

## Supporting Information

### An Oxidative Coupling between C-H/ C-H Bonds of Indoles and Cyclic Ethers or Cycloalkanes

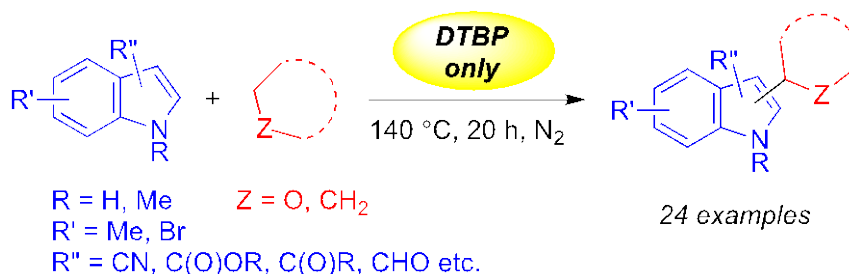
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## 1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All the reactions were performed in Rotaflo®(England) resealable screw-cap tube (approx. 10 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). Dioxane and tetrahydrofuran were freshly distilled over sodium under nitrogen.<sup>1</sup> Thin layer chromatography was performed on precoated silica gel 60 F<sub>254</sub> plates. Silica gel (230-400 mesh) was used for column chromatography. <sup>1</sup>H NMR spectra were recorded on a 400 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl<sub>3</sub> (δ 7.26 ppm), or with TMS (δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. <sup>13</sup>C NMR spectra were recorded on a 100 MHz spectrometer and the spectra were referenced to CDCl<sub>3</sub> (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on an ESI-QToF mass spectrometer which the ionization method is electrospray ionization (ESI) and the mass analyzer is a quadrupole time-of-flight mass analyzer.

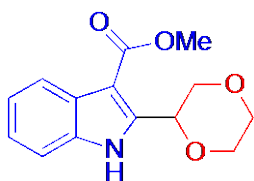
## 2. General procedures for CDC of ethers/ cycloalkanes with indoles

DTBP was added to a mixture of indole (0.50 mmol) and ether/cycloalkane (2 mL) in a Schlenk tube at room temperature under nitrogen atmosphere. The tube was then placed into a preheated oil bath (140 °C) and stirred for 20 hours. After completion of reaction,

the reaction tube was allowed to cool to room temperature and quenched with water and diluted with ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (230-400 mesh) to afford the desired product.

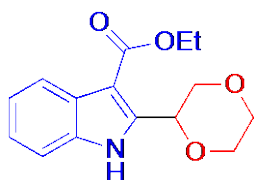
### 3. Characterization data

#### Methyl 2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3aa)



EA:hexane = 1:2,  $R_f$  = 0.4, white solid, 78% (102 mg), m.p. = 167-168 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.13 (s, 1H), 7.43-7.40 (m, 1H), 7.29-7.26 (m, 2H), 5.54 (dd,  $J$  = 11.28, 2.72 Hz, 1H), 4.33 (dd,  $J$  = 11.2, 2.8 Hz, 1H), 4.02-4.0 (m, 2H), 3.96 (s, 3H), 3.87 (d,  $J$  = 11.52 Hz, 1H), 3.78-3.71 (m, 1H), 3.38 (t,  $J$  = 9.2 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.4, 142.8, 134.5, 126.8, 123.0, 122.1, 121.6, 111.3, 103.5, 72.3, 70.2, 67.0, 66.4, 51.0. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_4$   $[\text{M} + \text{H}]^+$  262.1079, found 262.1082.

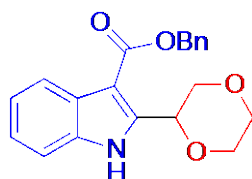
#### Ethyl 2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3ba)



EA:hexane = 1:3,  $R_f$  = 0.3, white solid, 64% (88 mg), m.p. = 160-161 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.06 (s, 1H), 8.16-8.13 (m, 1H), 7.39-7.36 (m, 1H), 7.25-7.23 (m, 2H), 5.51 (dd,  $J$  = 9.64, 2.80 Hz, 1H), 4.45-4.42 (m, 2H), 4.34 (dd,  $J$  = 14.20, 7.08 Hz, 1H),

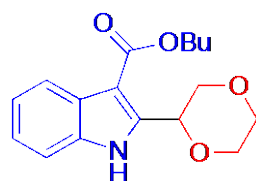
3.99-3.96 (m, 2H), 3.84 (d,  $J = 11.52$  Hz, 1H), 3.74-3.68 (m, 1H), 3.34 (t,  $J = 10.40$  Hz, 1H), 1.44 (t,  $J = 7.00$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.0, 142.7, 134.5, 126.9, 122.9, 122.0, 121.6, 111.2, 103.7, 72.3, 70.2, 67.0, 66.4, 59.8, 14.6. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_4$   $[\text{M} + \text{H}]^+$  276.1230, found 276.1233.

**Benzyl 2-(1,4-dioxan-2-yl)-1H-indole-3-carboxylate (Table 2, product 3ca)**



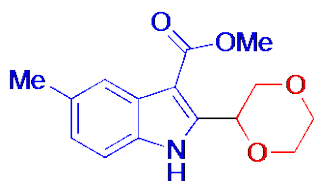
EA:hexane = 1:2,  $R_f = 0.4$ , white solid, 67% (113 mg), m.p. = 149-150 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.26 (s, 1H), 8.19 (d,  $J = 4.80$  Hz, 1H), 7.55-7.53 (m, 2H), 7.45-7.38 (m, 4H), 7.28 (s, 2H), 5.58 (d,  $J = 8.00$  Hz, 1H), 5.47 (s, 2H), 4.34 (d,  $J = 10.40$  Hz, 1H), 3.99-3.98 (m, 2H), 3.86 (d,  $J = 11.60$  Hz, 1H), 3.76-3.72 (m, 1H), 3.38 (t,  $J = 10.40$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 143.3, 136.6, 134.6, 128.6, 128.2, 128.1, 126.8, 123.0, 122.2, 121.7, 111.4, 103.4, 72.3, 70.2, 67.0, 66.4, 65.7. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_4$   $[\text{M} + \text{H}]^+$  338.1387, found 338.1388.

**Butyl 2-(1,4-dioxan-2-yl)-1H-indole-3-carboxylate (Table 2, product 3da)**



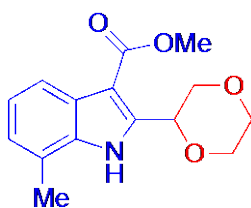
EA:hexane = 1:2,  $R_f = 0.5$ , white solid, 62% (94 mg), m.p. = 113-114 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.12 (s, 1H), 8.17-8.15 (m, 1H), 7.42-7.40 (m, 1H), 7.29-7.25 (m, 2H), 5.54 (dd,  $J = 9.60, 2.80$  Hz, 1H), 4.38 (t,  $J = 6.6$  Hz, 2H), 4.32 (dd,  $J = 11.2, 2.40$  Hz, 1H), 4.01 (d,  $J = 6.40$  Hz, 2H), 3.87 (d,  $J = 11.60$  Hz, 1H), 3.77-3.71 (m, 1H), 3.37 (t,  $J = 10.40$  Hz, 1H), 1.87-1.84 (m, 2H), 1.82-1.58 (m, 2H), 1.55 (t,  $J = 7.60$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.2, 142.7, 134.5, 126.9, 122.9, 122.0, 121.6, 111.3, 103.8, 72.4, 70.2, 67.0, 66.4, 63.8, 31.0, 19.4, 13.8. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{22}\text{NO}_4$   $[\text{M} + \text{H}]^+$  304.1543, found 304.1547.

**Methyl 2-(1,4-dioxan-2-yl)-5-methyl-1H-indole-3-carboxylate (Table 2, product 3ea)**



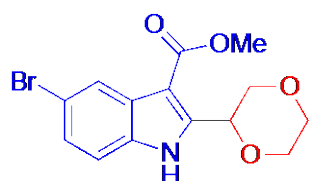
EA:hexane = 1:2,  $R_f$  = 0.3, white solid, 66% (91 mg), m.p. = 167-168 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.01 (s, 1H), 7.94 (s, 1H), 7.30 (s, 1H), 7.09 (d,  $J$  = 7.60 Hz, 1H), 5.52 (dd,  $J$  = 9.60, 2.80 Hz, 1H), 4.28 (dd,  $J$  = 11.60, 2.80 Hz, 1H), 4.27-3.99 (m, 2H), 3.96 (s, 3H), 3.87 (d,  $J$  = 11.60 Hz, 1H), 3.77-3.39 (m, 1H), 3.36 (t,  $J$  = 5.60 Hz, 1H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.5, 142.7, 132.8, 131.6, 127.1, 124.5, 121.2, 110.9, 103.0, 72.3, 70.2, 67.0, 66.4, 51.0, 21.6. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_4$  [ $\text{M} + \text{H}$ ] $^+$  276.1236, found 276.1237.

**Methyl 2-(1,4-dioxan-2-yl)-7-methyl-1H-indole-3-carboxylate (Table 2, product 3fa)**



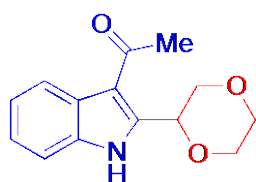
EA:hexane = 1:2,  $R_f$  = 0.4, white solid, 63% (87mg), m.p. = 151-152 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.96 (s, 1H), 7.99 (d,  $J$  = 8.0 Hz, 1H), 7.21-7.17 (t,  $J$  = 7.60 Hz, 1H), 7.08 (d,  $J$  = 7.20 Hz, 1H), 5.55 (dd,  $J$  = 9.60, 2.80 Hz, 1H), 4.30 (dd,  $J$  = 11.60, 2.80 Hz, 1H), 4.02 (dd,  $J$  = 7.20, 1.60 Hz, 2H), 3.97 (s, 3H), 3.96 (dd,  $J$  = 8.40, 5.2 Hz, 1H), 3.89-3.74 (m, 1H), 3.38 (t,  $J$  = 10.6 Hz, 1H), 2.55 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.5, 142.4, 134.0, 126.5, 123.6, 122.3, 120.5, 119.2, 103.9, 72.4, 70.2, 67.0, 66.4, 51.0, 16.5. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_4$  [ $\text{M} + \text{H}$ ] $^+$  276.1236, found 276.1234.

**Methyl 5-bromo-2-(1,4-dioxan-2-yl)-1H-indole-3-carboxylate (Table 2, product 3ga)**



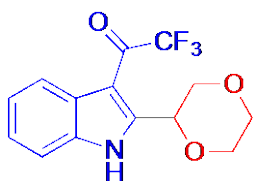
EA:hexane = 1:2,  $R_f$  = 0.3, yellow solid, 60% (102 mg), m.p. = 196-197 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.19 (s, 1H), 8.27 (s, 1H), 7.36-7.33 (m, 1H), 7.25 (s, 1H), 5.50 (dd,  $J$  = 10.00, 2.80 Hz, 1H), 4.32 (dd,  $J$  = 11.60, 2.80 Hz, 1H), 4.00-3.98 (m, 2H), 3.96 (s, 1H), 3.87 (d,  $J$  = 11.60 Hz, 1H), 3.72-3.69 (m, 1H), 3.35 (t,  $J$  = 10.6 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.0, 143.9, 133.1, 128.4, 126.0, 124.2, 115.6, 112.7, 103.2, 72.1, 70.0, 67.0, 66.4, 51.2. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{14}\text{BrNO}_4$   $[\text{M} + \text{H}]^+$  340.0184, found 340.0177.

**1-(2-(1,4-Dioxan-2-yl)-1H-indol-3-yl)ethanone (Table 2, product 3ha)**



EA:hexane = 1:2,  $R_f$  = 0.3, white solid, 60% (73.5 mg), m.p. = 212-213 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.34 (s, 1H), 7.94 (d,  $J$  = 7.20 Hz, 1H), 7.47 (d,  $J$  = 7.20 Hz, 1H), 7.33-7.30 (m, 2H), 5.55 (d,  $J$  = 7.60 Hz, 1H), 4.38 (d,  $J$  = 10.8 Hz, 1H), 3.99 (s, 2H), 3.89 (d,  $J$  = 11.20 Hz, 1H), 3.77-3.72 (m, 1H), 3.34 (t,  $J$  = 10.40 Hz, 1H), 2.73 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.1, 143.4, 134.7, 126.3, 122.8, 122.2, 120.5, 113.5, 111.9, 72.8, 69.7, 67.0, 66.4, 31.2. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_3$   $[\text{M} + \text{H}]^+$  246.1125, found 246.1129.

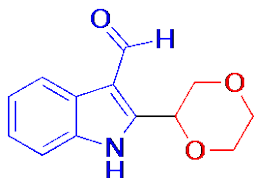
**1-(2-(1,4-Dioxan-2-yl)-1H-indol-3-yl)-2,2,2-trifluoroethanone (Table 2, product 3ia)**



EA:hexane = 1:2,  $R_f$  = 0.4, yellow solid, 77% (115 mg), m.p. = 209-210 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.59 (s, 1H), 8.00 (d,  $J$  = 5.2 Hz, 1H), 7.49-7.47 (m, 1H), 7.36-7.34 (m, 2H), 5.49 (dd,  $J$  = 9.60, 2.80 Hz, 1H), 4.37 (dd,  $J$  = 11.6, 2.8 Hz, 1H), 4.04 (d,  $J$  = 6.0 Hz, 2H), 3.91 (d,  $J$  = 11.6 Hz, 1H), 3.79-3.35 (m, 1H), 3.35 (t,  $J$  = 5.40 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.3 (q,  $J$  = 36.5 Hz), 149.2, 134.8, 124.6, 124.0, 123.5, 121.1 (q,

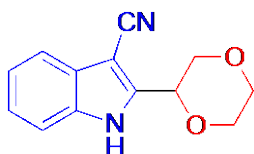
$J = 5.33$  Hz), 118.4 (d,  $J = 287$  Hz), 115.6, 112.0, 107.6, 72.9, 69.3, 67.1, 66.3. HRMS (ESI)  $m/z$ : calcd for  $C_{14}H_{13}F_3NO_3$   $[M + H]^+$  300.0848, found 300.0852.

**2-(1,4-Dioxan-2-yl)-1H-indole-3-carbaldehyde (Table 2, product 3ja)**



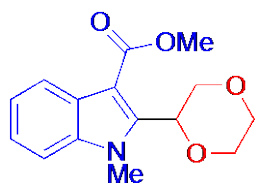
EA:hexane = 1:2,  $R_f = 0.2$ , light yellow solid, 46% (53 mg), m.p. = 211-212 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  10.27 (s, 1H), 9.20 (s, 1H), 8.17-8.15 (m, 1H), 7.44-7.43 (m, 1H), 7.33-7.31 (m, 2H), 5.46 (dd,  $J = 9.60, 2.40$  Hz, 1H), 4.25 (d,  $J = 11.60$  Hz, 1H), 4.03 (d,  $J = 6.40$  Hz, 2H), 3.91 (d,  $J = 11.60$  Hz, 1H), 3.80-3.74 (m, 1H), 3.52 (t,  $J = 10.60$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  183.7, 143.9, 134.7, 126.6, 123.8, 122.9, 120.1, 113.1, 111.5, 71.4, 70.8, 66.9, 66.4. HRMS (ESI)  $m/z$ : calcd for  $C_{13}H_{14}NO_3$   $[M + H]^+$  232.0968, found 232.0967.

**2-(1,4-Dioxan-2-yl)-1H-indole-3-carbonitrile (Table 2, product 3ka)**



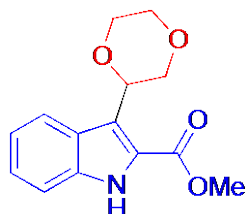
EA:hexane = 1:2,  $R_f = 0.4$ , light yellow solid, 50% (57 mg), m.p. = 152-153 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.07 (s, 1H), 7.73 (d,  $J = 7.20$  Hz, 1H), 7.46 (d,  $J = 7.60$  Hz, 1H), 7.34-7.29 (m, 2H), 5.17 (dd,  $J = 9.60, 2.40$  Hz, 1H), 4.28 (dd,  $J = 11.60, 2.40$  Hz, 1H), 4.01-3.98 (m, 2H), 3.90 (d,  $J = 11.60$  Hz, 1H), 3.80-3.74 (m, 1H), 3.62 (t,  $J = 10.8$  Hz, 1H).  $^{13}C$  NMR (100MHz,  $CDCl_3$ ):  $\delta$  143.5, 134.1, 127.6, 124.1, 122.4, 119.4, 115.2, 112.0, 83.4, 71.0, 70.0, 66.8, 66.4. HRMS (ESI)  $m/z$ : calcd for  $C_{13}H_{13}N_2O_2$   $[M + H]^+$  229.0972, found 229.0970.

**Methyl 2-(1,4-dioxan-2-yl)-1-methyl-1H-indole-3-carboxylate (Table 2, product 3la)**



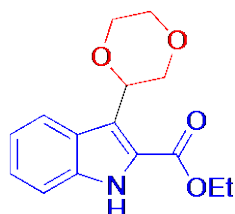
EA:hexane = 1:2,  $R_f$  = 0.5, yellow oil, 40% (55 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 (d,  $J$  = 7.20 Hz, 1H), 7.38-7.26 (m, 3H), 6.17 (dd,  $J$  = 10.80, 3.20 Hz, 1H), 4.09 (s, 3H), 4.01 (d,  $J$  = 2.80 Hz, 1H), 3.97 (s, 3H), 3.95 (d,  $J$  = 2.80 Hz, 1H), 3.89-3.75 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.7, 141.8, 137.6, 125.9, 123.1, 122.0, 109.5, 105.1, 74.9, 72.2, 68.7, 68.6, 67.4, 66.6, 66.4, 51.0, 32.8. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_4$  [ $\text{M} + \text{H}$ ] $^+$  276.1236, found 276.1235.

**Methyl 3-(1,4-dioxan-2-yl)-1H-indole-2-carboxylate (Table 2, product 3ma)**



EA:hexane = 1:3,  $R_f$  = 0.3, white solid, 48% (63 mg), m.p. = 169-170 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.97 (s, 1H), 8.20 (d,  $J$  = 8.0 Hz, 1H), 7.40-7.32 (m, 2H), 7.19-7.15 (m, 1H), 5.69 (dd,  $J$  = 9.2, 4.0 Hz, 1H), 4.04-3.98 (m, 2H), 3.97 (s, 3H), 3.92-3.86 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.2, 136.2, 126.5, 125.8, 123.7, 122.8, 120.6, 119.7, 111.8, 73.7, 70.7, 67.3, 66.6, 52.1. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_4$  [ $\text{M} + \text{H}$ ] $^+$  262.1079, found 262.1076.

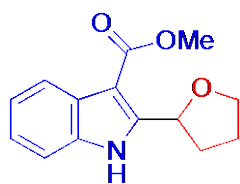
**Ethyl 3-(1,4-dioxan-2-yl)-1H-indole-2-carboxylate (Table 2, product 3na)**





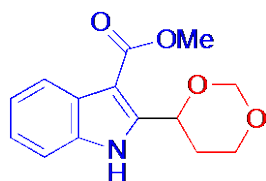
EA:hexane = 1:2,  $R_f$  = 0.4, white solid, 45% (62 mg), m.p. = 125-126 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.97 (s, 1H), 8.20 (d,  $J$  = 8.4 Hz, 1H), 7.40-7.32 (m, 2H), 7.19 (t,  $J$  = 7.40 Hz, 1H), 5.71 (dd,  $J$  = 9.6, 3.2 Hz, 1H), 4.49-4.44 (m, 2H), 4.07-3.99 (m, 2H), 3.96-3.83 (m, 4H), 1.48 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.8, 136.2, 126.5, 125.6, 123.7, 123.1, 120.5, 119.5, 111.8, 73.5, 70.7, 67.4, 66.6, 61.3, 14.4. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_4$   $[\text{M} + \text{H}]^+$  276.1236, found 276.1232.

**Methyl 2-(tetrahydrofuran-2-yl)-1H-indole-3-carboxylate (Table 3, product 3ab)**



EA:hexane = 1:2,  $R_f$  = 0.4, colourless oil, 57% (70 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.15 (s, 1H), 8.14 (d,  $J$  = 2.0 Hz, 1H), 7.40 (dd,  $J$  = 6.80, 2.80 Hz, 1H), 7.26 - 7.22 (m, 2H), 5.67 (t,  $J$  = 7.20 Hz, 1H), 4.22 - 4.17 (m, 1H), 4.03 - 3.98 (m, 1H), 3.95 (s, 3H), 2.76 - 2.72 (m, 1H), 2.10 - 2.01 (m, 1H), 1.99 - 1.95 (m, 1H), 1.93 - 1.86 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.8, 149.5, 133.8, 127.5, 122.5, 121.9, 121.3, 111.2, 102.2, 75.5, 69.35, 50.85, 33.4, 26.0. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{15}\text{NO}_3\text{Na}$   $[\text{M} + \text{Na}]^+$  268.0944, found 268.0946.

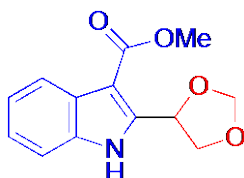
**Methyl 2-(1,3-dioxan-4-yl)-1H-indole-3-carboxylate (Table 3, product 3ac)**



EA:hexane = 1:2,  $R_f$  = 0.4, white solid, 44% (57 mg), m.p. = 190-191 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.10 (s, 1H), 8.03 - 8.01 (m, 1H), 7.33 - 7.31 (m, 1H), 7.19 - 7.16 (m, 2H), 5.53 (dd,  $J$  = 11.20, 2.80 Hz, 1H), 5.19 (d,  $J$  = 6.40 Hz, 1H), 4.89 (d,  $J$  = 6.40 Hz, 1H), 4.14 - 4.10 (m, 1H), 3.94 - 3.93 (m, 1H), 3.86 (s, 3H), 2.14 (d,  $J$  = 13.20 Hz, 1H), 1.92 - 1.81 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.8, 146.6, 134.4, 126.6, 122.9, 122.0,

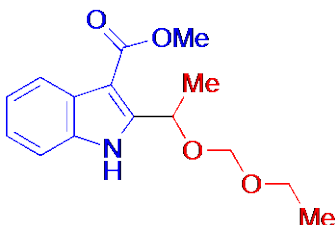
121.6, 111.4, 102.3, 94.0, 72.9, 66.7, 51.0, 32.0. HRMS (ESI)  $m/z$ : calcd for  $C_{14}H_{15}NO_4Na$   $[M + Na]^+$  284.0893, found 284.0890.

**Methyl 2-(1,3-dioxolan-4-yl)-1*H*-indole-3-carboxylate (Table 3, product 3ad)**



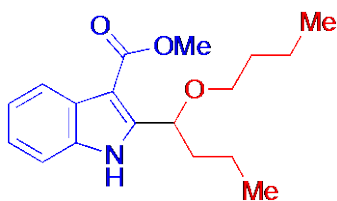
EA:hexane = 1:2,  $R_f$  = 0.5, colourless oil, 45% (55.5 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.19 (s, 1H), 8.13-8.11 (m, 1H), 7.42-7.40 (m, 1H), 7.30-7.25 (m, 2H), 5.82 (dd,  $J$  = 7.6, 5.6 Hz, 1H), 5.35 (s, 1H), 5.06 (s, 1H), 3.53 (t,  $J$  = 8.0 Hz, 1H), 3.97-3.94 (m, 4H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  165.9, 146.1, 134.1, 127.0, 123.0, 122.1, 121.3, 111.4, 103.1, 95.9, 71.9, 71.6, 51.1. HRMS (ESI)  $m/z$ : calcd for  $C_{13}H_{13}NO_4Na$   $[M + Na]^+$  270.0737, found 270.0738.

**Methyl 2-(1-(ethoxymethoxy)ethyl)-1*H*-indole-3-carboxylate (Table 3, product 3ae)**



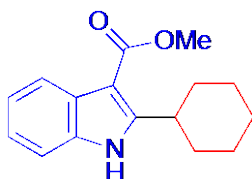
EA:hexane = 1:2,  $R_f$  = 0.5, white solid, 50% (69 mg), m.p. = 74-75 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.98 (s, 1H), 8.15 – 8.13 (m, 1H), 7.41 – 7.39 (m, 1H), 7.27 – 7.25 (m, 2H), 5.74 (dd,  $J$  = 12.80, 6.40 Hz, 1H), 4.75 (dd,  $J$  = 29.60, 6.80 Hz, 2H), 3.96 (s, 3H), 3.73 – 3.67 (m, 1H), 3.63 – 3.57 (m, 1H), 1.61 (d,  $J$  = 6.80 Hz, 3H), 1.21 (t,  $J$  = 7.00 Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  165.7, 149.1, 134.3, 127.1, 122.8, 121.9, 121.6, 111.1, 103.1, 94.0, 68.9, 64.0, 50.9, 22.1, 15.1. HRMS (ESI)  $m/z$ : calcd for  $C_{15}H_{19}NO_4Na$   $[M + Na]^+$  300.1206, found 300.1214.

**Methyl 2-(1-butoxybutyl)-1*H*-indole-3-carboxylate (Table 3, product 3af)**



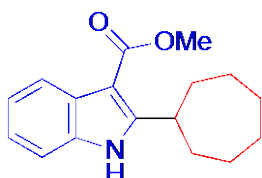
EA:hexane = 1:10,  $R_f$  = 0.5, colourless oil, 74% (103 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94 (s, 1H), 8.16-8.14 (m, 1H), 7.43-7.40 (m, 1H), 7.28-7.26 (m, 2H), 5.33 (dd,  $J$  = 7.20, 5.24 Hz, 1H), 3.97 (s, 3H), 3.49 (t,  $J$  = 6.50 Hz, 2H), 1.85-1.79 (m, 2H), 1.64-1.59 (m, 2H), 1.54-1.49 (m, 2H), 1.45-1.39 (m, 2H), 0.96 (dd,  $J$  = 15.20, 7.65 Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.0, 149.4, 134.3, 127.1, 122.7, 121.8, 121.5, 111.1, 103.9, 75.1, 70.3, 50.8, 38.6, 32.0, 19.4, 18.8, 13.9, 13.8. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{26}\text{NO}_3$  [ $\text{M} + \text{H}$ ] $^+$  304.1913, found 304.1958.

**Methyl 2-cyclohexyl-1*H*-indole-3-carboxylate (Table 3, product 3ag)**



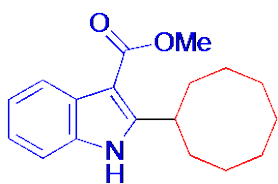
EA:hexane = 1:8,  $R_f$  = 0.5, colourless oil, 60% (77 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.59 (s, 1H), 8.14 (d,  $J$  = 7.06 Hz, 1H), 7.38-7.36 (m, 1H), 7.27-7.20 (m, 2H), 3.96 (s, 3H), 3.86-3.79 (m, 1H), 2.12 (d,  $J$  = 11.93 Hz, 2H), 1.91-1.81 (m, 3H), 1.51-1.43 (m, 4H), 1.33-1.26 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.7, 153.3, 134.6, 127.1, 122.3, 121.7, 121.5, 110.9, 102.7, 50.8, 36.4, 32.4, 26.5, 26.1. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$  258.1494, found 258.1476.

**Methyl 2-cycloheptyl-1*H*-indole-3-carboxylate (Table 3, product 3ah)**



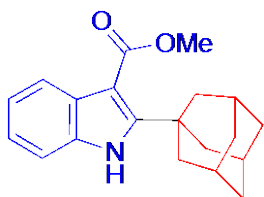
EA:hexane = 1:10,  $R_f$  = 0.6, colourless oil, 77% (104 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54 (s, 1H), 8.14-8.11 (m, 1H), 7.37-7.35 (m, 1H), 7.26-7.21 (m, 2H), 4.03-3.99 (m, 1H), 3.96 (s, 3H), 2.15-2.09 (m, 2H), 1.86-1.83 (m, 2H), 1.78-1.74 (m, 2H), 1.71-1.60 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.6, 154.7, 134.6, 126.9, 122.3, 121.7, 121.6, 110.8, 102.1, 50.8, 37.9, 34.5, 27.8, 27.2. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{22}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$  272.1651, found 272.1658.

**Methyl 2-cyclooctyl-1*H*-indole-3-carboxylate (Table 3, product 3ai)**



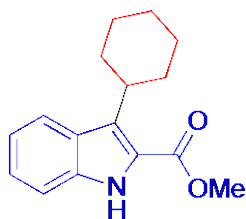
EA:hexane = 1:10,  $R_f$  = 0.6, colourless oil, 73% (100 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54 (s, 1H), 8.14 (d,  $J$  = 7.02 Hz, 1H), 7.37-7.34 (m, 1H), 7.26-7.19 (m, 2H), 4.21-4.16 (m, 1H), 3.97 (s, 3H), 2.03-1.97 (m, 2H), 1.85-1.68 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.7, 155.3, 134.8, 127.0, 122.2, 121.7, 121.6, 110.9, 101.9, 50.8, 35.2, 32.7, 26.7, 26.6, 25.9. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{24}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$  286.1807, found 286.1807.

**Methyl 2-((1*S*,3*S*)-adamantan-1-yl)-1*H*-indole-3-carboxylate (Table 3, product 3aj)**



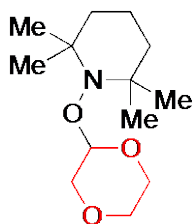
EA:hexane = 1:10,  $R_f$  = 0.5, colourless oil, 42% (65 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72 (s, 1H), 8.17 (d,  $J$  = .2 Hz, 1H), 7.39-7.37 (m, 1H), 7.25-7.21 (m, 2H), 3.99 (s, 3H), 2.33 (s, 6H), 2.15 (s, 3H), 1.88-1.82 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.2, 154.9, 133.2, 128.4, 122.2, 122.0, 121.8, 110.8, 103.4, 50.9, 39.3, 36.6, 35.9, 28.6. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$  310.1807, found 310.1821.

**Methyl 3-cyclohexyl-1*H*-indole-2-carboxylate (Table 3, product 3og)**



EA:hexane = 1:8,  $R_f$  = 0.5, colourless oil, 35% (45 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.74 (s, 1H), 7.97 (d,  $J$  = 8.40 Hz, 1H), 7.40-7.38 (m, 1H), 7.34-7.28 (m, 1H), 7.14-7.11 (m, 1H), 3.97 (s, 3H), 3.78 (t,  $J$  = 12.2 Hz, 1H), 2.08-1.99 (m, 2H), 1.89-1.86 (m, 5H), 1.54-1.39 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.8, 136.3, 130.6, 126.7, 125.2, 123.0, 121.7, 119.5, 111.9, 51.7, 36.3, 32.8, 27.2, 26.4. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_2$   $[\text{M} + \text{H}]^+$  258.1494, found 258.1476.

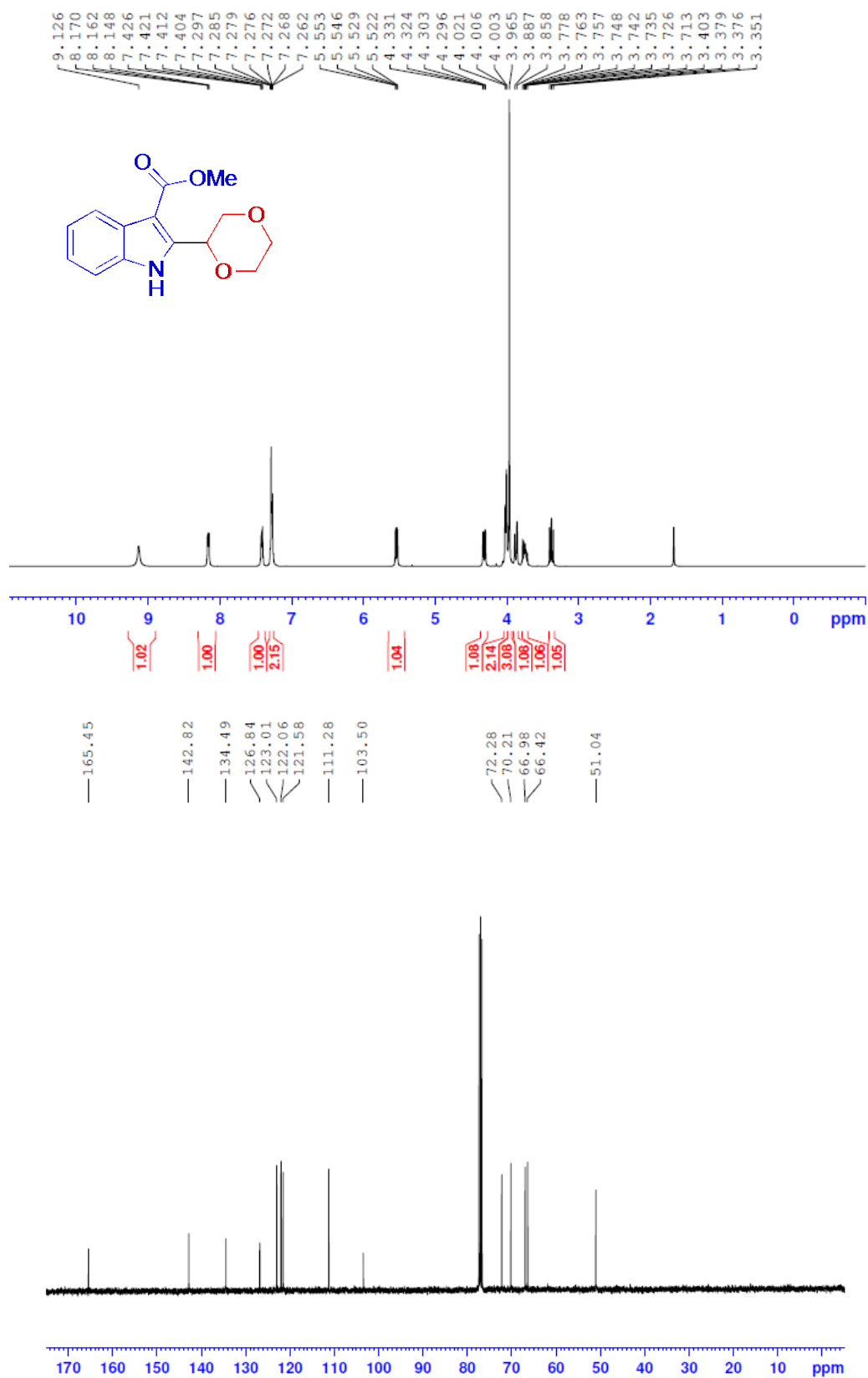
**1-((1,4-Dioxan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (Scheme 2, product 4)<sup>2</sup>**



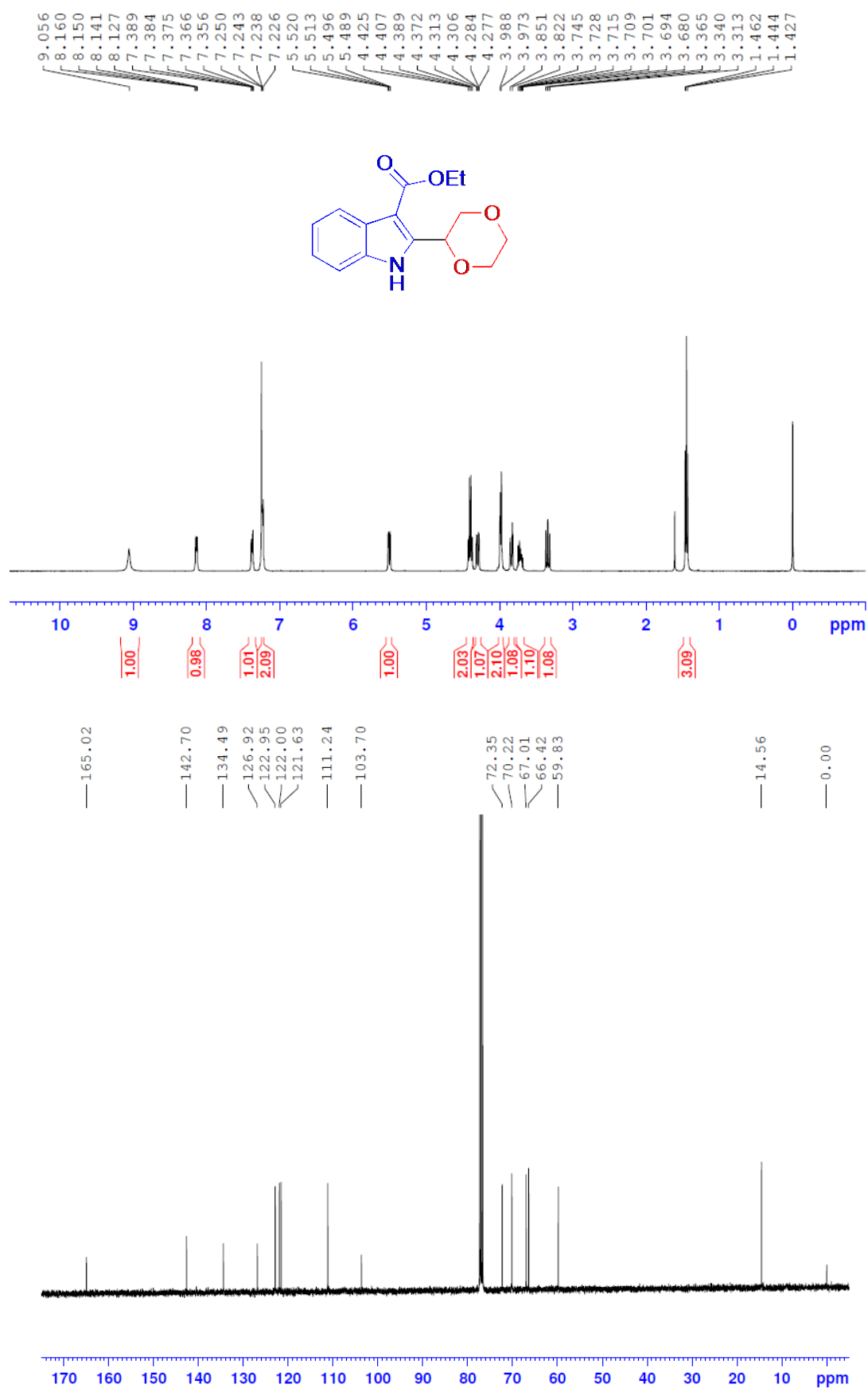
Colourless oil, 60%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.80-4.78 (m, 1H), 3.99-3.96 (m, 1H), 3.83-3.80 (m, 1H), 3.64-3.58 (m, 3H), 3.52-3.49 (m, 1H), 1.47 (d,  $J$  = 8.8 Hz, 5H), 1.31-1.28 (m, 4H), 1.10 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  101.4, 67.9, 65.8, 63.3, 60.5, 59.3, 40.4, 39.9, 33.8, 33.3, 20.6, 20.0, 17.1.

#### 4. $^1\text{H}$ and $^{13}\text{C}$ spectra

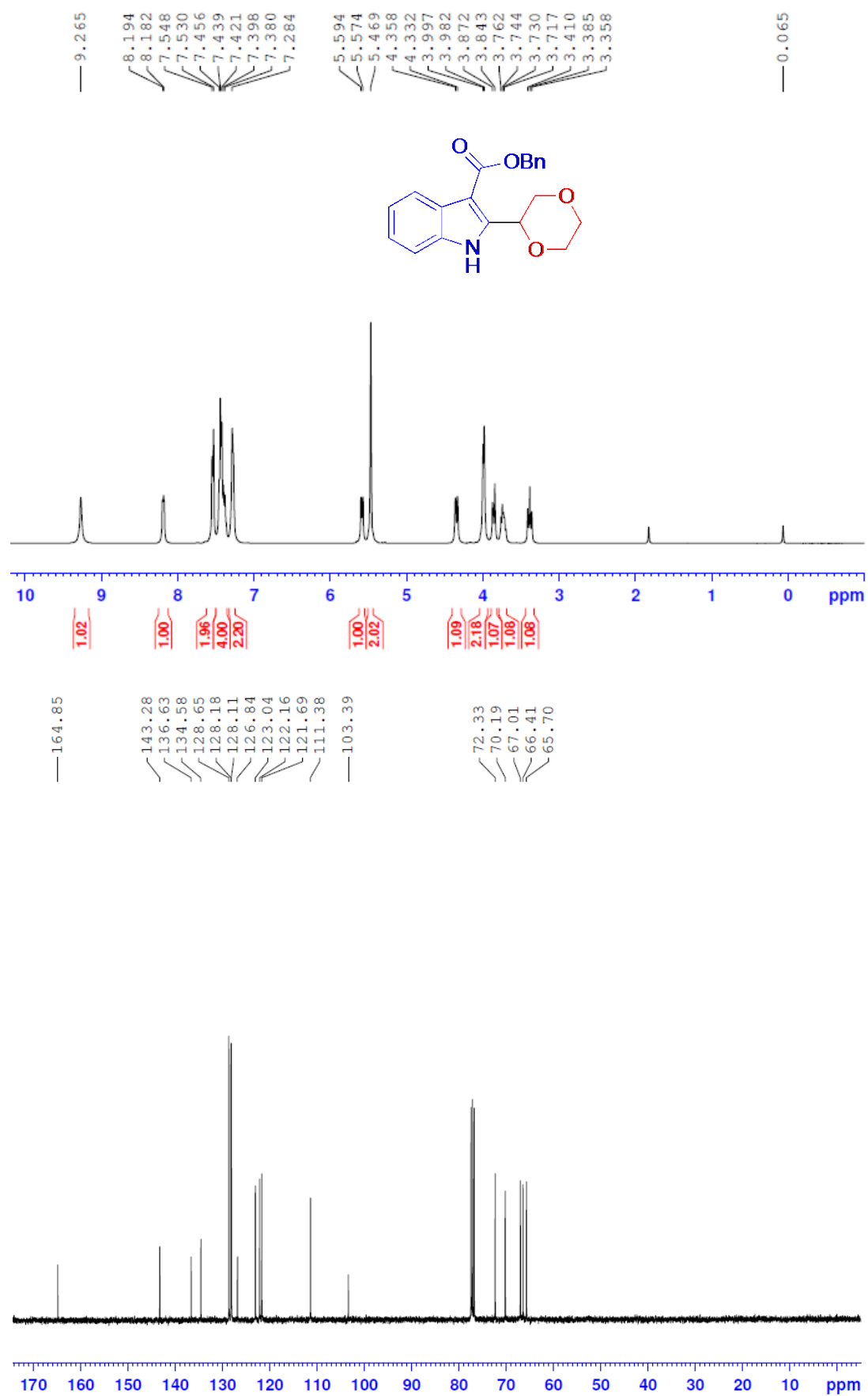
Methyl 2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3aa)



Ethyl 2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3ba)

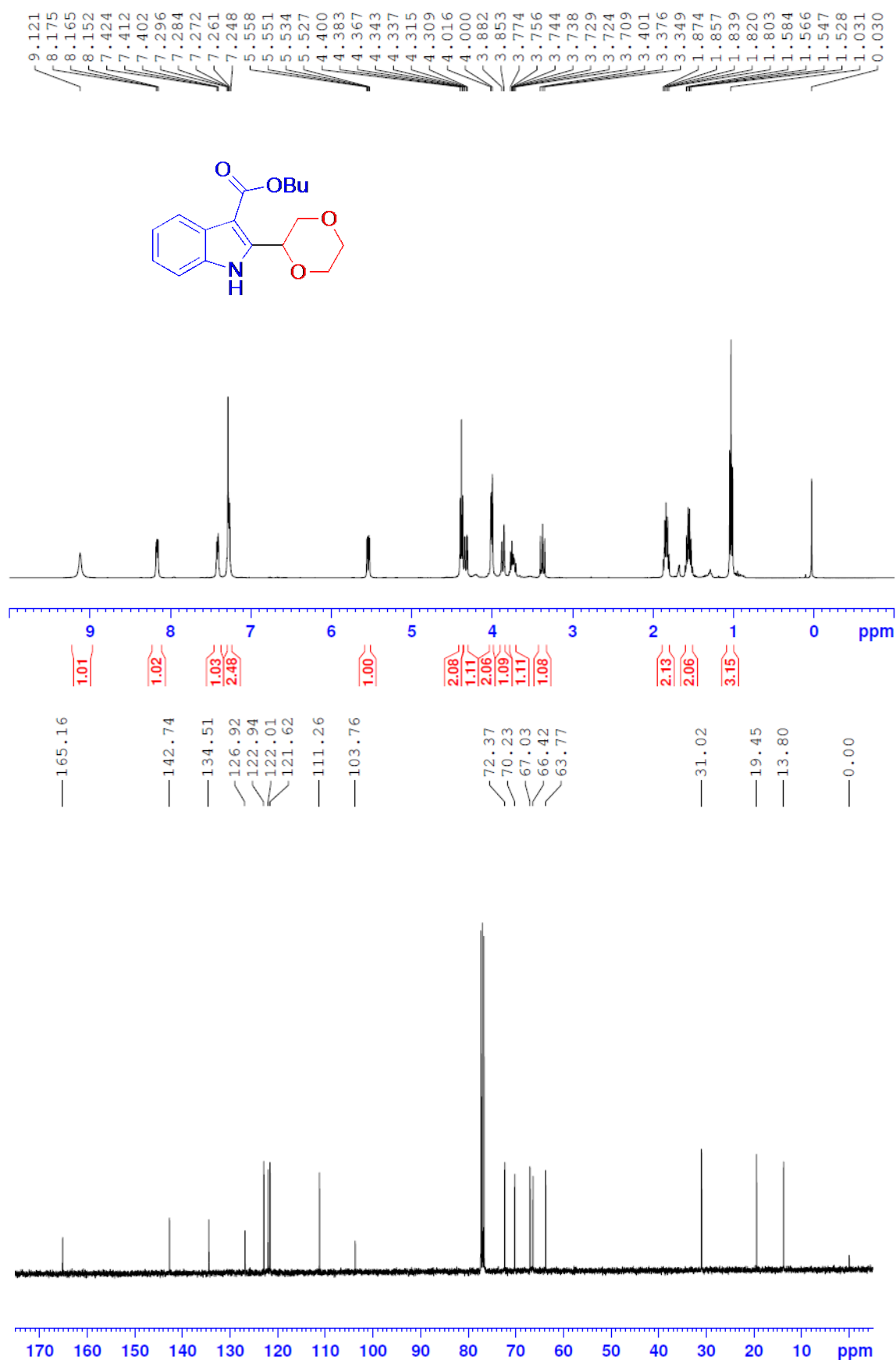


**Benzyl 2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3ca)**

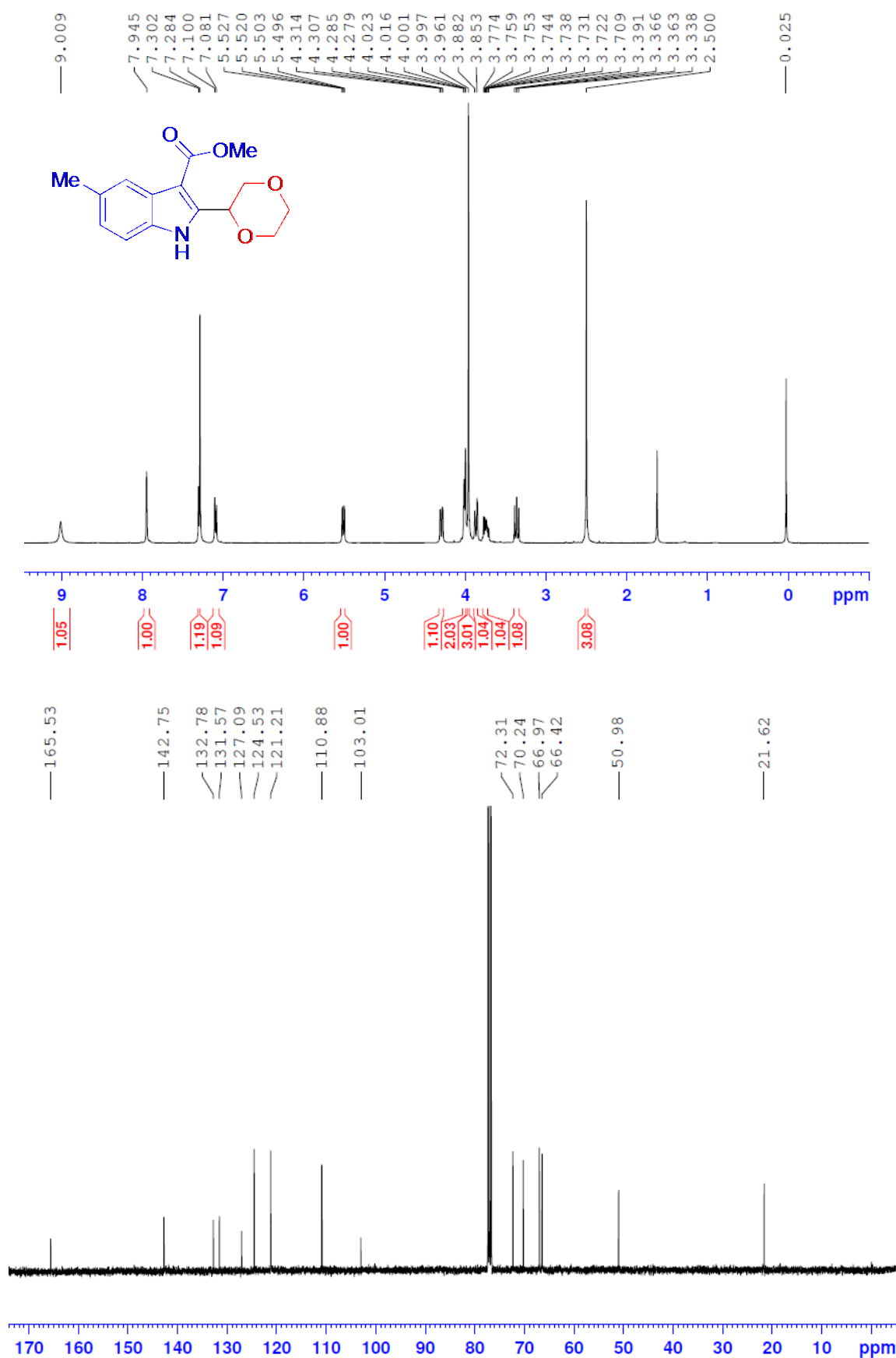




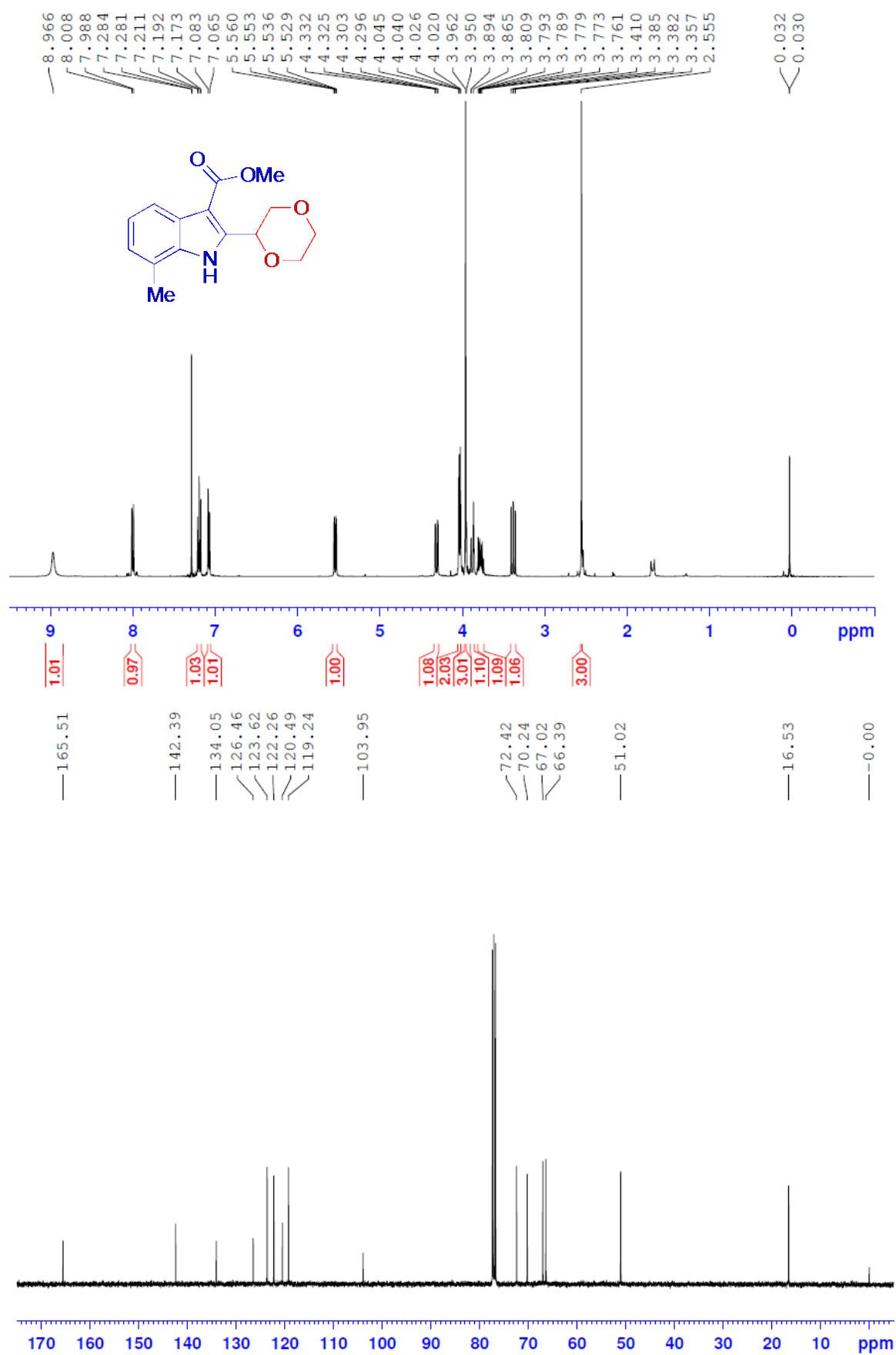
Butyl 2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3da)



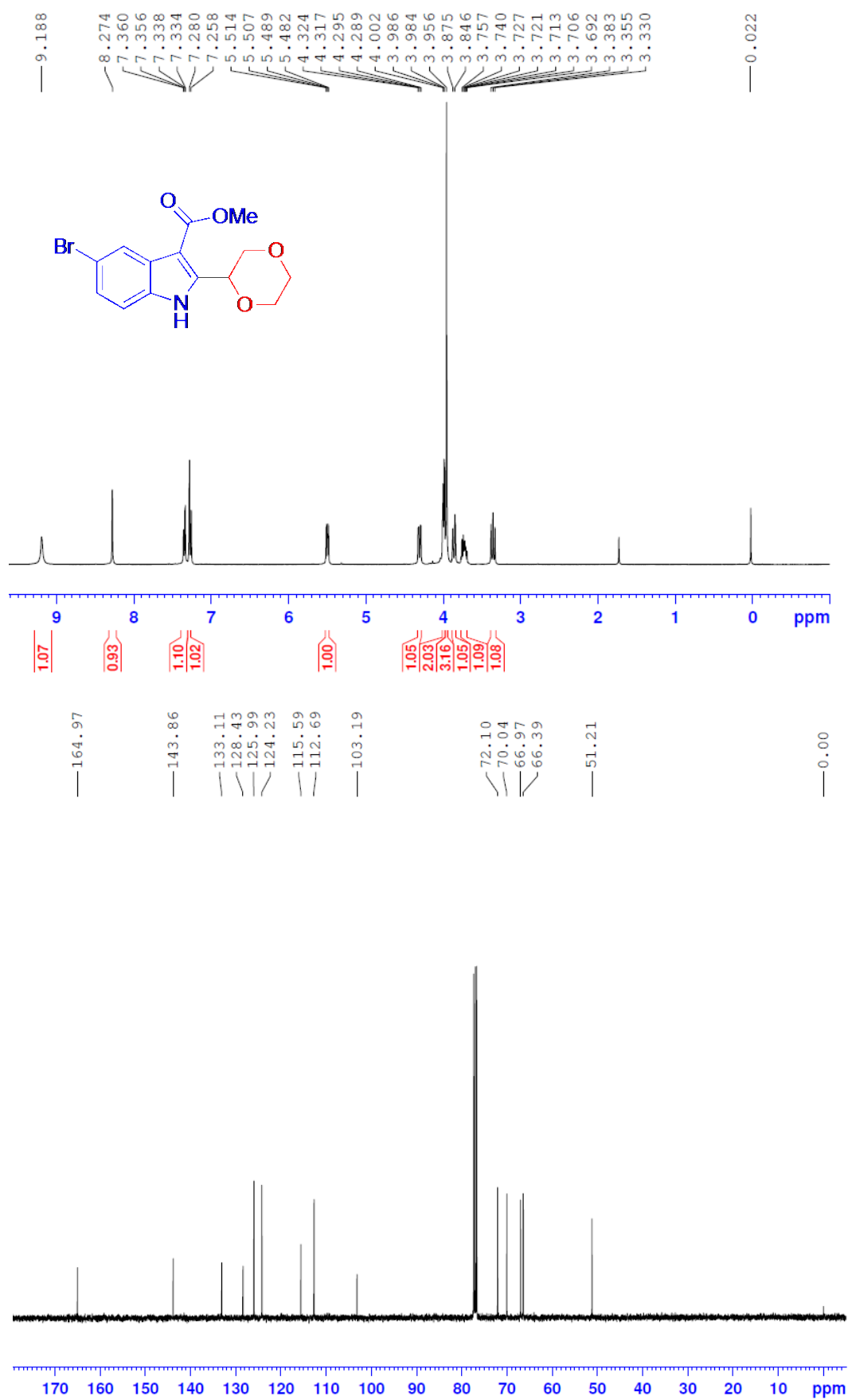
Methyl 2-(1,4-dioxan-2-yl)-5-methyl-1*H*-indole-3-carboxylate (Table 2, product 3ea)



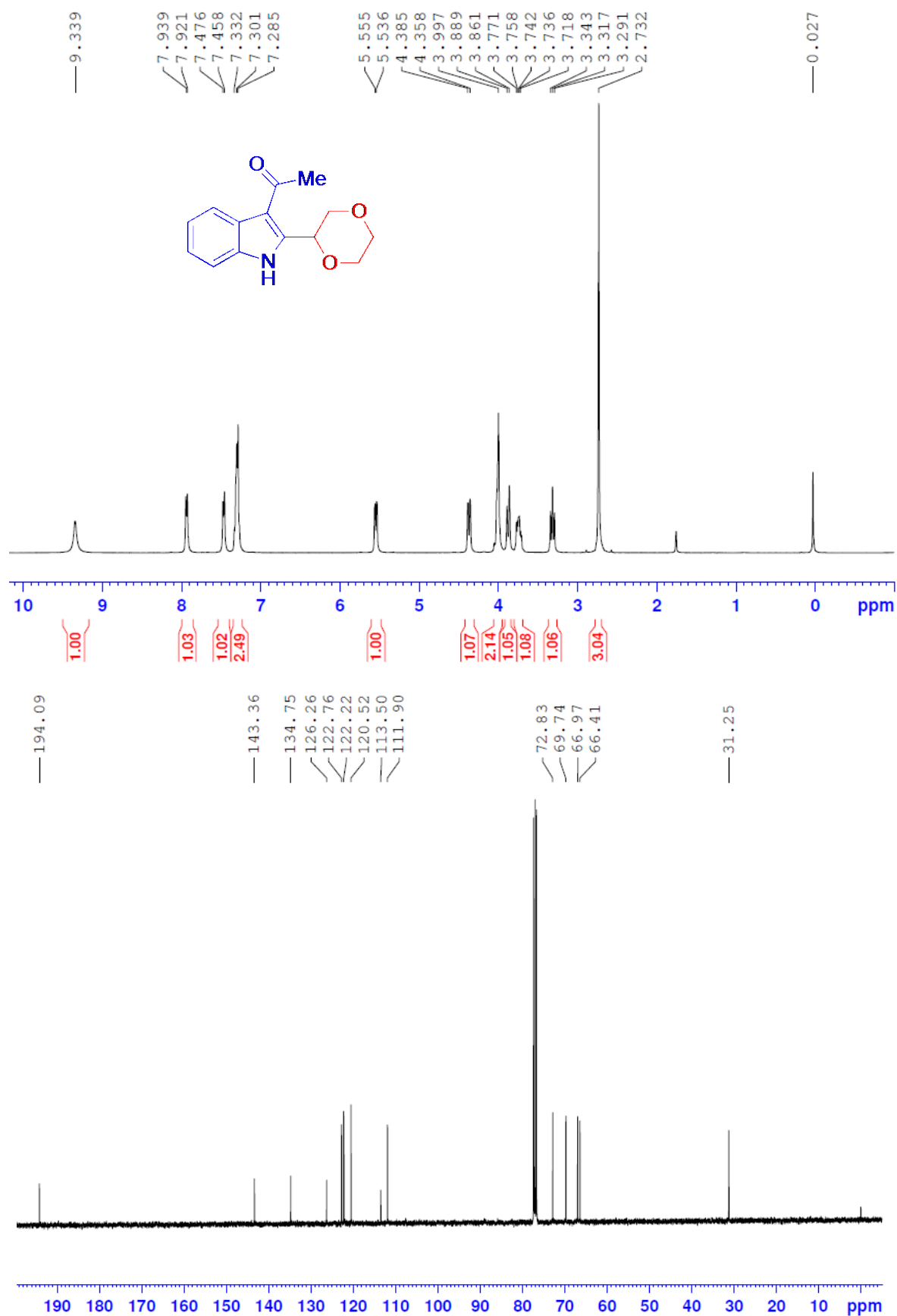
Methyl 2-(1,4-dioxan-2-yl)-7-methyl-1*H*-indole-3-carboxylate (Table 2, product 3fa)



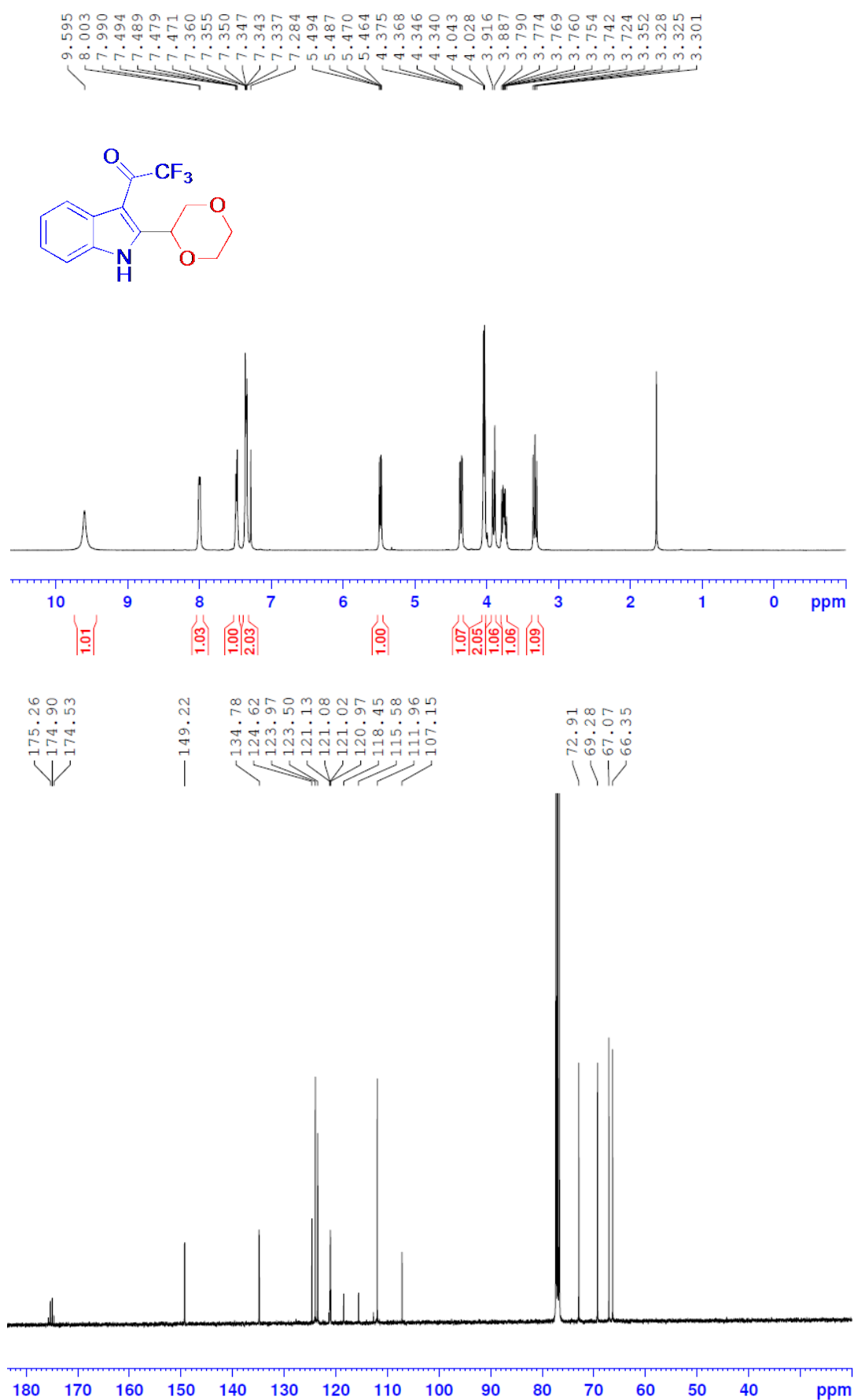
Methyl 5-bromo-2-(1,4-dioxan-2-yl)-1*H*-indole-3-carboxylate (Table 2, product 3ga)



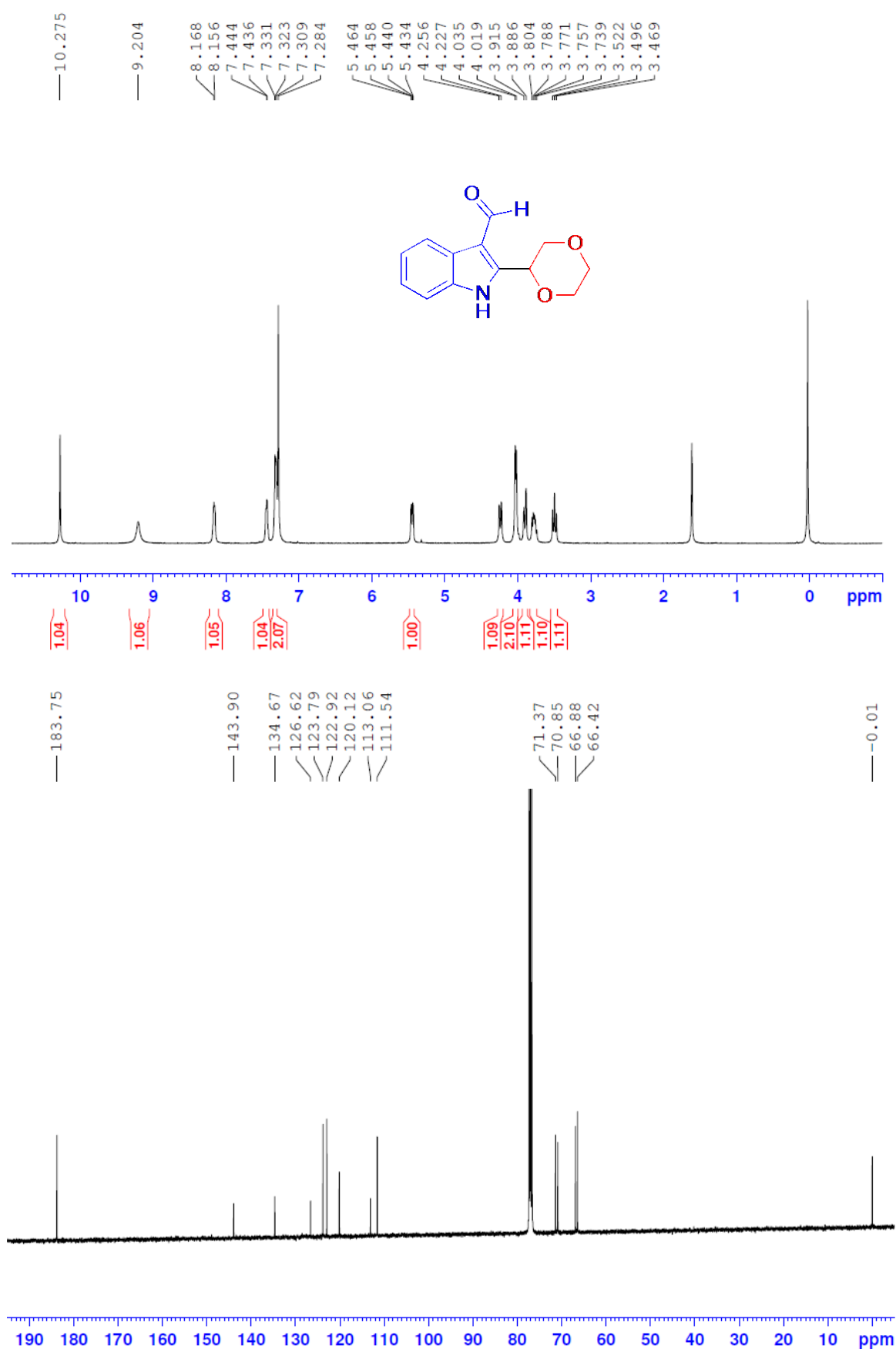
1-(2-(1,4-Dioxan-2-yl)-1*H*-indol-3-yl)ethanone (Table 2, product 3ha)



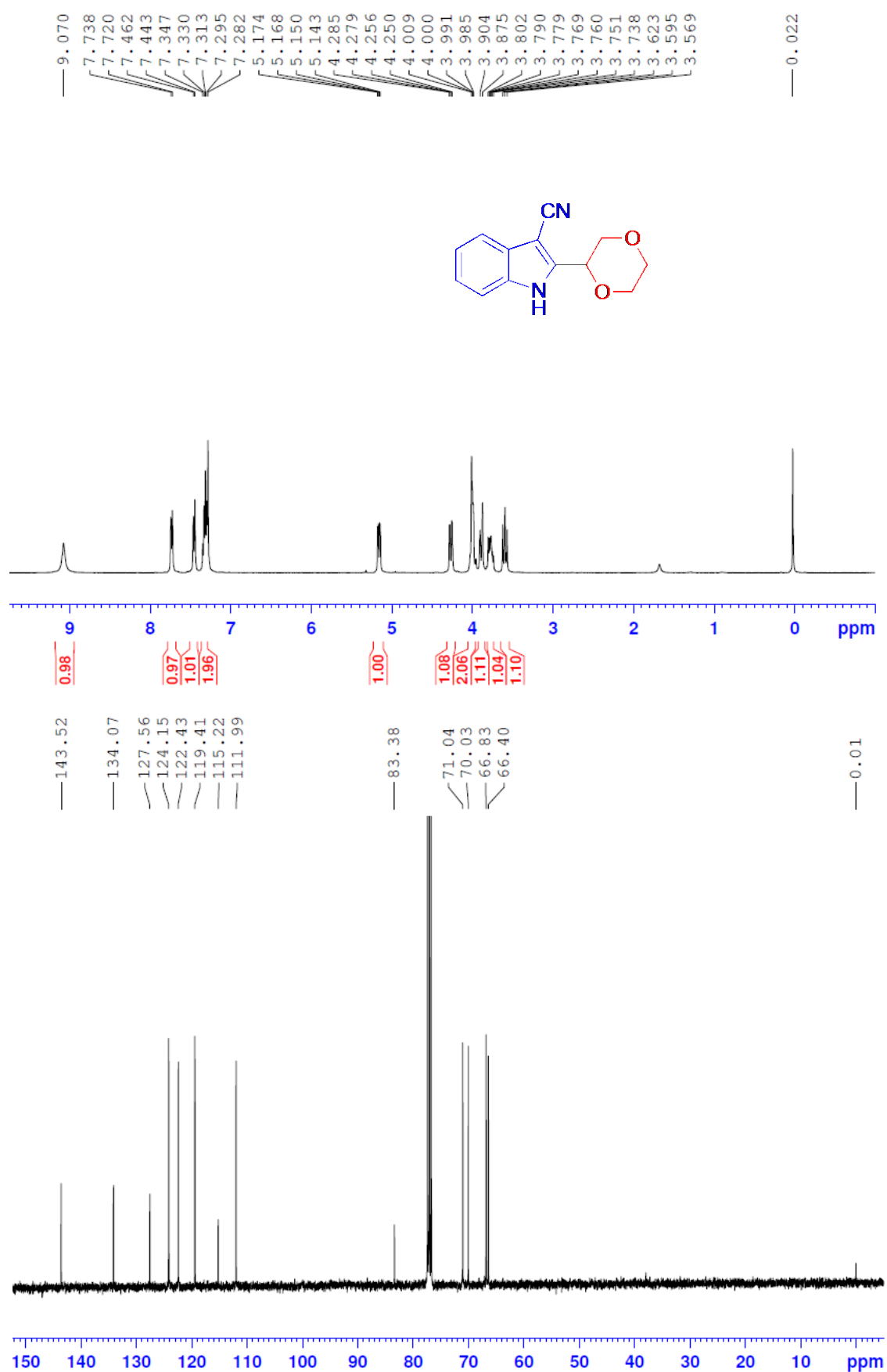
**1-(2-(1,4-Dioxan-2-yl)-1*H*-indol-3-yl)-2,2,2-trifluoroethanone (Table 2, product 3ia)**



**2-(1,4-Dioxan-2-yl)-1*H*-indole-3-carbaldehyde (Table 2, product 3ja)**

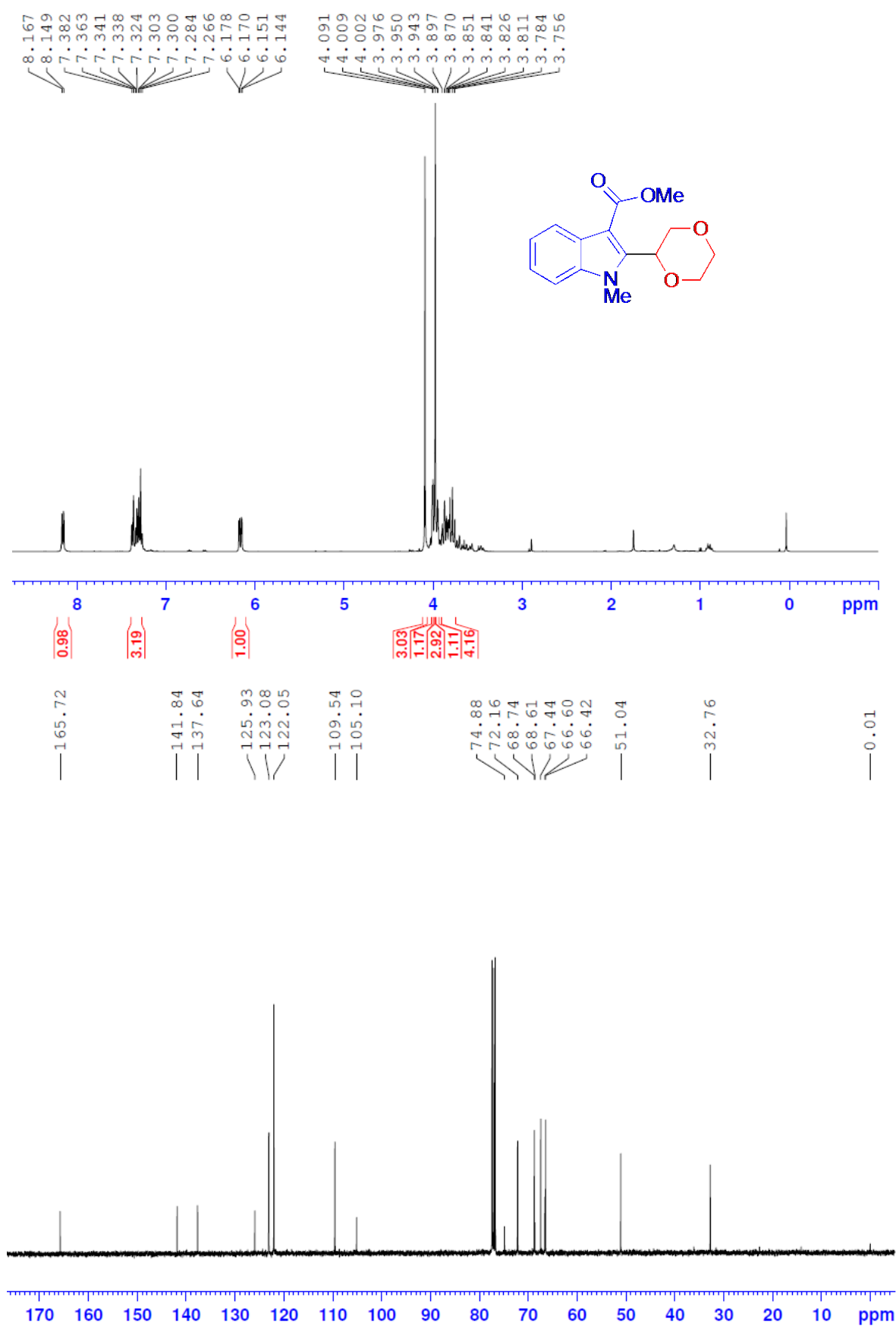


**2-(1,4-Dioxan-2-yl)-1*H*-indole-3-carbonitrile (Table 2, product 3ka)**

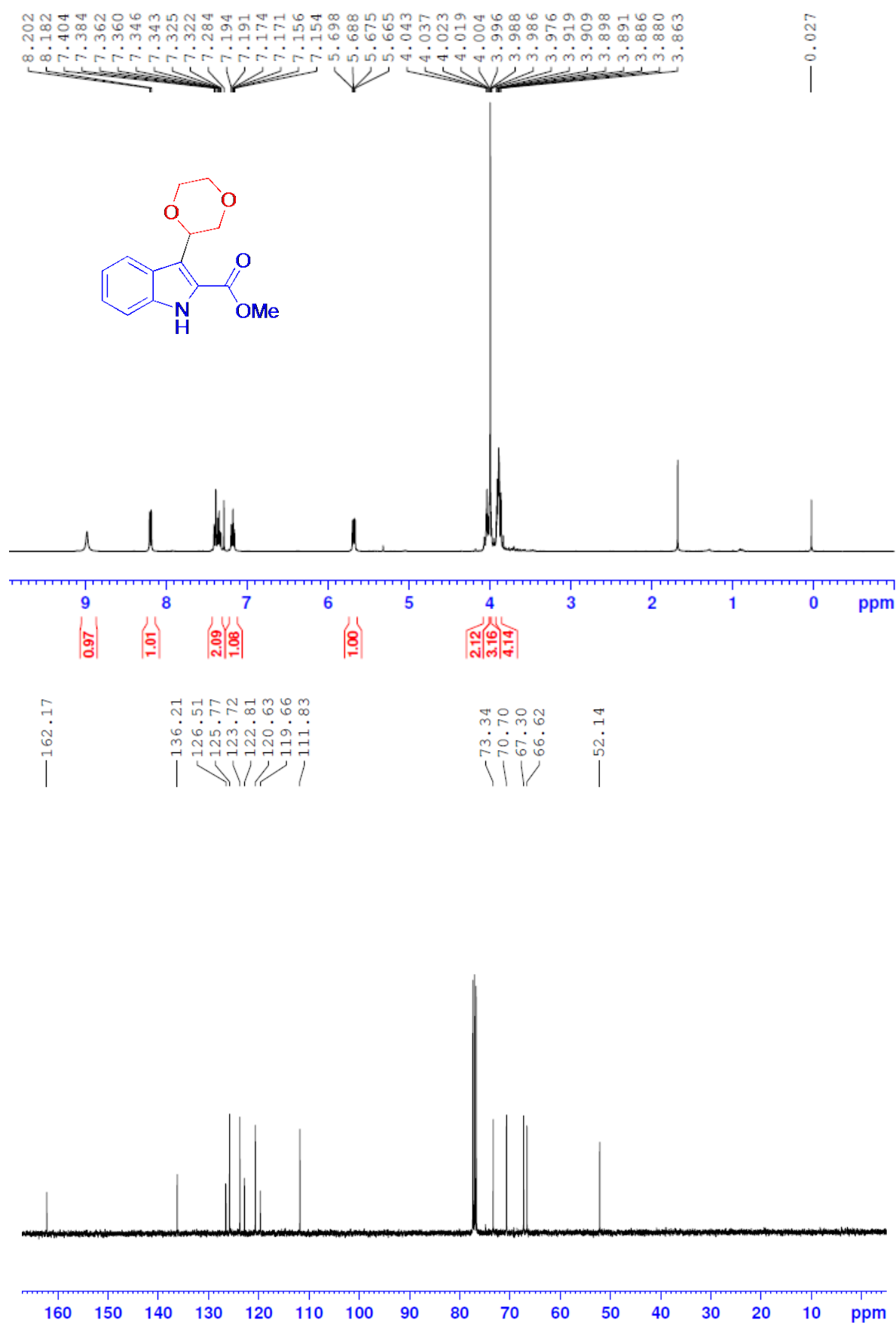




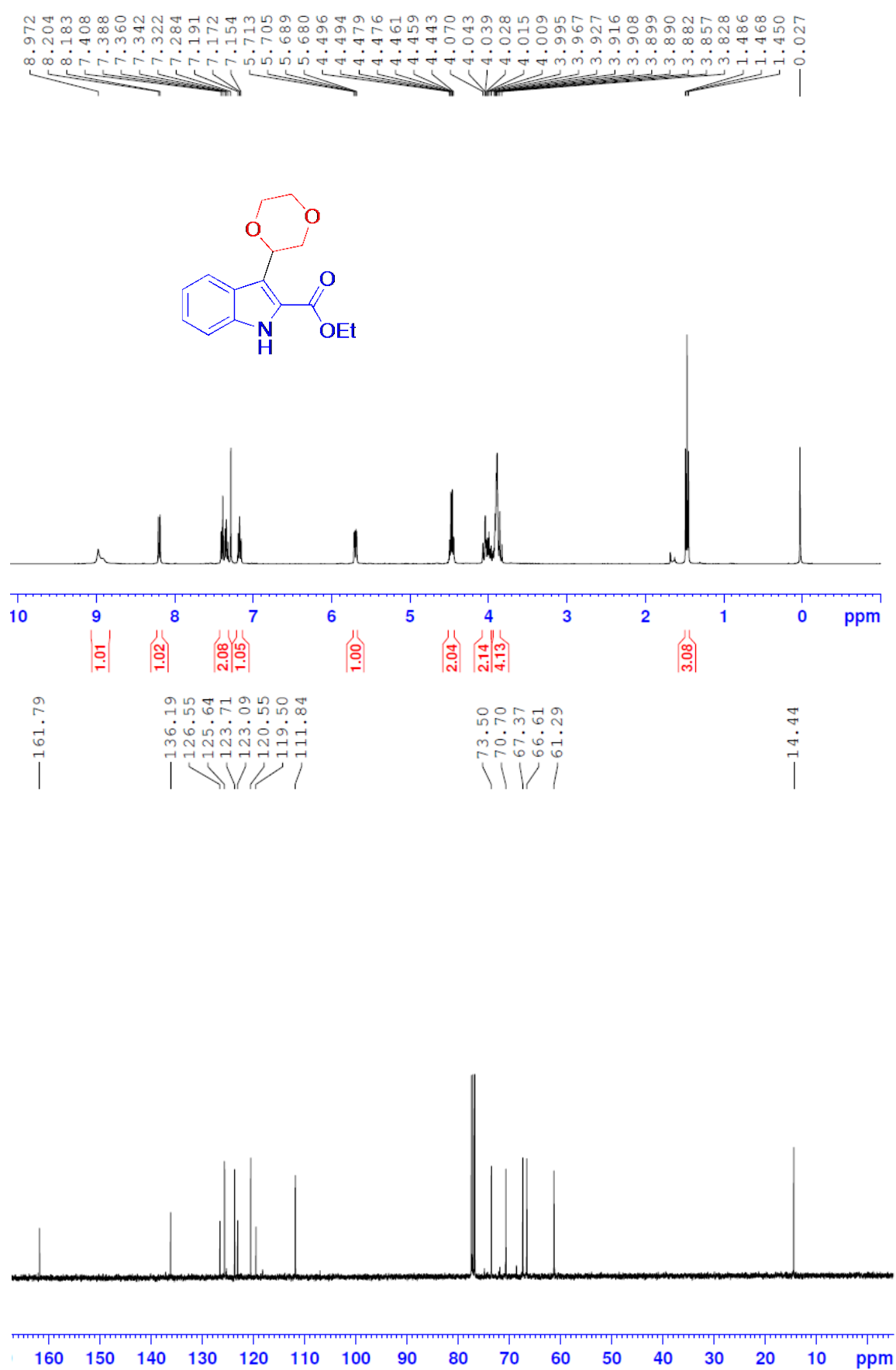
**Methyl 2-(1,4-dioxan-2-yl)-1-methyl-1*H*-indole-3-carboxylate (Table 2, product 3la)**



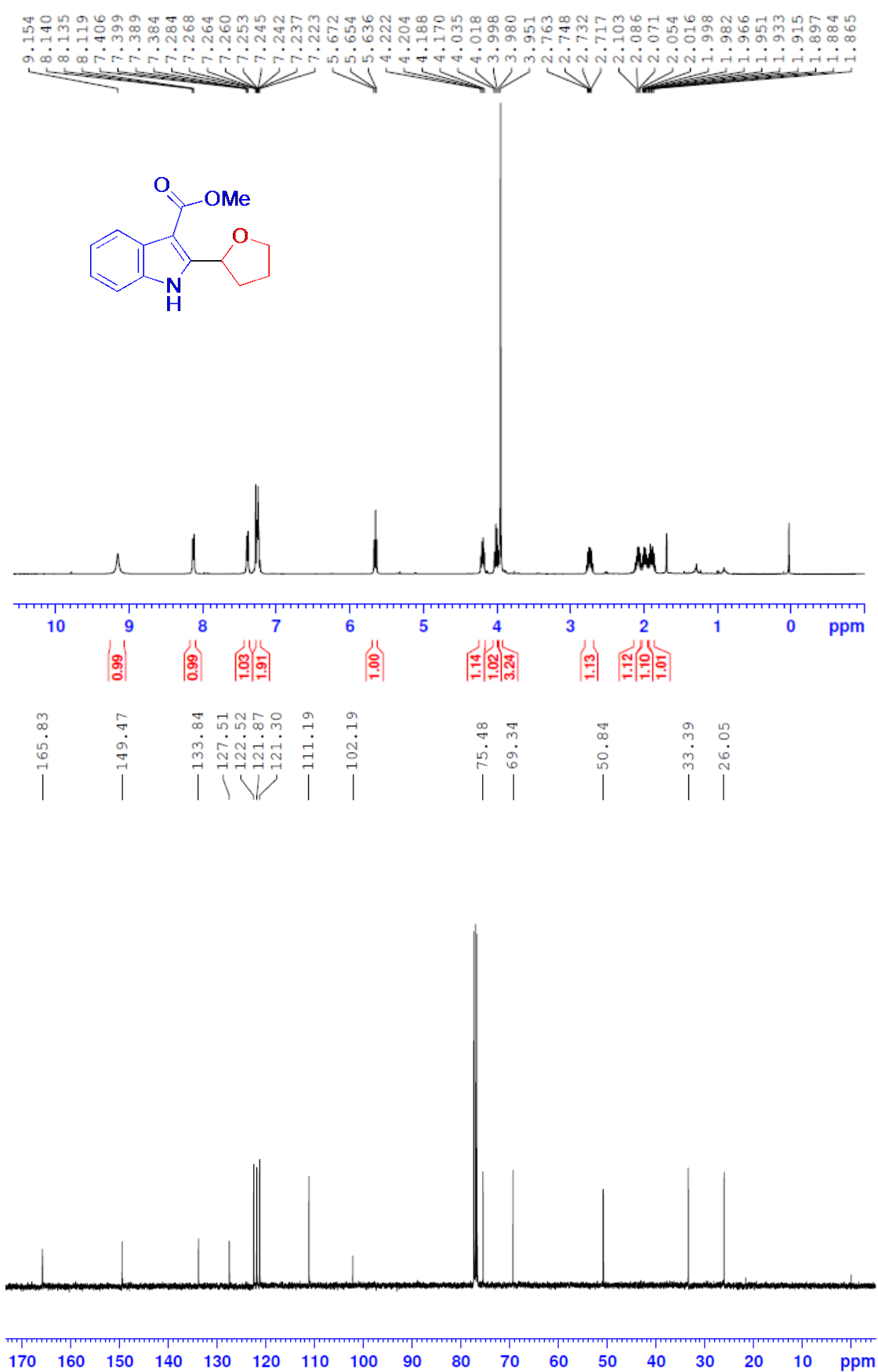
Methyl 3-(1,4-dioxan-2-yl)-1*H*-indole-2-carboxylate (Table 2, product 3ma)



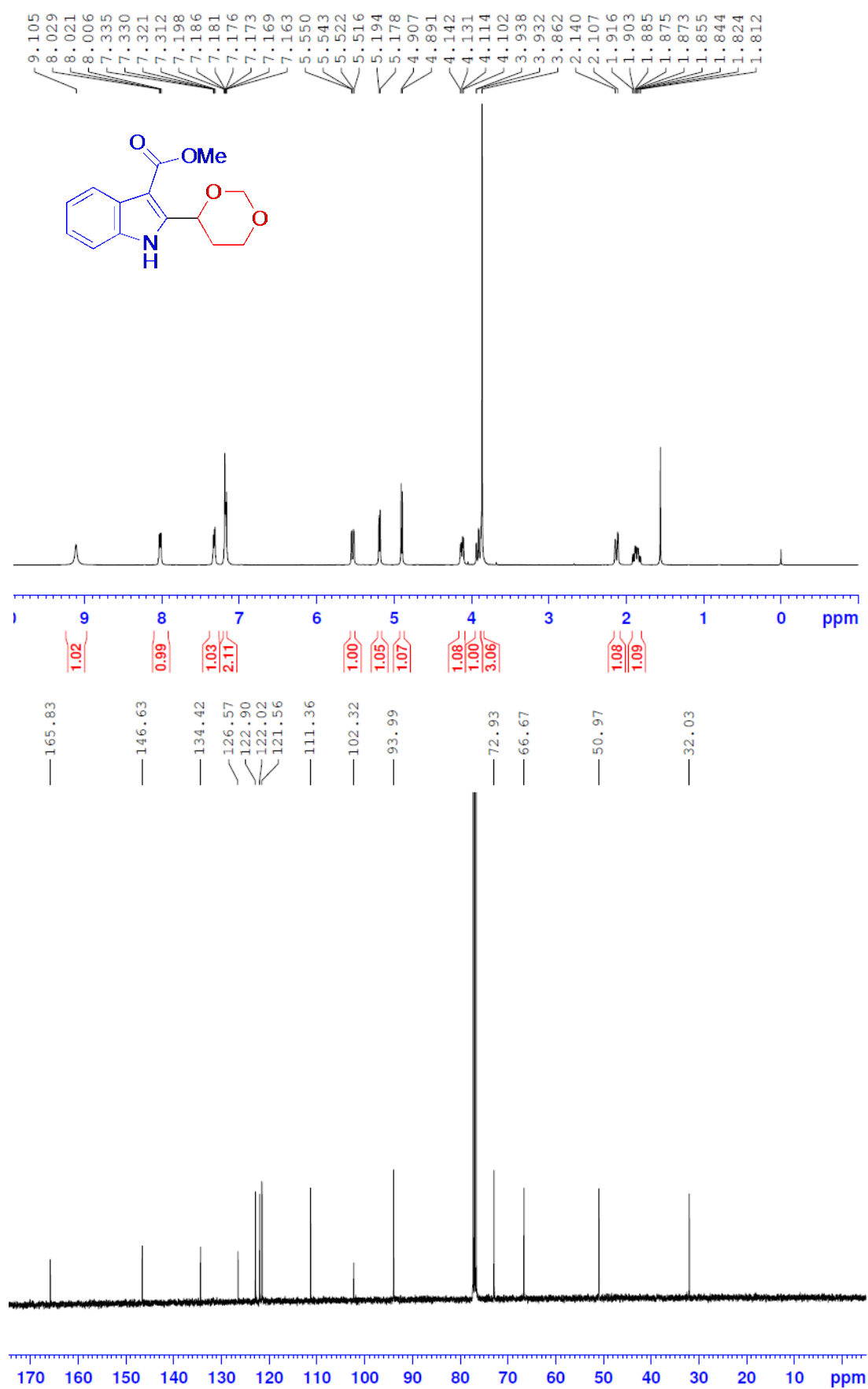
**Ethyl 3-(1,4-dioxan-2-yl)-1*H*-indole-2-carboxylate (Table 2, product 3na)**



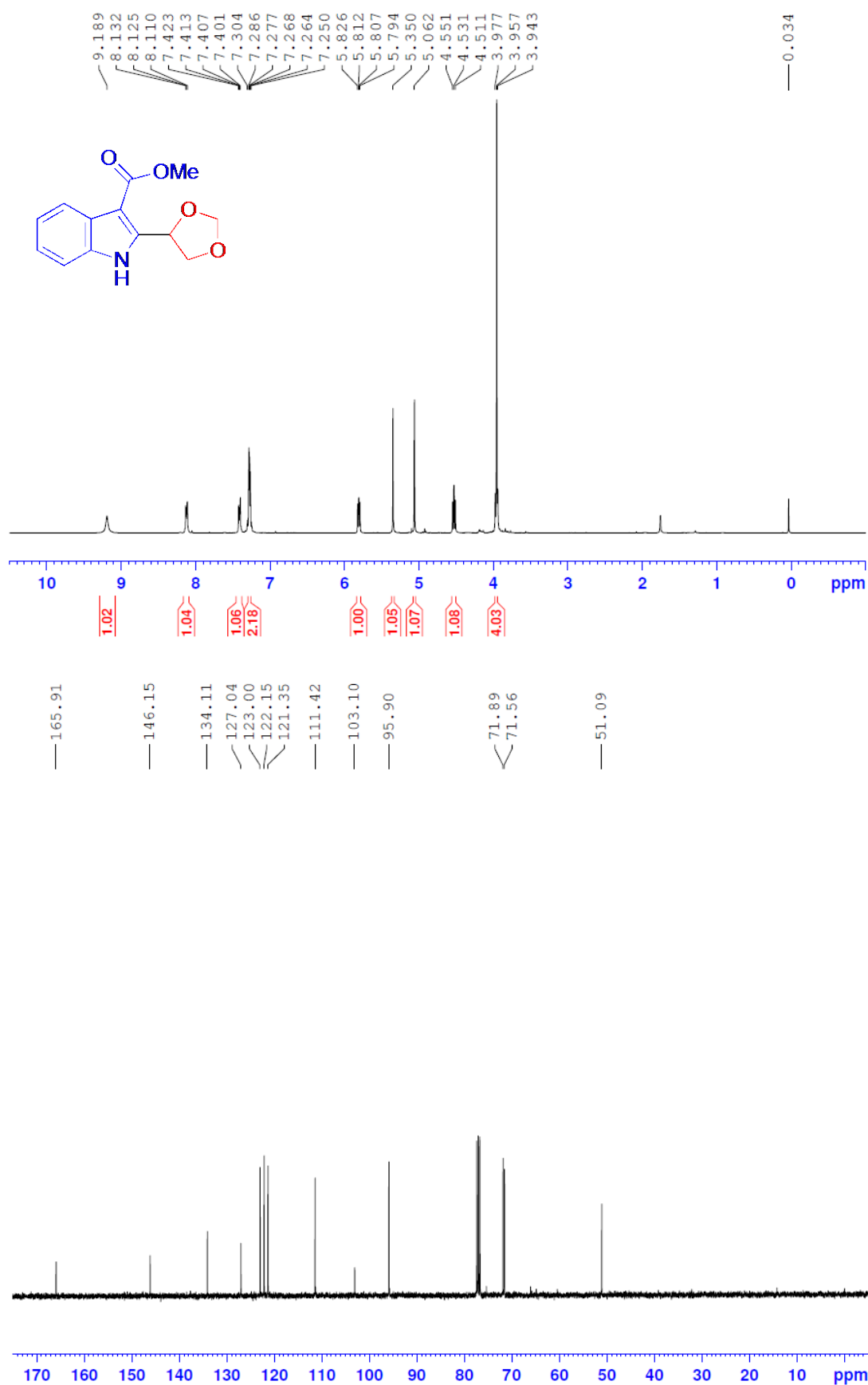
Methyl 2-(tetrahydrofuran-2-yl)-1*H*-indole-3-carboxylate (Table 3, product 3ab)



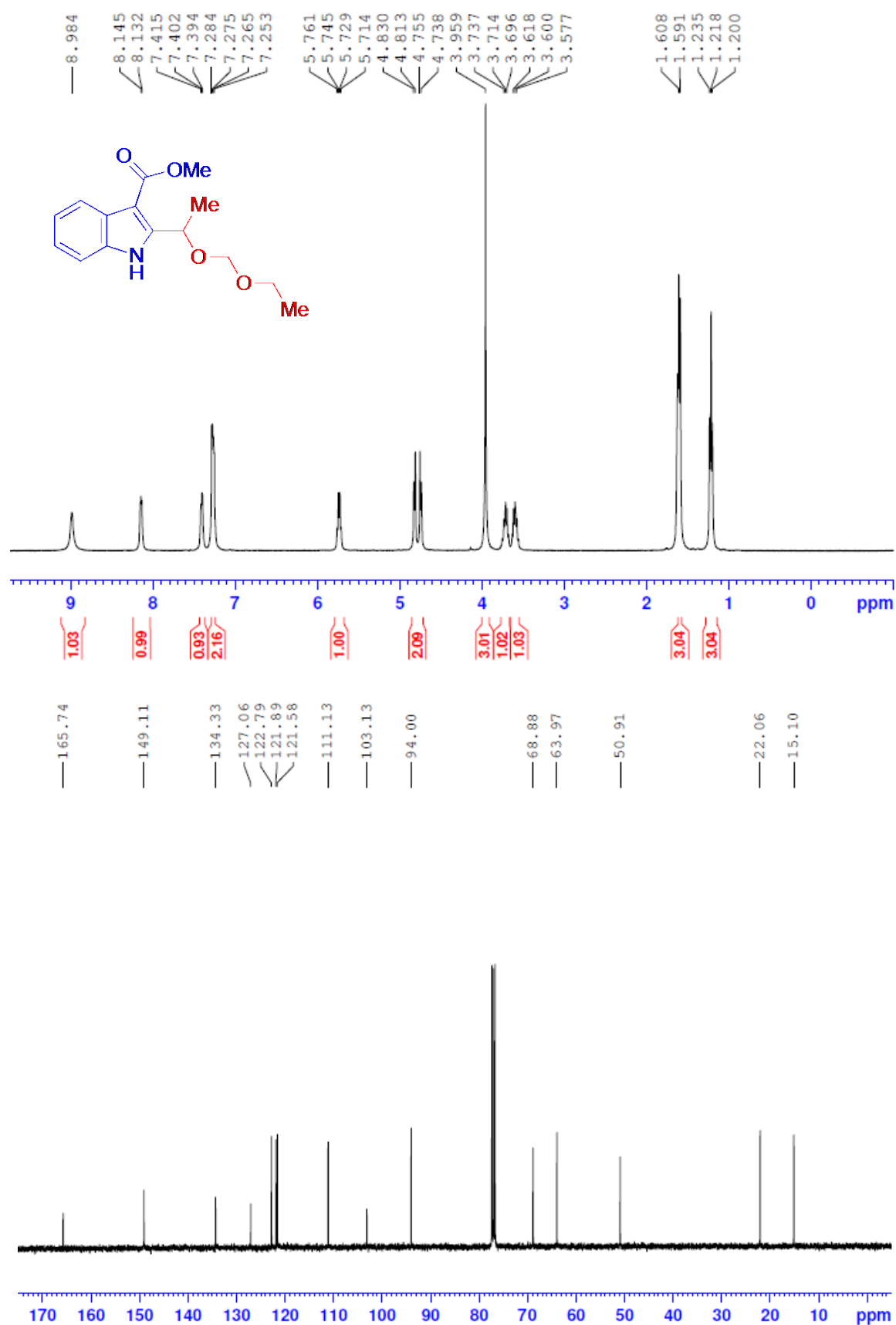
**Methyl 2-(1,3-dioxan-4-yl)-1*H*-indole-3-carboxylate (Table 3, product 3ac)**



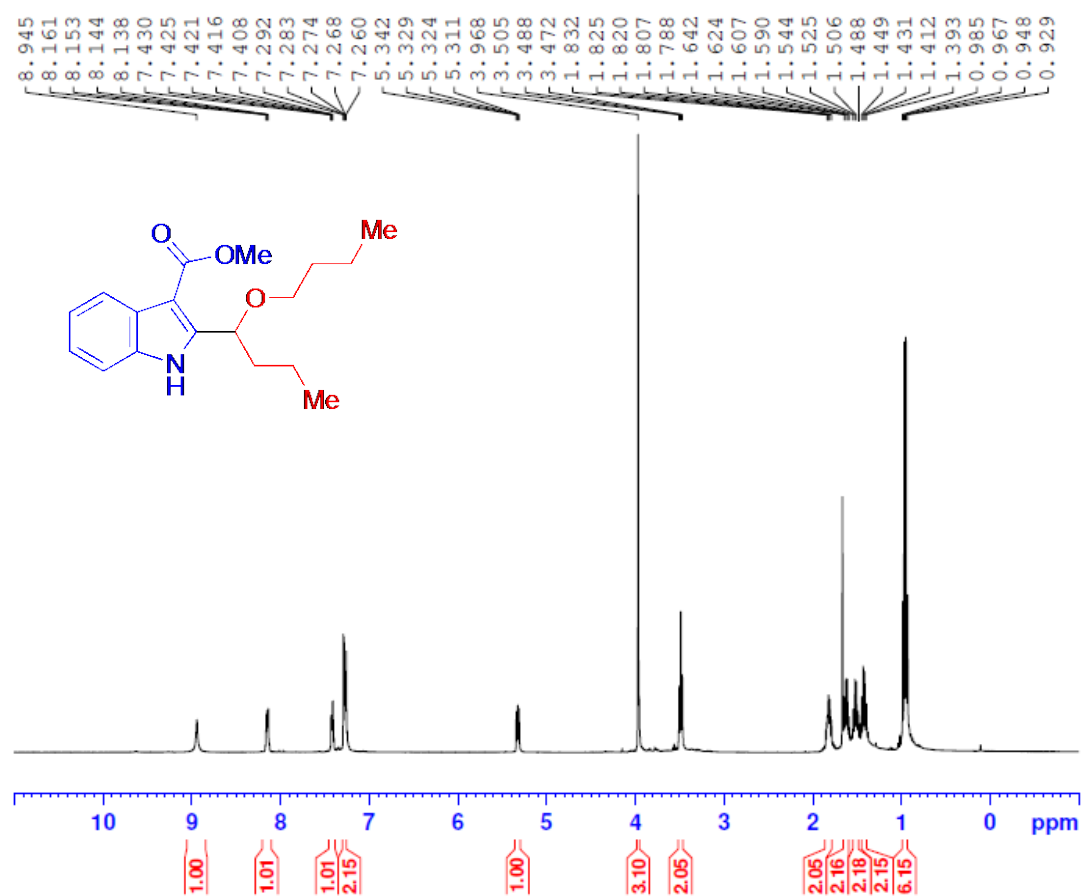
Methyl 2-(1,3-dioxolan-4-yl)-1*H*-indole-3-carboxylate (Table 3, product 3ad)



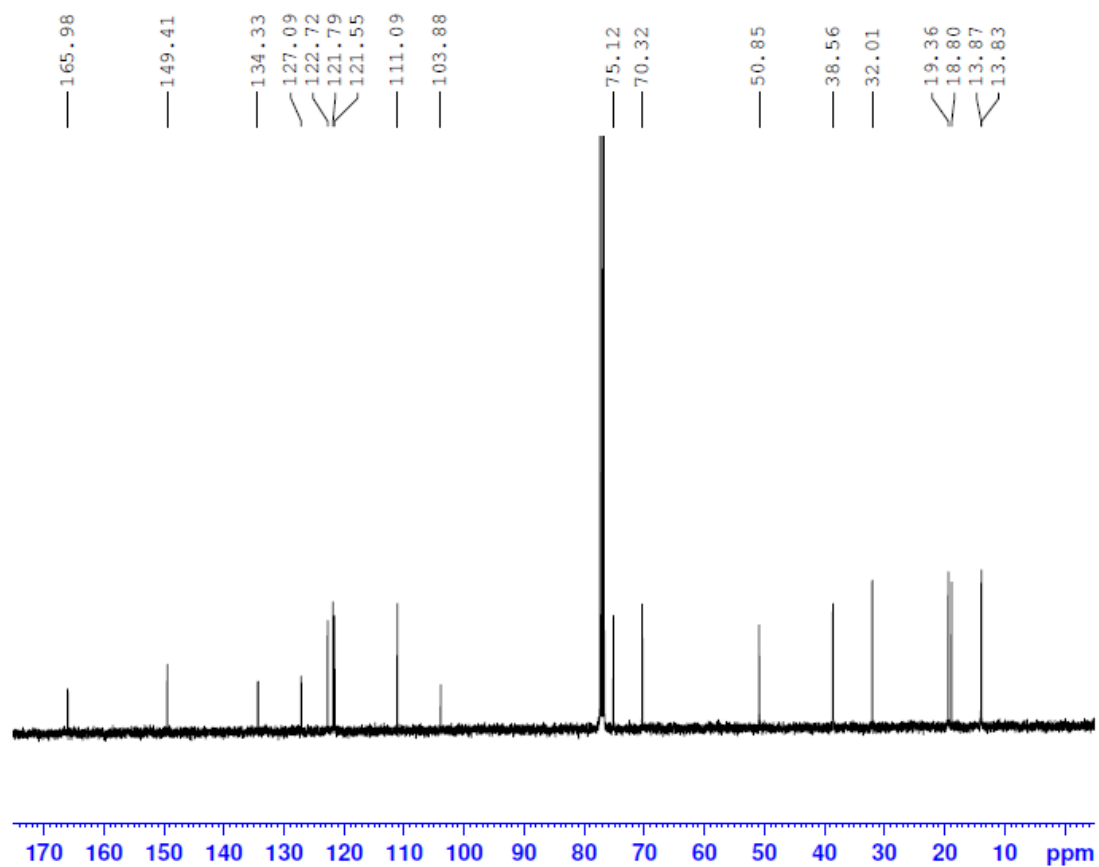
Methyl 2-(1-(ethoxymethoxy)ethyl)-1*H*-indole-3-carboxylate (Table 3, product 3ae)



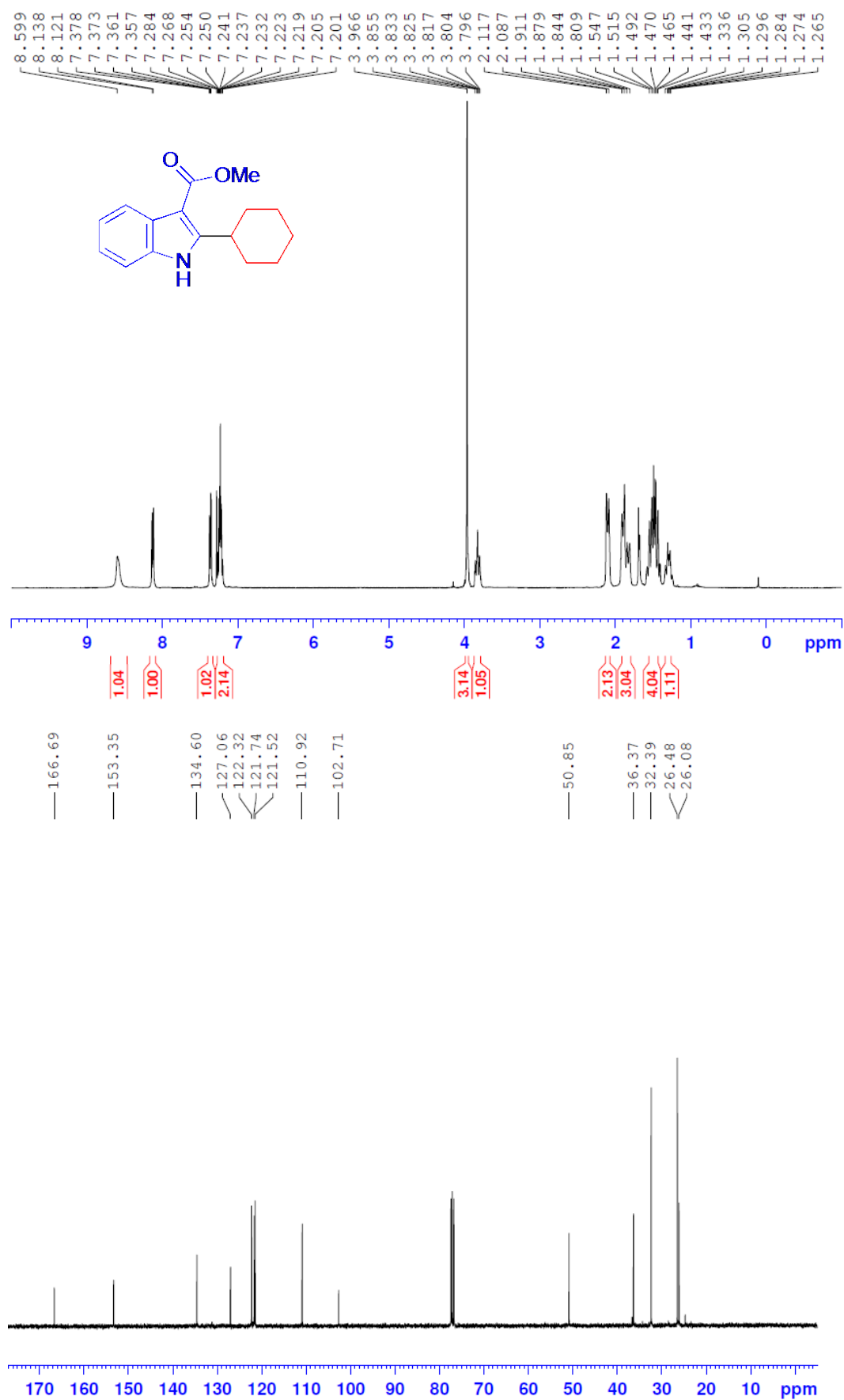
Methyl 2-(1-butoxybutyl)-1H-indole-3-carboxylate (Table 3, product 3af)



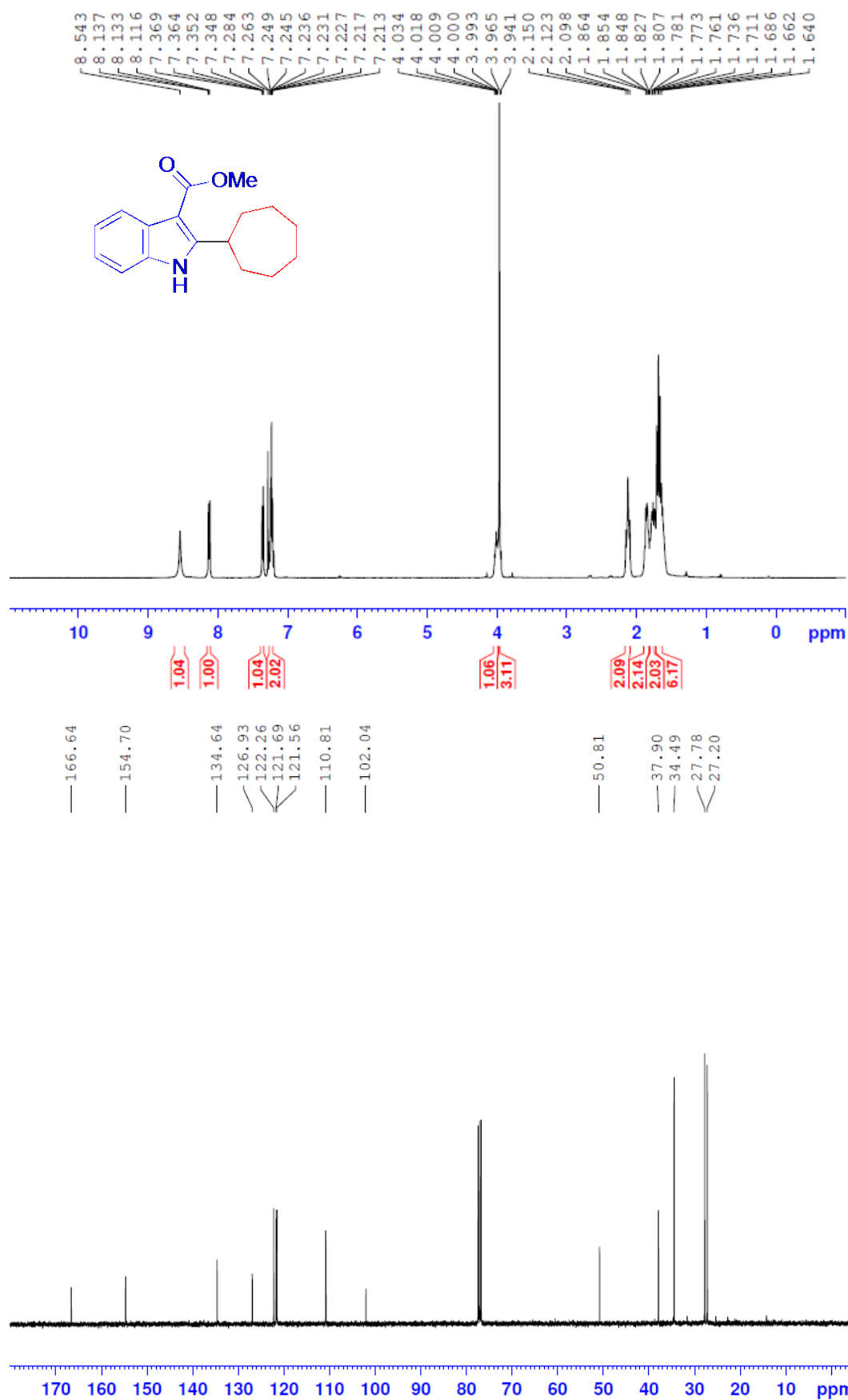




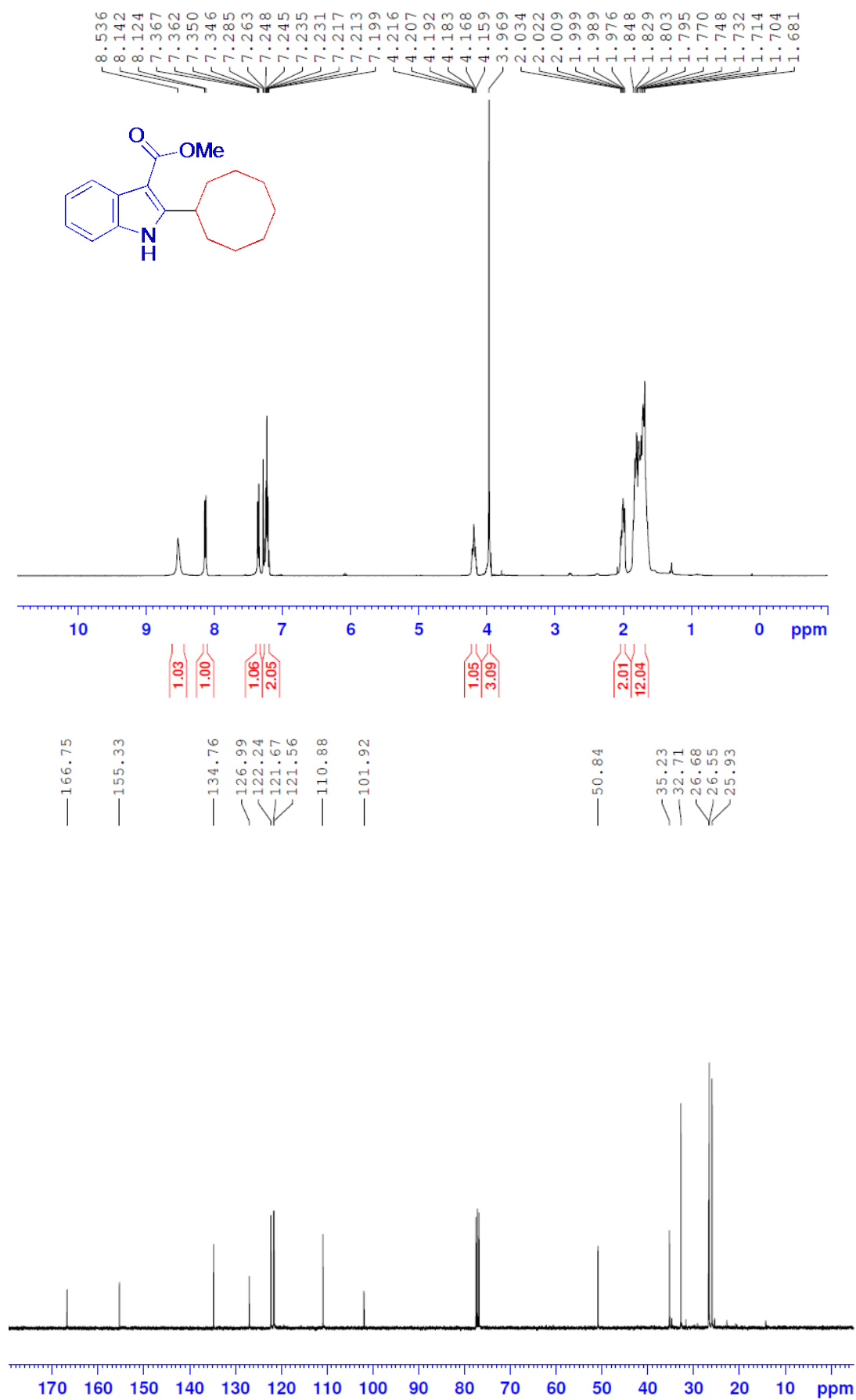
Methyl 2-cyclohexyl-1*H*-indole-3-carboxylate (Table 3, product 3ag)



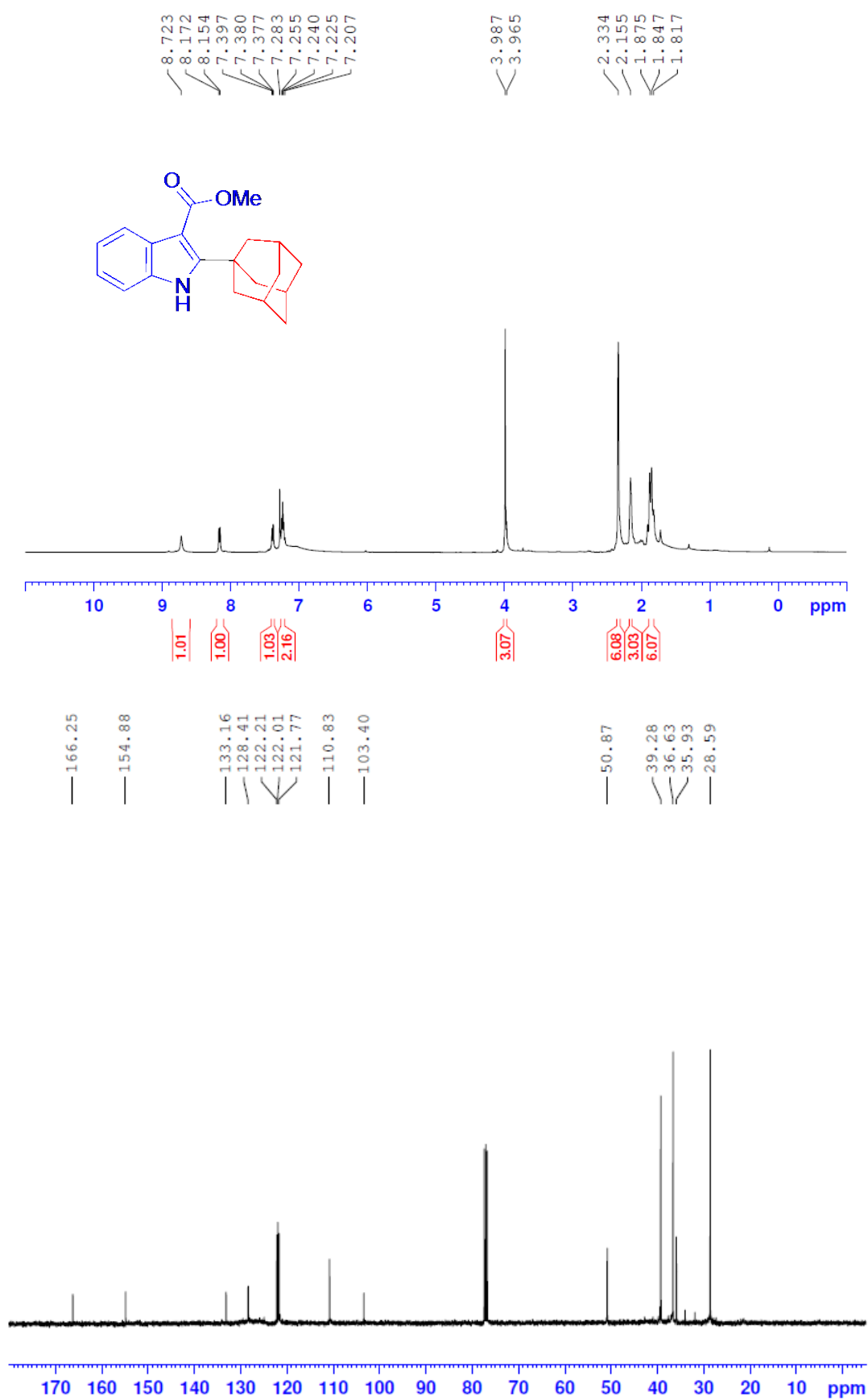
Methyl 2-cycloheptyl-1H-indole-3-carboxylate (Table 3, product 3ah)



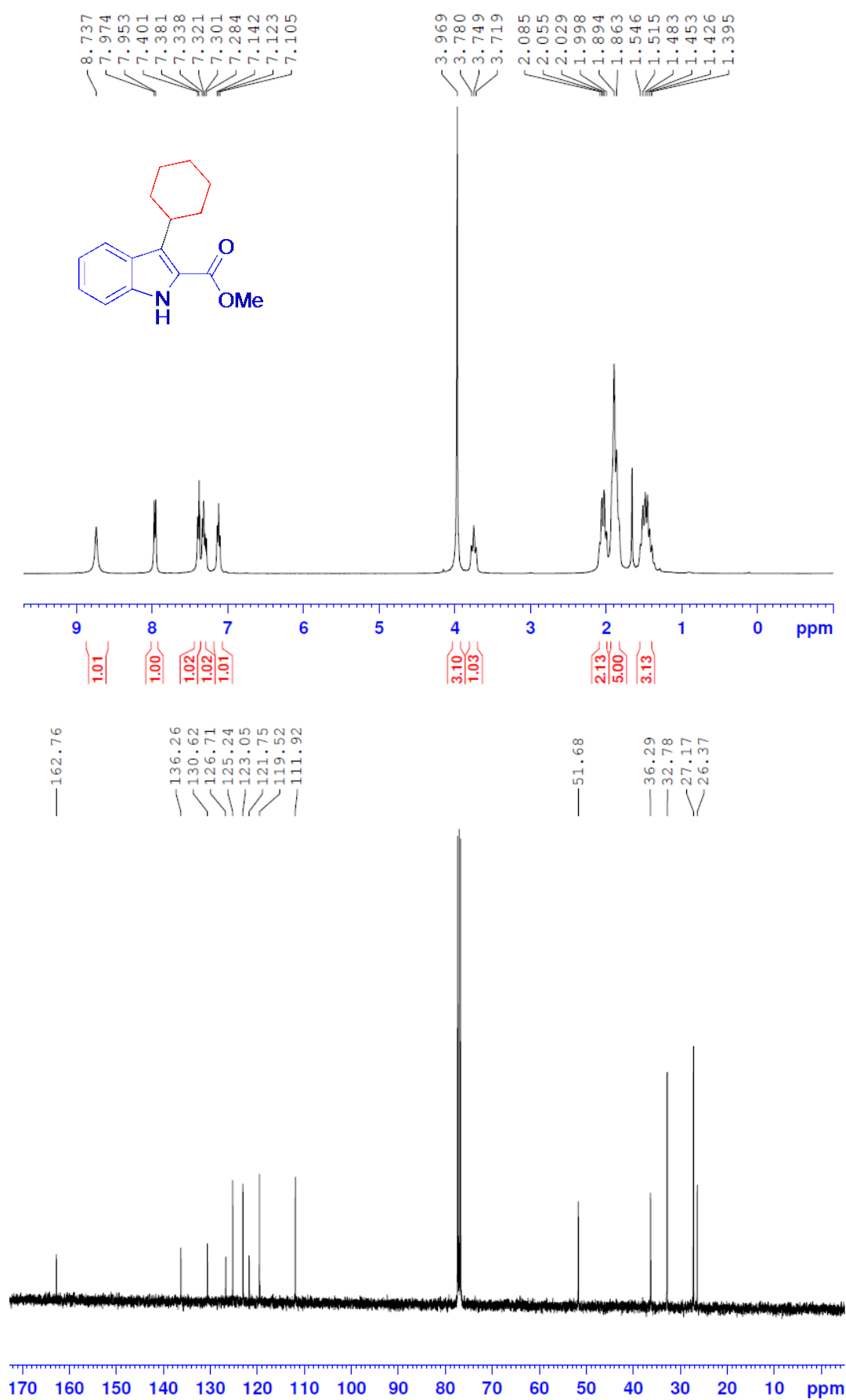
Methyl 2-cyclooctyl-1H-indole-3-carboxylate (Table 3, product 3ai)



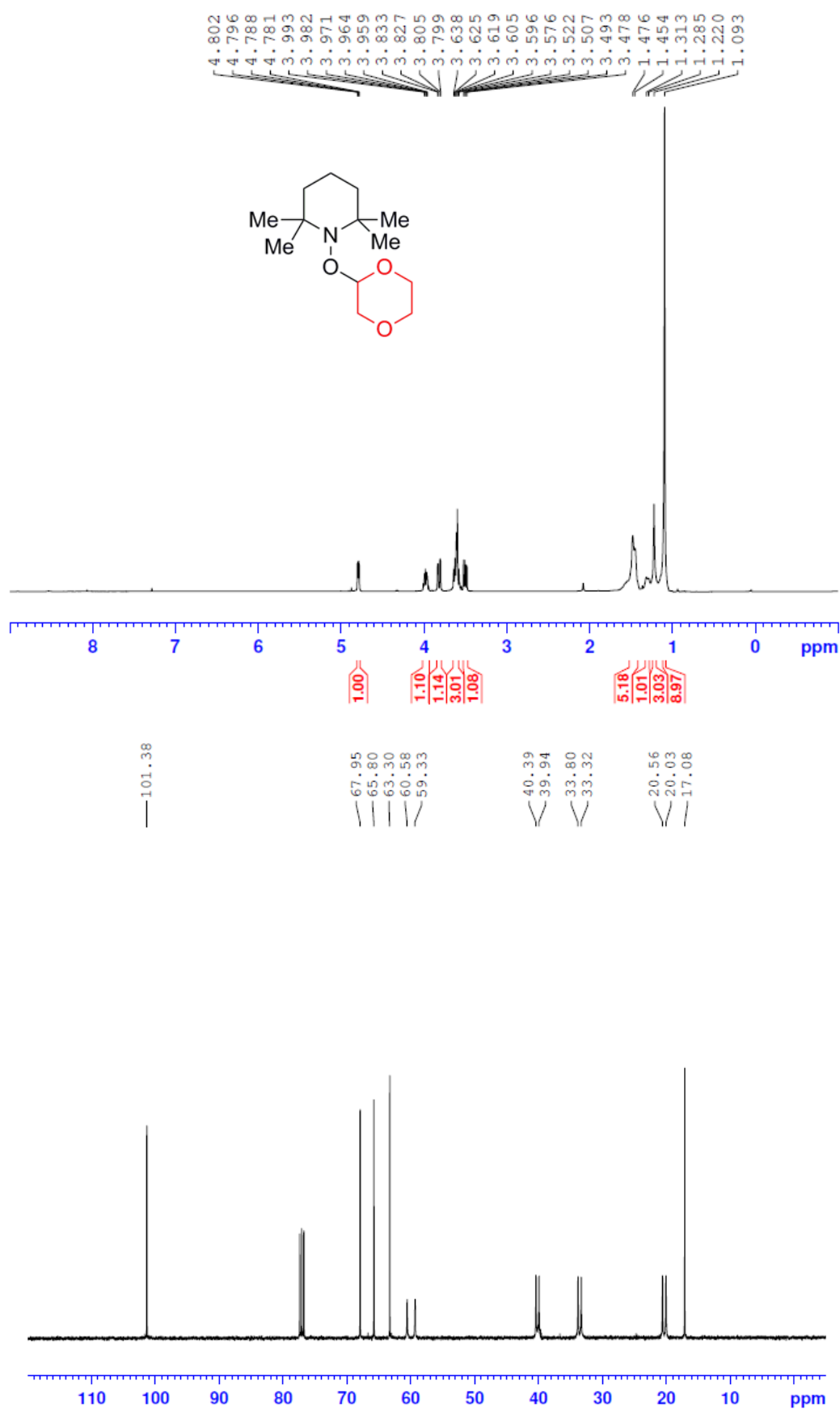
Methyl 2-((1S,3S)-adamantan-1-yl)-1H-indole-3-carboxylate (Table 3, product 3aj)



Methyl 3-cyclohexyl-1*H*-indole-2-carboxylate (Table 3, product 3og)



1-((1,4-Dioxan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (Scheme 2, product 4)



## References

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- 2 M. Hu, J. H. Fan, Y. Liu, X. H. Ouyang, R. J. Song and J. H. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 9577.