Supporting Information

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1. General Information

Unless otherwise stated, all commercial reagents were used as received. Reactions were conducted in dry glassware using anhydrous solvents (pass through activated alumina columns). Reaction temperatures were controlled using IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately, 24 ^{o}C). Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silica gel (200-300 mesh) supplied by Tsingdao Haiyang Chemicals (China) was used for flash column chromatography. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker spectrometers (400 MHz, 500 MHz). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16); proton (dimethyl sulfoxide-d_6 δ 2.50), carbon (dimethyl sulfoxide-d_6 δ 39.52); proton (acetone-d_6 δ 2.05), carbon (acetone-d_6 δ 206.26) and tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained on UHPLC-QTOF-MS^{E} from Tianjin University of Traditional Chinese Medicine. The melting points of all compounds in this communication were measured by YRT-3 melting point meter.

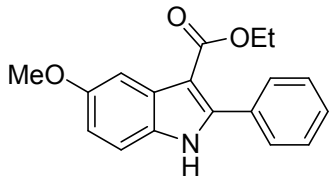
2. Experimental Procedure

(A) Materials.

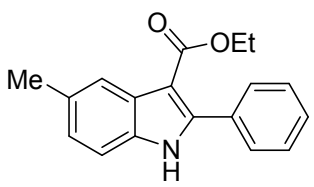
Substrates (Enamines) were prepared according to the known procedures. [1]

(B) Experimental procedure for the synthesis of indoles.

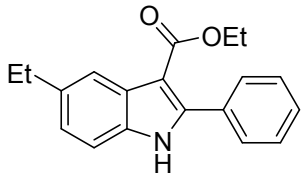
To a 15 mL sealed tube was added **1** (0.50 mmol), CBr_4 (0.75 mmol), K_2CO_3 (1.00 mmol) and dry DMSO (5 mL). The resulting mixture was heated at 100 °C for the indicated time until the complete consumption of starting material as monitored by TLC or GC-MS analysis. After cooling, the mixture was filtered through a pad of Celite, the filter cake was washed with EA. The reaction was then diluted with EA and organic phase was washed successively with water (3×25 mL) and brine (3×25 mL), dried over anhydrous Na_2S0_4, and filtered. The filtrate was concentrated in vacuo and purified by silica gel column chromatography (EA/Hexane) to afford desired product.



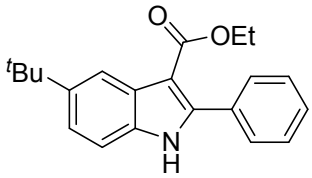
Ethyl 5-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-1): 125 mg, 85% yield; White solid; R_f = 0.24 (EA-Hexane = 1:5, *V:V*); m.p. 186-188 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.43 – 7.35 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.70, 155.79, 144.96, 132.23, 130.28, 129.64, 129.14, 128.60, 128.11, 113.50, 112.04, 104.36, 103.61, 59.75, 55.78, 14.34; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{17}NNaO_3$ $[M+Na]^+$: 318.1101, found: 318.1097.



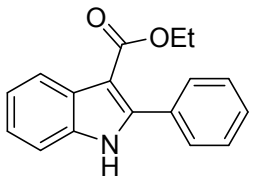
Ethyl 5-methyl-2-phenyl-1*H*-indole-3-carboxylate (2-2): 117 mg, 84% yield; White solid; R_f = 0.32 (EA-Hexane = 1:5, *V:V*); m.p. 137-139 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (brs, 1H), 8.04 (s, 1H), 7.66 – 7.55 (m, 2H), 7.45 – 7.34 (m, 3H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.08 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.69, 144.62, 133.65, 132.35, 131.58, 129.69, 129.11, 128.11, 128.03, 124.80, 121.82, 110.85, 104.25, 59.75, 21.85, 14.39; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{17}NNaO_2$ [M+Na]$^+$: 302.1151, found: 302.1145.



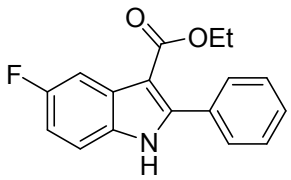
Ethyl 5-ethyl-2-phenyl-1*H*-indole-3-carboxylate (2-3): 122 mg, 83% yield; White solid; R_f = 0.28 (EA-Hexane = 1:5, *V:V*); m.p. 161-163 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.08 (s, 1H), 7.65 – 7.58 (m, 2H), 7.46 – 7.37 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.13 (dd, *J* = 8.2, 1.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.67, 144.63, 138.35, 133.80, 132.39, 129.70, 129.13, 128.14, 128.04, 123.85, 120.68, 110.94, 104.46, 59.74, 29.37, 16.55, 14.39; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{19}NNaO_2$ [M+Na]$^+$: 316.1308, found: 316.1301.



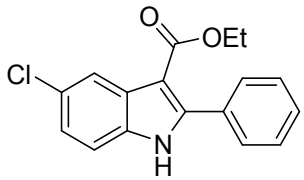
Ethyl 5-(tert-butyl)-2-phenyl-1*H*-indole-3-carboxylate (2-4): 138 mg, 86% yield; White solid; R_f = 0.32 (EA-Hexane = 1:5, *V:V*); m.p. 158-160 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 8.30 (s, 1H), 7.67 – 7.59 (m, 2H), 7.47 – 7.40 (m, 3H), 7.37 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.44 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.65, 145.27, 144.72, 133.47, 132.41, 129.70, 129.17, 128.19, 127.62, 121.61, 118.16, 110.65, 104.76, 59.73, 34.99, 31.99, 14.37; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{23}NNaO_2$ [M+Na]$^+$: 344.1621, found: 344.1615.



Ethyl 2-phenyl-1*H*-indole-3-carboxylate (2-5): 107 mg, 81% yield; White solid; R_f = 0.39 (EA-Hexane = 1:5, *V:V*); m.p. 147-158 °C; ^{1}H NMR (500 MHz, Acetone-d_6) δ 11.01 (brs, 1H), 8.21 (d, *J* = 6.0 Hz, 1H), 7.81 – 7.65 (m, 2H), 7.53 – 7.41 (m, 4H), 7.27 – 7.17 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 165.51, 145.31, 136.80, 133.40, 130.83, 129.63, 128.89, 128.66, 123.57, 122.68, 122.28, 112.36, 104.84, 59.80, 14.65; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{15}NNaO_2$ $[M+Na]^+$: 288.0995, found: 288.0990.

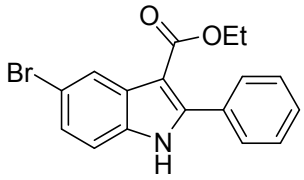


Ethyl 5-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-6): 105 mg, 74% yield; White solid; R_f = 0.40 (EA-Hexane = 1:5, *V:V*); m.p. 152-154 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (brs, 1H), 7.85 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.40 (d, *J* = 6.3 Hz, 3H), 7.26 – 7.22 (m, 1H), 6.97 (td, *J* = 9.0, 2.5 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.39, 159.33 (d, *J* = 236.5 Hz), 146.22, 131.81, 129.60, 129.40, 128.47 (d, *J* = 11.3 Hz), 128.18, 112.06 (d, *J* = 9.7 Hz), 111.61 (d, *J* = 26.4 Hz), 107.48 (d, *J* = 25.2 Hz), 104.85 (d, *J* = 4.5 Hz), 59.98, 14.37; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.19 (td, *J* = 9.5, 4.4 Hz); HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{14}FNNaO_2$ $[M+Na]^+$: 306.0901, found: 306.0893.

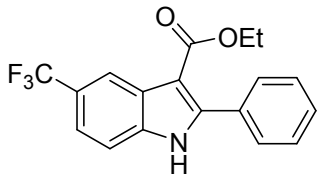


Ethyl 5-chloro-2-phenyl-1*H*-indole-3-carboxylate (2-7): 105 mg, 70% yield; White solid; R_f = 0.41 (EA-Hexane = 1:5, *V:V*); m.p. 149-151 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.42 – 7.35 (m, 3H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.19 (dd, *J* = 8.6,

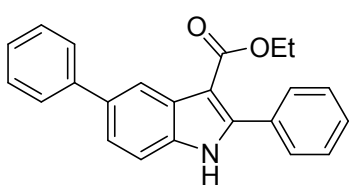
2.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.21, 145.81, 133.66, 131.63, 129.63, 129.51, 128.80, 128.23, 127.93, 123.62, 121.78, 112.27, 104.44, 60.06, 14.40; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{14}ClNNaO_2$ $[M+Na]^+$: 322.0605, found: 322.0601.



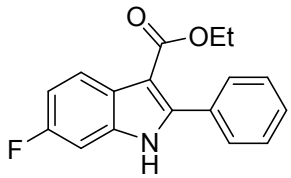
Ethyl 5-bromo-2-phenyl-1*H*-indole-3-carboxylate (2-8): 125 mg, 73% yield; White solid; R_f = 0.40 (EA-Hexane = 1:5, *V:V*); m.p. 103-105 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 8.35 (s, 1H), 7.63 – 7.54 (m, 2H), 7.42 – 7.35 (m, 3H), 7.33 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.18, 145.62, 133.94, 131.58, 129.64, 129.53, 129.37, 128.24, 126.22, 124.84, 115.63, 112.67, 104.34, 60.08, 14.39; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{14}BrNNaO_2$ $[M+Na]^+$: 366.0100, found: 366.0103.



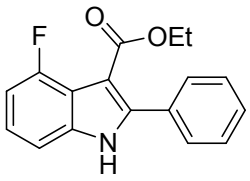
Ethyl 2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (2-9): 103 mg, 62% yield; White solid; R_f = 0.39 (EA-Hexane = 1:5, *V:V*); m.p. 177-179 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.53 (s, 1H), 7.65 – 7.57 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.38 (m, 4H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.05, 146.19, 136.59, 131.36, 129.74, 129.65, 128.34, 127.16, 126.95 (q, *J* = 270.2 Hz), 124.48 (q, *J* = 31.3 Hz), 120.20 – 120.01 (m), 119.90, 111.55, 105.42, 60.24, 14.34; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.65; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{14}F_3NNaO_2$ $[M+Na]^+$: 356.0869, found: 356.0861.



Ethyl 2,5-diphenyl-1*H*-indole-3-carboxylate (2-10): 128 mg, 75% yield; White solid; R_f = 0.34 (EA-Hexane = 1:4, *V:V*); m.p. 175-177 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.50 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.53 - 7.46 (m, 3H), 7.43 – 7.35 (m, 5H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.64, 145.28, 142.38, 135.54, 134.85, 132.03, 129.67, 129.25, 128.83, 128.25, 128.14, 127.54, 126.72, 123.02, 120.65, 111.54, 104.85, 59.89, 14.39; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{19}NNaO_2$ $[M+Na]^+$: 364.1308, found:364.1314.

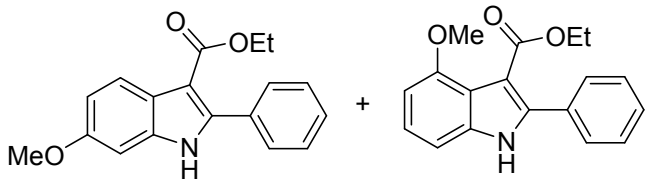


Ethyl 6-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-11): 44 mg, 31% yield; White solid; R_f = 0.43 (EA-Hexane = 1:5, *V:V*); m.p. 157-159 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 8.19 – 8.09 (m, 1H), 7.64 – 7.56 (m, 2H), 7.44 – 7.36 (m, 3H), 7.06 – 6.98 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.35, 160.32 (d, *J* = 239.9 Hz), 145.04 (d, *J* = 3.0 Hz), 135.31 (d, *J* = 12.3 Hz), 131.92, 129.64, 129.36, 128.24, 124.21, 123.30 (d, *J* = 9.6 Hz), 110.75 (d, *J* = 23.9 Hz), 104.79, 97.63 (d, *J* = 26.2 Hz), 59.98, 14.38; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.20 (td, *J* = 9.3, 5.5 Hz); HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{14}FNNaO_2$ $[M+Na]^+$: 306.0901, found: 306.0898.

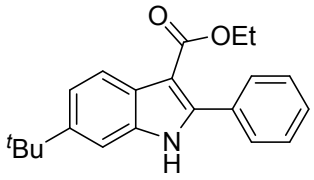


Ethyl 4-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-11'): 44 mg, 31% yield; White solid; R_f = 0.29 (EA-Hexane = 1:5, *V:V*); m.p. 166-168 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 7.60 – 7.47 (m, 2H), 7.42 – 7.32 (m, 3H), 7.20 – 7.10 (m, 2H), 6.90 (dd, *J* = 11.0, 7.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.27, 156.27 (d, *J* = 251.7 Hz), 143.30, 137.95 (d, *J* = 10.1 Hz), 131.69, 129.35, 129.26, 128.32, 123.89 (d, *J* = 8.0 Hz), 115.76 (d, *J* = 19.1 Hz), 107.85 (d, *J* = 21.3 Hz), 107.39 (d, *J* = 4.0 Hz), 104.50 (d, *J* = 3.6 Hz), 60.55, 14.08; ^{19}F

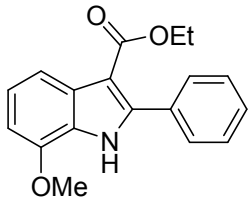
NMR (376 MHz, Chloroform-*d*) δ -113.74 (dd, *J* = 11.3, 3.0 Hz); HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{14}FNNaO_2$ [M+Na]$^+$: 306.0901, found: 306.0906.



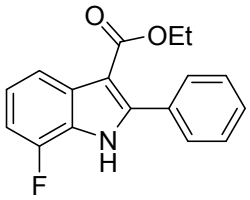
Ethyl 6-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-12) and ethyl-4-methoxy-2-phenyl-1*H*-indol-3-carboxylate (2-12'): 127 mg, 86% yield; White solid; R_f = 0.25 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.17 (s, 1H), 9.03 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.51 – 7.47 (m, 2H), 7.34 – 7.30 (m, 6H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.76 (d, *J* = 2.1 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 4H), 3.84 (s, 3H), 3.72 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 167.39, 165.76, 156.88, 153.63, 143.80, 138.81, 137.05, 136.24, 132.15, 131.89, 129.58, 128.81, 128.49, 128.43, 128.33, 127.95, 124.02, 122.73, 121.87, 117.01, 111.79, 106.12, 104.55, 104.19, 101.76, 94.63, 60.81, 59.74, 55.54, 55.44, 14.34, 14.08; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{17}NNaO_3$ [M+Na]$^+$: 318.1101, found: 318.1108.



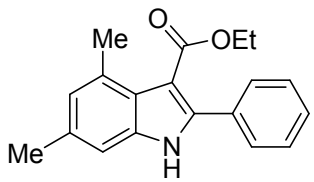
Ethyl 6-(*tert*-butyl)-2-phenyl-1*H*-indole-3-carboxylate (2-13): 132 mg, 82% yield; White solid; R_f = 0.47 (EA-Hexane = 1:5, *V:V*); m.p. 157-159 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (brs, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.46 – 7.40 (m, 3H), 7.40 – 7.35 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.40 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.63, 146.95, 144.37, 135.52, 132.37, 129.69, 129.12, 128.18, 125.47, 121.77, 120.50, 107.39, 104.58, 59.73, 34.93, 31.80, 14.44; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{23}NNaO_2$ [M+Na]$^+$: 344.1621, found: 344.1613.



Ethyl 7-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-14): 130 mg, 88% yield; White solid; R_f = 0.36 (EA-Hexane = 1:5, *V:V*); m.p. 158-160 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.74 – 7.62 (m, 2H), 7.53 – 7.38 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 4.32 (d, *J* = 7.0 Hz, 2H), 3.97 (s, 3H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.47, 145.89, 143.97, 132.25, 129.78, 129.25, 129.11, 128.23, 125.85, 122.64, 114.83, 105.39, 103.16, 59.80, 55.55, 14.46; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{17}NNaO_3$ $[M+Na]^+$: 318.1101, found:318.1106.

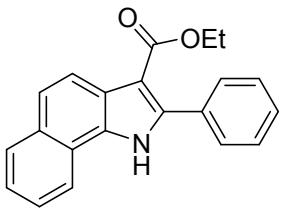


Ethyl 7-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-15): 95 mg, 67% yield; White solid; R_f = 0.39 (EA-Hexane = 1:5, *V:V*); m.p. 143-145 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.87 (brs, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.46 – 7.38 (m, 3H), 7.18 (td, *J* = 8.0, 5.0 Hz, 1H), 6.98 (dd, *J* = 10.7, 8.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.18, 149.22 (d, *J* = 244.4 Hz), 145.18, 131.61, 131.10 (d, *J* = 4.5 Hz), 129.75, 129.50, 128.22, 123.72 (d, *J* = 13.6 Hz), 122.39 (d, *J* = 6.2 Hz), 117.99 (d, *J* = 3.6 Hz), 108.10 (d, *J* = 15.6 Hz), 105.60, 60.01, 14.36; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -135.10 (dd, *J* = 10.8, 4.9 Hz); HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{14}FNNaO_2$ $[M+Na]^+$: 306.0901, found: 306.0905.

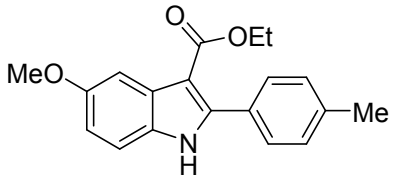


Ethyl 4,6-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (2-16): 122 mg, 83% yield; White solid; R_f = 0.35 (EA-Hexane = 1:5, *V:V*); m.p. 120-122 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 6.87 (s, 1H), 6.86 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.67 (s,

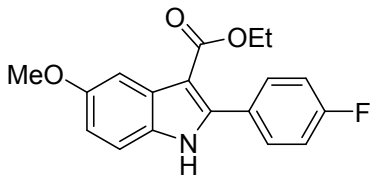
3H), 2.39 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 167.37, 140.63, 136.28, 133.02, 132.50, 130.81, 128.73, 128.47, 128.25, 125.30, 123.66, 108.97, 106.83, 60.53, 21.42, 21.16, 13.94; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$: 316.1308, found:316.1310.



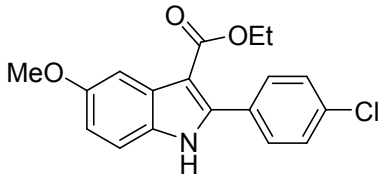
Ethyl 2-phenyl-1*H*-benzo[*g*]indole-3-carboxylate (2-17): 99 mg, 63% yield; White solid; R_f = 0.42 (EA-Hexane = 1:5, *V:V*); m.p. 198-200 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.40 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43 – 7.32 (m, 3H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.71, 142.48, 132.31, 130.87, 130.24, 129.83, 129.03, 128.21, 125.99, 124.71, 124.24, 122.91, 121.44, 121.26, 119.65, 106.53, 60.00, 14.43; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1151, found: 338.1156.



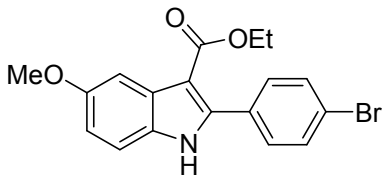
Ethyl 5-methoxy-2-(*p*-tolyl)-1*H*-indole-3-carboxylate (2-18): 128 mg, 83% yield; White solid; R_f = 0.38 (EA-Hexane = 1:5, *V:V*); m.p. 140-142 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.72 (d, *J* = 2.5 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.21 – 7.14 (m, 3H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.36 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.79, 155.76, 145.29, 139.17, 130.29, 129.47, 129.26, 128.80, 128.69, 113.25, 111.96, 104.12, 103.78, 59.69, 55.80, 21.45, 14.40; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$: 332.1257, found: 332.1249.



Ethyl 2-(4-fluorophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-19): 125 mg, 80% yield; White solid; R_f = 0.38 (EA-Hexane = 1:5, *V:V*); m.p. 167-168 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.93 (brs, 1H), 7.82 – 7.74 (m, 2H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.19 (m, 2H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 165.55, 163.91 (d, *J* = 246.5 Hz), 156.67, 144.45, 132.96 (d, *J* = 8.4 Hz), 131.73, 129.86 (d, *J* = 3.3 Hz), 129.68, 115.48 (d, *J* = 21.8 Hz), 113.83, 113.11, 104.82, 104.40, 59.80, 55.80, 14.64; ^{19}F NMR (376 MHz, Acetone-d_6) δ -114.35 (tt, *J* = 9.0, 4.9 Hz); HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}FNNaO_3$ $[M+Na]^+$: 336.1006, found: 336.1001.

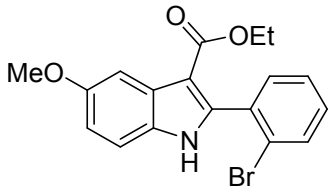


Ethyl 2-(4-chlorophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-20): 135 mg, 82% yield; White solid; R_f = 0.36 (EA-Hexane = 1:5, *V:V*); m.p. 140-142 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.55, 155.99, 143.46, 135.28, 130.97, 130.68, 130.35, 128.56, 128.40, 113.88, 112.02, 104.85, 103.80, 59.89, 55.83, 14.42; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}ClNNaO_3$ $[M+Na]^+$: 352.0711, found: 352.0707.

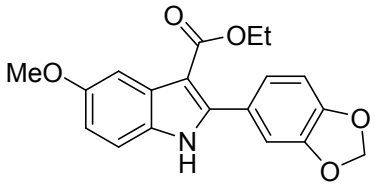


Ethyl 2-(4-bromophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-21): 158 mg, 85% yield; White solid; R_f = 0.36 (EA-Hexane = 1:5, *V:V*); m.p. 164-165 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.52, 156.00, 143.44, 131.37, 131.21, 131.15, 130.36, 128.57,

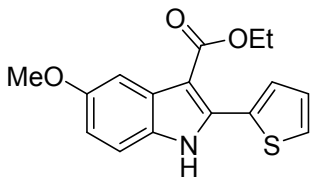
123.59, 113.93, 112.03, 104.89, 103.81, 59.90, 55.84, 14.43; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}BrNNaO_3$ $[M+Na]^+$: 396.0206, found: 396.0210.



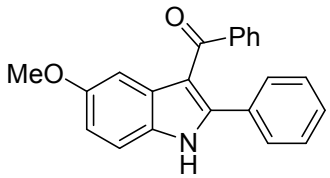
Ethyl 2-(2-bromophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-22): 132 mg, 71% yield; White solid; R_f = 0.36 (EA-Hexane = 1:5, *V:V*); m.p. 163-165 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.75 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.24 (m, 2H), 6.93 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.14, 155.94, 142.68, 134.21, 132.66, 132.01, 130.52, 130.14, 127.72, 126.93, 123.96, 114.01, 112.20, 106.47, 103.36, 59.64, 55.85, 14.12; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}BrNNaO_3$ $[M+Na]^+$: 396.0206, found: 396.0200.



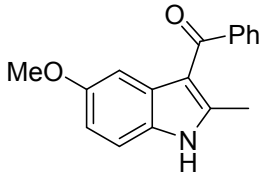
Ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-5-methoxy-1*H*-indole-3-carboxylate (2-23): 115 mg, 68% yield; White solid; R_f = 0.25 (EA-Hexane = 1:3, *V:V*); m.p. 168-170 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.06 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.82, 155.73, 148.34, 147.28, 144.85, 130.15, 128.57, 125.76, 123.36, 113.20, 111.96, 110.30, 107.96, 103.88, 103.73, 101.42, 59.76, 55.78, 14.41; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{17}NNaO_5$ $[M+Na]^+$: 362.0999, found: 362.0996.



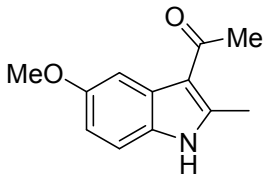
Ethyl 5-methoxy-2-(thiophen-2-yl)-1*H*-indole-3-carboxylate (2-24): 90 mg, 60% yield; White solid; R_f = 0.43 (EA-Hexane = 1:5, *V:V*); m.p. 147-150 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 2.9 Hz, 1H), 7.43 (d, *J* = 4.8 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.14 – 7.06 (m, 1H), 6.91 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.50, 155.93, 137.53, 132.84, 130.24, 129.32, 128.70, 127.78, 127.39, 113.96, 111.79, 104.81, 104.00, 60.01, 55.80, 14.55; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{15}NNaO_3S$ $[M+Na]^+$: 324.0665, found: 324.0669.



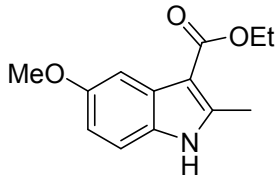
(5-methoxy-2-phenyl-1*H*-indol-3-yl)(phenyl)methanone (2-25): 75 mg, 46% yield; White solid; R_f = 0.56 (EA-Hexane = 1:5, *V:V*); m.p. 186-188 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.04 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.51 (s, 1H), 7.29 – 7.23 (m, 4H), 7.15 – 7.07 (m, 5H), 6.90 (dd, *J* = 8.7, 1.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.75, 156.14, 144.75, 139.88, 131.90, 131.51, 130.73, 129.71, 129.60, 129.35, 128.69, 128.32, 127.79, 114.24, 113.60, 112.14, 103.11, 55.82; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{17}NNaO_2$ $[M+Na]^+$: 350.1151, found: 350.1148.



(5-methoxy-2-methyl-1*H*-indol-3-yl)(phenyl)methanone (2-26): 57 mg, 43% yield; White solid; R_f = 0.33 (EA-Hexane = 1:3, *V:V*); m.p. 220-222 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.87 (s, 1H), 7.60 – 7.55 (m, 3H), 7.53 – 7.48 (m, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 6.87 (s, 1H), 6.76 (dd, *J* = 8.7, 1.6 Hz, 1H), 3.60 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 191.75, 154.74, 144.93, 141.90, 130.91, 129.92, 128.45, 128.16, 127.92, 112.51, 111.97, 111.15, 102.74, 55.03, 14.51; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{15}NNaO_2$ $[M+Na]^+$: 288.0995, found: 288.0998.



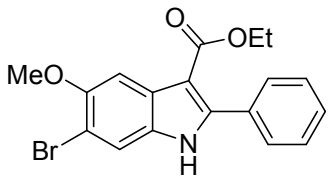
1-(5-methoxy-2-methyl-1*H*-indol-3-yl)ethan-1-one (2-27): 49 mg, 48% yield; White solid; R_f = 0.38 (EA-Hexane = 1:3, *V:V*); m.p. 227-229 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.66 (s, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.77 (s, 3H), 2.65 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 192.76, 155.01, 144.27, 129.52, 127.75, 113.54, 111.66, 110.90, 103.37, 55.27, 30.70, 15.14; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}NNaO_2$ $[M+Na]^+$: 226.0838, found: 226.0845.



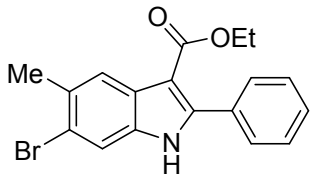
Ethyl 5-methoxy-2-methyl-1*H*-indole-3-carboxylate (2-28): 45 mg, 39% yield; White solid; R_f = 0.53 (EA-Hexane = 1:5, *V:V*); m.p. 161-163 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.70 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 166.31, 155.67, 144.30, 129.52, 128.29, 112.19, 111.32, 104.58, 103.61, 59.58, 55.85, 14.72, 14.56; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{15}NNaO_3$ $[M+Na]^+$: 256.0944, found: 256.0940.

(C) Experimental procedure for the synthesis of brominated indoles.

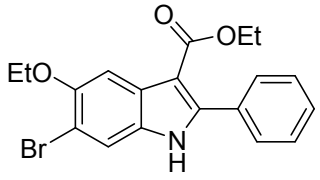
To a 15 mL sealed tube was added **1** (0.50 mmol), CBr_4 (1.50 mmol), and dry DMSO (5 mL). The mixture was stirred at room temperature and then EtONa (1.00 mmol) was added. The resulting mixture was heated at 100 ^{o}C for the indicated time until the complete consumption of starting material as monitored by TLC or GC-MS analysis. After cooling, the mixture was filtered through a pad of Celite, the filter cake was washed with EA. The reaction was then diluted with EA and organic phase was washed successively with water (3×25 mL) and brine (3×25 mL), dried over anhydrous Na_2S0_4, and filtered. The filtrate was concentrated in vacuo and purified by silica gel column chromatography (EA/Hexane) to afford desired product.



Ethyl 6-bromo-5-methoxy-2-phenyl-1*H*-indole-3-carboxylate (3-1): 123 mg, 66% yield; White solid; R_f = 0.35 (EA-Hexane = 1:5, *V:V*); m.p. 212-214 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.11 (s, 1H), 7.72 – 7.64 (m, 3H), 7.62 (s, 1H), 7.53 – 7.44 (m, 3H), 4.18 (d, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.22 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.25, 150.76, 145.14, 131.57, 130.68, 129.87, 129.02, 127.84, 127.60, 115.79, 106.75, 103.20, 102.78, 59.11, 56.14, 14.05; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}BrNNaO_3$ $[M+Na]^+$:396.0206, found: 396.0205.

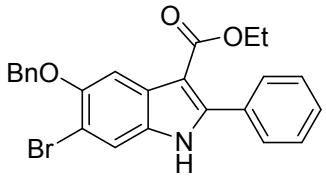


Ethyl 6-bromo-5-methyl-2-phenyl-1*H*-indole-3-carboxylate (3-2): 111 mg, 62% yield; White solid; R_f = 0.42 (EA-Hexane = 1:5, *V:V*); m.p. 187-189 °C; ^{1}H NMR (500 MHz, Acetone-d_6) δ 11.08 (brs, 1H), 8.13 (s, 1H), 7.76 – 7.72 (m, 2H), 7.70 (s, 1H), 7.52 – 7.43 (m, 3H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 165.14, 146.03, 136.06, 132.93, 130.76, 130.74, 129.84, 128.71, 128.62, 123.90, 119.49, 115.65, 104.41, 59.94, 23.48, 14.56; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}BrNNaO_2$ $[M+Na]^+$: 380.0257, found: 380.0252.

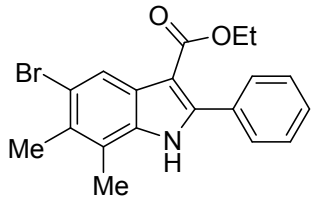


Ethyl 6-bromo-5-ethoxy-2-phenyl-1*H*-indole-3-carboxylate (3-29): 122 mg, 63% yield; White solid; R_f = 0.34 (EA-Hexane = 1:5, *V:V*); m.p. 196-198 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.75 (brs, 1H), 7.73 (s, 1H), 7.60 – 7.53 (m, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.32 (m, 3H), 4.23 (d, *J* = 7.0 Hz, 2H), 4.15 (d, *J* = 6.7 Hz, 2H), 1.50 (t, *J* = 6.7 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.47, 151.21, 145.24, 131.83, 130.47, 129.59, 129.35, 128.17, 127.97, 115.60,

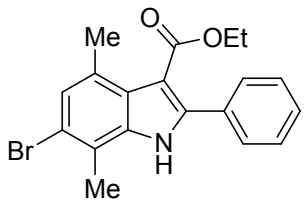
109.00, 105.50, 104.34, 65.43, 59.90, 14.93, 14.31; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}BrNNaO_3$ $[M+Na]^+$: 410.0362, found: 410.0366.



Ethyl 5-(benzyloxy)-6-bromo-2-phenyl-1*H*-indole-3-carboxylate (3-30): 130 mg, 58% yield; White solid; R_f = 0.33 (EA-Hexane = 1:5, *V:V*); m.p. 197-199 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.82 (s, 1H), 7.60 – 7.57 (m, 2H), 7.57 – 7.53 (m, 3H), 7.44 – 7.37 (m, 5H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.22 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.26, 150.96, 145.21, 137.12, 131.84, 130.63, 129.62, 129.44, 128.64, 128.24, 127.96, 127.92, 127.29, 115.61, 109.25, 106.20, 104.63, 71.48, 59.90, 14.35; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{20}BrNNaO_3$ $[M+Na]^+$: 472.0519, found: 472.0522.

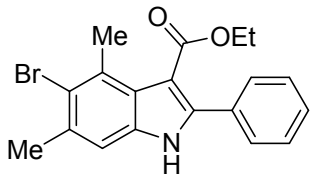


Ethyl 5-bromo-6,7-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-31): 121 mg, 65% yield; White solid; R_f = 0.52 (EA-Hexane = 1:5, *V:V*); m.p. 146-148 °C; ^{1}H NMR (500 MHz, Acetone-d_6) δ 10.82 (brs, 1H), 8.29 (s, 1H), 7.72 – 7.63 (m, 2H), 7.49 – 7.41 (m, 3H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 2.46 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 165.08, 146.07, 135.98, 132.92, 131.06, 129.74, 129.66, 128.43, 127.81, 123.18, 121.86, 119.76, 104.46, 59.87, 19.41, 14.74, 14.55; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}BrNNaO_2$ $[M+Na]^+$: 394.0413, found: 394.0416.

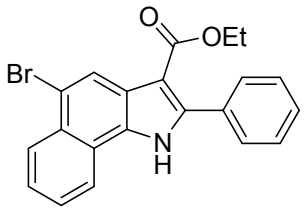


Ethyl 6-bromo-4,7-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-32): 104 mg, 56% yield; White solid; R_f = 0.62 (EA-Hexane = 1:5, *V:V*); m.p. 169-171 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22

(s, 1H), 7.62 – 7.54 (m, 2H), 7.51 – 7.41 (m, 3H), 7.19 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 2.52 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 166.56, 141.07, 135.50, 132.16, 130.48, 129.03, 128.83, 128.55, 127.38, 124.72, 118.87, 117.58, 108.30, 60.74, 20.64, 16.50, 14.02; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}BrNNaO_2$ $[M+Na]^+$: 394.0413, found: 394.0409.



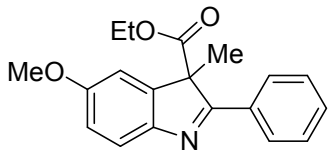
Ethyl 5-bromo-4,6-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-16): 115 mg, 62% yield; White solid; R_f = 0.36 (EA-Hexane = 1:5, *V:V*); m.p. 147-1494 °C; ^{1}H NMR (500 MHz, Acetone-d_6) δ 10.89 (s, 1H), 7.66 – 7.59 (m, 2H), 7.51 – 7.41 (m, 3H), 7.31 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 2.49 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 167.64, 141.29, 135.87, 133.09, 133.07, 130.58, 129.40, 129.37, 129.22, 126.10, 121.59, 111.75, 108.01, 61.09, 25.03, 21.13, 14.22; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}BrNNaO_2$ $[M+Na]^+$: 394.0413, found: 394.0416.



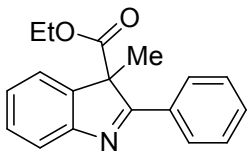
Ethyl 5-bromo-2-phenyl-1*H*-benzo[g]indole-3-carboxylate (3-17): 69 mg, 35% yield; Yellowish solid; R_f = 0.31 (EA-Hexane = 1:5, *V:V*); m.p. 235-237 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.96 (s, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.53 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.67 (m, 3H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.56 – 7.48 (m, 3H), 4.22 (d, *J* = 7.0 Hz, 2H), 1.22 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.12, 143.36, 131.52, 130.38, 130.20, 128.92, 127.78, 127.46, 127.32, 127.01, 125.98, 124.44, 123.85, 122.52, 121.92, 115.17, 104.40, 59.36, 14.10; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{16}BrNNaO_2$ $[M+Na]^+$: 416.0257, found: 416.0251.

(D) Experimental procedure for the synthesis of 3*H*-indoles.

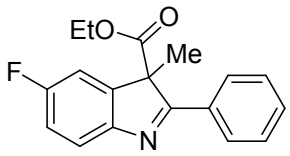
To a 15 mL sealed tube was added **4** (0.50 mmol), CBr_4 (0.75 mmol), K_2CO_3 (1.00 mmol) and dry DMSO (5 mL). The resulting mixture was heated at 110 °C for the indicated time until the complete consumption of starting material as monitored by TLC or GC-MS analysis. After cooling, the mixture was filtered through a pad of Celite, the filter cake was washed with EA. The reaction was then diluted with EA and organic phase was washed successively with water (3×25 mL) and brine (3×25 mL), dried over anhydrous Na_2S0_4, and filtered. The filtrate was concentrated in vacuo and purified by silica gel column chromatography (EA/Hexane) to afford desired product.



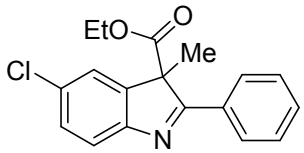
Ethyl 5-methoxy-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-1): 117 mg, 76% yield; Yellow oil; R_f = 0.28 (EA-Hexane = 1:10, *V:V*); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 – 7.88 (m, 2H), 7.65 – 7.59 (m, 1H), 7.50 – 7.42 (m, 3H), 6.99 – 6.89 (m, 2H), 4.21 – 4.11 (m, 1H), 4.03 – 3.94 (m, 1H), 3.85 (s, 3H), 1.70 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 176.15, 171.80, 158.87, 148.68, 143.54, 132.30, 130.77, 128.85, 128.09, 121.76, 114.19, 107.70, 62.33, 61.96, 55.91, 21.36, 13.91; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$: 332.1257, found: 332.1261.



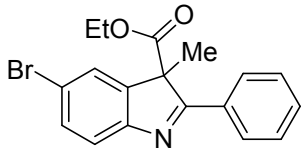
Ethyl 3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-2): 98 mg, 70% yield; Yellowish oil; R_f = 0.36 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.46 – 7.36 (m, 2H), 7.30 – 7.25 (m, 1H), 4.19 – 4.06 (m, 1H), 4.04 – 3.92 (m, 1H), 1.72 (s, 3H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.15, 171.70, 155.06, 141.89, 132.13, 131.20, 129.11, 128.89, 128.46, 126.42, 121.42, 121.30, 62.20, 61.92, 21.13, 13.87; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$: 302.1151, found: 302.1154.



Ethyl 5-fluoro-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-3): 92 mg, 62% yield; Colorless oil; R_f = 0.67 (EA-Hexane = 1:10, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.89 (m, 2H), 7.69 – 7.61 (m, 1H), 7.51 – 7.44 (m, 3H), 7.16 – 7.07 (m, 2H), 4.19 – 4.09 (m, 1H), 4.06 – 3.97 (m, 1H), 1.71 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.02 (d, *J* = 4.3 Hz), 171.14, 161.68 (d, *J* = 244.4 Hz), 151.14 (d, *J* = 2.2 Hz), 143.68 (d, *J* = 9.0 Hz), 131.97, 131.25, 128.95, 128.32, 122.10 (d, *J* = 9.0 Hz), 115.87 (d, *J* = 23.2 Hz), 109.36 (d, *J* = 25.1 Hz), 62.69 (d, *J* = 2.2 Hz), 62.16, 21.12, 13.88; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.92; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}FNNaO_2$ $[M+Na]^+$: 320.1057, found: 320.1051.

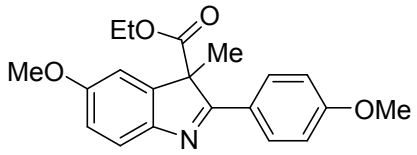


Ethyl 5-chloro-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-4): 88 mg, 56% yield; Yellowish oil; R_f = 0.53 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.41 – 7.34 (m, 2H), 4.19 – 4.10 (m, 1H), 4.03 – 3.94 (m, 1H), 1.71 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 178.44, 170.93, 153.50, 143.37, 132.02, 131.70, 131.46, 129.32, 128.94, 128.44, 122.08, 122.01, 62.42, 62.17, 21.06, 13.83; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}ClNNaO_2$ $[M+Na]^+$: 336.0762, found: 336.0758.

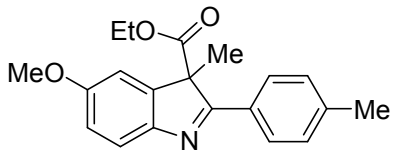


Ethyl 5-bromo-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-5): 109 mg, 61% yield; Yellowish oil; R_f = 0.53 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 2H), 7.58 – 7.51 (m, 3H), 7.51 – 7.44 (m, 3H), 4.20 – 4.11 (m, 1H), 4.04 – 3.95 (m, 1H), 1.71 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 178.45, 170.96, 154.02, 143.72, 132.25, 131.72,

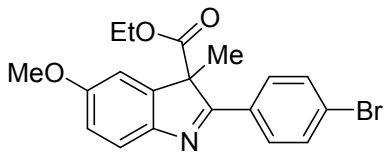
131.49, 128.96, 128.47, 124.89, 122.57, 119.86, 62.44, 62.21, 21.08, 13.86; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}BrNNaO_2$ $[M+Na]^+$: 380.0257, found: 380.0253.



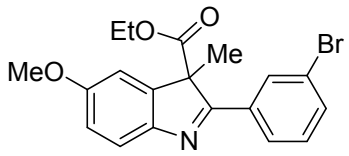
Ethyl 5-methoxy-2-(4-methoxyphenyl)-3-methyl-3*H*-indole-3-carboxylate (5-6): 119 mg, 70% yield; Yellowish oil; R_f =0.29 (EA-Hexane = 1:10, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 2H), 7.61 – 7.55 (m, 1H), 7.00 – 6.94 (m, 2H), 6.94 – 6.90 (m, 2H), 4.19 – 4.09 (m, 1H), 4.02 – 3.93 (m, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 1.69 (s, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.77, 171.97, 161.76, 158.48, 148.92, 143.37, 129.79, 125.11, 121.24, 114.27, 114.04, 107.72, 62.20, 61.90, 55.90, 55.53, 21.66, 13.95; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NNaO_4$ $[M+Na]^+$: 362.1363, found: 362.1360.



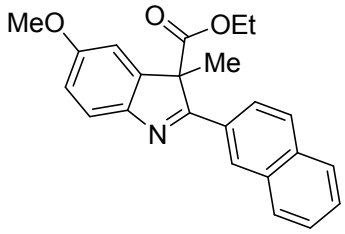
Ethyl 5-methoxy-3-methyl-2-(*p*-tolyl)-3*H*-indole-3-carboxylate (5-7): 115 mg, 71% yield; Colorless oil; R_f = 0.46 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 2H), 7.63 – 7.56 (m, 1H), 7.29 – 7.21 (m, 2H), 6.97 – 6.90 (m, 2H), 4.18 – 4.09 (m, 1H), 4.03 – 3.93 (m, 1H), 3.84 (s, 3H), 2.41 (s, 3H), 1.69 (s, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.19, 171.89, 158.70, 148.82, 143.48, 141.20, 129.61, 129.59, 128.07, 121.53, 114.11, 107.69, 62.27, 61.89, 55.89, 21.63, 21.49, 13.91; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$: 346.1414, found: 346.1408.



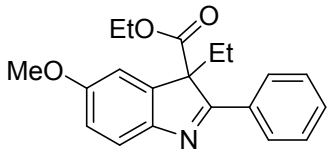
Ethyl 2-(4-bromophenyl)-5-methoxy-3-methyl-3*H*-indole-3-carboxylate (5-8): 132 mg, 68% yield; White solid; R_f = 0.57 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 2H), 7.64 – 7.56 (m, 3H), 6.98 – 6.91 (m, 2H), 4.19 – 4.09 (m, 1H), 4.04 – 3.93 (m, 1H), 3.84 (s, 3H), 1.68 (s, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.96, 171.55, 159.08, 148.48, 143.51, 132.11, 131.26, 129.47, 125.38, 121.92, 114.31, 107.76, 62.26, 62.07, 55.92, 21.27, 13.94; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}BrNNaO_3$ $[M+Na]^+$: 410.0362, found: 410.0354.



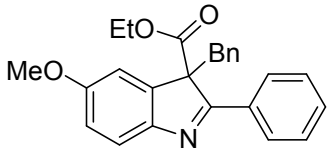
Ethyl 2-(3-bromophenyl)-5-methoxy-3-methyl-3*H*-indole-3-carboxylate (5-9): 114 mg, 59% yield; Colorless oil; R_f = 0.42 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (t, *J* = 2.0 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.65 – 7.56 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.97 – 6.93 (m, 2H), 4.22 – 4.13 (m, 1H), 4.03 – 3.93 (m, 1H), 3.85 (s, 3H), 1.69 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.55, 171.42, 159.21, 148.31, 143.53, 134.36, 133.58, 130.95, 130.27, 126.48, 123.19, 122.09, 114.39, 107.76, 62.35, 62.11, 55.94, 21.24, 13.95; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}BrNNaO_3$ $[M+Na]^+$: 410.0362, found: 410.0367.



Ethyl 5-methoxy-3-methyl-2-(naphthalen-2-yl)-3*H*-indole-3-carboxylate (5-10): 118 mg, 66% yield; Yellowish oil; R_f = 0.35 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.18 (m, 2H), 7.95 – 7.90 (m, 2H), 7.89 – 7.84 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.01 – 6.94 (m, 2H), 4.23 – 4.13 (m, 1H), 4.06 – 3.95 (m, 1H), 3.86 (s, 3H), 1.79 (s, 3H), 0.99 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.07, 171.93, 158.97, 143.68, 134.48, 133.19, 129.82, 129.07, 128.62, 128.37, 127.88, 127.59, 126.74, 125.01, 121.83, 114.28, 107.72, 62.42, 62.00, 55.92, 21.71, 13.94; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{21}NNaO_3$ $[M+Na]^+$: 382.1414, found: 382.1419.

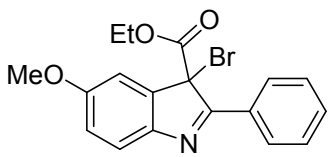


Ethyl 3-ethyl-5-methoxy-2-phenyl-3*H*-indole-3-carboxylate (5-11): 121 mg, 75% yield; Yellow oil; R_f = 0.49 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.89 (m, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.43 (m, 3H), 6.94 (dd, *J* = 8.0, 3.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 4.19 – 4.10 (m, 1H), 4.03 – 3.93 (m, 1H), 3.85 (s, 3H), 2.56 – 2.36 (m, 2H), 0.99 (t, *J* = 7.0 Hz, 3H), 0.28 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.88, 171.71, 158.87, 149.73, 141.28, 132.83, 130.78, 128.85, 127.80, 121.50, 114.13, 107.87, 67.51, 61.79, 55.89, 27.92, 13.90, 7.20; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$: 346.1414, found: 346.1406.



Ethyl 3-benzyl-5-methoxy-2-phenyl-3*H*-indole-3-carboxylate (5-12): 140 mg, 73% yield; Yellowish oil; R_f = 0.33 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.87 (m, 2H), 7.53 – 7.46 (m, 3H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.91 – 6.81 (m, 3H), 6.40 (d, *J* = 7.0 Hz, 2H), 4.20 (dq, *J* = 11.0, 7.0 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.87 (s, 3H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.66 (d, *J* = 14.0 Hz, 1H), 1.02 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.14, 171.46, 158.58, 149.63, 140.99, 134.17, 133.36, 130.72, 129.48, 128.93, 128.01, 127.50, 126.82, 121.59, 114.37, 108.41, 67.52, 62.06, 55.95, 40.49, 13.91; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{23}NNaO_3$ $[M+Na]^+$: 408.1570, found: 408.1575.

(E) NMR data of compound 9



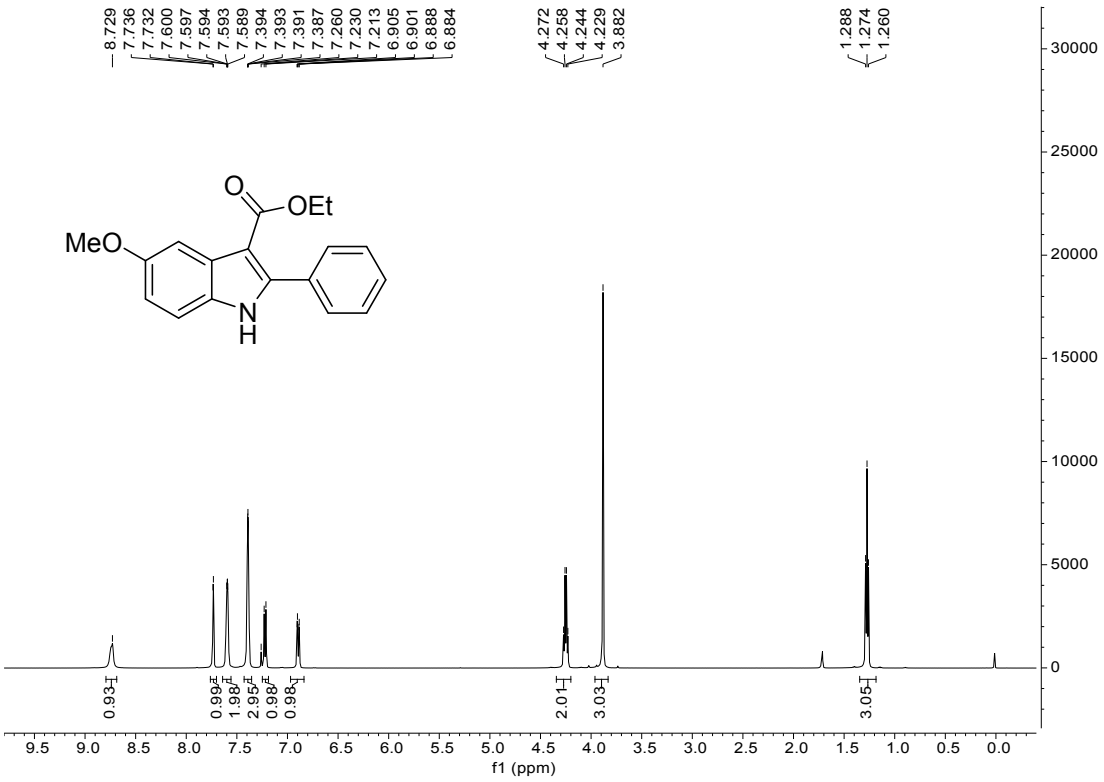
Ethyl 3-bromo-5-methoxy-2-phenyl-3*H*-indole-3-carboxylate (9): Yello oil; R_f = 0.52 (EA-Hexane = 1:5, *V:V*); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 – 8.01 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.27 – 4.18 (m, 1H), 4.13 – 4.03 (m, 1H), 3.85 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ171.89, 166.51, 159.51, 146.84, 139.80, 131.38, 130.70, 128.66, 128.65, 122.46, 116.08, 109.32, 63.77, 59.46, 56.01, 13.86; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{16}BrNNaO_3$ $[M+Na]^+$: 396.0206, found: 396.0210.

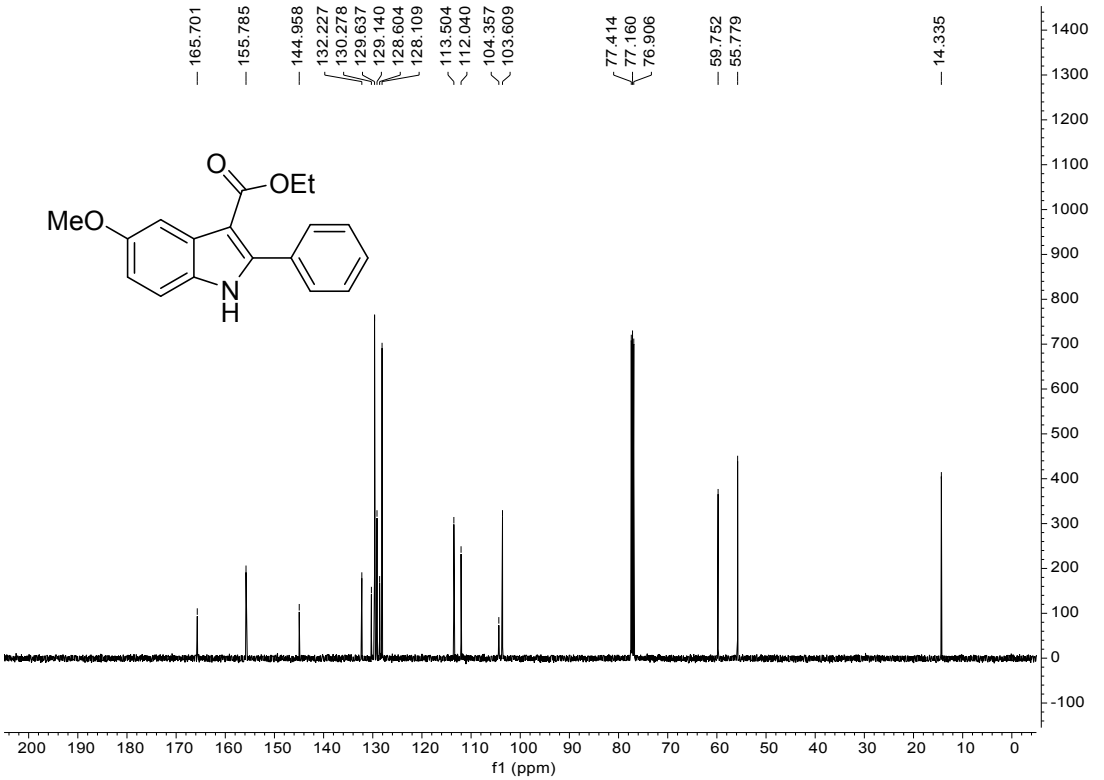
Reference:

[1] (a) C. A. Brandt, A. C. Silva, C. G. Pancote, C. L. Brito and M. Solveira, *Synthesis*, 2004, **10**, 1557. (b) W. Xie, J. Fang, J. Li and P. G. Wang, *Tetrahedron*, 1999, **55**, 12929. (c) W. Yu, Y. Du and K. Zhao, *Org. Lett.*, 2009, **11**, 2417. (d) A. V. Malkov, S. Stoncius, K. Vrankova, M. Arndt, *Chem, Eur. J.*, 2008, **14**, 8082. (e) P. Drouhin and R. J. K. Taylor, *Eur. J. Org. Chem.,* 2015, 2333. (f) Z. H. He, H. R. Li and Z. P. Li, *J. Org. Chem.,* 2010, **75**, 4636.

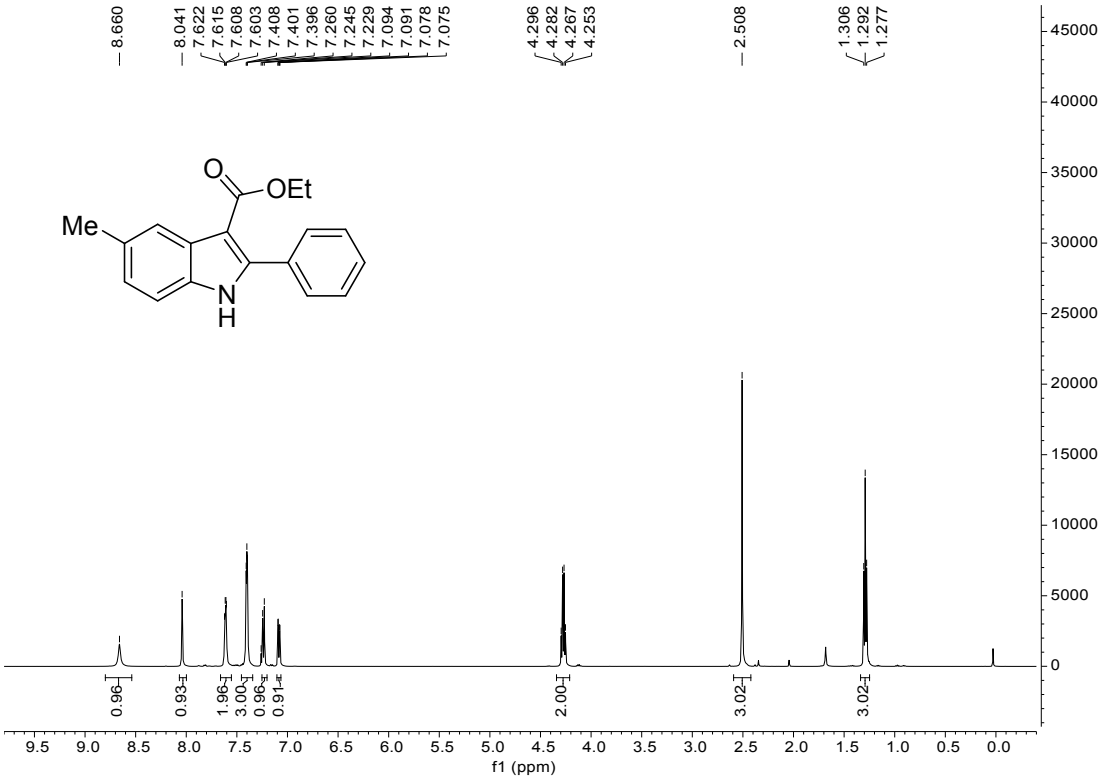
3. NMR Spectra

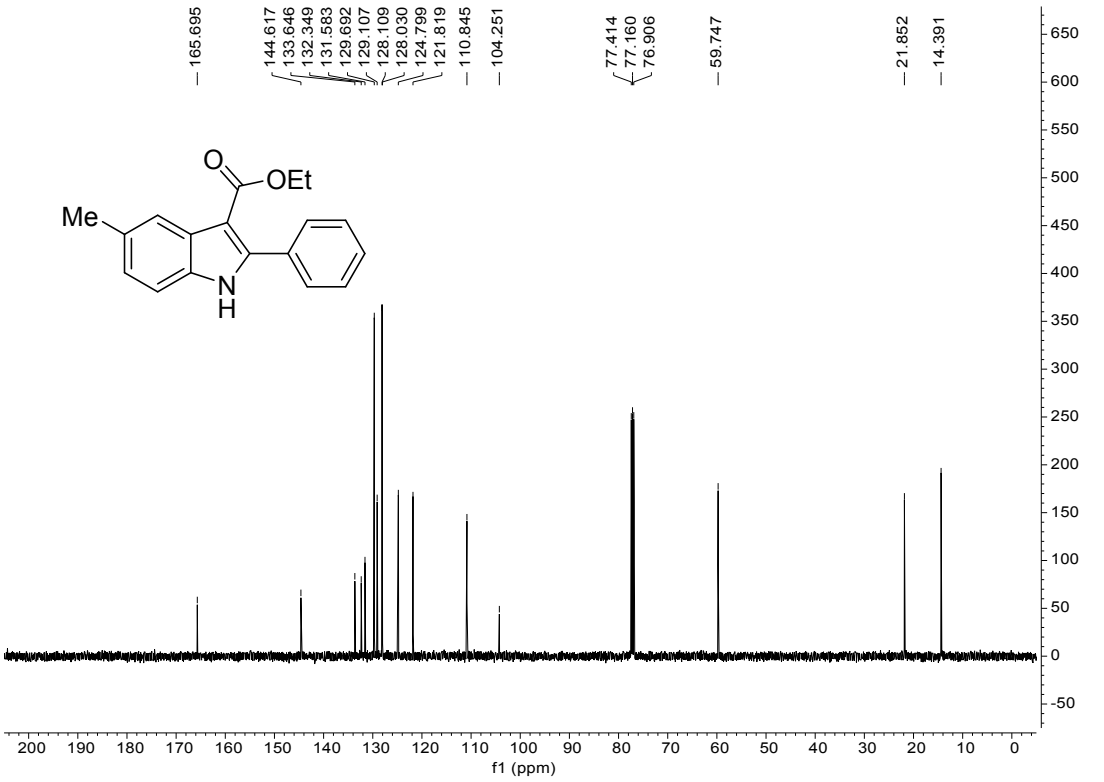
Ethyl 5-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-1)



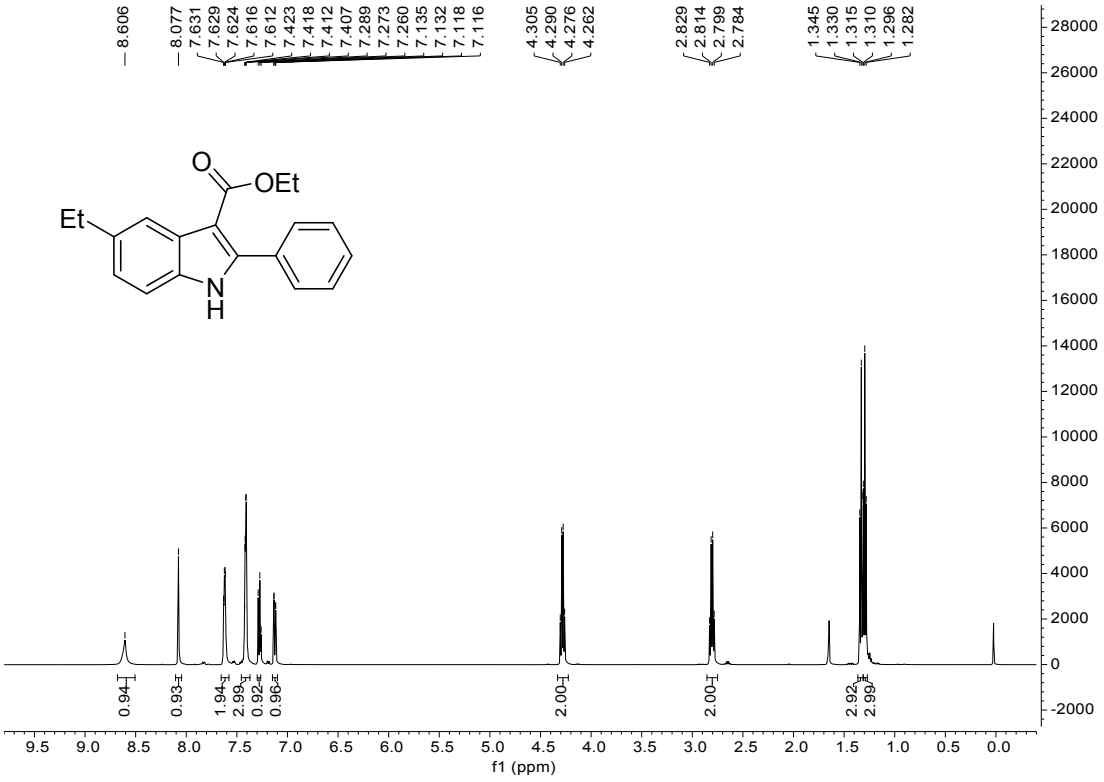


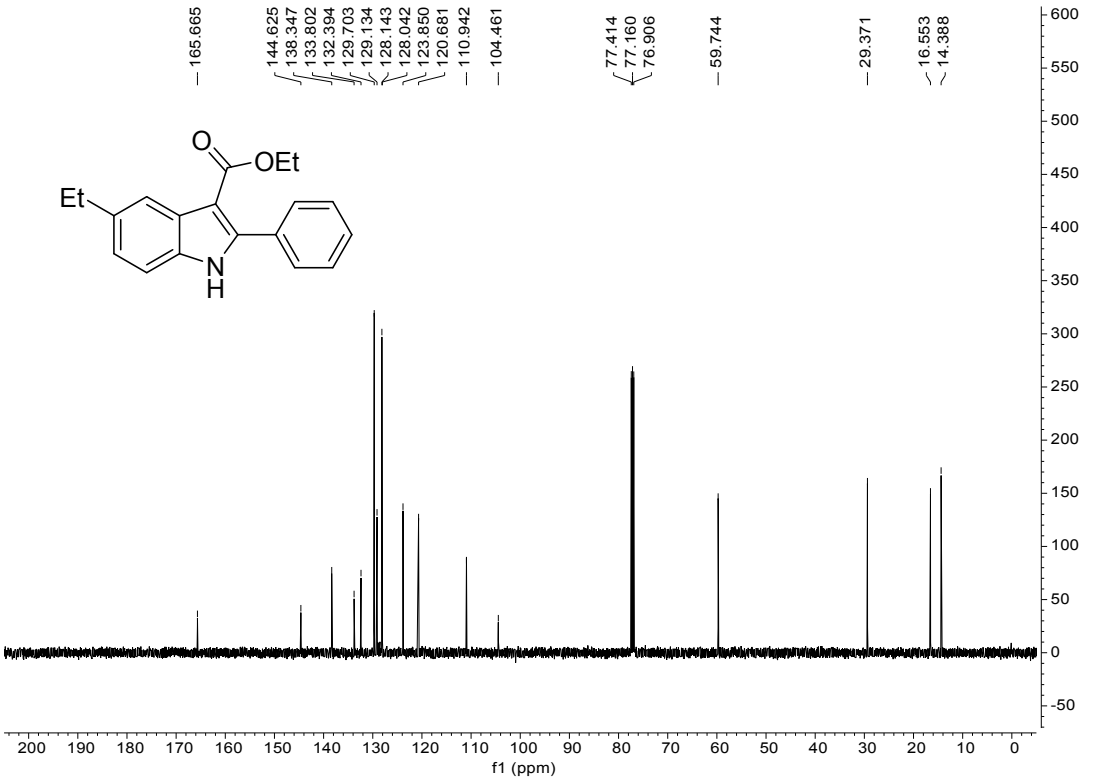
Ethyl 5-methyl-2-phenyl-1*H*-indole-3-carboxylate (2-2)



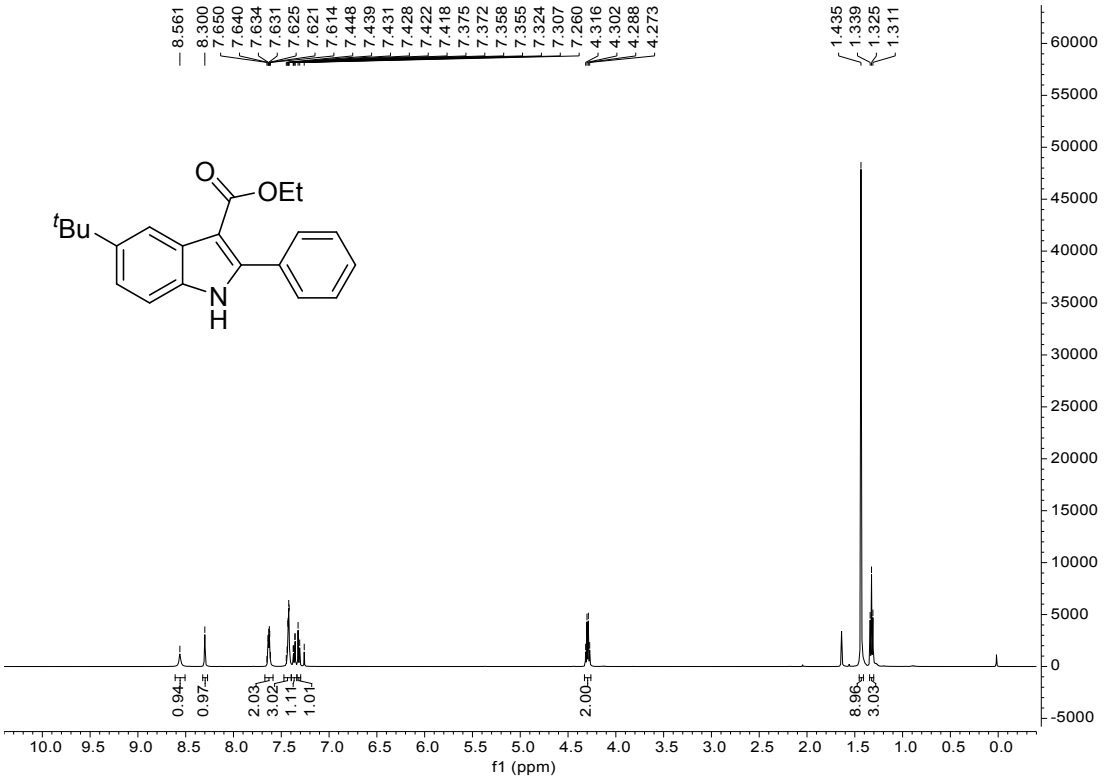


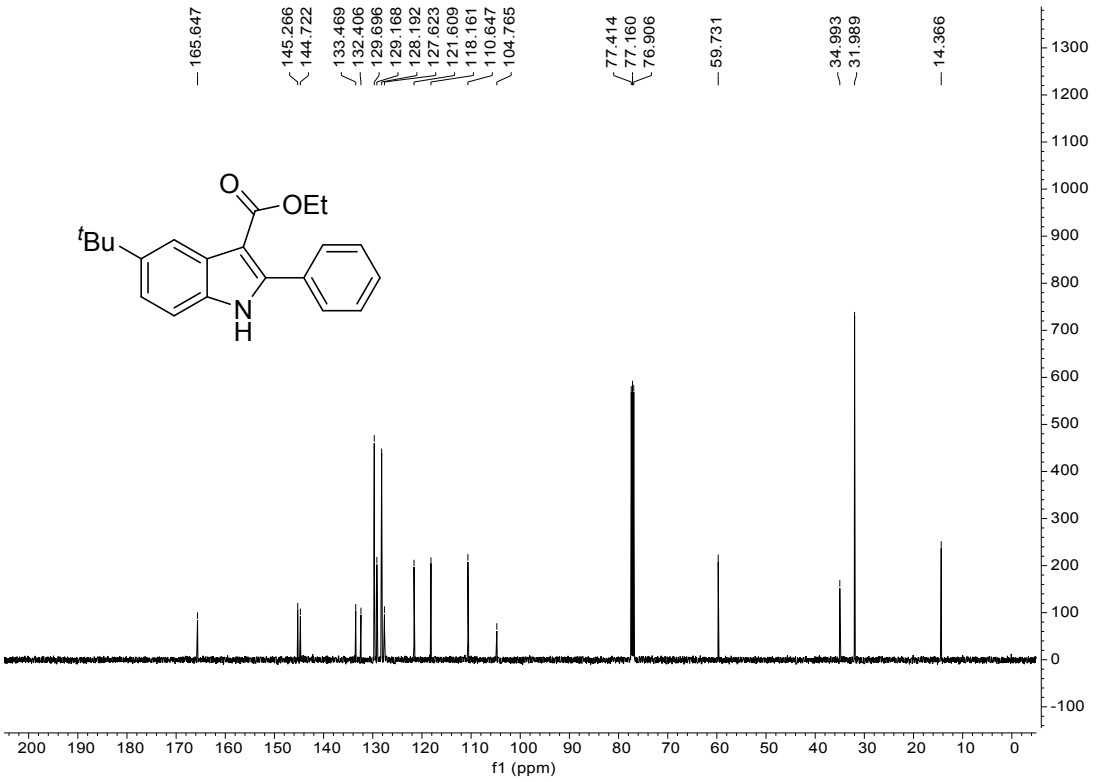
Ethyl 5-ethyl-2-phenyl-1*H*-indole-3-carboxylate (2-3)



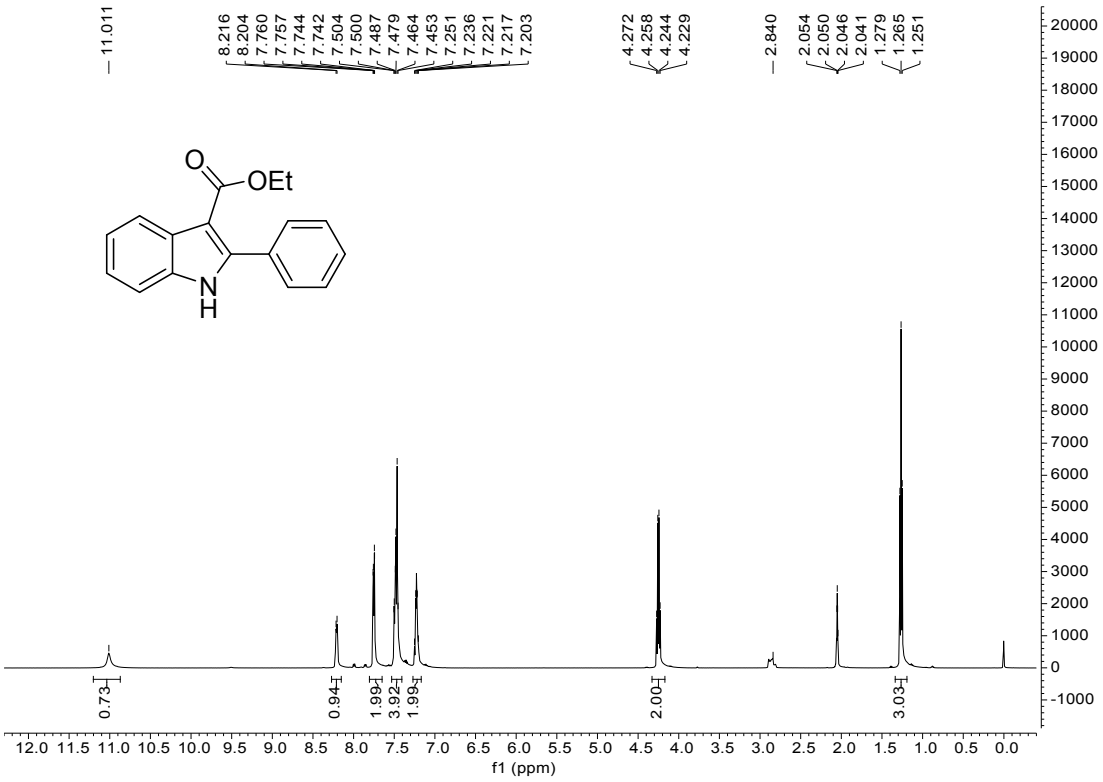


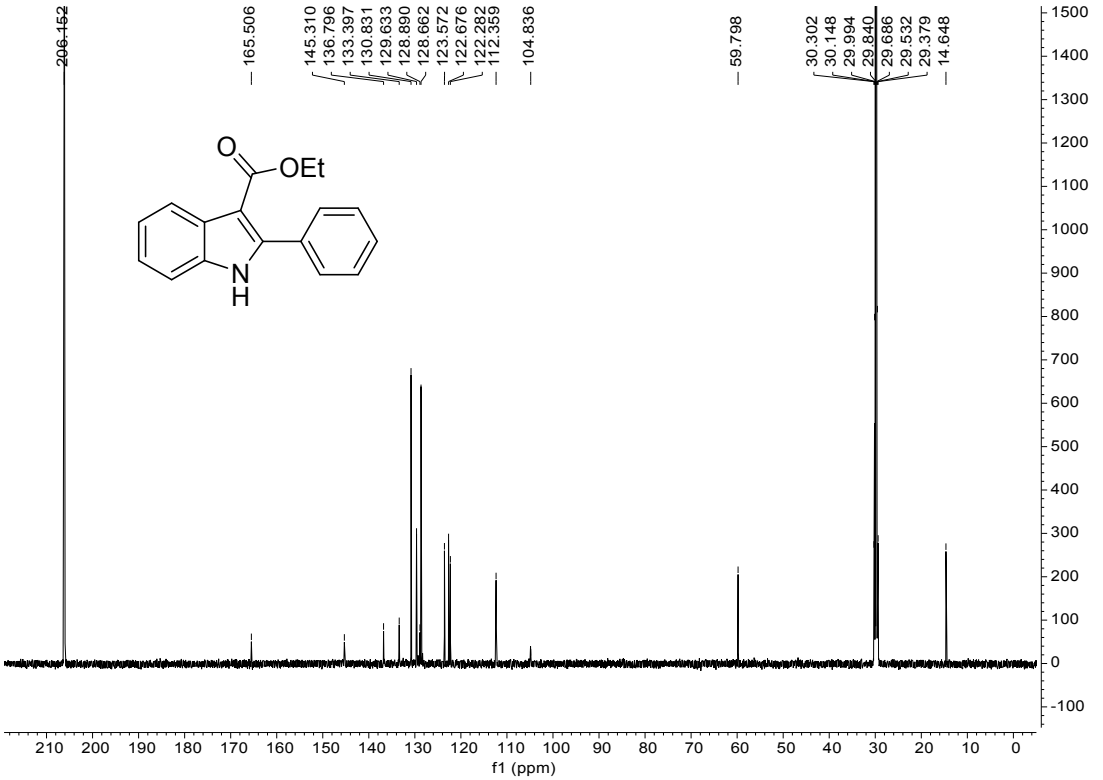
Ethyl 5-(tert-butyl)-2-phenyl-1*H*-indole-3-carboxylate (2-4)



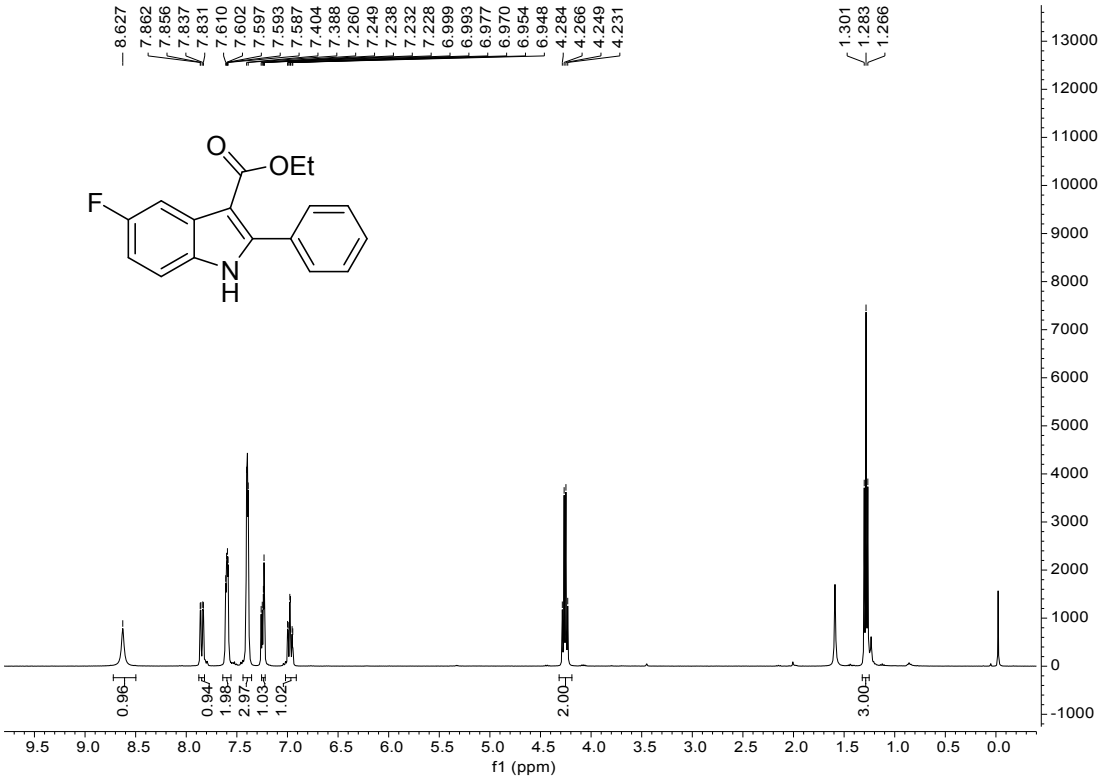


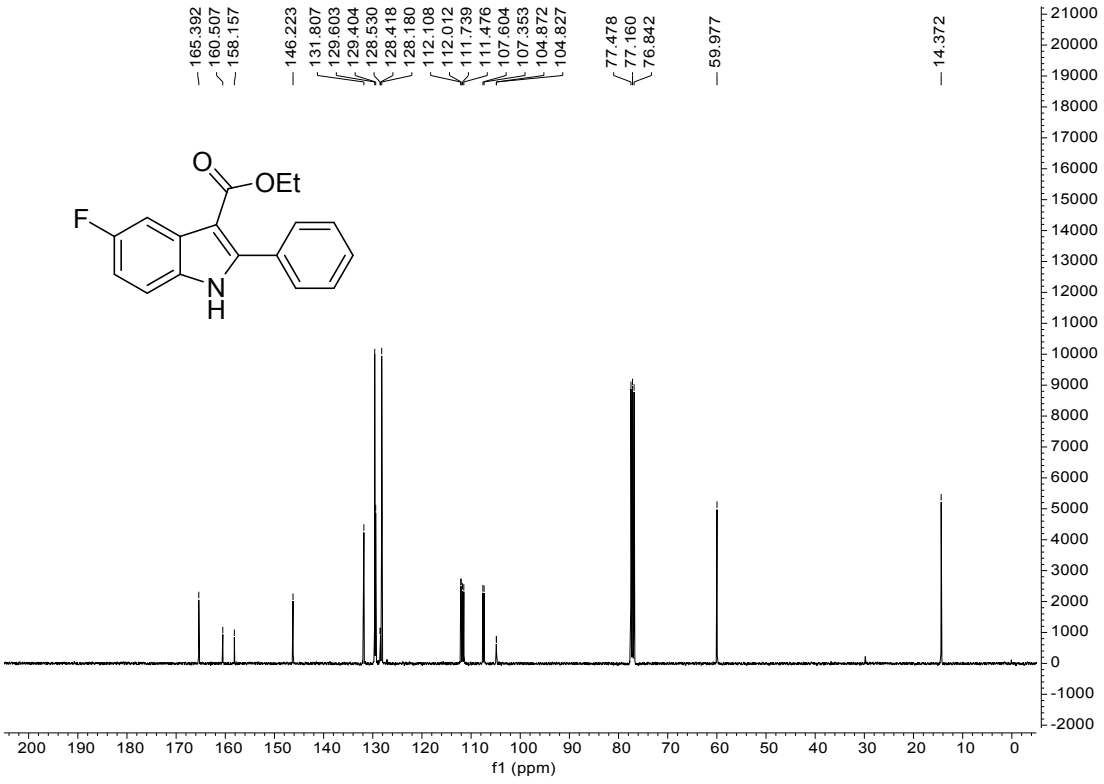
Ethyl 2-phenyl-1*H*-indole-3-carboxylate (2-5)

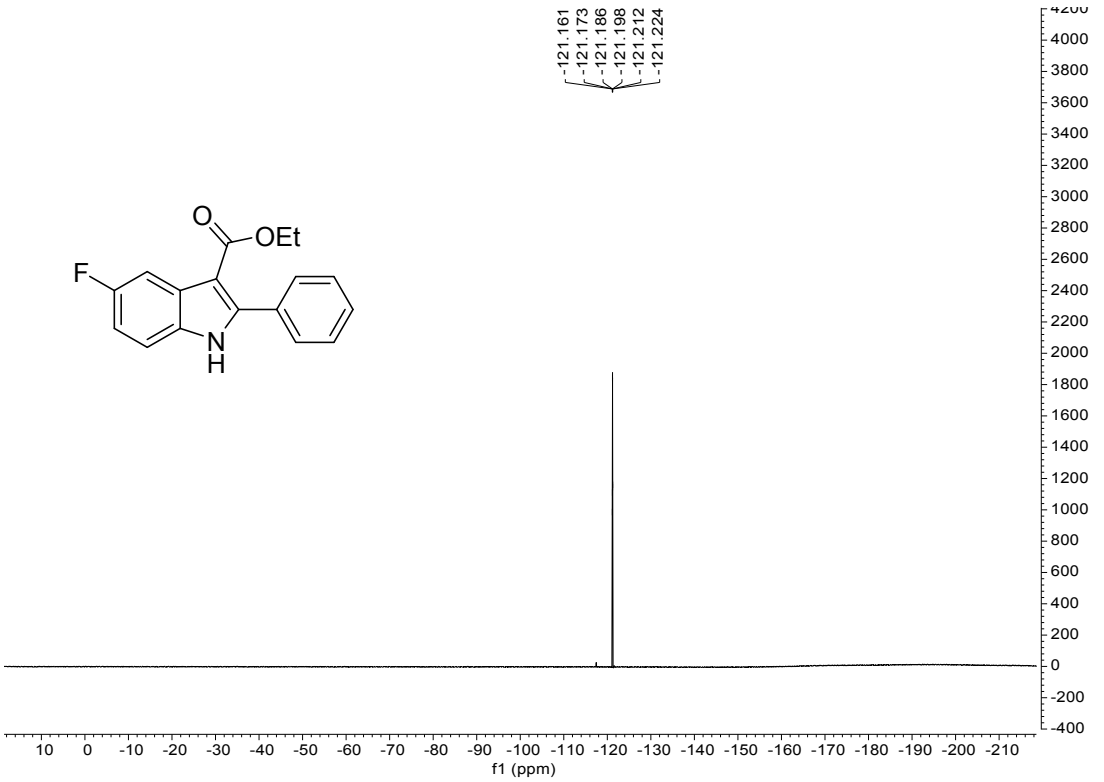




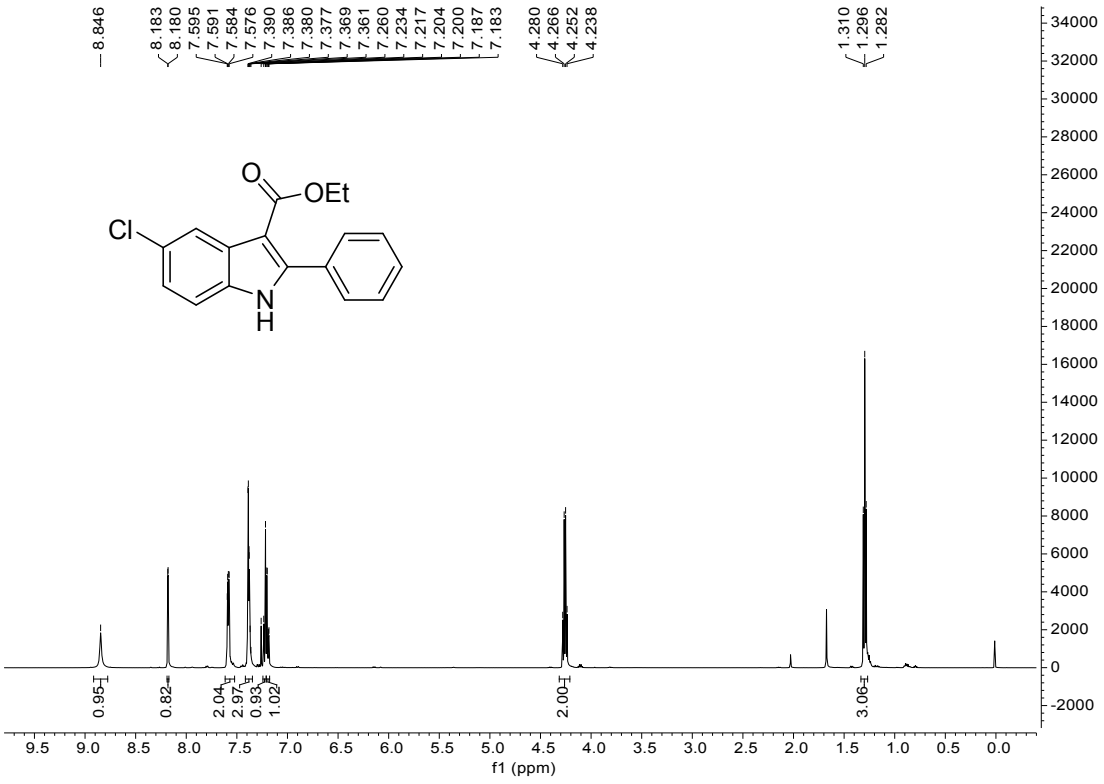
Ethyl 5-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-6)

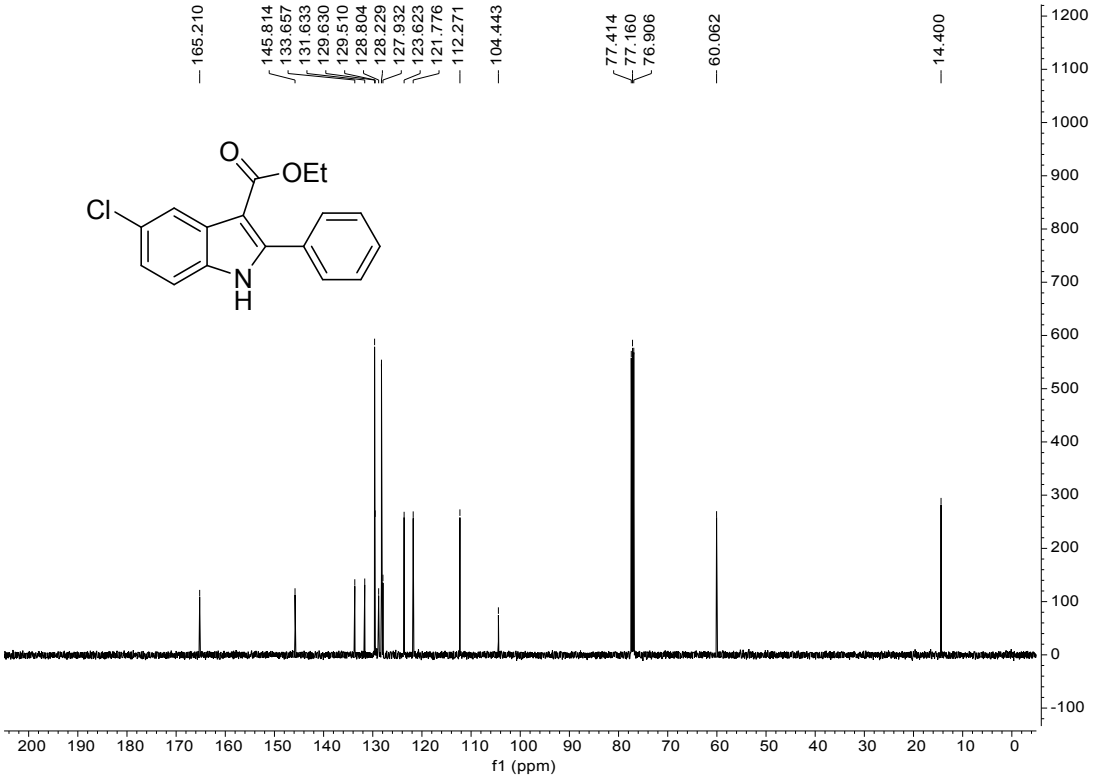




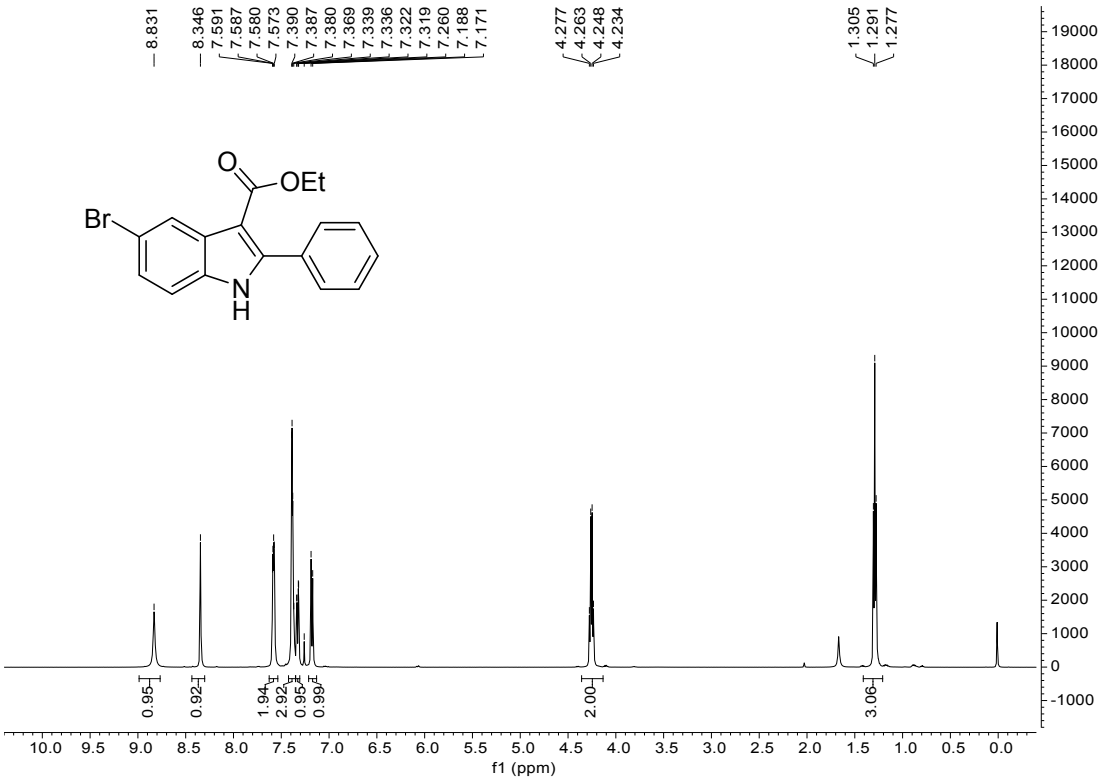


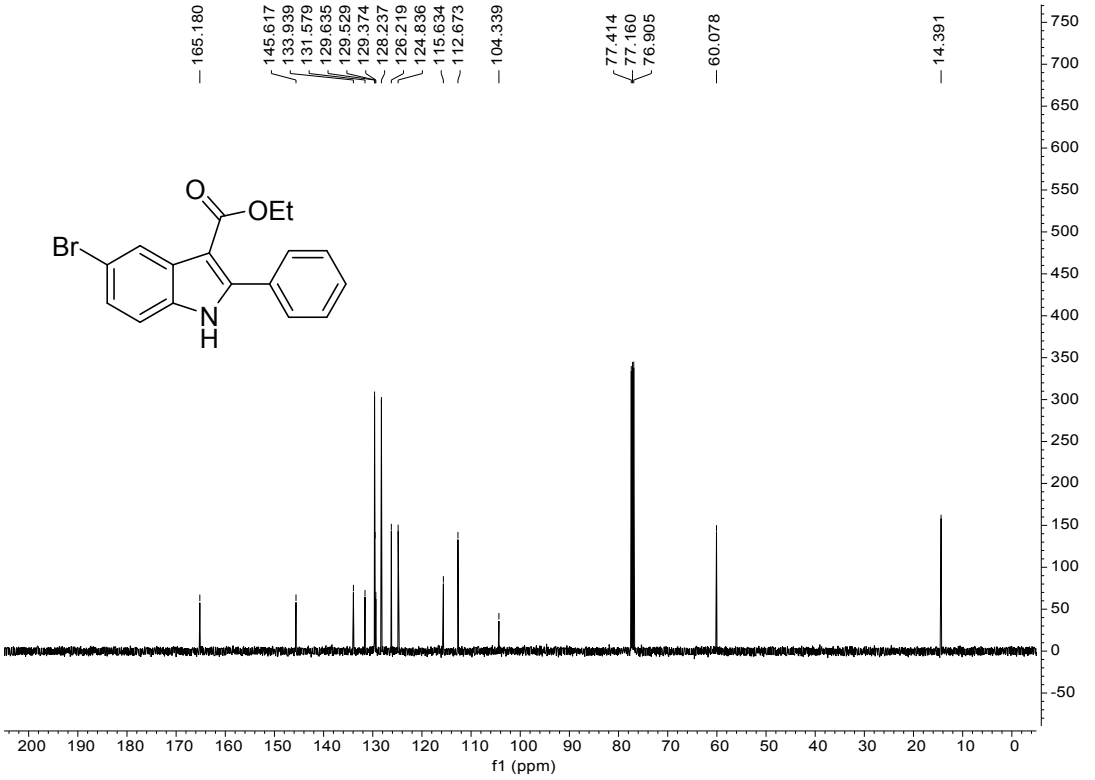
Ethyl 5-chloro-2-phenyl-1*H*-indole-3-carboxylate (2-7)



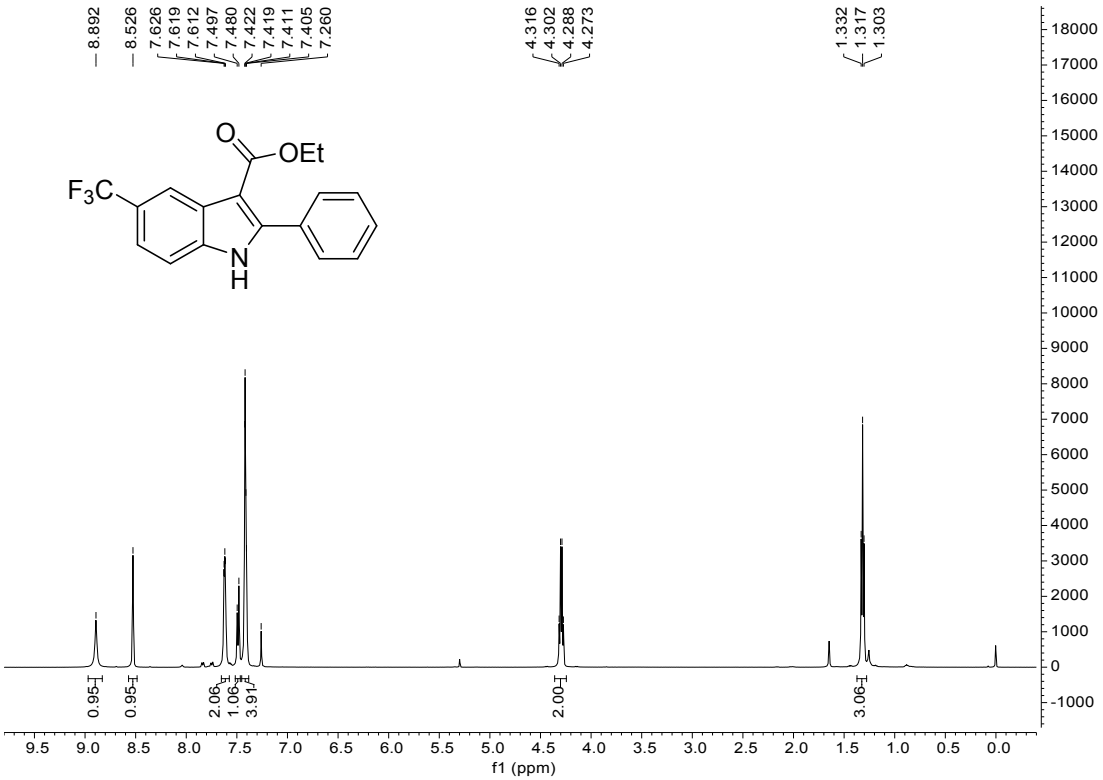


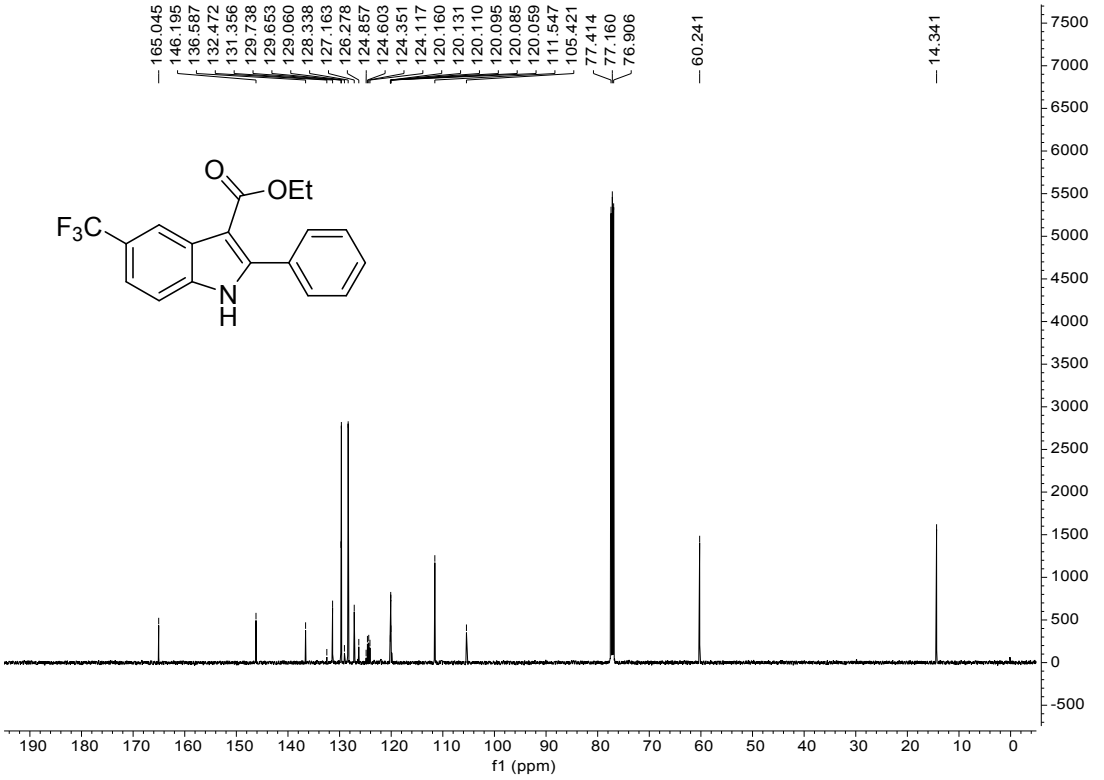
Ethyl 5-bromo-2-phenyl-1*H*-indole-3-carboxylate (2-8)





Ethyl 2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (2-9)

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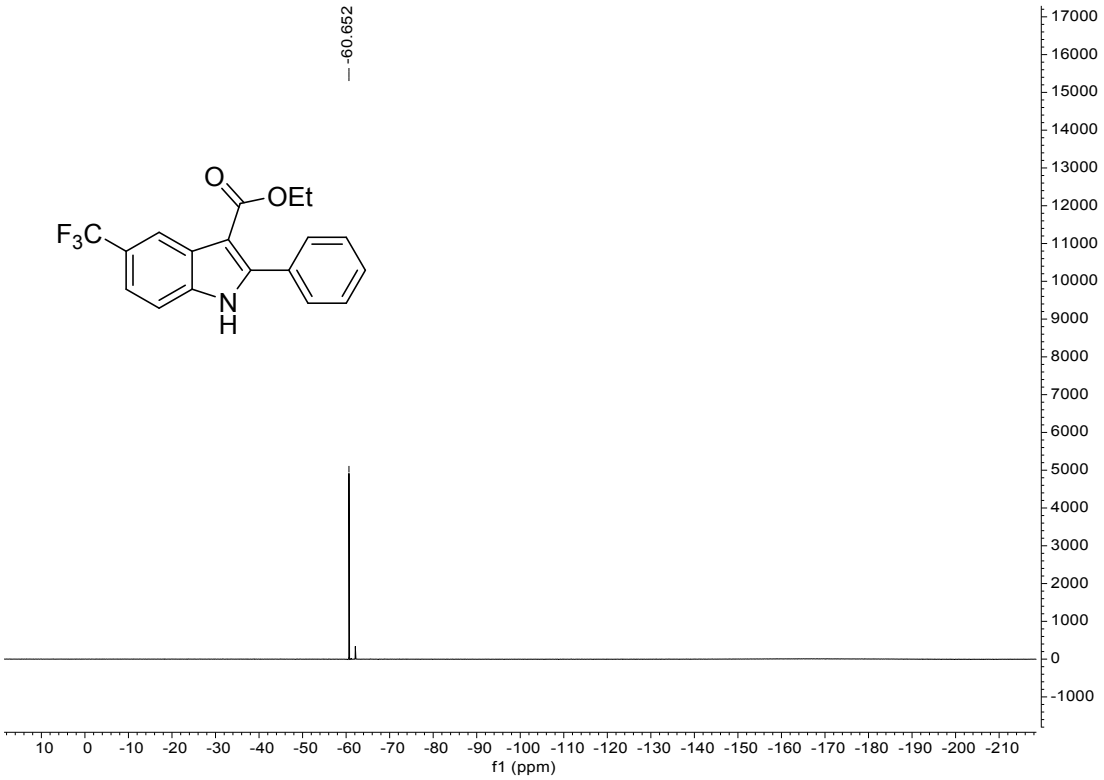
14.341
O
OEt
F3C
N
H
f1 (ppm)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N
H
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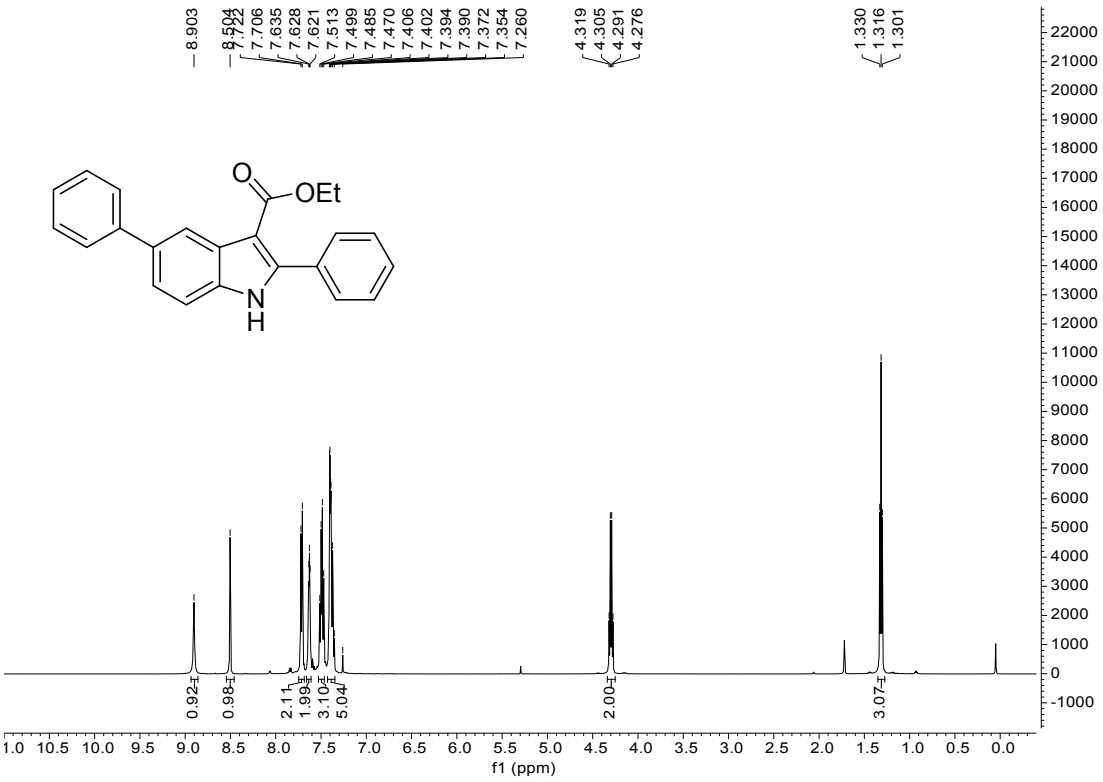
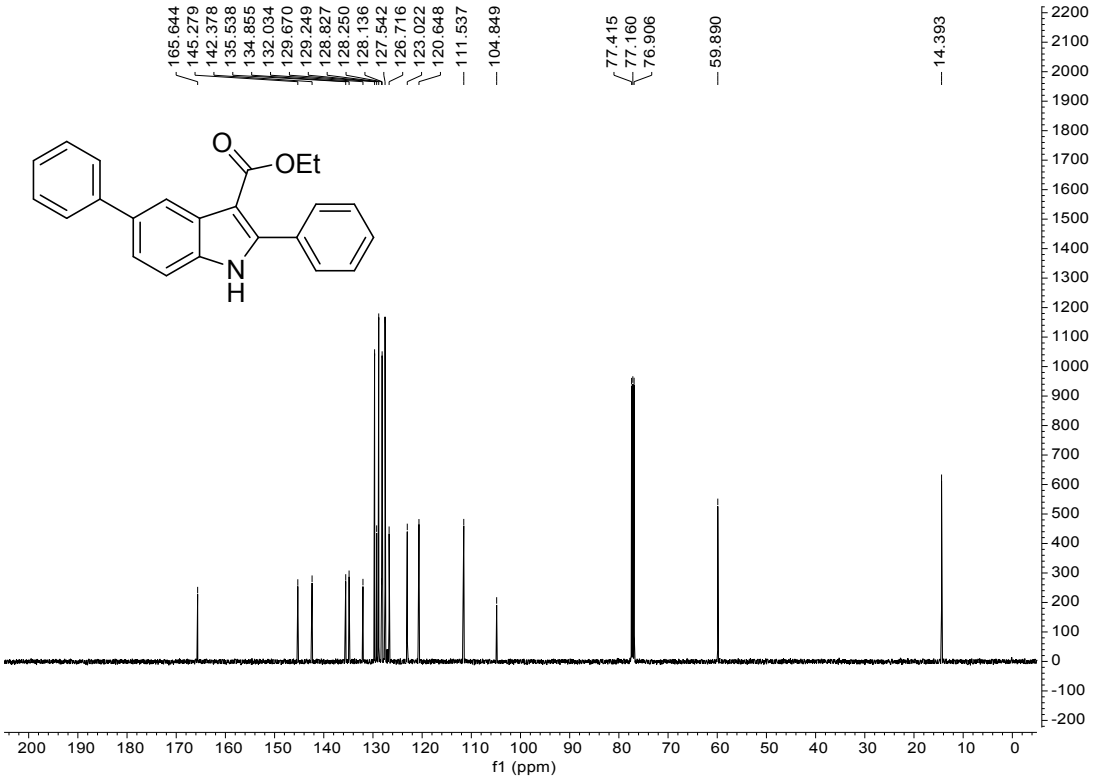
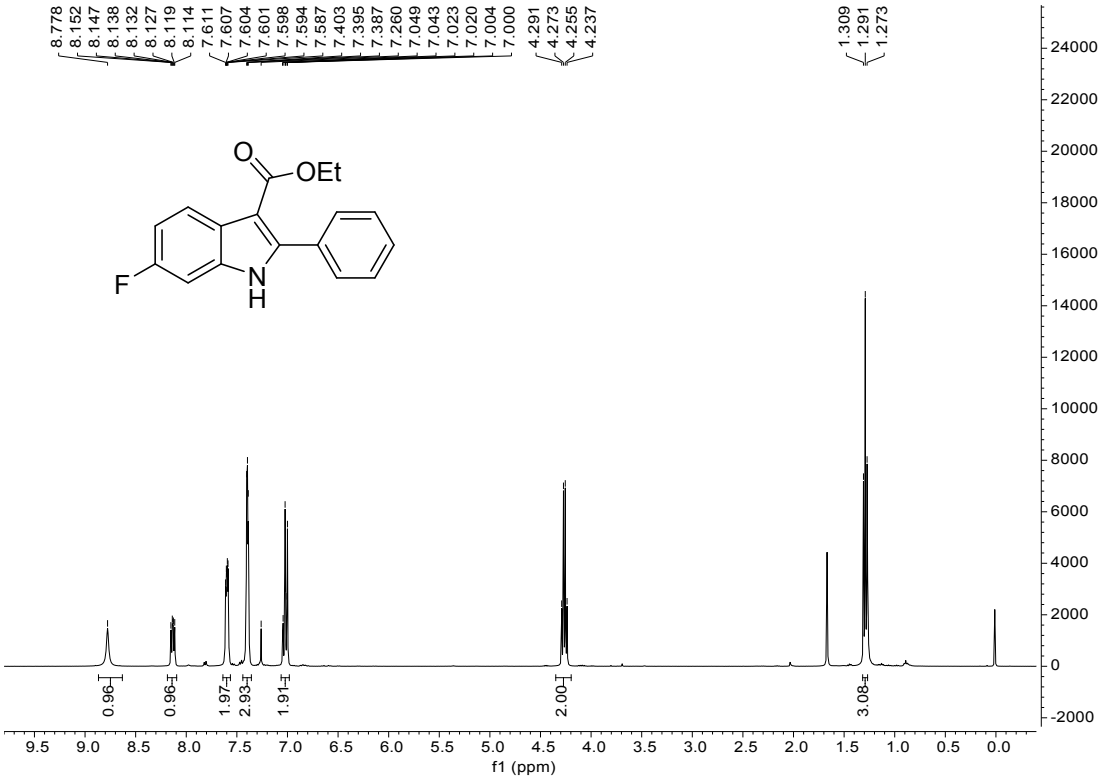
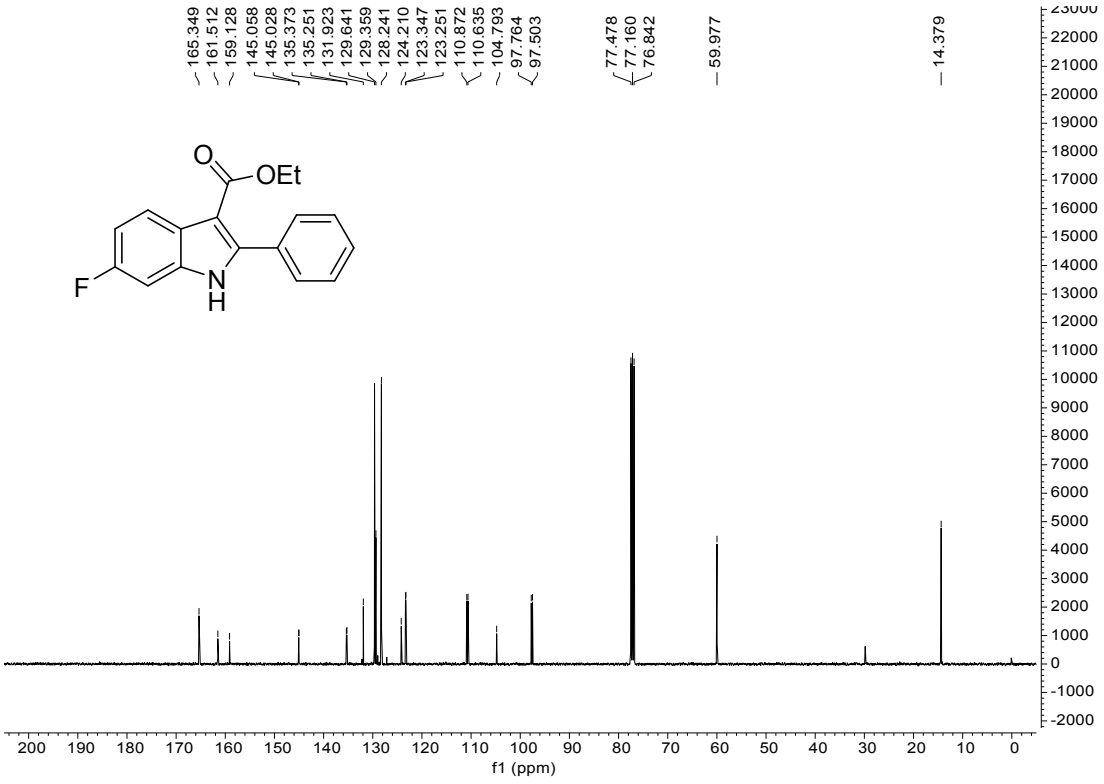
Ethyl 2,5-diphenyl-1*H*-indole-3-carboxylate (2-10)

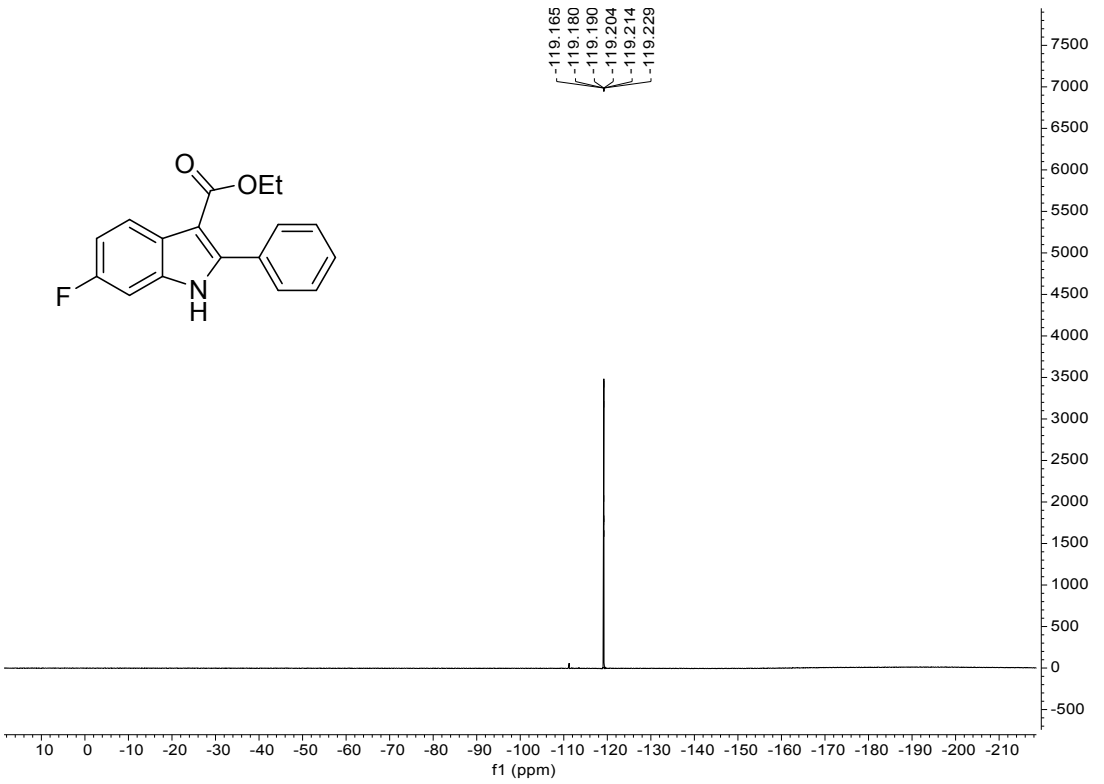




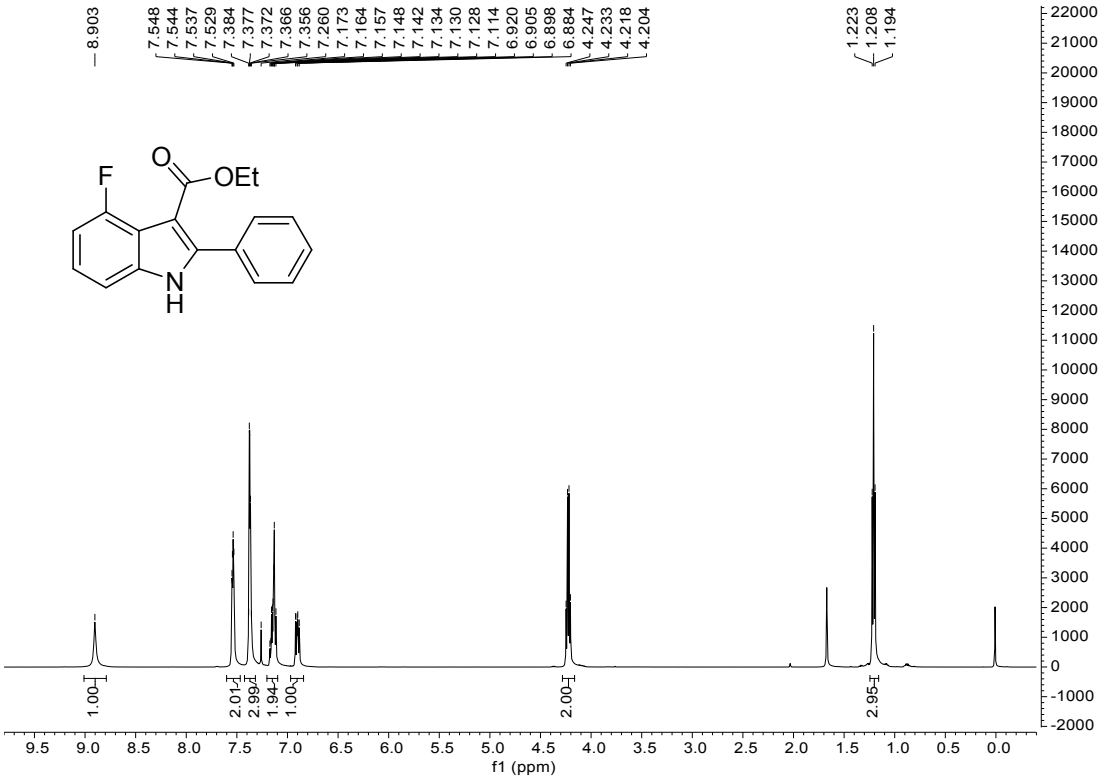
Ethyl 6-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-11)

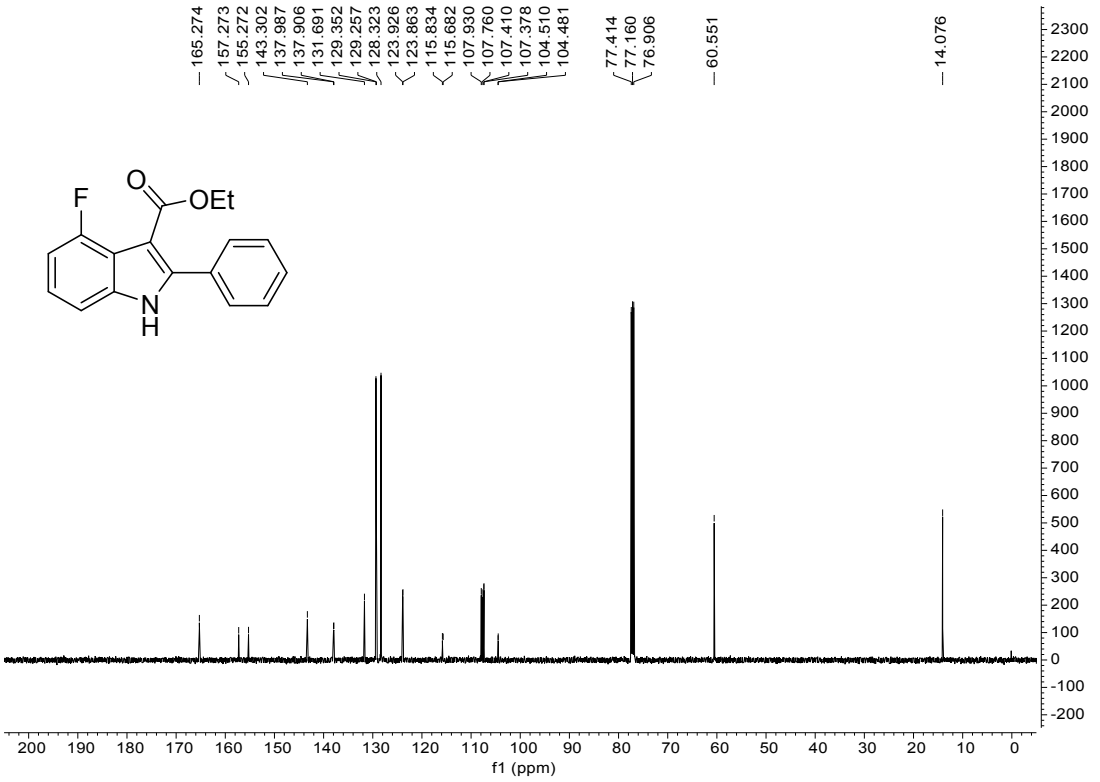






Ethyl 4-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-11')

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107.760
107.410
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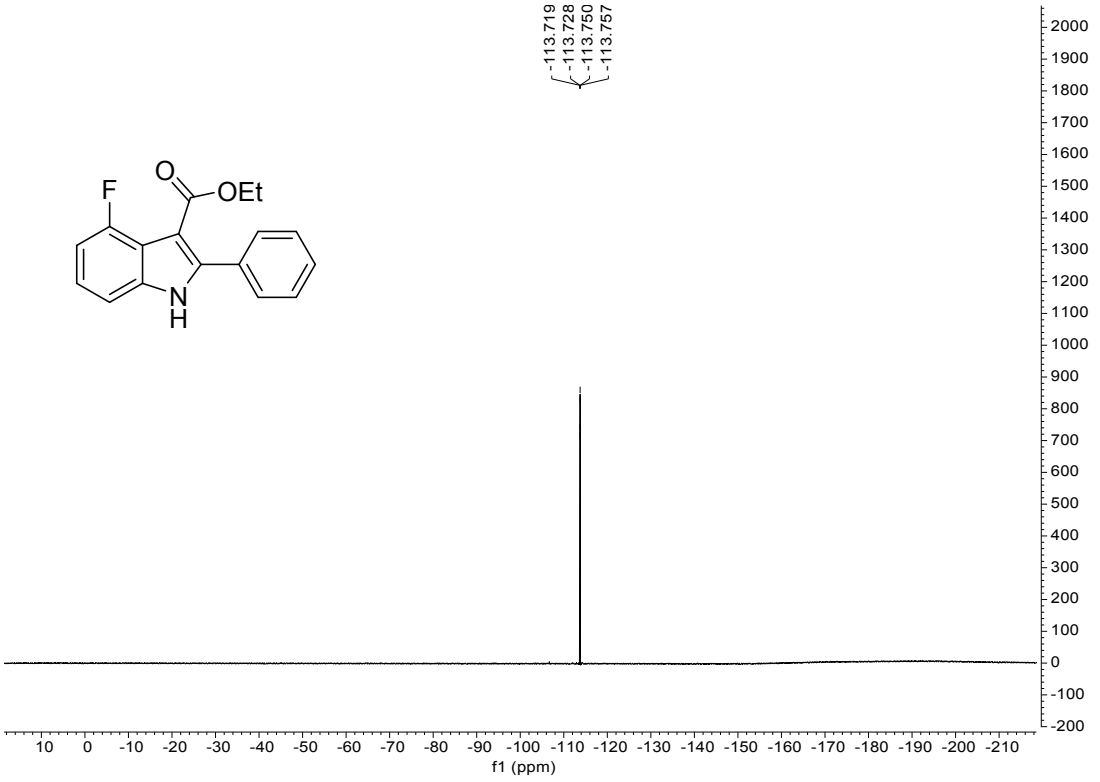
F
O
OEt
N
H
f1 (ppm)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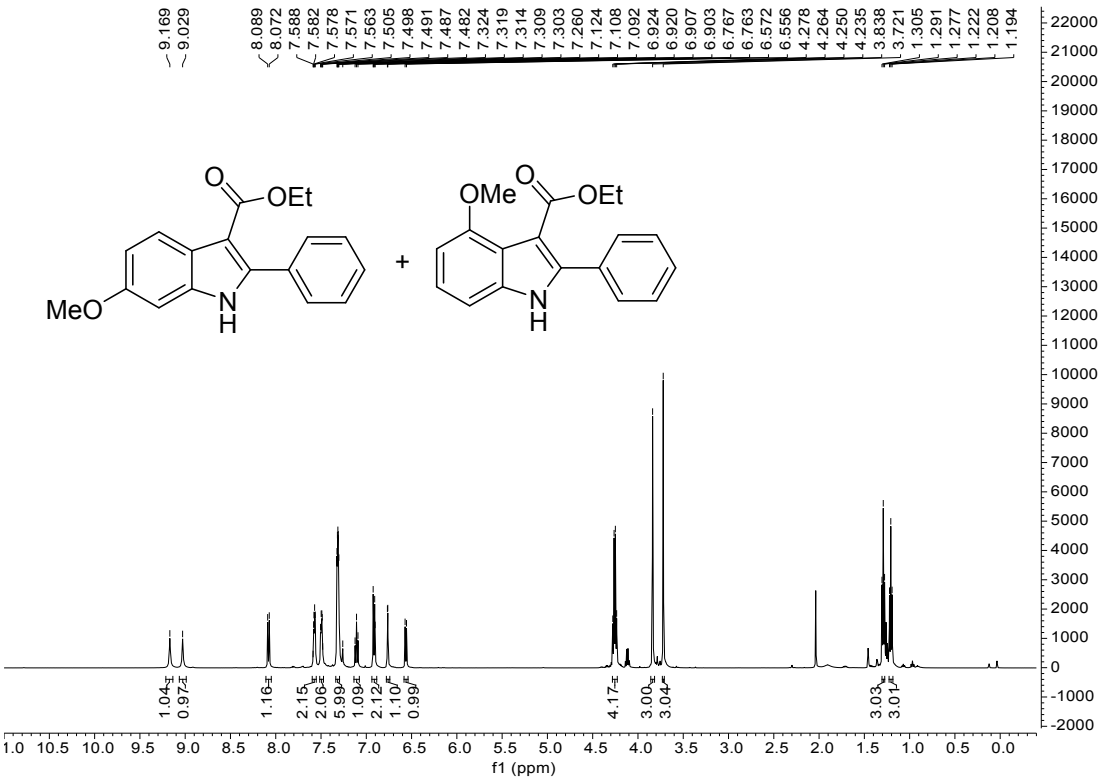
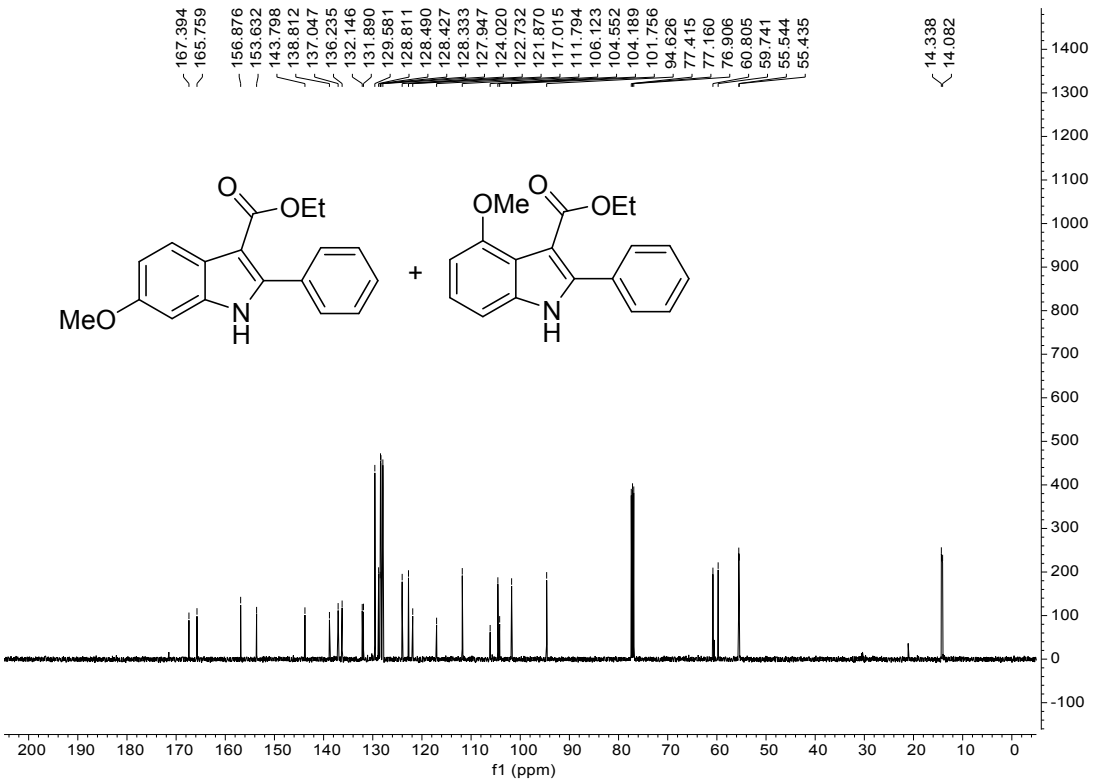
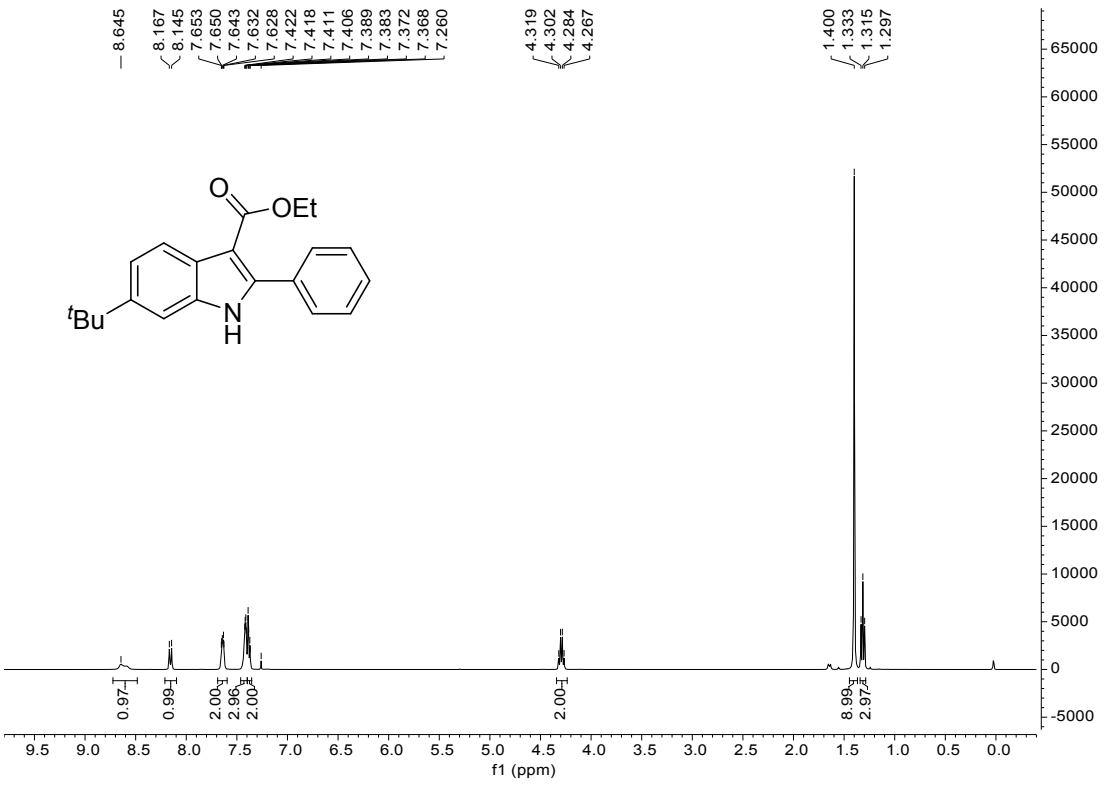
O
OEt
N
H
f1 (ppm)

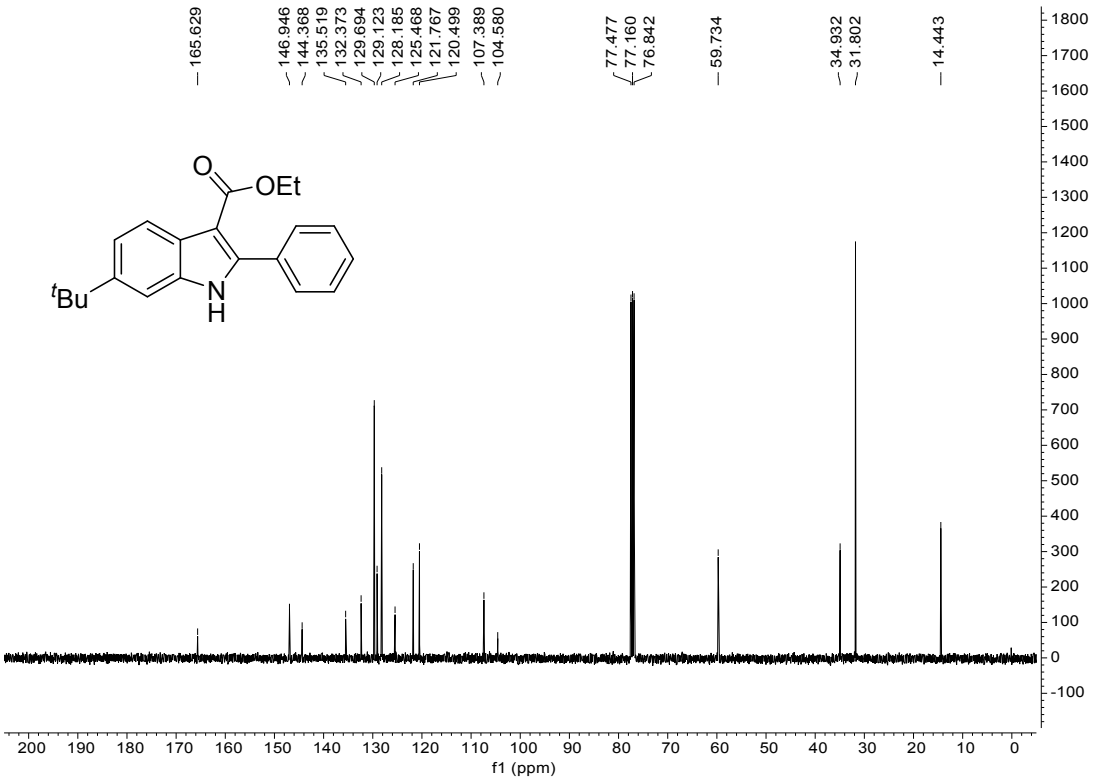
Ethyl 6-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-12) and ethyl 4-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-12')



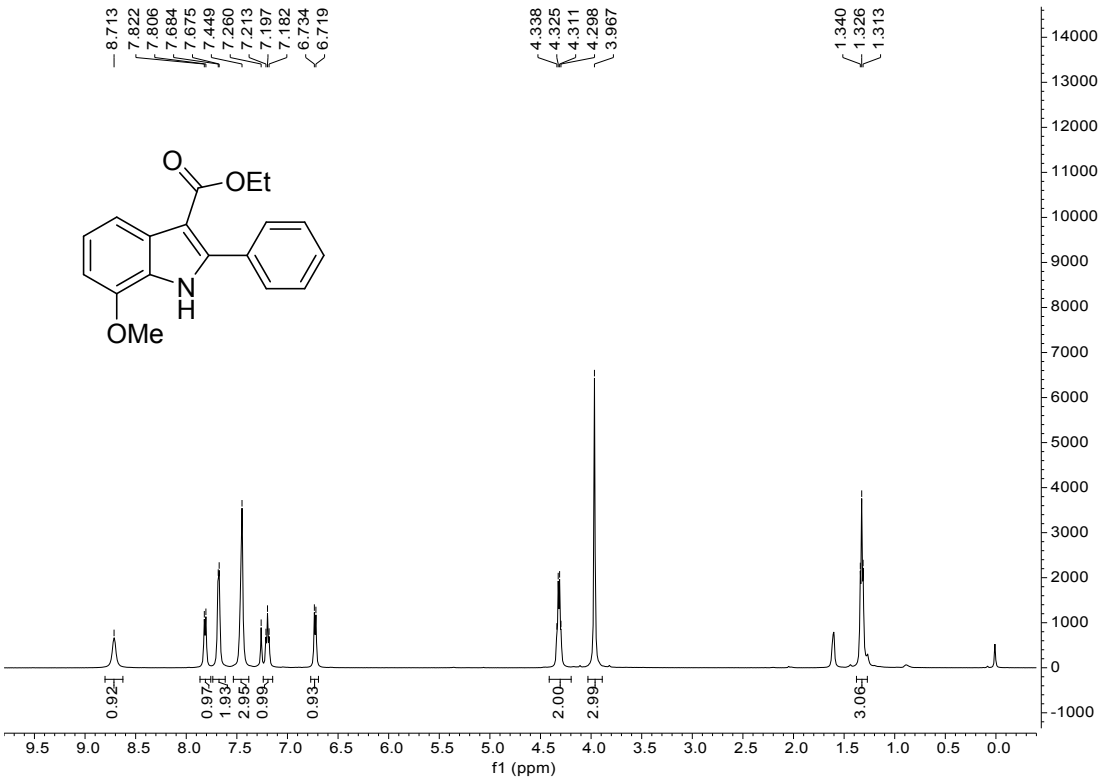


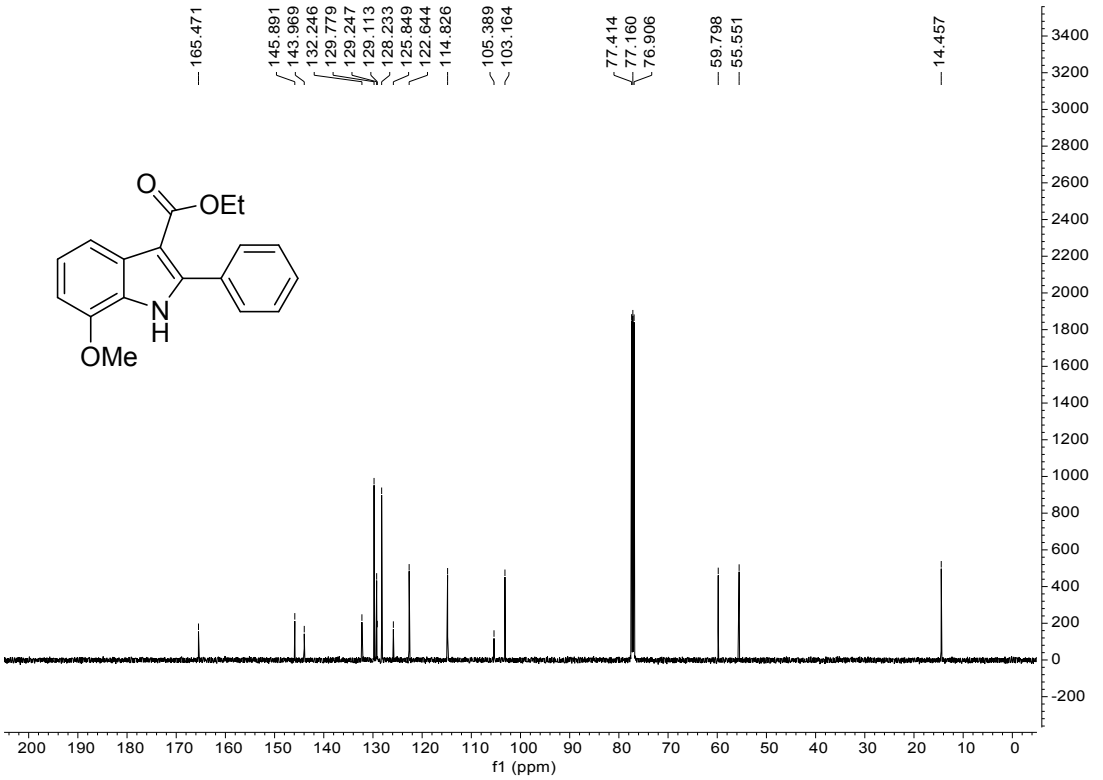
Ethyl 6-(*tert*-butyl)-2-phenyl-1*H*-indole-3-carboxylate (2-13)



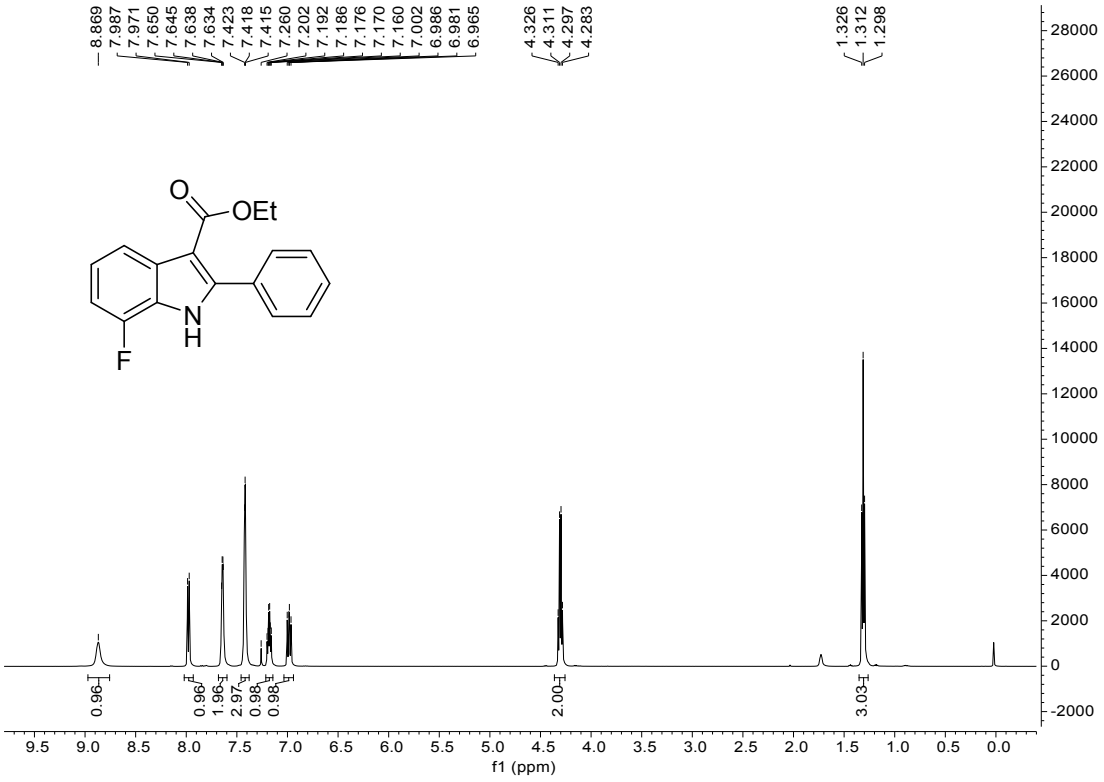


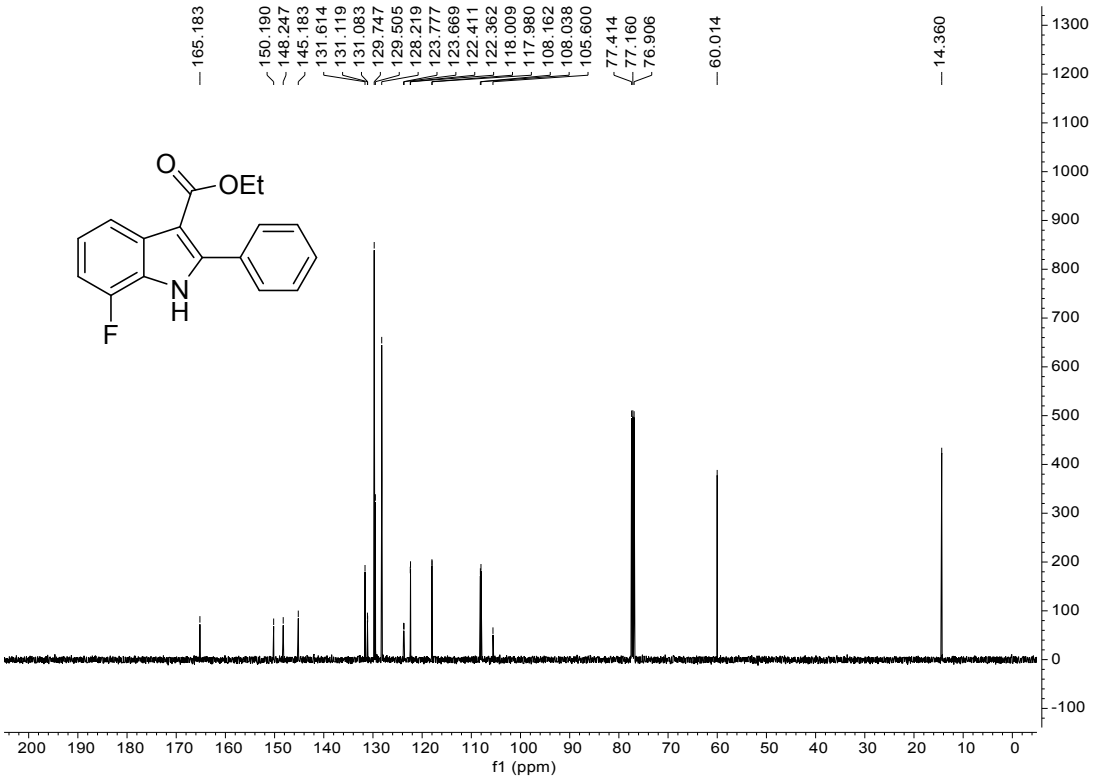
Ethyl 7-methoxy-2-phenyl-1*H*-indole-3-carboxylate (2-14)

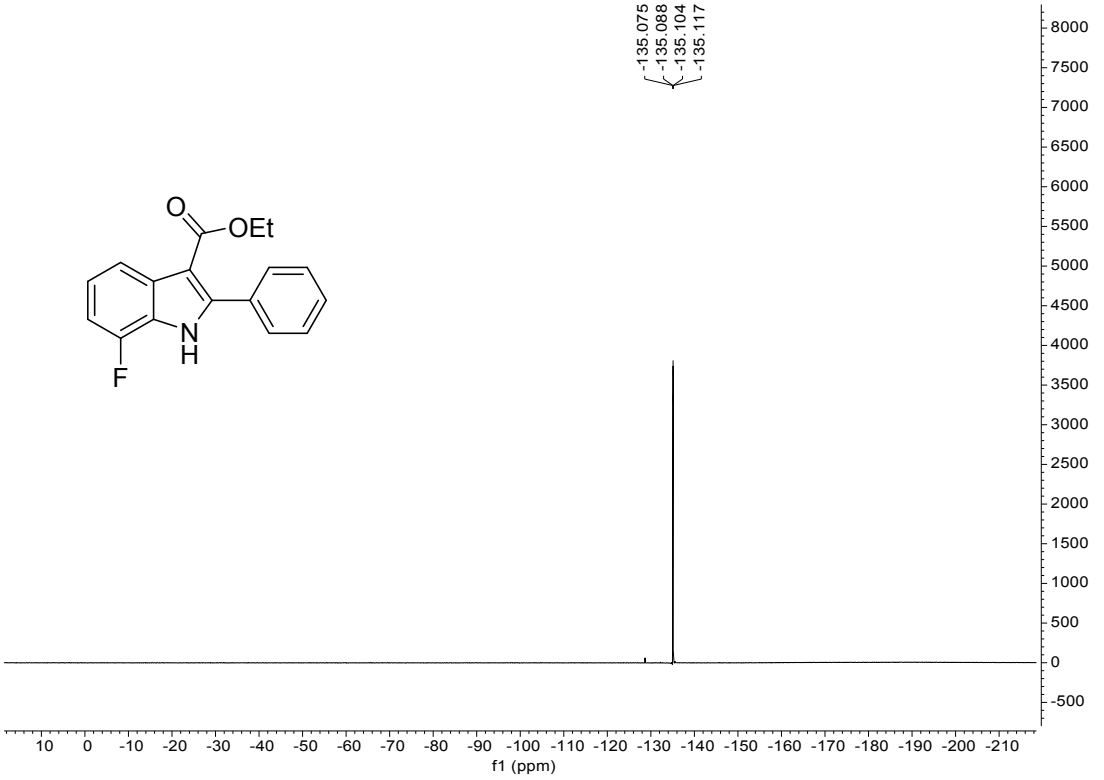




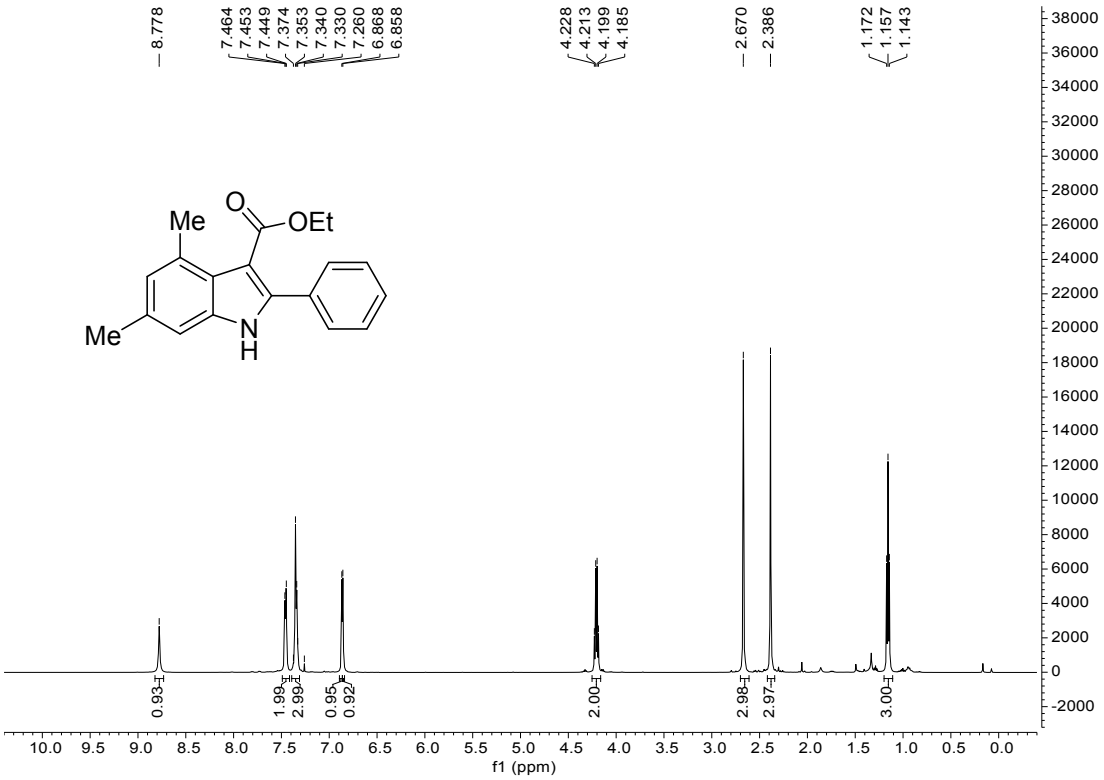
Ethyl 7-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2-15)

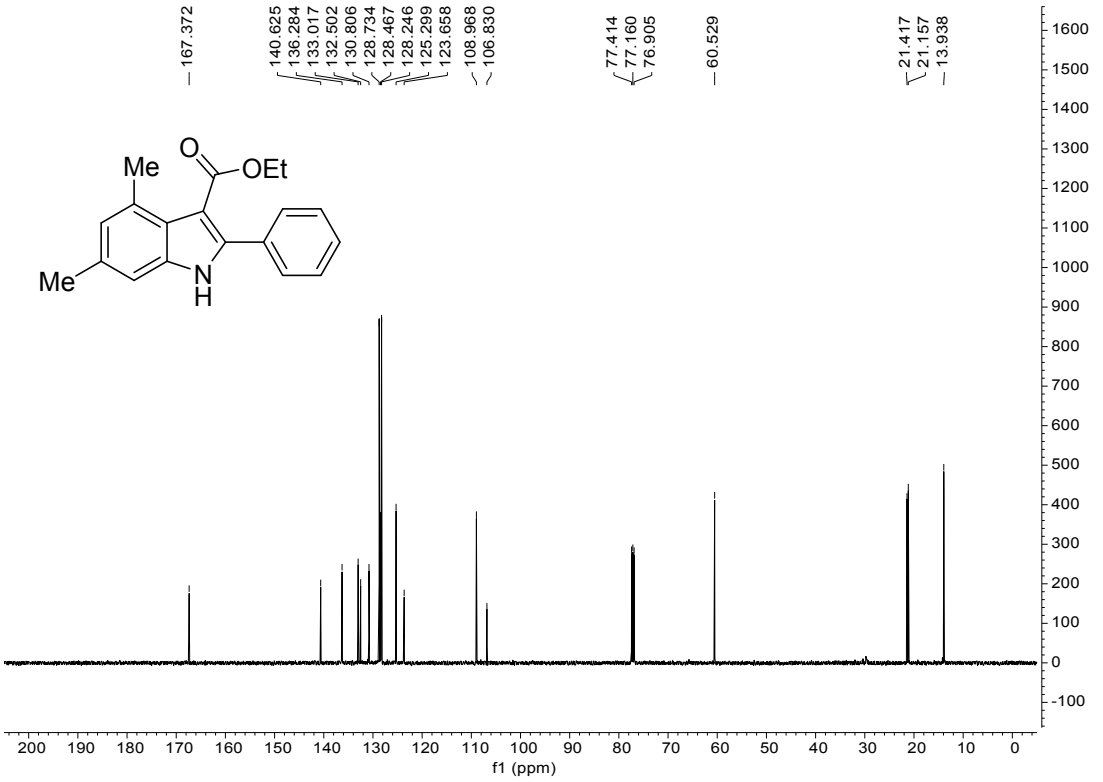




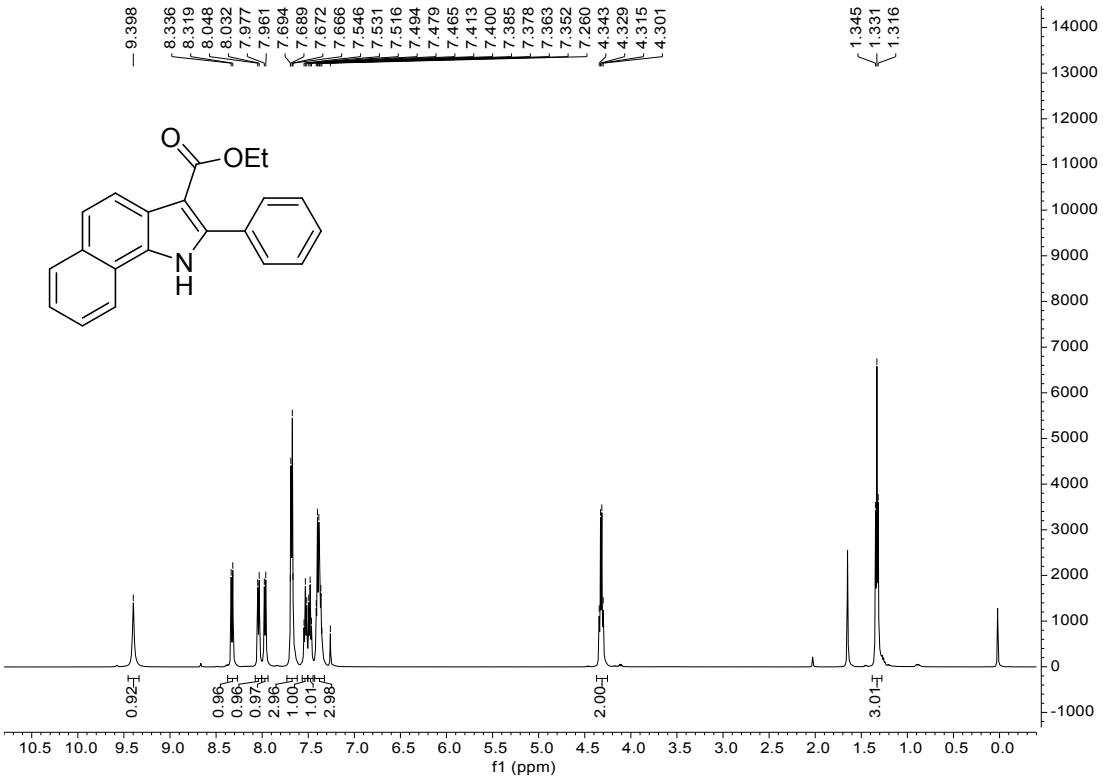


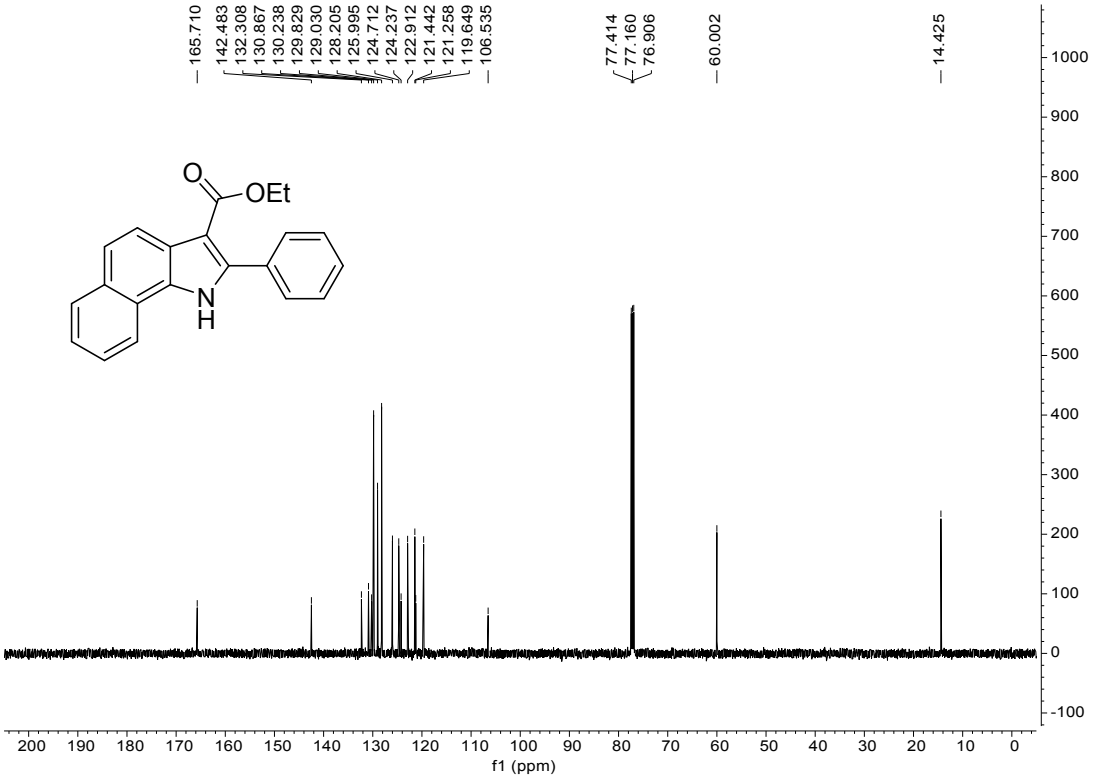
Ethyl 4,6-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (2-16)



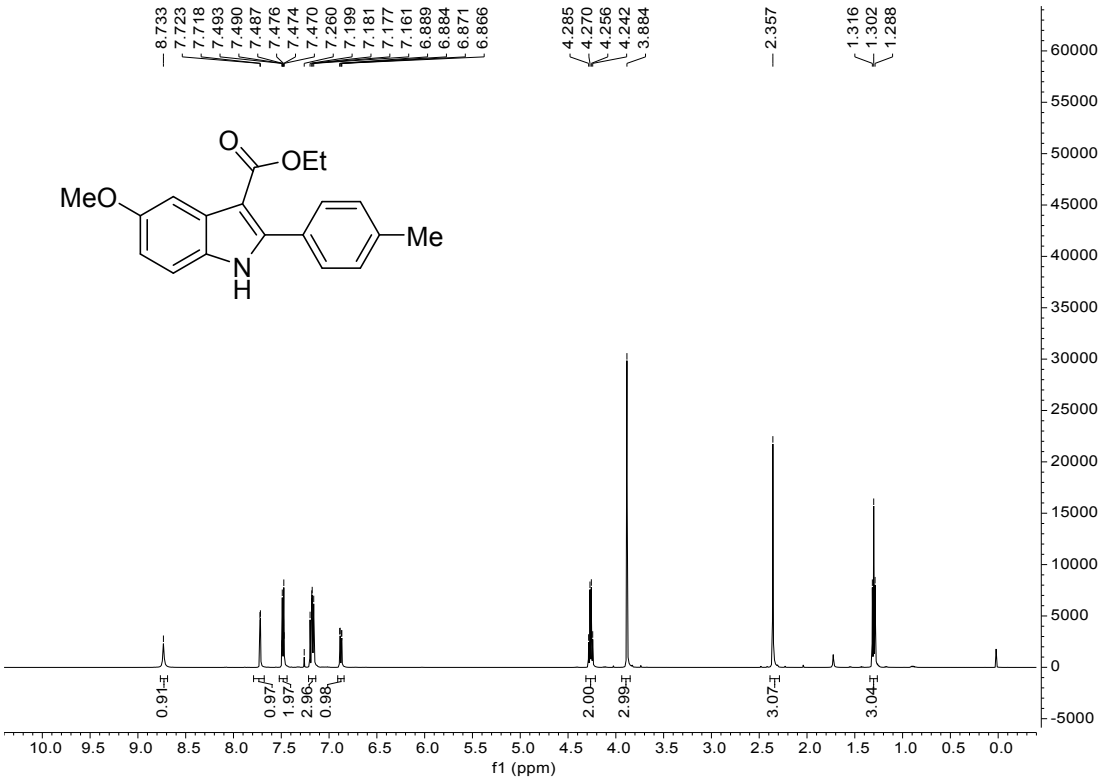


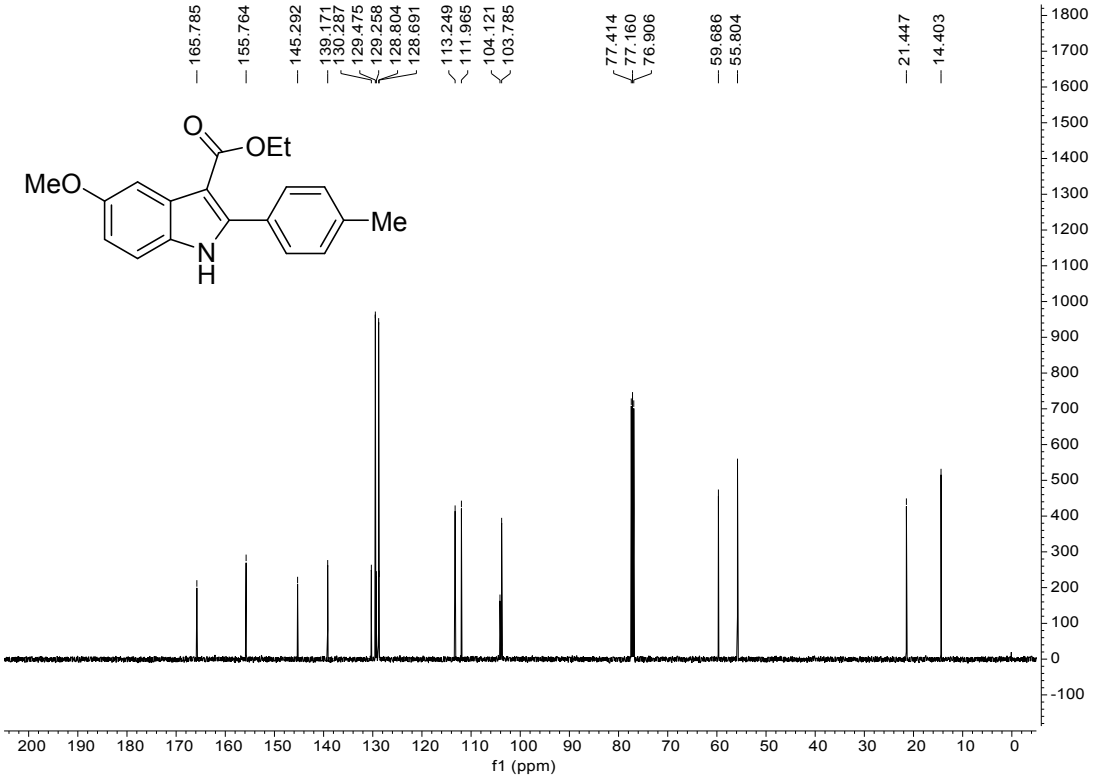
Ethyl 2-phenyl-1*H*-benzo[*g*]indole-3-carboxylate (2-17)



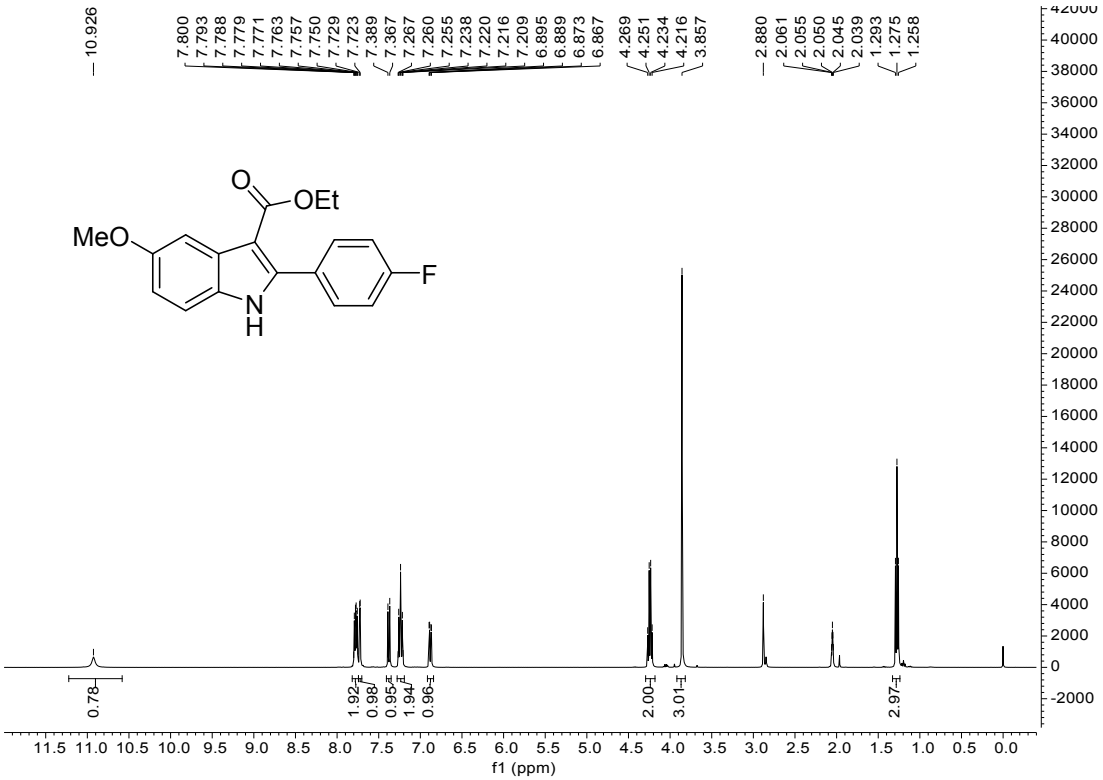


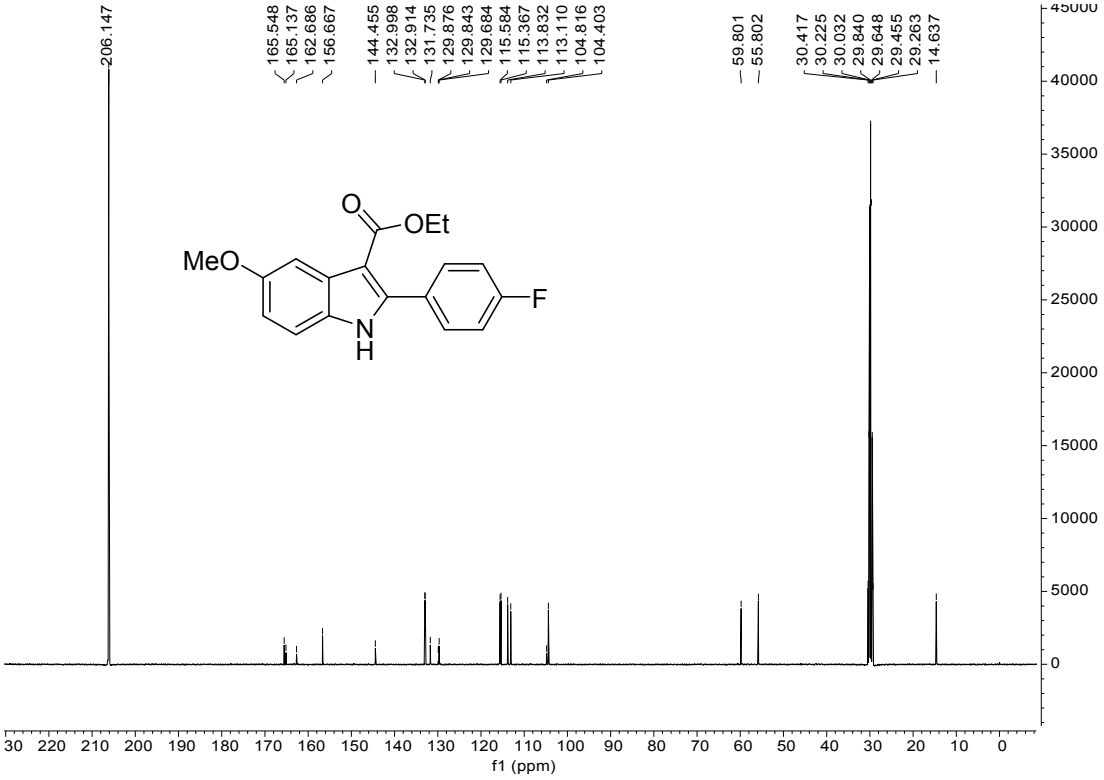
Ethyl 5-methoxy-2-(*p*-tolyl)-1*H*-indole-3-carboxylate (2-18)





Ethyl 2-(4-fluorophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-19)

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104.816
104.403
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55.802
30.417
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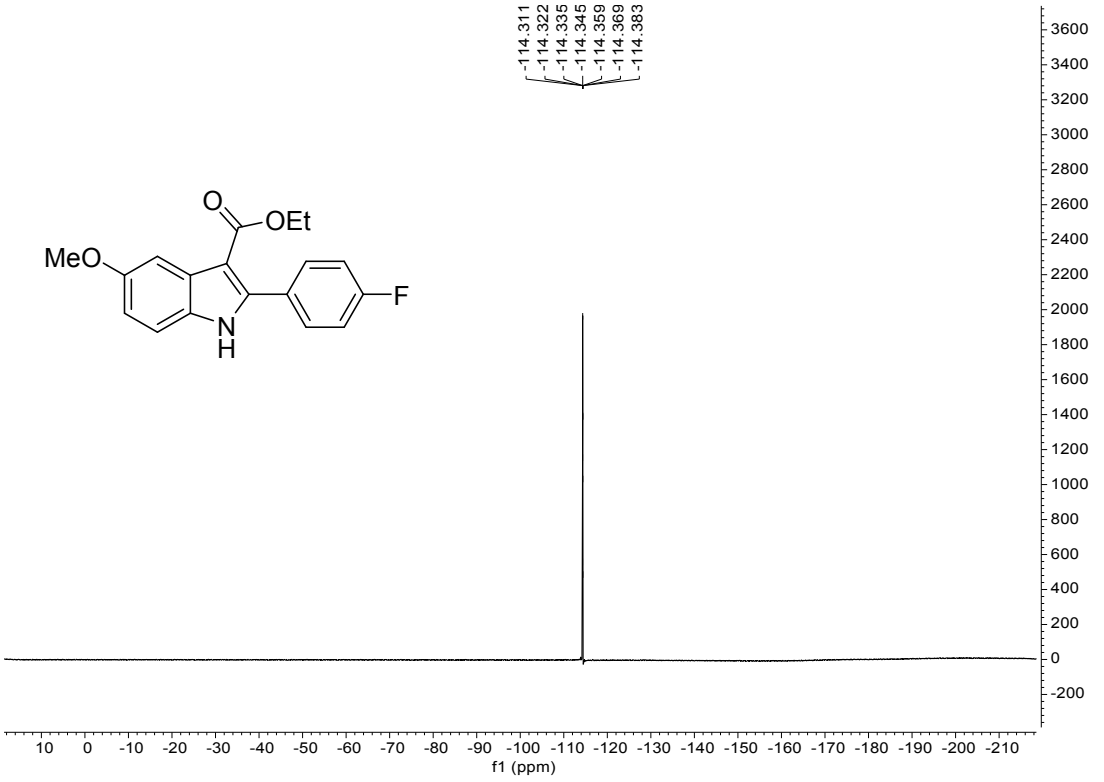
29.263
14.637
O
OEt
MeO
F
N
H
f1 (ppm)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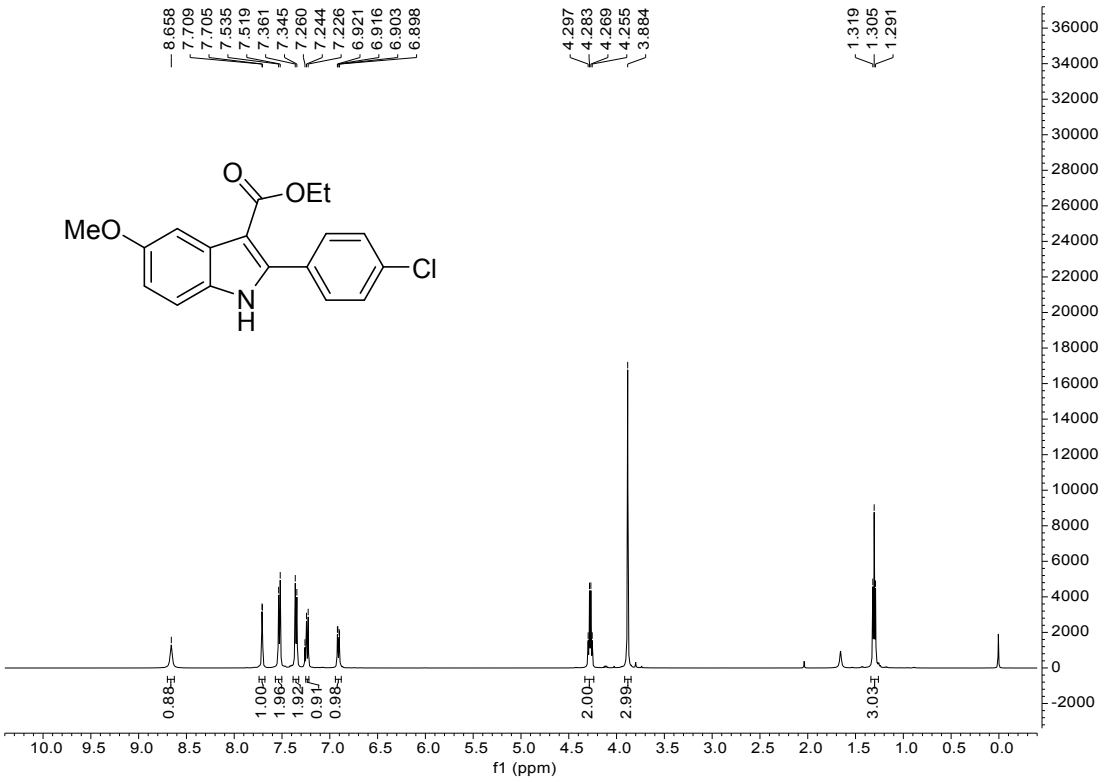
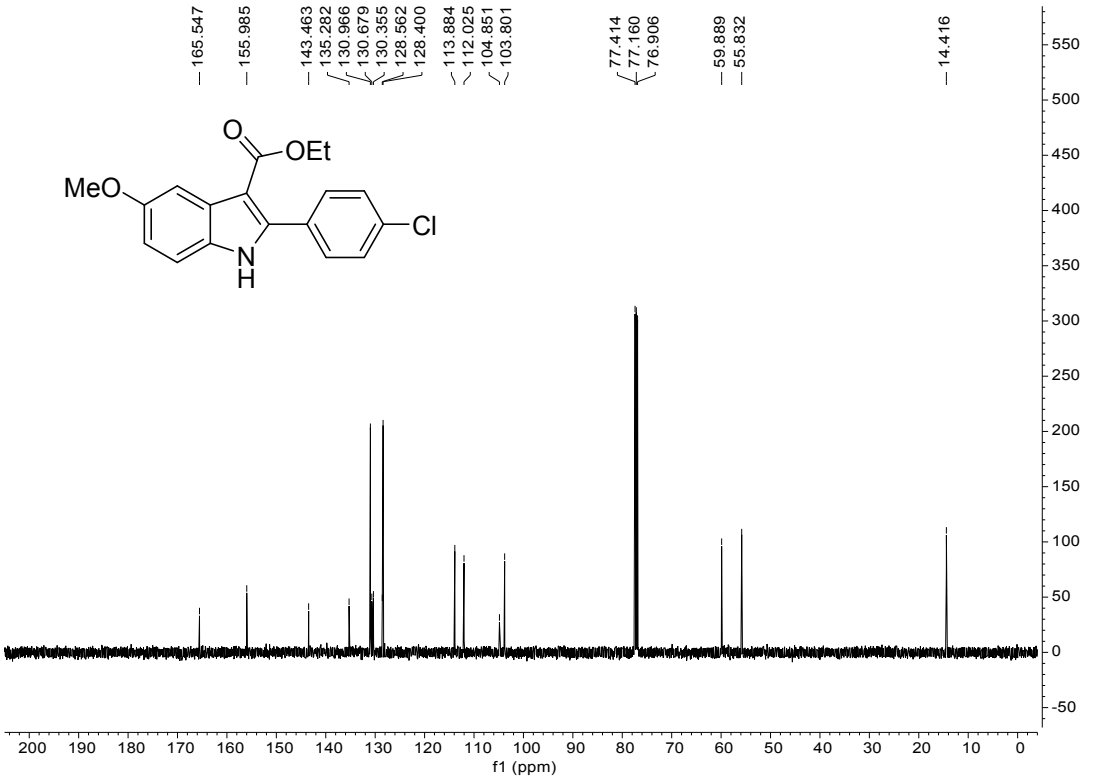
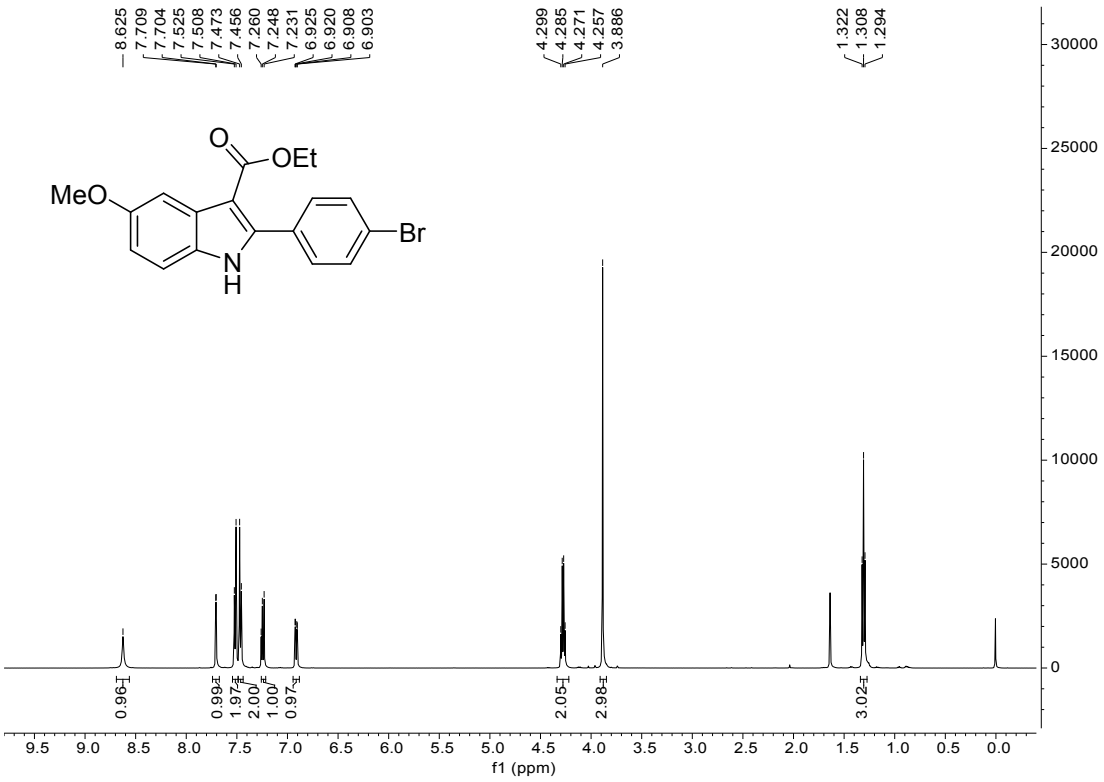
O
OEt
MeO
F
N
H
f1 (ppm)

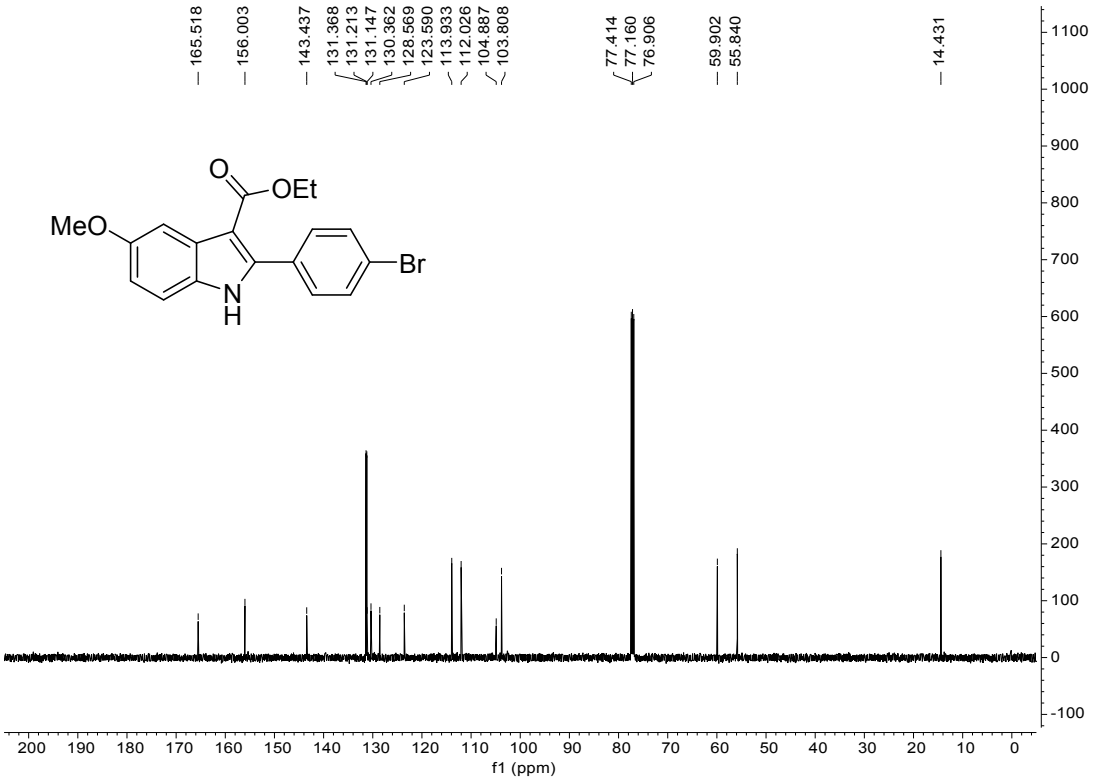
Ethyl 2-(4-chlorophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-20)



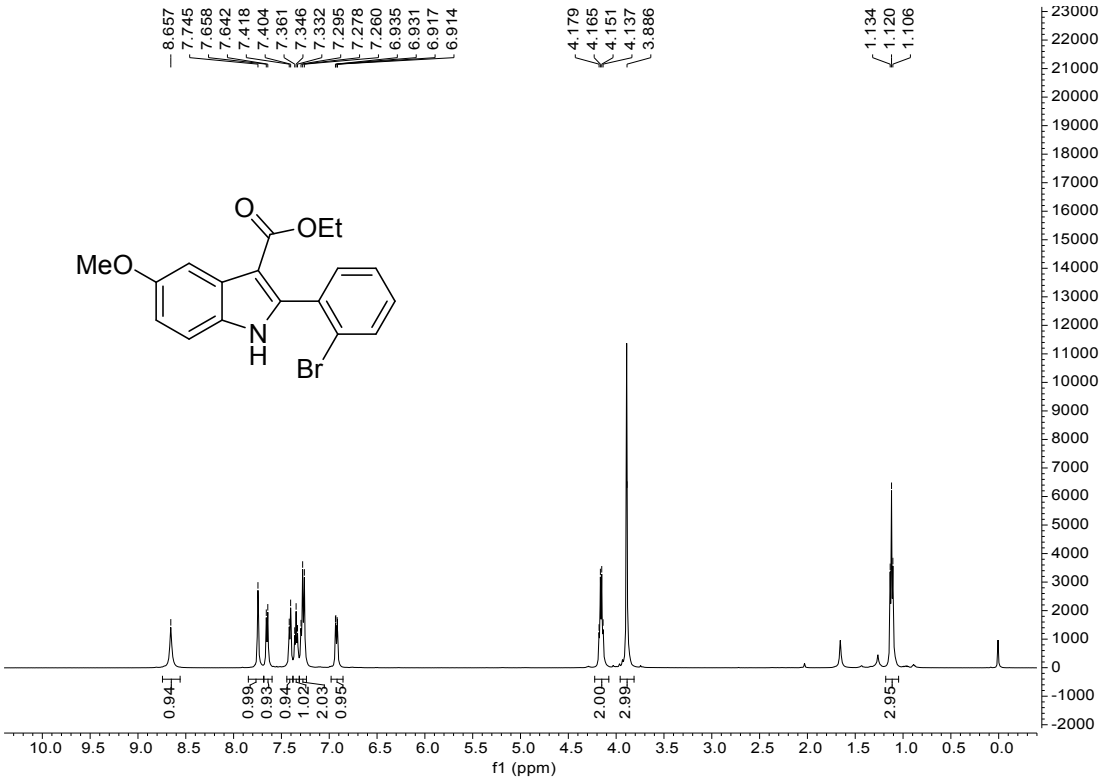


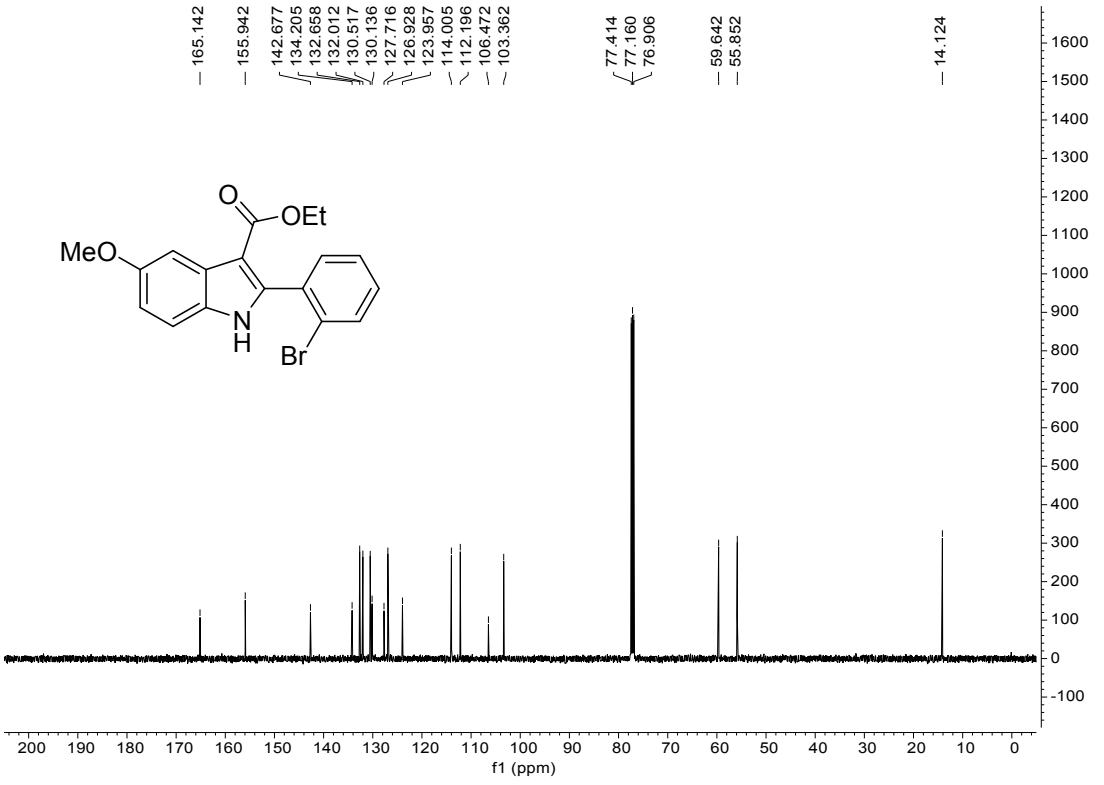
Ethyl 2-(4-bromophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-21)



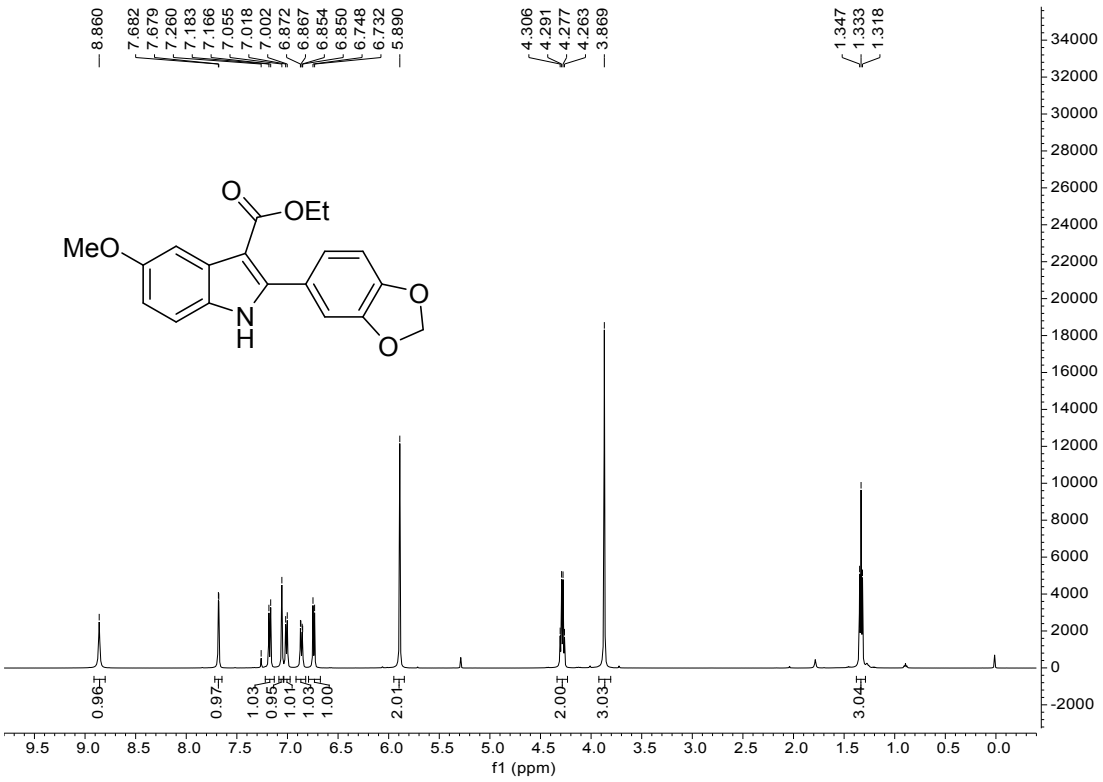


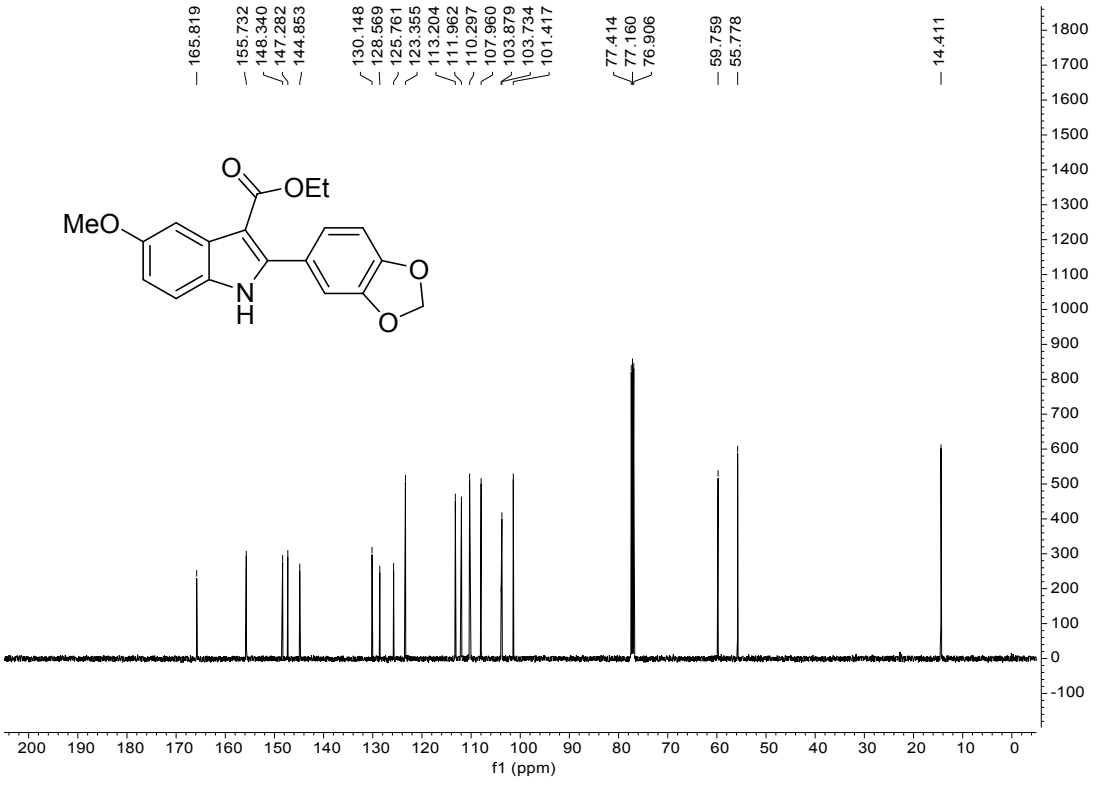
Ethyl 2-(2-bromophenyl)-5-methoxy-1*H*-indole-3-carboxylate (2-22)



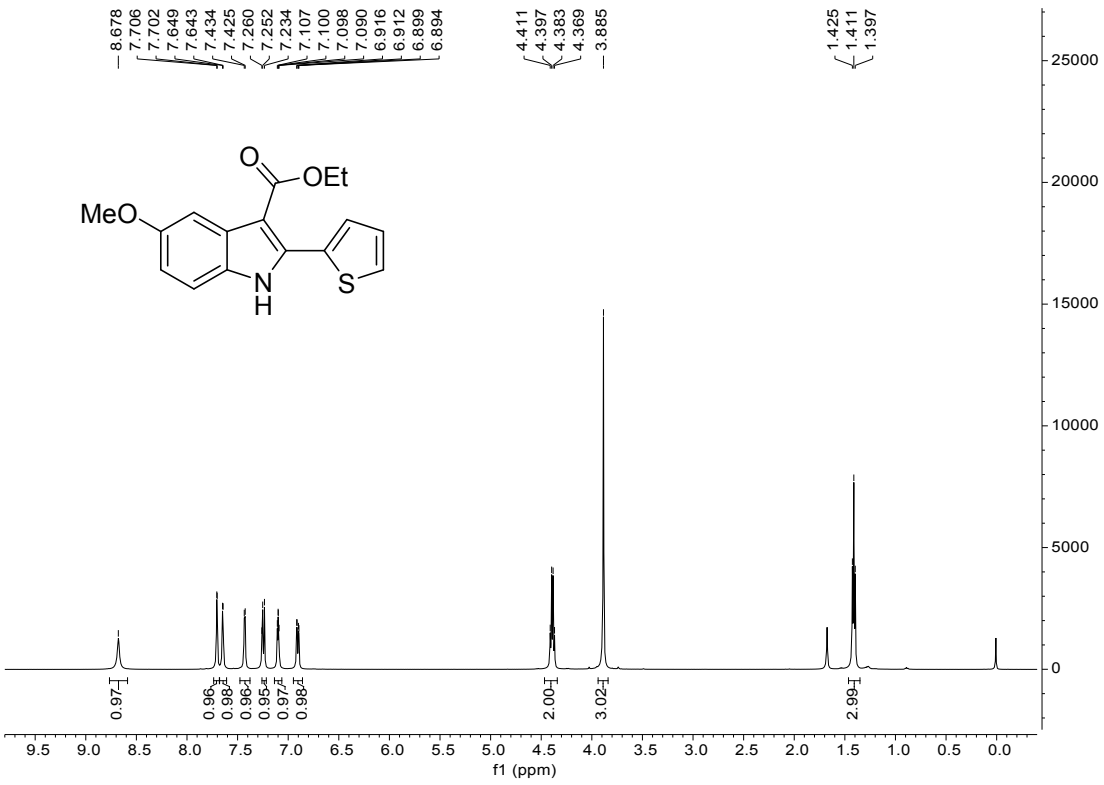


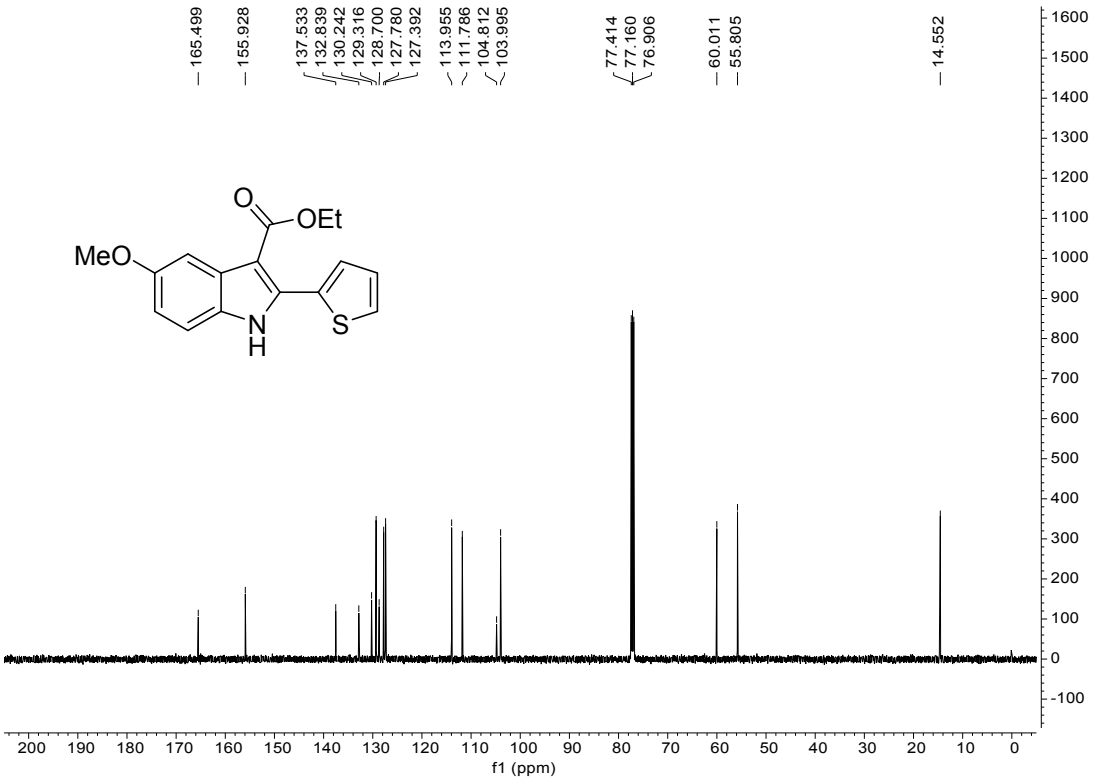
Ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-5-methoxy-1*H*-indole-3-carboxylate (2-23)



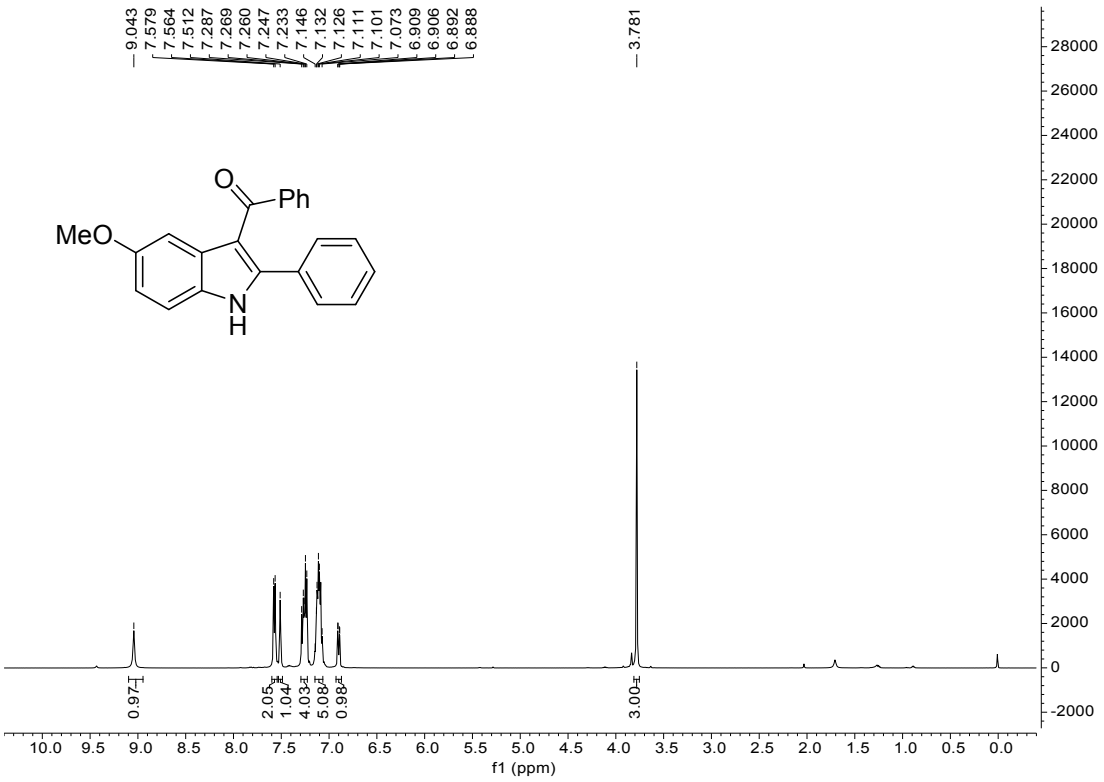


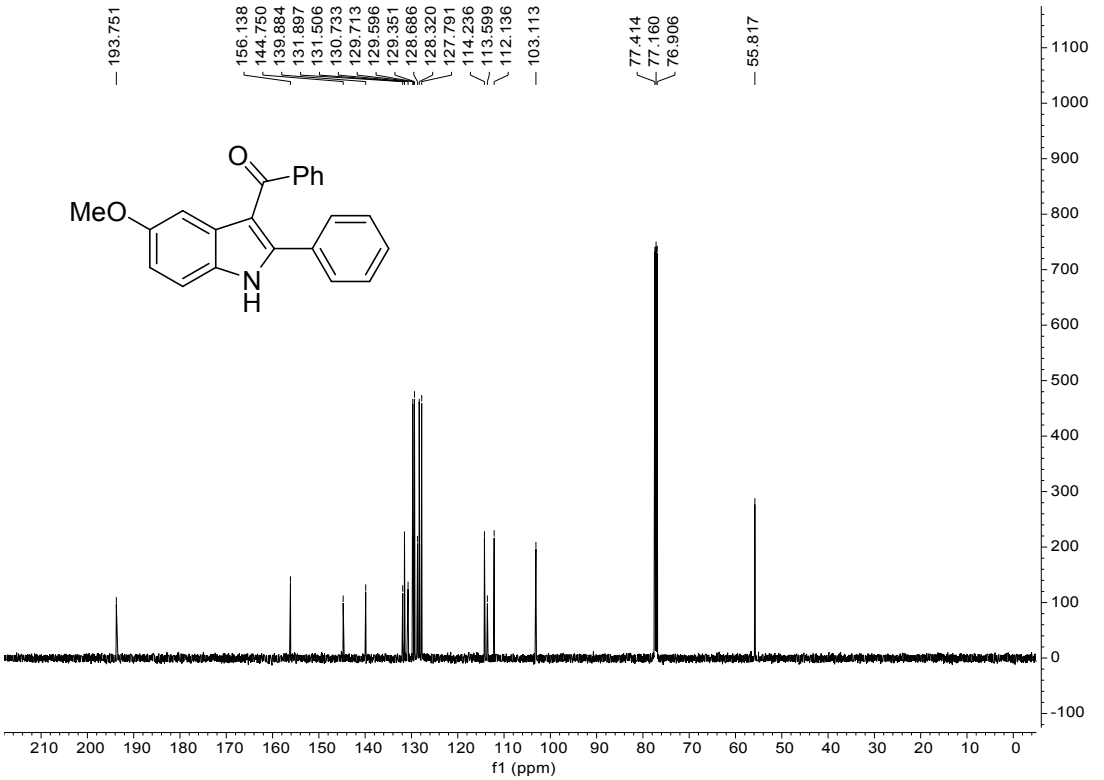
Ethyl 5-methoxy-2-(thiophen-2-yl)-1*H*-indole-3-carboxylate (2-24)



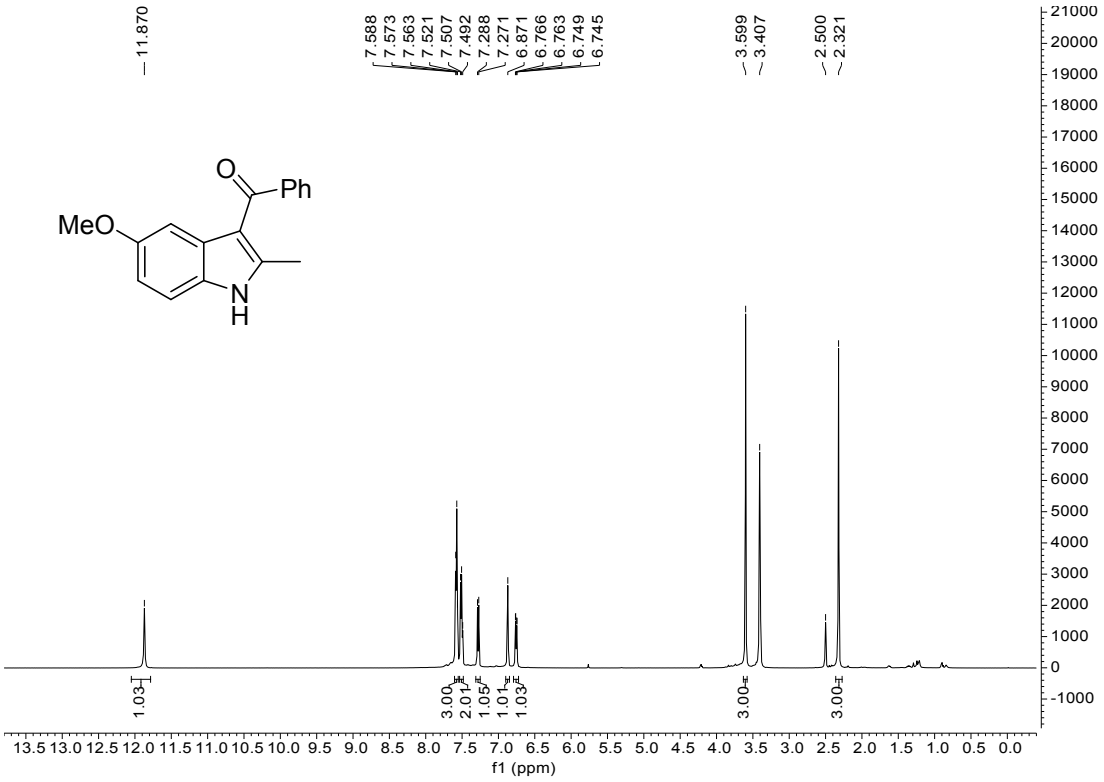


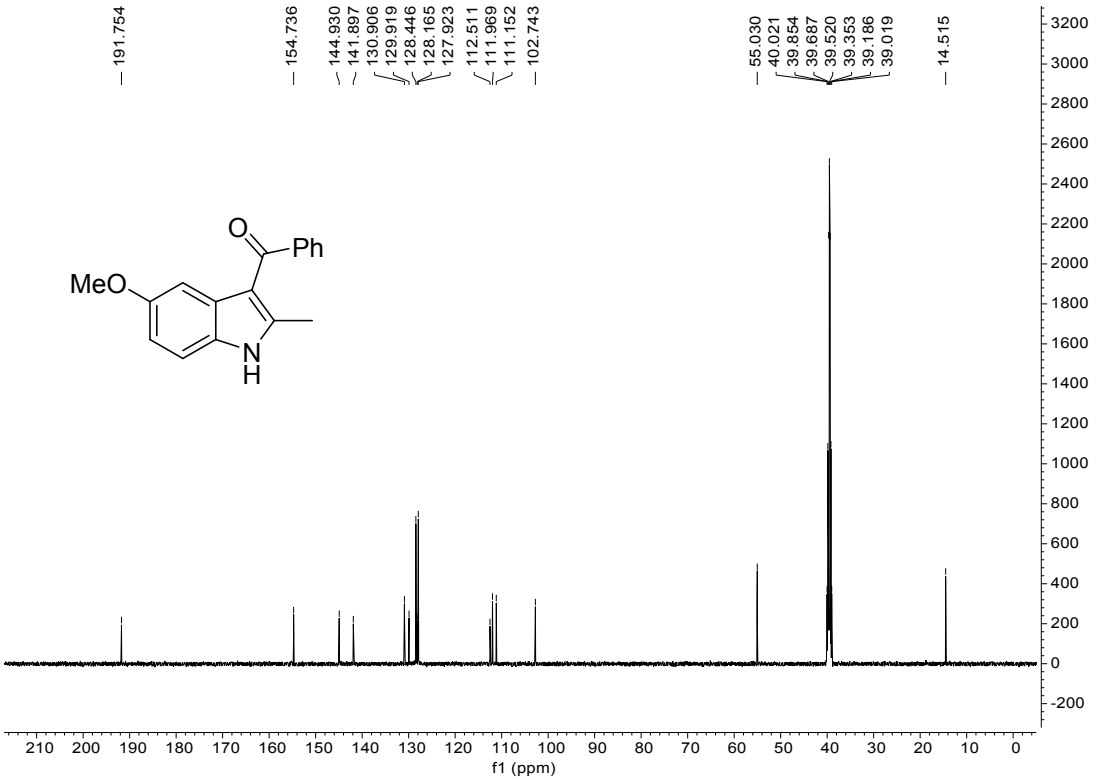
(5-methoxy-2-phenyl-1*H*-indol-3-yl)(phenyl)methanone (2-25)



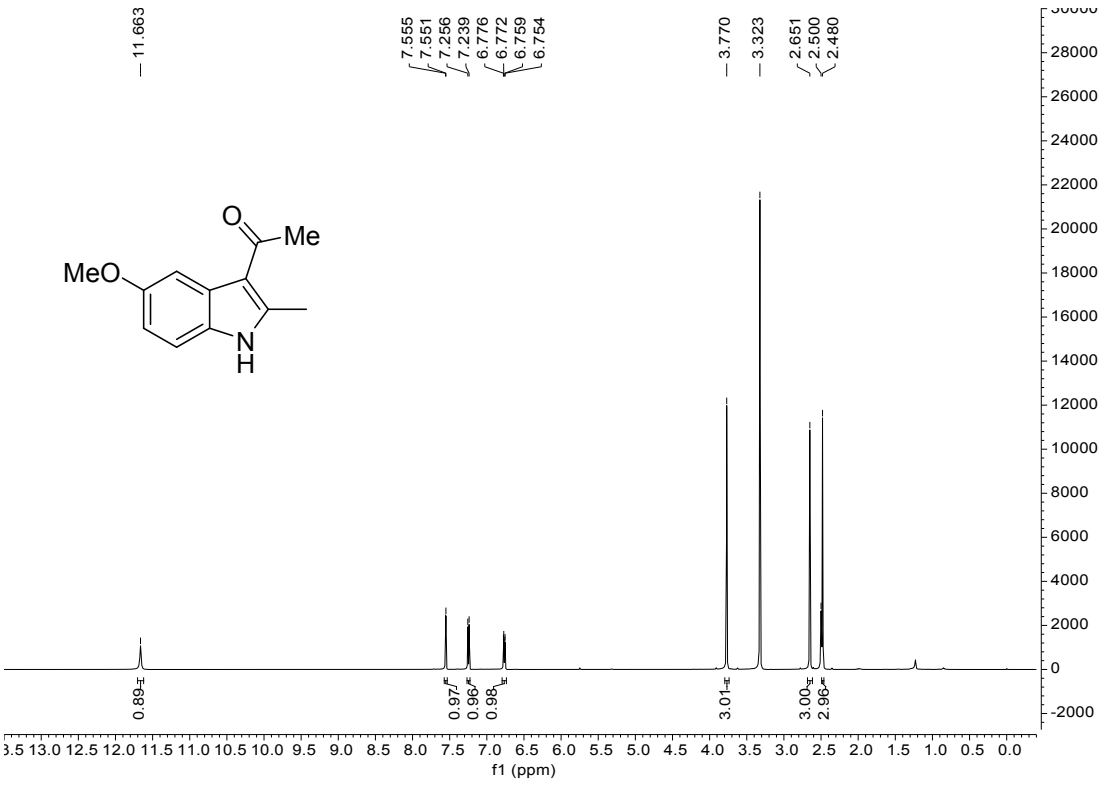


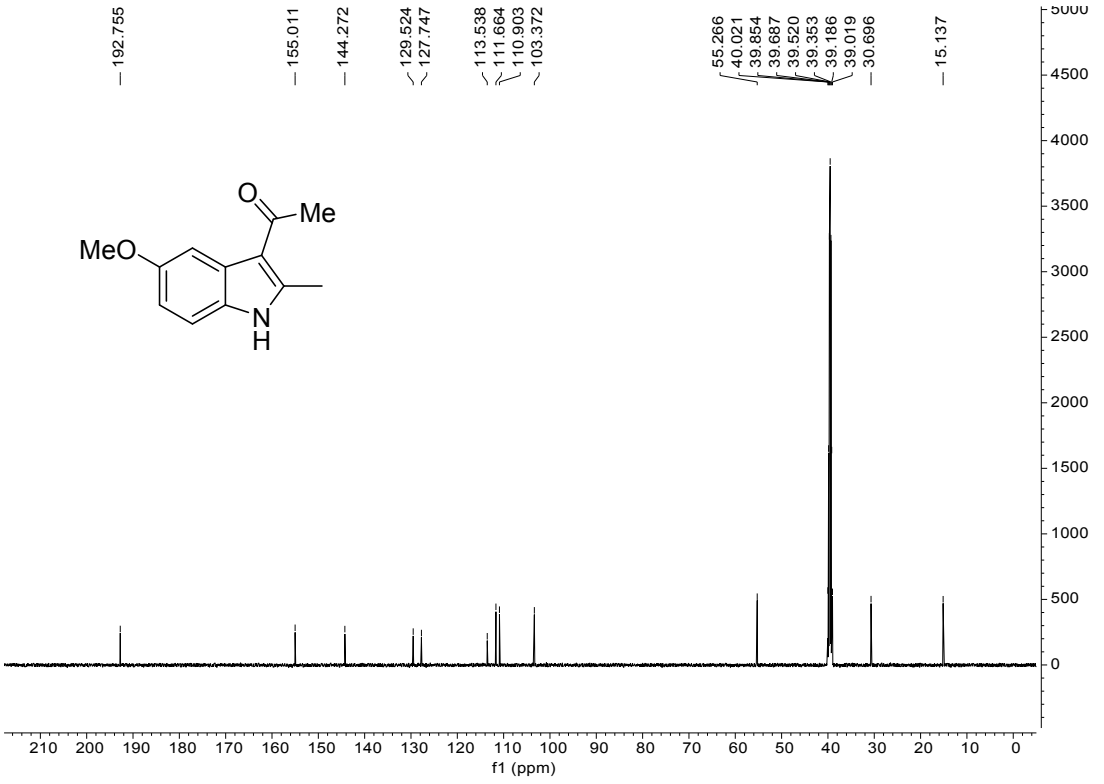
(5-methoxy-2-methyl-1*H*-indol-3-yl)(phenyl)methanone (2-26)



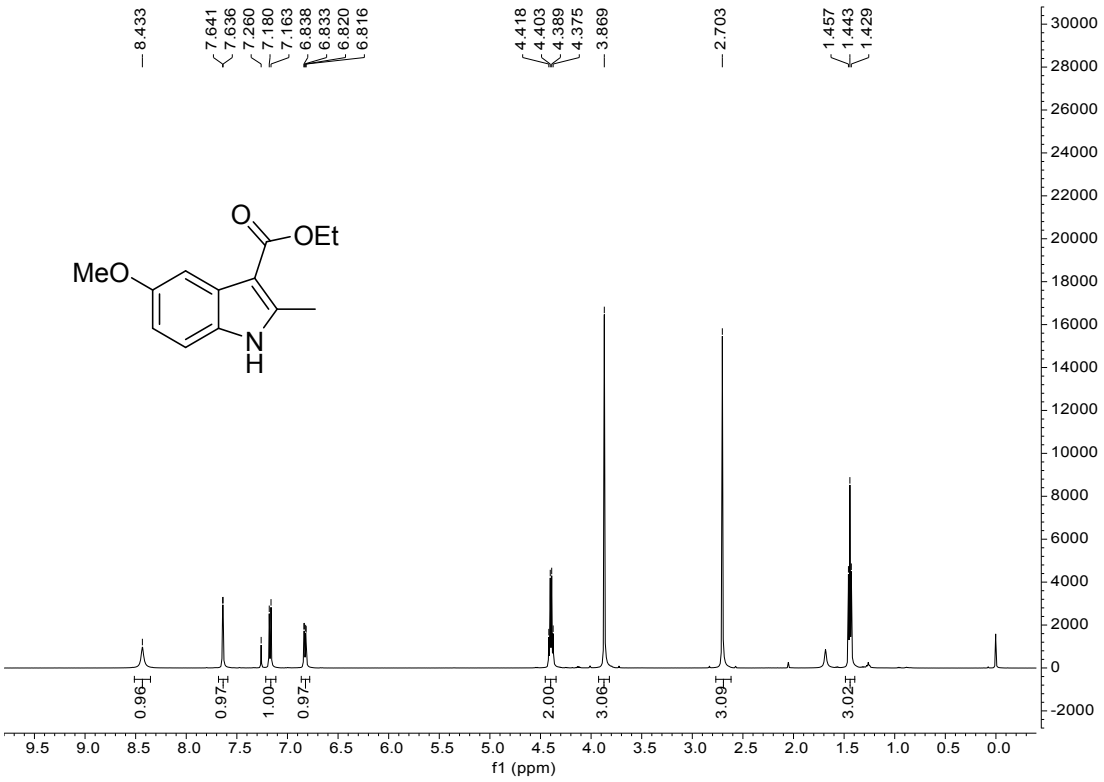


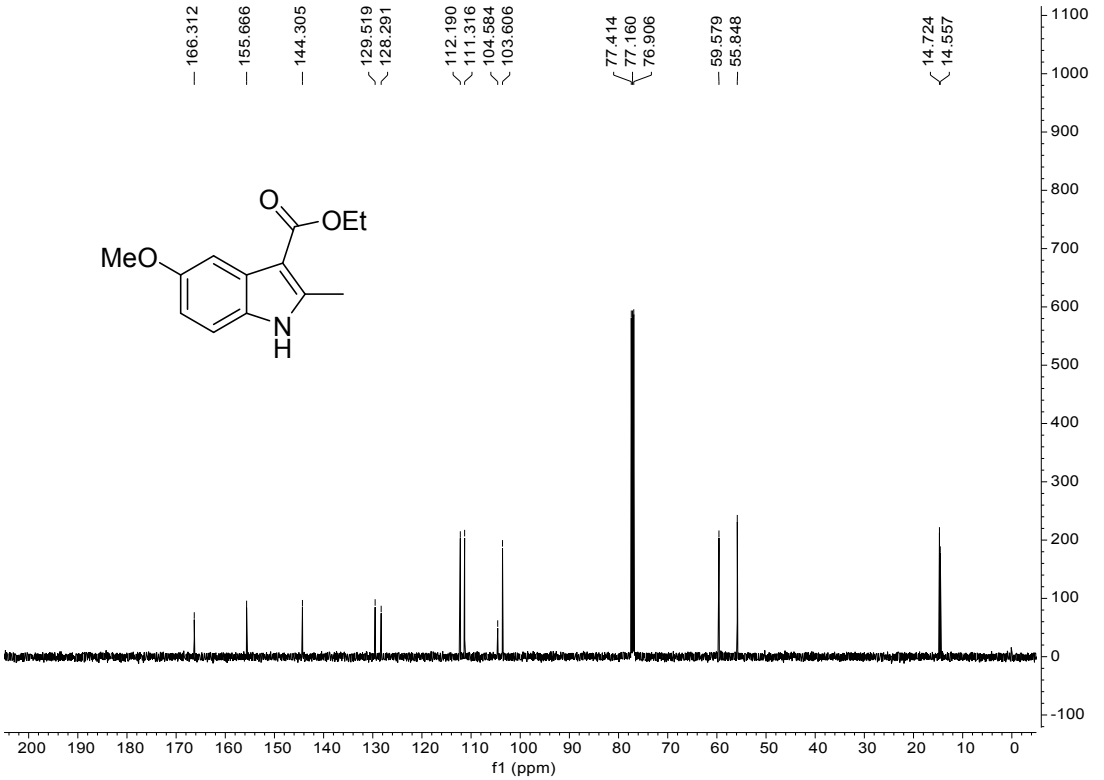
1-(5-methoxy-2-methyl-1*H*-indol-3-yl)ethan-1-one (2-27)



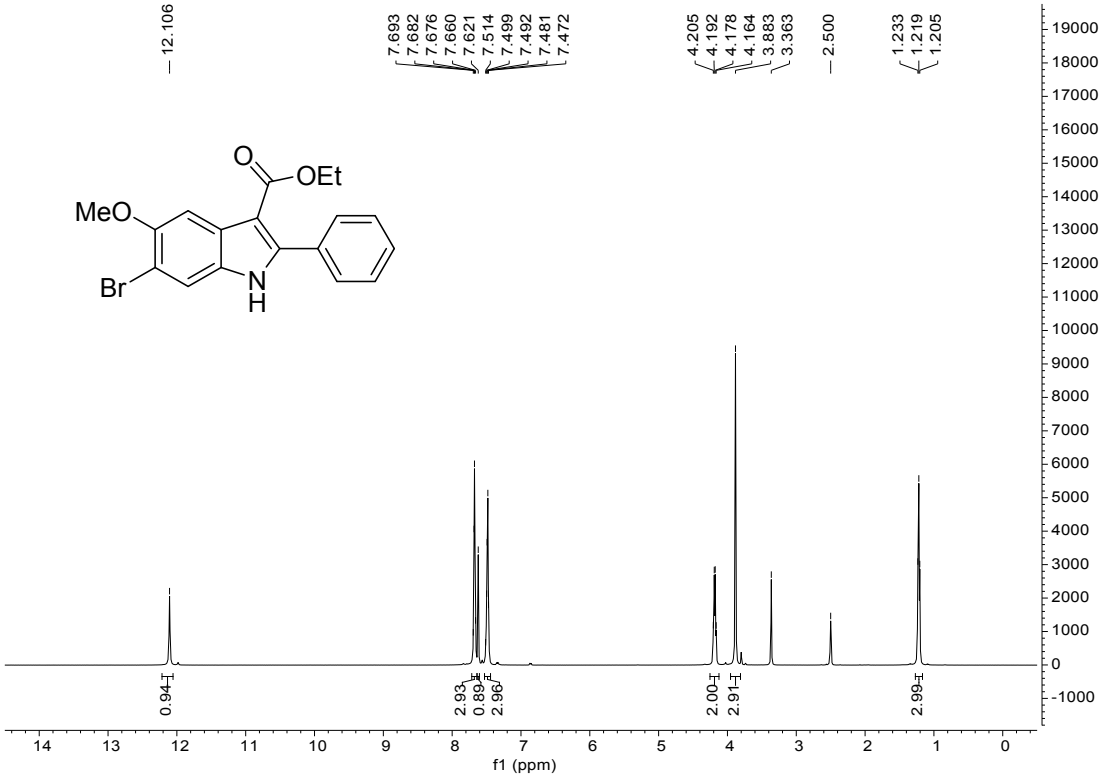


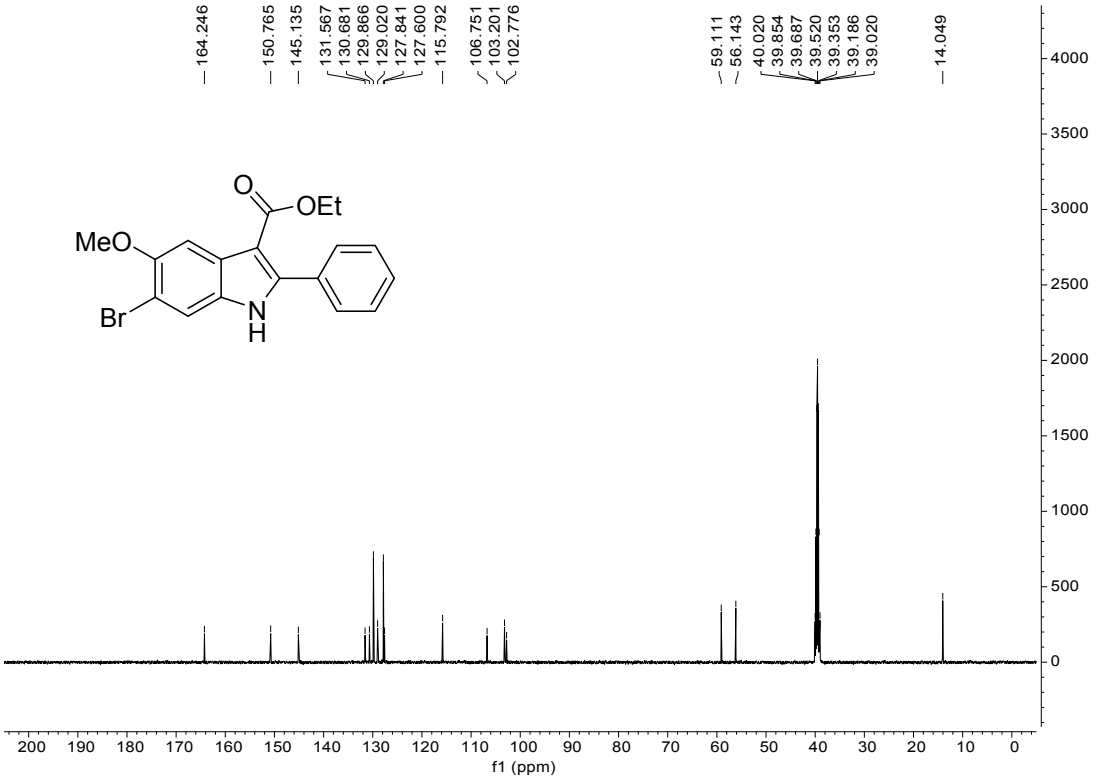
Ethyl 5-methoxy-2-methyl-1*H*-indole-3-carboxylate (2-28)



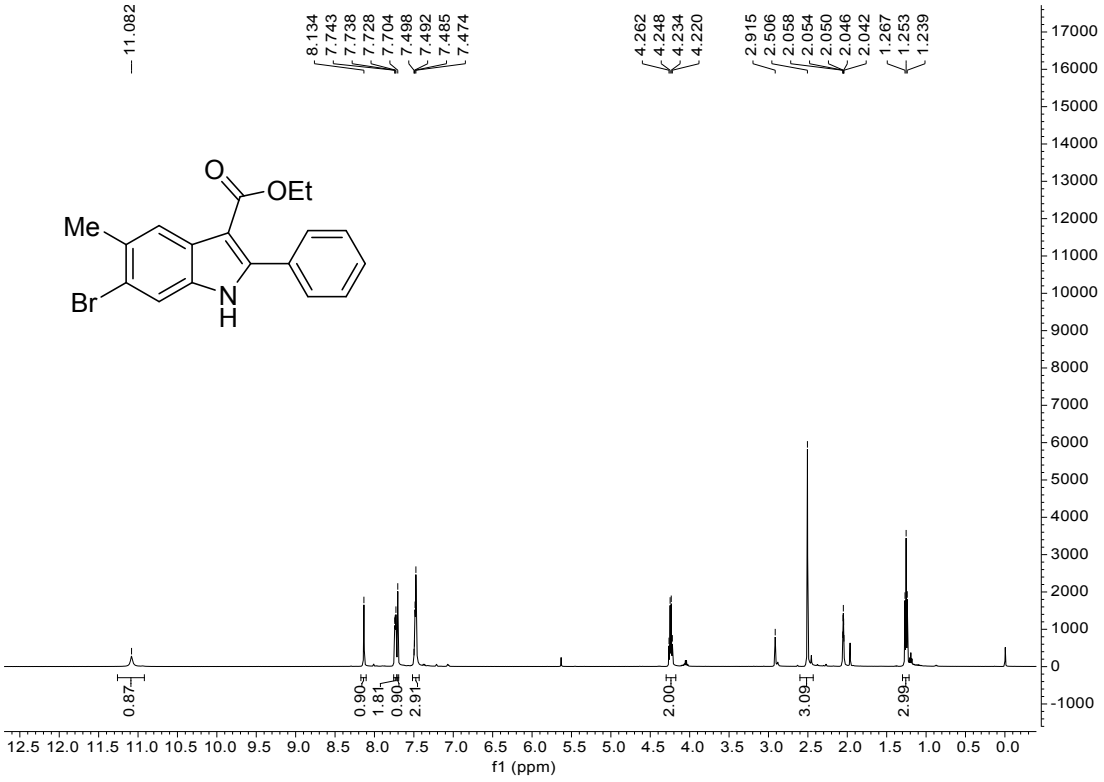


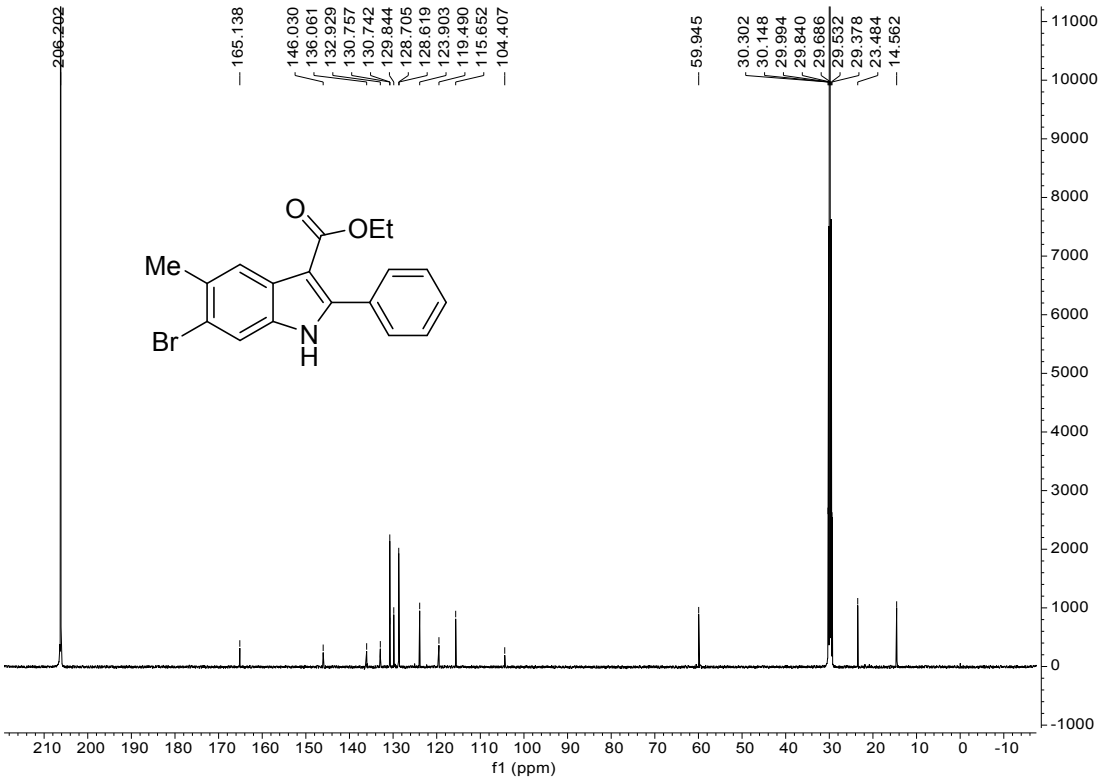
Ethyl 6-bromo-5-methoxy-2-phenyl-1*H*-indole-3-carboxylate (3-1)



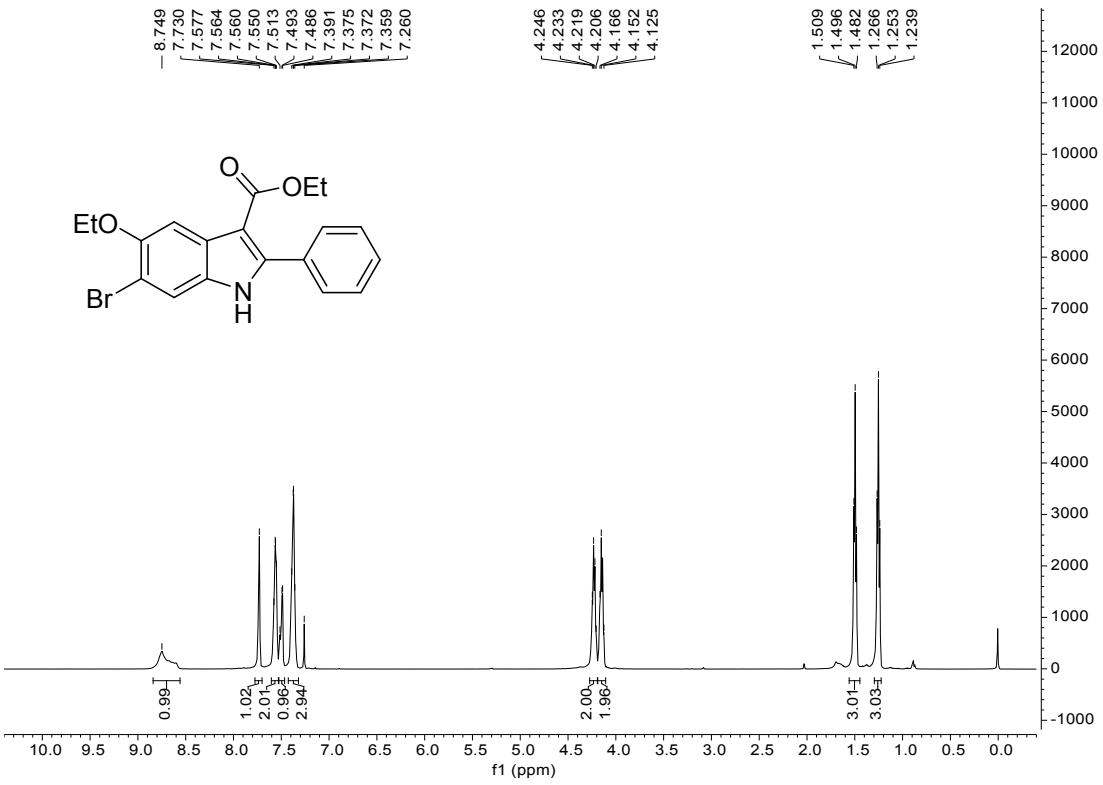


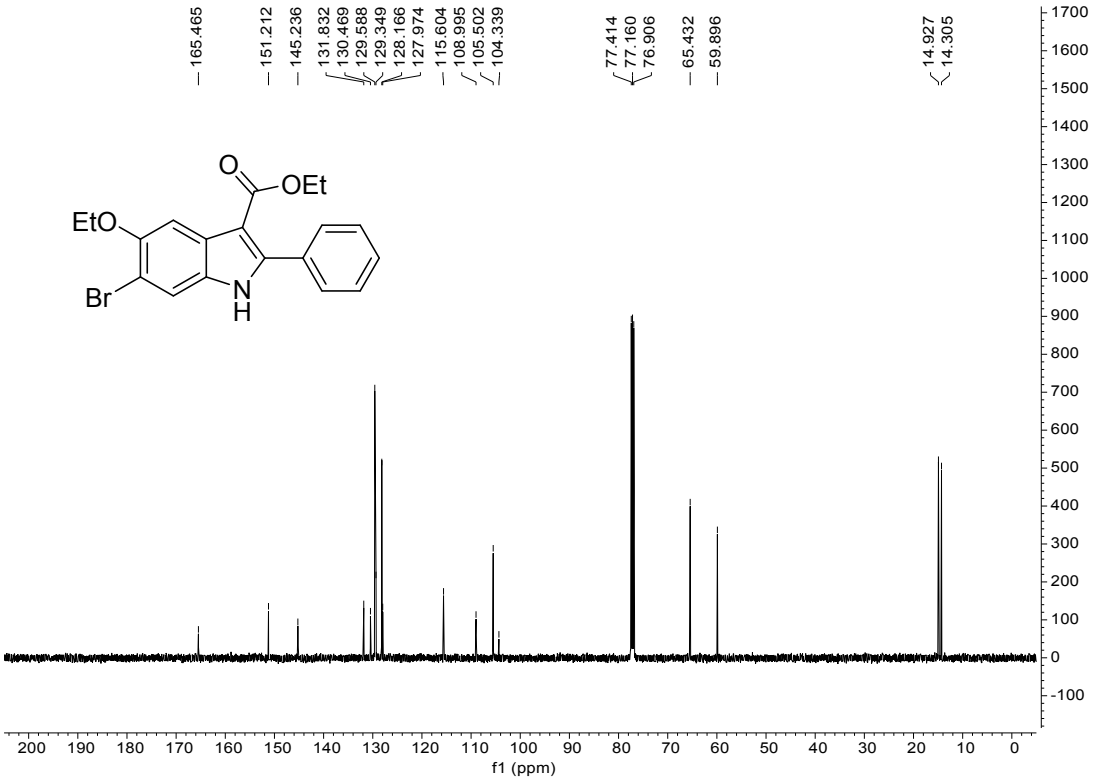
Ethyl 6-bromo-5-methyl-2-phenyl-1*H*-indole-3-carboxylate (3-2)



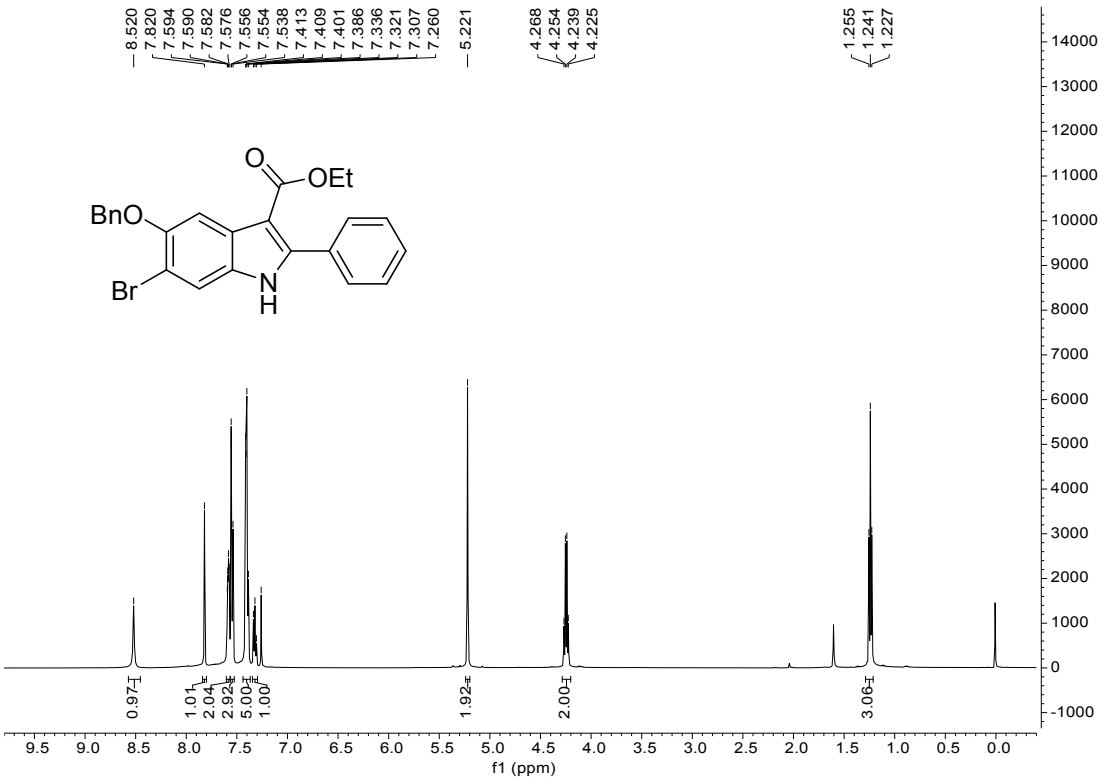


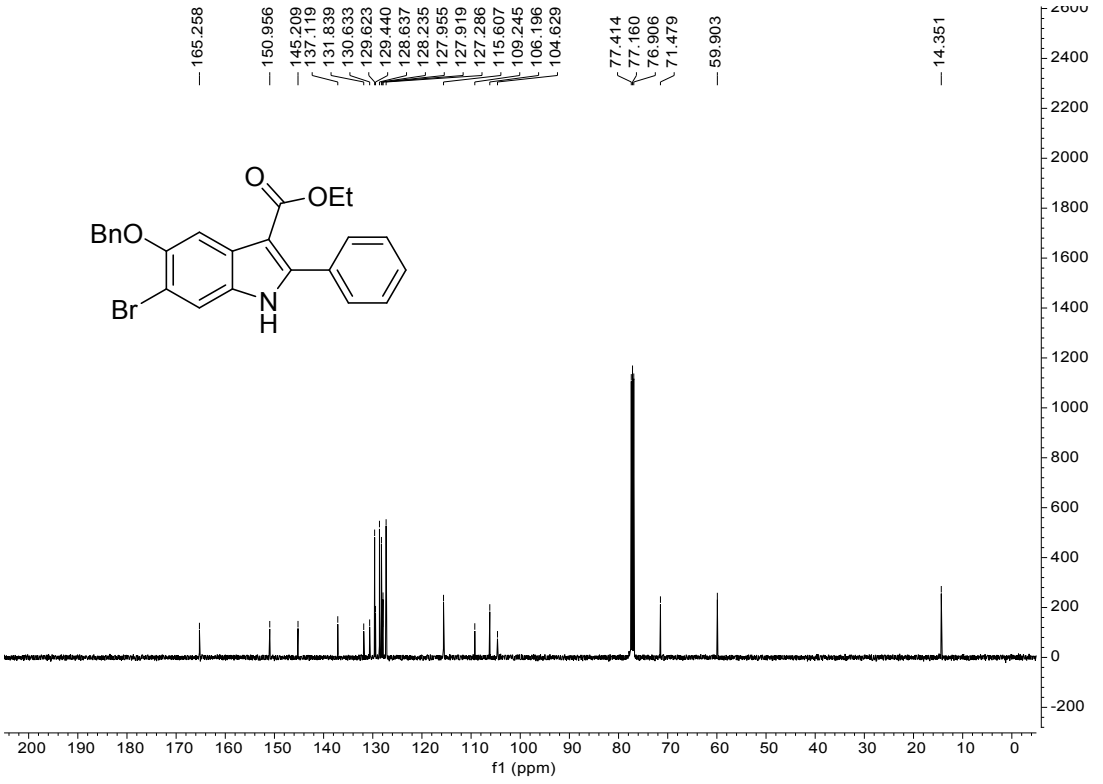
Ethyl 6-bromo-5-ethoxy-2-phenyl-1*H*-indole-3-carboxylate (3-29)



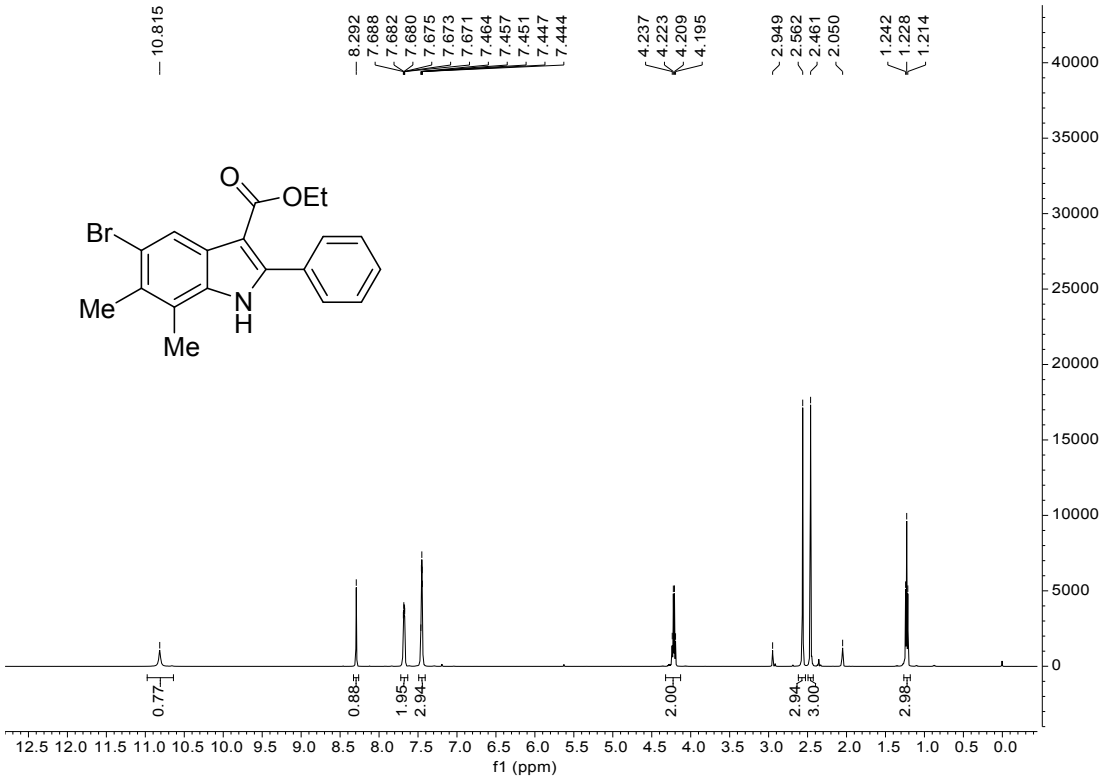


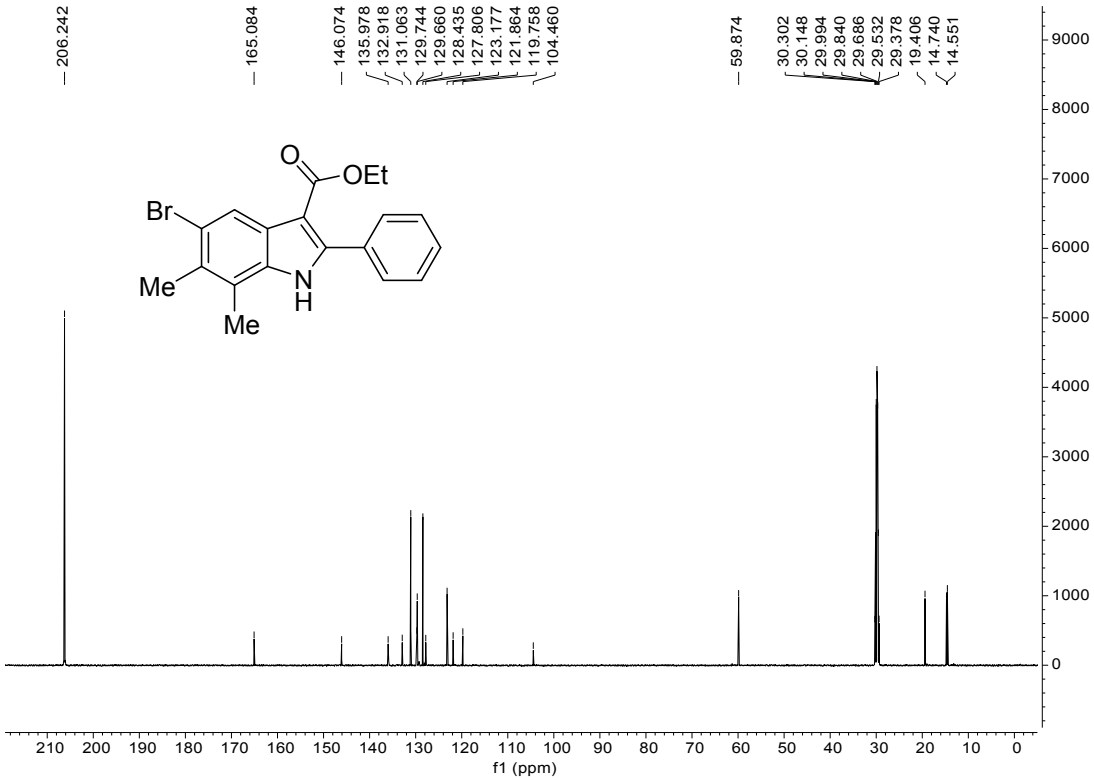
Ethyl 5-(benzyloxy)-6-bromo-2-phenyl-1*H*-indole-3-carboxylate (3-30)



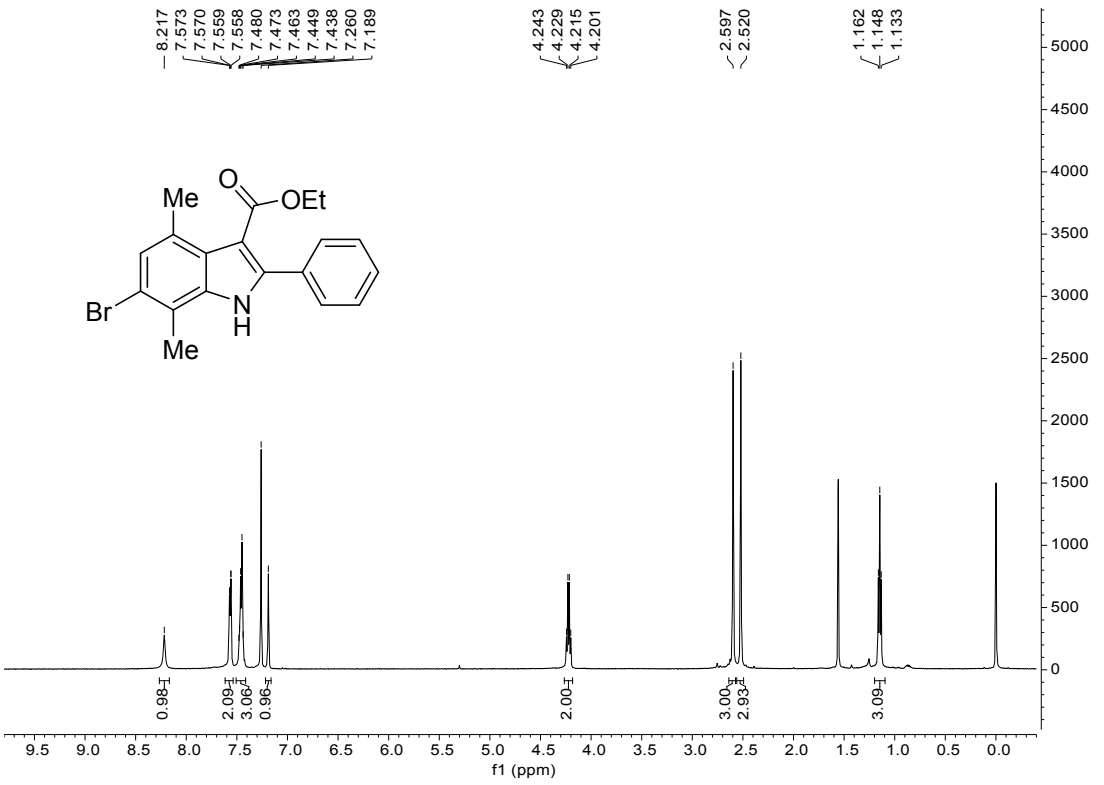


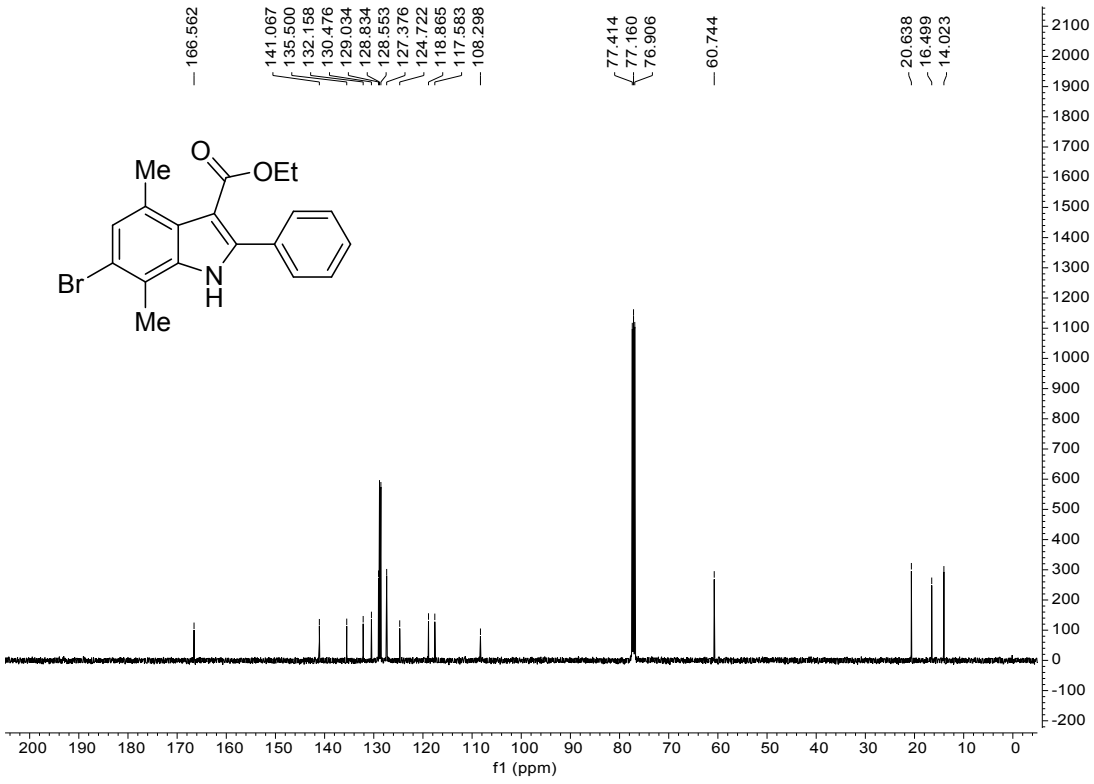
Ethyl 5-bromo-6,7-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-31)



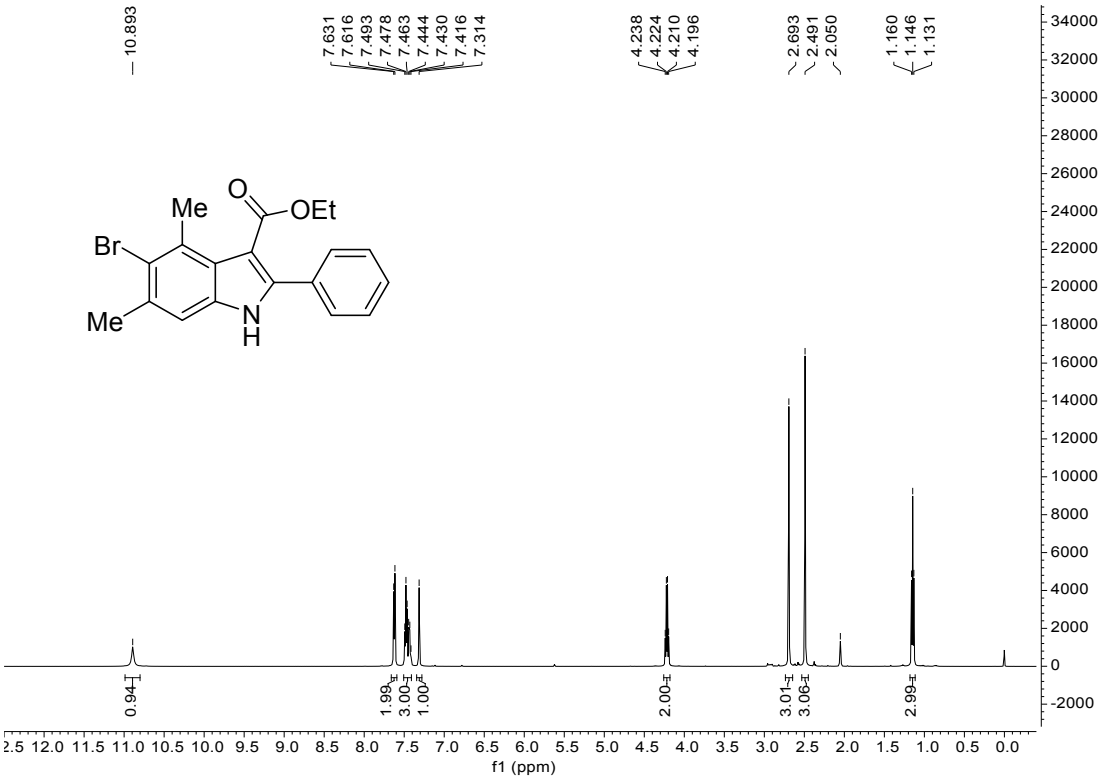


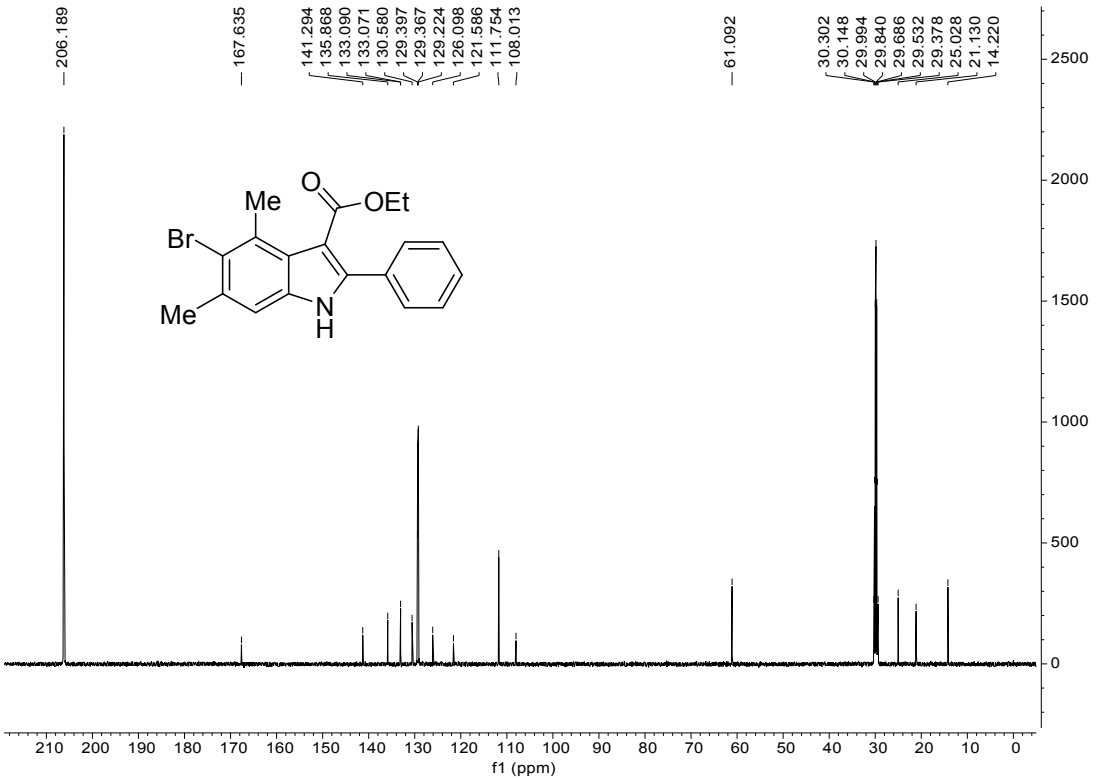
Ethyl 6-bromo-4,7-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-32)



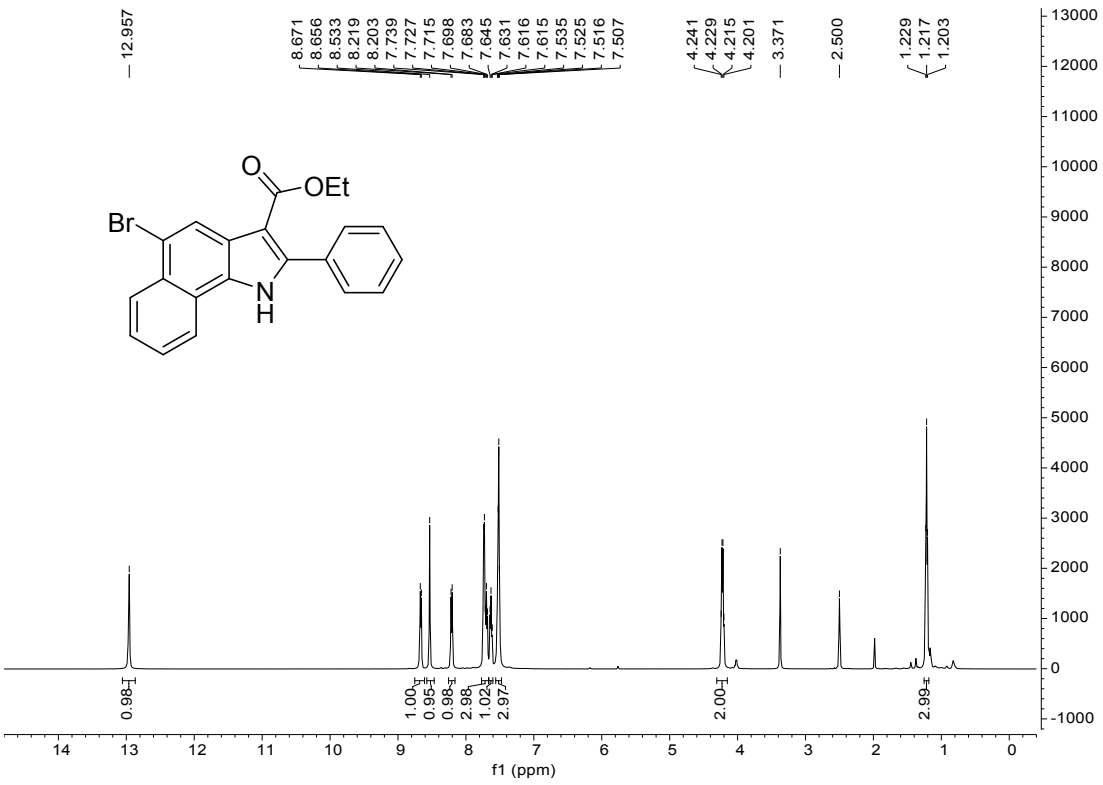


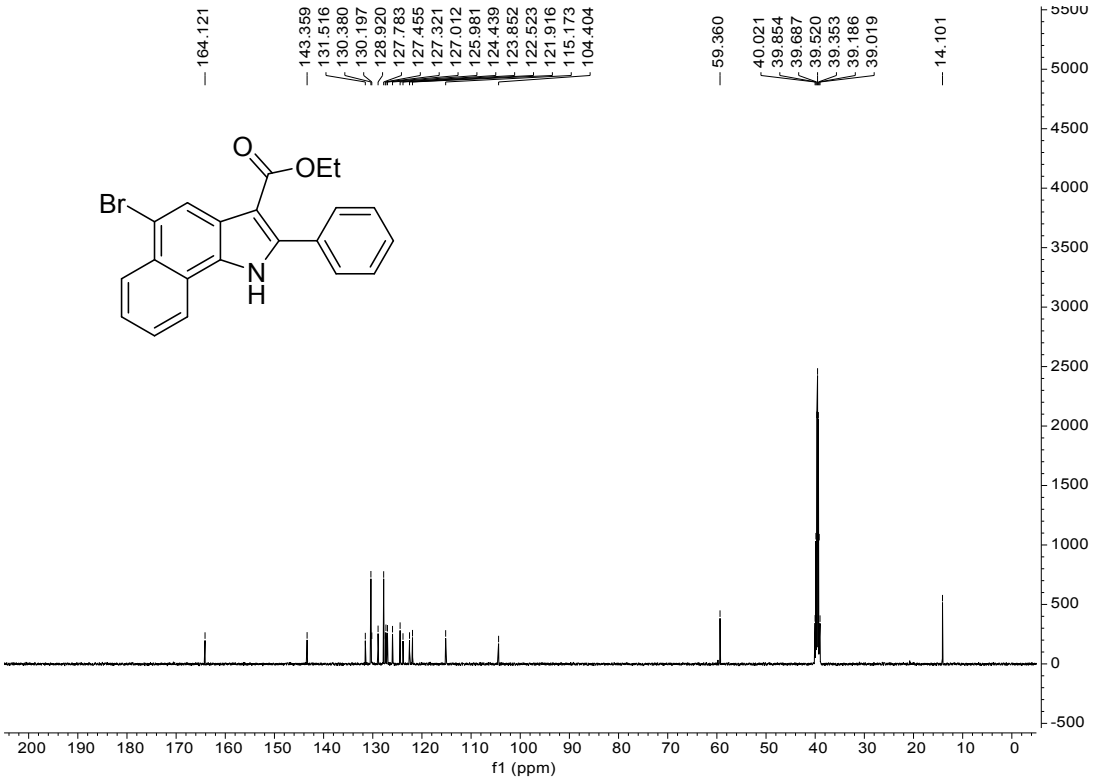
Ethyl 5-bromo-4,6-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-16)



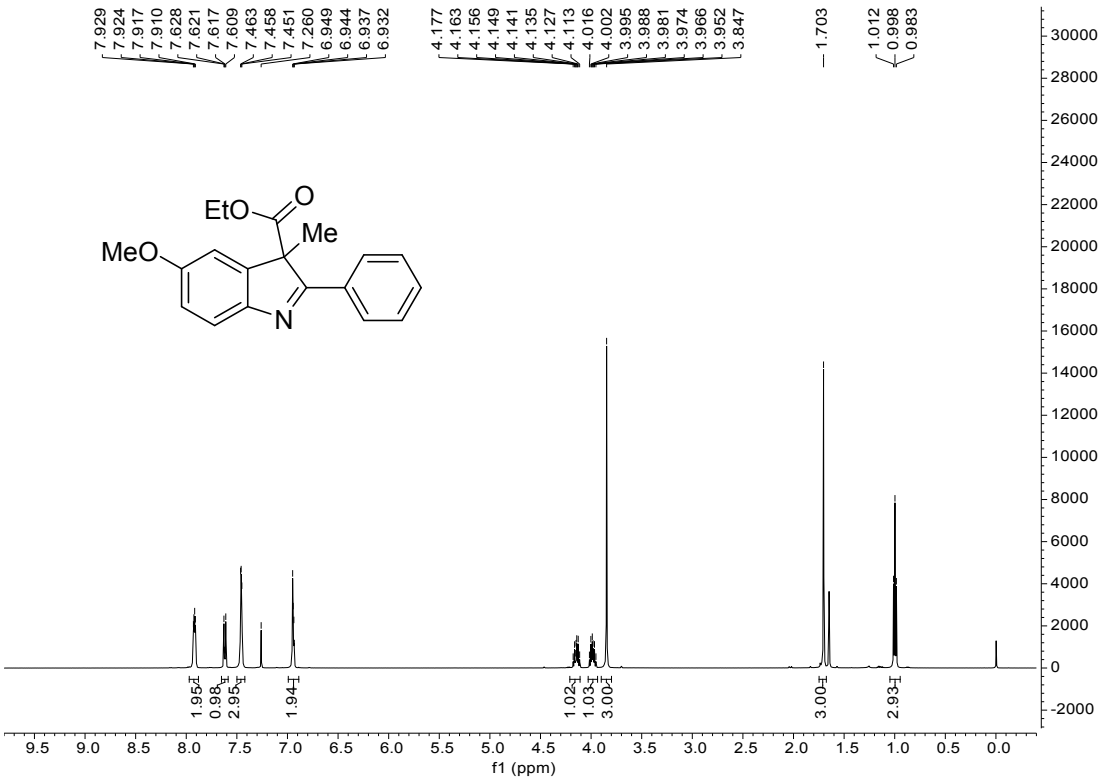


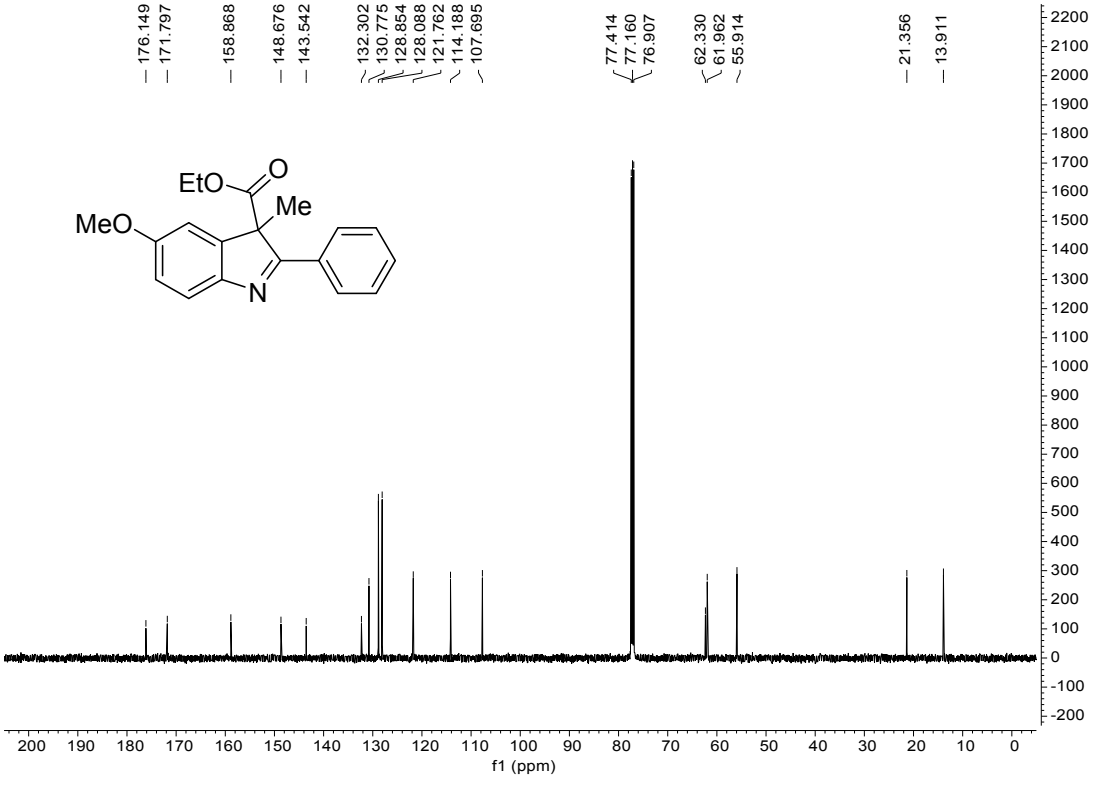
Ethyl 5-bromo-2-phenyl-1*H*-benzo[g]indole-3-carboxylate (3-17)



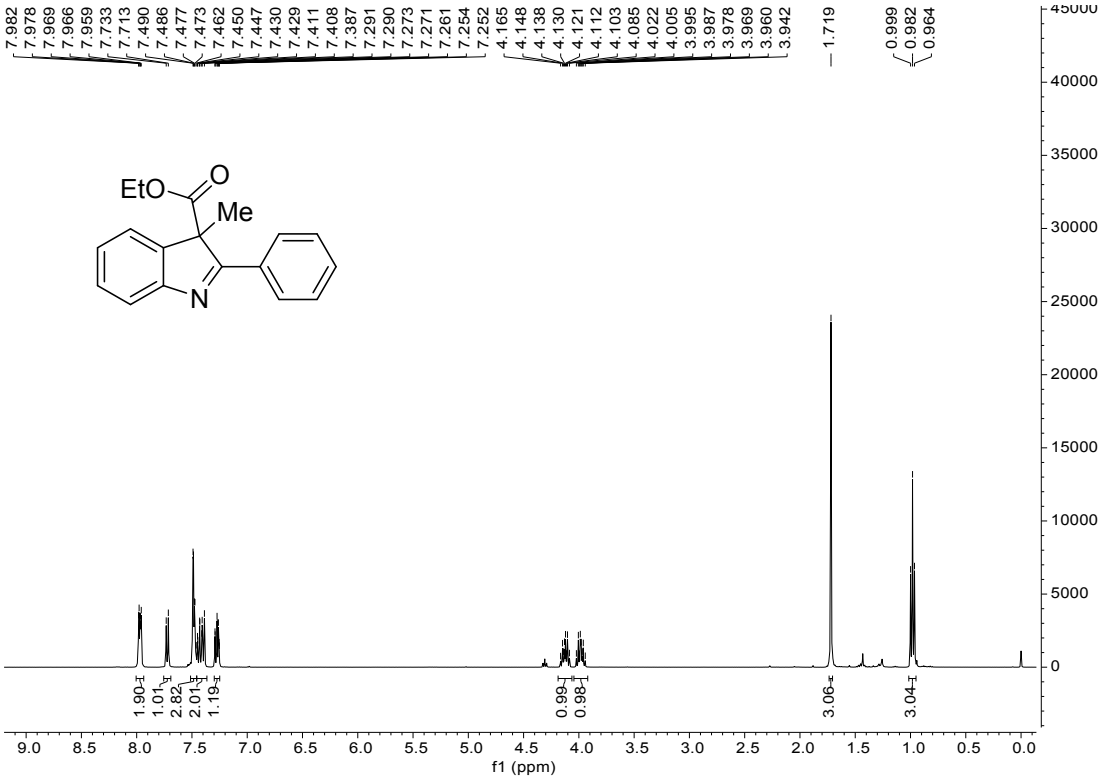


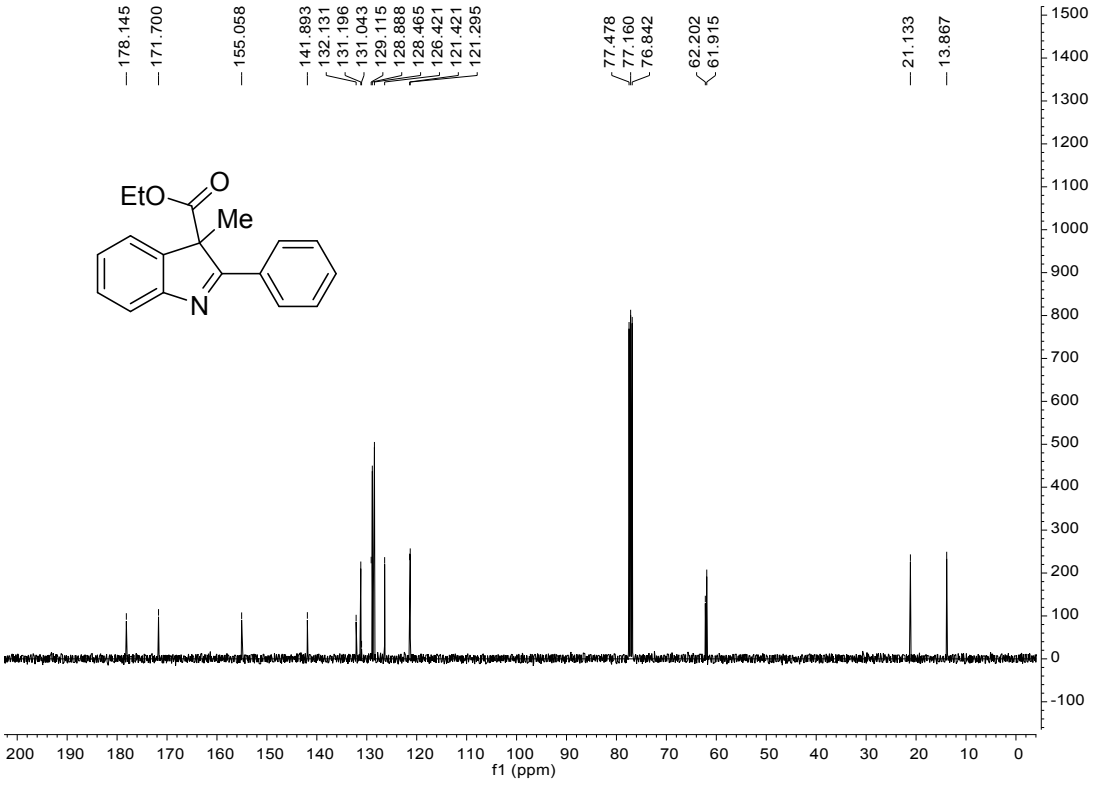
Ethyl 5-methoxy-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-1)



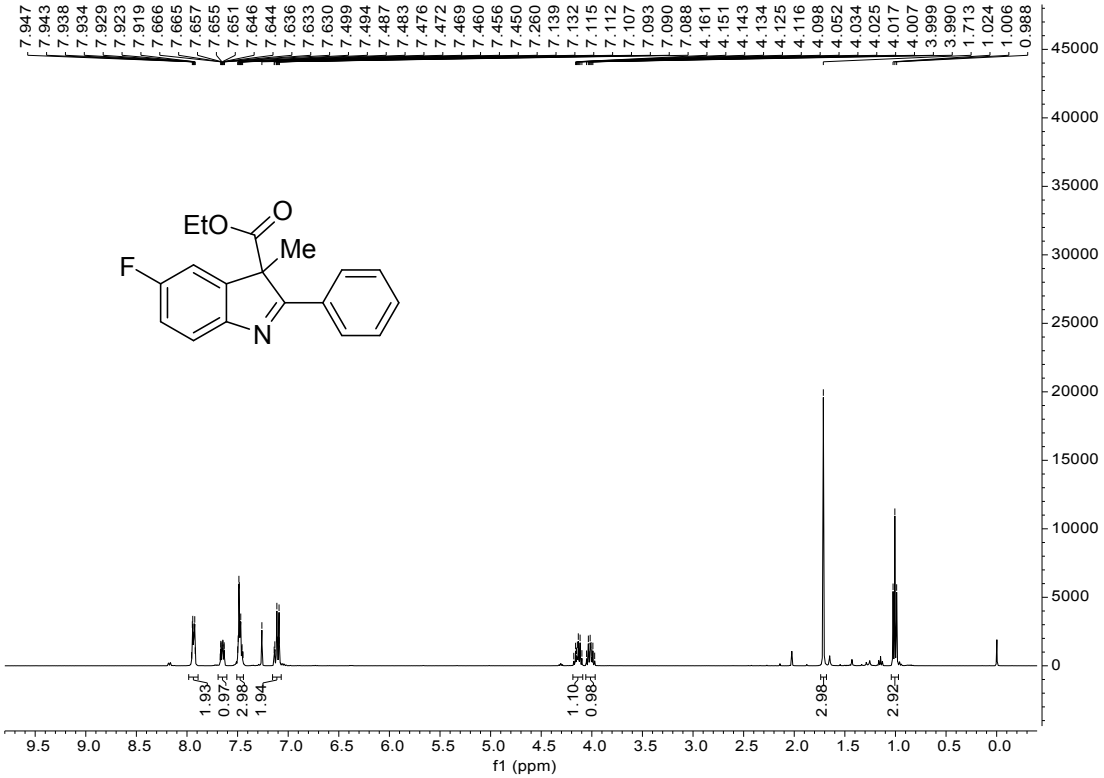


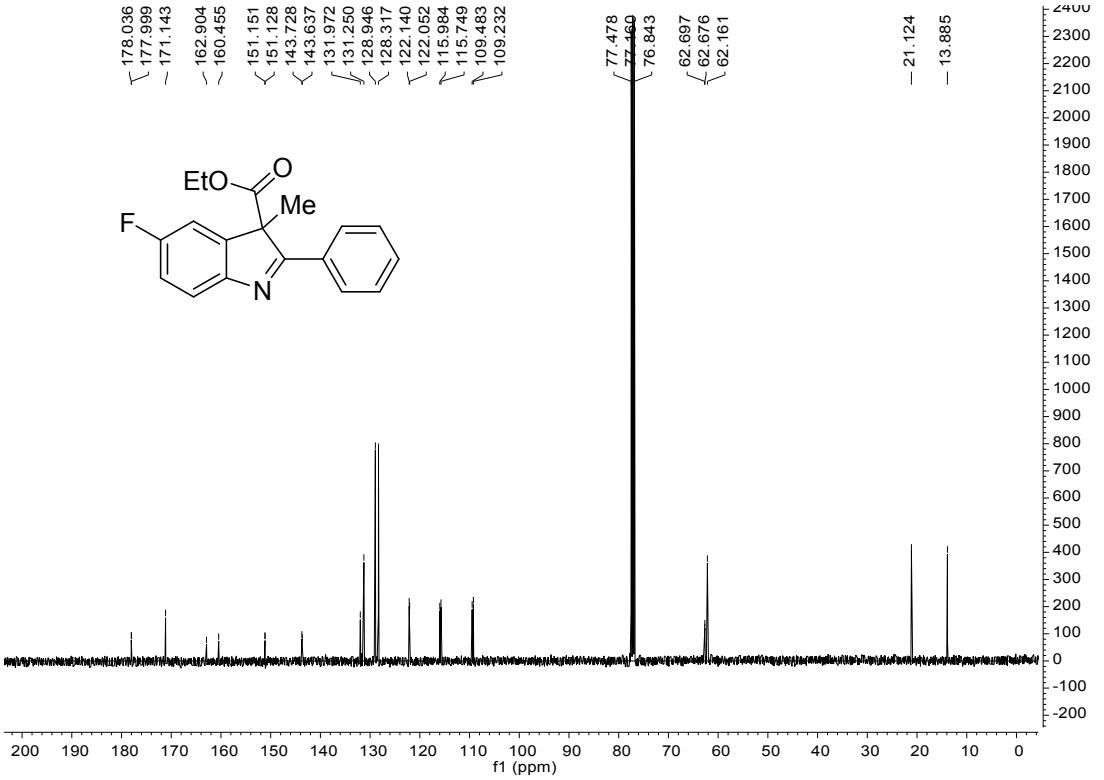
Ethyl 3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-2)

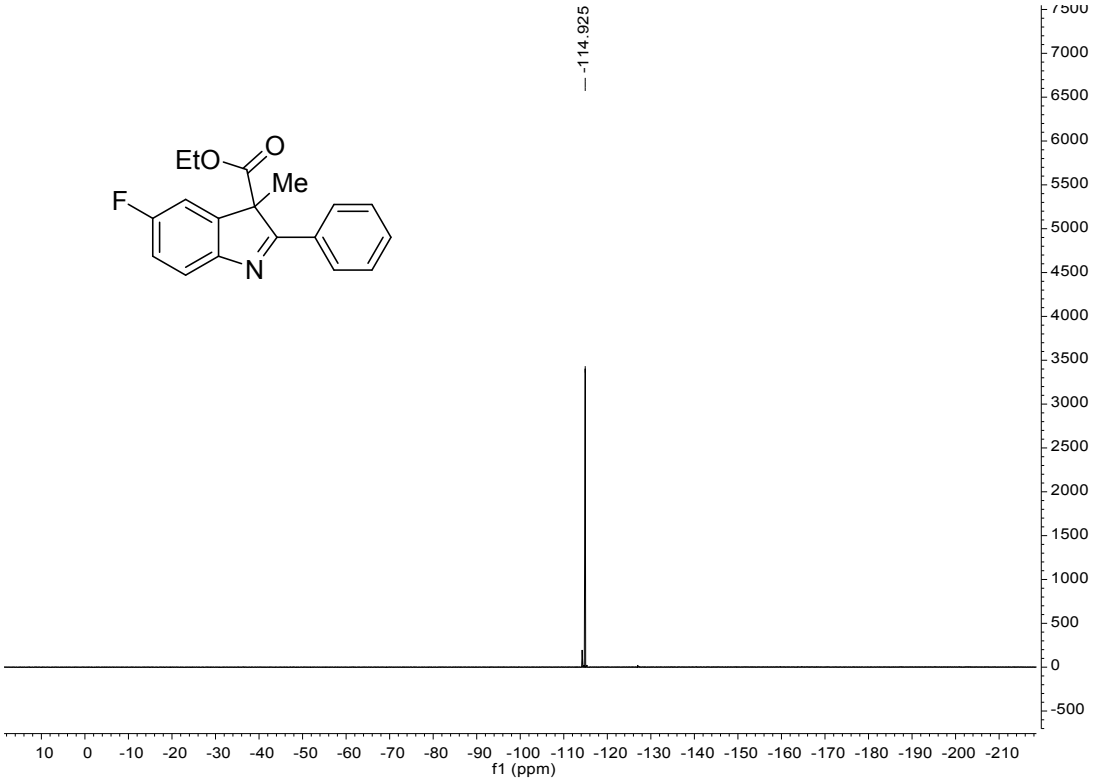




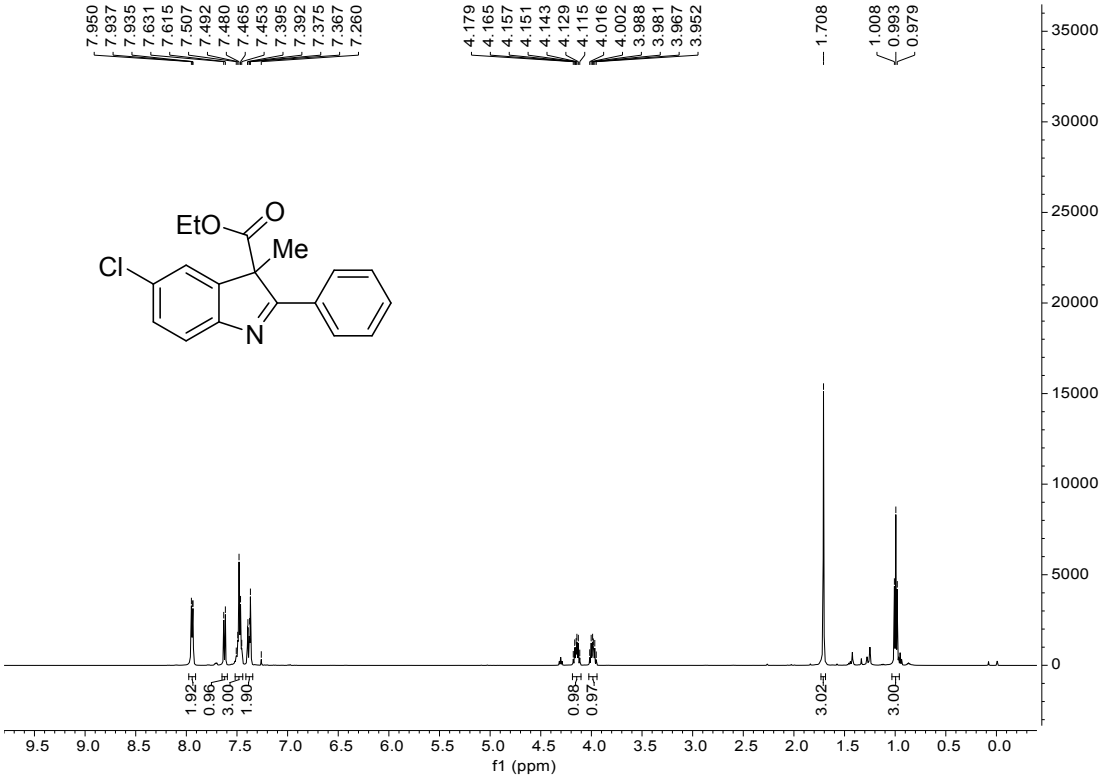
Ethyl 5-fluoro-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-3)

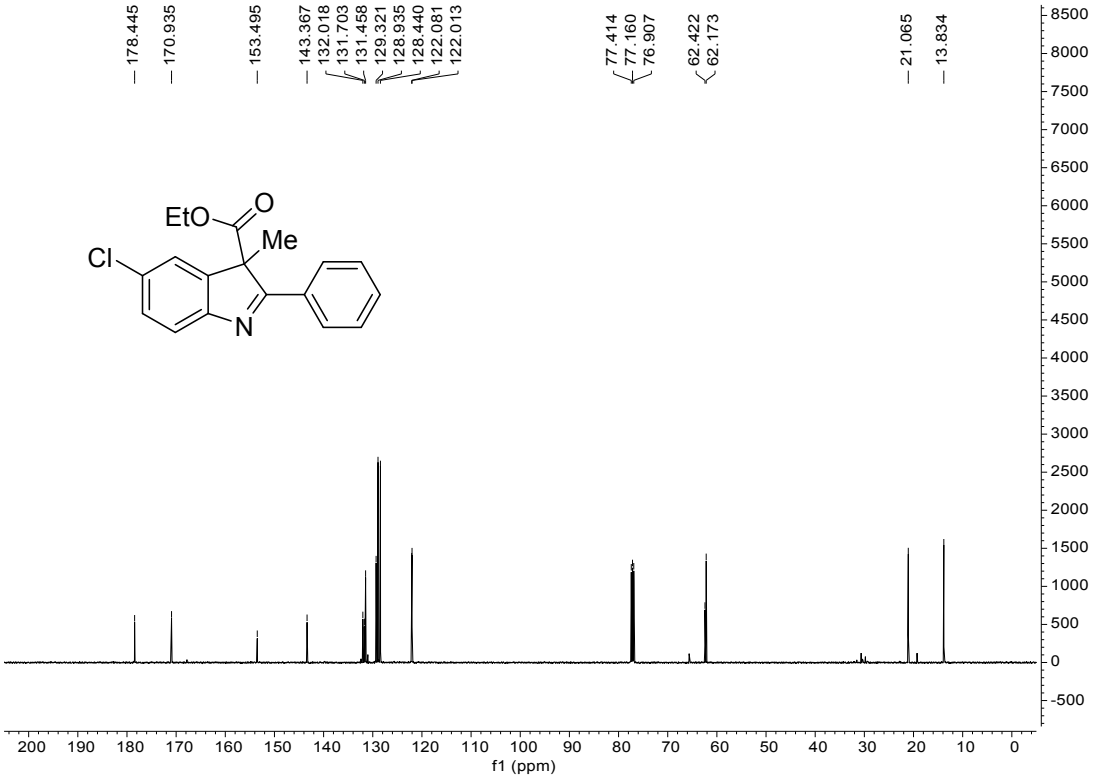




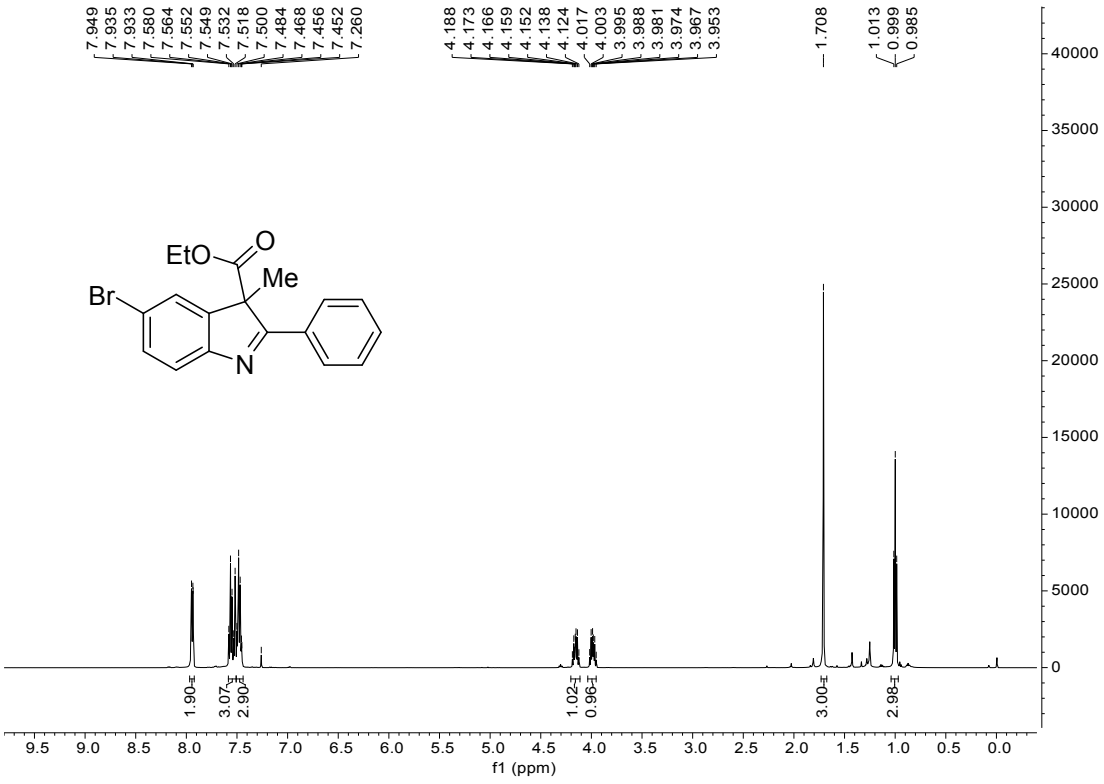


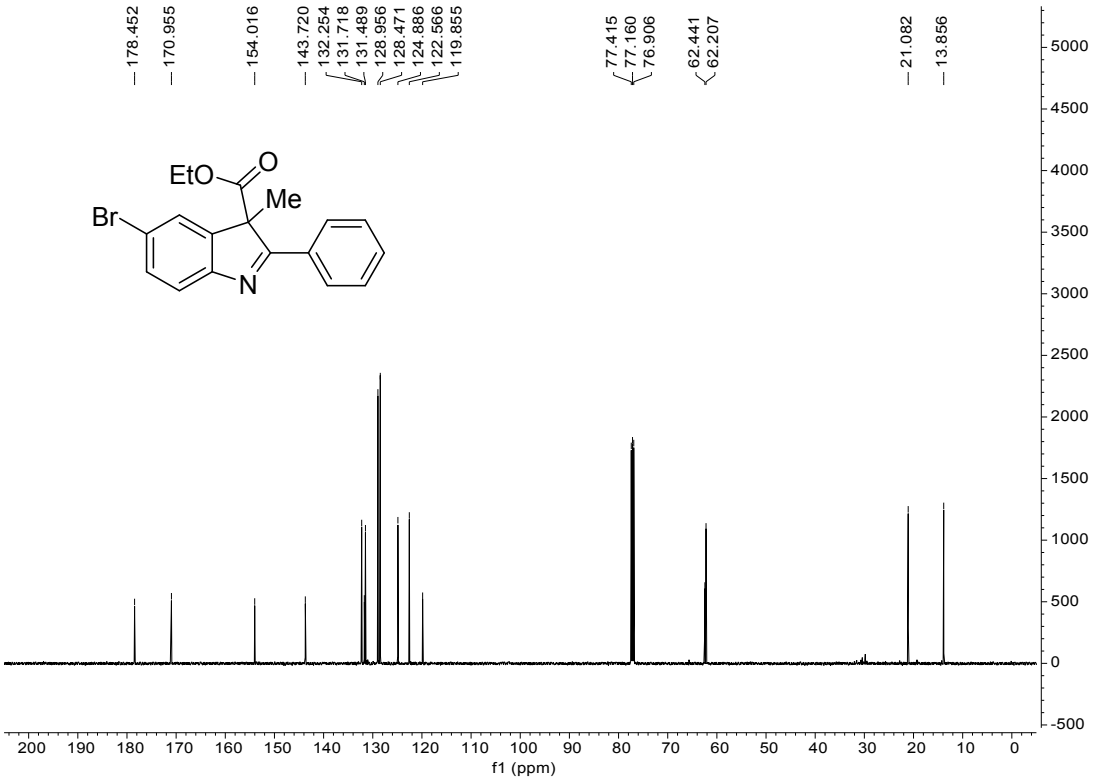
Ethyl 5-chloro-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-4)



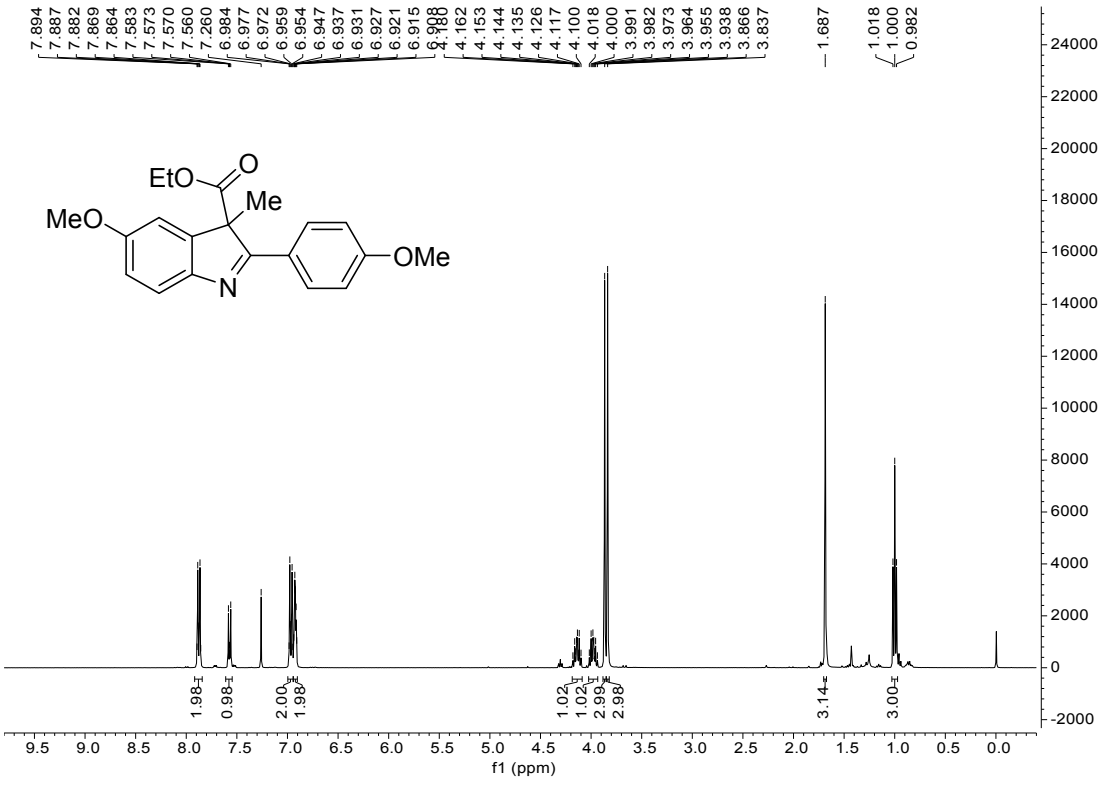


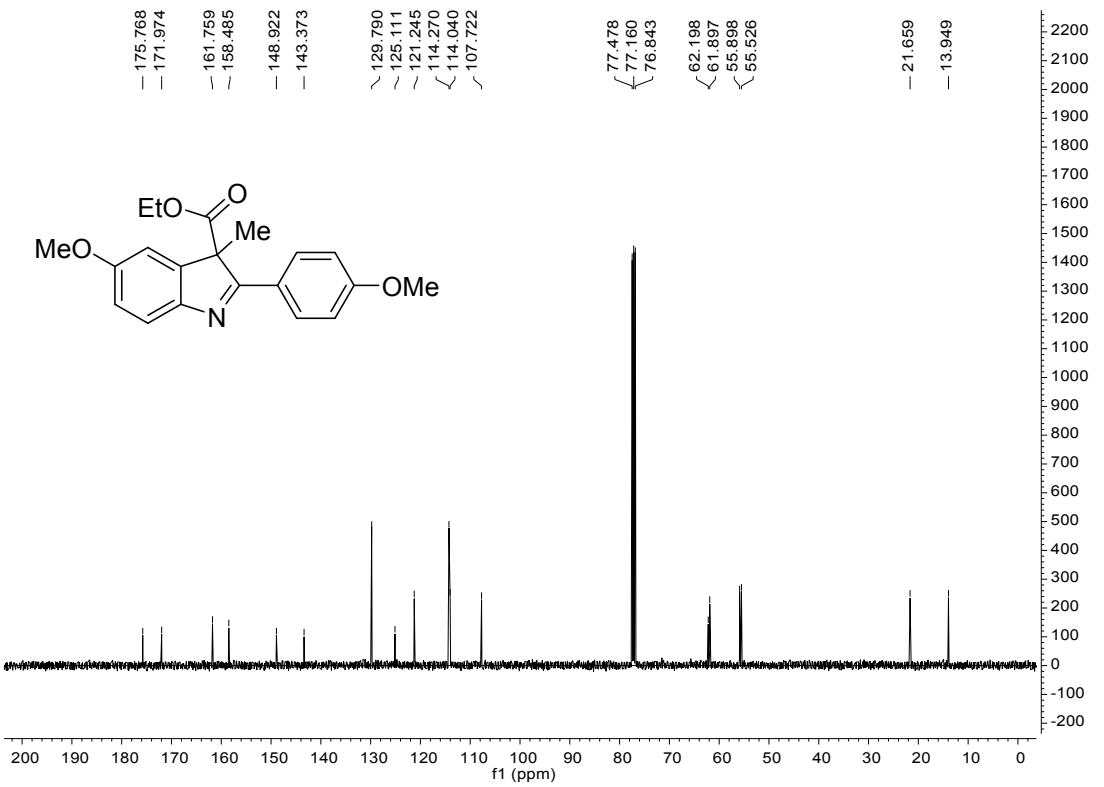
Ethyl 5-bromo-3-methyl-2-phenyl-3*H*-indole-3-carboxylate (5-5)



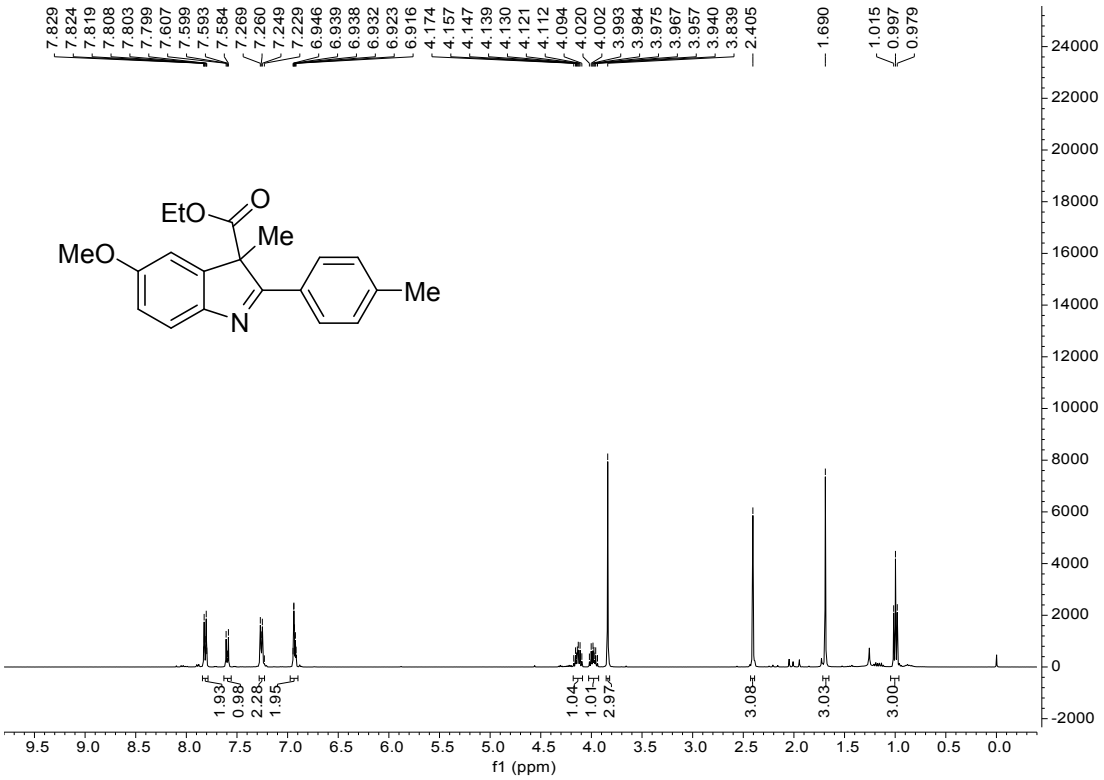


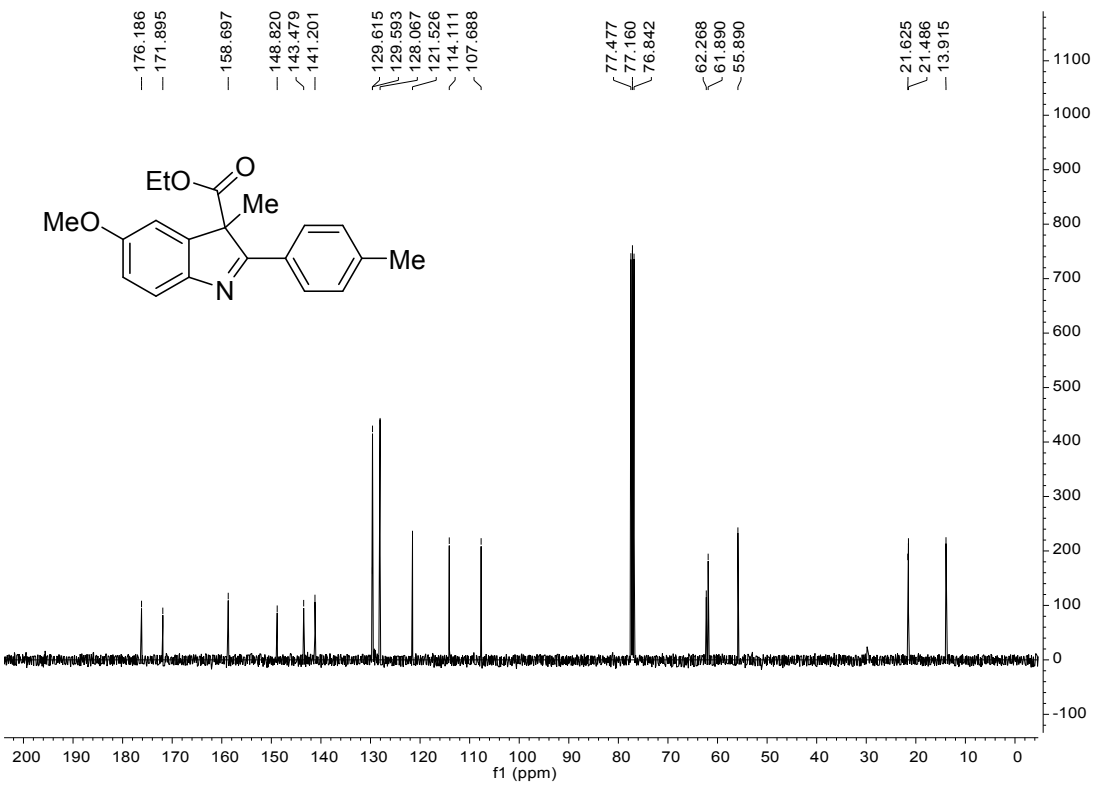
Ethyl 5-methoxy-2-(4-methoxyphenyl)-3-methyl-3*H*-indole-3-carboxylate (5-6)



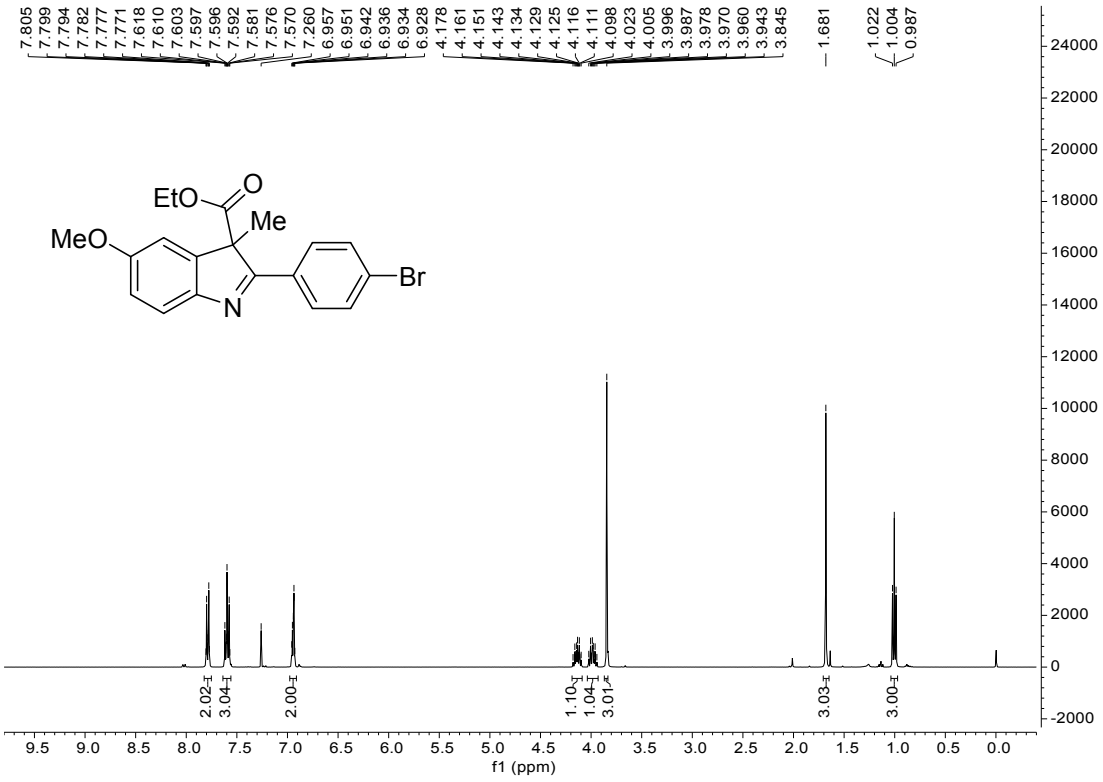


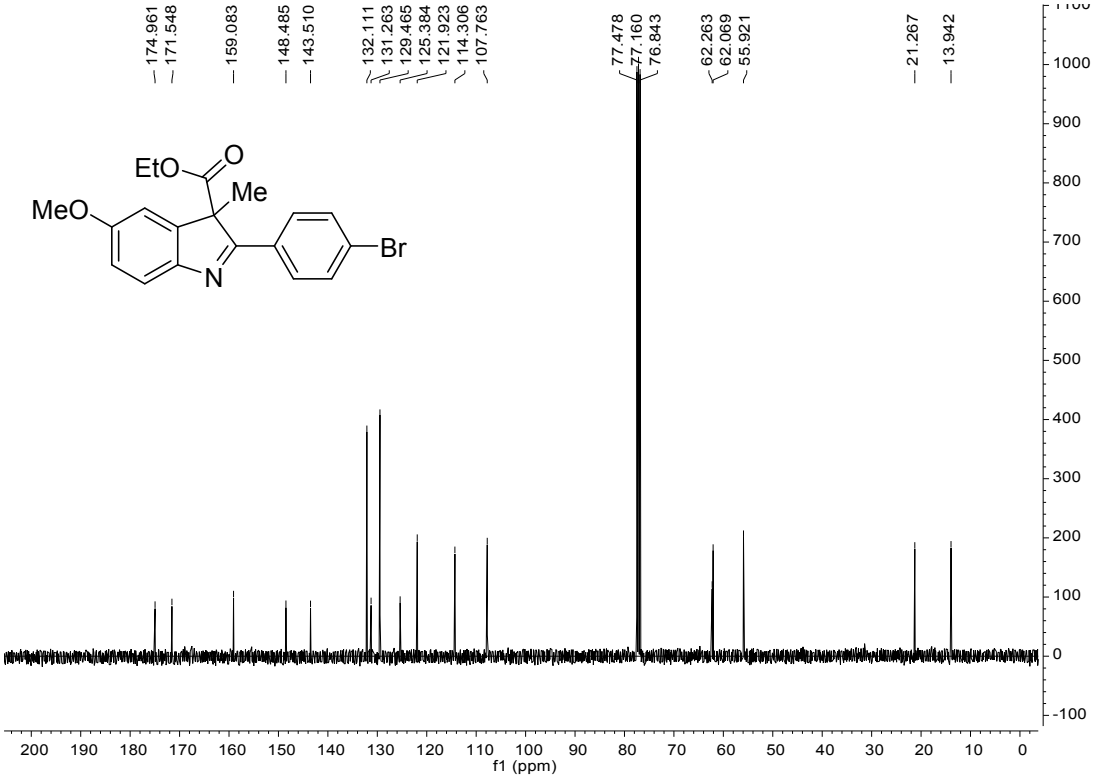
Ethyl 5-methoxy-3-methyl-2-(*p*-tolyl)-3*H*-indole-3-carboxylate (5-7)



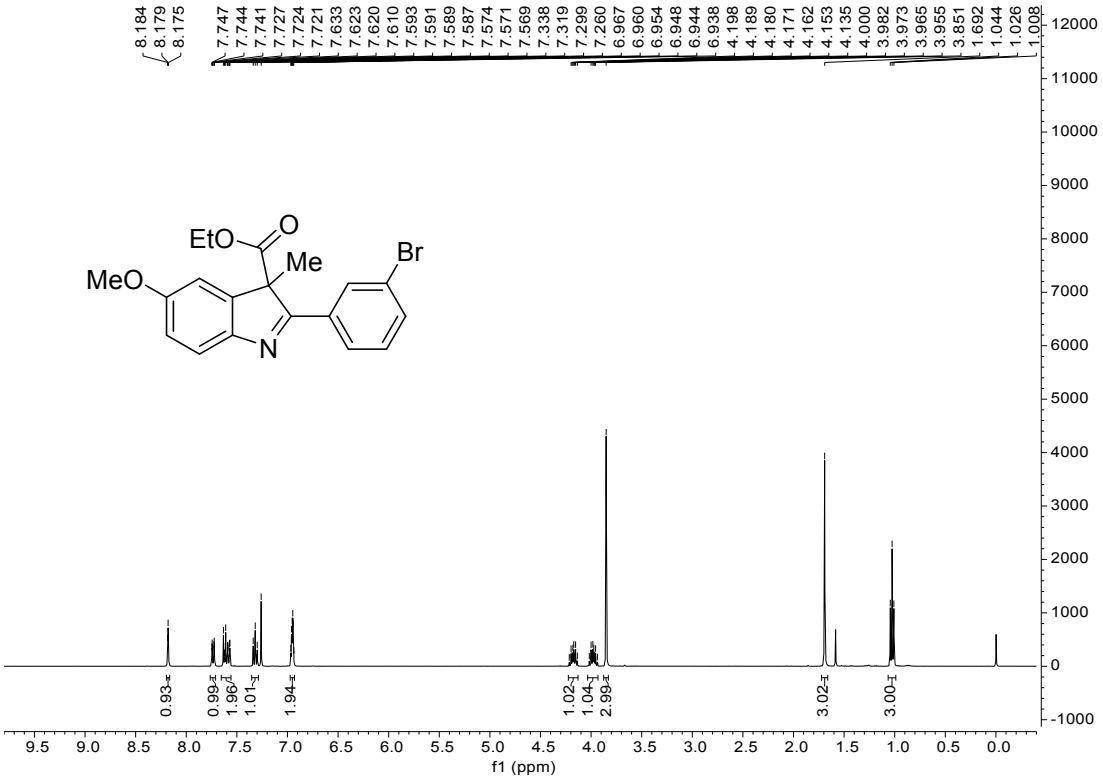


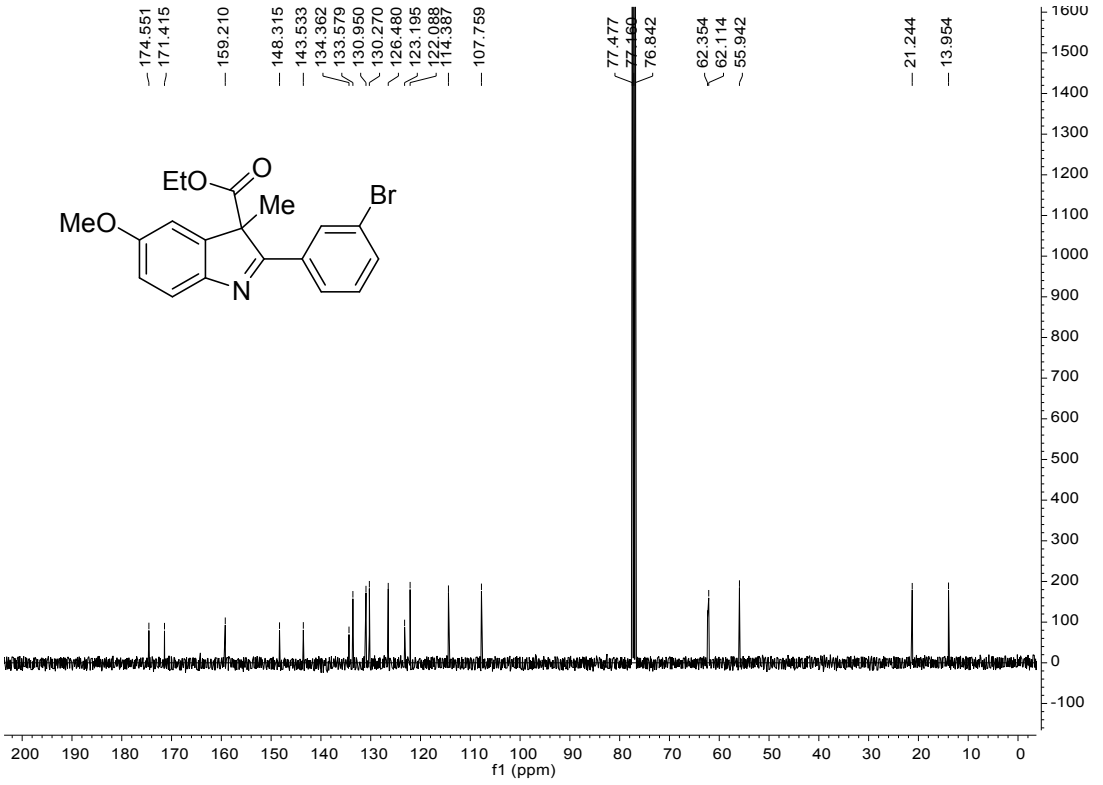
Ethyl 2-(4-bromophenyl)-5-methoxy-3-methyl-3*H*-indole-3-carboxylate (5-8)



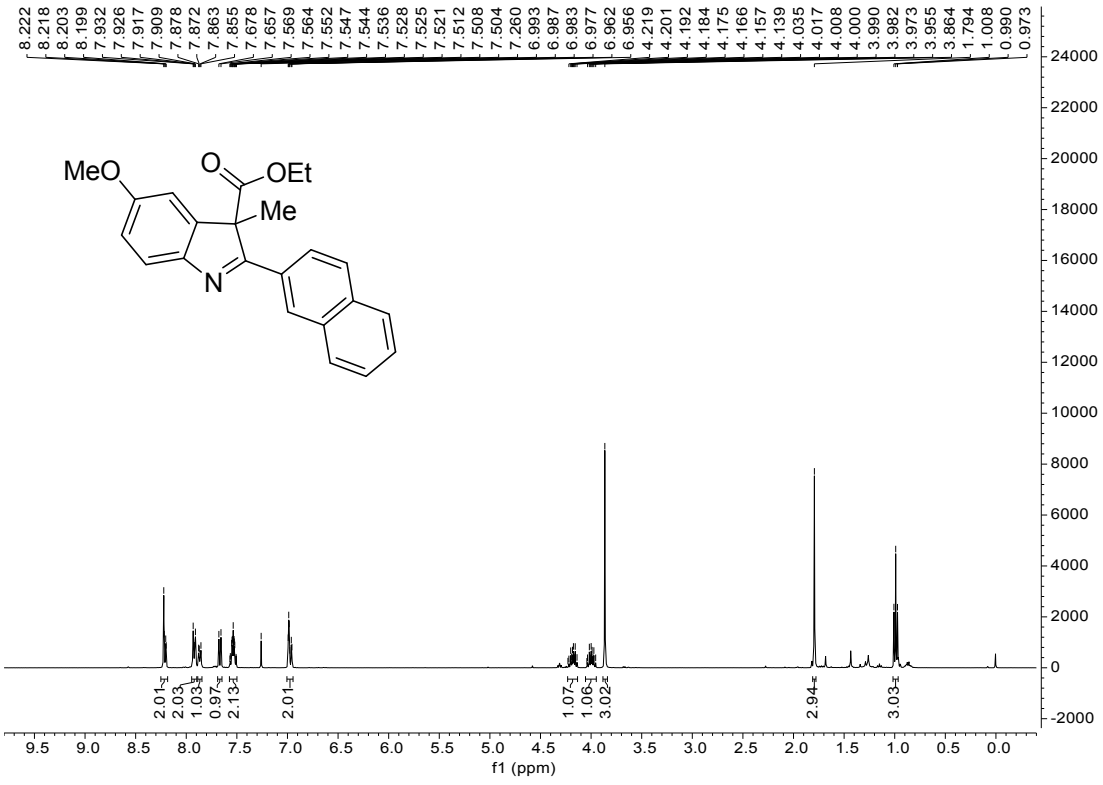


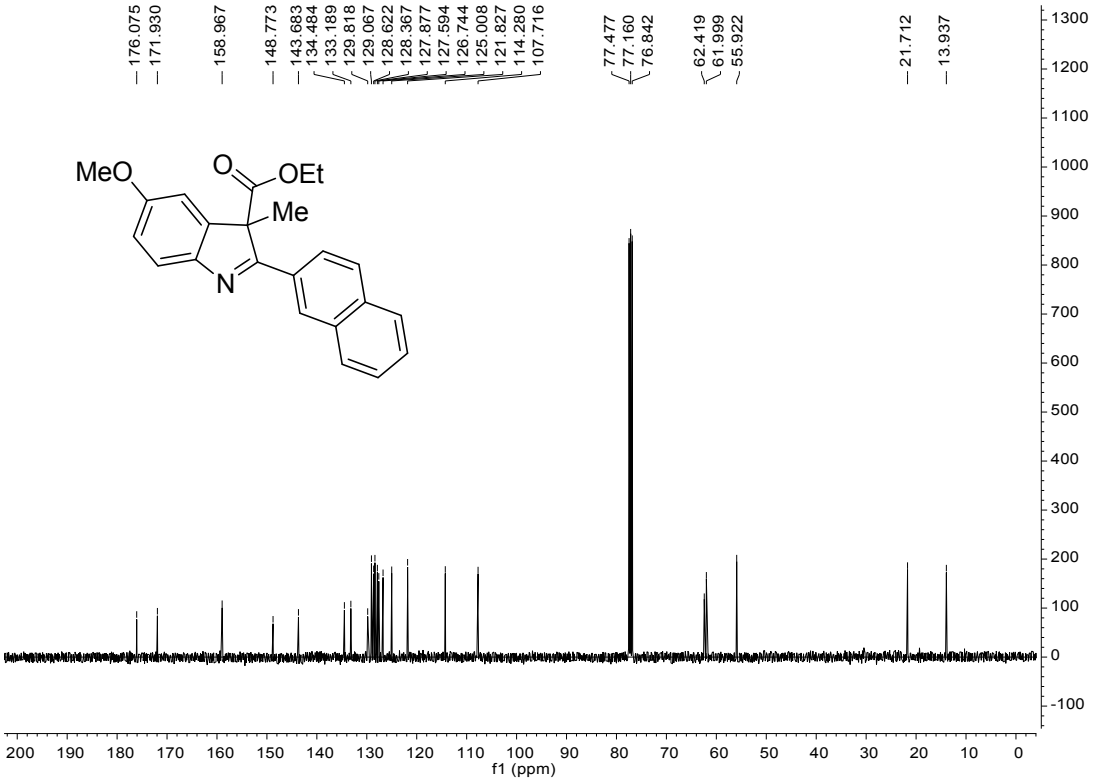
Ethyl 2-(3-bromophenyl)-5-methoxy-3-methyl-3*H*-indole-3-carboxylate (5-9)



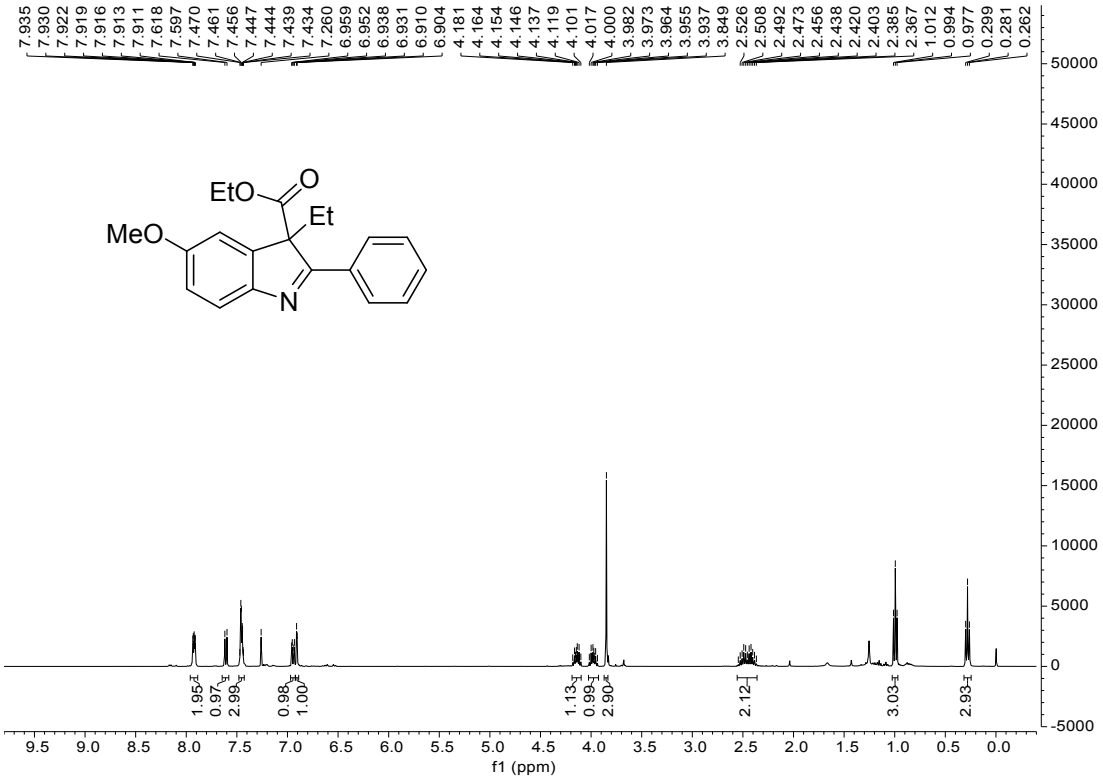


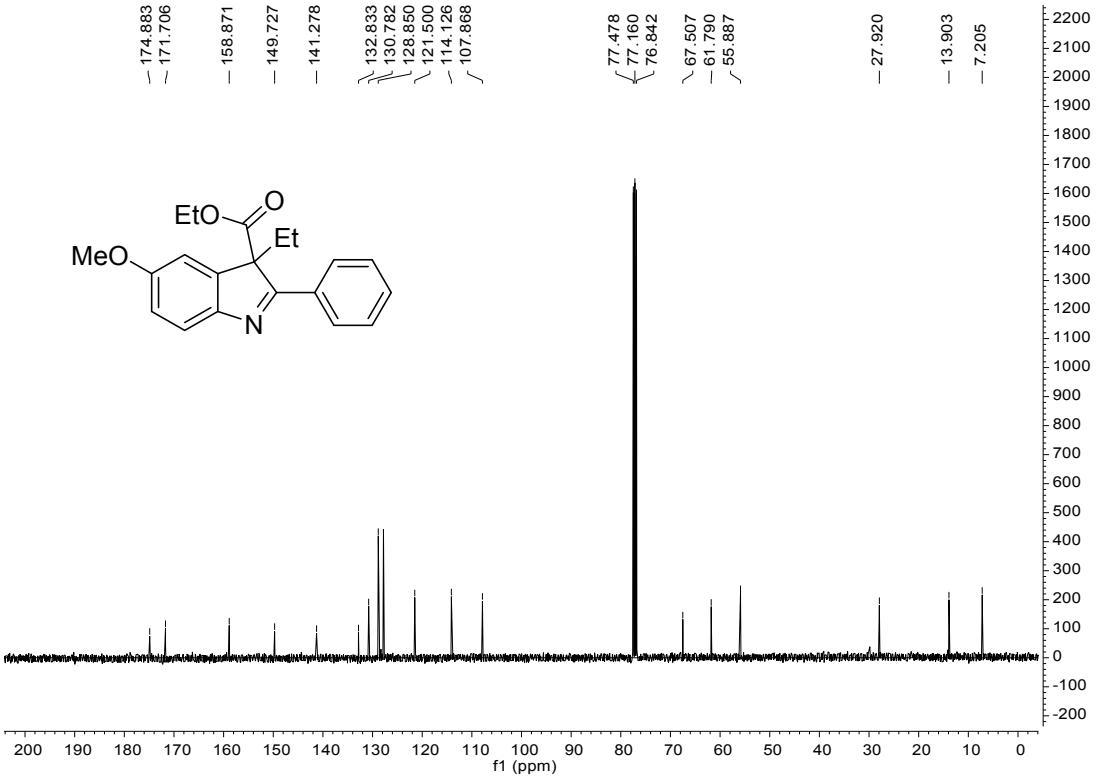
Ethyl 5-methoxy-3-methyl-2-(naphthalen-2-yl)-3*H*-indole-3-carboxylate (5-10)



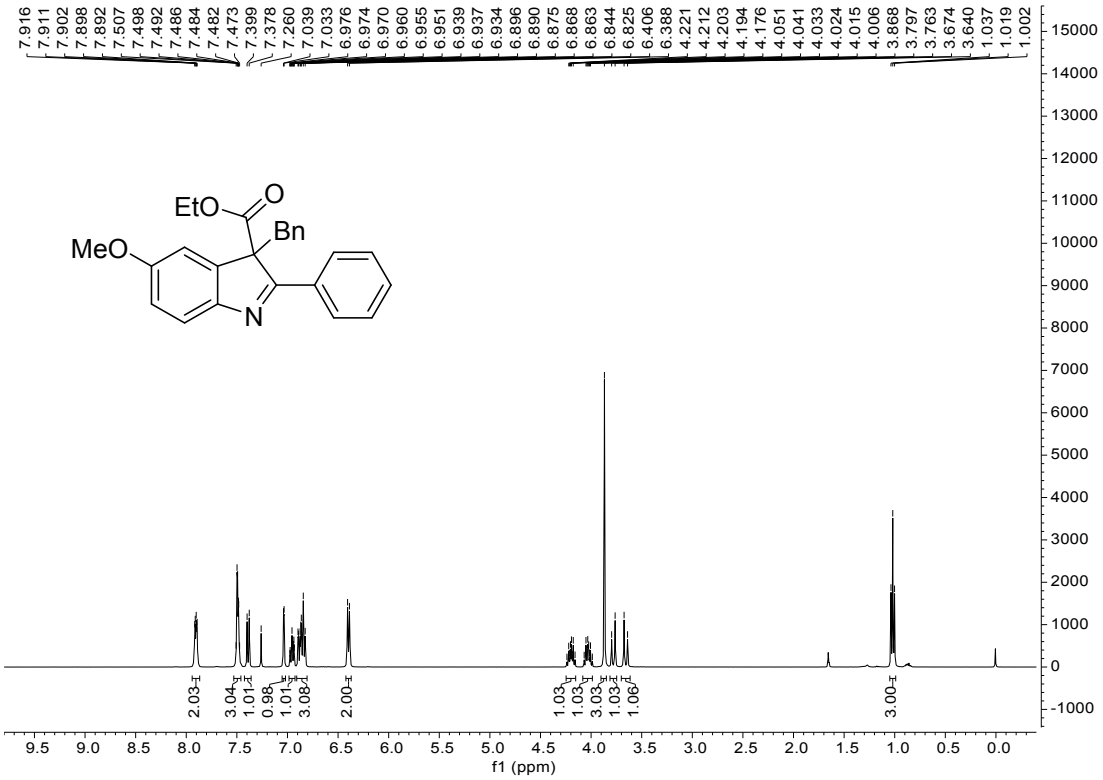


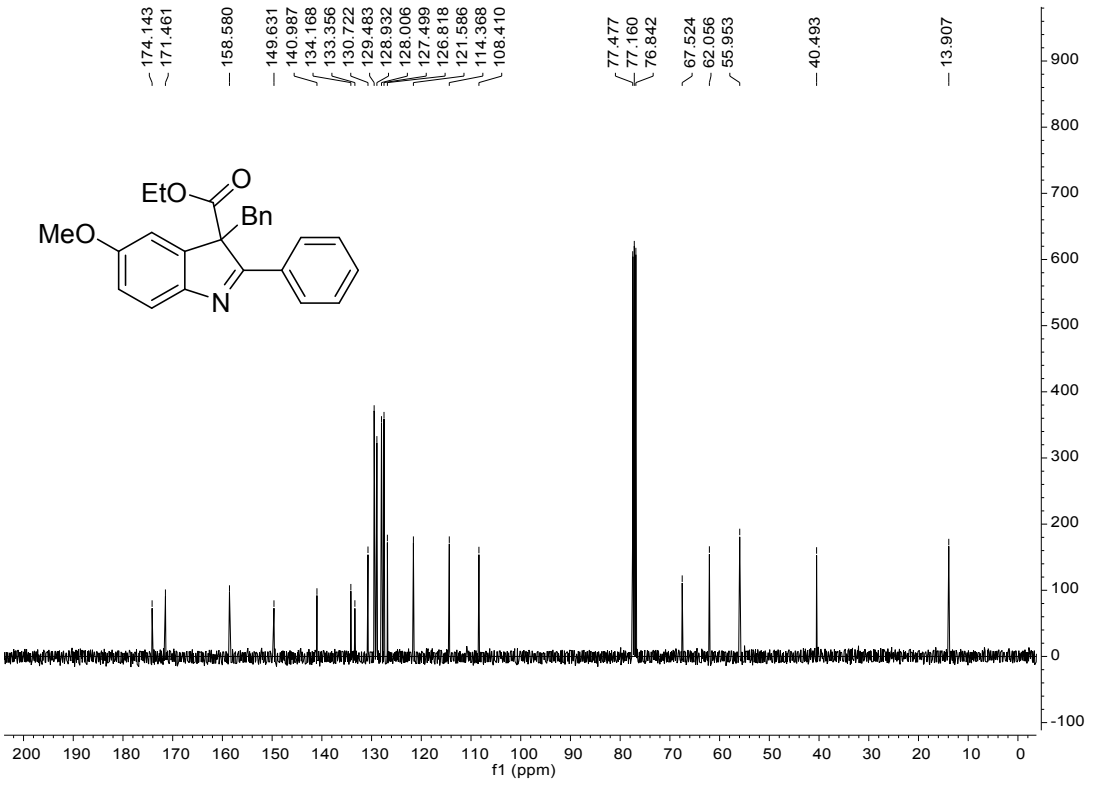
Ethyl 3-ethyl-5-methoxy-2-phenyl-3*H*-indole-3-carboxylate (5-11)



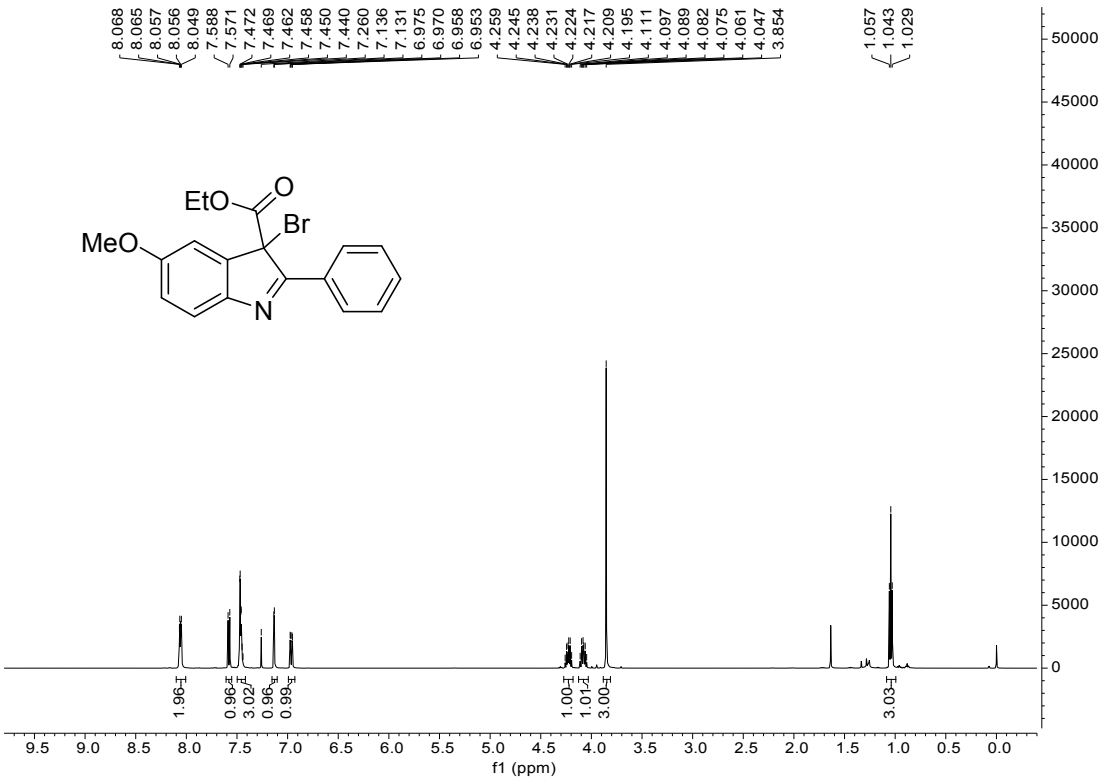


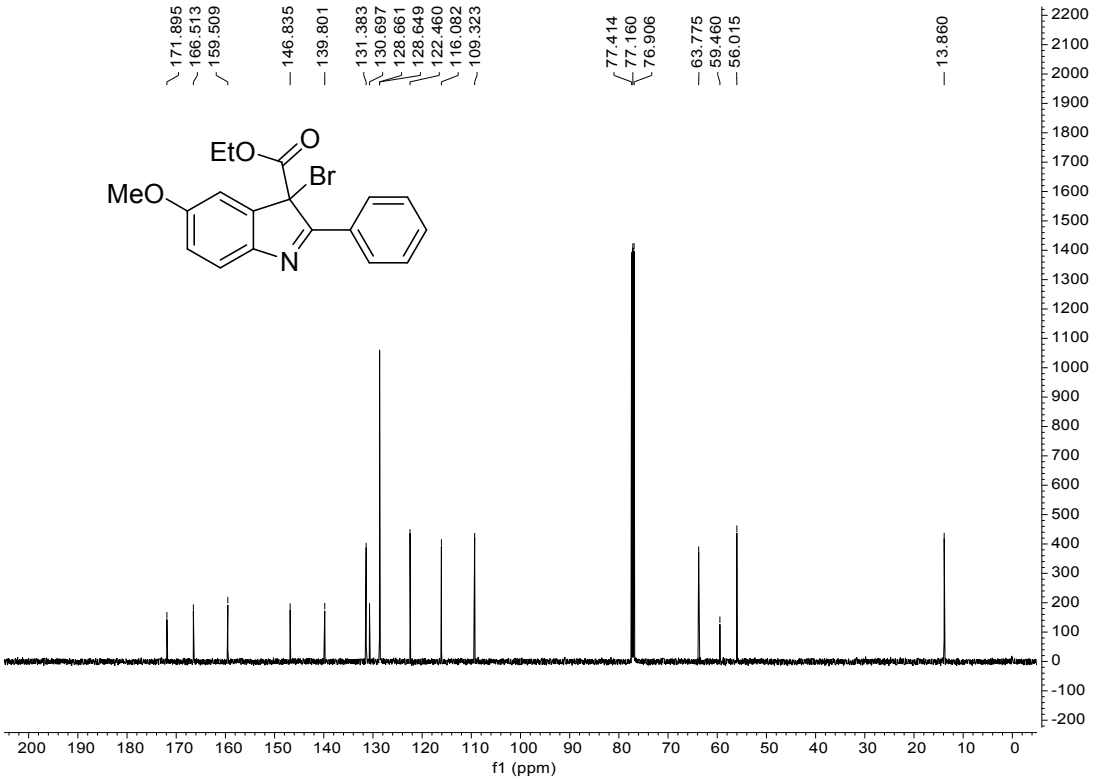
Ethyl 3-benzyl-5-methoxy-2-phenyl-3*H*-indole-3-carboxylate (5-12)





Ethyl 3-bromo-5-methoxy-2-phenyl-3*H*-indole-3-carboxylate (9)

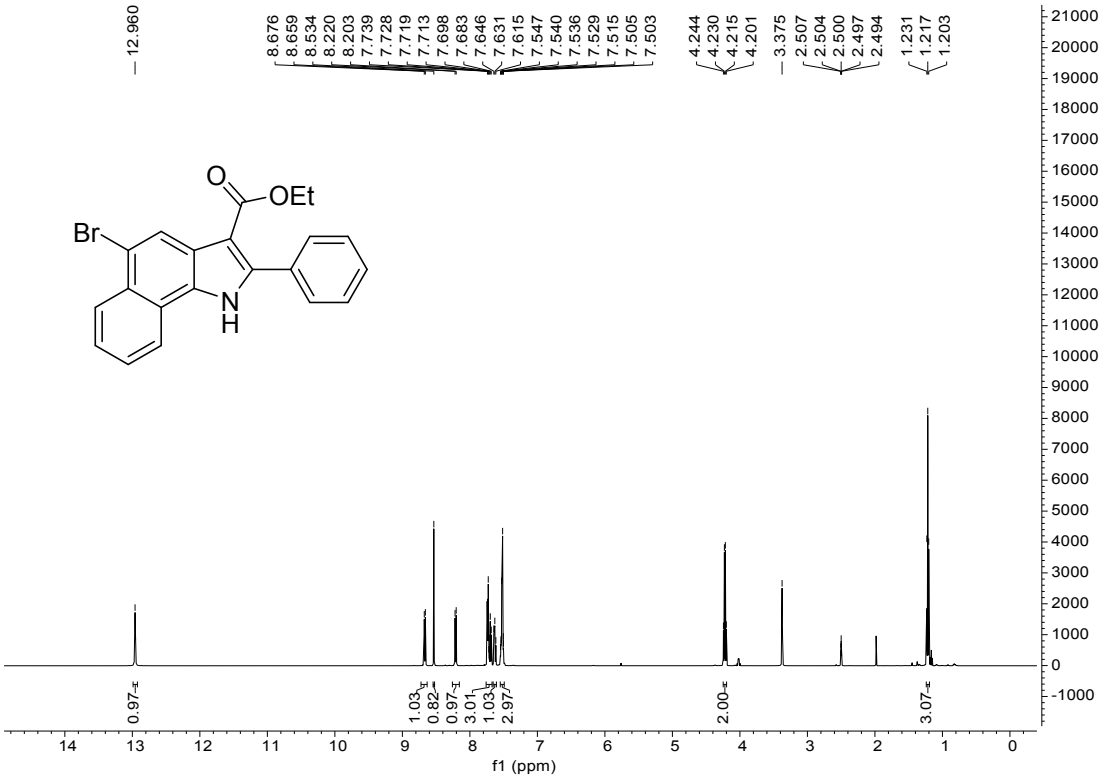


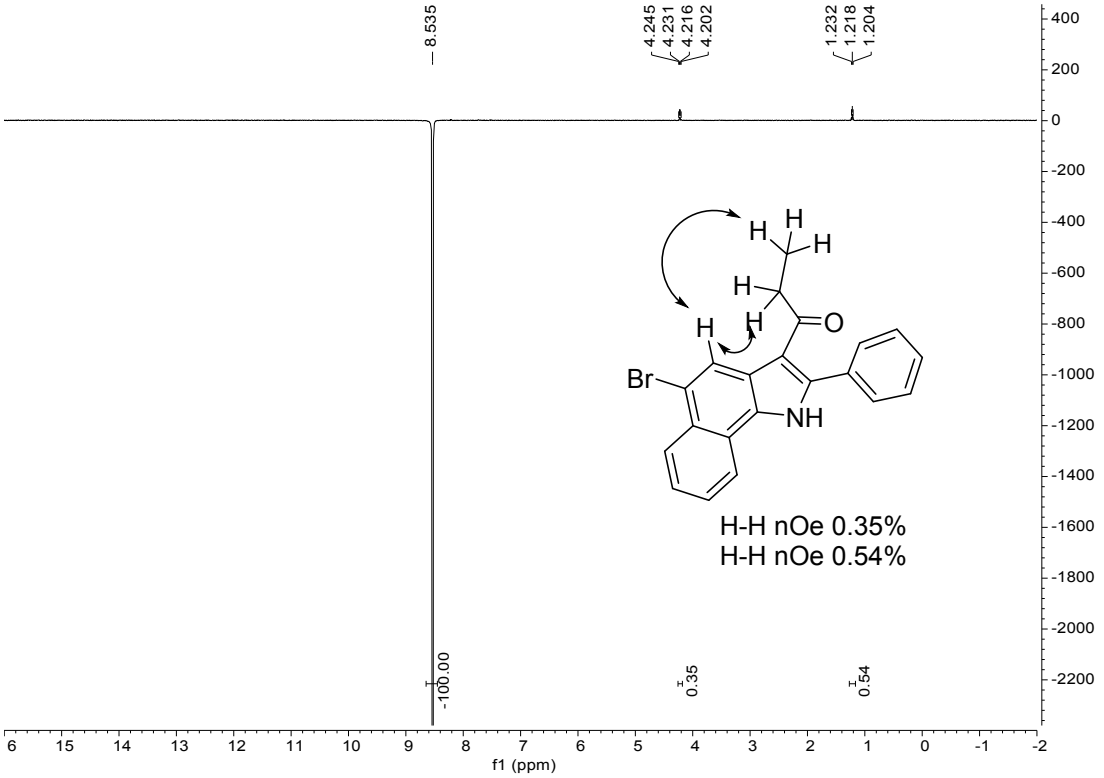

171.895
166.513
159.509
146.835
139.801
131.383
130.697
128.661
128.649
122.460
116.082
109.323
77.414
77.160
76.906
63.775
59.460
56.015
13.860
EtO
O
Br
MeO
N
f1 (ppm)

4. ^{1}H-^{1}H NOESY experiments (3-17 and 3-32)

NOESY experiment of **3-17**

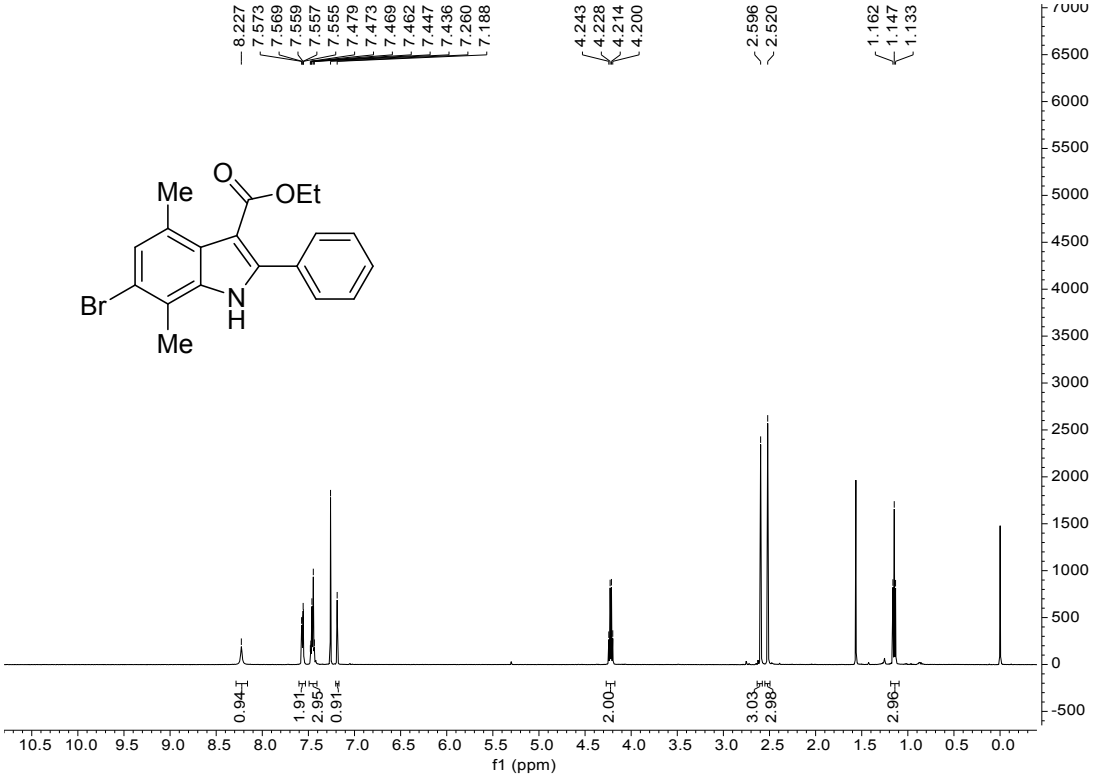
Ethyl 5-bromo-2-phenyl-1*H*-benzo[g]indole-3-carboxylate (3-17)

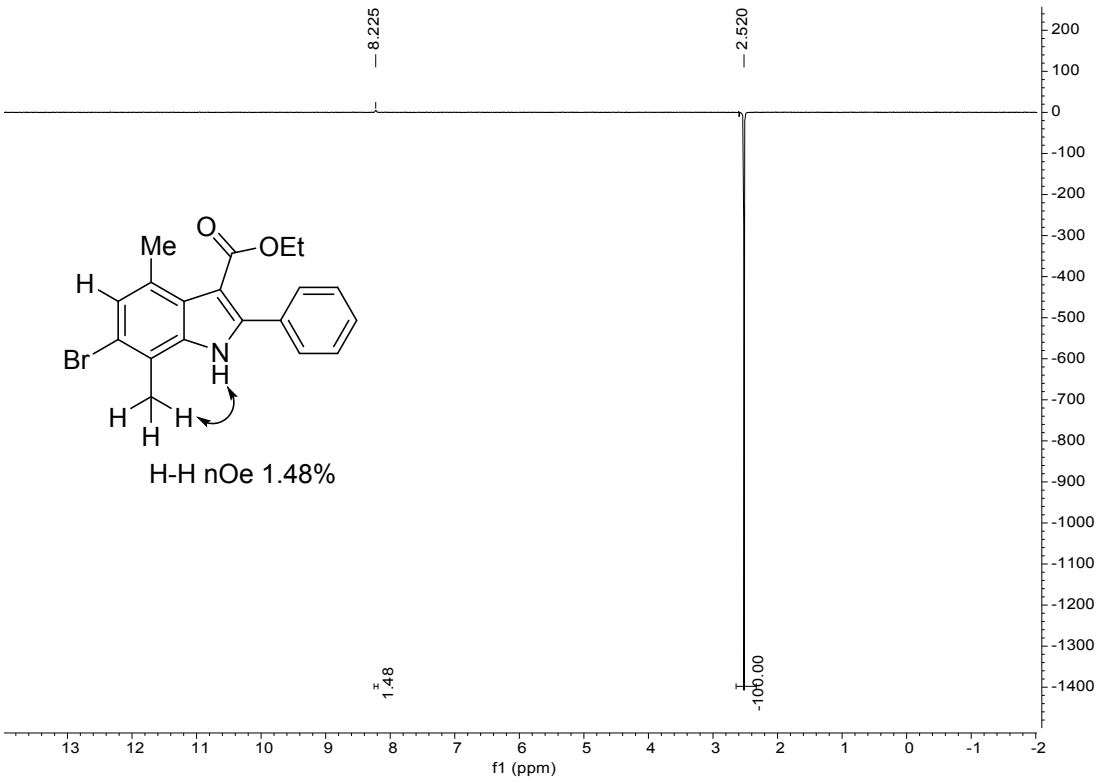


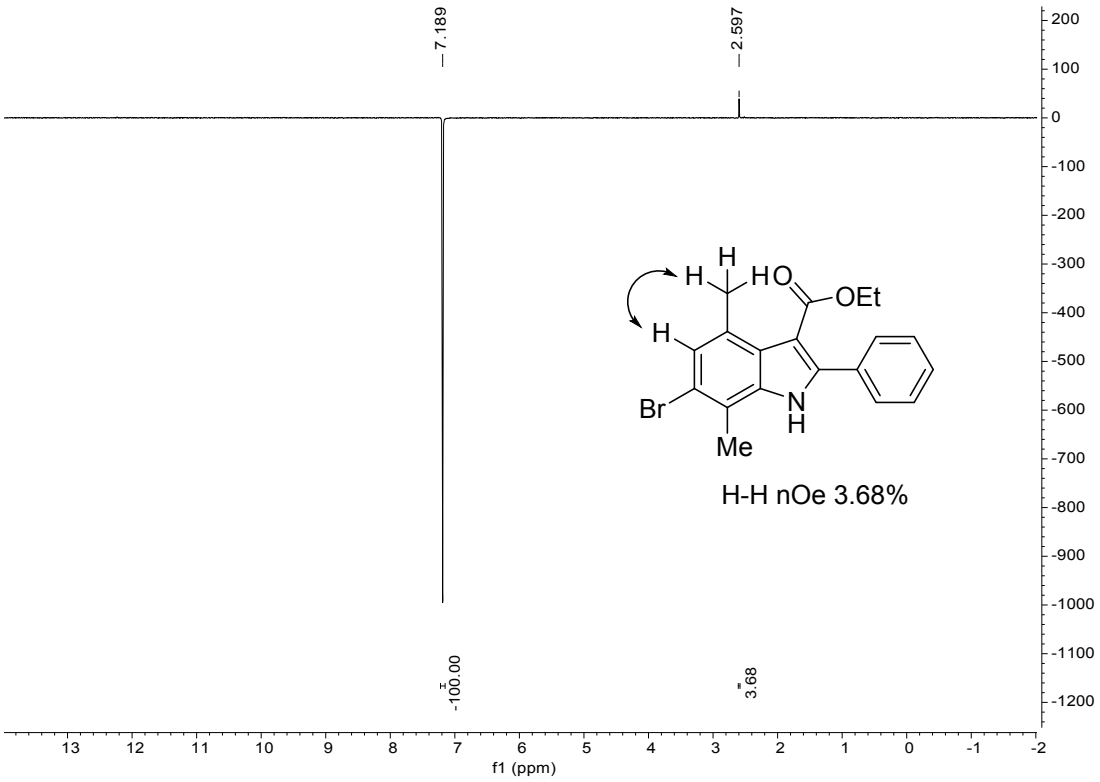


NOESY experiment of **3-32**

Ethyl 6-bromo-4,7-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (3-32)



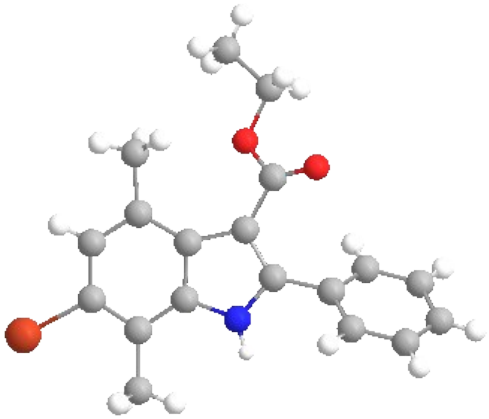




5. X-ray structure of 3-32 (CCDC 2085362)

The structure of **3-32** was further determined by single crystal X-ray analysis. (CCDC 2085362 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre).

X-ray structure of product 3-32 (ellipsoid contour at 50% probability)



Experimental

Single crystals of **3-32** ($C_{19}H_{18}BrNO_2$) were grown by slow evaporation in ethyl acetate/

acetonitrile = 5/2 under air atmosphere. A suitable crystal was selected and mounted on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 160(10) K during data collection. Using Olex2, the structure was solved with the Shelxs structure solution program using Direct Methods.

Crystal structure determination of 3-32

Crystal Data for **3-32** ($C_{19}H_{18}BrNO_2$), MW = 374.23, P21/n, Cell: a = 12.178Å, b = 7.563Å, c = 17.663Å, α = 90°, β = 90.5451(16)°, γ = 90°, V = 1626.75(5) Å^3, T = 160(10) K, Z = 4, *Dcalc* = 1.520g/cm^3.

Table 1. Crystal data and structure refinement for 3-32

Bond precision:	C-C = 0.0064 A		Wavelength=1.54184
Cell:	a=12.1783(2)	b=7.56305(18)	c=17.6627(3)
	alpha=90	beta=90.5451(16)	gamma=90
Temperature:	160 K		
	Calculated		Reported
Volume	1626.75(5)		1626.75(6)
Space group	P 21/c		P 1 21/c 1
Hall group	-P 2ybc		-P 2ybc
Moiety formula	C19 H18 Br N O2		C19 H18 Br N O2
Sum formula	C19 H18 Br N O2		C19 H18 Br N O2
Mr	372.24		372.25
Dx,g cm-3	1.520		1.520
Z	4		4
Mu (mm-1)	3.516		3.516
F000	760.0		760.0
F000'	759.10		
h,k,lmax	15,9,22		15,9,22
Nref	3417		3234
Tmin,Tmax	0.881,0.900		0.588,1.000
Tmin'	0.839		
Correction method= # Reported T Limits: Tmin=0.588 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.946			Theta(max)= 76.360
R(reflections)= 0.0641(2463)			wR2(reflections)= 0.1987(3234)
S = 1.098			Npar= 211