

Supporting Information For

Preparation of Pyridyltriazole Ruthenium Complexes as Effective Catalysts for the Selective Alkylation and One-Pot C-H Hydroxylation of 2-Oxindole with Alcohols under Solvent-Free Fashion and Mechanism Exploration

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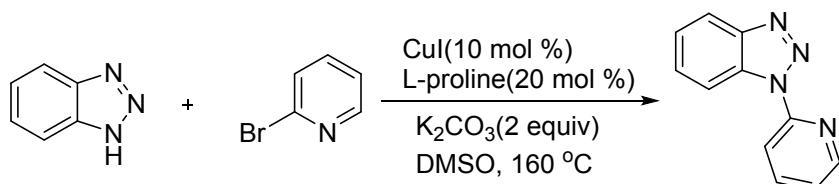
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1. General Methods and Materials

All of the reactions dealing with air were carried out in a high purity argon or nitrogen atmosphere using standard Schlenk techniques or glovebox techniques. All the obtained products were characterized by ¹H-NMR, ¹³C-NMR and melting points (m.p), melting points were measured on an Electrothermal WRS X-4A microscopy digital apparatus and without correction. ¹H NMR and ¹³C NMR spectra were obtained on Bruker Advance III HD 400 MHz spectrometer and referenced to CDCl₃ (7.26 ppm for ¹H, and 77.1 ppm for ¹³C) or DMSO-d₆ (2.50 ppm for ¹H, and 39.5 ppm for ¹³C) with tetramethylsilane as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm δ) downfield from TMS and coupling constants are reported in Hertz. The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. High resolution mass spectra (HRMS) were recorded on LTQ-FTUHRA mass spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at shortwave UV light (254 nm) and KMnO₄. Flash column chromatography was performed on 230-430 mesh silica gel. Unless otherwise stated, all the reagents were purchased from commercial sources (J&K Chemic, Acros, TCI, SCRC, Energy Chemical), used without further purification.

2. Preparation of Pyridyltriazole Ruthenium Complexes

2.1 Procedure for synthesis of 1-(pyridin-2-yl)-1H-benzo[d][1,2,3]triazole¹



To an oven-dried 250-mL Schlenk tube were successively added *1H*-benzotriazole (1.430 g, 12 mmol), 2-bromopyridine (1.580 g, 10 mmol), copper (I) iodide (0.190 g, 1 mmol), potassium carbonate (2.764 g, 20 mmol), L-proline (0.230 g, 2 mmol), and dimethylsulfoxide (40 mL) under N₂ atmosphere. Then, the resulting mixture was stirred at 160 °C for 18 h and monitored by TLC until complete disappearance of 2-bromopyridine. After cooling down to ambient temperature, the reaction mixture was added water and extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous MgSO₄ and concentrated by removing the solvent under vacuum. Finally, the residue was purified by flash column chromatography with ethyl acetate/ petroleum ether to give the desired product (1.334 g, 68% yield).

2.2 Preparation of pyridyltriazole ruthenium complexes

Procedure for the synthesis of [{Ru(*p*-cymene)}(Pyridyltriazole)Cl][Cl]

In an oven-dried 50-mL Schlenk tube equipped with a stir bar were successively added $[\text{RuCl}_2(p\text{-cymene})]_2$ (1.224 g, 2 mmol), triazole ligand (0.804 g, 4.1 mmol) and methanol (20 mL). The tube was evacuated and refilled with high purity nitrogen, and the mixture was vigorously stirred for 24 h at room temperature. All the volatiles were evaporated under reduced pressure, and the resultant residue was purified by column chromatography on silica gel with methanol/dichloromethane to give the PTA-Ru product **1a**.

Yellow solid, 89% yield; ^1H NMR (400 MHz, DMSO- d_6) δ 9.72 (d, J = 4.9 Hz, 1H), 8.85 (d, J = 8.4 Hz, 1H), 8.76 (d, J = 8.7 Hz, 1H), 8.47 (dd, J = 17.9, 8.0 Hz, 2H), 7.97 (t, J = 7.6 Hz, 1H), 7.82 (dd, J = 14.6, 7.6 Hz, 2H), 6.44 (d, J = 6.2 Hz, 1H), 6.40 (d, J = 6.4 Hz, 1H), 6.25 (d, J = 6.3 Hz, 1H), 6.11 (d, J = 6.2 Hz, 1H), 2.81 (dq, J = 13.8, 6.9 Hz, 1H), 2.17 (s, 3H), 1.15 (dd, J = 6.9, 2.8 Hz, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 156.06, 147.14, 146.96, 143.39, 132.40, 131.07, 128.16, 125.65, 120.50, 114.17, 112.76, 106.66, 103.86, 88.72, 87.19, 85.71, 85.65, 30.92, 22.59, 21.81, 18.43. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{N}_4\text{Ru}$: C, 50.20; H, 4.41; N, 11.15. Found: C, 50.08; H, 4.36; N, 11.08.

Procedure for the synthesis of $[\{\text{Ru}(p\text{-cymene})\}(\text{pyridyltriazole})\text{Cl}][\text{PF}_6]$

Under N_2 atmosphere, $[\{\text{Ru}(p\text{-cymene})\}(\text{pyridyltriazole})\text{Cl}][\text{Cl}]$ (0.934 g, 2 mmol) and methanol (20 mL) was added to an oven-dried 100-mL Schlenk tube equipped with a stir bar. Then, the tube was closed and the resulting mixture was stirred at room temperature for 1 h. After water (20 mL) were introduced into the solution, NH_4PF_6 (0.815 g, 5 mmol, 2.5 equiv) was added in portions with vigorously stirring for 2 h. The precipitate was isolated by vacuum filtration and washed with diethyl ether three times. The remaining residue was purified through recrystallization to give the PTA-Ru product **1b**.

Yellow solid, 84% yield; ^1H NMR (400 MHz, DMSO- d_6) δ 9.58 (d, J = 5.4 Hz, 1H), 8.74 (s, 1H), 8.67 (d, J = 8.6 Hz, 1H), 8.47 (dd, J = 12.7, 8.2 Hz, 2H), 7.99 (t, J = 7.8 Hz, 1H), 7.90 – 7.71 (m, 2H), 6.38 (t, J = 6.9 Hz, 2H), 6.19 (d, J = 6.2 Hz, 1H), 6.06 (d, J = 6.1 Hz, 1H), 2.83 (dt, J = 13.6, 6.8 Hz, 1H), 2.16 (s, 3H), 1.16 (dd, J = 6.7, 2.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 155.71, 147.25, 146.99, 143.30, 132.39, 131.11, 128.16, 125.59, 120.54, 114.03, 112.62, 106.75, 103.84, 88.71, 87.15, 85.68, 85.65, 30.93, 22.54, 21.79, 18.40. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{ClF}_6\text{N}_4\text{PRu}$: C, 41.22; H, 3.62; N, 9.16. Found: C, 41.09; H, 3.54; N, 9.07. CCDC number: 1846966.

For further analysis of thermogravimetric curves of pyridyltriazole ruthenium complexes, as follows:

“For compound **1a**, the weight loss at 242 °C should be caused by the loss of chlorine element, while the weight loss at 261 °C might be attributed to the loss in ligand. In comparison, after the loss of one chlorine element in the beginning, the great weight loss at 218 °C might be attributed to the quick loss of non-coordinating anions (PF_6^-) and then the loss of ligand at 223 °C happened.”

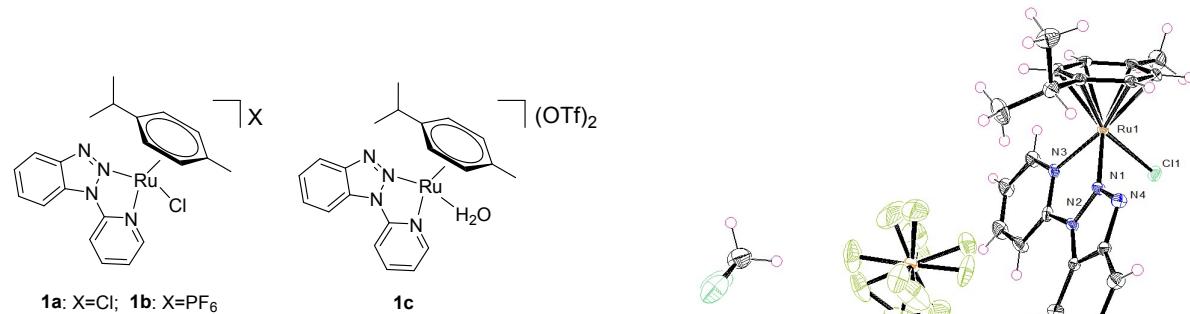


Figure S1. ORTEP structure of [{Ru(*p*-cymene)}(Pyridyltriazole)Cl][PF₆] (thermal ellipsoids set at 50% probability, DCM as co-crystallized solvent molecules).

Table S1. Crystallographic data for [{Ru(*p*-cymene)}(Pyridyltriazole)Cl][PF₆]

Empirical formula	C ₂₂ H ₂₄ Cl ₃ F ₆ N ₄ P Ru
Formula weight	696.84
Temperature	100 K
Wavelength	0.71075 Å
Crystal system, space group	Monoclinic, P 1 21/n1
Unit cell dimensions	a=8.1716(4) Å, alpha=90° b=30.1115(13) Å, beta=95.159(2)° c=10.9853(5) Å, gamma=90°
Volume	2692.1(2) Å ³
Z, Calculated density	4, 1.719 mg/m ³
Absorption coefficient	1.001 mm ⁻¹
F(000)	1392
Theta range for data collection	2.982 to 26.413°
Limiting indices	-10<=h<=10, -37<=k<=37, -13<=l<=13
Reflections collected / unique	30775/5494 [R(int) = 0.0283]
Completeness to theta = 25.242°	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6661
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5494/198/392
Goodness-of-fit on F ²	1.266
Final R indices [I>2sigma(I)]	R1=0.0457, wR2=0.0973
R indices (all data)	R1 = 0.0490, wR2 = 0.0986
Largest diff. peak and hole	1.247 and -1.152 e. Å ⁻³
CCDC number	1846966

Procedure for the synthesis of [{Ru(*p*-cymene)}(pyridyltriazole)H₂O]**[OTf]₂**

Under N₂ atmosphere, [{Ru(*p*-cymene)}(pyridyltriazole)Cl][Cl] (0.467 g, 1 mmol) and water (10 mL) was added to an oven-dried 100-mL Schlenk tube equipped with a stir bar. Then, the tube was closed and the resulting mixture was stirred at room temperature for 1 h. AgOTf (0.642 g, 2.5 mmol, 2.5 equiv) was added in portions with vigorously stirring for 2 h. After completion, the suspensions were filtered through a syringe filter (0.2 μm, nylon)

into a clean round-bottom flask. The solvent was removed under vacuum and the resulting solid was dried overnight in vacuo to give the PTA-Ru product **1c**.

Yellow oil, 75 % yield; ¹H NMR (400 MHz, D₂O) δ 9.52 (d, *J* = 5.6 Hz, 1H), 8.51 – 8.36 (m, 2H), 8.27 (dd, *J* = 20.2, 8.6 Hz, 2H), 7.90 (t, *J* = 7.9 Hz, 1H), 7.83 – 7.66 (m, 2H), 6.36 (dd, *J* = 15.4, 6.3 Hz, 2H), 6.11 (t, *J* = 6.1 Hz, 2H), 2.64 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.13 (s, 3H), 1.01 (dd, *J* = 11.3, 6.9 Hz, 6H). ¹³C NMR (101 MHz, D₂O) δ 154.99, 147.76, 147.56, 144.35, 133.36, 131.41, 128.30, 126.13, 120.61, 114.16, 111.66, 104.97, 104.82, 87.85, 86.88, 84.27, 84.18, 30.59, 21.34, 21.00, 17.76. Anal. Calcd for C₂₃H₂₂F₆N₄O₆RuS₂: C, 37.86; H, 3.04; N, 7.68. Found: C, 37.71; H, 3.13; N, 7.60.

3. General procedure for the alkylation of 2-oxindole with alcohols

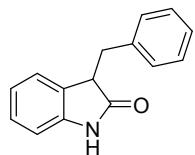
Under N₂ atmosphere, 2-oxindole (0.5 mmol), alcohols (1.0 mmol), pyridyltriazole ruthenium(II) catalyst **1b** (1 mol%), KOH (2.0 equiv.), were introduced in a Schlenk tube (25 mL), successively. The tube was evacuated and refilled with high purity nitrogen for three times. Then, the Schlenk tube was closed and the resulting mixture was stirred at 130 °C for 1 h under solvent-free conditions. After cooling down to room temperature, water was added to quench the reaction and extracted with EtOAc (3x5 mL), the organic phases were concentrated by removing the solvent under vacuum. Finally, the residue was purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 10:1) as eluent to give the desired product.

4. General procedure for the C-H hydroxylation process

Under N₂ atmosphere, 2-oxindole (0.5 mmol), alcohols (1.0 mmol), pyridyltriazole ruthenium(II) catalyst **1b** (1 mol%), KOH (2.0 equiv.) were introduced in a Schlenk tube (50 mL), successively. The tube was evacuated and refilled with high purity nitrogen for three times. Then, the Schlenk tube was closed and the resulting mixture was stirred at 130 °C for 1 h. After cooling down to room temperature, EtOAc (5 mL) was introduced, the reaction mixture was stirred under air for 12 h. Finally, concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 3:1) as eluent to give the desired product.

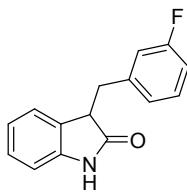
5. Analytical data of the obtained compounds

(1) 3-benzyl-1,3-dihydroindol-2-one (**4aa**).²



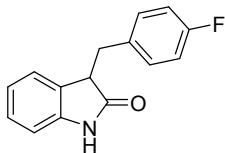
Pale yellow needles; Mp. 128-130 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 7.28 – 7.13 (m, 6H), 6.88 (dd, *J* = 14.1, 7.4 Hz, 2H), 6.73 (d, *J* = 7.4 Hz, 1H), 3.75 (dd, *J* = 9.3, 4.5 Hz, 1H), 3.50 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.93 (dd, *J* = 13.7, 9.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 180.05, 141.56, 137.81, 129.41, 128.99, 128.33, 127.95, 126.66, 124.79, 121.98, 109.84, 47.60, 36.61.

(2) 3-(3-fluoro-benzyl)-1,3-dihydroindol-2-one (**4ab**)



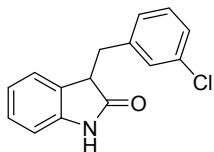
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.36 (s, 1H), 7.23 – 7.14 (m, 2H), 6.99 – 6.84 (m, 5H), 6.78 (d, J = 7.4 Hz, 1H), 3.74 (dd, J = 8.9, 4.6 Hz, 1H), 3.46 (dd, J = 13.8, 4.6 Hz, 1H), 2.96 (dd, J = 13.8, 9.0 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.91, 162.71 (d, J = 245.8 Hz), 141.64, 140.36 (d, J = 7.3 Hz), 129.81 (d, J = 8.3 Hz), 128.66, 128.20, 125.15 (d, J = 2.8 Hz), 124.66, 122.20, 116.30 (d, J = 21.2 Hz), 113.68 (d, J = 21.0 Hz), 110.07, 47.38, 36.24. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{FNO} [\text{M}+\text{H}]^+$ 242.0981, found 242.0985.

(3) 3-(4-fluoro-benzyl)-1,3-dihydroindol-2-one (4ac).²



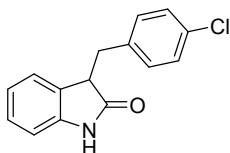
Colorless needles; Mp. 150-151 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.96 – 6.80 (m, 5H), 3.72 (dd, J = 8.5, 4.6 Hz, 1H), 3.42 (dd, J = 13.8, 4.6 Hz, 1H), 2.99 (dd, J = 13.8, 8.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.56, 161.76 (d, J = 244.7 Hz), 141.51, 133.23 (d, J = 3.3 Hz), 130.92 (d, J = 7.9 Hz), 128.69, 128.13, 124.71, 122.15, 115.13 (d, J = 21.2 Hz), 109.84, 47.59, 35.69.

(4) 3-(3-chloro-benzyl)-1,3-dihydroindol-2-one (4ad)



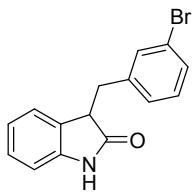
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 9.04 (s, 1H), 7.22–7.13 (m, 4H), 7.06 (d, J = 6.7 Hz, 1H), 6.93 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 7.4 Hz, 1H), 3.74 (dd, J = 8.9, 4.7 Hz, 1H), 3.44 (dd, J = 13.8, 4.7 Hz, 1H), 2.95 (dd, J = 13.8, 9.0 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.58, 141.52, 139.83, 134.11, 129.60, 129.53, 128.56, 128.23, 127.64, 126.97, 124.68, 122.22, 110.00, 47.30, 36.20. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{ClNO} [\text{M}+\text{H}]^+$ 258.0686, found 258.0685.

(5) 3-(4-chloro-benzyl)-1,3-dihydroindol-2-one (4ae).²



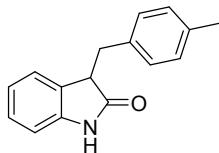
Pale yellow crystals; Mp. 138-140 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 7.25 – 7.17 (m, 3H), 7.10 (d, J = 8.4 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H), 6.86 (t, J = 8.3 Hz, 2H), 3.75 (dd, J = 8.4, 4.6 Hz, 1H), 3.43 (dd, J = 13.8, 4.6 Hz, 1H), 3.03 (dd, J = 13.8, 8.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.88, 141.65, 136.12, 132.54, 130.82, 128.64, 128.46, 128.20, 124.65, 122.19, 110.05, 47.47, 35.84.

(6) 3-(3-bromo-benzyl)-1,3-dihydroindol-2-one (4af)



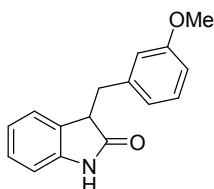
Pale yellow crystals; Mp. 158-160 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.34 (s, 1H), 7.36 – 7.30 (m, 2H), 7.18 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 5.5 Hz, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 6.78 (d, J = 7.4 Hz, 1H), 3.72 (dd, J = 8.9, 4.7 Hz, 1H), 3.43 (dd, J = 13.8, 4.7 Hz, 1H), 2.92 (dd, J = 13.8, 9.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 179.68, 141.53, 140.09, 132.39, 129.85, 129.83, 128.51, 128.18, 128.04, 124.61, 122.31, 122.16, 110.02, 47.28, 36.11. HRMS (ESI) m/z Calculated for C₁₅H₁₂BrNO [M+H]⁺ 302.0181, found 302.0183.

(7) 3-(4-methyl-benzyl)-1,3-dihydroindol-2-one (4ag).²



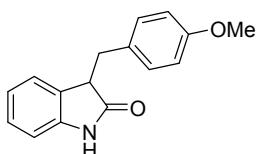
White powder; Mp. 149-150 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.35 (s, 1H), 7.15 (t, J = 7.7 Hz, 1H), 7.09 – 7.02 (m, 4H), 6.92 – 6.84 (m, 2H), 6.74 (d, J = 7.4 Hz, 1H), 3.72 (dd, J = 9.3, 4.5 Hz, 1H), 3.45 (dd, J = 13.7, 4.5 Hz, 1H), 2.88 (dd, J = 13.7, 9.4 Hz, 1H), 2.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 180.22, 141.64, 136.18, 134.76, 129.32, 129.21, 129.08, 127.95, 124.85, 122.00, 109.89, 47.73, 36.25, 21.11.

(8) 3-(3-methoxy-benzyl)-1,3-dihydroindol-2-one (4ah)



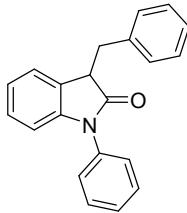
Colorless needles; Mp. 121-121 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.47 (s, 1H), 7.15 (t, J = 7.8 Hz, 2H), 6.92 – 6.84 (m, 2H), 6.81 – 6.70 (m, 4H), 3.74 (dd, J = 9.3, 4.5 Hz, 1H), 3.70 (s, 3H), 3.47 (dd, J = 13.7, 4.5 Hz, 1H), 2.89 (dd, J = 13.7, 9.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 180.27, 159.55, 141.73, 139.48, 129.36, 129.10, 128.03, 124.85, 122.05, 121.87, 114.78, 112.46, 110.00, 55.15, 47.60, 36.70. HRMS (ESI) m/z Calculated for C₁₆H₁₅NO₂ [M+H]⁺ 254.1181, found 254.1186.

(9) 3-(4-methoxy-benzyl)-1,3-dihydroindol-2-one (4ai).²



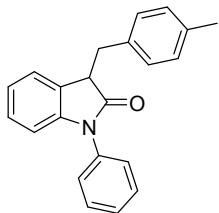
Colorless needles; Mp. 110-111 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 6.81 (t, J = 8.0 Hz, 3H), 3.79 (s, 3H), 3.74 (dd, J = 8.8, 4.3 Hz, 1H), 3.45 (dd, J = 13.8, 4.4 Hz, 1H), 2.94 (dd, J = 13.8, 9.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 180.17, 158.28, 141.64, 130.38, 129.73, 129.10, 127.90, 124.76, 121.95, 113.67, 109.85, 55.13, 47.81, 35.71.

(10) 3-benzyl-1-phenylindolin-2-one (4aj).²



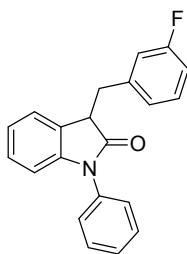
Pale yellow needles; Mp. 158-161 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (t, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.29 – 7.22 (m, 5H), 7.21 – 7.14 (m, 3H), 7.05 – 6.99 (m, 2H), 6.69 (d, $J = 7.9$ Hz, 1H), 3.96 (dd, $J = 8.1, 4.4$ Hz, 1H), 3.56 (dd, $J = 13.5, 4.4$ Hz, 1H), 3.21 (dd, $J = 13.5, 8.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.46, 144.43, 137.31, 134.50, 129.62, 129.61, 128.22, 128.14, 128.08, 127.91, 126.74, 126.69, 124.74, 122.55, 109.21, 47.26, 37.16.

(11) 3-(4-methyl-benzyl)-1-phenylindolin-2-one (4ak)



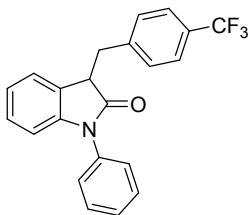
Pale yellow needles; Mp. 169-171 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (t, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.21 – 7.15 (m, 1H), 7.09 (s, 4H), 7.05 – 6.99 (m, 2H), 6.71 (d, $J = 7.9$ Hz, 1H), 3.94 (dd, $J = 8.3, 4.4$ Hz, 1H), 3.53 (dd, $J = 13.6, 4.4$ Hz, 1H), 3.16 (dd, $J = 13.6, 8.3$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.55, 144.42, 136.21, 134.59, 134.28, 129.59, 129.47, 128.93, 128.32, 128.04, 127.84, 126.70, 124.78, 122.51, 109.19, 47.32, 36.77, 21.10. HRMS (ESI) m/z Calculated for $\text{C}_{22}\text{H}_{19}\text{NO}$ [M+H] $^+$ 314.1545, found 314.1546.

(12) 3-(3-fluoro-benzyl)-1-phenylindolin-2-one (4al)



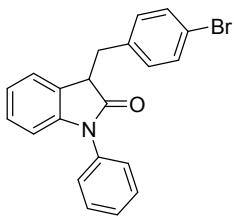
Pale yellow needles; Mp. 131-134 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (t, $J = 7.7$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.22 – 7.17 (m, 2H), 7.12 (dtd, $J = 9.8, 7.8, 2.9$ Hz, 2H), 6.97 (dd, $J = 6.6, 5.7$ Hz, 2H), 6.93 – 6.80 (m, 3H), 6.64 (d, $J = 7.9$ Hz, 1H), 3.87 (dd, $J = 7.8, 4.6$ Hz, 1H), 3.45 (dd, $J = 13.6, 4.5$ Hz, 1H), 3.17 (dd, $J = 13.6, 7.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 175.09, 161.52 (d, $J = 245.7$ Hz), 143.28, 138.77 (d, $J = 7.3$ Hz), 133.32, 128.60, 128.55, 128.52, 127.04 (d, $J = 3.6$ Hz), 126.64, 125.52, 124.25 (d, $J = 2.8$ Hz), 123.50, 121.62, 115.31 (d, $J = 21.2$ Hz), 112.57 (d, $J = 20.9$ Hz), 108.26, 45.85, 35.60. HRMS (ESI) m/z Calculated for $\text{C}_{21}\text{H}_{16}\text{FNO}$ [M+H] $^+$ 318.1294, found 318.1289.

(13) 1-phenyl-3-(4-(trifluoromethyl)-benzyl)indolin-2-one (4am)



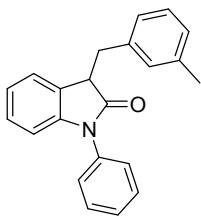
White needles; Mp. 138-140 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 7.5, 6.2 Hz, 4H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.09 (m, 3H), 7.08 – 6.93 (m, 2H), 6.64 (d, *J* = 7.9 Hz, 1H), 3.93 (dd, *J* = 7.4, 4.5 Hz, 1H), 3.49 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.29 (dd, *J* = 13.5, 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 175.95, 144.44, 141.37, 134.33, 130.00, 129.66, 129.11 (d, *J* = 32.4 Hz), 128.23 (d, *J* = 6.2 Hz), 127.54, 126.55, 125.65, 125.07 (q, *J* = 3.7 Hz), 124.52, 122.95, 122.78, 109.46, 46.89, 36.81. HRMS (ESI) m/z Calculated for C₂₂H₁₆F₃NO [M+H]⁺ 368.1262, found 368.1263.

(14) 3-(4-bromo-benzyl)-1-phenylindolin-2-one (4an)



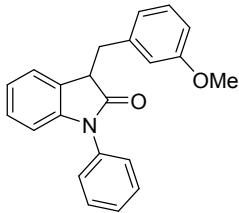
Pale yellow needles; Mp. 170-171 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.11 (ddd, *J* = 8.1, 4.6, 1.4 Hz, 1H), 6.99 (dt, *J* = 16.3, 7.0 Hz, 4H), 6.63 (d, *J* = 7.9 Hz, 1H), 3.85 (dd, *J* = 7.5, 4.5 Hz, 1H), 3.38 (dd, *J* = 13.6, 4.5 Hz, 1H), 3.16 (dd, *J* = 13.6, 7.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.14, 144.41, 136.24, 134.40, 131.41, 131.29, 129.68, 128.18, 128.16, 127.71, 126.61, 124.61, 122.73, 120.77, 109.43, 46.99, 36.42. HRMS (ESI) m/z Calculated for C₂₁H₁₆BrNO [M+H]⁺ 378.0494, found 378.0492.

(15) 3-(3-methyl-benzyl)-1-phenylindolin-2-one (4ao)



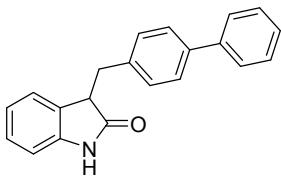
Pale yellow needles; Mp. 155-157 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.87 (m, 2H), 6.63 (d, *J* = 7.9 Hz, 1H), 3.87 (dd, *J* = 8.2, 4.5 Hz, 1H), 3.46 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.08 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.25 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 175.42, 143.29, 136.65, 136.20, 133.48, 129.23, 128.48, 127.16, 126.98, 126.93, 126.75, 126.33, 125.58, 125.54, 123.70, 121.39, 108.06, 46.12, 36.03, 20.27. HRMS (ESI) m/z Calculated for C₂₂H₁₉NO [M+H]⁺ 314.1545, found 314.1549.

(16) 3-(3-methoxy-benzyl)-1-phenylindolin-2-one (4ap)



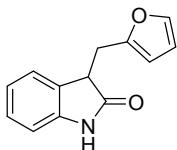
Pale yellow needles; Mp. 141-142 °C ; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (t, $J = 7.7$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.21 (dd, $J = 5.8, 4.5$ Hz, 2H), 7.15 – 7.07 (m, 2H), 6.97 (dd, $J = 6.5, 5.6$ Hz, 2H), 6.79 – 6.71 (m, 2H), 6.64 (d, $J = 7.8$ Hz, 2H), 3.89 (dd, $J = 8.2, 4.4$ Hz, 1H), 3.66 (s, 3H), 3.48 (dd, $J = 13.5, 4.4$ Hz, 1H), 3.12 (dd, $J = 13.5, 8.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.43, 159.48, 144.46, 138.91, 134.55, 129.62, 129.21, 128.20, 128.08, 127.93, 126.70, 124.79, 122.56, 122.05, 114.68, 112.77, 109.25, 55.15, 47.18, 37.24. HRMS (ESI) m/z Calculated for $\text{C}_{22}\text{H}_{19}\text{NO}_2$ [M+H] $^+$ 330.1494, found 330.1495.

(17) 3-((1,1'-biphenyl)-4-ylmethyl)-1-phenylindolin-2-one (4aq).²



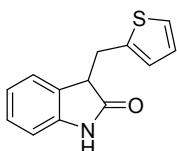
White solid; Mp. 153-154 °C ; ^1H NMR (400 MHz, CDCl_3) δ 9.08 (s, 1H), 7.60 – 7.52 (m, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 (t, $J = 7.7$ Hz, 1H), 6.87 (ddd, $J = 28.4, 17.5, 7.4$ Hz, 3H), 3.78 (dd, $J = 9.1, 4.5$ Hz, 1H), 3.52 (dd, $J = 13.7, 4.5$ Hz, 1H), 2.98 (dd, $J = 13.7, 9.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.67, 141.47, 140.70, 139.42, 136.87, 129.84, 128.97, 128.73, 128.02, 127.18, 126.96, 126.93, 124.83, 122.07, 109.80, 47.49, 36.24.

(18) 3-(furan-2-ylmethyl)indolin-2-one (4ar).²



White powder; Mp. 146-147 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.29 (s, 1H), 7.33 (d, $J = 1.3$ Hz, 1H), 7.19 (t, $J = 7.7$ Hz, 1H), 6.92 (dd, $J = 14.2, 7.5$ Hz, 2H), 6.78 (d, $J = 7.4$ Hz, 1H), 6.28 (dd, $J = 3.0, 1.9$ Hz, 1H), 6.03 (d, $J = 3.1$ Hz, 1H), 3.82 (dd, $J = 9.5, 4.6$ Hz, 1H), 3.48 (dd, $J = 15.0, 4.6$ Hz, 1H), 2.98 (dd, $J = 15.1, 9.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.62, 151.92, 141.55, 141.47, 128.77, 128.10, 124.64, 122.25, 110.36, 109.82, 107.30, 45.21, 29.04.

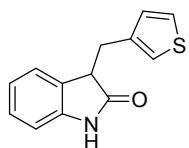
(19) 3-(thiophen-2-ylmethyl)indolin-2-one (4as).²



Yellow needles; Mp. 154-155 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.90 (s, 1H), 7.12 (ddd, $J = 7.1, 4.7, 1.6$ Hz, 1H), 7.01 (dd, $J = 5.1, 0.7$ Hz, 1H), 6.92 – 6.85 (m, 2H), 6.79 (dd, $J = 8.1, 4.6$ Hz, 2H), 6.70 (d, $J = 3.2$ Hz, 1H), 3.68

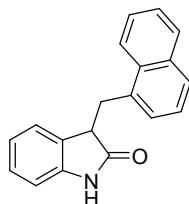
(dd, $J = 8.2, 4.4$ Hz, 1H), 3.53 (dd, $J = 14.8, 4.3$ Hz, 1H), 3.26 (dd, $J = 14.8, 8.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.20, 140.70, 138.62, 127.53, 127.21, 125.64, 125.38, 123.61, 123.25, 121.21, 108.84, 46.65, 29.64.

(20) 3-(thiophen-3-ylmethyl)indolin-2-one (4at)



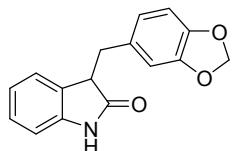
Yellow needles; Mp. 141-142 °C ^1H NMR (400 MHz, CDCl_3) δ 8.73 (s, 1H), 7.22 – 7.14 (m, 2H), 6.94 (dd, $J = 13.2, 5.4$ Hz, 2H), 6.90 – 6.82 (m, 3H), 3.72 (dd, $J = 8.5, 4.4$ Hz, 1H), 3.43 (dd, $J = 14.2, 4.4$ Hz, 1H), 3.10 (dd, $J = 14.2, 8.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.46, 141.48, 137.82, 129.04, 128.44, 128.05, 125.49, 124.59, 122.45, 122.17, 109.70, 47.04, 30.96. HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_{11}\text{NOS}$ [M+H]⁺ 230.0640, found 230.0644.

(21) 3-(naphthalen-1-ylmethyl)indolin-2-one (4au).²



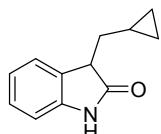
Yellow needles; Mp. 112-113 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.37 (s, 1H), 7.78 (dd, $J = 6.0, 3.4$ Hz, 1H), 7.74 – 7.68 (m, 2H), 7.59 (s, 1H), 7.45 – 7.39 (m, 2H), 7.33 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.13 (t, $J = 7.7$ Hz, 1H), 6.83 (t, $J = 7.6$ Hz, 2H), 6.70 (d, $J = 7.4$ Hz, 1H), 3.83 (dd, $J = 9.4, 4.5$ Hz, 1H), 3.63 (dd, $J = 13.7, 4.5$ Hz, 1H), 3.05 (dd, $J = 13.7, 9.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 180.15, 141.68, 135.50, 133.43, 132.39, 129.11, 128.14, 128.10, 128.08, 127.73, 127.70, 127.63, 126.08, 125.63, 124.89, 122.11, 110.01, 47.57, 36.90.

(22) 3-(benzo[d][1,3]dioxol-5-ylmethyl)indolin-2-one (4av).²



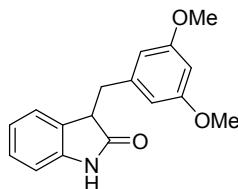
Pale yellow needles; Mp. 135-136 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.99 (s, 1H), 7.20 (t, $J = 7.7$ Hz, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.87 (dd, $J = 13.9, 7.6$ Hz, 2H), 6.70 (dd, $J = 4.7, 3.1$ Hz, 2H), 6.63 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.93 (s, 2H), 3.71 (dd, $J = 9.0, 4.6$ Hz, 1H), 3.42 (dd, $J = 13.8, 4.6$ Hz, 1H), 2.91 (dd, $J = 13.8, 9.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.66, 147.55, 146.30, 141.50, 131.47, 128.93, 128.00, 124.82, 122.57, 122.08, 109.79, 109.65, 108.06, 100.88, 47.71, 36.33.

(23) 3-(cyclopropylmethyl)indolin-2-one (4aw)



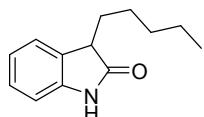
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 7.33 (d, $J = 7.4$ Hz, 1H), 7.23 (t, $J = 7.7$ Hz, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 7.7$ Hz, 1H), 3.61 – 3.54 (m, 1H), 2.11 – 2.01 (m, 1H), 1.85 – 1.73 (m, 1H), 0.91 – 0.80 (m, 1H), 0.51 – 0.37 (m, 2H), 0.28 – 0.20 (m, 1H), 0.14 – 0.08 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.35, 141.98, 130.00, 127.79, 124.42, 122.08, 109.90, 46.83, 35.58, 8.05, 5.31, 4.16. HRMS (ESI) m/z Calculated for $\text{C}_{12}\text{H}_{13}\text{NO} [\text{M}+\text{H}]^+$ 188.1075, found 188.1073.

(24) 3-(3,5-dimethoxybenzyl)indolin-2-one (4ax)



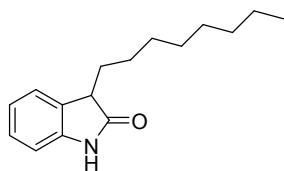
Yellow needleless; Mp. 166–168 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.24 (s, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 6.98 – 6.83 (m, 3H), 6.42 – 6.33 (m, 3H), 3.77 (dd, $J = 9.4, 4.3$ Hz, 1H), 3.73 (s, 6H), 3.47 (dd, $J = 13.7, 4.4$ Hz, 1H), 2.87 (dd, $J = 13.7, 9.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.95, 160.68, 141.60, 140.22, 129.07, 128.00, 124.92, 122.05, 109.86, 107.34, 99.02, 55.26, 47.45, 36.94. HRMS (ESI) m/z Calculated for $\text{C}_{17}\text{H}_{17}\text{NO}_3 [\text{M}+\text{H}]^+$ 284.1287, found 284.1291.

(25) 3-pentylindolin-2-one (4ay).²



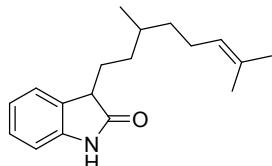
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 9.34 (d, $J = 44.7$ Hz, 1H), 7.24 (dd, $J = 12.2, 7.5$ Hz, 2H), 7.04 (t, $J = 7.3$ Hz, 1H), 6.95 (d, $J = 7.7$ Hz, 1H), 3.50 (t, $J = 6.0$ Hz, 1H), 2.09 – 1.89 (m, 2H), 1.54 – 1.41 (m, 1H), 1.38 – 1.22 (m, 5H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.15, 141.78, 129.99, 127.76, 124.08, 122.18, 109.82, 46.23, 31.79, 30.52, 25.47, 22.40, 14.00.

(26) 3-octylindolin-2-one (4az)



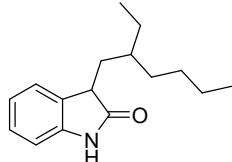
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 9.56 (s, 1H), 7.23 (dd, $J = 12.5, 7.5$ Hz, 2H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 7.7$ Hz, 1H), 3.50 (t, $J = 6.0$ Hz, 1H), 2.08 – 1.91 (m, 2H), 1.51 – 1.39 (m, 1H), 1.37 – 1.21 (m, 11H), 0.89 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.28, 141.88, 130.00, 127.76, 124.06, 122.16, 109.87, 46.27, 31.83, 30.57, 29.63, 29.34, 29.24, 25.82, 22.63, 14.08. HRMS (ESI) m/z Calculated for $\text{C}_{16}\text{H}_{23}\text{NO} [\text{M}+\text{H}]^+$ 246.1858, found 246.1855.

(27) 3-(3,7-dimethyloct-6-en-1-yl)indolin-2-one (4b)



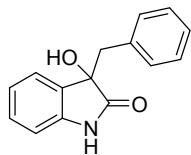
Colorless oil ; ^1H NMR (400 MHz, CDCl_3) δ 9.50 (d, $J = 15.2$ Hz, 1H), 7.23 (dd, $J = 12.1, 7.5$ Hz, 2H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 7.7$ Hz, 1H), 5.15 – 5.02 (m, 1H), 3.49 (t, $J = 5.9$ Hz, 1H), 2.07 – 1.86 (m, 4H), 1.69 (s, 3H), 1.60 (s, 3H), 1.52 – 1.24 (m, 4H), 1.22 – 1.08 (m, 2H), 0.90 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.21, 141.87, 131.13, 129.96, 127.78, 124.82, 124.07, 122.19, 109.86, 46.36, 36.88, 32.69, 32.45, 28.08, 25.71, 25.46, 19.41, 17.64. HRMS (ESI) m/z Calculated for $\text{C}_{18}\text{H}_{25}\text{NO} [\text{M}+\text{H}]^+$ 272.2014, found 272.2018.

(28) 3-(2-ethylhexyl)indolin-2-one (4c)



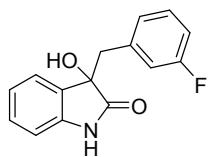
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 9.34 (s, 1H), 7.23 (t, $J = 7.7$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 7.7$ Hz, 1H), 3.50 (t, $J = 7.2$ Hz, 1H), 2.02 – 1.89 (m, 1H), 1.85 – 1.67 (m, 2H), 1.48 – 1.23 (m, 8H), 0.98 – 0.86 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.58, 141.65, 130.52, 127.71, 124.30, 122.06, 109.88, 44.10, 35.72, 35.27, 32.76, 28.57, 25.99, 23.04, 14.08, 10.23. HRMS (ESI) m/z Calculated for $\text{C}_{16}\text{H}_{23}\text{NO} [\text{M}+\text{H}]^+$ 246.1858, found 246.1855.

(29) 3-benzyl-3-hydroxyindolin-2-one (5aa)



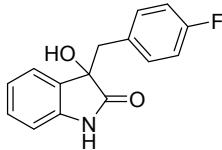
White solid; Mp. 122-124 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 7.17 – 7.04 (m, 5H), 6.99 – 6.84 (m, 3H), 6.61 (d, $J = 7.5$ Hz, 1H), 6.12 (s, 1H), 3.17 (d, $J = 12.6$ Hz, 1H), 3.01 (d, $J = 12.6$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.24, 142.14, 135.56, 131.44, 130.60, 129.31, 127.94, 126.79, 125.05, 121.64, 109.74, 77.06, 43.96. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{NO}_2 [\text{M}+\text{H}]^+$ 240.1025, found 240.1029.

(30) 3-(3-fluorobenzyl)-3-hydroxyindolin-2-one (5ab)



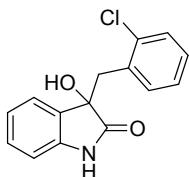
Pale yellow solid; Mp. 144-145 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 10.17 (s, 1H), 7.18 – 7.11 (m, 3H), 6.98 – 6.90 (m, 2H), 6.75 (dd, $J = 15.9, 8.9$ Hz, 2H), 6.67 (d, $J = 7.7$ Hz, 1H), 6.24 (s, 1H), 3.22 (d, $J = 12.7$ Hz, 1H), 3.05 (d, $J = 12.7$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.16, 161.91 (d, $J = 242.4$ Hz), 142.08, 138.50 (d, $J = 7.6$ Hz), 131.21, 129.73 (d, $J = 8.3$ Hz), 129.49, 126.80 (d, $J = 2.5$ Hz), 125.05, 121.78, 117.19 (d, $J = 21.1$ Hz), 113.66 (d, $J = 20.8$ Hz), 109.89, 76.90, 43.47. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{FNO}_2 [\text{M}+\text{H}]^+$ 258.0930, found 258.0926.

(31) 3-(4-fluorobenzyl)-3-hydroxyindolin-2-one (5ac)



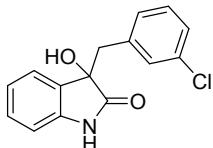
Pale yellow solid; Mp. 126-127 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.09 (s, 1H), 7.12 (ddd, J = 10.4, 8.4, 4.3 Hz, 2H), 6.93 (d, J = 7.4 Hz, 5H), 6.63 (d, J = 7.6 Hz, 1H), 6.14 (s, 1H), 3.15 (d, J = 12.8 Hz, 1H), 2.98 (d, J = 12.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.20, 161.45 (d, J = 242.1 Hz), 142.08, 132.37 (d, J = 8.0 Hz), 131.74 (d, J = 3.0 Hz), 131.28, 129.40, 125.03, 121.72, 114.69 (d, J = 21.0 Hz), 109.79, 76.95, 42.98. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{FNO}_2$ [M+H] $^+$ 258.0930, found 258.0931.

(32) 3-(2-chlorobenzyl)-3-hydroxyindolin-2-one (5ad)



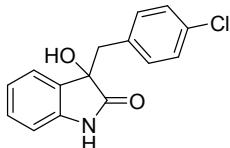
White solid; Mp. 168-171 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.15 (s, 1H), 7.21 – 7.07 (m, 4H), 6.99 – 6.82 (m, 3H), 6.64 (d, J = 7.6 Hz, 1H), 6.20 (s, 1H), 3.20 – 3.14 (m, 1H), 3.02 – 2.97 (m, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.05, 142.04, 138.17, 132.52, 131.13, 130.38, 129.75, 129.51, 129.37, 126.85, 125.06, 121.75, 109.88, 76.82, 43.31. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{ClNO}_2$ [M+H] $^+$ 274.0635, found 274.0630.

(33) 3-(3-chlorobenzyl)-3-hydroxyindolin-2-one (5ae)



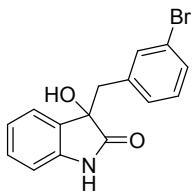
Pale yellow needles; Mp. 155-157 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.26 (s, 1H), 7.39 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 7.23 – 7.16 (m, 2H), 7.12 (ddd, J = 7.7, 6.5, 2.5 Hz, 1H), 6.85 – 6.78 (m, 2H), 6.70 (d, J = 7.7 Hz, 1H), 6.20 (s, 1H), 3.30 (d, J = 13.5 Hz, 1H), 3.13 (d, J = 13.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.47, 141.84, 134.57, 133.65, 132.61, 131.07, 129.42, 129.36, 128.81, 126.87, 125.08, 121.60, 109.80, 76.34, 76.34. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{ClNO}_2$ [M+H] $^+$ 274.0635, found 274.0636.

(34) 3-(4-chlorobenzyl)-3-hydroxyindolin-2-one (5af)



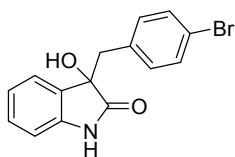
Pale yellow needles; Mp. 142-143 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.10 (s, 1H), 7.19 – 7.08 (m, 4H), 6.92 (dt, J = 6.6, 2.8 Hz, 3H), 6.63 (d, J = 7.6 Hz, 1H), 6.17 (s, 1H), 3.16 (d, J = 12.7 Hz, 1H), 2.99 (d, J = 12.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.09, 142.05, 134.63, 132.40, 131.62, 131.19, 129.46, 127.94, 125.03, 121.78, 109.84, 76.88, 43.14. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{ClNO}_2$ [M+H] $^+$ 274.0635, found 274.0638.

(35) 3-(3-bromobenzyl)-3-hydroxyindolin-2-one (5ag)



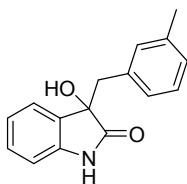
Pale yellow needles; Mp. 135-136 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.15 (s, 1H), 7.31 (dd, J = 8.0, 1.0 Hz, 1H), 7.12 (ddt, J = 15.6, 12.4, 4.5 Hz, 4H), 6.92 (ddd, J = 10.3, 5.6, 1.7 Hz, 2H), 6.65 (d, J = 7.7 Hz, 1H), 6.20 (s, 1H), 3.17 (d, J = 12.7 Hz, 1H), 2.98 (d, J = 12.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.04, 142.04, 138.45, 133.29, 131.12, 130.06, 129.75, 129.74, 129.51, 125.06, 121.75, 121.21, 109.90, 76.84, 43.30. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{BrNO}_2$ [M+H] $^+$ 318.0130, found 318.0129.

(36) 3-(4-bromobenzyl)-3-hydroxyindolin-2-one (5ah)



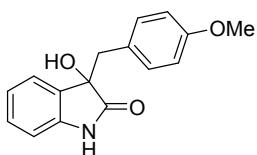
Pale yellow needles; Mp. 161-162 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.12 (s, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.16 – 7.09 (m, 2H), 6.93 (td, J = 7.5, 0.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 7.6 Hz, 1H), 6.19 (s, 1H), 3.15 (d, J = 12.7 Hz, 1H), 2.98 (d, J = 12.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.09, 142.06, 135.04, 132.80, 131.19, 130.86, 129.48, 125.03, 121.80, 120.21, 109.87, 76.84, 43.22. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{12}\text{BrNO}_2$ [M+H] $^+$ 318.0130, found 318.0133.

(37) 3-hydroxy-3-(3-methylbenzyl)indolin-2-one (5ai)



Pale yellow needles; Mp. 155-156 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.06 (s, 1H), 7.15 – 7.08 (m, 2H), 6.92 (tt, J = 4.8, 2.9 Hz, 3H), 6.73 (s, 1H), 6.68 (d, J = 7.4 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 6.11 (s, 1H), 3.14 (d, J = 12.6 Hz, 1H), 2.98 (d, J = 12.6 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.29, 142.18, 136.76, 135.46, 131.55, 131.36, 129.29, 127.80, 127.69, 127.45, 125.09, 121.61, 109.76, 77.10, 43.96, 21.43. HRMS (ESI) m/z Calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_2$ [M+H] $^+$ 254.1181, found 254.1179.

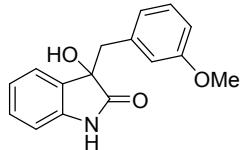
(38) 3-hydroxy-3-(4-methoxybenzyl)indolin-2-one (5aj)



Pale yellow needles; Mp. 122-124 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.03 (s, 1H), 7.12 (t, J = 7.7 Hz, 2H), 6.92 (t, J = 7.1 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 6.63 (dd, J = 15.1, 8.1 Hz, 3H), 6.06 (s, 1H), 3.64 (s, 3H), 3.09 (d, J = 12.8 Hz, 1H), 2.94 (d, J = 12.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 179.32, 158.21, 142.18, 131.58,

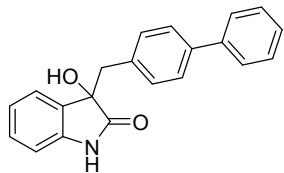
131.55, 129.28, 127.35, 125.01, 121.66, 113.38, 109.72, 77.12, 55.28, 43.07. HRMS (ESI) m/z Calculated for C₁₆H₁₅NO₃ [M+H]⁺ 270.1130, found 270.1135.

(39) 3-hydroxy-3-(3-methoxybenzyl)indolin-2-one (5ak)



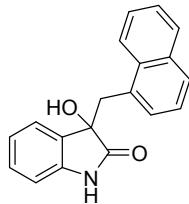
Pale yellow needles; Mp. 136-137 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.06 (s, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.67 – 6.60 (m, 2H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 6.14 (s, 1H), 3.54 (s, 3H), 3.15 (d, *J* = 12.6 Hz, 1H), 3.01 (d, *J* = 12.5 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 179.21, 158.84, 142.22, 137.00, 131.51, 129.36, 128.93, 125.08, 122.96, 121.68, 116.03, 112.37, 109.79, 77.09, 55.10, 43.97. HRMS (ESI) m/z Calculated for C₁₆H₁₅NO₃ [M+H]⁺ 270.1130, found 270.1131.

(40) 3-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxyindolin-2-one (5al)



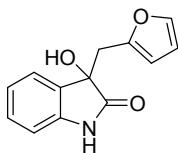
Pale yellow needles; Mp. 149-151 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.13 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 8.4 Hz, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.11 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.19 (s, 1H), 3.23 (d, *J* = 12.7 Hz, 1H), 3.07 (d, *J* = 12.6 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 179.23, 142.17, 140.14, 138.43, 134.90, 131.49, 131.23, 129.38, 129.32, 127.70, 126.85, 126.12, 125.07, 121.74, 109.81, 77.00, 43.54. HRMS (ESI) m/z Calculated for C₂₁H₁₇NO₂ [M+H]⁺ 316.1338, found 316.1336.

(41) 3-hydroxy-3-(naphthalen-1-ylmethyl)indolin-2-one (5am)



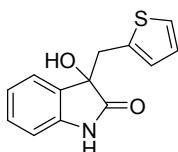
Pale yellow needles; Mp. 145-146 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.12 (s, 1H), 7.84 – 7.78 (m, 1H), 7.73 – 7.67 (m, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.48 (s, 1H), 7.43 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.30 (s, 1H), 3.40 (d, *J* = 12.6 Hz, 1H), 3.26 (d, *J* = 12.6 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 179.29, 142.13, 133.37, 133.04, 132.20, 131.50, 129.39, 129.17, 129.13, 127.86, 127.82, 127.16, 126.28, 125.93, 125.14, 121.73, 109.81, 77.25, 44.16. HRMS (ESI) m/z Calculated for C₁₉H₁₅NO₂ [M+H]⁺ 290.1181, found 290.1182.

(42) 3-(furan-2-ylmethyl)-3-hydroxyindolin-2-one (5an)



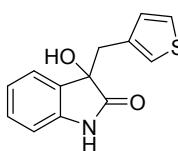
White needles; Mp. 119-121 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.19 (s, 1H), 7.35 (d, *J* = 1.1 Hz, 1H), 7.15 (td, *J* = 7.6, 1.1 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.21 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.16 (s, 1H), 5.78 (d, *J* = 3.1 Hz, 1H), 3.21 (d, *J* = 14.4 Hz, 1H), 3.06 (d, *J* = 14.4 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 183.67, 155.09, 147.03, 146.73, 136.30, 134.22, 129.53, 126.59, 115.52, 114.58, 112.68, 80.17, 41.20. HRMS (ESI) m/z Calculated for C₁₃H₁₁NO₃ [M+H]⁺ 230.0817, found 230.0821.

(43) 3-hydroxy-3-(thiophen-2-ylmethyl)indolin-2-one (5ao)



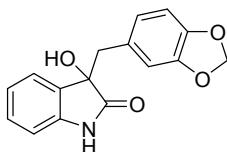
Pale yellow needles; Mp. 115-116 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.21 (s, 1H), 7.27 – 7.14 (m, 3H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.28 (s, 1H), 3.39 (d, *J* = 14.0 Hz, 1H), 3.30 (d, *J* = 14.0 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 178.91, 142.53, 137.14, 131.32, 129.63, 127.56, 126.59, 125.40, 124.89, 121.85, 109.90, 76.36, 38.22. HRMS (ESI) m/z Calculated for C₁₃H₁₁NO₂S [M+H]⁺ 246.0589, found 246.0591.

(44) 3-hydroxy-3-(thiophen-3-ylmethyl)indolin-2-one (5ap)



Pale yellow needles; Mp. 105-106 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.10 (s, 1H), 7.25 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.13 (td, *J* = 7.7, 1.1 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.60 (dd, *J* = 4.9, 0.8 Hz, 1H), 6.11 (s, 1H), 3.17 (d, *J* = 13.3 Hz, 1H), 3.03 (d, *J* = 13.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.32, 142.25, 135.91, 131.74, 129.76, 129.34, 125.11, 124.79, 123.68, 121.71, 109.79, 76.45, 38.41. HRMS (ESI) m/z Calculated for C₁₃H₁₁NO₂S [M+H]⁺ 246.0589, found 246.0593.

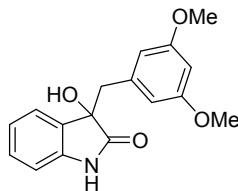
(45) 3-(benzo[d][1,3]dioxol-5-ylmethyl)-3-hydroxyindolin-2-one (5aq)



Pale yellow needles; Mp. 160-162 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.10 (s, 1H), 7.13 (t, *J* = 7.1 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.65 (dd, *J* = 7.7, 5.1 Hz, 2H), 6.45 (d, *J* = 1.4 Hz, 1H), 6.36 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.10 (s, 1H), 5.90 (d, *J* = 0.8 Hz, 2H), 3.10 (d, *J* = 12.8 Hz, 1H), 2.94 (d, *J* = 12.8 Hz, 1H). ¹³C NMR (101 MHz,

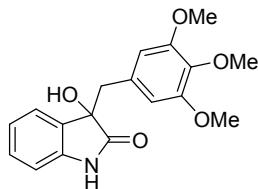
DMSO-*d*₆) δ 179.31, 146.83, 146.11, 142.17, 131.49, 129.34, 129.21, 125.05, 123.78, 121.70, 110.76, 109.80, 107.89, 101.05, 77.07, 43.48. HRMS (ESI) m/z Calculated for C₁₆H₁₃NO₄ [M+H]⁺ 284.0923, found 284.0925.

(46) 3-(3,5-dimethoxybenzyl)-3-hydroxyindolin-2-one (5ar)



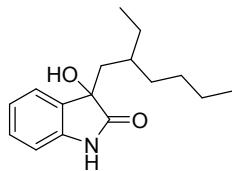
White solid; Mp. 127-128 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.07 (s, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.14 (s, 1H), 6.04 (d, *J* = 2.1 Hz, 2H), 3.54 (s, 6H), 3.12 (d, *J* = 12.5 Hz, 1H), 2.99 (d, *J* = 12.5 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.14, 159.96, 142.31, 137.66, 131.61, 129.34, 125.08, 121.64, 109.80, 108.59, 98.82, 77.07, 55.25, 44.23. HRMS (ESI) m/z Calculated for C₁₇H₁₇NO₄ [M+H]⁺ 300.1236, found 300.1239.

(47) 3-hydroxy-3-(3,4,5-trimethoxybenzyl)indolin-2-one (5as)



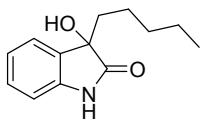
White solid; Mp. 160-161°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.34 (s, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.44 (s, 2H), 3.82 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.65 (s, 5H), 3.61 (s, 3H), 3.28 (dd, *J* = 13.8, 4.8 Hz, 1H), 2.93 – 2.82 (m, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 178.64, 152.80, 143.18, 136.41, 134.09, 129.59, 128.05, 124.90, 121.35, 109.60, 106.99, 60.42, 56.12, 46.86, 36.12. HRMS (ESI) m/z Calculated for C₁₈H₁₉NO₅ [M+H]⁺ 330.1341, found 330.1342.

(48) 3-(2-ethylhexyl)-3-hydroxyindolin-2-one (5at)



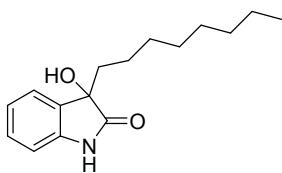
Colorless oil; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.46 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 10.9 Hz, 1H), 3.10 – 2.81 (m, 1H), 1.72 – 1.51 (m, 2H), 1.52 – 1.31 (m, 2H), 1.33 – 1.09 (m, 4H), 0.99 – 0.67 (m, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.52, 145.89, 142.68, 129.43, 128.75, 123.76, 122.52, 121.82, 110.28, 40.49, 34.56, 29.69, 28.02, 22.77, 14.32, 12.15. HRMS (ESI) m/z Calculated for C₁₆H₂₃NO₂ [M+H]⁺ 262.1807, found 262.1805.

(49) 3-hydroxy-3-pentylindolin-2-one (5au)



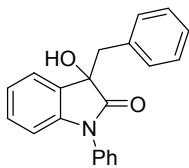
Pale yellow needles; Mp. 135-136 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.21 (s, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 5.82 (s, 1H), 1.82 – 1.67 (m, 2H), 1.22 – 1.09 (m, 4H), 1.09 – 0.99 (m, 1H), 0.98 – 0.87 (m, 1H), 0.77 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.86, 142.22, 132.63, 129.20, 124.21, 121.98, 109.89, 76.13, 38.16, 31.77, 22.80, 22.29, 14.21. HRMS (ESI) m/z Calculated for C₁₃H₁₇NO₂ [M+H]⁺ 220.1338, found 220.1340.

(50) 3-hydroxy-3-octylindolin-2-one (5av)



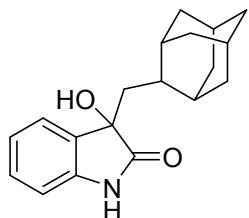
Colorless oil; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.21 (s, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 5.82 (s, 1H), 1.86 – 1.68 (m, 2H), 1.14 (s, 9H), 1.08 – 0.99 (m, 1H), 0.91 (td, *J* = 12.9, 7.4 Hz, 1H), 0.82 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.88, 142.23, 132.62, 129.16, 124.19, 121.94, 109.88, 76.13, 38.22, 31.65, 29.58, 29.21, 28.98, 23.13, 22.52, 14.36. HRMS (ESI) m/z Calculated for C₁₆H₂₃NO₂ [M+H]⁺ 262.1807, found 262.1805.

(51) 3-benzyl-3-hydroxy-1-phenylindolin-2-one (5aw)



Yellow solid; Mp. 163-165 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.44 (ddd, *J* = 29.6, 15.0, 7.5 Hz, 1H), 7.18 – 7.06 (m, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 6.9 Hz, 1H), 6.52 (s, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 3.32 (d, *J* = 12.4 Hz, 1H), 3.25 (d, *J* = 12.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 176.96, 143.29, 135.00, 134.47, 130.79, 130.45, 129.98, 129.53, 128.40, 128.00, 127.03, 126.77, 125.06, 123.12, 108.88, 77.42, 45.00. HRMS (ESI) m/z Calculated for C₂₁H₁₇NO₂ [M+H]⁺ 316.1338, found 316.1339.

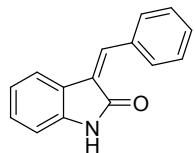
(52) (5ax)



White solid; Mp. 123-124 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.22 (s, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 5.67 (s, 1H), 1.89 (d, *J* = 13.8 Hz, 1H), 1.81 (d, *J* =

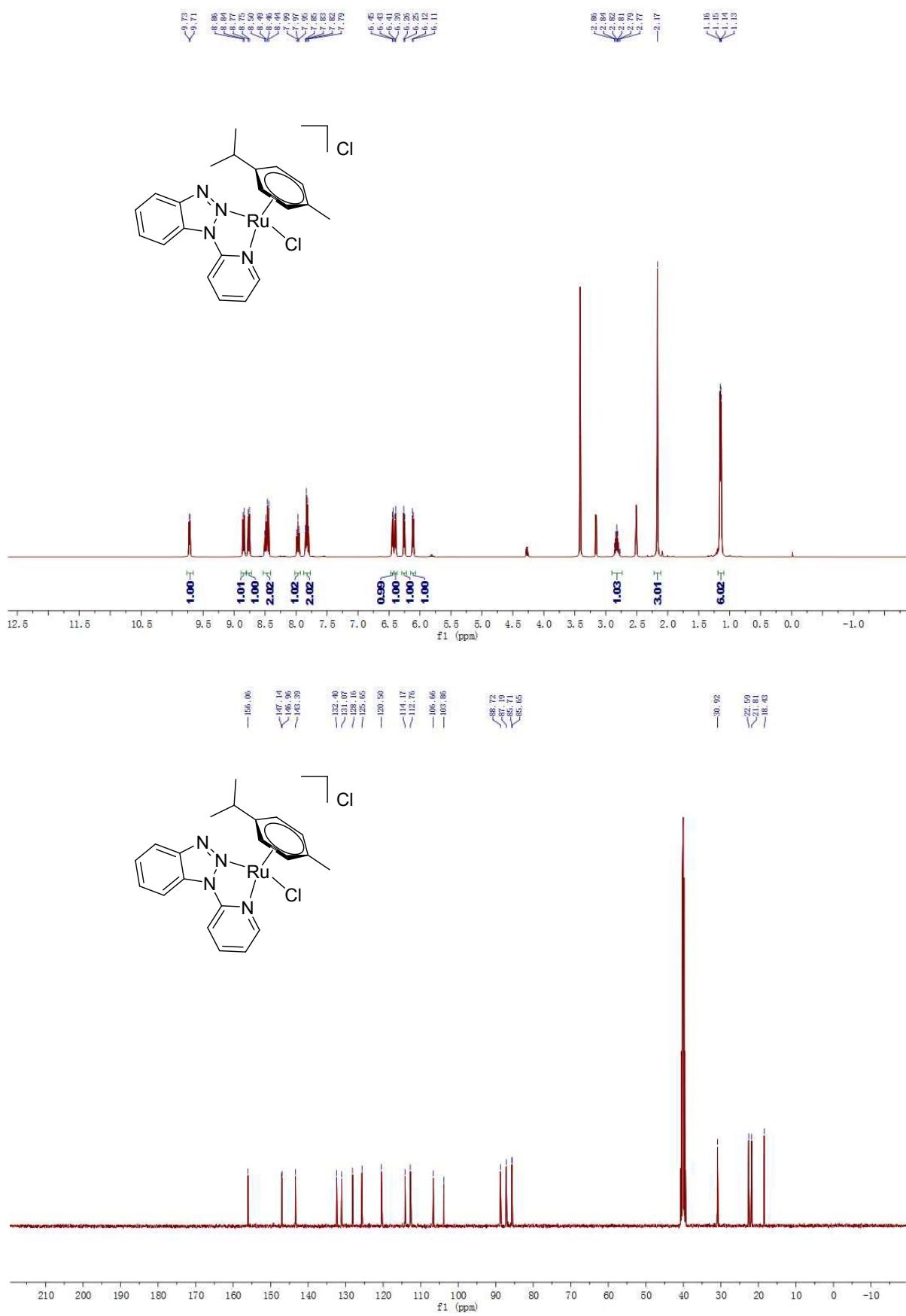
13.8 Hz, 1H), 1.71 (s, 3H), 1.51 (d, J = 11.8 Hz, 3H), 1.37 (d, J = 11.5 Hz, 3H), 1.22 (q, J = 12.1 Hz, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 180.08, 142.17, 133.03, 129.43, 125.48, 121.63, 109.96, 74.23, 52.07, 43.27, 36.75, 31.93, 28.36. HRMS (ESI) m/z Calculated for $\text{C}_{19}\text{H}_{23}\text{NO}_2$ [M+H] $^+$ 298.1807, found 298.1808.

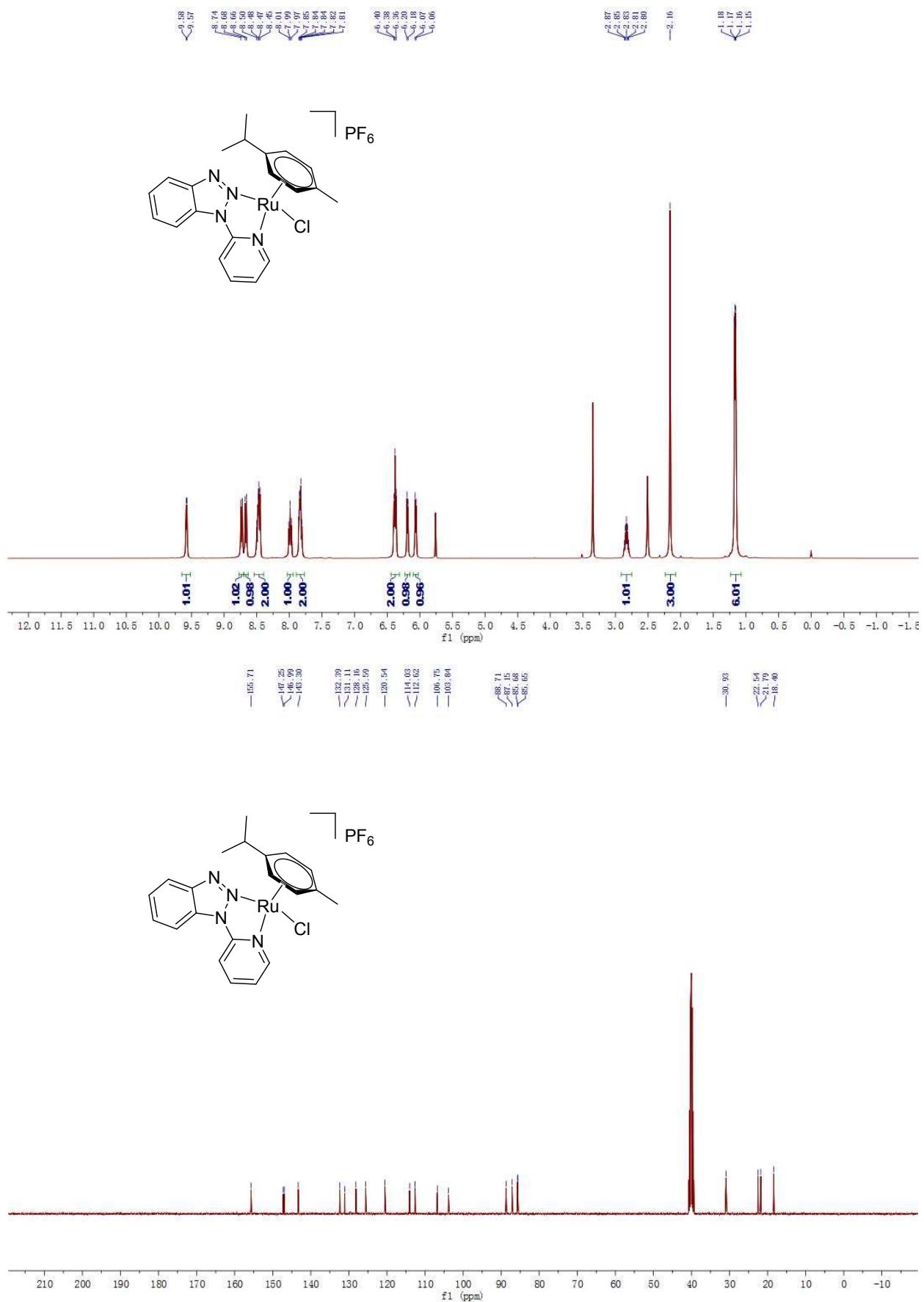
Intermediate C

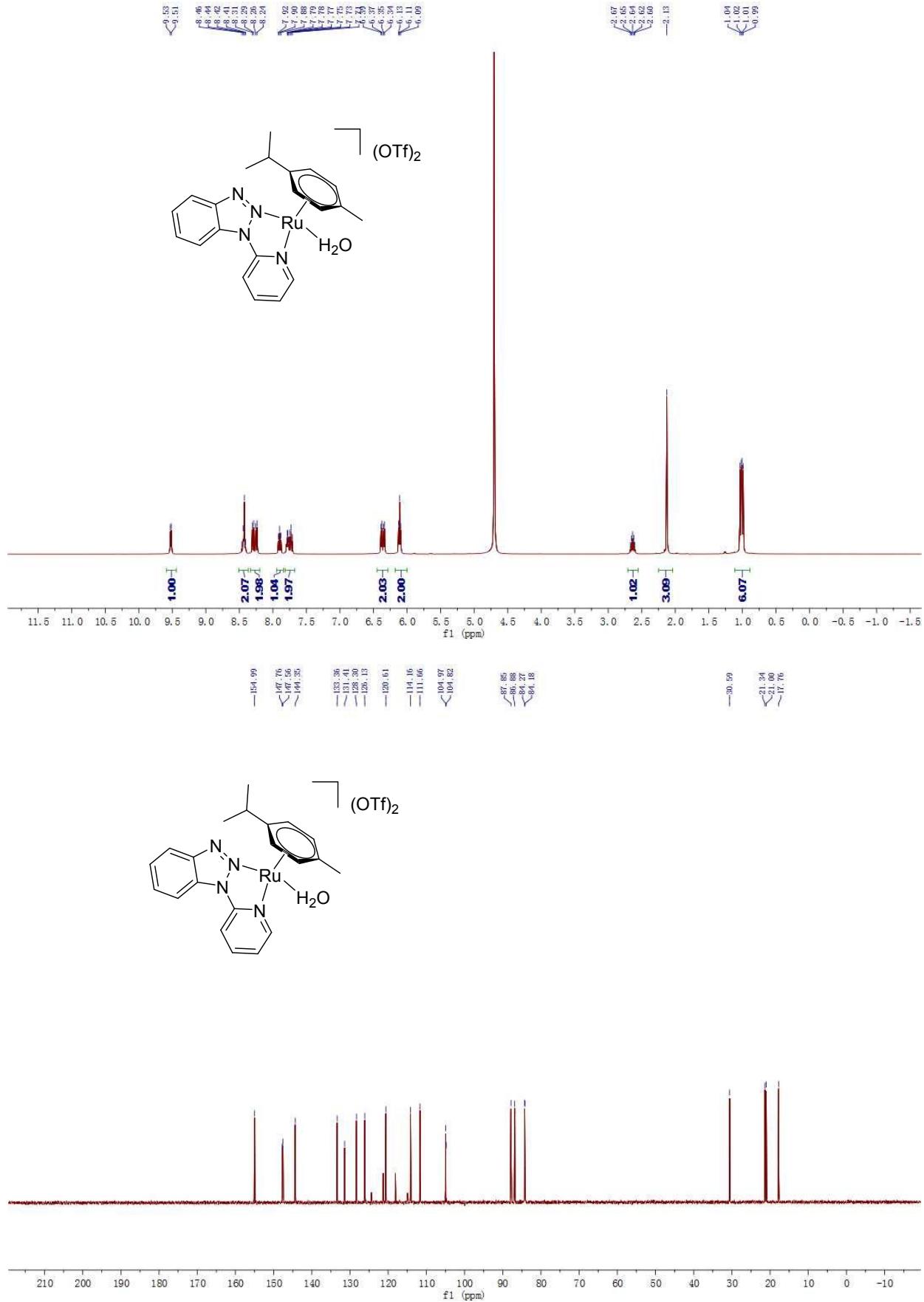


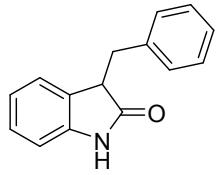
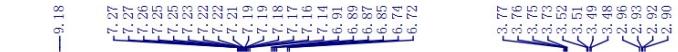
Yellow needles; Mp. 175-176 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.33 (s, 1H), 7.89 (s, 1H), 7.68 (dd, J = 13.7, 7.4 Hz, 3H), 7.58 – 7.42 (m, 3H), 7.24 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.89 (t, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.67, 141.84, 137.54, 134.90, 129.93, 129.68, 129.36, 128.68, 127.77, 123.04, 121.83, 121.73, 110.40. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{11}\text{NO}$ [M+H] $^+$ 222.0919, found 222.0917.

6. NMR spectra of obtained compounds

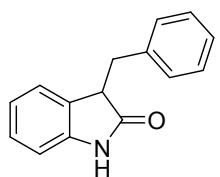
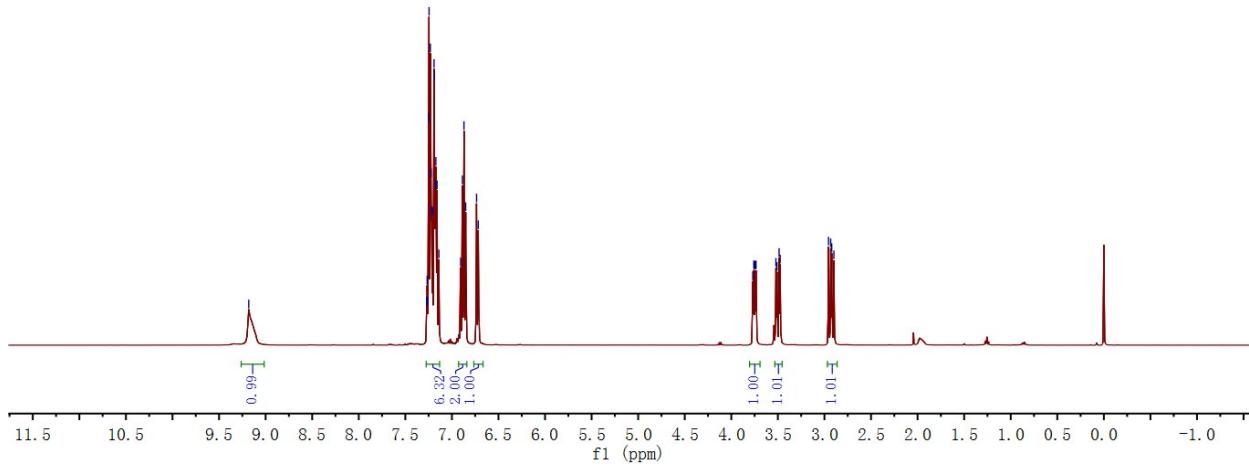




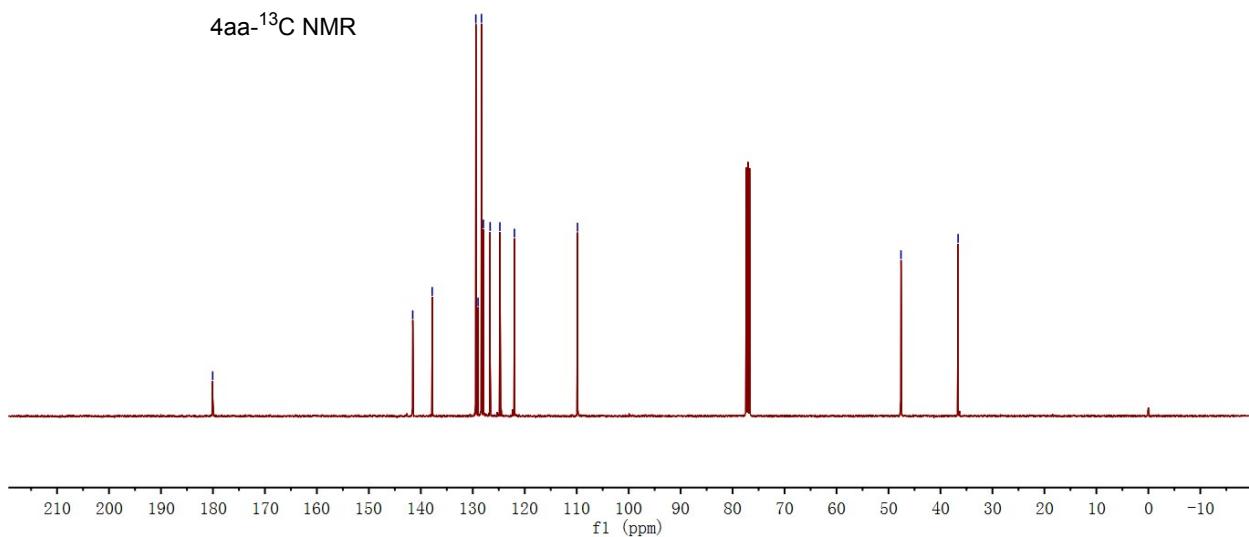


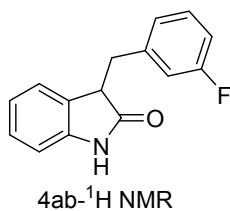


4aa-¹H NMR

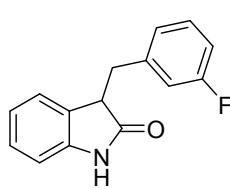
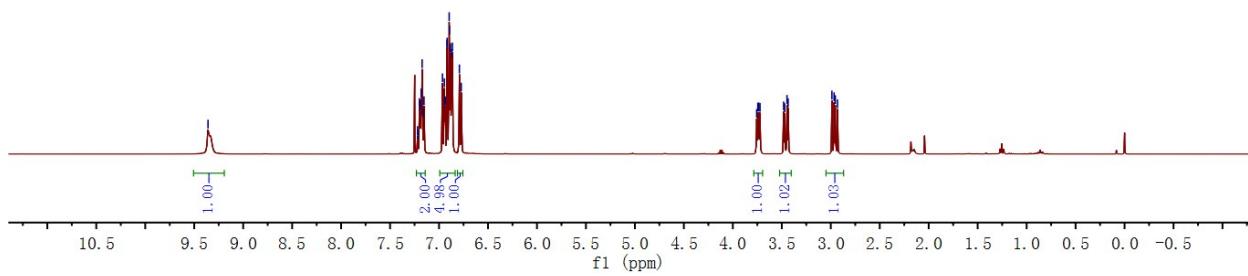


4aa-¹³C NMR

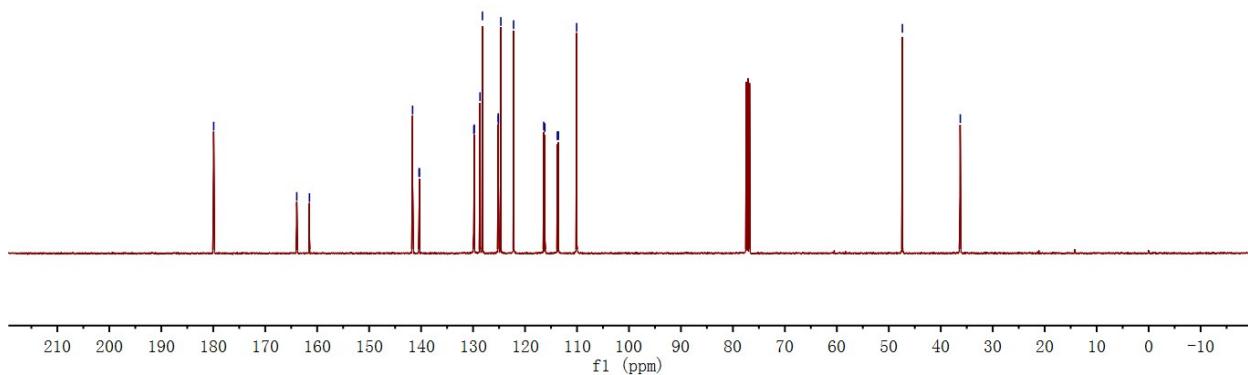


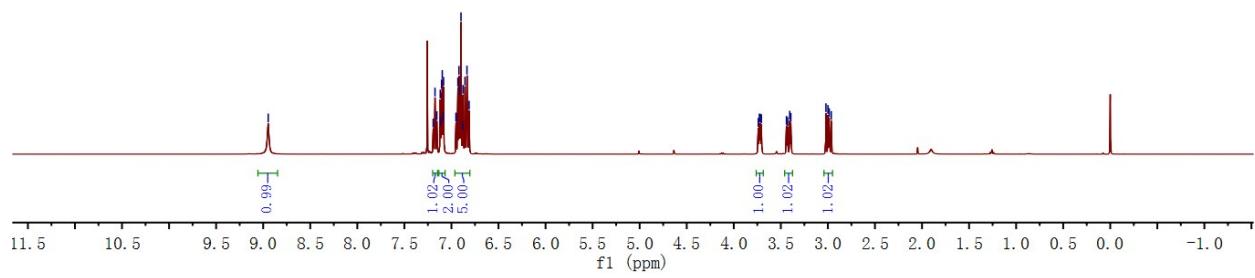
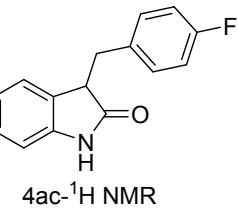
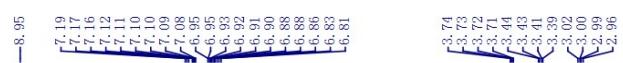


4ab⁻¹H NMR



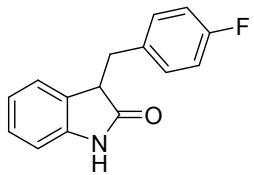
4ab-¹³C NMR



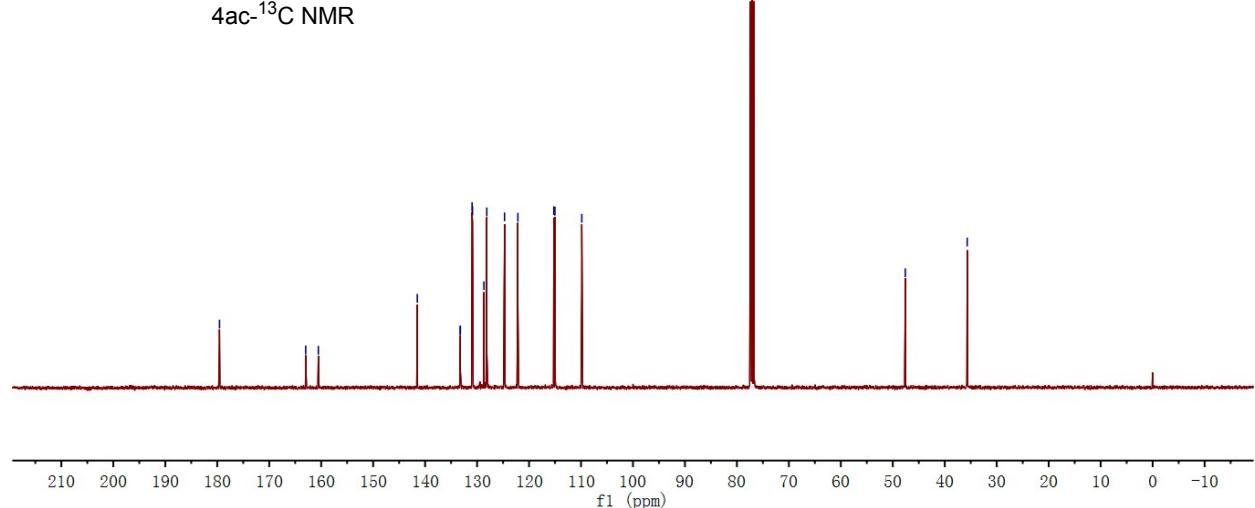


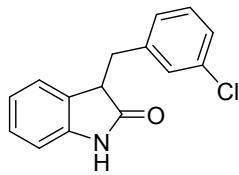
—141.51
—133.25
—133.21
—130.96
—130.88
—128.69
—128.63
—128.13
—124.71
—122.15
—115.23
—115.02
—109.84

—47.59
—35.69

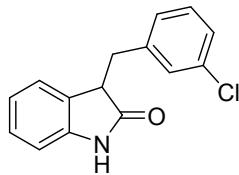
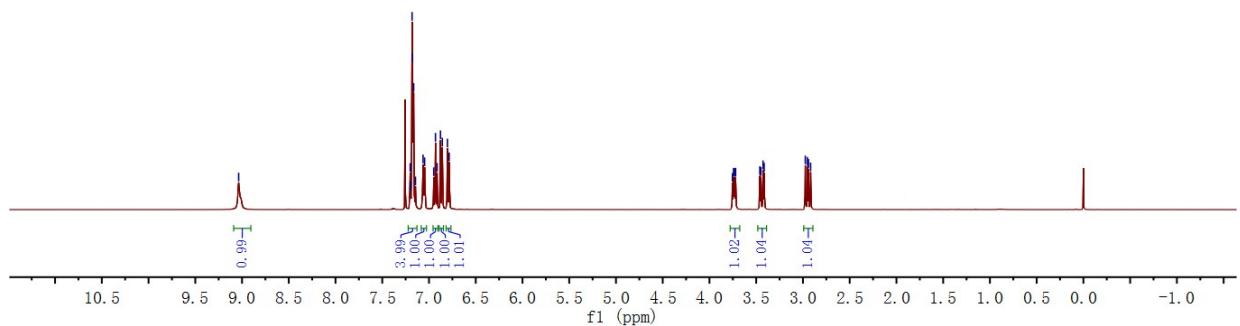


4ac- ^{13}C NMR

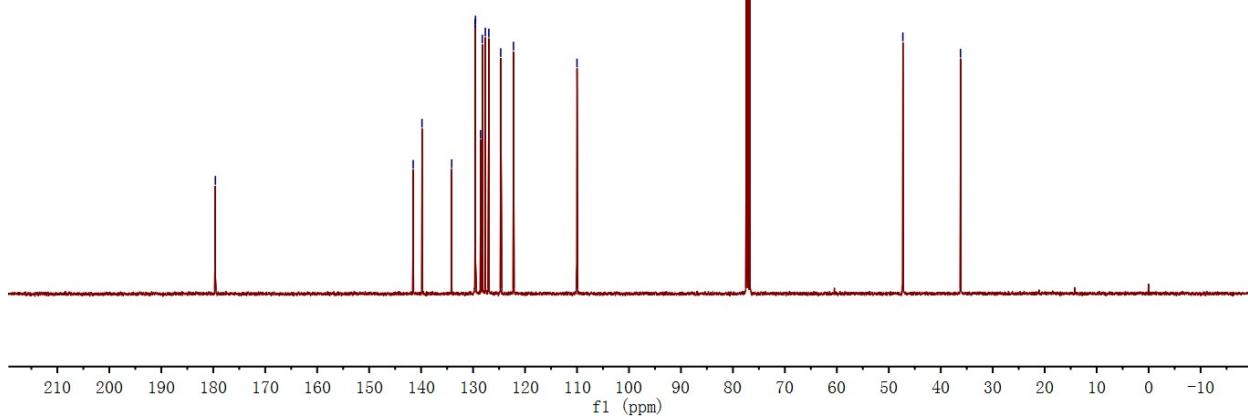


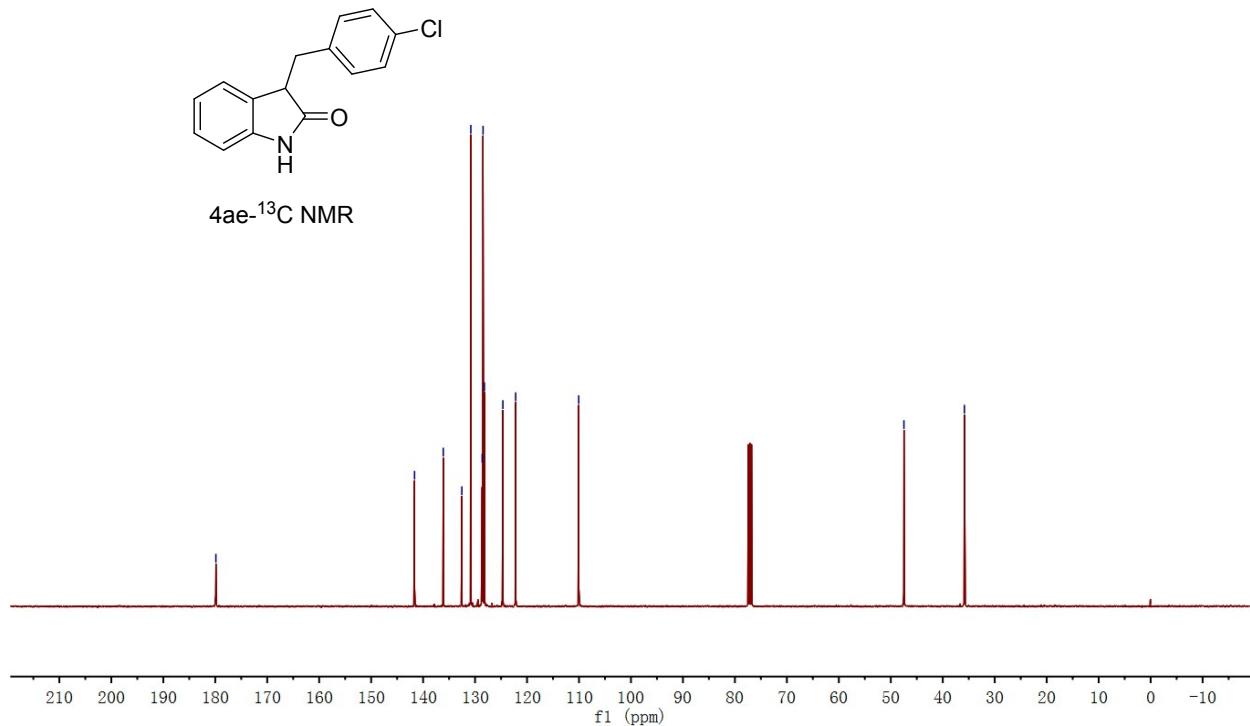
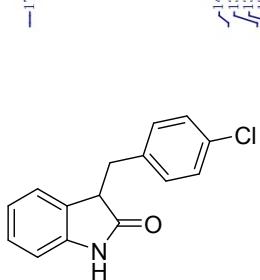
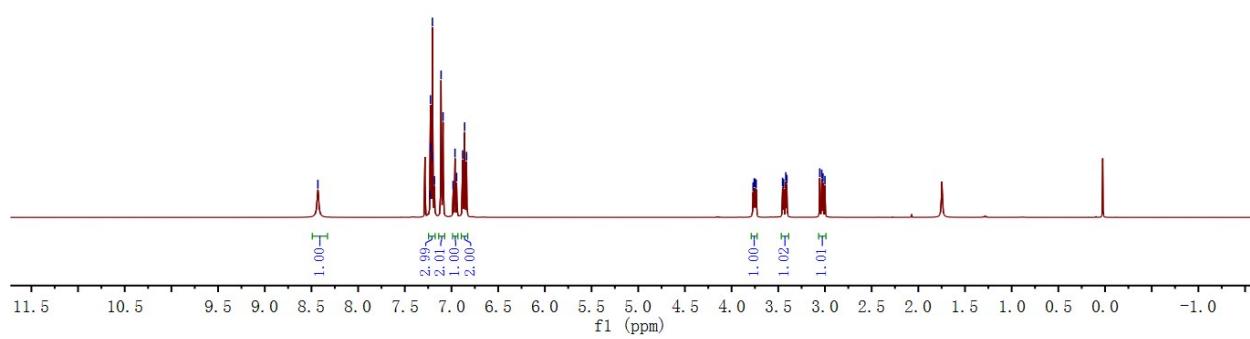
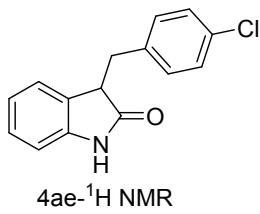


4ad⁻¹H NMR



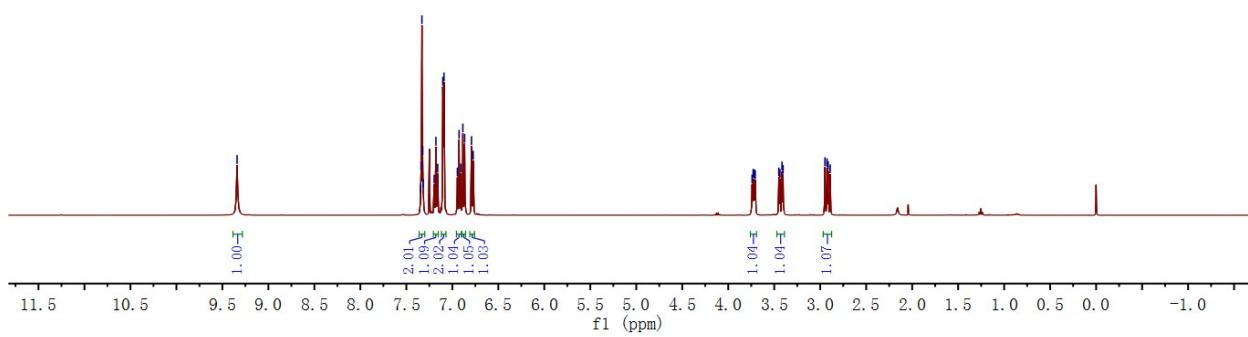
4ad-¹³C NMR



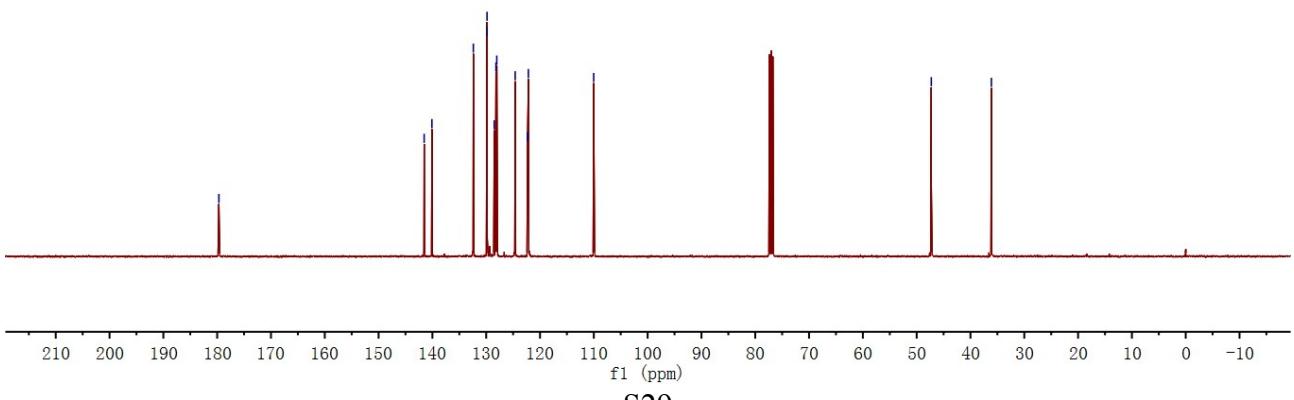


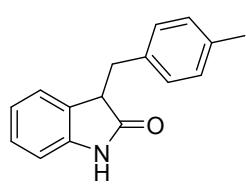
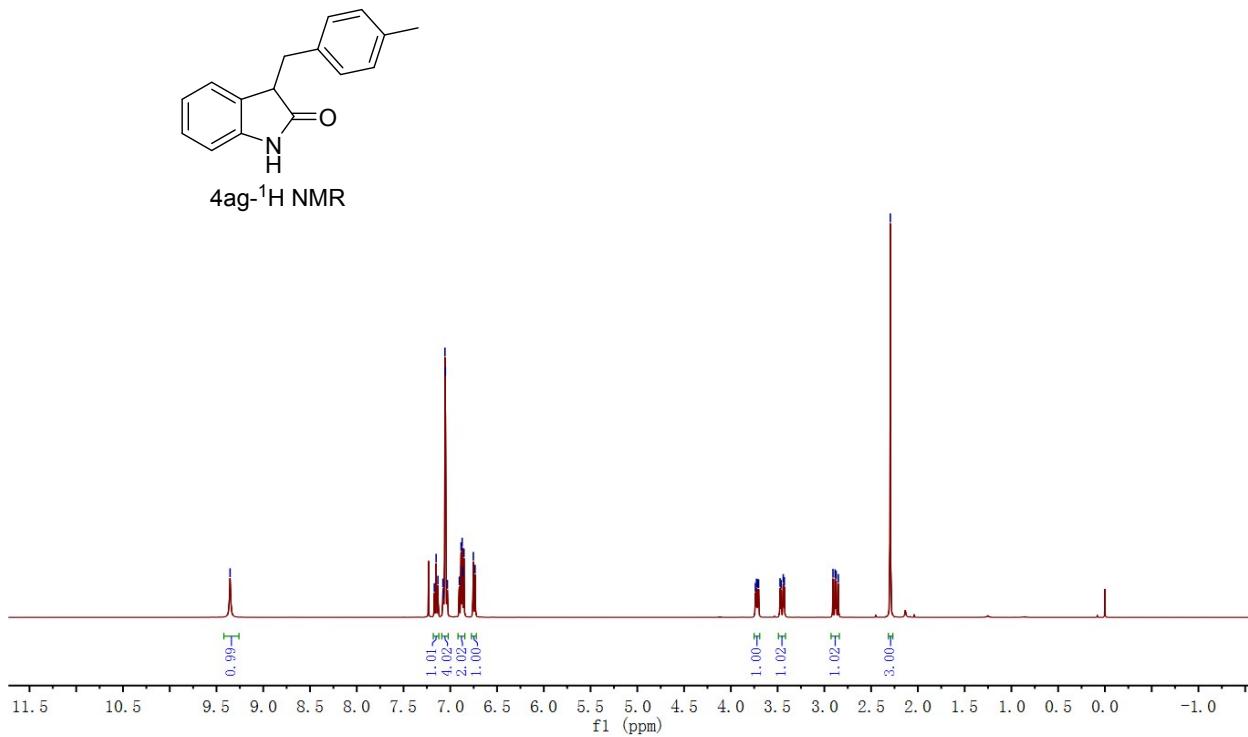


4af-¹H NMR

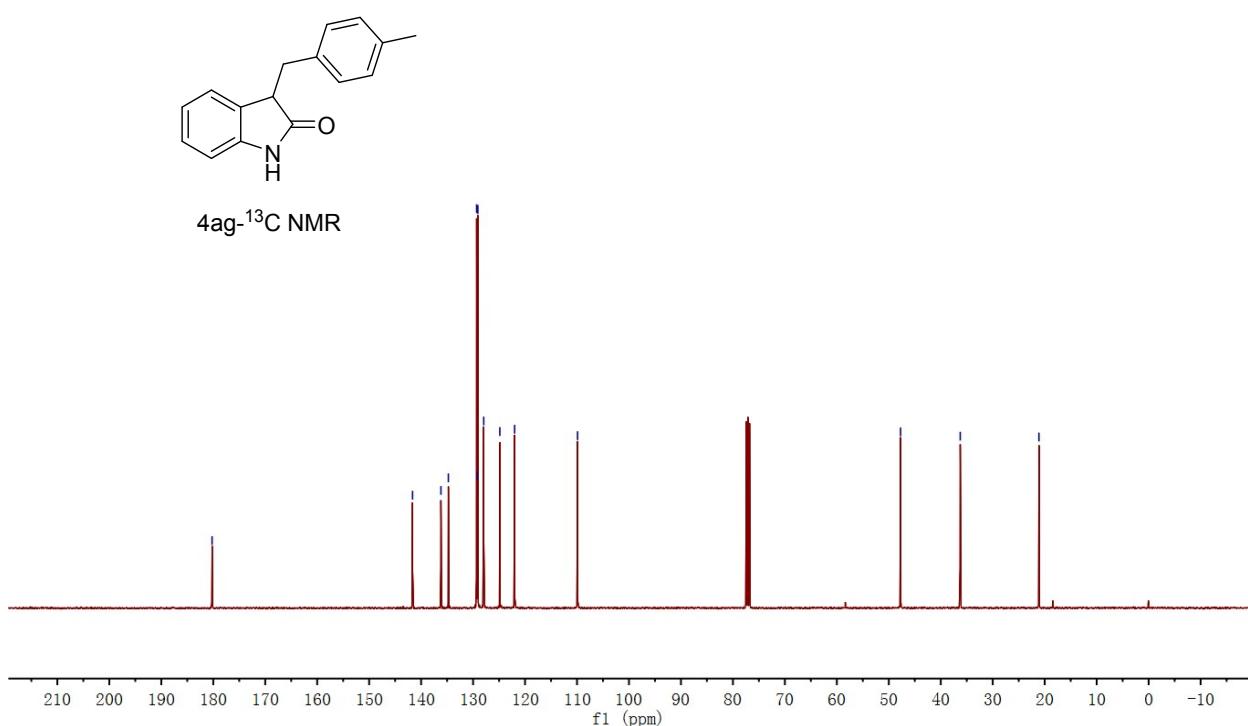


4af-¹³C NMR



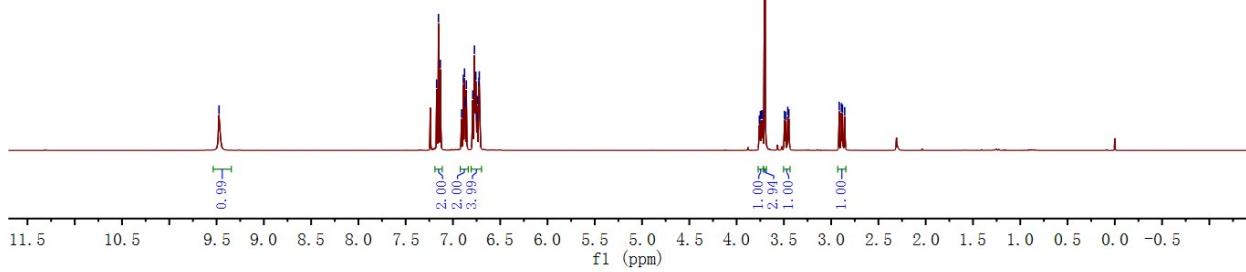


^1H NMR





4ah-¹H NMR



—190.27

—159.55

—141.73

—139.48

—129.36

—128.03

—124.85

—122.05

—121.87

—114.78

—112.46

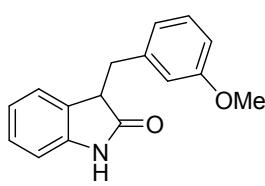
—110.00

—55.15

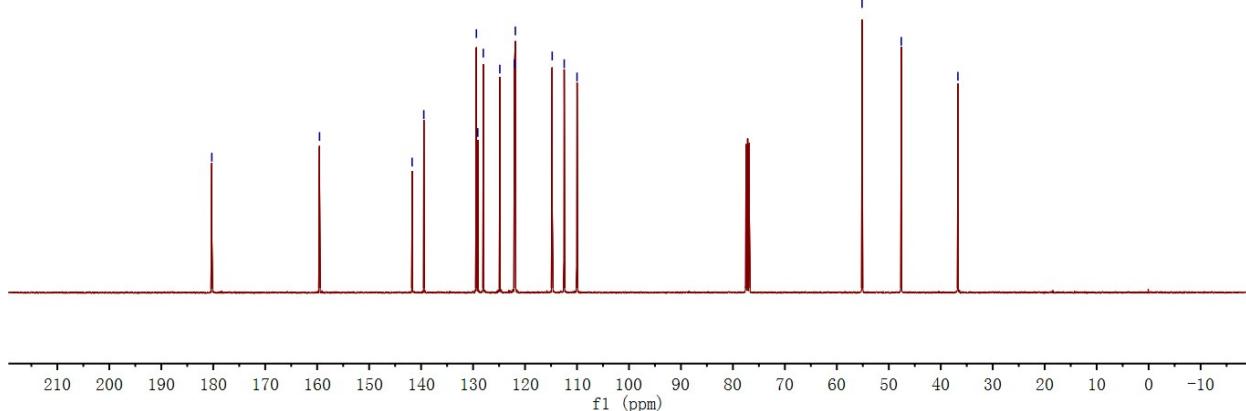
—47.60

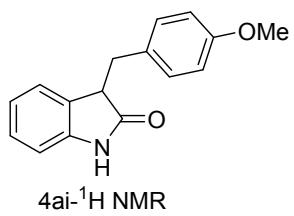
—36.70

f1 (ppm)

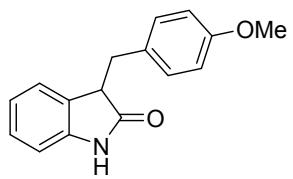
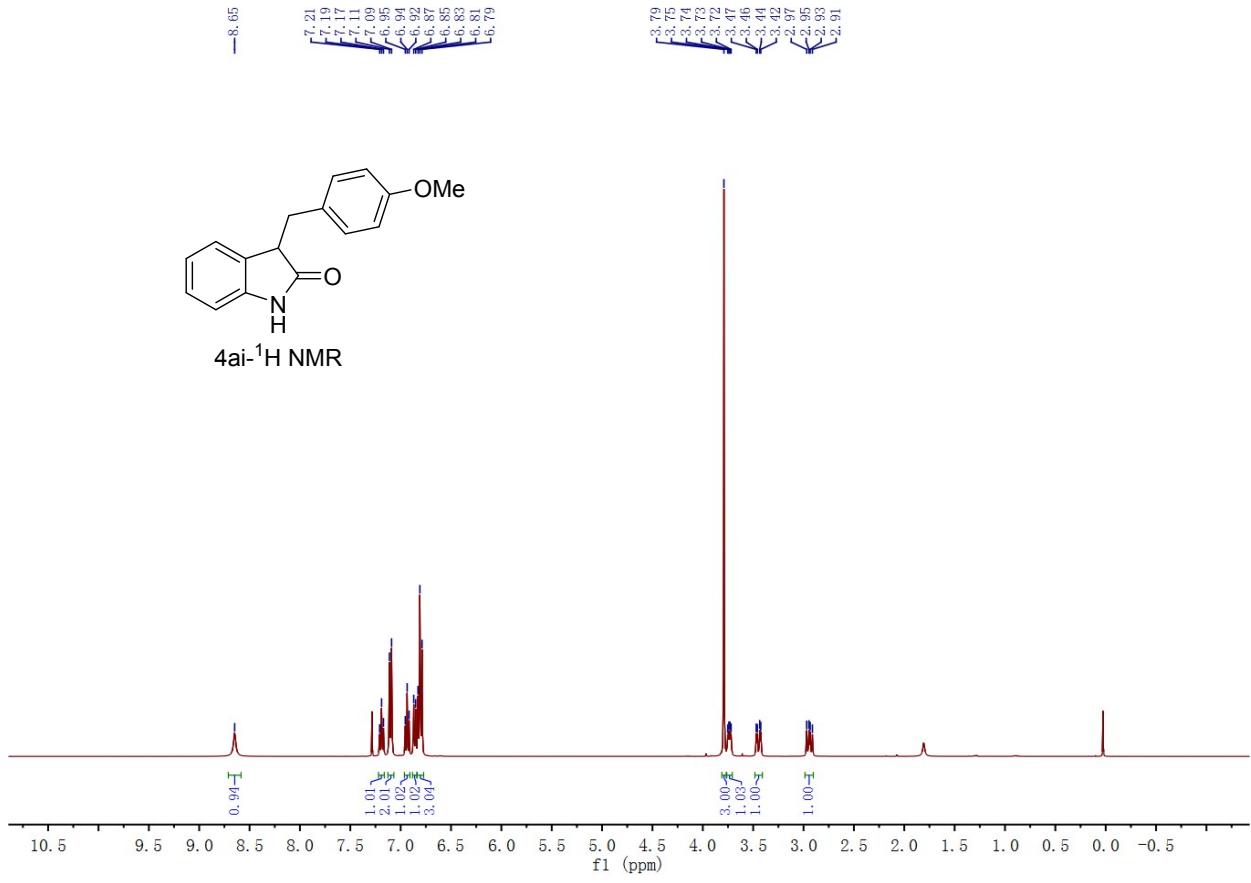


4ah-¹³C NMR

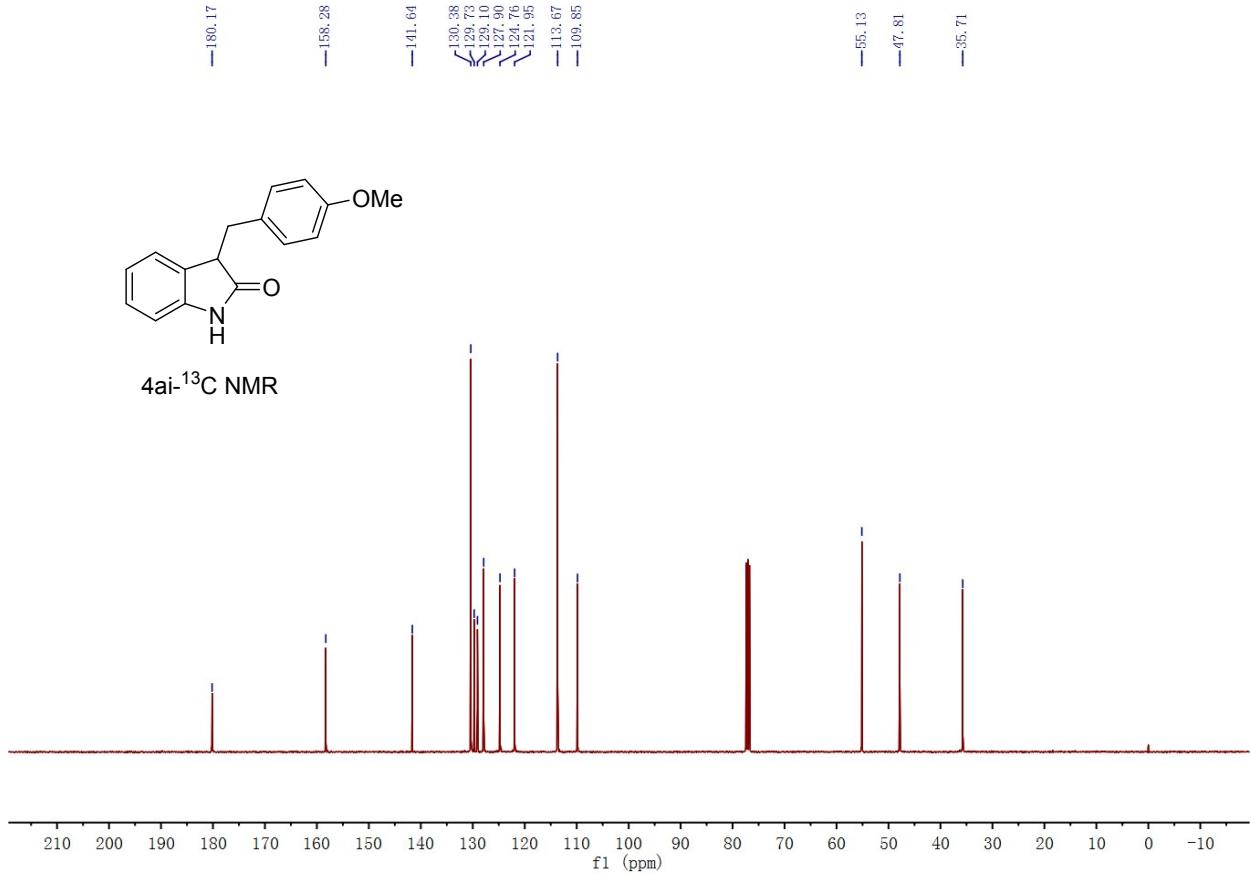




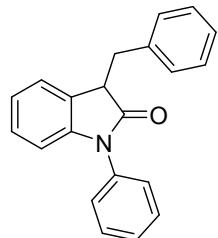
4ai-¹H NMR



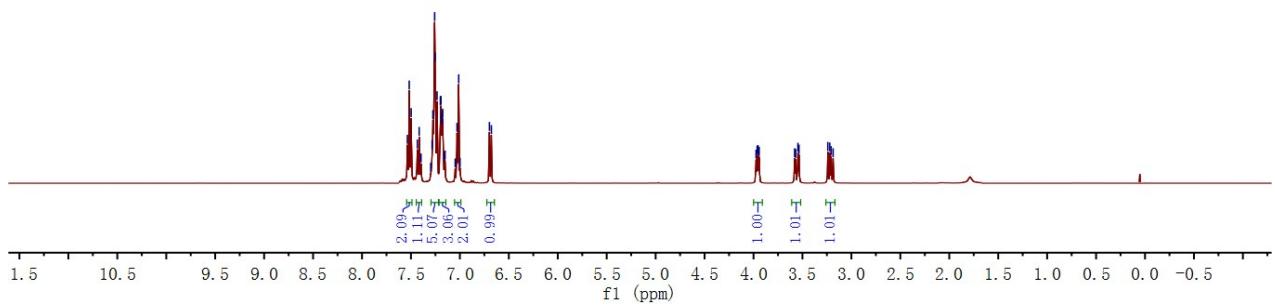
4ai-¹³C NMR



7.54
 7.52
 7.43
 7.42
 7.40
 7.30
 7.28
 7.26
 7.25
 7.23
 7.20
 7.19
 7.18
 7.16
 7.15
 7.05
 7.03
 7.01
 7.00
 6.70
 6.68

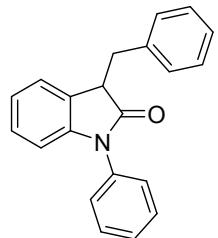


4aj-¹H NMR

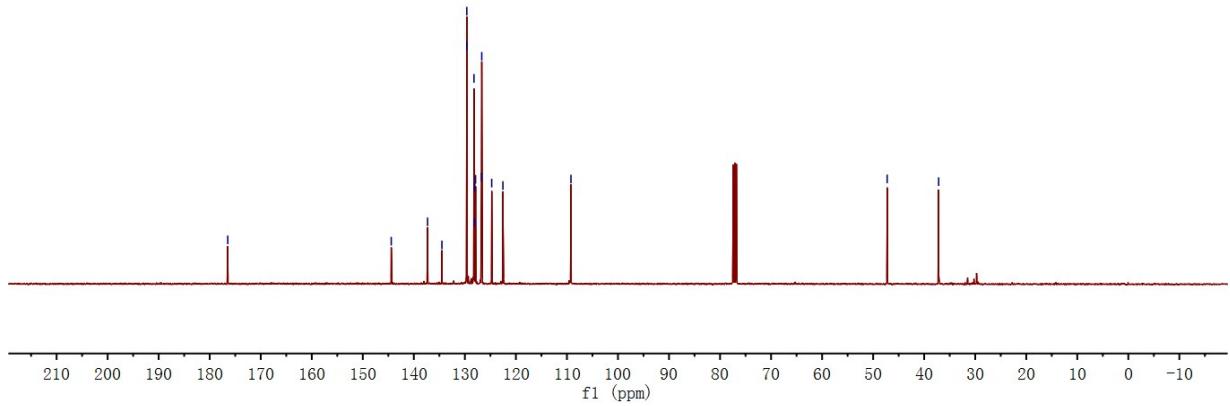


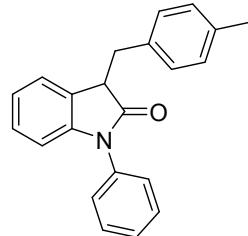
-144.43
 137.31
 129.62
 129.61
 128.22
 128.14
 128.08
 127.91
 126.74
 126.69
 126.71
 126.25

-47.26
 -37.16

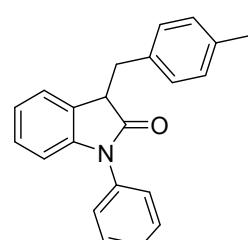
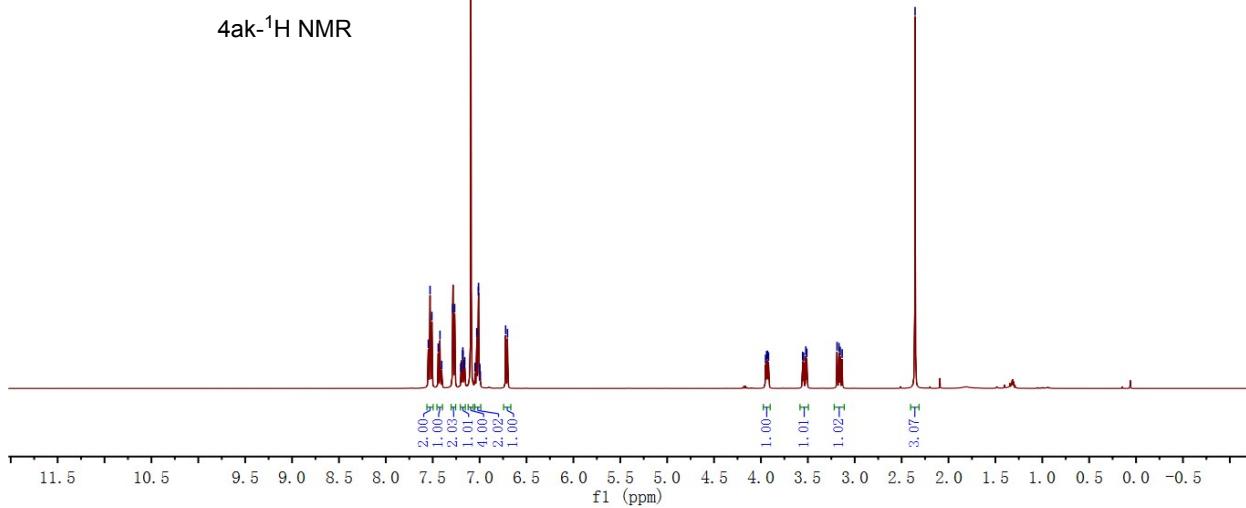


4aj-¹³C NMR

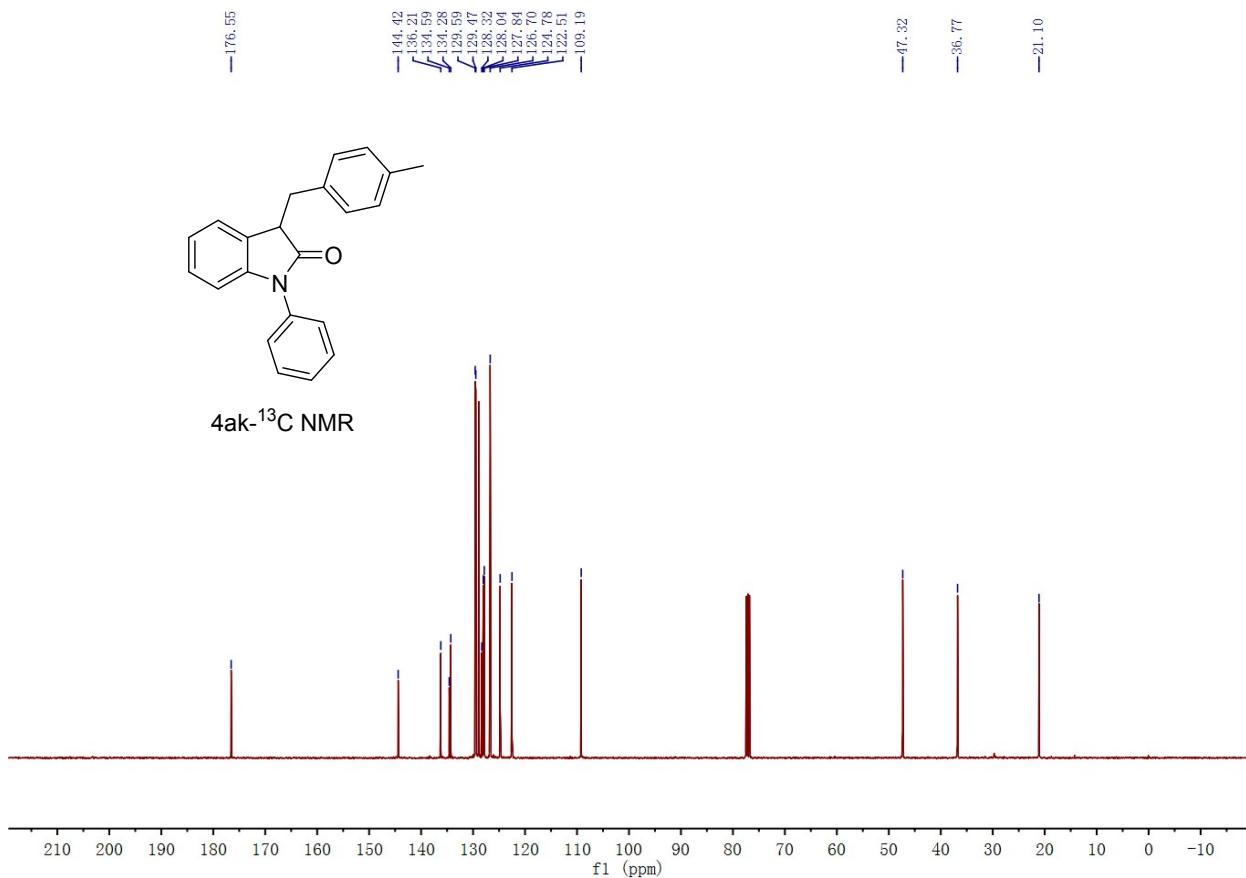


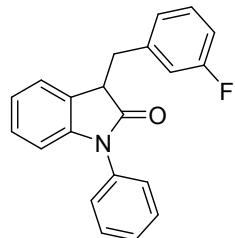


4ak⁻¹H NMR

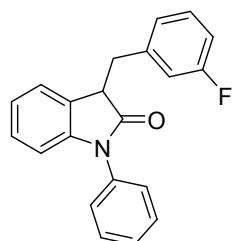
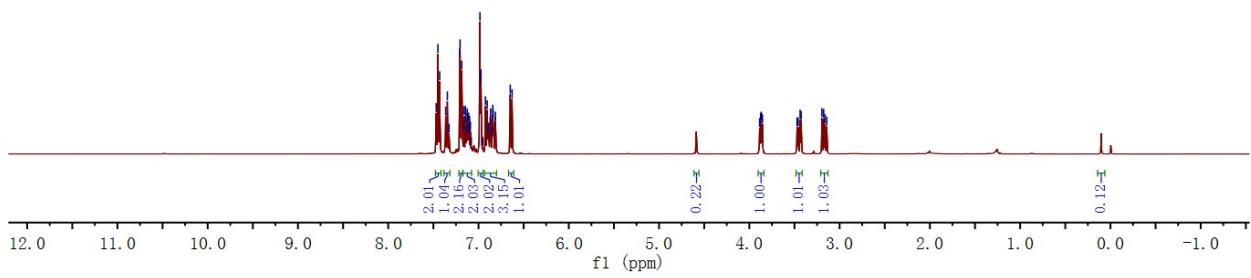


4ak-¹³C NMR

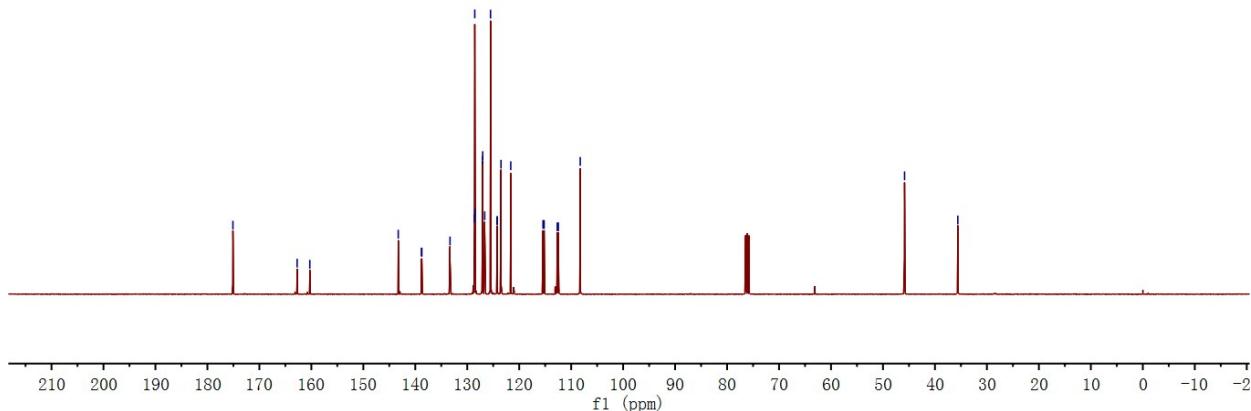




4al-¹H NMR

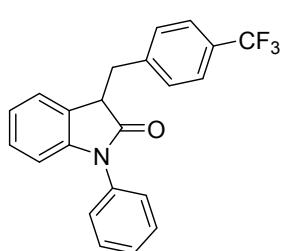
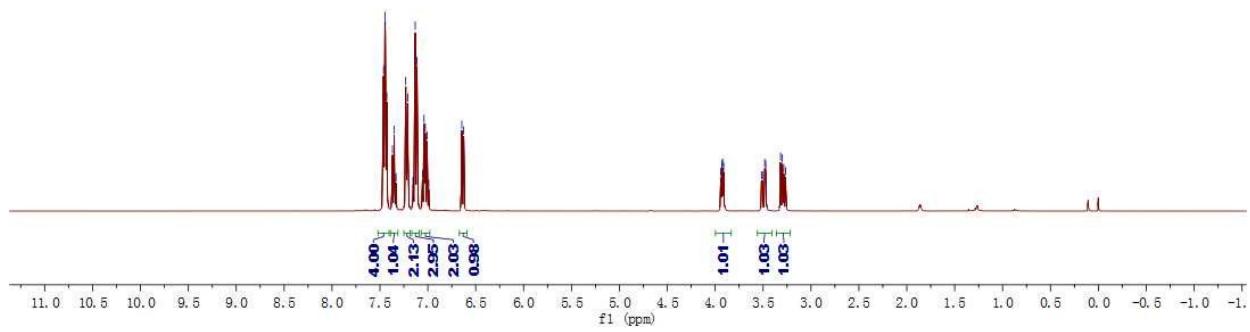


4al-¹³C NMR

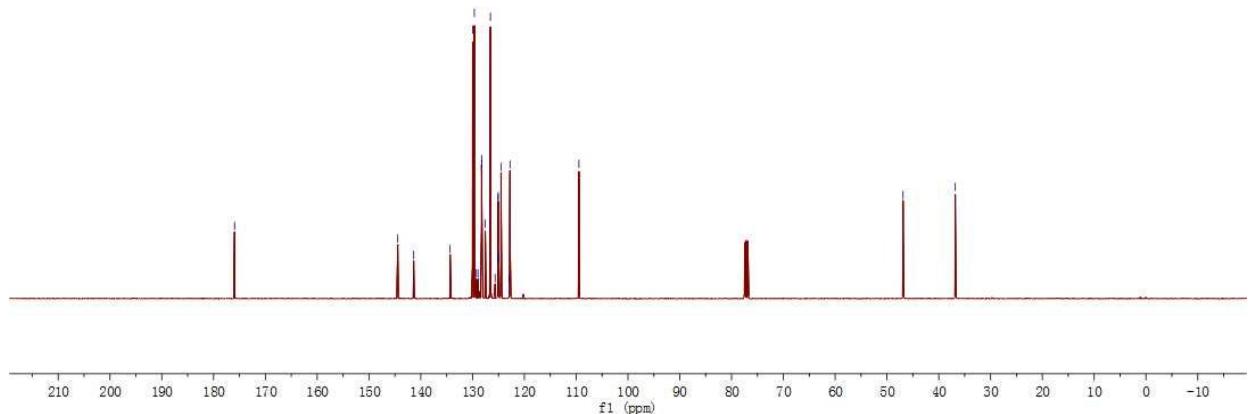


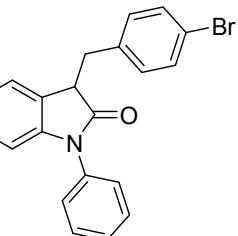


4am-¹H NMR

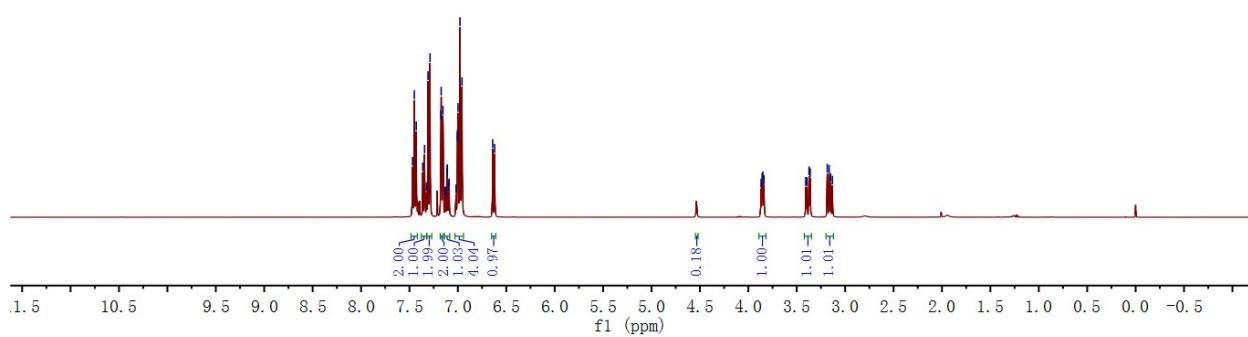


4am-¹³C NMR





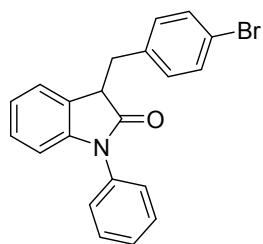
4an-¹H NMR



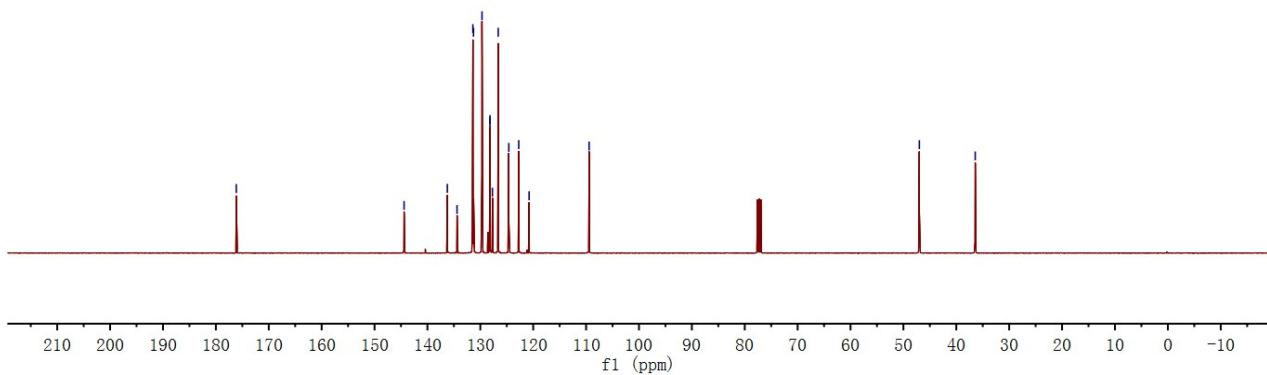
-176, 14

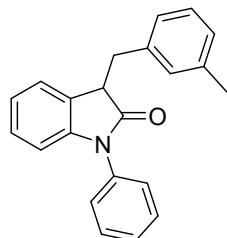
-144, 41
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-131, 41
-131, 29
-129, 68
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-126, 61
-124, 61
-122, 73
-120, 43

-36, 99
-46, 42

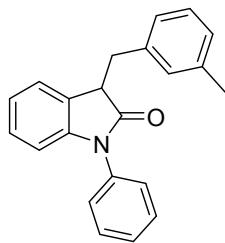
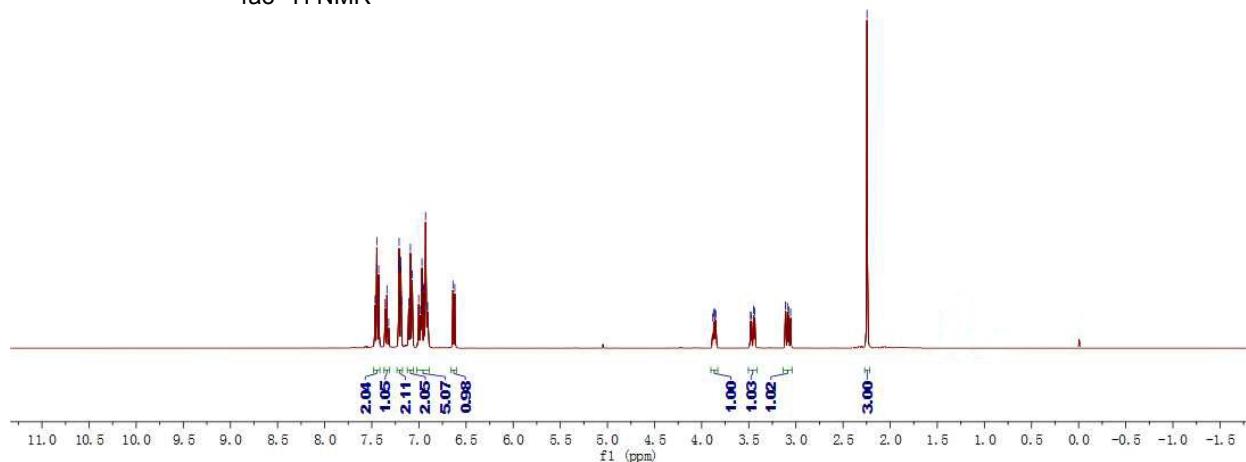


4an-¹³C NMR

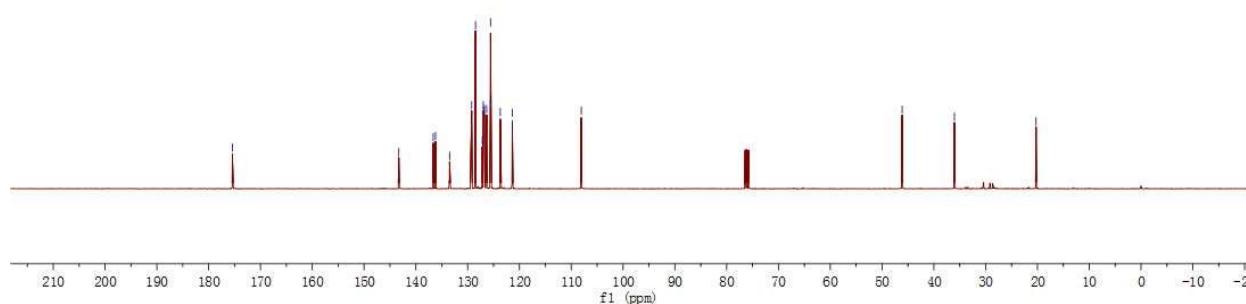


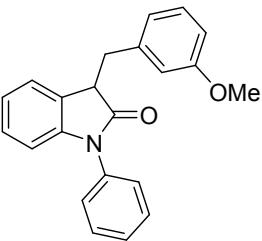


4a^o-¹H NMR

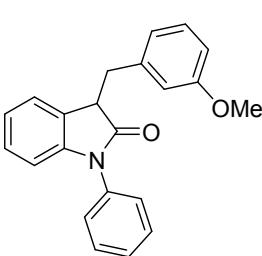
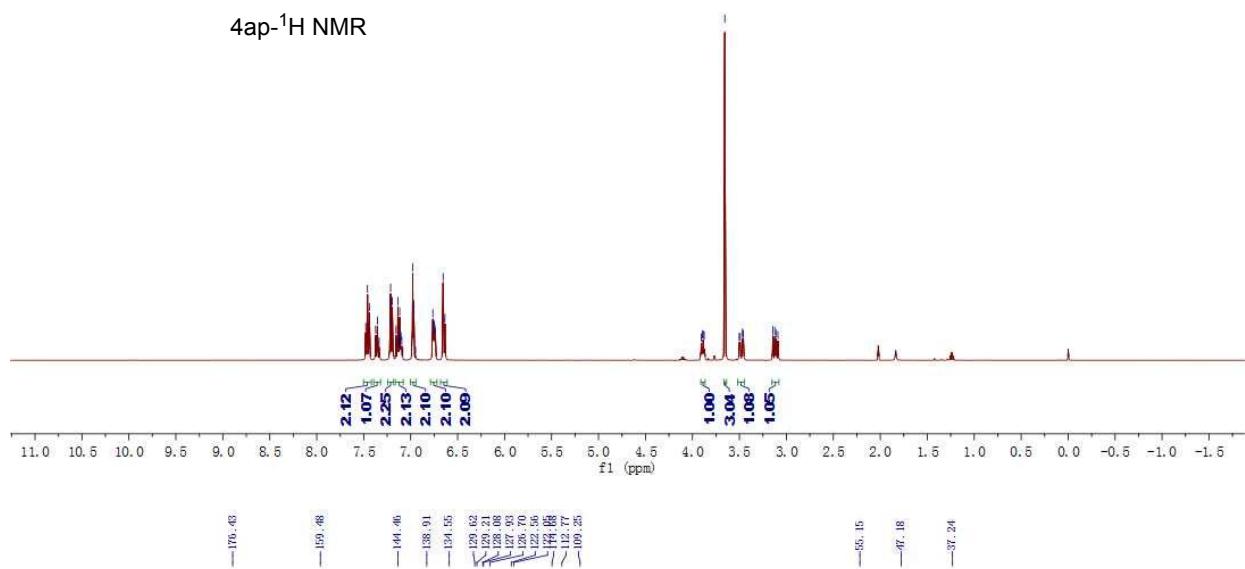


4ao-¹³C NMR

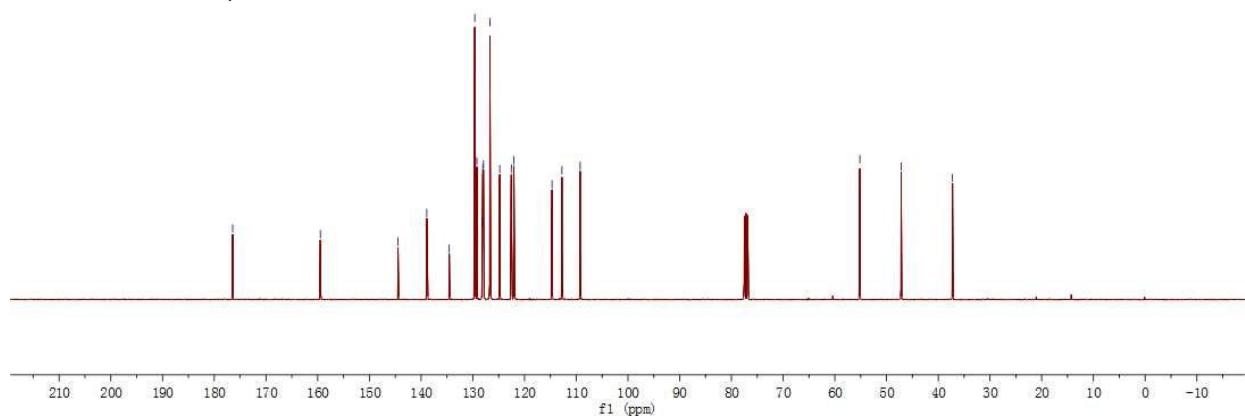


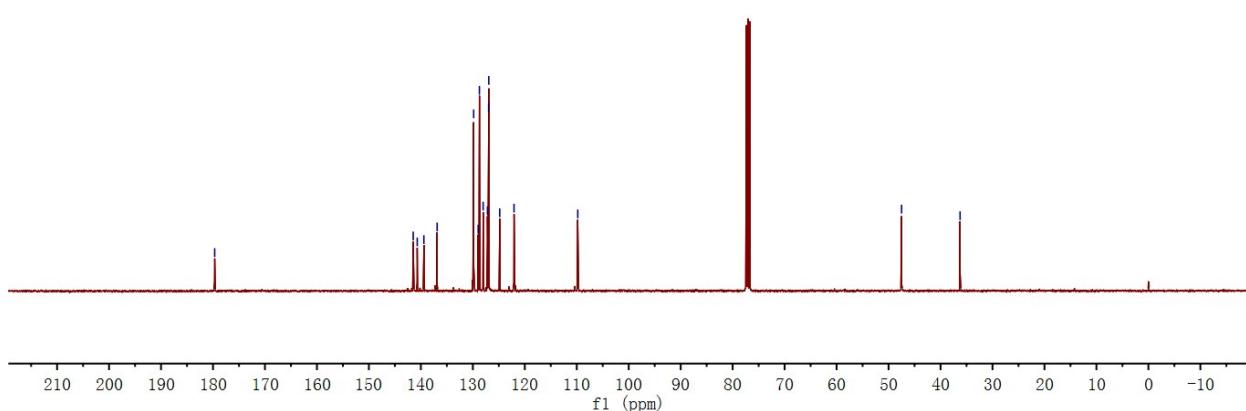
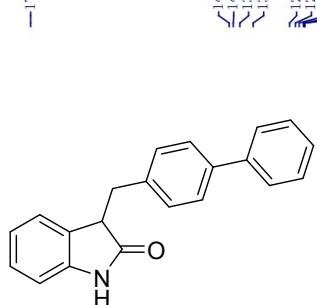
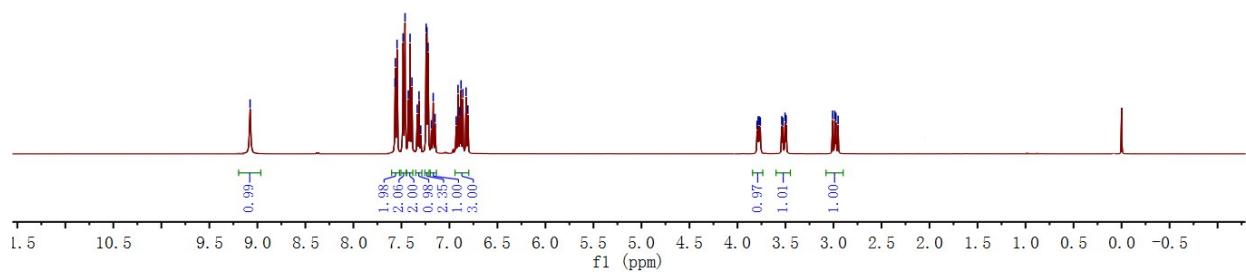
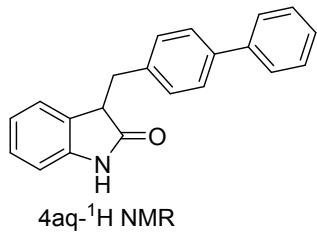
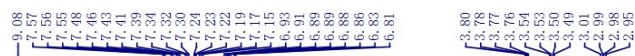


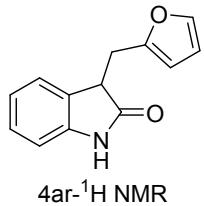
4ap-¹H NMR



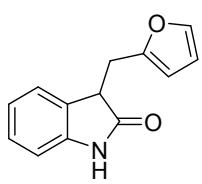
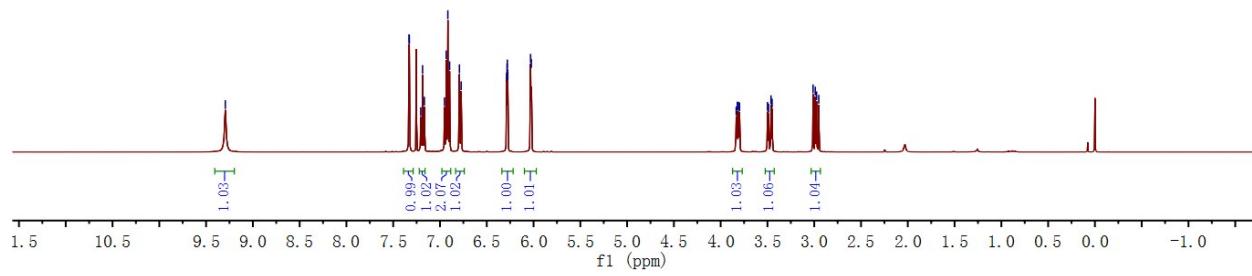
4ap-¹³C NMR



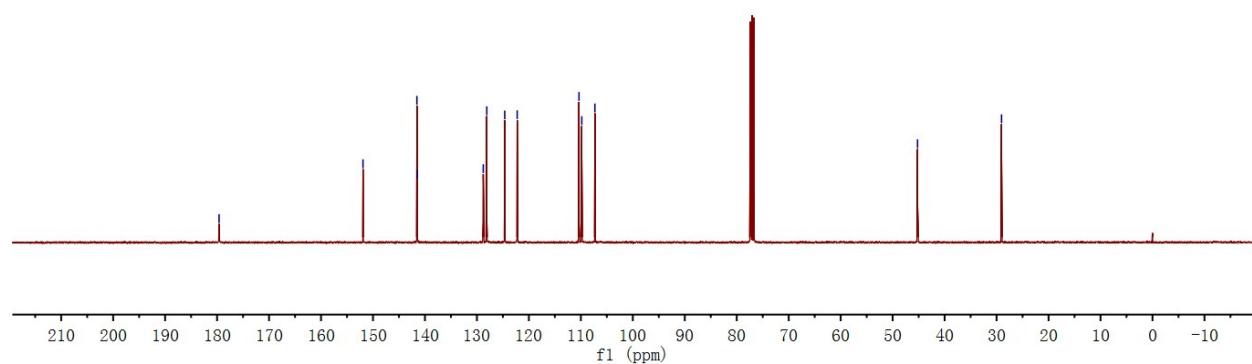


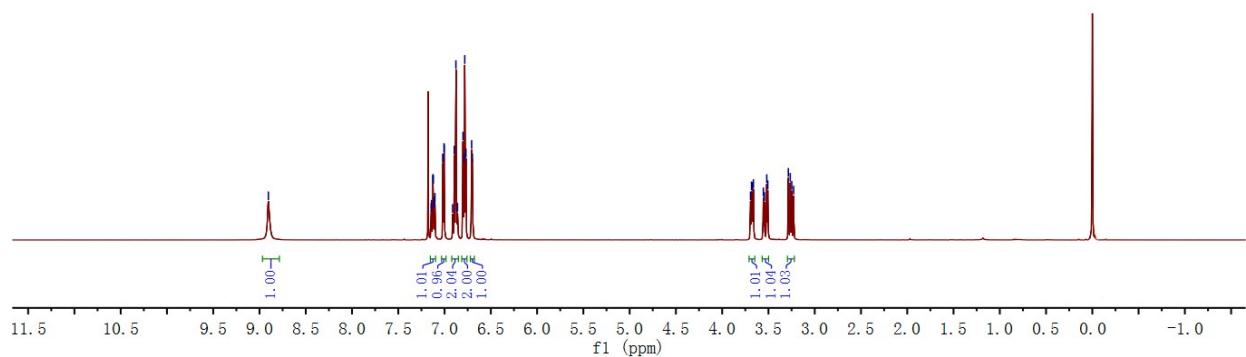
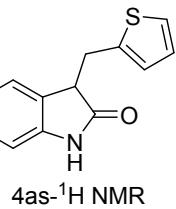


4ar⁻¹H NMR

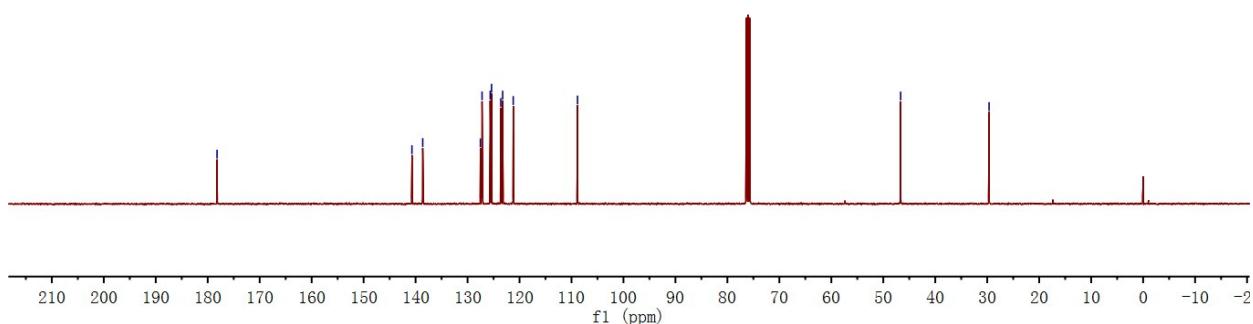


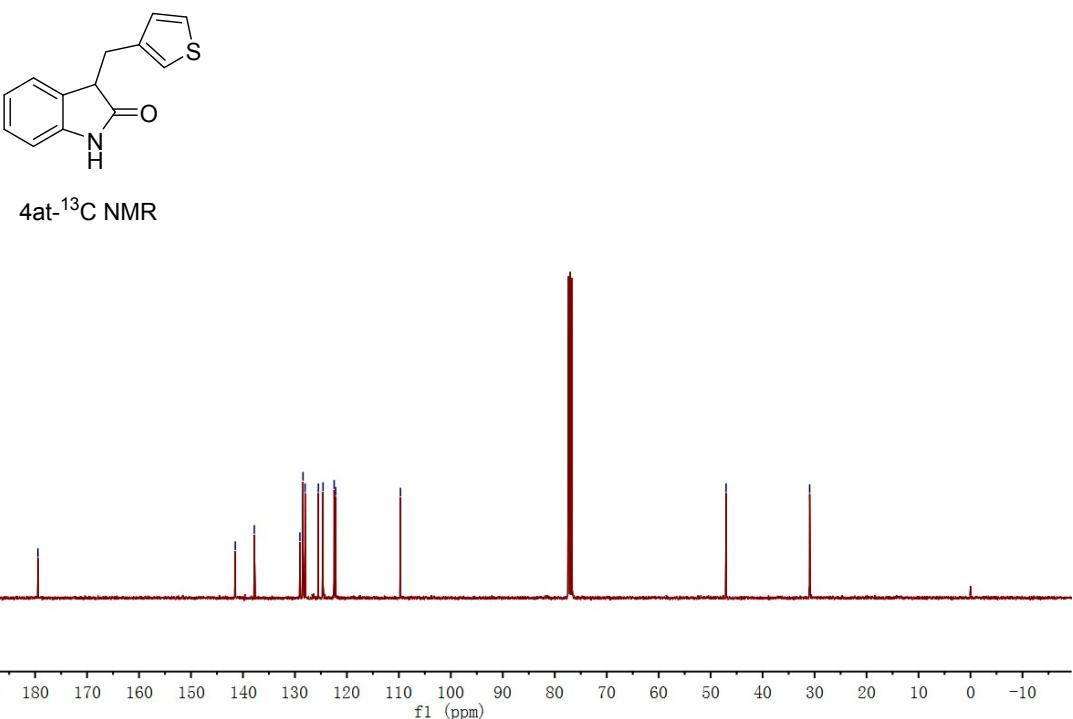
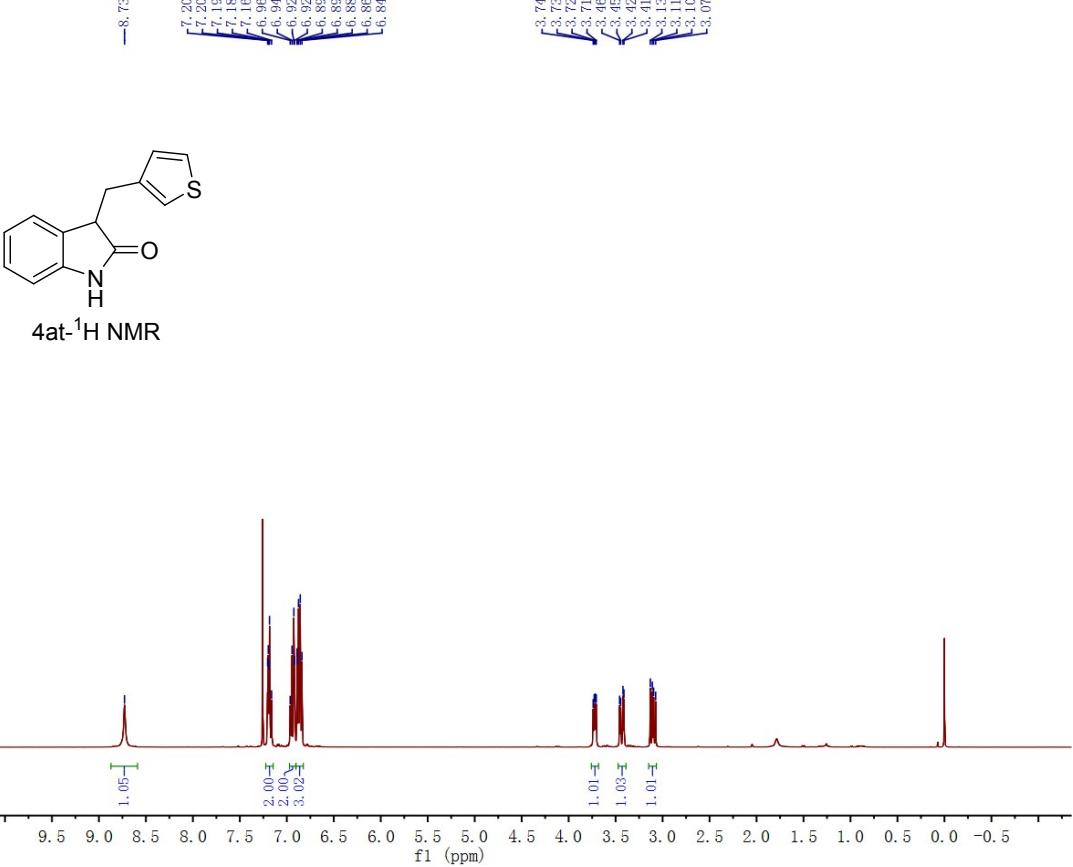
4ar-¹³C NMR





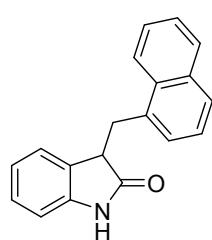
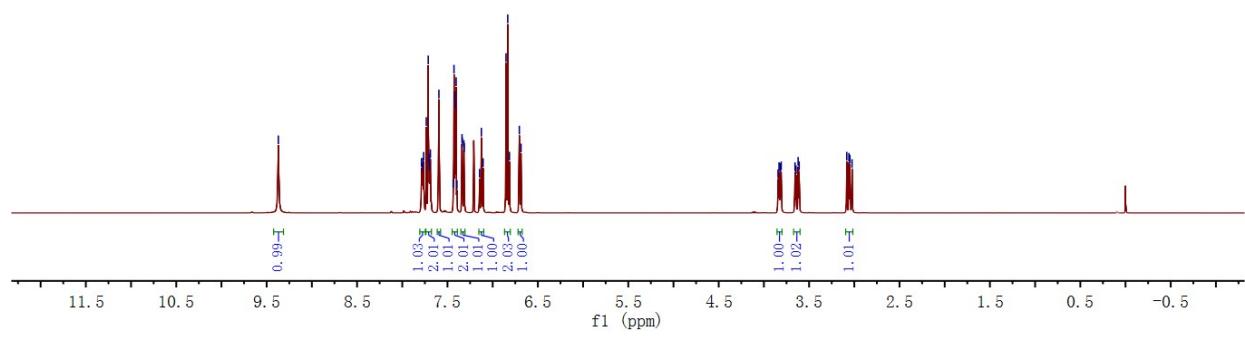
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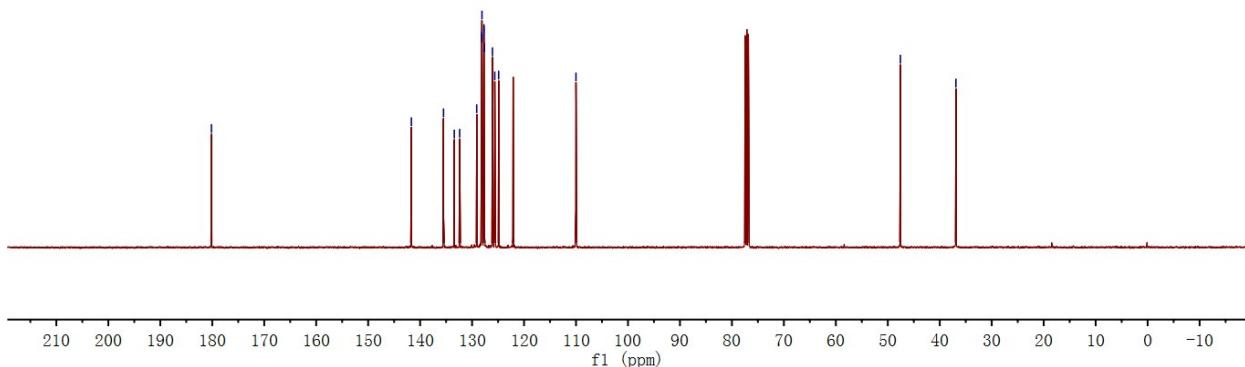


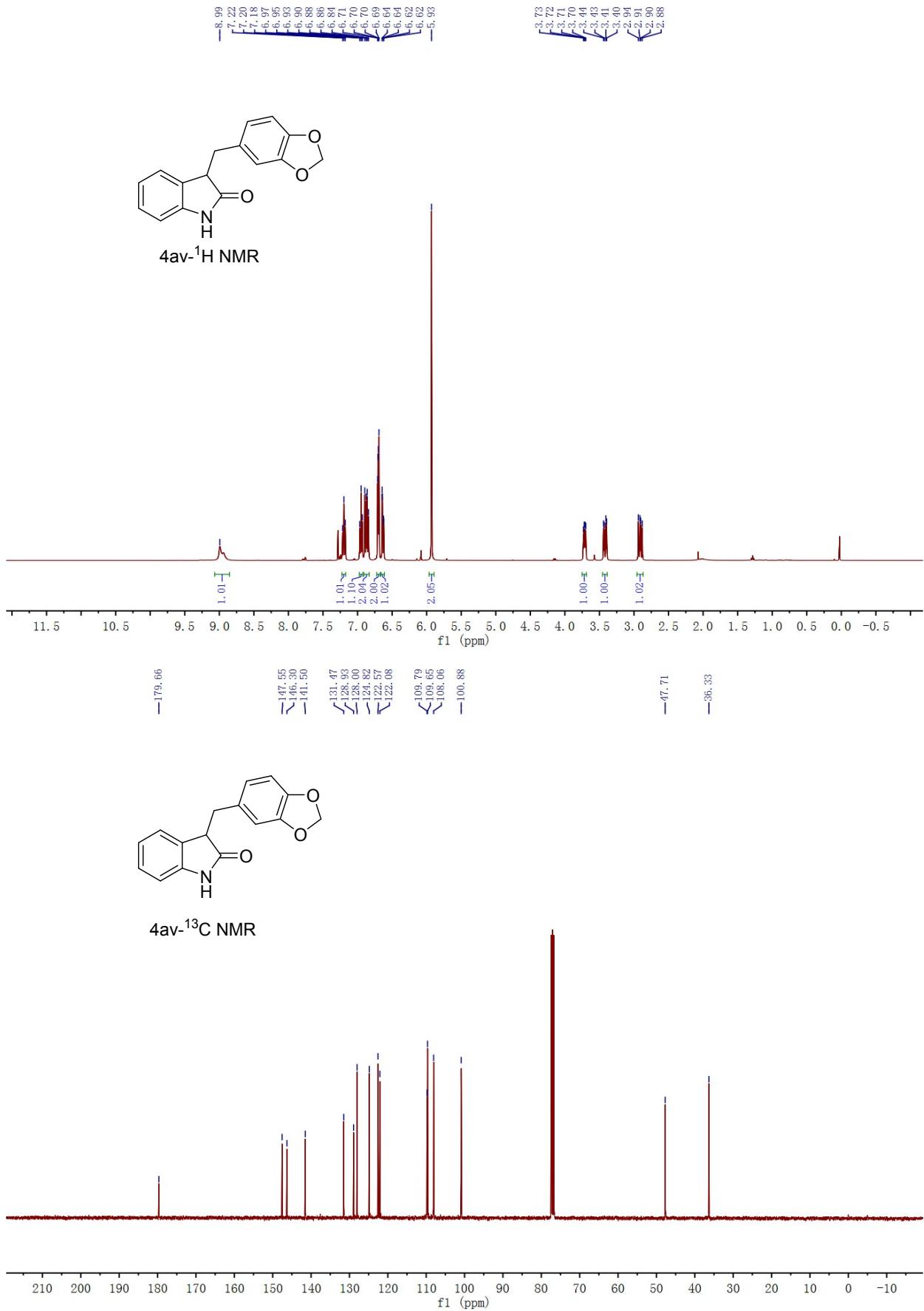


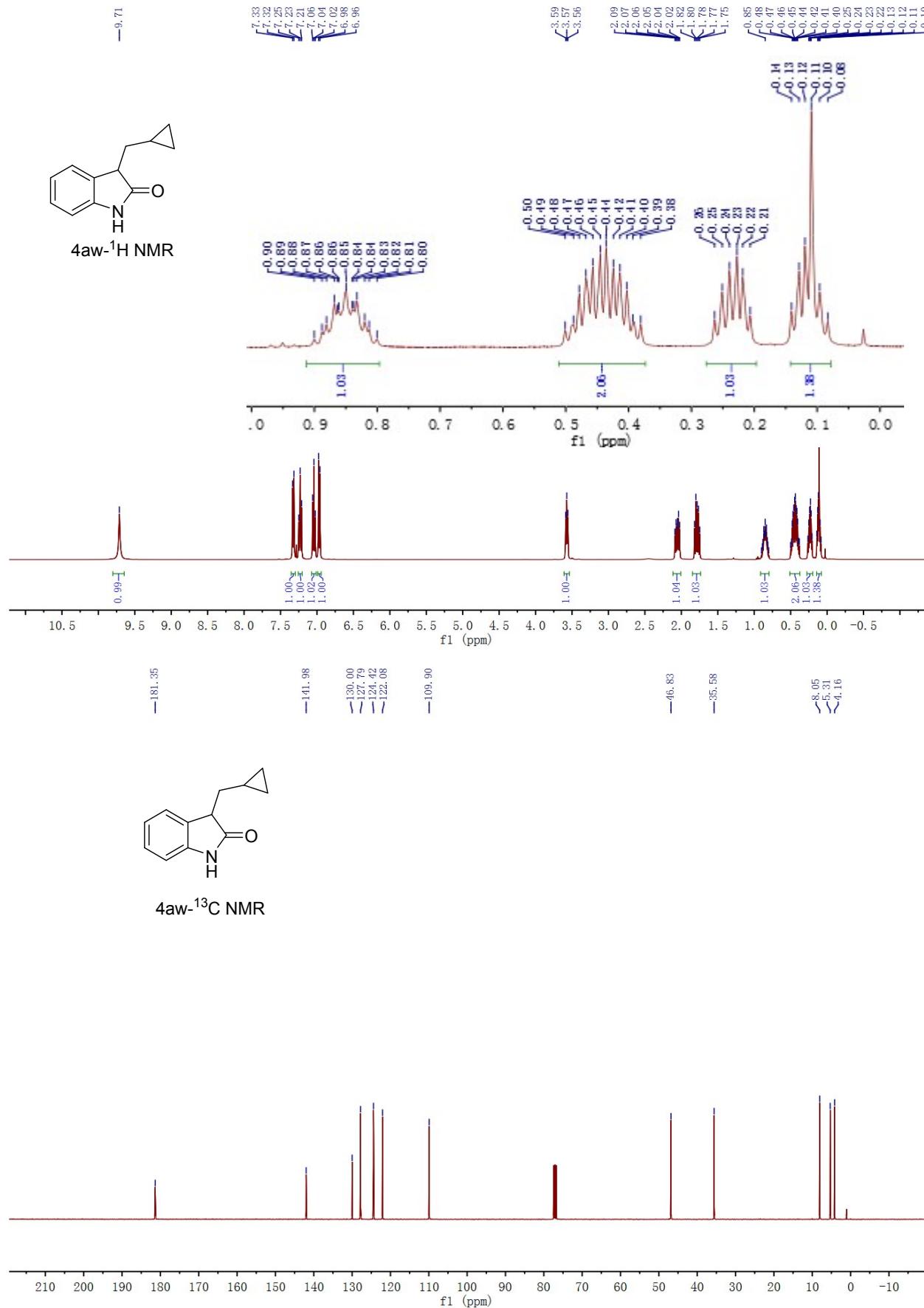
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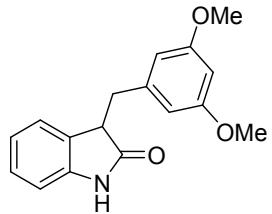


4au-¹³C NMR

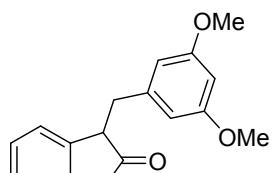
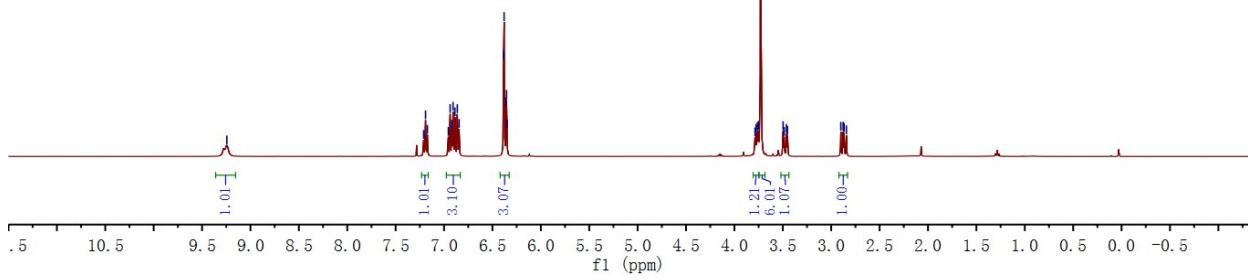




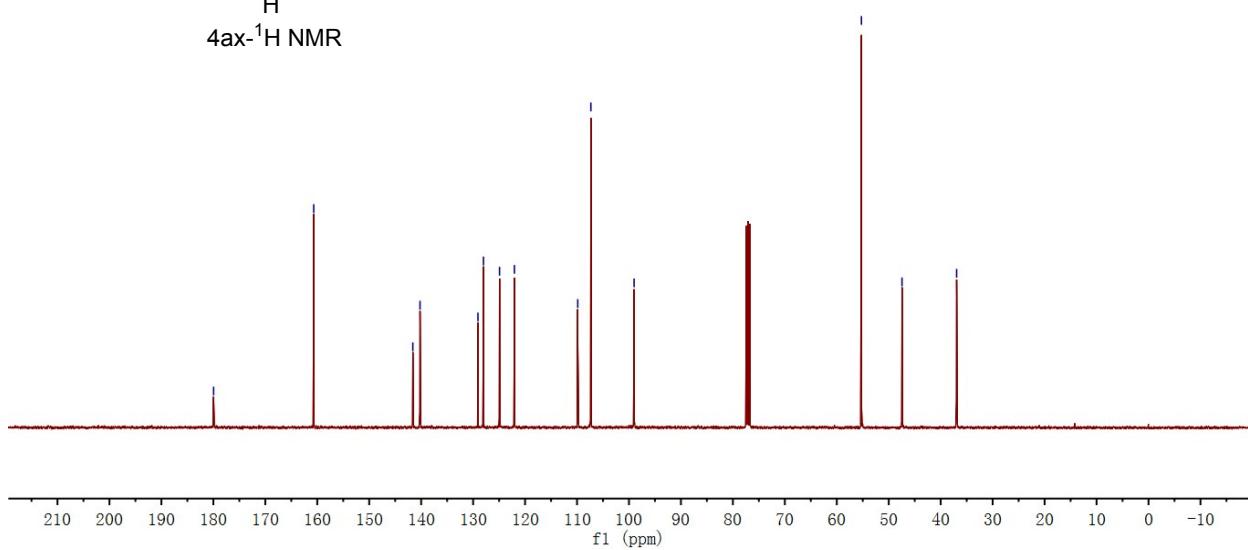




4ax-¹³C NMR

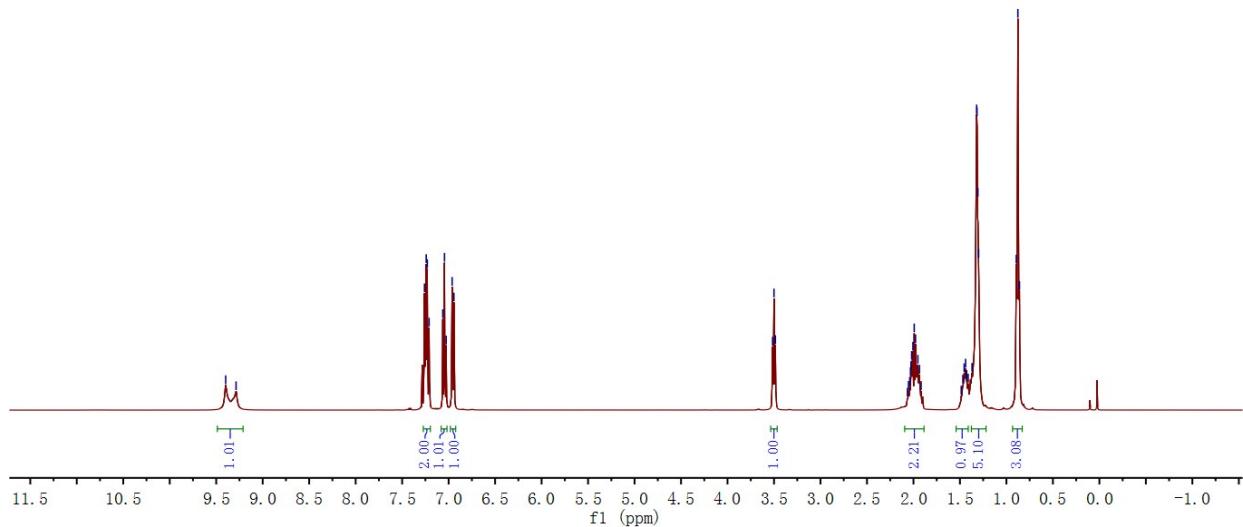


4ax-¹H NMR

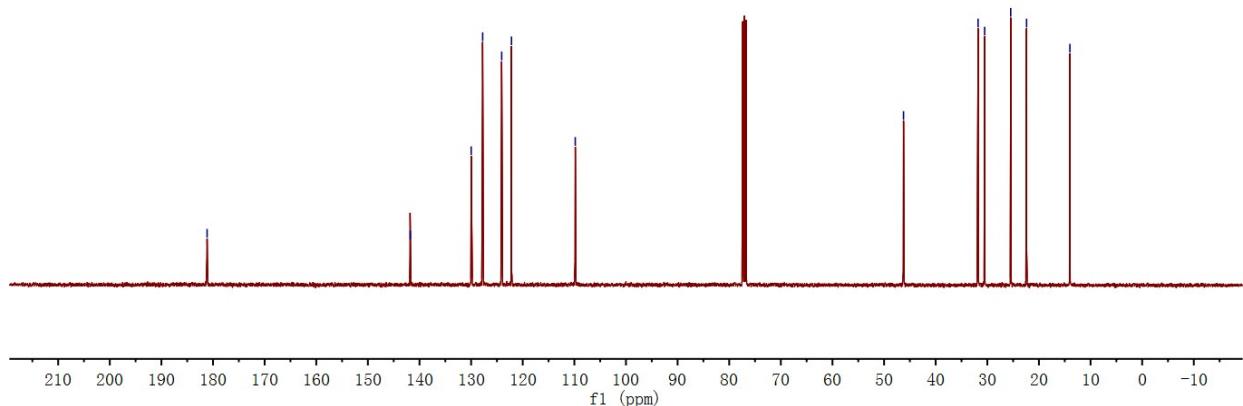


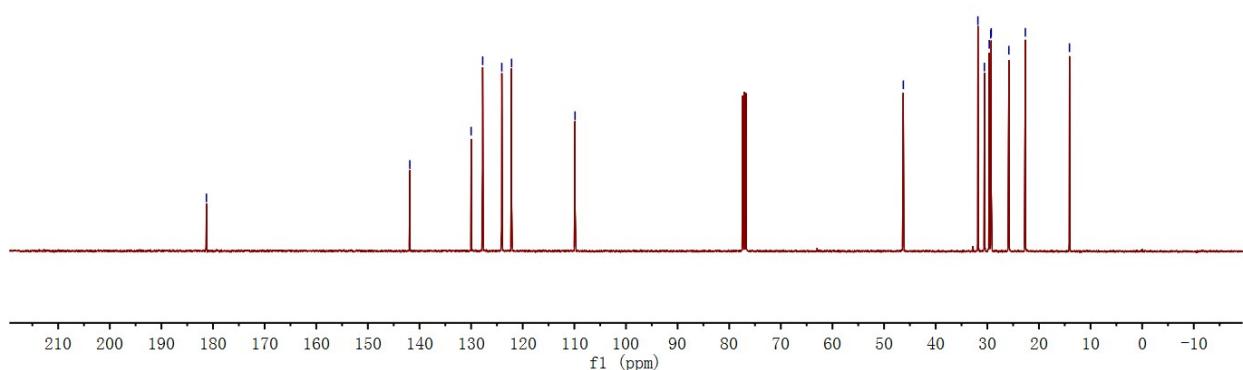
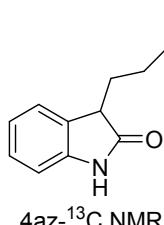
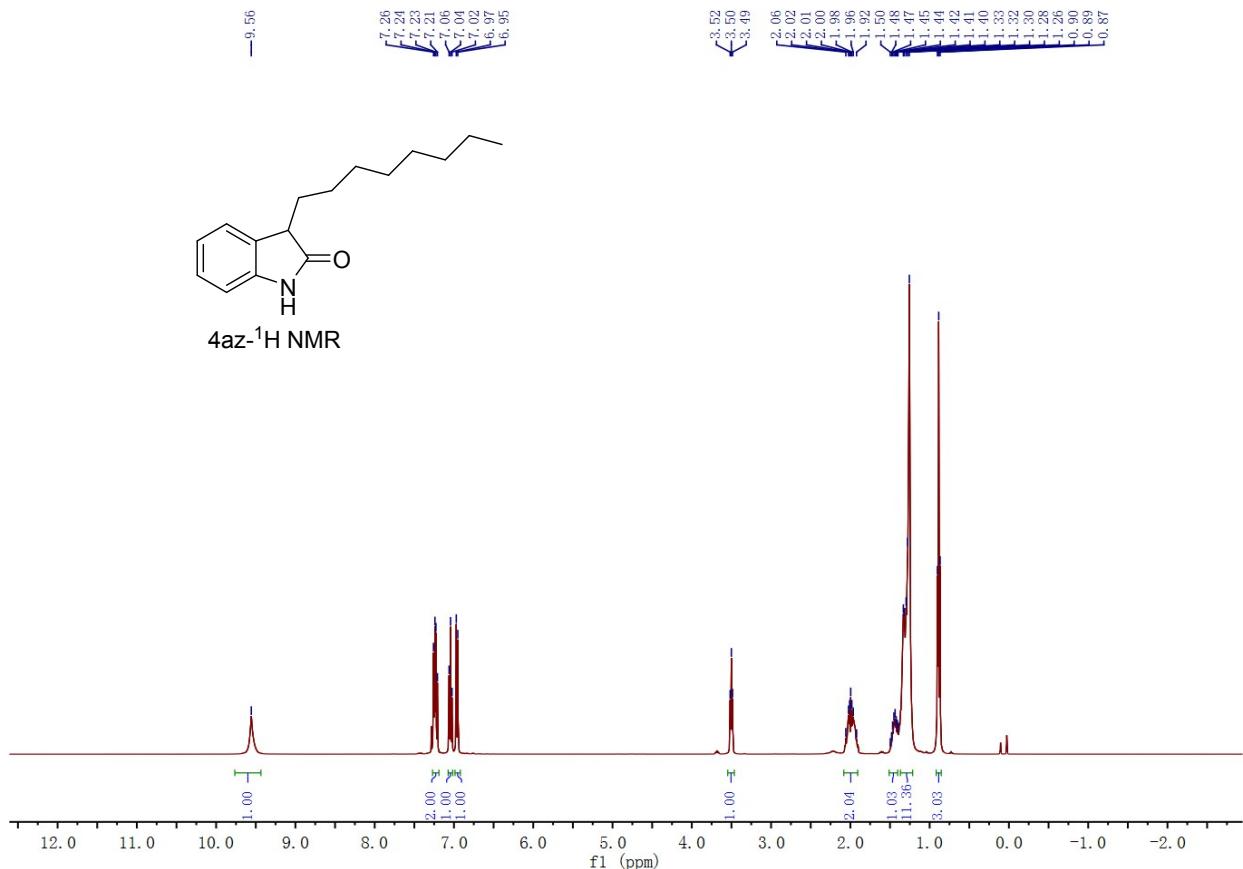
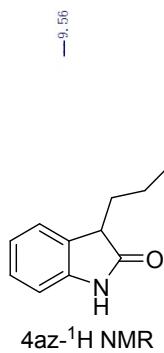


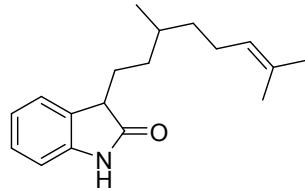
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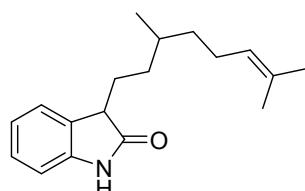
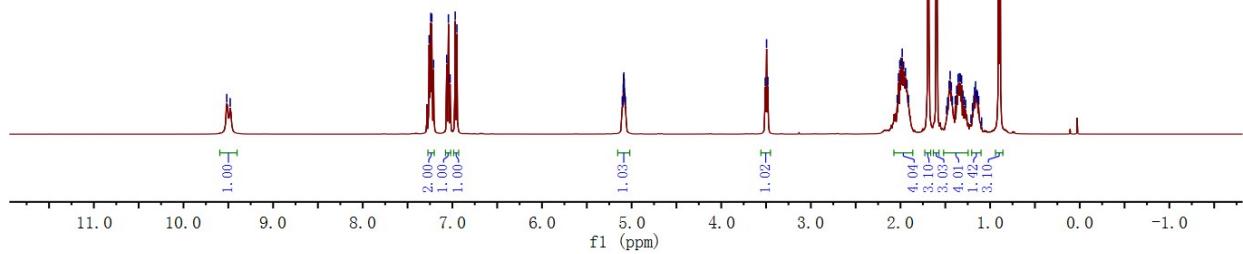
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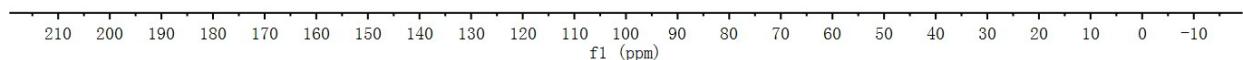


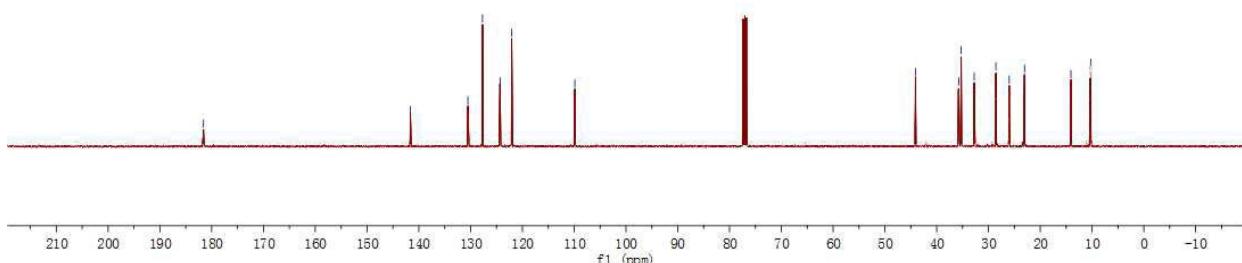
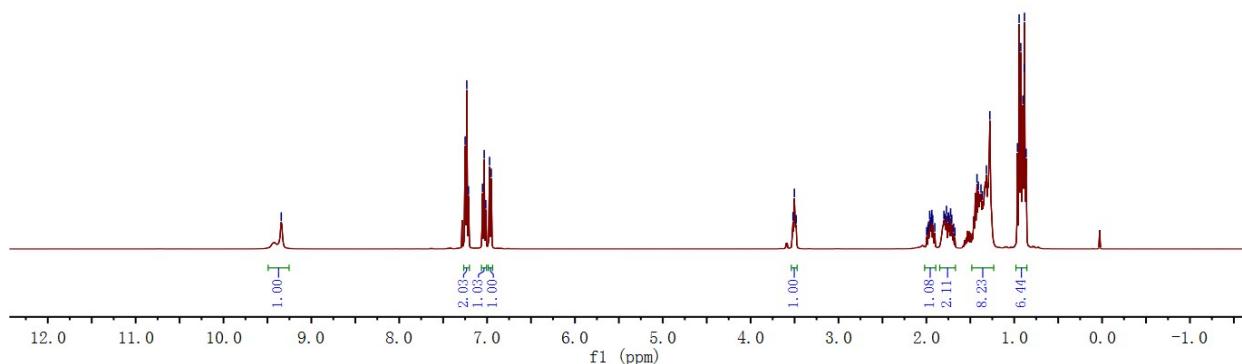


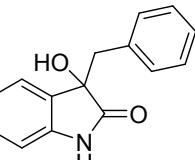
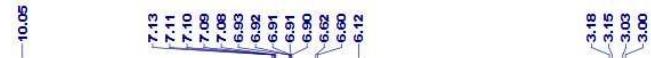
4b-¹H NMR



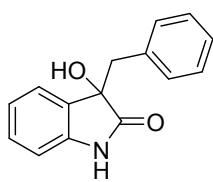
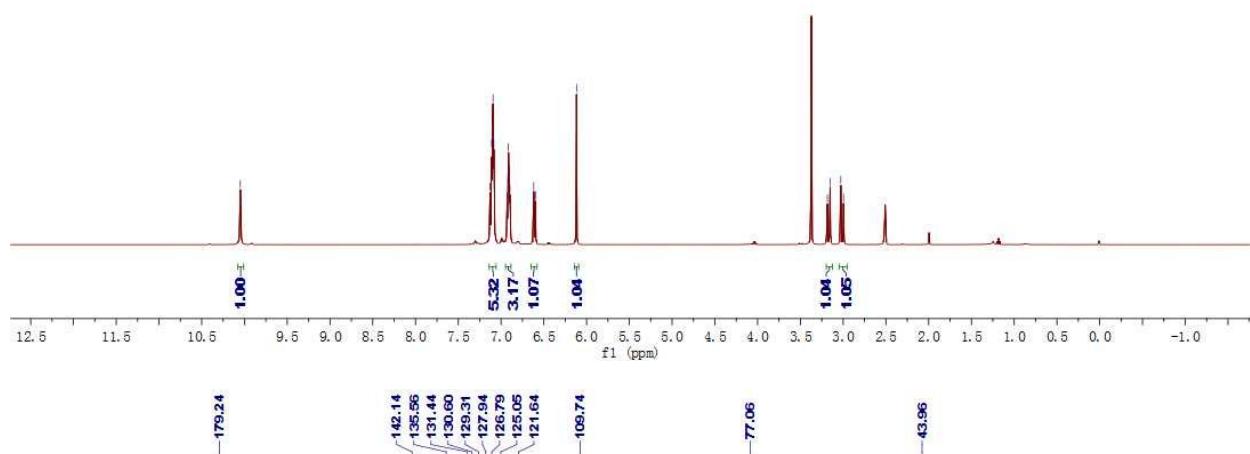
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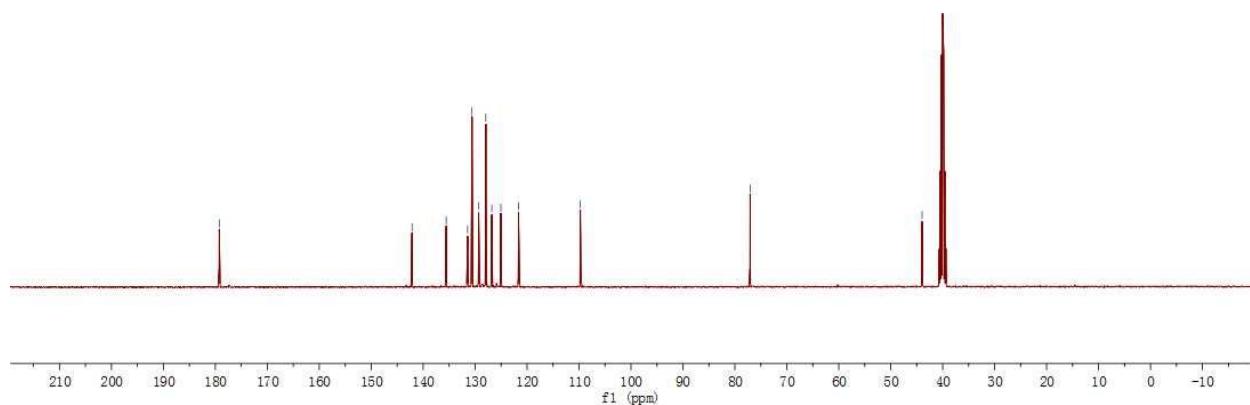




5aa-¹H NMR

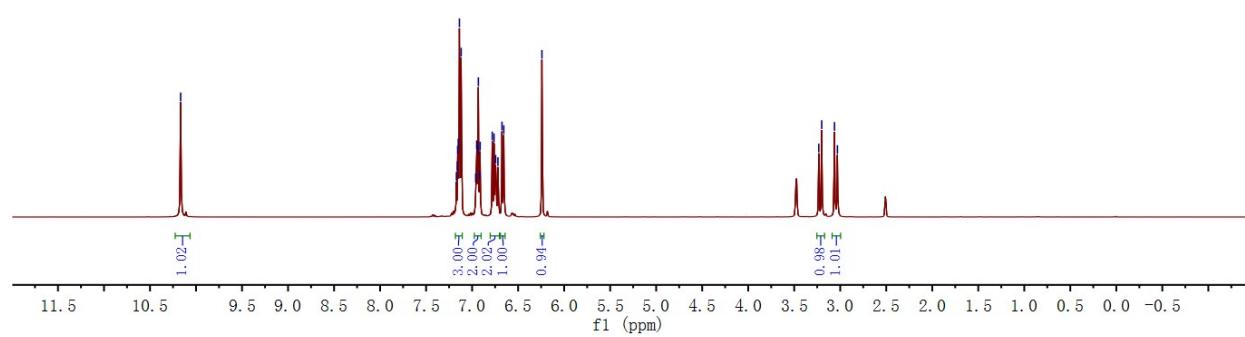


5aa-¹³C NMR

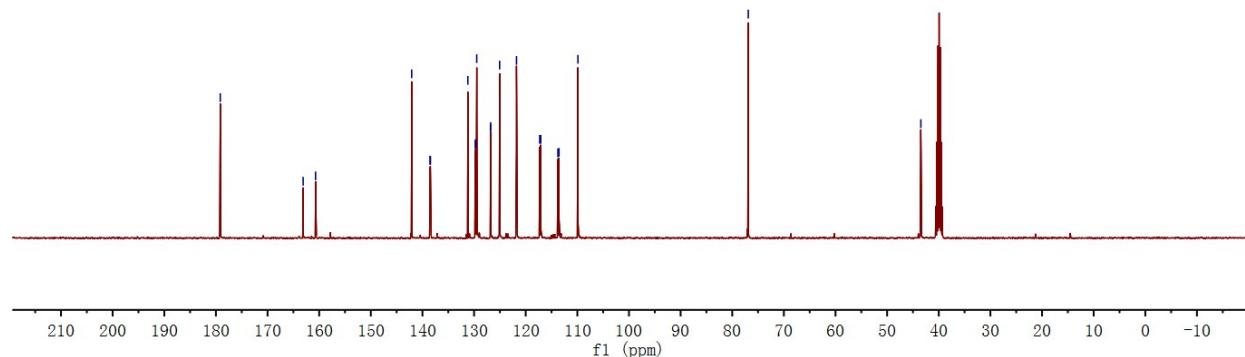


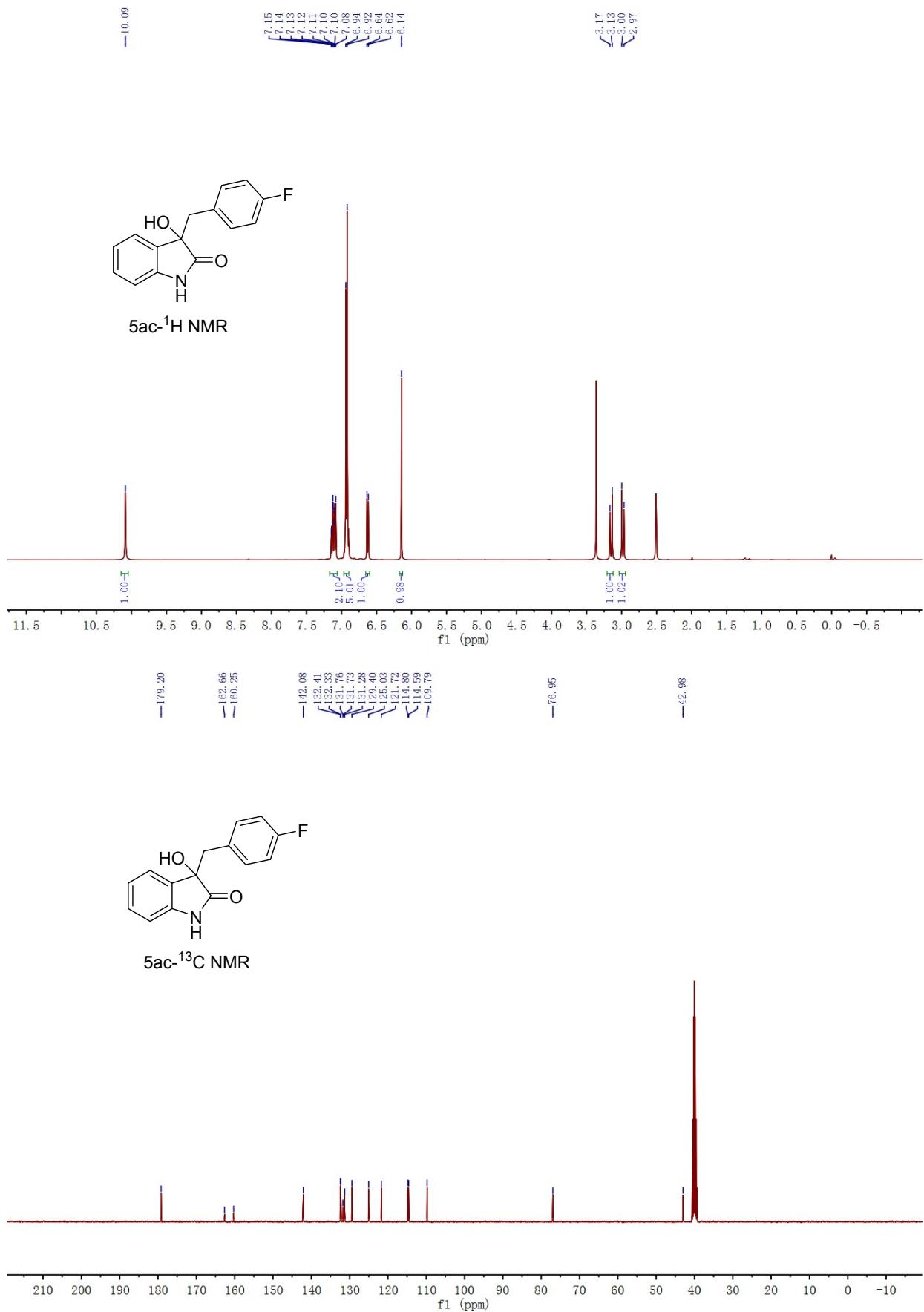


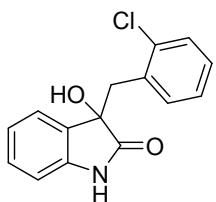
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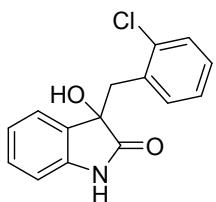
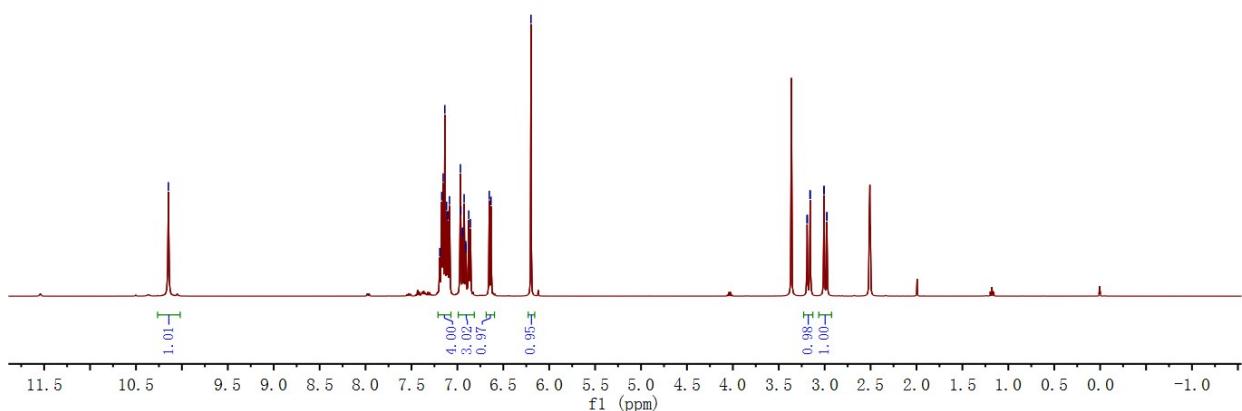
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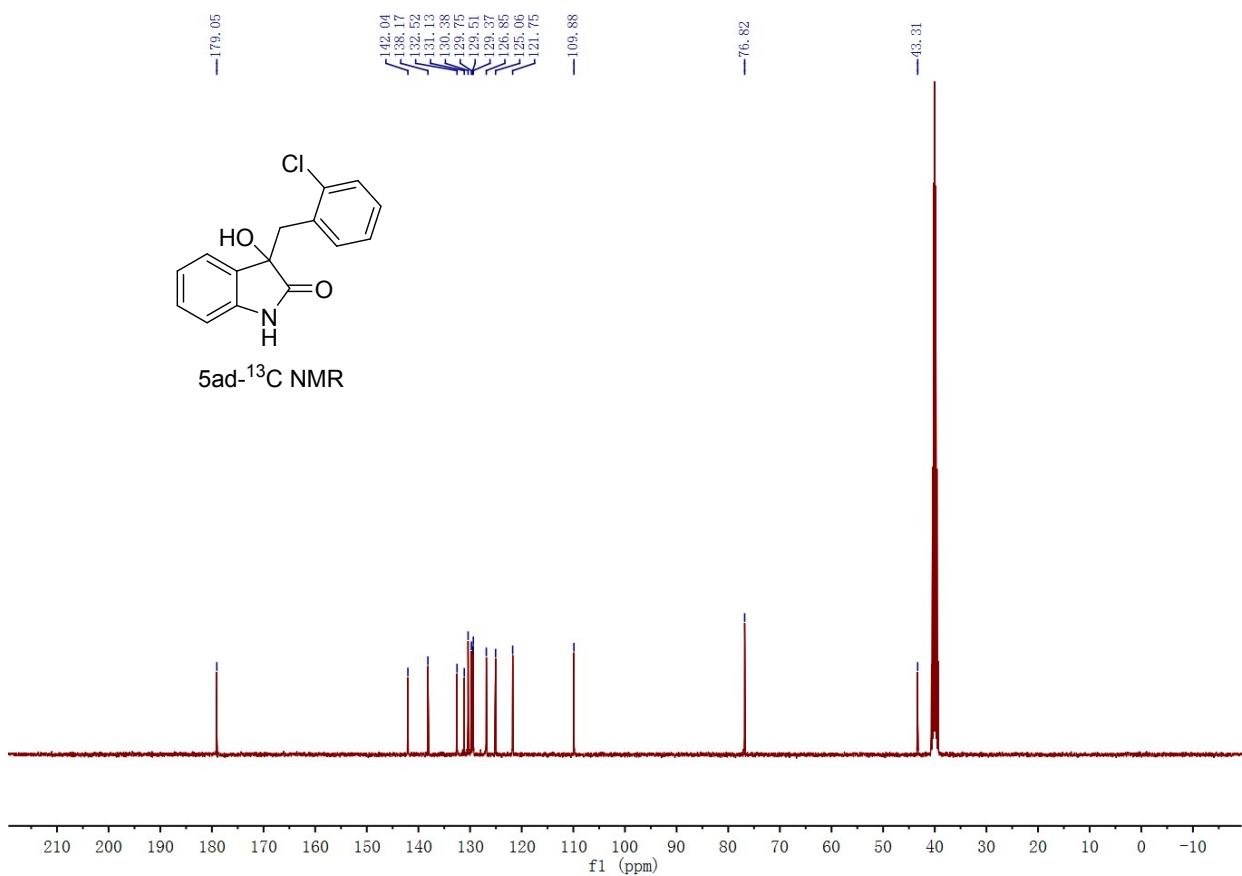


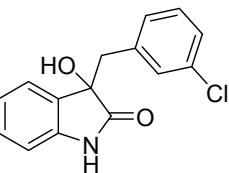
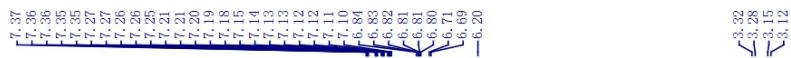


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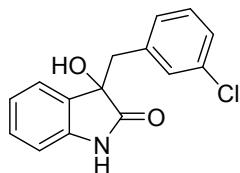
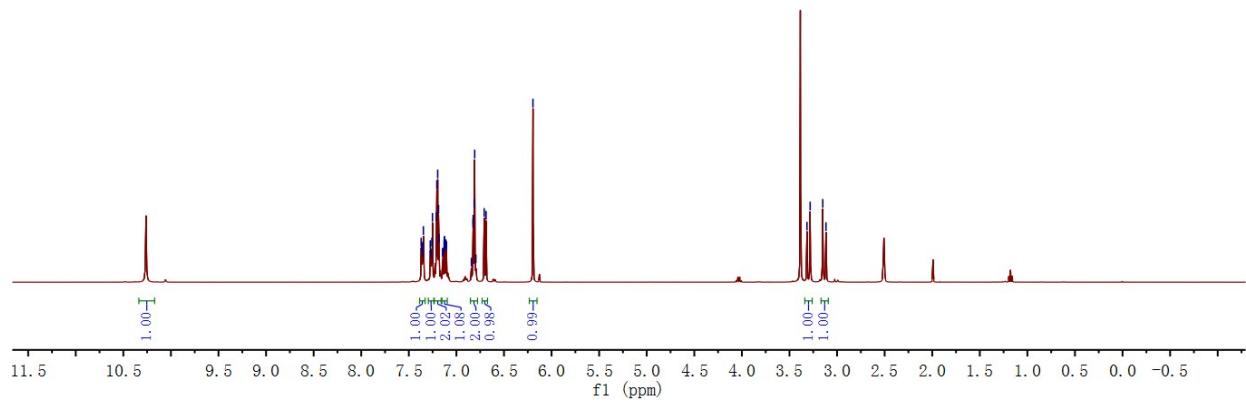


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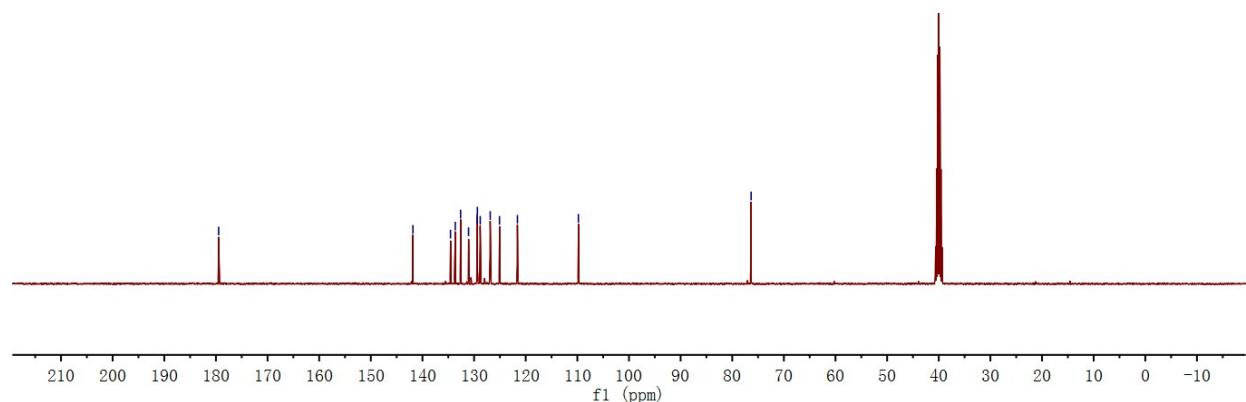




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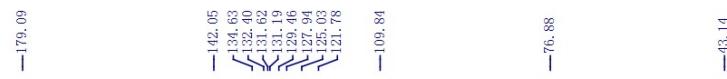
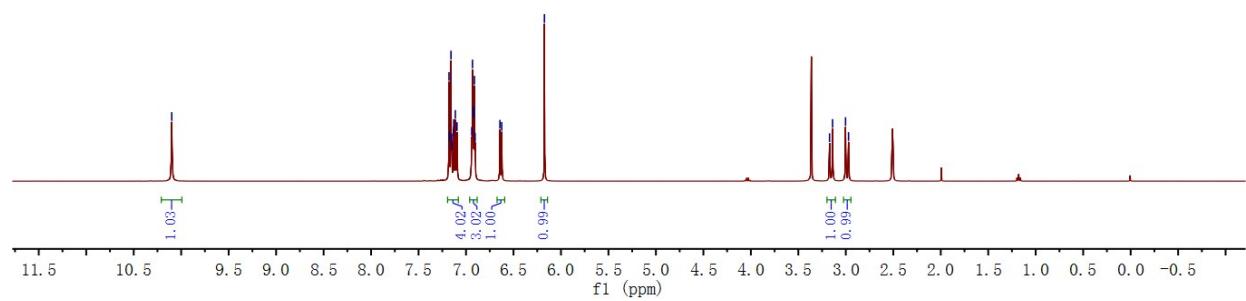


5ae-¹³C NMR

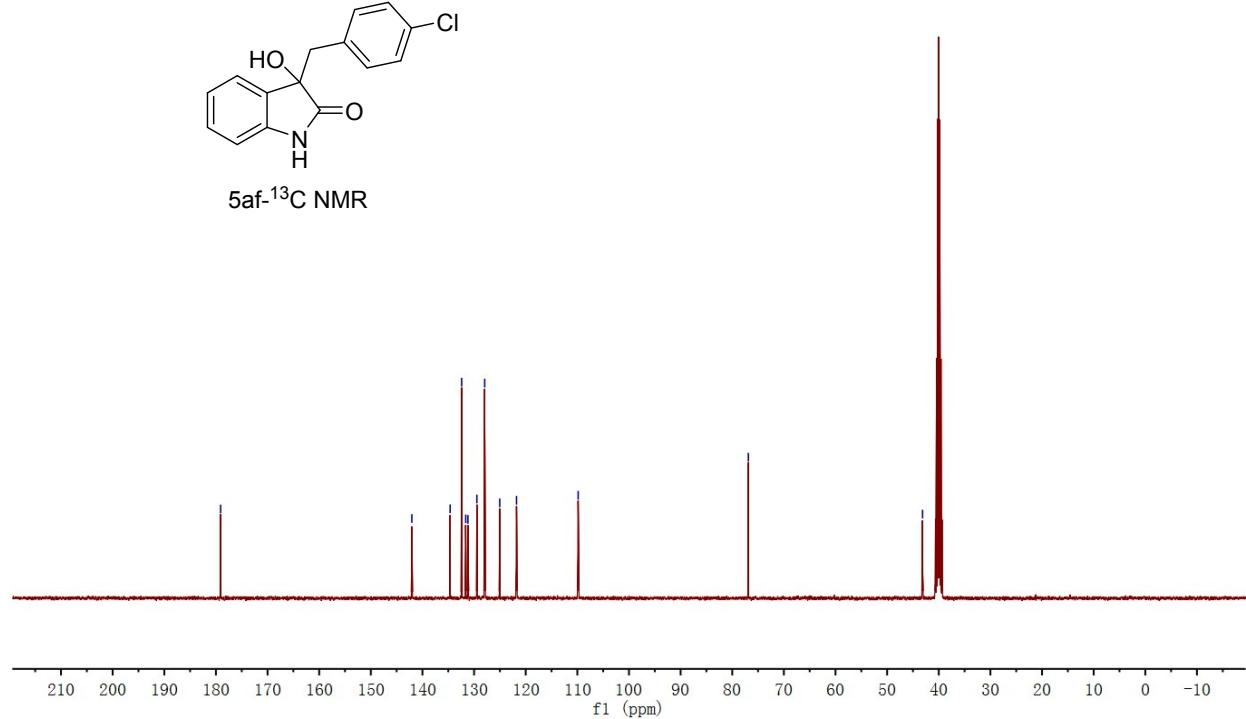


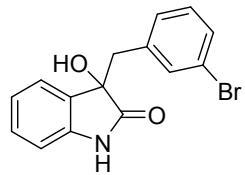


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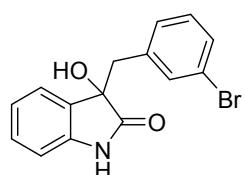
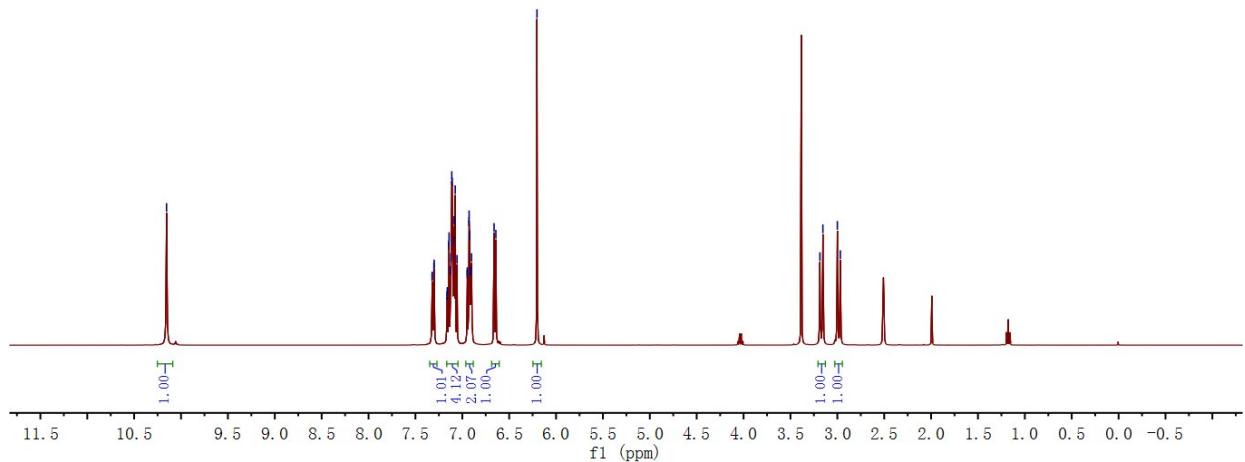


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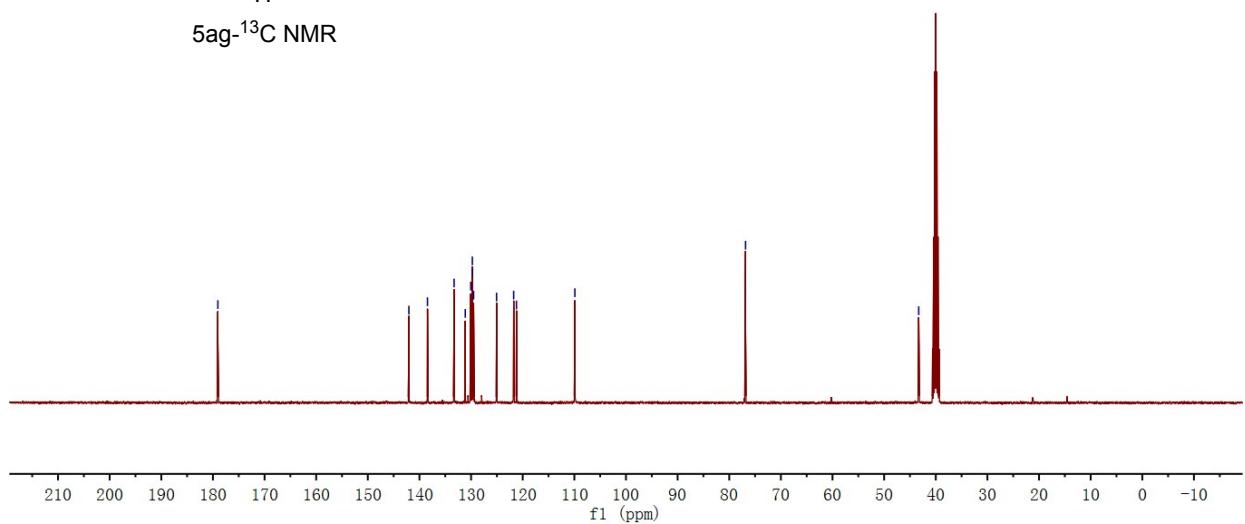


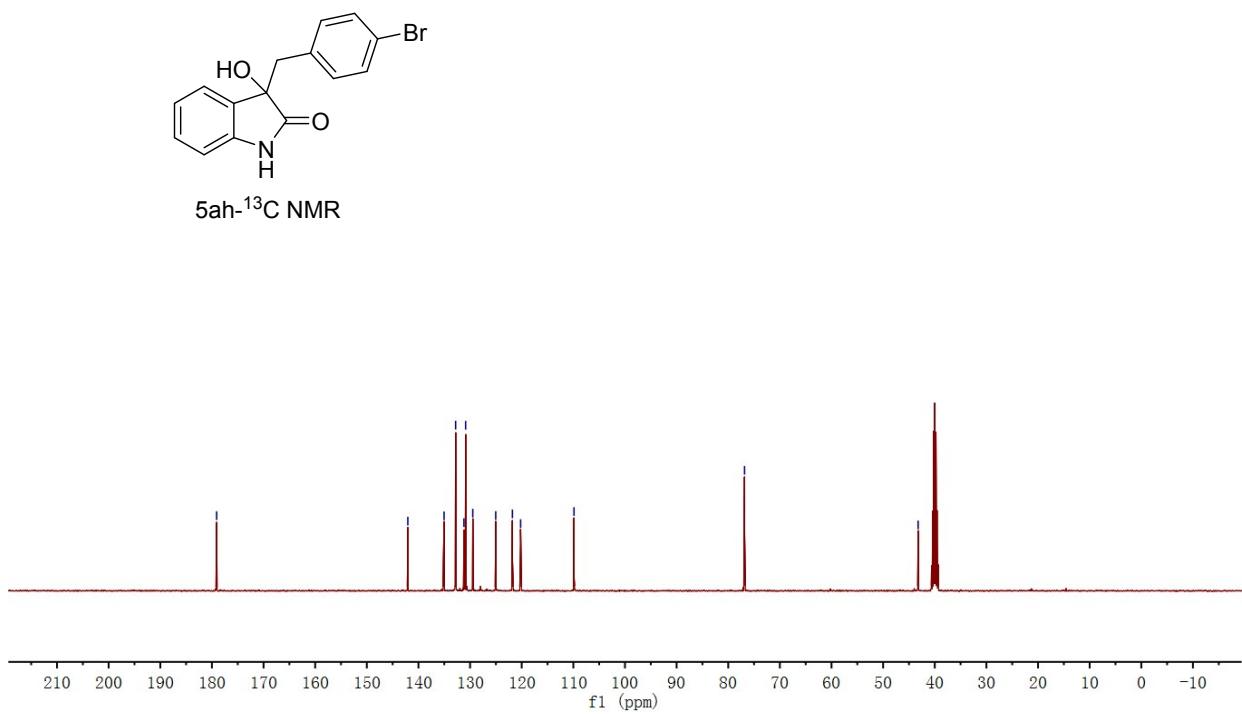
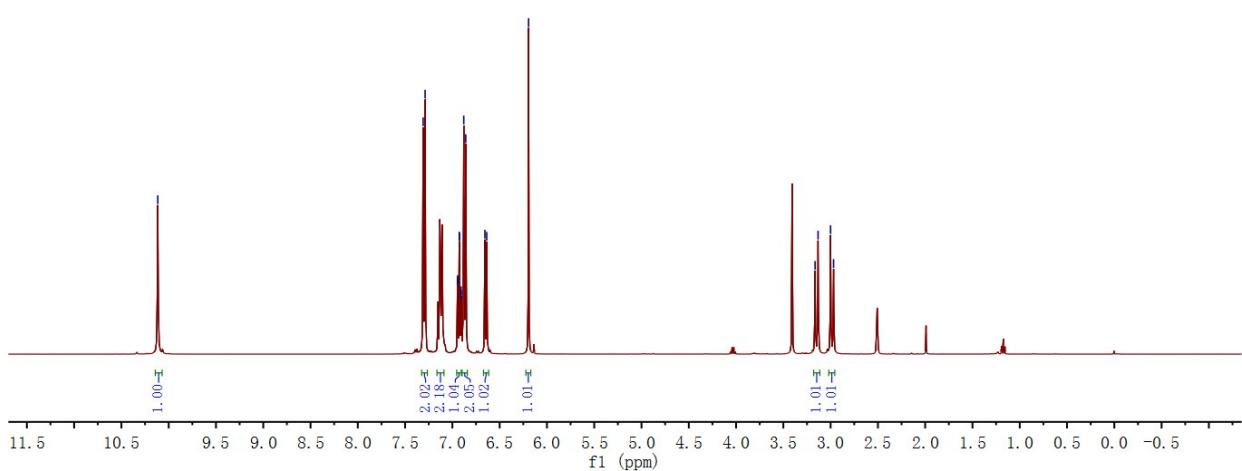


5ag-¹H NMR



5ag-¹³C NMR

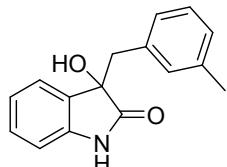




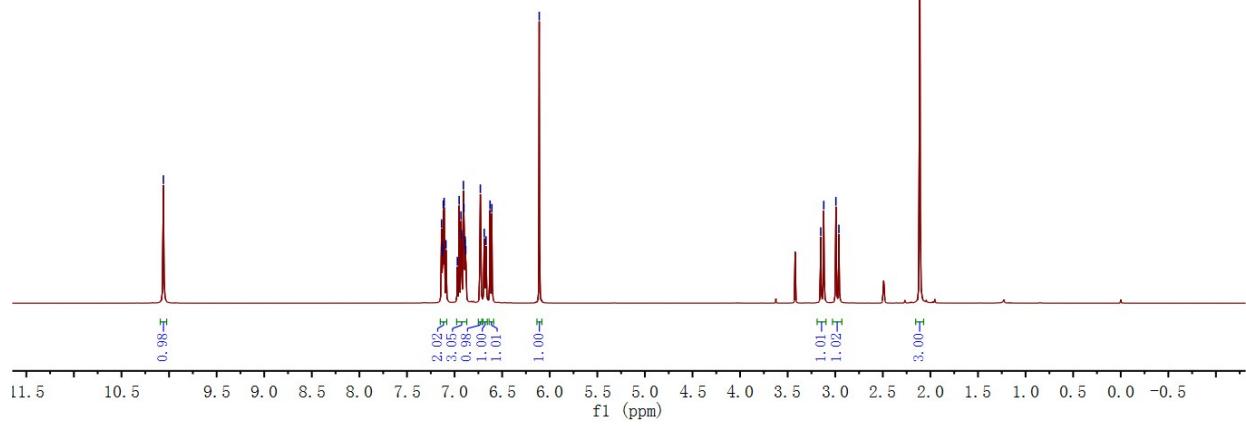
-10.06

7.14
7.13
7.13
7.12
7.11
7.09
6.97
6.95
6.93
6.93
6.91
6.89
6.89
6.88
6.73
6.69
6.67
6.63
6.61
6.11

-2.11



5ai-¹H NMR



-179.29

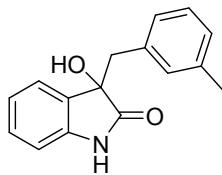
142.18
136.76
135.46
131.55
131.36
129.29
127.80
127.69
127.45
125.09
121.61

-109.76

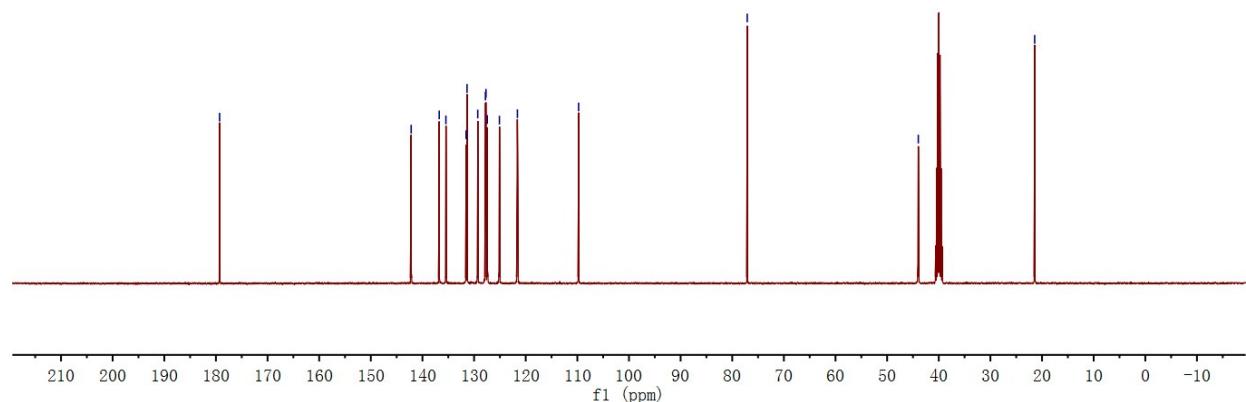
-77.10

-43.96

-21.43



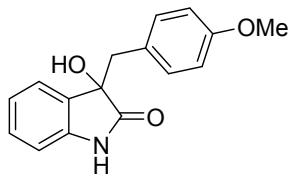
5ai-¹³C NMR



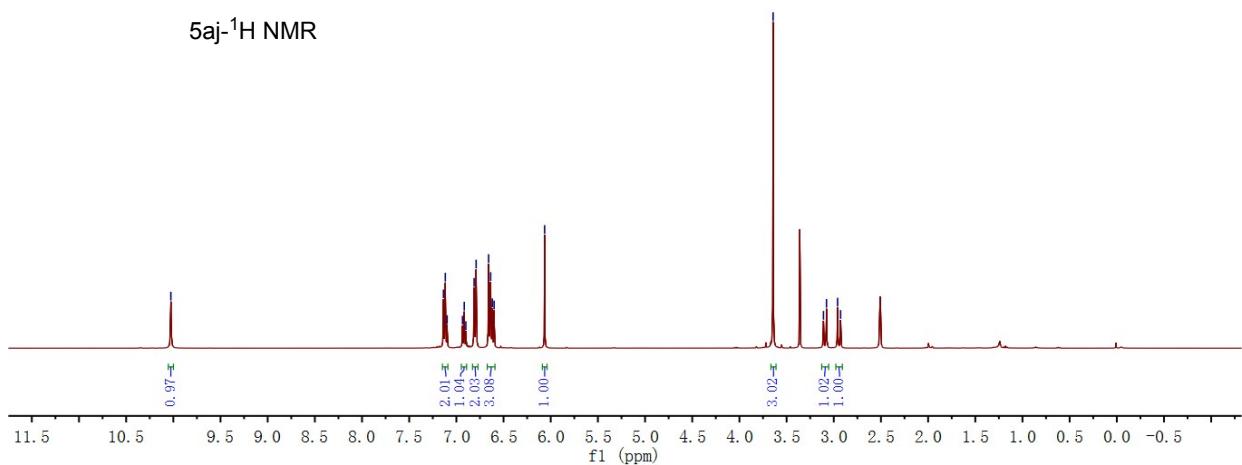
-10.03

7.14
7.12
7.10
6.93
6.92
6.90
6.81
6.79
6.66
6.64
6.62
6.60
6.06

-3.64
-3.11
-3.08
-2.96
-2.93



5aj-¹H NMR



-158.21

-142.18

-131.58

-131.55

-129.28

-127.35

-125.01

-121.66

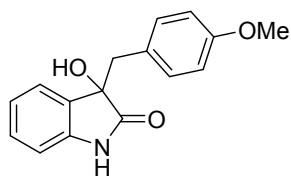
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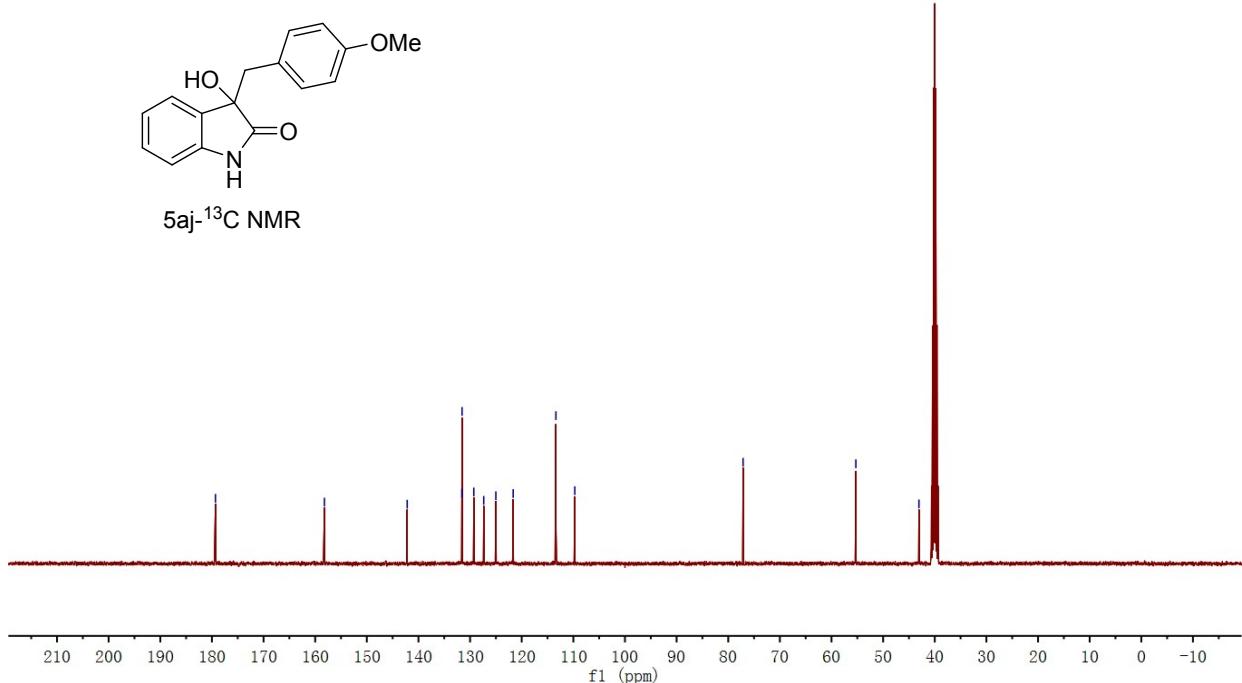
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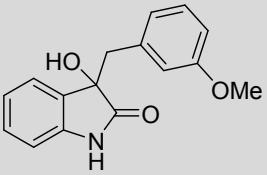
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-43.07



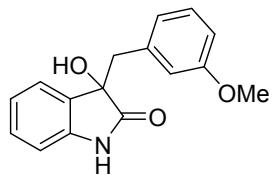
5aj-¹³C NMR



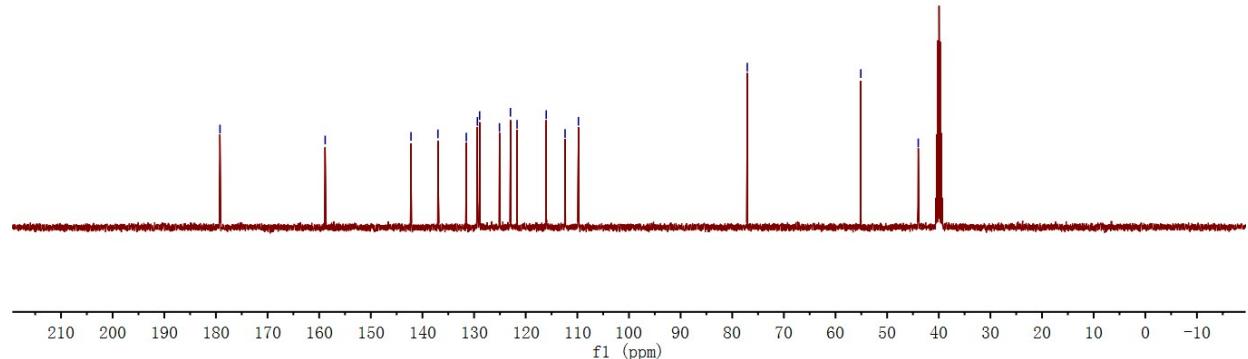


5ak-¹H NMR

—179.21
—158.84
—142.22
—137.00
—131.51
—129.36
—128.93
—125.08
—122.96
—121.68
—116.03
—112.37
—109.79
—77.09
—55.10
—43.97

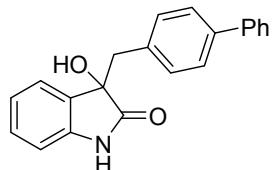
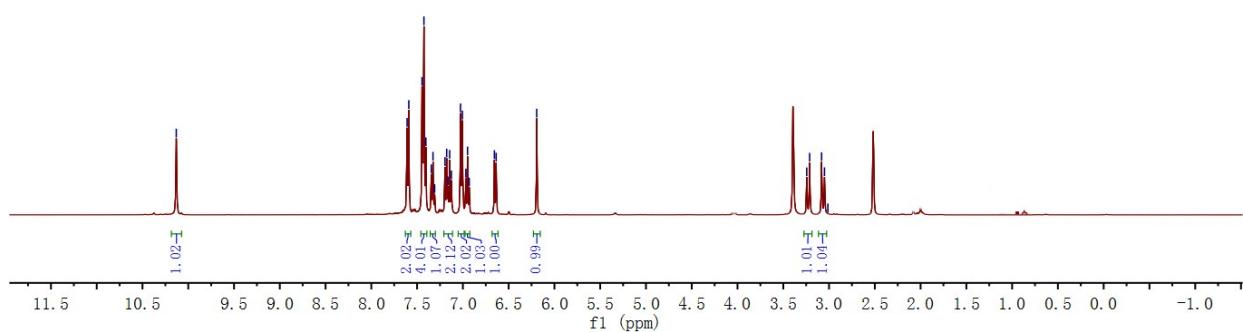


5ak-¹³C NMR

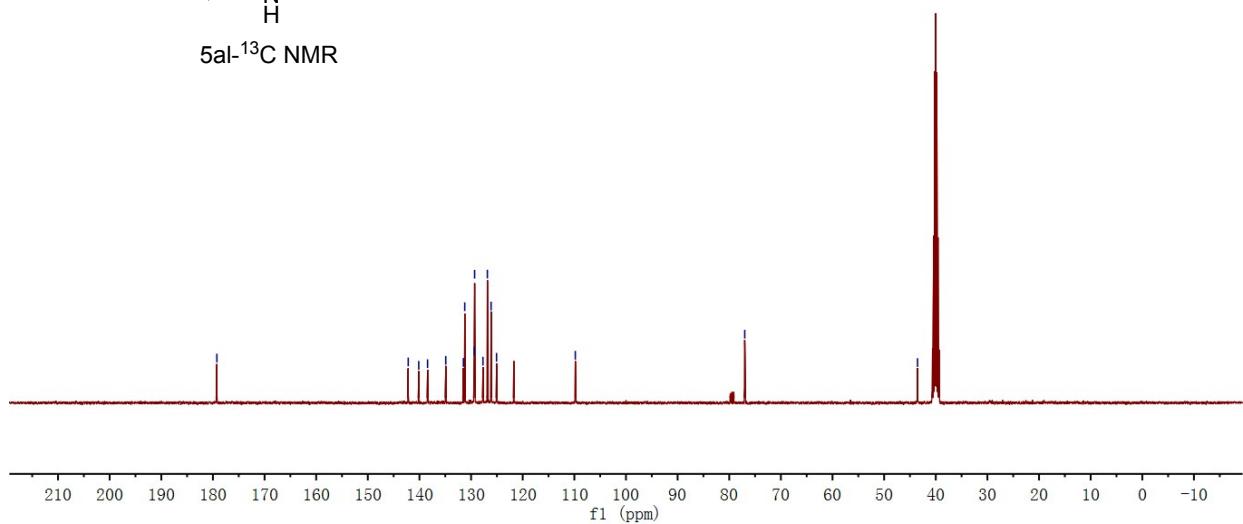


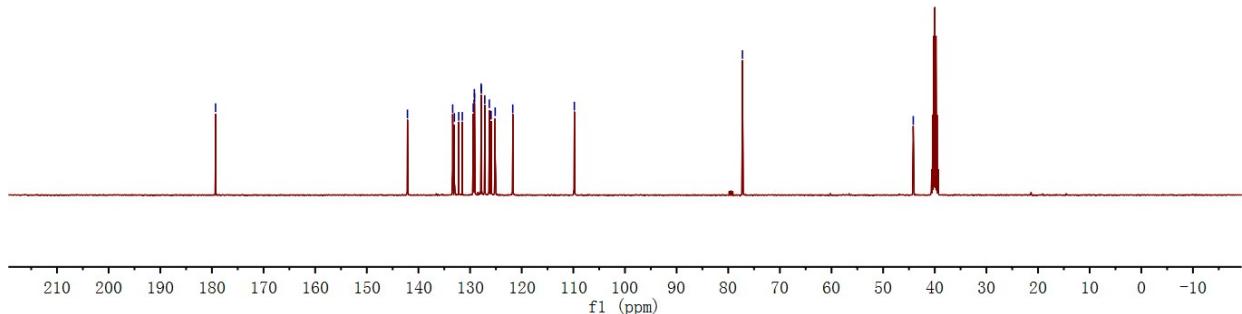
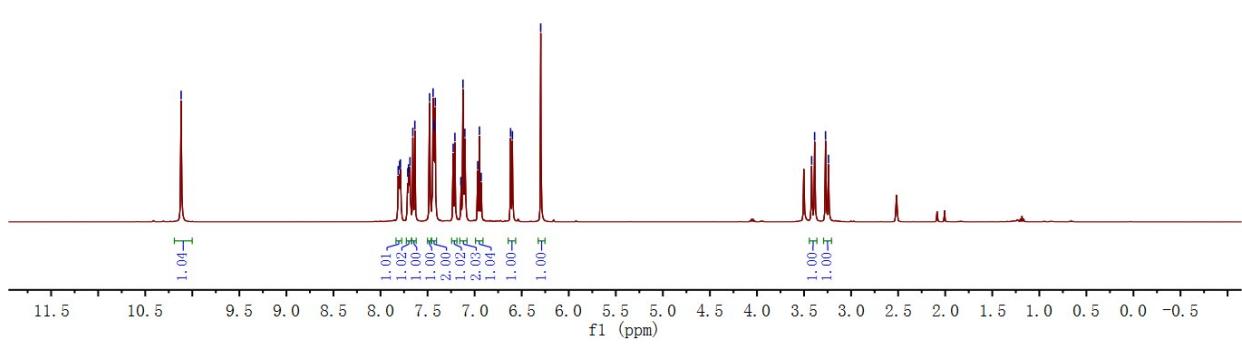


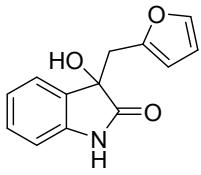
5al-¹H NMR



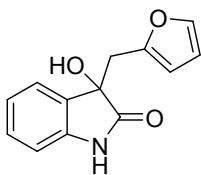
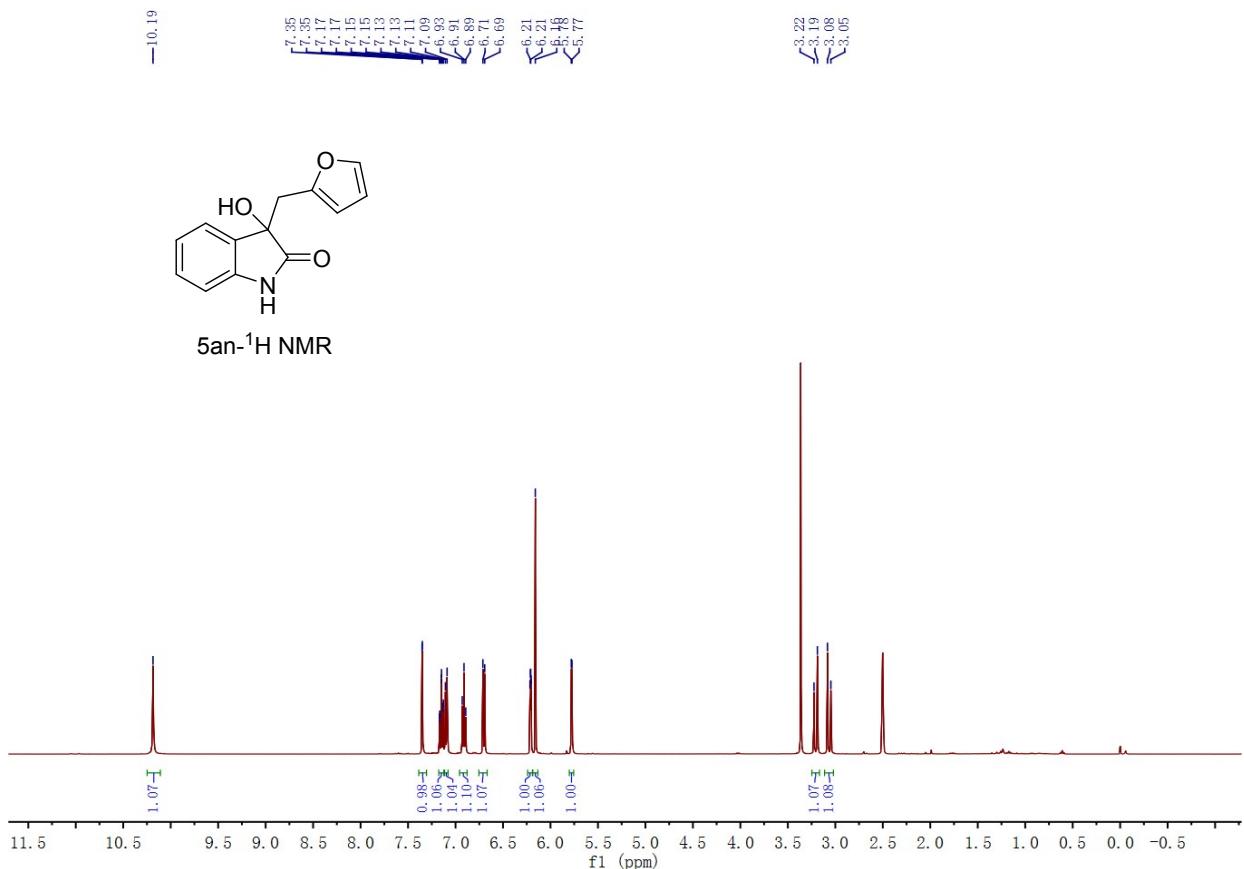
5al-¹³C NMR



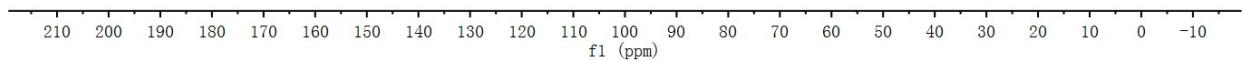


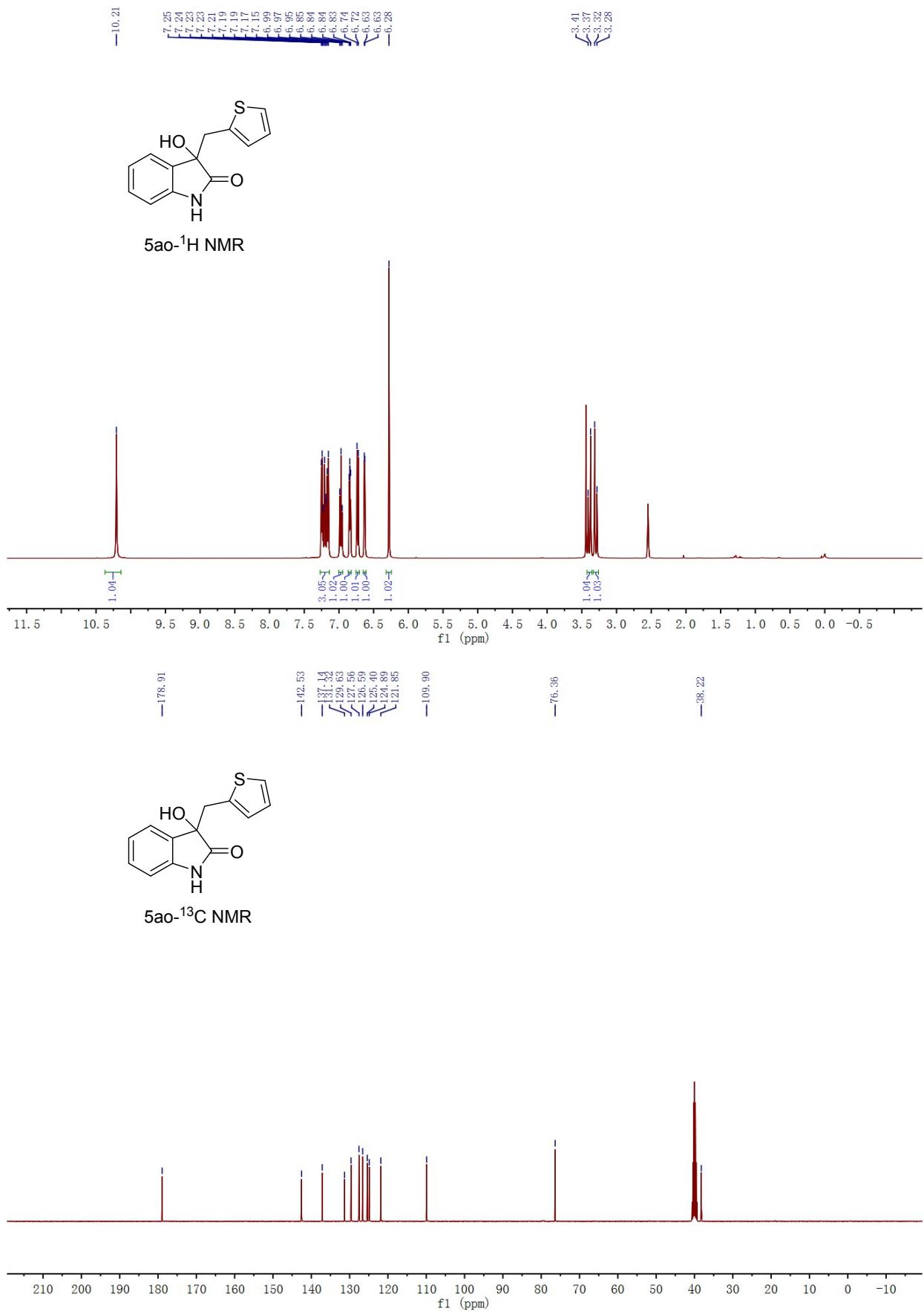


5an-¹H NMR



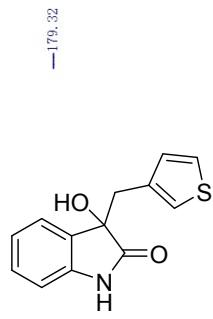
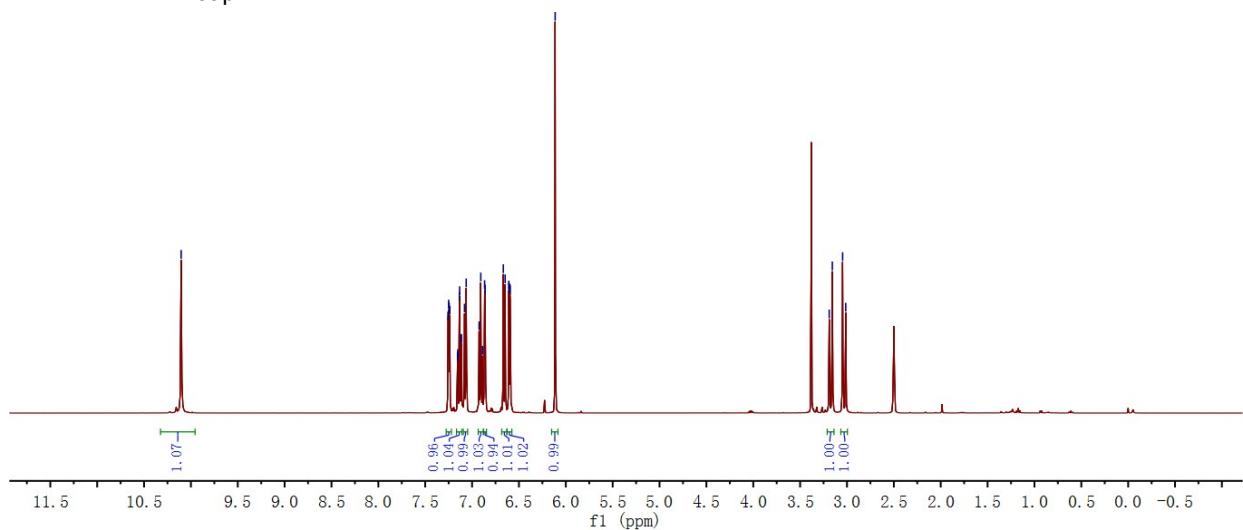
5an-¹³C NMR



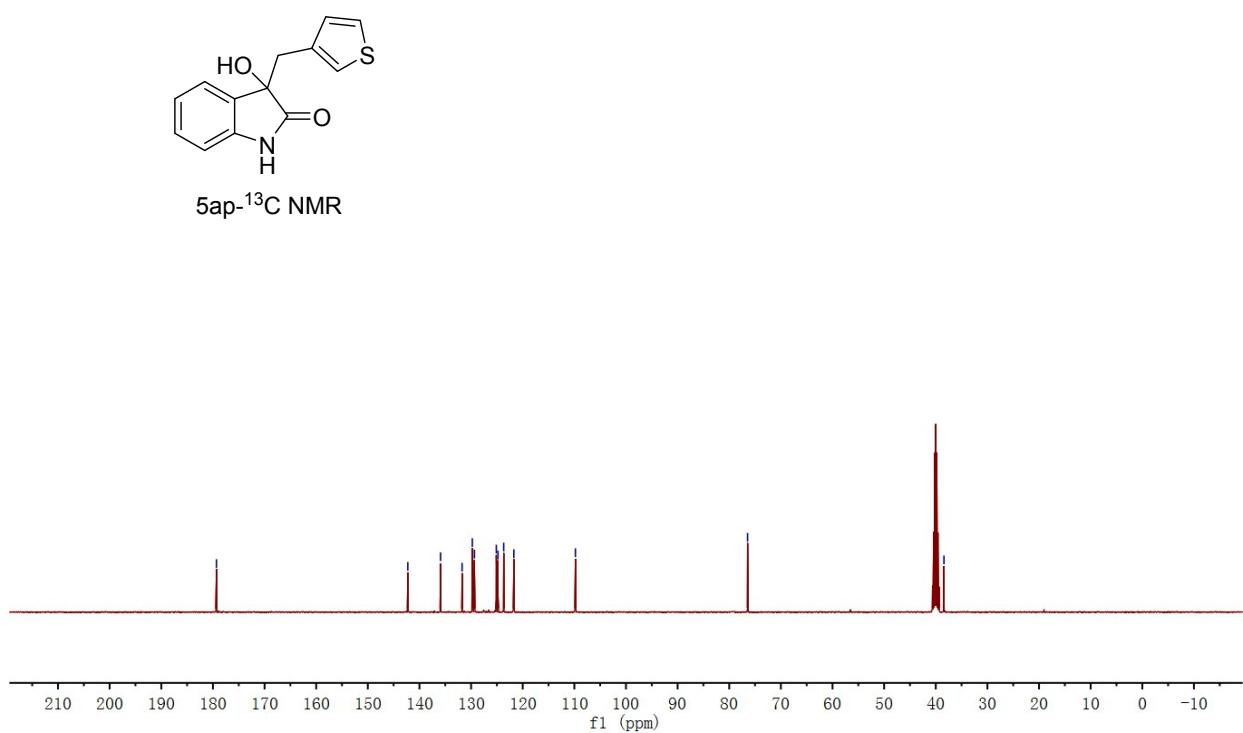


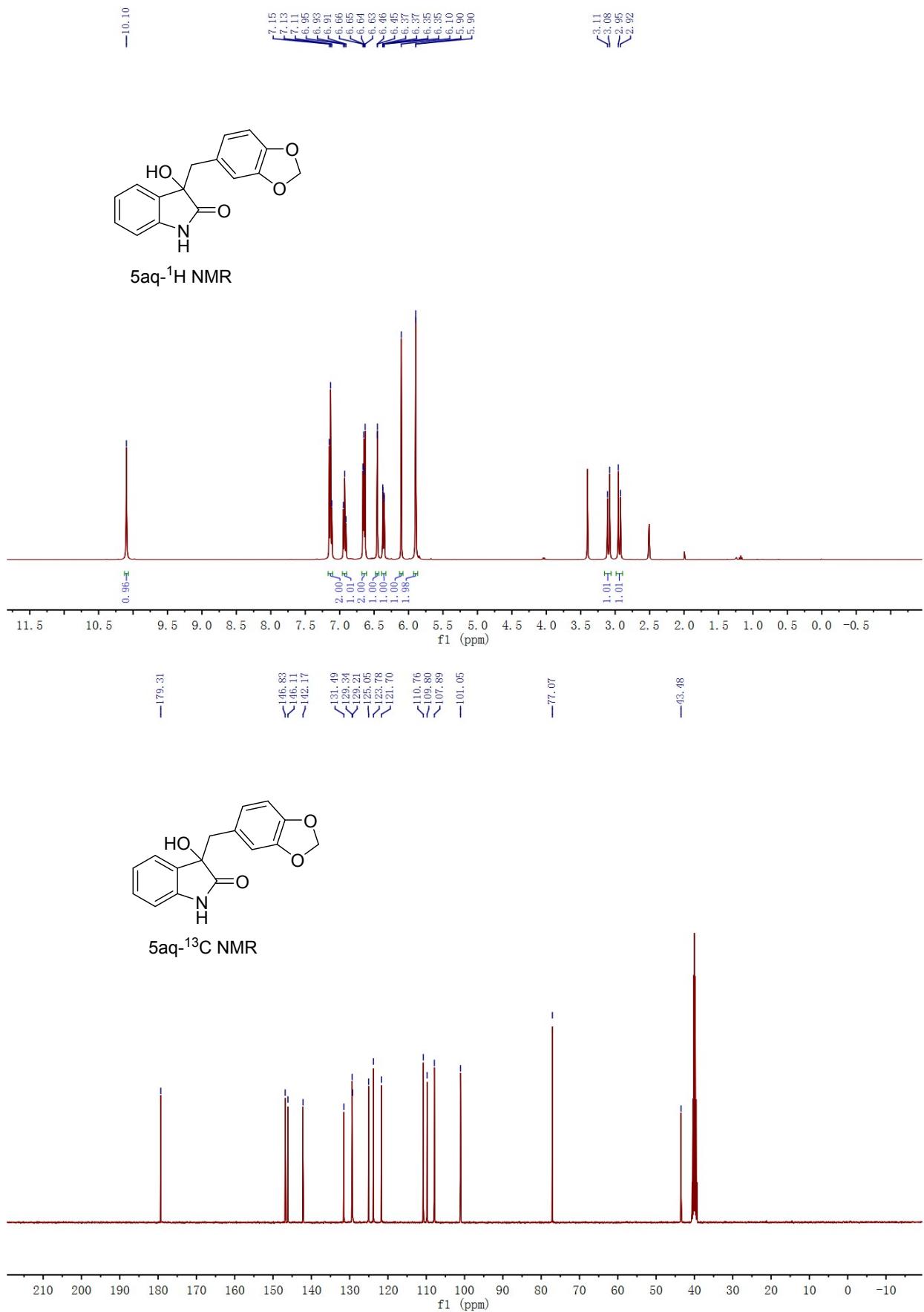


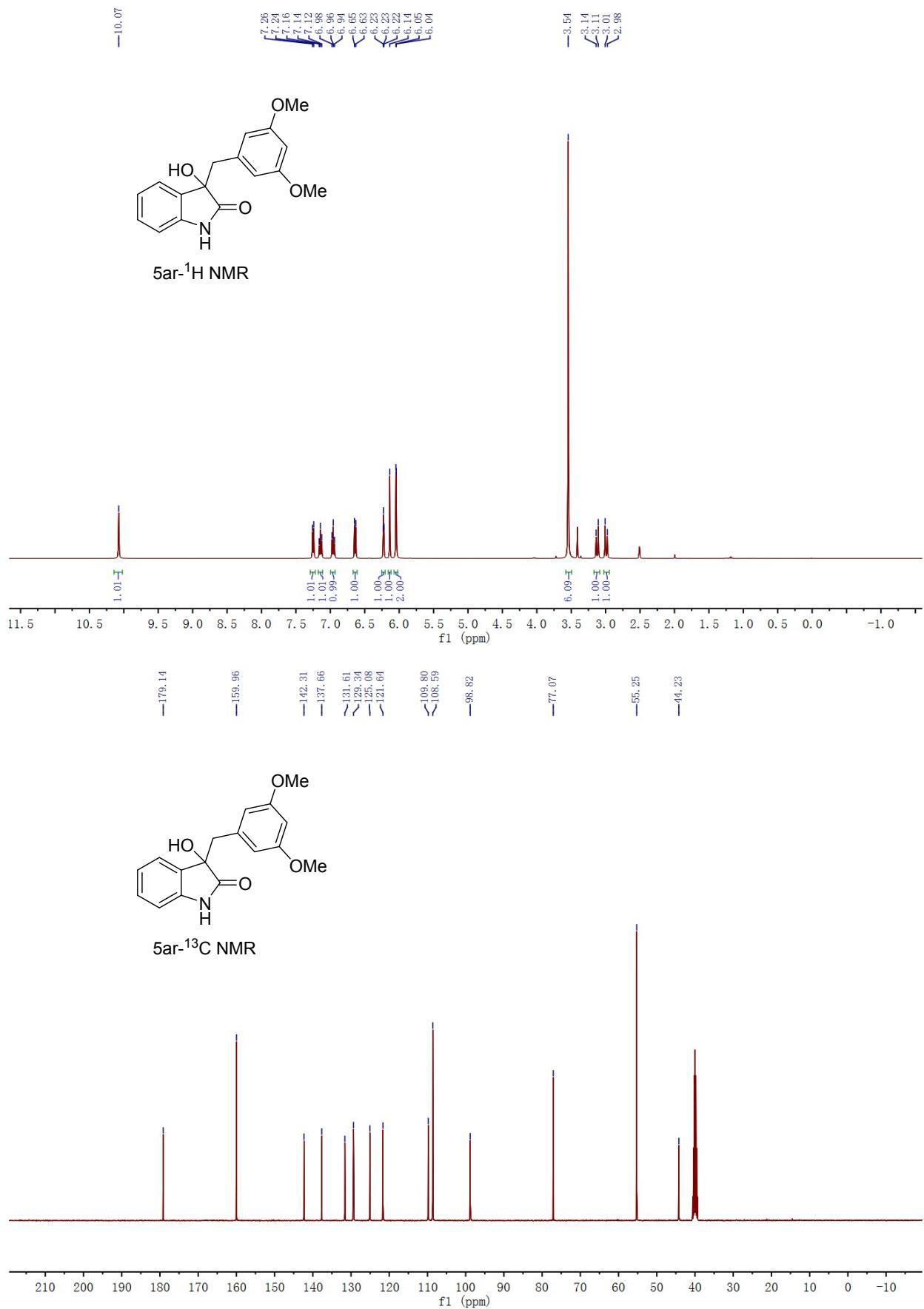
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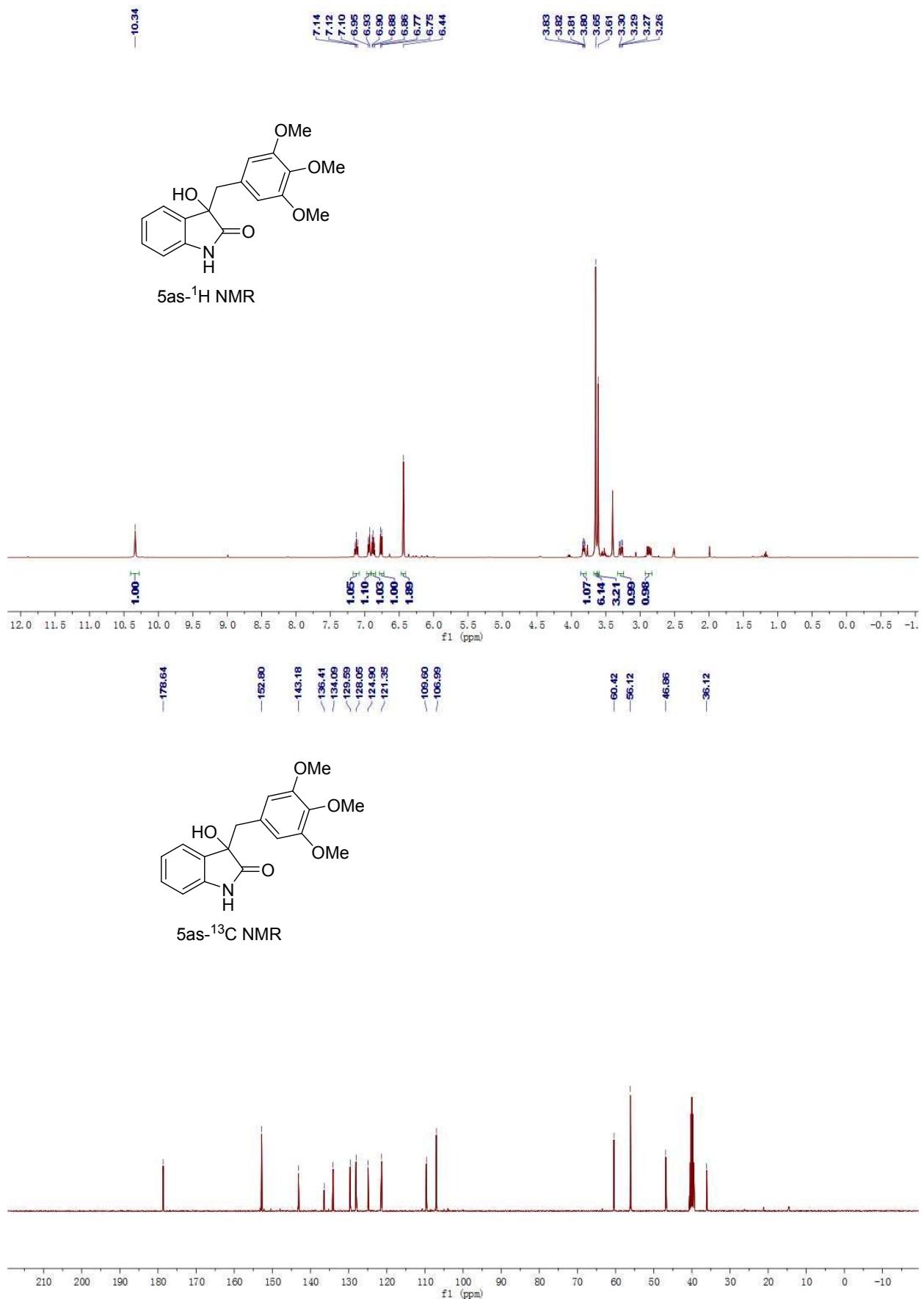


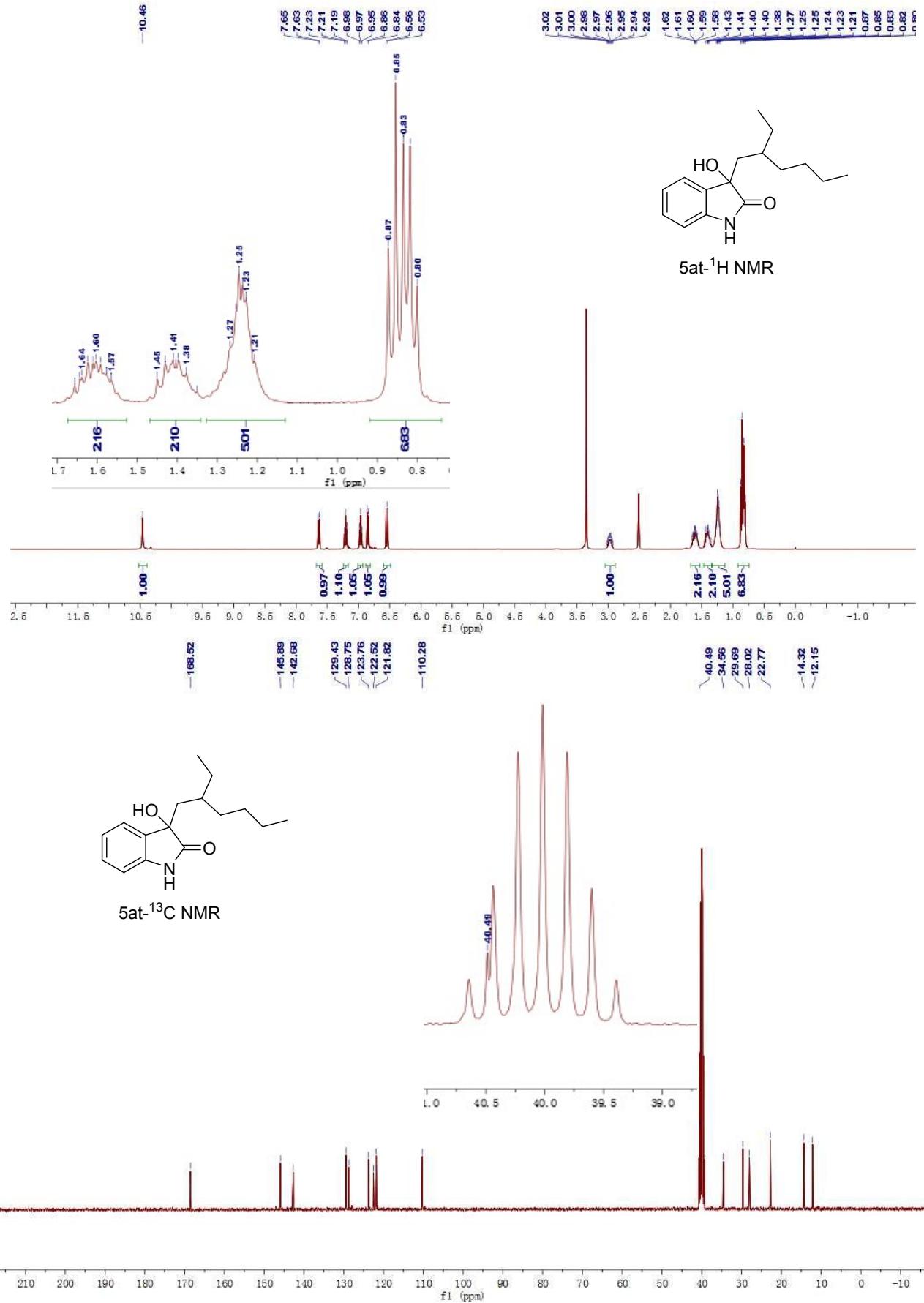
5ap-¹³C NMR

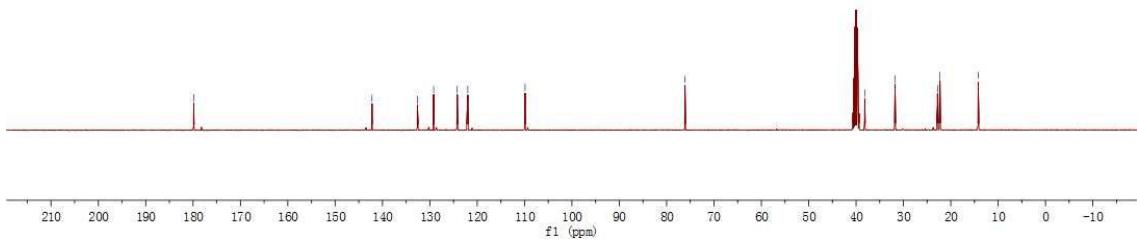
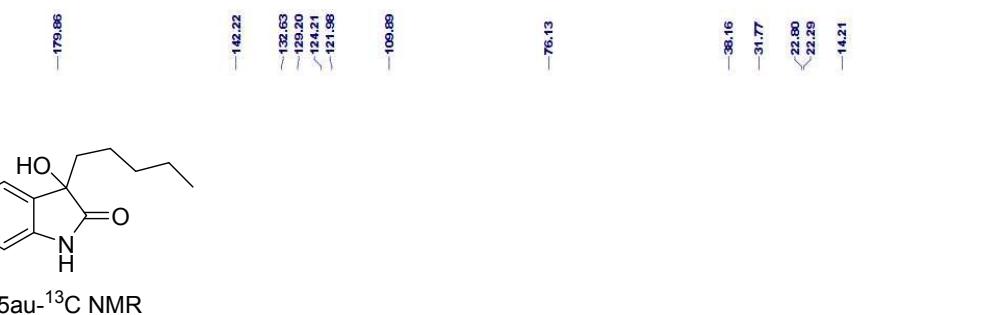
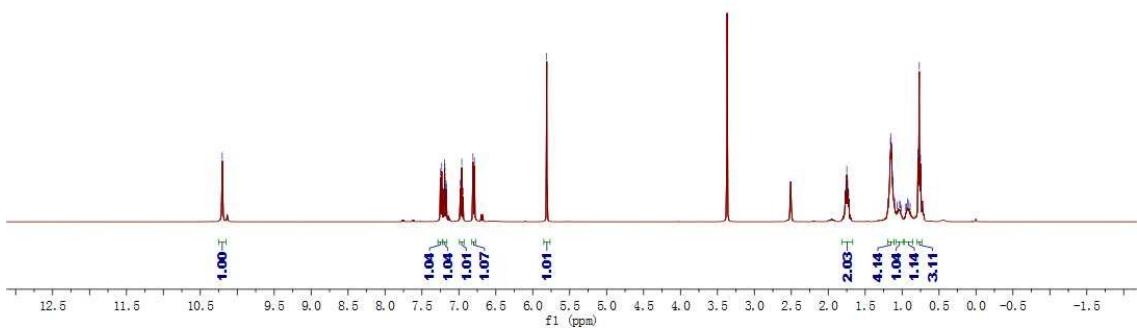
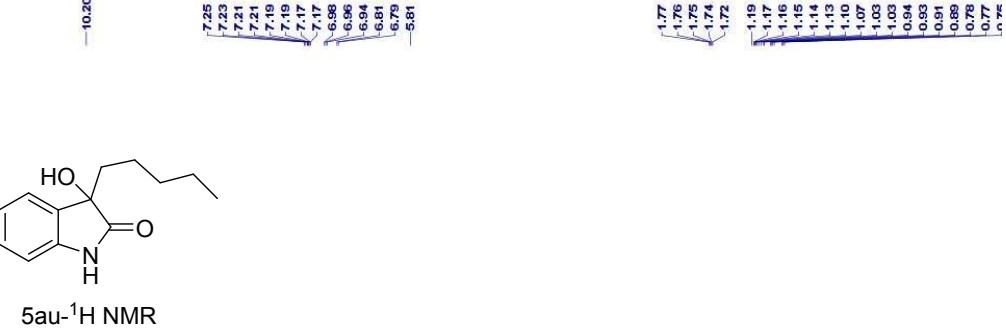


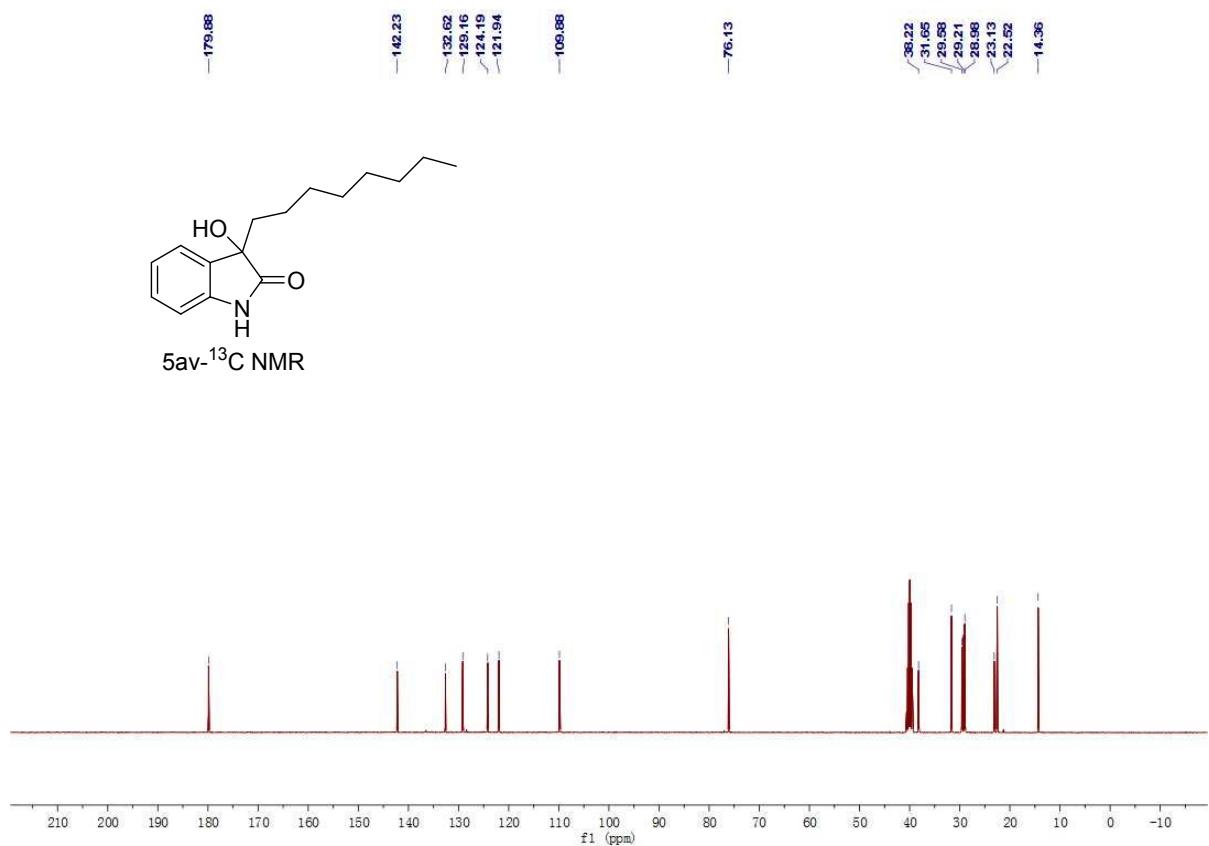
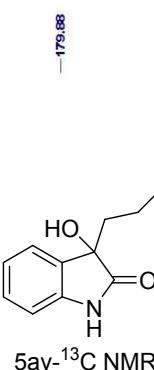
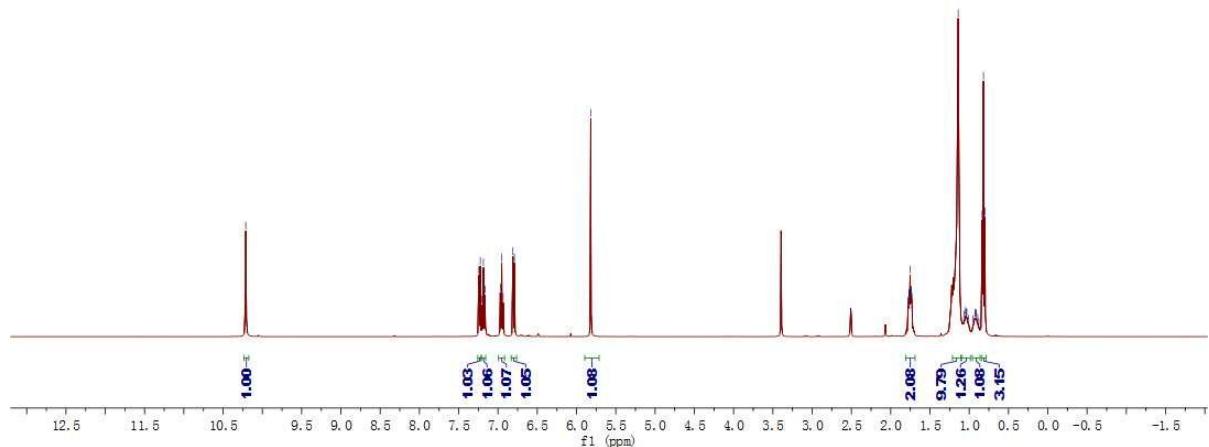
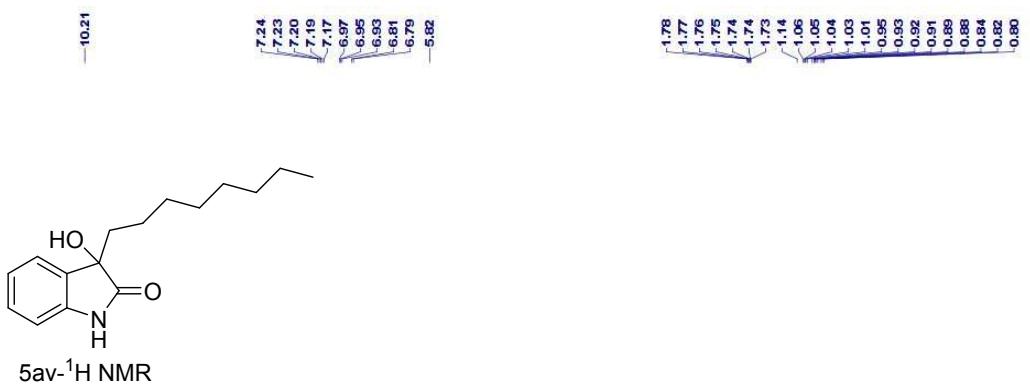


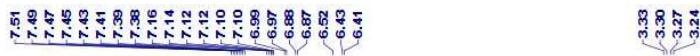




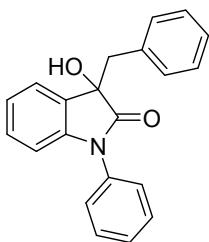
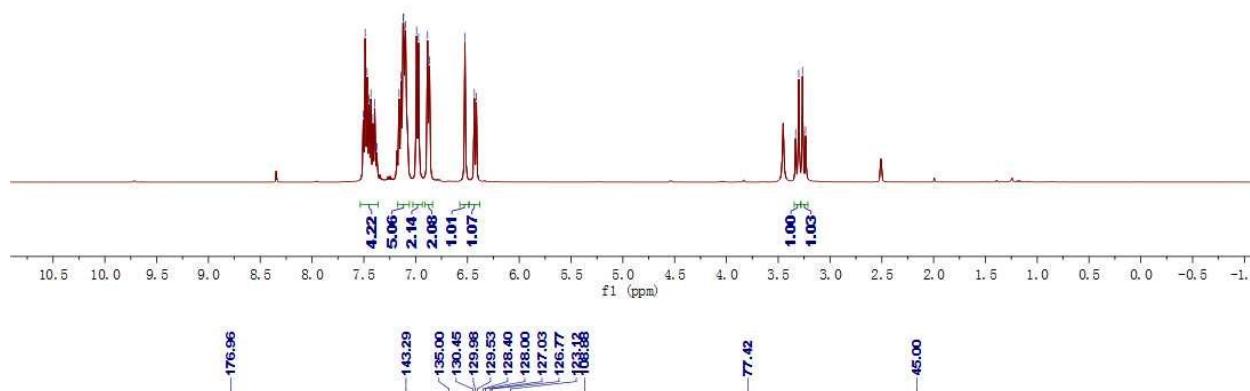




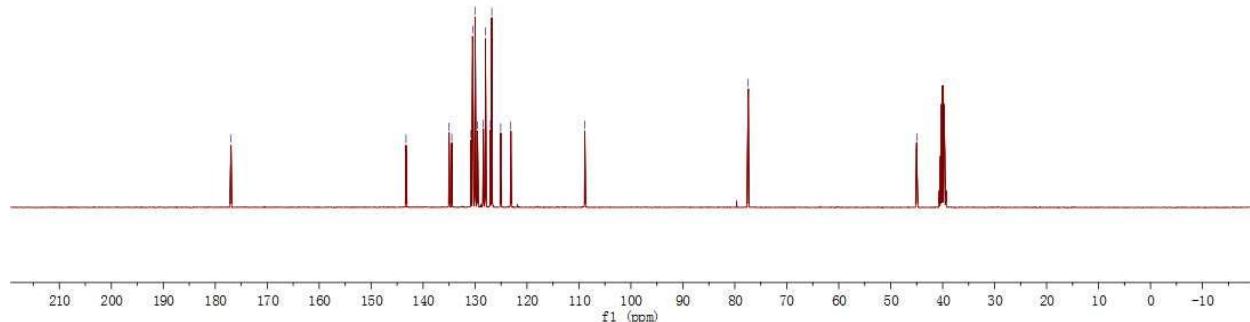


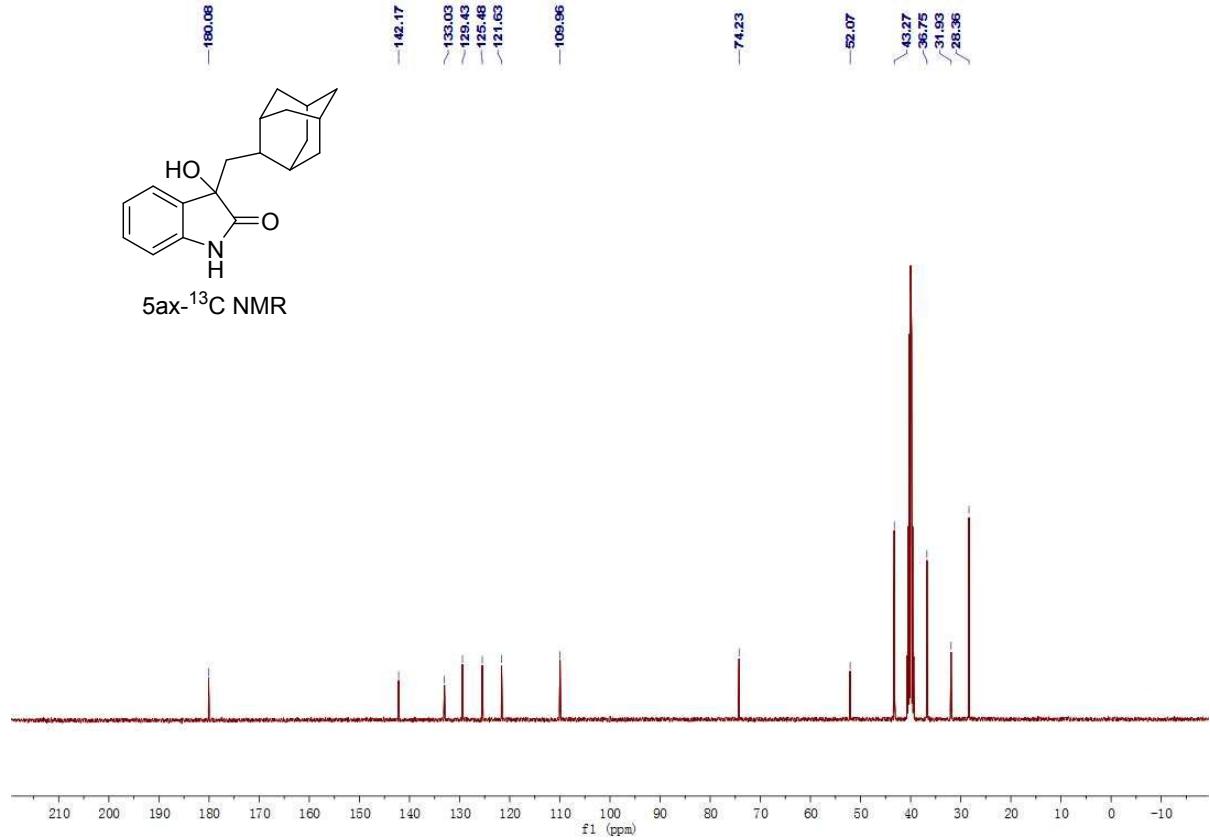
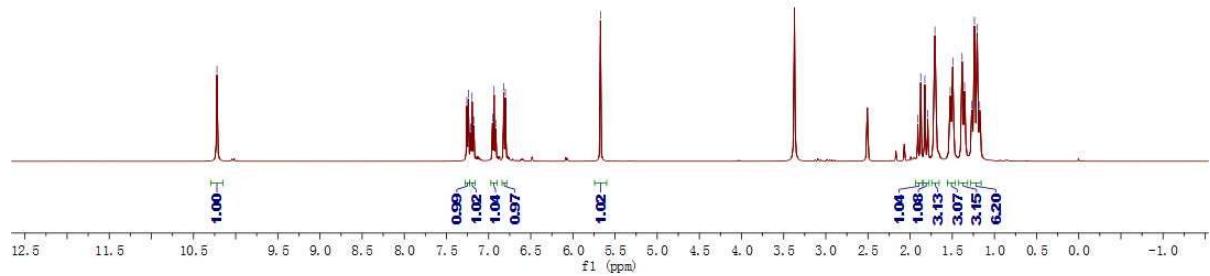
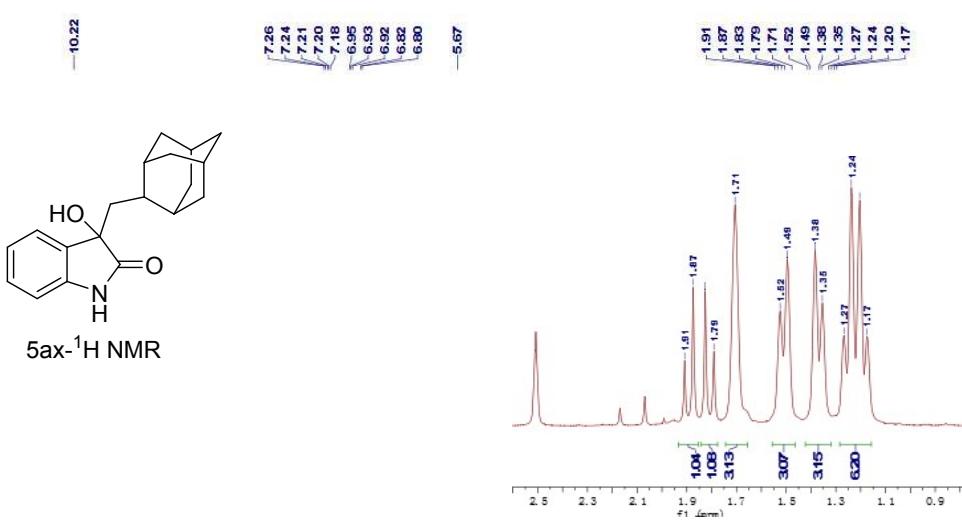


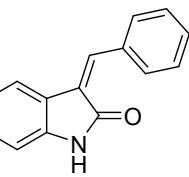
5aw- ^1H NMR



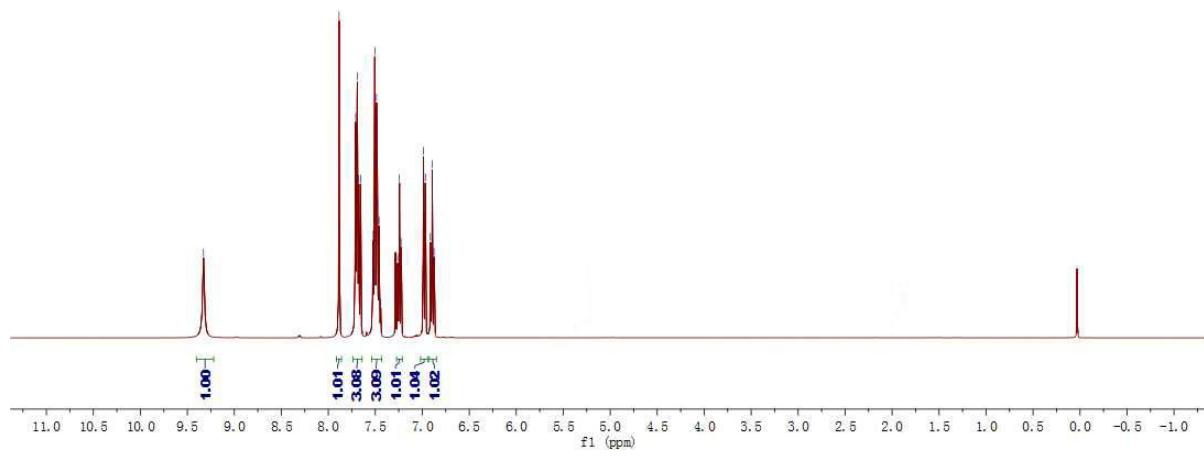
5aw- ^{13}C NMR



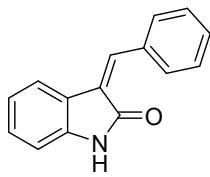




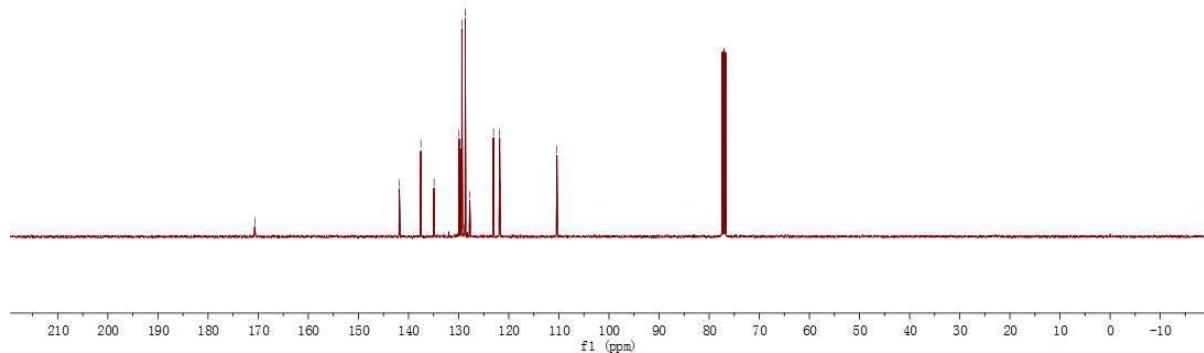
B-¹H NMR



170.67
144.34
137.54
134.90
129.93
129.88
129.36
128.88
127.77
123.04
121.83
121.73
110.40



B-¹³C NMR



7. Reference

1. R. Huang, Y. Yang, D.-S. Wang, L. Zhang and D. Wang, *Organic Chemistry Frontiers*, 2018, 5, 203-209; Z. Xu, D.-S. Wang, X. Yu, Y. Yang and D. Wang, *Advanced Synthesis & Catalysis*, 2017, 359, 3332-3340.
2. A. E. Putra, Y. Oe and T. Ohta, *European Journal of Organic Chemistry*, 2015, 2015, 7799-7805; Thomas Jensen and Robert Madsen*, *J. Org. Chem.* 2009, 74, 3990–3992; C. Chaudhari, S. M. A. H. Siddiki, K. Kon, A. Tomita, Y. Tai and K.-i. Shimizu, *Catal. Sci. Technol.*, 2014, 4, 1064-1069.