

Supporting Information

Rhodium-Catalyzed Annulation of Hydrazines with Vinylene Carbonate to Synthesize Unsubstituted 1-Aminoindole Derivatives

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Experimental Section

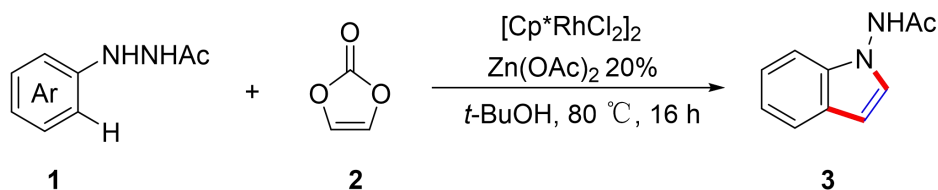
General Information:

All the reactions were carried out under N₂ atmosphere using standard Schlenk technique. ¹H NMR (400 MHz), ¹⁹F (376 M Hz) and ¹³C NMR (101 MHz) were recorded on a NMR spectrometer with DMSO-*d*₆ as solvent. Chemical shifts of ¹H, ¹⁹F and ¹³C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (DMSO-*d*₆: δ H = 2.50 ppm, δ C = 39.52 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh or alumina 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) was done on an Agilent 6210 ESI/TOF mass spectrometer. [Cp**RhCl*₂]₂ was prepared from RhCl₃·*x*H₂O following a literature procedure.¹ [Cp**Rh*(CH₃CN)₃](SbF₆)₂ was prepared from [Cp**RhCl*₂]₂ following a literature procedure.² Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

General Procedure: Preparation of the Substrates

The substrates **1b-1u**,^[3] were prepared according to the literature reports.

General Procedure for Synthesis of **3** via Rh(III)-Catalyzed C-H Activation and Annulation with Vinylene Carbonate

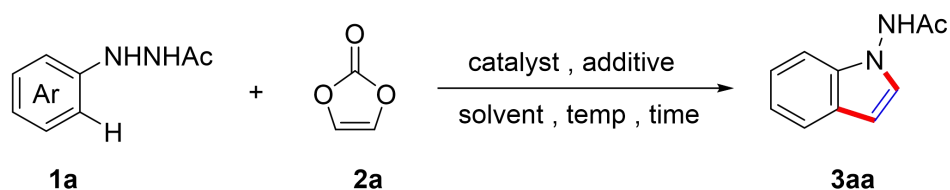


A mixture of **1** (0.2 mmol), **2** (0.4 mmol, 2 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (6.2 mg, 0.01 mmol, 5.0 mol%), and $\text{Zn}(\text{OAc})_2$ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the mixture was stirred at 80°C for 16 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EA:PE=1:2).

Gram-scale synthesis of **3aa**:

A mixture of **1a** (6 mmol), **2a** (12 mmol, 2 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (185.4 mg, 0.3 mmol, 5.0 mol%), and $\text{Zn}(\text{OAc})_2$ (220.2 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (60 mL) was added and the mixture was stirred at 80°C for 16 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel and good yield of **3aa** 86% (0.9020 g) was still attained (eluent: EA:PE=1:2).

Optimization Studies:

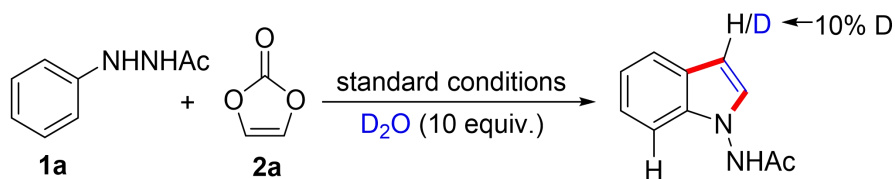


Entry	Catalyst(mol%)	Additive(mol%)	Solvent	T(°C)	Time(h)	Yield(%) ^[b]
1	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	DMF	80	16	66
2	[Cp*Rh(MeCN) ₃][SbF ₆] ₂ (6.0)	Zn(OAc) ₂ (20)	DMF	80	16	41
3	Cp*Co(CO)I ₂	Zn(OAc) ₂ (20)	DMF	80	16	nd
4	[Cp*IrCl ₂] ₂	Zn(OAc) ₂ (20)	DMF	80	16	nd
5	[<i>p</i> -CymeneRuCl ₂] ₂	Zn(OAc) ₂ (20)	DMF	80	16	nd
6	none	Zn(OAc) ₂ (20)	DMF	80	16	nd
7	[Cp*RhCl ₂] ₂ (5.0)	NaOAc(40)	DMF	80	16	nd
8	[Cp*RhCl ₂] ₂ (5.0)	KOAc(40)	DMF	80	16	nd
9	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	<i>t</i> -BuOH	80	16	94
10	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	MeCN	80	16	91
11	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	DME	80	16	86
12	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	DCE	80	16	85
13	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	Dioxane	80	16	80
14	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	TAA	80	16	76
15	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	Toluene	80	16	70
16	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	CH ₃ OH	80	16	nd
17	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	<i>t</i> -BuOH	60	16	66
18	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	<i>t</i> -BuOH	100	16	80
19	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	<i>t</i> -BuOH	80	12	90
20	[Cp*RhCl ₂] ₂ (5.0)	Zn(OAc) ₂ (20)	<i>t</i> -BuOH	80	20	90

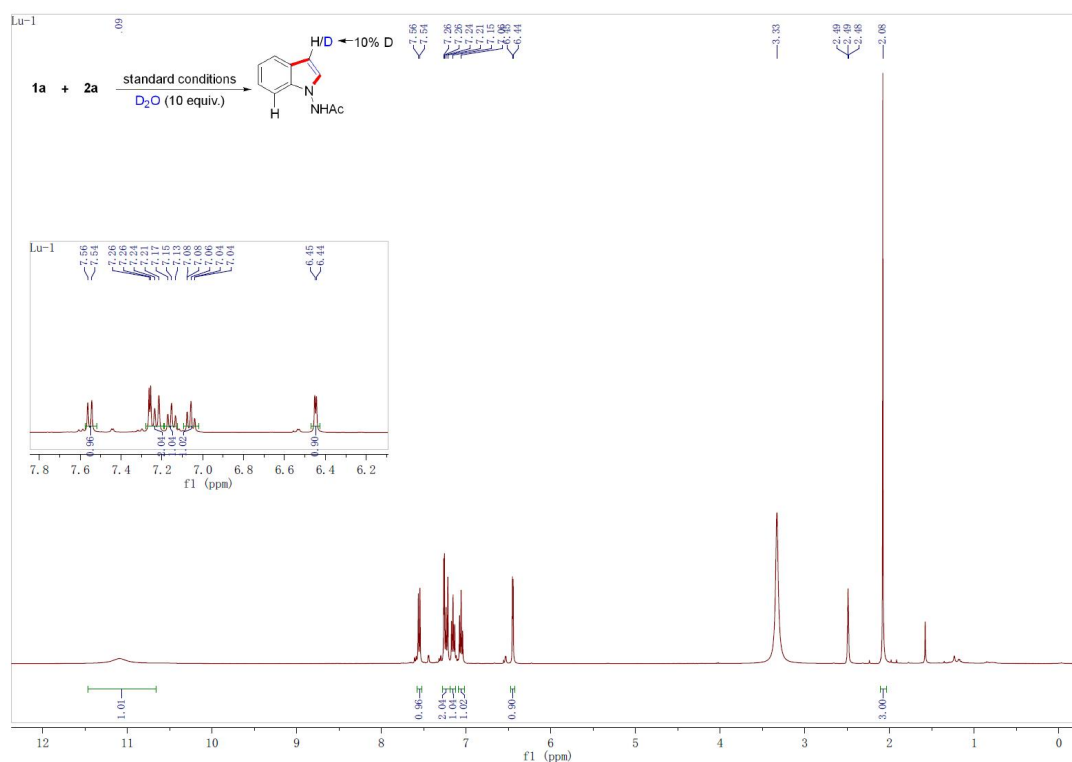
[a] Reaction conditions: **1a**(0.2mmol), **2**(0.4mmol), solvent (2 mL).

[b] Isolated yield.

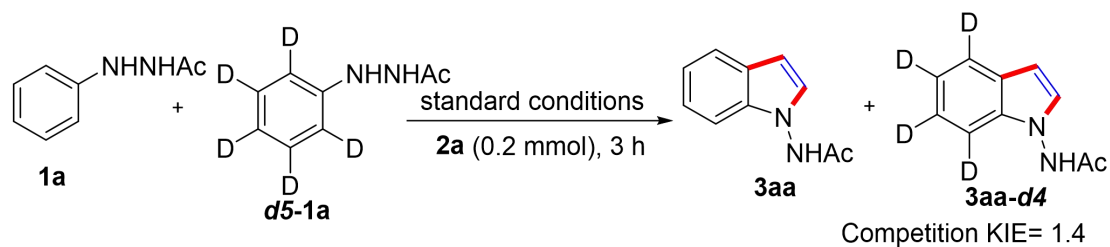
H/D Exchange Experiments:



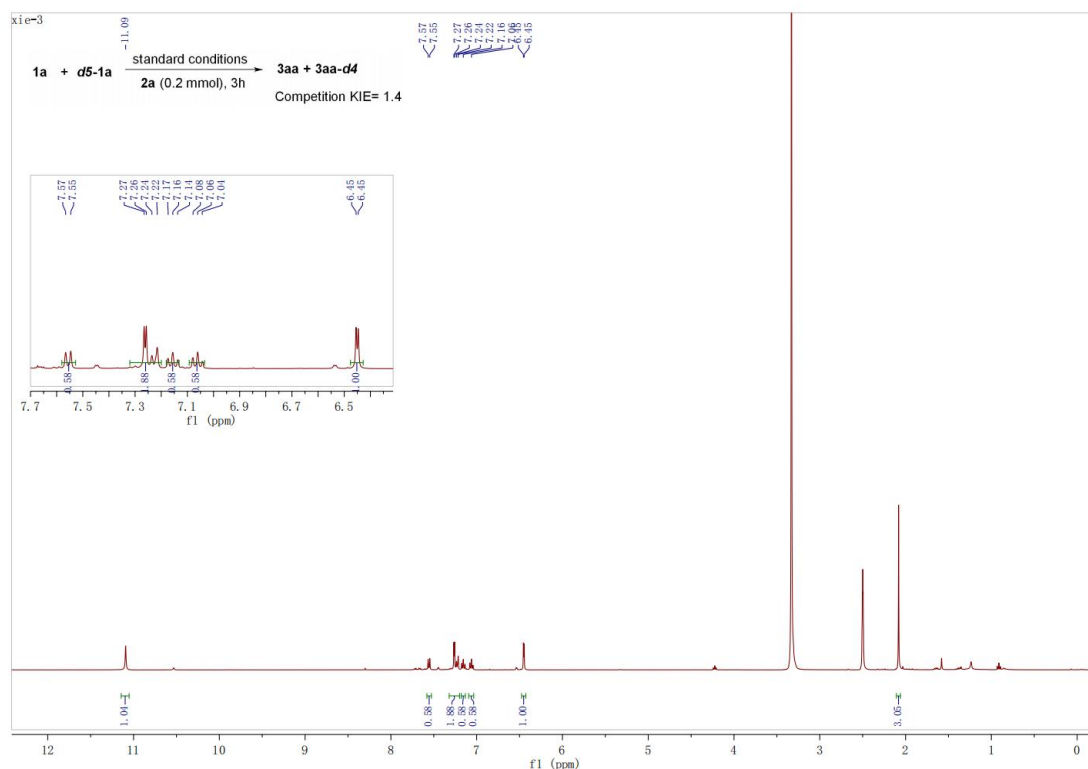
Procedure for the reaction in the presence of 2a: A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), vinylene carbonate **2a** (0.4 mmol, 2 equiv), [Cp*RhCl₂]₂ (6.2 mg, 0.01 mmol, 5.0 mol%), and Zn(OAc)₂ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) and D₂O (2.0 mmol, 10.0 equiv) was added and the mixture was stirred at 80°C for 16 h under N₂ atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA:PE=1:2) to give the product **3aa** (18.7 mg).



Competition KIE Experiment:

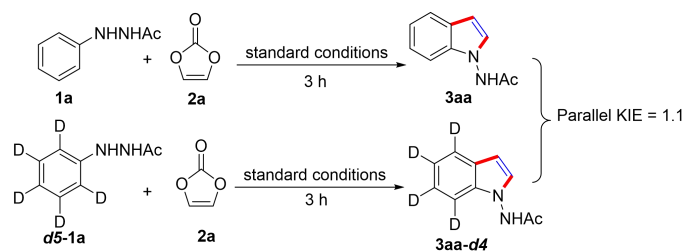


A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol, 1.0 equiv), **1a-d5** (0.2 mmol, 1.0 equiv), vinylene carbonate **2a** (0.4 mmol, 2 equiv), [Cp**Rh*Cl₂]₂ (6.2 mg, 0.01 mmol, 5.0 mol%), and Zn(OAc)₂ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the mixture was stirred at 80°C for 3 h under N₂ atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA:PE=1:2) to give the product **3aa** and **d4-3aa** (8.1 mg). The KIE value was determined to be $k_H/k_D = 1.4$ on the basis of ¹H NMR analysis.

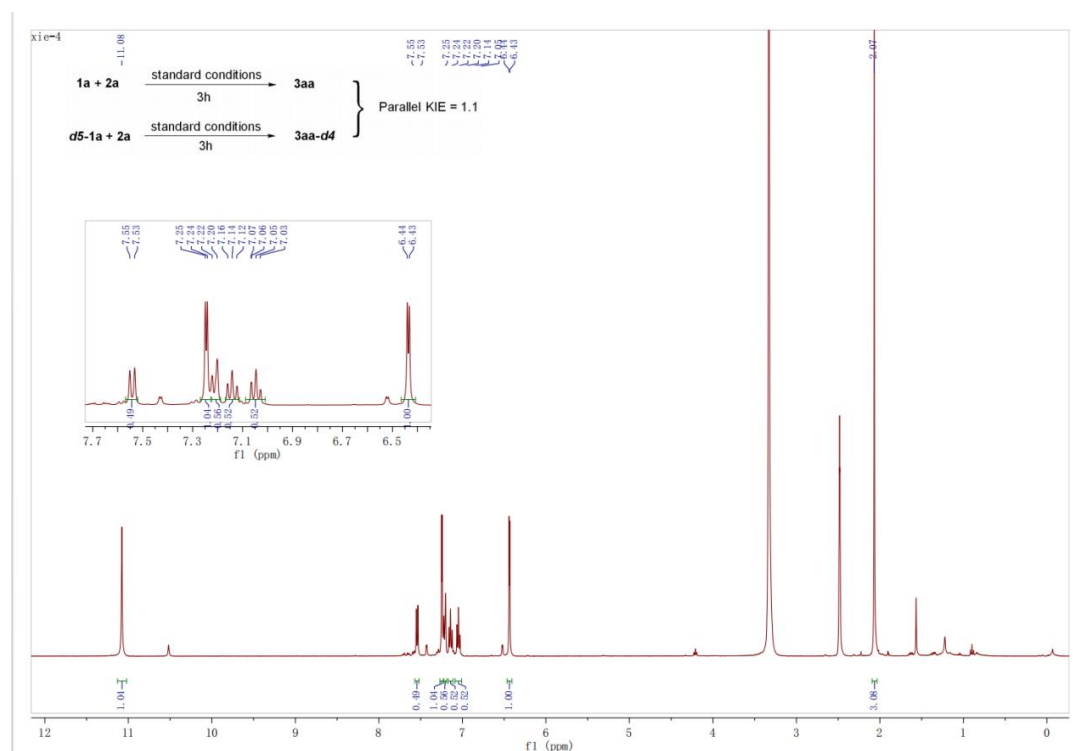


¹H NMR of product **3aa** and **d4-3aa** obtained from the competition KIE experiment

Parallel KIE Experiment:

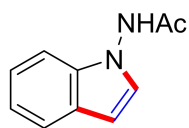


A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), vinylene carbonate **2a** (0.4 mmol), [Cp*RhCl₂]₂ (6.2 mg, 0.01 mmol), Zn(OAc)₂ (7.3 mg) and *t*-BuOH (2.0 mL) were charged into Schlenk tube. To another tube **1a-d5** (0.2 mmol), vinylene carbonate **2a** (0.4 mmol), [Cp*RhCl₂]₂ (6.2 mg, 0.01 mmol), Zn(OAc)₂ (7.3 mg) and *t*-BuOH (2.0 mL) were added. These two reaction mixtures were stirred side-by-side at 80°C for 3h under N₂ atmosphere. The reactions tubes were quenched at 0°C and these two mixtures were rapidly combined. The combined mixture was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA:PE=1:2) to give the product **3aa** and **d4-3aa** (16.3 mg). The KIE value was determined to be $k_H/k_D = 1.1$ on the basis of ¹H NMR analysis.

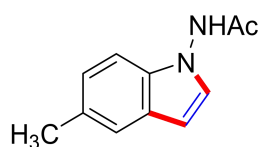


¹H NMR of product **3aa** and **d4-3aa** obtained from the parallel KIE experiment

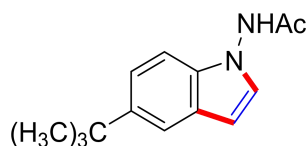
Characterization of Products:



N-(1*H*-indol-1-yl)acetamide (**3aa**): white crystalline solid (32.9 mg, 94%); M.p.:135-136 °C. IR (cm⁻¹): ν 3252, 1678, 1528, 1265, 1221, 741. ¹H NMR (400 MHz, DMSO-d₆): δ 11.15 (s, 1H), 7.60 (dt, $J = 7.9, 1.0$ Hz, 1H), 7.33 – 7.25 (m, 2H), 7.20 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.11 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 1H), 6.50 (dd, $J = 3.3, 0.9$ Hz, 1H), 2.13 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.19, 135.58, 129.16 (d, $J = 6.9$ Hz), 125.92, 122.05 – 121.70 (m), 120.59, 119.98 – 119.60 (m), 108.97 (d, $J = 2.9$ Hz), 99.95 (d, $J = 8.5$ Hz), 20.55 (q, $J = 4.8$ Hz). HRMS (ESI): Calcd for C₁₀H₁₀N₂O [M+Na]⁺ 197.0685, Found 197.0693.

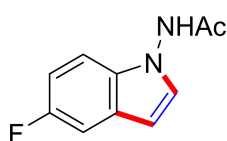


N-(5-methyl-1*H*-indol-1-yl)acetamide (**3ba**): white solid (26.8 mg, 71%); M.P.:137-139 °C. IR (cm⁻¹): ν 3240, 3026, 1682, 1530, 1265, 719. ¹H NMR (400 MHz, DMSO-d₆): δ 11.06 (s, 1H), 7.35 (s, 1H), 7.21 (d, $J = 3.4$ Hz, 1H), 7.13 (d, $J = 8.3$ Hz, 1H), 7.00 (dd, $J = 8.3, 1.6$ Hz, 1H), 6.39 – 6.34 (m, 1H), 2.39 (s, 3H), 2.09 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.09, 134.01, 129.12 (d, $J = 8.5$ Hz), 128.38, 126.14, 123.51 – 123.25 (m), 120.15 (d, $J = 5.3$ Hz), 108.66 (dd, $J = 5.2, 3.1$ Hz), 99.38 (d, $J = 6.8$ Hz), 21.03 (q, $J = 9.1$ Hz), 20.51 (q, $J = 4.3$ Hz). HRMS(ESI): Calcd for C₁₁H₁₃N₂O [M+H]⁺ 189.1022, Found 189.1025.

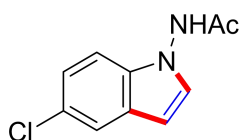


N-(5-(*tert*-butyl)-1*H*-indol-1-yl)acetamide (**3ca**): pale brown solid (36.7 mg, 80%); M.p.:190.5-191.2 °C. IR(cm⁻¹): ν 3246, 2959, 1688, 1528, 1273, 876. ¹H NMR (400

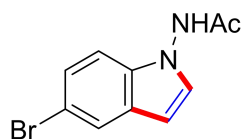
MHz, DMSO-d₆): δ 11.01 (s, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.24 – 7.05 (m, 3H), 6.35 (d, J = 3.3 Hz, 1H), 2.02 (s, 3H), 1.29 (s, 9H); ¹³C NMR (101 MHz, DMSO): δ 169.14, 142.22, 133.83, 129.05 (d, J = 8.2 Hz), 125.72, 120.01 (d, J = 3.2 Hz), 116.27 (d, J = 2.1 Hz), 108.66 – 108.26 (m), 99.97 (d, J = 7.5 Hz), 34.22, 31.80 (q, J = 7.3 Hz), 20.52 (q, J = 4.4 Hz). HRMS(ESI): Calcd for C₁₄H₁₉N₂O [M+H]⁺ 231.1492, Found 1231.1497.



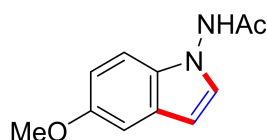
***N*-(5-fluoro-1*H*-indol-1-yl)acetamide (3da)**: brown crystalline solid (29.6 mg, 68%); M.p.:116.5-117.5 °C. IR(cm⁻¹): ν 3203, 1684, 1547, 1373, 1225, 856. ¹H NMR (400 MHz, DMSO-d₆): δ 11.07 (s, 1H), 7.29 – 7.23 (m, 2H), 7.16 (dd, J = 8.9, 4.5 Hz, 1H), 6.93 (td, J = 9.2, 2.5 Hz, 1H), 6.38 (d, J = 3.3 Hz, 1H), 2.01 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.28, 132.30, 131.04 (d, J = 6.3 Hz), 126.20 (d, J = 10.4 Hz), 110.25 – 109.83 (m), 100.03 (dd, J = 8.4, 4.5 Hz), 20.53 (q, J = 4.4 Hz); ¹⁹F NMR (376 MHz, DMSO): δ -124.54. HRMS(ESI): Calcd for C₁₀H₁₀FN₂O [M+H]⁺ 193.0772, Found 193.0784.



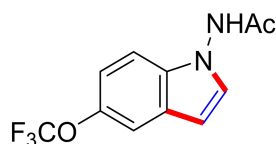
***N*-(5-chloro-1*H*-indol-1-yl)acetamide (3ea)**: pale yellow crystalline solid (32.2 mg, 77%); M.p.:139-141 °C. IR (cm⁻¹): ν 3244 1672 1524 1464 708. ¹H NMR (400 MHz, DMSO-d₆): δ 11.18 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 3.4 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 7.18 (dd, J = 8.7, 2.0 Hz, 1H), 6.49 – 6.45 (m, 1H), 2.09 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.15, 134.09, 130.87 (d, J = 6.0 Hz), 126.99, 124.46, 122.08 – 121.70 (m), 119.77, 110.57 (t, J = 3.3 Hz), 99.70 (d, J = 8.8 Hz), 20.49 (q, J = 4.4 Hz). HRMS(ESI): Calcd for C₁₀H₉ClN₂O [M+Na]⁺ 231.0296, Found 231.0305.



N-(5-bromo-1H-indol-1-yl)acetamide (**3fa**): pale yellow solid (40.4 mg, 80%); M.p.:167-169 °C. IR(cm^{-1}): ν 3233, 1684, 1530, 1458, 798. ^1H NMR (400 MHz, DMSO- d_6): δ 11.19 (s, 1H), 7.78 (d, $J = 1.9$ Hz, 1H), 7.35 (d, $J = 3.4$ Hz, 1H), 7.32 – 7.21 (m, 2H), 6.47 (d, $J = 3.4$ Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.13, 134.34, 130.71 (d, $J = 6.2$ Hz), 127.69, 124.41 (t, $J = 3.1$ Hz), 122.81 (d, $J = 1.8$ Hz), 112.34, 111.23 – 110.90 (m), 99.62 (d, $J = 8.7$ Hz), 20.50 (q, $J = 4.5$ Hz). HRMS(ESI): Calcd for $\text{C}_{10}\text{H}_9\text{BrN}_2\text{O}$ $[\text{M}+\text{Na}]^+$ 274.9790, Found 274.9799.

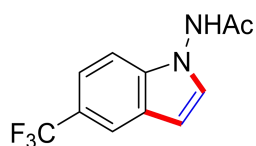


N-(5-methoxy-1H-indol-1-yl)acetamide (**3ga**): pale yellow solid (26.8 mg, 66%); M.p.:106-107 °C. IR(cm^{-1}): ν 3265, 1674, 1477, 1240, 806. ^1H NMR (400 MHz, DMSO- d_6): δ 11.05 (s, 1H), 7.23 (d, $J = 3.3$ Hz, 1H), 7.14 (d, $J = 8.9$ Hz, 1H), 7.08 (d, $J = 2.4$ Hz, 1H), 6.82 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.39 – 6.36 (m, 1H), 3.77 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.13, 154.04, 130.75, 129.56 (d, $J = 8.0$ Hz), 126.32, 111.88 (d, $J = 8.4$ Hz), 109.85 – 109.52 (m), 102.48 (d, $J = 8.8$ Hz), 99.56 (d, $J = 6.8$ Hz), 55.42 (q, $J = 12.0$ Hz), 20.50 (q, $J = 4.1$ Hz). HRMS(ESI): Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$ 227.0791, Found 227.0801.

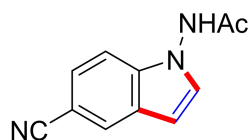


N-(5-(trifluoromethoxy)-1H-indol-1-yl)acetamide (**3ha**): pale yellow solid (43.4 mg, 84%); M.p.:145-147 °C. IR(cm^{-1}): ν 3026, 1680, 1284, 1159, 880. ^1H NMR (400 MHz,

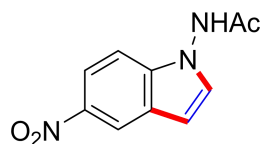
DMSO-d₆): δ 11.24 (s, 1H), 7.60 – 7.57 (m, 1H), 7.43 (d, J = 3.4 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.18 – 7.13 (m, 1H), 6.56 (d, J = 3.4 Hz, 1H), 2.11 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.25, 142.47 (q, J = 1.9 Hz), 134.06, 131.43 (d, J = 4.9 Hz), 126.07, 121.74, 115.58 (d, J = 6.8 Hz), 112.96, 110.18 (t, J = 2.7 Hz), 100.43 (d, J = 9.7 Hz), 20.48 (q, J = 4.8 Hz); ¹⁹F NMR (376 MHz, DMSO): δ -57.08. HRMS(ESI): Calcd for C₁₁H₉F₃N₂O₂ [M+Na]⁺ 281.0508, Found 281.0513.



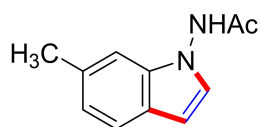
N-(5-(trifluoromethyl)-1H-indol-1-yl)acetamide (**3ia**): pale yellow solid (42.6 mg, 88%); M.p.: 168-170 °C. IR(cm⁻¹): ν 3020, 1680, 1109, 901, 814, 733. ¹H NMR (400 MHz, DMSO-d₆): δ 11.30 (s, 1H), 7.99 (s, 1H), 7.50 – 7.43 (m, 3H), 6.65 (d, J = 3.4 Hz, 1H), 2.12 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.68, 137.54, 131.99 (d, J = 4.1 Hz), 127.22, 125.81, 124.52, 121.39 (q, J = 31.1 Hz), 118.84 (d, J = 4.3 Hz), 110.34, 101.59 (d, J = 10.7 Hz), 20.98 (q, J = 4.9 Hz); ¹⁹F NMR (376 MHz, DMSO): δ -58.64. HRMS(ESI): Calcd for C₁₁H₁₀F₃N₂O [M+H]⁺ 243.0740, Found 243.0751.



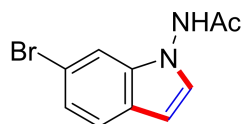
N-(5-cyano-1H-indol-1-yl)acetamide (**3ja**): pale yellow solid (30.0 mg, 75%); M.p.: 157-158 °C. IR(cm⁻¹): ν 3244, 2222, 1668, 1520, 806, 577. ¹H NMR (400 MHz, DMSO-d₆): δ 11.33 (s, 1H), 8.13 (d, J = 1.6 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 (d, J = 8.5 Hz, 1H), 6.66 – 6.62 (m, 1H), 2.12 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.23, 137.25, 131.92 (d, J = 3.5 Hz), 126.28 (d, J = 5.9 Hz), 125.71, 124.85, 120.33, 110.41 (t, J = 2.0 Hz), 102.23, 101.04 (d, J = 10.9 Hz), 20.52 (d, J = 5.2 Hz). HRMS(ESI): Calcd for C₁₁H₁₀N₃O [M+H]⁺ 200.0818, Found 200.0821.



***N*-(5-nitro-1*H*-indol-1-yl)acetamide (3ka)**: pale yellow solid (25.4 mg, 58%); M.p.: 189-191 °C. IR(cm^{-1}): ν 3246, 1672, 1514, 1339, 741. ^1H NMR (400 MHz, DMSO- d_6): δ 11.40 (s, 1H), 8.60 (d, $J = 2.3$ Hz, 1H), 8.07 (dd, $J = 9.0, 2.3$ Hz, 1H), 7.57 (d, $J = 3.4$ Hz, 1H), 7.46 (d, $J = 9.0$ Hz, 1H), 6.82 – 6.75 (m, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.17, 141.54, 138.51, 132.96 (d, $J = 2.5$ Hz), 125.22, 117.77 (d, $J = 6.2$ Hz), 117.32 (d, $J = 3.5$ Hz), 109.65 (d, $J = 3.0$ Hz), 102.65 (d, $J = 11.4$ Hz), 20.51 (q, $J = 5.1$ Hz). HRMS(ESI): Calcd for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_3$ [$\text{M}+\text{Na}$] $^+$ 242.0536, Found 242.0545.

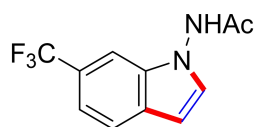


***N*-(6-methyl-1*H*-indol-1-yl)acetamide (3la)**: pale yellow solid (28.4 mg, 75%); M.p.: 141-142 °C. IR(cm^{-1}): ν 3564, 2351, 1682, 1456, 1269, 802. ^1H NMR (400 MHz, DMSO- d_6): δ 11.05 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 3.3$ Hz, 1H), 7.05 (s, 1H), 6.92 (dd, $J = 8.0, 1.5$ Hz, 1H), 6.40 (d, $J = 3.4$ Hz, 1H), 2.42 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.58, 136.43, 131.66, 128.95 (d, $J = 9.1$ Hz), 124.28, 122.01 (d, $J = 9.1$ Hz), 120.76 (d, $J = 3.3$ Hz), 109.21 (d, $J = 9.2$ Hz), 100.23 (d, $J = 7.6$ Hz), 21.84 (q, $J = 9.5$ Hz), 21.02 (q, $J = 4.5$ Hz). HRMS(ESI): Calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$ 189.1022, Found 189.1025.

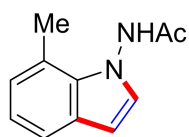


***N*-(6-bromo-1*H*-indol-1-yl)acetamide (3ma)**: pale yellow solid (40.6 mg, 80%); M.p.: 181-183 °C. IR(cm^{-1}): ν 3242, 2318, 1682, 1267, 891, 719. ^1H NMR (400 MHz, DMSO- d_6): δ 11.17 (s, 1H), 7.56 – 7.47 (m, 2H), 7.32 (d, $J = 3.4$ Hz, 1H), 7.22 (dd, J

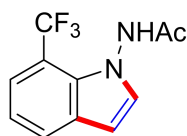
= 8.4, 1.8 Hz, 1H), 6.51 (dd, J = 3.3, 1.0 Hz, 1H), 2.11 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.25, 136.42, 130.21 (d, J = 7.0 Hz), 124.95, 122.91 – 122.63 (m), 122.40, 114.91, 111.77 (d, J = 3.4 Hz), 100.28 (d, J = 9.2 Hz), 20.56 (q, J = 4.8 Hz). HRMS(ESI): Calcd for C₁₀H₉BrN₂O [M+Na]⁺ 274.9790, Found 274.9797.



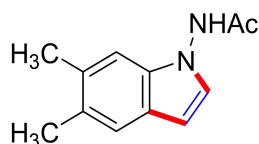
***N*-(6-(trifluoromethyl)-1*H*-indol-1-yl)acetamide (3na)**: pale yellow solid (23.4 mg, 48%); M.p.:191-193 °C. IR (cm⁻¹): ν 3250, 1686, 1458, 1275, 1115, 729. ¹H NMR (400 MHz, DMSO-d₆): δ 11.28 (s, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.55 (d, J = 3.3 Hz, 1H), 7.38 (dd, J = 8.3, 1.7 Hz, 1H), 6.66 – 6.55 (m, 1H), 2.13 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.83, 135.02, 133.09 (d, J = 2.9 Hz), 129.03, 124.36, 123.06 (q, J = 31.4 Hz), 122.05, 116.60 (d, J = 5.1 Hz), 106.92 (q, J = 4.5 Hz), 100.90 (d, J = 10.5 Hz), 21.04 (q, J = 5.1 Hz); ¹⁹F NMR (376 MHz, DMSO): δ -58.94. HRMS(ESI): Calcd for C₁₁H₉F₃N₂O [M+Na]⁺ 265.0559, Found 265.0565.



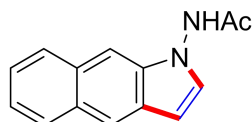
***N*-(7-methyl-1*H*-indol-1-yl)acetamide (3oa)**: orange solid (24.3 mg, 64%); M.p.:130-132 °C. IR(cm⁻¹): ν 3238, 1682, 1524, 1265, 897, 785. ¹H NMR (400 MHz, DMSO-d₆) δ 11.20 (s, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.15 (d, J = 3.4 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.1 Hz, 1H), 6.42 (d, J = 3.4 Hz, 1H), 2.47 (s, 3H), 2.04 (s, 3H); ¹³C NMR (101 MHz, DMSO): δ 169.49, 133.81, 130.10, 130.01, 126.59, 120.05, 119.85, 118.65 (d, J = 4.6 Hz), 100.19, 100.12, 20.37 (d, J = 3.5 Hz). HRMS(ESI): Calcd for C₁₁H₁₃N₂O [M+H]⁺ 189.1022, Found 189.1026.



***N*-(7-(trifluoromethyl)-1*H*-indol-1-yl)acetamide (3pa)**: pale yellow solid (12.0 mg, 25%); M.p.:189-191 °C. IR(cm^{-1}): ν 3210, 1684, 1535, 1321, 1115, 725. ^1H NMR (400 MHz, DMSO- d_6): δ 11.24 (s, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.54 (d, $J = 7.5$ Hz, 1H), 7.37 (d, $J = 3.4$ Hz, 1H), 7.22 (t, $J = 7.7$ Hz, 1H), 6.68 (d, $J = 3.4$ Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.26, 132.62 (d, $J = 5.9$ Hz), 130.97, 128.80, 125.84, 120.56 (q, $J = 6.0$ Hz), 119.28 – 119.07 (m), 112.05, 111.57 (q, $J = 32.6$ Hz), 101.65, 101.54, 20.39 (q, $J = 2.7$ Hz); ^{19}F NMR (376 MHz, DMSO): δ -56.05. HRMS(ESI): Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 243.0740, Found 243.0750.

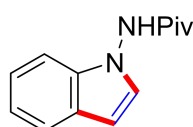


***N*-(5,6-dimethyl-1*H*-indol-1-yl)acetamide (3qa)**: brown solid (16.7 mg, 36%); M.p.:118.9-121.2 °C. IR(cm^{-1}): ν 3232, 3022, 1678, 1369, 1273, 706. ^{13}C NMR (101 MHz, DMSO): δ 169.04, 134.52, 130.46, 128.13 (d, $J = 9.1$ Hz), 127.85, 124.16, 120.61, 120.55, 109.16 (d, $J = 8.8$ Hz), 99.17 (d, $J = 5.0$ Hz), 20.52 (q, $J = 3.8$ Hz), 20.03 (q, $J = 7.5$ Hz), 19.64 (d, $J = 7.7$ Hz); ^1H NMR (400 MHz, DMSO- d_6): δ 10.98 (s, 1H), 7.29 (s, 1H), 7.09 (d, $J = 3.3$ Hz, 1H), 6.98 (s, 1H), 6.31 – 6.26 (m, 1H), 2.28 (d, $J = 8.2$ Hz, 6H), 2.06 (s, 3H). HRMS(ESI): Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$ 225.0998, Found 225.1004.

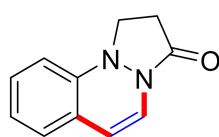


***N*-(1*H*-benzof[5,6]indol-1-yl)acetamide (3sa, major)**: pale brown solid (39.7 mg, **3sa:3sa'** = 5:1, 88%); M.p.:118-120°C. IR(cm^{-1}): ν 3231, 1674, 1371, 1219, 851, 733.

^1H NMR (400 MHz, DMSO- d_6): δ 11.19 (s, 1H), 8.14 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.75 (s, 1H), 7.55 (d, J = 3.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 6.64 (d, J = 3.5 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.27 (d, J = 11.0 Hz), 136.35, 133.76 (d, J = 2.7 Hz), 132.00, 129.78, 128.91, 128.45, 127.97, 127.66, 127.23, 125.90, 123.90, 123.36, 122.63 (d, J = 8.1 Hz), 120.57, 118.04 (d, J = 5.6 Hz), 110.88, 104.04, 99.47 (d, J = 10.4 Hz), 20.60 (dd, J = 6.1, 4.2 Hz). HRMS(ESI): Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$ 247.0842, Found 247.0847.



O-(1*H*-indol-1-yl)pivalamide (**3ta**): pale pink solid (25.3 mg, 58%); M.p.:110.7-111.3 °C. IR(cm^{-1}): ν 3275, 2978, 1709, 1526, 1267, 1161, 750. ^1H NMR (400 MHz, DMSO- d_6): δ 7.54 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 3.4 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.05 (ddd, J = 8.0, 5.6, 2.4 Hz, 1H), 6.41 (d, J = 3.4 Hz, 1H), 2.48 (d, J = 1.9 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, DMSO): δ 154.78, 135.81, 129.55 (d, J = 7.2 Hz), 125.92, 120.59, 108.66, 99.80 (d, J = 7.7 Hz), 80.42, 27.94 (d, J = 7.4 Hz). HRMS(ESI): Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$ 239.1155, Found 239.1158.



1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one (**3va**): brown solid (15.6 mg, 42%); M.p.: 72.8-74.7 °C. IR(cm^{-1}): ν 3287, 2311, 1684, 1456, 752. ^1H NMR(400 MHz, DMSO): δ 7.03 (t, J = 7.2 Hz, 1H), 6.76 (d, J = 9.1 Hz, 2H), 6.62 (d, J = 7.3 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H), 5.74 (d, J = 7.3 Hz, 1H), 3.52 (t, J = 7.7 Hz, 2H), 2.67 (t, J = 7.7 Hz, 2H); ^{13}C NMR(101 MHz, DMSO): δ 162.95, 146.28, 129.31, 129.27, 124.56, 124.52, 123.44, 122.66, 122.61, 122.09, 122.05, 122.01, 111.28, 111.23, 110.27, 110.19, 47.27, 30.43. HRMS(ESI): Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$ 209.0685, Found 209.0685.

The crystallographic data of **3aa**:

Compound **3aa** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu K α radiation. The data were collected and processed using CrysAlisPro⁴. The structures were solved by direct methods using Olex2 software⁵, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018⁶ using a full-matrix least squares procedure based on F^2 . The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2 . The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2302860 for compounds **3aa**.

The crystallographic data for the complex is summarized in the table below.

Compounds	3aa
Identification code	23-2
Empirical formula	C ₁₀ H ₁₀ N ₂ O
Formula weight	174.20
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	9.4933(3)
b/Å	9.0418(3)
c/Å	21.8135(9)
α /°	90
β /°	101.356(4)
γ /°	90
Volume/Å ³	1835.74(12)

Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.261
μ/mm^{-1}	0.678
F(000)	736.0
Crystal size/ mm^3	$0.14 \times 0.12 \times 0.1$
Radiation	Cu K α ($\lambda = 1.54184$)
2 Θ range for data collection/ $^\circ$	8.268 to 146.59
Index ranges	$-11 \leq h \leq 11, -7 \leq k \leq 10, -26 \leq l \leq 26$
Reflections collected	3227
Independent reflections	1793 [$R_{\text{int}} = 0.0185, R_{\text{sigma}} = 0.0244$]
Data/restraints/parameters	1793/7/119
Goodness-of-fit on F^2	1.035
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0490, wR_2 = 0.1323$
Final R indexes [all data]	$R_1 = 0.0542, wR_2 = 0.1388$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.22/-0.25

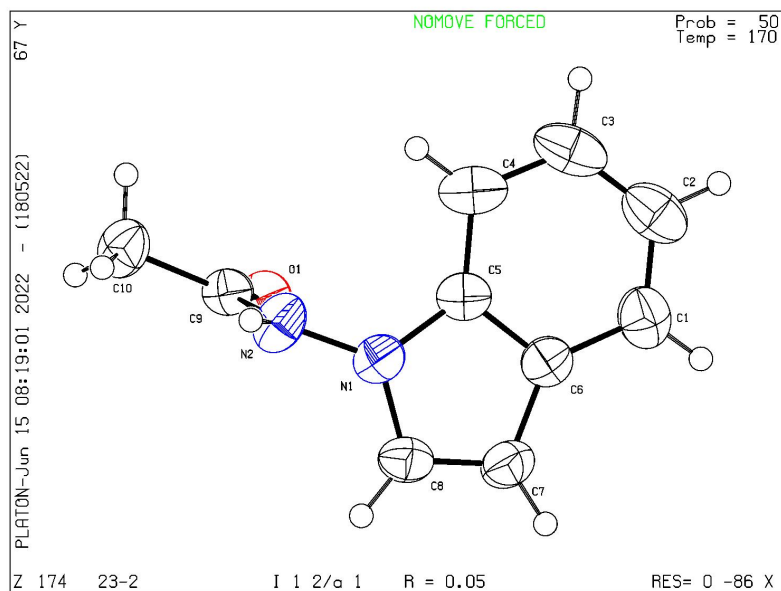
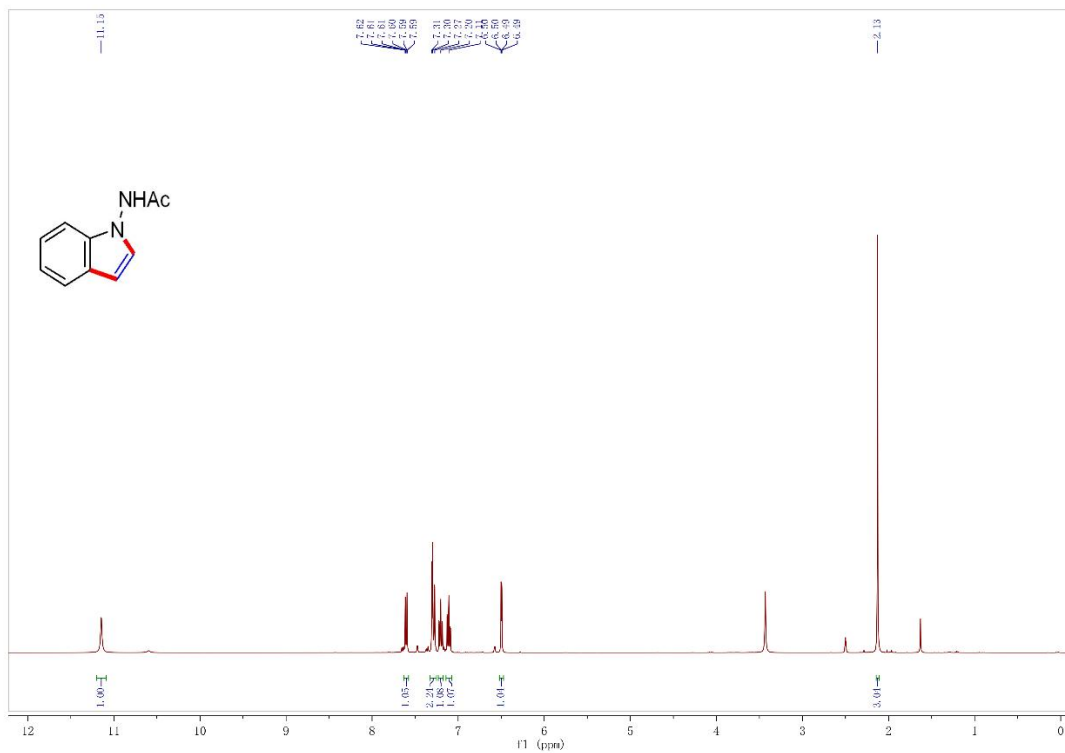
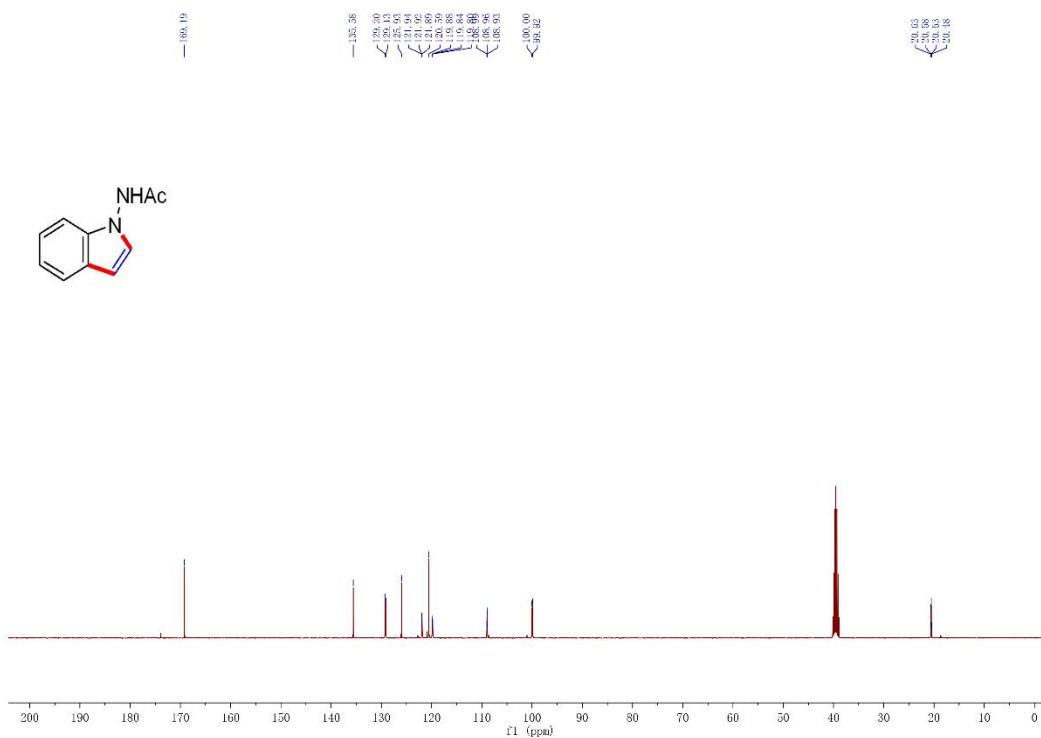


Figure S1. The molecular structure of **3aa**.

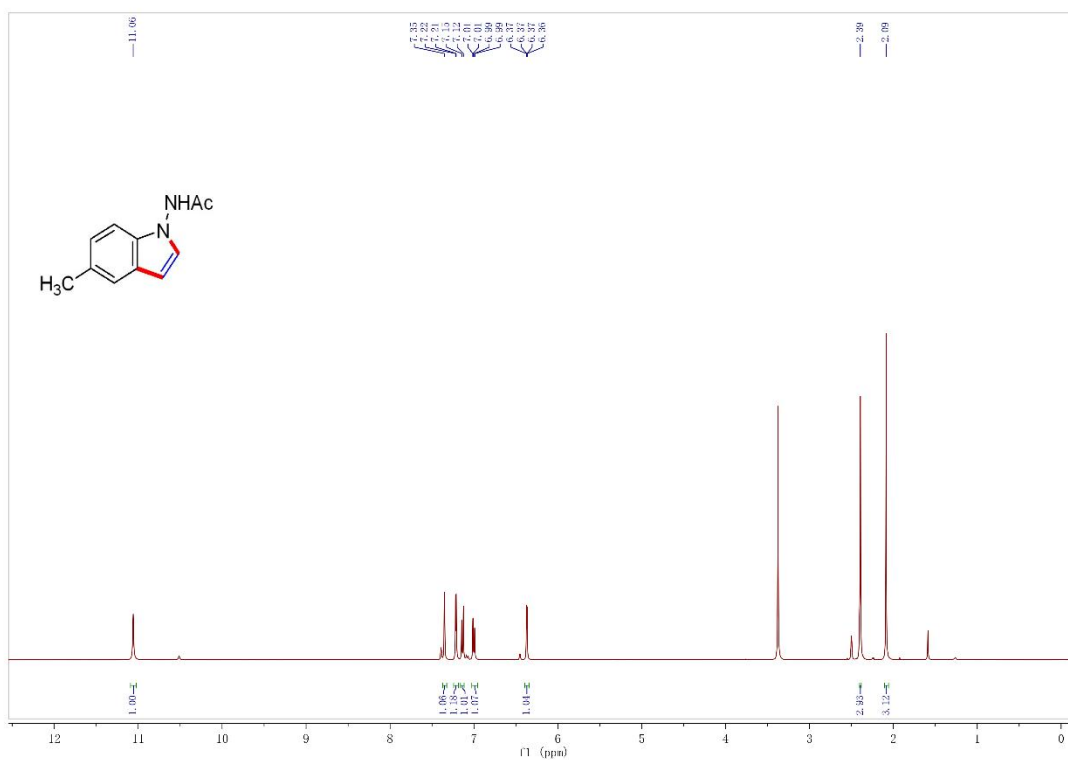
**Spectral Copies of ^1H , ^{13}C , and ^{19}F NMR
of Compounds Obtained in This Study**



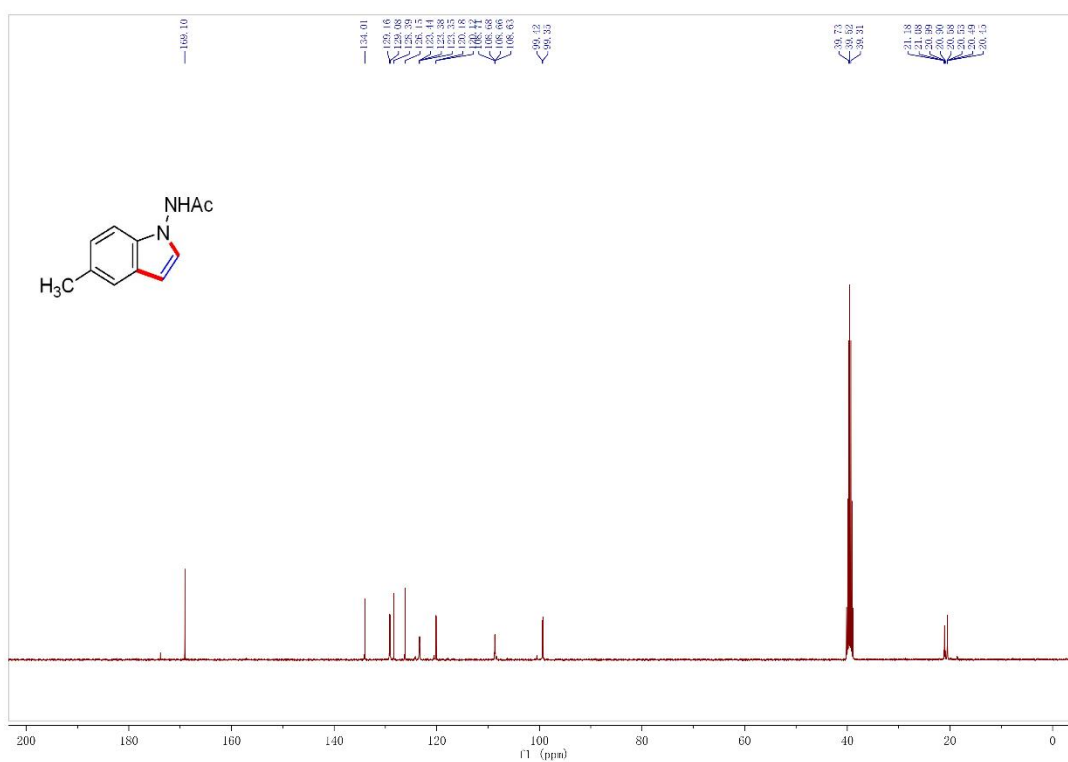
¹H NMR spectrum of compound 3aa



¹³C NMR spectrum of compound 3aa



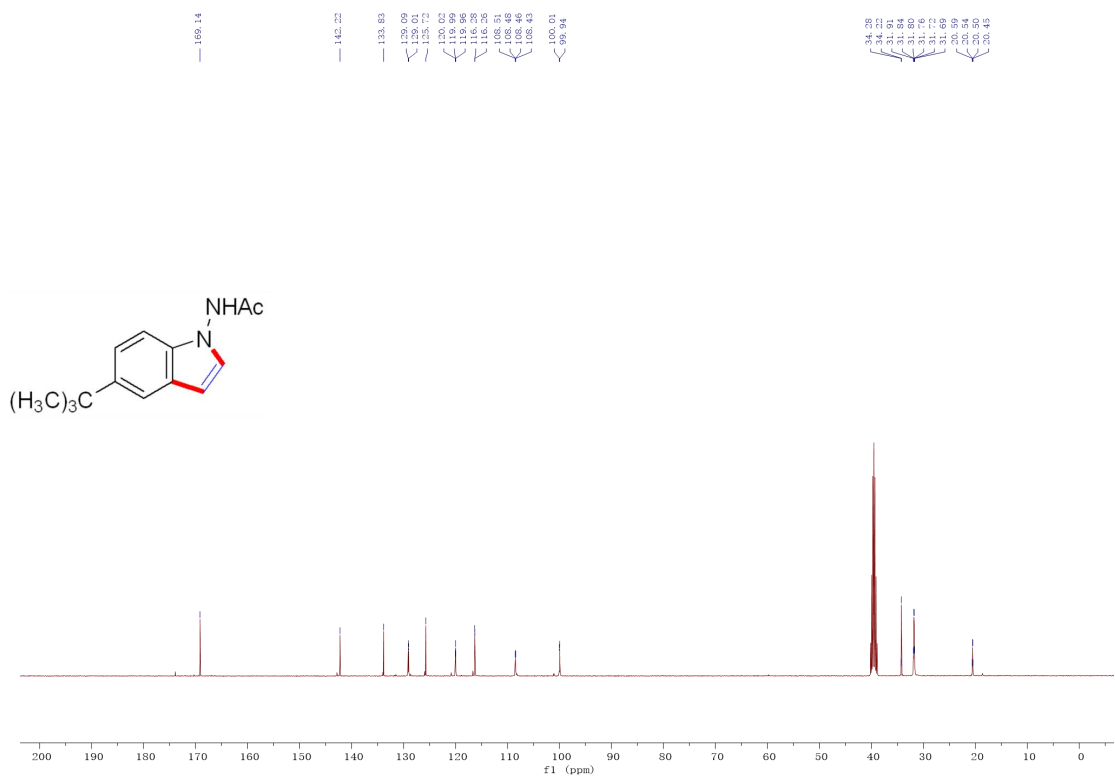
¹H NMR spectrum of compound **3ba**



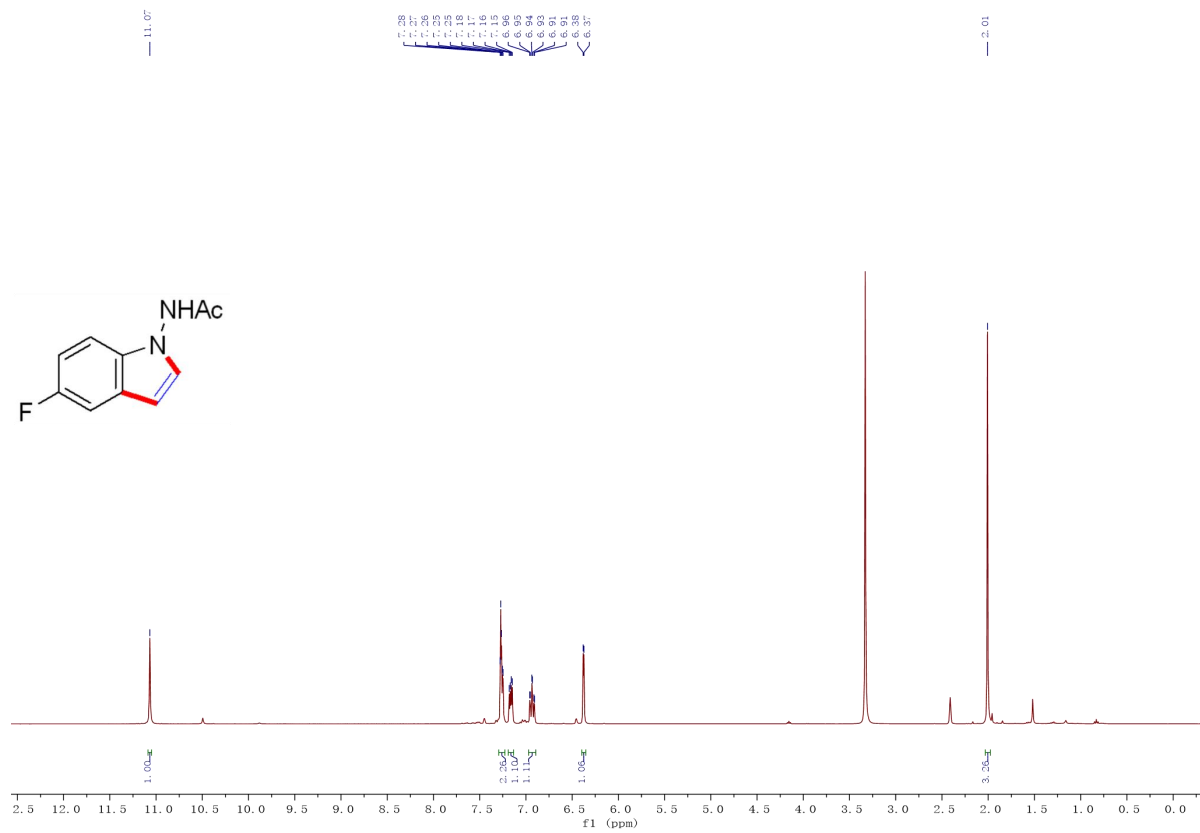
¹³C NMR spectrum of compound **3ba**



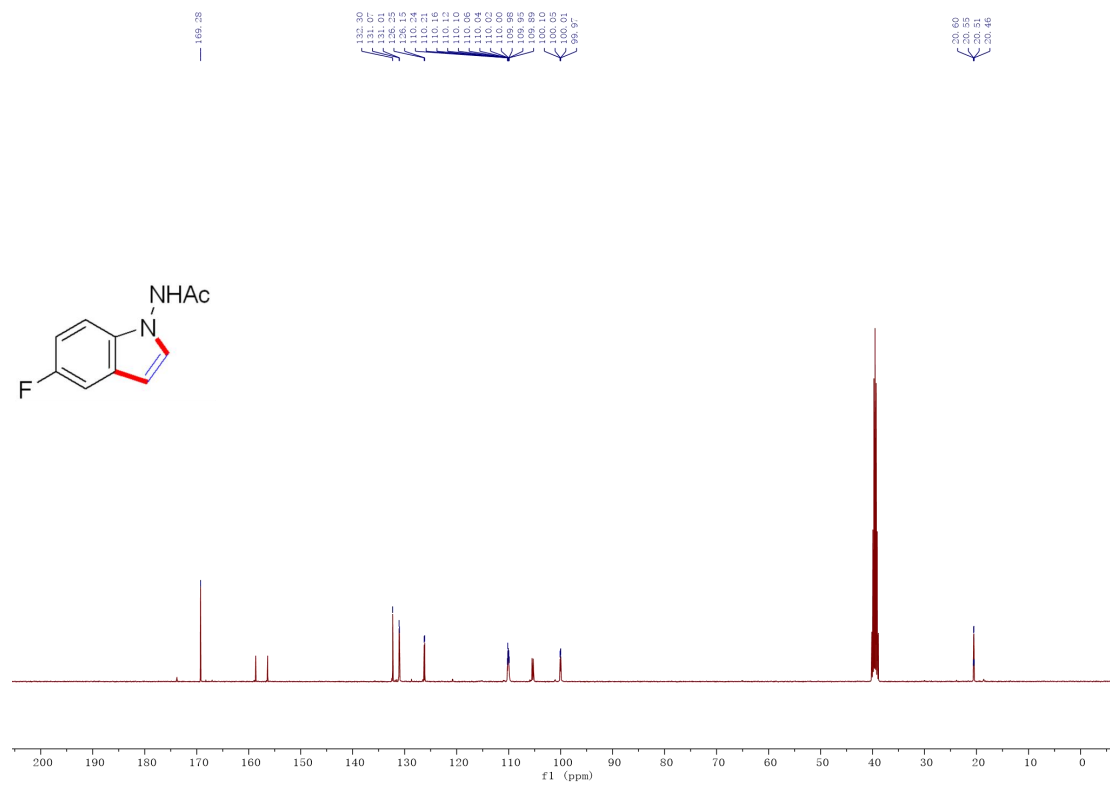
¹H NMR spectrum of compound **3ca**



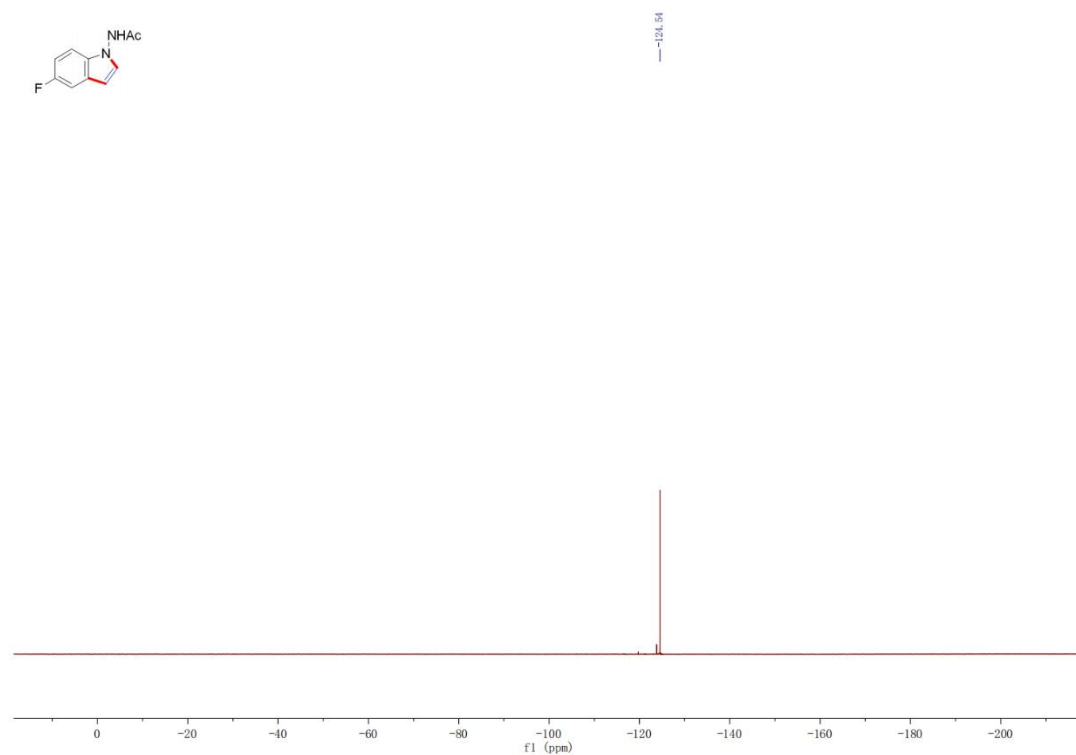
¹³C NMR spectrum of compound **3ca**



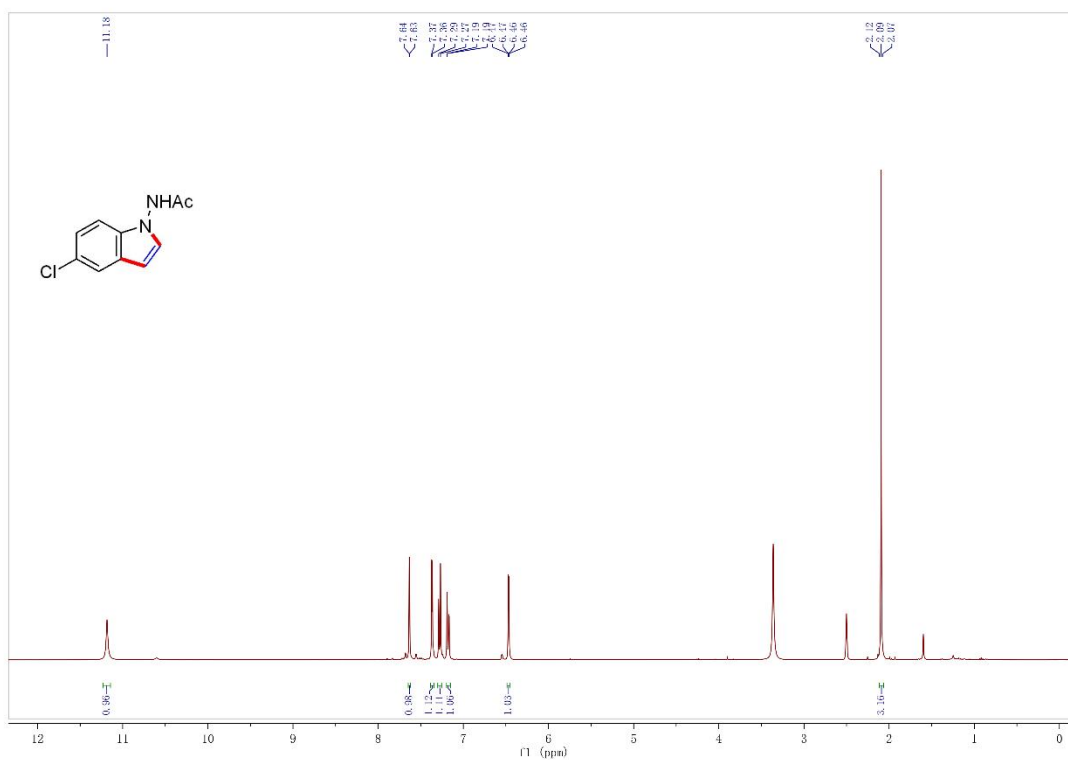
¹H NMR spectrum of compound **3da**



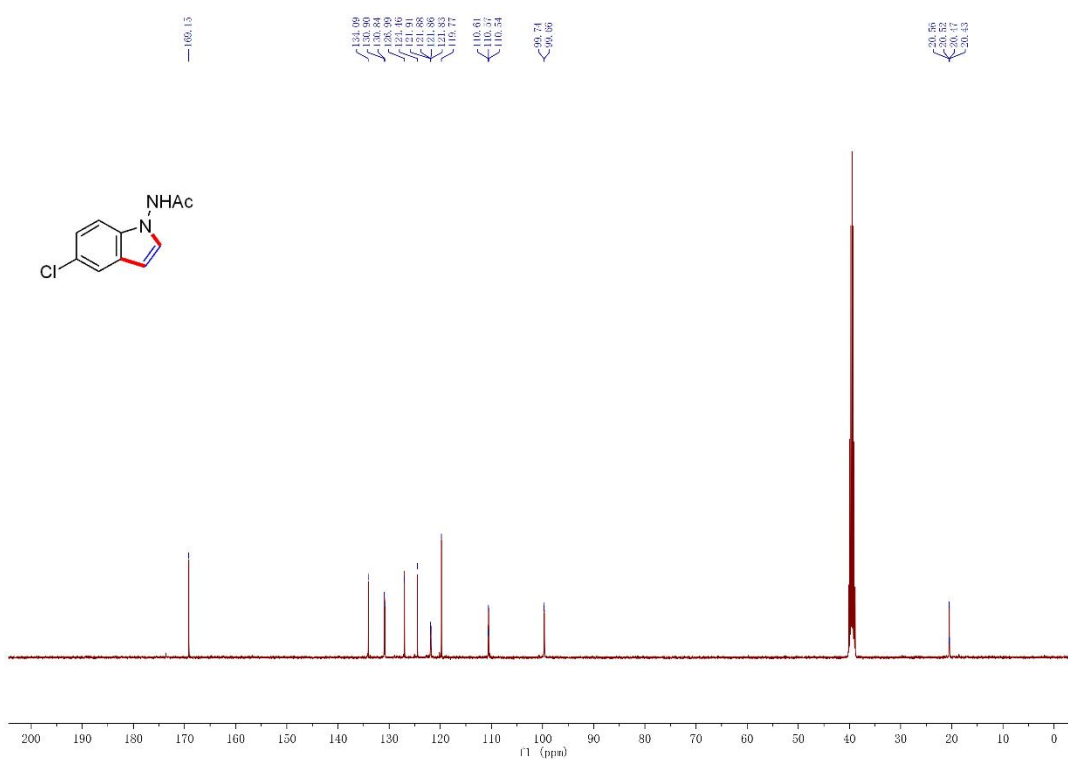
¹³C NMR spectrum of compound **3da**



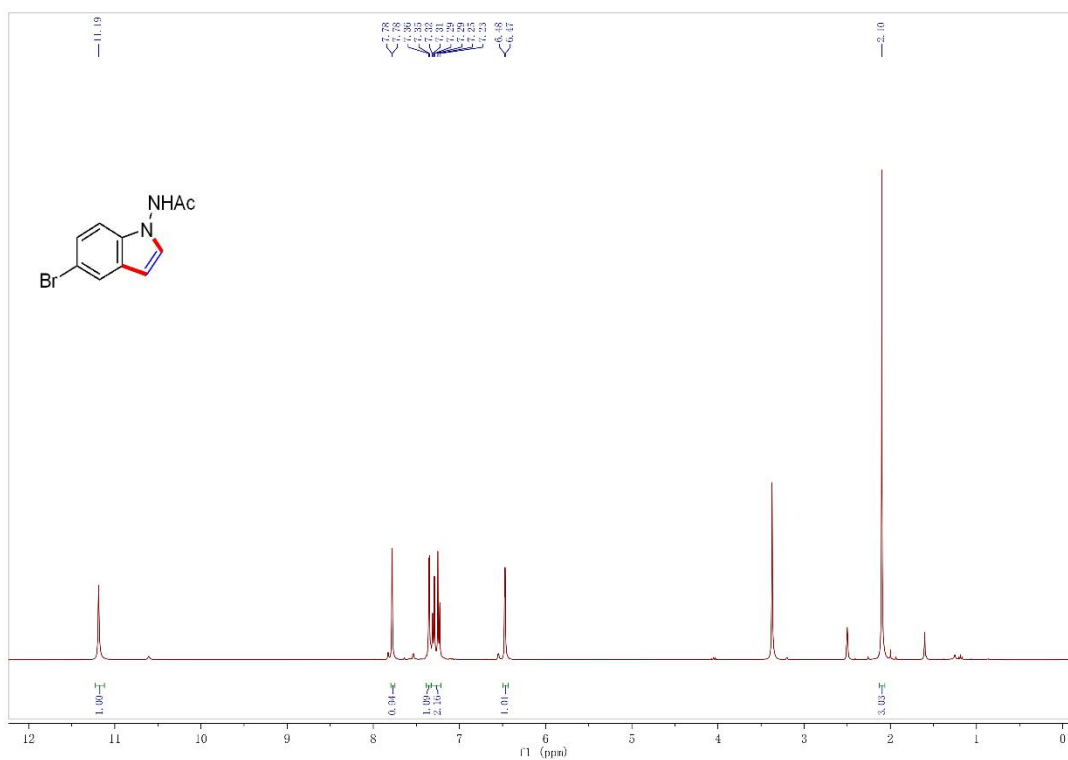
¹⁹F NMR spectrum of compound **3da**



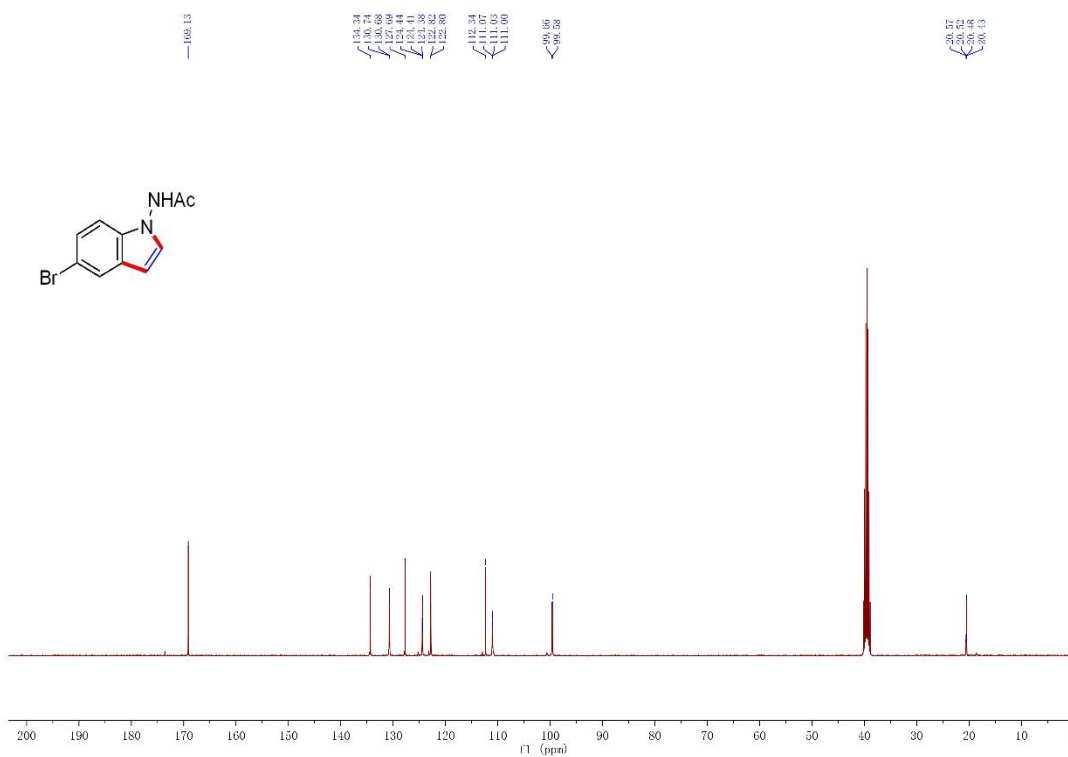
¹H NMR spectrum of compound 3ea



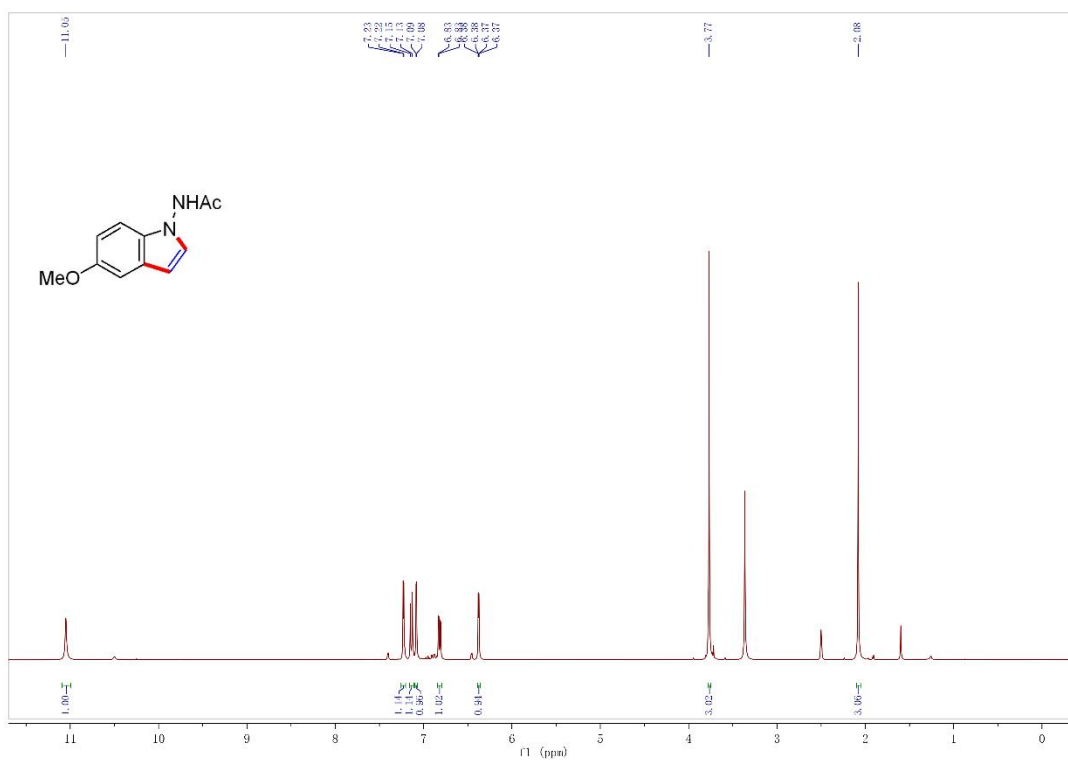
¹³C NMR spectrum of compound 3ea



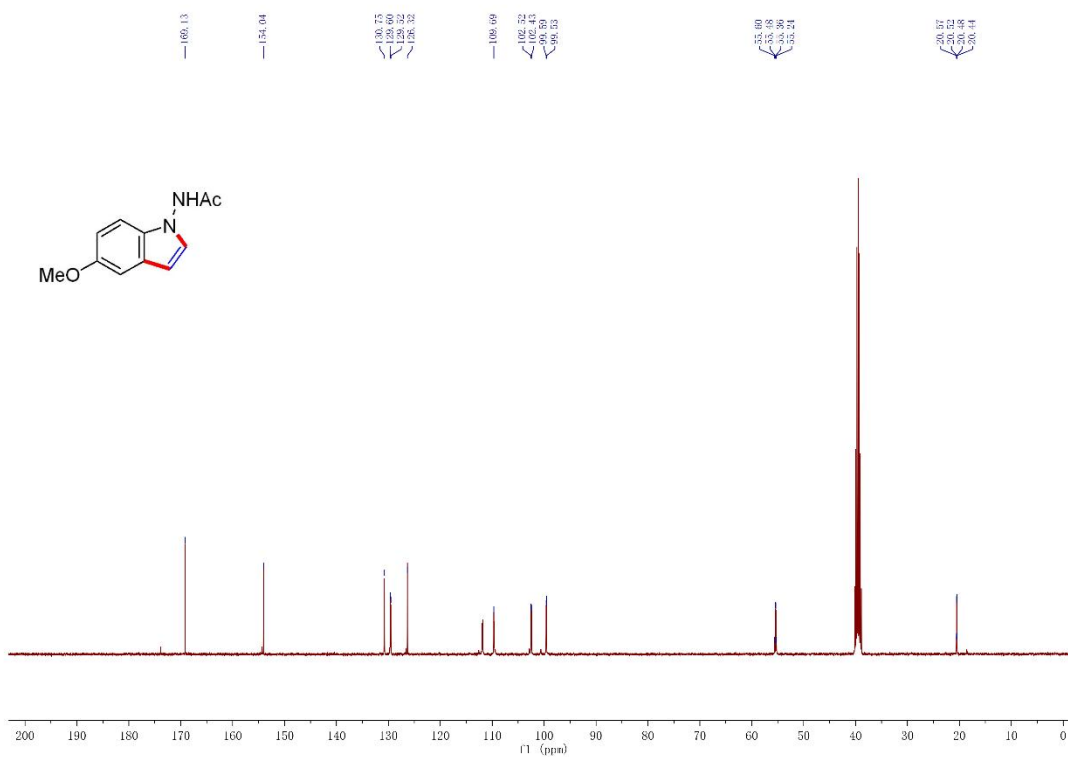
¹H NMR spectrum of compound **3fa**



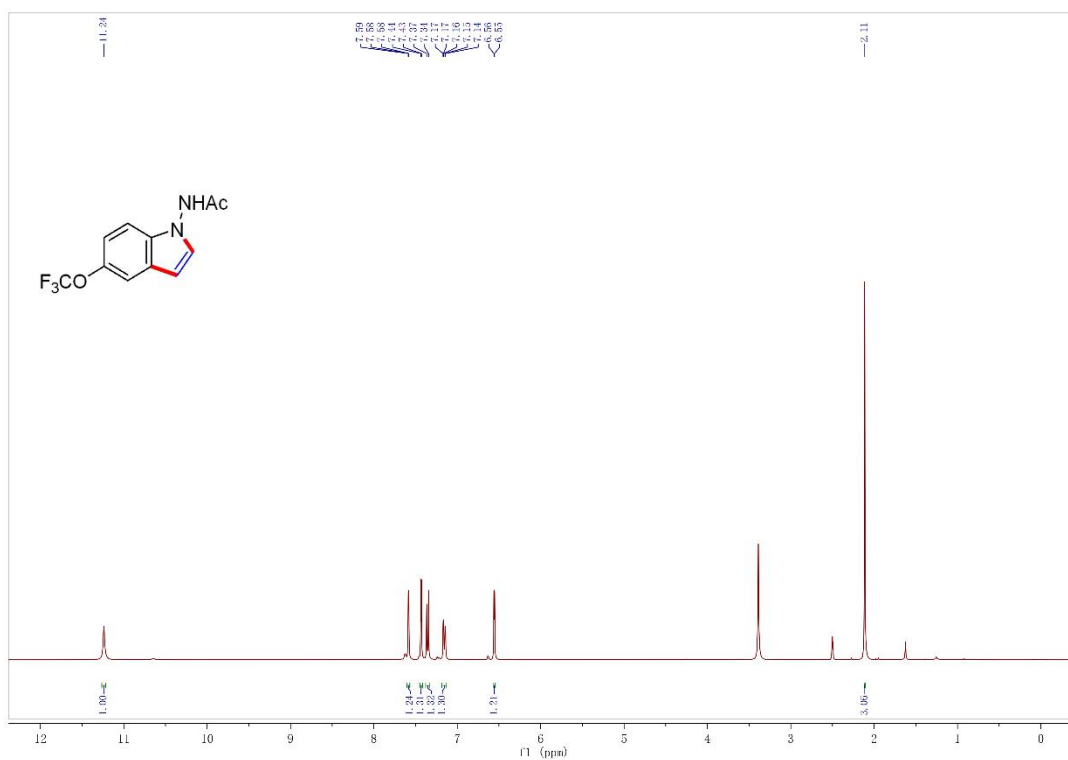
¹³C NMR spectrum of compound **3fa**



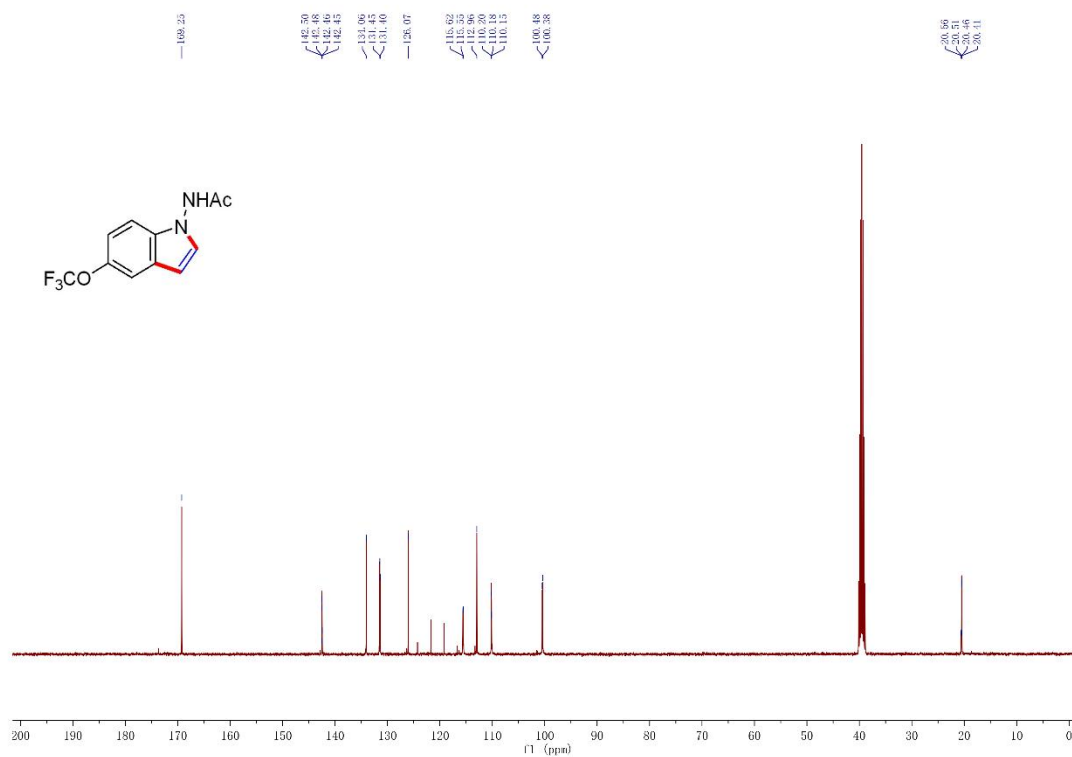
¹H NMR spectrum of compound 3ga



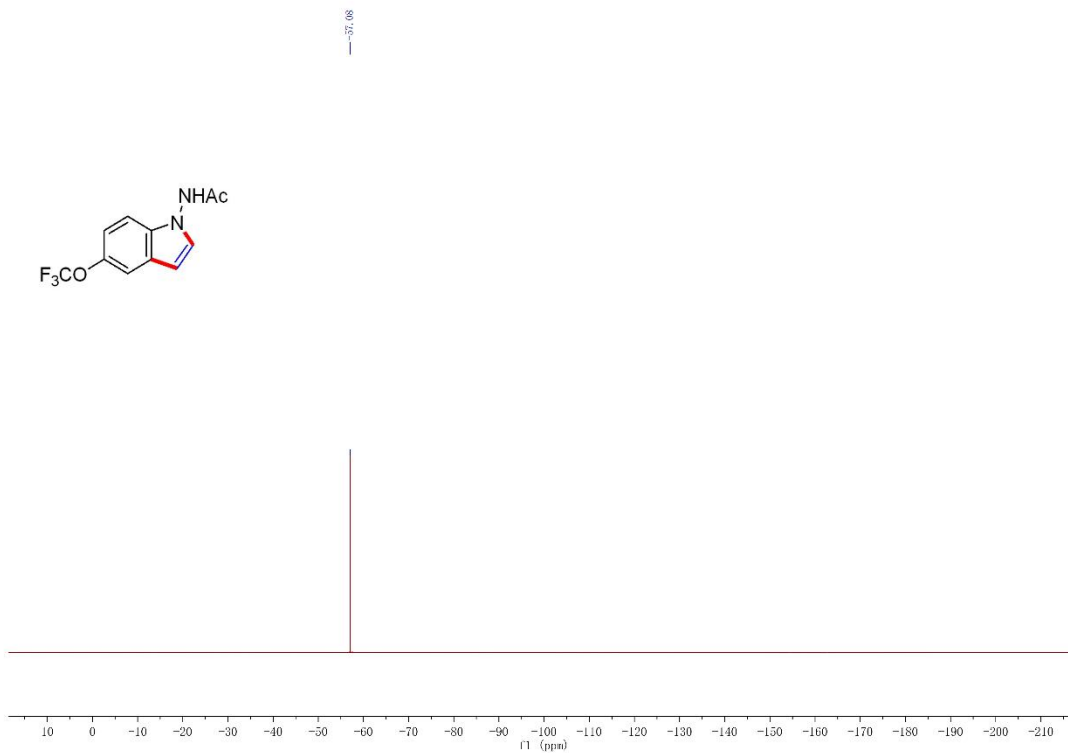
¹³C NMR spectrum of compound 3ga



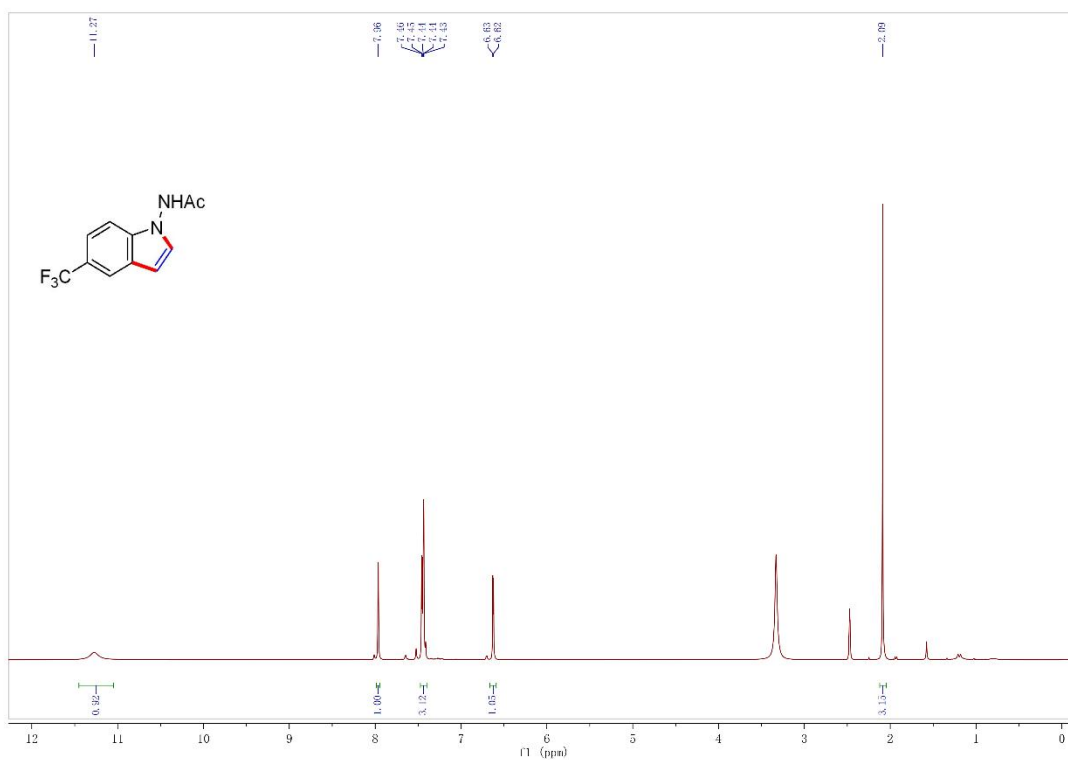
¹H NMR spectrum of compound **3ha**



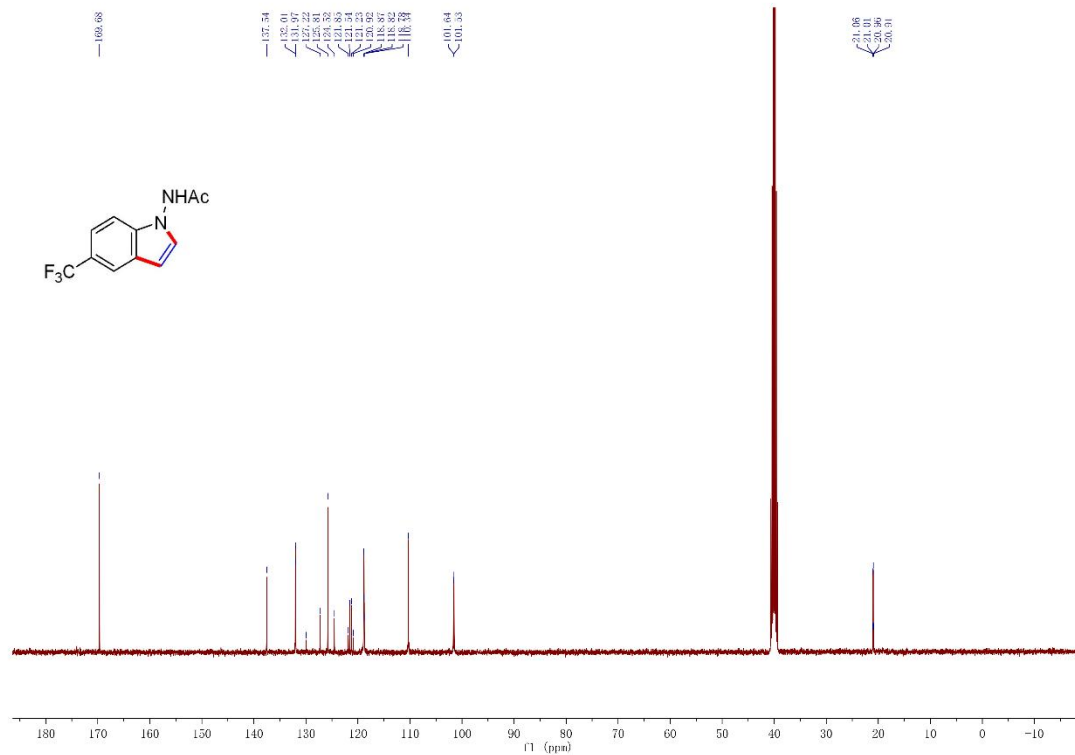
¹³C NMR spectrum of compound **3ha**



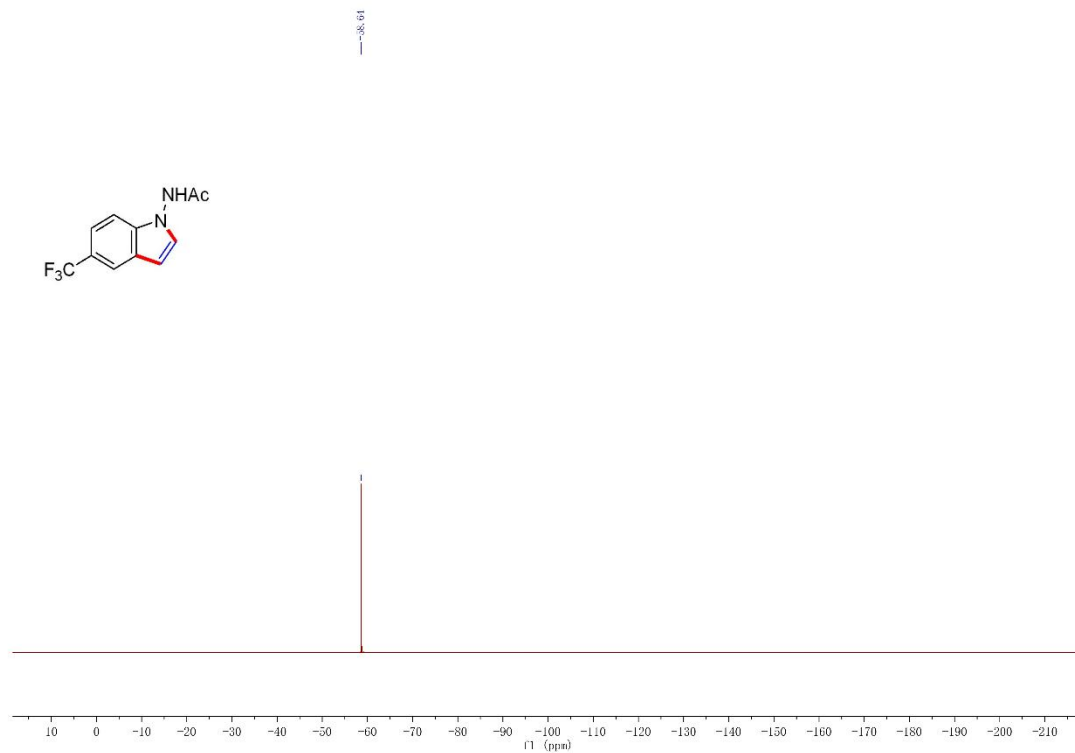
^{19}F NMR spectrum of compound **3ha**



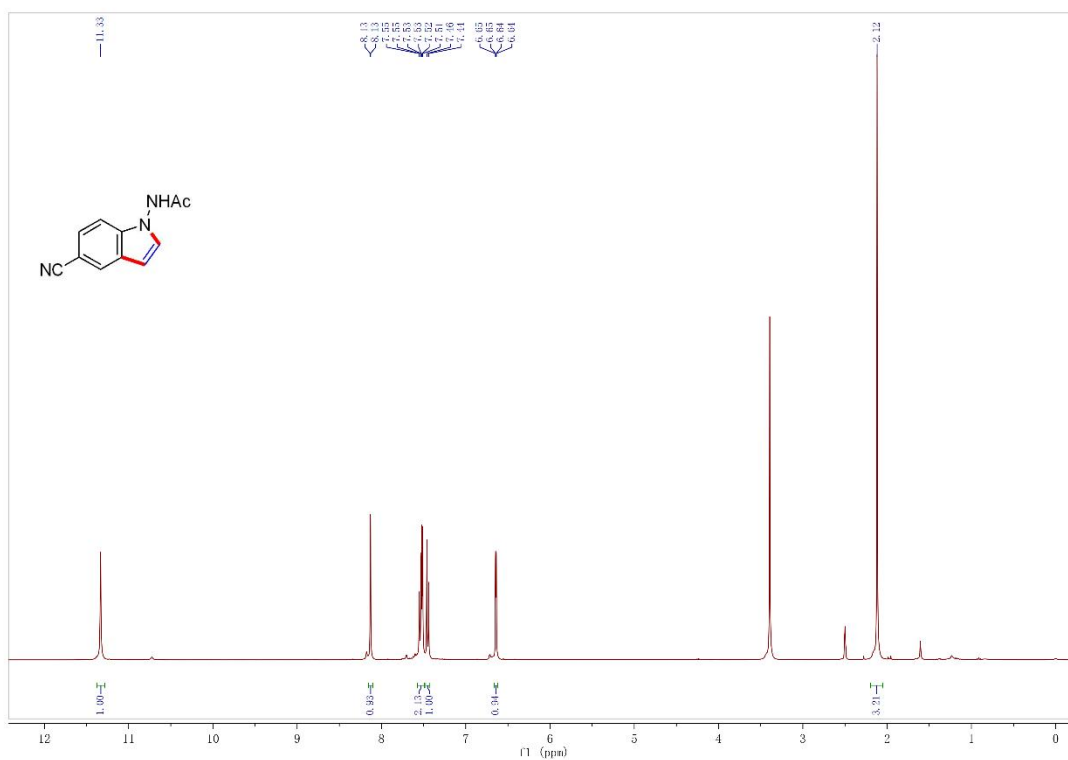
^1H NMR spectrum of compound **3ia**



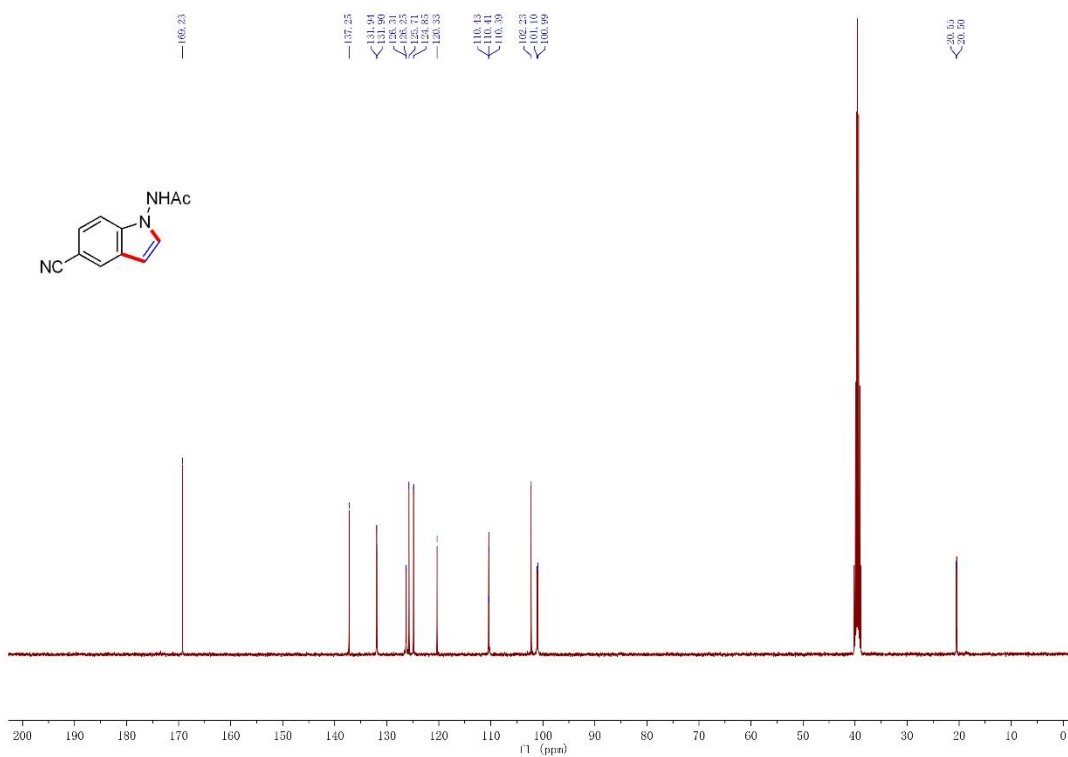
¹³C NMR spectrum of compound **3ia**



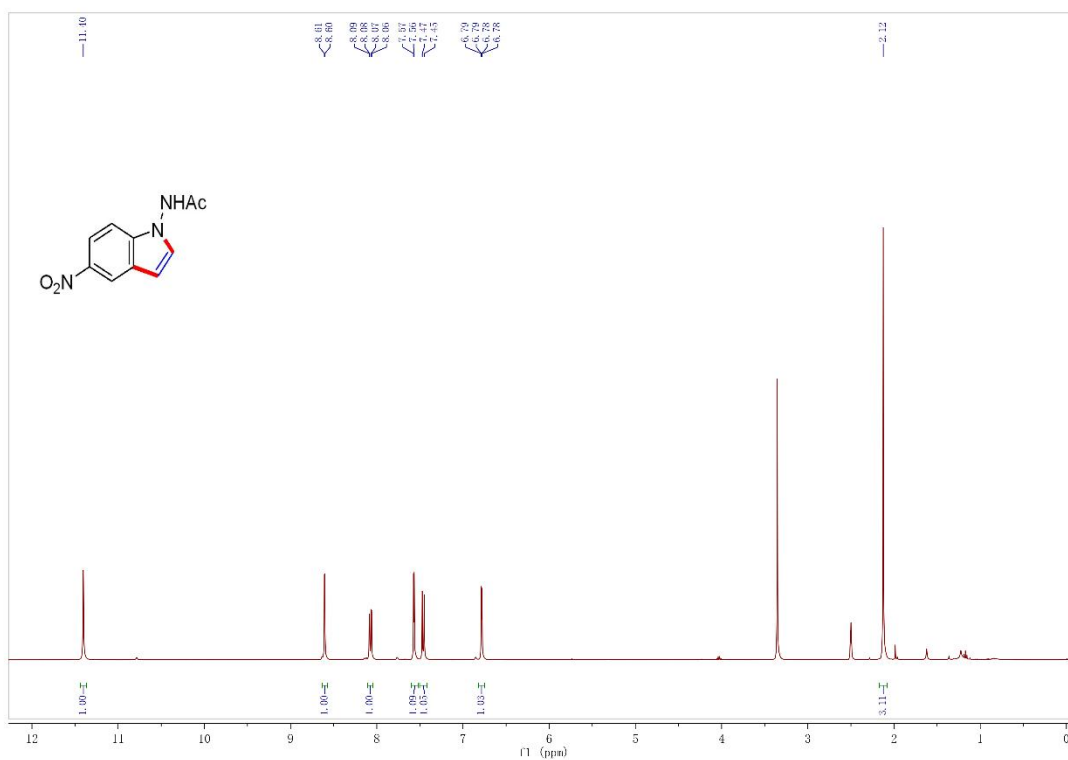
¹⁹F NMR spectrum of compound **3ia**



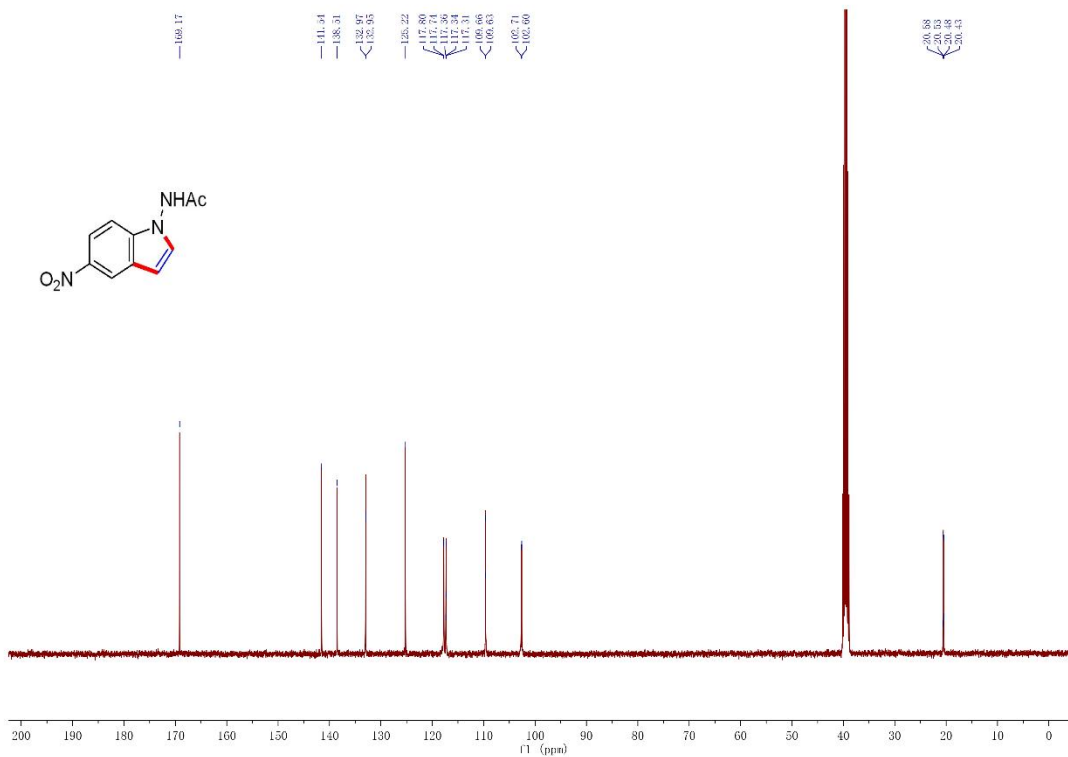
¹H NMR spectrum of compound 3ja



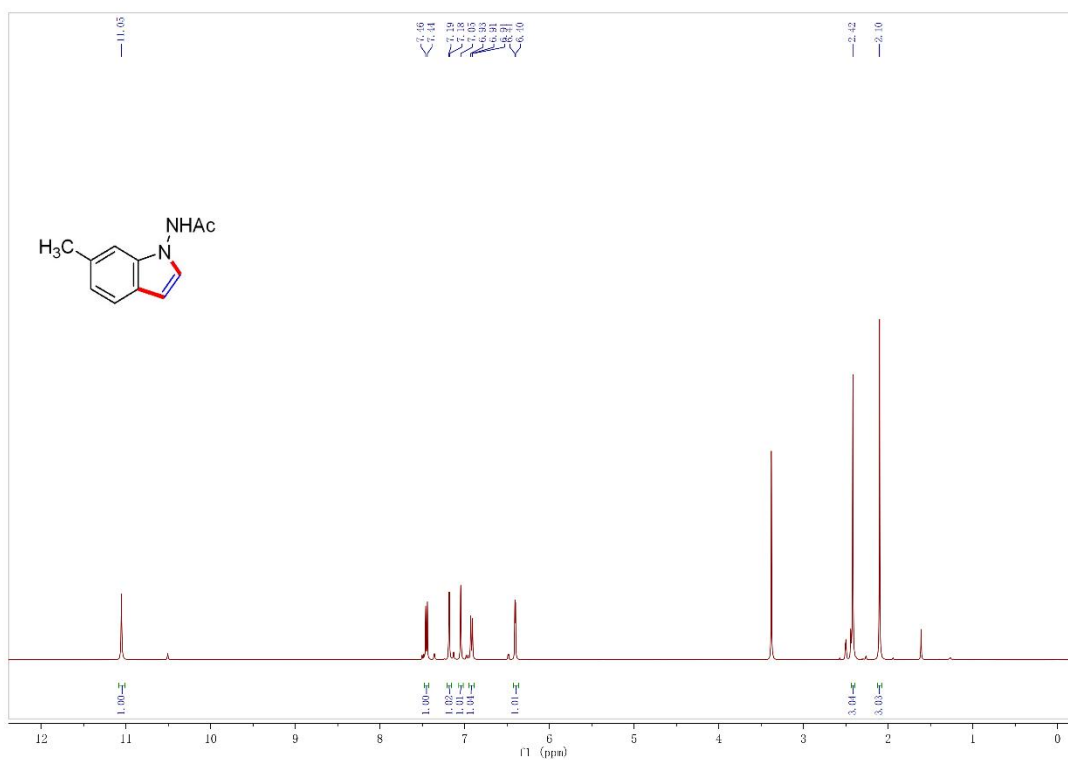
¹³C NMR spectrum of compound 3ja



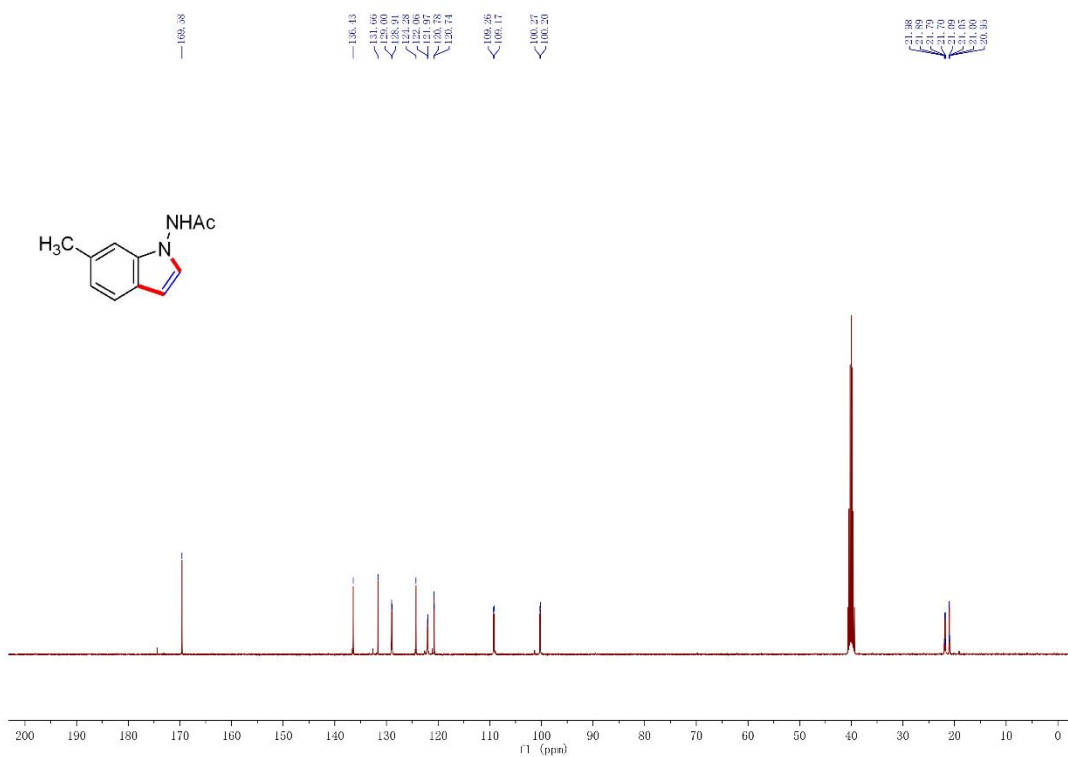
¹H NMR spectrum of compound 3ka



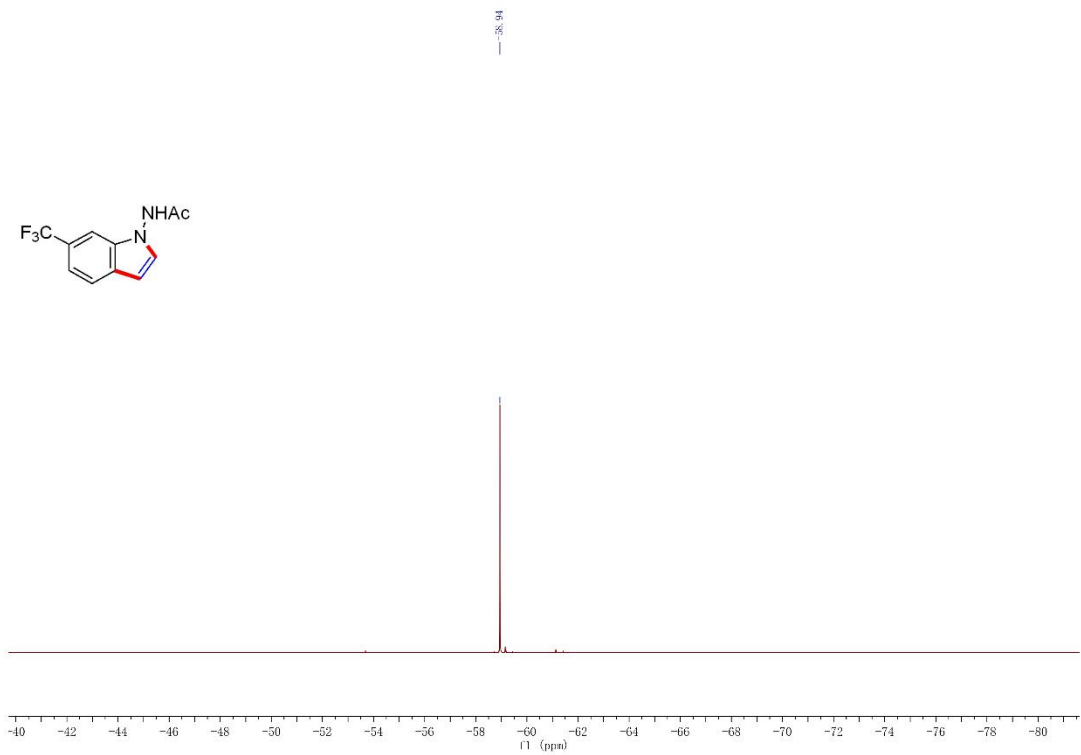
¹³C NMR spectrum of compound 3ka



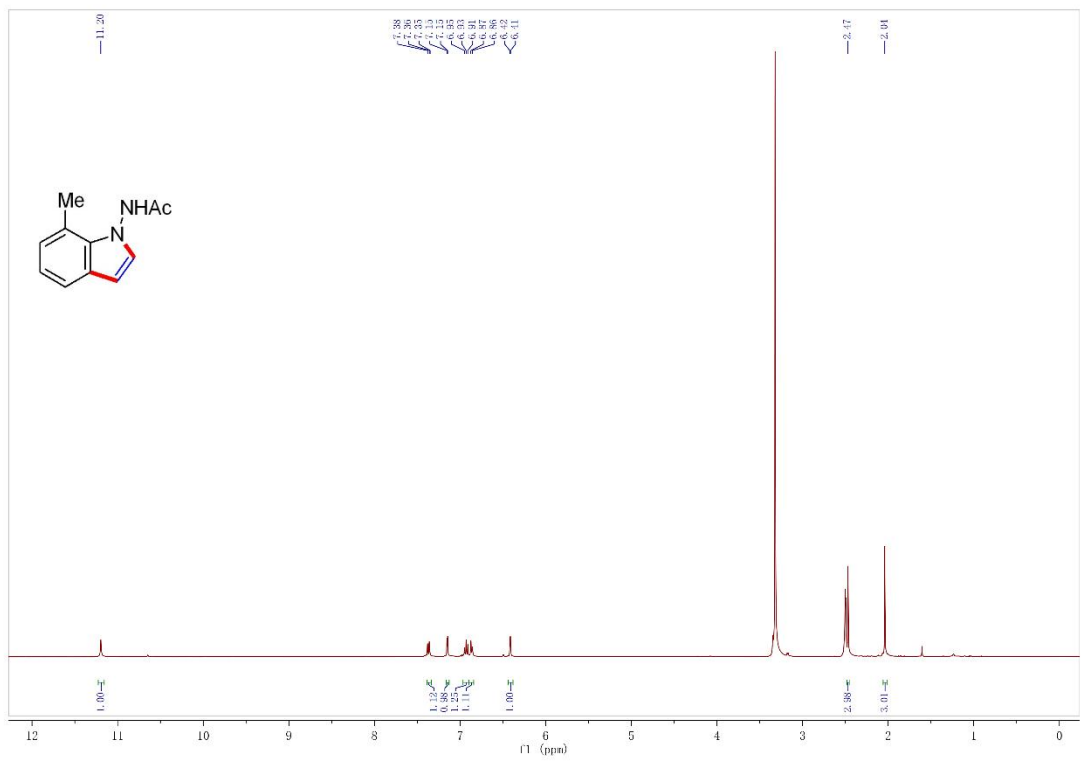
¹H NMR spectrum of compound **3la**



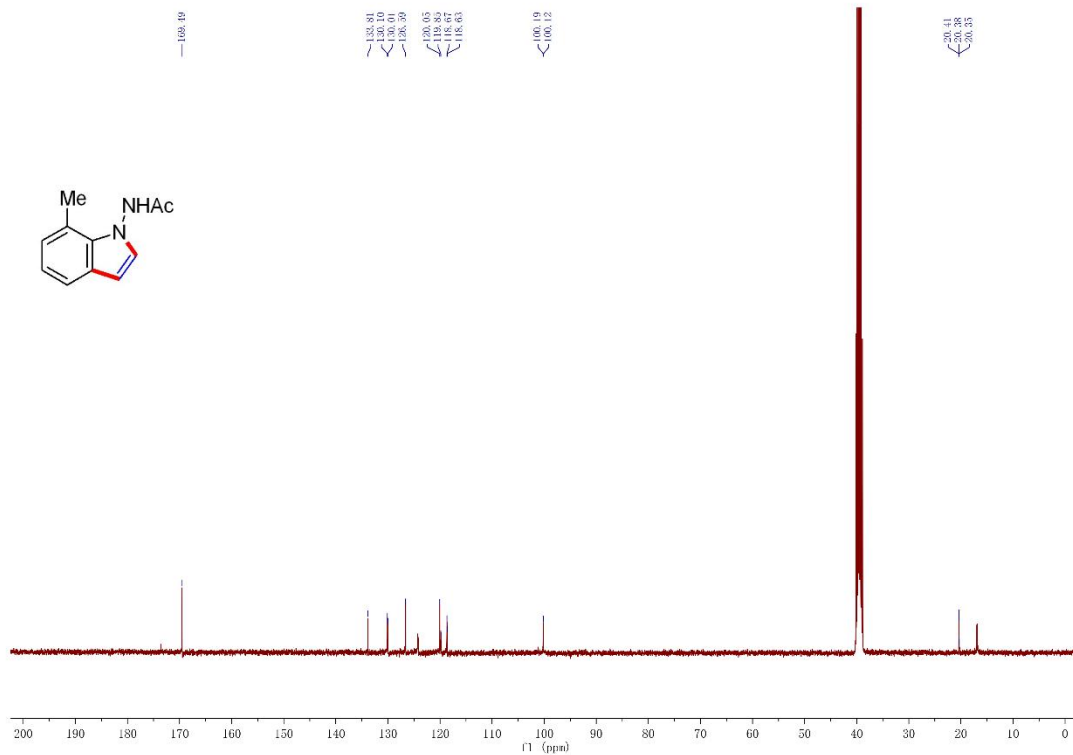
¹³C NMR spectrum of compound **3la**



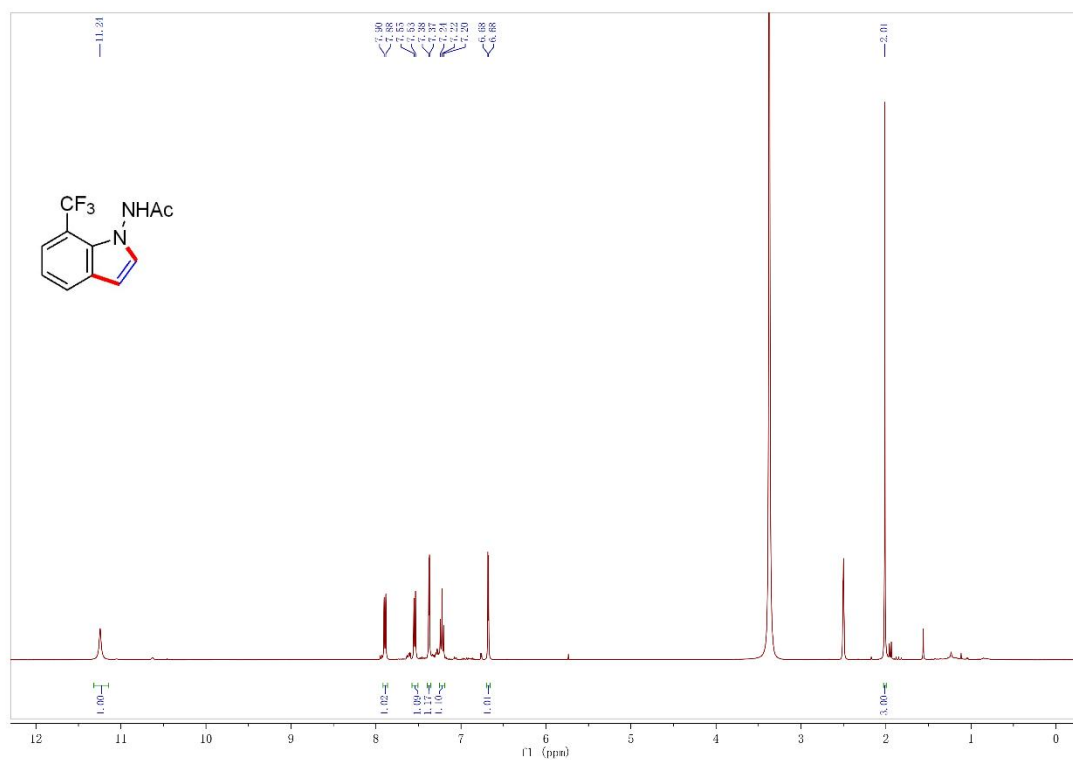
^{19}F NMR spectrum of compound **3na**



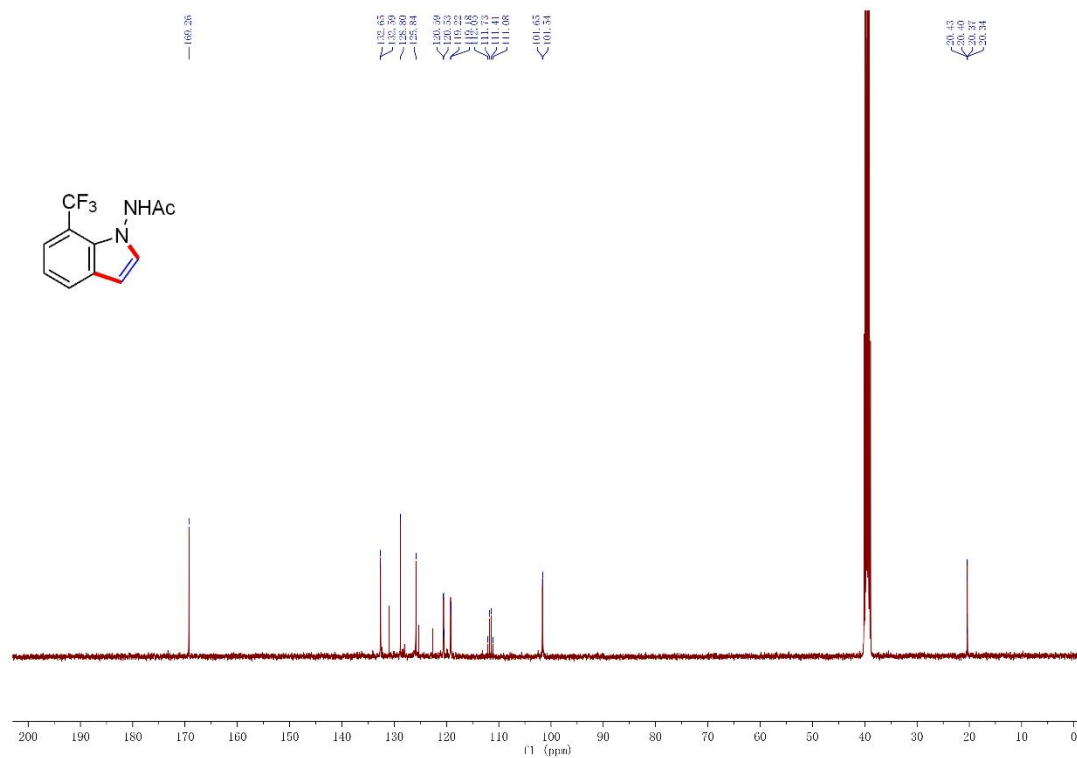
^1H NMR spectrum of compound **3oa**

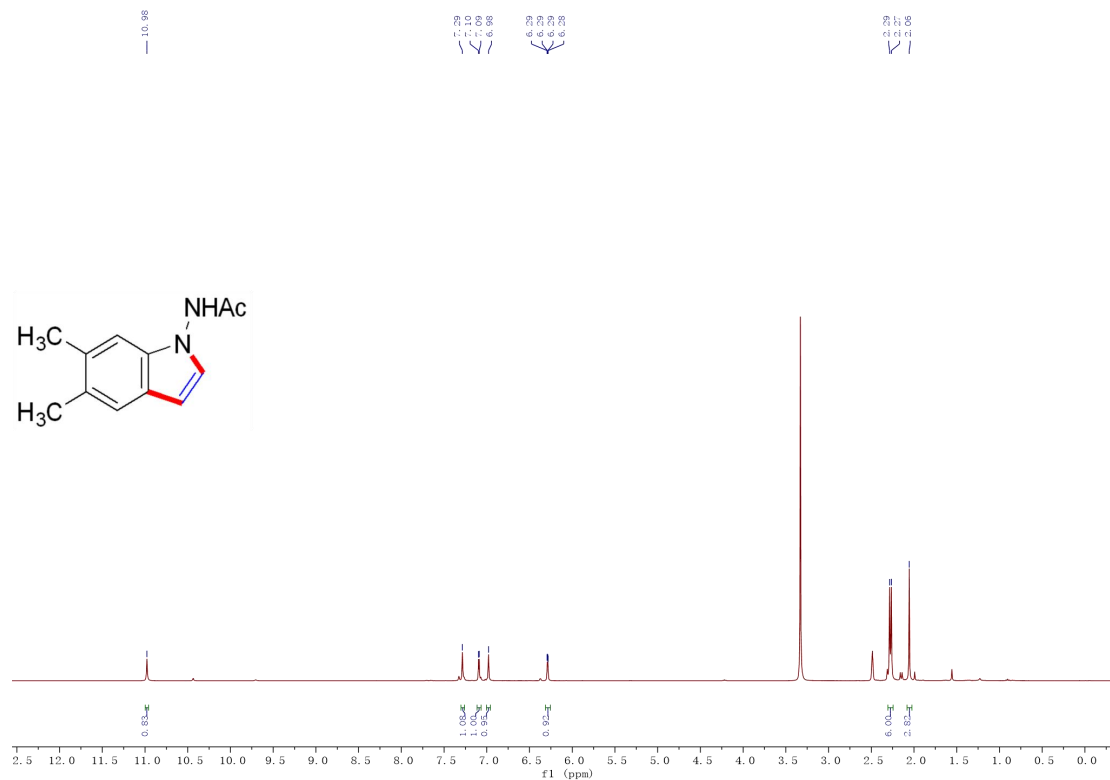


^{13}C NMR spectrum of compound **30a**

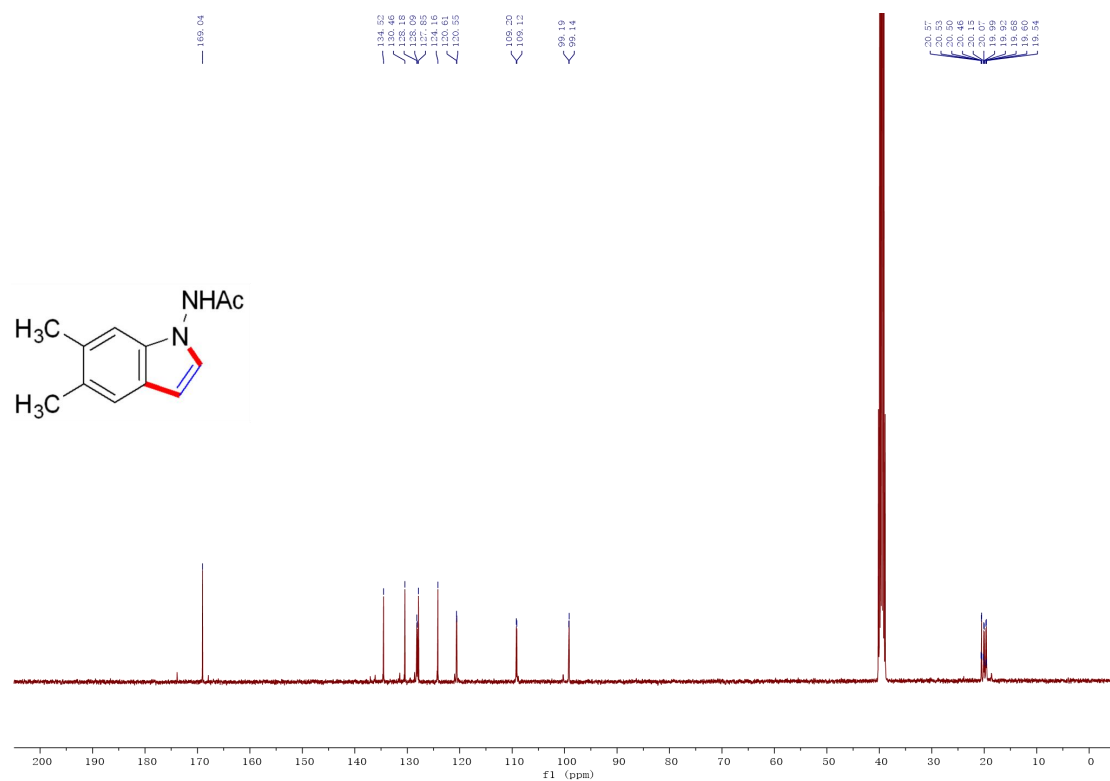


^1H NMR spectrum of compound **30a**

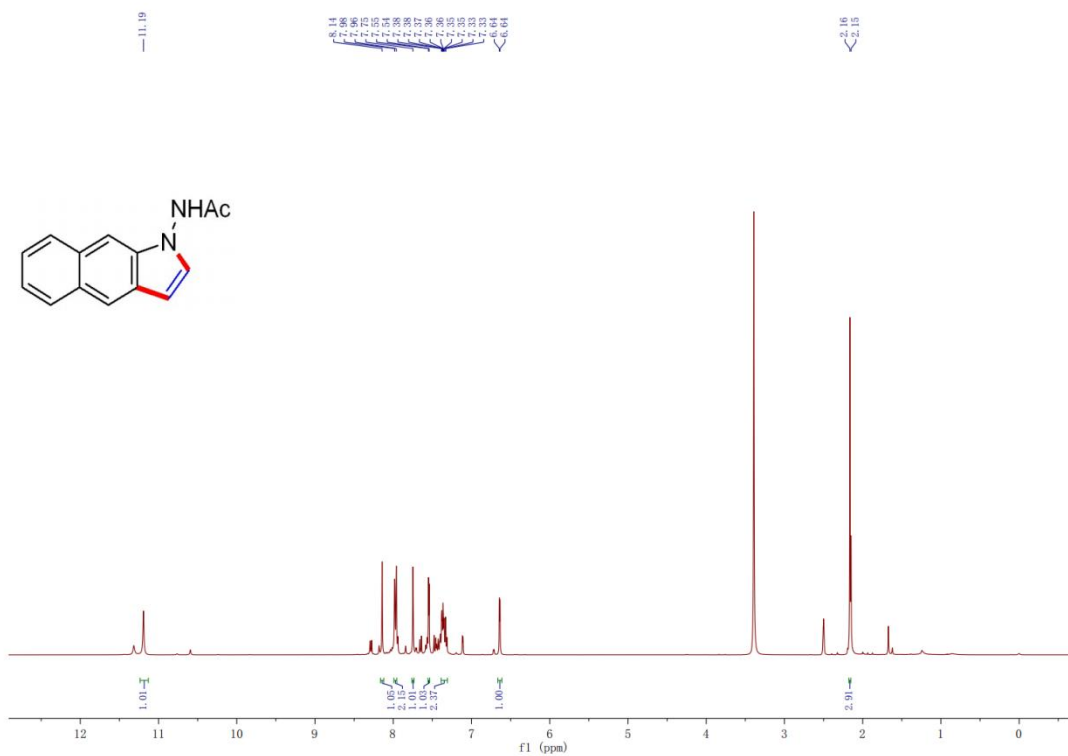




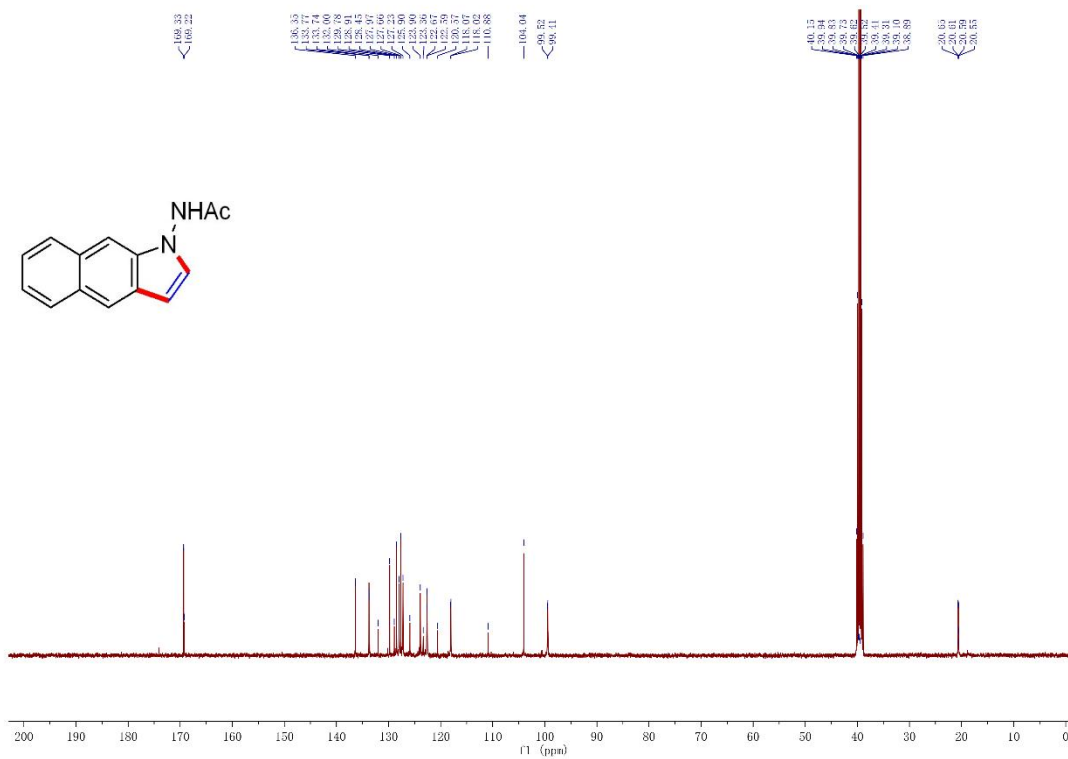
¹H NMR spectrum of compound 3qa



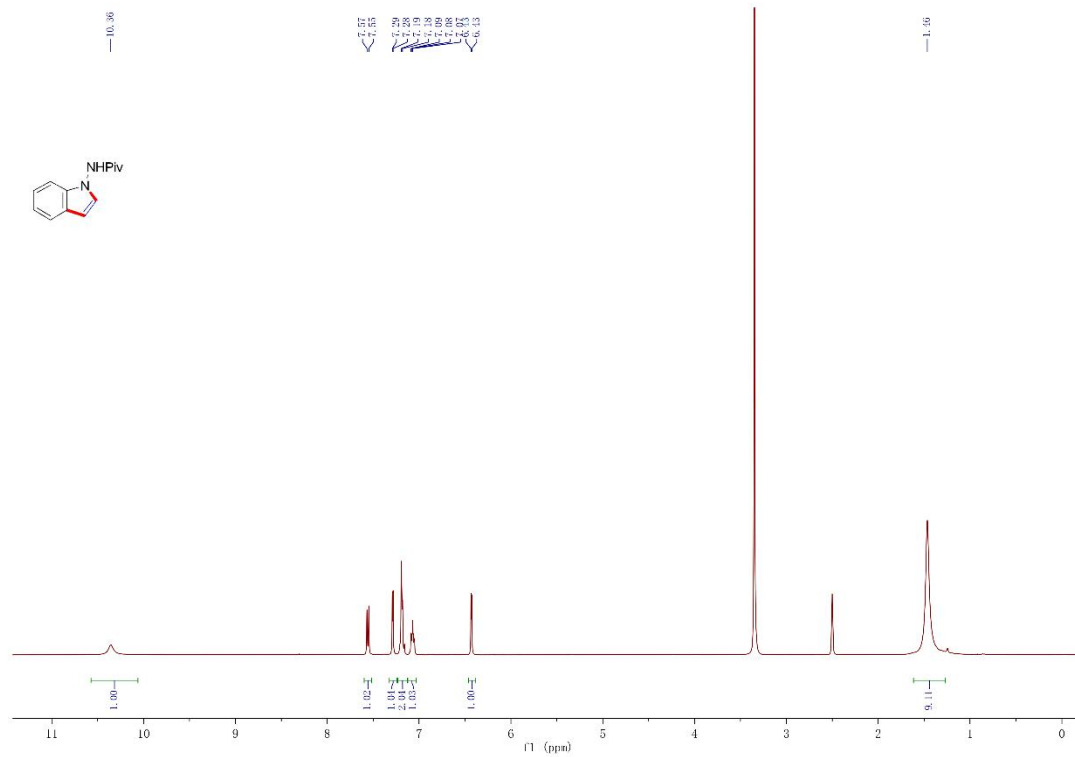
¹³C NMR spectrum of compound 3qa



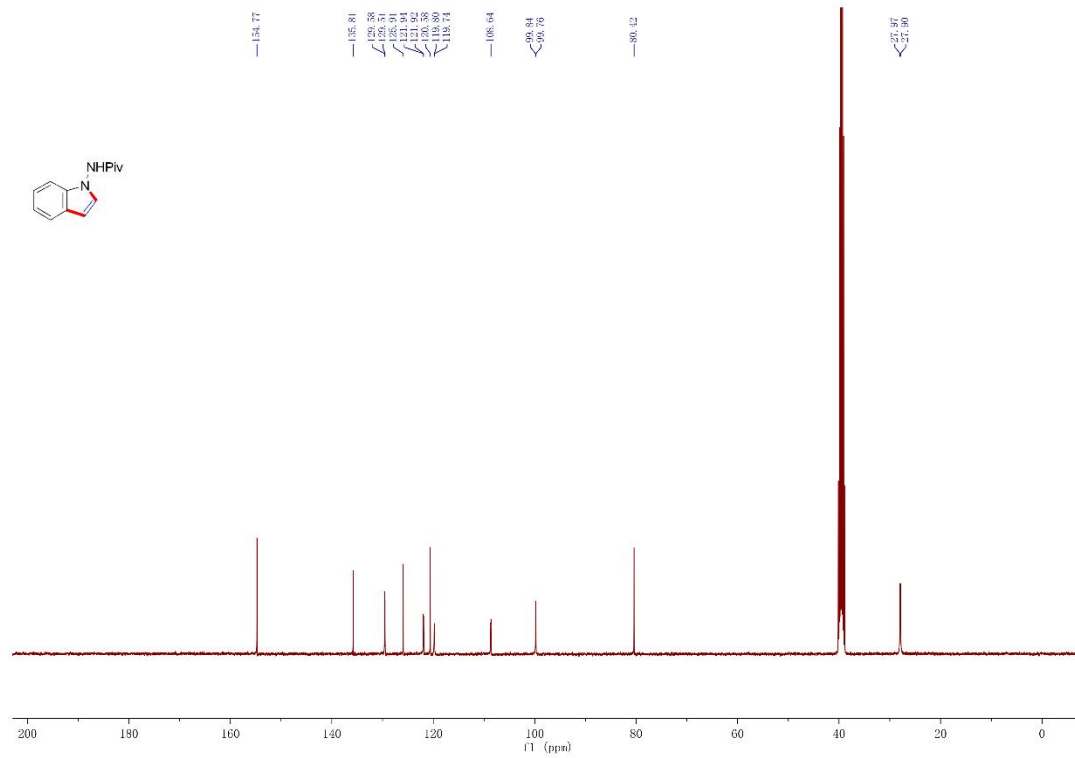
¹H NMR spectrum of compound 3sa



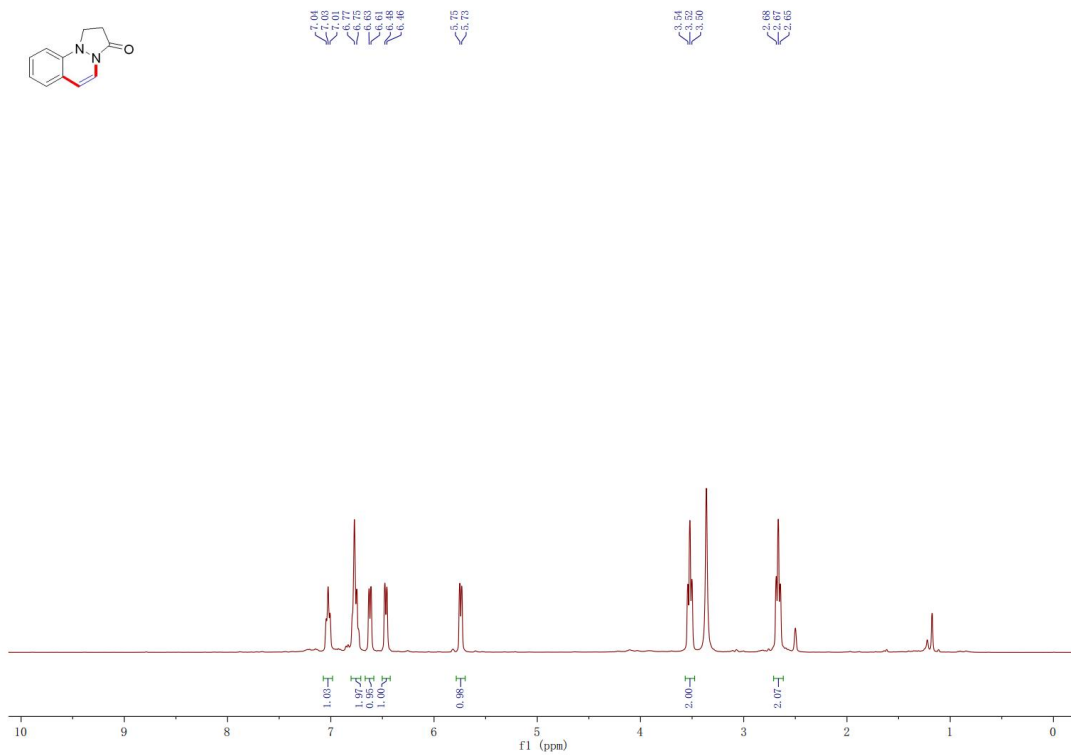
¹³C NMR spectrum of compound 3sa



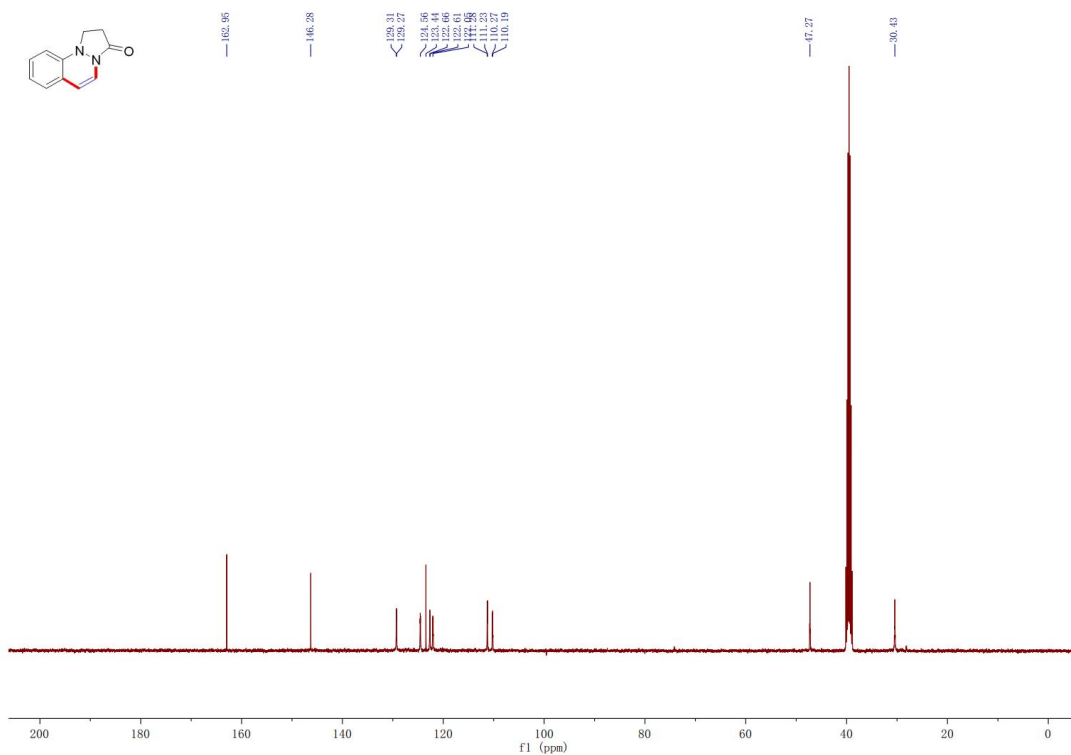
¹H NMR spectrum of compound **3ta**



¹³C NMR spectrum of compound **3ta**



¹H NMR spectrum of compound 3va



¹³C NMR spectrum of compound 3va

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