

Supporting Information For

Preparation of Indoles via Iron-Catalyzed Direct Oxidative Coupling

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Context

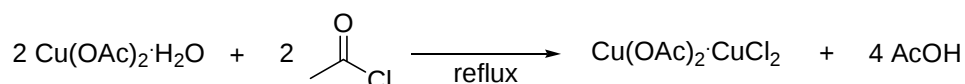
1. General information	-----S2
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General information:

Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 or DMSO (d^6) and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 or DMSO (d^6). Copies of ^1H NMR and ^{13}C NMR spectra are provided. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. The substrates **1** were prepared according to the following literatures:

- (a) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* 2008, **47**, 7230.

Preparation of $\text{Cu}(\text{OAc})_2\cdot\text{CuCl}_2$:

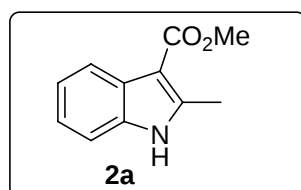


A 100 mL, twp-necked, flask charged with 10 g of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ was equipped with a magnetic stirring bar, a 50 mL pressure-equalizing dropping funnel, and a reflux condenser. Acetyl chloride (30 mL) was added dropwise over a 10 min period, and then the mixture was refluxed with stirring for 2 h. After the flask was cooled to room temperature, the precipitate was collected by filtration using a Büchner funnel, the collected solid was washed with 20 mL of anhydrous diethyl ether, and dried in vacuo to afford $\text{Cu}(\text{OAc})_2\cdot\text{CuCl}_2$ as yellow brown solid. (**Caution!** Acetyl chloride is eye irritants. All operations with this reagent should be carried out in a well-ventilated hood.)

Typical procedure for Fe-Catalyzed intramolecular oxidative coupling of **1**:

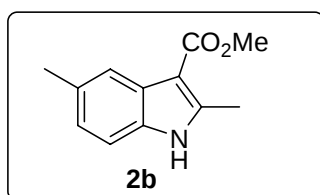
The mixture of methyl (Z)-3-(phenylamino)but-2-enoate (**1a**; 57 mg, 0.3 mmol), FeCl_3 (4.8 mg, 10 mol%), $\text{Cu}(\text{OAc})_2\cdot\text{CuCl}_2$ (142 mg, 0.45 mmol) and K_2CO_3 (124 mg, 0.9 mmol) was stirred in DMF (3 mL) at 120 °C for 2h. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (15 mL), and washed with $\text{NH}_3\cdot\text{H}_2\text{O}$ (10%, aq) (20 mL). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The desired indole **2a** (41 mg) was obtained in 72% yield after purification by flash chromatography on silica gel with hexane/ethyl acetate/triethylamine (100:20:3) as the eluent.

Spectroscopic data for products **2**

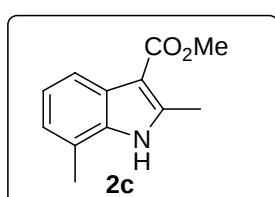


Methyl 2-methyl-indole-3-carboxylate 2a: ^1H NMR (400 MHz, CDCl_3) δ 8.66 (s, 1H), 8.12-8.10 (d, $J = 7.6$ Hz, 1H), 7.32-7.30 (d, $J = 7.6$ Hz, 1H), 7.24-6.18 (m, 2H), 3.95 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 144.1, 134.5, 127.1,

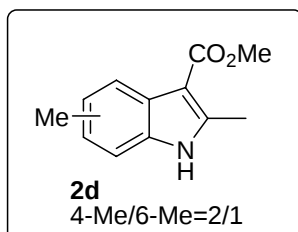
122.3, 121.7, 121.2, 110.5, 104.4, 50.8, 14.1. m/z (EI): 189.0, 174.0, 158.0.



Methyl-2,5-dimethyl-3-indolecarboxylate 2b: ^1H NMR (400 MHz, CDCl_3) δ 8.62 (s, 1H), 7.89 (s, 1H), 7.16-7.14 (d, $J = 8.0$ Hz, 1H), 7.01-6.99 (d, $J = 8.0$ Hz, 1H), 3.93 (s, 3H), 2.68 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 144.2, 132.7, 131.1, 127.3, 123.7, 120.9, 110.2, 103.8, 50.7, 21.6, 14.2. m/z (EI): 203.0, 172.0, 143.0.

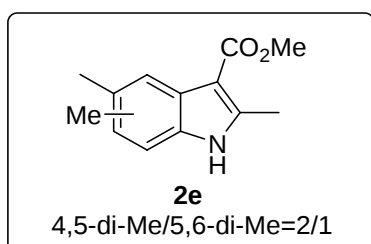


Methyl-2,7-dimethyl-3-indolecarboxylate 2c: ^1H NMR (400 MHz, CDCl_3) δ 8.66 (s, 1H), 7.94-7.92 (d, $J = 8.0$ Hz, 1H), 7.15-7.11 (t, $J = 7.6$ Hz, 1H), 6.99-6.97 (d, $J = 7.2$ Hz, 1H), 3.93 (s, 3H), 2.73 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 143.8, 133.9, 126.7, 122.9, 121.8, 119.7, 118.8, 104.7, 50.8, 16.4, 14.2. m/z (EI): 203.0, 172.0, 143.0.



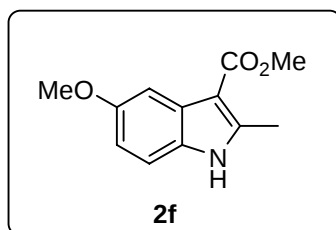
2d: Methyl-2,4-dimethyl-3-indolecarboxylate ^1H NMR (400 MHz, CDCl_3) δ 8.59 (s, 1H), 7.12-7.09 (d, $J = 7.6$ Hz, 1H), 7.04-7.02 (m, 1H), 6.97-6.95 (d, $J = 6.8$ Hz, 1H), 3.89 (s, 3H), 2.69 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 142.3, 135.1, 131.2, 125.4, 123.8, 122.4, 108.4, 105.9, 50.9, 22.2, 14.4. m/z (EI): 203.0, 172.0, 143.0.

Methyl-2,6-dimethyl-3-indolecarboxylate ^1H NMR (400 MHz, CDCl_3) δ 8.52 (s, 1H), 7.95-7.93 (d, $J = 8.4$ Hz, 1H), 7.08-7.06 (m, 2H), 3.92 (s, 3H), 2.68 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 143.5, 134.9, 132.1, 124.8, 123.2, 120.8, 110.6, 104.1, 50.7, 21.5, 14.1. m/z (EI): 203.0, 172.0, 143.0.

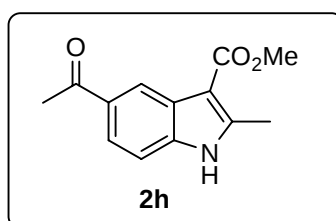


2e: Methyl-2,4,5-trimethyl-3-indolecarboxylate ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 6.99-6.94 (m, 2H), 3.89 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 141.9, 133.9, 131.1, 129.4, 126.1, 124.9, 107.8, 105.6, 50.9, 20.3, 17.2, 14.2. m/z (EI): 217.0, 186.0, 185.0, 157.0.

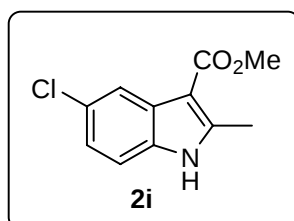
Methyl-2,5,6-trimethyl-3-indolecarboxylate ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 7.82 (s, 1H), 6.93 (s, 1H), 3.91 (s, 3H), 2.61 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 143.5, 133.4, 130.2, 128.6, 125.3, 121.1, 111.1, 103.4, 50.7, 20.2, 20.1, 14.0. m/z (EI): 217.0, 186.0, 185.0, 157.0.



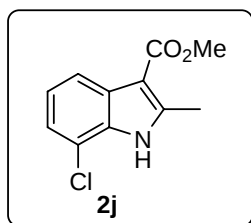
Methyl 5-methoxy-2-methyl-indole-3-carboxylate 2f: ^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 7.62 (s, 1H), 7.20-7.18 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1H), 6.85-6.83 (d, $J = 8.8$ Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 155.6, 144.2, 129.3, 128.1, 112.1, 111.2, 104.3, 103.4, 55.8, 50.8, 14.4. m/z (EI): 219.0, 204.0, 188.0.



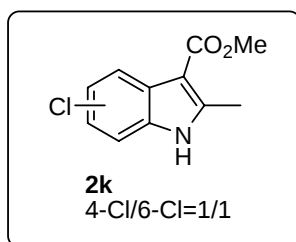
Methyl 5-acetyl-2-methyl-indole-3-carboxylate 2h: ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 12.19 (s, 1H), 8.57 (s, 1H), 7.79-7.77 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1H), 7.45-7.43 (d, $J = 8.4$ Hz, 1H), 3.85 (s, 3H), 2.68 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 197.9, 165.6, 147.1, 137.9, 130.9, 126.8, 122.6, 122.2, 111.6, 104.3, 51.2, 27.2, 14.2.



Methyl-5-chloro-2-methyl-indole-3-carboxylate 2i: ^1H NMR (400 MHz, CDCl_3) δ 8.66 (s, 1H), 8.05 (d, $J = 1.2$ Hz, 1H), 7.21-7.19 (d, $J = 8.4$ Hz, 1H), 7.15-7.12 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1H), 3.93 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 145.3, 132.8, 128.2, 127.5, 122.6, 120.9, 111.5, 104.3, 50.9, 14.2. m/z (EI): 225.0, 223.0, 210.0, 208.0, 194.0, 192.0, 128.0.

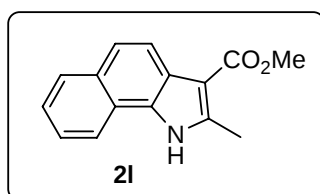


Methyl-7-chloro-2-methyl-indole-3-carboxylate 2j: ^1H NMR (400 MHz, CDCl_3) δ 8.60 (s, 1H), 8.00 (m, 1H), 7.21-7.14 (m, 2H), 3.95 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 144.5, 131.7, 128.5, 122.4, 121.7, 119.9, 115.9, 105.6, 50.9, 14.2. m/z (EI): 225.0, 223.0, 208.0, 192.0.

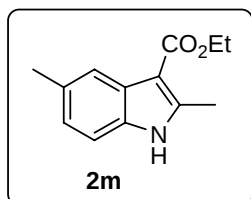


2k: Methyl-4-chloro-2-methyl-indole-3-carboxylate: ^1H NMR (400 MHz, CDCl_3) δ 9.19 (s, 1H), 7.18-7.16 (d, $J = 8.4$ Hz, 2H), 7.06-7.02 (t, $J = 8.4$ Hz, 1H), 3.92 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 142.4, 136.4, 125.5, 123.9, 123.1, 122.7, 109.4, 105.5, 51.2, 13.6. m/z (EI): 225.0, 223.0, 208.0, 192.0.

Methyl-6-chloro-2-methyl-indole-3-carboxylate: ^1H NMR (400 MHz, $\text{DMSO}-d^6$) δ 11.97 (s, 1H), 7.88-7.86 (d, $J = 8.4$ Hz, 1H), 7.39 (s, 1H), 7.14-7.11 (d, $J = 8.4$ Hz, 1H), 3.80 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d^6$) δ 165.6, 146.2, 135.7, 126.7, 125.9, 122.0, 121.6, 111.4, 103.2, 51.0, 14.1. m/z (EI): 225.0, 223.0, 208.0, 192.0.

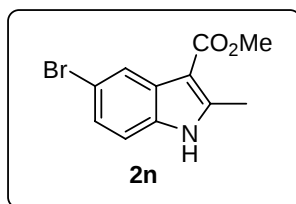


Methyl 2-methyl-benz[gl]indole-3-carboxylate 2l: ^1H NMR (400 MHz, $\text{DMSO}-d^6$) δ 12.57 (s, 1H), 8.36-8.34 (d, $J = 8.4$ Hz, 1H), 8.08-8.06 (d, $J = 8.8$ Hz, 1H), 7.94-7.92 (d, $J = 8.0$ Hz, 1H), 7.59-7.54 (m, 2H), 7.45-7.41 (t, $J = 8.0$ Hz, 1H), 3.84 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d^6$) δ 166.0, 142.7, 130.1, 129.6, 128.8, 126.2, 124.4, 123.3, 121.9, 121.7, 120.9, 120.8, 104.9, 51.0, 14.2. m/z (EI): 239.0, 208.0.

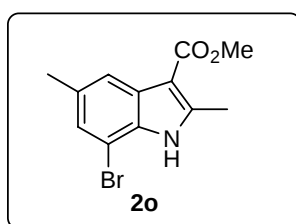


Ethyl 2,5-dimethyl-indole-3-carboxylate 2m: ^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.90 (s, 1H), 7.18-7.16 (d, $J = 8.0$ Hz, 1H), 7.01-6.99 (d, $J = 8.0$ Hz, 1H),

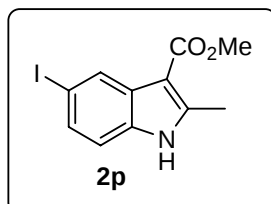
4.41-4.37 (m, 2H), 2.71 (s, 3H), 2.46 (s, 3H), 1.46-1.43 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 143.8, 132.7, 131.0, 127.4, 123.7, 121.0, 110.1, 104.1, 50.4, 21.6, 14.6, 14.3. m/z (EI): 217.0, 172.0.



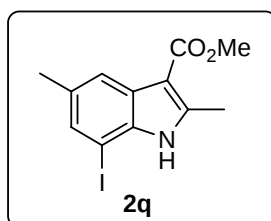
Methyl 5-bromo-2-methyl-indole-3-carboxylate 2n: ^1H NMR (400 MHz, CDCl_3) δ 8.67 (s, 1H), 8.21 (s, 1H), 7.28-7.26 (d, $J = 8.8$ Hz, 1H), 7.17-7.15 (d, $J = 8.4$ Hz, 1H), 3.93 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 145.2, 133.1, 128.7, 125.2, 123.8, 115.2, 111.9, 104.1, 50.9, 14.2.



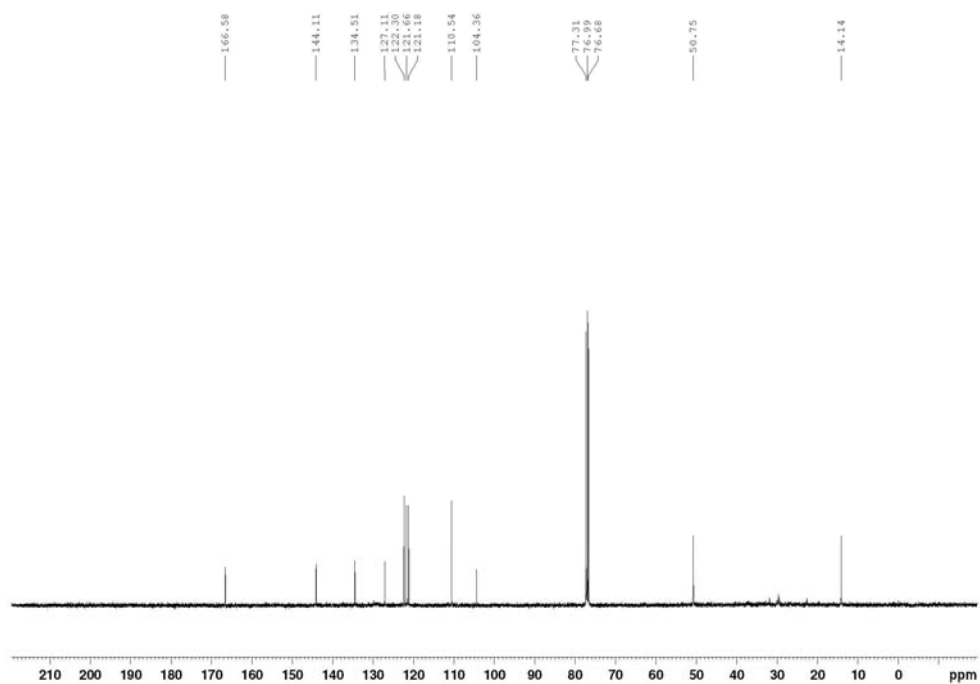
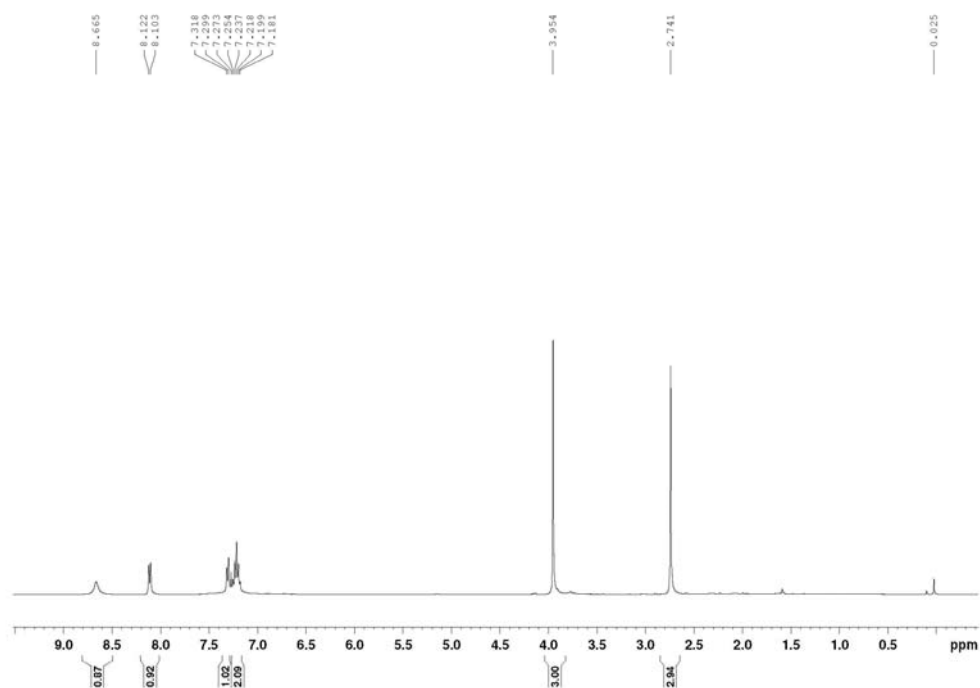
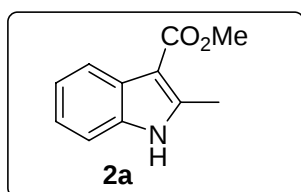
Methyl 7-bromo-2,5-dimethyl-indole-3-carboxylate 2o: ^1H NMR (400 MHz, CDCl_3) δ 8.51 (s, 1H), 7.81 (s, 1H), 7.17 (s, 1H), 3.93 (s, 3H), 2.75 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 144.4, 132.7, 131.4, 128.4, 125.9, 120.3, 105.2, 103.4, 50.9, 21.3, 14.2.

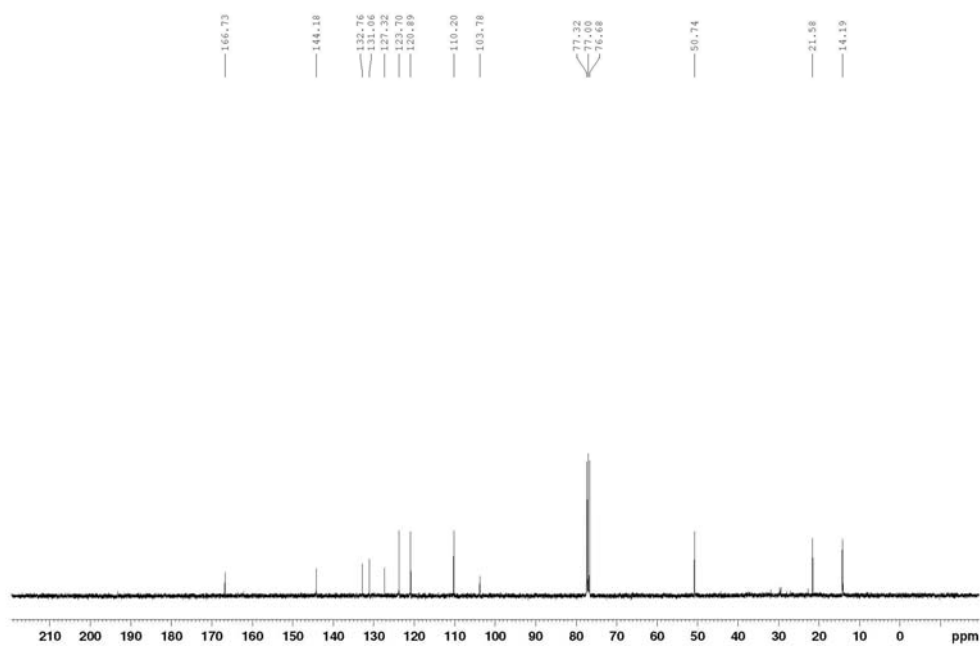
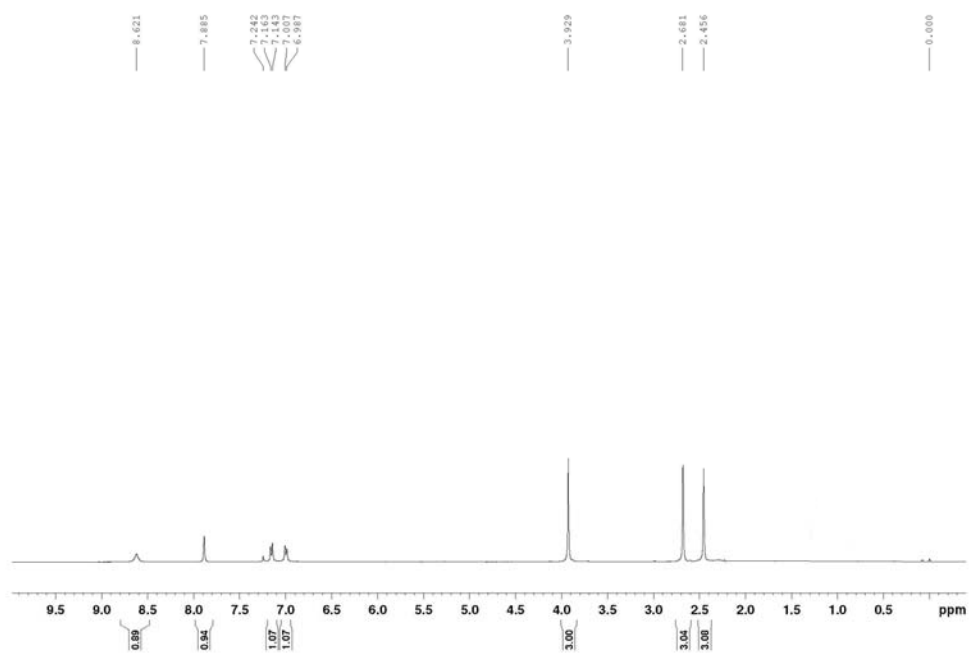
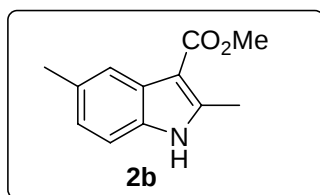


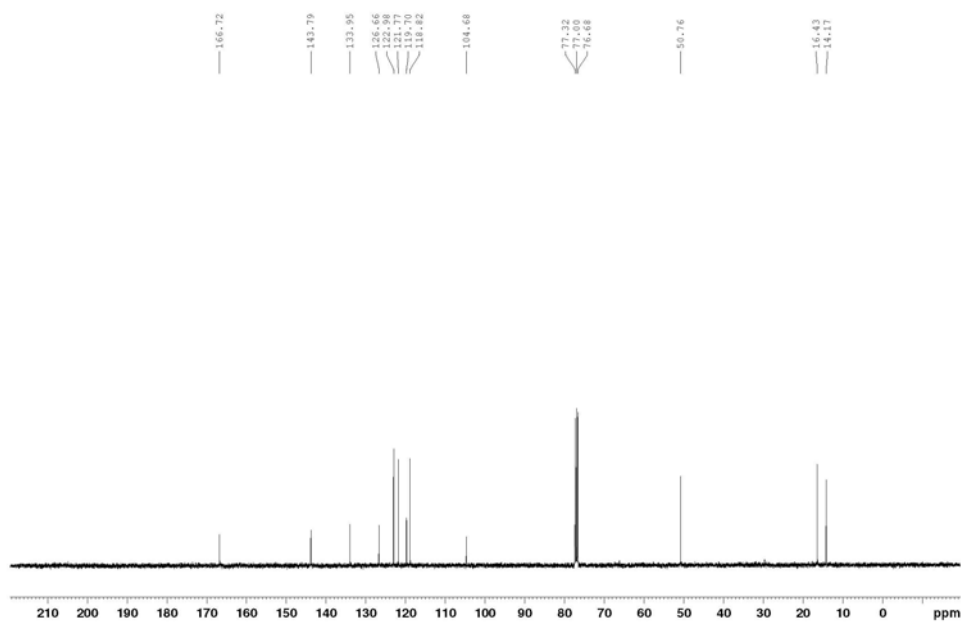
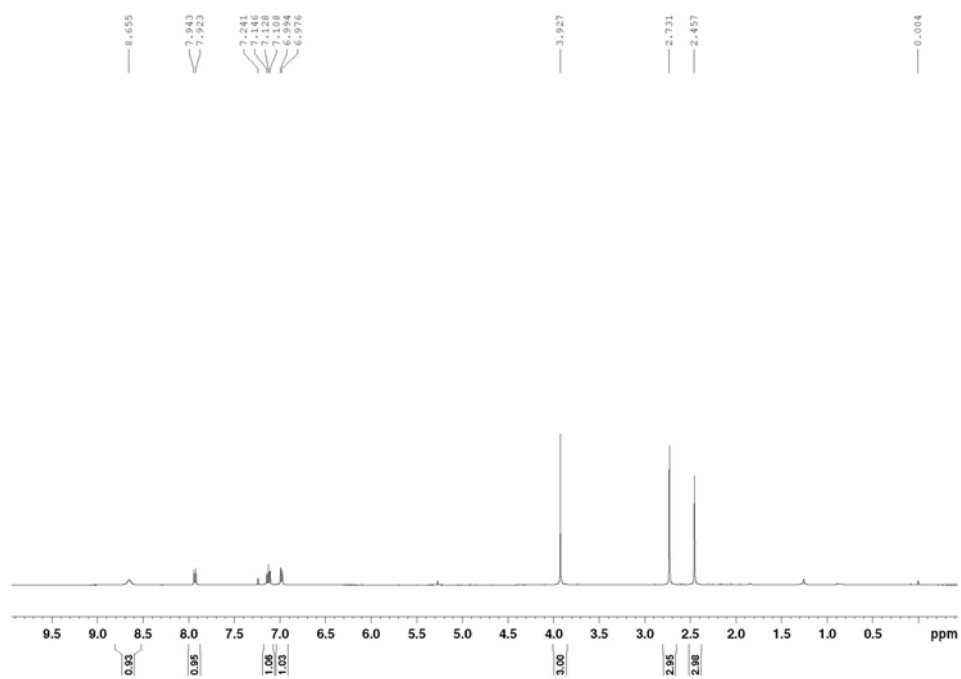
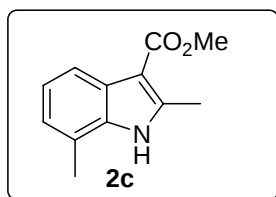
Methyl 5-iodo-2-methyl-indole-3-carboxylate 2p: ^1H NMR (400 MHz, $\text{DMSO}-d^6$) δ 12.02 (s, 1H), 8.22 (s, 1H), 7.41-7.38 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1H), 7.22-7.20 (d, $J = 8.4$ Hz, 1H), 3.80 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d^6$) δ 165.5, 146.1, 134.4, 130.2, 129.7, 129.0, 114.1, 102.4, 85.9, 51.1, 14.1.

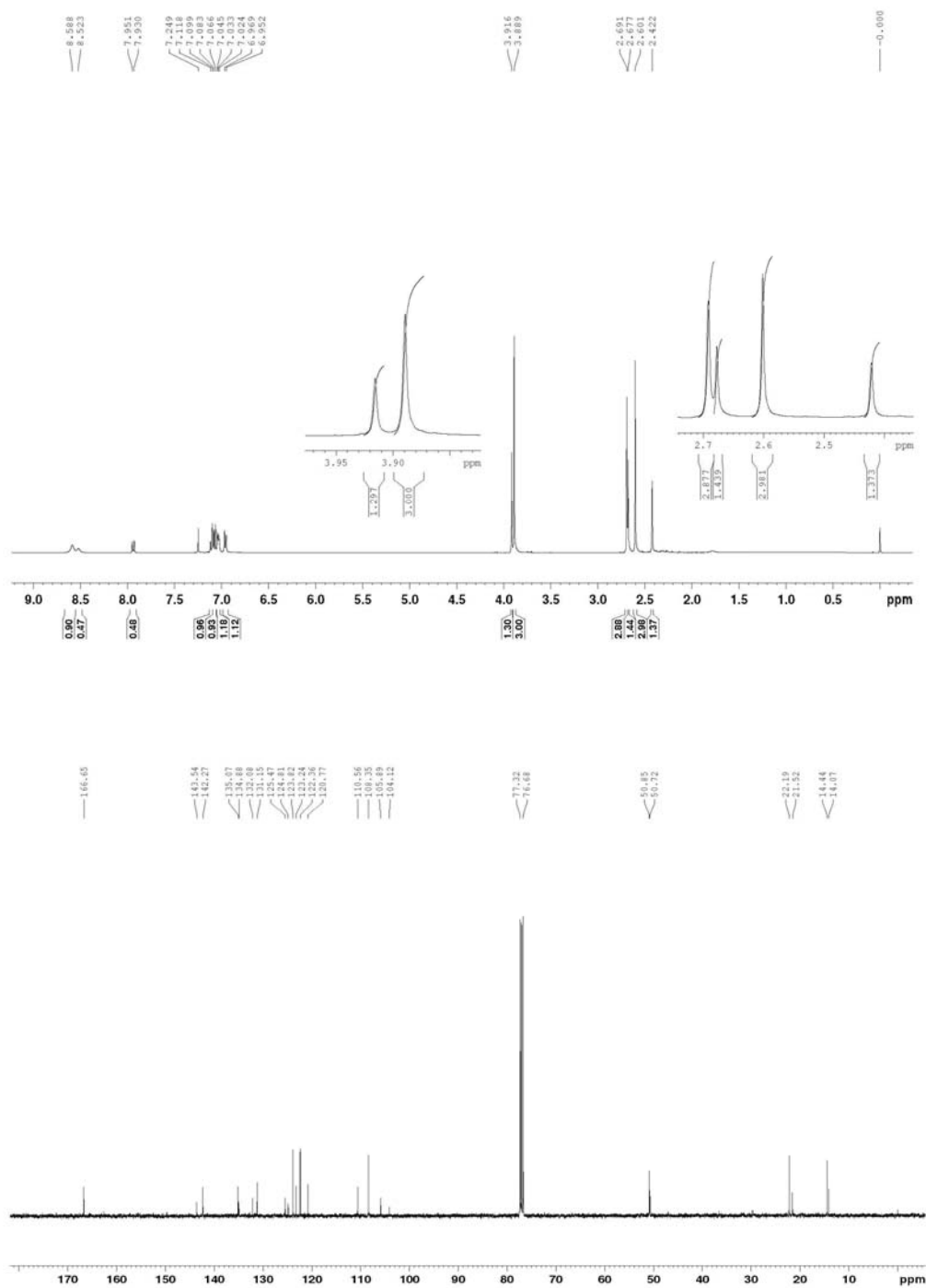
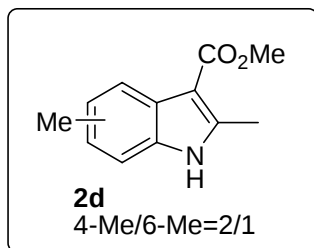


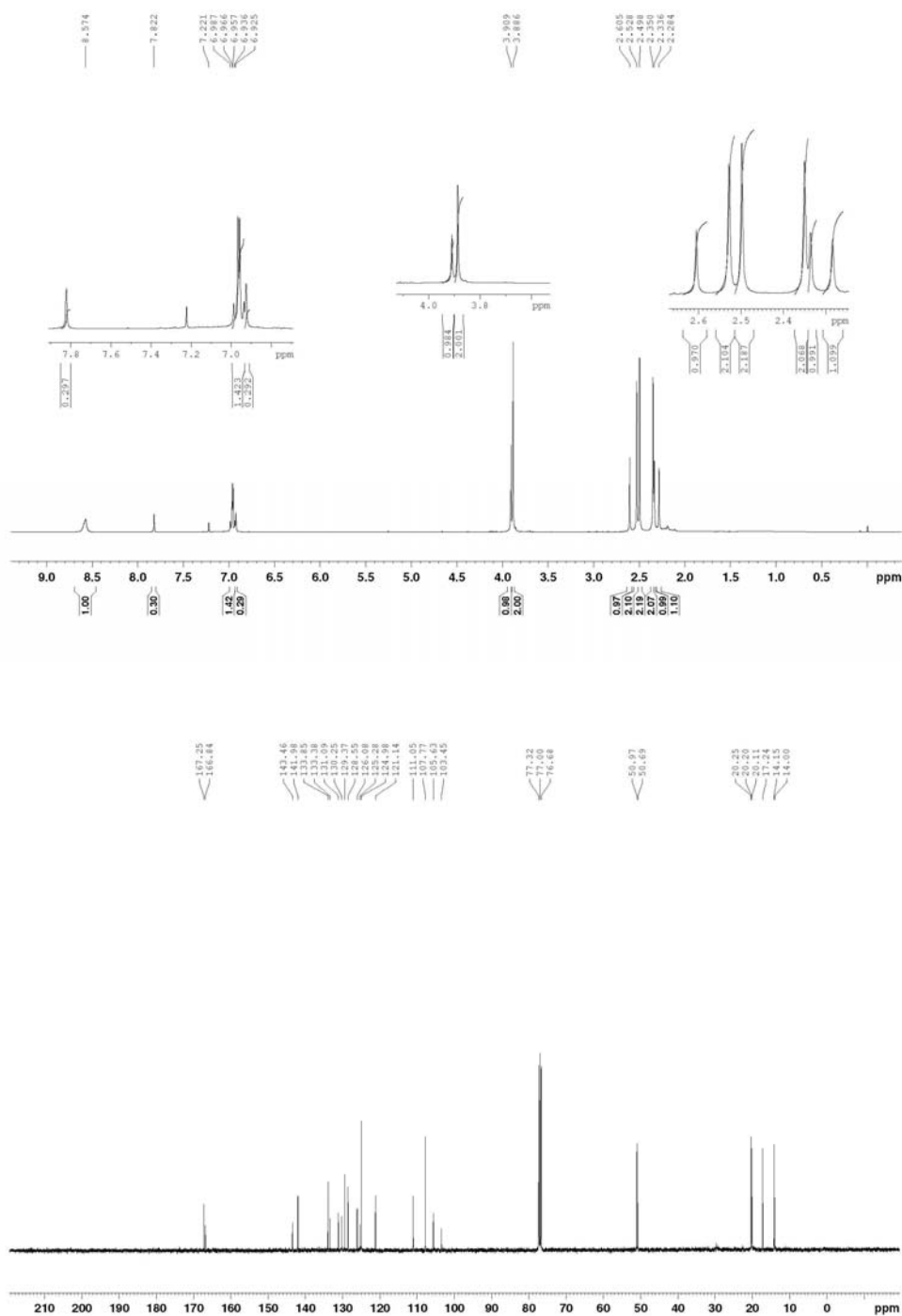
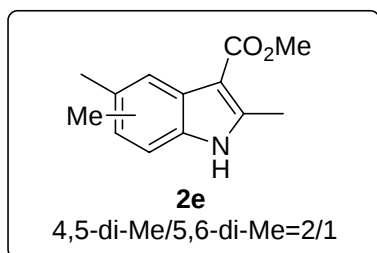
Methyl 7-iodo-2,5-dimethyl-indole-3-carboxylate 2q: ^1H NMR (400 MHz, $\text{DMSO}-d^6$) δ 11.52 (s, 1H), 7.72 (s, 1H), 7.36 (s, 1H), 3.79 (s, 3H), 2.66 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d^6$) δ 165.8, 146.4, 135.7, 132.3, 132.2, 127.8, 120.7, 103.9, 76.6, 51.0, 21.1, 14.0.

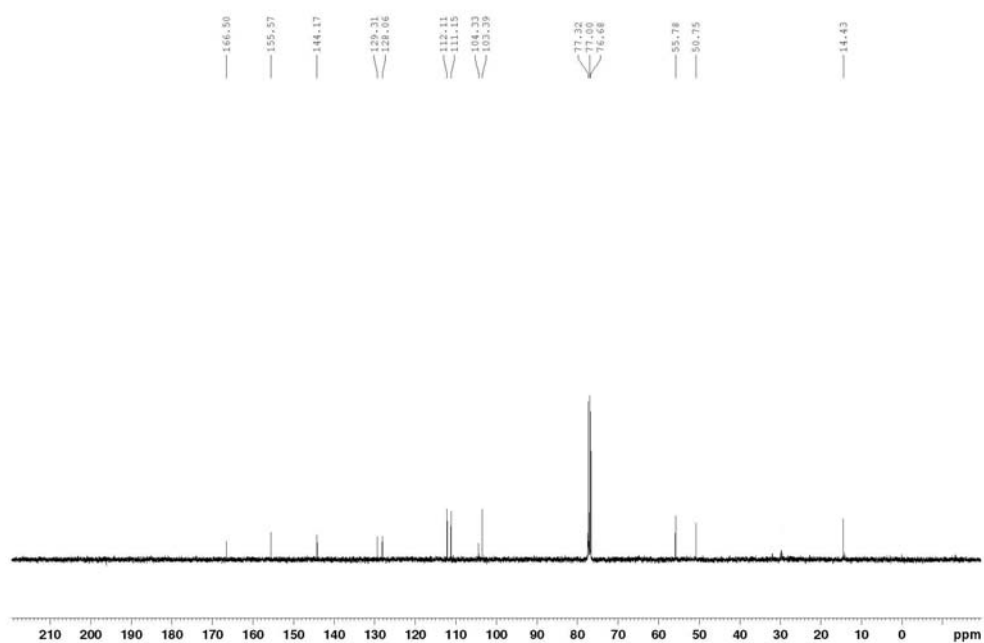
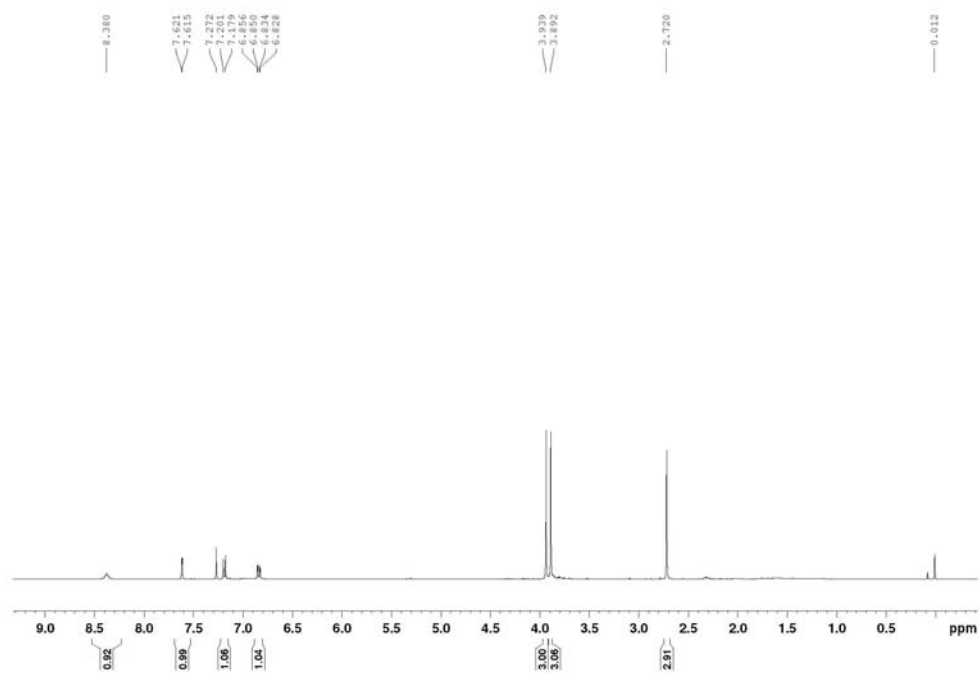
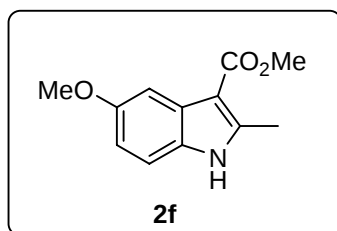


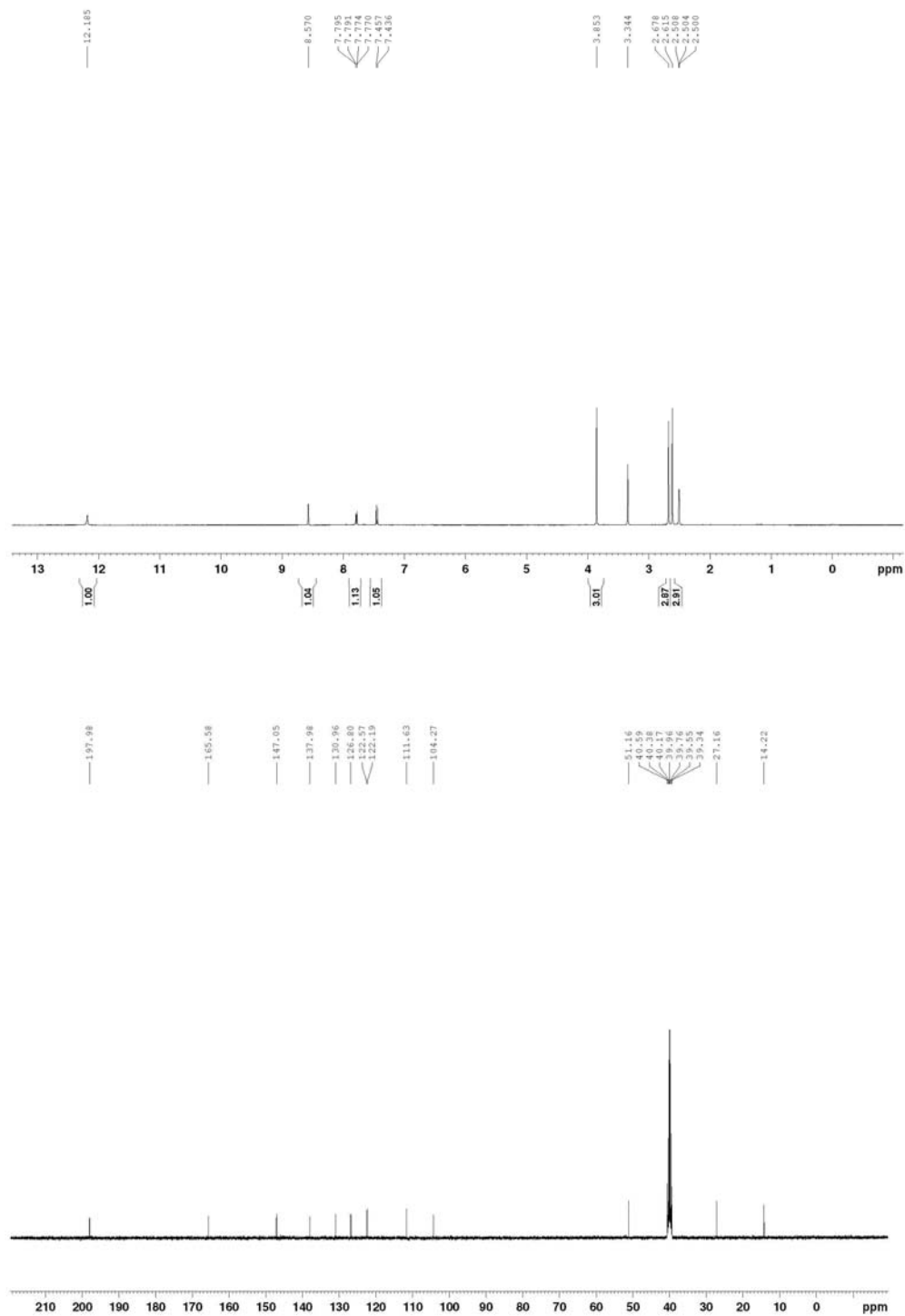
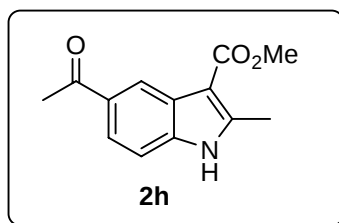


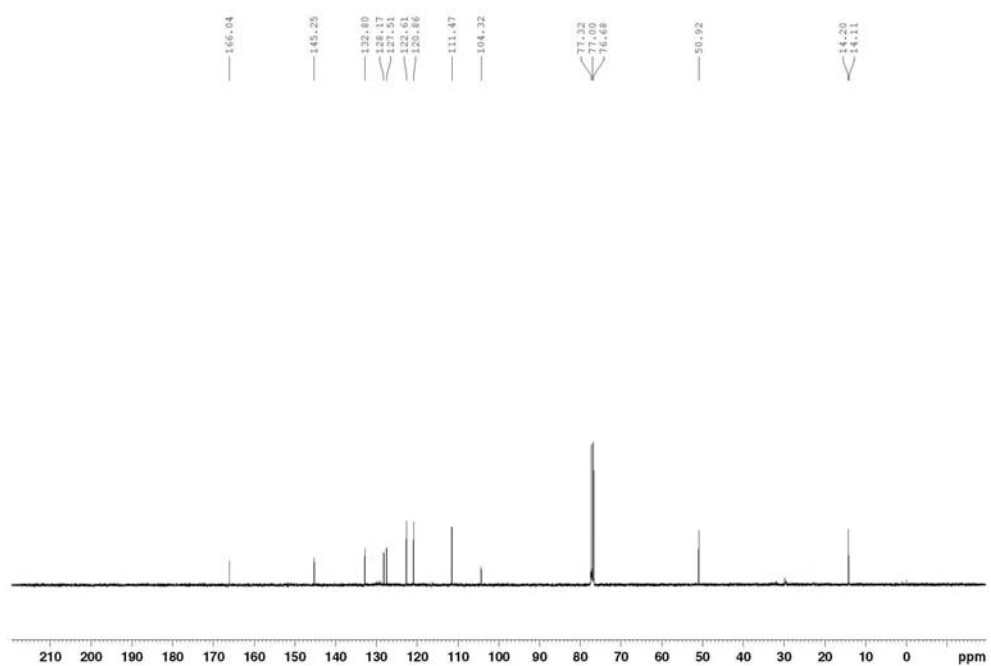
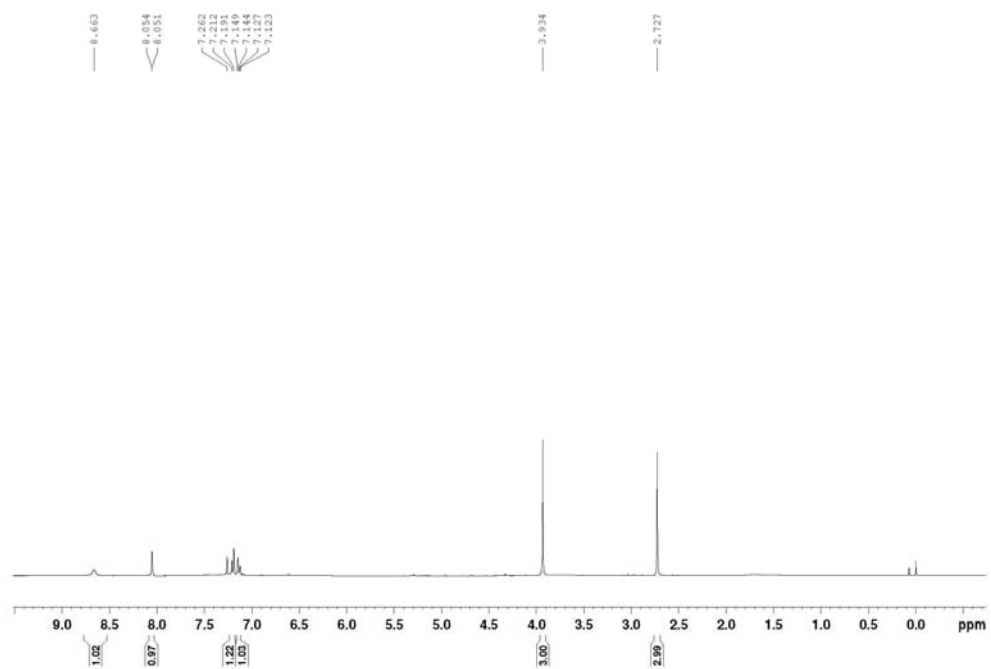
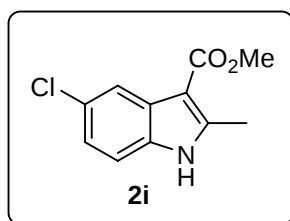


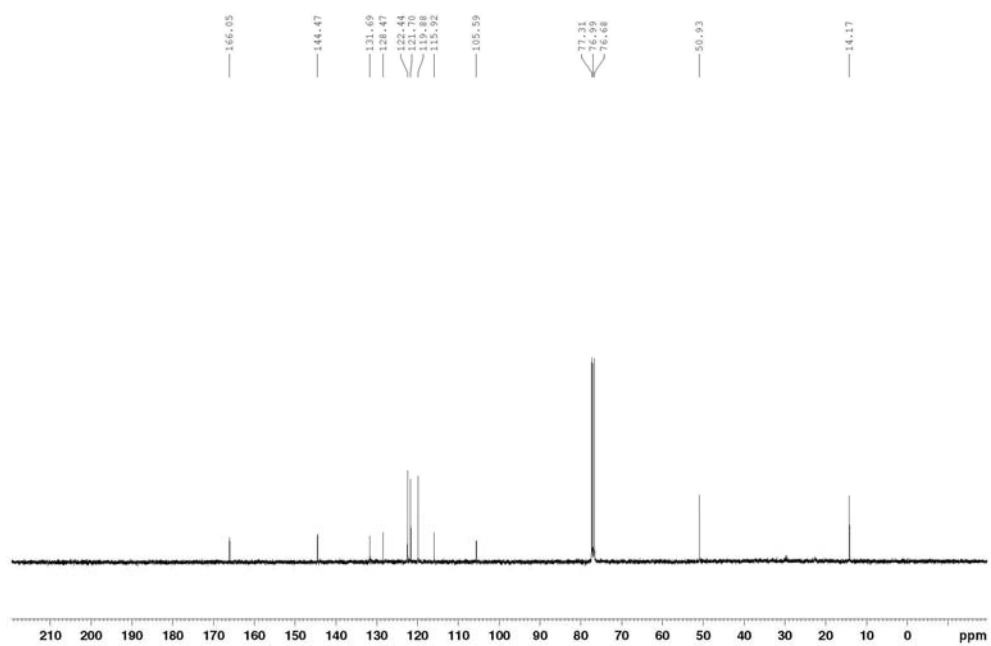
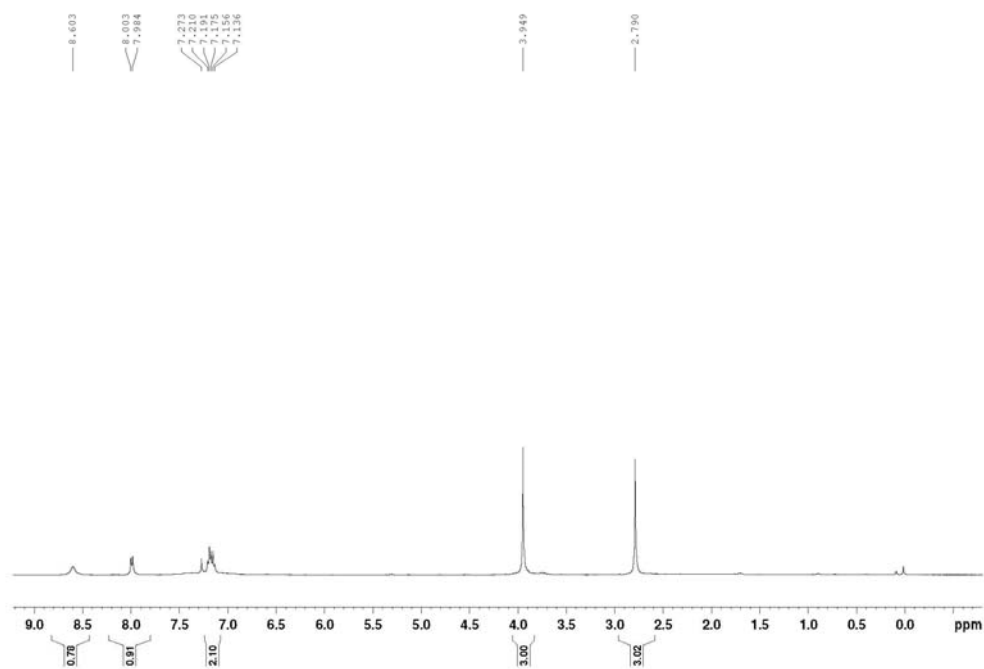
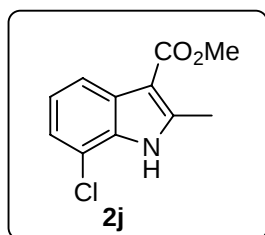


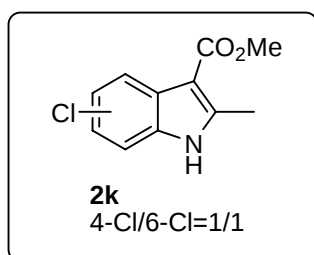




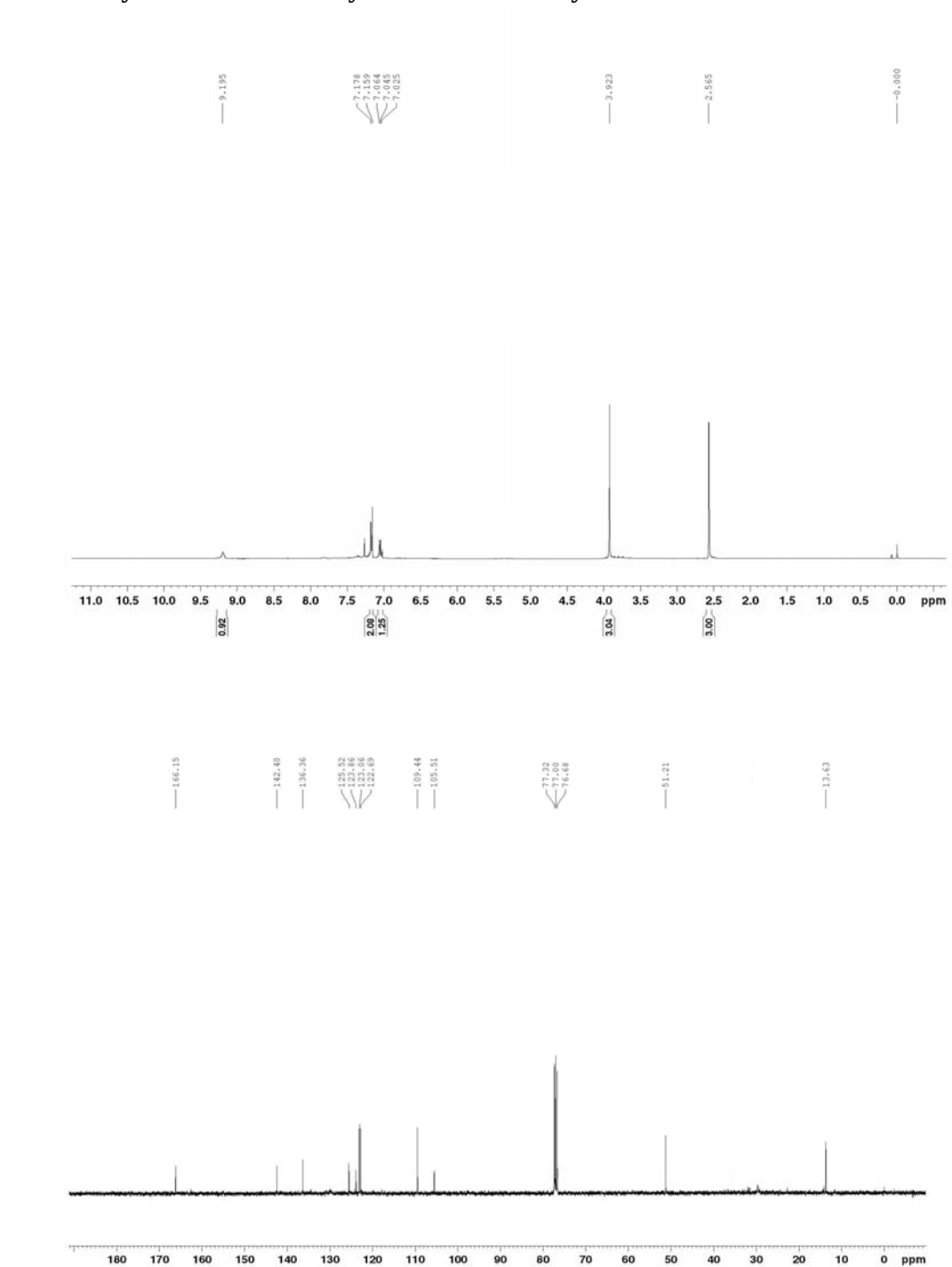


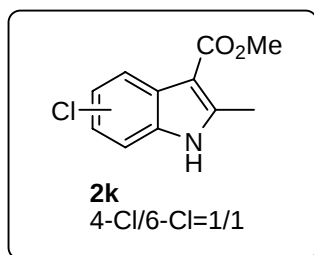






2k: Methyl-4-chloro-2-methyl-indole-3-carboxylate:





2k: Methyl-6-chloro-2-methyl-indole-3-carboxylate:

