Supporting Information

Rh(III)-catalyzed C(sp^2)-H functionalization/cyclization cascade of *N*-carboxamide indole and iodonium reagent for access to indoloquinazolinone derivatives

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Experimental Section:

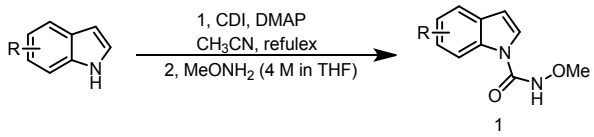
1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under air, and undistilled solvent was used unless otherwise noted. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded in $CDCl_3$ on 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^{1}H NMR and ^{13}C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

2. Synthesis of the starting materials

2.1 General procedure for the synthesis of substrate 1.

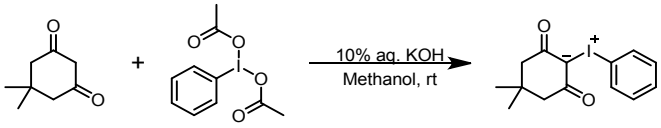
The *N*-methoxy-1H-indole-1-carboxamides **1** were prepared according to previously described methods. [1]



1

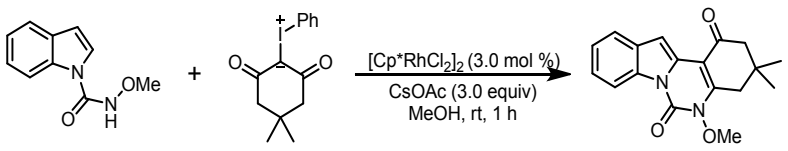
2.2 General procedure for the synthesis of substrate 2.

The iodonium ylides **2** were prepared according to previously described methods. [2]



2

3. Typical procedure for the synthesis of 3aa

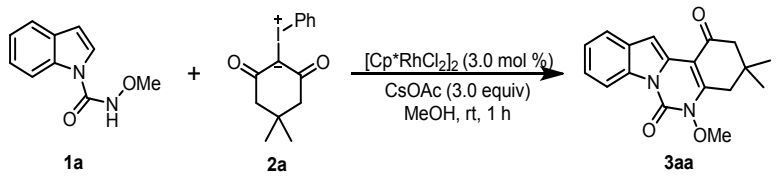


1a **2a** **3aa**

To a 15 mL reaction tube was sequentially added *N*-methoxy-1H-indole-1-carboxamide **1a** (0.2 mmol, 1.0 equiv), 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium ylide **2a** (0.24 mmol, 2.0

equiv), $[Cp^*RhCl_2]_2$ (3 mol %), CsOAc (3 equiv) and MeOH (2 mL). The reaction mixture was stirred at room temperature for about 1 h. Afterwards, the target product was obtained by filtration and washing with MeOH.

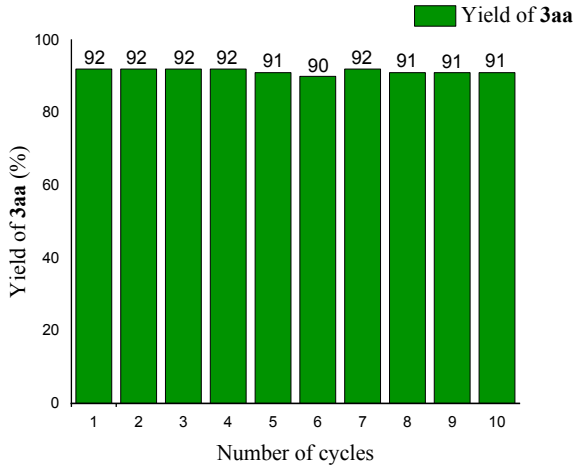
4.Gram-scale synthesis



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

To a 250 mL reaction flask was sequentially added *N*-methoxy-1H-indole-1-carboxamide **1a** (4.0 mmol, 1.0 equiv), 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium ylide **2a** (4.8 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3 mol %), CsOAc (3.0 equiv) and MeOH (40 mL). The reaction mixture was stirred at room temperature until the **1a** was consumed completely detected by TLC. Afterwards, the target product (1.11 g, 90%) was obtained by filtration and washing with MeOH.

5.Recycling study of the catalytic system



To a 15 mL reaction flask was sequentially added *N*-methoxy-1H-indole-1-carboxamide **1a** (0.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium ylide **2a** (1.0 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), CsOAc (3.0 equiv) and MeOH (5 mL). The reaction mixture was stirred at room temperature until the **1a** was consumed completely detected by TLC. Afterwards, the product was

filtered directly. The filtrate was transferred to the flask, and to which, *N*-methoxy-1H-indole-1-carboxamide **1a** (0.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium ylide **2a** (1.0 mmol, 2.0 equiv) was added. The reaction mixture was stirred at room temperature until the **1a** was consumed completely detected by TLC. The product was filtered directly. The filtrate was transferr -ed to the flask again for the next eight times.

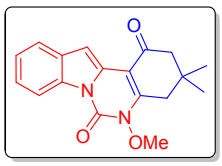
6.References

[1] Lin-Bao Zhang, Ming-Hui Zhu, Shao-Fei Ni, Li-Rong Wen, and Ming Li. *ACS Catal*. **2019**, *9*, 1680-1685

[2] Sivakalai Mayakrishnan, Masilamani Tamizmani and Naryanan Uma Maheswari. *Chem. Commun.* **2020**, *56,* 15462-15465.

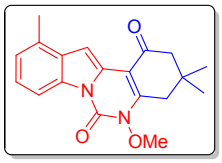
7.Analytical and spectral data of substrates

5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3aa**):



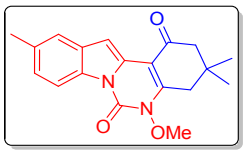
According to the general procedure, **3aa** was obtained in 92% yield (57 mg). Yellow solid, mp = 169 °C-170 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 – 8.51 (m, 1H), 7.72 – 7.65 (m, 1H), 7.53 (s, 1H), 7.41 – 7.33 (m, 2H), 4.12 (s, 3H), 2.89 (s, 2H), 2.47 (s, 2H), 1.20 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.1, 148.8, 145.0, 132.6, 131.2, 129.1, 124.5, 123.4, 120.7, 115.7, 104.6, 102.2, 65.1, 50.9, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{19}N_2O_3$, m/z: 311.1396, found: 311.1396. **IR (thin film):** ν_{max} 3672, 2969, 2902, 1723 cm^{-1}.

5-methoxy-3,3,11-trimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ab**):



According to the general procedure, **3ab** was obtained in 90% yield (58 mg). White solid, mp = 170 °C-171 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.29 – 7.25 (m, 1H), 7.17 (d, J = 4.0 Hz, 1H), 4.11 (s, 3H), 2.87 (s, 2H), 2.60 (s, 3H), 2.46 (s, 2H), 1.19 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.3, 148.7, 145.0, 132.3, 130.9, 130.2, 128.5, 124.6, 123.5, 113.2, 104.7, 100.7, 65.1, 50.9, 37.2, 32.6, 28.4, 18.8 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{19}N_2O_3$, m/z: 325.1552, found: 325.1551. **IR (thin film):** ν_{max} 2962, 2899, 1713 cm^{-1}.

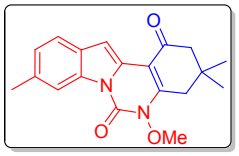
5-methoxy-3,3,10-trimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ac**):



According to the general procedure, **3ac** was obtained in 94% yield (61 mg). White solid, mp = 179 °C-181 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 (d, J

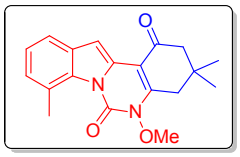
= 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 4.11 (s, 3H), 2.88 (s, 2H), 2.49 (s, 3H), 2.46 (s, 2H), 1.20 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.2, 148.6, 144.9, 134.1, 131.5, 130.8, 129.1, 124.9, 120.4, 115.3, 104.7, 101.9, 65.1, 50.9, 37.2, 32.6, 28.4, 21.6 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{19}N_2O_3$, m/z: 325.1552, found: 325.1551. **IR (thin film):** ν_{max} 2969, 2902, 1717 cm^{-1}.

5-methoxy-3,3,9-trimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ad**):



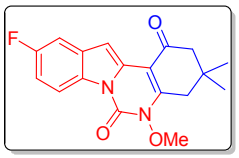
According to the general procedure, **3ad** was obtained in 84% yield (54 mg). White solid, mp = 155 °C-157 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.38 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.47 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 4.11 (s, 3H), 2.87 (s, 2H), 2.54 (s, 3H), 2.45 (s, 2H), 1.19 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.2, 148.4, 145.1, 133.5, 133.0, 129.0, 128.5, 126.1, 120.2, 115.7, 104.8, 102.1, 65.1, 50.8, 37.2, 32.6, 28.4, 22.0 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{19}N_2O_3$, m/z: 325.1552 , found: 325.1550. **IR (thin film):** ν_{max} 3623, 3662, 2968, 2901, 1722 cm^{-1}.

5-methoxy-3,3,8-trimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ae**):



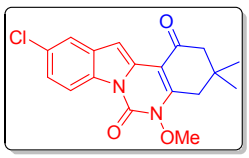
According to the general procedure, **3ae** was obtained in 90% yield (58 mg). White solid, mp = 166 °C-167 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.57 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.16 (d, J = 8.0 Hz, 1H), 4.08 (s, 3H), 2.88 (d, J = 3.6 Hz, 5H), 2.47 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 192.9, 148.9, 145.7, 132.9, 132.5, 130.0, 127.6, 126.5, 125.0, 118.6, 104.6, 104.0, 64.8, 51.0, 37.3, 32.61, 28.4, 24.0 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{19}N_2O_3$, m/z: 325.1552, found: 325.1551. **IR (thin film):** ν_{max} 3673, 2983, 2901, 1717 cm^{-1}.

10-fluoro-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3af**):



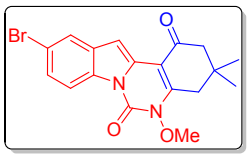
According to the general procedure, **3af** was obtained in 81% yield (53 mg). Yellow solid, mp = 189 °C-190 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.50 (dd, J = 8.0, 4.0 Hz, 1H), 7.49 (s, 1H), 7.31 (m, 1H), 7.08 (m, 1H), 4.13 (s, 3H), 2.91 (s, 2H), 2.49 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.0, 160.2 (d, $J_{C\text{-}F}$ = 239.0 Hz), 149.1, 144.8, 132.4 (d, $J_{C\text{-}F}$ = 11.0 Hz), 130.6, 128.9, 116.8 (d, $J_{C\text{-}F}$ = 10.0 Hz), 111.4 (d, $J_{C\text{-}F}$ = 26.0 Hz), 105.8 (d, $J_{C\text{-}F}$ = 23.0 Hz), 104.4, 101.9 (d, $J_{C\text{-}F}$ = 4.0 Hz), 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ = -117.9 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}FN_2O_3$, m/z: 329.1301, found: 329.1298. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

10-chloro-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ag**):



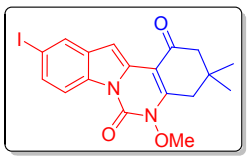
According to the general procedure, **3ag** was obtained in 94% yield (64 mg). Yellow solid, mp = 189 °C-190 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.44 (s, 1H), 7.32 – 7.25 (m, 1H), 4.12 (s, 3H), 2.89 (s, 2H), 2.48 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 149.3, 144.7, 132.4, 130.9, 130.4, 130.1, 123.5, 120.0, 116.7, 104.5, 101.3, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}ClN_2O_3$, m/z: 345.1006, found: 345.1005. **IR (thin film):** ν_{max} 3671, 2957, 2901, 1722 cm^{-1}.

10-bromo-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3ah):



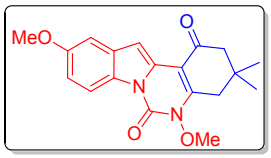
According to the general procedure, **3ah** was obtained in 86% yield (67 mg). Yellow solid, mp = 189 °C-190 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.41 (d, J = 8.0 Hz, 1H), 7.79 (s, 1H), 7.44 – 7.42 (m, 2H), 4.12 (s, 3H), 2.89 (s, 2H), 2.48 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 149.4, 144.7, 132.9, 131.2, 130.2, 126.2, 123.1, 118.0, 117.0, 104.5, 101.2, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}BrN_2O_3$, m/z: 389.0501, found: 389.0501. **IR (thin film):** ν_{max} = 3671, 2957, 2902, 1720 cm^{-1}.

10-iodo-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3ai):



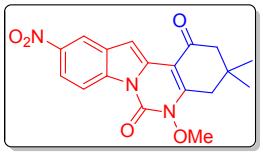
According to the general procedure, **3ai** was obtained in 90%yield (78 mg). Yellow solid, mp = 189 °C-190 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, J = 8.0 Hz, 1H), 8.00 – 7.97 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 4.12 (s, 3H), 2.88 (s, 2H), 2.46 (s, 2H), 1.20 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 149.4, 144.7, 133.5, 131.8, 129.9, 129.4, 117.4, 104.4, 100.9, 89.1, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}IN_2O_3$, m/z: 437.0362, found: 437.0360. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

5,10-dimethoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3aj):



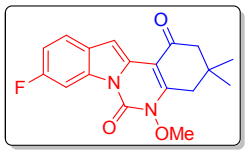
According to the general procedure, **3aj** was obtained in 89% yield (60 mg). Yellow solid, mp = 187 °C-188 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 (d, J = 8.0 Hz, 1H), 7.44 (s, 1H), 7.10 (d, J = 4.0 Hz, 1H), 6.98 – 6.95(m, 1H), 4.11 (s, 3H), 3.88 (s, 3H), 2.87 (s, 2H), 2.45 (s, 2H), 1.19 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.2 157.1, 148.6, 144.7, 132.3, 129.7, 127.3, 116.4, 112.7, 104.5 102.4, 101.9, 65.1, 55.6, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{19}H_{21}N_2O_4$, m/z: 341.1501, found:341.1501. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

5-methoxy-3,3-dimethyl-10-nitro-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3ak):



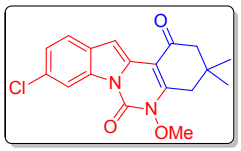
According to the general procedure, **3ak** was obtained in 45% yield (32 mg). Yellow solid, mp = 189 °C-190 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, J = 12.0 Hz, 1H), 8.56 (d, J = 1.7 Hz, 1H), 8.22 – 8.20 (m, 1H), 7.67 (s, 1H), 4.16 (s, 3H), 2.94 (s, 2H), 2.52 (s, 2H), 1.23 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.9, 149.9, 145.0, 144.8, 135.4, 131.9, 131.1, 118.3, 116.8, 116.0, 104.5, 102.7, 65.3, 50.8, 37.3, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}N_3O_5$, m/z: 356.1246, found: 356.1245. **IR (thin film):** ν_{max} 3673, 3651, 2966, 2902, 1731 cm^{-1}.

9-fluoro-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3al):



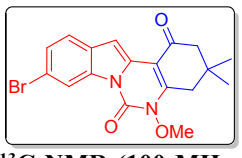
According to the general procedure, **3al** was obtained in 82% yield (53 mg). Yellow solid, mp = 172 °C-173 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (d, J = 8.0 Hz, 1H), 7.59 (m, 1H), 7.46 (s, 1H), 7.14 (t, J = 8.0 Hz, 1H), 4.12 (s, 3H), 2.89 (s, 2H), 2.47 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 159.8 (d, $J_{C\text{-}F}$ = 239.0 Hz), 148.6, 144.9, 132.4 (d, $J_{C\text{-}F}$ = 12.0 Hz), 129.5, 127.5, 121.3 (d, $J_{C\text{-}F}$ = 11.0 Hz), 113.0 (d, $J_{C\text{-}F}$ = 24.0 Hz), 104.8, 102.8 (d, $J_{C\text{-}F}$ = 28.0 Hz), 101.8, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ = -117.5 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}FN_2O_3$, m/z: 329.1301, found: 329.1300. **IR (thin film):** ν_{max} 2969, 2901, 1711 cm^{-1}.

9-chloro-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3am):



According to the general procedure, **3am** was obtained in 92% yield (63 mg). Yellow solid, mp = 188 °C-189 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.55 – 8.51 (m, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.41 (s, 1H), 7.32 (dd, J = 4.0, 8.0 Hz, 1H), 4.12 (s, 3H), 2.87 (s, 2H), 2.45 (s, 2H), 1.20 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0 149.0, 144.7, 132.6, 129.7, 129.7, 128.9, 125.0, 121.3, 115.7, 104.6, 101.7, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{18}ClN_2O_3$, m/z: 345.1006, found: 345.1003. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

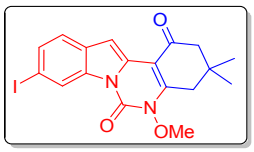
9-bromo-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (3an):



According to the general procedure, **3an** was obtained in 82% yield (64 mg). Yellow solid, mp = 188 °C-189 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (s, 1H), 7.53 – 7.45 (m, 3H), 4.12 (s, 3H), 2.89 (s, 2H), 2.47 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 149.1, 144.8, 133.0, 130.0, 129.6, 127.7, 121.7, 118.6, 116.5,

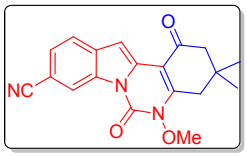
104.5, 101.8, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+Na]^+$ $C_{18}H_{17}BrNaN_2O_3$, m/z: 411.0320, found:411.0316. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

9-iodo-5-methoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ao**):



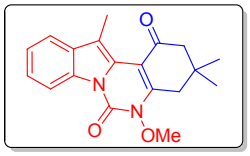
According to the general procedure, **3ao** was obtained in 84% yield (73 mg). Yellow solid, mp = 188 °C-189 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (s, 1H), 7.66 – 7.64 (m, 1H), 7.45 – 7.41 (m, 2H), 4.12 (s, 3H), 2.89 (s, 2H), 2.47 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 149.2, 144.7, 133.3, 133.2, 130.5, 129.4, 124.4, 122.1, 104.4, 101.8, 86.9, 65.2, 50.8, 37.2, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+C_{18}H_{18}IN_2O_3$, m/z: 437.0362, found: 437.0363. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

5-methoxy-3,3-dimethyl-1,6-dioxo-1,2,3,4,5,6-hexahydroindolo[1,2-c]quinazoline-9-carbonitrile (**3ap**):



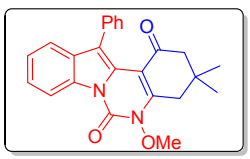
According to the general procedure, **3ap** was obtained in 67% yield (44 mg). Yellow solid, mp = 176 °C-177 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.61 – 7.54 (m, 2H), 4.16 (s, 3H), 2.96 (s, 2H), 2.52 (s, 2H), 1.23 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.9, 150.4, 144.5, 134.4, 132.4, 131.4, 127.4, 121.3, 120.2, 120.0, 105.6, 104.4, 102.0, 65.3, 50.8, 37.3, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{19}H_{18}N_3O_3$, m/z: 336.1348, found: 336.1345. **IR (thin film):** ν_{max} 2951, 2867, 1720 cm^{-1}.

5-methoxy-3,3,12-trimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3aq**):



According to the general procedure, **3aq** was obtained in 83% yield (53 mg). White solid, mp = 151 °C-152 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 – 8.51 (m, 1H), 7.67 – 7.61 (m, 1H), 7.42 – 7.34 (m, 2H), 4.06 (s, 3H), 2.86 (s, 2H), 2.52 (s, 3H), 2.47 (s, 2H), 1.20 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.8, 148.1, 145.0, 132.8 132.7, 124.9, 124.1, 123.8, 118.6, 115.7, 111.4, 106.9, 65.0, 51.6, 37.6, 32.3, 28.4, 11.9 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{19}H_{21}N_2O_3$, m/z: 325.1552, found: 325.1550. **IR (thin film):** ν_{max} 2949, 2913, 1716 cm^{-1}.

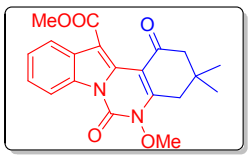
5-methoxy-3,3-dimethyl-12-phenyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ar**):



According to the general procedure, **3ar** was obtained in 75% yield (58 mg). Yellow solid, mp = 166 °C-167 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (d, J = 12.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.40 (m, 5H), 7.30 (d, J = 8.0 Hz, 2H), 4.13 (s, 3H), 2.91 (s, 2H), 2.33 (s, 2H), 1.17 (s, 6H). **^{13}C NMR (100**

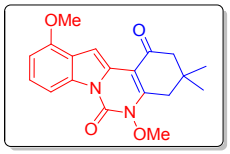
MHz, $CDCl_3$) δ 190.8, 148.8, 145.0, 135.9, 132.7, 131.8, 129.5, 127.7, 126.7, 124.6, 124.1, 119.7, 116.8, 115.8, 106.1, 65.1, 51.0, 37.6, 32.5, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{24}H_{23}N_2O_3$, m/z: 387.1709, found: 387.1704. **IR (thin film):** ν_{max} 2953, 2867, 1722 cm^{-1}.

methyl 5-methoxy-3,3-dimethyl-1,6-dioxo-1,2,3,4,5,6-hexahydroindolo[1,2-c]quinazoline-12-carboxylate (**3as**):



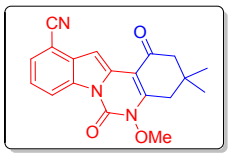
According to the general procedure, **3as** was obtained in 65% yield (48 mg). Yellow solid, mp = 188 °C-189 °C. M.p. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.54 (d, J = 8.0 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.47 – 7.37 (m, 2H), 4.10 (s, 3H), 3.94 (s, 3H), 2.89 (s, 2H), 2.39 (s, 2H), 1.17 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.2, 165.8, 150.4, 144.3, 132.0, 128.9, 128.1, 125.3 124.5, 119.8, 115.7, 107.9, 104.9, 65.2, 51.8, 50.4, 37.3, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{20}H_{21}N_2O_5$, m/z: 369.1450, found: 369.1449. **IR (thin film):** ν_{max} 2949, 2867, 1735 cm^{-1}.

5,11-dimethoxy-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3at**):



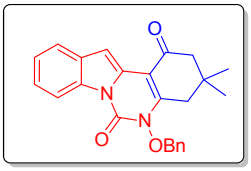
According to the general procedure, **3at** was obtained in 82% yield (55 mg). Yellow solid, mp = 172 °C-173 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.33 – 7.27 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.13 (s, 3H), 4.00 (s, 3H), 2.85 (s, 2H), 2.42 (s, 2H), 1.19 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.9, 152.8, 148.3, 145.1, 133.7, 127.8, 124.3, 121.9, 108.7, 104.8, 104.4, 99.3, 65.1, 55.6, 50.7, 37.1, 32.5, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{19}H_{21}N_2O_4$, m/z: 341.1501, found: 341.1505. **IR (thin film):** ν_{max} 2960, 2867, 1735 cm^{-1}.

5-methoxy-3,3-dimethyl-1,6-dioxo-1,2,3,4,5,6-hexahydroindolo[1,2-c]quinazoline-11-carbonitrile (**3au**):



According to the general procedure, **3au** was obtained in 82% yield (55 mg). Yellow solid, mp = 175 °C-176 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, J = 8.3 Hz, 1H), 7.81 – 7.59 (m, 2H), 7.38 (t, J = 8.0 Hz, 1H), 4.16 (s, 3H), 2.95 (s, 2H), 2.51 (s, 2H), 1.22 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.6, 150.2, 144.6, 132.9, 132.3, 131.7, 129.2, 122.9, 120.1, 117.9, 104.3, 103.0, 100.2, 65.3, 50.7, 37.3, 32.6, 28.4 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{19}H_{18}N_3O_3$, m/z: 336.1348, found: 336.1343. **IR (thin film):** ν_{max} 2969, 2867, 1735 cm^{-1}.

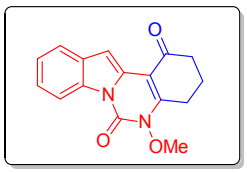
5-(benzyloxy)-3,3-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3av**):



According to the general procedure, **3av** was obtained in 83% yield (64 mg). Yellow solid, mp = 178 °C-179 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62

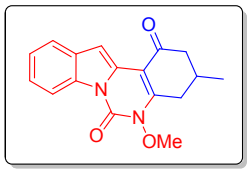
(s, 1H), 7.70 (s, 1H), 7.53 (s, 3H), 7.44 – 7.40 (m, 5H), 5.29 (s, 2H), 2.65 (s, 2H), 2.38 (s, 2H), 1.05 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.3, 149.5, 145.4, 133.3, 132.6, 131.3, 130.2, 129.8, 129.2, 129.0, 124.5, 123.4, 120.7, 115.7, 104.4, 102.1, 79.4, 50.8, 37.7, 32.4, 28.2 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{24}H_{23}N_2O_3$, m/z: 387.1709, found:387.1704. **IR (thin film):** ν_{max} 2963, 2967, 1722 cm^{-1}.

5-methoxy-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3ba**):



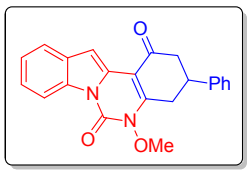
According to the general procedure, **3ba** was obtained in 89% yield (50 mg). Yellow solid, mp = 168 ^{o}C-170 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.59 – 8.49 (m, 1H), 7.72 – 7.64 (m, 1H), 7.57 – 7.48 (m, 1H), 7.36 (m, 2H), 4.12 (s, 3H), 3.09 – 2.96 (m, 2H), 2.64 – 2.54 (m, 2H), 2.28 – 2.15 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.1, 150.5, 132.6, 131.19, 129.2, 124.4, 123.4, 120.7, 115.7, 105.6, 102.4, 65.1, 37.1, 23.7, 20.9 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{16}H_{15}N_2O_3$, m/z: 283.1083, found: 283.1080. **IR (thin film):** ν_{max} 2938, 2867, 1735 cm^{-1}.

5-methoxy-3-methyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3bb**):



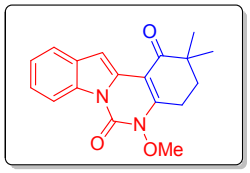
According to the general procedure, **3bb** was obtained in 85% yield (50 mg). Yellow solid, mp = 184 ^{o}C-185 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.60 – 8.54 (m, 1H), 7.72 – 7.70 (m, 1H), 7.55 (s, 1H), 7.42 – 7.36 (m, 2H), 4.15 (s, 3H), 3.20 (dd, J = 4.0 Hz, 20.0Hz, 1H), 2.72 – 2.54 (m, 2H), 2.47 – 2.38 (m, 1H), 2.33 – 2.26 (m, 1H), 1.24 (d, J = 8.0 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.2, 149.9, 144.9, 132.6, 131.2, 129.2, 124.4, 123.4, 120.7, 115.7, 105.2, 102.2, 65.1, 45.3, 31.5, 28.6, 21.1 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{17}H_{17}N_2O_3$, m/z: 297.1239, found: 297.1238. **IR (thin film):** ν_{max} 2949, 2867, 1735 cm^{-1}.

5-methoxy-3-phenyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3bc**):



According to the general procedure, **3bc** was obtained in 79% yield (56 mg). Yellow solid, mp = 195 ^{o}C-196 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.60 – 8.51 (m, 1H), 7.72 – 7.67 (m, 1H), 7.56 (s, 1H), 7.42 – 7.30 (m, 7H), 4.10 (s, 3H), 3.56 – 3.48 (m, 1H), 3.40 (dd, J = 4.0, 20.0 Hz, 1H), 3.06 – 2.98 (m, 1H), 2.90 – 2.76 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 192.4, 149.5, 144.8, 141.8, 132.6, 131.2, 129.1, 129.0, 127.6, 126.8, 124.5, 123.5, 120.8, 115.7, 102.5, 65.2, 43.9, 39.1, 31.3 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{22}H_{19}N_2O_3$, m/z: 359.1396, found: 359.1395. **IR (thin film):** ν_{max} 2974, 2901, 1723 cm^{-1}.

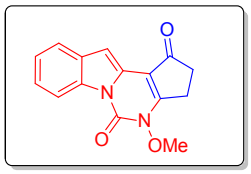
5-methoxy-2,2-dimethyl-3,4-dihydroindolo[1,2-c]quinazoline-1,6(2H,5H)-dione (**3bd**):



According to the general procedure, **3bd** was obtained in 80% yield (50 mg). Yellow solid, mp = 141 ^{o}C-143 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.60

– 8.52 (m, 1H), 7.71 – 7.64 (m, 1H), 7.55 (s, 1H), 7.40 – 7.31 (m, 2H), 4.13 (s, 3H), 3.05 – 3.02 (m, 2H), 2.06 – 2.03 (m, 2H), 1.25 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.3, 148.9, 145.0, 132.6, 131.2, 129.7, 124.4, 123.3, 120.7, 115.7, 103.8, 102.5, 65.1, 40.4, 34.2 24.4, 20.6 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{18}H_{19}N_2O_3$, m/z: 311.1396, found: 311.1395. **IR (thin film):** ν_{max} 3628, 2970, 2938, 1719 cm^{-1}.

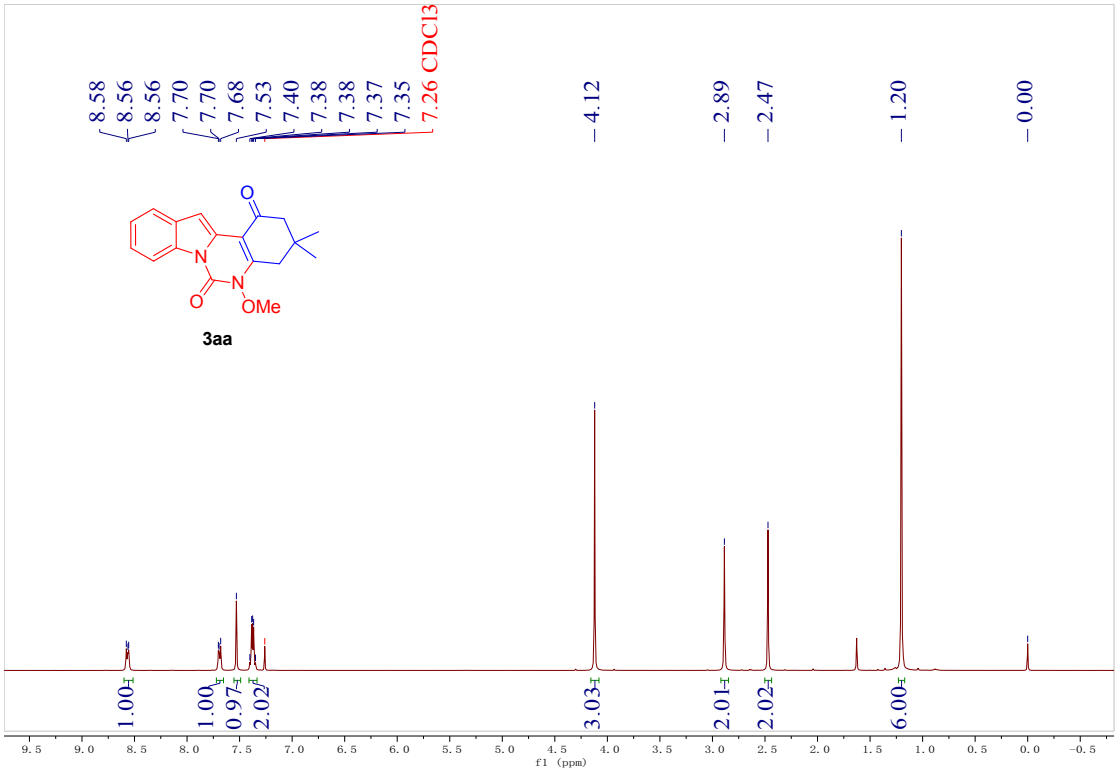
4-methoxy-2,3-dihydro-1H-cyclopenta[4,5]pyrimido[1,6-a]indole-1,5(4H)-dione (**3be**):



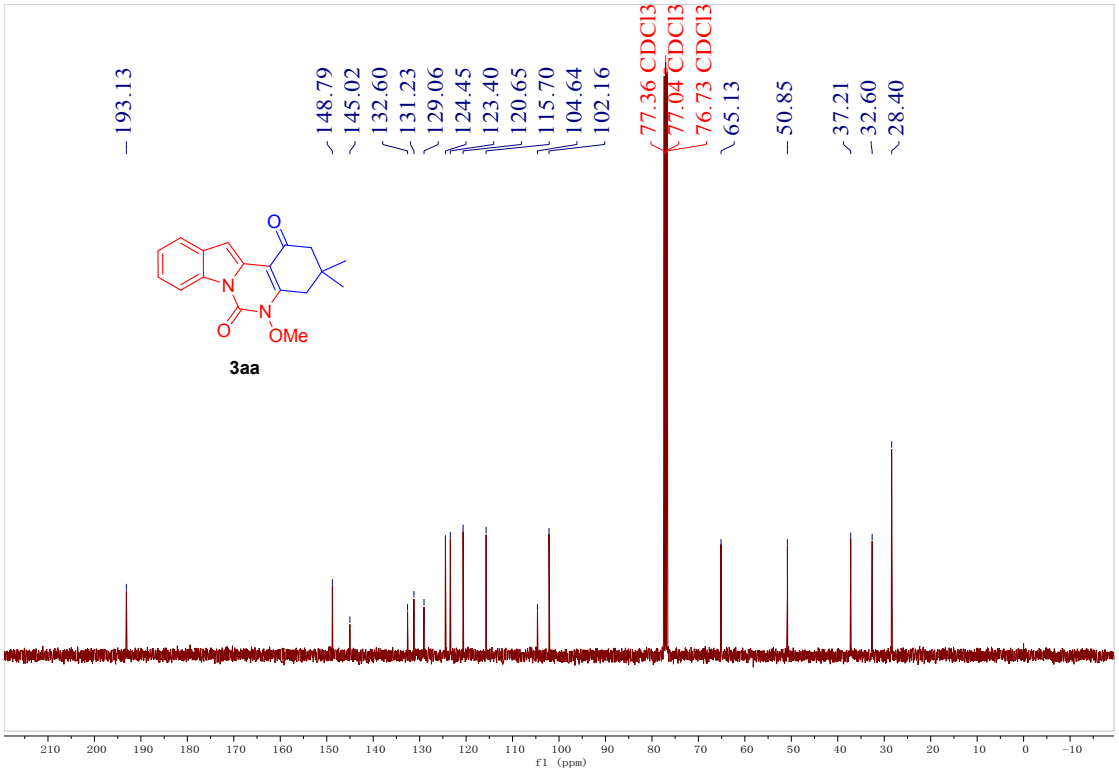
According to the general procedure, **3be** was obtained in 82% yield (44 mg). White solid, mp = 197 ^{o}C-198 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 – 8.51 (m, 1H), 7.70 – 7.65 (m, 1H), 7.41 – 7.36 (m, 2H), 7.08 (s, 1H), 4.20 (s, 3H), 3.15 – 3.09 (m, 2H), 2.76 – 2.71 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.2, 160.9, 145.2, 133.1, 130.9, 127.7, 124.6, 123.8, 120.8, 115.5, 109.5, 100.0, 65.6, 34.7, 23.2 ppm. **HRMS (ESI)**: calcd for $[M+H]^+$ $C_{15}H_{13}N_2O_3$, m/z: 269.0926, found: 269.0924. **IR** ν = 2964, 2867, 1735 cm^{-1}.

8.The ^{1}H, ^{13}C, ^{19}F NMR spectra of products:

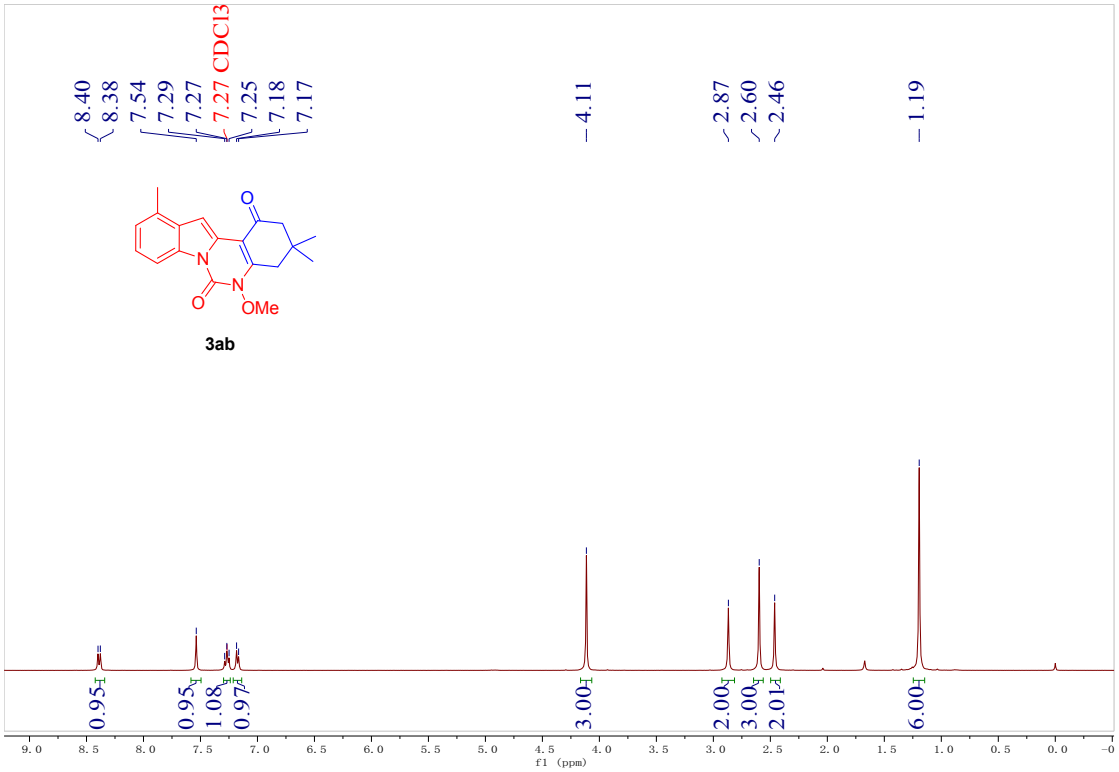
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



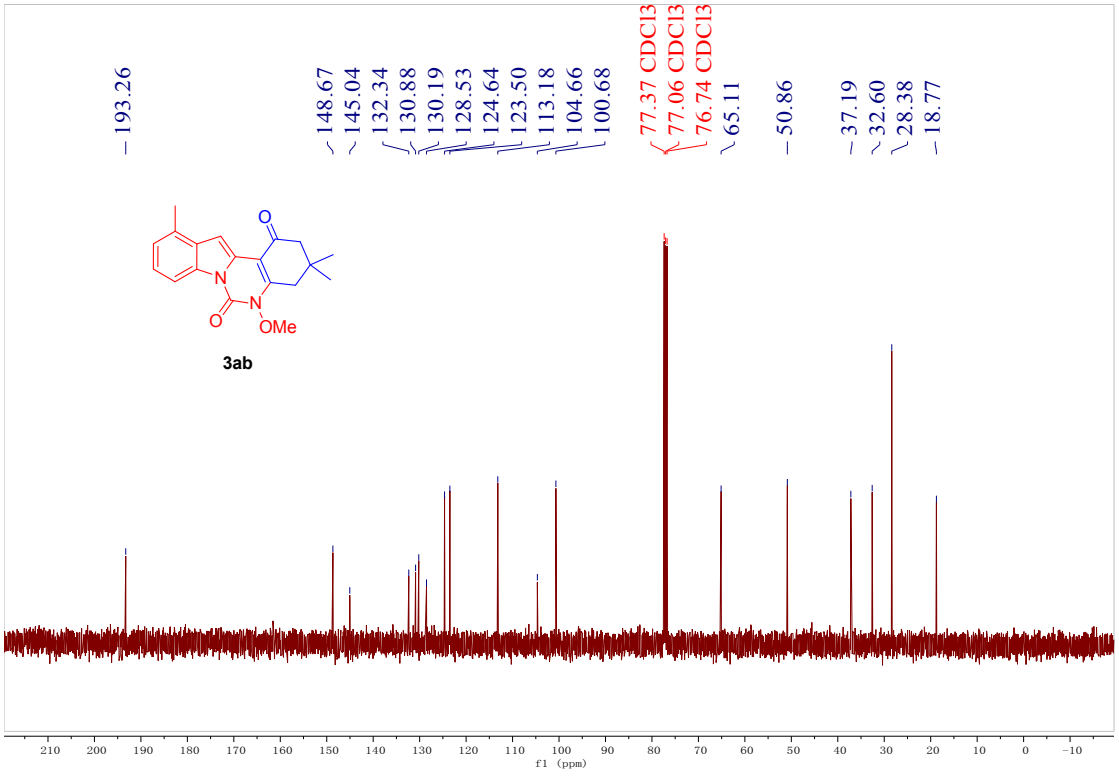
^{13}**C**{^{1}**H**} NMR (100 MHz, $CDCl_3$) spectrum of **3aa**



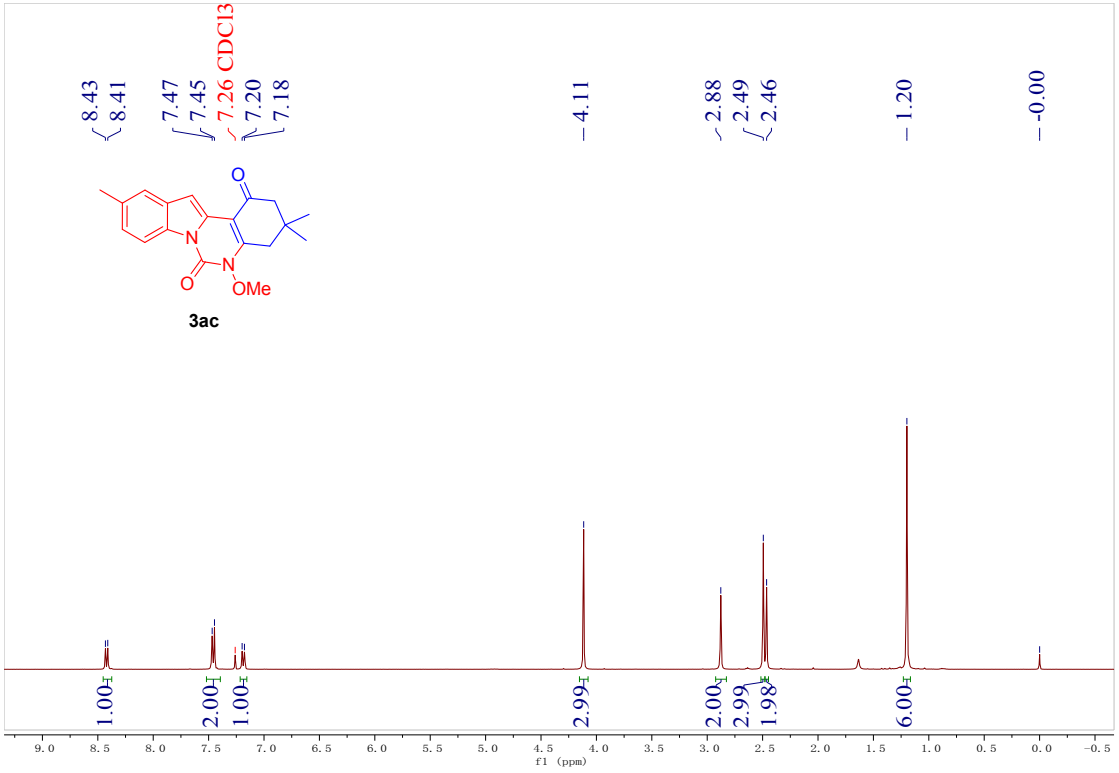
^{1}**H** NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



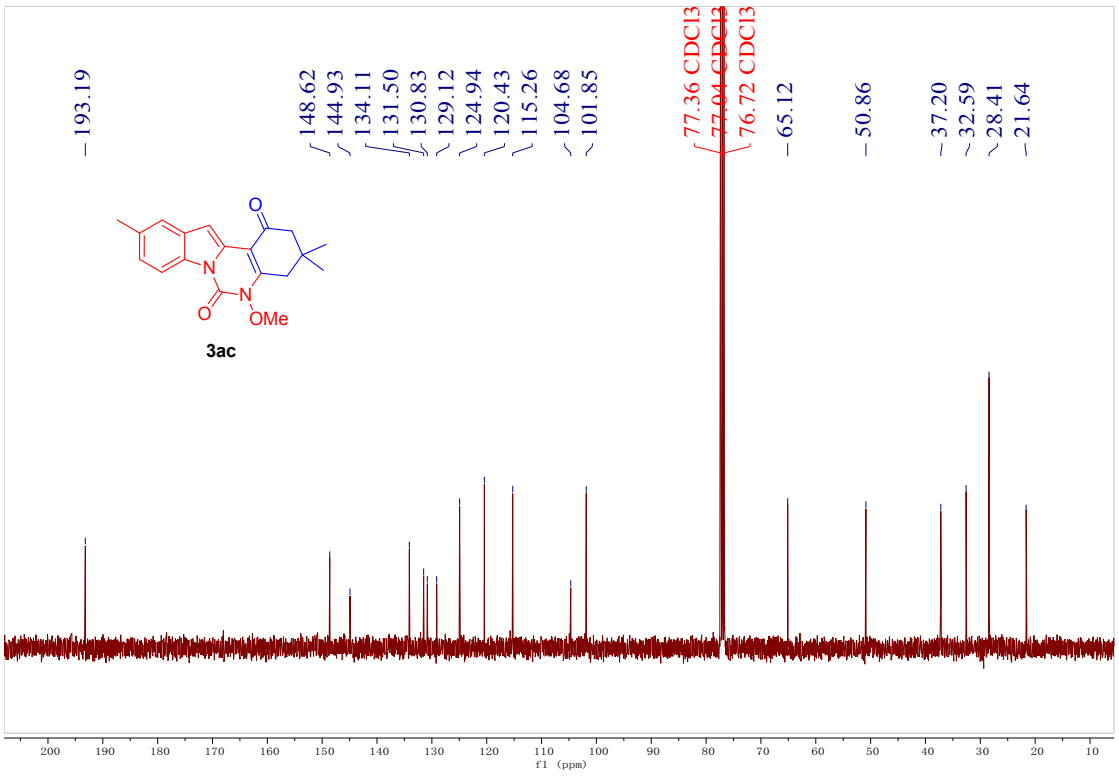
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3ab**



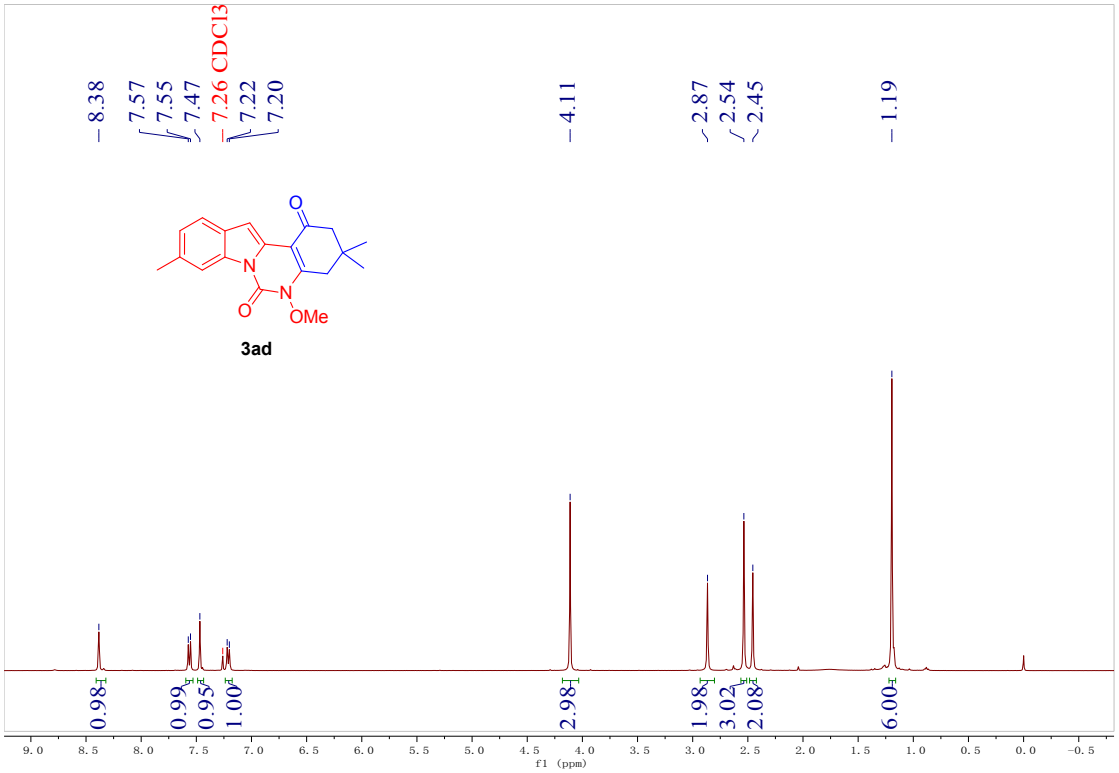
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



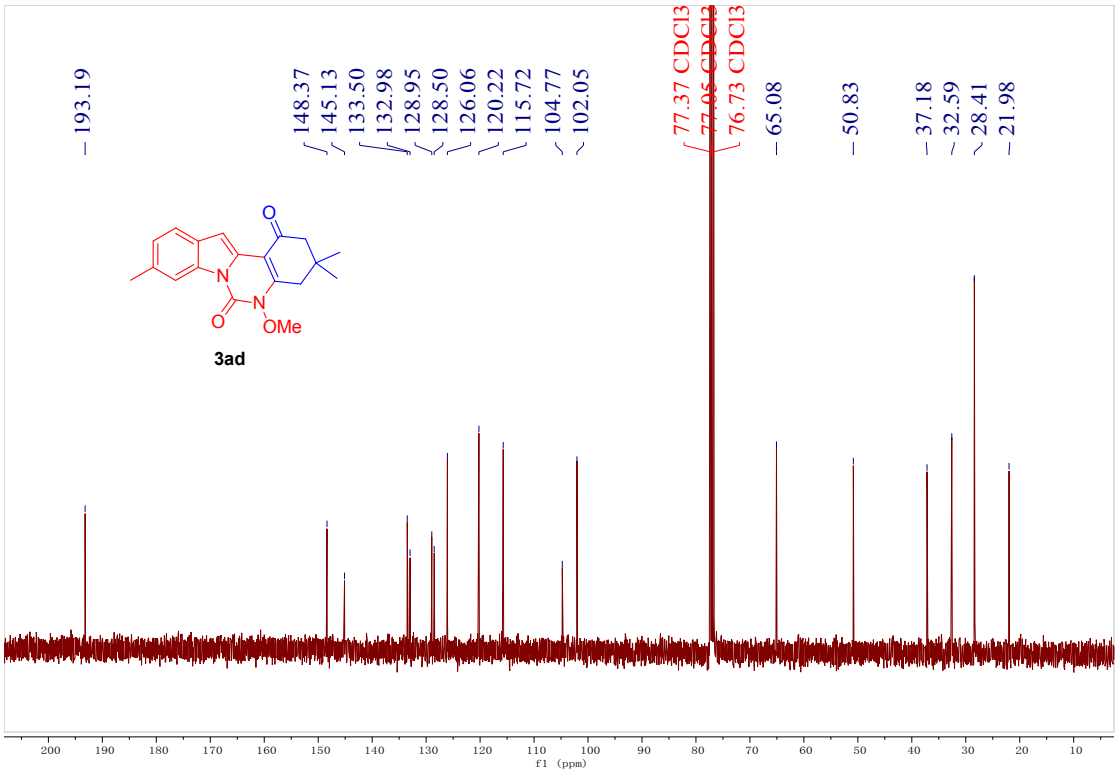
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ac**



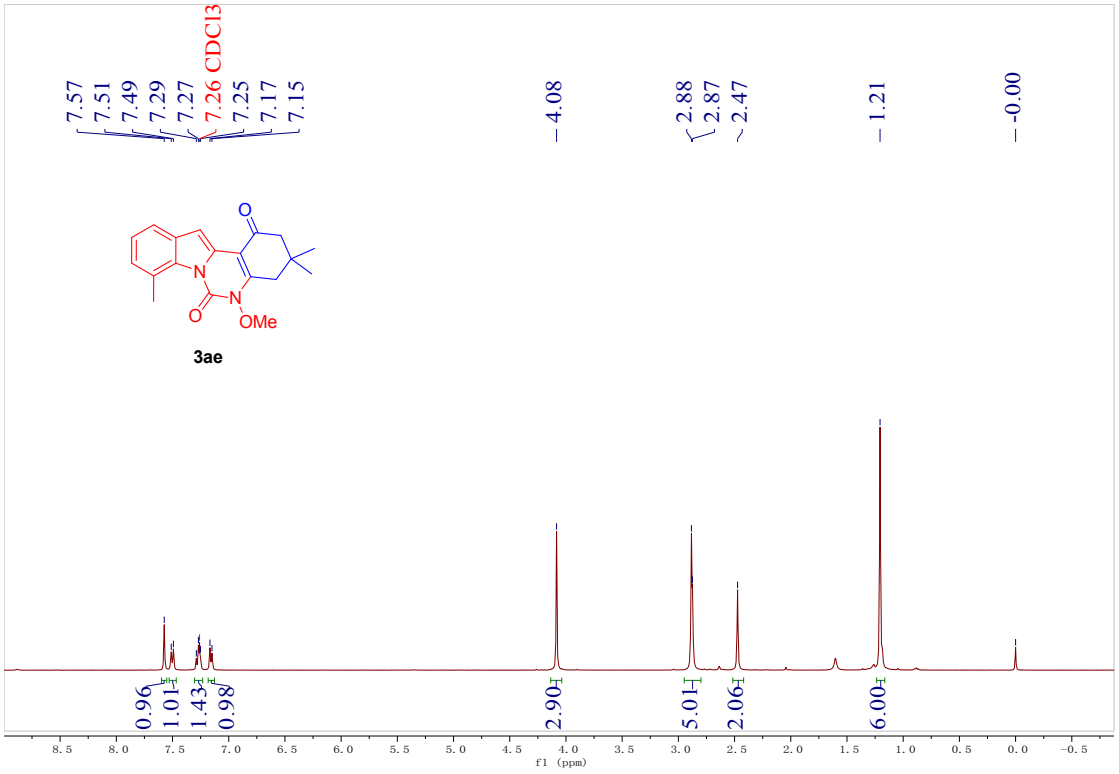
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



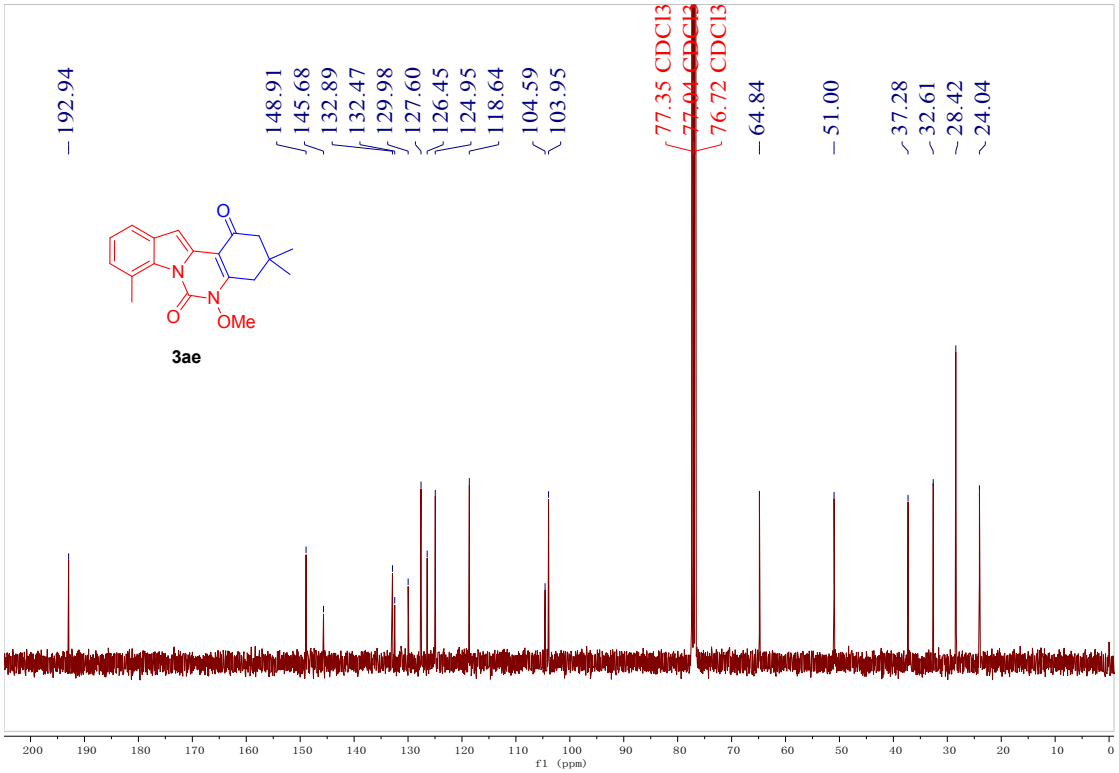
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ad**



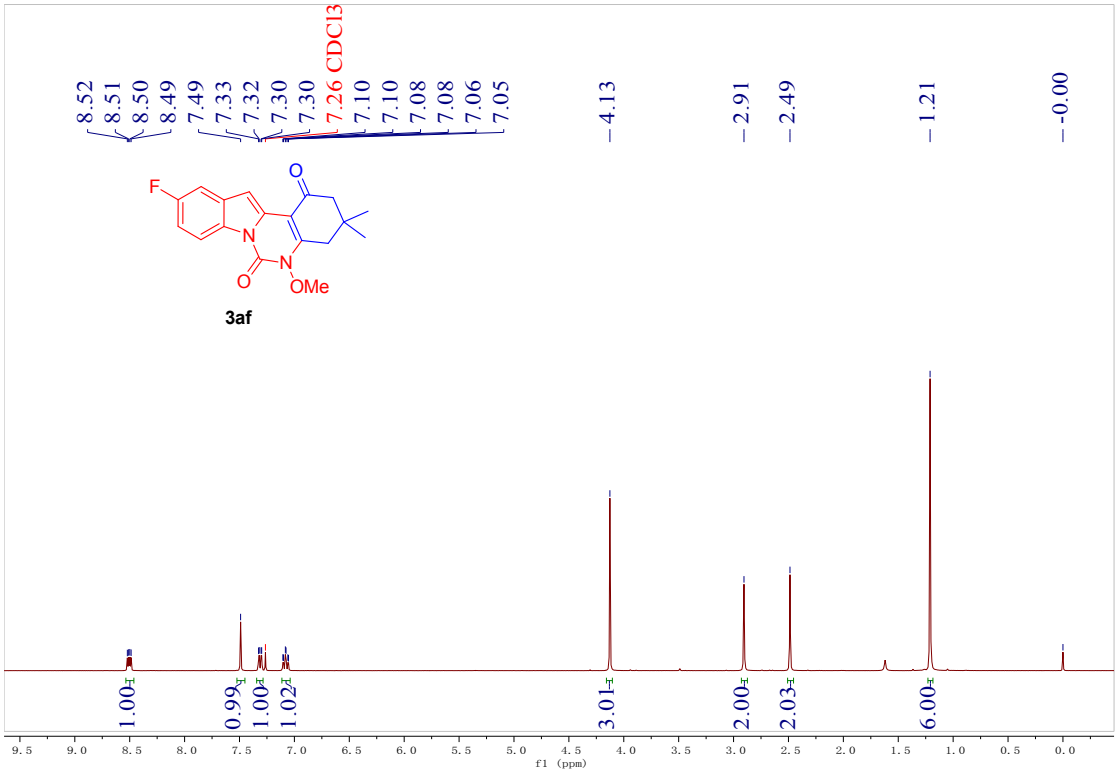
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



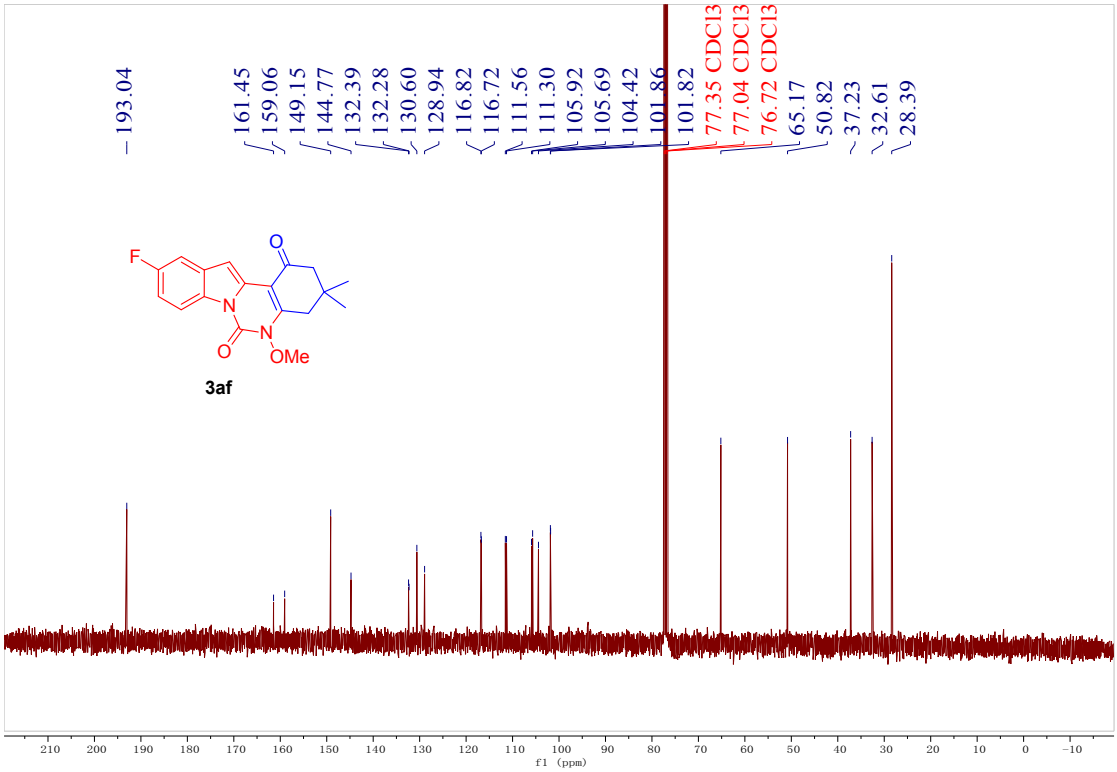
^{13}**C**{^{1}**H**} NMR (100 MHz, $CDCl_3$) spectrum of **3ae**



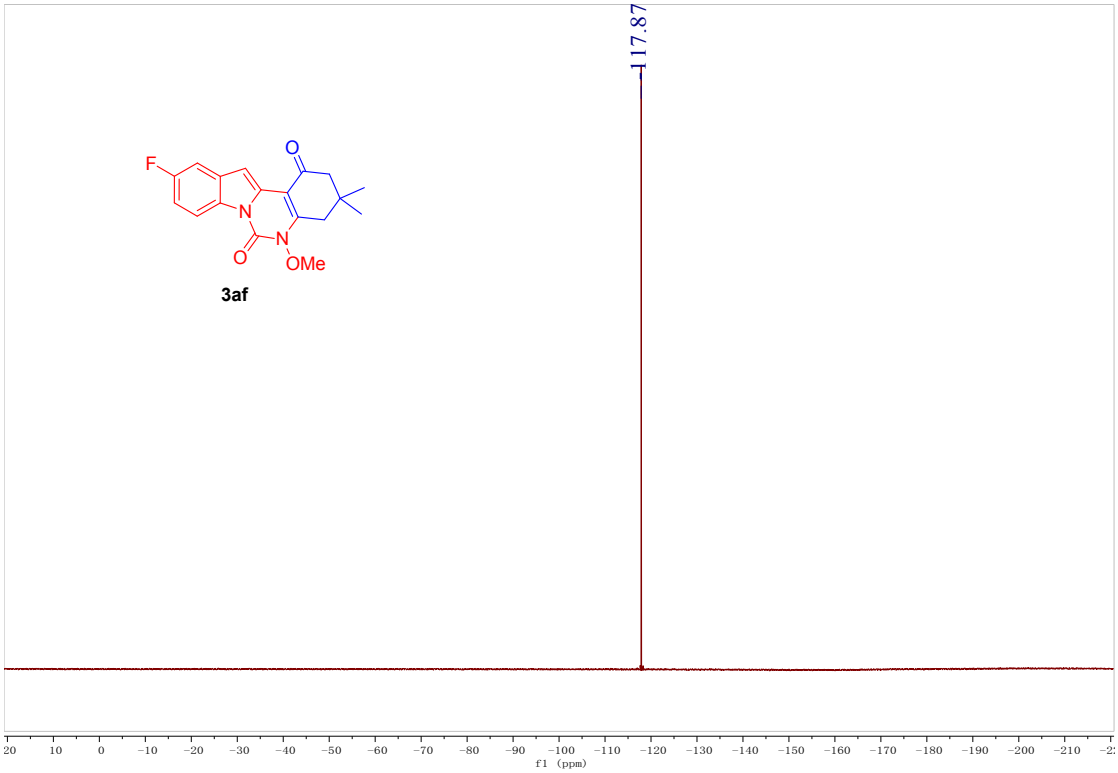
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



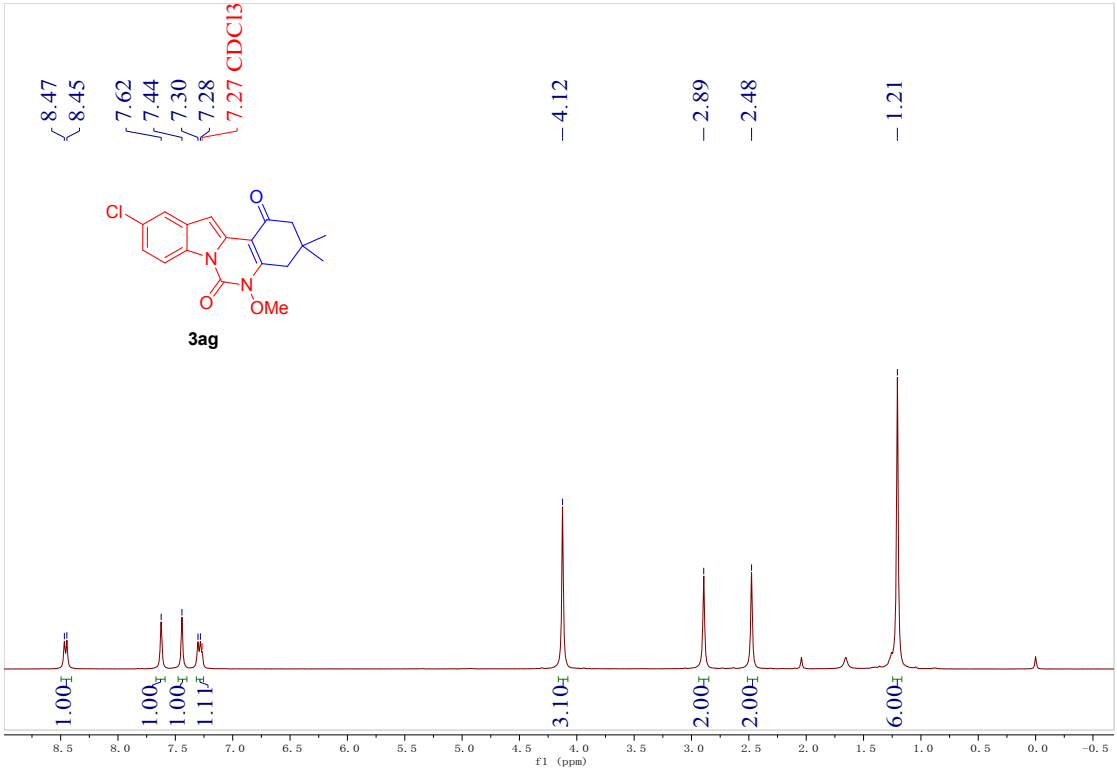
[13]C{[1]H} NMR (100 MHz, $CDCl_3$) spectrum of **3af**



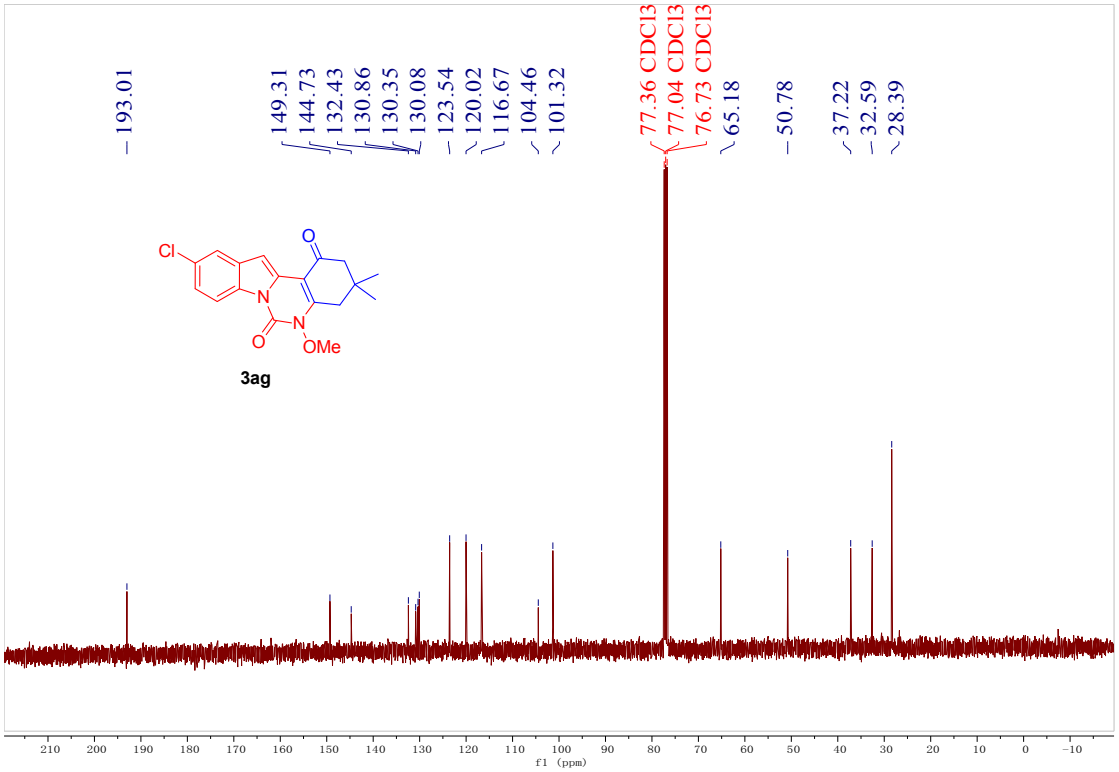
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3af**



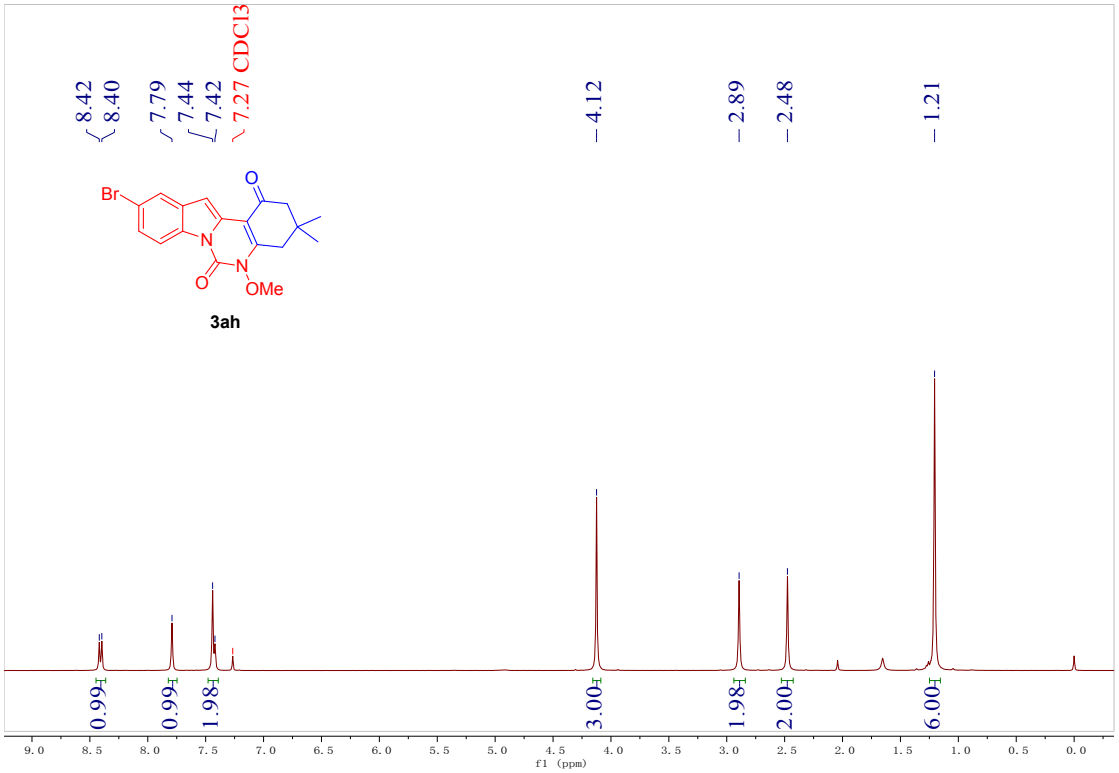
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**



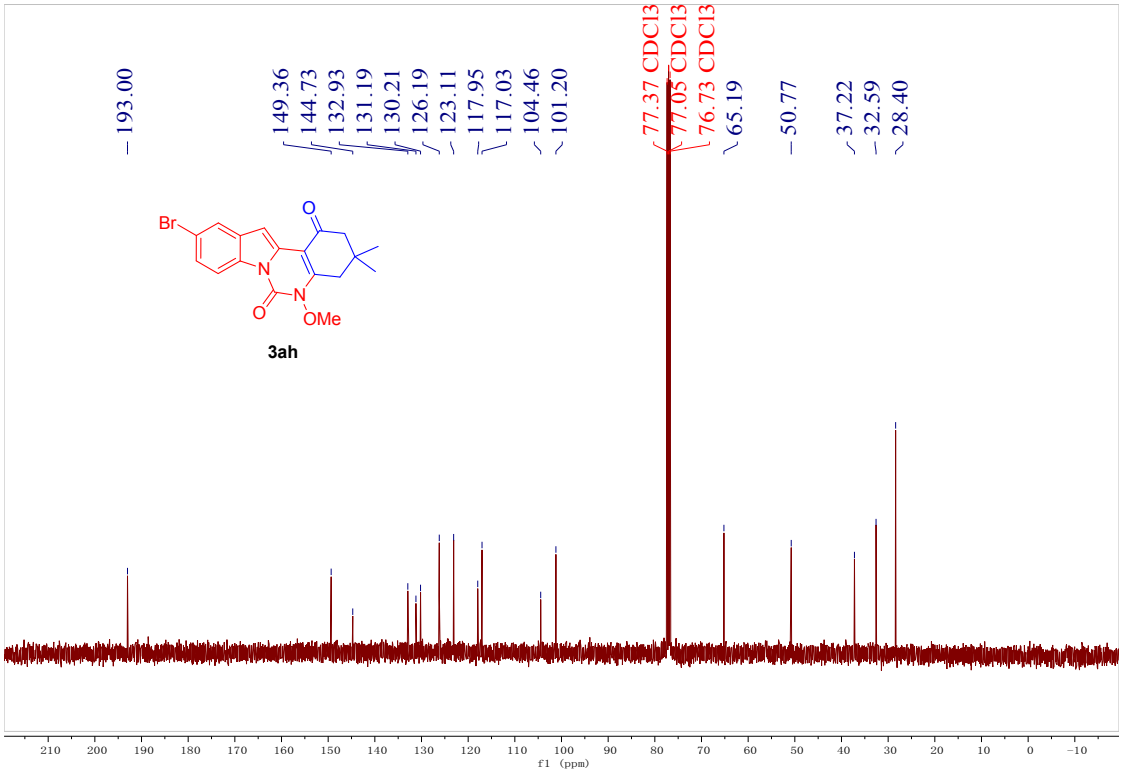
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ag**



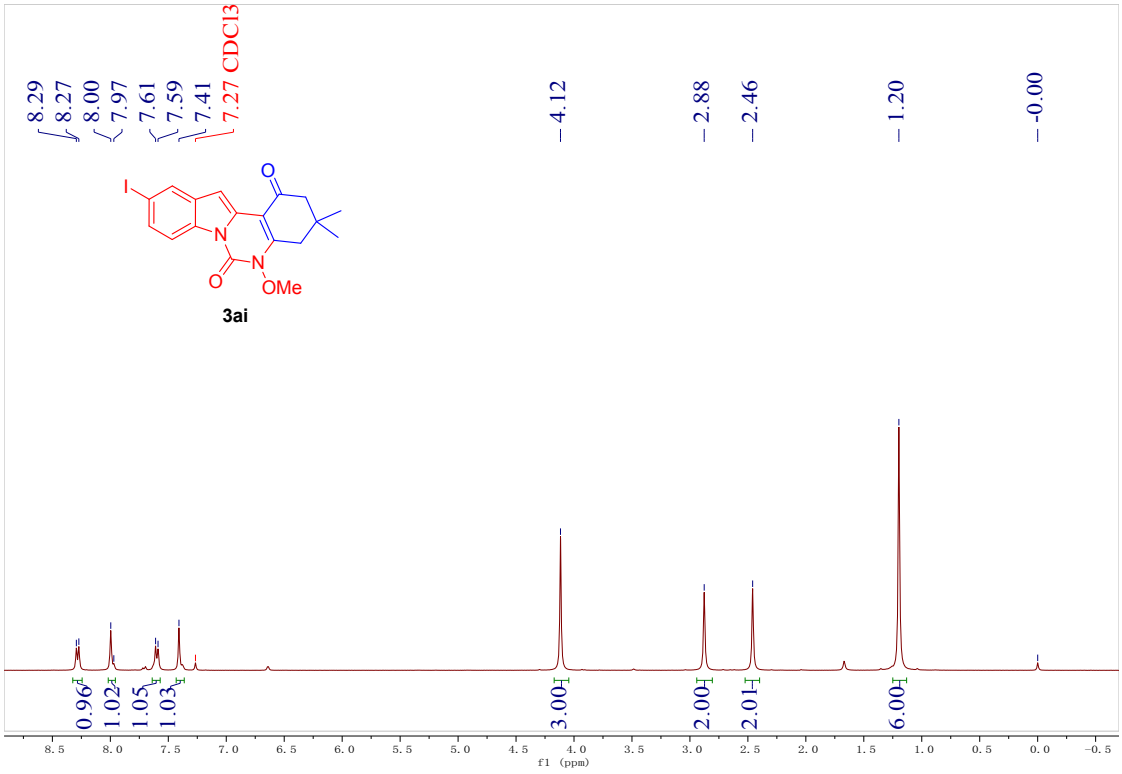
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



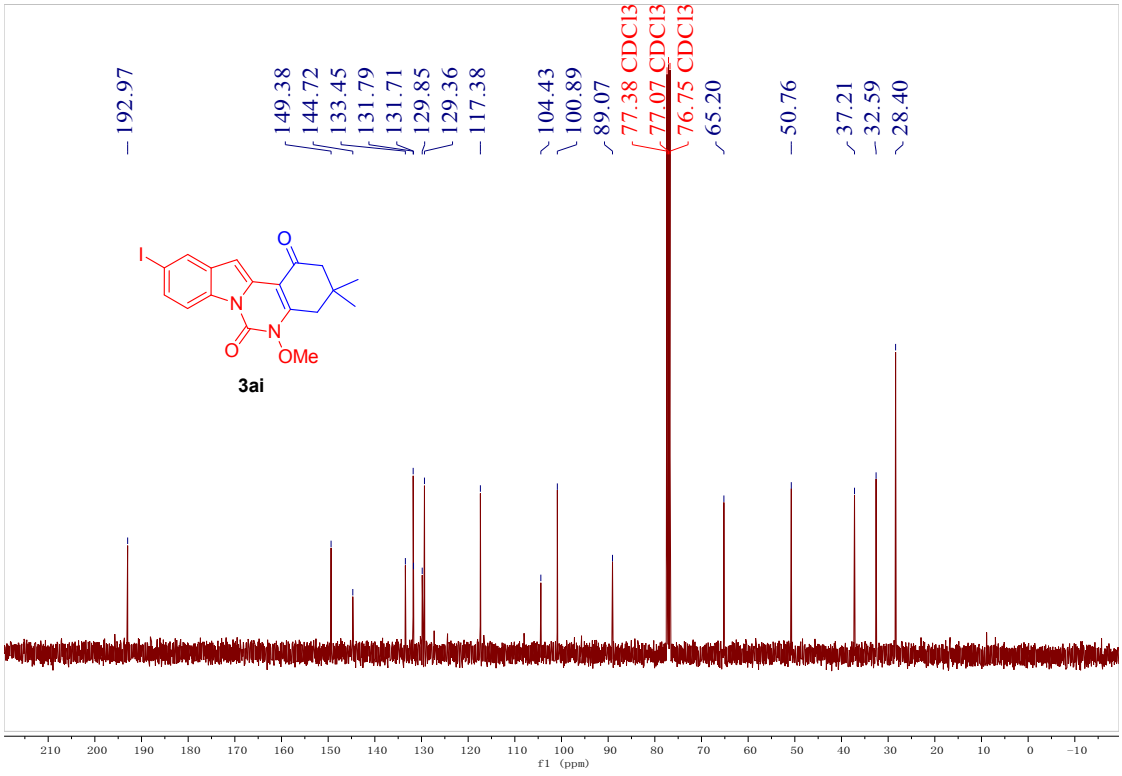
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ah**



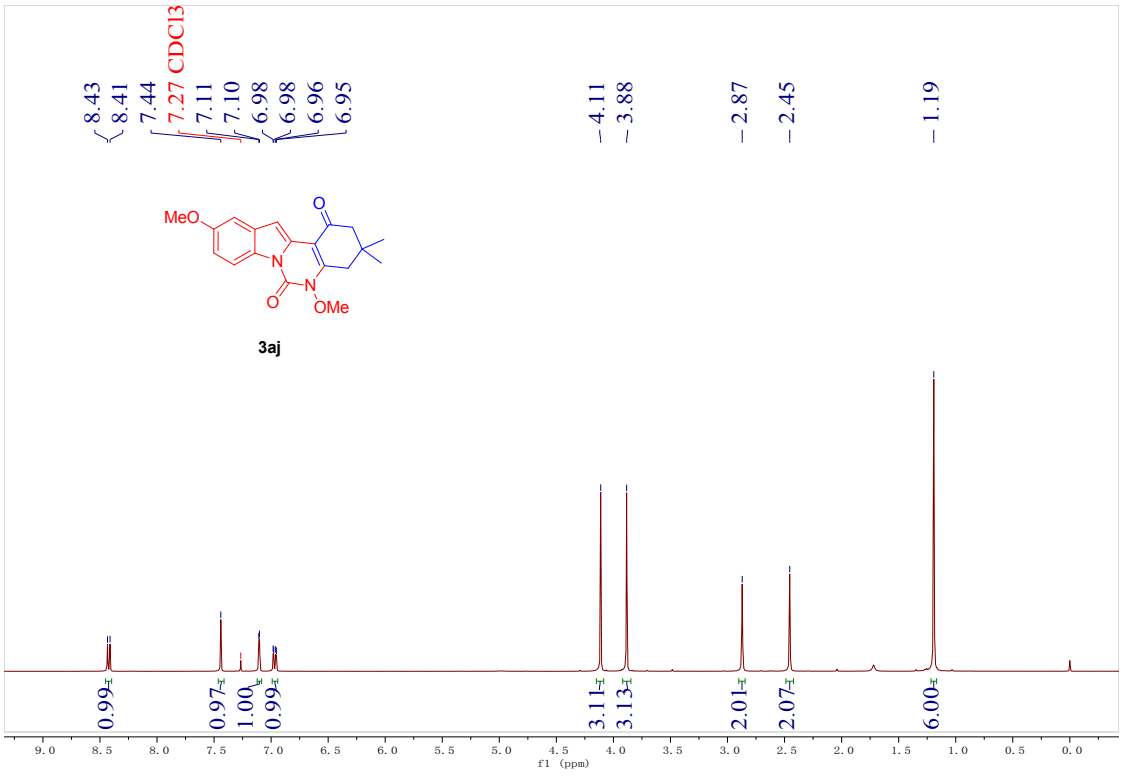
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai**



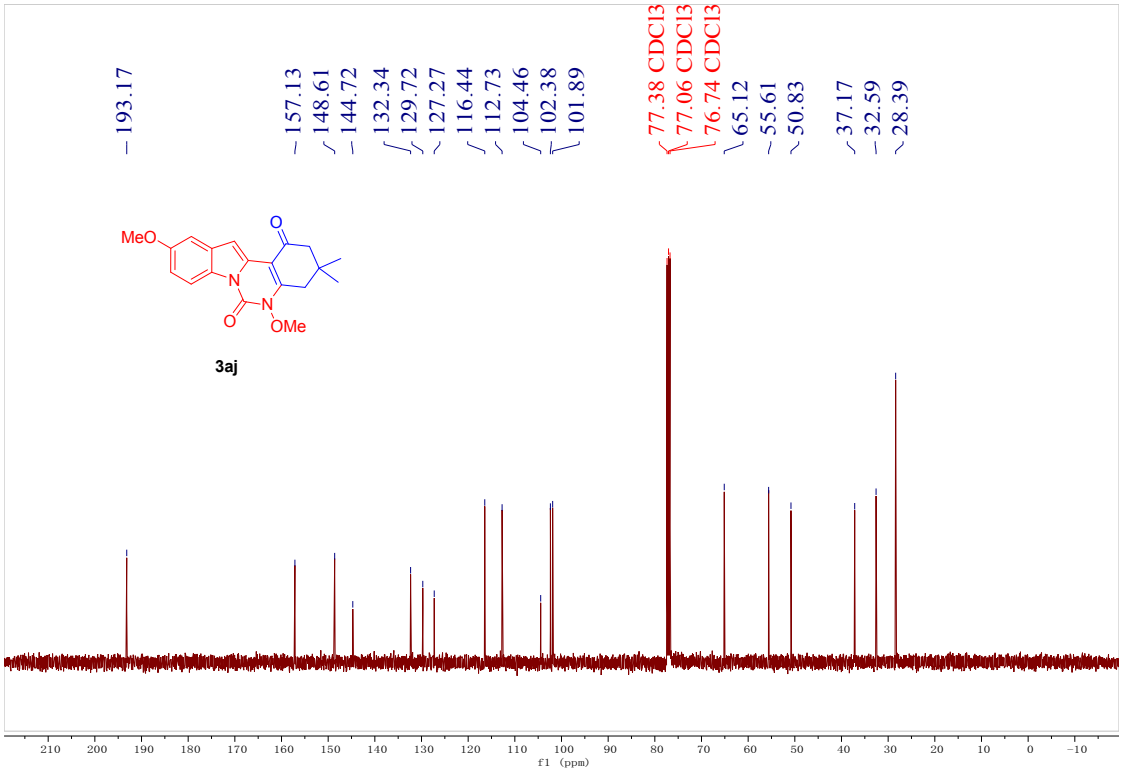
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3ai**



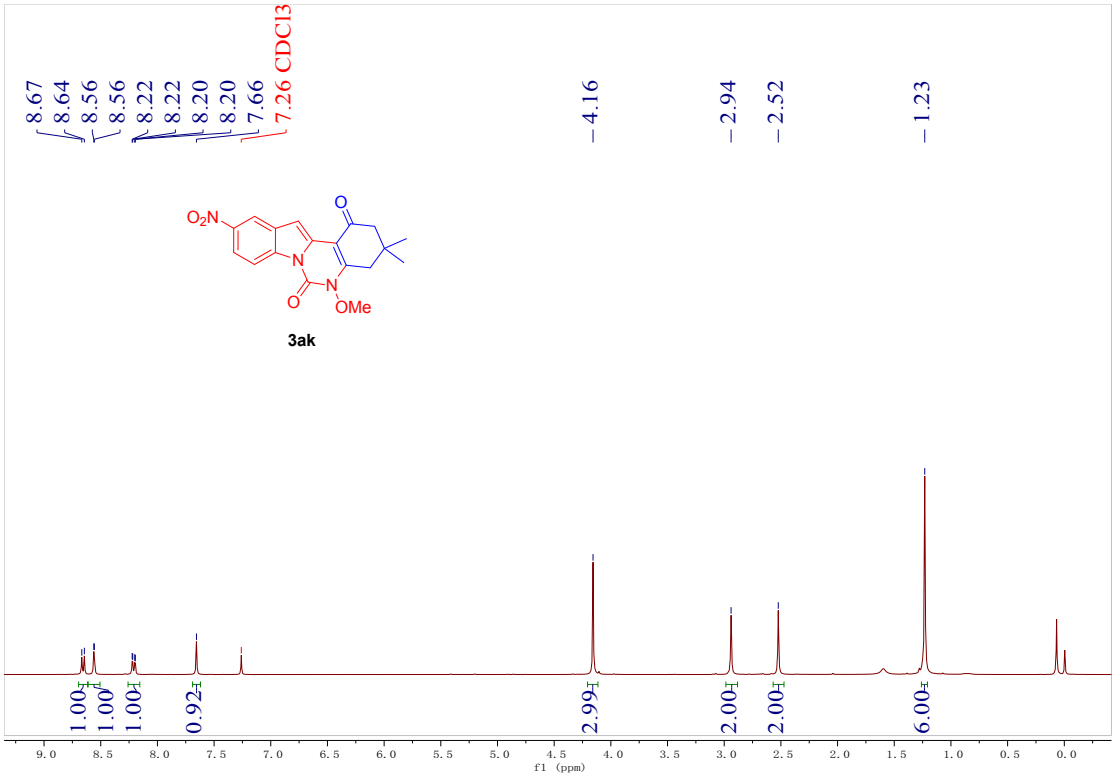
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aj**



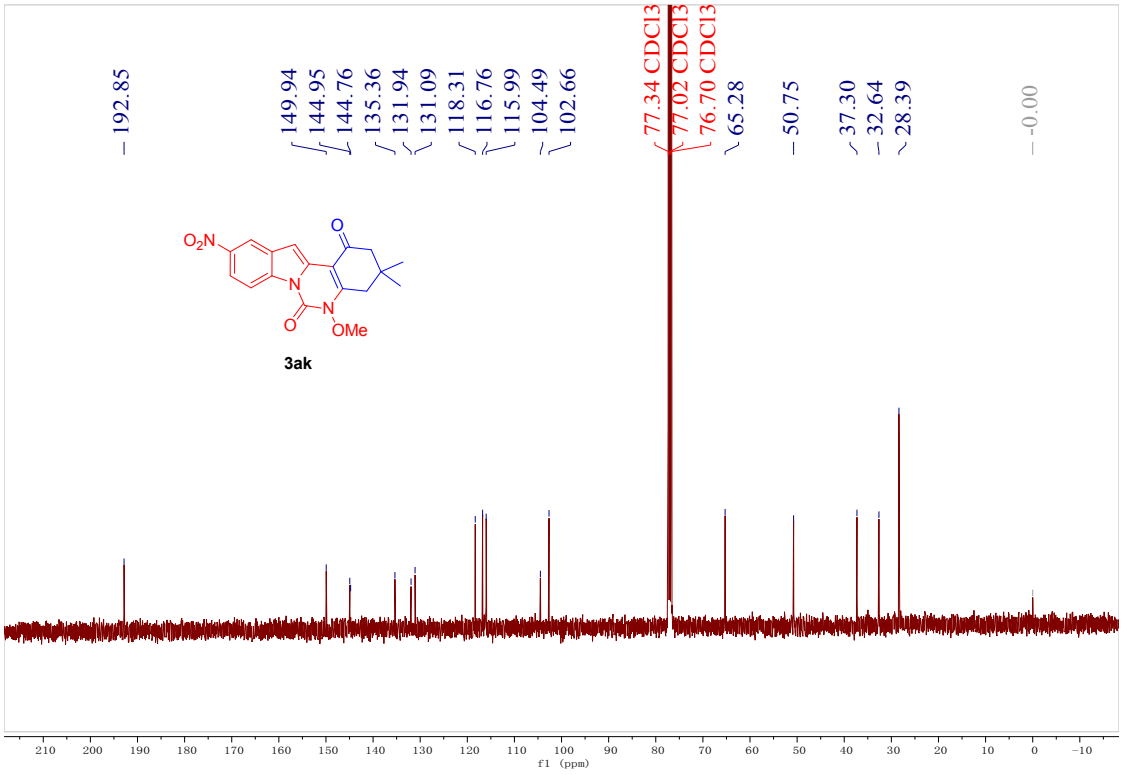
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3aj**



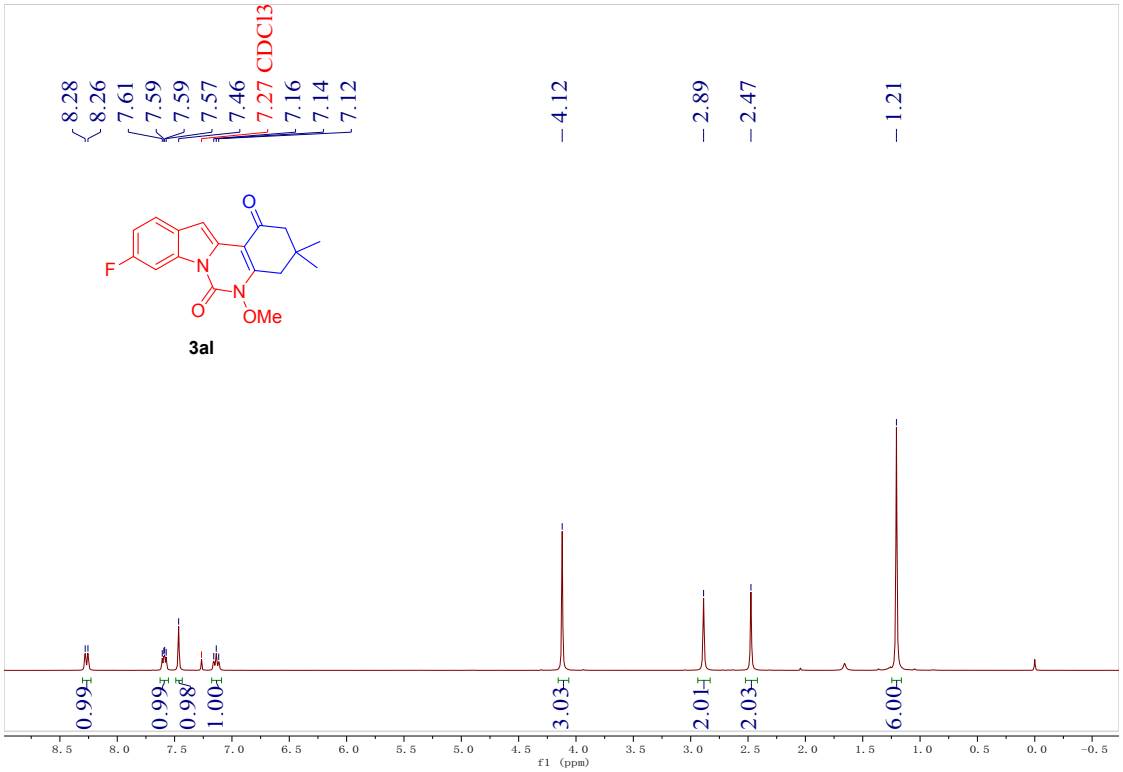
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ak**



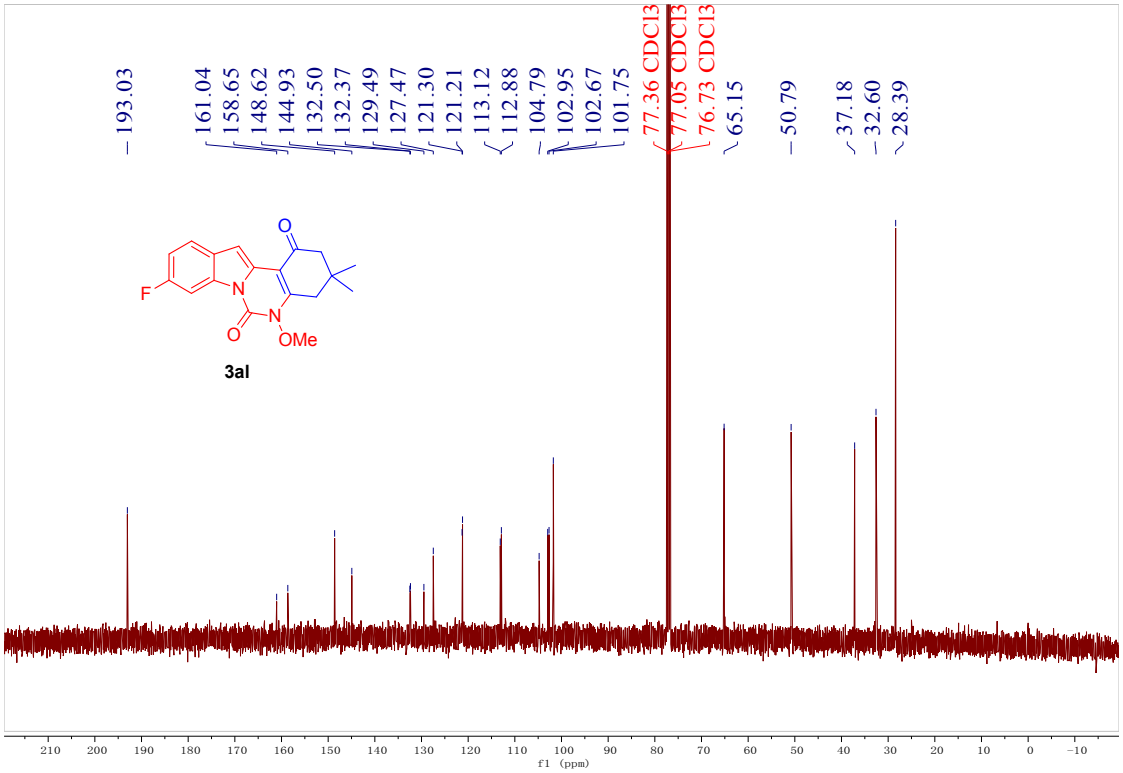
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3ak**



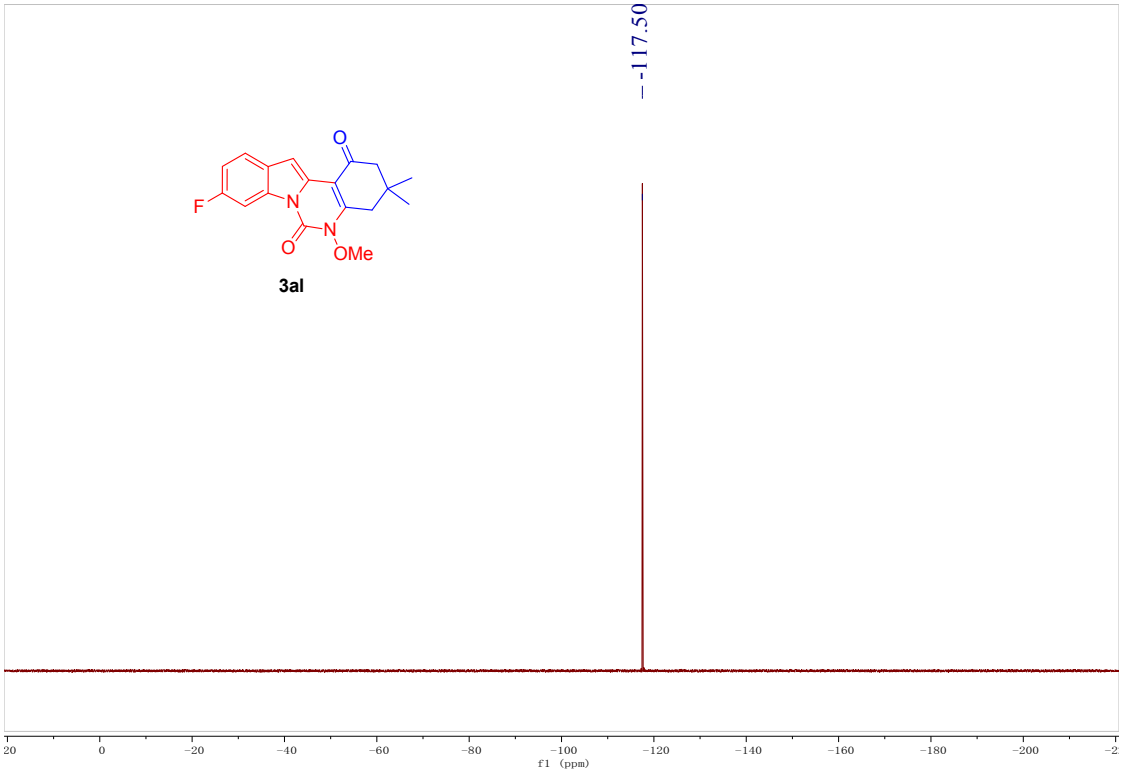
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3al**



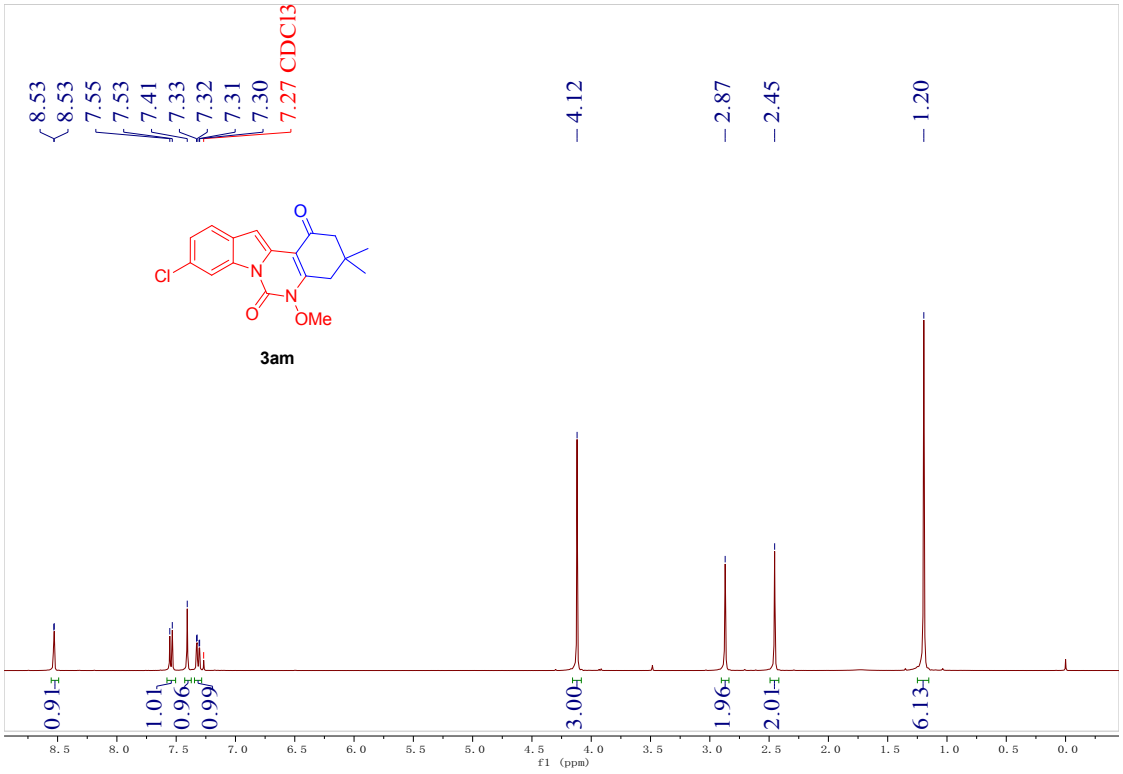
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3al**



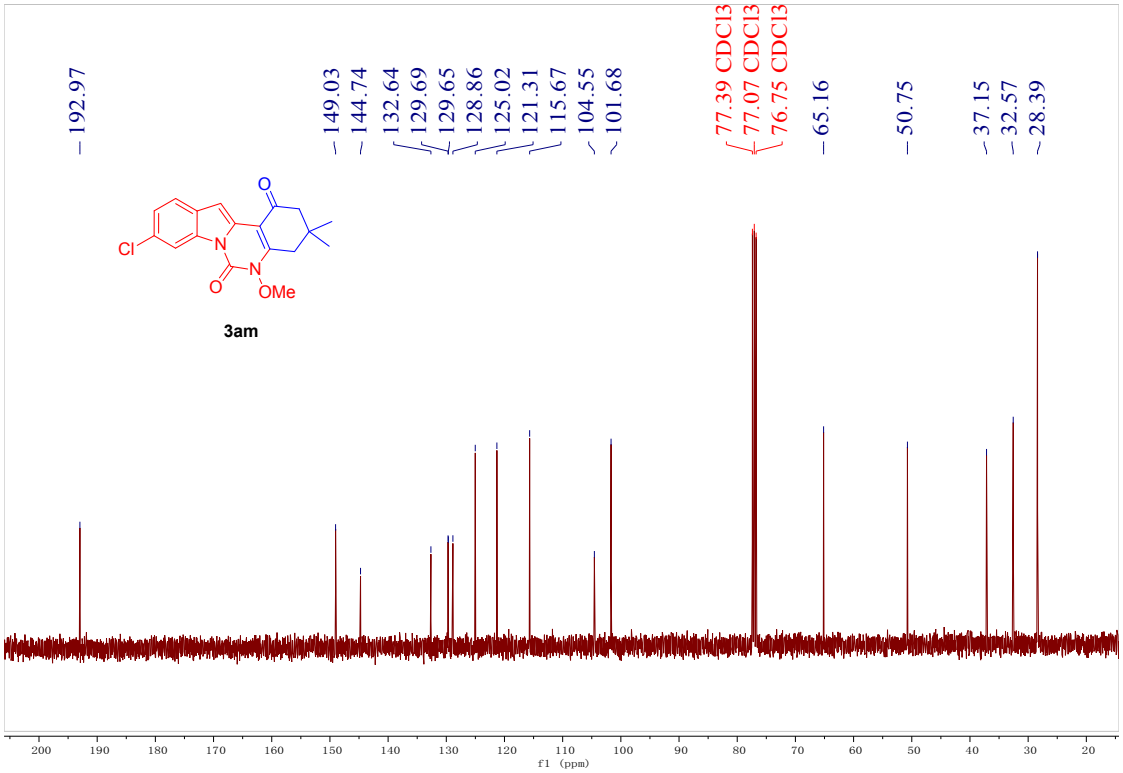
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3al**



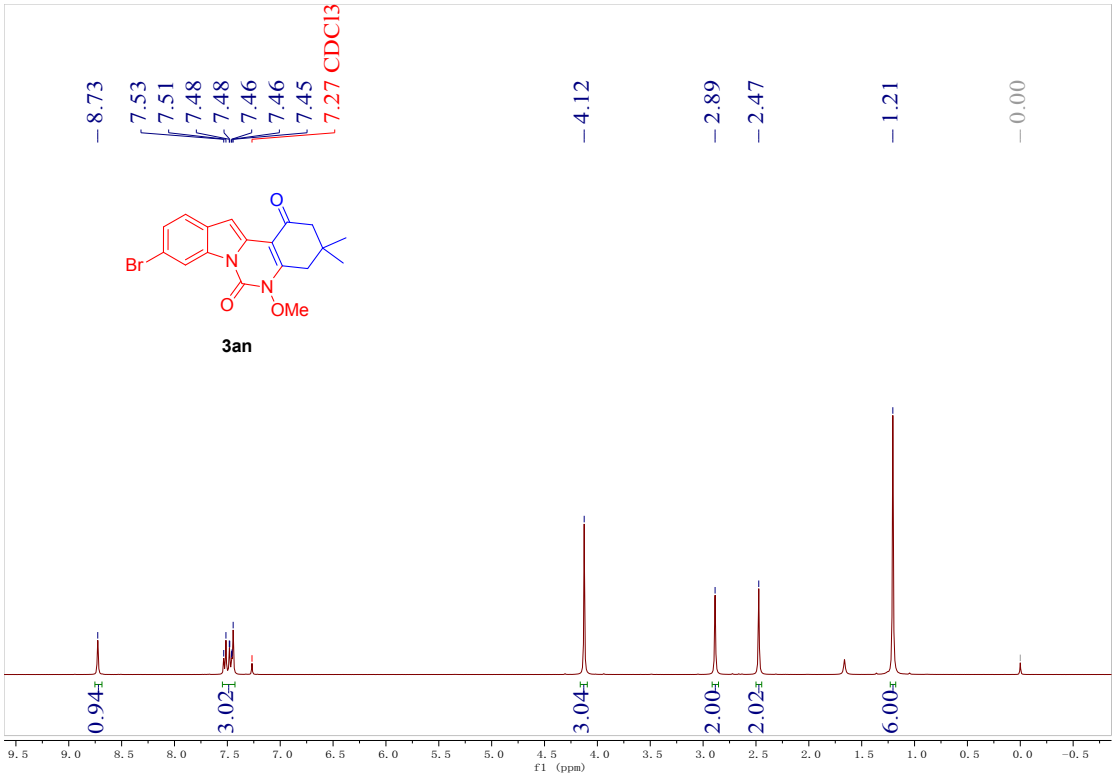
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3am**



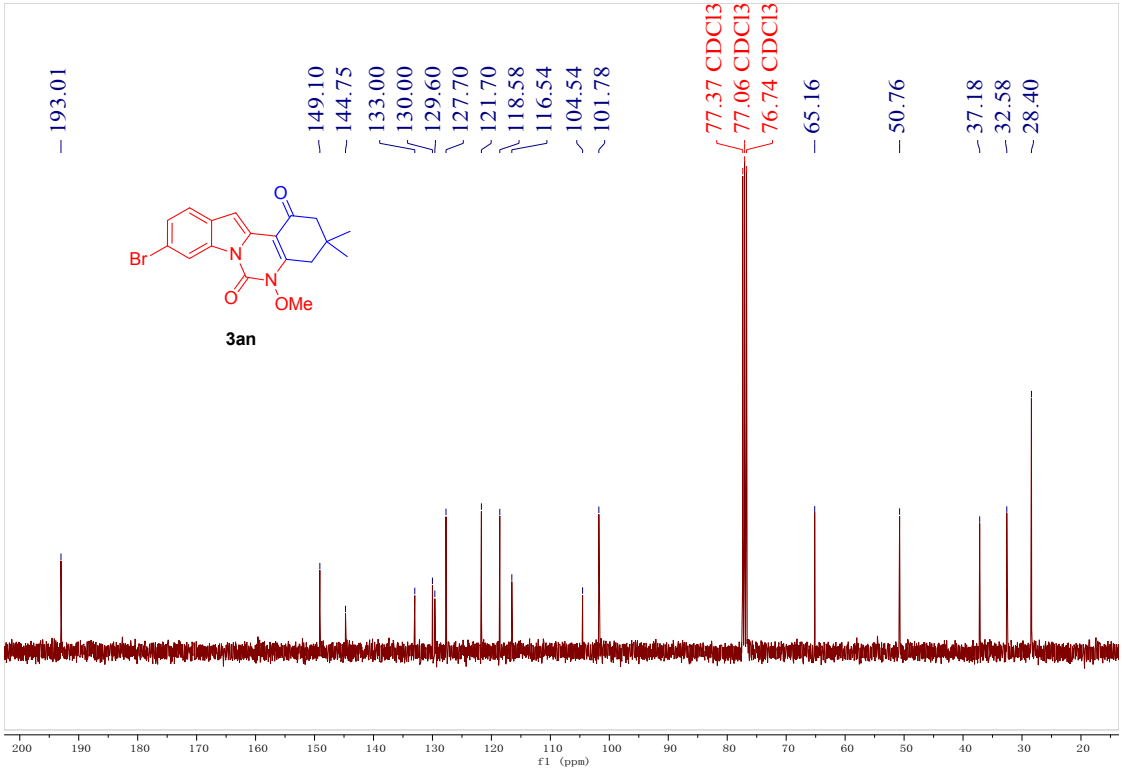
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3am**



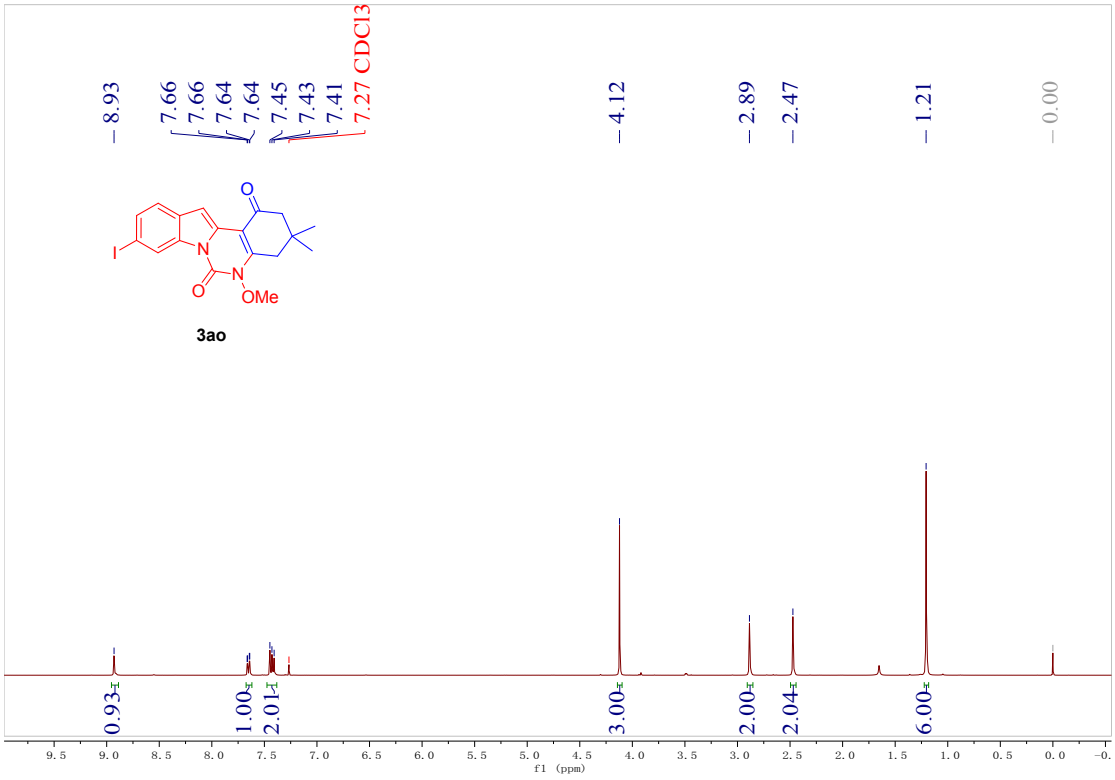
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3an**



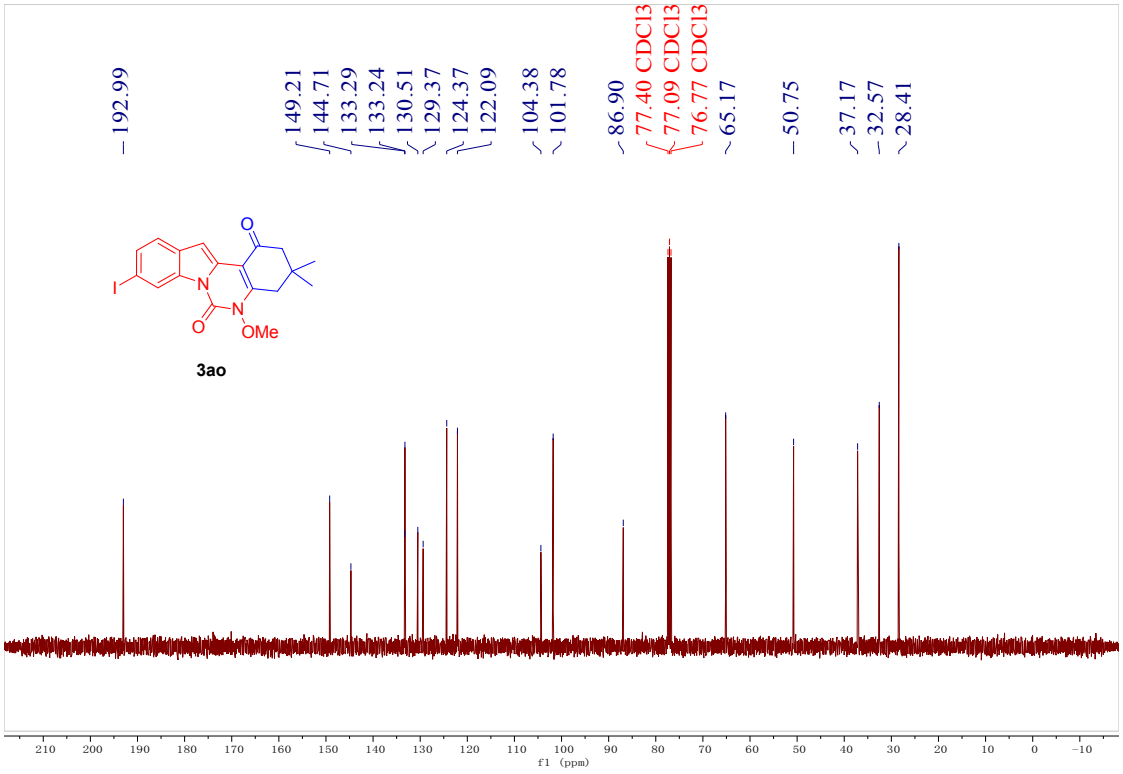
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3an**



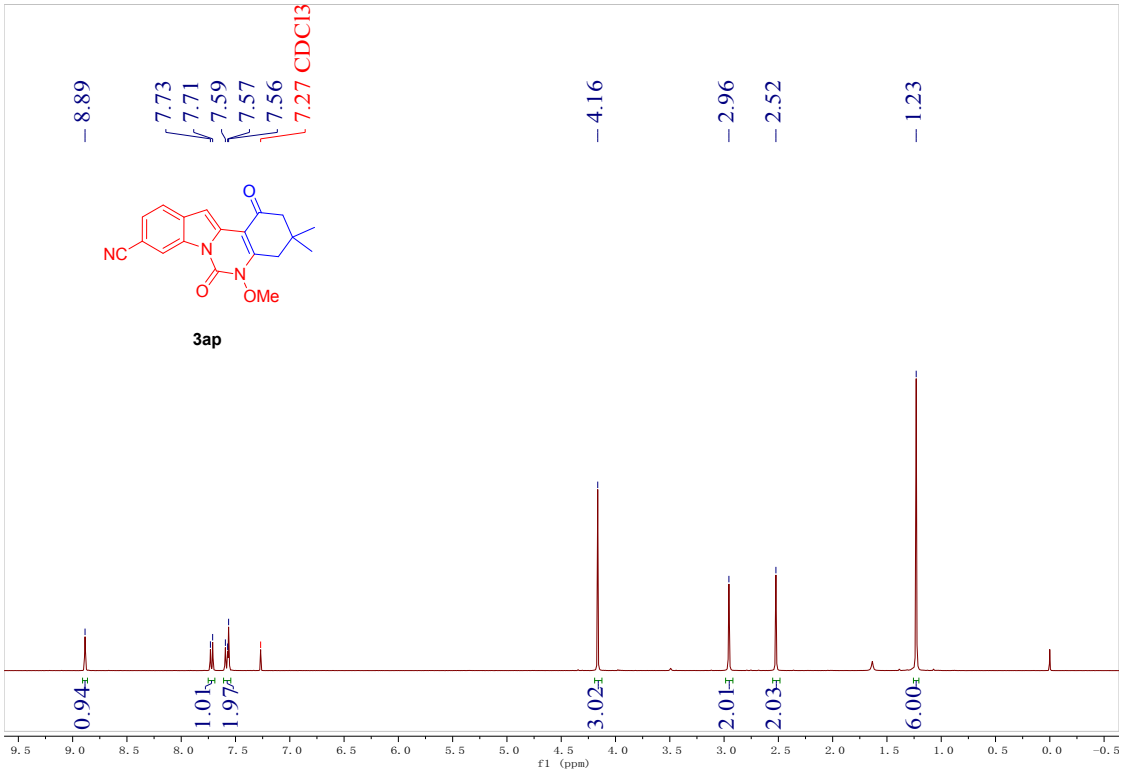
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ao**



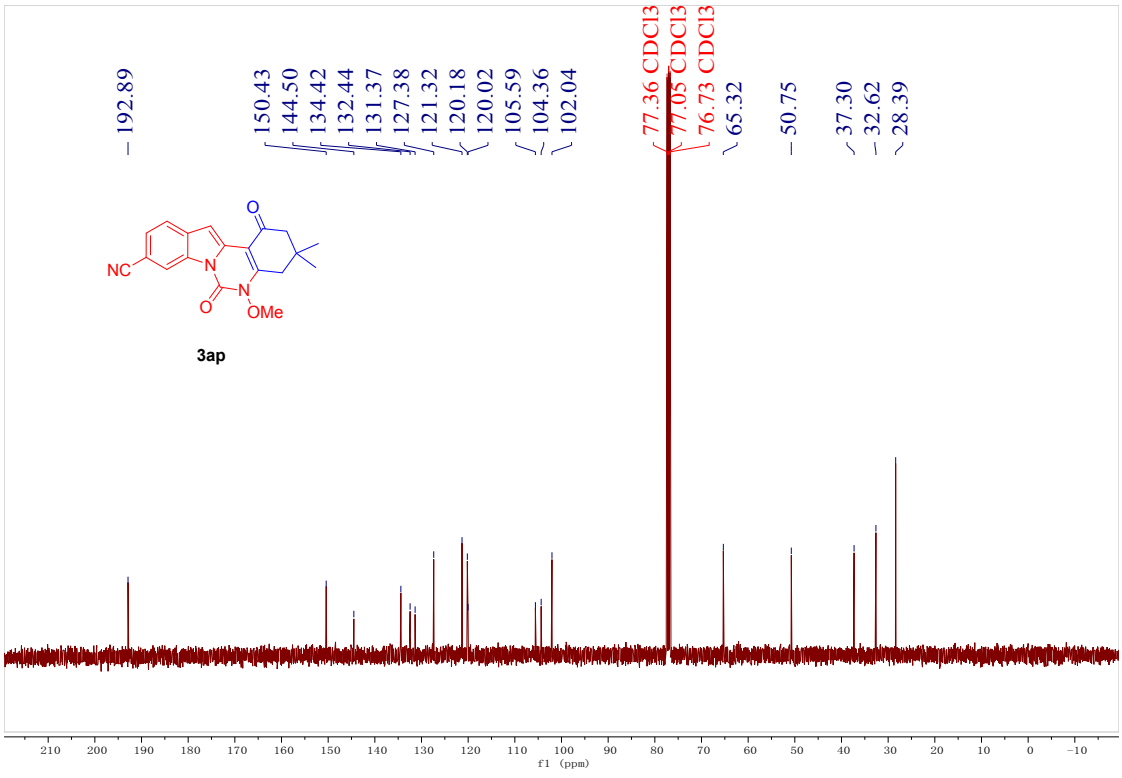
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ao**



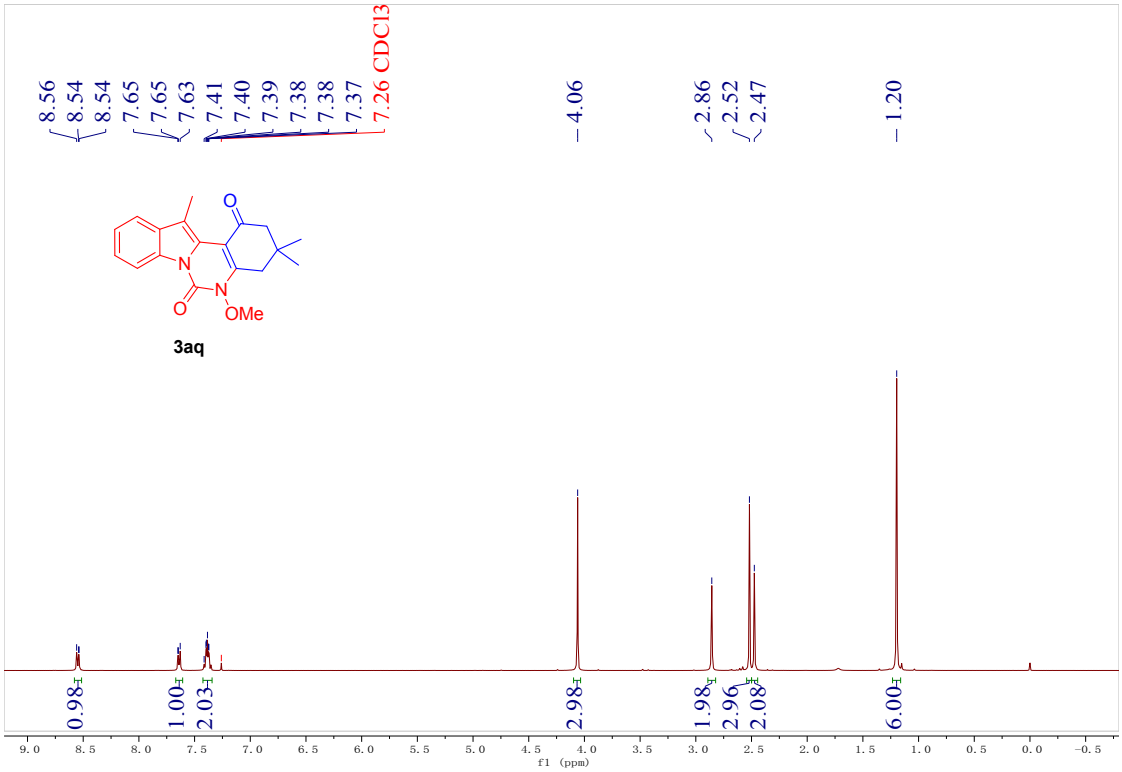
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ap**



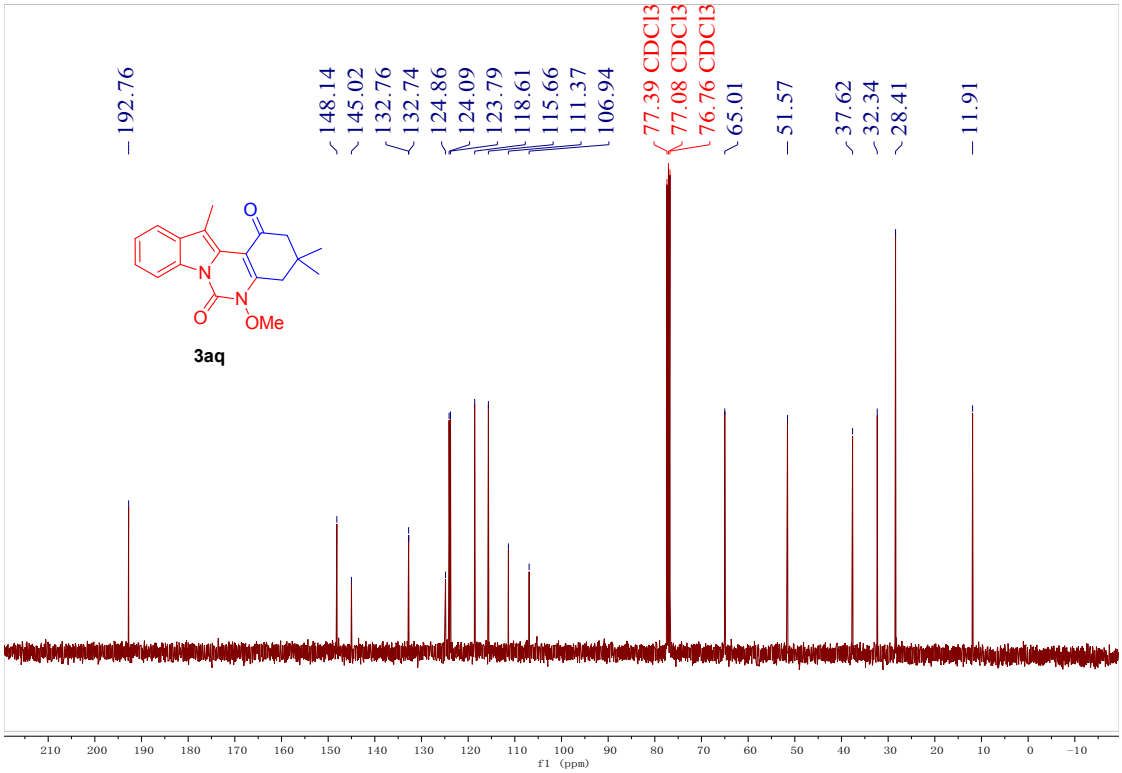
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3ap**



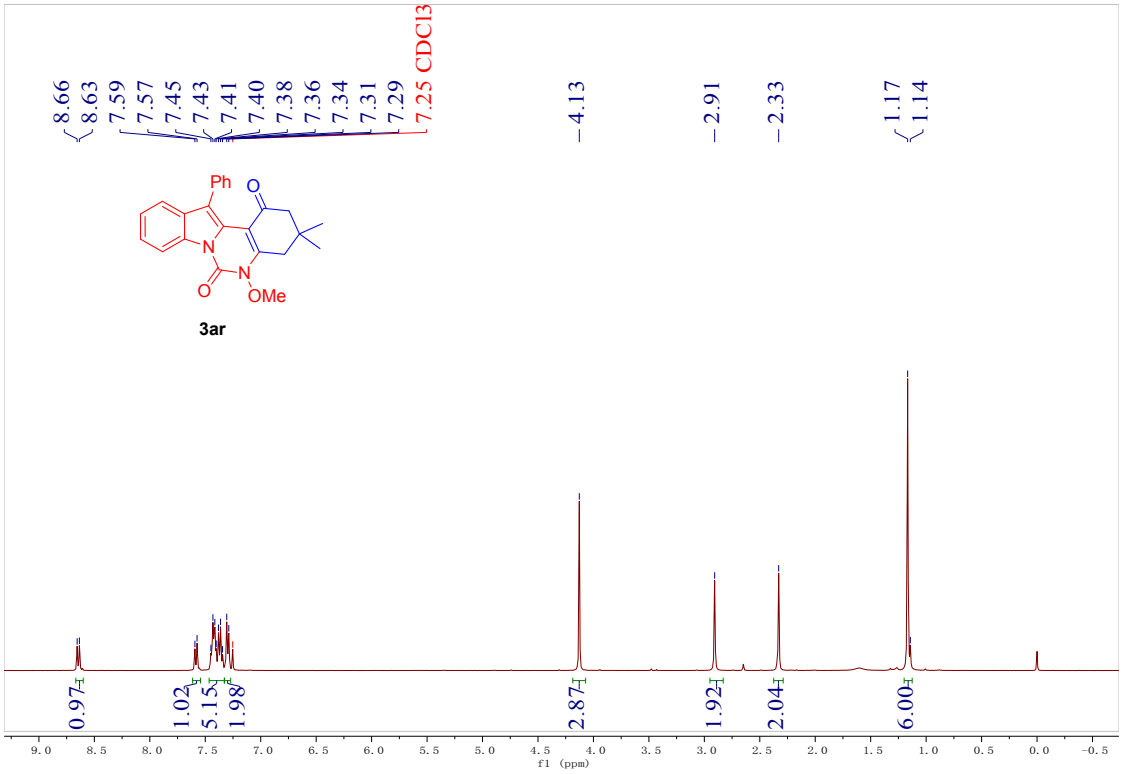
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aq**



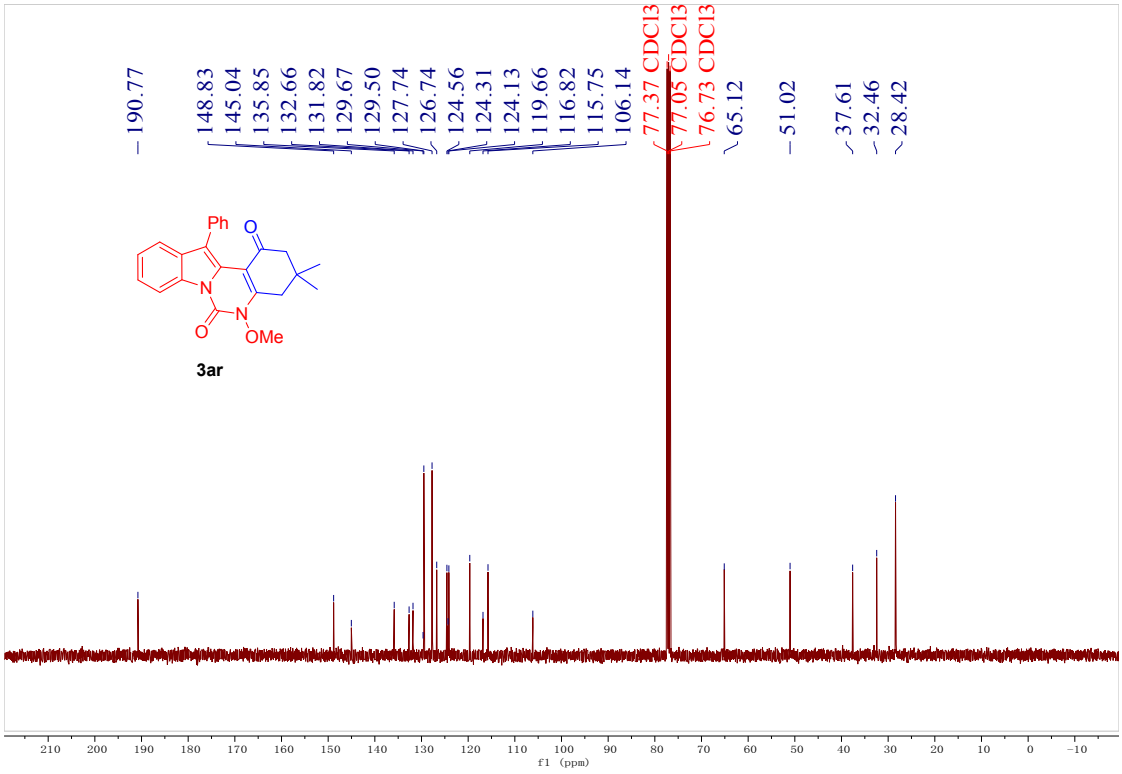
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3aq**



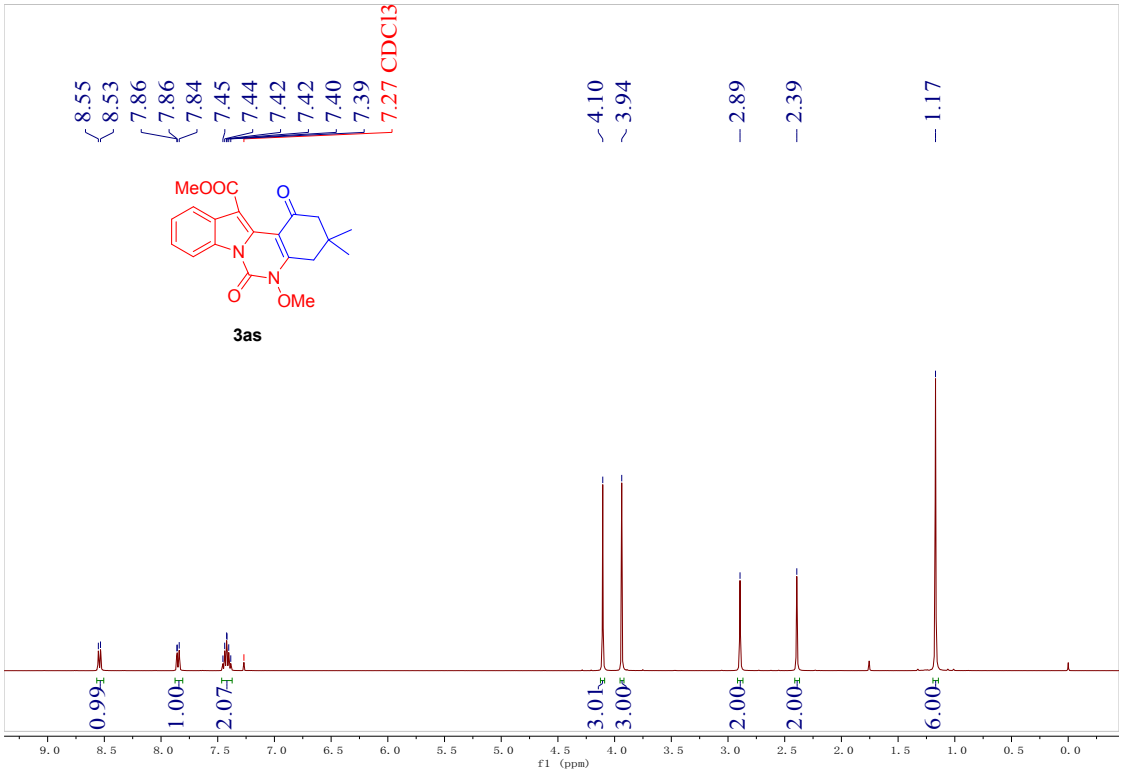
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ar**



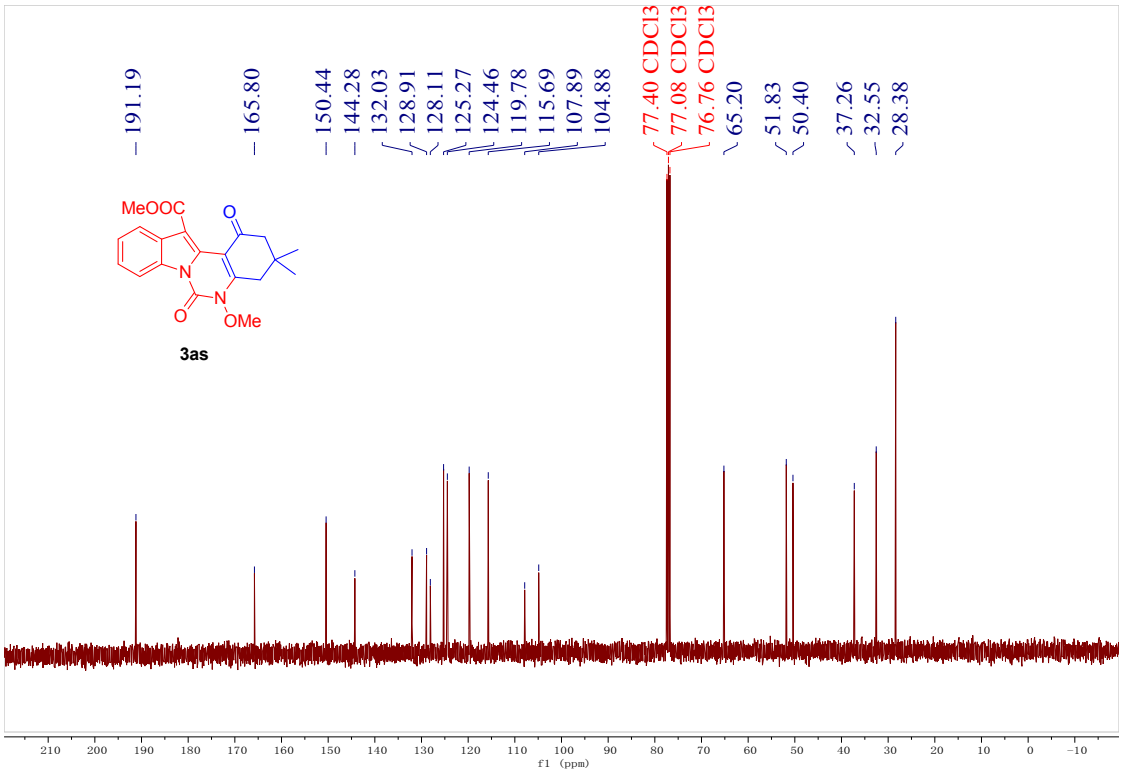
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ar**



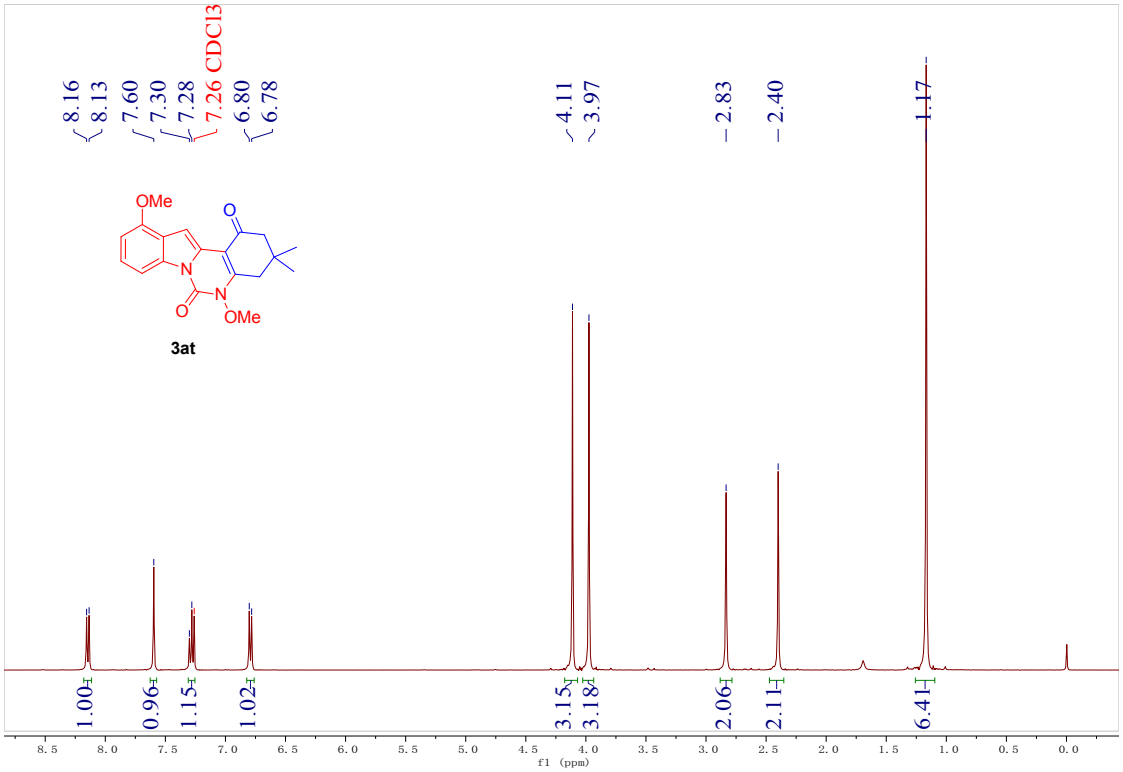
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **3as**



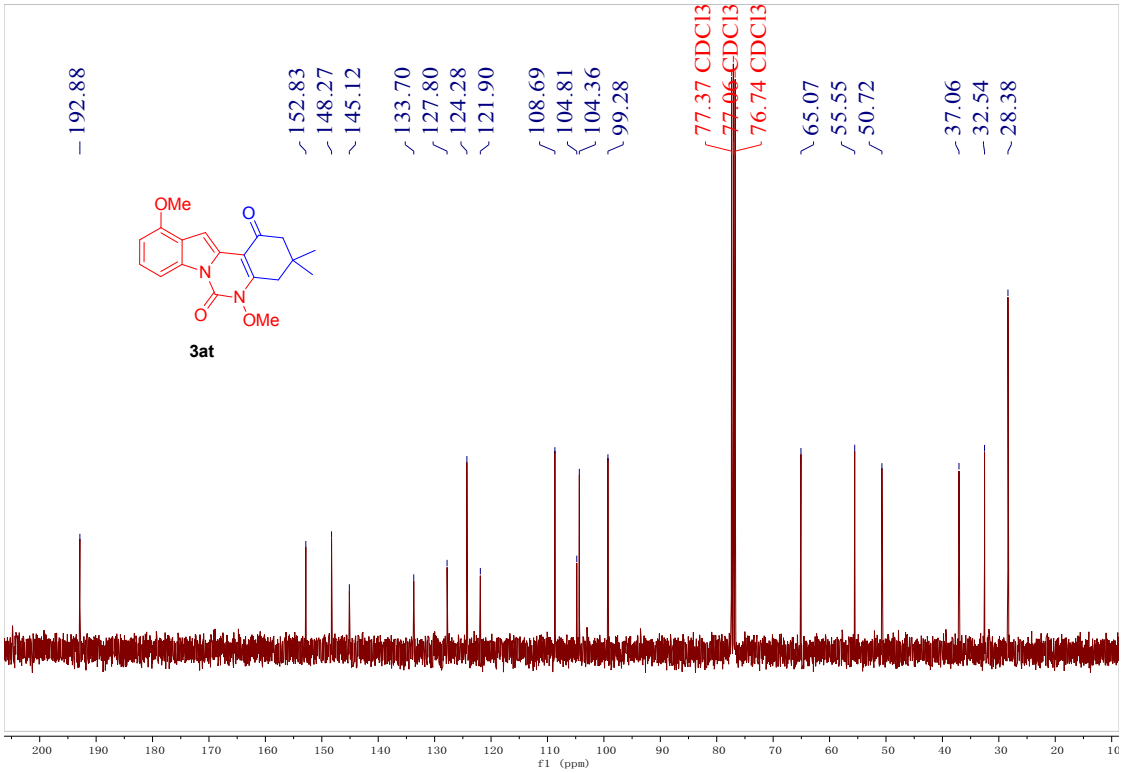
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3as**



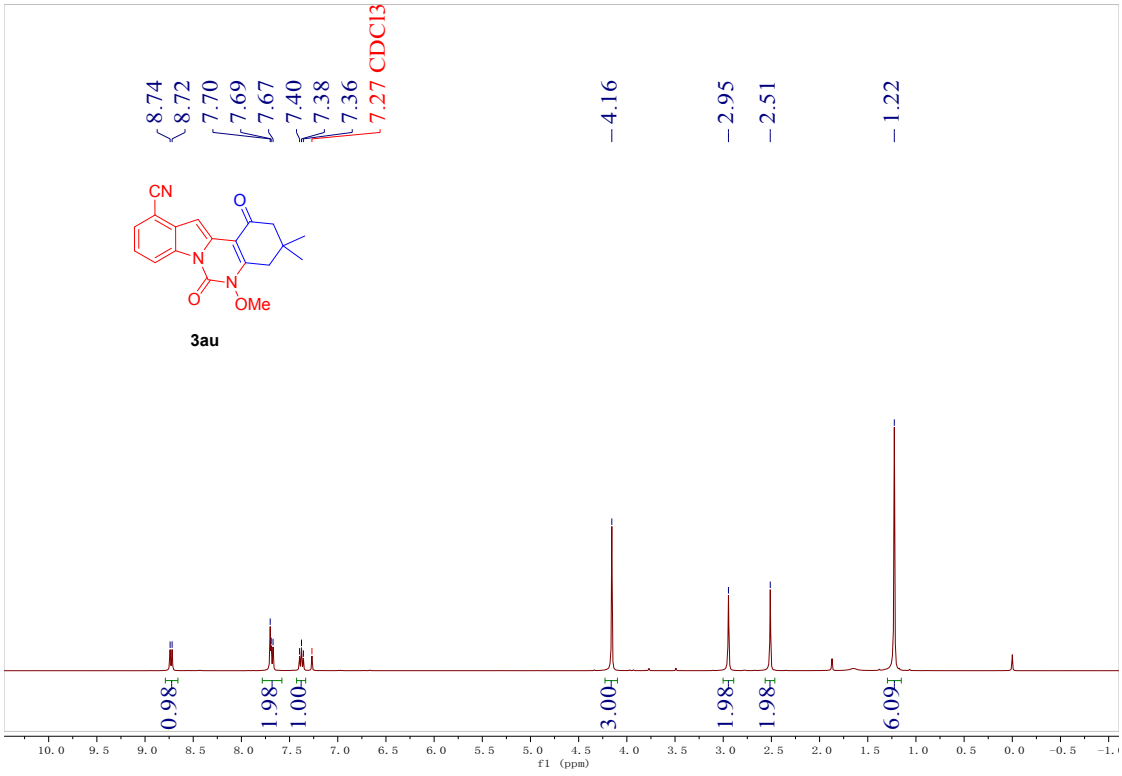
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3at**



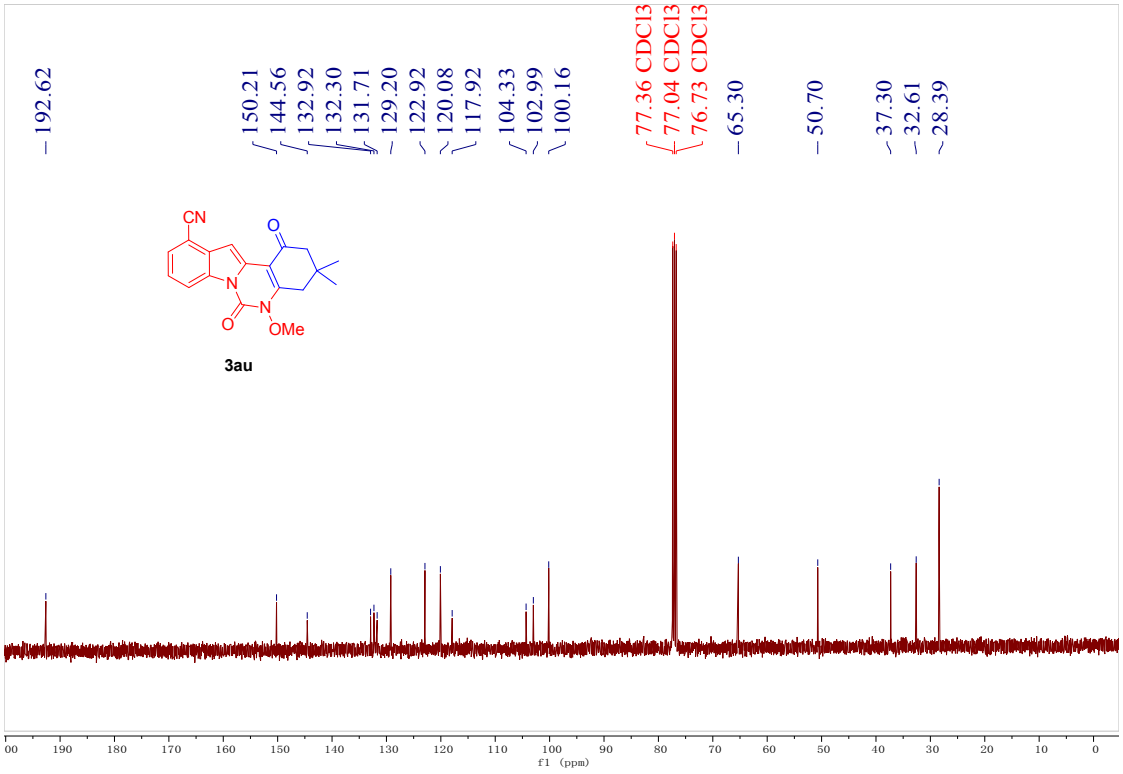
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3at**



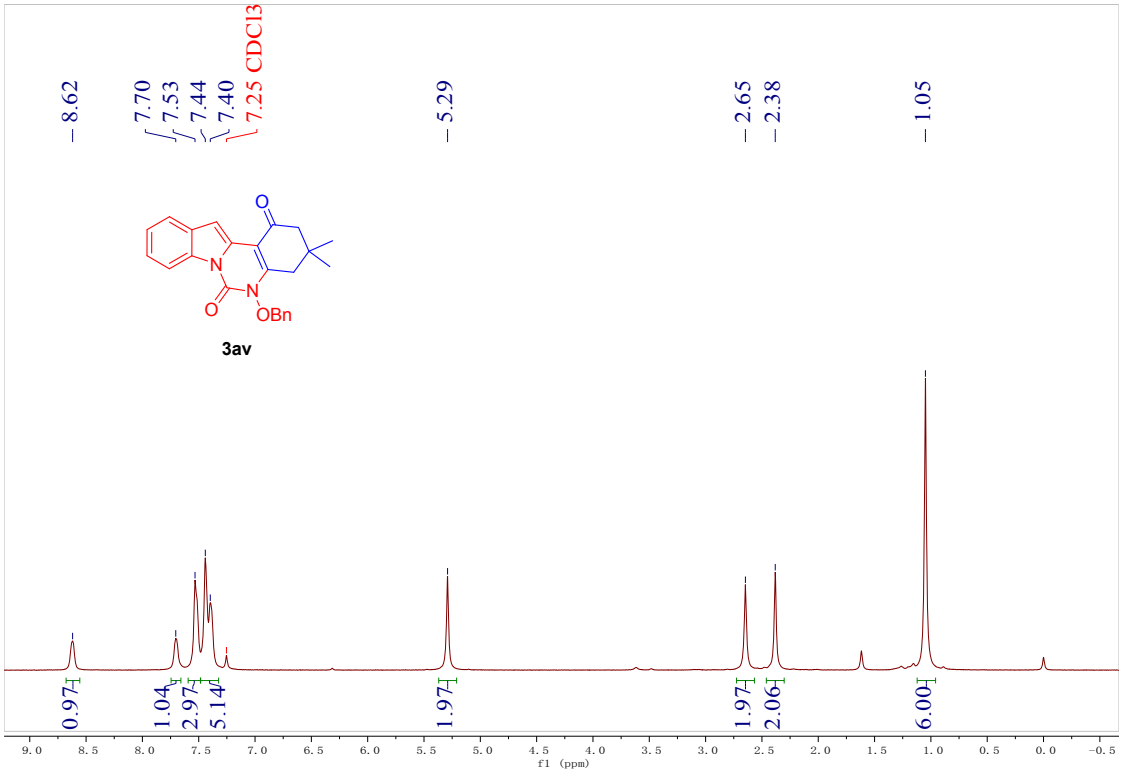
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3au**



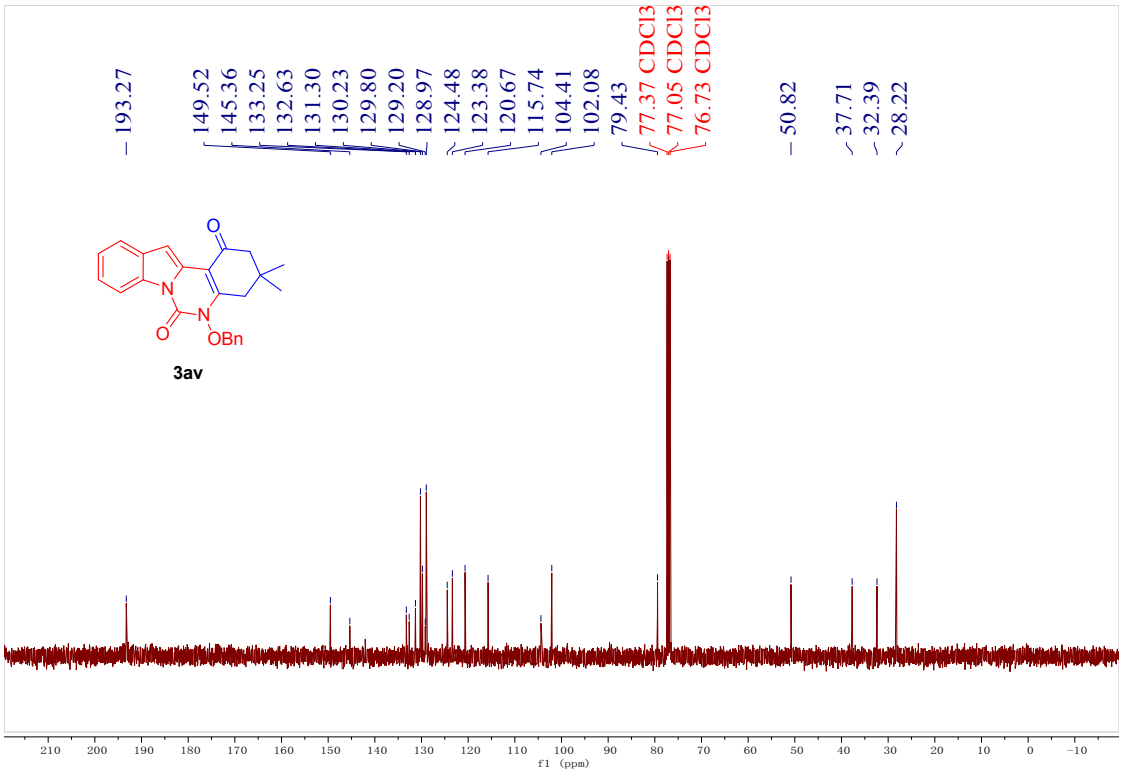
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3au**



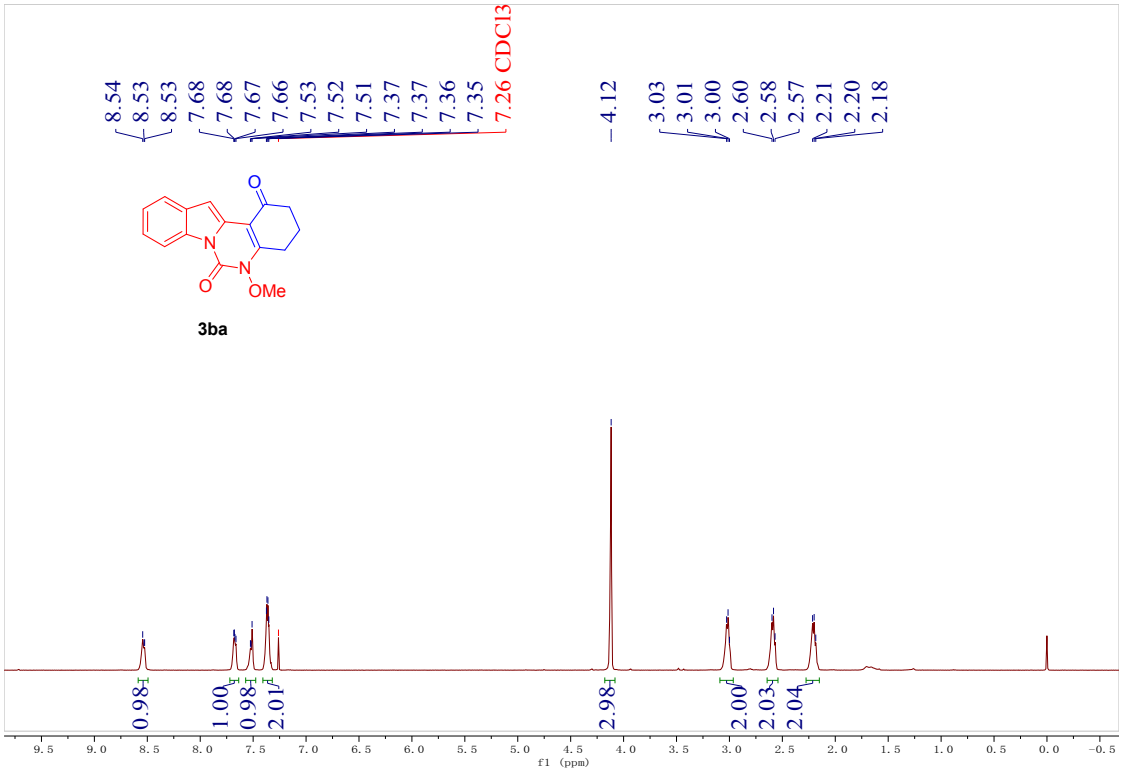
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3av**



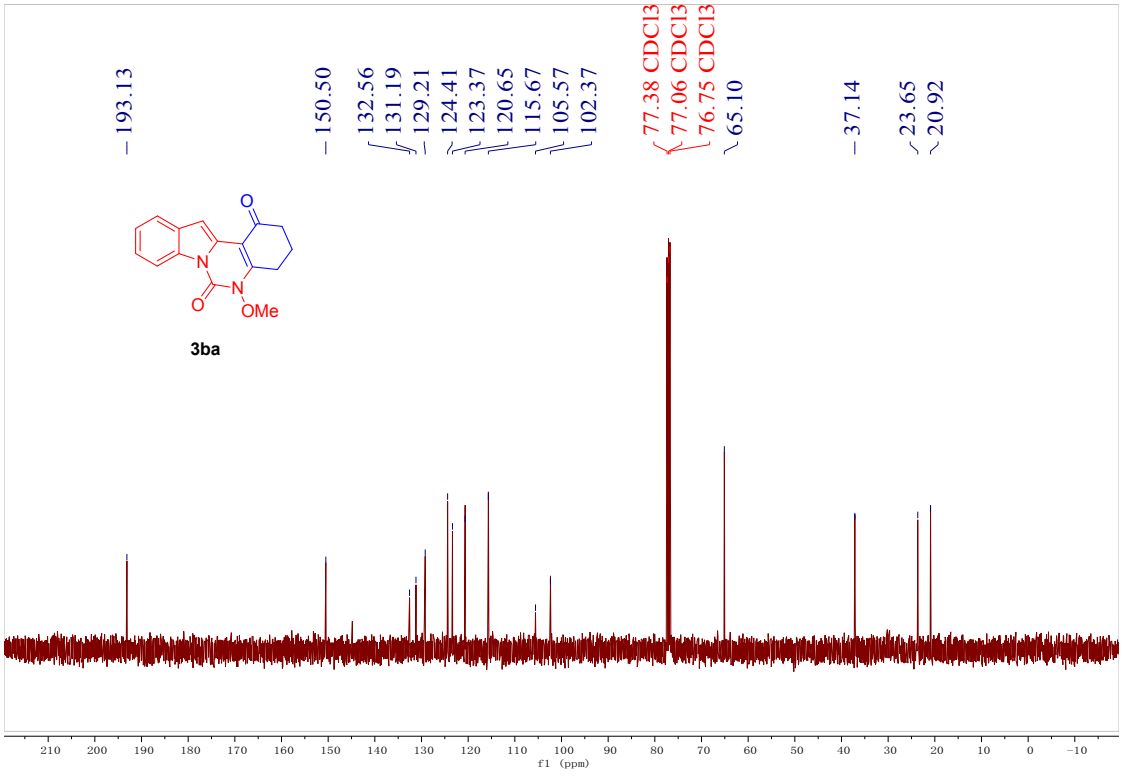
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3av**



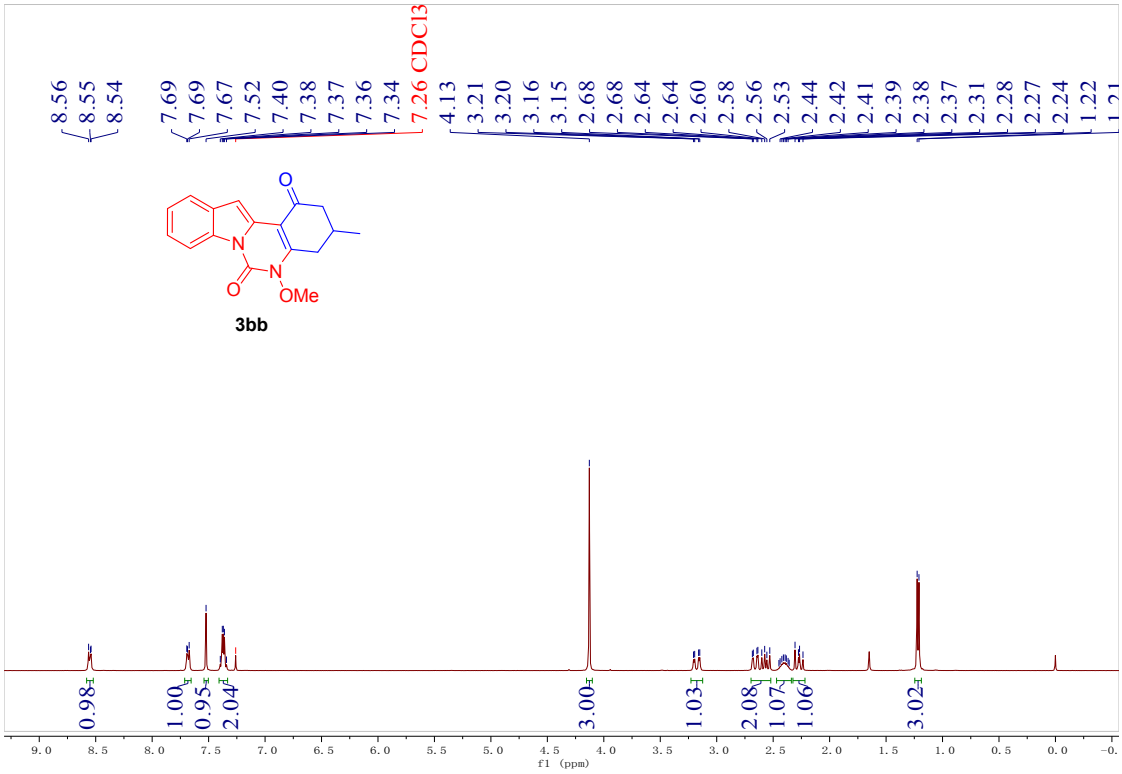
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



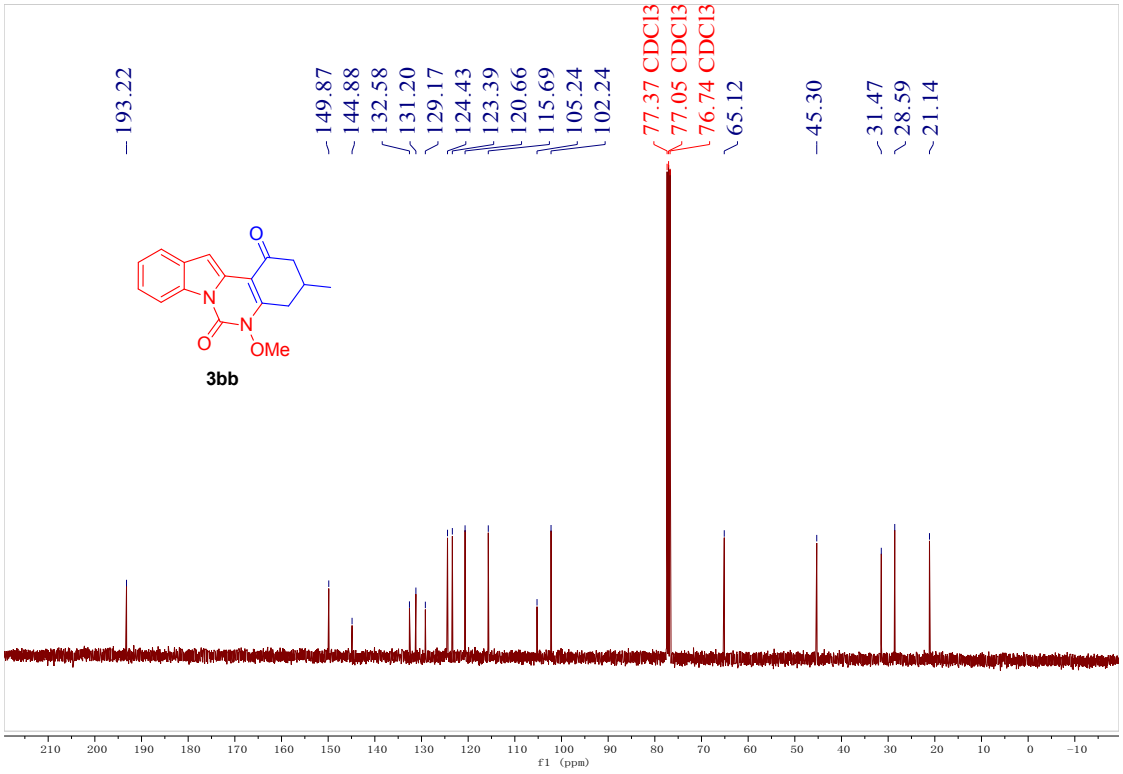
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3ba**



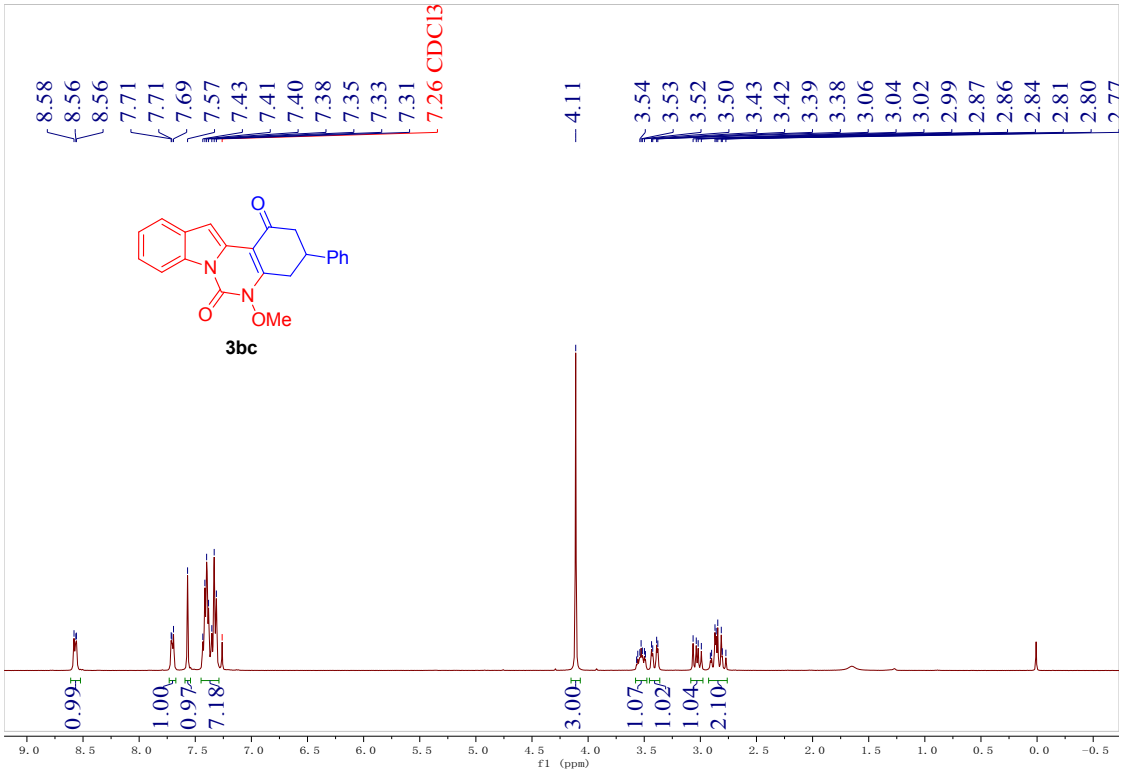
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3bb**



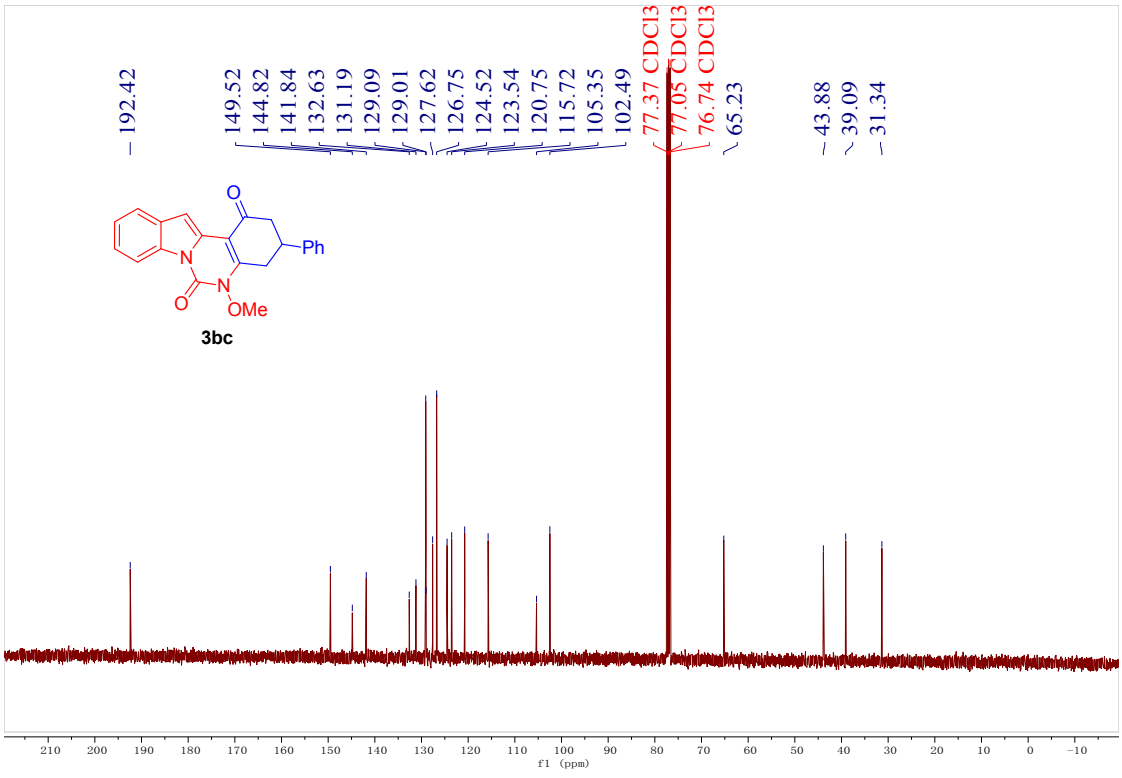
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3bb**



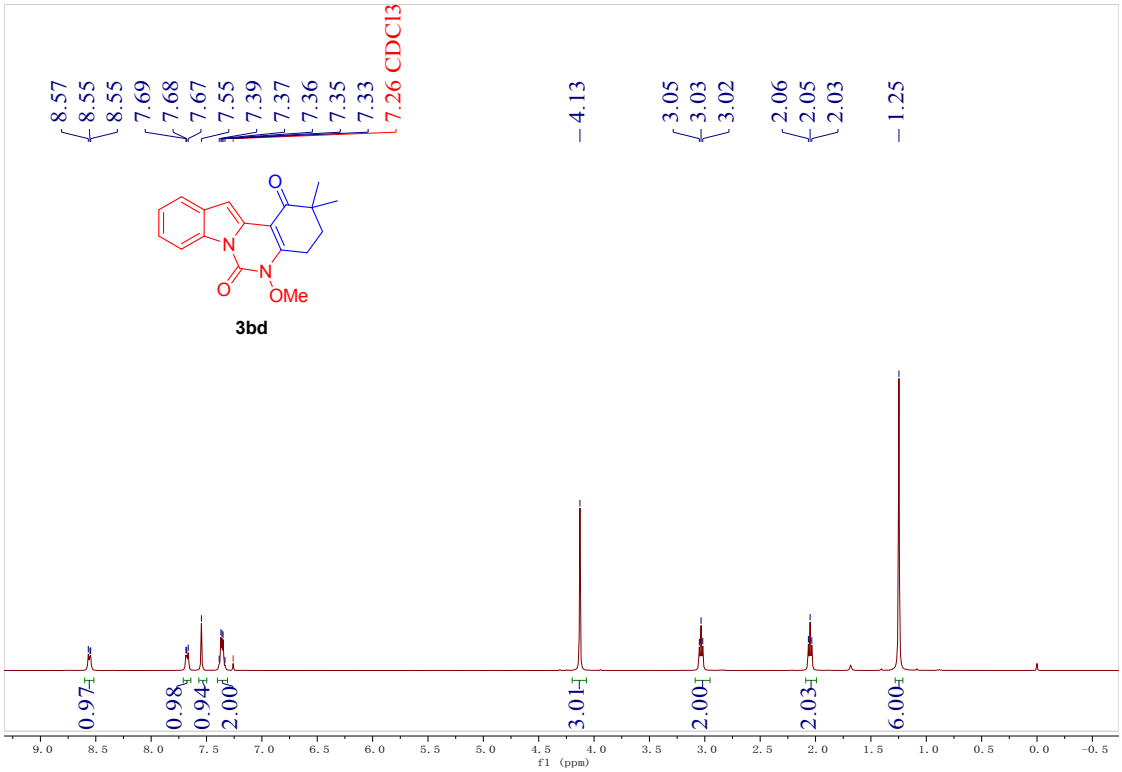
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **3bc**



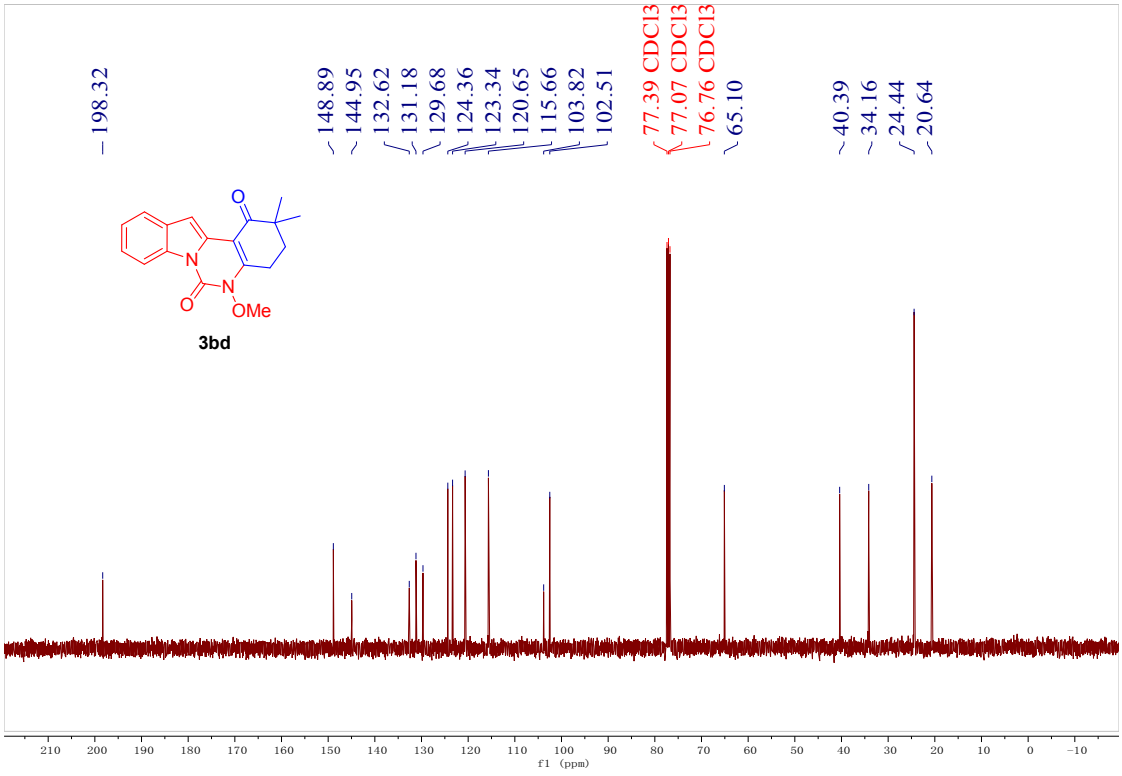
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3bc**



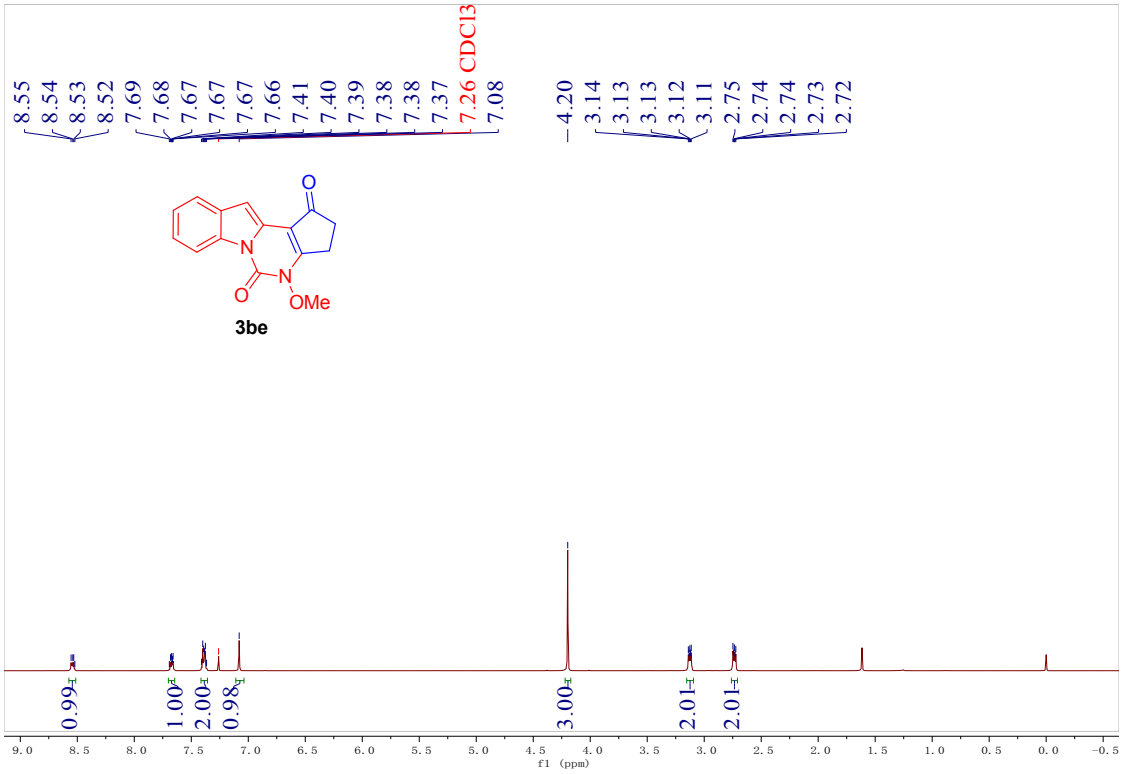
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3bd**



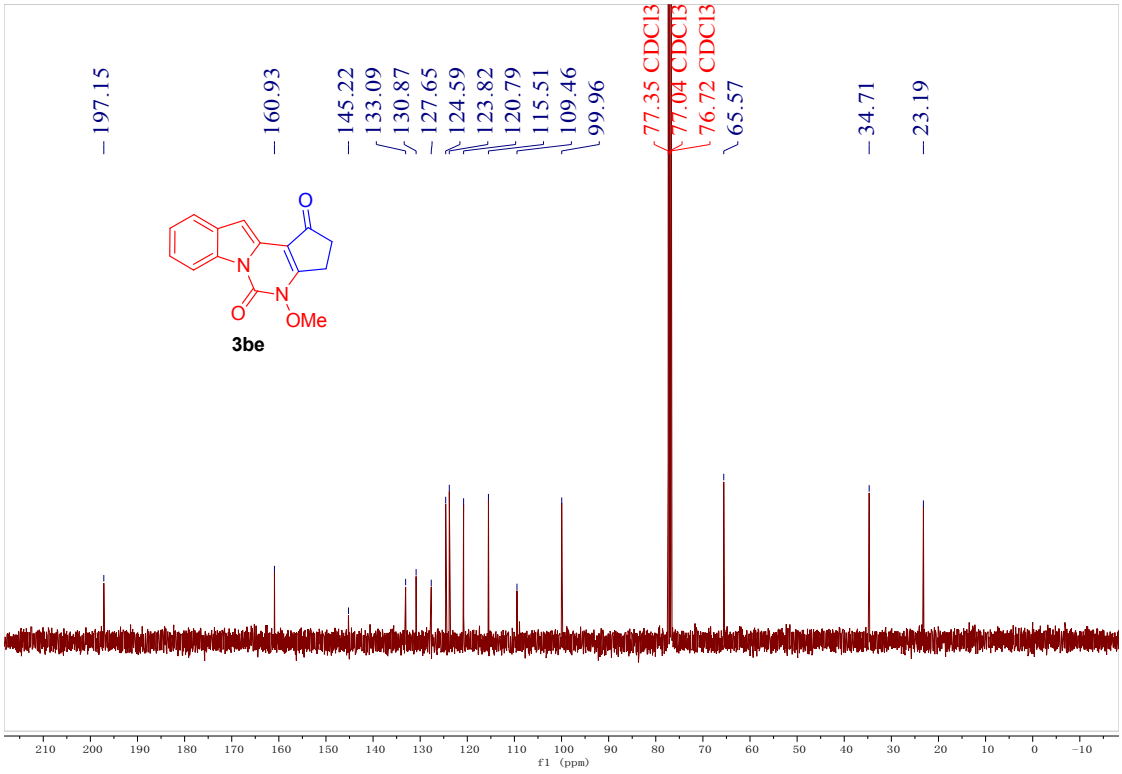
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3bd**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3be**

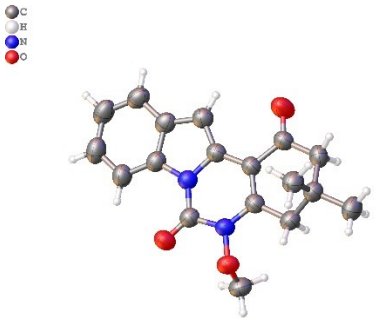


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3be**



9. Crystal data and structure refinement for 3aa

Figure S1 Single crystal structure of 3aa.



The crystal of **3aa** were prepared by recrystallization from ethyl acetate and petroleum ether (5:1).

The thermal ellipsoid was drawn at the 40% probability level.

Crystal Number: CCDC 2070972

Empirical formula: $C_{18}H_{18}N_2O_3$

Formula weight: 310.34

Unit cell parameters: a = 8.4879(10) Å, b = 9.8238(14) Å, c = 10.6092(11) Å,

α = 110.924, β = 95.681, γ = 108.558

Temperature: 293 K

Wavelength: 1.54184 Å

Volume: 760.4(2)
F (000): 328.0
h, k, l max: 10,12,13