

Supporting Information for

Regioselective C5–H Direct Iodination of Indoles

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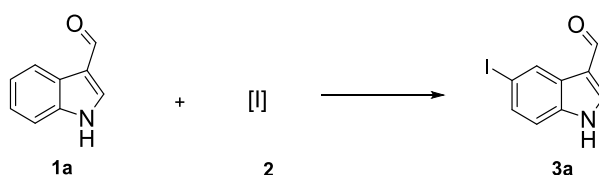
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1. General information

All reactions were carried out under air. All reagents were used as received unless otherwise noted. Flash chromatography was performed with silica gel (200-300 mesh). NMR spectra were recorded on a Bruker Ascend 400 spectrometer at 400 MHz (^1H NMR), 101 MHz (^{13}C NMR), on a JEOL ECZ400R spectrometer at 101 MHz (^{13}C NMR). ^1H NMR chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. ^1H NMR spectra was recorded with CDCl_3 (TMS, $\delta = 0.00$ ppm) or DMSO-d_6 ($\delta = 2.50$ ppm) as internal reference; ^{13}C NMR spectra was recorded with CDCl_3 ($\delta = 77.1$ ppm) or DMSO-d_6 ($\delta = 39.6$ ppm) as internal reference. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br. s = broad singlet. Most of reagents bought from Adamas-beta. Infrared (IR) data were acquired on a Bruker Invenio-R FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a Bruker Daltonics S2 MicroTof-Q II mass spectrometer. X-ray crystal structure analyses were measured on Bruker Smart APEXIICCD instrument using Mo-K α radiation. The structures were solved and refined using the SHELXTL software package.

2. Optimization of conditions for the synthesis of

5-iodo-1H-indole-3-carbaldehyde



entry	Iodine source	Acid (equiv.)	Solvent	Temp. ($^{\circ}\text{C}$)	Yield (%) ^[b]
1 ^[c]	NIS	TFA	DCM	60	33
2	NIS	TFA	DCM	60	33

3	NIS	-	DCM	60	Trace
4	NIS	TfOH	DCM	60	61
5	NIS	HCl	DCM	60	25
6	NIS	AcOH	DCM	60	19
7	NIS	H ₂ SO ₄	DCM	60	21
8	NIS	BF ₃ ·Et ₂ O	DCM	60	63
9	NIS	FeCl ₃	DCM	60	Trace
10	NIS	AlCl ₃	DCM	60	Trace
11	NIS	SnCl ₄	DCM	60	Trace
12	I ₂	BF ₃ ·Et ₂ O	DCM	60	0
13	KI	BF ₃ ·Et ₂ O	DCM	60	0
14	IOAc	BF ₃ ·Et ₂ O	DCM	60	0
15	NIS	BF ₃ ·Et ₂ O	DCE	60	57
16	NIS	BF ₃ ·Et ₂ O	CH ₃ Cl	60	51
17	NIS	BF ₃ ·Et ₂ O	CH ₃ CN	60	0
18	NIS	BF ₃ ·Et ₂ O	DMSO	60	0
19	NIS	BF ₃ ·Et ₂ O	DMF	60	0
20	NIS	BF ₃ ·Et ₂ O	DCM	40	61
21	NIS	BF ₃ ·Et ₂ O	DCM	r.t.	60
22	NIS	BF ₃ ·Et ₂ O	DCM	0	17
23	NIS	BF ₃ ·Et ₂ O (0.5)	DCM	r.t.	47
24	NIS	BF ₃ ·Et ₂ O (2)	DCM	r.t.	78
25	NIS	BF ₃ ·Et ₂ O (5)	DCM	r.t.	77

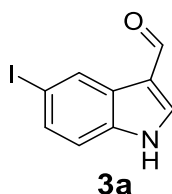
^[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), acid (0.5 mmol), solvent (3 mL) and at ambient temperature and under air for 4 h. ^[b]Isolated yields. ^[c]Pd(OAc)₂ (10 mol %) was added.

3. General procedure

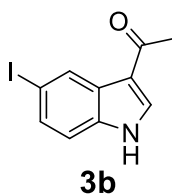
A 10 mL round-bottom flask was charged with indole derivatives (0.5 mmol), NIS (0.5 mmol) and

dichloromethane (3 mL). After $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.0 mmol) was added, and stirred at room temperature for 4 h under air. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4 , concentrated in vacuo and directly subjected for column chromatography to afford product.

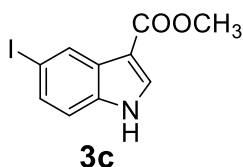
4. Characterization data for 3a-3ac



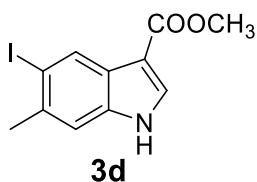
5-iodo-1H-indole-3-carbaldehyde:¹ 178.1 mg, 78% yield; White solid; m. p. = 185 – 186 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.27 (s, 1H), 9.92 (s, 1H), 8.44 (s, 1H), 8.29 (d, J = 3.1 Hz, 1H), 7.53 (dd, J = 8.5, 1.4 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 185.2, 138.9, 136.2, 131.6, 129.2, 126.7, 117.2, 115.0, 86.6; IR: 3239, 2924, 2804, 2749, 2360, 1650, 1435, 1386, 1285, 1232, 1124, 1088, 878, 789, 666, 608 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_6\text{INNaO}$ [$\text{M} + \text{Na}$]⁺: 293.9386; found 293.9385.



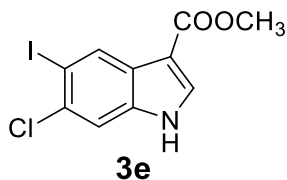
1-(5-iodo-1H-indol-3-yl)ethan-1-one:² 134.4 mg, 73% yield; White solid; m. p. = 133 – 134 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.08 (s, 1H), 8.52 (d, J = 1.6 Hz, 1H), 8.31 (s, 1H), 7.48 (dd, J = 8.5, 1.7 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 192.8, 135.8, 135.1, 130.8, 129.7, 127.8, 116.0, 114.6, 86.2, 27.2; IR: 3285, 2853, 2361, 1681, 1532, 1427, 1211, 1174, 1134, 1052, 880, 786, 737, 529 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_8\text{INNaO}$ [$\text{M} + \text{Na}$]⁺: 307.9543; found 307.9541.



methyl 5-iodo-1H-indole-3-carboxylate:³ 148.9 mg, 71% yield; Yellow solid; m. p. = 184 – 185 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 8.33 (s, 1H), 8.09 (s, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 164.5, 135.6, 133.4, 130.5, 128.8, 128.2, 115.0, 105.7, 85.9, 50.9; IR: 3273, 2923, 1680, 1446, 1357, 1194, 1177, 1057, 879, 767, 536 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_8\text{INNaO}_2$ [$\text{M} + \text{Na}$]⁺: 323.9492; found 323.9490.

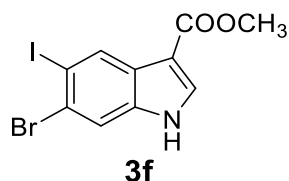


methyl 5-iodo-6-methyl-1H-indole-3-carboxylate: 120.9 mg, 74% yield; Yellow solid; m. p. = 194 – 195 °C; Eluant: ethyl acetate/petroleum ether (1:6, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 11.97 (s, 1H), 8.42 (s, 1H), 8.04 (d, J = 2.9 Hz, 1H), 7.47 (s, 1H), 3.80 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 140.0, 117.6, 115.2, 114.7, 112.2, 109.1, 98.8, 92.5, 82.8, 49.0, 30.7; IR: 3649, 2923, 2361, 1716, 1684, 1541, 1197, 1144, 1053, 810, 518, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{11}\text{INO}_2$ [$\text{M} + \text{H}$]⁺: 315.9829; found 315.9821.

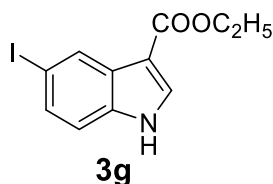


methyl 6-chloro-5-iodo-1H-indole-3-carboxylate: 130.8 mg, 69% yield; Yellow solid; m. p. = 198 – 199 °C; Eluant: ethyl acetate/petroleum ether (1:4, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.14 (s, 1H), 8.50 (s, 1H), 8.15 (s, 1H), 7.73 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 139.7, 117.6, 115.7, 113.1, 112.6, 109.5, 98.7, 92.7, 78.0, 49.1; IR: 3246, 1673, 1508, 1449, 1194, 1171,

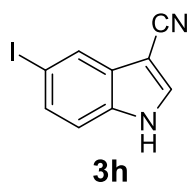
1054, 914, 771, 550, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_7\text{I}\text{Cl}\text{INaO}_2$ $[\text{M} + \text{Na}]^+$: 357.9102; found 357.9102.



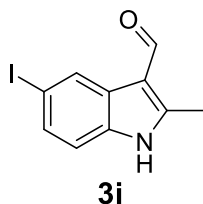
methyl 6-bromo-5-iodo-1H-indole-3-carboxylate: ³ 115.9 mg, 63% yield; Yellow solid; m. p. = 205 – 206 °C; Eluant: ethyl acetate/petroleum ether (1:4, R_f = 0.30). ¹H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 8.51 (s, 1H), 8.12 (d, J = 2.9 Hz, 1H), 7.87 (s, 1H), 3.81 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 139.3, 117.5, 115.4, 112.9, 109.6, 105.1, 101.0, 92.5, 82.0, 48.8; IR: 3649, 1709, 1508, 1360, 1220, 1092, 529 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_8\text{Br}\text{INO}_2$ $[\text{M} + \text{H}]^+$: 379.8778; found 379.8777.



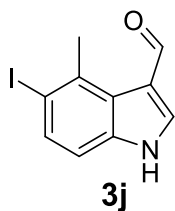
ethyl 5-iodo-1H-indole-3-carboxylate: 163.4 mg, 70% yield; Yellow solid; m. p. = 142 – 143 °C; Eluant: ethyl acetate/petroleum ether (1:3, R_f = 0.30). ¹H NMR (400 MHz, DMSO) δ 12.10 (s, 1H), 8.34 (d, J = 1.5 Hz, 1H), 8.07 (s, 1H), 7.47 (dd, J = 8.5, 1.6 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, DMSO) δ 164.1, 135.6, 133.2, 130.5, 128.9, 128.2, 114.9, 106.0, 85.8, 59.3, 14.5; IR: 3276, 1672, 1526, 1473, 1180, 1136, 1049, 890, 808, 588, 420 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{10}\text{INO}_2$ $[\text{M} + \text{Na}]^+$: 337.9648; found 337.9646.



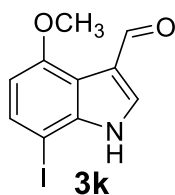
5-iodo-1H-indole-3-carbonitrile:⁴ 147.5 mg, 77% yield; White solid; m. p. = 190 – 191 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ¹H NMR (400 MHz, DMSO) δ 12.35 (s, 1H), 8.25 (s, 1H), 7.95 (d, J = 1.3 Hz, 1H), 7.55 (dd, J = 8.6, 1.6 Hz, 1H), 7.40 (d, J = 8.6 Hz, 1H); ¹³C NMR (101 MHz, DMSO) δ 135.5, 134.5, 131.7, 129.2, 126.8, 115.8, 115.4, 86.0, 83.7; IR: 3276, 2923, 2360, 2218, 1508, 1418, 1240, 883, 796, 611, 418 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_5\text{IN}_2\text{Na}$ [$\text{M} + \text{Na}$]⁺: 268.9570; found 268.9574.



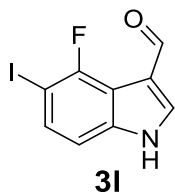
5-iodo-2-methyl-1H-indole-3-carbaldehyde: 132.6 mg, 67% yield; Yellow solid; m. p. = 223 – 224 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ¹H NMR (400 MHz, DMSO) δ 12.14 (s, 1H), 10.02 (s, 1H), 8.38 (s, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 2.67 (s, 3H); ¹³C NMR (101 MHz, DMSO) δ 184.5, 149.3, 134.6, 130.7, 128.3, 128.1, 113.9, 112.9, 86.3, 11.5; IR: 3199, 2922, 2853, 2360, 1633, 1572, 1458, 1375, 1234, 870, 797, 635, 584, 434 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_8\text{INNaO}$ [$\text{M} + \text{Na}$]⁺: 307.9543; found 307.9542.



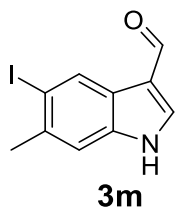
5-iodo-4-methyl-1H-indole-3-carbaldehyde: 121.4 mg, 74% yield; Yellow solid; m. p. = 196 – 197 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ¹H NMR (400 MHz, DMSO) δ 12.34 (s, 1H), 9.88 (s, 1H), 8.28 (d, J = 3.2 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 8.5 Hz, 1H), 2.95 (s, 3H); ¹³C NMR (101 MHz, DMSO) δ 184.2, 141.4, 138.1, 134.2, 133.7, 124.2, 119.3, 112.4, 95.3, 27.8; IR: 3228, 2851, 2743, 2361, 1705, 1646, 1508, 1384, 1140, 1087, 970, 844, 793, 753, 606, 544, 501 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INO}$ [$\text{M} + \text{H}$]⁺: 285.9723; found 285.9729.



7-iodo-4-methoxy-1H-indole-3-carbaldehyde: 131.9 mg, 91% yield; Yellow solid; m. p. = 208 – 209 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 10.31 (s, 1H), 7.98 (d, J = 3.1 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 6.64 (d, J = 8.2 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 186.5, 154.4, 139.2, 132.3, 123.0, 119.3, 116.4, 105.0, 67.5, 55.7; IR: 3214, 2924, 1648, 1517, 1382, 1273, 1091, 972, 789, 636, 583, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INO}_2$ $[\text{M} + \text{H}]^+$: 301.9672; found 301.9673.

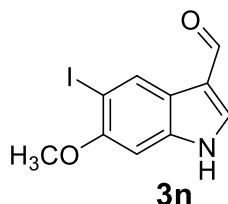


4-fluoro-5-iodo-1H-indole-3-carbaldehyde:⁵ 136.5 mg, 67% yield; Yellow solid; m. p. = 208 – 209 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 9.98 (d, J = 2.8 Hz, 1H), 8.25 (s, 1H), 7.61 – 7.48 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 183.5, 154.7 (d, J = 246.4 Hz), 140.6 (d, J = 11.2 Hz), 137.1, 132.1, 116.3 (d, J = 6.6 Hz), 113.7 (d, J = 24.2 Hz), 111.7 (d, J = 3.6 Hz), 72.6 (d, J = 24.8 Hz); IR: 3283, 2955, 2360, 1647, 1622, 1121, 1097, 857, 780, 699, 599, 546, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_6\text{FINO}$ $[\text{M} + \text{H}]^+$: 289.9473; found 289.9471.

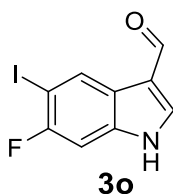


5-iodo-6-methyl-1H-indole-3-carbaldehyde: 143.8 mg, 77% yield; Yellow solid; m. p. = 228 – 229 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.25 (s, 1H), 9.88 (s, 1H), 8.53 (s, 1H), 8.25 (s, 1H), 7.51 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ

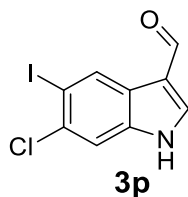
185.0, 138.8, 137.4, 134.7, 130.4, 124.6, 117.0, 113.3, 93.9, 28.1; IR: 2920, 2850, 2360, 1633, 1523, 1450, 1259, 1158, 1092, 953, 717, 424 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INNaO}$ [$\text{M} + \text{Na}$] $^+$: 307.9543; found 307.9536.



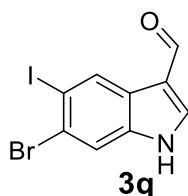
5-iodo-6-methoxy-1H-indole-3-carbaldehyde: 122.7 mg, 75% yield; Yellow solid; m. p. = 330 – 331 $^{\circ}\text{C}$; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.05 (s, 1H), 9.86 (s, 1H), 8.45 (s, 1H), 8.19 (d, J = 2.5 Hz, 1H), 7.08 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 185.0, 154.3, 138.0 (2C), 130.6, 120.2, 117.2, 95.2, 80.8, 56.5; IR: 3107, 3005, 2924, 2756, 2360, 1638, 1568, 1521, 1440, 1402, 1226, 1160, 1040, 876, 836, 727, 658, 584, 433 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INO}_2$ [$\text{M} + \text{H}$] $^+$: 301.9672; found 301.9670.



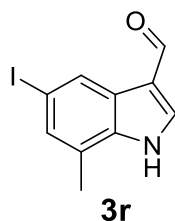
6-fluoro-5-iodo-1H-indole-3-carbaldehyde: 140.0 mg, 73% yield; Yellow solid; m. p. = 185 – 186 $^{\circ}\text{C}$; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 12.28 (s, 1H), 9.90 (s, 1H), 8.47 (d, J = 6.3 Hz, 1H), 8.33 (s, 1H), 7.44 (d, J = 8.7 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 185.2, 157.5 (d, J = 235.9 Hz), 139.6, 137.1 (d, J = 11.5 Hz), 130.3, 130.3 (d, J = 3.2 Hz), 117.0, 99.6 (d, J = 29.1 Hz), 75.5 (d, J = 28.2 Hz); IR: 3365, 2921, 2851, 1699, 1624, 1524, 1472, 1360, 1149, 1099, 976, 833, 721, 667, 599, 532, 437 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_5\text{FINaO}$ [$\text{M} + \text{Na}$] $^+$: 311.9292; found 311.9289.



6-chloro-5-iodo-1H-indole-3-carbaldehyde: 119.1 mg, 71% yield; White solid; m. p. = 244 – 245 °C; Eluant: ethyl acetate/petroleum ether (1:2, $R_f = 0.30$). ^1H NMR (400 MHz, DMSO) δ 12.29 (s, 1H), 9.91 (s, 1H), 8.61 (s, 1H), 8.35 (s, 1H), 7.76 (s, 1H); ^{13}C NMR (101 MHz, DMSO) δ 185.3, 140.0, 137.4, 131.5, 131.3, 125.2, 116.8, 113.2, 90.6; IR: 2955, 2922, 2852, 1637, 1576, 1541, 1457, 1251, 820, 526, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_5\text{ClINNaO}$ $[\text{M} + \text{Na}]^+$: 327.8997; found 327.8991.

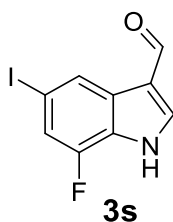


6-bromo-5-iodo-1H-indole-3-carbaldehyde: 128.9 mg, 70% yield; Yellow solid; m. p. = 298 – 299 °C; Eluant: ethyl acetate/petroleum ether (1:2, $R_f = 0.30$). ^1H NMR (400 MHz, DMSO) δ 12.27 (s, 1H), 9.91 (s, 1H), 8.63 (s, 1H), 8.33 (s, 1H), 7.91 (s, 1H); ^{13}C NMR (101 MHz, DMSO) δ 185.3, 139.8, 137.6, 131.5, 125.6, 122.4, 116.8, 116.5, 93.5; IR: 3213, 2921, 2852, 1638, 1522, 1249, 1092, 1021, 811, 776, 686, 595, 518, 421 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_6\text{BrINO}$ $[\text{M} + \text{H}]^+$: 349.8672; found 349.8662.

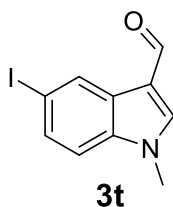


5-iodo-7-methyl-1H-indole-3-carbaldehyde: 102.8 mg, 47% yield; Yellow solid; m. p. = 208 – 209 °C; Eluant: ethyl acetate/petroleum ether (1:2, $R_f = 0.40$). ^1H NMR (400 MHz, DMSO) δ 12.32 (s, 1H), 9.91 (s, 1H), 8.29 (d, $J = 3.2$ Hz, 1H), 8.26 (s, 1H), 7.38 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 185.2, 138.5, 135.9, 131.9, 126.8, 126.3, 124.8, 117.6, 86.8, 16.3; IR: 3179, 2920, 2360,

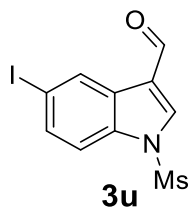
638, 1526, 1449, 1386, 1221, 1170, 1128, 866, 782, 611, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INO}$ $[\text{M} + \text{H}]^+$: 285.9723; found 285.9712.



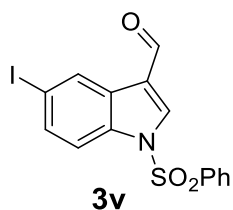
7-fluoro-5-iodo-1H-indole-3-carbaldehyde:¹⁰ 100.9 mg, 63% yield; Yellow solid; m. p. = 185 – 186 °C; Eluant: ethyl acetate/petroleum ether (1:2, R_f = 0.40). ^1H NMR (400 MHz, DMSO) δ 12.80 (s, 1H), 9.96 (s, 1H), 8.33 (s, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.54 (dd, J = 8.2, 5.5 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 185.4, 148.4 (d, J = 243.2 Hz), 139.2, 131.6, 128.0 (d, J = 4.8 Hz), 125.0 (d, J = 15.3 Hz), 118.9, 118.8 (d, J = 3.8 Hz), 74.1 (d, J = 21.1 Hz); IR: 3111, 2958, 2360, 1619, 1525, 1452, 1271, 1138, 799, 687, 664, 539, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_5\text{FINNaO}$ $[\text{M} + \text{Na}]^+$: 311.9292; found 311.9295.



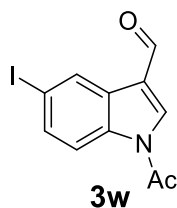
5-iodo-1-methyl-1H-indole-3-carbaldehyde:⁶ 124.8 mg, 79% yield; Yellow solid; m. p. = 130 – 131 °C; Eluant: ethyl acetate/petroleum ether (1:7, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 9.91 (s, 1H), 8.64 (d, J = 1.4 Hz, 1H), 7.59 (dd, J = 7.6, 2.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 184.2, 139.4, 137.1, 132.6, 130.9, 127.4, 117.2, 111.8, 87.3, 33.9; IR: 2921, 1655, 1508, 1466, 1370, 1075, 1028, 802, 731, 611, 587, 420 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INO}$ $[\text{M} + \text{H}]^+$: 285.9723; found 285.9719.



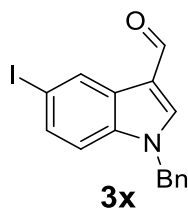
5-iodo-1-(methylsulfonyl)-1H-indole-3-carbaldehyde: 127.2 mg, 77% yield; White solid; m. p. = 203 – 204 °C; Eluant: ethyl acetate/petroleum ether (1:8, $R_f = 0.30$). ^1H NMR (400 MHz, DMSO) δ 10.07 (s, 1H), 8.62 (s, 1H), 8.51 (d, $J = 1.5$ Hz, 1H), 7.79 (d, $J = 1.7$ Hz, 1H), 7.74 (d, $J = 8.7$ Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 186.9, 139.1, 134.2, 134.1, 130.1, 127.9, 119.5, 115.6, 89.9, 41.8; IR: 3122, 2924, 1670, 1541, 1441, 1362, 1330, 1233, 1173, 1124, 970, 784, 744, 581, 534, 507, 424 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_9\text{INO}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 349.9342; found 349.9340.



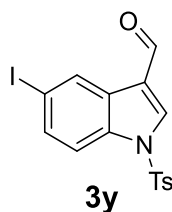
5-iodo-1-(phenylsulfonyl)-1H-indole-3-carbaldehyde: 128.9 mg, 73% yield; Yellow solid; m. p. = 217 – 218 °C; Eluant: ethyl acetate/petroleum ether (1:5, $R_f = 0.30$). ^1H NMR (400 MHz, DMSO) δ 10.04 (s, 1H), 8.89 (s, 1H), 8.42 (s, 1H), 8.11 (d, $J = 7.5$ Hz, 2H), 7.86 – 7.71 (m, 3H), 7.65 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 185.0, 137.2, 136.4, 135.2, 135.1, 134.6, 131.6, 129.9, 128.4, 127.2, 121.5, 115.1, 89.8; IR: 2955, 2921, 2360, 1734, 1683, 1541, 1473, 1232, 1129, 968, 784, 731, 684, 594, 575, 553, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{11}\text{INO}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 411.9499; found 411.9500.



1-acetyl-5-iodo-1H-indole-3-carbaldehyde: 143.8 mg, 70% yield; White solid; m. p. = 190 – 191 °C; Eluant: ethyl acetate/petroleum ether (1:8, $R_f = 0.30$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.08 (s, 1H), 8.64 (s, 1H), 8.16 (d, $J = 8.8$ Hz, 1H), 8.01 (s, 1H), 7.72 (dd, $J = 8.8, 1.3$ Hz, 1H), 2.73 (s, 3H); (101 MHz, CDCl_3) δ 185.2, 168.4, 135.6 (2C), 135.3, 130.9, 128.1, 121.7, 118.3, 90.1, 23.9; IR: 2923, 2853, 2360, 1772, 1681, 1654, 1542, 1438, 1397, 1338, 1213, 1134, 1011, 787, 649, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_9\text{INO}_2$ $[\text{M} + \text{H}]^+$: 313.9672; found 313.9670.



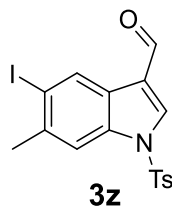
1-benzyl-5-iodo-1H-indole-3-carbaldehyde:⁷ 150.7 mg, 69% yield; Yellow liquid; Eluant: ethyl acetate/petroleum ether (1:9, $R_f = 0.30$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.90 (s, 1H), 8.67 (d, $J = 1.1$ Hz, 1H), 7.62 (s, 1H), 7.51 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.34 (dd, $J = 8.3, 2.2$ Hz, 3H), 7.17 – 7.12 (m, 2H), 7.05 (d, $J = 8.6$ Hz, 1H), 5.30 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 184.3, 138.8, 136.6, 134.9, 132.6, 130.9, 129.2, 128.6, 127.6, 127.2, 117.5, 112.4, 87.3, 51.1; IR: 3649, 1707, 1652, 1529, 1441, 1385, 1355, 1220, 1164, 1027, 764, 724, 696, 609, 529, 422 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{13}\text{INO}$ $[\text{M} + \text{H}]^+$: 362.0036; found 362.0026.



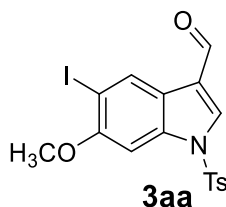
5-iodo-1-tosyl-1H-indole-3-carbaldehyde:⁸ 166.3 mg, 85% yield; White solid; m. p. = 230 – 231 °C; Eluant: ethyl acetate/petroleum ether (1:5, $R_f = 0.30$). $^1\text{H NMR}$ (400 MHz, DMSO) δ 10.04 (s, 1H), 8.87 (s, 1H), 8.42 (d, $J = 1.3$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 8.7$ Hz, 1H), 7.72 (dd, $J = 8.7, 1.5$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 186.7, 146.8, 138.9, 134.5, 133.7, 133.2, 130.7, 130.1, 128.0, 127.3, 120.4, 115.5, 90.3, 21.2; IR: 2923, 2852,

2361, 1717, 1683, 1541, 1457, 1437, 1376, 1178, 1130, 1105, 967, 783, 665, 581, 538, 419 cm^{-1} ;

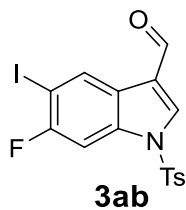
HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{13}\text{INO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 425.9655; found 425.9636.



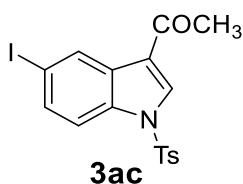
5-iodo-6-methyl-1-tosyl-1H-indole-3-carbaldehyde: 132.7 mg, 87% yield; White solid; m. p. = 206 – 207 $^{\circ}\text{C}$; Eluant: ethyl acetate/petroleum ether (1:5, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 10.02 (s, 1H), 8.71 (s, 1H), 8.12 (s, 1H), 7.85 – 7.79 (m, 3H), 7.30 (d, J = 8.2 Hz, 2H), 2.56 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 185.0, 146.4, 139.2, 136.2, 135.6, 134.3, 132.5, 130.5, 127.2, 126.1, 121.3, 113.6, 97.2, 29.2, 21.8; IR: 2922, 2362, 1683, 1558, 1541, 1457, 1177, 1108, 887, 685, 666, 582, 541, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{15}\text{INO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 439.9812; found 439.9800.



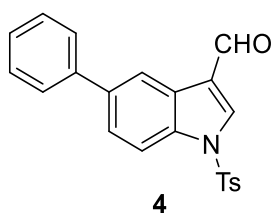
5-iodo-6-methoxy-1-tosyl-1H-indole-3-carbaldehyde: 112.7 mg, 75% yield; White solid; m. p. = 106 – 107 $^{\circ}\text{C}$; Eluant: ethyl acetate/petroleum ether (1:6, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 10.00 (s, 1H), 8.65 (s, 1H), 8.08 (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.40 (s, 1H), 7.30 (d, J = 8.2 Hz, 2H), 3.96 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 185.1, 156.8, 146.5, 136.4, 135.3, 134.3, 132.9, 130.5, 127.1, 121.6, 121.6, 95.7, 84.1, 56.8, 21.8; IR: 2838, 2360, 1676, 1618, 1542, 1494, 1434, 1378, 1287, 1217, 1177, 1100, 1030, 982, 813, 673, 580, 541 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{15}\text{INO}_4\text{S}$ $[\text{M} + \text{H}]^+$: 455.9761; found 455.9764.



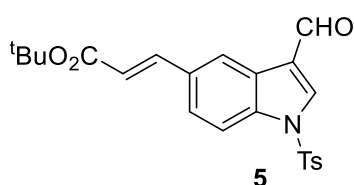
6-fluoro-5-iodo-1-tosyl-1H-indole-3-carbaldehyde: 130.5 mg, 81% yield; Yellow solid; m. p. = 190 – 191 °C; Eluant: ethyl acetate/petroleum ether (1:6, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 10.02 (s, 1H), 8.64 (d, J = 6.2 Hz, 1H), 8.19 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 184.9, 159.7 (d, J = 243.5 Hz), 146.8, 136.7 (d, J = 3.2 Hz), 135.5 (d, J = 11.2 Hz), 134.0, 132.8 (d, J = 2.7 Hz), 130.7, 127.3, 124.4 (d, J = 1.9 Hz), 121.1, 100.9 (d, J = 31.5 Hz), 78.6 (d, J = 27.8 Hz), 21.8; IR: 3126, 2924, 2360, 1675, 1596, 1542, 1459, 1418, 1381, 1176, 1113, 1086, 1010, 901, 666, 583, 541, 438 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{12}\text{FINO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 443.9561; found 443.9555.



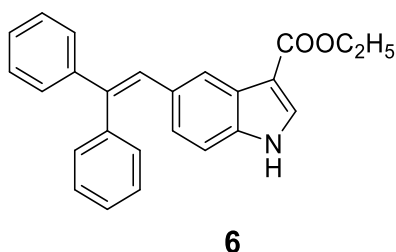
1-(5-iodo-1-tosyl-1H-indol-3-yl)ethan-1-one:² 140.9 mg, 81% yield; White solid; m. p. = 197 – 198 °C; Eluant: ethyl acetate/petroleum ether (1:5, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 8.10 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.63 (dd, J = 8.4, 1.1 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 2.55 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.2, 146.4, 135.8, 134.4, 134.0, 132.2, 130.5, 127.2, 127.0, 124.7, 122.1, 121.4, 90.4, 27.84, 21.79; IR: 3750, 2921, 1670, 1541, 1418, 1171, 1090, 973, 815, 669, 576, 535, 419 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{14}\text{INNaO}_3\text{S}$ $[\text{M} + \text{Na}]^+$: 461.9631; found 461.9614.



5-phenyl-1-tosyl-1H-indole-3-carbaldehyde:⁹ 51 mg, 89% yield; White solid; m. p. = 198 – 199 °C; Eluant: ethyl acetate/petroleum ether (1:4, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 10.12 (s, 1H), 8.47 (d, J = 1.5 Hz, 1H), 8.25 (s, 1H), 8.00 (d, J = 8.7 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.68 – 7.59 (m, 3H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 185.4, 146.3, 140.7, 138.7, 136.8, 134.7, 134.47, 130.46, 128.9, 127.6, 127.5, 127.3, 127.0, 125.9, 122.6, 121.0, 113.5, 21.8; IR: 3360, 2956, 2920, 2850, 1646, 1469, 1177, 974, 580, 457, 421 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NO}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 376.1002; found 376.1014.



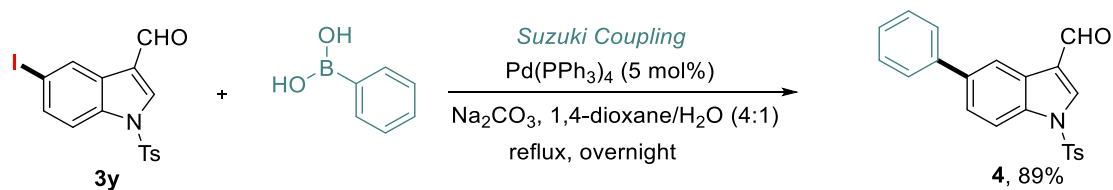
tert-butyl (E)-3-(3-formyl-1-tosyl-1H-indol-5-yl)acrylate: 53 mg, 91% yield; Yellow liquid; Eluant: ethyl acetate/petroleum ether (1:4, R_f = 0.30). ^1H NMR (400 MHz, CDCl_3) δ 10.07 (s, 1H), 8.39 (s, 1H), 8.23 (s, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 16.0 Hz, 1H), 7.53 (dd, J = 8.7, 1.2 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 2.36 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 185.2, 166.2, 146.5, 143.0, 137.0, 135.9, 134.2, 132.0, 130.5, 127.3, 126.8, 126.0, 122.4, 122.3, 120.7, 113.6, 80.6, 28.2, 21.7; IR: 3588, 3004, 1709, 1638, 1220, 1093, 978, 902, 529, 441, 428 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{23}\text{NNaO}_4\text{S}$ [$\text{M} + \text{Na}$] $^+$: 432.1240; found 432.1258.



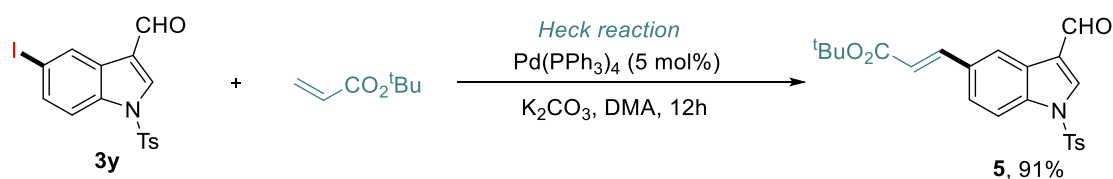
ethyl 5-(2,2-diphenylvinyl)-1H-indole-3-carboxylate: 34 mg, 43% yield; Yellow liquid; Eluant: ethyl acetate/petroleum ether (1:5, R_f = 0.30). ^1H NMR (400 MHz, DMSO) δ 11.74 (s, 1H), 8.00 (d, J = 2.6 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.25 (dt, J = 30.9, 7.2 Hz, 7H), 7.07 (d, J = 7.4 Hz, 4H), 7.00

(d, $J = 8.7$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 164.4, 149.5, 142.0, 134.7, 132.7, 128.5, 127.9, 125.9, 125.2, 123.6, 120.3, 111.8, 106.9, 58.9, 52.3, 30.6, 14.4. IR: 3638, 3070, 2953, 2852, 1708, 1649, 1530, 1325, 1228, 1121, 1065, 877, 839, 641 cm^{-1} ; HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{21}\text{NNaO}_2$ ($M + \text{Na}^+$): 390.1465; found 390.1460.

5. Procedures for synthetic application

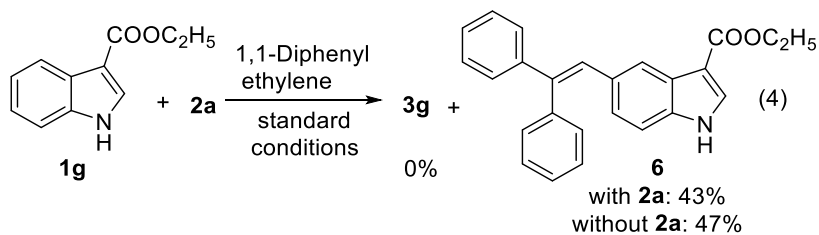
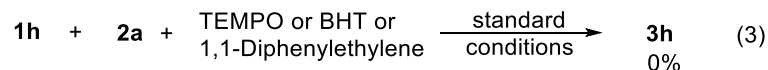
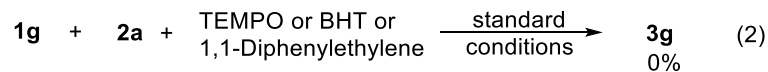
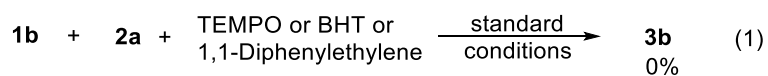


To a mixture of **3y** (63 mg, 0.15 mmol), sodium carbonate (31 mg, 0.29 mmol), phenylboronic acid (26 mg, 0.21 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (17 mg, 0.015 mmol) in 1, 4-dioxane: water (4:1) 2 mL was taken under argon atmosphere in a sealed tube vial. The reaction mixture was stirred at 100 °C for 12 h in oil bath. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4 , concentrated via rotavapor and subjected for column chromatography to afford product **4** (51 mg, 89%) as white solid.



To a mixture of **3y** (63 mg, 0.15 mmol), potassium carbonate (41 mg, 0.3 mmol), tert-butylacrylate (57 mg, 0.45 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (17 mg, 0.015) in DMA 1 mL was taken under argon atmosphere in a sealed tube vial. The reaction mixture was stirred at 100 °C for 12 h in oil bath. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4 , concentrated via rotavapor and subjected for column chromatography to afford product **5** (53 mg, 91%) as yellow liquid.

6. Procedures for radical-trapping experiments



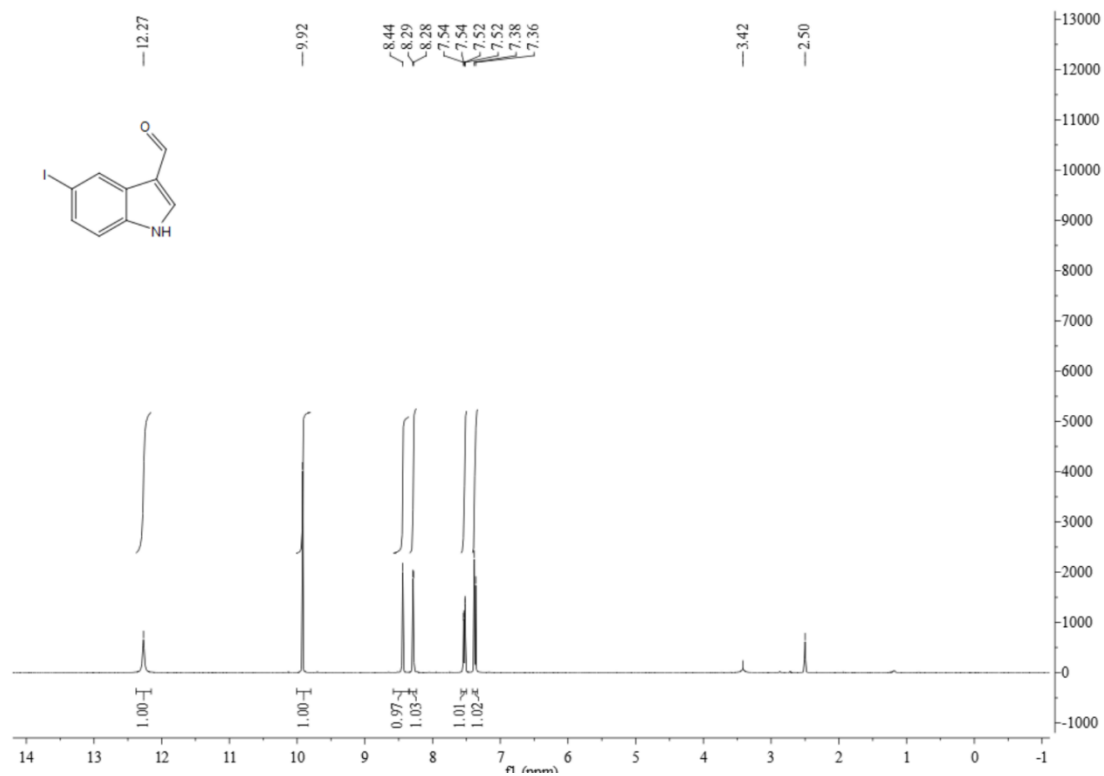
A 10 mL round bottomed flask equipped with a stirring bar was charged with **1b**, **1g** or **1h** (0.5 mmol), **2a** (0.5 mmol), and DCM (3 mL) followed by sequential addition of three radical-trapping reagents, TEMPO (1.5 mmol, 3.0 equiv), BHT (1.5 mmol, 3.0 equiv) or 1,1-diphenylethylene (1.5 mmol, 3.0 equiv), respectively. Then $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.0 mmol) was added, and stirred at room temperature under air. No product **3b**, **3g** and **3h** were detected after 12 h (eq. 1, 2 and 3). But an adduct of ethyl 1H-indole-3-carboxylate and 1,1-diphenylethylene **6** was detected in the reaction mixture (eq.4).

7. References

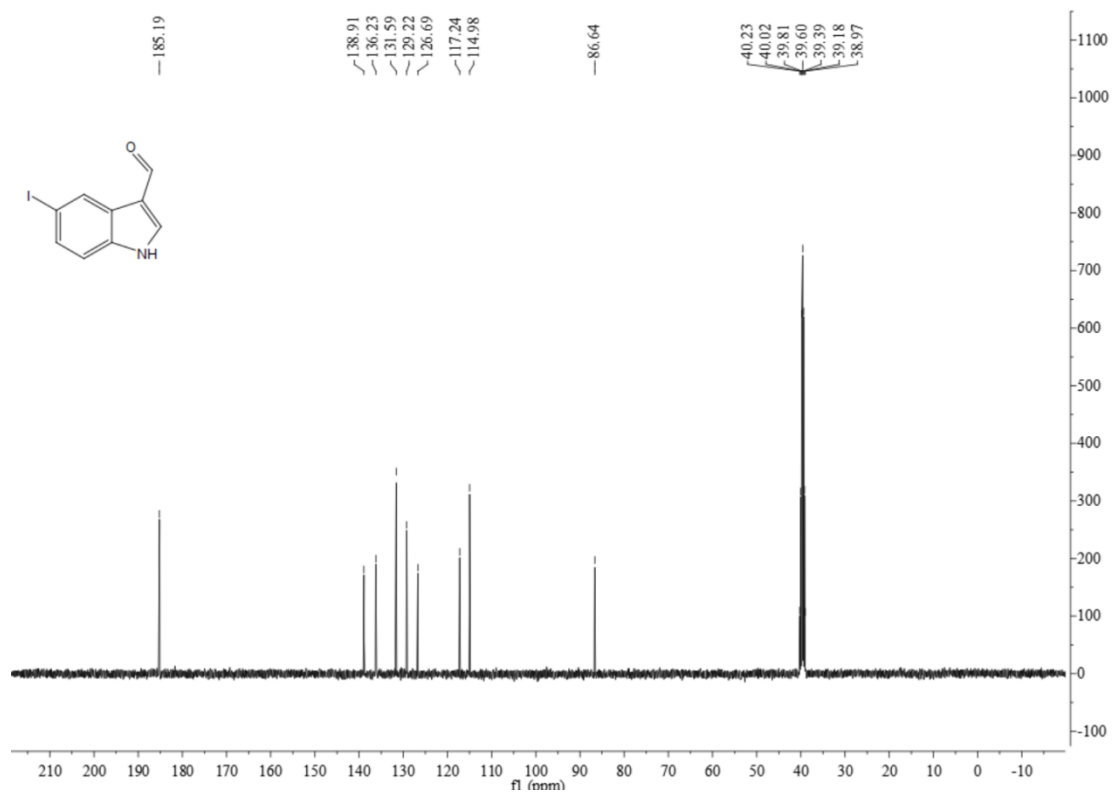
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8. NMR spectra

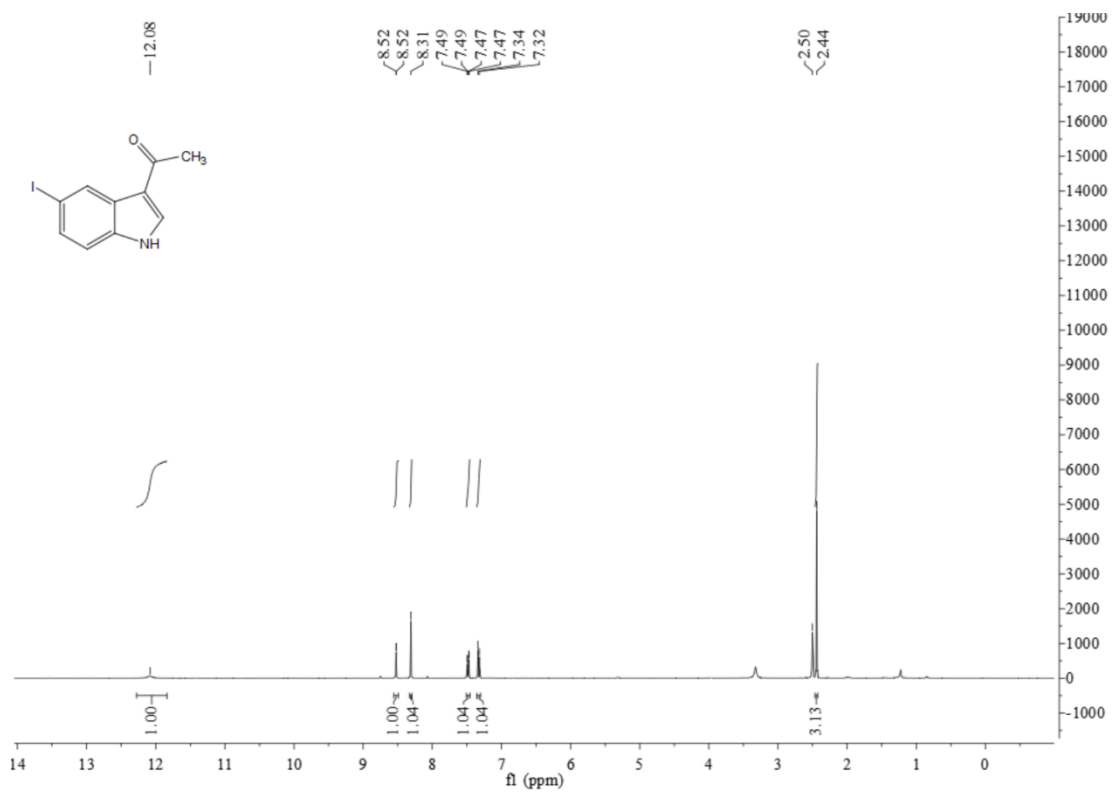
^1H NMR spectra of compound **3a**



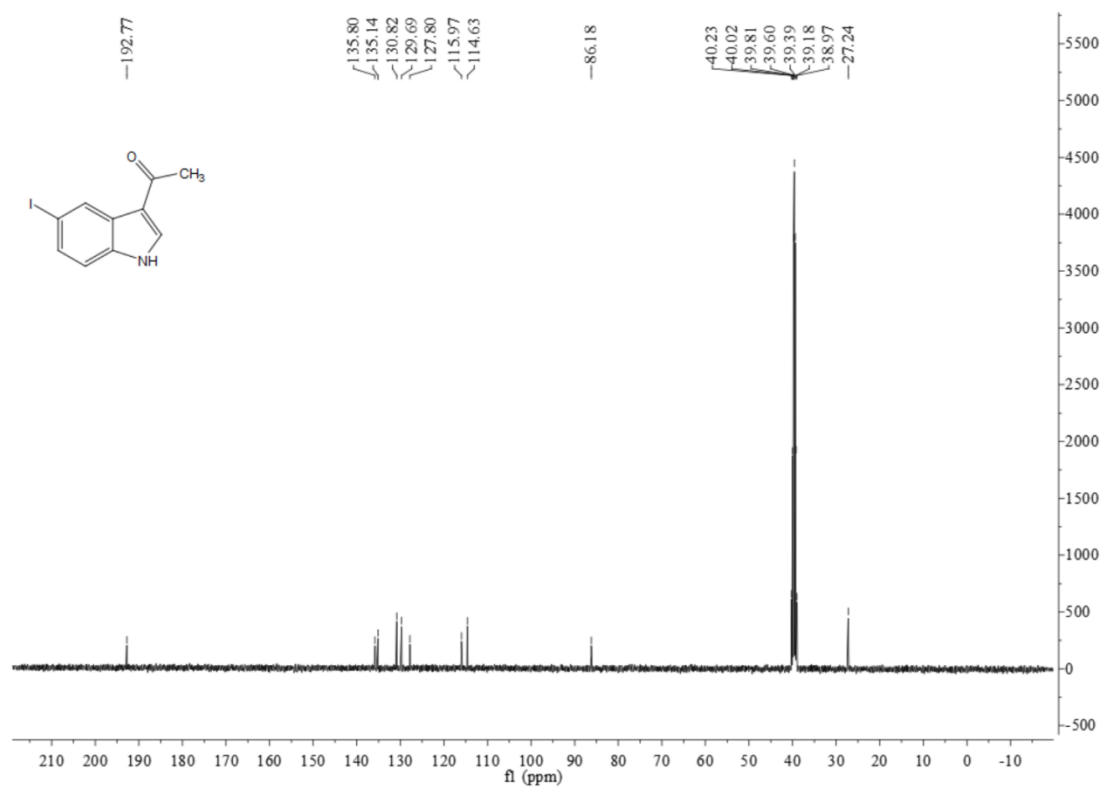
^{13}C NMR spectra of compound **3a**



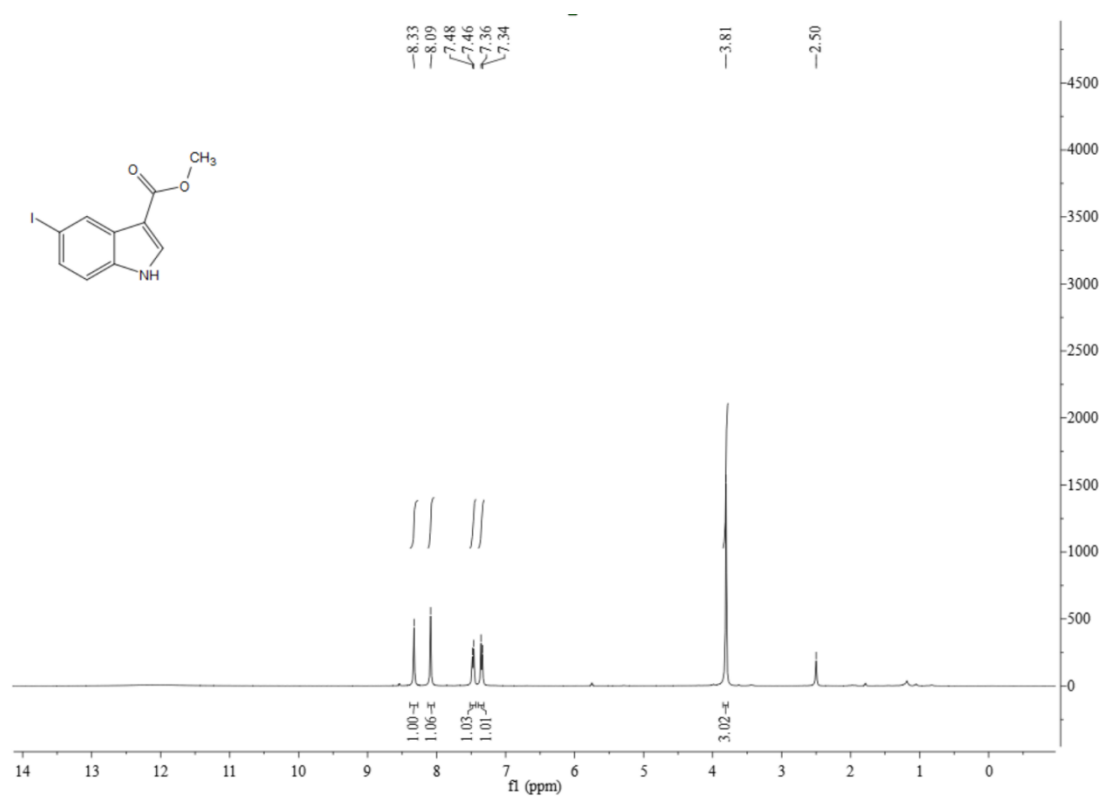
¹H NMR spectra of compound **3b**



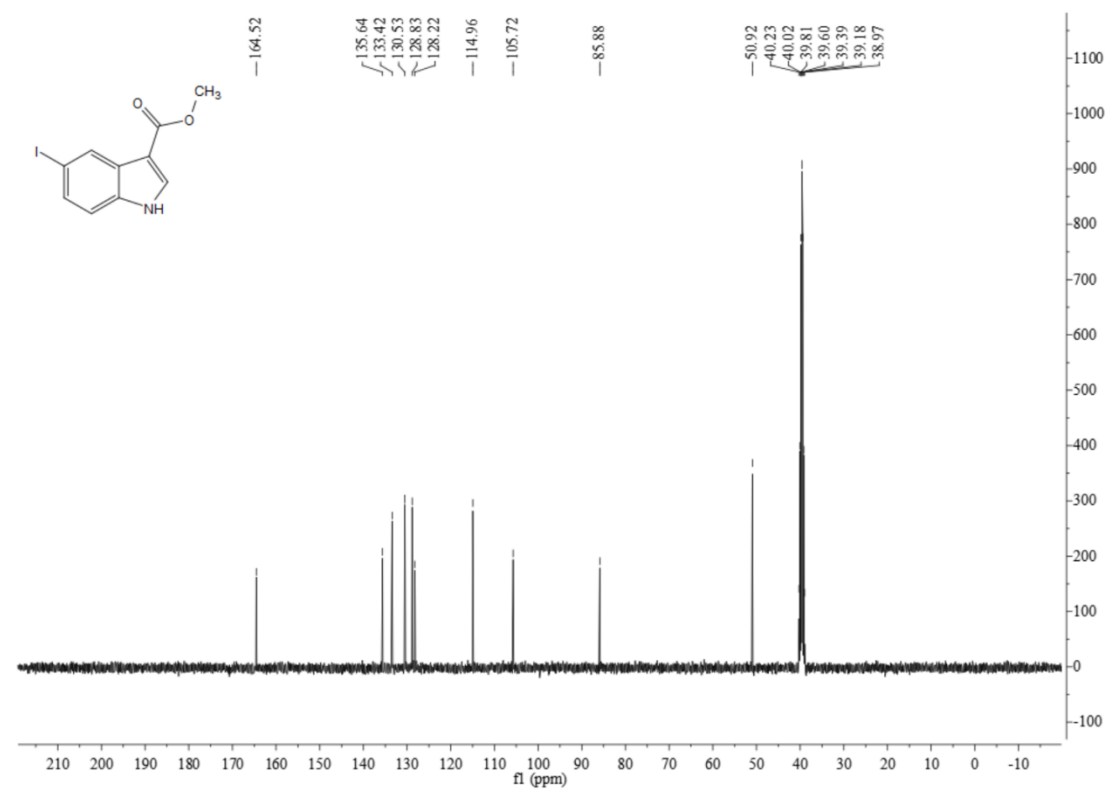
¹³C NMR spectra of compound **3b**



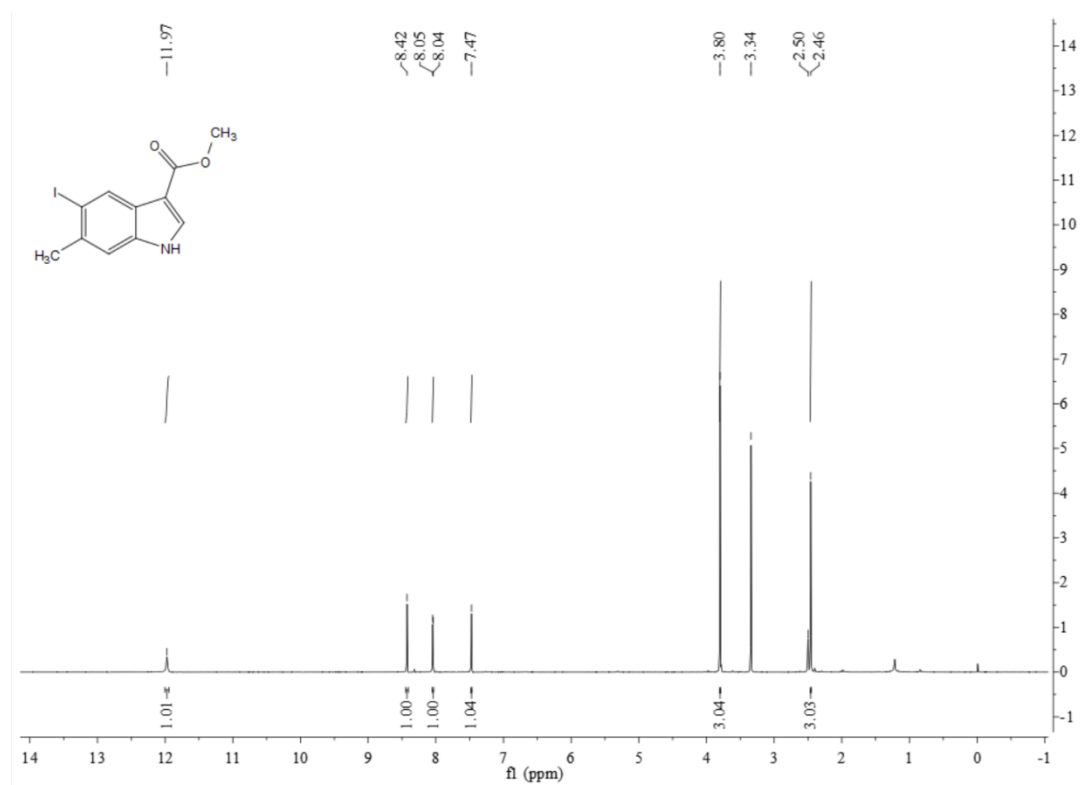
¹H NMR spectra of compound **3c**



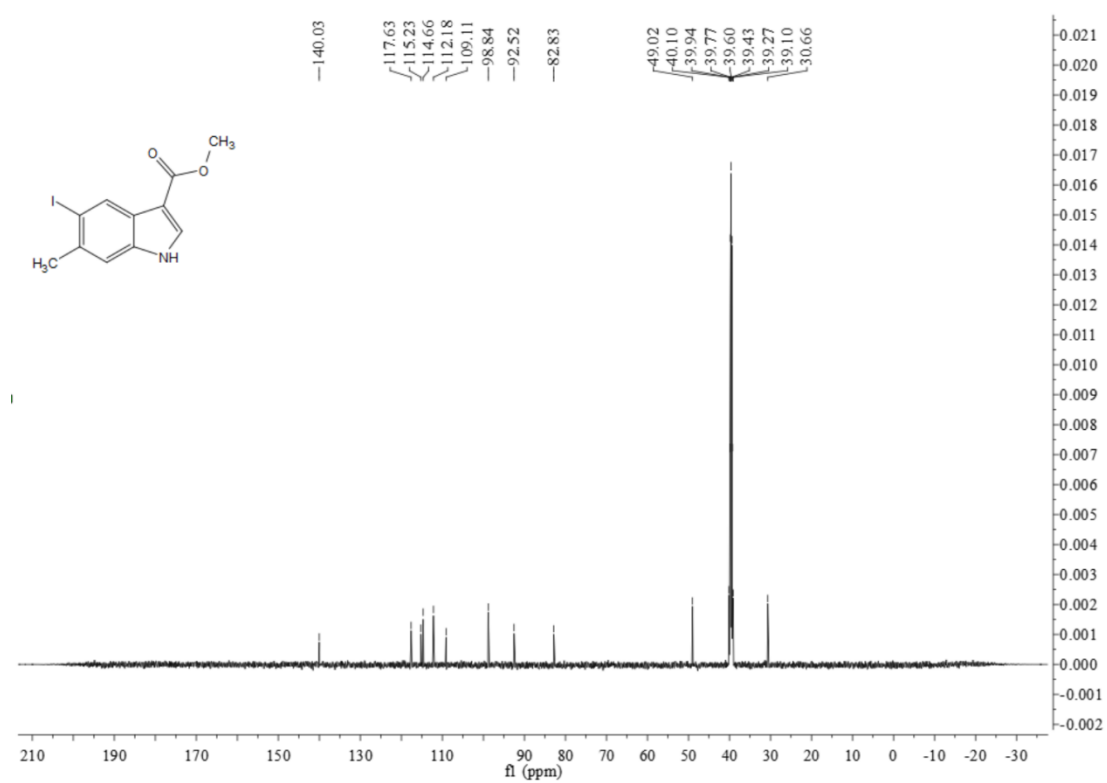
¹³C NMR spectra of compound **3c**



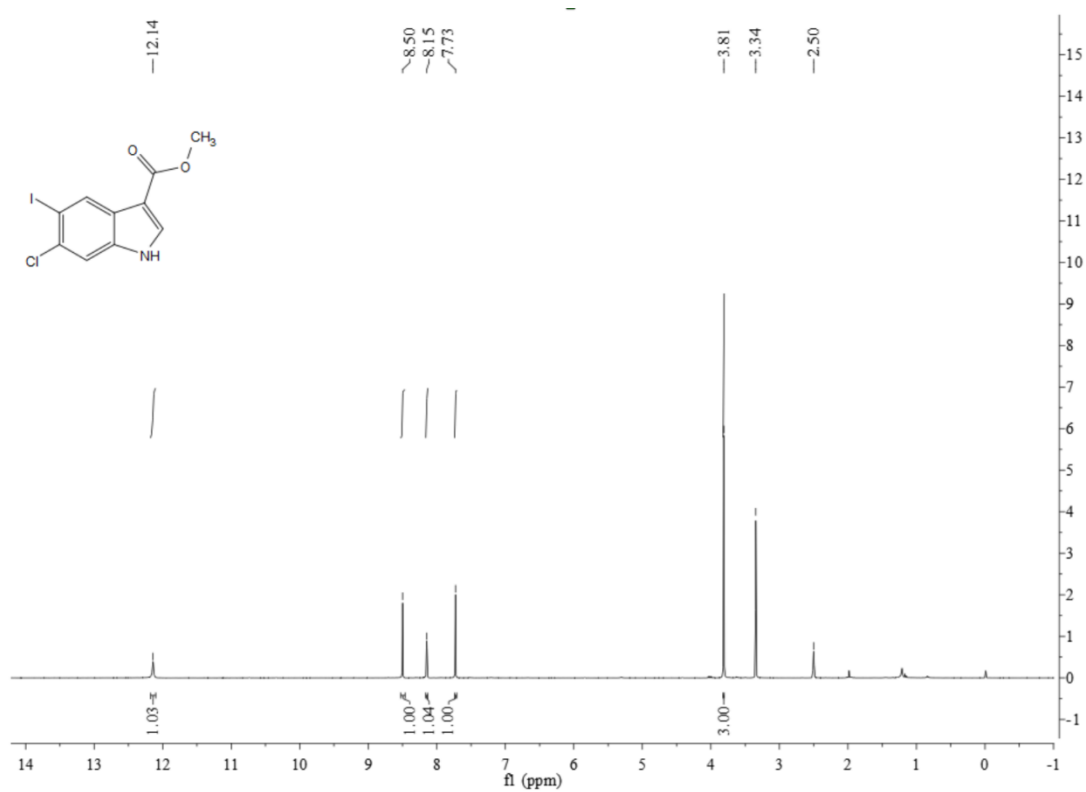
¹H NMR spectra of compound **3d**



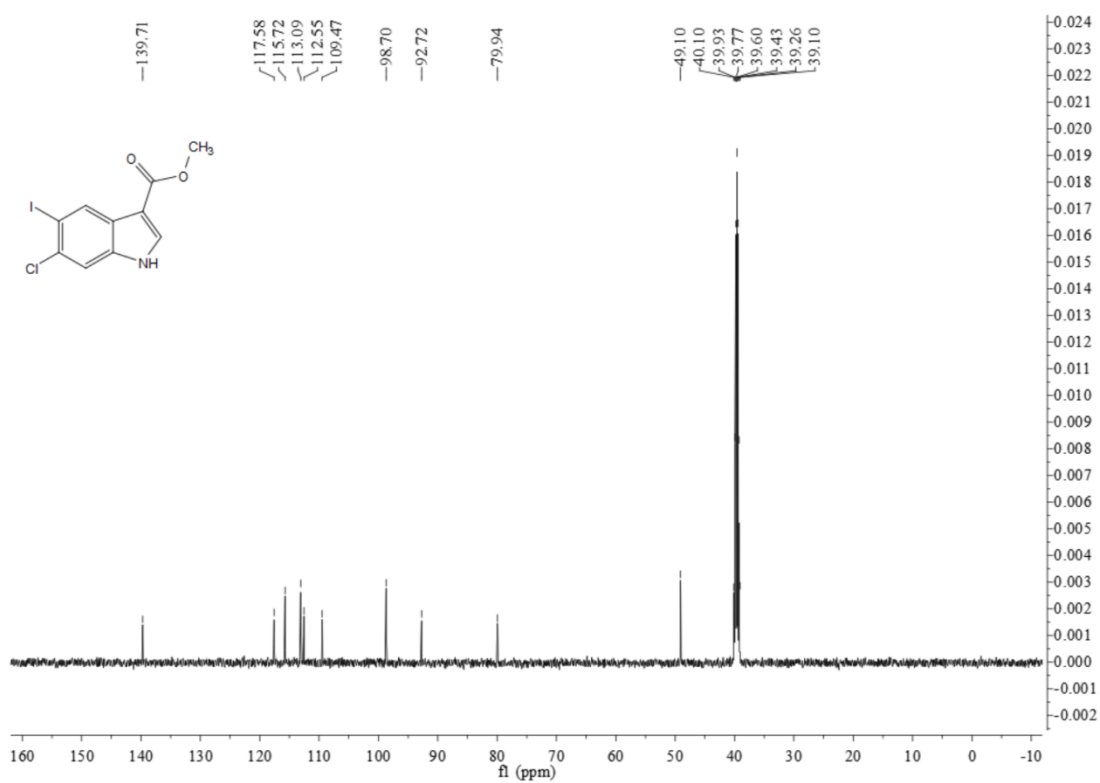
¹³C NMR spectra of compound **3d**



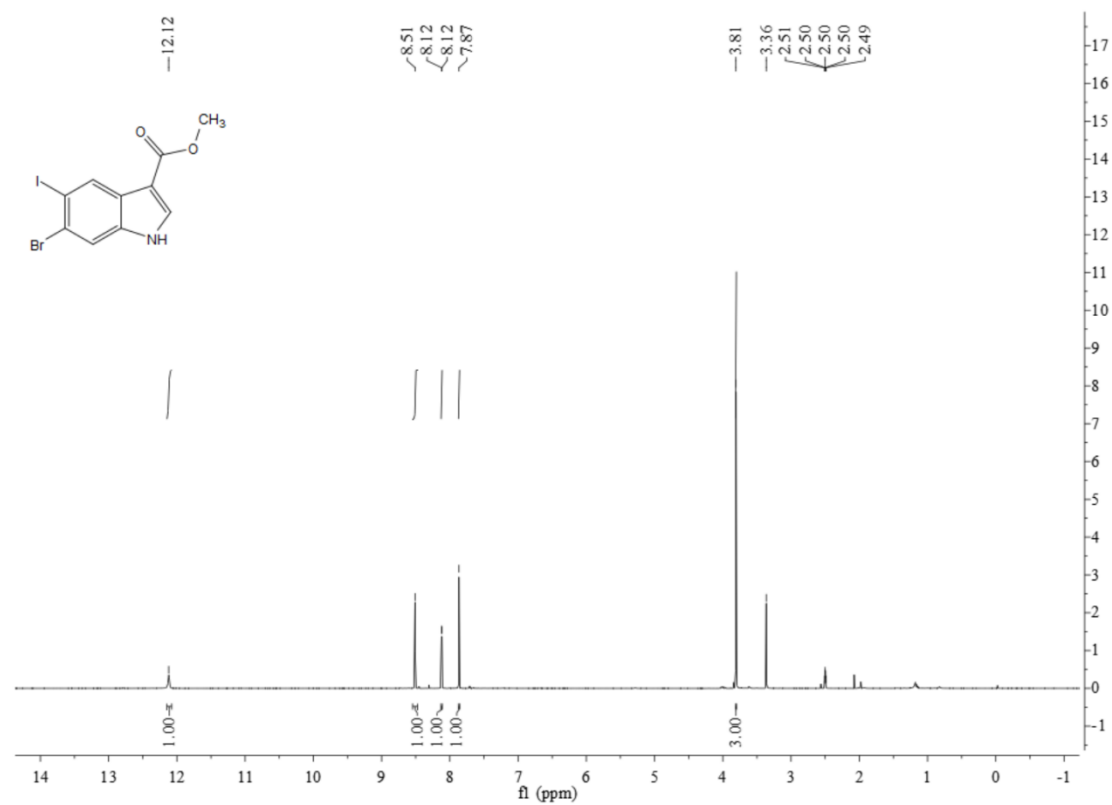
¹H NMR spectra of compound **3e**



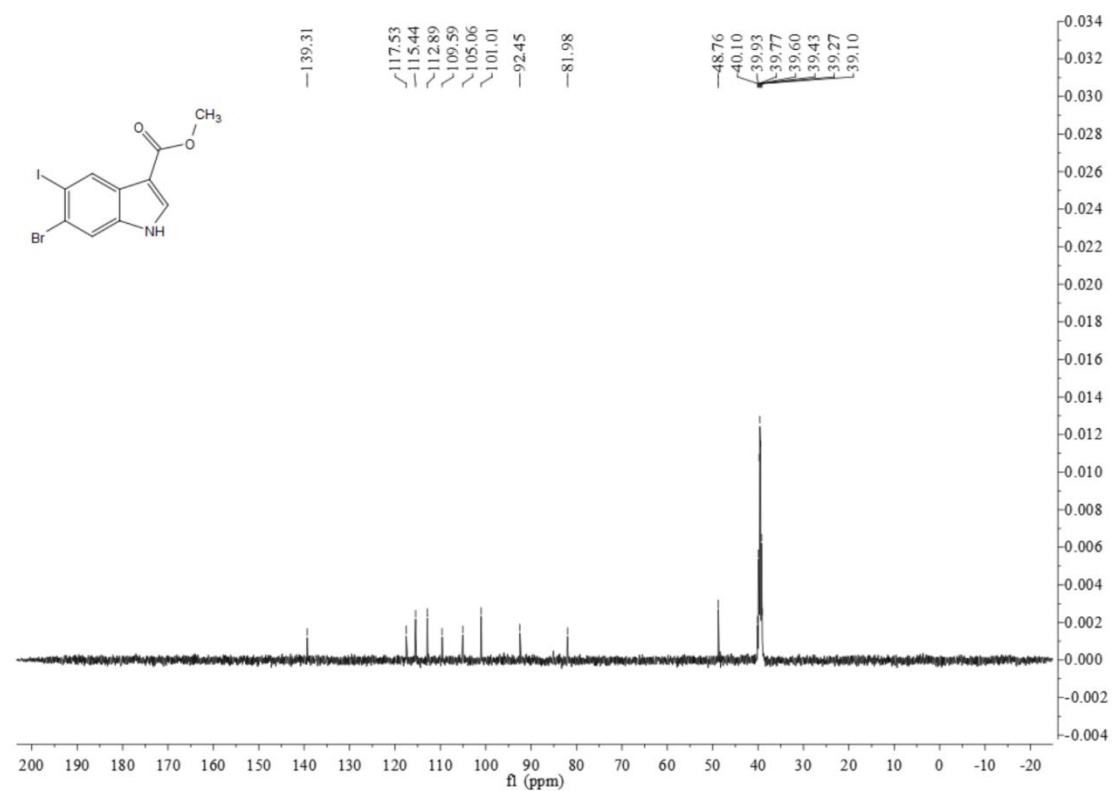
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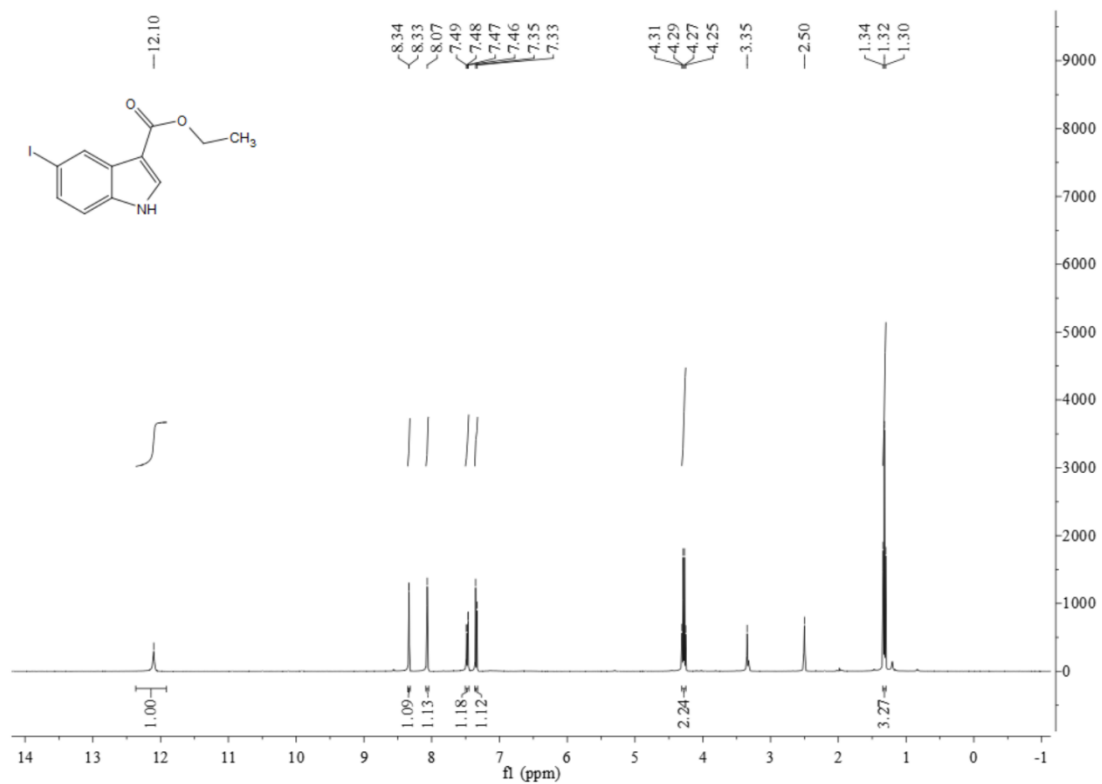
^1H NMR spectra of compound **3f**



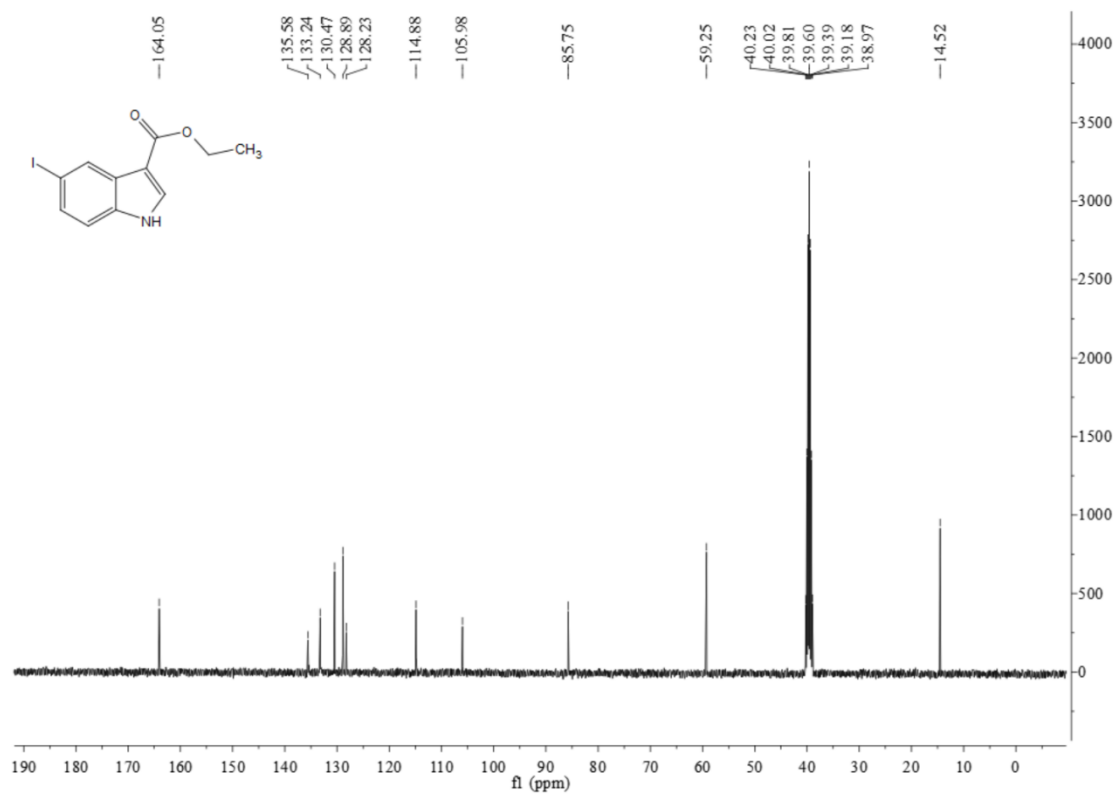
^{13}C NMR spectra of compound **3f**



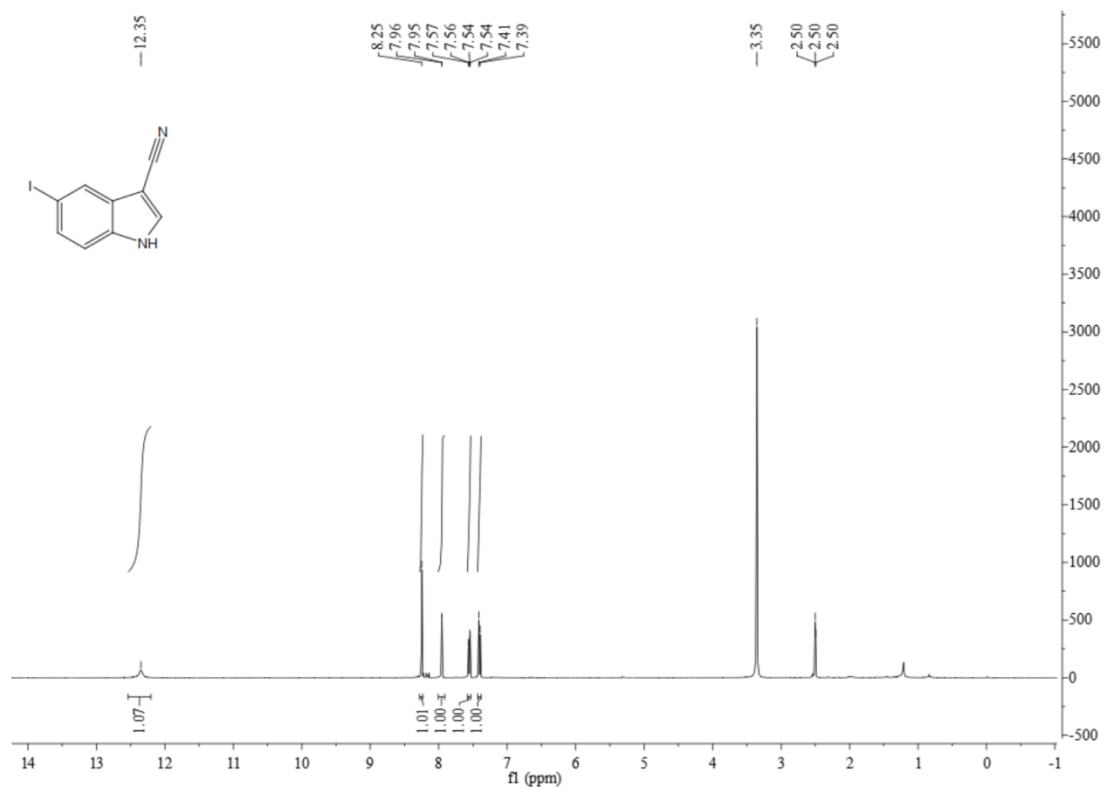
¹H NMR spectra of compound **3g**



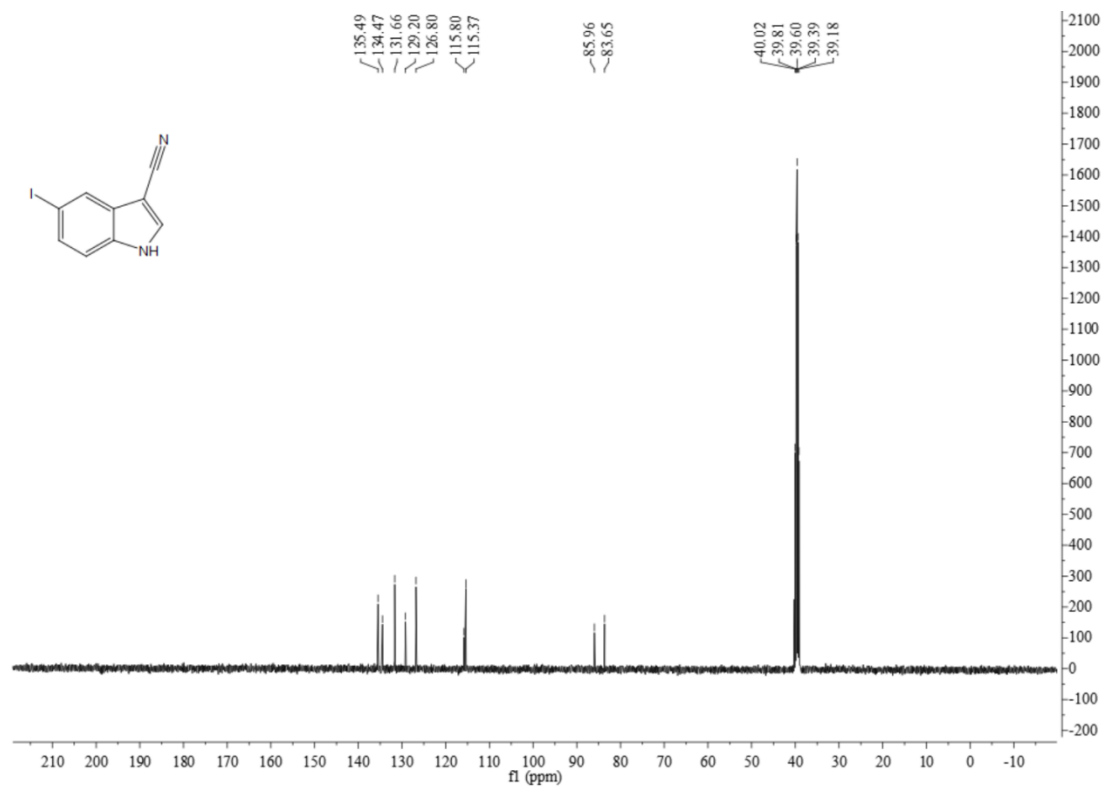
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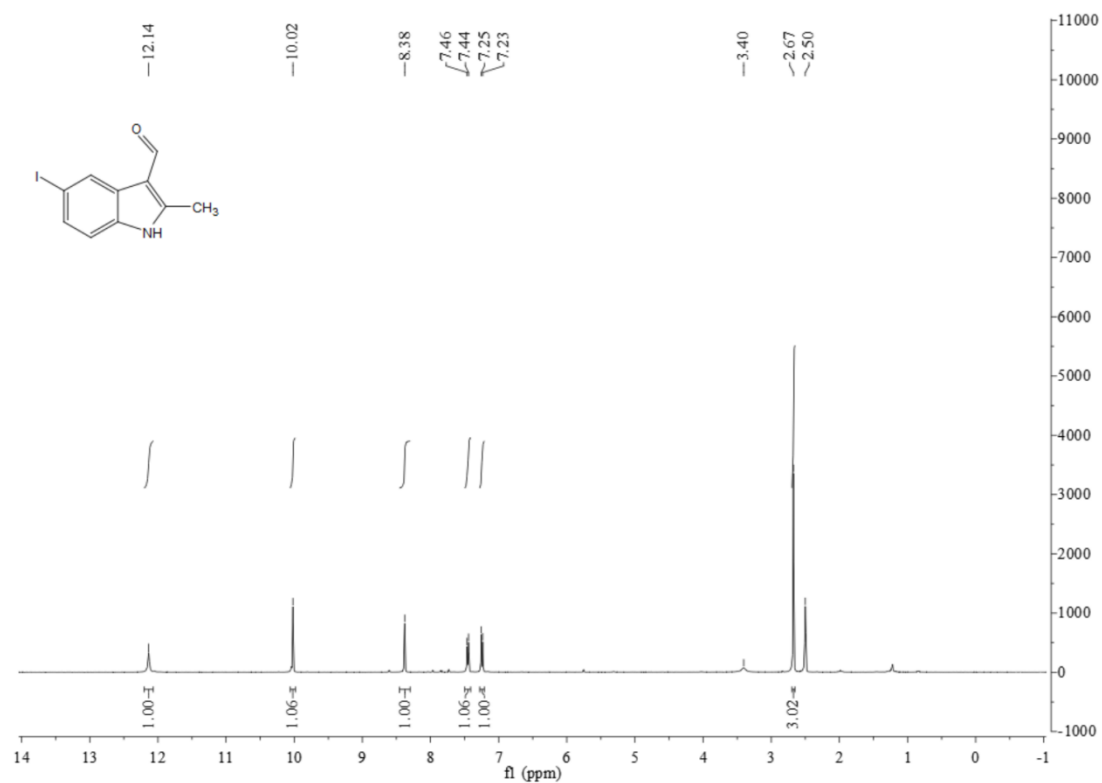
¹H NMR spectra of compound **3h**



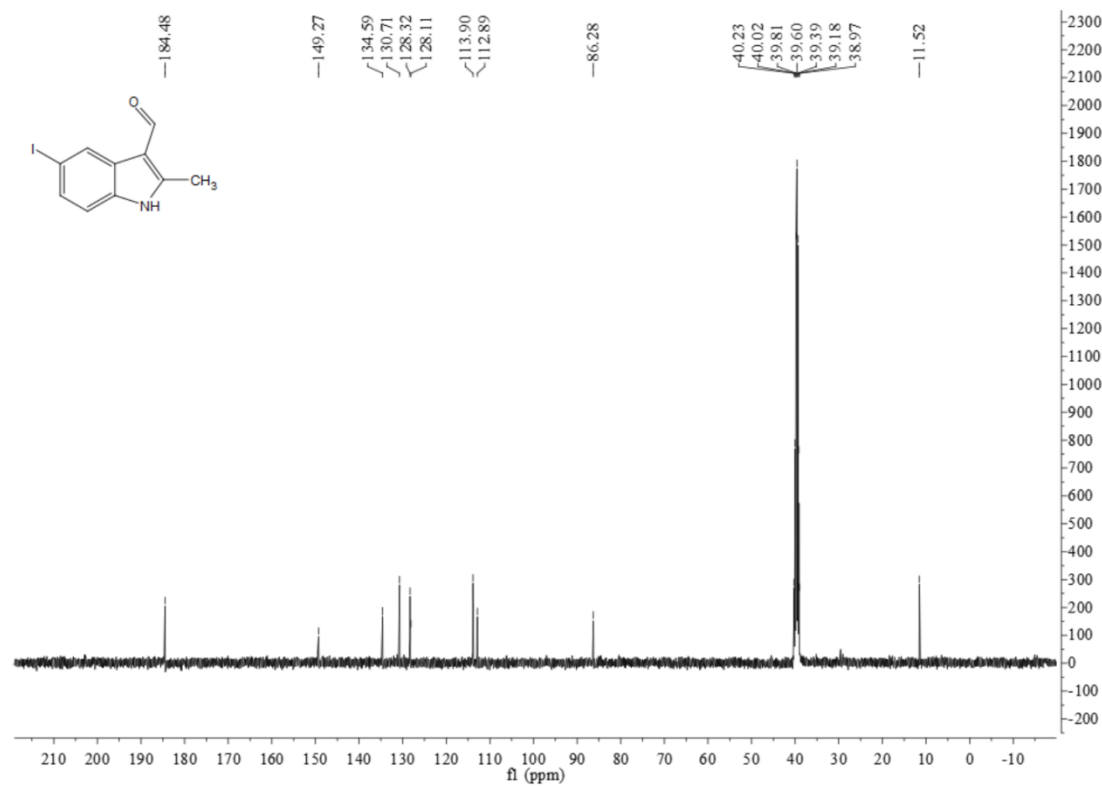
¹³C NMR spectra of compound **3h**



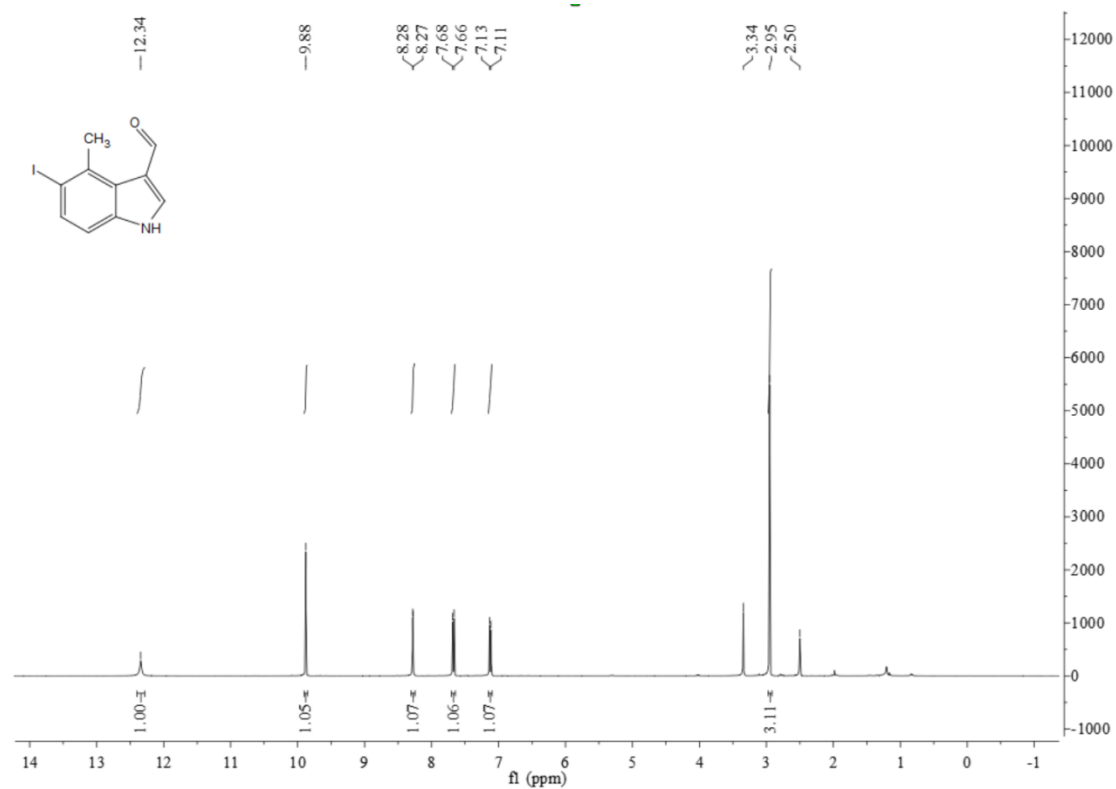
¹H NMR spectra of compound **3i**



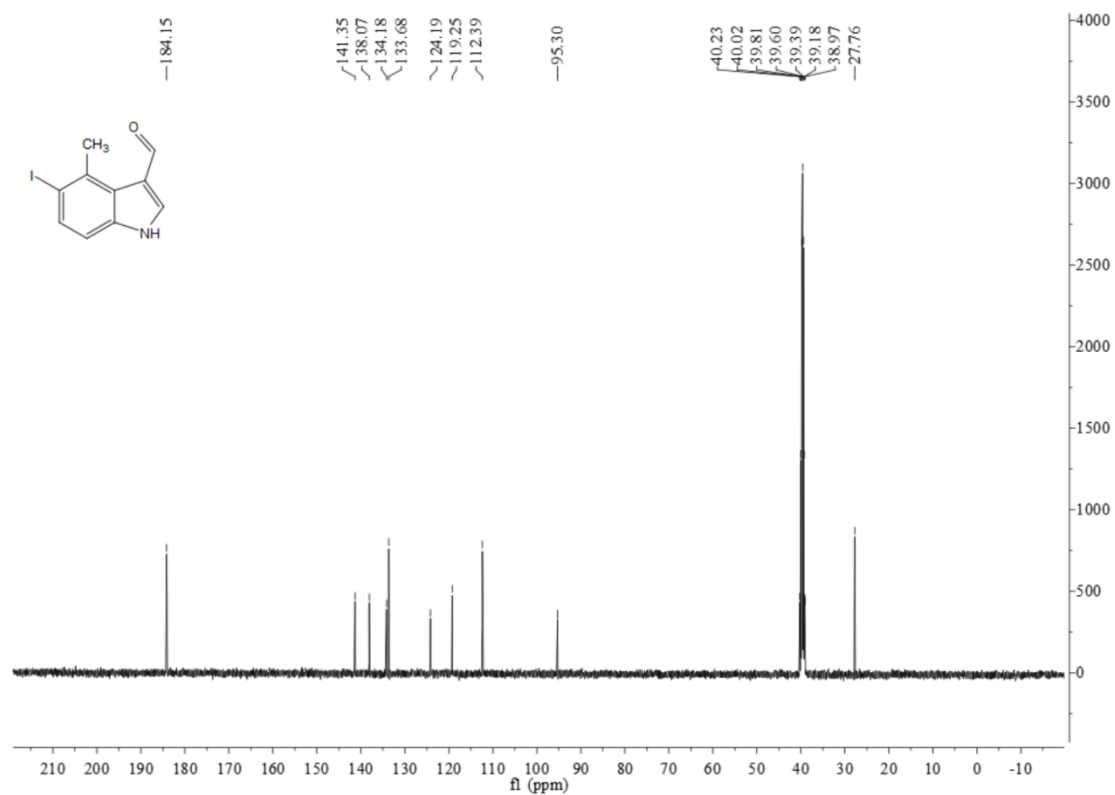
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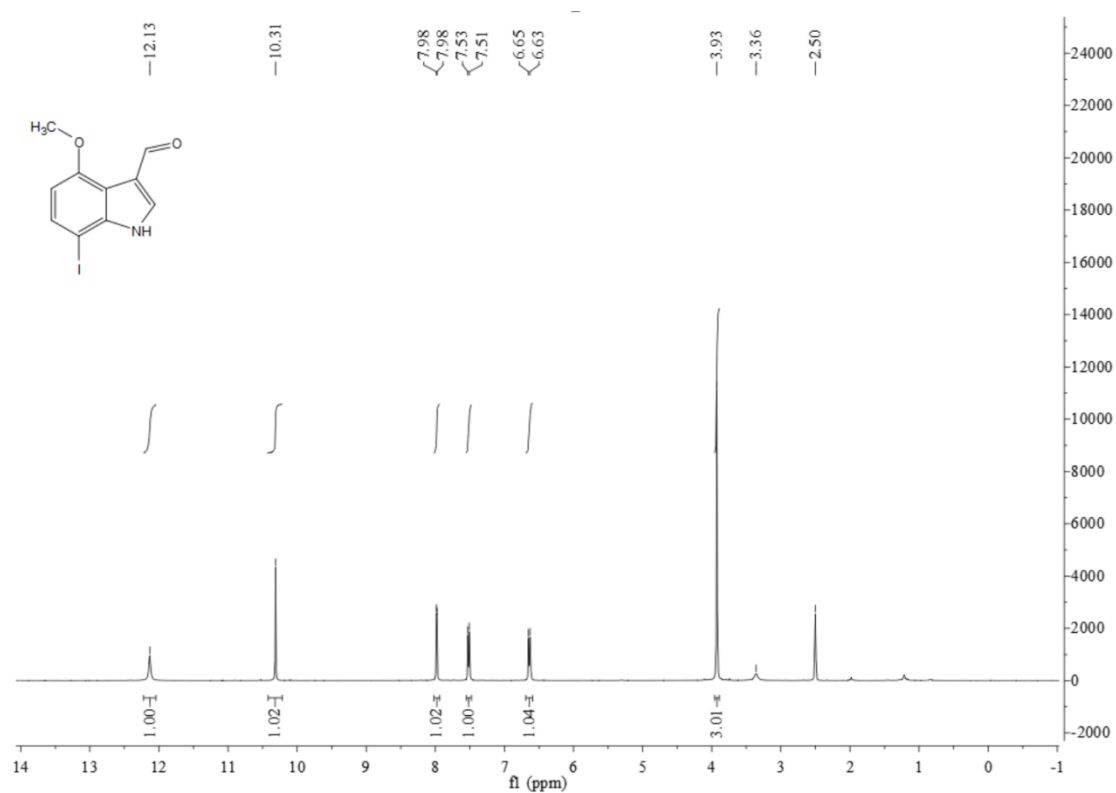
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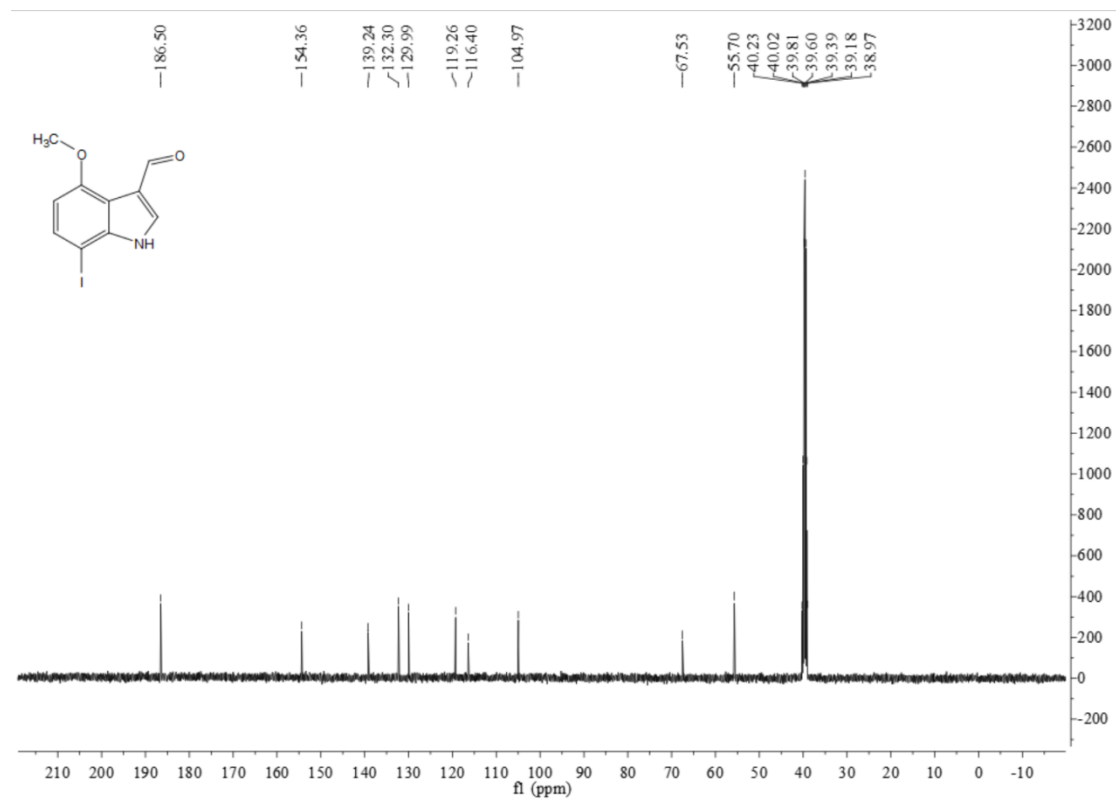
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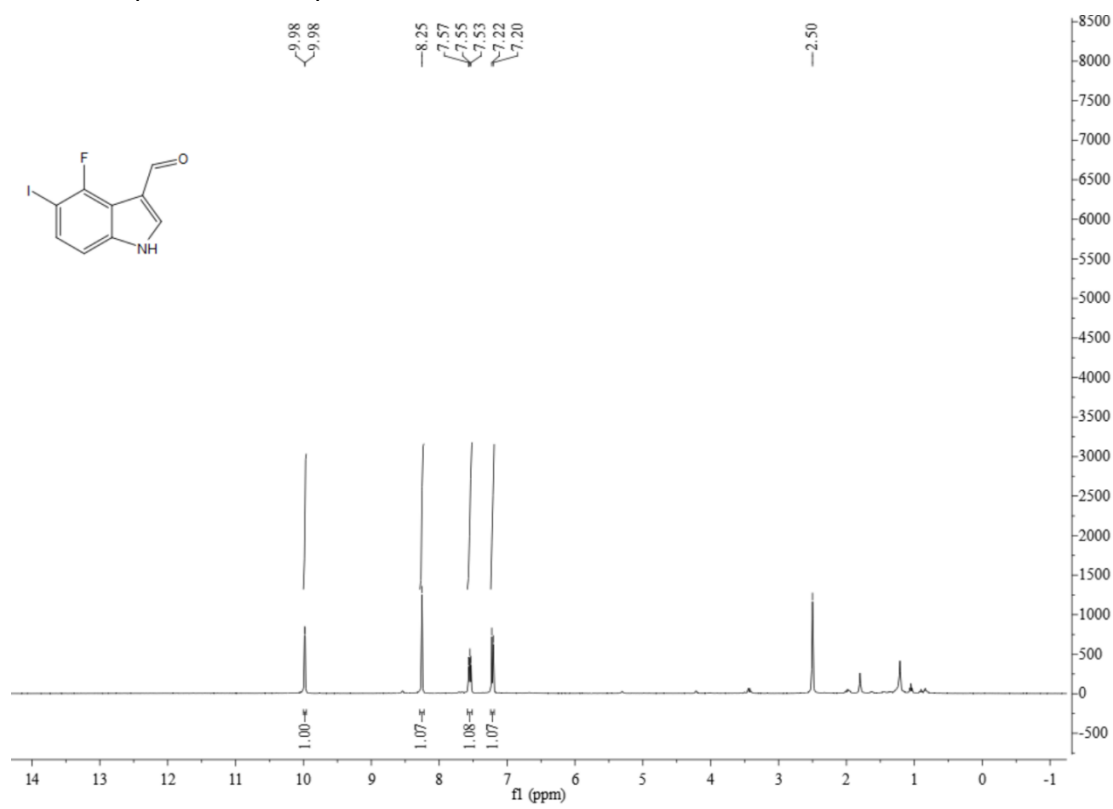
¹H NMR spectra of compound **3k**



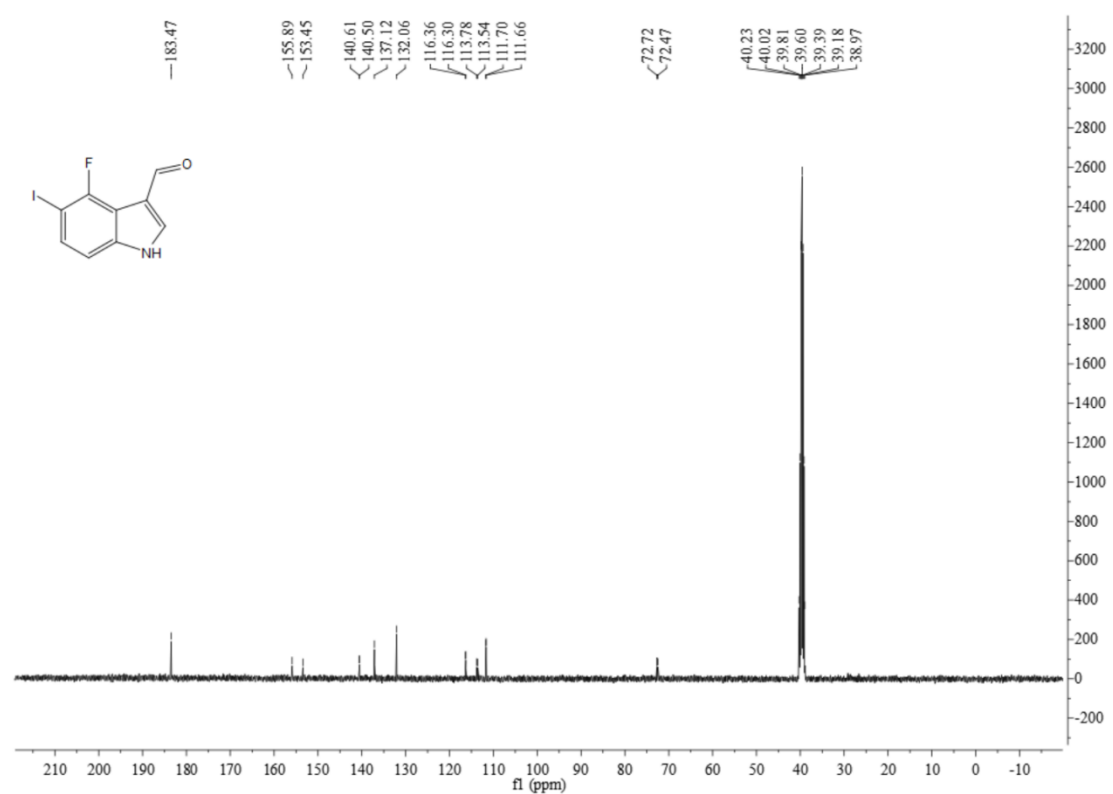
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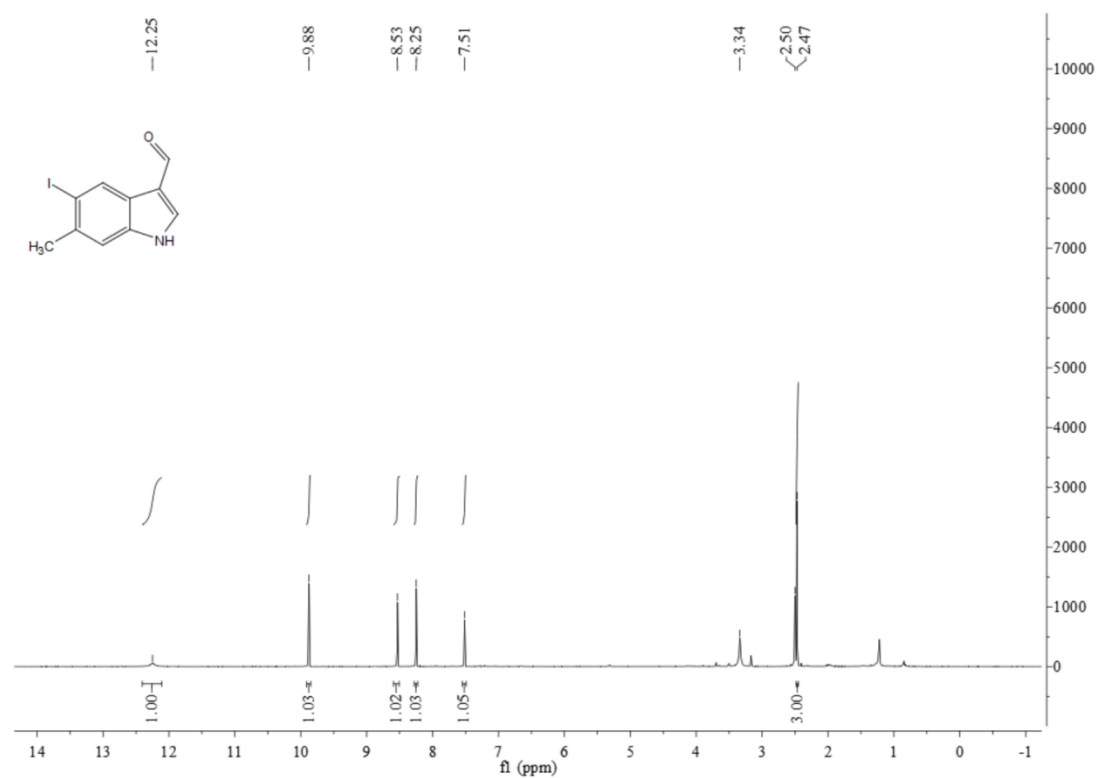
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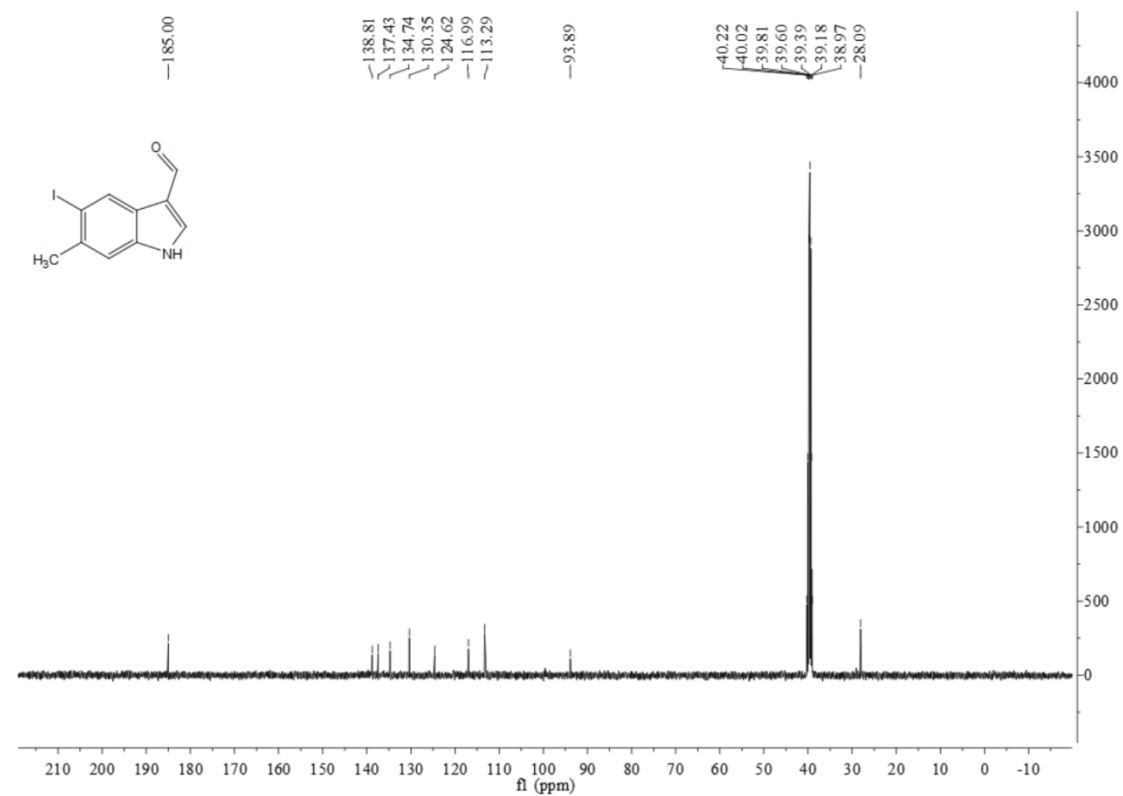
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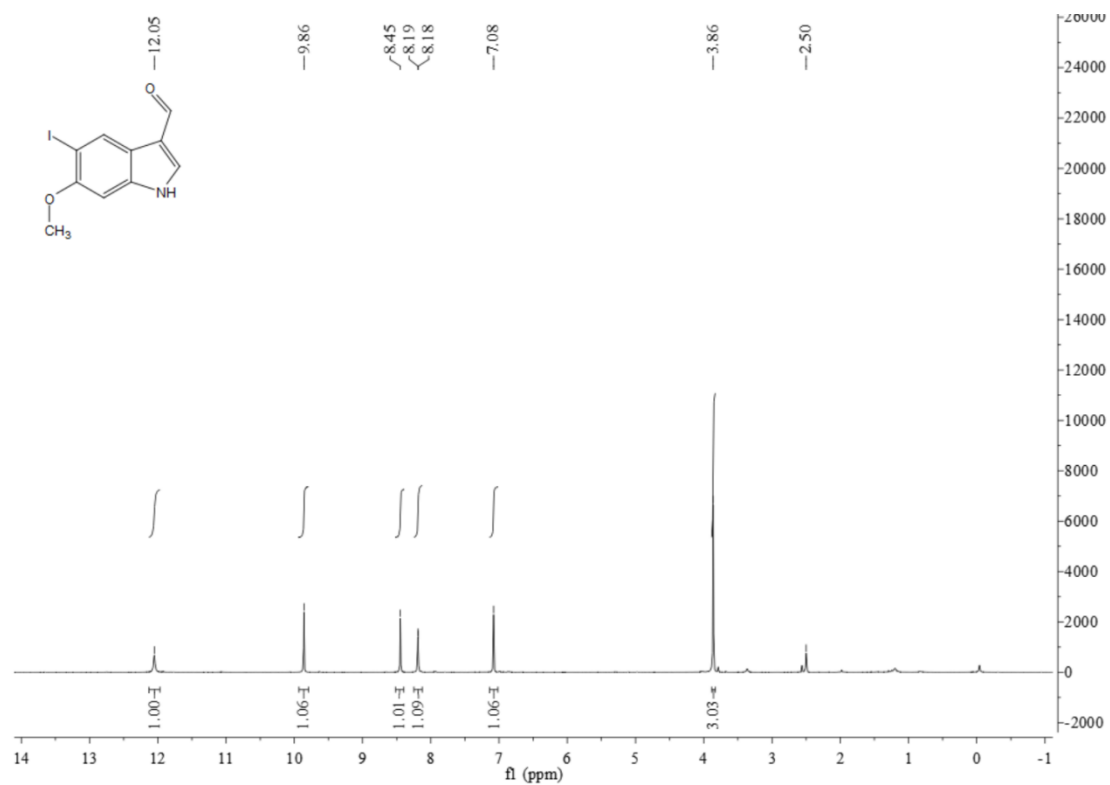
^1H NMR spectra of compound **3m**



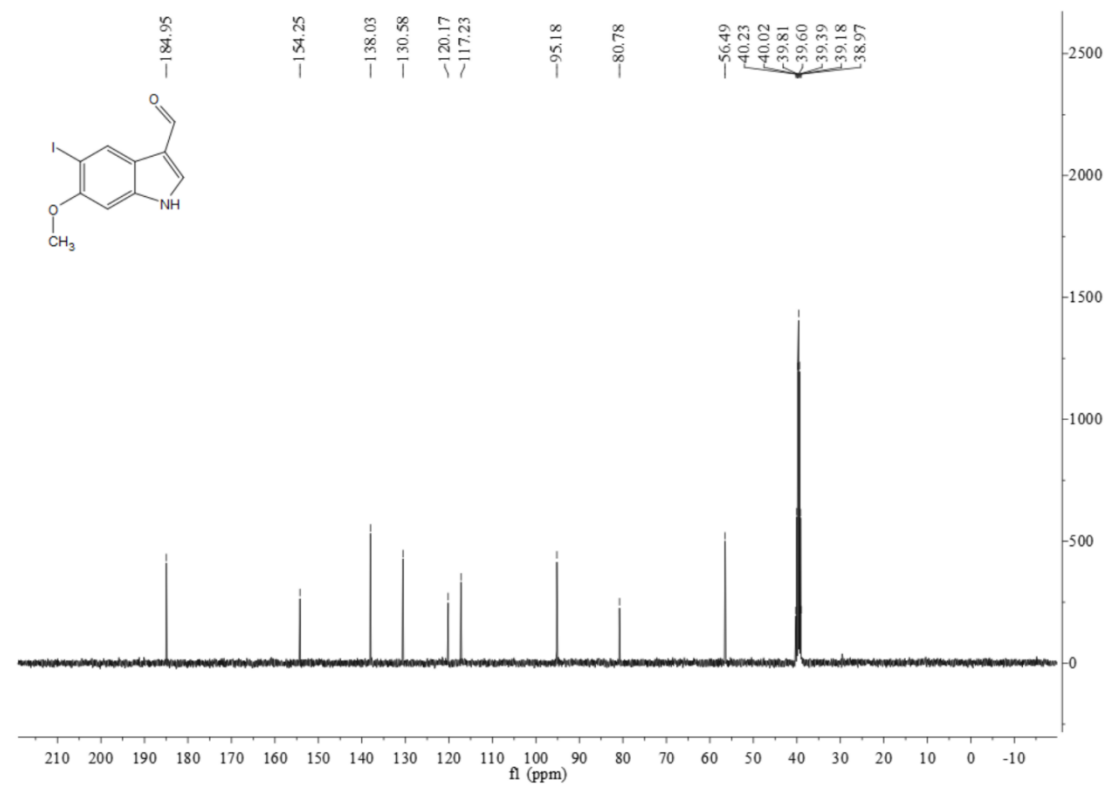
^{13}C NMR spectra of compound **3m**



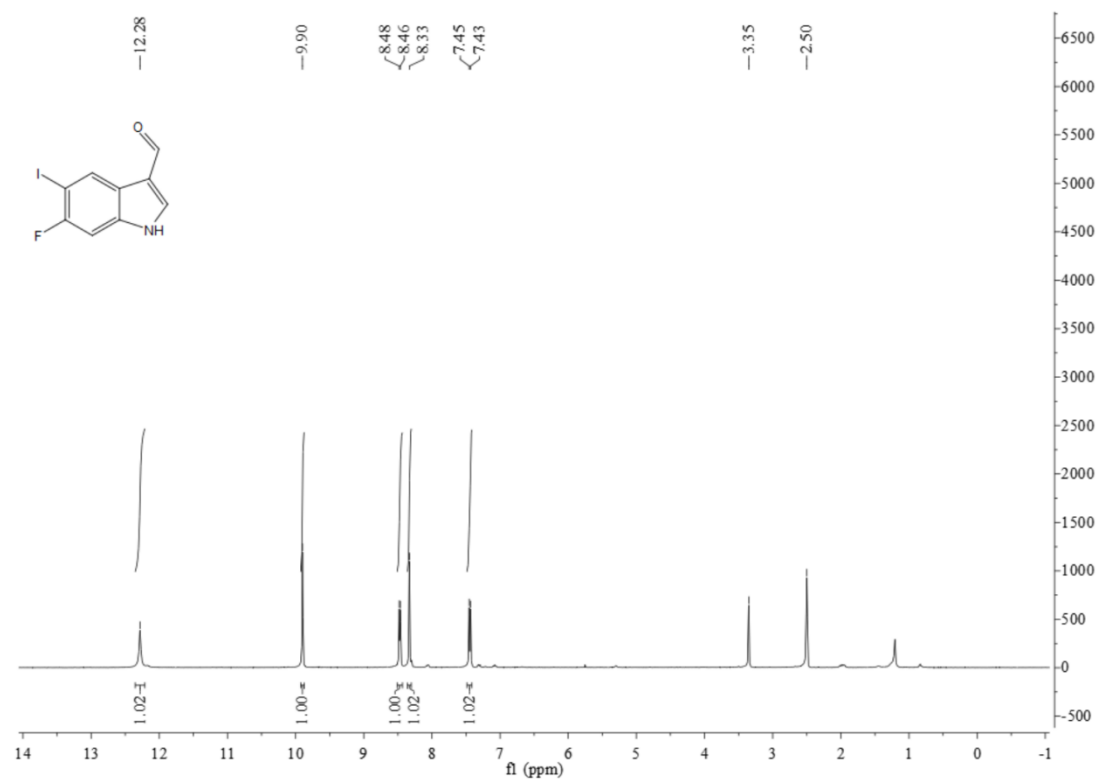
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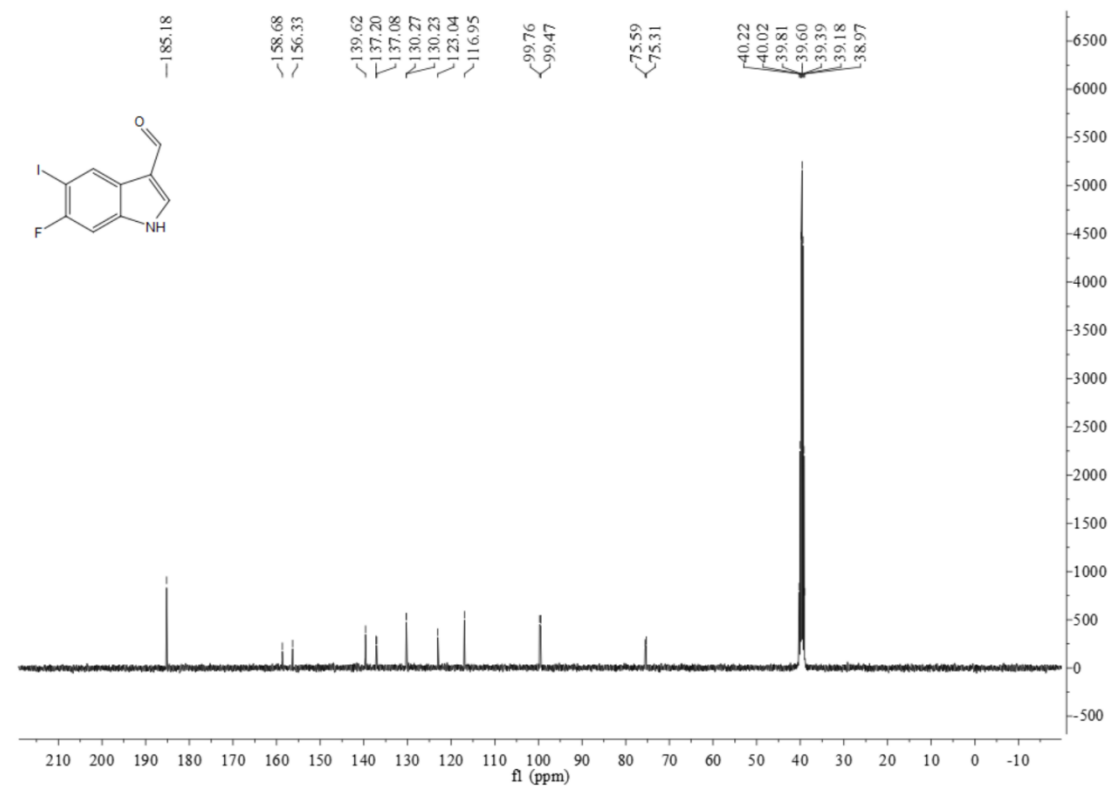
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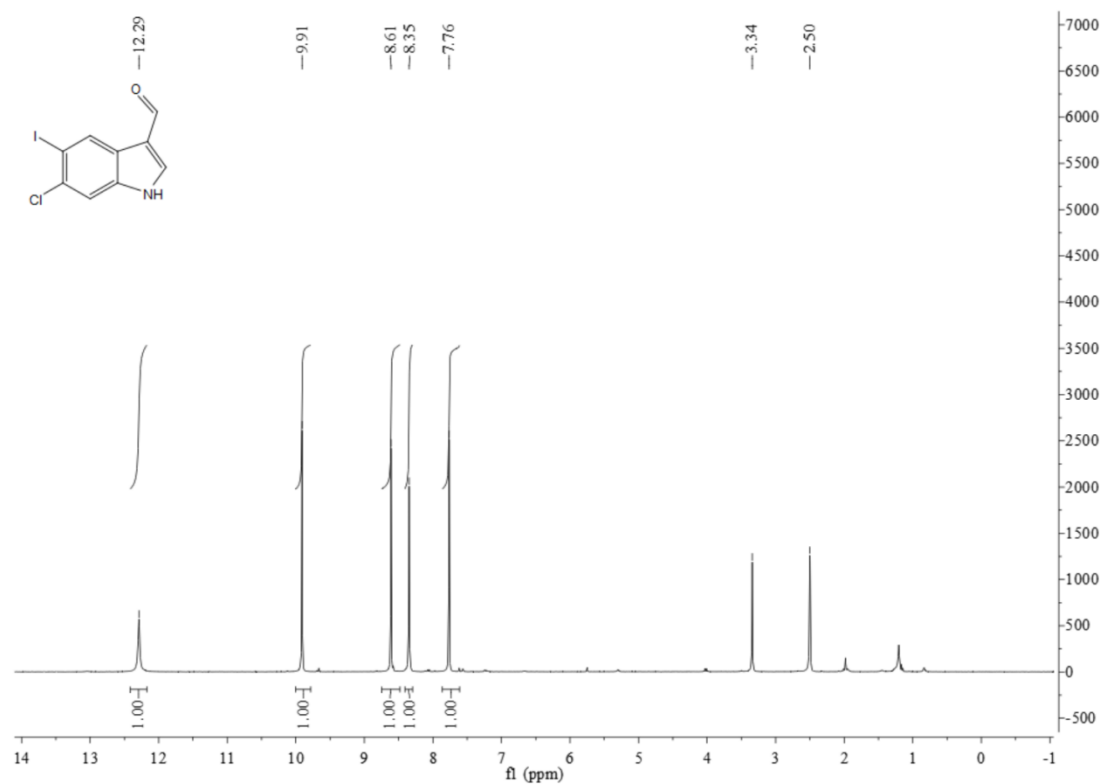
¹H NMR spectra of compound **3o**



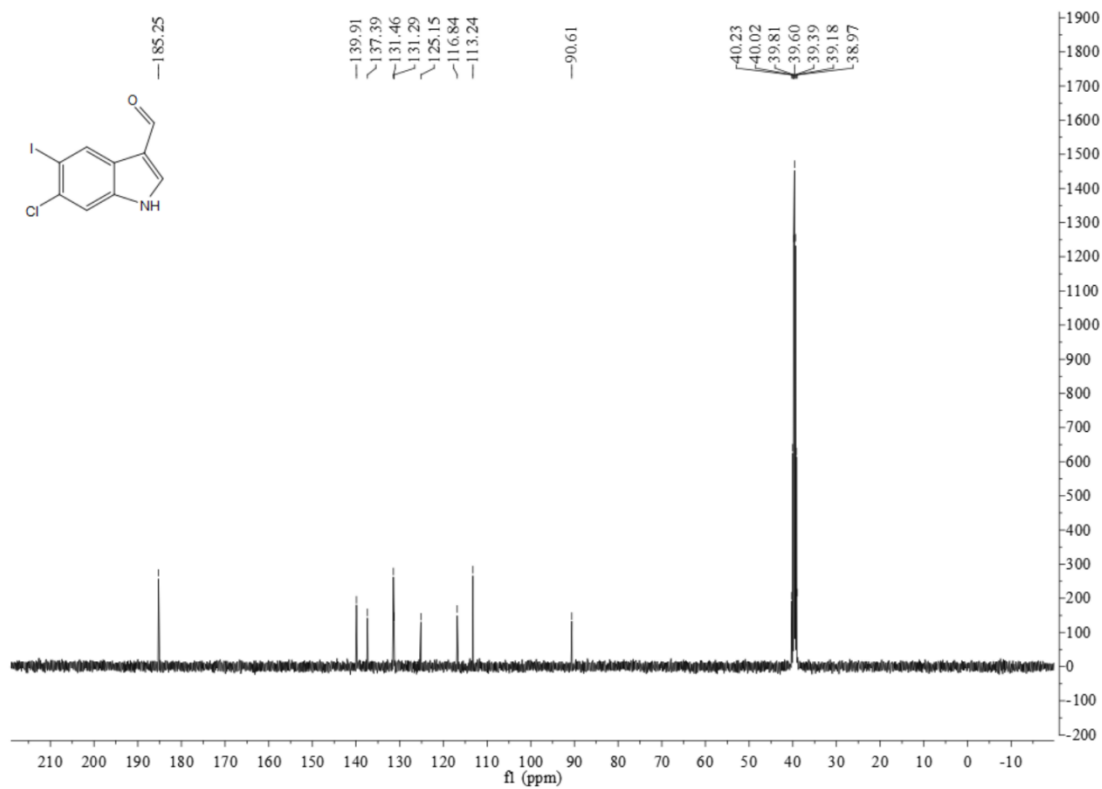
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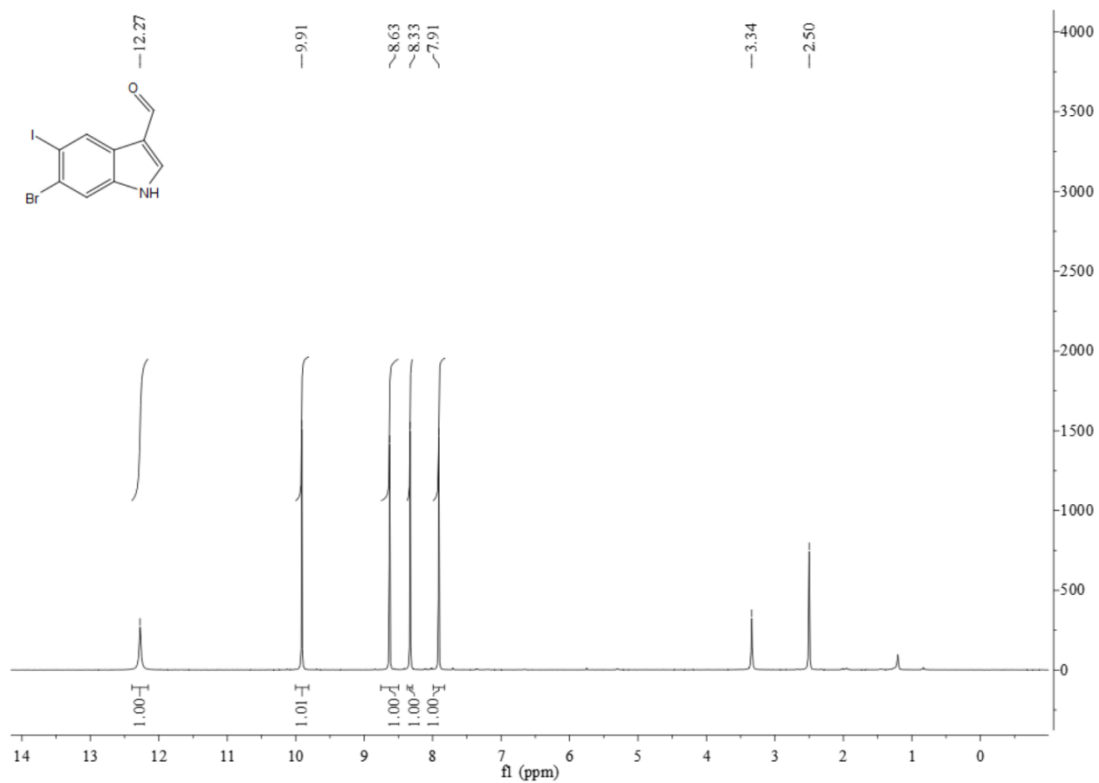
^1H NMR spectra of compound **3p**



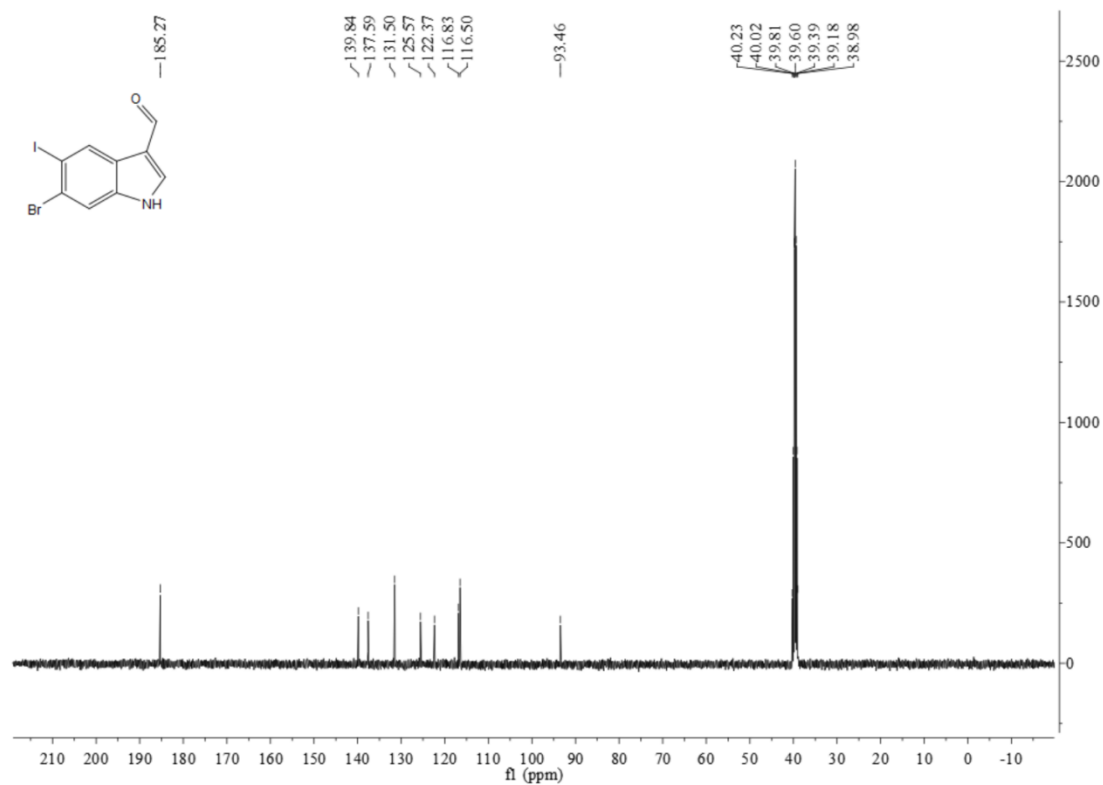
^{13}C NMR spectra of compound **3p**



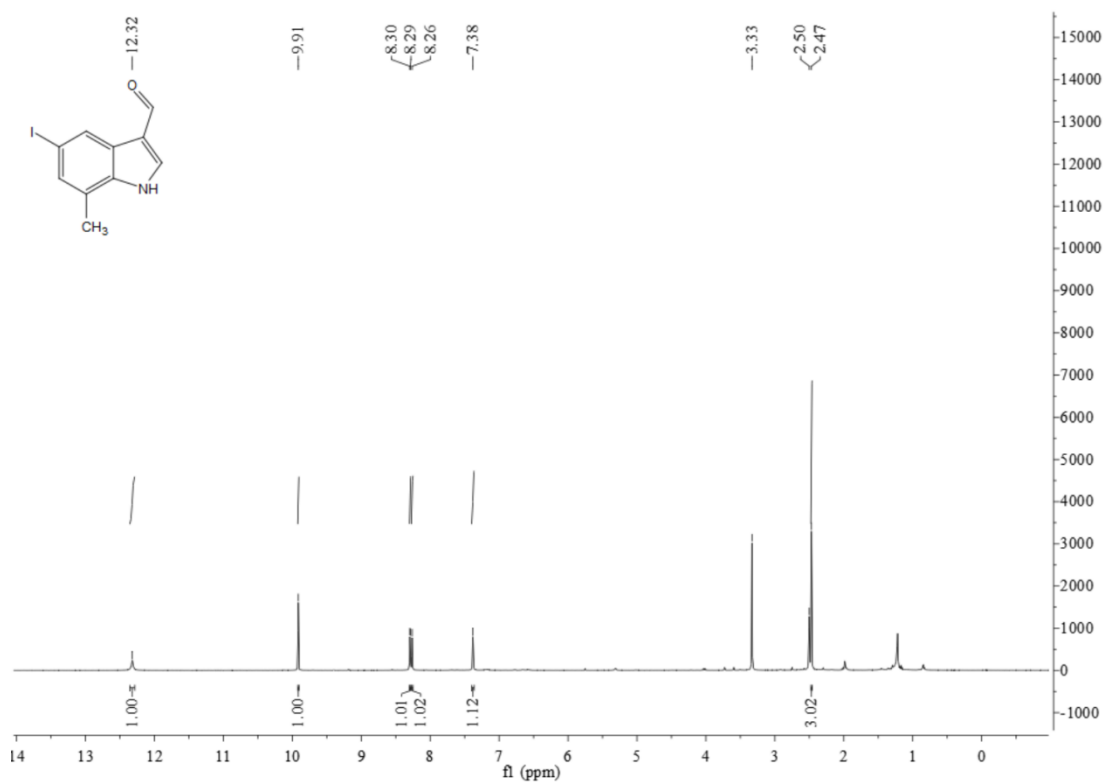
^1H NMR spectra of compound **3q**



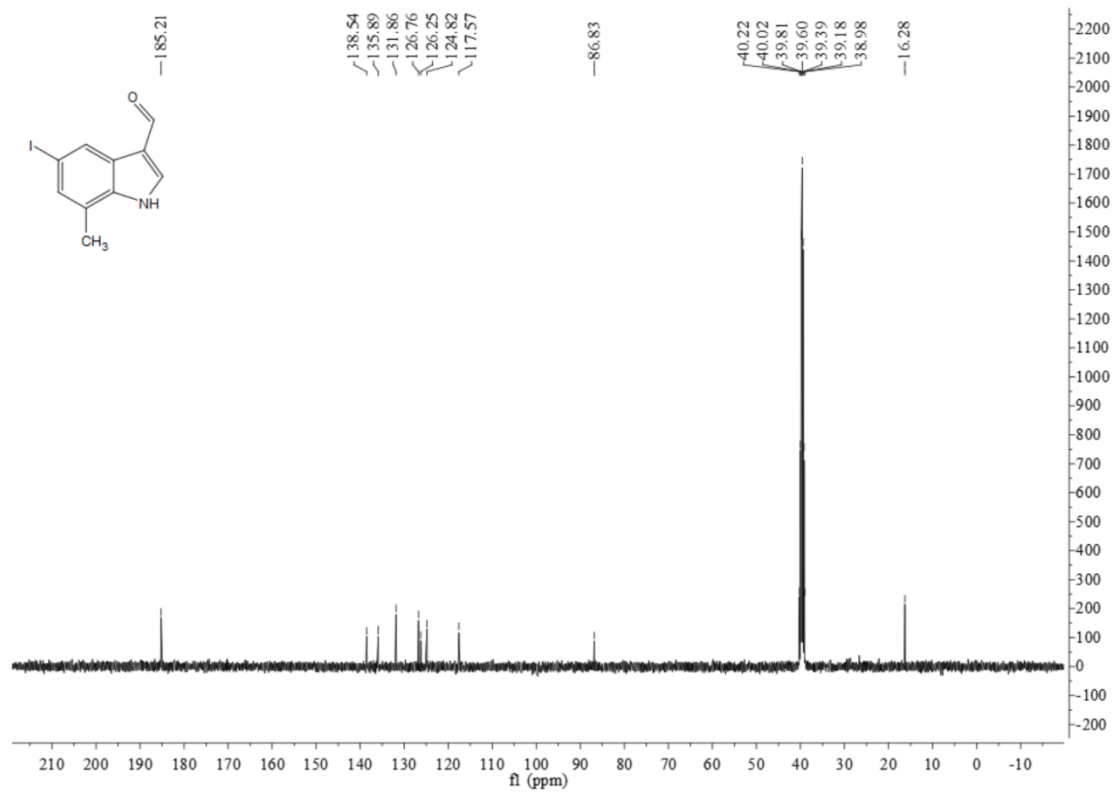
^{13}C NMR spectra of compound **3q**



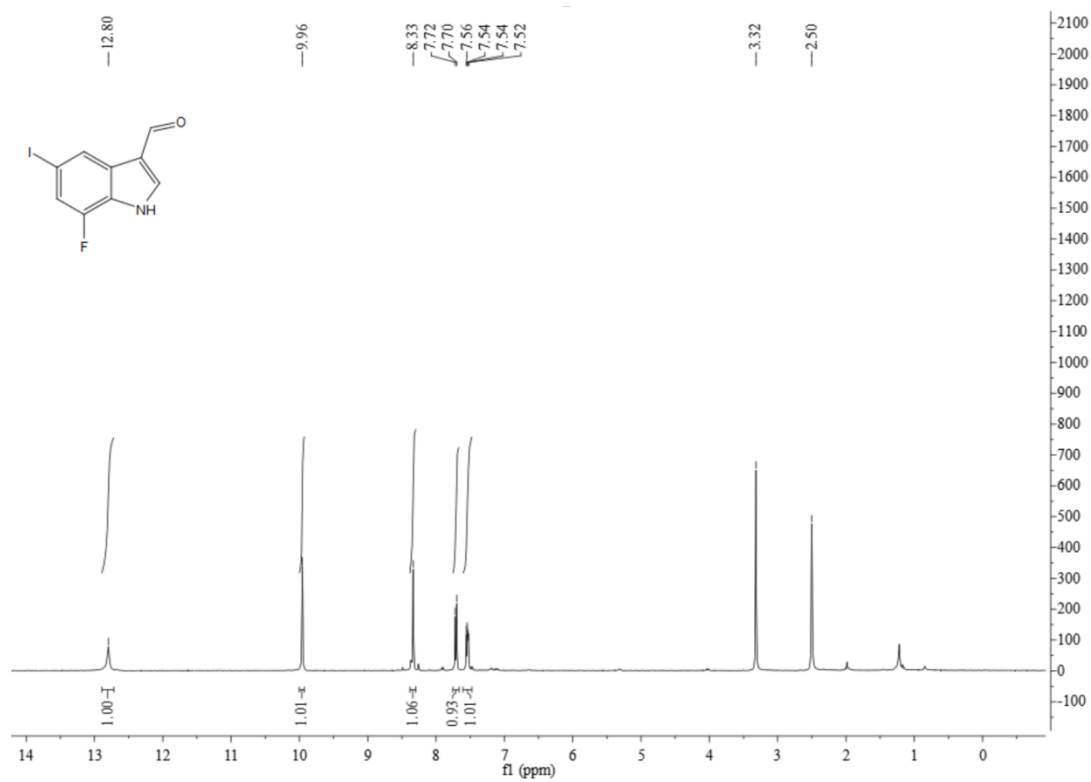
¹H NMR spectra of compound **3r**



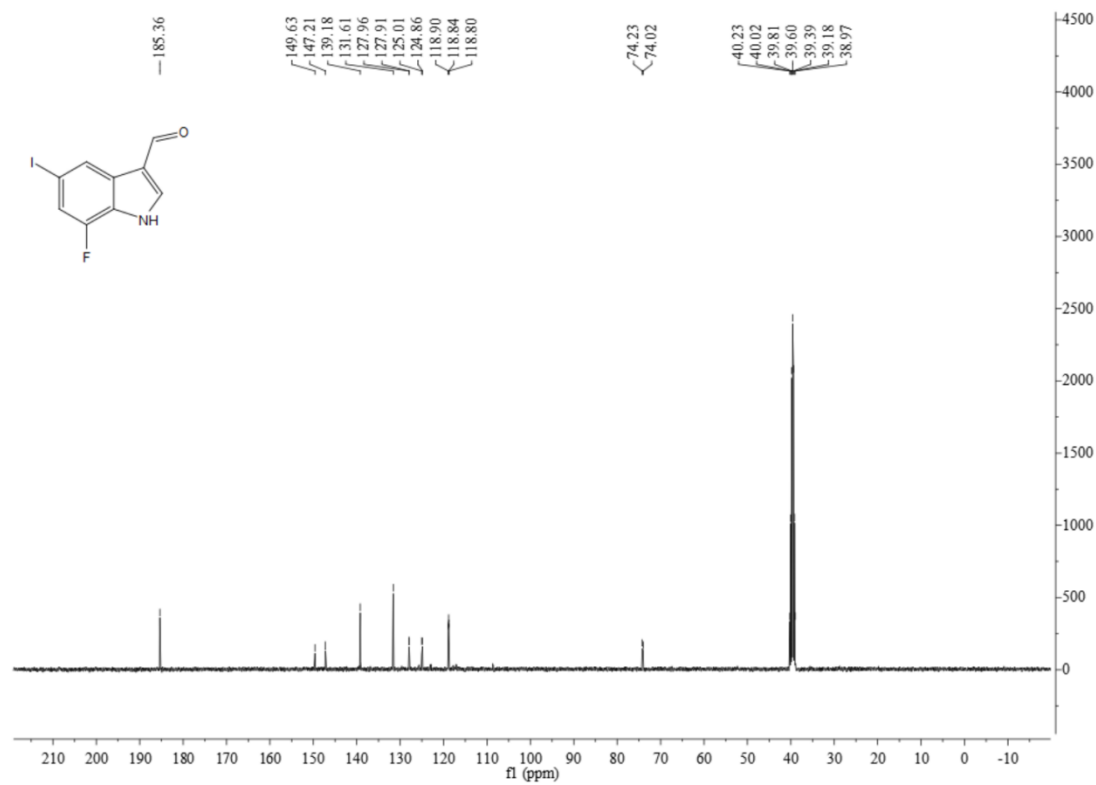
¹³C NMR spectra of compound **3r**



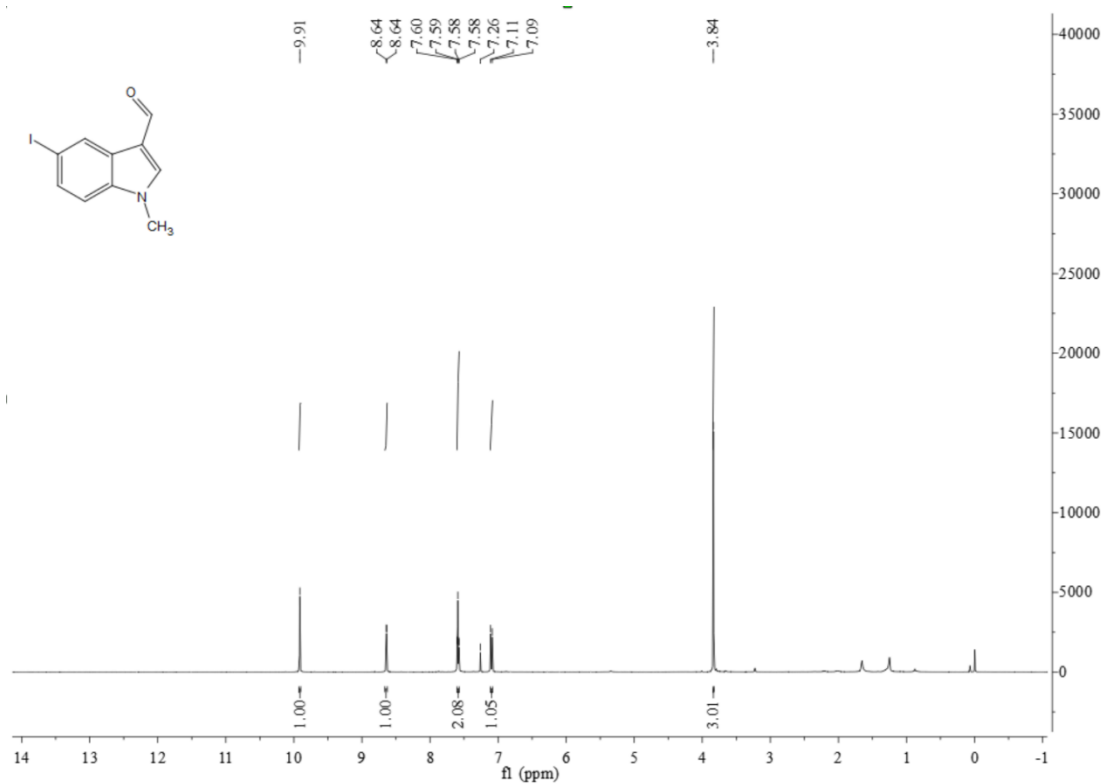
¹H NMR spectra of compound **3s**



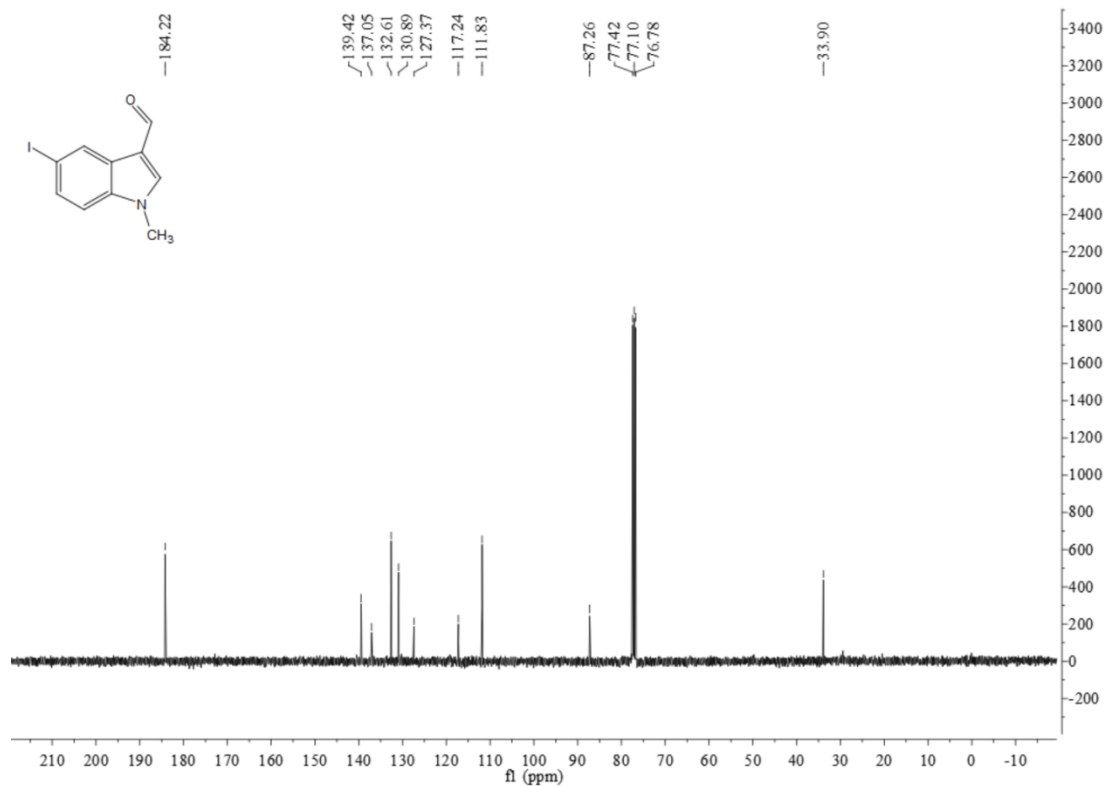
¹³C NMR spectra of compound **3s**



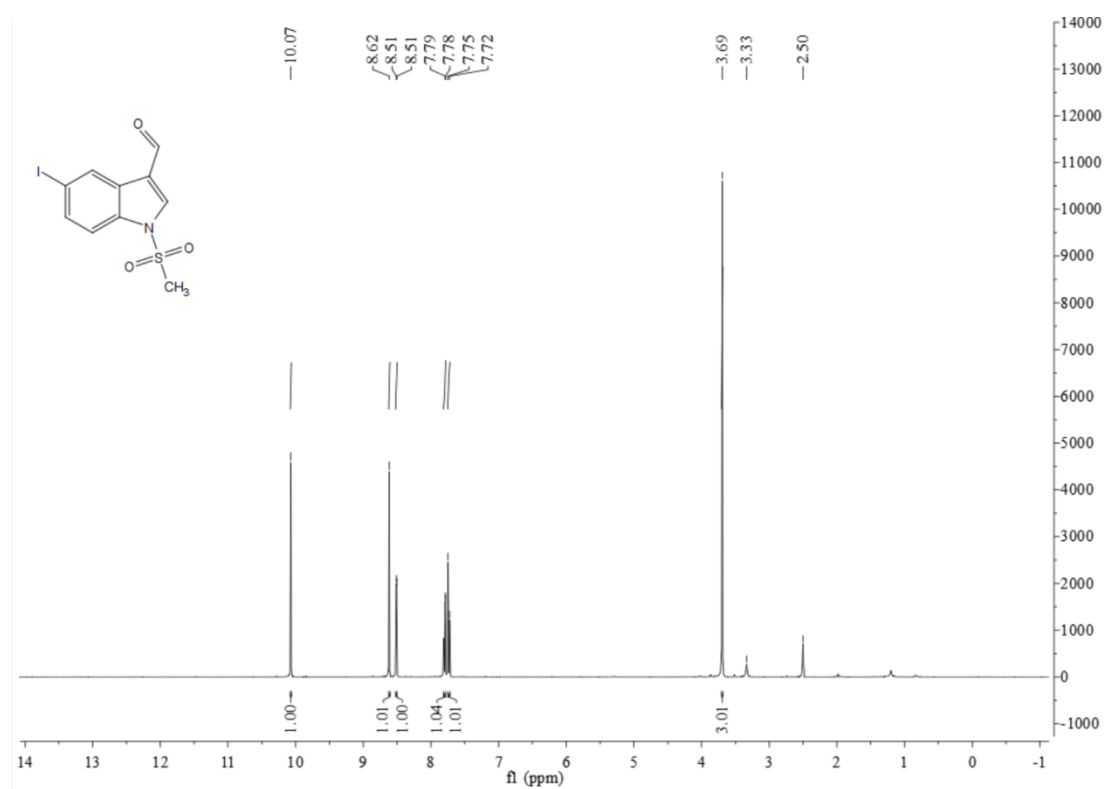
¹H NMR spectra of compound **3t**



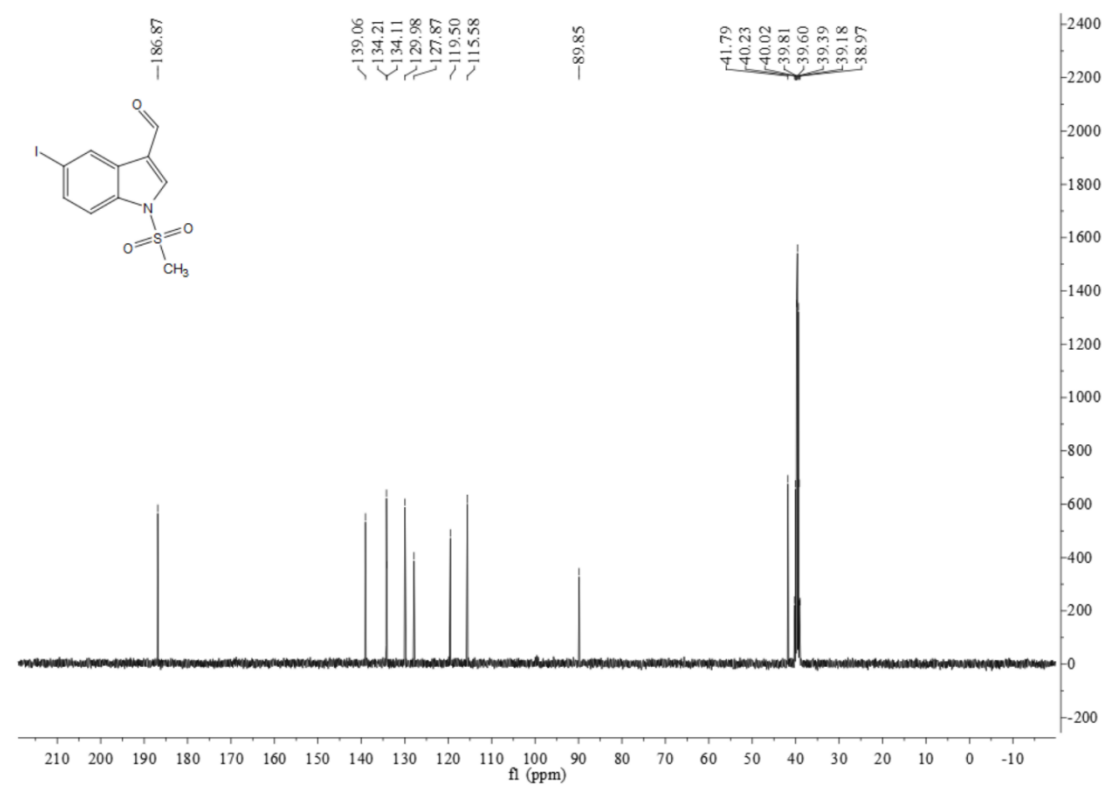
¹³C NMR spectra of compound **3t**



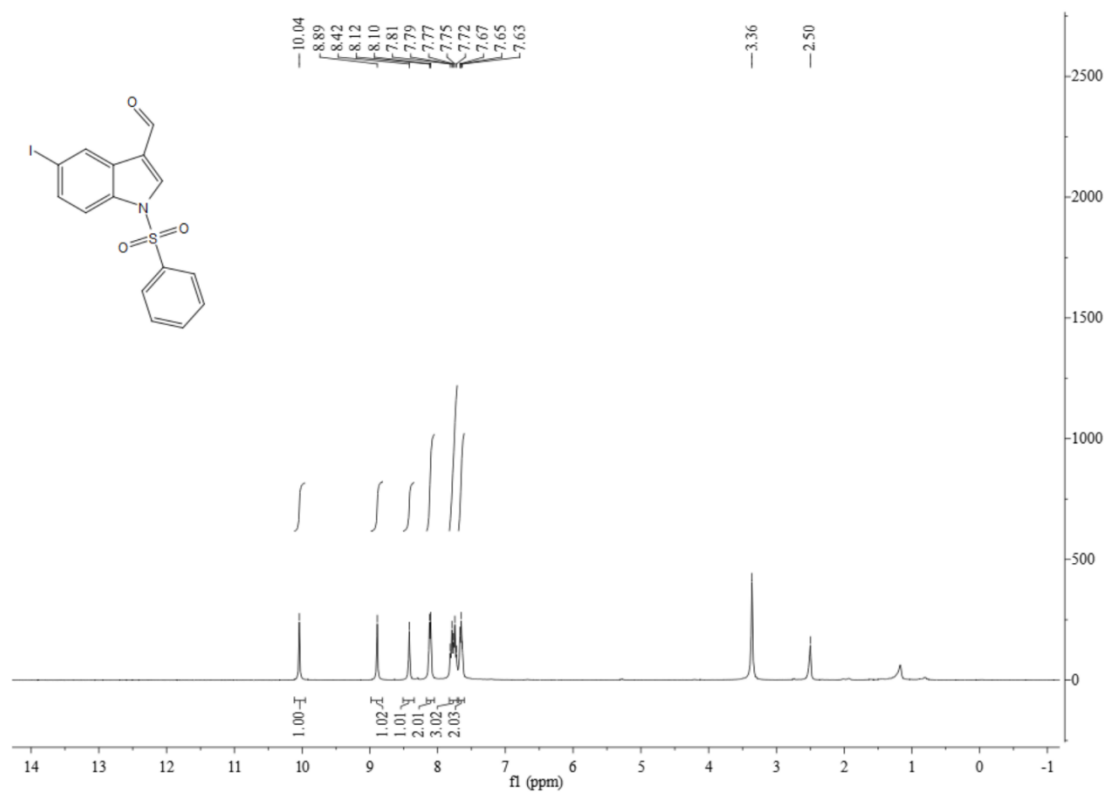
¹H NMR spectra of compound **3u**



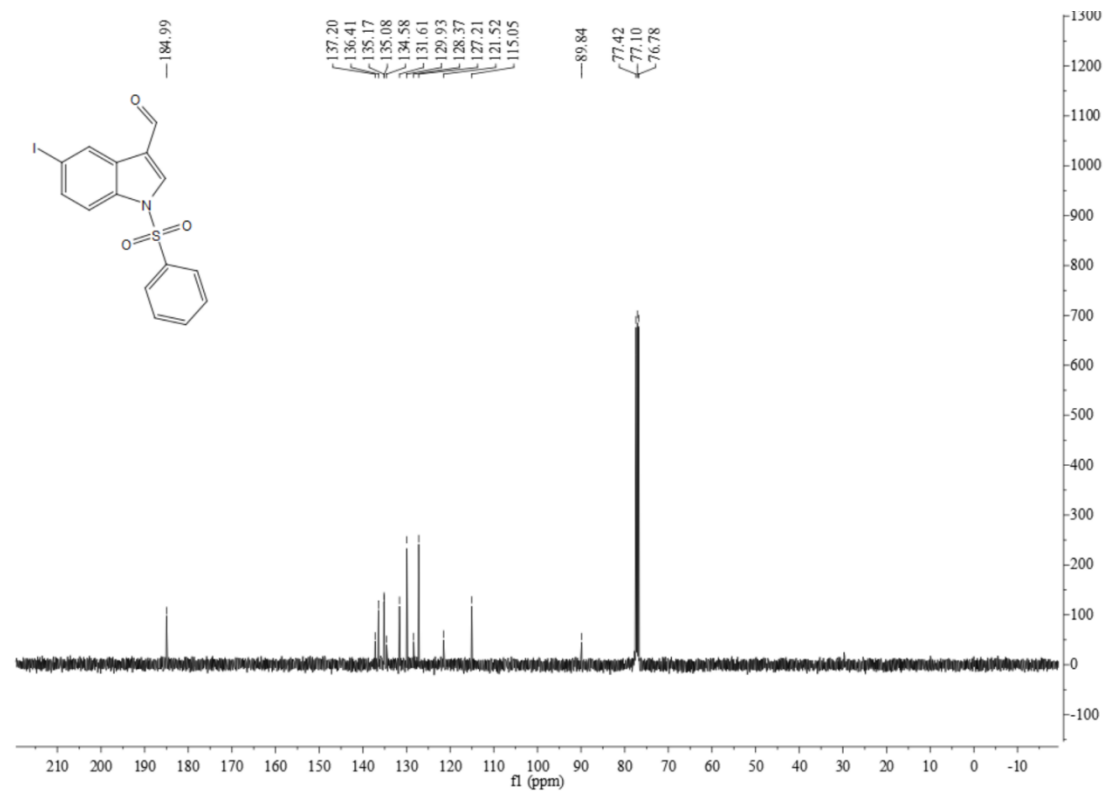
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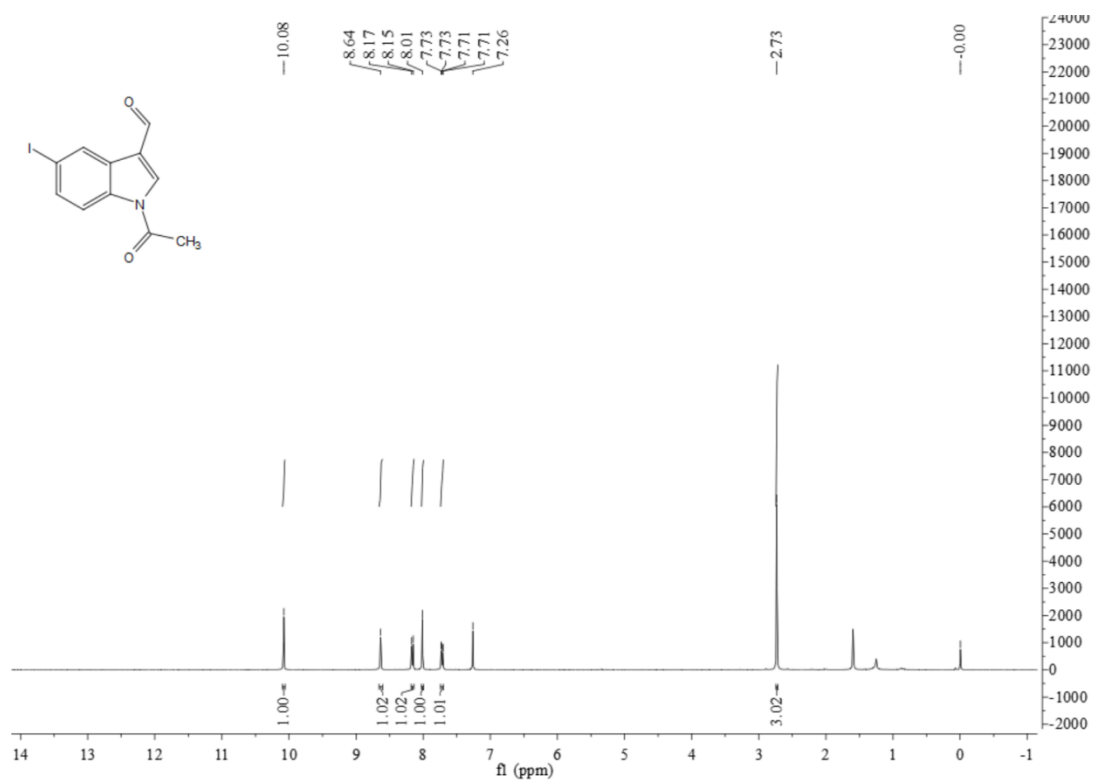
¹H NMR spectra of compound **3v**



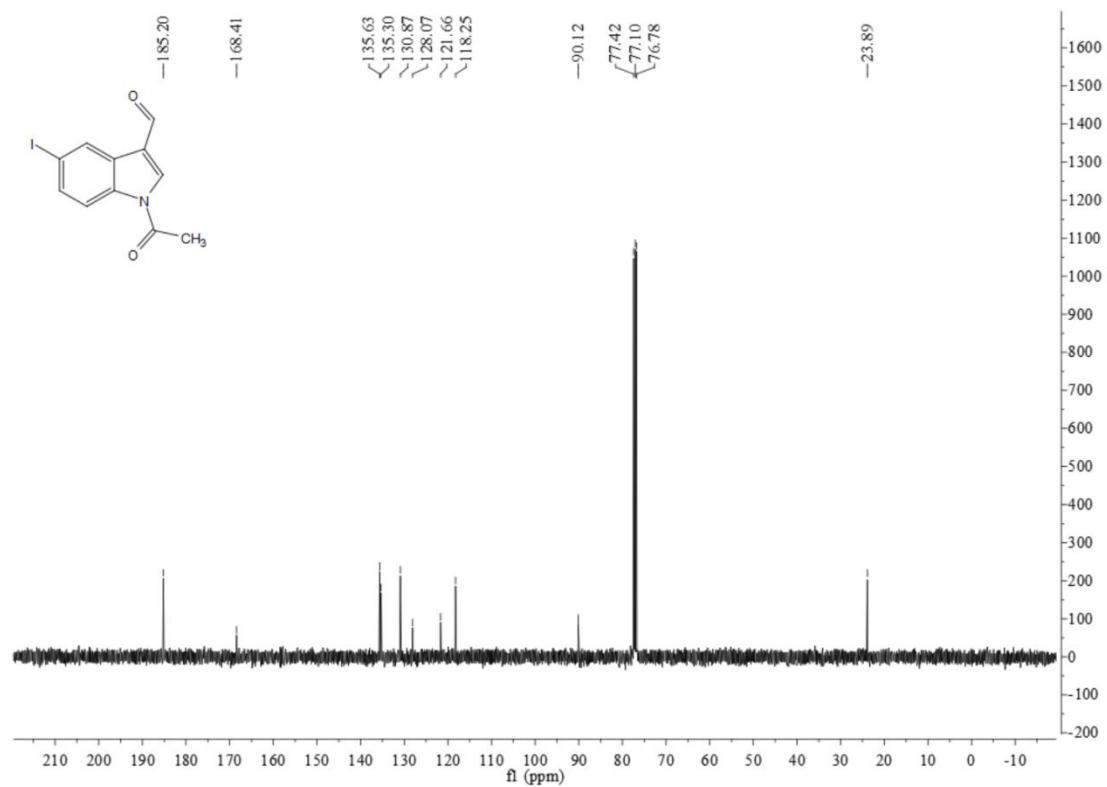
¹³C NMR spectra of compound **3v**



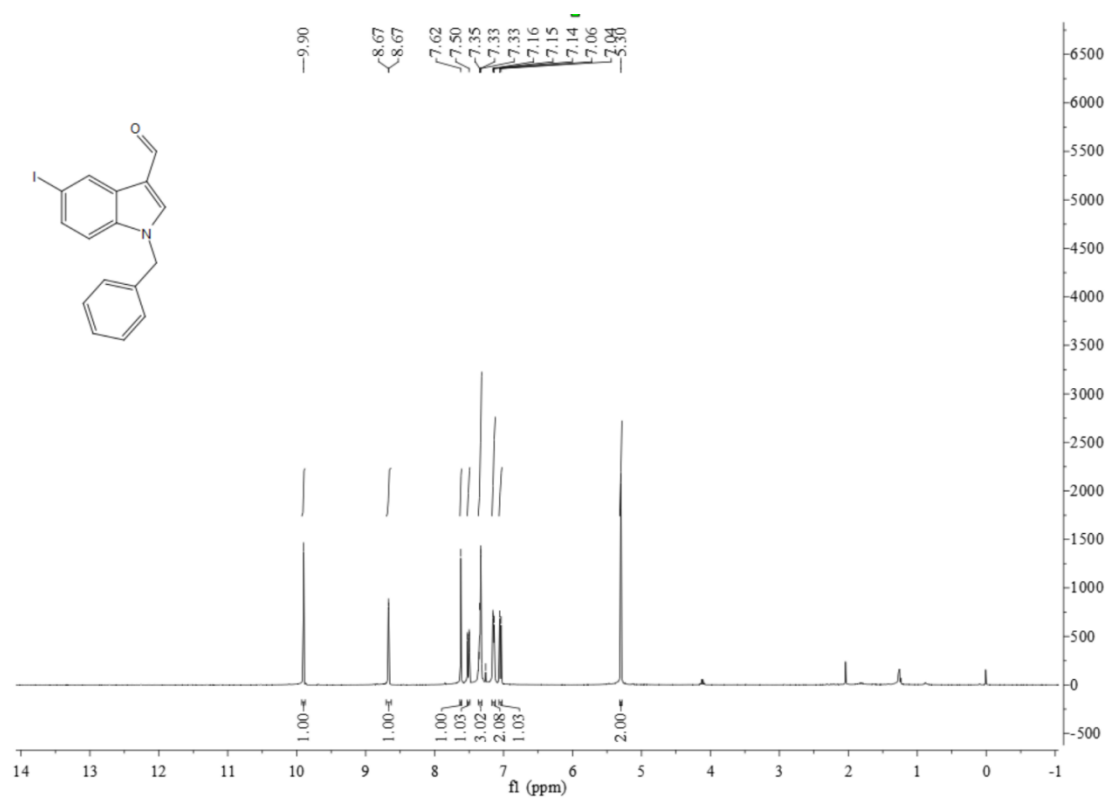
¹H NMR spectra of compound **3w**



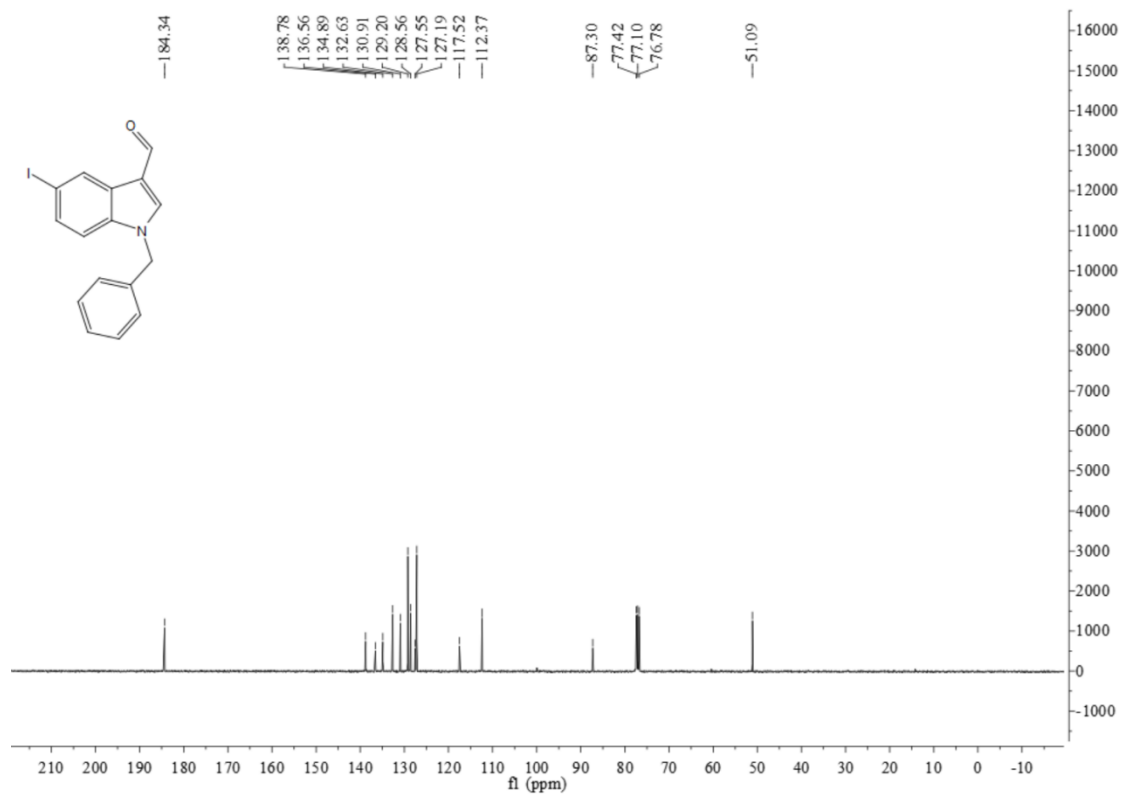
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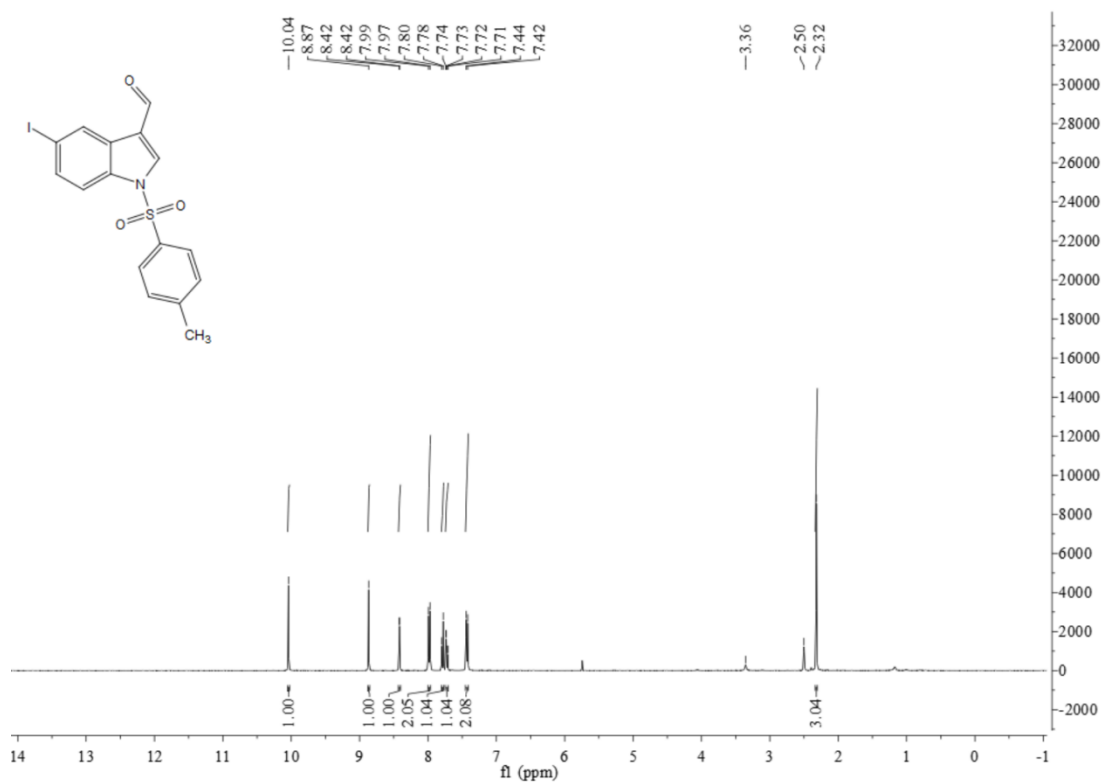
¹H NMR spectra of compound **3x**



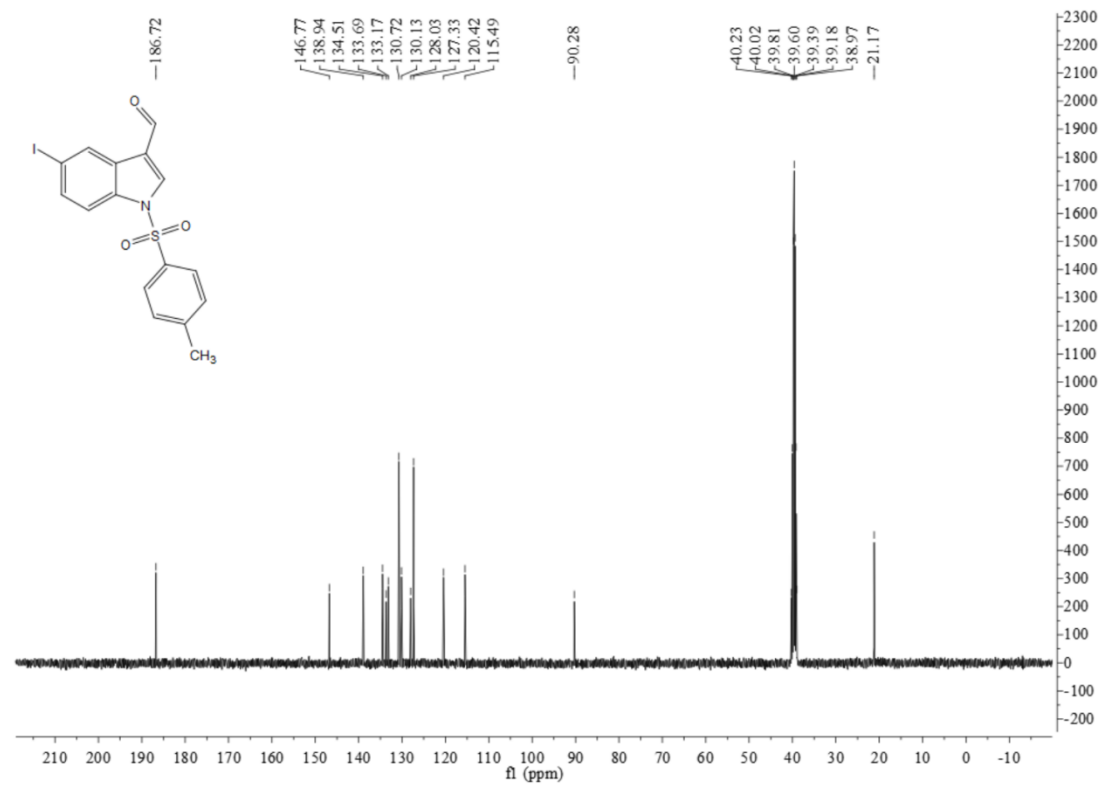
¹³C NMR spectra of compound **3x**



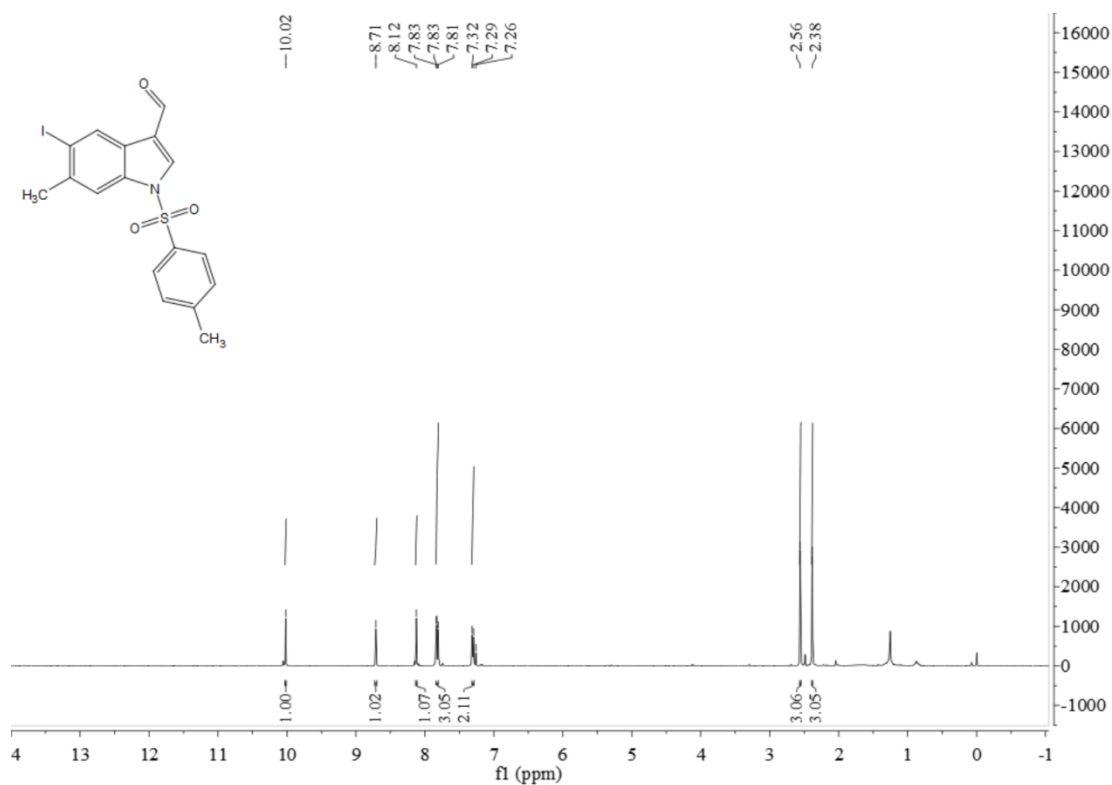
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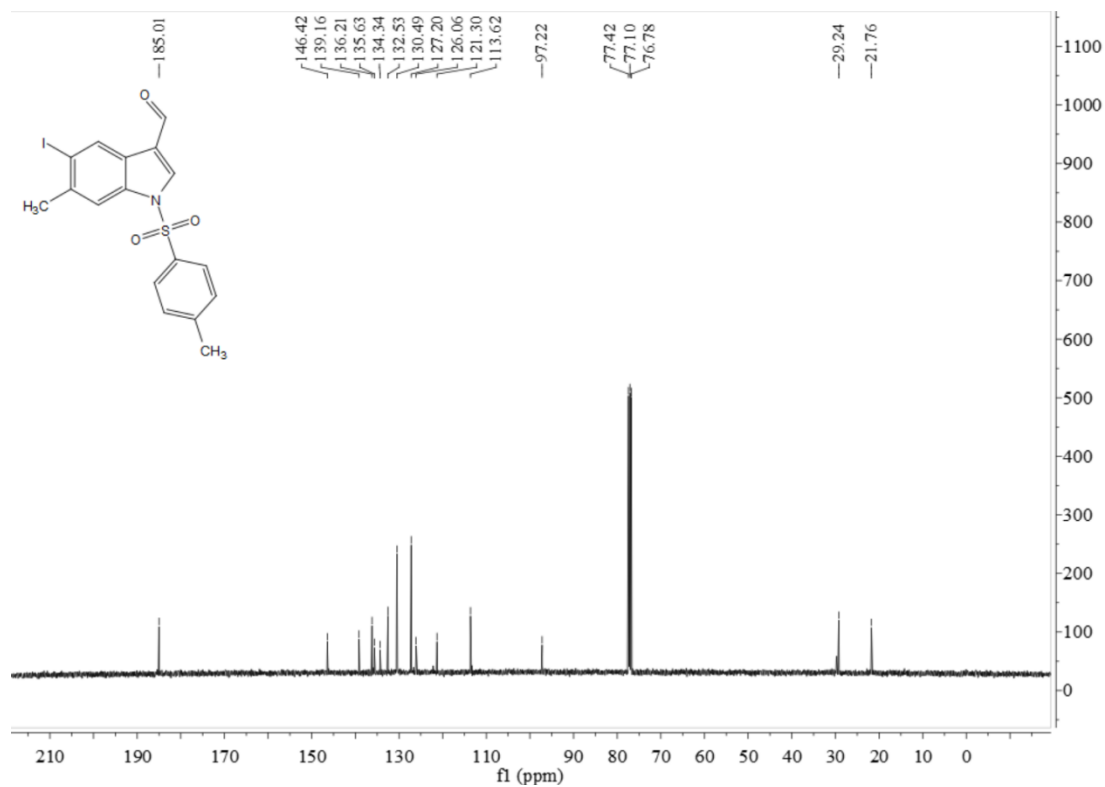
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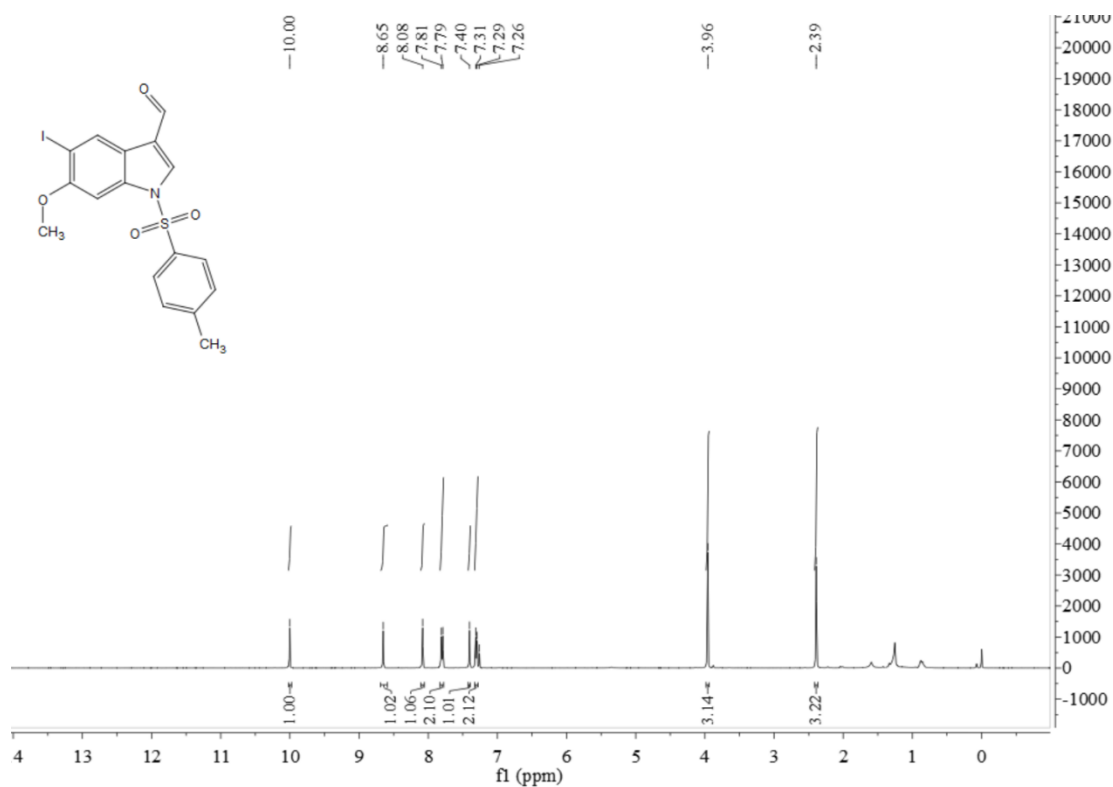
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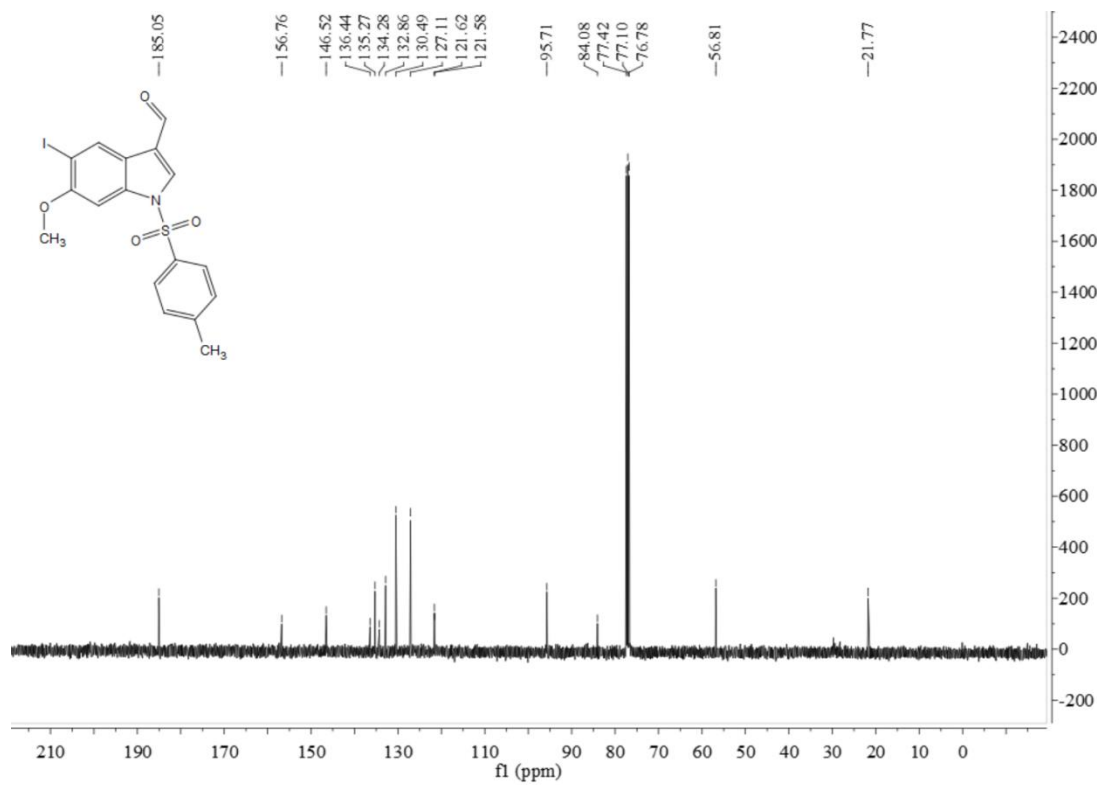
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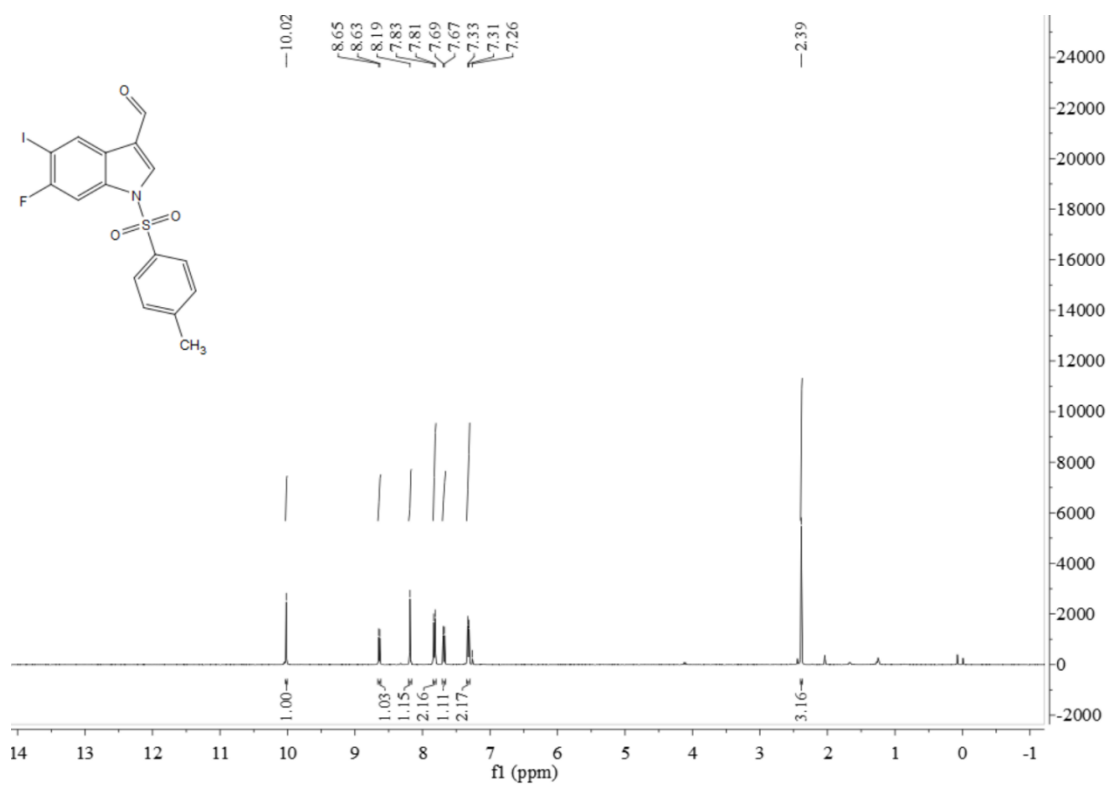
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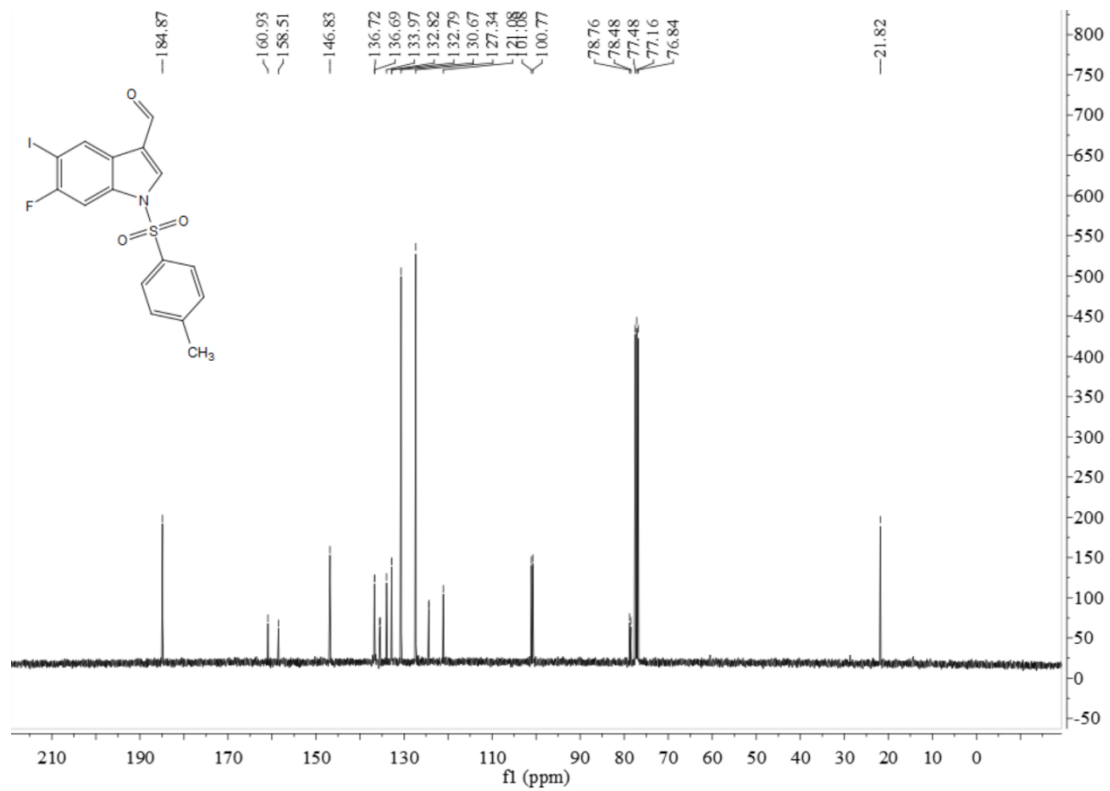
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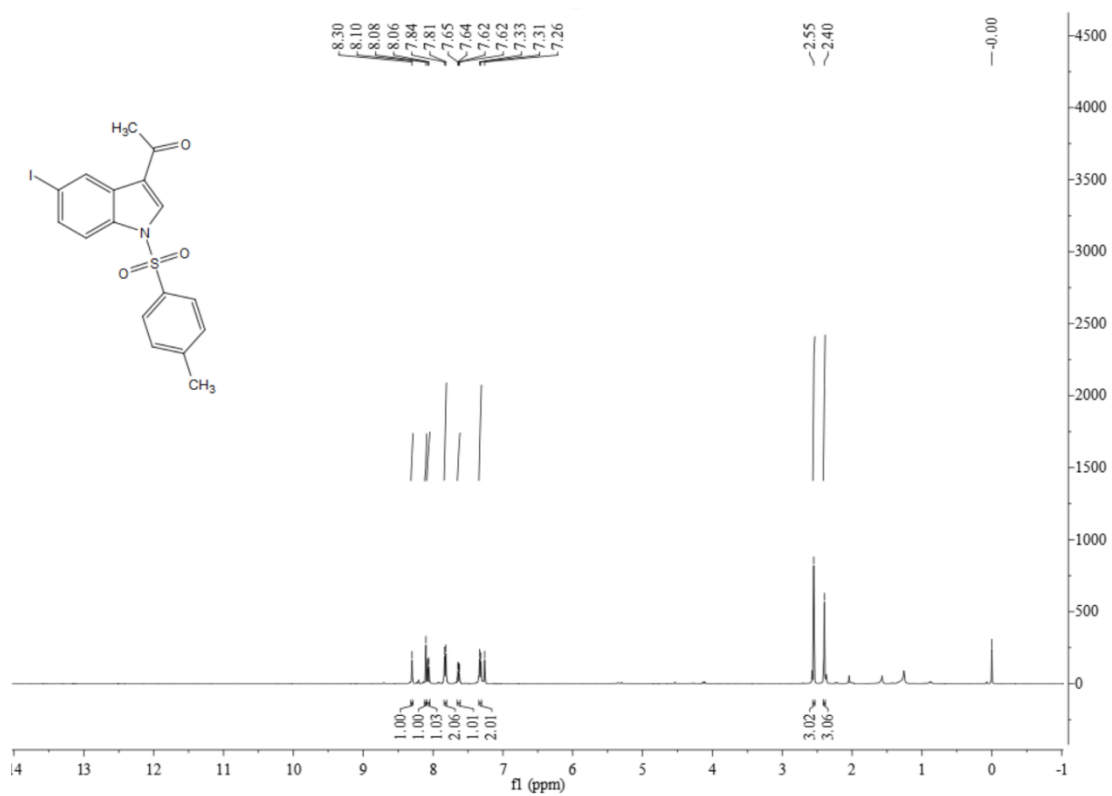
¹H NMR spectra of compound **3ab**



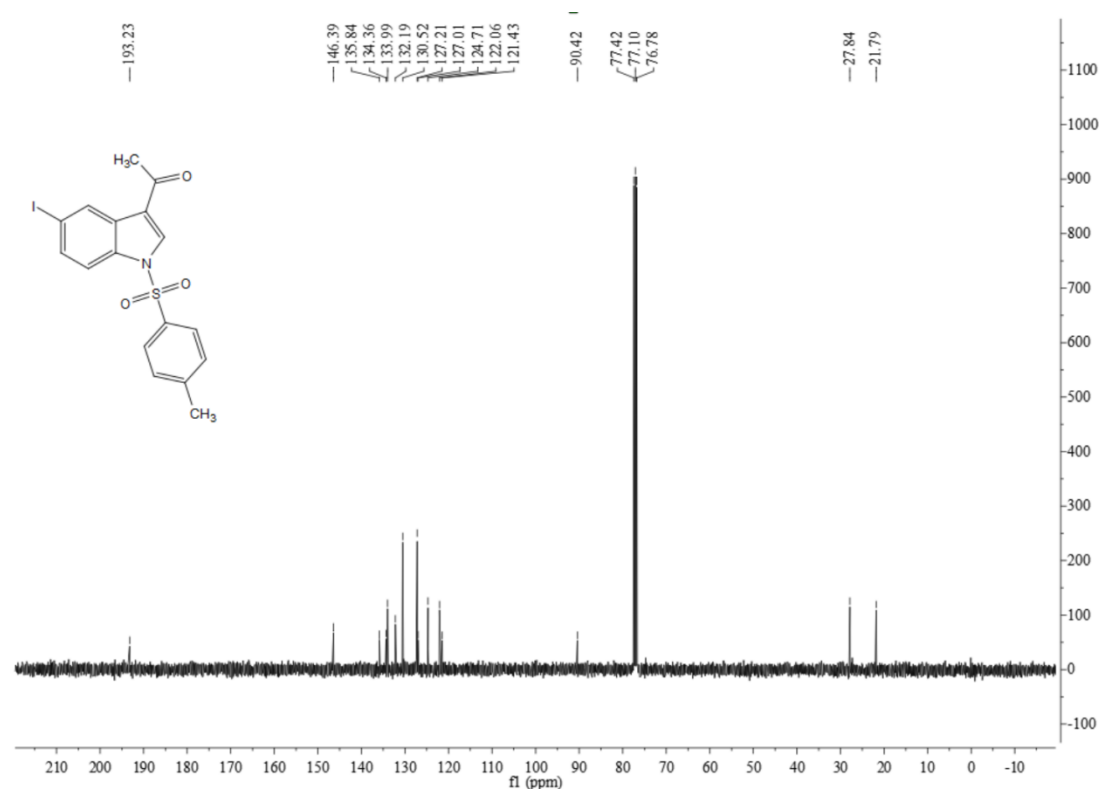
¹³C NMR spectra of compound **3ab**



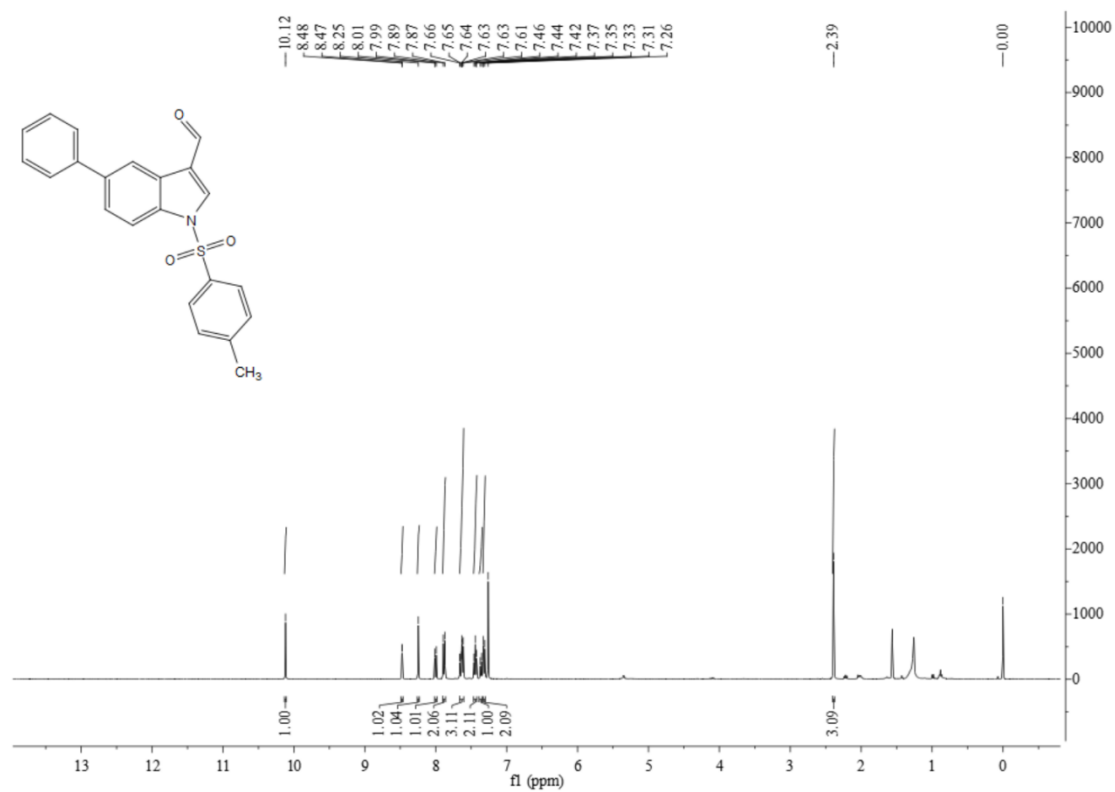
¹H NMR spectra of compound **3ac**



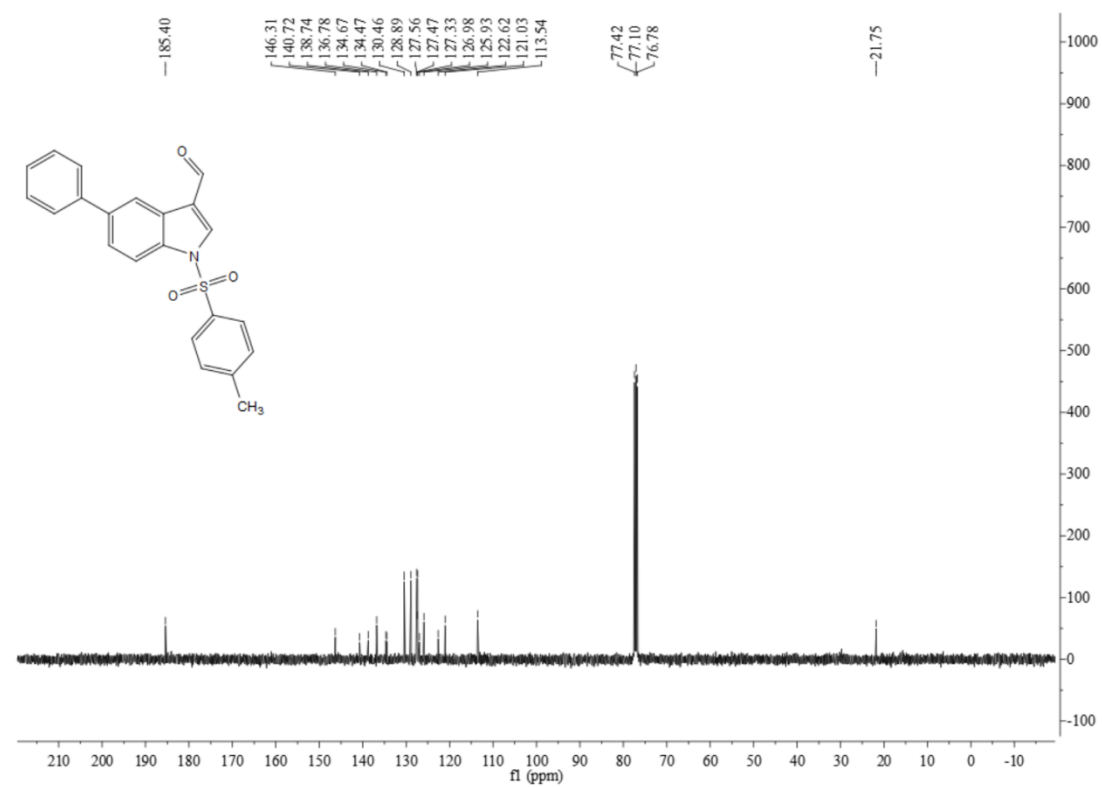
¹³C NMR spectra of compound **3ac**



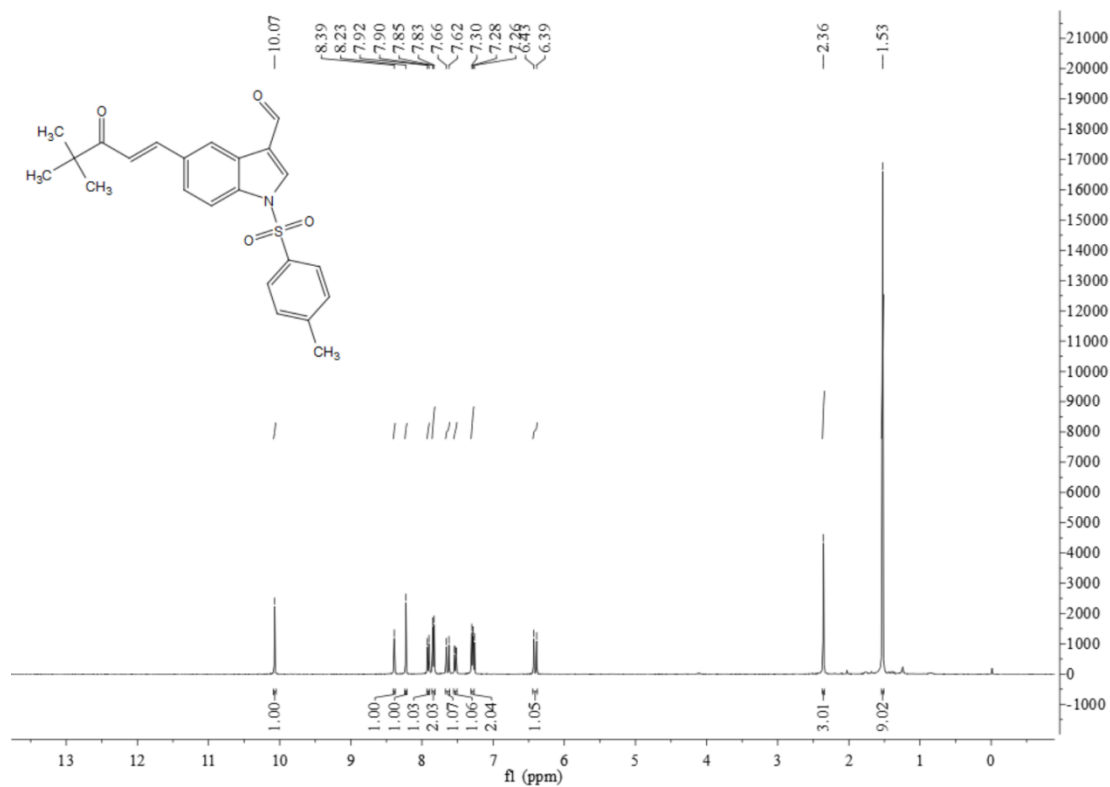
¹H NMR spectra of compound 4



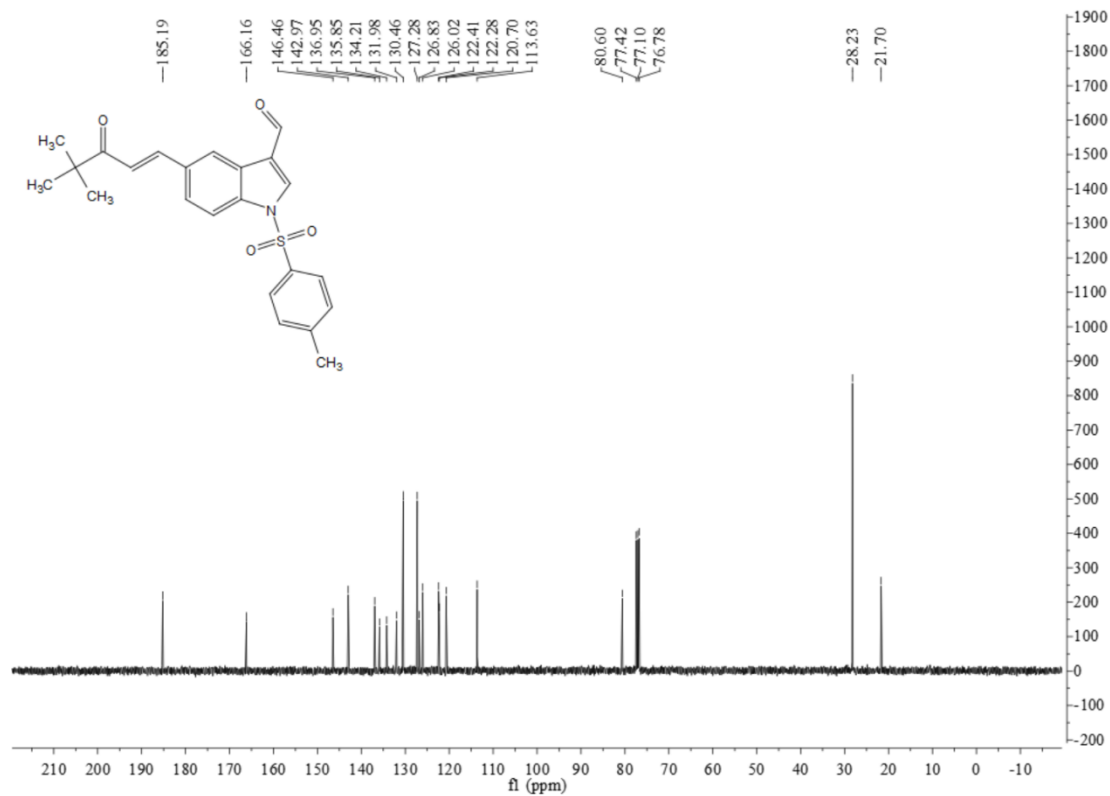
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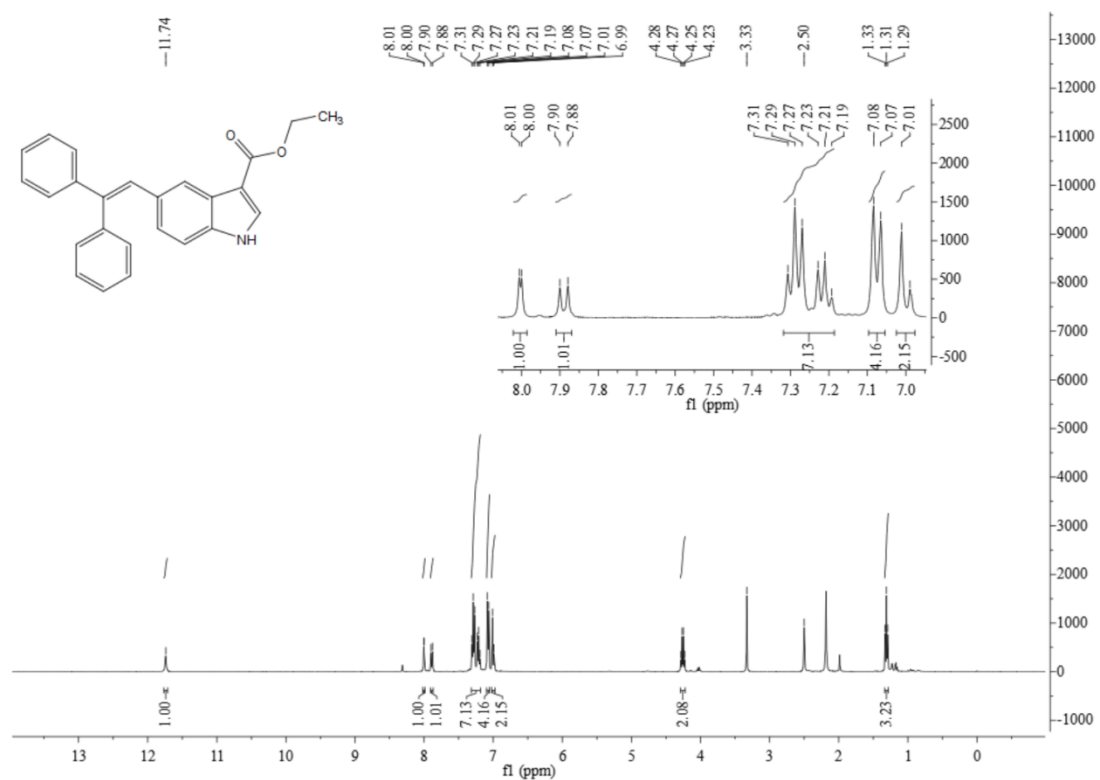
¹H NMR spectra of compound 5



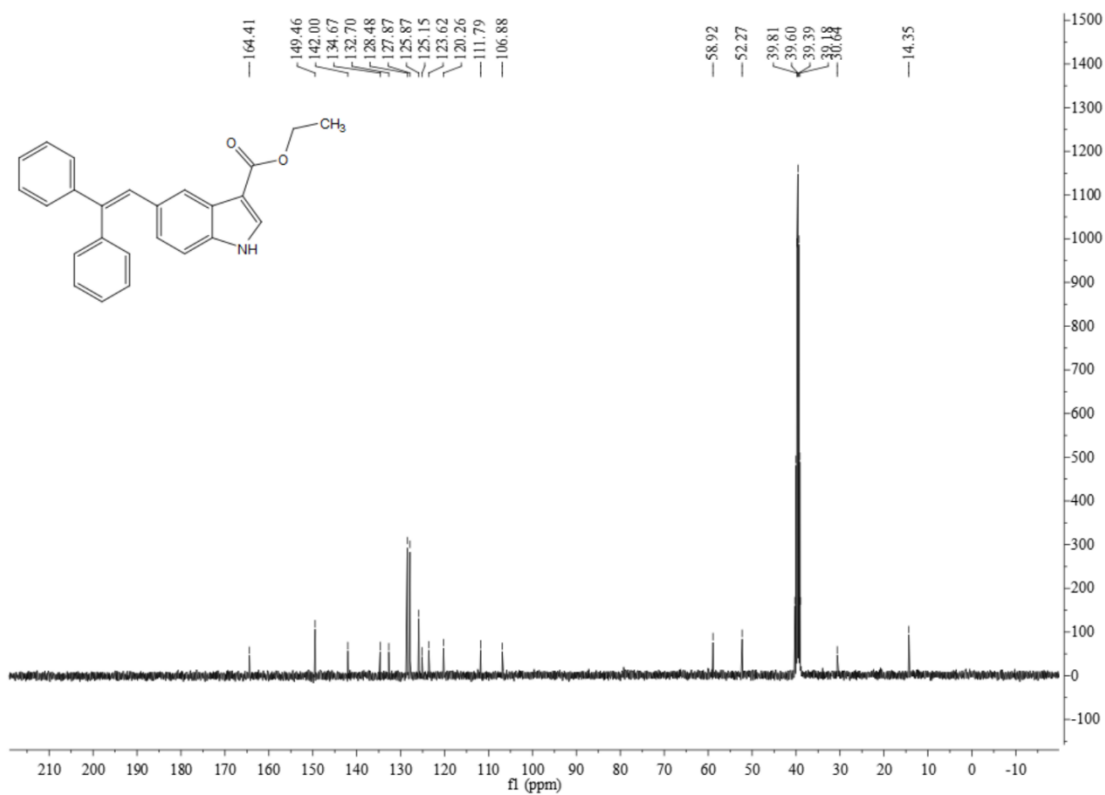
¹³C NMR spectra of compound 5



¹H NMR spectra of compound 6

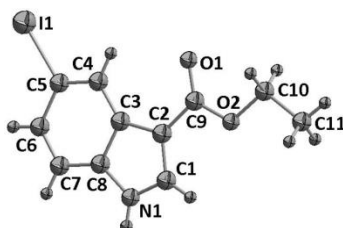


¹³C NMR spectra of compound 6



9. X-ray crystal structure of compounds 3g and 3k

X-ray Crystal Structure of ethyl 5-iodo-1H-indole-3-carboxylate (**3g**) (CCDC:2052806)



X-ray Crystal Structure of 7-iodo-4-methoxy-1H-indole-3-carbaldehyde (**3k**) (CCDC:2052807)

