

## Electronic Supplementary Information

### 2-Substituted 3-Arylindoles Through Palladium-Catalyzed Arylative Cyclization of 2-Alkynyltrifluoroacetanilides with Arylboronic Acids under Oxidative Conditions

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## GENERAL INFORMATION

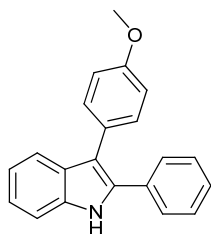
Melting points are uncorrected. All of the reagents, catalysts, and solvents are commercially available and were used as purchased, without further purification. The appropriate 2-alkynyltrifluoroacetanilides were prepared, usually in high yields, from 2-iodoaniline via a two-step process involving a Sonogashira cross-coupling with terminal alkynes followed by a trifluoroacetylation step.<sup>1</sup> Reaction products were purified on axially compressed columns, packed with SiO<sub>2</sub> 25-40 μm, connected to a preparative pump for solvent delivery and to a refractive index detector, and eluting with *n*-hexane/EtOAc mixtures. <sup>1</sup>H NMR (400.13 MHz), <sup>13</sup>CNMR (100.6 MHz) and <sup>19</sup>F NMR (376.5 MHz) spectra were recorded with a Bruker Avance 400 spectrometer. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer. Mass spectra were determined with a QP2010 Gas Chromatograph Mass spectrometer (EI ion source).

### General Procedure.

#### Preparation of 2-phenyl-3-(4-methoxyphenyl)indole 3a

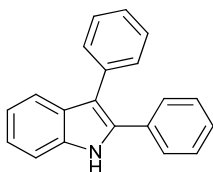
In a 50 mL Carousel Tube Reactor (Radely Discovery Technology) containing a magnetic stirring bar Pd(OAc)<sub>2</sub> (3.8 mg, 0.0172 mmol) and dppp (7.1 mg, 0.0172 mmol) were dissolved at room temperature with 1.0 mL of anhydrous MeOH. Then, *o*-(phenylethynyl)trifluoroacetanilide (100.0 mg, 0.345 mmol), 4-methoxyphenylboronic acid (105.0 mg, 0.690 mmol), K<sub>3</sub>PO<sub>4</sub> (146.7 mg, 0.690 mmol), and 1.0 mL of solvent were added. The mixture was stirred for 1.5 h at 60 °C under a balloon of molecular oxygen. After this time, the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with water. The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc 85/15 v/v) to afford 78.4 mg (76% yield) of 3-(4-methoxyphenyl)-2-phenyl-1*H*-indole: mp: 184-185 °C; IR (KBr): 3419, 1603, 1510 cm<sup>-1</sup>; <sup>1</sup>H NMR (400.13 MHz) (CDCl<sub>3</sub>) δ 8.24 (bs, 1 H), 7.68 (d, *J* = 7.4 Hz, 1 H), 7.52-7.13 (m, 10 H), 6.97 (d, *J* = 8.7 Hz, 2 H), 3.88 (s, 3 H); <sup>13</sup>CNMR (100.6 MHz) (CDCl<sub>3</sub>) δ 158.2, 135.9, 133.8, 132.9, 131.2, 129.1, 128.7, 128.1, 127.6, 127.4, 122.7, 120.4, 119.8, 114.8, 114.1, 110.9, 55.3. MS *M/e* (relative intensity): 299 (*M*<sup>+</sup>, 74), 103 (33), 77 (65), 51 (100).

## CHARACTERIZATION DATA



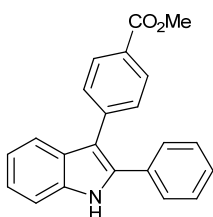
#### 3-(4-methoxyphenyl)-2-phenyl-1*H*-indole (3a)

mp.: 184-5 °C; lit.<sup>2</sup> mp.: 184-5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.24 (bs, 1 H), 7.68 (d, *J* = 7.4 Hz, 1 H), 7.52-7.13 (m, 10 H), 6.97 (d, *J* = 8.7 Hz, 2 H), 3.88 (s, 3 H); <sup>13</sup>CNMR (CDCl<sub>3</sub>) δ 158.2, 135.9, 133.8, 132.9, 131.2, 129.1, 128.7, 128.1, 127.6, 127.4, 122.7, 120.4, 119.8, 114.8, 114.1, 110.9, 55.3.



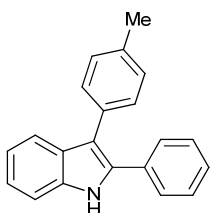
**2,3-diphenyl-1H-indole (3b)**

mp.: 120-121 °C; lit.<sup>2</sup> mp.: 120-121 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.22 (bs, 1 H), 7.80 (d, *J* = 7.9 Hz, 1 H), 7.57-7.23 (m, 13 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 136.0, 135.2, 134.2, 132.8, 130.3, 128.9, 128.8, 128.6, 128.3, 127.8, 126.4, 122.8, 120.6, 119.8, 115.2, 111.1.



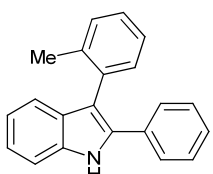
**methyl 4-(2-phenyl-1H-indol-3-yl)benzoate (3c)**

mp.: 134-135 °C; IR (KBr): 3347, 1693, 1602, 1282, 1116 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.24 (bs, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.50-7.24 (m, 9 H), 7.19 (t, *J* = 7.7 Hz, 1 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 3.89 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 158.2, 135.9, 133.7, 132.9, 131.2, 129.0, 128.7, 128.1, 127.6, 127.4, 122.7, 120.3, 119.7, 114.7, 114.1, 110.9, 55.3. MS: *m/z* (%): 327 (M<sup>+</sup>, 100), 267 (40). Anal calcd for C<sub>22</sub>H<sub>14</sub>NO<sub>2</sub> C, 80.71; H, 5.23; N, 4.28; found: C, 80.79; H, 5.24; N, 4.26.



**2-phenyl-3-*p*-tolyl-1H-indole (3d)**

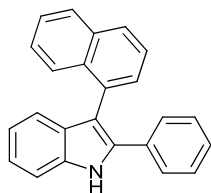
mp.: 123-124 °C; lit.<sup>2</sup> mp.: 123-124 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.22 (bs, 1 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.50-7.24 (m, 12 H), 2.47 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 136.0, 135.9, 134.0, 132.9, 132.1, 130.1, 129.4, 129.0, 128.7, 128.2, 127.7, 122.7, 120.4, 119.9, 115.1, 111.0, 21.4.



**2-phenyl-3-*o*-tolyl-1H-indole (3e)**

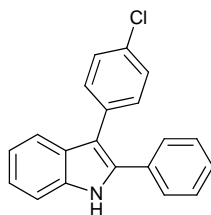
mp: 170-171 °C; lit.<sup>3</sup> mp.: 170-171 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.34 (bs, 1 H), 7.48 (d, *J* = 8.4 Hz, 1 H), 7.50-7.24 (m, 11 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 2.06 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 137.8, 135.9,

134.6, 133.9, 133.0, 131.7, 131.1, 129.7, 127.5, 127.3, 127.2, 126.8, 126.0, 122.7, 120.8, 120.1, 114.9, 110.0, 20.2.



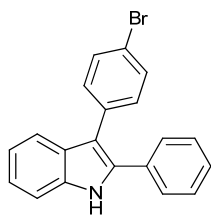
**3-(naphthalen-1-yl)-2-phenyl-1H-indole (3f)**

wax. IR (neat): 3415, 1602  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.28 (bs, 1 H), 7.97 (d,  $J = 8.0$  Hz, 1 H), 7.93 (d,  $J = 8.0$  Hz, 1 H), 7.84 (d,  $J = 8.2$  Hz, 1 H), 7.58-7.46 (m, 4 H), 7.40-7.19 (m, 8 H), 7.11 (t,  $J = 7.6$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  135.8, 135.0, 134.0, 133.0, 132.9, 132.5, 130.4, 129.1, 128.6, 128.2, 127.6, 127.5, 127.2, 126.8, 125.9, 125.8, 125.7, 122.7, 120.3, 120.2, 113.5, 110.9. MS:  $m/z$  (%): 319 ( $\text{M}^+$ , 100). Anal calcd for  $\text{C}_{24}\text{H}_{17}\text{N}$  C, 90.25; H, 5.36; N, 4.39; found: C, 90.31; H, 5.35; N, 4.41.



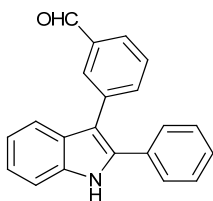
**3-(4-chlorophenyl)-2-phenyl-1H-indole (3g)**

mp.: 140-141  $^\circ\text{C}$ ; lit.<sup>4</sup> mp.: 140-141  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.30 (bs, 1 H), 7.67 (d,  $J = 7.7$  Hz, 1 H), 7.51-7.24 (m, 11 H), 7.19 (t,  $J = 8.0$  Hz, 1 H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.0, 134.6, 133.7, 132.5, 132.1, 131.5, 128.91, 128.89, 128.6, 128.3, 128.0, 122.9, 120.8, 119.5, 114.0, 111.2.



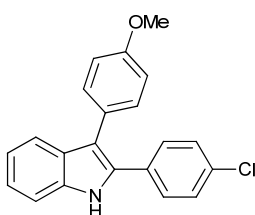
**3-(4-bromophenyl)-2-phenyl-1H-indole (3h)**

mp: 125-117  $^\circ\text{C}$ . IR (KBr): 3399, 1030, 744  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.28 (bs, 1 H), 7.70 (d,  $J = 8.0$  Hz, 1 H), 7.54 (d,  $J = 7.2$  Hz, 2 H), 7.51-7.30 (m, 9 H), 7.22 (t,  $J = 7.2$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  135.9, 134.4, 134.2, 132.4, 131.77, 131.75, 128.8, 128.4, 128.3, 128.0, 122.9, 120.7, 120.2, 119.4, 113.8, 111.1. MS:  $m/z$  (%): 349 ( $\text{M}^{+2}$ , 96), 347 ( $\text{M}^+$ , 100). Anal calcd for  $\text{C}_{20}\text{H}_{14}\text{BrNO}$  C, 68.98; H, 4.05; N, 4.02; found: C, 68.90; H, 4.03; N, 3.99.



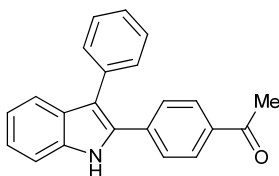
**3-(2-phenyl-1H-indol-3-yl)benzaldehyde (3i)**

mp.: 212-213 °C; lit.<sup>2</sup> mp.: 212-3 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.02 (s, 1 H), 8.36 (bs, 1 H), 8.00 (s, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 7.72-7.66 (m, 2 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 1 H), 7.46-7.29 (m, 6 H), 7.21 (t, *J* = 8.0 Hz, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 193.0, 136.8, 136.4, 136.0, 135.8, 134.6, 132.1, 130.5, 129.5, 128.7, 128.1, 127.8, 127.6, 127.1, 122.2, 120.0, 118.4, 111.9, 111.7.



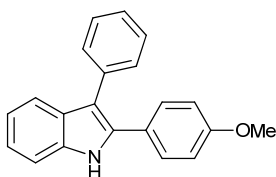
**2-(4-chlorophenyl)-3-(4-methoxyphenyl)-1H-indole (3j)**

mp: 160-162 °C. IR (KBr): 3407, 1486, 1033, 1245 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.22 (bs, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.40-7.25 (m, 7 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 158.4, 136.0, 133.4, 132.5, 131.3, 131.2, 129.2, 129.0, 128.9, 127.0, 123.0, 120.5, 119.8, 115.3, 114.2, 110.9, 55.3. MS: *m/z* (%): 333 (M<sup>+</sup>, 100). Anal calcd for C<sub>21</sub>H<sub>16</sub>ClNO C, 75.56; H, 4.83; N, 4.20; found: C, 75.47; H, 4.84; N, 4.17.



**1-(4-(3-phenyl-1H-indol-2-yl)phenyl)ethanone (3k)**

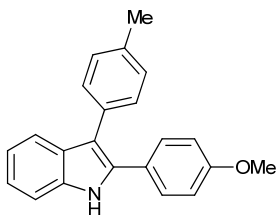
mp: 188-189 °C; lit.<sup>3</sup> mp: 188-189 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.41 (bs, 1 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.50-7.26 (m, 7 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 2.61 (s, 3 H). <sup>13</sup>CNMR (CDCl<sub>3</sub>) δ 197.8, 137.4, 136.3, 135.8, 134.7, 132.6, 130.0, 128.9, 128.82, 128.83, 127.9, 126.8, 123.5, 120.8, 120.1, 116.9, 111.1, 26.8.



**2-(4-methoxyphenyl)-3-phenyl-1H-indole (3l)**

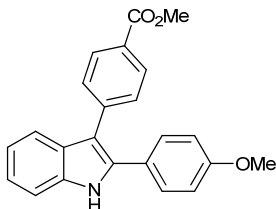
mp: 103-104 °C; lit.<sup>3</sup> mp 103-104 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.20 (bs, 1 H), 7.75 (d, *J* = 7.8 Hz, 1 H), 7.53-7.26 (m, 9 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). <sup>13</sup>CNMR

(CDCl<sub>3</sub>) δ 159.3, 135.9, 135.4, 134.3, 130.2, 129.6, 128.9, 128.6, 126.2, 125.3, 122.5, 120.4, 119.6, 114.3, 110.9, 55.3.



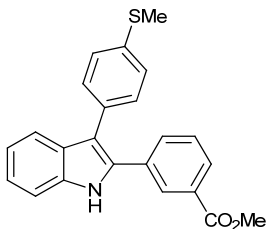
**2-(4-methoxyphenyl)-3-*p*-tolyl-1*H*-indole (3m)**

mp.: 94-95 °C; lit.<sup>4</sup> mp.: 94-95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.21 (bs, 1 H), 7.75 (d, *J* = 7.8 Hz, 1 H), 7.44-7.17 (m, 9 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 2.47 (s, 3 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 159.1, 135.8, 135.7, 133.9, 132.2, 130.1, 129.5, 129.3, 128.9, 125.4, 122.4, 120.3, 119.6, 114.2, 114.1, 110.9, 55.3, 21.4.



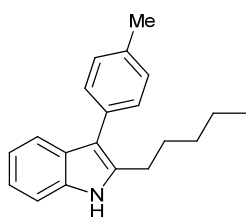
**methyl 4-(2-(4-methoxyphenyl)-1*H*-indol-3-yl)benzoate (3n)**

mp: 140-142 °C. IR (KBr): 3330, 1693, 1604, 1290, 1024 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.53 (bs, 1 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.28 (t, *J* = 8.2 Hz, 2 H), 7.21 (t, *J* = 7.6 Hz, 2 H), 6.96-6.86 (m, 2 H), 3.98 (s, 3 H), 3.84 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 167.6, 159.5, 140.8, 135.9, 135.3, 131.9, 129.9, 129.7, 128.2, 127.3, 124.7, 122.7, 120.7, 119.2, 115.3, 114.3, 111.1, 55.3, 52.2. MS: *m/z* (%): 357 (M<sup>+</sup>, 100), 298 (38), 267 (30). Anal calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub> C, 77.29; H, 5.36; N, 3.92; found: C, 77.38; H, 5.35; N, 3.95.



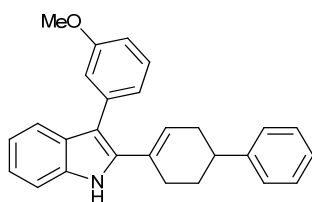
**methyl 3-(3-(4-(methylthio)phenyl)-1*H*-indol-2-yl)benzoate (3p)**

m.p.: 37-39 °C. IR (KBr) 3360, 1722, 1436. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.64 (bs, 1 H), 8.18 (td, *J*<sub>1</sub> = 1.8 Hz, *J*<sub>2</sub> = 0.4 Hz, 1 H), 7.91 (ddd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.7 Hz, *J*<sub>3</sub> = 1.1 Hz, 1 H), 7.64 (d, *J*<sub>2</sub> = 7.8 Hz, 1 H), 7.50 (ddd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 2.1 Hz, *J*<sub>3</sub> = 1.1 Hz, 1 H), 7.41 (dt, *J*<sub>1</sub> = 8.1 Hz, *J*<sub>2</sub> = 0.9 Hz, 1 H), 7.34-7.19 (m, 6 H), 7.14 (t, *J*<sub>2</sub> = 7.5 Hz, 1 H), 3.89 (s, 3 H), 2.50 (s, 3 H). <sup>13</sup>C NMR cm<sup>-1</sup>; (CDCl<sub>3</sub>): δ 166.8, 136.2, 136.1, 133.1, 133.4, 132.8, 131.6, 130.7, 130.5, 128.7, 128.6, 128.5, 128.3, 126.9, 123.0, 120.5, 120.0, 115.1, 111.1, 52.3, 15.8; MS: *m/z* (%): 375 (M<sup>+</sup>, 5), 373 (M<sup>+</sup>, 27), 372 (100), 327(8). Anal calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>S C, 73.97; H, 5.13; N, 3.75; found: C, 73.89; H, 5.14; N, 3.72.



**2-pentyl-3-p-tolyl-1H-indole (3q)**

oil; lit.<sup>4</sup> oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.97 (bs, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 2 H), 7.41-7.34 (m, 3 H), 7.25-7.16 (m, 2 H), 2.90 (t, *J* = 7.9 Hz, 2 H), 2.51 (s, 3 H), 1.80-1.69 (m, 2 H), 1.42-1.30 (m, 4 H), 0.99-0.90 (m, 3 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 136.0, 135.5, 135.3, 132.6, 129.6, 129.3, 128.2, 121.5, 119.9, 119.1, 114.4, 110.5, 31.7, 29.7, 26.5, 22.6, 21.3, 14.1.



**3-(3-methoxyphenyl)-2-(4-phenylcyclohex-1-enyl)-1H-indole (3r)**

m.p.: 58-60. IR (KBr) 3410, 1600, 1488 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.16 (bs, 1 H), 7.68 (d quint, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 0.6 Hz, 1 H), 7.44-7.11 (m, 11 H), 6.92 (ddd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.7 Hz, *J*<sub>3</sub> = 0.9 Hz, 1 H), 6.23-6.19 (m, 1 H), 3.90 (s, 3 H), 3.00-2.86 (m, 1 H), 2.61-2.48 (m, 1 H), 2.44-2.33 (m, 3 H), 2.06-1.97 (m, 1 H), 1.90-1.81 (m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 159.6, 146.5, 137.2, 135.9, 134.9, 131.0, 129.2, 128.7, 128.6, 128.4, 127.6, 126.8, 126.1, 122.5, 122.2, 120.1, 119.3, 115.3, 111.8, 110.6, 55.2, 39.5, 33.8, 29.9, 28.1. MS: *m/z* (%): 379 (M<sup>+</sup>, 100). Anal calcd for C<sub>27</sub>H<sub>25</sub>NO C, 85.45; H, 6.64; N, 3.69; found: C, 85.37; H, 6.63; N, 3.71.

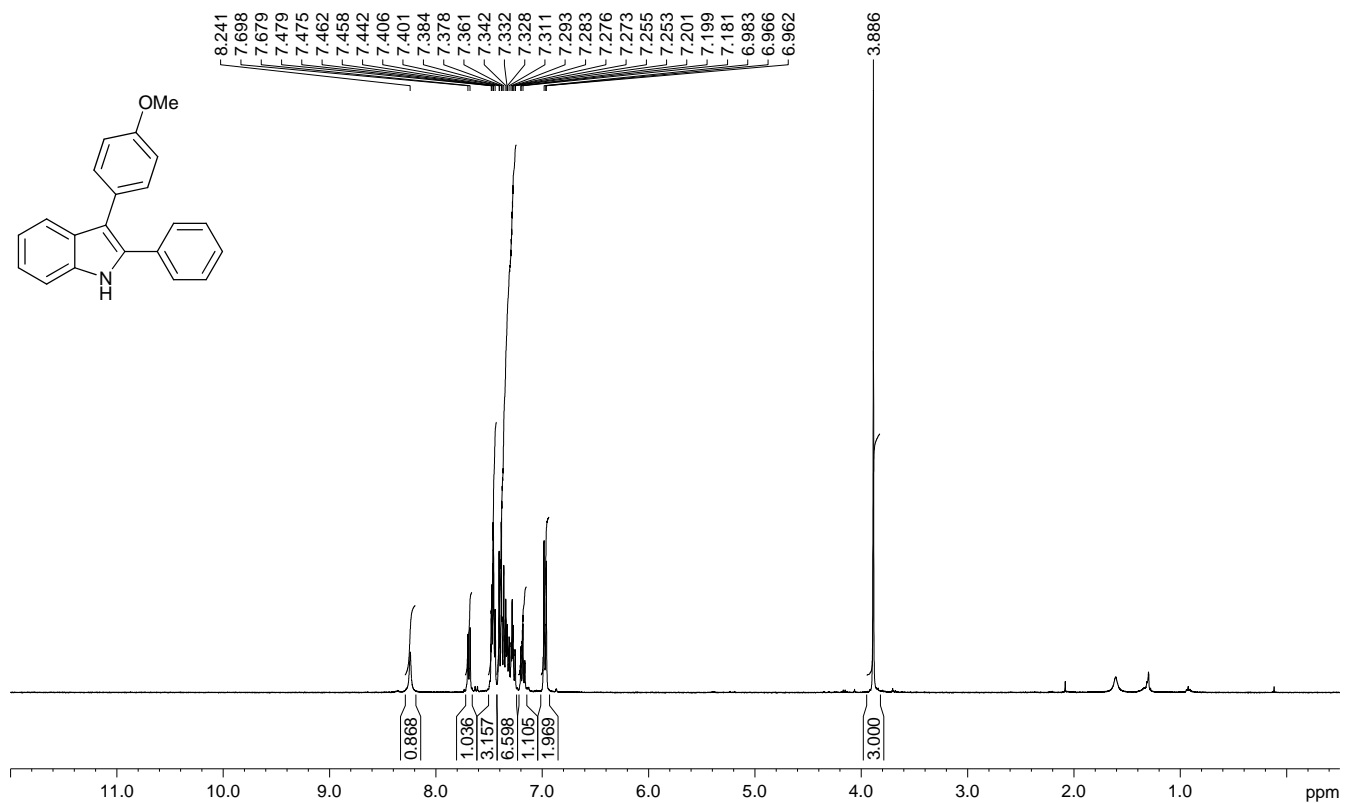
## REFERENCES

- <sup>1</sup> S. Cacchi, G. Fabrizi, P. Pace, *J. Org. Chem.* 1998, **63**, 1001.
- <sup>2</sup> S. Cacchi, G. Fabrizi, D. Lamba, F. Marinelli, L. M. Parisi, *Synthesis* 2003, 728.
- <sup>3</sup> S. Cacchi, S.; G. Fabrizi, A. Goggiamani, *Adv. Synth. Cat.* 2006, 1301.
- <sup>4</sup> S. Cacchi, G. Fabrizi, A. Goggiamani, A. Perboni, A. Sferrazza, P. Stabile *Org. Lett.*, 2010, **63**, 3279.

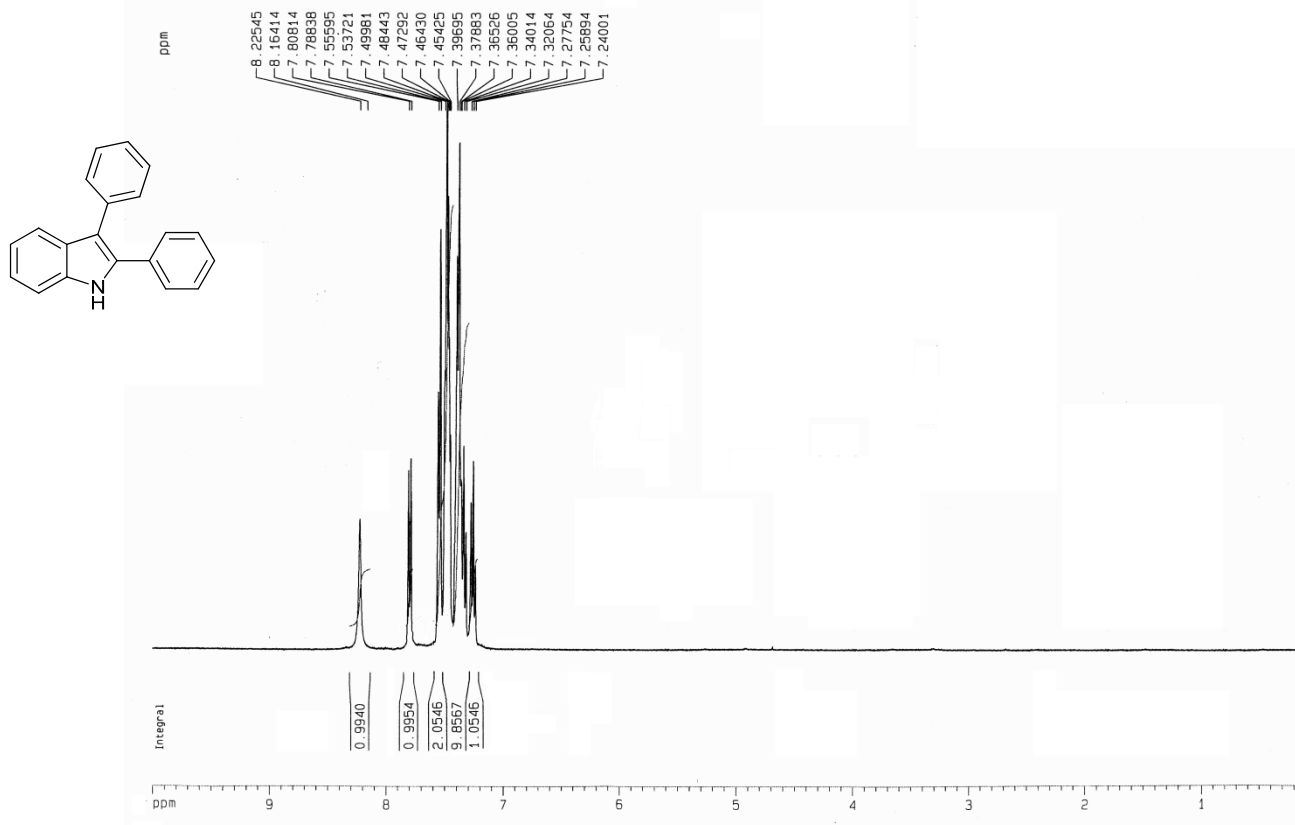


### NMR Spectra (known compounds)

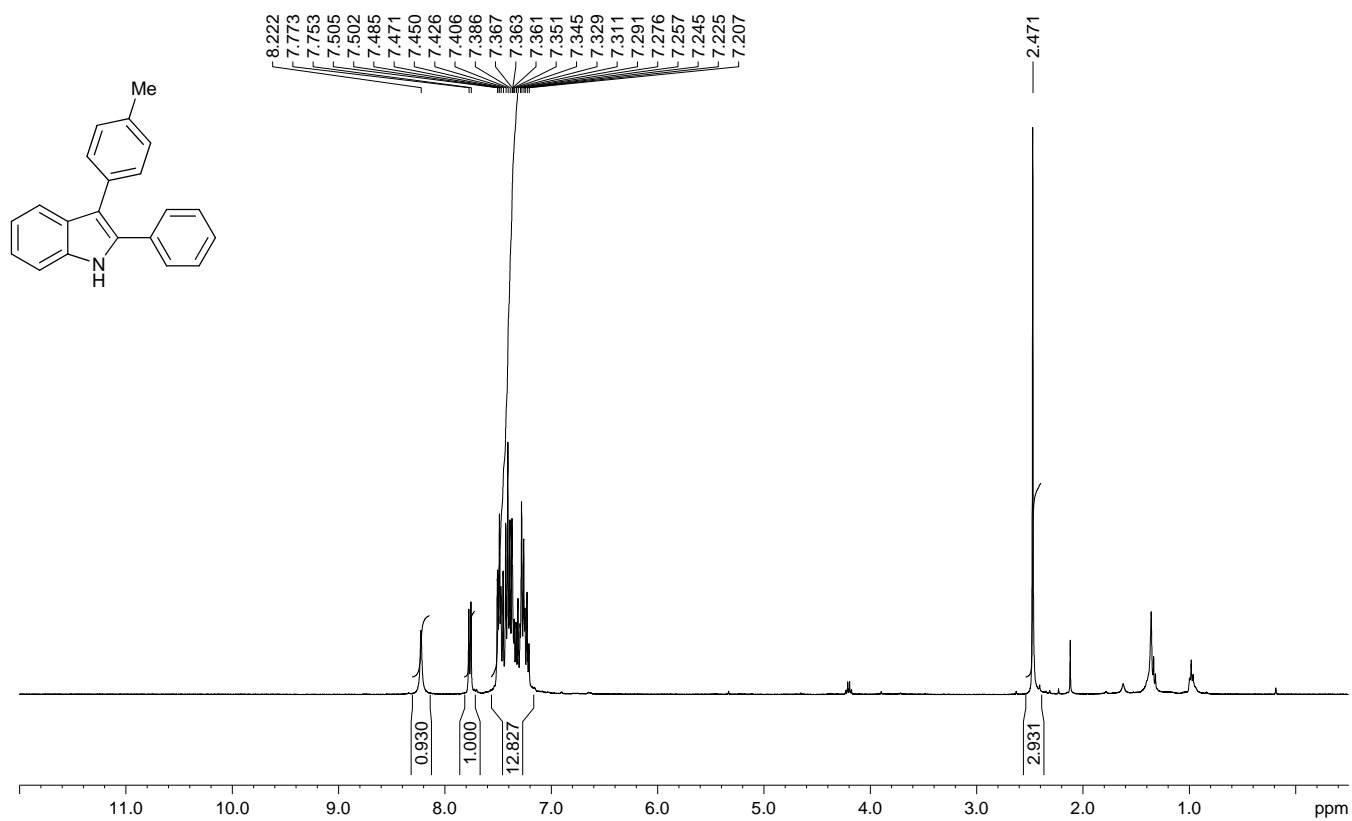
3a



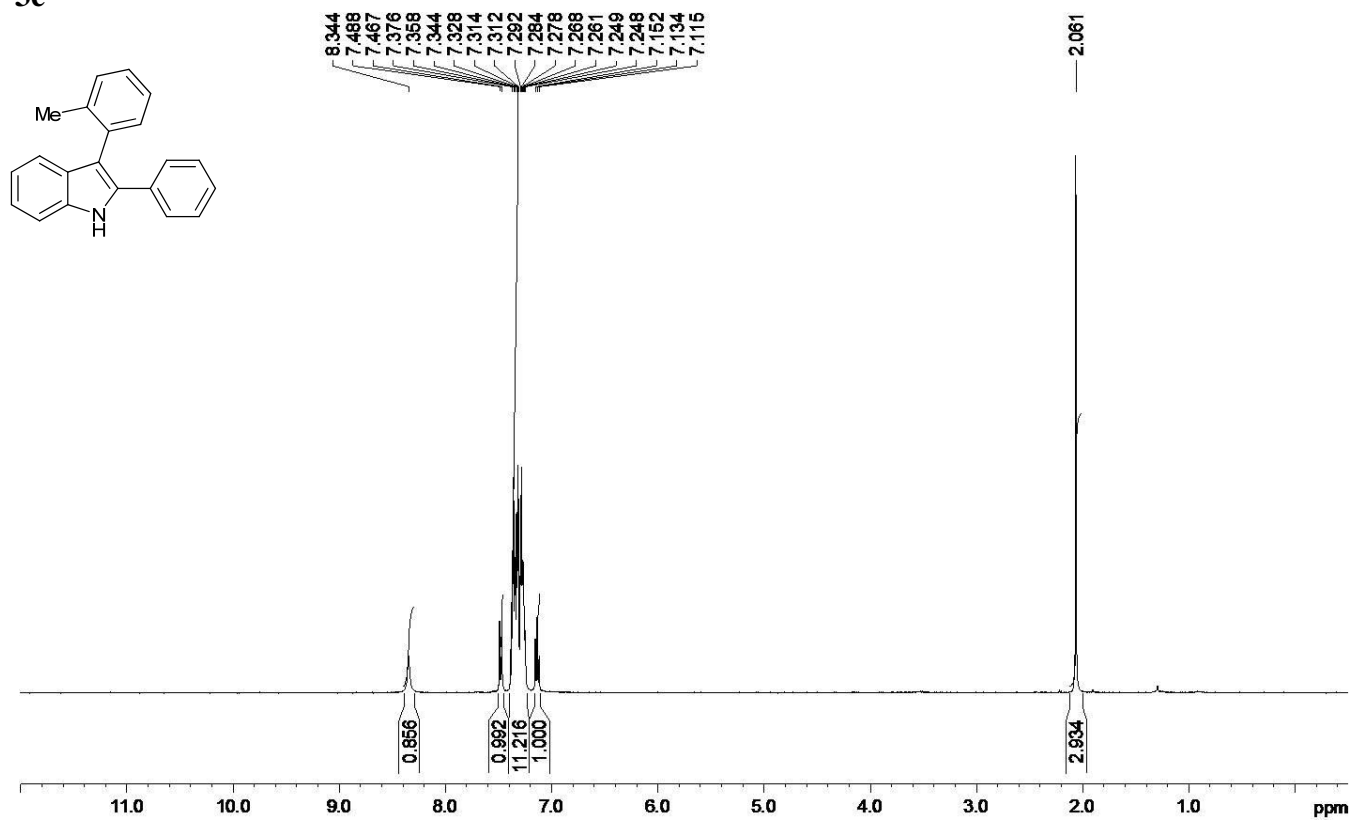
3b



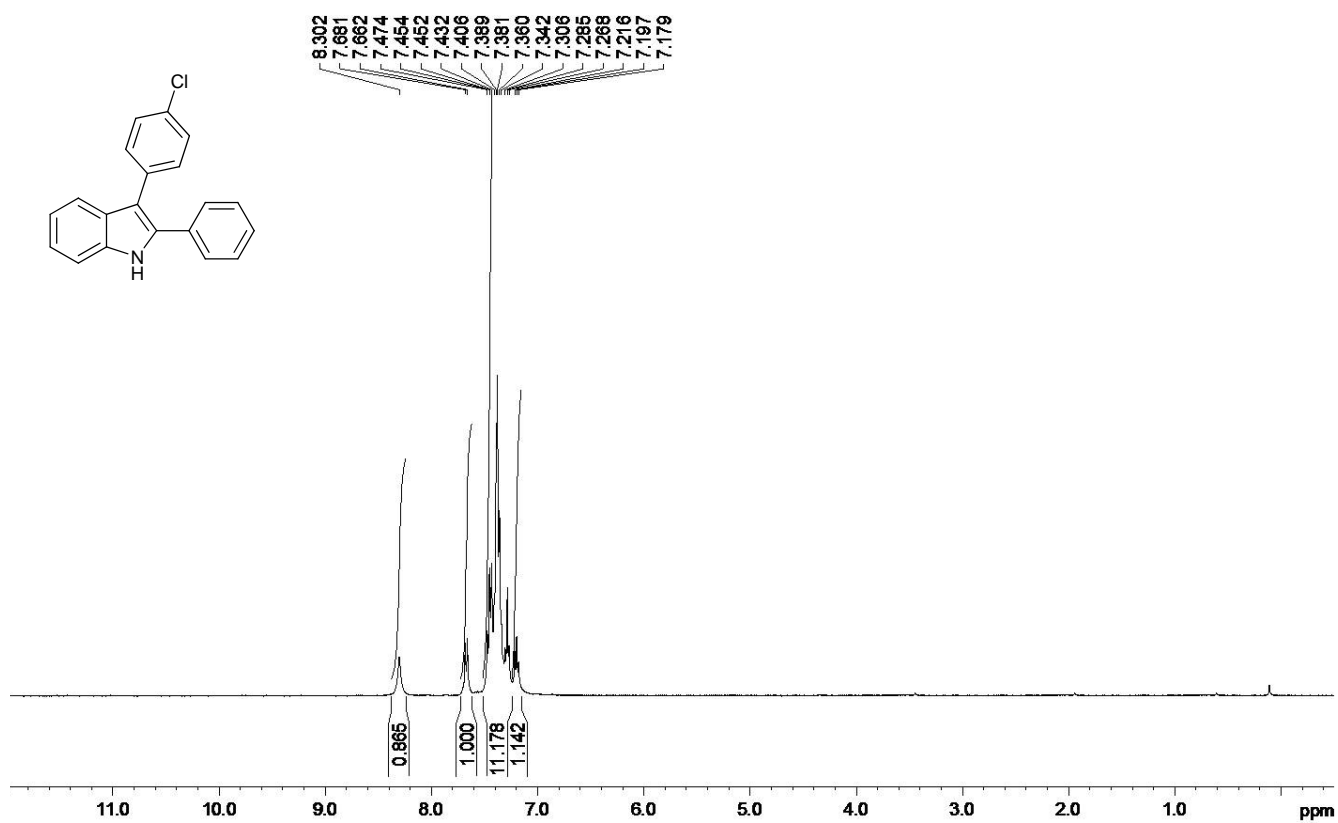
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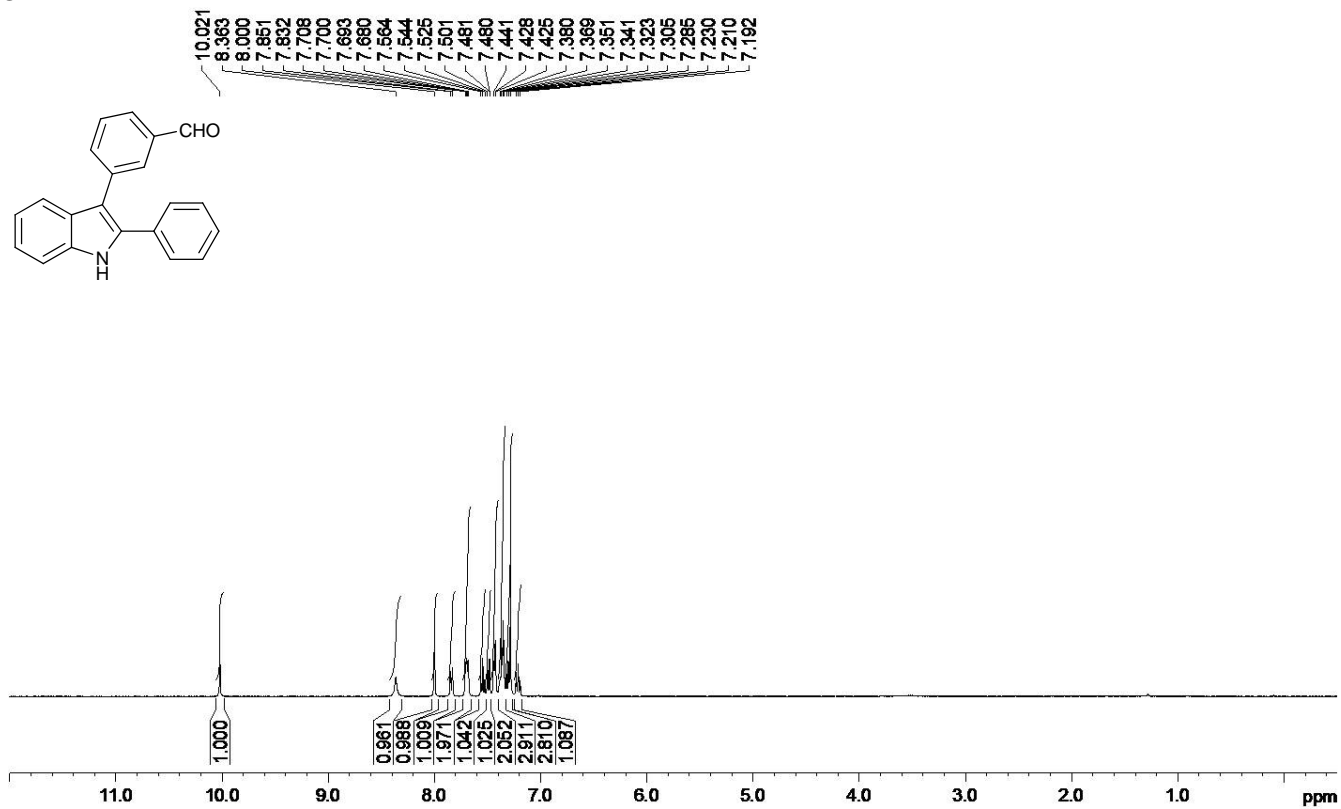
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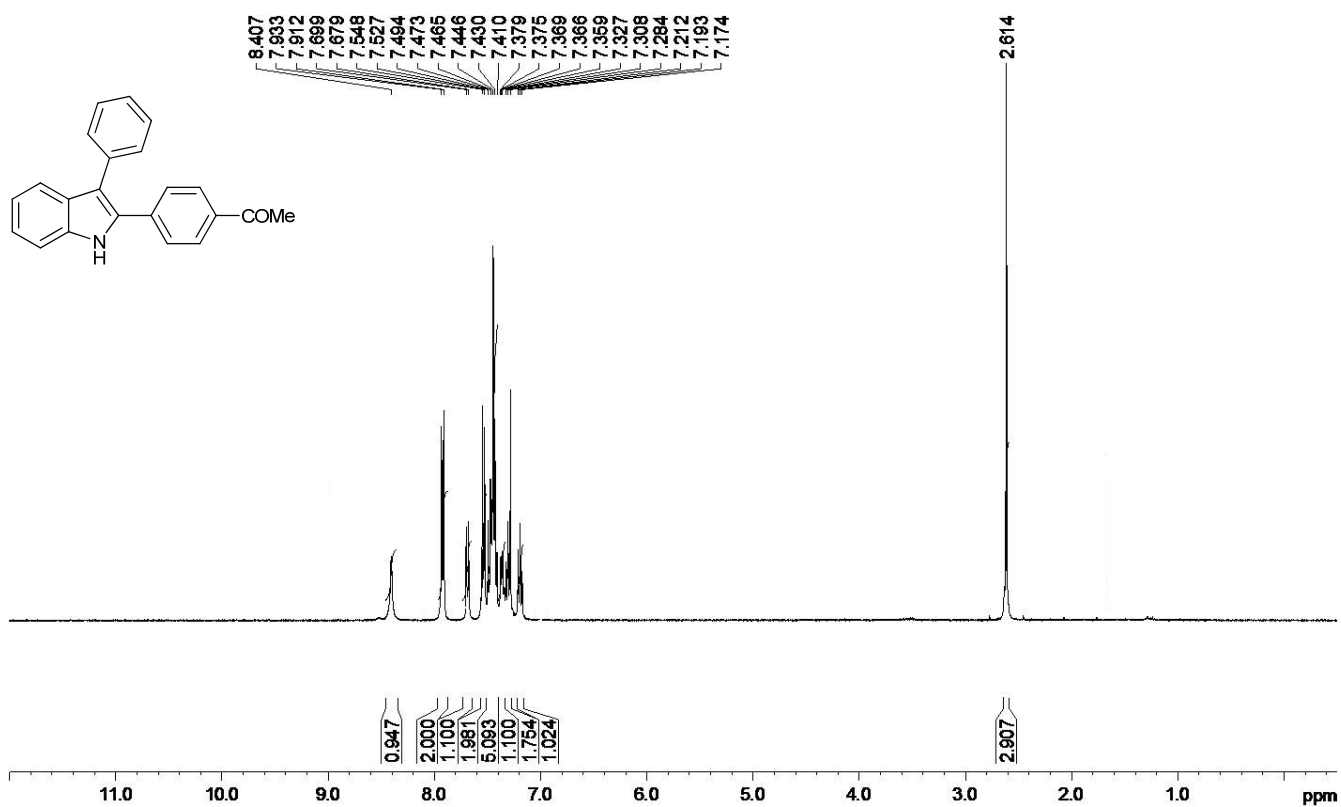
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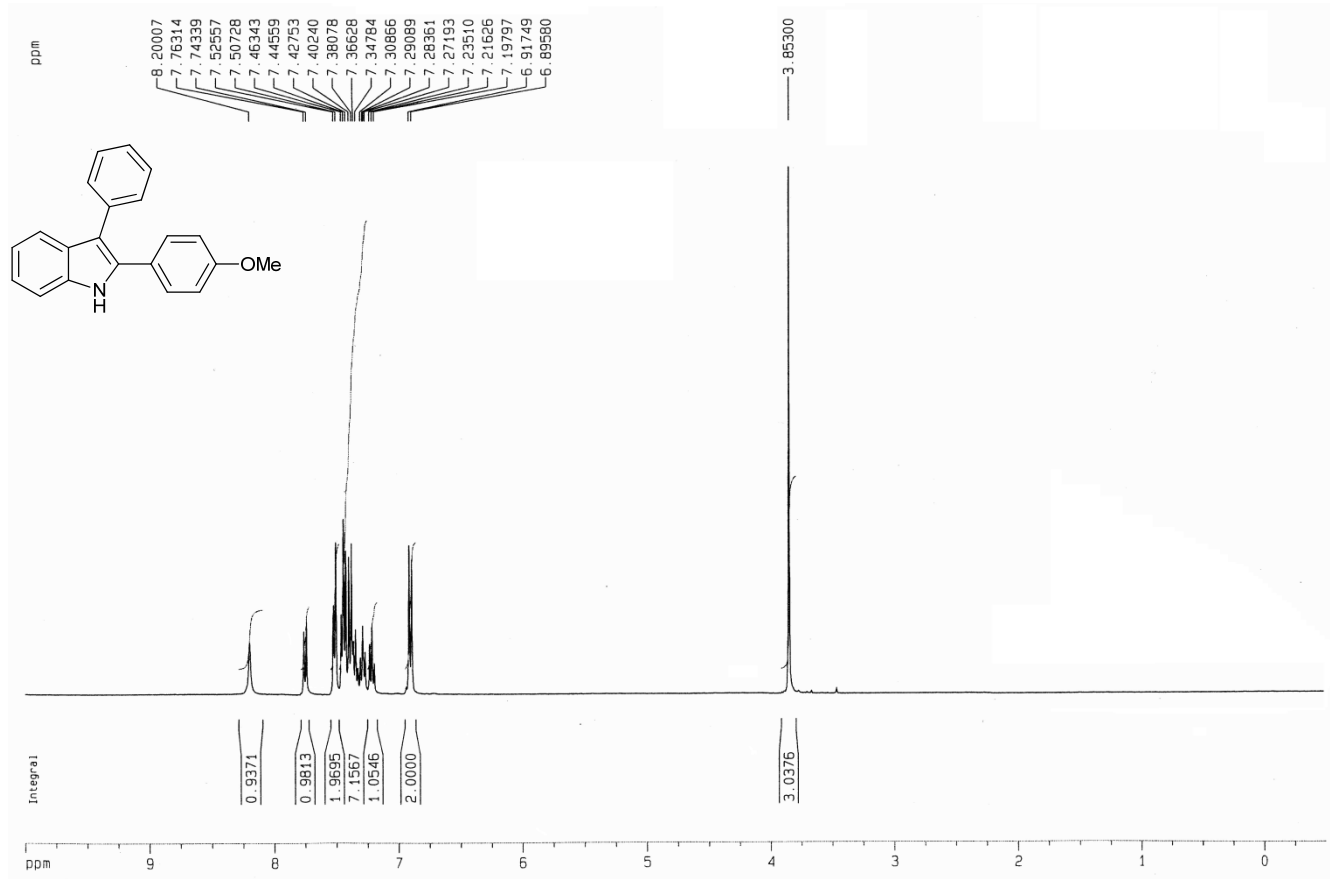
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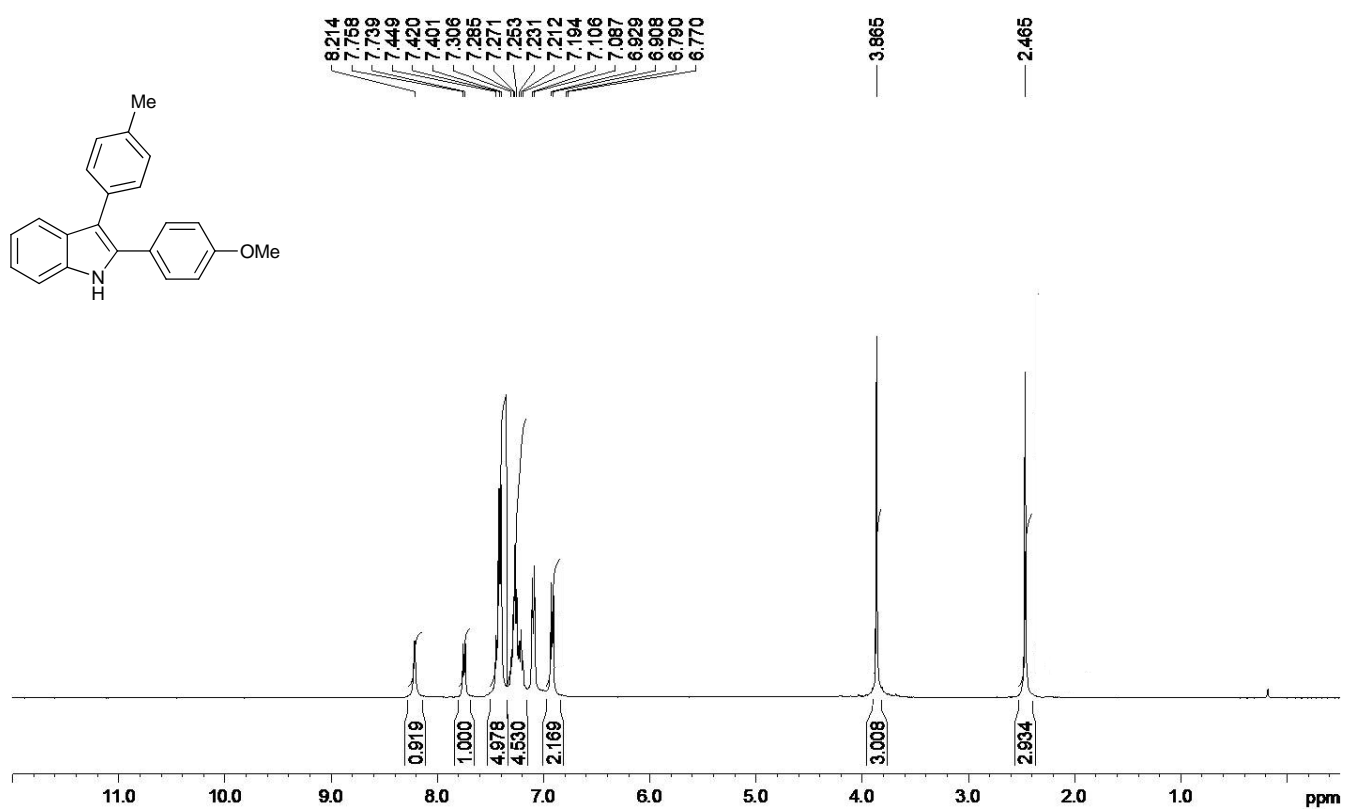
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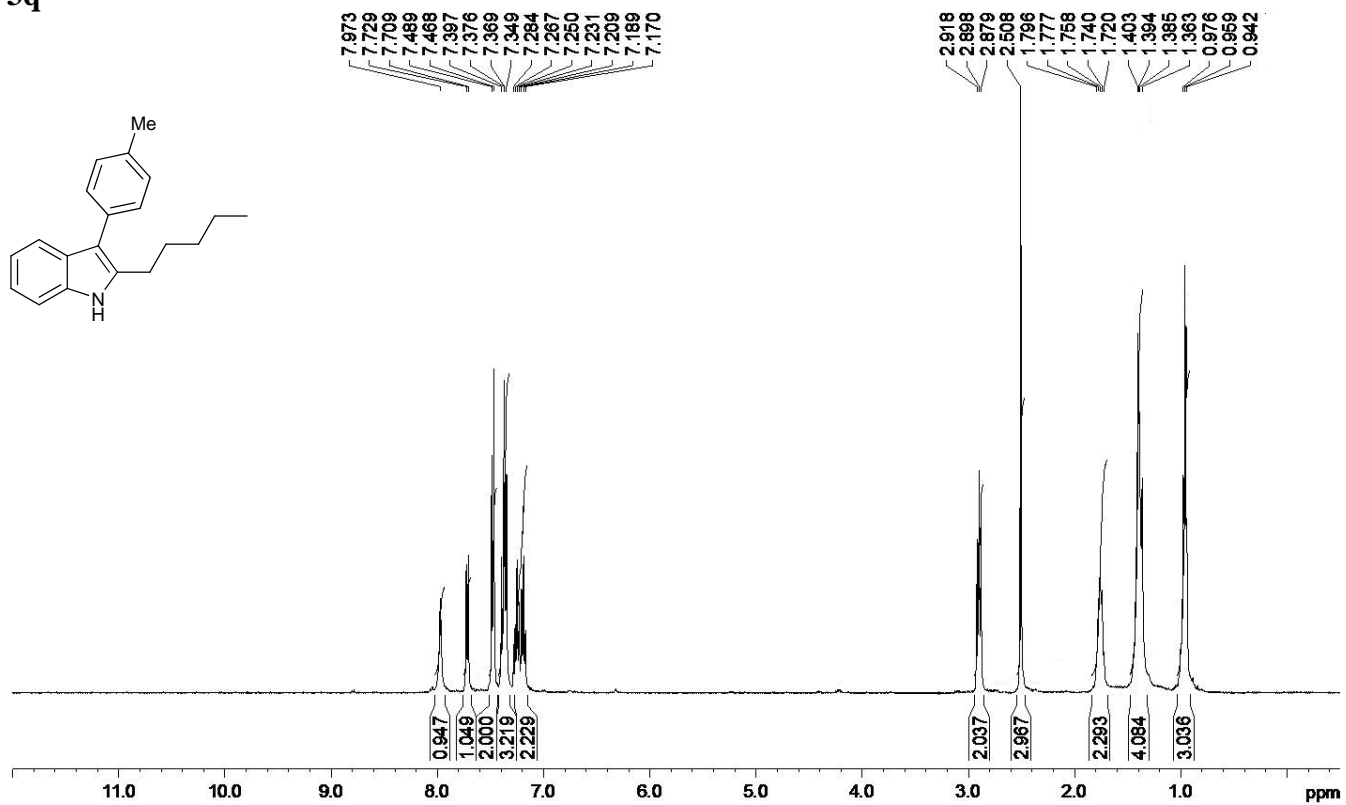
3l



### 3m

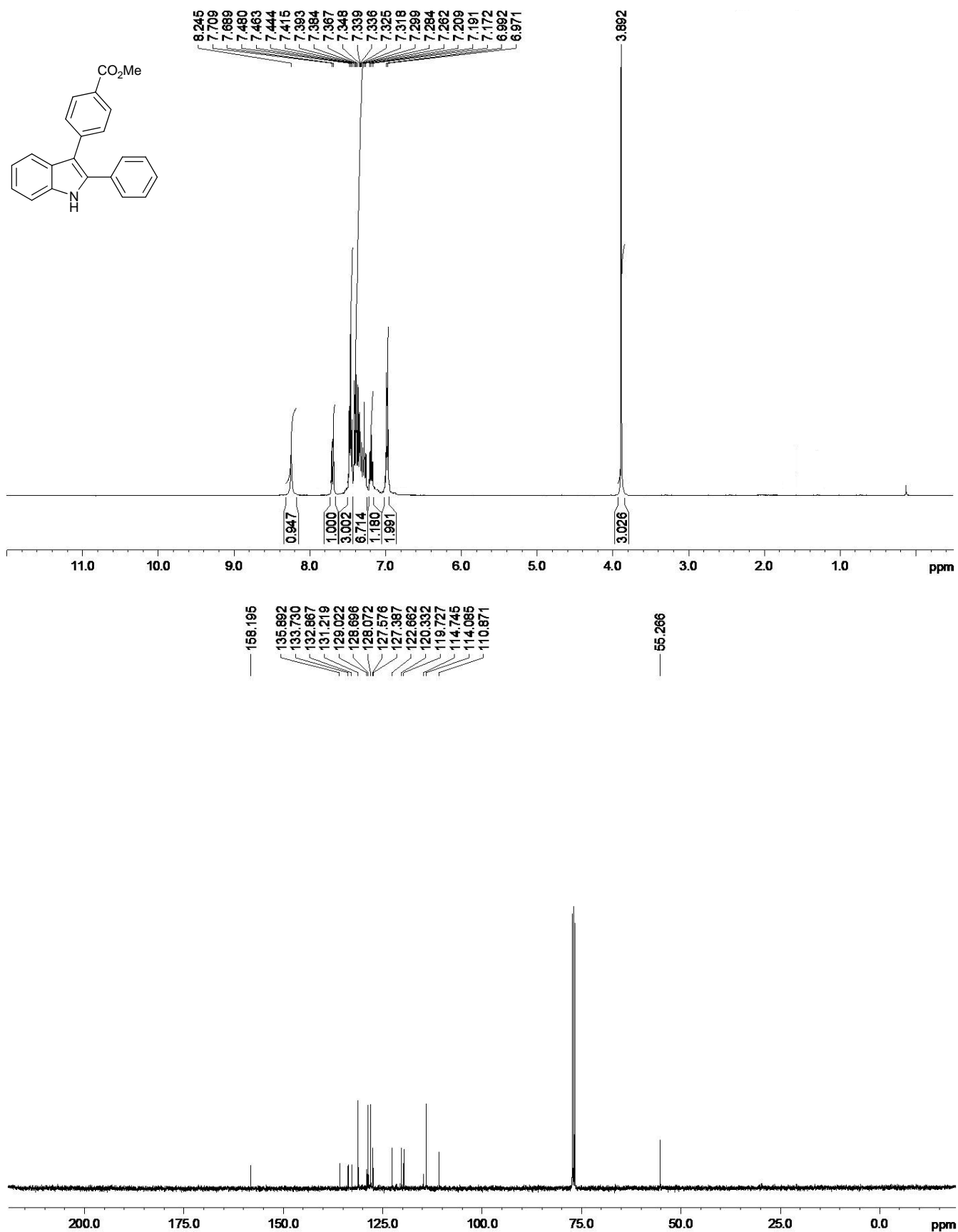


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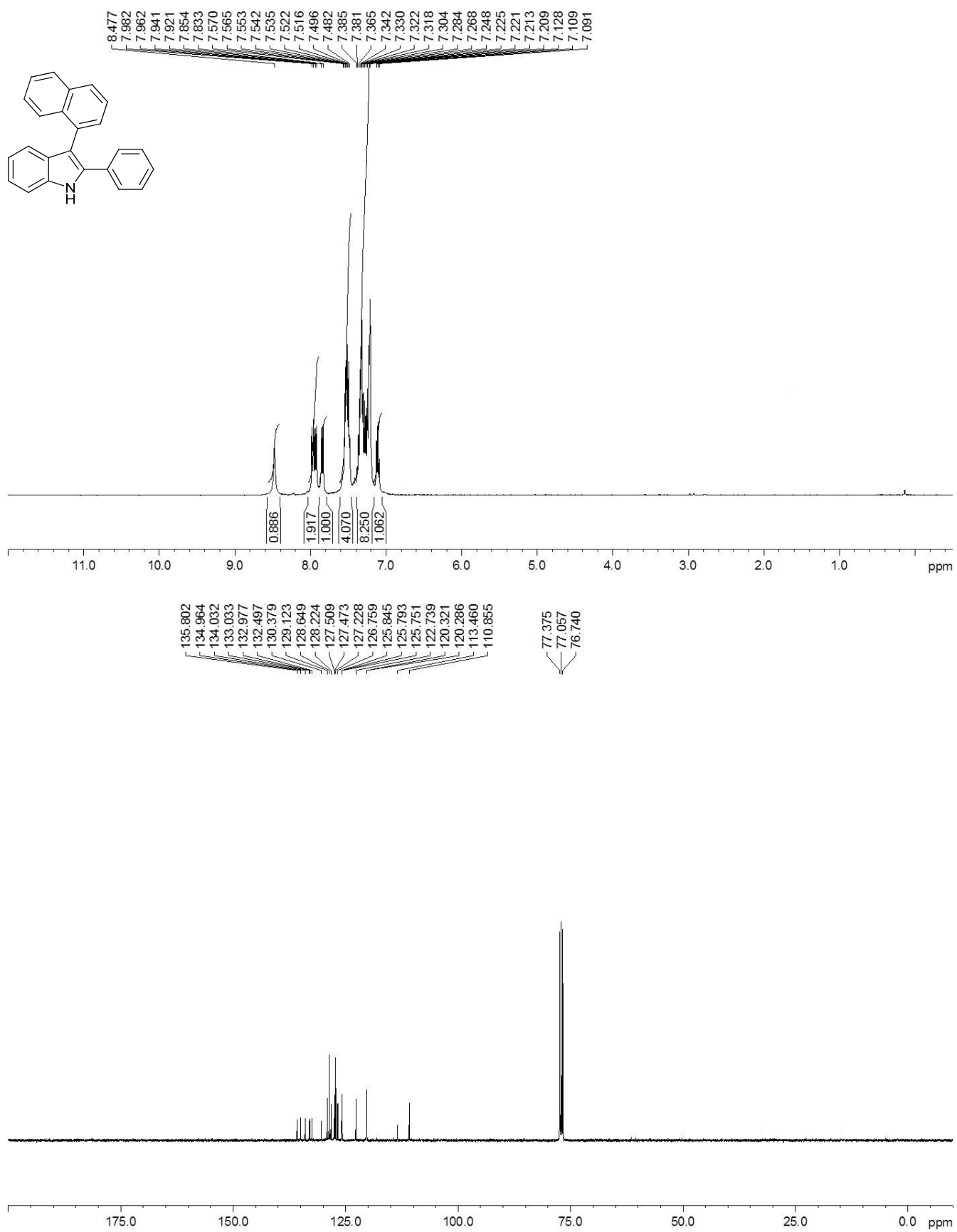


### NMR Spectra (new compounds)

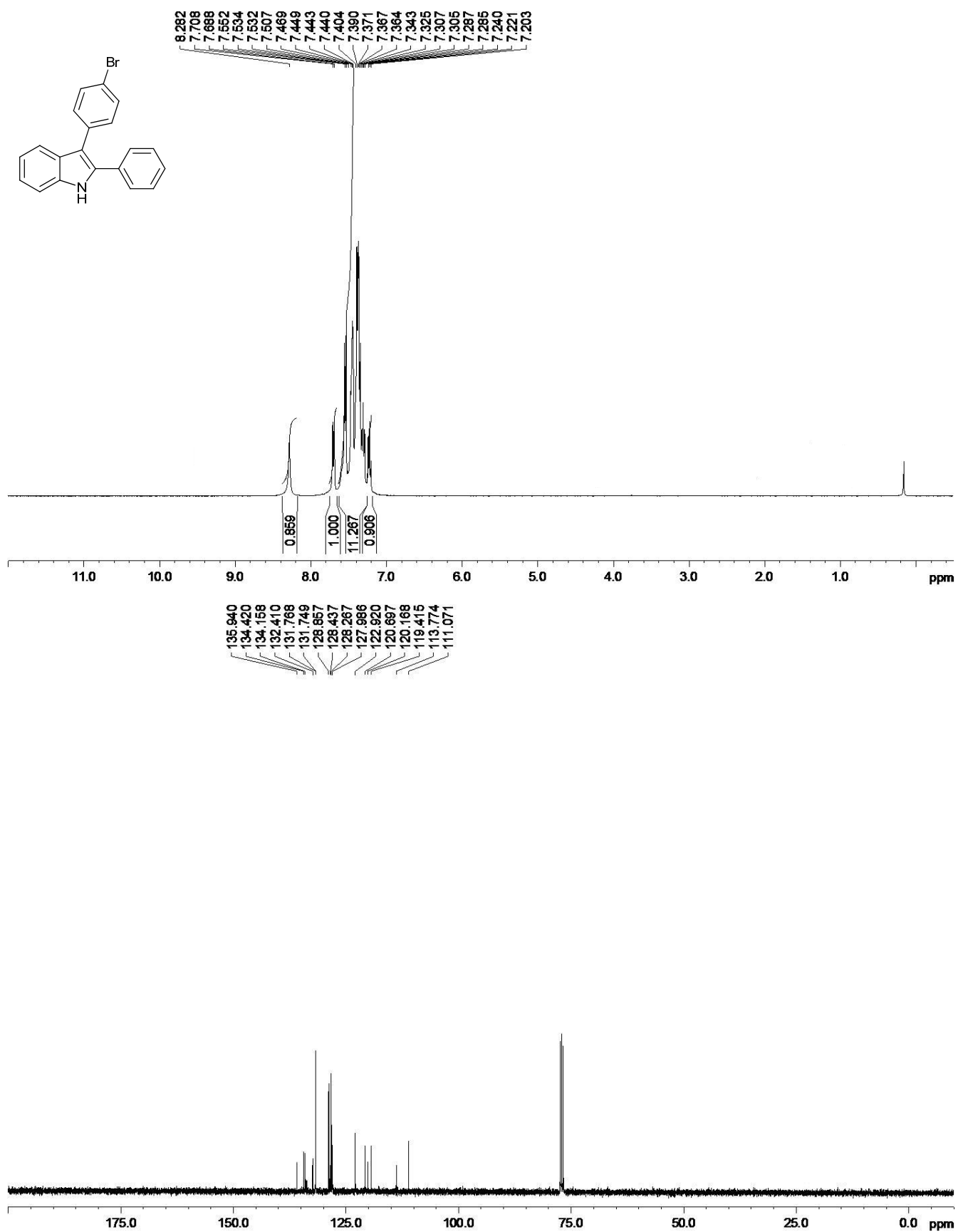
3c



3f

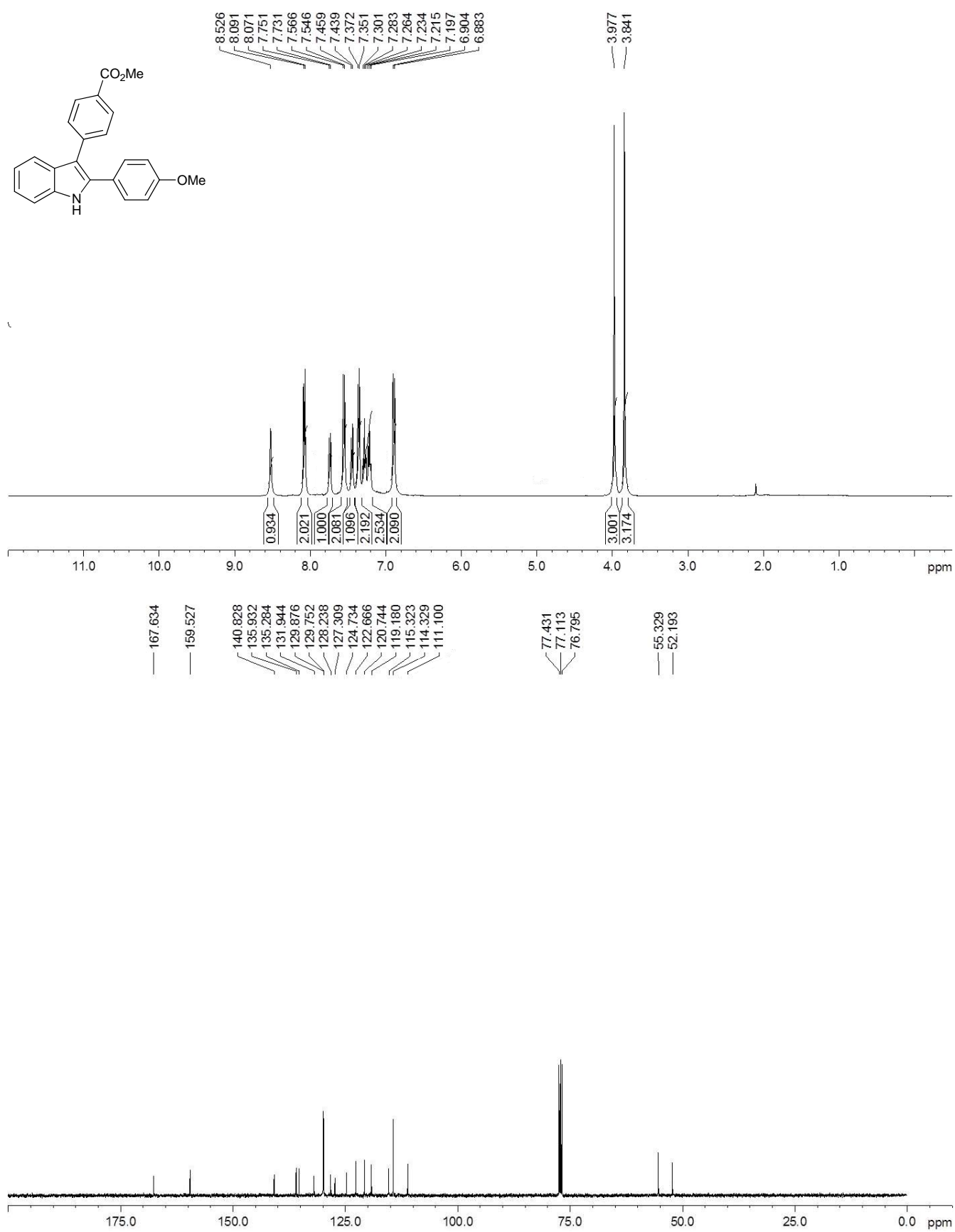


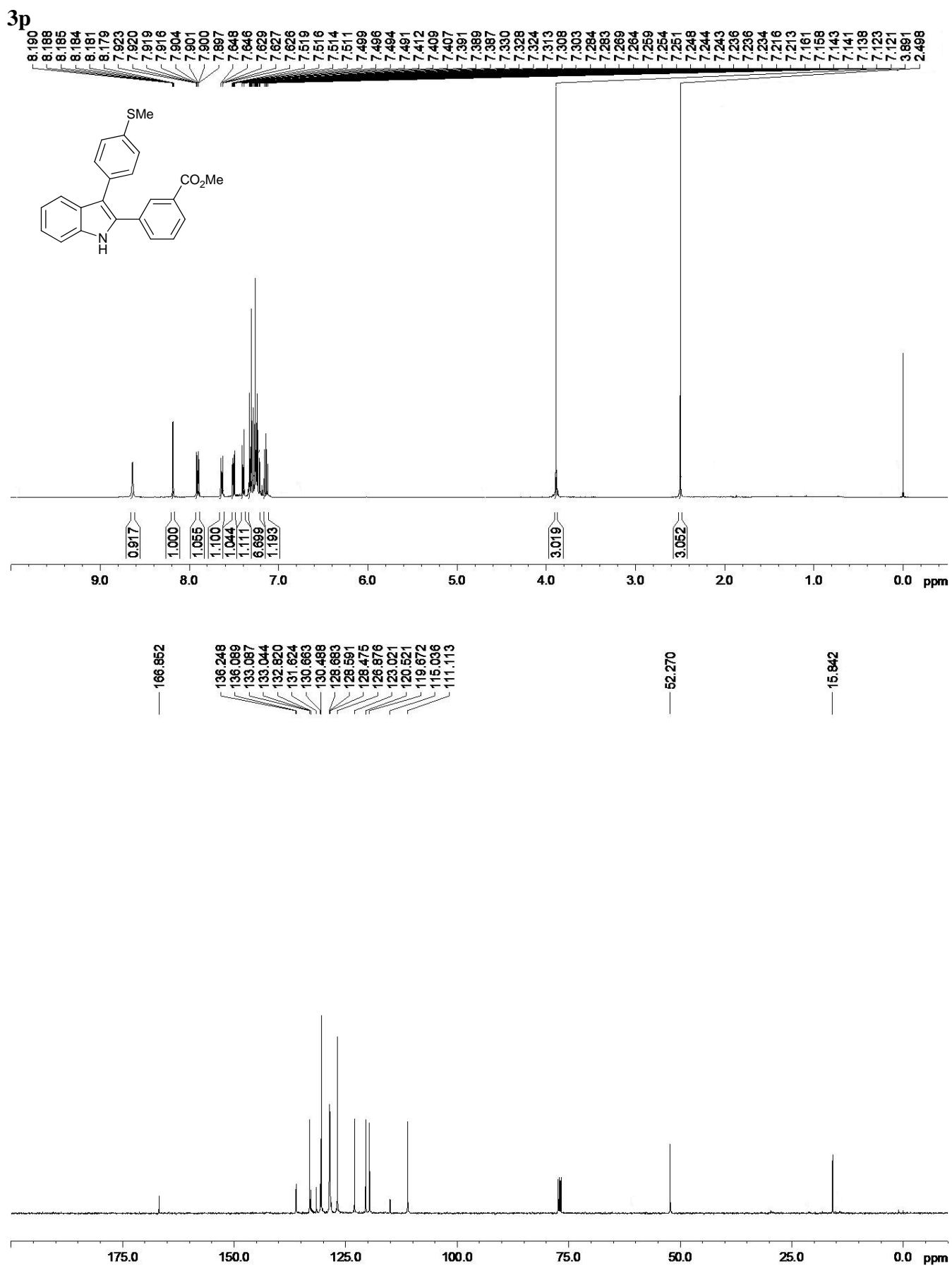
3h





3n





**3n**

