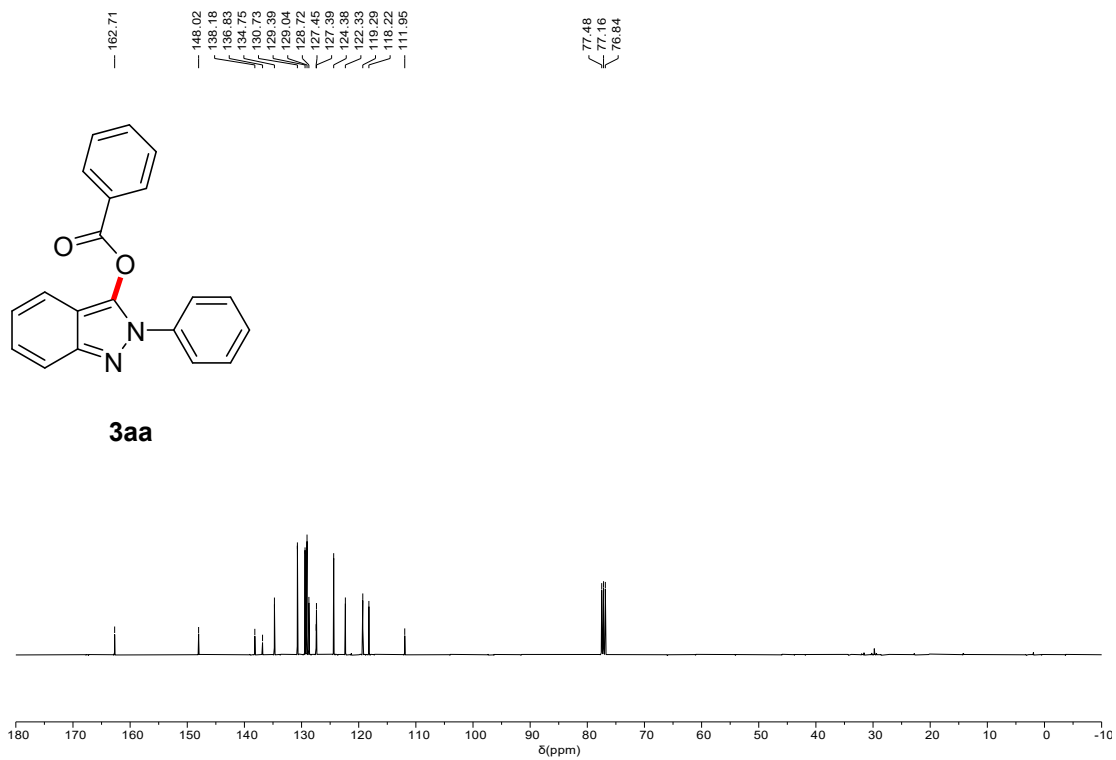
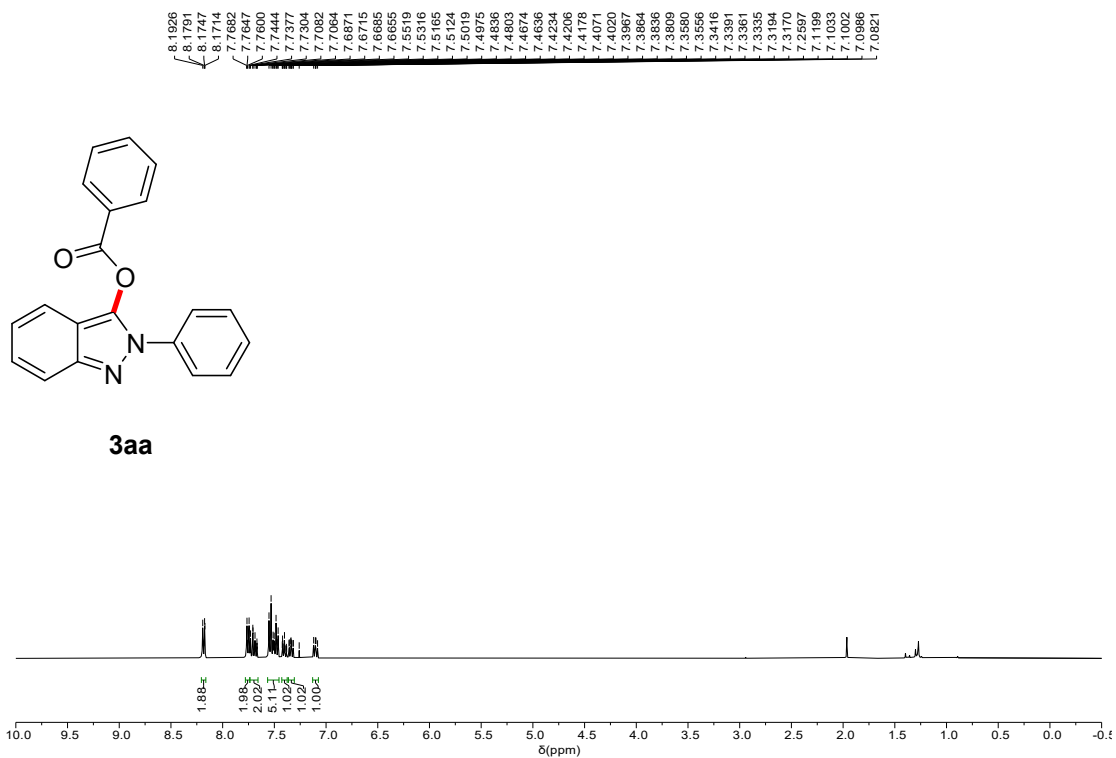
Spectrum from 0718.wiff2 (sample 5) - LX-1, +TOF MS (50 - 850) from 0.14...F MS (50 - 850) from 0.264 to 0.478 min], Gaussian smoothed (5.0 points)

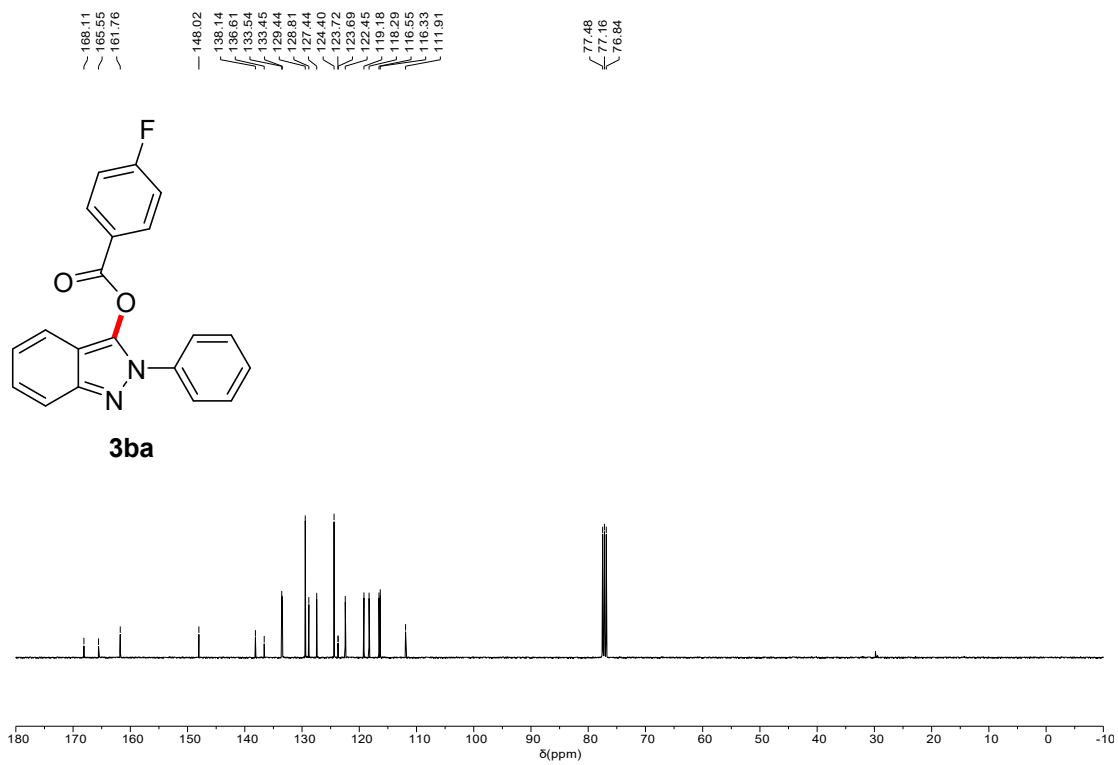
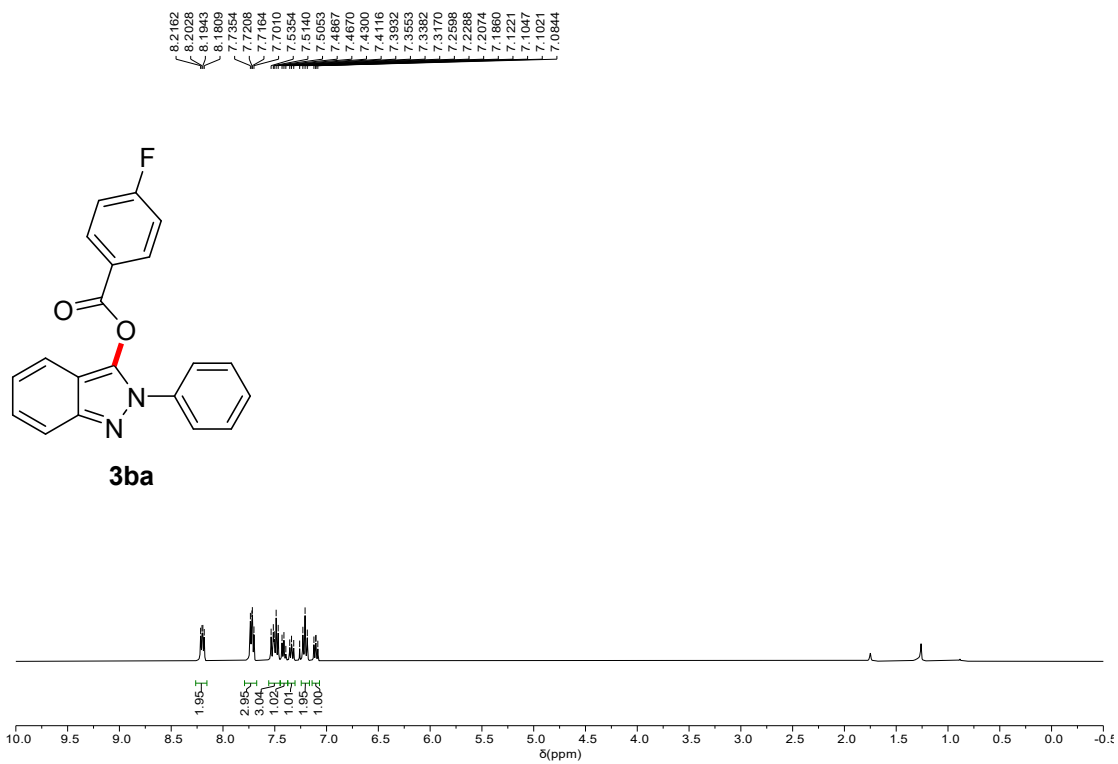


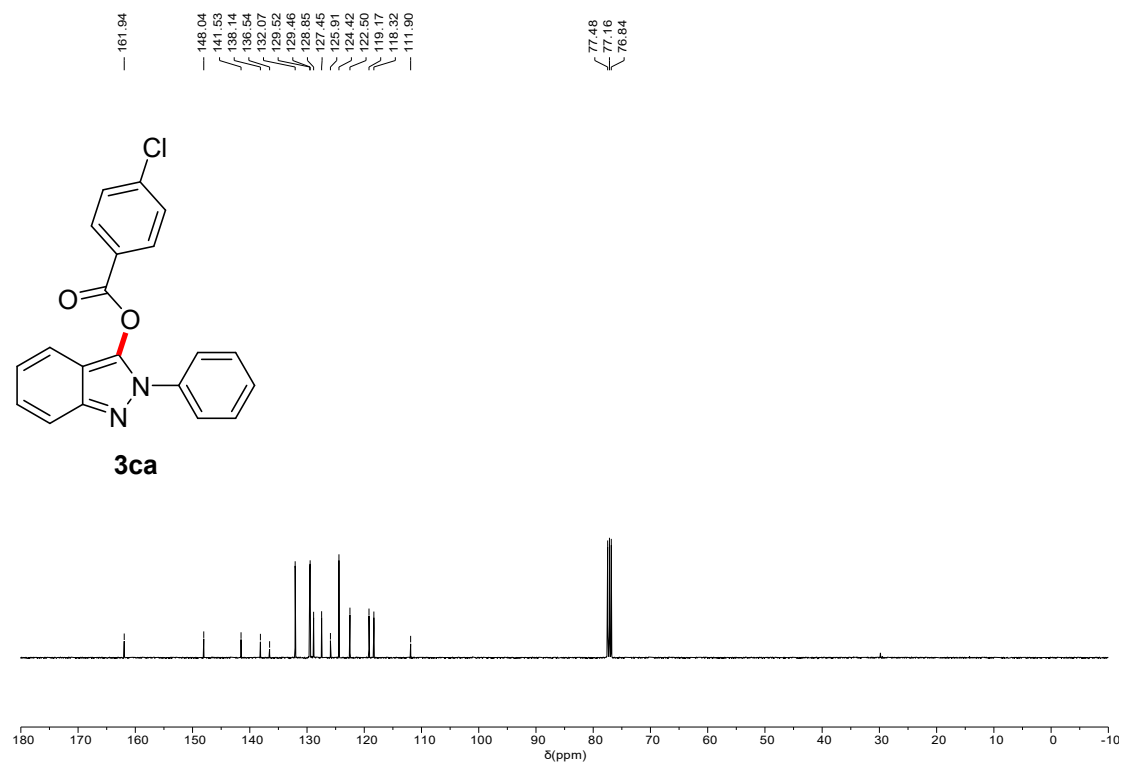
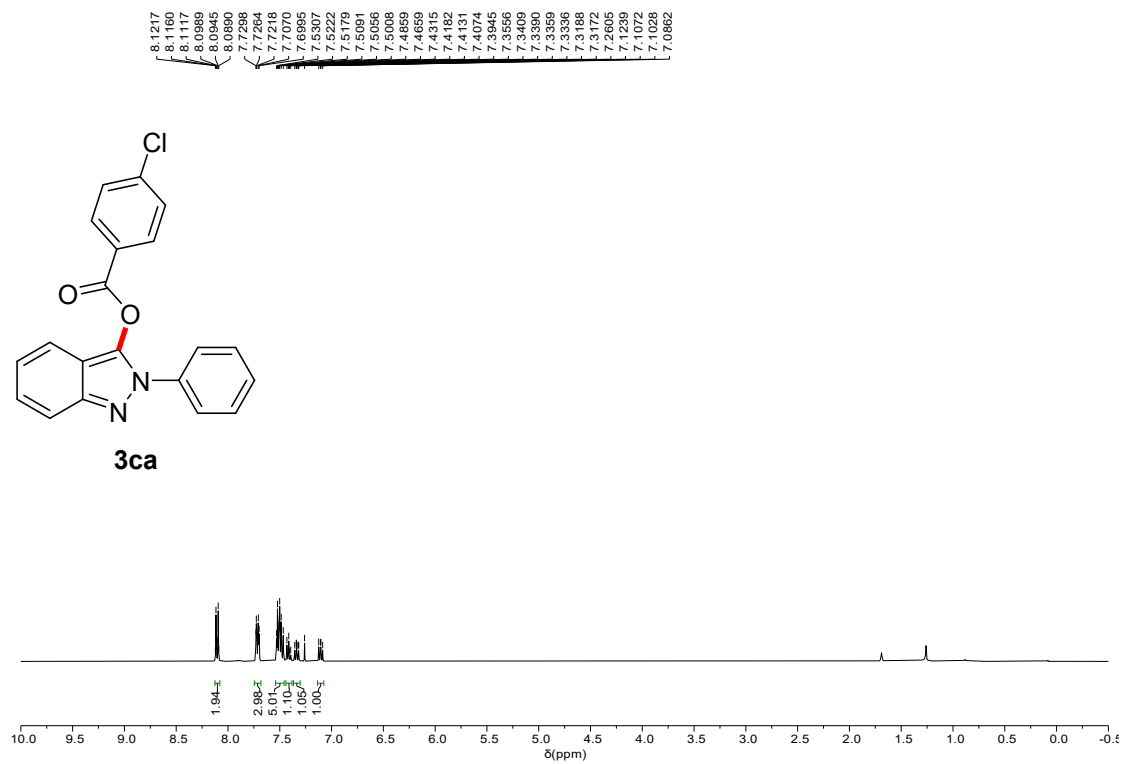
## 7 References

1. M. Kondo, S. Takizawa, Y. Z. Jiang and H. Sasai, *Chem. Eur. J.*, 2019, **25**, 9866-9869.
2. M. R. Kumar, A. Park, N. Park and S. Lee, *Org. Lett.*, 2011, **13**, 3542-3545.

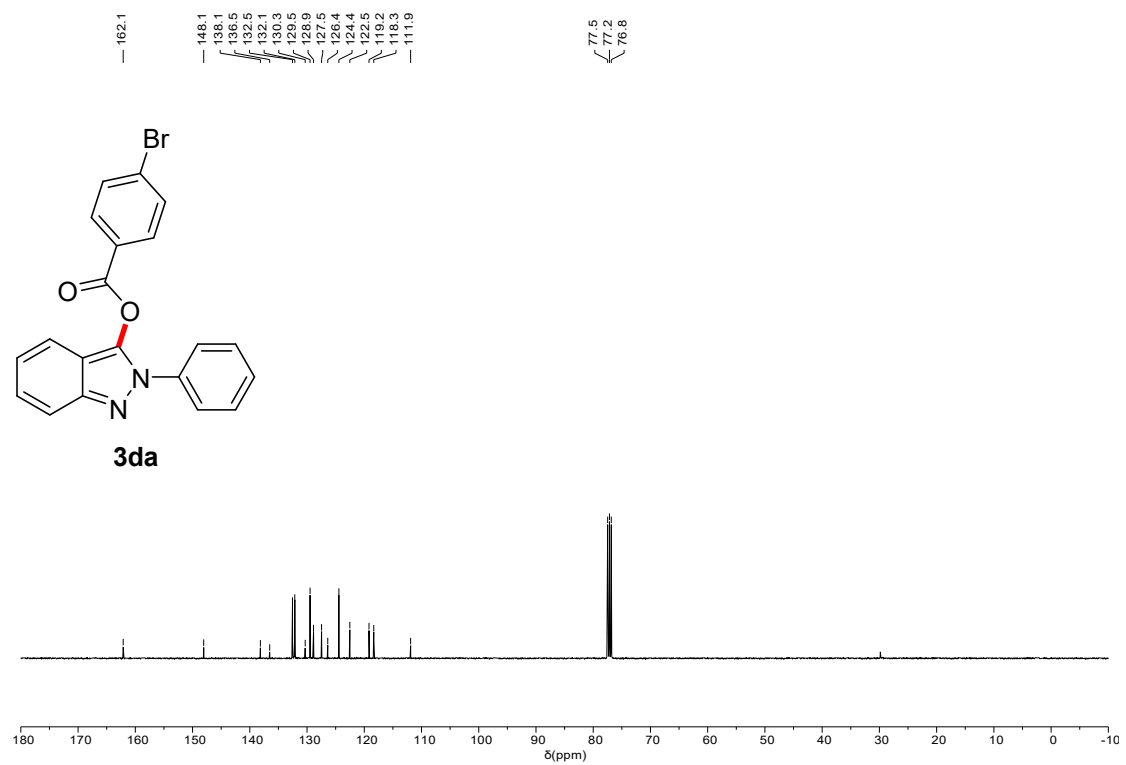
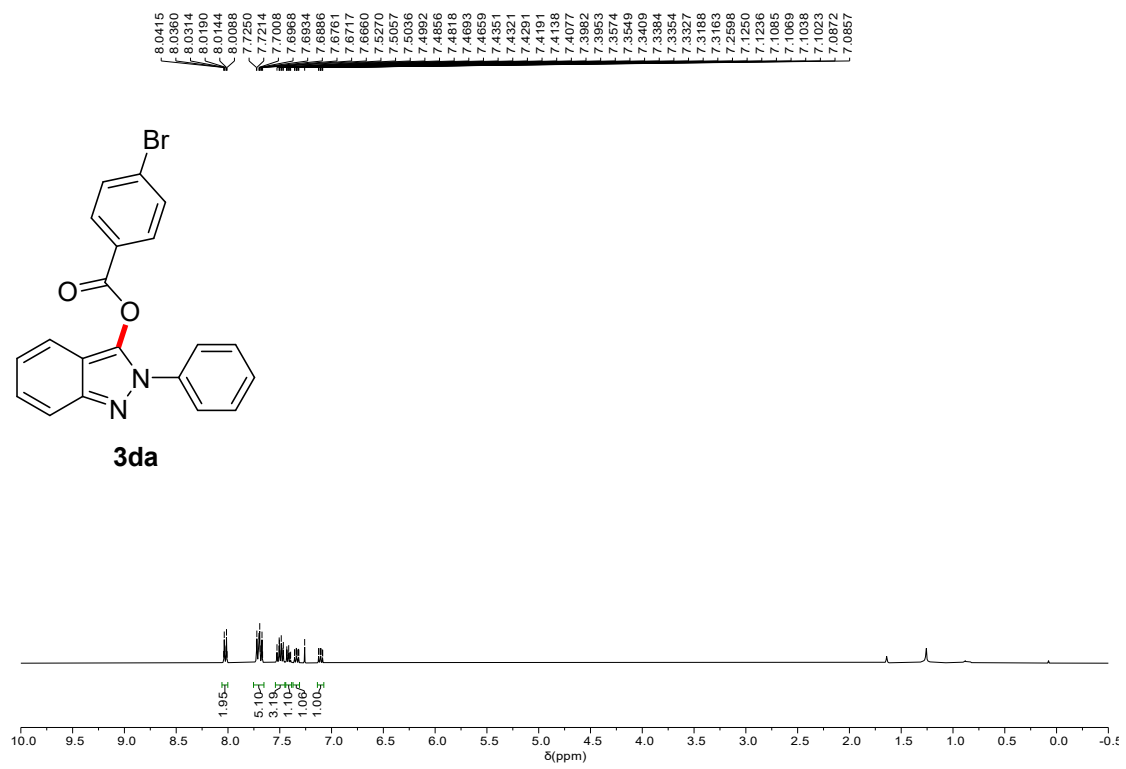
## 8 NMR spectra of prepared compounds



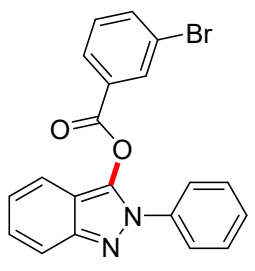




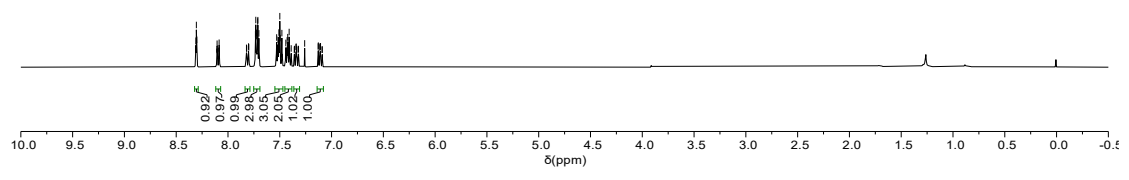




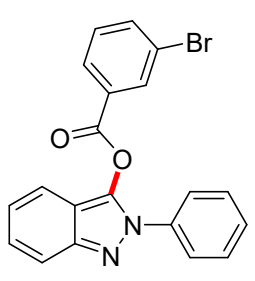
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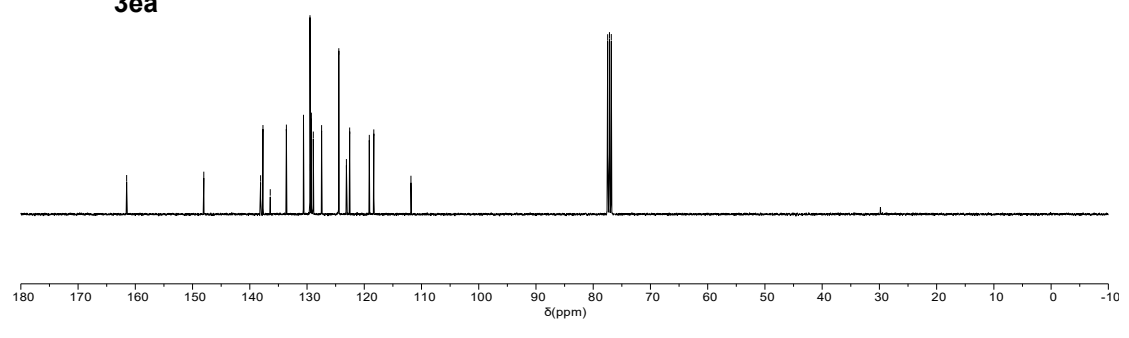
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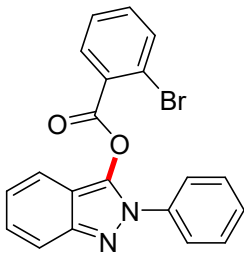
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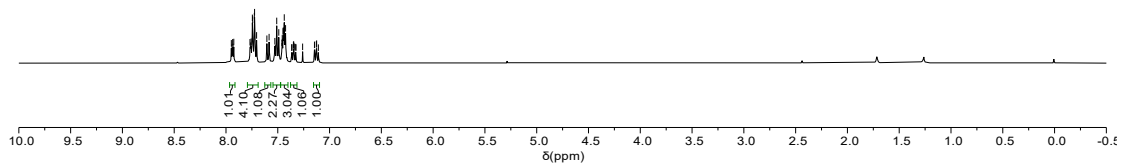
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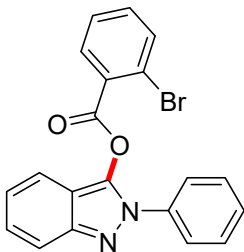
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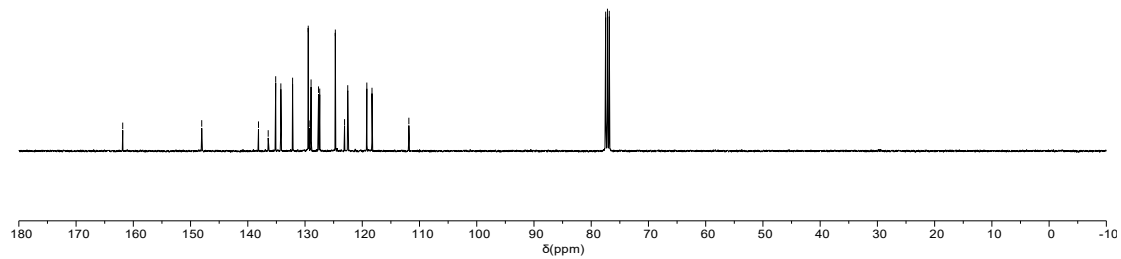
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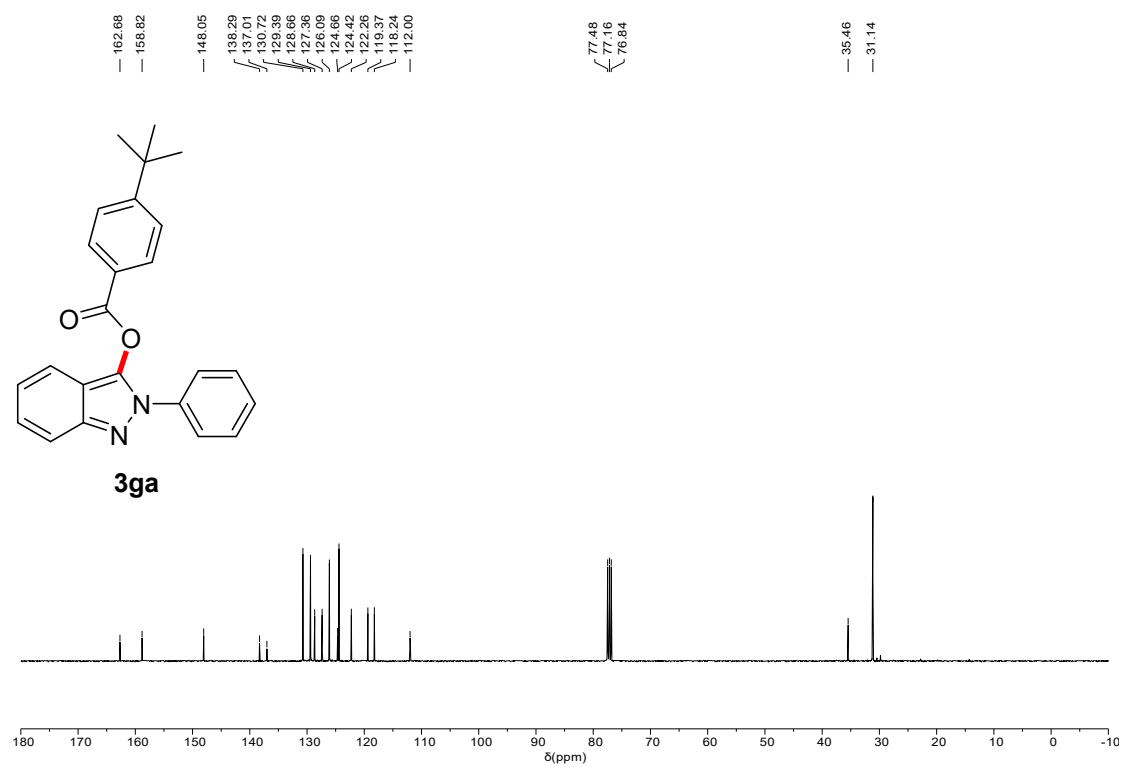
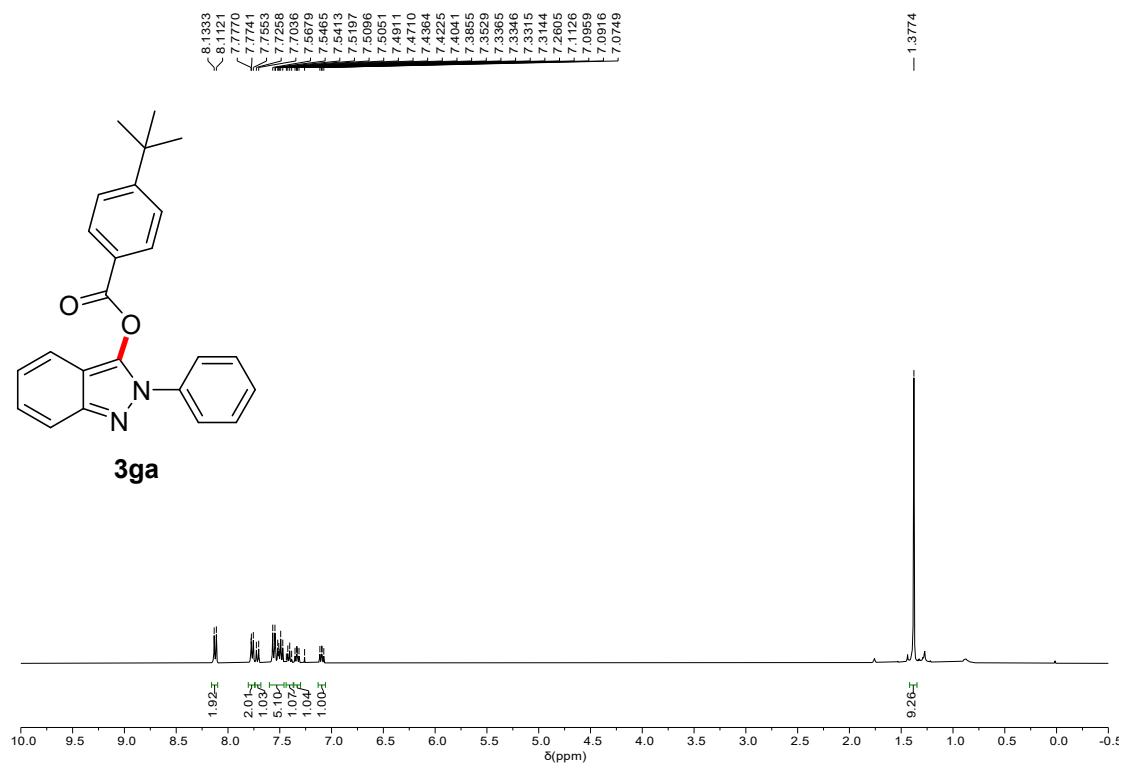


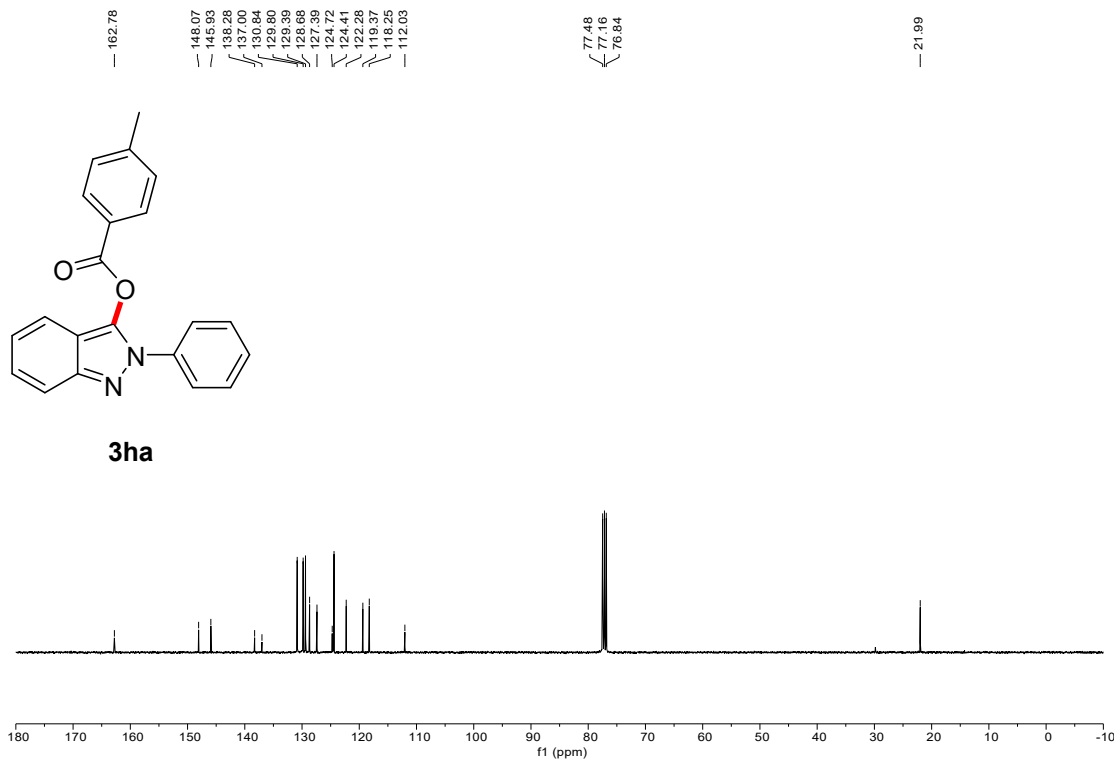
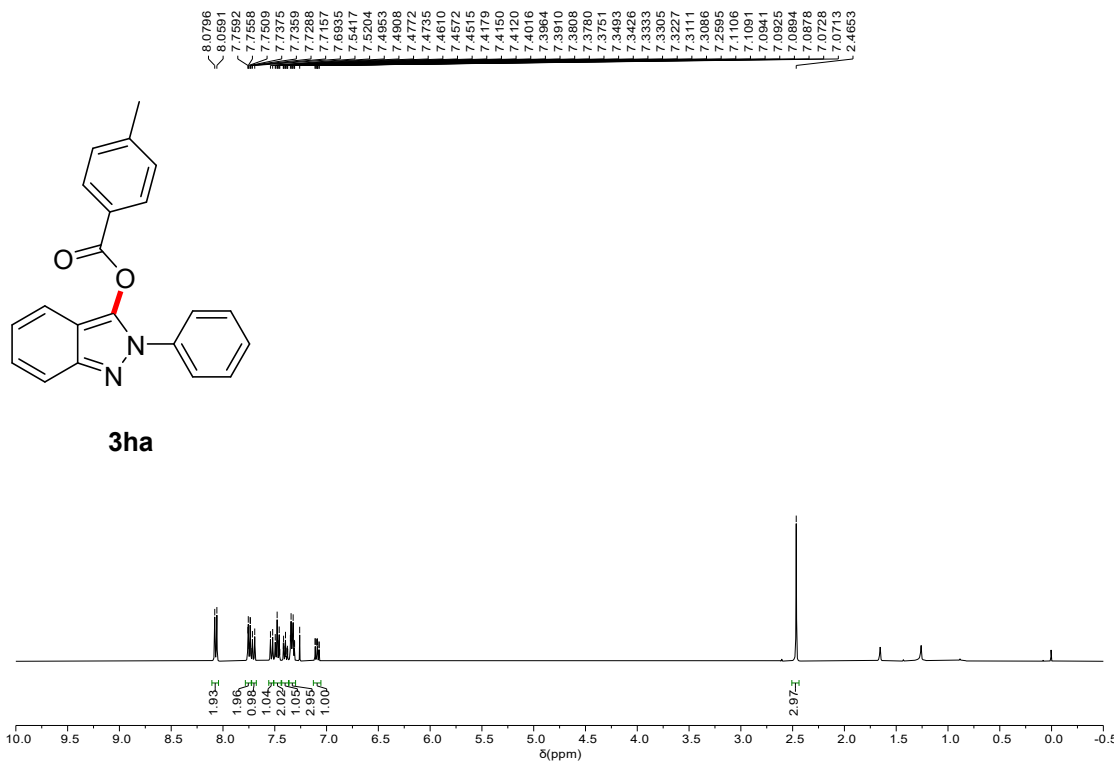
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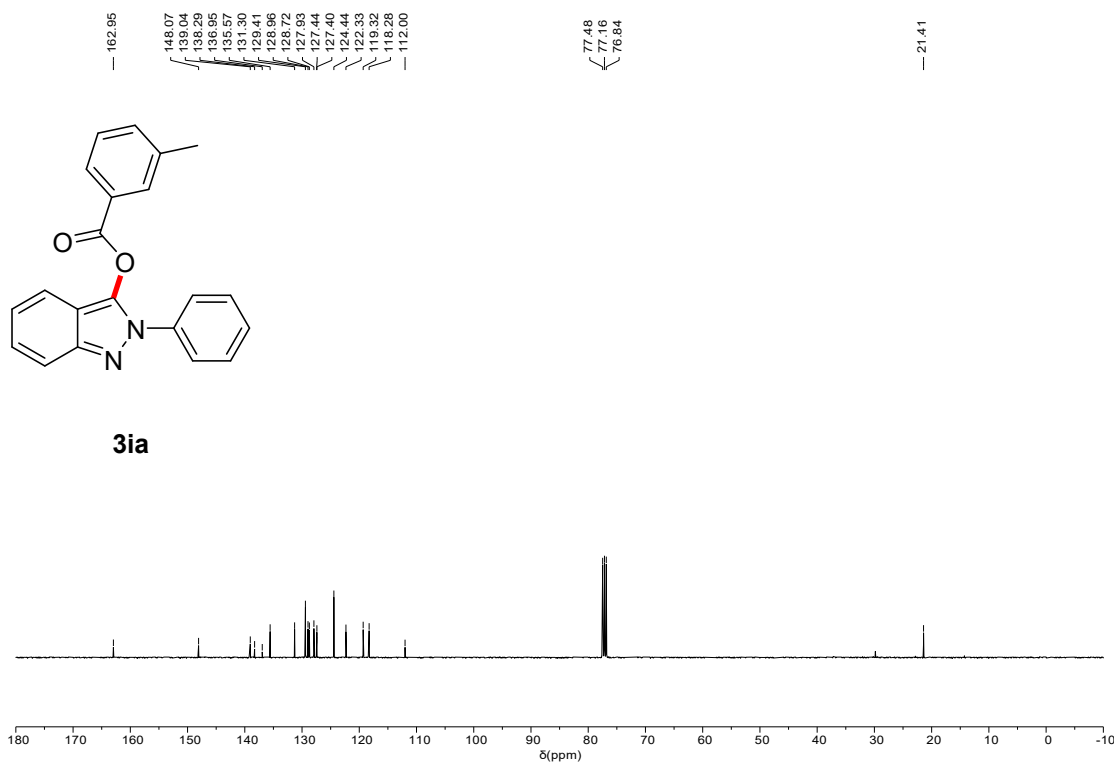
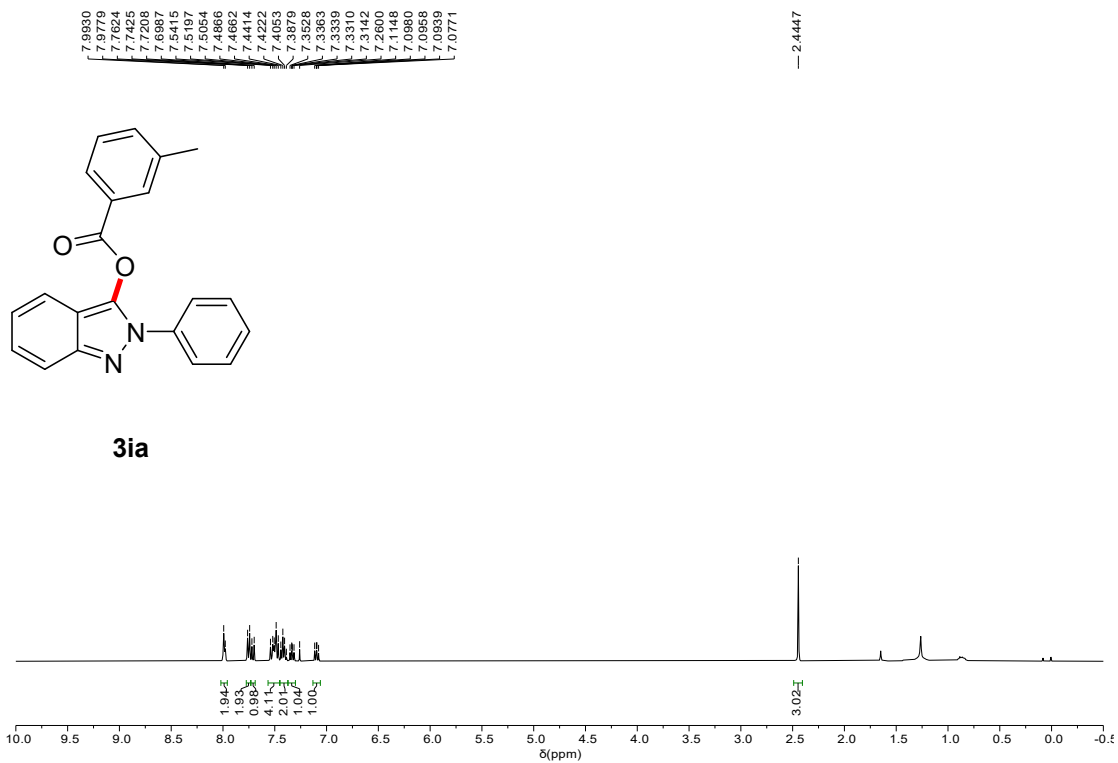


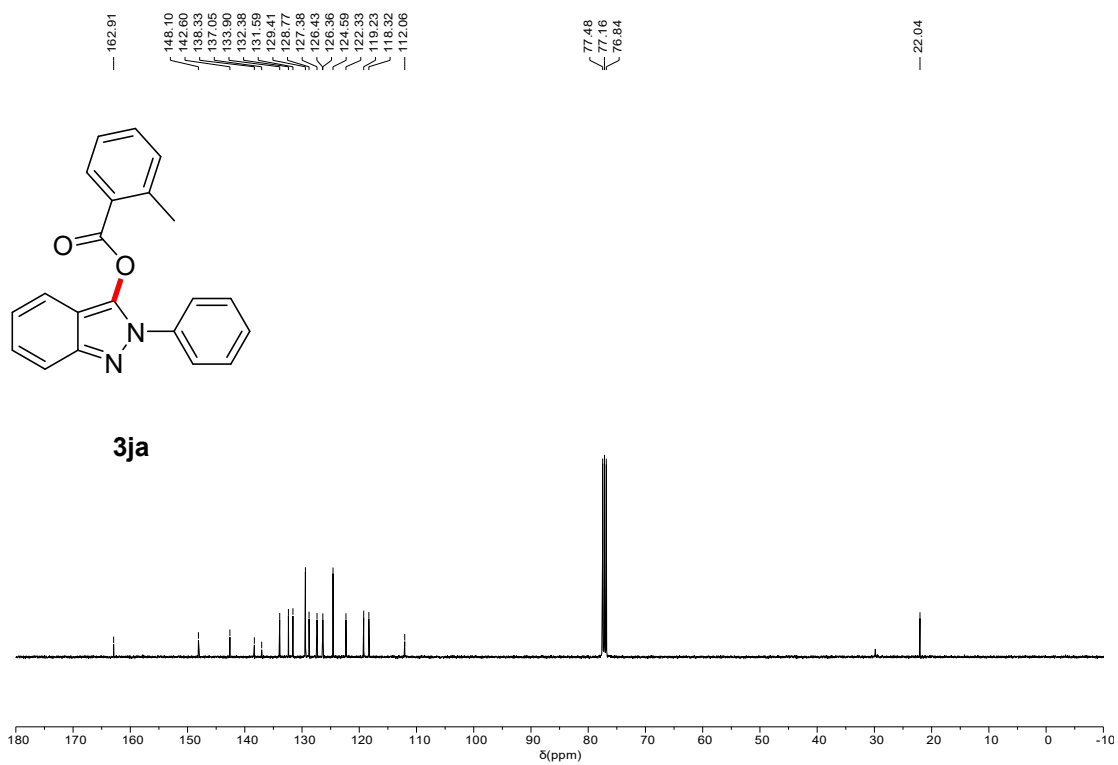
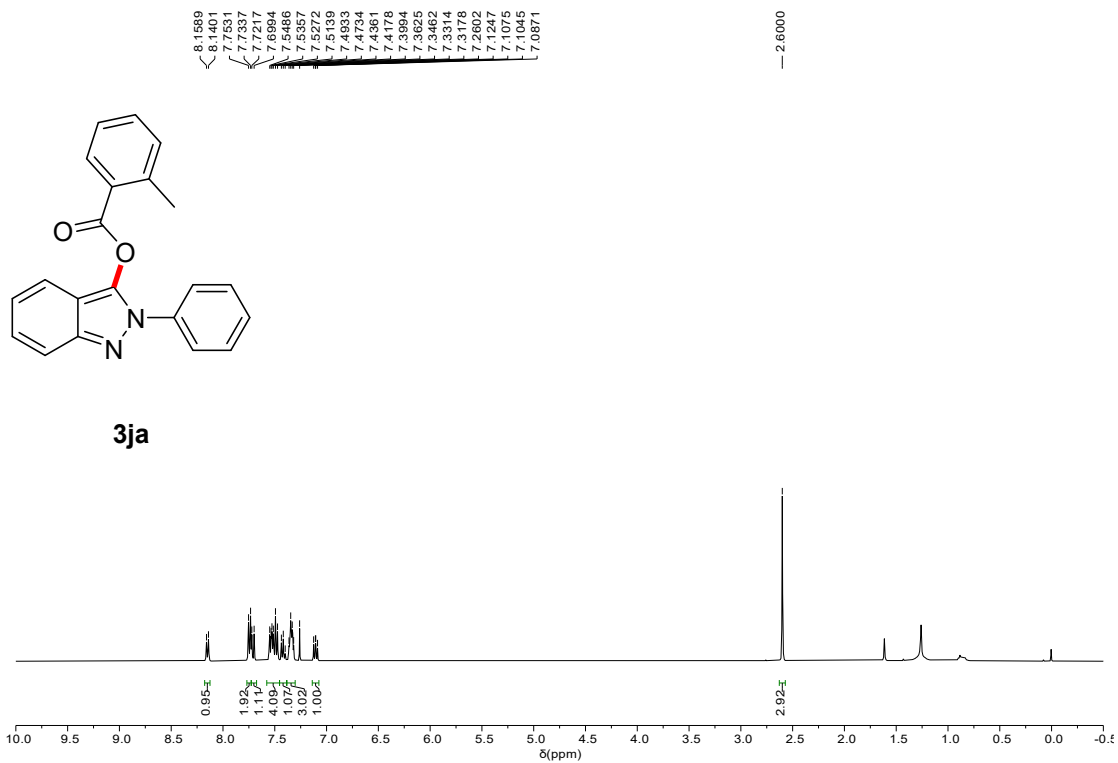
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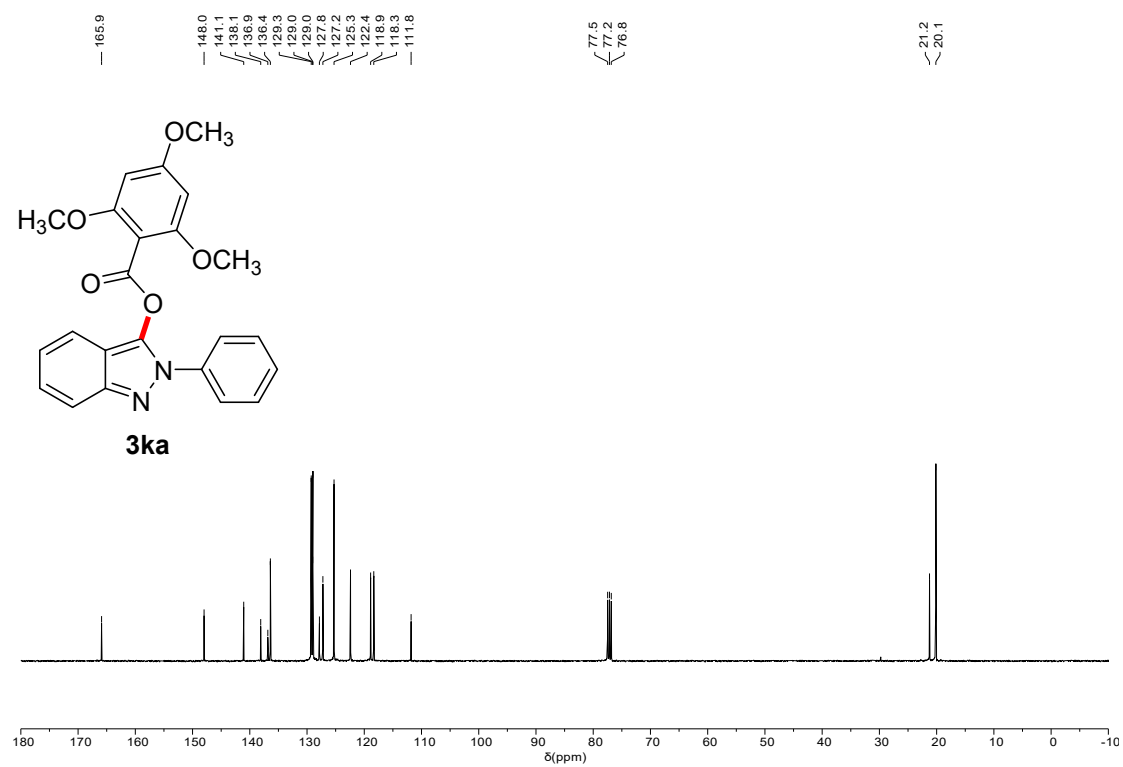
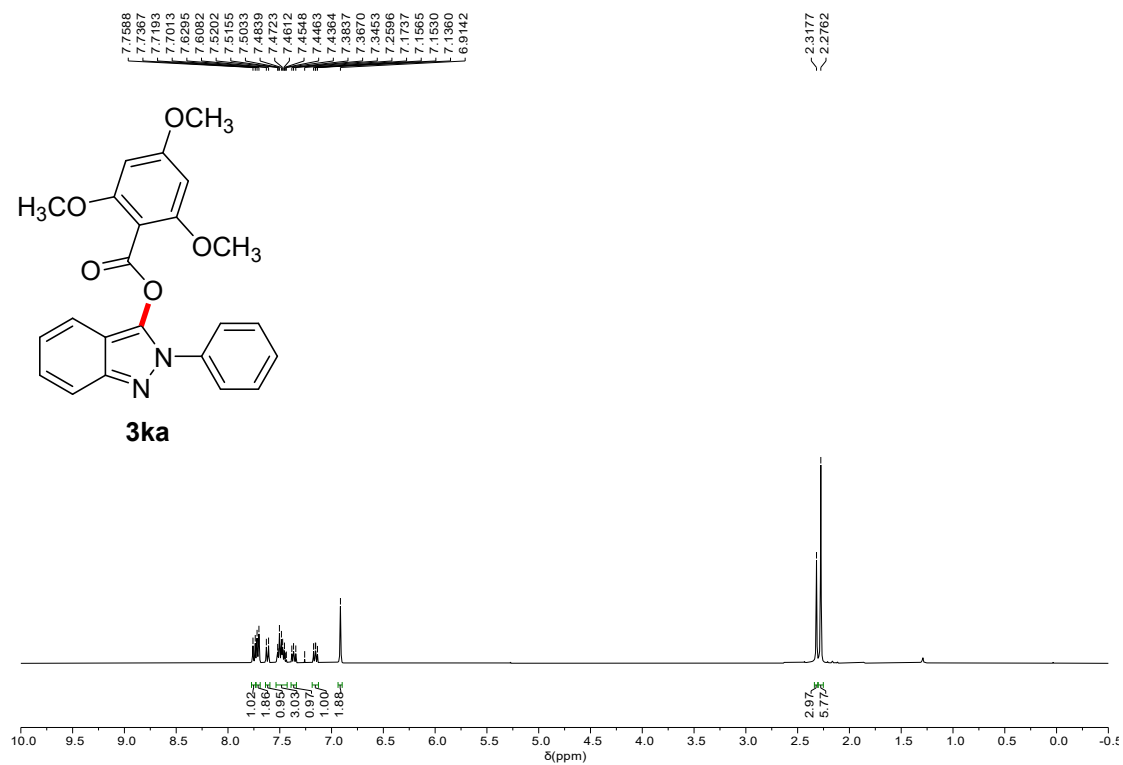




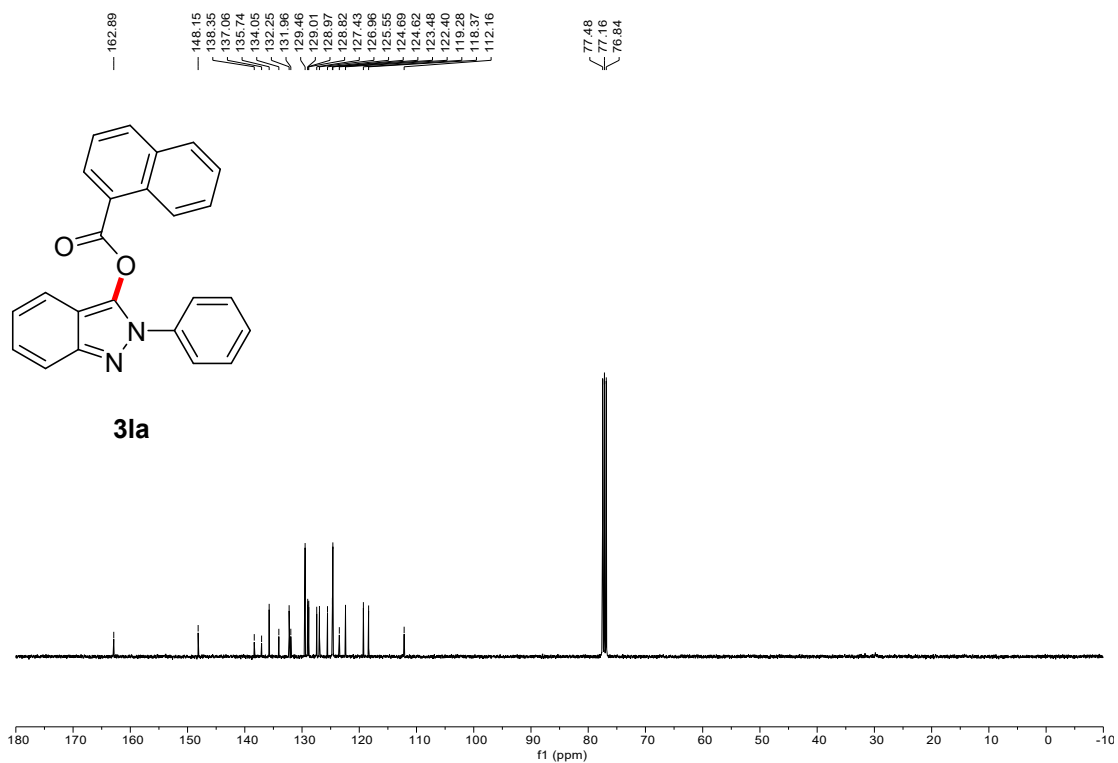
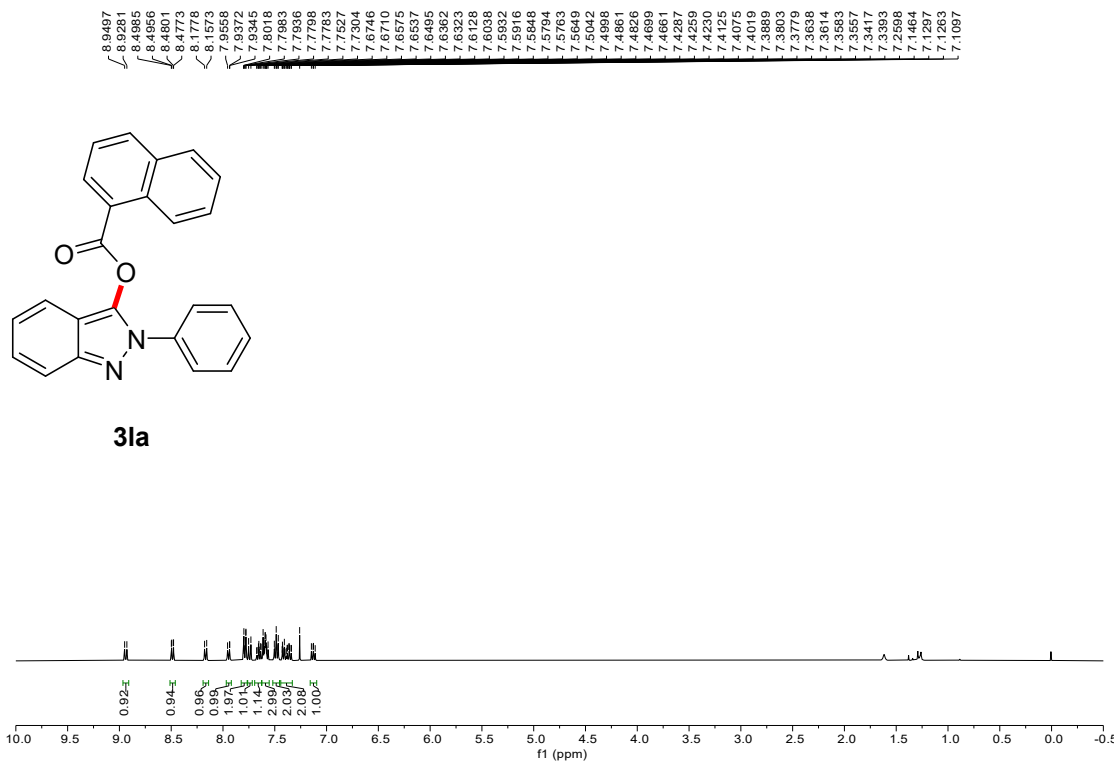


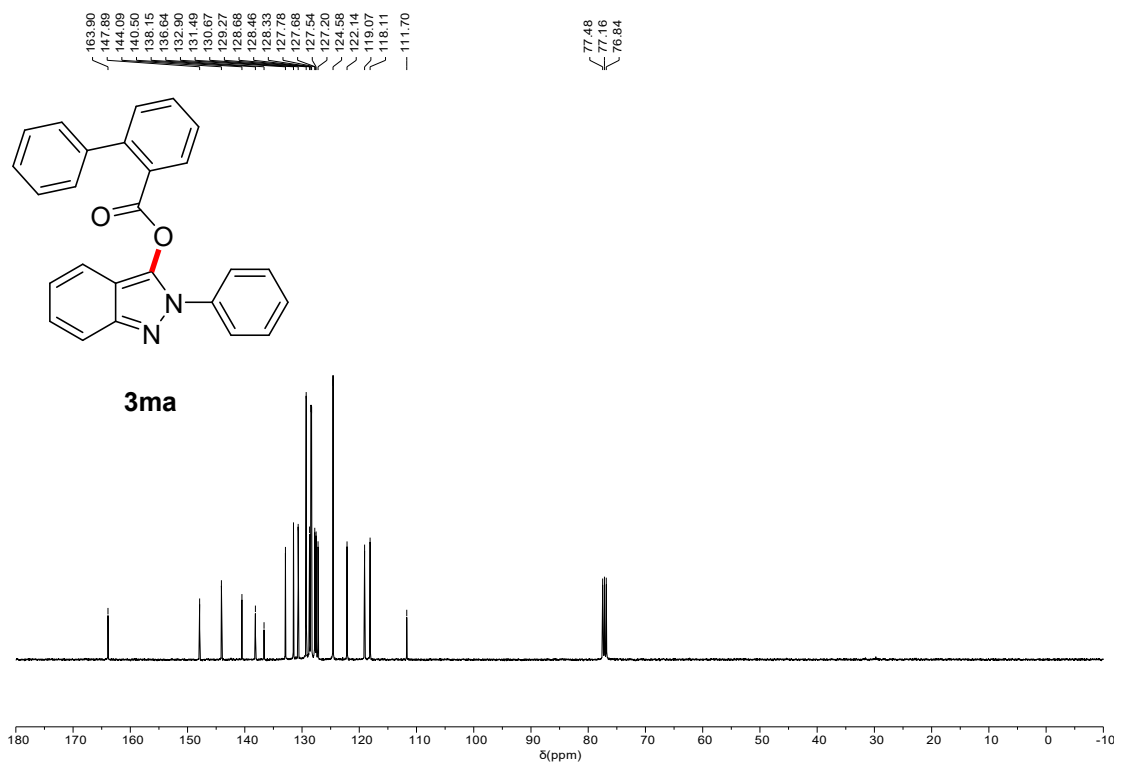
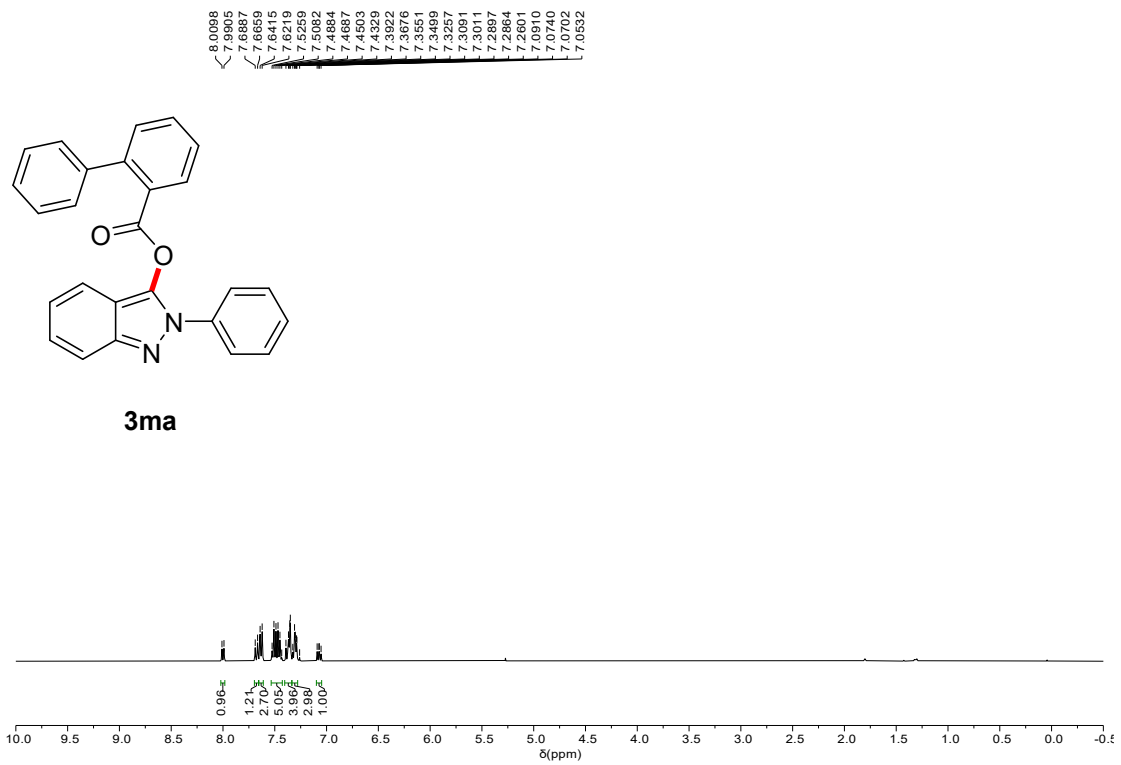


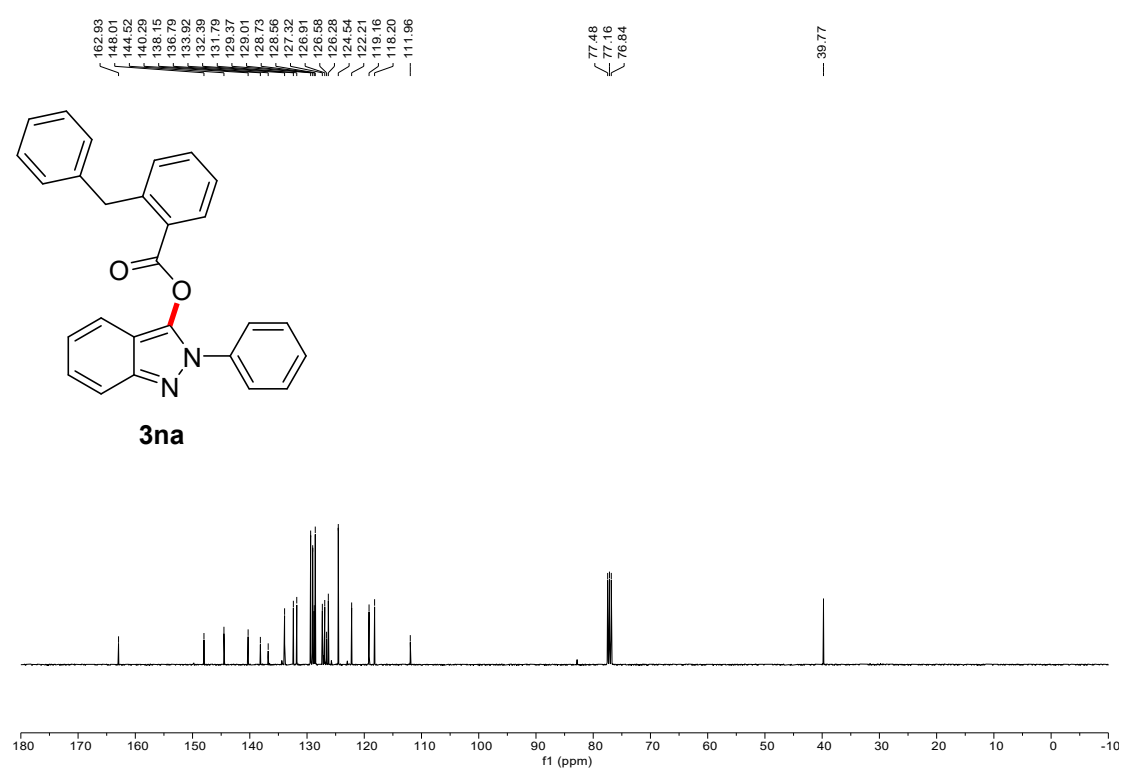
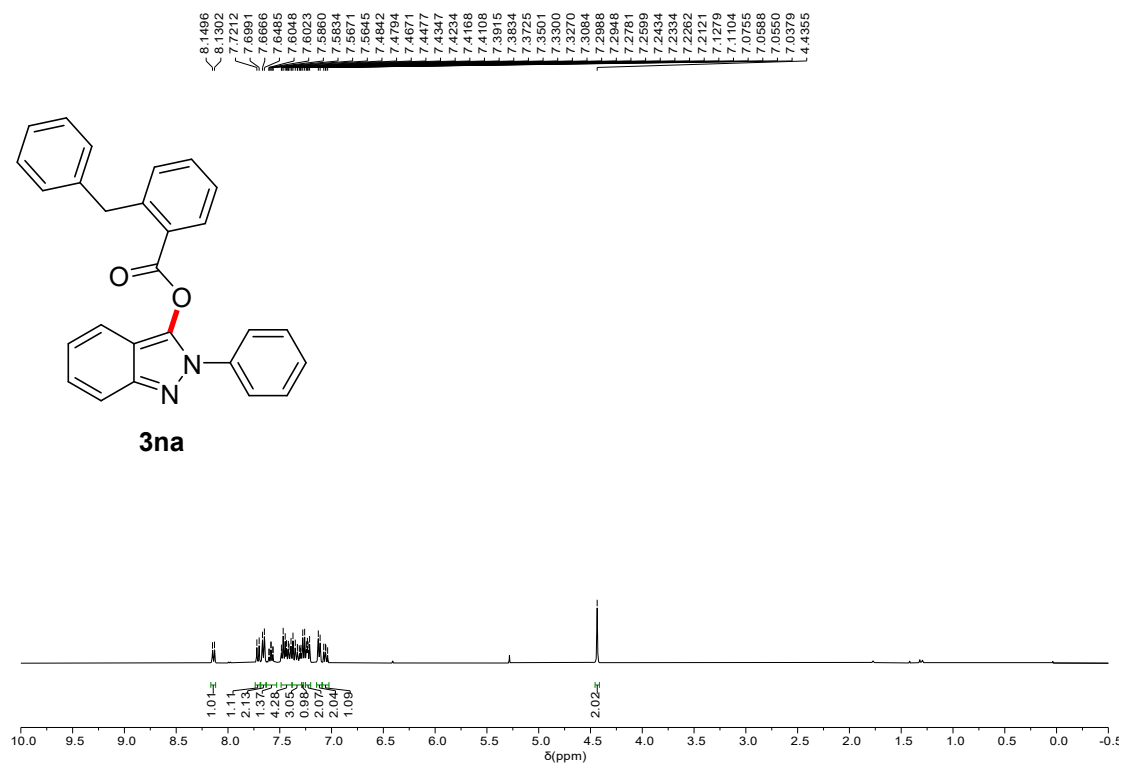


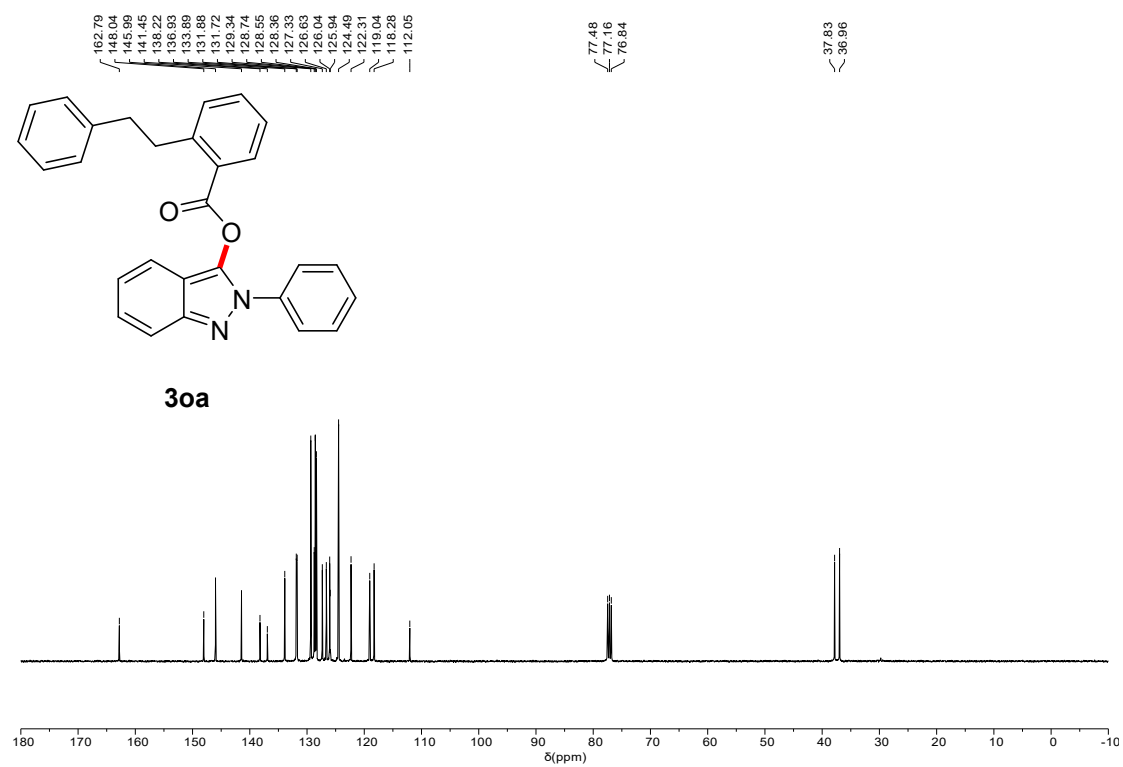
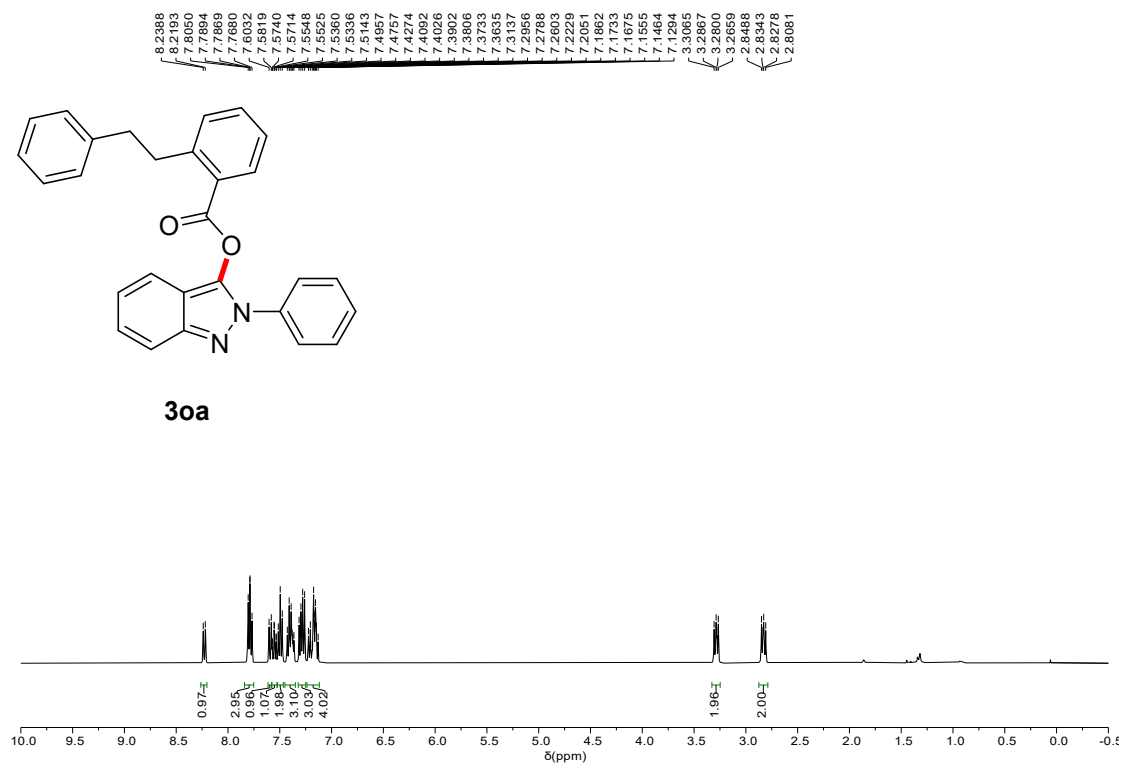




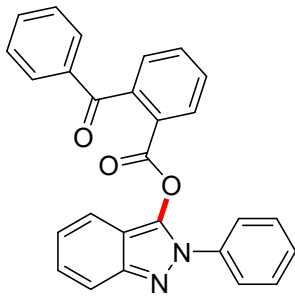




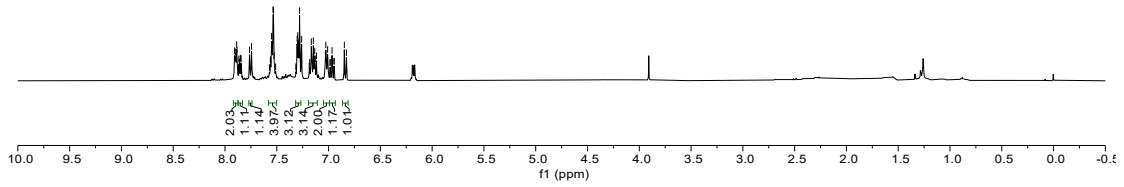




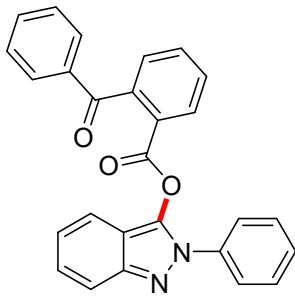
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3pa



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76.84



3pa

