Supporting Information for:

Synthesis of Spirooxindoles *via* Palladium-Catalyzed Dearomative Reductive-Heck Reaction

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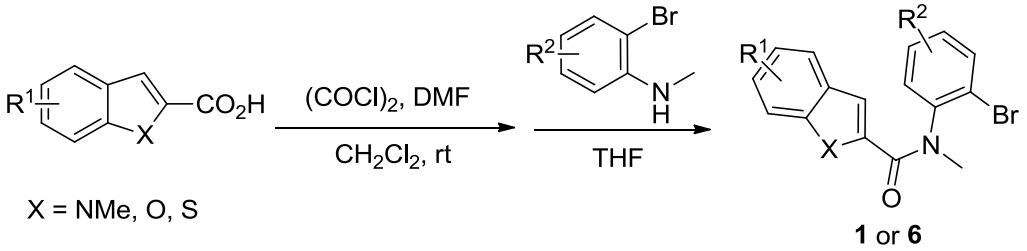
Contents:

1. General information:

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated with heating gun prior to use. ^{1}H, ^{13}C NMR spectra were recorded on Bruker AVANCE III 500MHz with TMS as internal standard. Anhydrous THF, toluene were freshly distilled over Na and benzophenone. Anhydrous CH_2Cl_2 was freshly distilled over calcium hydride. Melting points were measured on a Büchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 TOF LC/MS mass spectrometer. Column chromatography was carried out using silica gel (200-300 mesh).

2. Substrate synthesis

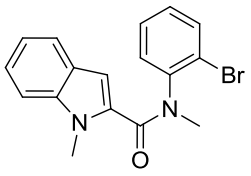
Substrates **1** were prepared according to the known procedure by the condensation of indole-2-carboxylic acids (or benzofuran-2-carboxylic acid and benzo[b]thiophene-2-carboxylic acid) with *N*-methyl-2-bromoanilines shown in Scheme S1.[1] 1-Methyl-1H-indole-2-carboxylic acids were prepared according to the known method in literature.[2]



Scheme S1 Substrate synthesis

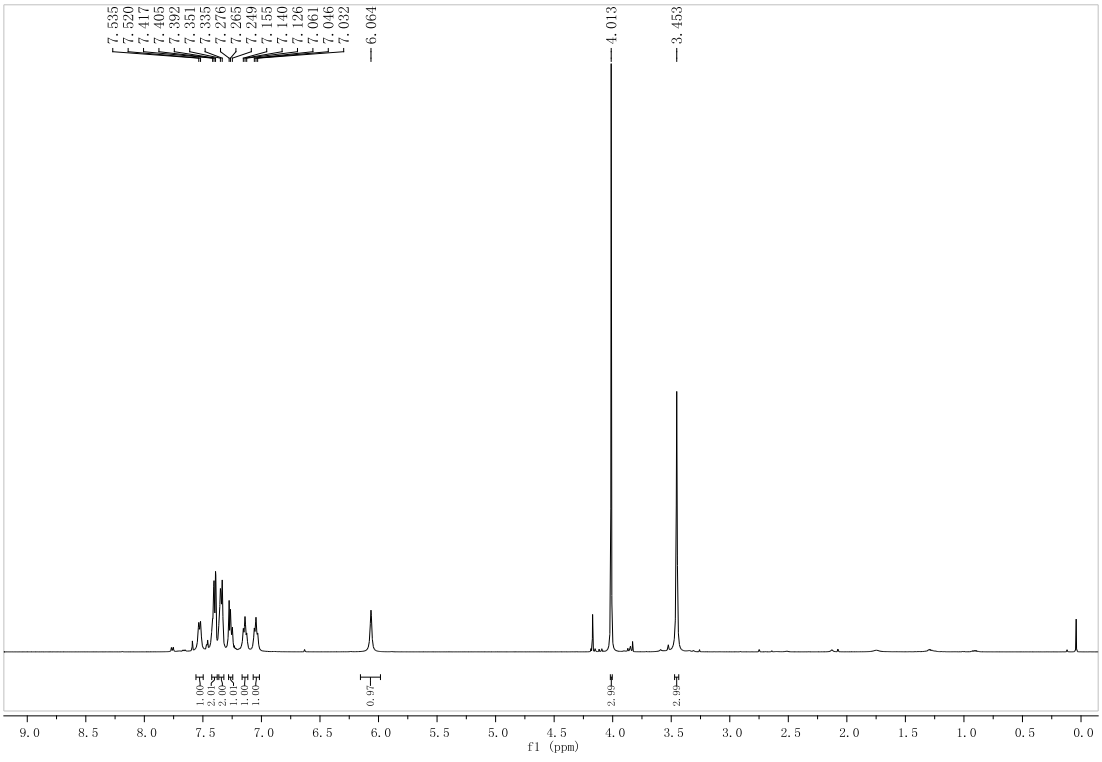
To a stirred solution of carboxylic acid (3.0 mmol, 1.0 equiv.) in CH_2Cl_2 (12 mL) were added a catalytic amount of DMF (6 μL) and $(COCl)_2$ (0.6 mL) and the mixture was stirred for 1 h at room temperature. The mixture was then concentrated under reduced pressure. To a stirred solution of this residue in THF (5.0 mL) was added a mixture of N-methyl 2-bromoaniline and Et_3N (1.8 mL) in THF (35 mL). The mixture was stirred at room temperature for 20 h and then concentrated under vacuum. The left residue was diluted with EtOAc, washed with brine, and dried over $MgSO_4$. After filtration, the solvent was concentrated under vacuum and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v) to afford the substrates **1** and **6**.

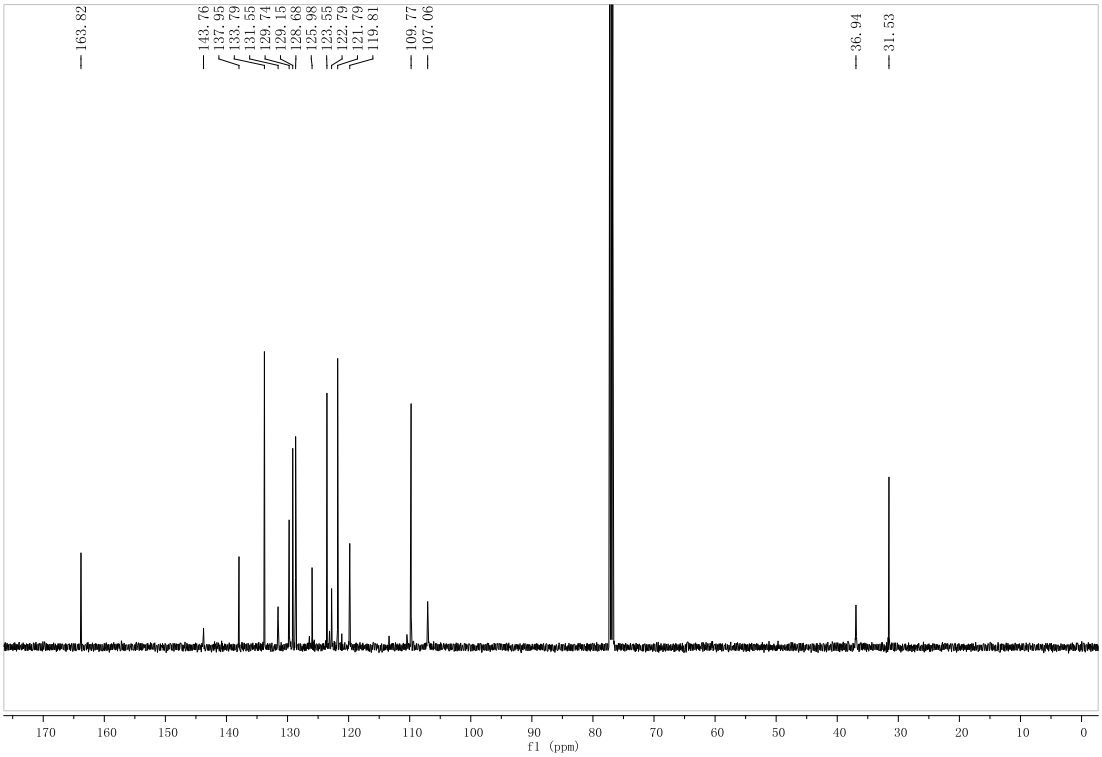
N-(2-bromophenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1a**



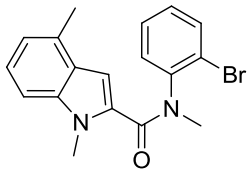
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 48% yield, m.p. 112-115 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 6.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 5.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.0 Hz, 1H), 6.06 (s, 1H), 4.01 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 143.8, 138.0, 133.8, 131.6,

129.7, 129.2, 128.7, 126.0, 123.6, 122.8, 121.8, 119.8, 109.8, 107.1, 36.9, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{16}BrN_2O$ ($[M+H]^+$): 343.0441, found 343.0451.

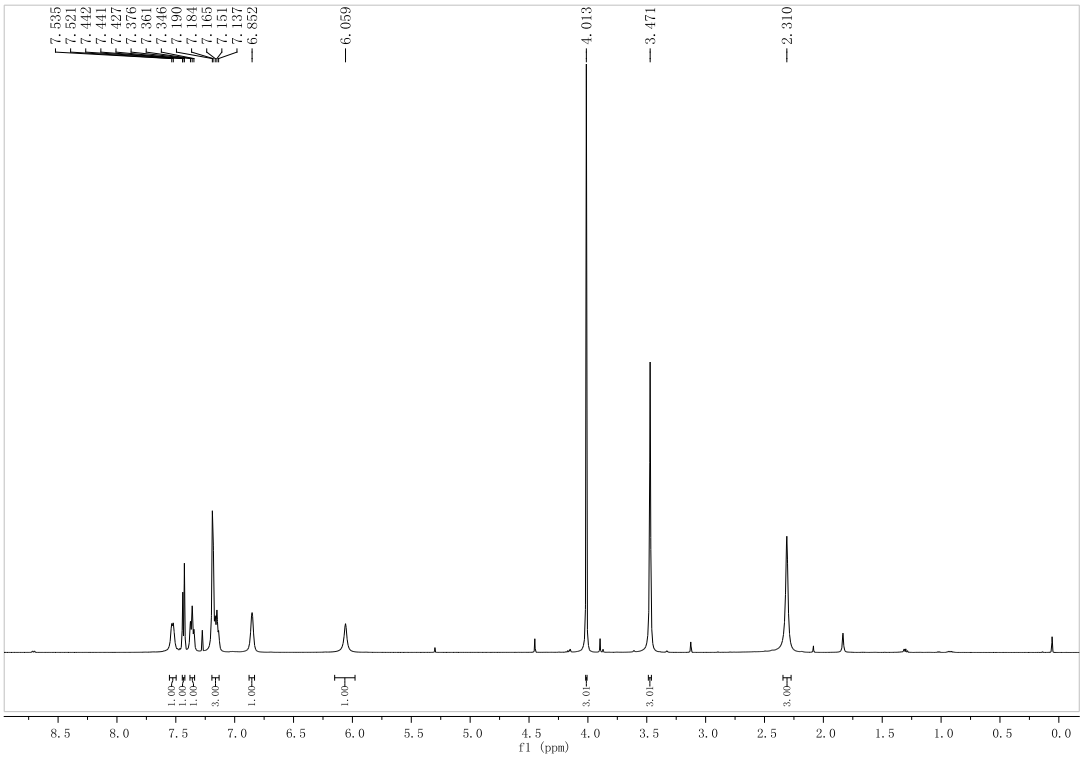


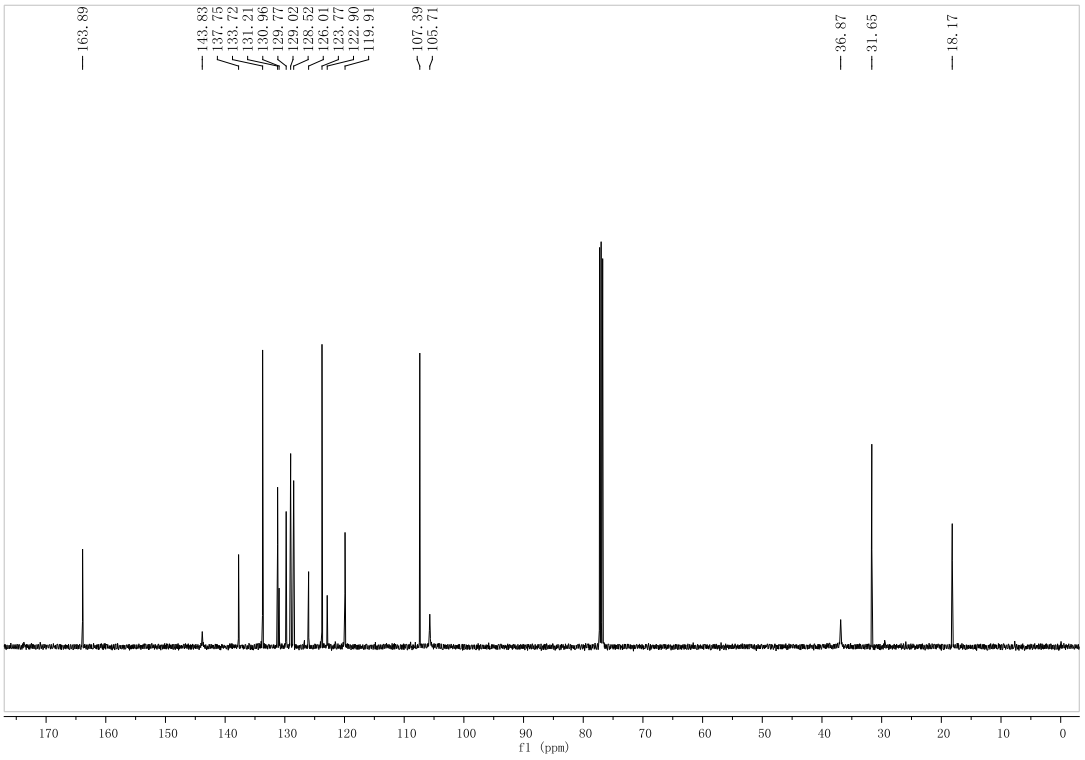


N-(2-Bromophenyl)-N,1,4-trimethyl-1H-indole-2-carboxamide **1b**

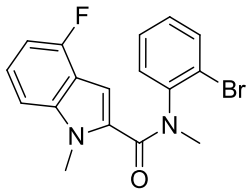


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 63% yield, m.p. 101-103 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.0 Hz, 1H), 7.42-7.45 (m, 1H), 7.36 (t, *J* = 7.5Hz, 1H), 7.13-7.19 (m, 3H), 6.85 (s, 1H), 6.06 (s, 1H), 4.01 (s, 3H), 3.47 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 143.8, 137.8, 133.7, 131.2, 131.0, 129.8, 129.0, 128.5, 126.0, 123.8, 122.9, 119.9, 107.4, 105.7, 36.9, 31.6, 18.2. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O$ ($[M+H]^+$): 357.0597, found 357.0589.

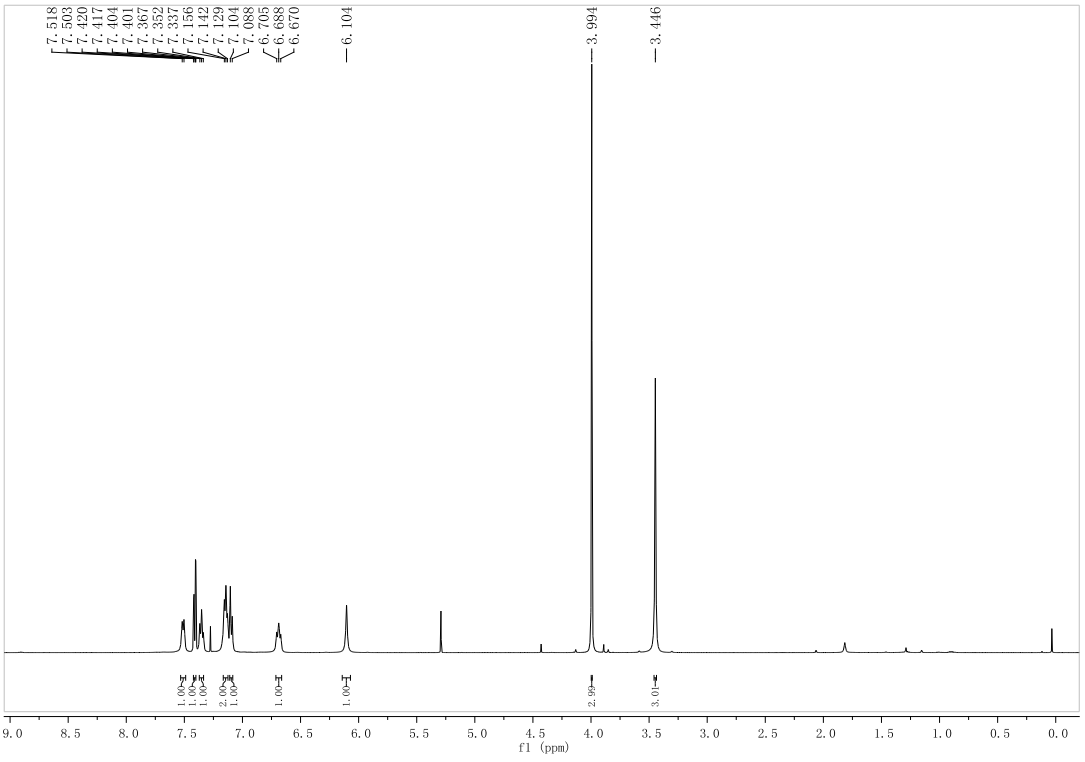




N-(2-Bromophenyl)-4-fluoro-N,1-dimethyl-1H-indole-2-carboxamide **1c**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); pale yellow solid, 65% yield, m.p. 100-103 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 8.5 Hz, 1H), 6.10 (s, 1H), 3.99 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 156.7 (d, *J* = 249.2 Hz), 143.4, 140.3 (d, *J* = 10.6 Hz), 133.8, 131.7, 129.7, 129.4, 128.8, 124.0 (d, *J* = 7.9 Hz), 122.7, 115.4 (d, *J* = 22.5 Hz), 105.9 (d, *J* = 3.6 Hz), 104.41 (d, *J* = 18.8 Hz), 102.63, 36.92, 32.00. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{15}BrFN_2O$ ($[M+H]^+$): 361.0346, found 361.0334.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7.420
7.417
7.404
7.401
7.367
7.352
7.337
7.156
7.142
7.129
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7.088
6.705
6.688
6.670
6.104
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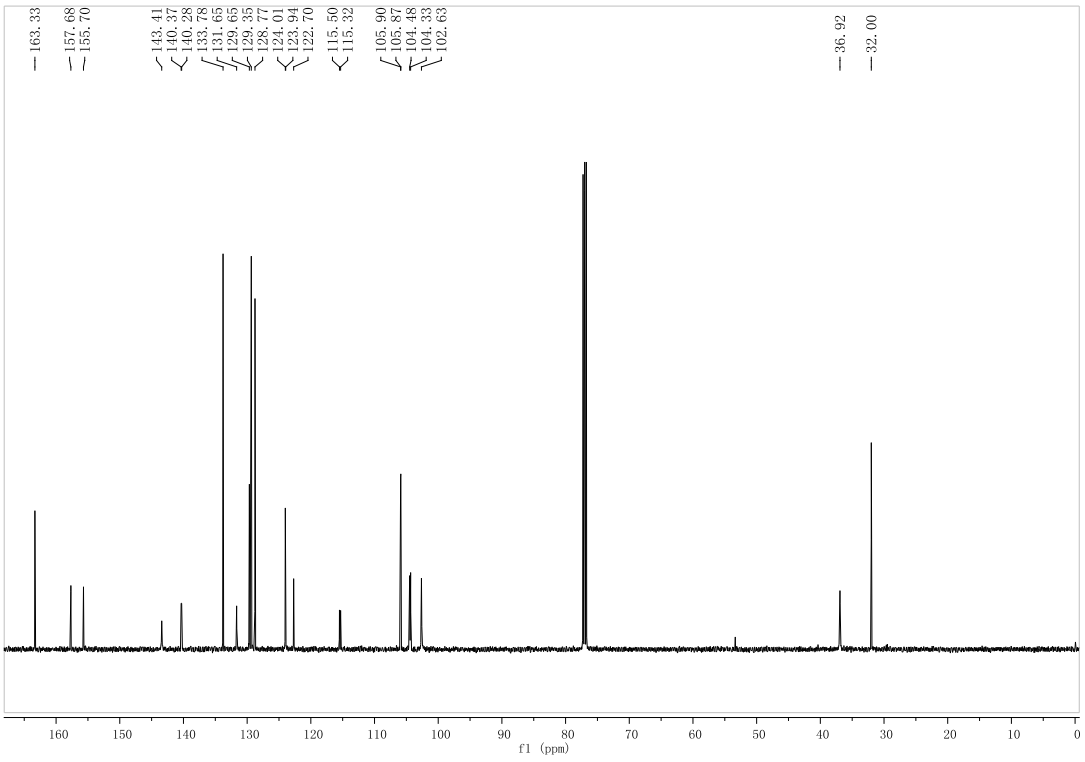
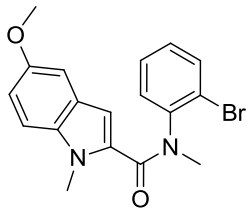
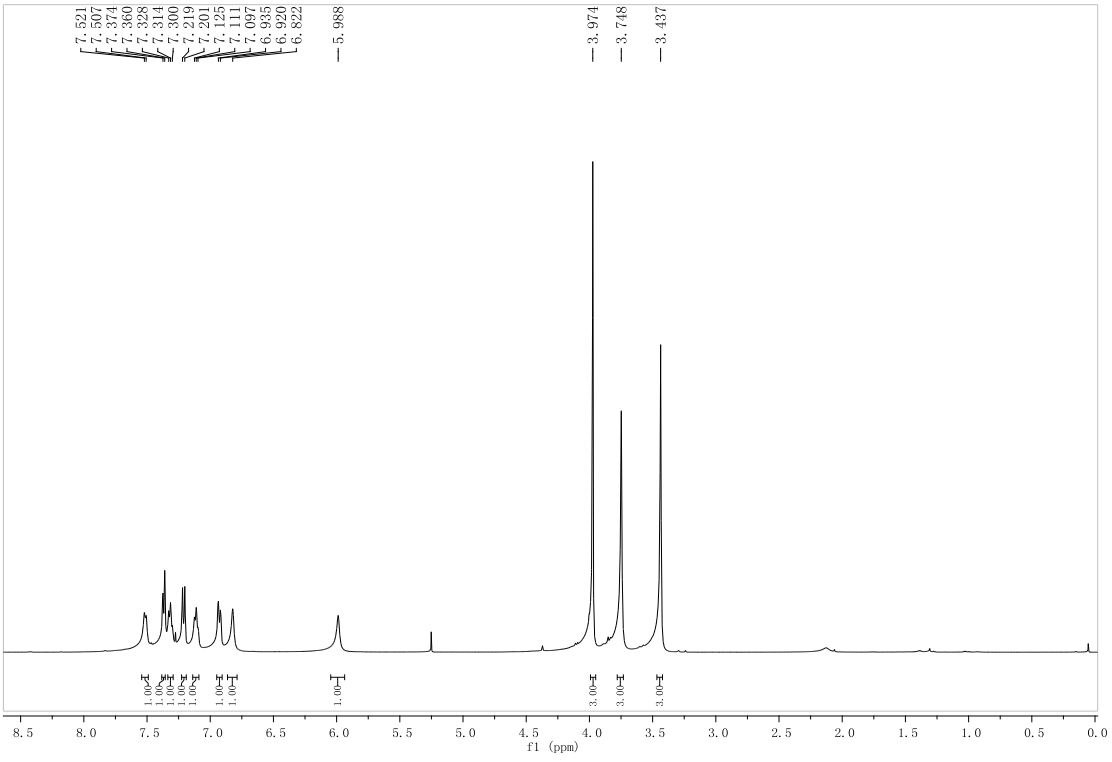
1.04
1.04
2.99
3.01
f1 (ppm)

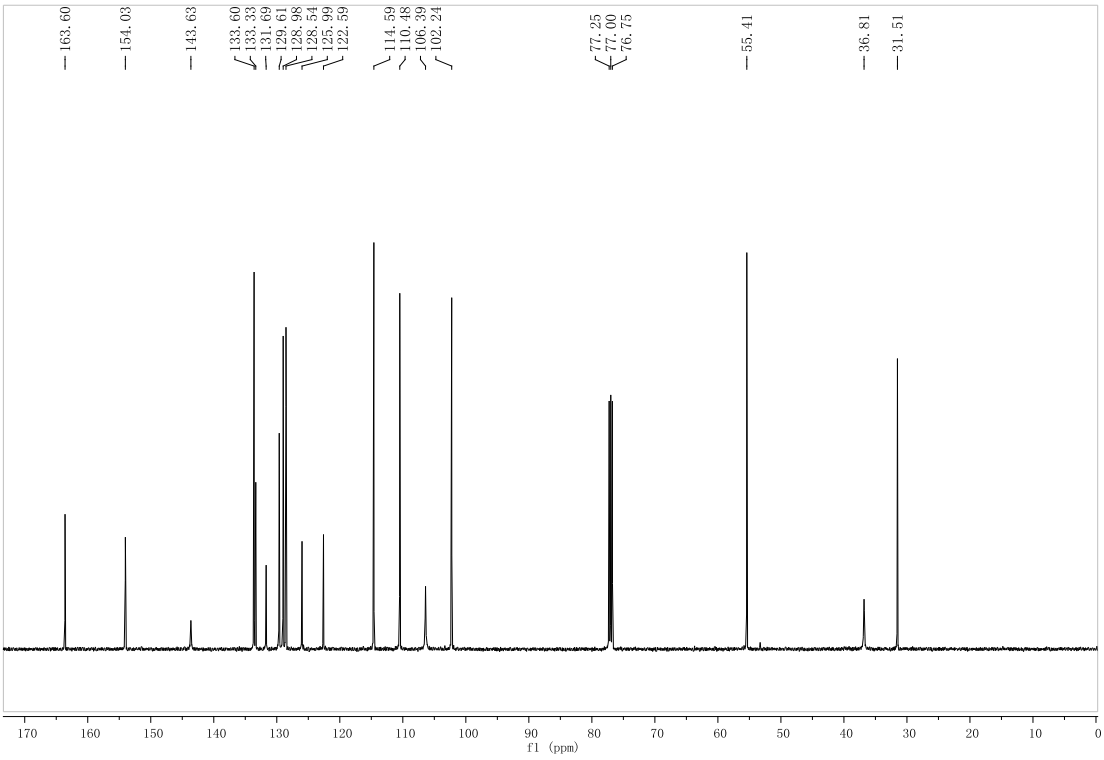

163.33
157.68
155.70
143.41
140.37
140.28
133.78
131.65
129.65
129.35
128.77
124.01
123.94
122.70
115.50
115.32
105.90
105.87
104.48
104.33
102.63
36.92
32.00
f1 (ppm)

N-(2-Bromophenyl)-5-methoxy-N,1-dimethyl-1H-indole-2-carboxamide **1d**

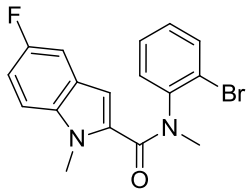


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 45% yield, m.p. 119-122 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 5.99 (s, 1H), 3.97 (s, 3H), 3.75 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 154.0, 143.6, 133.6, 133.3, 131.7, 129.6, 129.0, 128.5, 126.0, 123.0, 114.6, 110.5, 106.4, 102.2, 77.3, 77.0, 76.8, 55.4, 36.8, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O_2$ ($[M+H]^+$): 373.0546, found 373.0538.

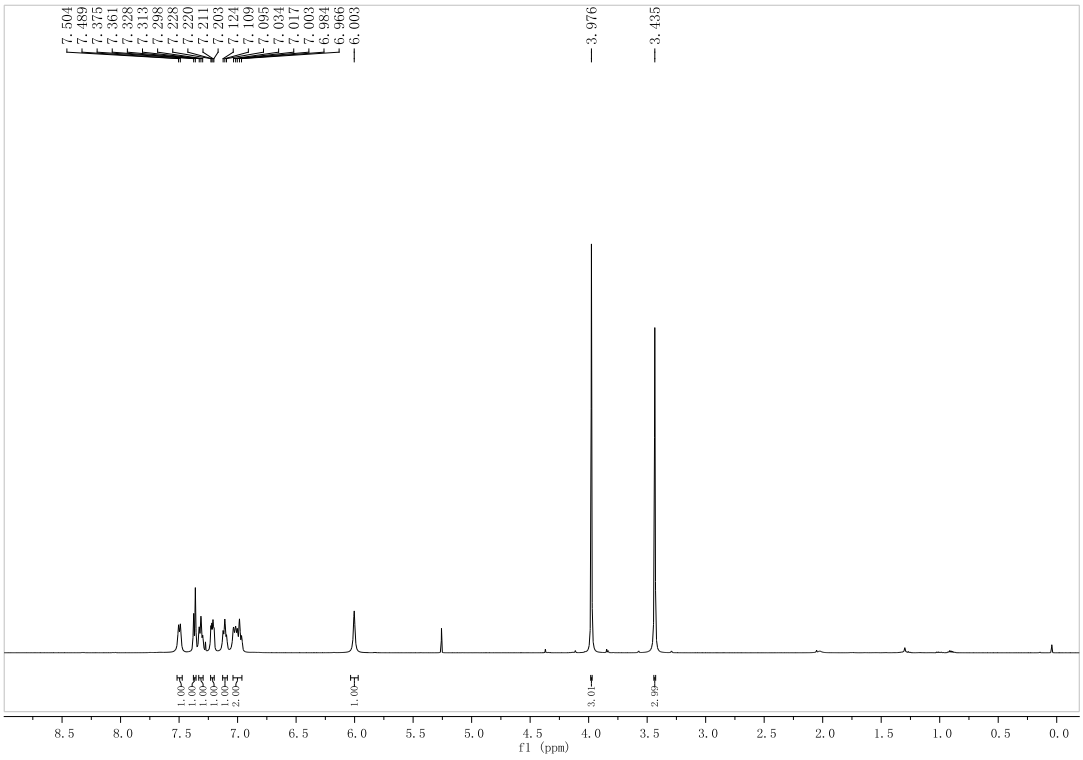




N-(2-Bromophenyl)-5-fluoro-N,1-dimethyl-1H-indole-2-carboxamide **1e**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); pale yellow solid, 55% yield, m.p. 123-125 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 8.5, 4.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96-7.03 (m, 2H), 6.00 (s, 1H), 3.98 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 157.7 (d, *J* = 235.4 Hz), 143.4, 134.5, 133.7, 132.9, 129.6, 129.2, 128.6, 125.8 (d, *J* = 10.0 Hz), 122.6, 112.2 (d, *J* = 26.6 Hz), 110.5 (d, *J* = 10.0 Hz), 106.4, 105.9 (d, *J* = 23.2 Hz), 36.8, 31.6. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{19}BrN_2O_2$ ($[M+H]^+$): 361.0346, found 361.0344.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7.228
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7.211
7.203
7.124
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7.095
7.034
7.017
7.003
6.984
6.966
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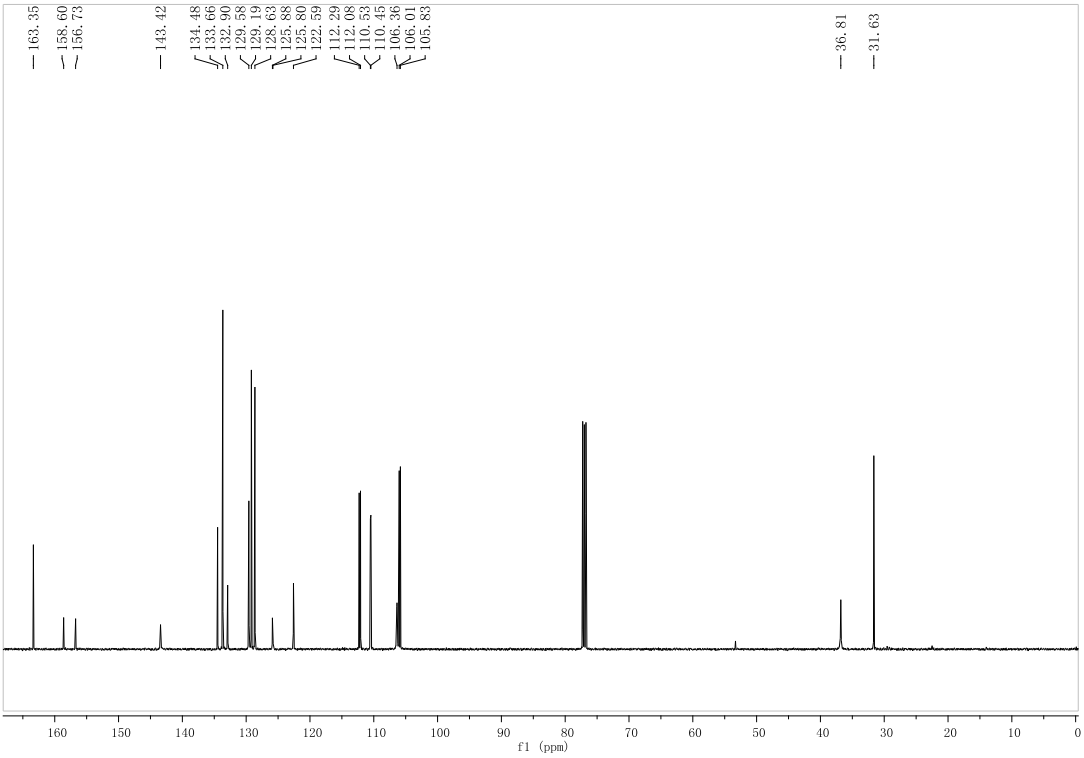
1.00
2.00
1.00
3.01
2.99
f1 (ppm)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128.63
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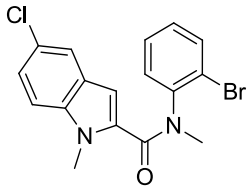
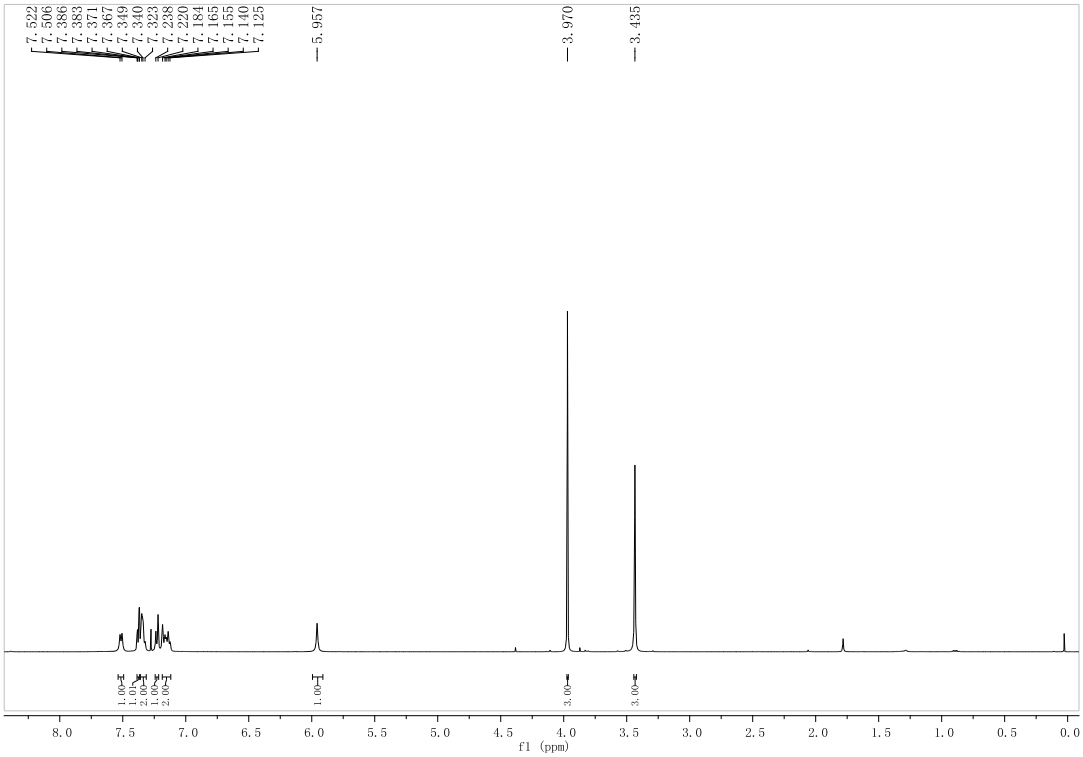
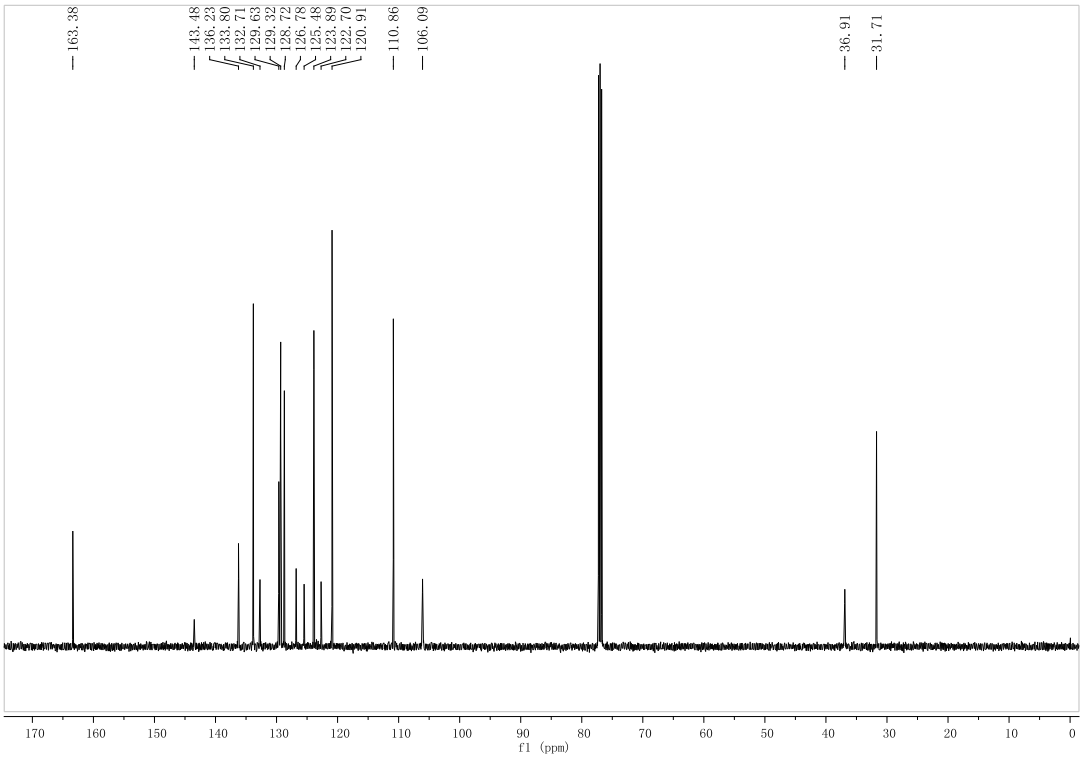
125.80
122.59
112.29
112.08
110.53
110.45
106.36
106.01
105.83
36.81
31.63
f1 (ppm)

N-(2-Bromophenyl)-5-chloro-N,1-dimethyl-1H-indole-2-carboxamide **1f**

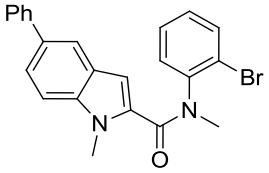


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); pale yellow solid, 56% yield, m.p. 128-129 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.32-7.35 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.12-7.19 (m, 2H), 5.96 (s, 1H), 3.97 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 143.5, 136.2, 133.8, 132.7, 129.6, 129.3, 128.7, 126.8, 125.5, 123.9, 122.7, 120.9, 110.9, 106.1, 36.9, 31.7. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{15}BrClN_2O$ ($[M+H]^+$): 377.0051, found 377.0045.

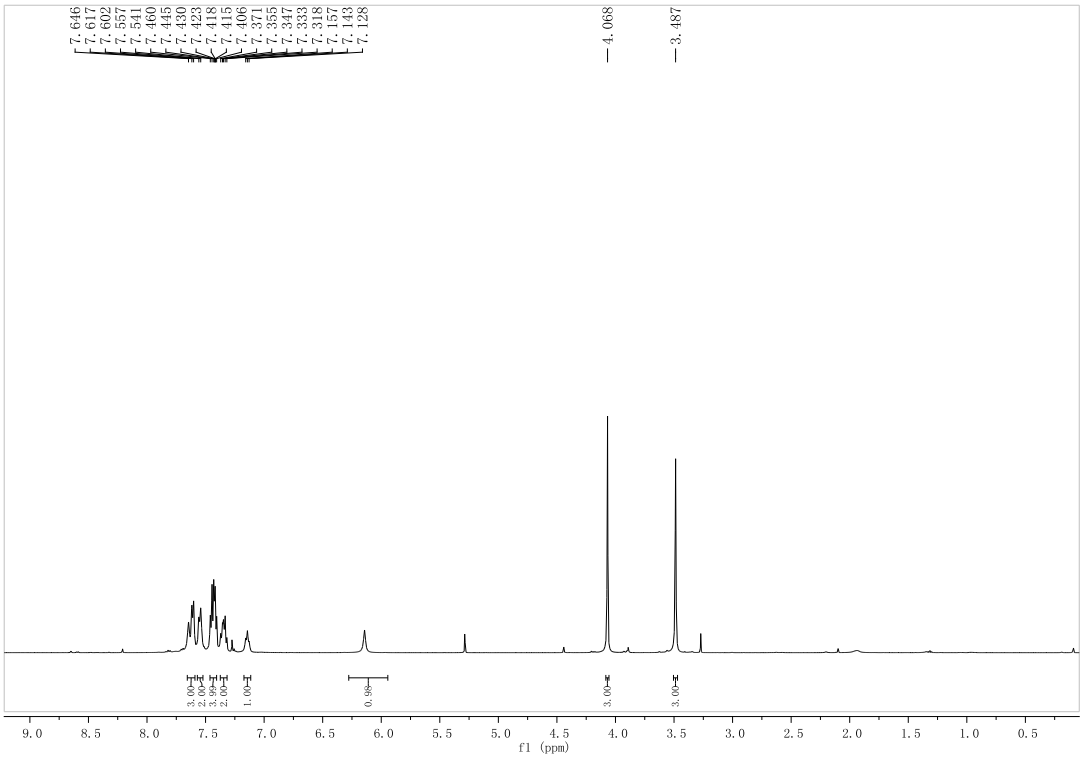




N-(2-Bromophenyl)-N,1-dimethyl-5-phenyl-1H-indole-2-carboxamide **1g**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 48% yield, m.p. 157-159 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (t, *J* = 14.5 Hz, 3H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.40-7.46 (m, 4H), 7.31-7.38 (m, 2H), 7.14 (t, *J* = 7.0 Hz, 1H), 6.14 (s, 1H), 4.07 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 143.6, 141.9, 137.4, 133.7, 133.3, 132.1, 129.7, 129.1, 128.6 (d, *J* = 17.3 Hz), 127.1, 126.3 (d, *J* = 11.3 Hz), 123.4, 122.7, 120.1, 110.0, 107.3, 36.9, 31.6. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{20}BrN_2O_2$ ($[M+H]^+$): 419.0754, found 419.0743.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7.430
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7.415
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7.355
7.347
7.333
7.318
7.157
7.143
7.128
4.068
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3.00
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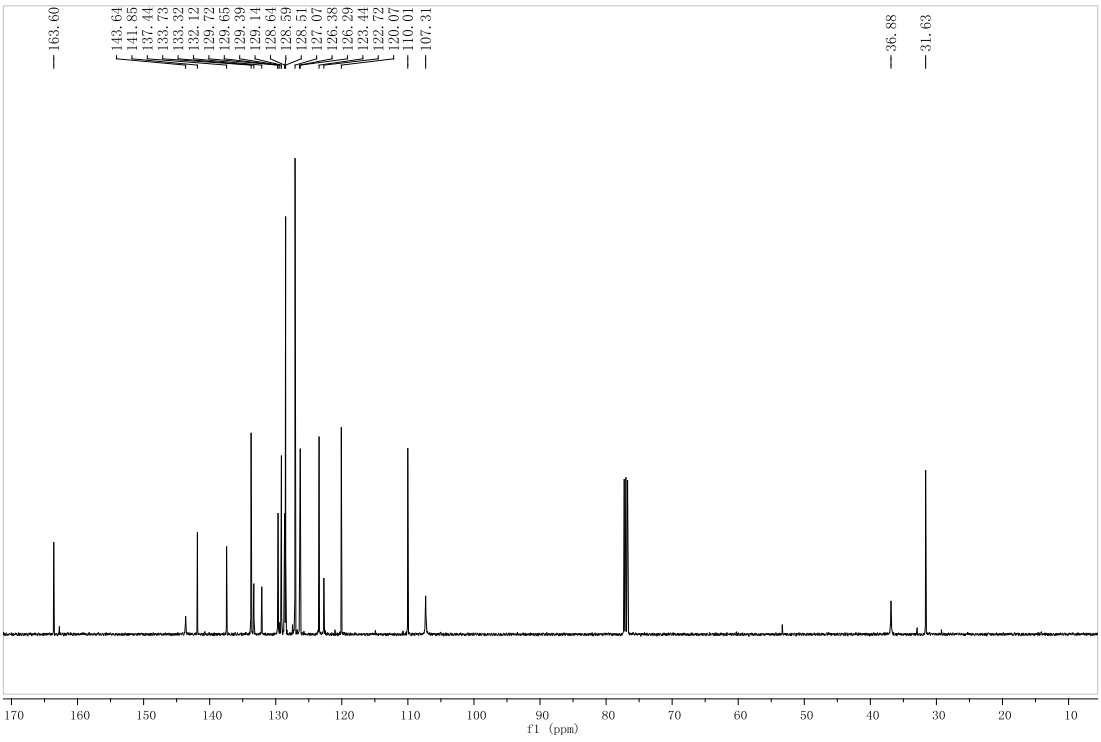
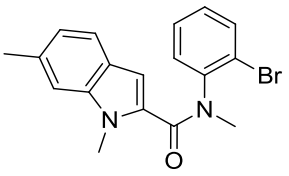
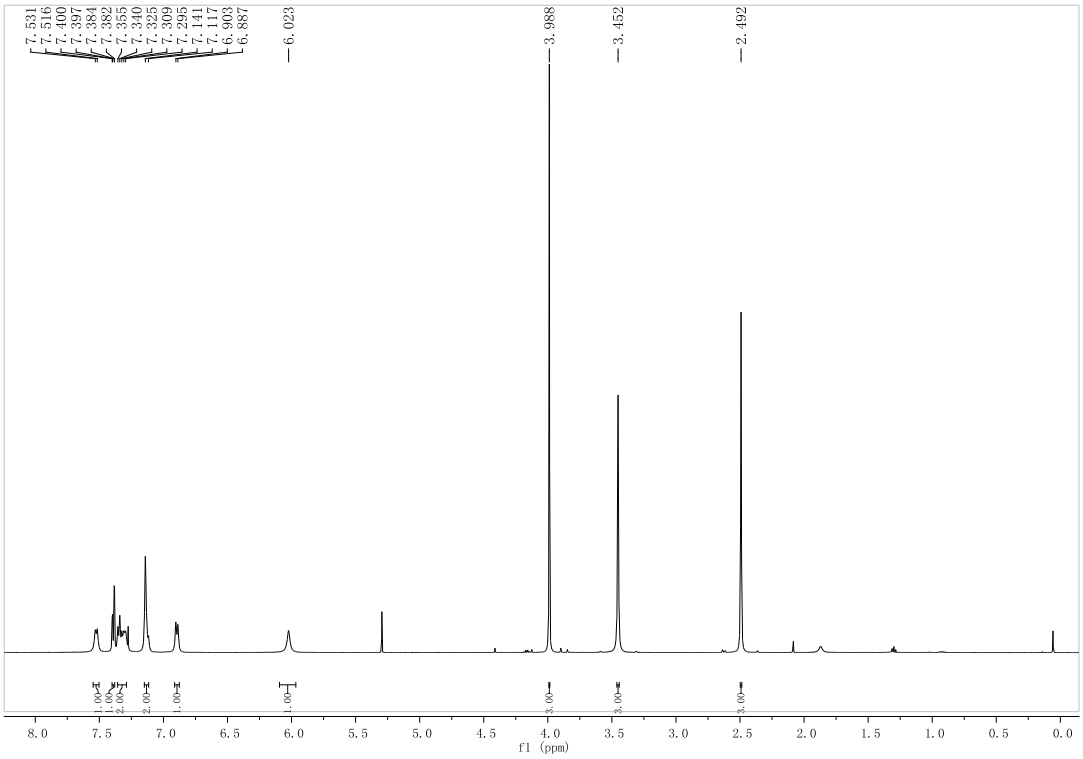
2.99
2.04
1.00
0.98
3.00
3.00
f1 (ppm)

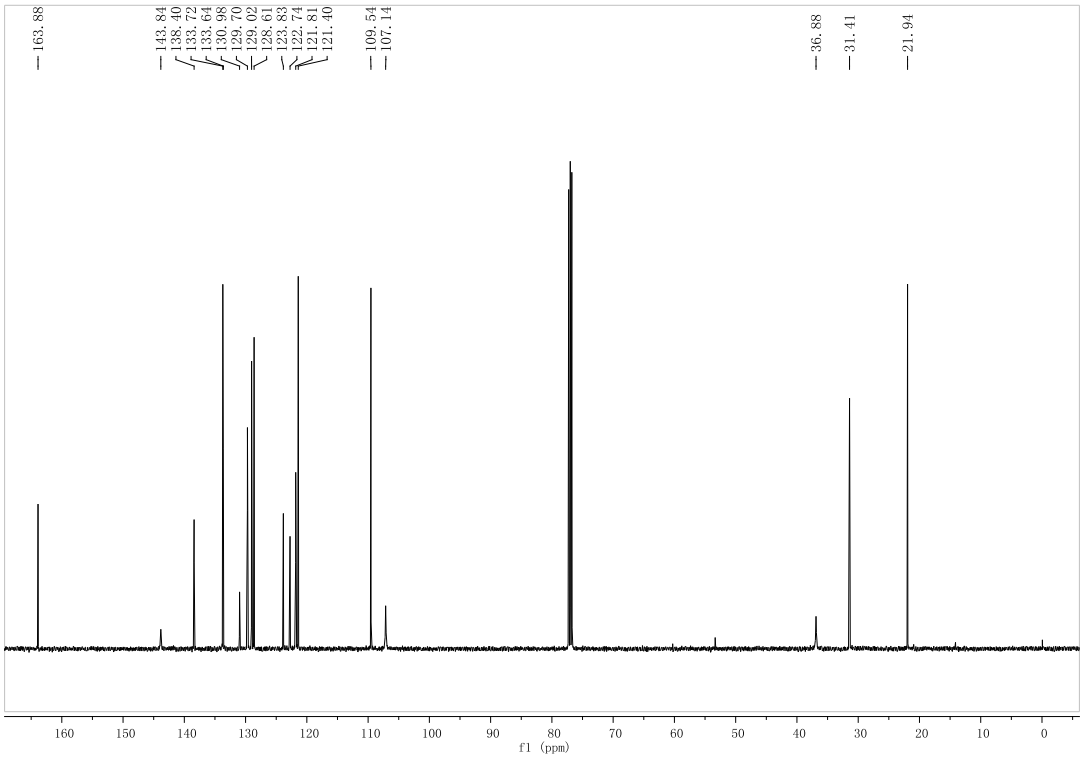

163.60
143.64
141.85
137.44
133.73
133.32
132.12
129.72
129.65
129.39
129.14
128.64
128.59
128.51
127.07
126.38
126.29
123.44
122.72
120.07
110.01
107.31
36.88
31.63
f1 (ppm)

N-(2-Bromophenyl)-N,1,6-trimethyl-1H-indole-2-carboxamide **1h**

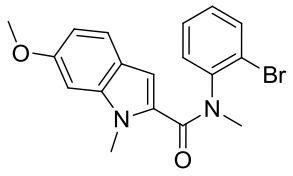


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 54% yield, m.p. 115-117 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29-7.36 (m, 2H), 7.13 (d, *J* = 12.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 1H), 3.99 (s, 3H), 3.45 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 143.8, 138.4, 133.7, 113.6, 131.0, 129.7, 129.0, 128.6, 123.8, 122.7, 121.8, 121.4, 109.5, 107.1, 36.9, 31, 21.9. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O$ ($[M+H]^+$): 357.0597, found 357.0584.

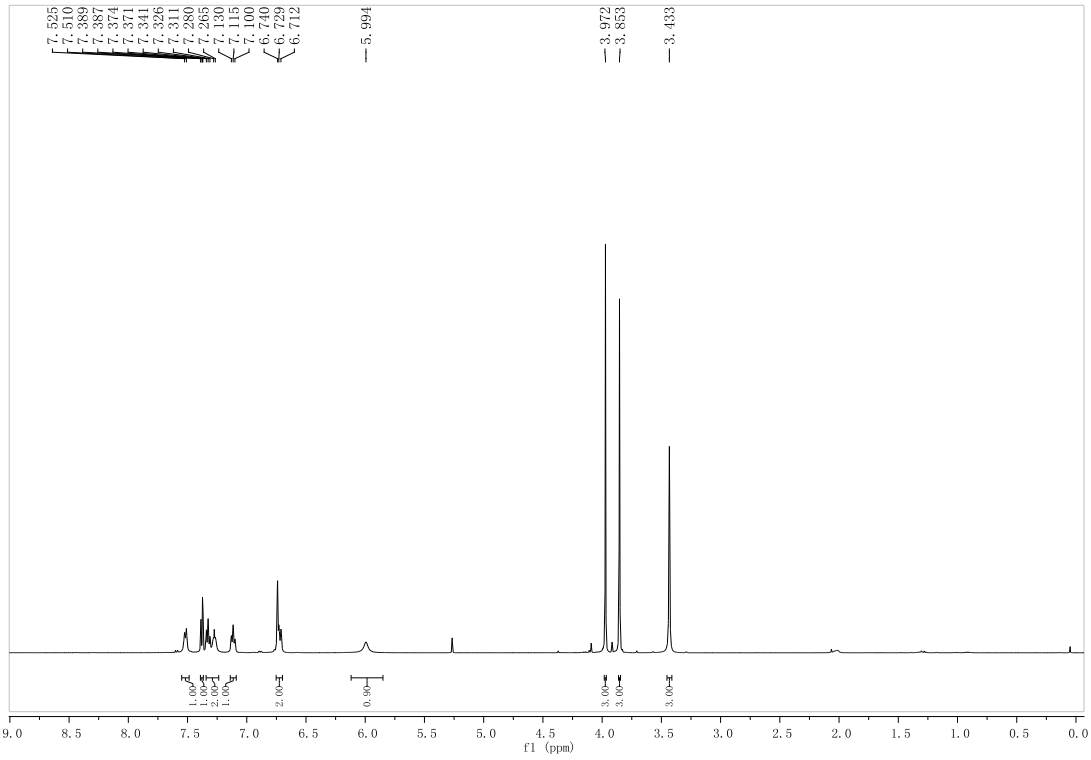


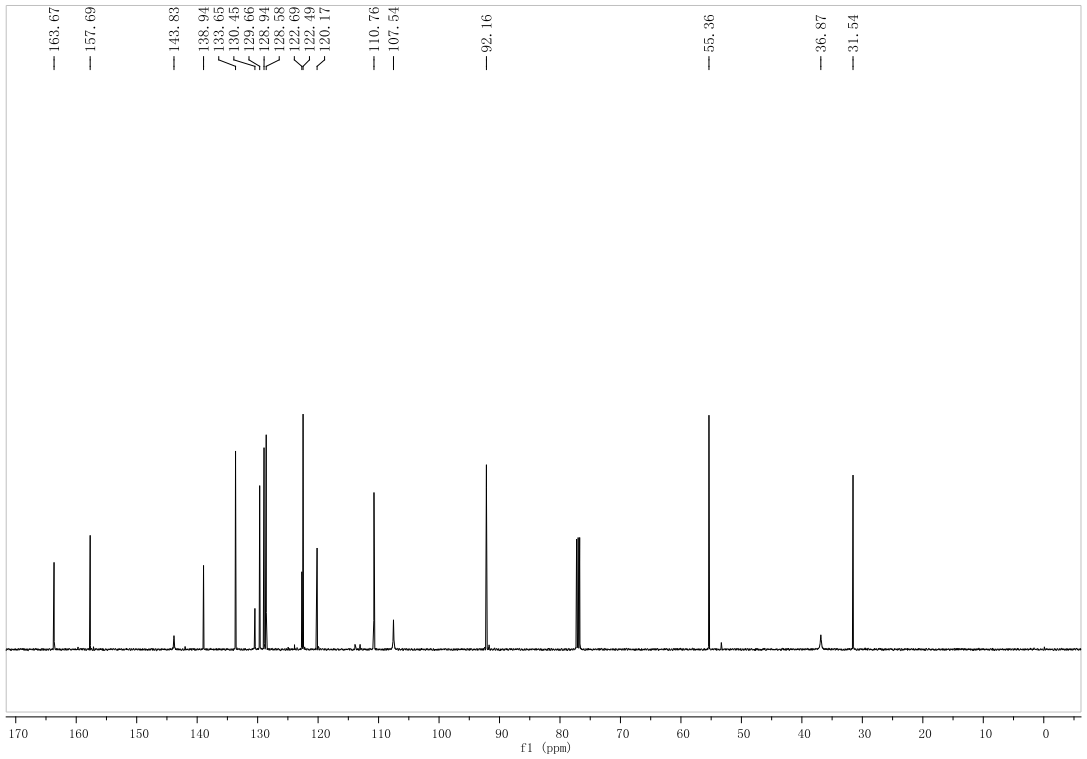


N-(2-Bromophenyl)-6-methoxy-N,1-dimethyl-1H-indole-2-carboxamide **1i**

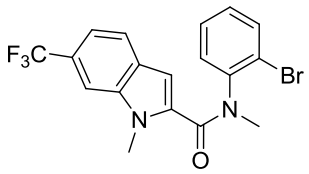


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 43% yield, m.p. 113-115 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.38 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.26-7.35 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.71-6.74 (m, 2H), 5.99 (s, 1H), 3.97 (s, 3H), 3.85 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 157.7, 143.8, 138.9, 133.7, 130.5, 129.7, 128.9, 128.6, 122.7, 122.5, 120.2, 110.8, 107.5, 92.2, 55.4, 36.9, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O_2$ ($[M+H]^+$): 373.0546, found 373.0539.

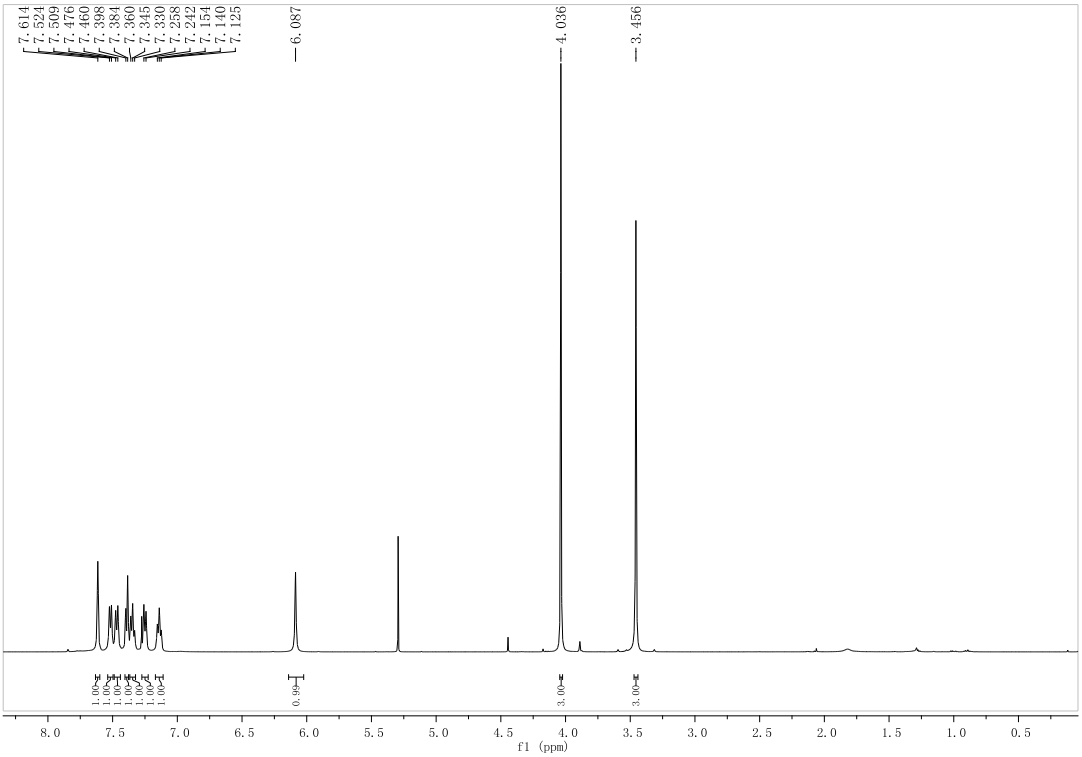

7.525
7.510
7.389
7.387
7.374
7.371
7.341
7.326
7.311
7.280
7.265
7.130
7.115
7.100
6.740
6.729
6.712
5.994
3.972
3.853
3.433
f1 (ppm)

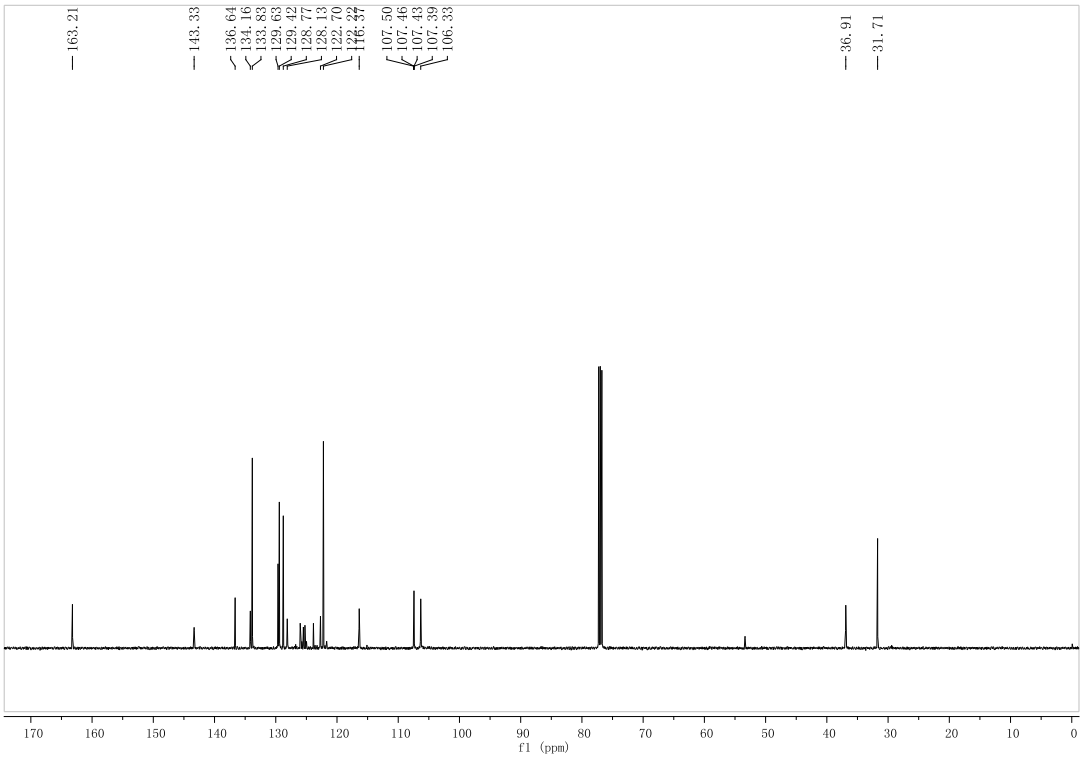

163.67
157.69
143.83
138.94
133.65
130.45
129.66
128.94
128.58
122.69
122.49
120.17
110.76
107.54
92.16
55.36
36.87
31.54
f1 (ppm)

N-(2-Bromophenyl)-N,1-dimethyl-6-(trifluoromethyl)-1H-indole-2-carboxamide **1j**

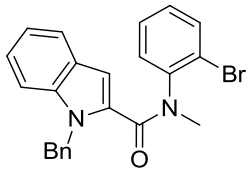


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 43% yield, m.p. 99-101 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.0 Hz, 1H), 6.09 (s, 1H), 4.04 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 143.3, 136.6, 134.2, 133.8, 129.6, 129.4, 128.8, 128.1, 126.0, 125.4 (q, *J* = 31.9 Hz) , 123.9, 122.7, 122.2, 121.7, 116.4, 107.4 (q, *J* = 6.0 Hz), 106.3, 36.9, 31.7. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{15}BrF_3N_2O$ ($[M+H]^+$): 411.0314, found 411.0304.

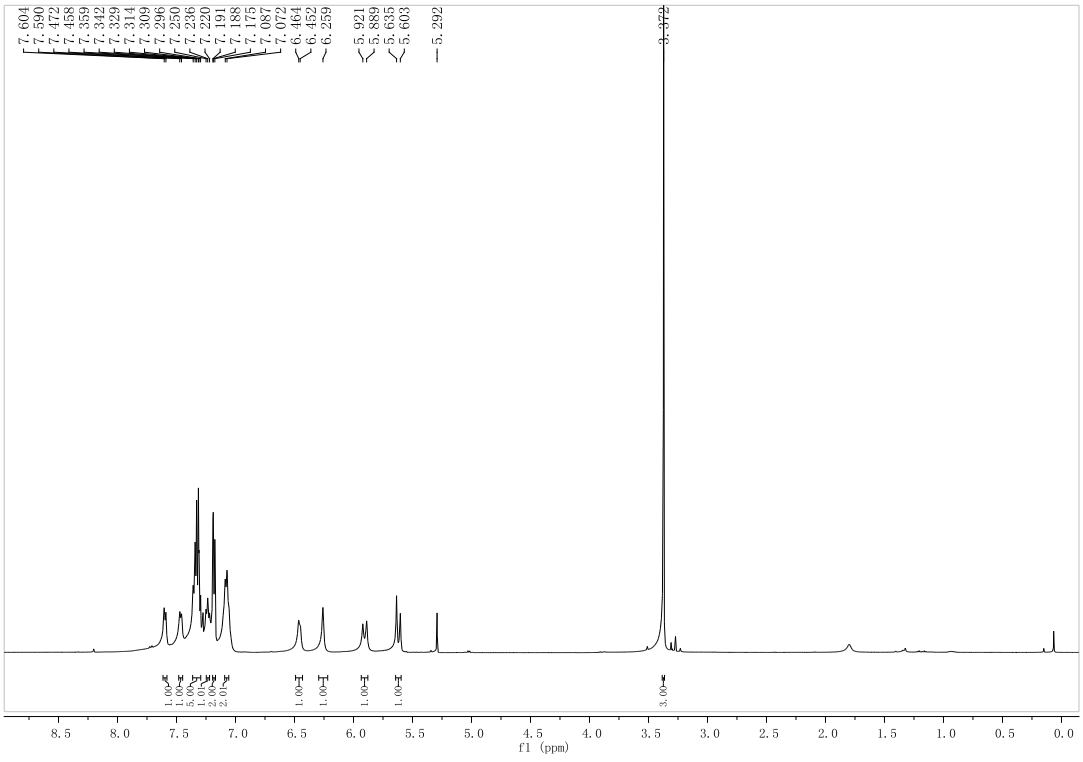


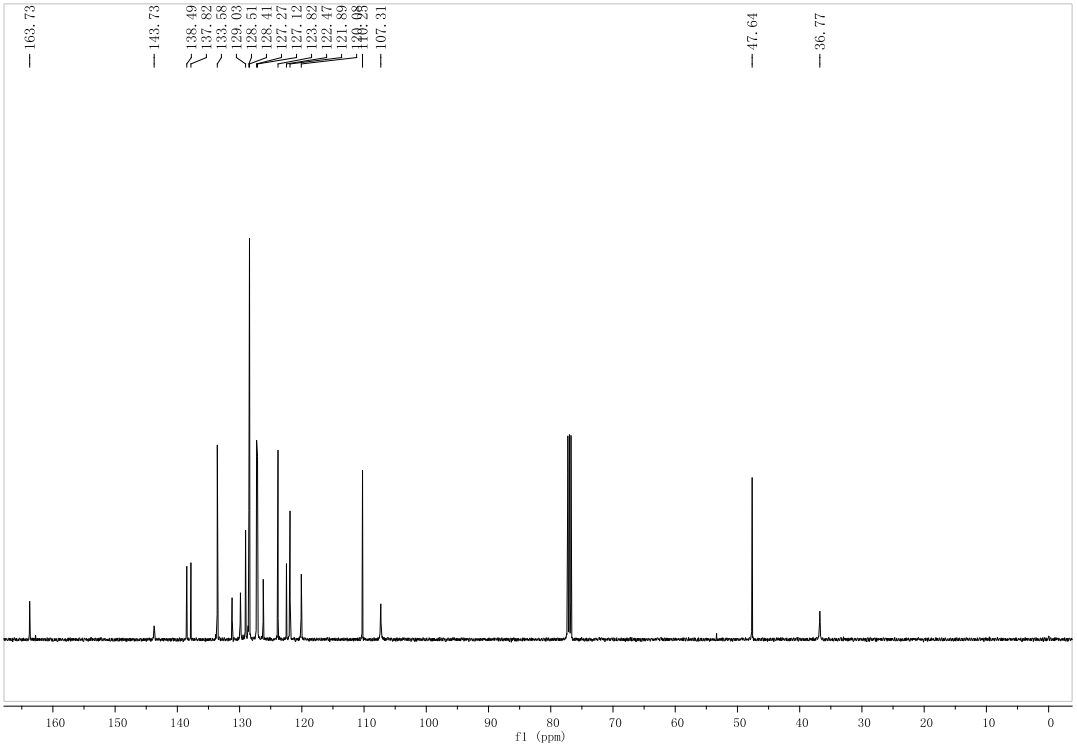


1-Benzyl-N-(2-bromophenyl)-N-methyl-1H-indole-2-carboxamide **1k**

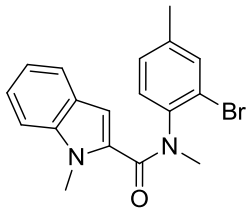


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 54% yield, m.p. 150-154 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.29-7.36 (m, 5H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.17-7.20 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.46 (d, *J* = 6.0 Hz, 1H), 6.26 (s, 1H), 5.90 (d, *J* = 16.0 Hz, 1H), 5.62 (d, *J* = 16.0 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 143.7, 138.5, 137.8, 133.9, 133.6, 131.2, 129.9, 129.0, 128.5 (d, *J* = 12.5 Hz), 127.2 (d, *J* = 18.8 Hz), 126.2, 123.8, 122.5, 121.9, 120.1, 110.3, 107.3, 47.6, 36.8. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{20}BrN_2O$ ($[M+H]^+$): 419.0754, found 419.0756.

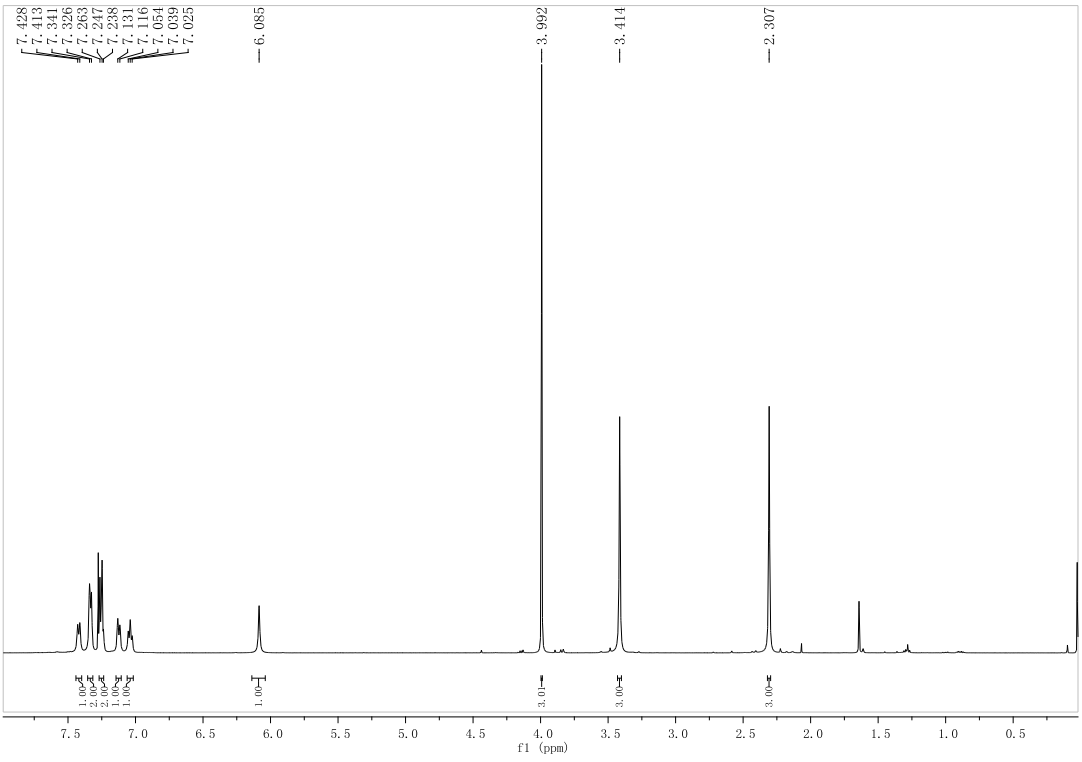

7.604
7.590
7.472
7.458
7.359
7.342
7.329
7.314
7.309
7.296
7.250
7.236
7.220
7.191
7.188
7.175
7.087
7.072
6.464
6.452
6.259
5.921
5.889
5.635
5.603
5.292
3.372
f1 (ppm)

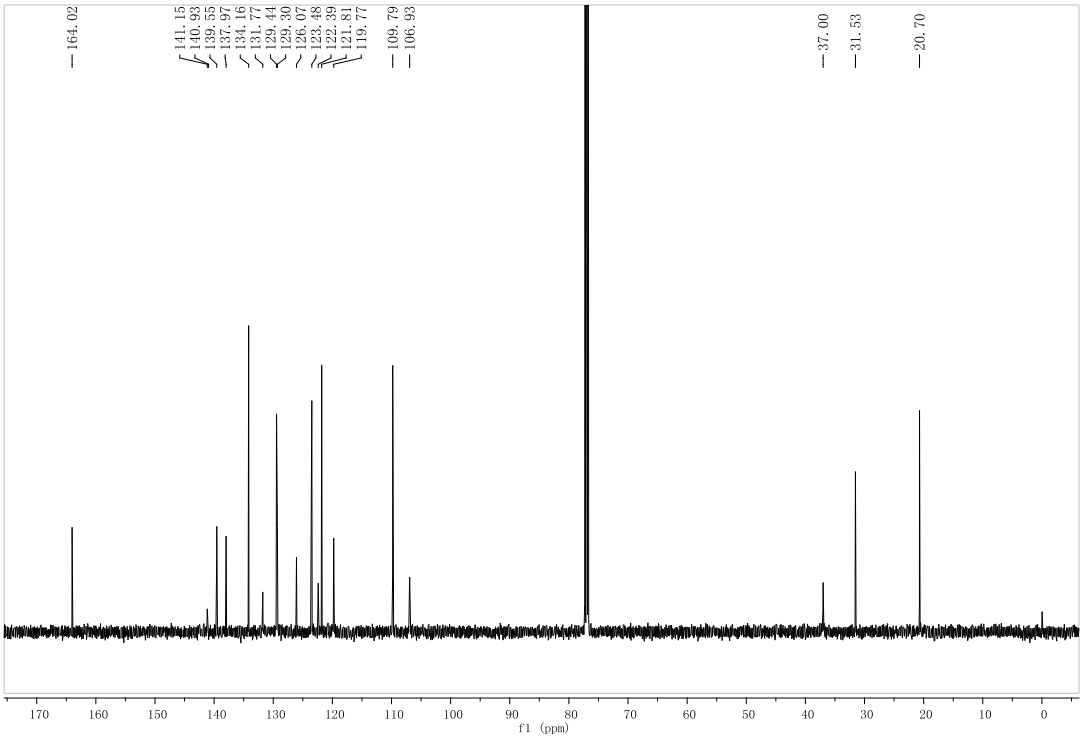

163.73
143.73
138.49
137.82
133.58
129.03
128.51
128.41
127.27
127.12
123.82
122.47
121.89
107.31
47.64
36.77
f1 (ppm)

N-(2-Bromo-4-methylphenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1l**

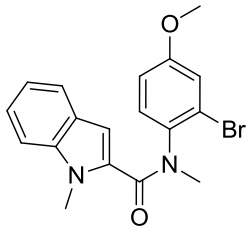


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 38% yield, m.p. 131-133 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.08 (s, 1H), 3.99 (s, 3H), 3.41 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 141.2, 139.6, 138.0, 134.2, 131.8, 129.4, 129.3, 126.1, 123.5, 122.4, 121.8, 119.8, 109.8, 106.9, 37.0, 31.5, 20.7. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O$ ($[M+H]^+$): 357.0594, found 357.0594.

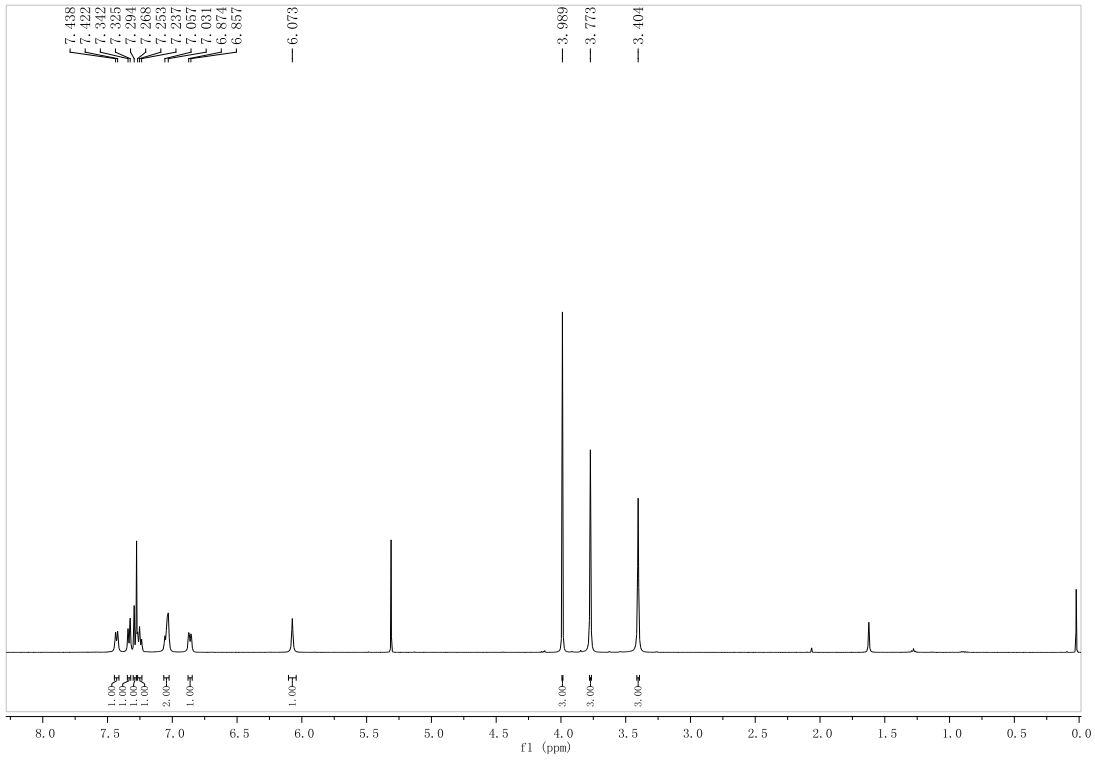




N-(2-Bromo-4-methoxyphenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1m**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 40% yield, m.p. 142-144 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.29 (s, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 13.0 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.07 (s, 1H), 3.99 (s, 3H), 3.77 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 159.2, 138.0, 136.6, 131.8, 130.1, 126.1, 123.5, 123.3, 121.8, 119.8, 118.4, 114.7, 109.8, 106.8, 55.7, 37.1, 31.6. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O_2$ ($[M+H]^+$): 373.0546, found 373.0536


7.438
7.422
7.342
7.325
7.294
7.268
7.253
7.237
7.057
7.031
6.874
6.857
6.073
3.989
3.773
3.404
1.00
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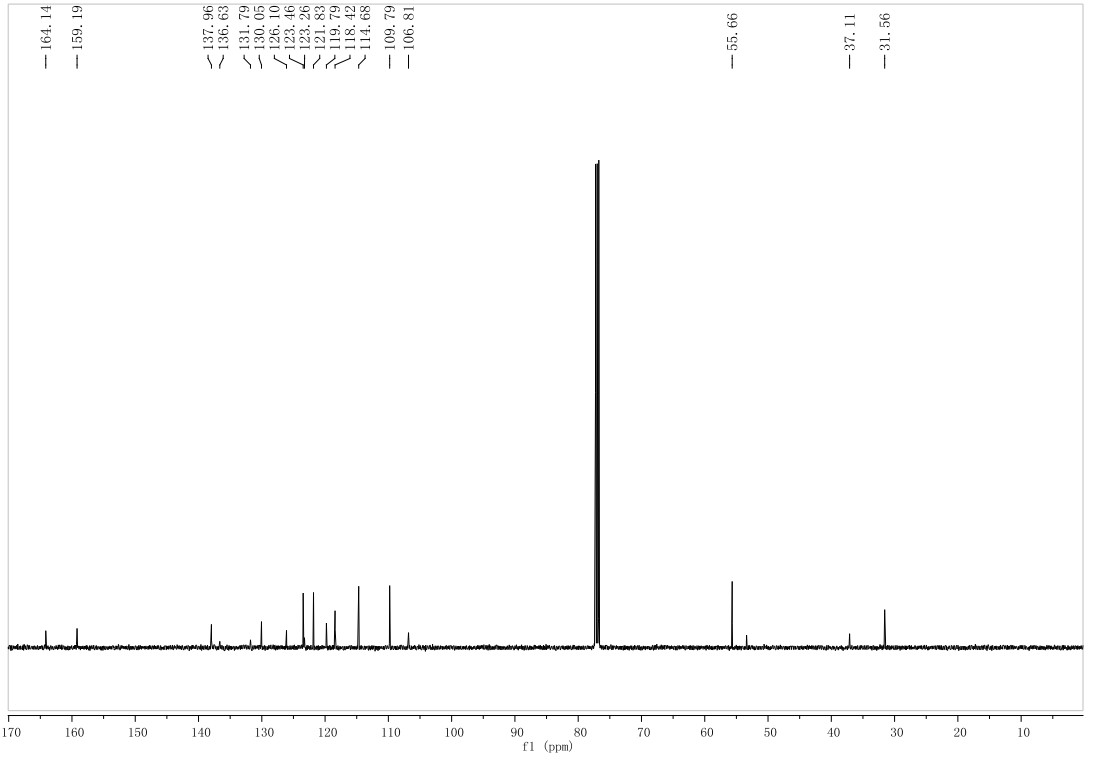
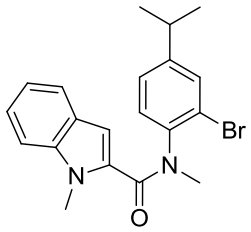
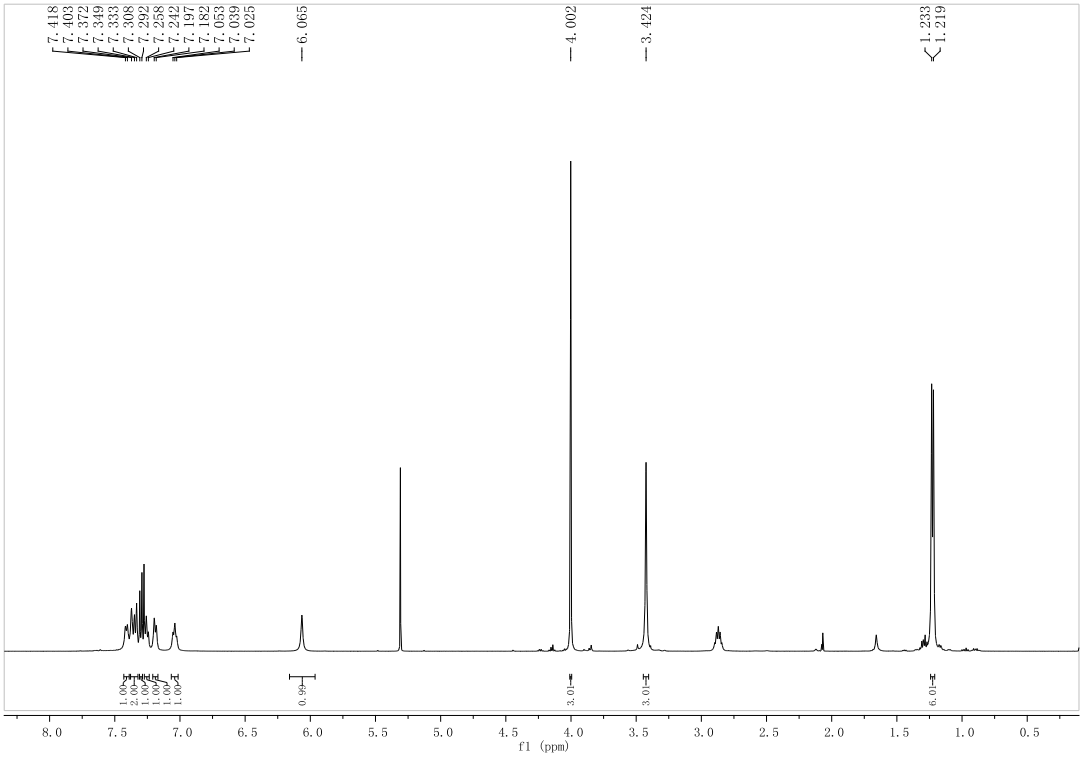
1.00
1.00
2.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

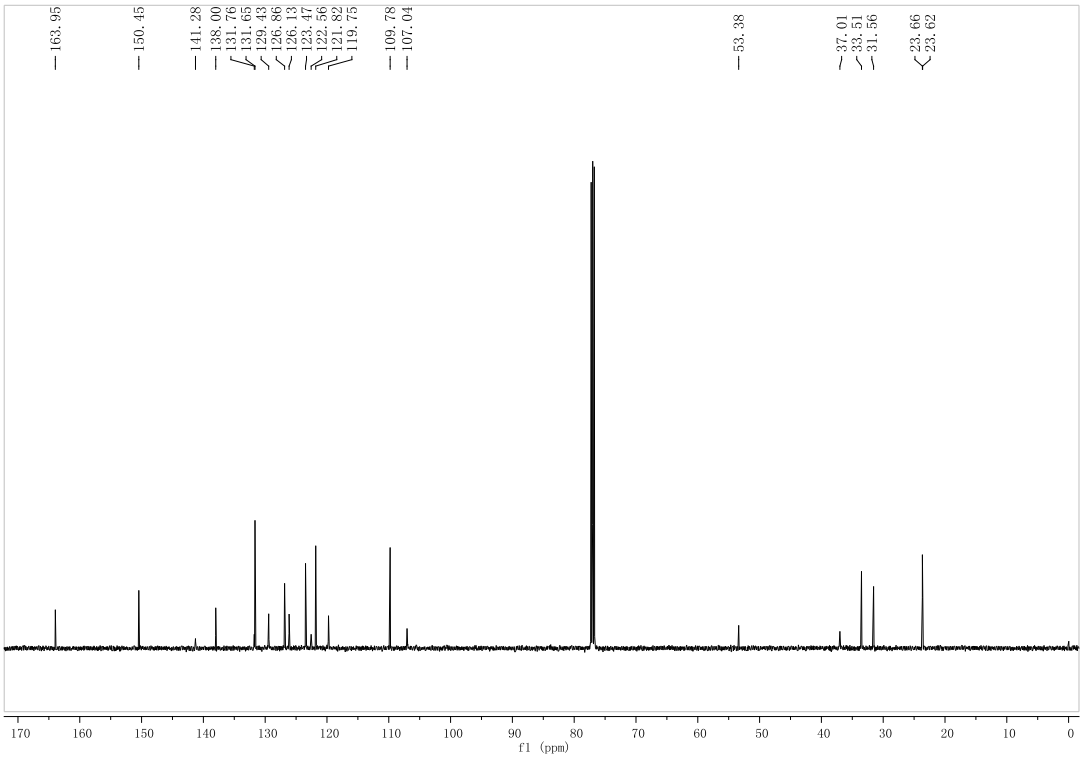

164.14
159.19
137.96
136.63
131.79
130.05
126.10
123.46
123.26
121.83
119.79
118.42
114.68
109.79
106.81
55.66
37.11
31.56
f1 (ppm)

N-(2-Bromo-4-isopropylphenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1n**

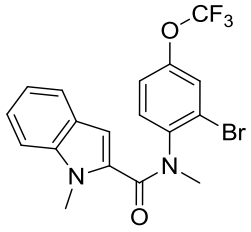


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 36% yield, m.p. 133-134 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 11.5 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.0 Hz, 1H), 6.06 (s, 1H), 4.00 (s, 3H), 3.42 (s, 3H), 1.23 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 150.5, 141.3, 138.0, 131.7 (d, *J* = 13.8 Hz), 129.4, 126.9, 126.1, 123.5, 122.6, 121.8, 119.8, 109.8, 107.0, 53.4, 37.0, 33.5, 31.6, 23.6 (d, *J* = 5.0 Hz). HRMS *m/z* (ESI+): Calculated for $C_{20}H_{21}BrN_2O$ ($[M+H]^+$): 385.0910, found 385.0918.

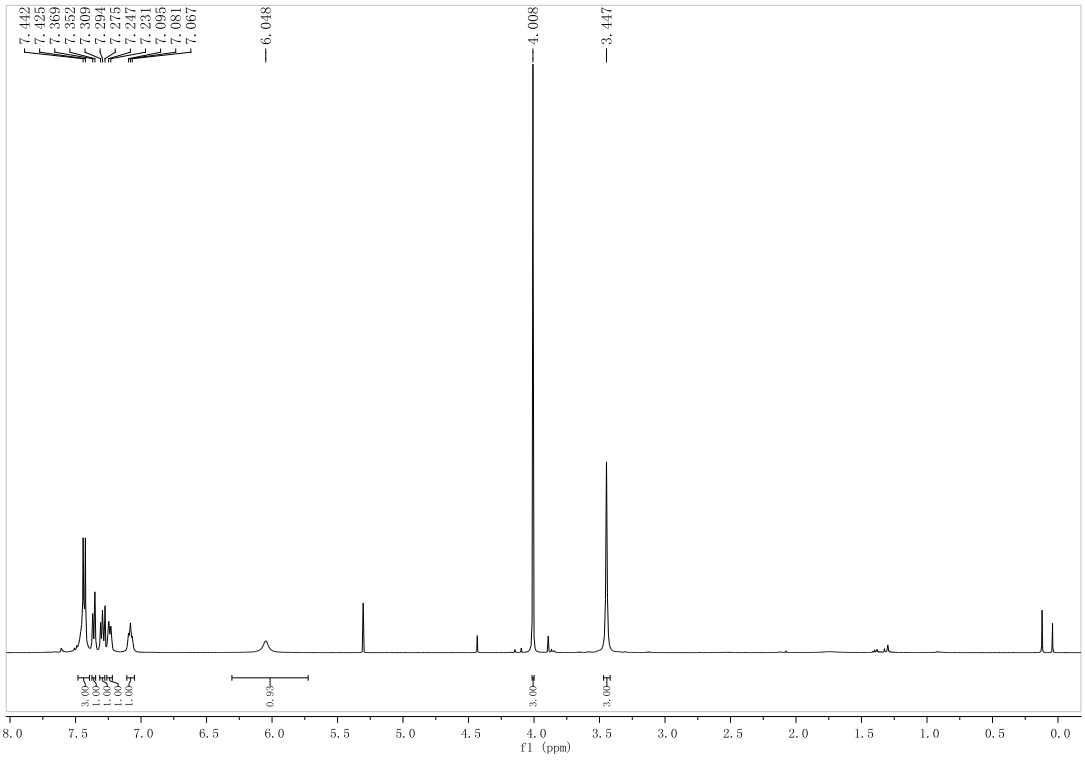


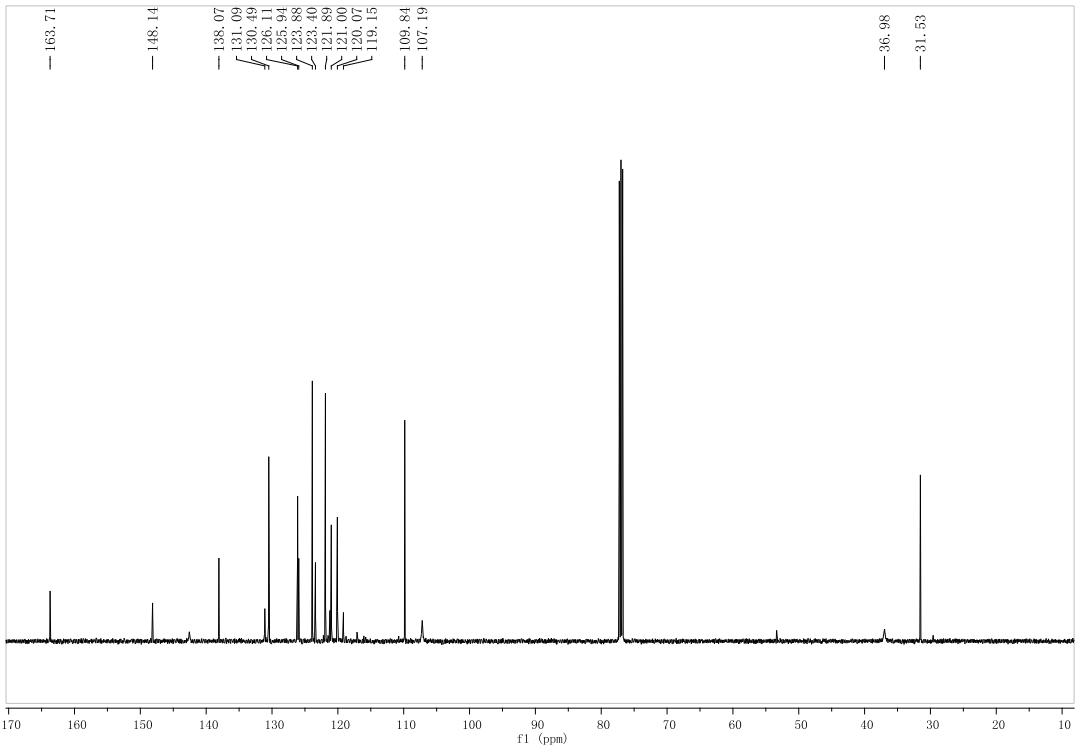


N-(2-Bromo-4-(trifluoromethoxy)phenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1o**

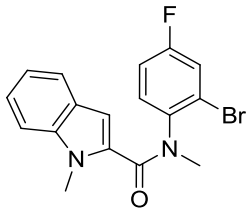


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 38% yield, m.p. 97-99 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 3H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.05 (s, 1H), 4.01 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 148.1, 138.1, 131.1, 130.5, 126.1, 125.9, 123.9, 123.4, 121.9, 121.2, 121.0, 120.1, 119.2, 109.8, 107.2, 37.0, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{14}BrF_3N_2O_2$ ($[M+H]^+$): 427.0264, found 427.0265.

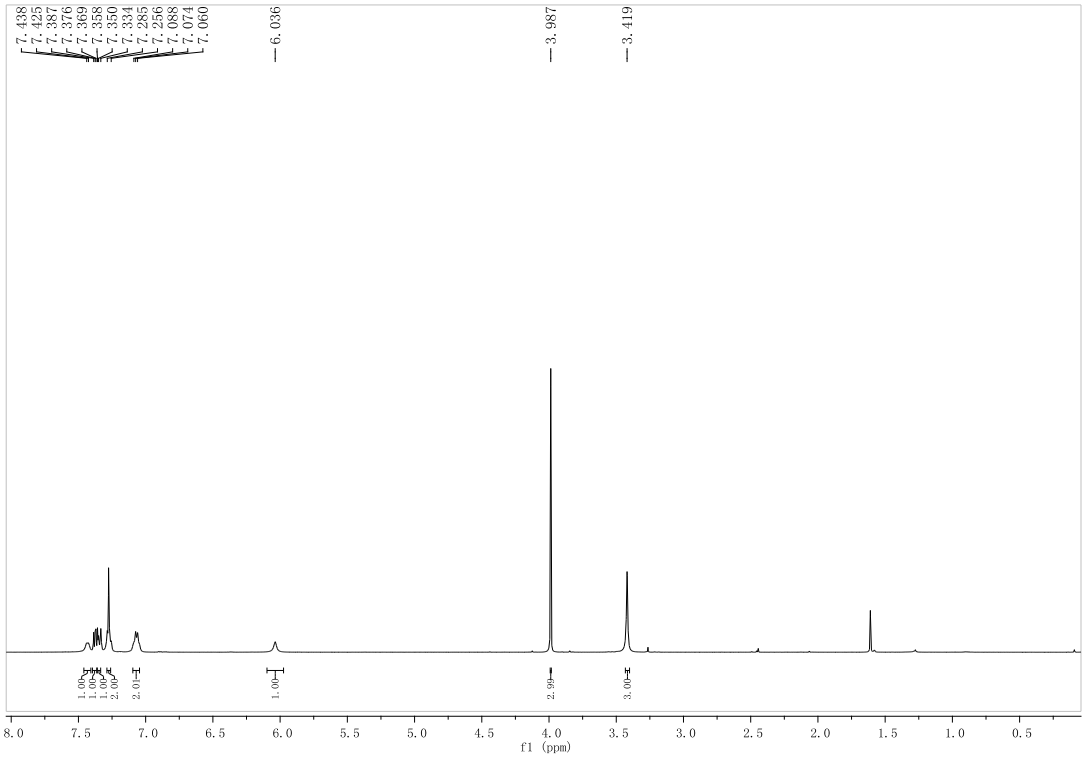

7.442
7.425
7.369
7.352
7.309
7.294
7.275
7.247
7.231
7.095
7.081
7.067
6.048
4.008
3.447
f1 (ppm)

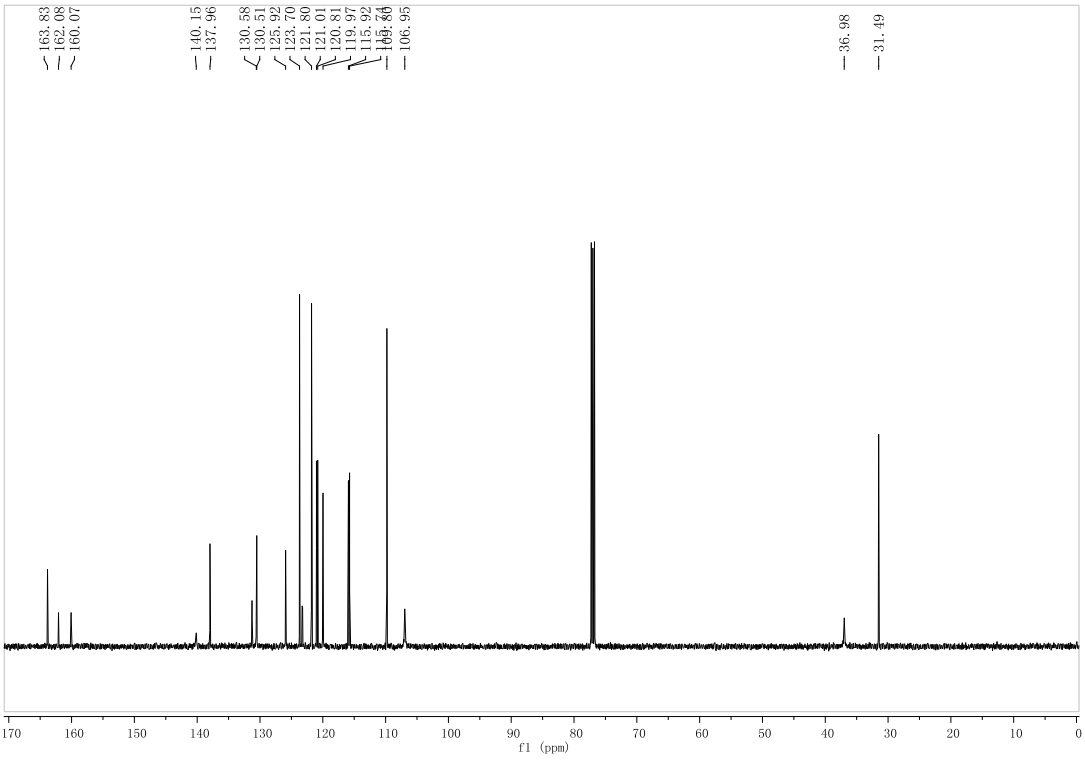

163.71
148.14
138.07
131.09
130.49
126.11
125.94
123.88
123.40
121.89
121.00
120.07
119.15
109.84
107.19
36.98
31.53
f1 (ppm)

N-(2-Bromo-4-fluorophenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1p**

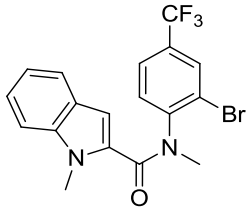


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 32% yield, m.p. 110-113 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.5 Hz, 1H), 7.38 (t, *J* = 3.0 Hz, 1H), 7.35 (t, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 5.0 Hz, 2H), 7.05-7.10 (m, 2H), 6.04 (s, 1H), 3.99 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 161.1 (d, *J* = 252.7 Hz), 140.2, 138.0, 131.3, 130.55 (d, *J* = 8.8 Hz), 125.9, 123.7, 123.3 (d, *J* = 10.0 Hz), 121.8, 120.9 (d, *J* = 25.4 Hz), 120.0, 115.8 (d, *J* = 22.3 Hz), 109.8, 107.0, 37.0, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{15}BrFN_2O$ ($[M+H]^+$): 361.0346, found 361.0338.

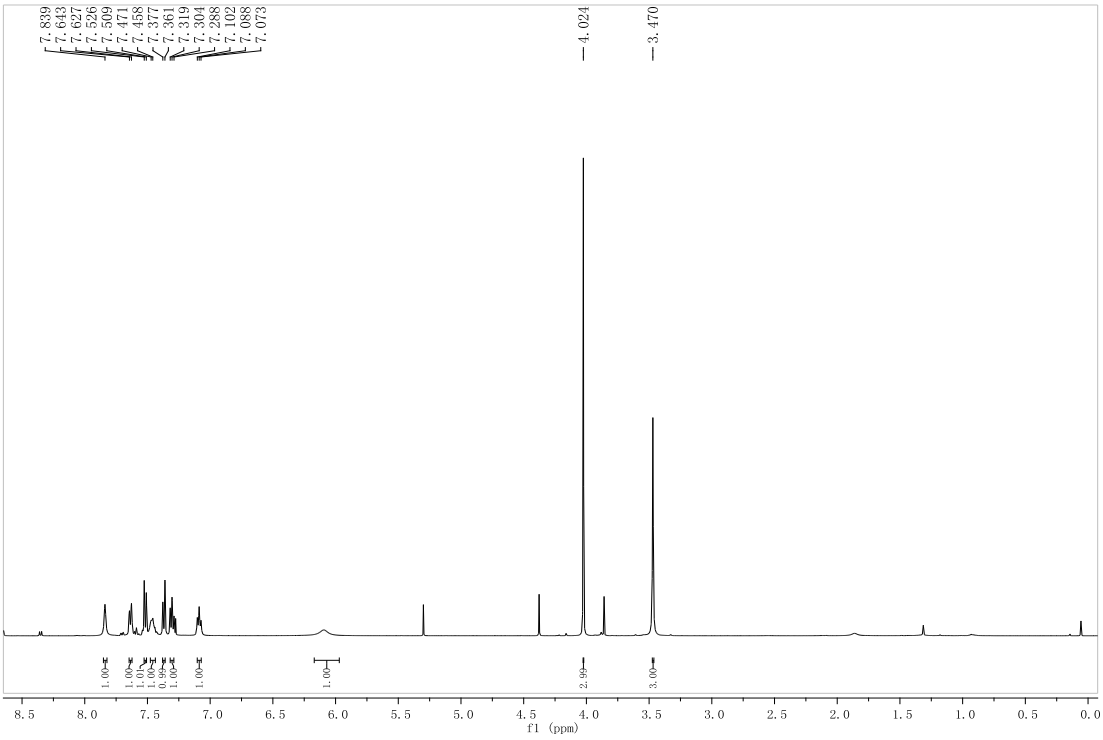


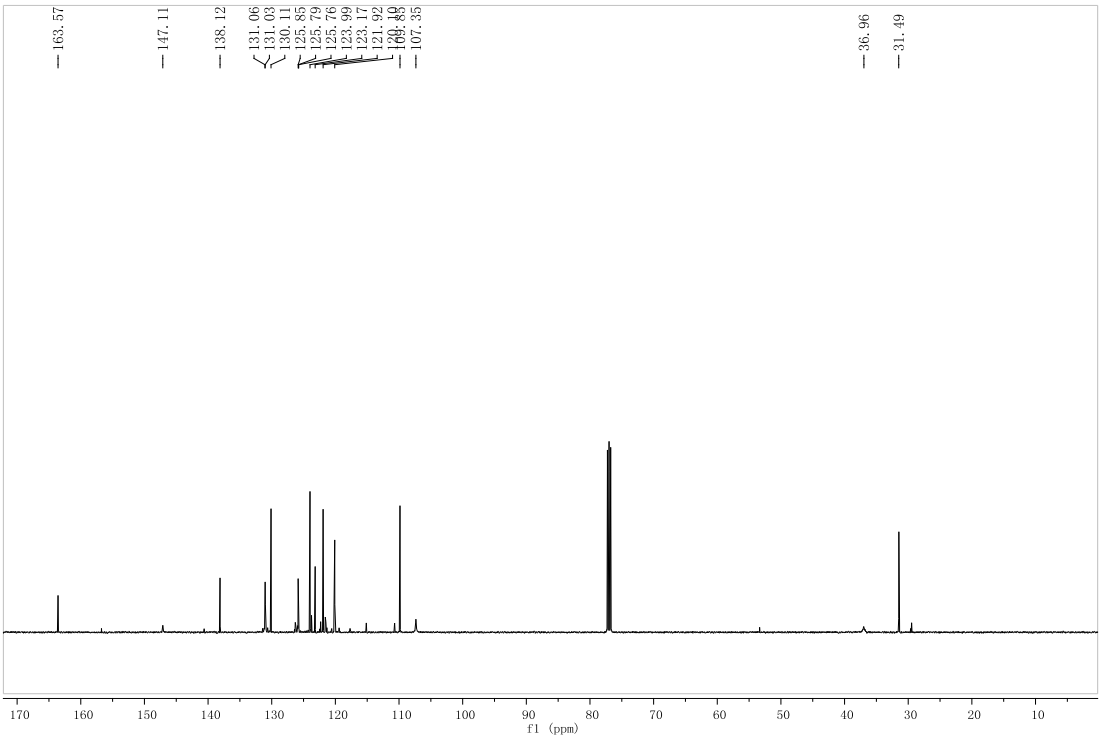


N-(2-Bromo-4-(trifluoromethyl)phenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1q**

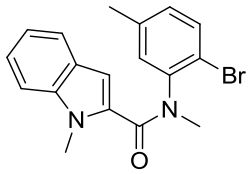


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 15% yield, m.p. 96-98 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 6.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.09 (s, 1H), 4.02 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 147.1, 138.1, 131.02 (q, *J* = 3.5 Hz), 130.9, 130.1, 125.8, 125.7 (q, *J* = 3.5 Hz), 124.0, 123.8, 123.2, 121.9, 120.1, 109.9, 107.4, 37.0, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{15}BrF_3N_2O$ ($[M+H]^+$): 411.0314, found 411.0316.

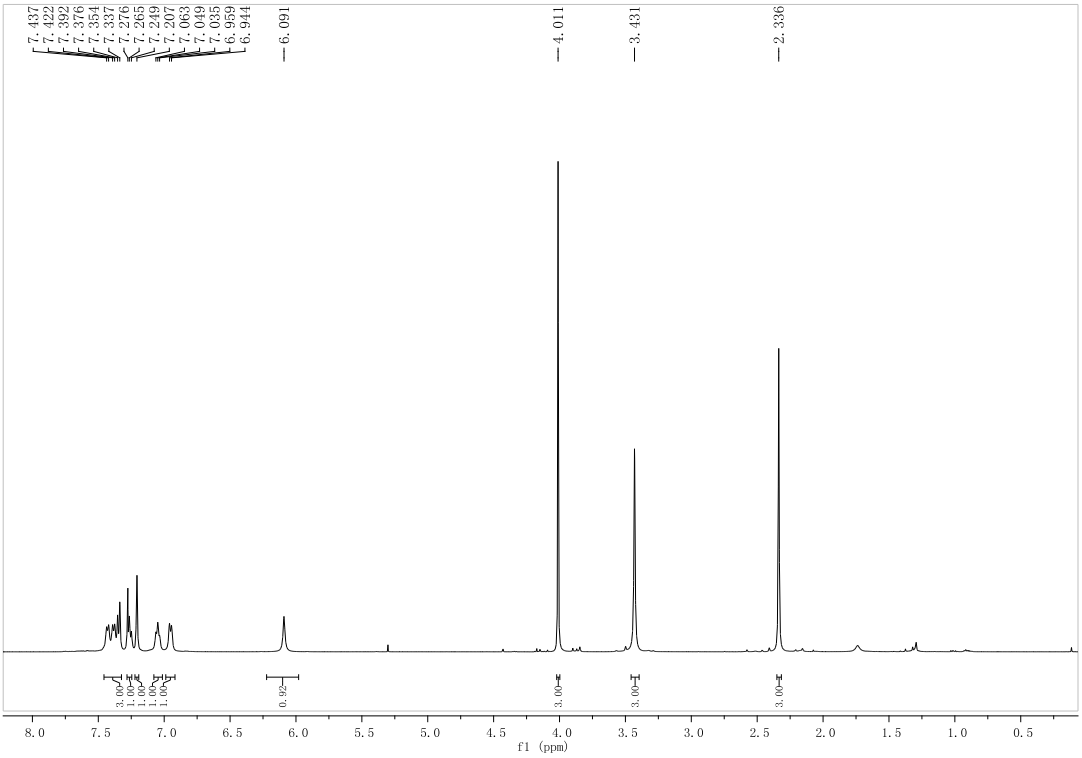

7.839
7.643
7.627
7.526
7.509
7.471
7.458
7.377
7.361
7.319
7.304
7.288
7.102
7.088
7.073
4.024
3.470
f1 (ppm)

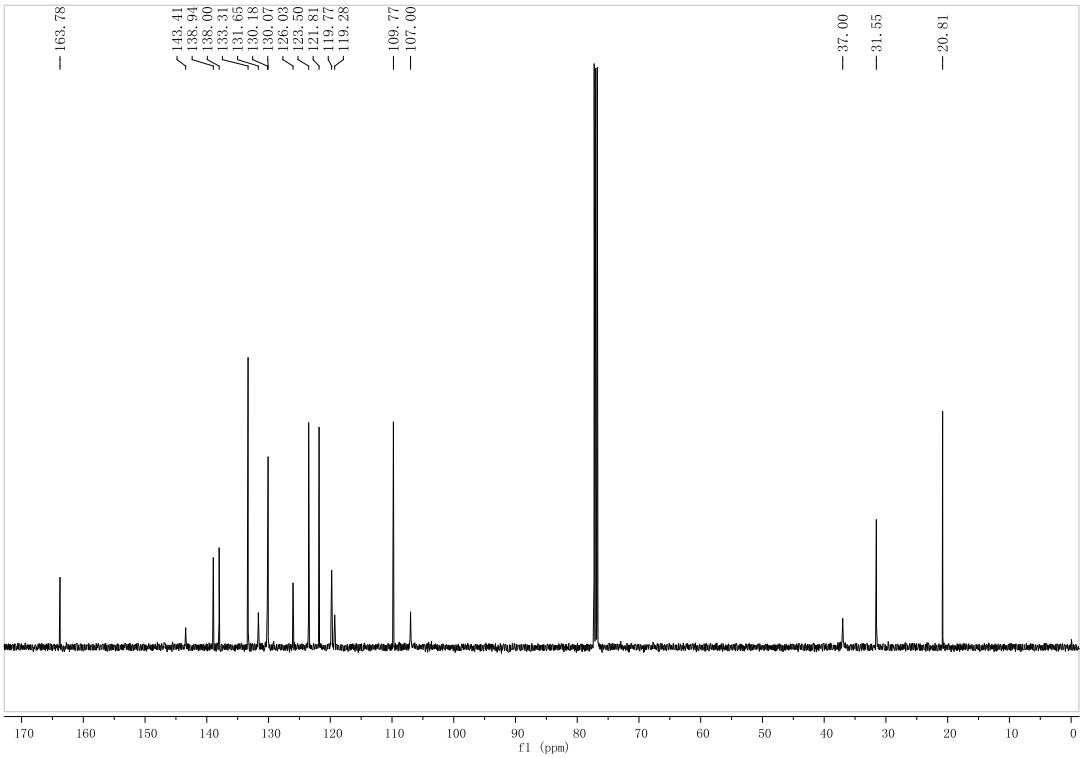

163.57
147.11
138.12
131.06
131.03
130.11
125.85
125.79
125.76
123.99
123.17
121.92
107.35
36.96
31.49
f1 (ppm)

N-(2-Bromo-5-methylphenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1r**

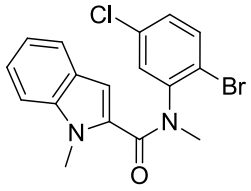


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 38% yield, m.p. 157-160 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.33 (m, 3H), 7.26 (t, *J* = 5.5 Hz, 1H), 7.21 (s, 1H), 7.05 (t, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.09 (s, 1H), 4.01 (s, 3H), 3.43 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 143.4, 138.9, 138.0, 133.3, 131.7, 130.2, 130.1, 126.0, 123.5, 121.8, 119.8, 119.3, 109.8, 107.0, 37.0, 31.6, 20.8. HRMS *m/z* (ESI^{+}): Calculated for $C_{18}H_{18}BrN_2O$ ($[M+H]^{+}$): 357.0594, found 357.0593.

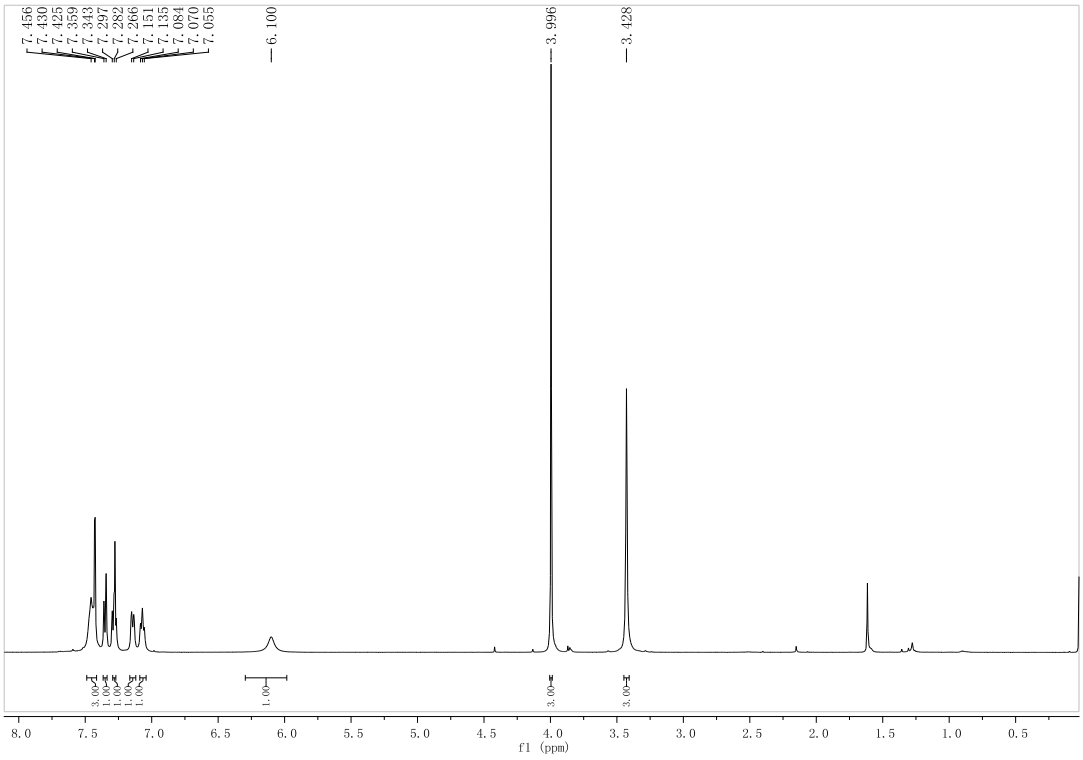


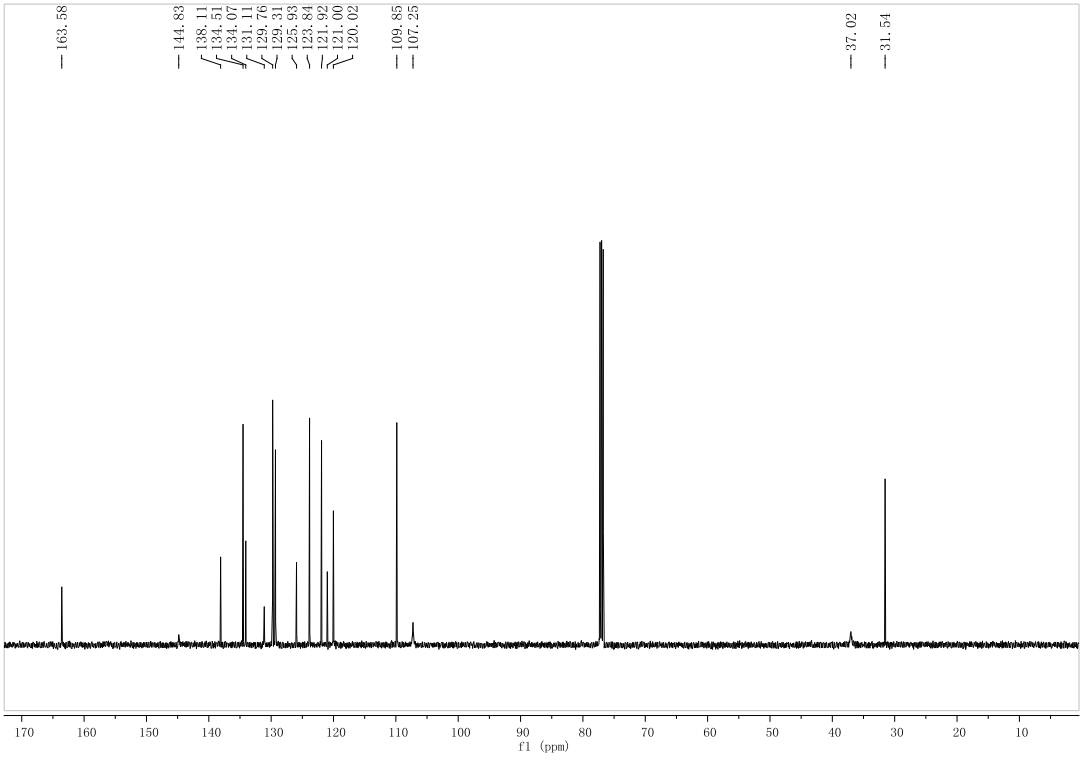


N-(2-Bromo-5-chlorophenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1s**

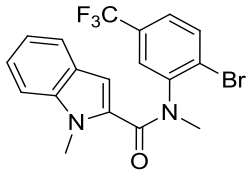


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 46% yield, m.p. 151-155 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H),, 7.14 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.10 (s, 1H), 4.00 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 144.8, 138.1, 134.5, 134.1, 131.1, 129.8, 129.3, 125.9, 123.8, 121.9, 121.0, 120.0, 109.9, 107.3, 37.0, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{15}BrClN_2O$ ($[M+H]^+$): 377.0051, found 377.0043.

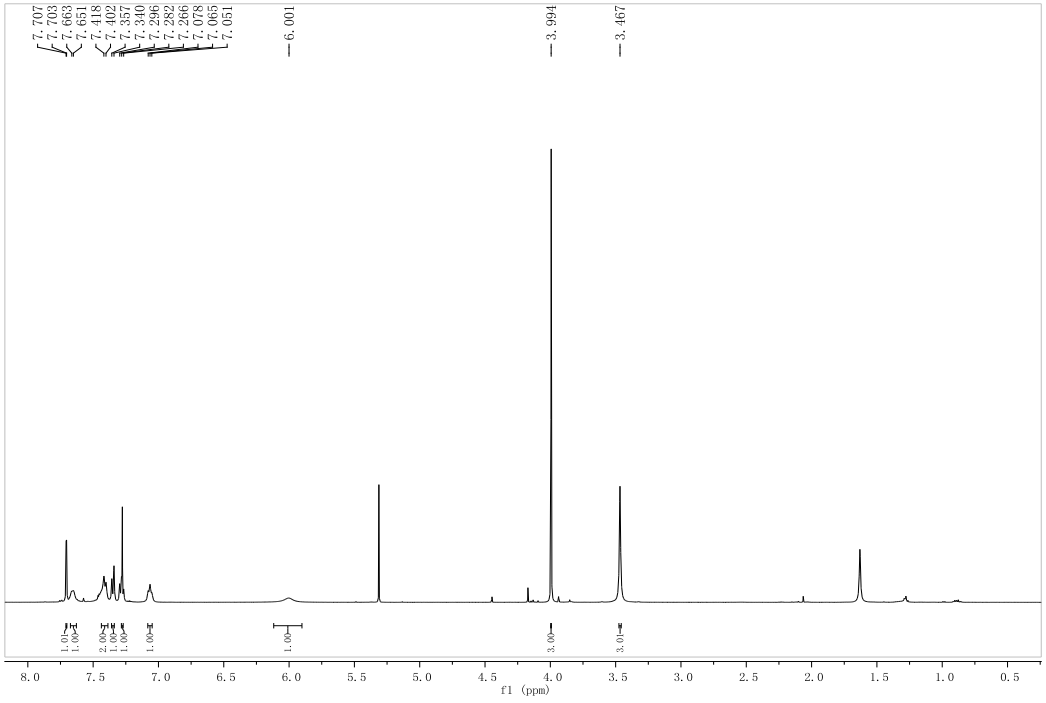

7.456
7.430
7.425
7.359
7.343
7.297
7.282
7.266
7.151
7.135
7.084
7.070
7.055
6.100
3.996
3.428
3.04
1.06
1.06
1.06
1.06
1.04
3.00
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

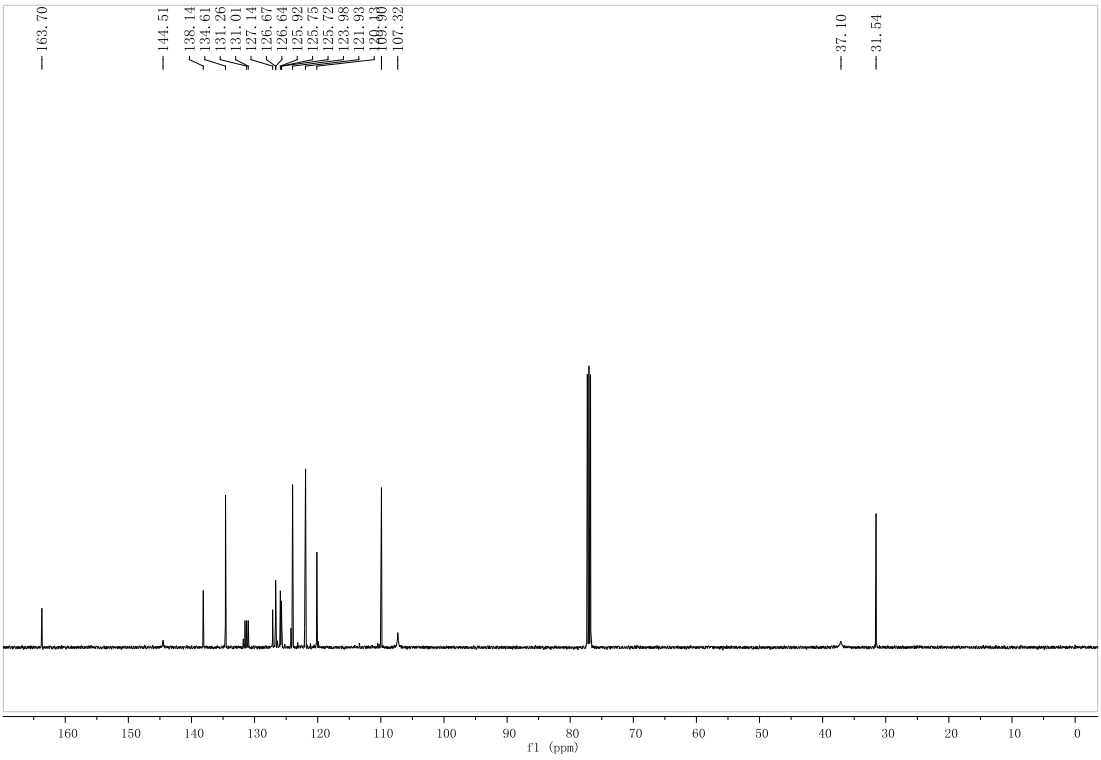

163.58
144.83
138.11
134.51
134.07
131.11
129.76
129.31
125.93
123.84
121.92
121.00
120.02
109.85
107.25
37.02
31.54
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

N-(2-Bromo-5-(trifluoromethyl)phenyl)-N,1-dimethyl-1H-indole-2-carboxamide **2t**

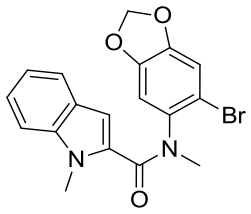


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 16% yield, m.p. 128-131 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 6.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 1H), 7.06 (t, *J* = 6.5 Hz, 1H), 6.00 (s, 1H), 3.99 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 144.5, 138.1, 134.6, 131.4 (q, *J* = 32.8 Hz), 131.0, 127.1, 126.6 (q, *J* = 3.5 Hz), 125.9, 125.7 (d, *J* = 3.5 Hz), 124.0, 121.9, 120.1, 109.9, 107.3, 37.1, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{15}BrF_3N_2O$ ($[M+H]^+$): 411.0314, found 411.0311.

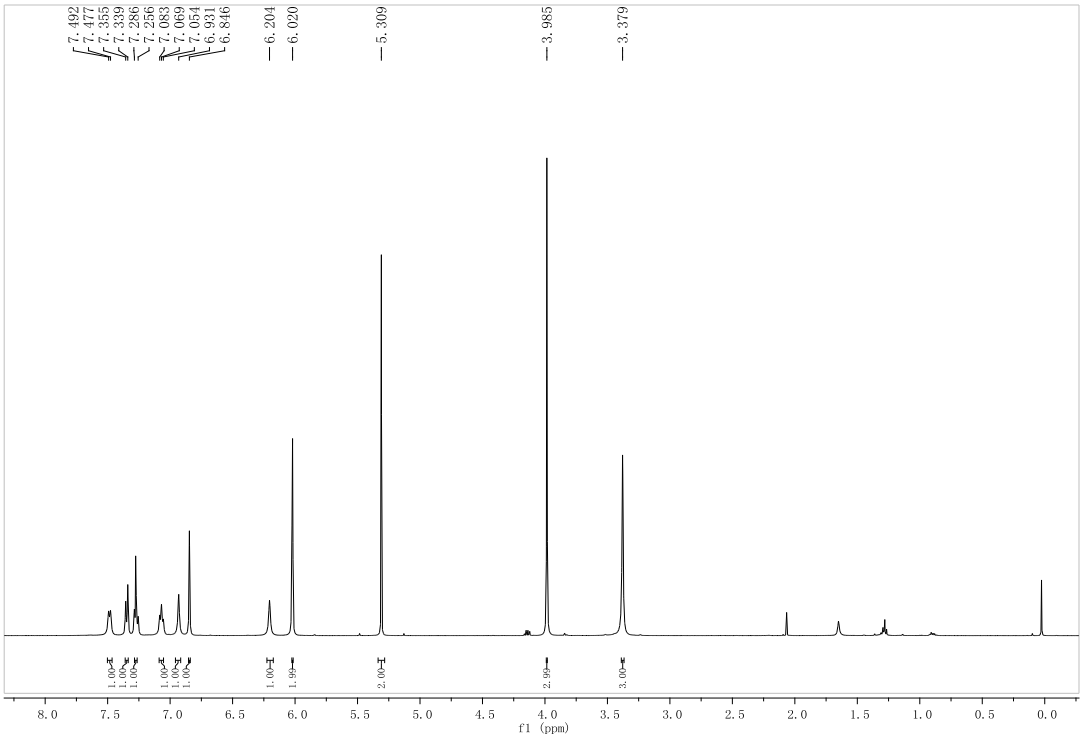


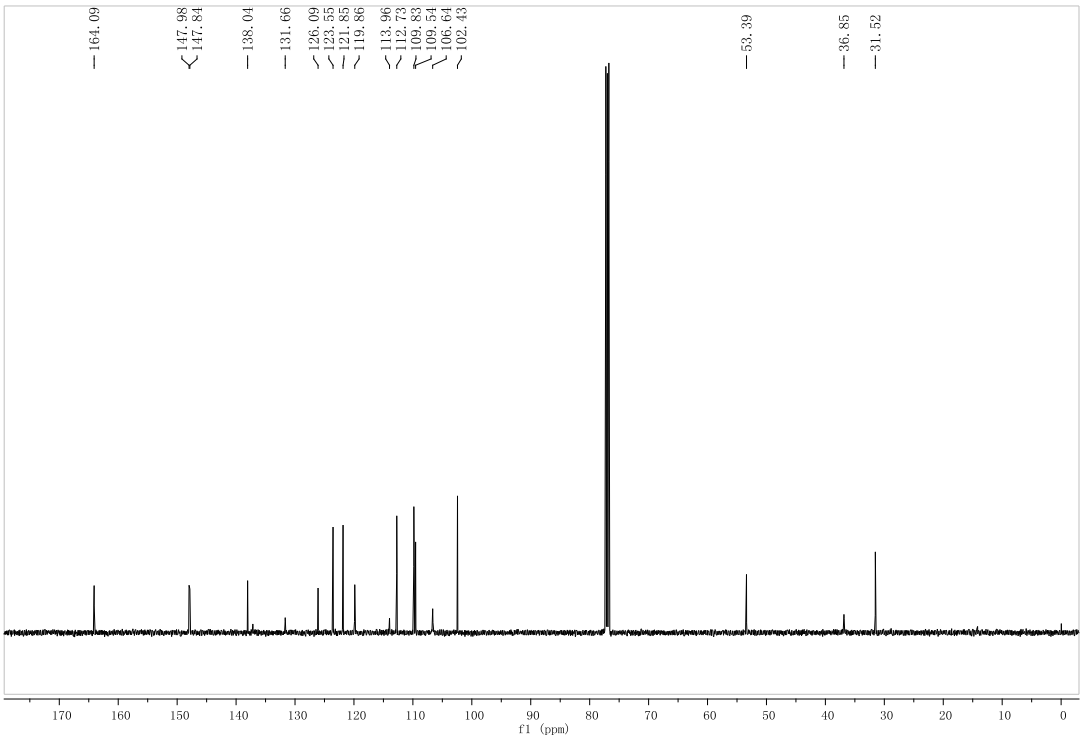


N-(6-Bromobenzo[d][1,3]dioxol-5-yl)-N,1-dimethyl-1H-indole-2-carboxamide **1u**

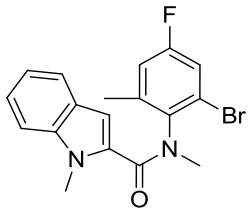


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 52% yield, m.p. 154-156 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 5.0 Hz, 1H) 7.07 (t, *J* = 7.0 Hz, 1H), 6.93 (s, 1H), 6.85 (s, 1H), 6.20 (s, 1H), 6.02 (s, 2H), 5.31 (s, 2H), 3.98 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 148.0, 147.8, 138.0, 131.7, 126.1, 123.6, 121.9, 119.9, 114.0, 112.7, 109.8, 109.5, 106.6, 102.4, 53.4, 36.9, 31.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}BrN_2O_3$ ($[M+H]^+$): 387.0339, found 387.0329.

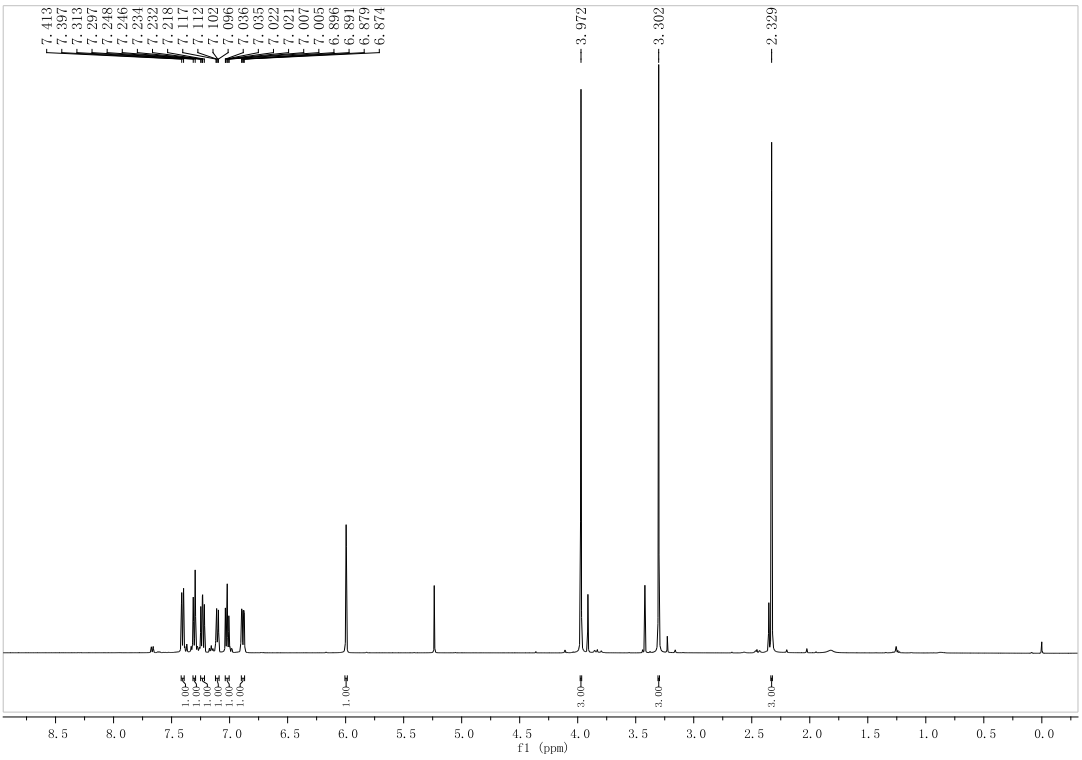

7.492
7.477
7.355
7.339
7.286
7.256
7.083
7.069
7.054
6.931
6.846
6.204
6.020
5.309
3.985
3.379
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.99
2.00
2.99
3.00
f1 (ppm)

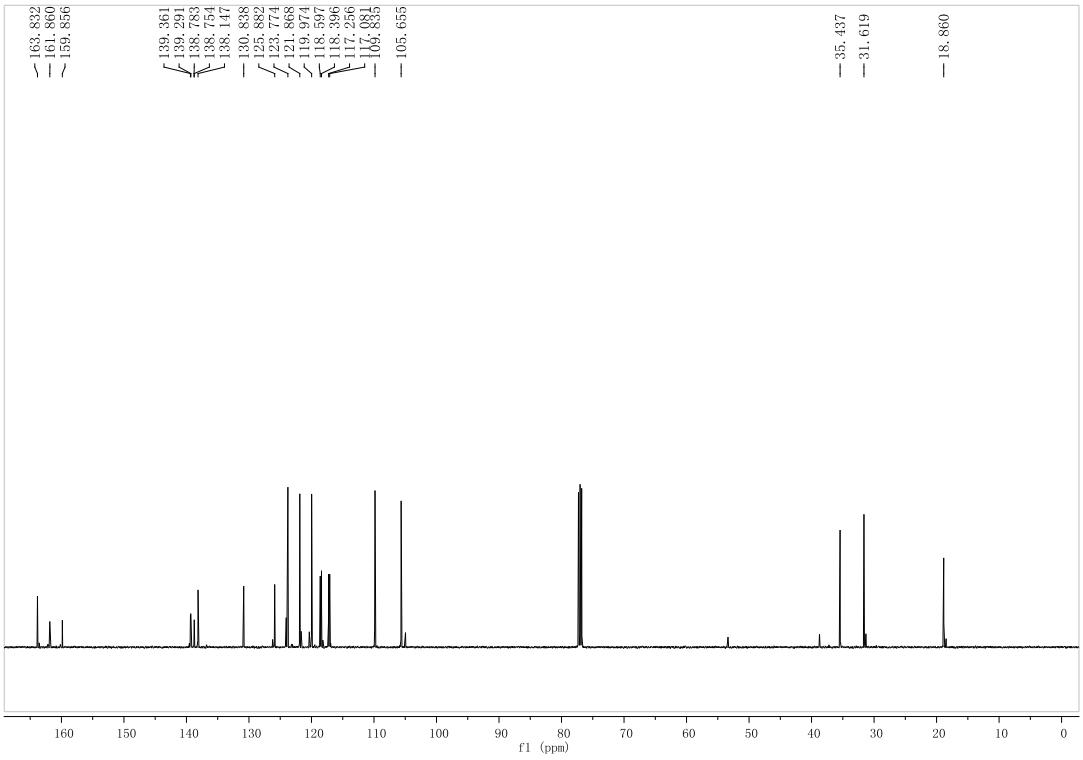

164.09
147.98
147.84
138.04
131.66
126.09
123.55
121.85
119.86
113.96
112.73
109.83
109.54
106.64
102.43
53.39
36.85
31.52
f1 (ppm)

N-(2-Bromo-4-fluoro-6-methylphenyl)-N,1-dimethyl-1H-indole-2-carboxamide **1v**

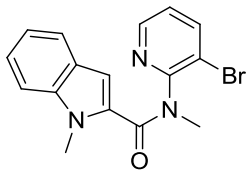


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 36% yield, m.p. 151-154 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.21-7.25 (m, 1H), 7.11 (dd, *J* = 7.5, 2.5 Hz, 1H), 7.02 (td, *J* = 7.0, 0.5 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.00 (s, 1H), 3.97 (s, 3H), 3.30 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 160.86 (d, *J* = 252.1 Hz), 139.33 (d, *J* = 8.8 Hz), 138.77 (d, *J* = 3.6 Hz), 138.2, 130.8, 125.9, 124.08 (d, *J* = 10.6 Hz), 123.8 121.9, 120.0, 118.50 (d, *J* = 25.3 Hz), 117.17 (d, *J* = 21.9 Hz), 109.8, 105.7, 35.4, 31.6, 18.9. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{17}BrFN_2O$ ([M+H]$^{+}$): 375.0503, found 375.0494.

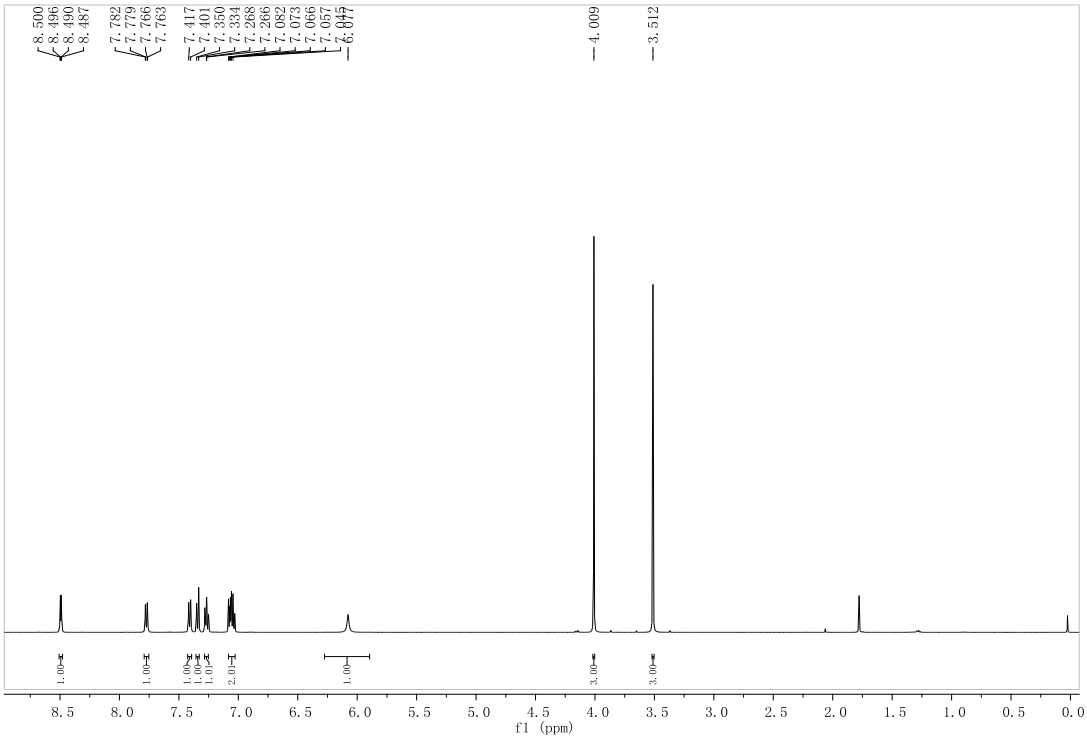


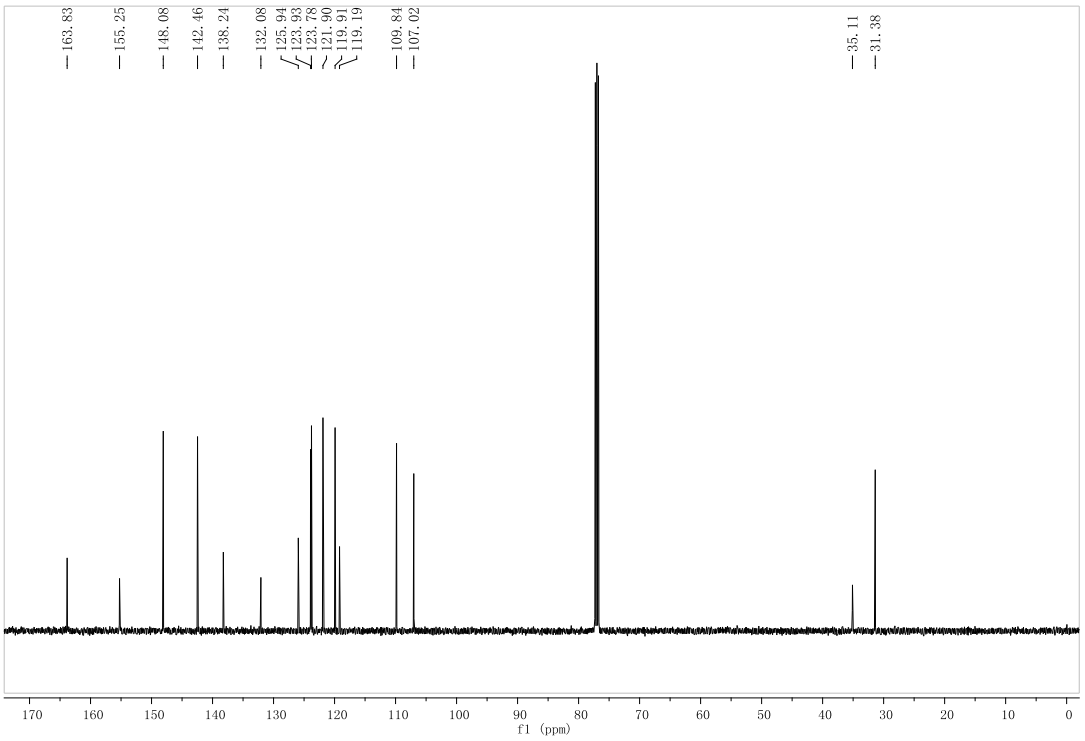


N-(3-Bromopyridin-2-yl)-N,1-dimethyl-1H-indole-2-carboxamide **1w**

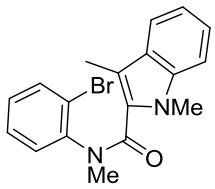


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 54% yield, m.p. 118-121 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.25-7.29 (m, 1H), 7.03-7.09 (m, 2H), 6.08 (s, 1H), 4.01 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 155.3, 148.1, 142.5, 138.2, 132.1, 125.9, 123.9 (d, *J* = 18.7 Hz), 121.9, 119.9, 119.2, 109.8, 107.0, 35.1, 31.4. HRMS *m/z* (ESI+): Calculated for $C_{16}H_{15}BrN_3O$ ($[M+H]^+$): 344.0393, found 344.0397.

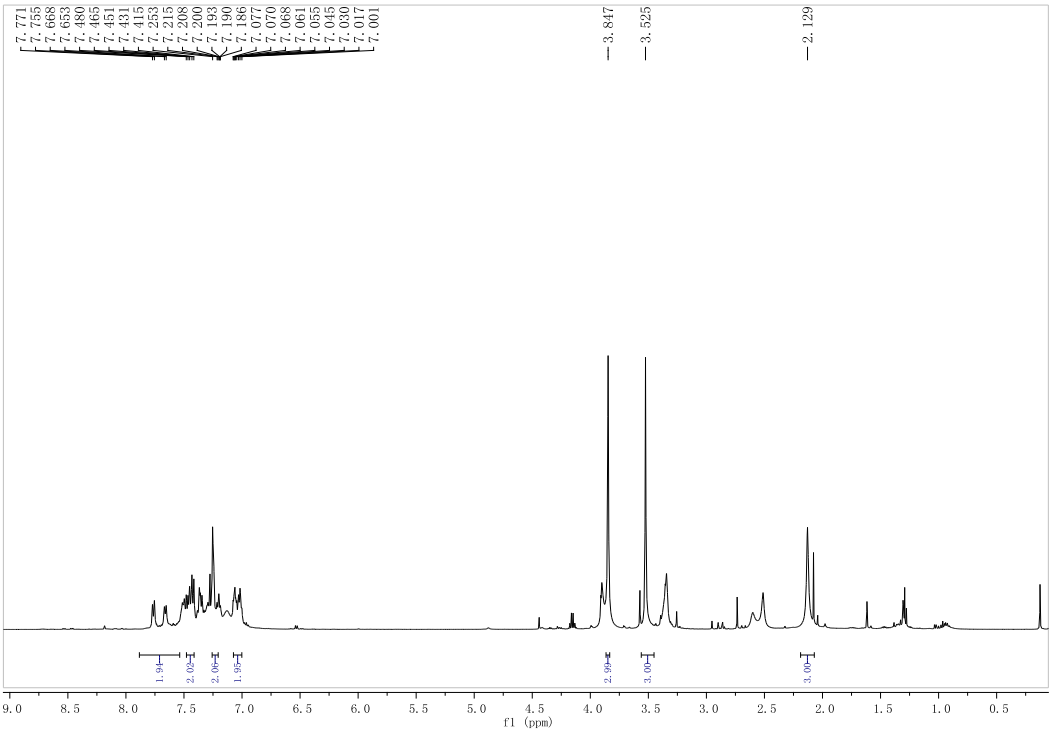

8.500
8.496
8.490
8.487
7.782
7.779
7.766
7.763
7.417
7.401
7.350
7.334
7.268
7.266
7.082
7.073
7.066
7.057
7.045
6.047
4.009
3.512
1.00
1.00
1.00
1.00
1.00
2.01
1.00
3.00
3.00
f1 (ppm)

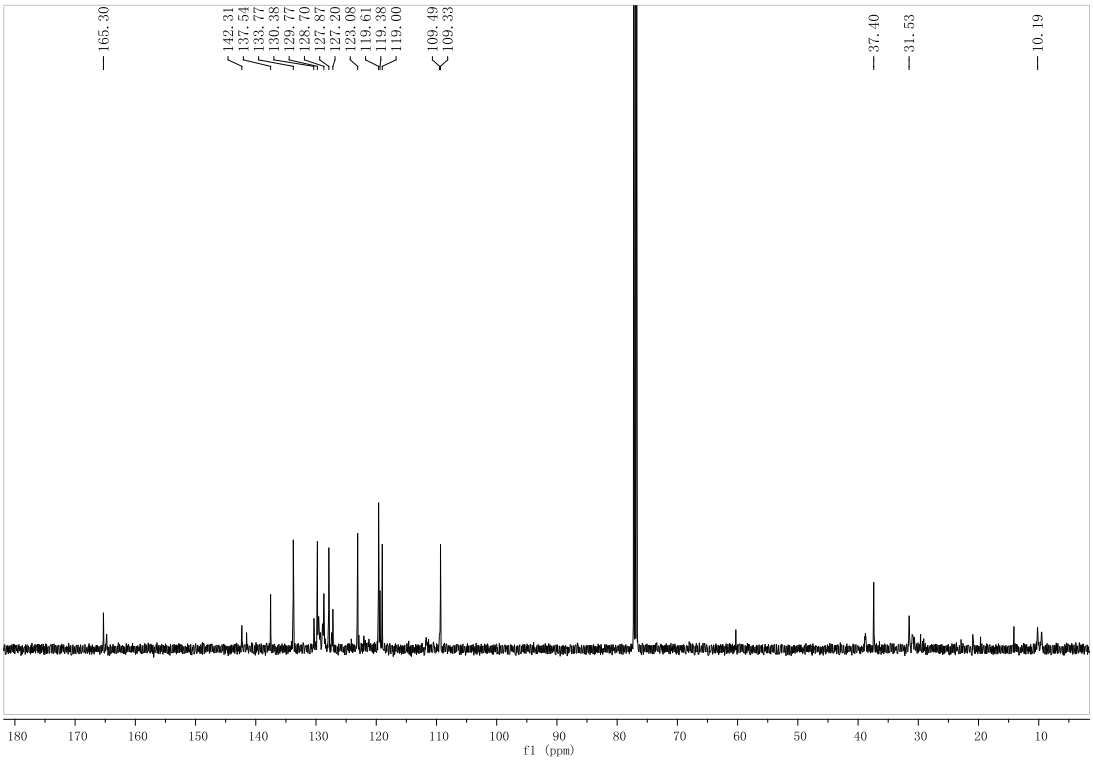

163.83
155.25
148.08
142.46
138.24
132.08
125.94
123.93
123.78
121.90
119.91
119.19
109.84
107.02
35.11
31.38
f1 (ppm)

N-(2-bromophenyl)-N,1,3-trimethyl-1H-indole-2-carboxamide **1x**

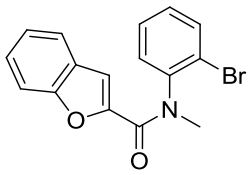


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, 46% yield from ethyl 1,3-dimethyl-1H-indole-2-carboxylate, m.p. 124-127 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 51.0, 8.0 Hz, 2H), 7.44 (dd, *J* = 17.5, 7.5 Hz, 2H), 7.21-7.26 (m, 2H), 7.00-7.07 (m, 2H), 3.85 (s, 3H), 3.52 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 142.3, 137.6, 133.8, 130.4, 129.8, 128.7, 127.9, 127.2, 123.1, 119.6, 119.4, 119.0, 109.5, 109.4, 37.4, 31.6, 10.2. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}BrN_2O$ ($[M+H]^+$): 357.0594, found 357.0614.

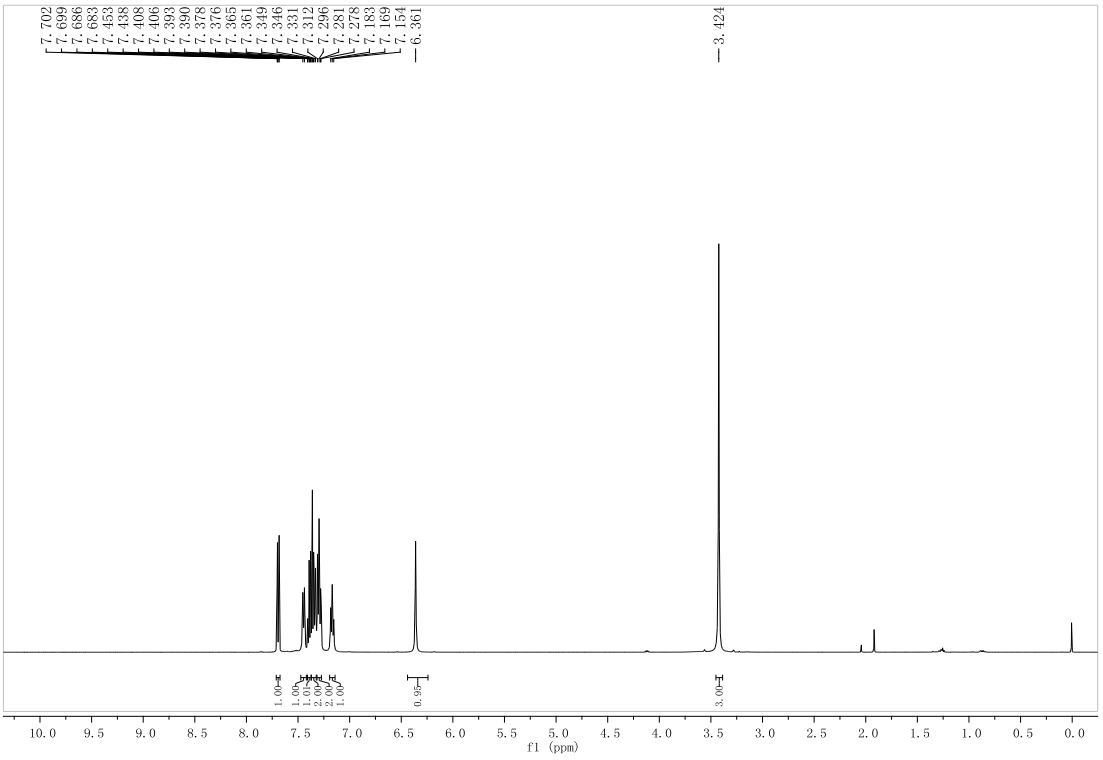


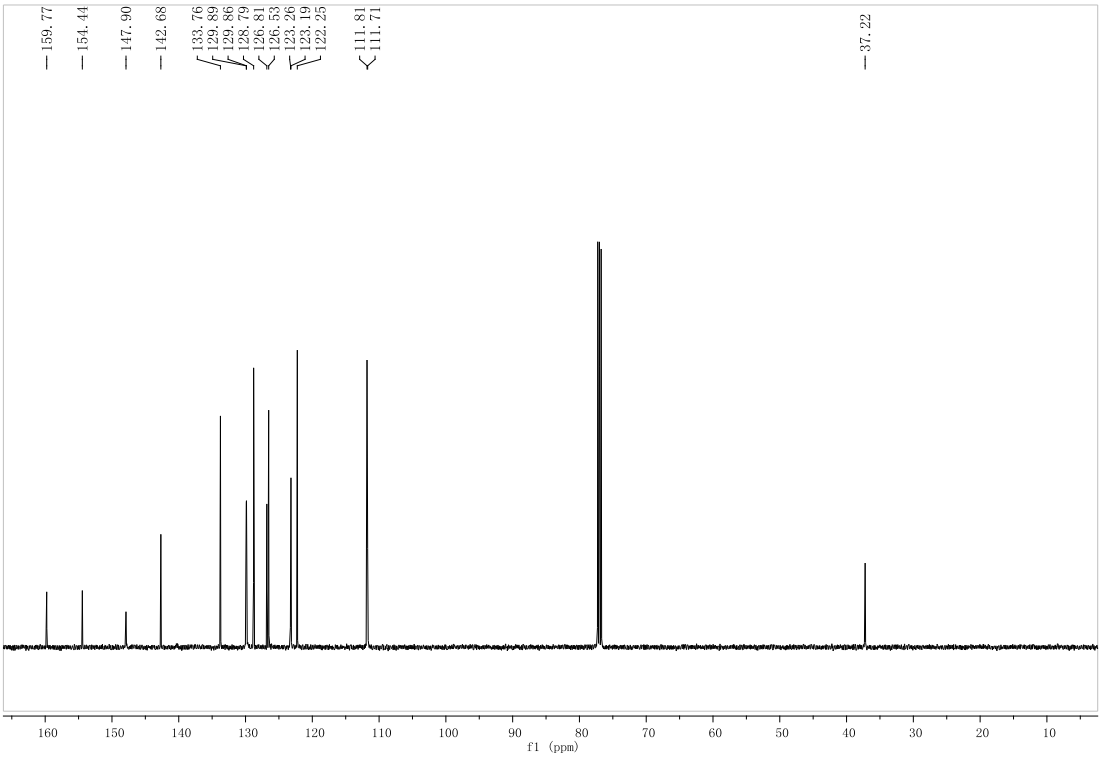


N-(2-bromophenyl)-N-methylbenzofuran-2-carboxamide **6a**

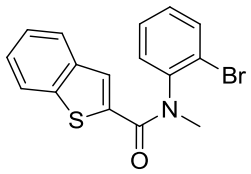


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 65% yield from ethyl benzofuran-2-carboxylate, m.p. 118-121 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.37-7.41 (m, 1H), 7.32-7.37 (m, 2H), 7.29 (dd, *J* = 15.5, 8.0 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 6.36 (s, 1H), 3.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 154.4, 147.9, 142.7, 133.8, 129.9 (d, *J* = 3.8 Hz), 128.8, 126.8, 126.5, 123.2 (d, *J* = 10.0 Hz), 122.3, 111.8 (d, *J* = 12.5 Hz), 37.2. HRMS *m/z* (ESI+): Calculated for $C_{16}H_{12}BrNO_3$ ($[M+H]^+$): 330.0124, found 330.119.

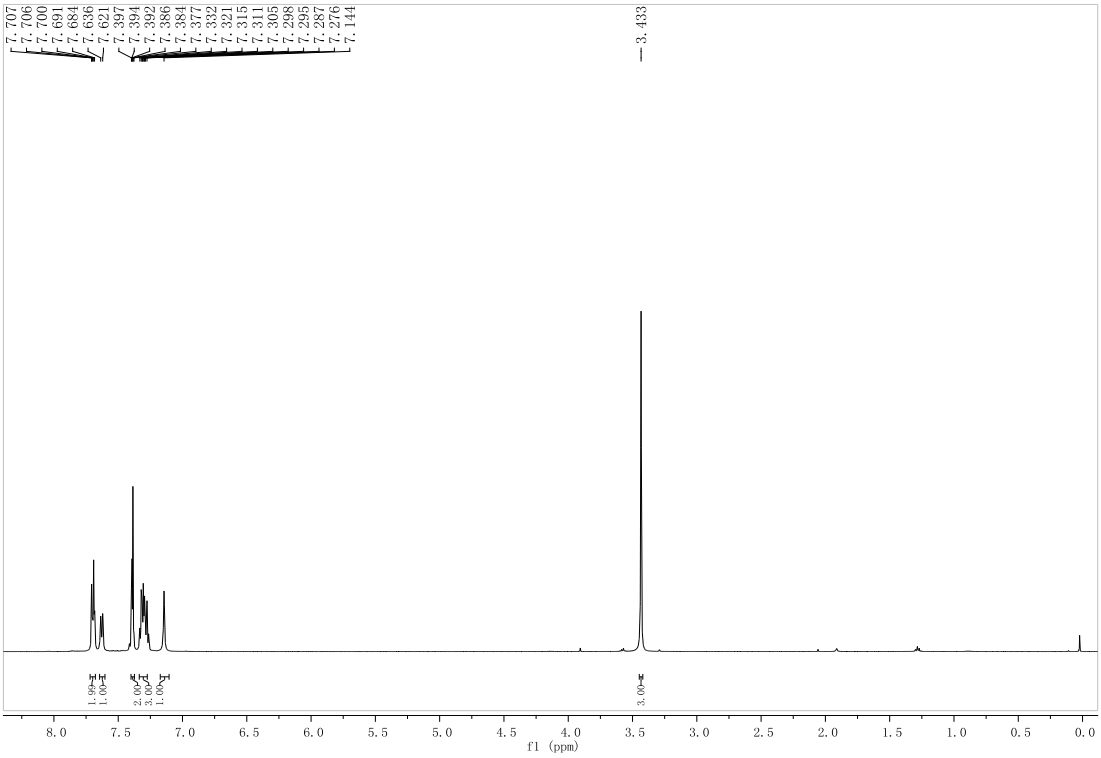

7.702
7.699
7.686
7.683
7.453
7.438
7.408
7.406
7.393
7.390
7.378
7.376
7.365
7.361
7.349
7.346
7.331
7.312
7.296
7.281
7.278
7.183
7.169
7.154
6.361
3.424
1.04
1.00
1.05
2.04
1.00
0.95
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

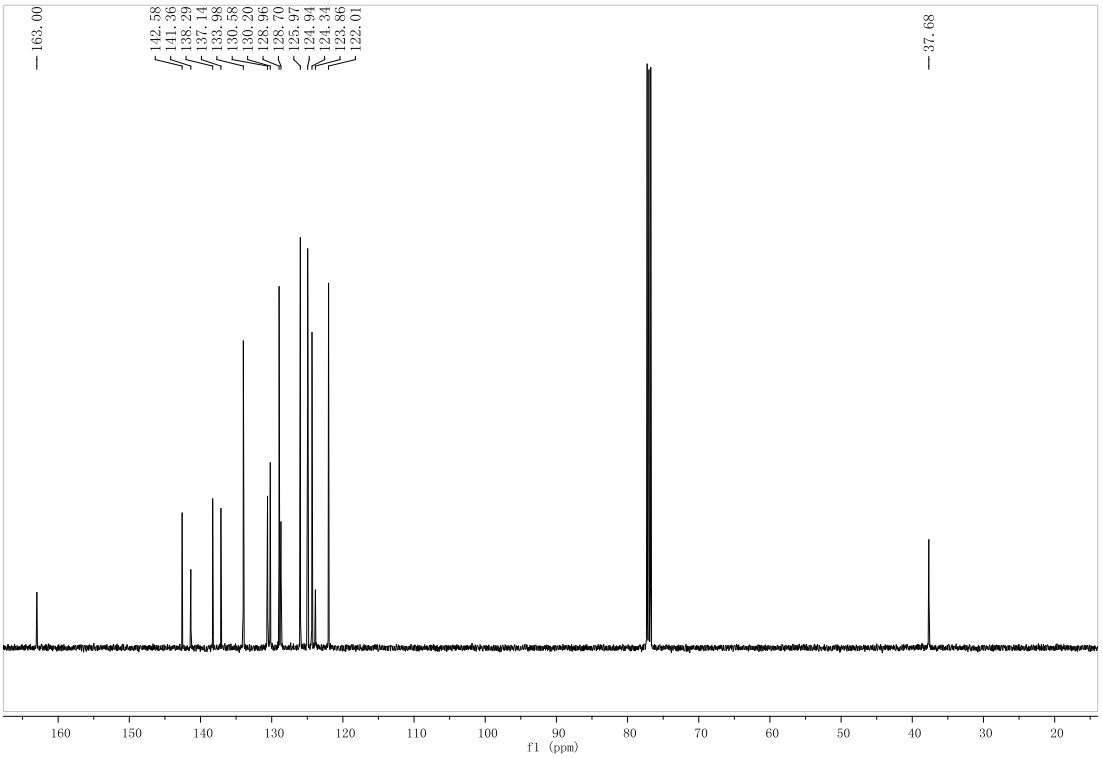

159.77
154.44
147.90
142.68
133.76
129.89
129.86
128.79
126.81
126.53
123.26
123.19
122.25
111.81
111.71
37.22
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

N-(2-bromophenyl)-N-methylbenzo[b]thiophene-2-carboxamide **6b**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55% yield from ethyl benzo[b]thiophene-2-carboxylate, m.p. 118-121 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.72 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.37-7.40 (m, 2H), 7.27-7.34 (m, 3H), 7.14 (s, 1H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 142.6, 141.4, 138.3, 137.1, 134.0, 130.6, 130.2, 129.0 (s), 128.7, 126.0, 124.9, 124.3, 123.9, 122.0, 37.7. HRMS *m/z* (ESI+): Calculated for $C_{16}H_{12}BrNOS$ ($[M+H]^+$): 345.9896, found 345.9890.

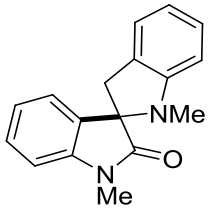




3. General procedure for Pd-catalyzed dearomative reductive-Heck reaction

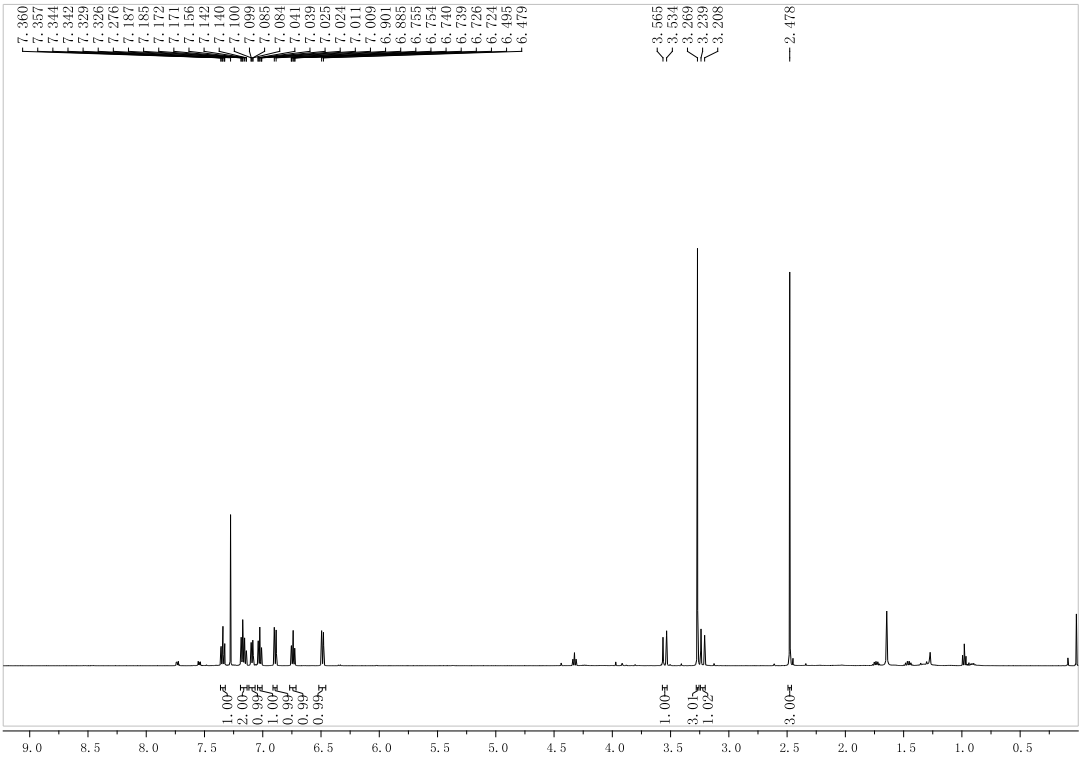
To a dried Schlenk tube was added C2-substitued indole **1** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), $PCy_3 \cdot HBF_4$ (0.02 mmol) and HCO_2Na (0.6 mmol) under N_2, 2.0 mL MeOH was then introduced via syringe. The mixture was stirred at 100 ^oC (oil bath) until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting withethyl/petroleum ether 1:10 (v/v) to afford the products. **2a** and **6a** are known compounds.[1]

1,1'-Dimethyl-2,3'-spirobi[indolin]-2'-one **2a**

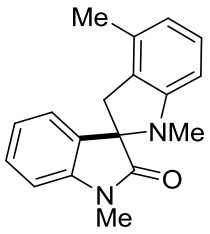


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); 94% yield, ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (td, *J* = 8.0, 1.5 Hz, 1H), 7.14-7.19 (m, 2H), 7.09 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.02 (td, *J* = 8.0, 1.0 Hz, 1H), 6.89

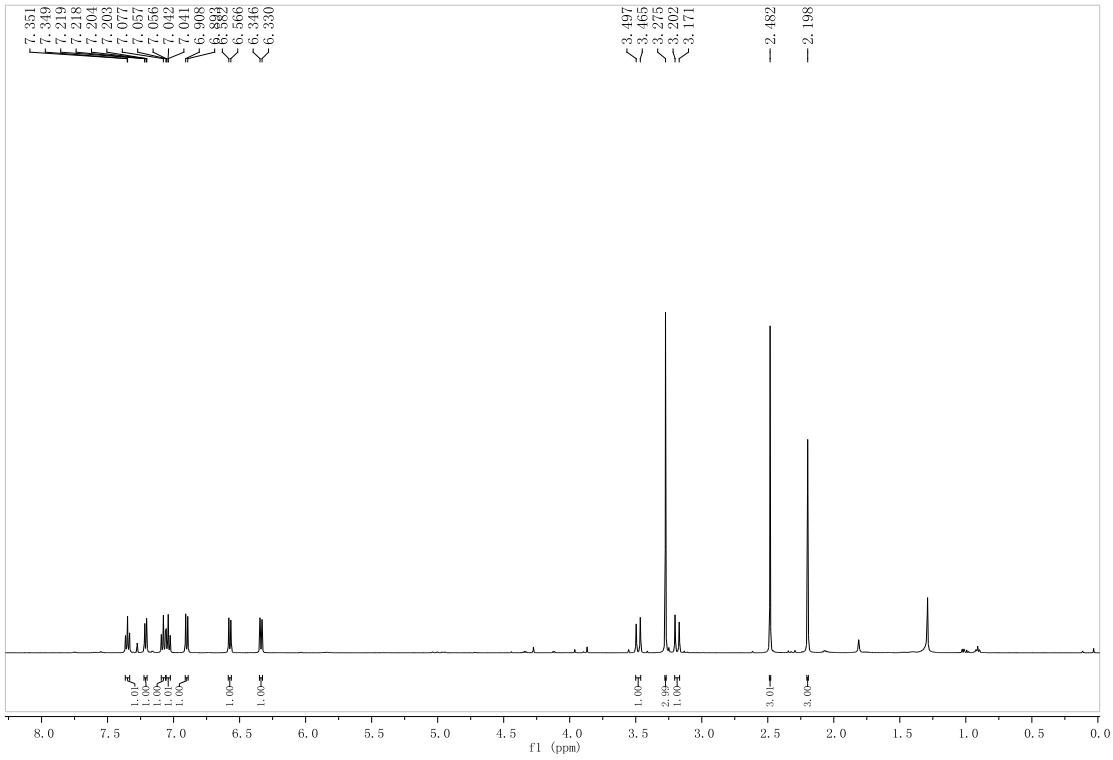
(d, *J* = 8.0 Hz, 1H), 6.74 (td, *J* = 7.5, 0.5 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.55 (d, *J* = 15.5 Hz, 1H), 3.27 (s, 3H), 3.22 (d, *J* = 15.5 Hz, 1H), 2.48 (s, 3H).

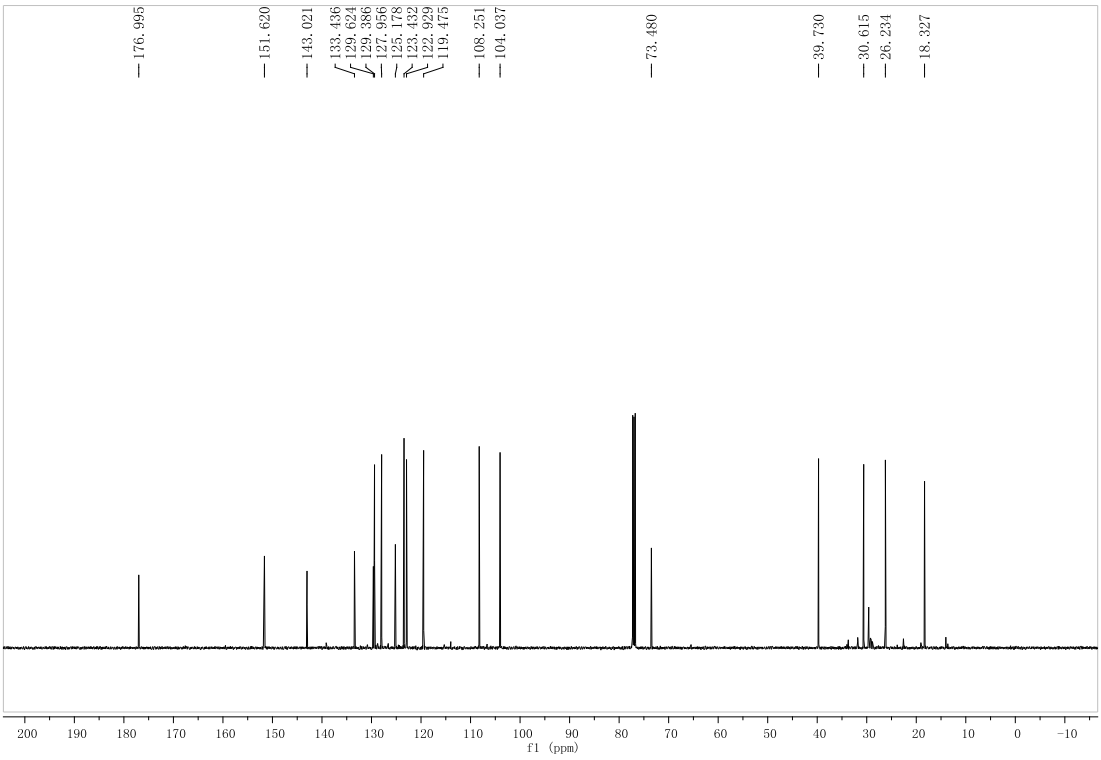


1,1',4'-Trimethyl-2,3'-spirobi[indolin]-2-one **2b**

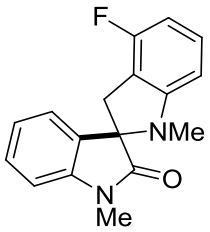


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 90% yield, m.p. 130-134 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.37 (m, 1H), 7.21 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.02-7.07 (m, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 3.48 (d, *J* = 16.0 Hz, 1H), 3.27 (s, 3H), 3.19 (d, *J* = 15.5 Hz, 1H), 2.48 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 151.6, 143.0, 133.4, 129.6, 129.4, 128.0, 125.2, 123.4, 122.9, 119.5, 108.3, 104.0, 73.5, 39.7, 30.6, 26.2, 18.3. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{19}N_2O$ ($[M+H]^+$): 279.1492, found 279.1492.

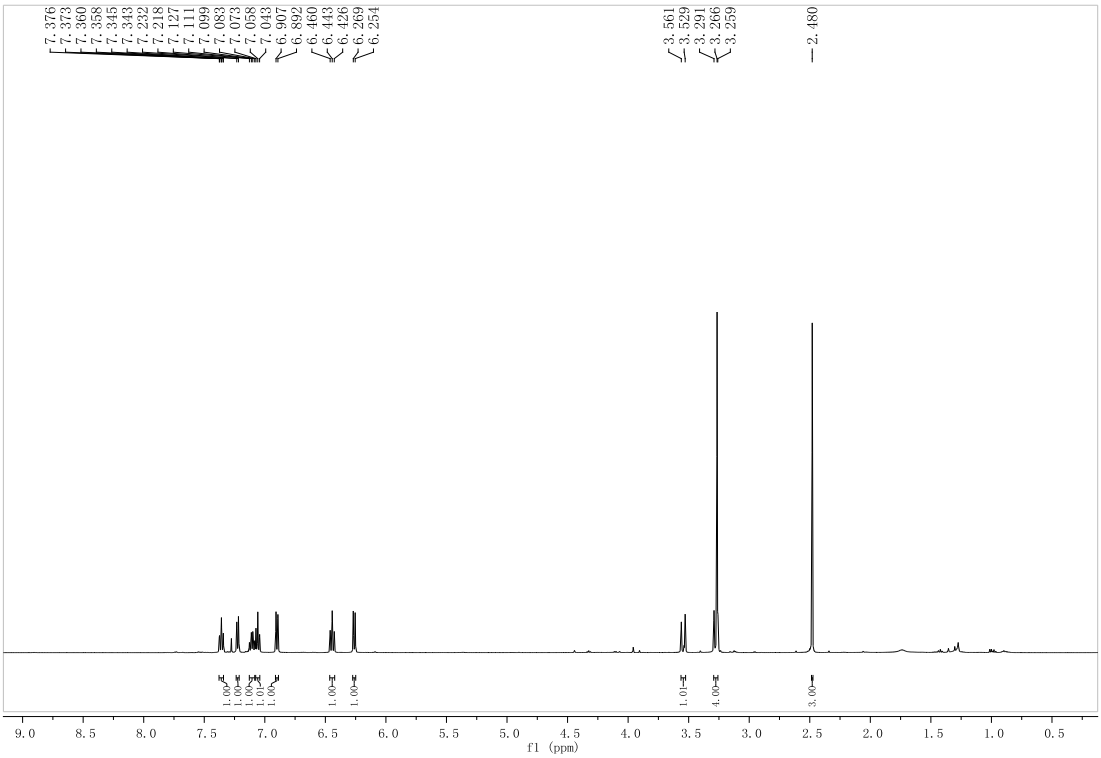

7.351
7.349
7.219
7.218
7.204
7.203
7.077
7.057
7.056
7.042
7.041
6.908
6.566
6.346
6.330
3.497
3.465
3.275
3.202
3.171
2.482
2.198
f1 (ppm)

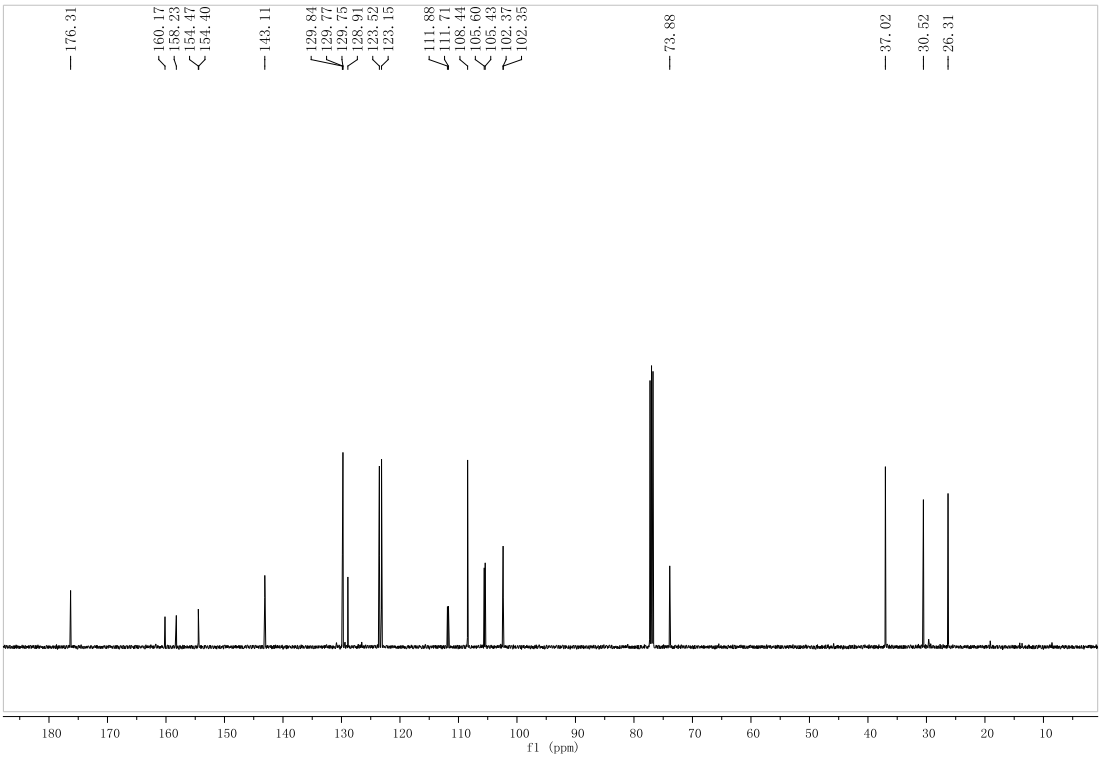

176.995
151.620
143.021
133.436
129.624
129.386
127.956
125.178
123.432
122.929
119.475
108.251
104.037
73.480
39.730
30.615
26.234
18.327
f1 (ppm)

4-Fluoro-1,1'-dimethyl-2,3'-spirobi[indolin]-2'-one **2c**

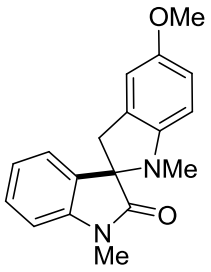


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 91% yield, m.p. 157-161 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (td, *J* = 8.0, 1.5 Hz, 1H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.11 (dd, *J* = 14.0, 8.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.44 (t, *J* = 8.5 Hz, 1H), 6.26 (d, *J* = 7.5 Hz, 1H), 3.54 (d, *J* = 16.0 Hz, 1H), 3.27 (t, *J* = 12.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 159.2 (d, *J* = 243.9 Hz), 154.4 (d, *J* = 8.9 Hz), 143.1, 129.8, 129.7 (d, *J* = 2.5 Hz), 128.9, 123.5, 123.2, 111.8 (d, *J* = 21.3 Hz), 108.4, 105.5 (d, *J* = 21.1 Hz), 102.4 (d, *J* = 2.5 Hz), 73.9, 37.0, 30.5, 26.3. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{16}FN_2O$ ($[M+H]^+$): 283.1241, found 283.1236.

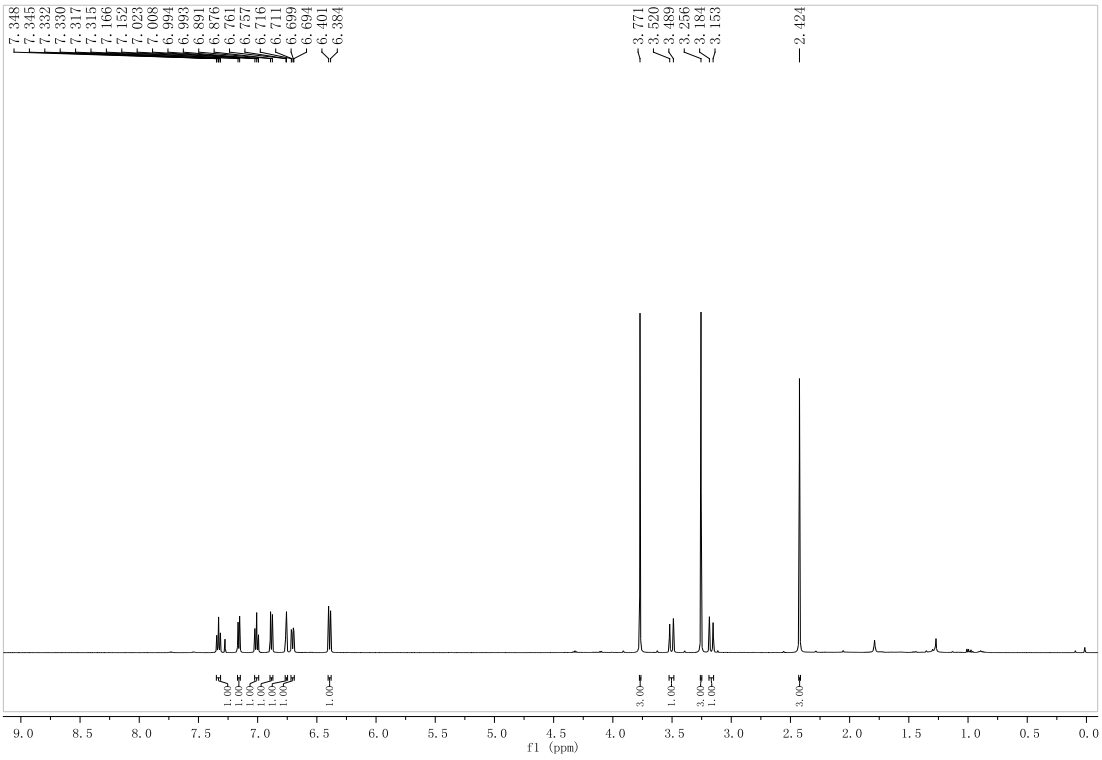




5'-Methoxy-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2d**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 90% yield, m.p. 150-155 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (td, *J* = 8.0, 1.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.00 (dd, *J* = 11.0, 4.0 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 2.0 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.39 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 3H), 3.50 (d, *J* = 15.5 Hz, 1H), 3.26 (s, 3H), 3.17 (d, *J* = 15.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 153.1, 146.1, 143.0, 129.4, 129.1, 128.4, 123.4, 122.8, 112.0 (d, *J* = 1.3 Hz), 108.3, 106.8, 77.3, 77.0, 76.8, 74.2, 55.9, 40.7, 31.3, 26.2. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{19}N_2O_2$ ($[M+H]^+$): 295.1441, found 295.1466.


7.348
7.345
7.332
7.330
7.317
7.315
7.166
7.152
7.023
7.008
6.994
6.993
6.891
6.876
6.761
6.757
6.716
6.711
6.699
6.694
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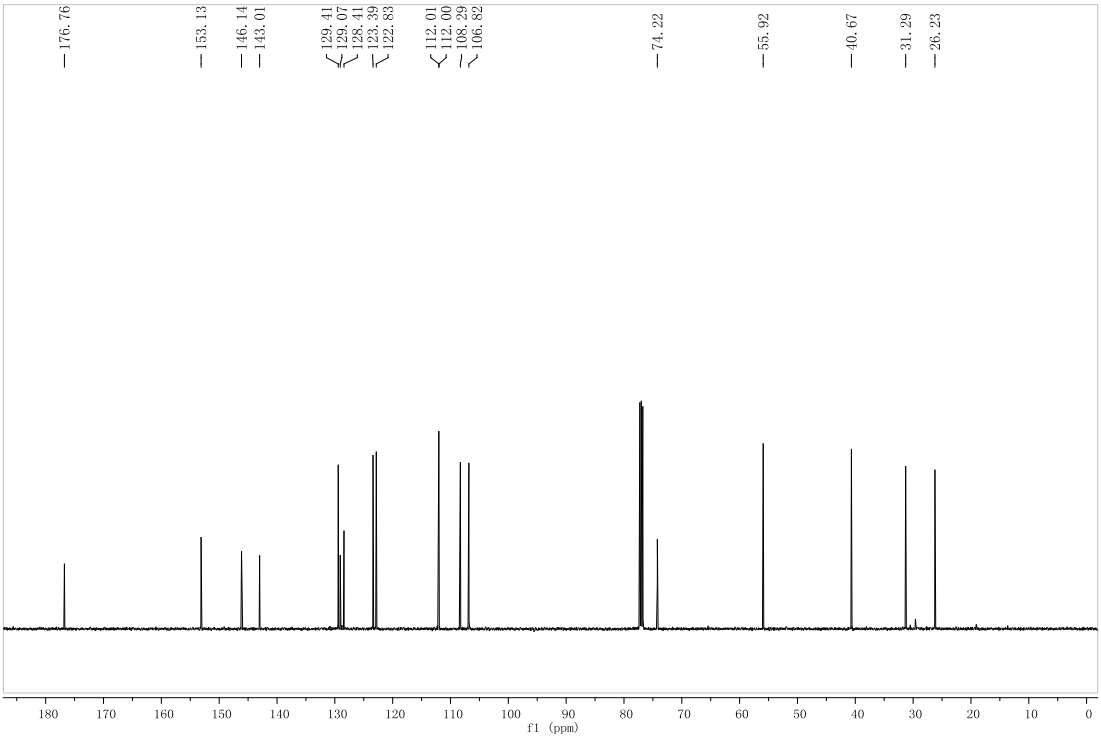
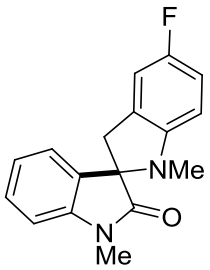
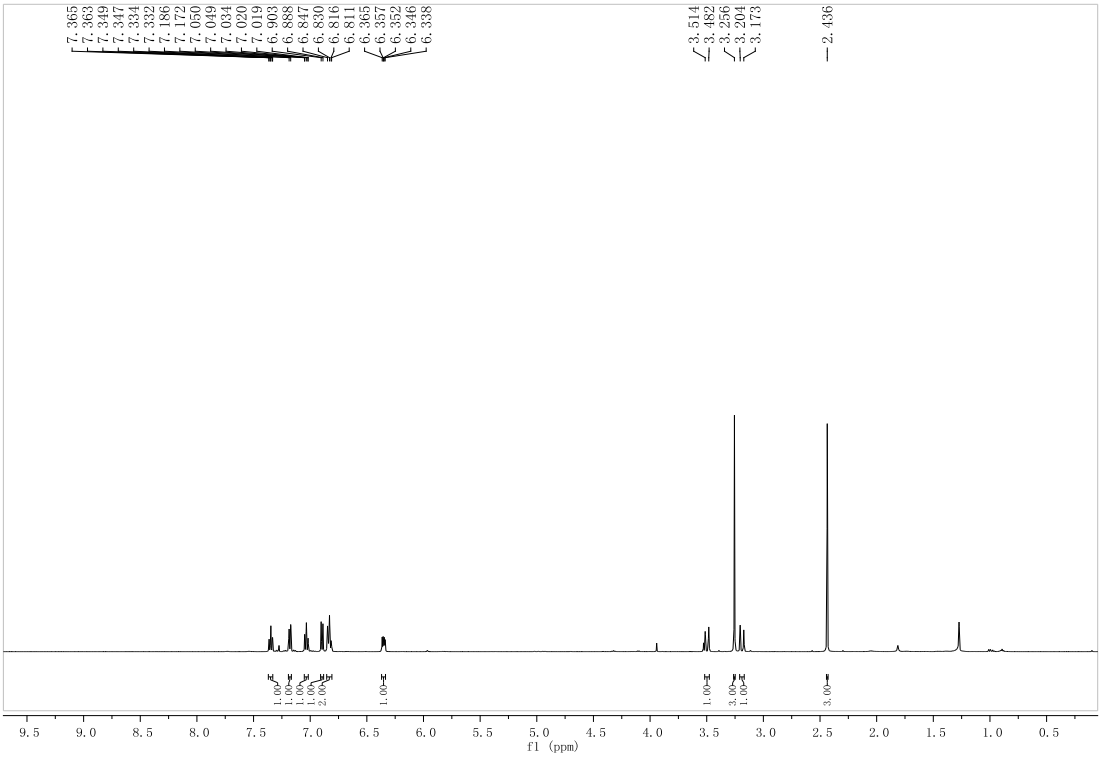
6.384
3.771
3.520
3.489
3.256
3.184
3.153
2.424
f1 (ppm)

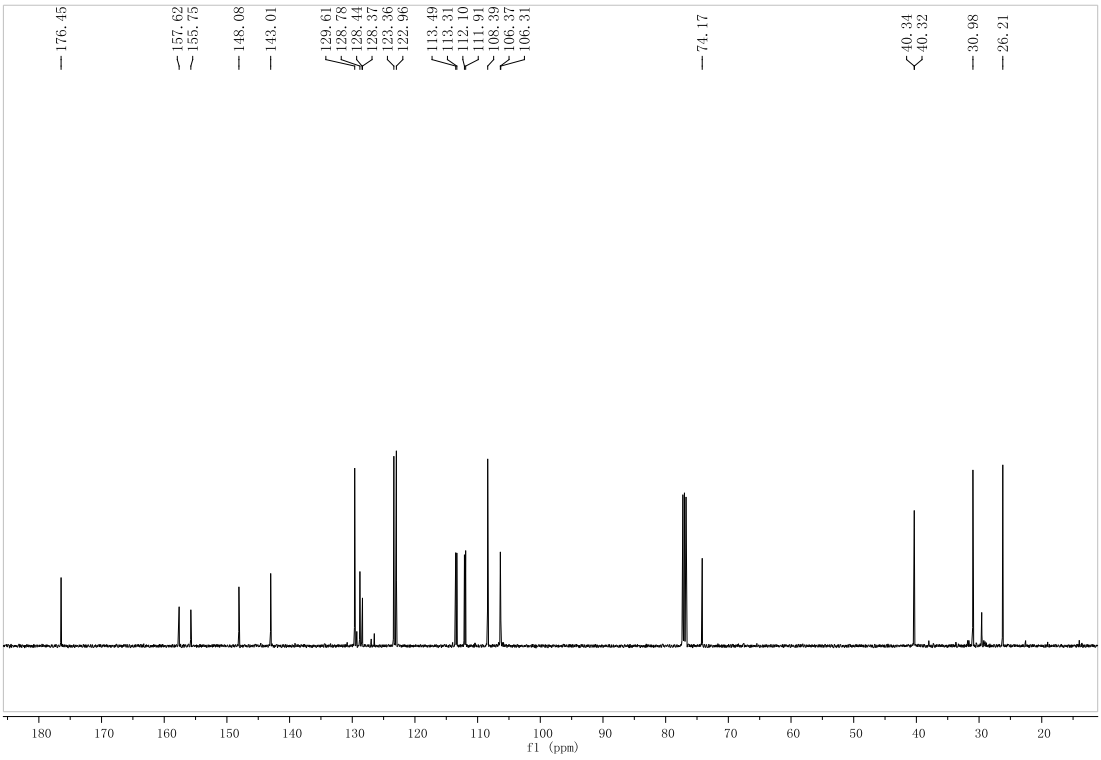

176.76
153.13
146.14
143.01
129.41
129.07
128.41
123.39
122.83
112.01
112.00
108.29
106.82
74.22
55.92
40.67
31.29
26.23
f1 (ppm)

5'-Fluoro-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2e**

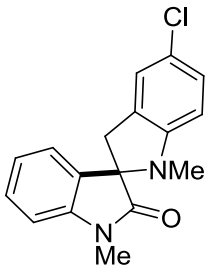


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 89% yield, m.p. 140-142 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 8.0, 1.0 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 7.01-7.05 (m, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.81-6.85 (m, 2H), 6.33-6.37 (m, 1H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.26 (s, 3H), 3.19 (d, *J* = 16.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4, 157.6, 155.8, 148.1, 143.0, 129.6, 128.8, 128.4 (d, *J* = 8.8 Hz), 123.4, 123.0, 113.5, 113.3, 112.1, 111.9, 108.4, 106.3 (d, *J* = 7.5 Hz), 74.2, 40.3 (d, *J* = 2.5 Hz), 31.0, 26.2. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}FN_2O$ ($[M+H]^+$): 283.1241, found 283.1234.

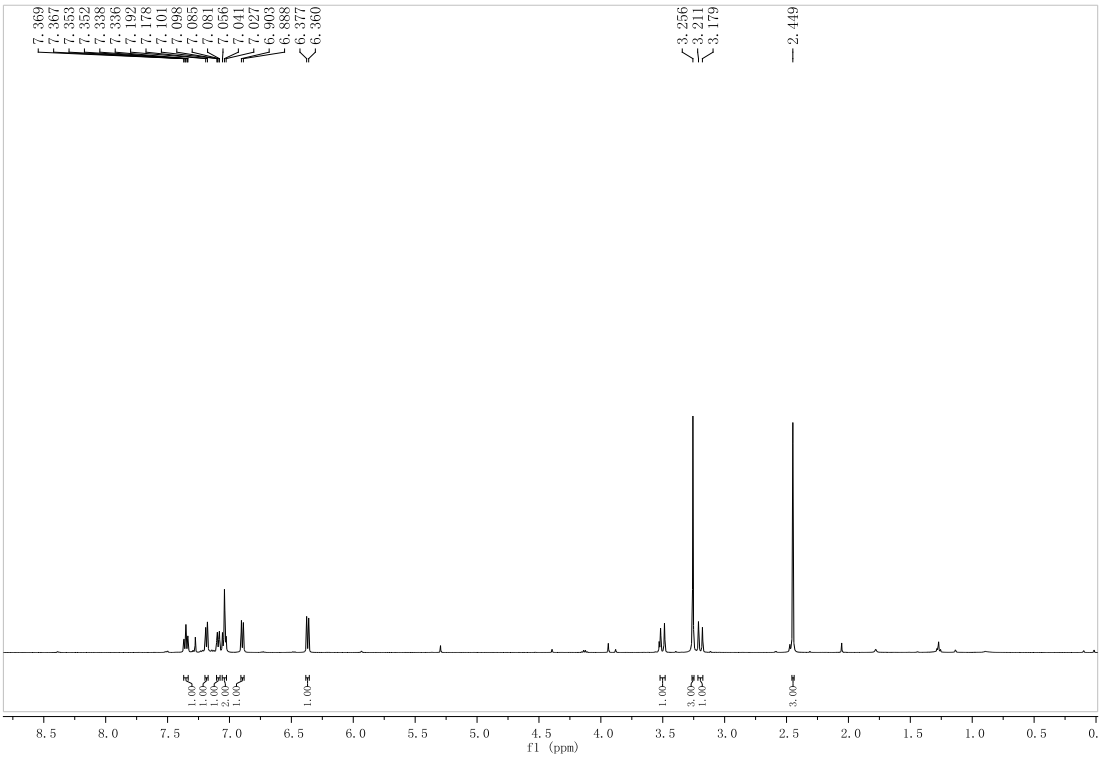




5'-Chloro-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2f**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); pale yellow solid, 90% yield, m.p. 156-158 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 8.0, 1.0 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 8.5 Hz, 1H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.26 (s, 3H), 3.20 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 150.5, 143.0, 129.7, 128.7 (d, *J* = 6.0 Hz), 128.7, 127.5, 124.3, 123.4, 123.0, 122.6, 108.4, 107.0, 77.3, 77.0, 76.8, 73.8, 40.2, 30.5, 26.2. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{16}ClN_2O$ ($[M+H]^+$): 299.0946, found 299.0936.


7.369
7.367
7.353
7.352
7.338
7.336
7.192
7.178
7.101
7.098
7.085
7.081
7.056
7.041
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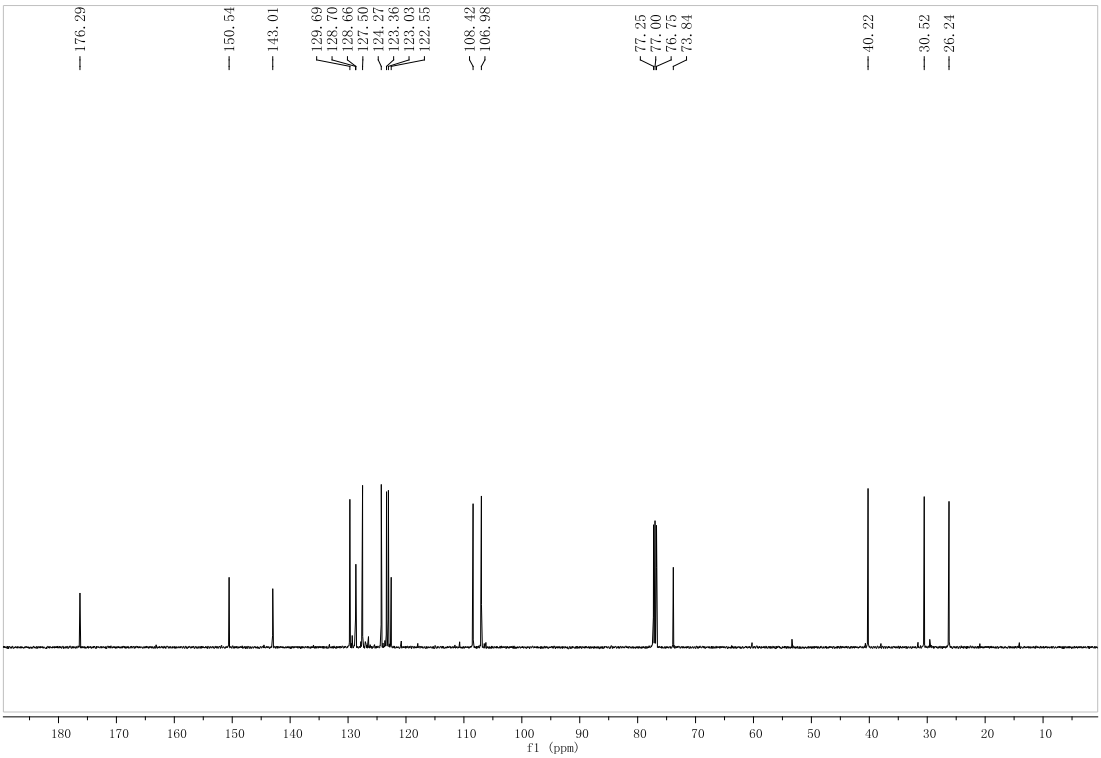
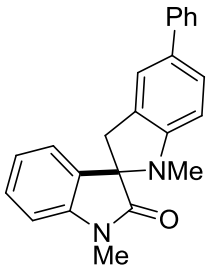
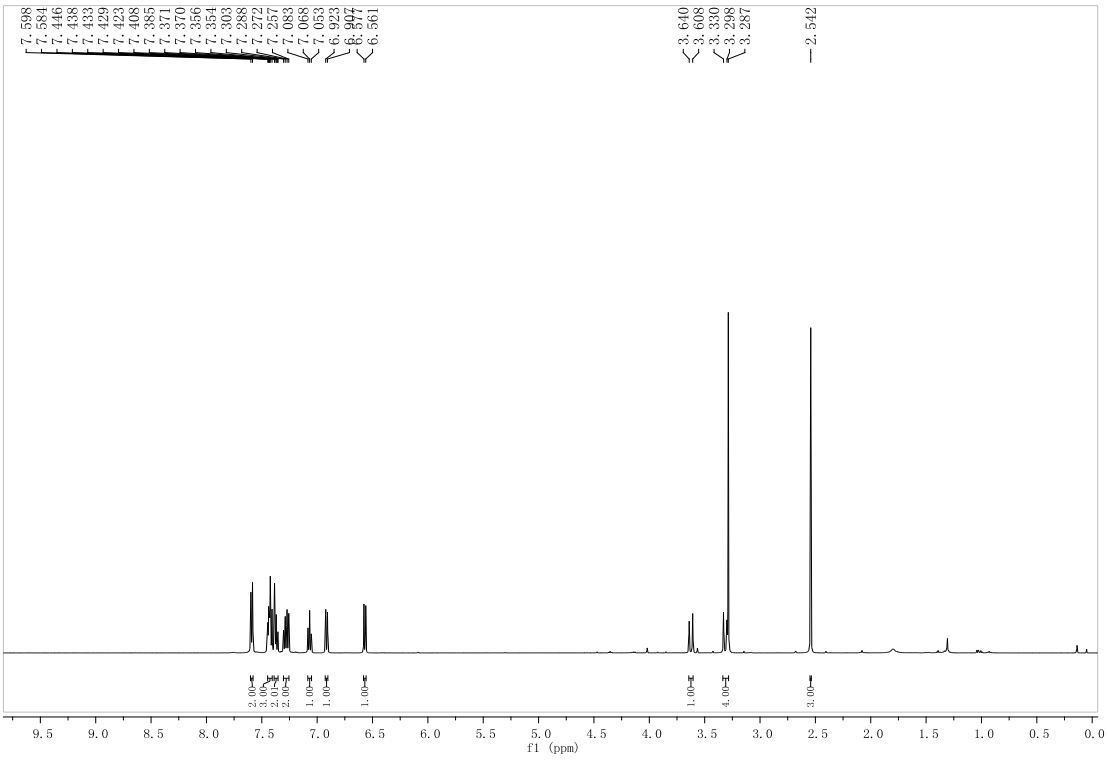
6.903
6.888
6.377
6.360
3.256
3.211
3.179
2.449
f1 (ppm)

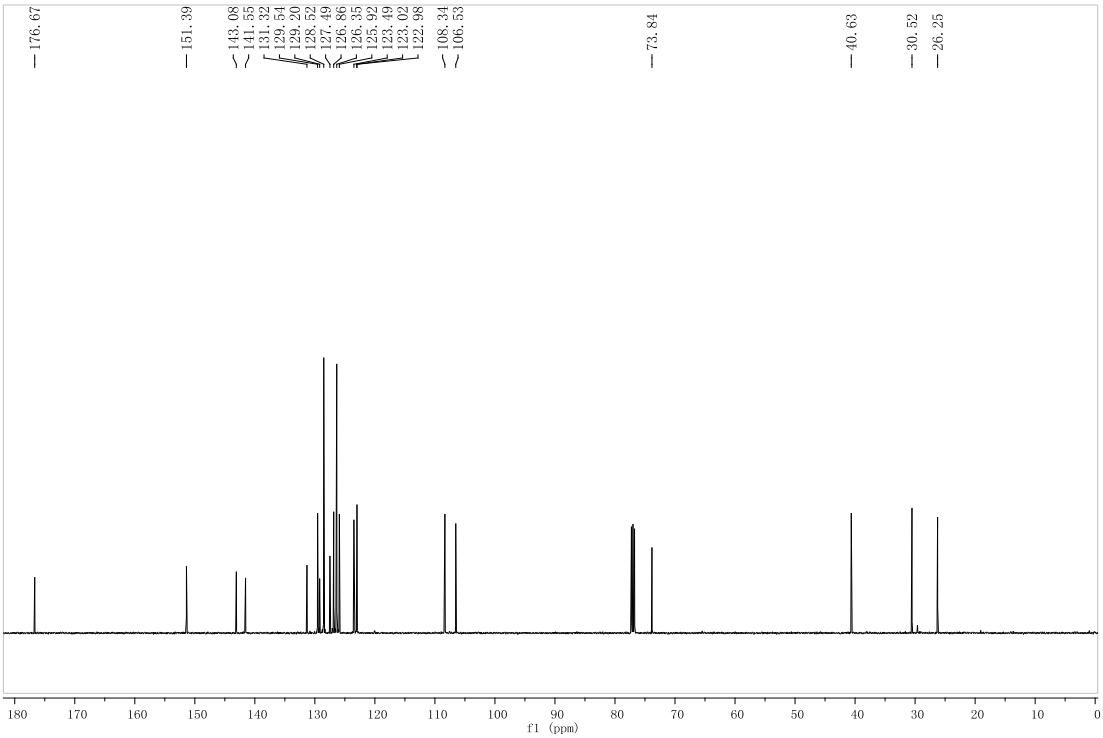

176.29
150.54
143.01
129.69
128.70
128.66
127.50
124.27
123.36
123.03
122.55
108.42
106.98
77.25
77.00
76.75
73.84
40.22
30.52
26.24
f1 (ppm)

1,1'-Dimethyl-5'-phenyl-2,3'-spirobi[indolin]-2-one **2g**

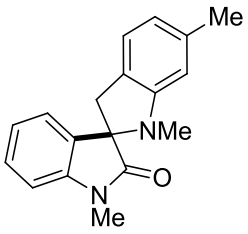


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); pale yellow solid, 78% yield, m.p. 160-164 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.40-7.45 (m, 3H), 7.35-7.39 (m, 2H), 7.28 (dd, *J* = 15.5, 7.5 Hz, 2H), 7.06 (dd, *J* = 14.5, 7.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.62 (d, *J* = 16.0 Hz, 1H), 3.28-3.33 (m, 4H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 151.4, 143.1, 141.6, 131.3, 129.5, 129.2, 128.5, 127.5, 126.9, 126.4, 125.9, 123.5, 123.0 (d, *J* = 2.8 Hz), 108.3, 106.5, 77.3, 77.0, 76.8, 73.8, 40.6, 30.5, 26.3. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{21}N_2O$ ($[M+H]^+$): 341.1648, found 341.1638.

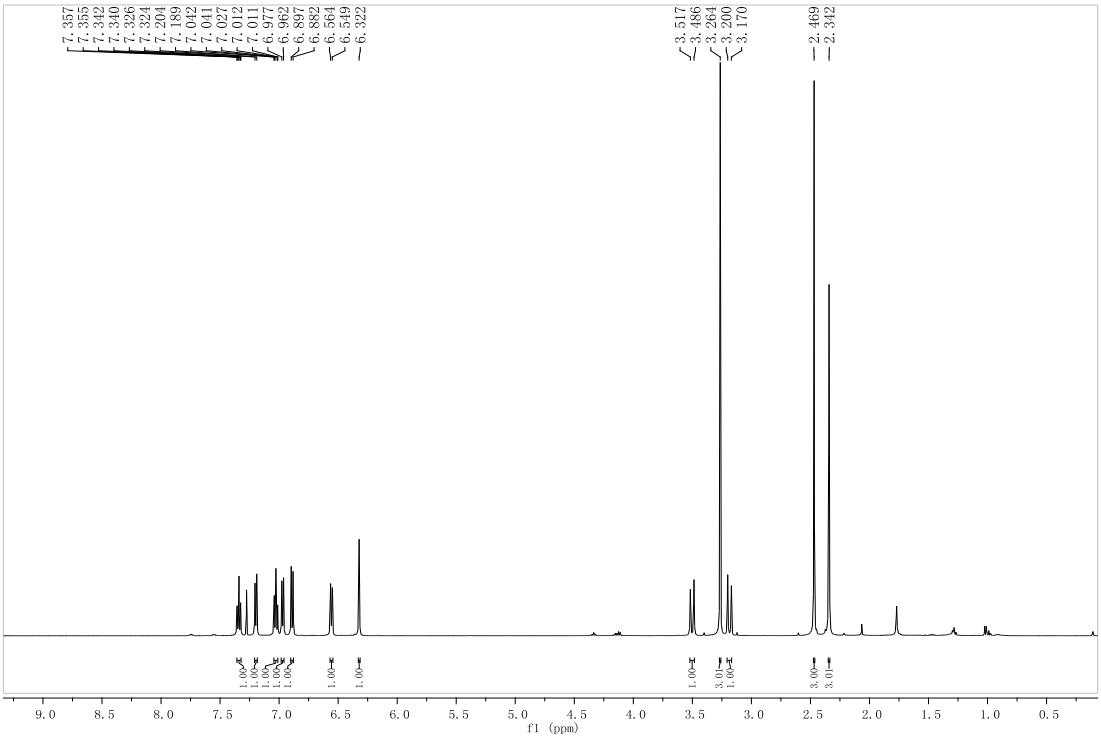


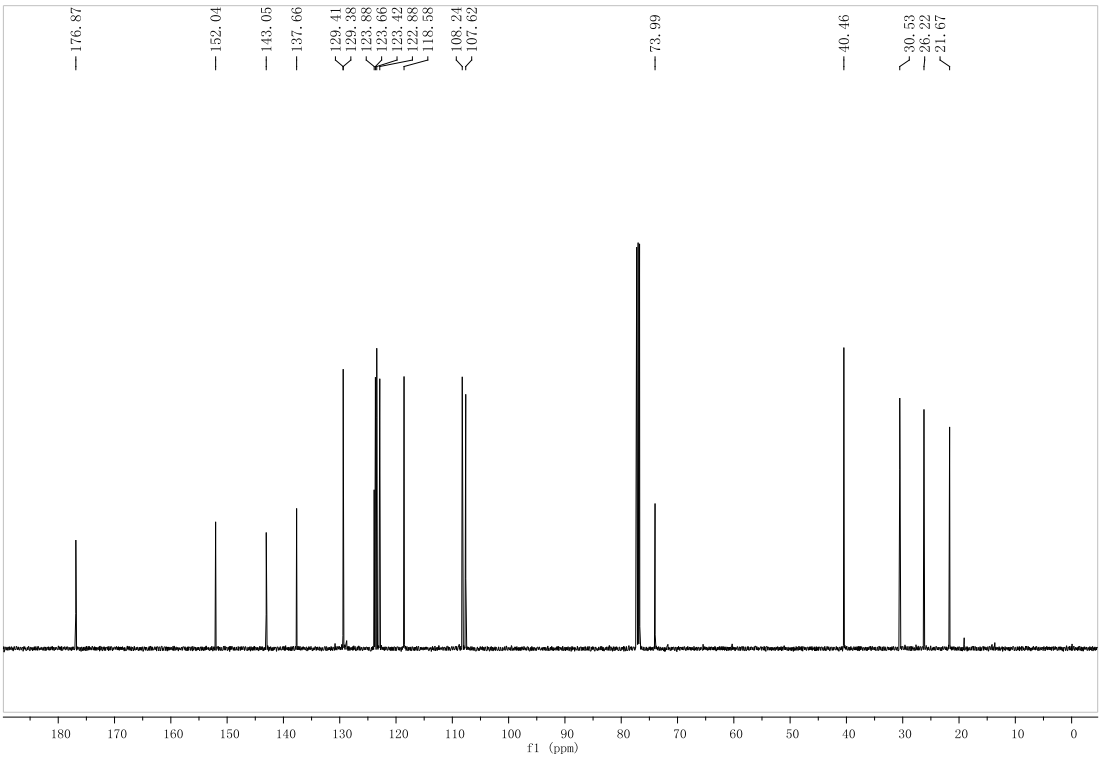


1,1',6'-Trimethyl-2,3'-spirobi[indolin]-2-one **2h**

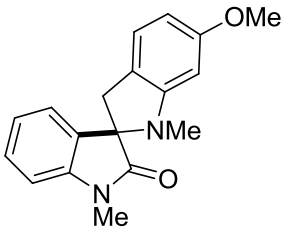


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 92% yield, m.p. 180-182 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (td, *J* = 7.5, 1.1 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.01-7.05 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 3.50 (d, *J* = 15.5 Hz, 1H), 3.26 (s, 3H), 3.18 (d, *J* = 15.5 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 152.0, 143.1, 137.7, 129.4 (d, *J* = 3.8 Hz), 123.9, 123.7, 123.4, 122.9, 118.6, 108.2, 107.6, 74.0, 40.5, 30.5, 26.2, 21.7. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{19}N_2O$ ($[M+H]^+$): 279.1492, found 279.1497.

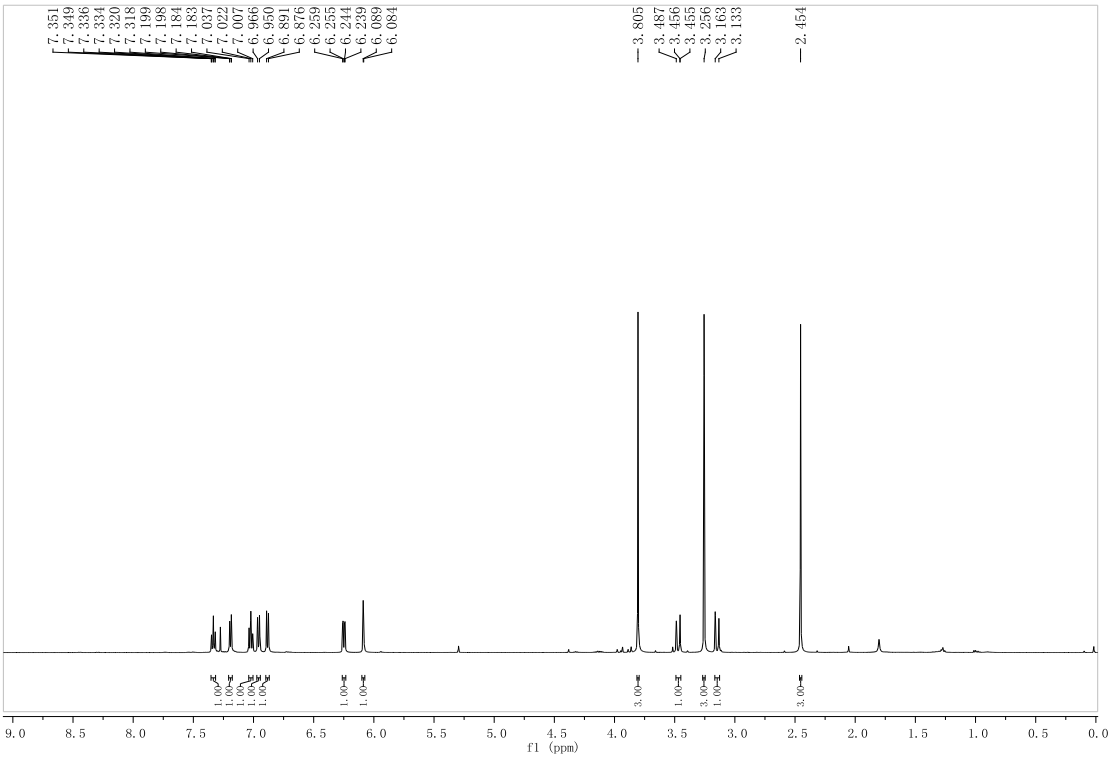

7.357
7.355
7.342
7.340
7.326
7.324
7.204
7.189
7.042
7.041
7.027
7.012
7.011
6.977
6.962
6.897
6.882
6.564
6.549
6.322
3.517
3.486
3.264
3.200
3.170
2.469
2.342
f1 (ppm)

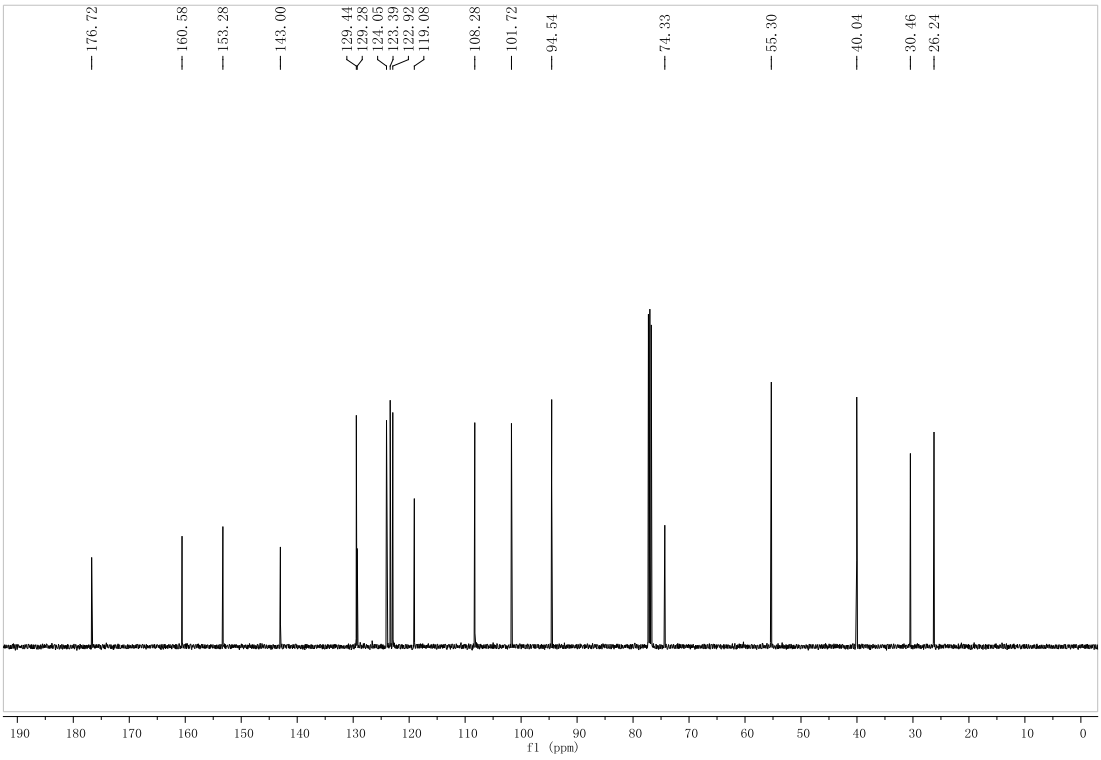

176.87
152.04
143.05
137.66
129.41
129.38
123.88
123.66
123.42
122.88
118.58
108.24
107.62
73.99
40.46
30.53
26.22
21.67
f1 (ppm)

6'-Methoxy-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2i**

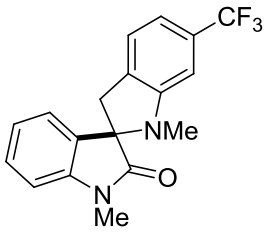


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 93% yield, m.p. 179-182 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.7, 1.0 Hz, 1H), 7.19 (dd, *J* = 7.3, 0.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.25 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.09 (d, *J* = 2.1 Hz, 1H), 3.81 (s, 3H), 3.45-3.49 (m, 1H), 3.26 (s, 3H), 3.15 (d, *J* = 15.3 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 160.6, 153.3, 143.0, 129.4, 129.3, 124.1, 123.4, 122.9, 119.1, 108.3, 101.7, 94.5, 74.3, 55.3, 40.0, 30.5, 26.2. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{19}BrN_2O_2$ ($[M+H]^+$): 295.1441, found 295.1434.

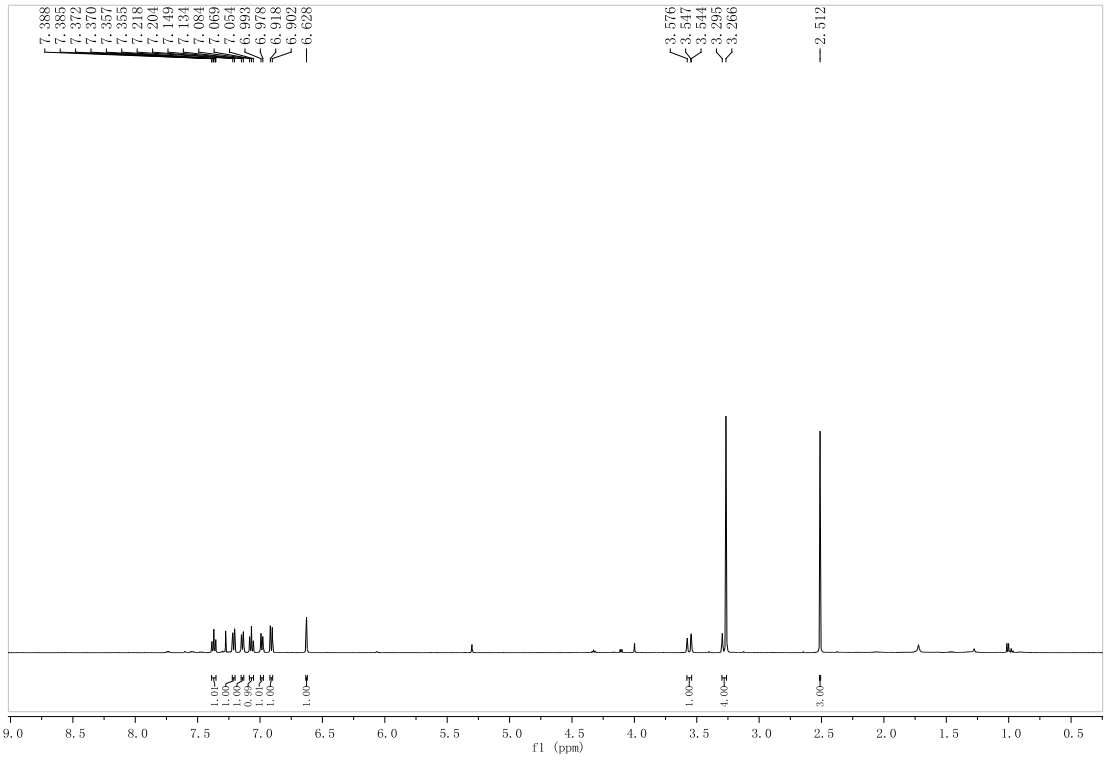


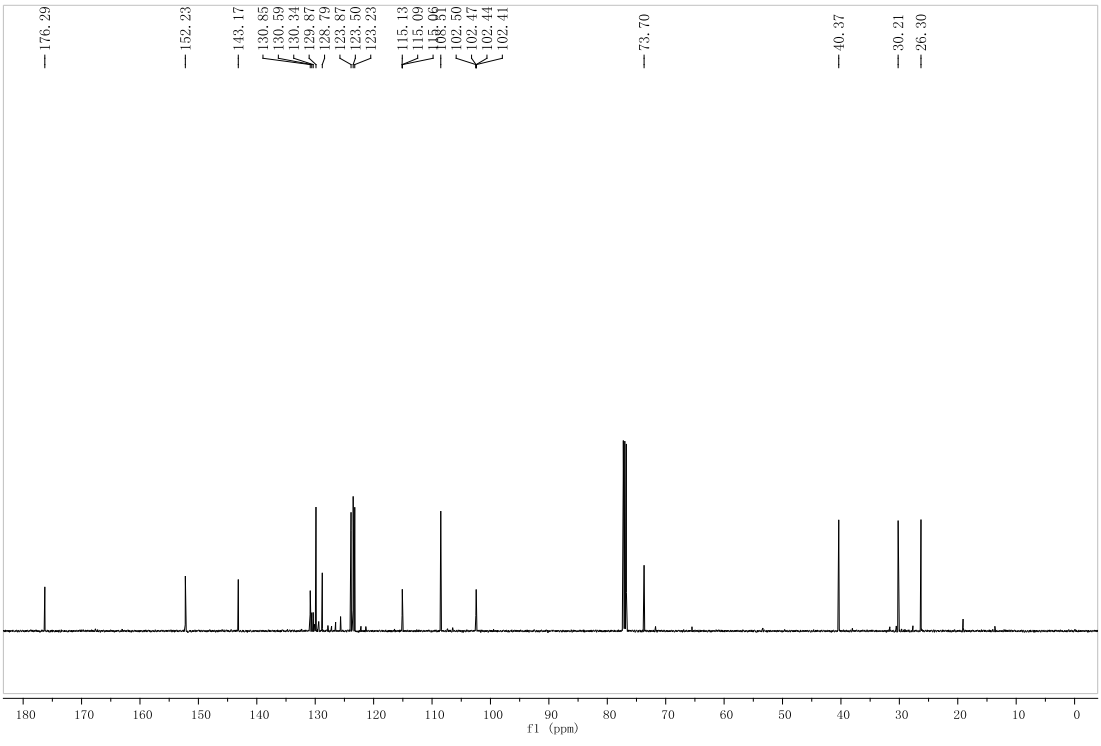


1,1'-Dimethyl-6'-(trifluoromethyl)-2,3'-spirobi[indolin]-2-one **2j**

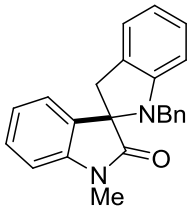


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 85% yield, m.p. 146-150 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (td, *J* = 8.0, 1.5 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 3.54-3.58 (m, 1H), 3.28 (d, *J* = 15.5 Hz, 4H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 152.2, 143.2, 130.9, 130.6, 130.3, 129.9, 128.8, 123.9, 123.5, 123.2, 115.1 (q, *J* = 5.0 Hz), 108.5, 102.5 (q, *J* = 3.8 Hz), 73.7, 40.4, 30.2, 26.3. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}BrF_3N_2O$ ($[M+H]^+$): 411.0314, found 411.0304.

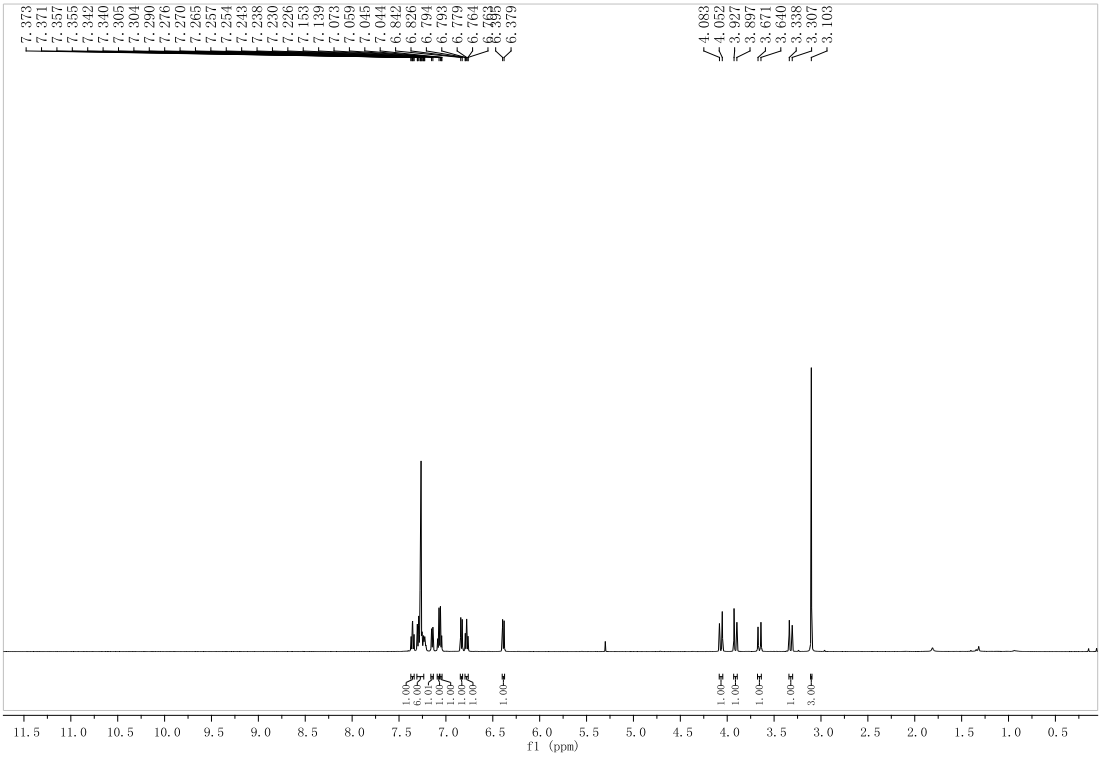

7.388
7.385
7.372
7.370
7.357
7.355
7.218
7.204
7.149
7.134
7.084
7.069
7.054
6.993
6.978
6.918
6.902
6.628
3.576
3.547
3.544
3.295
3.266
2.512
1.01
1.06
1.06
1.06
1.01
1.06
1.00
1.00
4.00
3.00
f1 (ppm)

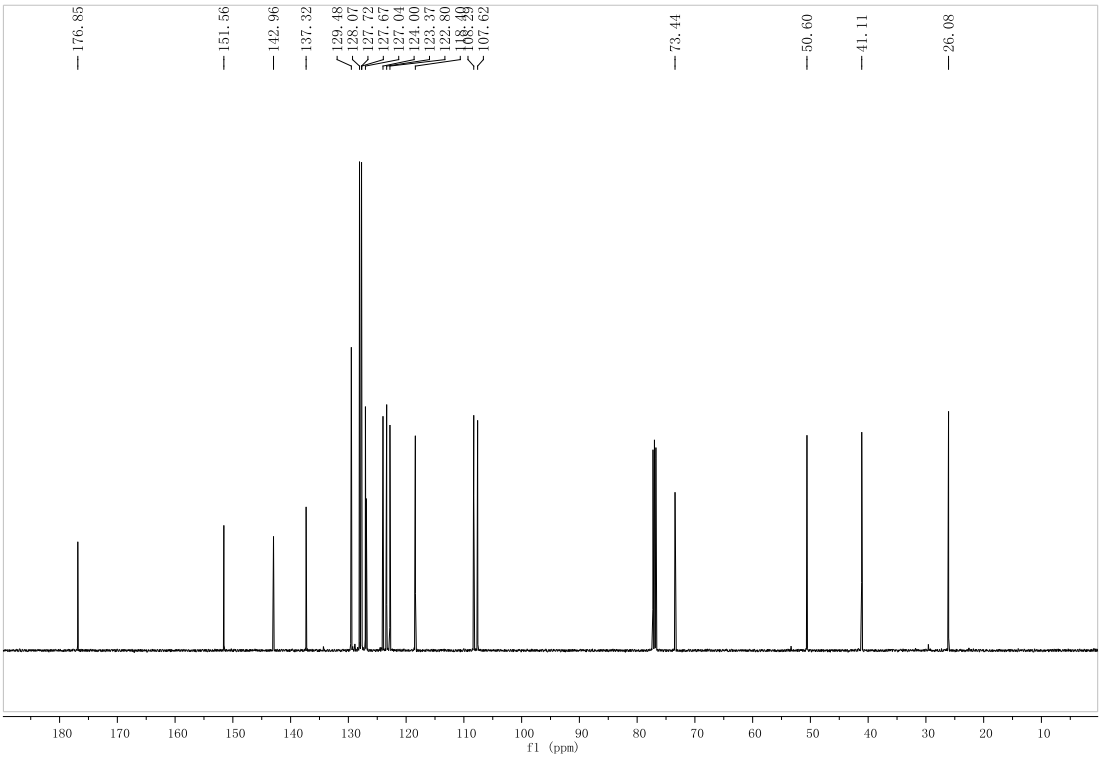

176.29
152.23
143.17
130.85
130.59
130.34
129.87
128.79
123.87
123.50
123.23
115.13
115.09
108.31
102.50
102.47
102.44
102.41
73.70
40.37
30.21
26.30
f1 (ppm)

1-Benzyl-1'-methyl-2,3'-spirobi[indolin]-2'-one **2k**

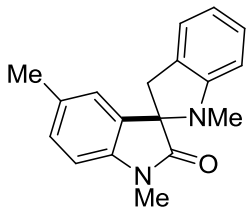


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 91% yield, m.p. 133-137 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (td, *J* = 8.0, 1.0 Hz, 1H), 7.22-7.31 (m, 6H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.04-7.06 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.76-6.80 (m, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 4.07 (d, *J* = 15.5 Hz, 1H), 3.91 (d, *J* = 15.0 Hz, 1H), 3.66 (d, *J* = 15.5 Hz, 1H), 3.32 (d, *J* = 15.5 Hz, 1H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 151.6, 143.0, 137.3, 129.5, 128.1, 127.7 (d, *J* = 6.0 Hz), 127.0, 126.9, 124.0, 123.4, 122.8, 118.4, 108.3, 107.6, 73.4, 50.6, 41.1, 26.1. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{20}KN_2O$ ($[M+K]^+$): 379.1207, found 379.1199.

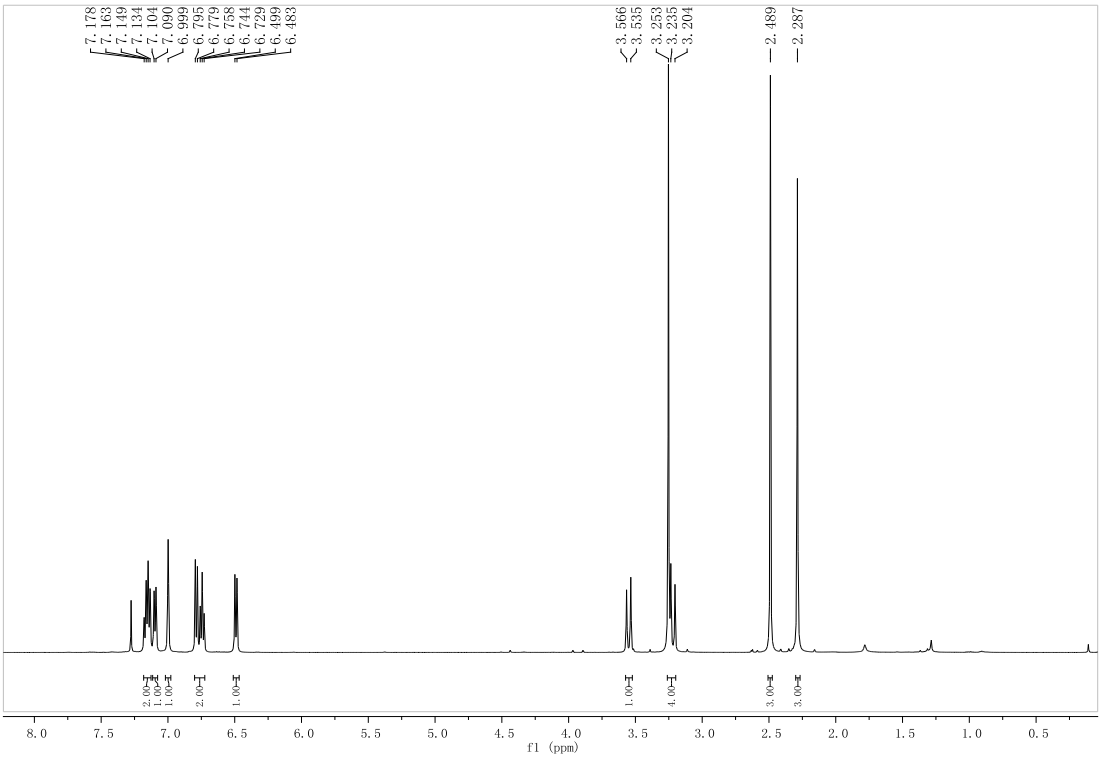


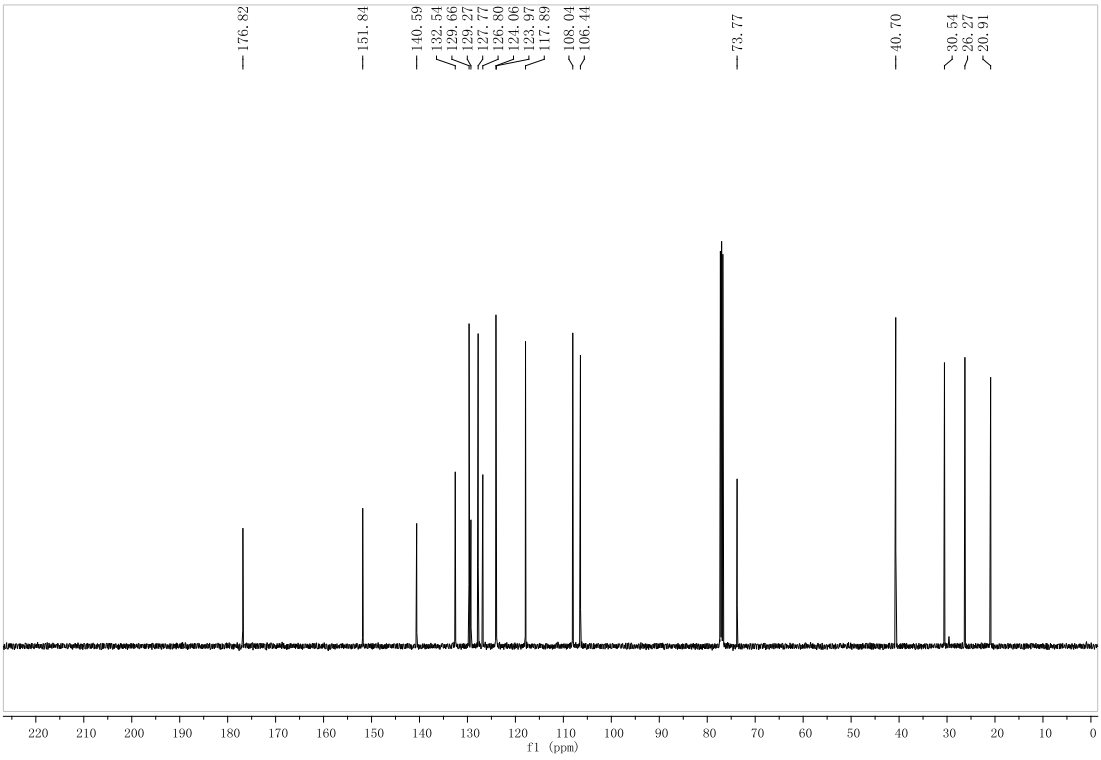


1,1',5-Trimethyl-2,3'-spirobi[indolin]-2-one **2l**

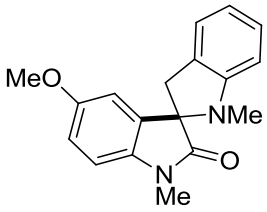


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 99% yield, m.p. 125-127 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 14.5, 7.5 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.00 (s, 1H), 6.72-6.80 (m, 2H), 6.49 (d, *J* = 7.5 Hz, 1H), 3.55 (d, *J* = 15.5 Hz, 1H), 3.20-3.26 (m, 4H), 2.49 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 151.8, 140.6, 132.5, 129.7, 129.3, 127.8, 126.8, 124.0 (d, *J* = 11.25 Hz), 117.9, 108.0, 106.4, 73.8, 40.7, 30.5, 26.3, 20.9. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}KN_2O$ ($[M+H]^+$): 317.1056, found 317.1047.

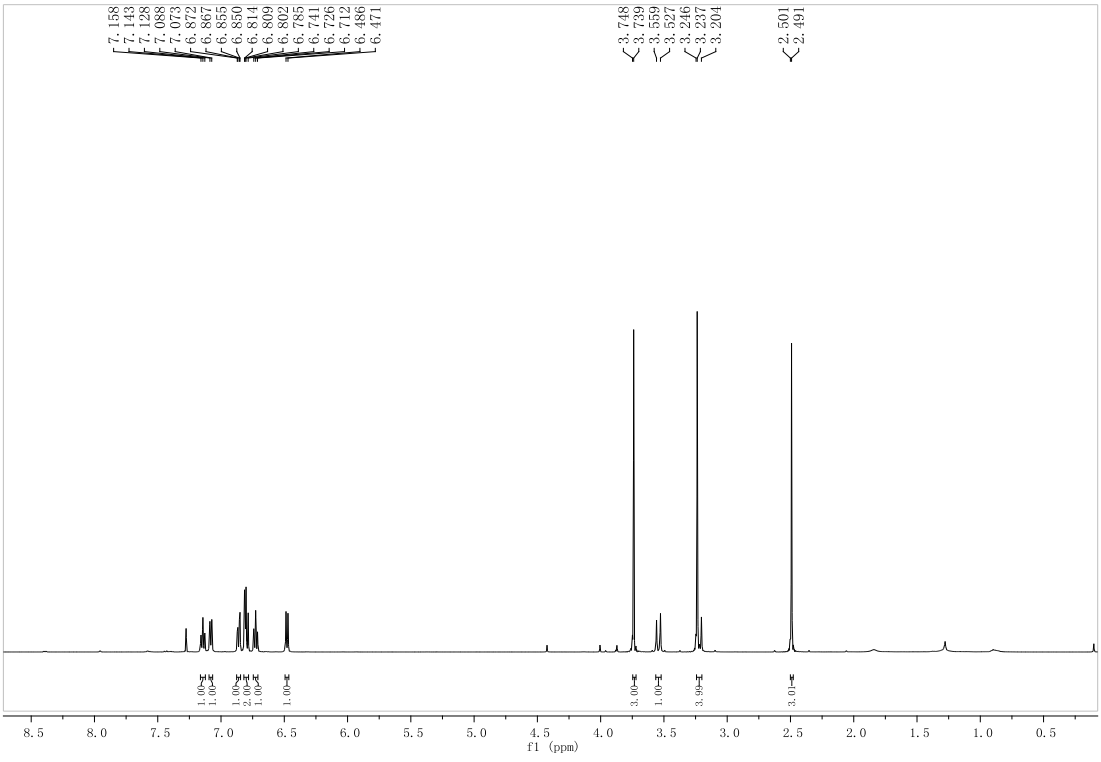

7.178
7.163
7.149
7.134
7.104
7.090
6.999
6.795
6.779
6.758
6.744
6.729
6.499
6.483
3.566
3.535
3.253
3.235
3.204
2.489
2.287
f1 (ppm)

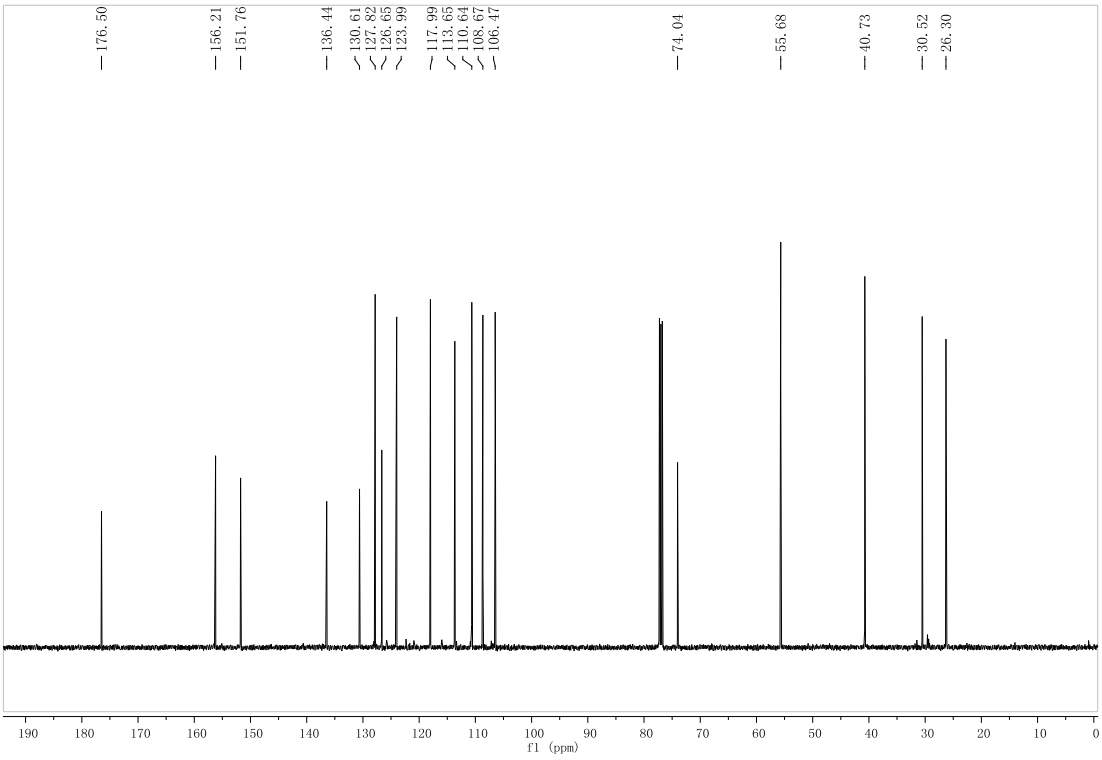

176.82
151.84
140.59
132.54
129.66
129.27
127.77
126.80
124.06
123.97
117.89
108.04
106.44
73.77
40.70
30.54
26.27
20.91
f1 (ppm)

5-Methoxy-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2m**

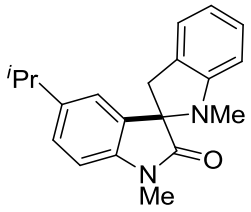


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 98% yield, m.p. 123-125 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.80 (dd, *J* = 6.0, 2.5 Hz, 2H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 3.54 (d, *J* = 16.0 Hz, 1H), 3.22 (d, *J* = 16.5 Hz, 4H), 2.50 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 156.2, 151.8, 136.4, 130.6, 127.8, 126.7, 124.0, 118.0, 113.7, 110.6, 108.7, 106.5, 74.0, 55.7, 40.7, 30.5, 26.3. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{18}NaN_2O_2$ ([M+H]$^{+}$): 317.1260, found 317.1248.

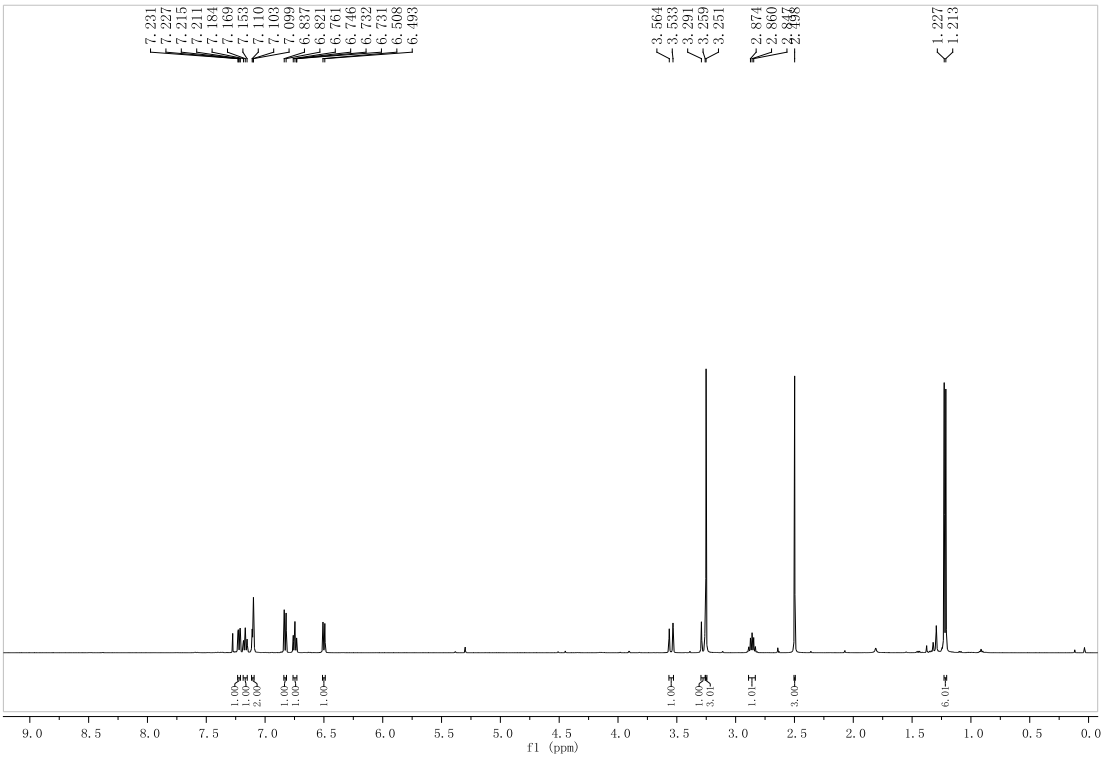




5-Isopropyl-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2n**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 95% yield, m.p. 80-84 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.09-7.12 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.74 (dd, *J* = 7.5, 7.0 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 3.55 (d, *J* = 15.5 Hz, 1H), 3.28 (d, *J* = 16.0 Hz, 1H), 3.25 (s, 3H), 2.87 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.50 (s, 3H), 1.22 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 151.9, 144.0, 141.0, 129.4, 127.8, 126.9, 126.8, 124.0, 121.8, 117.9, 108.0, 106.4, 73.7, 40.8, 33.7, 30.5, 26.2, 24.1, 24.1. HRMS *m/z* (ESI+): Calculated for $C_{20}H_{23}N_2O$ ($[M+H]^+$): 307.1805, found 307.1802.


7.231
7.227
7.215
7.211
7.184
7.169
7.153
7.110
7.103
7.099
6.837
6.821
6.761
6.746
6.732
6.731
6.508
6.493
3.564
3.533
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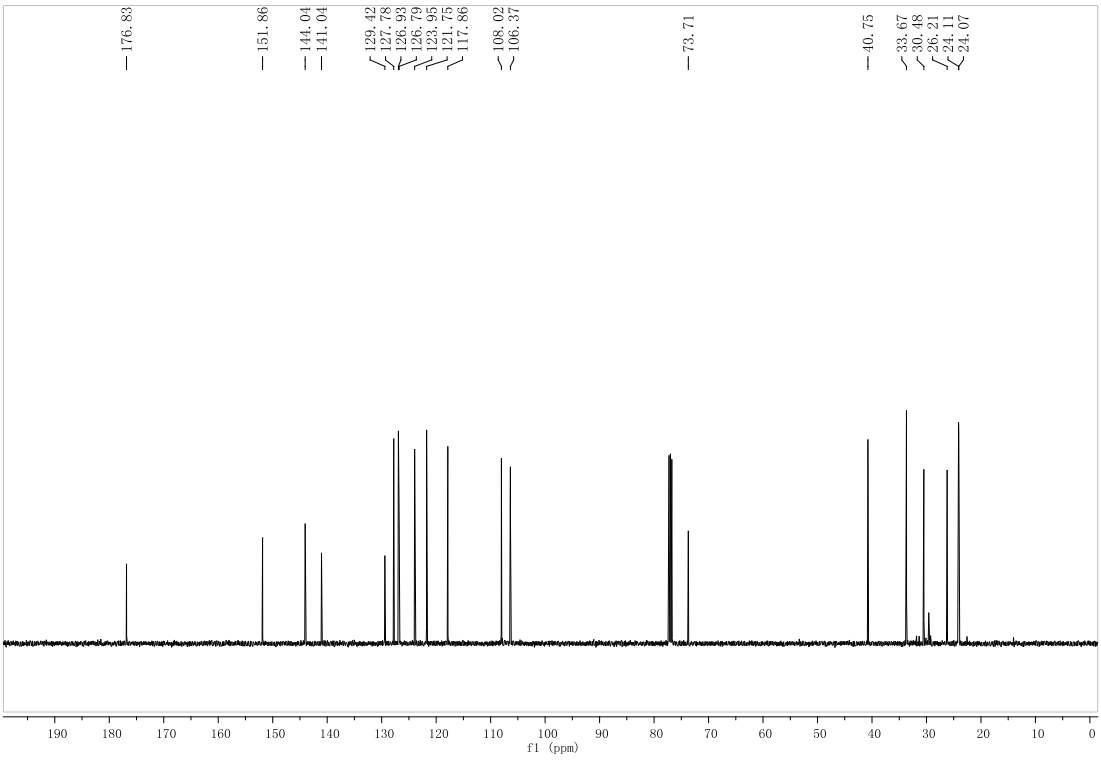
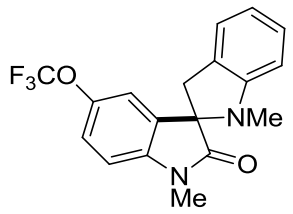
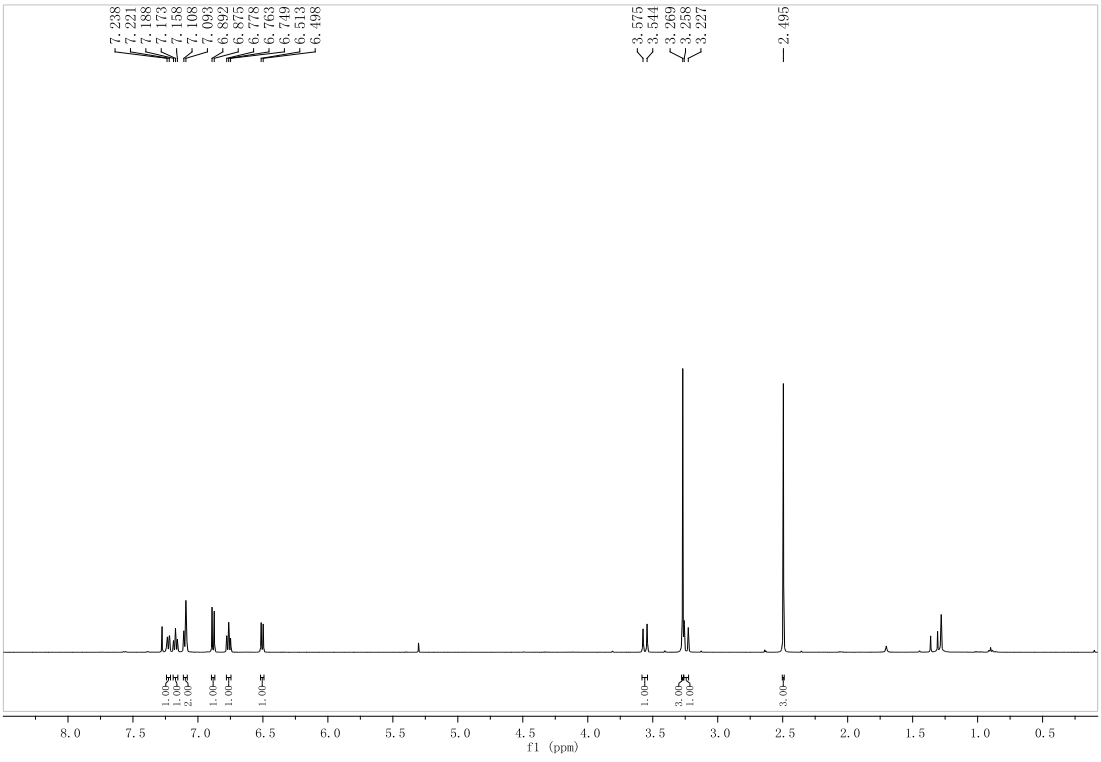
3.259
3.251
2.874
2.860
2.847
2.498
1.227
1.213
f1 (ppm)

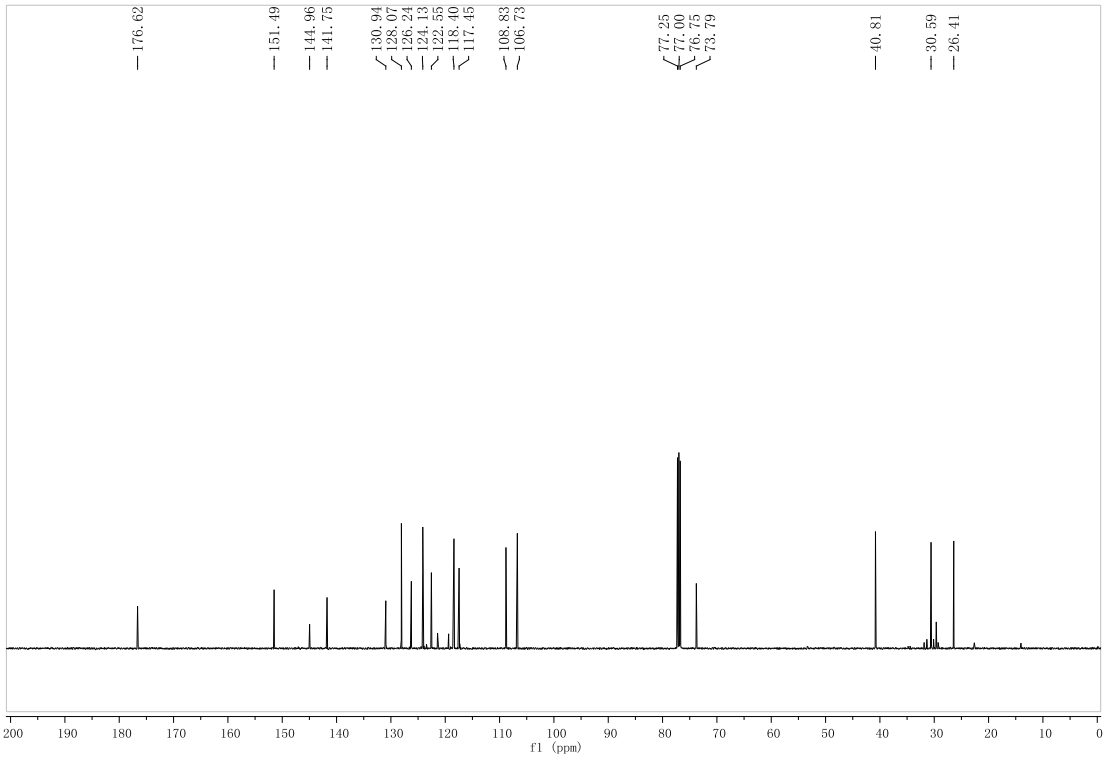

176.83
151.86
144.04
141.04
129.42
127.78
126.93
126.79
123.95
121.75
117.86
108.02
106.37
73.71
40.75
33.67
30.48
26.21
24.11
24.07
f1 (ppm)

1,1'-Dimethyl-5-(trifluoromethoxy)-2,3'-spirobi[indolin]-2-one **2o**

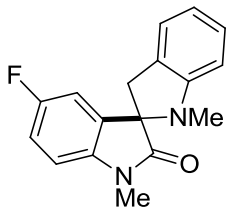


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 90% yield, m.p. 91-93 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 3.56 (d, *J* = 15.5 Hz, 1H), 3.27 (s, 3H), 3.24 (d, *J* = 15.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 151.5, 145.0, 141.8, 130.9, 128.1, 126.2, 124.1, 122.6 118.4, 117.5, 108.8, 106.7, 77.3, 77.00, 76.8, 73.8, 40.8, 30.6, 26.4. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}F_3N_2O_2$ ($[M+H]^+$): 349.1158, found 349.1150.

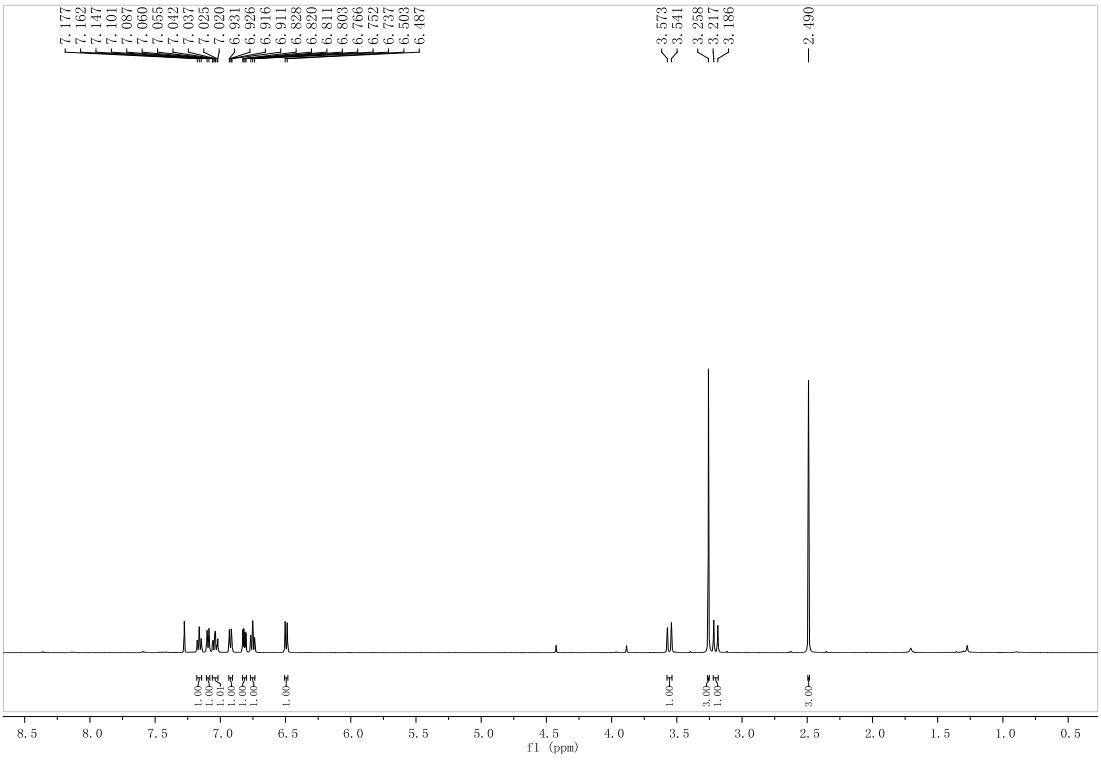




5-Fluoro-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2p**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 89% yield, m.p. 157-161 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 1H), 7.04 (td, *J* = 9.0, 2.5 Hz, 1H), 6.92 (dd, *J* = 7.5, 2.5 Hz, 1H), 6.82 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.75 (t, *J* = 7.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.56 (d, *J* = 16.0 Hz, 1H), 3.26 (s, 3H), 3.20 (d, *J* = 15.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 159.33 (d, *J* = 242.1 Hz), 151.6, 138.9 (d, *J* = 1.8 Hz), 130.9 (d, *J* = 7.9 Hz), 128.0, 124.1, 118.3, 115.7 (d, *J* = 23.4 Hz), 111.5 (d, *J* = 24.5 Hz), 108.92 (d, *J* = 7.9 Hz), 106.7, 74.1, 40.7, 30.6, 26.4. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{16}FN_2O$ ($[M+H]^+$): 283.1241, found 283.1236.


7.177
7.162
7.147
7.101
7.087
7.060
7.055
7.042
7.037
7.025
7.020
6.931
6.926
6.916
6.911
6.828
6.820
6.811
6.803
6.766
6.752
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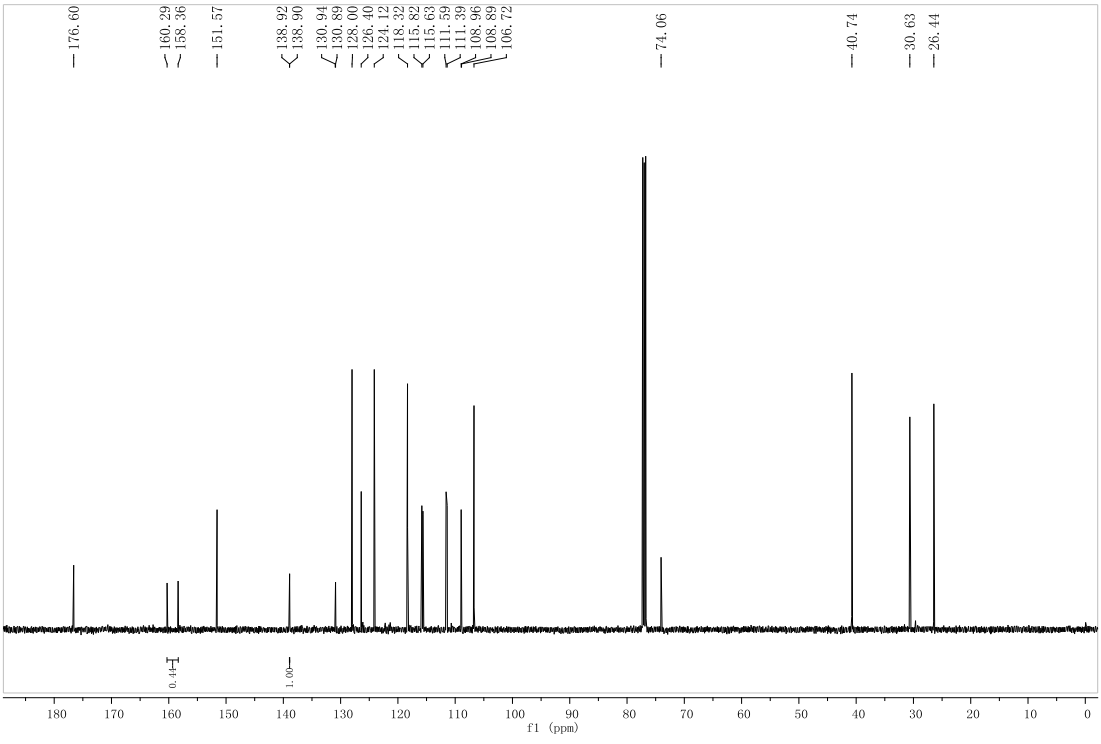
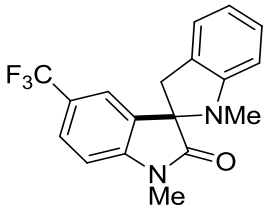
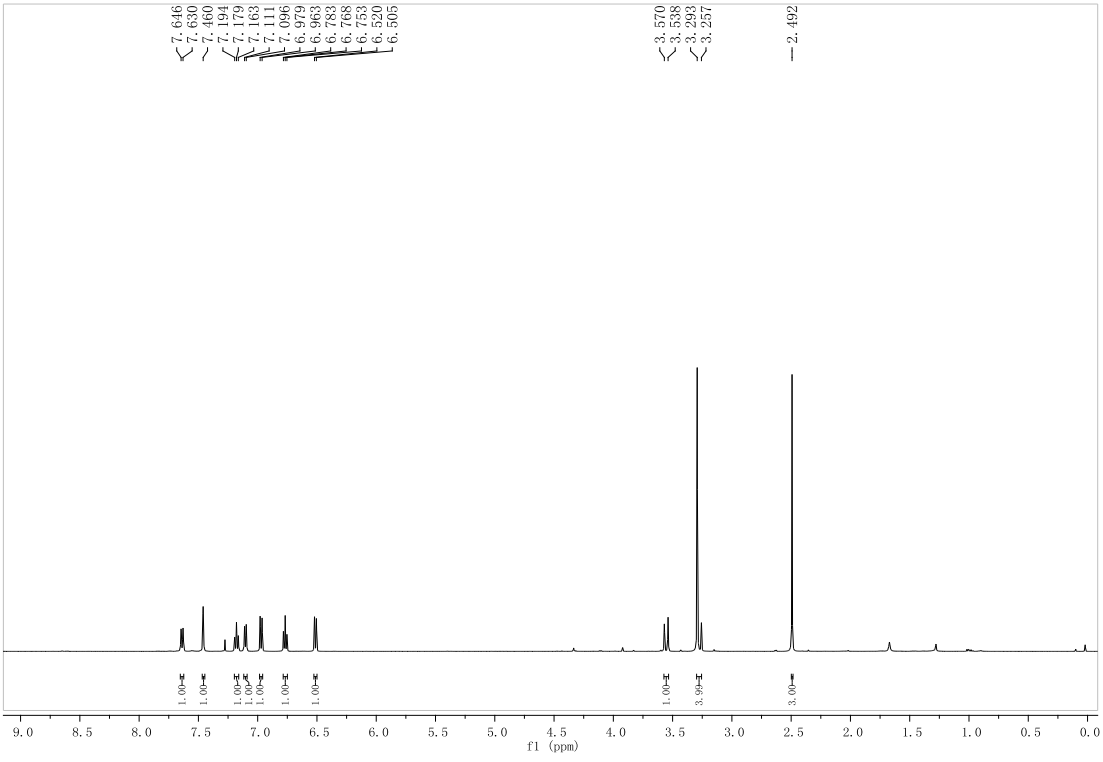
6.503
6.487
3.573
3.541
3.258
3.217
3.186
2.490
f1 (ppm)

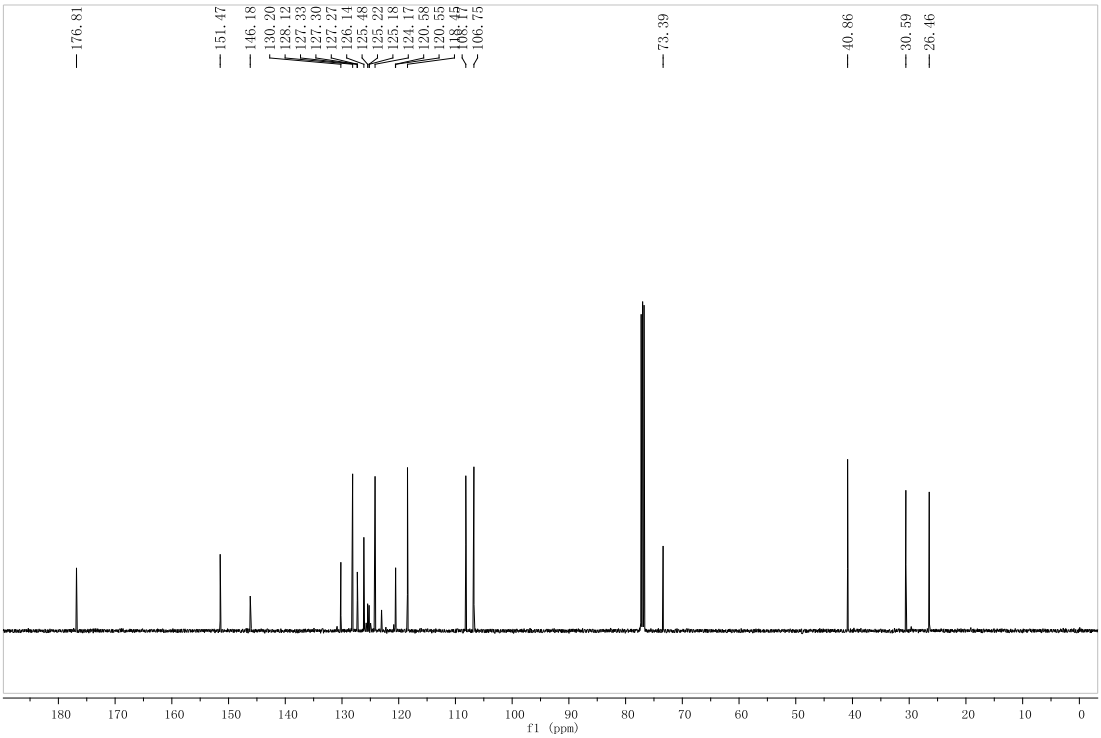

176.60
160.29
158.36
151.57
138.92
138.90
130.94
130.89
128.00
126.40
124.12
118.32
115.82
115.63
111.59
111.39
108.96
108.89
106.72
74.06
40.74
30.63
26.44
f1 (ppm)

1,1'-Dimethyl-5-(trifluoromethyl)-2,3'-spirobi[indolin]-2-one **2q**

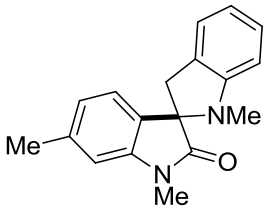


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 85% yield, m.p. 127-128 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 3.55 (d, *J* = 16.0 Hz, 1H), 3.27 (d, *J* = 18.0 Hz, 4H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 151.5, 146.2, 130.2, 128.1, 127.3 (q, *J* = 3.8 Hz), 126.1, 124.2, 123.0, 125.21 (q, *J* = 30.6 Hz), 120.6 (q, *J* = 2.5 Hz), 118.5, 108.2, 106.8, 73.4, 40.9, 30.6, 26.5. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}F_3N_2O$ ($[M+H]^+$): 333.1209, found 333.1205.

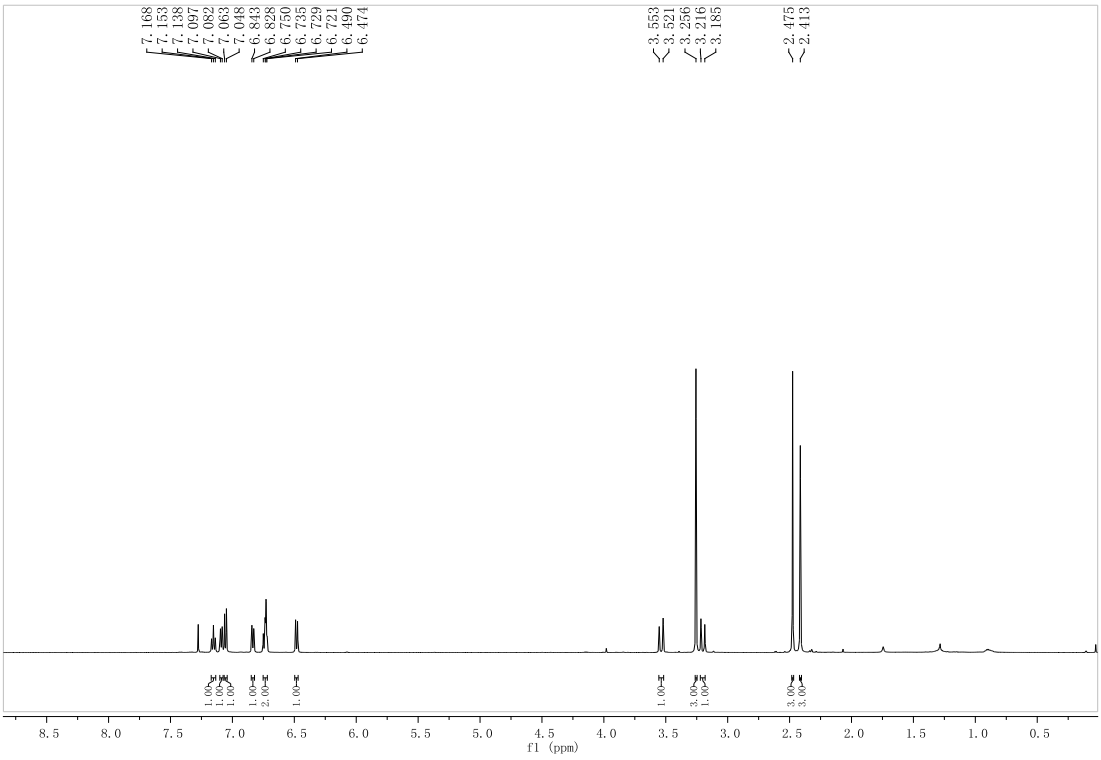


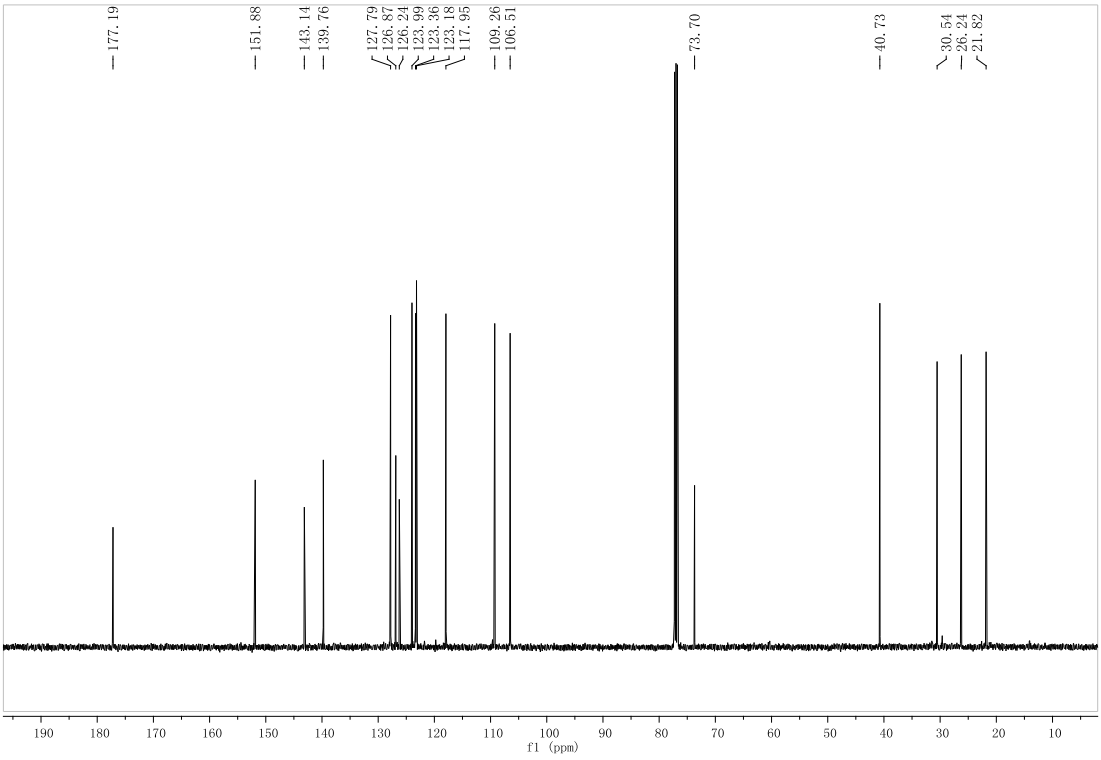


1,1',6-Trimethyl-2,3'-spirobi[indolin]-2-one **2r**

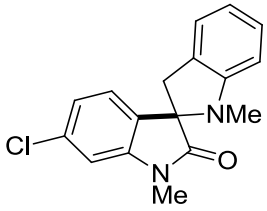


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 95% yield, m.p. 156-157 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.73 (dd, *J* = 7.5, 3.0 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 3.54 (d, *J* = 16.0 Hz, 1H), 3.26 (s, 3H), 3.20 (d, *J* = 15.5 Hz, 1H), 2.48 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 151.9, 143.1, 139.8, 127.8, 126.87, 126.2, 124.0, 123.4, 123.2, 118.0, 109.3, 106.5, 73.7, 40.7, 30.5, 26.2, 21.8. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{19}N_2O$ ($[M+H]^+$): 279.1492, found 279.1501.

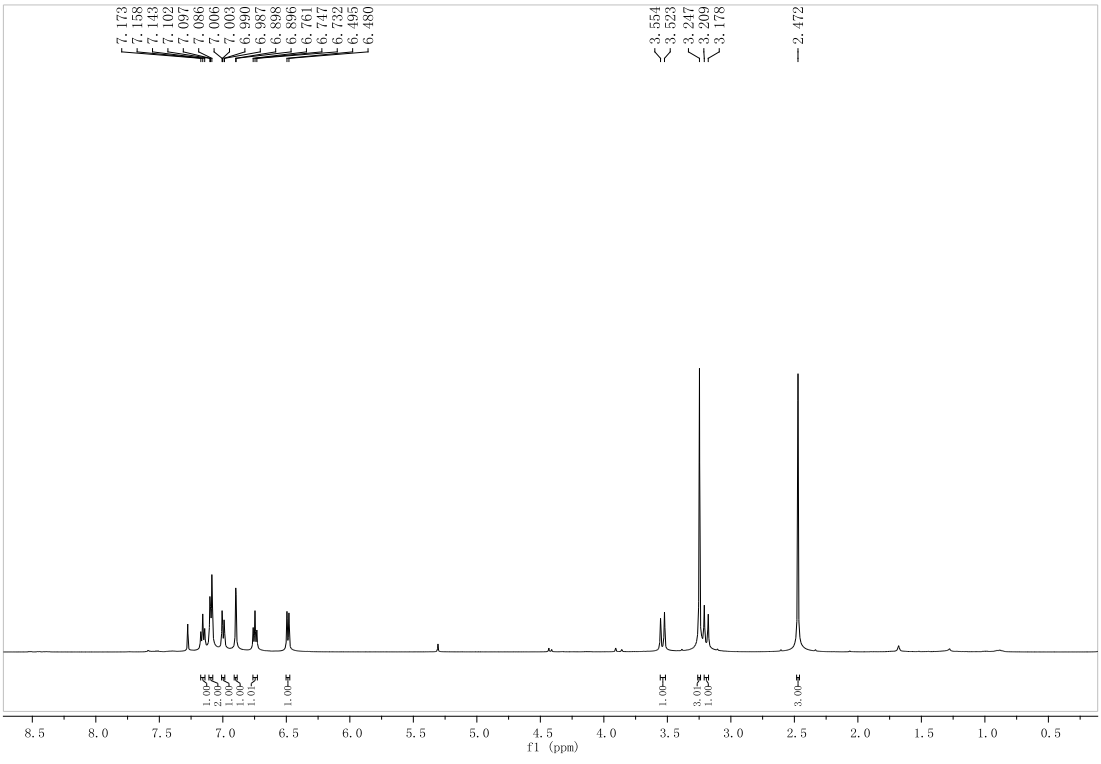

7.168
7.153
7.138
7.097
7.082
7.063
7.048
6.843
6.828
6.750
6.735
6.729
6.721
6.490
6.474
3.553
3.521
3.256
3.216
3.185
2.475
2.413
f1 (ppm)

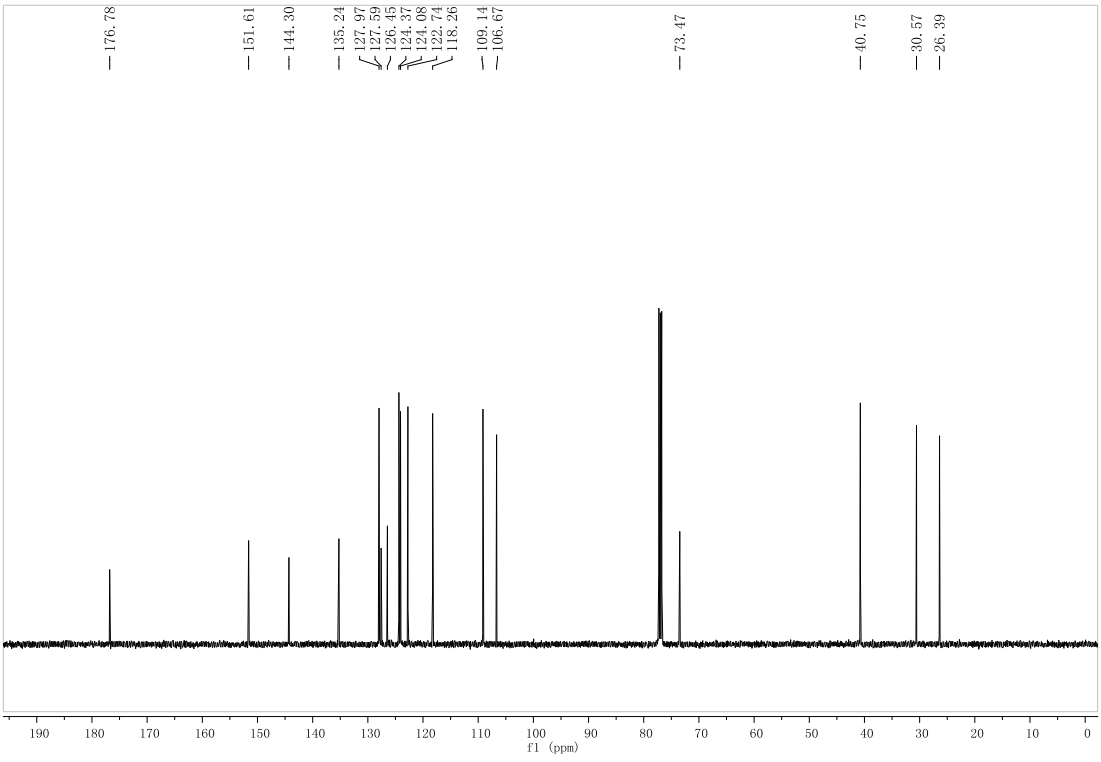

177.19
151.88
143.14
139.76
127.79
126.87
126.24
123.99
123.36
123.18
117.95
109.26
106.51
73.70
40.73
30.54
26.24
21.82
f1 (ppm)

6-Chloro-1,1'-dimethyl-2,3'-spirobi[indolin]-2-one **2s**

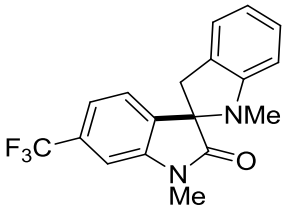


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); pale yellow solid, 71% yield, m.p. 140-146 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.5 Hz, 1H), 7.08-7.11 (m, 2H), 7.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.90 (d, *J* = 1.0 Hz, 1H), 6.75 (t, *J* = 7.0 Hz, 1H), 6.49 (d, *J* = 7.5 Hz, 1H), 3.54 (d, *J* = 15.5 Hz, 1H), 3.25 (s, 3H), 3.19 (d, *J* = 15.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 151.6, 144.3, 135.2, 128.0, 127.6, 126.5, 124.4, 124.1, 122.7, 118.3, 109.1, 106.7, 73.5, 40.8, 30.6, 26.4. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{16}ClN_2O$ ($[M+H]^+$): 299.0946, found 299.0938.

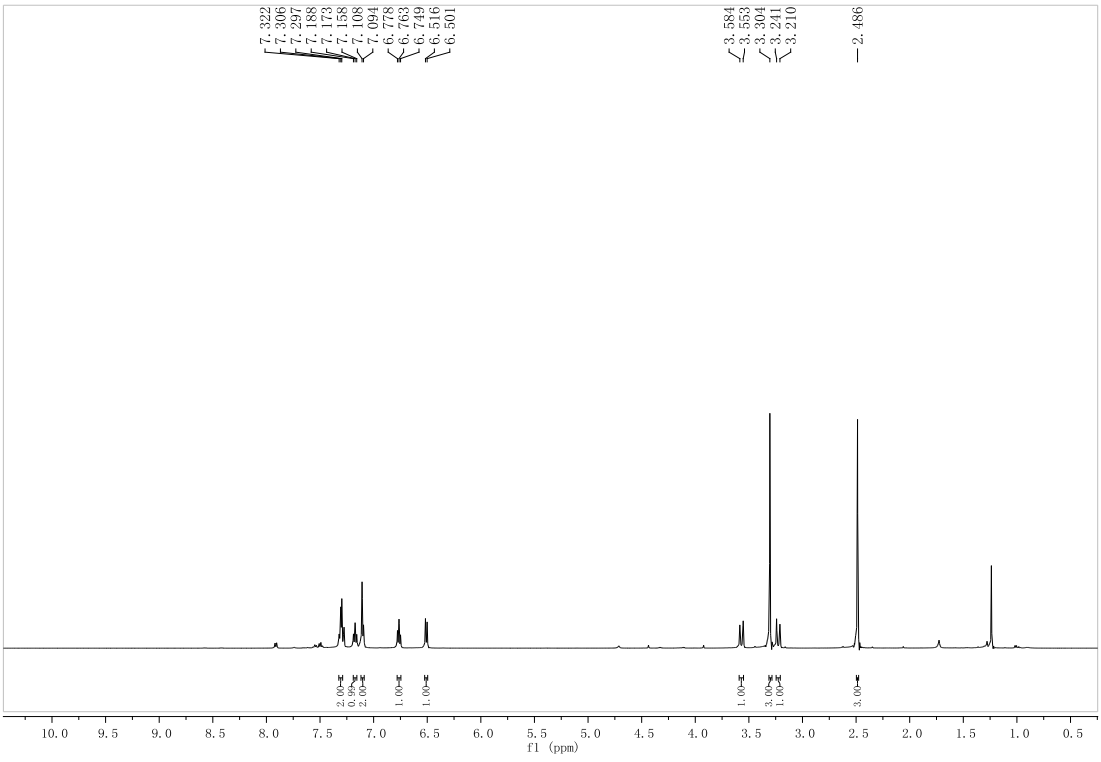


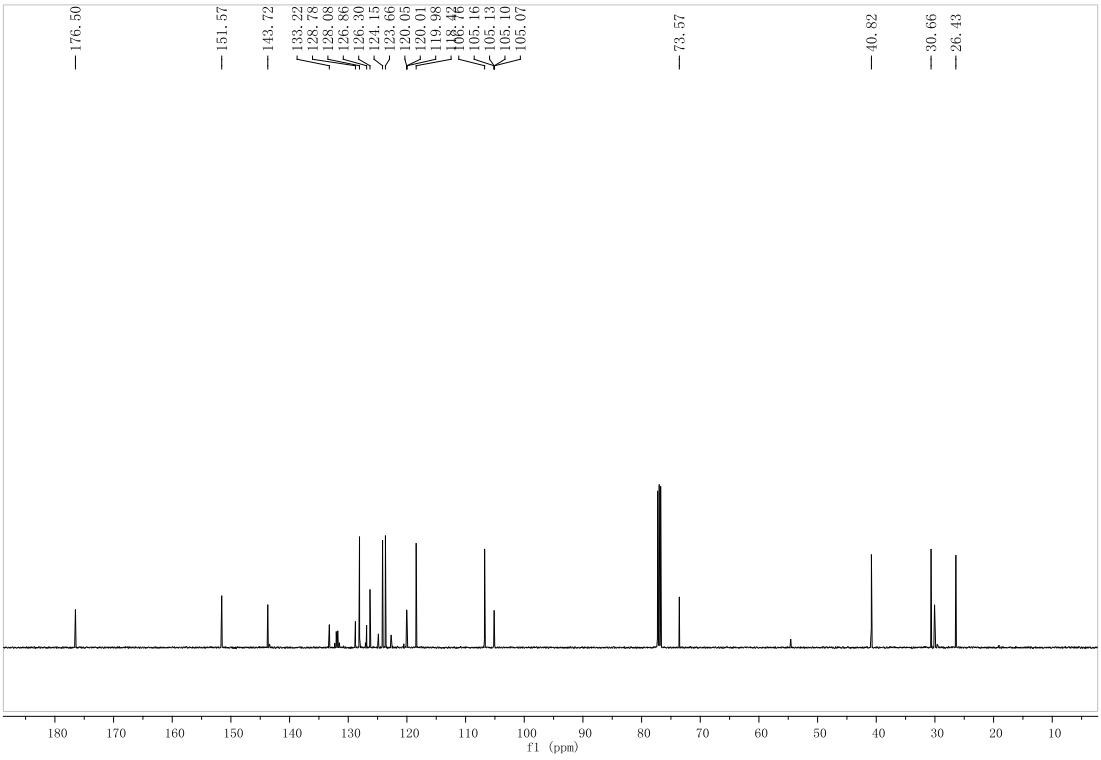


1,1'-Dimethyl-6-(trifluoromethyl)-2,3'-spirobi[indolin]-2-one **2t**

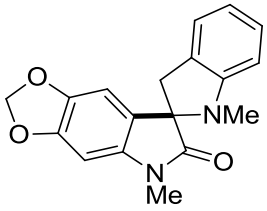


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 95% yield, m.p. 84-88 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.33 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 3.57 (d, *J* = 15.5 Hz, 1H), 3.30 (s, 3H), 3.23 (d, *J* = 15.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 151.6, 143.7, 133.2, 128.8, 128.1, 126.9, 126.3, 124.2, 123.7, 120.0 (q, *J* = 4.0 Hz), 118.4, 106.8, 105.1 (q, *J* = 3.7 Hz), 73.6, 40.8, 30.7, 26.4. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}F_3N_2O$ ($[M+H]^+$): 333.1209, found 333.1200.

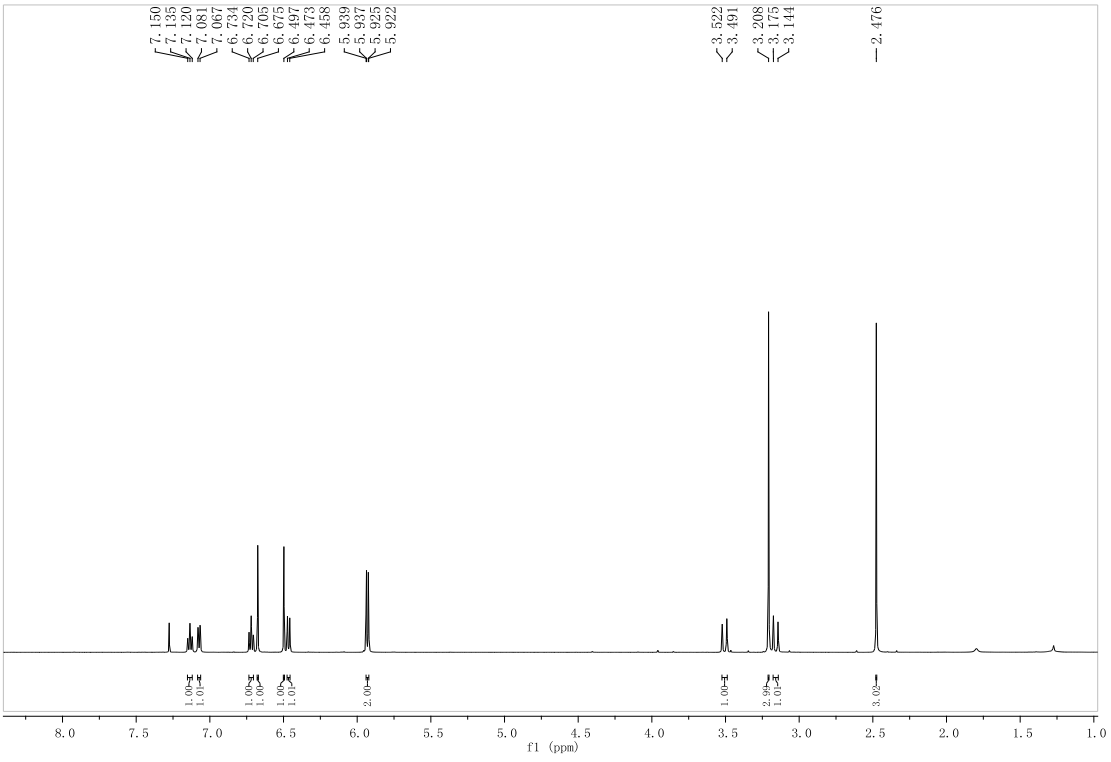

7.322
7.306
7.297
7.188
7.173
7.158
7.108
7.094
6.778
6.763
6.749
6.516
6.501
3.584
3.553
3.304
3.241
3.210
2.486
2.04
0.99
2.04
1.00
1.00
1.04
3.04
1.00
3.04
f1 (ppm)

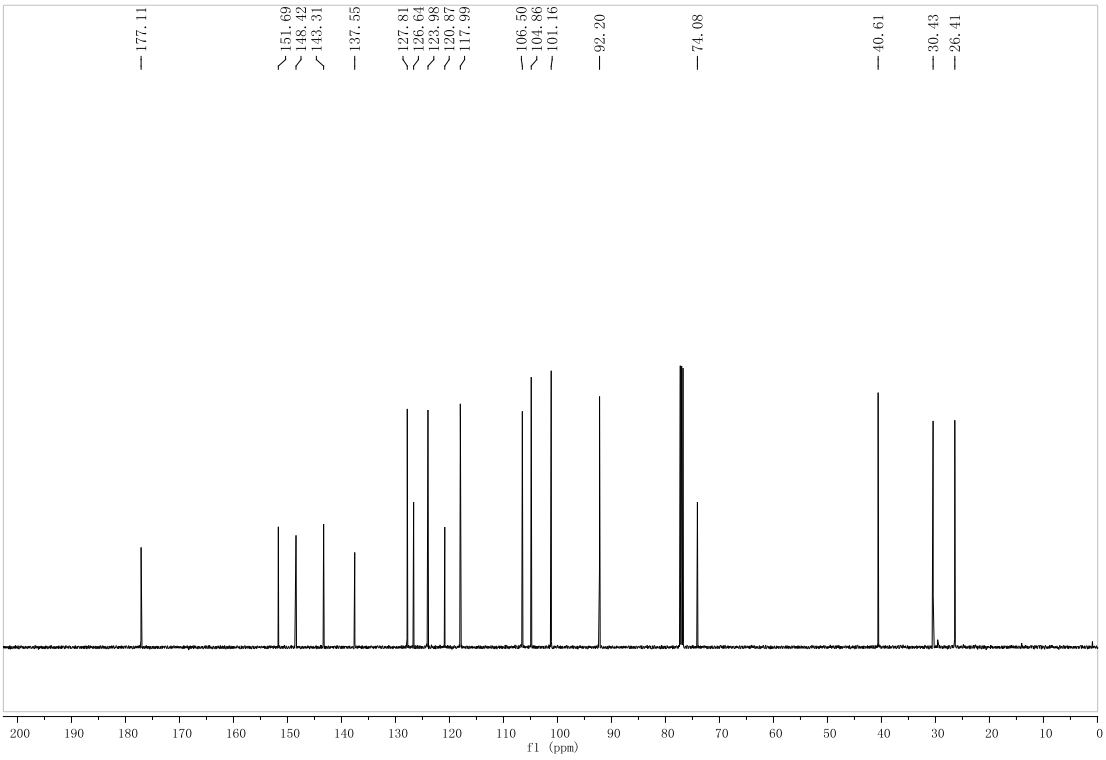

176.50
151.57
143.72
133.22
128.78
128.08
126.86
126.30
124.15
123.66
120.05
120.01
119.98
118.42
108.76
105.16
105.13
105.10
105.07
73.57
40.82
30.66
26.43
f1 (ppm)

1',5-Dimethylspiro[[1,3]dioxolo[4,5-f]indole-7,2'-indolin]-6(5H)-one **2u**

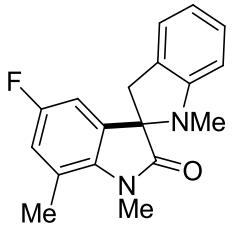


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 96% yield, m.p. 169-172 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 6.72 (t, *J* = 7.0 Hz, 1H), 6.68 (s, 1H), 6.50 (s, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 5.93 (dd, *J* = 7.0, 1.0 Hz, 2H), 3.51 (d, *J* = 15.5 Hz, 1H), 3.21 (s, 3H), 3.16 (d, *J* = 15.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 151.7, 148.4, 143.3, 137.6, 127.8, 126.6, 124.0, 120.9, 118.0, 106.5, 104.9, 101.2, 92.2, 74.1, 40.6, 30.4, 26.4. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}NaN_2O_3$ ($[M+H]^+$): 331.1053, found 331.1042.

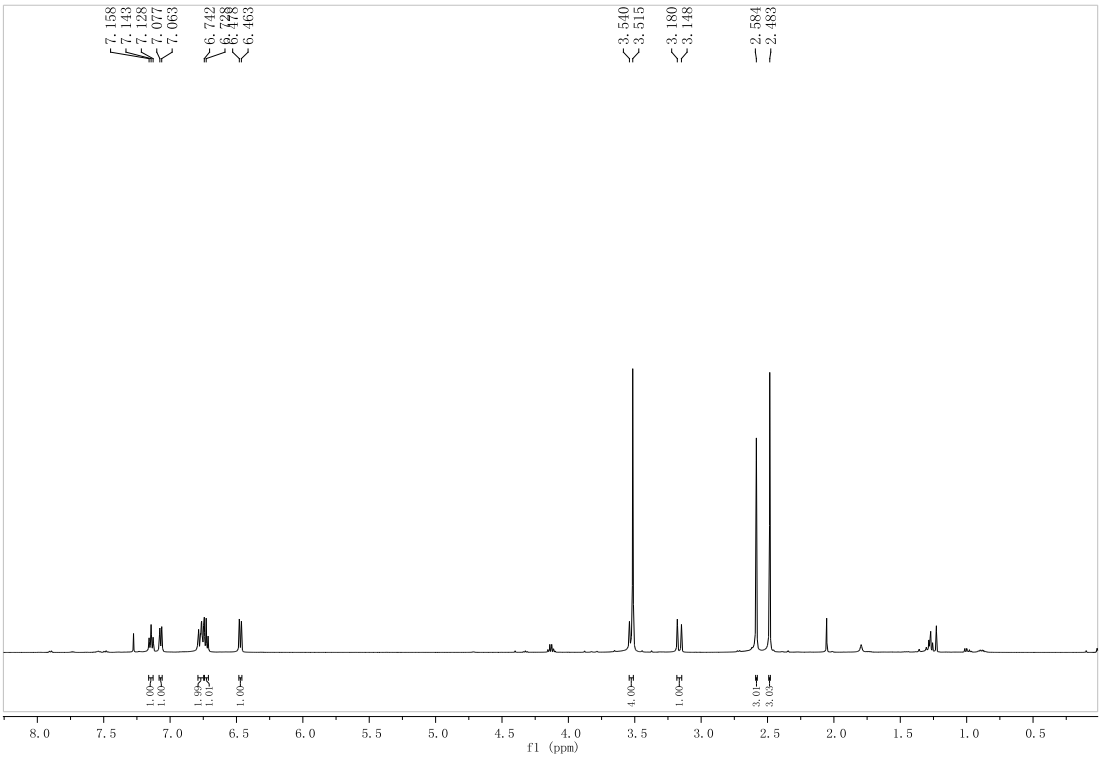




5-Fluoro-1,1',7-trimethyl-2,3'-spirobi[indolin]-2-one **2v**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 98% yield, m.p. 74-77 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 6.74-6.79 (m, 2H), 6.71-6.75 (m, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 3.53 (d, *J* = 12.5 Hz, 4H), 3.16 (d, *J* = 15.5Hz, 1H), 2.58 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 158.72 (d, *J* = 242.7 Hz), 151.6, 136.5 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 7.5 Hz), 127.9, 126.4, 124.0, 121.6 (d, *J* = 7.5 Hz), 119.2, 119.0, 118.1, 108.78 (d, *J* = 23.9 Hz), 106.5, 73.4 (d, *J* = 2.5 Hz), 41.1, 30.5, 29.7, 18.8. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{17}FN_2O$ ($[M+H]^+$): 297.1398, found 297.1389.


7.158
7.143
7.128
7.077
7.063
6.742
6.728
6.478
6.463
3.540
3.515
3.180
3.148
2.584
2.483
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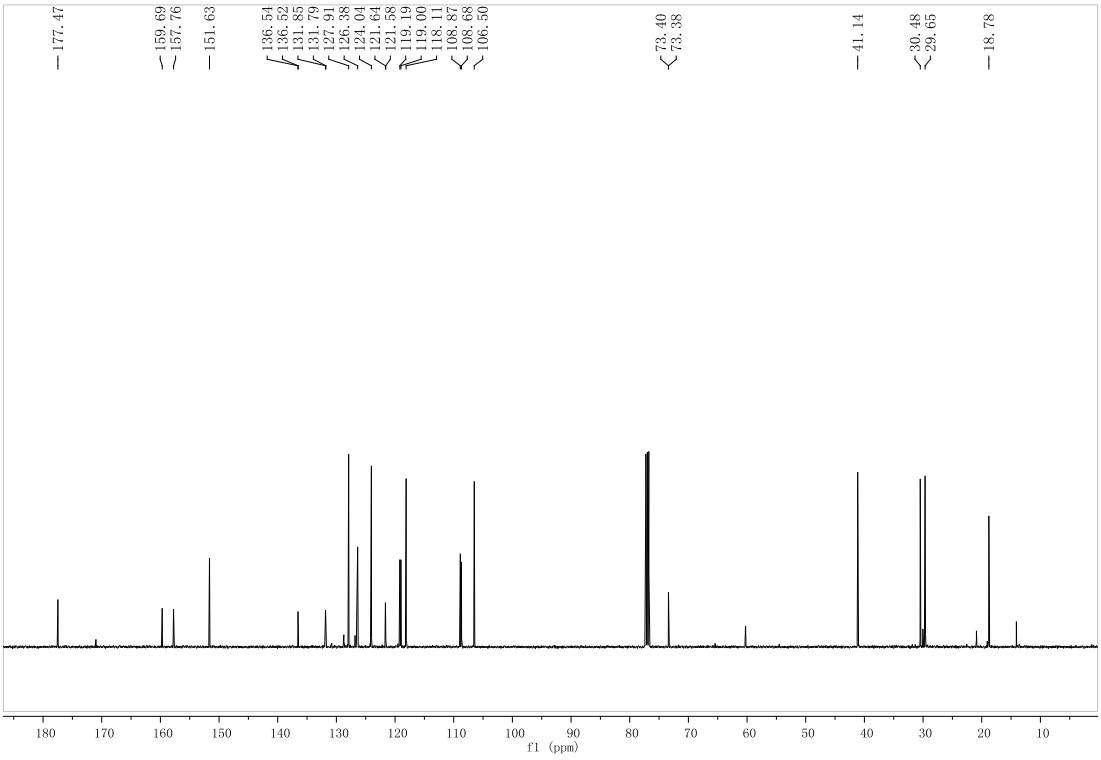
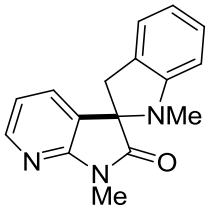
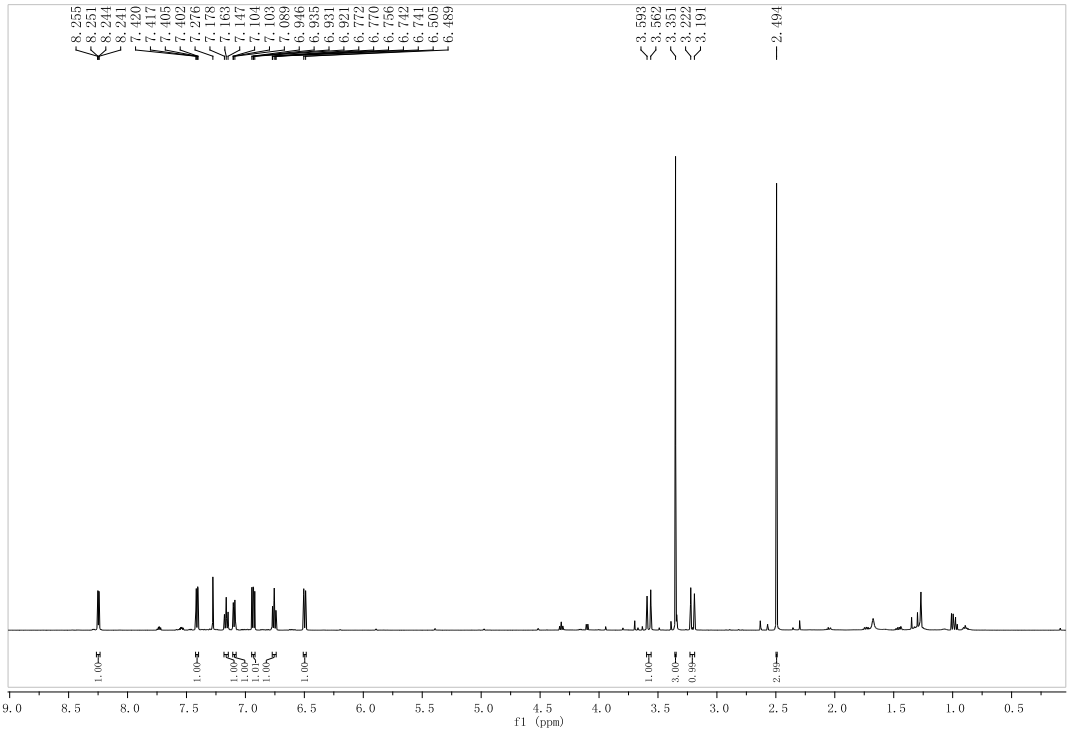
1.00
1.99
1.01
1.00
4.00
1.00
3.01
3.03
f1 (ppm)

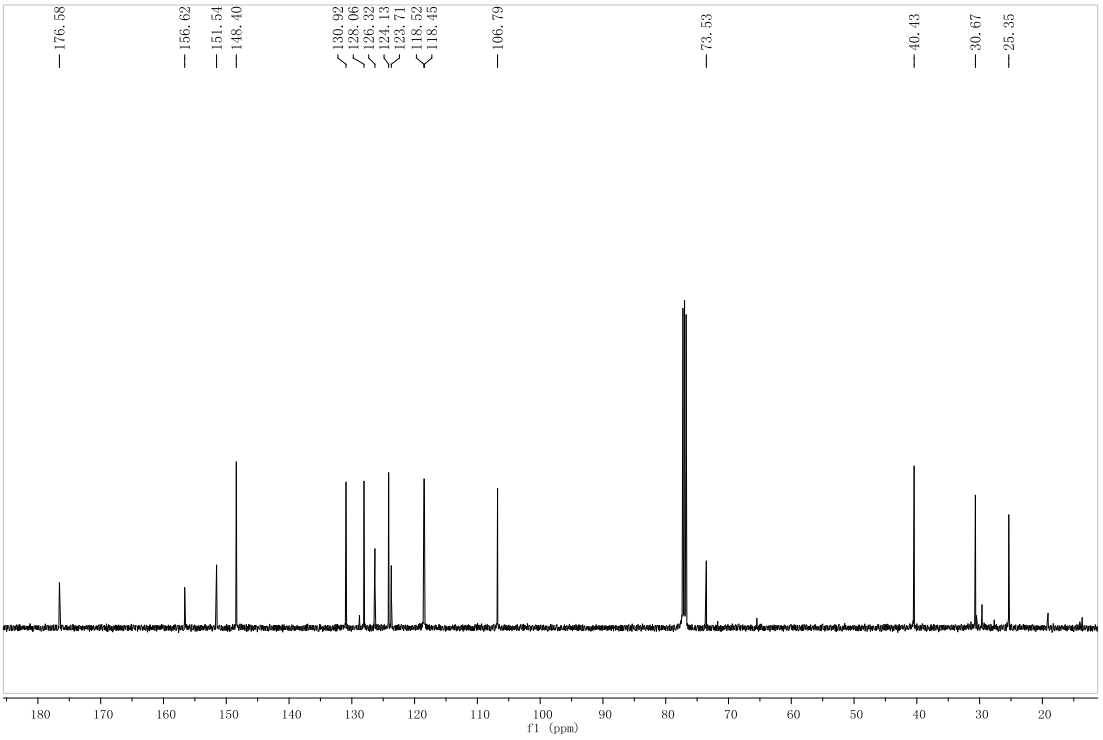

177.47
159.69
157.76
151.63
136.54
136.52
131.85
131.79
127.91
126.38
124.04
121.64
121.58
119.19
119.00
118.11
108.87
108.68
106.50
73.40
73.38
41.14
30.48
29.65
18.78
f1 (ppm)

1,1'-Dimethylspiro[indoline-2,3'-pyrrolo[2,3-b]pyridin]-2'(1'H)-one **2w**

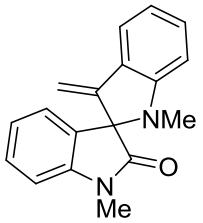


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 90% yield, m.p. 210-213 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 5.5, 2.0 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7..5 Hz, 1H), 6.93 (dd, *J* = 7.5, 5.5 Hz, 1H), 6.74-6.78 (m, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 3.58 (d, *J* = 15.5 Hz, 1H), 3.35 (s, 3H), 3.21 (d, *J* = 15.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 156.6, 151.5, 148.4, 130.9, 128.1, 126.3, 124.1, 123.7, 118.5, 118.4, 106.8, 73.5, 40.4, 30.7, 25.4. HRMS *m/z* (ESI+): Calculated for $C_{16}H_{16}N_3O$ ($[M+H]^+$): 266.1288, found 266.1281.

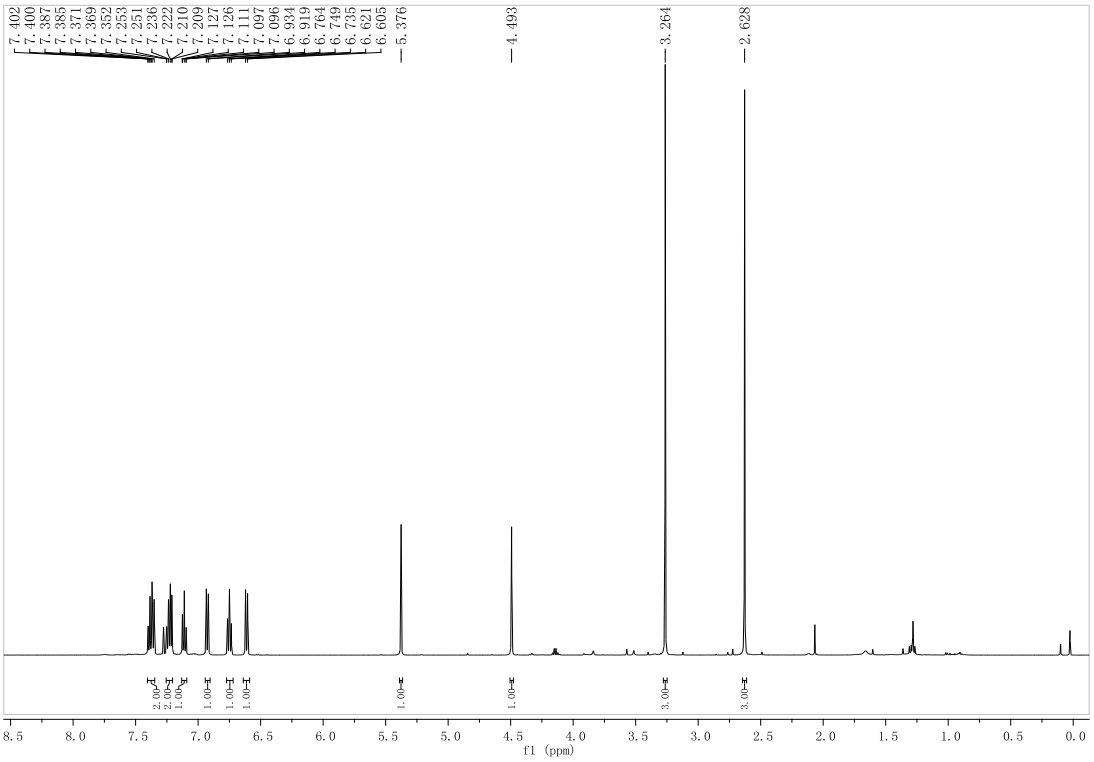


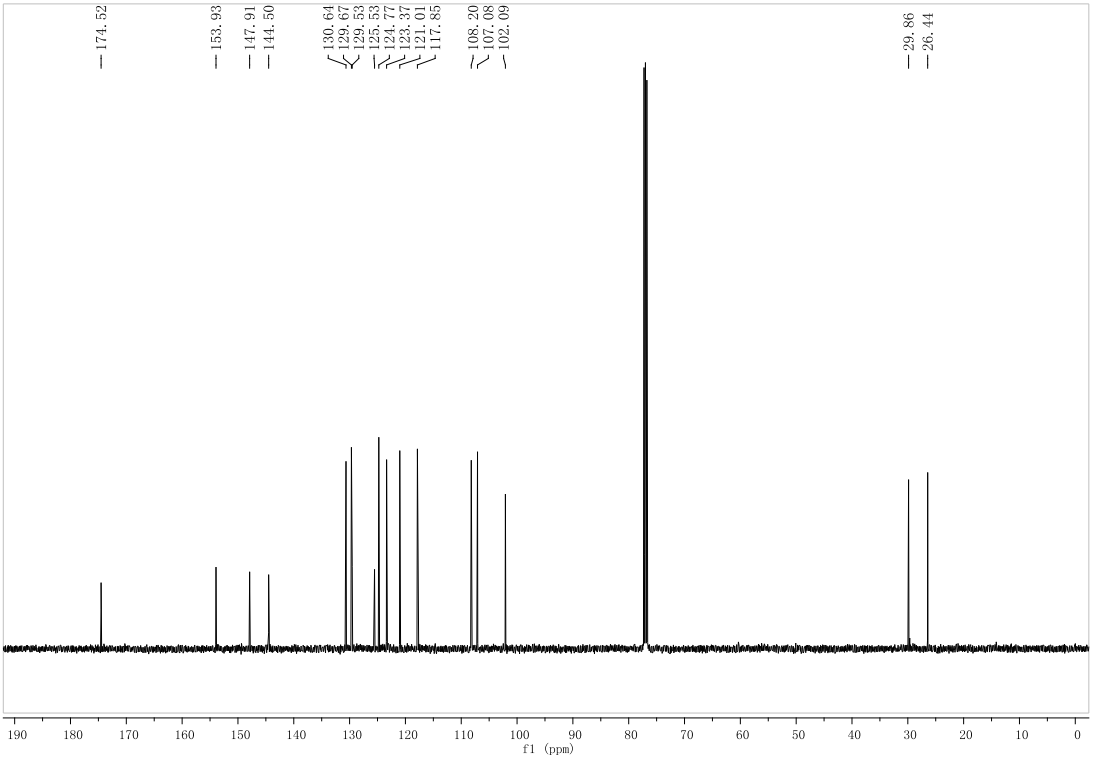


1,1'-dimethyl-3'-methylene-2,3'-spirobi[indolin]-2-one **5**

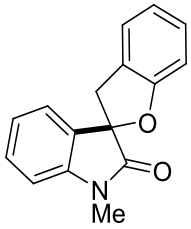


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, 52% yield, m.p. 166-169 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.41 (m, 2H), 7.20-7.26 (m, 2H), 7.09-7.13 (m, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 1H), 4.49 (s, 1H), 3.26 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 153.9, 147.9, 144.5, 130.6, 129.7, 129.5, 125.5, 124.8, 123.4, 121.0, 117.9, 108.2, 107.1, 102.1, 29.9, 26.4. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{17}N_2O$ ($[M+H]^+$): 277.1335, found 277.1343.

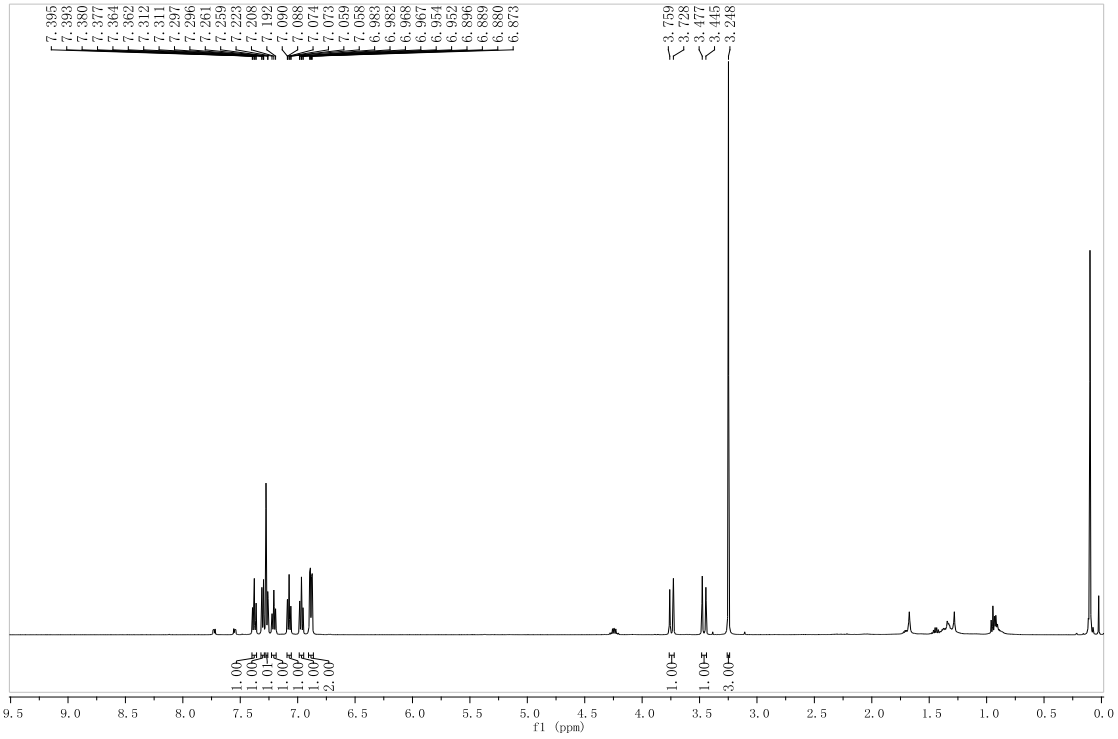

7.402
7.400
7.387
7.385
7.371
7.369
7.352
7.253
7.251
7.236
7.222
7.210
7.209
7.127
7.126
7.111
7.097
7.096
6.934
6.919
6.764
6.749
6.735
6.621
6.605
5.376
4.493
3.264
2.628
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


174.52
153.93
147.91
144.50
130.64
129.67
129.53
125.53
124.77
123.37
121.01
117.85
108.20
107.08
102.09
29.86
26.44
f1 (ppm)

1'-Methyl-3H-spiro[benzofuran-2,3'-indolin]-2'-one **7a**



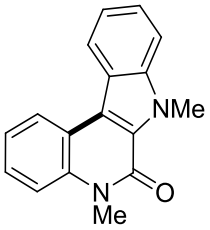
Purified by chromatography on silica gel, eluting with dichloromethane/petroleum ether/ethyl acetate 4:2:0.1 (v/v); white solid, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (td, *J* = 7.5, 1.0 Hz, 1H), 7.30 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.26 (s, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.07 (td, *J* = 8.0, 1.0 Hz, 1H), 6.97 (td, *J* = 7.5, 0.5 Hz, 1H), 6.88 (dd, *J* = 8.0, 3.5 Hz, 2H), 3.74 (d, *J* = 15.5 Hz, 1H), 3.46 (d, *J* = 16.0 Hz, 1H), 3.25 (s, 3H).



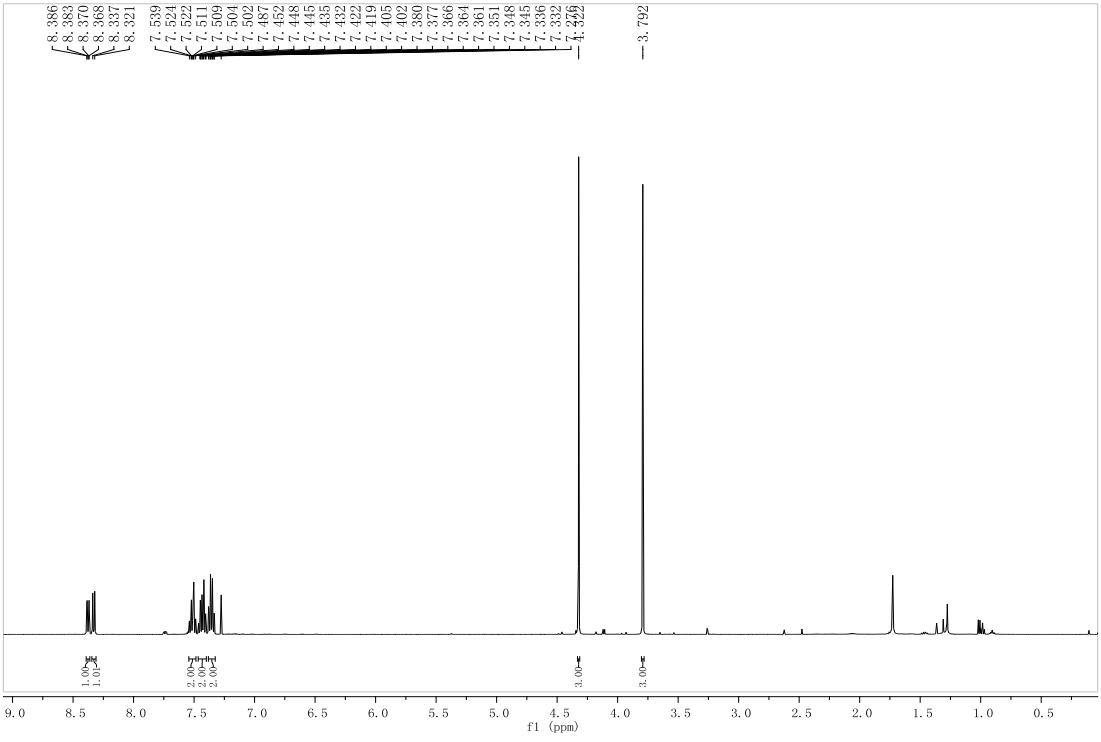
4. General procedure for direct C3-arylation reaction

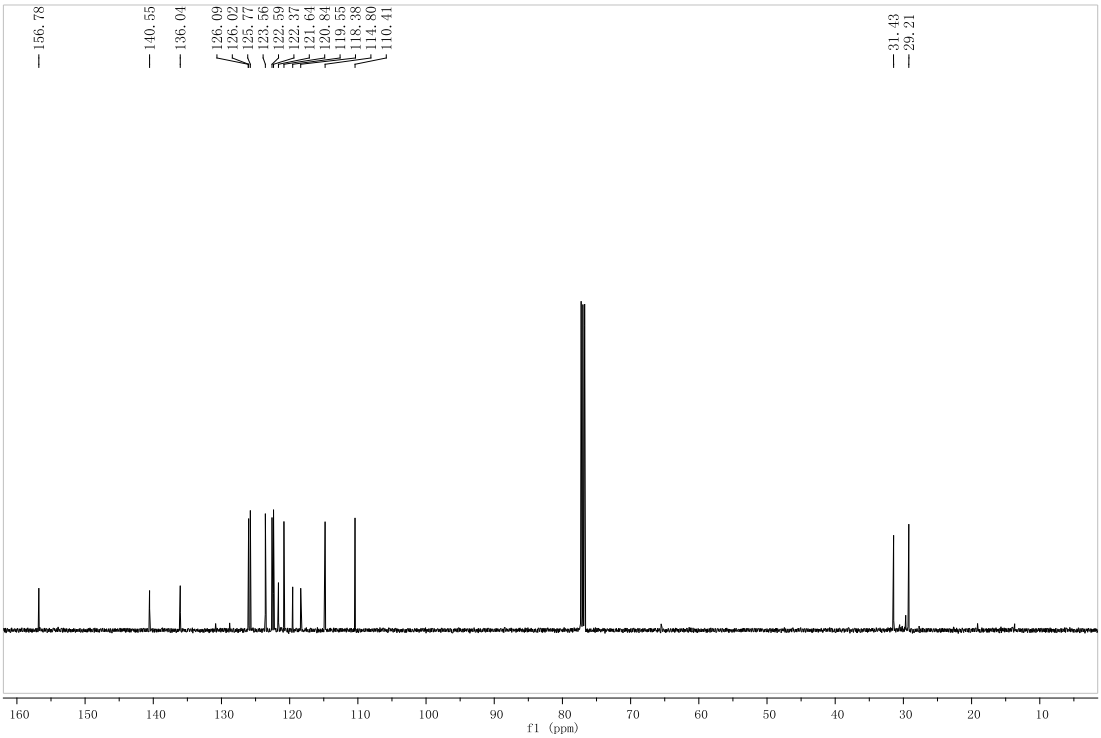
To a dried Schlenk tube was added C2-substitued indole **1** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), $PCy_3 \cdot HBF_4$ (0.02 mmol) and AcONa (0.6 mmol) under N_2, 2.0 mL MeOH was then introduced via syringe. The mixture was stirred at 100 ^{o}C (oil bath) until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting withethyl/petroleum ether 1:10 (v/v) to afford the products.

5,7-Dimethyl-5H-indolo[2,3-c]quinolin-6(7H)-one **3a**

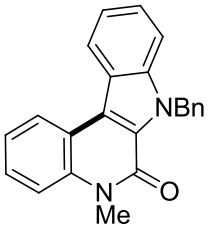


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 92% yield, m.p. 233-235 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.48-7.55 (m, 2H), 7.40-7.47 (m, 2H), 7.33-7.38 (m, 2H), 4.32 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 140.6, 136.0, 126.0 , 126.1, 125.8, 123.6, 122.6, 122.4, 121.6, 120.8, 119.6, 118.4, 114.8, 110.4, 31.4, 29.2. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{15}N_2O$ ($[M+H]^+$): 263.1179, found 263.1189.

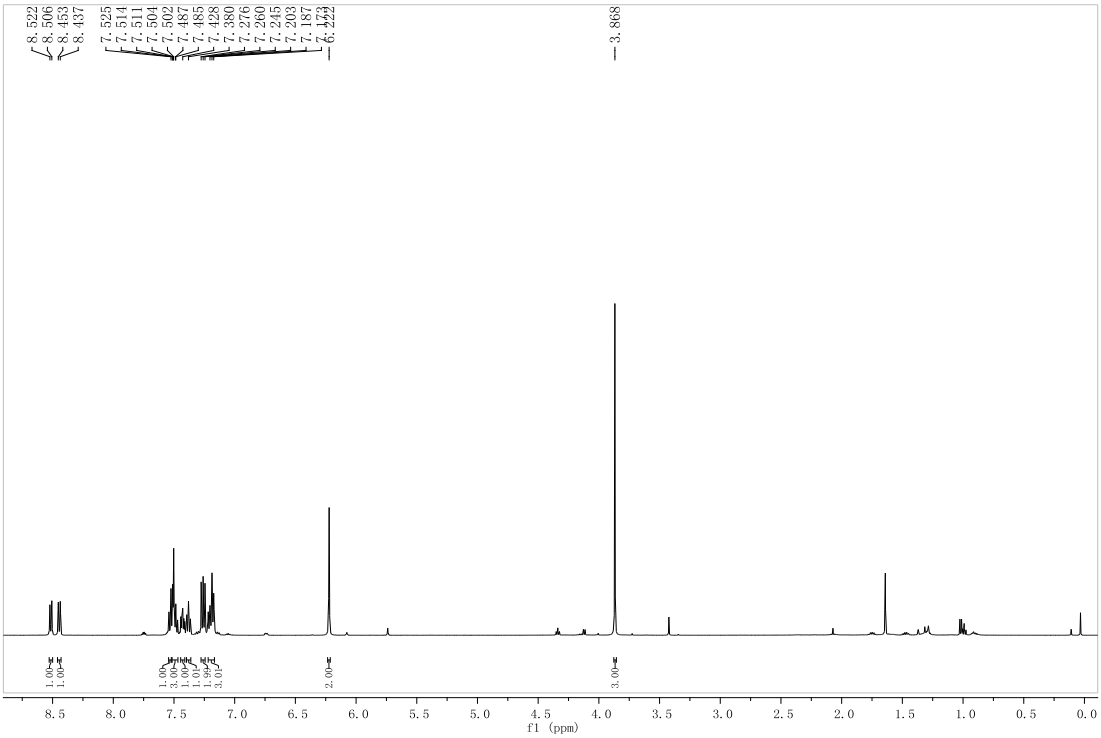




7-Benzyl-5-methyl-5H-indolo[2,3-c]quinolin-6(7H)-one **3b**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 90% yield, m.p. 165-167 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46-7.50 (m, 3H), 7.41-7.45 (m, 1H), 7.36-7.40 (m, 1H), 7.24-7.28 (m, 2H), 7.20 (dd, *J* = 15.5, 7.5 Hz, 3H), 6.22 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 140.3, 138.4, 136.3, 128.6, 127.1, 126.5, 126.5, 126.4, 126.1, 125.9, 123.8, 122.8, 122.5, 122.1, 121.2, 119.6, 119.1, 115.0, 111.3, 47.9, 29.4. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{19}N_2O$ ($[M+H]^+$): 339.1492, found 339.1503.


8.522
8.506
8.453
8.437
7.525
7.514
7.511
7.504
7.502
7.487
7.485
7.428
7.380
7.276
7.260
7.245
7.203
7.187
7.173
6.222
3.868
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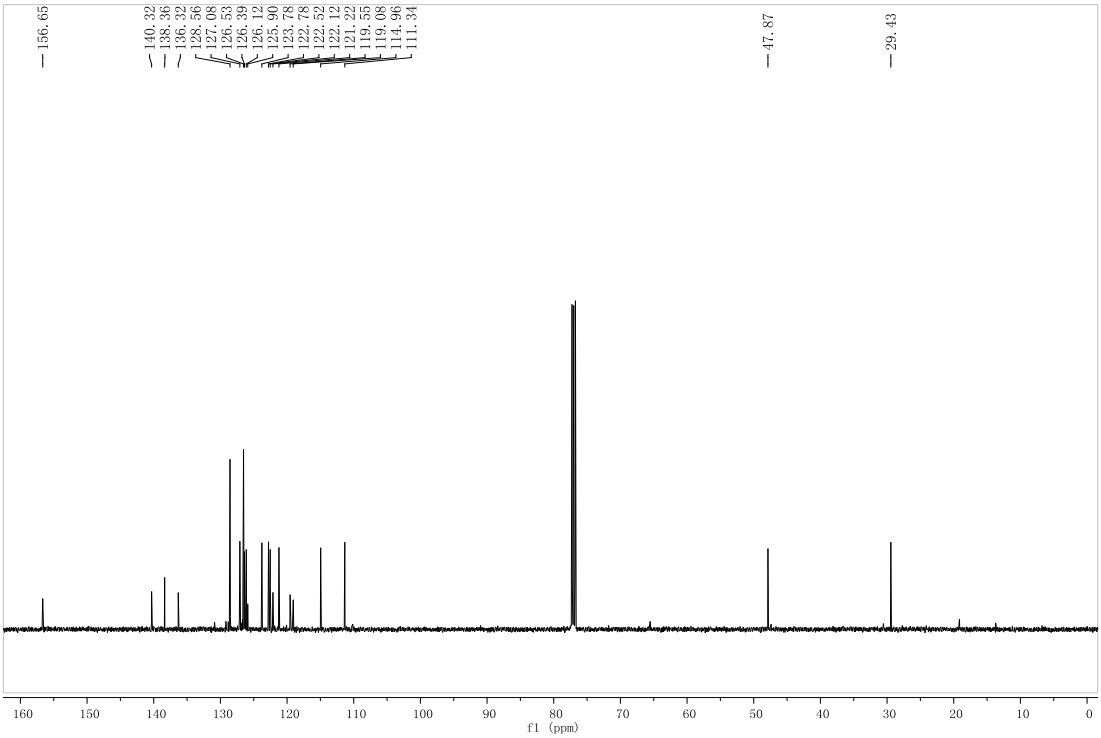
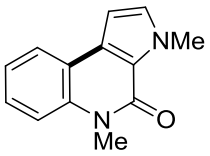
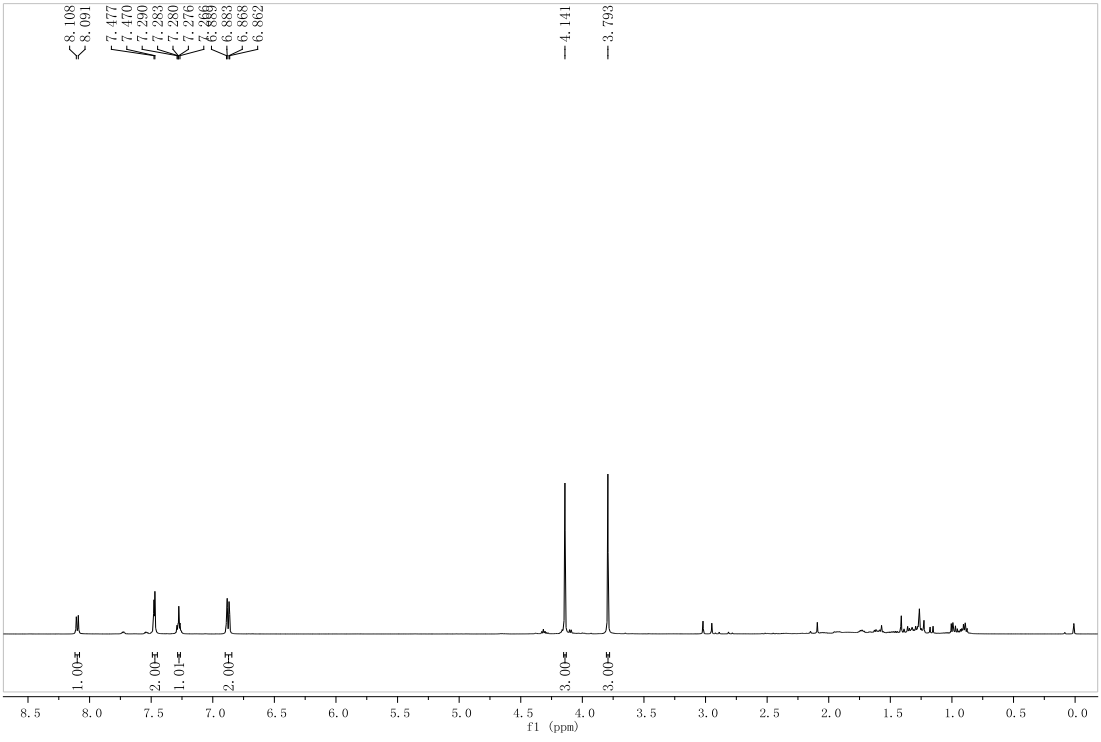
1.08
1.06
3.08
1.01
1.96
3.01
2.00
3.00
f1 (ppm)

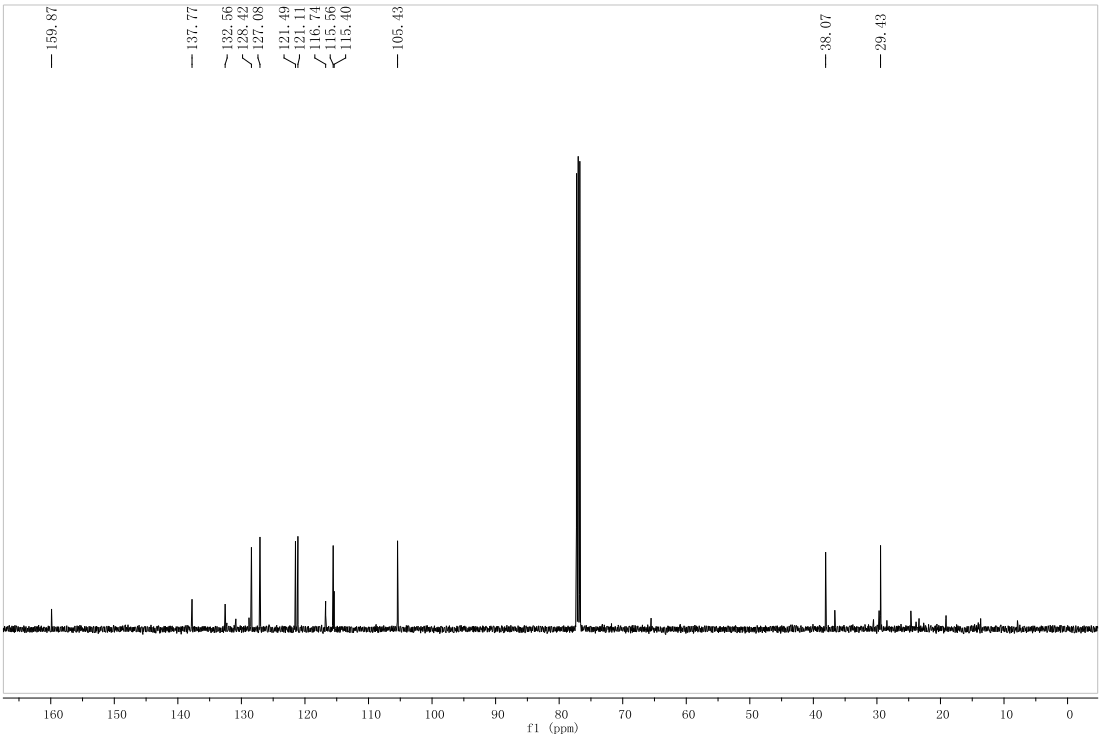

156.65
140.32
138.36
136.32
128.56
127.08
126.53
126.39
126.12
125.90
123.78
122.78
122.52
122.12
121.22
119.55
119.08
114.96
111.34
47.87
29.43
f1 (ppm)

3-Benzyl-5-methyl-3H-pyrrolo[2,3-c]quinolin-4(5H)-one **3c**

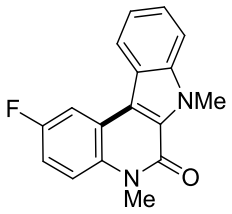


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, 64% yield, m.p. 140-142 ^{o}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 3.5 Hz, 2H), 7.28 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.88 (dd, *J* = 10.5, 3.0 Hz, 2H), 4.14 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 137.8, 132.6, 128.4, 127.1, 121.5, 121.1, 116.7, 115.6, 115.4, 105.4, 38.1, 29.4. HRMS *m/z* (ESI+): Calculated for $C_{13}H_{12}N_2O$ ($[M+H]^+$): 213.1022, found 213.1031.

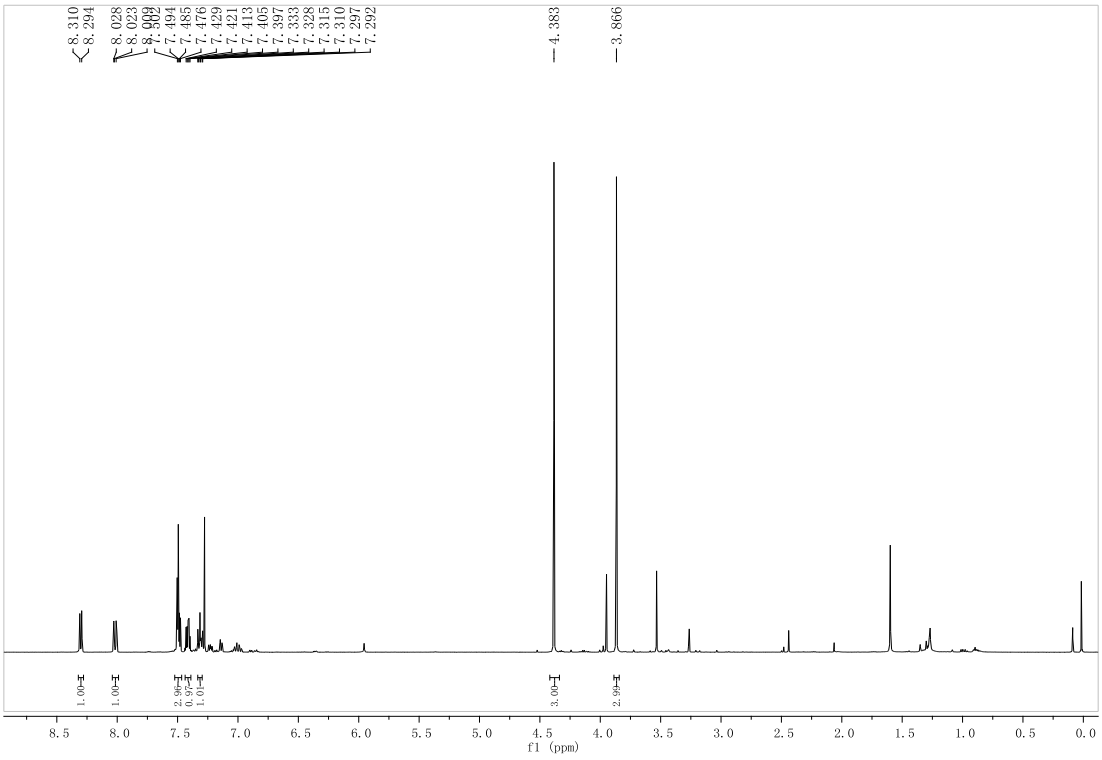




7-benzyl-2-fluoro-5-methyl-5H-indolo[2,3-c]quinolin-6(7H)-one **3d**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 80% yield, m.p. 236-239 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.02 (dd, *J* = 9.5, 1.5 Hz, 1H), 7.49 (dd, *J* = 8.5, 4.0 Hz, 3H), 7.39-7.44 (m, 1H), 7.30 -7.33 (m, 1H), 4.38 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 137.3, 136.1, 129.4, 127.2 (d, *J* = 31.3 Hz), 126.6, 126.3, 123.3, 122.7, 119.4, 115.0, 114.6 (d, *J* = 26.3 Hz), 111.4 (d, *J* = 8.8 Hz), 107.6 (d, *J* = 23.8 Hz), 107.5, 31.8, 29.4. HRMS *m/z* (ESI+): Calculated for $C_{17}H_{14}FN_2O$ ($[M+H]^+$): 281.1085, found 281.1079.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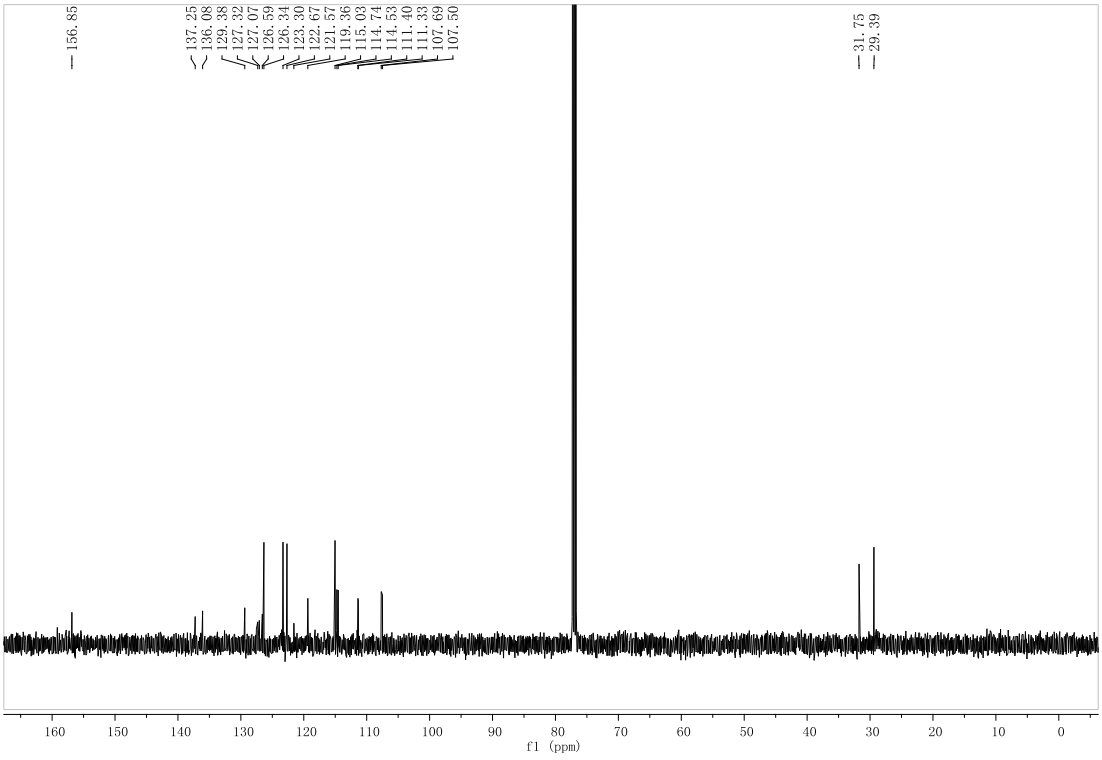
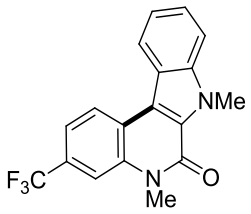
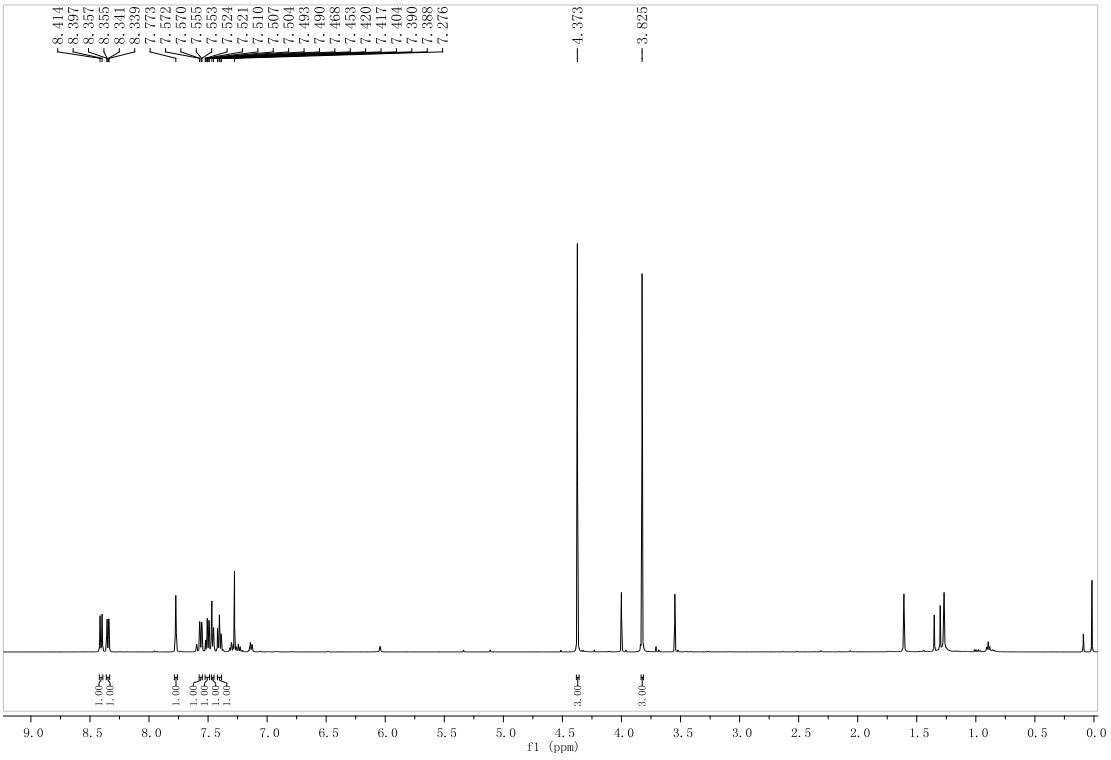
8.028
8.023
7.494
7.485
7.476
7.429
7.421
7.413
7.405
7.397
7.333
7.328
7.315
7.310
7.297
7.292
4.383
3.866
1.00
1.04
2.96
0.97
1.04
3.00
2.99
f1 (ppm)

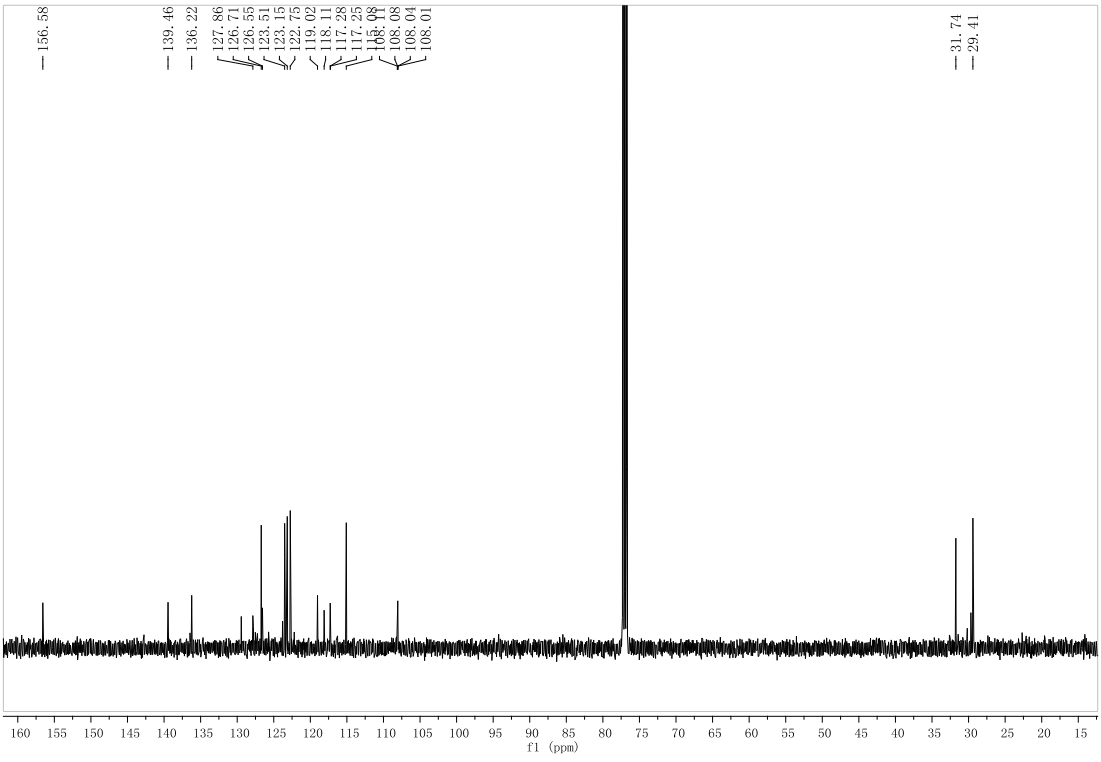

156.85
137.25
136.08
129.38
127.32
127.07
126.59
126.34
123.30
122.67
121.57
119.36
115.03
114.74
114.53
111.40
111.33
107.69
107.50
31.75
29.39
f1 (ppm)

5,7-dimethyl-3-(trifluoromethyl)-5H-indolo[2,3-c]quinolin-6(7H)-one **3e**

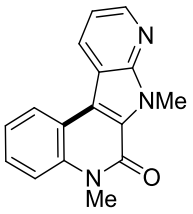


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 83% yield, m.p. 216-218 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 1H), 8.35 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.77 (s, 1H), 7.56 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.49-7.58 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.39-7.42 (m, 1H), 4.37 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 139.5, 136.2, 129.4, 127.9, 126.7, 126.6, 123.5, 123.2, 122.8, 119.0, 118.1, 117.27 (q, *J* = 6.6 Hz), 115.1, 108.0 (q, *J* = 8.5 Hz), 31.7 29.4. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{13}F_3N_2O$ ($[M+H]^+$): 331.1053, found 331.1058.

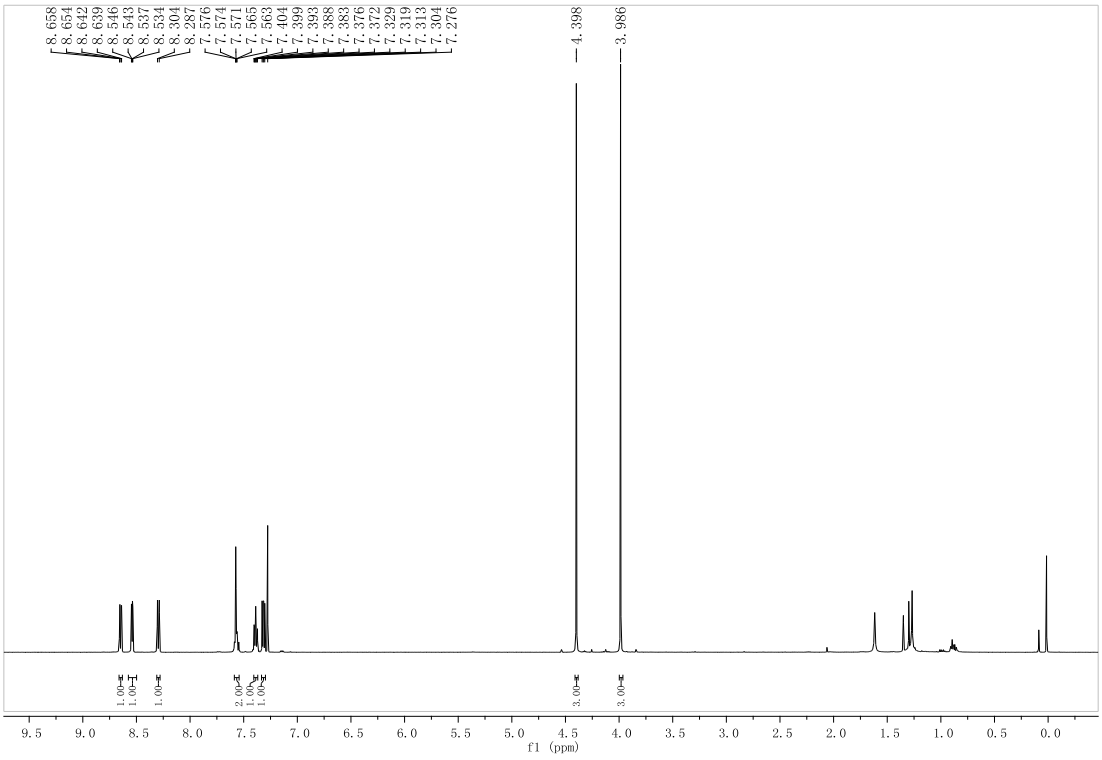




5,7-dimethyl-5H-pyrido[3',2':4,5]pyrrolo[2,3-c]quinolin-6(7H)-one **3f**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, 92% yield, m.p. 226-228 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.54 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.54-7.59 (m, 2H), 7.39 (ddd, *J* = 8.0, 5.5, 2.5 Hz, 1H), 7.32 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.40 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 146.8, 145.1, 140.7, 131.0, 126.6, 126.2, 122.2, 121.8, 121.3, 118.1, 116.6, 115.1, 110.8, 31.6, 28.5. HRMS *m/z* (ESI+): Calculated for $C_{16}H_{14}N_3O$ ($[M+H]^+$): 213.1022, found 213.1031.


8.658
8.654
8.642
8.639
8.546
8.543
8.537
8.534
8.304
8.287
7.576
7.574
7.571
7.565
7.563
7.404
7.399
7.393
7.388
7.383
7.376
7.372
7.329
7.319
7.313
7.304
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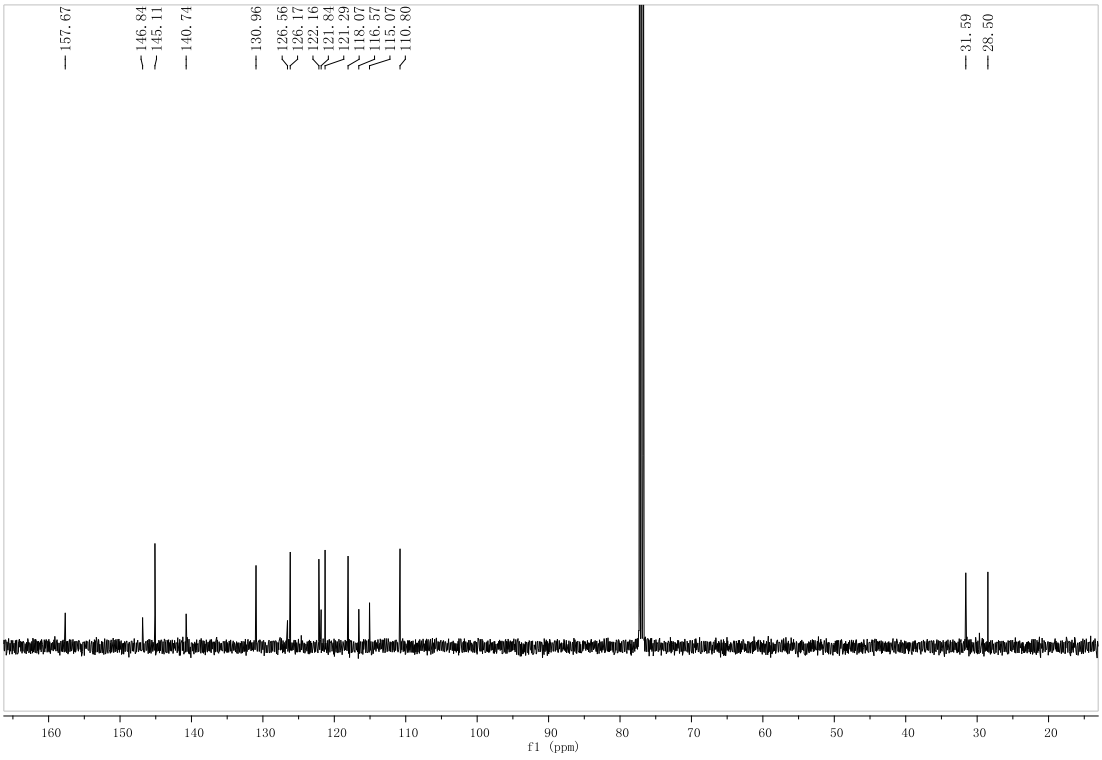
1.00
1.00
3.00
3.00
f1 (ppm)


157.67
146.84
145.11
140.74
130.96
126.56
126.17
122.16
121.84
121.29
118.07
116.57
115.07
110.80
31.59
28.50
f1 (ppm)

5. References

1. A. S. Kyei, K. Tchabanenko, J. E. Baldwin and R. M. Adlington, *Tetrahedron Lett*. 2004, **45**, 8931.

2. M. Sechi, M. Derudas, R. Dallocchio, A. Dess ì, A. Bacchi , L. Sannia, F. Carta, M. Palomba, O. Ragab, C. Chan, R. Shoemaker, S. Sei, R. Dayam and N. Neamati, *J. Med. Chem.*, 2004, **47**, 5298.