Supporting Information

Electrophotoredox Cerium-catalyzed Decarboxylative Radical Cyclization Cascade for the Synthesis of Alkylated Benzimidazo-fused Isoquinolinones

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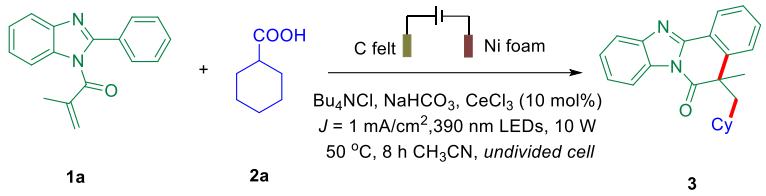
1. General information

Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. And all the solvents were used without any purification. Thin-layer chromatography (TLC) was performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness (Yantai Yuanbo Biological Technology Co., Ltd.) and all compounds were visualized with a UV light at 254 nm. Flash column chromatography was performed using silica gel (200-300 mesh, Yantai Yuanbo Biological Technology Co., Ltd.). NMR spectra were recorded on a Bruker Avance III spectrometer operating at 600 MHz (^{1}H NMR) and 150 MHz (^{13}C NMR) or at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H: residual internal $CHCl_3$ (δ 7.26 ppm); ^{13}C: internal $CDCl_3$ (δ 77.2 ppm). Coupling constants were quoted in Hz(*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

2. General procedure for the synthesis of starting materials

The alkene substrates were known compounds, and were synthesized according to the literature procedures[1,2,3]. To the solution of benzimidazole (5 mmol, 1 equiv.) and DMAP (2.0 mmol, 0.4 equiv) in DCM was added Et_3N (10 mmol, 2.0 equiv) at 0 °C. Then, methacryloyl chloride (10 mmol, 2.0 equiv) was slowly added to the solution. The solution was warmed up to room temperature and stirred for 10 h. The mixture was diluted with DCM (20 mL) and saturated NaCl aqueous solution (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with DCM (20 mL x 3 times). The combined organic layer was washed with brine, dried over Na_2SO_4. After evaporation of solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1-6:1) as the eluent.

3. General procedure for the synthesis of 3-27



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

An undivided cell was equipped with a carbon felt anode (1.0 × 3.0 cm^2) and a nickel foam cathode (1.0 × 3.0 cm^2). To the cell was added **1a** (0.3 mmol), **2a** (1.5 mmol), $NaHCO_3$ (0.5 mmol), $CeCl_3$ (0.03 mmol, 10 mol %), *n*-Bu_4NCl (0.3 mmol) and *CH_3CN* (10 mL) sequentially. The reaction cell was placed 0.5 cm away from the LEDs (Kessil, 390 nm, 10 W). Then, the resulting mixture was electrolyzed under constant current conditions (1 mA/cm^2) at 50 °C under light irradiation (390 nm, 10 W). After the reaction (8 h), the solvent was removed by distillation. The product was then extracted with DCM (3×20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired pure product.

4. CV experiments using n-Bu$_4$NI or n-Bu$_4$NBr as the supporting electrolyte

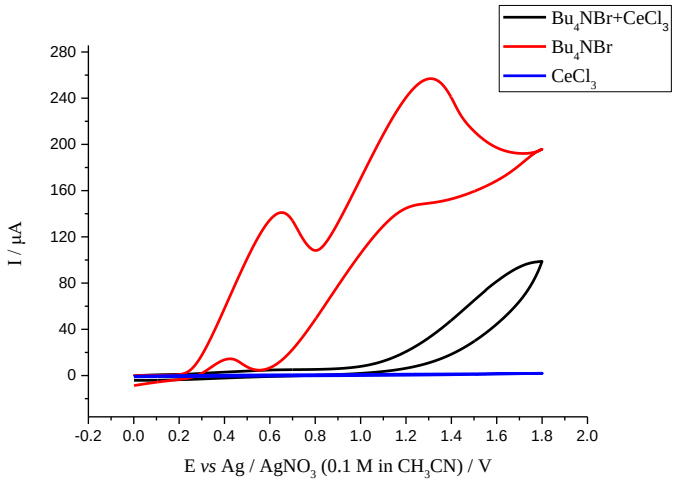


Figure S1. CV experiments. CV of related compound at a platinum disk electrode in CH_3CN at a scan rate of 0.1 Vs^{-1}: $CeCl_3$ (3 mM), *n*-Bu_4NBr (9 mM), $CeCl_3$ (3 mM) + *n*-Bu_4NBr (9 mM).

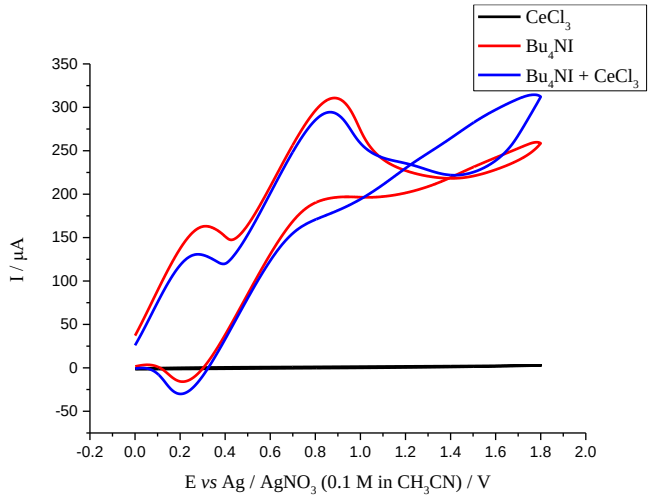
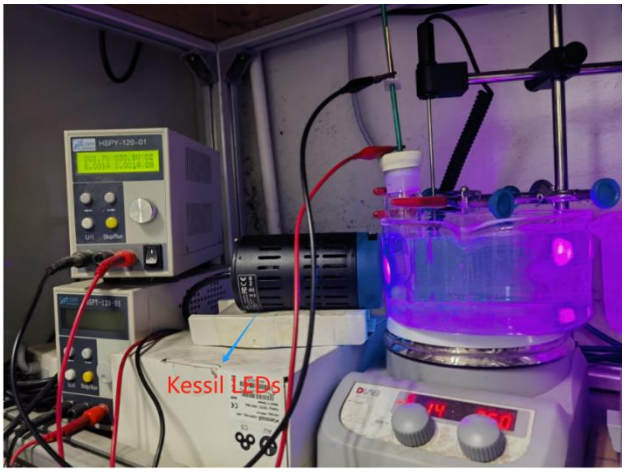
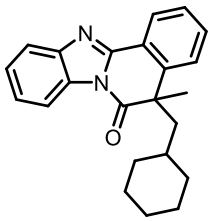


Figure S2. CV experiments. CV of related compound at a platinum disk electrode in CH_3CN at a scan rate of 0.1 Vs^{-1}: $CeCl_3$ (3 mM), *n*-Bu_4NI (9 mM), $CeCl_3$ (3 mM) + *n*-Bu_4NI (9 mM).

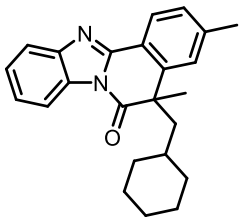
5. A photo of the reaction setup



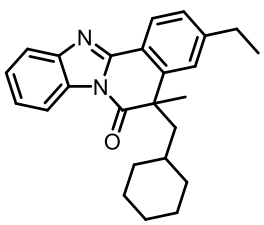
6. Characterization data of 3-27



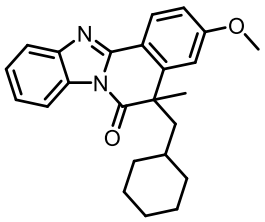
5-(cyclohexylmethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (3)[3]**,** white solid (89.2 mg, 86%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 7.7 Hz, 1H), 8.38 (d, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.42 (m, 4H), 2.50 – 2.47 (m,1H), 2.06 (d, 4.4 Hz, 1H), 1.72 (s, 1H), 1.67 (s, 3H), 1.48 – 1.37 (m, 3H), 1.26 (s, 2H), 1.17 (s, 1H), 0.99 (s, 1H), 0.94 (d, *J* = 9.6 Hz, 2H), 0.80 (s, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.7, 145.0, 144.2, 142.0, 131.8, 127.7, 126.7, 126.09, 125.96, 125.6, 122.7, 119.9, 115.9, 77.4, 77.2, 77.0, 49.0, 48.5, 35.1, 34.4, 33.1, 31.9, 26.1.



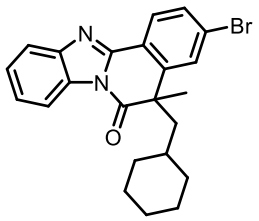
6-(cyclohexylmethyl)-3,5-dimethylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (4)[4]**,** white solid (47.3 mg, 44%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.37 (d, *J* = 7.1 Hz, 2H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 2.48 (s, 3H), 2.46 – 2.44 (m, 1H), 2.05 (d, *J* = 14.3 Hz, 1H), 1.65 (s, 3H), 1.47 (s, 1H), 1.43 – 1.36 (m, 2H), 1.28 (s, 1H), 1.16 (s, 1H), 0.99 (s, 1H), 0.94 (s, 2H), 0.80 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.8, 150.1, 144.1, 142.2, 141.9, 131.4, 128.7, 127.0, 125.9, 125.8, 125.3, 119.9, 119.6, 115.8, 77.3, 77.1, 76.9, 48.8, 48.2, 34.9, 34.3, 32.9, 31.9, 26.0, 25.94, 25.92, 22.1.



6-(cyclohexylmethyl)-3-ethyl-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (5)[5]**,** white solid (45.8 mg, 41%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.44 – 8.34 (m, 2H), 7.82 (d, J = 7.6 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.26 (s, 1H), 2.77 (d, J = 7.8 Hz, 2H), 2.46 (d, J = 14.2 Hz, 1H), 2.08 – 2.04 (m, 1H), 1.66 (s, 3H), 1.48 – 1.44 (m, 1H), 1.40 (s, 2H), 1.31 (t, J = 7.7 Hz, 3H), 1.25 (s, 2H), 1.18 (s, 1H), 0.98 (s, 1H), 0.94 (d, J = 10.1 Hz, 1H), 0.81 (d, J = 8.1 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.8, 150.1, 148.4, 144.1, 142.0, 131.4, 127.5, 126.0, 125.9, 125.8, 125.3, 120.1, 119.6, 115.8, 77.3, 77.1, 76.9, 48.8, 48.4, 34.9, 34.3, 33.0, 31.8, 29.3, 26.0, 25.94, 25.90, 15.5.

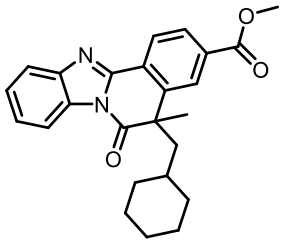


5-(cyclohexylmethyl)-3-methoxy-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (6)[5]**,** white solid (106.6 mg, 95%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.56 (d, J = 8.2 Hz, 1H), 8.42 – 8.37 (m, 1H), 8.15 (d, J = 1.4 Hz, 1H), 8.15 – 8.15 (m, 2H), 7.89 – 7.83 (m, 1H), 7.51 – 7.44 (m, 2H), 4.00 (s, 3H), 2.50 (d, J = 14.4 Hz, 1H), 2.13 (d, J = 14.4 Hz, 1H), 1.70 (s, 3H), 1.47 – 1.37 (m, 3H), 1.24 – 1.15 (m, 2H), 0.96 – 0.90 (m, 3H), 0.84 – 0.76 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.0, 166.3, 148.8, 144.1, 142.1, 132.7, 131.5, 128.4, 128.1, 126.4, 126.14, 126.07, 120.10, 115.9, 77.2, 77.0, 76.8, 52.6, 48.9, 48.5, 35.0, 34.2, 33.0, 31.6, 25.9.

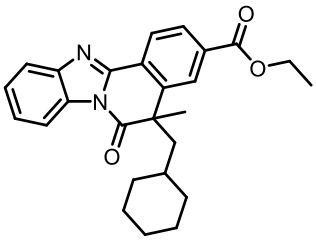


3-bromo-5-(cyclohexylmethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (7)[5]**,** white solid (62.2 mg, 49%). **^{1}H NMR (600 MHz, $CDCl_3$)** ^{1}H NMR (600 MHz, Chlorof orm-*d*) δ 8.43 – 8.30 (m, 2H), 7.83 (d, *J* = 5.6 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.46 (s, 2H), 2.49 (d, *J* = 14.5 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.66 (s, 3H), 1.49 (s, 1H), 1.43-1.

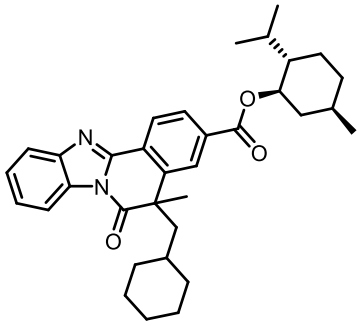
39 (m, 2H), 1.25 (s, 3H), 0.98 – 0.95 (m, 2H), 0.84 – 0.81 (m, 3H). **^{13}C NMR (150 M Hz, $CDCl_3$)** δ 172.7, 149.0, 144.0, 143.7, 131.4, 131.1, 129.8, 127.5, 126.3, 126.1, 125.8, 121.6, 119.8, 115.8, 77.3, 77.1, 76.9, 48.8, 48.3, 34.9, 34.2, 32.9, 31.8, 29.7, 25.94, 25.87.



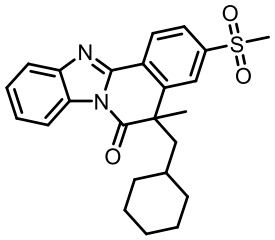
Methyl 5-(cyclohexylmethyl)-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline-3-carboxylate (8)[4], white solid (59.2 mg, 49%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.56 (d, *J* = 8.1 Hz, 1H), 8.39 (d, *J* = 4.8 Hz, 1H), 8.13 (d, *J* = 14.2 Hz, 2H), 7.86 (s, 1H), 7.50 – 7.45 (m, 2H), 3.99 (s, 3H), 2.52 – 2.48 (d, 8.1 Hz, 1H), 2.14 (d, *J* = 14.1 Hz, 1 H), 1.69 (s, 3H), 1.44 (d, *J* = 10.6 Hz, 1H), 1.39 (t, *J* = 13.0 Hz, 2H), 1.25 (s, 1H), 1.1 4 (s, 1H), 0.94 – 0.89 (m, 3H), 0.81 – 0.77 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 1 73.1, 166.3, 148.8, 144.1, 142.0, 132.7, 131.5, 128.4, 128.1, 126.4, 126.2, 126.1, 120.1, 11 5.9, 77.3, 77.1, 76.8, 52.7, 48.8, 48.5, 35.0, 34.2, 32.9, 31.7, 29.7, 25.92, 25.90, 25.85.



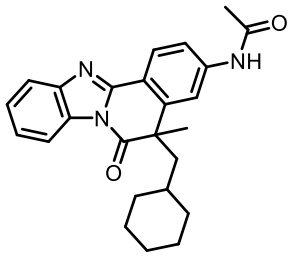
ethyl 5-(cyclohexylmethyl)-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline-3-carboxylate (9), white solid (68.7 mg, 55%)， m.p. 165-166 °C. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.56 (d, J = 8.0 Hz, 1H), 8.45 – 8.35 (m, 1H), 8.16 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.87 (s, 1H), 7.48 (s, 2H), 4.46 (s, 2H), 2.59 – 2.44 (m, 1H), 2.14 (d, J = 14.6 Hz, 1H), 1.71 (s, 3H), 1.46 (s, 4H), 1.40 (t, J = 12.7 Hz, 2H), 1.26 (s, 1H), 1.16 (d, J = 8.7 Hz, 1H), 1.02 – 0.89 (m, 3H), 0.85 – 0.79 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.1, 165.8, 148.8, 144.1, 142.0, 133.0, 131.5, 128.4, 128.1, 126.3, 126.1, 126.0, 120.1, 115.9, 77.3, 77.1, 76.8, 61.6, 48.8, 48.5, 35.0, 34.2, 32.9, 31.7, 25.9, 14.4. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{26}H_{29}N_2O_3^+$ 417.2173, Found 417.2170.



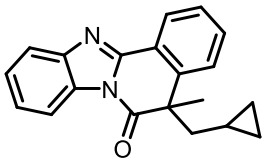
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 5-(cyclohexylmethyl)-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline-3-carboxylate (10)[4]**,** white solid (56.9 mg, 36%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.55 (d, J = 7.2 Hz, 1H), 8.40 (d, J = 4.8 Hz, 1H), 8.14 – 8.10 (m, 2H), 7.87 (d, J = 5.3 Hz, 1H), 7.48 (d, J = 3.3 Hz, 2H), 4.99 (t, J = 11.3 Hz, 1H), 2.59 – 2.44 (m, 1H), 2.20 – 2.13 (m, 2H), 2.10 – 1.96 (m, 1H), 1.76 (s, 2H), 1.70 (s, 3H), 1.63 – 1.61 (m, 3H), 1.47 (s, 1H), 1.42 – 1.40 (m, 2H), 1.29 – 1.26 (m, 3H), 1.18 – 1.15 (m, 1H), 0.96 (s, 9H), 0.84 – 0.79 (m, 6H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.5, 165.7, 149.2, 144.4, 142.4, 133.8, 133.6, 131.8, 128.7, 128.6, 128.5, 128.4, 126.4, 120.4, 116.3, 77.6, 77.4, 77.2, 76.1, 48.8, 47.6, 41.2, 35.2, 34.6, 34.5, 33.3, 32.4, 31.8, 30.1, 27.2, 27.0, 26.2, 24.0, 22.4, 21.1, 17.2, 17.0.



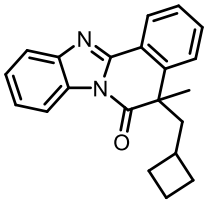
5-(cyclohexylmethyl)-5-methyl-3-(methylsulfonyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (11)[2]**,** white solid (95.3 mg, 75%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.71 (d, J = 7.6 Hz, 1H), 8.40 (d, J = 4.3 Hz, 1H), 8.06 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.89 (s, 1H), 7.51 (d, J = 3.3 Hz, 2H), 3.15 (s, 3H), 2.53 (d, J = 14.1 Hz, 1H), 2.12 (d, J = 14.3 Hz, 1H), 1.72 (s, 3H), 1.48 – 1.38 (m, 3H), 1.29 – 1.15 (m, 3H), 0.95 – 0.94 (m, 2H), 0.85 – 0.75 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 172.2, 147.8, 144.0, 143.2, 142.8, 131.4, 127.4, 127.2, 126.6, 126.4, 126.3, 126.0, 120.3, 116.0, 77.3, 77.1, 76.9, 48.8, 48.7, 44.5, 35.1, 34.2, 33.0, 31.5, 25.9, 25.83, 25.77.



N-(5-(cyclohexylmethyl)-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-3-yl)acetamide (12)[5]**,** white solid (79.4 mg, 66%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.42 (d, *J* = 8.5 Hz, 1H), 8.36 (d, *J* = 7.6 Hz, 1H), 7.91 (s, 1H), 7.80 (d, *J* = 9.5 Hz, 1H), 7.52 (s, 1H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.42 (d, *J* = 9.1 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.26 (s, 3H), 2.06 (d, *J* = 14.7 Hz, 1H), 1.66 (s, 3H), 1.47 – 1.40(d, *J* = 39.0 Hz, 2H), 1.29 (d, *J* = 11.3 Hz, 2H), 1.17 (s, 1H), 1.02 (s, 1H), 0.94 – 0.91 (m, 2H), 0.82 – 0.80 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.5, 168.6, 149.6, 143.4, 141.1, 131.4, 126.9, 125.9, 125.4, 119.5 118.7, 117.0., 115.8, 77.3, 77.1, 76.8, 48.8, 48.6, 34.9, 34.2, 32.9, 31.9, 29.7, 25.9, 25.0.

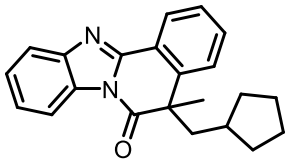


5-(cyclopropylmethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (13)[3]**,** white solid (51.6 mg, 57%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, J = 7.9 Hz, 1H), 8.38 (d, J = 6.9 Hz, 1H), 7.83 (d, J = 6.9 Hz, 1H), 7.58 (t, J = 8.2 Hz, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.45 – 7.41 (m, 2H), 2.20 – 2.16 (m, 1H), 2.02 – 1.99 (m, 1H), 1.77 (s, 3H), 0.20 – 0.13 (m, 1H), 0.19 – 0.14 (m, 1H), -0.04 – -0.10 (m, 2H), -0.21 – -0.25 (m, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.8, 150.3, 144.2, 142.2, 131.8, 131.6, 127.8, 126.4, 125.9, 125.7, 123.4, 119.9, 115.7, 77.4, 77.2, 77.0, 49.9, 49.7, 27.0, 7.00, 4.0, 3.8.

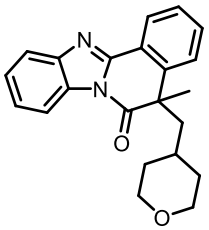


5-(cyclobutylmethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (14)[3]**,** white solid (42.7 mg, 45%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.47 (d, J = 7.6 Hz, 1H), 8.36 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 7.3 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.47 (t, J = 7.1 Hz,

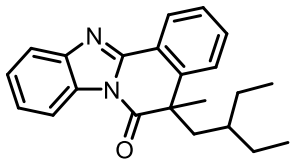
2H), 7.43 (pd, J = 7.3, 1.3 Hz, 2H), 2.47 (m, 1H), 2.08 (m, 1H), 1.88 – 1.83 (m, 1H), 1.74 (s, 3H), 1.51 – 1.42 (m, 5H), 1.33 – 1.27 (m, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.3, 150.0, 144.1, 141.8, 131.6, 131.4, 127.6, 126.5, 125.82, 125.75, 125.5, 122.9, 119. 8, 115.7, 77.3, 77.0, 76.8, 51.3, 48.6, 32.9, 28.9, 28.5, 27.9, 18.6.



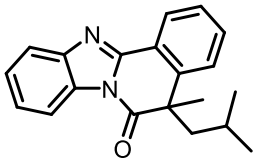
5-(cyclopentylmethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (15)[3]**,** white solid (54.5 mg, 55%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, J = 8.1 Hz, 1H), 8.39 (d, J = 7.3 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.43 (q, J = 7.2 Hz, 2H), 2.54 – 2.51 (m, 1H), 2.20 – 2.17 (m, 1H), 1.73 (s, 3 H), 1.40 – 1.29 (m, 3H), 1.25 – 1.16 (m, 4H), 0.98 – 0.92 (m, 1H), 0.83 – 0.76 (m, 1 H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.6, 149.9, 144.1, 142.1, 131.6, 131.4, 127.6, 126. 6, 125.9, 125.5, 122.8, 119.8, 115.8, 77.3, 77.0, 76.8, 49.2, 49.1, 37.5, 33.6, 32.4, 30.1, 2 4.9, 24.6.



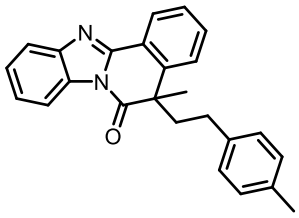
5-methyl-5-((tetrahydro-2H-pyran-4-yl)methyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-o ne (16)[5]**,** white solid (55.3 mg, 53%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.50 (d, J = 7.8, Hz, 1H), 8.38 (d, J = 6.9 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.5 1 – 7.47 (m, 2H), 7.47 – 7.43 (m, 2H), 3.75 – 3.61 (m, 2H), 3.03 (t, J = 11.6 Hz, 1H), 2.97 (t, J = 11.5 Hz, 1H), 2.56 – 2.52 (m, 1H), 2.11 (d, J = 14.4 Hz, 1H), 1.69 (s, 3H), 1.26 – 1.21 (m, 2H), 1.17 – 1.03 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.2, 149. 6, 144.1, 141.6, 131.8, 131.4, 127.8, 126.5, 126.1, 126.0, 125.7, 122.6, 119.8, 115.8, 77.3, 77.0, 76.8, 67.5, 48.5, 48.2, 33.8, 32.9, 32.5, 31.7.



5-(2-ethylbutyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (17)[3]**,** yellow oil (59.9 mg, 60%). **^{1}H NMR (600 MHz, CDCl$_3$)** 1H NMR (600 MHz, Chloroform-d) δ 8.51 – 8.46 (m, 1H), 8.40 – 8.34 (m, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.50 – 7.41 (m, 4H), 2.42 – 2.39 (m, 1H), 2.02 – 1.99 (m, 1H), 1.73 (s, 3H), 0.99 – 0.88 (m, 5H), 0.59 – 0.53 (m, 5H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 173.5, 149.9, 144.1, 141.9, 131.9, 131.6, 127.6, 126.7, 125.85, 125.82, 125.5, 122.9, 119.7, 115.7, 77.2, 77.0, 76.8, 48.7, 46.4, 37.3, 29.9, 25.8, 25.3, 10.3, 10.0.

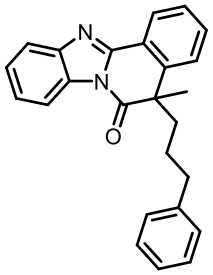


6-isobutyl-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (18)[3]**,** yellow oil (64.8 mg, 71%). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.50 (d, J = 7.6 Hz, 1H), 8.39 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 7.1 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.51 – 7.41 (m, 4H), 2.48 – 2.44 (m, 1H), 2.10 – 2.06 (m,f 1H), 1.69 (s, 3H), 1.33 – 1.27 (m, 1H), 0.63 (d, J = 6.7 Hz, 3H), 0.57 (d, J = 6.6 Hz, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 173.6, 149.8, 144.1, 141.8, 131.6, 131.4, 127.6, 126.6, 126.0, 125.9, 125.5, 122.8, 119.8, 115.8, 77.3, 77.0, 76.8, 50.6, 48.6, 31.4, 25.7, 23.9, 22.4.

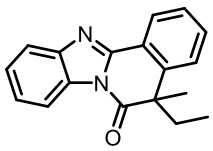


5-methyl-5-(4-methylphenethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (19)[6]**,** white solid (56.2 mg, 51%). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.51 (d, *J* = 7.0 Hz, 1H), 8.27 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.62 (t, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.44 – 73.38 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 2.85 – 2.79 (m, 1H), 2.37 – 2.14 (m, 4H), 2.08 (s, 3H), 1.75 (s, 1H), 1.73 (s, 3H). **^{13}C**

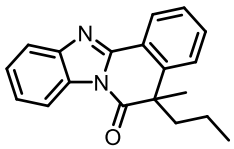
NMR (150 MHz, $CDCl_3$) δ 173.0, 149.8, 144.0, 141.4, 136.8, 135.7, 131.9, 131.3, 128.8, 128.1, 127.8, 126.1, 126.0, 125.8, 125.4, 123.3, 119.7, 115.7, 77.3, 77.0, 76.8, 49.1, 44.3, 31.2, 29.7, 29.0, 20.8.



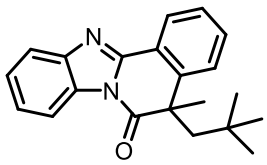
5-methyl-5-(3-phenylpropyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (20)[2]**,** white so lid (59.3 mg, 54%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.47 (d, J = 7.8 Hz, 1H), 8.37 (d, J = 6.6 Hz, 1H), 7.81 (d, J = 6.5 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.48 – 7.45 (m, 1H), 7.44 – 7.41 (m, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.17 (t, J = 7.4 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H), 6.95 (d, J = 7.2 Hz, 2H), 2.55 – 2.50 (m, 1H), 2.45 – 2.41 (m, 1H), 2.03 – 1.98 (m, 1H), 1.74 (s, 1H), 1.69 (s, 3H), 1.36 – 1.29 (m, 1H), 1.19 – 1.11 (m, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.3, 149.9, 144.1, 141.6, 141.2, 131.9, 131.3, 128.29, 128.27, 128.25, 127.7, 126.0, 125.92, 125.90, 125.6, 123.0, 119.8, 115.7, 77.3, 77.1, 76.9, 49.4, 42.2, 35.6, 29.2, 26.6.



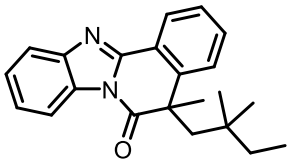
5-ethyl-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (21)[3]**,** white solid (53.8 mg, 65%). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.52 – 8.45 (m, 1H), 8.40 – 8.33 (m, 1H), 7.86 – 7.79 (m, 1H), 7.61 – 7.55 (m, 1H), 7.52 – 7.40 (m, 4H), 2.51 – 2.39 (m, 1H), 2.06 – 1.96 (m, 1H), 1.74 (s, 3H), 0.58 (t, J = 7.4 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.4, 150.0, 144.1, 141.6, 131.9, 131.3, 127.7, 126.1, 125.9, 125.8, 125.5, 123.3, 119.8, 115.7, 77.5, 77.0, 76.6, 50.1, 36.4, 28.3, 9.6.



5-methyl-5-propylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (22)[3]**,** white solid (53.9 mg, 62%). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1H NMR (300 MHz, Chloroform-d) δ 8.51 – 8.44 (m, 1H), 8.38 – 8.35 (m, 1H), 7.84 – 7.80 (m, 1H), 7.63 – 7.53 (m, 1H), 7.51 – 7. 39 (m, 4H), 2.47 – 2.29 (m, 1H), 2.00 – 1.90 (m, 1H), 1.73 (s, 3H), 1.01 – 0.81 (m, 2 H), 0.74 (t, J = 7.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.6, 150.4, 144.2, 142.0, 132.0, 131.4, 127.7, 126.2, 126.0, 125.9, 125.6, 123.1, 119.9, 115.8, 77.6, 77.2, 76.7, 49.6, 45.7, 28.8, 18.6, 14.1.

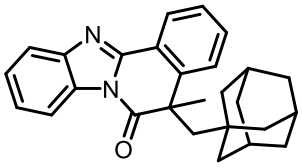


5-methyl-5-neopentylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (23)[3]**,** white solid (38. 7 mg, 41%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, J = 7.7 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.53 (t, J = 8.5 Hz, 2H), 7.49 – 7.41 (m, 3H), 2.64 (d, J = 14.5 Hz, 1H), 2.17 (d, J = 14.5 Hz, 1H), 1.71 (s, 3H), 0.54 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.5, 149.8, 144.1, 142.0, 131.5, 131.2, 127.64, 127.57, 125.9, 125. 5, 122.4, 119.7, 115.8, 77.2, 77.0, 76.8, 55.3, 47.7, 33.1, 32.0, 30.8.

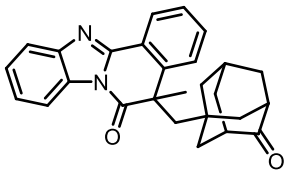


5-(2,2-dimethylbutyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (24)[3]**,** white solid (72.7 mg, 73%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, J = 7.7 Hz, 1H), 8.39 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 6.4 Hz, 2H), 7.48 – 7.41 (m, 3H), 2.61 (d, J = 14.5 Hz, 1H), 2.16 (d, J = 14.5 Hz, 1H), 1.71 (s, 3H), 1.01 – 0.95 (m, 1H), 0.93 – 0.87 (m, 1H), 0.68 (t, J = 7.4 Hz, 3H), 0.48 (s, 3H), 0.36 (s, 3H). **^{13}C N MR (150 MHz, $CDCl_3$)** δ 173.5, 149.8, 144.1, 142.2, 131.5, 131.1, 127.6, 127.5, 125.89, 125.86, 125.5, 122.4, 119.7, 115.8, 77.2, 77.0, 76.8, 53.2, 47.5, 36.6, 34.5, 33.2, 27.6, 26.

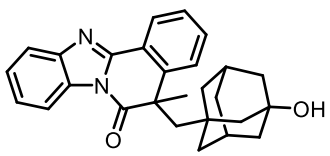
9, 8.3.



5-(((3r,5r,7r)-adamantan-1-yl)methyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (25)[3]**,** white solid (99.8 mg, 84%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, J = 7.7 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.52 (s, 2H), 7.50 – 7.42 (m, 3H), 2.51 (d, J = 14.6 Hz, 1H), 2.07 (d, J = 14.6 Hz, 1H), 1.67 (s, 3H), 1.63 (s, 3 H), 1.43 (d, J = 12.0 Hz, 3H), 1.30 (d, J = 11.6 Hz, 3H), 1.16 – 1.08 (m, 6H). **^{13}C NM R (150 MHz, $CDCl_3$)** δ 173.5, 149.8, 144.1, 142.3, 131.5, 131.1, 127.6, 125.9, 125.5, 12 2.1, 119.7, 115.9, 77.2, 77.0, 76.8, 56.2, 46.9, 43.5, 36.5, 34.2, 33.7, 28.4.



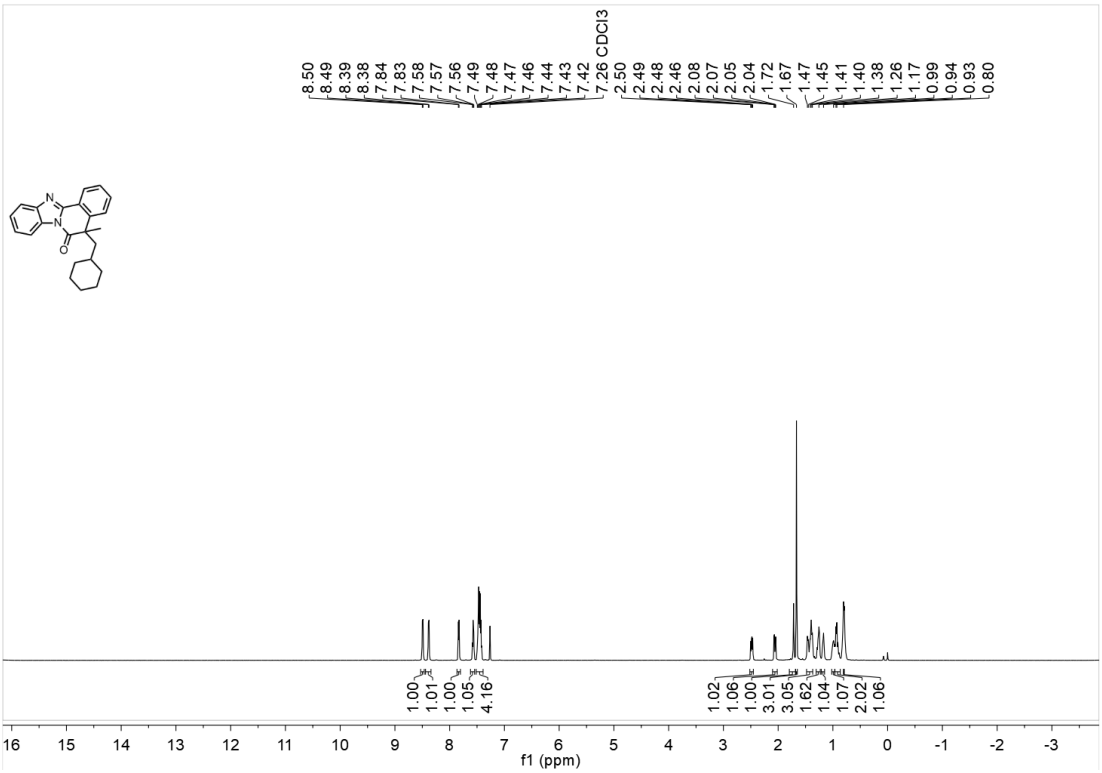
5-methyl-5-(((1s,3R,5S,7s)-4-oxoadamantan-1-yl)methyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (26)[3]**,** white solid (61.5 mg, 50%). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.50 (d, J = 7.0 Hz, 1H), 8.38 (d, J = 6.7 Hz, 1H), 7.84 (d, J = 6.7 Hz, 1H), 7.56 – 7.45 (m, 5 H), 2.64 (d, J = 14.6 Hz, 1H), 2.24 (d, J = 16.5 Hz, 2H), 2.15 – 2.11 (m, 1H), 1.80 (s, 1H), 1.68 (s, 6H), 1.62 – 1.53 (m, 2H), 1.52 – 1.38 (m, 3H), 1.33 – 1.25 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 217.6, 173.2, 141.6, 131.5, 128.1, 127.4, 126.30, 126.25, 125. 9, 122.2, 120.0, 116.0, 77.6, 77.2, 76.7, 53.7, 47.0, 46.4, 46.2, 45.1, 44.4, 41.8, 38.34, 38. 31, 34.2, 33.9, 27.7.



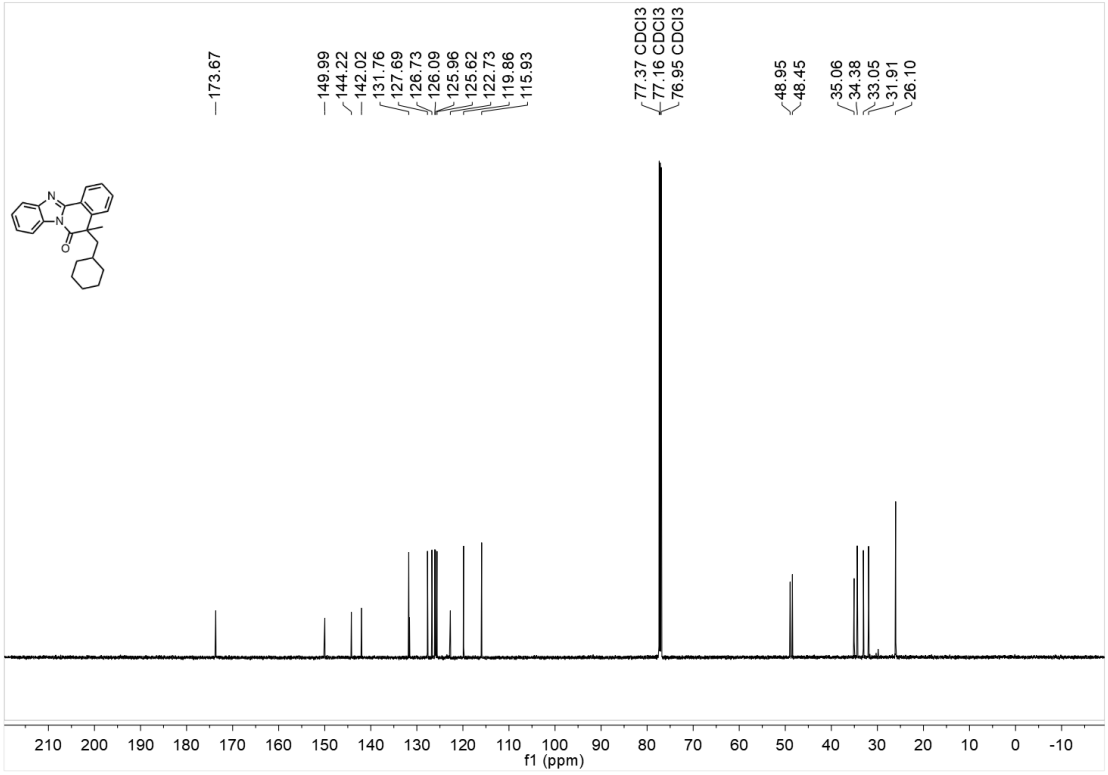
5-(((1s,3s,5R,7S)-3-hydroxyadamantan-1-yl)methyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (27)[3]**,** white solid (68.1 mg, 55%). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.53

– 8.46 (m, 1H), 8.43 – 8.34 (m, 1H), 7.88 – 7.80 (m, 1H), 7.57 – 7.41 (m, 5H), 2.60 (d, *J* = 14.6 Hz, 1H), 2.14 (d, *J* = 14.6 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.67 (s, 3H), 1.43 – 1.26 (m, 5H), 1.16 – 0.93 (m, 7H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.4, 149.8, 144.1, 142.1, 131.5, 131.4, 127.9, 127.6, 126.1, 126.0, 125.8, 122.1, 119.9, 116.0, 77.6, 77.2, 7 6.7, 68.6, 55.0, 51.7, 47.0, 44.6, 44.1, 41.7, 41.0, 37.8, 35.0, 33.9, 30.7, 30.5.

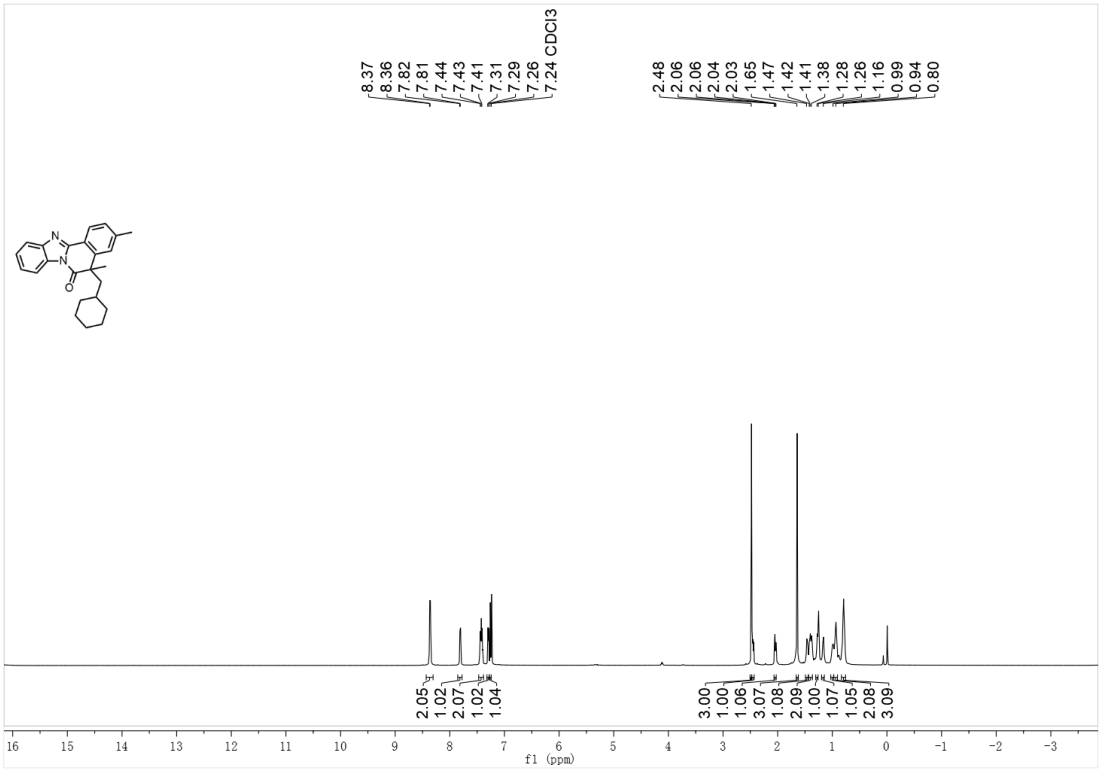
7. Spectra of prepared compounds



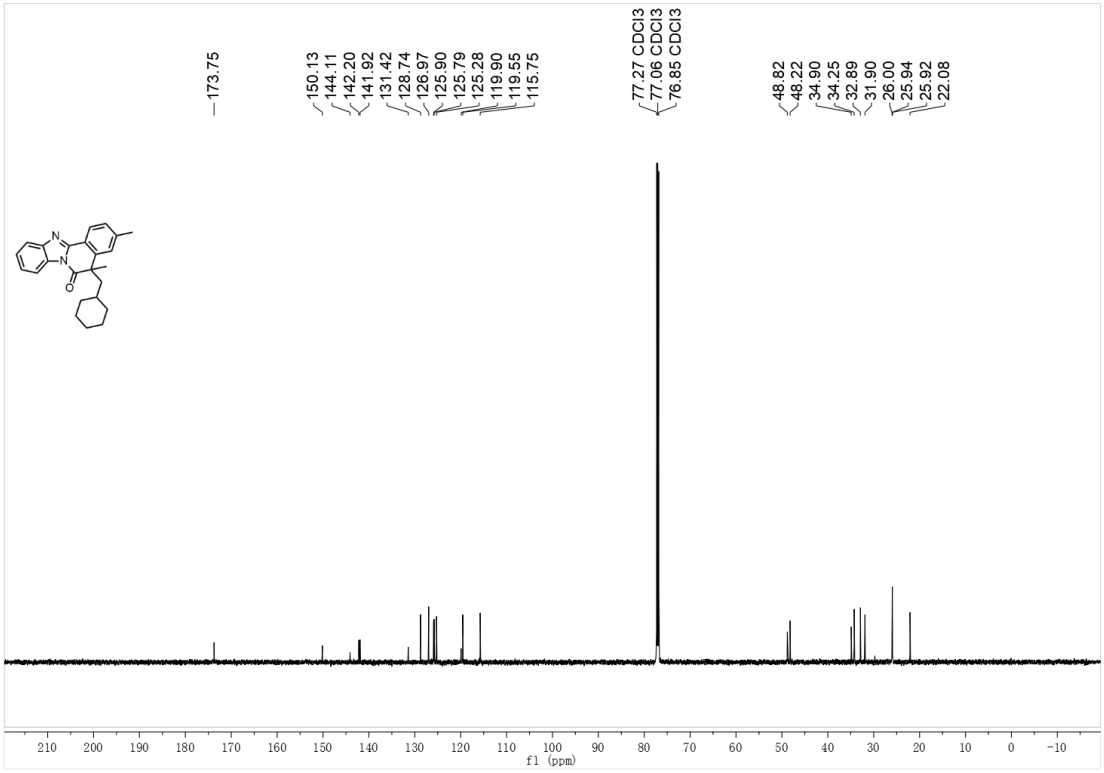
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3**



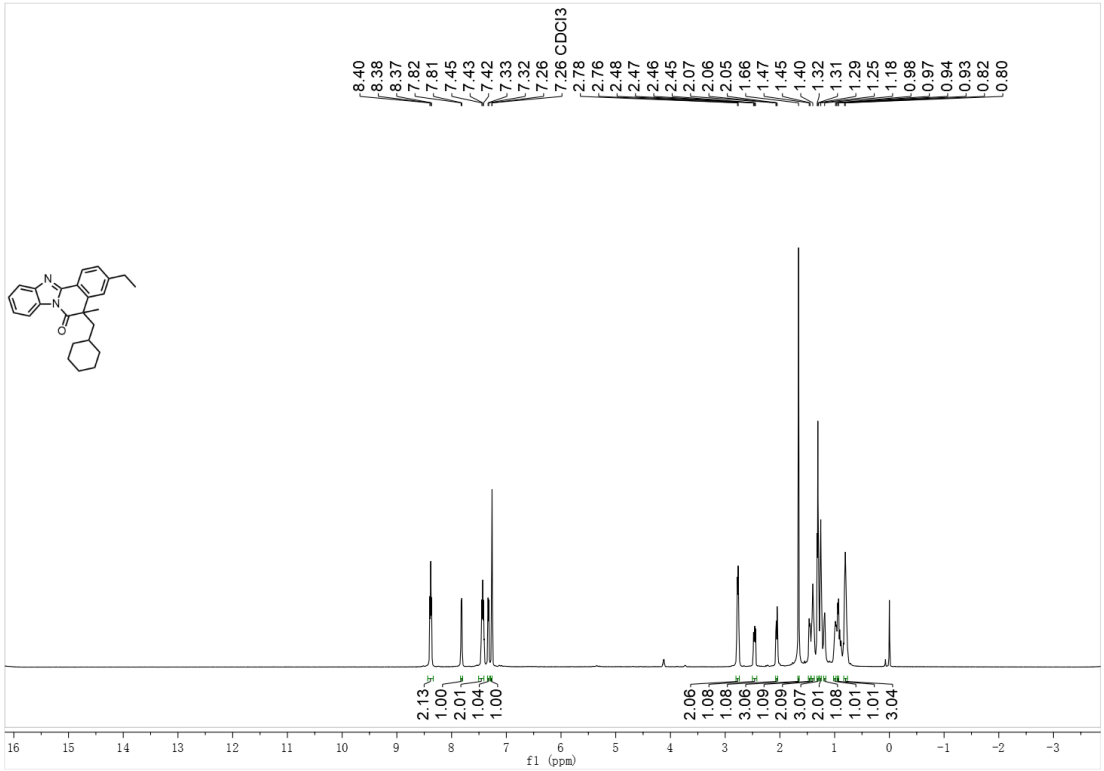
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **3**



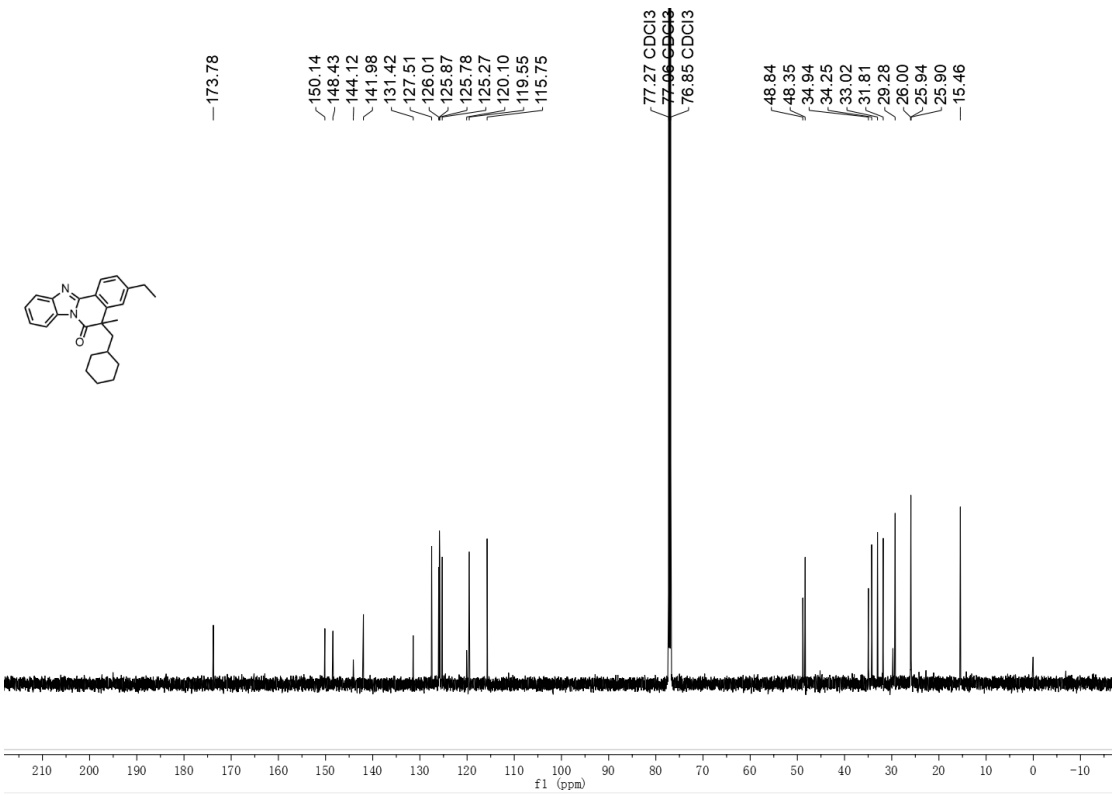
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4**



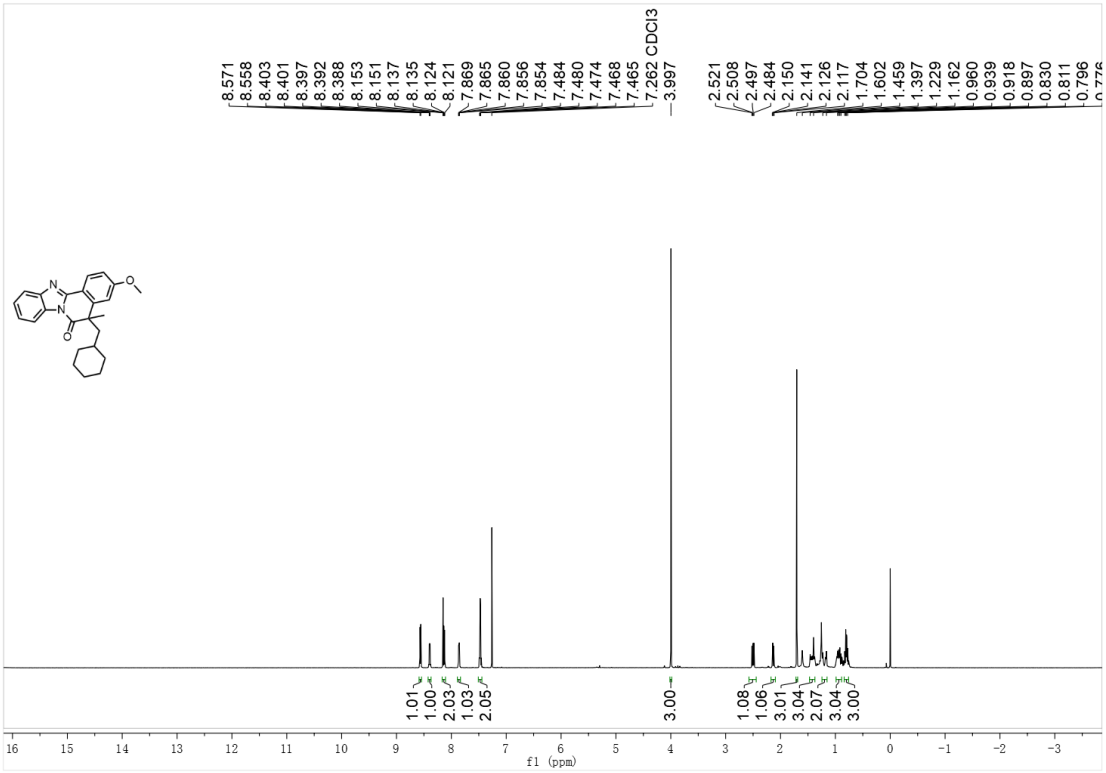
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **4**



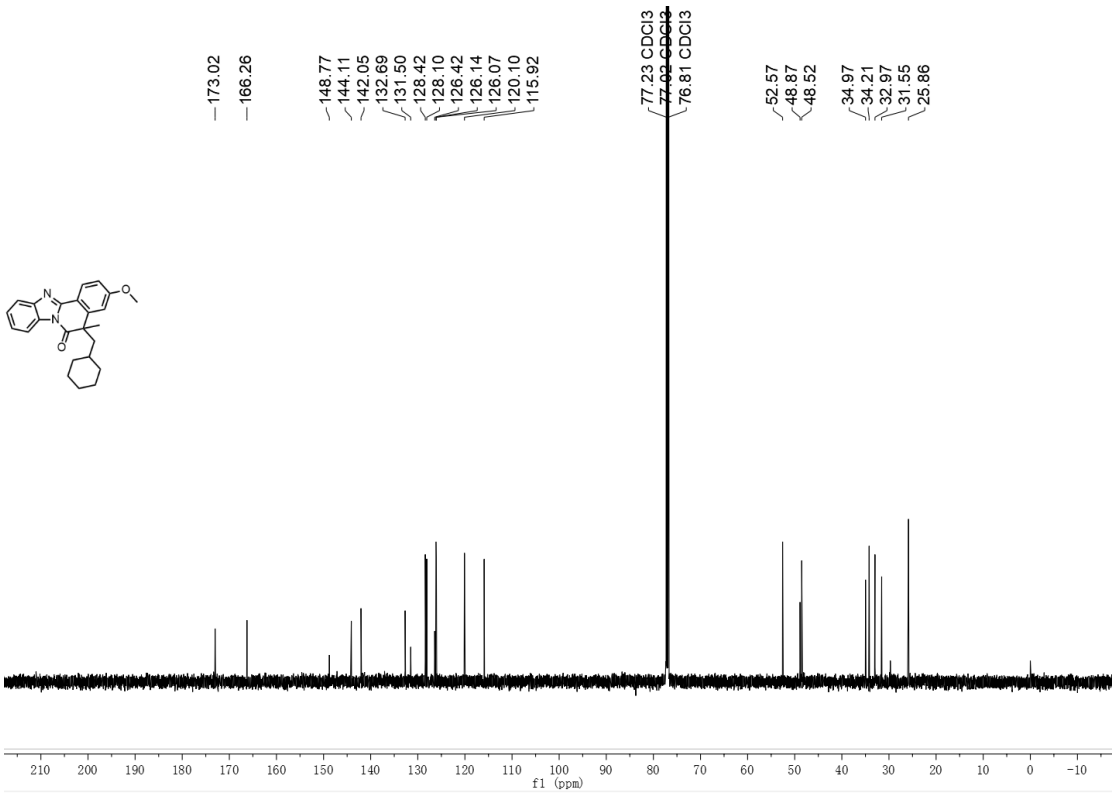
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5**



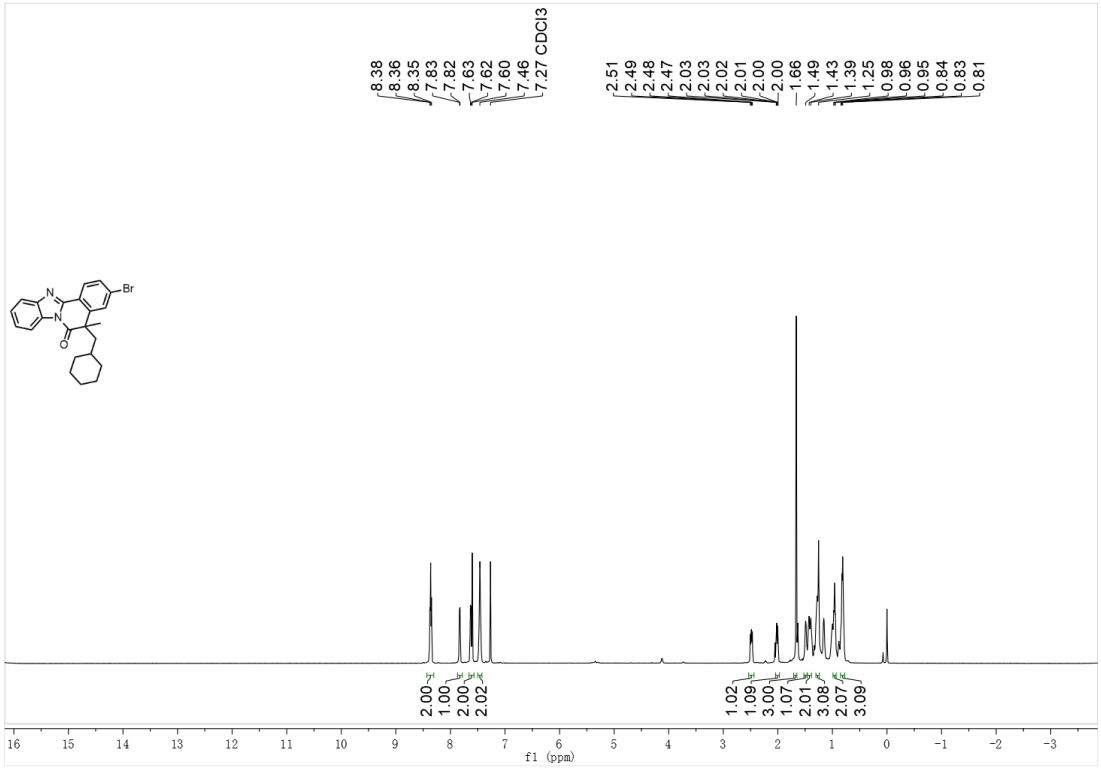
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **5**



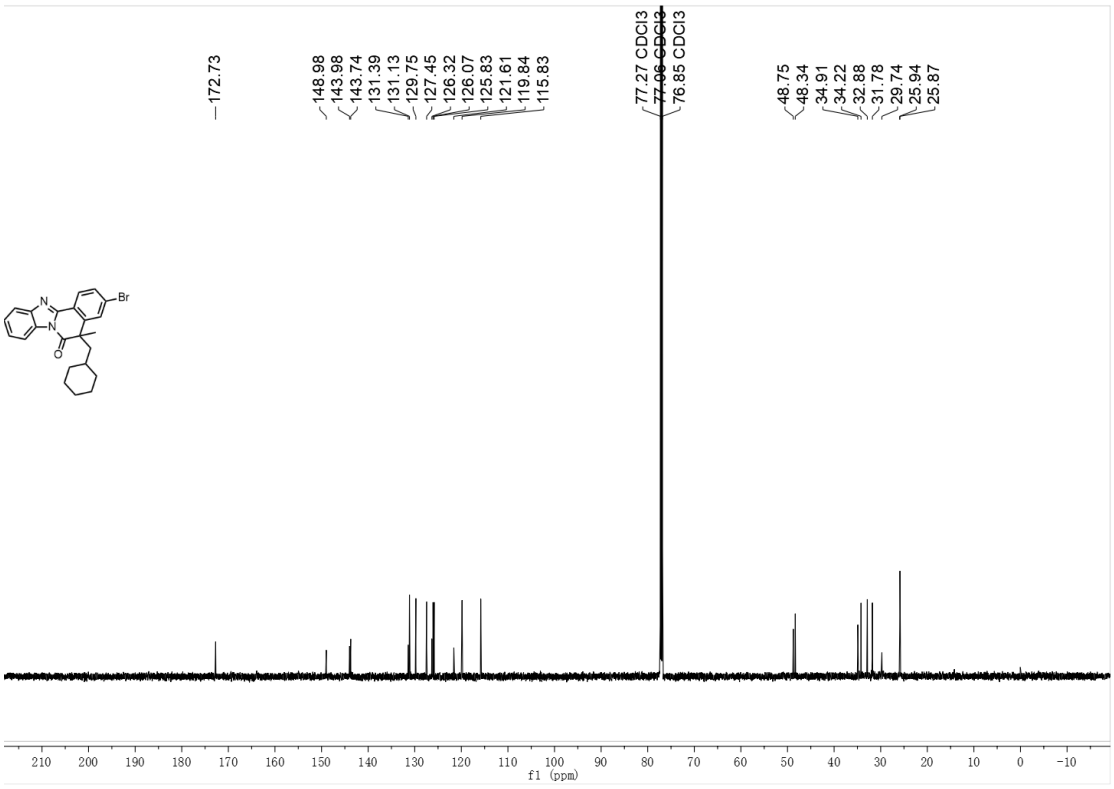
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6**



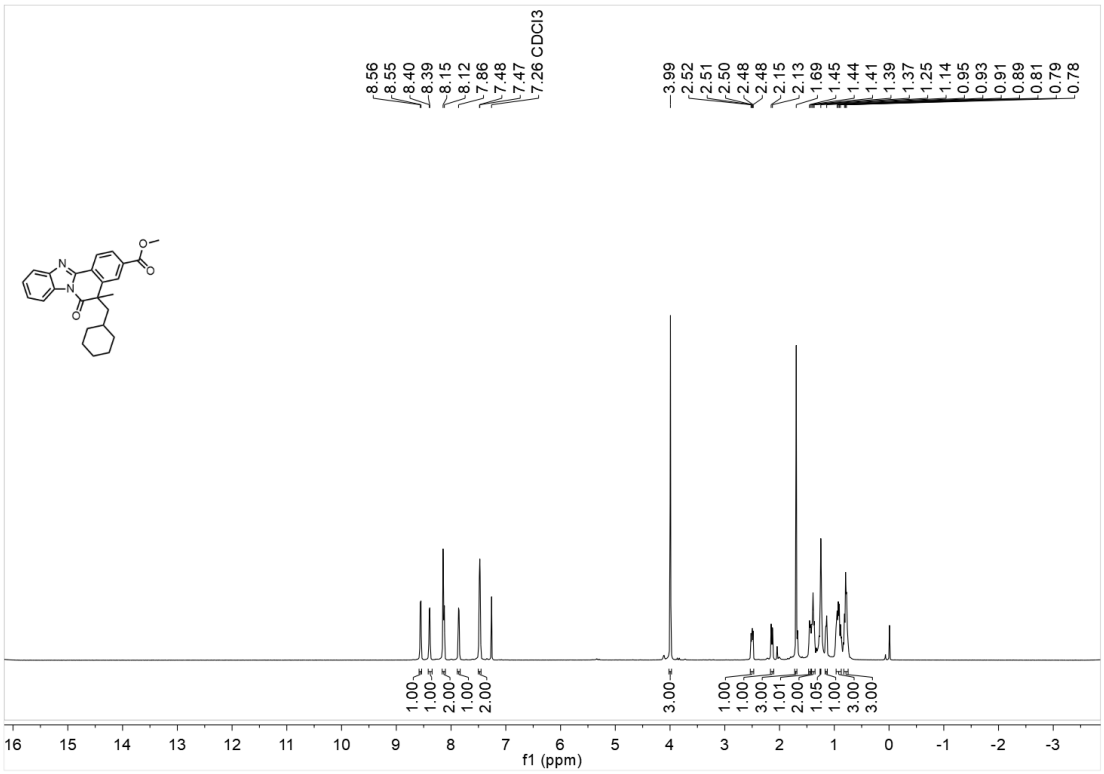
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6**



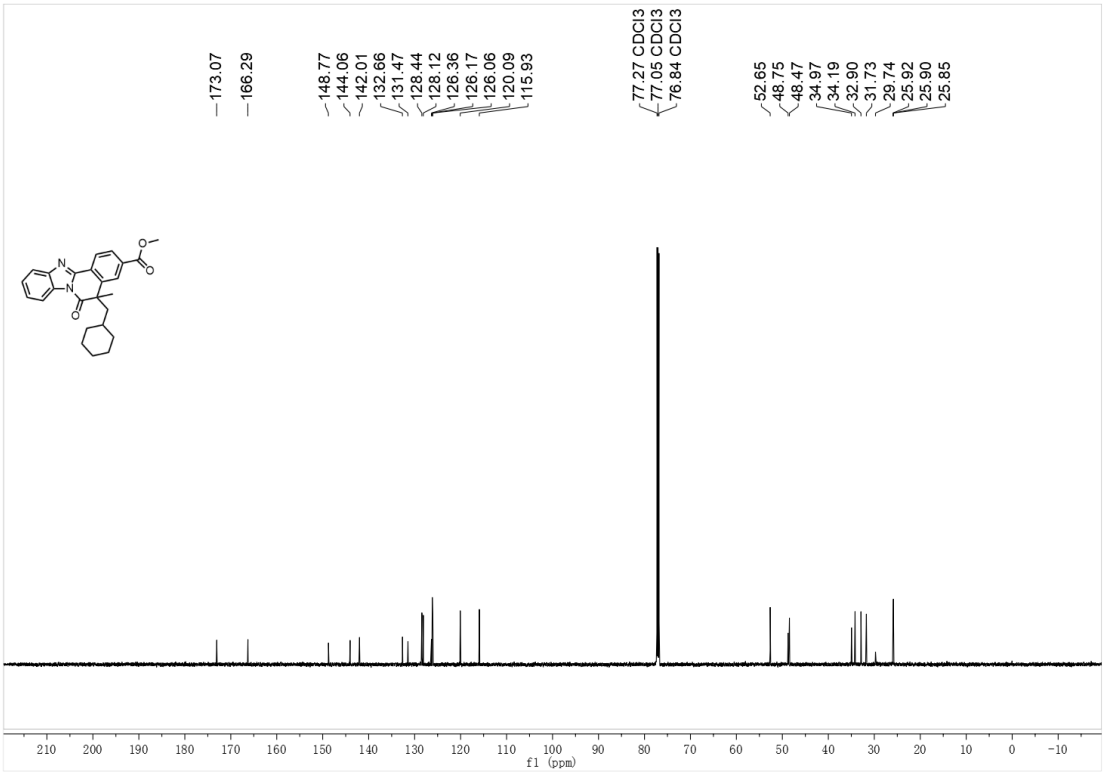
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **7**



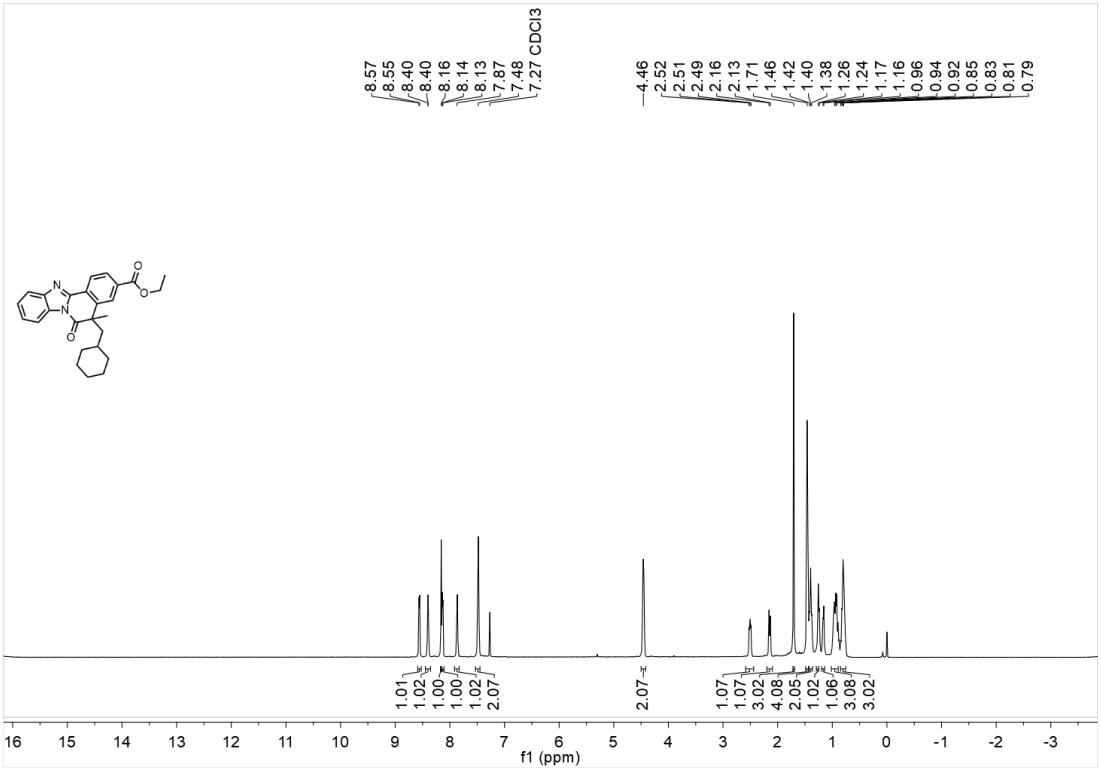
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **7**



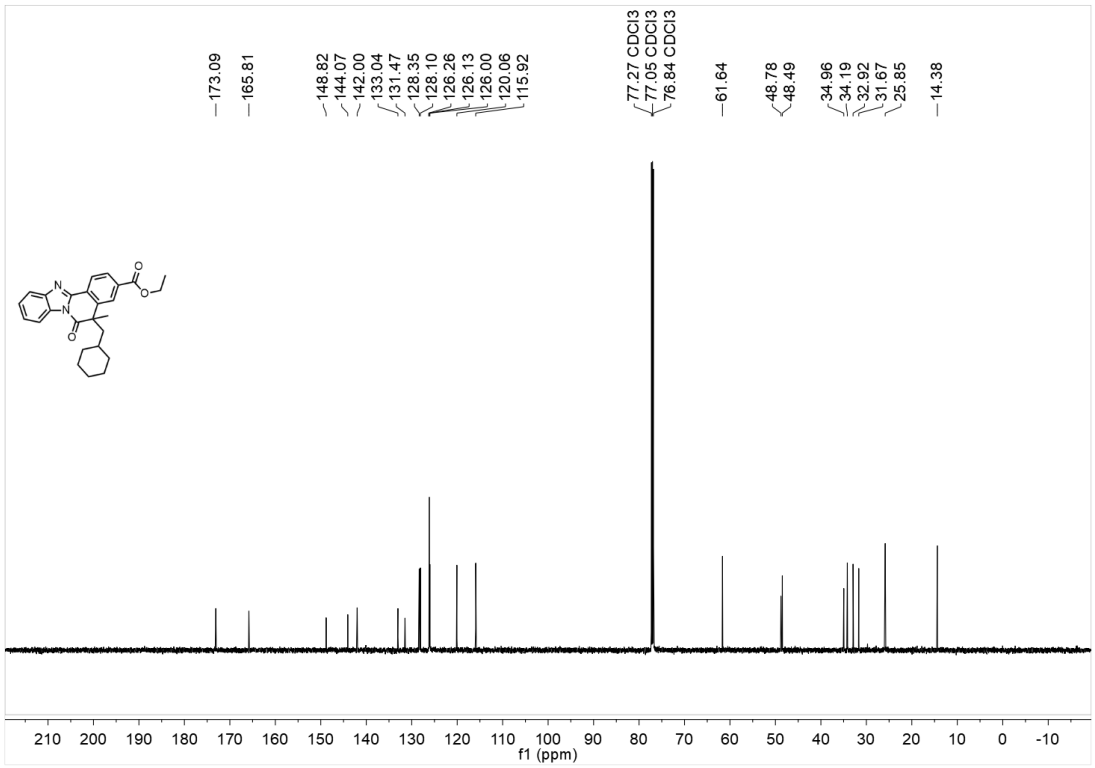
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **8**



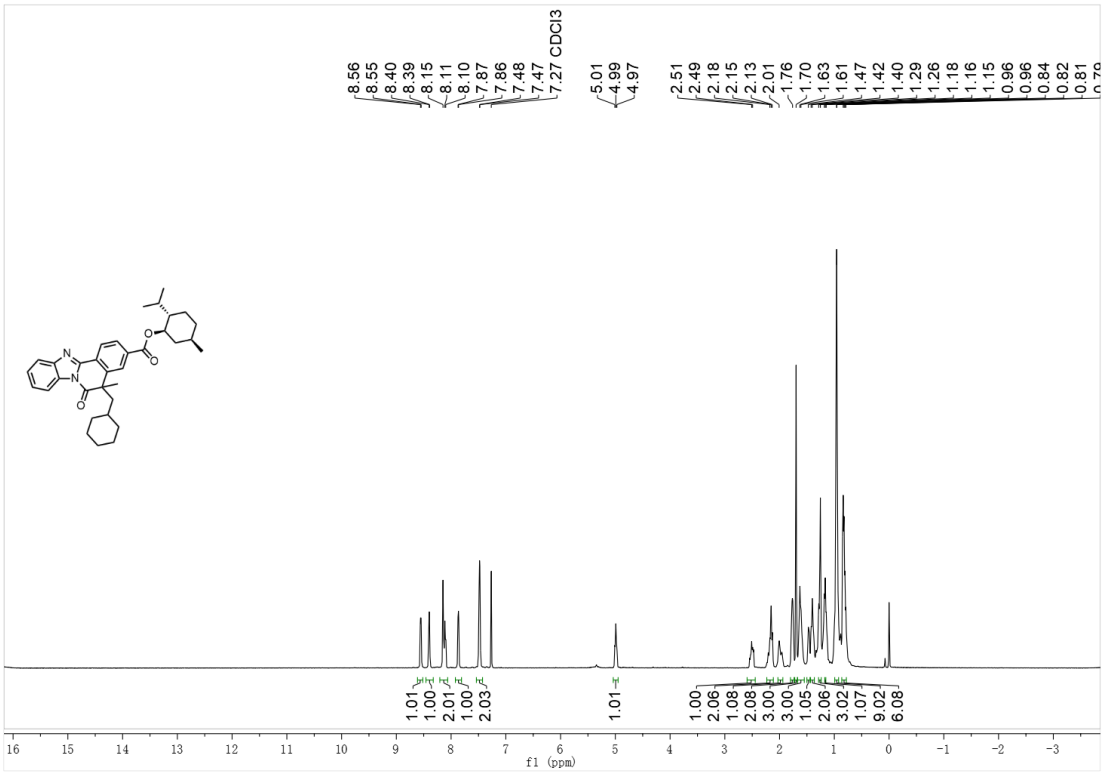
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **8**



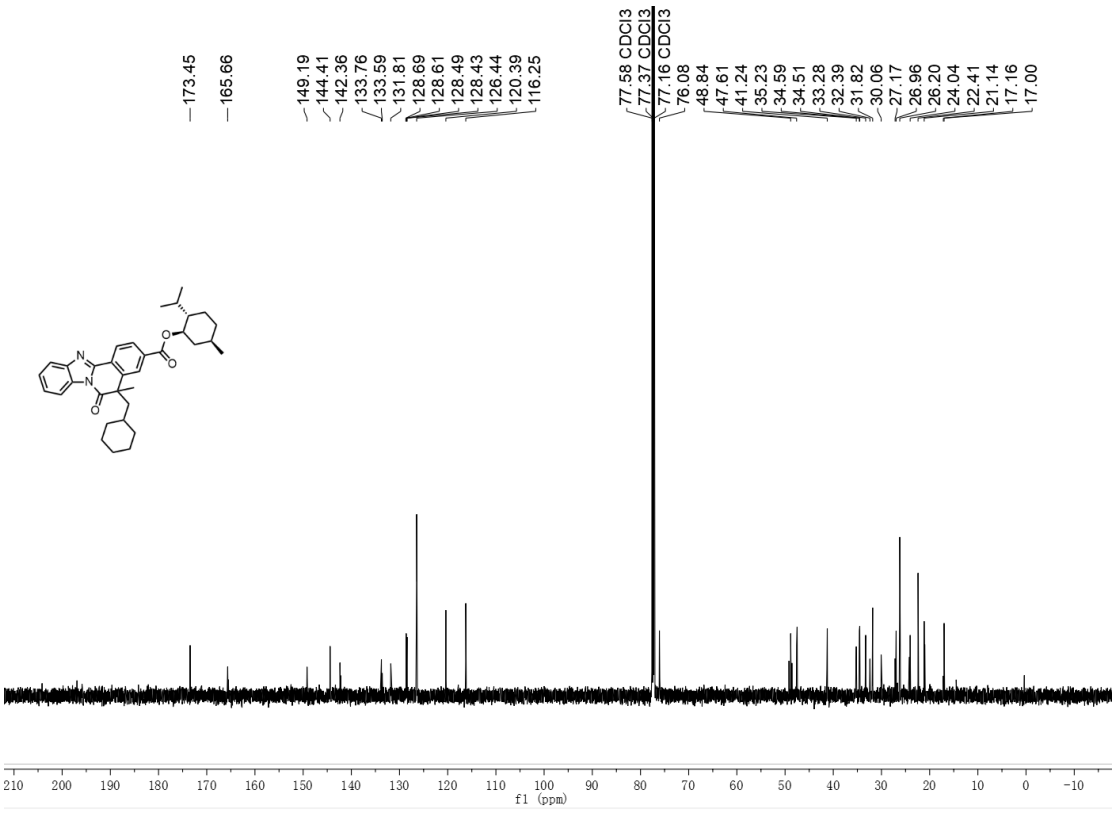
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9**



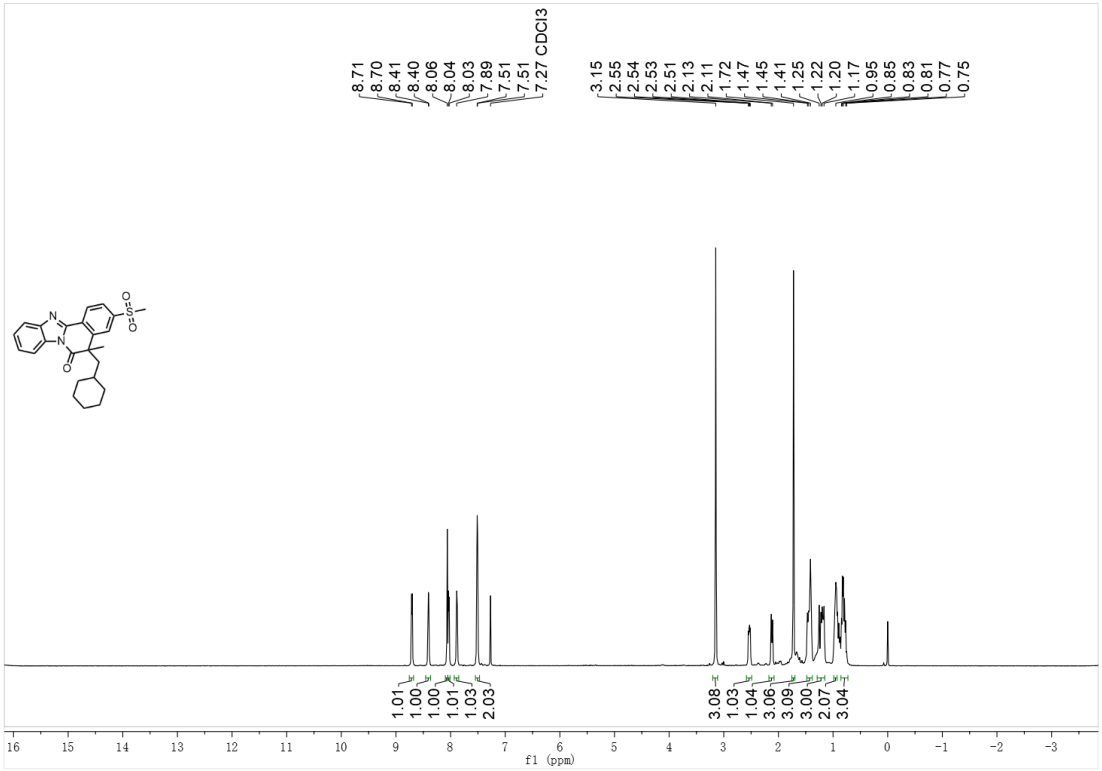
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **9**



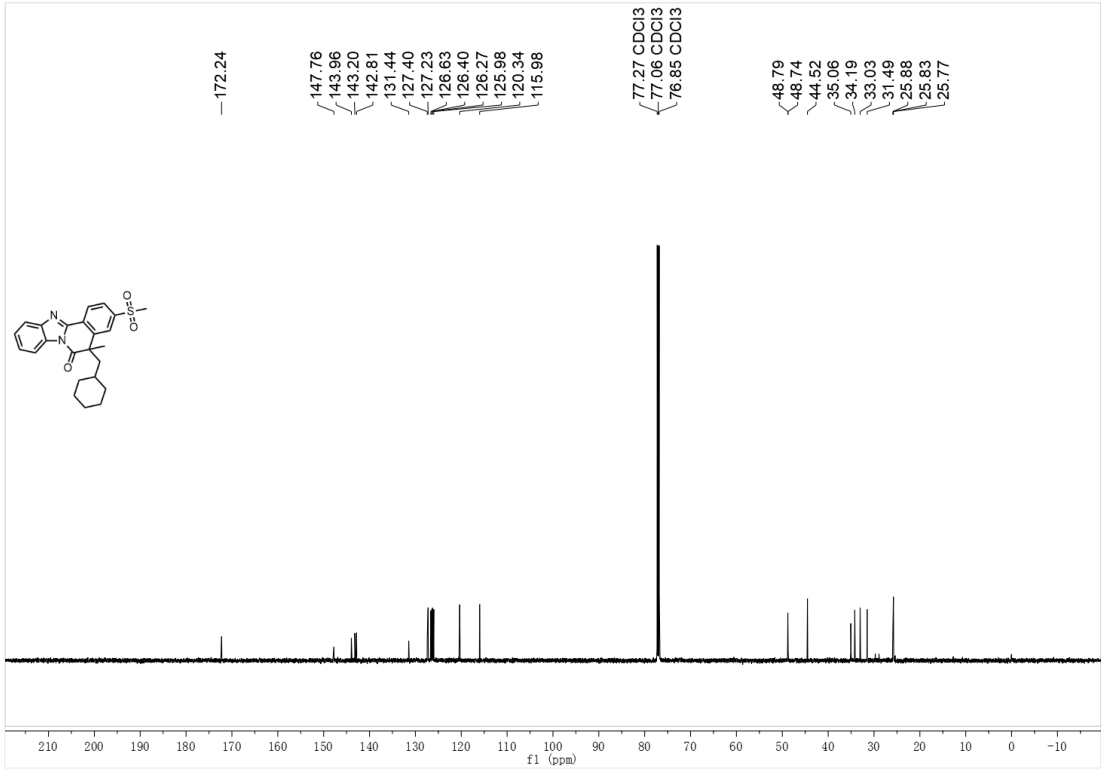
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **10**



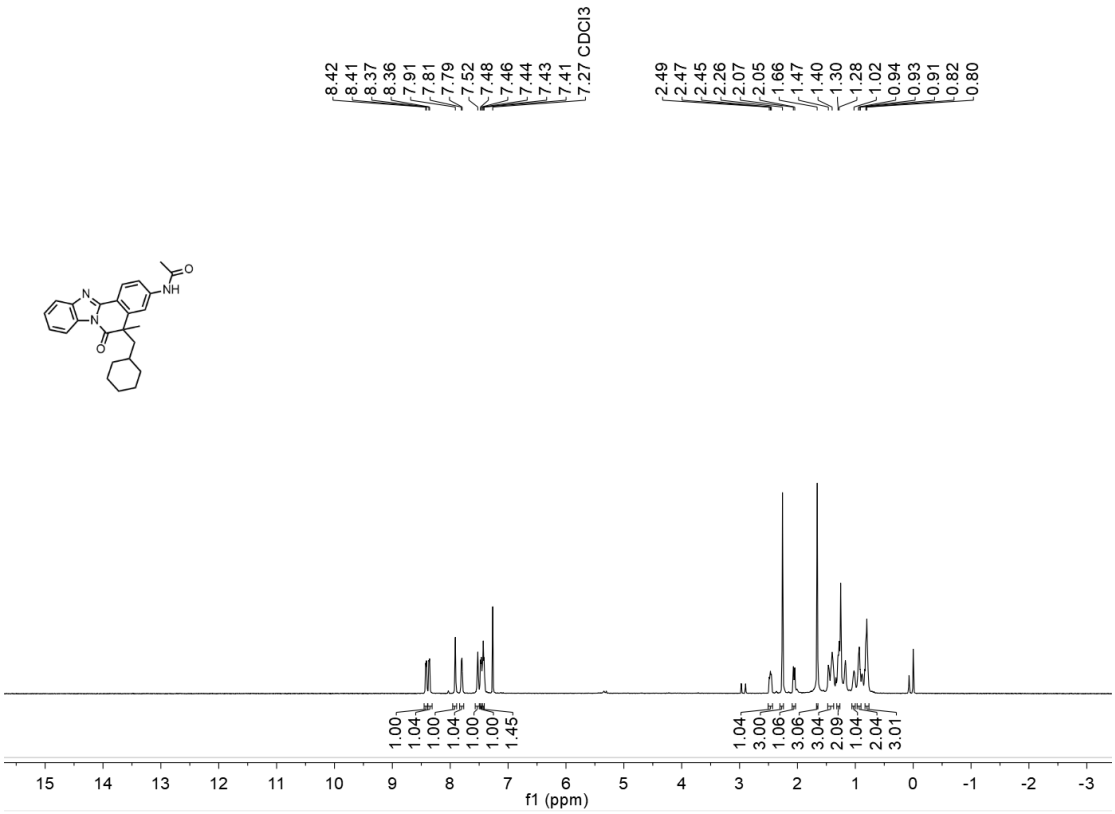
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **10**



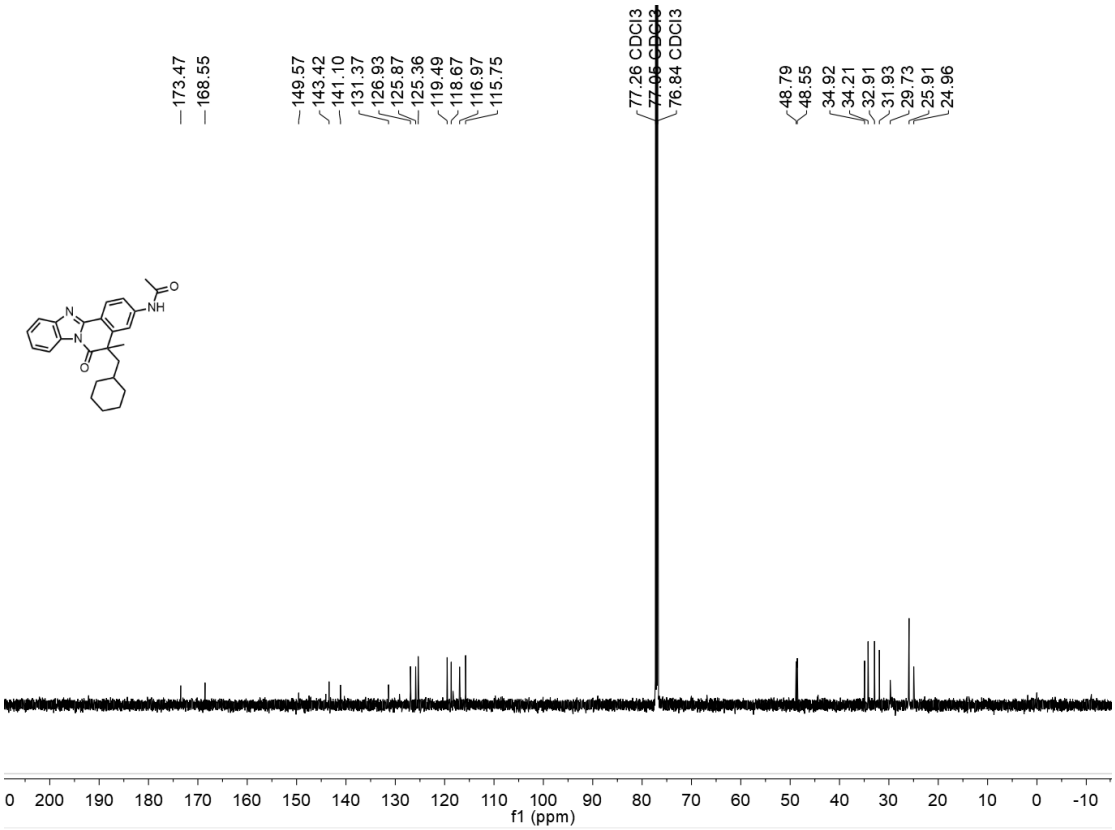
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **11**



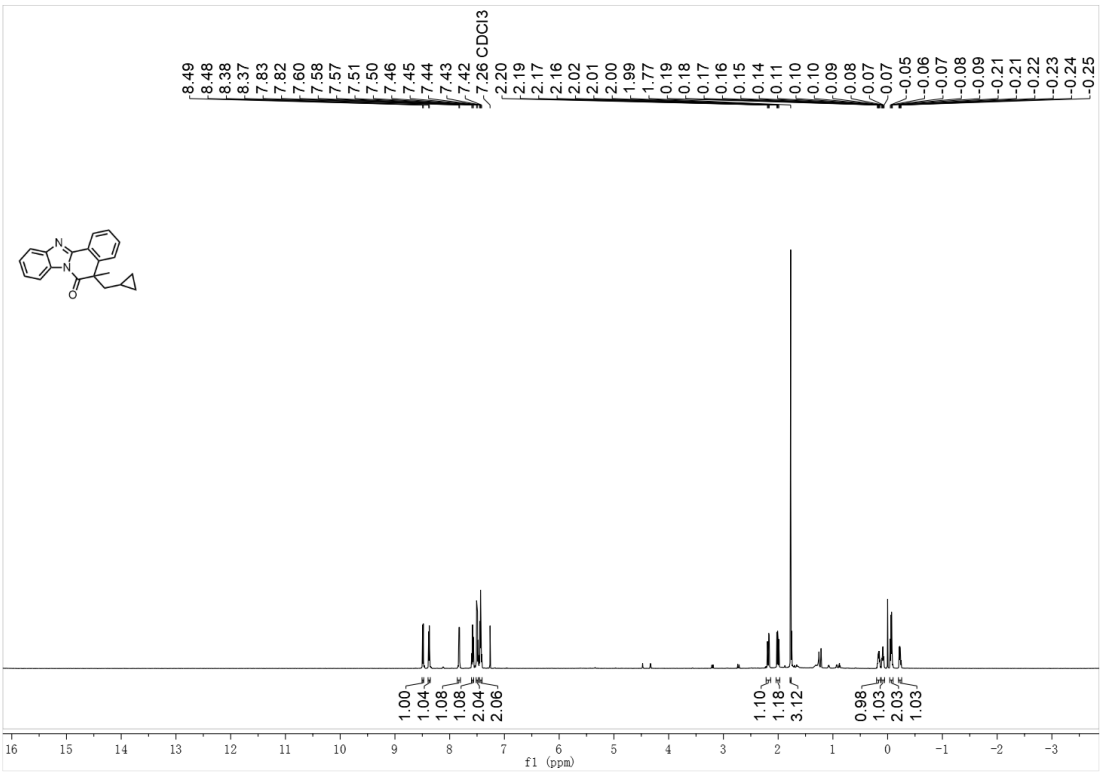
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **11**



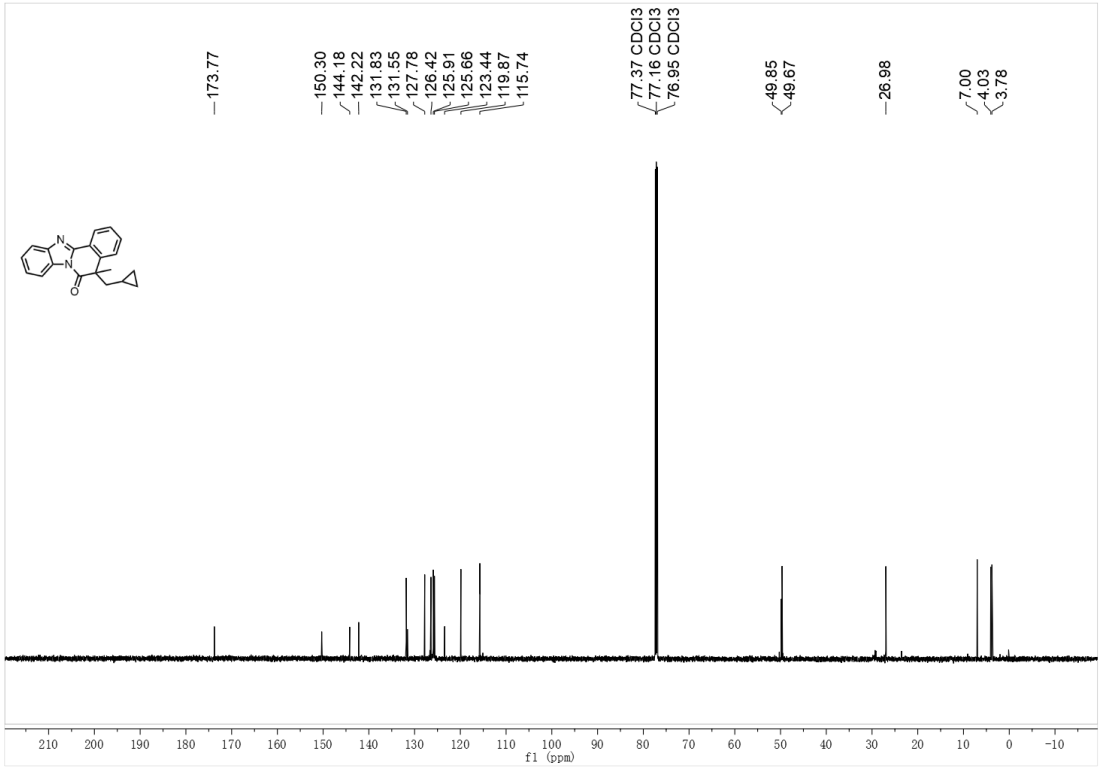
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **12**



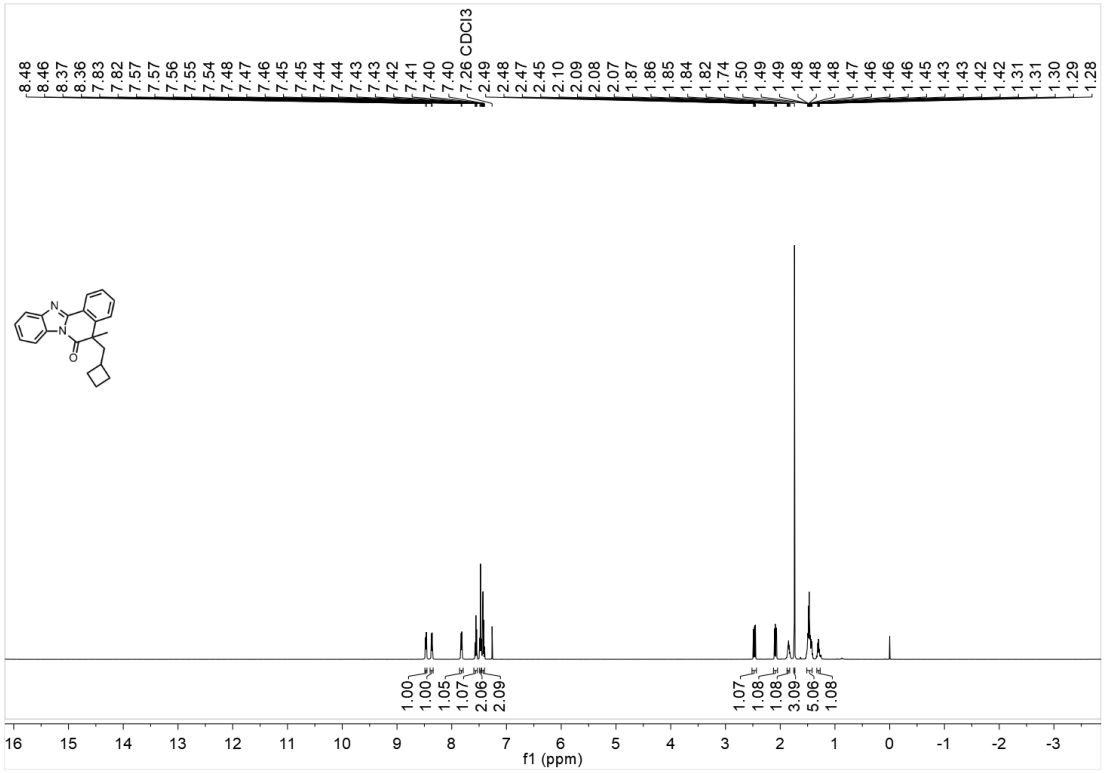
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **12**



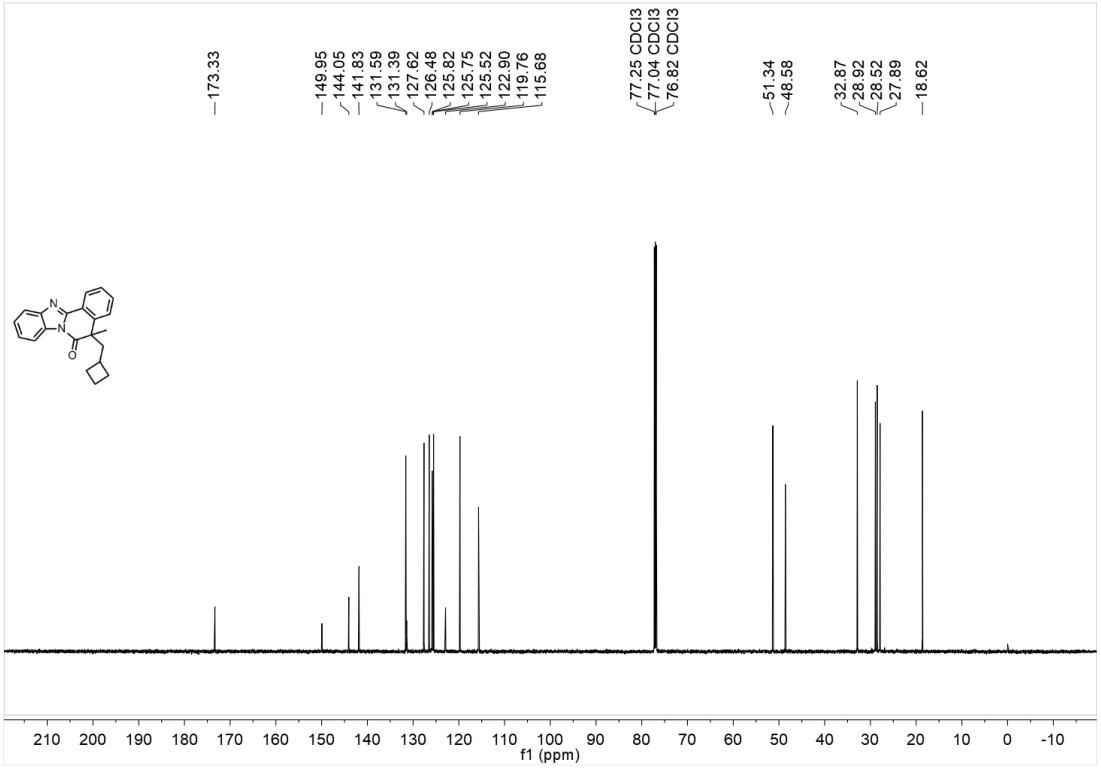
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **13**



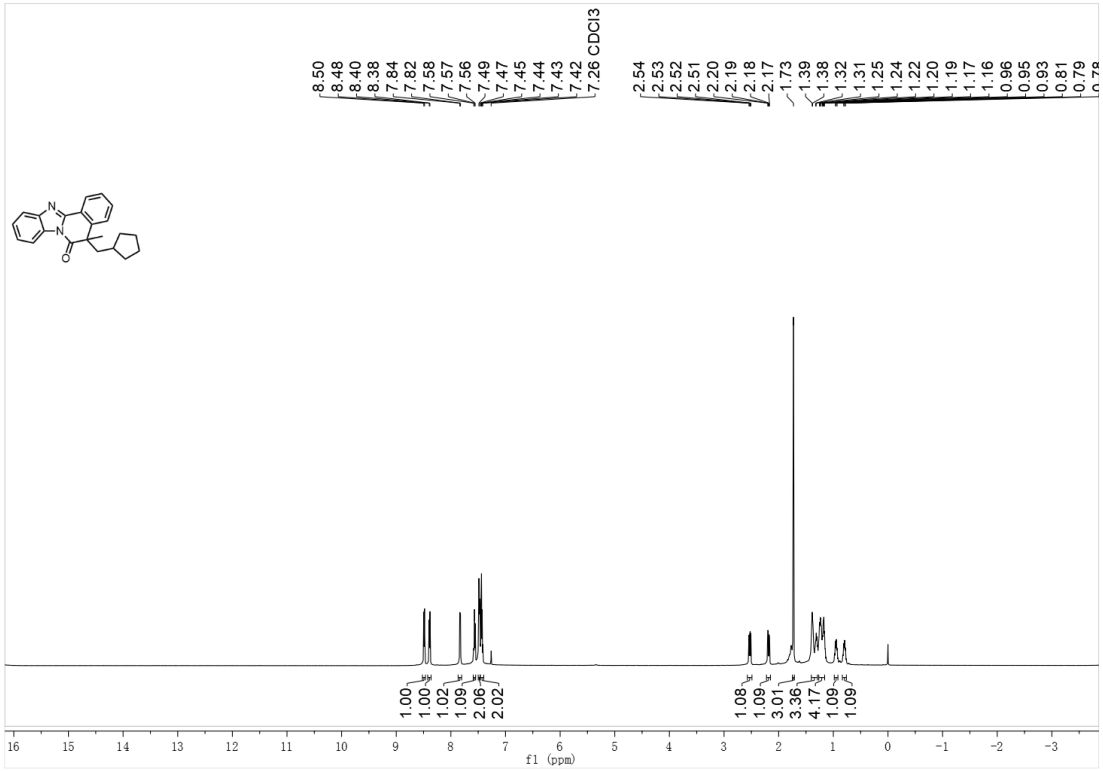
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **13**



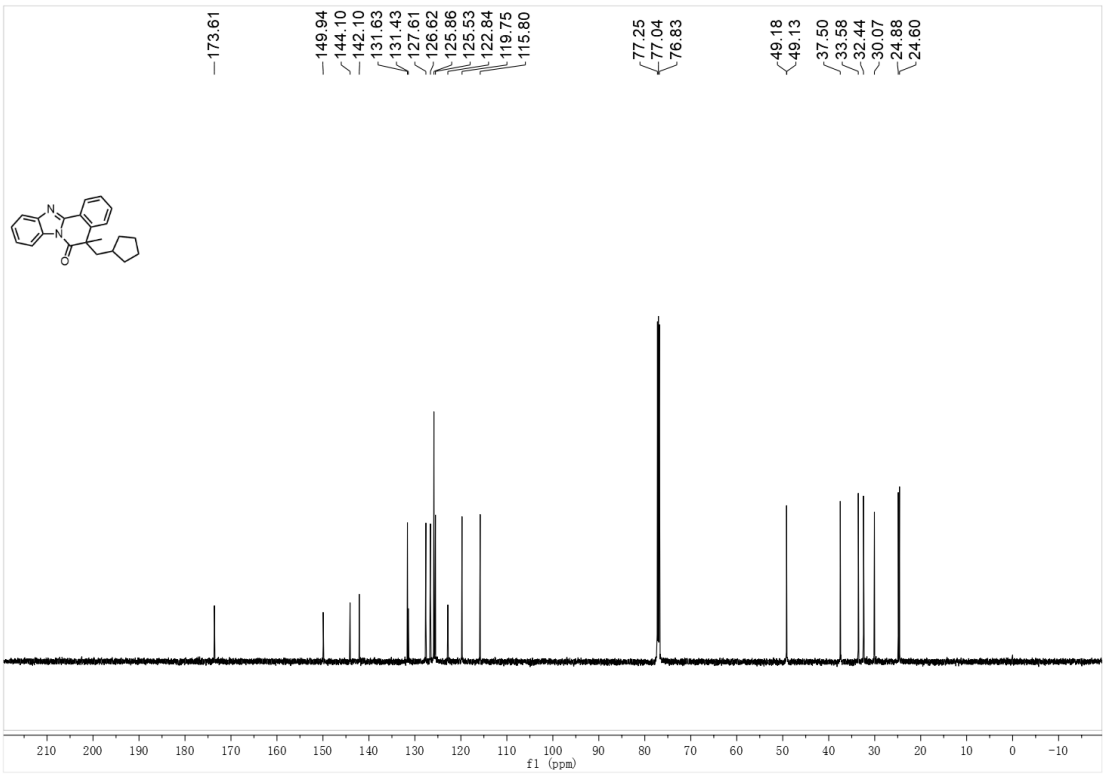
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14**



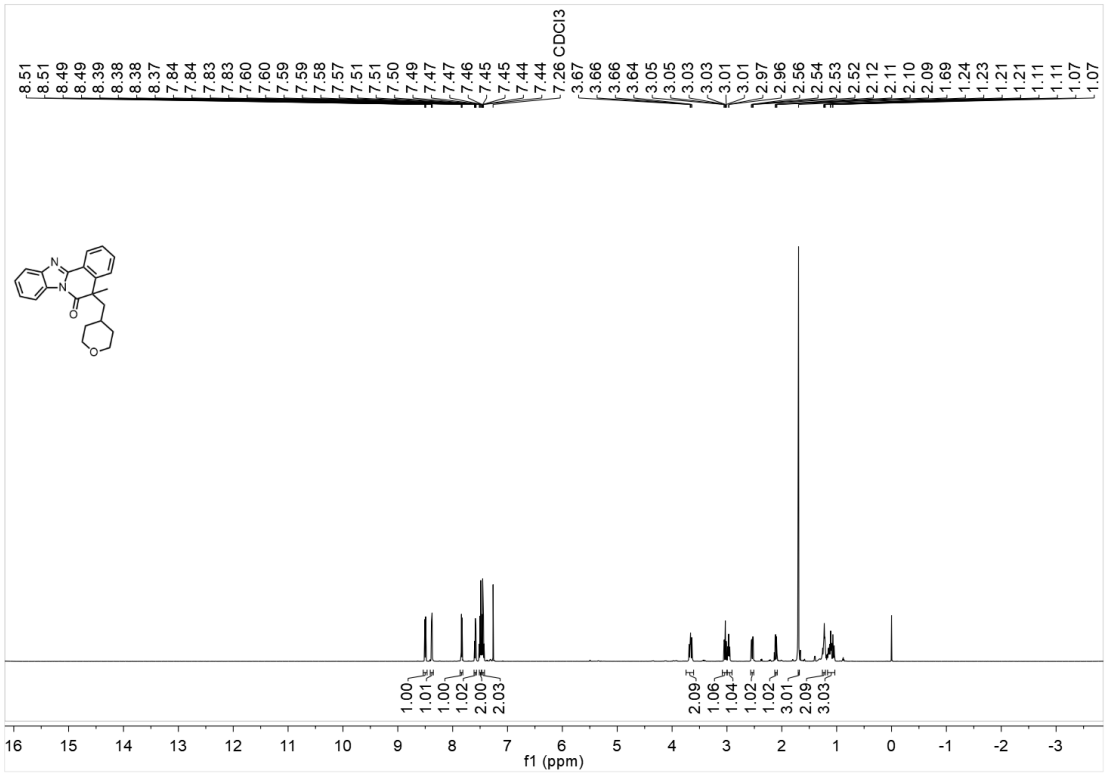
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14**



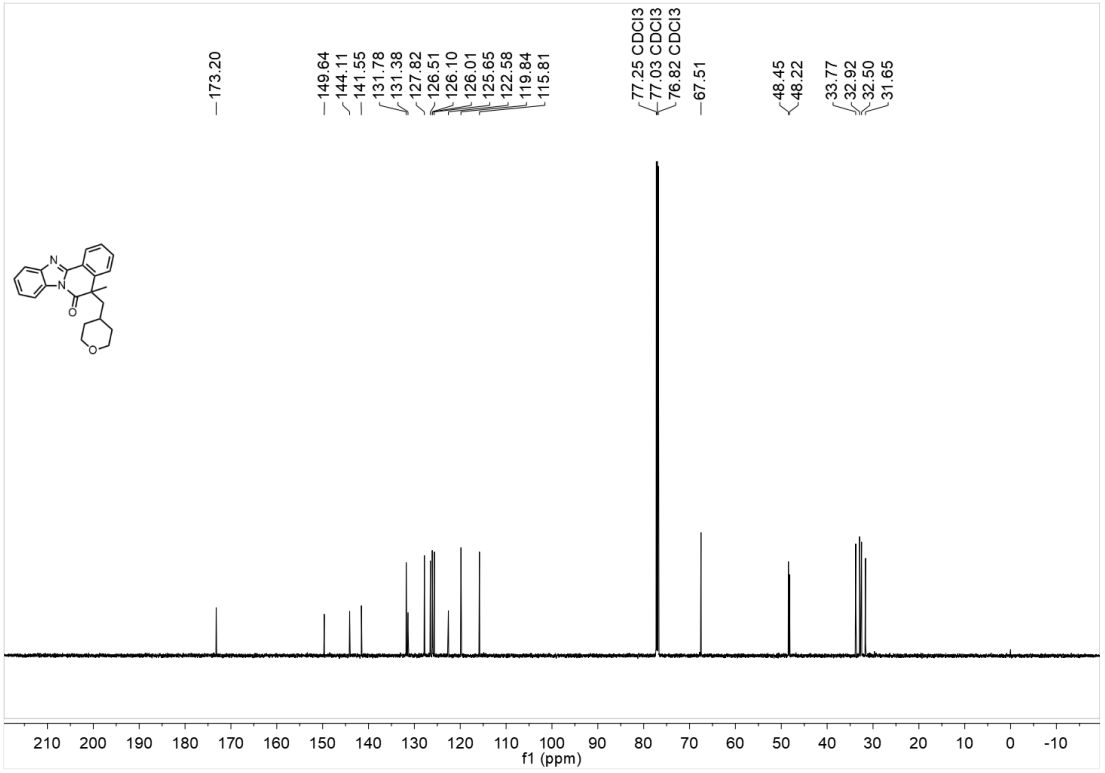
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **15**



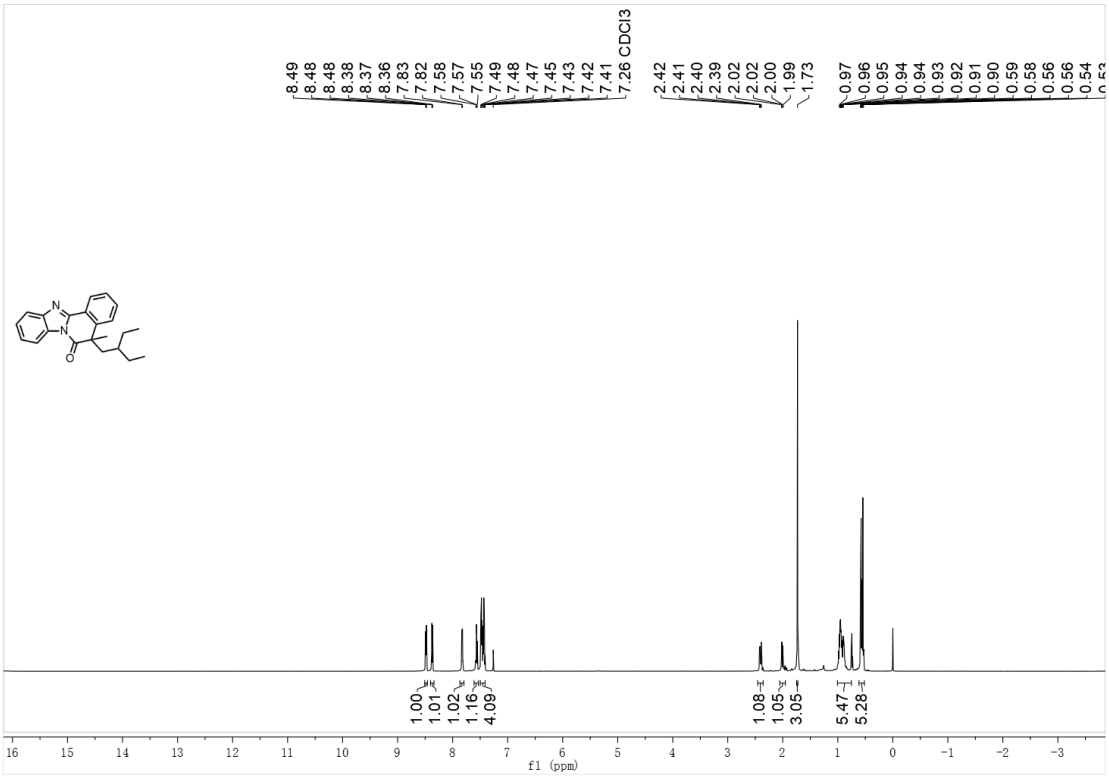
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **15**



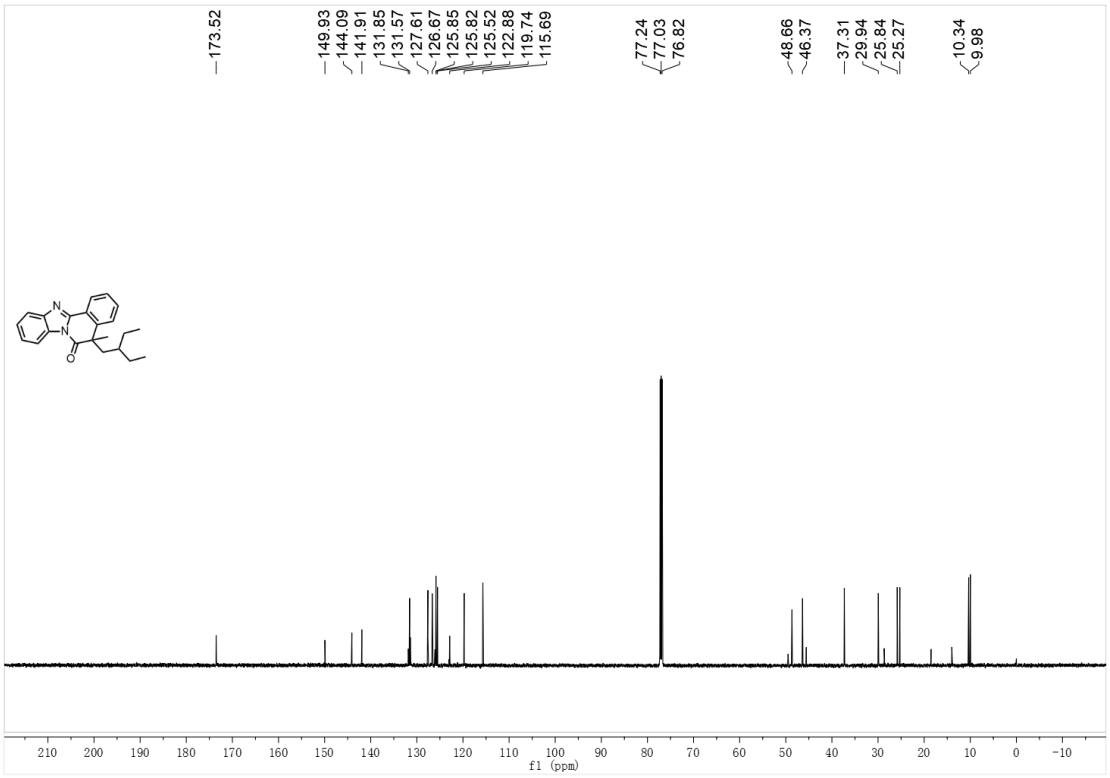
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16**



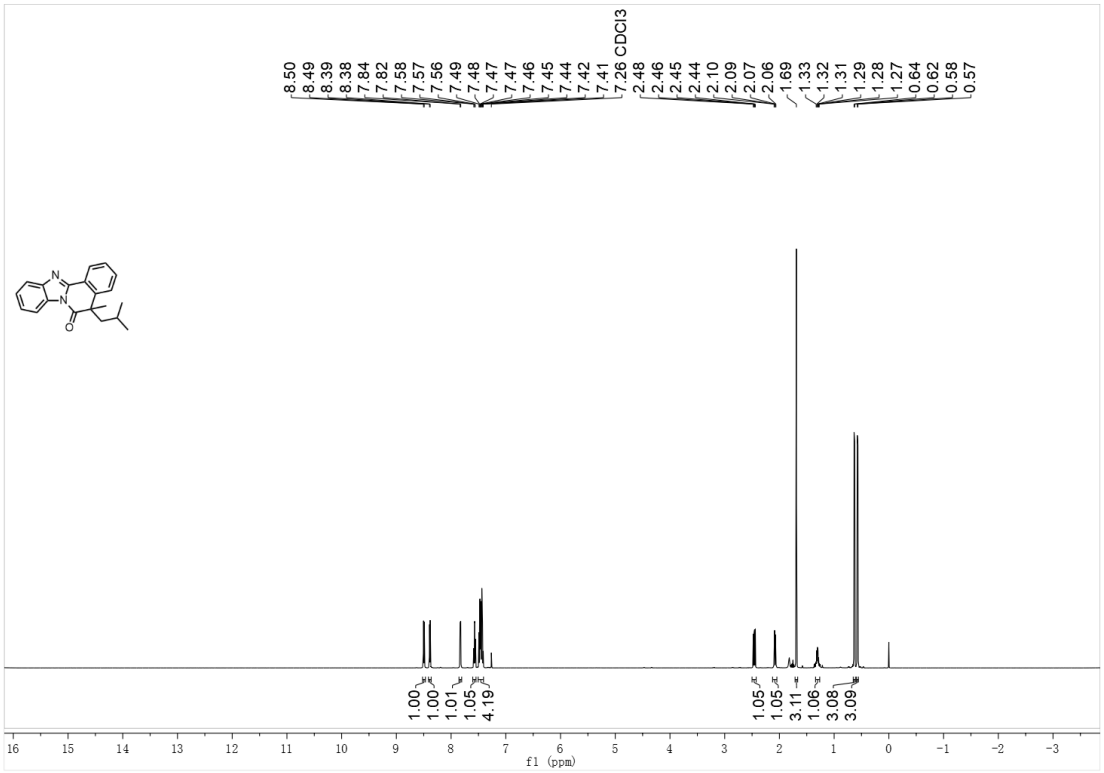
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **16**



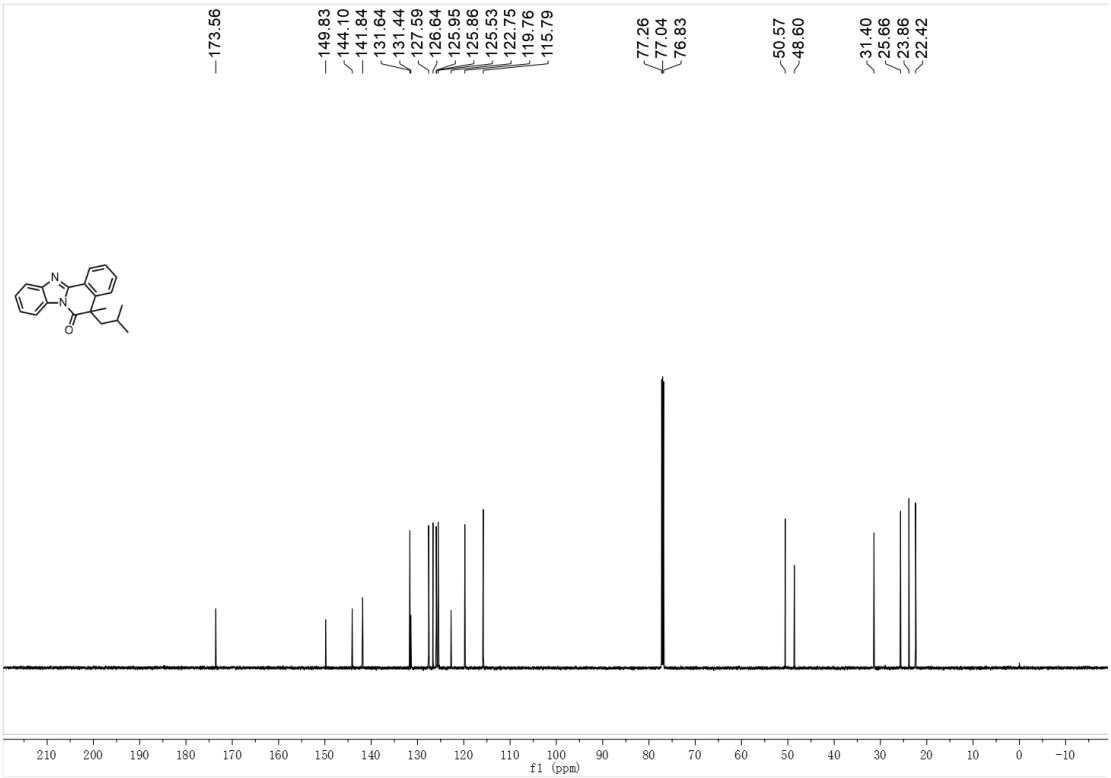
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **17**



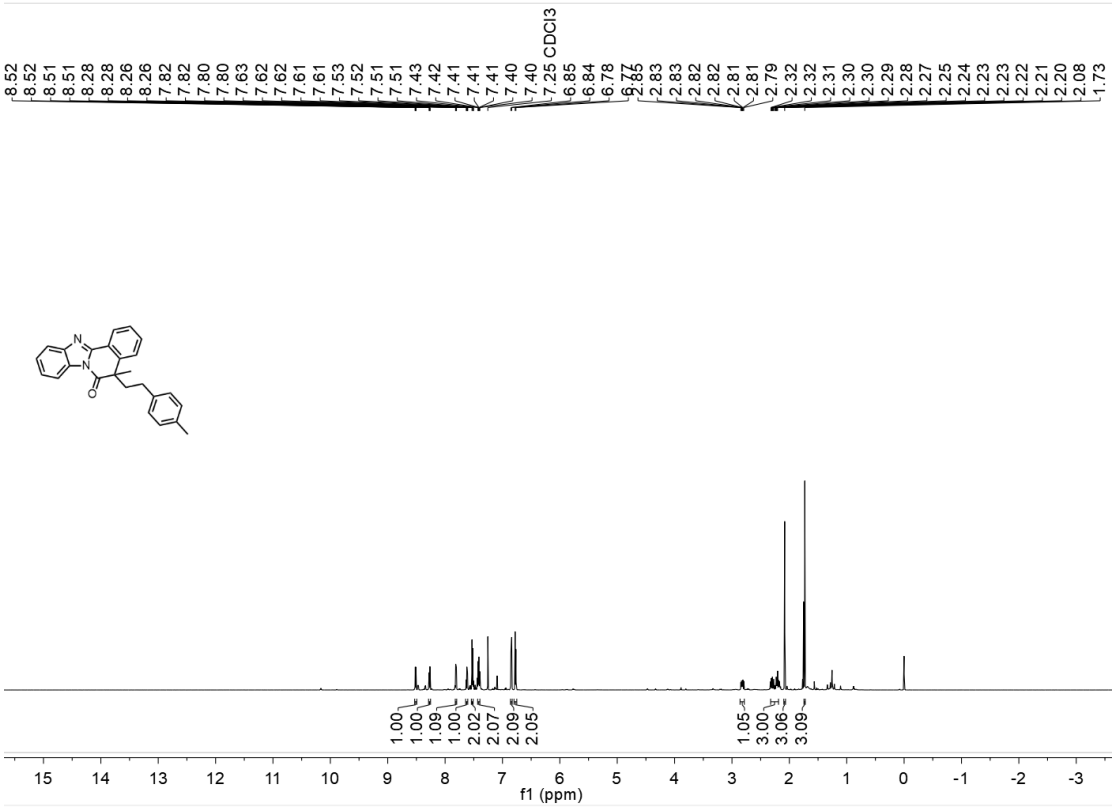
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **17**



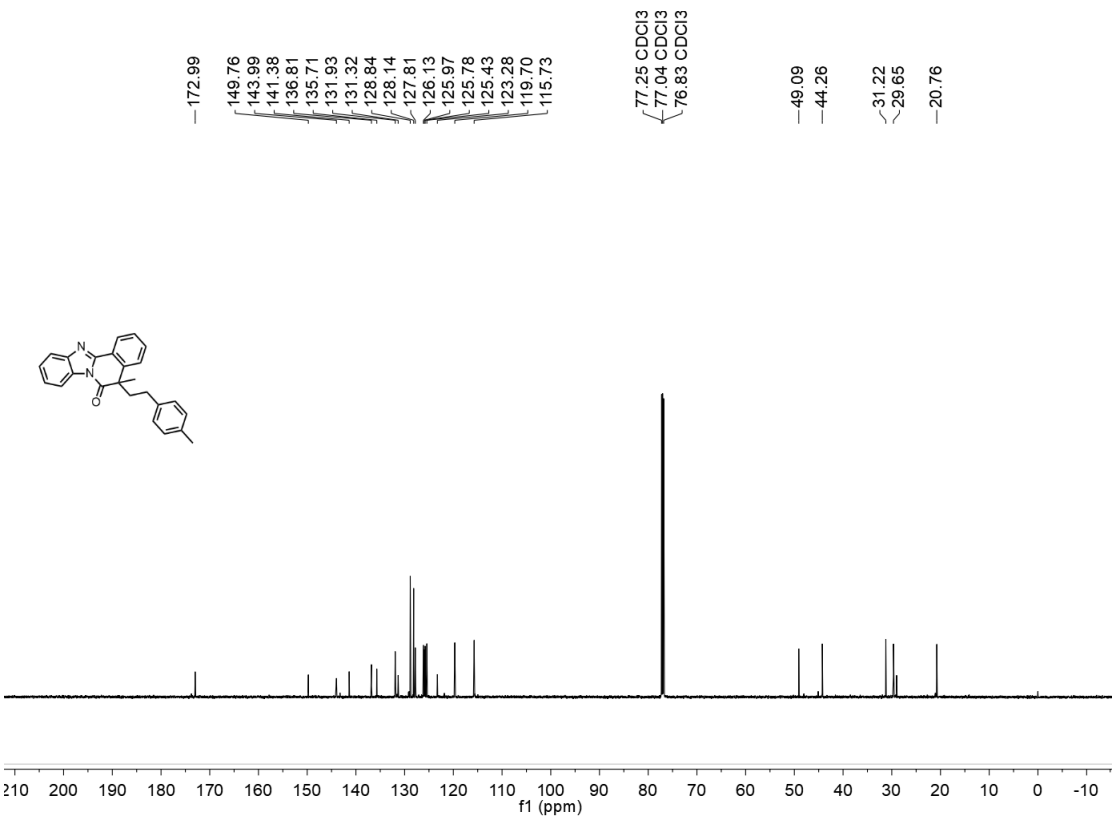
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **18**



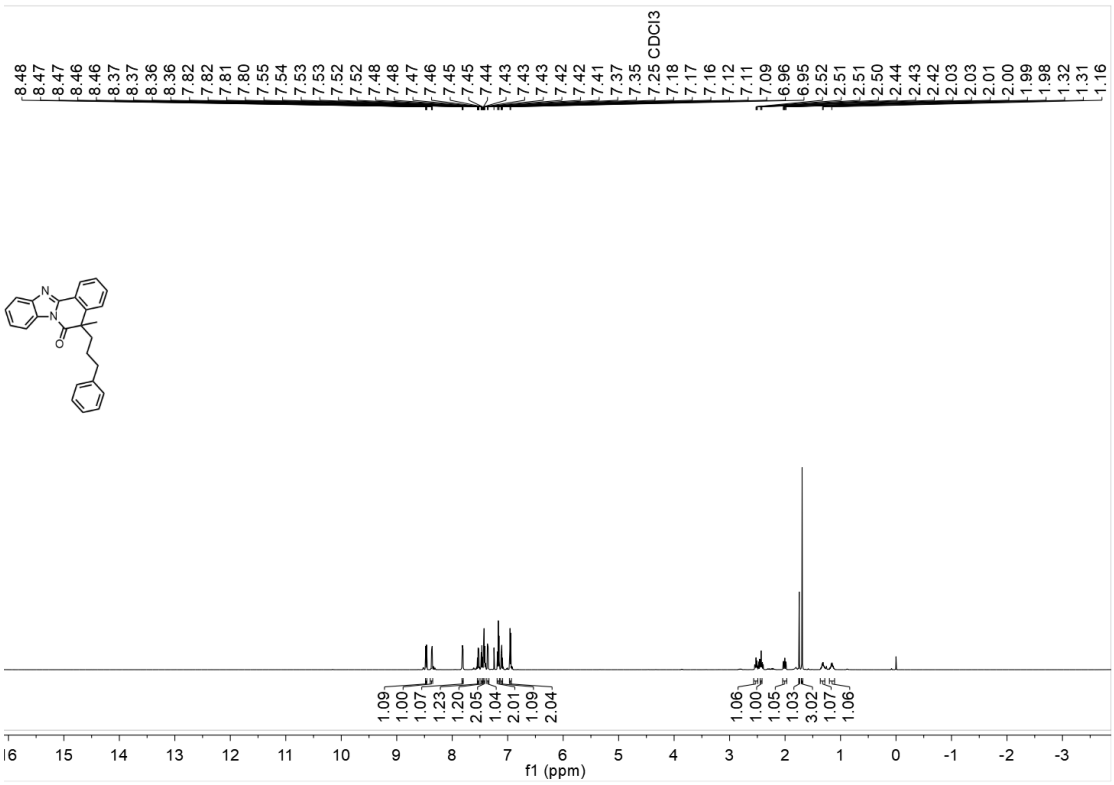
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **18**



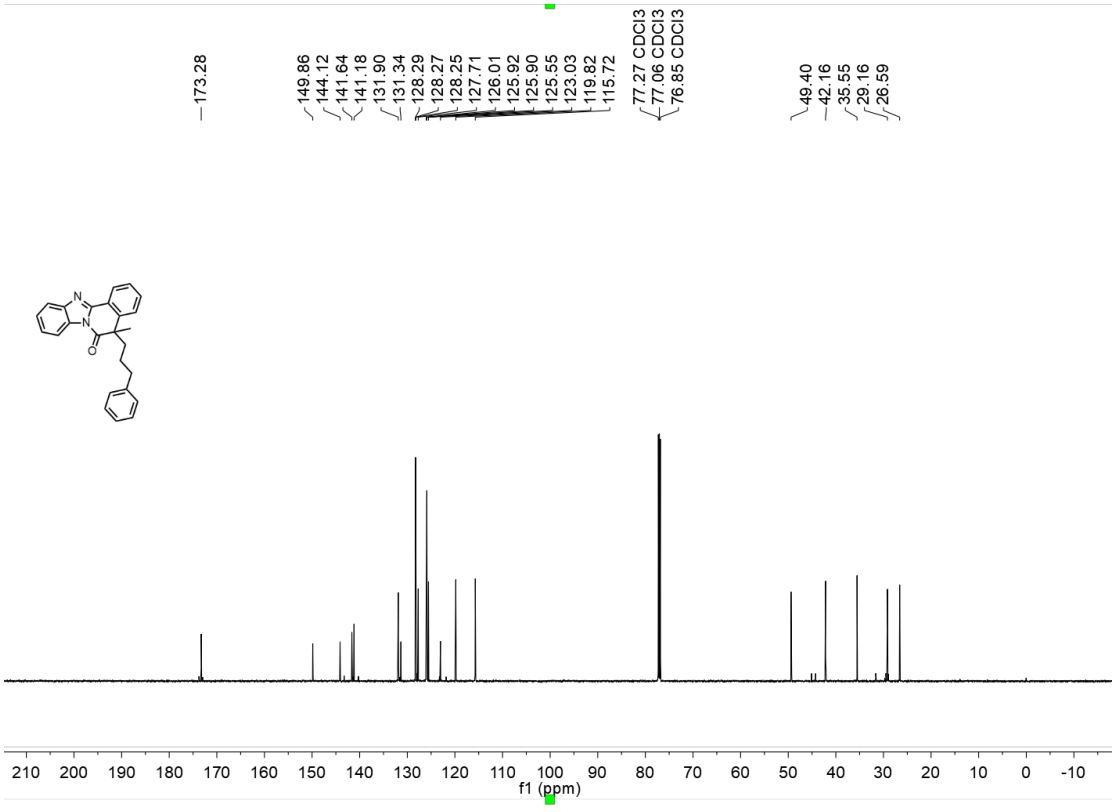
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **19**



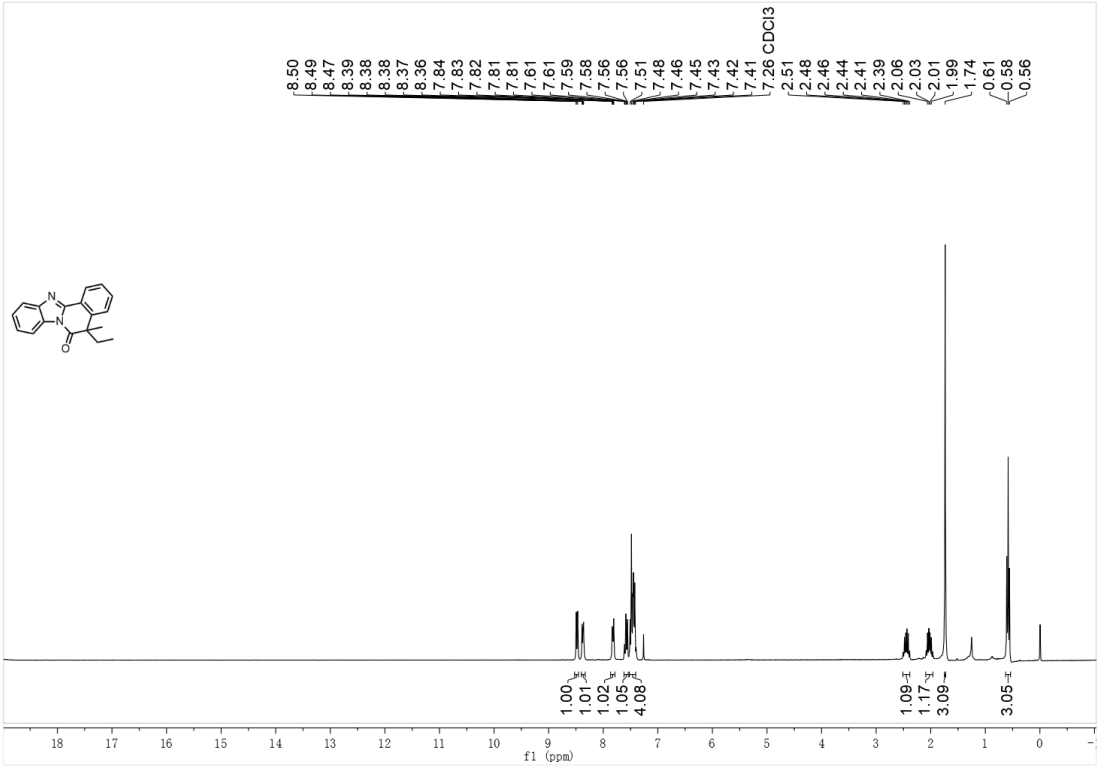
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **19**



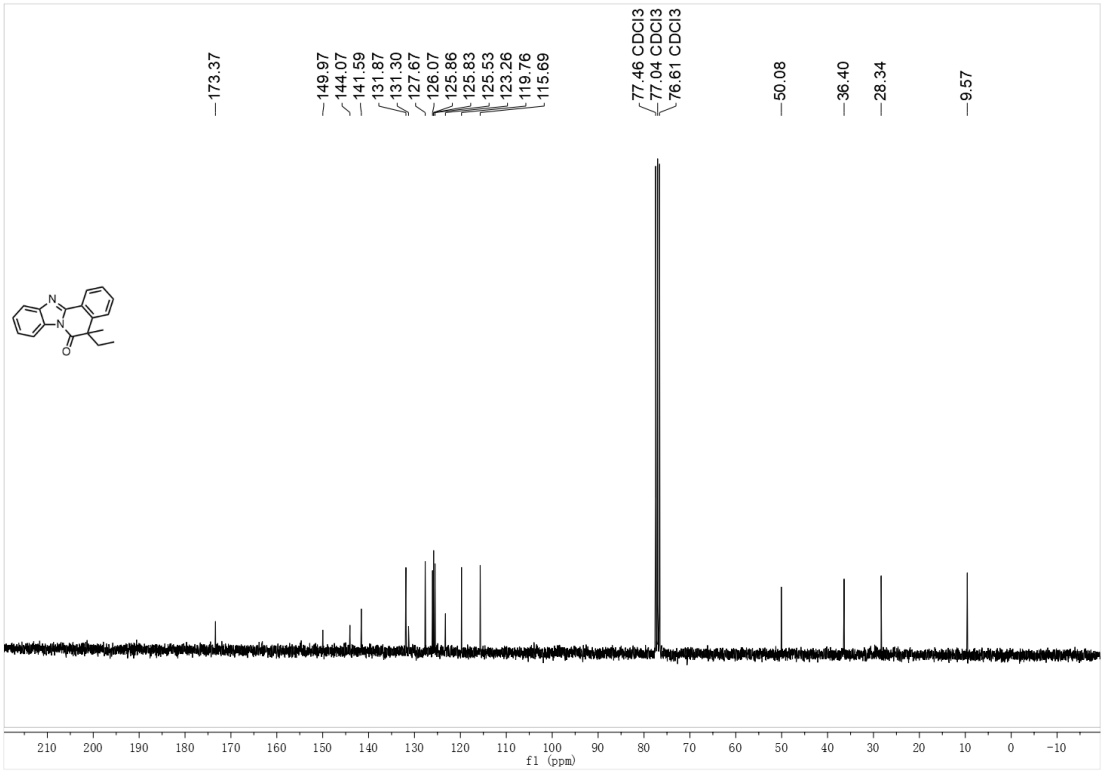
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **20**



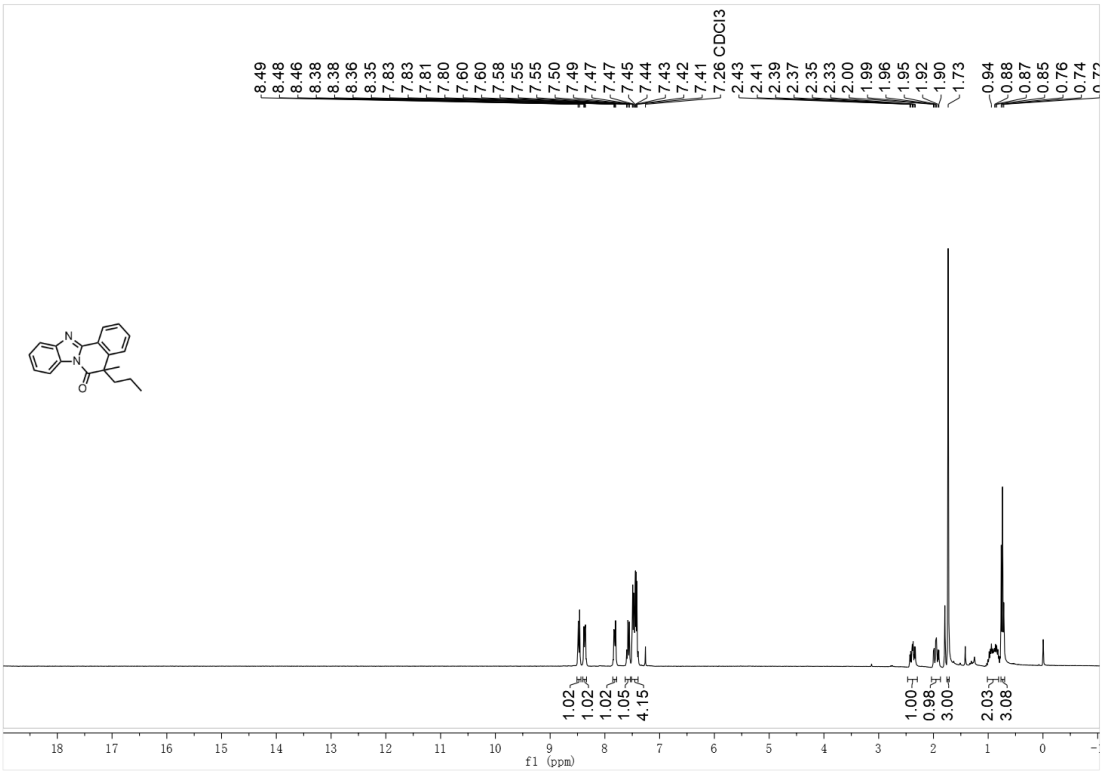
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **20**



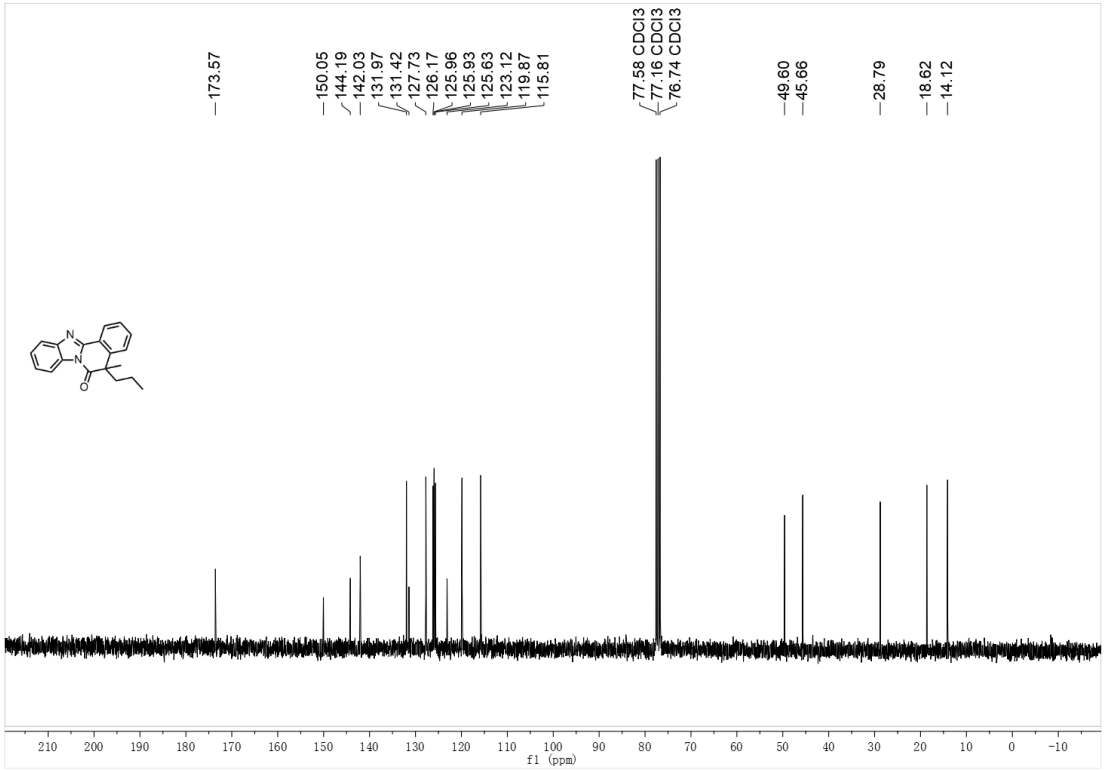
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **21**



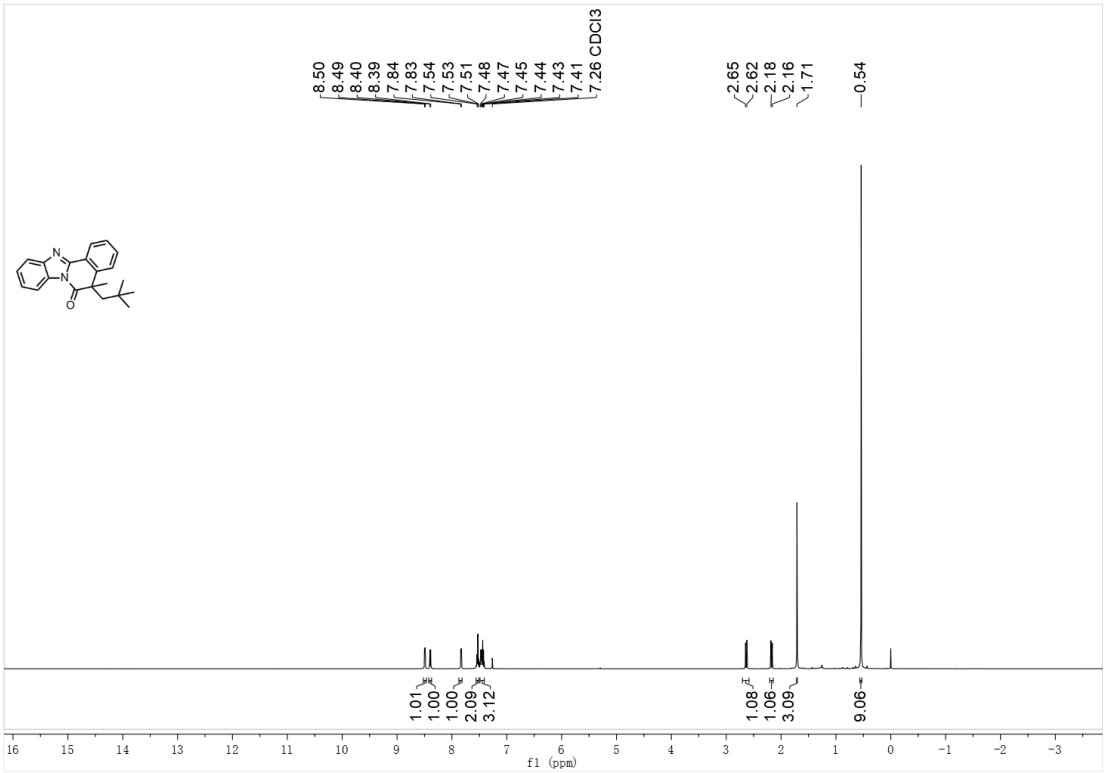
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **21**



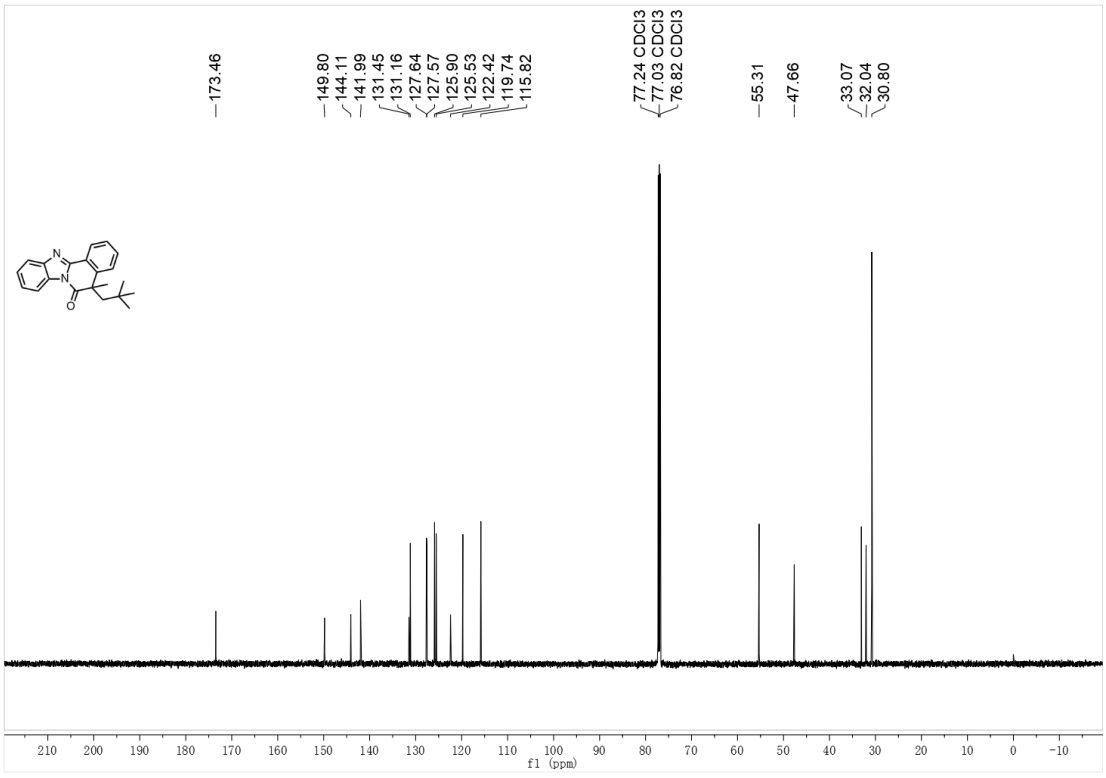
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **22**



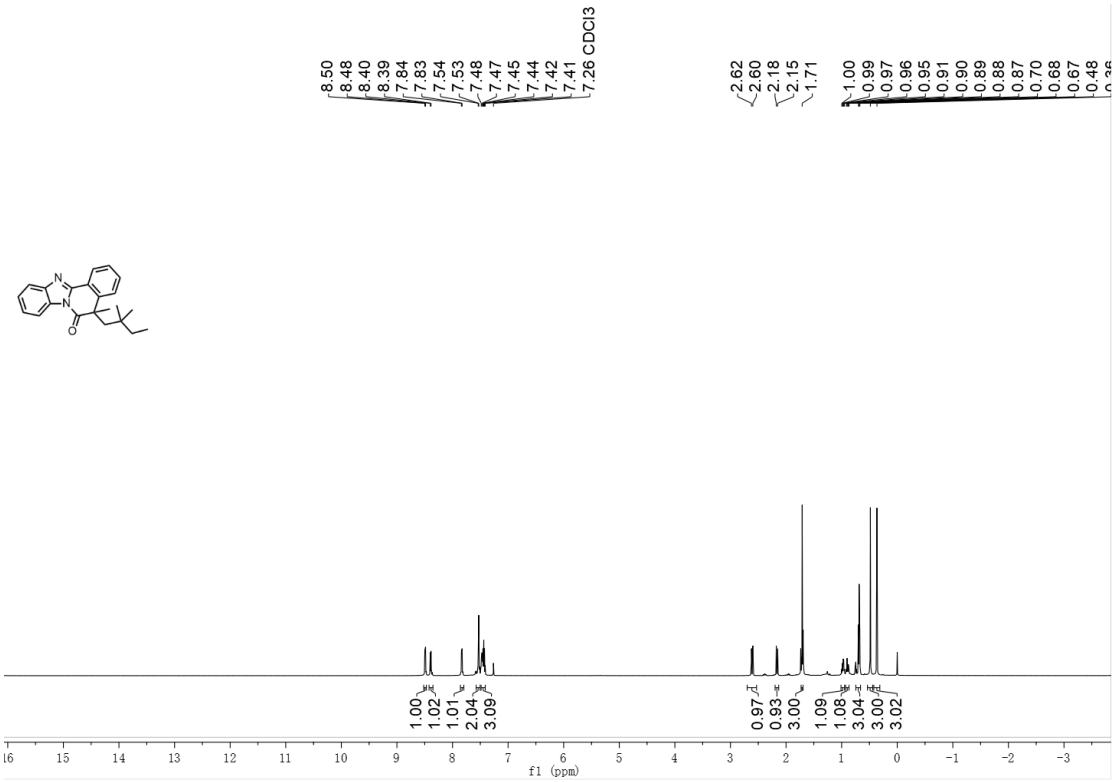
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **22**



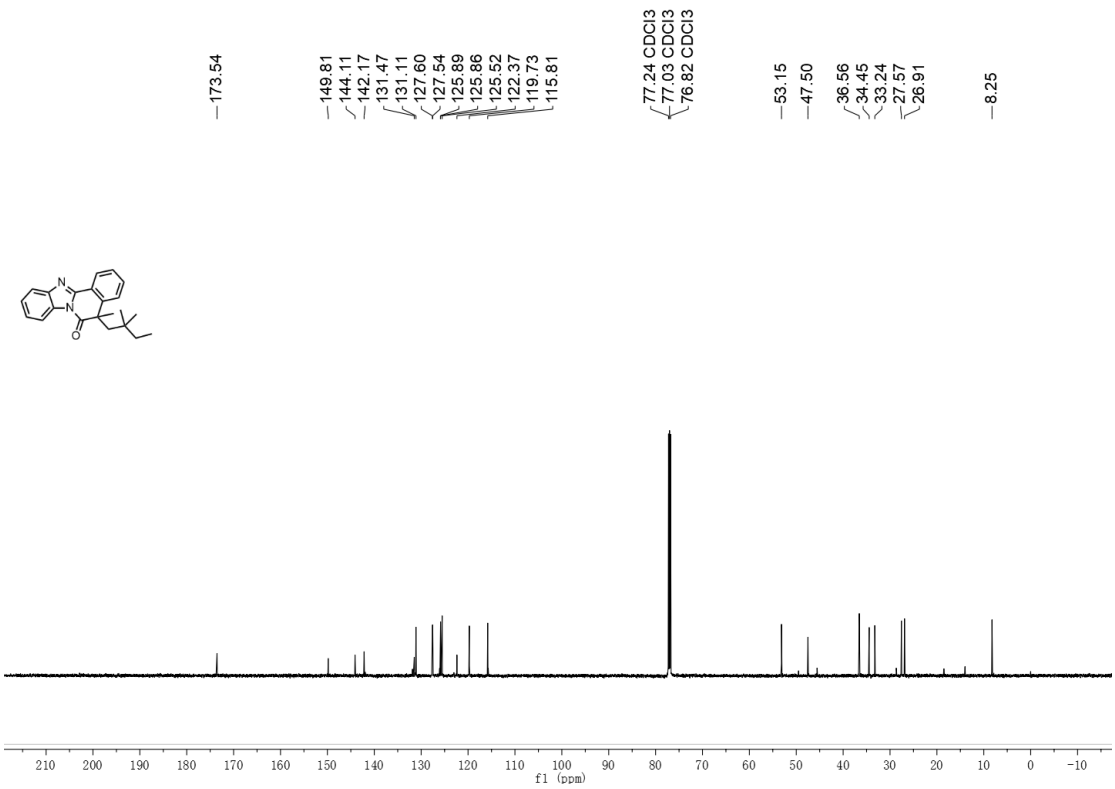
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **23**



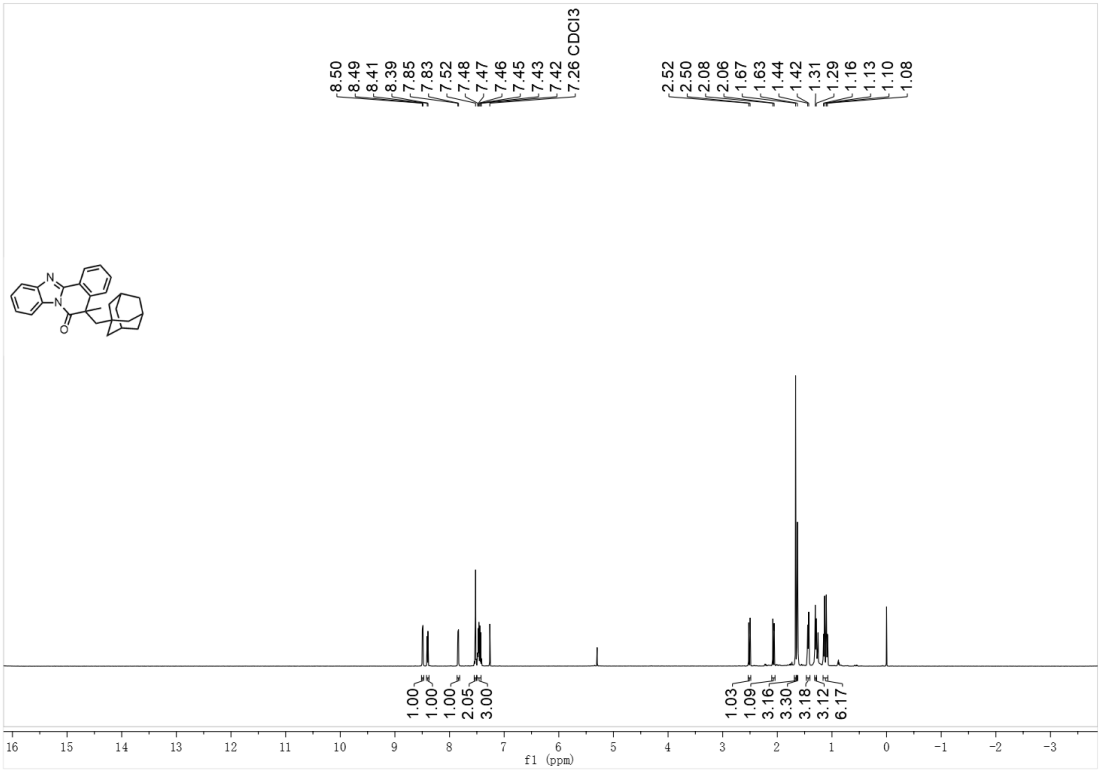
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **23**



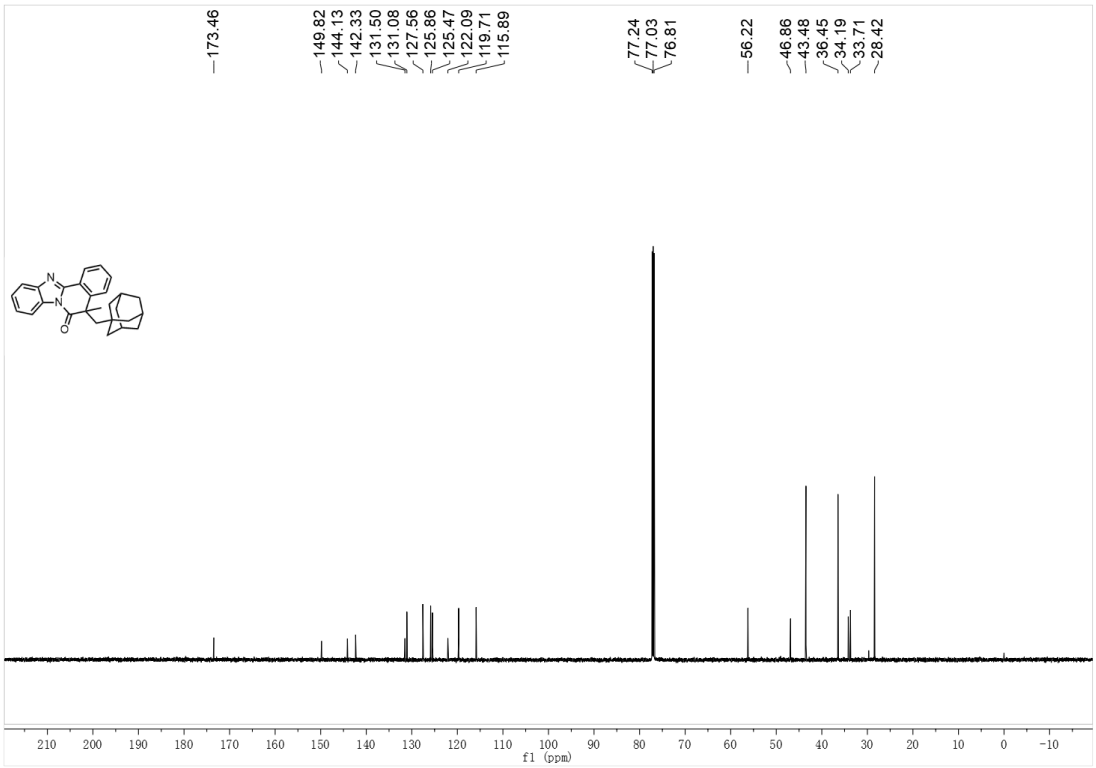
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **24**



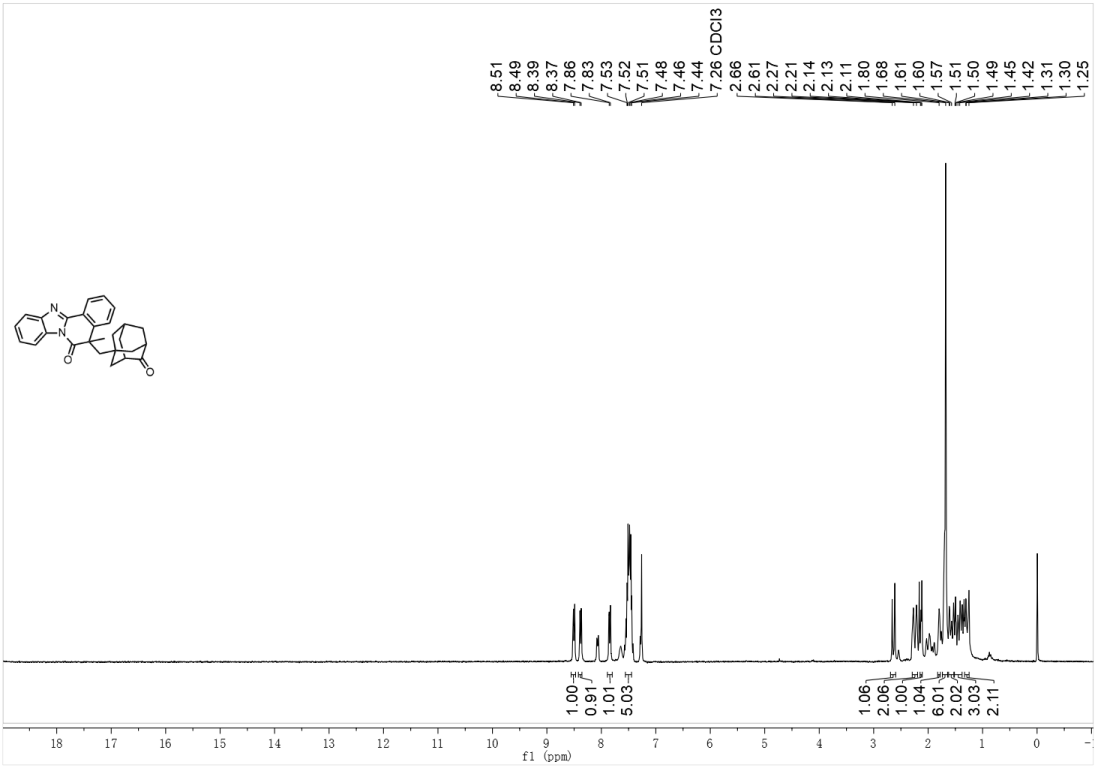
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **24**



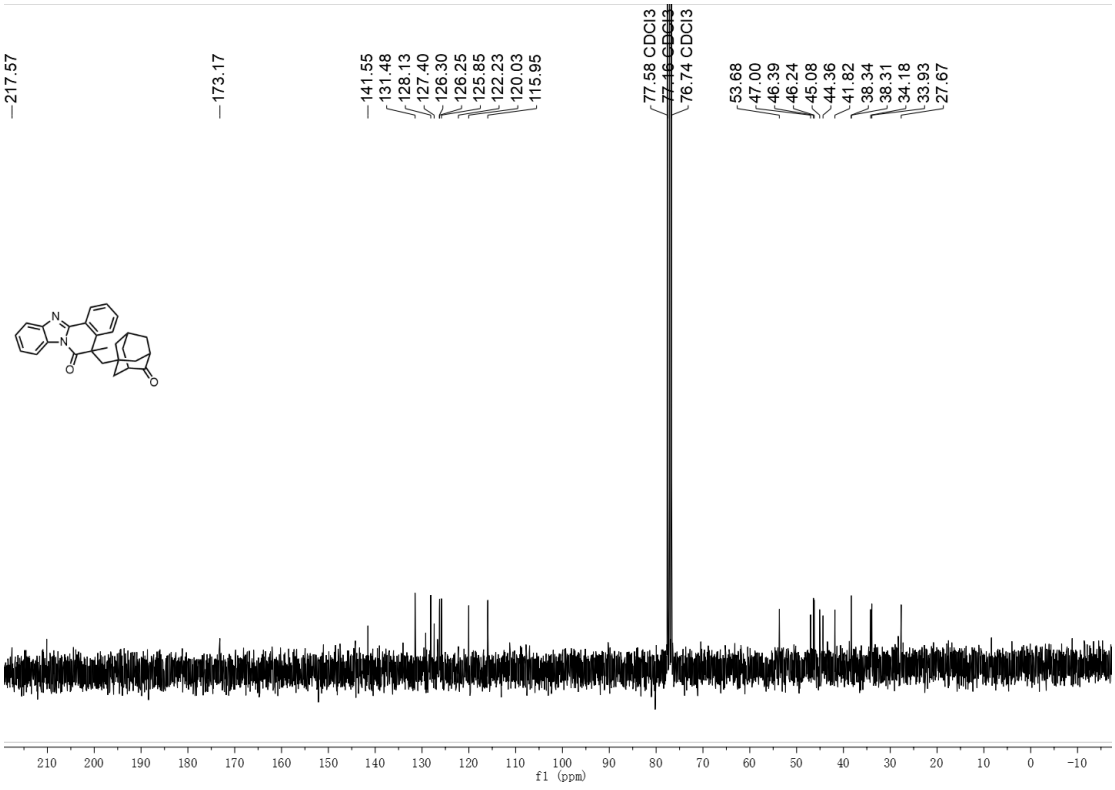
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **25**



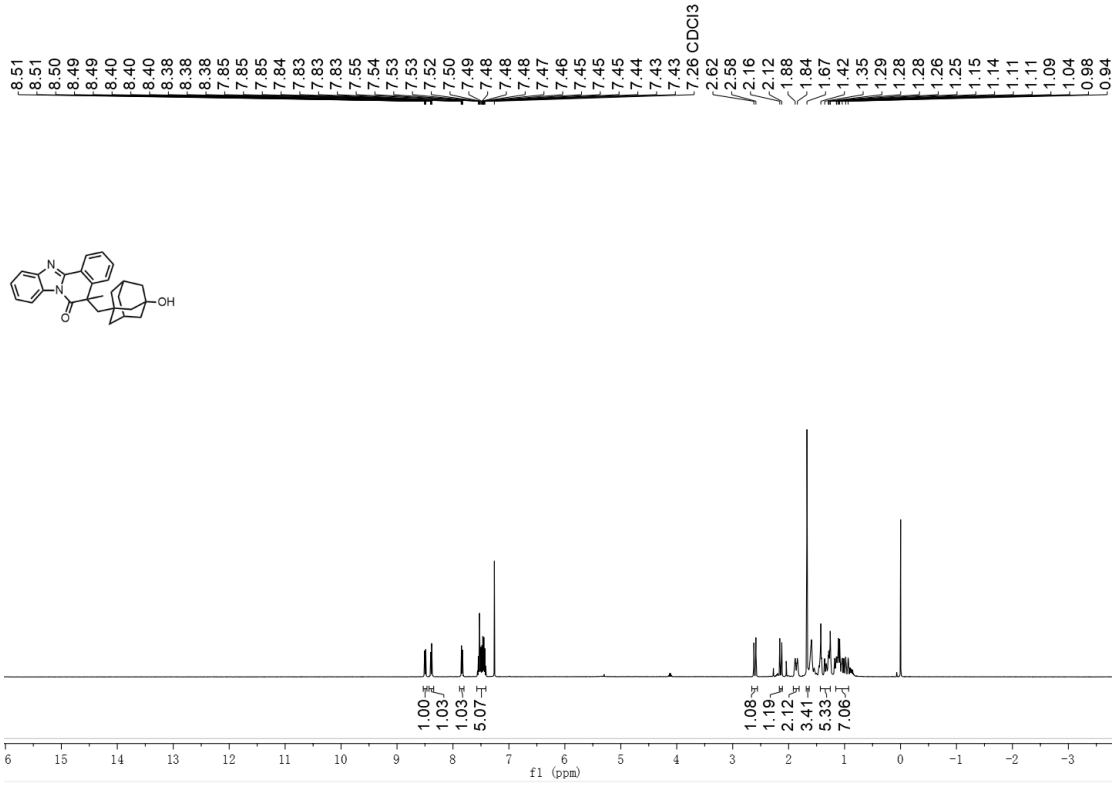
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **25**



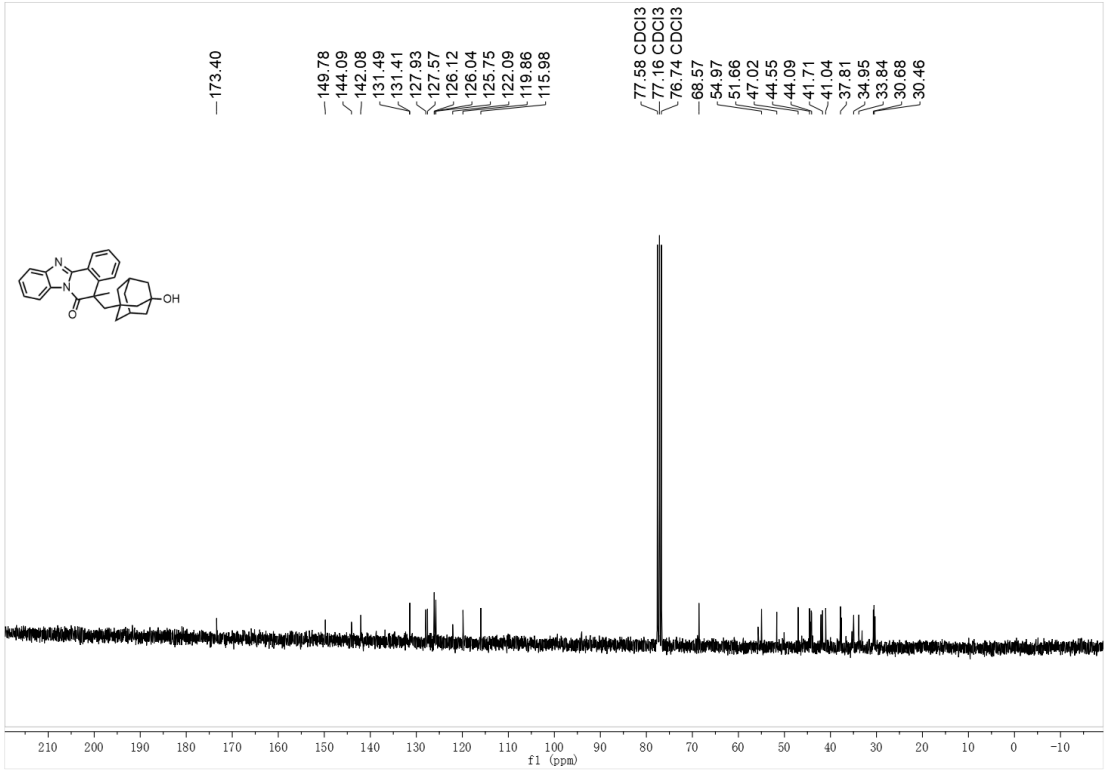
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **26**



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **26**



^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **27**



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **27**

8. References

[1] D. R. Stuart, E. Villemure, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 12072.

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