

**Synthesis of 2,3'-Spirobi[indolin]-2-ones Enabled by a Tandem Nucleophilic
Benzoylation/C(sp²)-N Cross-Coupling Reaction Sequence**

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Supporting Information

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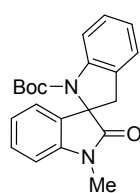
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1. General methods

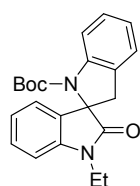
Reagents were purchased from commercial sources and were directly used unless otherwise noted. ^1H NMR and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded in CDCl_3 . ^1H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl_3 at 7.26 ppm). Data are reported as the follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl_3 at 77.16 ppm).

2. General procedure for synthesis of 2,3'-spirobi[indoline]-2-ones **3**

In a 5 mL of flame-dried vial with a stir bar, the mixture of 3-aminooxindoles **1** (0.2 mmol), 2-bromobenzyl bromides **2** (0.22 mmol, 1.1 equiv.), CuBr (0.01 mmol, 1.4 mg), $t\text{BuONa}$ (0.8 mmol, 76.8 mg, 4.0 equiv.) in 2.0 mL of DMF was stirred at 100 or 170 °C for specified time. After completion of the reaction indicated by TLC, 10.0 mL of water was added into the mixture and the solution was extracted with EtOAc (6×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, concentrated, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford the products **3**. It was noted that the reaction mixtures could be directly purified by flash column chromatography on silica gel when the reactions were performed in mesitylene.

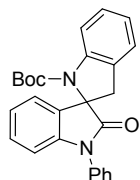


Tert-butyl 1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3a: Yellow oil; 60.3 mg, yield 86%. ^1H NMR (400 MHz, CDCl_3): δ 1.12 (s, 9H), 3.21 (d, $J = 16.7$ Hz, 1H), 3.25 (s, 3H), 3.65 (d, $J = 16.1$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 6.98-7.03 (m, 2H), 7.10-7.15 (m, 2H), 7.24-7.27 (m, 1H), 7.30-7.34 (m, 1H), 7.98 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 26.6, 27.9, 41.6, 68.8, 81.5, 108.1, 115.1, 121.8, 123.0, 123.2, 124.5, 127.0, 128.1, 129.2, 132.6, 142.7, 143.3, 151.1, 176.7. HRMS (ESI-TOF) calcd. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{NaO}_3$ [$\text{M} + \text{Na}$] $^+$ 373.1523; found: 373.1523.

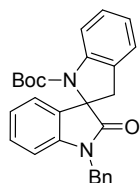


Tert-butyl 1-ethyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3b: White solid; 40.1 mg, yield 55%; mp 206.7-207.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (s, 9H), 1.33 (t, $J = 7.2$ Hz, 3H), 3.23 (d, $J = 16.0$ Hz, 1H), 3.44-3.50 (m, 1H), 3.63 (d,

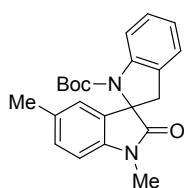
$J = 16.1$ Hz, 1H), 4.05-4.12 (m, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 6.97-7.02 (m, 2H), 7.10-7.14 (m, 2H), 7.23 (d, $J = 7.7$ Hz, 1H), 7.28-7.32 (m, 1H), 7.98 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.1, 27.9, 35.2, 41.7, 68.8, 81.6, 108.2, 115.1, 121.9, 123.0, 124.4, 127.0, 128.1, 129.1, 132.8, 142.0, 143.5, 151.1, 176.2. HRMS (ESI-TOF) calcd. for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$ 365.1860; found: 365.1869.



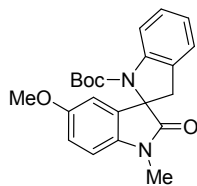
Tert-butyl 2-oxo-1-phenyl-2,3'-spirobi[indoline]-1'-carboxylate 3c: White solid; 42.1 mg, yield 51%; mp 202.4-203.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.17 (s, 9H), 3.39 (d, $J = 16.1$ Hz, 1H), 3.75 (d, $J = 16.1$ Hz, 1H), 7.02-7.09 (m, 3H), 7.16-7.22 (m, 3H), 7.28 (s, 1H), 7.39-7.42 (m, 1H), 7.55-7.56 (m, 4H), 8.04 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 28.1, 42.5, 69.0, 82.0, 109.7, 115.2, 122.2, 123.1, 123.8, 124.5, 125.6, 126.8, 127.8, 128.2, 129.0, 129.6, 132.7, 134.5, 142.2, 143.5, 151.2, 175.8. HRMS (ESI-TOF) calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 435.1679; found: 435.1686.



Tert-butyl 1-benzyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3d: Yellow oil; 40.1 mg, yield 47%. ^1H NMR (400 MHz, CDCl_3): δ 1.12 (s, 9H), 3.31 (d, $J = 16.0$ Hz, 1H), 3.73 (d, $J = 16.0$ Hz, 1H), 4.41 (d, $J = 15.4$ Hz, 1H), 5.42 (d, $J = 15.4$ Hz, 1H), 6.78 (d, $J = 7.1$ Hz, 1H), 6.96-7.01 (m, 1H), 7.03 (d, $J = 7.3$ Hz, 1H), 7.12-7.17 (m, 2H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 10.0$ Hz, 2H), 7.36 (s, 4H), 8.02 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 27.8, 41.8, 44.1, 68.8, 81.7, 109.0, 115.1, 121.8, 123.0, 123.2, 124.5, 126.9, 127.6, 127.9, 128.1, 129.0, 129.1, 132.7, 135.9, 141.9, 143.5, 151.1, 176.8. HRMS (ESI-TOF) calcd. for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 449.1836; found: 449.1851.



Tert-butyl 1,5-dimethyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3e: Colourless oil; 51.0 mg, yield 70%. ^1H NMR (400 MHz, CDCl_3): δ 1.13 (s, 9H), 2.24 (s, 3H), 3.19 (d, $J = 16.1$ Hz, 1H), 3.22 (s, 3H), 3.63 (d, $J = 16.1$ Hz, 1H), 6.73 (d, $J = 7.8$ Hz, 1H), 6.91 (s, 1H), 6.99-7.03 (m, 1H), 7.10 (d, $J = 7.7$ Hz, 1H), 7.14 (d, $J = 7.4$ Hz, 1H), 7.23-7.27 (m, 1H), 7.98 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.1, 26.6, 27.9, 41.6, 68.9, 81.5, 107.9, 115.1, 122.5, 123.0, 124.5, 127.2, 128.1, 129.4, 132.6, 132.9, 140.3, 143.4, 151.2, 176.6. HRMS (ESI-TOF) calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 387.1679; found: 387.1686.



Tert-butyl 5-methoxy-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate

3f: White solid; 54.0 mg, yield 71%; mp 163.2-164.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.14 (s, 9H), 3.20 (d, *J* = 16.2 Hz, 1H), 3.22 (s, 3H), 3.64 (d, *J* =

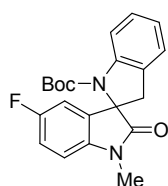
16.2 Hz, 1H), 3.70 (s, 3H), 6.71 (d, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H),

6.82-6.84 (m, 1H), 6.98-7.02 (m, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* =

8.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.6, 27.9, 41.6, 56.0, 69.1, 81.5, 108.6, 109.0,

113.6, 115.1, 123.0, 124.5, 127.0, 128.1, 133.7, 136.2, 143.3, 151.0, 156.6, 176.4. HRMS (ESI-

TOF) calcd. for C₂₂H₂₄N₂NaO₄ [M + Na]⁺ 403.1628; found: 403.1626.



Tert-butyl 5-fluoro-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3g:

White solid; 59.0 mg, yield 80%; mp 190.3-192.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.15 (s, 9H), 3.19 (d, *J* = 16.5 Hz, 1H), 3.24 (s, 3H), 3.65 (d, *J* = 16.0

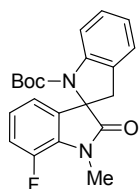
Hz, 1H), 6.76-6.78 (m, 1H), 6.87 (d, *J* = 6.5 Hz, 1H), 7.00-7.04 (m, 2H), 7.14 (d,

J = 7.0 Hz, 1H), 7.24-7.27 (m, 1H), 7.97 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.8,

27.9, 41.6, 68.9, 81.8, 108.7 (d, *J* = 7.6 Hz, 1C), 110.1 (d, *J* = 24.8 Hz, 1C), 115.2, 115.4 (d, *J* =

23.4 Hz, 1C), 123.2, 124.5, 126.6, 128.3, 134.0, 138.7, 143.2, 150.8, 159.6 (d, *J* = 240.9 Hz, 1C),

176.4. HRMS (ESI-TOF) calcd. for C₂₁H₂₁FN₂NaO₃ [M + Na]⁺ 391.1428; found: 391.1436.



Tert-butyl 7-fluoro-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3h:

Yellow solid; 41.3 mg, yield 56%; mp 161.2-162.7 °C. ¹H NMR (400 MHz, CDCl₃):

δ 1.18 (s, 9H), 3.20 (d, *J* = 16.1 Hz, 1H), 3.46 (s, 3H), 3.64 (d, *J* = 16.0 Hz, 1H),

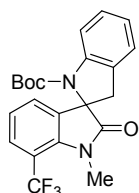
6.88-6.94 (m, 2H), 6.99-7.07 (m, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.23-7.27 (m, 1H),

7.97 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 27.9, 28.4, 41.7, 68.8, 81.8, 115.1, 117.1

(d, *J* = 19.2 Hz, 1C), 117.7, 123.1, 123.9 (d, *J* = 6.2 Hz, 1C), 124.5, 126.7, 128.2, 129.8, 135.4,

143.2, 147.7 (d, *J* = 242.3 Hz, 1C), 150.9, 176.3. HRMS (ESI-TOF) calcd. for C₂₁H₂₁FN₂NaO₃ [M

+ Na]⁺ 391.1428; found: 391.1424.



Tert-butyl 1-methyl-2-oxo-7-(trifluoromethyl)-2,3'-spirobi[indoline]-1'-

carboxyl -ate 3i: Yellow oil; 49.4 mg, yield 59%. ¹H NMR (400 MHz, CDCl₃): δ

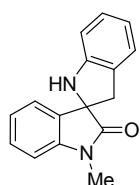
1.14 (s, 9H), 3.19 (d, *J* = 16.1 Hz, 1H), 3.47 (s, 3H), 3.65 (d, *J* = 15.9 Hz, 1H),

7.03-7.08 (m, 2H), 7.15 (d, *J* = 6.3 Hz, 1H), 7.28 (s, 2H), 7.61 (d, *J* = 7.4 Hz, 1H),

7.98 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 27.8, 28.4, 42.1, 67.1, 82.1, 112.6 (q, *J* =

33.2 Hz, 1C), 115.1, 122.3, 122.6, 123.3, 124.6, 125.2, 126.5, 127.0 (q, *J* = 5.9 Hz, 1C), 128.4,

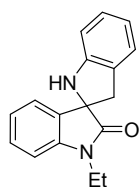
135.2, 140.5, 143.2, 150.7, 176.3. HRMS (ESI-TOF) calcd. for $C_{22}H_{21}F_3N_2NaO_3$ $[M + Na]^+$ 441.1397; found: 441.1401.



1-Methyl-2,3'-spirobi[indolin]-2-one 3j: Yellow solid; 31.0 mg, yield 62%; mp

259.9-262.1 °C. 1H NMR (400 MHz, $CDCl_3$): δ 3.23 (s, 3H), 3.25 (d, $J = 15.8$ Hz, 1H), 3.61 (d, $J = 15.8$ Hz, 1H), 4.18 (s, 1H), 6.71 (d, $J = 7.6$ Hz, 1H), 6.79-6.86 (m, 2H), 6.99-7.02 (m, 1H), 7.08-7.14 (m, 2H), 7.24 (d, $J = 7.7$ Hz, 1H), 7.29-7.33 (m,

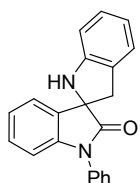
1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 41.9, 68.3, 108.5, 110.0, 119.8, 122.8, 123.4, 124.7, 126.7, 127.9, 129.6, 133.1, 142.6, 149.9, 178.5. HRMS (ESI-TOF) calcd. for $C_{16}H_{15}N_2O$ $[M + H]^+$ 251.1179; found: 251.1182.



1-Ethyl-2,3'-spirobi[indolin]-2-one 3k: Yellow solid; 44.9 mg, yield 85%; mp

252.1-253.2 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.30 (t, $J = 7.1$ Hz, 3H), 3.25 (d, $J = 15.7$ Hz, 1H), 3.62 (d, $J = 15.8$ Hz, 1H), 3.78-3.81 (m, 2H), 4.19 (s, 1H), 6.71 (d, $J = 7.6$ Hz, 1H), 6.78-6.83 (m, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.98-7.01 (m, 1H), 7.09-

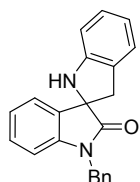
7.14 (m, 2H), 7.25 (d, $J = 7.4$ Hz, 1H), 7.29-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.8, 35.1, 42.0, 68.3, 108.6, 110.1, 119.8, 123.0, 123.2, 124.7, 126.8, 127.9, 129.5, 133.4, 141.7, 149.9, 178.1. HRMS (ESI-TOF) calcd. for $C_{17}H_{17}N_2O$ $[M + H]^+$ 265.1335; found: 265.1339.



1-Phenyl-2,3'-spirobi[indolin]-2-one 3l: White solid; 29.4 mg, yield 47%; mp

223.8-224.6 °C. 1H NMR (400 MHz, $CDCl_3$): δ 3.39 (d, $J = 15.8$ Hz, 1H), 3.75 (d, $J = 15.7$ Hz, 1H), 4.35 (s, 1H), 6.75 (d, $J = 7.5$ Hz, 1H), 6.82-6.88 (m, 2H), 7.03-7.07

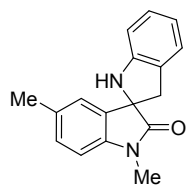
(m, 1H), 7.11-7.17 (m, 2H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 7.4$ Hz, 1H), 7.40-7.47 (m, 3H), 7.52-7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.6, 68.4, 109.8, 110.1, 119.9, 123.2, 123.9, 124.8, 126.5, 126.6, 128.0, 128.2, 129.5, 129.8, 133.0, 134.4, 142.4, 149.9, 177.9. HRMS (ESI-TOF) calcd. for $C_{21}H_{17}N_2O$ $[M + H]^+$ 313.1335; found: 313.1347.



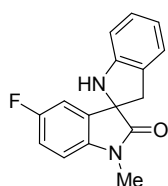
1-Benzyl-2,3'-spirobi[indolin]-2-one 3m: Yellow solid; 48.3 mg, yield 74%; mp

211.9-213.4 °C. 1H NMR (400 MHz, $CDCl_3$): δ 3.32 (d, $J = 15.7$ Hz, 1H), 3.69 (d, $J = 15.8$ Hz, 1H), 4.26 (s, 1H), 4.89 (d, $J = 15.5$ Hz, 1H), 4.96 (d, $J = 15.6$ Hz, 1H),

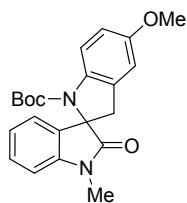
6.73-6.76 (m, 2H), 6.81-6.85 (m, 1H), 6.95-6.99 (m, 1H), 7.10-7.21 (m, 3H), 7.25-7.29 (m, 2H), 7.33 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.2, 44.1, 68.3, 109.5, 110.1, 119.9, 123.0, 123.4, 124.8, 126.7, 127.5, 127.9, 128.0, 129.0, 129.5, 133.1, 135.8, 141.7, 149.9, 178.7. HRMS (ESI-TOF) calcd. for $C_{22}H_{18}N_2NaO$ $[M + Na]^+$ 349.1311; found: 349.1323.



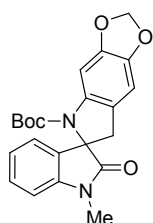
1,5-Dimethyl-2,3'-spirobi[indolin]-2-one 3n: Yellow solid; 40.2 mg, yield 76%; mp 251.8-252.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.26 (s, 3H), 3.21 (s, 3H), 3.24 (d, *J* = 15.8 Hz, 1H), 3.61 (d, *J* = 15.8 Hz, 1H), 4.17 (s, 1H), 6.70-6.75 (m, 2H), 6.80-6.83 (m, 1H), 7.06 (s, 1H), 7.09-7.12 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 21.1, 26.6, 42.0, 68.3, 108.2, 110.0, 119.8, 123.6, 124.7, 126.8, 127.9, 129.8, 133.1, 133.2, 140.2, 149.9, 178.5. HRMS (ESI-TOF) calcd. for C₁₇H₁₇N₂O [M + H]⁺ 265.1335; found: 265.1339.



5-Fluoro-1-methyl-2,3'-spirobi[indolin]-2-one 3o: White solid; 39.2 mg, yield 73%; mp 190.9-192.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.22 (s, 3H), 3.23 (d, *J* = 15.8 Hz, 1H), 3.61 (d, *J* = 15.8 Hz, 1H), 4.21 (s, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.76-6.83 (m, 2H), 6.98-7.02 (m, 2H), 7.08-7.13 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 26.7, 42.0, 68.5, 109.1 (d, *J* = 7.9 Hz, 1C), 110.1, 111.1 (d, *J* = 24.7 Hz, 1C), 115.7 (d, *J* = 23.4 Hz, 1C), 120.0, 124.8, 126.3, 128.1, 134.6 (d, *J* = 7.6 Hz, 1C), 138.4, 149.6, 159.7 (d, *J* = 240.9 Hz, 1C), 178.2. HRMS (ESI-TOF) calcd. for C₁₆H₁₃FN₂NaO [M + Na]⁺ 291.0904; found: 291.0911.

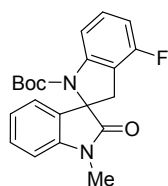


Tert-butyl 5'-methoxy-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3p: Yellow solid; 50.2 mg, yield 66%; mp 168.7-169.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.11 (s, 9H), 3.16 (d, *J* = 16.2 Hz, 1H), 3.24 (s, 3H), 3.61 (d, *J* = 16.1 Hz, 1H), 3.78 (s, 3H), 6.72 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.98-7.01 (m, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.29-7.33 (m, 1H), 7.87 (d, *J* = 8.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.6, 27.9, 41.6, 55.8, 68.9, 81.3, 108.1, 110.9, 112.7, 115.5, 121.8, 123.2, 128.4, 129.2, 132.6, 137.0, 142.8, 151.1, 156.0, 176.6. HRMS (ESI-TOF) calcd. for C₂₂H₂₄N₂NaO₄ [M + Na]⁺ 403.1628; found: 403.1636.



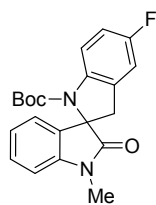
Tert-butyl 5'-methyl-2'-oxospiro[[1,3]dioxolo[4,5-f]indole-6,3'-indoline]-5(7H)-carboxylate 3q: Yellow solid; 51.3 mg, yield 65%; mp 228.0-229.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.10 (s, 9H), 3.09 (d, *J* = 15.8 Hz, 1H), 3.23 (s, 3H), 3.54 (d, *J* = 15.7 Hz, 1H), 5.93 (d, *J* = 7.6 Hz, 2H), 6.61 (s, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 7.00-7.02 (m, 1H), 7.13 (d, *J* = 6.8 Hz, 1H), 7.29-7.31 (m, 1H), 7.63 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.6, 27.9, 41.3, 69.4, 81.4, 98.4, 101.4, 104.9, 108.1, 118.7, 121.7, 123.2, 129.3, 132.5, 137.6, 142.7, 143.5, 147.5, 151.0, 176.5. HRMS (ESI-TOF) calcd. for

C₂₂H₂₂N₂NaO₅ [M + Na]⁺ 417.1421; found: 417.1428.



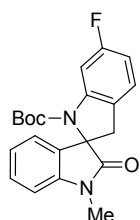
Tert-butyl 4'-fluoro-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3r:

White solid; 48.0 mg, yield 65%; mp 162.8-164.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.12 (s, 9H), 3.23 (d, *J* = 16.4 Hz, 1H), 3.25 (s, 3H), 3.62 (d, *J* = 16.4 Hz, 1H), 6.71-6.75 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 7.01-7.05 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.20-7.24 (m, 1H), 7.31-7.35 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.7, 27.8, 42.8, 69.3, 82.0, 108.3, 109.9 (d, *J* = 19.4 Hz, 1C), 111.0, 113.9, 121.9, 123.4, 125.8, 129.5, 130.1 (d, *J* = 7.6 Hz, 1C), 132.2, 142.8, 150.9, 158.9 (d, *J* = 245.1 Hz, 1C), 176.2. HRMS (ESI-TOF) calcd. for C₂₁H₂₁FN₂NaO₃ [M + Na]⁺ 391.1428; found: 391.1436.



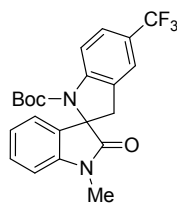
Tert-butyl 5'-fluoro-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3s:

White solid; 58.2 mg, yield 79%; mp 191.8-192.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.11 (s, 9H), 3.18 (d, *J* = 16.4 Hz, 1H), 3.24 (s, 3H), 3.62 (d, *J* = 16.4 Hz, 1H), 6.84-6.87 (m, 2H), 6.92-6.96 (m, 1H), 7.00-7.04 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.31-7.35 (m, 1H), 7.91-7.94 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.6, 27.9, 41.3, 69.1, 81.7, 108.2, 111.8 (d, *J* = 24.4 Hz, 1C), 114.3 (d, *J* = 22.7 Hz, 1C), 115.7 (d, *J* = 8.1 Hz, 1C), 121.8, 123.3, 128.8 (d, *J* = 8.6 Hz, 1C), 129.4, 132.2, 139.4, 142.7, 151.0, 159.2 (d, *J* = 239.3 Hz, 1C), 176.4. HRMS (ESI-TOF) calcd. for C₂₁H₂₁FN₂NaO₃ [M + Na]⁺ 391.1428; found: 391.1441.



Tert-butyl 6'-fluoro-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3t:

Yellow oil; 58.2 mg, yield 79%. ¹H NMR (400 MHz, CDCl₃): δ 1.11 (s, 9H), 3.16 (d, *J* = 15.9 Hz, 1H), 3.24 (s, 3H), 3.58 (d, *J* = 15.9 Hz, 1H), 6.67-6.72 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 7.00-7.06 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.31-7.34 (m, 1H), 7.74 (d, *J* = 10.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.6, 27.8, 40.8, 69.6, 82.0, 103.5 (d, *J* = 29.6 Hz, 1C), 108.2, 109.4 (d, *J* = 22.8 Hz, 1C), 121.8, 122.3, 123.3, 124.8 (d, *J* = 9.9 Hz, 1C), 129.4, 132.2, 142.7, 144.7 (d, *J* = 12.3 Hz, 1C), 150.9, 163.1 (d, *J* = 241.0 Hz, 1C), 176.3. HRMS (ESI-TOF) calcd. for C₂₁H₂₁FN₂NaO₃ [M + Na]⁺ 391.1428; found: 391.1437.

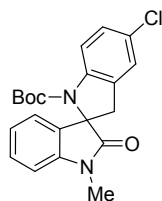


Tert-butyl 1-methyl-2-oxo-5'-(trifluoromethyl)-2,3'-spirobi[indoline]-1'-car-

boxylate 3u: Yellow solid; 52.0 mg, yield 62%; mp 169.7-170.8 °C. ¹H NMR

(400 MHz, CDCl₃): δ 1.13 (s, 9H), 3.26 (s, 3H), 3.26 (d, *J* = 16.4 Hz, 1H), 3.67 (d, *J* = 16.4 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 7.01-7.05 (m, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 7.32-7.36 (m, 1H), 7.39 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H);

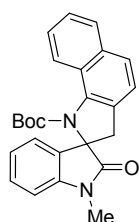
^{13}C NMR (100 MHz, CDCl_3): δ 26.6, 27.8, 41.1, 69.1, 82.3, 108.4, 114.8, 121.6, 121.7, 123.4, 124.5 (q, $J = 270.0$ Hz, 1C), 125.0 (q, $J = 32.0$ Hz, 1C), 125.8 (q, $J = 4.0$ Hz, 1C), 127.9, 129.6, 131.9, 142.8, 146.3, 150.8, 176.1. HRMS (ESI-TOF) calcd. for $\text{C}_{22}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$ 419.1577; found: 419.1573.



Tert-butyl 5'-chloro-1-methyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3v:

White solid; 56.5 mg, yield 74%; mp 190.9-192.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (s, 9H), 3.18 (d, $J = 16.4$ Hz, 1H), 3.24 (s, 3H), 3.62 (d, $J = 16.3$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 7.00-7.04 (m, 1H), 7.09-7.12 (m, 2H), 7.22 (d,

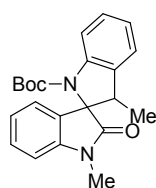
$J = 8.7$ Hz, 1H), 7.31-7.35 (m, 1H), 7.91 (d, $J = 8.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 26.7, 27.9, 41.2, 69.0, 81.9, 108.3, 116.0, 121.8, 123.4, 124.6, 128.0, 128.1, 129.0, 129.5, 132.1, 142.1, 142.8, 150.9, 176.3. HRMS (ESI-TOF) calcd. for $\text{C}_{21}\text{H}_{21}\text{ClN}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 407.1133; found: 407.1141.



Tert-butyl 1'-methyl-2'-oxospiro[benzo[g]indole-2,3'-indoline]-1(3H)-carboxylate 3w:

Yellow oil; 44.1 mg, yield 55%. ^1H NMR (400 MHz, CDCl_3): δ 1.28 (s, 9H), 3.27 (d, $J = 16.0$ Hz, 1H), 3.31 (s, 3H), 3.92 (d, $J = 16.0$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.94-6.98 (m, 1H), 7.06 (d, $J = 7.4$ Hz, 1H), 7.29-7.34 (m, 2H), 7.43-

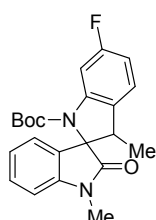
7.48 (m, 2H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 7.4$ Hz, 1H), 8.04 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 26.7, 27.8, 43.0, 70.6, 82.0, 108.2, 122.1, 123.2, 123.3, 124.9, 125.2, 125.3, 125.5, 125.6, 128.4, 129.4, 132.6, 134.6, 138.4, 142.5, 152.0, 176.3. HRMS (ESI-TOF) calcd. for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 423.1679; found: 423.1697.



Tert-butyl 1,3'-dimethyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3x:

Yellow oil; 48.1 mg, yield 66%, dr 4:1. ^1H NMR (400 MHz, CDCl_3): δ (major) 0.93 (d, $J = 7.1$ Hz, 3H), 1.13 (s, 9H), 3.25 (s, 3H), 3.90 (q, $J = 6.9$ Hz, 1H), 6.84-6.95 (m, 3H), 7.01-7.10 (m, 2H), 7.20-7.23 (m, 1H), 7.28-7.32 (m, 1H), 7.97 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (major) 13.3, 26.7, 27.8, 45.1, 74.3, 81.4, 108.0,

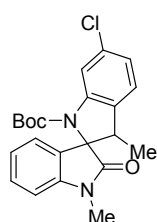
114.8, 122.6, 122.8, 123.0, 123.3, 128.9, 129.4, 131.0, 132.7, 142.8, 143.2, 151.2, 177.1. HRMS (ESI-TOF) calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 387.1679; found: 387.1681.



Tert-butyl 6'-fluoro-1,3'-dimethyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3y:

Yellow solid; 39.8 mg, yield 52%, dr 2:1; mp 108.7-110.2 °C. ^1H NMR (400 MHz, CDCl_3): δ (major + minor) 0.91 (d, $J = 7.0$ Hz, 3H), 1.12 (s, 9H), 3.21 (s,

1H), 3.25 (s, 2H), 3.84 (q, $J = 7.1$ Hz, 1H), 6.69-6.73 (m, 1H), 6.82-6.90 (m, 2H), 6.94-7.01 (m, 2H), 7.30-7.34 (m, 1H), 7.74 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (major + minor) 13.5, 14.5, 26.7, 27.8, 44.6, 74.2, 74.9, 82.0, 103.2 (d, $J = 29.5$ Hz, 1C), 103.3 (d, $J = 29.4$ Hz, 1C), 108.1, 109.3 (d, $J = 22.8$ Hz, 1C), 122.1, 122.7, 123.2, 123.3, 123.4, 127.5, 128.1, 129.1, 129.6, 143.2, 143.4, 144.1, 144.2, 151.0, 151.2, 163.2 (d, $J = 241.2$ Hz, 1C), 173.9, 176.7. HRMS (ESI-TOF) calcd. for $\text{C}_{22}\text{H}_{23}\text{FN}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 405.1585; found: 405.1592.



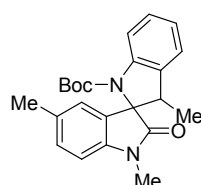
Tert-butyl 6'-chloro-1,3'-dimethyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate

3z: White solid; 55.8 mg, yield 70%, dr 3:1; mp 79.3-81.2 °C. ^1H NMR (400 MHz,

CDCl_3): δ (major + minor) 0.91 (d, $J = 7.1$ Hz, 3H), 1.12 (s, 9H), 3.20 (s, 0.75H),

3.25 (s, 2.25H), 3.84 (q, $J = 7.0$ Hz, 1H), 6.84-6.89 (m, 2H), 6.93-6.99 (m, 3H),

7.30-7.33 (m, 1H), 8.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (major + minor) 13.4, 14.3, 26.7, 27.8, 44.7, 74.0, 74.6, 82.0, 108.2, 115.2, 115.3, 122.0, 122.7, 122.9, 123.0, 123.2, 123.3, 123.6, 127.4, 129.2, 129.6, 131.3, 134.0, 143.2, 143.4, 143.9, 151.0, 173.8, 176.7. HRMS (ESI-TOF) calcd. for $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 421.1289; found: 421.1297.



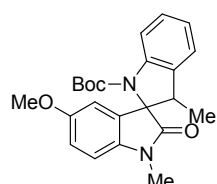
Tert-butyl 1,3',5-trimethyl-2-oxo-2,3'-spirobi[indoline]-1'-carboxylate 3a':

Yellow solid; 52.2 mg, yield 69%, dr 3:1; mp 86.6-88.1 °C. ^1H NMR (400

MHz, CDCl_3): δ (major + minor) 0.93 (d, $J = 7.0$ Hz, 3H), 1.13 (s, 9H), 2.20

(s, 2.25H), 2.29 (s, 0.75H), 3.18 (s, 0.75H), 3.23 (s, 2.25H), 3.89 (q, $J = 6.8$

Hz, 1H), 6.68 (s, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 9.0$ Hz, 1H), 7.10 (d, $J = 6.7$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.98 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (major + minor) 13.3, 14.7, 21.0, 26.7, 27.8, 45.1, 73.5, 74.4, 81.4, 107.8, 114.6, 114.8, 122.7, 122.8, 123.0, 123.9, 127.8, 128.2, 129.0, 129.6, 132.2, 132.8, 140.8, 141.0, 142.9, 151.3, 174.0, 177.1. HRMS (ESI-TOF) calcd. for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 401.1836; found: 401.1842.



Tert-butyl 5-methoxy-1,3'-dimethyl-2-oxo-2,3'-spirobi[indoline]-1'-carbo-

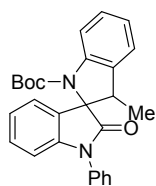
-xylate 3b': Yellow oil; 49.7 mg, yield 63%, dr 4:1. ^1H NMR (400 MHz,

CDCl_3): δ (major) 0.95 (d, $J = 7.3$ Hz, 3H), 1.15 (s, 9H), 3.23 (s, 3H), 3.67 (s,

3H), 3.90 (q, $J = 6.8$ Hz, 1H), 6.49 (s, 1H), 6.75 (d, $J = 8.9$ Hz, 1H), 6.83 (d,

$J = 9.7$ Hz, 1H), 7.03 (d, $J = 7.1$ Hz, 1H), 7.09 (d, $J = 7.0$ Hz, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.96 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (major) 13.3, 26.7, 27.9, 45.1, 56.0, 74.6, 81.5, 108.3, 110.9, 113.4, 114.8, 122.9, 123.1, 128.3, 128.9, 131.0, 136.8, 142.8, 151.2, 156.0,

176.8. HRMS (ESI-TOF) calcd. for $C_{23}H_{26}N_2NaO_4$ $[M + Na]^+$ 417.1785; found: 417.1779.



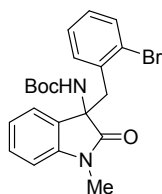
Tert-butyl 3'-methyl-2-oxo-1-phenyl-2,3'-spirobi[indoline]-1'-carboxylate 3c':

Yellow solid; 41.8 mg, yield 49%, dr 3:1; mp 107.3-108.8 °C. 1H NMR (400 MHz, $CDCl_3$): δ (major) 1.06 (d, $J = 7.0$ Hz, 3H), 1.19 (s, 9H), 3.99 (q, $J = 7.0$ Hz, 1H), 6.94-6.98 (m, 1H), 7.02-7.08 (m, 2H), 7.09-7.14 (m, 2H), 7.40-7.41 (m, 1H), 7.48-

7.57 (m, 6H), 8.01-8.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 13.8, 28.1, 46.2, 74.5, 82.0, 109.4, 109.7, 114.7, 114.9, 122.9, 123.6, 125.5, 127.9, 128.7, 129.2, 129.6, 129.7, 132.4, 133.1, 142.5, 143.0, 151.4, 176.2. HRMS (ESI-TOF) calcd. for $C_{27}H_{26}N_2NaO_3$ $[M + Na]^+$ 449.1836; found: 449.1839.

3. Control experiments

In a 5 mL of flame-dried vial with a stir bar, the mixture of 3-aminooxindole **1a** (0.2 mmol, 52.5 mg), 2-bromobenzyl bromide **2a** (0.22 mmol, 55.0 mg, 1.1 equiv.), $tBuONa$ (0.8 mmol, 76.8 mg, 4.0 equiv.) in 2.0 mL of DMF was stirred at 50 °C for 6 h. After completion of the reaction indicated by TLC, $CuBr$ (0.01 mmol, 1.4 mg) was added into the mixture and the resulting solution was continually stirred at 100°C for 16 h. Then 10.0 mL of water was added into the mixture and the solution was extracted with EtOAc (6×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, concentrated, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford compound **3a** with 82% yield (57.5 mg). It was emphasized that the non-cyclic intermediate **4** could be isolated and the characterized data was listed as follows.

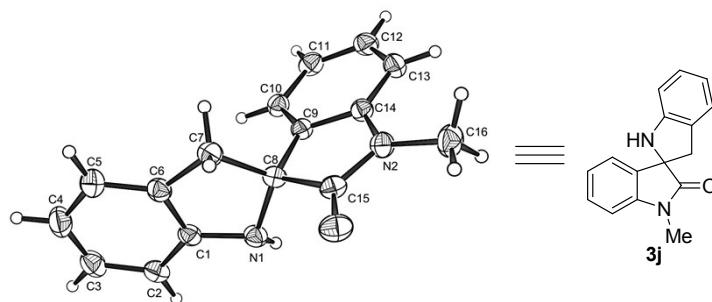


Tert-butyl (3-(2-bromobenzyl)-1-methyl-2-oxoindolin-3-yl)carbamate 4:

White solid; 59.5 mg, yield 69%; mp 143.8-145.3 °C; 1H NMR (400 MHz, $CDCl_3$), δ 1.19-1.25 (m, 9H), 3.14 (d, $J = 13.5$ Hz, 1H), 3.16 (s, 3H), 3.51 (d, $J = 13.5$ Hz, 1H), 5.54 (s, 1H), 6.69 (d, $J = 7.7$ Hz, 1H), 6.94-7.08 (m, 4H), 7.14-7.17

(m, 1H), 7.21-7.25 (m, 1H), 7.44 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ 26.5, 28.1, 41.8, 62.9, 80.5, 107.8, 122.2, 124.4, 125.9, 127.0, 128.9, 129.2, 132.4, 133.1, 133.5, 143.1, 153.9, 176.7. HRMS (ESI-TOF) calcd. for $C_{21}H_{23}BrN_2NaO_3$ $[M + Na]^+$: 453.0784; found: 453.0824.

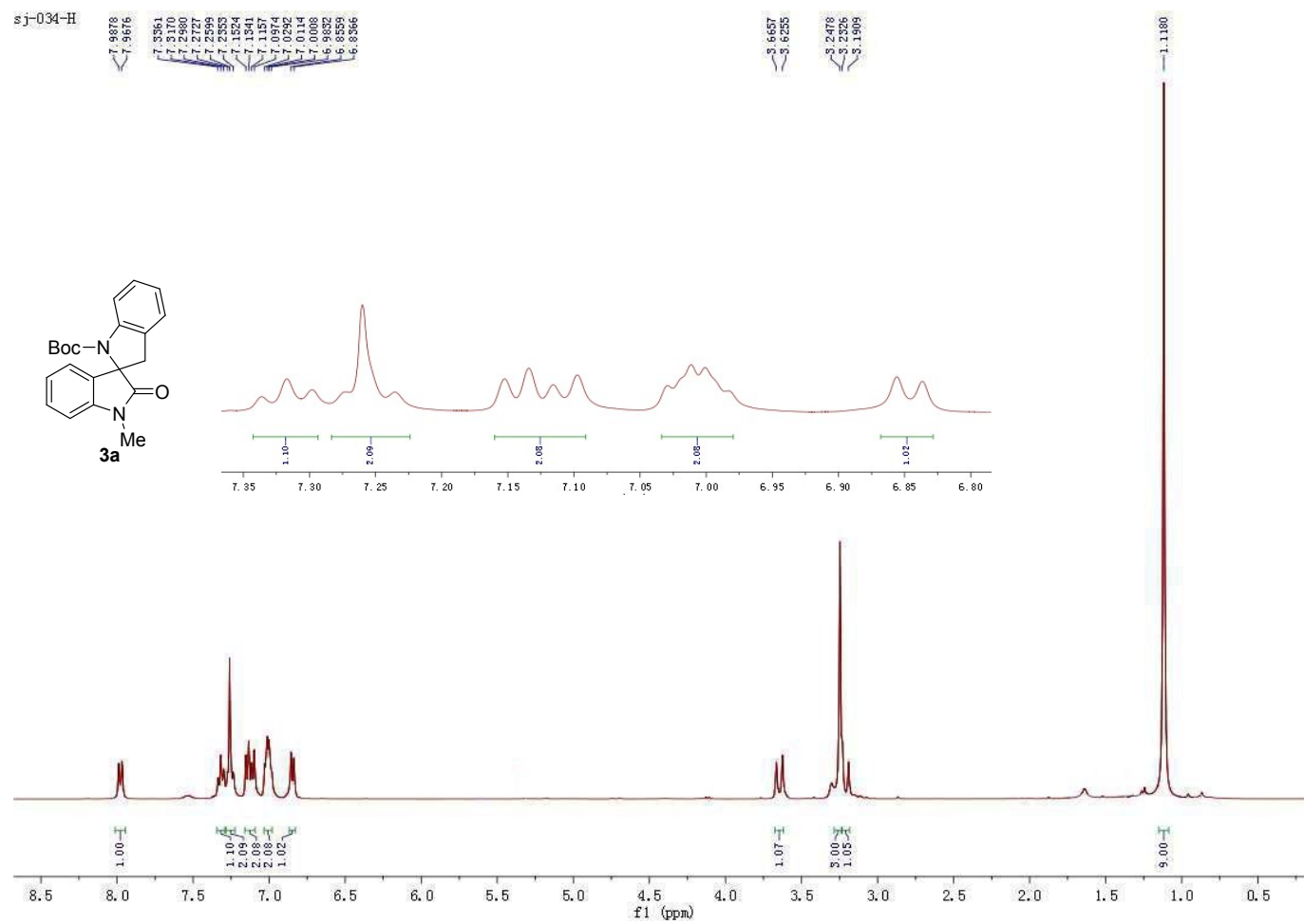
4. Crystallographic information for compound 3j



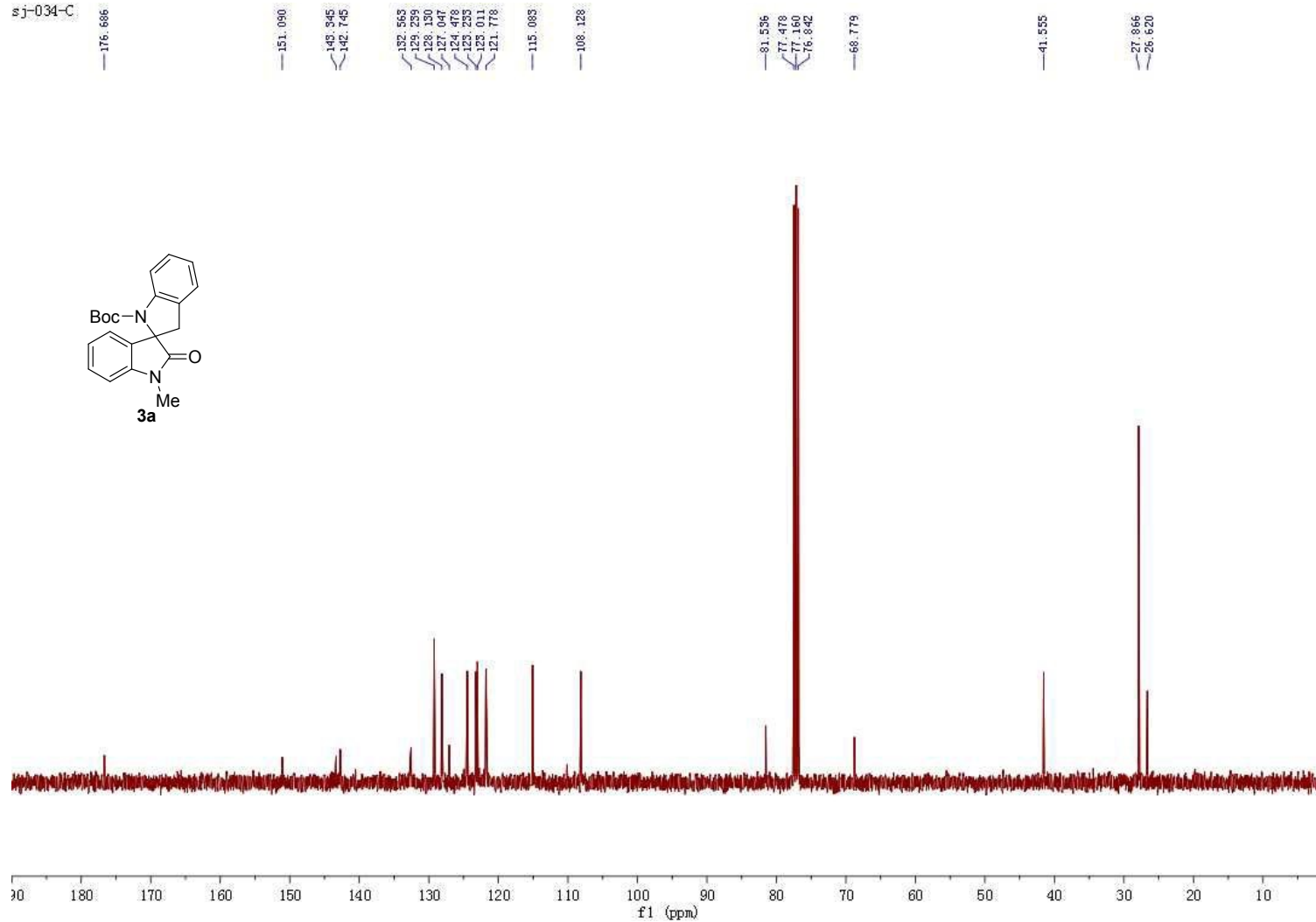
Compound 3j	Data
Empirical formula	C ₁₆ H ₁₄ N ₂ O
Formula weight	250.29
Temperature/K	290(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	5.57110(10)
b/Å	14.4715(4)
c/Å	15.8198(5)
α/°	90
β/°	94.691(2)
γ/°	90
Volume/Å ³	1271.15(6)
Z	4
ρ _{calc} /cm ³	1.308
μ/mm ⁻¹	0.660
F(000)	528.0
Crystal size/mm ³	0.390 × 0.330 × 0.320
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.294 to 140.08
Index ranges	-4 ≤ h ≤ 6, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	5613
Independent reflections	2369 [R _{int} = 0.0166, R _{sigma} = 0.0214]
Data/restraints/parameters	2369/0/173
Goodness-of-fit on F ²	1.047
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0394, wR ₂ = 0.1050
Final R indexes [all data]	R ₁ = 0.0437, wR ₂ = 0.1104
Largest diff. peak/hole / e Å ⁻³	0.19/-0.16

5. NMR spectra for compounds 3 and 4

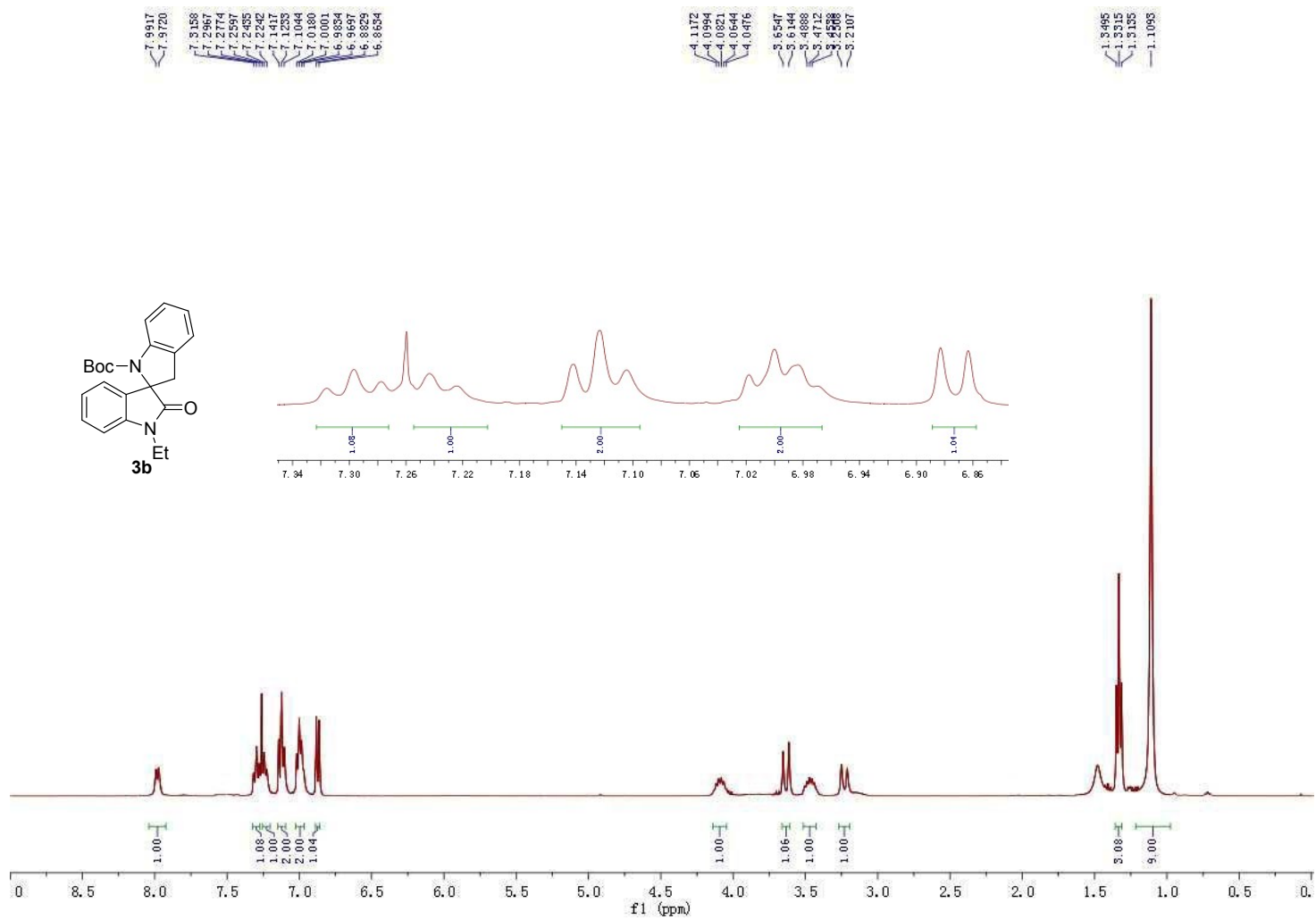
^1H and ^{13}C NMR of 3a

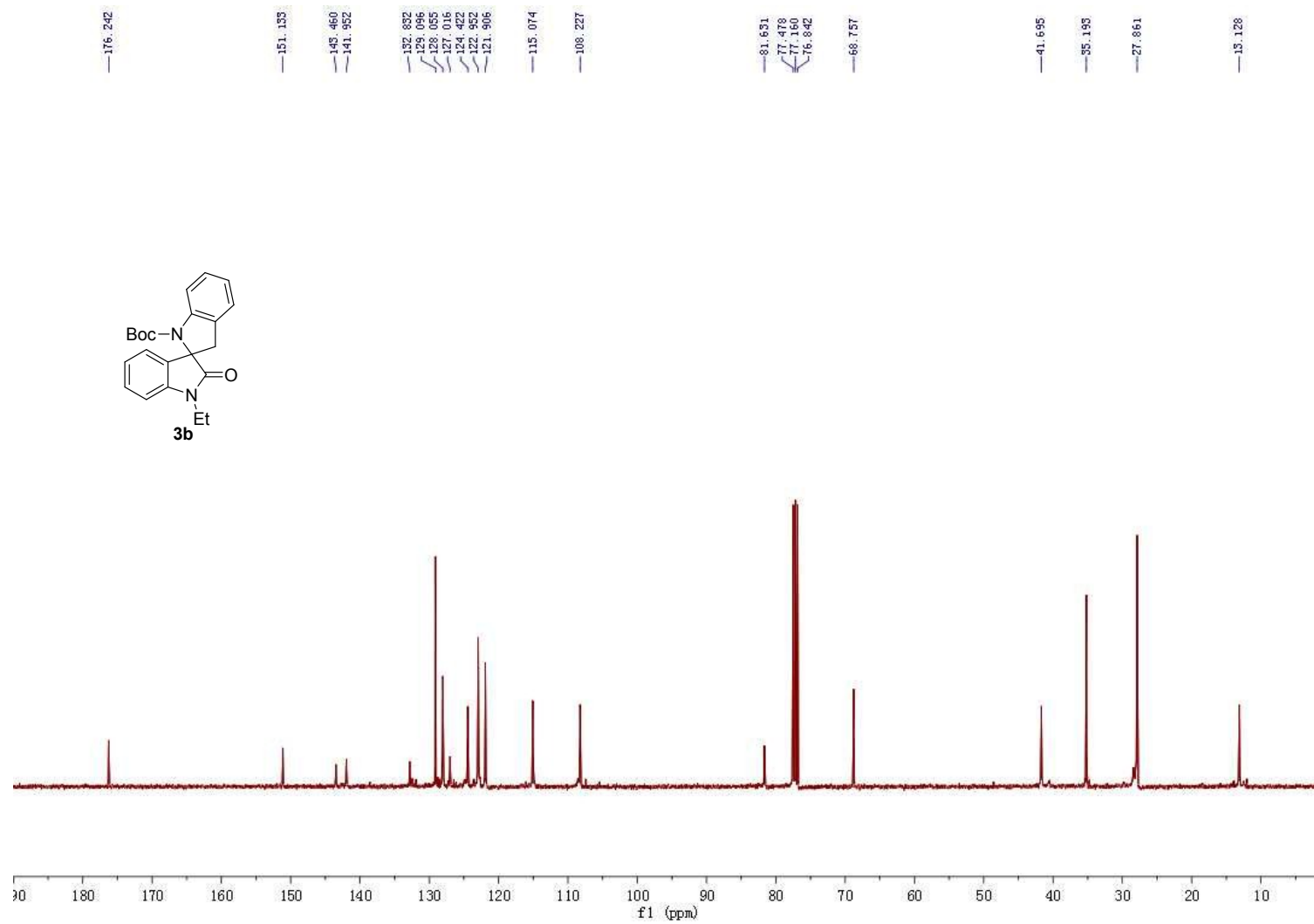


2
34-C

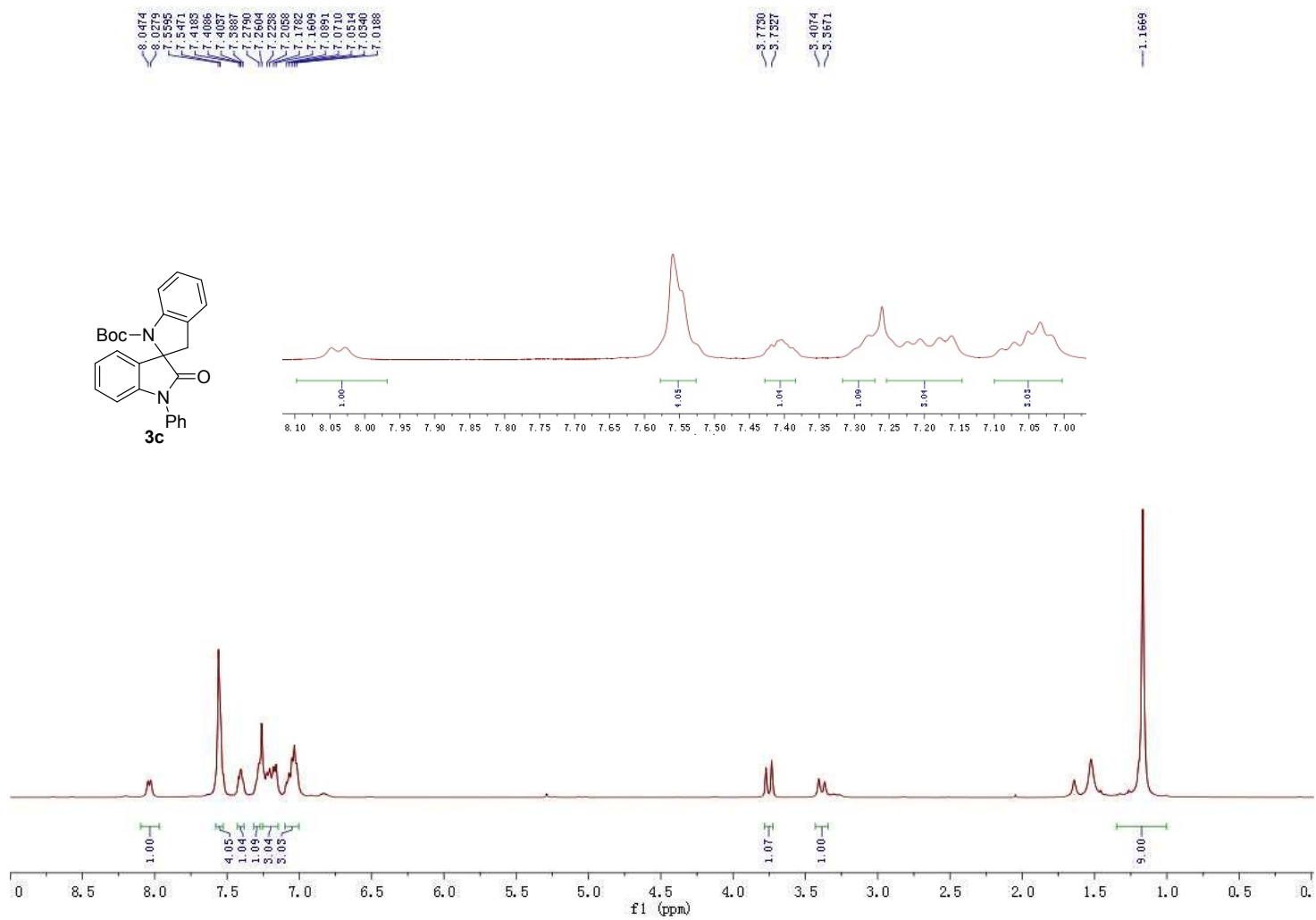


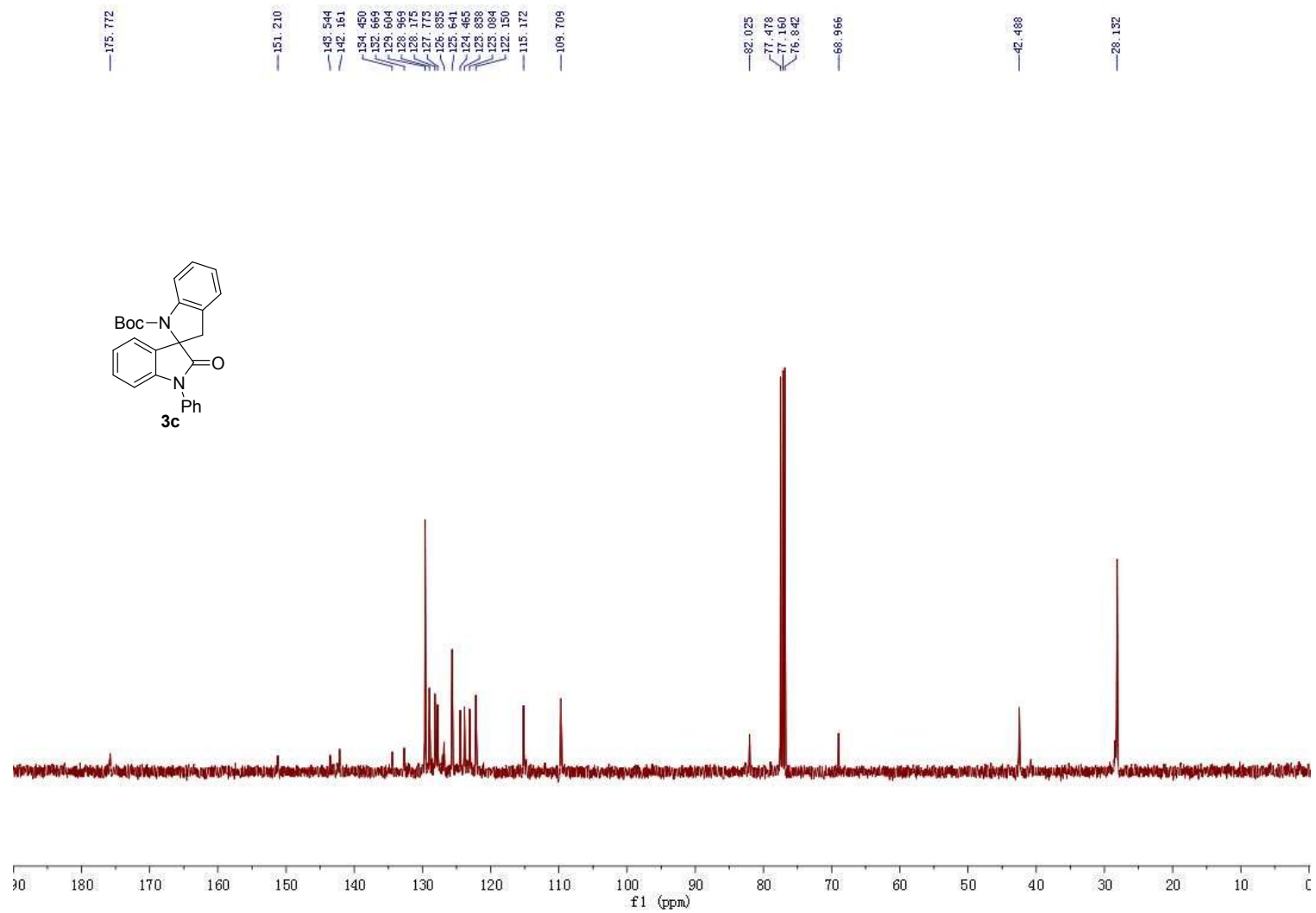
¹H and ¹³C NMR of 3b



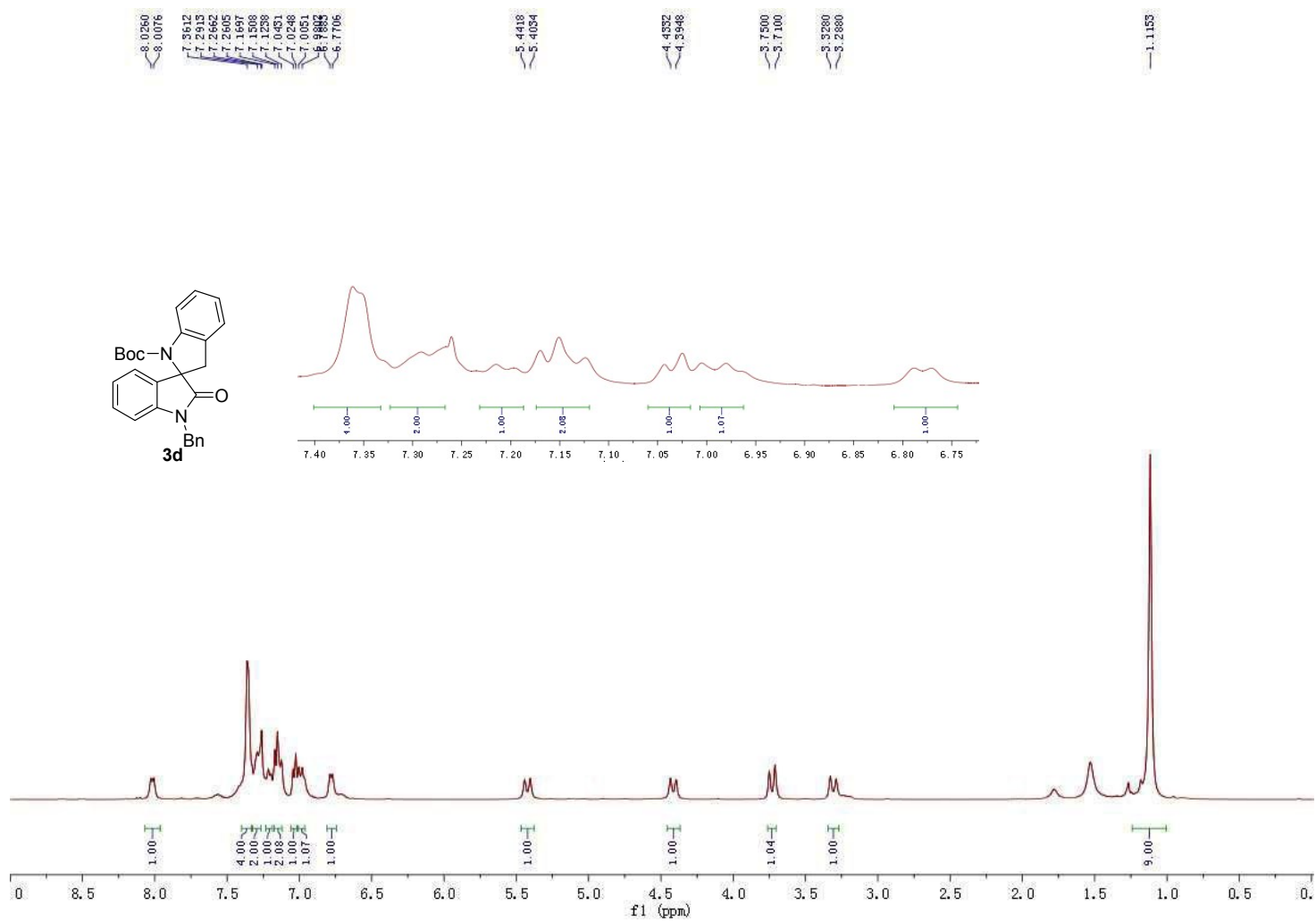


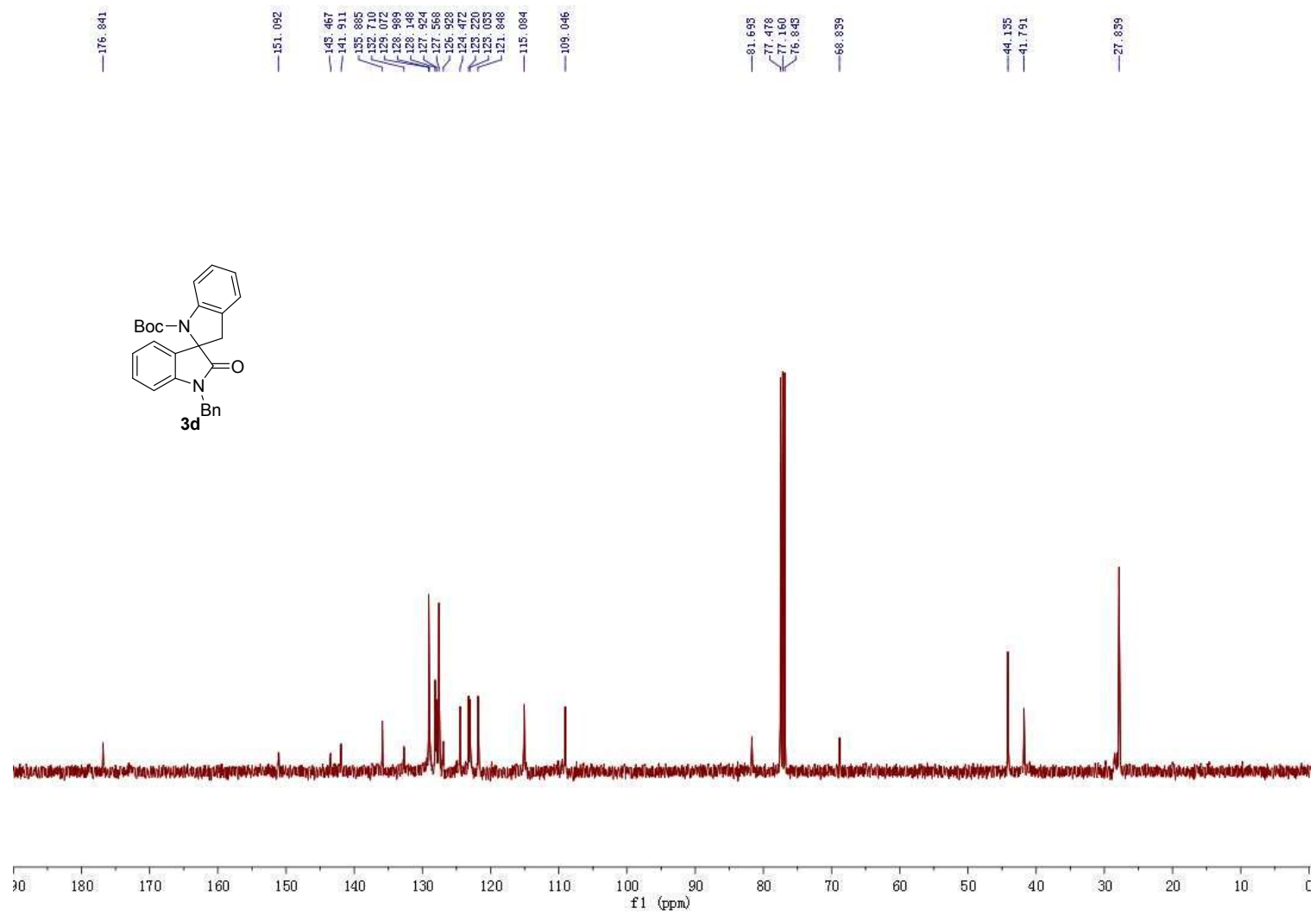
¹H and ¹³C NMR of 3c



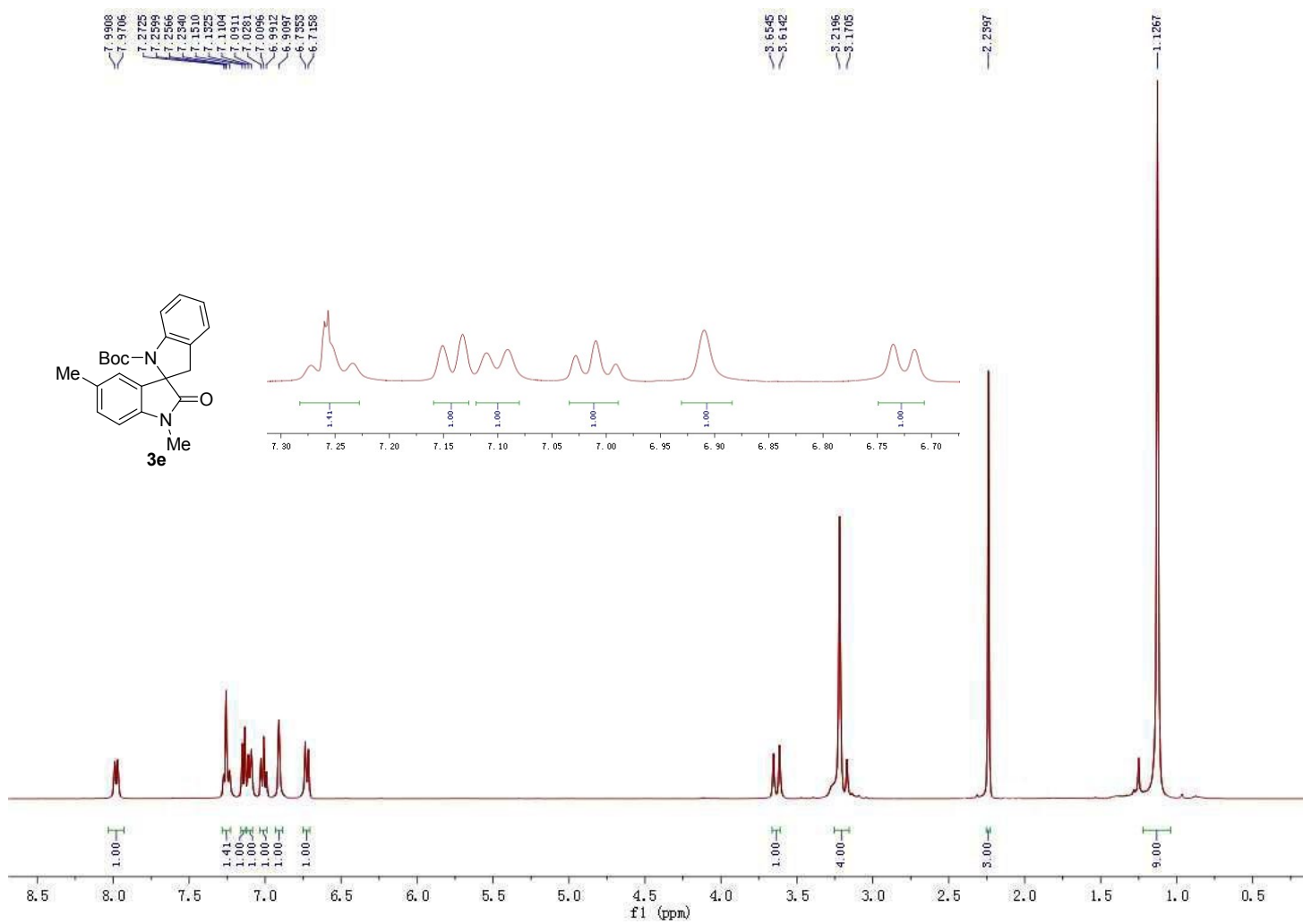


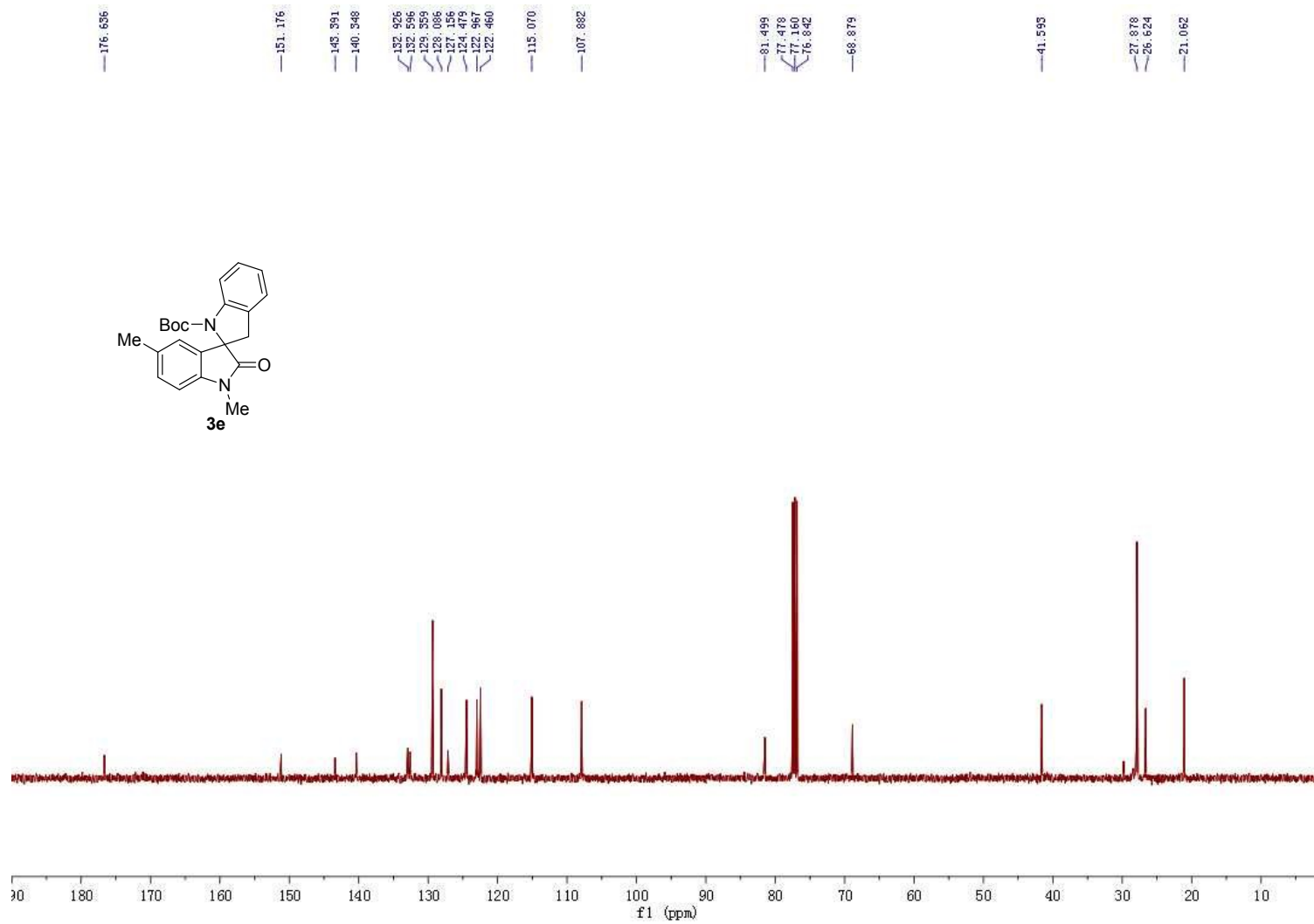
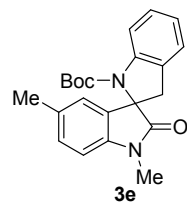
¹H and ¹³C NMR of 3d



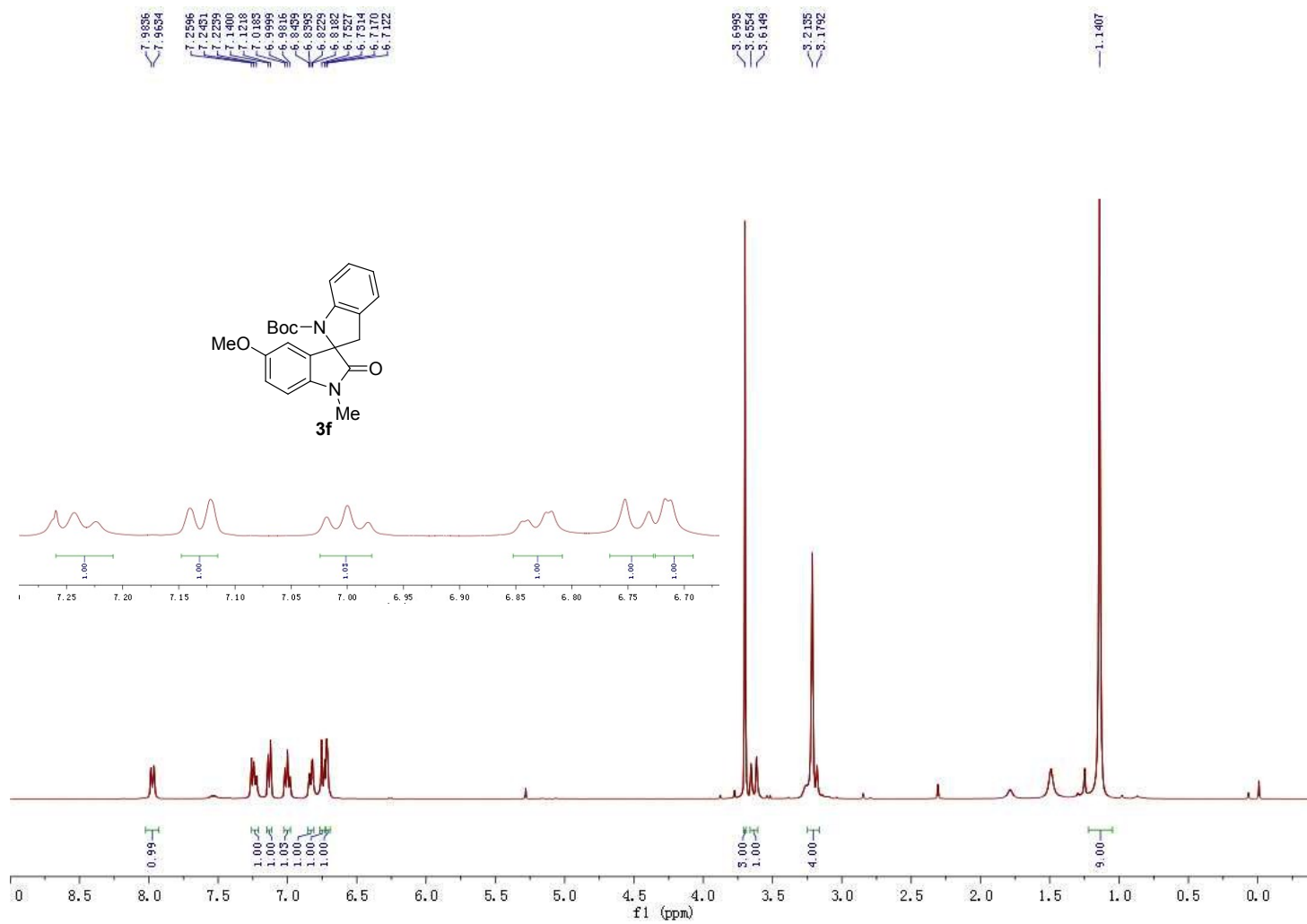


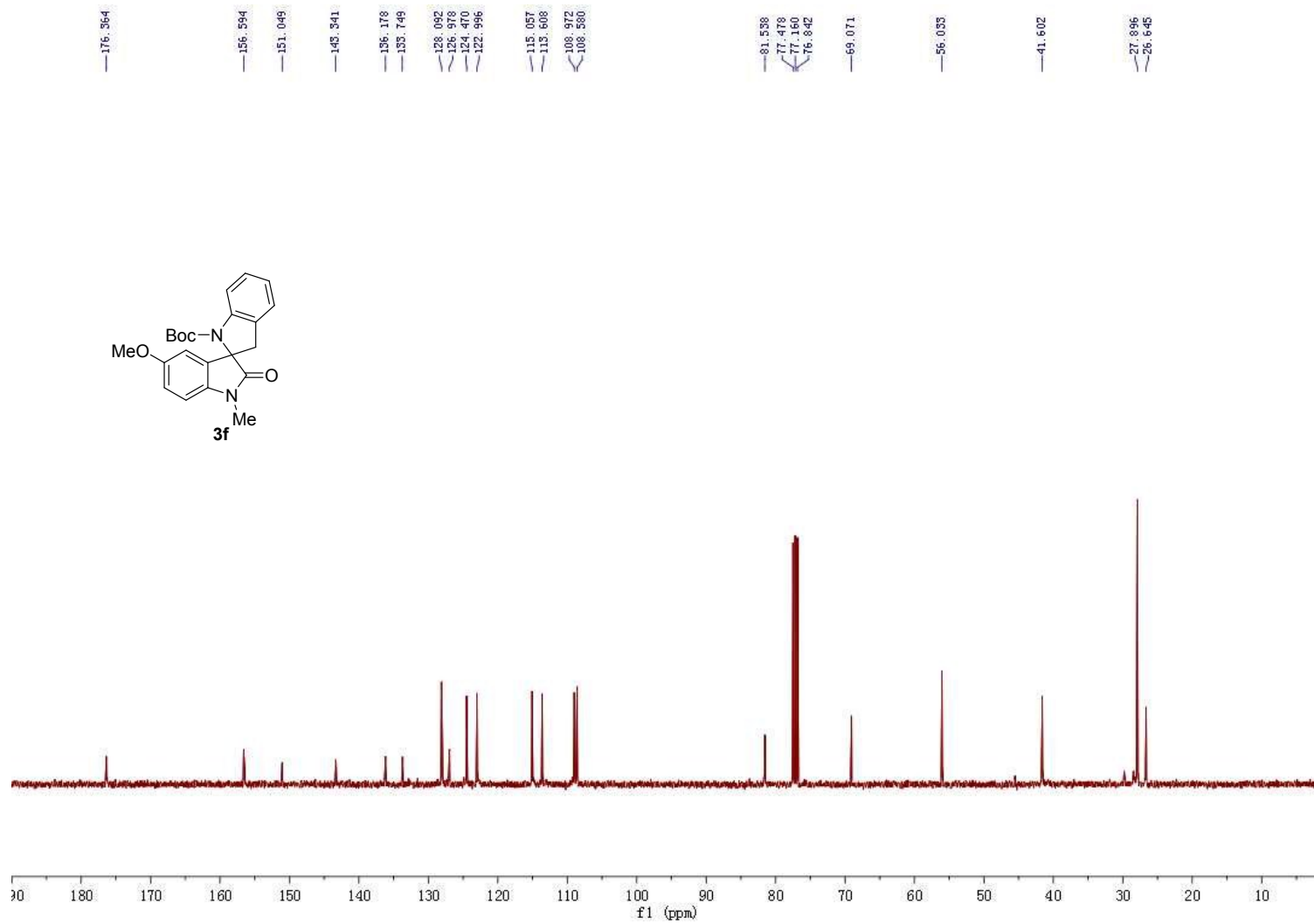
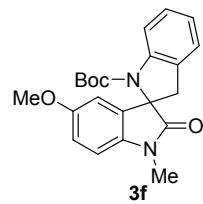
¹H and ¹³C NMR of 3e



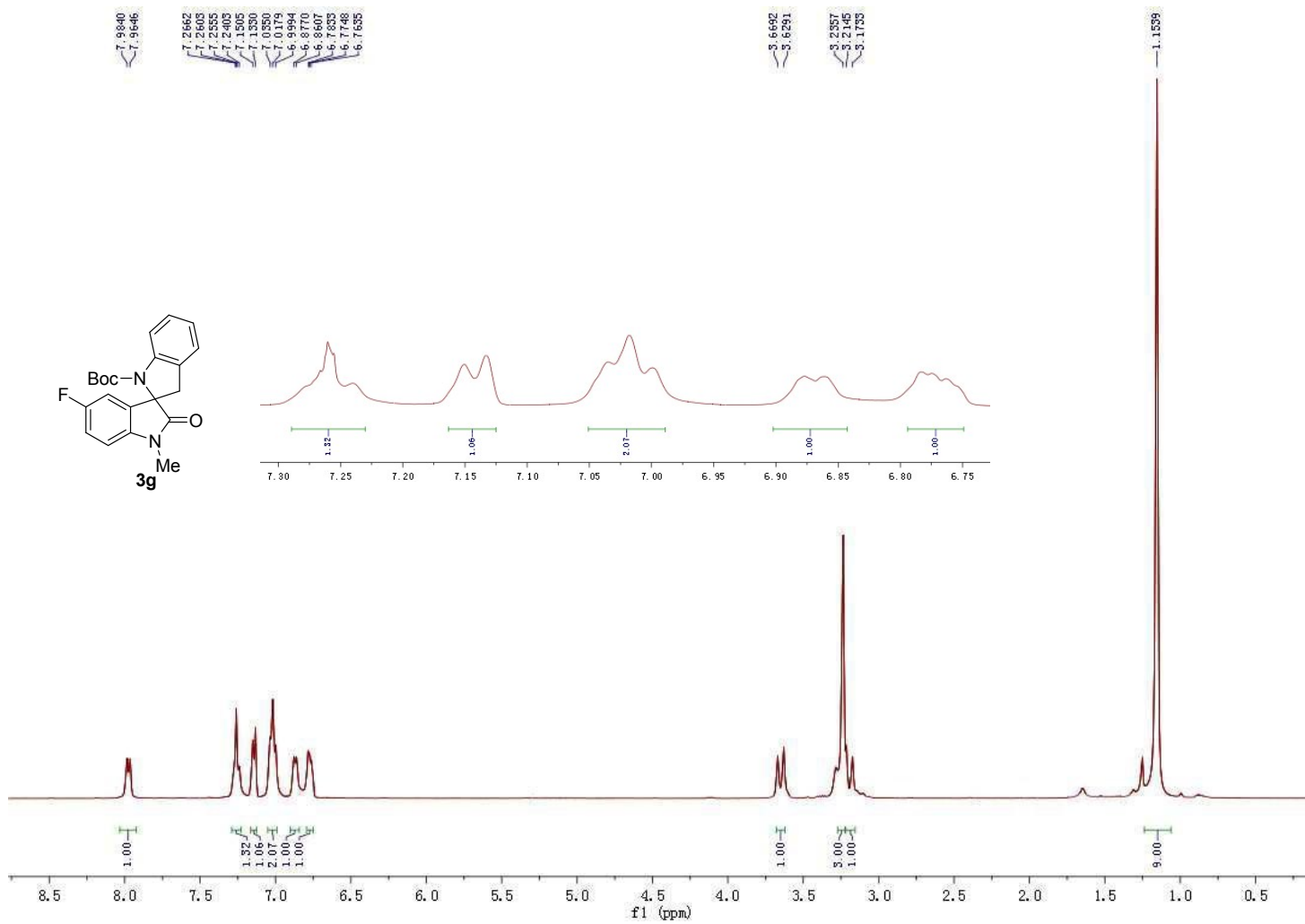


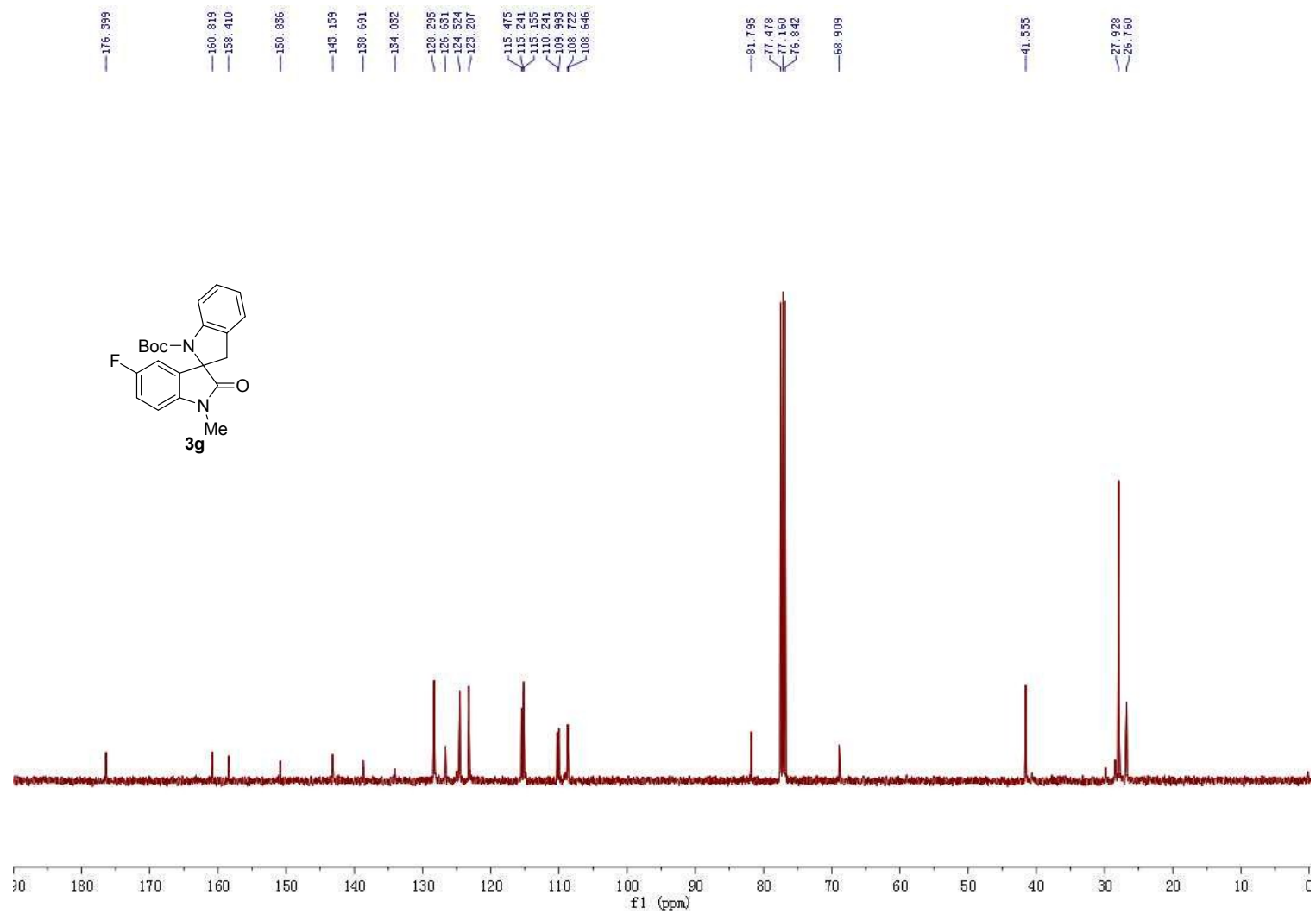
¹H and ¹³C NMR of 3f



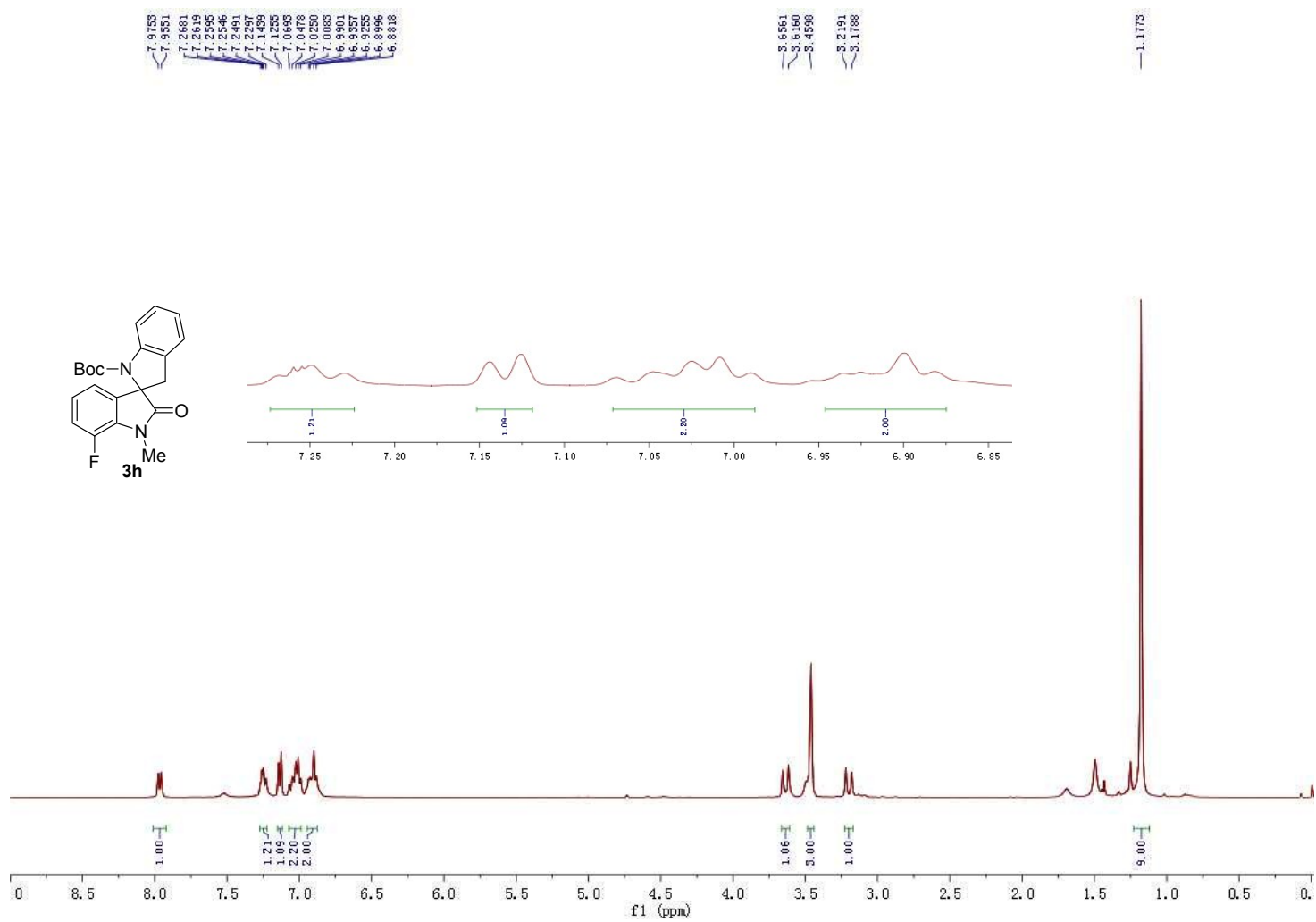


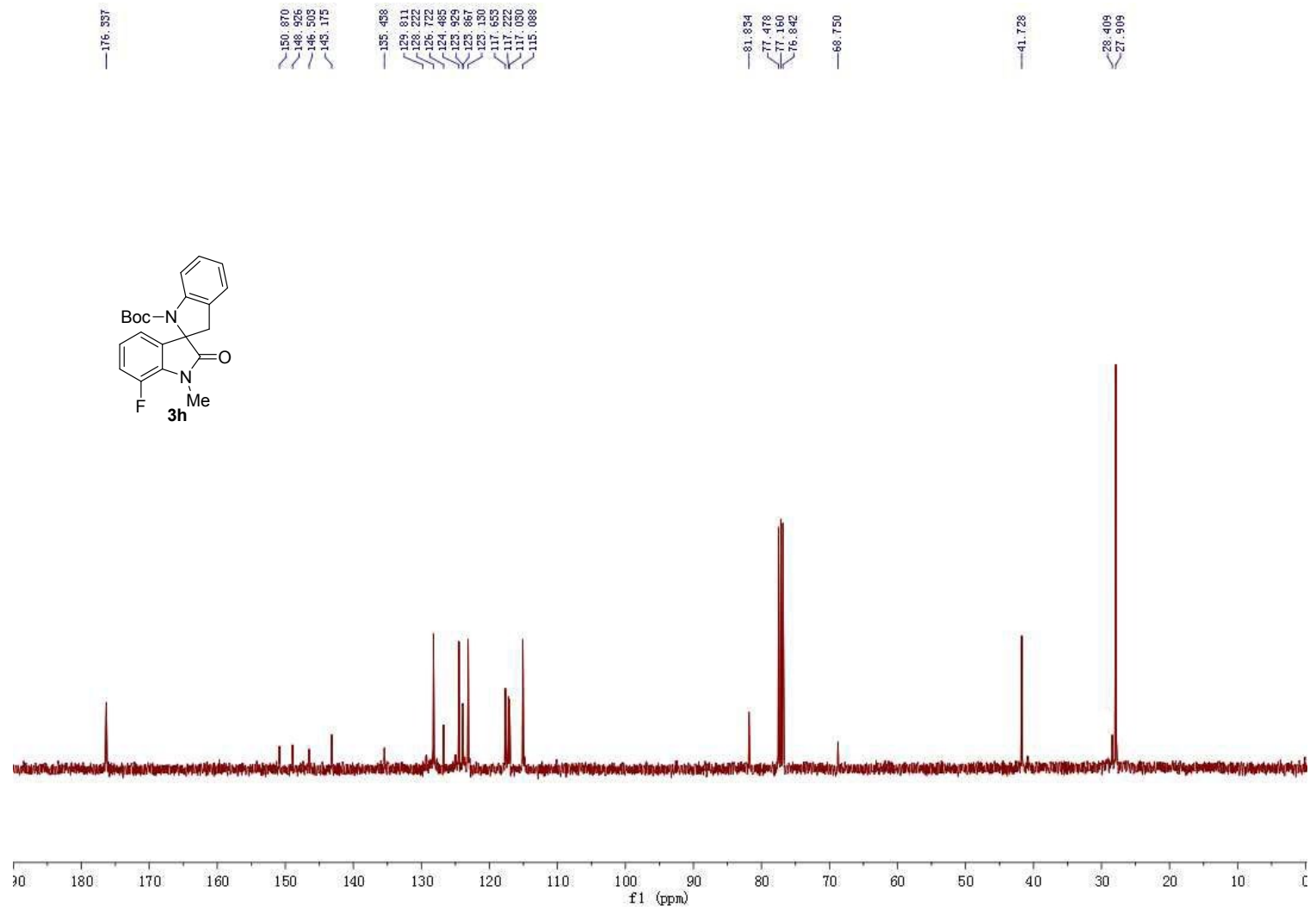
¹H and ¹³C NMR of 3g



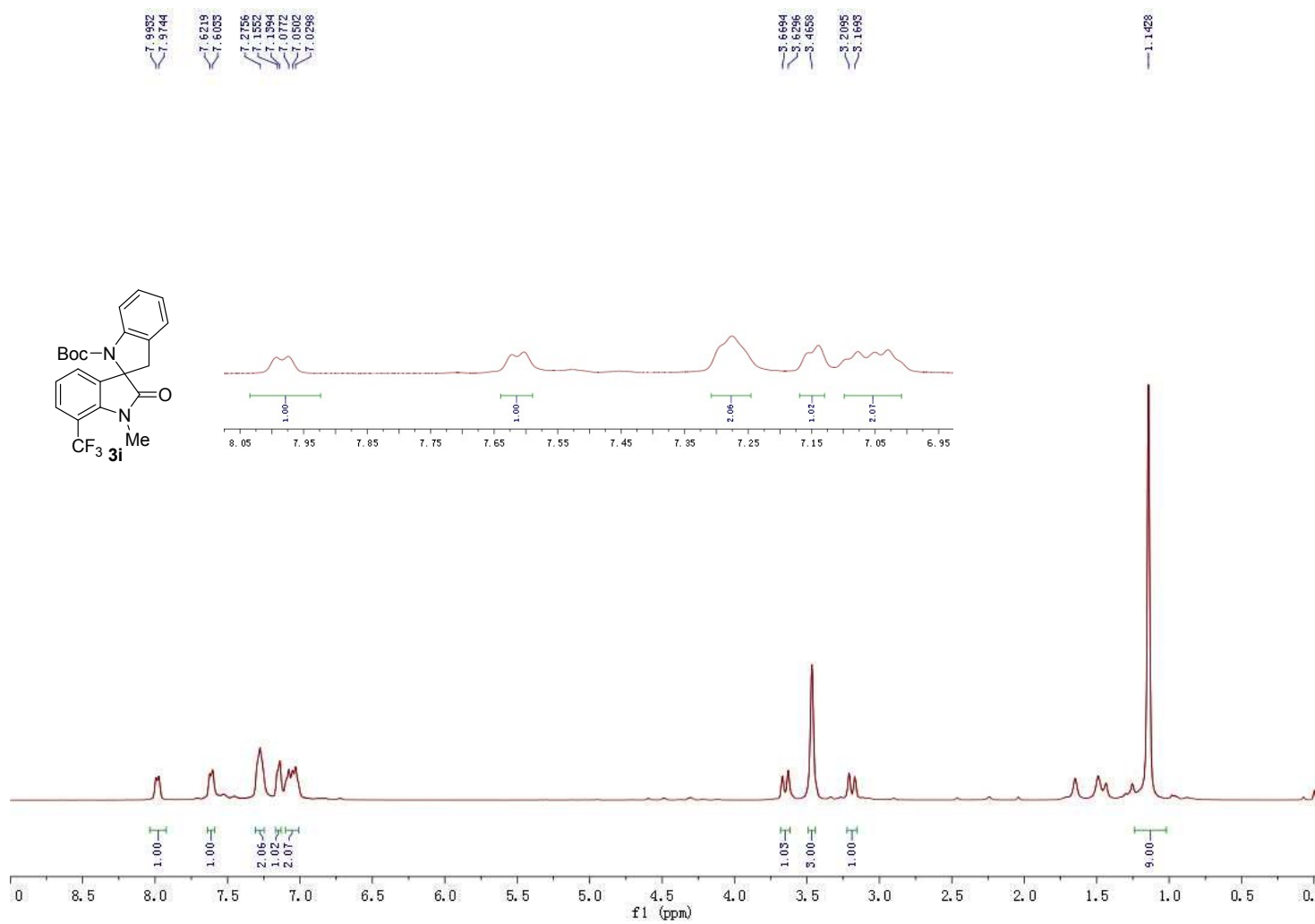


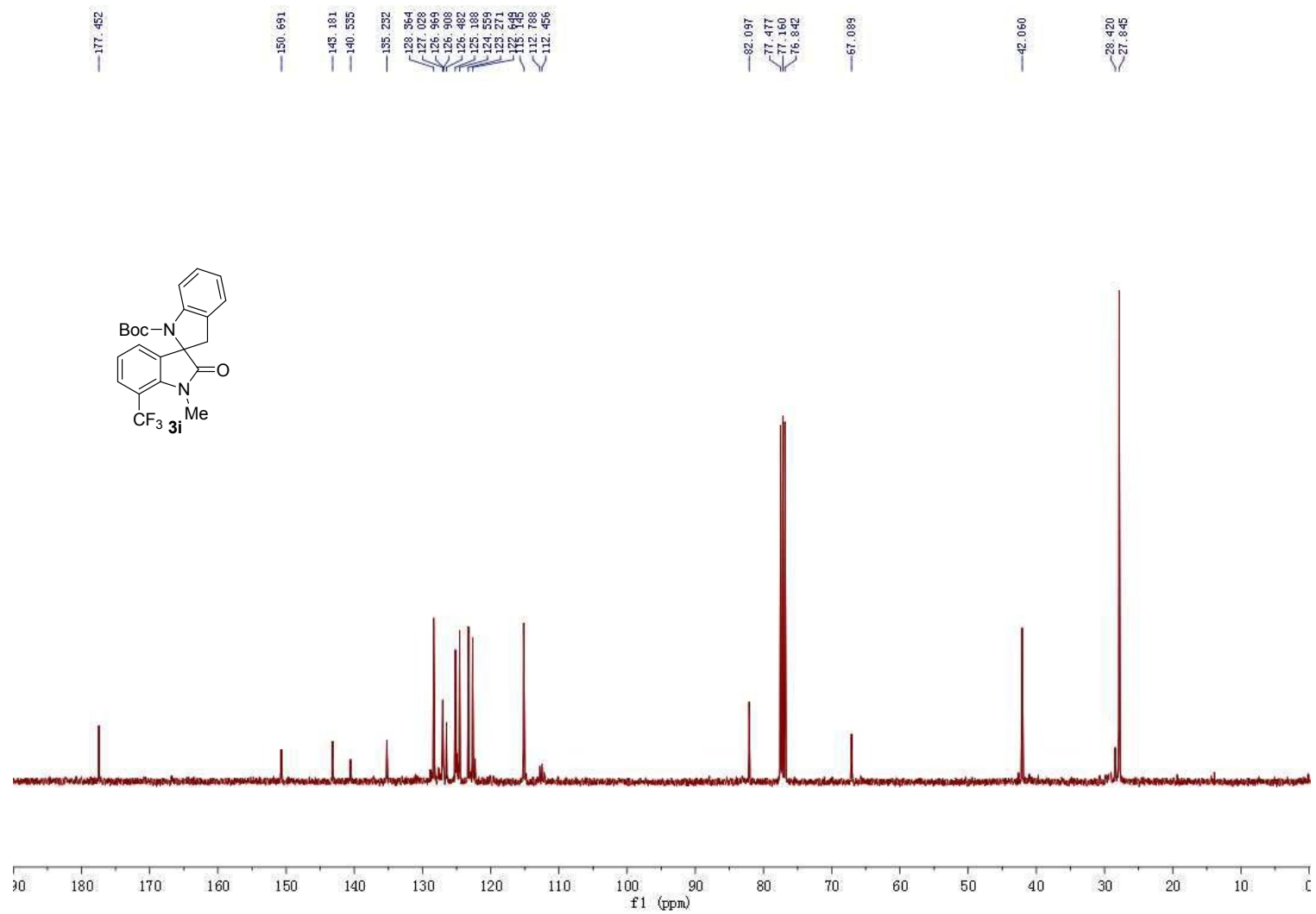
¹H and ¹³C NMR of 3h

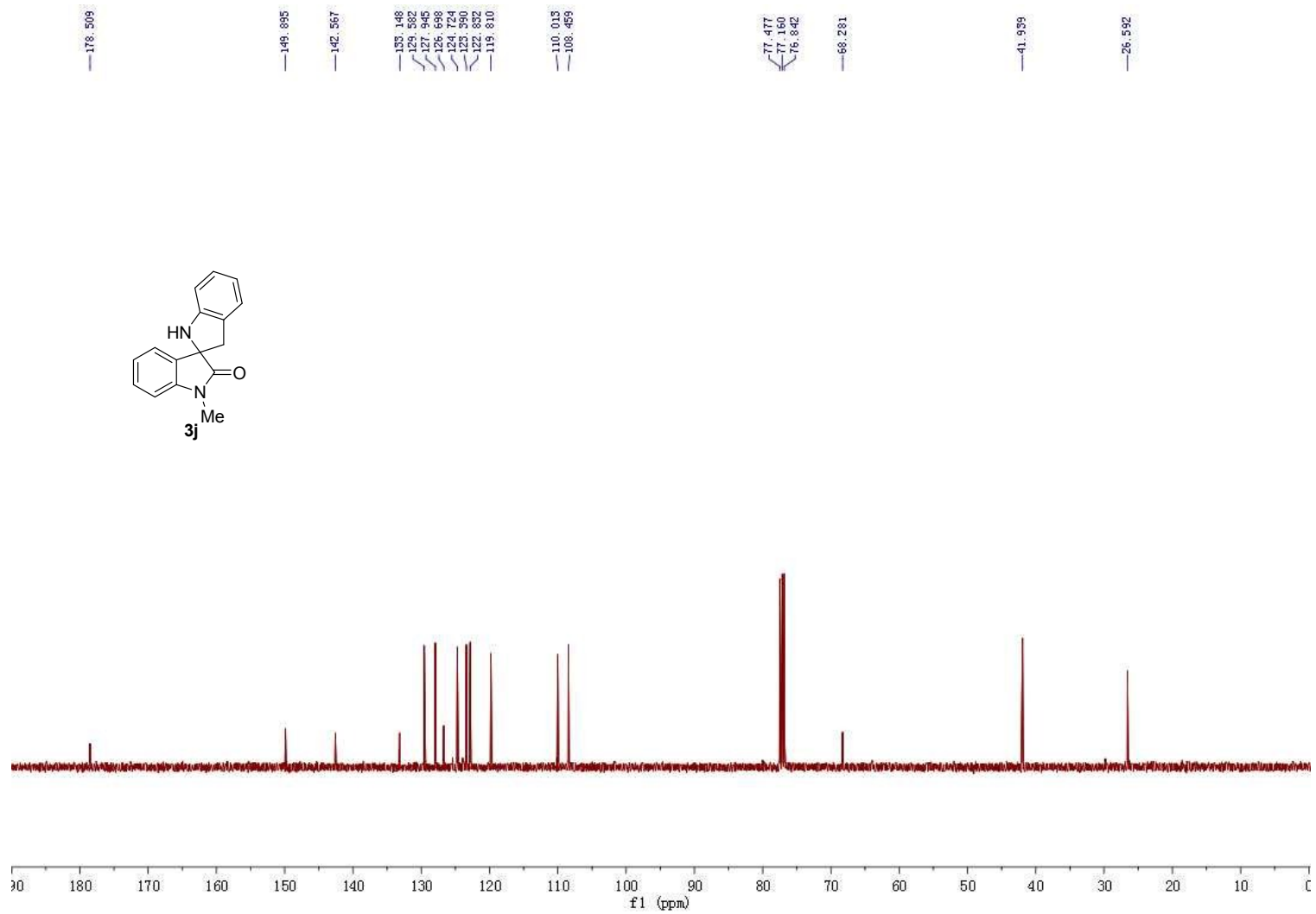
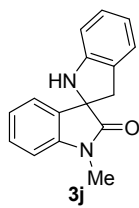




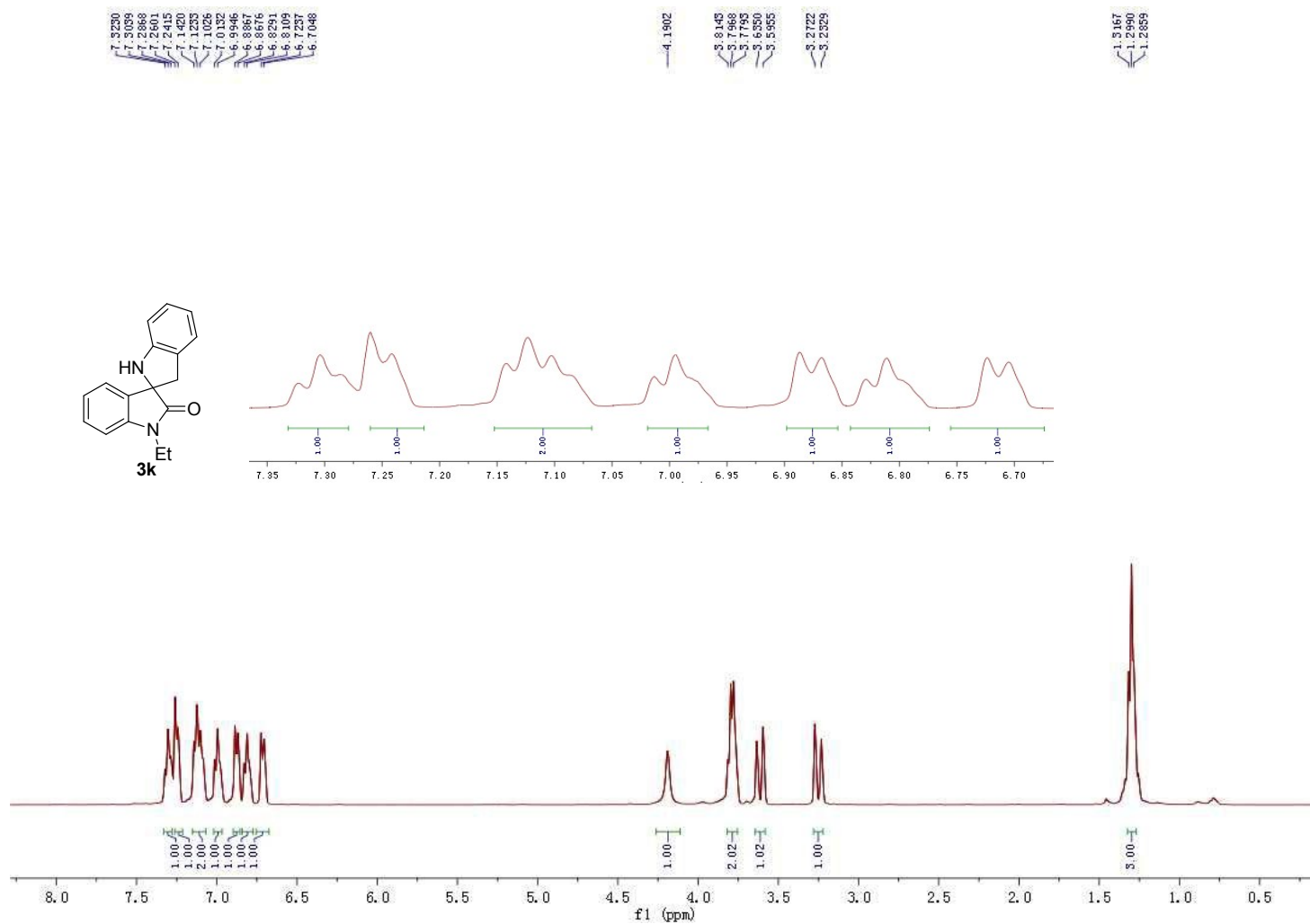
¹H and ¹³C NMR of 3i

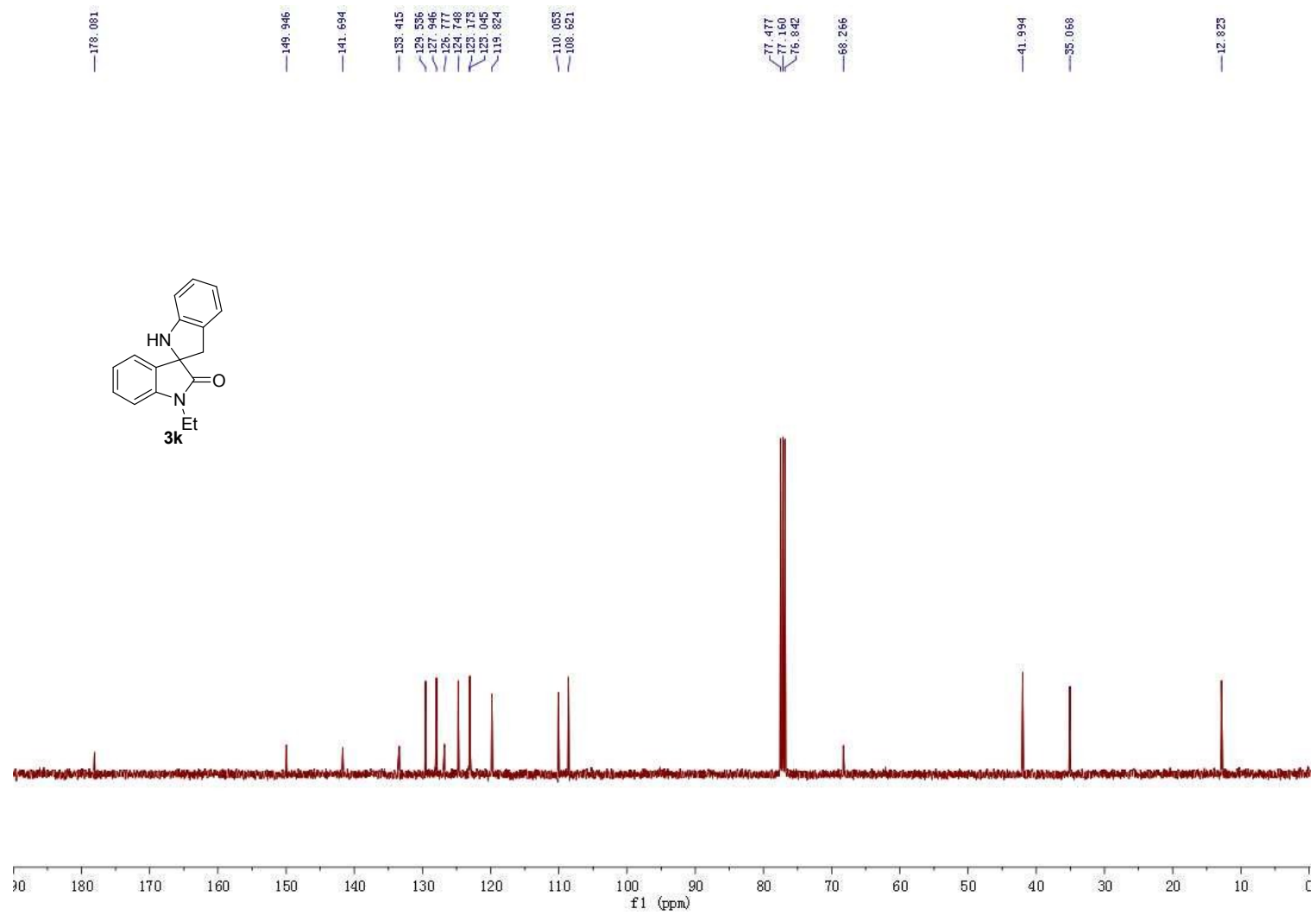




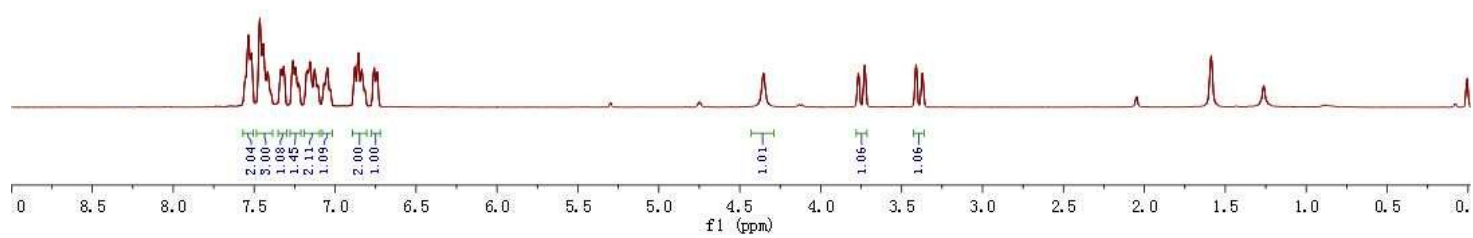
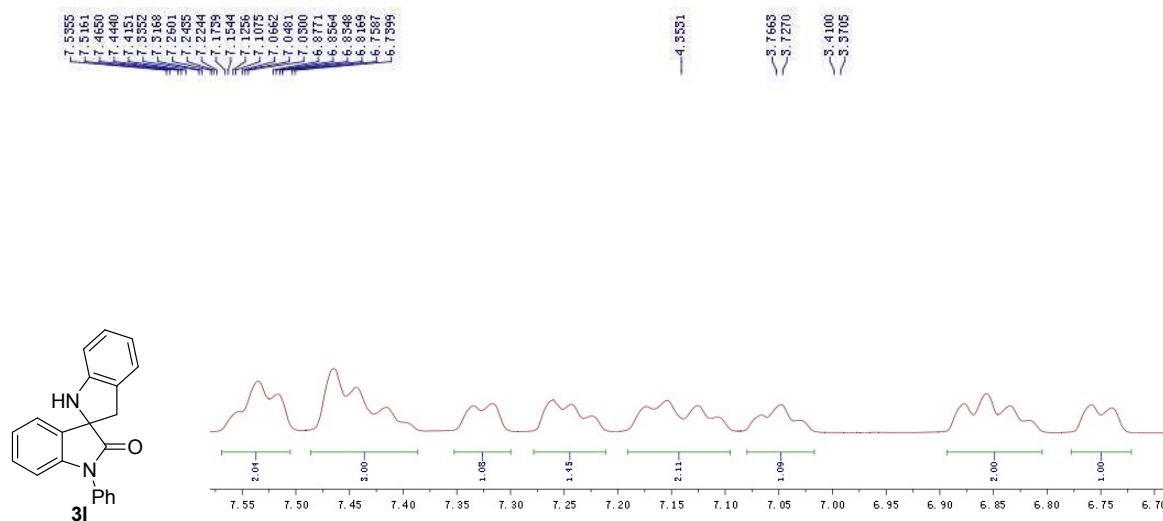


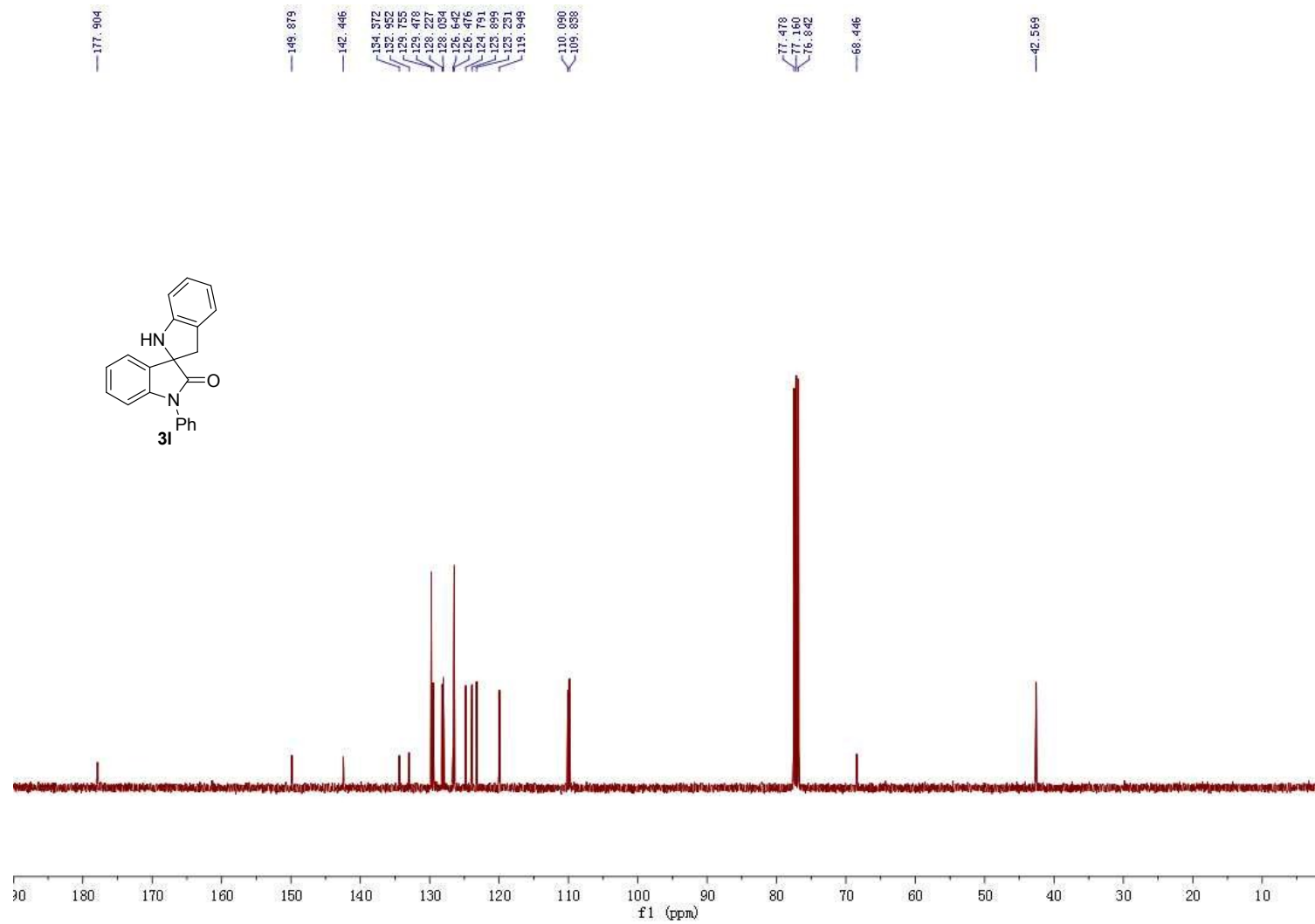
¹H and ¹³C NMR of 3k





¹H and ¹³C NMR of 3l





^1H and ^{13}C NMR of 3m

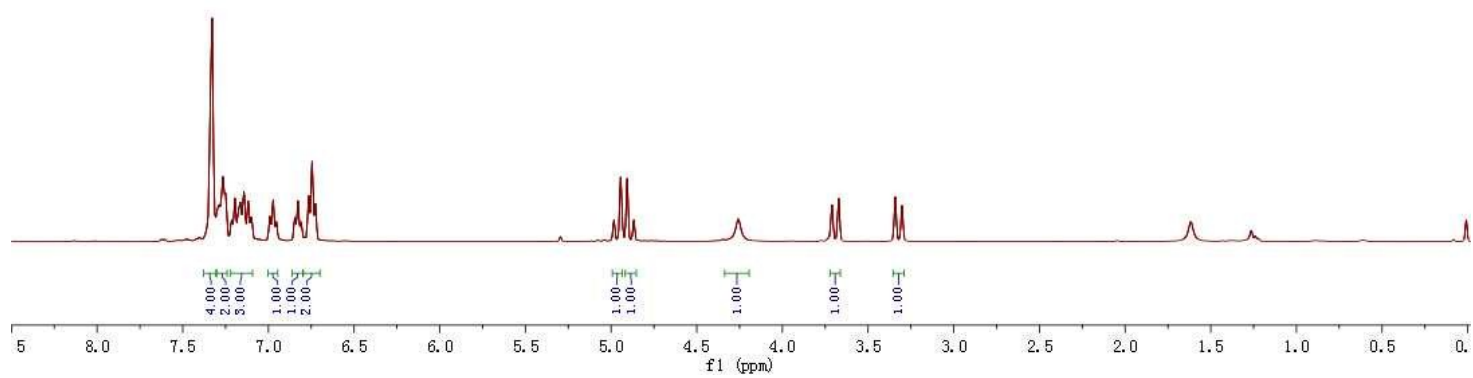
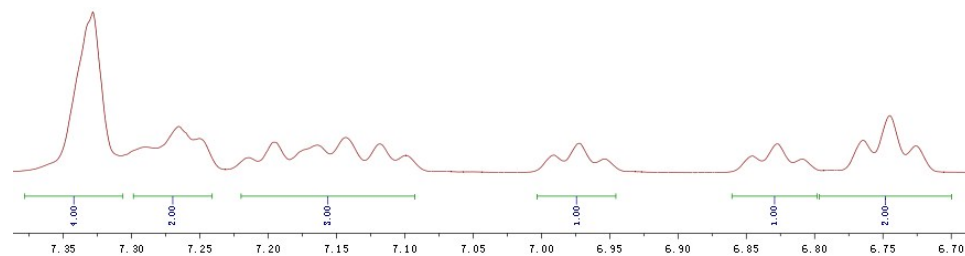
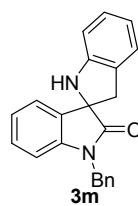
7.3283
7.3254
7.2956
7.2902
7.2137
7.1959
7.1641
7.1481
7.1183
7.0992
6.9906
6.9721
6.9352
6.9252
6.8271
6.8089
6.7646
6.7451
6.7260

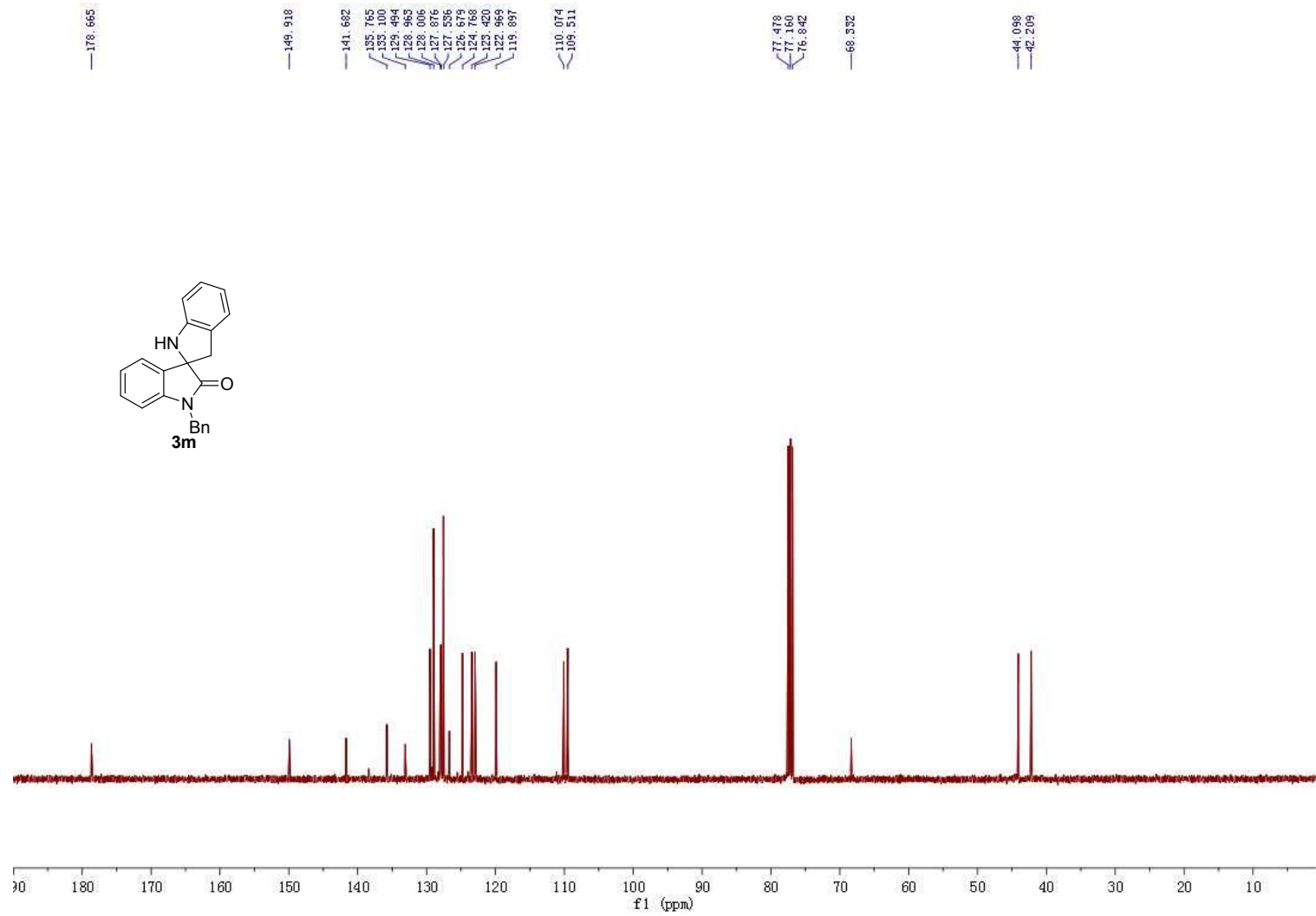
4.9880
4.9441
4.9060
4.8672

4.2584

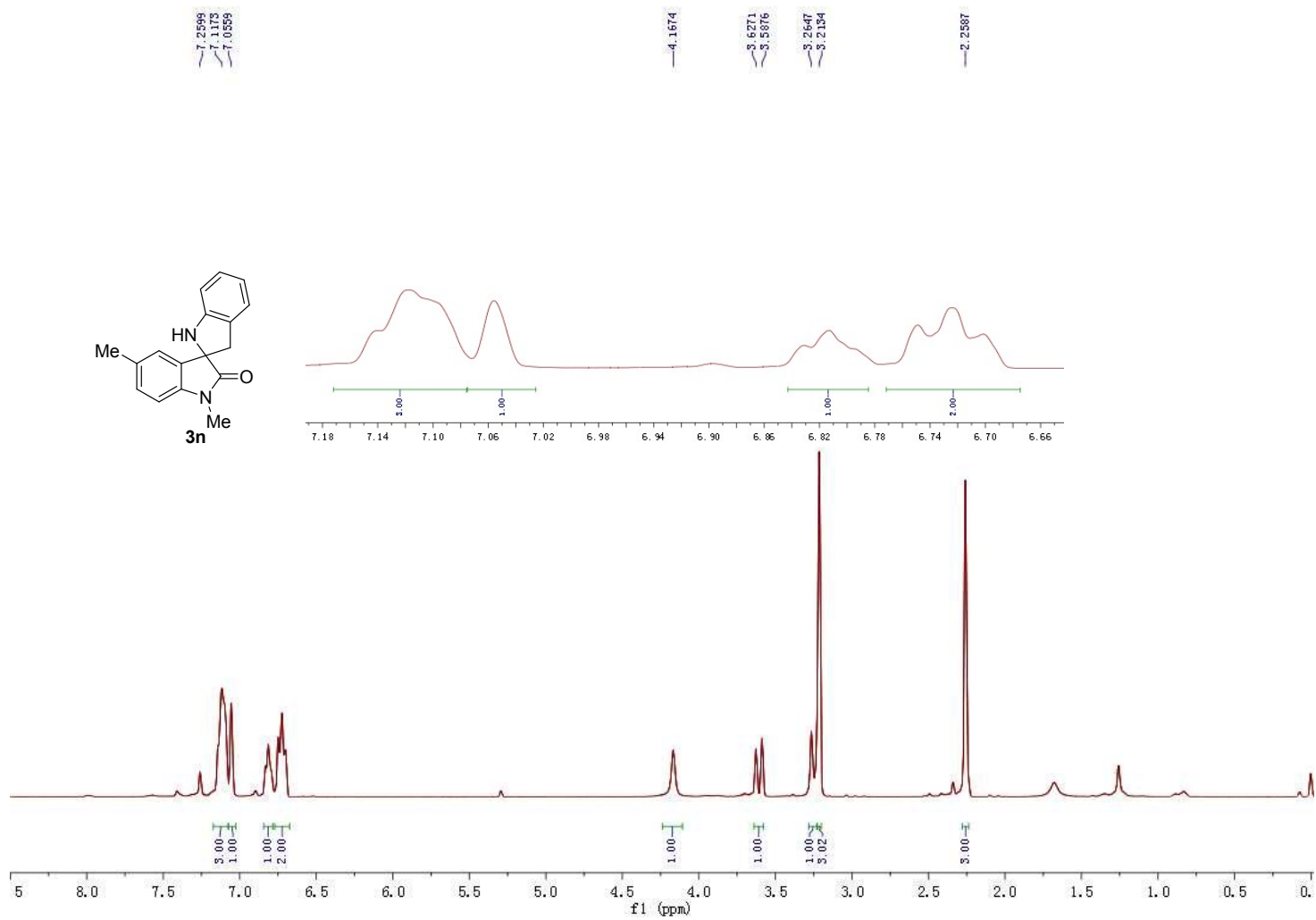
3.7109
3.6715

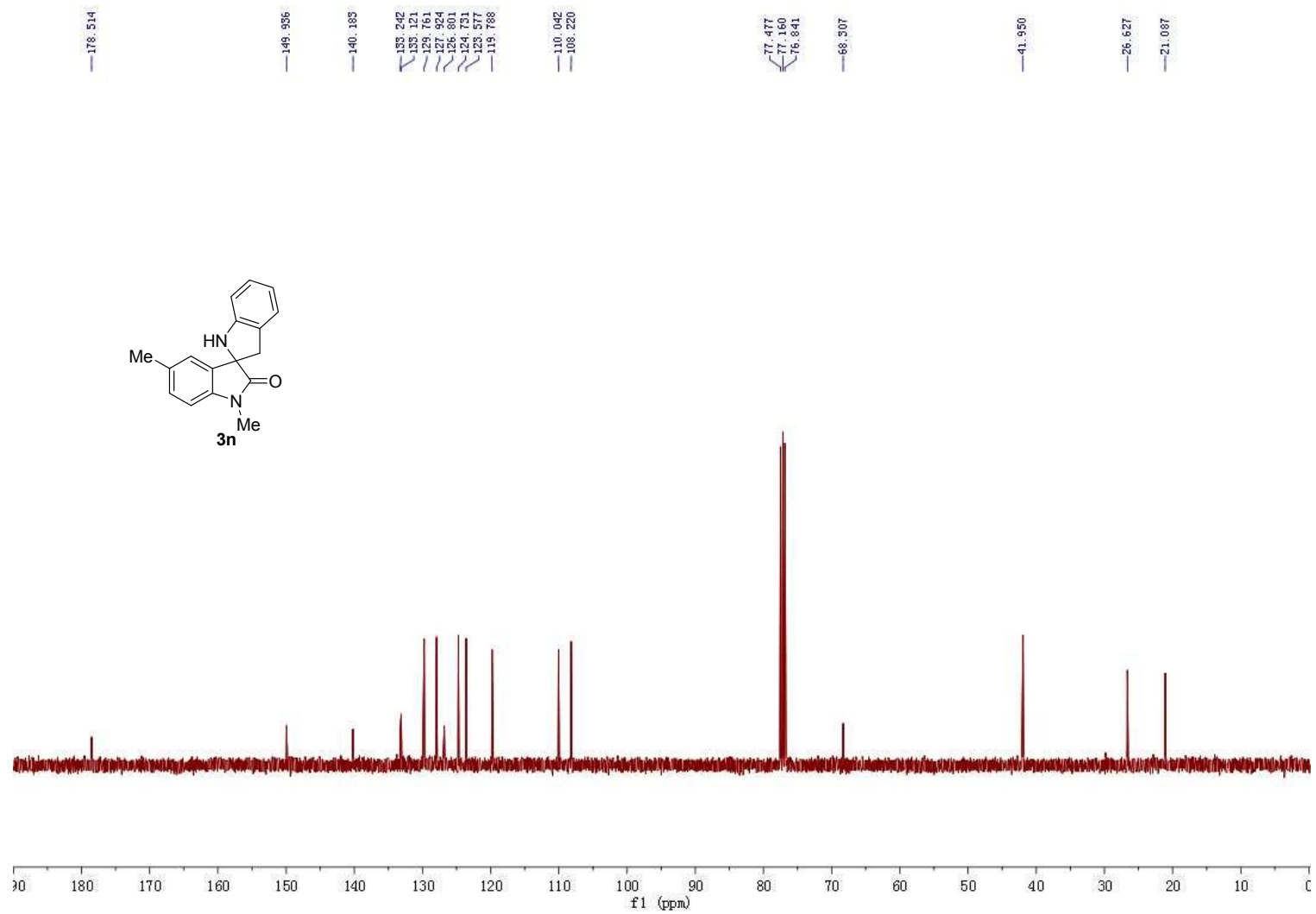
3.3412
3.3019





¹H and ¹³C NMR of 3n





¹H and ¹³C NMR of 3o

7.2601
7.1186
7.0837
7.0222
6.9950
6.9760
6.9322
6.8138
6.7885
6.7772
6.7669
6.7570
6.7162
6.6971

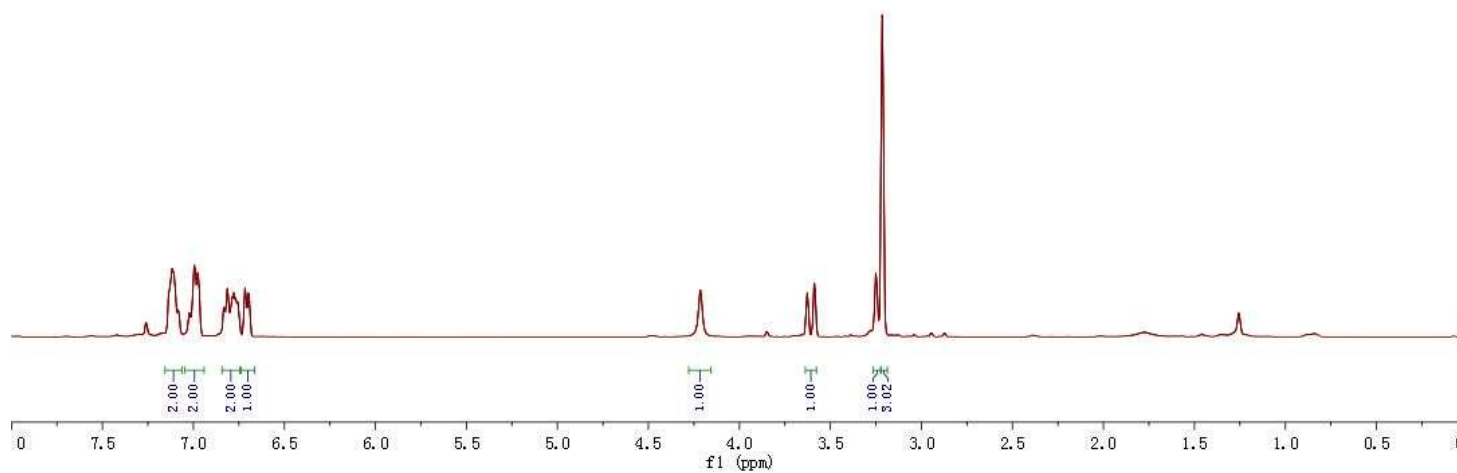
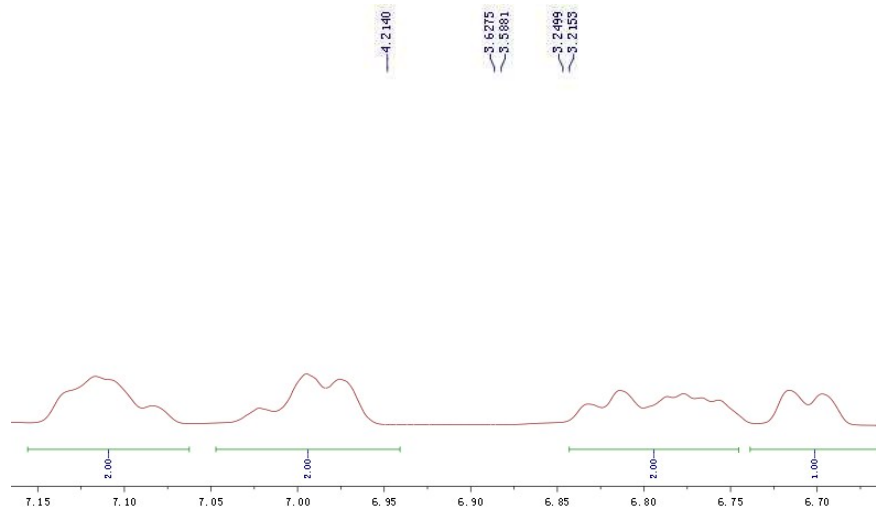
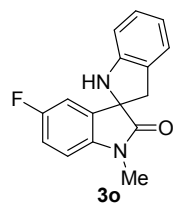
4.2140

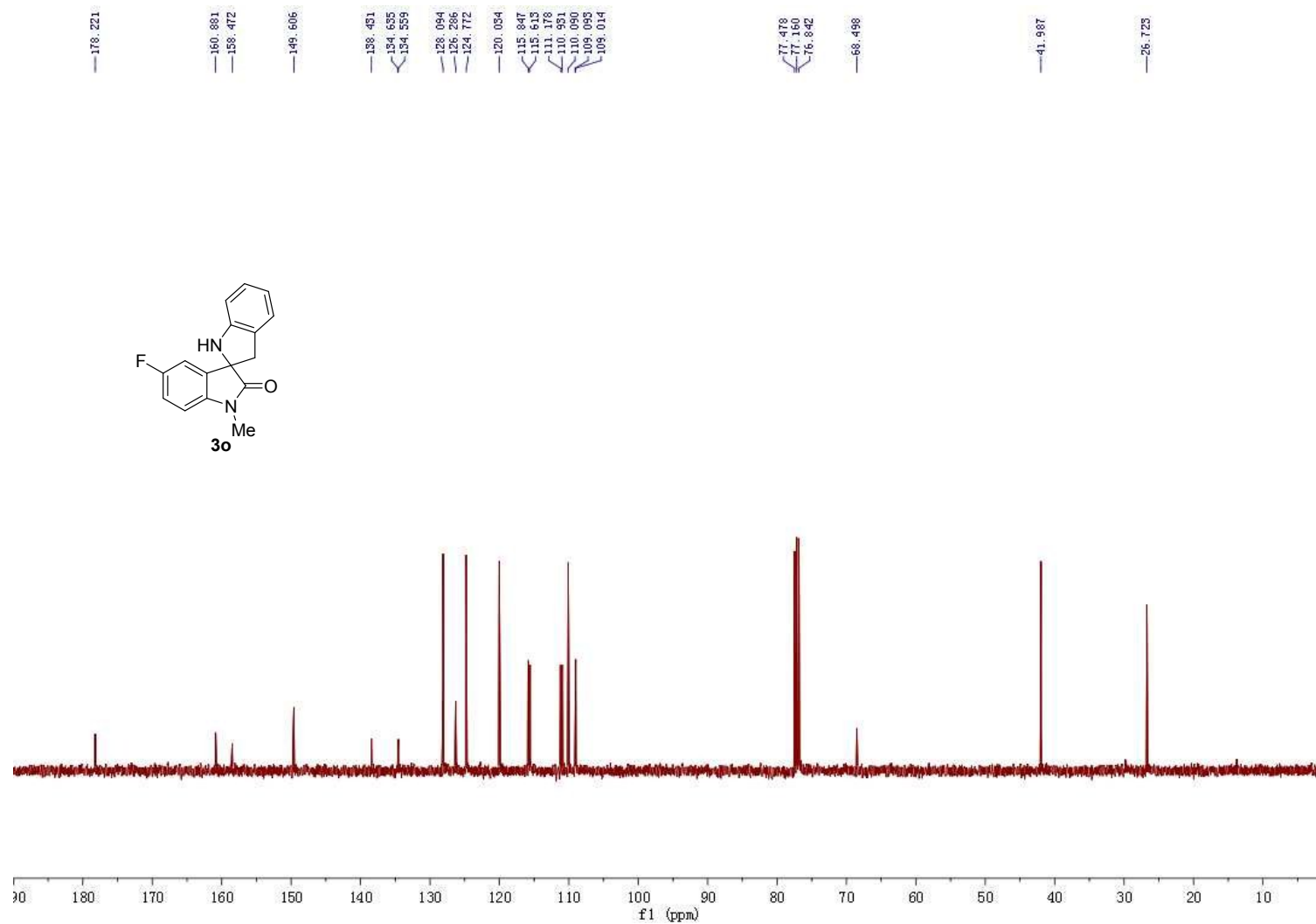
3.6275

3.5881

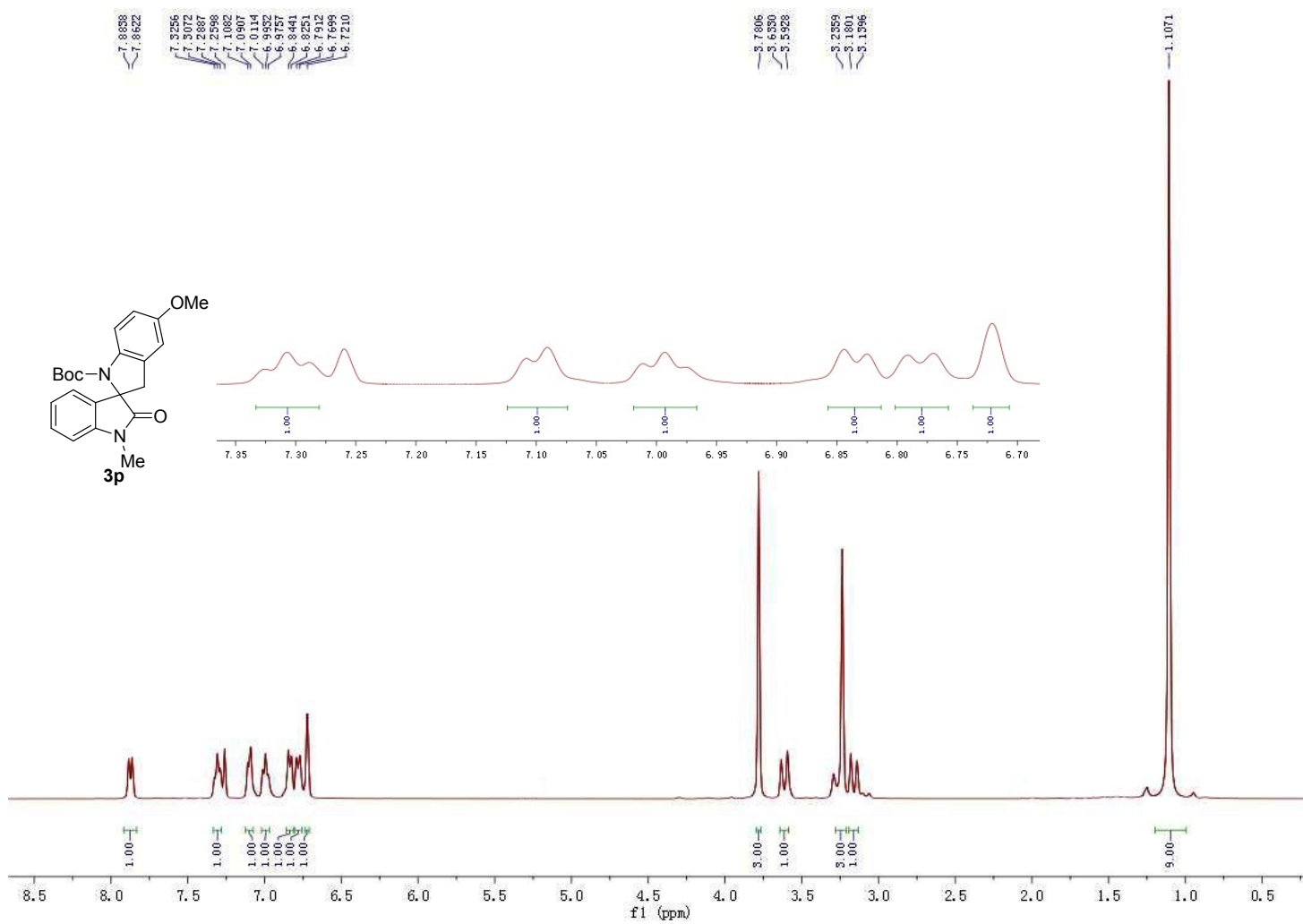
3.2499

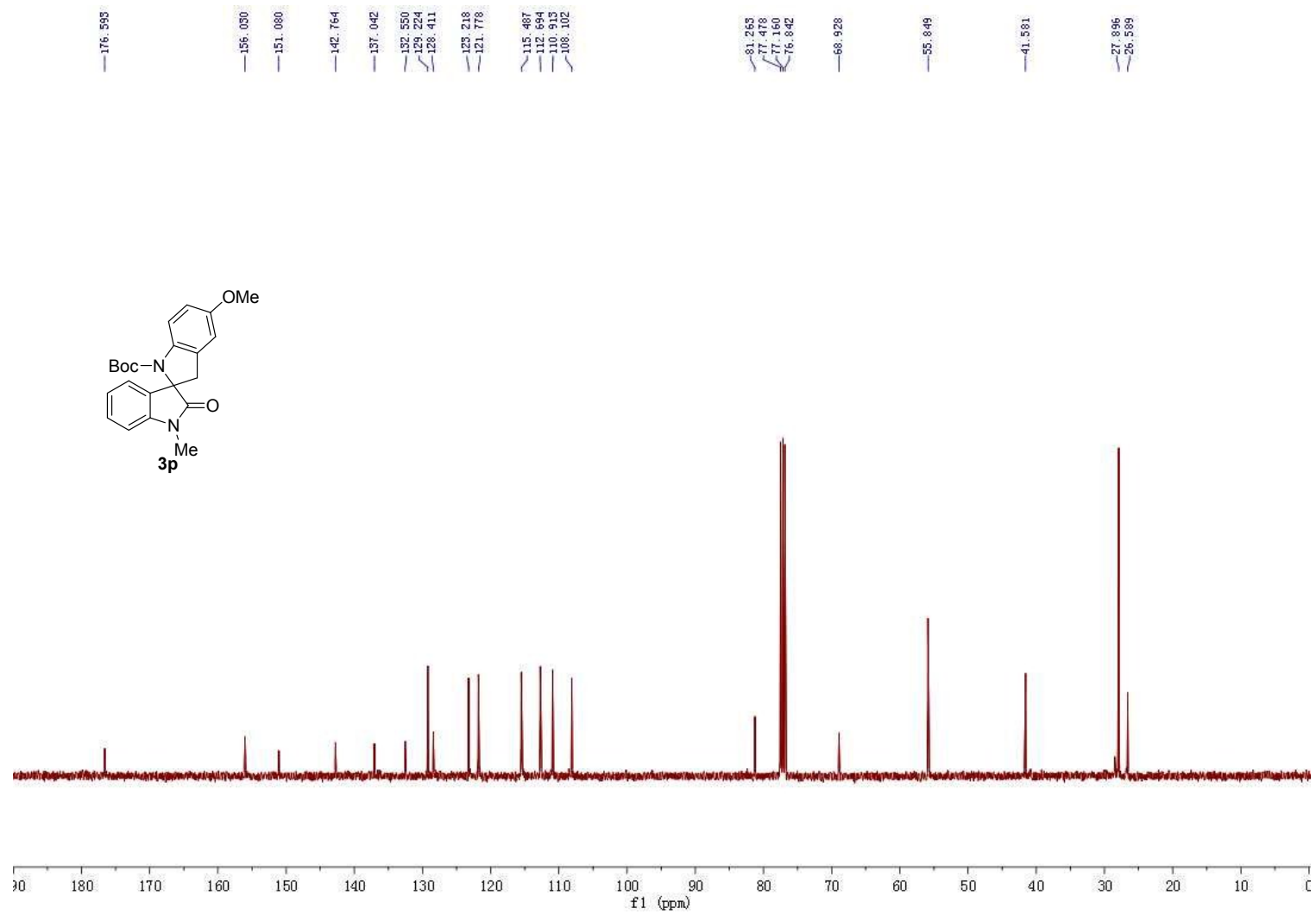
3.2155



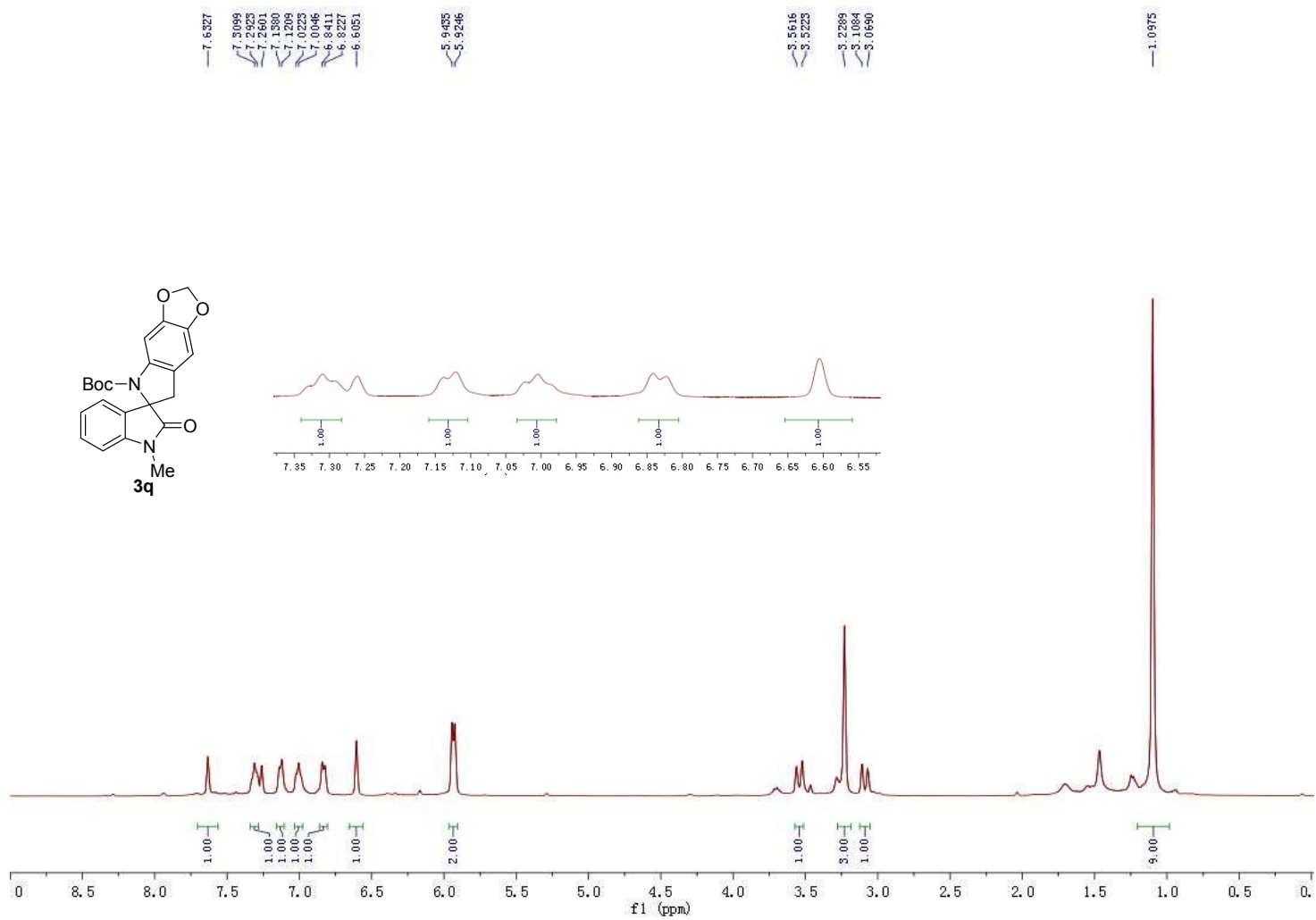


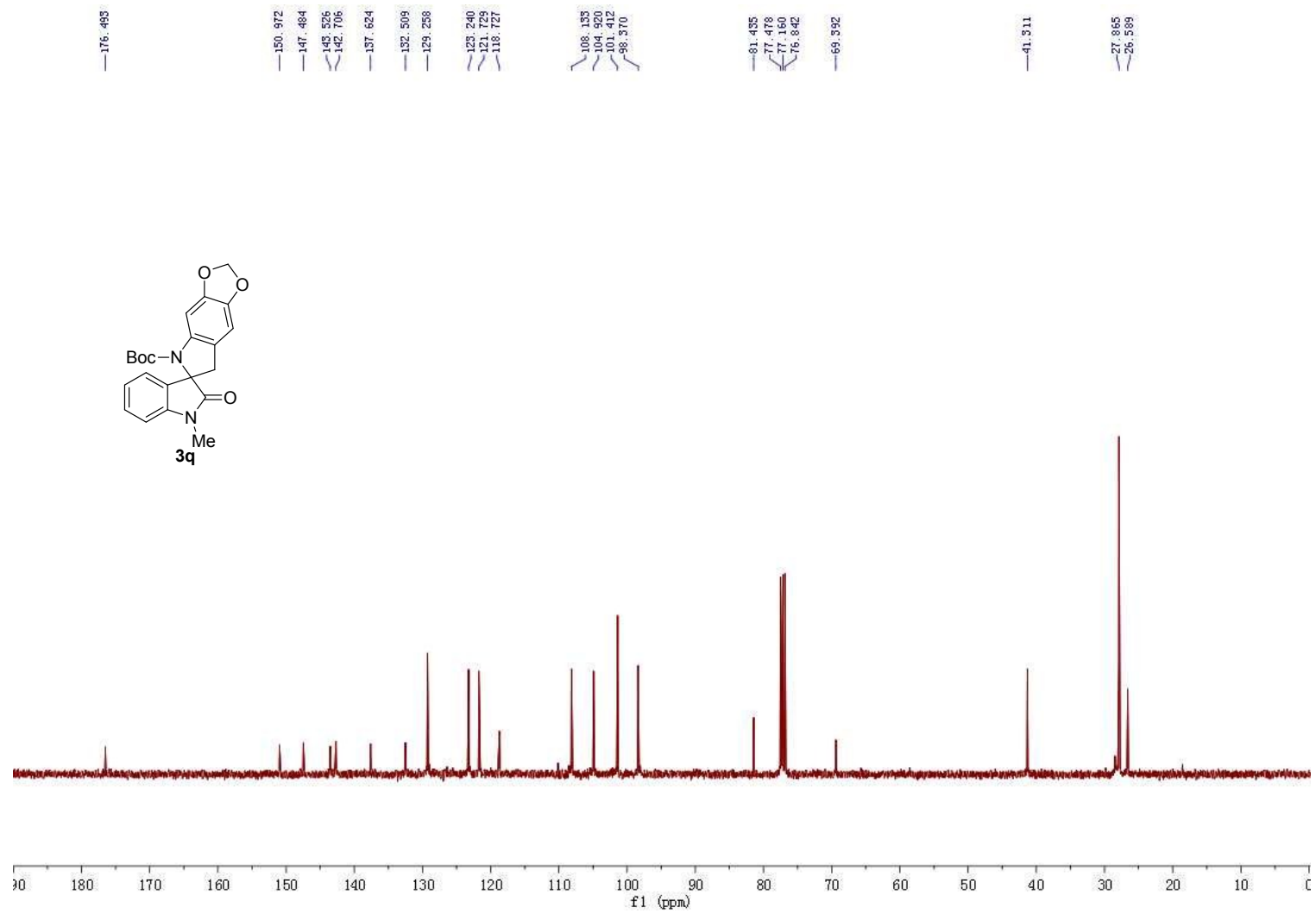
¹H and ¹³C NMR of 3p



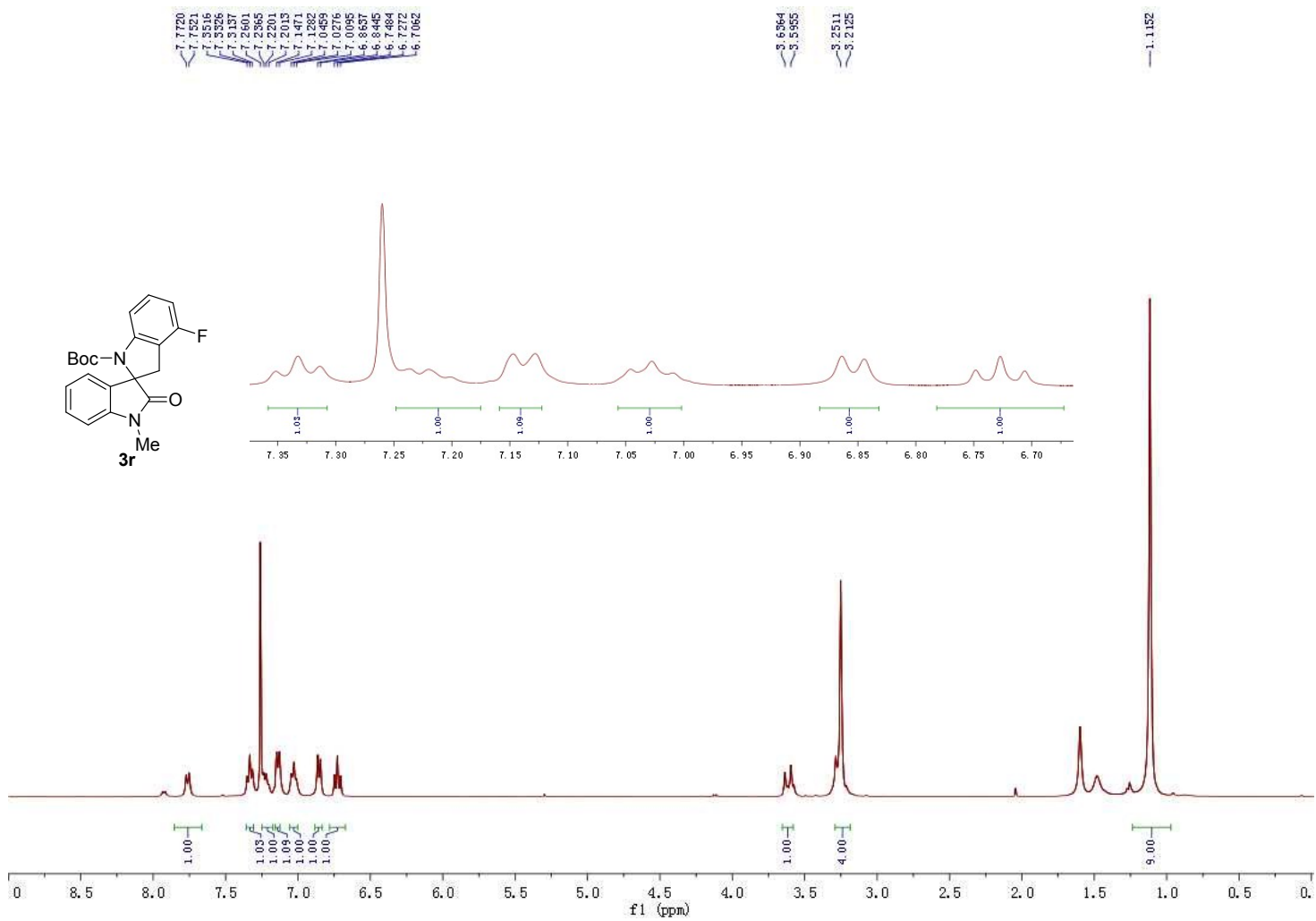


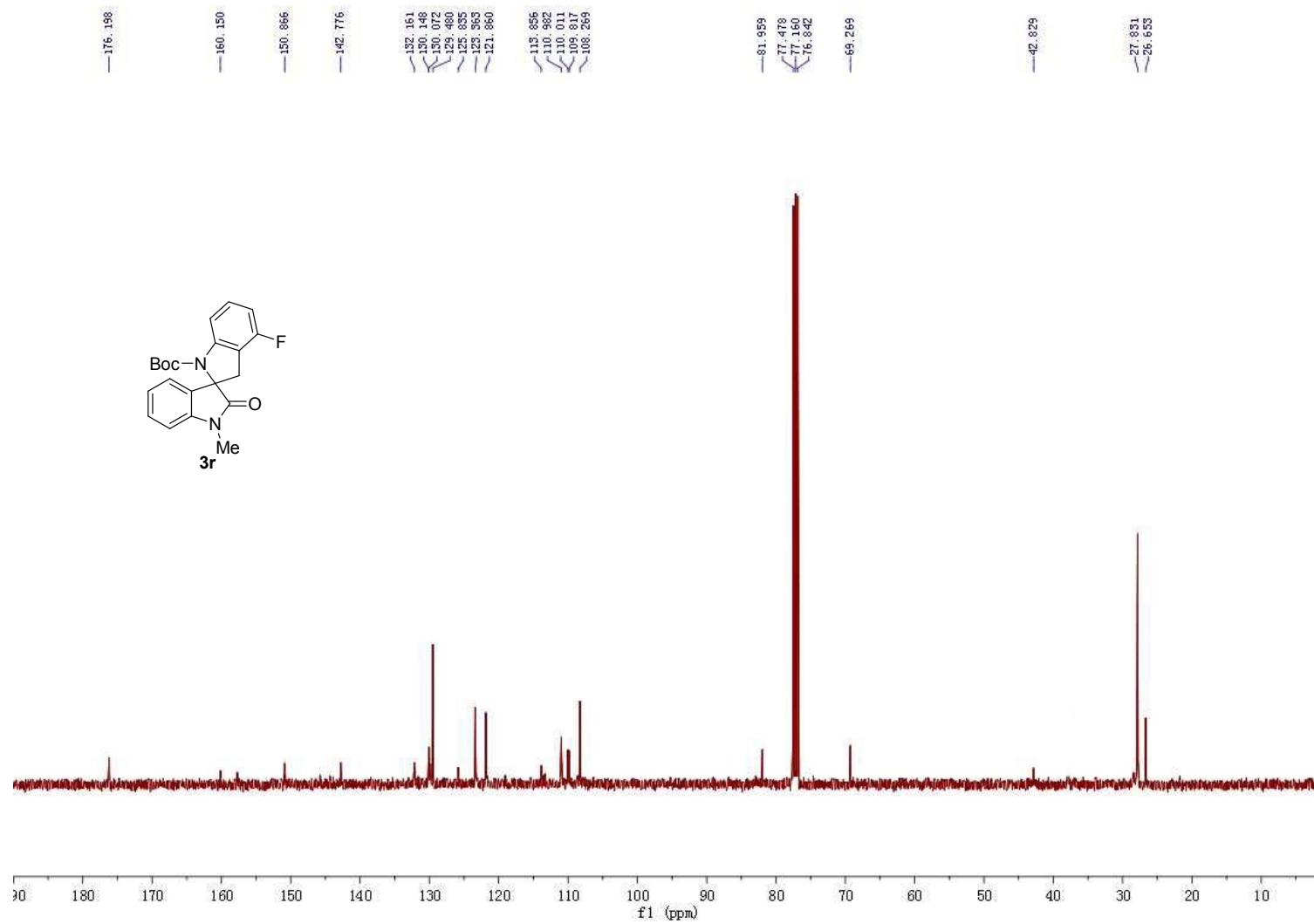
¹H and ¹³C NMR of 3q



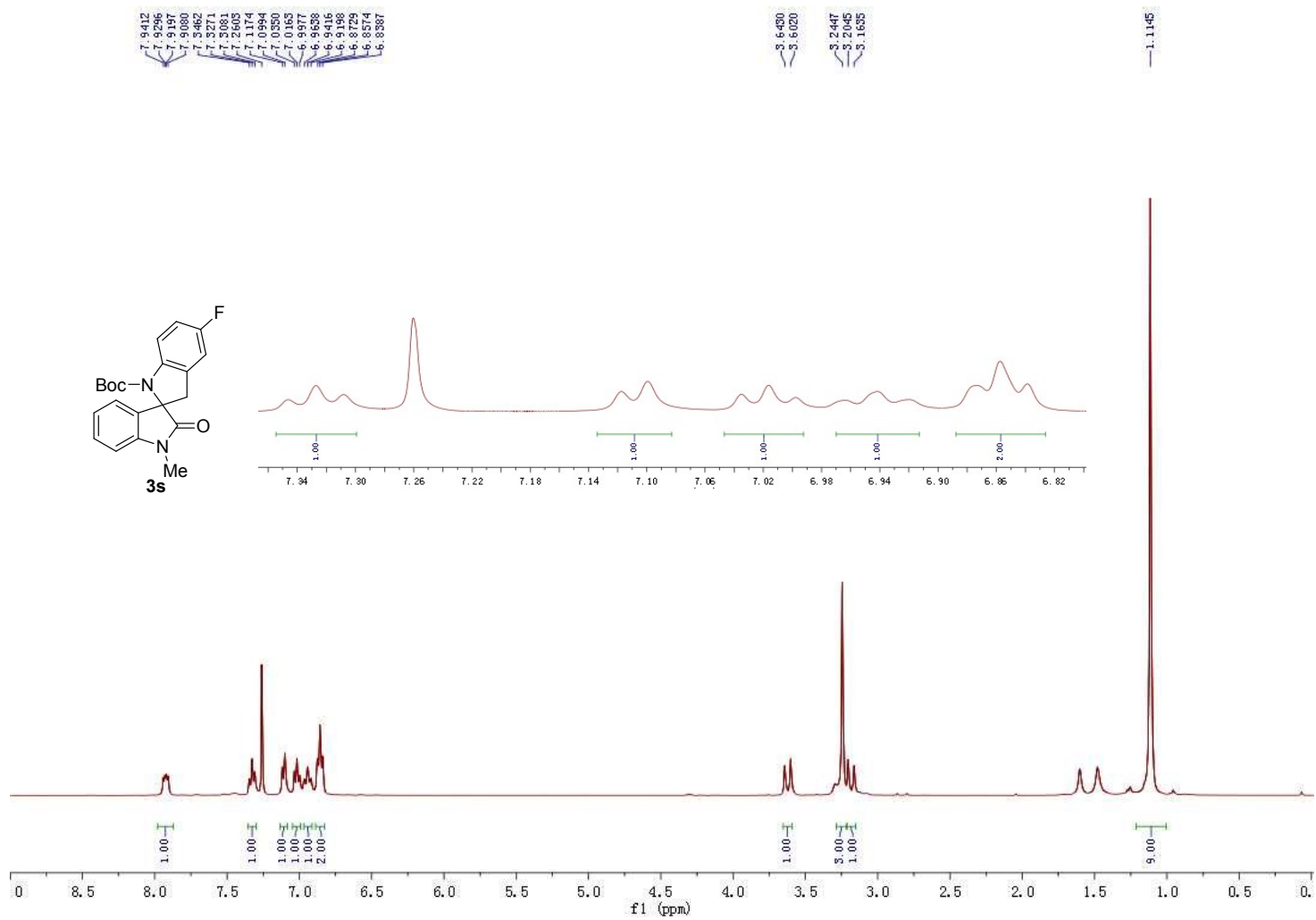


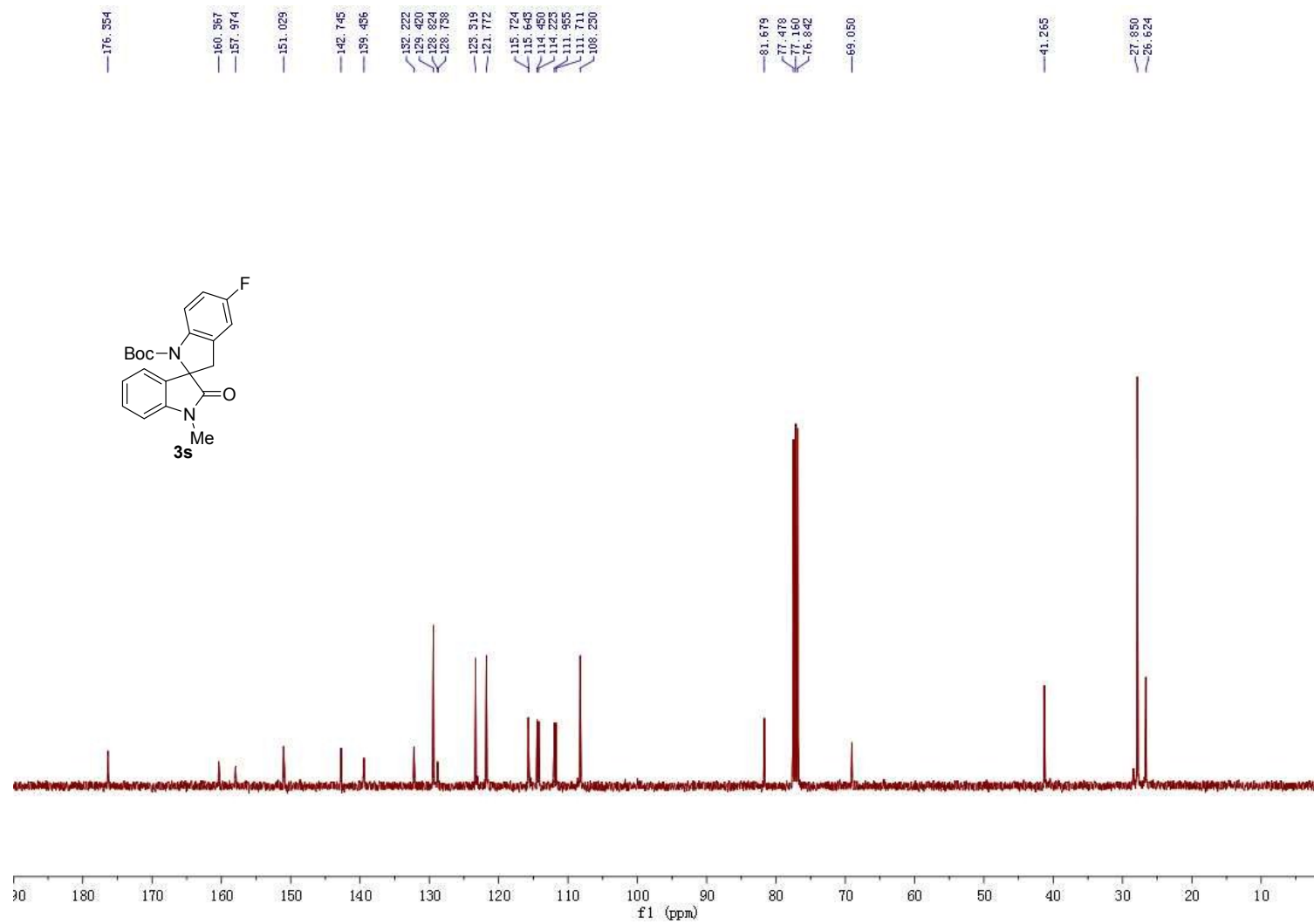
¹H and ¹³C NMR of 3r

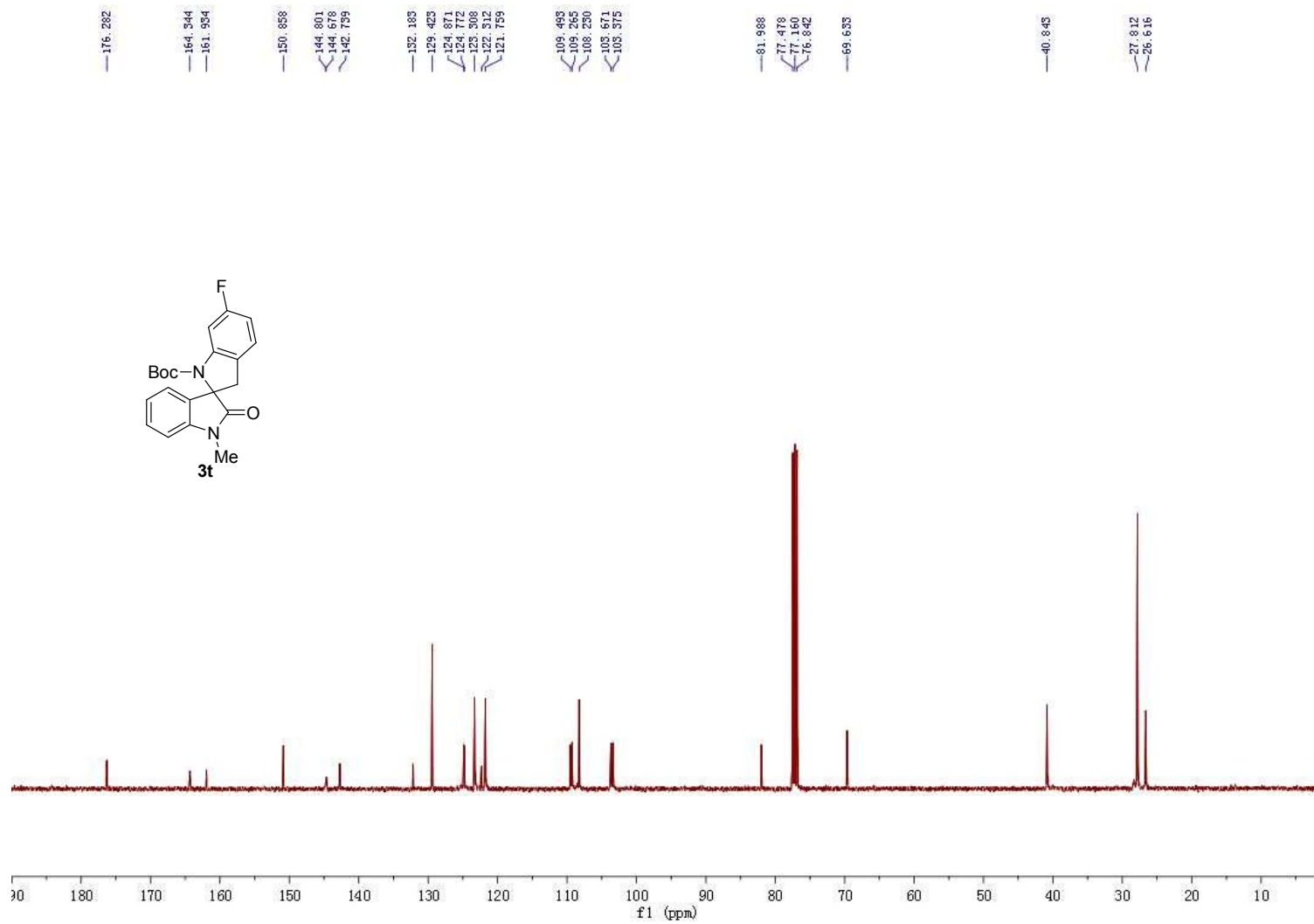




¹H and ¹³C NMR of 3s





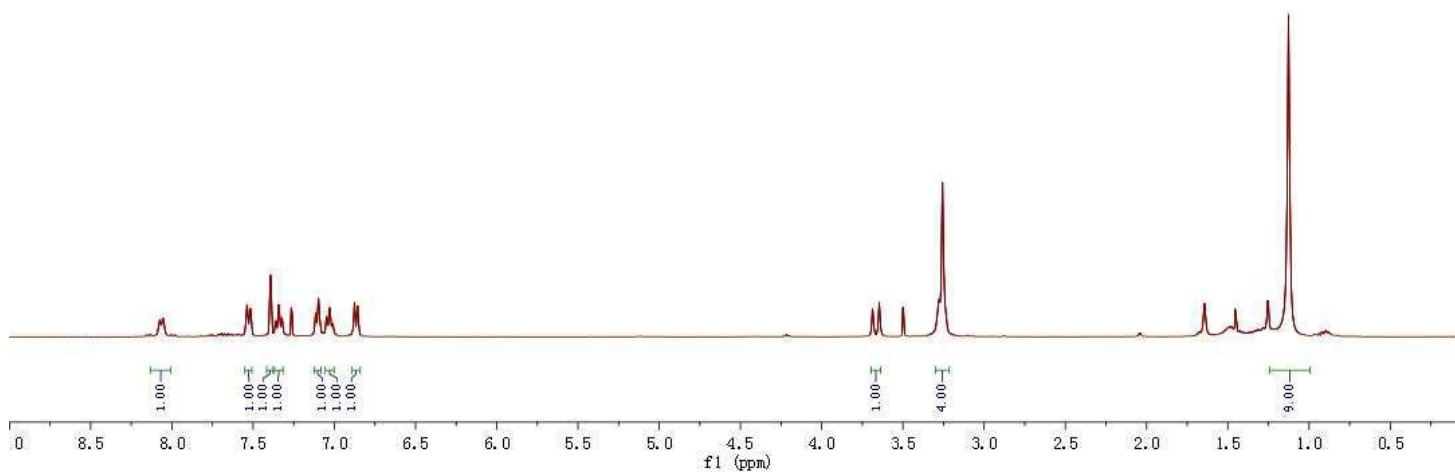
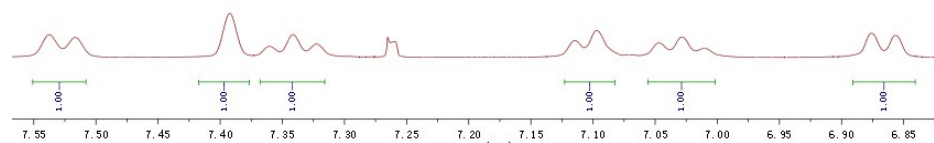
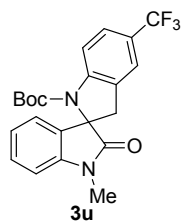


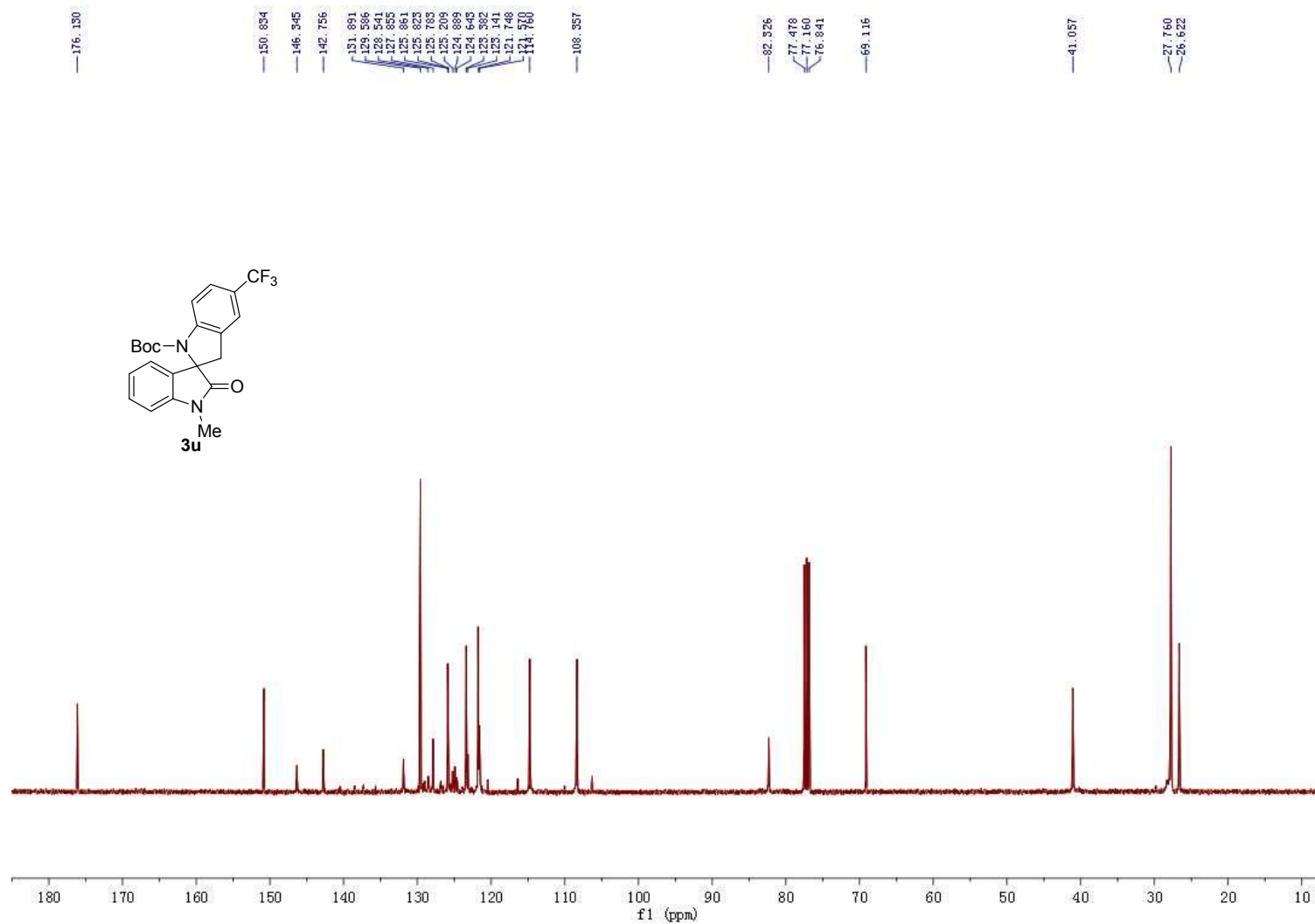
¹H and ¹³C NMR of 3u

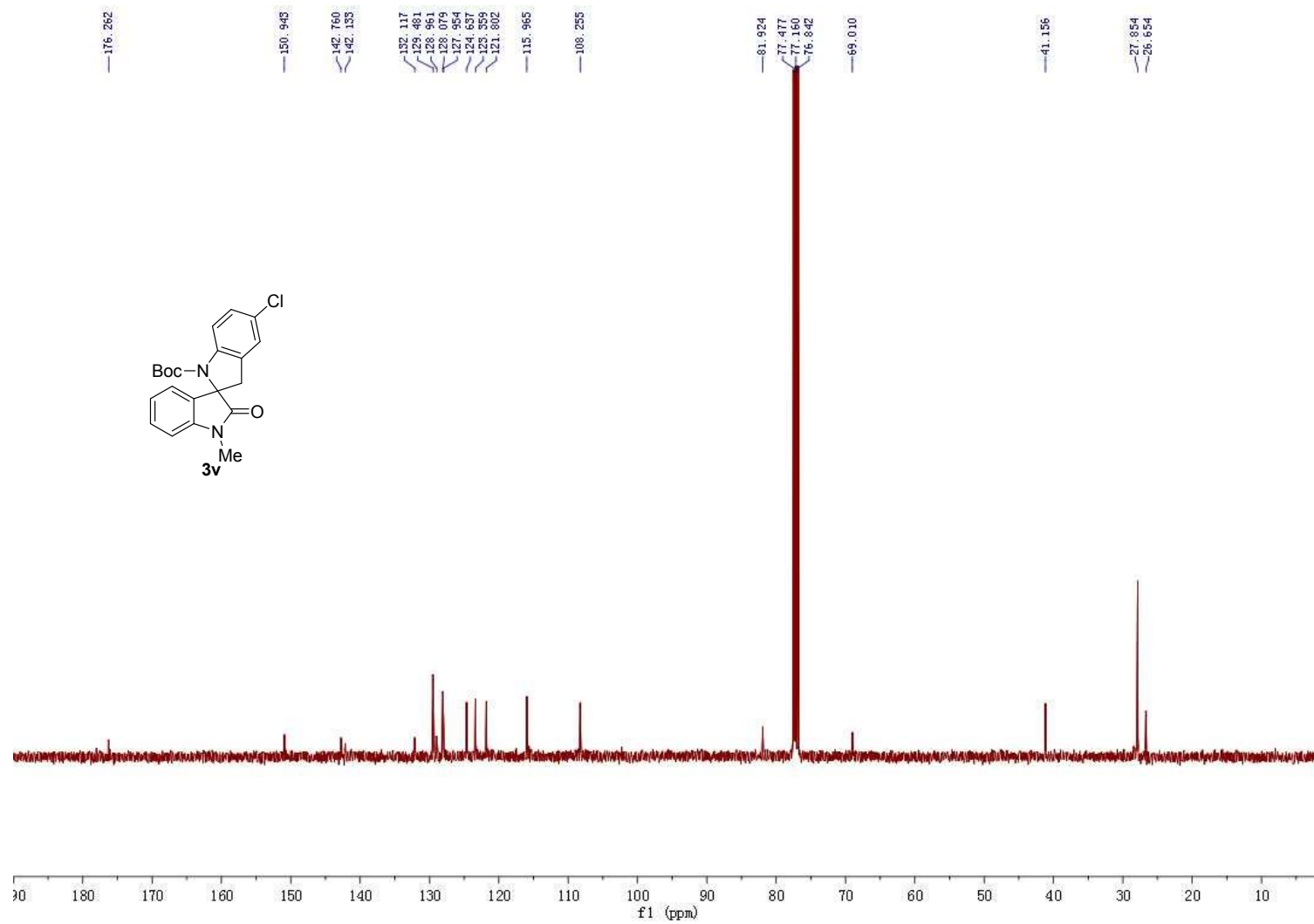
8.0742
8.0537
7.5975
7.5765
7.5423
7.5416
7.5226
7.5254
7.1147
7.0970
7.0728
7.0285
7.0104
6.8759
6.8566

3.6865
3.6465
3.2780
3.2561

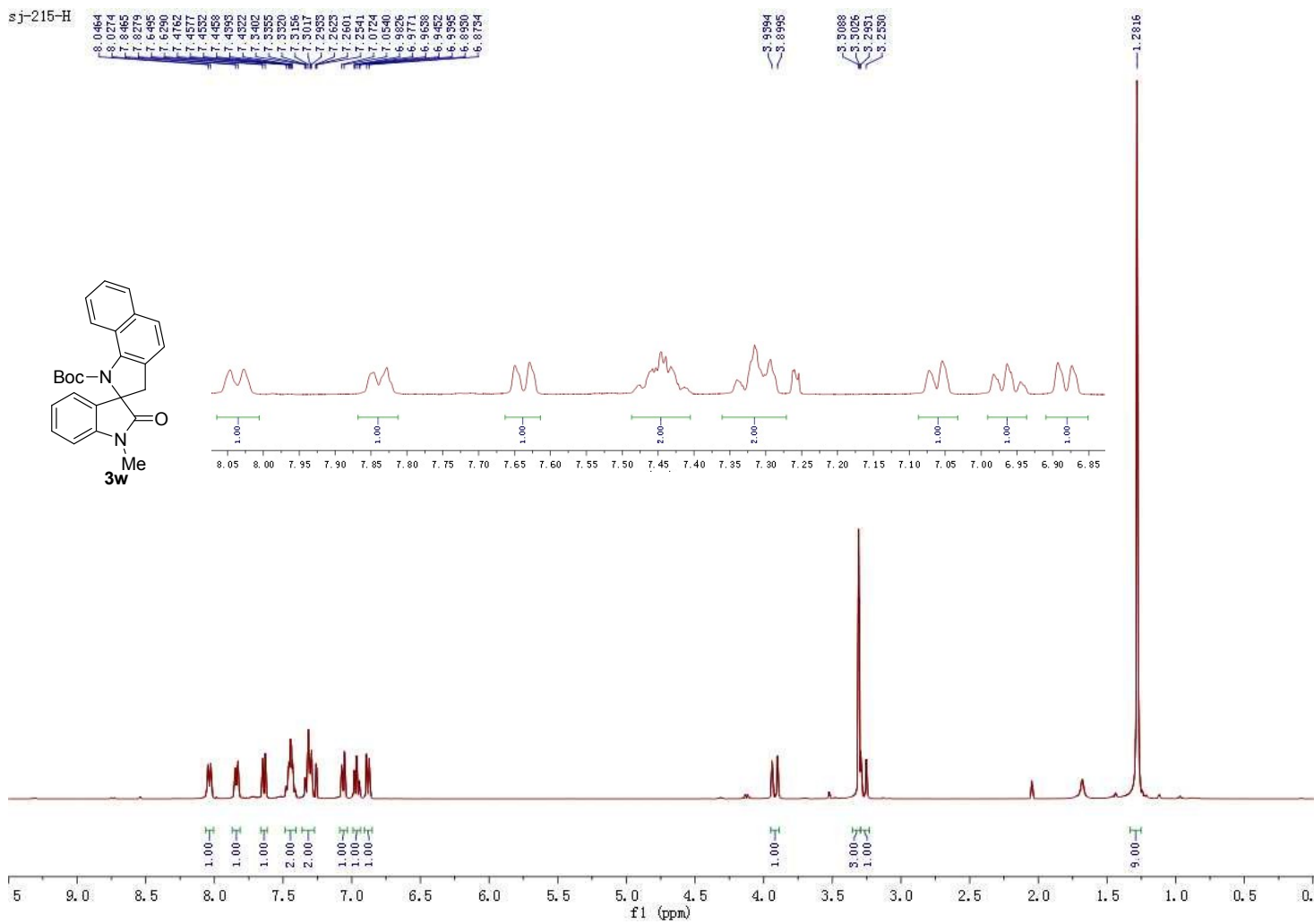
1.1263







¹H and ¹³C NMR of 3w



215-C

176.324

152.080

142.521
138.355
134.624
132.578
129.380
128.430
125.649
125.915
125.265
124.886
123.204
122.131

108.245

81.982

77.478

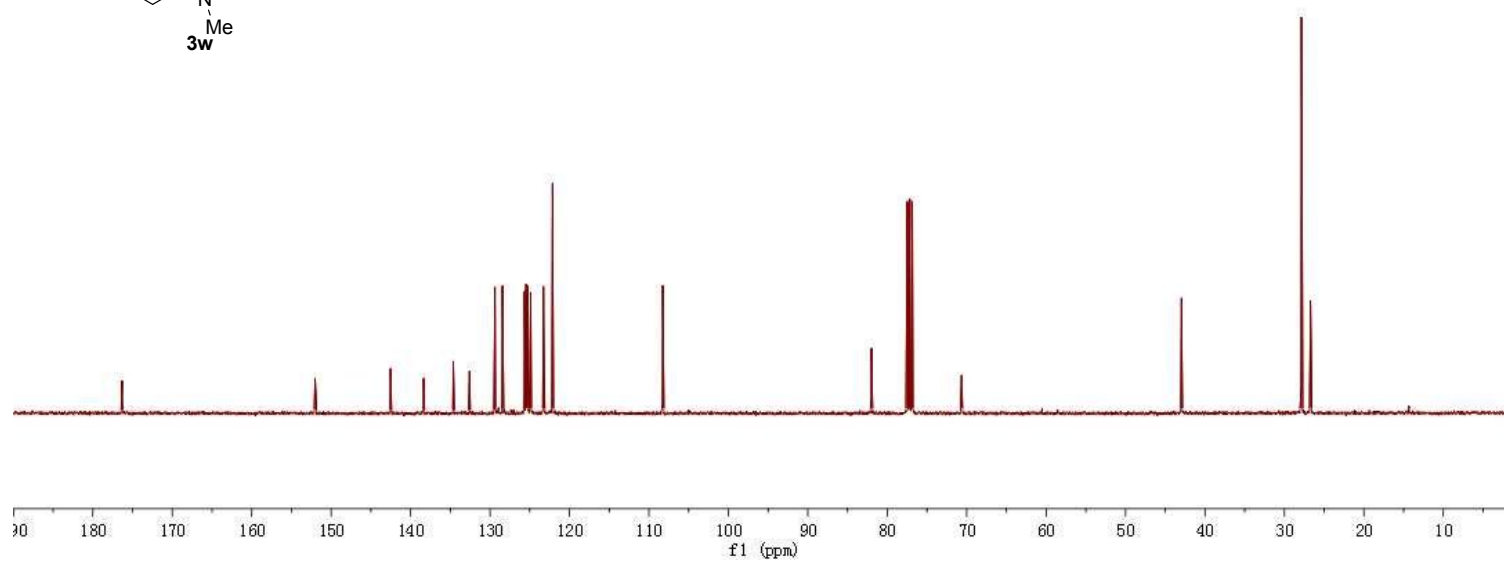
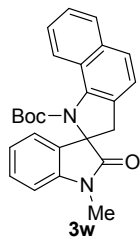
76.842

70.636

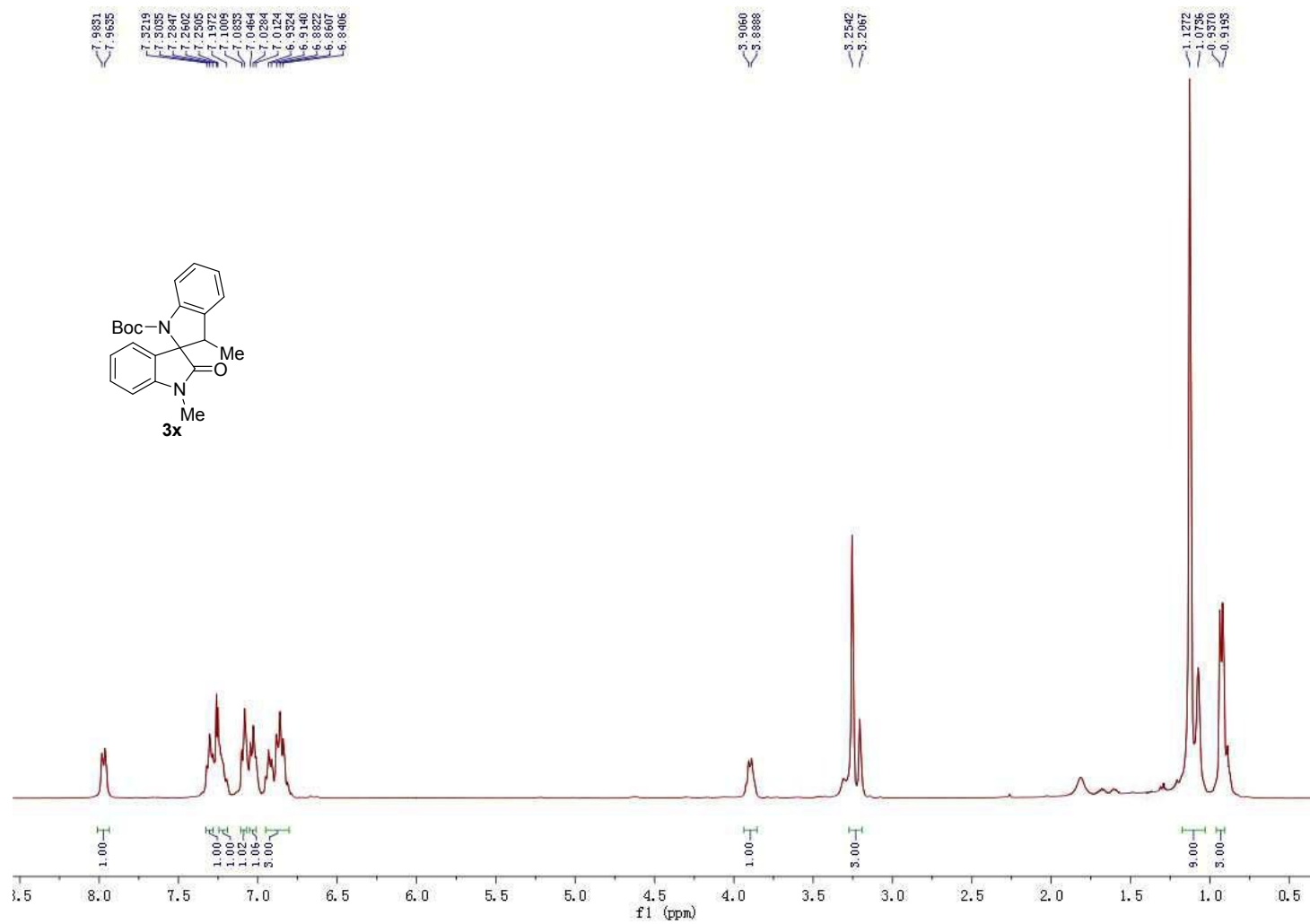
42.956

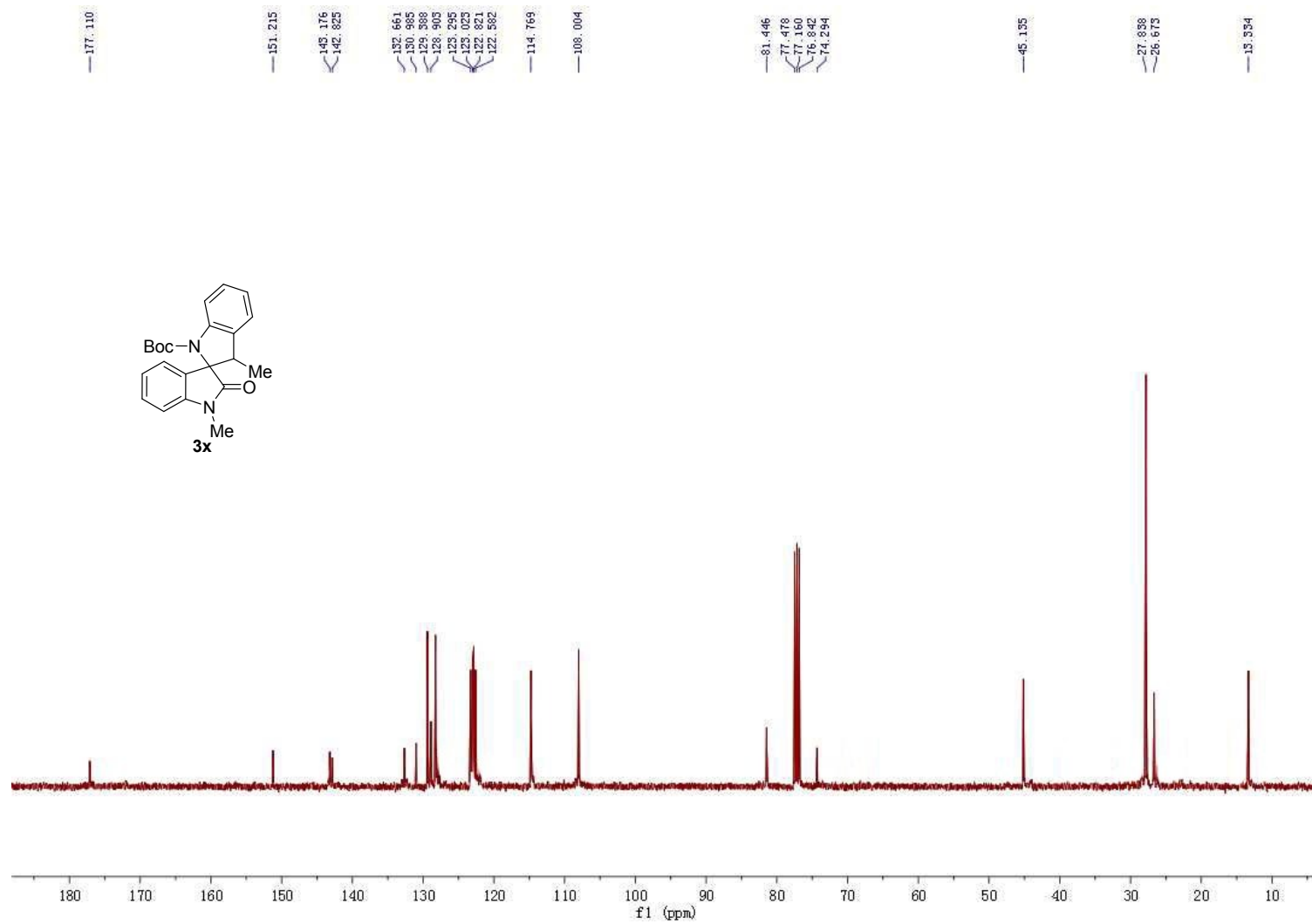
27.841

26.718

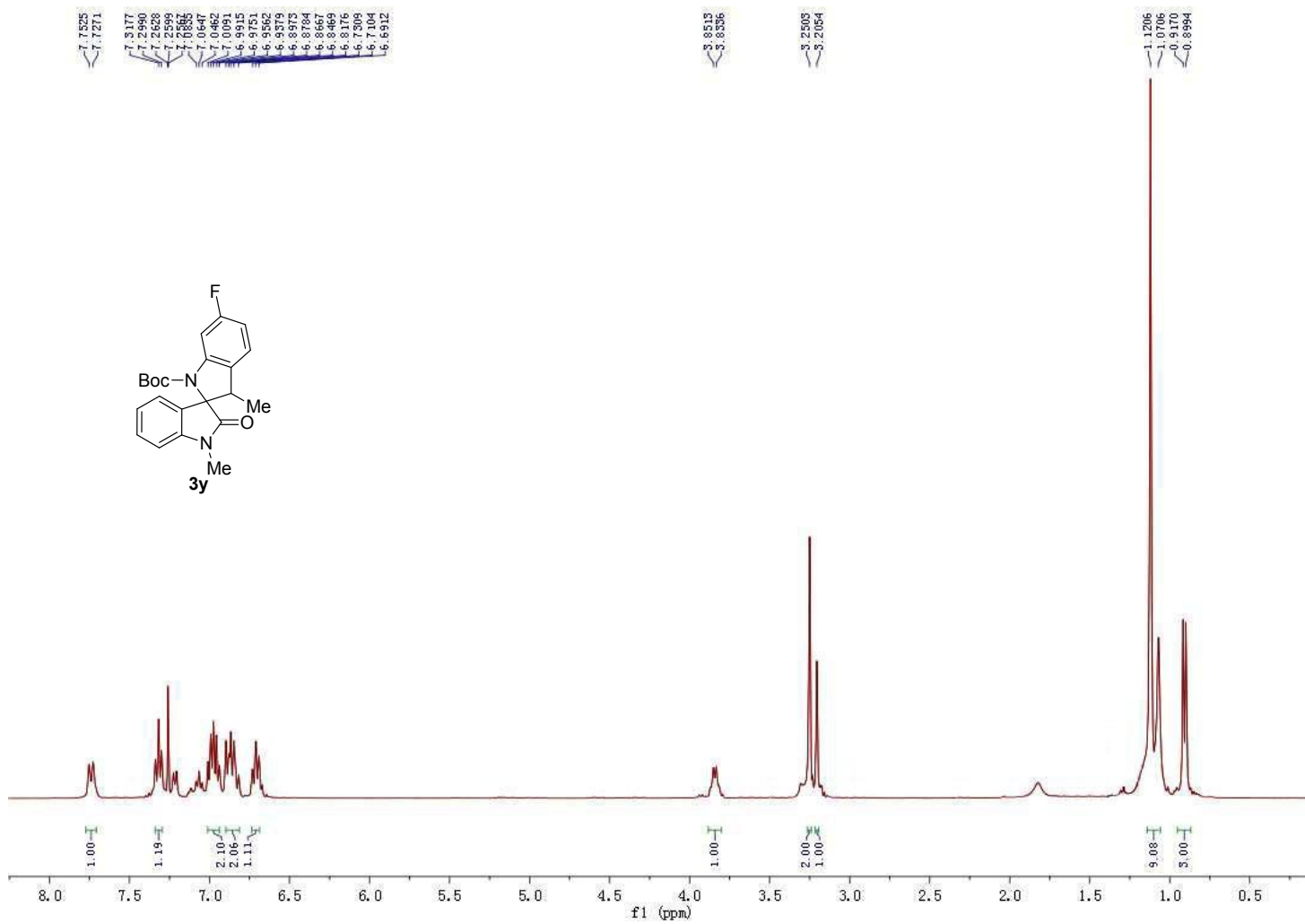


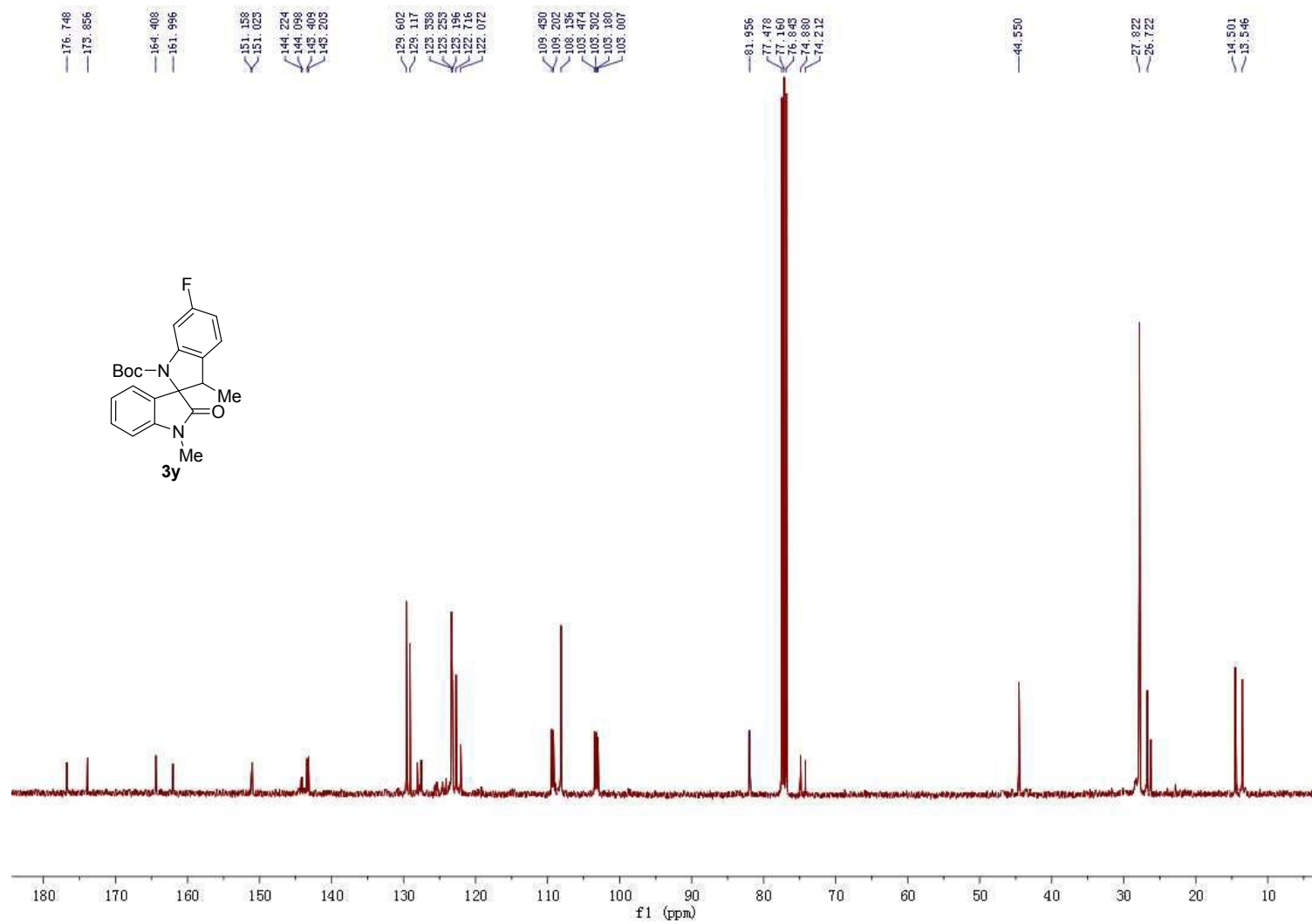
¹H and ¹³C NMR of 3x



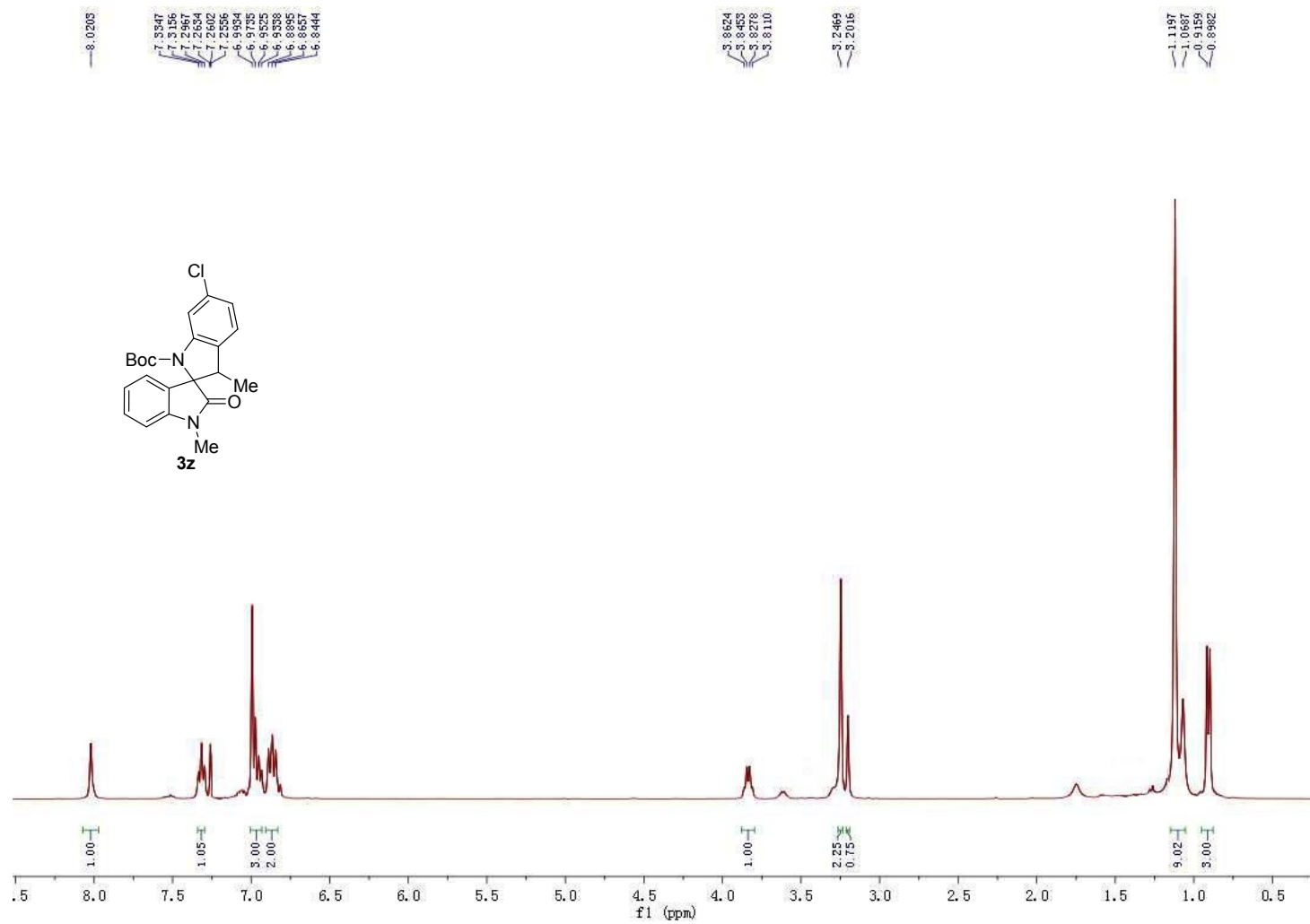


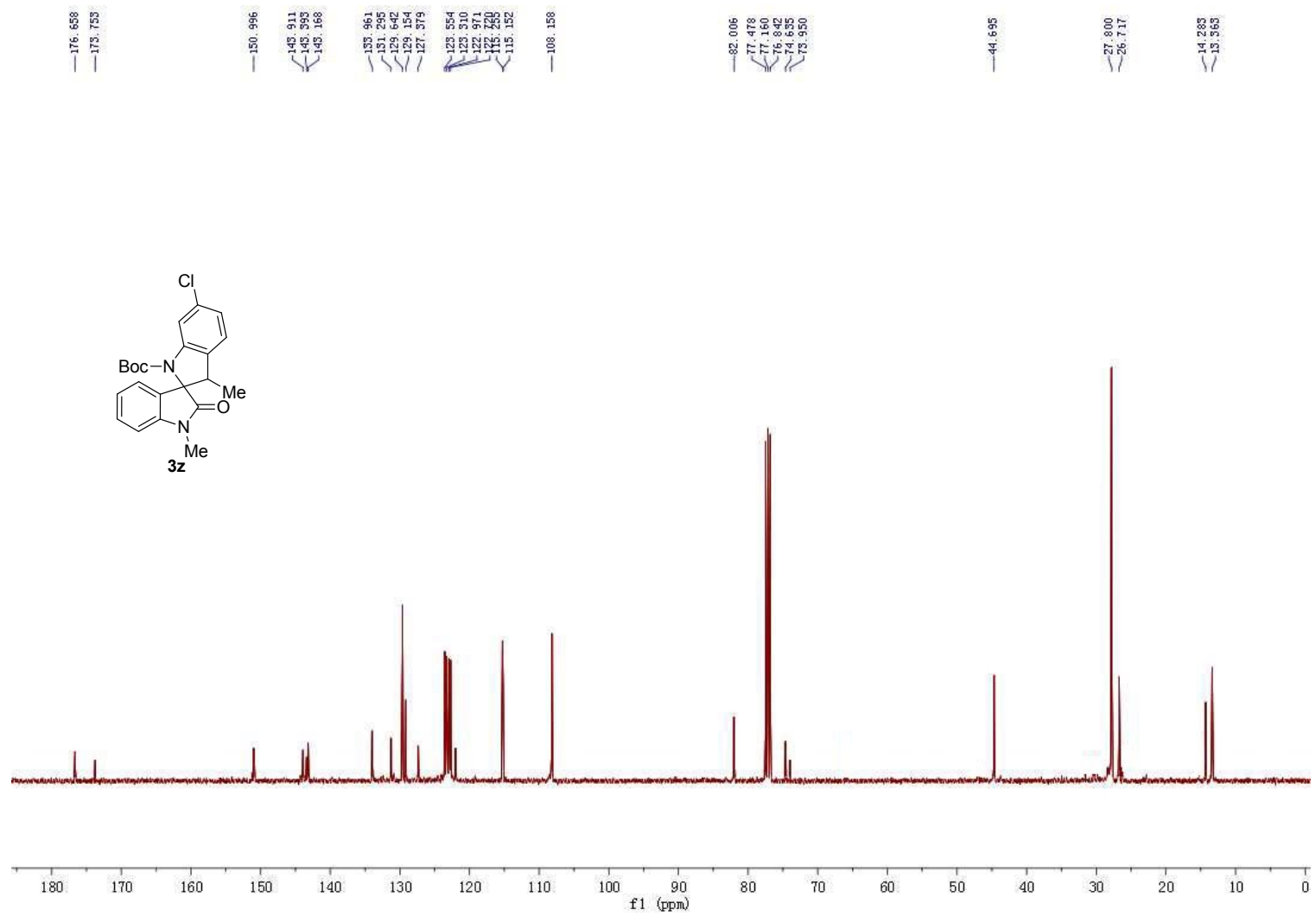
¹H and ¹³C NMR of 3y



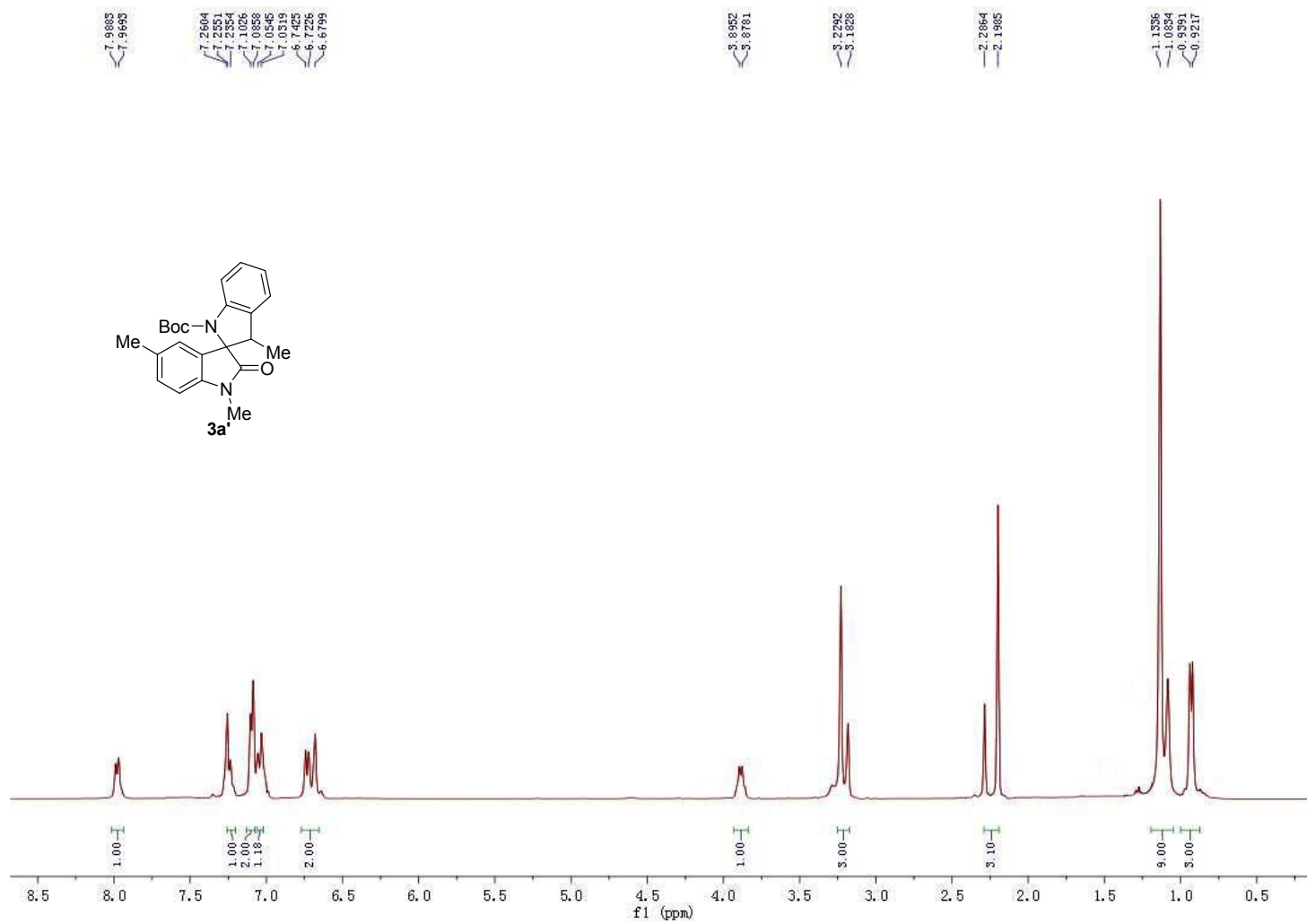


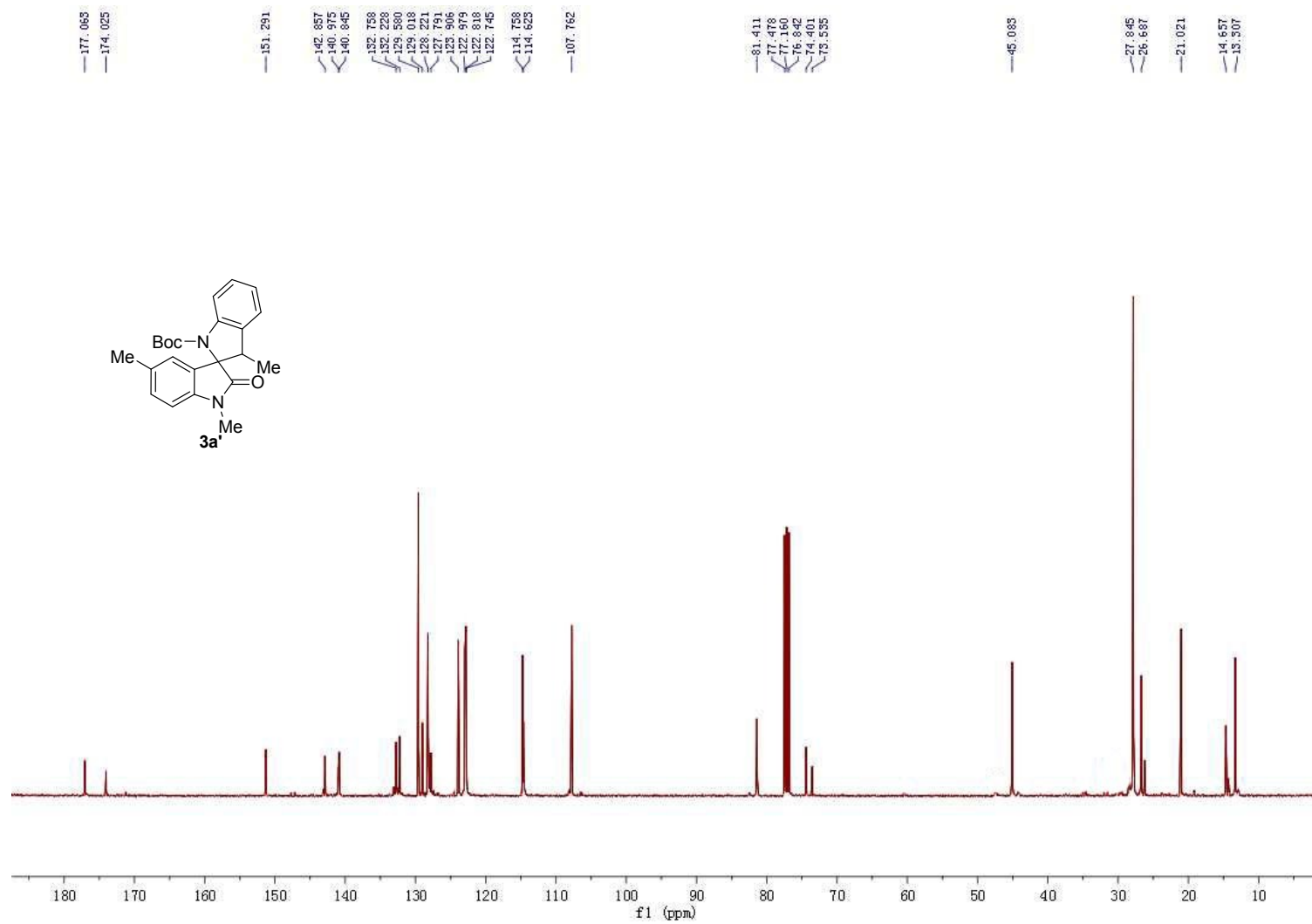
¹H and ¹³C NMR of 3z



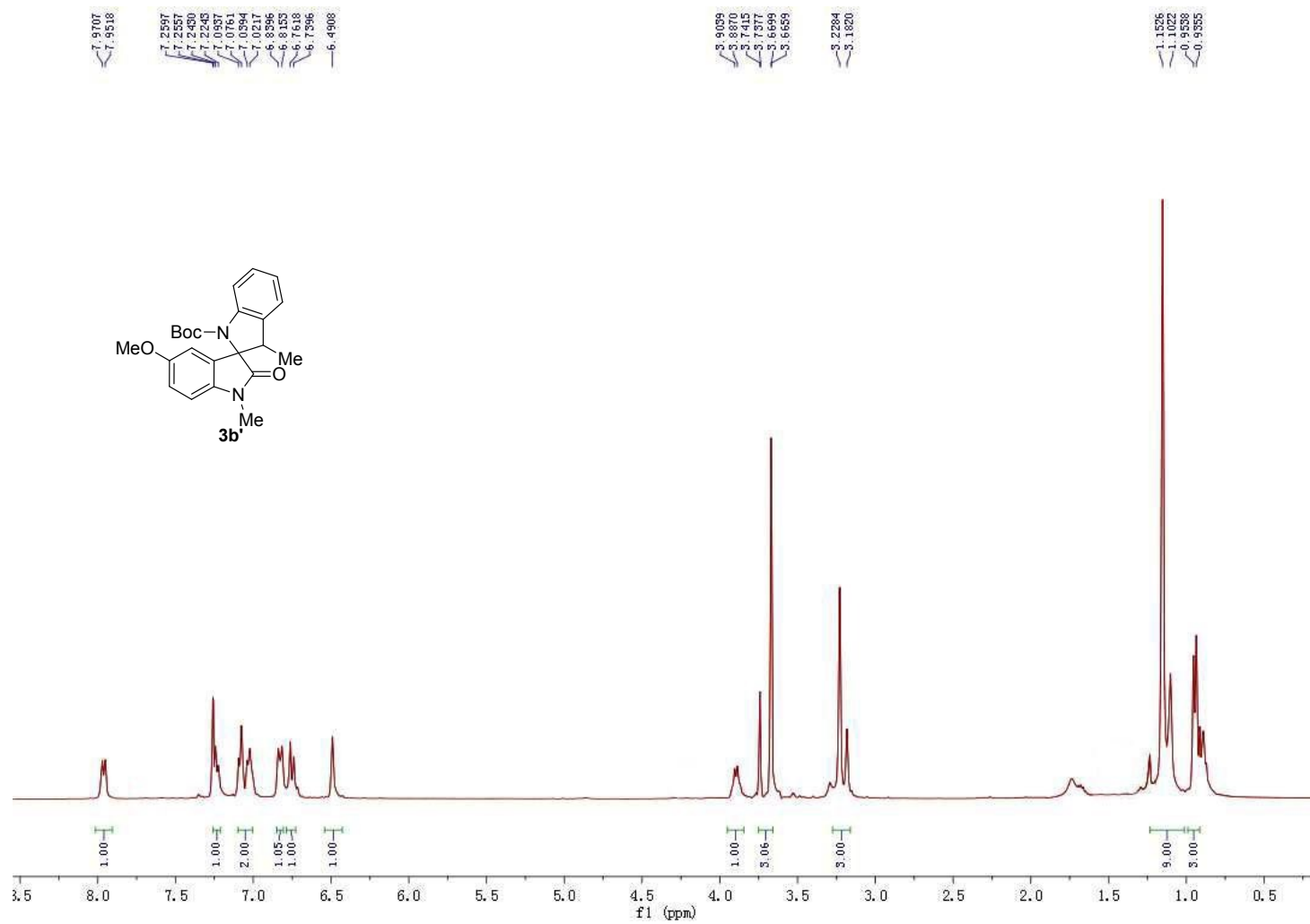


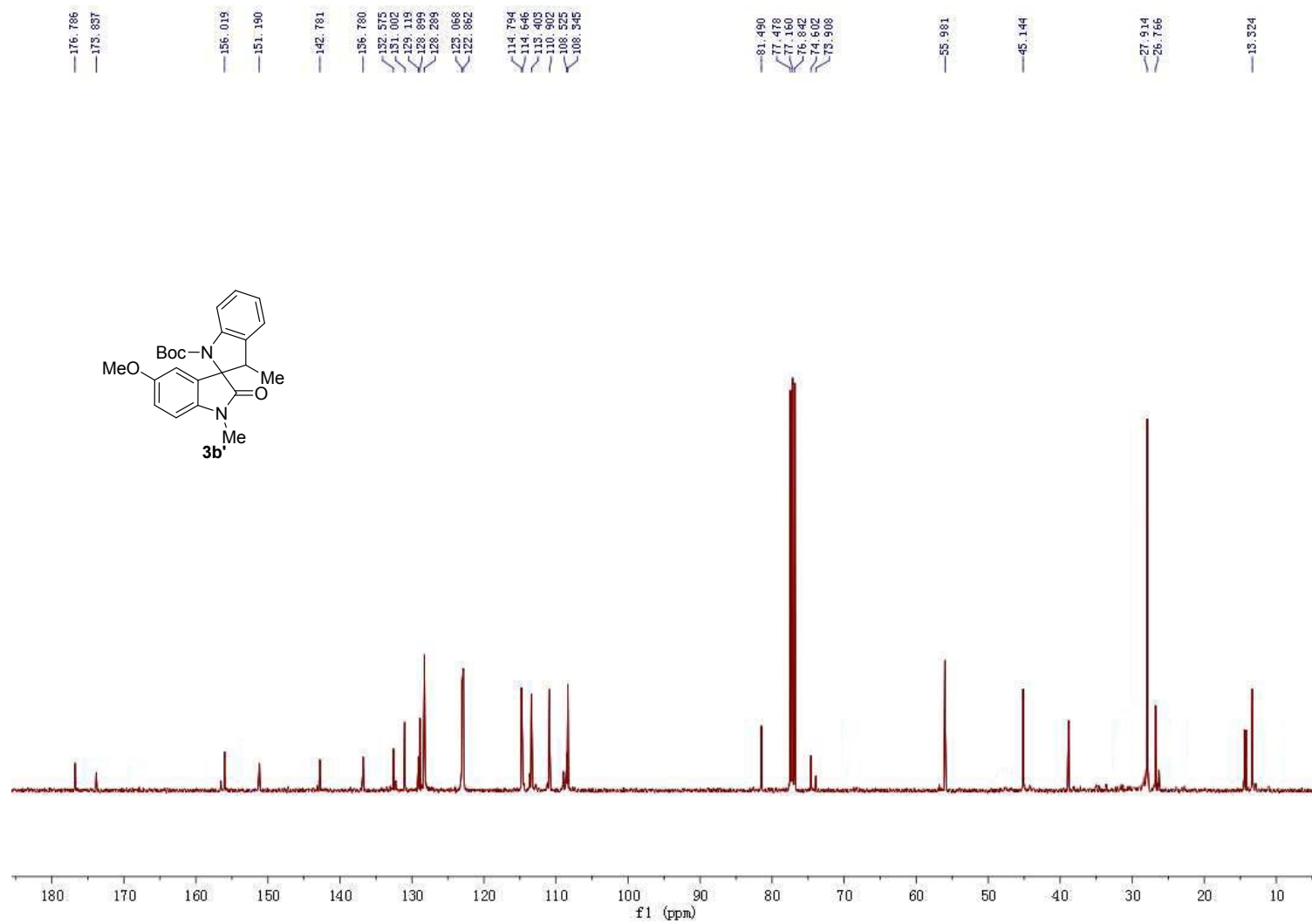
¹H and ¹³C NMR of 3a'



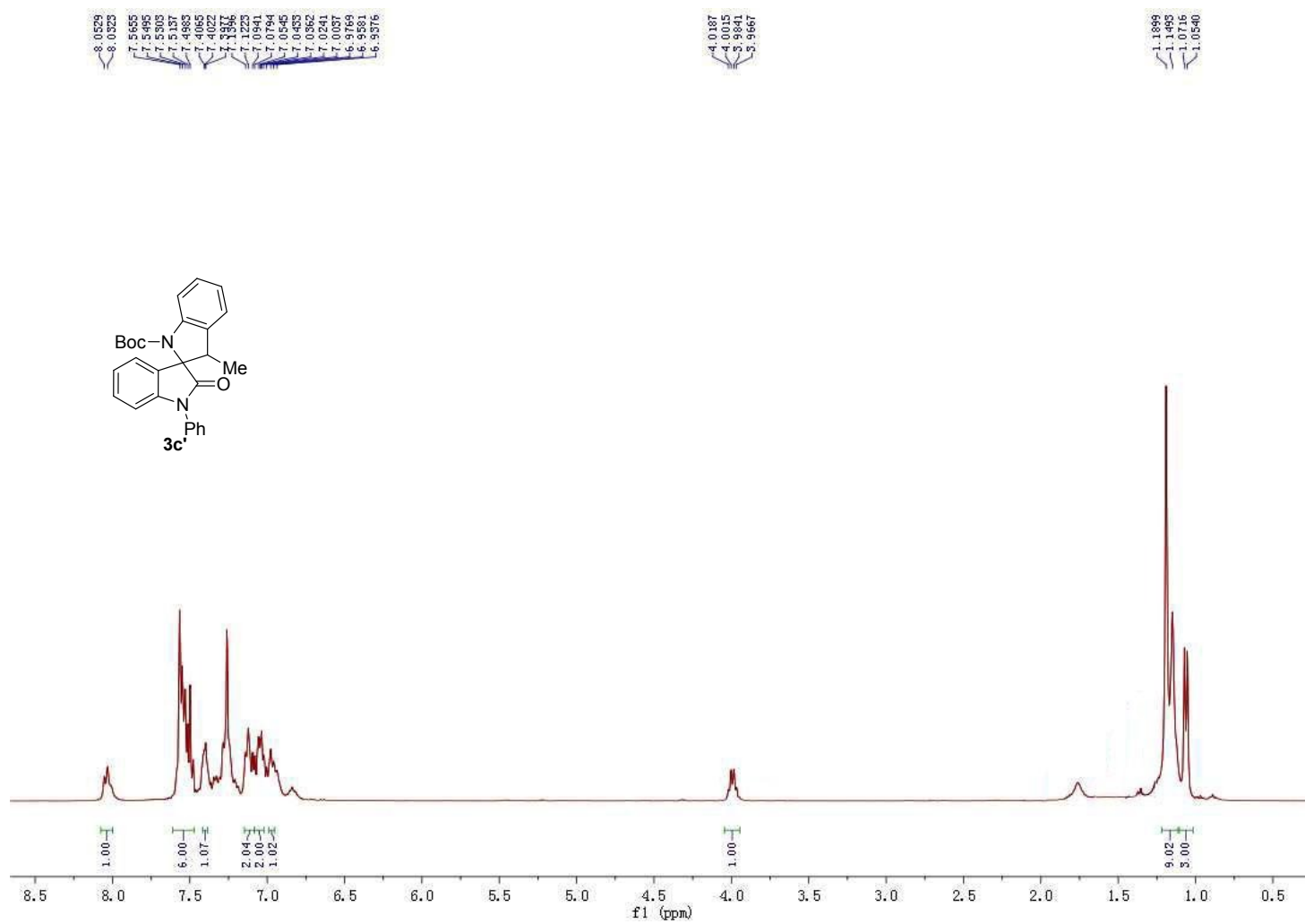


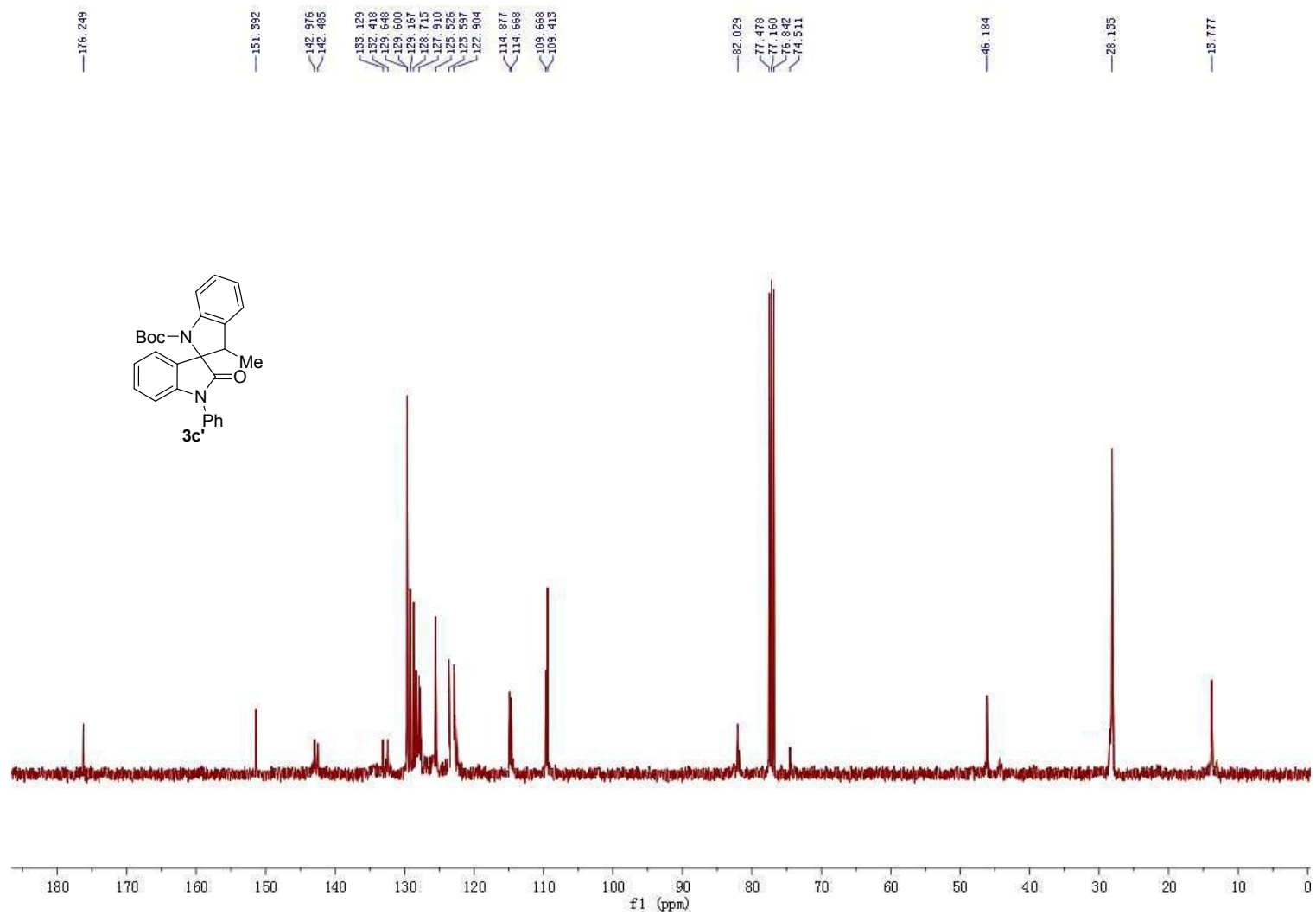
¹H and ¹³C NMR of 3b'





¹H and ¹³C NMR of 3c'





¹H and ¹³C NMR of 4

