

Supporting Information

NMM-promoted decarboxylative C(sp³)-C(sp³) coupling of coumarin-3-carboxylic acids and indolin-3-ones

Zhan-Yong Wang,^a Can Zhang,^a Xiao-Tian Wang,^a Xiao-Jin Sun,^a Yi-Lin Wang,^a
Ting Yang,^b Chenyang Ma,^c Ran Xia*^a and Hongxin Liu*^{c, d}

- a. School of Pharmacy, Xinxiang University, Xinxiang, China.
- b. Nursing College, Xinxiang University, Xinxiang, China.
- c. Henan Run Catalysts Co., Ltd., Xinxiang, China.
- d. College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, China.
- e. Institute of New Materials & Industrial Technology, Wenzhou University, Wenzhou, China.

Table of contents

1. General Information	1
2. The data of the products 3 and 4a	4
3. The NMR of 3 and 4a	17
4. Scanned copies of ¹H-NMR spectra of 3a (isolated from the experiment carried out in the presence of TEMPO, BHT as a radical scavenger) and the crude spectrum of 3ac	47
5. The HPLC of 3a	49
6 The data of crystal structure	51

1. General Information

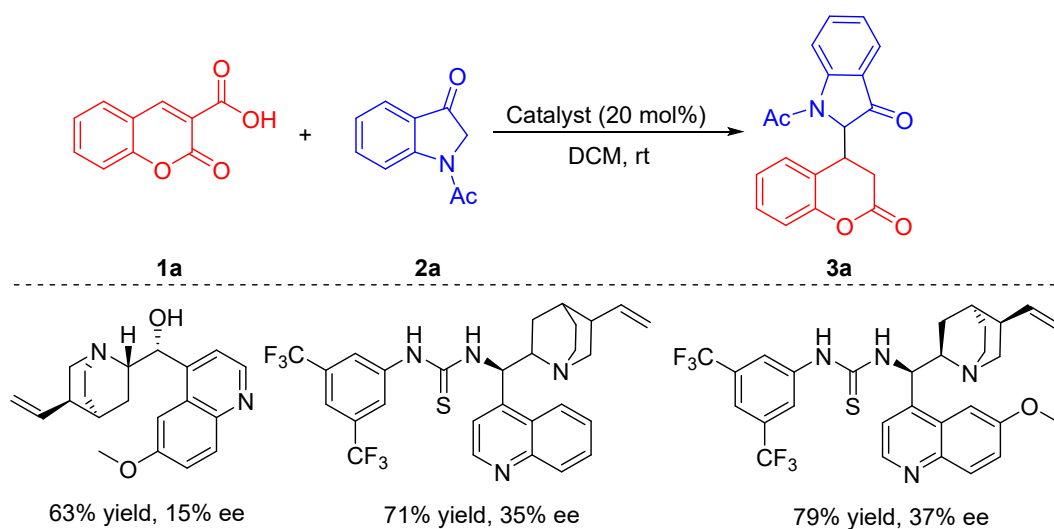
NMR spectra were obtained in CDCl₃ using TMS as the internal standard at 400 (for ¹H NMR) or 100 MHz (for ¹³C NMR), respectively. ¹H NMR spectra: J-values are reported in Hz. Organic solvents used were treated by general methods. Commercially obtained reagents were used without further purification. Column chromatography was performed using Huanghai 300-400 mesh silica gel at increased pressure. HRMS (m/z) were measured using Bruker Daltonics (TOF). The coumarin-3-carboxylic acids **1**¹ and the 1-acetyl-3-indolinone **2**² were prepared according to literature methods.

1. L. Wei, J. Wang, X. Zhang, P. Wang, Y. Zhao, J. Li, T. Hou, L. Qu, L. Shi, X. Liang and Y. Fang, *J. Med. Chem.* **2017**, 60, 362–372.
2. Q.-q. Zhang, F. Jin, J.-h. Yu, C. Zhang, M. Zhang, M.-z. Deng, S.-x. Lin, L. Chen, Y.-l. Zhao, B. He and Y. Li, *J. Org. Chem.* **2024**, 89, 10099–10111.

General procedure for the NMM-promoted decarboxylation of coumarin-3-carboxylic acids with indolin-3-ones.

Under N₂ atmosphere, coumarin-3-carboxylic acids **1** (0.1 mmol), indolin-3-ones **2** (0.12 mmol), DCM (2.0 ml) were successively added into a reaction tube, then NMM (0.02 mmol) was added with stirring. The resulting mixture was continuously stirred at rt for 48 h. After completion and removal of the solvent, the product **3** was obtained by column chromatography on a silica gel column eluting with petroleum ether-ethyl acetate mixture (PE:EA = 3:1) in 51 - 98% yields.

The preliminary investigation of enantioselectivity of coumarin-3-carboxylic acids **1a with the 1-acetyl-3-indolinone **2a**.**



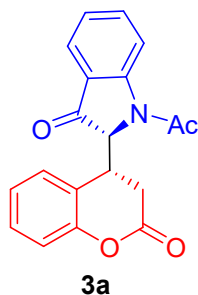
The preliminary investigation of enantioselectivity of coumarin-3-carboxylic acid **1a** and indolin-3-one **2b**.

Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (20 mol%) in dichloromethane (2.0 mL) at room temperature for 48 h. Isolated yields. Dr values (all the products >20:1) were determined by crude ¹H NMR. Ee was determined via HPLC on chiral stationary phase: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C.

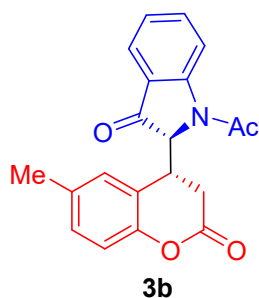
Preparation of methyl 3-(1-acetyl-3-oxoindolin-2-yl)-3-(2-hydroxyphenyl)propanoate (**4a**)

To a solution of **3a** (0.1 mmol) in methanol (1 ml), NaOH (0.1 mmol) was added. The reaction mixture was stirred at rt until no more starting product was detectable by TLC analysis (0.5 h). Subsequently it was concentrated, and the resulting residue was purified by flash chromatography on SiO₂ gel (PE/EA= 3:1) to yield **4a** (99%) as a white solid.

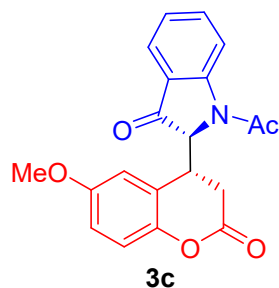
2. The data of the products 3 and 4a



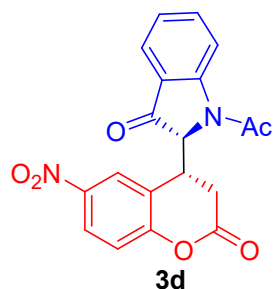
1-acetyl-2-(2-oxochroman-4-yl)indolin-3-one 3a: white solid, 88%, ^1H NMR (400 MHz, DMSO) δ 8.13 (s, 1H), 7.62 (t, $J = 7.7$ Hz, 1H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.11 (dt, $J = 20.2, 7.3$ Hz, 3H), 6.96 – 6.81 (m, 2H), 4.96 (s, 1H), 3.94 (d, $J = 6.9$ Hz, 1H), 3.26 (dd, $J = 17.4, 8.9$ Hz, 1H), 3.04 (d, $J = 17.4$ Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 198.4, 169.6, 166.0, 153.8, 151.7, 137.5, 129.9, 129.8, 124.8, 124.4, 124.2, 123.3, 119.4, 118.2, 117.0, 69.2, 37.0, 30.7, 24.4; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{NNaO}_4^+$: 344.0893; found: 344.0905.



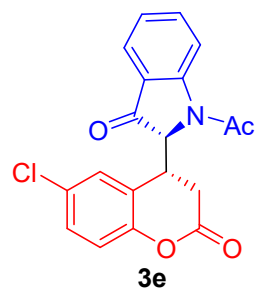
1-acetyl-2-(6-methyl-2-oxochroman-4-yl)indolin-3-one 3b: white solid, 74%, ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.64 (t, $J = 7.1$ Hz, 2H), 7.16 (t, $J = 7.0$ Hz, 1H), 7.00 (d, $J = 10.5$ Hz, 2H), 6.84 (d, $J = 7.9$ Hz, 1H), 4.68 (s, 1H), 3.85 (d, $J = 5.2$ Hz, 1H), 2.84 – 2.57 (m, 2H), 2.23 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 168.8, 166.1, 153.4, 149.8, 137.5, 134.2, 130.2, 128.9, 125.2, 124.7, 124.1, 120.0, 117.1, 69.3, 38.7, 30.3, 24.2, 20.6; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_4^+$: 358.1050; found: 358.1055.



1-acetyl-2-(6-methoxy-2-oxochroman-4-yl)indolin-3-one 3c: white solid, 70%, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.65 (t, $J = 6.5$ Hz, 2H), 7.17 (t, $J = 7.3$ Hz, 1H), 6.89 (d, $J = 8.8$ Hz, 1H), 6.79 – 6.66 (m, 2H), 4.70 (s, 1H), 3.86 (d, $J = 6.1$ Hz, 1H), 3.71 (s, 3H), 2.85 – 2.68 (m, 2H), 2.25 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.1, 168.8, 166.1, 156.2, 153.3, 145.8, 137.6, 125.2, 124.6, 124.2, 121.2, 118.2, 115.3, 113.1, 69.2, 55.7, 38.8, 30.2, 24.3; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_5^+$: 374.0999; found: 374.1008.

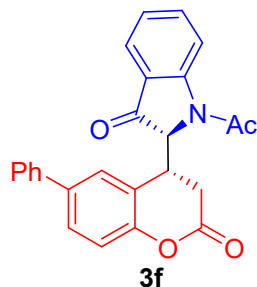


1-acetyl-2-(6-nitro-2-oxochroman-4-yl)indolin-3-one 3d: pale yellow solid, 51%, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (s, 2H), 7.67 (s, 2H), 7.57 (s, 1H), 7.15 (d, $J = 41.5$ Hz, 2H), 4.83 (s, 1H), 4.15 (s, 1H), 2.99 (s, 2H), 2.56 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.5, 169.0, 164.2, 156.3, 152.4, 143.7, 137.9, 125.22, 125.16, 124.8, 124.7, 124.5, 121.6, 118.1, 116.3, 68.5, 37.3, 29.8, 25.1; HRMS-TOF: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_6^+$: 367.0925; found: 367.0936.

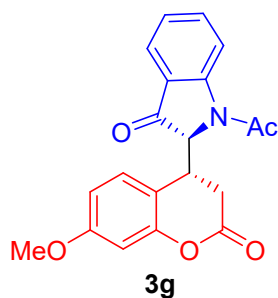


1-acetyl-2-(6-chloro-2-oxochroman-4-yl)indolin-3-one 3e: white solid, 62%, $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.15 (s, 1H), 7.65 (s, 1H), 7.42 (s, 1H), 7.11 (s, 1H), 6.96 (d, $J = 6.8$ Hz, 3H), 4.98 (s, 1H), 3.93 (s, 1H), 3.28 (d, $J = 18.5$ Hz, 1H), 3.06 (d, $J = 16.9$ Hz, 1H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (100 MHz,

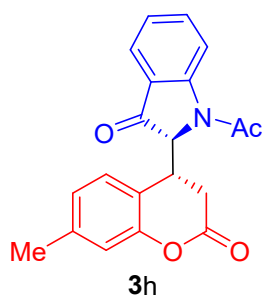
DMSO) δ 198.3, 169.7, 165.8, 153.8, 148.0, 137.7, 124.8, 124.5, 123.4, 121.3, 118.6, 118.2, 116.5, 116.4, 116.1, 69.0, 37.0, 30.2, 24.4; HRMS-TOF: $[M + Na]^+$ calcd for $C_{19}H_{14}ClNNaO_4^+$: 378.0504; found: 378.0508.



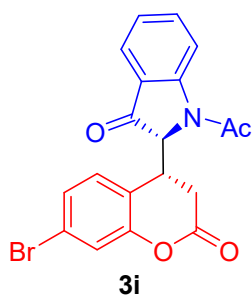
1-acetyl-2-(2-oxo-6-phenylchroman-4-yl)indolin-3-one 3f: white solid, 80%, 1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.63 (d, $J = 10.5$ Hz, 2H), 7.39 (d, $J = 19.5$ Hz, 7H), 7.16 (t, $J = 6.9$ Hz, 1H), 7.03 (d, $J = 8.2$ Hz, 1H), 4.75 (s, 1H), 4.01 (s, 1H), 3.04 – 2.88 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 168.7, 165.8, 153.2, 151.3, 139.6, 137.7, 137.6, 128.9, 128.3, 127.6, 127.2, 126.8, 125.2, 124.6, 124.3, 120.3, 117.7, 69.2, 38.4, 30.5, 24.4; HRMS-TOF: $[M + Na]^+$ calcd for $C_{25}H_{19}NNaO_4^+$: 420.1206; found: 420.1213.



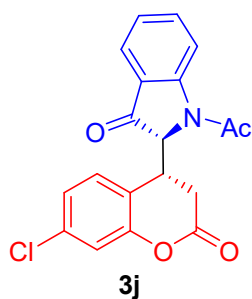
1-acetyl-2-(7-methoxy-2-oxochroman-4-yl)indolin-3-one 3g: white solid, 78%, 1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 1H), 7.38 – 7.53 (m, 1H), 7.30 – 7.27 (m, 3H), 7.13 – 7.11 (m, 1H), 6.92 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.2$ Hz, 1H), 4.64 (dd, $J = 8.9, 2.6$ Hz, 1H), 3.77 (s, 3H), 3.35 (dd, $J = 16.7, 8.9$ Hz, 1H), 3.08 (dd, $J = 16.7, 2.7$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 168.8, 165.9, 160.6, 152.8, 151.3, 137.5, 131.8, 129.3, 125.1, 124.7, 124.1, 115.2, 111.6, 111.0, 69.4, 55.5, 37.7, 30.6, 24.4; HRMS-TOF: $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_5^+$: 374.0999; found: 374.1007.



1-acetyl-2-(7-methyl-2-oxochroman-4-yl)indolin-3-one 3h: white solid, 81%, ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.62 (t, $J = 8.8$ Hz, 2H), 7.14 (t, $J = 7.3$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 1H), 6.75 (s, 1H), 4.67 (s, 1H), 3.89 (d, $J = 5.6$ Hz, 1H), 2.91 – 2.70 (m, 2H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 168.8, 166.1, 153.3, 151.7, 140.1, 137.5, 128.4, 125.4, 125.1, 124.5, 124.1, 117.7, 117.0, 69.3, 38.0, 30.5, 24.3, 21.1; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_4^+$: 358.1050; found: 358.1059.

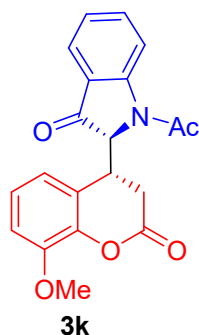


1-acetyl-2-(7-bromo-2-oxochroman-4-yl)indolin-3-one 3i: white solid, 70%, ^1H NMR (400 MHz, CDCl_3) δ 7.65 (t, $J = 7.3$ Hz, 3H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 1H), 4.71 (s, 1H), 3.92 (s, 1H), 2.93 – 2.78 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 168.9, 165.2, 152.9, 152.4, 137.7, 129.7, 127.5, 125.1, 124.7, 124.5, 122.6, 120.6, 119.4, 68.9, 37.7, 30.3, 24.7; HRMS-TOF: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_4^+$: 400.0179; found: 400.0188.

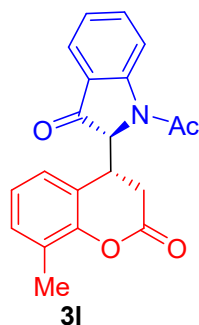


1-acetyl-2-(7-chloro-2-oxochroman-4-yl)indolin-3-one 3j: white solid, 80%, ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 6.9$ Hz, 3H), 7.20 (t, $J = 6.6$ Hz, 1H), 7.10 (d, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 4.73 (s, 1H), 3.95 (s, 1H), 2.98 – 2.80 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9,

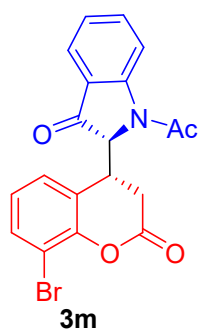
168.8, 165.2, 152.9, 152.3, 137.7, 134.9, 129.5, 125.1, 124.7, 124.6, 124.5, 118.9, 117.7, 68.9, 37.6, 30.3, 24.7; HRMS-TOF: $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_4^+$: 356.0684; found: 356.0693.



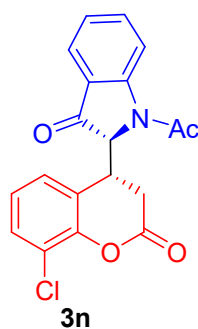
1-acetyl-2-(8-methoxy-2-oxochroman-4-yl)indolin-3-one 3k: white solid, 82%, 1H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.63 (d, $J = 6.8$ Hz, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 6.97 (t, $J = 7.7$ Hz, 1H), 6.79 (dd, $J = 13.9, 7.9$ Hz, 2H), 4.72 (s, 1H), 3.92 (s, 1H), 3.81 (s, 3H), 2.85 (dd, $J = 16.8, 7.8$ Hz, 1H), 2.74 (d, $J = 16.8$ Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 168.9, 165.3, 153.3, 147.7, 141.4, 137.5, 125.1, 124.6, 124.1, 121.4, 119.9, 117.8, 112.1, 69.2, 56.1, 38.7, 30.2, 24.3; HRMS-TOF: $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_5^+$: 374.0999; found: 374.1006.



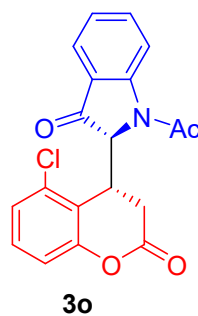
1-acetyl-2-(8-methyl-2-oxochroman-4-yl)indolin-3-one 3l: white solid, 89%, 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.63 (t, $J = 7.0$ Hz, 2H), 7.16 (t, $J = 7.3$ Hz, 1H), 7.07 (d, $J = 7.1$ Hz, 1H), 7.01 (d, $J = 7.0$ Hz, 1H), 6.92 (t, $J = 7.3$ Hz, 1H), 4.68 (s, 1H), 3.90 (d, $J = 5.6$ Hz, 1H), 2.81 (dt, $J = 30.6, 12.3$ Hz, 2H), 2.24 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 168.8, 166.0, 153.4, 150.2, 137.5, 131.2, 126.8, 126.1, 125.2, 124.6, 124.1, 120.1, 117.7, 69.4, 38.8, 30.3, 24.1, 15.7; HRMS-TOF: $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_4^+$: 358.1050; found: 358.1063.



1-acetyl-2-(8-bromo-2-oxochroman-4-yl)indolin-3-one 3m: white solid, 65%, ^1H NMR (400 MHz, CDCl_3) δ 7.67 (dd, $J = 13.3, 7.5$ Hz, 3H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 6.91 (t, $J = 7.6$ Hz, 1H), 4.75 (s, 1H), 3.94 (d, $J = 6.0$ Hz, 1H), 2.82 (dt, $J = 30.9, 12.2$ Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 168.9, 164.9, 153.0, 149.0, 137.7, 133.5, 127.6, 125.24, 125.16, 124.7, 124.5, 122.7, 117.2, 111.2, 69.0, 38.9, 30.2, 24.5; HRMS-TOF: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_4^+$: 400.0179; found: 400.0185.

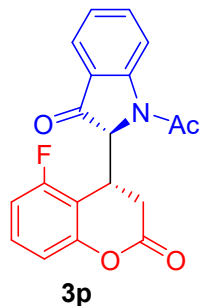


1-acetyl-2-(8-chloro-2-oxochroman-4-yl)indolin-3-one 3n: white solid, 69%, ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 6.5$ Hz, 3H), 7.26 (s, 1H), 7.19 (s, 1H), 7.10 (d, $J = 7.1$ Hz, 1H), 6.96 (t, $J = 7.4$ Hz, 1H), 4.75 (s, 1H), 3.94 (s, 1H), 2.83 (dt, $J = 29.1, 12.1$ Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 168.8, 164.8, 153.0, 148.0, 137.7, 130.4, 126.8, 125.2, 124.7, 124.6, 124.5, 122.7, 122.3, 117.2, 69.0, 38.7, 30.1, 24.5; HRMS-TOF: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_4^+$: 356.0684; found: 356.0690.

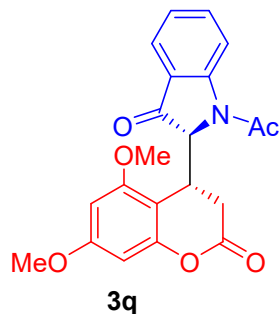


1-acetyl-2-(5-chloro-2-oxochroman-4-yl)indolin-3-one 3o: white solid, 65%, ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.67 (m, 3H), 7.25 (dd, $J = 13.7, 7.3$ Hz, 3H), 6.97 (d, $J = 7.6$ Hz, 1H), 4.95 (s, 1H),

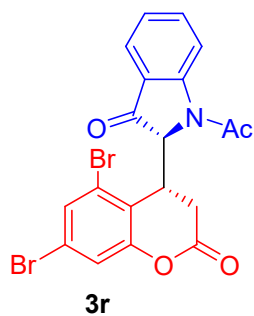
4.24 (d, $J = 6.8$ Hz, 1H), 2.65 (dd, $J = 17.0, 7.3$ Hz, 1H), 2.41 (s, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 169.1, 165.6, 153.7, 153.2, 137.7, 133.6, 130.2, 125.7, 124.8, 124.2, 121.0, 118.0, 116.0, 67.2, 37.9, 29.5, 23.7; HRMS-TOF: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_4^+$: 356.0684; found: 356.0689.



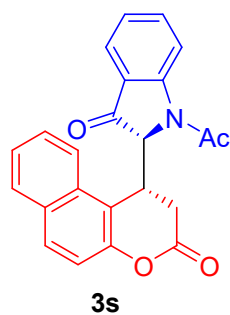
1-acetyl-2-(5-fluoro-2-oxochroman-4-yl)indolin-3-one 3p: white solid, 68%, ^1H NMR (400 MHz, CDCl_3) δ 7.66 (t, $J = 15.3$ Hz, 3H), 7.24 – 7.10 (m, 2H), 6.77 (d, $J = 6.1$ Hz, 2H), 4.78 (s, 1H), 4.31 (s, 1H), 2.93 – 2.77 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 168.8, 165.1, 161.3, 158.8, 152.9 (d, $J = 6.3$ Hz), 137.5, 130.3 (d, $J = 9.8$ Hz), 125.0, 124.4, 116.9, 113.1 (d, $J = 3.0$ Hz), 111.1 (d, $J = 22.0$ Hz), 109.1 (d, $J = 21.0$ Hz), 68.1, 32.5, 30.0, 24.4; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{14}\text{FNNaO}_4^+$: 362.0799; found: 362.0809.



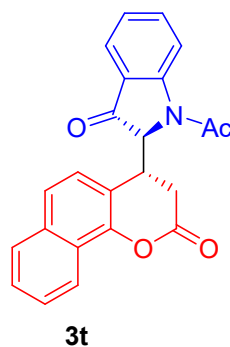
1-acetyl-2-(5,7-dimethoxy-2-oxochroman-4-yl)indolin-3-one 3q: white solid, 92%, ^1H NMR (400 MHz, CDCl_3) δ 8.11 (s, 1H), 7.65 (dd, $J = 17.0, 7.9$ Hz, 2H), 7.19 (t, $J = 7.2$ Hz, 1H), 6.18 (d, $J = 9.7$ Hz, 2H), 4.69 (s, 1H), 4.15 (d, $J = 6.0$ Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 2.75 – 2.56 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 168.8, 165.9, 161.4, 157.8, 153.9, 153.5, 137.5, 125.0, 124.5, 123.7, 118.4, 101.7, 94.8, 94.0, 68.3, 56.0, 55.6, 33.7, 30.2, 23.5; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{NNaO}_6^+$: 404.1105; found: 404.1112.



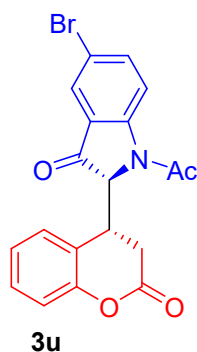
1-acetyl-2-(5,7-dibromo-2-oxochroman-4-yl)indolin-3-one 3r: yellow solid, 66%, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 (d, $J = 7.2$ Hz, 3H), 7.62 (s, 1H), 7.31 (s, 1H), 7.25 (t, $J = 7.2$ Hz, 1H), 4.79 (s, 1H), 3.93 (d, $J = 5.7$ Hz, 1H), 2.81 (dt, $J = 28.1, 12.4$ Hz, 2H), 2.45 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.5, 168.9, 164.4, 152.8, 148.3, 137.9, 135.5, 130.4, 125.3, 124.8, 124.7, 124.5, 116.8, 111.8, 68.7, 38.6, 29.8, 24.7; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{13}\text{Br}_2\text{NNaO}_4^+$: 499.9104; found: 499.9109.



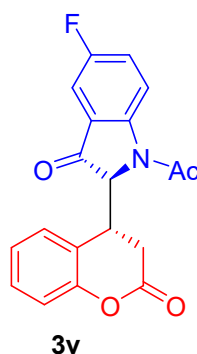
1-acetyl-2-(2-oxo-3,4-dihydro-2H-benzo[g]chromen-4-yl)indolin-3-one 3s: yellow solid, 61%, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.55 (s, 1H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.74 (dd, $J = 14.1, 7.1$ Hz, 2H), 7.67 (s, 1H), 7.52 (d, $J = 7.0$ Hz, 2H), 7.28 (d, $J = 7.9$ Hz, 2H), 4.96 (s, 1H), 4.81 (s, 1H), 2.81 (s, 2H), 2.64 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.9, 168.8, 166.2, 151.9, 150.9, 137.4, 131.2, 131.1, 130.7, 129.0, 127.9, 125.4, 125.2, 124.9, 123.4, 117.4, 65.9, 33.1, 29.0, 25.6; HRMS-TOF: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{18}\text{NO}_4^+$: 372.1230; found: 372.1237.



1-acetyl-2-(2-oxo-3,4-dihydro-2H-benzo[h]chromen-4-yl)indolin-3-one 3t: yellow solid, 80%, ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 7.2 Hz, 1H), 7.87 (s, 1H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.59 (dd, *J* = 13.8, 7.4 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 3H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 4.77 (s, 1H), 4.06 (d, *J* = 5.4 Hz, 1H), 2.95 (dt, *J* = 31.9, 12.3 Hz, 2H), 2.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 168.8, 165.8, 153.3, 147.3, 137.5, 133.9, 127.5, 127.2, 126.8, 125.1, 124.6, 124.3, 124.2, 123.5, 121.6, 117.6, 114.7, 69.2, 38.7, 30.5, 24.3; HRMS-TOF: [M + Na]⁺ calcd for C₂₃H₁₇NNaO₄⁺: 394.1050; found: 394.1061.

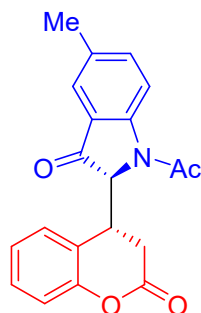


1-acetyl-5-bromo-2-(2-oxochroman-4-yl)indolin-3-one 3u: yellow solid, 95%, ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.72 (d, *J* = 11.2 Hz, 2H), 7.28 (d, *J* = 6.1 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 4.71 (s, 1H), 3.92 (d, *J* = 5.5 Hz, 1H), 2.90 (dd, *J* = 16.9, 7.7 Hz, 1H), 2.79 (d, *J* = 17.0 Hz, 1H), 2.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 168.6, 165.6, 152.2, 151.9, 140.1, 130.1, 128.6, 126.6, 124.7, 119.9, 117.8, 117.6, 69.6, 38.7, 30.3, 24.0; HRMS-TOF: [M + Na]⁺ calcd for C₁₉H₁₄BrNNaO₄⁺: 421.9998; found: 421.9985.



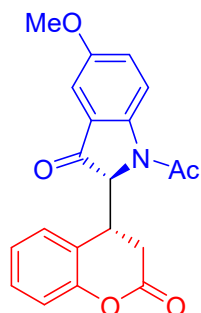
1-acetyl-5-fluoro-2-(2-oxochroman-4-yl)indolin-3-one 3v: yellow solid, 92%, ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.34 (td, *J* = 8.7, 2.8 Hz, 1H), 7.24 (dt, *J* = 5.0, 2.2 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 4.71 (s, 1H), 3.90 (d, *J* = 6.9 Hz, 1H), 2.86 (dt, *J* = 38.2, 12.4 Hz, 2H), 2.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.4 (d, *J* = 2.9 Hz), 168.5, 165.6, 160.5, 158.0, 151.9, 149.8, 130.0, 128.7, 126.3, 124.9 (d, *J* = 24.0 Hz), 124.7, 119.8,

117.6, 109.5 (d, $J = 24.0$ Hz), 69.9, 38.7, 30.3, 23.8; HRMS-TOF: $[M + Na]^+$ calcd for $C_{19}H_{14}FNNaO_4^+$: 362.0799; found: 362.0793.



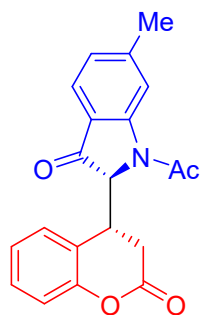
3w

1-acetyl-5-methyl-2-(2-oxochroman-4-yl)indolin-3-one 3w: yellow solid, 82%, 1H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 2H), 7.25 – 7.18 (m, 2H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 8.2$ Hz, 1H), 4.69 (s, 1H), 3.92 (d, $J = 7.2$ Hz, 1H), 2.88 – 2.74 (m, 2H), 2.33 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 168.7, 166.0, 151.9, 138.6, 134.5, 129.6, 128.7, 125.3, 124.5, 123.8, 120.4, 117.4, 69.4, 38.3, 30.3, 24.2, 20.6; HRMS-TOF: $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_4^+$: 358.1050; found: 358.1046.



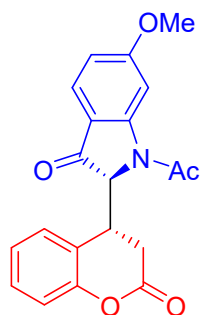
3x

1-acetyl-5-methoxy-2-(2-oxochroman-4-yl)indolin-3-one 3x: yellow solid, 80%, 1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.20 (dt, $J = 11.4, 8.4$ Hz, 3H), 7.05 – 6.98 (m, 2H), 6.95 (d, $J = 8.1$ Hz, 1H), 4.69 (s, 1H), 3.92 (d, $J = 5.3$ Hz, 1H), 3.77 (s, 3H), 2.91 – 2.76 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 168.4, 165.9, 156.7, 151.9, 129.7, 128.7, 126.3, 126.0, 124.5, 120.1, 117.4, 104.8, 69.7, 55.8, 38.3, 30.3, 24.0; HRMS-TOF: $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_5^+$: 374.0999; found: 374.0993.



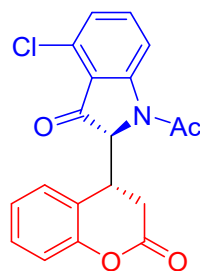
3y

1-acetyl-6-methyl-2-(2-oxochroman-4-yl)indolin-3-one 3y: yellow solid, 91%, ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.21 (dd, $J = 16.9, 8.1$ Hz, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.96 (dd, $J = 7.9, 1.6$ Hz, 2H), 4.67 (s, 1H), 3.91 (d, $J = 7.3$ Hz, 1H), 2.91 – 2.75 (m, 2H), 2.45 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 168.8, 165.9, 153.7, 152.0, 149.6, 129.7, 128.6, 125.9, 124.5, 123.8, 122.9, 120.5, 117.4, 69.6, 38.4, 30.3, 24.3, 22.9; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_4^+$: 358.1050; found: 358.1052.



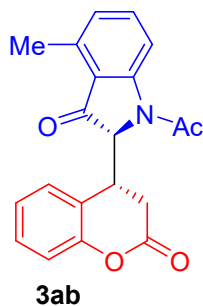
3z

1-acetyl-6-methoxy-2-(2-oxochroman-4-yl)indolin-3-one 3z: yellow solid, 88%, ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.6$ Hz, 1H), 7.46 (d, $J = 7.1$ Hz, 1H), 7.27 – 7.18 (m, 2H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.98 (d, $J = 8.1$ Hz, 1H), 6.69 (dd, $J = 8.6, 2.1$ Hz, 1H), 4.63 (s, 1H), 3.89 (d, $J = 6.7$ Hz, 4H), 2.81 (qd, $J = 16.9, 4.6$ Hz, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.6, 169.0, 167.5, 165.9, 155.8, 152.0, 129.8, 128.6, 125.5, 124.7, 120.6, 118.2, 117.5, 112.6, 102.3, 70.0, 56.1, 38.8, 30.1, 24.0; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_5^+$: 374.0999; found: 374.0997.

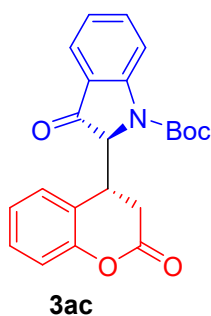


3aa

1-acetyl-4-chloro-2-(2-oxochroman-4-yl)indolin-3-one 3aa: yellow solid, 68%, ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.63 (ddd, $J = 7.3, 4.1, 2.8$ Hz, 2H), 7.20 – 7.15 (m, 2H), 7.02 (d, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 8.2$ Hz, 1H), 4.70 (s, 1H), 3.93 (d, $J = 7.0$ Hz, 1H), 2.93 – 2.80 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 168.7, 165.9, 151.9, 137.5, 129.7, 128.6, 125.2, 124.54, 124.51, 124.2, 120.2, 117.4, 69.2, 38.4, 30.4, 24.3; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{14}\text{ClNNaO}_4^+$: 378.0504; found: 378.0500.

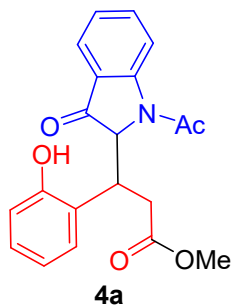


1-acetyl-4-methyl-2-(2-oxochroman-4-yl)indolin-3-one 3ab: white solid, 74%, ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.43 (t, $J = 7.9$ Hz, 1H), 7.20 – 7.13 (m, 2H), 7.00 – 6.92 (m, 2H), 6.87 (d, $J = 7.5$ Hz, 1H), 4.64 (d, $J = 1.7$ Hz, 1H), 3.94 – 3.87 (m, 1H), 2.90 – 2.84 (m, 2H), 2.49 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.9, 168.7, 165.9, 153.6, 151.9, 140.0, 136.6, 129.6, 128.7, 126.2, 124.4, 122.9, 120.1, 117.2, 114.7, 69.1, 38.3, 30.5, 24.4, 18.3; HRMS-TOF: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_4^+$: 358.1050; found: 358.1055.



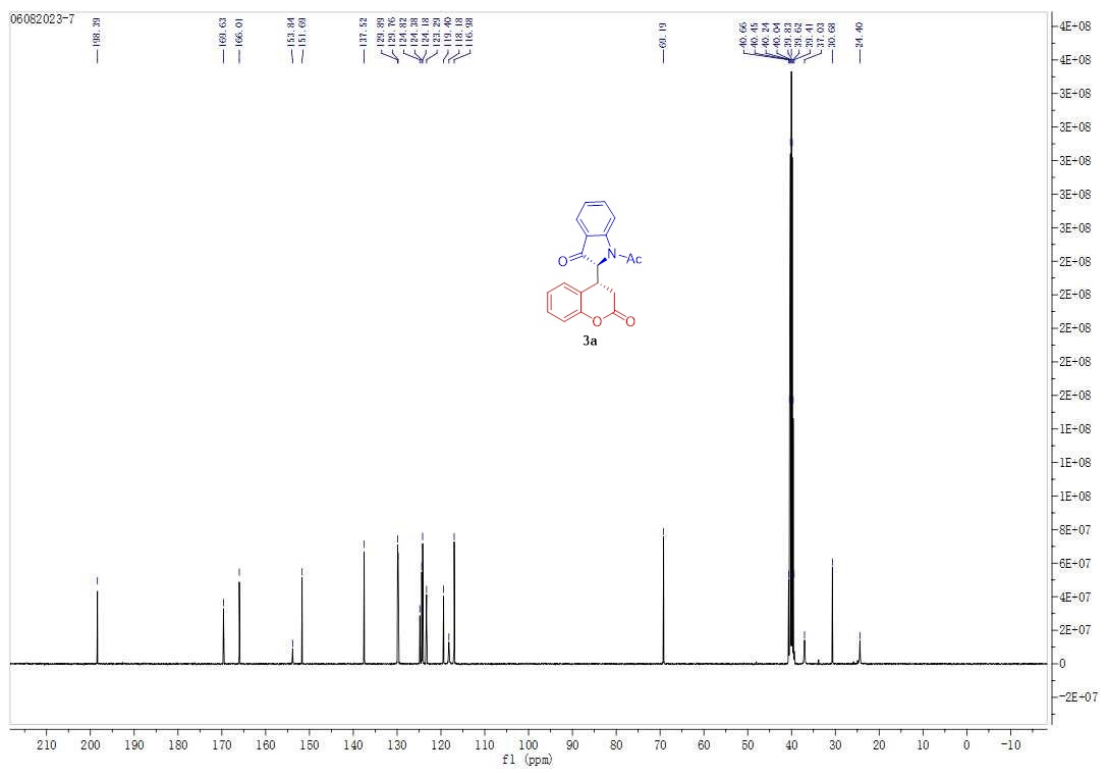
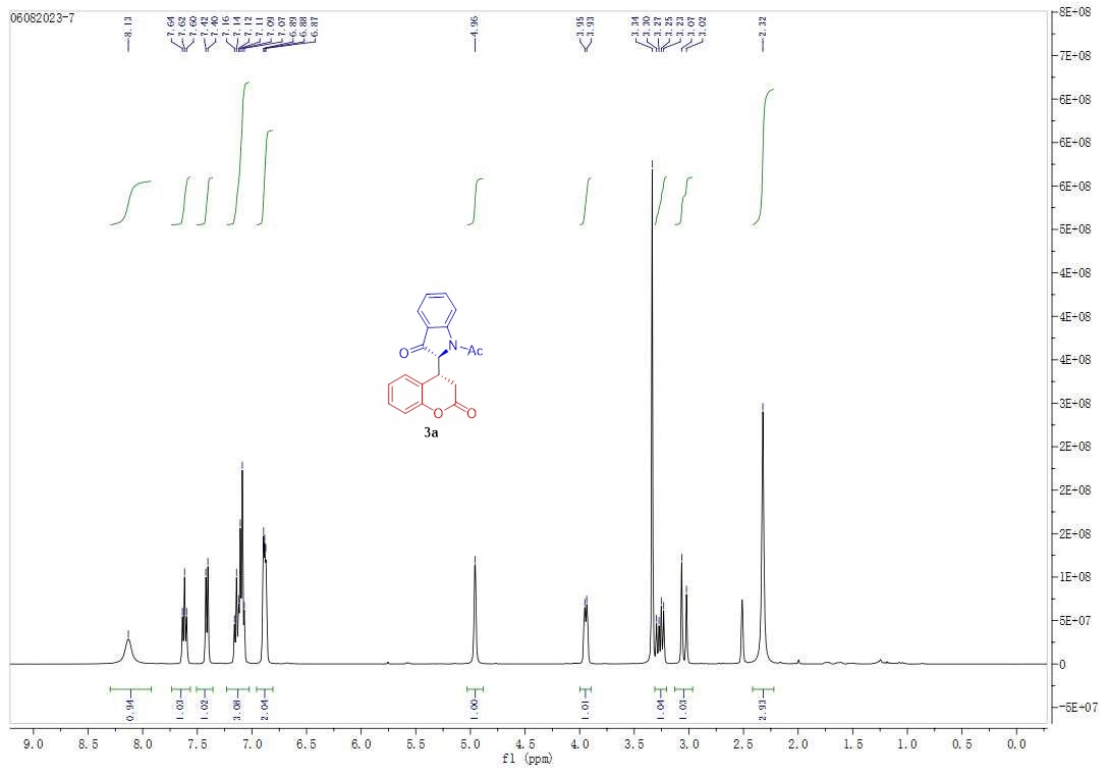
tert-butyl 3-oxo-2-(2-oxochroman-4-yl)indoline-1-carboxylate 3ac: yellow solid, 98% (dr 2:1), ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.0$ Hz, 1H), 7.60 (t, $J = 6.3$ Hz, 2H), 7.20 (dd, $J = 17.3, 8.1$ Hz, 2H), 7.09 (t, $J = 7.4$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 1H), 4.55 (s, 1H), 3.93 (d, $J = 7.0$ Hz, 1H), 2.84 (dd, $J = 16.9, 7.7$ Hz, 1H), 2.76 (d, $J = 16.8$ Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 166.2, 153.9, 152.1, 151.1, 137.6, 129.3, 128.6, 124.4, 124.3, 123.74,

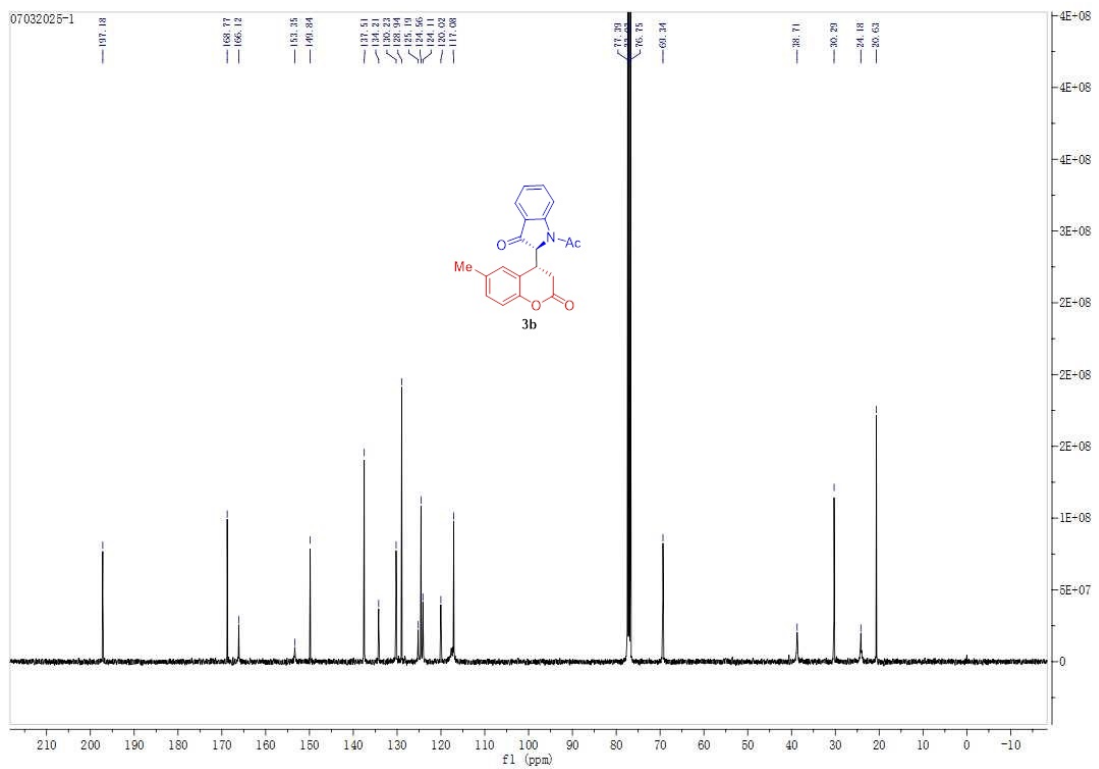
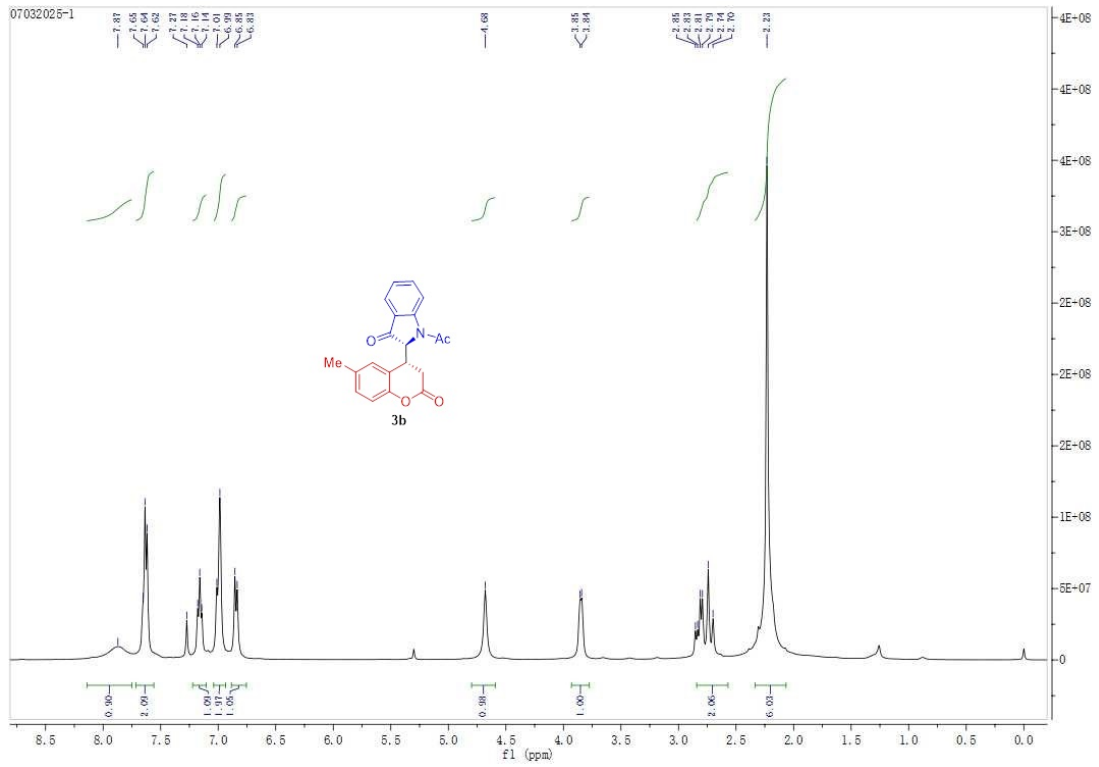
123.66, 121.1, 117.6, 117.3, 83.5, 69.0, 38.1, 30.3, 28.0; HRMS-TOF: $[M + Na]^+$ calcd for $C_{22}H_{21}NNaO_5^+$: 402.1312; found: 402.1315.

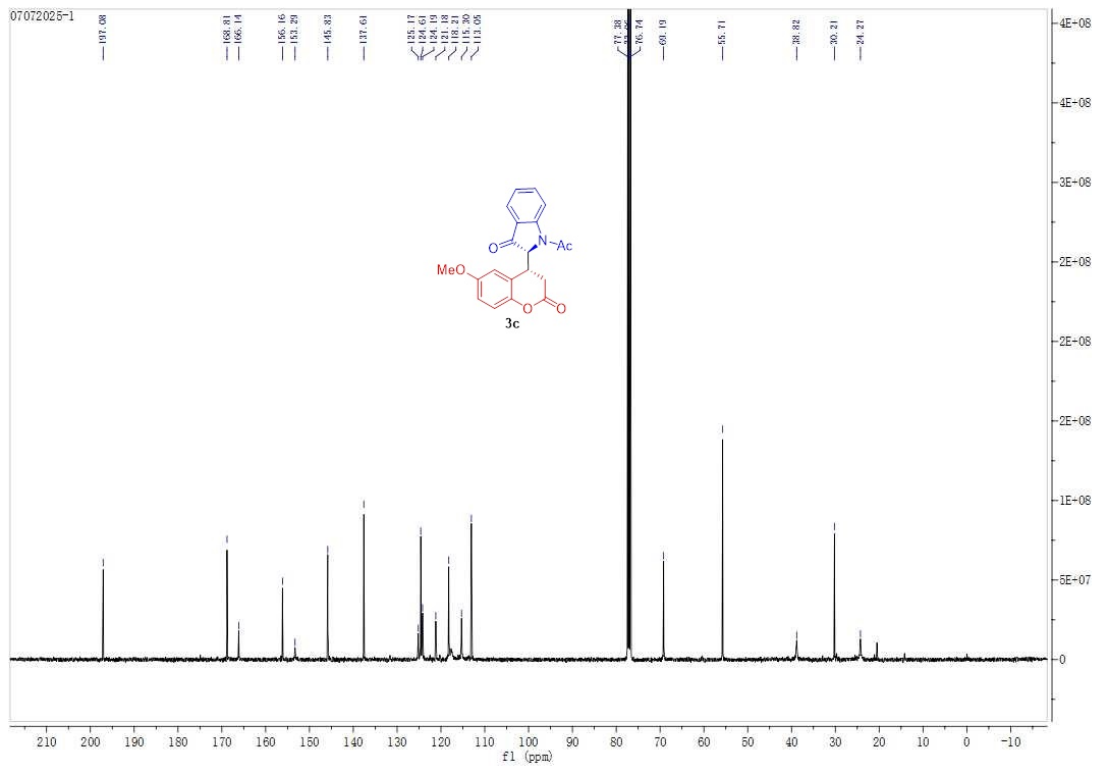
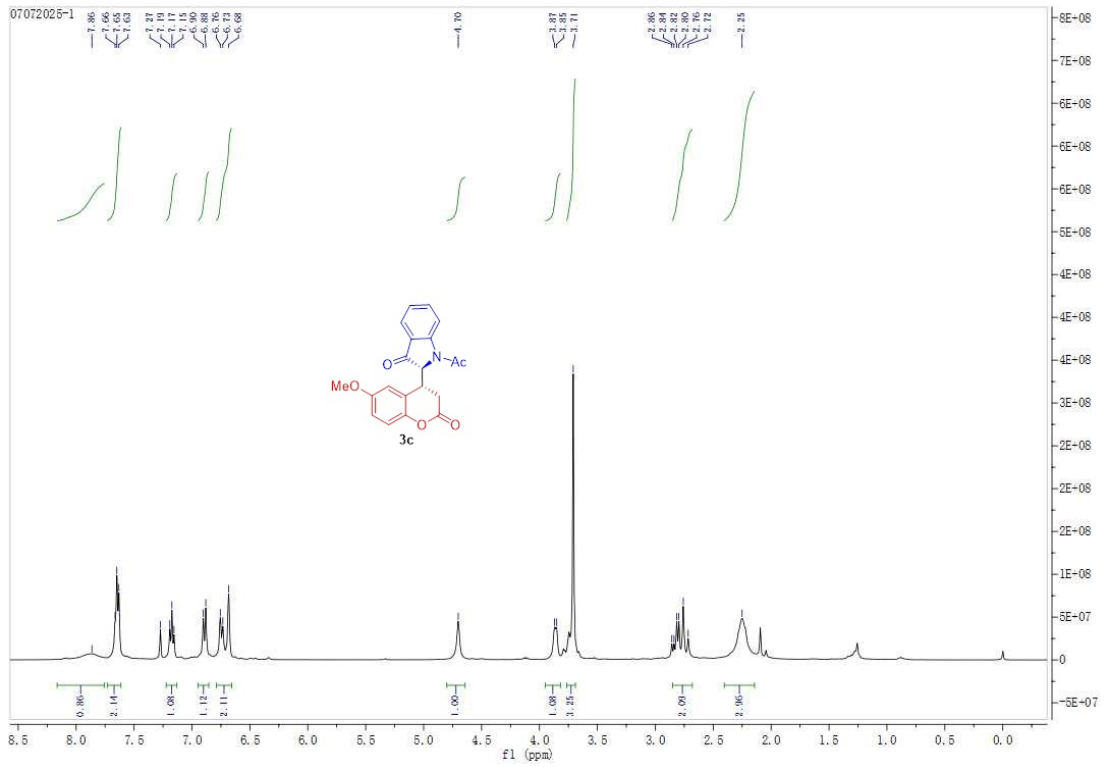


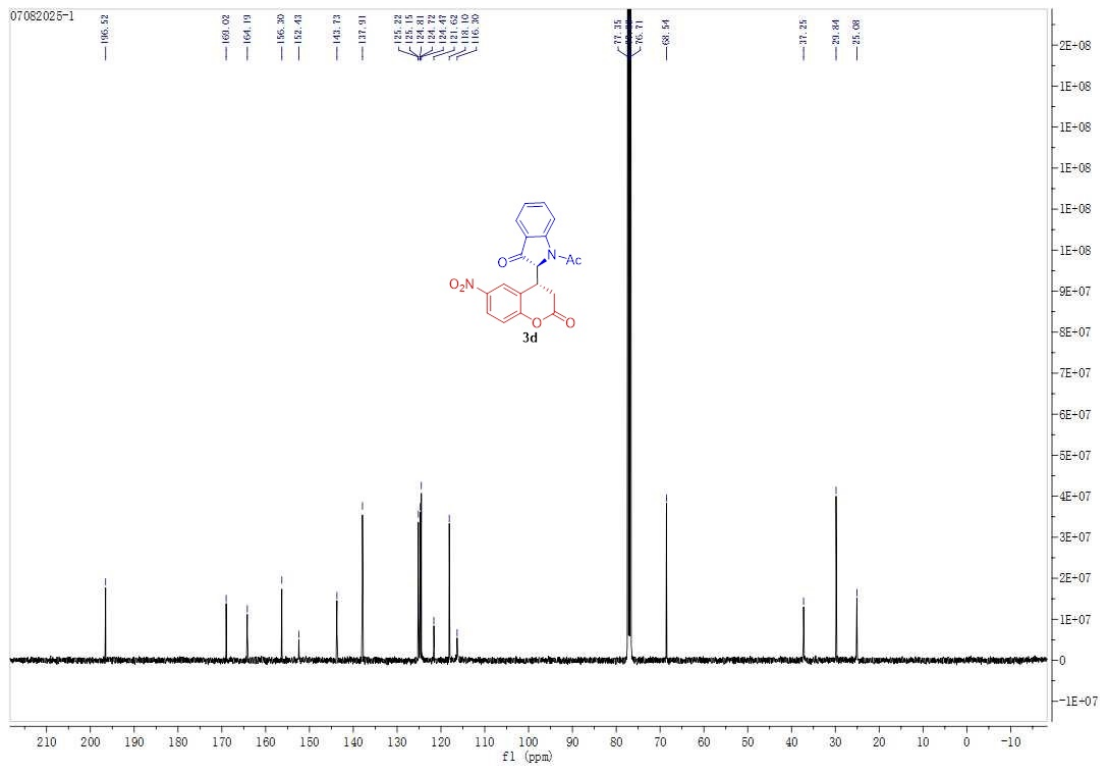
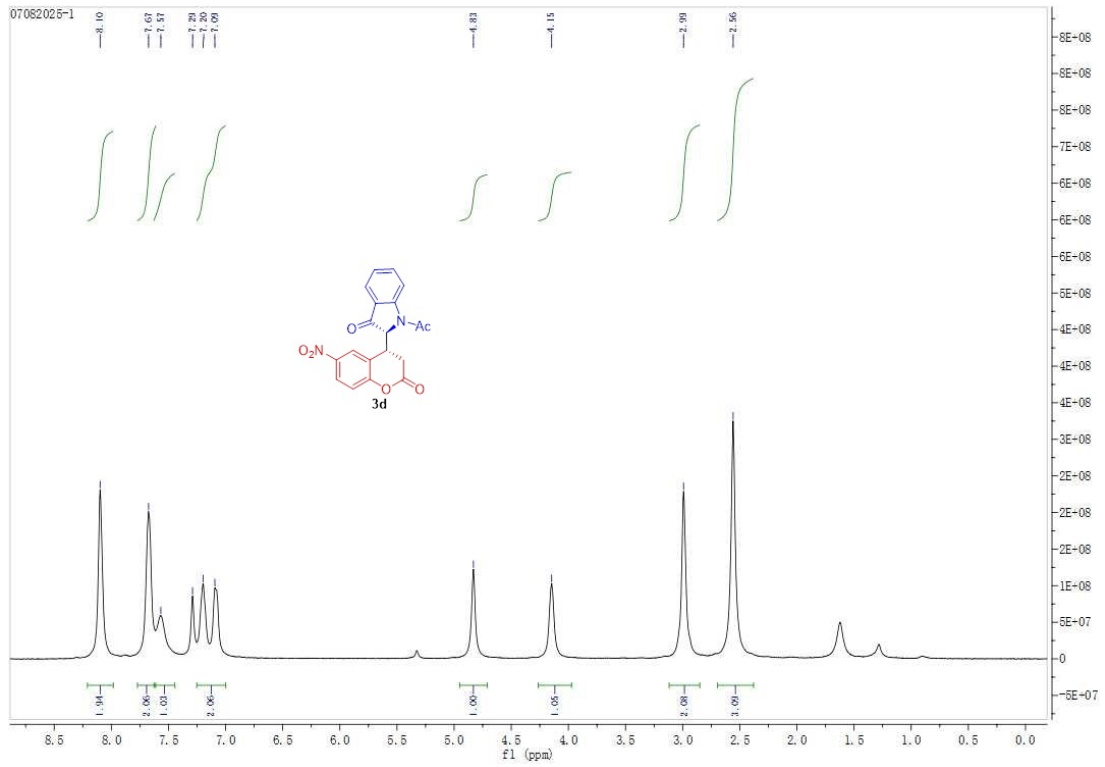
methyl 3-(1-acetyl-3-oxoindolin-2-yl)-3-(2-hydroxyphenyl)propanoate 4a: white solid, 99%,
 1H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, $J = 86.1$ Hz, 2H), 7.50 (d, $J = 7.1$ Hz, 1H), 7.37 (t, $J = 7.3$ Hz, 1H), 6.99 (t, $J = 7.1$ Hz, 1H), 6.82 (d, $J = 6.4$ Hz, 2H), 6.75 (d, $J = 7.6$ Hz, 1H), 6.49 (t, $J = 6.9$ Hz, 1H), 4.88 – 4.73 (m, 2H), 3.79 (s, 4H), 2.74 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 173.5, 171.2, 154.9, 153.2, 136.6, 128.4, 128.1, 125.6, 124.0, 122.8, 122.6, 119.5, 118.2, 115.1, 67.2, 52.0, 34.6, 32.5, 23.8; HRMS-TOF: $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_5^+$: 376.1155; found: 376.1159.

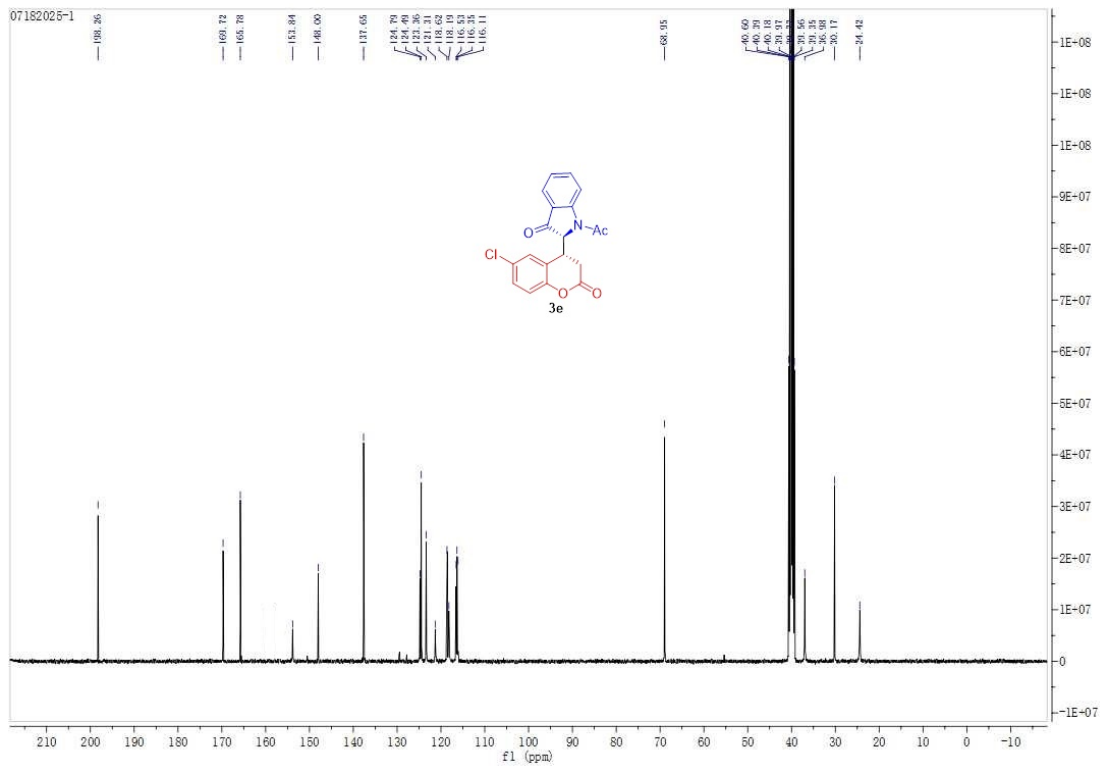
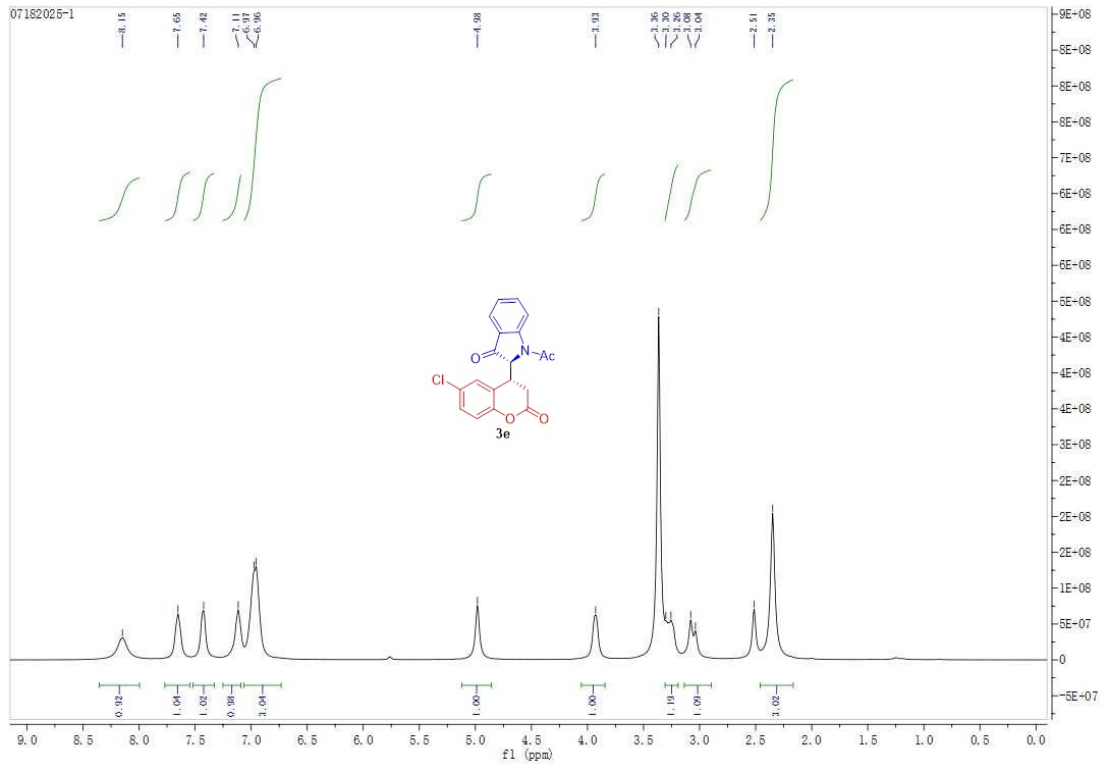
3. The NMR of 3 and 4a

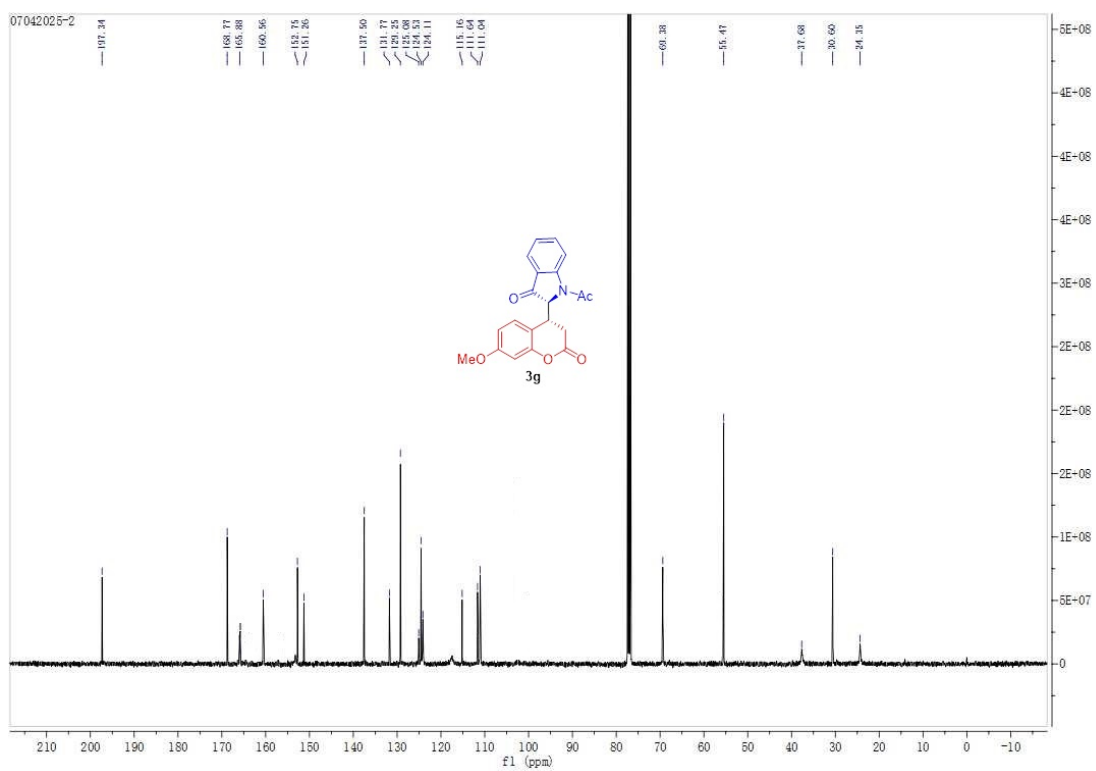
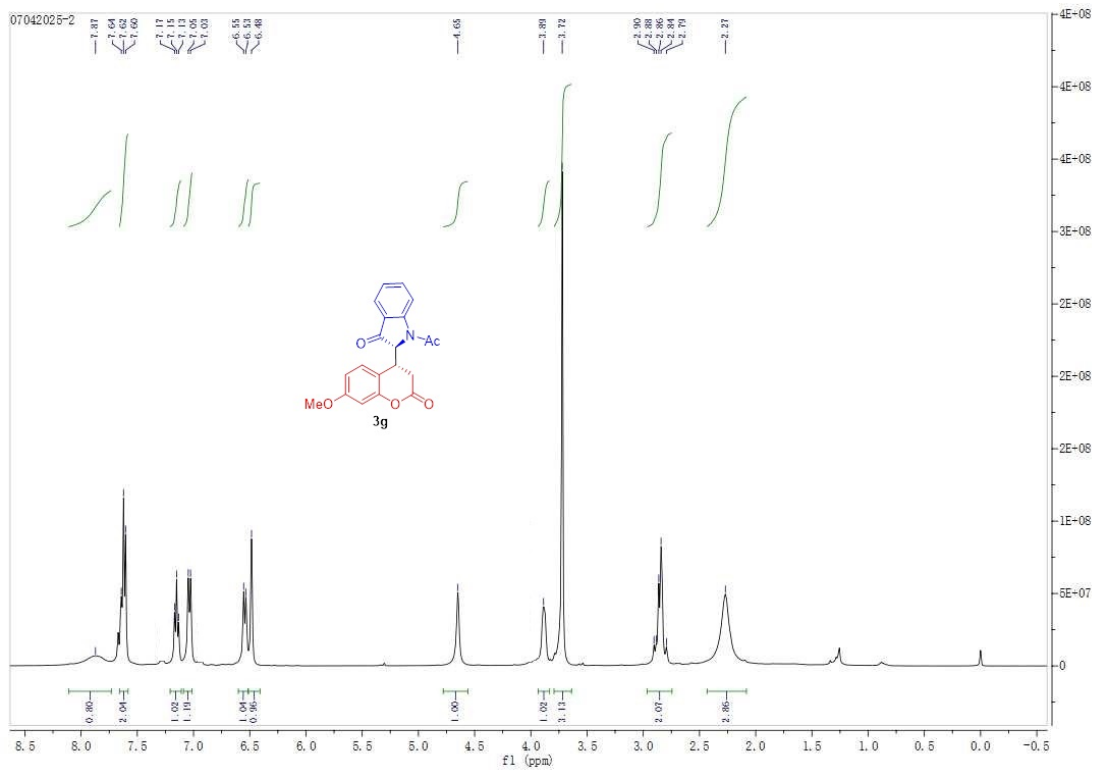


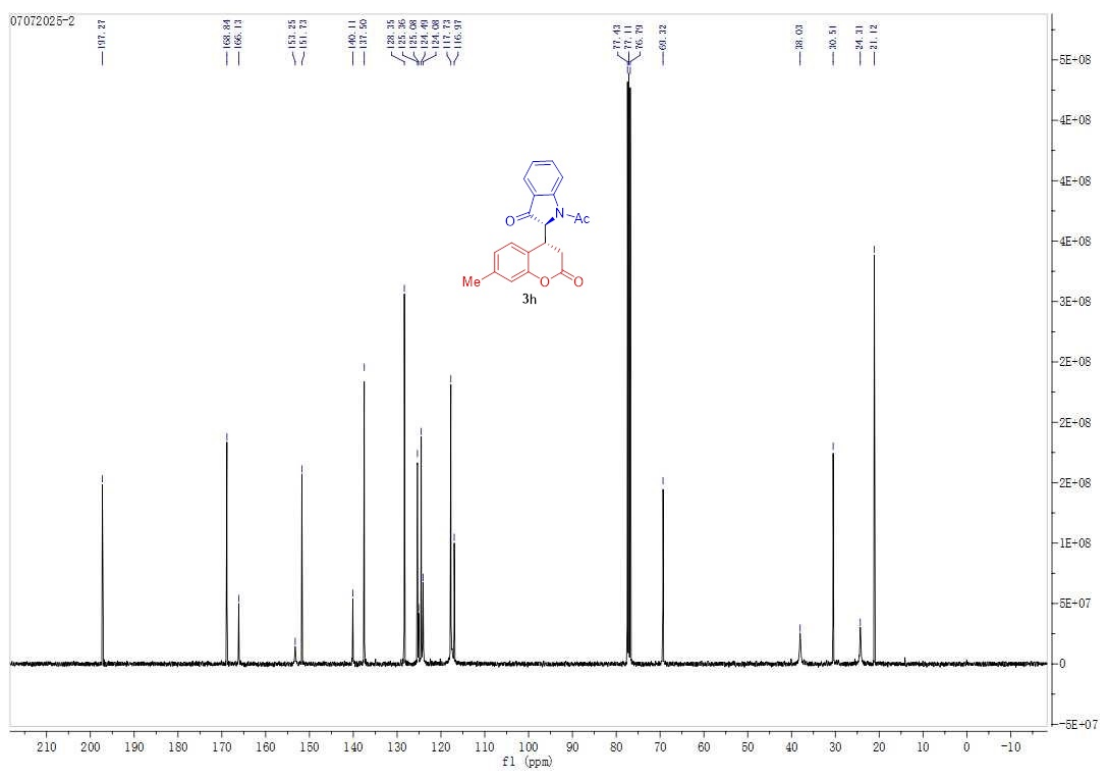
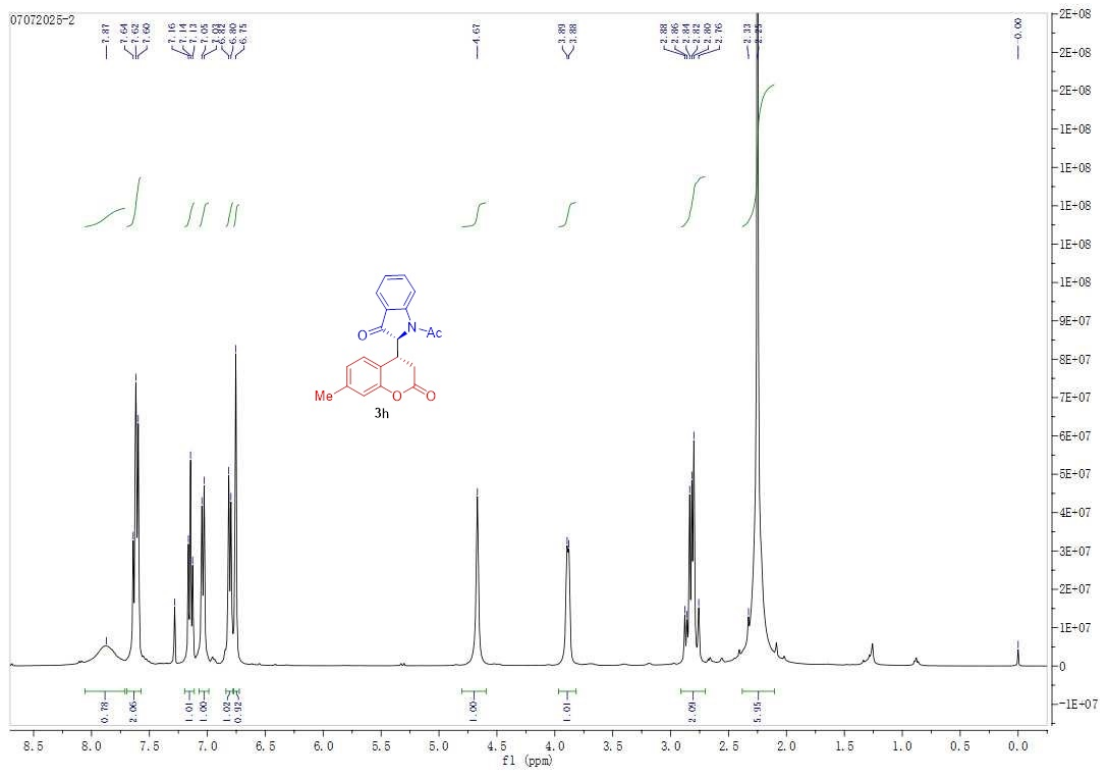


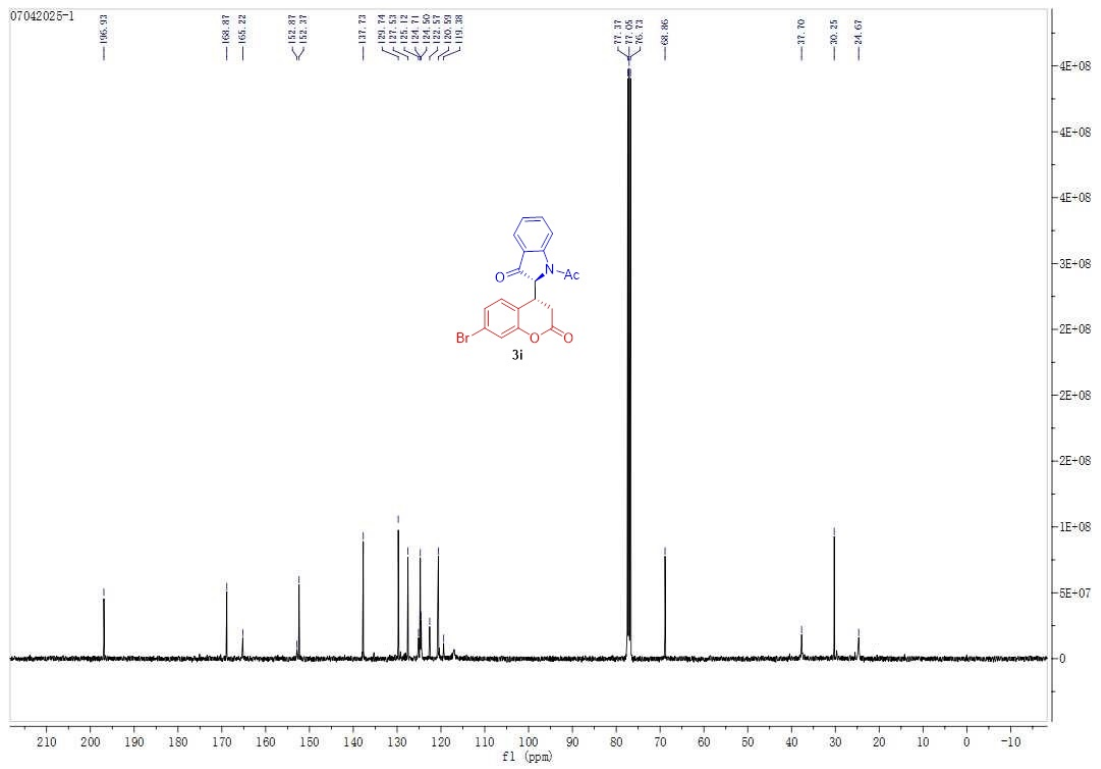
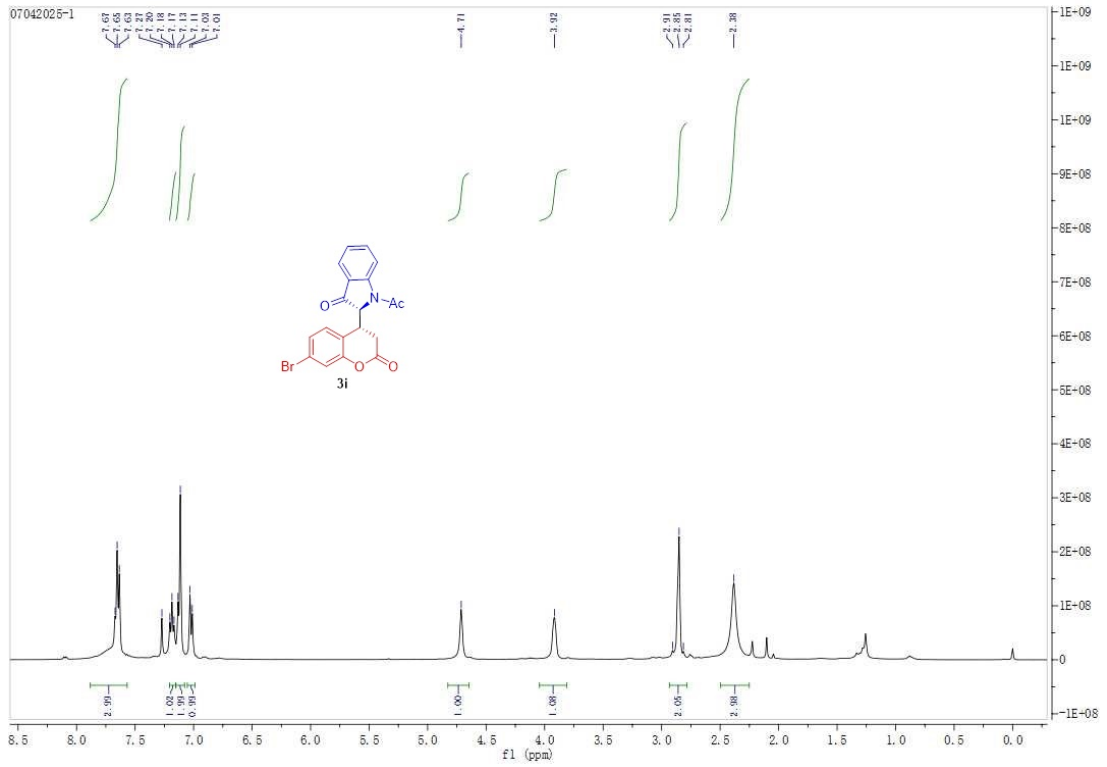


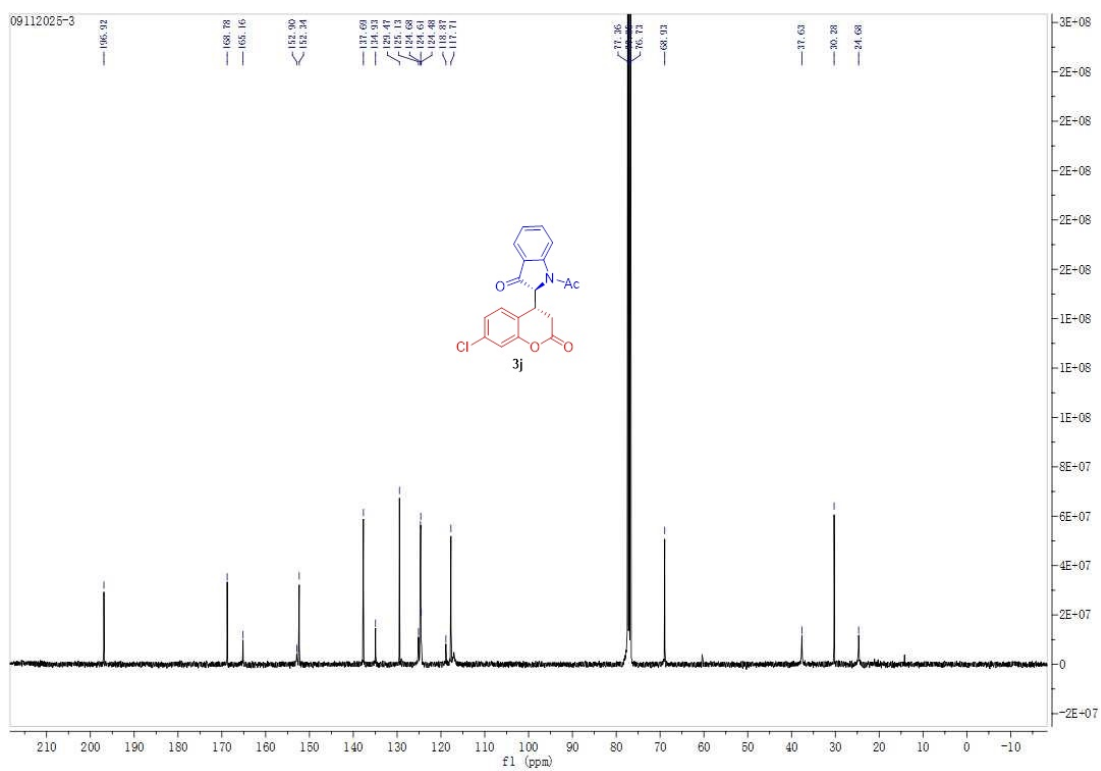
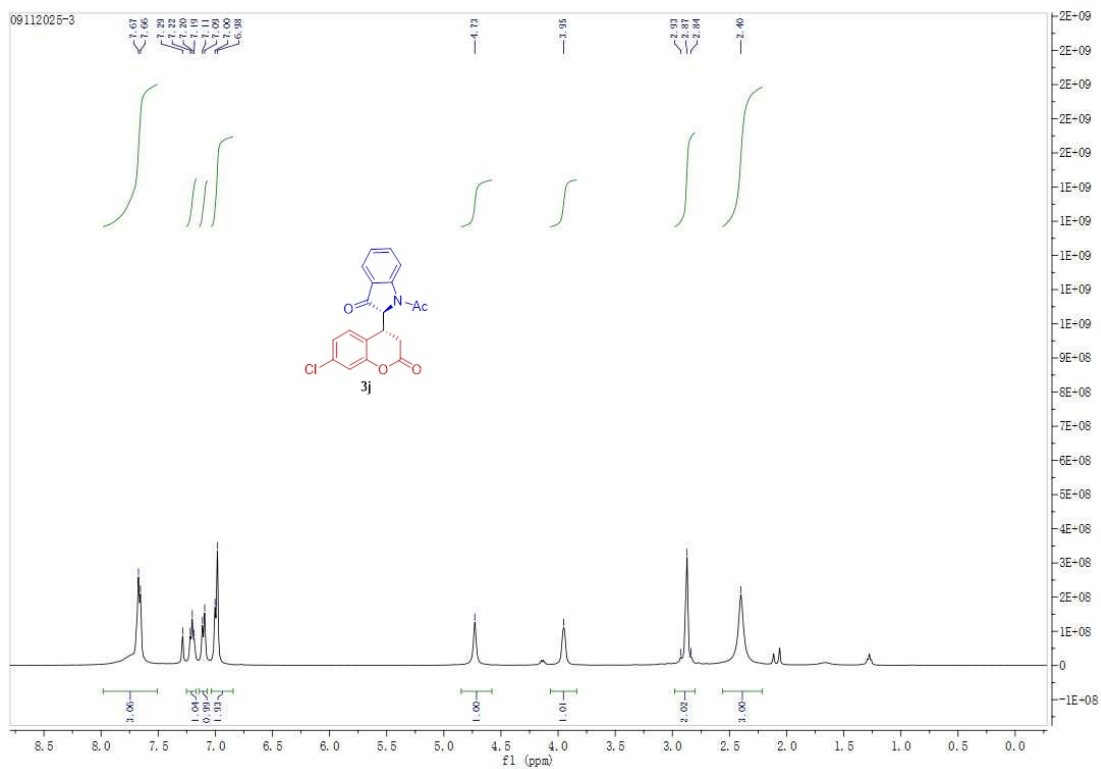


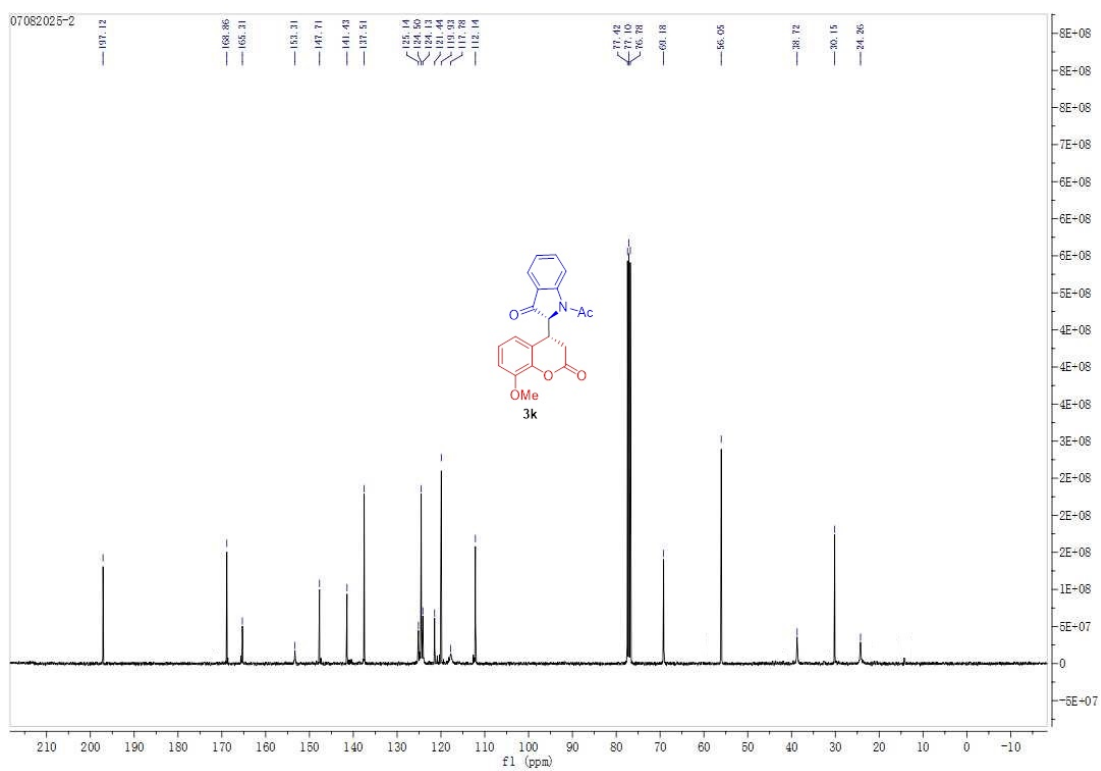
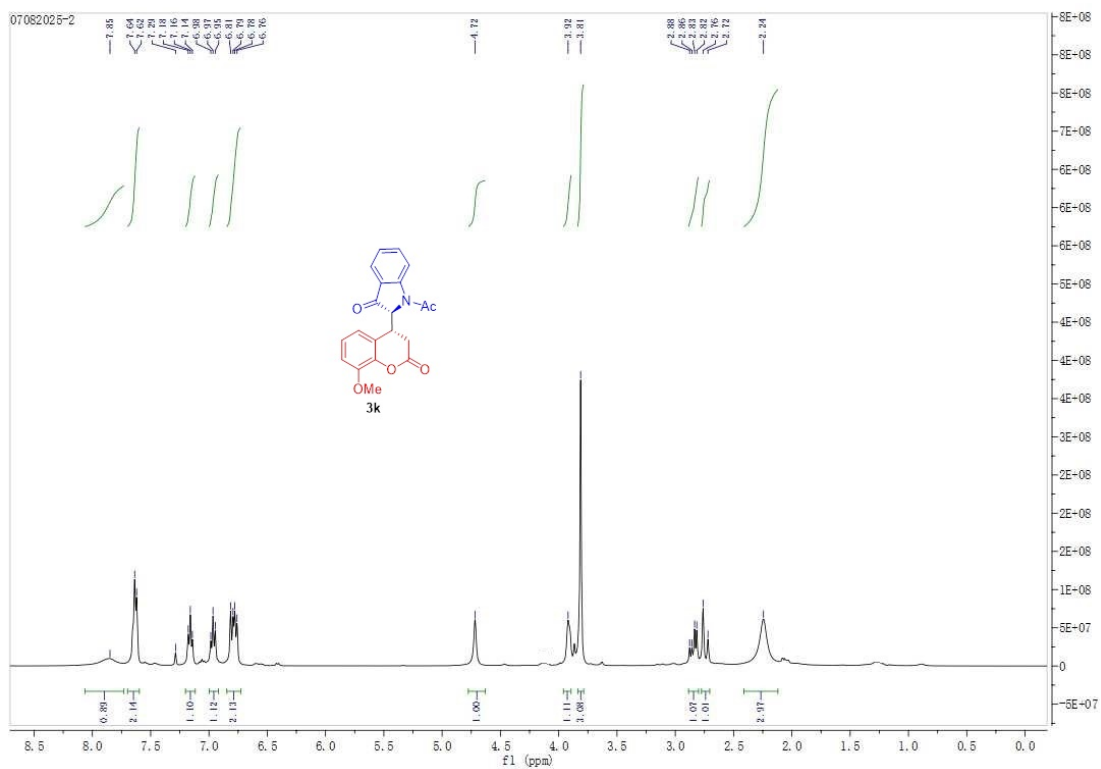


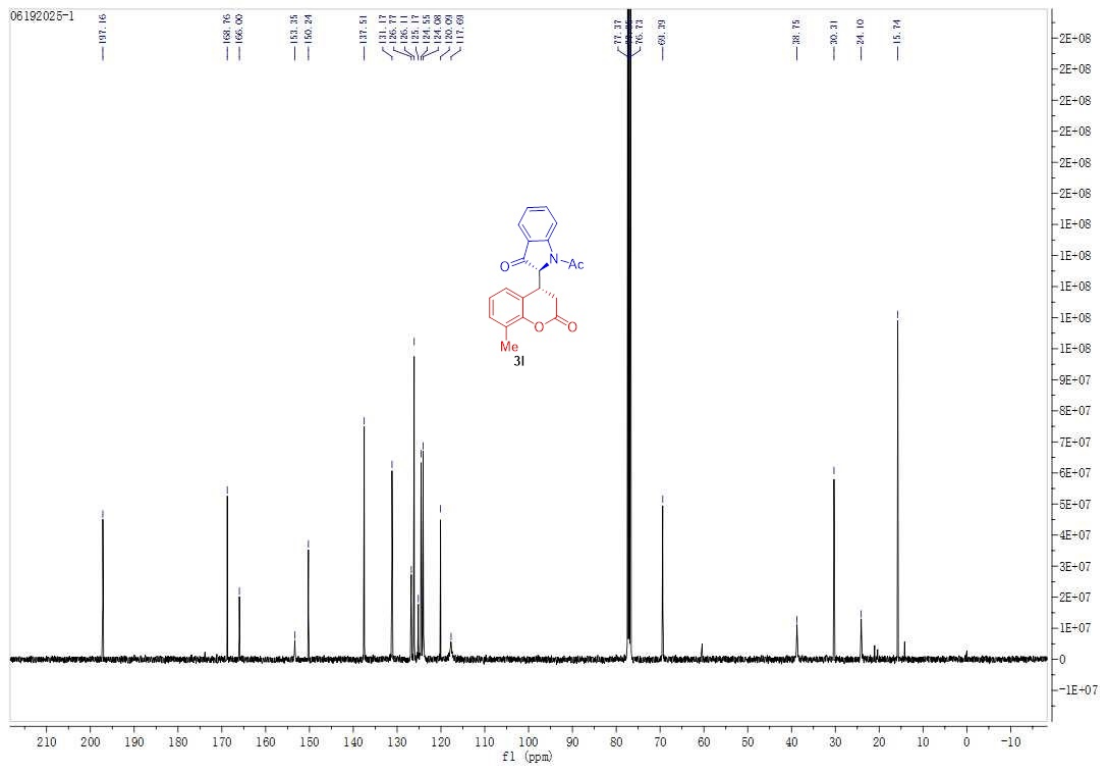
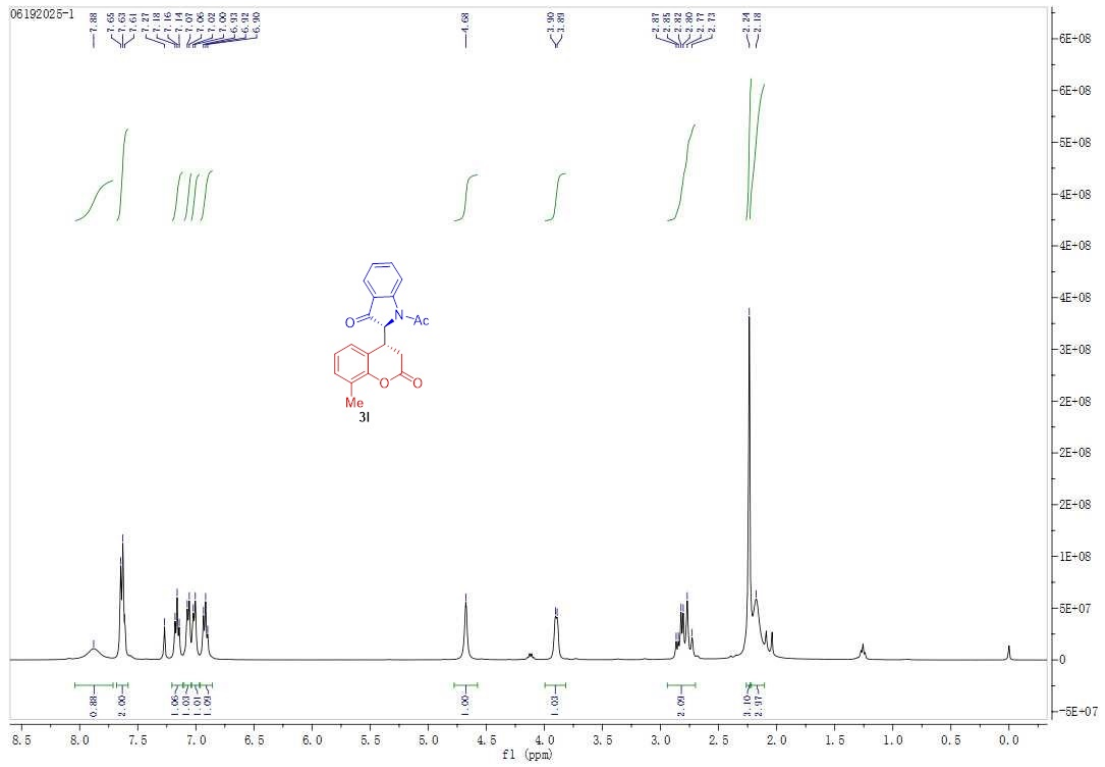


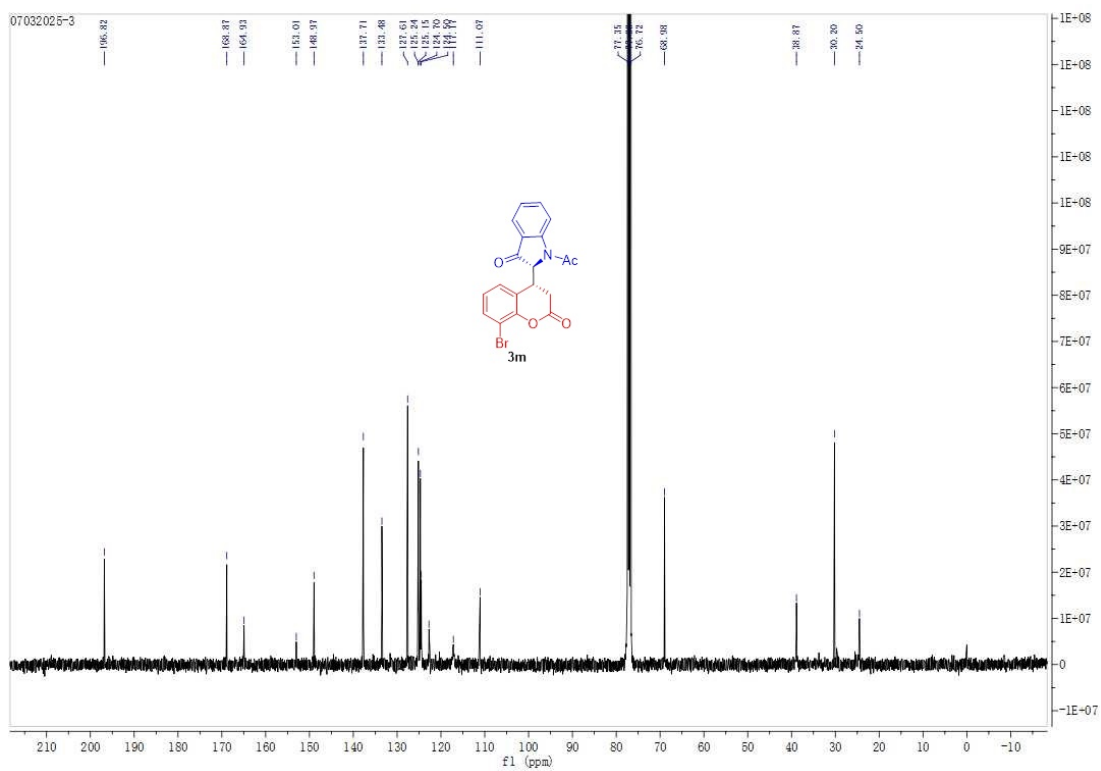
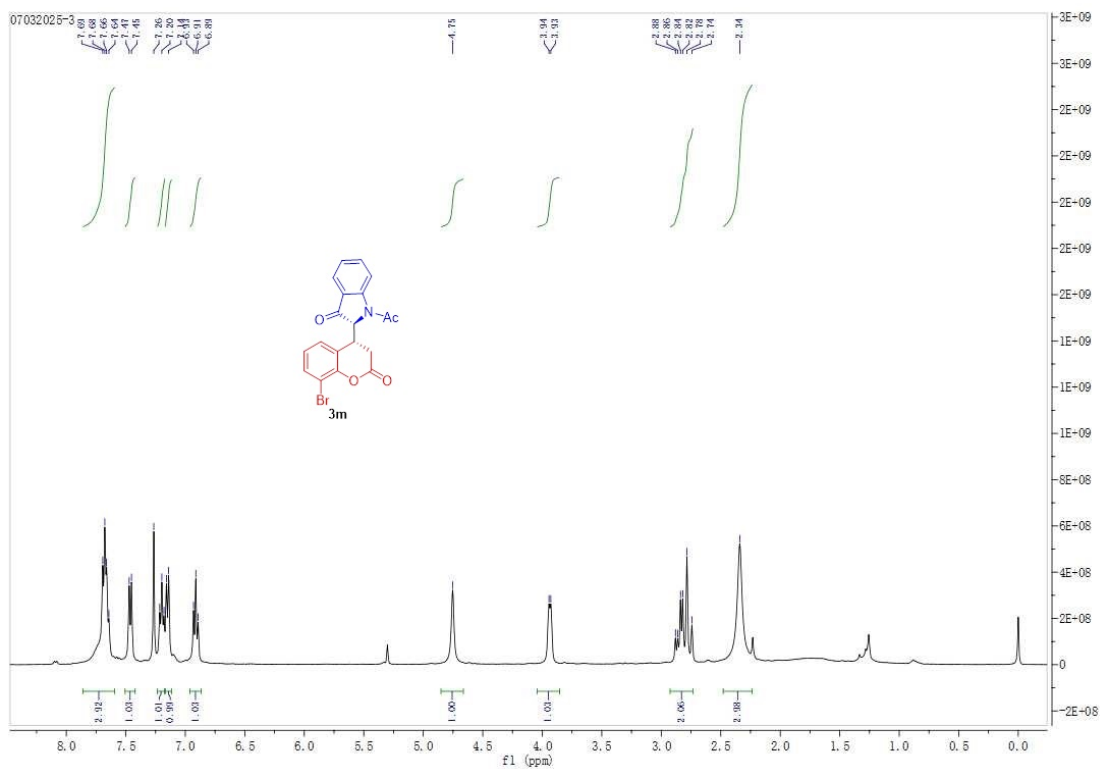


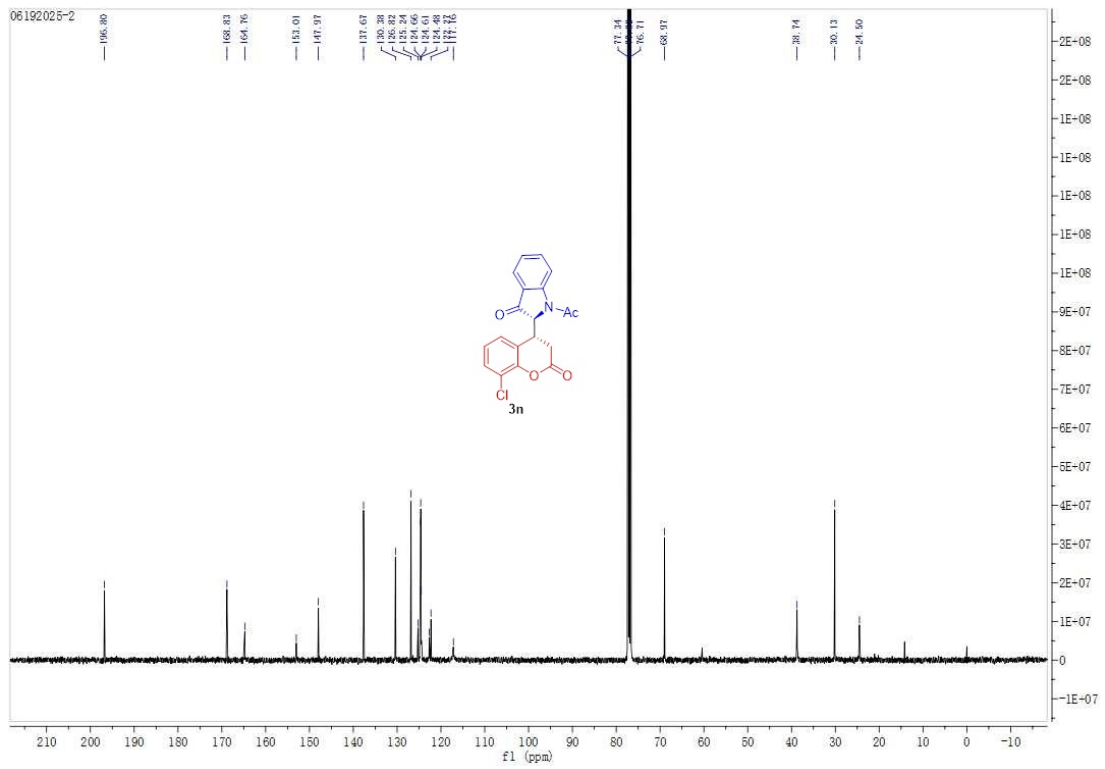
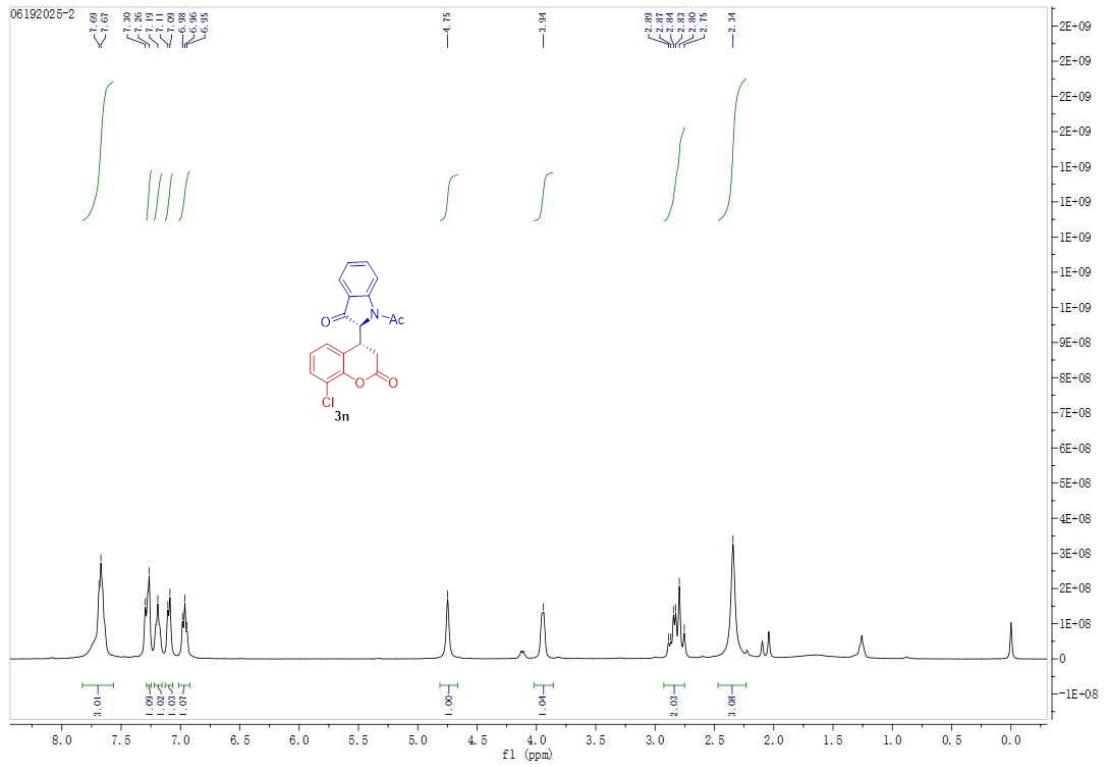


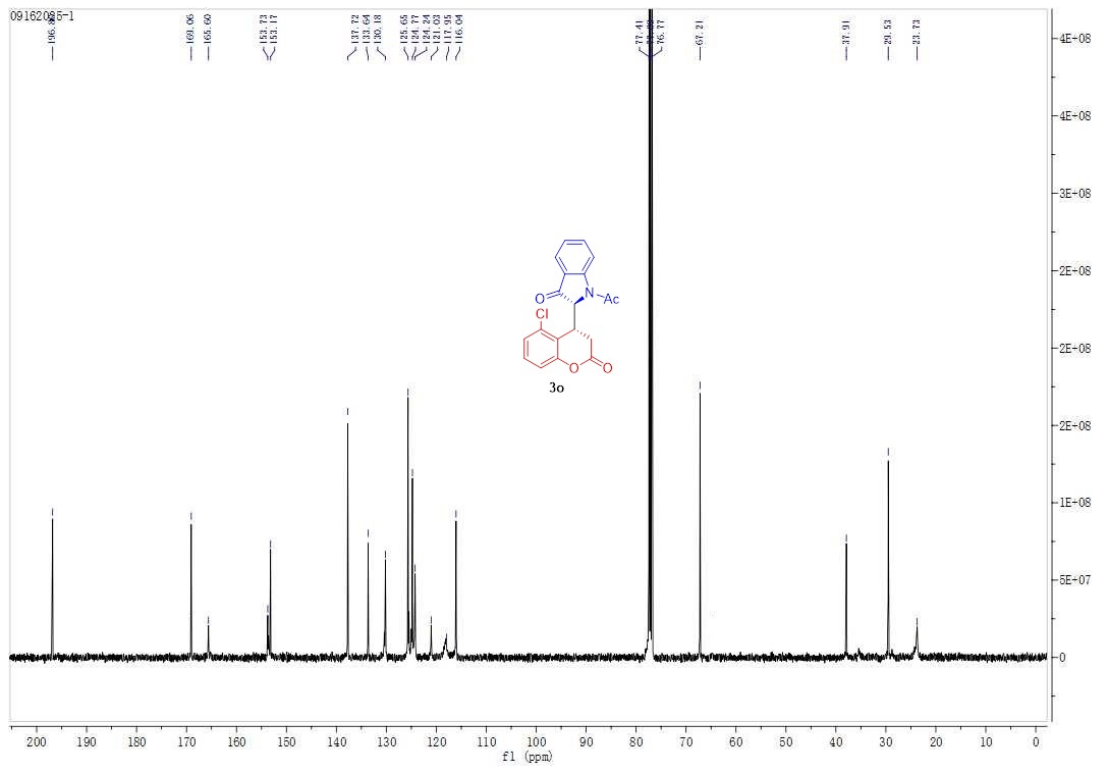
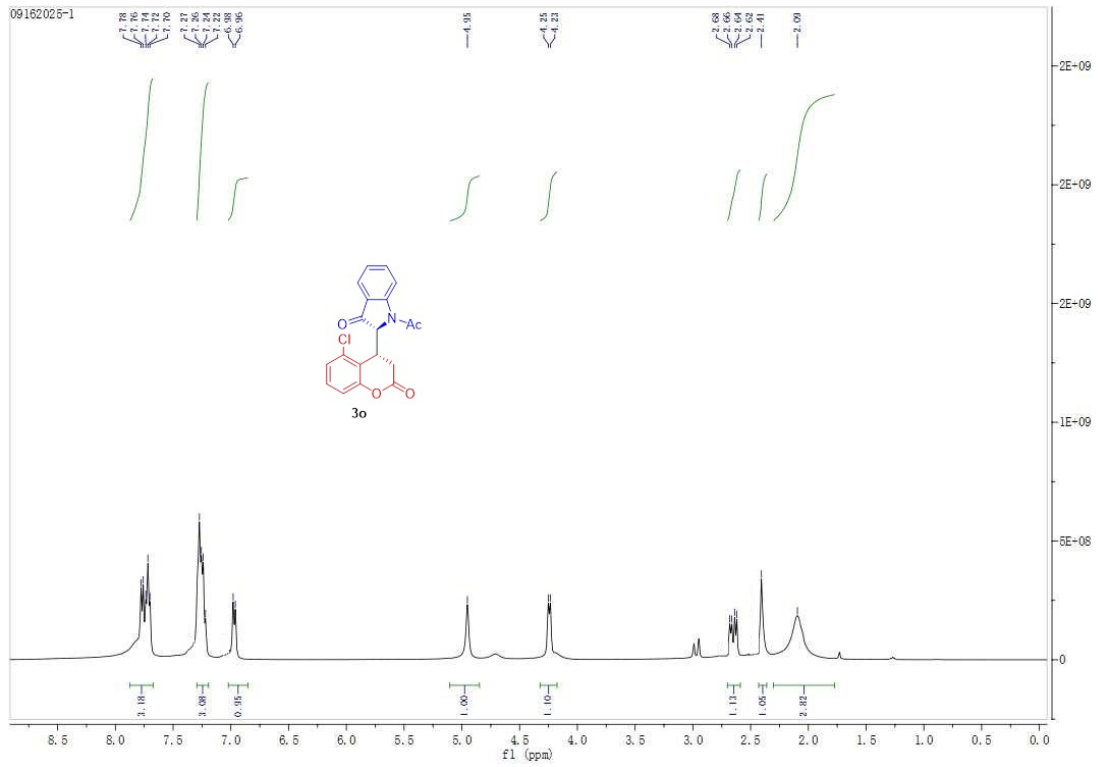


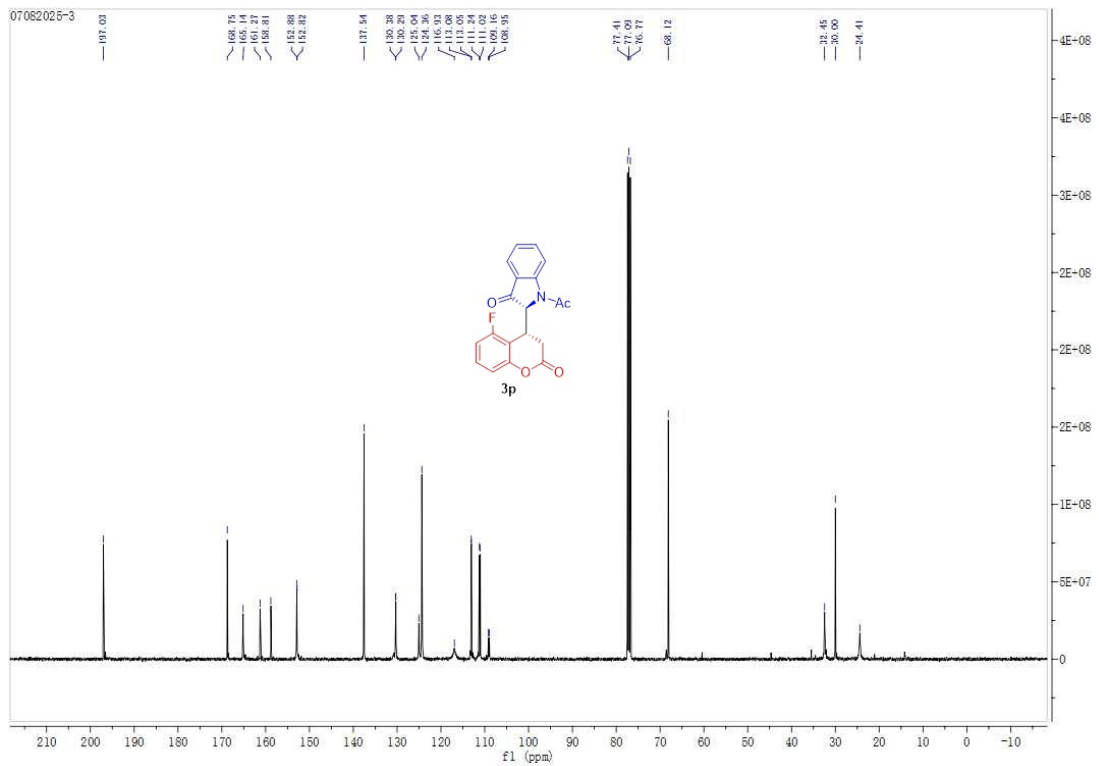
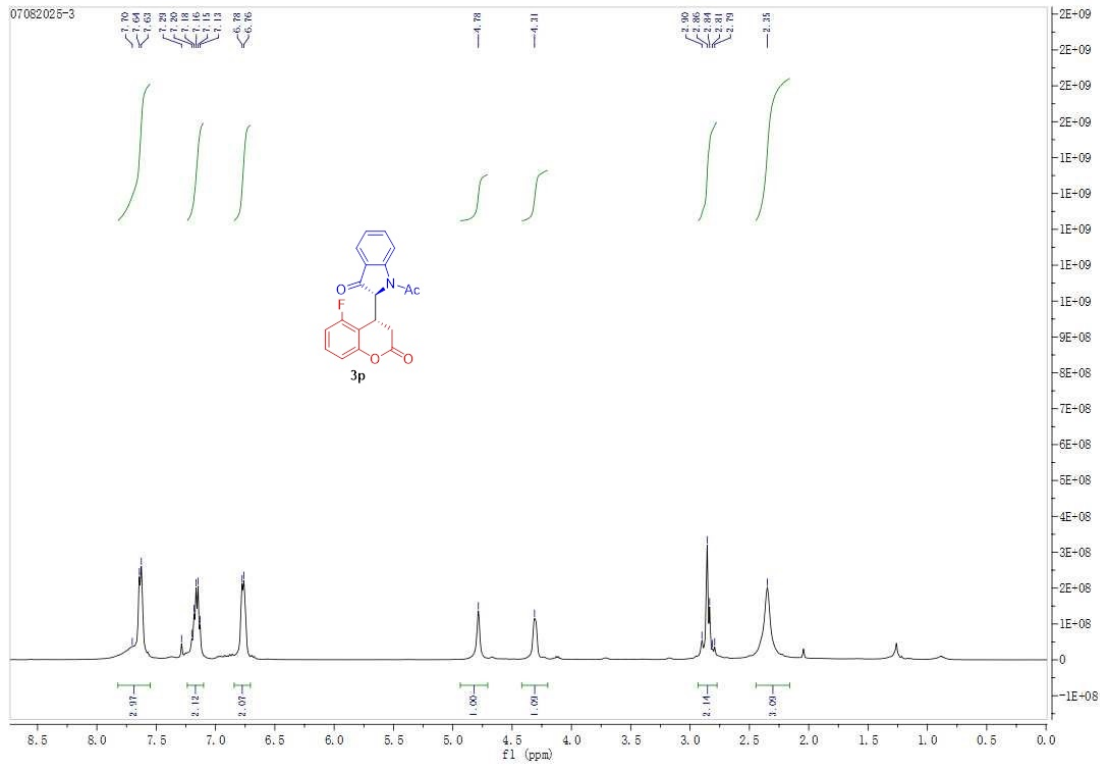


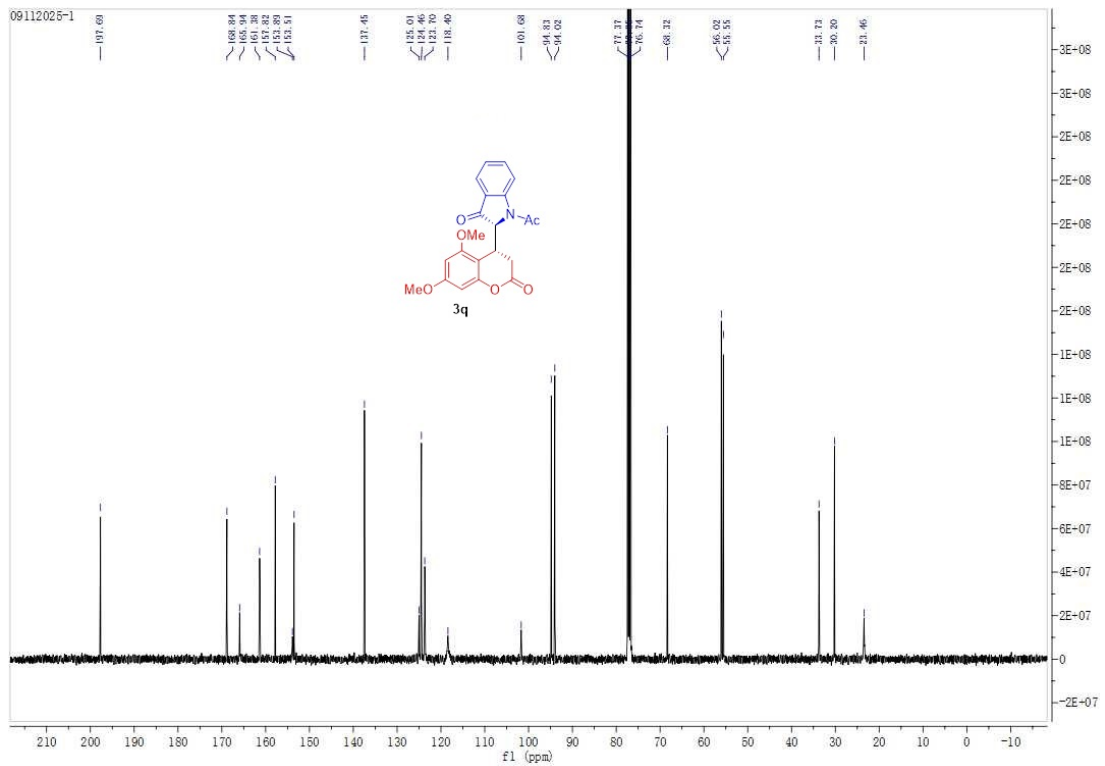
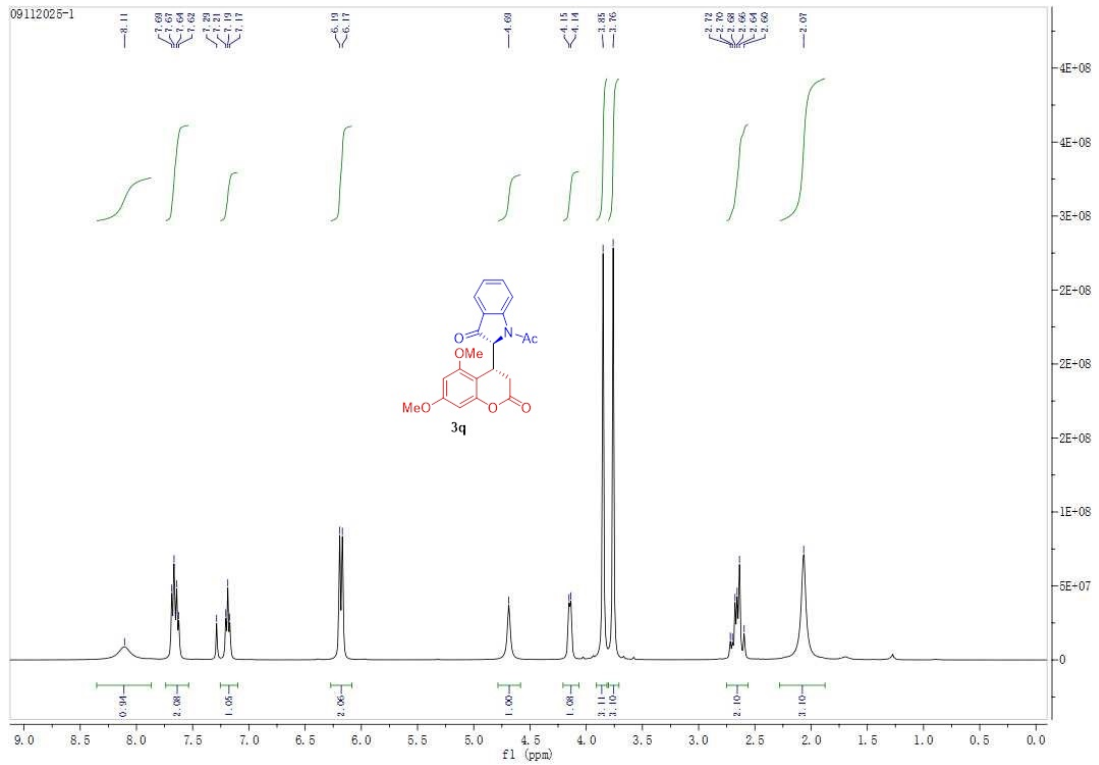


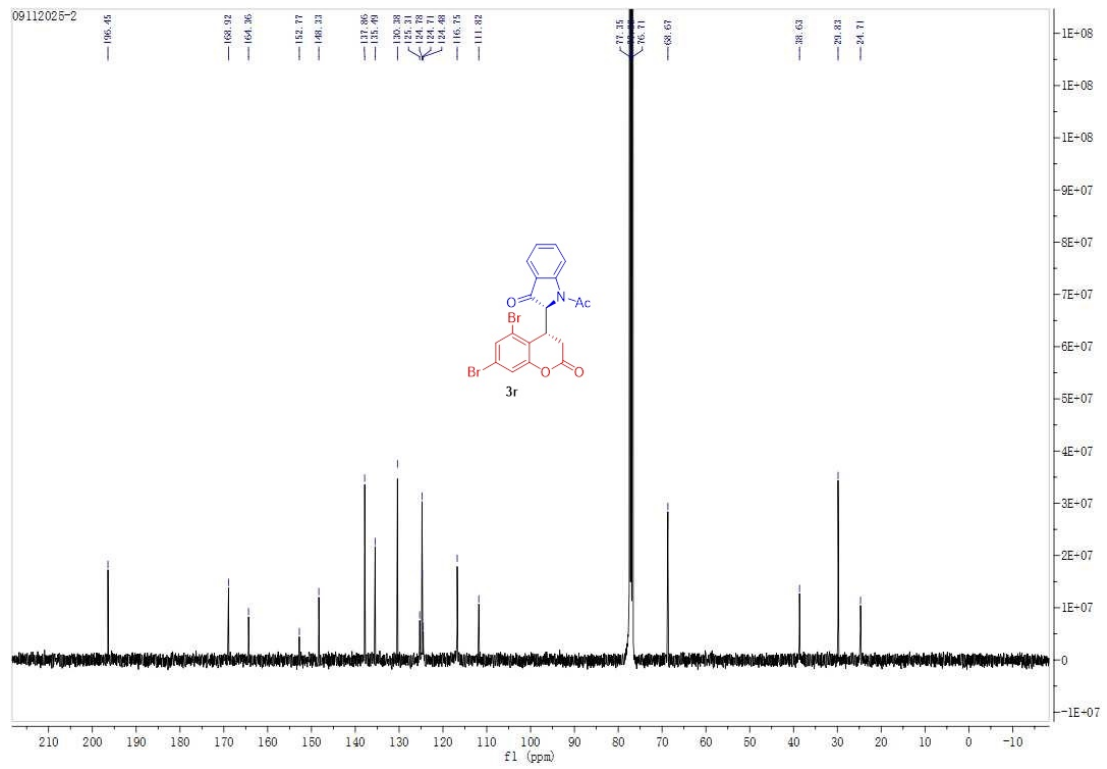
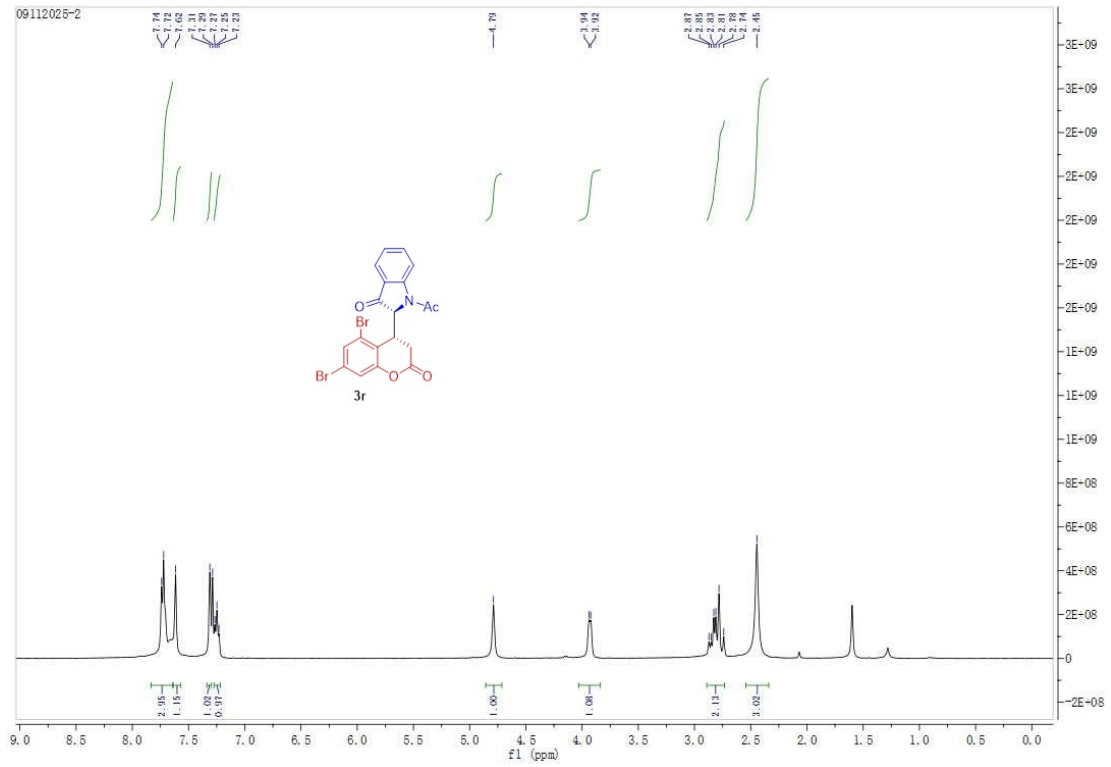


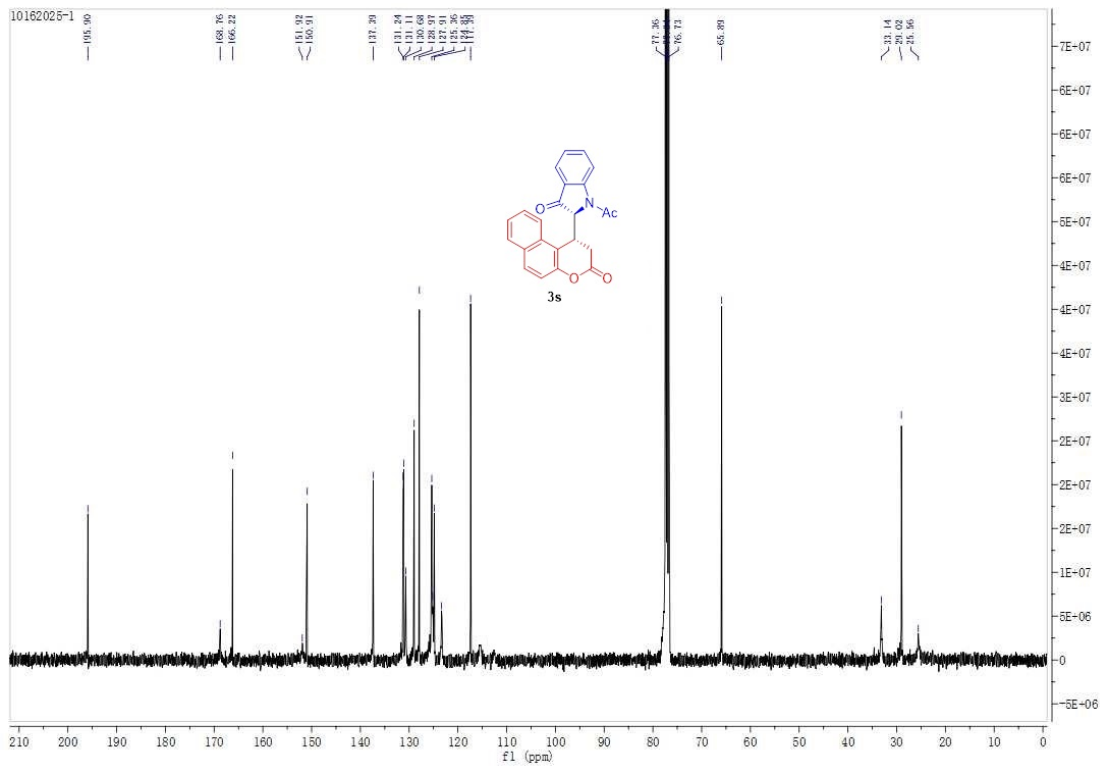
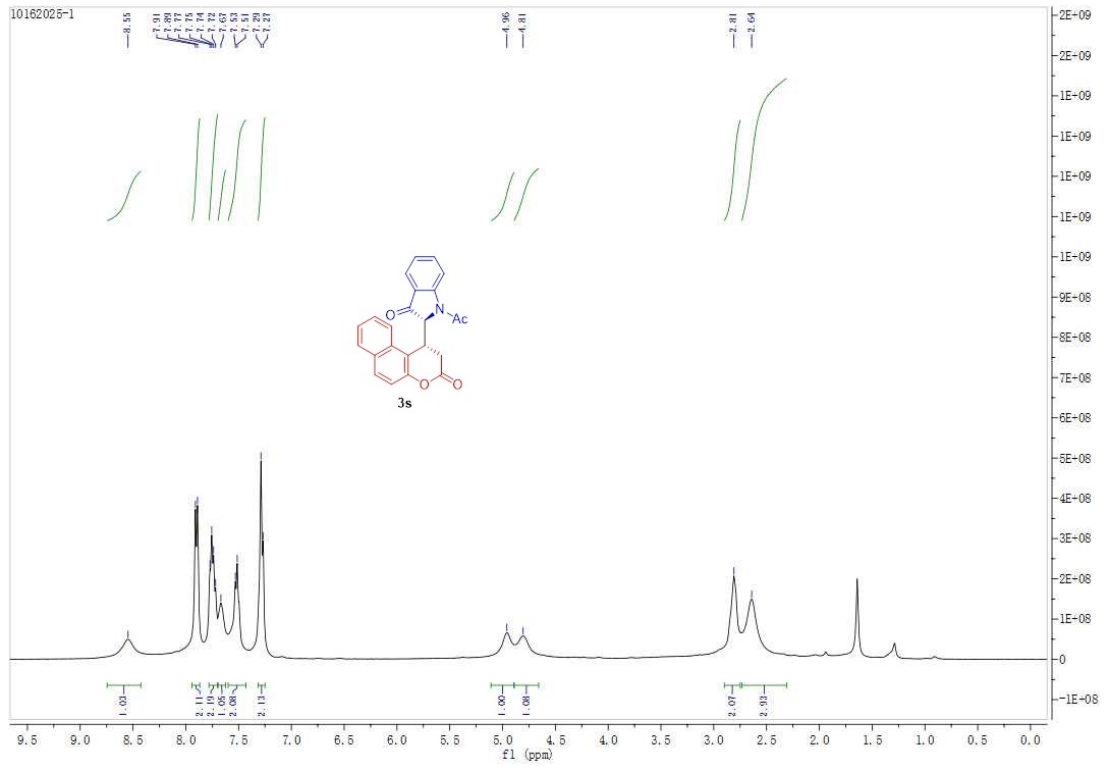


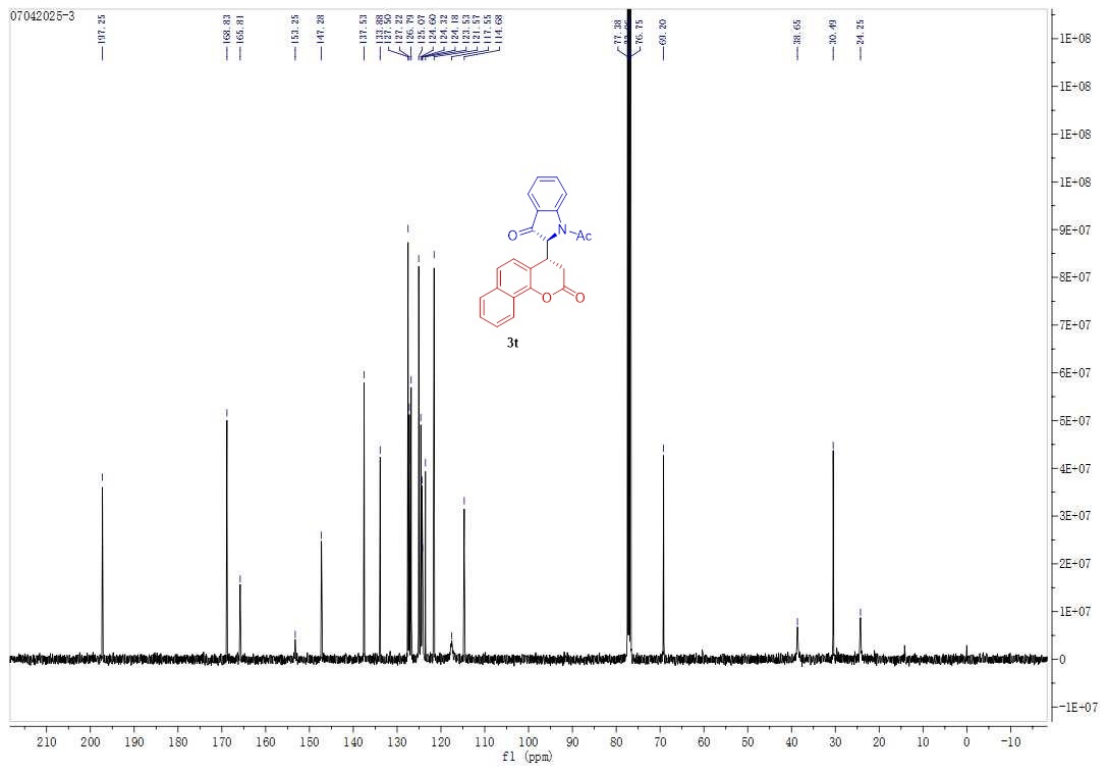
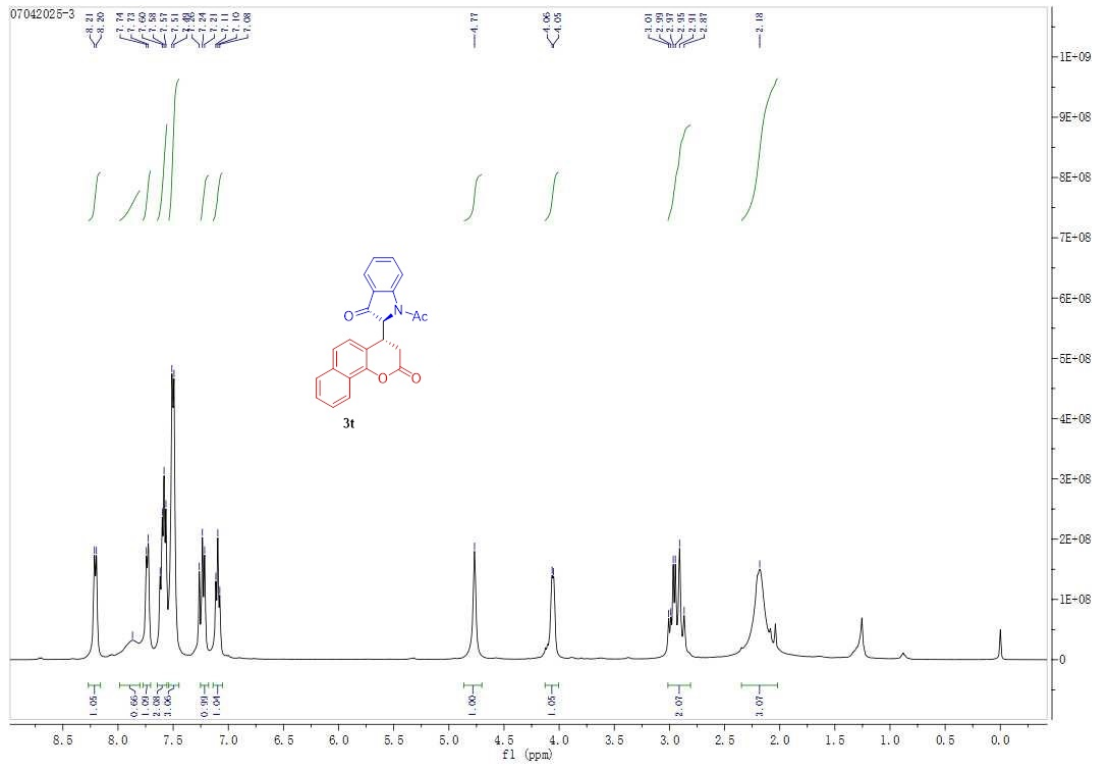


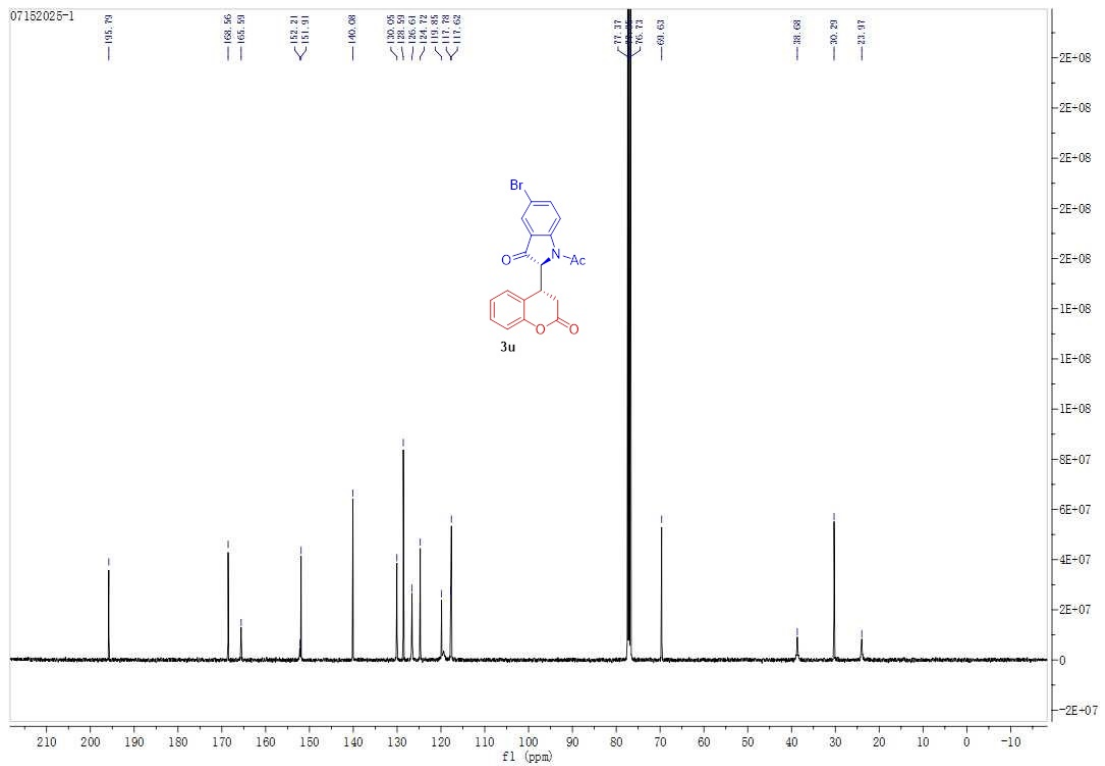
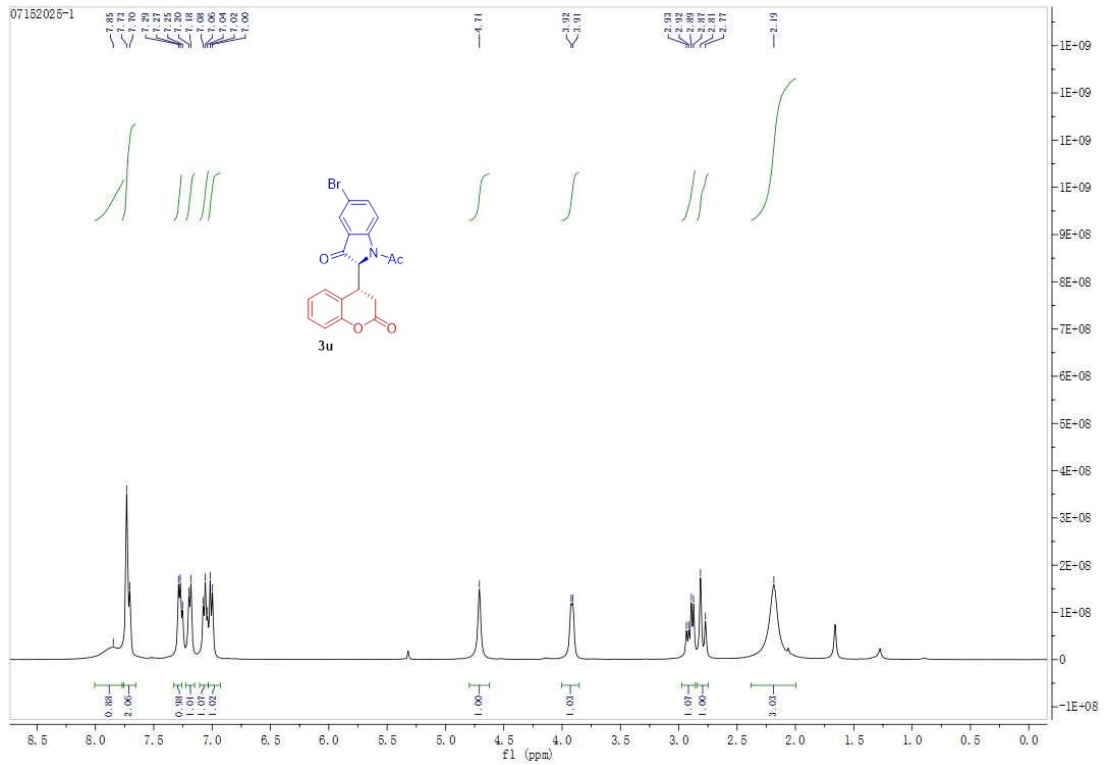


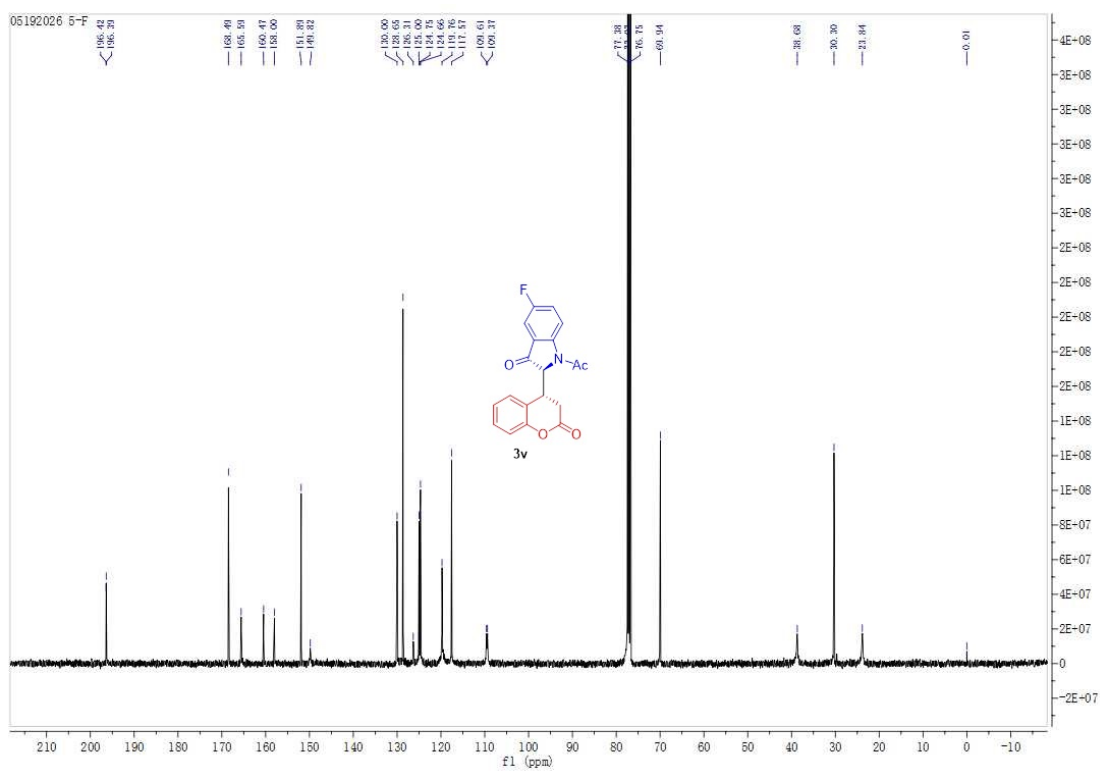
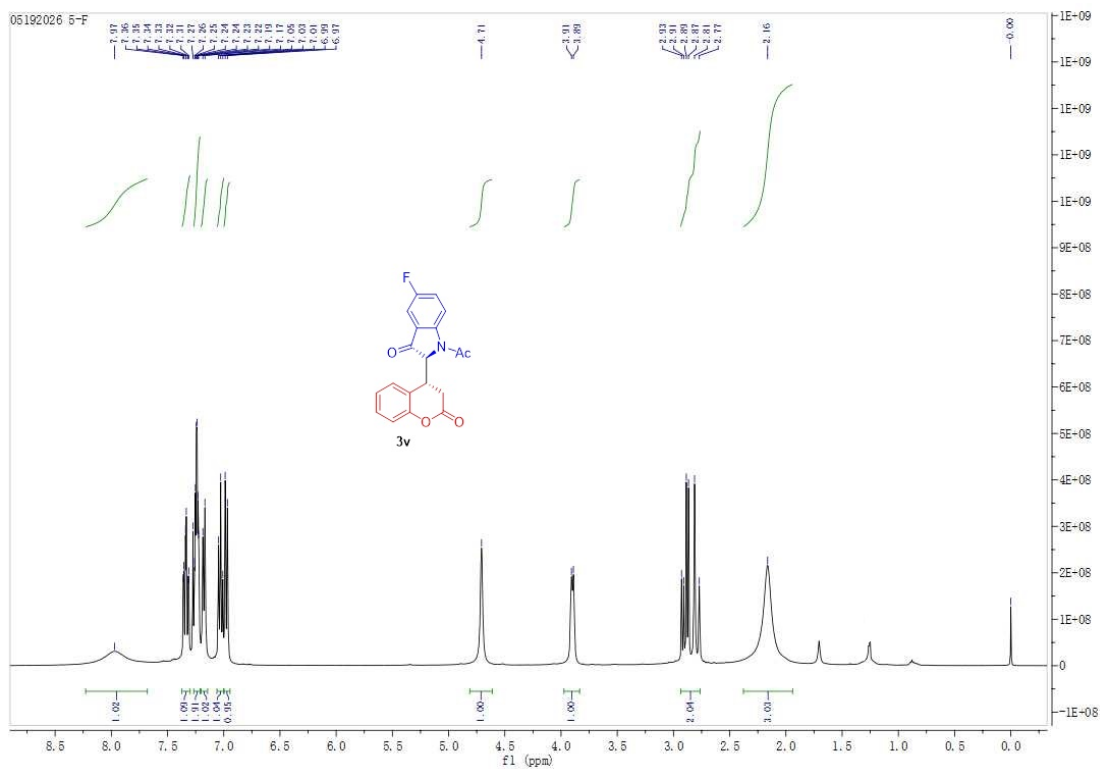


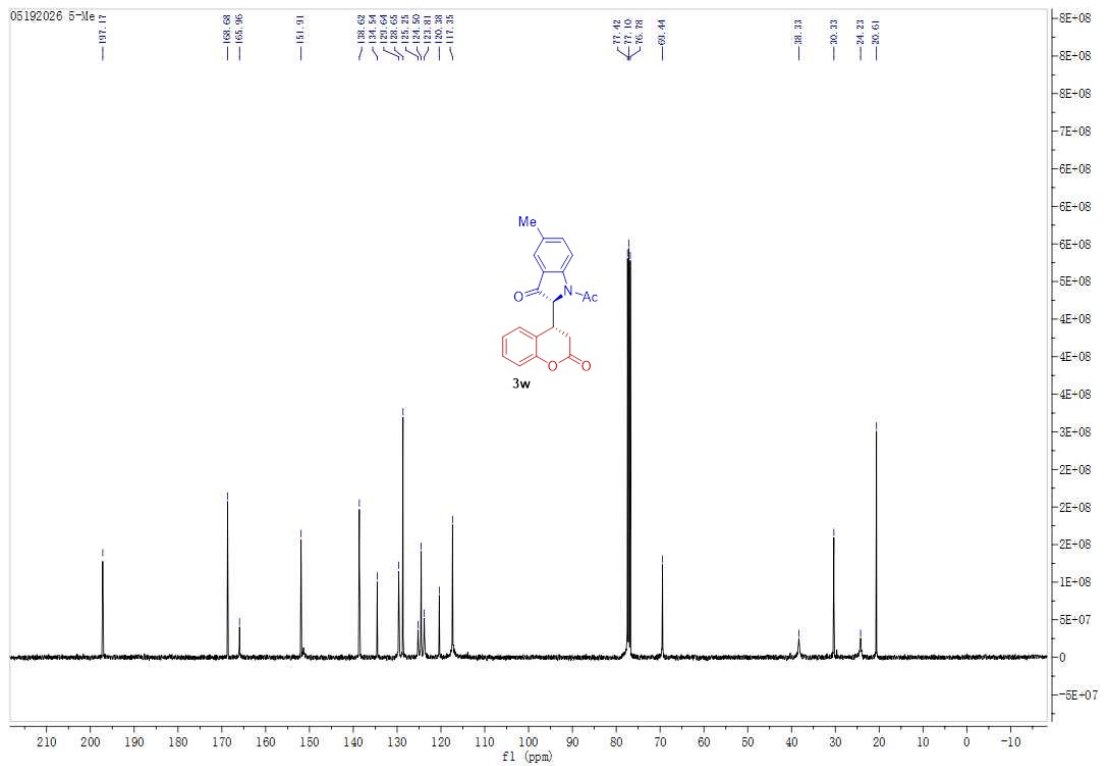
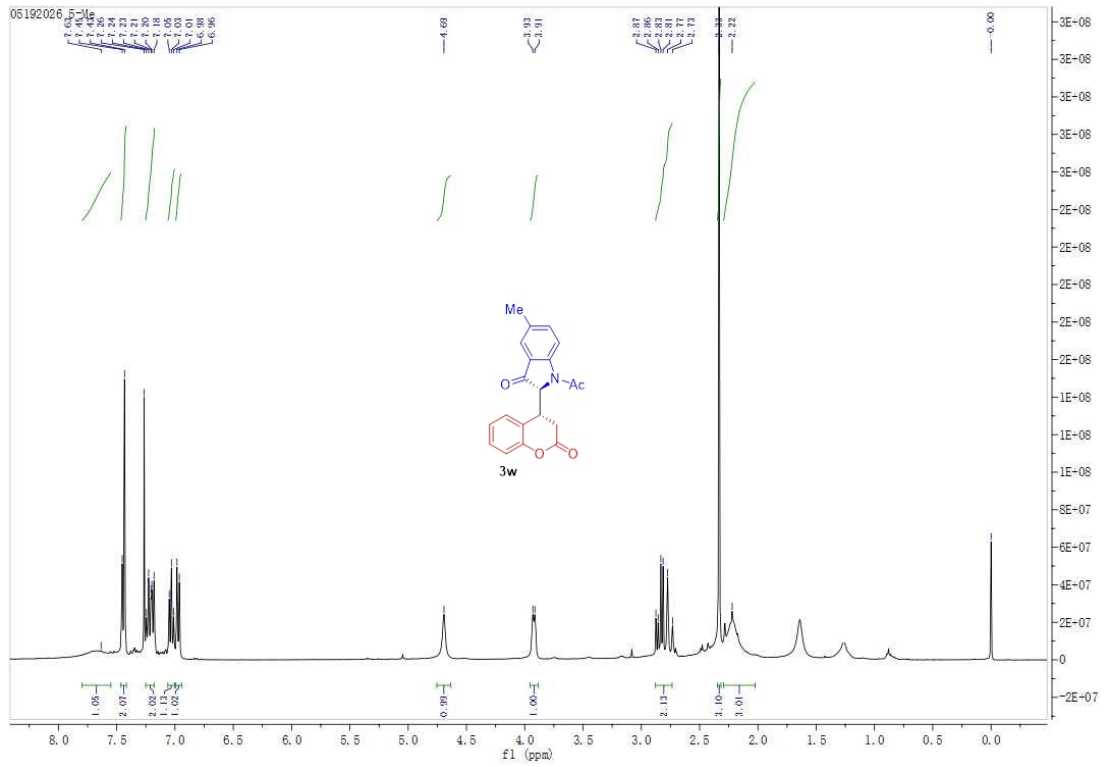


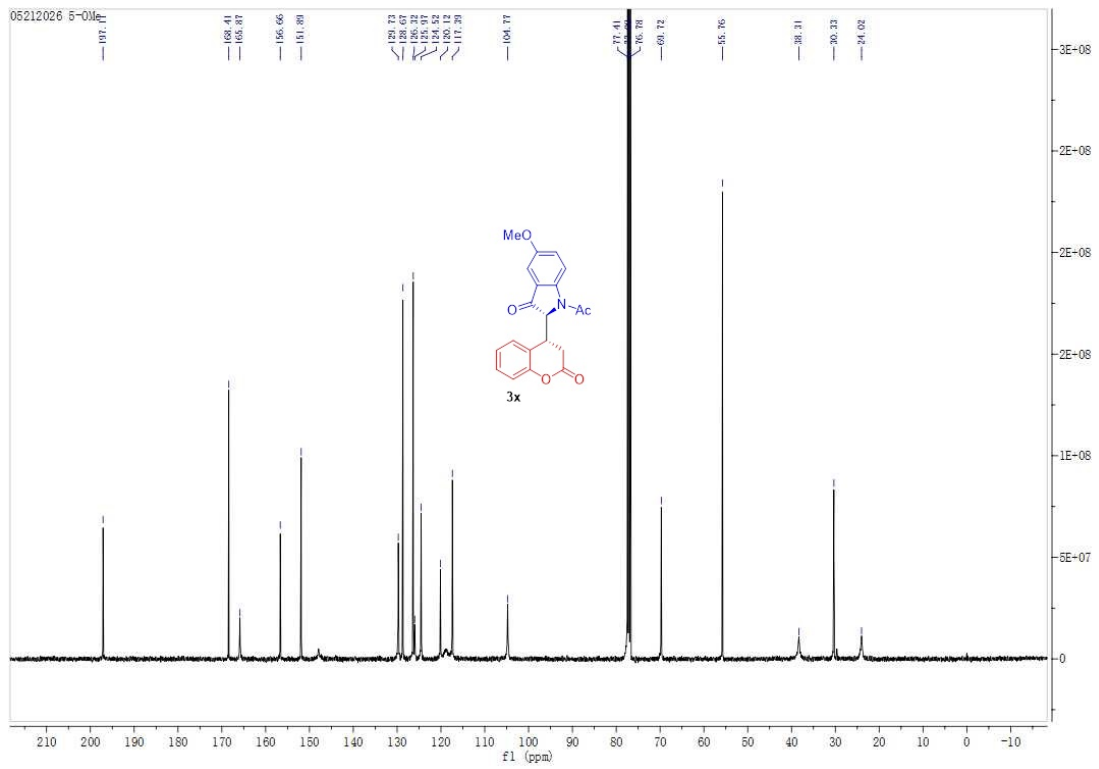
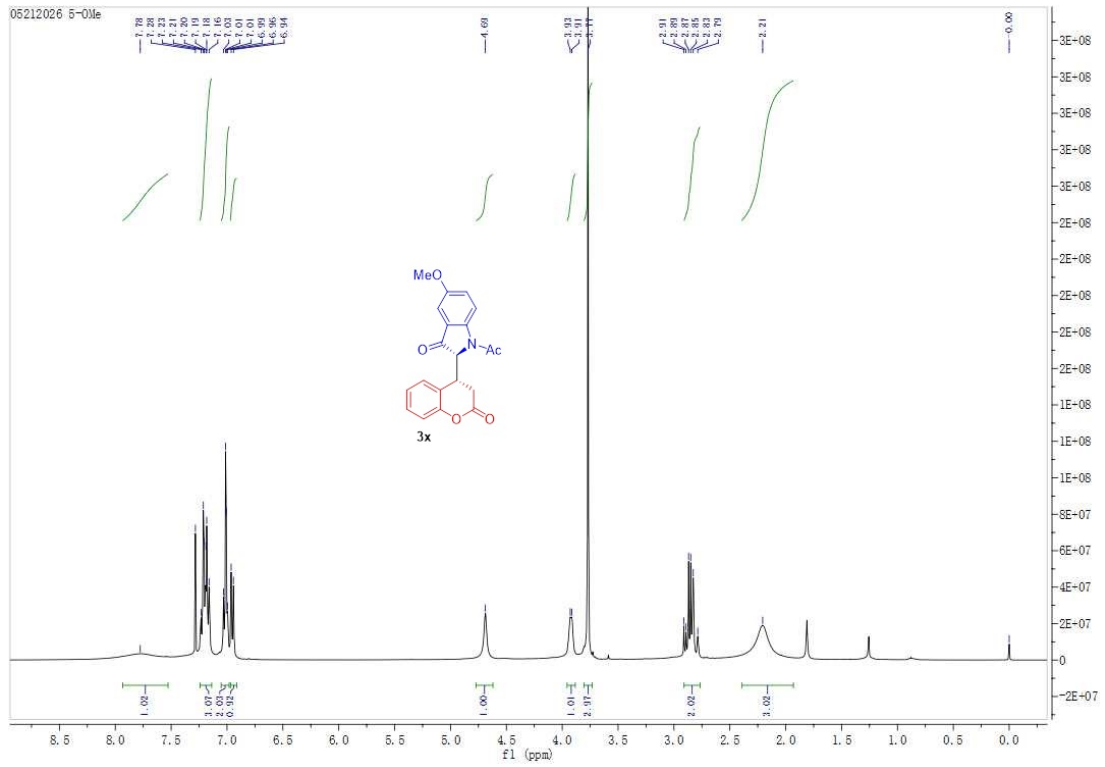


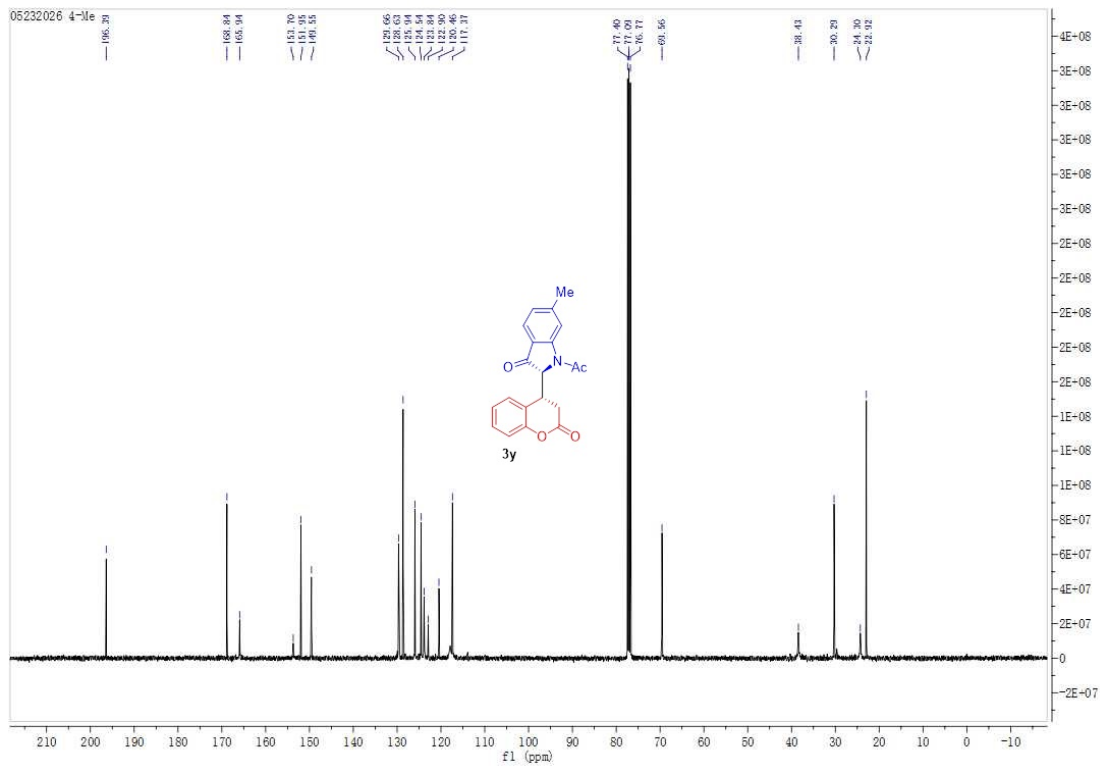
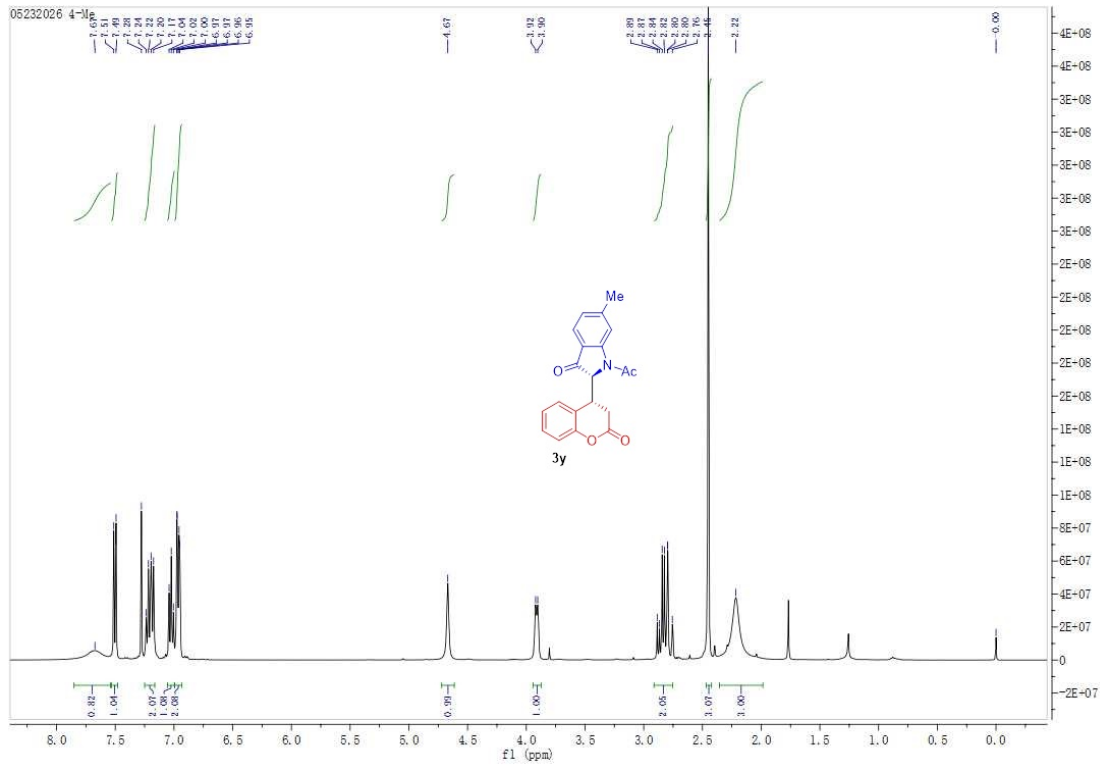


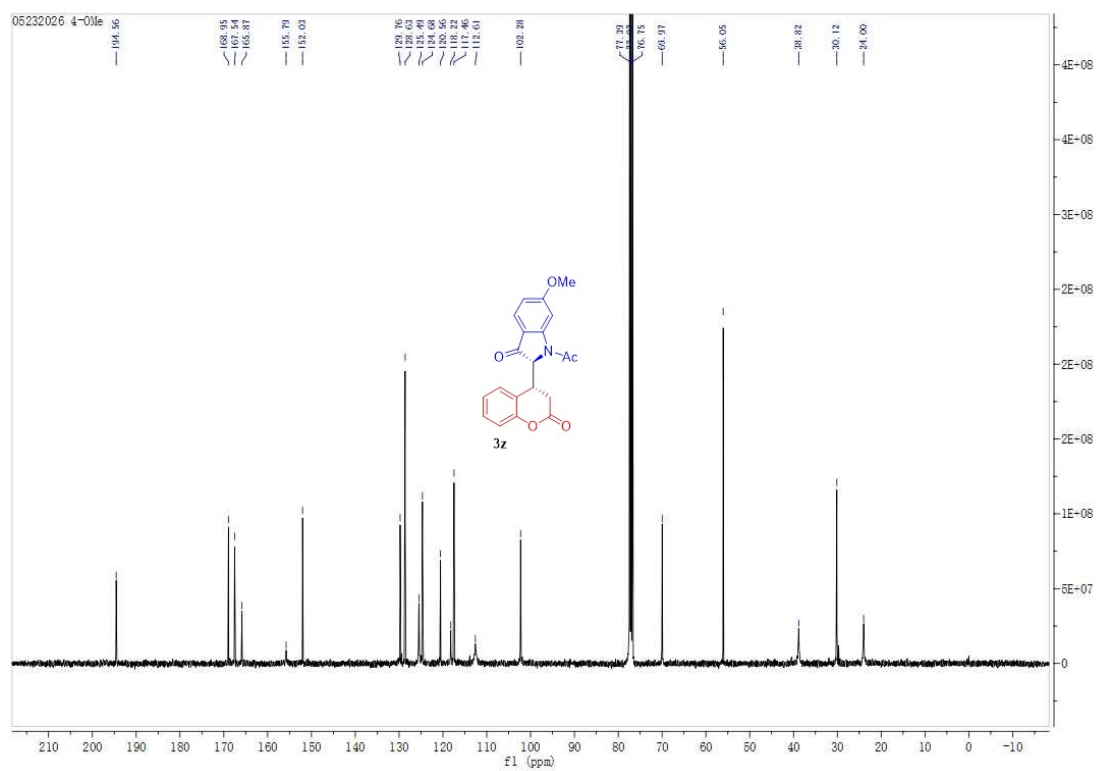
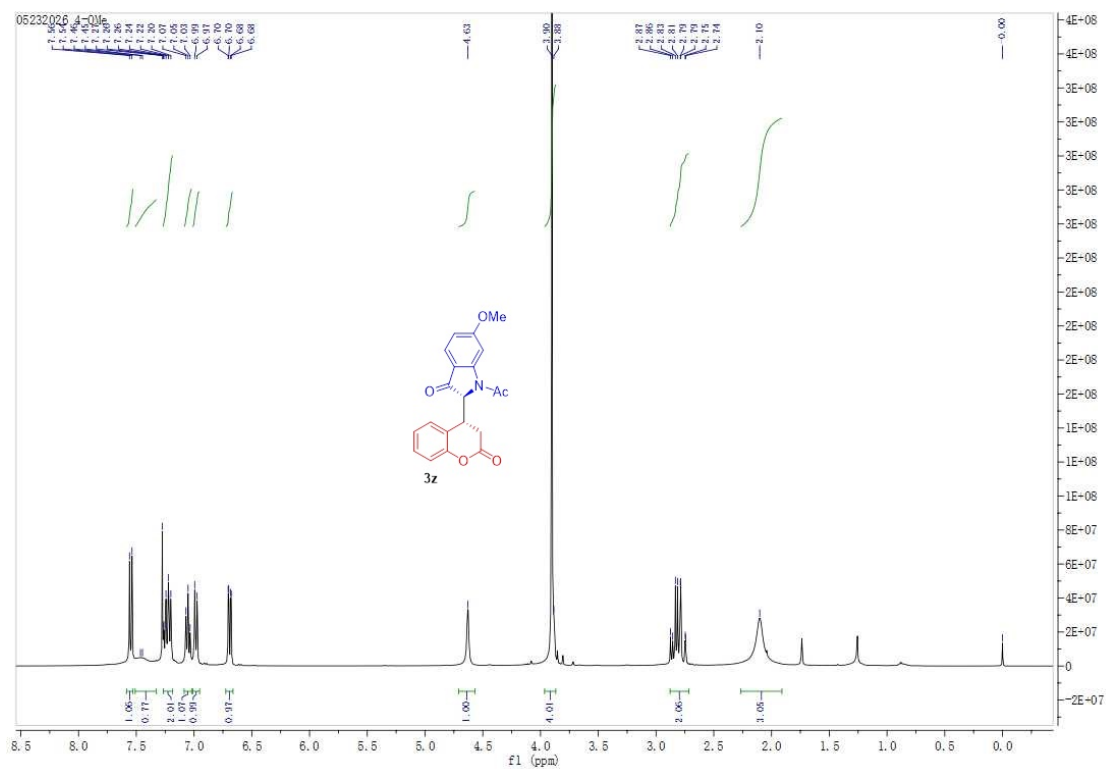


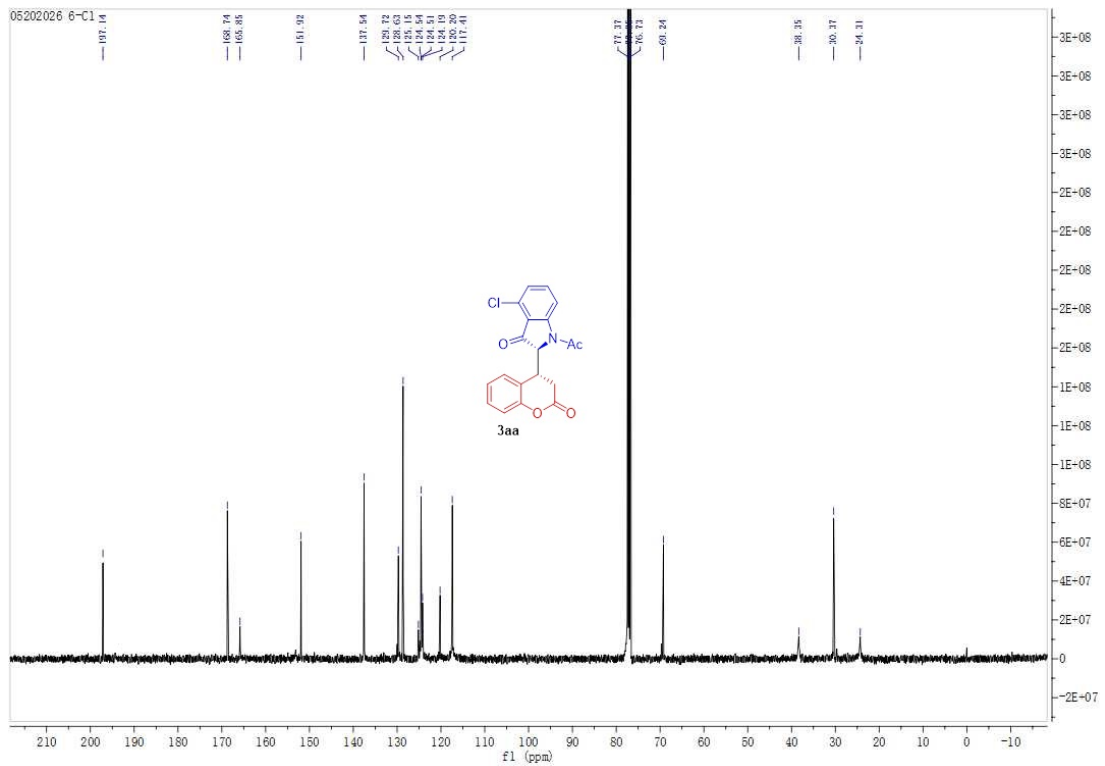
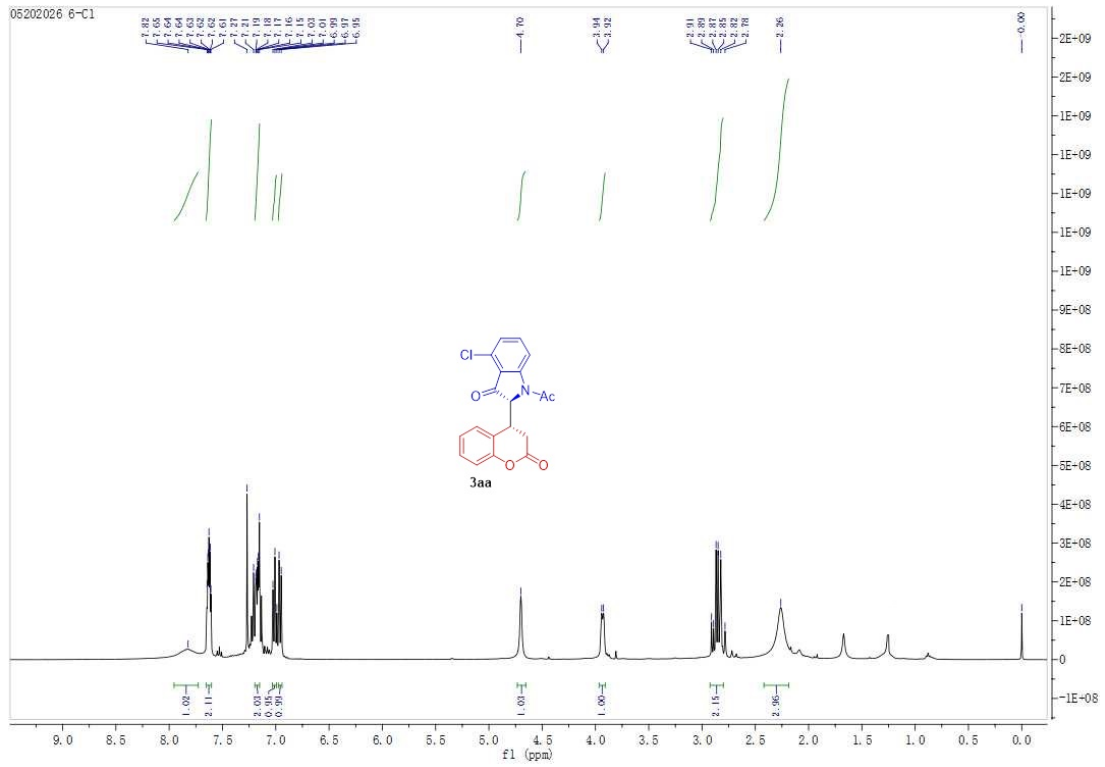


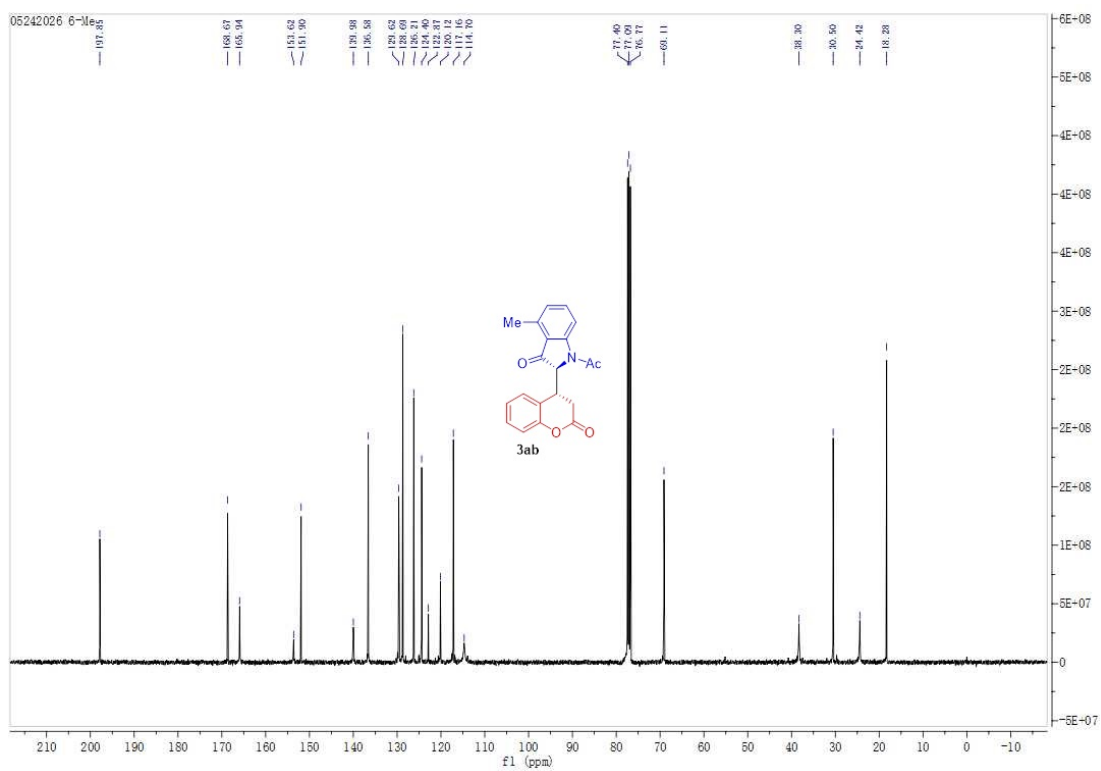
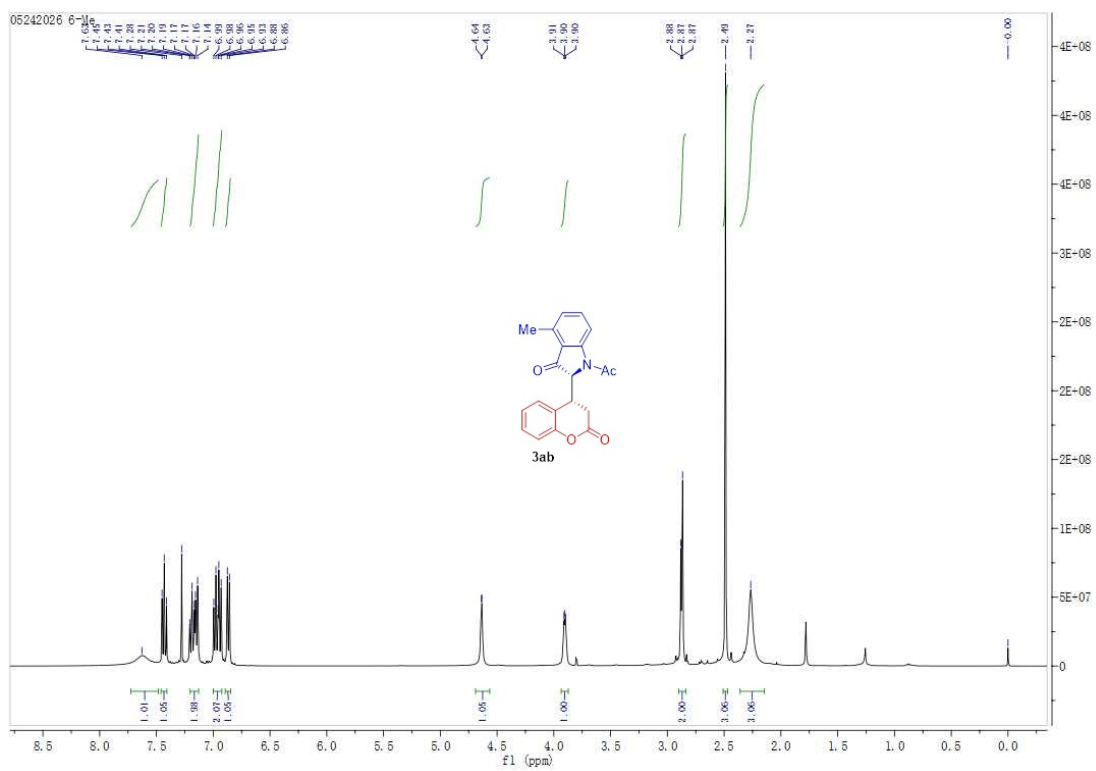


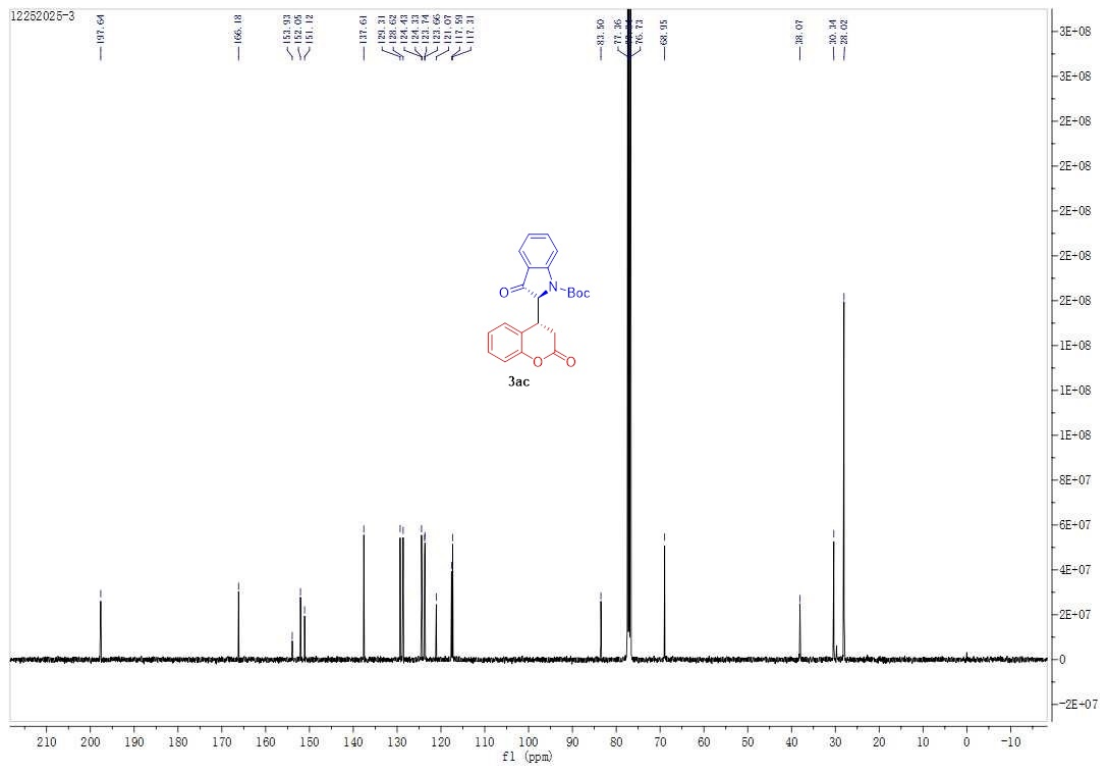
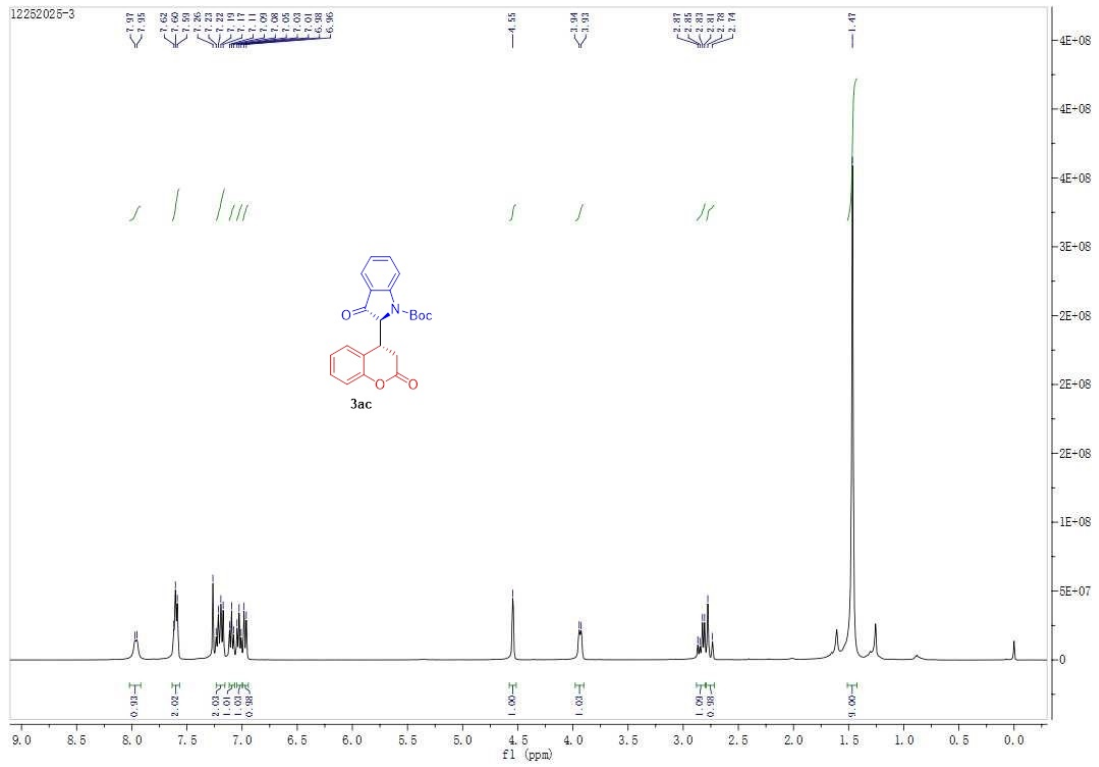


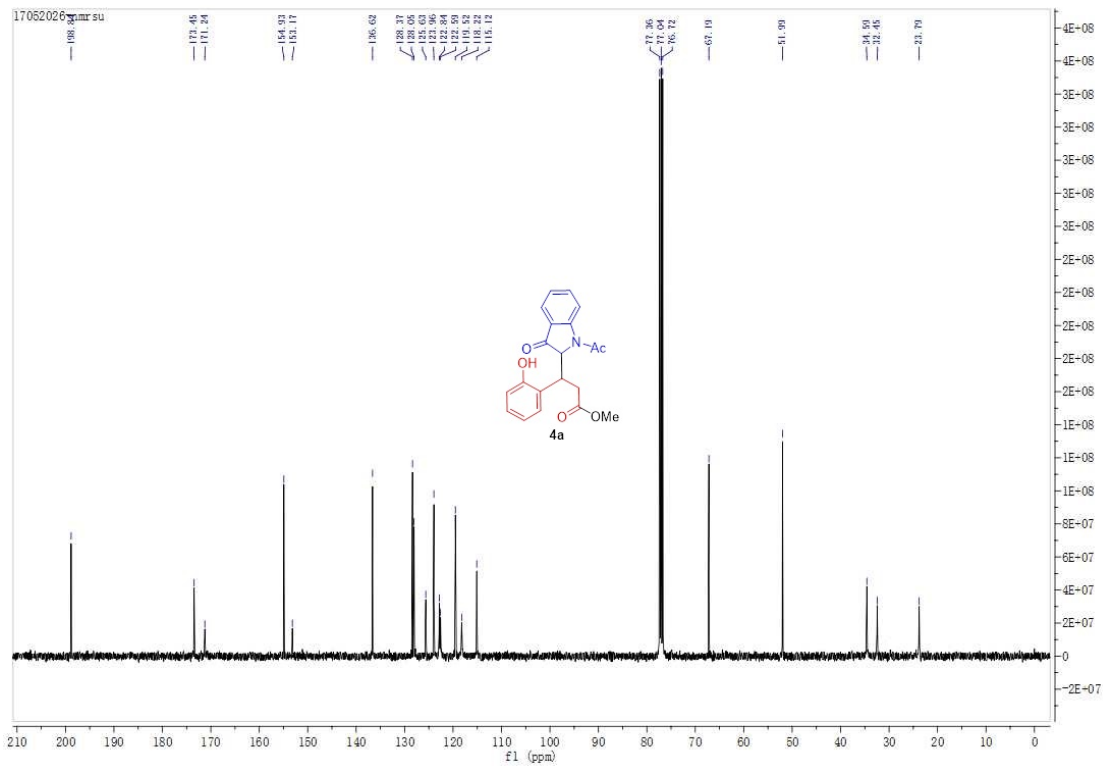
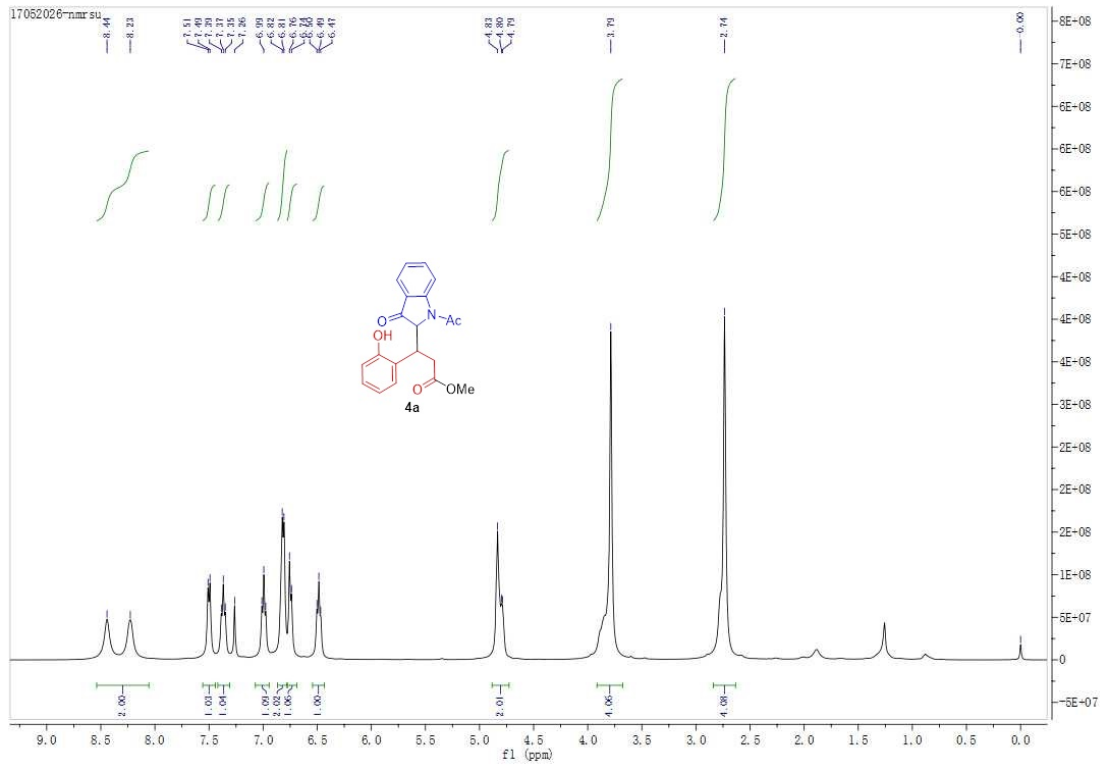




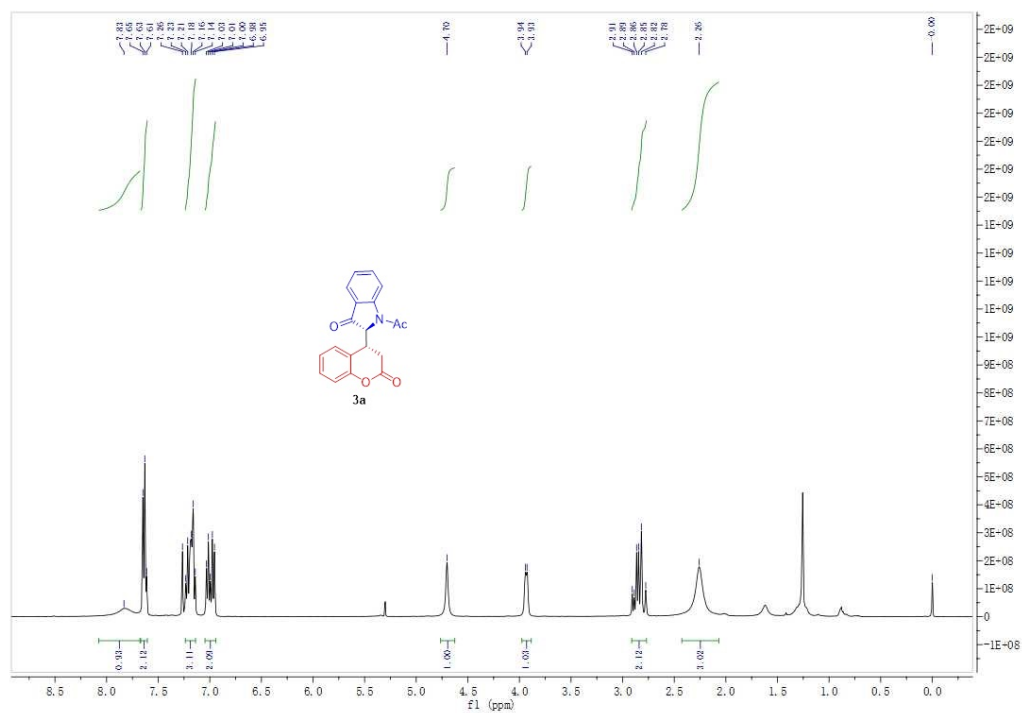




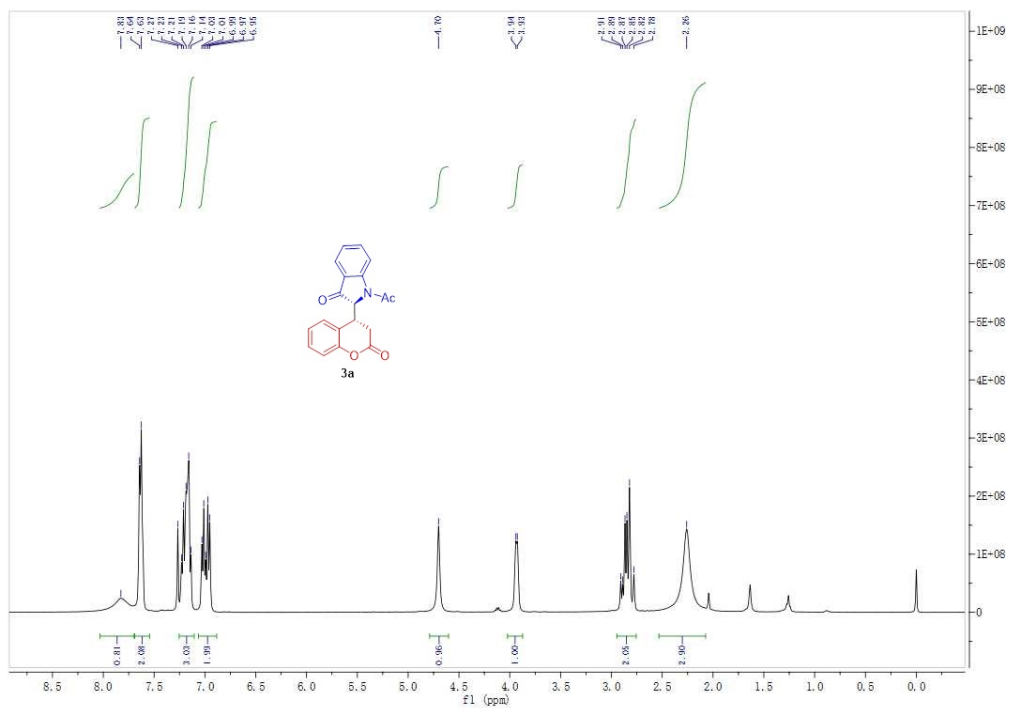




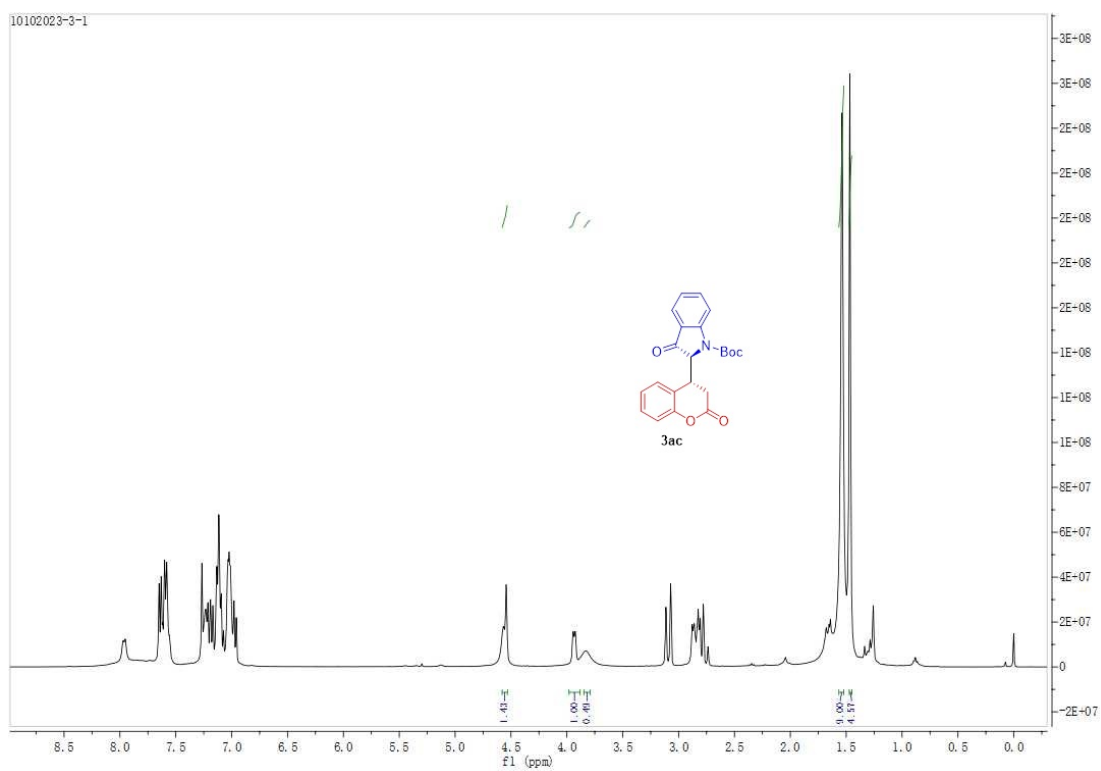
4. Scanned copies of $^1\text{H-NMR}$ spectra of **3a** (isolated from the experiment carried out in the presence of TEMPO, BHT as a radical scavenger) and the crude spectrum of **3ac**



(Isolated from the experiment carried out in the presence of TEMPO as a radical scavenger)



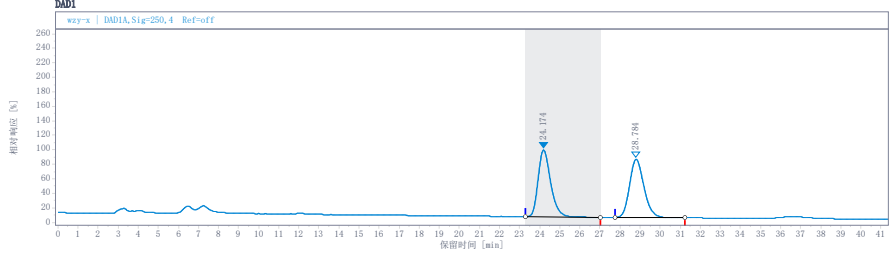
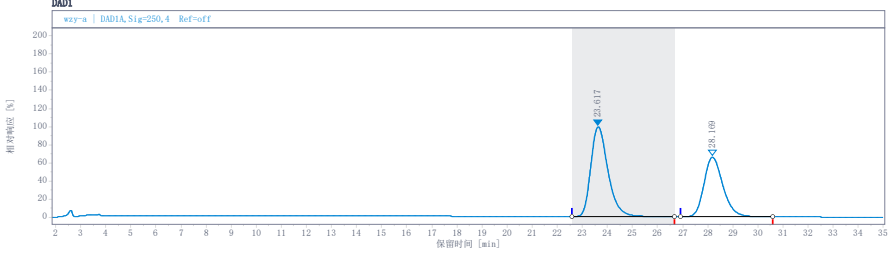
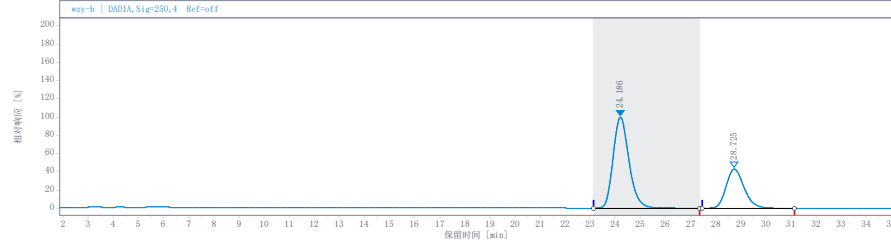
(Isolated from the experiment carried out in the presence of BHT as a radical scavenger)

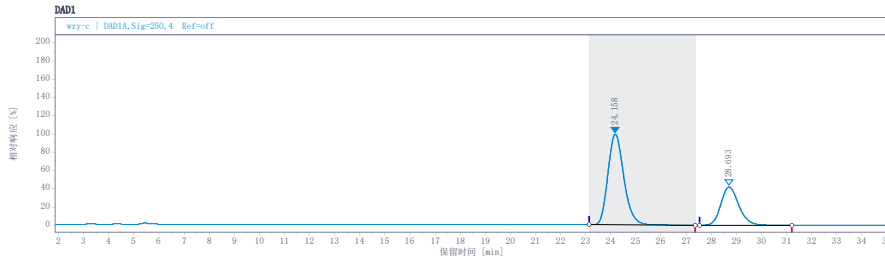


(The crude spectrum of **3ac**)

5. The HPLC of 3a

HPLC data of compound **3a**: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C.

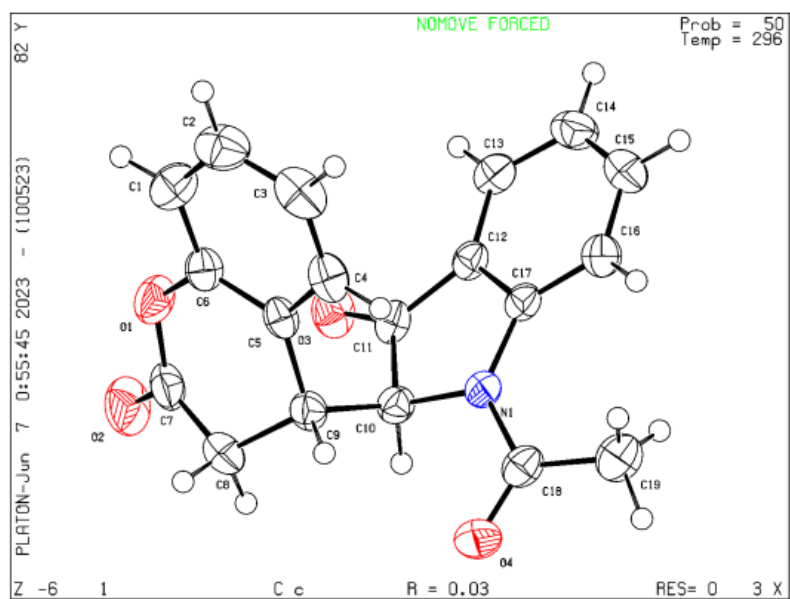
			
Peak	Ret.time	area	Area%
1	24.174	1022.681	50.190
2	28.784	1014.918	49.810
CAS: 130-95-0, 15%ee			
			
Peak	Ret.time	area	Area%
1	23.617	2825.797	57.739
2	28.169	2068.300	42.261
CAS: 851477-19-5, 35%ee			
			
Peak	Ret.time	area	Area%
1	24.186	7124.723	67.258
2	28.725	3468.406	32.742
CAS: 852913-25-8, 37%ee			



Peak	Ret.time	area	Area%
1	24.158	7672.008	68.208
2	28.693	3575.978	31.792

6 The data of crystal structure

Datablock 1 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1

Bond precision:	C-C = 0.0034 A	Wavelength=0.71073	
Cell:	a=11.3469(11)	b=13.9960(14)	c=9.8736(10)
	alpha=90	beta=106.705(2)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1501.9(3)	1501.9(3)	
Space group	C c	C c	
Hall group	C -2yc	C -2yc	
Moiety formula	C19 H15 N O4	?	
Sum formula	C19 H15 N O4	C19 H15 N O4	
Mr	321.32	321.32	
Dx, g cm-3	1.421	1.421	
Z	4	4	
Mu (mm-1)	0.101	0.101	
F000	672.0	672.0	
F000'	672.35		
h, k, lmax	13, 16, 11	13, 16, 11	
Nref	2648[1328]	2409	
Tmin, Tmax	0.974, 0.978		
Tmin'	0.974		
Correction method=	Not given		
Data completeness=	1.81/0.91	Theta(max)=	24.997
R(reflections)=	0.0283(2296)	wR2(reflections)=	0.0673(2409)
S =	1.070	Npar=	218