Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Supporting Information

# Metal-Free $(Boc)_2O$-Mediated C4-Selective Direct Indolation of Pyridines Using TEMPO

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**CONTENTS**

## 1. General Methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for $^{1}H$ and $^{13}C$ NMR spectra. $CDCl_3$ or DMSO-*d6* was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. HRFABMS spectra were recorded on a FTMS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

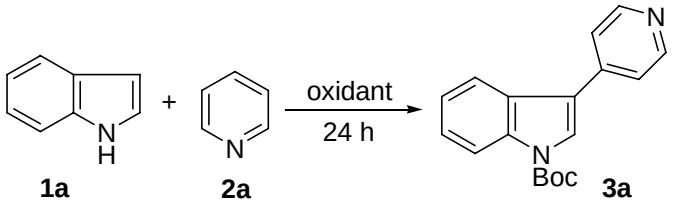
**Materials**

Commercially available starting materials and solvents were used as supplied, without further purification.

## 2. General Procedure and Characterization Data of the Products 3a-w, 4, 6b and 8a-c

### 2.1. More Details for the Model Reaction Optimization

**Table S1**. Optimization of Reaction Conditions[a]

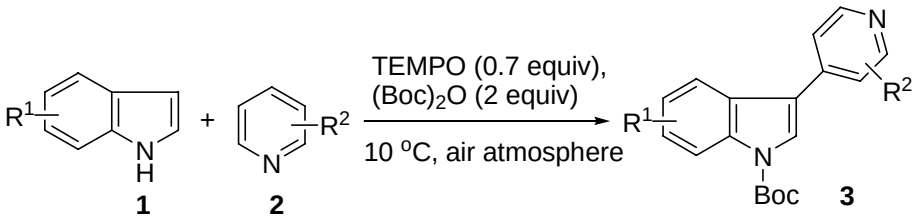



**1a** **2a** **3a**

| Entry | TEMPO (equiv) | $(Boc)_2O$ (equiv) | additive (equiv) | Temp. ($^{o}C$) | Solvent | Isolated yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | 0.3 | 2 | benzoic acid (0.3) | r.t. | - | 12 |
| 2 | 0.3 | 2 | *t*-BuOK (0.3) | r.t. | - | trace |
| 3 | 0.3 | 2 | 0 | r.t. | - | 35 |
| 4 | 0 | 2 | 0 | r.t. | - | trace |
| 5 | 0.3 | 2 | 0 | 0 | - | 36 |
| 6 | 0.3 | 2 | 0 | 10 | - | 45 |
| 7 | 0.3 | 2 | 0 | 35 | - | 23 |
| 8 | 0.3 | 2 | 0 | 45 | - | trace |
| 9 | 0.2 | 2 | 0 | 10 | - | 20 |
| 10 | 0.5 | 2 | 0 | 10 | - | 53 |
| 11 | 0.6 | 2 | 0 | 10 | - | 62 |
| **12** | **0.7** | **2** | **0** | **10** | **-** | **80** |
| 13 | 0.8 | 2 | 0 | 10 | - | 78 |
| 14 | 0.7 | 1 | 0 | 10 | - | 36 |
| 15 | 0.7 | 1.5 | 0 | 10 | - | 70 |
| 16 | 0.7 | 2.5 | 0 | 10 | - | 79 |
| 17 | 0.7 | 2 | 0 | 10 | benzene | trace |
| 18 | 0.7 | 2 | 0 | 10 | toluene | trace |
| 19 | 0.7 | 2 | 0 | 10 | DCM | trace |
| 20 | 0.7 | 2 | 0 | 10 | THF | trace |

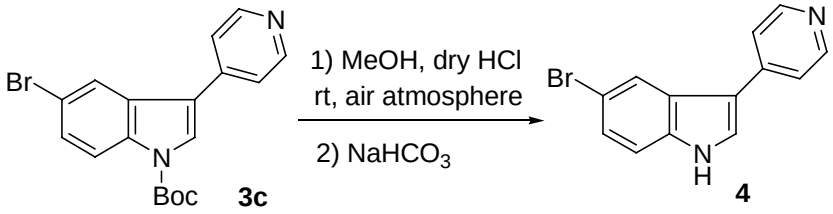
[a] Reaction conditions: indole (0.5 mmol), pyridine (0.8 mmol). [b] Isolated yield.

**2.2 General Procedure for the Indolation of Pyridines.**



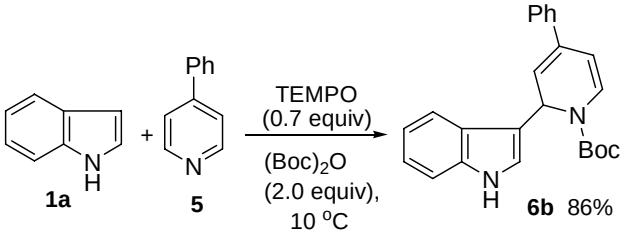

To a solution of indole (0.5 mmol) and TEMPO (0.35 mmol ) in pyridine (0.8 mmol) was added $(Boc)_2O$ (1.0 mmol) under air atmosphere and the mixture was stirred at 10 °C for 24-48 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product **3**.

**2.3 General Procedure for the Synthesis of 4.**



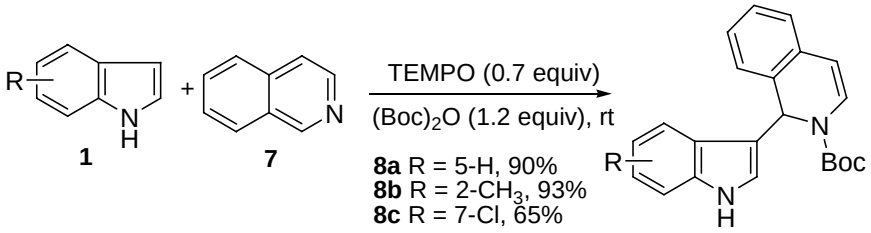

To a solution of **3c** (75 mg, 0.2 mmol) in THF (1 mL) was added a methanolic solution of hydrochloric acid (0.2 mL) at 0 °C under air atmosphere. It was stirred for 2 h at room temperature and quenched with saturated aq. $NaHCO_3$ (1 mL) and water (5 mL). It was extracted with ethyl acetate (8 mL × 3). Combined organic layer was washed with brine and dried over $Na_2SO_4$. Concentration of organic layer in vacuo. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:2) to give the corresponding product **4** (49 mg, 90%).

**2.4 General Procedure for the Synthesis of 6b.**



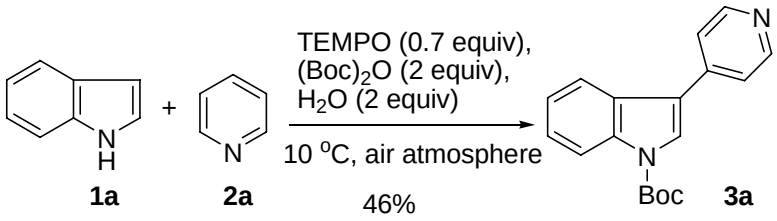

To a solution of indole (85 mg, 0.5 mmol) and TEMPO (55 mg, 0.35 mmol ) in 4-phenylpyridine (124 mg, 0.8 mmol) was added $(Boc)_2O$ (202 mg, 1.0 mmol) under air atmosphere and the mixture was stirred at 10 °C for 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product **6b** (159 mg, 86%).

**2.5 General Procedure for the Indolation of Isoquinoline.**



To a solution of indole (0.5 mmol), TEMPO (0.35 mmol ) and isoquinoline (0.55 mmol) in THF (1 mL) was added $(Boc)_2O$ (0.6 mmol) under air atmosphere and the mixture was stirred at room temperature for 3 h. The reaction mitxure was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:8) to yield the corresponding product **8**.

**2.6 Control Experiments**

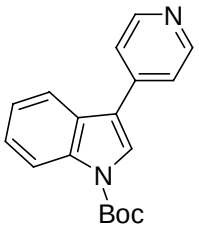



**1a** **2a** **3a**

To a solution of indole (85 mg, 0.5 mmol), TEMPO (55 mg, 0.35 mmol ) and $H_2O$ (18 mg, 1 mmol) in pyridine (63 mg, 0.8 mmol) was added $(Boc)_2O$ (202 mg, 1 mmol) under air atmosphere and the mixture was stirred at 10 $^oC$ for 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product **3a** (67 mg, 46%).

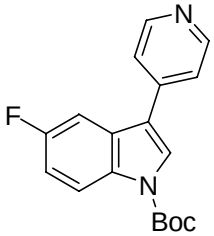
**2.7 Spectroscopic Data of the Products 3a-w, 4, 6b and 8a-c.**

***tert*-Butyl 3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3a)**




*Rf* 0.25 (EtOAc/PE = 1/4). White solid, m.p. 90.3-91.8 °C. IR (KBr) $\nu_{max}$: 1727, 1378, 1243, 1160, 756 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.70 (d, $J$ = 5.8 Hz, 2H, Ar-H), 8.26 (d, $J$ = 8.0 Hz, 1H, Ar-H), 7.89 (s, 1H, Ar-H), 7.87 (d, $J$ = 8.0 Hz, 1H, Ar-H), 7.59 (d, $J$ = 5.8 Hz, 2H, Ar-H), 7.43 (t, $J$ = 7.5 Hz, 1H, Ar-H), 7.35 (t, $J$ = 7.5 Hz, 1H, Ar-H), 1.73 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.3, 149.4, 141.8, 136.0, 127.9, 125.1, 124.4, 123.4, 122.2, 119.6, 119.4, 115.7, 84.5, 28.2. HRESIMS calcd for $[C_{18}H_{18}N_2O_2 + H]^+$ 295.14465 (100%), found 295.14389 (100%).

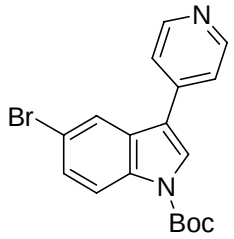
***tert*-Butyl 5-fluoro-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3b)**




*Rf* 0.20 (EtOAc/PE = 1/4). White solid, m.p. 139-140 °C. IR (KBr) $\nu_{max}$: 1737, 1598, 1464, 1377, 1258, 1152, 1098, 1051, 804 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.71 (s, 2H, Ar-H), 8.22-8.17 (m, 1H, Ar-H), 7.90 (s, 1H, Ar-H), 7.54 (d, $J$ = 5.6 Hz, 2H, Ar-H), 7.50 (dd, $J$ = 9.1, 2.6 Hz, 1H, Ar-H), 7.14 (dt, $J$ = 2.6, 9.1 Hz, 1H, Ar-H), 1.72 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 159.7 (d, $J$ = 240.2 Hz), 150.4, 149.1, 141.3, 132.4, 128.8 (d, $J$ = 9.6 Hz), 125.7, 122.0, 119.1 (d, $J$ = 4.2 Hz), 116.7 (d, $J$ = 9.1 Hz), 112.9 (d, $J$ = 25.0 Hz), 105.3 (d, $J$ = 24.7 Hz), 84.8, 28.1.

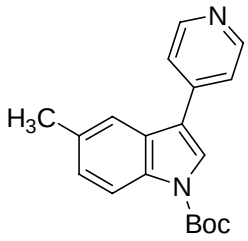
HRESIMS calcd for $[C_{18}H_{17}FN_2O_2 + H]^+$ 313.13523 (100%), found 313.13361 (100%).

***tert*-Butyl 5-bromo-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3c)**



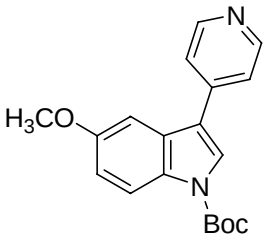

*Rf* 0.20 (EtOAc/PE = 1:4). Pale yellow, m.p. 130.7-132.6 °C. IR (KBr) $\nu_{max}$: 1744, 1379, 1245, 1160, 756 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.70 (d, $J$ = 6.0 Hz, 2H, Ar-H), 8.13 (d, $J$ = 8.8 Hz, 1H, Ar-H), 7.96 (d, $J$ = 1.8 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H), 7.54 (d, $J$ = 6.0 Hz, 1H, Ar-H), 7.52 (d, $J$ = 6.0 Hz, 1H, Ar-H), 7.50 (dd, $J$ = 8.8, 1.8 Hz, 1H, Ar-H), 1.72 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.4, 149.0, 141.1, 134.7, 129.6, 128.0, 125.3, 122.3, 122.2, 118.7, 117.1, 116.9, 85.0, 28.2. HRESIMS calcd for $[C_{18}H_{17}BrN_2O_2 + H]^+$ 373.05517 (100%), 375.05312 (100%), found 373.05420 (100%), 375.05197 (100%).

***tert*-Butyl 5-methyl-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3d)**



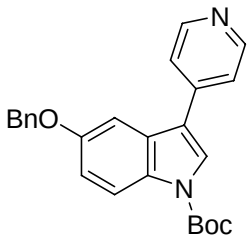

*Rf* 0.20 (EtOAc/PE = 1/4). White solid, m.p. 124-125 °C. IR (KBr) $\nu_{max}$: 1725, 1601, 1371, 1243, 1150 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.70 (d, $J$ = 5.7 Hz, 2H, Ar-H), 8.12 (d, $J$ = 8.3 Hz, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.65 (s, 1H, Ar-H), 7.59 (d, $J$ = 5.7 Hz, 2H, Ar-H), 7.24 (d, $J$ = 8.3 Hz, 1H, Ar-H), 2.51 (s, 3H, $CH_3$), 1.72 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.2, 149.5, 141.9, 134.2, 133.0, 128.1, 126.4, 124.4, 122.3, 119.5, 119.1, 115.3, 84.3, 28.2, 21.5. HRESIMS calcd for $[C_{19}H_{20}N_2O_2 + H]^+$ 309.16030 (100%), found 309.15875 (100%).

***tert*-Butyl 5-methoxy-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3e)**



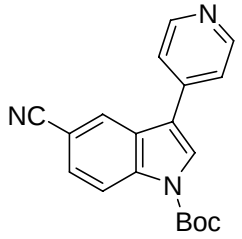

*Rf* 0.40 (EtOAc/PE = 1/2). White solid, m.p. 106-107 °C. IR (KBr) $\nu_{max}$: 1723, 1608, 1385, 1249, 1164, 1115 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.85-8.60 (br s, 2H, Ar-H), 8.14 (d, $J$ = 9.0 Hz, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.63-7.54 (br s, 2H, Ar-H), 7.30 (d, $J$ = 2.5 Hz, 1H, Ar-H), 7.04 (dd, $J$ = 9.0, 2.5 Hz, 1H, Ar-H), 3.90 (s, 3H, $OCH_3$), 1.72 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 156.5, 150.3, 149.4, 141.9, 130.7, 128.8, 125.0, 122.3, 119.2, 116.4, 113.6, 102.5, 84.3, 55.8, 28.2. HRESIMS calcd for $[C_{19}H_{20}N_2O_3 + H]^+$ 325.15522 (100%), found 325.15341 (100%).

***tert*-Butyl 5-(benzyloxy)-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3f)**



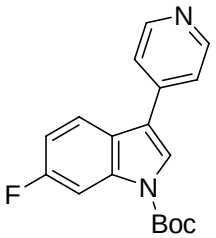

*Rf* 0.40 (EtOAc/PE = 1/2). White solid, m.p. 136-137 °C. IR (KBr) $\nu_{max}$: 1730, 1605, 1371, 1225, 1156, 816 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.73 (s, 2H, Ar-H), 8.14 (d, $J$ = 8.7 Hz, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.56-7.48 (m, 4H, Ar-H), 7.43 (dt, $J$ = 6.1, 1.6 Hz, 2H, Ar-H), 7.39-7.35 (m, 2H, Ar-H), 7.12 (dd, $J$ = 9.1, 2.4 Hz, 1H, Ar-H), 5.16 (s, 2H, $OCH_2$), 1.72 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 155.5, 150.2, 149.4, 141.9, 137.1, 130.9, 128.7, 128.6, 128.0, 127.5, 125.0, 122.1, 119.2, 116.4, 114.3, 104.2, 84.4, 70.8, 28.2. HRESIMS calcd for $[C_{25}H_{24}N_2O_3 + H]^+$ 401.18652 (100%), found 401.18503 (100%).

***tert*-Butyl 5-cyano-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3g)**



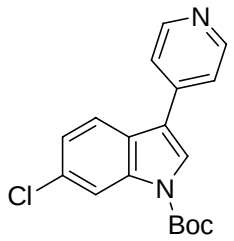

*Rf* 0.20 (EtOAc/PE = 1/4). Pale yellow solid, m.p. 144-145 °C. IR (KBr) $\nu_{max}$: 2225, 1743, 1603, 1465, 1372, 1289, 1254, 1157, 815 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.77 (s, 2H, Ar-H), 8.38 (d, $J$ = 8.7 Hz, 1H, Ar-H), 8.18 (d, $J$ = 1.3 Hz, 1H, Ar-H), 7.97 (s, 1H, Ar-H), 7.68 (dd, $J$ = 8.7, 1.3 Hz, 1H, Ar-H), 7.56 (s, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 1.74 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.6, 148.7, 140.4, 137.8, 128.1, 128.0, 126.2, 124.6, 122.3, 119.4, 119.3, 116.6, 107.0, 85.8, 28.1. MS (ESI): 320 ($M+H^+$, 100). Anal calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found C, 71.27; H, 5.63; N, 12.85.

***tert*-Butyl 6-fluoro-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3h)**



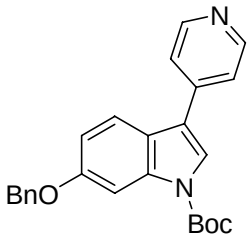

*Rf* 0.20 (EtOAc/PE = 1/4). White solid, m.p. 113-114 °C. IR (KBr) $\nu_{max}$: 1731, 1601, 1483, 1444, 1388, 1252, 1167, 807 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.71 (d, $J$ = 4.8 Hz, 2H, Ar-H), 7.98 (dd, $J$ = 8.8, 1.4 Hz, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.76 (dd, $J$ = 8.8, 5.3 Hz, 1H, Ar-H), 7.56 (dd, $J$ = 4.8, 1.4 Hz, 2H, Ar-H), 7.10 (dt, $J$ = 2.4, 8.8 Hz, 1H, Ar-H), 1.72 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 161.2 (d, $J$ = 240.7 Hz), 150.4, 149.1, 141.4, 136.3 (d, $J$ = 12.8 Hz), 124.4 (d, $J$ = 3.6 Hz), 124.3, 122.1, 120.4 (d, $J$ = 10.0 Hz), 119.3, 117.0 (d, $J$ = 24.3 Hz), 103.0 (d, $J$ = 28.6 Hz), 84.9, 28.1. HRESIMS calcd for $[C_{18}H_{17}FN_2O_2 + H]^+$ 313.13523 (100%), found 313.13358 (100%).

***tert*-Butyl 6-chloro-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3i)**



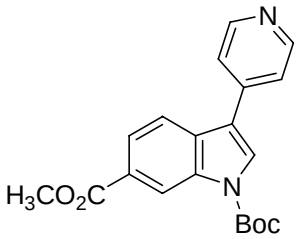

*Rf* 0.30 (EtOAc/PE = 1/4). White solid, m.p. 164-165 °C. IR (KBr) $\nu_{max}$: 1729, 1600, 1463, 1437, 1382, 1252, 1171, 805 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.70 (d, $J$ = 5.9 Hz, 2H, Ar-H), 8.30 (s, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.76 (d, $J$ = 8.5 Hz, 1H, Ar-H), 7.55 (d, $J$ = 5.9 Hz, 2H, Ar-H), 7.32 (dd, $J$ = 8.5, 1.9 Hz, 1H, Ar-H), 1.73 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.4, 149.0, 141.2, 136.4, 131.1, 126.4, 124.7, 124.0, 122.2, 120.4, 119.3, 116.0, 85.1, 28.1. HRESIMS calcd for $[C_{18}H_{17}ClN_2O_2 + H]^+$ 329.10568 (100%), 331.10273 (33%), found 329.10403 (100%), 331.10080 (33%).

***tert*-Butyl 6-(benzyloxy)-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3j)**



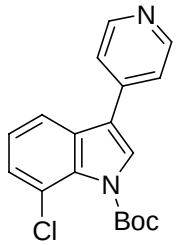

*Rf* 0.38 (EtOAc/PE = 1/2). White solid, m.p. 135-136 °C. IR (KBr) $\nu_{max}$: 1733, 1601, 1374, 1227, 1152, 815 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.68 (s, 2H, Ar-H), 7.94 (s, 1H, Ar-H), 7.78 (s, 1H, Ar-H), 7.74 (d, $J$ = 8.7 Hz, 1H, Ar-H), 7.58 (d, $J$ = 4.3 Hz, 2H, Ar-H), 7.51 (dd, $J$ = 8.4, 1.3 Hz, 2H, Ar-H), 7.44 (dt, $J$ = 1.3, 8.4 Hz, 2H, Ar-H), 7.37 (dt, $J$ = 2.4, 8.4 Hz, 1H, Ar-H), 7.07 (dd, $J$ = 8.7, 2.4 Hz, 1H, Ar-H), 5.19 (s, 1H, $OCH_2$), 1.71 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 157.4, 150.2, 149.5, 141.9, 137.1, 136.9, 128.6, 128.0, 127.6, 123.1, 122.2, 121.9, 120.2, 119.4, 113.4, 100.9, 84.3, 70.5, 28.2. HRESIMS calcd for $[C_{25}H_{24}N_2O_3 + H]^+$ 401.18652 (100%), found 401.18460 (100%).

**1-*tert*-Butyl 6-methyl 3-(pyridin-4-yl)-1*H*-indole-1,6-dicarboxylate (3k)**



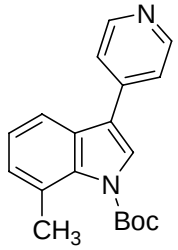

*Rf* 0.30 (EtOAc/PE = 1/2). Pale yellow solid, m.p. 135-137 °C. IR (KBr) $\nu_{max}$: 1740, 1717, 1604, 1438, 1377, 1298, 1241, 1189, 1155, 1100 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.97 (s, 1H, Ar-H), 8.73 (dd, $J$ = 5.9, 1.4 Hz, 2H, Ar-H), 8.05 (dd, $J$ = 8.4, 1.4 Hz, 1H, Ar-H), 8.02 (s, 1H, Ar-H), 7.89 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.58 (d, $J$ = 5.9 Hz, 2H, Ar-H), 3.99 (s, 3H, $OCH_3$), 1.75 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 167.3, 150.4, 149.0, 141.1, 135.5, 131.5, 127.0, 126.8, 124.5, 112.2, 119.4, 119.3, 117.6, 85.2, 52.2, 28.1. MS (ESI): 353 ($M+H^+$, 100). Anal calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found C, 67.83; H, 6.01; N, 7.72.

***tert*-Butyl 7-chloro-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3l)**



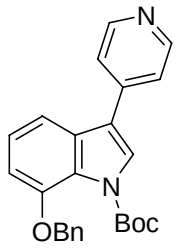

*Rf* 0.30 (EtOAc/PE = 1/2). Amorphous solid. IR (KBr) $\nu_{max}$: 1753, 1605, 1353, 1266, 1152 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.71 (s, 2H, Ar-H), 7.80 (s, 1H, Ar-H), 7.75 (dd, $J$ = 7.9, 0.9 Hz, 1H, Ar-H), 7.54 (d, $J$ = 7.9 Hz, 2H, Ar-H), 7.43 (dd, $J$ = 7.9, 0.9 Hz, 1H, Ar-H), 7.27 (t, $J$ = 7.9 Hz, 1H, Ar-H), 1.70 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.3, 148.5, 141.2, 132.9, 131.4, 127.8, 127.2, 124.3, 122.4, 121.0, 119.2, 118.2, 85.2, 27.9. MS (ESI): 329 ($M+H^+$, 100), 331 ($M+H^+$, 30). Anal calcd for $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 5.21; N, 8.52. Found C, 65.61; H, 5.36; N, 8.20.

***tert*-Butyl 7-methyl-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3m)**




*Rf* 0.35 (EtOAc/PE = 1/2). Amorphous solid. IR (KBr) $\nu_{max}$: 1750, 1604, 1355, 1260, 1225, 1152 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.70 (s, 2H, Ar-H), 7.77 (s, 1H, Ar-H), 7.68 (d, $J$ = 7.5 Hz, 1H, Ar-H), 7.57 (d, $J$ = 5.6 Hz, 2H, Ar-H), 7.27 (t, $J$ = 7.5 Hz, 1H, Ar-H), 7.22 (d, $J$ = 5.6 Hz, 1H, Ar-H), 2.68 (s, 3H, $CH_3$), 1.69 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.2, 149.2, 141.9, 135.6, 129.3, 128.4, 126.6, 126.0, 123.8, 122.5, 119.5, 117.1, 84.1, 28.0, 22.1. MS (ESI): 309 ($M+H^+$, 100). Anal calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found C, 73.63; H, 6.91; N, 8.71.

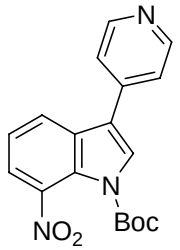
***tert*-Butyl 7-(benzyloxy)-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3n)**




*Rf* 0.38 (EtOAc/PE = 1/2). White solid, m.p. 112-113 °C. IR (KBr) $\nu_{max}$: 1744, 1604, 1366, 1239, 1152, 1047 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.68 (s, 2H, Ar-H), 7.77 (s, 1H, Ar-H), 7.58 (d, $J$ = 7.1 Hz, 2H, Ar-H), 7.56 (d, $J$ = 8.5 Hz, 2H, Ar-H), 7.48 (dd, $J$ = 7.1, 1.0 Hz, 1H, Ar-H), 7.40 (dt, $J$ = 1.0, 8.5 Hz, 2H, Ar-H), 7.36 (dt, $J$ = 1.0, 7.1 Hz, 1H, Ar-H), 7.28 (t, $J$ = 8.0 Hz, 1H, Ar-H), 6.99 (d, $J$ = 8.0 Hz, 1H, Ar-H), 5.27 (s, 2H, $OCH_2$), 1.58 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.2, 148.9, 147.9, 141.9, 137.0, 130.9, 128.4, 127.8, 127.5, 127.0, 125.9, 124.5, 122.3, 119.1, 112.5, 109.0, 84.1, 71.1, 27.8. MS (ESI): 401 ($M+H^+$, 100). Anal calcd for $C_{25}H_{24}N_2O_3$: C,

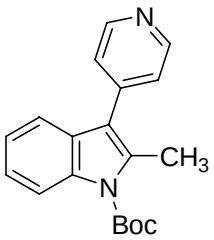
74.98; H, 6.04; N, 7.00. Found C, 74.67; H, 6.32; N, 6.86.

***tert*-Butyl 7-nitro-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3o)**



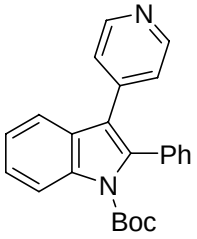

*Rf* 0.20 (EtOAc/PE = 1/2). Yellow solid, m.p. 116-118 °C. IR (KBr) $\nu_{max}$: 1745, 1606, 1531, 1371, 1259, 1149, 818 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.75 (s, 2H, Ar-H), 8.08 (dd, $J$ = 8.0, 0.8 Hz, 1H, Ar-H), 7.91 (s, 1H, Ar-H), 7.88 (dd, $J$ = 8.0, 0.8 Hz, 1H, Ar-H), 7.56 (d, $J$ = 8.0 Hz, 2H, Ar-H), 7.45 (t, $J$ = 8.0 Hz, 1H, Ar-H), 1.65 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.5, 148.3, 140.5, 139.5, 131.6, 127.8, 126.2, 124.6, 123.1, 122.5, 120.9, 119.5, 86.8, 27.9. MS (ESI): 340 ($M+H^+$, 100), 362 ($M+Na^+$, 15). Anal calcd for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38. Found C, 63.98; H, 4.89; N, 12.02.

***tert*-Butyl 2-methyl-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3p)**



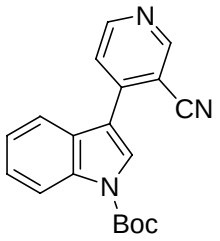

*Rf* 0.20 (EtOAc/PE = 1/6). Pale yellow solid, m.p. 80-81 °C. IR (KBr) $\nu_{max}$: 1736, 1603, 1358, 1319, 1152, 1119, 834 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.73 (s, 2H, Ar-H), 8.19 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.49 (d, $J$ = 7.6 Hz, 1H, Ar-H), 7.40 (d, $J$ = 7.6 Hz, 2H, Ar-H), 7.33 (dt, $J$ = 1.0, 7.6 Hz, 1H, Ar-H), 7.25 (dt, $J$ = 8.4, 1.0 Hz, 1H, Ar-H), 2.65 (s, 3H, $CH_3$), 1.74 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.5, 150.0, 142.4, 135.8, 134.8, 128.3, 125.0, 124.1, 123.1, 118.5, 118.2, 115.6, 84.3, 28.3, 14.8. MS (ESI): 309 ($M+H^+$, 100). Anal calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found C, 73.88; H, 6.73; N, 8.89.

***tert*-Butyl 2-phenyl-3-(pyridin-4-yl)-1*H*-indole-1-carboxylate (3q)**



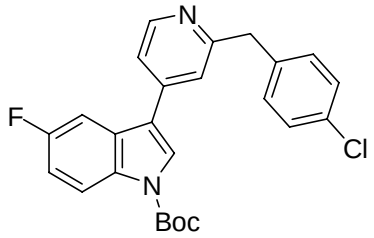

*Rf* 0.31 (EtOAc/PE = 1/4). Pale yellow solid, m.p. 136-138 °C. IR (KBr) $\nu_{max}$: 1727, 1604, 1357, 1321, 1154 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.52 (d, $J$ = 3.4 Hz, 2H, Ar-H), 8.35 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.63 (d, $J$ = 7.8 Hz, 1H, Ar-H), 7.44 (dt, $J$ = 1.2, 7.3 Hz, 1H, Ar-H), 7.39-7.31 (m, 4H, Ar-H), 7.30-7.26 (m, 2H, Ar-H), 7.15 (d, $J$ = 5.9 Hz, 2H, Ar-H) ), 1.28 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 149.9, 149.6, 142.0, 136.9, 136.6, 133.2, 130.2, 130.1, 128.1, 128.0, 125.1, 124.8, 124.7, 123.4, 119.0, 115.5, 83.8, 27.5. MS (ESI): 371 ($M+H^+$, 100). Anal calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found C, 77.65; H, 6.18; N, 7.39.

***tert*-Butyl 3-(3-cyanopyridin-4-yl)-1*H*-indole-1-carboxylate (3r)**



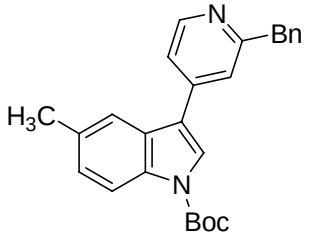

*Rf* 0.33 (EtOAc/PE = 1/4). Pale yellow solid, m.p. 116-118 °C. IR (KBr) $\nu_{max}$: 2231, 1725, 1608, 1374, 1259, 1160, 1094, 1055, 798 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 9.15 (s, 2H, Ar-H), 8.30 (d, $J$ = 8.3 Hz, 1H, Ar-H), 8.22 (s, 1H, Ar-H), 7.95-7.80 (br s, 1H, Ar-H), 7.72 (d, $J$ = 7.9 Hz, 1H, Ar-H), 7.47 (dt, $J$ = 0.9, 8.3 Hz, 1H, Ar-H), 7.38 (dt, $J$ = 0.9, 7.9 Hz, 1H, Ar-H), 1.73 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 153.9, 152.0, 149.0, 145.1, 135.7, 127.4, 126.9, 125.6, 123.7, 119.2, 116.9, 115.9, 115.4, 85.1, 28.1. MS (ESI): 320 ($M+H^+$, 100). Anal calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found C, 71.20; H, 5.61; N, 12.83.

***tert*-Butyl 3-(2-(4-chlorobenzyl)pyridin-4-yl)-5-fluoro-1*H*-indole-1-carboxylate (3s)**




*Rf* 0.25 (EtOAc/PE = 1/6). Pale yellow solid, m.p. 131-133 °C. IR (KBr) $\nu_{max}$: 1725, 1609, 1374, 1260, 1161, 798 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.64 (d, $J$ = 5.2 Hz, 1H, Ar-H), 8.18 (dd, $J$ = 8.5, 4.1 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H), 7.41 (dd, $J$ = 8.9, 2.4 Hz, 1H, Ar-H), 7.38 (dd, $J$ = 4.1, 1.6 Hz, 1H, Ar-H), 7.35 (s, 1H, Ar-H), 7.31 (d, $J$ = 8.5 Hz, 1H, Ar-H), 7.30 (s, 1H, Ar-H), 7.29-7.26 (m, 2H, Ar-H), 7.13 (dd, $J$ = 8.9, 2.4 Hz, 1H, Ar-H), 4.21 (s, 2H, $CH_2$), 1.71 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 161.1, 159.6 (d, $J$ = 240.1 Hz), 150.1, 149.3 (d, $J$ = 30.5 Hz), 142.0, 137.9, 136.7, 132.4, 130.4, 128.8, 128.7, 125.7, 121.4, 119.9, 119.2 (d, $J$ = 4.1 Hz), 116.7 (d, $J$ = 9.2 Hz), 112.9 (d, $J$ = 25.0 Hz), 105.3 (d, $J$ = 24.7 Hz), 84.8, 44.0, 28.1. MS (ESI): 437 ($M+H^+$, 100), 439 ($M+H^+$, 30). Anal calcd for $C_{25}H_{22}ClFN_2O_2$: C, 68.73; H, 5.08; N, 6.41. Found C, 68.39; H, 5.37; N, 6.14.

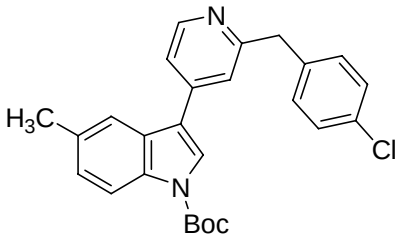
***tert*-Butyl 3-(3-benzylpyridin-4-yl)-5-methyl-1*H*-indole-1-carboxylate (3t)**




*Rf* 0.19 (EtOAc/PE = 1/8). Amorphous solid. IR (KBr) $\nu_{max}$: 1735, 1372, 1248, 1156 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.64 (d, $J$ = 5.2 Hz, 1H, Ar-H), 8.09 (d, $J$ = 8.3 Hz, 1H, Ar-H), 7.80 (s, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.42 (dd, $J$ = 5.2, 1.6 Hz, 1H, Ar-H), 7.40 (s, 1H, Ar-H), 7.39-7.35 (m, 4H, Ar-H), 7.30-7.26 (m, 1H, Ar-H), 7.23 (dd, $J$ = 8.3, 1.0 Hz, 1H, Ar-H), 4.27 (s, 2H, $CH_2$), 2.48 (s, 3H, $CH_3$), 1.73 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 161.6, 149.8, 149.5, 142.4, 139.6, 132.9, 129.2, 128.7, 126.5, 126.3, 124.3, 121.7, 119.9, 119.5, 119.3, 115.2, 84.3,

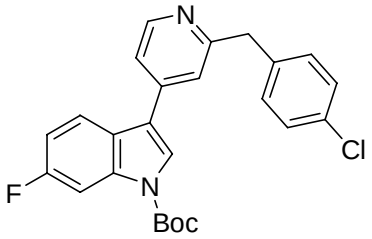
44.7, 28.2, 21.5. MS (ESI): 399 ($M+H^+$, 100). Anal calcd for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.58; N, 7.03. Found C, 78.04; H, 6.91; N, 6.70.

***tert*-Butyl 3-(2-(4-chlorobenzyl)pyridin-4-yl)-5-methyl-1*H*-indole-1-carboxylate (3u)**



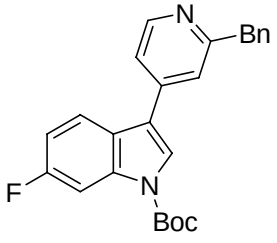

*Rf* 0.32 (EtOAc/PE = 1/6). Amorphous solid. IR (KBr) $\nu_{max}$: 1736, 1604, 1371, 1248, 1155 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.63 (d, $J$ = 5.2 Hz, 1H, Ar-H), 8.09 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.79 (s, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.43 (dd, $J$ = 5.2, 1.6 Hz, 1H, Ar-H), 7.37 (s, 1H, Ar-H), 7.31 (t, $J$ = 1.6 Hz, 2H, Ar-H), 7.30 (s, 1H, Ar-H), 7.27 (dd, $J$ = 5.2, 1.2 Hz, 1H, Ar-H), 7.22 (dd, $J$ = 8.4, 1.2 Hz, 1H, Ar-H), 4.22 (s, 2H, $CH_2$), 2.48 (s, 3H, $CH_3$), 1.72 (s, 9H, 3X$CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 161.0, 149.9, 149.5, 142.6, 138.0, 132.9, 132.3, 130.5, 130.4, 128.7, 128.2, 126.4, 124.3, 121.6, 120.1, 119.4, 119.2, 115.3, 84.3, 44.0, 28.2, 21.4. MS (ESI): 433 ($M+H^+$, 100), 435 ($M+H^+$, 30). Anal calcd for $C_{26}H_{25}ClN_2O_2$: C, 72.13; H, 5.82; N, 6.47. Found C, 72.51; H, 5.59; N, 6.13.

***tert*-Butyl 3-(2-(4-chlorobenzyl)pyridin-4-yl)-6-fluoro-1*H*-indole-1-carboxylate (3v)**




*Rf* 0.29 (EtOAc/PE = 1/6). Pale yellow solid, m.p. 141-143 °C. IR (KBr) $\nu_{max}$: 1734, 1605, 1484, 1380, 1274, 1155 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.63 (d, $J$ = 6.1 Hz, 1H, Ar-H), 7.95 (d, $J$ = 8.8 Hz, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 7.66 (dd, $J$ = 8.8, 5.3 Hz, 1H, Ar-H), 7.40 (dd, $J$ = 5.3, 1.6 Hz, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 7.32 (d, $J$ = 6.1 Hz, 1H, Ar-H), 7.30 (t, $J$ = 1.6 Hz, 2H, Ar-H), 7.27 (dd, $J$ = 6.1, 2.3 Hz, 1H, Ar-H), 7.08 (dd, $J$ = 8.8, 2.3 Hz, 1H, Ar-H), 4.21 (s, 2H, $CH_2$), 1.72 (s, 9H, 3X$CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 161.1 (d, $J$ = 241.6 Hz), 161.0, 150.0, 149.1, 142.1, 137.9, 132.4, 130.4, 128.9, 128.7, 124.4 (d, $J$ = 3.6 Hz), 124.3, 121.5, 120.3 (d, $J$ = 9.8 Hz), 120.0, 119.3, 111.6 (d, $J$ = 24.2 Hz), 103.1 (d, $J$ = 28.6 Hz), 84.9, 44.0, 28.1. MS (ESI): 437 ($M+H^+$, 100), 439 ($M+H^+$, 30). Anal calcd for $C_{25}H_{22}ClFN_2O_2$: C, 68.73; H, 5.08; N, 6.41. Found C, 68.50; H, 5.47; N, 6.62.

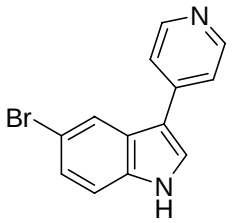
***tert*-Butyl 3-(3-benzylpyridin-4-yl)-6-fluoro-1*H*-indole-1-carboxylate (3w)**




*Rf* 0.19 (EtOAc/PE = 1/6). Amorphous solid. IR (KBr) $\nu_{max}$: 1739, 1602, 1374, 1222, 1153 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.64 (d, $J$ = 5.1 Hz, 1H, Ar-H), 7.95 (d, $J$ = 9.3 Hz, 1H, Ar-H),

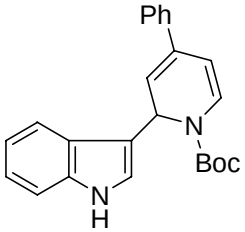
7.79 (s, 1H, Ar-H), 7.65 (dd, *J* = 8.8, 5.3 Hz, 1H, Ar-H), 7.41-7.33 (m, 6H, Ar-H), 7.30-7.23 (m, 1H, Ar-H), 7.07 (dd, *J* = 8.8, 2.4 Hz, 1H, Ar-H), 4.26 (s, 2H, $CH_2$), 1.73 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 161.7, 161.1 (d, *J* = 241.6 Hz), 149.9, 149.2, 141.9, 139.4, 129.2, 129.1, 128.8, 128.6, 126.5, 124.3 (d, *J* = 3.9 Hz), 121.6, 120.4 (d, *J* = 9.8 Hz), 119.9, 119.5, 111.6 (d, *J* = 24.2 Hz), 103.0 (d, *J* = 28.6 Hz), 84.9, 44.8, 28.1. MS (ESI): 403 ($M+H^+$, 100). Anal calcd for $C_{25}H_{23}FN_2O_2$: C, 74.61; H, 5.76; N, 6.96. Found C, 74.27; H, 6.13; N, 6.61.

**5-Bromo-3-(pyridin-4-yl)-1*H*-indole (4)**



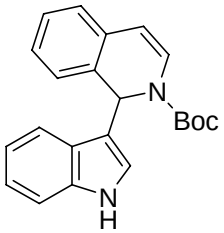

*Rf* 0.15 (EtOAc/PE = 1:1). Waxy solid. IR (KBr) $\nu_{max}$: 3410, 1685, 1602, 1208, 802 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-*d6*): $\delta$ 12.11 (s, 1H, NH), 8.55 (d, *J* = 6.0 Hz, 2H, Ar-H), 8.12 (d, *J* = 1.2 Hz, 2H, Ar-H), 7.74 (d, *J* = 6.0 Hz, 2H, Ar-H), 7.49 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.32 (dd, *J* = 8.6, 1.2 Hz, 1H, Ar-H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 149.9, 143.5, 136.4, 128.2, 126.8, 125.0, 121.8, 121.0, 114.8, 113.7, 112.8. HRESIMS calcd for $[C_{13}H_9BrN_2 + H]^+$ 273.00274 (100%), 275.00069 (100%), found 273.00177 (100%), 274.99942 (100%).

***tert*-Butyl 2-(1*H*-indol-3-yl)-4-phenylpyridine-1(2*H*)-carboxylate (6b)**




*Rf* 0.3 (EtOAc/PE = 1/8). Amorphous solid. IR (KBr) $\nu_{max}$: 1680, 1615, 1371, 1232, 1151 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.15 (s, 1H, NH), 8.03 (s, 1H, Ar-H), 7.55-7.45 (m, 2H, Ar-H), 7.43-7.30 (m, 4H, Ar-H), 7.25-7.19 (m, 2H, Ar-H), 8.64 (dt, *J* = 0.8, 7.9 Hz, 1H, Ar-H), 6.84 (s, 1H), 6.42 (s, 1H), 6.00 (s, 1H), 5.80 (s, 1H), 1.53 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 152.3, 139.1, 136.6, 133.1, 128.5, 127.5, 126.4, 125.9, 125.7, 124.5, 122.1, 120.8, 119.8, 117.8, 116.0, 111.1, 105.9, 81.4, 48.3, 28.3. MS (ESI): 373 ($M+H^+$, 100). Anal calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found C, 77.05; H, 6.80; N, 7.31.

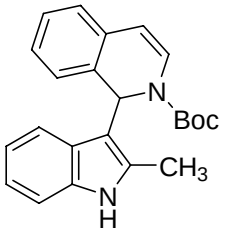
***tert*-Butyl 1-(1*H*-indol-3-yl)isoquinoline-2(1*H*)-carboxylate (8a)**




*Rf* 0.20 (EtOAc/PE = 1/10). White amorphous solid. IR (KBr) $\nu_{max}$: 1686, 1634, 1362, 1240, 1164, 772 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.00 (s, 2H, Ar-H), 7.32 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.29-7.24 (br s, 1H, Ar-H), 7.21-7.11 (m, 5H, Ar-H), 6.89 (s, 1H, Ar-H), 6.77 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.00 (s, 1H, Ar-H), 1.57 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 152.1,

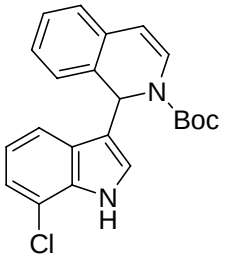
136.3, 132.5, 130.8, 127.5, 126.9, 126.8, 125.7, 125.6, 124.5, 124.4, 122.1, 120.5, 119.8, 117.8, 111.0, 108.6, 81.5, 50.8, 28.3. MS (ESI): 347 ($M+H^+$, 100). Anal calcd for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found C, 75.91; H, 6.73; N, 7.86.

***tert*-Butyl 1-(2-methyl-1*H*-indol-3-yl)isoquinoline-2(1*H*)-carboxylate (8b)**




*Rf* 0.23 (EtOAc/PE = 1/8). White amorphous solid. IR (KBr) $\nu_{max}$: 1682, 1635, 1456, 1341, 1290, 1236, 1164, 769 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.87 (s, 1H, Ar-H), 7.68 (d, $J$ = 6.8 Hz, 1H, Ar-H), 7.22 (d, $J$ = 8.0 Hz, 1H, Ar-H), 7.14-7.04 (m, 4H, Ar-H), 7.02 (dd, $J$ = 8.0, 1.7 Hz, 2H, Ar-H), 7.00 (d, $J$ = 6.8 Hz, 1H, Ar-H), 6.75 (s, 1H, Ar-H), 5.98 (d, $J$ = 8.0 Hz, 1H, Ar-H), 2.58 (s, 3H, $CH_3$), 1.43 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 152.4, 135.1, 132.9, 131.8, 129.9, 127.1, 127.0, 126.8, 126.7, 126.5, 124.4, 120.9, 120.2, 119.6, 119.4, 116.7, 110.0, 106.4, 81.3, 51.7, 28.3, 12.6. MS (ESI): 361 ($M+H^+$, 100). Anal calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found C, 76.93; H, 6.57; N, 7.61.

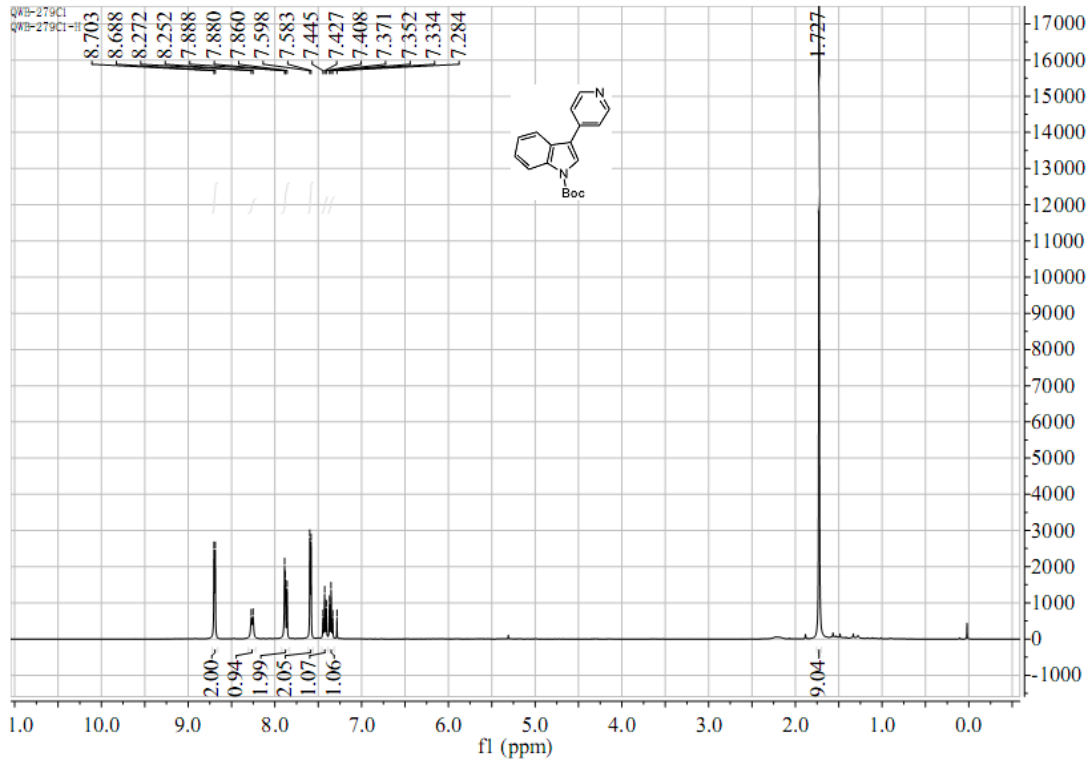
***tert*-Butyl 1-(7-chloro-1*H*-indol-3-yl)isoquinoline-2(1*H*)-carboxylate (8c)**

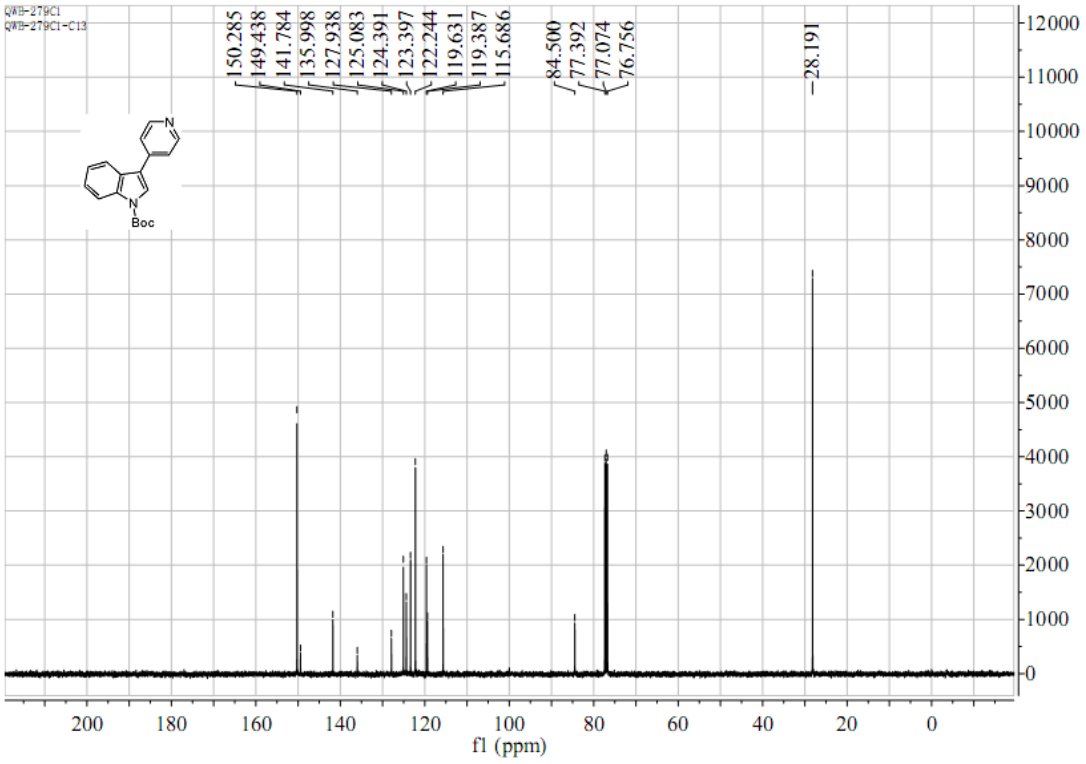



*Rf* 0.22 (EtOAc/PE = 1/16). White amorphous solid. IR (KBr) $\nu_{max}$: 1694, 1634, 1446, 1342, 1241, 1122, 771 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.21 (s, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.32-7.12 (m, 5H, Ar-H), 7.06 (d, $J$ = 7.9 Hz, 1H, Ar-H), 6.86 (s, 1H, Ar-H), 6.76 (s, 1H, Ar-H), 6.70 (s, 1H, Ar-H), 5.99 (s, 1H, Ar-H), 1.54 (s, 9H, $3XCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 152.1, 133.5, 132.1, 130.8, 127.7, 127.0, 126.9, 126.8, 125.5, 125.0, 124.6, 121.4, 120.6, 119.2, 118.9, 116.5, 108.5, 81.6, 50.7, 28.3. MS (ESI): 381 ($M+H^+$, 100), 383 ($M+H^+$, 30). Anal calcd for $C_{22}H_{21}ClN_2O_2$: C, 69.38; H, 5.56; N, 7.36. Found C, 69.25; H, 5.87; N, 7.13.

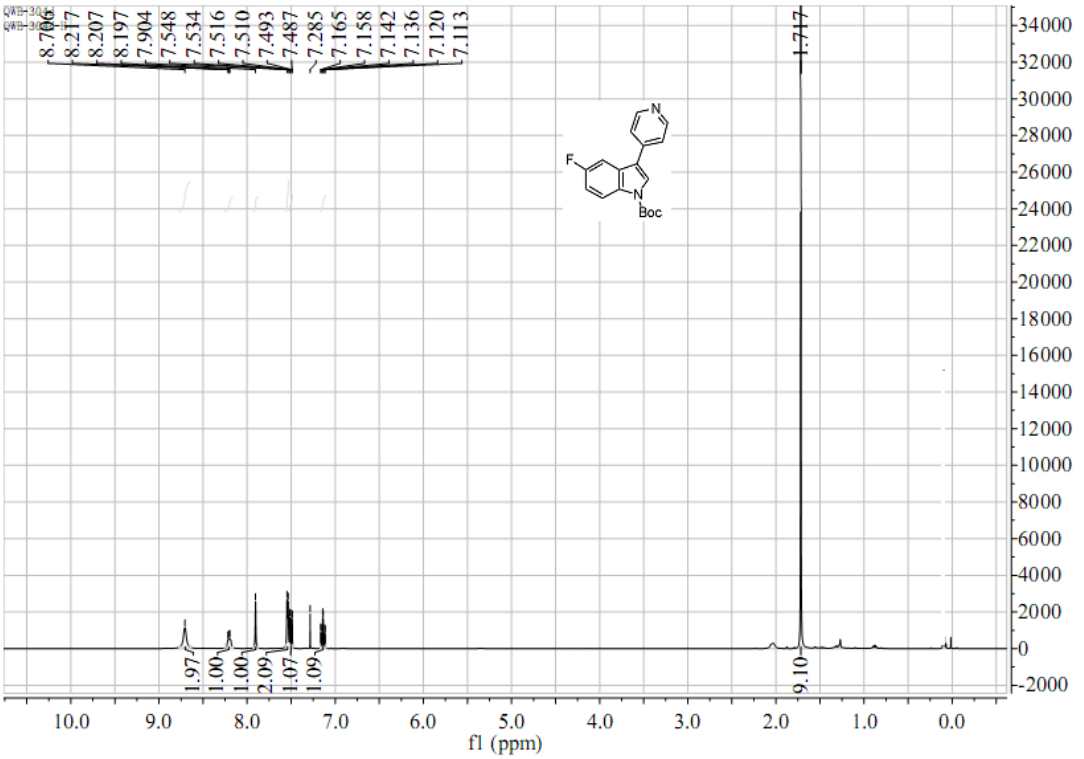
## 3. Copies of $^{1}H$, $^{13}C$ NMR Spectra

Compound **3a**



Compound **3b**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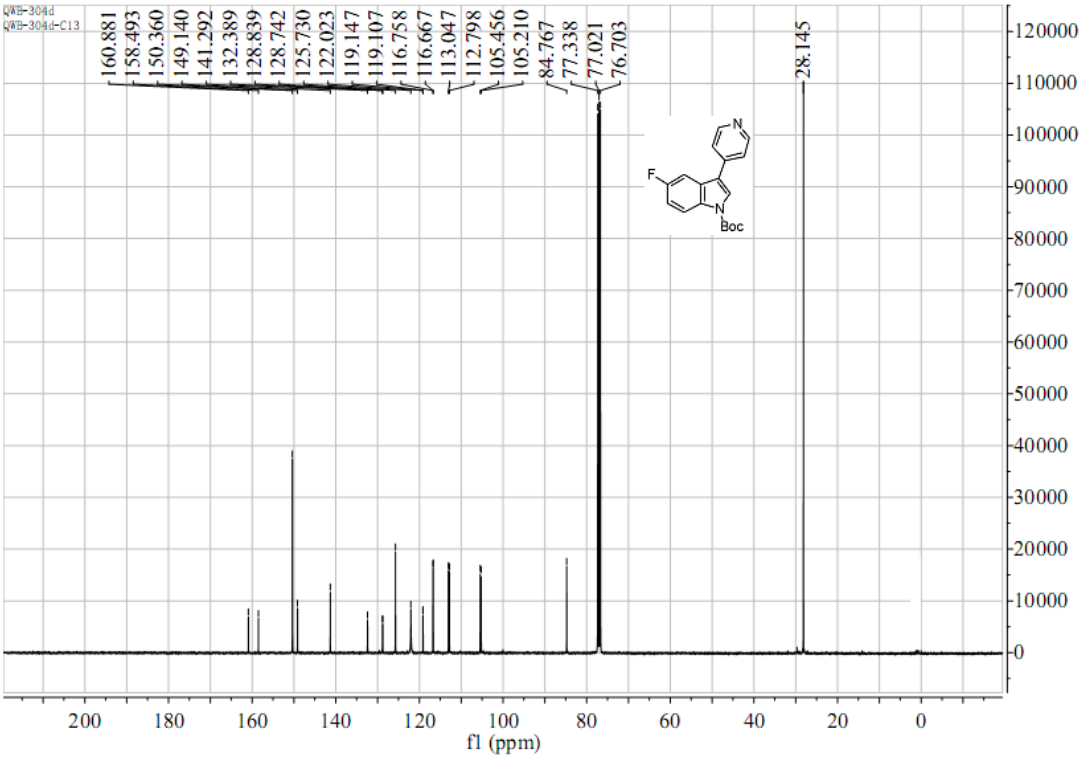
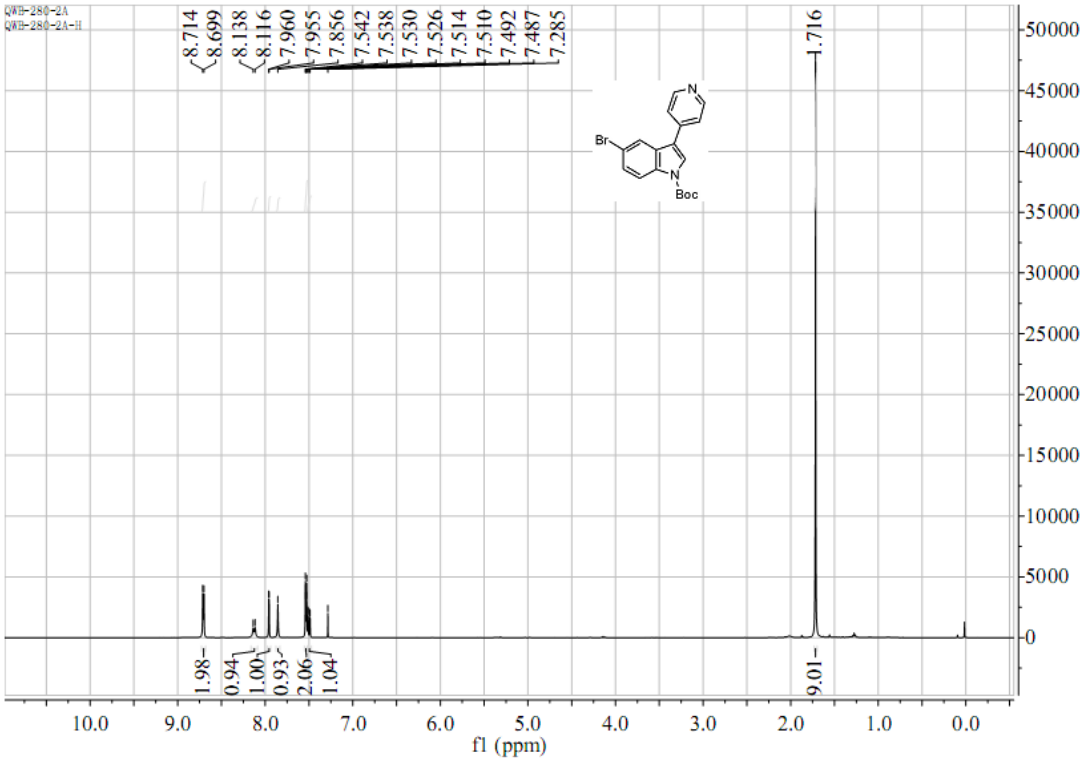
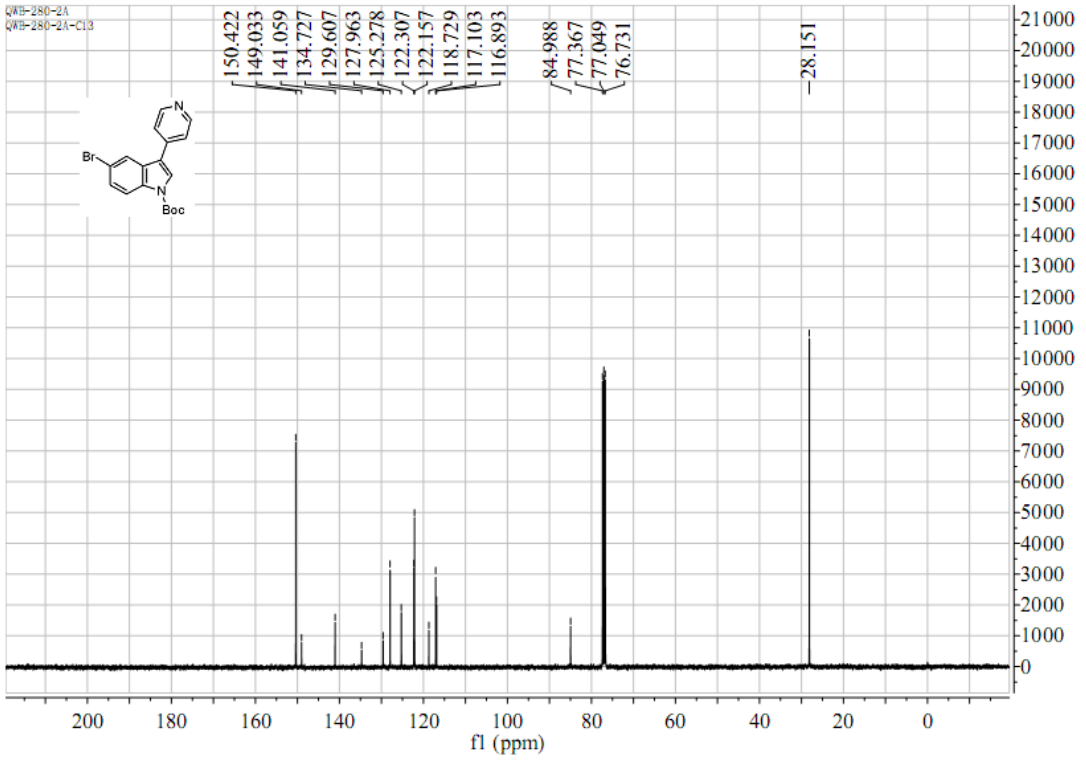
8.207
8.197
7.904
7.548
7.534
7.516
7.510
7.493
7.487
7.285
7.165
7.158
7.142
7.136
7.120
7.113
1.717
F
N
Boc
1.97
1.00
1.00
2.09
1.07
1.09
9.10
f1 (ppm)

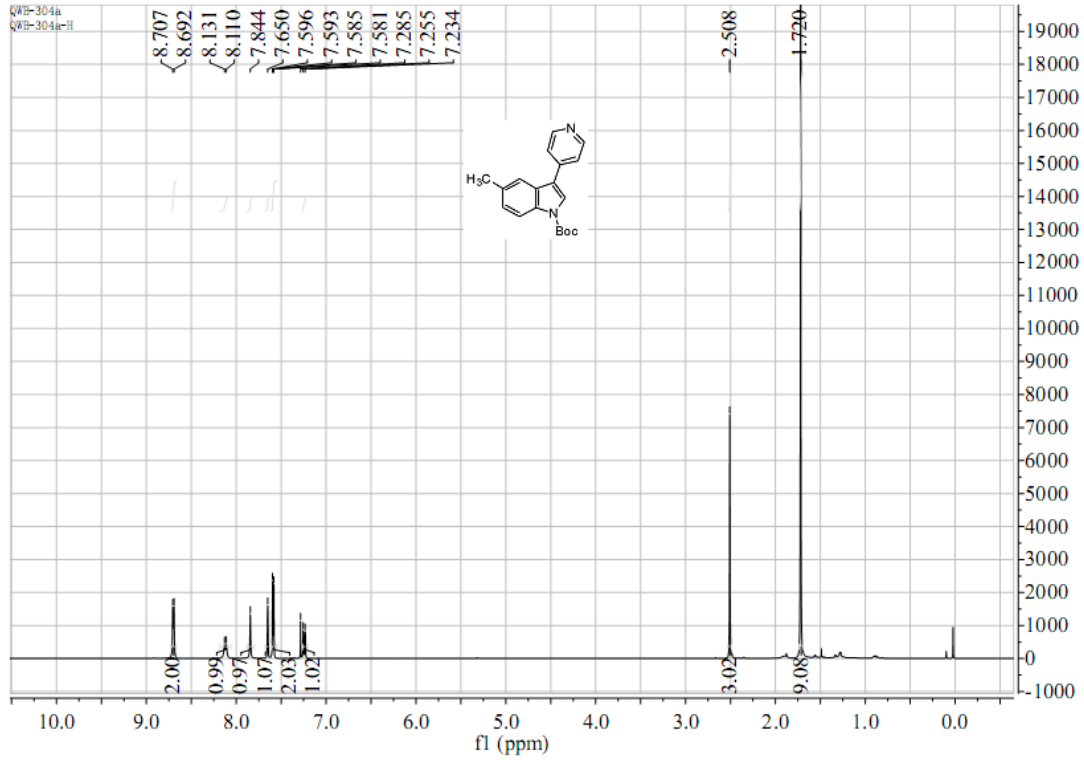

160.881
158.493
150.360
149.140
141.292
132.389
128.839
128.742
125.730
122.023
119.147
119.107
116.758
116.667
113.047
112.798
105.456
105.210
84.767
77.338
77.021
76.703
28.145
F
N
Boc
f1 (ppm)

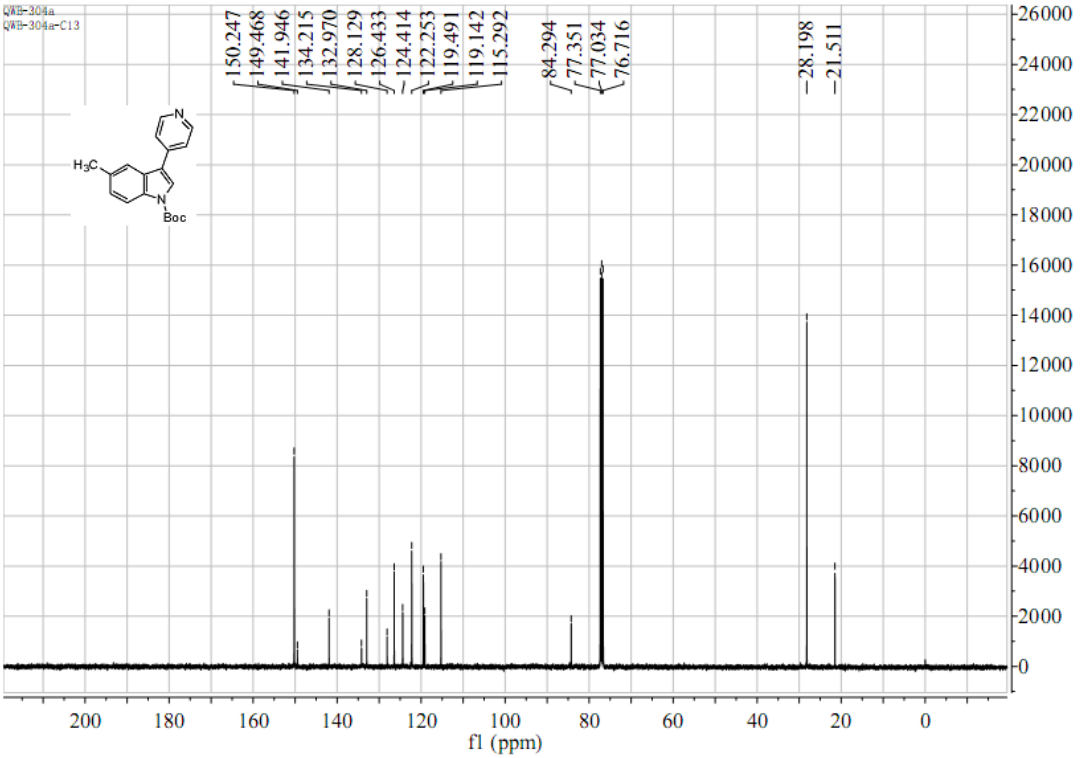
Compound **3c**


8.714
8.699
8.138
8.116
7.960
7.955
7.856
7.542
7.538
7.530
7.526
7.514
7.510
7.492
7.487
7.285
1.716
Br
N
Boc
1.98
0.94
1.00
0.93
2.06
1.04
9.01
fl (ppm)

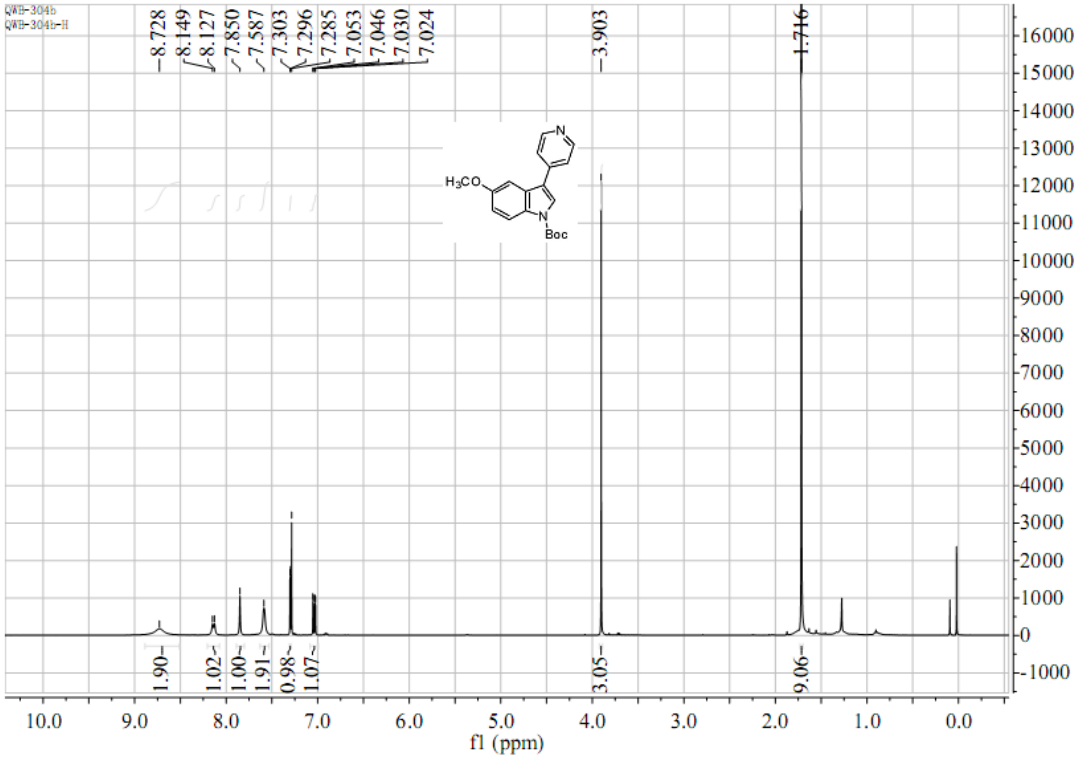

150.422
149.033
141.059
134.727
129.607
127.963
125.278
122.307
122.157
118.729
117.103
116.893
84.988
77.367
77.049
76.731
28.151
Br
N
Boc
fl (ppm)

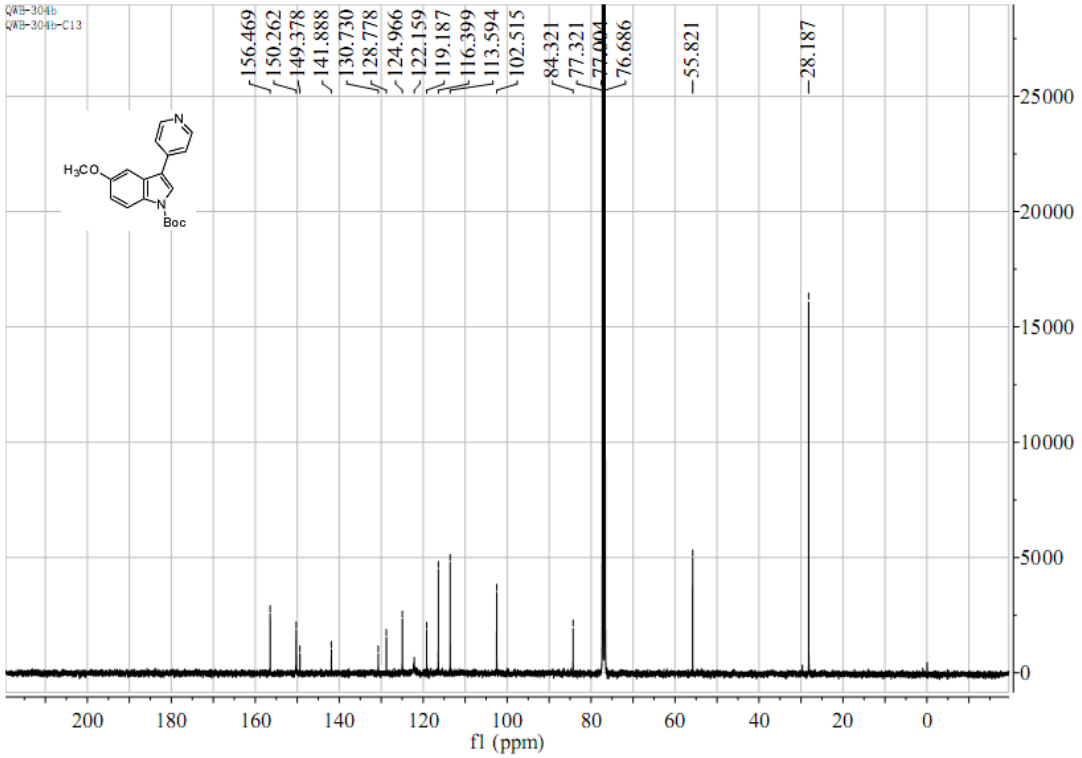
Compound **3d**


8.707
8.692
8.131
8.110
7.844
7.650
7.596
7.593
7.585
7.581
7.285
7.255
7.234
2.508
1.720
2.00
0.99
0.97
1.07
2.03
1.02
3.02
9.08
H3C
N
Boc
f1 (ppm)

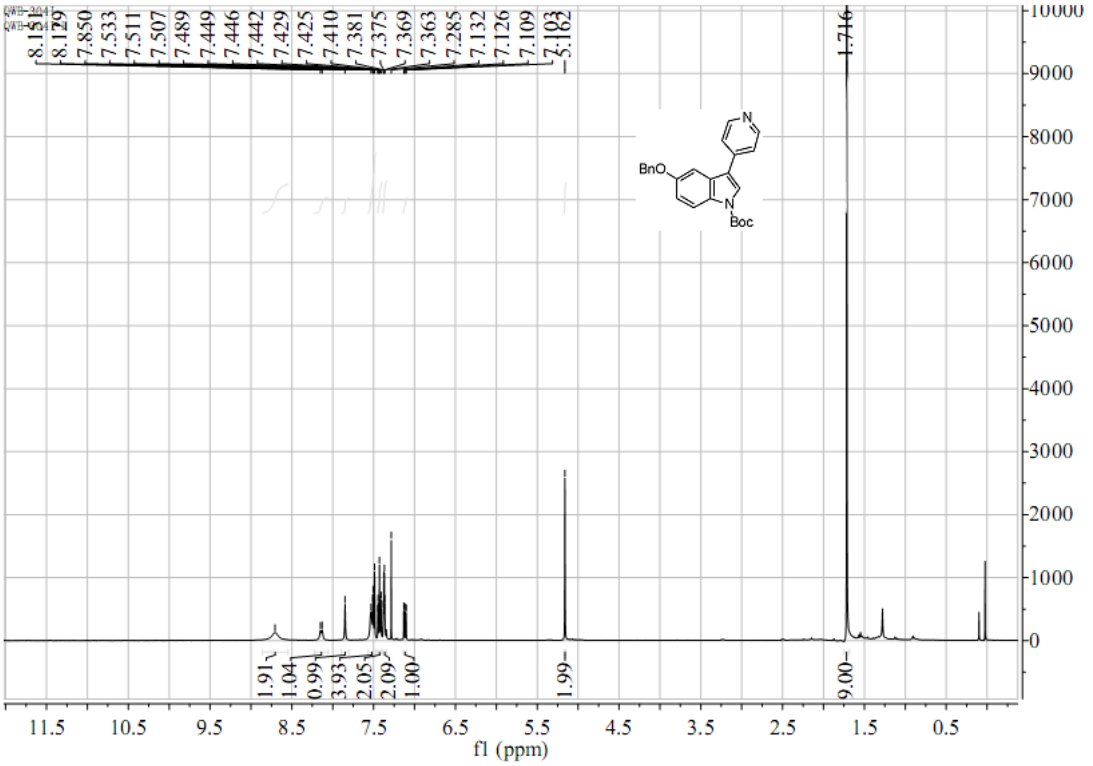

150.247
149.468
141.946
134.215
132.970
128.129
126.433
124.414
122.253
119.491
119.142
115.292
84.294
77.351
77.034
76.716
28.198
21.511
H3C
N
Boc
f1 (ppm)

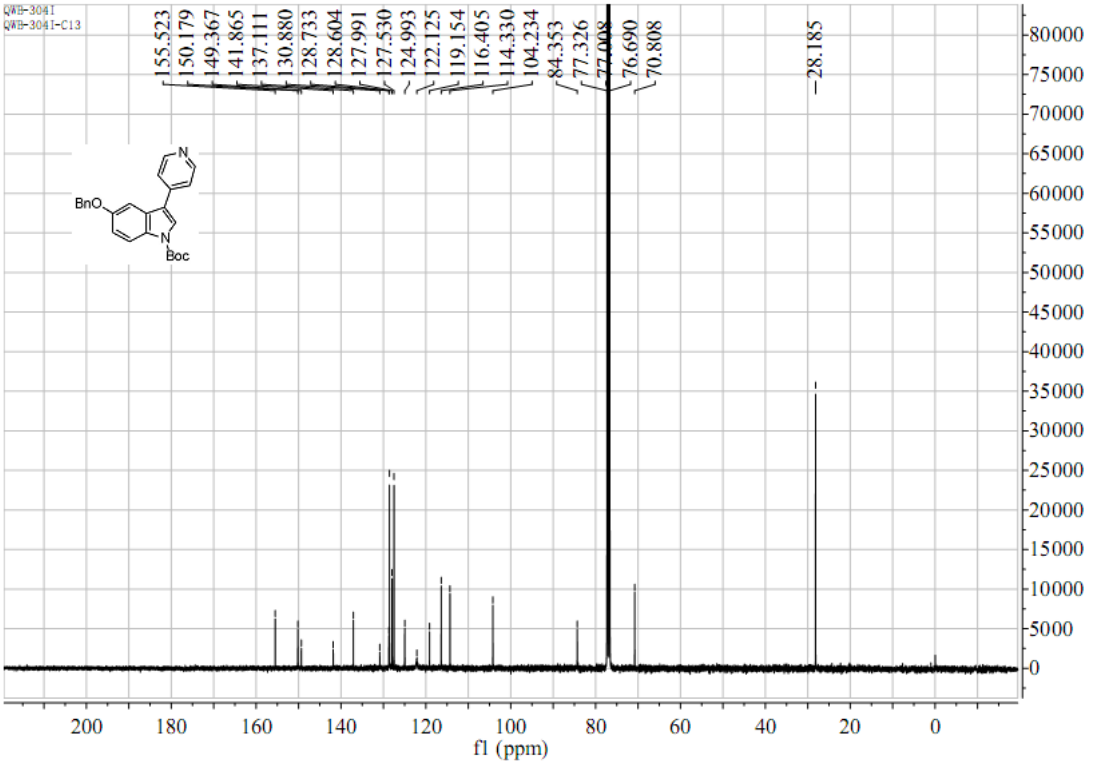
Compound **3e**


8.728
8.149
8.127
7.850
7.587
7.303
7.296
7.285
7.053
7.046
7.030
7.024
3.903
1.716
1.90
1.02
1.00
1.91
0.98
1.07
3.05
9.06
f1 (ppm)

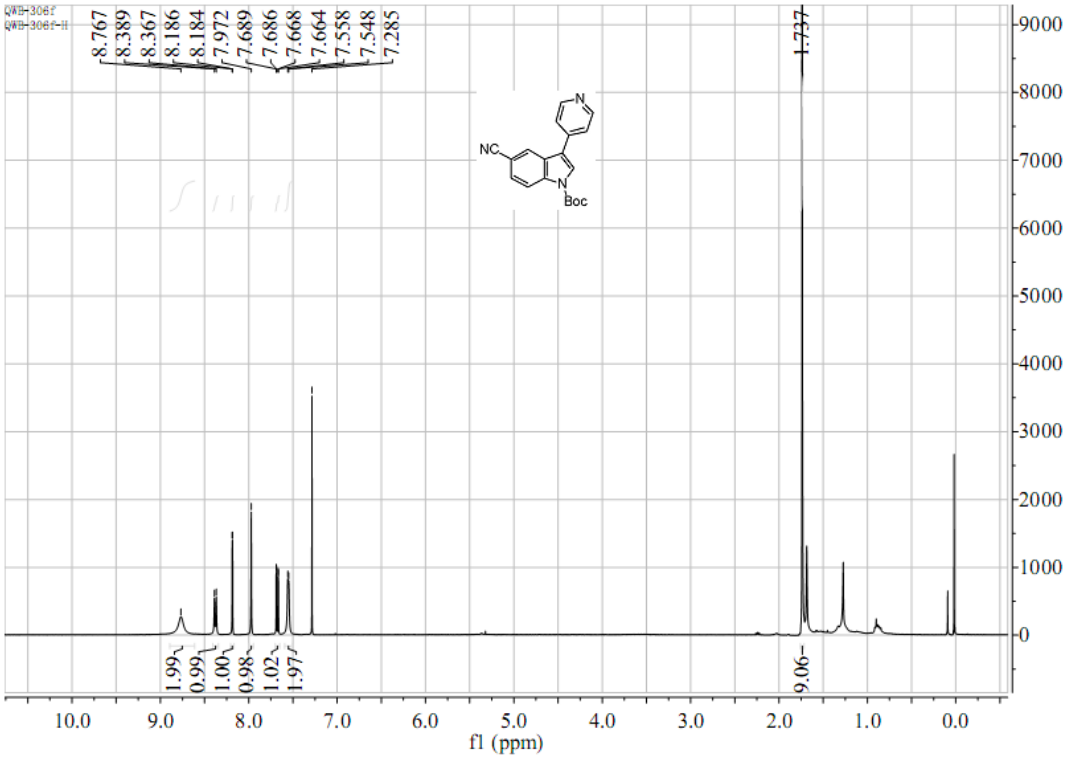

156.469
150.262
149.378
141.888
130.730
128.778
124.966
122.159
119.187
116.399
113.594
102.515
84.321
77.321
77.004
76.686
55.821
28.187
f1 (ppm)

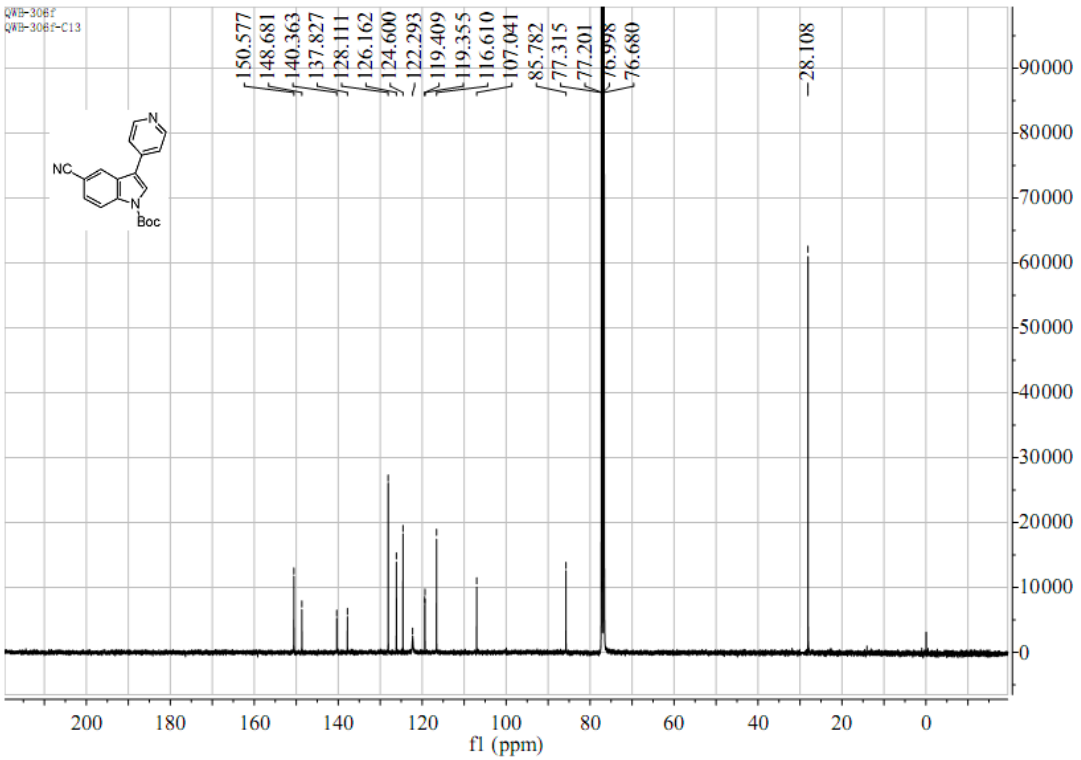
Compound **3f**


8.151
8.129
7.850
7.533
7.511
7.507
7.489
7.449
7.446
7.442
7.429
7.425
7.410
7.381
7.375
7.369
7.363
7.285
7.132
7.126
7.109
7.103
5.162
1.716
BnO
N
Boc
1.91
1.04
0.99
3.93
2.05
2.09
1.00
1.99
9.00
fl (ppm)

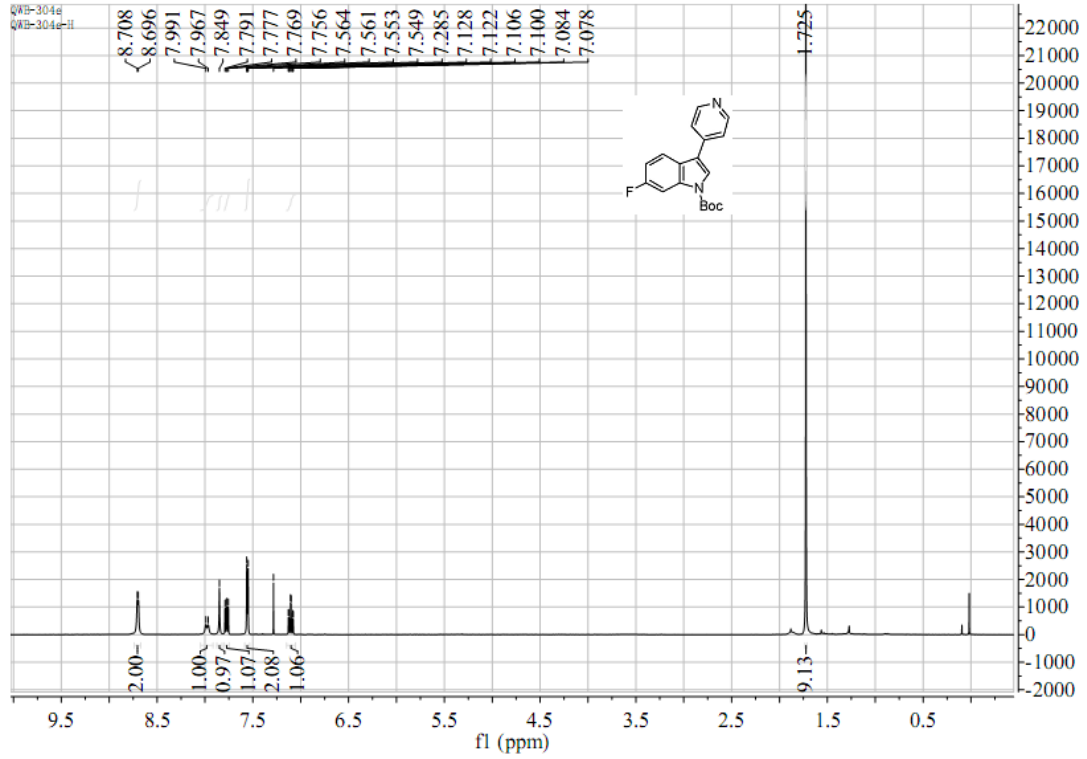

155.523
150.179
149.367
141.865
137.111
130.880
128.733
128.604
127.991
127.530
124.993
122.125
119.154
116.405
114.330
104.234
84.353
77.326
77.008
76.690
70.808
28.185
BnO
N
Boc
fl (ppm)

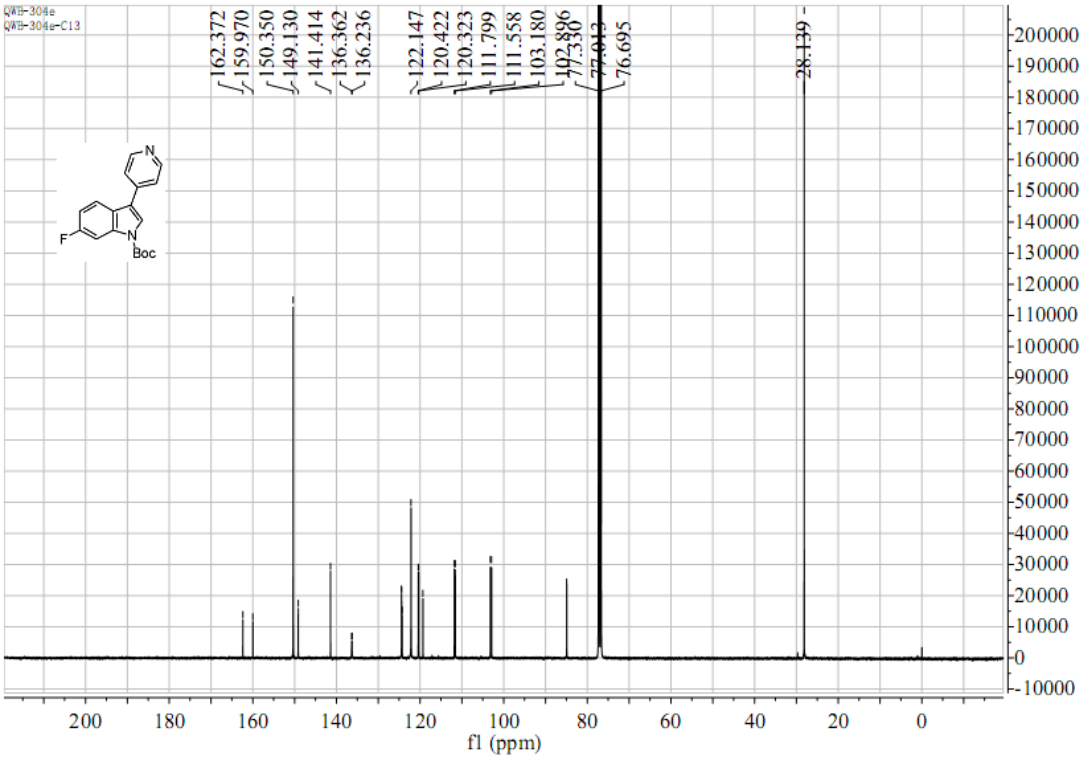
Compound **3g**


8.767
8.389
8.367
8.186
8.184
7.972
7.689
7.686
7.668
7.664
7.558
7.548
7.285
1.737
NC
N
Boc
1.99
0.99
1.00
0.98
1.02
1.97
9.06
fl (ppm)

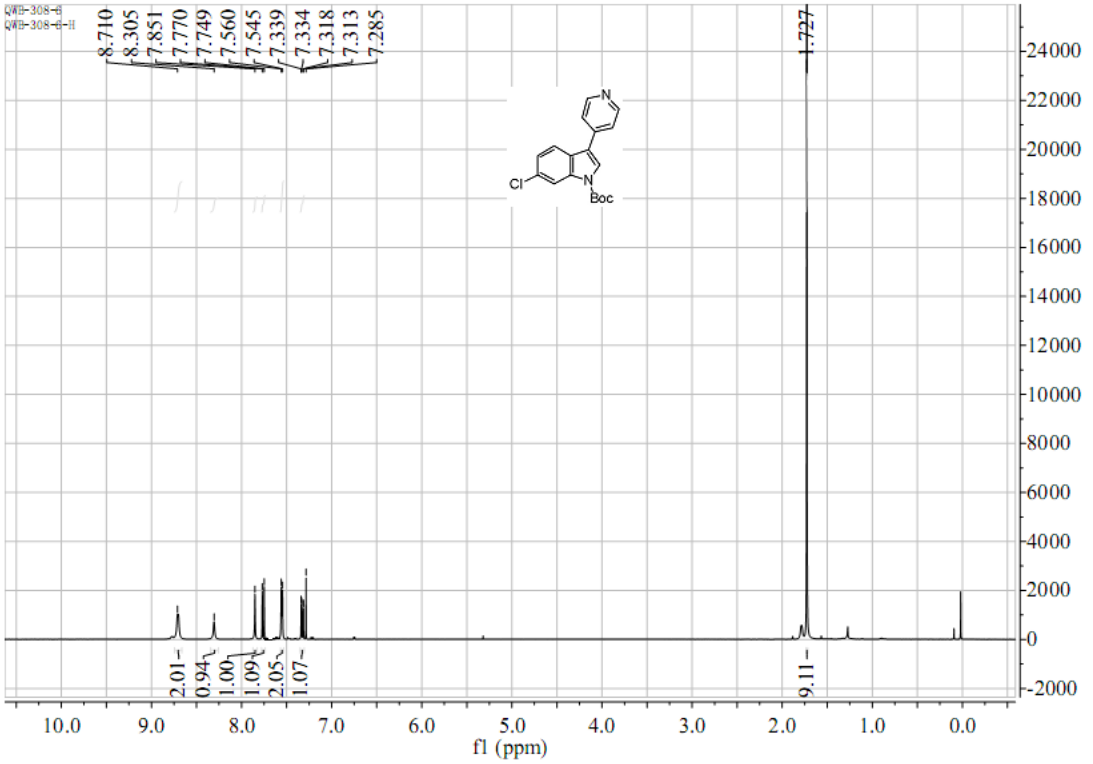

150.577
148.681
140.363
137.827
128.111
126.162
124.600
122.293
119.409
119.355
116.610
107.041
85.782
77.315
77.201
76.998
76.680
28.108
NC
N
Boc
fl (ppm)

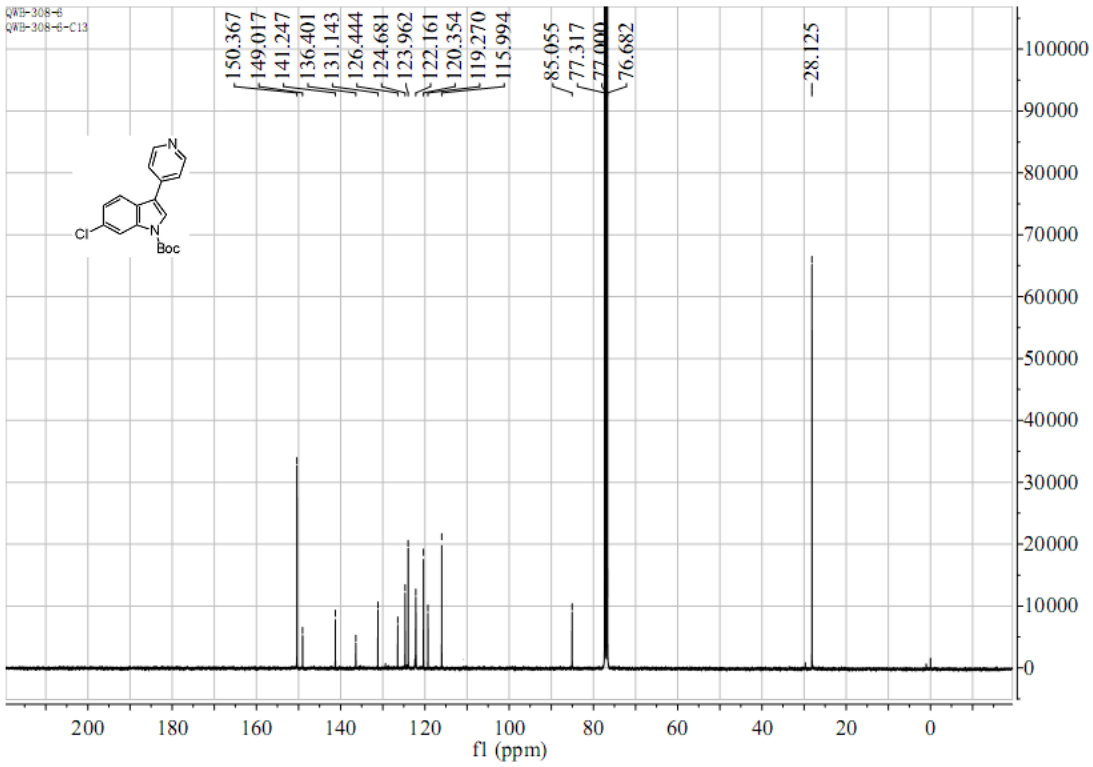
Compound **3h**


QWB-304e
QWB-304e-H
8.708
8.696
7.991
7.967
7.849
7.791
7.777
7.769
7.756
7.564
7.561
7.553
7.549
7.285
7.128
7.122
7.106
7.100
7.084
7.078
1.725
2.00
1.00
0.97
1.07
2.08
1.06
9.13
f1 (ppm)

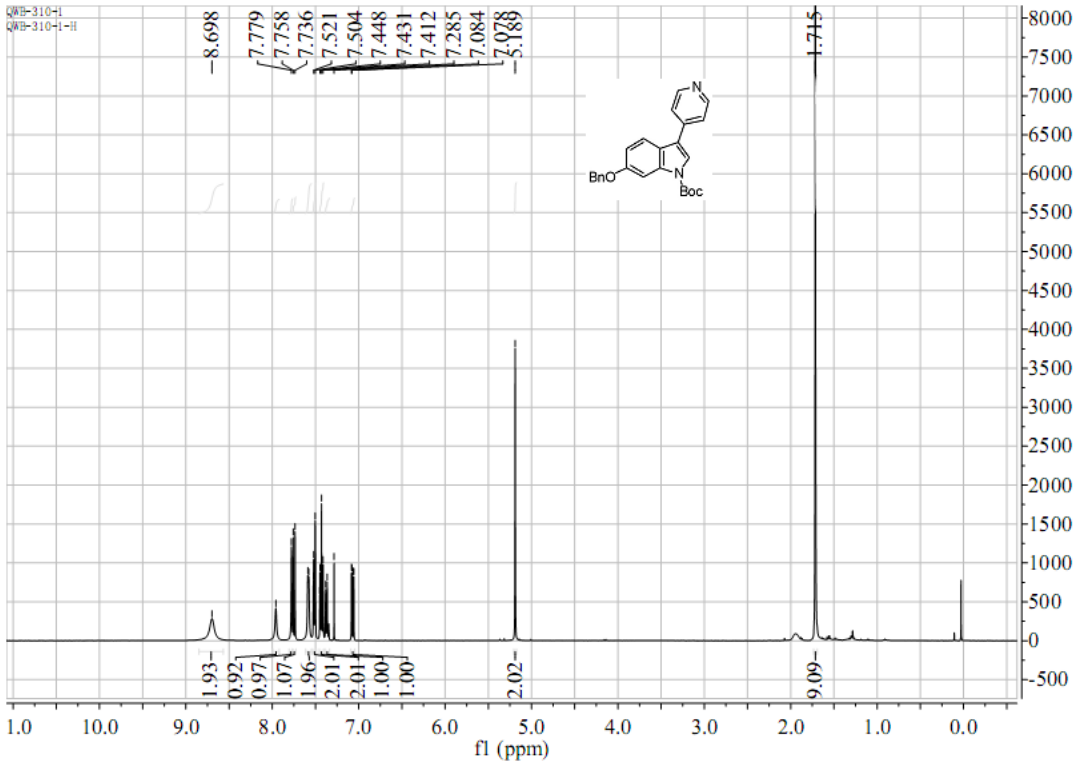

QWB-304e
QWB-304e-C13
162.372
159.970
150.350
149.130
141.414
136.362
136.236
122.147
120.422
120.323
111.799
111.558
103.180
102.896
77.330
77.013
76.695
28.139
f1 (ppm)

Compound **3i**


8.710
8.305
7.851
7.770
7.749
7.560
7.545
7.339
7.334
7.318
7.313
7.285
1.727
2.01
0.94
1.00
1.09
2.05
1.07
9.11
Cl
N
Boc
f1 (ppm)


150.367
149.017
141.247
136.401
131.143
126.444
124.681
123.962
122.161
120.354
119.270
115.994
85.055
77.317
77.000
76.682
28.125
Cl
N
Boc
f1 (ppm)

Compound **3j**


QWH-310-1
QWH-310-1-H1
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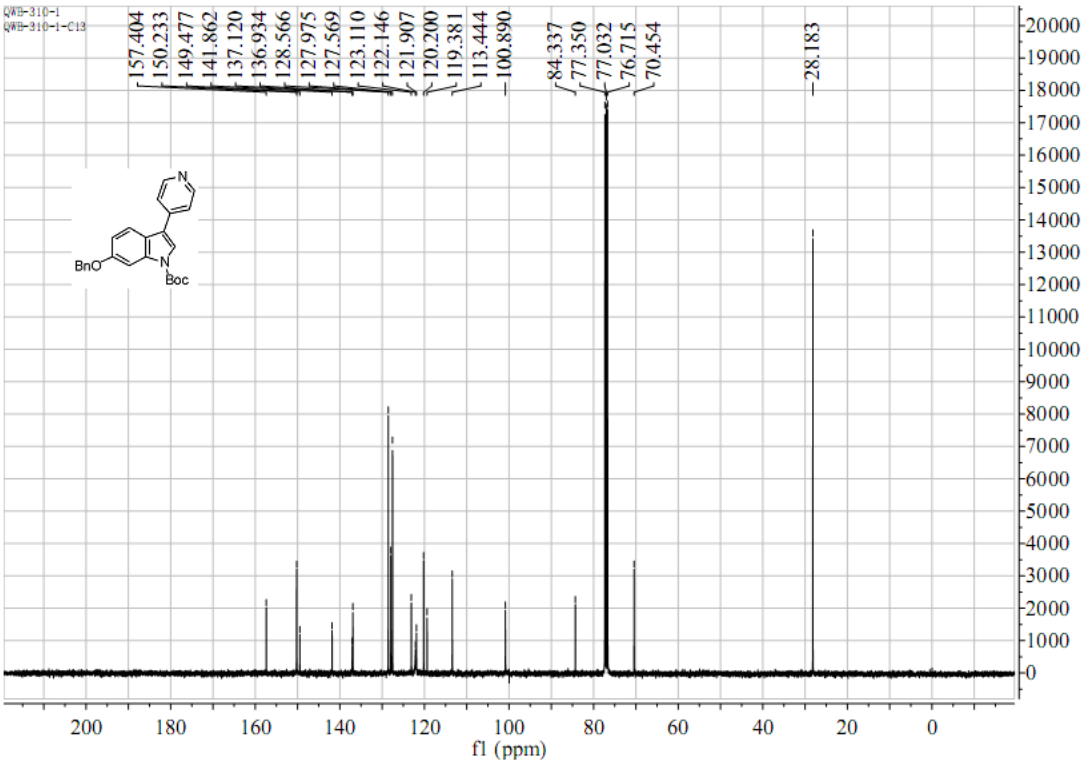
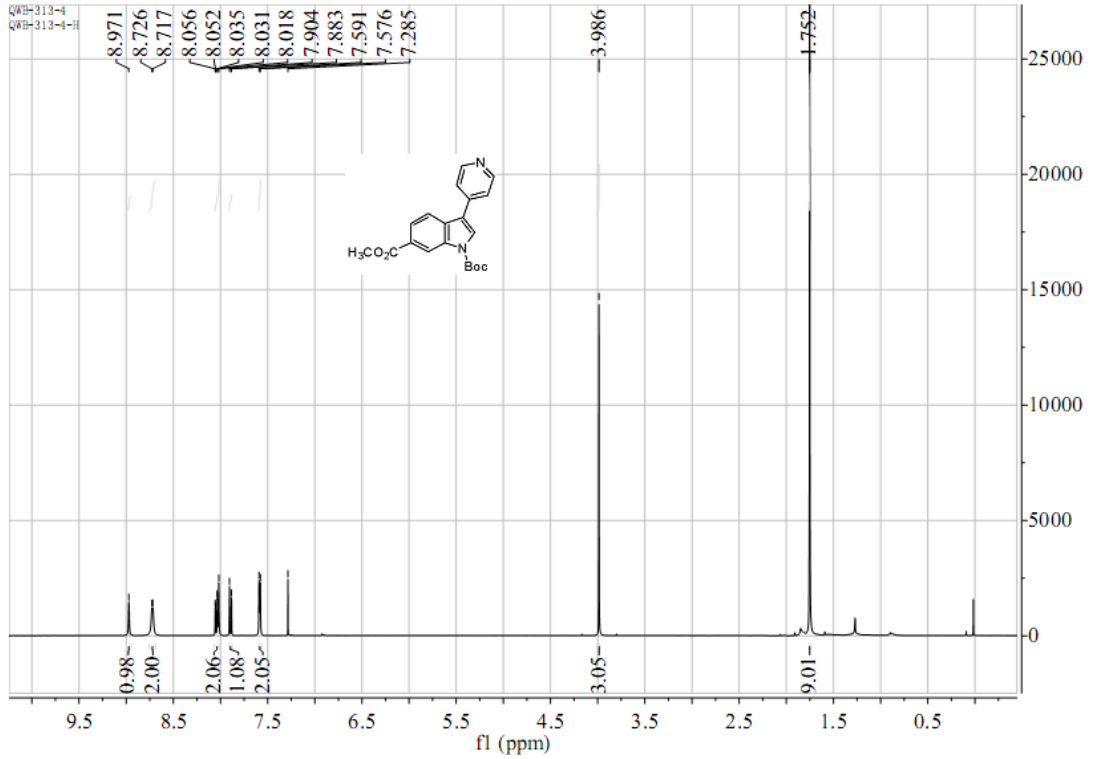
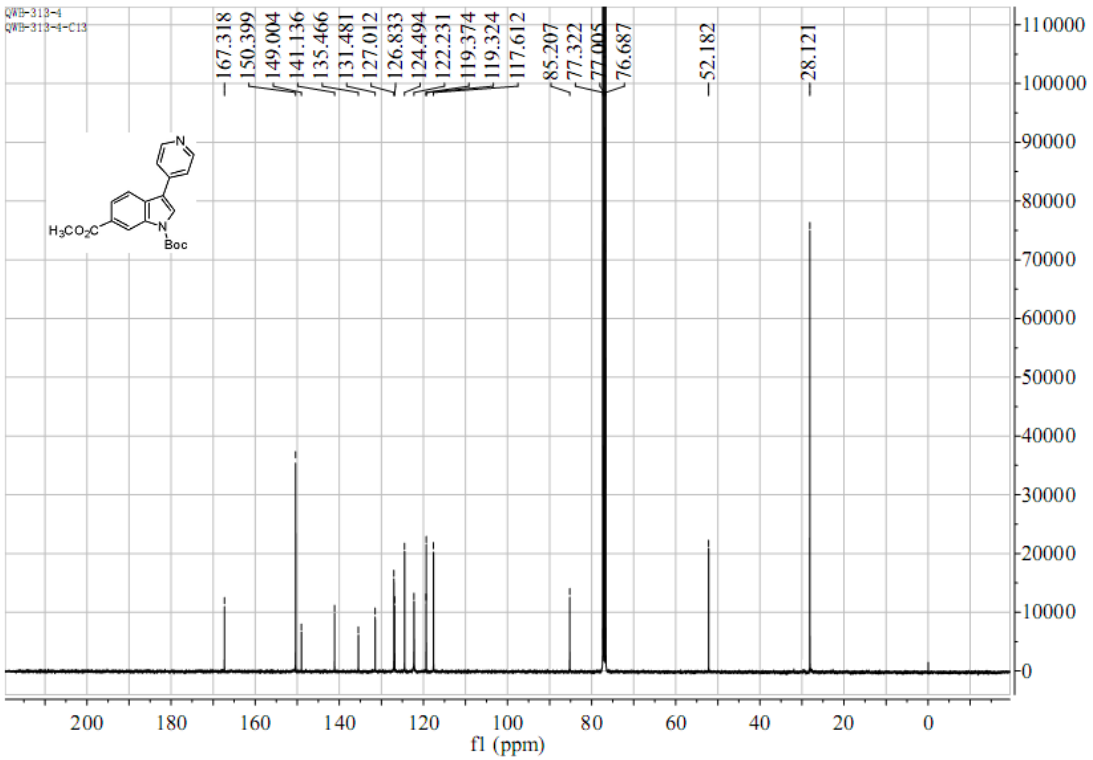
7.779
7.758
7.736
7.521
7.504
7.448
7.431
7.412
7.285
7.084
7.078
5.189
1.715
BnO
N
Boc
1.93
0.92
0.97
1.07
1.96
2.01
2.01
1.00
1.00
2.02
9.09
f1 (ppm)

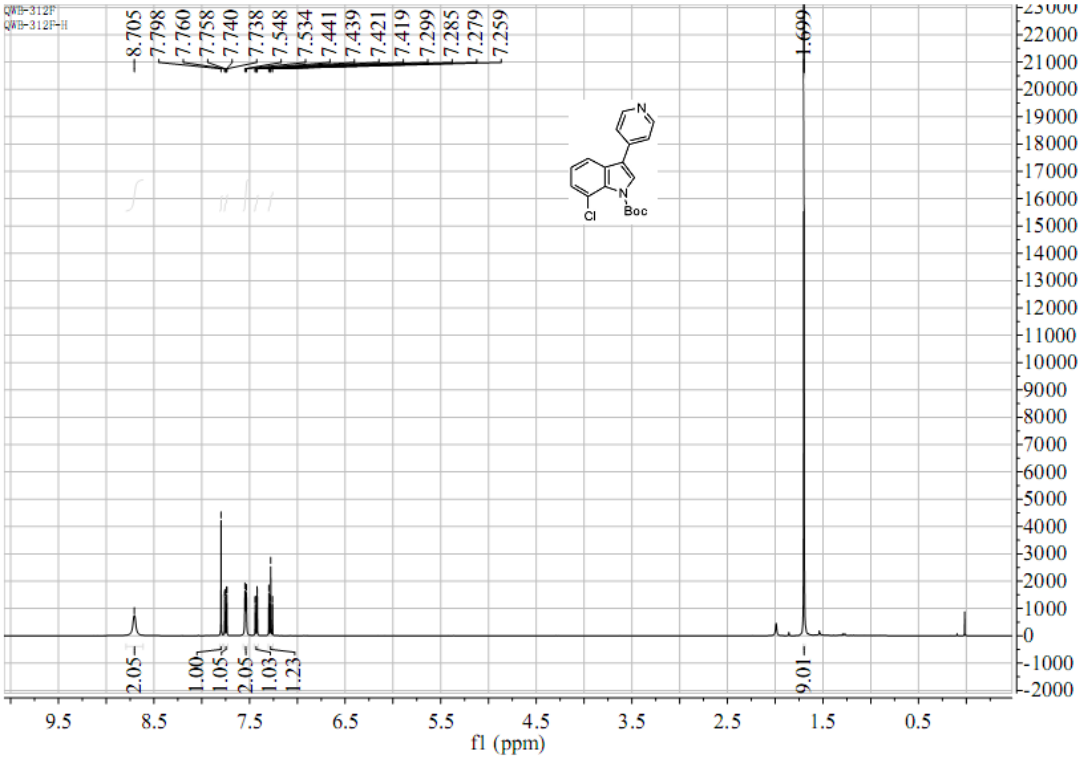

QWH-310-1
QWH-310-1-C13
157.404
150.233
149.477
141.862
137.120
136.934
128.566
127.975
127.569
123.110
122.146
121.907
120.200
119.381
113.444
100.890
84.337
77.350
77.032
76.715
70.454
28.183
BnO
N
Boc
f1 (ppm)

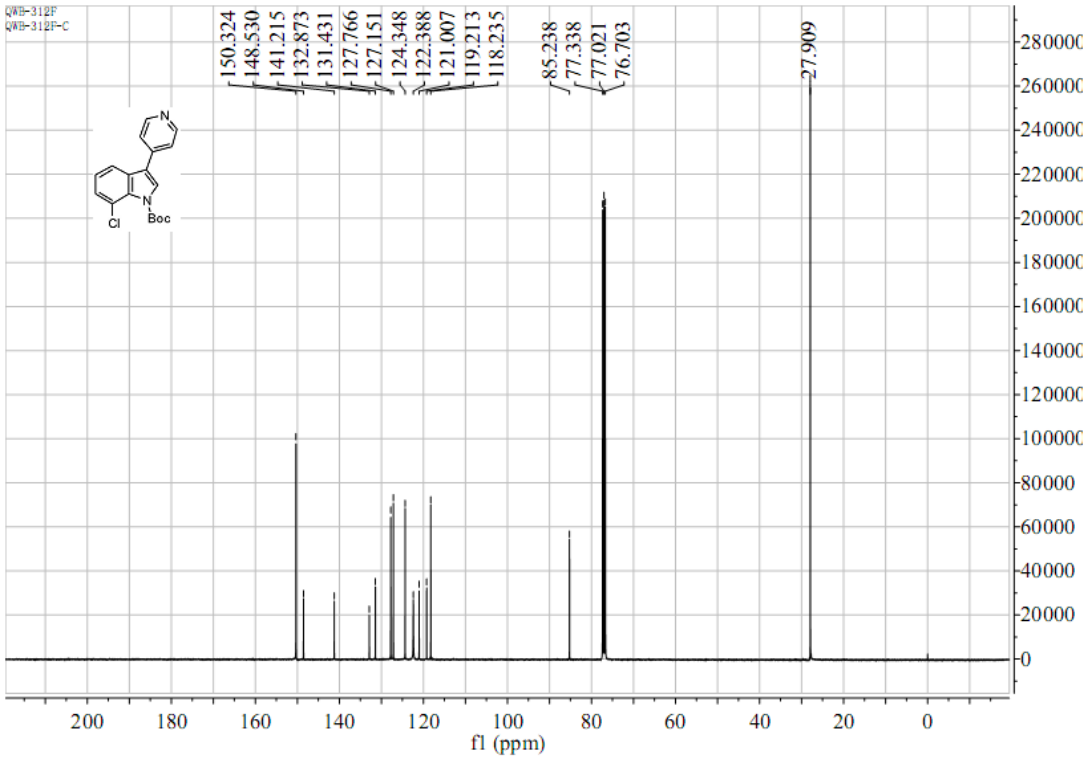
Compound **3k**


QWH-313-4
QWH-313-4-H
8.971
8.726
8.717
8.056
8.052
8.035
8.031
8.018
7.904
7.883
7.591
7.576
7.285
3.986
1.752
0.98
2.00
2.06
1.08
2.05
3.05
9.01
f1 (ppm)

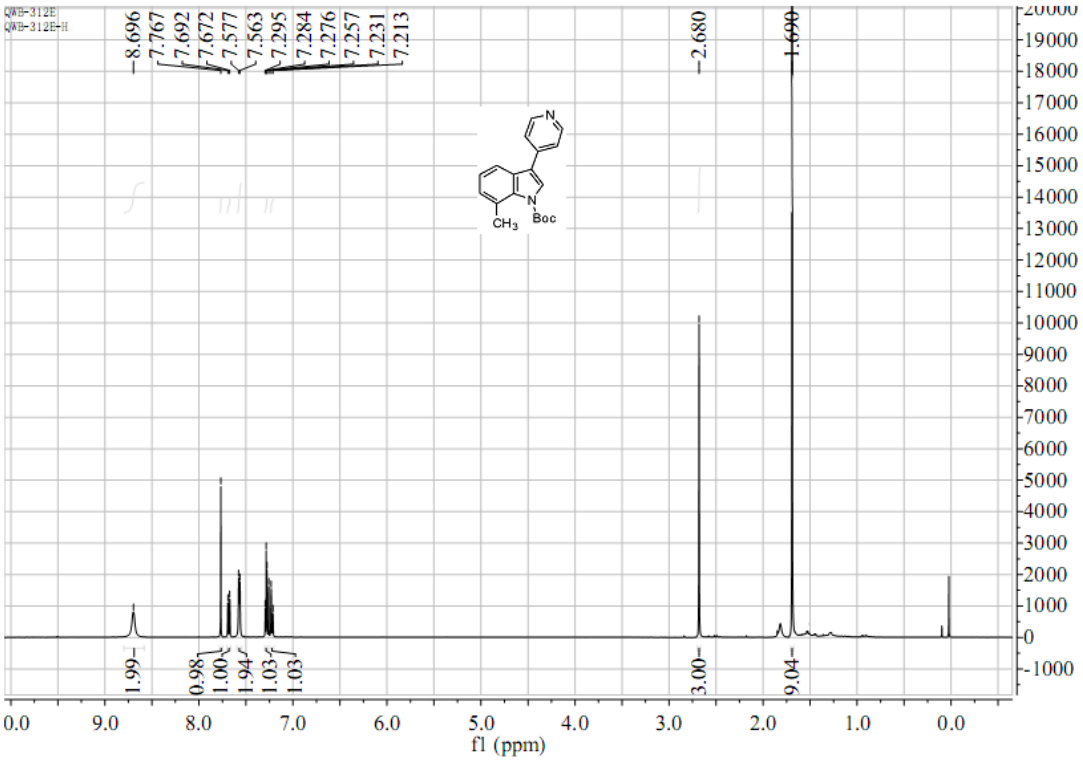

QWH-313-4
QWH-313-4-C13
167.318
150.399
149.004
141.136
135.466
131.481
127.012
126.833
124.494
122.231
119.374
119.324
117.612
85.207
77.322
77.005
76.687
52.182
28.121
f1 (ppm)

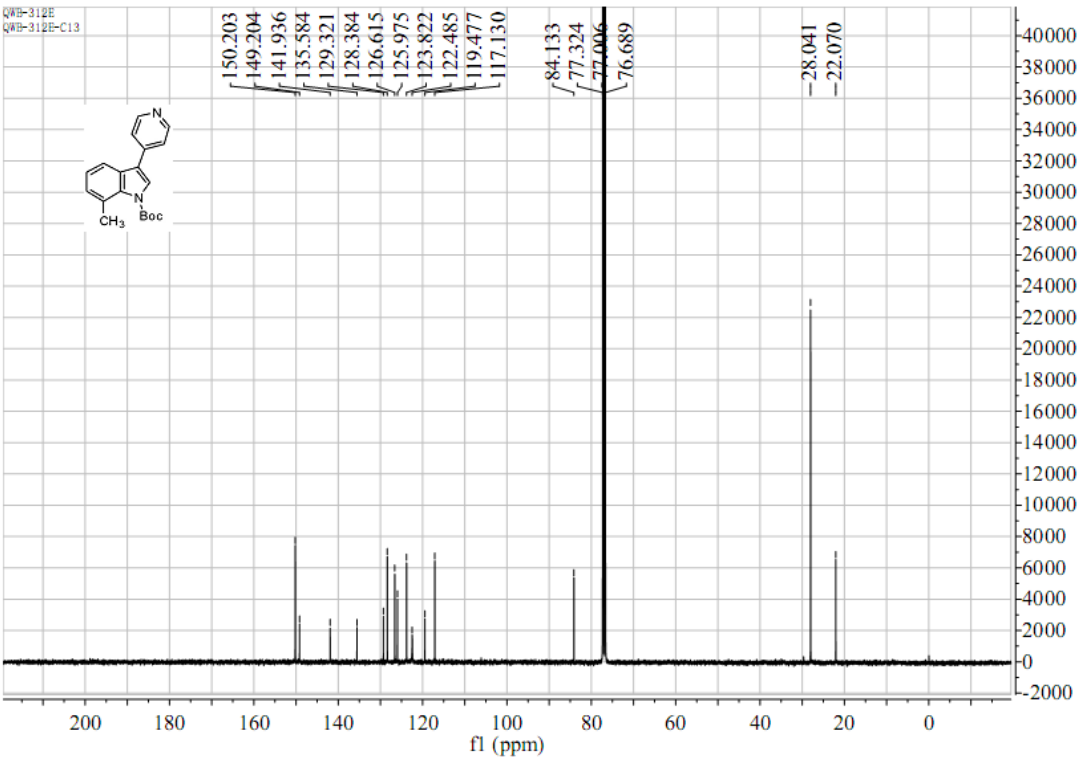
Compound **3l**


8.705
7.798
7.760
7.758
7.740
7.738
7.548
7.534
7.441
7.439
7.421
7.419
7.299
7.285
7.279
7.259
1.699
2.05
1.00
1.05
2.05
1.03
1.23
9.01
f1 (ppm)

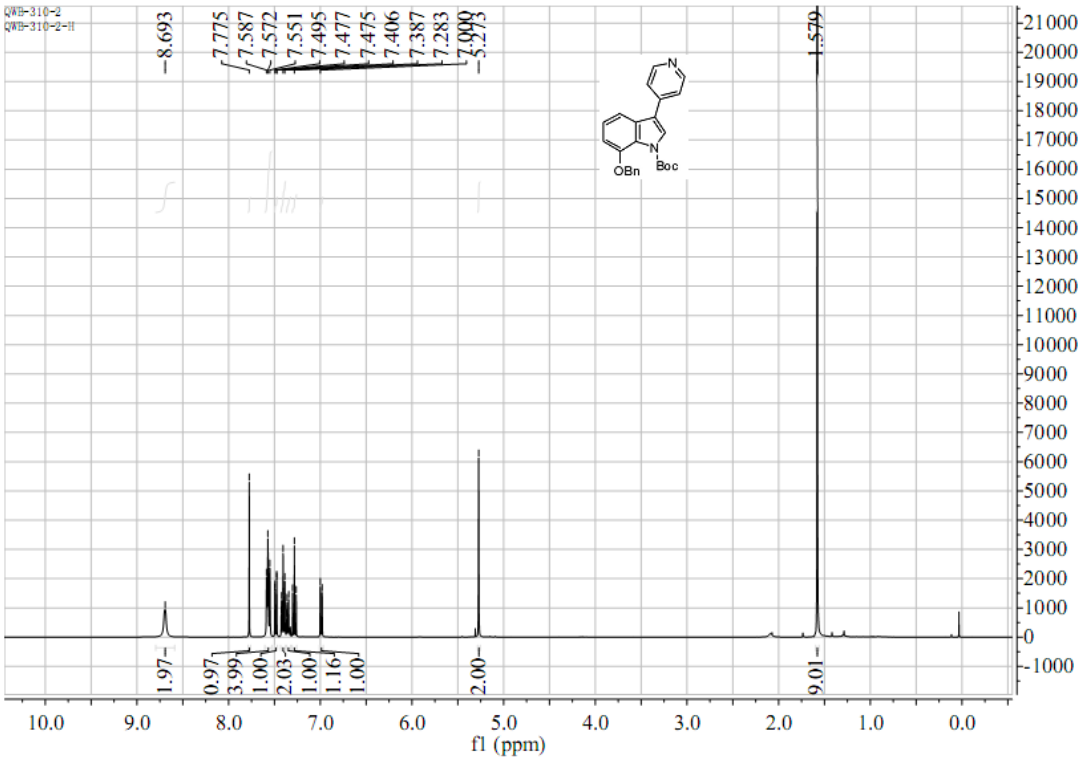

150.324
148.530
141.215
132.873
131.431
127.766
127.151
124.348
122.388
121.007
119.213
118.235
85.238
77.338
77.021
76.703
27.909
f1 (ppm)

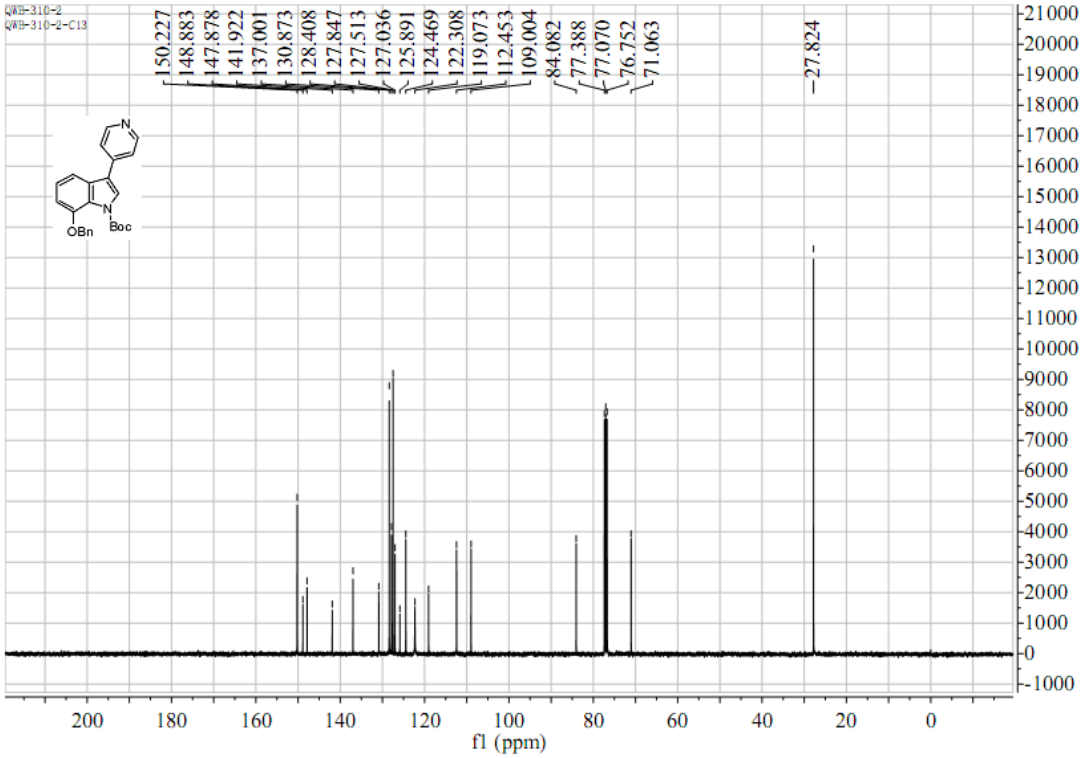
Compound **3m**


QWH-312E
QWH-312E-H
8.696
7.767
7.692
7.672
7.577
7.563
7.295
7.284
7.276
7.257
7.231
7.213
2.680
1.690
1.99
0.98
1.00
1.94
1.03
1.03
3.00
9.04
fl (ppm)

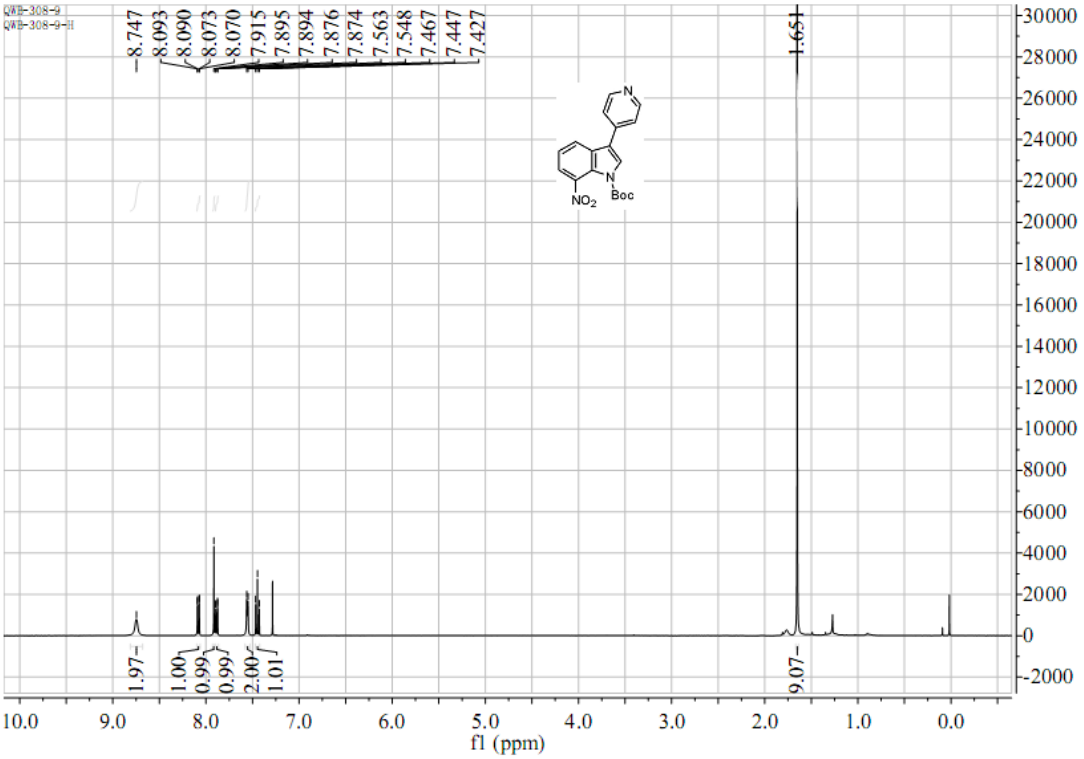

QWH-312E
QWH-312E-C13
150.203
149.204
141.936
135.584
129.321
128.384
126.615
125.975
123.822
122.485
119.477
117.130
84.133
77.324
77.006
76.689
28.041
22.070
fl (ppm)

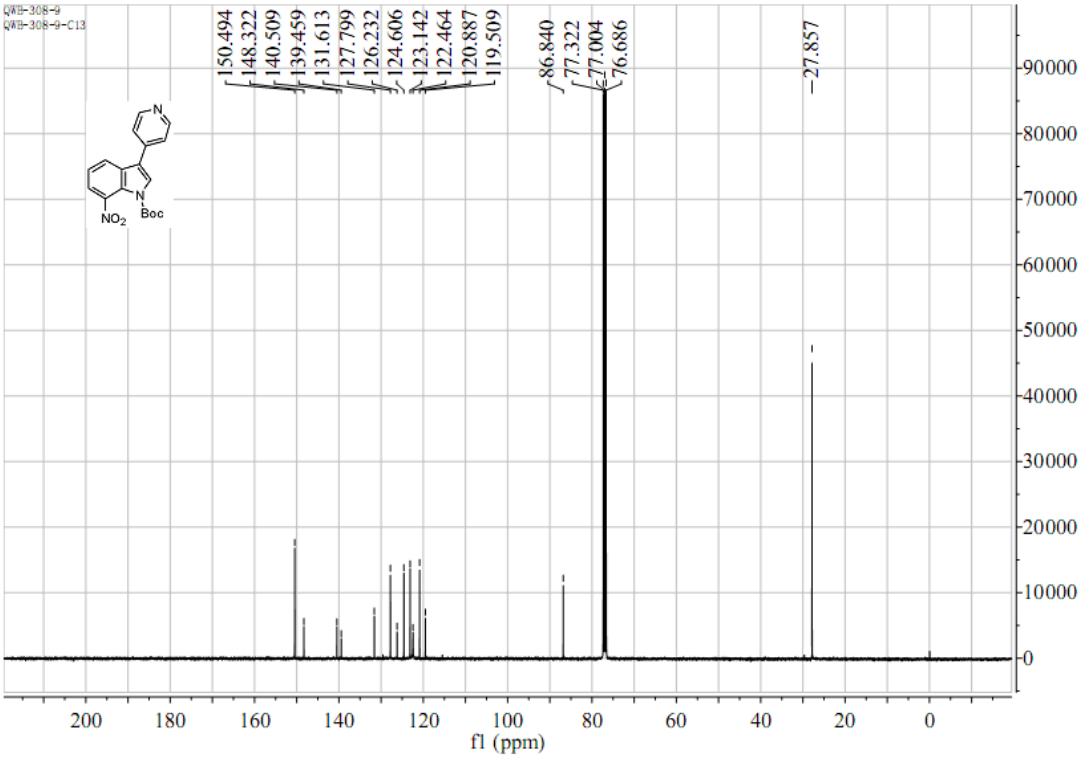
Compound **3n**


QWH-310-2
QWH-310-2-H
8.693
7.775
7.587
7.572
7.551
7.495
7.477
7.475
7.406
7.387
7.283
7.000
5.273
1.579
OBn
Boc
1.97
0.97
3.99
1.00
2.03
1.00
1.16
1.00
2.00
9.01
f1 (ppm)

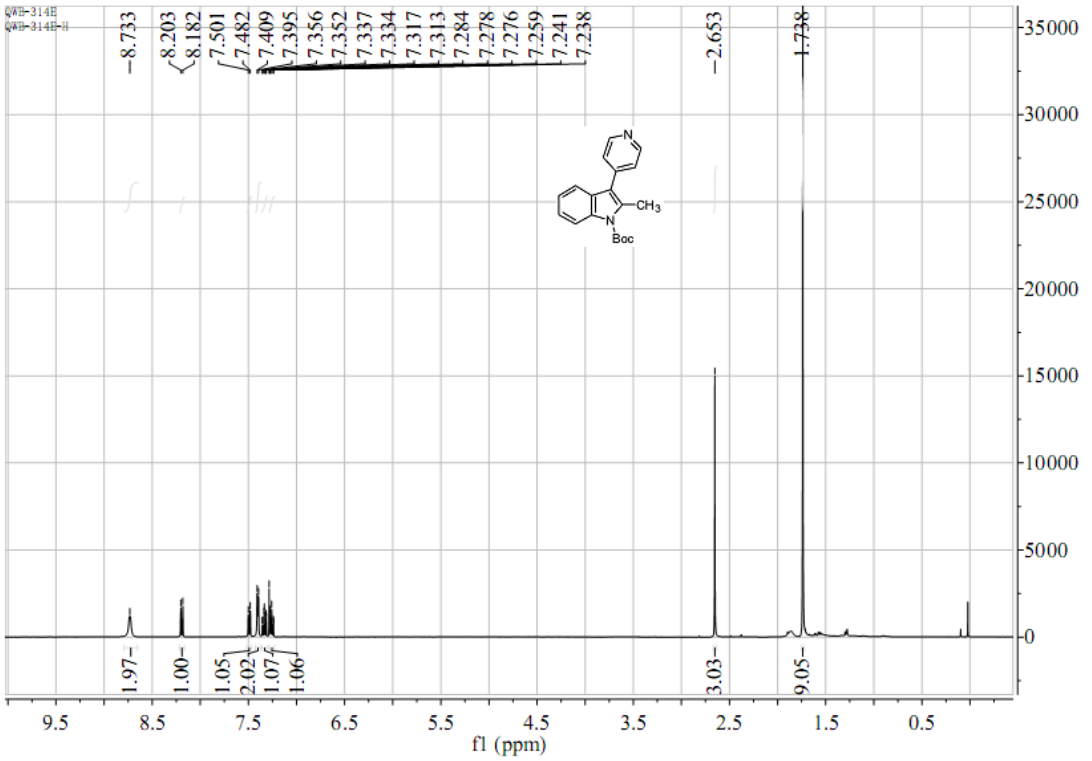

QWH-310-2
QWH-310-2-C13
150.227
148.883
147.878
141.922
137.001
130.873
128.408
127.847
127.513
127.036
125.891
124.469
122.308
119.073
112.453
109.004
84.082
77.388
77.070
76.752
71.063
27.824
OBn
Boc
f1 (ppm)

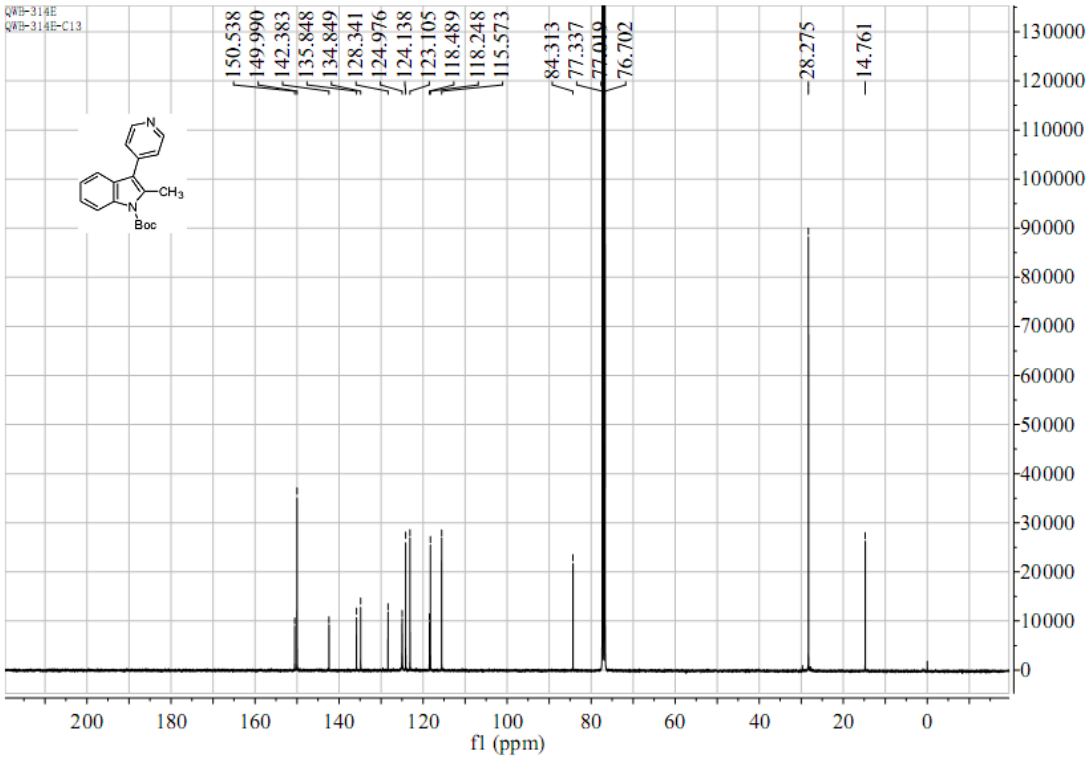
Compound **3o**


8.747
8.093
8.090
8.073
8.070
7.915
7.895
7.894
7.876
7.874
7.563
7.548
7.467
7.447
7.427
1.651
1.97
1.00
0.99
0.99
2.00
1.01
9.07
NO2
Boc
f1 (ppm)

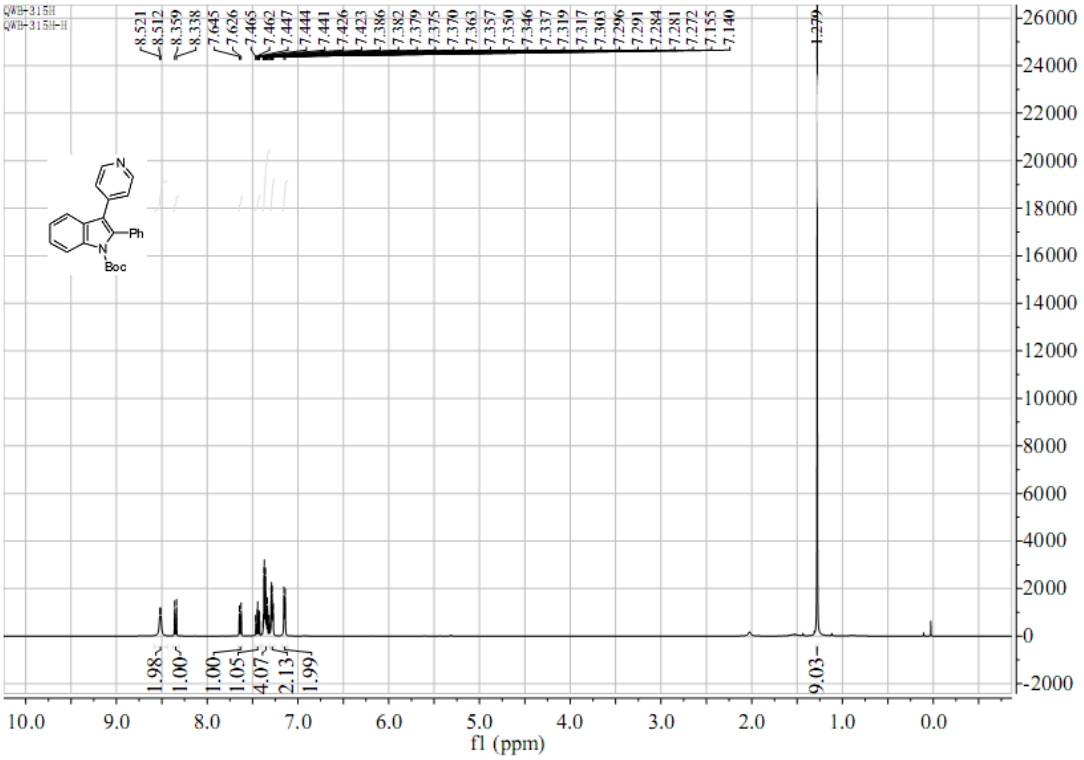

150.494
148.322
140.509
139.459
131.613
127.799
126.232
124.606
123.142
122.464
120.887
119.509
86.840
77.322
77.004
76.686
27.857
NO2
Boc
f1 (ppm)

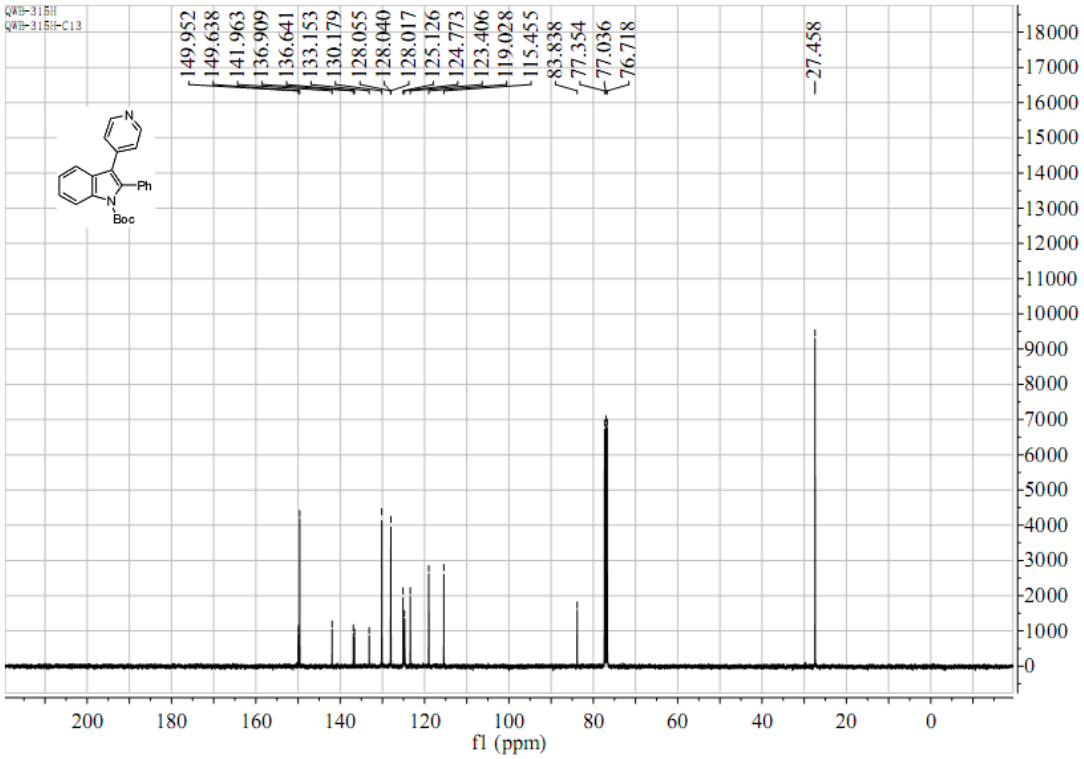
Compound **3p**


8.733
8.203
8.182
7.501
7.482
7.409
7.395
7.356
7.352
7.337
7.334
7.317
7.313
7.284
7.278
7.276
7.259
7.241
7.238
2.653
1.738
1.97
1.00
1.05
2.02
1.07
1.06
3.03
9.05
CH3
N
Boc
f1 (ppm)

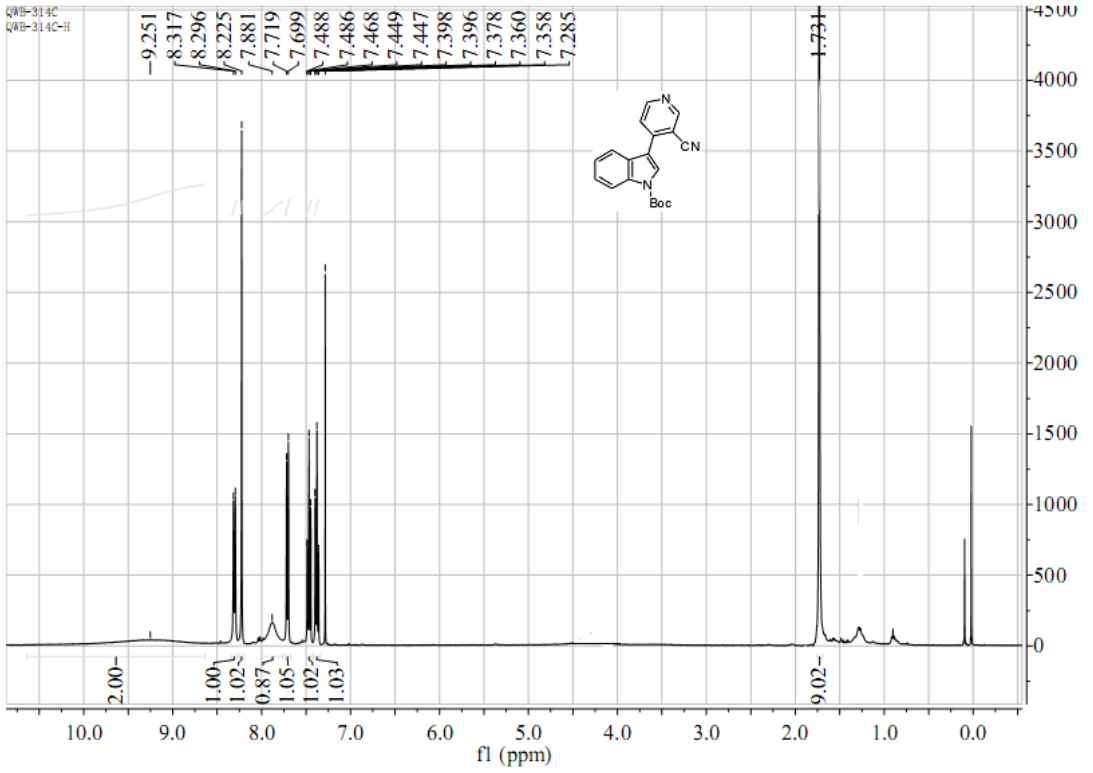

150.538
149.990
142.383
135.848
134.849
128.341
124.976
124.138
123.105
118.489
118.248
115.573
84.313
77.337
77.019
76.702
28.275
14.761
CH3
N
Boc
f1 (ppm)

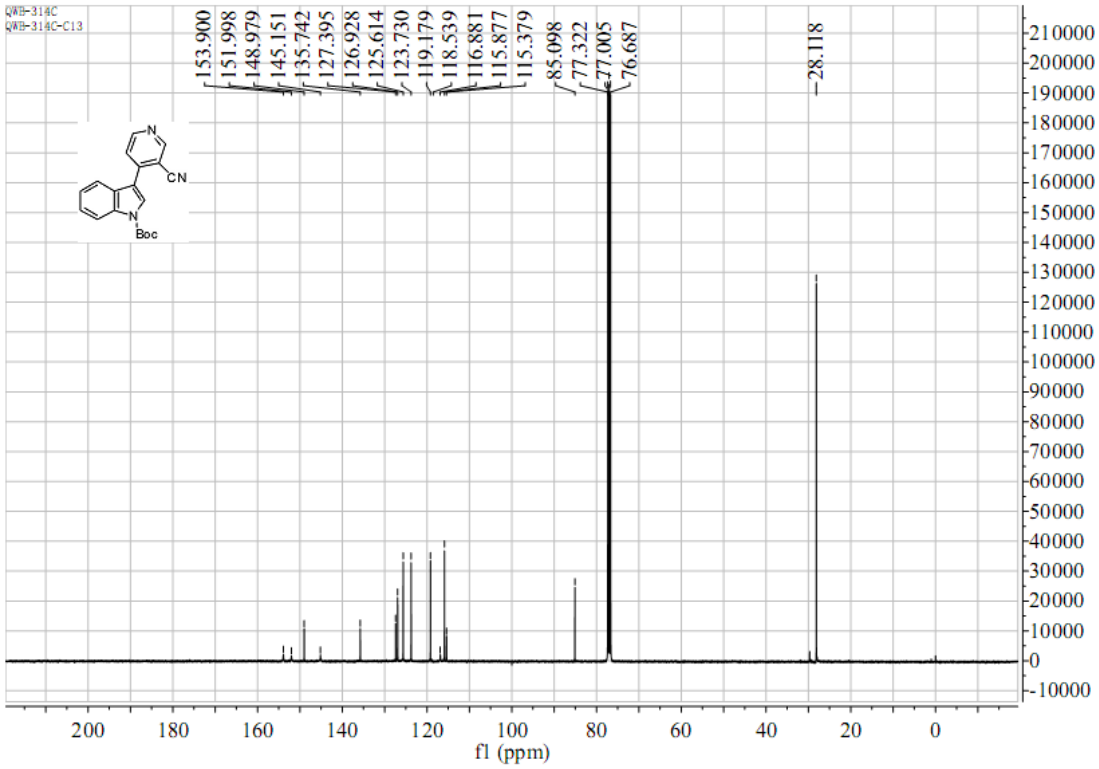
Compound **3q**


8.521
8.512
8.359
8.338
7.645
7.626
7.465
7.462
7.447
7.444
7.441
7.426
7.423
7.386
7.382
7.379
7.375
7.370
7.363
7.357
7.350
7.346
7.337
7.319
7.317
7.303
7.296
7.291
7.284
7.281
7.272
7.155
7.140
1.279
Ph
N
Boc
1.98
1.00
1.00
1.05
4.07
2.13
1.99
9.03
f1 (ppm)

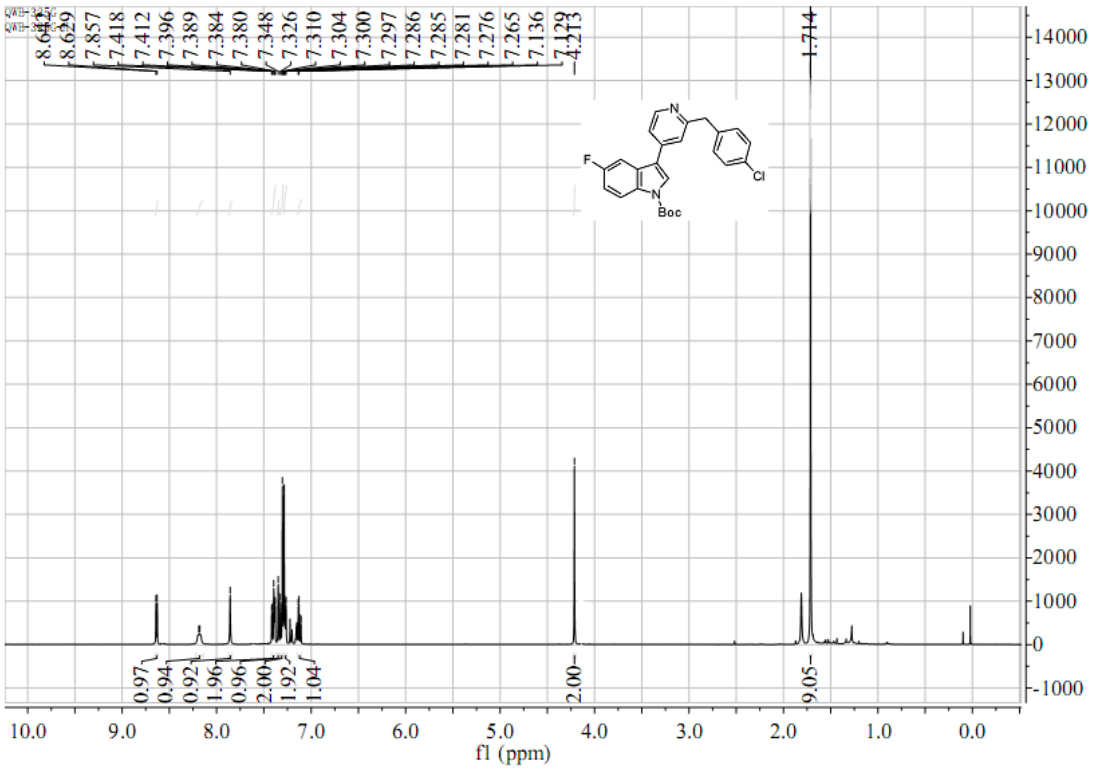

149.952
149.638
141.963
136.909
136.641
133.153
130.179
128.055
128.040
128.017
125.126
124.773
123.406
119.028
115.455
83.838
77.354
77.036
76.718
27.458
Ph
N
Boc
f1 (ppm)

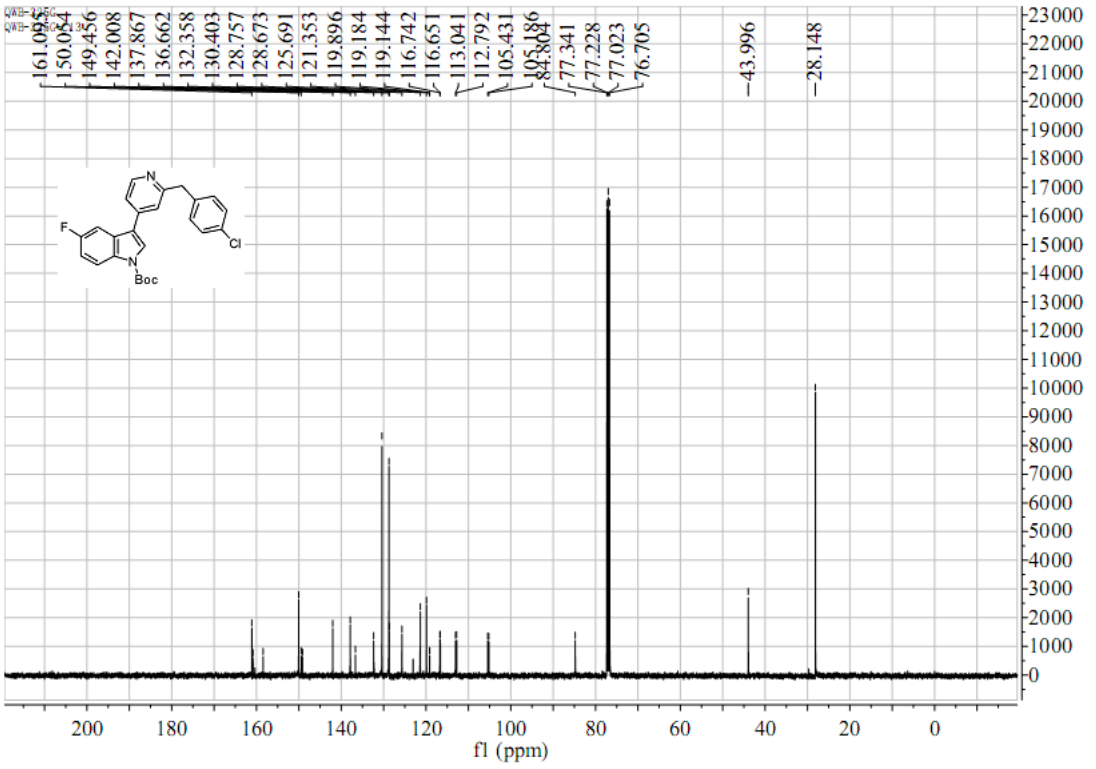
Compound **3r**


QWB-314C
QWB-314C-H
9.251
8.317
8.296
8.225
7.881
7.719
7.699
7.488
7.486
7.468
7.449
7.447
7.398
7.396
7.378
7.360
7.358
7.285
1.731
CN
N
Boc
2.00
1.00
1.02
0.87
1.05
1.02
1.03
9.02
f1 (ppm)

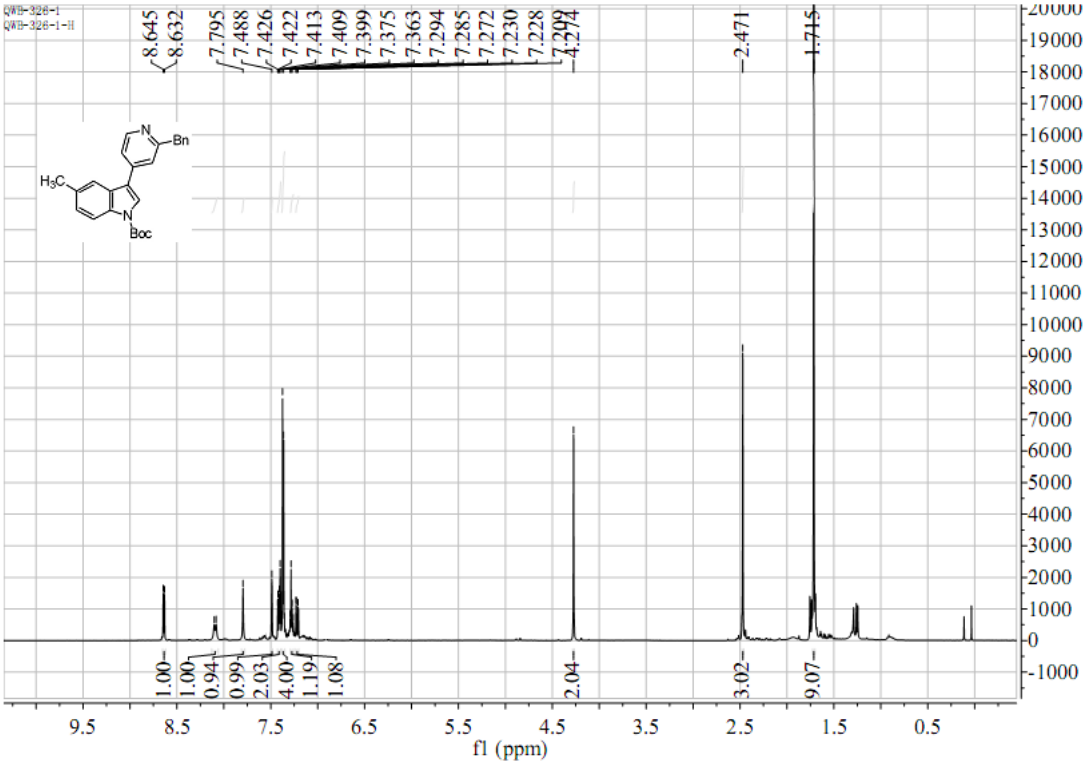

QWB-314C
QWB-314C-C13
153.900
151.998
148.979
145.151
135.742
127.395
126.928
125.614
123.730
119.179
118.539
116.881
115.877
115.379
85.098
77.322
77.005
76.687
28.118
CN
N
Boc
f1 (ppm)

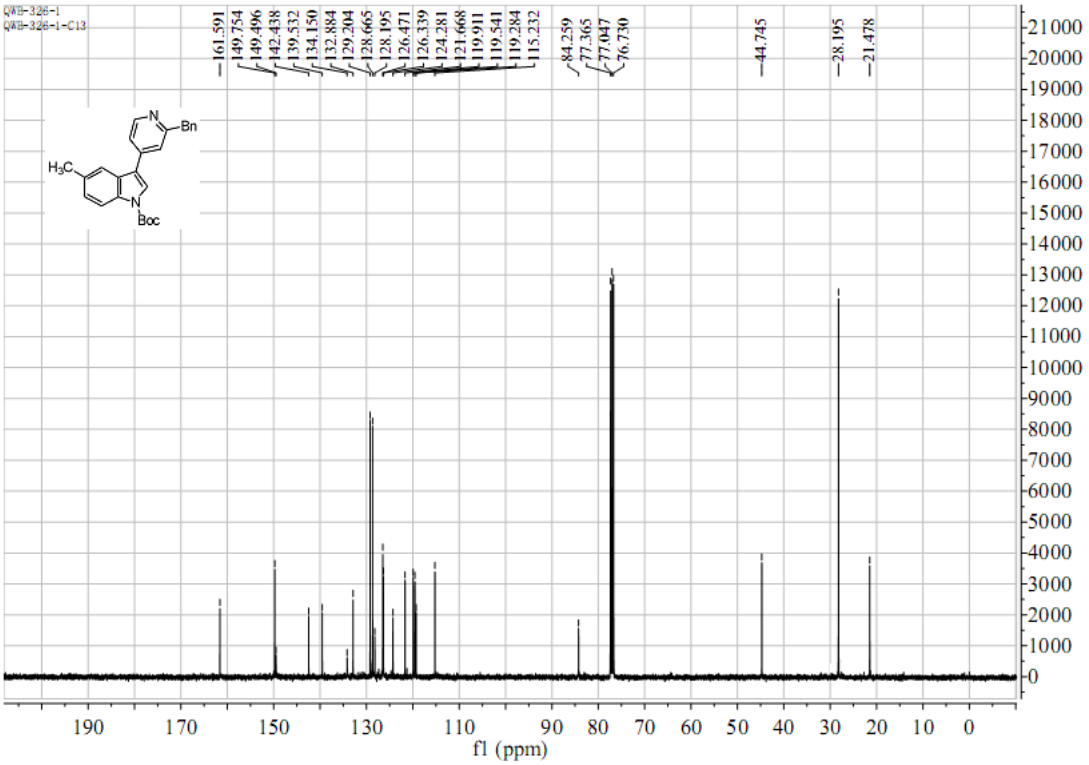
Compound **3s**


8.644
8.629
7.857
7.418
7.412
7.396
7.389
7.384
7.380
7.348
7.326
7.310
7.304
7.300
7.297
7.286
7.285
7.281
7.276
7.265
7.136
7.129
4.213
1.714
0.97
0.94
0.92
1.96
0.96
2.00
1.92
1.04
2.00
9.05
F
N
Cl
Boc
f1 (ppm)

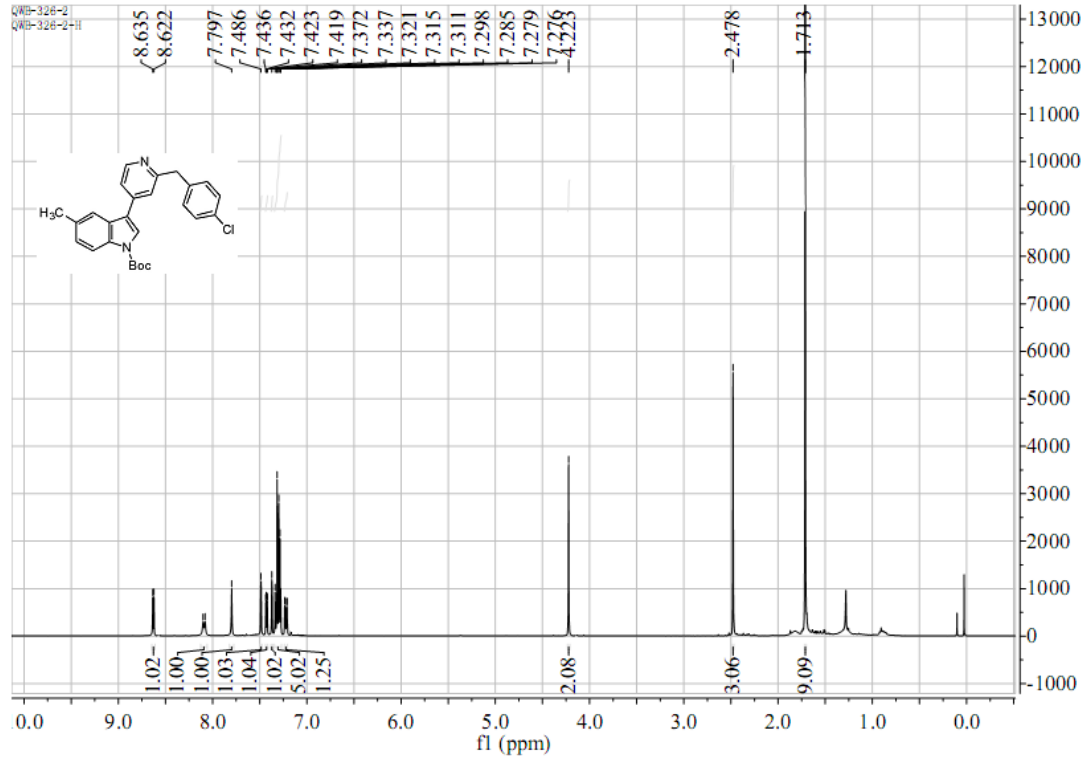

161.095
150.054
149.456
142.008
137.867
136.662
132.358
130.403
128.757
128.673
125.691
121.353
119.896
119.184
119.144
116.742
116.651
113.041
112.792
105.431
105.186
84.804
77.341
77.228
77.023
76.705
43.996
28.148
F
N
Cl
Boc
f1 (ppm)

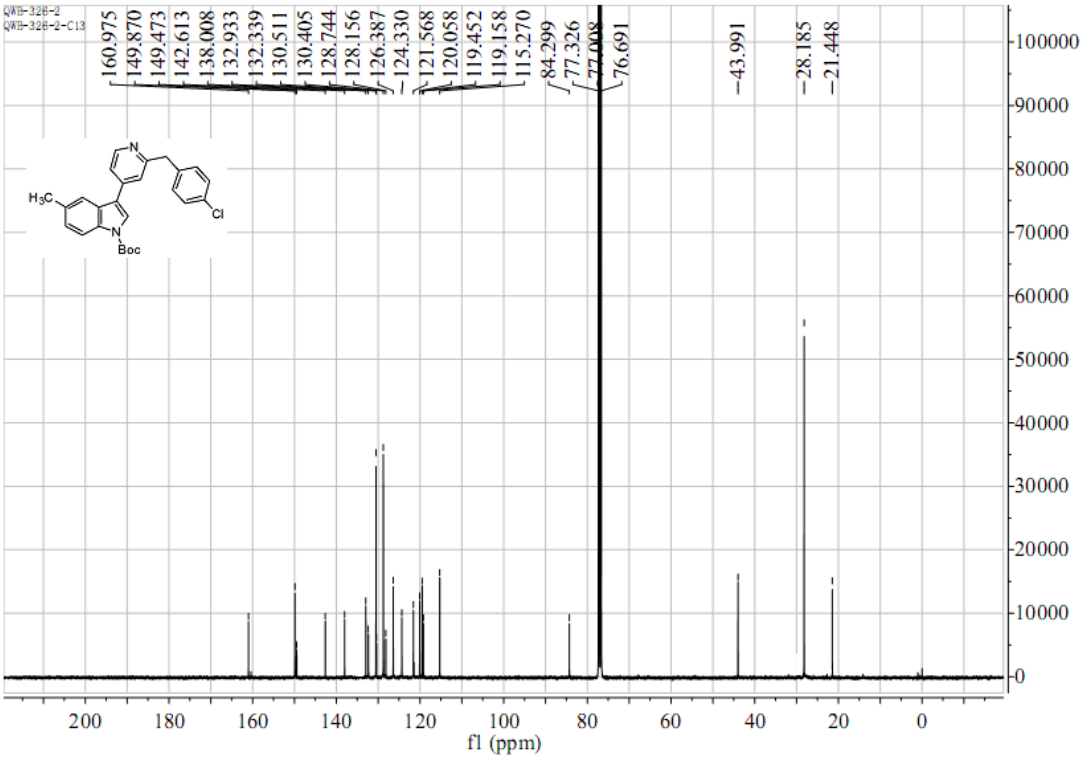
Compound **3t**


8.645
8.632
7.795
7.488
7.426
7.422
7.413
7.409
7.399
7.375
7.363
7.294
7.285
7.272
7.230
7.228
7.209
4.274
2.471
1.715
Bn
H3C
Boc
1.00
1.00
0.94
0.99
2.03
4.00
1.19
1.08
2.04
3.02
9.07
f1 (ppm)

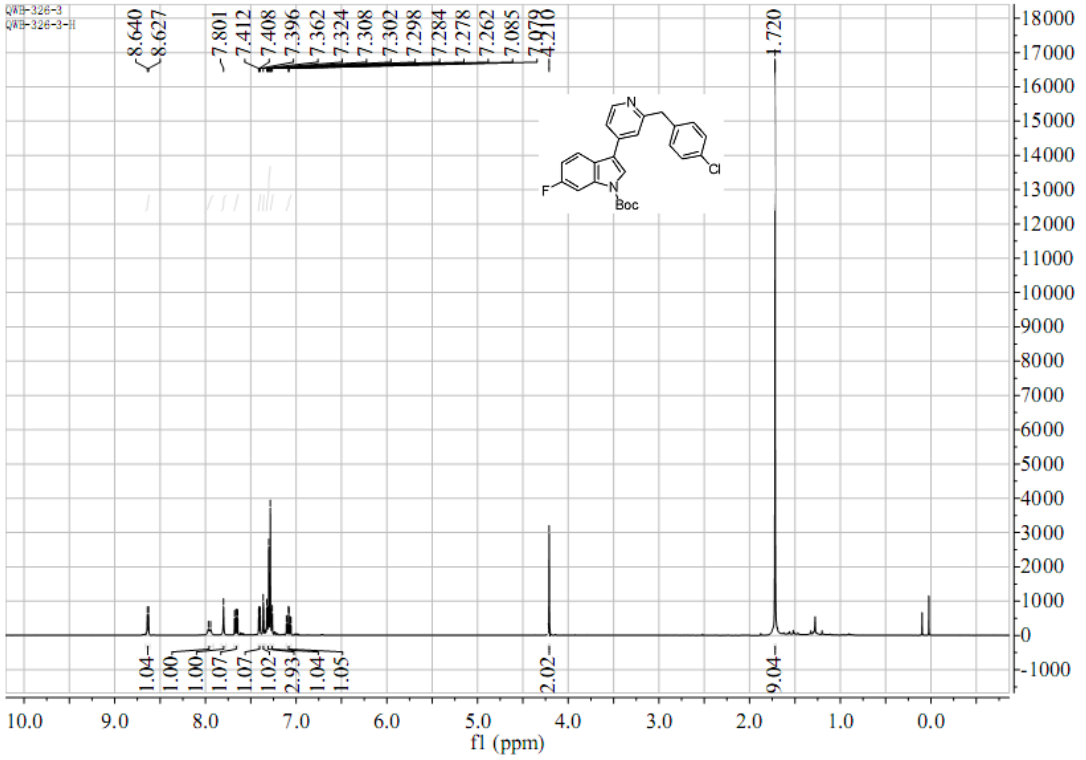

161.591
149.754
149.496
142.438
139.532
134.150
132.884
129.204
128.665
128.195
126.471
126.339
124.281
121.668
119.911
119.541
119.284
115.232
84.259
77.365
77.047
76.730
44.745
28.195
21.478
Bn
H3C
Boc
f1 (ppm)

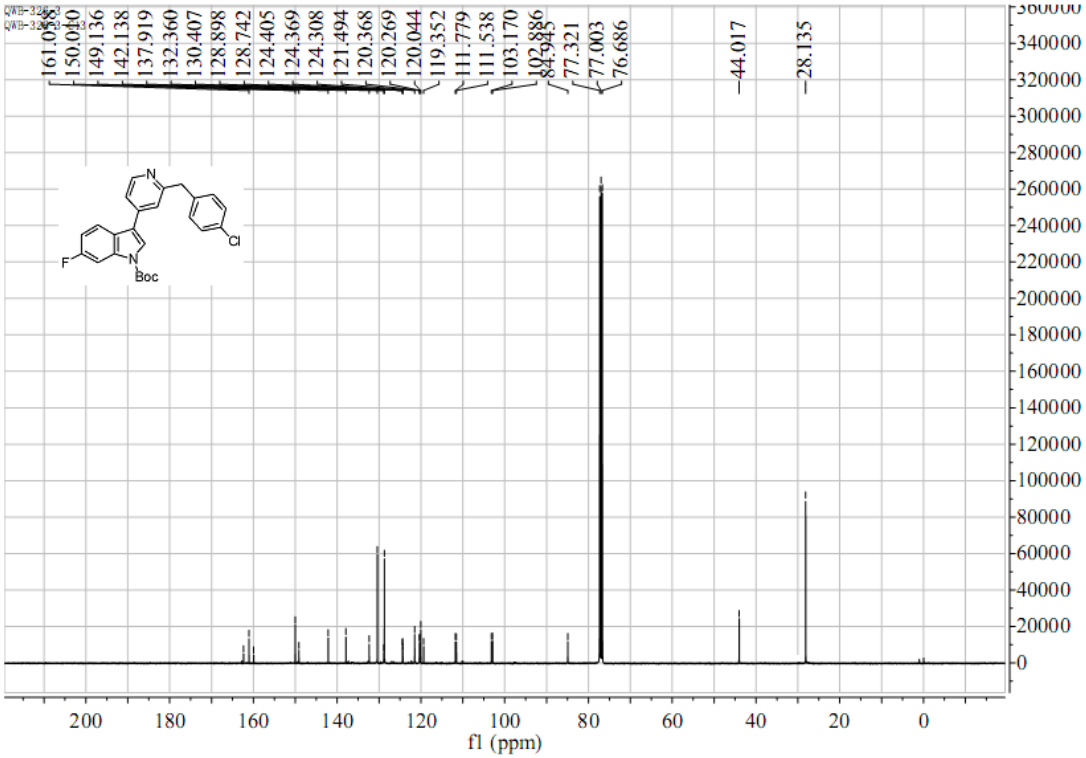
Compound **3u**


8.635
8.622
7.797
7.486
7.436
7.432
7.423
7.419
7.372
7.337
7.321
7.315
7.311
7.298
7.285
7.279
7.276
4.223
2.478
1.713
1.02
1.00
1.00
1.03
1.04
1.02
5.02
1.25
2.08
3.06
9.09
fl (ppm)

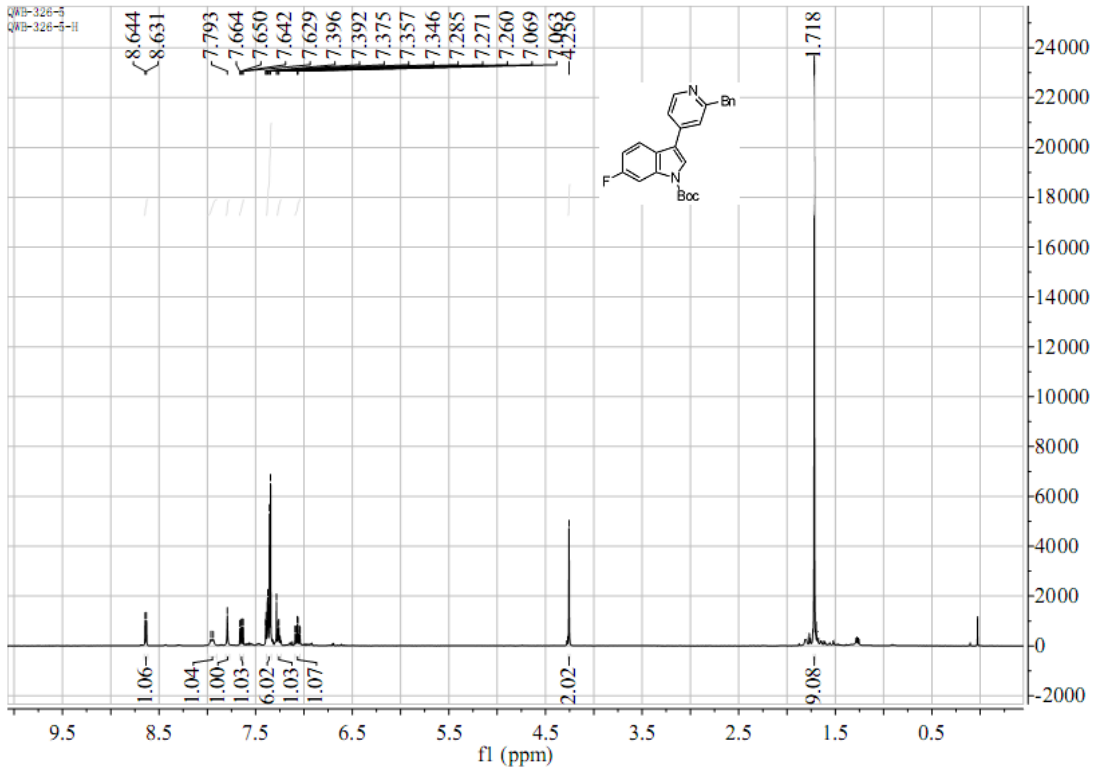

160.975
149.870
149.473
142.613
138.008
132.933
132.339
130.511
130.405
128.744
128.156
126.387
124.330
121.568
120.058
119.452
119.158
115.270
84.299
77.326
77.008
76.691
43.991
28.185
21.448
fl (ppm)

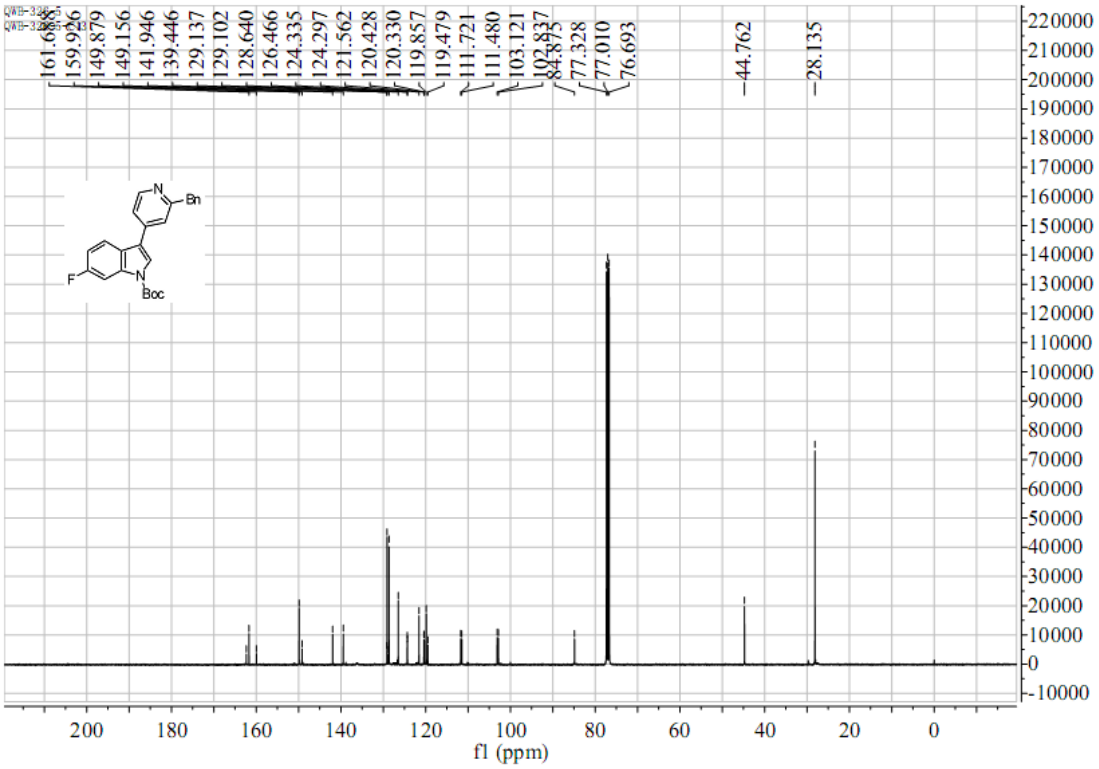
Compound **3v**


8.640
8.627
7.801
7.412
7.408
7.396
7.362
7.324
7.308
7.302
7.298
7.284
7.278
7.262
7.085
4.210
1.720
1.04
1.00
1.00
1.07
1.07
1.02
2.93
1.04
1.05
2.02
9.04
F
N
Boc
Cl
f1 (ppm)

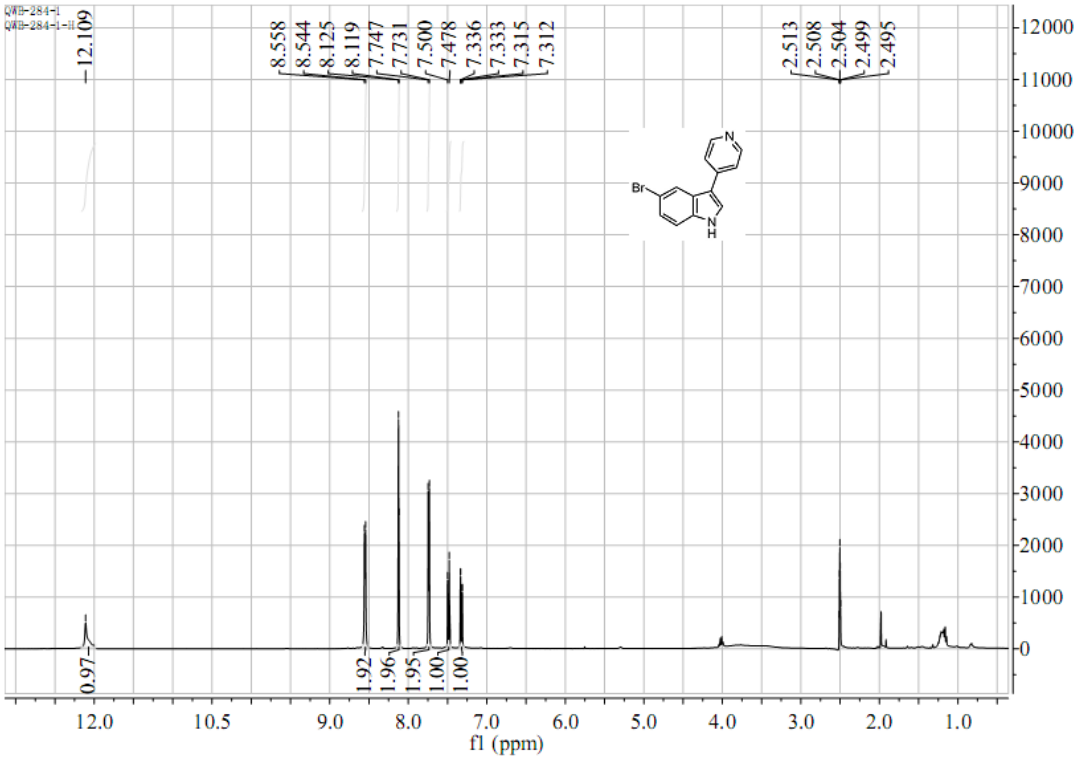

161.058
150.044
149.136
142.138
137.919
132.360
130.407
128.898
128.742
124.405
124.369
124.308
121.494
120.368
120.269
120.044
119.352
111.779
111.538
103.170
84.945
77.321
77.003
76.686
44.017
28.135
F
N
Boc
Cl
f1 (ppm)

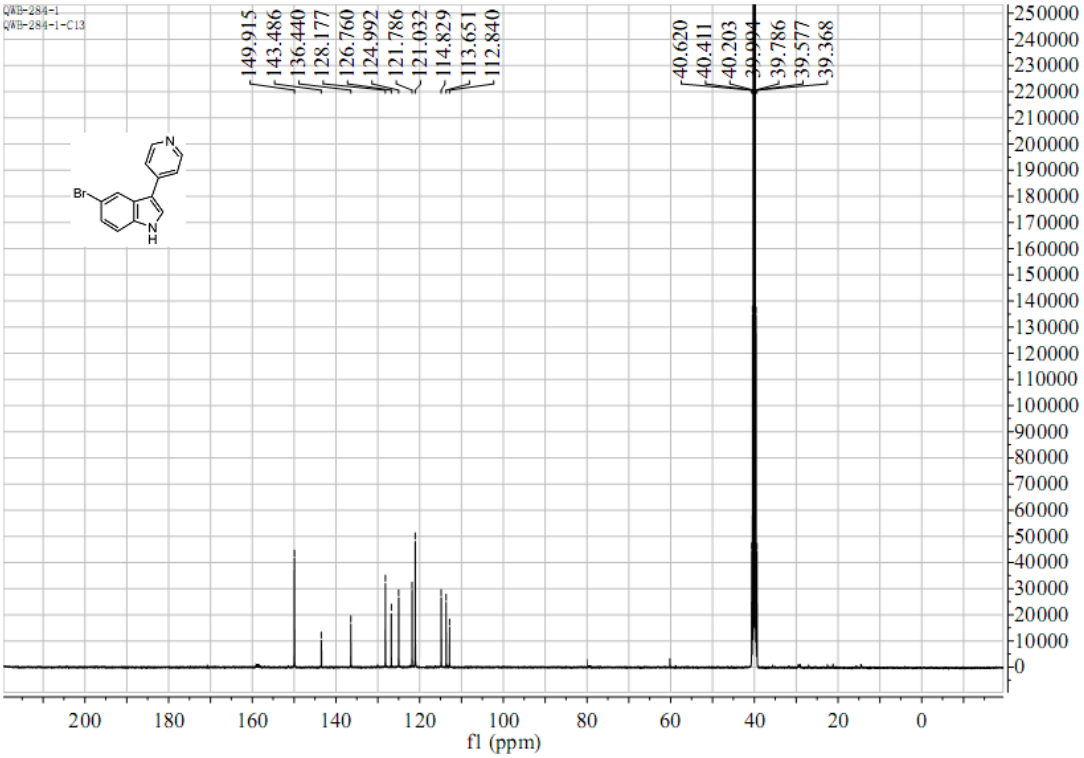
Compound **3w**


8.644
8.631
7.793
7.664
7.650
7.642
7.629
7.396
7.392
7.375
7.357
7.346
7.285
7.271
7.260
7.069
7.063
4.256
1.718
Bn
F
N
Boc
1.06
1.04
1.00
1.03
6.02
1.03
1.07
2.02
9.08
f1 (ppm)

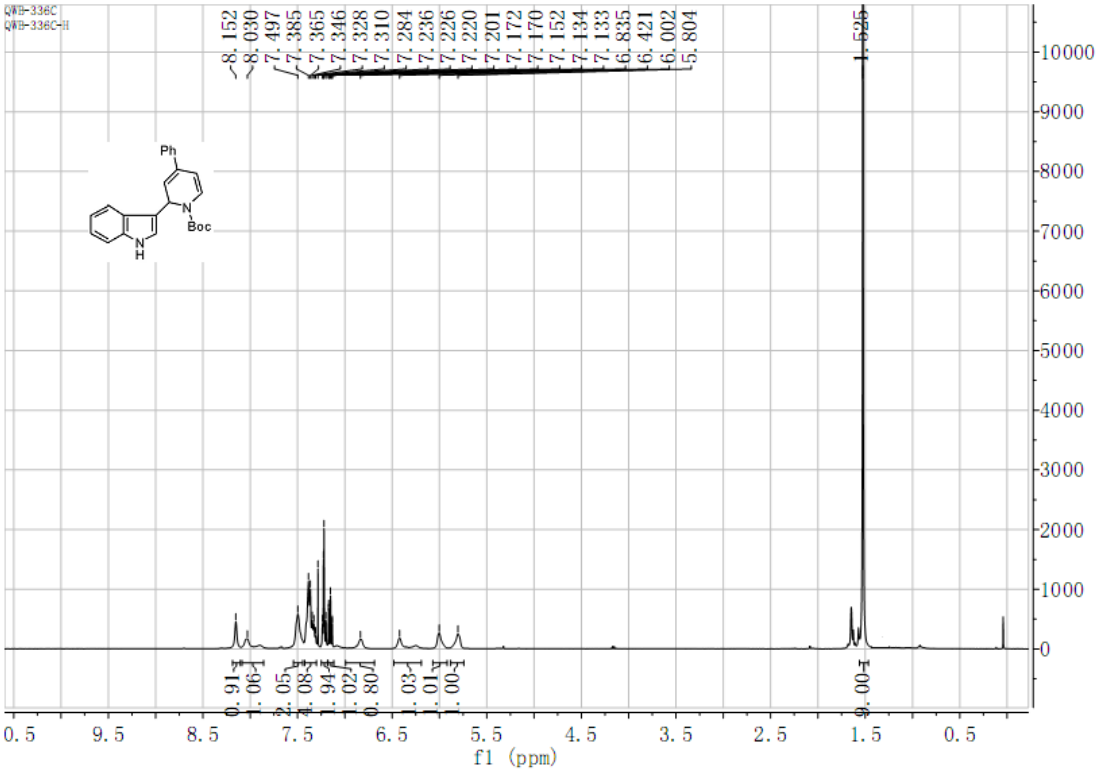

161.688
159.926
149.879
149.156
141.946
139.446
129.137
129.102
128.640
126.466
124.335
124.297
121.562
120.428
120.330
119.857
119.479
111.721
111.480
103.121
102.837
84.875
77.328
77.010
76.693
44.762
28.135
Bn
F
N
Boc
f1 (ppm)

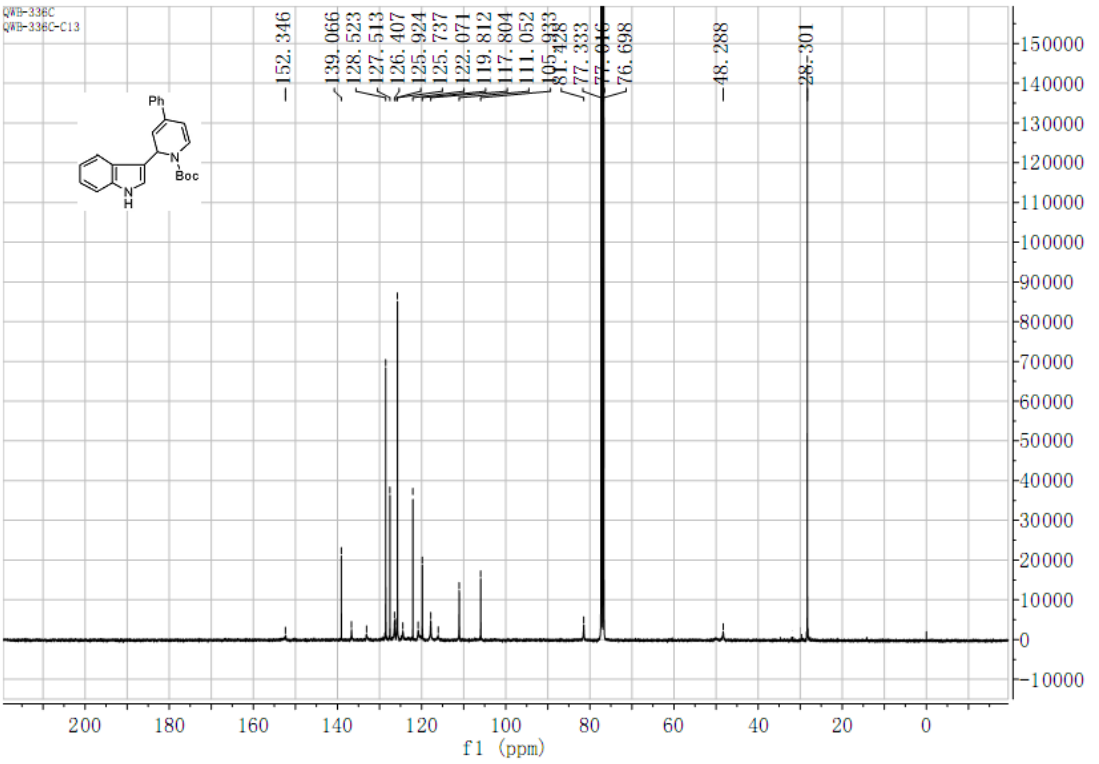
Compound **4**


12.109
8.558
8.544
8.125
8.119
7.747
7.731
7.500
7.478
7.336
7.333
7.315
7.312
2.513
2.508
2.504
2.499
2.495
0.97
1.92
1.96
1.95
1.00
1.00
f1 (ppm)

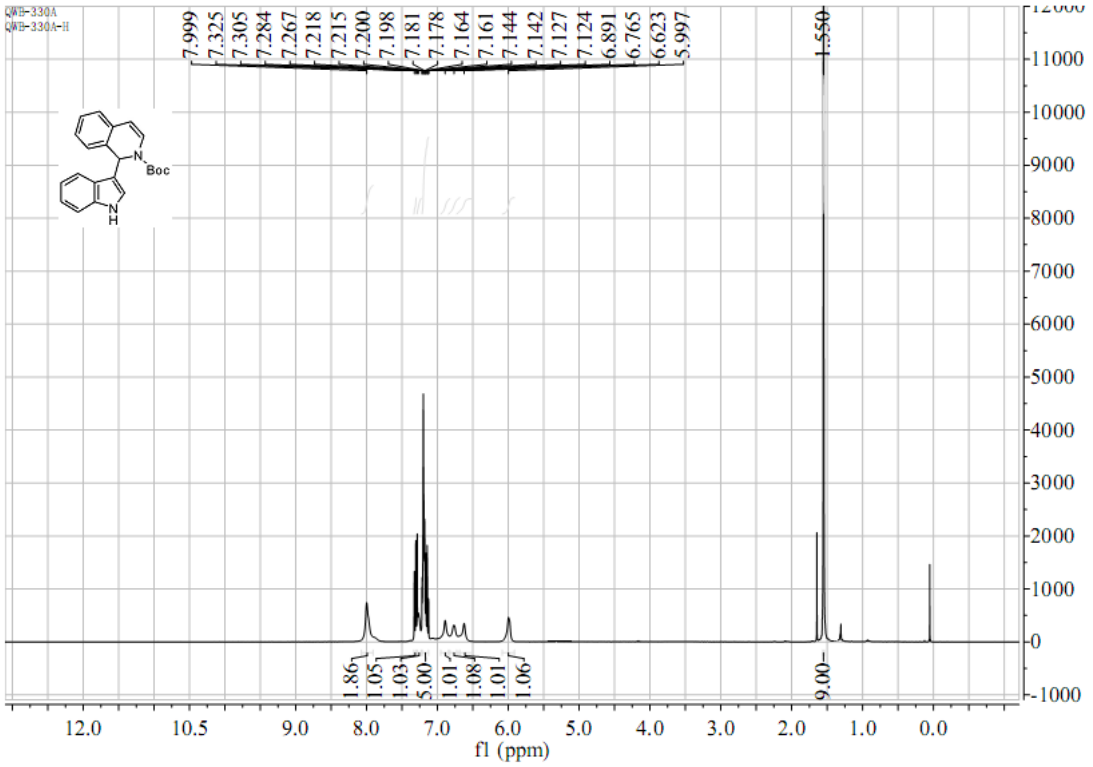

149.915
143.486
136.440
128.177
126.760
124.992
121.786
121.032
114.829
113.651
112.840
40.620
40.411
40.203
39.994
39.786
39.577
39.368
f1 (ppm)

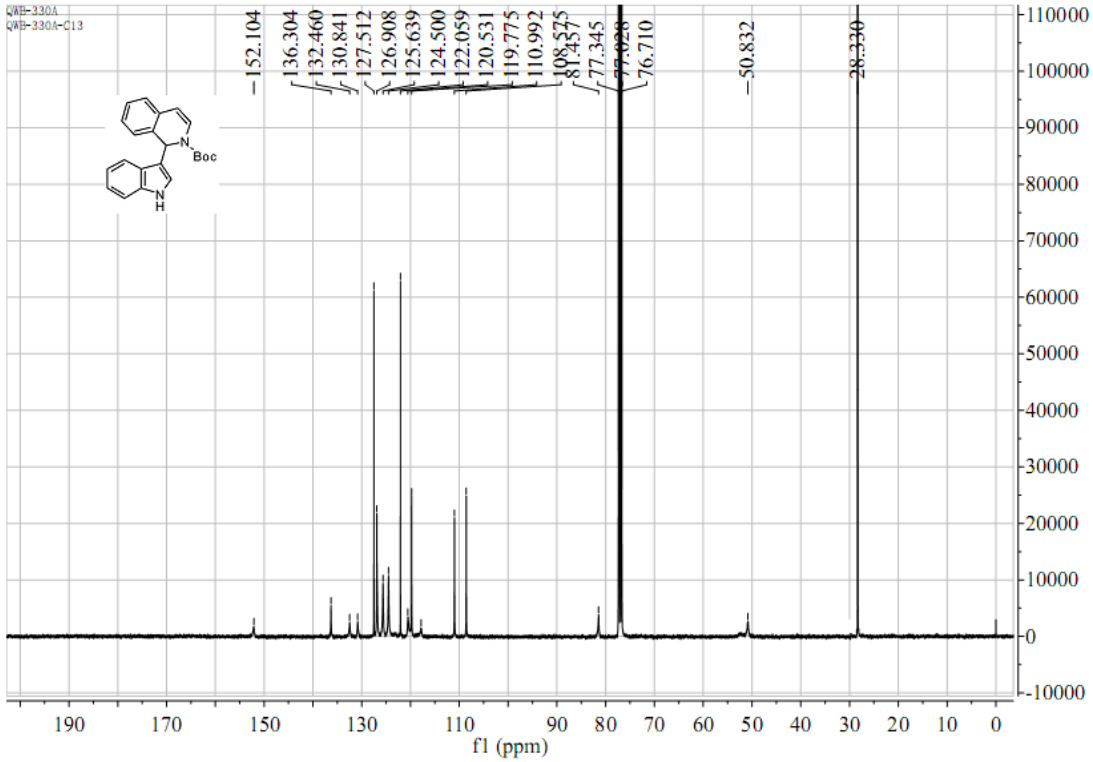
Compound **6b**


QWB-336C
QWB-336C-H
8.152
8.030
7.497
7.385
7.365
7.346
7.328
7.310
7.284
7.236
7.226
7.220
7.201
7.172
7.170
7.152
7.134
7.133
6.835
6.421
6.002
5.804
1.525
Ph
N
Boc
H
0.91
1.06
2.05
4.08
1.94
1.02
0.80
1.03
1.01
1.00
9.00
f1 (ppm)

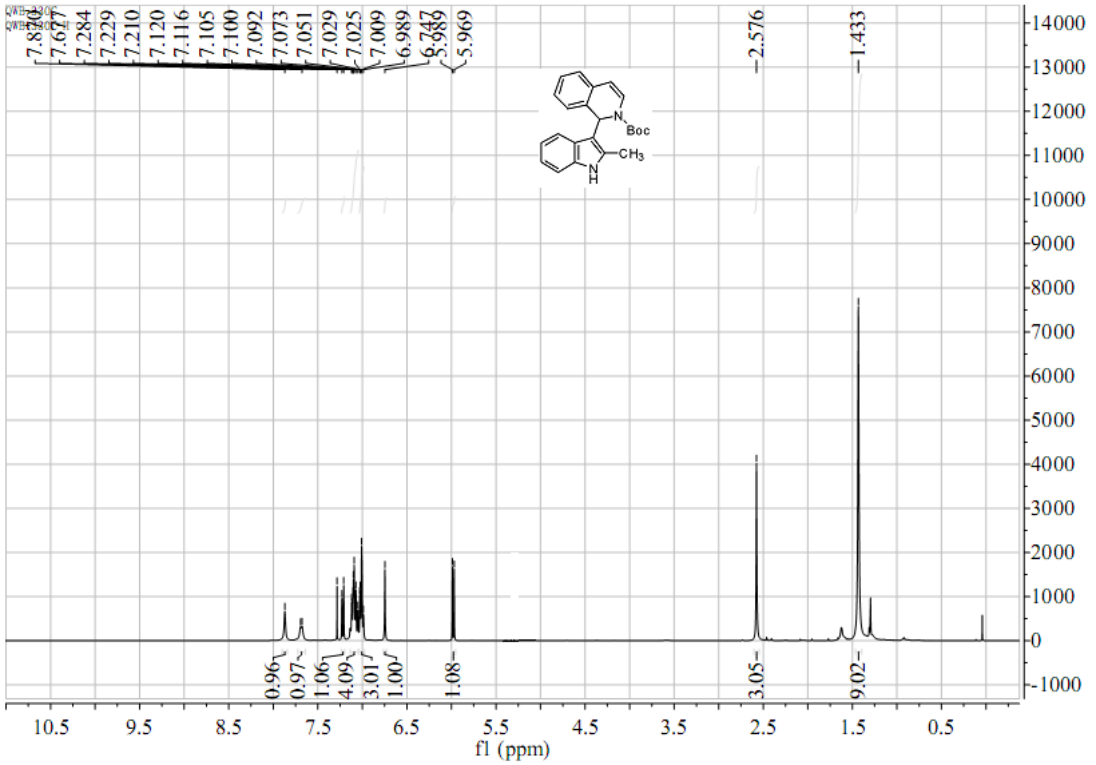

QWB-336C
QWB-336C-C13
152.346
139.066
128.523
127.513
126.407
125.924
125.737
122.071
119.812
117.804
111.052
105.933
81.428
77.333
77.046
76.698
48.288
28.301
Ph
N
Boc
H
f1 (ppm)

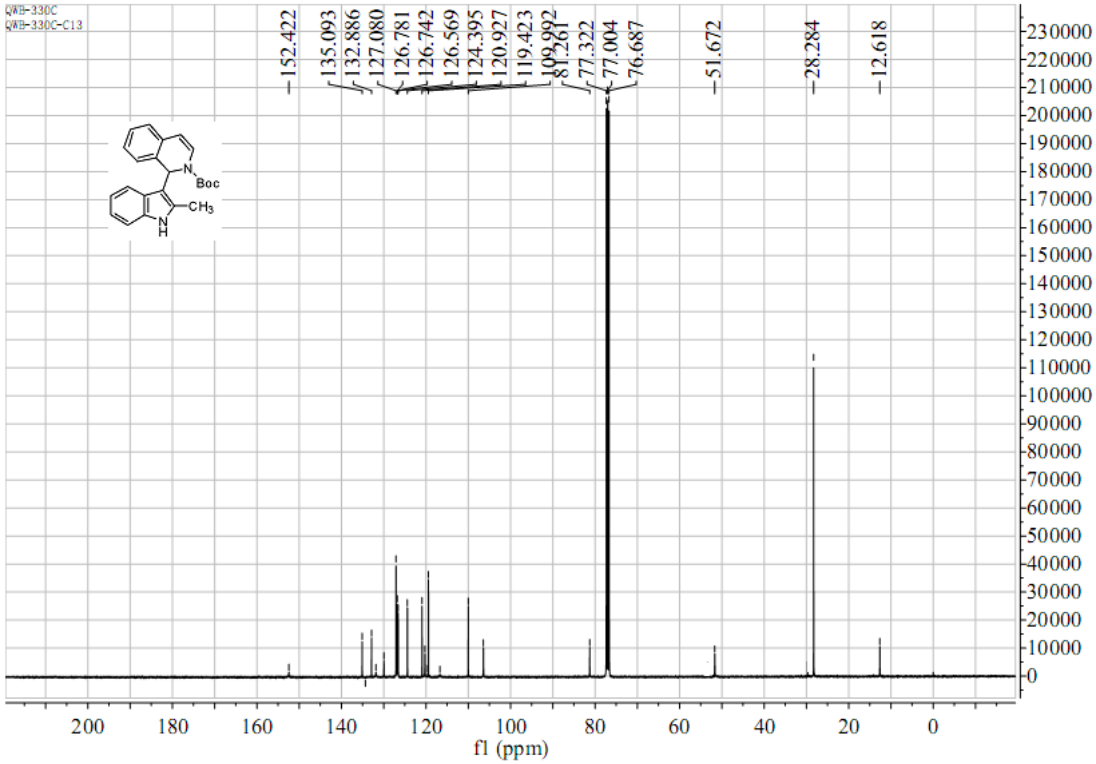
Compound **8a**


QWB-330A
QWB-330A-H
7.999
7.325
7.305
7.284
7.267
7.218
7.215
7.200
7.198
7.181
7.178
7.164
7.161
7.144
7.142
7.127
7.124
6.891
6.765
6.623
5.997
1.550
Boc
N
H
1.86
1.05
1.03
5.00
1.01
1.08
1.01
1.06
9.00
f1 (ppm)

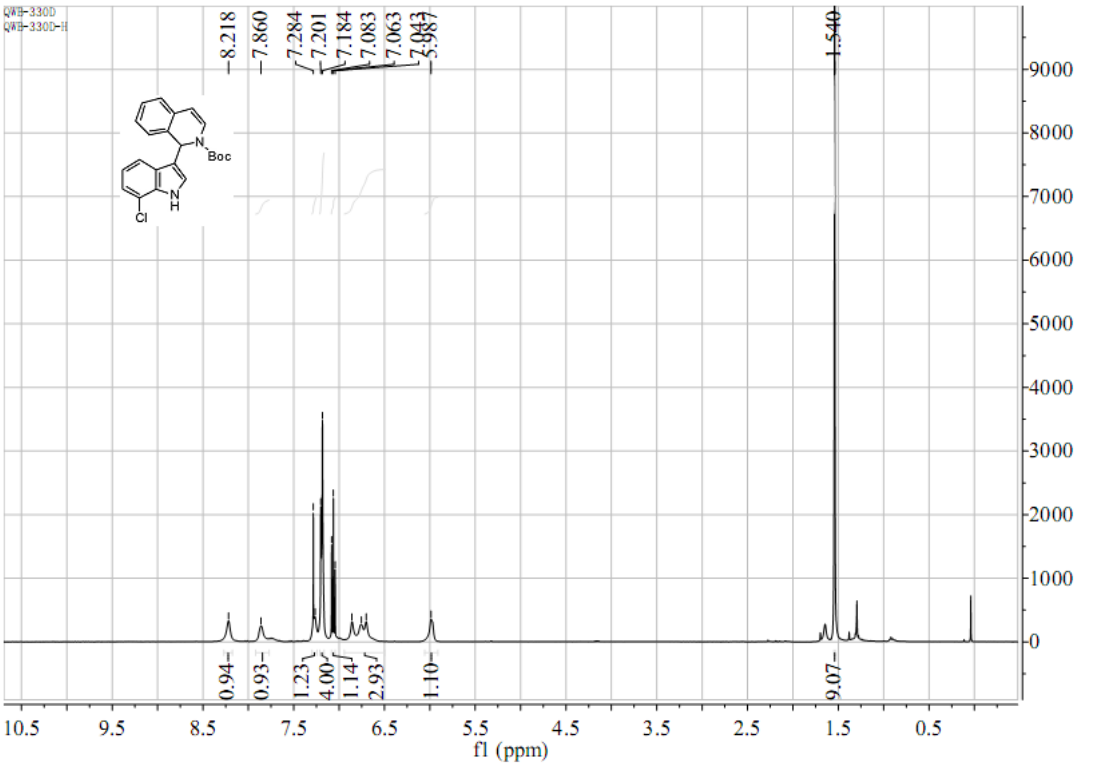

QWB-330A
QWB-330A-C13
152.104
136.304
132.460
130.841
127.512
126.908
125.639
124.500
122.059
120.531
119.775
110.992
108.525
81.457
77.345
76.710
50.832
28.330
Boc
N
H
f1 (ppm)

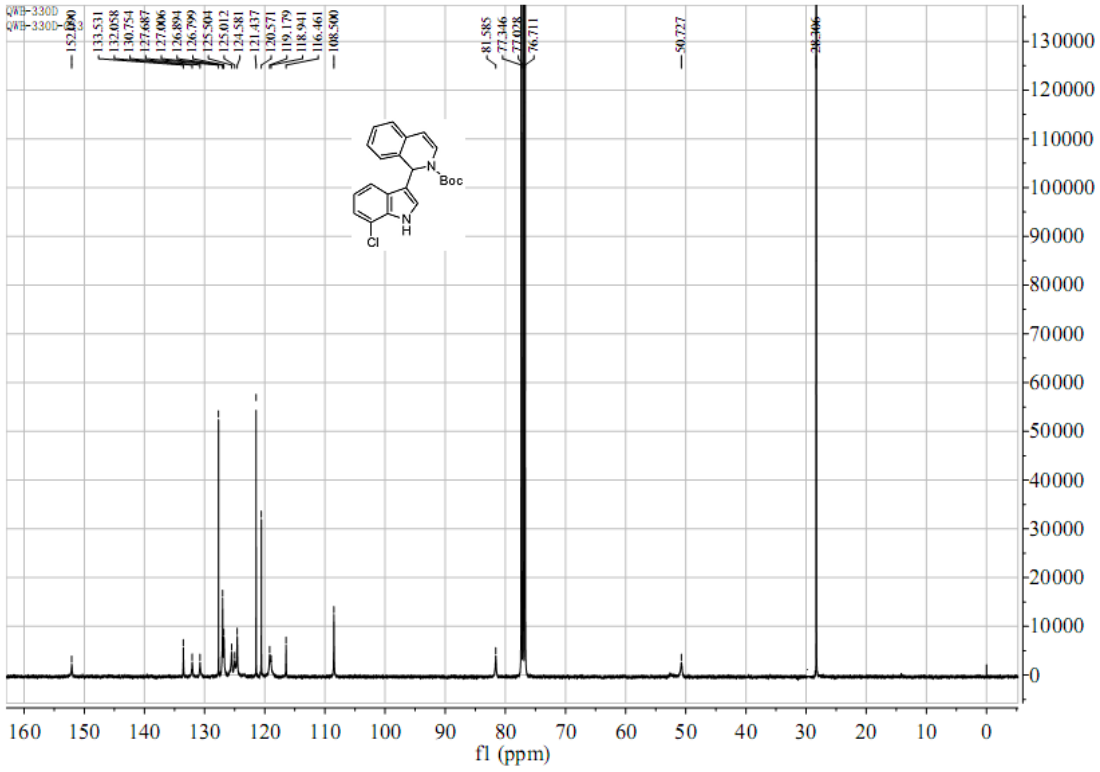
Compound **8b**


7.827
7.627
7.284
7.229
7.210
7.120
7.116
7.105
7.100
7.092
7.073
7.051
7.029
7.025
7.009
6.989
6.747
5.983
5.969
2.576
1.433
Boc
CH3
0.96
0.97
1.06
4.09
3.01
1.00
1.08
3.05
9.02
f1 (ppm)


QWB-330C
QWB-330C-C13
152.422
135.093
132.886
127.080
126.781
126.742
126.569
124.395
120.927
119.423
109.992
81.261
77.322
77.004
76.687
51.672
28.284
12.618
Boc
CH3
f1 (ppm)

Compound **8c**


8.218
7.860
7.284
7.201
7.184
7.083
7.063
1.540
Boc
Cl
H
N
0.94
0.93
1.23
4.00
1.14
2.93
1.10
9.07
f1 (ppm)


133.531
132.058
130.754
127.687
127.006
126.894
126.799
125.504
125.012
124.581
121.437
120.571
119.179
118.941
116.461
108.500
81.585
77.346
77.028
76.711
50.727
28.306
Boc
Cl
H
N
f1 (ppm)

**4. X-ray Data of Compound 4.**

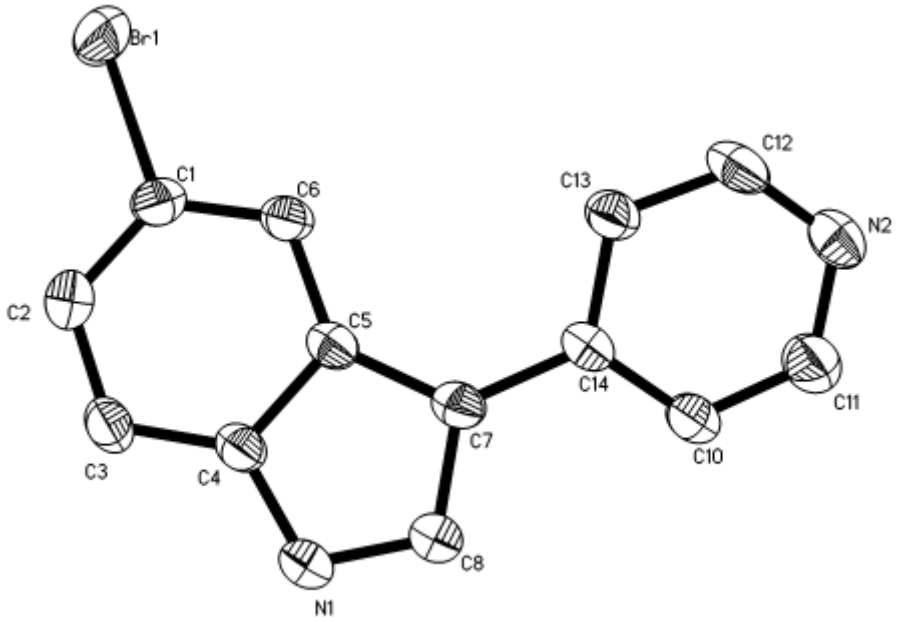



**Figure 1**. ORTEP representation of the molecular structure of **4** with H atoms omitted for clarity.