# Supporting Information

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

Yichun Chen,[a]† Ziqi Lu,[a]† Wenfen He,[a] Huanyi Zhu,[a] WeiLong Lu,[a] Junjun Shi,[a] Jie Sheng,[a] Wucheng Xie*[a]

*† Y. Chen and Z. Lu contributed to this work equally.*

[a] *School of Environment and Chemical Engineering, Foshan University, Foshan 528000, China*

Phone/Fax: +86 (0757) 82781287, E-mail: wuchengxie@fosu.edu.cn

## Experimental Section

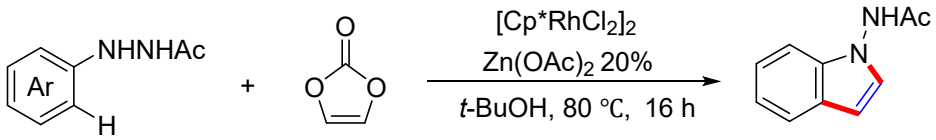
### General Information:

All the reactions were carried out under $N_2$ atmosphere using standard Schlenk technique. $^1$H NMR (400 MHz), $^{19}$F (376 M Hz) and $^{13}$C NMR (101 MHz) were recorded on a NMR spectrometer with DMSO-$d_6$ as solvent. Chemical shifts of $^1$H, $^{19}$F and $^{13}$C 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 $RhCl_3 \cdot xH_2O$ following a literature procedure.[1] $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ 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**



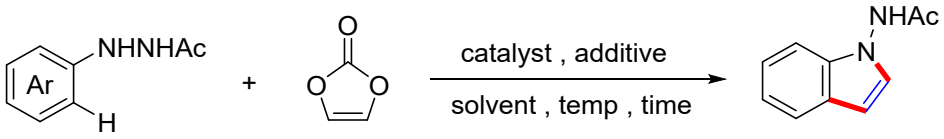

**1** **2** **3**

A mixture of **1** (0.2 mmol), **2** (0.4 mmol, 2 equiv), $[Cp^*RhCl_2]_2$ (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℃ 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), $[Cp^*RhCl_2]_2$ (185.4 mg, 0.3 mmol, 5.0 mol%), and $Zn(OAc)_2$ (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℃ 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:



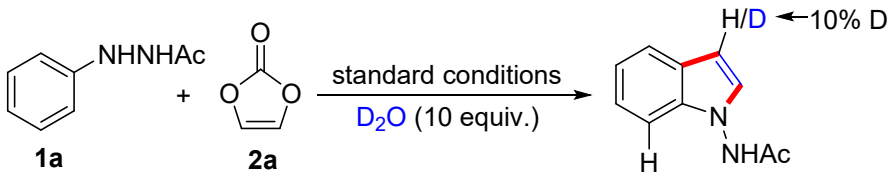

**1a** **2a** **3aa**

| 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 | $[p$-CymeneRu$Cl_2]_2$ | $Zn(OAc)_2$(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) | *t*-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) | $CH_3OH$ | 80 | 16 | nd |
| 17 | $[Cp^*RhCl_2]_2$(5.0) | $Zn(OAc)_2$(20) | *t*-BuOH | 60 | 16 | 66 |
| 18 | $[Cp^*RhCl_2]_2$(5.0) | $Zn(OAc)_2$(20) | *t*-BuOH | 100 | 16 | 80 |
| 19 | $[Cp^*RhCl_2]_2$(5.0) | $Zn(OAc)_2$(20) | *t*-BuOH | 80 | 12 | 90 |
| 20 | $[Cp^*RhCl_2]_2$(5.0) | $Zn(OAc)_2$(20) | *t*-BuOH | 80 | 20 | 90 |

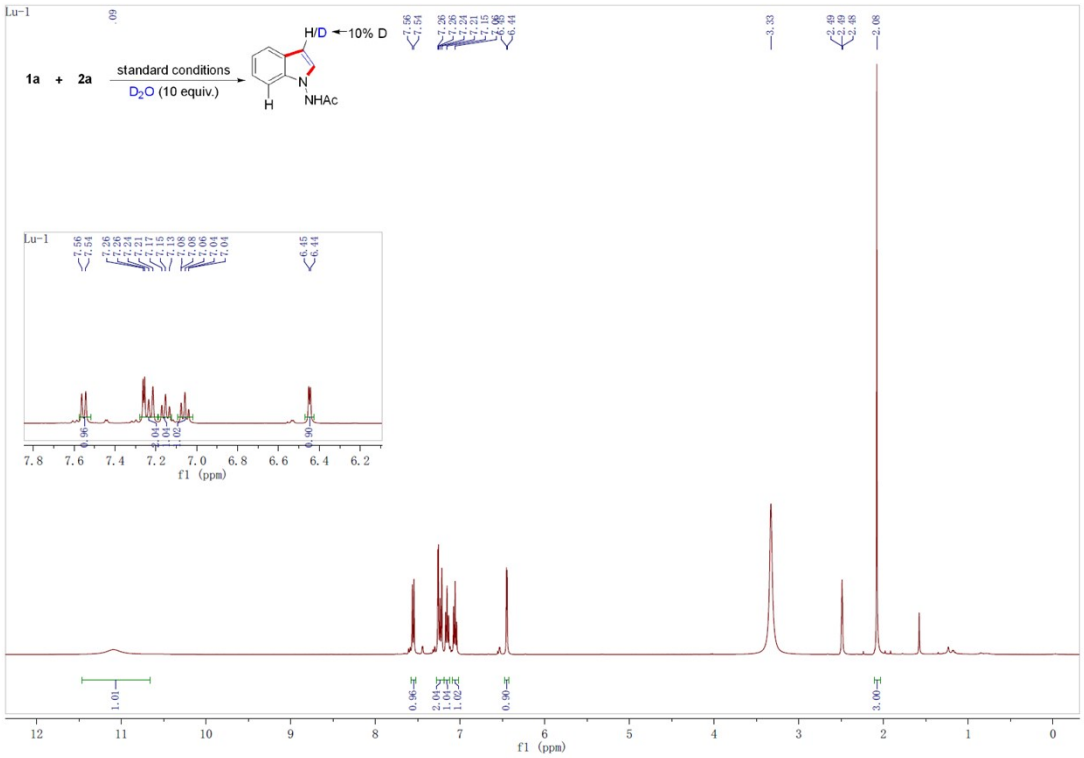
[a] Reaction conditions: **1a**(0.2mmol), 2(0.4mmol), solvent (2 mL).

[b] Isolated yield.

**H/D Exchange Experiments:**

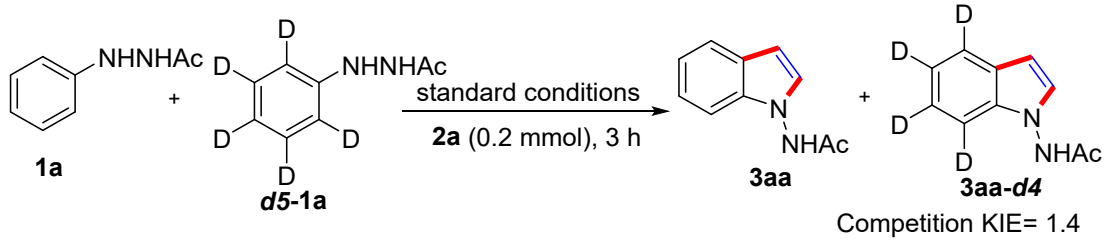



**Procedure for the reaction in the presence of 2a:** A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), vinylene carbonate **2a** (0.4 mmol, 2 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5.0 mol%), and $Zn(OAc)_2$ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) and $D_2O$ (2.0 mmol, 10.0 equiv) 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 residue was purified by flash column chromatography on silica gel (eluent: EA:PE=1:2) to give the product **3aa** (18.7 mg).




$^1$H NMR of the product **3aa** for the H/D exchange reaction in presence of **2a**

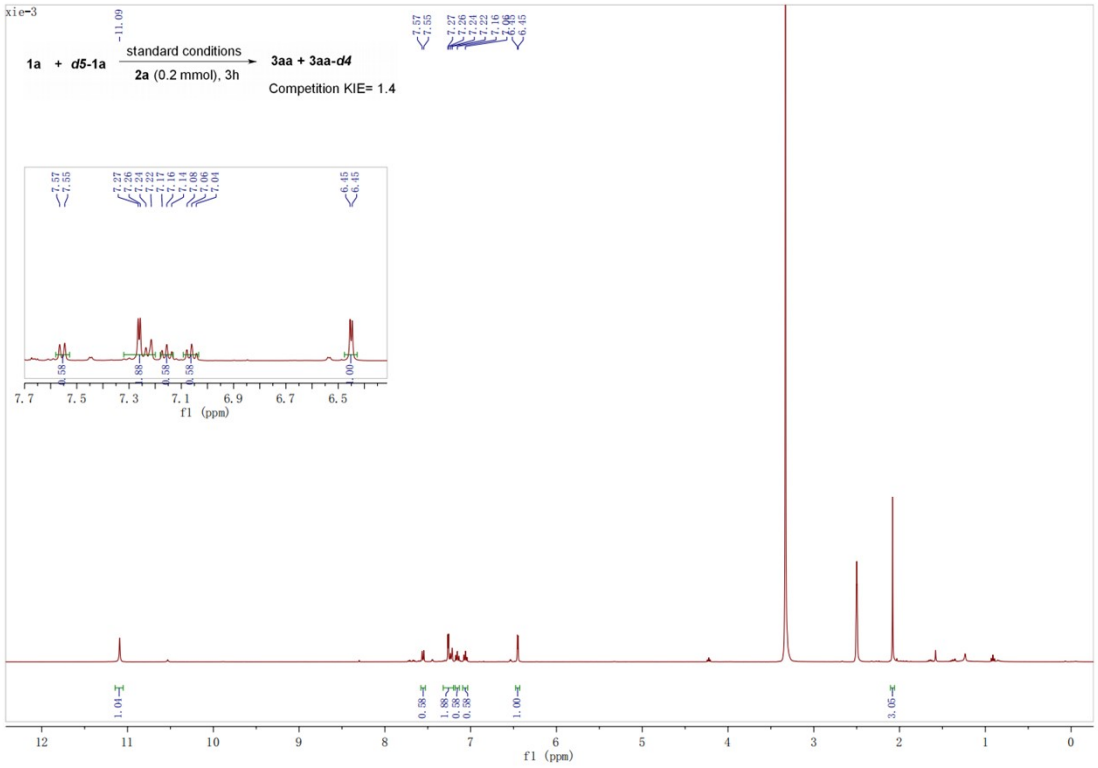
**Competition KIE Experiment:**




**1a** ***d5*-1a** **3aa** **3aa-*d4***

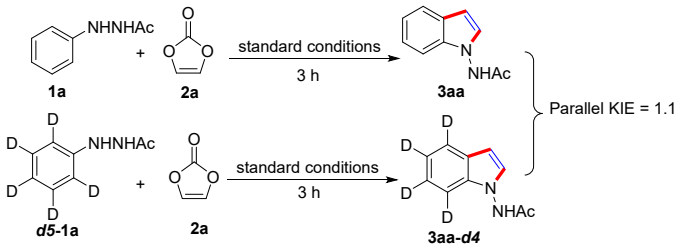
Competition KIE= 1.4

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), $[Cp^*RhCl_2]_2$ (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℃ for 3 h under $N_2$ 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 $^1$H NMR analysis.

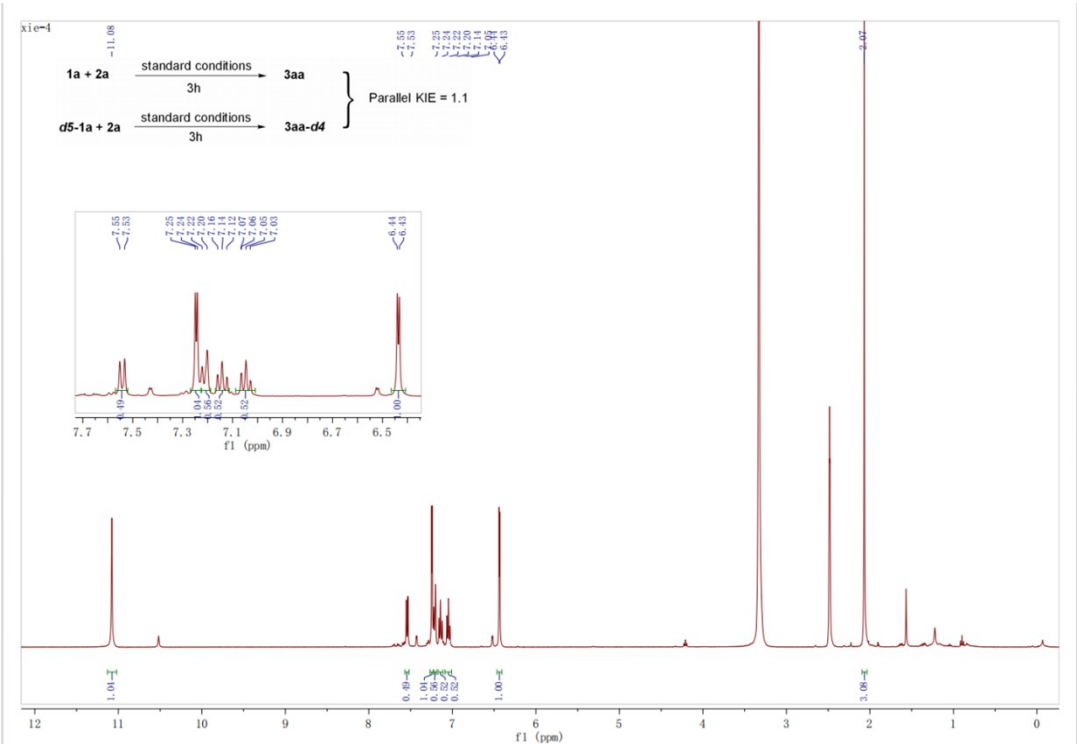



$^1$H NMR of product **3aa** and ***d4*-3aa** obtained from the competition KIE experiment

**Parallel KIE Experiment:**

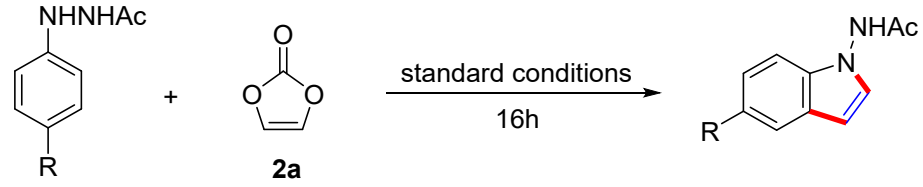



A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), vinylene carbonate **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Zn(OAc)_2$ (7.3 mg) and *t*-BuOH (2.0 mL) were charged into Schlenk tube. To another tube **1a-*d5*** (0.2 mmol), vinylene carbonate **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (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 $N_2$ 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 $^1$H NMR analysis.



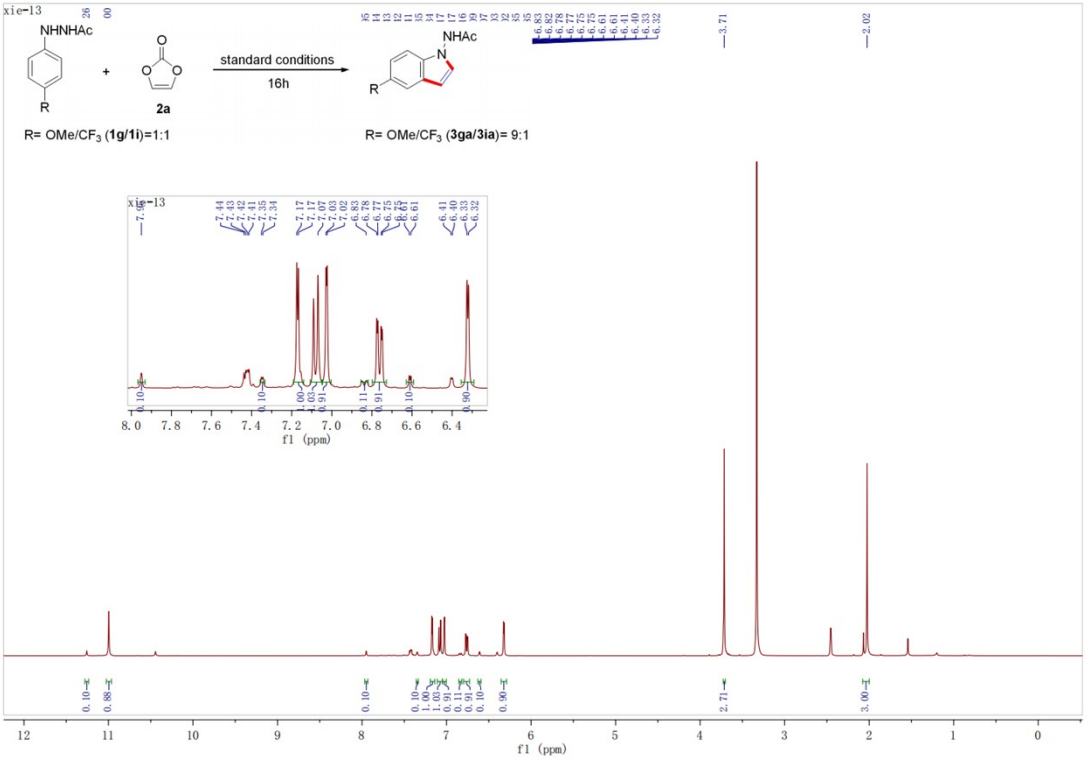

$^1$H NMR of product **3aa** and ***d4*-3aa** obtained from the parallel KIE experiment

**Competition Experiment:**



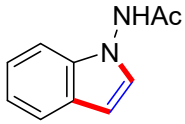

R= OMe/$CF_3$ (**1g/1i**)=1:1 R= OMe/$CF_3$ (**3ga/3ia**)= 9:1

A mixture of *N*′-(4-methoxyphenyl)acetohydrazide **1g** (0.2 mmol, 1.0 equiv.), *N*′-(4-(trifluoromethyl)phenyl)acetohydrazide **1i** (0.2 mmol, 1.0 equiv.), vinylene carbonate **2a** (0.4 mmol, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (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 16 h under $N_2$ 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 with EtOAc/petroleum ether to give a mixture of products **3ga** and **3ia** at a ratio of 0.91:0.10 = 9:1.

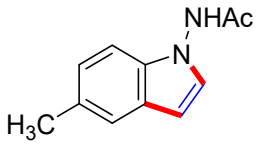



$^1$H NMR of products **3ga** and **3ia** obtained from the competition experiment

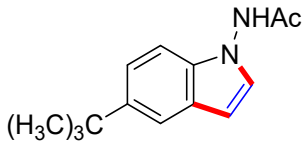
**Characterization of Products:**




N-***(1H-indol-1-yl)acetamide (3aa)***: white crystalline solid (32.9 mg, 94%); M.p.:135-136 ℃. IR ($cm^{-1}$): *v* 3252, 1678, 1528, 1265, 1221, 741. $^{1}H$ 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); $^{13}C$ 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 $C_{10}H_{10}N_2O$ $[M+Na]^+$ 197.0685, Found 197.0693.

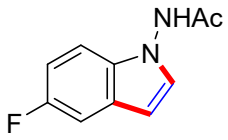



***N-(5-methyl-1H-indol-1-yl)acetamide (3ba)***: white solid (26.8 mg, 71%); M.P.:137-139 ℃. IR ($cm^{-1}$): *v* 3240, 3026, 1682, 1530, 1265, 719. $^{1}H$ NMR (400 MHz, DMSO-d6): δ 11.06 (s, 1H), 7.35 (s, 1H), 7.21 (d, J = 3.4 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 7.00 (dd, J = 8.3, 1.6 Hz, 1H), 6.39 – 6.34 (m, 1H), 2.39 (s, 3H), 2.09 (s, 3H); $^{13}C$ 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 $C_{11}H_{13}N_2O$ $[M+H]^+$ 189.1022, Found 189.1025.

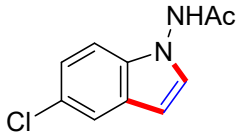



***N-(5-(tert-butyl)-1H-indol-1-yl)acetamide (3ca):*** pale brown solid (36.7 mg, 80%); M.p.:190.5-191.2 ℃. IR($cm^{-1}$): *v* 3246, 2959, 1688, 1528, 1273, 876. $^{1}H$ NMR (400

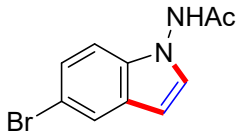
MHz, DMSO-d6): δ 11.01 (s, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.24 – 7.05 (m, 3H), 6.35 (d, J = 3.3 Hz, 1H), 2.02 (s, 3H), 1.29 (s, 9H); $^{13}$C NMR (101 MHz, DMSO): δ 169.14, 142.22, 133.83, 129.05 (d, J = 8.2 Hz), 125.72, 120.01 (d, J = 3.2 Hz), 116.27 (d, J = 2.1 Hz), 108.66 – 108.26 (m), 99.97 (d, J = 7.5 Hz), 34.22, 31.80 (q, J = 7.3 Hz), 20.52 (q, J = 4.4 Hz). HRMS(ESI): Calcd for $C_{14}H_{19}N_2O$ $[M+H]^+$ 231.1492, Found 1231.1497.



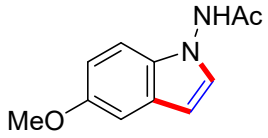

***N-(5-fluoro-1H-indol-1-yl)acetamide (3da):*** brown crystalline solid (29.6 mg, 68%); M.p.:116.5-117.5 ℃. IR(cm$^{-1}$): *v* 3203, 1684, 1547, 1373, 1225, 856. $^1$H NMR (400 MHz, DMSO-d6): δ 11.07 (s, 1H), 7.29 – 7.23 (m, 2H), 7.16 (dd, J = 8.9, 4.5 Hz, 1H), 6.93 (td, J = 9.2, 2.5 Hz, 1H), 6.38 (d, J = 3.3 Hz, 1H), 2.01 (s, 3H); $^{13}$C 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); $^{19}$F NMR (376 MHz, DMSO): δ -124.54. HRMS(ESI): Calcd for $C_{10}H_{10}FN_2O$ $[M+H]^+$ 193.0772, Found 193.0784.



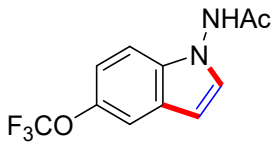

***N-(5-chloro-1H-indol-1-yl)acetamide (3ea)***: pale yellow crystalline solid (32.2 mg, 77%); M.p.:139-141 ℃. IR (cm$^{-1}$): *v* 3244 1672 1524 1464 708. $^1$H NMR (400 MHz, DMSO-d6): δ 11.18 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 3.4 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 7.18 (dd, J = 8.7, 2.0 Hz, 1H), 6.49 – 6.45 (m, 1H), 2.09 (s, 3H); $^{13}$C 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 $C_{10}H_9ClN_2O$ $[M+Na]^+$ 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($cm^{-1}$): *v* 3233, 1684, 1530, 1458, 798. $^{1}H$ NMR (400 MHz, DMSO-d6): 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 $C_{10}H_9BrN_2O$ $[M+Na]^+$ 274.9790, Found 274.9799.

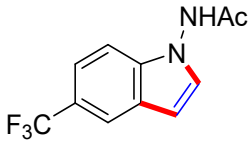



***N-(5-methoxy-1H-indol-1-yl)acetamide (3ga)***: pale yellow solid (26.8 mg, 66%); M.p.:106-107 °C. IR($cm^{-1}$): *v* 3265, 1674, 1477, 1240, 806. $^{1}H$ NMR (400 MHz, DMSO-d6): δ 11.05 (s, 1H), 7.23 (d, J = 3.3 Hz, 1H), 7.14 (d, J = 8.9 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 6.82 (dd, J = 8.8, 2.4 Hz, 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 $C_{11}H_{12}N_2O_2$ $[M+Na]^+$ 227.0791, Found 227.0801.

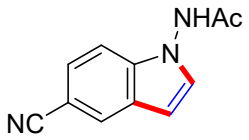



***N-(5-(trifluoromethoxy)-1H-indol-1-yl)acetamide (3ha)***: pale yellow solid (43.4 mg, 84%); M.p.:145-147 °C. IR($cm^{-1}$): *v* 3026, 1680, 1284, 1159, 880. $^{1}H$ NMR (400 MHz, DMSO-d6): δ 11.24 (s, 1H), 7.60 – 7.57 (m, 1H), 7.43 (d, J = 3.4 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.18 – 7.13 (m, 1H), 6.56 (d, J = 3.4 Hz, 1H), 2.11 (s, 3H); $^{13}C$ NMR (101

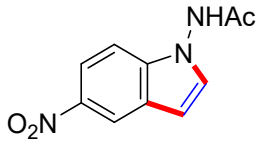
MHz, DMSO): δ 169.25, 142.47 (q, J = 1.9 Hz), 134.06, 131.43 (d, J = 4.9 Hz), 126.07, 121.74, 115.58 (d, J = 6.8 Hz), 112.96, 110.18 (t, J = 2.7 Hz), 100.43 (d, J = 9.7 Hz), 20.48 (q, J = 4.8 Hz); $^{19}$F NMR (376 MHz, DMSO): δ -57.08. HRMS(ESI): Calcd for $C_{11}H_9F_3N_2O_2$ $[M+Na]^+$ 281.0508, Found 281.0513.



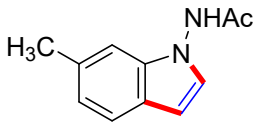

***N-(5-(trifluoromethyl)-1H-indol-1-yl)acetamide (3ia)***: pale yellow solid (42.6 mg, 88%); M.p.:168-170 °C. IR($cm^{-1}$): *v* 3020, 1680, 1109, 901, 814, 733. $^1$H NMR (400 MHz, DMSO-d6): δ 11.30 (s, 1H), 7.99 (s, 1H), 7.50 – 7.43 (m, 3H), 6.65 (d, J = 3.4 Hz, 1H), 2.12 (s, 3H); $^{13}$C NMR (101 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); $^{19}$F NMR (376 MHz, DMSO): δ -58.64. HRMS(ESI): Calcd for $C_{11}H_{10}F_3N_2O$ $[M+H]^+$ 243.0740, Found 243.0751.



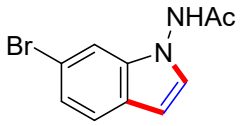

***N-(5-cyano-1H-indol-1-yl)acetamide (3ja)***: pale yellow solid (30.0 mg, 75%); M.p.:157-158 °C. IR($cm^{-1}$): *v* 3244, 2222, 1668, 1520, 806, 577. $^1$H NMR (400 MHz, DMSO-d6): δ 11.33 (s, 1H), 8.13 (d, J = 1.6 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 (d, J = 8.5 Hz, 1H), 6.66 – 6.62 (m, 1H), 2.12 (s, 3H); $^{13}$C 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 $C_{11}H_{10}N_3O$ $[M+H]^+$ 200.0818, Found 200.0821.



***N-(5-nitro-1H-indol-1-yl)acetamide (3ka)***: pale yellow solid (25.4 mg, 58%); M.p.:189-191 ℃. IR($cm^{-1}$): *v* 3246, 1672, 1514, 1339, 741. $^{1}H$ NMR (400 MHz, DMSO-d6): 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 $C_{10}H_9N_3O_3$ $[M+Na]^+$ 242.0536, Found 242.0545.

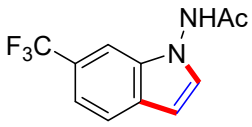



***N-(6-methyl-1H-indol-1-yl)acetamide (3la)***: pale yellow solid (28.4 mg, 75%); M.p.:141-142 ℃. IR($cm^{-1}$): *v* 3564, 2351, 1682, 1456, 1269, 802. $^{1}H$ NMR (400 MHz, DMSO-d6): δ 11.05 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 3.3 Hz, 1H), 7.05 (s, 1H), 6.92 (dd, J = 8.0, 1.5 Hz, 1H), 6.40 (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 $C_{11}H_{13}N_2O$ $[M+H]^+$ 189.1022, Found 189.1025.

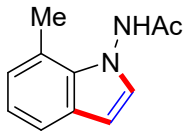



***N-(6-bromo-1H-indol-1-yl)acetamide (3ma)***: pale yellow solid (40.6 mg, 80%); M.p.:181-183 ℃. IR($cm^{-1}$): *v* 3242, 2318, 1682, 1267, 891, 719. $^{1}H$ NMR (400 MHz, DMSO-d6): δ 11.17 (s, 1H), 7.56 – 7.47 (m, 2H), 7.32 (d, J = 3.4 Hz, 1H), 7.22 (dd, J = 8.4, 1.8 Hz, 1H), 6.51 (dd, J = 3.3, 1.0 Hz, 1H), 2.11 (s, 3H); $^{13}C$ 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,

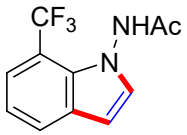
114.91, 111.77 (d, J = 3.4 Hz), 100.28 (d, J = 9.2 Hz), 20.56 (q, J = 4.8 Hz). HRMS(ESI): Calcd for $C_{10}H_9BrN_2O$ $[M+Na]^+$ 274.9790, Found 274.9797.



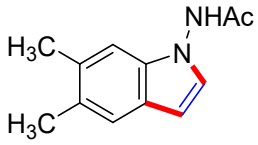

***N-(6-(trifluoromethyl)-1H-indol-1-yl)acetamide (3na)***: pale yellow solid (23.4 mg, 48%); M.p.:191-193 ℃. IR ($cm^{-1}$): *v* 3250, 1686, 1458, 1275, 1115, 729. $^1H$ NMR (400 MHz, DMSO-d6): δ 11.28 (s, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.55 (d, J = 3.3 Hz, 1H), 7.38 (dd, J = 8.3, 1.7 Hz, 1H), 6.66 – 6.55 (m, 1H), 2.13 (s, 3H); $^{13}C$ 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); $^{19}F$ NMR (376 MHz, DMSO): δ -58.94. HRMS(ESI): Calcd for $C_{11}H_9F_3N_2O$ $[M+Na]^+$ 265.0559, Found 265.0565.



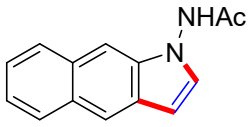

***N-(7-methyl-1H-indol-1-yl)acetamide (3oa)***: orange solid (24.3 mg, 64%); M.p.:130-132 ℃. IR($cm^{-1}$): *v* 3238, 1682, 1524, 1265, 897, 785. $^1H$ NMR (400 MHz, DMSO-d6) δ 11.20 (s, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.15 (d, J = 3.4 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.1 Hz, 1H), 6.42 (d, J = 3.4 Hz, 1H), 2.47 (s, 3H), 2.04 (s, 3H); $^{13}C$ 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 $C_{11}H_{13}N_2O$ $[M+H]^+$ 189.1022, Found 189.1026.



***N-(7-(trifluoromethyl)-1H-indol-1-yl)acetamide (3pa)***: pale yellow solid (12.0 mg, 25%); M.p.:189-191 ℃. IR($cm^{-1}$): *v* 3210, 1684, 1535, 1321, 1115, 725. $^{1}H$ NMR (400 MHz, DMSO-d6): 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 $C_{11}H_{10}F_3N_2O$ $[M+H]^+$ 243.0740, Found 243.0750.

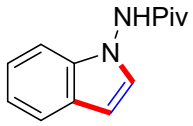



***N-(5,6-dimethyl-1H-indol-1-yl)acetamide (3qa):*** brown solid (16.7 mg, 36%); M.p.:118.9-121.2 ℃. IR($cm^{-1}$): *v* 3232, 3022, 1678, 1369, 1273, 706. $^{13}C$ NMR (101 MHz, DMSO): δ169.04, 134.52, 130.46, 128.13 (d, J = 9.1 Hz), 127.85, 124.16, 120.61, 120.55, 109.16 (d, J = 8.8 Hz), 99.17 (d, J = 5.0 Hz), 20.52 (q, J = 3.8 Hz), 20.03 (q, J = 7.5 Hz), 19.64 (d, J = 7.7 Hz); $^{1}H$ NMR (400 MHz, DMSO-d6): 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 $C_{12}H_{14}N_2O$ $[M+Na]^+$ 225.0998, Found 225.1004.

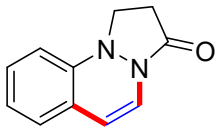



***N-(1H-benzo[f]indol-1-yl)acetamide (3sa, major)***: pale brown solid (39.7 mg, **3sa:3sa'** = 5:1, 88%); M.p.:118-120℃. IR($cm^{-1}$): *v* 3231, 1674, 1371, 1219, 851, 733. $^{1}H$ NMR (400 MHz, DMSO-d6): δ 11.19 (s, 1H), 8.14 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.75 (s, 1H), 7.55 (d, J = 3.5 Hz, 1H), 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 $C_{14}H_{12}N_2O$ $[M+Na]^+$ 247.0842, Found 247.0847.




O-***(1H-indol-1-yl)pivalamide (3ta)***: pale pink solid (25.3 mg, 58%); M.p.:110.7-111.3 °C. IR($cm^{-1}$): *v* 3275, 2978, 1709, 1526, 1267, 1161, 750. $^1H$ NMR (400 MHz, DMSO-d6): 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 $C_{11}H_{10}N_2O$ $[M+Na]^+$ 239.1155, Found 239.1158.




***1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (3va):*** brown solid (15.6 mg, 42%); M.p.: 72.8-74.7 °C. IR($cm^{-1}$): *v* 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 $C_{11}H_{10}N_2O$ $[M+Na]^+$ 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 Kα radiation. The data were collected and processed using CrysAlisPro[4]. The structures were solved by direct methods using Olex2 software[5], and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018[6] 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 | $C_{10}H_{10}N_2O$ |
| 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 |

| | |
|---|---|
| $\rho_{calc}$g/cm$^3$ | 1.261 |
| μ/mm$^{-1}$ | 0.678 |
| F(000) | 736.0 |
| Crystal size/mm$^3$ | 0.14 × 0.12 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.268 to 146.59 |
| Index ranges | -11 ≤ h ≤ 11, -7 ≤ k ≤ 10, -26 ≤ l ≤ 26 |
| Reflections collected | 3227 |
| Independent reflections | 1793 [$R_{int}$ = 0.0185, $R_{sigma}$ = 0.0244] |
| Data/restraints/parameters | 1793/7/119 |
| Goodness-of-fit on F$^2$ | 1.035 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0490, w$R_2$ = 0.1323 |
| Final R indexes [all data] | $R_1$ = 0.0542, w$R_2$ = 0.1388 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.22/-0.25 |

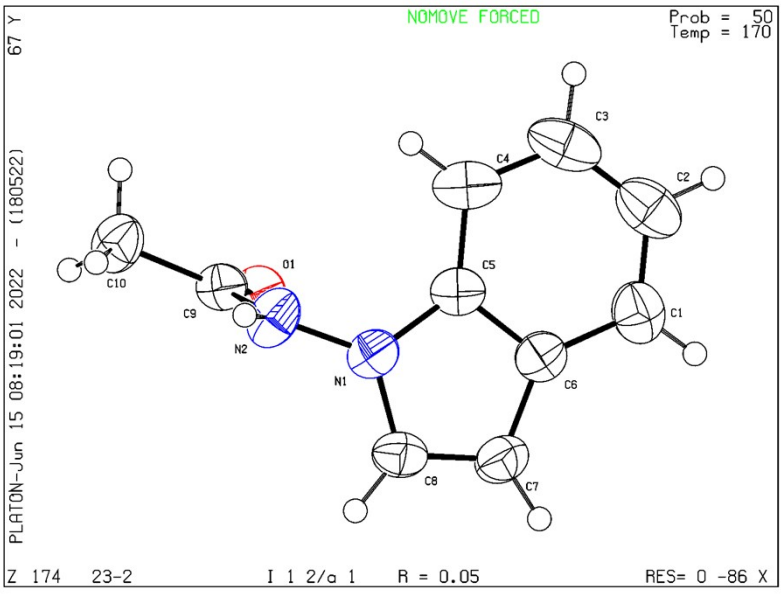
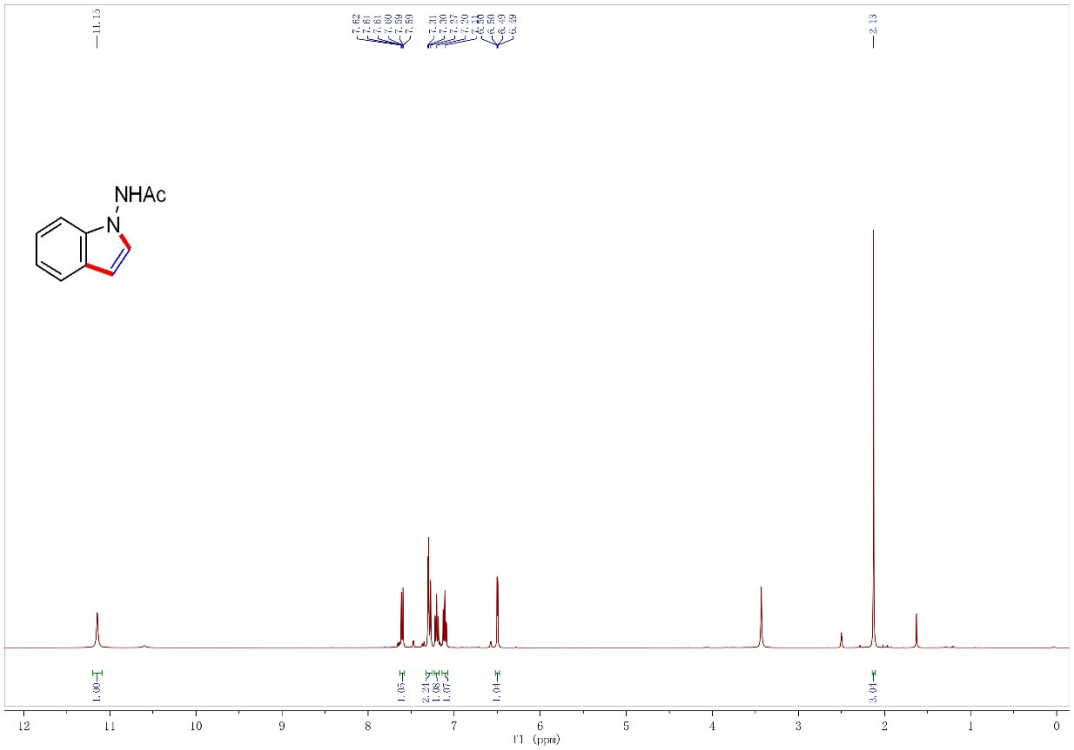
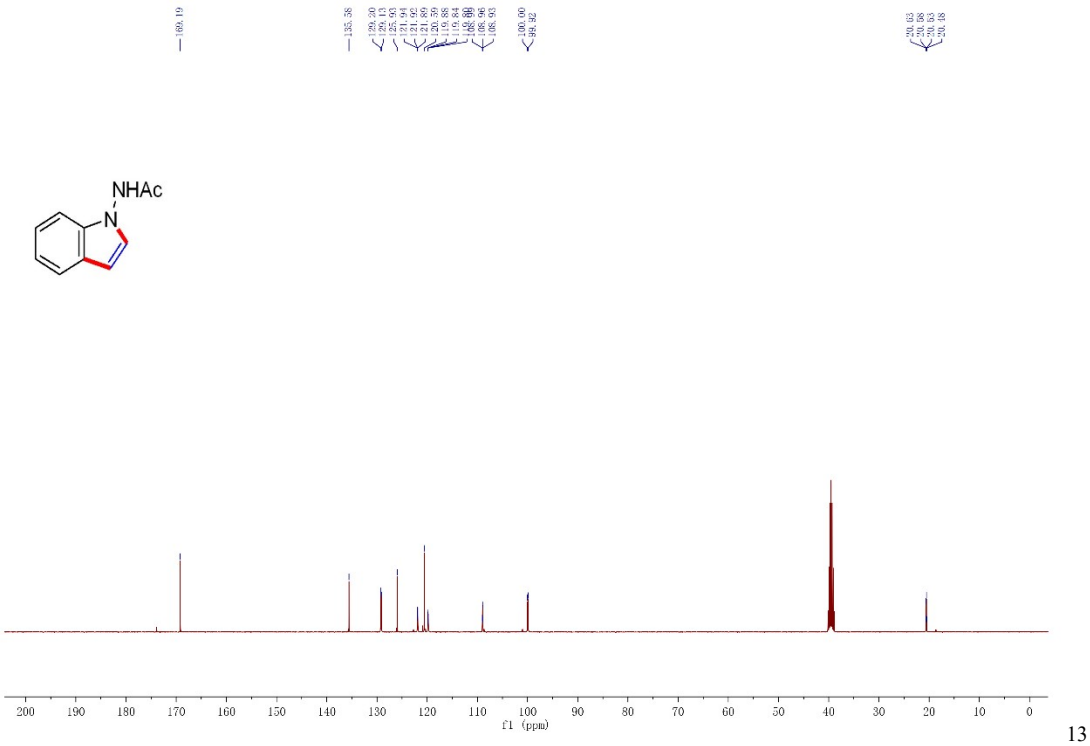



**Figure S1.** The molecular structure of **3aa.**

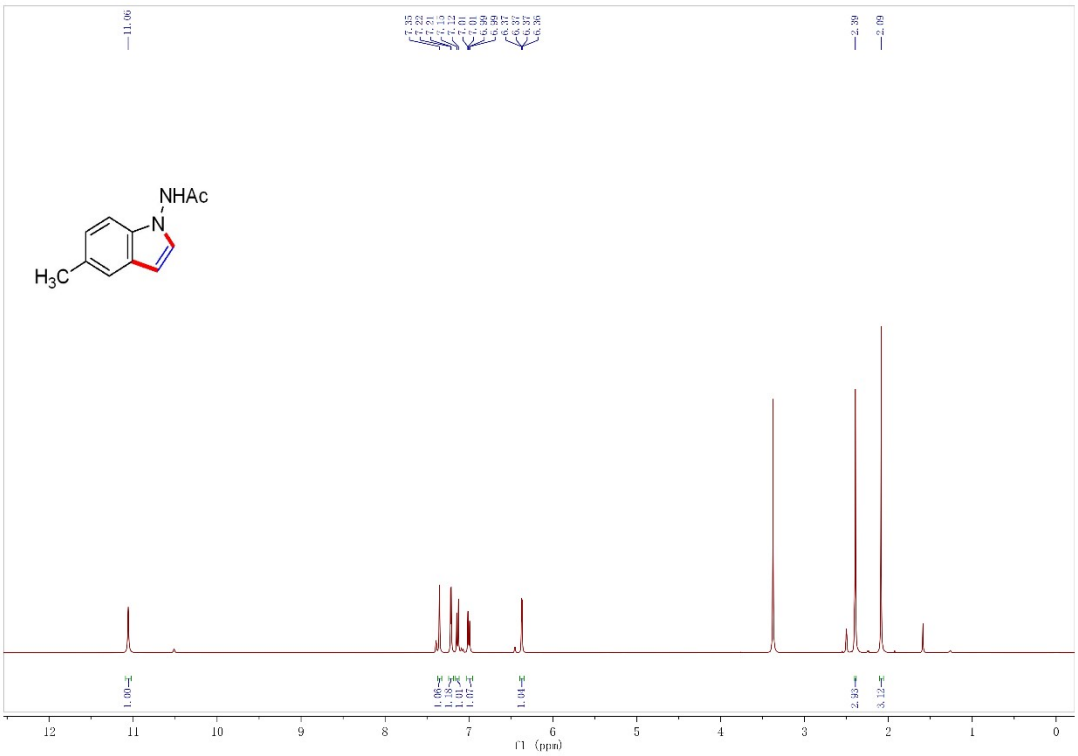
# Spectral Copies of $^{1}H$, $^{13}C$, and $^{19}F$ NMR of Compounds Obtained in This Study



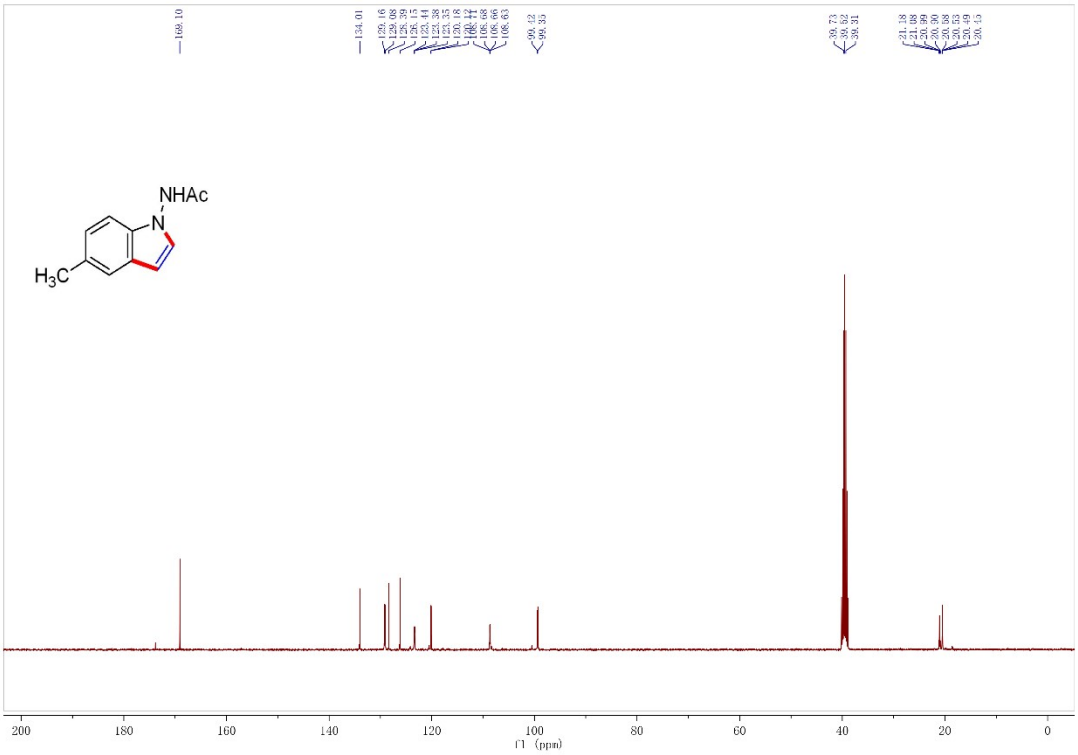

$^{1}$H NMR spectrum of compound **3aa**



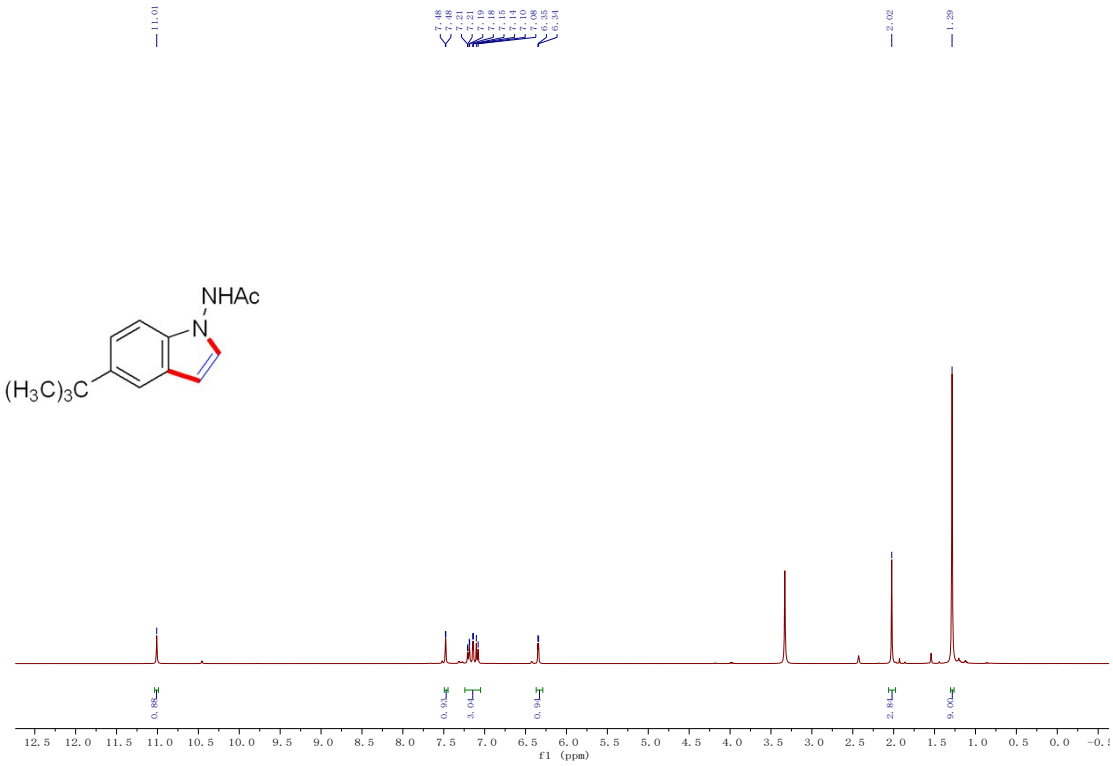

13C NMR spectrum of compound **3aa**



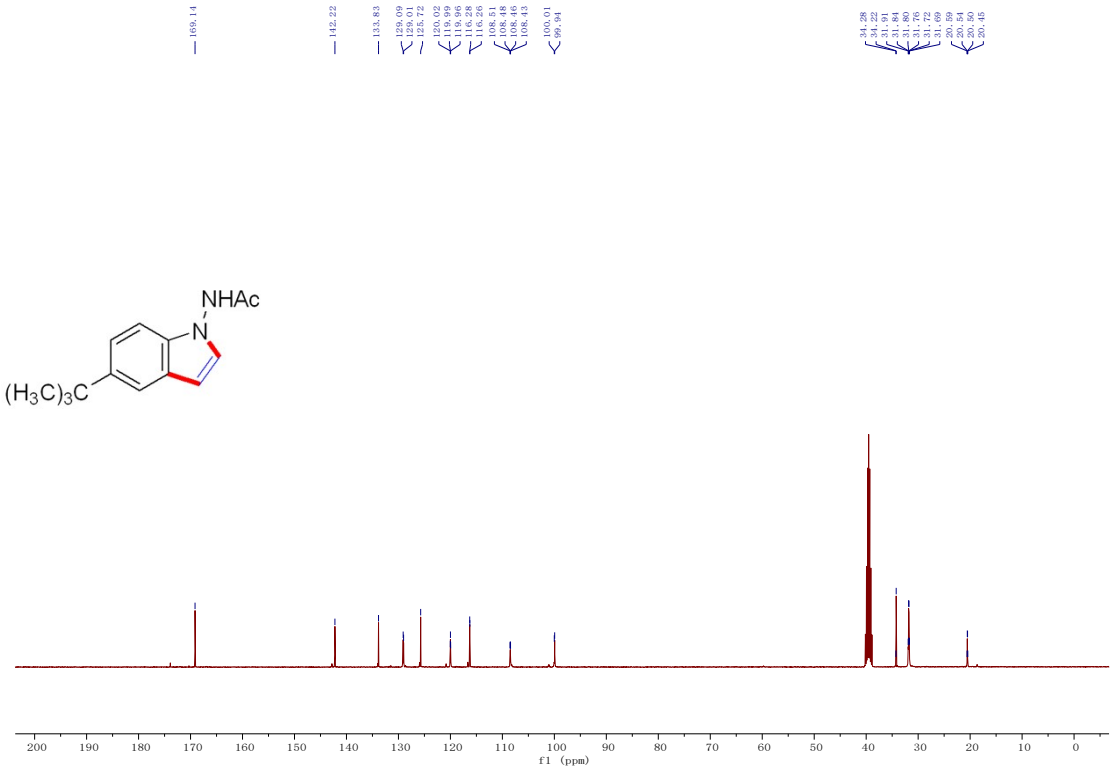

$^{1}$H NMR spectrum of compound **3ba**



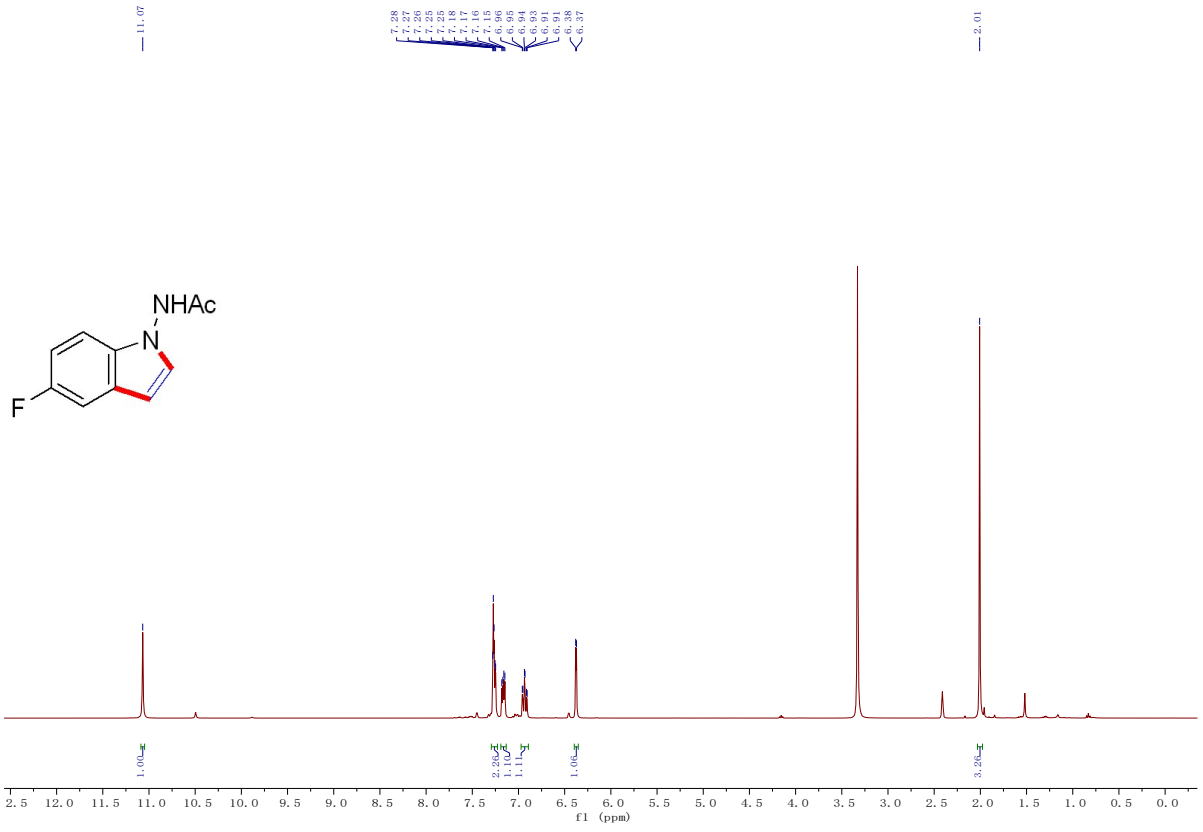

$^{13}$C NMR spectrum of compound **3ba**



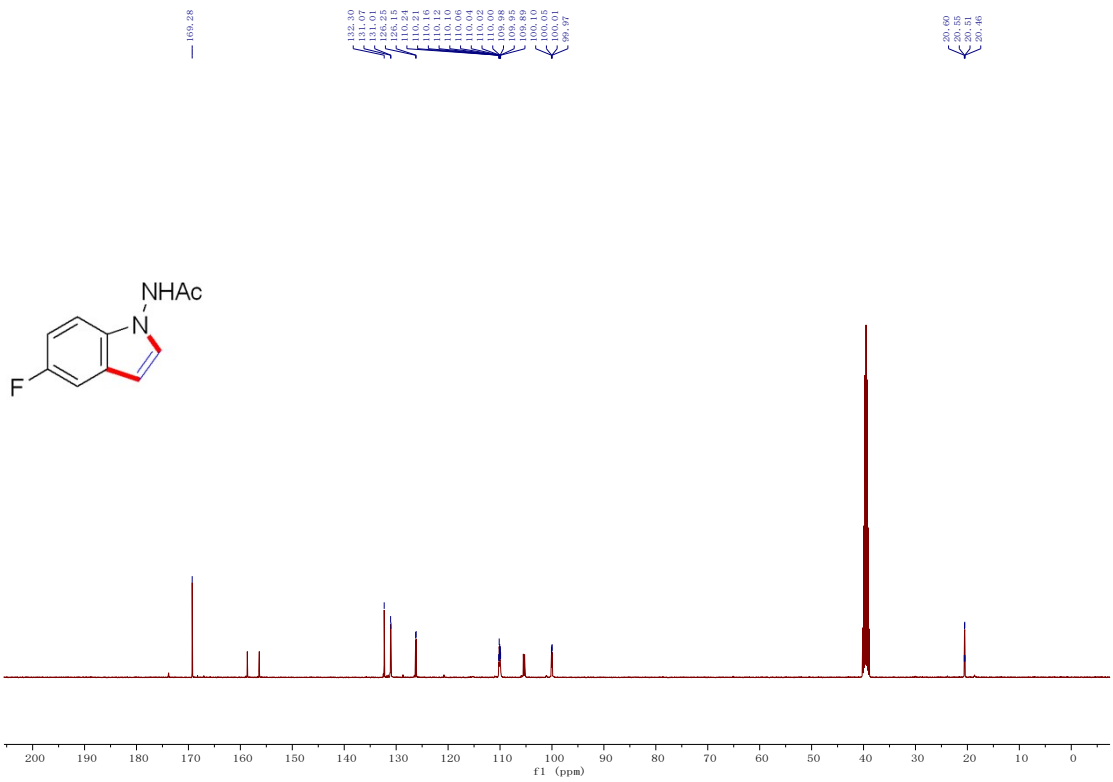

$^{1}$H NMR spectrum of compound **3ca**



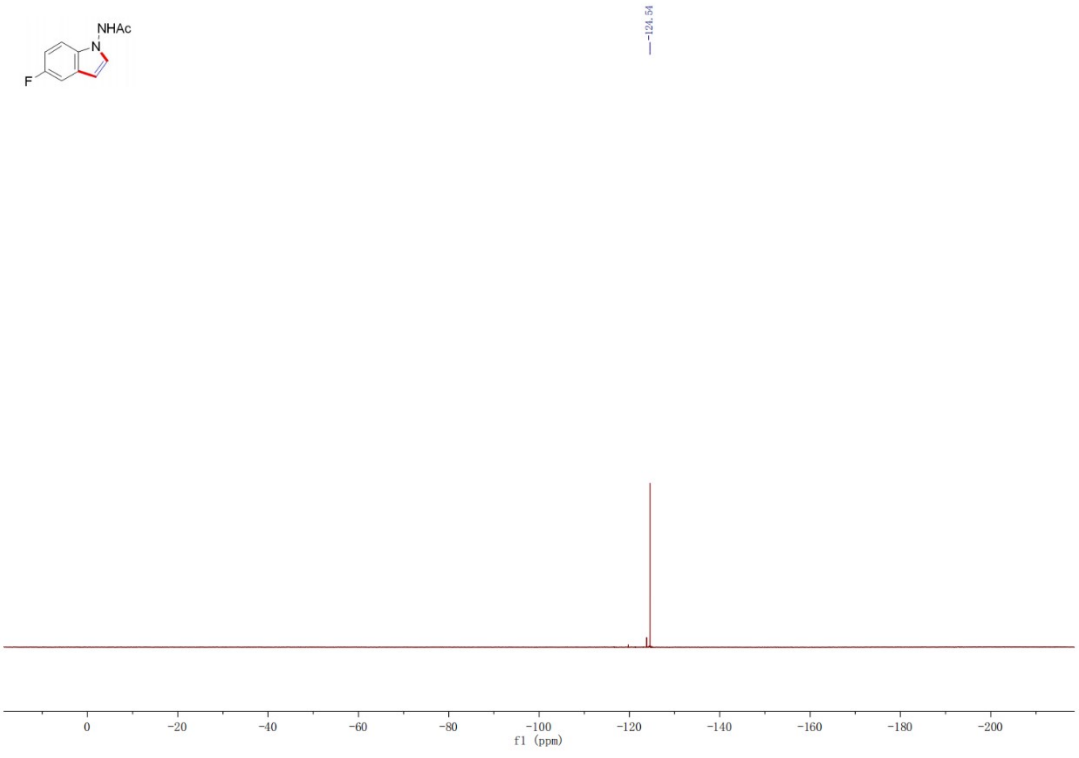

$^{13}$C NMR spectrum of compound **3ca**



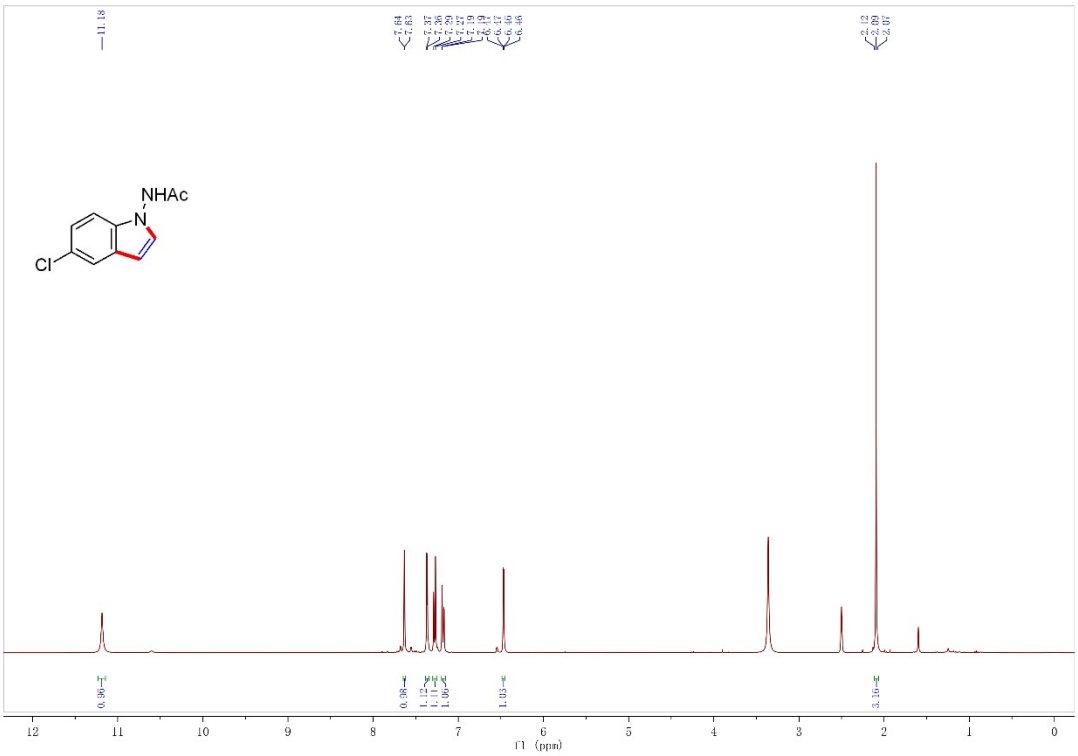

$^1$H NMR spectrum of compound **3da**



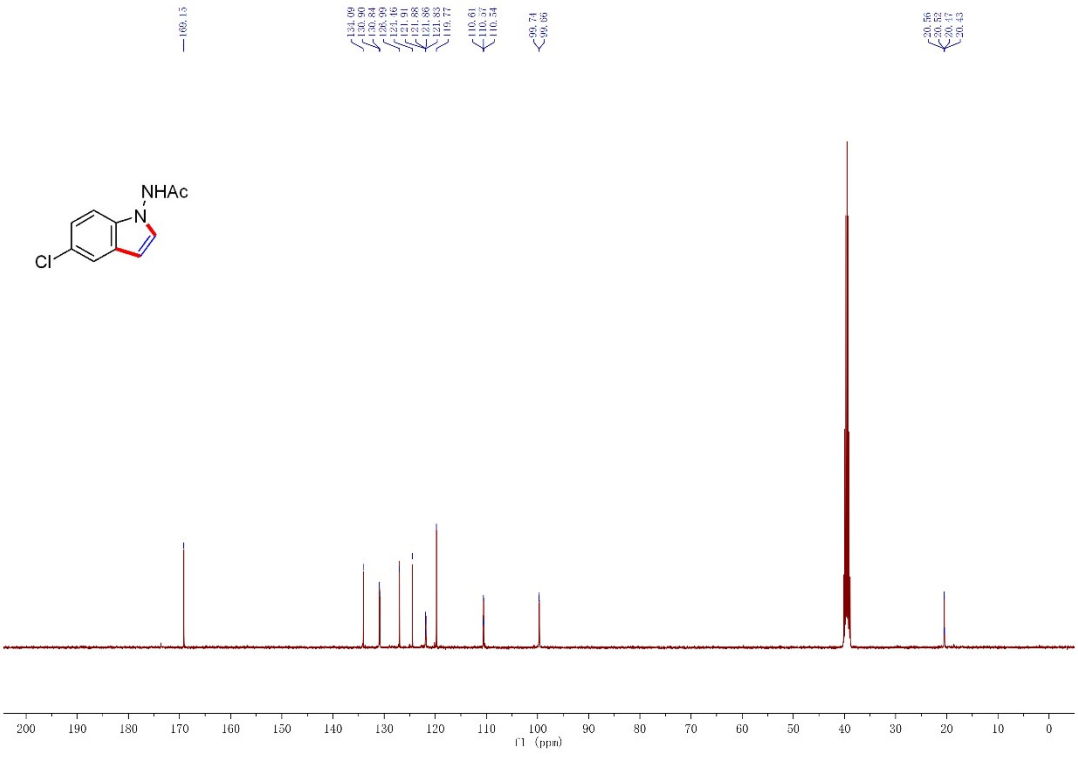

$^{13}$C NMR spectrum of compound **3da**



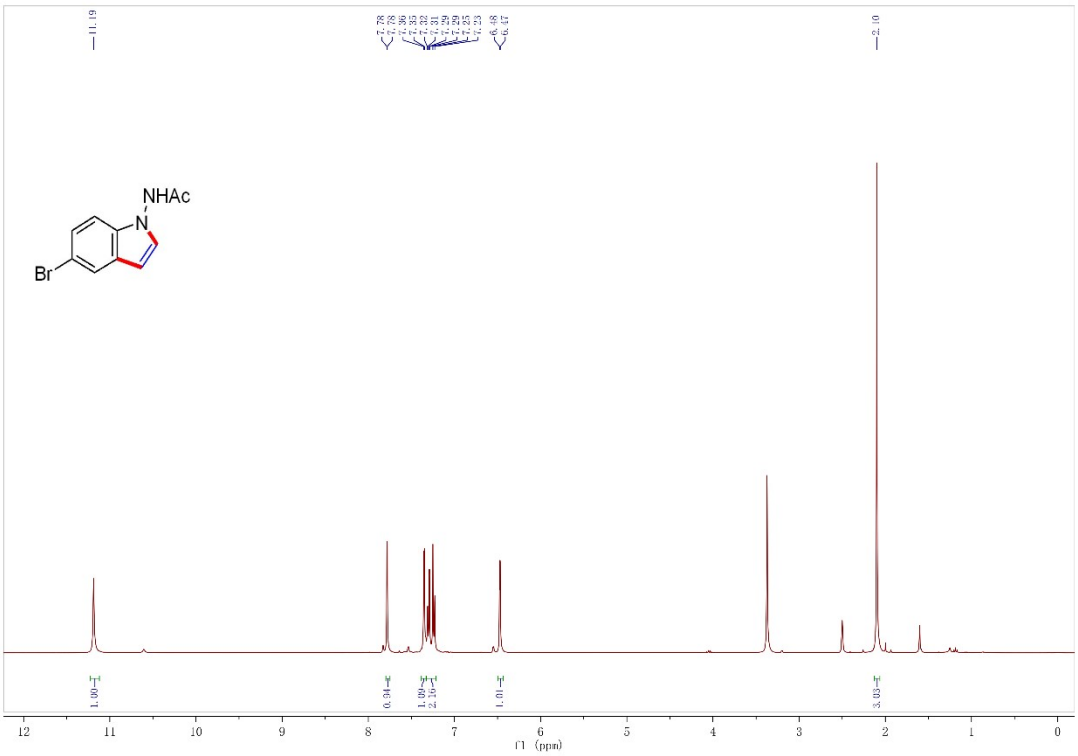

$^{19}$F NMR spectrum of compound **3da**



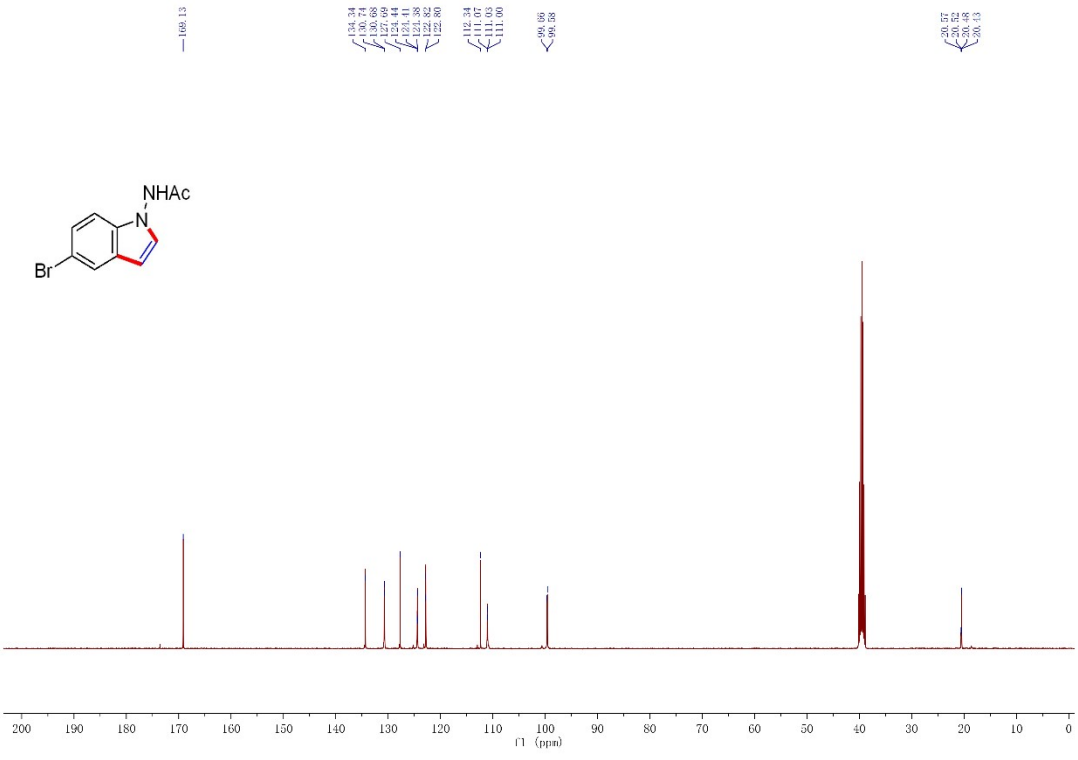

$^{1}$H NMR spectrum of compound **3ea**



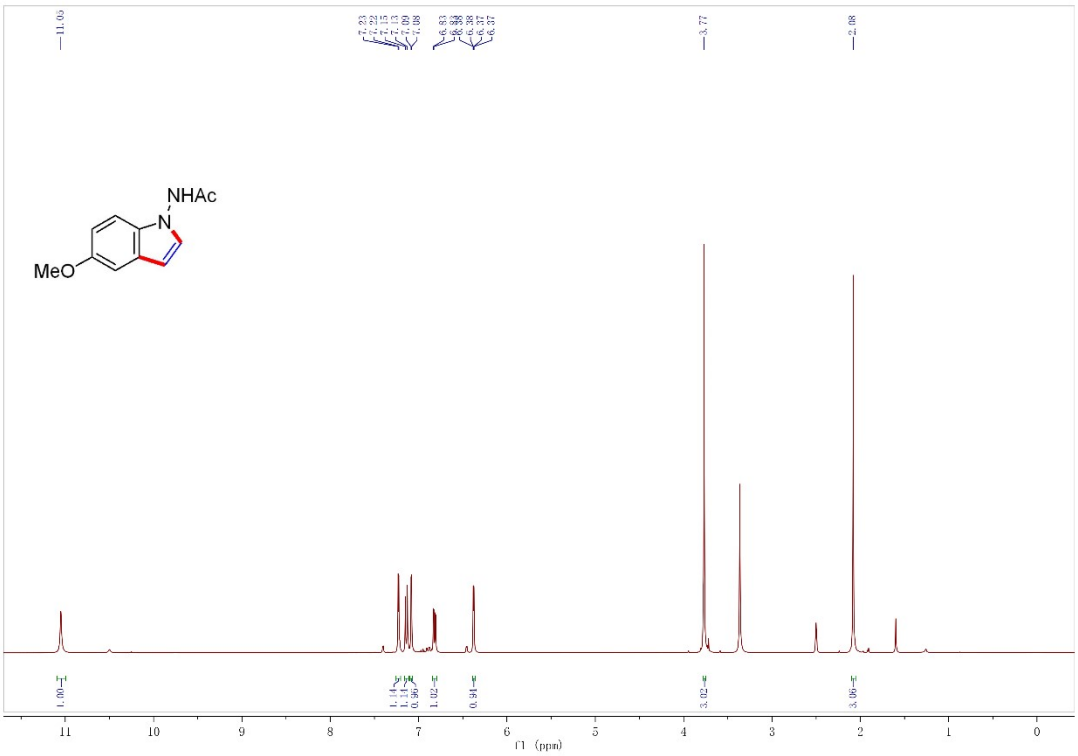

$^{13}$C NMR spectrum of compound **3ea**



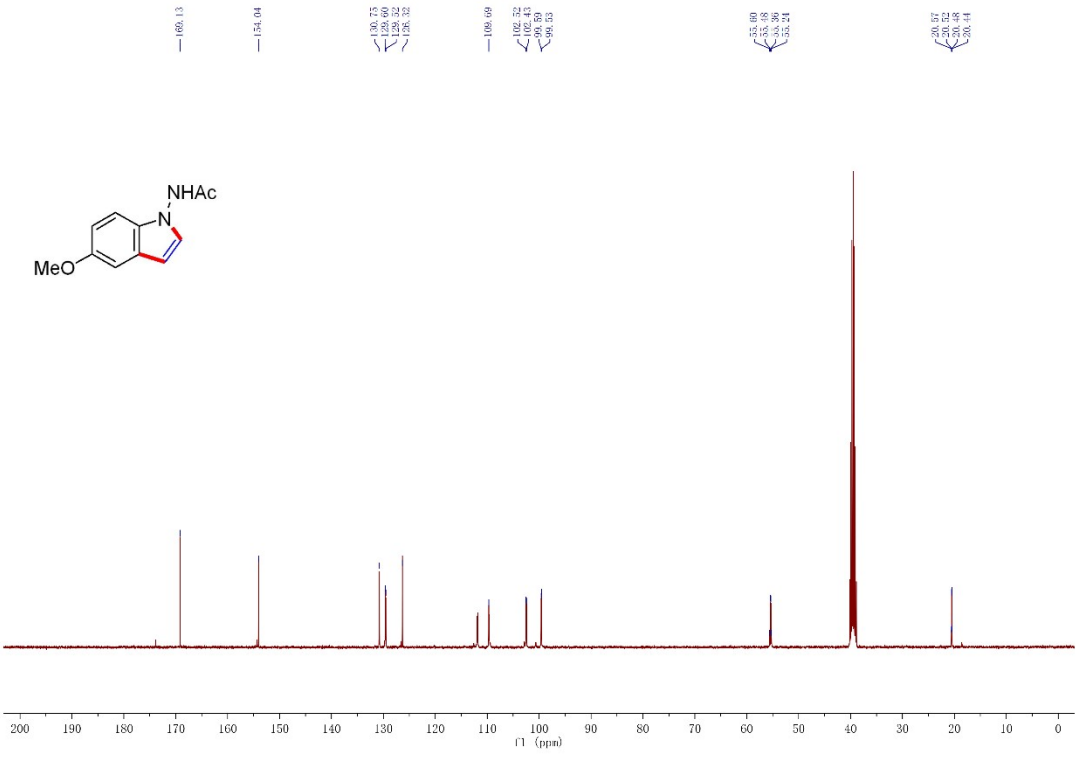

$^{1}$H NMR spectrum of compound **3fa**



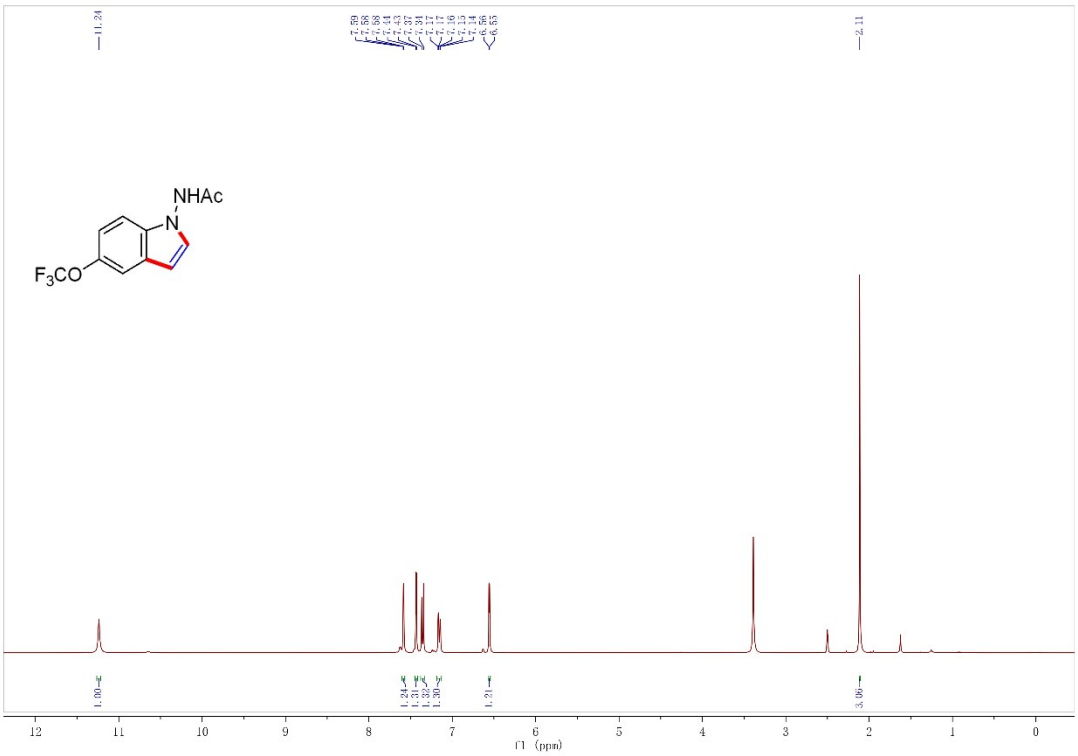

$^{13}$C NMR spectrum of compound **3fa**



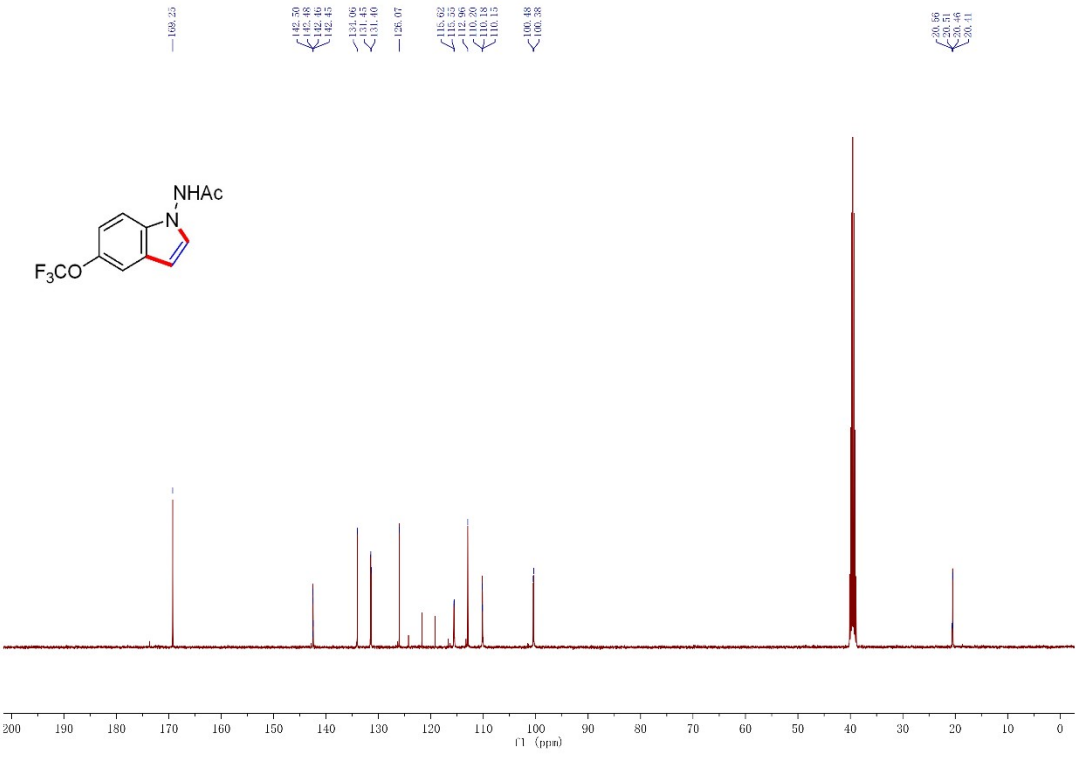

$^{1}$H NMR spectrum of compound **3ga**



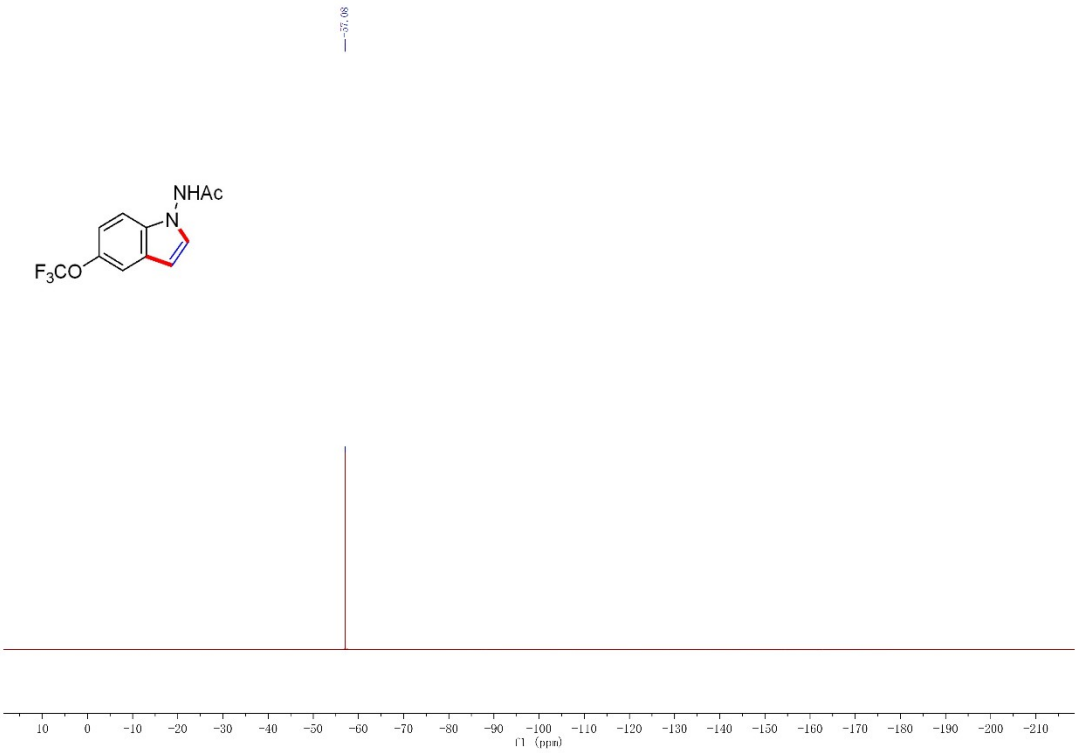

$^{13}$C NMR spectrum of compound **3ga**



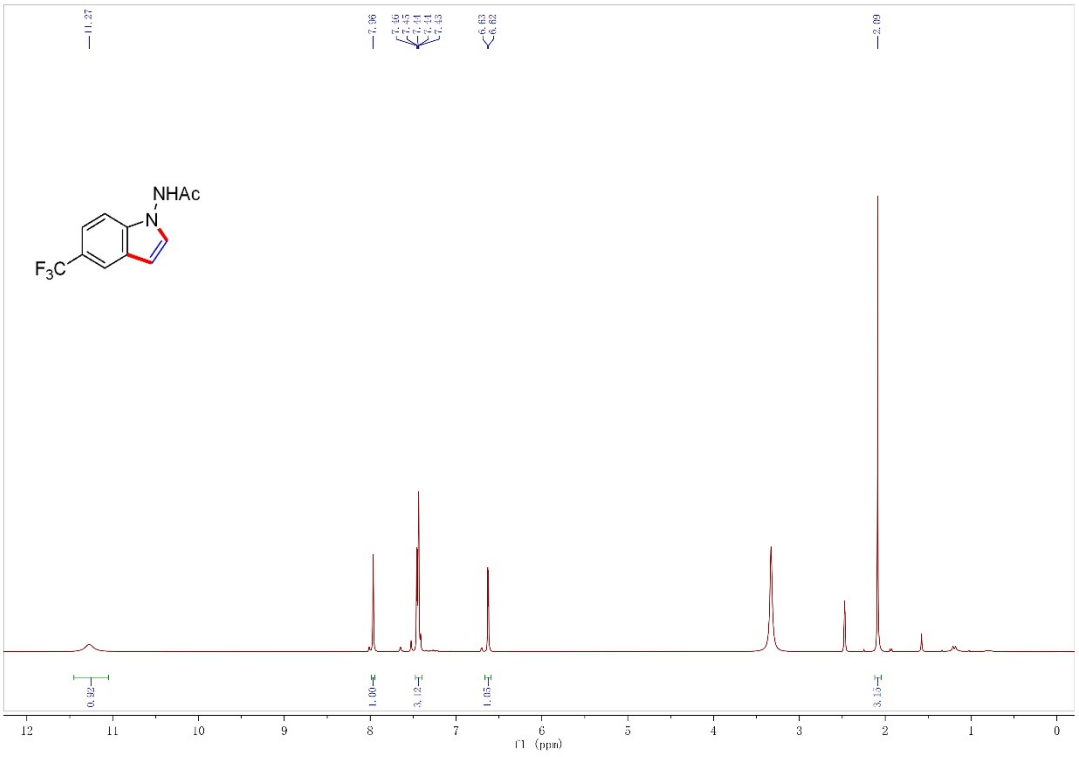

$^{1}$H NMR spectrum of compound **3ha**



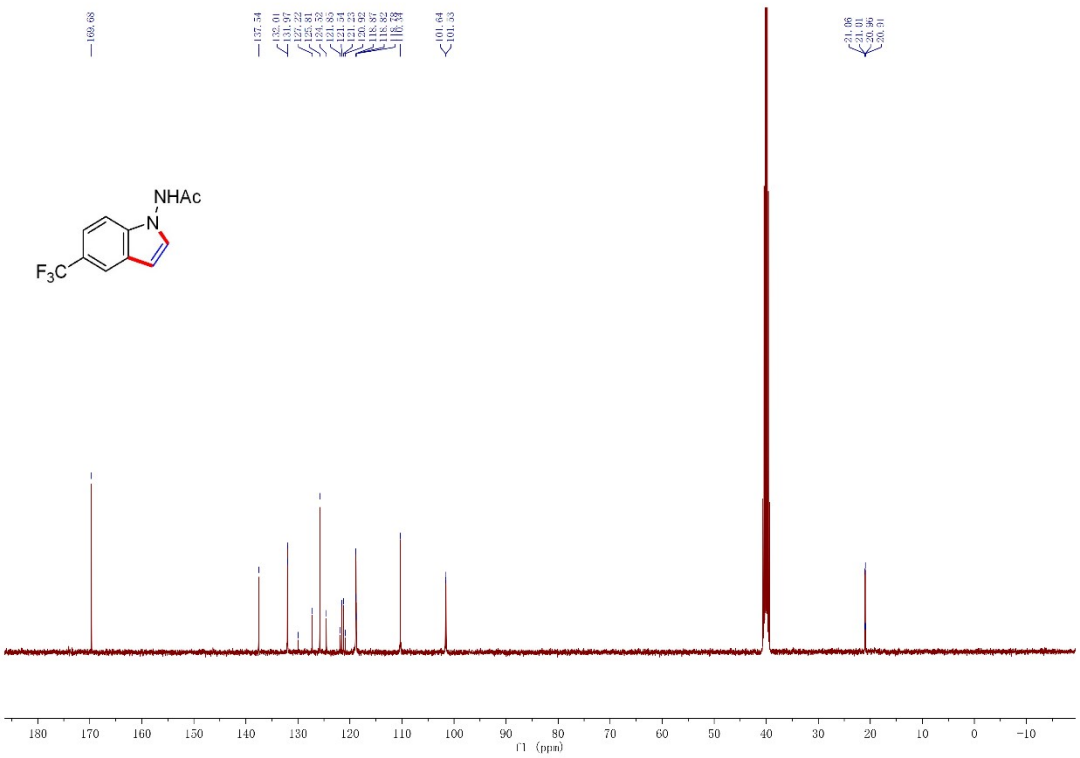

$^{13}$C NMR spectrum of compound **3ha**



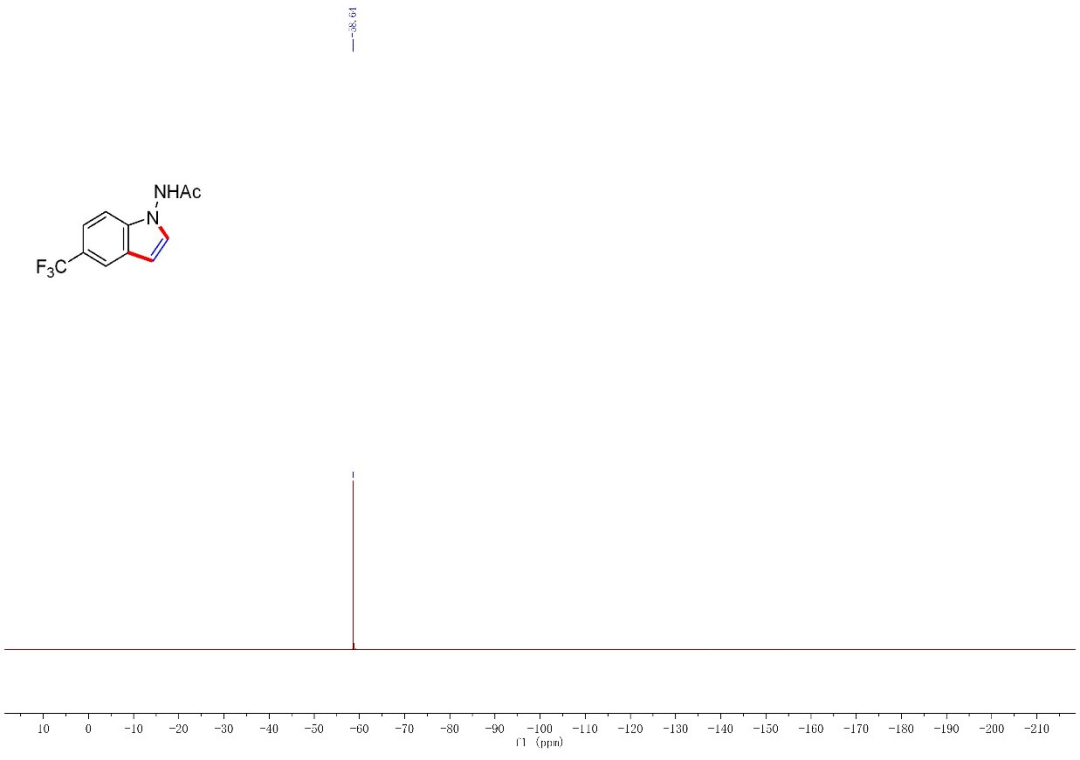

$^{19}$F NMR spectrum of compound **3ha**



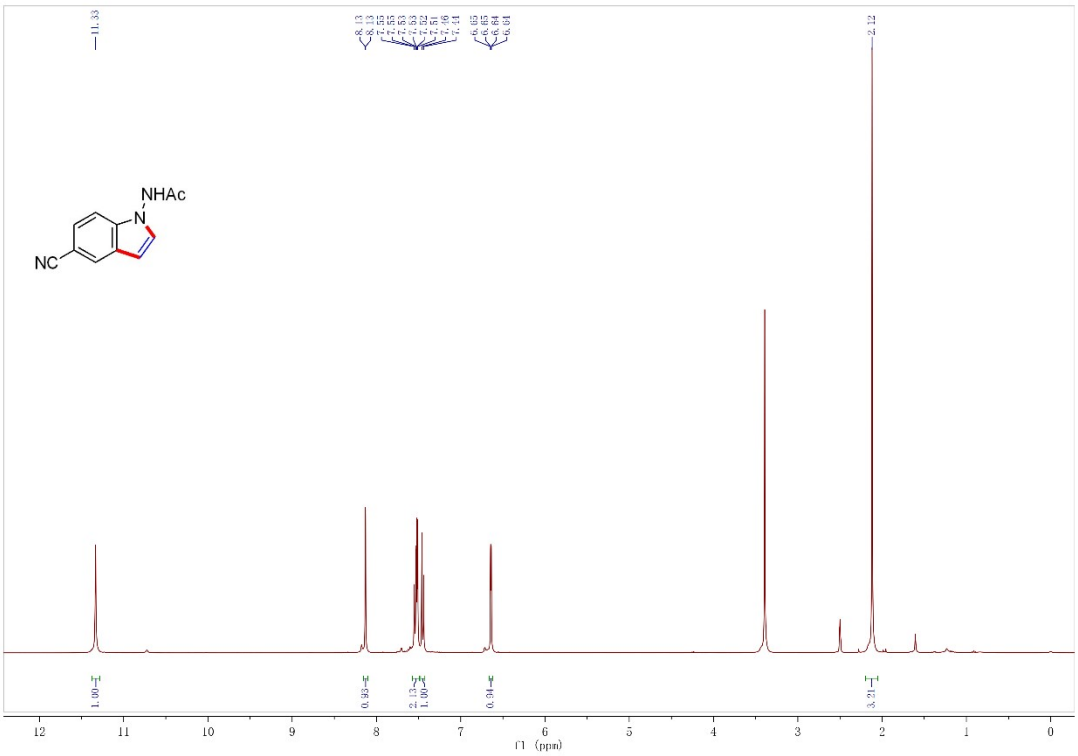

$^{1}$H NMR spectrum of compound **3ia**



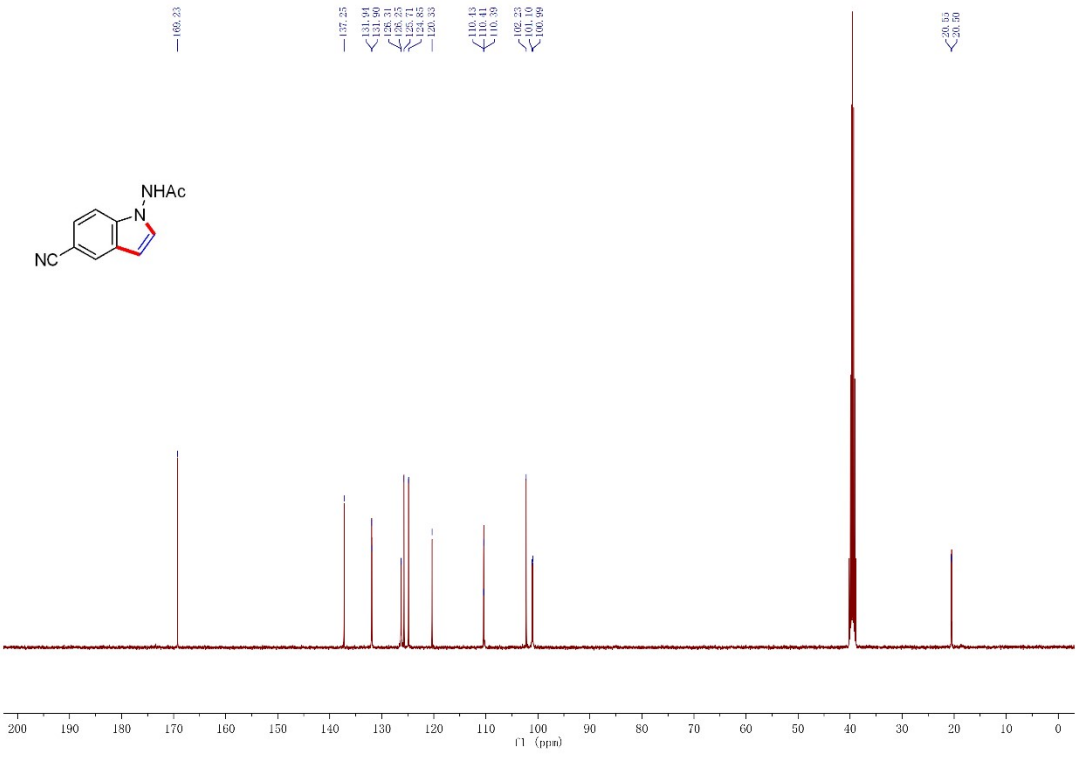

$^{13}$C NMR spectrum of compound **3ia**



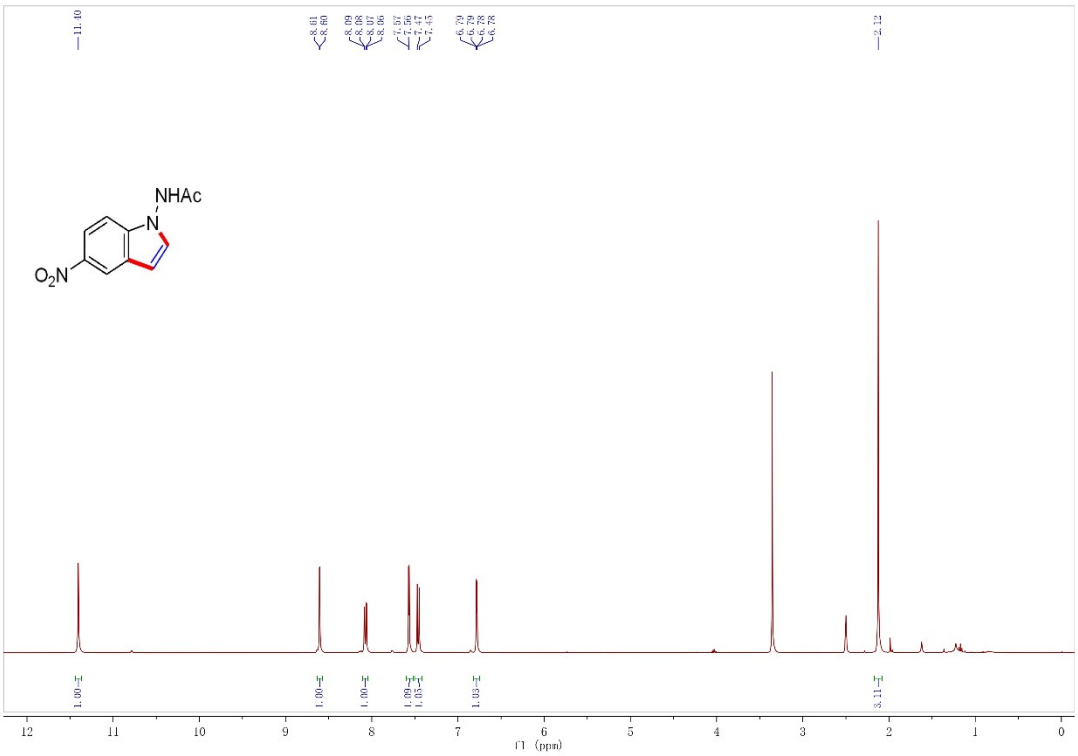

$^{19}$F NMR spectrum of compound **3ia**



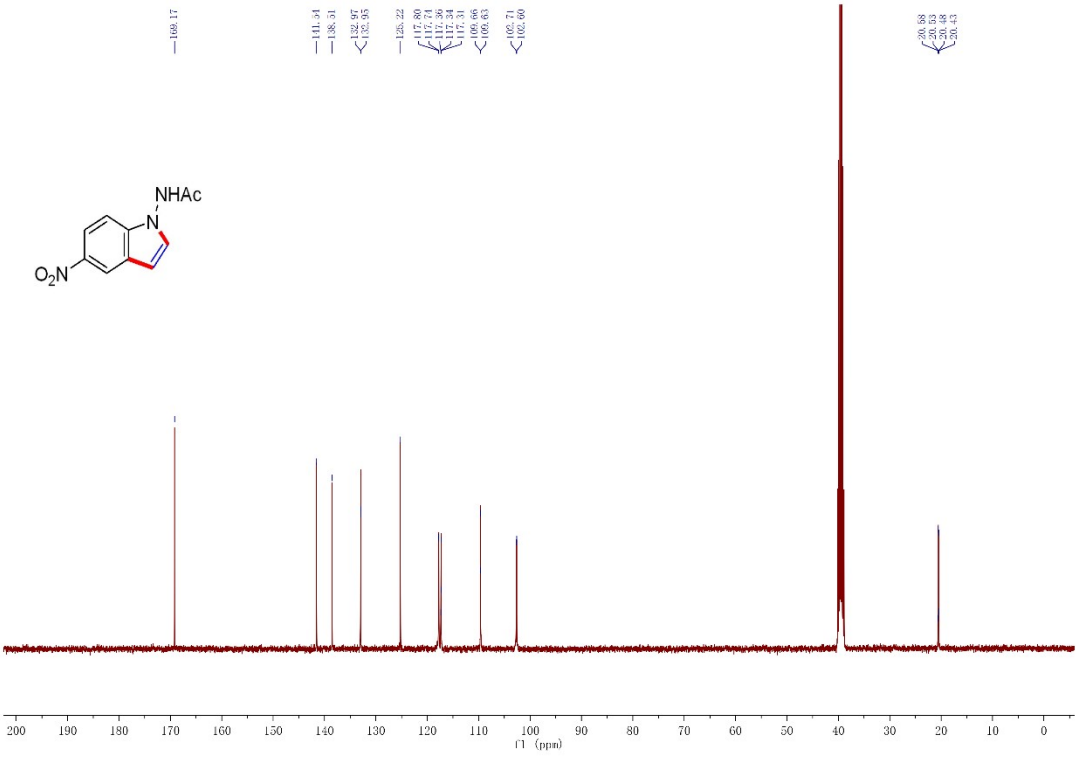

$^{1}$H NMR spectrum of compound **3ja**



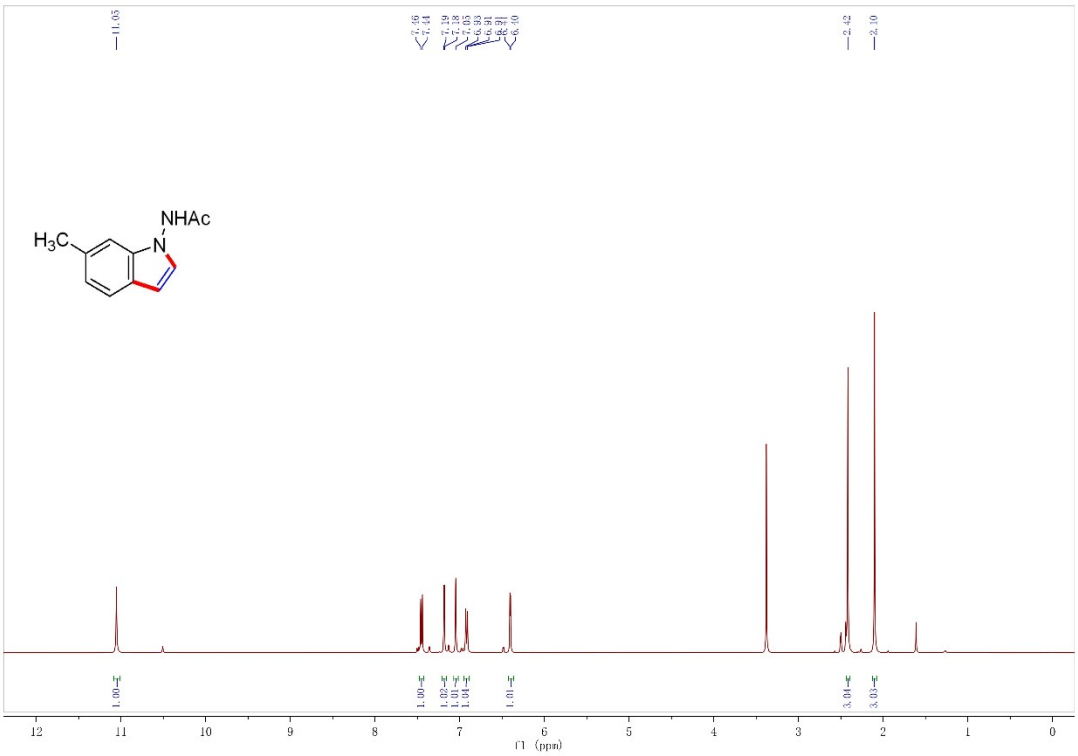

$^{13}$C NMR spectrum of compound **3ja**



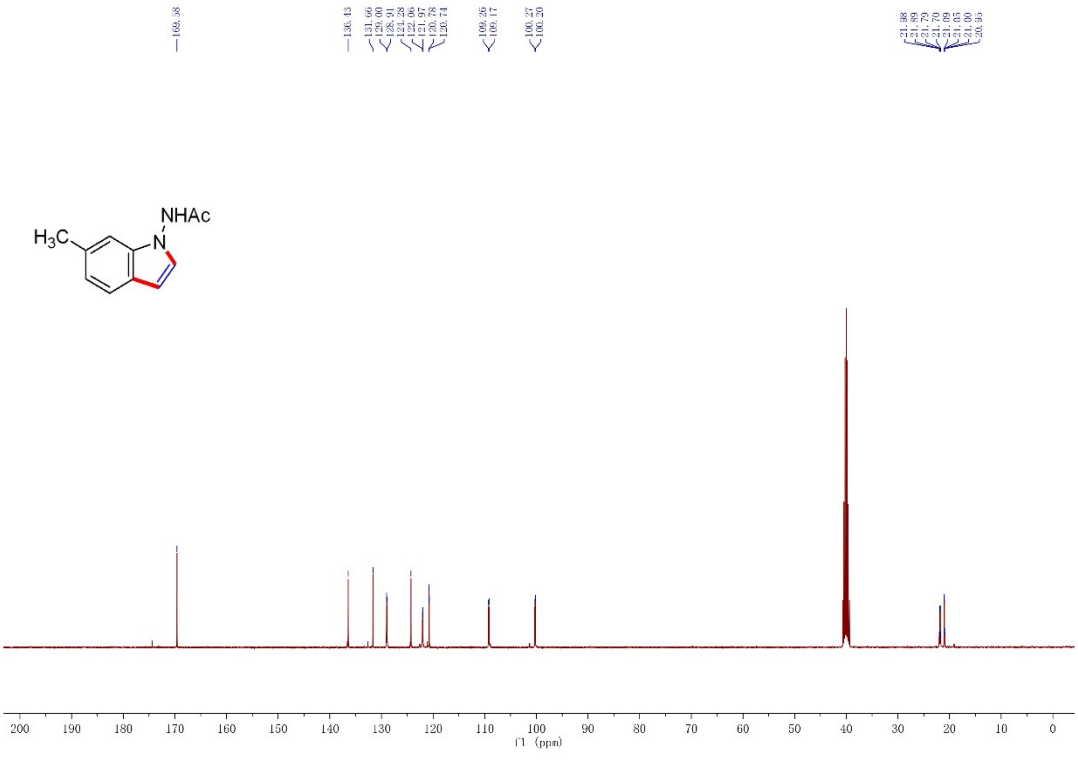

$^{1}$H NMR spectrum of compound **3ka**



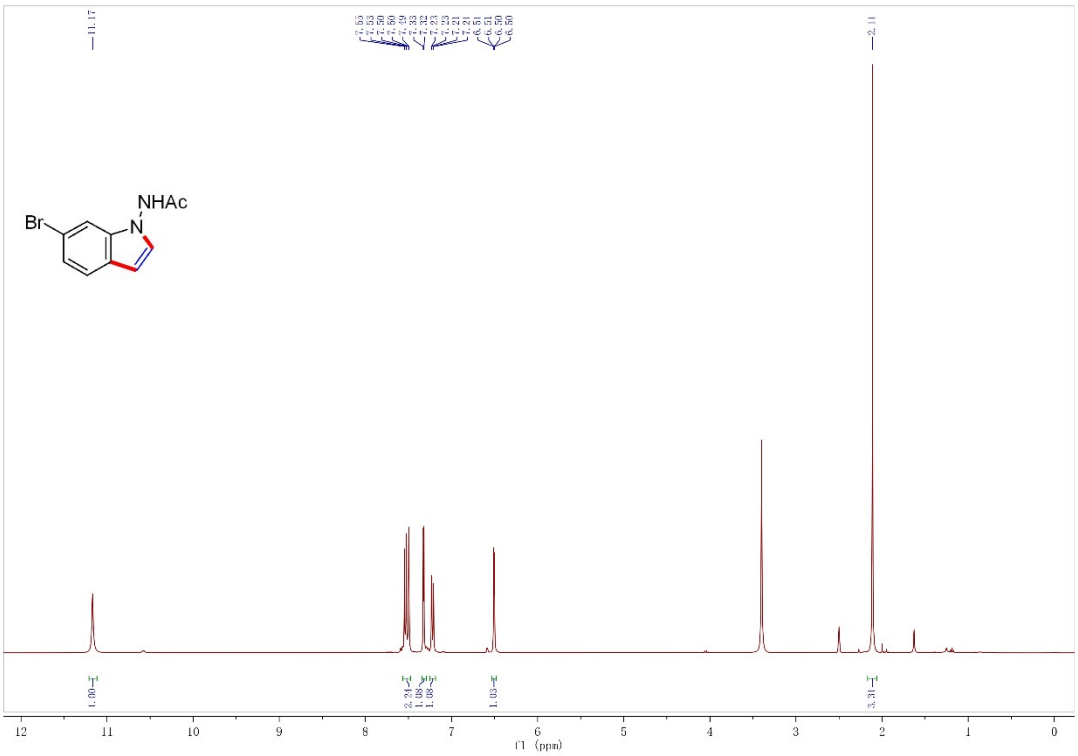

$^{13}$C NMR spectrum of compound **3ka**



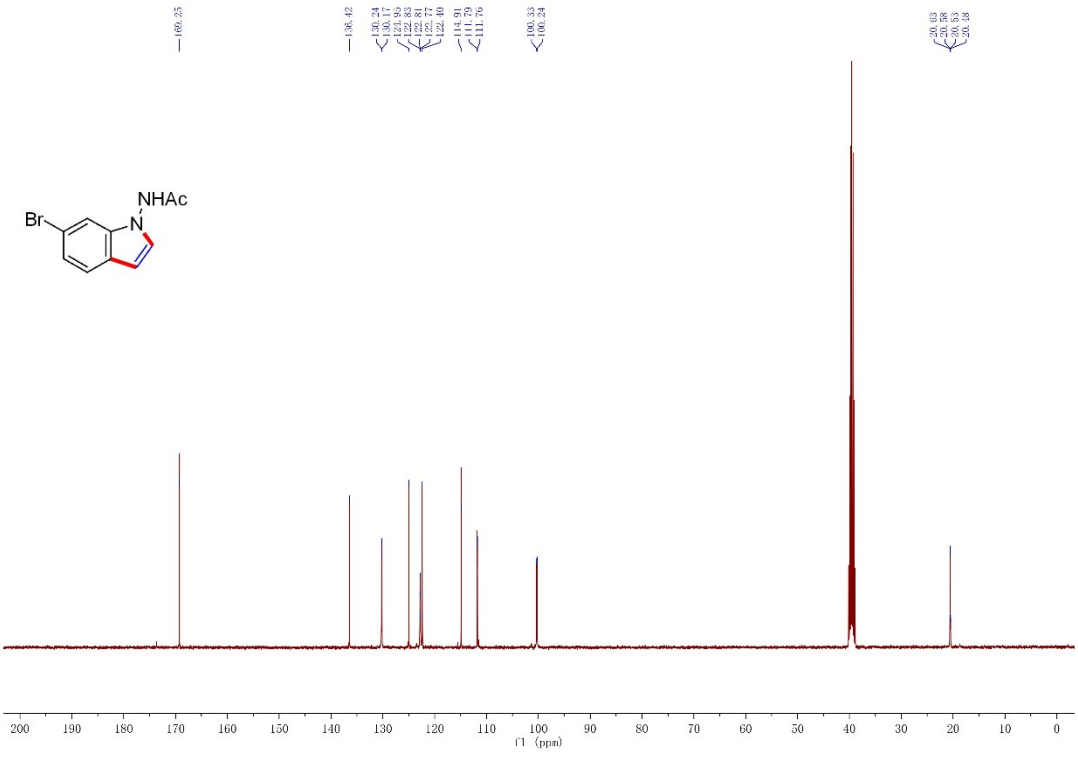

$^{1}$H NMR spectrum of compound **3la**



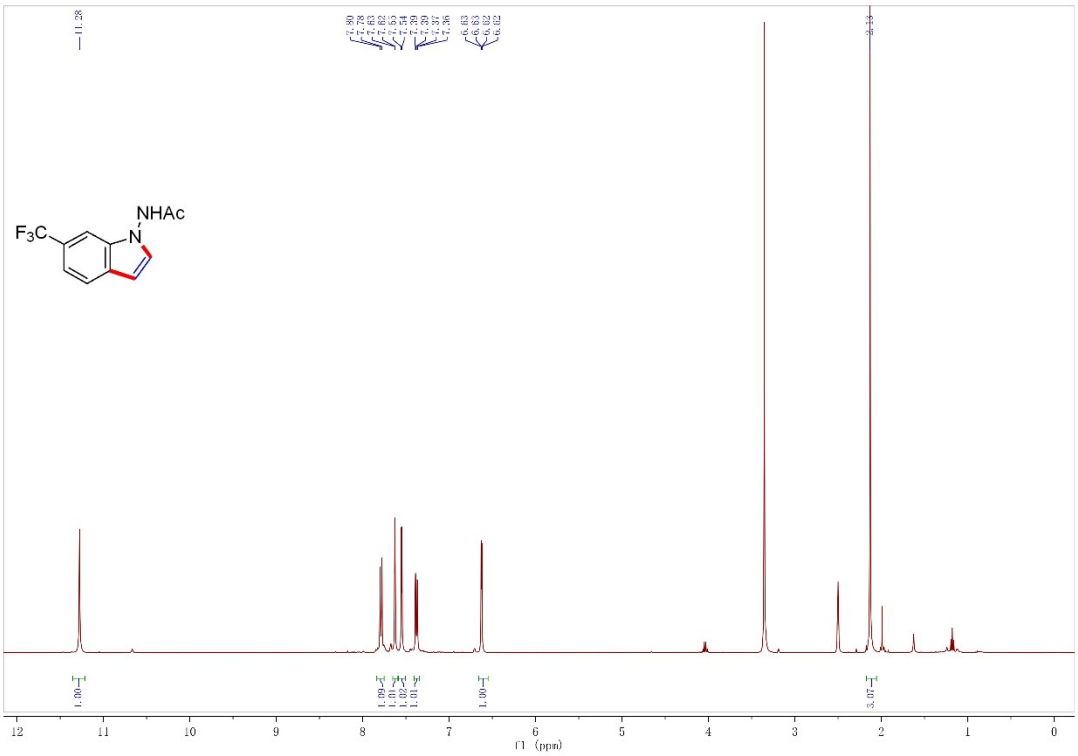

$^{13}$C NMR spectrum of compound **3la**



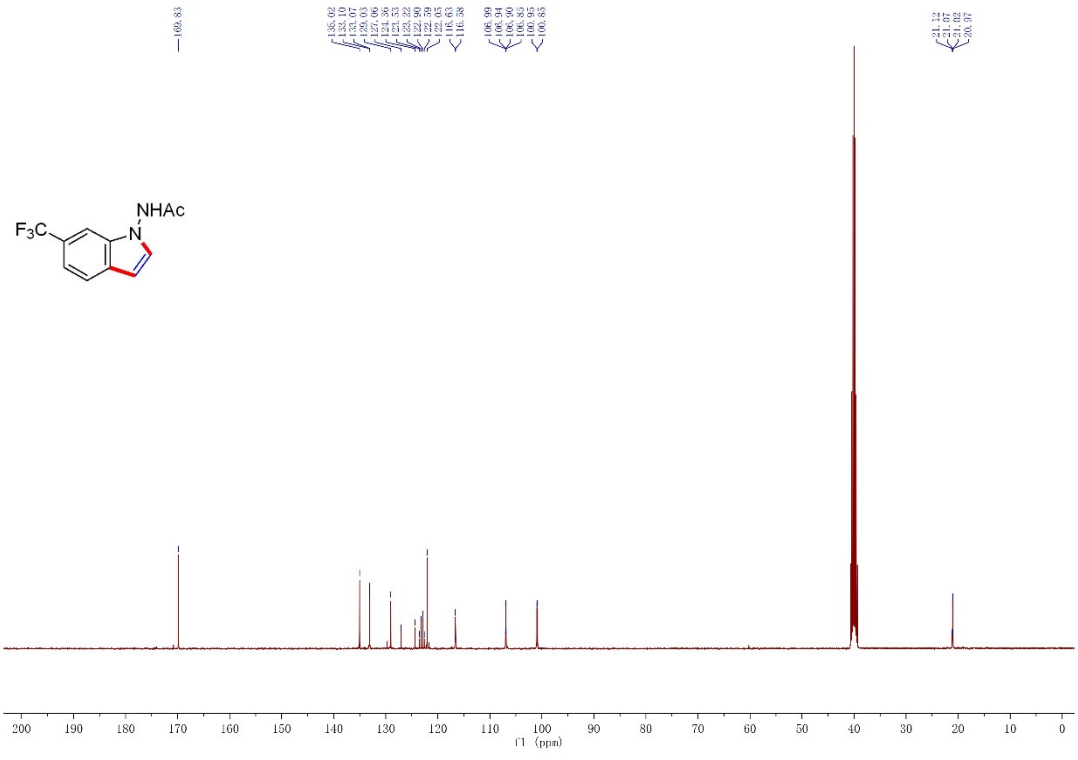

$^{1}$H NMR spectrum of compound **3ma**



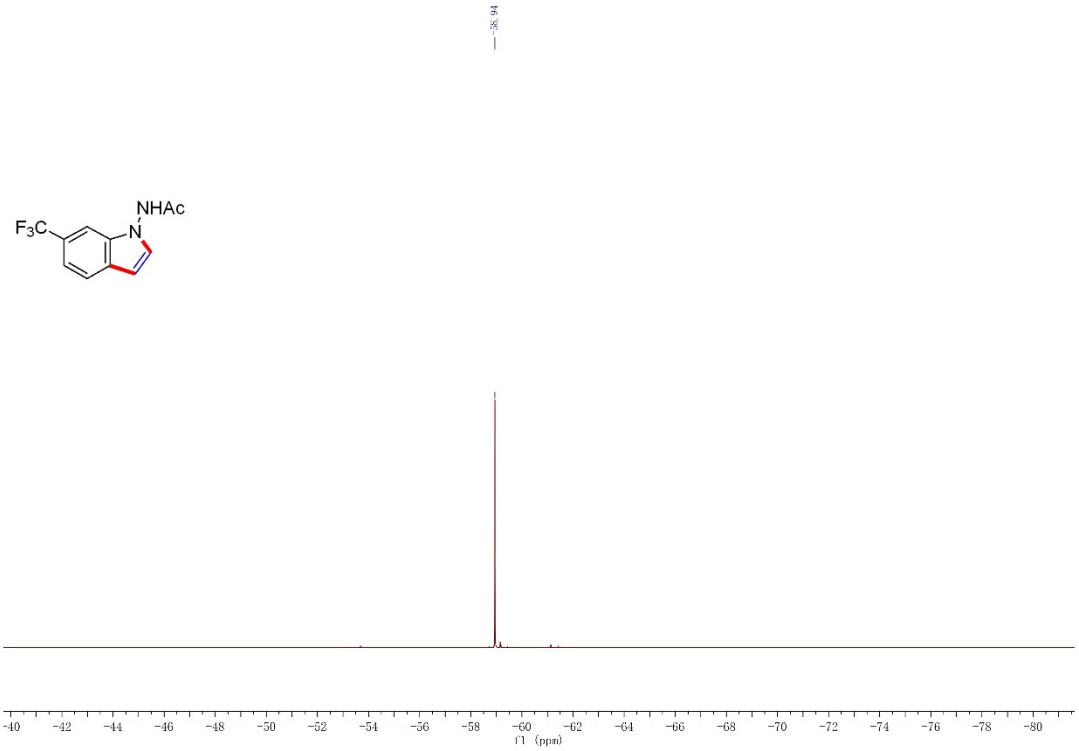

$^{13}$C NMR spectrum of compound **3ma**



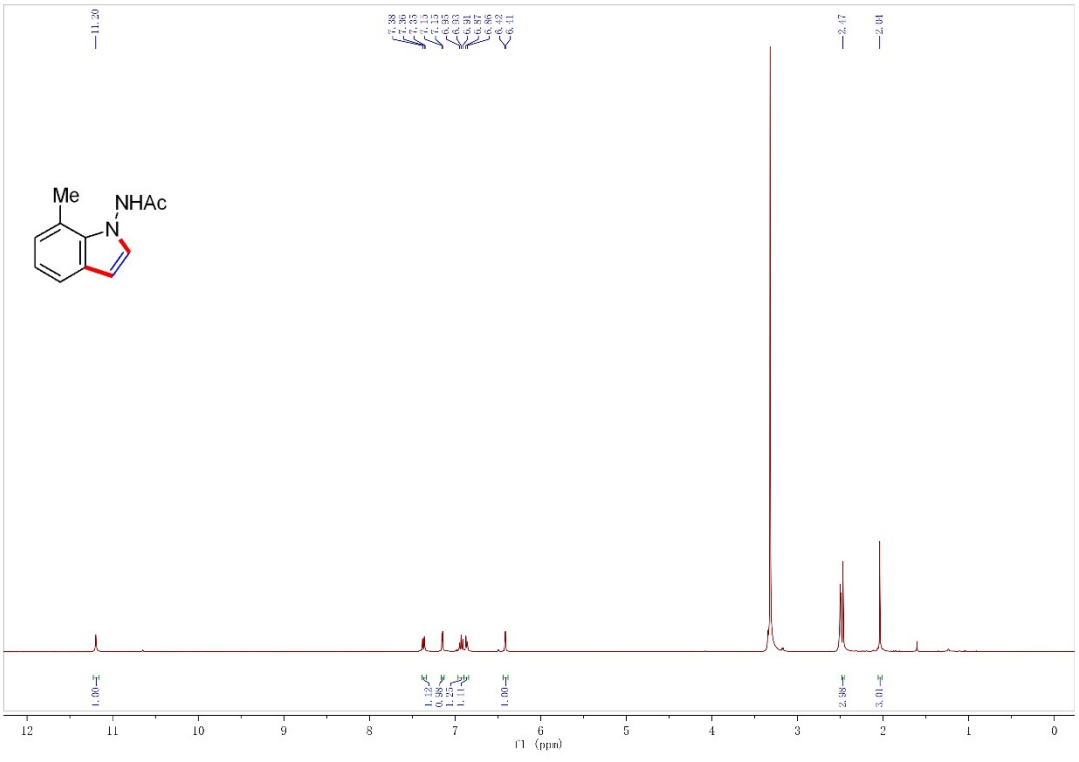

$^{1}$H NMR spectrum of compound **3na**



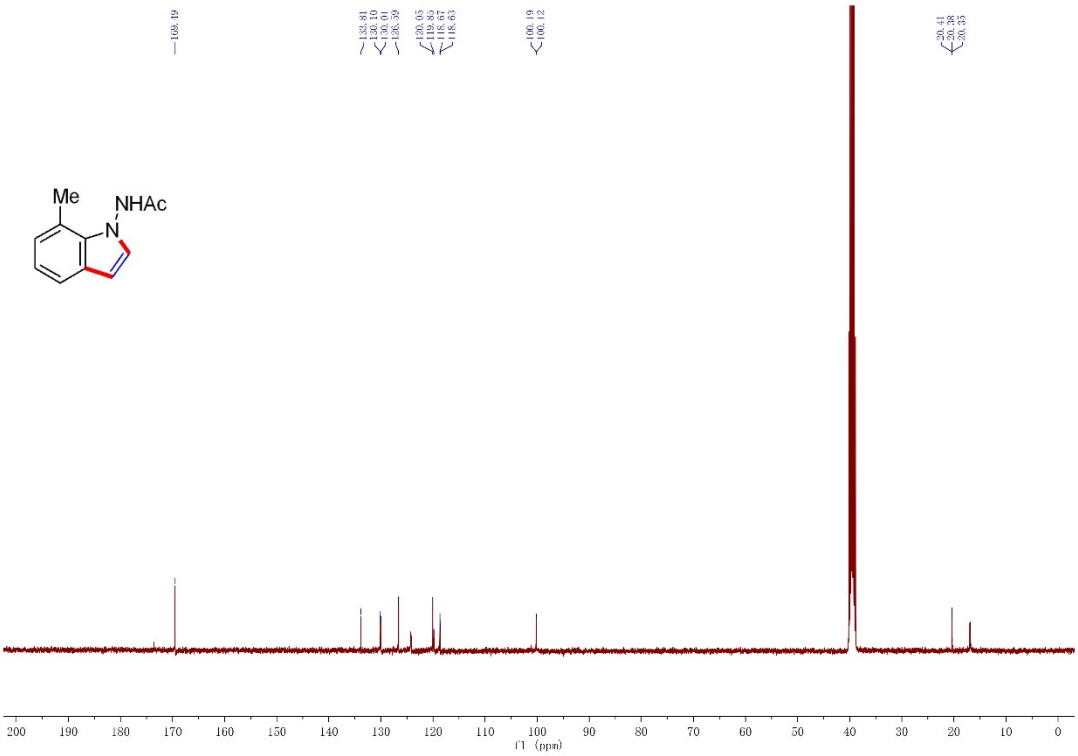

$^{13}$C NMR spectrum of compound **3na**



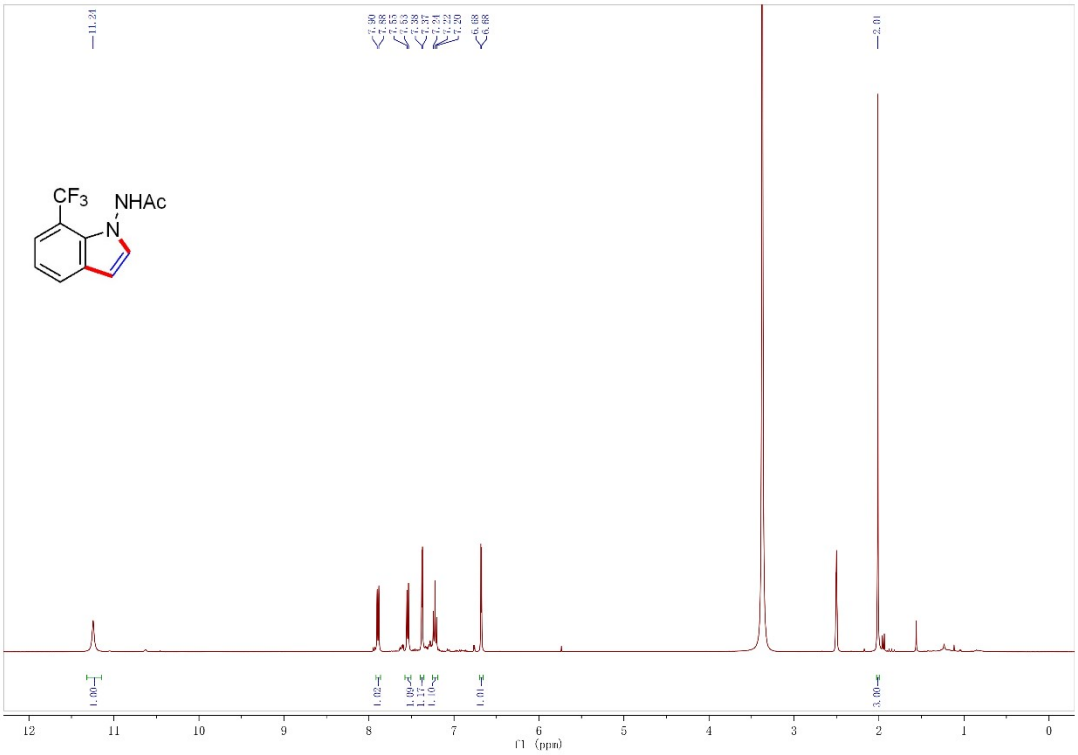

$^{19}$F NMR spectrum of compound **3na**



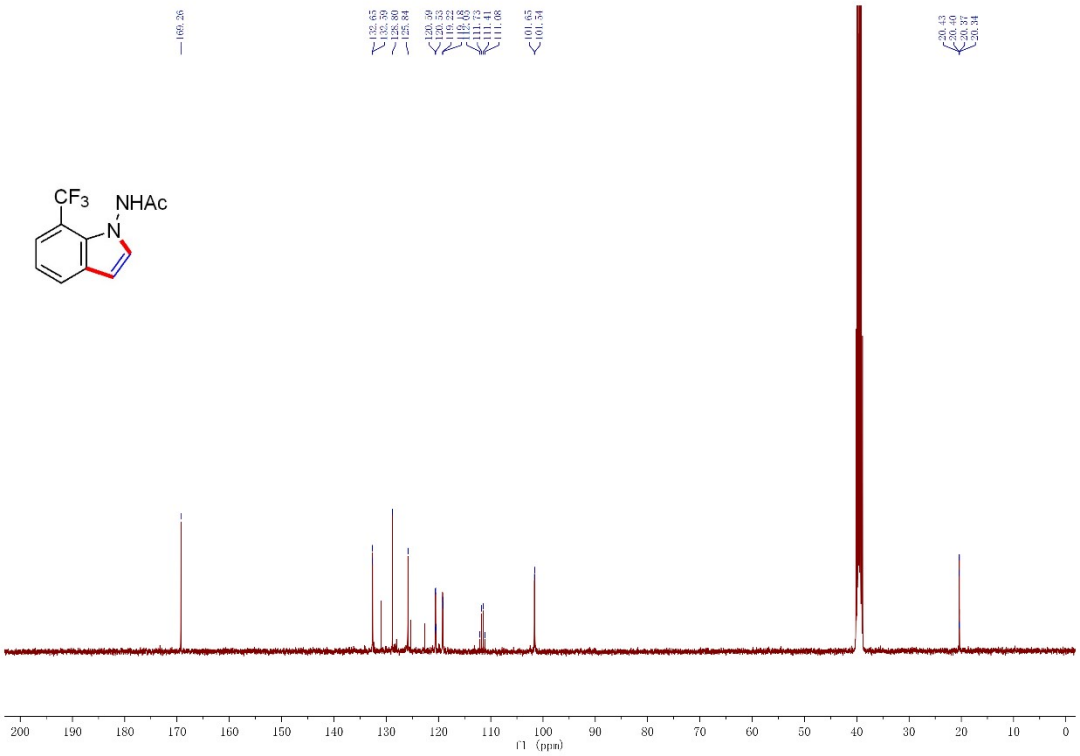

$^{1}$H NMR spectrum of compound **3oa**



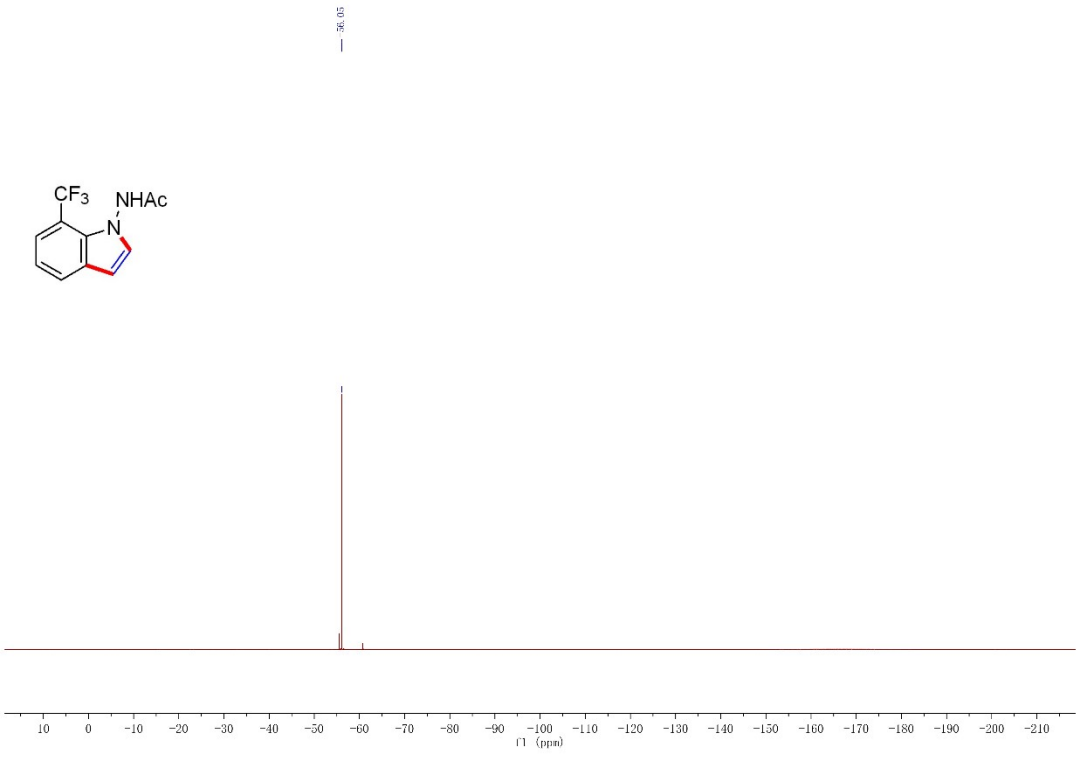

$^{13}$C NMR spectrum of compound **3oa**



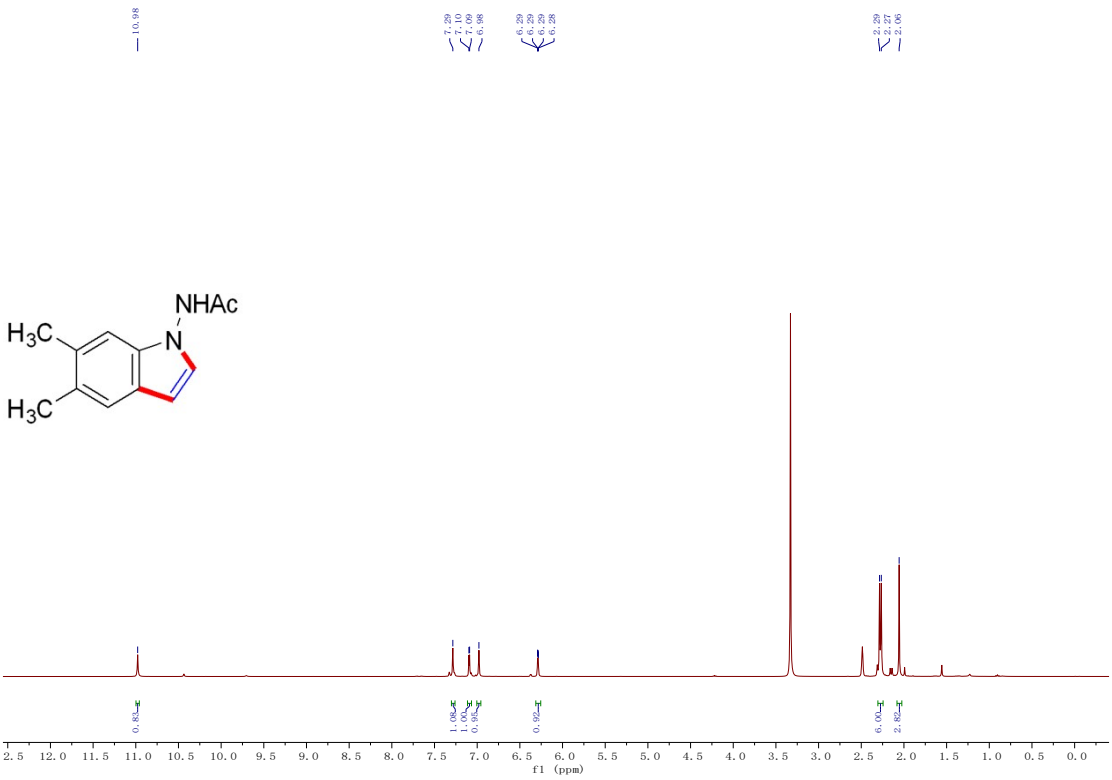

$^{1}$H NMR spectrum of compound **3pa**



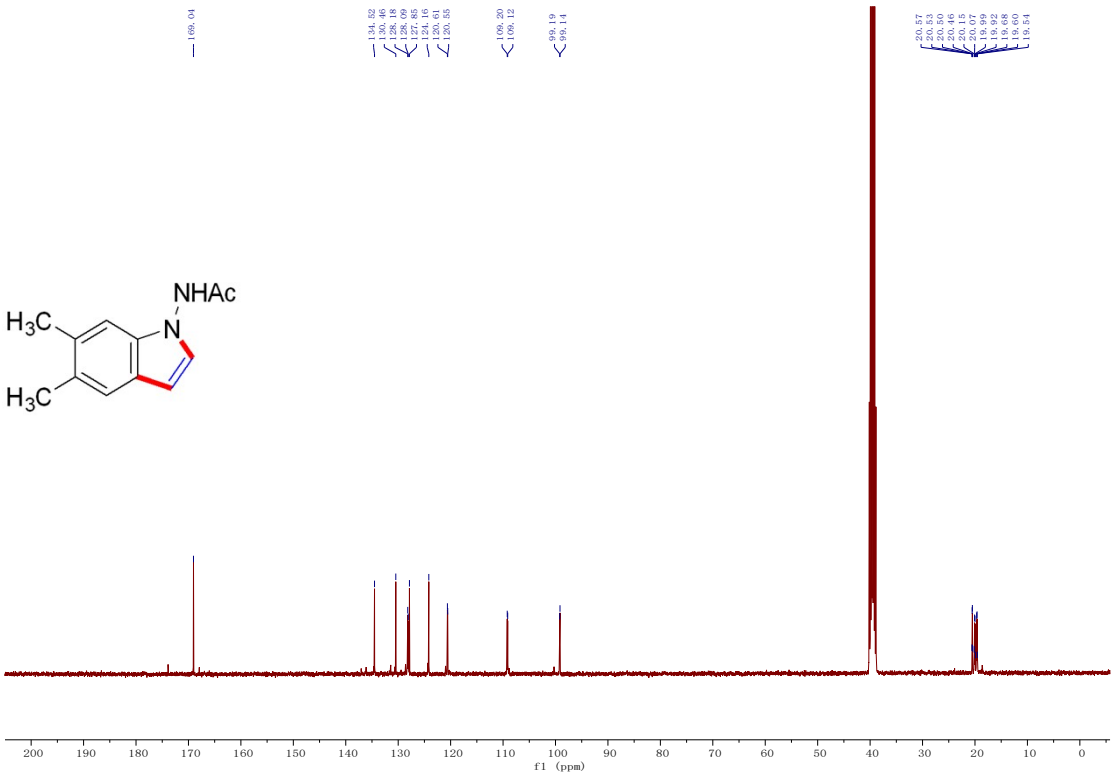

$^{13}$C NMR spectrum of compound **3pa**



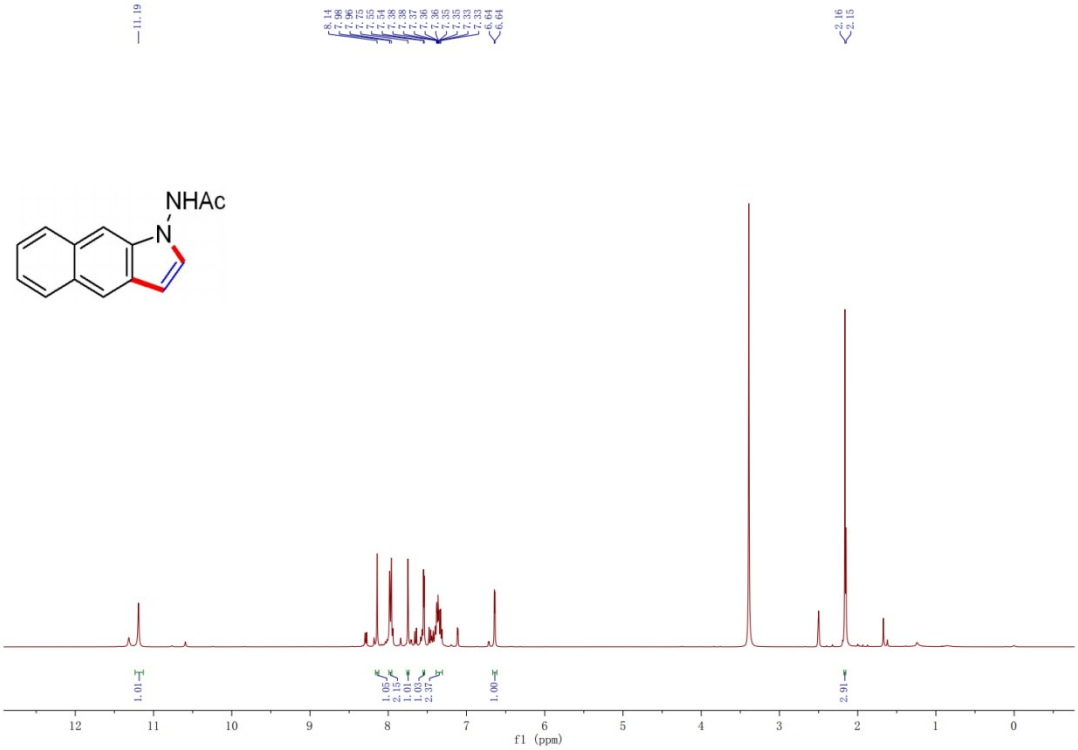

$^{19}$F NMR spectrum of compound **3pa**



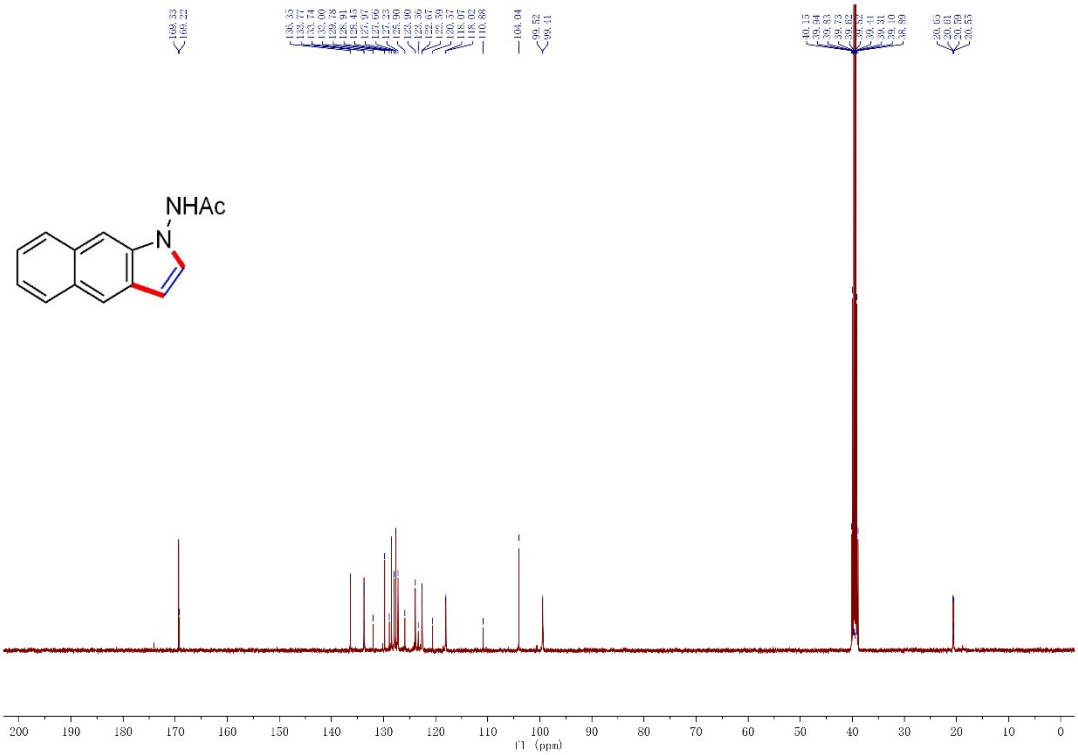

$^{1}$H NMR spectrum of compound **3qa**



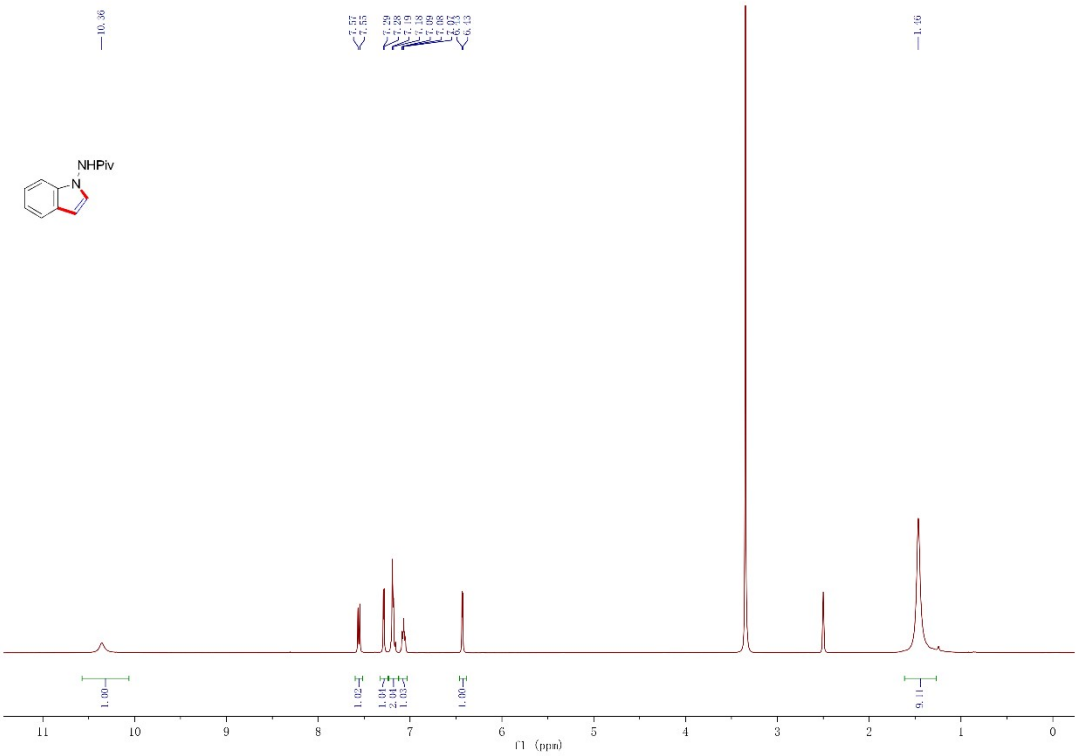
$^{13}$C NMR spectrum of compound **3qa**



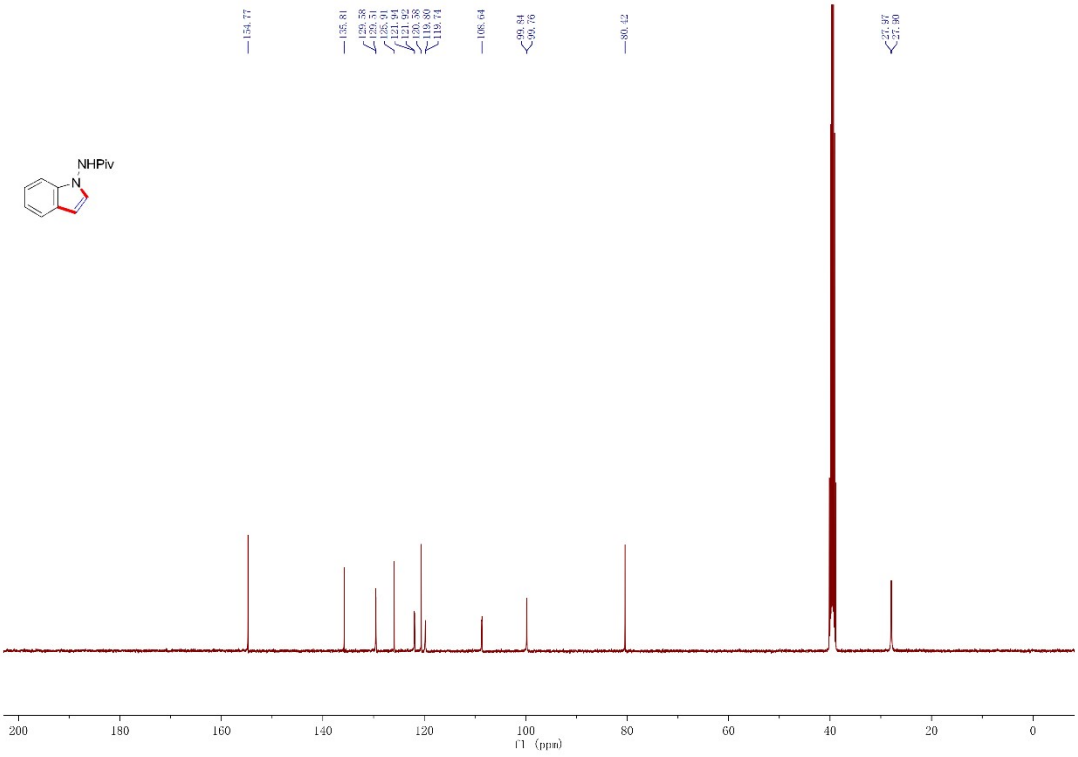

$^{1}$H NMR spectrum of compound **3sa**



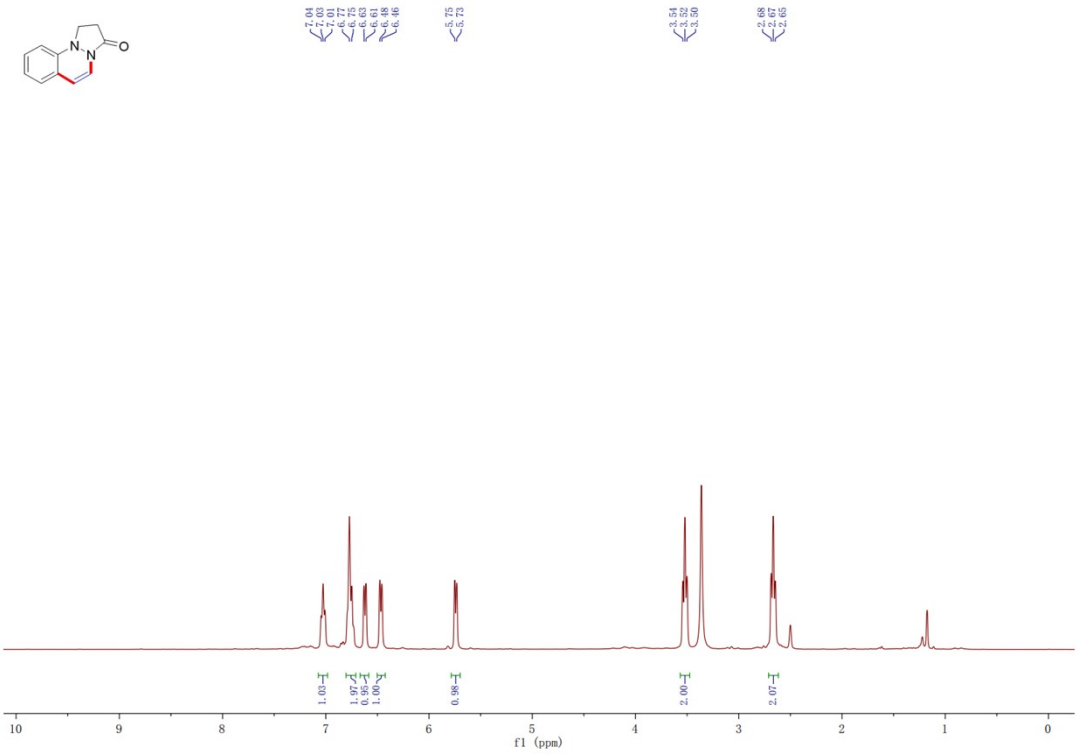

$^{13}$C NMR spectrum of compound **3sa**



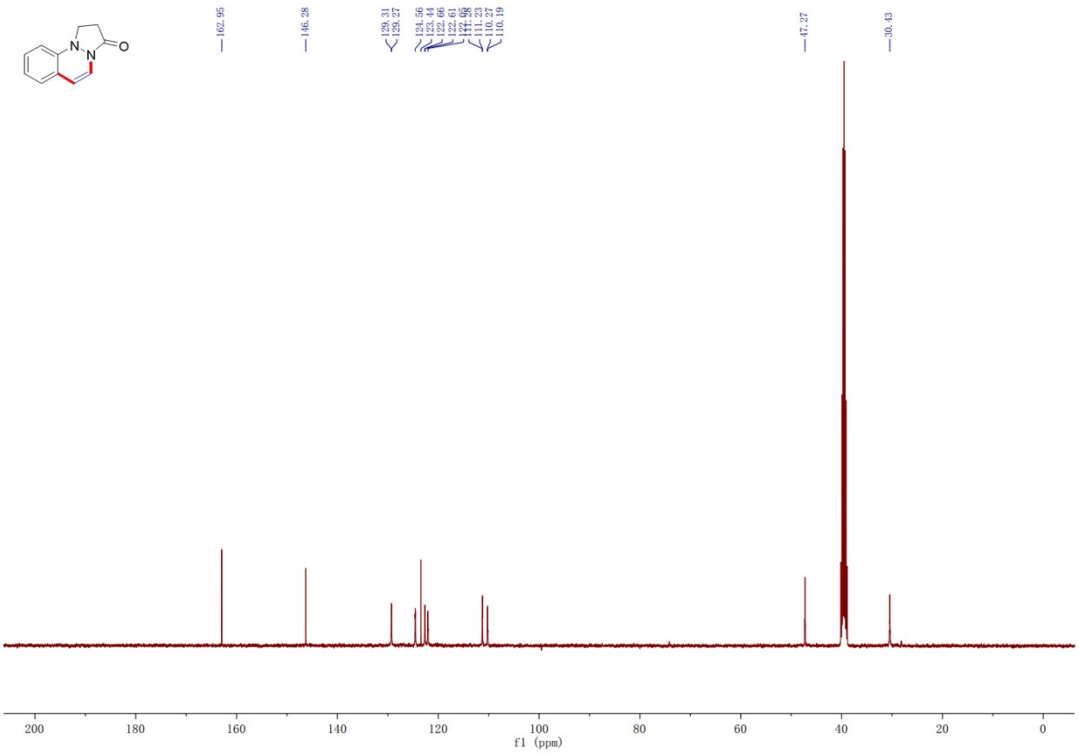

$^{1}$H NMR spectrum of compound **3ta**




$^{13}$C NMR spectrum of compound **3ta**




$^{1}$H NMR spectrum of compound **3va**




$^{13}$C NMR spectrum of compound **3va**

## References:


[1] C. White, A. Yates andP. M. Maitlis, *Inorg. Synth.,* 1992, **29**, 228.

[2] P. M. Boyer, C. P. Roy, J. M. Bielski and J. S. Merpla, *Inorg. Chim. Acta,* 1996, **245**, 7.

[3] Y. Liang, K. Yu, B. Li, S. Xu, H. Song and B. Wang, *Chem. Commun.,* 2014, **50**, 6130.

[4] Oxford Diffraction, Xcalibur CCD System. CrysAlisPro. Oxford Diffraction Ltd: Abingdon, England, UK, 201024.

[5] O. V. Dolomanov, L. J. Bourhis and R. J. Gildea, *J. Appl. Cryst.*, 2009, **42**, 339.

[6] D. Kratzert, J. J. Holstein and I. Krossing, *J. Appl. Crystallogr.*, 2015, **48**, 933.