Supporting Information

Copper catalyzed radical cyclization from phenylboronic acid and *N*-acryloyl indole or benzimidazole derivatives with air as oxidant

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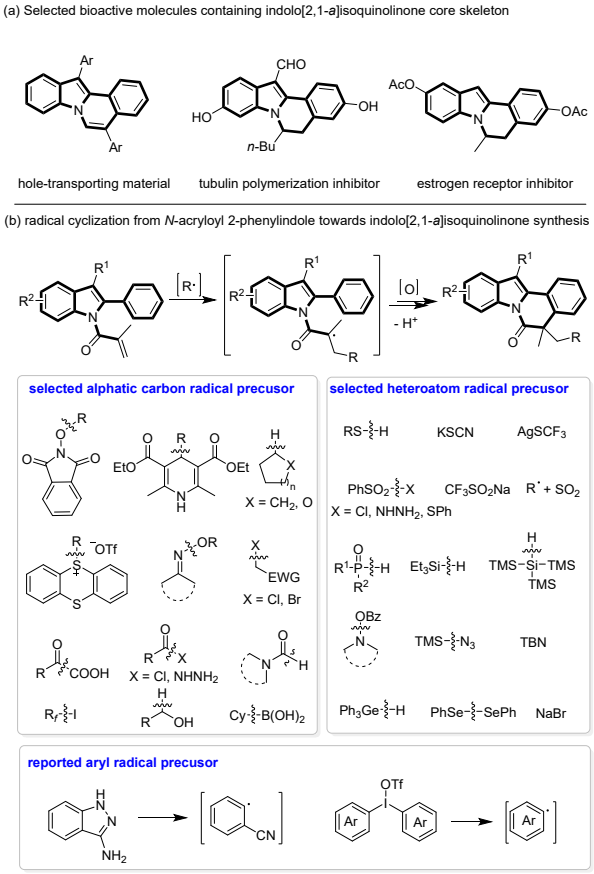
Contents

1. General information

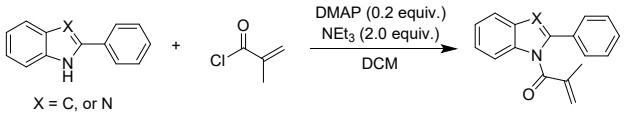
All the materials were purchased from Bidepharm, Energy Chemical, Adamas-beta® etc. and used as received unless otherwise noted. Unless specially indicated, all chemical reagents were purchased from commercial sources and were used as received without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Thin-layer chromatography plates were homemade using GF254 silica gel. Flash chromatography columns were packed with 200-300 mesh silica gels using the indicated solvents. The HRMS and GC-MS analyses were performed on BRUKER FT-ICR-MS SolariX 7T and Agilent 5975C MS paired with the 7890A GC, respectively. The spin-trapping Electron Paramagnetic Resonance (EPR) Spectroscopy was collected by Bruker EleXsys E500 EPR Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-*d6* on a Bruker AV400 instrument at room temperature. Chemical shifts were reported in parts per million (ppm) and the residual solvent signals were used as references for ^{1}H (TMS: $\delta H = 0.00$ ppm) and ^{13}C NMR spectra ($CDCl_3$: $\delta C = 77.16$ ppm, middle line). Data were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constants (Hz), and integration.

2. The importance of indolo[2,1-a]isoquinolinone derivatives and their synthesis *via* radical cyclization from *N*-acryloyl 2-phenylindole (Figure S1)



3. Experimental section

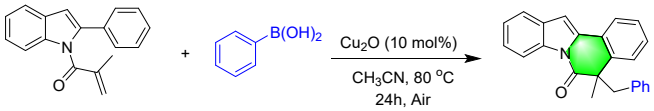
(1) The general procedure for synthesis of *N*-acryloyl indole or benzimidazole



In a 100 mL round-bottom flask equipped with a magnetic stir bar, 4-dimethylaminopyridine (4 mmol), the corresponding indole or benzimidazole derivative (20 mmol), and dichloromethane (DCM, 35 mL) were combined. The mixture was stirred at 0 °C, followed by the addition of triethylamine (40 mmol) and the slow dropwise addition of methacryloyl chloride (40 mmol). The reaction was then allowed to warm to room temperature and stirred for 2–3 days. [1] After full consumption of the starting material as monitored by TLC, the reaction was quenched with saturated

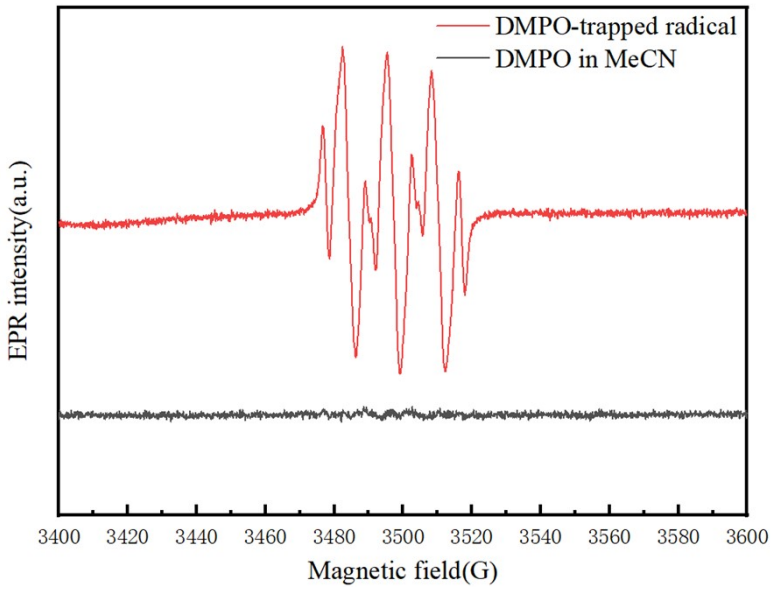
brine and extracted with ethyl acetate. The combined organic phases were dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to deliver the desired product.

(2) Representative Procedure for the Synthesis of Indolo[2,1-a]isoquinolinone Derivatives



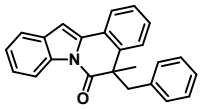
N-acryl-2-phenylindole (0.1 mmol), phenylboronic acid (0.3 mmol) and Cu_2O (10 mol%) were loaded into a 10 mL Schlenk tube equipped with a magnetic stir bar and a rubber septum. Acetonitrile (1.0 mL) was then added. At the initial stage, the reaction mixture existed as a brick-red suspension due to insoluble solid Cu_2O powder. After heating at 80 °C for 24 h, the reaction system underwent a distinct color transition from brick-red to pale green. Upon completion of the reaction, the mixture was cooled to room temperature. The crude product was directly purified *via* preparative thin-layer chromatography (TLC) with petroleum ether/ethyl acetate (10:1, v/v) as the eluent. All substrate scope evaluations and the synthesis of benzoimidazo[2,1-a]isoquinolinone derivatives were performed following the same standard procedure.

4. EPR Experiment



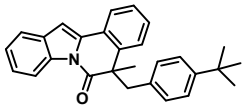
To a dry 10 mL reaction tube equipped with a magnetic stir bar were added phenylboronic acid (0.2 mmol), Cu_2O (50 mol%), acetonitrile (1 mL), and the spin-trapping reagent DMPO (0.4 mL). For the blank control experiment, only DMPO (0.4 mL) was dissolved in acetonitrile (1 mL). Both systems were heated with stirring in an oil bath at 80 °C for 10 min. Afterwards, an aliquot of the reaction mixture was collected with a capillary tube for electron paramagnetic resonance (EPR) measurement.

5. Characterization of products



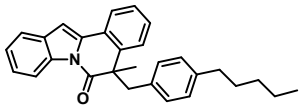
5-benzyl-5-methylindolo[2,1-*a*]isoquinolin-6(5H)-one

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.56 (d, J = 8.2 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.47 (d, J = 7.7 Hz, 2H), 7.43 – 7.26 (m, 4H), 6.90 (t, J = 7.4 Hz, 1H), 6.80 (t, J = 7.5 Hz, 2H), 6.72 (s, 1H), 6.57 (d, J = 7.3 Hz, 2H), 3.53 (d, J = 13.0 Hz, 1H), 3.10 (d, J = 13.0 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.49, 137.37, 135.86, 135.25, 135.05, 130.49, 129.27, 128.52, 127.54, 127.29, 126.81, 126.54, 125.33, 125.03, 124.34, 123.49, 120.28, 116.51, 102.48, 50.45, 50.40, 26.06. IR: v = 3035, 2940, 2864, 1712, 1626, 1493, 1488, 1419, 1372, 1325, 1301, 1208, 804, 771, 723, 701 cm^{-1} HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}NO$ 338.1540; Found 338.1541.



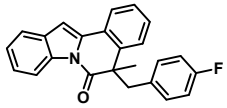
5-(4-(tert-butyl)benzyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

white solid, mp: 142-145℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.52 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 6.9 Hz, 1H), 7.46 (t, J = 8.5 Hz, 2H), 7.41 (d, J = 4.9 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.24 – 7.20 (m, 1H), 6.74 (d, J = 8.3 Hz, 2H), 6.61 (s, 1H), 6.43 (d, J = 8.2 Hz, 2H), 3.43 (d, J = 12.9 Hz, 1H), 3.03 (d, J = 13.0 Hz, 1H), 1.89 (s, 3H), 1.40 (s, 3H), 1.25 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.44, 149.45, 137.47, 135.36, 135.09, 132.54, 130.47, 128.78, 128.53, 127.24, 126.64, 125.73, 125.68, 124.92, 124.26, 124.18, 123.39, 120.16, 116.38, 102.23, 50.56, 34.11, 31.13, 29.72, 25.28. IR: v = 3027, 2964, 2939, 2854, 1694, 1600, 1451, 1381, 1336, 1198, 1169, 1020, 934, 815, 751 cm^{-1} HRMS (ESI) *m*/*z*: [M + H]$^+$ Calcd for $C_{28}H_{27}NO$ 394.2166; Found 394.2167.



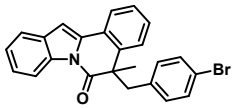
5-methyl-5-(4-pentylbenzyl)indolo[2,1-a]isoquinolin-6(5H)-one

white solid, mp: 150-151℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.55 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 6.6 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 7.29 – 7.24 (m, 2H), 6.67 (s, 1H), 6.58 (d, J = 8.0 Hz, 2H), 6.44 (d, J = 8.0 Hz, 2H), 3.46 (d, J = 13.0 Hz, 1H), 3.04 (d, J = 13.0 Hz, 1H), 2.34 – 2.25 (m, 2H), 1.88 (s, 3H), 1.37 – 1.29 (m, 4H), 1.18 – 1.05 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.55, 141.17, 137.52, 135.33, 135.07, 132.87, 130.50, 129.06, 128.48, 127.53, 127.22, 126.77, 124.95, 124.25, 123.42, 120.20, 116.47, 102.35, 50.43, 35.27, 31.19, 30.99, 29.72, 25.62, 22.47, 14.02. IR: v = 2954, 2925, 2854, 1696, 1600, 1512, 1485, 1450, 1379, 1360, 1340, 1315, 1196, 1168, 934, 807, 750 cm^{-1} HRMS (ESI) *m*/*z*: [M + H]$^+$ Calcd for $C_{29}H_{29}NO$ 408.2322; Found 408.2323.



5-(4-fluorobenzyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

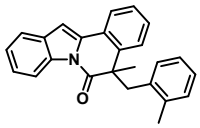
pale yellow solid, mp: 135-138℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.55 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 7.1 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.44 – 7.27 (m, 5H), 6.74 (s, 1H), 6.52 – 6.48 (m, 3H), 3.51 (d, J = 13.1 Hz, 1H), 3.06 (d, J = 13.1 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.32, 137.12, 135.03 (d, $J_{F,C}$ = 9.6 Hz), 131.61, 130.67 (d, $J_{F,C}$ = 8.0 Hz), 130.48, 128.60, 127.40, 126.69, 125.40, 125.12, 124.46, 123.53, 120.39, 116.45, 114.36 (d, $J_{F,C}$ = 21.1 Hz), 102.71, 50.41, 49.65, 26.02. ^{19}F NMR (376 MHz, $CDCl_3$, 25° C) δ = -116.24. IR: v = 2928, 2157, 2024, 1961, 1694, 1602, 1508, 1450, 1379, 1360, 1340, 1223, 834, 809, 754, 604 cm^{-1} HRMS (ESI) *m*/*z*: [M + H]$^+$ Calcd for $C_{24}H_{18}FNO$ 356.1446; Found 356.1447.



5-(4-bromobenzyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

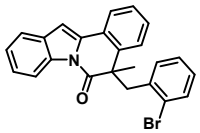
white solid, mp: 230-233℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.55 (d, J = 8.1 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.55 – 7.44 (m, 2H), 7.43 – 7.27 (m, 4H), 6.94 (d, J

= 8.4 Hz, 2H), 6.77 (s, 1H), 6.45 (d, *J* = 8.3 Hz, 2H), 3.51 (d, *J* = 13.1 Hz, 1H), 3.05 (d, *J* = 13.1 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.18, 136.95, 134.98, 130.95, 130.67, 130.54, 128.62, 127.46, 126.70, 125.32, 125.17, 124.53, 123.65, 120.69, 120.44, 116.47, 102.92, 50.24, 49.40, 26.43. IR: v = 3059, 2925, 2851, 1694, 1598, 1487, 1450, 1379, 1360, 1340, 1315, 1194, 1074, 1012, 838, 807, 752 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{18}BrNO$ 416.0645; Found 416.0646.



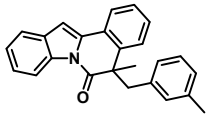
5-methyl-5-(2-methylbenzyl)indolo[2,1-a]isoquinolin-6(5H)-one

white solid, mp: 260-265℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) *δ* = 8.53 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.27 (m, 5H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H), 3.15 (d, *J* = 13.8 Hz, 1H), 1.91 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.76, 137.40, 137.12, 135.34, 135.24, 133.98, 130.54, 130.10, 129.96, 128.51, 127.41, 126.94, 126.57, 125.45, 125.09, 124.94, 124.31, 123.69, 120.34, 116.41, 102.54, 77.35, 49.96, 46.41, 24.95, 19.05. IR: v = 3066, 2926, 2858, 1694, 1598, 1487, 1448, 1379, 1358, 1340, 1315, 1198, 1172, 1149, 1037, 930, 807, 748 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{21}NO$ 352.1696; Found 352.1697.



5-(2-bromobenzyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

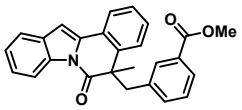
white solid, mp: 95-98℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) *δ* = 8.55 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.27 (m, 6H), 6.88 – 6.82 (m, 2H), 6.77 (t, *J* = 7.9 Hz, 1H), 6.70 – 6.60 (m, 1H), 3.65 (d, *J* = 14.3 Hz, 1H), 3.42 (d, *J* = 14.3 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.29, 137.00, 135.71, 135.37, 135.32, 132.63, 130.82, 130.59, 128.71, 128.08, 127.52, 127.10, 126.63, 125.60, 125.17, 124.43, 123.79, 120.38, 116.61, 102.72, 49.73, 47.39, 25.97. IR: v = 3063, 2984, 2926, 1696, 1596, 1471, 1448, 1379, 1358, 1340, 1194, 1149, 1039, 1024, 809, 750 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{18}BrNO$ 416.0645; Found 416.0646.



5-methyl-5-(3-methylbenzyl)indolo[2,1-a]isoquinolin-6(5H)-one

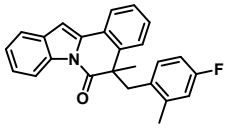
white solid, mp: 261-263℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) *δ* = 8.56 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 5.7 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.30 – 7.25 (m, 1H), 6.67 (d, *J* = 6.9 Hz, 3H), 6.38 (s, 1H), 6.23 (d, *J* = 6.2 Hz, 1H), 3.44 (d, *J* = 12.8 Hz, 1H), 3.00 (d, *J* = 12.8 Hz, 1H), 1.90 (s, 3H), 1.77 (s, 3H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ = 172.52, 137.38, 137.09, 135.52, 135.29, 135.02, 130.50, 130.03, 128.49, 127.24, 127.18, 126.65, 126.17, 125.57, 124.98, 124.28, 123.34, 120.24, 116.41, 102.31, 51.18, 50.50, 25.17, 20.66. IR: v = 3077, 3029, 2919, 2865, 1692, 1493, 1446, 1374, 1347, 1320, 1194, 1146, 1033, 936, 801, 740 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{21}NO$ 352.1696; Found 352.1698.



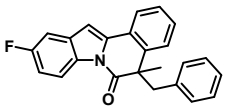
Methyl 3-((5-methyl-6-oxo-5,6-dihydroindolo[2,1-a]isoquinolin-5 -yl)methyl)benzoate

white solid, mp: 67-69°C; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.56 (d, J = 8.2 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.20 (m, 2H), 6.86 (t, J = 7.7 Hz, 1H), 6.68 (d, J = 7.7 Hz, 1H), 6.65 (s, 1H), 3.64 (s, 3H), 3.55 (d, J = 13.0 Hz, 1H), 3.09 (d, J = 13.0 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.17, 166.58, 136.79, 136.11, 134.97, 133.66, 130.33, 129.36, 128.73, 127.87, 127.57, 127.46, 126.58, 125.41, 125.05, 124.39, 123.50, 120.34, 116.52, 102.66, 51.77, 50.54, 50.36, 25.48. IR: v = 3068, 2948, 2849, 1721, 1692, 1600, 1448, 1436, 1379, 1360, 1340, 1280, 1239, 1201, 1108, 1088, 815, 750, 740, 697 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{26}H_{21}NO_3$ 396.1595; Found 396.1596.



5-(4-fluoro-2-methylbenzyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

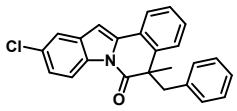
white solid, mp: 278-280°C; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.51 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 6.1 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.38 – 7.28 (m, 5H), 6.78 (s, 1H), 6.49 (dd, J = 9.9, 2.5 Hz, 1H), 6.46 – 6.38 (m, 1H), 6.34 – 6.26 (m, 1H), 3.42 (d, J = 13.8 Hz, 1H), 3.07 (d, J = 13.8 Hz, 1H), 1.91 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.57, 139.43 (d, $J_{F,C}$ = 7.4 Hz), 137.14, 135.17, 131.86, 131.45 (d, $J_{F,C}$ = 8.3 Hz), 130.52, 129.69, 128.58, 127.53, 126.86, 125.59, 125.18, 124.41, 123.71, 120.44, 116.32 (t, $J_{F,C}$ = 10.4 Hz), 111.65 (d, $J_{F,C}$ = 20.8 Hz), 102.72, 46.08, 29.71, 24.72, 19.16. ^{19}F NMR (376 MHz, $CDCl_3$, 25° C) δ = -116.85. IR: v = 3068, 2933, 2854, 1713, 1614, 1586, 1553, 1498, 1475, 1450, 1379, 1356, 1246, 1168, 1155, 762, 750 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{20}FNO$ 370.1602; Found 370.1603.



5-benzyl-10-fluoro-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

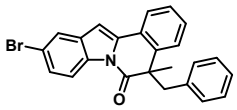
white solid, mp: 128-130°C; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.50 (dd, J = 8.9, 4.8 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.64 (s, 1H),

6.53 (d, J = 8.4 Hz, 2H), 3.51 (d, J = 12.9 Hz, 1H), 3.08 (d, J = 13.0 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.27, 137.59, 136.79, 135.67, 129.22, 129.15, 128.89, 127.53, 127.38, 126.80, 126.62, 123.57, 117.45 (d, $J_{F,C}$ = 9.2 Hz), 112.47 (d, $J_{F,C}$ = 24.8 Hz), 105.92 (d, $J_{F,C}$ = 24.2 Hz), 101.95 (d, $J_{F,C}$ = 4.1 Hz), 50.74, 50.36, 25.88. ^{19}F NMR (376 MHz, $CDCl_3$, 25° C) δ = -113.46, -118.41. IR: v = 3066, 3025, 2923, 2856, 1692, 1598, 1444, 1379, 1362, 1332, 1215, 1168, 1123, 959, 856, 803, 758, 729, 699 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{18}FNO$ 356.1446; Found 356.1447.



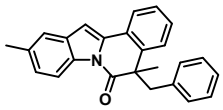
5-benzyl-10-chloro-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

white solid, mp: 133-136℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.47 (d, J = 8.7 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.79 (t, J = 7.5 Hz, 2H), 6.61 (s, 1H), 6.52 (d, J = 7.3 Hz, 2H), 3.50 (d, J = 12.9 Hz, 1H), 3.08 (d, J = 12.9 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.40, 137.56, 136.56, 135.59, 133.29, 131.78, 129.86, 129.12, 128.99, 127.55, 127.41, 126.79, 126.66, 125.03, 123.62, 119.86, 117.40, 101.47, 50.87, 50.45, 25.79. IR: v = 3023, 2926, 2858, 1701, 1609, 1446, 1356, 1324, 1218, 1153, 1027, 968, 925, 860, 799, 749, 731, 688 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{18}ClNO$ 372.1150; Found 372.1151.



5-benzyl-10-bromo-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

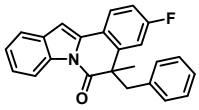
white solid, mp: 136-138℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.42 (d, J = 8.7 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 1.6 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.79 (t, J = 7.5 Hz, 2H), 6.60 (s, 1H), 6.51 (d, J = 7.3 Hz, 2H), 3.50 (d, J = 12.9 Hz, 1H), 3.07 (d, J = 12.9 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.44, 137.57, 136.43, 135.57, 133.63, 132.27, 129.19, 129.12, 129.01, 127.73, 127.56, 127.42, 126.79, 126.67, 124.91, 123.64, 122.90, 117.79, 101.33, 50.89, 50.48, 25.77. IR: v = 3077, 3020, 2921, 1965, 1692, 1590, 1451, 1419, 1360, 1324, 1090, 1009, 945, 817, 738, 702 cm^{-1} HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{18}BrNO$ 416.0645; Found 416.0646.



5-benzyl-5,10-dimethylindolo[2,1-a]isoquinolin-6(5H)-one

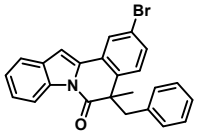
white solid, mp: 130-135℃;^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.42 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 6.90 (t, J = 7.3 Hz, 1H), 6.81 (t, J = 7.5 Hz, 2H), 6.65 (s, 1H), 6.57 (d, J = 7.4 Hz, 2H), 3.53 (d, J = 13.1 Hz, 1H), 3.09 (d, J = 13.0 Hz, 1H), 2.44 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.25,

137.38, 135.93, 135.28, 133.92, 133.25, 130.73, 130.09, 129.34, 129.27, 128.37, 127.53, 127.21, 126.80, 126.50, 126.32, 125.42, 123.42, 120.28, 116.12, 102.28, 50.39, 50.29, 26.11, 21.49. IR: v = 3028, 2923, 2854, 1690, 1596, 1493, 1455, 1379, 1362, 1325, 1311, 1201, 811, 760, 733, 701 cm^{-1}. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{21}NO$ 352.1696; Found 352.1698.



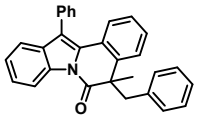
5-benzyl-3-fluoro-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

white solid, mp: 98-99℃; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.55 (d, J = 8.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.18 – 7.12 (m, 1H), 7.08 – 6.99 (m, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.82 (t, J = 7.4 Hz, 2H), 6.63 (s, 1H), 6.59 (d, J = 7.3 Hz, 2H), 3.54 (d, J = 13.1 Hz, 1H), 3.04 (d, J = 13.1 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.81, 162.77 (d, $J_{F,C}$ = 248.4 Hz), 139.87 (d, $J_{F,C}$ = 7.2 Hz), 135.47, 134.93, 134.42, 130.42, 130.03, 129.20, 127.66, 126.73, 125.53 (d, $J_{F,C}$ = 8.6 Hz), 125.11, 124.46, 121.84 (d, $J_{F,C}$ = 3.1 Hz), 120.27, 116.47, 115.13 (d, $J_{F,C}$ = 22.5 Hz), 113.48 (d, $J_{F,C}$ = 22.7 Hz), 102.26 (d, $J_{F,C}$ = 1.8 Hz), 50.58, 50.48, 25.92. ^{19}F NMR (376 MHz, $CDCl_3$, 25° C) δ = -111.48. IR: v = 3061, 3027, 2923, 1696, 1604, 1491, 1450, 1379, 1352, 1340, 1276, 1221, 1182, 950, 906, 807, 748, 733, 701 cm^{-1} HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{18}FNO$ 356.1446; Found 356.1447.



5-benzyl-2-bromo-5-methylindolo[2,1-a]isoquinolin-6(5H)-one

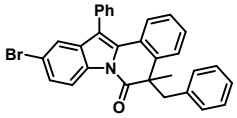
white solid, mp: 98-100℃; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.55 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.49 (d, J = 7.7 Hz, 2H), 7.41 – 7.29 (m, 3H), 6.92 (d, J = 7.3 Hz, 1H), 6.84 (t, J = 7.4 Hz, 2H), 6.73 (s, 1H), 6.59 (d, J = 7.1 Hz, 2H), 3.53 (d, J = 13.2 Hz, 1H), 3.06 (d, J = 13.1 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.90, 136.24, 135.50, 135.13, 133.66, 131.30, 130.18, 129.85, 129.22, 128.66, 127.71, 126.72, 126.17, 125.55, 124.53, 121.22, 120.57, 116.52, 103.52, 50.27, 50.26, 25.99. IR: v = 3066, 3032, 2926, 2155, 1973, 1961, 1696, 1594, 1479, 1450, 1422, 1379, 1346, 1203, 941, 815, 748, 733, 701, 623 cm^{-1} HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{18}BrNO$ 416.0645; Found 416.0647.



5-benzyl-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5H)-one

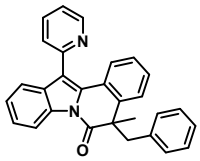
white solid, mp: 118-120℃; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.62 (d, J = 8.2 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.42 – 7.36 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 6.97 (q, J = 7.4 Hz, 2H), 6.82 (t, J = 7.6 Hz, 2H), 6.55 (d, J = 7.4 Hz, 2H), 3.49 (d, J = 12.8 Hz, 1H), 3.05 (d, J = 12.8 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ = 172.54, 137.77, 135.83, 134.04, 133.99, 131.87, 130.07, 129.34, 129.03, 128.15, 127.86, 127.47, 126.72, 126.65, 126.42, 126.24, 125.70, 125.04, 124.27, 119.60, 119.22, 116.31, 51.63, 50.36, 24.84. IR: v = 3066, 3027, 2923, 2849, 1692, 1608, 1450, 1389, 1377, 1362, 1334, 1235, 1168, 1139, 1031, 975, 916, 783, 774, 750, 733, 701 cm^{-1} HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{23}NO$ 414.1853; Found 414.1854.



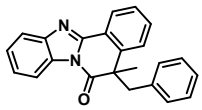
5-benzyl-10-bromo-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5H)-one

white solid, mp: 135-138℃; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) *δ* = 8.49 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.42 (m, 5H), 7.35 – 7.23 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.03 – 6.92 (m, 2H), 6.82 (t, *J* = 7.6 Hz, 2H), 6.51 (d, *J* = 7.4 Hz, 2H), 3.47 (d, *J* = 12.8 Hz, 1H), 3.03 (d, *J* = 12.8 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.51, 137.92, 135.59, 133.65, 133.25, 132.63, 132.19, 130.53, 129.96, 129.19, 128.63, 128.41, 128.15, 127.52, 126.87, 126.80, 126.42, 125.84, 125.13, 121.88, 118.52, 117.78, 117.70, 52.03, 50.43, 24.70. IR: v = 3059, 3025, 2921, 1694, 1606, 1442, 1412, 1385, 1360, 1325, 1315, 1268, 1169, 1056, 928, 912, 809, 758, 731, 701 cm^{-1} HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{22}BrNO$ 492.0958; Found 492.0961.



5-benzyl-5-methyl-12-(pyridin-2-yl)indolo[2,1-a]isoquinolin-6(5H)-one

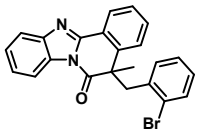
white solid, mp: 92-94℃; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) *δ* = 8.82 (d, *J* = 4.2 Hz, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.95 (q, *J* = 8.8, 8.1 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 2H), 6.61 (d, *J* = 7.3 Hz, 2H), 3.50 (d, *J* = 13.0 Hz, 1H), 3.10 (d, *J* = 13.0 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.63, 153.99, 153.82, 150.33, 138.11, 136.59, 135.89, 134.25, 133.01, 129.45, 128.62, 128.57, 127.52, 126.73, 126.70, 126.59, 125.87, 125.75, 125.67, 125.35, 124.55, 122.48, 119.60, 118.58, 116.25, 51.13, 50.41, 24.94. IR: v = 3063, 3027, 2921, 2849, 1696, 1604, 1588, 1561, 1475, 1450, 1385, 1360, 1332, 1282, 1168, 1151, 1103, 750, 733, 701 cm^{-1} HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{22}N_2O$ 415.1805; Found 415.1806.



5-benzyl-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one[1]

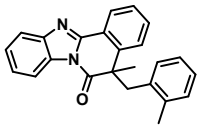
^1H NMR (400 MHz, $CDCl_3$, TMS, 25°C) *δ* = 8.39 – 8.30 (m, 1H), 8.27 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.63 – 7.56 (m, 2H), 7.50 – 7.42 (m, 1H), 7.42 – 7.34 (m, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 2H), 6.53 (d, *J* = 7.3 Hz, 2H), 3.56 (d, *J* = 13.0 Hz, 1H), 3.17 (d, *J* = 13.0 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.64, 149.50, 143.76, 140.66, 134.99, 131.49, 131.02, 128.97, 127.84, 127.77,

127.04, 126.60, 125.68, 125.64, 125.42, 123.55, 119.62, 115.40, 51.10, 50.84, 25.99.



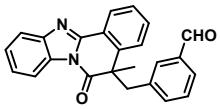
5-(2-bromobenzyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one[1]

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.37 – 8.30 (m, 2H), 7.78 – 7.71 (m, 1H), 7.53 – 7.45 (m, 3H), 7.42 (dd, J = 5.7, 3.4 Hz, 2H), 7.31 – 7.22 (m, 1H), 6.88 – 6.76 (m, 2H), 6.65 – 6.57 (m, 1H), 3.69 (d, J = 14.2 Hz, 1H), 3.45 (d, J = 14.2 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.38, 149.61, 143.93, 140.16, 134.89, 132.85, 132.11, 131.62, 131.33, 130.67, 128.56, 128.08, 126.99, 126.77, 125.93, 125.77, 125.53, 123.29, 119.71, 115.58, 50.31, 47.97, 25.59.



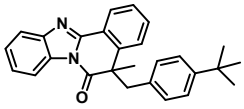
5-methyl-5-(2-methylbenzyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one[1]

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.36 – 8.26 (m, 2H), 7.74 – 7.68 (m, 1H), 7.56 – 7.45 (m, 2H), 7.44 – 7.37 (m, 3H), 6.88 – 6.77 (m, 2H), 6.62 (t, J = 7.2 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 3.51 (d, J = 13.7 Hz, 1H), 3.21 (d, J = 13.7 Hz, 1H), 1.97 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.90, 149.58, 143.89, 140.62, 136.92, 133.14, 131.44, 131.24, 130.23, 129.79, 127.95, 127.04, 126.77, 125.82, 125.63, 125.43, 125.11, 123.63, 119.68, 115.31, 50.65, 46.97, 24.88, 18.98.



3-((5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-5-yl)methyl)benzaldehyde

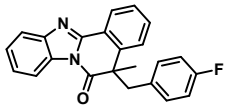
white solid, mp: 120-122℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 9.50 (s, 1H), 8.34 (d, J = 7.3 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.49 – 7.40 (m, 2H), 7.36 (s, 2H), 7.14 (d, J = 7.4 Hz, 2H), 7.04 – 6.95 (m, 1H), 6.76 (d, J = 7.6 Hz, 1H), 3.64 (d, J = 13.0 Hz, 1H), 3.23 (d, J = 13.0 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.21, 156.44, 137.92, 134.86, 131.96, 130.39, 128.53, 128.47, 128.32, 126.50, 126.07, 125.84, 123.34, 121.97, 119.53, 115.36, 114.83, 51.09, 50.57, 25.64. IR: v = 3652, 3136, 3097, 2157, 2147, 2026, 2016, 2006, 1961, 1950, 1944, 1715, 1696, 1453, 1356, 762, 756, 680 cm^{-1} HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}N_2O_2$ 367.1442; Found 367.1443.



5-(4-(tert-butyl)benzyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one[1]

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.33 – 8.24 (m, 2H), 7.68 – 7.62 (m,

1H), 7.62 – 7.57 (m, 2H), 7.51 – 7.44 (m, 1H), 7.41 – 7.32 (m, 2H), 6.78 (d, J = 8.3 Hz, 2H), 6.44 (d, J = 8.2 Hz, 2H), 3.49 (d, J = 13.0 Hz, 1H), 3.14 (d, J = 13.0 Hz, 1H), 1.93 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.65, 149.93, 149.54, 143.77, 140.80, 131.81, 131.45, 131.09, 128.58, 127.76, 126.53, 125.54, 125.50, 125.27, 124.56, 123.77, 119.54, 115.31, 51.23, 50.61, 34.12, 31.03, 25.63.



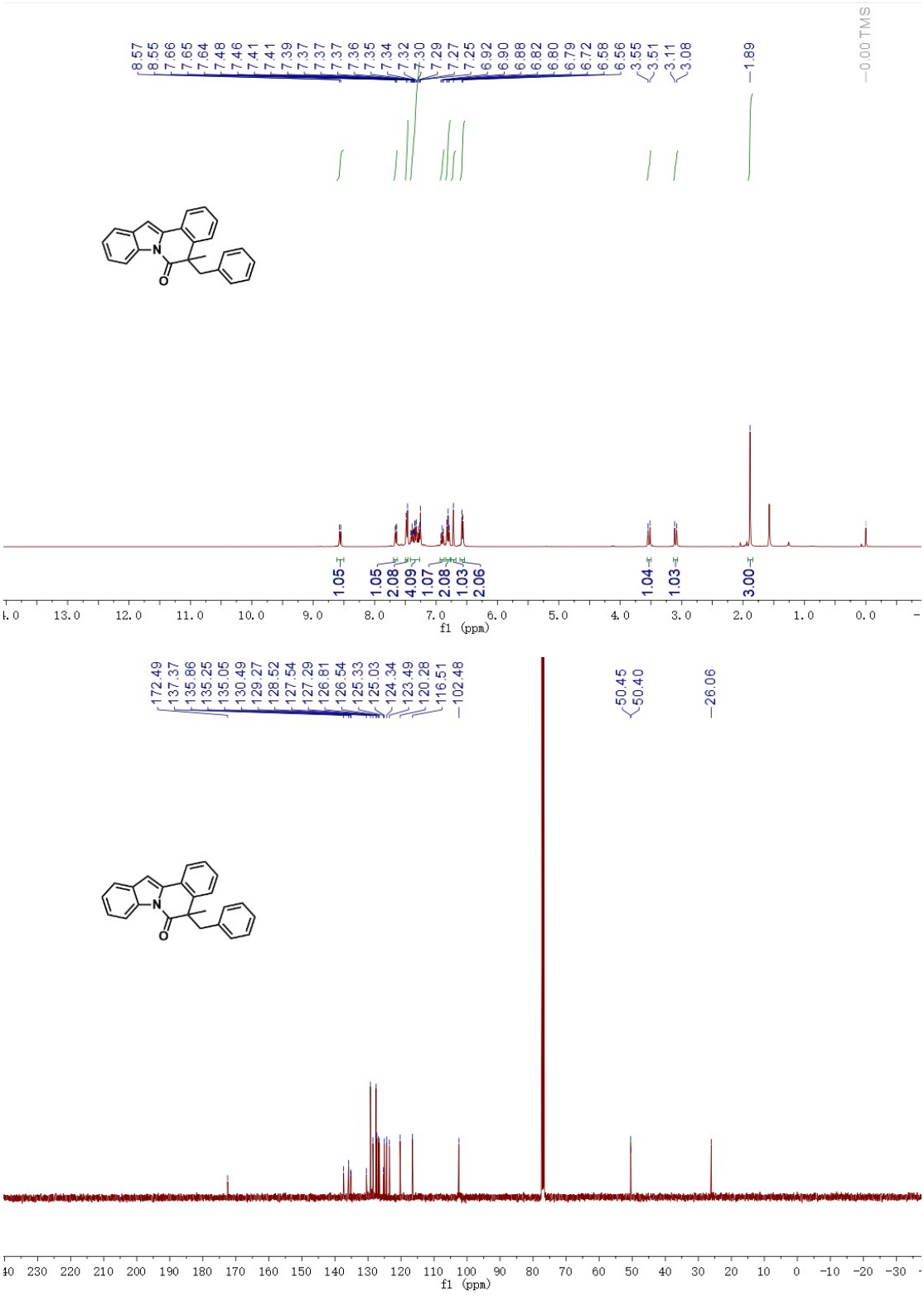
5-(4-fluorobenzyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one[1]

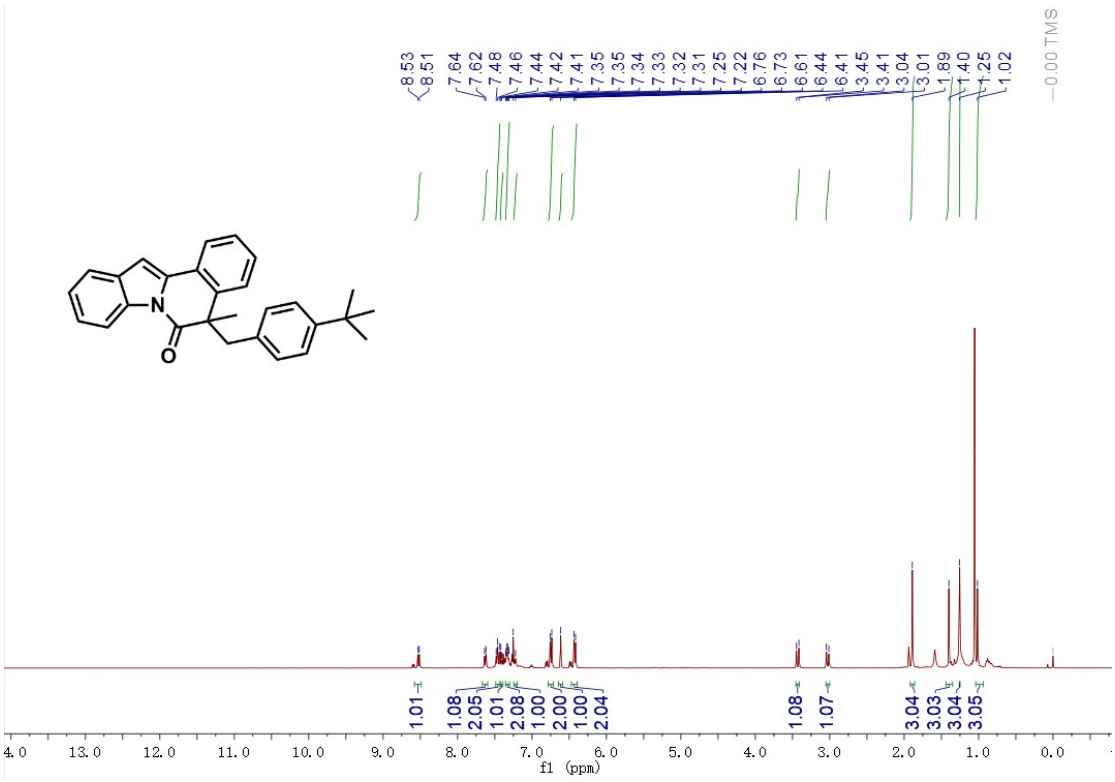
^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ = 8.38 – 8.26 (m, 2H), 7.74 – 7.68 (m, 1H), 7.65 – 7.57 (m, 2H), 7.52 – 7.44 (m, 1H), 7.43 – 7.37 (m, 2H), 6.50 (d, J = 7.0 Hz, 4H), 3.55 (d, J = 13.2 Hz, 1H), 3.15 (d, J = 13.2 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.50, 161.28 (d, $J_{F,C}$ = 32.0 Hz), 149.36, 143.91, 143.81, 140.45, 131.56, 130.90 (d, $J_{F,C}$ = 12.3 Hz), 130.56, 130.48, 127.96, 126.54, 125.82, 125.74, 125.52, 123.55, 119.76, 115.36, 114.72 (d, $J_{F,C}$ = 21.2 Hz), 51.07, 49.76, 26.16. ^{19}F NMR (376 MHz, $CDCl_3$, 25°C) δ = -115.18.

6. References

(1) Meher, P., Samanta, R. K., Manna, S., Murarka, S. Visible light photoredox-catalyzed arylative cyclization to access benzimidazo [2, 1-a] isoquinolin-6 (5 H)-ones. Chemical Communications, 2023, 59(40): 6092-6095.

7. NMR spectra

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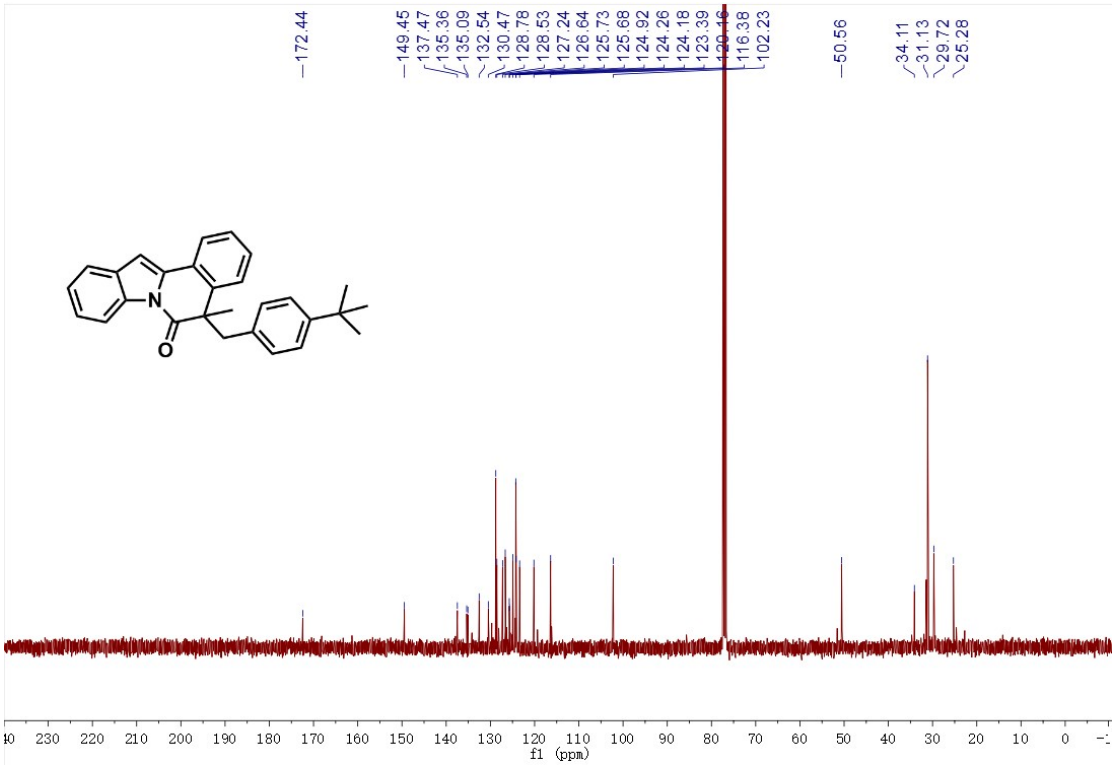
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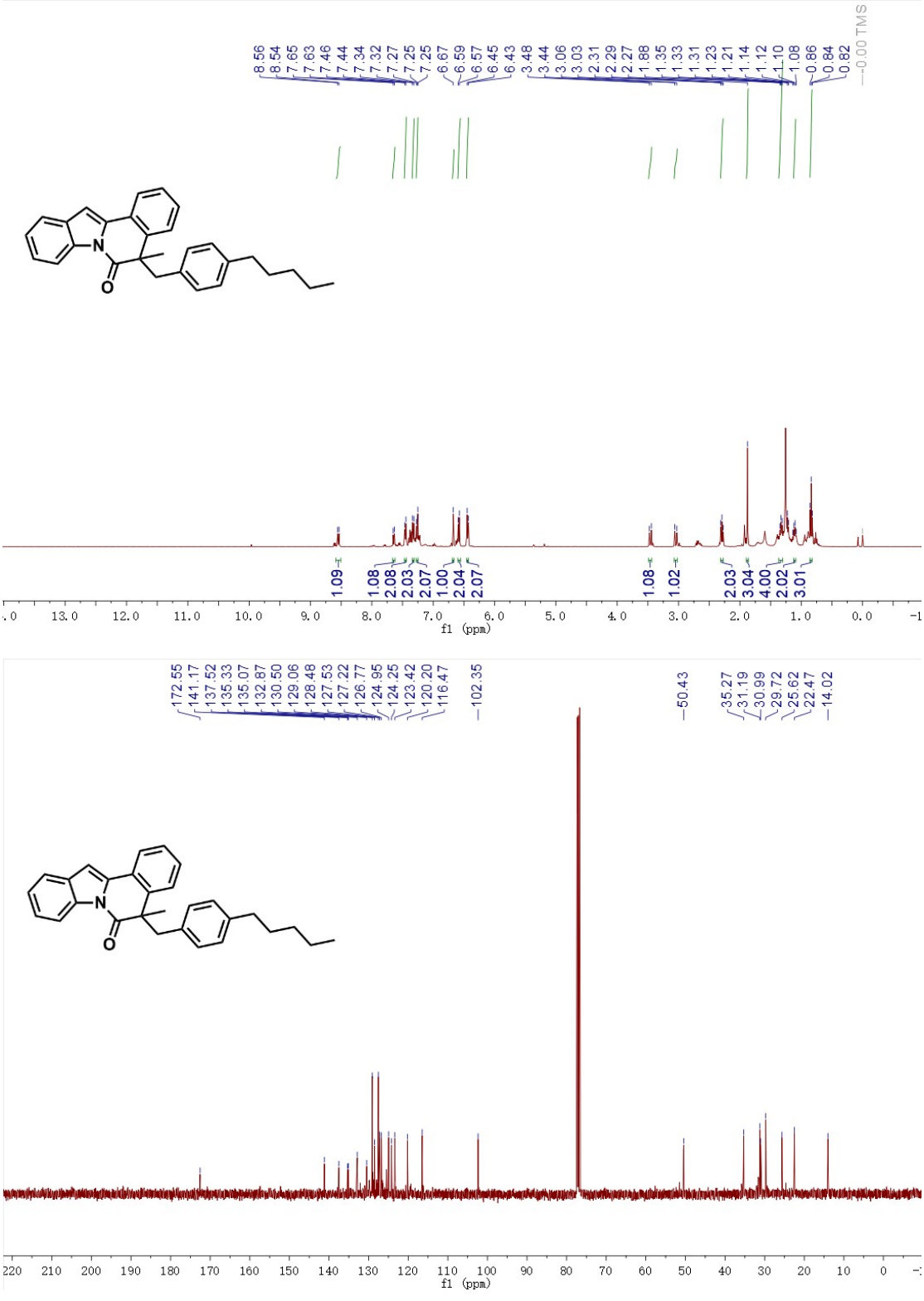
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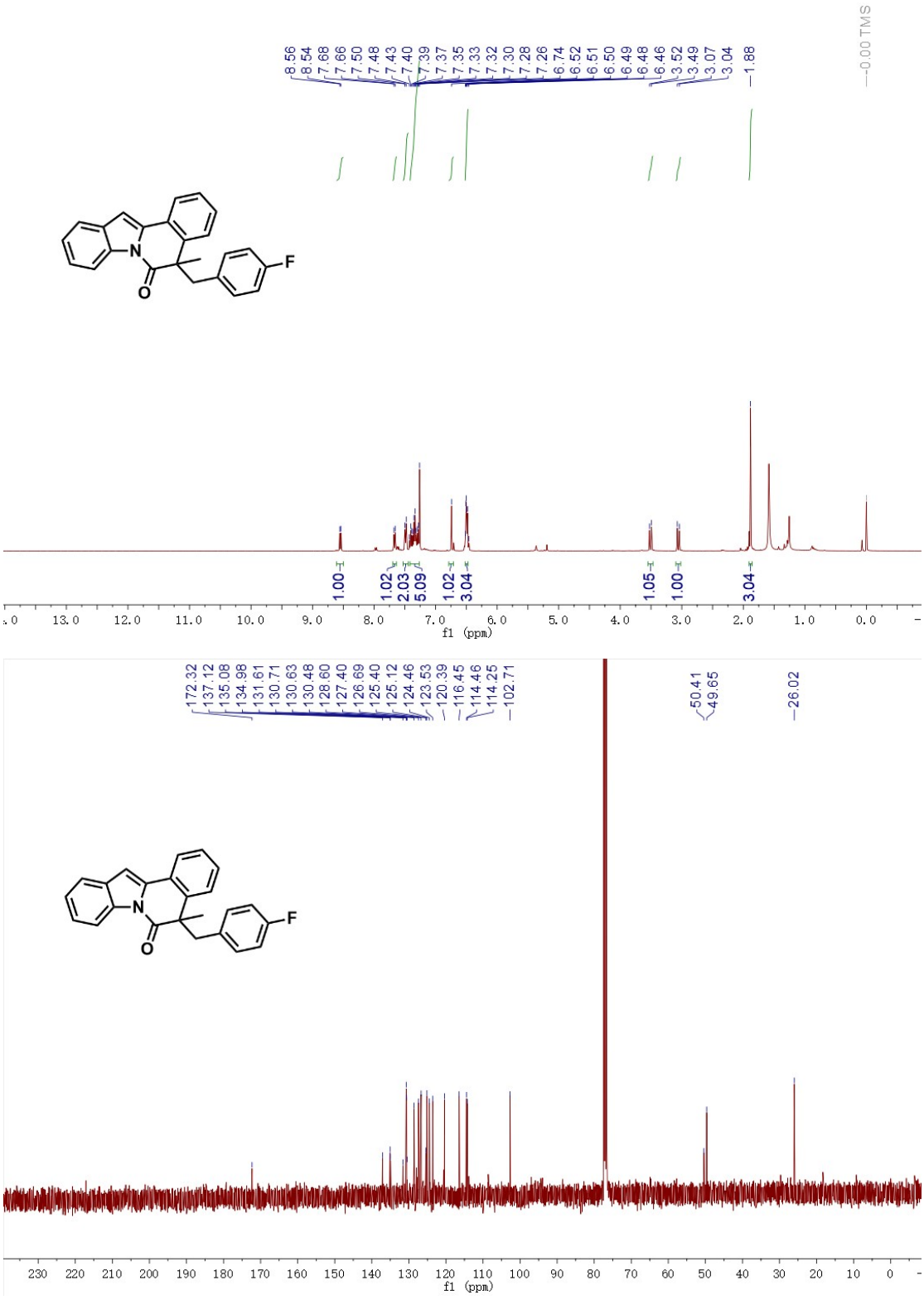
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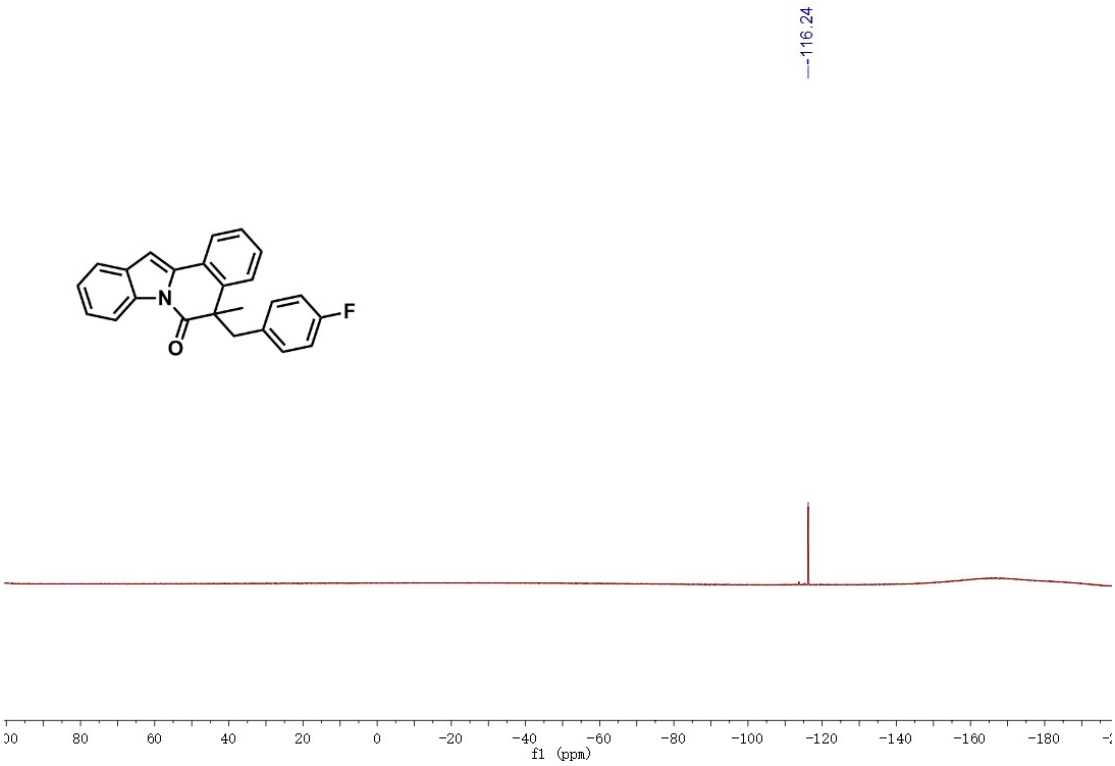
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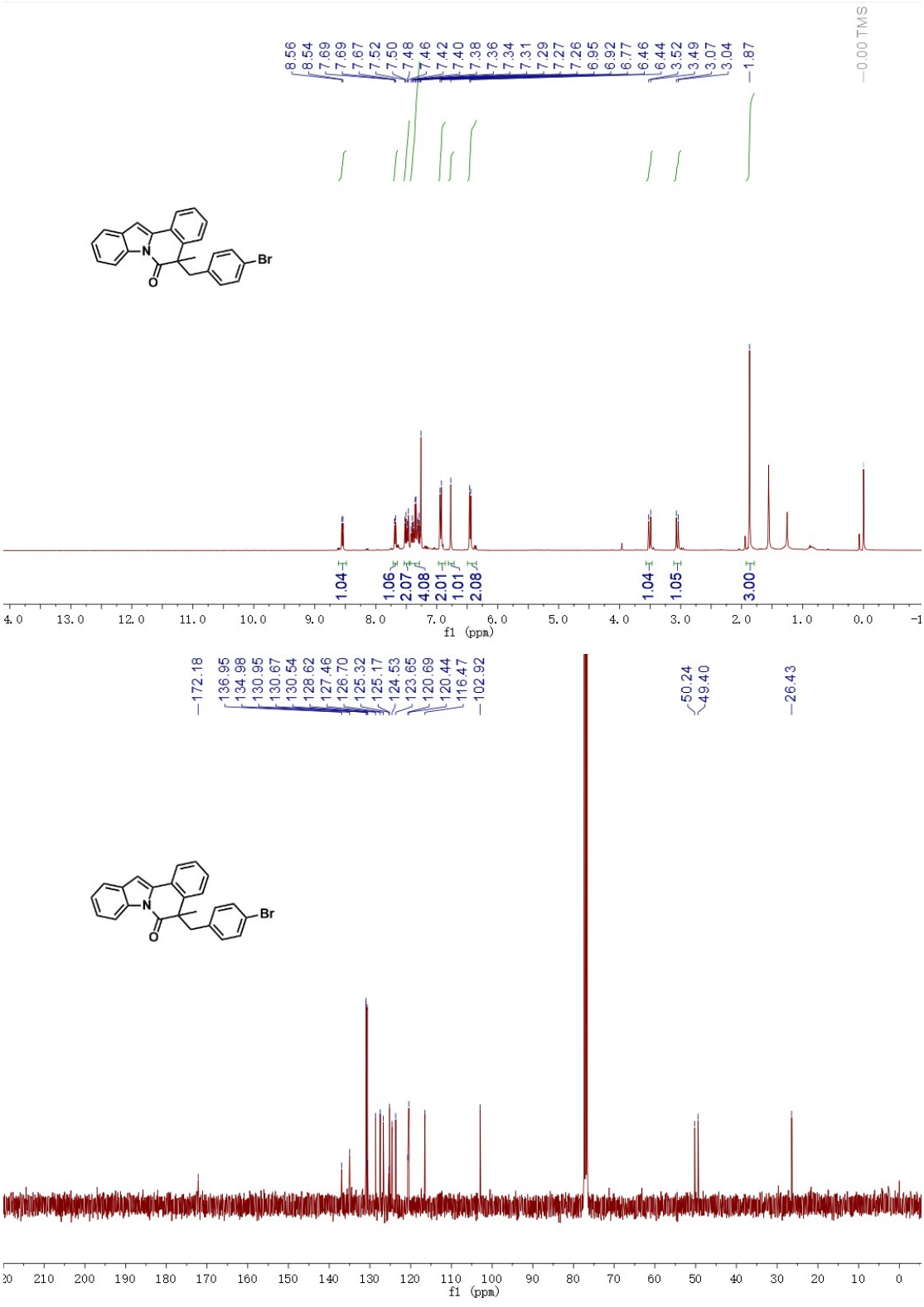
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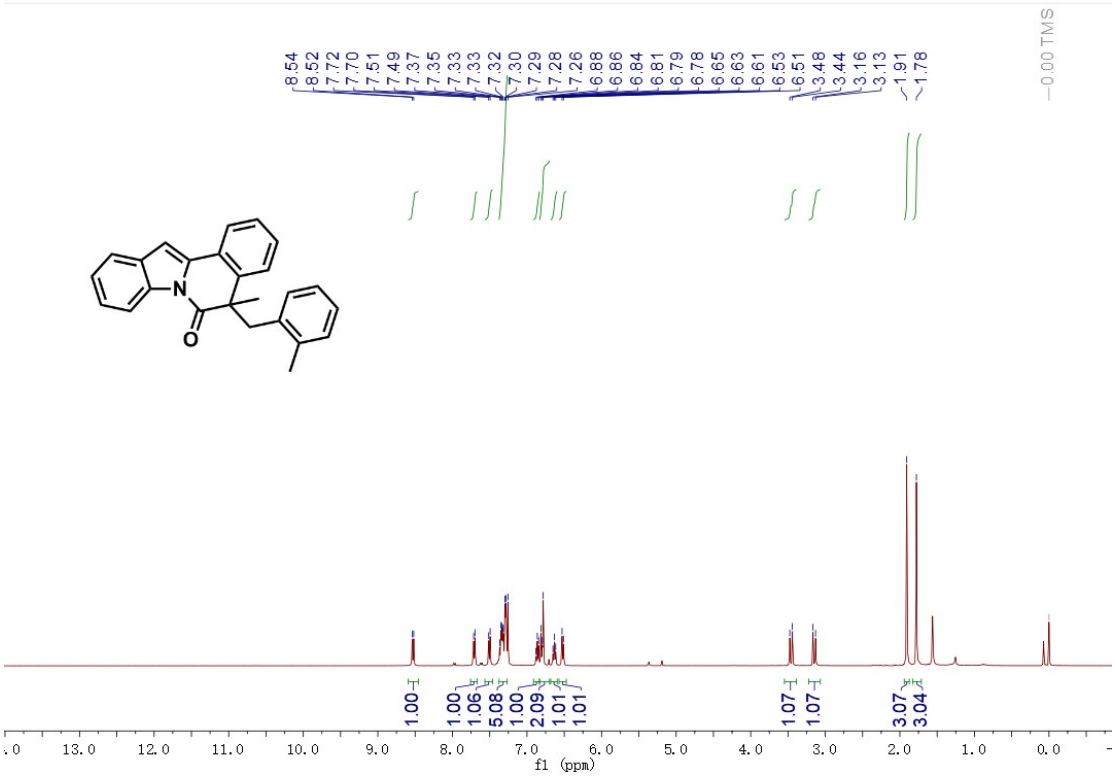
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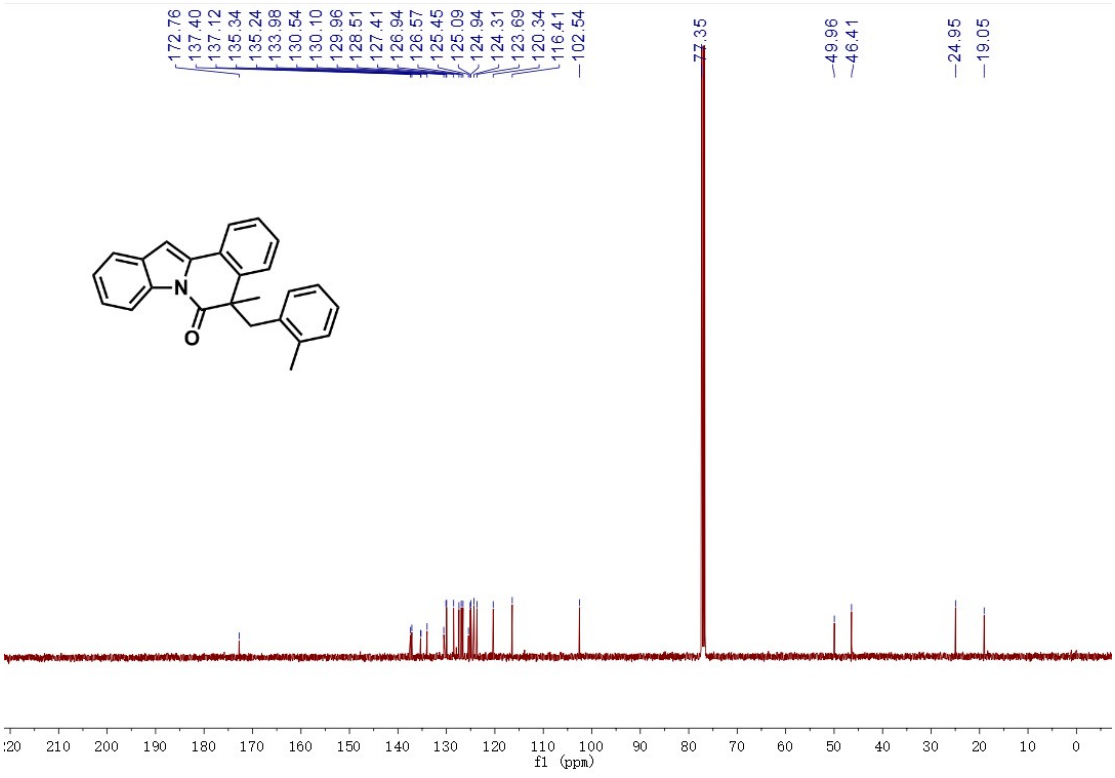
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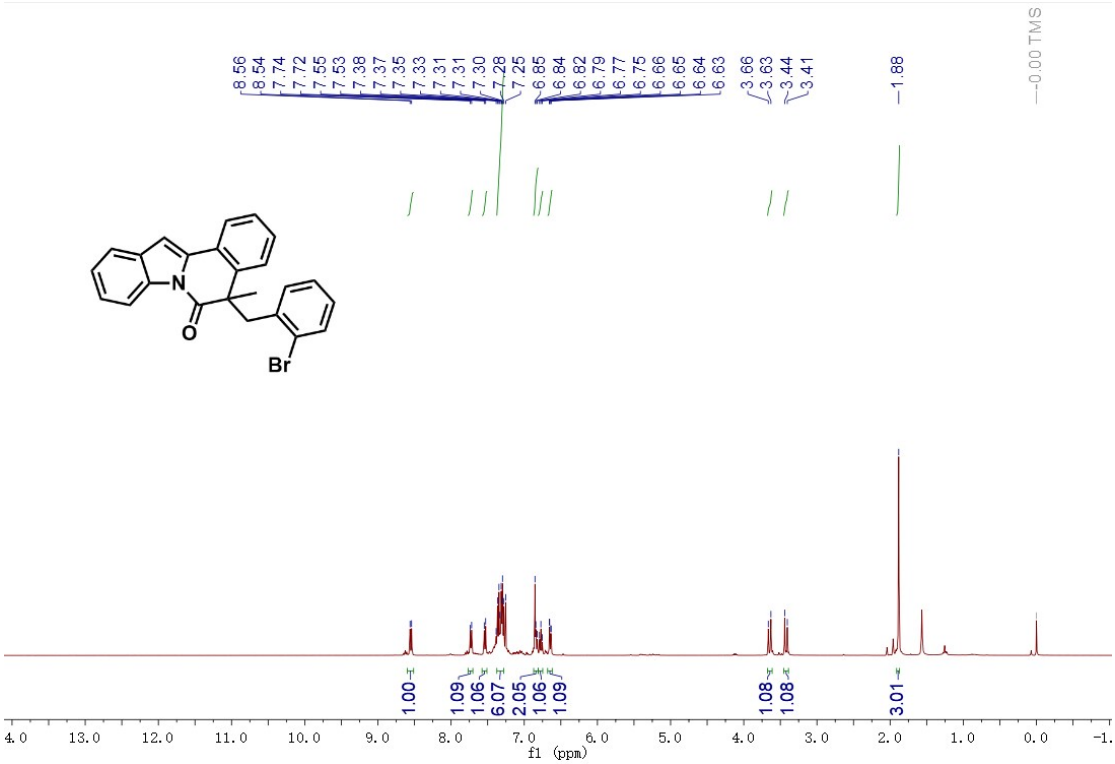
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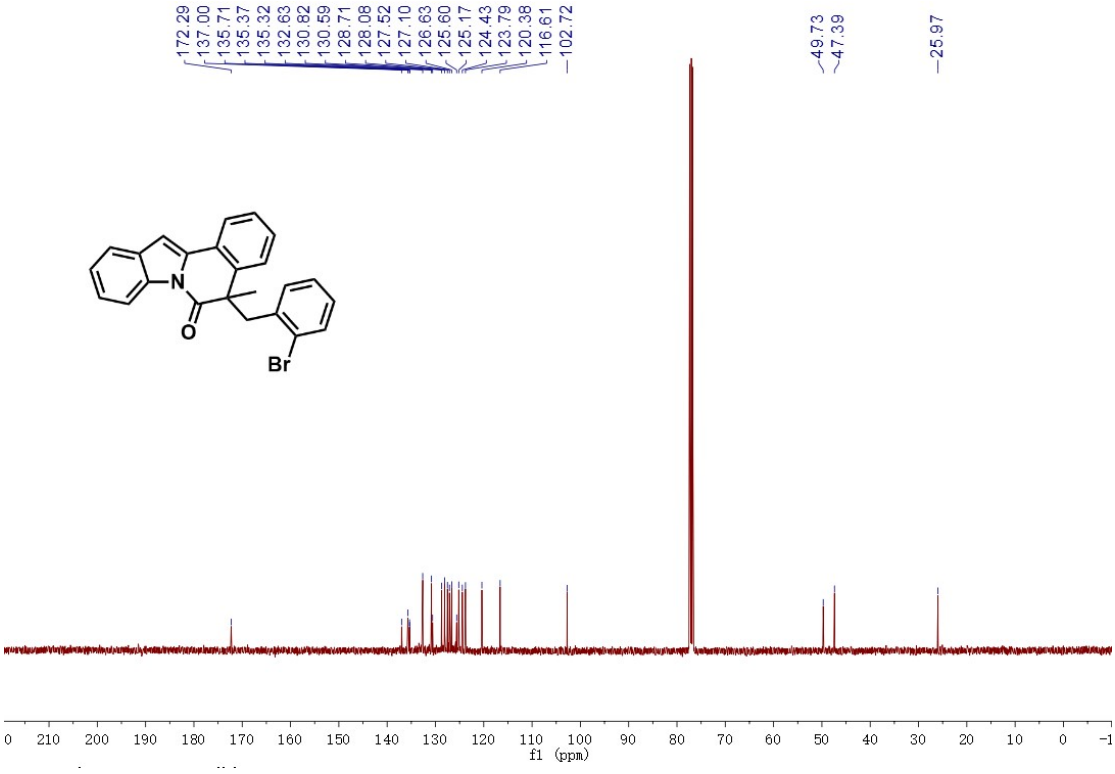
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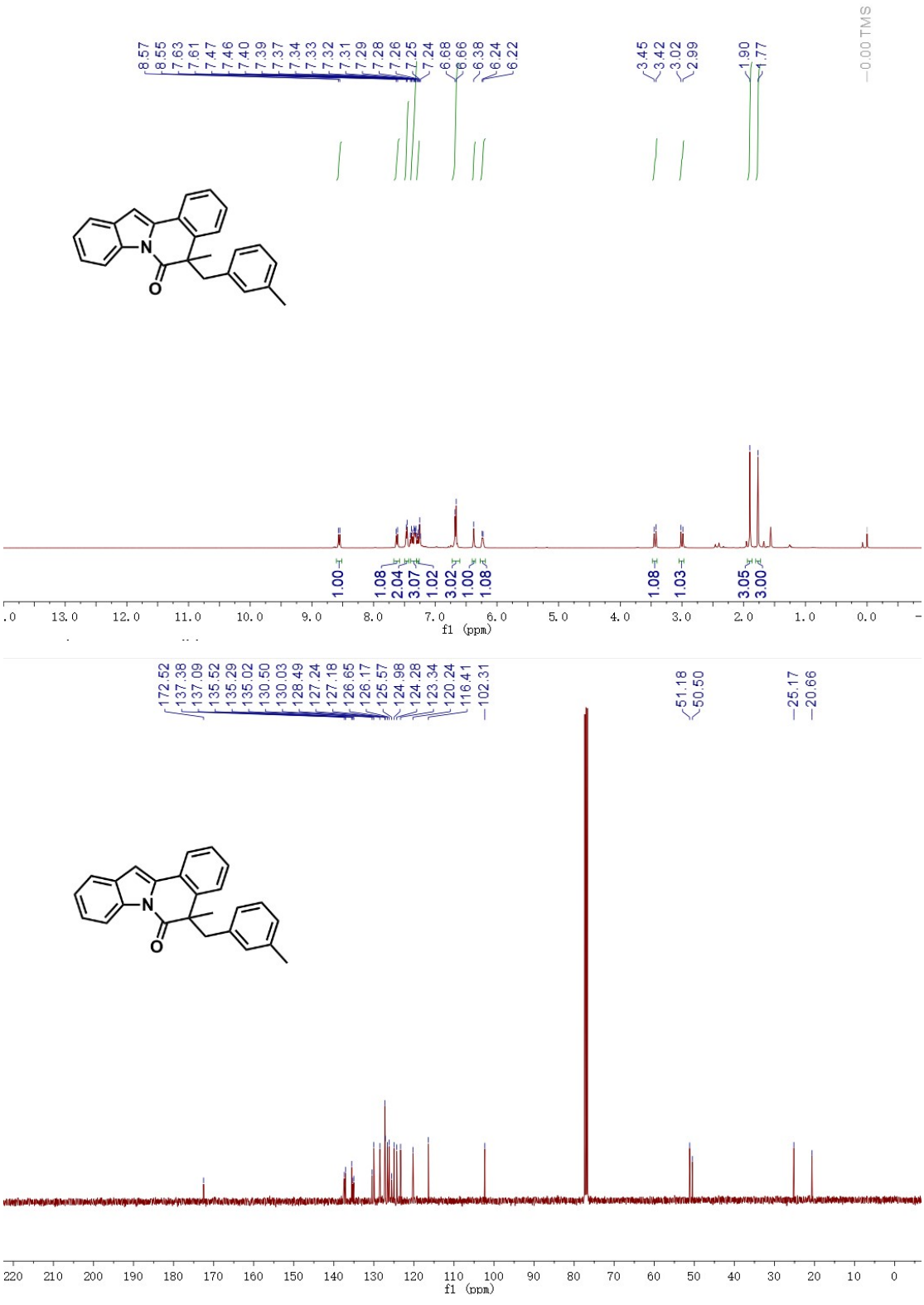
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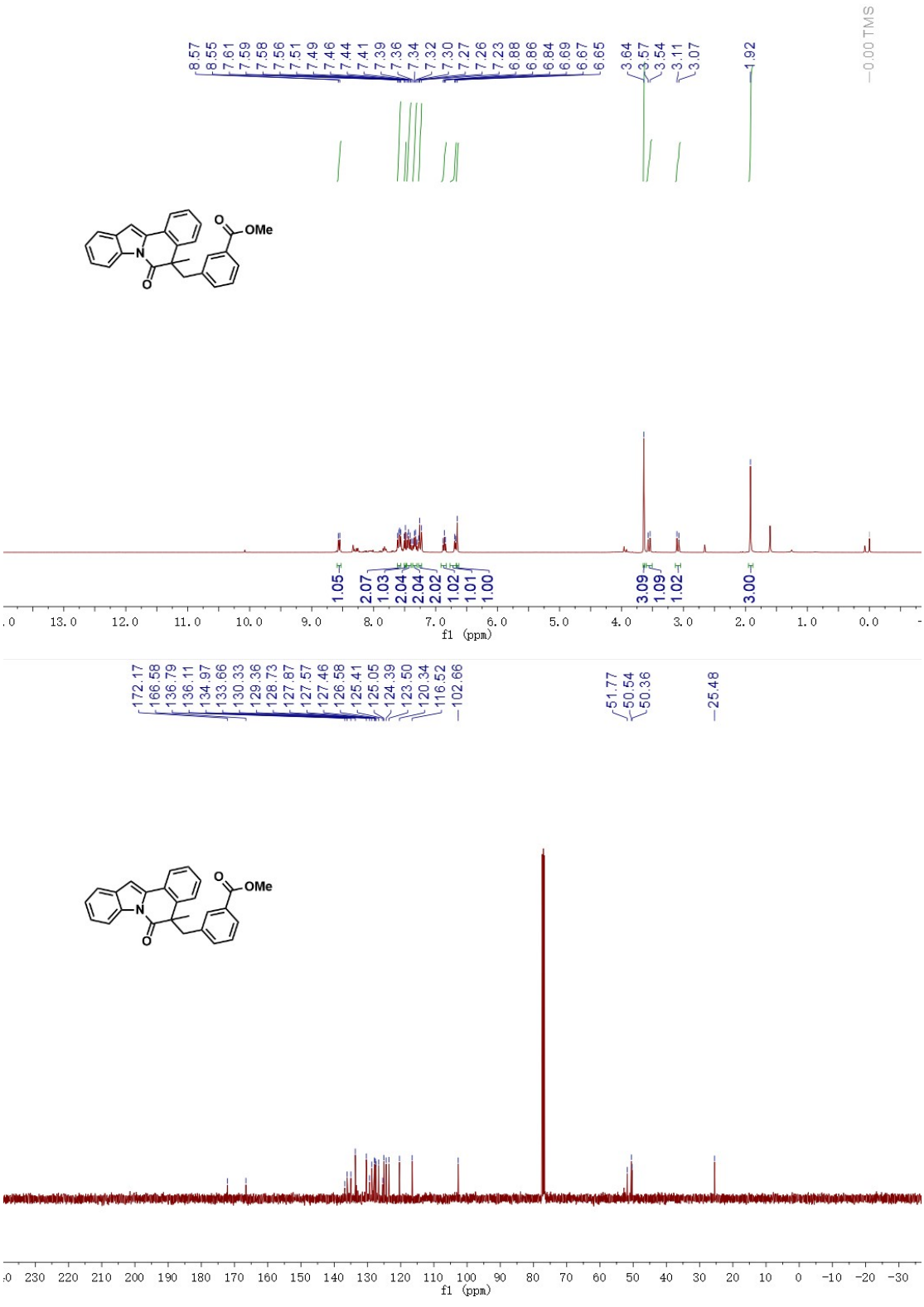
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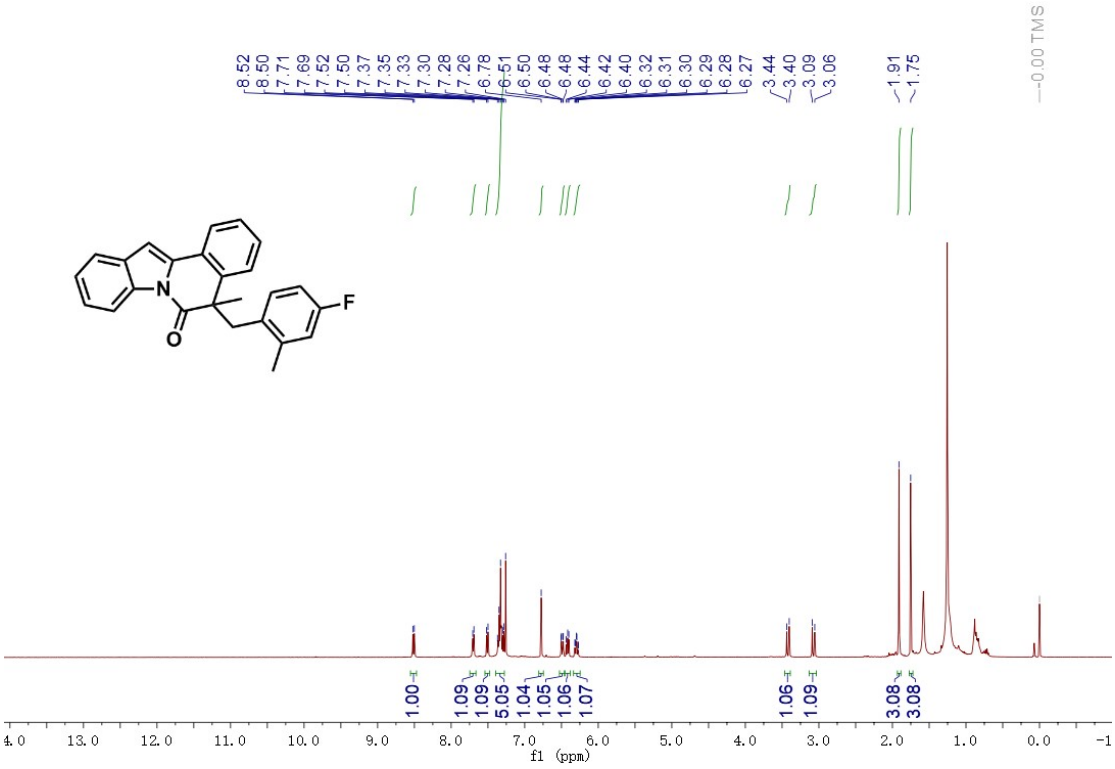
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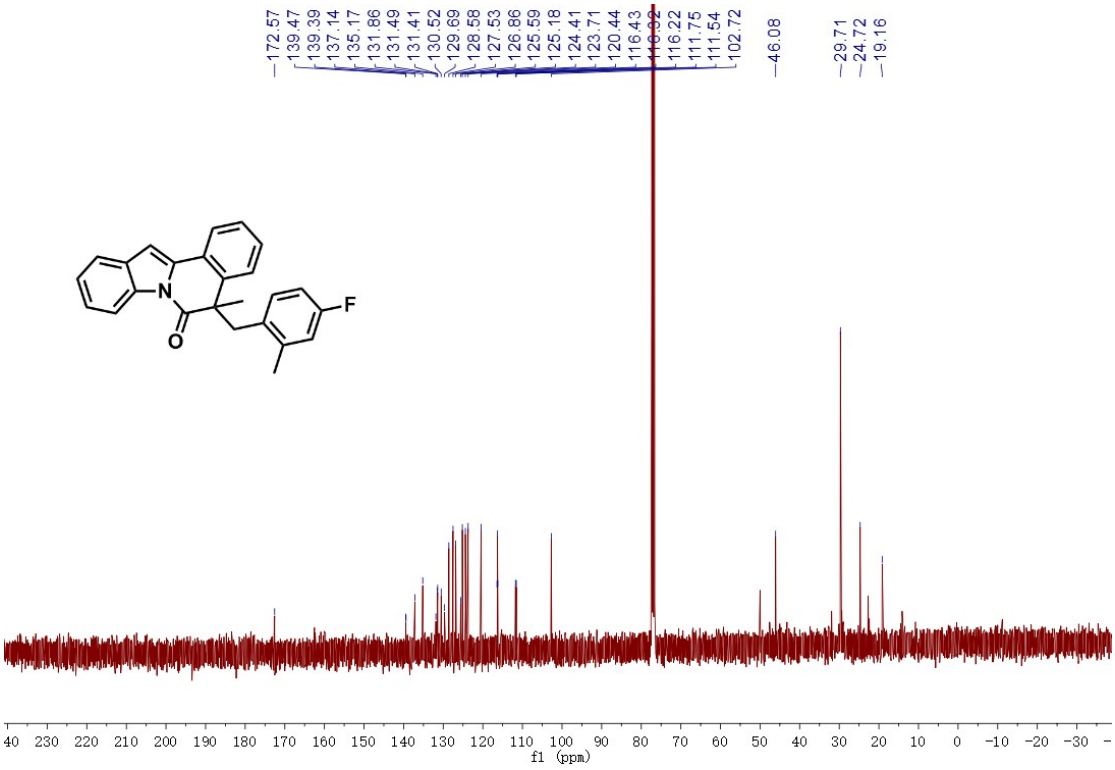
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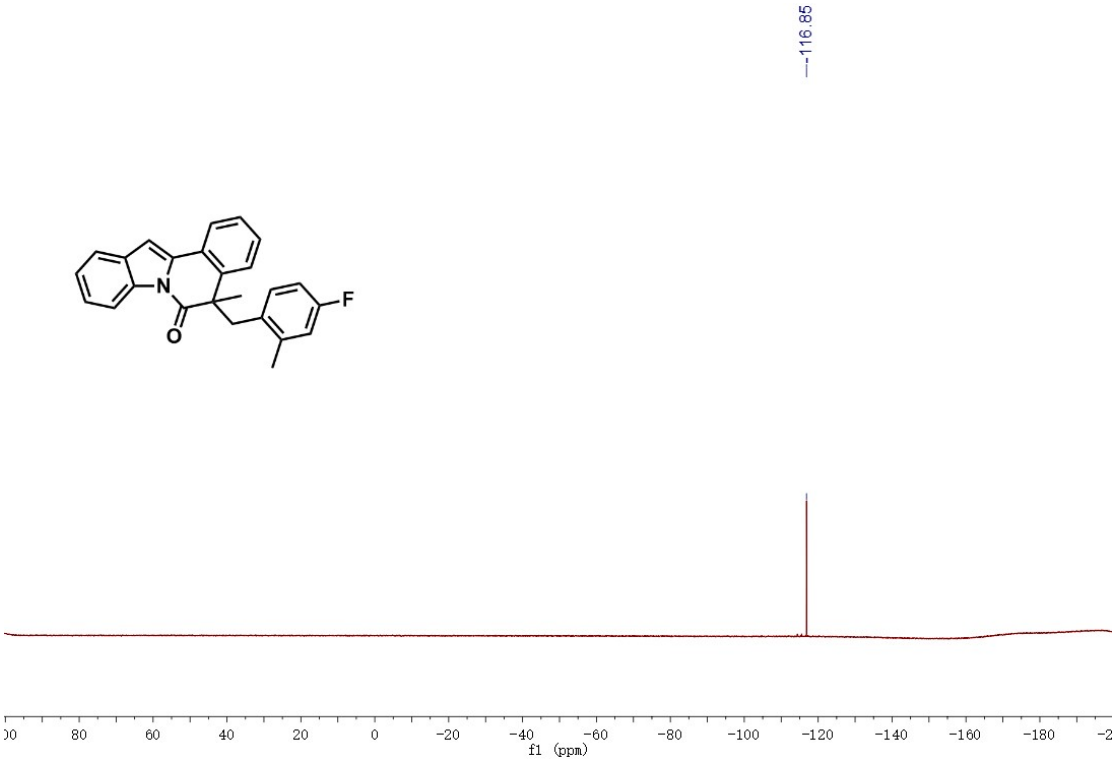
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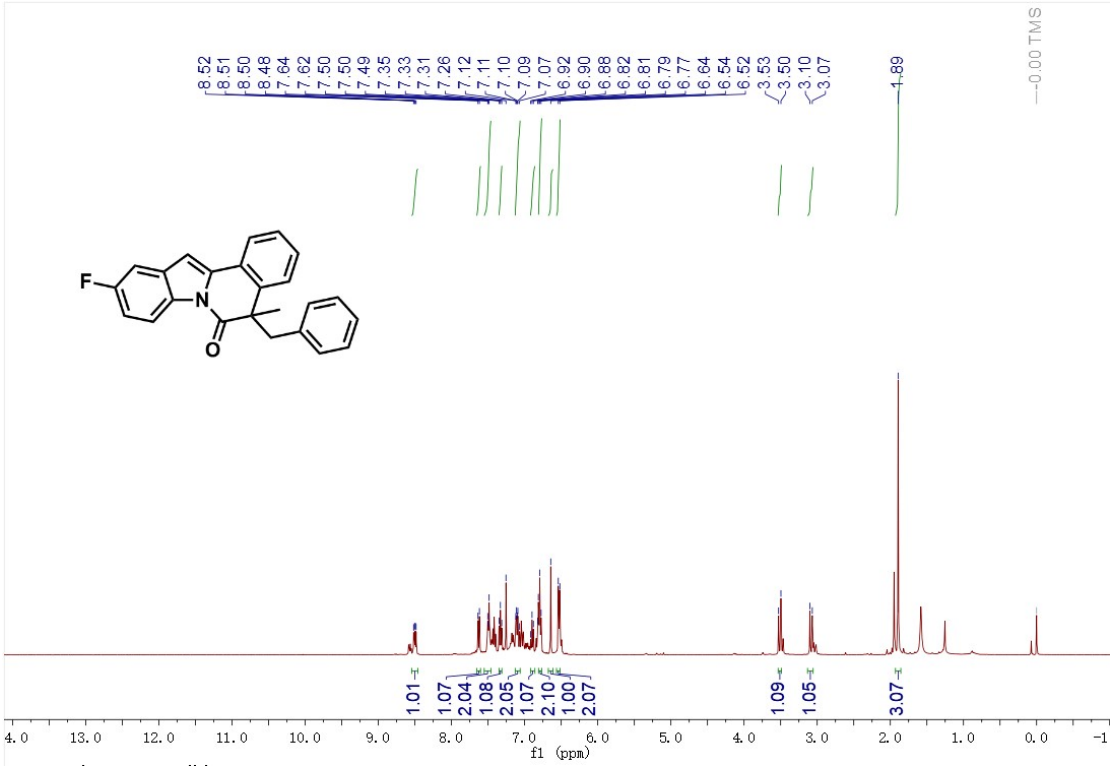
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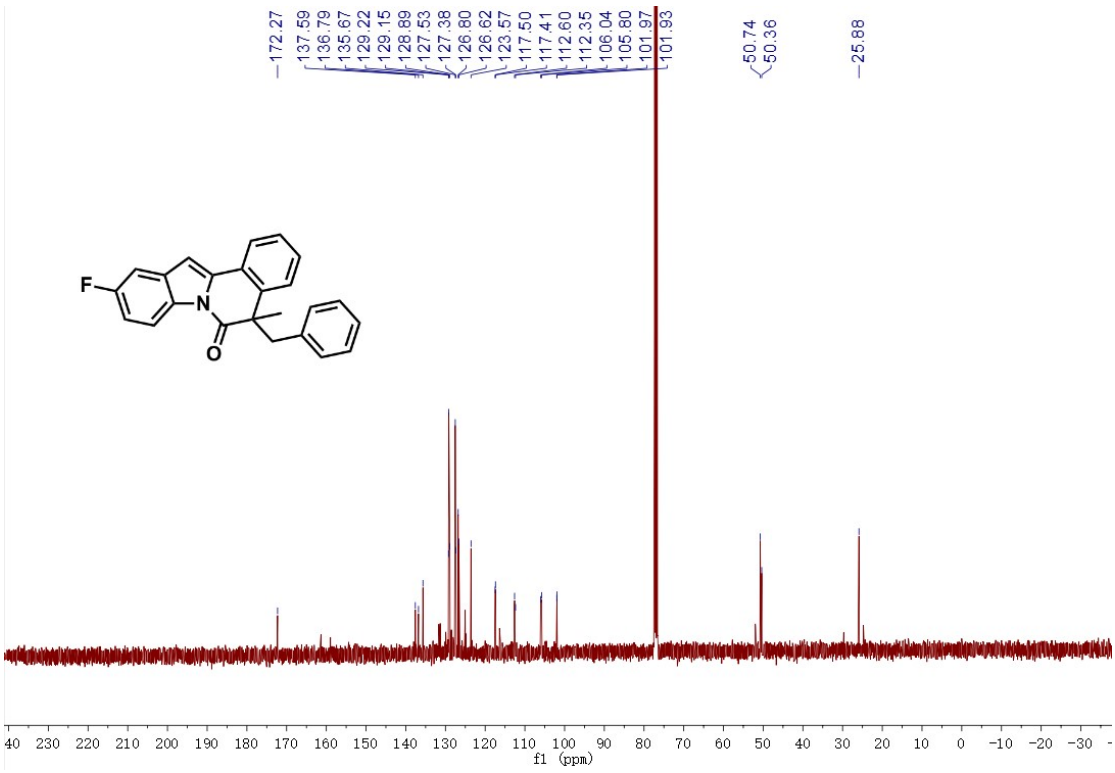
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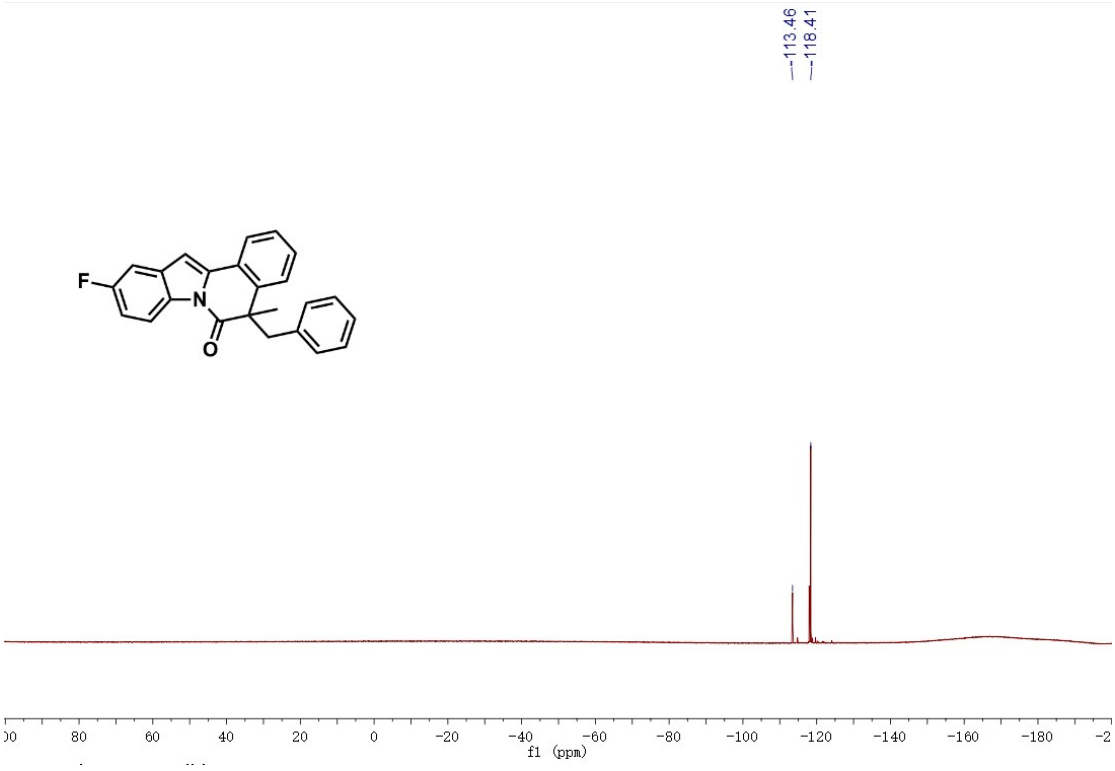
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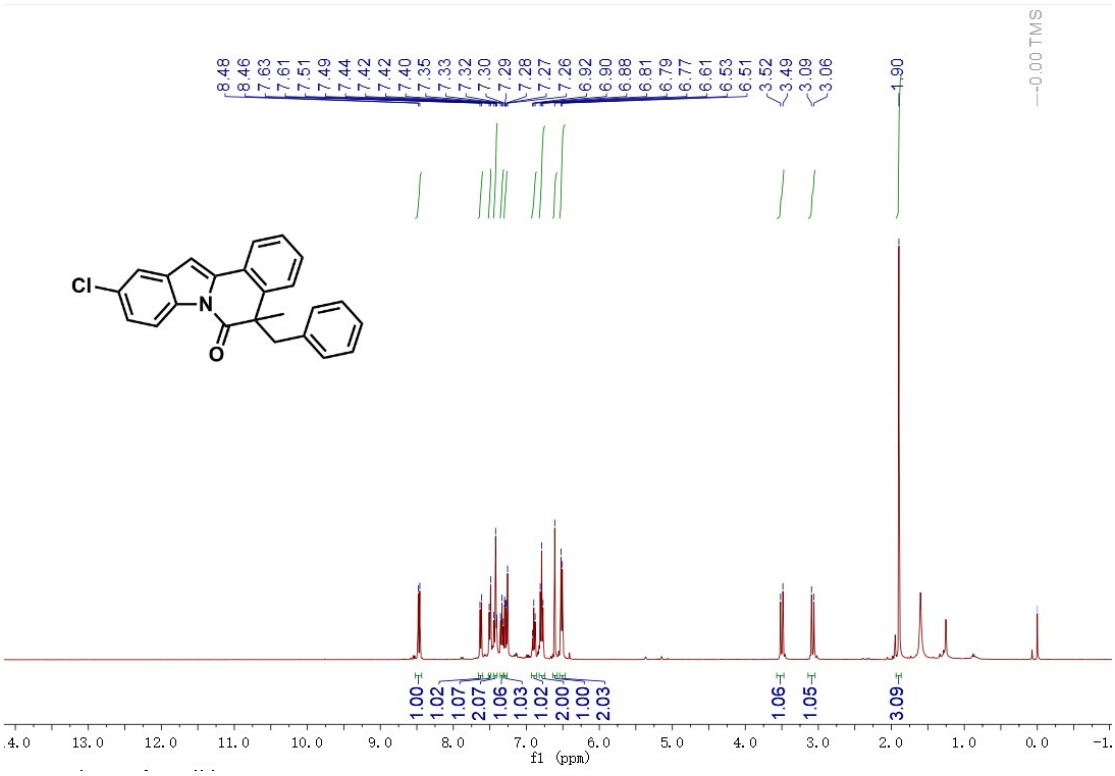
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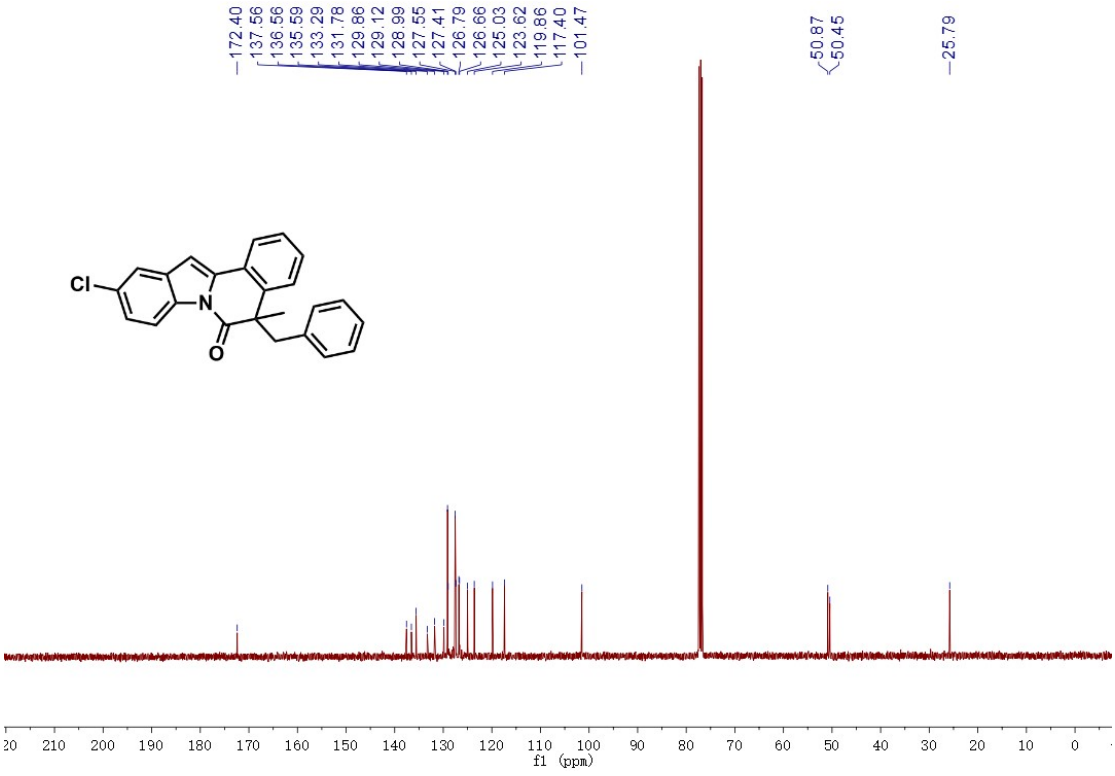
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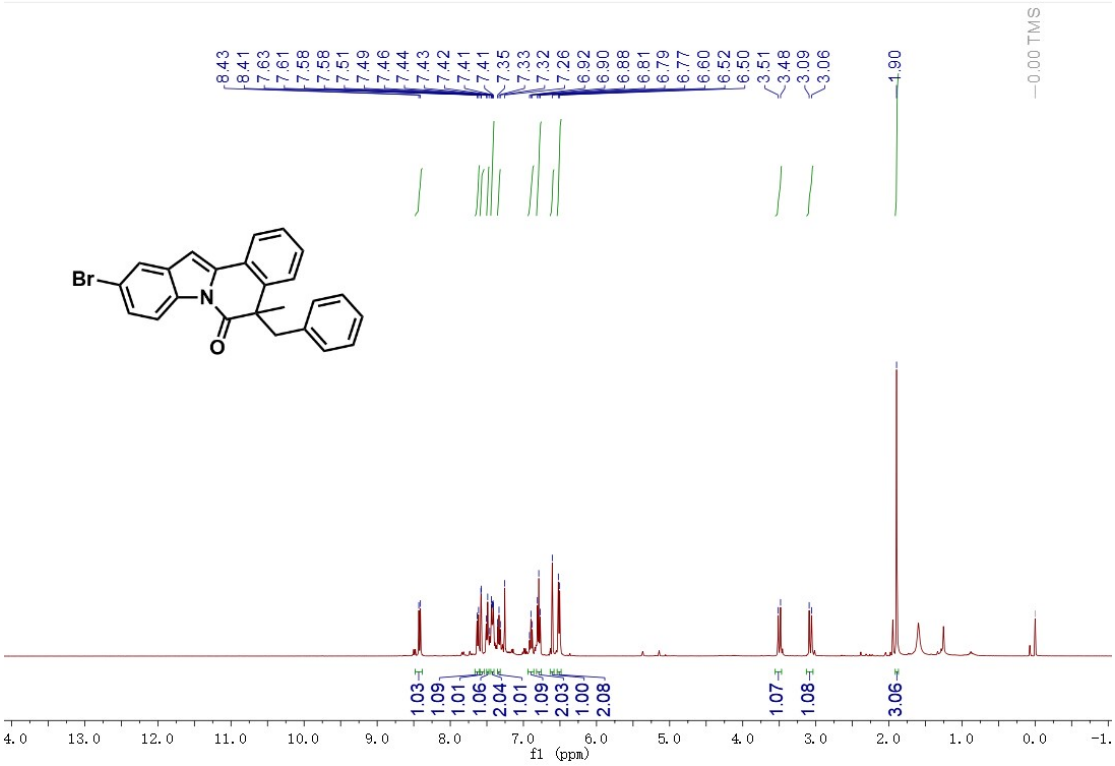
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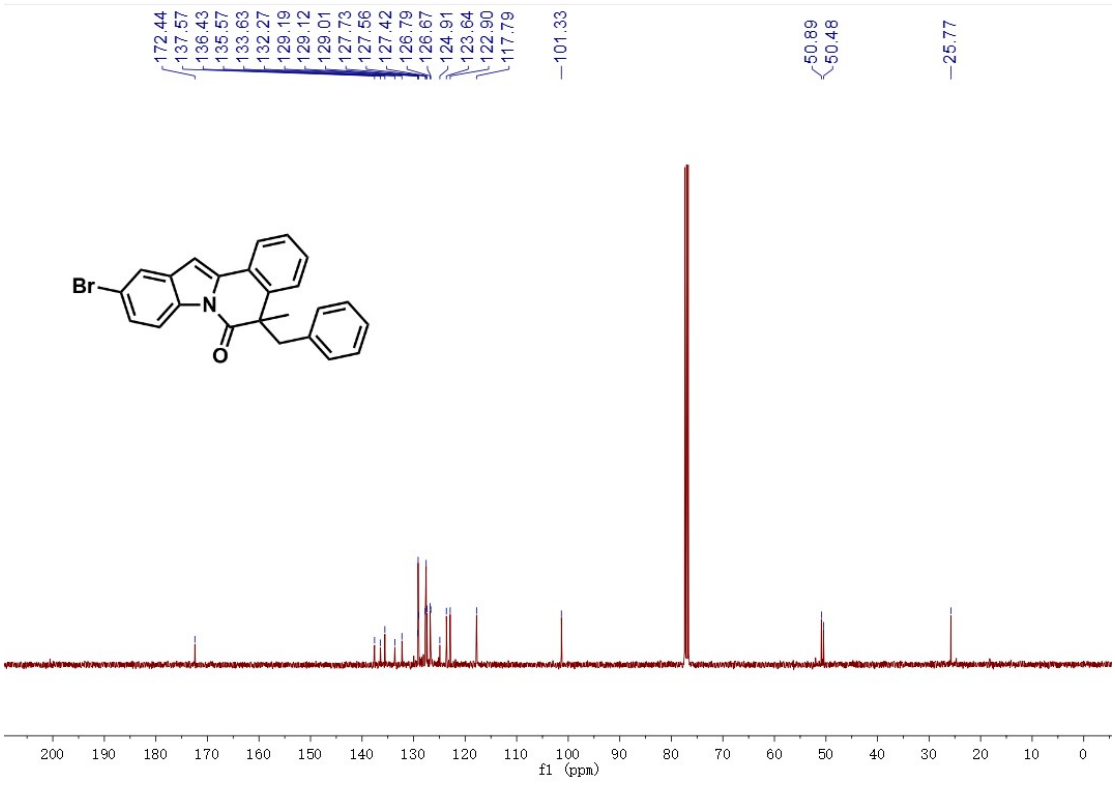
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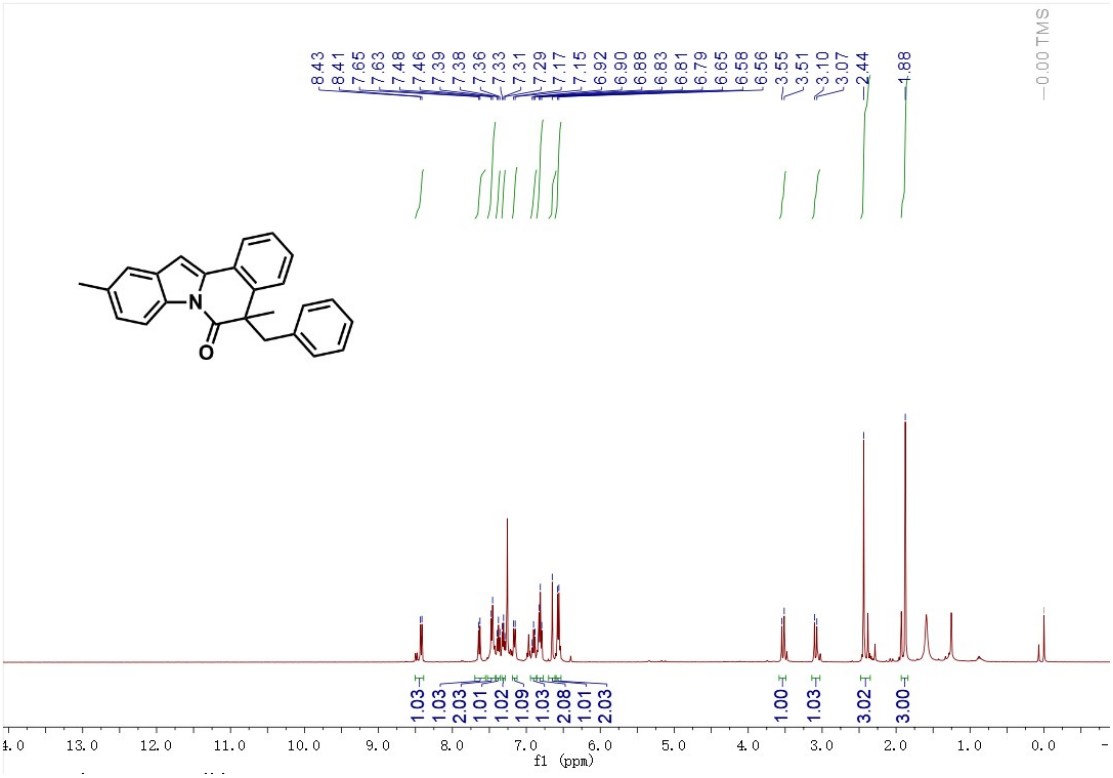
f1 (ppm)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7.38
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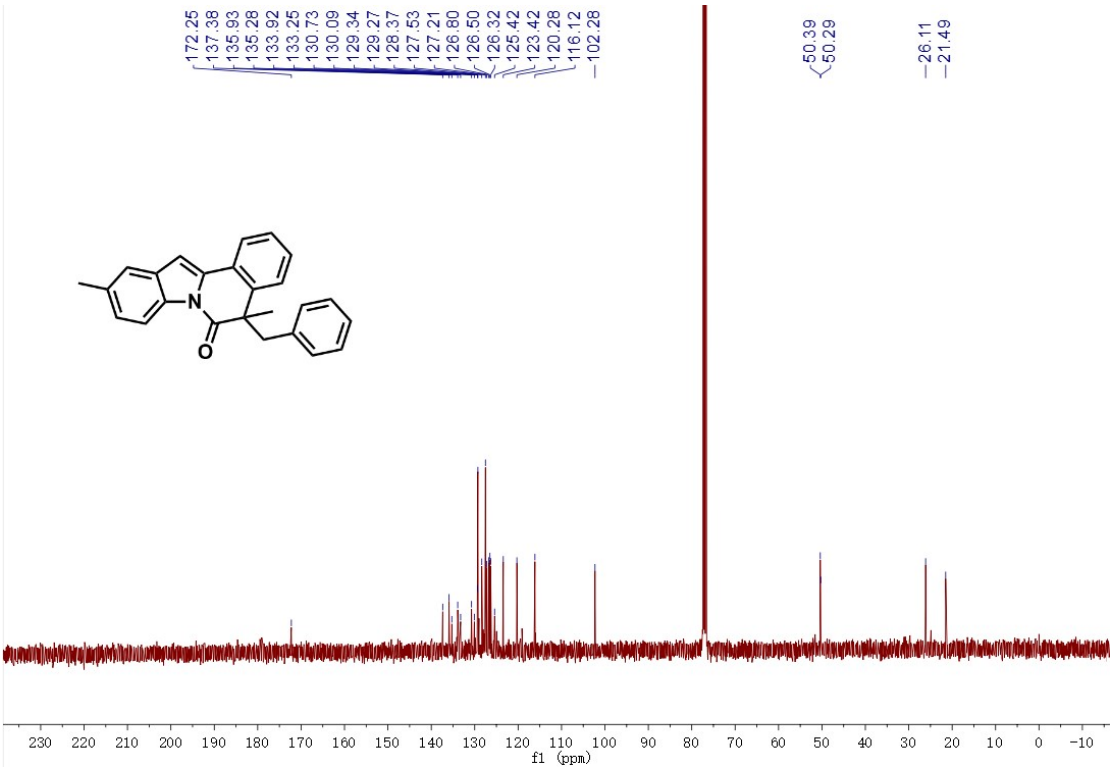
7.33
7.31
7.29
7.17
7.15
6.92
6.90
6.88
6.83
6.81
6.79
6.65
6.58
6.56
3.55
3.51
3.10
3.07
2.44
1.88
0.00 TMS
1.03
1.03
2.03
1.01
1.02
1.09
1.03
2.08
1.01
2.03
1.00
1.03
3.02
3.00
f1 (ppm)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135.28
133.92
133.25
130.73
130.09
129.34
129.27
128.37
127.53
127.21
126.80
126.50
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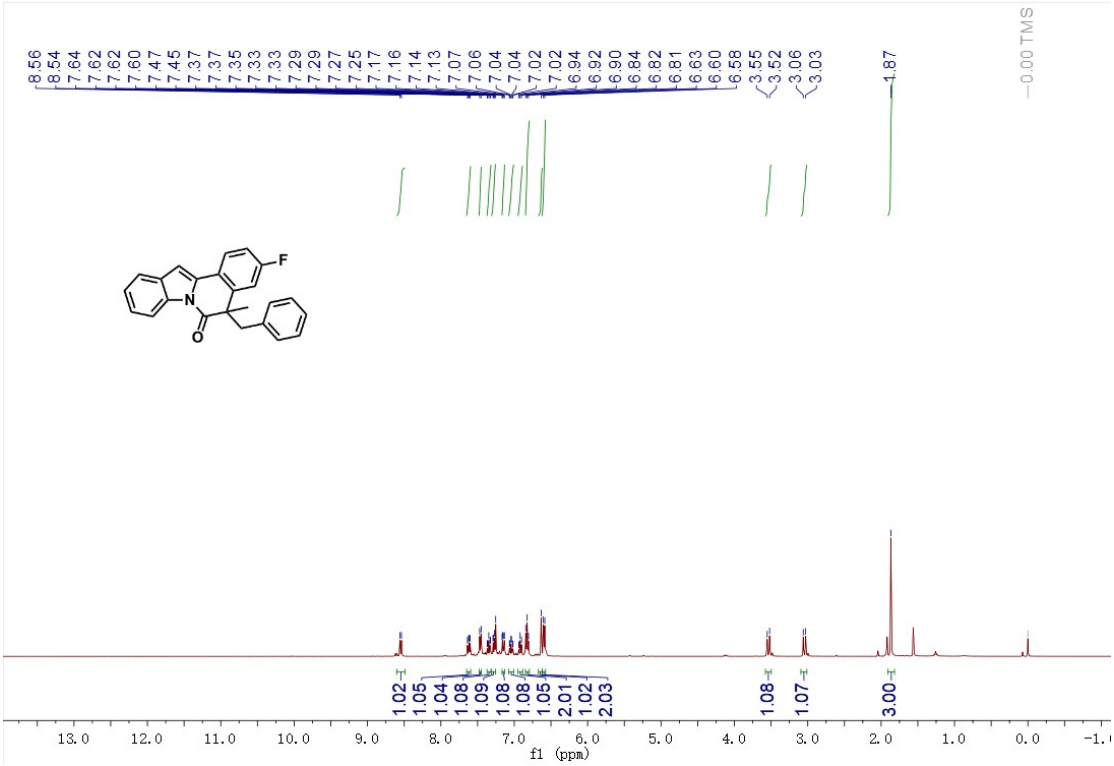
123.42
120.28
116.12
102.28
50.39
50.29
26.11
21.49
f1 (ppm)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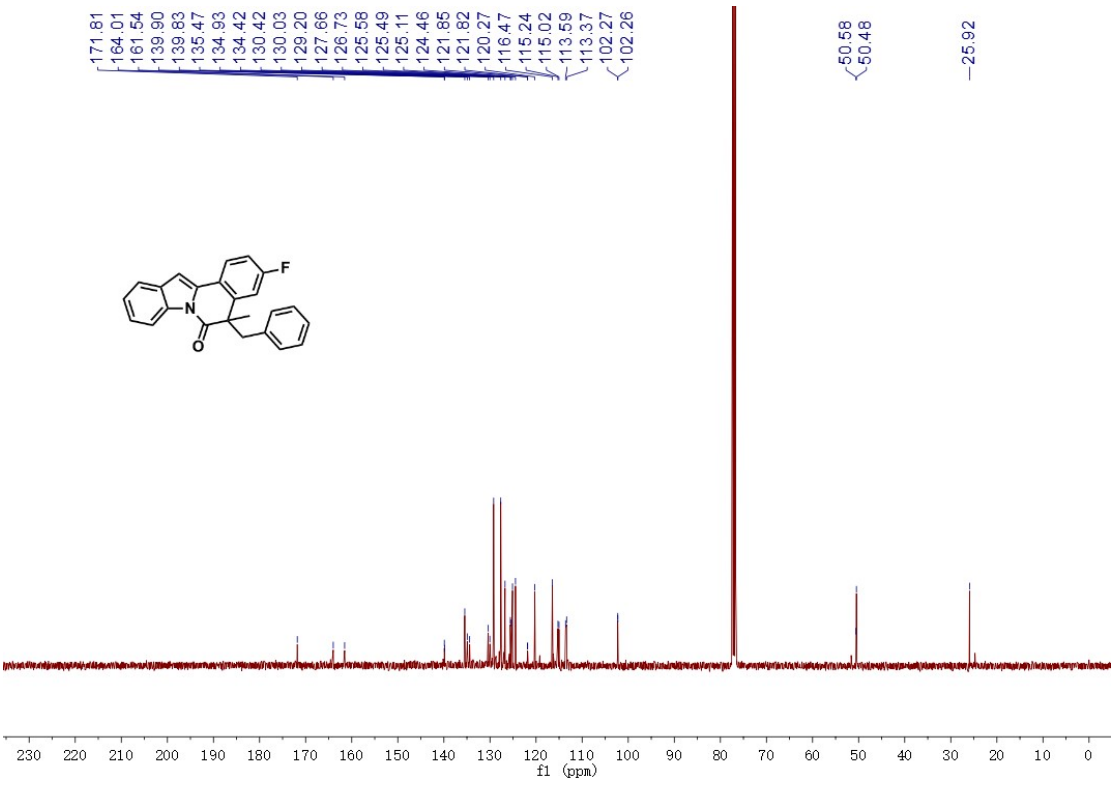
7.33
7.29
7.29
7.27
7.25
7.17
7.16
7.14
7.13
7.07
7.06
7.04
7.04
7.02
7.02
6.94
6.92
6.90
6.84
6.82
6.81
6.63
6.60
6.58
3.55
3.52
3.06
3.03
1.87
0.00 TMS
F
N
O
1.02
1.05
1.04
1.08
1.09
1.08
1.08
1.05
2.01
1.02
2.03
1.08
1.07
3.00
f1 (ppm)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135.47
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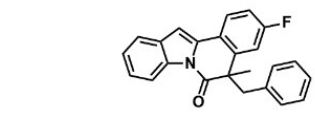
134.42
130.42
130.03
129.20
127.66
126.73
125.58
125.49
125.11
124.46
121.85
121.82
120.27
116.47
115.24
115.02
113.59
113.37
102.27
102.26
50.58
50.48
25.92
F
N
O
f1 (ppm)


F
N
O

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40
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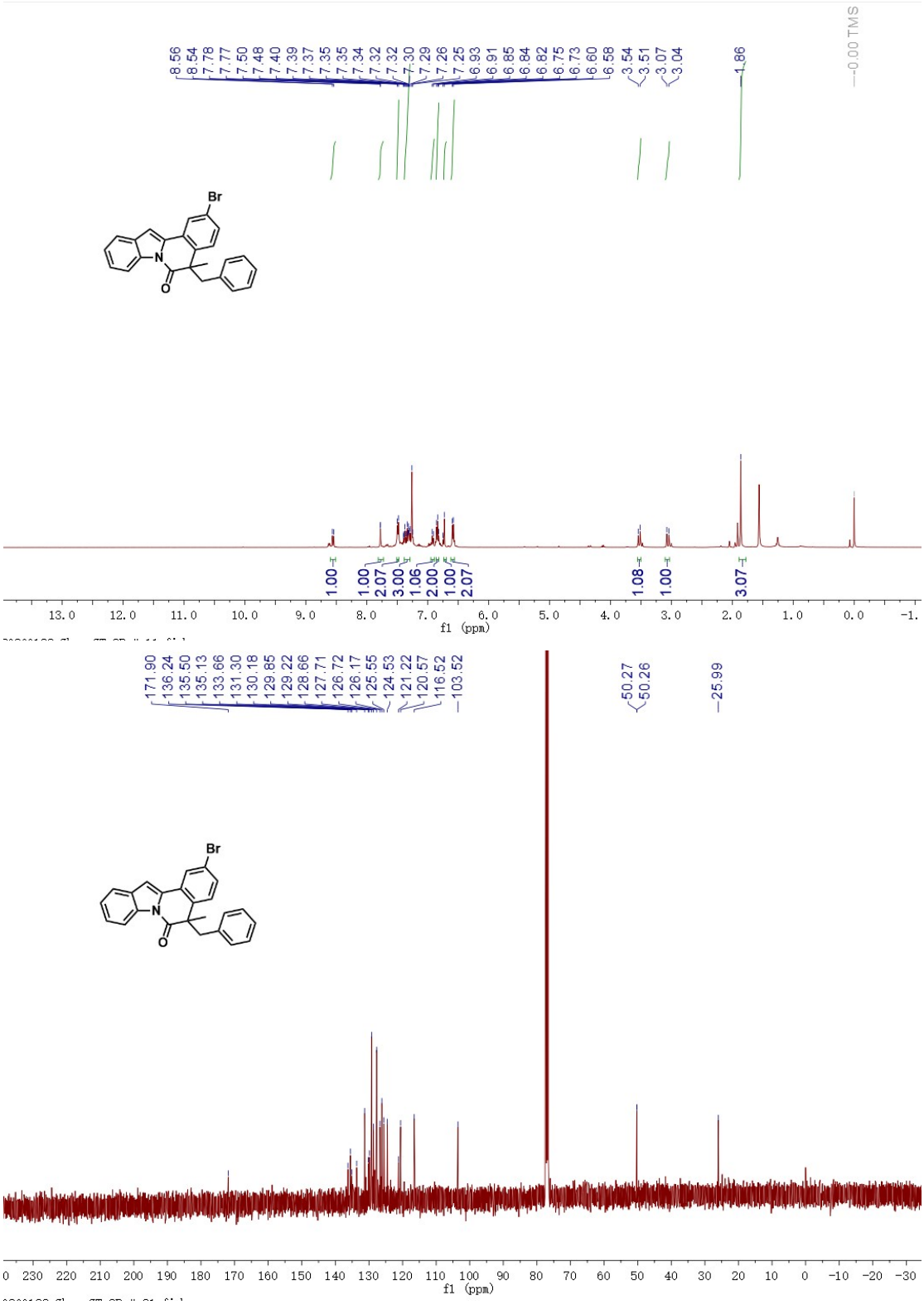
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)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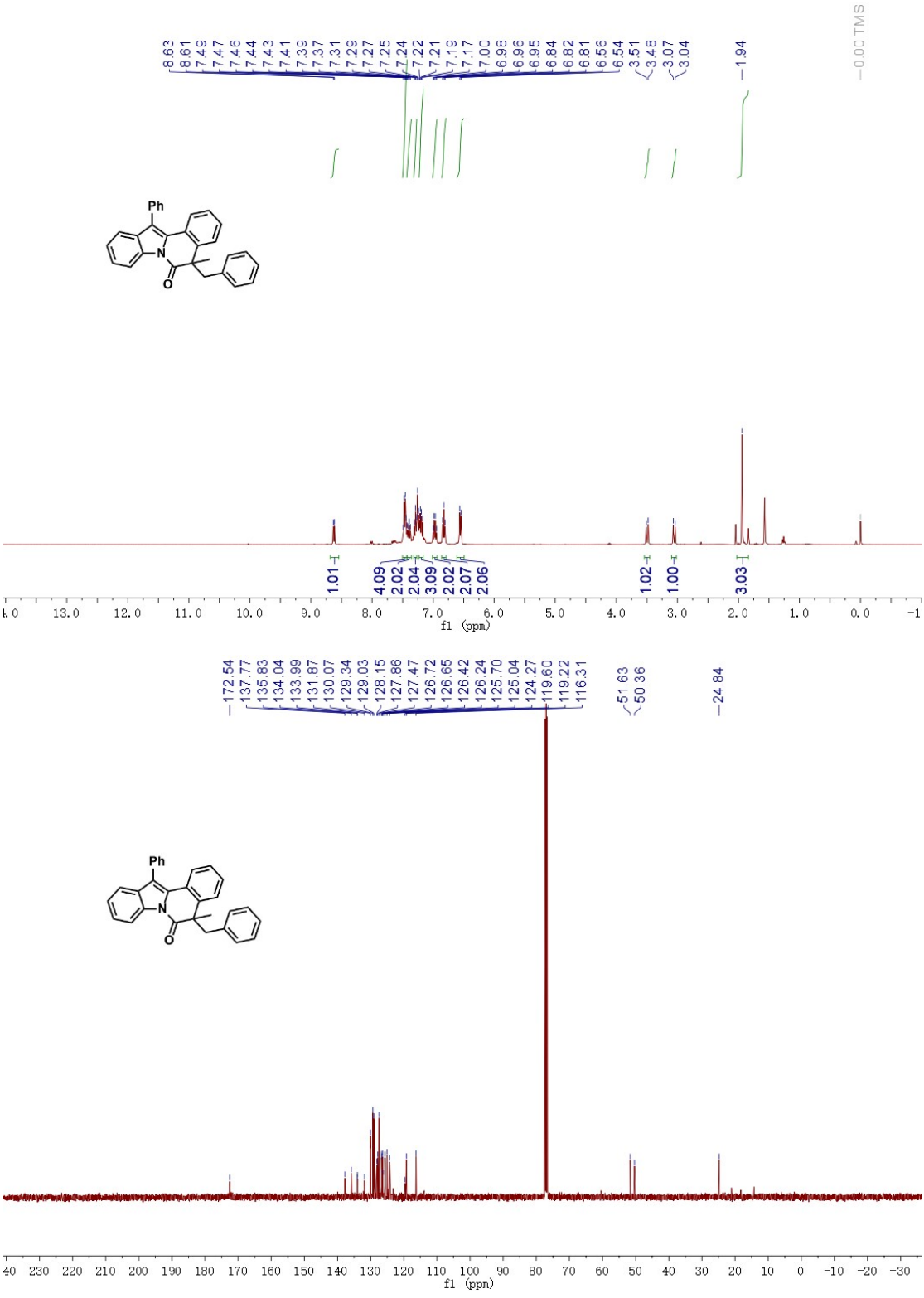
7.39
7.37
7.35
7.35
7.34
7.32
7.30
7.29
7.26
7.25
6.93
6.91
6.85
6.84
6.82
6.75
6.73
6.60
6.58
3.54
3.51
3.07
3.04
1.86
0.00 TMS
Br
N
O
1.00
1.00
2.07
3.00
1.06
2.00
1.00
2.07
1.08
1.00
3.07
f1 (ppm)
171.90
136.24
135.50
135.13
133.66
131.30
130.18
129.85
129.22
128.66
127.71
126.72
126.17
125.55
124.53
121.22
120.57
116.52
103.52
50.27
50.26
25.99
Br
N
O
f1 (ppm)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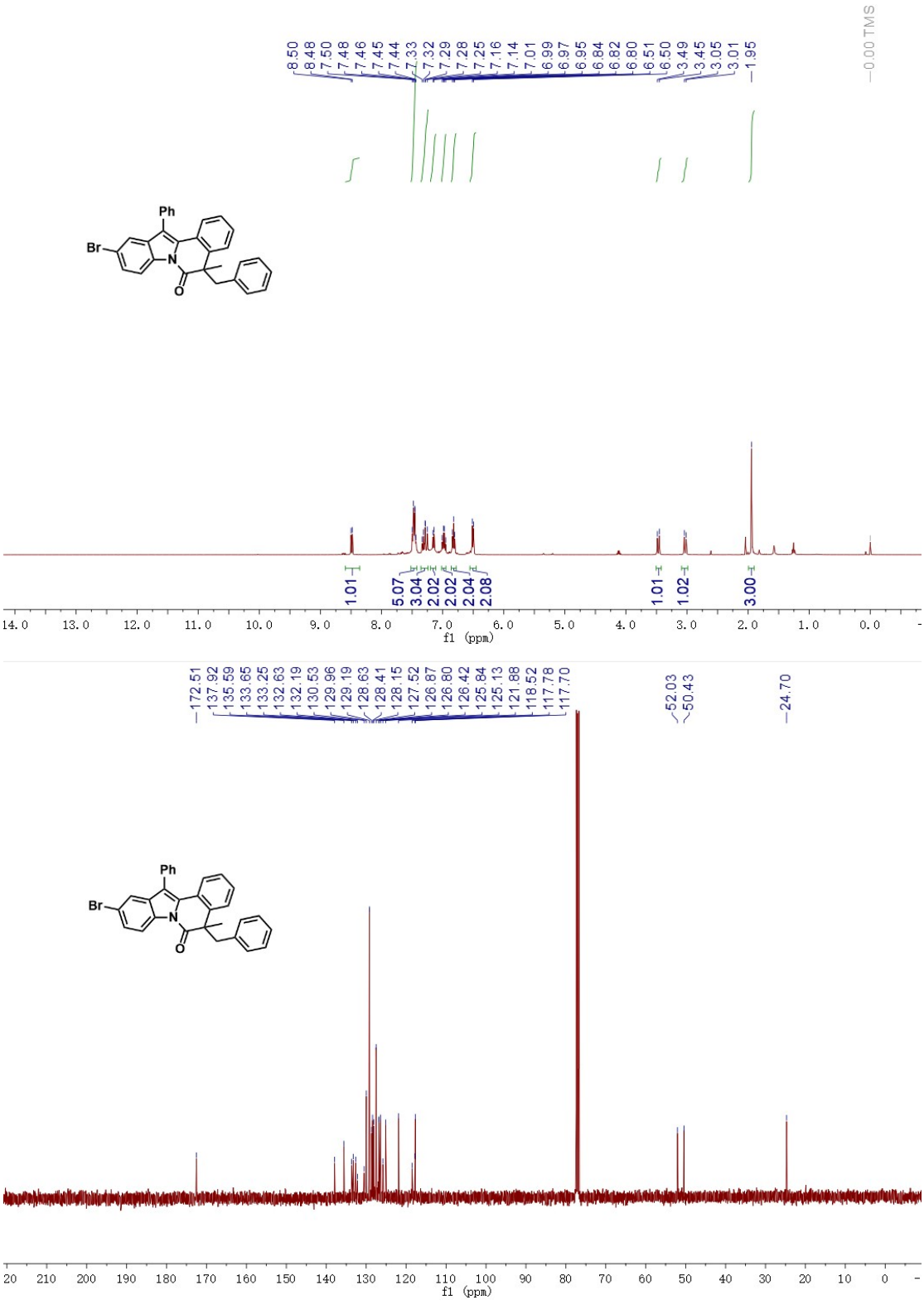
7.37
7.31
7.29
7.27
7.25
7.24
7.22
7.21
7.19
7.17
7.00
6.98
6.96
6.95
6.84
6.82
6.81
6.56
6.54
3.51
3.48
3.07
3.04
1.94
0.00 TMS
Ph
N
O
1.01
4.09
2.02
2.04
3.09
2.02
2.07
2.06
1.02
1.00
3.03
f1 (ppm)
172.54
137.77
135.83
134.04
133.99
131.87
130.07
129.34
129.03
128.15
127.86
127.47
126.72
126.65
126.42
126.24
125.70
125.04
124.27
119.60
119.22
116.31
51.63
50.36
24.84
Ph
N
O
f1 (ppm)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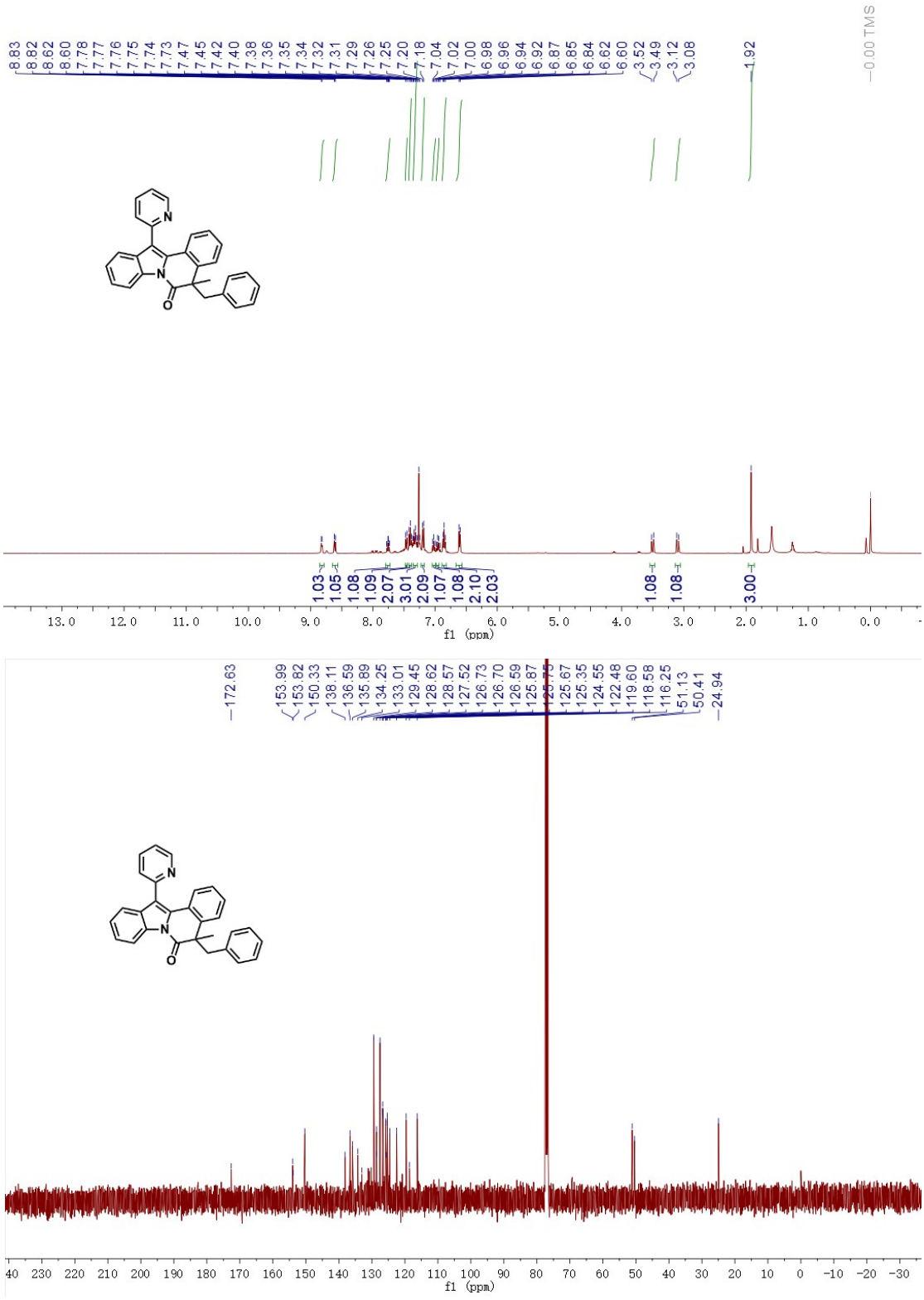
7.33
7.32
7.29
7.28
7.25
7.16
7.14
7.01
6.99
6.97
6.95
6.84
6.82
6.80
6.51
6.50
3.49
3.45
3.05
3.01
1.95
0.00 TMS
Ph
Br
N
O
1.01
5.07
3.04
2.02
2.02
2.04
2.08
1.01
1.02
3.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
172.51
137.92
135.59
133.65
133.25
132.63
132.19
130.53
129.96
129.19
128.63
128.41
128.15
127.52
126.87
126.80
126.42
125.84
125.13
121.88
118.52
117.78
117.70
52.03
50.43
24.70
Ph
Br
N
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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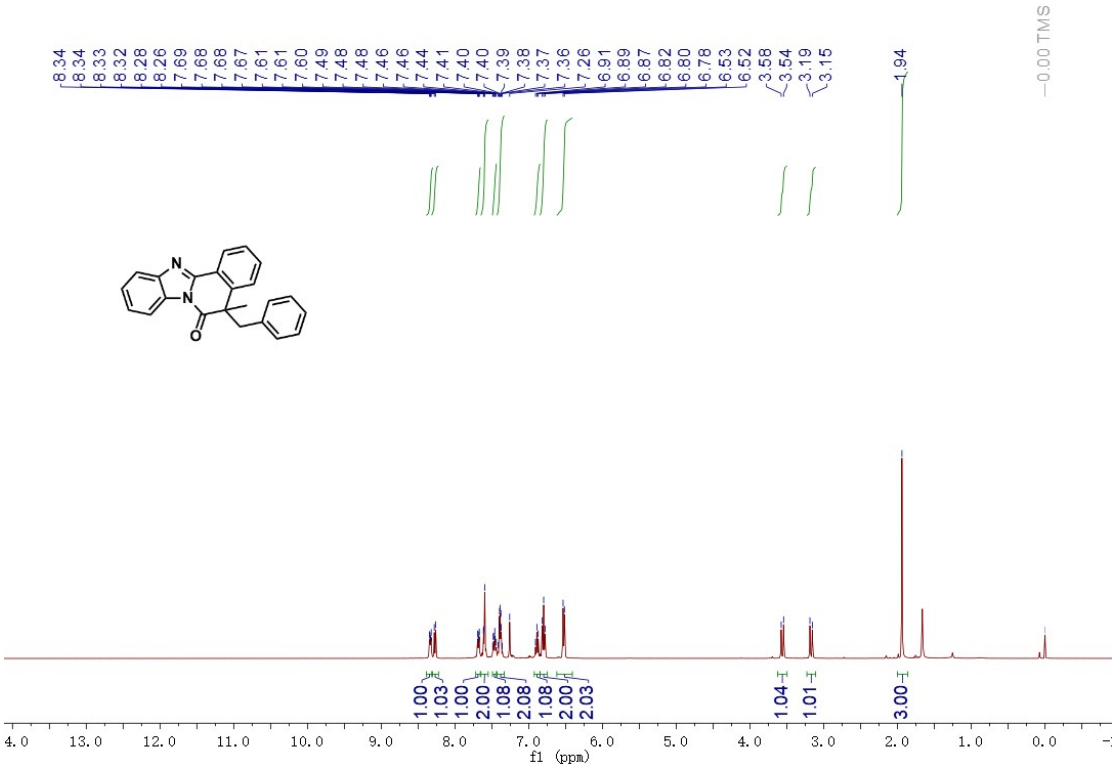
7.73
7.47
7.45
7.42
7.40
7.38
7.36
7.35
7.34
7.32
7.31
7.29
7.26
7.25
7.20
7.18
7.04
7.02
7.00
6.98
6.96
6.94
6.92
6.87
6.85
6.84
6.62
6.60
3.52
3.49
3.12
3.08
1.92
0.00 TMS
1.03
1.05
1.08
1.09
2.07
3.01
2.09
1.07
1.08
2.10
2.03
1.08
1.08
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
172.63
153.99
153.82
150.33
138.11
136.59
135.89
134.25
133.01
129.45
128.62
128.57
127.52
126.73
126.70
126.59
125.87
125.75
125.67
125.35
124.55
122.48
119.60
118.58
116.25
51.13
50.41
24.94
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)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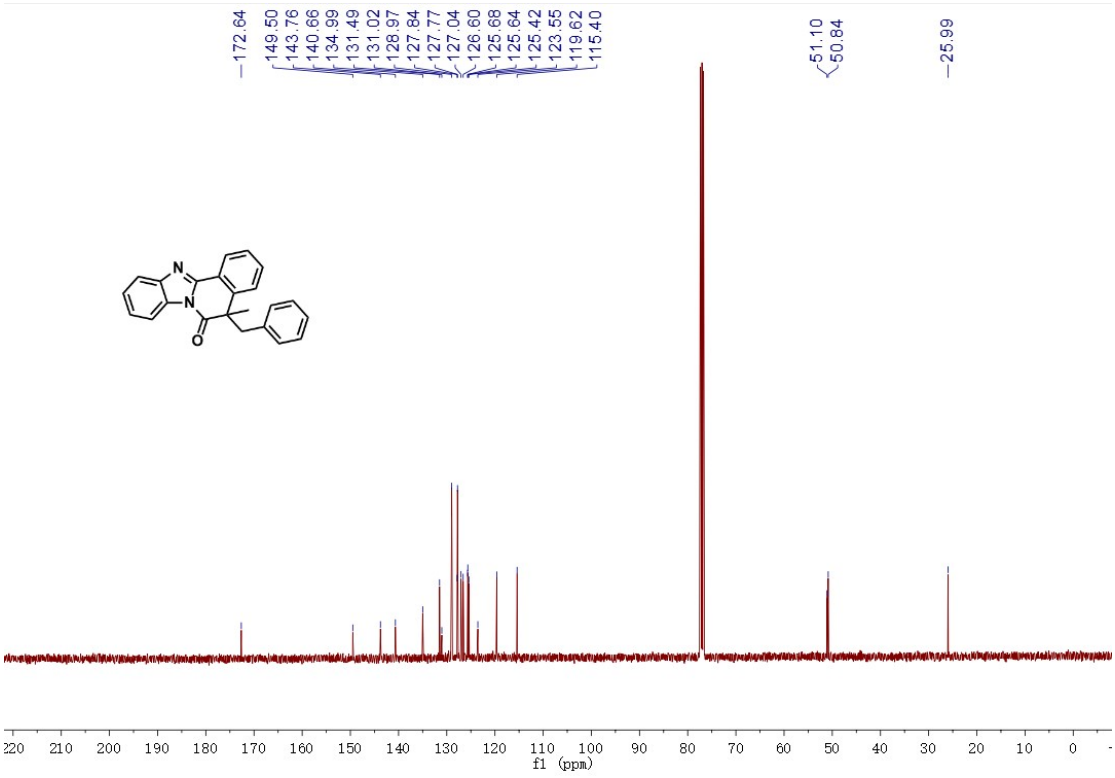
7.68
7.68
7.67
7.61
7.61
7.60
7.49
7.48
7.48
7.46
7.46
7.44
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.26
6.91
6.89
6.87
6.82
6.80
6.78
6.53
6.52
3.58
3.54
3.19
3.15
1.94
0.00 TMS
1.00
1.03
1.00
2.00
1.08
2.08
1.08
2.00
2.03
1.04
1.01
3.00
f1 (ppm)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131.49
131.02
128.97
127.84
127.77
127.04
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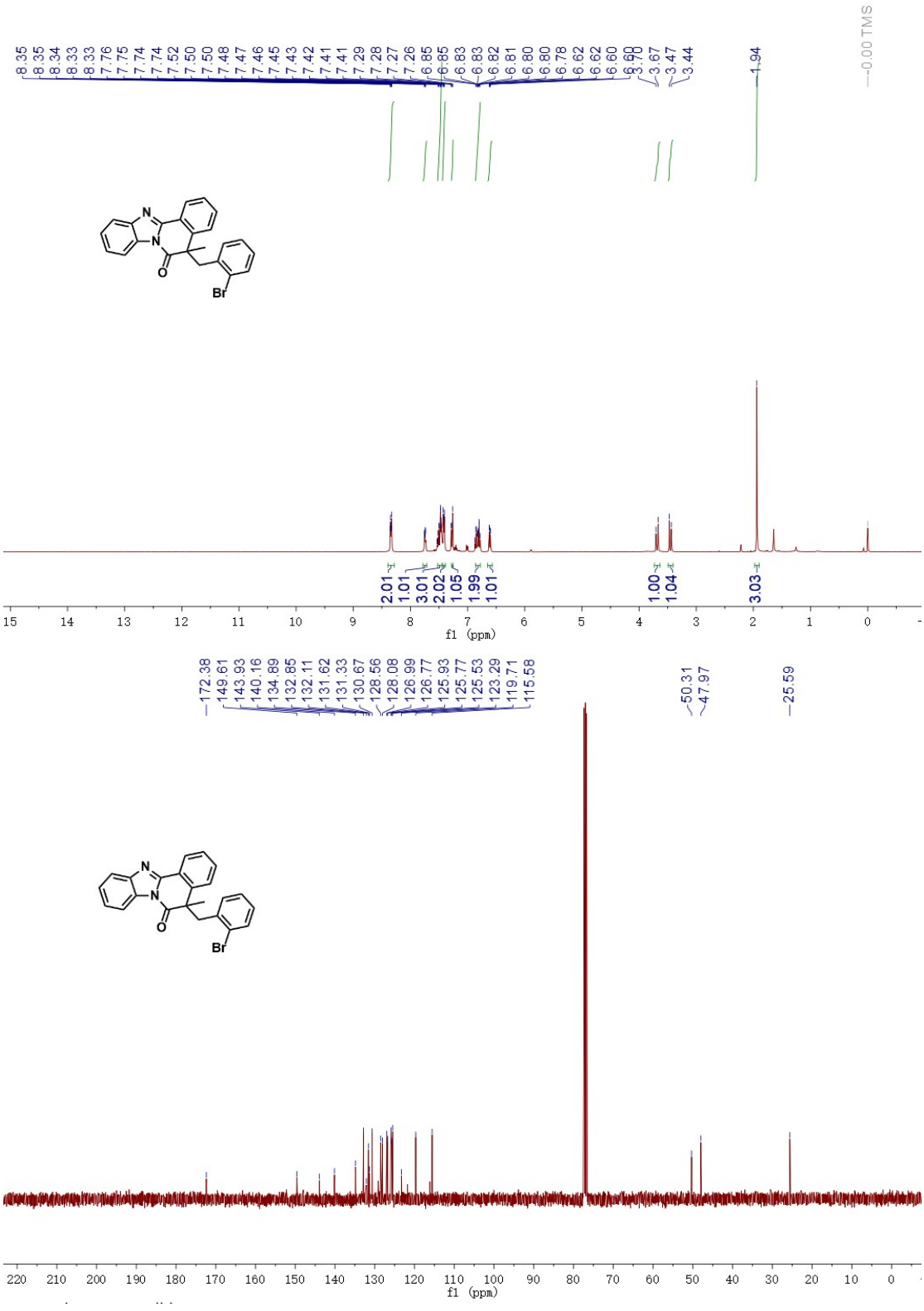
125.64
125.42
123.55
119.62
115.40
51.10
50.84
25.99
f1 (ppm)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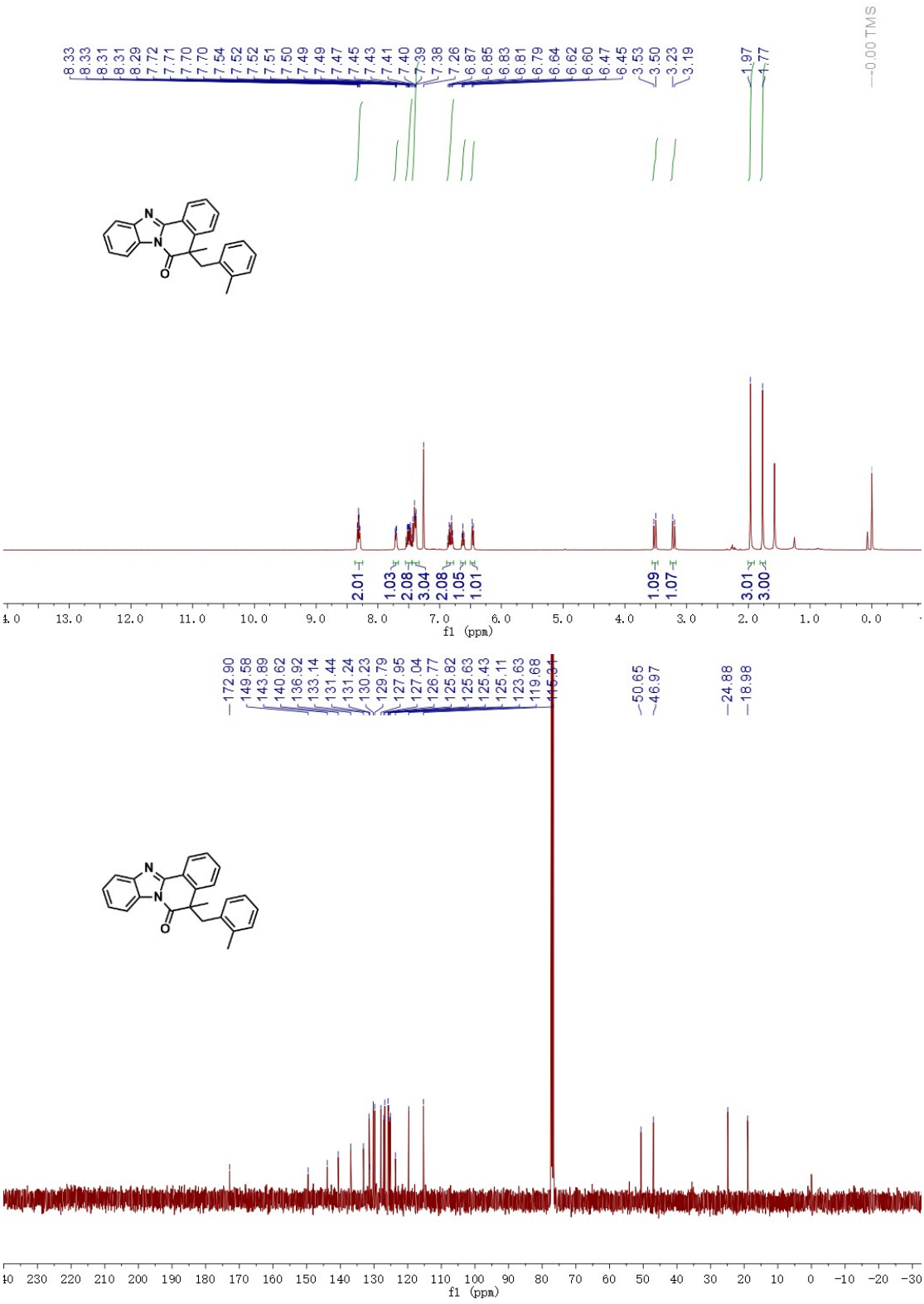
7.74
7.74
7.52
7.50
7.50
7.48
7.47
7.46
7.45
7.43
7.42
7.41
7.41
7.29
7.28
7.27
7.26
6.85
6.85
6.83
6.83
6.82
6.81
6.80
6.80
6.78
6.62
6.60
3.67
3.47
3.44
1.94
0.00 TMS
N
N
O
Br
2.01
1.01
3.01
2.02
1.05
1.99
1.01
1.00
1.04
3.03
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
172.38
149.61
143.93
140.16
134.89
132.85
132.11
131.62
131.33
130.67
128.56
128.08
126.99
126.77
125.93
125.77
125.53
123.29
119.71
115.58
50.31
47.97
25.59
N
N
O
Br
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.52
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7.49
7.49
7.47
7.45
7.43
7.41
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7.39
7.38
7.26
6.87
6.85
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6.81
6.79
6.64
6.62
6.60
6.47
6.45
3.53
3.50
3.23
3.19
1.97
1.77
0.00 TMS
2.01
1.03
2.08
3.04
2.08
1.05
1.01
1.09
1.07
3.01
3.00
f1 (ppm)
172.90
149.58
143.89
140.62
136.92
133.14
131.44
131.24
130.23
129.79
127.95
127.04
126.77
125.82
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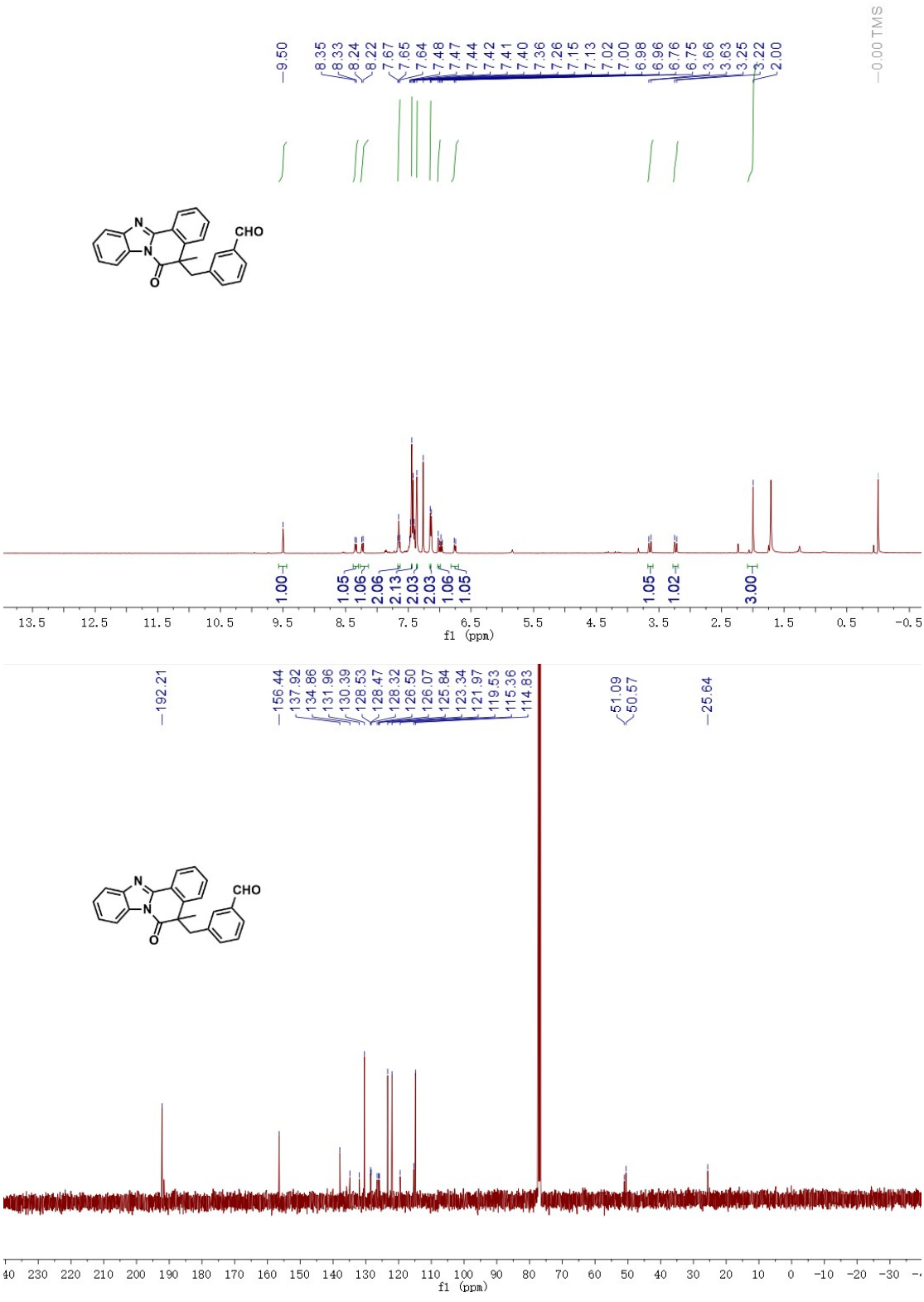
125.11
123.63
119.68
115.34
50.65
46.97
24.88
18.98
f1 (ppm)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8.33
8.24
8.22
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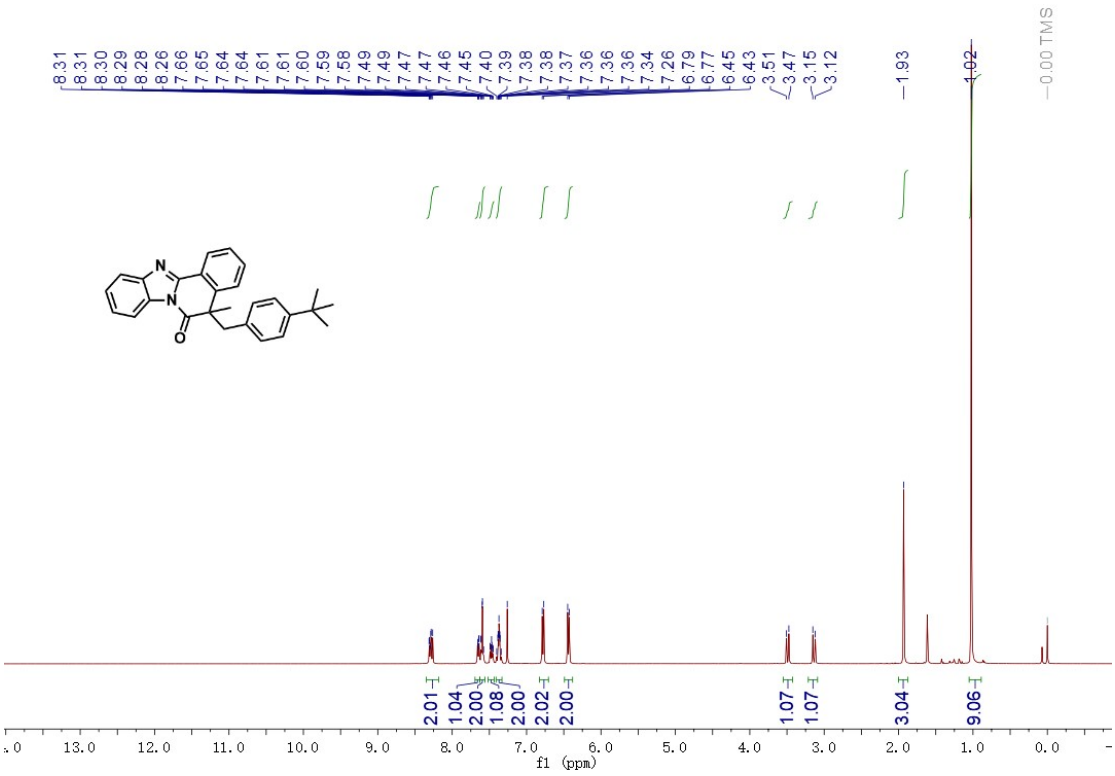
7.65
7.64
7.48
7.47
7.44
7.42
7.41
7.40
7.36
7.26
7.15
7.13
7.02
7.00
6.98
6.96
6.76
6.75
3.66
3.63
3.25
3.22
2.00
0.00 TMS
CHO
1.00
1.05
1.06
2.06
2.13
2.03
2.03
1.06
1.05
1.05
1.02
3.00
f1 (ppm)
192.21
156.44
137.92
134.86
131.96
130.39
128.53
128.47
128.32
126.50
126.07
125.84
123.34
121.97
119.53
115.36
114.83
51.09
50.57
25.64
CHO
f1 (ppm)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8.31
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7.65
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7.64
7.61
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7.59
7.58
7.49
7.49
7.47
7.47
7.46
7.45
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.34
7.26
6.79
6.77
6.45
6.43
3.51
3.47
3.15
3.12
1.93
1.92
0.00 TMS
2.01
1.04
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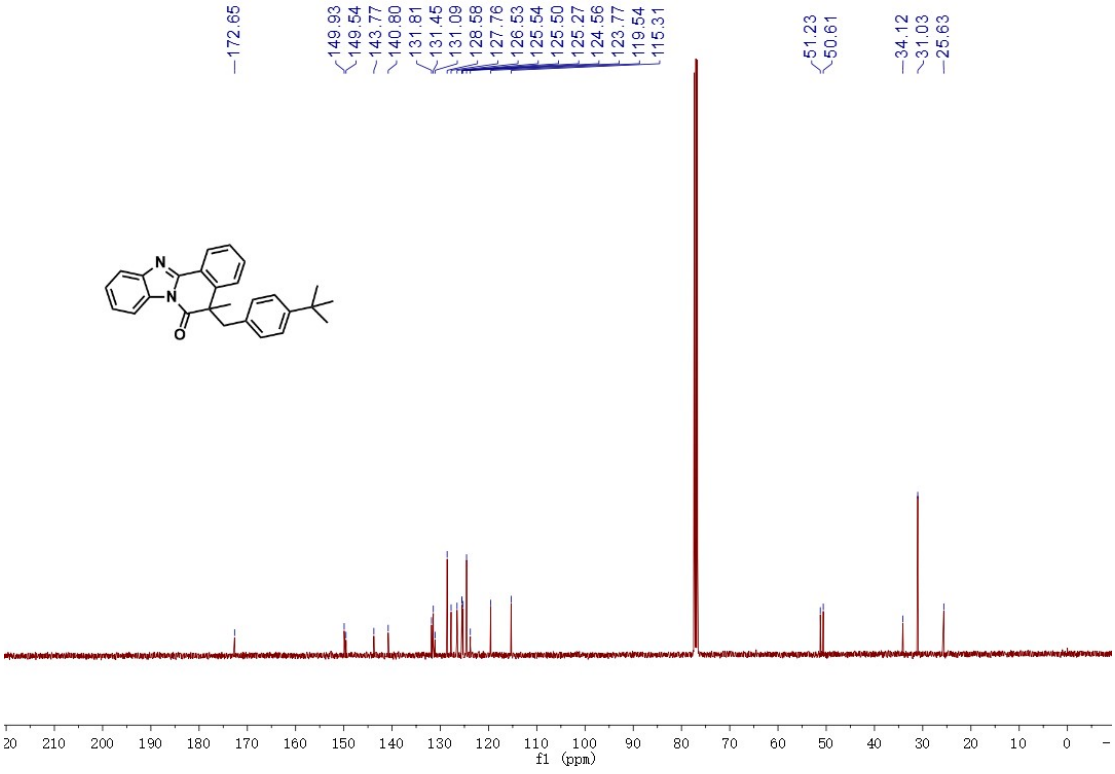
1.08
2.00
2.02
2.00
1.07
1.07
3.04
9.06
f1 (ppm)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149.93
149.54
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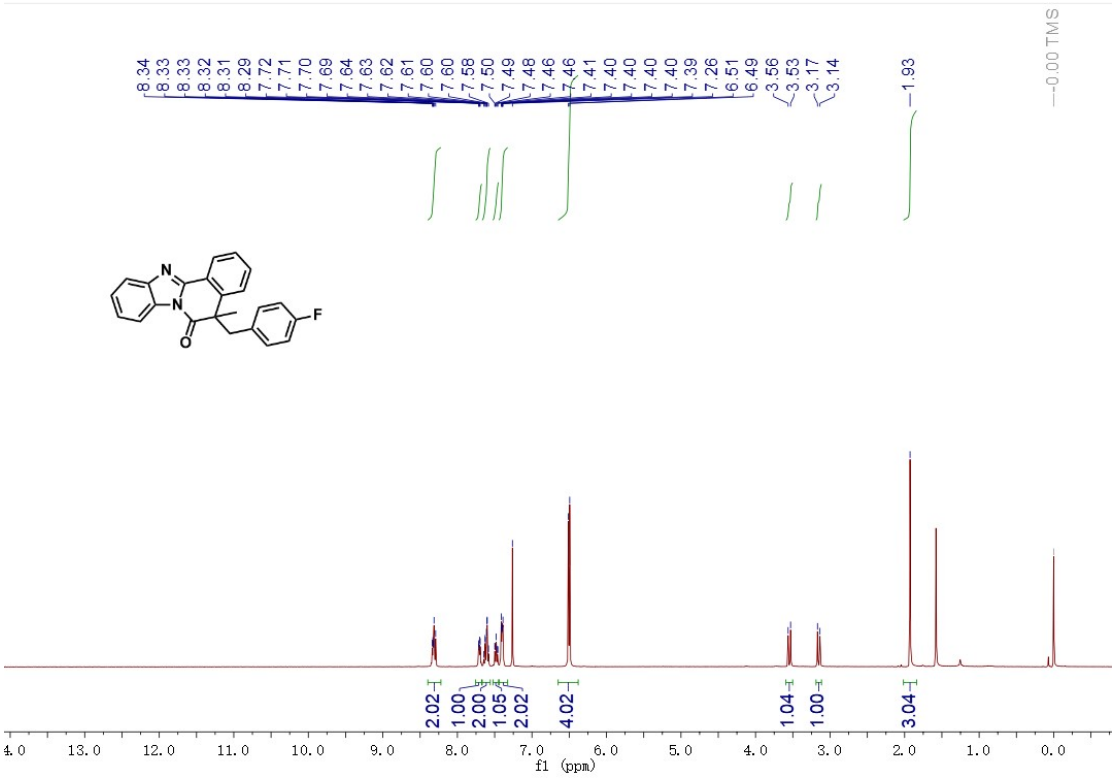
140.80
131.81
131.45
131.09
128.58
127.76
126.53
125.54
125.50
125.27
124.56
123.77
119.54
115.31
51.23
50.61
34.12
31.03
25.63
f1 (ppm)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8.33
8.32
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8.29
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7.71
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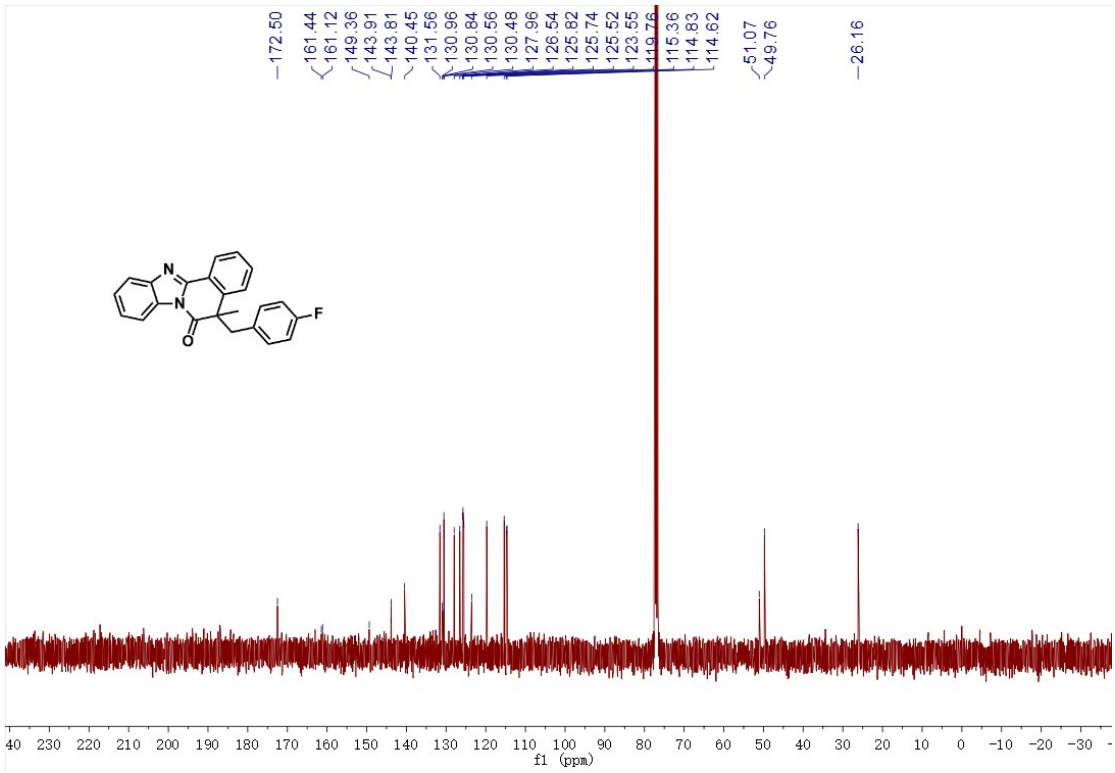
7.69
7.64
7.63
7.62
7.61
7.60
7.60
7.58
7.50
7.49
7.48
7.46
7.46
7.41
7.40
7.40
7.40
7.40
7.39
7.26
6.51
6.49
3.56
3.53
3.17
3.14
1.93
0.00 TMS
N
N
O
F
2.02
1.00
2.00
1.05
2.02
4.02
1.04
1.00
3.04
f1 (ppm)


172.50
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161.12
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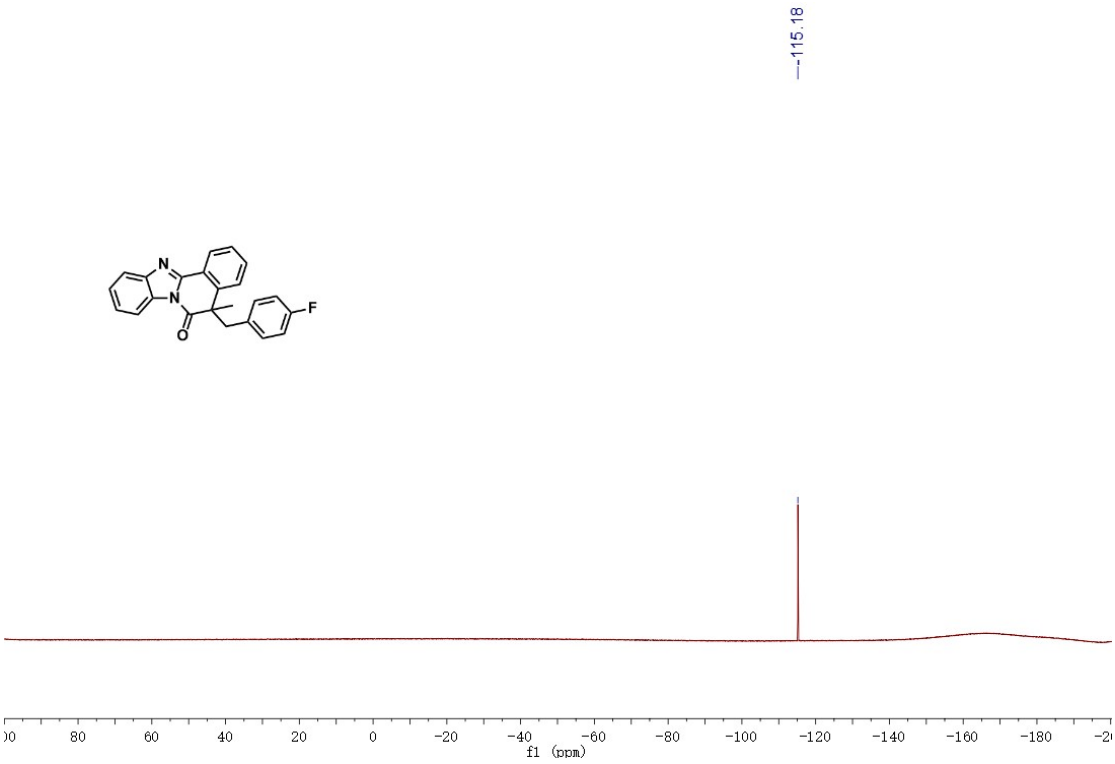
143.81
140.45
131.56
130.96
130.84
130.56
130.48
127.96
126.54
125.82
125.74
125.52
123.55
119.76
115.36
114.83
114.62
51.07
49.76
26.16
N
N
O
F
f1 (ppm)


-115.18
N
N
O
F
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)