Pictet-Spengler Reaction based on the in Situ Generated α-Amino Iminium through Heyns Rearrangement

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Content

General information

All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents from Adamas-beta were used as received. The solvents were dried by distillation over the appropriate drying reagents.

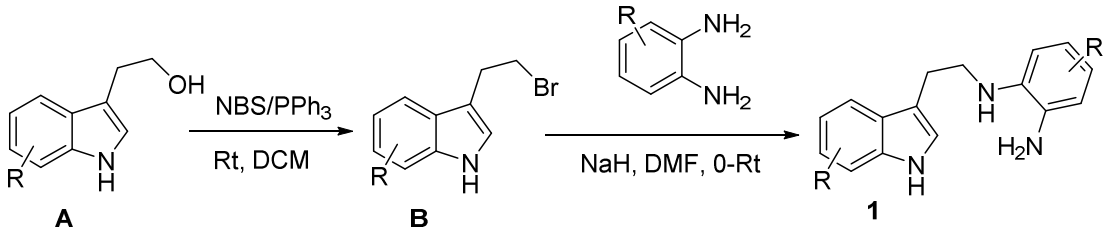
^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment.

^{13}C NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, $\delta = 77.0$).

Mass spectra were recorded on ThermoQuest Finnigan LCQ^{DECA} system equipped with an ESI source.

Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 30℃with UV detector at 254 nm.

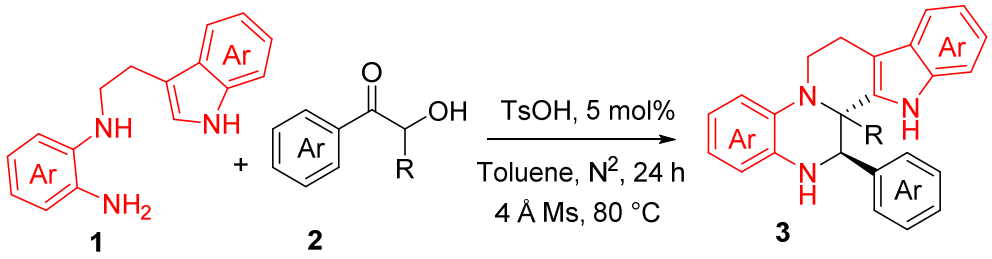
1. General procedural for synthesis of 1



To an ice bath cooled solution of 2-(1H-indol-3-yl) ethanol (16.1 g, 100 mmol) and PPh_3 (26.2 g, 100 mmol) in DCM (60 mL) was added NBS (18.0 g, 100 mmol) in small portions. The mixture was stirred for 2 hours and quenched with water. The organic phase was dried over sodium sulfate and concentrated. The crude material was purified by chromatography (petroleum/EtOAc 6:1) to give 3-(2-bromoethyl) indole **B** as a white solid (20 g, 80 %).

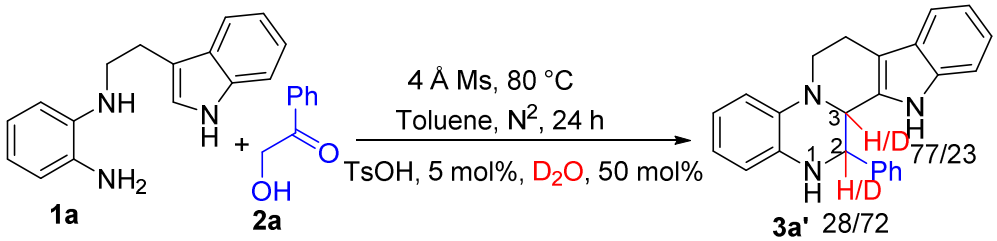
To a fume dried 100 mL bottle, 20 mL anhydrous DMF was added. Then the bottle was placed in ice cooled condition and NaH (60%, 0.98 g, 2.5 eq.) was added under nitrogen atmosphere. After that, the *o*-PDA (2.16 g, 20 mmol, 2 eq.) was added slowly. The mixture was stirred for 5 minutes and **B** (10 mmol, 2.24 g, 1 eq.) was added slowly under nitrogen atmosphere. Then the reaction mixture was stirred for 1 h and then 12 h at room temperature. Then the reaction mixture was diluted with 100 mL water and extracted with EtOAc (100 mL×3). The extracts was washed with water (100 mL) and dried over sodium sulfate and concentrated. The crude material was purified by chromatography (petroleum/EtOAc 4:1) to give **1a** as a black solid (1.88 g, 75%).

2. General procedural for synthesis of 3



0.2 mmol of **1**, 0.2 mmol of **2**, 0.01 mmol of PTSA and 50 mg 4 Ă molecular sieve were reacted in 2 mL toluene at 80 ℃ under argon for 24 h. Then, the reaction mixture was purified directly with flash silicon column eluted with EtOAc /petroleum ether (20%).

3. NMR experiment for exploring the reaction process



50 mol% D_2O was added into the reaction mixture obtained as the standard procedural. The obtained product was purified and analyzed with NMR. The results were depicted in Figure S1

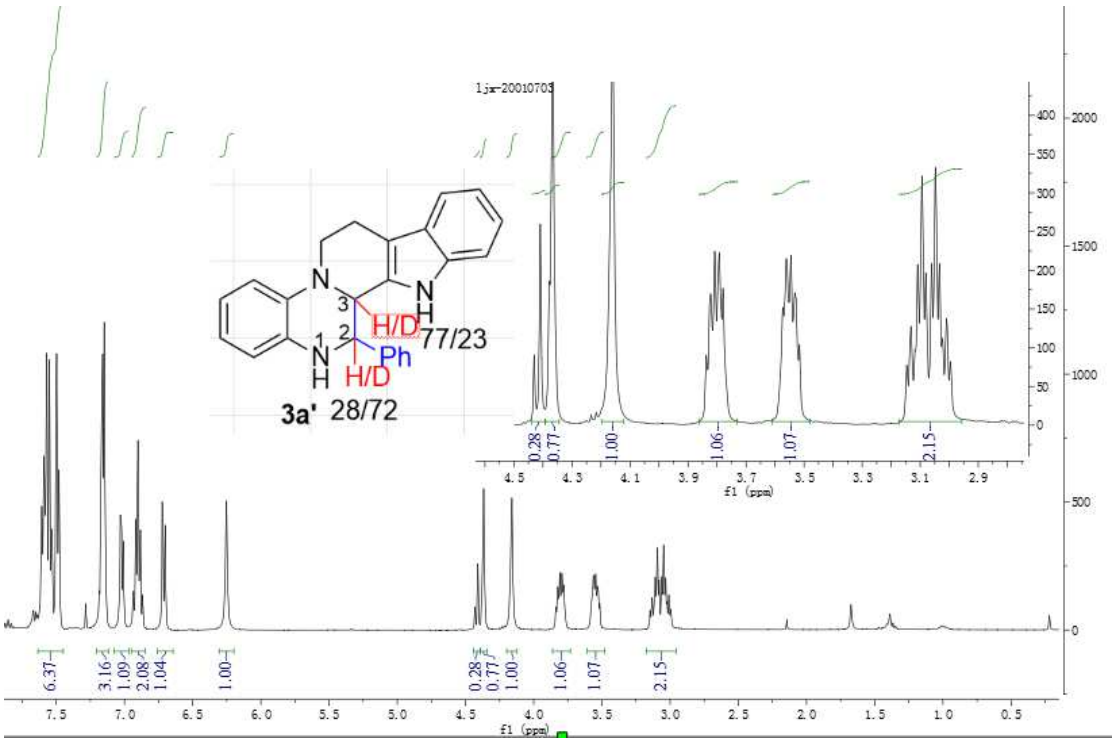
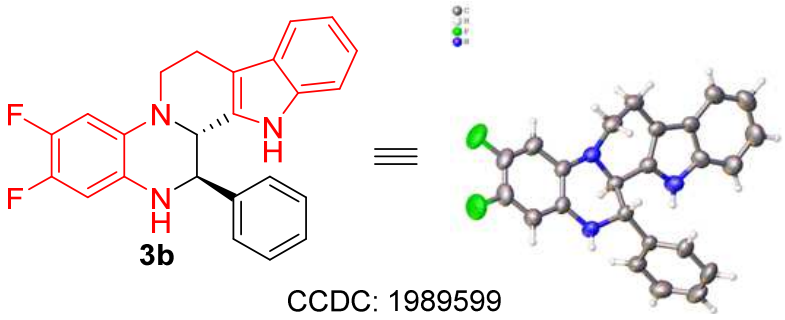


Fig. 1 the deuteration result

4. X-ray results of the product

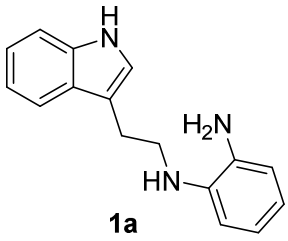


CCDC: 1989599

Chemical formula	$C_{24}H_{19}F_2N_3$
Formula weight	387.42
Space group	P 21/c

Hall group	-P 2ybc
Z	4
a/Å	5.7811(6)
b/Å	14.4499(13)
c/Å	22.9945(19)
α/°	90
β/°	94.696(8)
γ/°	90
Volume/Å^3	1914.4(3)
ρ_{calc}g/cm^3	1.344
Temperature/K	293 K

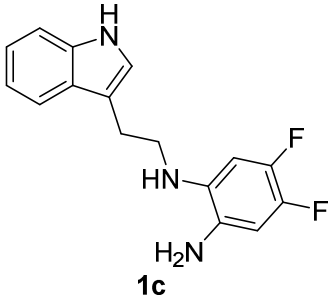
5. Characterization of selected new products



1a Black solid, m.p. 83-85 ℃. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.03 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.23 (dd, *J* = 10.9, 4.0 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.78 (ddd, *J* = 10.7, 9.7, 4.7 Hz, 3H), 3.53 (t, *J* = 6.8 Hz, 2H), 3.29 (s, 2H), 3.20 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.80, 136.44, 134.30, 127.56, 122.20, 122.13, 120.82, 119.48, 118.83, 118.69, 116.54, 113.47, 112.00, 111.40, 44.42, 25.28.

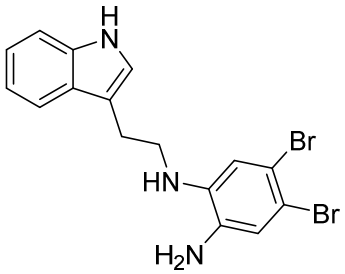
HRMS: $C_{17}H_{17}N_3$, Neutral mass: 251.14225, Observed m/z (M+H): 252.14952.



1c Brown solid, m.p. 92-93 ℃. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.05 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.1 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 6.58 – 6.44 (m, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 3.23 (s, 2H), 3.16 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.42, 134.02, 129.98, 127.44, 122.32, 121.97, 119.57, 118.69, 113.29, 111.33, 105.27, 105.06, 101.17, 100.95, 44.72, 25.04.

HRMS: $C_{16}H_{15}F_2N_3$, Neutral mass: 287.12340, Observed m/z (M+H): 288.13093.

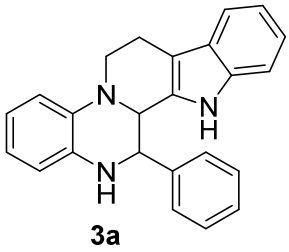


1e

Brown solid, m.p. 99-100 ℃. **^{1}H NMR (400 MHz, DMSO) δ** 10.86 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.83 (s, 1H), 6.65 (s, 1H), 4.98 (d, *J* = 20.8 Hz, 3H), 3.35 – 3.26 (m, 2H), 3.01 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.42, 134.02, 129.98, 127.44, 122.32, 121.97, 119.57, 118.69, 113.29, 111.33, 105.27, 105.06, 101.17, 100.95, 44.72, 25.04.

HRMS: $C_{16}H_{15}Br_2N_3$, Neutral mass: 406.96327, Observed m/z (M+H): 407.97029.

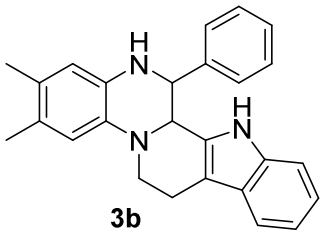


3a

Brown solid 66.7 mg, m.p. 169-170 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.58 – 7.44 (m, 6H), 7.15 – 7.06 (m, 3H), 6.97 (dt, *J* = 6.4, 2.5 Hz, 1H), 6.85 (pd, *J* = 7.3, 1.7 Hz, 2H), 6.69 (dd, *J* = 7.1, 2.0 Hz, 1H), 6.20 (s, 1H), 4.40 (d, *J* = 8.3 Hz, 1H), 4.34 (d, *J* = 8.2 Hz, 1H), 4.16 (s, 1H), 3.77 (ddd, *J* = 11.7, 6.5, 4.8 Hz, 1H), 3.58 – 3.45 (m, 1H), 3.11 – 2.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 136.32, 135.72, 135.02, 130.79, 129.21, 129.04, 128.73, 126.23, 121.80, 121.12, 119.27, 118.48, 118.36, 118.16, 114.10, 110.85, 110.60, 58.74, 58.17, 47.92, 21.98.

HRMS: $C_{24}H_{21}N_3$, Neutral mass: 351.17355, Observed m/z (M+H): 352.18069.

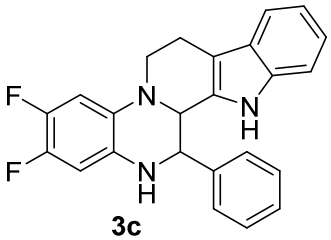


3b

Brown solid 62.9 mg, m.p. 164-166 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.58 – 7.49 (m, 4H), 7.49 – 7.44 (m, 2H), 7.12 (p, *J* = 5.6 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.54 (s, 1H), 6.18 (s, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 4.04 (s, 1H), 3.67 (ddd, *J* = 12.1, 7.7, 4.4 Hz, 1H), 3.61 – 3.52 (m, 1H), 3.17 – 3.06 (m, 1H), 2.98 (dt, *J* = 15.2, 4.6 Hz, 1H), 2.28 (d, *J* = 16.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.92, 135.79, 134.41, 132.92, 131.06, 129.66, 129.14, 128.87, 128.72, 126.32, 121.76, 121.11, 119.23, 118.19, 115.83, 110.85, 110.61, 59.21, 57.25, 49.14, 22.22, 19.26, 19.19.

HRMS: $C_{26}H_{25}N_3$, Neutral mass: 379.20485, Observed m/z (M+Na): 402.19508.

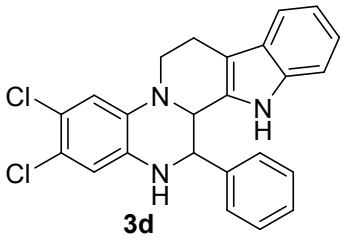


3c

Yellow solid 67.3 mg, m.p.117-118 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.58 – 7.50 (m, 4H), 7.43 (d, *J* = 6.6 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.00 – 6.96 (m, 1H), 6.88 (dd, *J* = 12.4, 7.8 Hz, 1H), 6.44 (dd, *J* = 11.4, 7.7 Hz, 1H), 6.21 (s, 1H), 4.34 (d, *J* = 8.2 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 4.06 (s, 1H), 3.71 – 3.59 (m, 1H), 3.49 – 3.37 (m, 1H), 3.09 – 2.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.04, 135.78, 130.25, 129.30, 129.24, 128.63, 126.15, 122.01, 119.42, 118.21, 110.73, 110.69, 107.16, 106.95, 102.21, 102.00, 58.52, 58.06, 48.19, 21.79.

HRMS: $C_{24}H_{19}F_2N_3$, Neutral mass: 387.15470, Observed m/z (M+H): 388.16224.



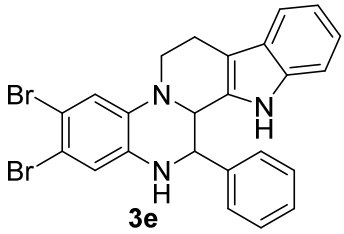
3d

Brown solid 69.7 mg, m.p. 107-108 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.61 – 7.48 (m, 4H), 7.44 (d, *J* = 6.7 Hz, 2H), 7.10 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.05 (s, 1H), 6.97 (d, *J* =

8.1 Hz, 1H), 6.68 (s, 1H), 6.23 (s, 1H), 4.36 (dd, *J* = 16.4, 8.0 Hz, 2H), 4.17 (s, 1H), 3.81 (dt, *J* = 10.1, 4.3 Hz, 1H), 3.43 – 3.32 (m, 1H), 3.01 (d, *J* = 4.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.74, 135.70, 135.48, 134.76, 129.94, 129.45, 129.39, 128.67, 126.08, 122.68, 122.08, 120.50, 119.49, 118.21, 117.36, 114.11, 110.75, 110.69, 59.34, 58.13, 46.43, 21.45.

HRMS: $C_{24}H_{19}Cl_2N_3$, Neutral mass: 419.09560, Observed m/z (M+H): 420.10226.

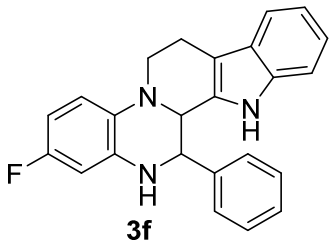


3e

Brown solid 88.6 mg, m.p. 122-123 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 – 7.49 (m, 4H), 7.43 (d, *J* = 6.5 Hz, 2H), 7.20 (s, 1H), 7.16 – 7.06 (m, 2H), 7.01 – 6.95 (m, 1H), 6.84 (s, 1H), 6.23 (s, 1H), 4.35 (q, *J* = 8.2 Hz, 2H), 4.17 (s, 1H), 3.81 (dt, *J* = 11.8, 4.8 Hz, 1H), 3.39 – 3.29 (m, 1H), 3.00 (t, *J* = 5.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.68, 136.20, 135.71, 135.56, 129.88, 129.47, 129.40, 128.67, 126.08, 122.09, 120.13, 119.50, 118.21, 117.09, 113.91, 111.58, 110.75, 110.69, 59.45, 58.05, 46.21, 21.40.

HRMS: $C_{24}H_{19}Br_2N_3$, Neutral mass: 506.99457, Observed m/z (M+H): 508.00086.

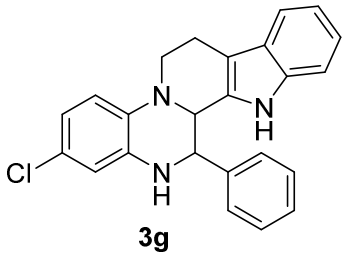


3f

Brown solid 64.2 mg, m.p. 177-179 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.61 – 7.48 (m, 4H), 7.47 – 7.39 (m, 2H), 7.17 – 7.08 (m, 2H), 7.04 – 6.94 (m, 2H), 6.58 – 6.45 (m, 1H), 6.39 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.17 (s, 1H), 4.38 (d, *J* = 8.3 Hz, 1H), 4.24 (s, 1H), 4.20 (d, *J* = 8.3 Hz, 1H), 3.61 (ddd, *J* = 12.1, 7.8, 4.5 Hz, 1H), 3.54 – 3.42 (m, 1H), 3.17 – 3.04 (m, 1H), 2.97 (dt, *J* = 15.2, 4.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.63, 157.26, 140.16, 137.64, 137.53, 135.79, 131.05, 131.03, 130.53, 129.26, 129.12, 128.63, 126.23, 121.90, 120.74, 120.64, 119.33, 118.22, 110.82, 110.65, 104.46, 104.24, 100.76, 100.50, 58.63, 57.18, 49.25, 22.13.

HRMS: $C_{24}H_{20}FN_3$, Neutral mass: 369.16413, Observed m/z (M+H): 370.17102.

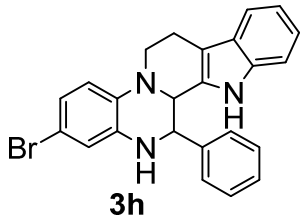


3g

Brown solid 67.9 mg, m.p. 187-188 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.57 – 7.49 (m, 4H), 7.46 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.13 – 7.06 (m, 2H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.76 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 6.23 (s, 1H), 4.41 – 4.33 (m, 2H), 4.12 (s, 1H), 3.82 (dt, *J* = 11.9, 5.0 Hz, 1H), 3.41 (ddd, *J* = 12.2, 7.1, 5.2 Hz, 1H), 3.06 – 2.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.18, 135.98, 135.69, 134.49, 130.34, 129.31, 129.27, 128.73, 126.14, 123.09, 121.95, 119.93, 119.40, 118.18, 116.46, 114.41, 110.80, 110.64, 59.15, 58.43, 46.66, 21.60.

HRMS: $C_{24}H_{20}ClN_3$, Neutral mass: 385.13458, Observed m/z (M+H): 386.14226.

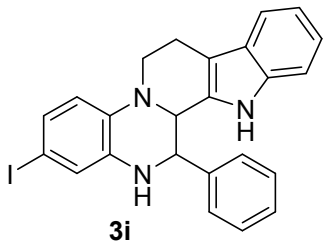


3h

Brown solid 77.4 mg, m.p. 207-208 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.57 – 7.49 (m, 4H), 7.44 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.97 (dt, *J* = 3.7, 2.5 Hz, 1H), 6.94 – 6.86 (m, 2H), 6.77 (d, *J* = 1.9 Hz, 1H), 6.20 (s, 1H), 4.38 (d, *J* = 8.2 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 4.18 (s, 1H), 3.77 – 3.69 (m, 1H), 3.47 – 3.39 (m, 1H), 3.08 – 2.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.02, 137.51, 135.72, 134.09, 130.29, 129.31, 129.25, 128.66, 126.14, 121.94, 120.85, 119.37, 119.10, 118.18, 116.16, 113.12, 110.80, 110.64, 58.40, 47.50, 21.77.

HRMS: $C_{26}H_{24}BrN_3$, Neutral mass: 457.11536, Observed m/z (M+H): 458.11995.



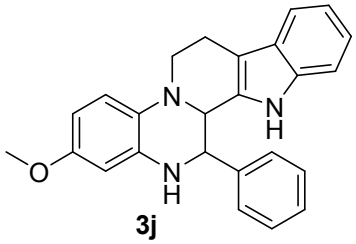
3i

Brown solid 80.1 mg, m.p. 163-164 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)**

δ 7.54 (q, *J* = 6.3 Hz, 4H), 7.49 (s, 1H), 7.17 – 7.09 (m, 3H), 7.03 – 6.95 (m, 1H), 6.92 – 6.83 (m, 2H), 6.70 (dd, *J* = 7.1, 1.6 Hz, 1H), 6.22 (s, 1H), 4.38 (dd, *J* = 22.1, 8.2 Hz, 2H), 4.16 (s, 1H), 3.83 – 3.73 (m, 1H), 3.57 – 3.47 (m, 1H), 3.05 (dtd, *J* = 20.5, 15.1, 5.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.62, 136.37, 135.77, 135.06, 130.85, 129.24, 129.06, 128.77, 126.28, 121.84, 121.16, 119.32, 118.51, 118.41, 118.21, 114.16, 110.89, 110.66, 58.77, 58.17, 47.96, 22.01.

HRMS: $C_{24}H_{20}IN_3$, Neutral mass: 477.07019, Observed m/z (M+H): 478.07780.

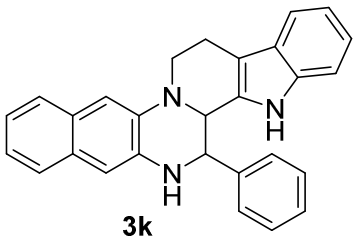


3j

Brown solid 73.2 mg, m.p.165-166 ℃; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.57 – 7.46 (m, 4H), 7.44 (d, *J* = 6.3 Hz, 2H), 7.13 – 7.03 (m, 3H), 6.99 – 6.90 (m, 1H), 6.41 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.28 (d, *J* = 2.6 Hz, 1H), 6.14 (s, 1H), 4.39 (d, *J* = 8.4 Hz, 1H), 4.26 – 4.16 (m, 2H), 3.80 (s, 3H), 3.58 – 3.48 (m, 2H), 3.15 – 3.05 (m, 1H), 2.94 (dt, *J* = 15.2, 4.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.28, 140.51, 137.59, 135.76, 130.83, 129.15, 128.92, 128.79, 128.61, 126.26, 121.74, 121.70, 119.19, 118.16, 110.78, 110.56, 103.85, 99.77, 58.97, 56.59, 55.50, 49.92, 22.28.

HRMS: $C_{24}H_{20}ON_3$, Neutral mass: 381.18411, Observed m/z (M+H): 382.19060.

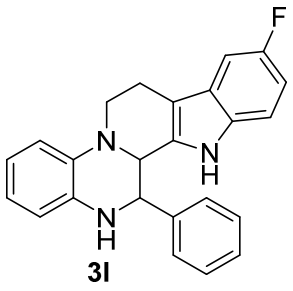


3k

Brown solid 64.2 mg, m.p.198-199 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.67 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.60 – 7.49 (m, 7H), 7.28 – 7.21 (m, 3H), 7.16 – 7.09 (m, 2H), 7.00 (dt, *J* = 6.3, 2.5 Hz, 1H), 6.89 (s, 1H), 6.34 (s, 1H), 4.59 (s, 2H), 4.40 (s, 1H), 4.27 (ddd, *J* = 11.9, 4.7, 2.9 Hz, 1H), 3.35 (ddd, *J* = 11.8, 10.2, 4.4 Hz, 1H), 3.16 – 3.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.45, 137.00, 136.29, 135.71, 130.61, 129.44, 129.39, 129.26, 128.86, 128.78, 126.26, 126.22, 124.84, 123.45, 122.53, 121.98, 119.47, 118.22, 110.76, 110.71, 108.76, 106.72, 61.60, 58.43, 44.49, 21.18.

HRMS: $C_{28}H_{23}N_3$, Neutral mass: 401.18920, Observed m/z (M+H): 402.19564

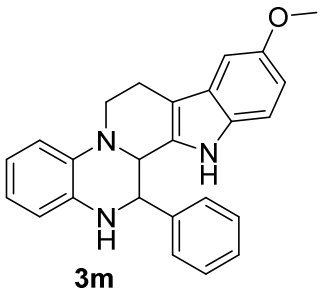


3l

Brown solid 62.8 mg, m.p. 83-84 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.58 – 7.49 (m, 3H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.17 (dd, *J* = 9.0, 1.3 Hz, 1H), 7.11 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.91 – 6.81 (m, 4H), 6.69 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.20 (s, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H), 4.16 (s, 1H), 3.76 (ddd, *J* = 11.6, 6.4, 4.8 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.07 – 2.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.89, 156.56, 140.51, 136.31, 134.90, 132.80, 132.23, 129.25, 129.08, 128.70, 126.65, 126.56, 121.26, 118.57, 118.52, 114.21, 111.19, 111.09, 111.07, 111.02, 110.07, 109.81, 103.36, 103.13, 58.79, 57.93, 47.97, 21.93.

HRMS: $C_{24}H_{20}FN_3$, Neutral mass: 369.16413, Observed m/z (M+H): 370.17096.

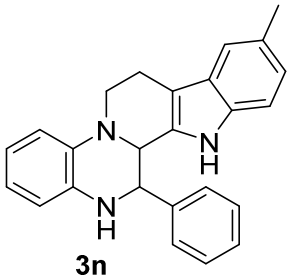


3m

Brown solid 69.4 mg, m.p. 145-146 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.57 – 7.41 (m, 5H), 7.11 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.89 – 6.80 (m, 3H), 6.76 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.68 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.11 (s, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 3.81 – 3.71 (m, 1H), 3.55 – 3.45 (m, 1H), 3.09 – 2.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.96, 140.62, 136.32, 135.01, 131.69, 130.90, 129.20, 129.01, 128.72, 126.60, 121.12, 118.48, 118.30, 114.11, 111.74, 111.31, 110.63, 100.33, 58.78, 58.18, 55.97, 47.92, 22.01.

HRMS: $C_{24}H_{20}ON_3$, Neutral mass: 381.18411, Observed m/z (M+H): 382.19010.

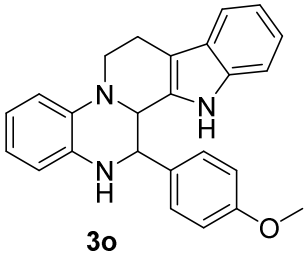


3n

Brown solid 65.1 mg, m.p. 120-121 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 – 7.42 (m, 5H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.15 – 7.08 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.81 (m, 3H), 6.69 (dd, *J* = 7.1, 1.7 Hz, 1H), 6.12 (s, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 4.15 (s, 1H), 3.82 – 3.69 (m, 1H), 3.57 – 3.44 (m, 1H), 3.01 (dtd, *J* = 20.3, 15.0, 5.1 Hz, 2H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.65, 136.37, 135.09, 134.09, 130.95, 129.17, 128.98, 128.74, 128.53, 126.51, 123.33, 121.11, 118.47, 118.40, 117.92, 114.12, 110.37, 110.28, 58.80, 58.19, 47.99, 22.00, 21.47.

HRMS: $C_{25}H_{23}N_3$, Neutral mass: 365.18920, Observed m/z (M+H): 366.19636.

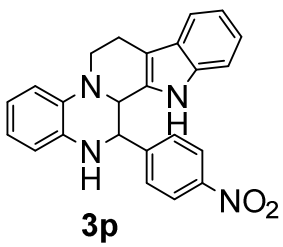


3o

Brown solid 64.9 mg, m.p.178-179 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.54 (d, *J* = 6.4 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.07 (ddd, *J* = 24.6, 10.7, 4.6 Hz, 6H), 6.89 – 6.78 (m, 2H), 6.67 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.34 (s, 1H), 4.34 (dd, *J* = 18.4, 8.3 Hz, 2H), 4.09 (s, 1H), 3.94 (s, 3H), 3.85 – 3.75 (m, 1H), 3.52 – 3.43 (m, 1H), 3.12 – 2.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.09, 136.28, 135.75, 134.99, 132.55, 131.07, 129.80, 126.30, 121.79, 120.93, 119.29, 118.40, 118.17, 117.79, 114.56, 113.95, 110.80, 110.68, 58.68, 57.85, 55.53, 47.53, 21.94.

HRMS: $C_{25}H_{23}N_3O$, Neutral mass: 381.18411, Observed m/z (M+H): 382.19145.



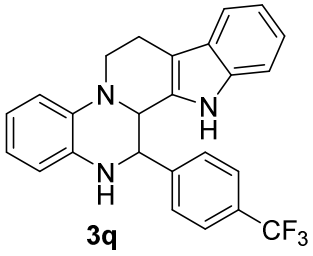
3p

Brown solid 69.8 mg, m.p.162-163 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ**

7.76 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.49 (m, 3H), 7.18 – 7.07 (m, 3H), 7.01 (dd, *J* = 6.2, 2.5 Hz, 1H), 6.88 (td, *J* = 6.9, 1.8 Hz, 2H), 6.71 (dd, *J* = 7.3, 2.0 Hz, 1H), 6.21 (s, 1H), 4.47 (d, *J* = 7.9 Hz, 1H), 4.32 (d, *J* = 7.9 Hz, 1H), 4.15 (s, 1H), 3.73 (ddd, *J* = 9.0, 6.9, 4.7 Hz, 1H), 3.62 – 3.41 (m, 1H), 3.03 (ddd, *J* = 20.3, 15.4, 10.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.81, 136.03, 135.75, 135.01, 130.18, 129.08, 126.29, 126.02, 125.98, 122.14, 121.52, 119.53, 119.16, 118.93, 118.25, 114.44, 111.21, 110.67, 58.80, 57.32, 48.49, 21.83.

HRMS: $C_{24}H_{20}N_4O_2$, Neutral mass: 396.15863, Observed m/z (M+H): 397.16722.

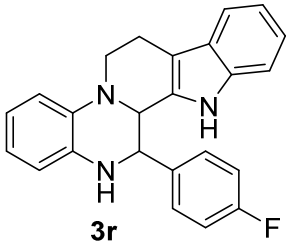


3q

Brown solid 75.5 mg, m.p. 97-99 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.33 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.54 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.19 – 7.08 (m, 3H), 7.04 (dd, *J* = 6.4, 2.1 Hz, 1H), 6.88 (pd, *J* = 7.3, 1.7 Hz, 2H), 6.72 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.33 (s, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 4.34 (d, *J* = 7.6 Hz, 1H), 4.16 (s, 1H), 3.72 (ddd, *J* = 12.1, 7.2, 4.8 Hz, 1H), 3.62 – 3.52 (m, 1H), 3.03 (qdd, *J* = 15.2, 7.4, 2.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.06, 148.03, 135.78, 135.72, 134.94, 129.86, 129.48, 126.35, 124.12, 122.30, 121.74, 119.67, 119.56, 119.20, 118.30, 114.60, 111.47, 110.78, 58.83, 56.88, 48.82, 21.69.

HRMS: $C_{25}H_{20}F_3N_3$, Neutral mass: 419.16093, Observed m/z (M+H): 420.16748.

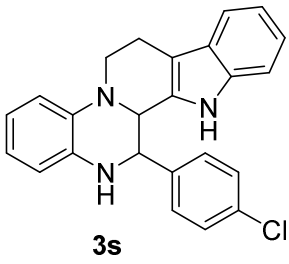


3r

Brown solid 68.7 mg, m.p. 83-85 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.21 (t, *J* = 8.6 Hz, 2H), 7.15 – 7.06 (m, 3H), 7.03 (dd, *J* = 6.4, 2.1 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.69 (dd, *J* = 6.9, 2.3 Hz, 1H), 6.25 (s, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 4.30 (d, *J* = 8.2 Hz, 1H), 4.11 (s, 1H), 3.75 (ddd, *J* = 11.6, 6.6, 4.7 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.12 – 3.02 (m, 1H), 3.01 – 2.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.49, 136.12, 135.74, 134.99, 130.52, 130.34, 130.26, 126.25, 121.97, 121.18, 119.41, 118.66, 118.42, 118.19, 116.27, 116.06, 114.15, 111.06, 110.66, 58.78, 57.38, 47.95, 21.92.

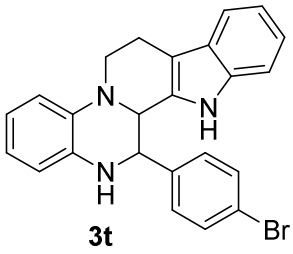
HRMS: $C_{24}H_{20}FN_3$, Neutral mass: 369.16413, Observed m/z (M+H): 370.17092.



3s Brown solid 70.2 mg, m.p. 87-88 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.63 – 7.54 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.05 (m, 4H), 6.95 – 6.80 (m, 2H), 6.74 – 6.61 (m, 1H), 6.31 (s, 1H), 4.38 (d, *J* = 8.1 Hz, 1H), 4.28 (d, *J* = 8.1 Hz, 1H), 4.10 (s, 1H), 3.75 (ddd, *J* = 11.7, 6.6, 4.8 Hz, 1H), 3.53 (dt, *J* = 11.9, 5.0 Hz, 1H), 3.13 – 2.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.22, 136.14, 135.78, 135.00, 134.74, 130.50, 130.01, 129.36, 126.31, 122.05, 121.32, 119.49, 118.74, 118.71, 118.25, 114.27, 111.09, 110.79, 58.72, 57.32, 48.16, 21.91.

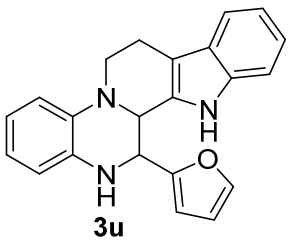
HRMS: $C_{24}H_{20}ClN_3$, Neutral mass: 385.13458, Observed m/z (M+H): 386.14134.



3t Brown solid 75.7 mg, m.p. 92-93 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.64 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.04 (m, 4H), 6.85 (pd, *J* = 7.3, 1.7 Hz, 2H), 6.68 (dd, *J* = 7.3, 2.0 Hz, 1H), 6.32 (s, 1H), 4.37 (d, *J* = 8.1 Hz, 1H), 4.28 (d, *J* = 8.1 Hz, 1H), 4.10 (s, 1H), 3.81 – 3.68 (m, 1H), 3.57 – 3.46 (m, 1H), 3.16 – 3.02 (m, 1H), 3.02 – 2.91 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.70, 136.08, 135.75, 134.95, 132.31, 130.41, 130.31, 126.26, 122.85, 122.03, 121.34, 119.46, 118.73, 118.21, 114.23, 111.08, 110.76, 58.66, 57.38, 48.17, 21.89.

HRMS: $C_{24}H_{20}BrN_3$, Neutral mass: 429.08406, Observed m/z (M+H): 430.09031.

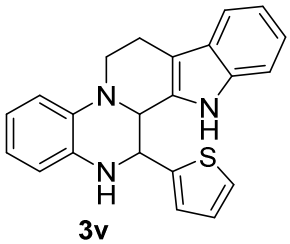


3u

Brown solid 60.1 mg, m.p. 77-78 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 (d, *J* = 1.1 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.07 (m, 4H), 6.89 – 6.81 (m, 2H), 6.73 (s, 1H), 6.71 – 6.67 (m, 1H), 6.59 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 4.58 (d, *J* = 8.1 Hz, 1H), 4.50 (d, *J* = 8.1 Hz, 1H), 4.12 (s, 1H), 3.76 – 3.66 (m, 1H), 3.55 – 3.43 (m, 1H), 3.11 – 2.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.88, 142.60, 136.09, 135.51, 135.15, 130.67, 126.45, 121.99, 121.33, 119.40, 118.99, 118.50, 118.31, 114.71, 111.34, 110.75, 108.93, 56.95, 52.12, 47.87, 21.71.

HRMS: $C_{22}H_{19}N_3O$, Neutral mass: 341.15281, Observed m/z (M+H): 342.15940.

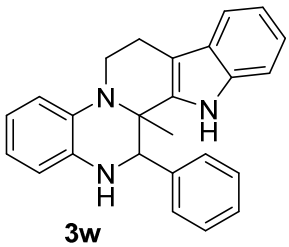


3v

Brown solid 60.1 mg, m.p. 89-91 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.54 (t, *J* = 6.6 Hz, 2H), 7.17 – 7.06 (m, 6H), 6.90 – 6.81 (m, 2H), 6.68 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.64 (s, 1H), 4.79 (d, *J* = 8.1 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.76 (ddd, *J* = 11.7, 6.5, 4.8 Hz, 1H), 3.56 – 3.48 (m, 1H), 3.15 – 3.04 (m, 1H), 2.99 (dt, *J* = 11.1, 5.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.29, 135.89, 135.58, 135.14, 130.62, 127.19, 126.83, 126.60, 126.29, 121.93, 121.20, 119.34, 118.95, 118.31, 118.25, 114.33, 110.93, 110.74, 59.74, 54.17, 47.90, 29.75, 21.87.

HRMS: $C_{22}H_{19}N_3S$, Neutral mass: 357.12997, Observed m/z (M+H): 358.13629.



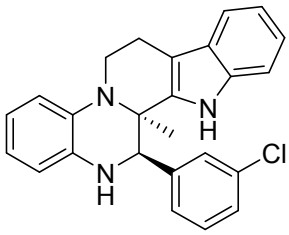
3w

Brown solid 63.6 mg, m.p. 52-54 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 – 7.55 (m, 1H), 7.53 – 7.32 (m, 4H), 7.18 – 7.09 (m, 3H), 7.08 – 7.00 (m, 1H), 6.93 – 6.80 (m, 2H), 6.71 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.36 (s, 1H), 4.55 (s, 1H), 4.24 (s, 1H), 3.70 (ddd, *J* = 12.0, 7.2, 4.6 Hz, 1H),

3.58 (dt, *J* = 10.8, 5.1 Hz, 1H), 3.09 (ddd, *J* = 15.0, 7.2, 4.8 Hz, 1H), 2.95 (dt, *J* = 10.2, 4.8 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.98, 136.07, 135.71, 135.50, 133.73, 128.69, 128.37, 126.39, 121.74, 121.14, 120.25, 119.29, 118.62, 118.27, 114.03, 110.61, 110.31, 60.06, 57.20, 47.94, 22.23, 18.85.

HRMS: $C_{25}H_{23}N_3$, Neutral mass: 365.18920, Observed m/z (M+H): 366.19703.

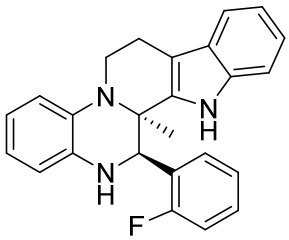


3x

Brown solid 41.5 mg, m.p.95-96℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ**7.63 – 7.59 (m, 1H), 7.60 – 7.53 (m, 1H), 7.49 (d, *J*=7.9, 1H), 7.32 (t, *J*=7.7, 1H), 7.23 – 7.15 (m, 3H), 7.13 (dd, *J*=8.5, 2.5, 2H), 6.91 (dt, *J*=20.5, 7.0, 2H), 6.74 (d, *J*=7.4, 1H), 6.50 (s, 1H), 4.54 (s, 1H), 4.19 (s, 1H), 3.69 (ddd, *J*=12.0, 7.3, 4.6, 1H), 3.65 – 3.57 (m, 1H), 3.17 – 3.07 (m, 1H), 2.97 (dt, *J*=15.1, 4.8, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.36 (s), 135.81 (d, *J*=4.4), 134.99 (s), 134.59 (s), 133.77 (s), 129.43 (s), 128.80 (s), 126.42 (s), 122.01 (s), 121.43 (s), 120.75 (s), 119.47 (s), 118.98 (s), 118.36 (s), 114.32 (s), 110.64 (d, *J*=15.1), 59.50 (s), 57.23 (s), 48.44 (s), 22.25 (s), 18.83 (s).

HRMS: $C_{25}H_{22}ClN_3$, Neutral mass:399.15023, Observed m/z (M+H):400.15490.



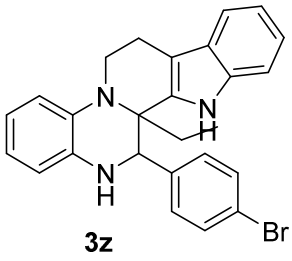
3y

Brown solid 43.7 mg, m.p.92-93℃. 1H NMR (400 MHz, CDCl3) δ7.85 (s, 1H), 7.60 – 7.54 (m, 1H), 7.45 (dd, J=13.1, 6.0, 1H), 7.37 (dd, J=14.3, 7.1, 1H), 7.18 – 7.10 (m, 3H), 7.07 (dd, J=6.2, 2.3, 1H), 7.01 (t, J=9.1, 1H), 6.94 – 6.83 (m, 2H), 6.72 (d, J=6.5, 1H), 6.58 (s, 1H), 4.99 (s, 1H), 4.09 (s, 1H), 3.70 (ddd, J=12.1, 7.6, 4.5, 1H), 3.65 – 3.56 (m, 1H), 3.08 (ddd, J=12.5, 7.4, 4.9, 1H), 2.97 (dt, J=15.1, 4.7, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56 (s), 160.07 (s), 136.02 (d, *J*=7.8), 135.25 (s), 133.99 (s), 129.92 (d, *J*=8.4), 126.51 (s), 124.41 (s), 121.71 (s), 121.37 (s), 121.04 (s), 119.27 (s), 118.95 (s), 118.38 (s),

114.55 (s), 110.44 (s), 110.00 (s), 57.02 (s), 48.71 (s), 29.74 (s), 22.13 (s), 19.21 (s).

HRMS: $C_{25}H_{22}FN_3$, Neutral mass:383.17978, Observed m/z (M+H):384.18646

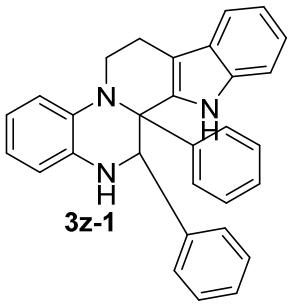


3z

Brown solid 75.2 mg, m.p.190-192 ℃; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.64 – 7.57 (m, 1H), 7.54 (d, *J* = 14.0 Hz, 2H), 7.20 – 7.08 (m, 5H), 6.92 (td, *J* = 7.5, 1.4 Hz, 1H), 6.85 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.45 (s, 1H), 4.48 (s, 1H), 4.18 (s, 1H), 3.76 (dt, *J* = 12.0, 4.5 Hz, 1H), 3.60 – 3.47 (m, 1H), 3.15 – 3.04 (m, 1H), 2.91 (dt, *J* = 15.0, 4.0 Hz, 1H), 1.94 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.58 – 1.52 (m, 1H), 0.51 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.06, 136.48, 135.74, 133.61, 133.04, 126.38, 122.77, 122.36, 121.81, 121.75, 119.33, 118.77, 118.17, 114.27, 112.72, 110.72, 60.57, 58.68, 51.36, 23.21, 22.33, 7.44.

HRMS: $C_{26}H_{24}BrN_3$, Neutral mass: 457.11536, Observed m/z (M+H): 458.11925.

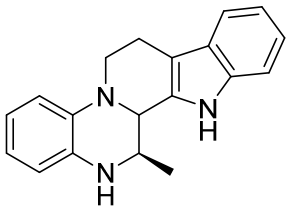


3z-1

Brown solid 77.8 mg, m.p.168-169 ℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.88 (s, 1H), 7.76 – 7.53 (m, 4H), 7.44 – 7.12 (m, 12H), 6.93 – 6.75 (m, 3H), 5.34 (s, 1H), 4.06 – 3.86 (m, 1H), 3.69 – 3.52 (m, 1H), 3.22 – 2.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.60, 139.23, 137.27, 136.38, 134.19, 129.94, 128.96, 128.86, 128.66, 128.38, 128.16, 127.17, 127.06, 127.00, 122.63, 122.07, 119.52, 118.51, 117.39, 112.88, 111.47, 111.15, 61.09, 49.00, 23.27.

HRMS: $C_{30}H_{25}N_3$, Neutral mass: 427.20485, Observed m/z (M+H): 428.21164.

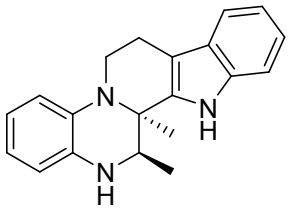


3z-2

Brown solid 52.0mg, m.p.164-165℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ**7.87 (s, 1H), 7.53 (d, *J*=7.7, 1H), 7.36 (d, *J*=8.0, 1H), 7.20 (t, *J*=7.5, 1H), 7.13 (t, *J*=7.1, 1H), 7.08 – 7.00 (m, 1H), 6.76 (dd, *J*=5.5, 3.7, 2H), 6.61 – 6.52 (m, 1H), 4.08 (d, *J*=6.3, 1H), 3.83 (dt, *J*=12.7, 5.1, 1H), 3.69 – 3.60 (m, 1H), 3.45 (ddd, *J*=12.6, 7.0, 5.2, 1H), 3.04 – 2.87 (m, 2H), 1.50 (d, *J*=6.3, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ136.09 (s), 135.53 (s), 134.73 (s), 132.17 (s), 127.03 (s), 121.97 (s), 120.98 (s), 119.54 (s), 118.64 (s), 118.26 (d, *J*=3.1), 114.71 (s), 110.86 (s), 58.35 (s), 48.22 (s), 47.69 (s), 29.72 (s), 20.75 (s), 20.18 (s).

HRMS:$C_{19}H_{19}N_3$, Neutral mass: 289.15790 Observed m/z (M+H):290.16539



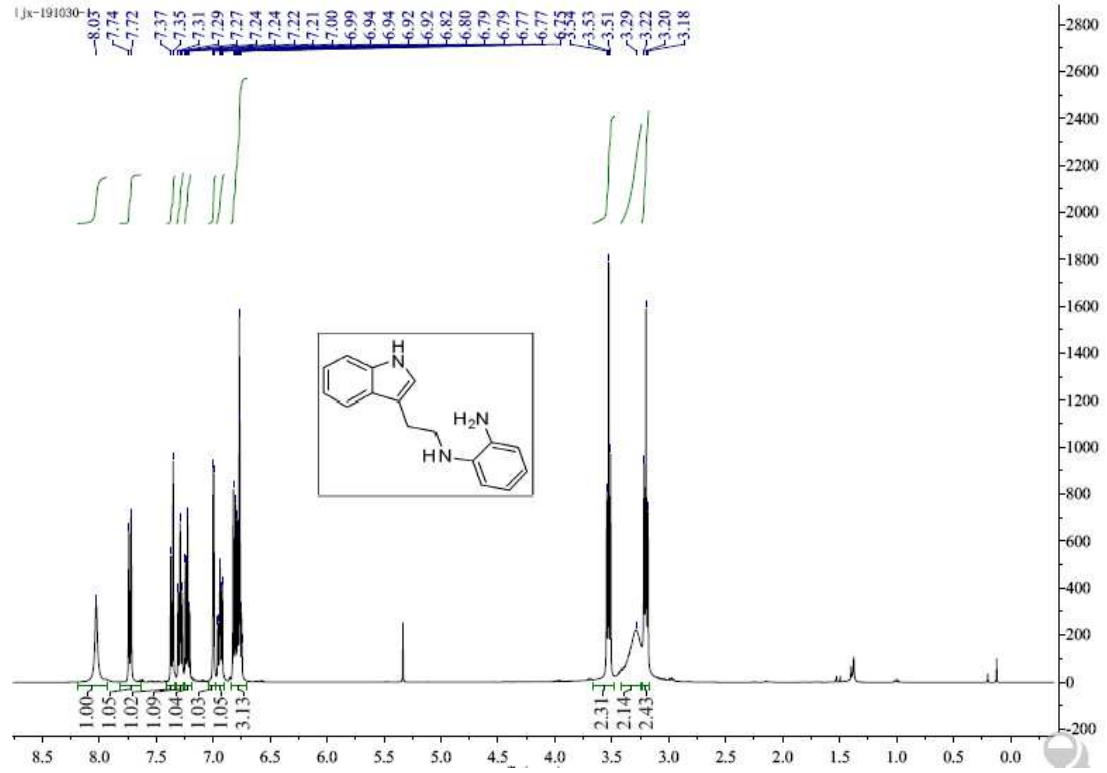
3z-3

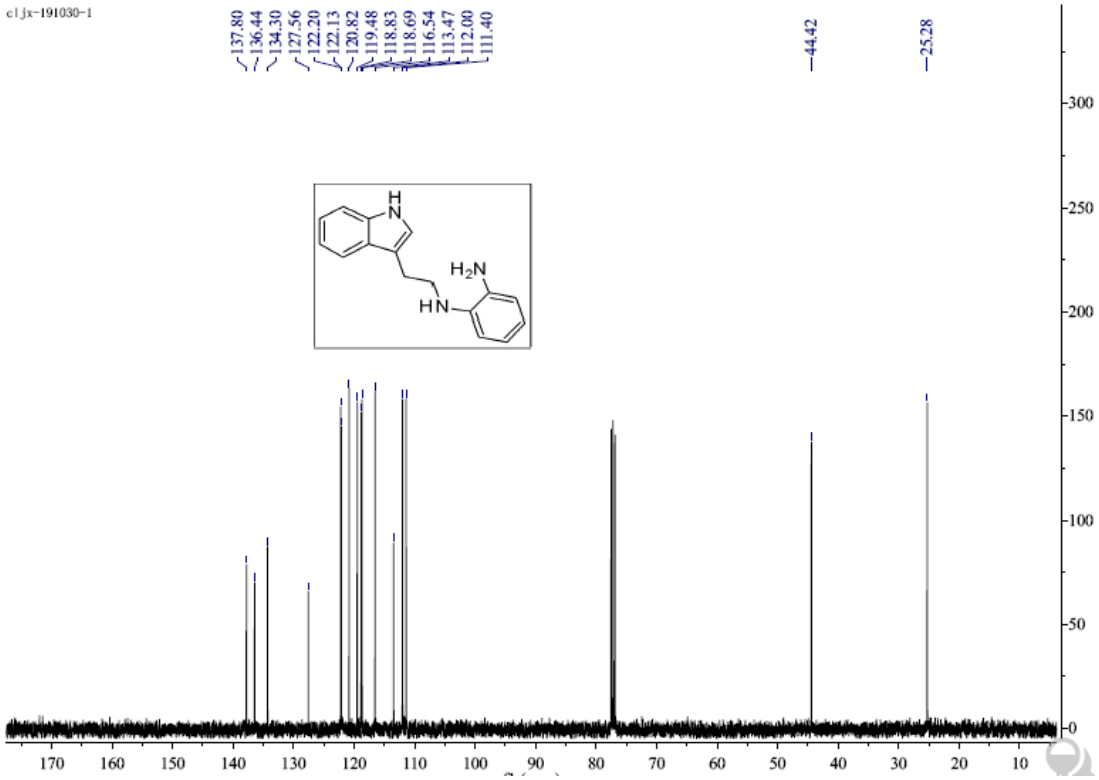
Brown solid 27.3 mg, m.p.140-141℃. **^{1}H NMR (400 MHz, $CDCl_3$) δ**7.82 (s, 1H), 7.58 (d, *J*=7.7, 1H), 7.40 (d, *J*=8.0, 1H), 7.24 (t, *J*=8.0, 1H), 7.17 (t, *J*=7.4, 1H), 7.05 (d, *J*=8.8, 1H), 6.81 (dt, *J*=14.3, 6.9, 2H), 6.62 (d, *J*=7.4, 1H), 3.63 (ddd, *J*=11.5, 8.2, 5.1, 2H), 3.53 – 3.43 (m, 1H), 3.02 (ddd, *J*=15.1, 6.7, 4.9, 1H), 2.94 – 2.85 (m, 1H), 1.44 (d, *J*=6.4, 3H), 1.30 (s, 3H).

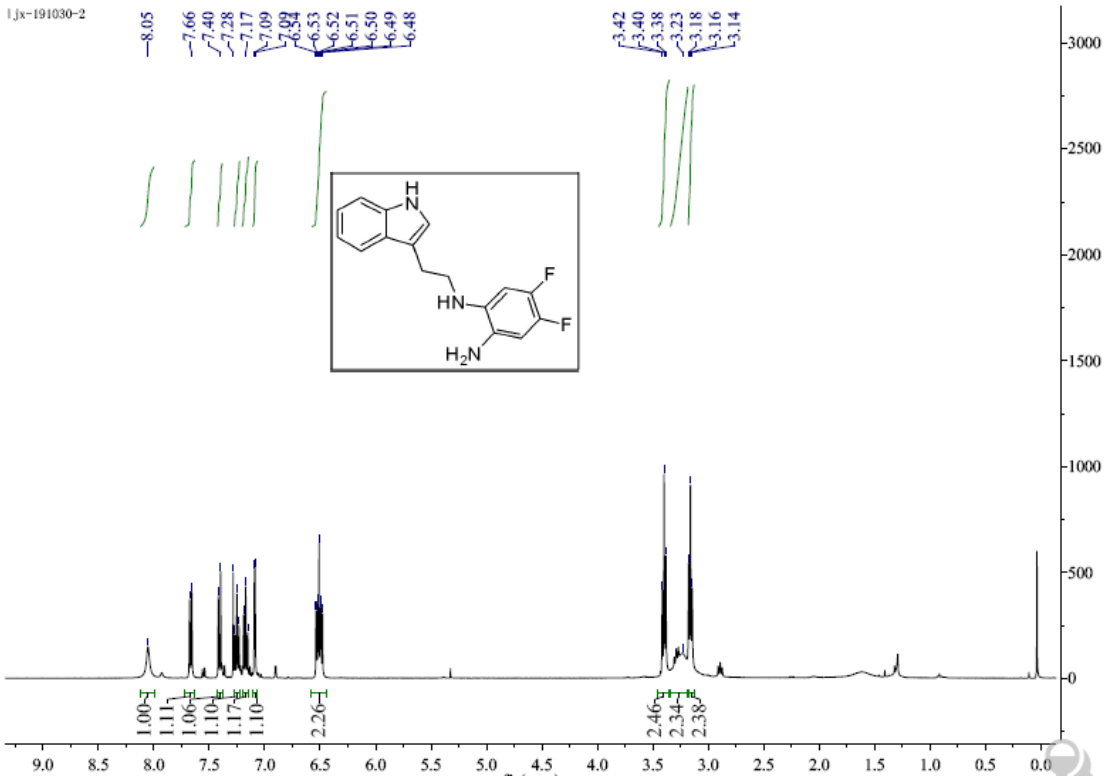
^{13}C NMR (101 MHz, $CDCl_3$) δ136.12 (s), 135.87 (s), 133.97 (s), 126.78 (s), 121.98 (s), 121.00 (s), 119.99 (s), 119.55 (s), 118.40 (s), 113.85 (s), 110.76 (s), 110.44 (s), 55.76 (s), 50.95 (s), 47.18 (s), 29.75 (s), 21.89 (s), 18.41 (s), 18.03 (s).

HRMS: $C_{20}H_{21}N_3$,Neutral mass:303.17355 Observed m/z (M+H):304.18042

Selected examples of the NMR spectrums



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7.09
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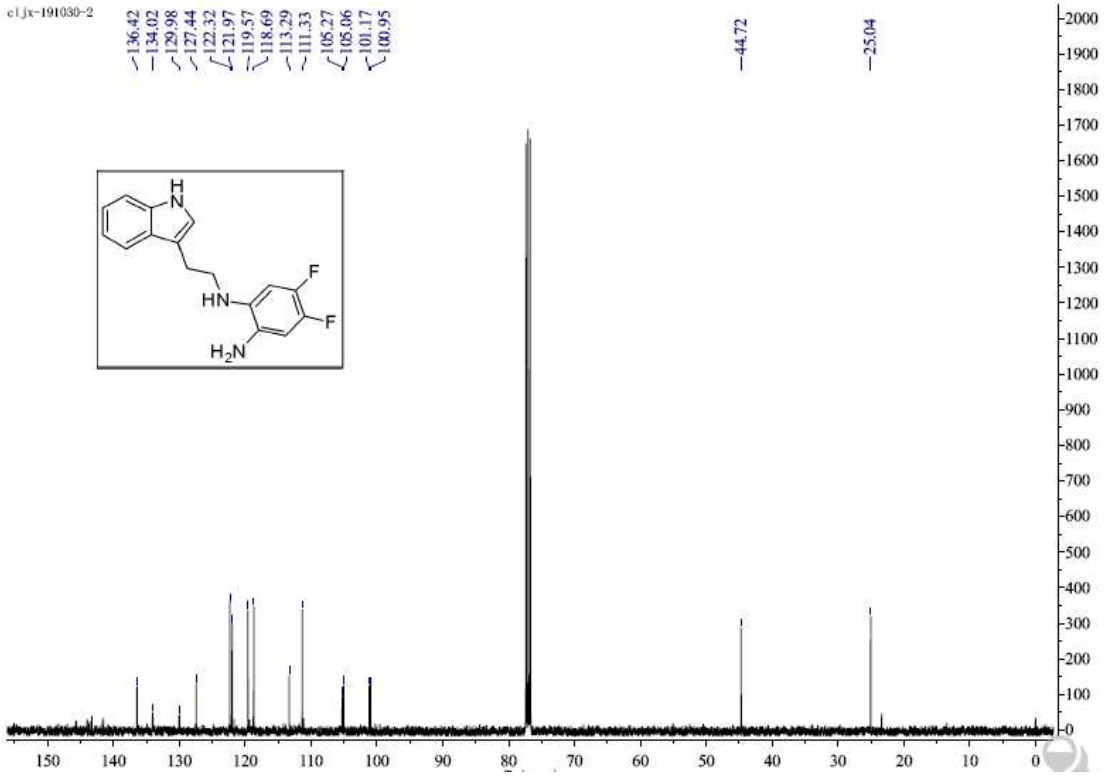
6.51
6.50
6.49
6.48
3.42
3.40
3.38
3.23
3.18
3.16
3.14
1.00
1.11
1.06
1.10
1.17
1.10
2.26
2.46
2.34
2.38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121.97
119.57
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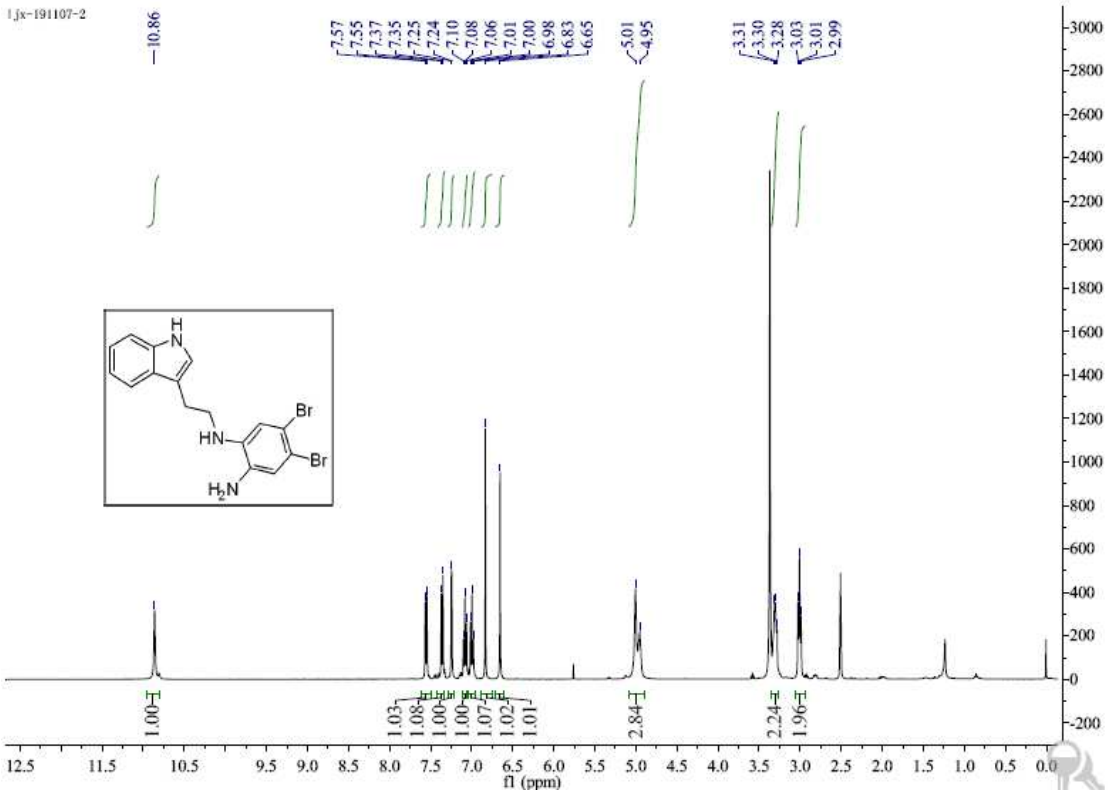
113.29
111.33
105.27
105.06
101.17
100.95
44.72
25.04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7.24
7.10
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7.00
6.98
6.83
6.65
5.01
4.95
3.31
3.30
3.28
3.03
3.01
2.99
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1.03
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1.01
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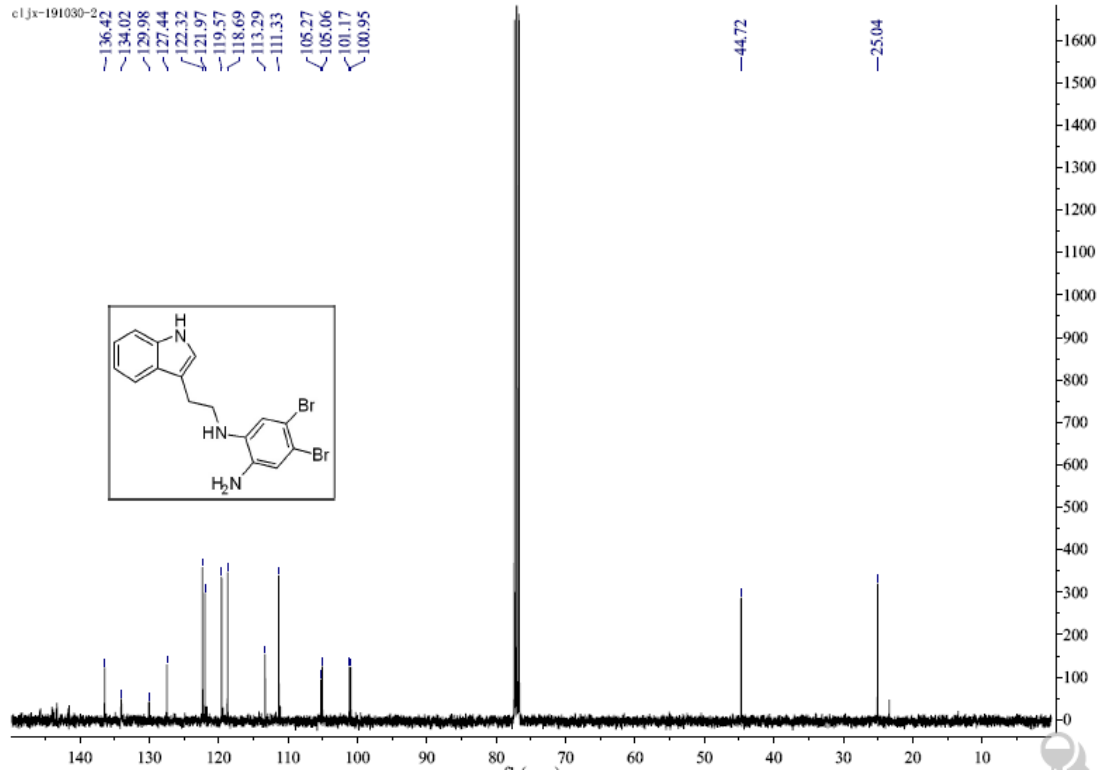
f1 (ppm)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134.02
129.98
127.44
122.32
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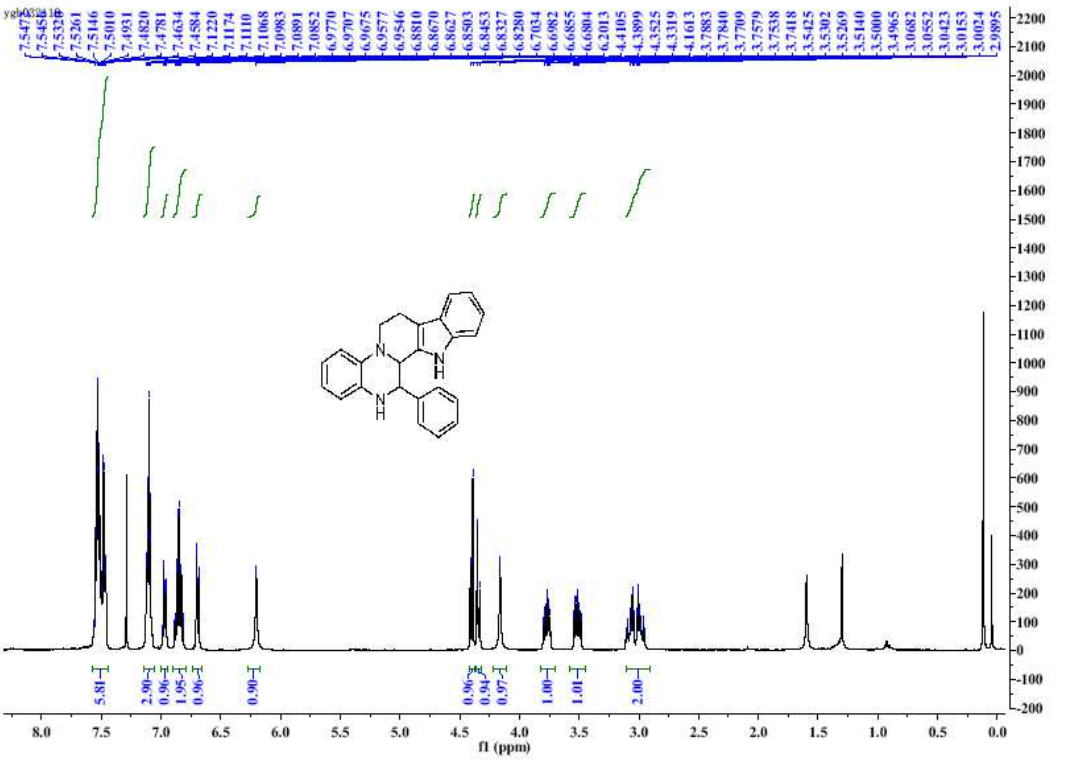
105.06
101.17
100.95
44.72
25.04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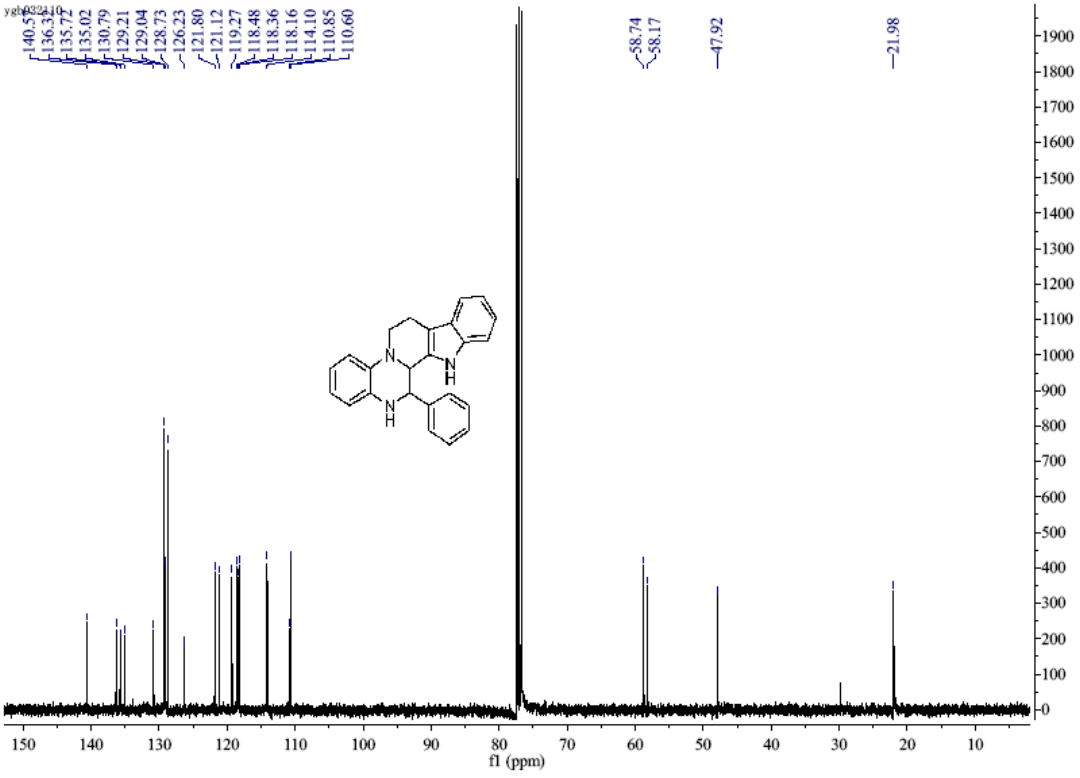
f1 (ppm)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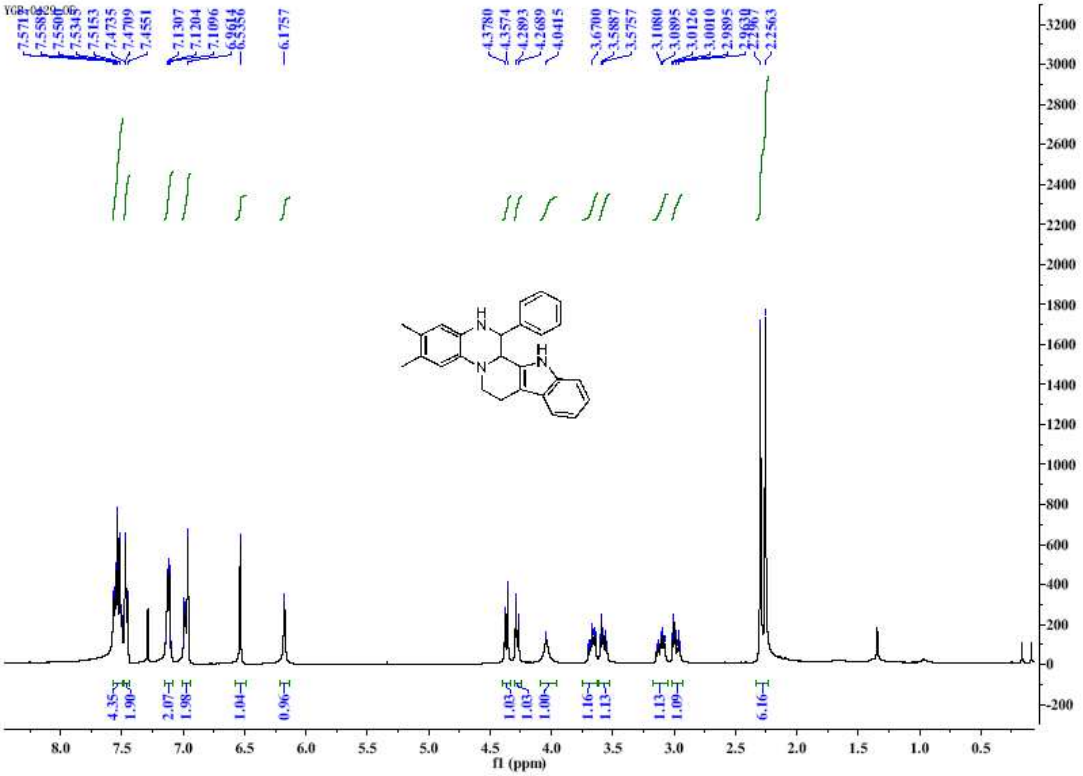
21.98
f1 (ppm)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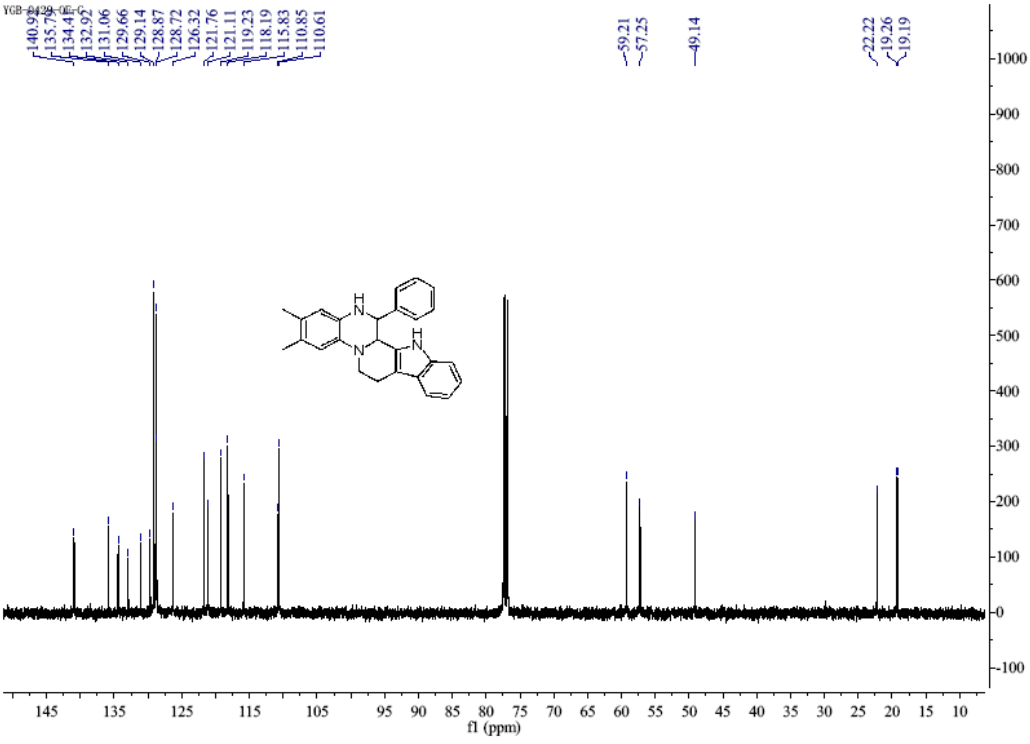
fl (ppm)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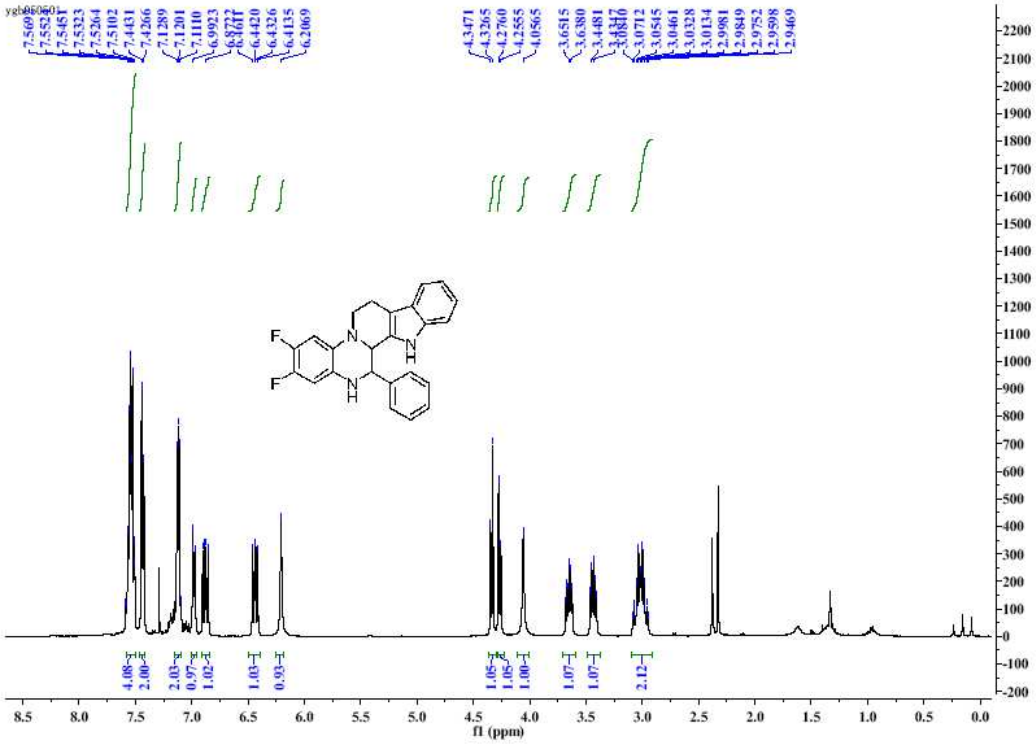
22.22
19.26
19.19
fl (ppm)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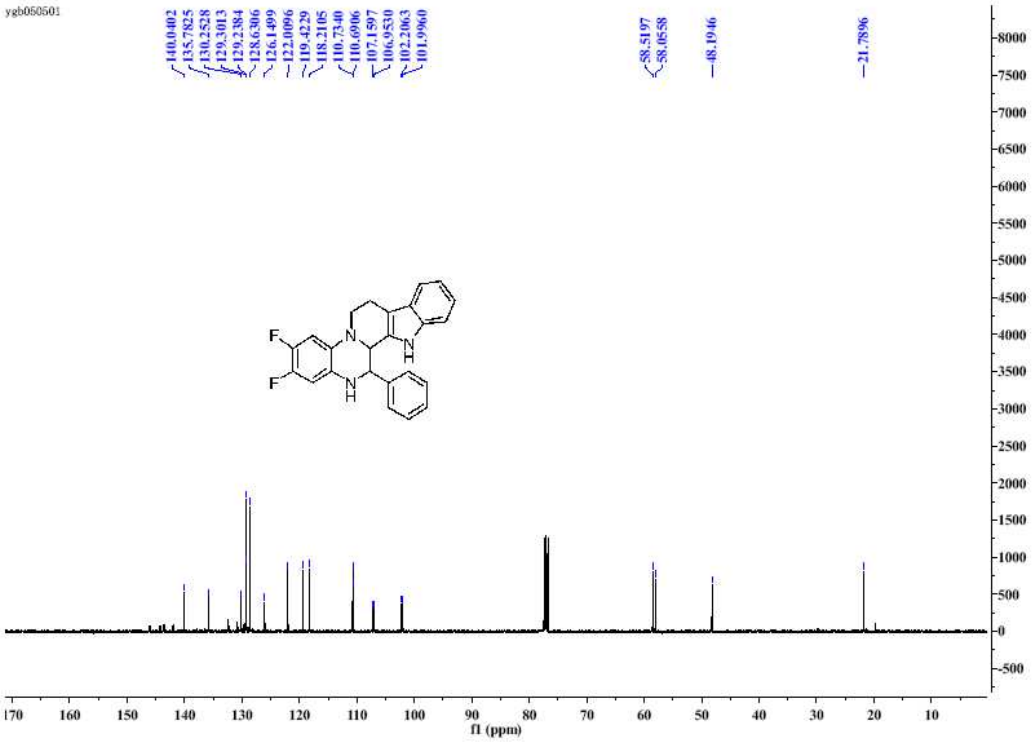
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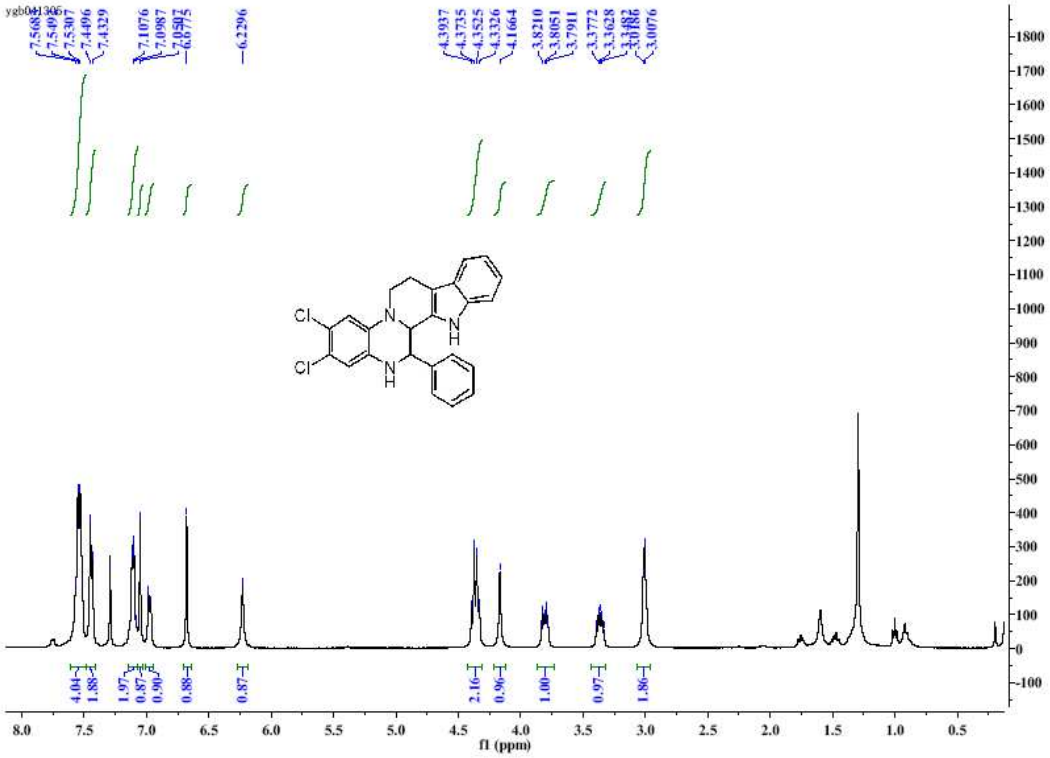
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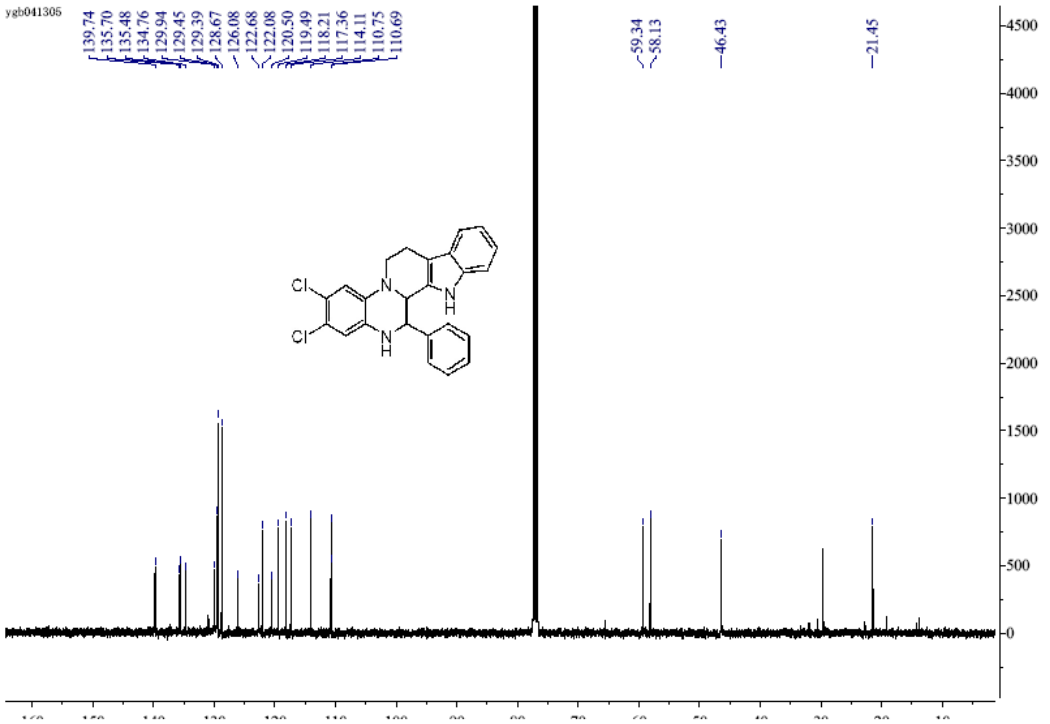
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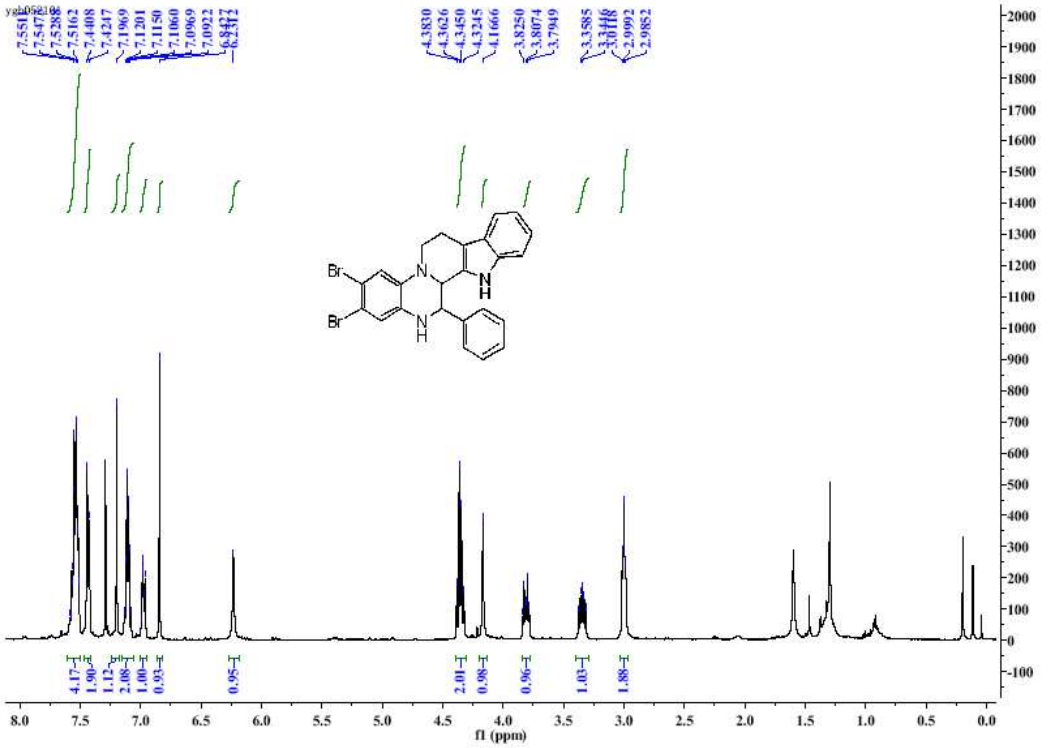
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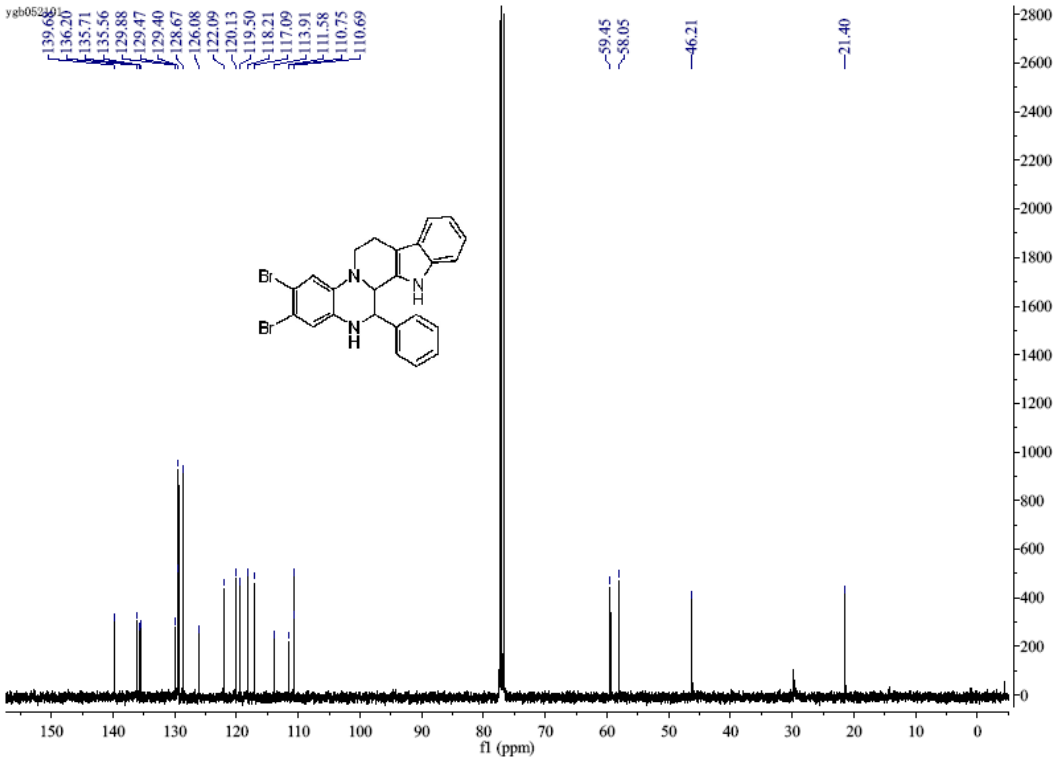
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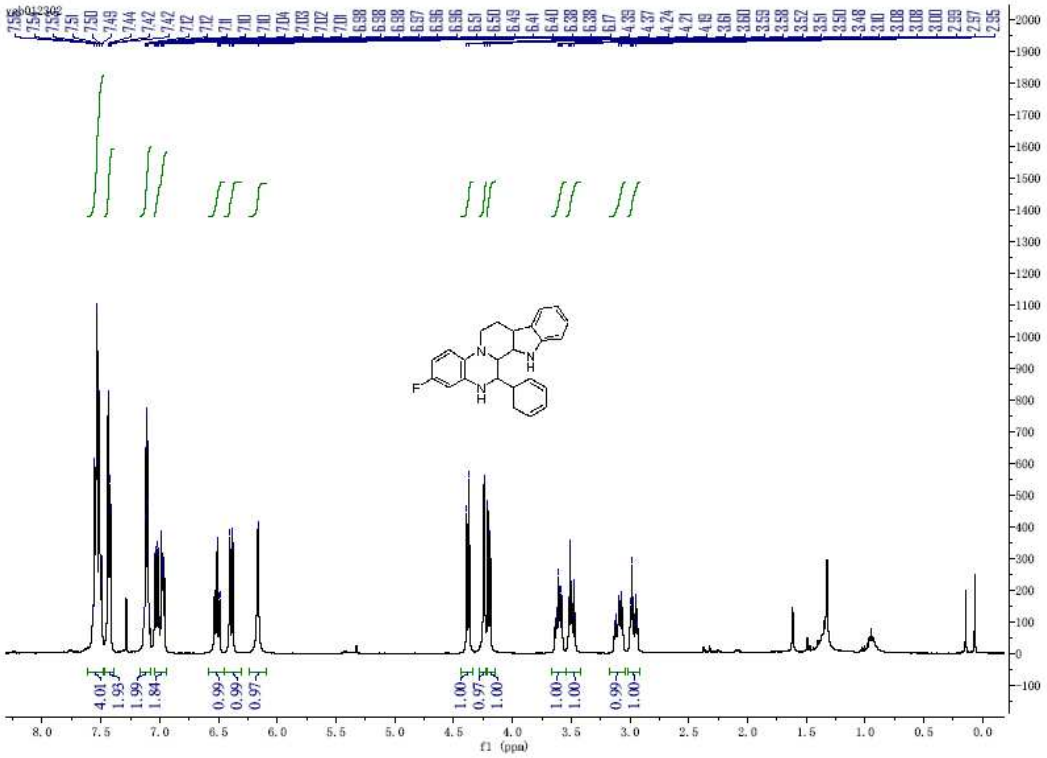
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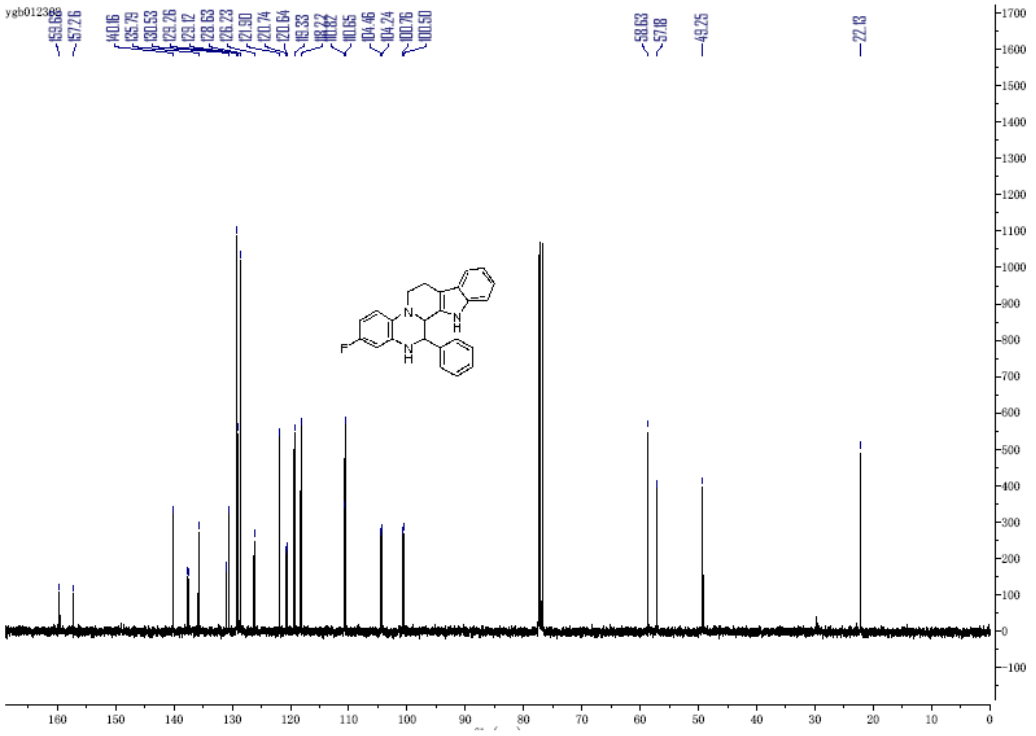

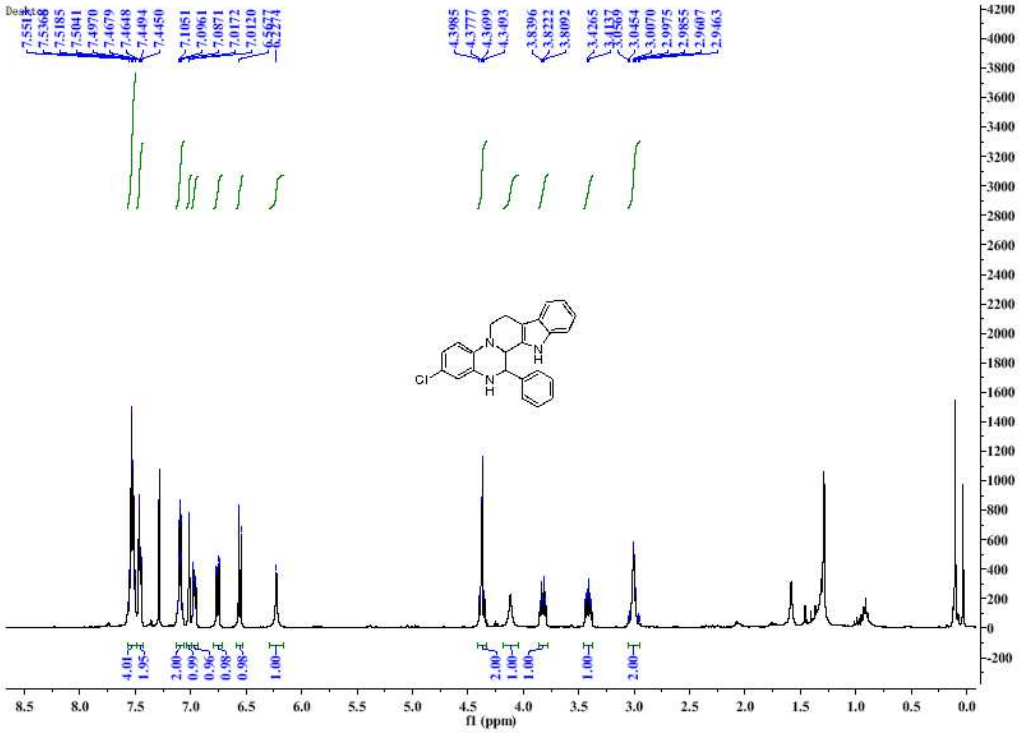
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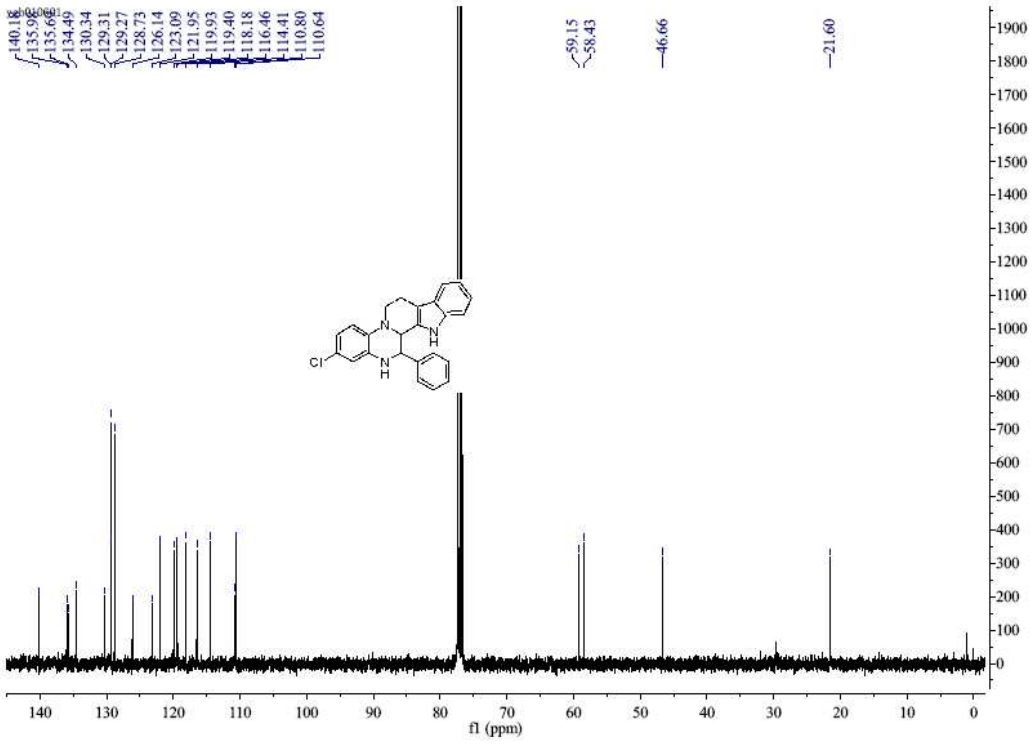
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110.64
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21.60
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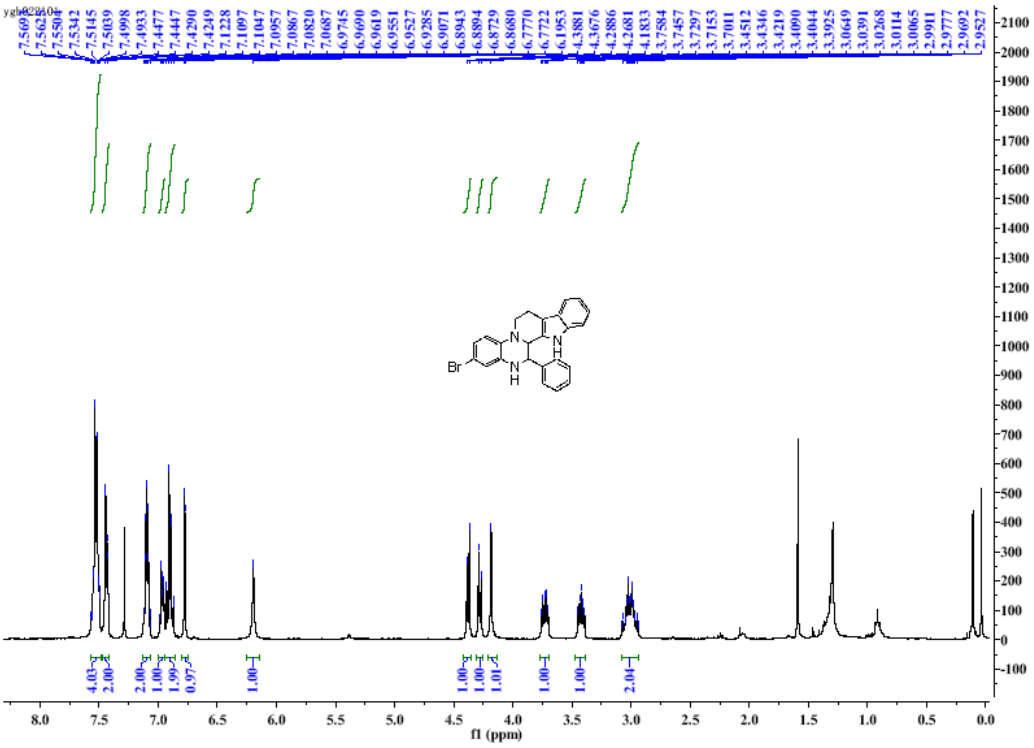
f1 (ppm)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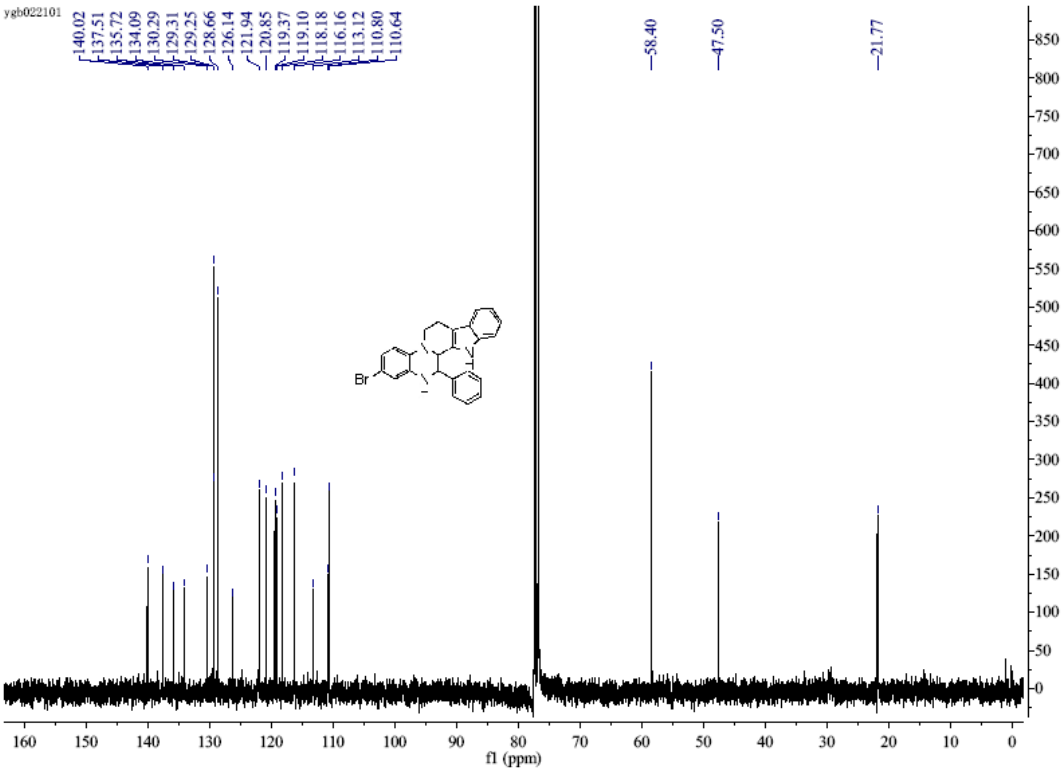
f1 (ppm)


ygb022101
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120.85
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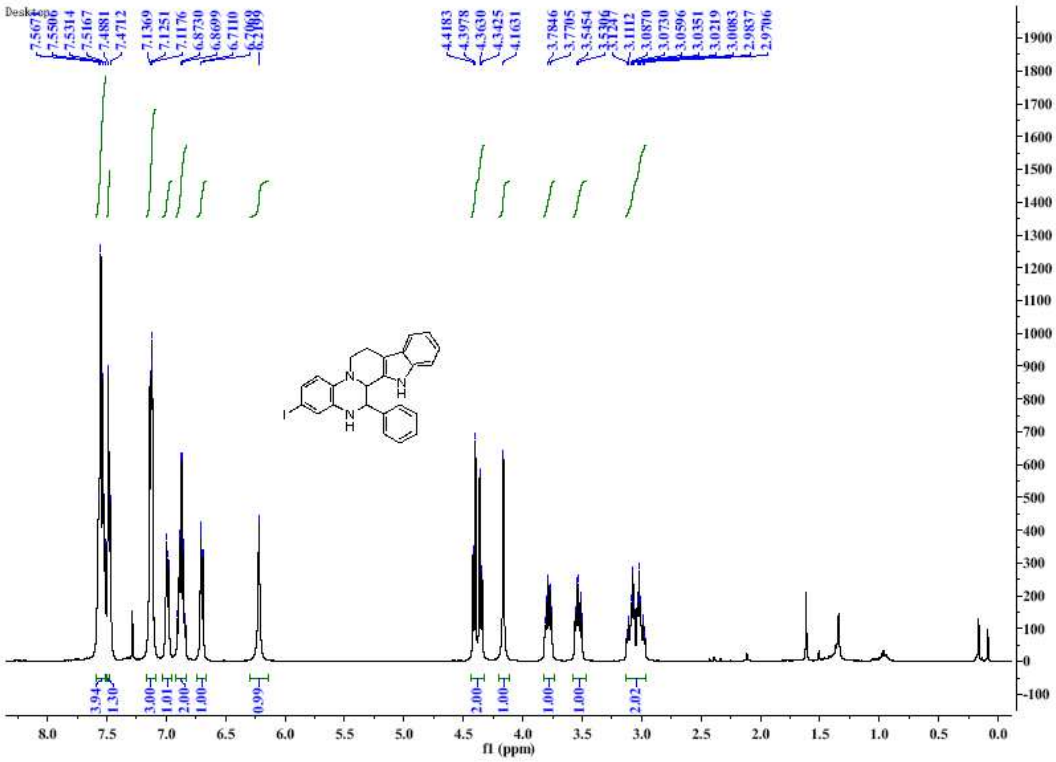
Br
f1 (ppm)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6.7110
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4.3425
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3.7705
3.5454
3.1112
3.0870
3.0730
3.0596
3.0351
3.0219
3.0083
2.9837
2.9706
3.94
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3.00
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2.00
1.00
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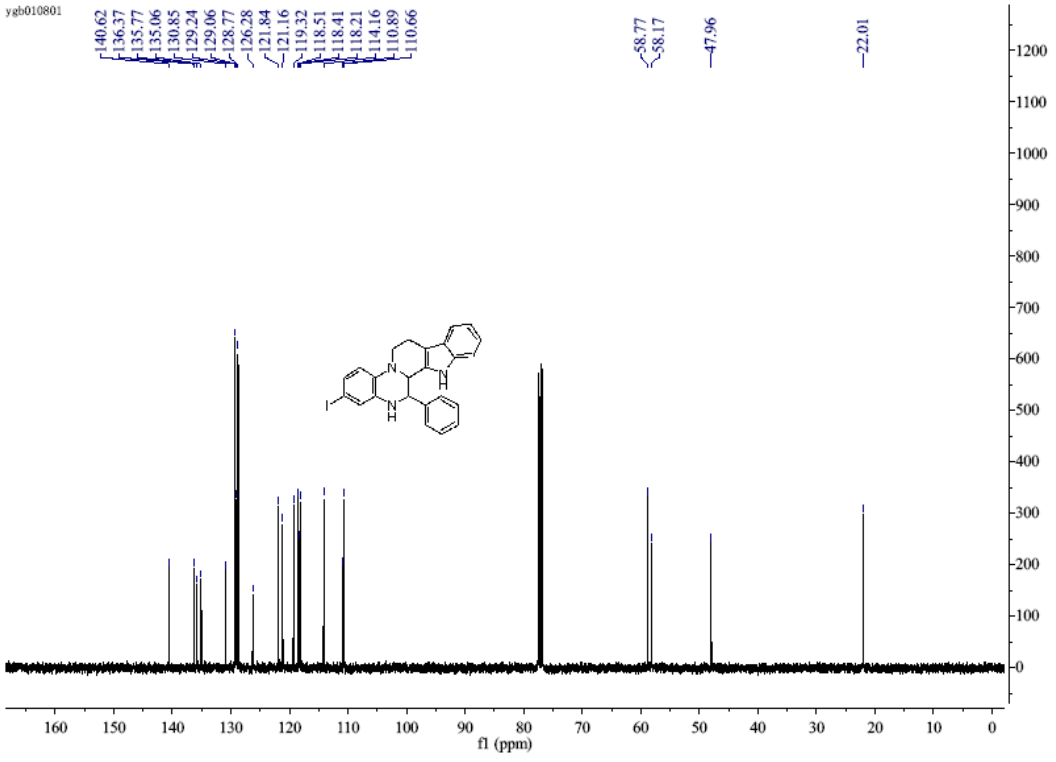
2.00
1.00
1.00
1.00
2.02
f1 (ppm)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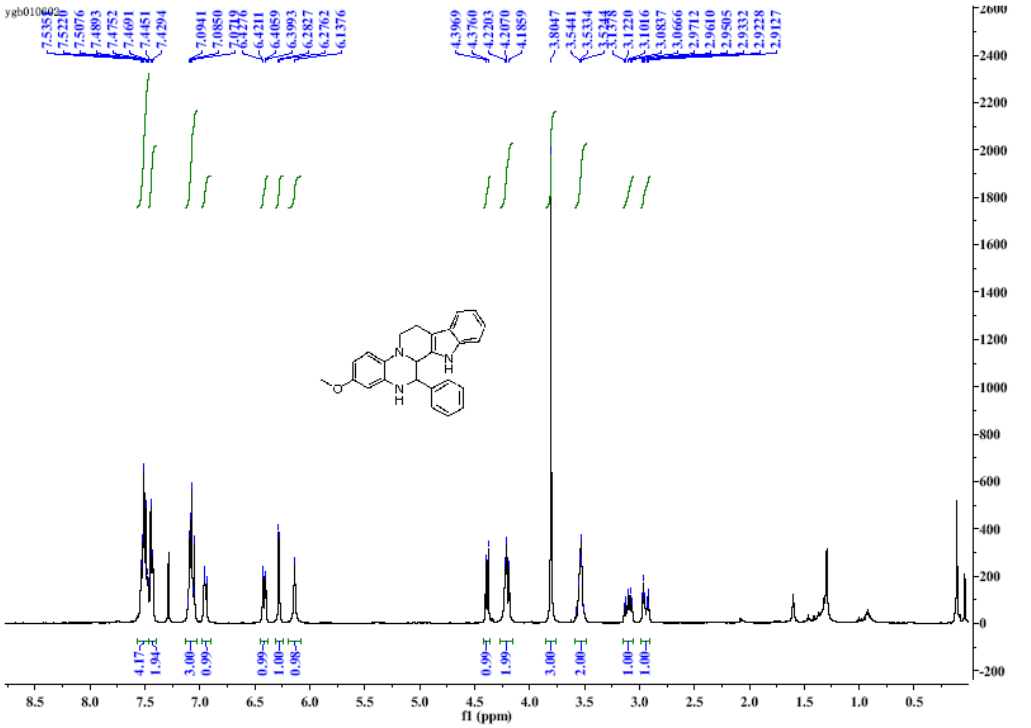
58.17
47.96
22.01
f1 (ppm)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7.4294
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7.0850
7.0719
6.4231
6.4059
6.3993
6.2827
6.2762
6.1376
4.3969
4.3760
4.2203
4.2070
4.1859
3.8047
3.5441
3.5334
3.1220
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3.0837
3.0666
2.9712
2.9610
2.9505
2.9332
2.9228
2.9127
4.17
1.94
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0.99
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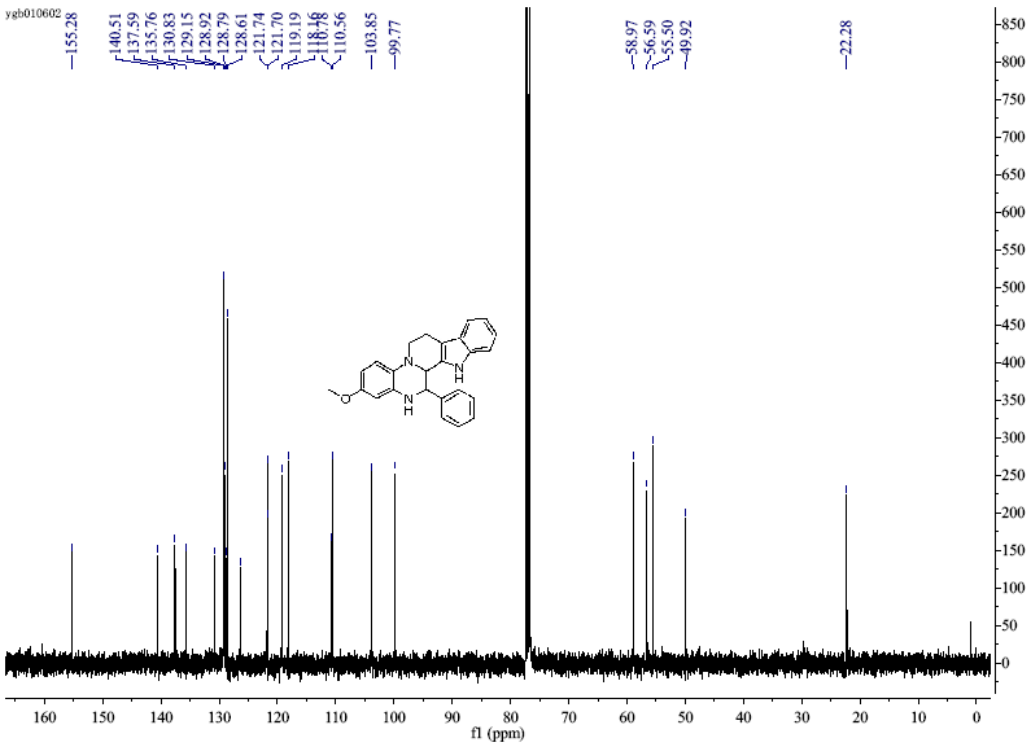
0.99
1.99
3.00
2.00
1.00
1.00
f1 (ppm)


ygb010602
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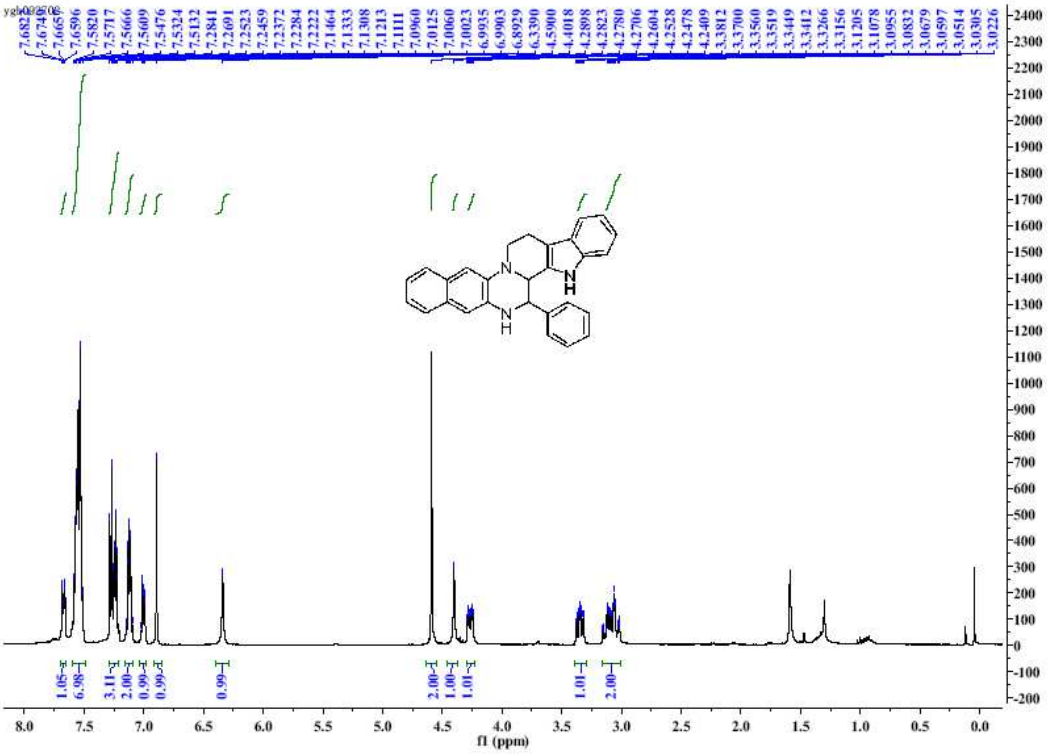
22.28
f1 (ppm)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7.2222
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7.1333
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7.1213
7.1111
7.0960
7.0125
7.0060
7.0023
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6.9903
6.8929
6.3390
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4.2898
4.2823
4.2780
4.2706
4.2604
4.2528
4.2478
4.2409
3.3812
3.3700
3.3560
3.3519
3.3449
3.3412
3.3266
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3.1078
3.0955
3.0832
3.0679
3.0597
3.0514
3.0305
3.0226
1.05
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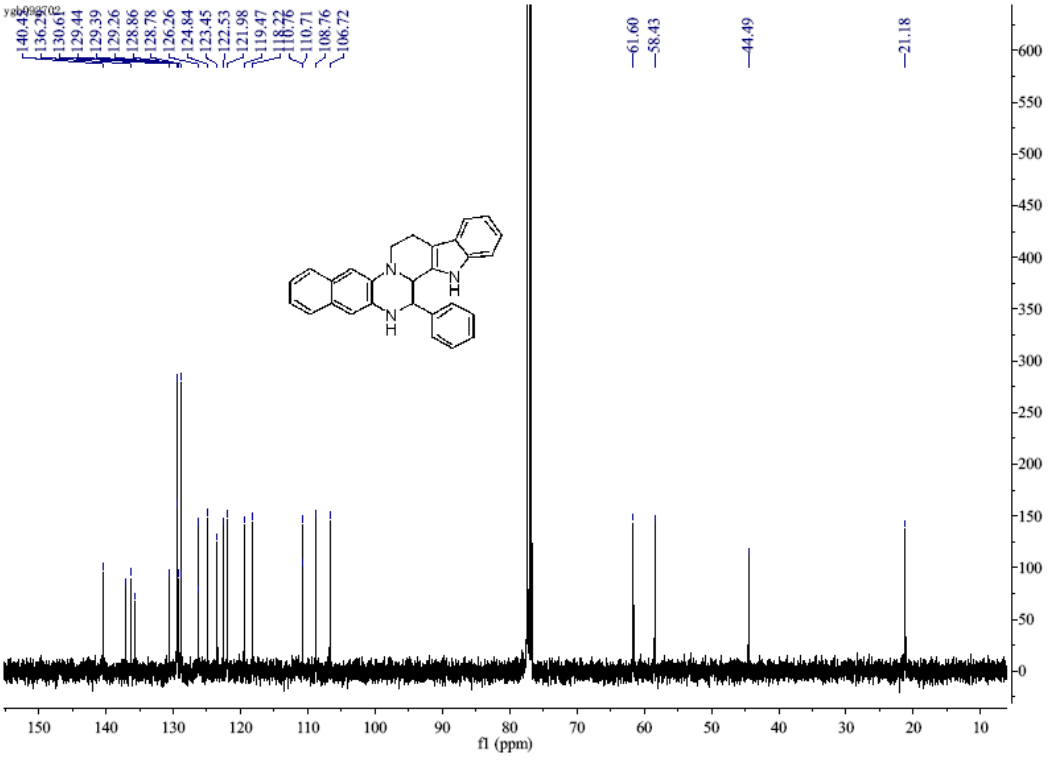
0.99
0.99
2.00
1.00
1.01
1.01
2.00
f1 (ppm)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123.45
122.53
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61.60
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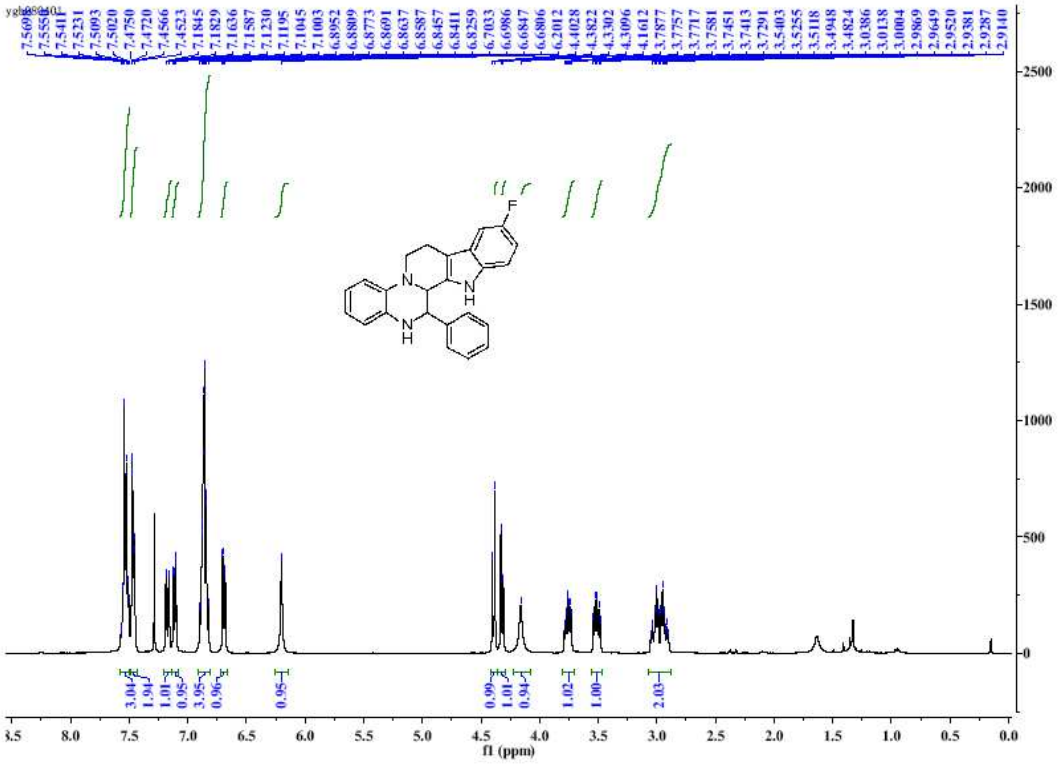
44.49
21.18
f1 (ppm)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7.4523
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7.1829
7.1636
7.1587
7.1230
7.1195
7.1045
7.1003
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6.8809
6.8773
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6.8637
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6.8457
6.8411
6.8259
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6.6847
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6.2012
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4.3822
4.3302
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3.7581
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3.7291
3.5403
3.5255
3.5118
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3.4824
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3.0138
3.0004
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2.9140
F
N
H
N
H
3.04
1.94
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0.94
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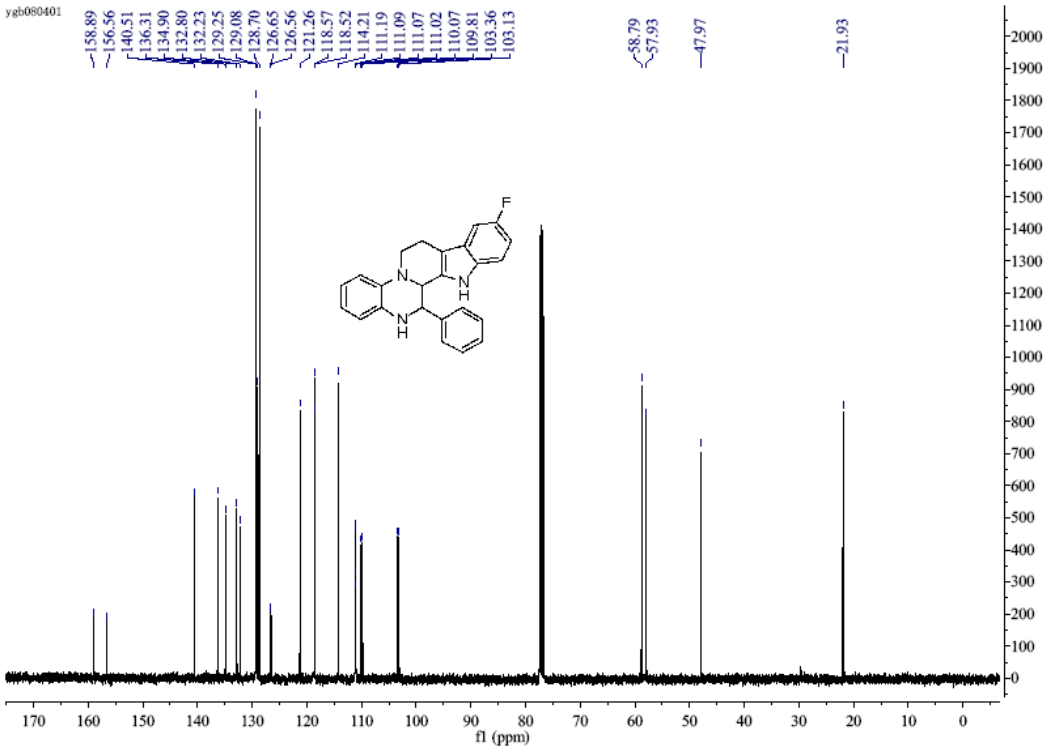
1.00
2.03
f1 (ppm)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118.57
118.52
114.21
111.19
111.09
111.07
111.02
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103.13
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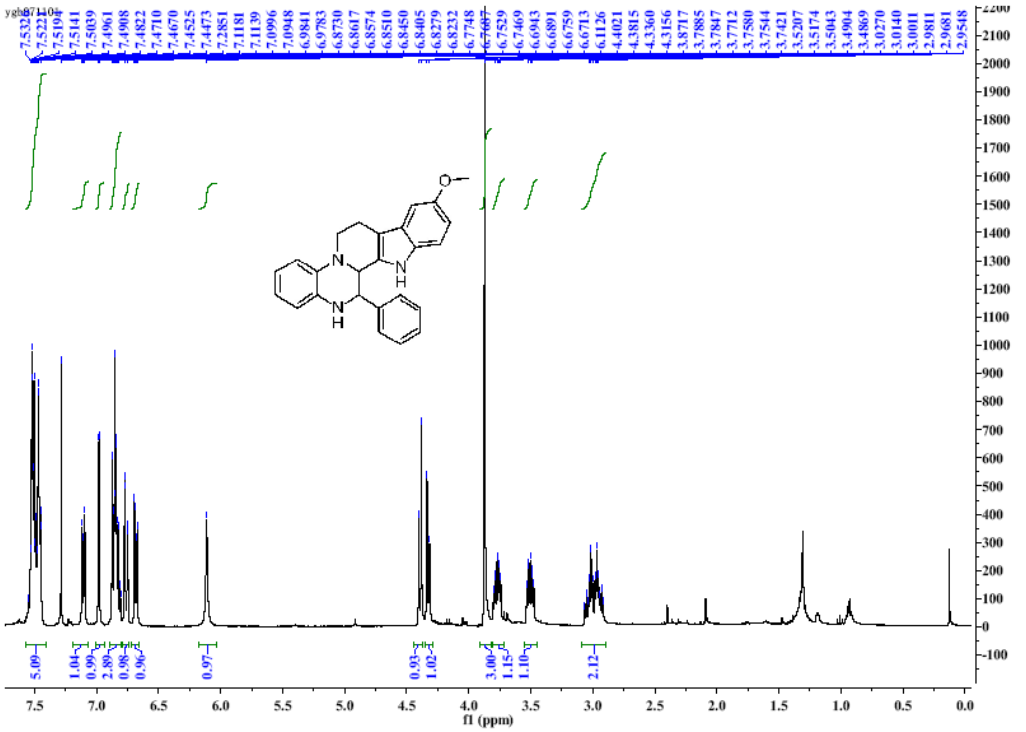
57.93
47.97
21.93
F
N
H
N
H
f1 (ppm)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7.1139
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6.8510
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4.3156
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3.7885
3.7847
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3.7580
3.7544
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3.0011
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0.93
1.02
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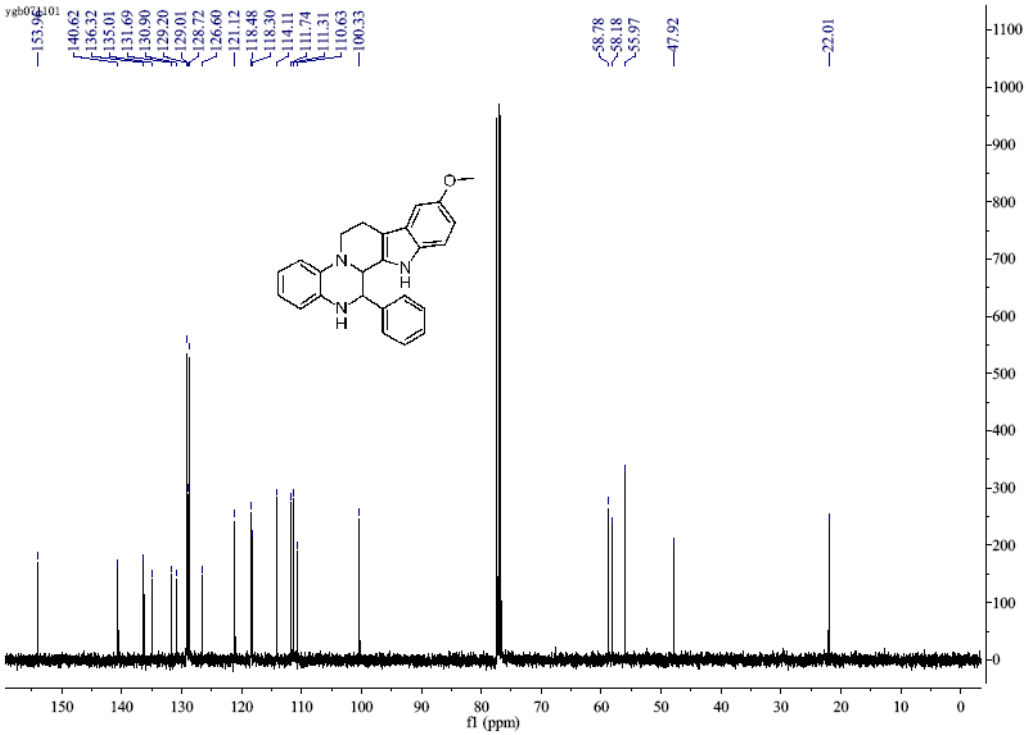
1.15
1.10
2.12
f1 (ppm)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111.31
110.63
100.33
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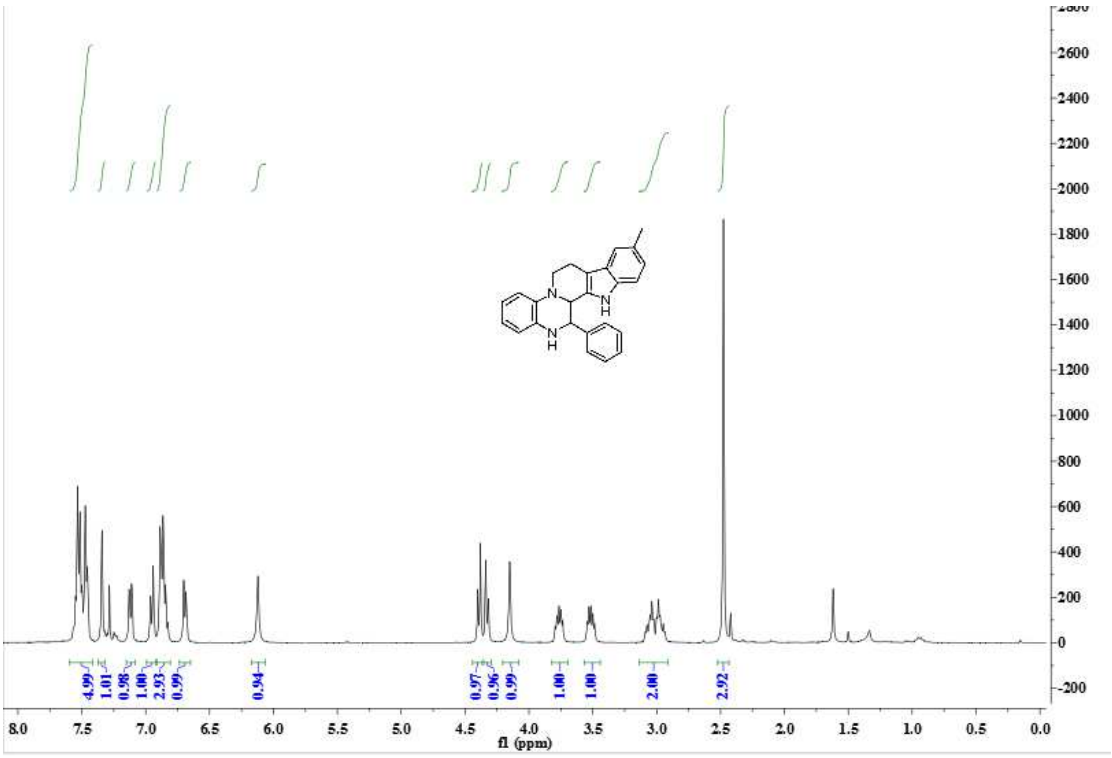
55.97
47.92
22.01
f1 (ppm)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0.96
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1.00
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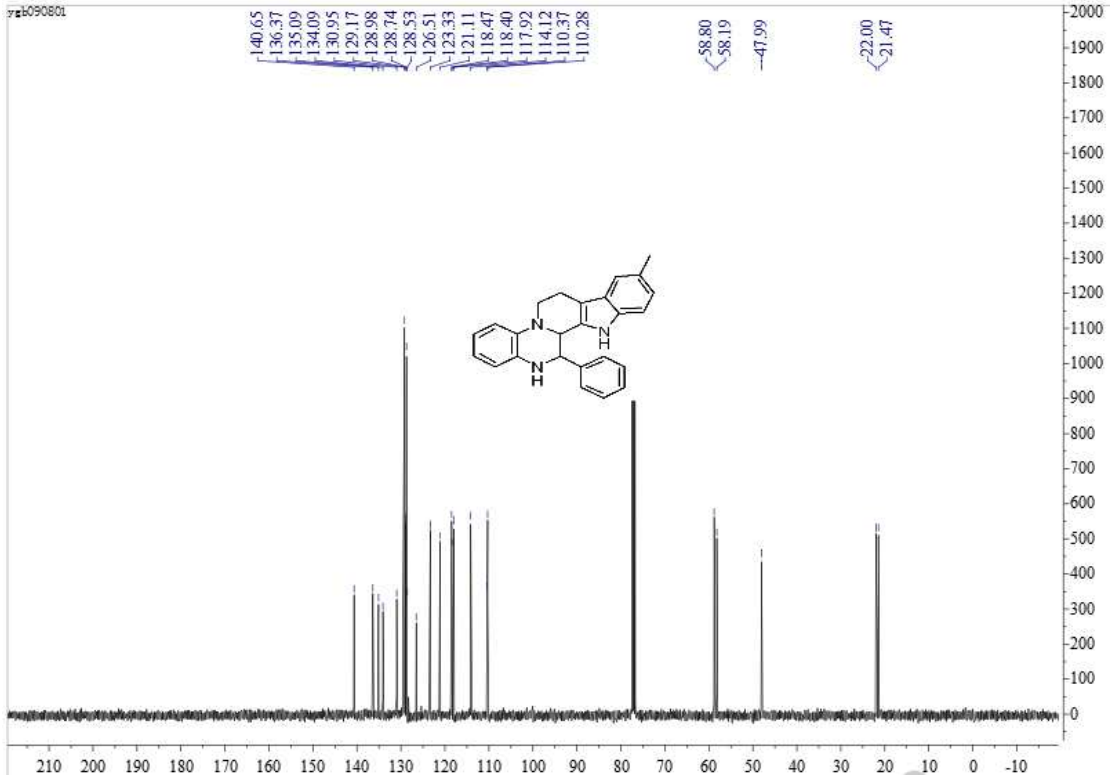
2.92
f1 (ppm)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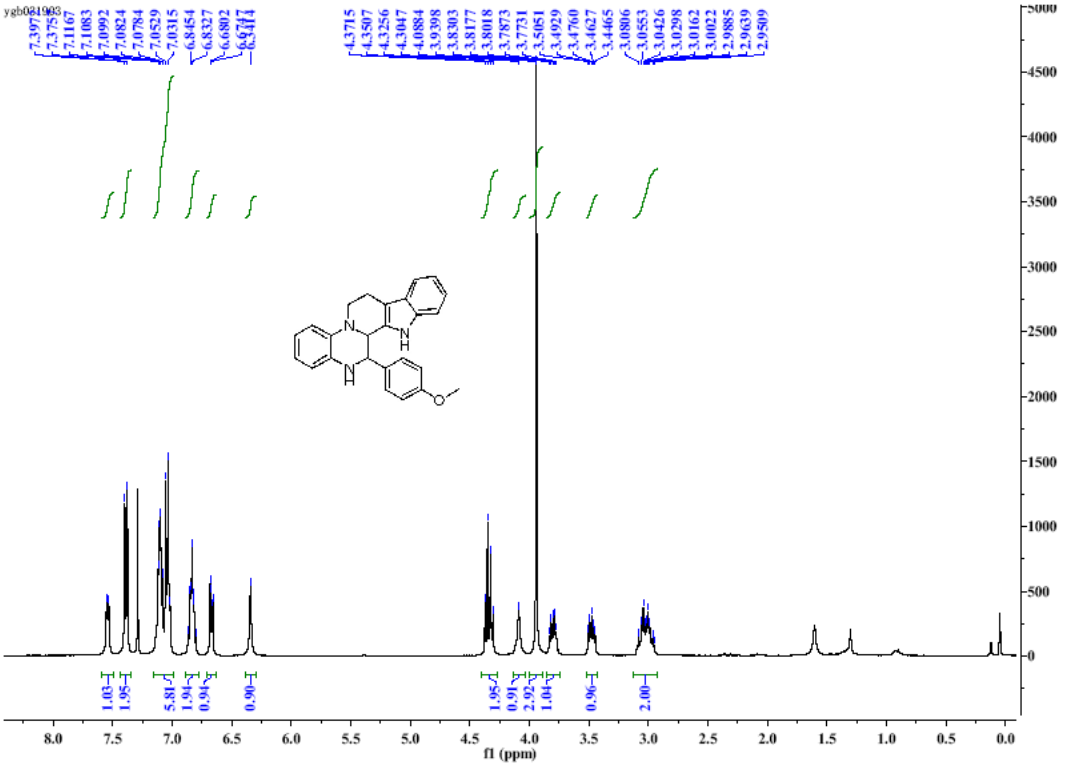
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1.95
0.91
2.92
1.04
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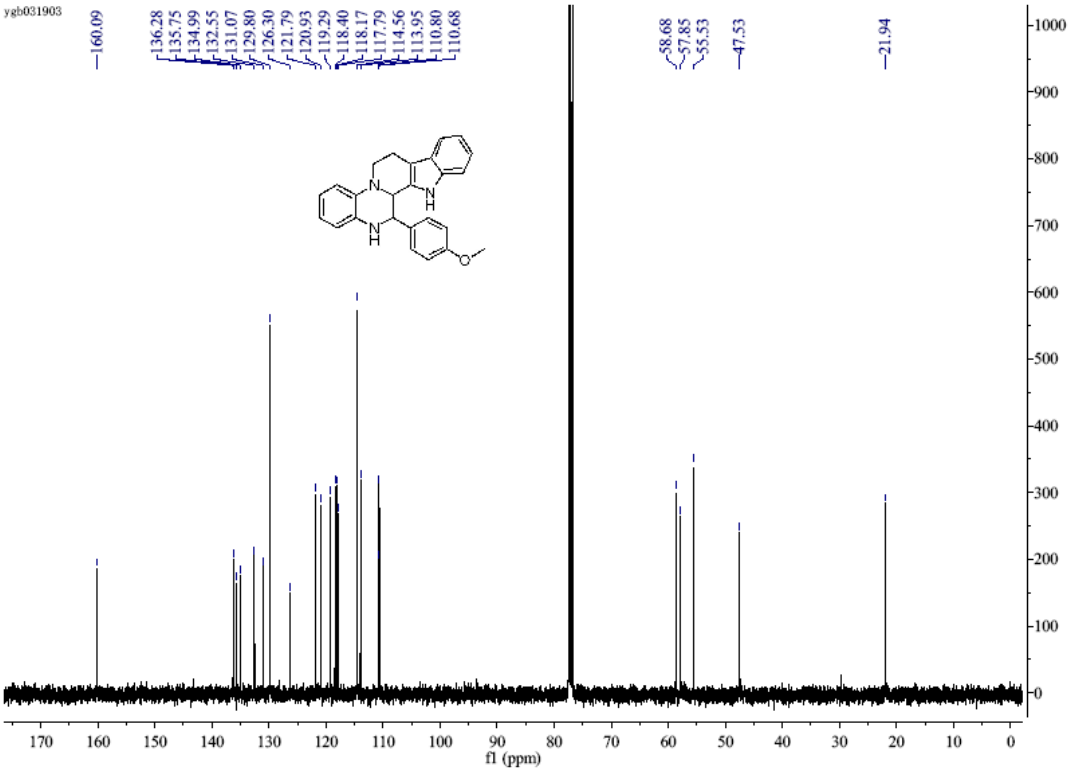
2.00
f1 (ppm)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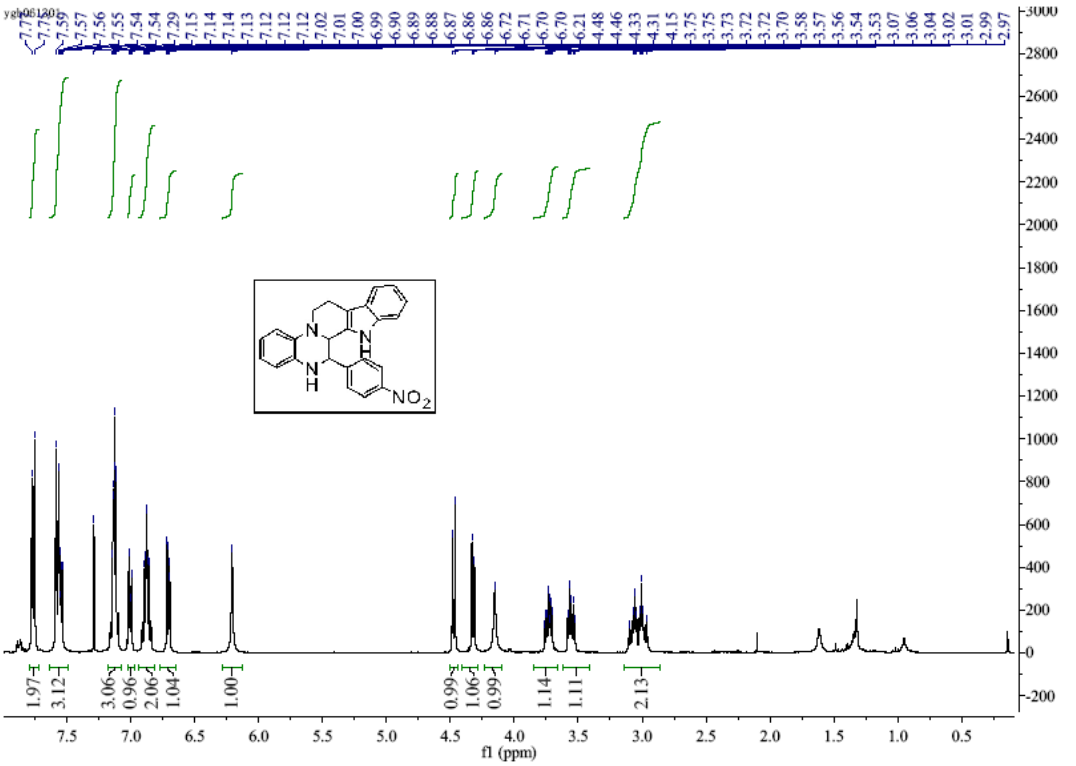
f1 (ppm)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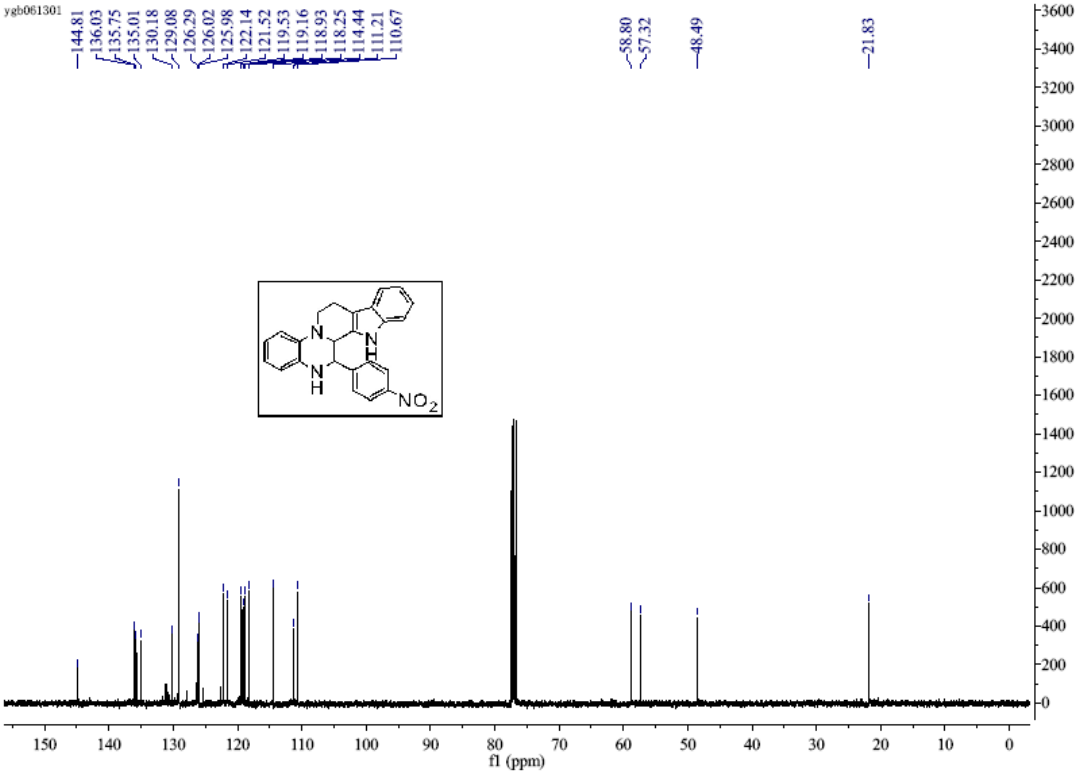
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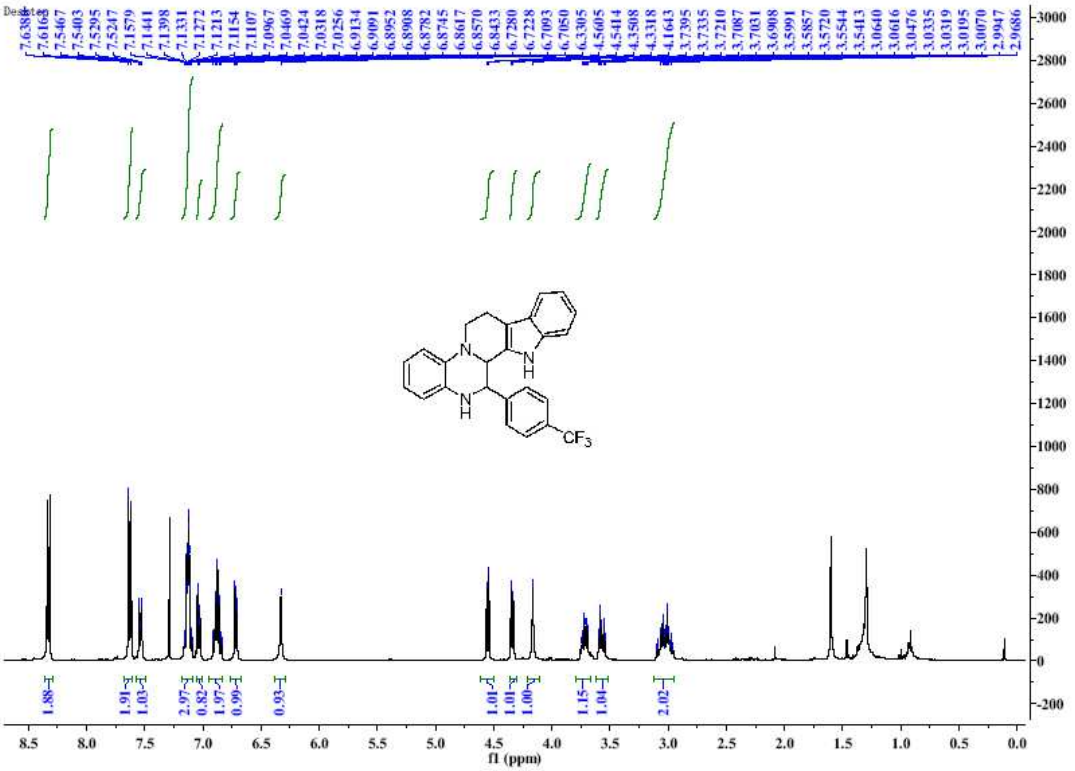
21.83
f1 (ppm)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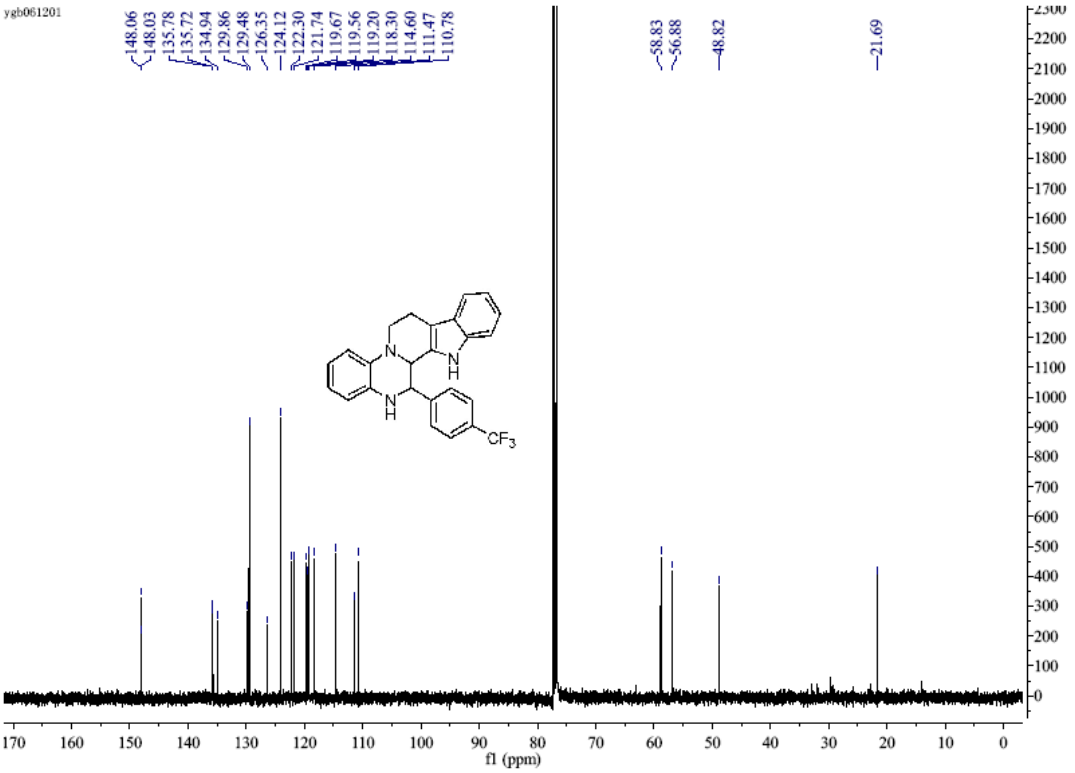
2.02
f1 (ppm)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119.20
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56.88
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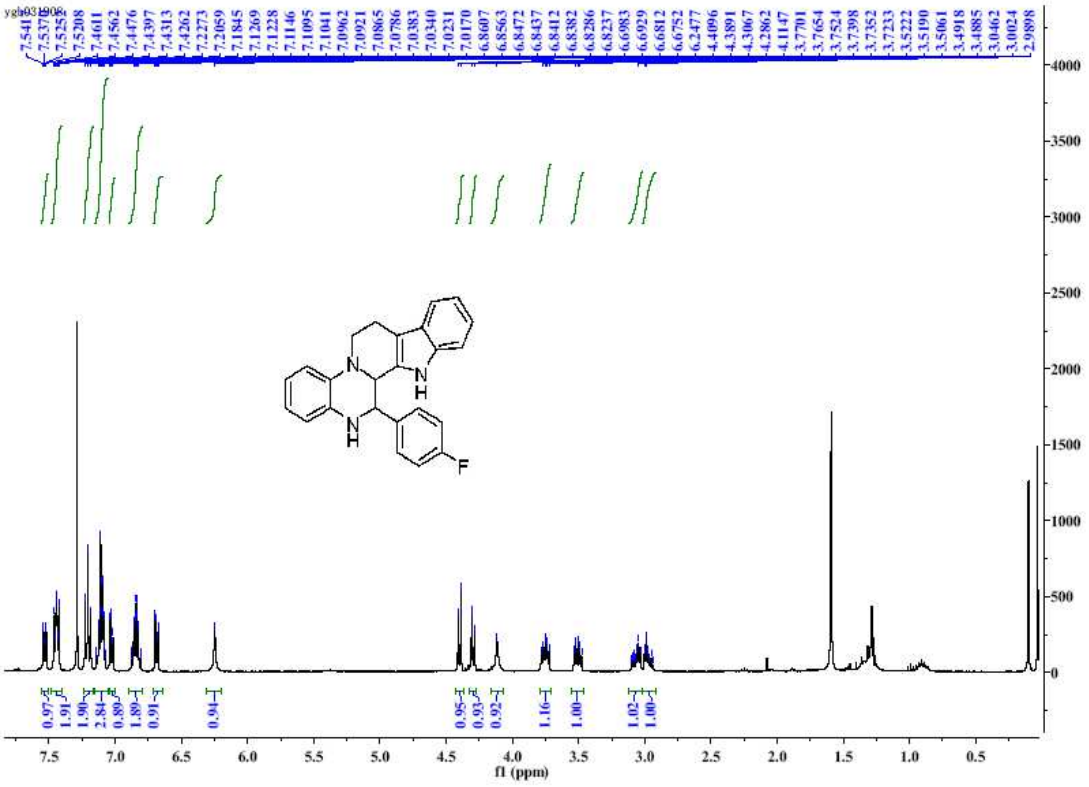
CF3
f1 (ppm)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0.92
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1.00
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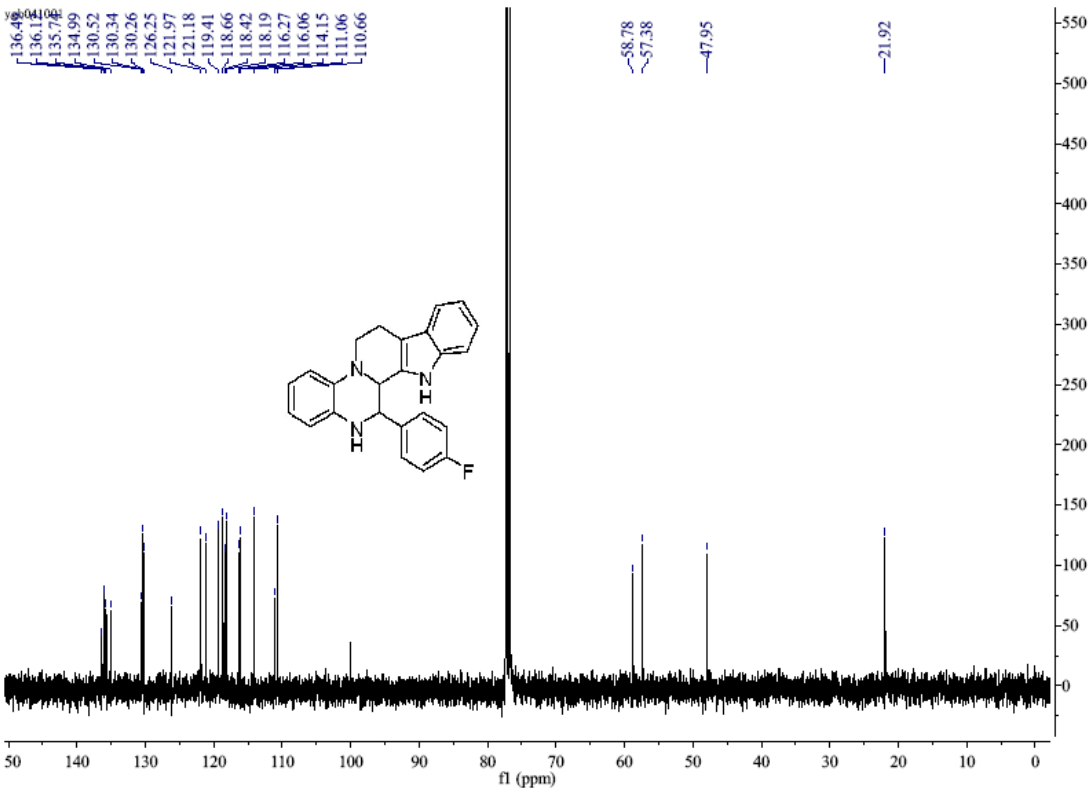
N
H
F
fl (ppm)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116.27
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110.66
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57.38
47.95
21.92
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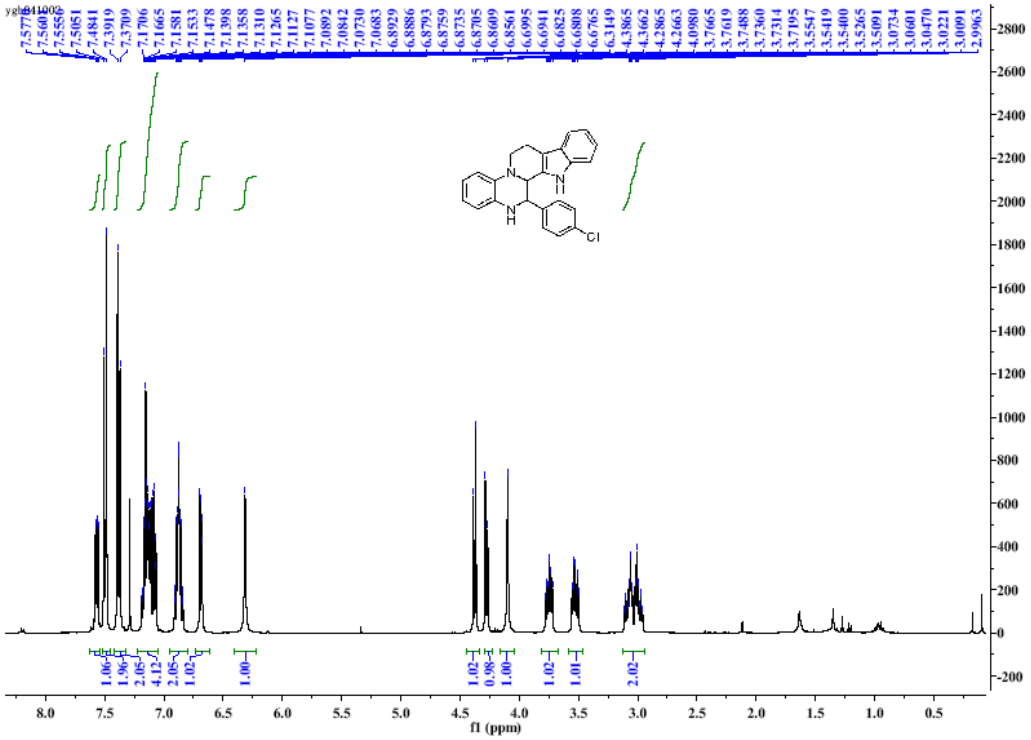
H
N
H
F
fl (ppm)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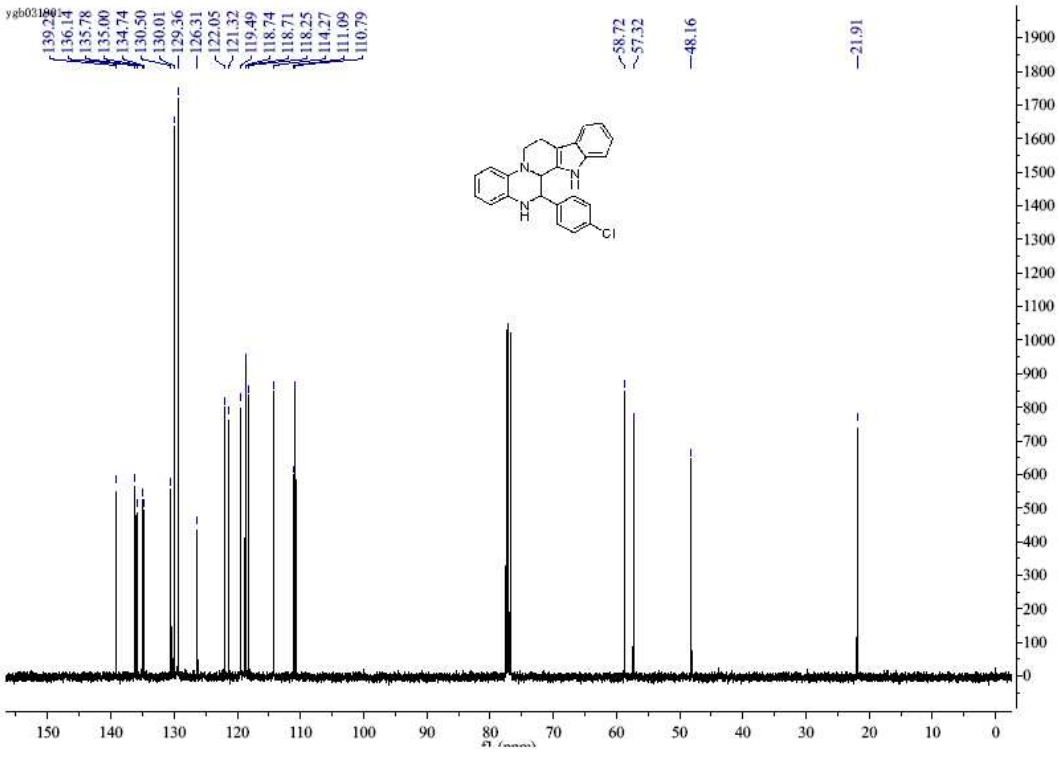
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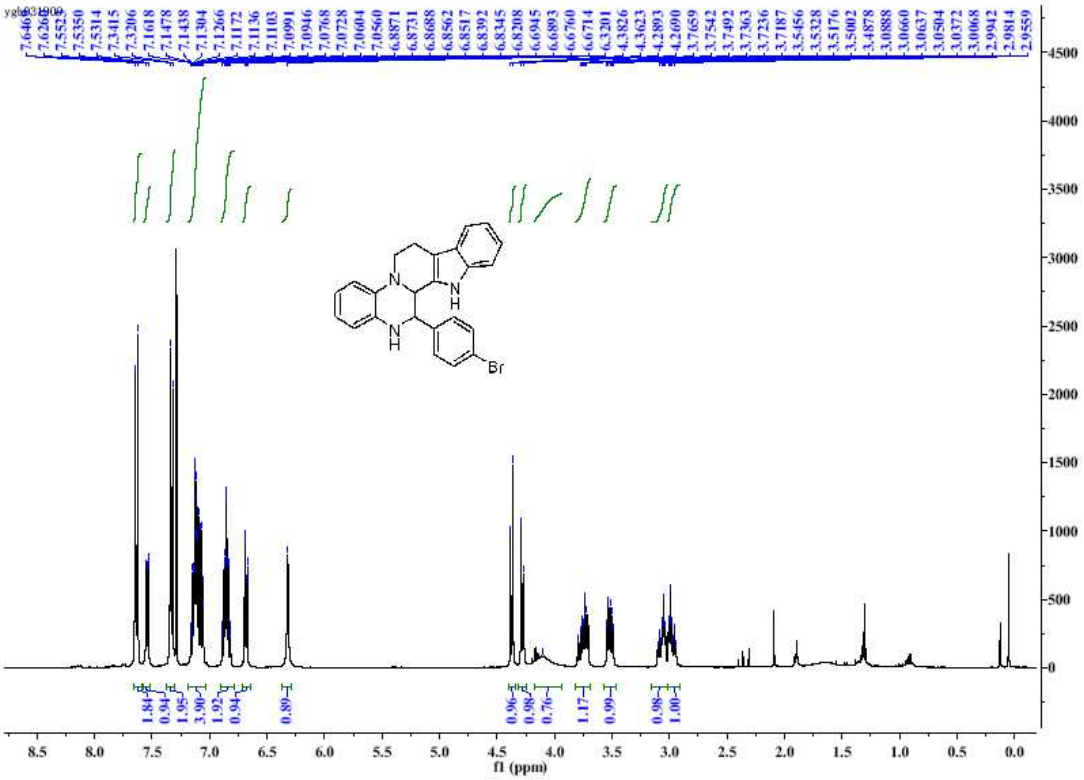
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0.76
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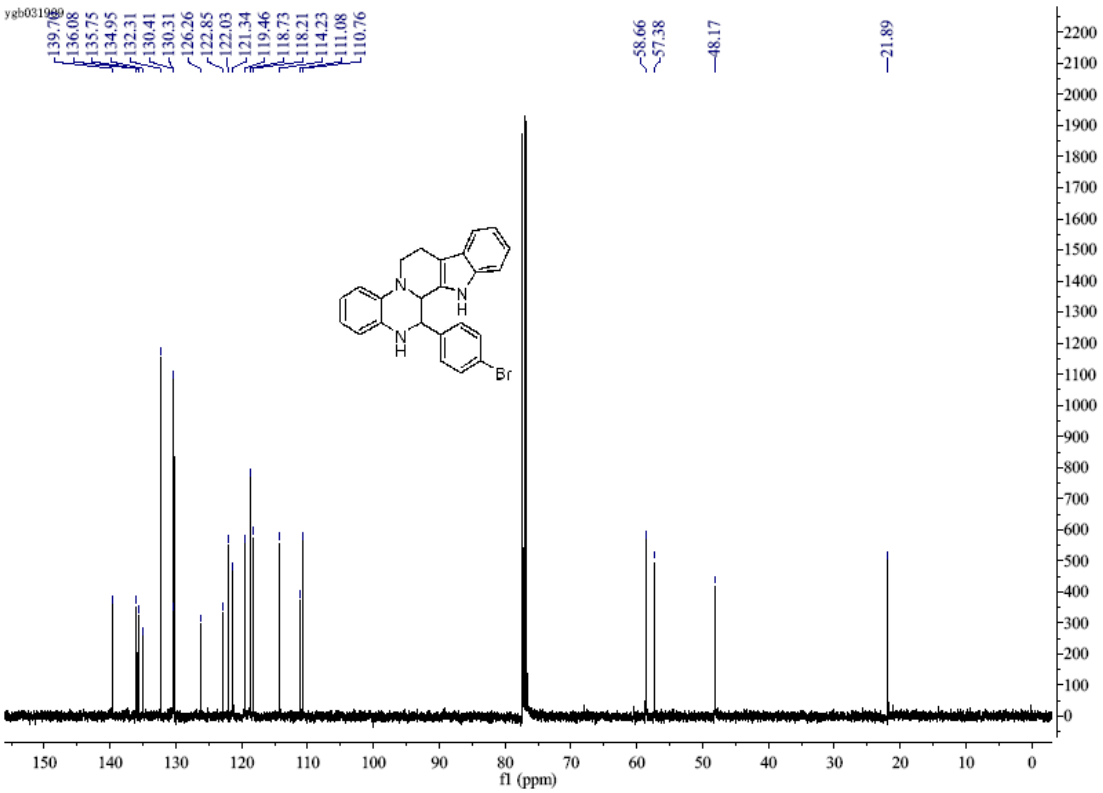
0.98
1.00
f1 (ppm)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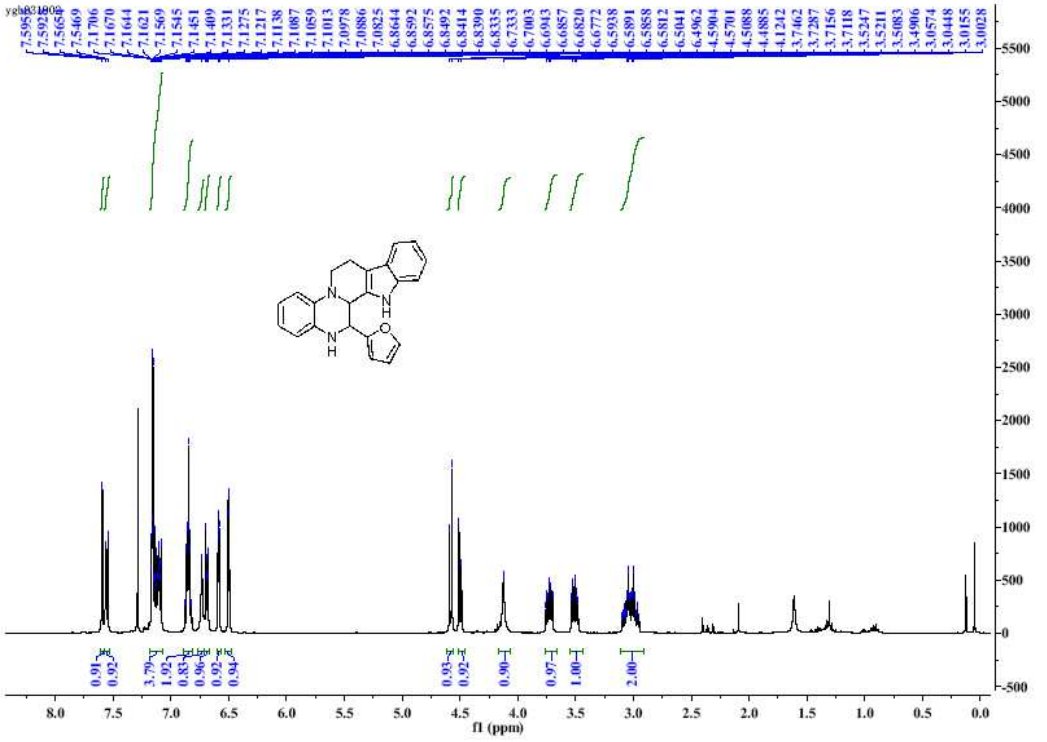
21.89
f1 (ppm)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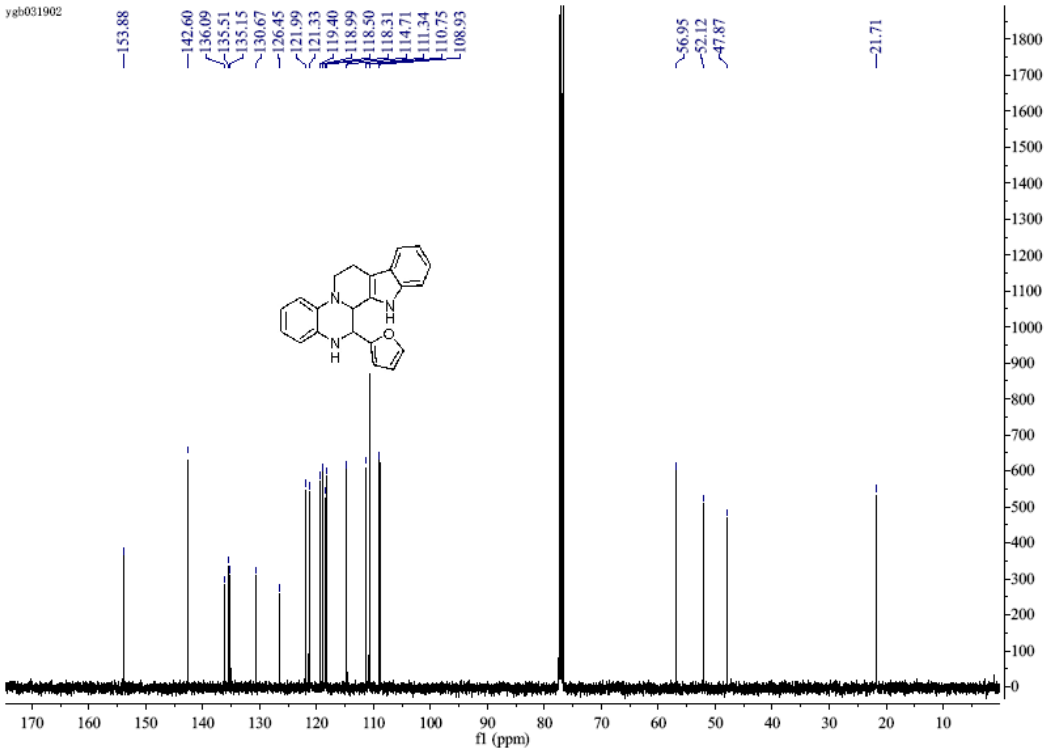
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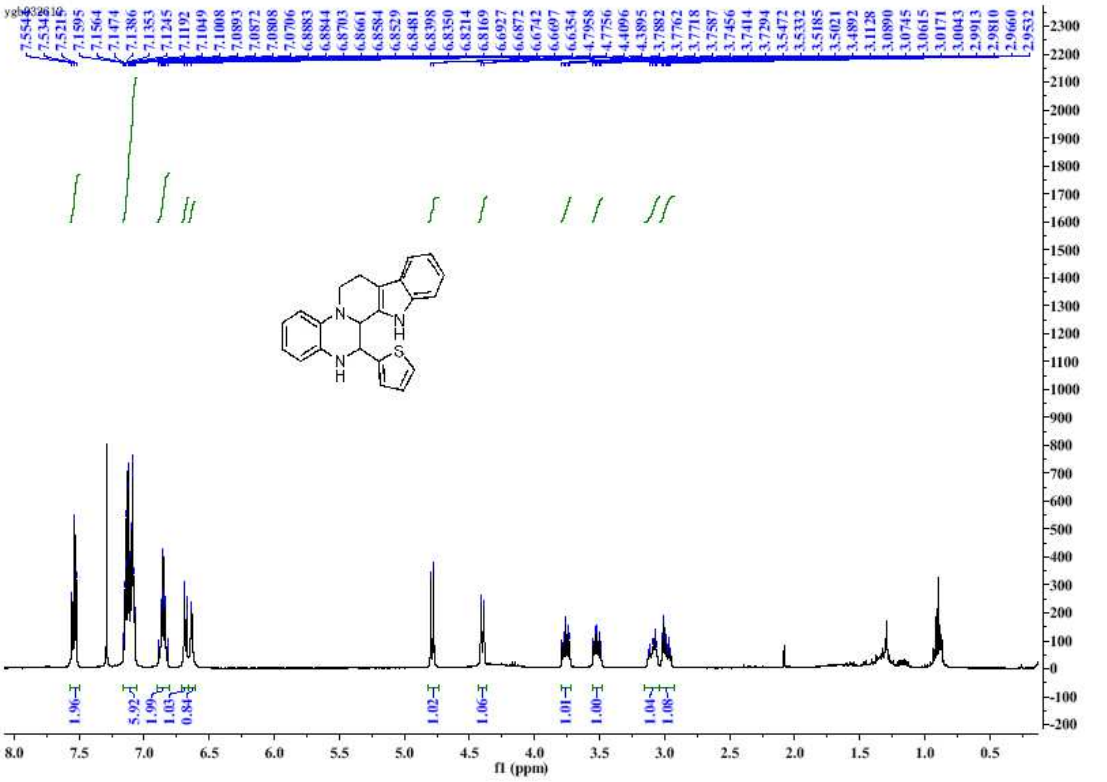
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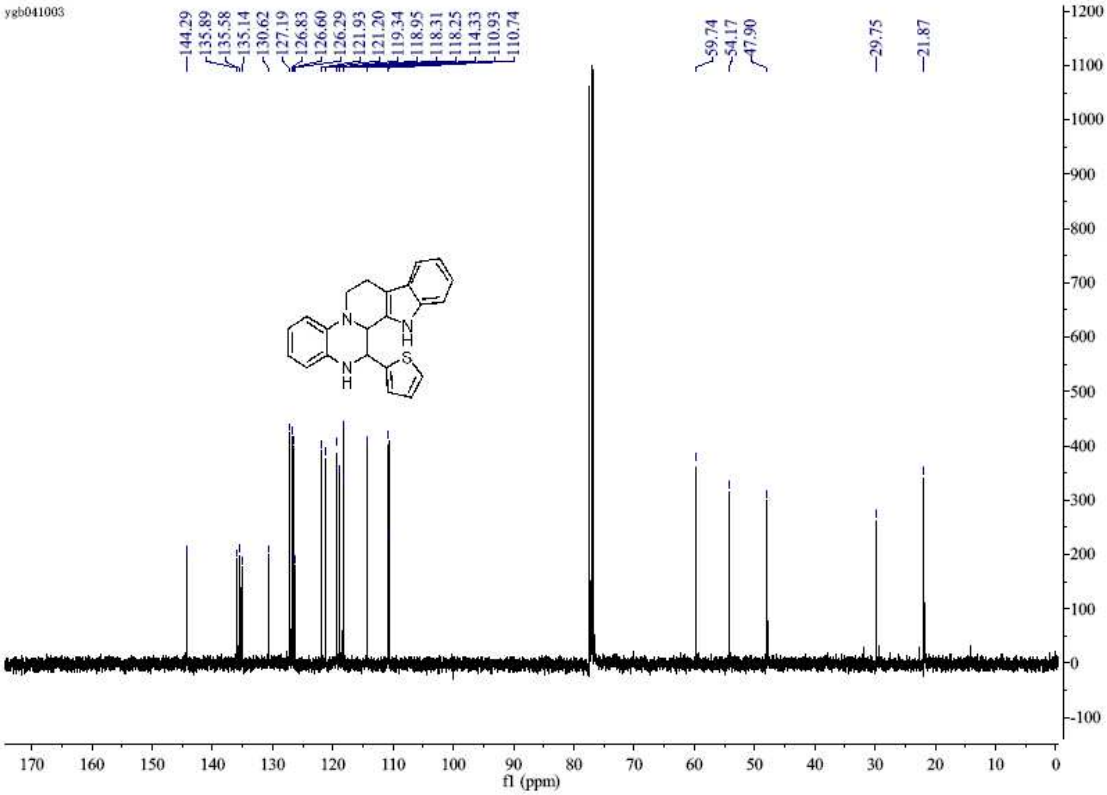
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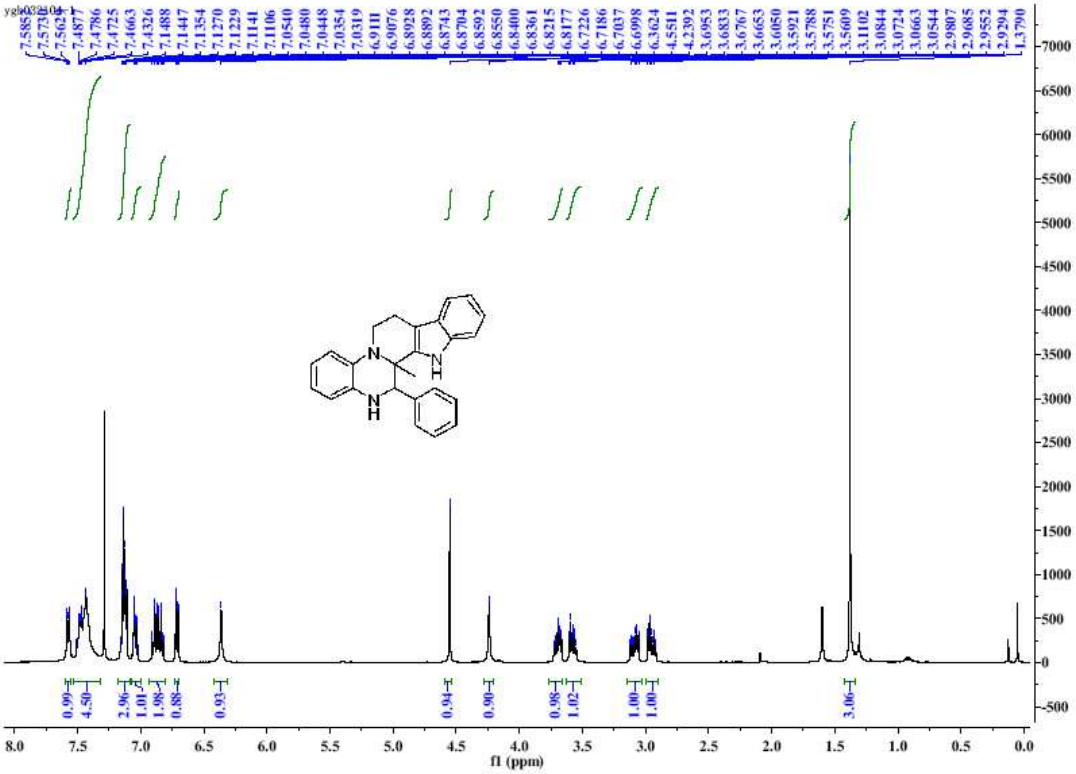
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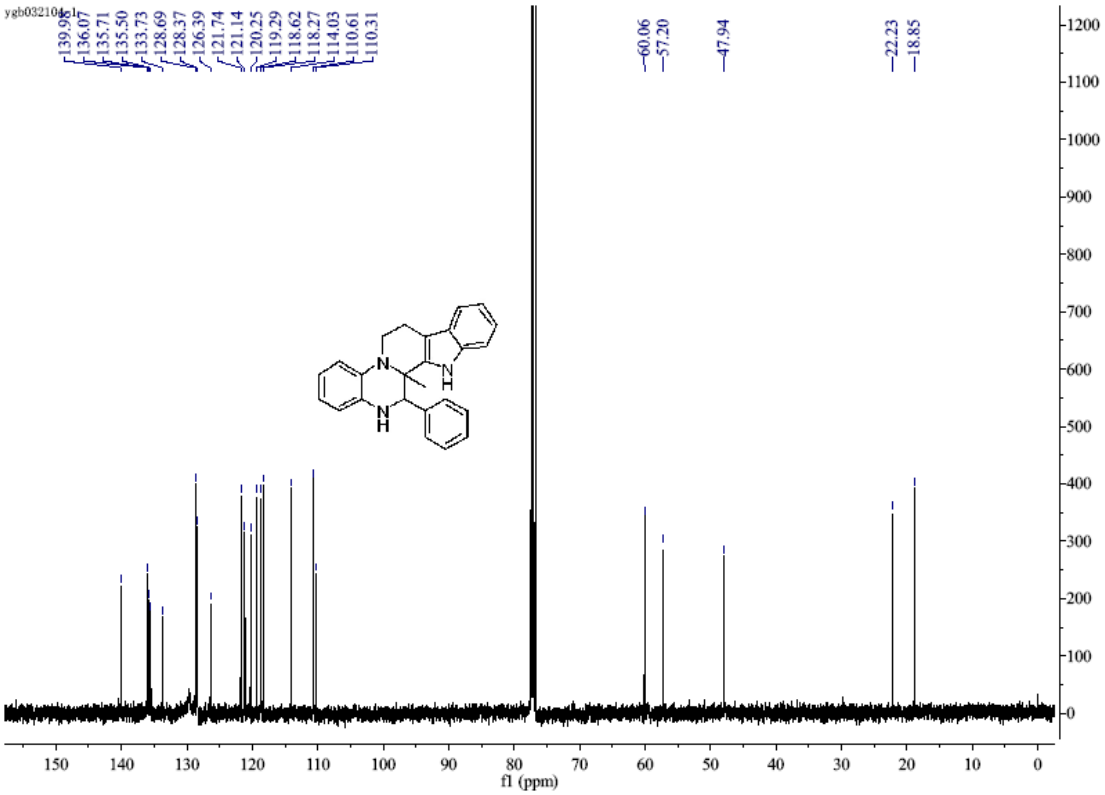
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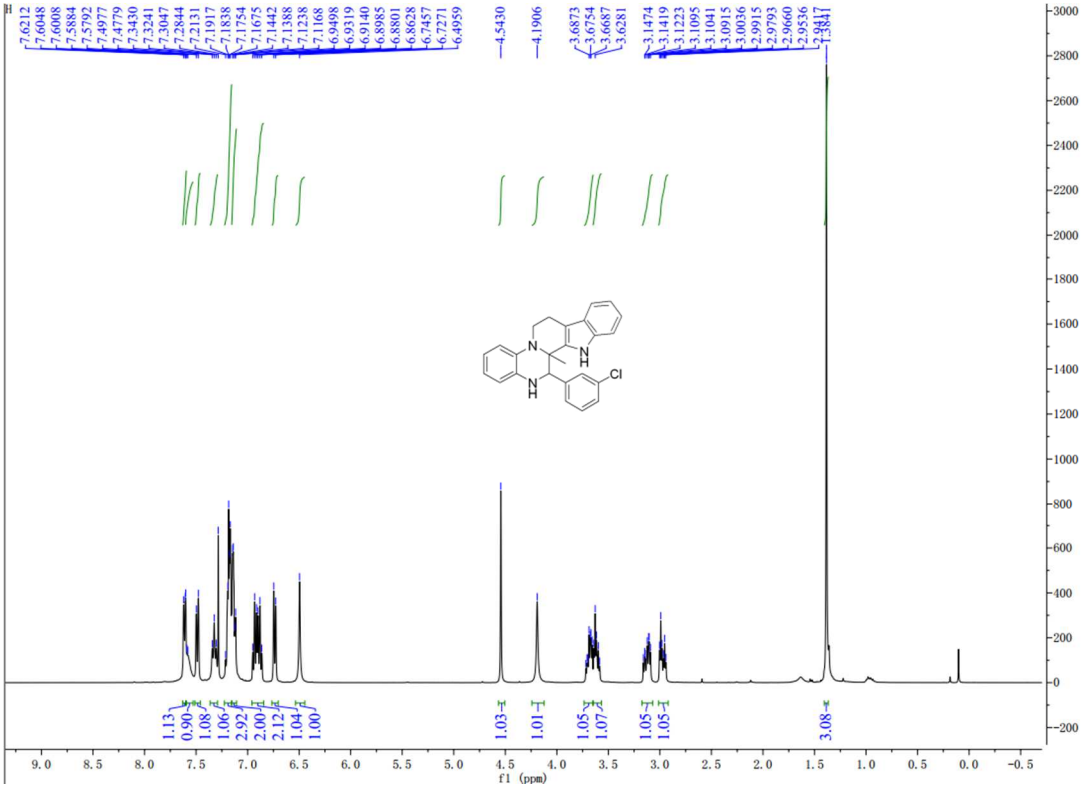
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7.1917
7.1838
7.1754
7.1675
7.1442
7.1388
7.1238
7.1168
6.9498
6.9319
6.9140
6.8985
6.8801
6.8628
6.7457
6.7271
6.4959
4.5430
4.1906
3.6873
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3.6687
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3.1474
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3.1223
3.1095
3.1041
3.0915
3.0036
2.9915
2.9793
2.9660
2.9536
1.5841
1.13
0.90
1.08
1.06
2.92
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2.12
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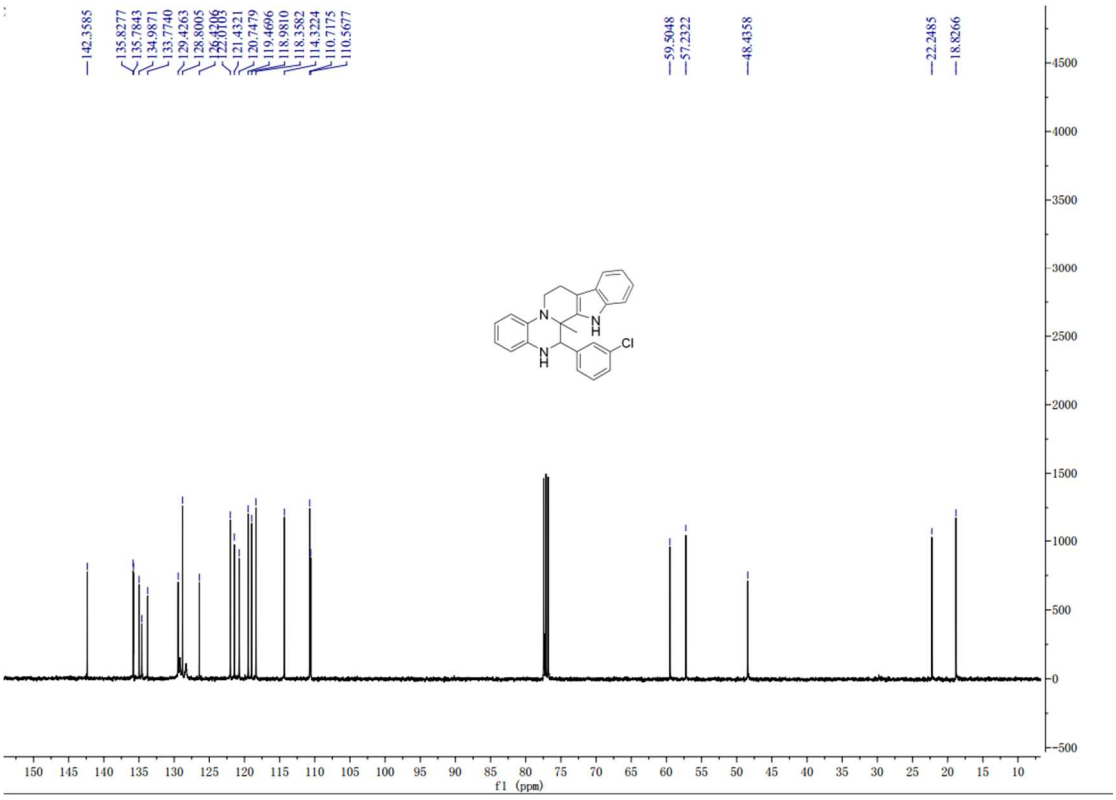
1.00
1.03
1.01
1.05
1.07
1.05
1.05
3.08
f1 (ppm)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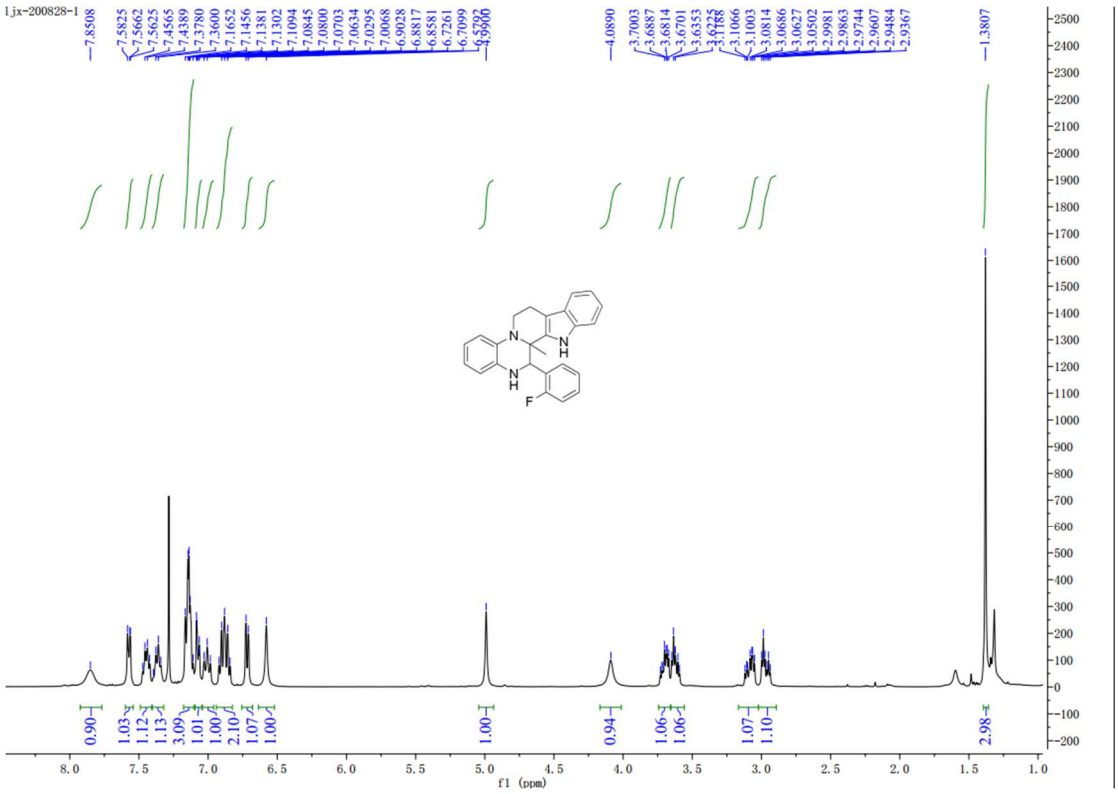
59.5048
57.2322
48.4358
22.2485
18.8266
f1 (ppm)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7.1381
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7.1094
7.0845
7.0800
7.0703
7.0634
7.0295
7.0068
6.9028
6.8817
6.8581
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6.7099
6.5792
4.9900
4.0890
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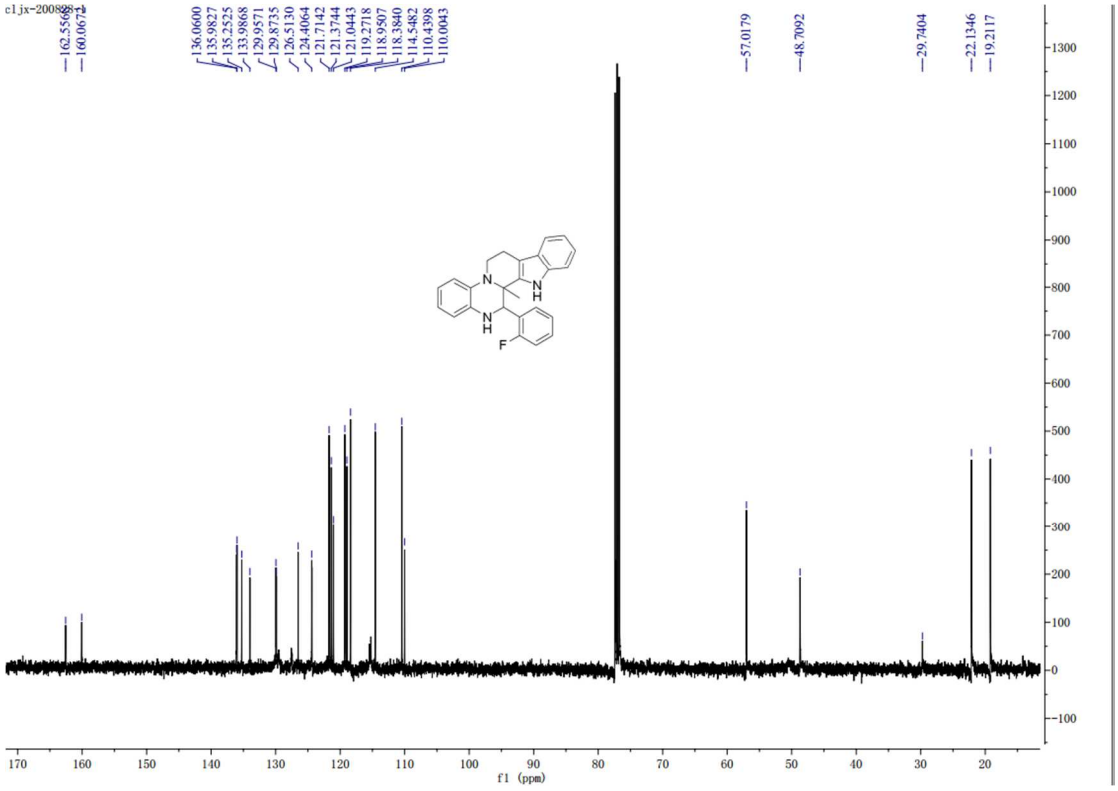
3.6814
3.6701
3.6353
3.6225
3.1188
3.1066
3.1003
3.0814
3.0686
3.0627
3.0502
2.9981
2.9863
2.9744
2.9607
2.9484
2.9367
1.3807
0.90
1.03
1.12
1.13
3.09
1.01
1.00
2.10
1.07
1.00
1.00
0.94
1.06
1.06
1.07
1.10
2.98
f1 (ppm)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124.4064
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29.7404
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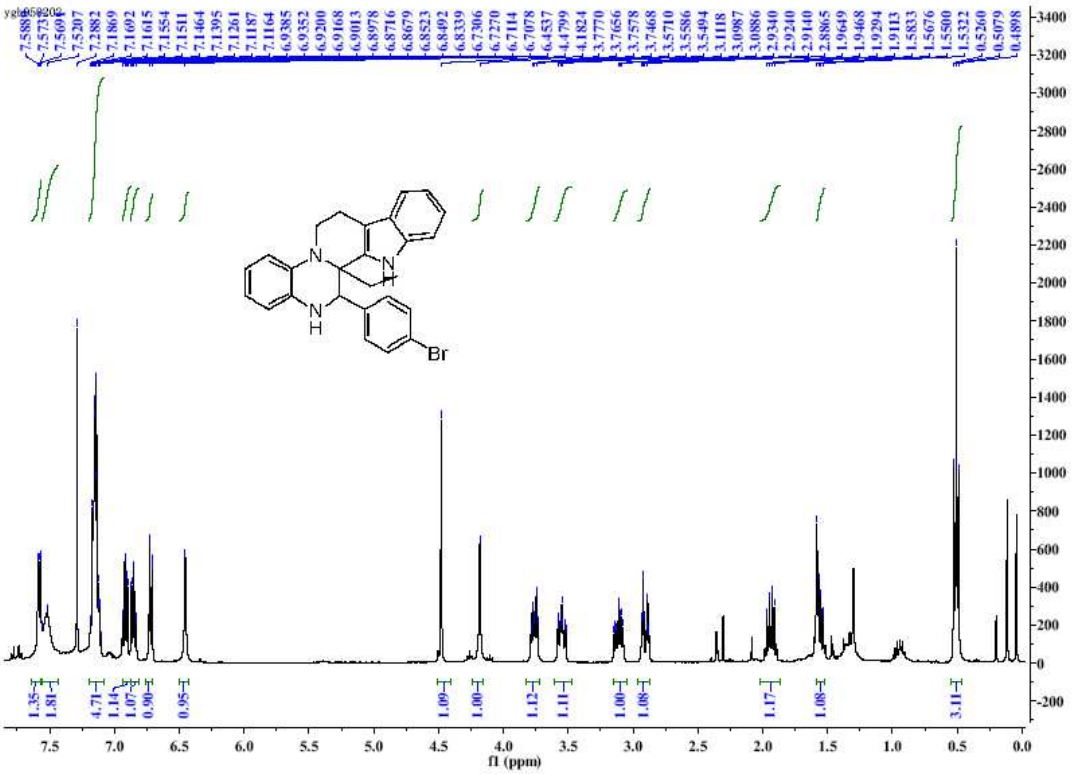
19.2117
f1 (ppm)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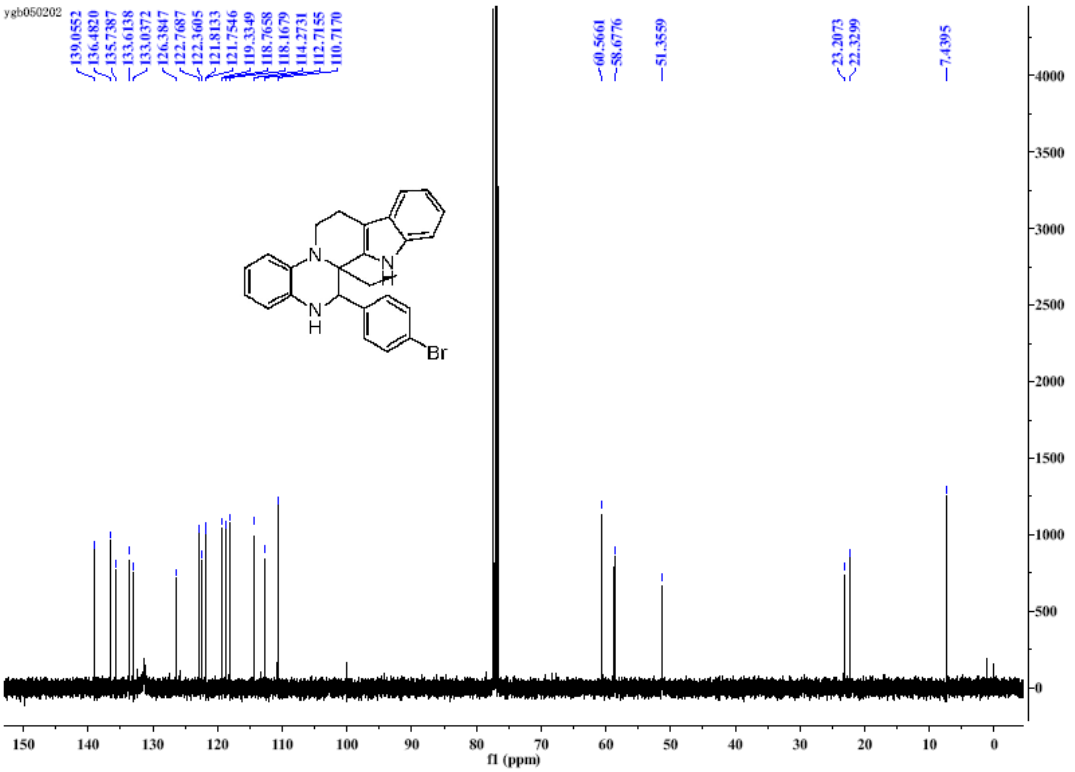
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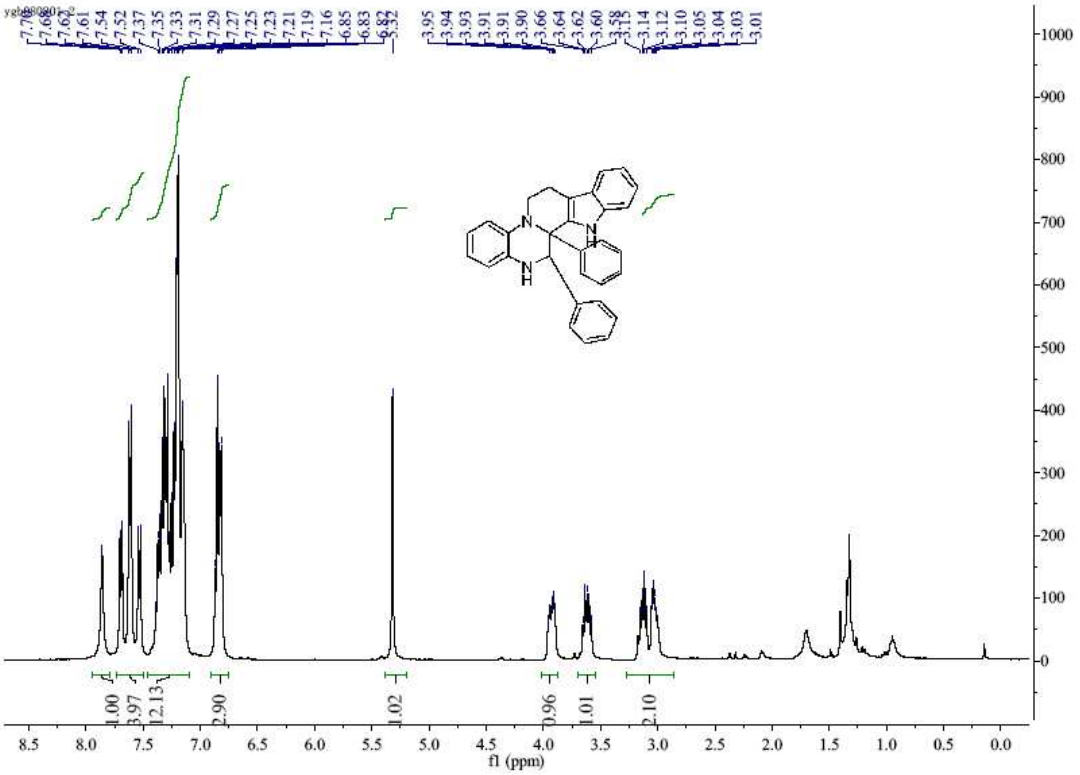
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7.31
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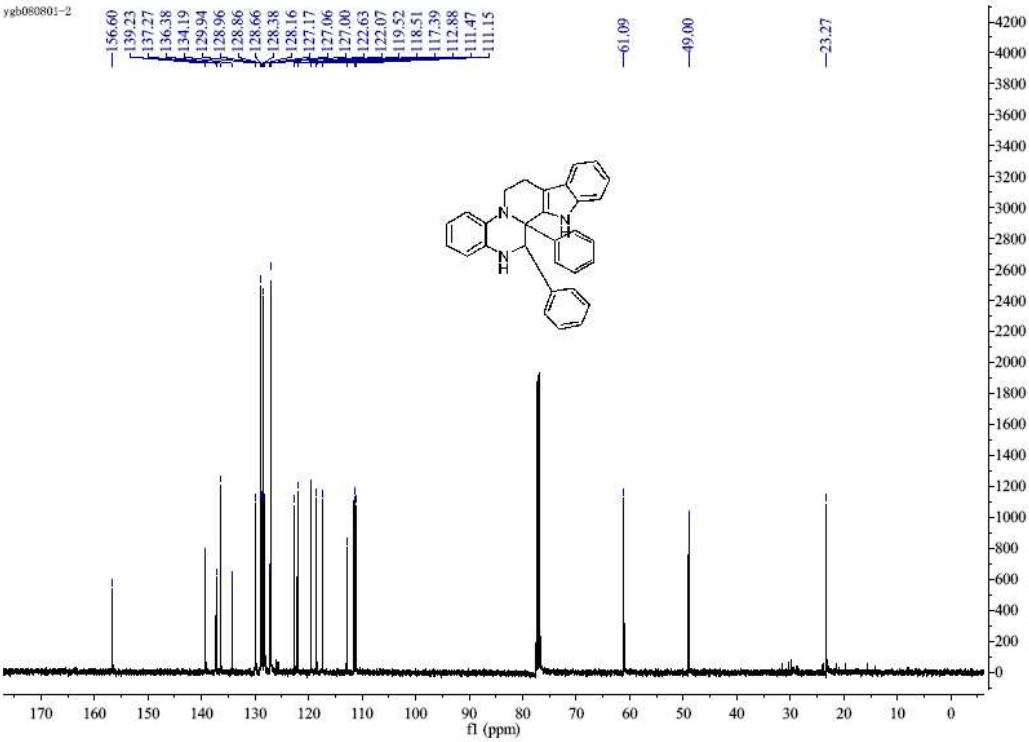
7.27
7.25
7.23
7.21
7.19
7.16
6.85
6.83
6.82
5.32
3.95
3.94
3.93
3.91
3.91
3.90
3.66
3.64
3.62
3.60
3.58
3.15
3.14
3.12
3.10
3.05
3.04
3.03
3.01
1.00
3.97
12.13
2.90
1.02
0.96
1.01
2.10
f1 (ppm)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128.86
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128.38
128.16
127.17
127.06
127.00
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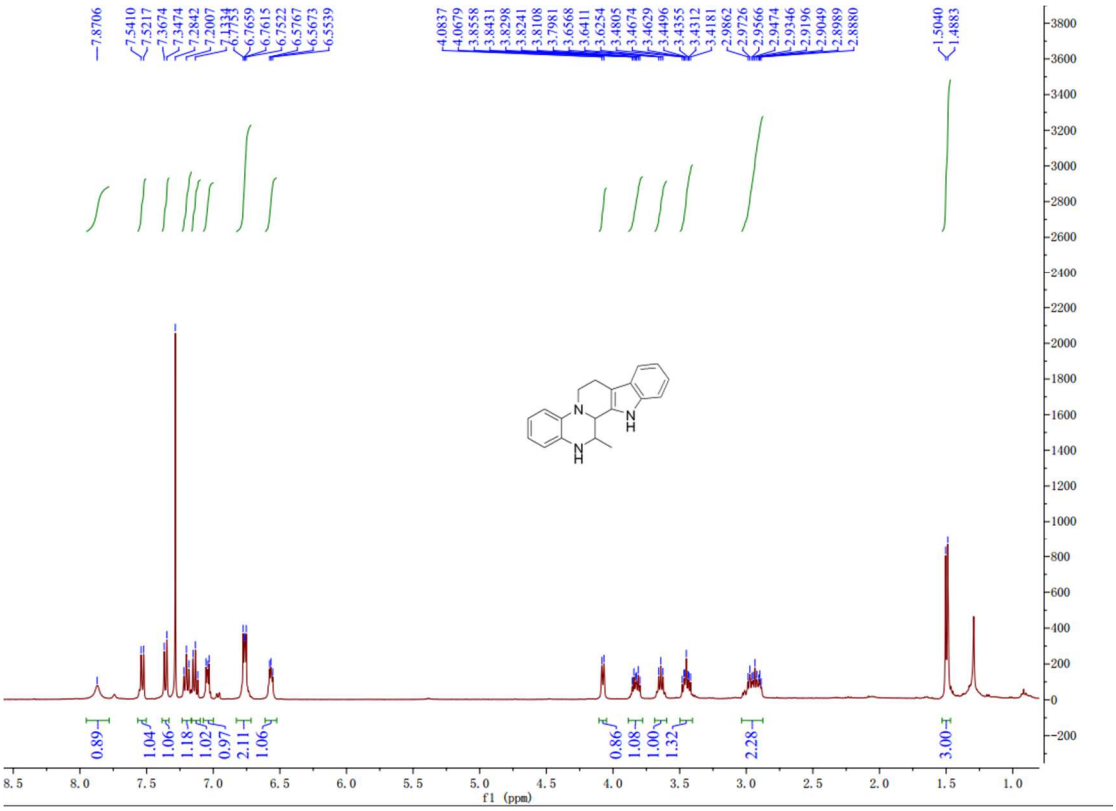
111.47
111.15
61.09
49.00
23.27
f1 (ppm)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6.5673
6.5539
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4.0679
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3.8241
3.8108
3.7981
3.6568
3.6411
3.6254
3.4805
3.4674
3.4629
3.4496
3.4355
3.4312
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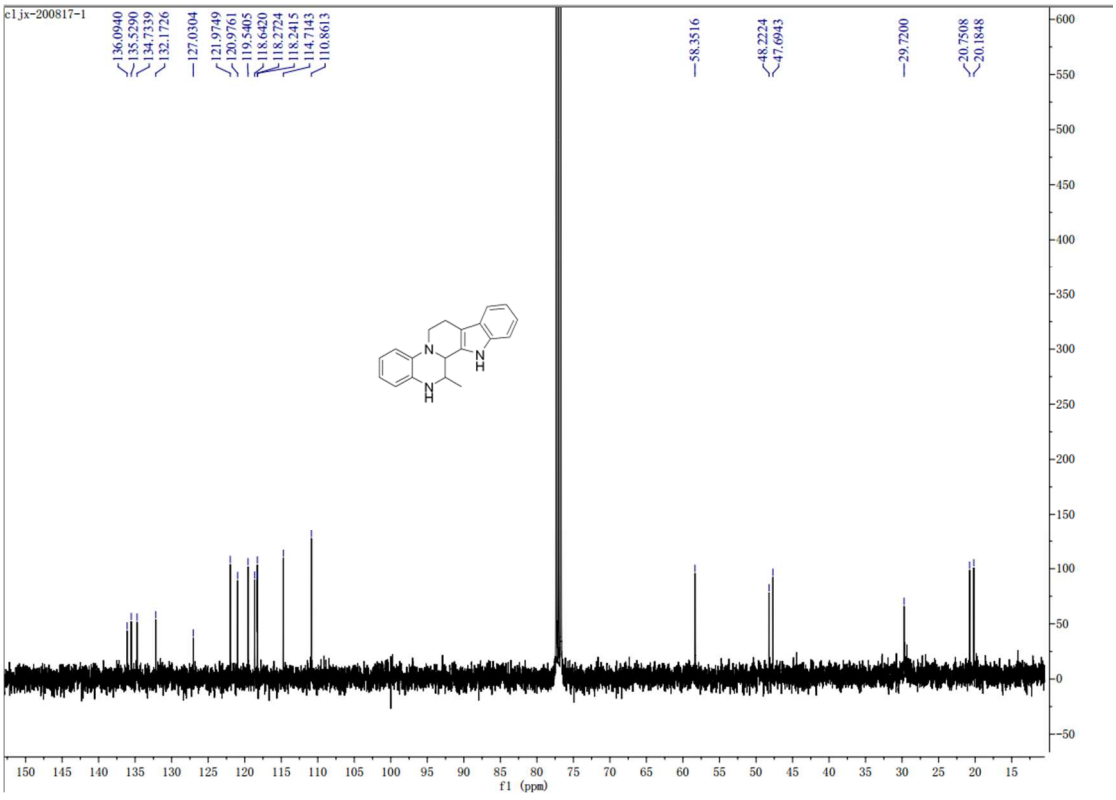
2.9862
2.9726
2.9566
2.9474
2.9346
2.9196
2.9049
2.8989
2.8880
1.5040
1.4883
0.89
1.04
1.06
1.18
1.02
0.97
2.11
1.06
0.86
1.08
1.00
1.32
2.28
3.00
f1 (ppm)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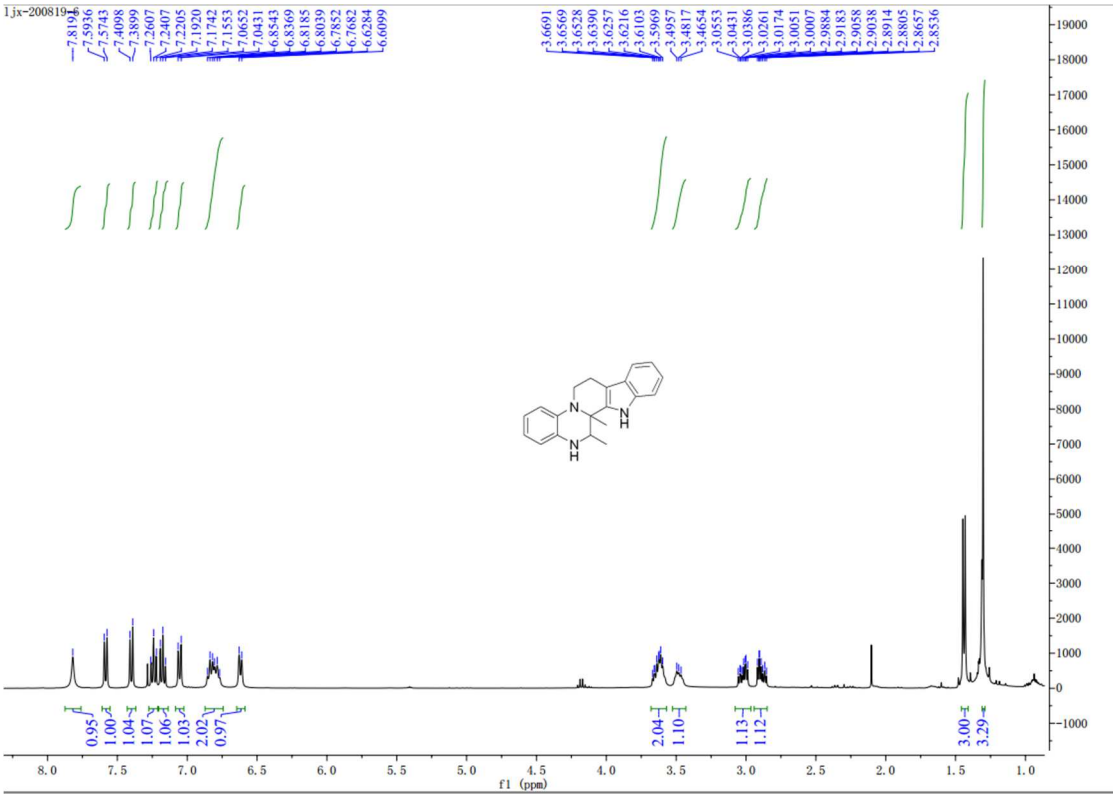
114.7143
110.8613
58.3516
48.2224
47.6943
29.7200
20.7508
20.1848
f1 (ppm)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3.6528
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3.4817
3.4654
3.0553
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3.0174
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3.0007
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2.9058
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2.8805
2.8657
2.8536
0.95
1.00
1.04
1.07
1.06
1.03
2.02
0.97
2.04
1.10
1.13
1.12
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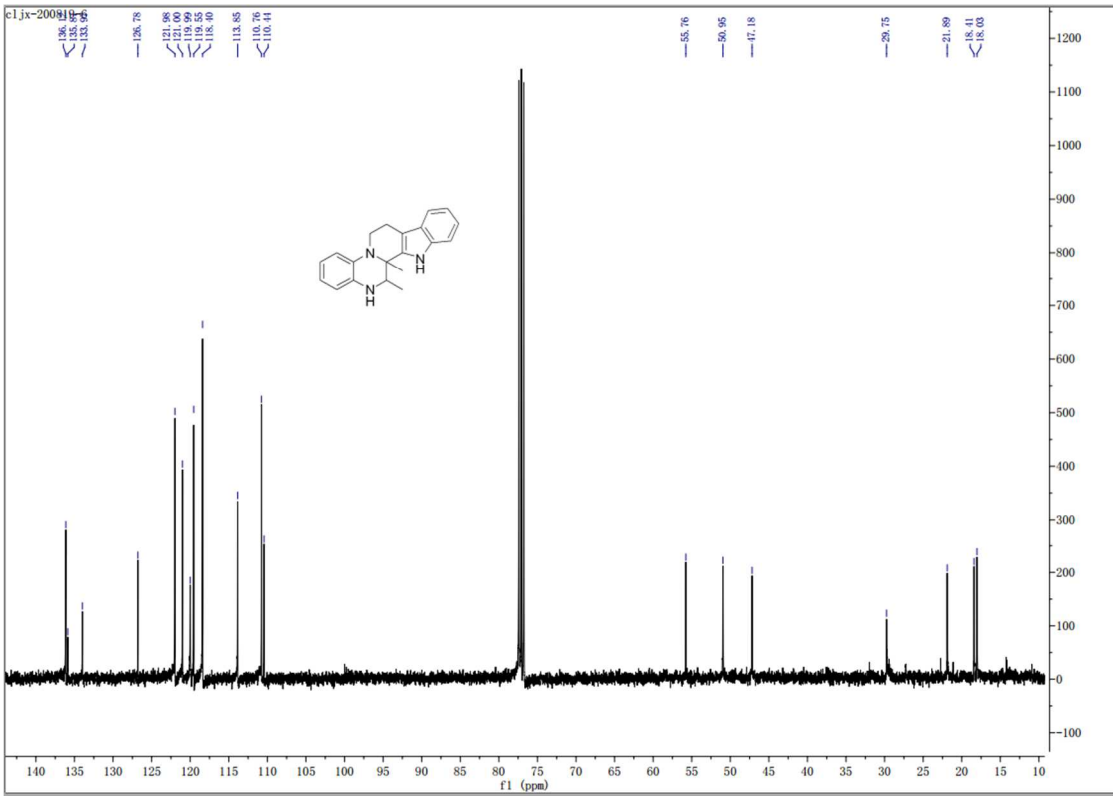
3.29
f1 (ppm)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55.76
50.95
47.18
29.75
21.89
18.41
18.03
f1 (ppm)