**Supporting information**

**Green Cyclocondensation of -Ethylthio--indolyl--unsaturated Ketones with Semicarbazide Hydrochloride as Hydrazine Equivalent in Water: Aqueous Synthesis of 3-Pyrazolyl Indoles**

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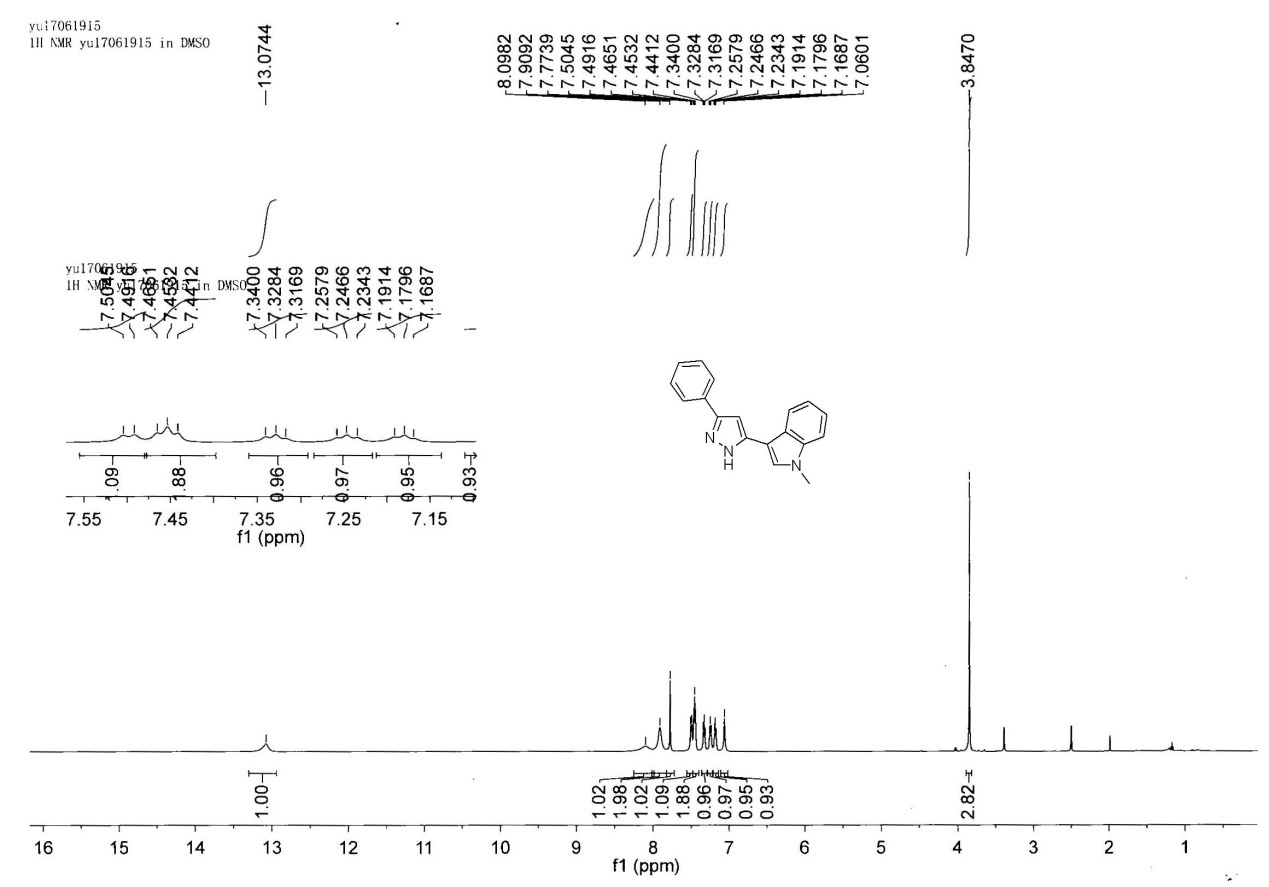
**General Considerations**

A 1H and 13C{1H} NMR spectra were recorded on a Bruker DRX-600 spectrometer and the chemical shift values refer to δ TMS=0.00 ppm; The HRMS analysis was achieved on Bruck micro Tof using ESI method. All the melting points were uncorrected. Analytical TLC plates, Sigma-Aldrich silica gel 60F200 were viewed by UV light (254 nm). Chromatographic purifications were performed on SDZF silica gel 160.

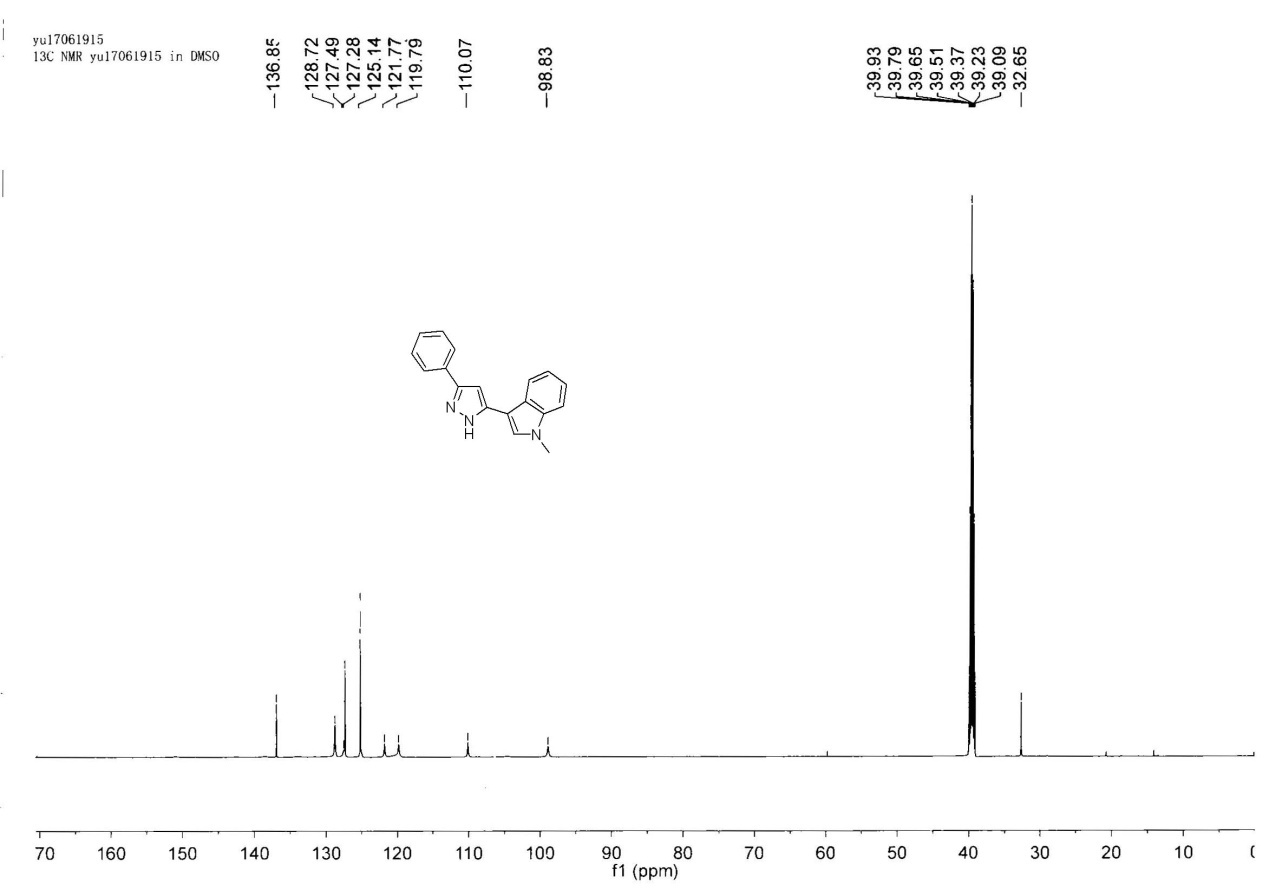
**Typical procedure for the preparation of 3-pyrazolyl indoles 3**

The mixture of **1** (0.25 mmol), **2** (56.2 mg, 0.50 mmol) and PEG-400 (0.25 mL, 0.75 mmol) in water (1 mL) in 20 mL reaction tube was stirred at reflux until **1** was completely consumed by TLC monitoring. After the mixture was allowed to cool down to ambient temperature, some white solid deposited from the reaction system. The white solid was collected by filtration and washed with water (3 × 25 mL) to give **3** in good yield.

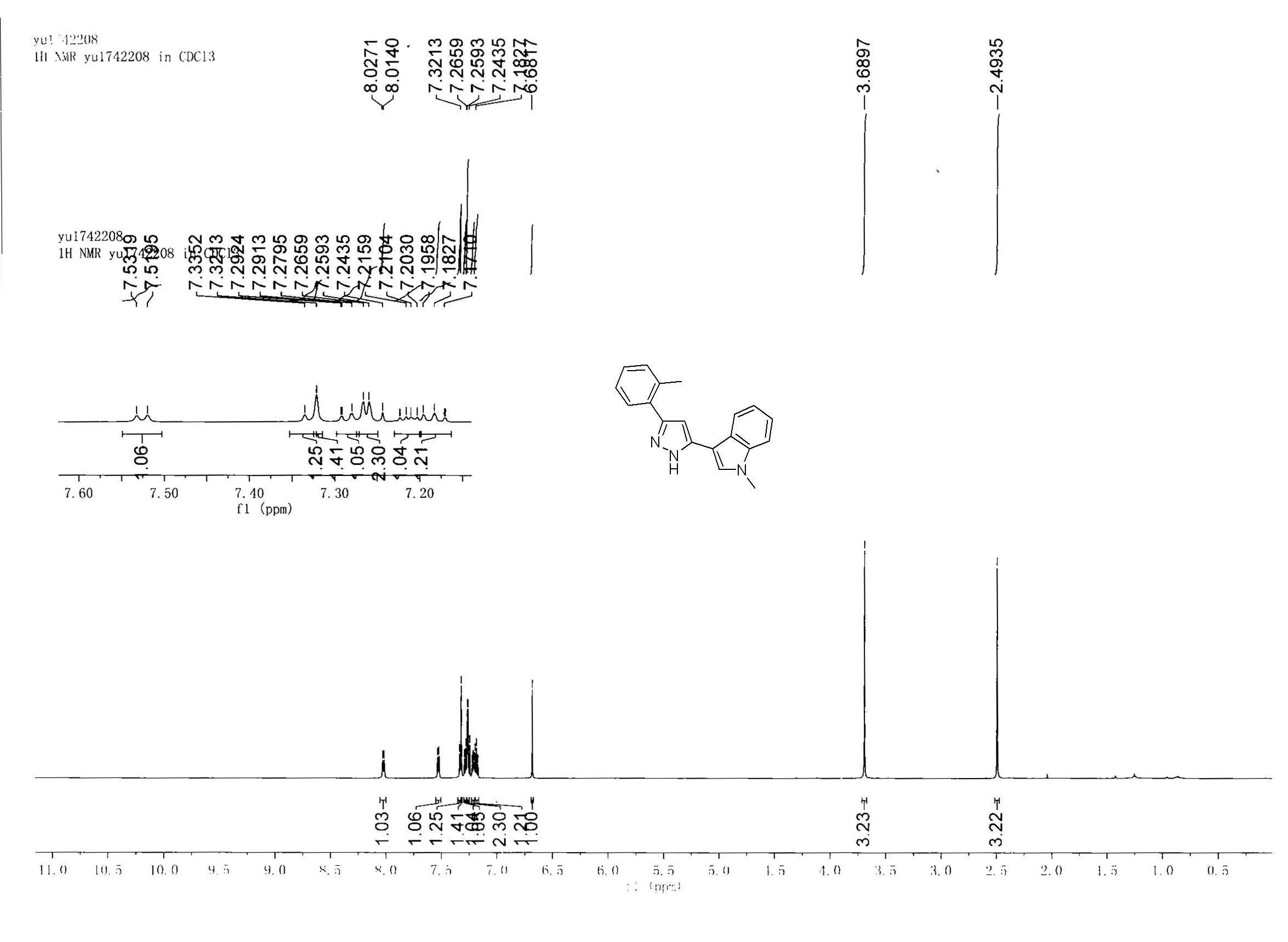
1. **1-methyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3a**: white solid; m.p. 220-222 oC.1H NMR (DMSO-*d*6, 600 MHz):**= 13.1 (br, 1 H), 8.10 (s, 1 H), 7.91 (s, 2 H), 7.77 (s, 1 H), 7.50 (d, *J*=7.7 Hz, 1 H), 7.45 (t, 2 H), 7.33( t, 1 H), 7.25 (t, 1 H), 7.18 (t, 1 H), 7.06 (s, 1 H), 3.85 (s, 3 H). 13C NMR (DMSO-*d*6, 150 MHz)**=136.9 (2 C), 128.7 (2 C), 127.5, 127.3 (3 C), 125.1 (5 C), 121.8, 119.8, 110.1, 98.8, 32.7. HRMS Cacldfor C18H16N3+: ([M+H]+) 274.1339; Found: 274.1349.
2. **1-methyl-3-(3-(o-tolyl)-1H-pyrazol-5-yl)-1H-indole 3b** white solid; m.p. 163-165oC. 1H NMR (CDCl3, 600 MHz): 8.02 (d, *J* = 7.9 Hz, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.33 (d, *J*=8.3 Hz, 1 H), 7.32 (s, 2 H), 7.28 (d, *J* = 7.7 Hz, 1 H), 7.26 ( d, *J* = 7.4 Hz, 2 H), 7.22-7.20 (m, 1 H), 7.18 (t, 1 H), 3.69 (s, 3 H), 2.49 (s, 3 H). 13C NMR (CDCl3, 150 MHz)**=137.2, 136.2, 131.0 (2 C), 129.2, 128.2, 126.9 (2 C), 126.1, 126.0 (2 C), 122.3, 120.4, 120.3 (2 C), 109.6, 103.1, 32.9, 21.1. HRMS Cacld for C19H18N3+: ([M+H]+) 288.1495; Found: 288.1488.
3. **1-methyl-3-(3-(m-tolyl)-1H-pyrazol-5-yl)-1H-indole 3c** white solid; m.p. 190-192oC. 1H NMR (Acetone-*d*6, 600 MHz):s, 1 H), 8.13 (d, *J* = 7.9 Hz, 1 H), 7.77 (s, 1 H), 7.72 (d, *J* = 7.7 Hz, 1 H), 7.68 (s, 1 H), 7.45 (d, *J* = 8.2 Hz, 1 H), 7.31( t, 1 H), 7.25(t, 1 H), 7.18-7.14 (m, 2 H), 7.01 (s, 1 H), 3.89 (s, 3 H), 2.39 (s, 3 H). 13C NMR (Acetone-*d*6, 150 MHz)**=138.9, 138.3, 129.4 (2 C), 129.0, 127.8(2 C), 126.9(2 C), 123.4 (2 C), 122.8 (2 C), 120.7 (2 C), 110.6, 99.9, 33.1, 21.5. HRMS Cacld for C19H18N3+: ([M+H]+) 288.1495; Found: 288.1490.
4. **1-methyl-3-(3-(p-tolyl)-1H-pyrazol-5-yl)-1H-indole 3d** white solid; m.p. 214-216oC. 1H NMR (CDCl3, 600 MHz):7.98 (d, *J* = 7.7 Hz, 1 H), 7.65 (d, *J* = 7.6 Hz, 2 H), 7.33-7.29 (m, 3 H), 7.22 (t, 1 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 6.78 (s, 1 H), 3.62 (s, 3 H), 2.37 (s, 3 H). 13C NMR (CDCl3, 150 MHz)**=137.7, 137.2, 129.5(3 C), 127.0 (2 C), 125.9, 125.7(4 C), 122.3, 120.3, 120.2 109.6, 99.8, 32.8, 21.4. HRMS Cacld for C19H18N3+: ([M+H]+) 288.1495; Found: 288.1498.
5. **3-(3-(4-methoxyphenyl)-1H-pyrazol-5-yl)-1-methyl-1H-indole 3e** white solid; m.p. 186-188oC. 1H NMR (CDCl3, 600 MHz):7.96 (d, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 7.6 Hz, 2 H), 7.30 (s, 3 H), 7.29 (s, 1 H), 7.25(s,1 H), 7.22-7.20 (m, 1 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 6.72 (s, 1 H), 3.79 (s, 3 H), 3.54 (s, 3 H). 13C NMR (CDCl3, 150 MHz)**=159.4, 137.1, 127.0 (6 C), 125.9, 122.2, 120.2, 120.1, 114.1(3 C), 109.6, 99.4, 55.4, 32.8. HRMS Cacld for C19H18N3O+: ([M+H]+) 304.1444; Found: 304.1448.
6. **3-(3-(4-chlorophenyl)-1H-pyrazol-5-yl)-1-methyl-1H-indole 3f** white solid; m.p. 247-249oC. 1H NMR (DMSO-*d*6, 600 MHz):13.1 (s, 1 H), 8.02-7.85 (m, 3 H), 7.80 (s, 1 H), 7.51 (s, 1 H),7.49 (s, 2 H), 7.19(t, 3 H), 3.85 (s, 3 H). 13C NMR (DMSO-*d*6, 150 MHz)**=150.3, 139.1, 137.3, 133.4, 132.1, 129.0, 127.8 (2 C), 127.3(2 C),125.2, 122.4, 120.5, 120.2, 110.7, 104.8, 99.2, 33.2. HRMS Cacld for C18H15ClN3+: ([M+H]+) 308.0949; Found: 308.0955.
7. **3-(3-(4-bromophenyl)-1H-pyrazol-5-yl)-1-methyl-1H-indole 3g** white solid; m.p. 167-169oC.1H NMR (DMSO-*d*6, 600 MHz):13.1 (s, 1 H), 8.0 (d, *J* = 7.3Hz, 1 H), 7.90 (d, *J* = 7.4Hz, 2 H), 7.77 (s, 1 H), 7.61 (d, *J* = 7.4Hz, 2 H), 7.52(d, *J* = 7.6 Hz,1 H), 7.25 (t, 1 H), 7.19 (t, 1 H), 7.12 (s, 1 H), 3.86 (s, 3 H). 13C NMR (DMSO-*d*6, 150 MHz)**=149.9, 138.7, 136.8, 133.3, 131.9, 131.5 (2 C), 127.2 (2 C), 124.7, 122.0, 120.2, 120.0, 119.7, 110.2, 104.3, 98.8, 32.8. HRMS Cacld for C18H15BrN3+: ([M+H]+) 352.0444; Found: 352.0440.
8. **1-methyl-3-(3-(thiophen-2-yl)-1H-pyrazol-5-yl)-1H-indole 3h** white solid; m.p. 248-250oC. 1H NMR (DMSO-*d*6, 600 MHz):13.0 (s, 1 H), 7.96 (d, *J* = 7.6Hz, 1 H), 7.77 (s, 1 H), 7.52 (d, *J* = 8.0Hz, 1 H), 7.51 (d, *J* = 3.4 Hz,1 H), 7.44 (s, 1 H), 7.27 (t, 1 H), 7.20 (t, 1 H), 7.11 (s, 1 H), 6.97 (s, 1 H), 3.86 (s, 3 H). 13C NMR (DMSO-*d*6, 150 MHz)**=146.7, 138.5, 137.4, 136.8, 127.6, 127.4, 124.7, 124.4, 123.6, 122.0, 120.0, 119.6, 110.3, 104.1, 98.4, 32.8. HRMS Cacld for C16H14N3S+: ([M+H]+) 280.0903; Found: 280.0910.
9. **1-methyl-3-(3-(naphthalen-1-yl)-1H-pyrazol-5-yl)-1H-indole 3i** white solid; m.p. 164-166oC. 1H NMR (CDCl3, 600 MHz):12.5 (s, 1 H), 8.43 (s, 1 H), 7.98 (s, 1 H), 7.81 (d, *J* = 7.7Hz, 1 H), 7.72 (d, *J* = 8.0Hz, 1 H), 7.58 (s, 1 H), 7.44-7.41 (m, 2 H), 7.25-7.23 (m, 3 H), 7.14 (t, 2 H), 6.84 (s, 1 H), 3.38 (s, 3 H). 13C NMR (CDCl3, 150 MHz)**=137.0, 133.7, 131.3, 128.4, 128.2 (2 C), 127.0 (2 C), 126.9 (2 C), 126.3, 125.8 (3 C), 125.2 (2 C), 122.0, 120.1 (2 C), 109.4, 103.7, 32.4. HRMS Cacld for C22H18N3+: ([M+H]+) 324.1495; Found: 324.1490.
10. **1,5-dimethyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3j** white solid; m.p. 227- 229oC. 1H NMR (Acetone-*d*6, 600 MHz):(br,7.94 (d, *J* = 7.7 Hz, 3 H), 7.63 (s, 1 H), 7.43 (t, 2 H), 7.33 (d, *J* = 8.3 Hz, 1 H), 7.31 (d, *J* = 7.4 Hz, 1 H), 7.08 (d, *J* = 8.3 Hz, 1 H), 7.02 (s, 1 H), 3.84 (s, 3 H), 2.47 (s, 3 H). 13C NMR (Acetone-*d*6, 150 MHz)**=136.8, 129.7, 129.5 (3 C), 128.3, 127.8(2 C), 126.9, 126.2 (4 C), 124.4, 110.3, 99.7, 99.7, 33.1, 21.6. HRMS Cacld for C19H18N3+: ([M+H]+) 288.1495; Found: 288.1500.
11. **5-methoxy-1-methyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3k** white solid; m.p. 225-227oC. 1H NMR (Acetone-*d*6, 600 MHz):(br,7.93 (d, *J* = 7.5 Hz, 2 H),7.64 (s, 1 H), 7.44 (t, 2 H), 7.35 (d, *J* = 8.9 Hz, 1 H), 7.32 (t, 1 H), 6.99 (s, 1 H), 6.90 (dd, *J*1= 8.8 Hz, *J*2 = 2.3 Hz, 1 H), 7.25-7.23 (m, 3 H), 7.14 (t, 2 H), 6.84 (s, 1 H), 3.38 (s, 3 H). 13C NMR (Acetone-*d*6, 150 MHz)**=155.8, 133.6, 129.6 (3 C), 128.4 (4 C), 127.1, 126.3 (4 C), 113.1, 111.4, 99.7, 56.0, 33.3. HRMS Cacld for C19H18N3O+: ([M+H]+) 304.1444; Found: 304.1441.
12. **5-bromo-1-methyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3l** white solid; m.p. 245-247oC.1H NMR (Acetone-*d*6, 600 MHz):(s,, 7.91 (d, *J* = 7.6 Hz, 2 H), 7.74 (s, 1 H), 7.47-7.43 (m, 3 H), 7.36-7.34 (m, 2 H), 7.04 (s, 1 H), 3.91 (s, 3 H). 13C NMR (Acetone-*d*6, 150 MHz)**=137.1, 129.7 (3 C), 129.4(2 C), 128.6, 128.3, 126.3 (4 C), 125.4, 124.1, 113.8, 112.6, 100.1,33.4. HRMS Cacld for C18H15BrN3+: ([M+H]+) 352.0444; Found: 352.0447.
13. **1-ethyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3m** white solid; m.p. 176-177oC. 1H NMR (Acetone-*d6*, 400 MHz):8.13 (d, *J* = 7.8 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.75 (s, 1 H), 7.48-8.41 (m, 3 H), 7.31 (t, 1 H), 7.23 (t, 1 H ), (t, 1 H), 7.04 (s, 1 H), 4.28-4.23 (m, 2 H), 1.44 (t, 3 H). 13C NMR (Acetone-*d6*, 100 MHz)**=137.3, 129.5 (4 C), 128.3, 126.8, 126.2 (4 C), 126.1, 122.7, 121.4, 120.7, 110.6, 99.9, 41.6, 15.7. HRMS Cacld for C19H18N3+: ([M+H]+) 288.1495; Found: 288.1502.
14. **1-benzyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3n** white solid; m.p. 193-195oC. 1H NMR (CDCl3, 600 MHz):(s,, 7.97 (d, *J* = 7.3 Hz, 1 H), 7.74 (d, *J* = 7.2 Hz, 2 H), 7.36 (s, 1 H), 7.32 (t, 2 H), 7.28 (d, *J* = 7.3 Hz, 1 H), 7.26 (t, 1 H), 7.23 (d, *J* = 7.2 Hz, 1 H ), 7.20-7.17 (m, 4 H), 7.03 (t, 2 H), 6.79 (s, 1 H), 5.05 (s, 2 H). 13C NMR (CDCl3, 150 MHz)**=136.8, 136.7, 128.8 (4 C), 128.7, 127.8, 128.6, 127.7, 126.8 (4 C), 126.3, 126.0, 125.6 (2 C), 122.4, 120.5, 120.2, 110.2, 100.0, 50.0. HRMS Cacld for C24H20N3+: ([M+H]+) 350.1652; Found: 350.1660.
15. **1-methyl-3-(3-methyl-1H-pyrazol-5-yl)-1H-indole 3o** white solid; m.p. 174-176oC. 1H NMR (DMSO-*d*6, 400 MHz): 8.01 (d, *J* = 7.8 Hz, 1 H),(s,, 7.44 (d, *J* = 8.1 Hz, 1 H), 7.19 (t, 1 H), 7.10 (t, 1 H), 6.30 (s, 1 H), 3.80 (s, 3 H), 2.26 (s, 3 H). 13C NMR (DMSO-*d*6, 100 MHz)**=138.0 (2 C), 128.2 (2 C), 126.4, 122.7 (2 C), 121.8, 120.6 (2 C), 111.0, 102.0, 33.7. HRMS Cacld for C13H14N3+: ([M+H]+) 212.1182; Found: 212.1179.
16. **2-methyl-3-(3-phenyl-1H-pyrazol-5-yl)-1H-indole 3p** white solid; m.p. 184-186oC.
17. 1 H NMR (CDCl3, 600 MHz):(s,, 7.80 (d, *J* = 7.6 Hz, 2 H), 7.75 (d, *J* = 7.7 Hz, 1 H), 7.33 (t, 2 H), 7.28 (t, 1 H), 7.24 (t, 1 H), 7.16 (t, 1 H), 7.13 (t, 1 H), 6.71 (s, 1 H), 2.41 (s, 3 H). 13C NMR (CDCl3, 150 MHz)**=135.1, 133.4, 128.7 (4 C), 127.7, 127.1, 125.7(4 C), 121.8, 120.5, 118.6, 110.5, 101.5, 12.7. HRMS Cacld for C18H16N3+: ([M+H]+) 274.1339; Found: 274.1330.



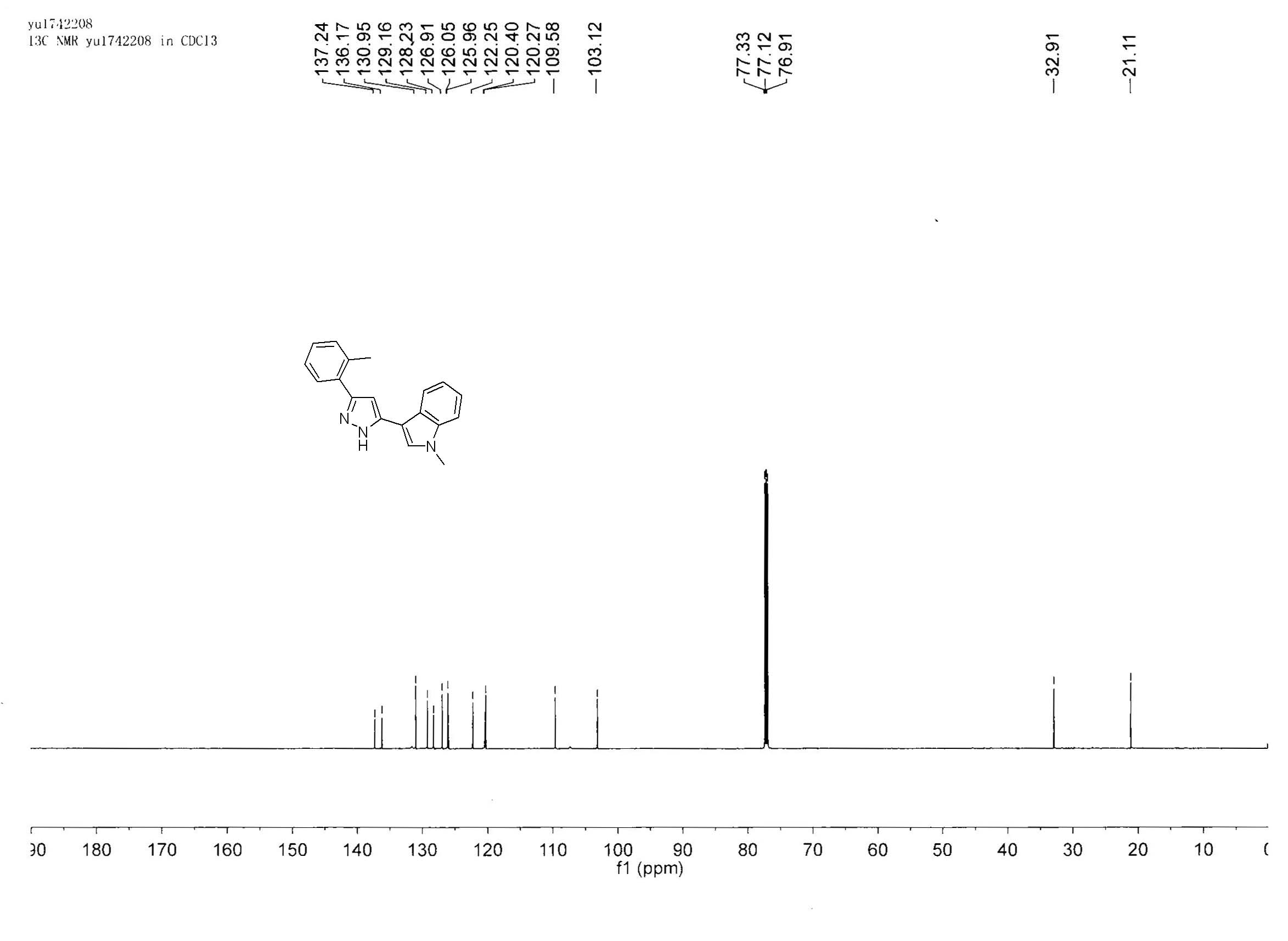
1H NMR of **3a**



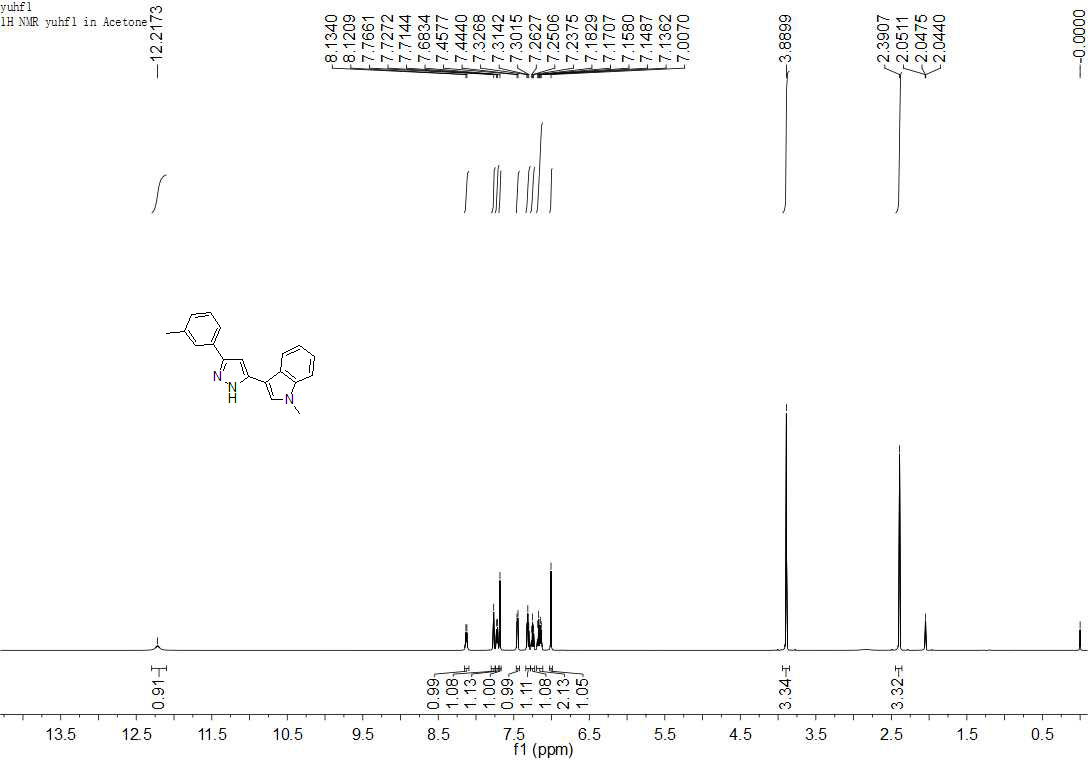
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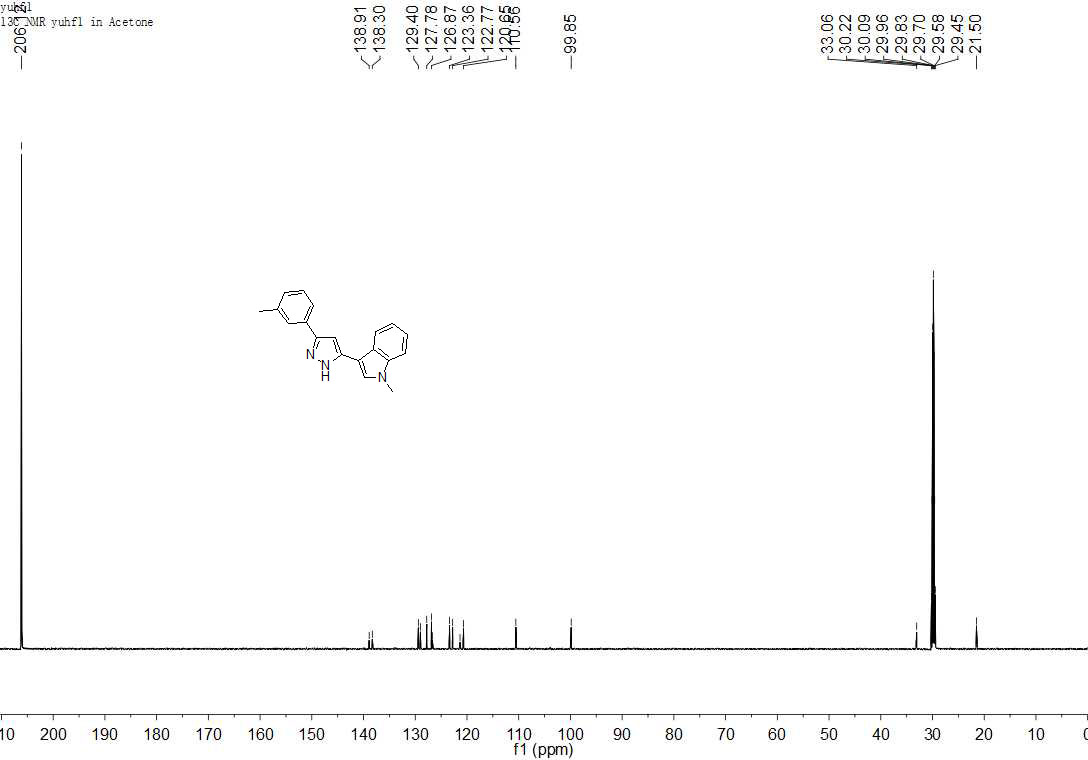
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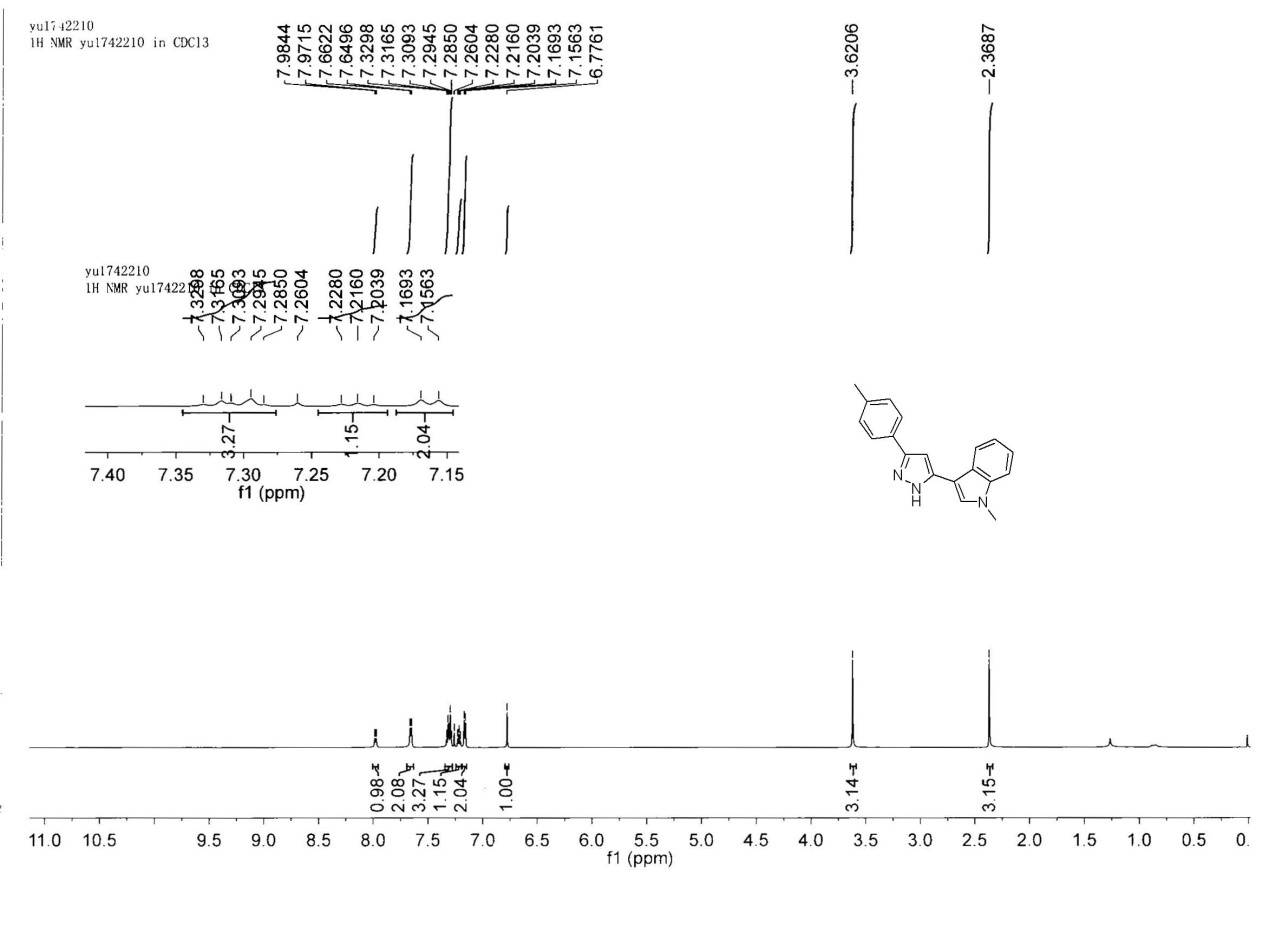
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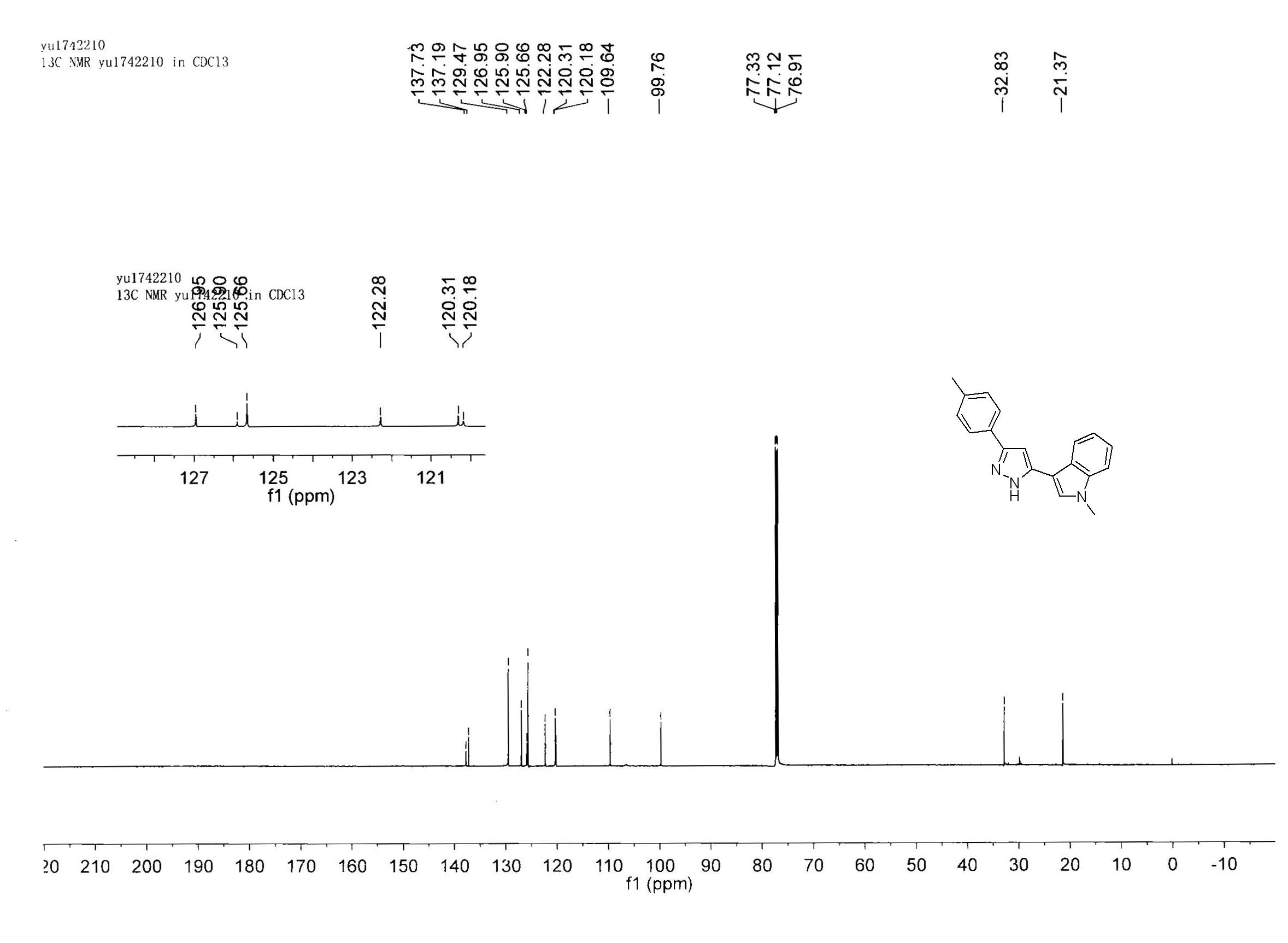
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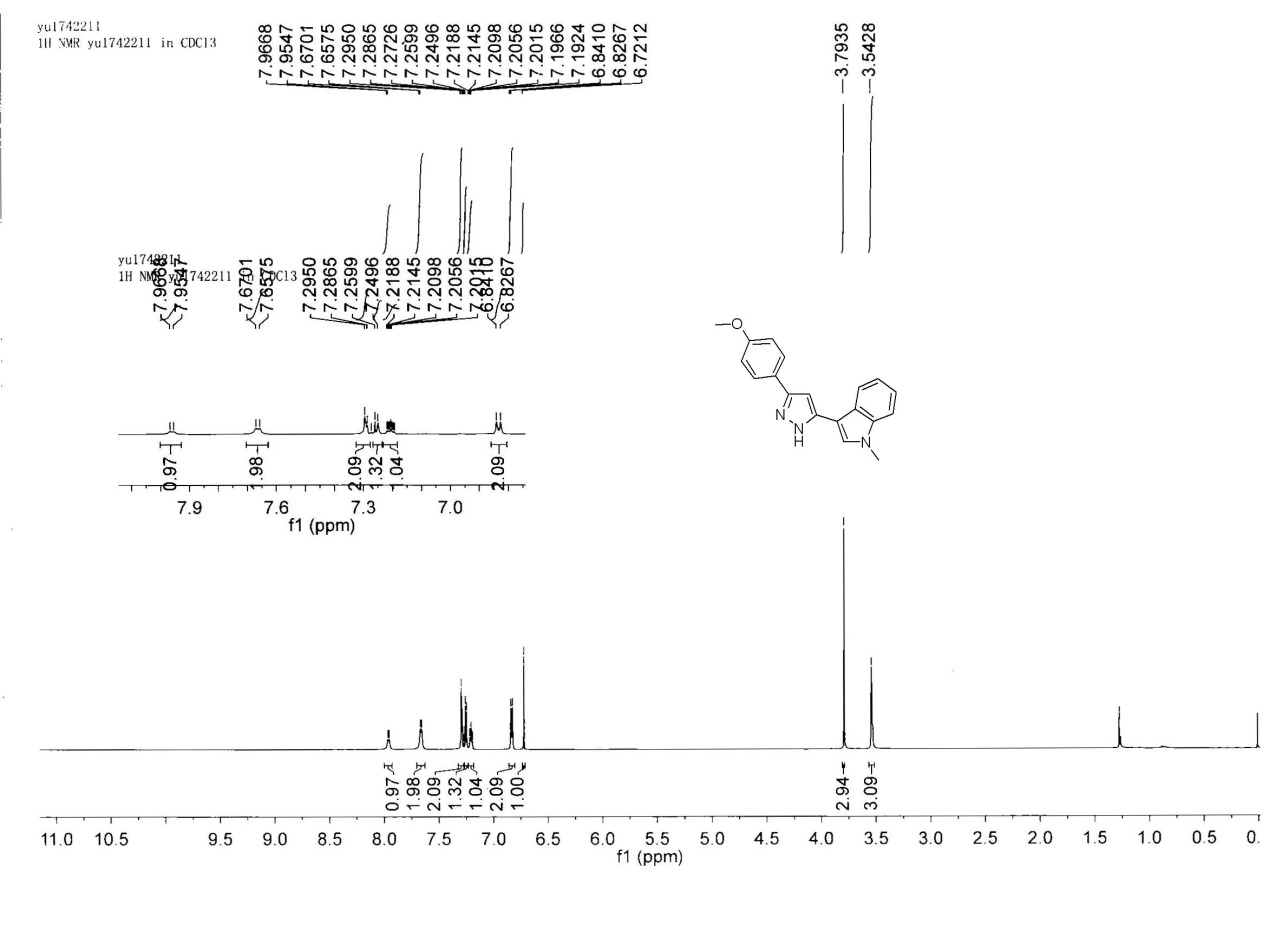
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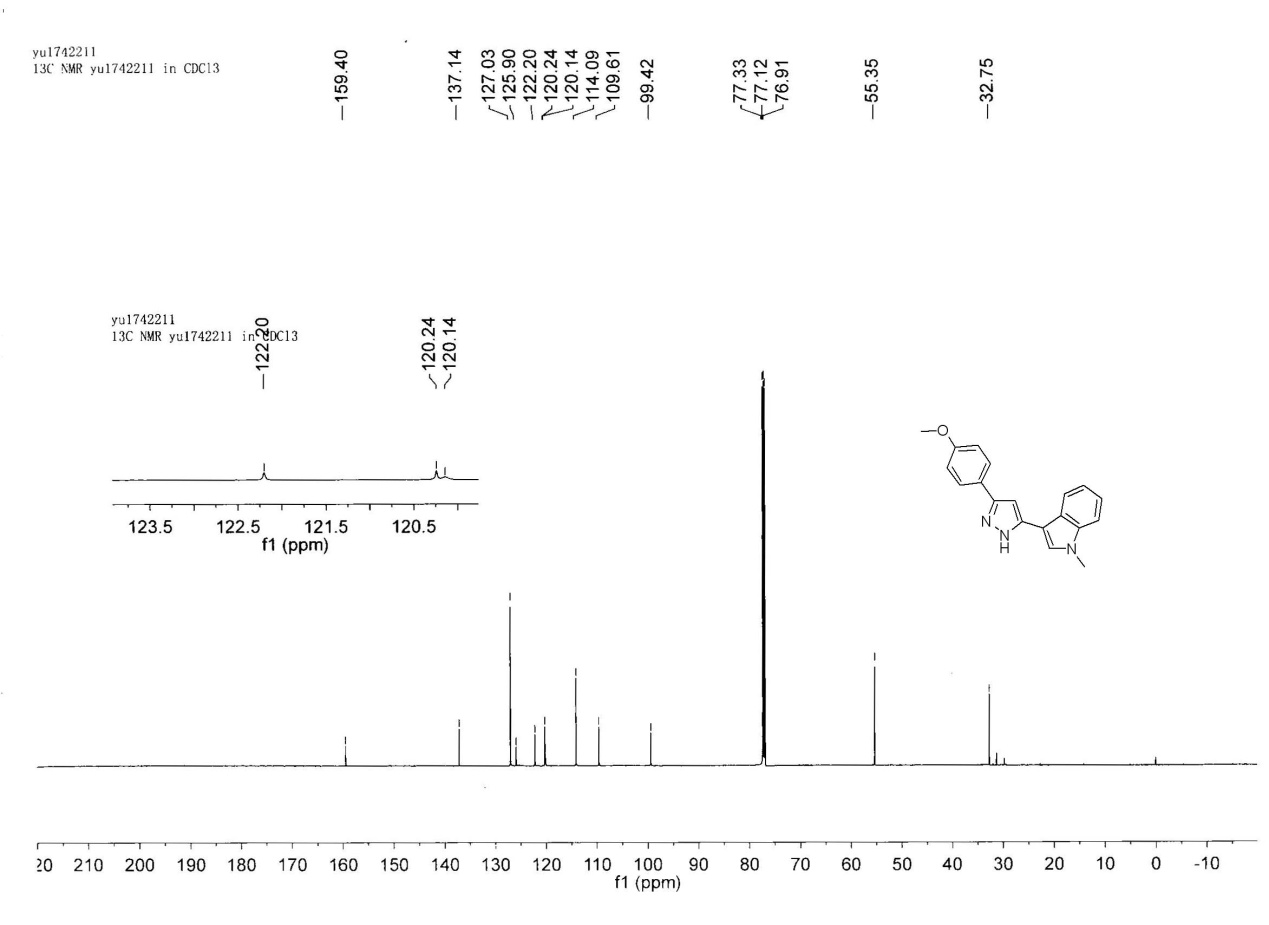
1H NMR of **3d**



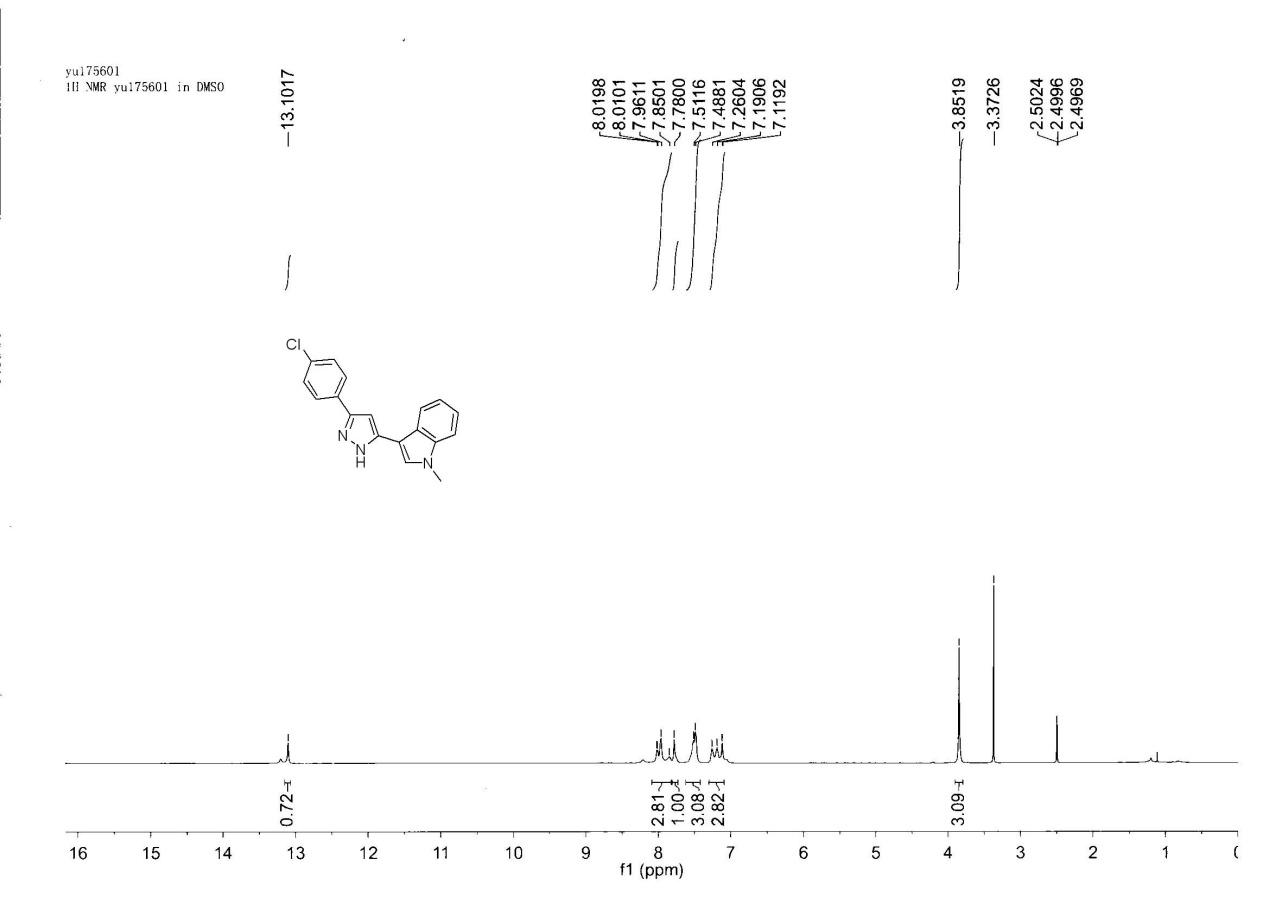
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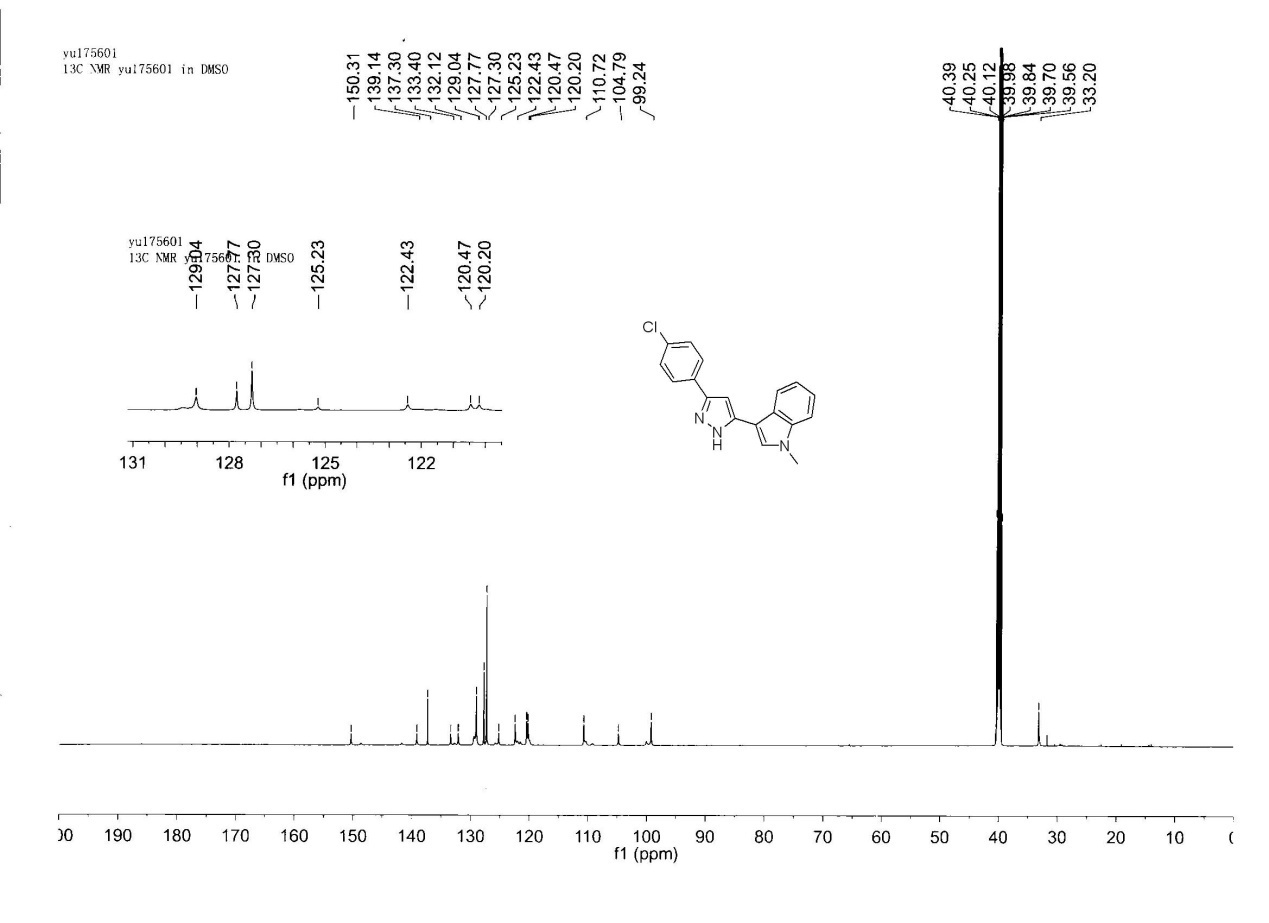
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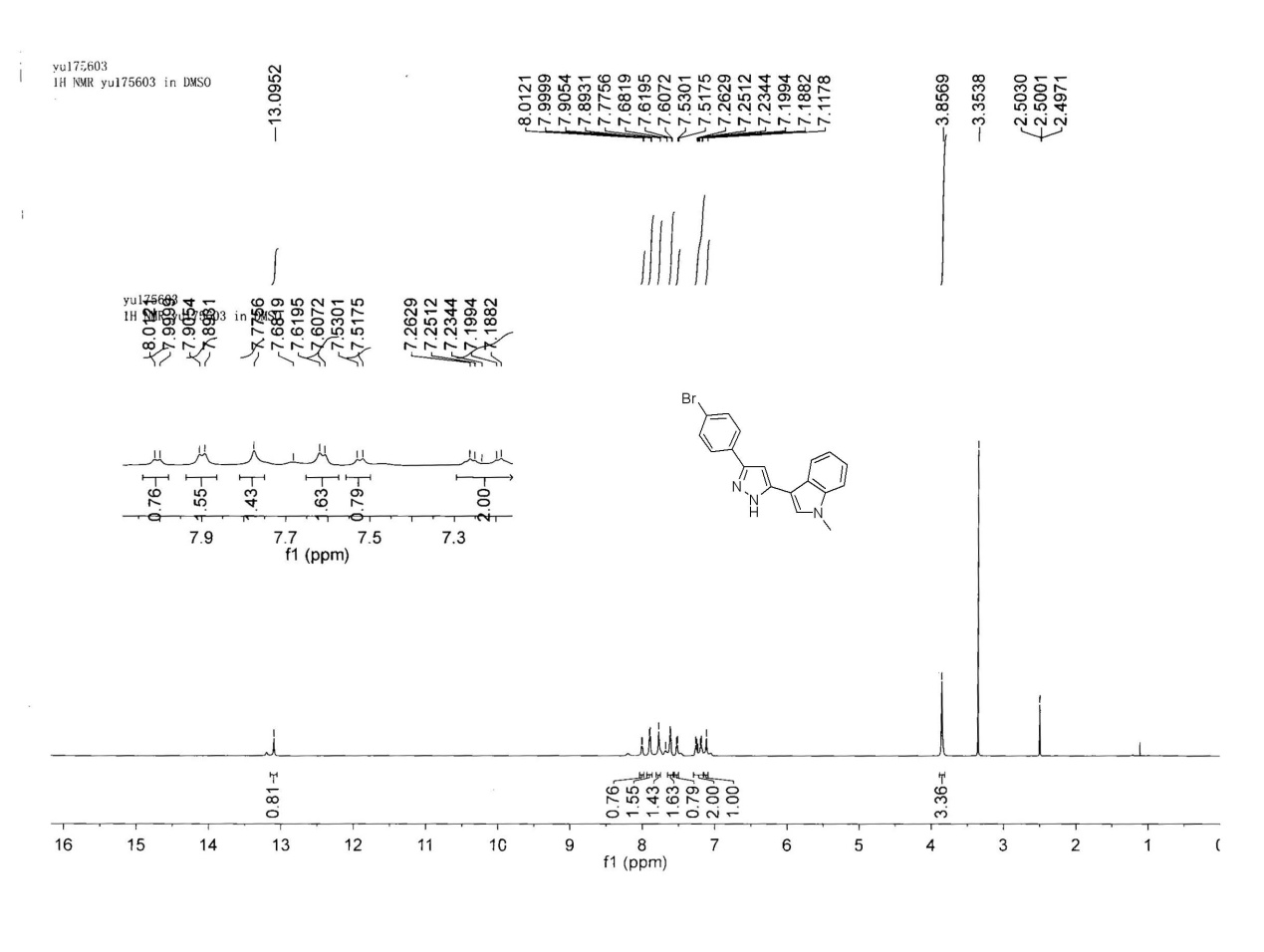
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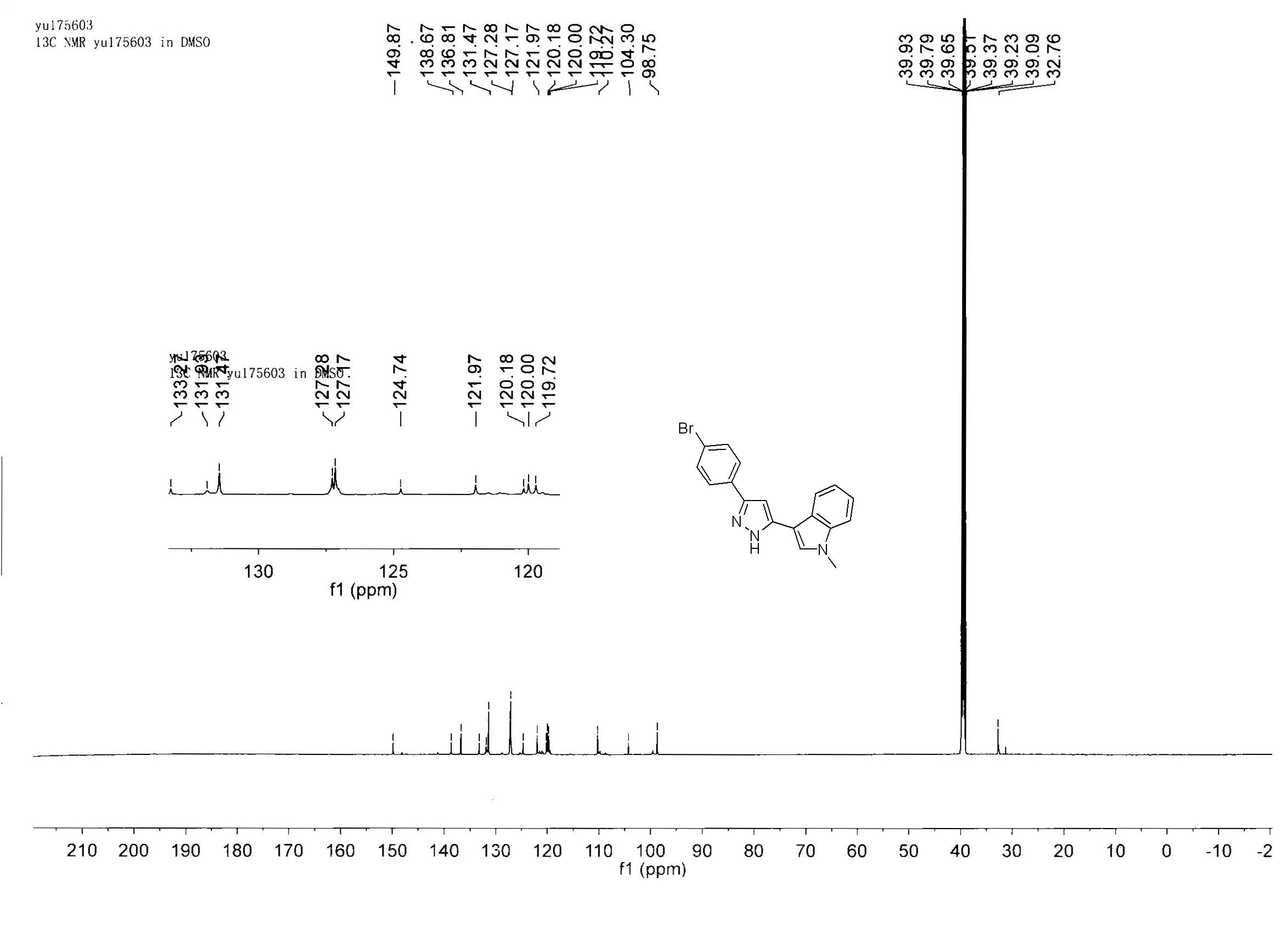
1H NMR of **3f**



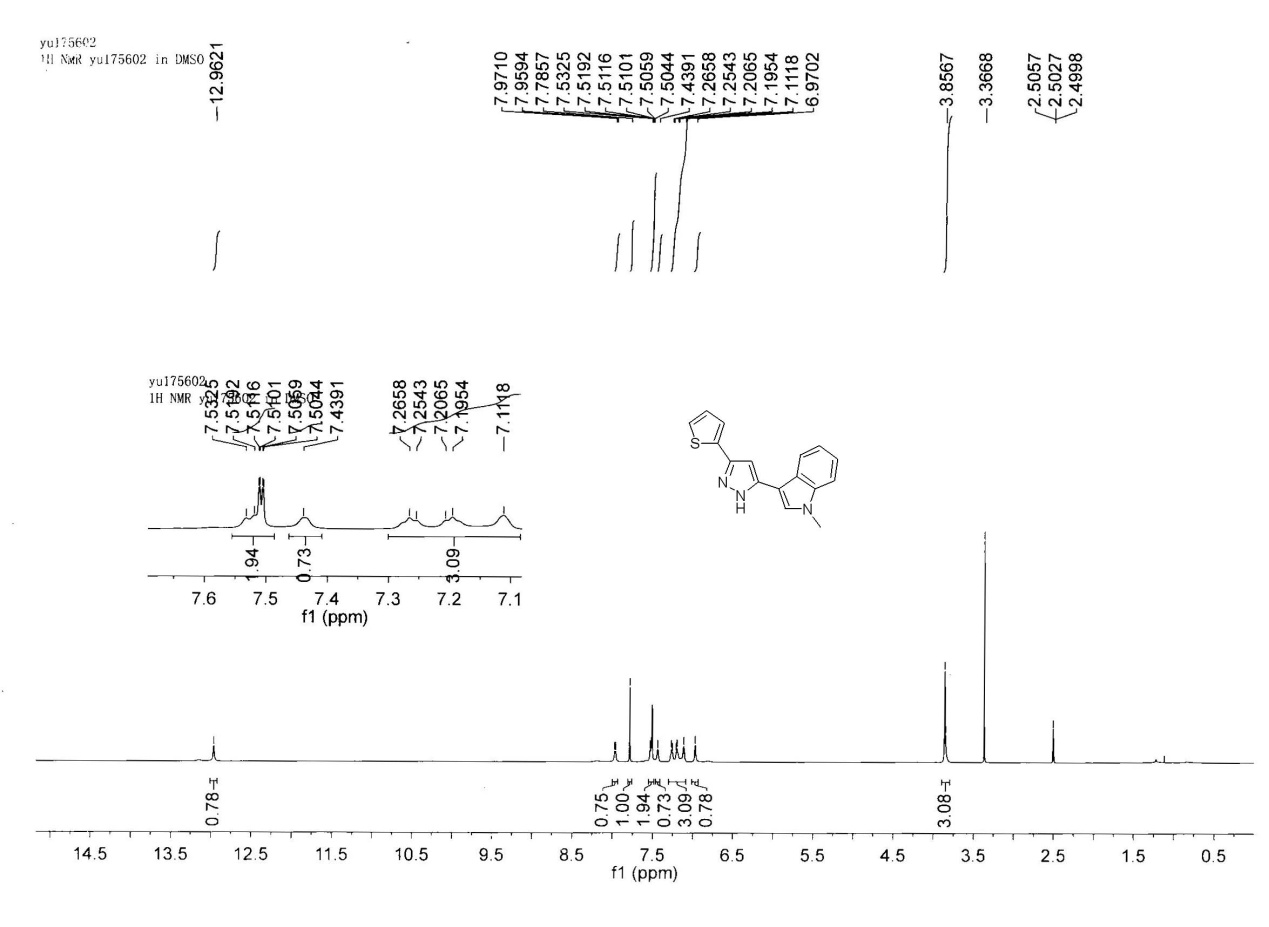
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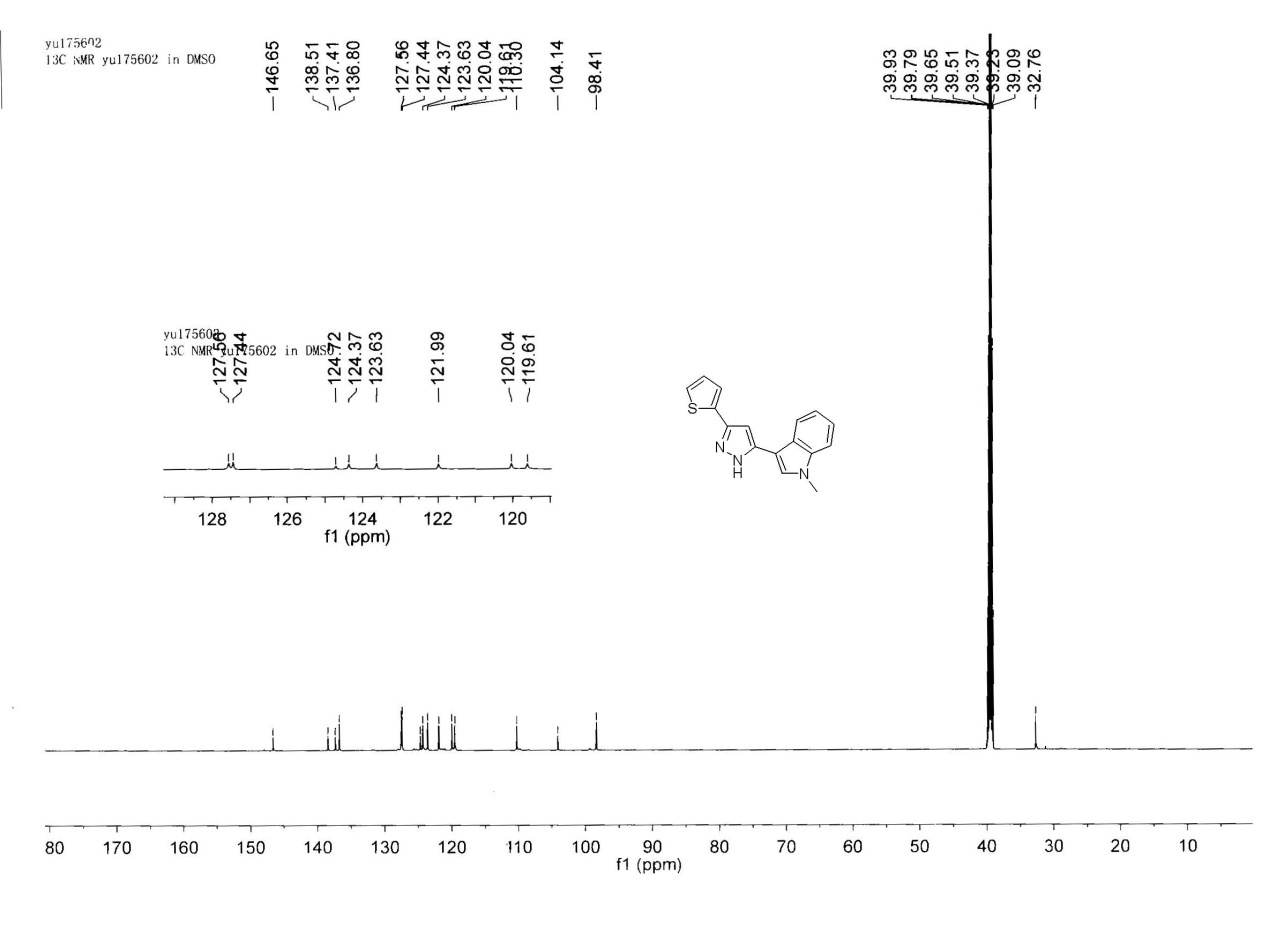
1H NMR of **3g**



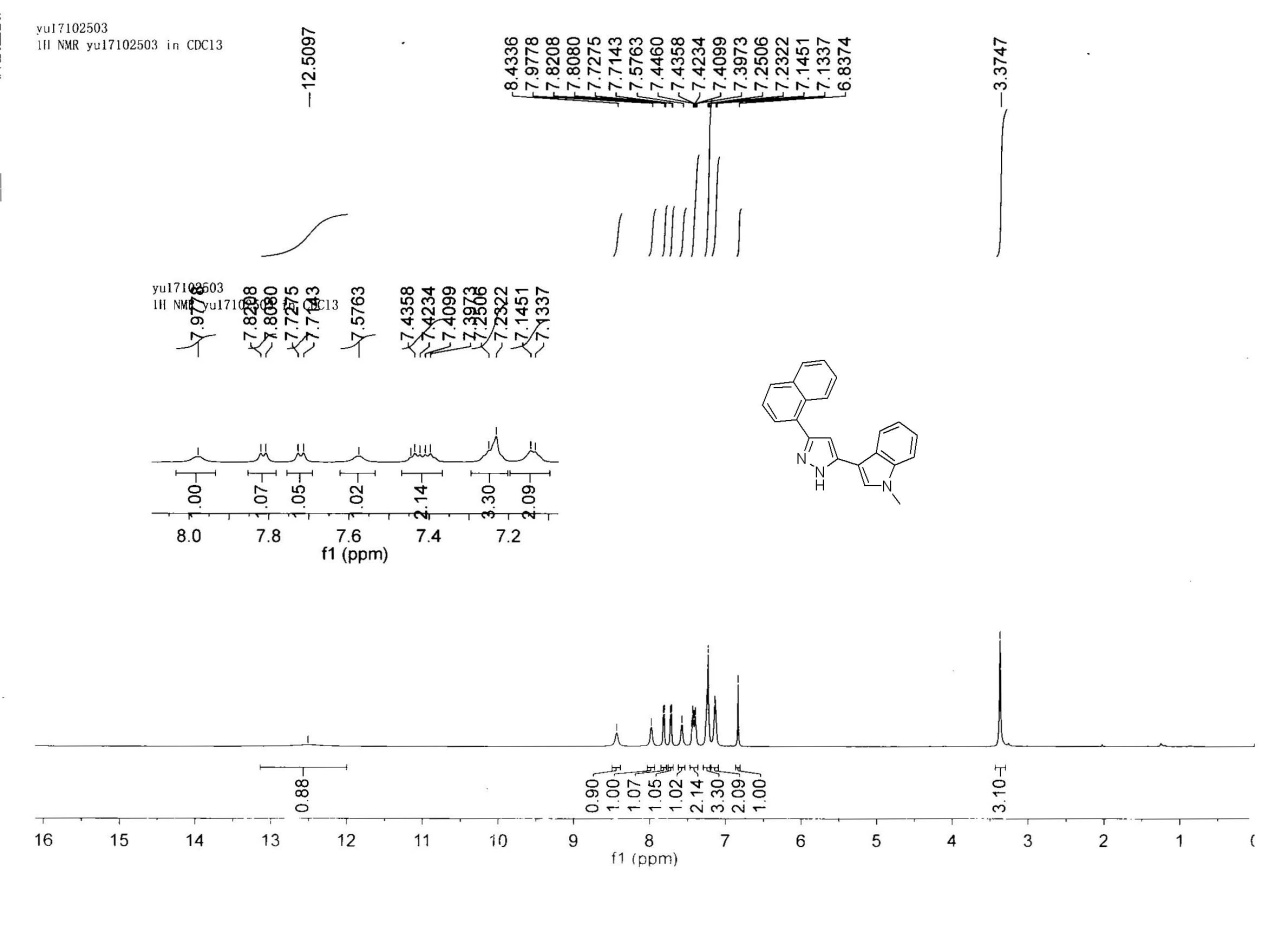
13C NMR of **3g**



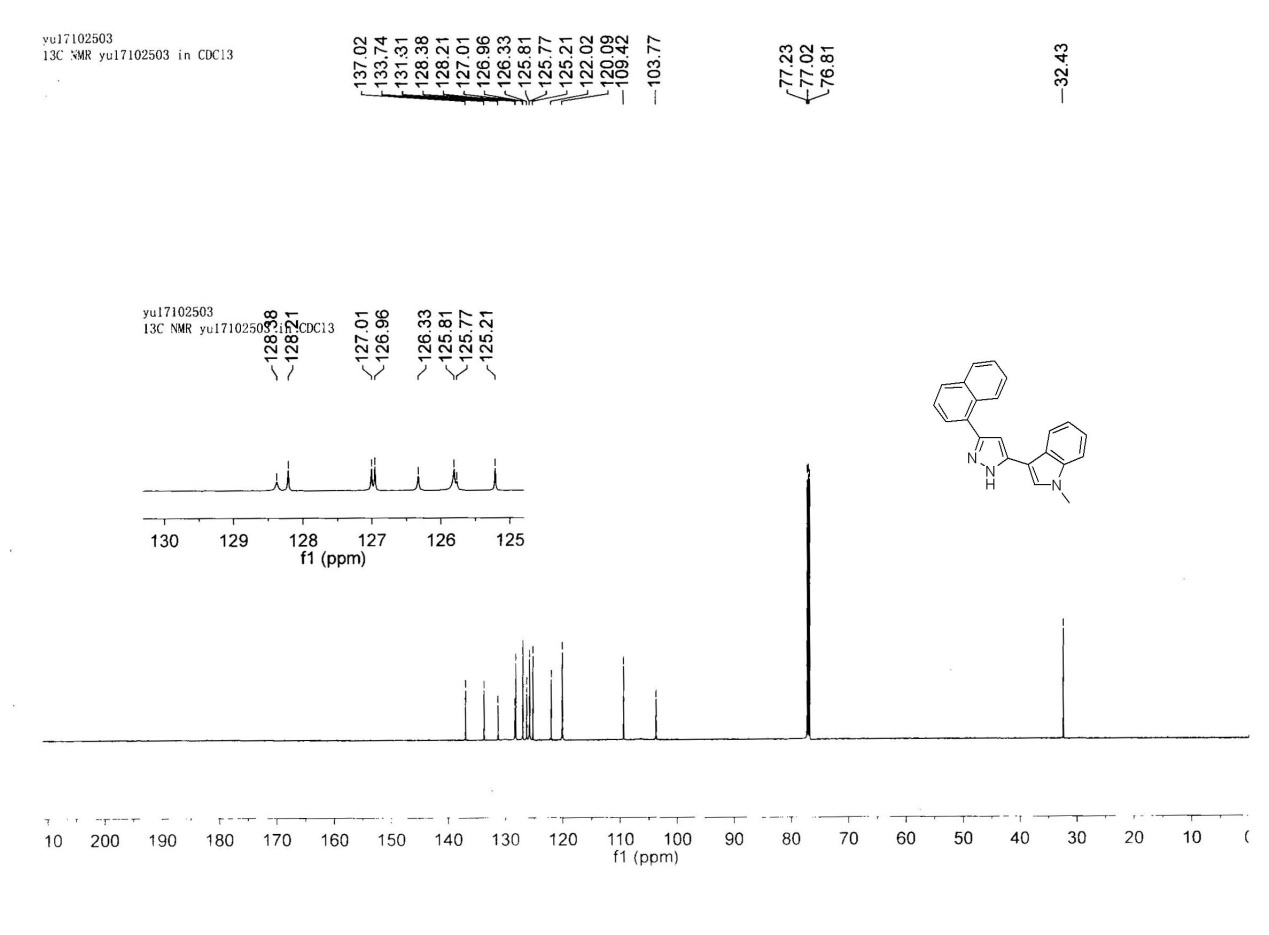
1H NMR of **3h**



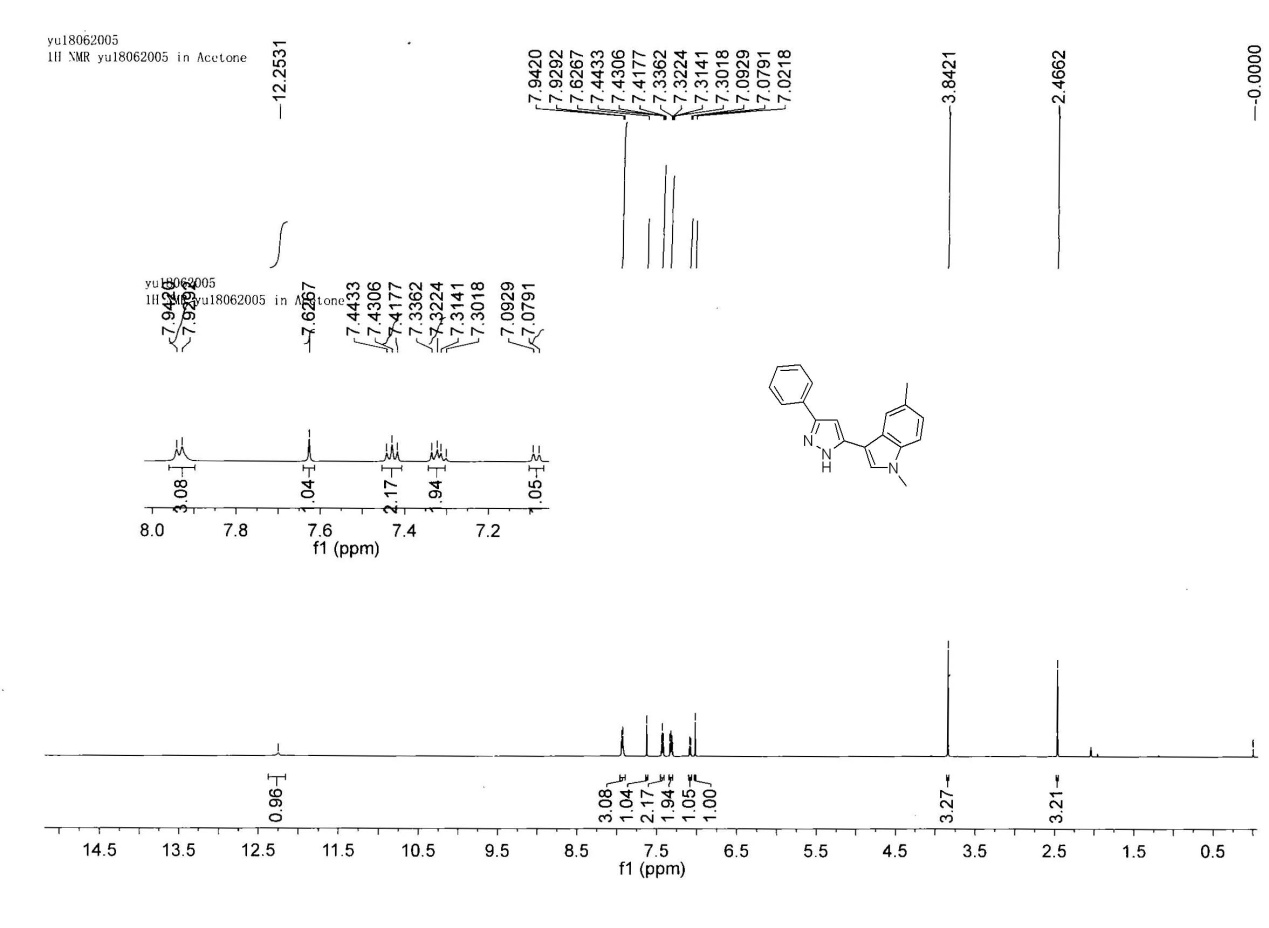
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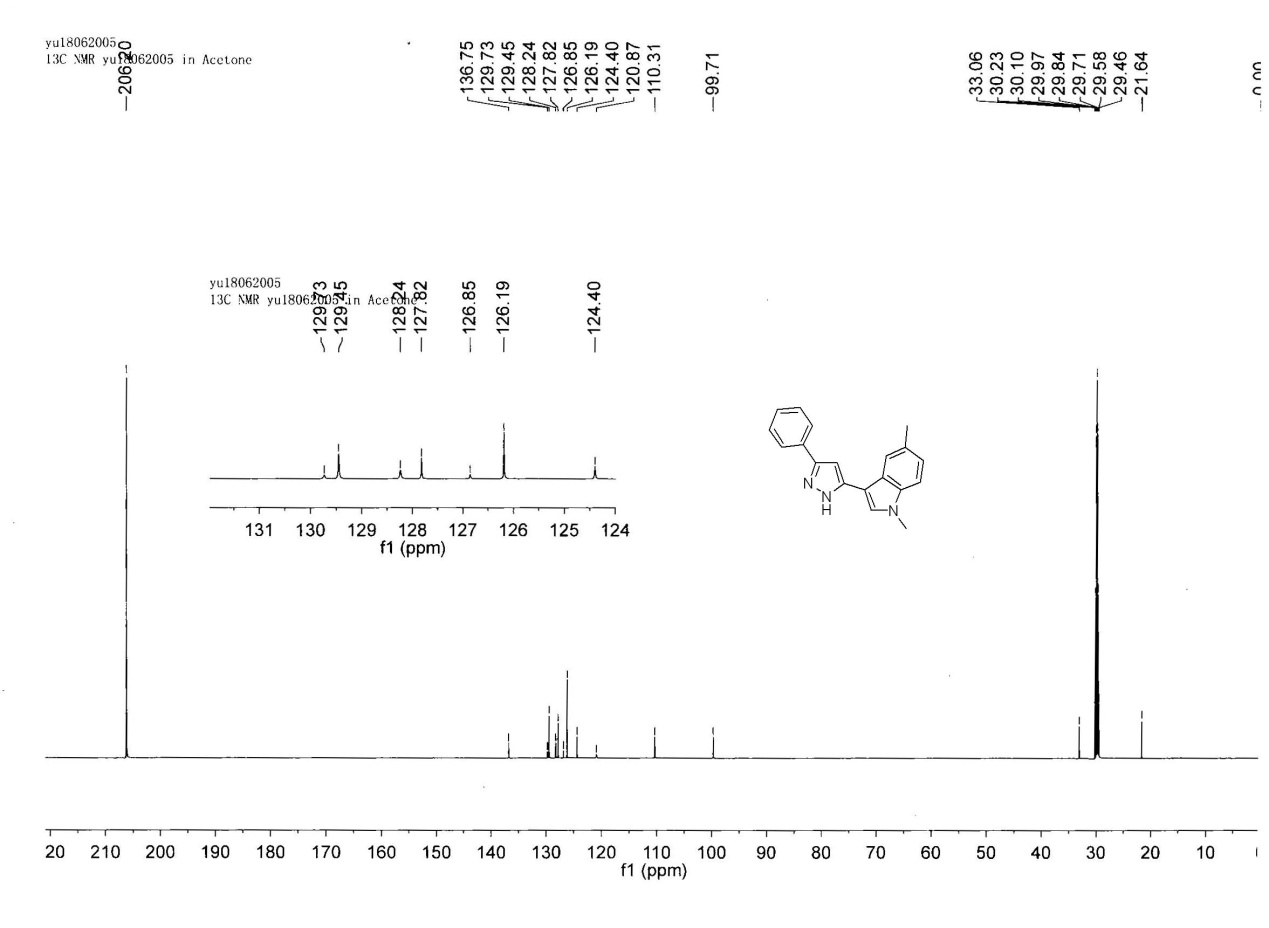
1H NMR of **3i**



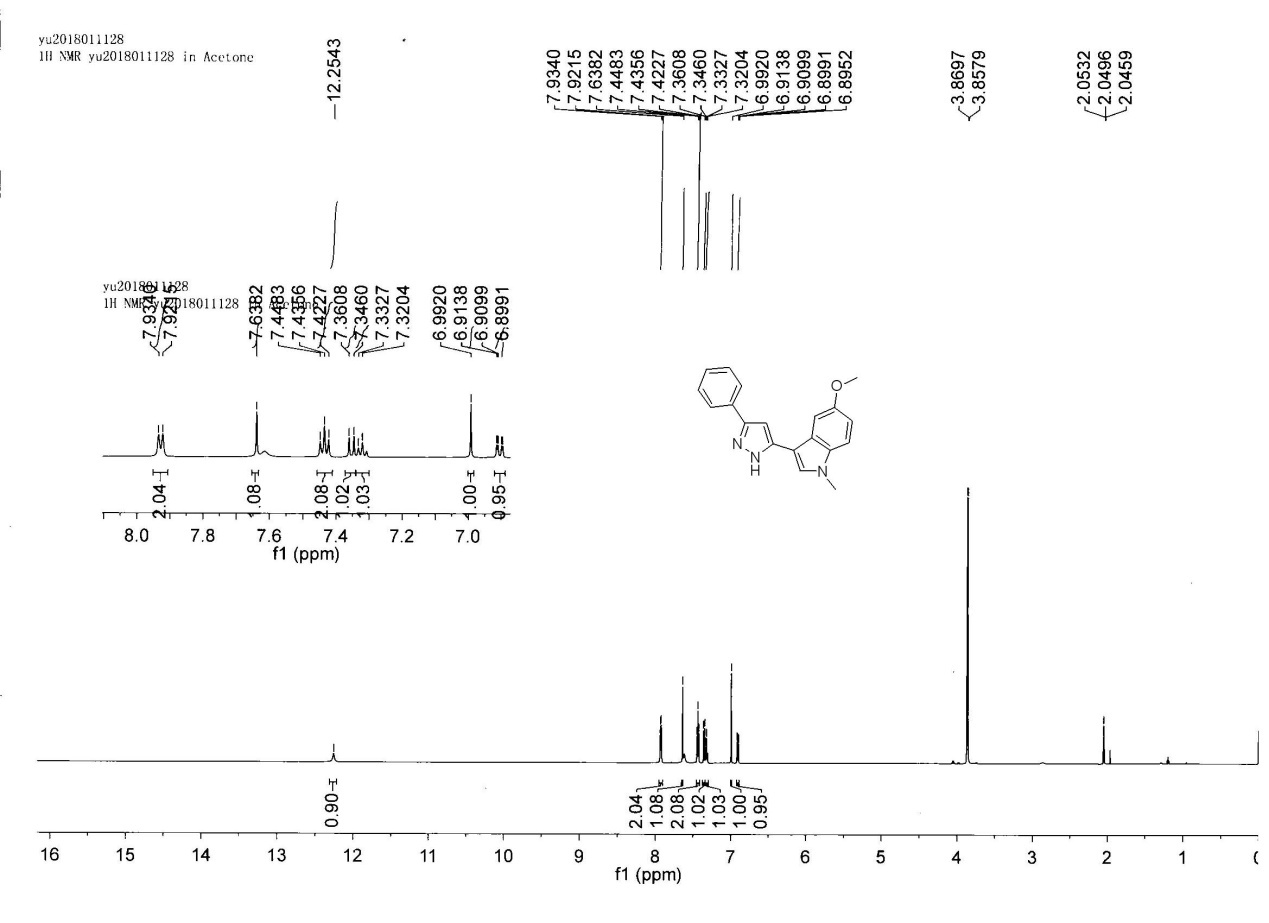
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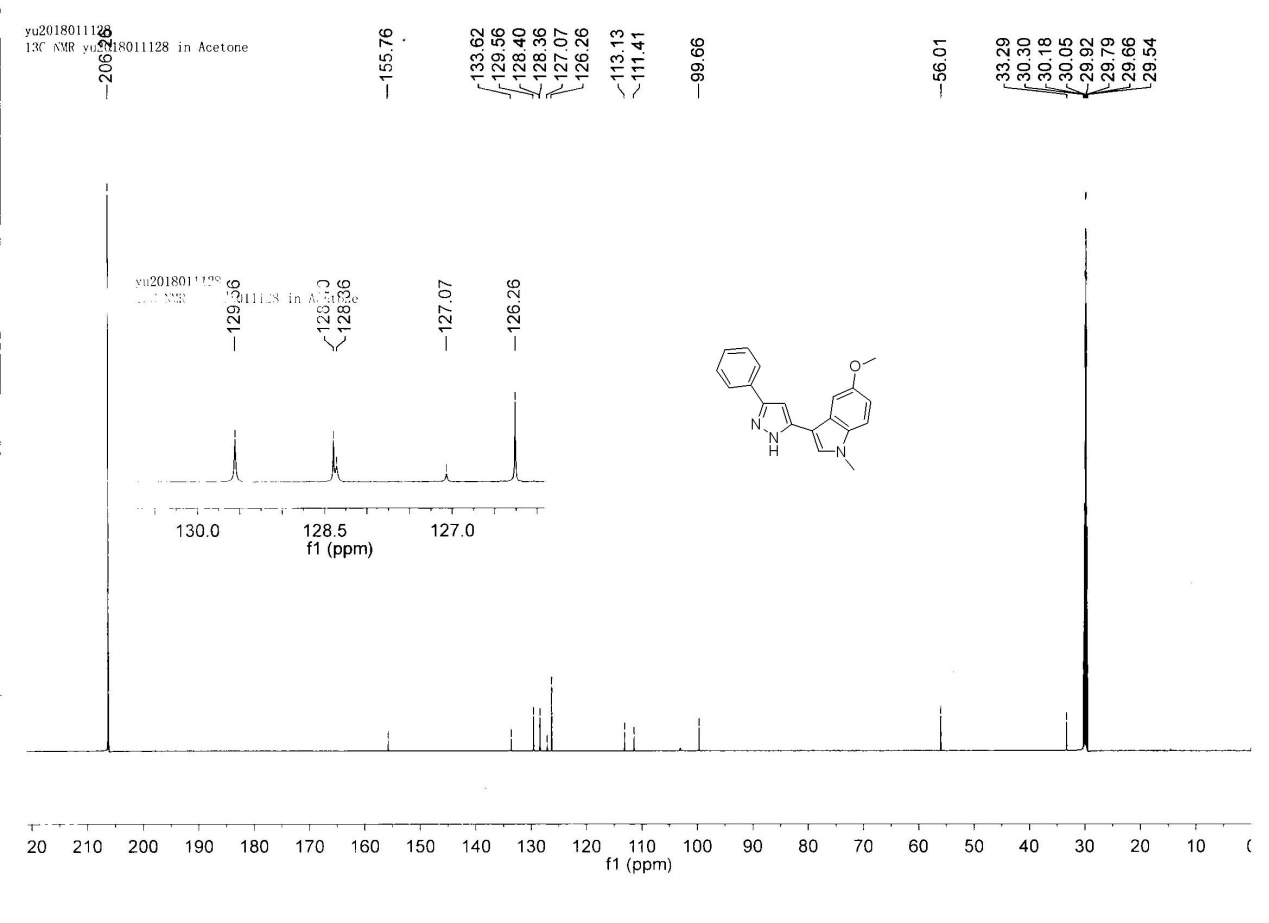
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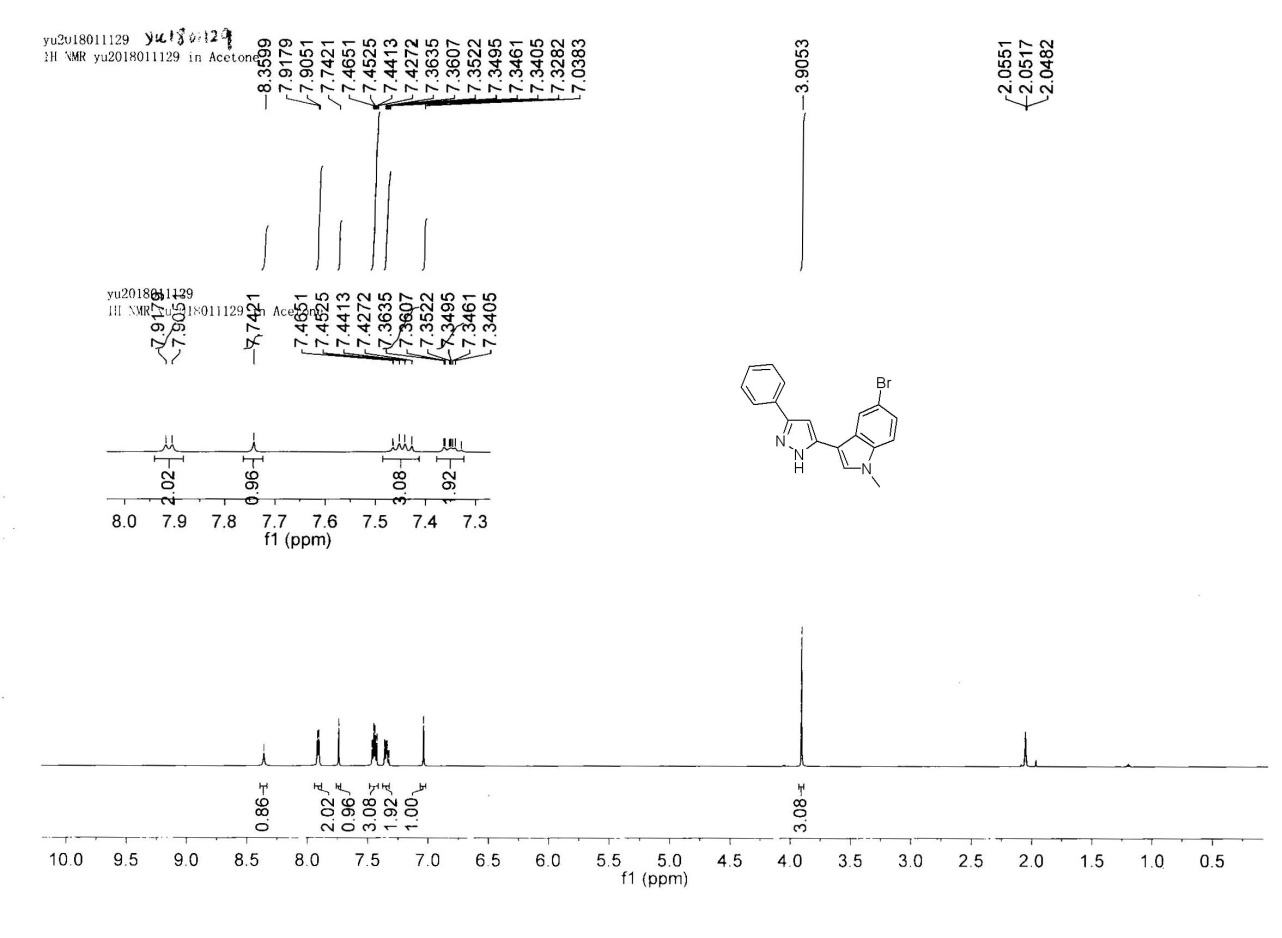
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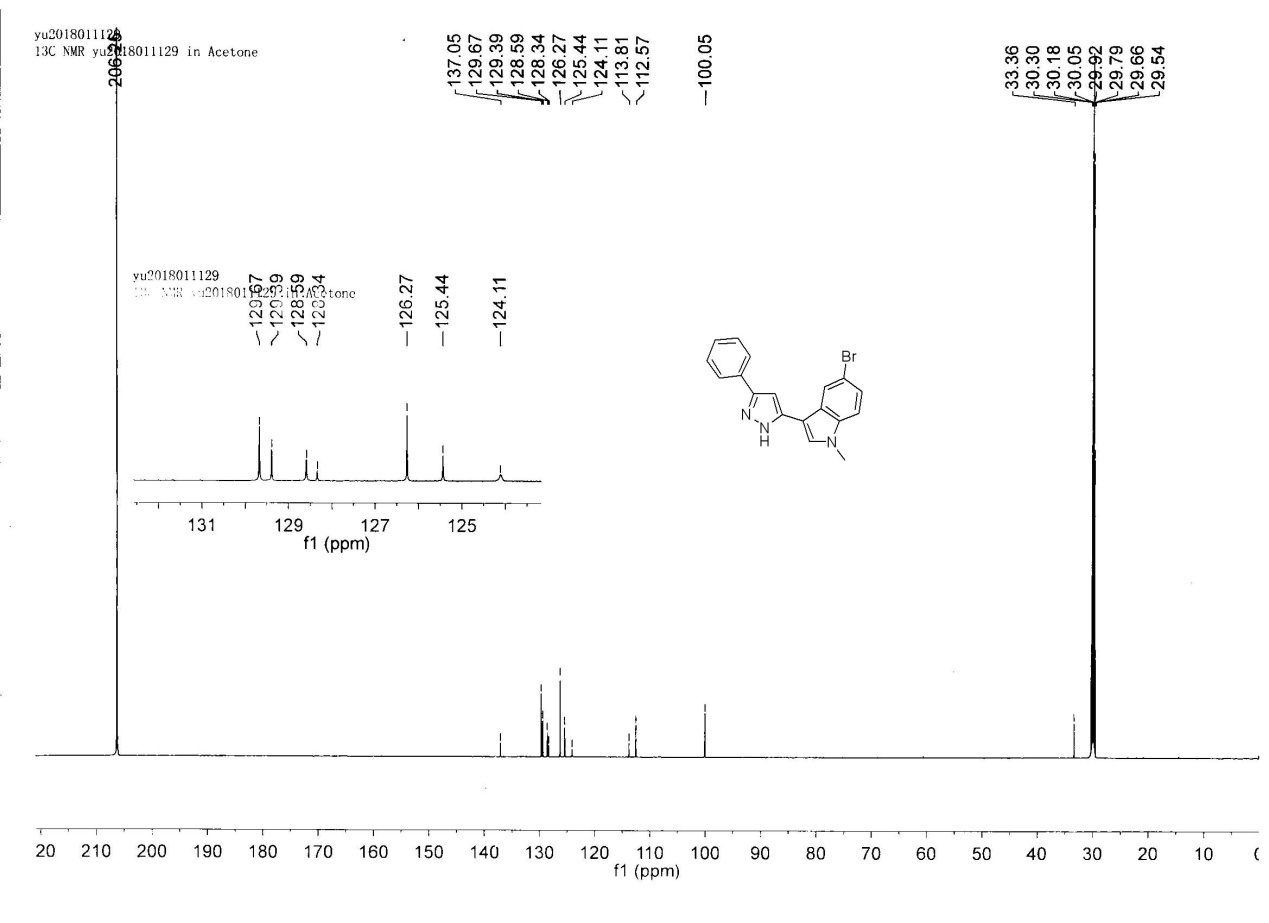
1H NMR of **3k**



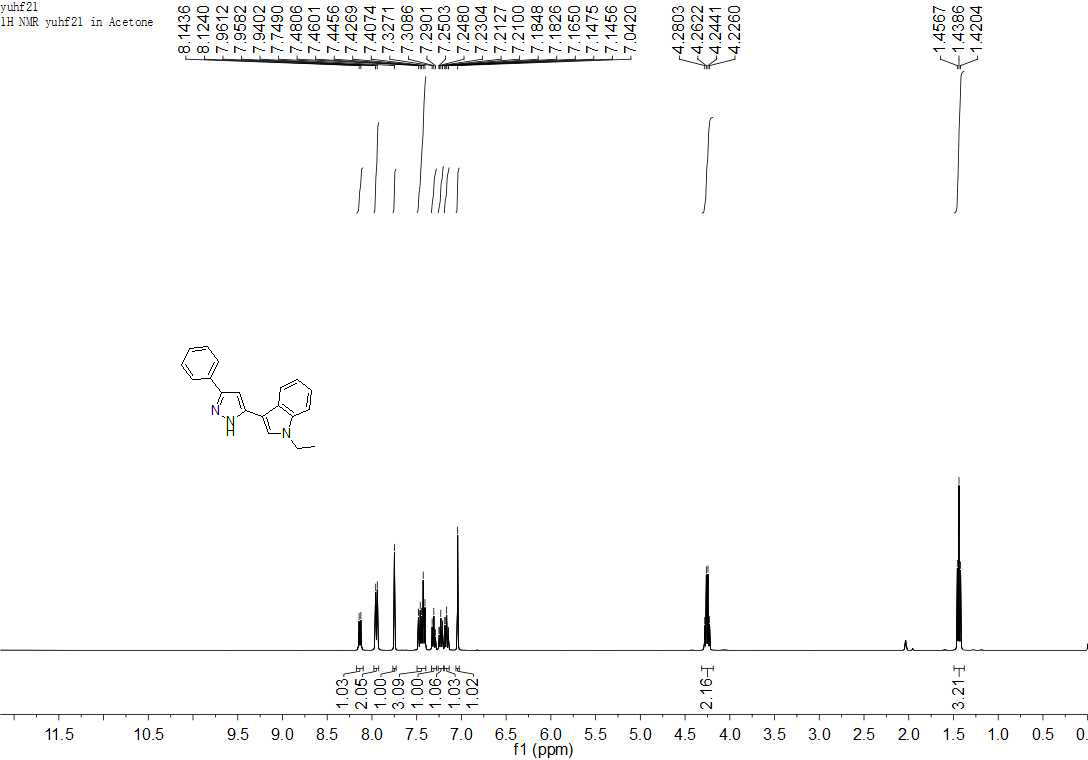
13C NMR of **3k**



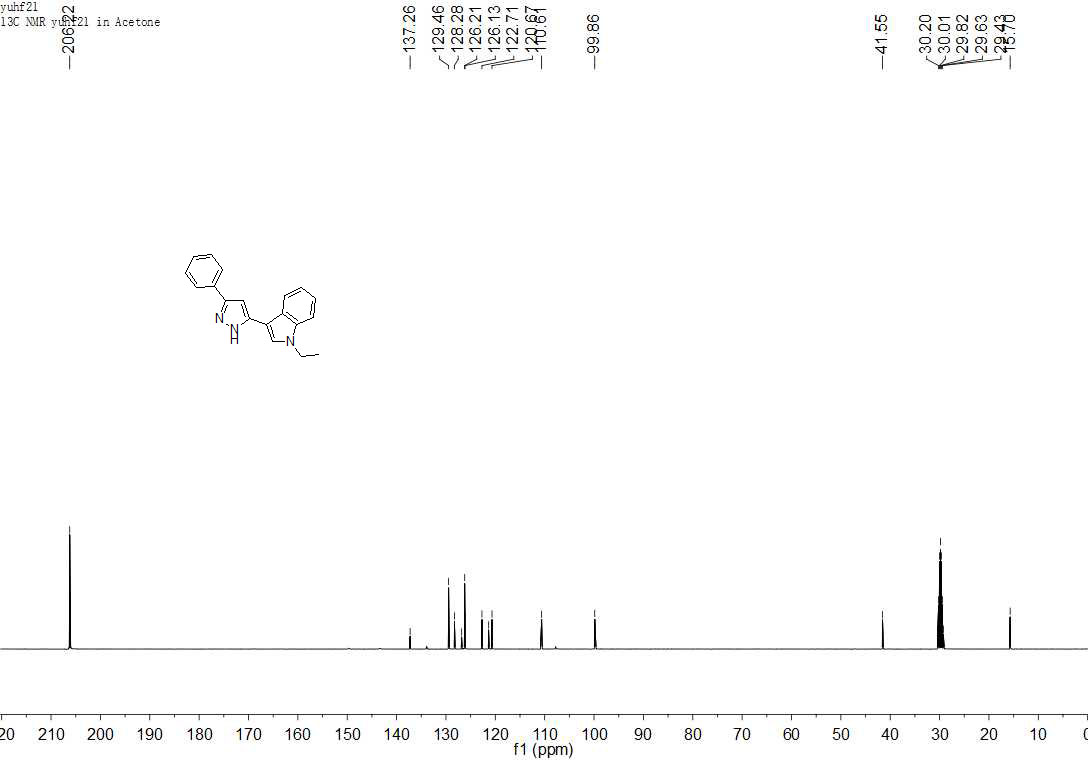
1H NMR of **3l**



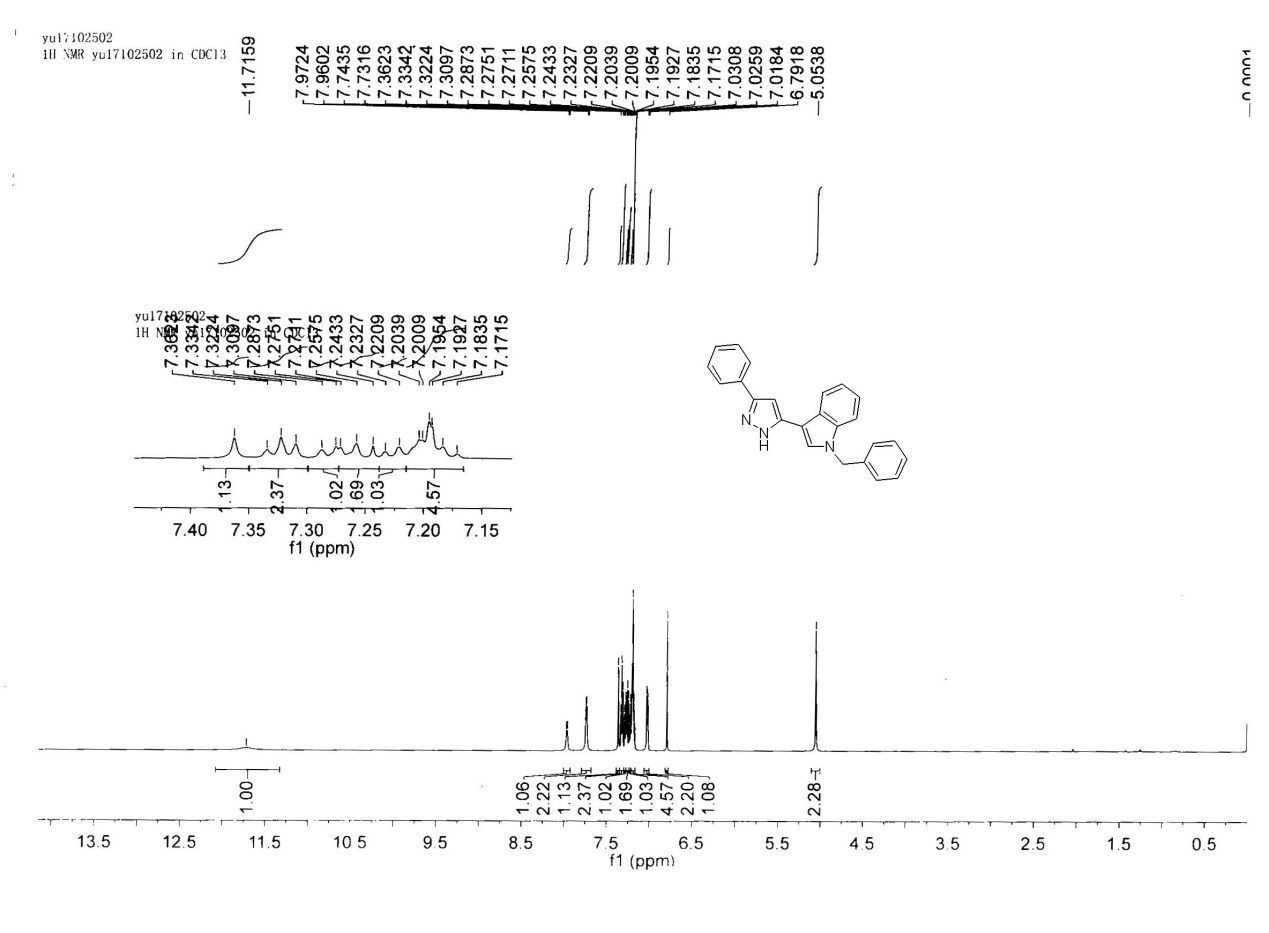
13C NMR of **3l**



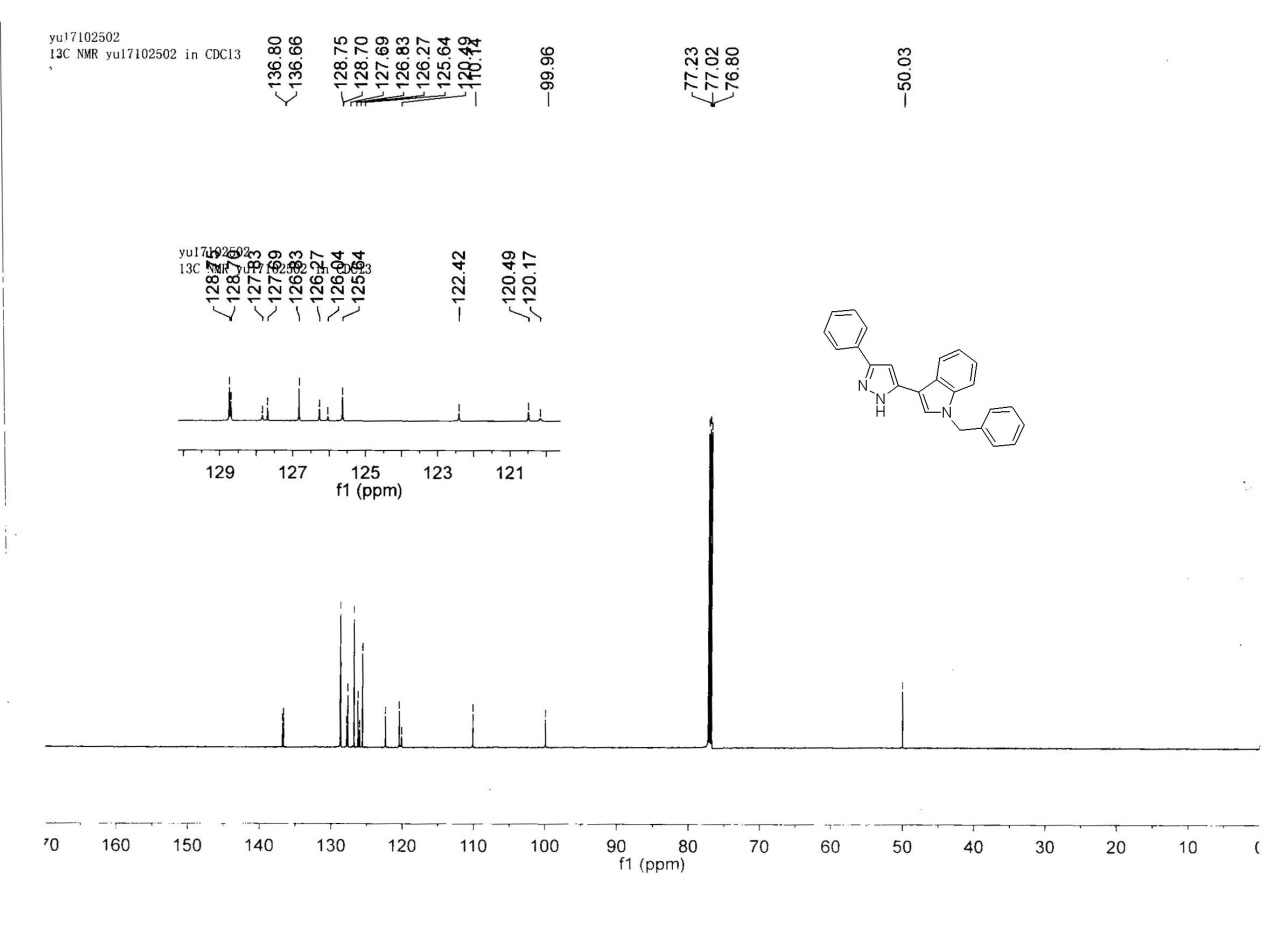
1H NMR of **3m**



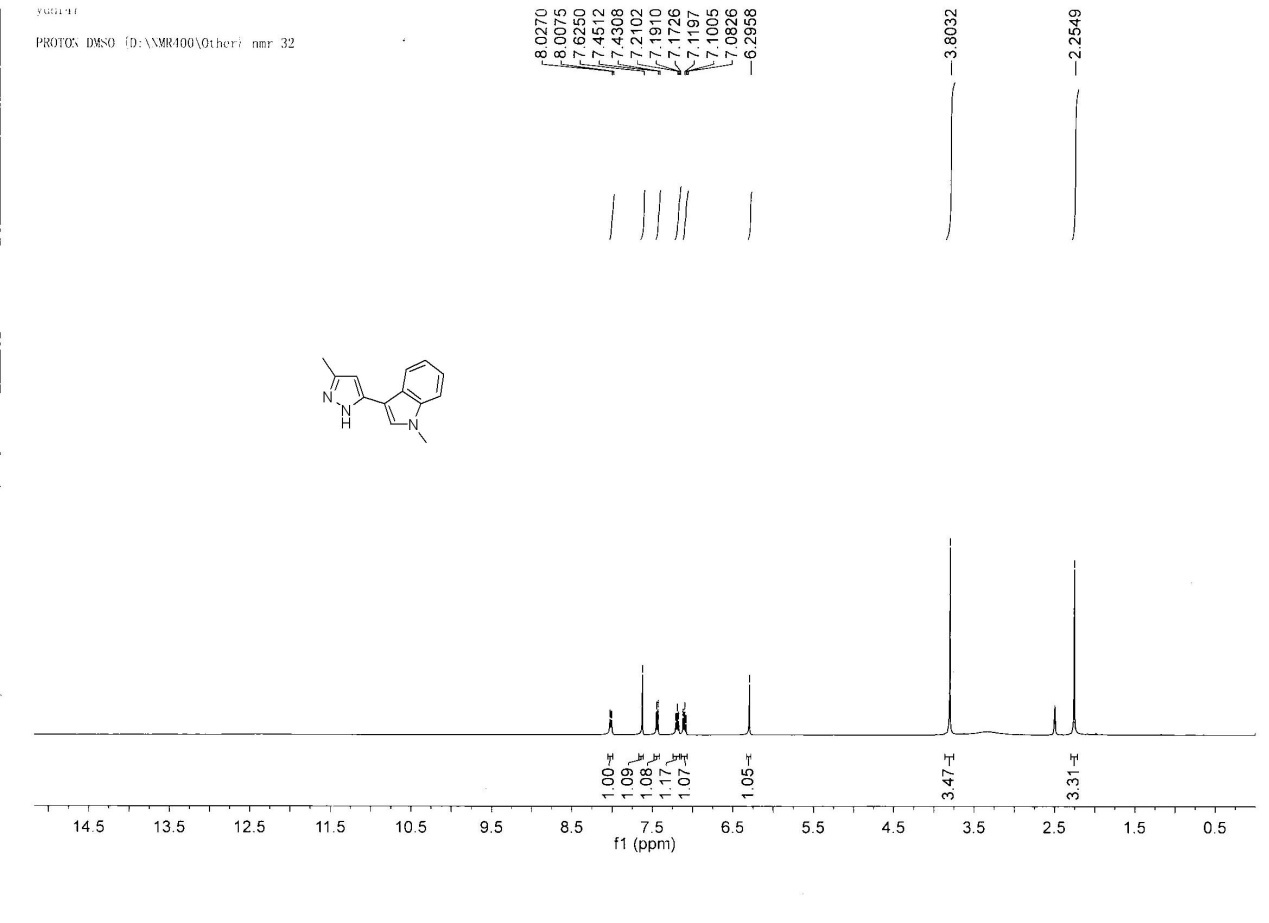
13C NMR of **3m**



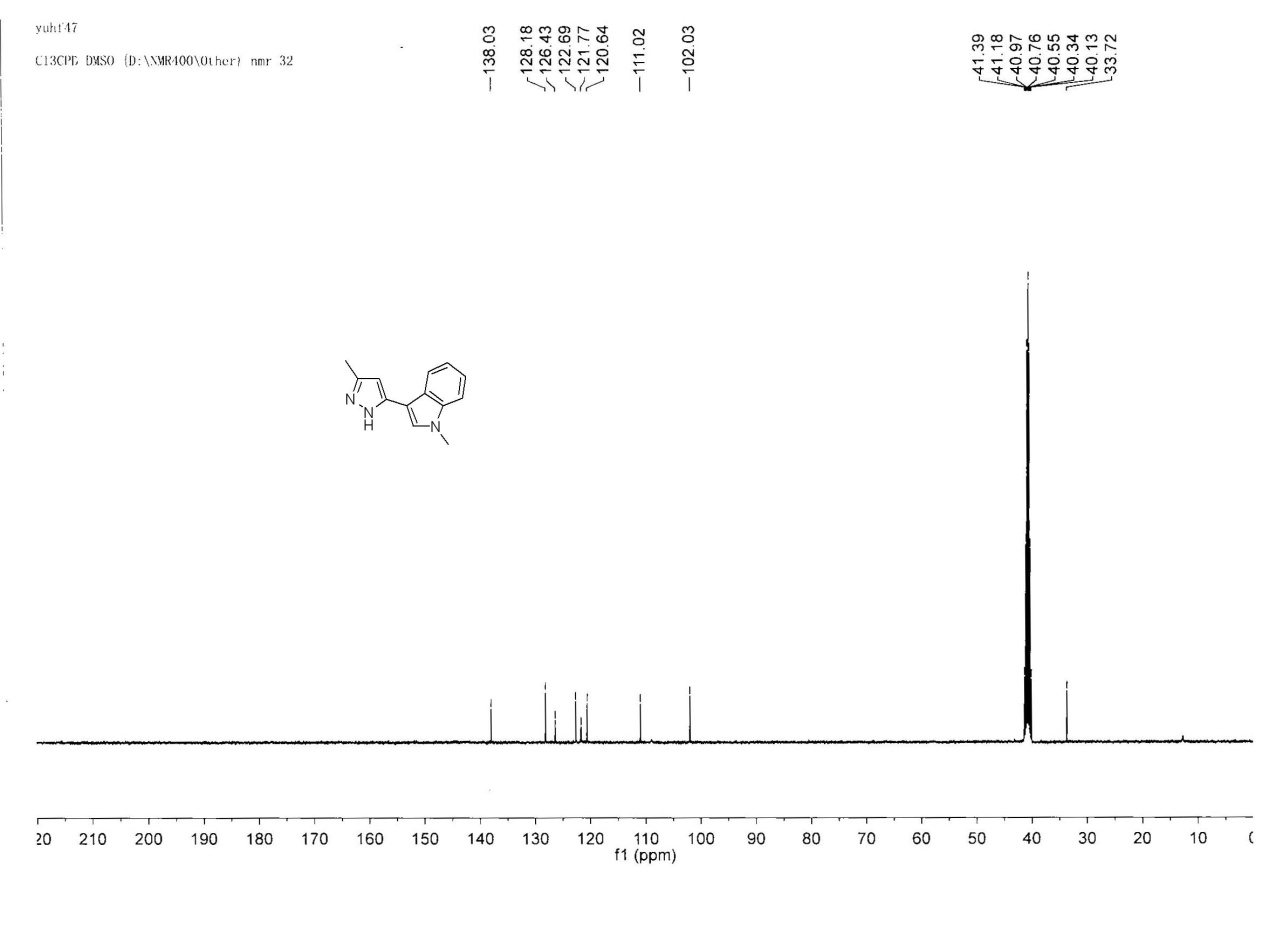
1H NMR of **3n**



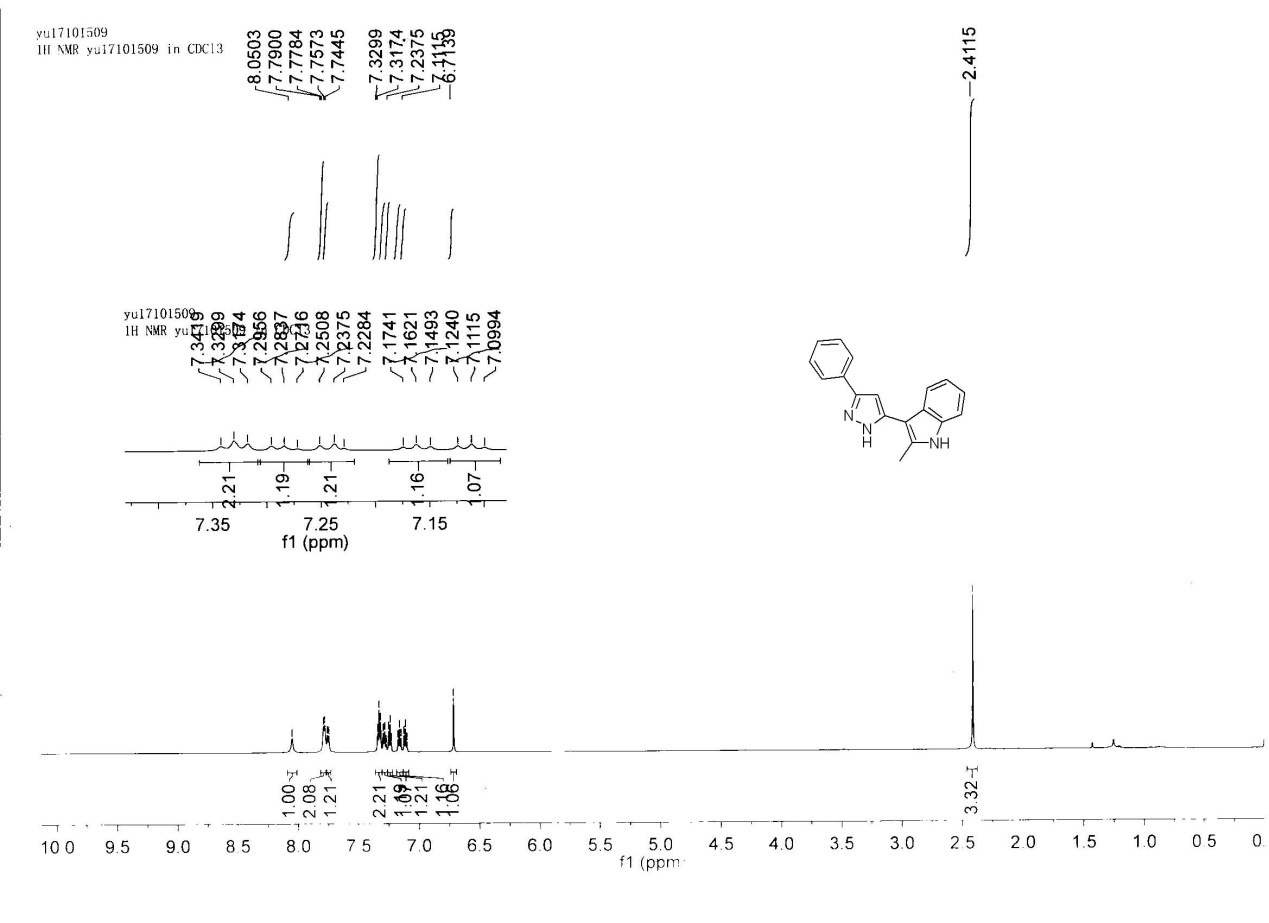
13C NMR of **3n**



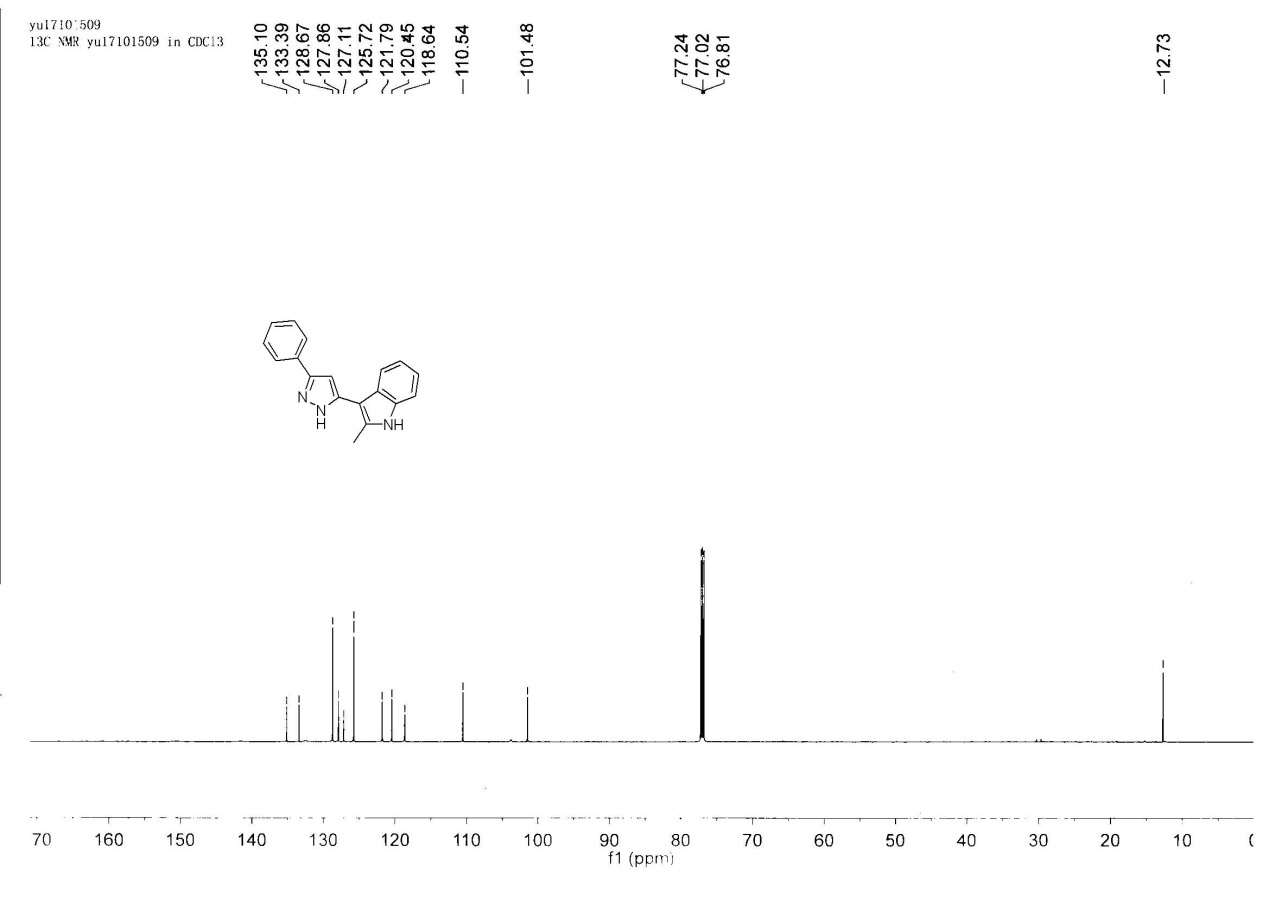
1H NMR of **3o**



13C NMR of **3o**



1H NMR of **3p**



13C NMR of **3p**