Rhodium(III)-Catalyzed Alkylation of Primary C(sp^3)-H Bonds with α-Diazocarbonyl Compounds

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Table of contents:

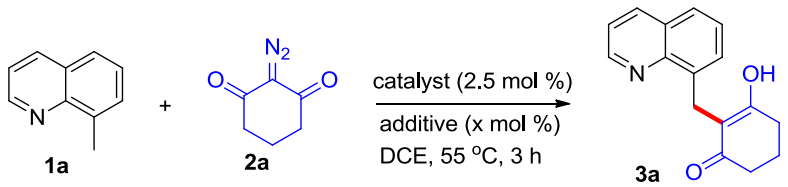
General methods:

All commercially available organic compounds were purchased from Sigma-Aldrich, Shanghai GeorGene Biotech Co., Ltd and adamas-beta in China.^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (125, 100 MHz) spectra were determined with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm from internal TMS (δ). All coupling constants (J values) were reported in hertz (Hz). High-resolution mass spectra were recorded using the ESI method. Reactions were monitored by thin-layer chromatography or LC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh).

Materials:

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. $[Cp^*RhCl_2]_2$,[S1] $[Cp^*Rh(MeCN)_3][SbF_6]_2$,[S2] 8-methyl-quinolines substrates,[S3] α-diazocarbonyl compounds[S4] were prepared according to the previously reported synthetic methods.

Table S1. Optimization of Rh(III)-catalyzed coupling of **1a** with **2a** [a]



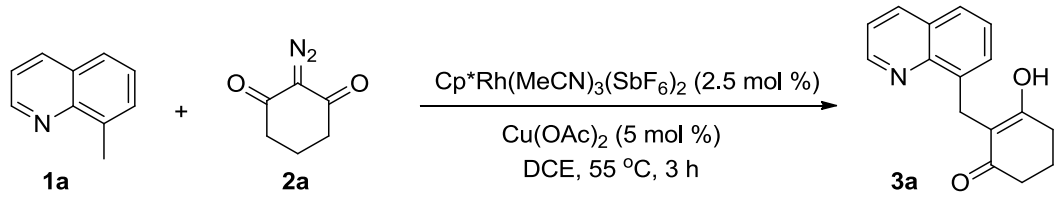
entry	catalyst (2.5 mol %)	additive (x mol %)	yield (%)
1	$(Cp^*RhCl_2)_2$	-	0
2	$(Cp^*RhCl_2)_2/AgSbF_6$	-	50
3	$Cp^*Rh(MeCN)_3(SbF_6)_2$	-	65
4	$Cp^*Rh(MeCN)_3(SbF_6)_2$	CsOAc (50 mol %)	60
5	$Cp^*Rh(MeCN)_3(SbF_6)_2$	AcOH (100 mol %)	95
6	$Cp^*Rh(MeCN)_3(SbF_6)_2$	$CuCl_2$ (5 mol %)	30

7	$Cp^*Rh(MeCN)_3(SbF_6)_2$	$Cu(OAc)_2$ (5 mol %)	99
8	-	$Cu(OAc)_2$ (5 mol %)	0

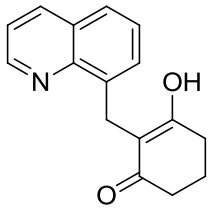
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2.5 mol%), additive (x mol %), DCE (1.0 mL), 55 ^oC, 3 h. Yields of isolated products.

Experimental Procedures and Characterizations:

a) General procedure for the synthesis of **3** (taking **3a** as an example):

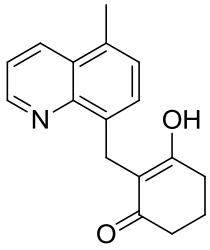


$Cp^*Rh(MeCN)_3(SbF_6)_2$ (2.5 mol %), $Cu(OAc)_2$ (5 mol %), 8-methylquinoline **1a** (0.2 mmol), diazo compound **2a** (0.3 mmol, 1.5 equiv) and DCE (2 mL, 0.1 M) were added to a test tube. The reaction mixture was stirred at 55 ^oC for 3 h. The solution was filtered through a celite pad and washed with dichloromethane. Then, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the title compound **3a**.

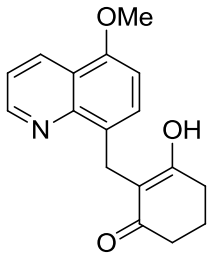


The title compound **3a** was isolated (PE:EA = 5:1) as a light brown solid, yield: 99%; ^1H NMR (400 MHz, $CDCl_3$) δ 13.95 (s, 1H), 8.84 (dd, J = 4.4, 1.6 Hz, 1H), 8.26 (dd, J = 8.4, 1.6 Hz, 1H), 8.07 (dd, J = 7.2, 1.2 Hz, 1H), 7.70 (dd, J = 8.0, 1.2 Hz, 1H), 7.52 (dd, J = 8.0, 7.2 Hz, 1H), 7.48 (dd, J = 8.4, 4.4 Hz, 1H), 4.08 (s, 2H), 2.42 (t, J = 6.0 Hz, 2H), 2.29 (t, J = 6.0 Hz, 2H), 1.90 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 174.3, 147.5, 145.0, 138.9, 138.4, 132.4, 128.7, 127.6, 125.9, 120.8, 114.7, 36.9, 29.9, 25.3, 20.7; HRMS (ESI): Calcd for $C_{16}H_{16}NO_2$ $[M+H]^+$ 254.1176,

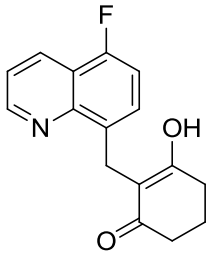
Found: 254.1171.



The title compound **3b** was isolated (PE:EA = 5:1) as a light brown solid, yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.04 (s, 1H), 8.83 (dd, J = 4.4, 1.6 Hz, 1H), 8.43 (dd, J = 8.4, 1.6 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.51 (dd, J = 8.4, 4.4 Hz, 1H), 7.35 (dd, J = 7.2, 0.8 Hz, 1H), 4.04 (s, 2H), 2.64 (s, 3H), 2.40 (t, J = 5.6 Hz, 2H), 2.28 (t, J = 5.6 Hz, 2H), 1.90 (p, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 174.3, 146.9, 145.2, 136.8, 134.8, 132.6, 132.0, 128.0, 120.4, 114.9, 36.9, 29.9, 25.2, 20.7, 18.4; HRMS (ESI): Calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$ 268.1332, Found: 268.1327.

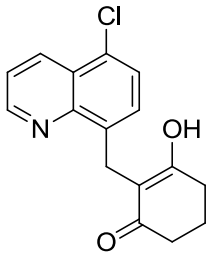


The title compound **3c** was isolated (PE:EA = 5:1) as a light brown solid, yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.95 (s, 1H), 8.82 (dd, J = 4.4, 1.6 Hz, 1H), 8.68 (dd, J = 8.4, 1.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.45 (dd, J = 8.4, 4.4 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.97 (s, 5H), 2.41 (t, J = 6.0 Hz, 2H), 2.28 (t, J = 6.0 Hz, 2H), 1.90 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 174.2, 153.5, 147.7, 145.3, 133.2, 132.1, 130.5, 121.3, 119.8, 115.2, 105.0, 55.8, 36.9, 29.9, 24.7, 20.7; HRMS (ESI): Calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$ 284.1281, Found: 284.1275.

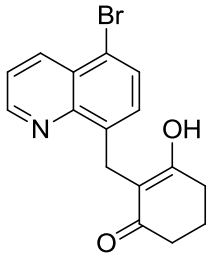


The title compound **3d** was isolated (PE:EA = 5:1) as a light brown solid, yield: 95%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.33 (s, 1H), 8.89 (dd, J = 4.4, 1.2 Hz, 1H), 8.79 – 8.33 (m, 1H), 8.00 (dd, J = 8.0, 6.4 Hz, 1H), 7.55 (dd, J = 8.4, 4.4 Hz, 1H), 7.24 – 7.12 (m, 1H), 4.02 (s, 2H), 2.42 (t, J = 6.0 Hz, 2H), 2.28 (t, J = 6.4 Hz, 2H), 1.90 (p, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 174.0, 156.1 (d, J = 253.7 Hz), 148.5, 145.1 (d, J = 2.8 Hz) , 134.7 (d, J = 4.6 Hz), 131.7 (d, J = 13.7 Hz), 131.7, 120.8 (d, J = 2.2 Hz), 119.4 (d, J = 17.3 Hz), 114.7, 110.9 (d, J = 18.5 Hz), 36.8, 29.8, 24.7, 20.6; HRMS (ESI): Calcd for $C_{16}H_{15}FNO_2$ $[M+H]^+$ 272.1081, Found: 272.1072.

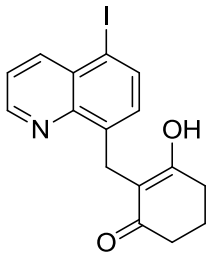


The title compound **3e** was isolated (PE:EA = 5:1) as a light brown solid, yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.34 (s, 1H), 8.89 (dd, J = 4.4, 1.6 Hz, 1H), 8.68 (dd, J = 8.4, 1.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.65 – 7.51 (m, 2H), 4.04 (s, 2H), 2.41 (t, J = 6.4 Hz, 2H), 2.28 (t, J = 6.4 Hz, 2H), 1.98 – 1.83 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 174.1, 148.2, 145.6, 138.2, 135.2, 132.1, 129.2, 127.5, 126.6, 121.6, 114.4, 36.8, 29.8, 25.0, 20.6; HRMS (ESI): Calcd for $C_{16}H_{15}ClNO_2$ $[M+H]^+$ 288.0785, Found: 288.0772.

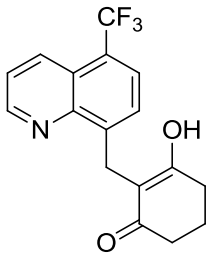


The title compound **3f** was isolated (PE:EA = 5:1) as a light brown solid, yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.30 (s, 1H), 8.86 (dd, J = 4.4, 1.6 Hz, 1H), 8.65 (dd, J = 8.4, 1.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 8.4, 4.4 Hz, 1H), 4.03 (s, 2H), 2.41 (s, *2*H), 2.29 (s, 2H), 1.90 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.2, 174.1, 148.3, 145.8, 138.9, 137.9, 132.6, 131.3, 127.9, 121.9, 119.5, 114.3, 36.8, 29.7, 25.0, 20.6; HRMS (ESI): Calcd for

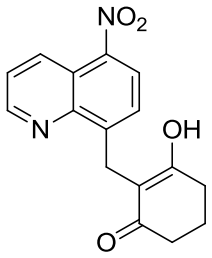
$C_{16}H_{15}BrNO_2$ $[M+H]^+$ 332.0281, Found: 332.0277.



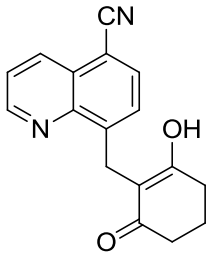
The title compound **3g** was isolated (PE:EA = 5:1) as a light brown solid, yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.34 (s, 1H), 8.82 (d, J = 4.4 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.55 (dd, J = 8.4, 4.4 Hz, 1H), 4.03 (s, 2H), 2.41 (t, J = 6.4 Hz, 2H), 2.28 (t, J = 6.4 Hz, 2H), 1.97 – 1.84 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.2, 174.2, 148.4, 145.7, 142.7, 140.0, 138.7, 133.4, 130.2, 122.4, 114.2, 95.6, 36.8, 29.7, 25.0, 20.6; HRMS (ESI): Calcd for $C_{16}H_{15}INO_2$ $[M+H]^+$ 380.0141, Found: 380.0135.



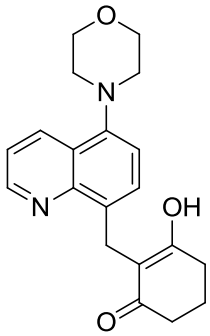
The title compound **3h** was isolated (PE:EA = 5:1) as a light brown solid, yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.27 (s, 1H), 8.95 (dd, J = 4.4, 1.6 Hz, 1H), 8.74 – 8.57 (m, 1H), 8.15 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.64 (dd, J = 8.8, 4.4 Hz, 1H), 4.12 (s, 2H), 2.43 (t, J = 6.4 Hz, 2H), 2.30 (t, J = 6.4 Hz, 2H), 1.92 (p, J = 6.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.2, 174.4, 148.3, 145.2, 143.9, 135.0, 130.8, 126.2(q, J = 5.7 Hz), 124.8, 124.5, 124.1, 124.0 (q, J = 273.5 Hz), 122.1, 113.9, 36.8, 29.8, 25.6, 20.6; HRMS (ESI): Calcd for $C_{17}H_{15}F_3NO_2$ $[M+H]^+$ 322.1050, Found: 322.1041.



The title compound **3i** was isolated (PE:EA = 2:1) as a light brown solid, yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.86 (s, 1H), 9.19 (dd, J = 8.8, 1.6 Hz, 1H), 8.98 (dd, J = 4.4, 1.6 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.75 (dd, J = 8.8, 4.4 Hz, 1H), 4.15 (s, 2H), 2.43 (t, J = 6.4 Hz, 2H), 2.30 (t, J = 6.4 Hz, 2H), 1.98 – 1.82 (p, J = 6.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 174.4, 148.9 146.9, 144.8, 143.6, 134.6, 130.6, 125.8, 123.7, 121.7, 113.3, 36.8, 29.6, 25.9, 20.6; HRMS (ESI): Calcd for $C_{16}H_{15}N_2O_4$ $[M+H]^+$ 299.1026, Found: 299.1031.

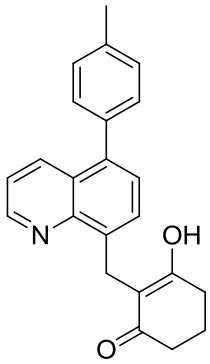


The title compound **3j** was isolated (PE:EA = 2:1) as a light brown solid, yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.93 (s, 1H), 8.99 (dd, J = 4.4, 1.6 Hz, 1H), 8.66 (dd, J = 8.4, 1.6 Hz, 1H), 8.18 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.72 (dd, J = 8.4, 4.4 Hz, 1H), 4.13 (s, 2H), 2.43 (t, J = 6.4 Hz, 2H), 2.29 (t, J = 6.4 Hz, 2H), 1.92 (p, J = 6.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2, 174.4, 149.4, 145.4, 144.6, 135.8, 134.0, 131.7, 128.2, 123.1, 116.6, 113.5, 108.3, 36.8, 29.8, 25.6, 20.6; HRMS (ESI): Calcd for $C_{17}H_{15}N_2O_2$ $[M+H]^+$ 279.1128, Found: 279.1133.

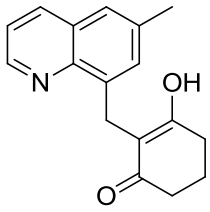


The title compound **3k** was isolated (PE:EA = 2:1) as a light brown solid, yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.96 (s, 1H), 8.82 (dd, J = 4.4, 1.6 Hz, 1H), 8.65 (dd, J = 8.4, 1.6 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.47 (dd, J = 8.4, 4.4 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 4.00 (s, 2H), 3.98 – 3.89 (m, 4H), 3.11 – 2.96 (m, 4H), 2.41 (s, 2H), 2.28 (s, 2H), 1.95 – 1.83 (p, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4,

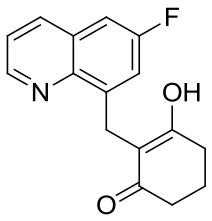
174.3, 147.8, 147.3, 145.8, 134.3, 134.2, 132.2, 124.5, 120.0, 116.4, 114.9, 67.2, 53.6, 36.8, 29.9, 25.0, 20.7; HRMS (ESI): Calcd for $C_{20}H_{23}N_2O_3$ $[M+H]^+$ 339.1703, Found: 339.1693.



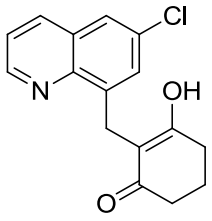
The title compound **3l** was isolated (PE:EA = 5:1) as a light brown solid, yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.06 (s, 1H), 8.84 (dd, J = 4.4, 1.6 Hz, 1H), 8.38 (dd, J = 8.4, 1.6 Hz, 1H), 8.11 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H), 7.43 (dd, J = 8.4, 4.4 Hz, 1H), 7.30 (s, 4H), 4.12 (s, 2H), 2.45 (s, 5H), 2.32 (s, 2H), 1.93 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 174.4, 147.2, 145.1, 138.7, 138.0, 137.5, 136.9, 136.0, 131.9, 129.9, 129.2, 128.2, 127.2, 120.6, 114.8, 36.9, 29.9, 25.4, 21.2, 20.7; HRMS (ESI): Calcd for $C_{23}H_{22}NO_2$ $[M+H]^+$ 344.1645, Found: 344.1641.



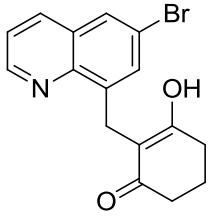
The title compound **3m** was isolated (PE:EA = 5:1) as a light brown solid, yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.15 (s, 1H), 8.75 (dd, J = 4.4, 1.6 Hz, 1H), 8.15 (dd, J = 8.4, 1.6 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 7.44 – 7.41 (m, 2H), 4.03 (s, 2H), 2.50 (s, 3H), 2.42 (s, 2H), 2.29 (s, 2H), 1.90 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 174.5, 146.5, 143.6, 138.5, 137.8, 137.6, 134.6, 128.8, 124.7, 120.8, 114.7, 36.9, 30.0, 25.2, 21.6, 20.7; HRMS (ESI): Calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$ 268.1332, Found: 268.1321.



The title compound **3n** was isolated (PE:EA = 5:1) as a light brown solid, yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.57 (s, 1H), 8.80 (dd, J = 4.4, 1.6 Hz, 1H), 8.20 (dd, J = 8.4, 1.6 Hz, 1H), 7.87 (dd, J = 9.2, 2.8 Hz, 1H), 7.50 (dd, J = 8.4, 4.4 Hz, 1H), 7.30 (dd, J = 8.4, 2.8 Hz, 1H), 4.06 (s, 2H), 2.42 (t, J = 6.4 Hz, 2H), 2.30 (t, J = 6.4 Hz, 2H), 2.00 – 1.82 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 174.3, 160.7 (d, J = 250.5 Hz), 146.8, 142.3 (d, J = 8.5 Hz), 137.7 (d, J = 5.2 Hz), 129.5 (d, J = 10.1 Hz), 122.5 (d, J = 25.9 Hz), 121.6, 114.0, 108.8 (d, J = 21.9 Hz), 36.79, 29.84, 25.30, 20.63; HRMS (ESI): Calcd for $C_{16}H_{15}FNO_2$ $[M+H]^+$ 272.1081, Found: 272.1077.

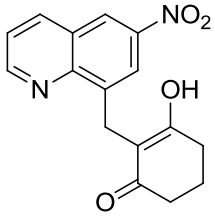


The title compound **3o** was isolated (PE:EA = 5:1) as a light brown solid, yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.47 (s, 1H), 8.82 (dd, J = 4.4, 1.6 Hz, 1H), 8.16 (dd, J = 8.4, 1.2 Hz, 1H), 8.03 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.51 (dd, J = 8.4, 4.4 Hz, 1H), 4.03 (s, 2H), 2.42 (t, J = 6.4 Hz, 2H), 2.30 (t, J = 6.4 Hz, 2H), 2.10 – 1.80 (p, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 174.2, 147.7, 143.6, 141.0, 137.4, 133.4, 133.0, 129.2, 124.5, 121.7, 114.0, 36.8, 29.8, 25.1, 20.6. HRMS (ESI): Calcd for $C_{16}H_{15}ClNO_2$ $[M+H]^+$ 288.0785, Found: 288.0773.

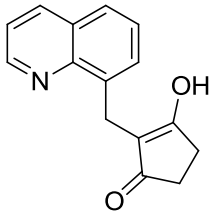


The title compound **3p** was isolated (PE:EA = 5:1) as a light brown solid, yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.46 (s, 1H), 8.84 (dd, J = 4.4, 1.6 Hz, 1H), 8.41 –

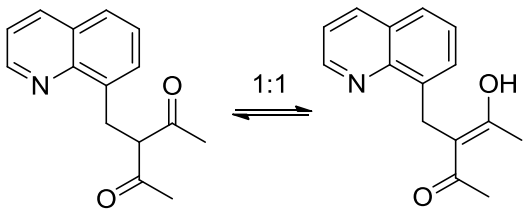
8.06 (m, 2H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.02 (s, 2H), 2.42 (t, *J* = 6.4 Hz, 2H), 2.30 (t, *J* = 6.4 Hz, 2H), 1.99 – 1.84 (p, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 174.2, 147.9, 143.8, 141.0, 137.3, 135.4, 129.7, 127.9, 121.7, 114.0, 36.8, 29.8, 25.0, 20.6; HRMS (ESI): Calcd for $C_{16}H_{15}BrNO_2$ $[M+H]^+$ 332.0281, Found: 332.0276.



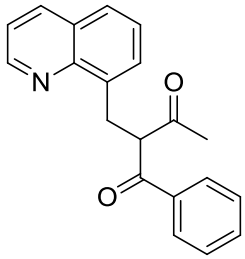
The title compound **3q** was isolated (PE:EA = 2:1) as a light brown solid, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.83 (s, 1H), 9.04 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.84 (d, *J* = 2.4 Hz, 1H), 8.66 (d, *J* = 2.4 Hz, 1H), 8.47 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.68 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.16 (s, 2H), 2.43 (t, *J* = 6.4 Hz, 2H), 2.30 (t, *J* = 6.4 Hz, 2H), 1.92 (p, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 174.0, 151.1, 147.1, 146.0, 141.8, 140.3, 127.6, 125.4, 122.7, 122.3, 113.7, 36.7, 29.7, 25.5, 20.5; HRMS (ESI): Calcd for $C_{16}H_{15}N_2O_4$ $[M+H]^+$ 299.1026, Found: 299.1033.



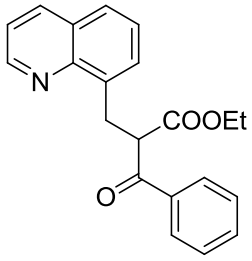
The title compound **3r** was isolated (PE:EA = 5:1) as a light brown solid, yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.88 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.59 – 7.47 (m, 2H), 3.93 (s, 2H), 2.46 (s, 2H), 2.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 186.9, 148.1, 145.1, 138.7, 138.0, 131.7, 129.0, 127.7, 126.5, 121.0, 116.8, 33.7, 27.1, 24.5; HRMS (ESI): Calcd for $C_{15}H_{14}NO_2$ $[M+H]^+$ 240.1020, Found: 240.1017.



The title compound **3s** was isolated (PE:EA = 5:1) as a light brown solid, yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.93 and 4.50 (s, t, J = 7.2 Hz, 1H), 8.97 and 8.91 (a pair of dd, J = 4.0, 1.6 Hz, 1H), 8.19 and 8.14 (a pair of dd, J = 8.0, 1.6 Hz, 1H), 7.60 – 7.33 (m, 3H), 4.33 and 3.75 (s, d, J = 7.2 Hz, 2H), 2.17 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.5, 192.3, 149.5, 149.4, 146.7, 146.6, 138.0, 136.8, 136.5, 136.4, 130.3, 128.4, 1 28.4, 127.4, 126.7, 126.4, 126.4, 126.3, 121.21, 121.1, 107.6, 68.4, 30.6, 29.8, 28.4, 23.1; HRMS (ESI): Calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1176, Found: 242.1168.

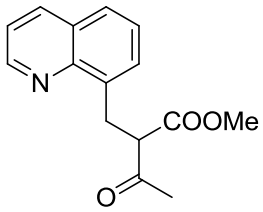


The title compound **3t** was isolated (PE:EA = 5:1) as a light brown solid, yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.0, 1.6 Hz, 1H), 8.13 (dd, J = 8.4, 1.6 Hz, 1H), 8.04 (dd, J = 5.2, 3.2 Hz, 2H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.61 (d, J = 6.4 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.45 – 7.35 (m, 4H), 5.42 (t, J = 7.2 Hz, 1H), 3.88 (qd, J = 13.2, 7.2 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 197.0, 149.3, 146.8, 136.9, 136.6, 136.4, 133.4, 130.9, 128.9, 128.6, 128.4, 127.0, 126.3, 121.0, 62.8, 31.9, 29.2; HRMS (ESI): Calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$ 304.1332, Found: 304.1337.

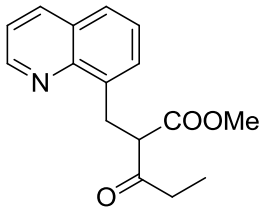


The title compound **3u** was isolated (PE:EA = 5:1) as a light brown solid, yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (dd, J = 4.0, 1.6 Hz, 1H), 8.19 – 8.16 (m, 2H), 8.14 (dd, J = 8.4, 1.6 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.45 – 7.39 (m, 4H), 5.30 (dd, J = 9.2, 5.6 Hz, 1H), 4.17 – 3.92 (m, 3H), 3.76 (dd, J = 13.2,

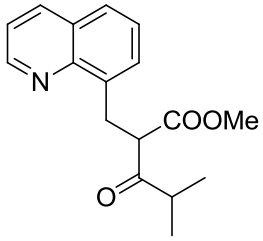
9.2 Hz, 1H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 169.8, 149.3, 146.9, 136.7, 136.4, 136.2, 133.3, 131.0, 129.0, 128.5, 128.3, 127.0, 126.3, 121.0, 61.1, 54.9, 32.3, 13.9; HRMS (ESI): Calcd for $C_{21}H_{20}NO_3$ $[M+H]^+$ 334.1437, Found: 334.1430.



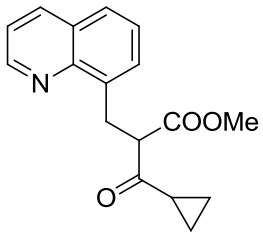
The title compound **3v** was isolated (PE:EA = 5:1) as a light brown oil, yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.0, 1.6 Hz, 1H), 8.13 (dd, J = 8.4, 1.6 Hz, 1H), 7.70 (dd, J = 8.4, 1.6 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.41 (ddd, J = 8.4, 7.6, 5.6 Hz, 2H), 4.38 (dd, J = 8.4, 6.6 Hz, 1H), 3.87 (dd, J = 13.6, 6.6 Hz, 1H), 3.70 – 3.58 (m, 4H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 170.0, 149.5, 146.7, 136.6, 136.3, 130.4, 128.4, 127.1, 126.2, 121.0, 59.9, 52.2, 30.9, 29.5; HRMS (ESI): Calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.1124, Found: 258.1119.



The title compound **3w** was isolated (PE:EA = 5:1) as a light brown oil, yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.0, 1.6 Hz, 1H), 8.13 (dd, J = 8.4, 1.6 Hz, 1H), 7.69 (dd, J = 8.0, 1.2 Hz, 1H), 7.56 (dd, J = 7.2, 1.2 Hz, 1H), 7.47 – 7.35 (m, 2H), 4.40 (dd, J = 8.0, 6.8 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.68 (dd, J = 13.2, 8.0 Hz, 1H), 3.64 (s, 3H), 2.58 (dq, J = 18.4, 7.2 Hz, 1H), 2.38 (dq, J = 18.4, 7.2 Hz, 1H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.2, 170.1, 149.4, 146.7, 136.6, 136.3, 130.5, 128.3, 127.0, 126.2, 121.0, 58.7, 52.2, 36.0, 31.0, 7.4; HRMS (ESI): Calcd for $C_{16}H_{18}NO_3$ $[M+H]^+$ 272.1281, Found: 272.1275.



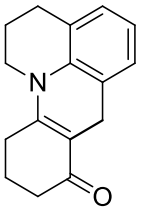
The title compound **3x** was isolated (PE:EA = 5:1) as a light brown oil, yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.0, 1.6 Hz, 1H), 8.13 (dd, J = 8.4, 1.6 Hz, 1H), 7.69 (dd, J = 8.0, 1.2 Hz, 1H), 7.56 (d, J = 6.0 Hz, 1H), 7.48 – 7.35 (m, 2H), 4.59 (t, J = 7.2 Hz, 1H), 3.73 (d, J = 7.2 Hz, 2H), 3.64 (s, 3H), 2.65 (hept, J = 6.8 Hz, 1H), 1.03 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.5, 170.0, 149.4, 146.7, 136.7, 136.4, 130.8, 128.3, 127.0, 126.2, 121.0, 56.8, 52.1, 41.2, 31.4, 17.8, 17.4; HRMS (ESI): Calcd for $C_{17}H_{20}NO_3$ $[M+H]^+$ 268.1438, Found: 268.1430.



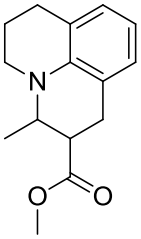
The title compound **3y** was isolated (PE:EA = 5:1) as a light brown oil, yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.0, 1.6 Hz, 1H), 8.14 (dd, J = 8.4, 1.6 Hz, 1H), 7.70 (dd, J = 8.0, 1.2 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.48 – 7.37 (m, 2H), 4.52 (dd, J = 8.4, 6.4 Hz, 1H), 3.91 (dd, J = 13.2, 6.4 Hz, 1H), 3.69 (dd, J = 13.2, 8.4 Hz, 1H), 3.65 (s, 3H), 2.15 – 2.09 (m, 1H), 1.11 – 1.05 (m, 1H), 1.03 – 0.97 (m, 1H), 0.92 – 0.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 170.2, 149.4, 146.8, 136.7, 136.3, 130.5, 128.4, 127.0, 126.2, 121.0, 59.8, 52.2, 31.1, 20.3, 11.6, 11.5; HRMS (ESI): Calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$ 284.1282, Found: 284.1276.

b) General procedure of hydrogenation of compounds **3a**, **3v**:

A solution of **3a** (24mg, 0.1mmol) and PtO_2 (1mg, 5 mol %) in 1.5mL methanol was stirred at 40℃ for 4 hours under a H_2 atmosphere. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **3a'**.



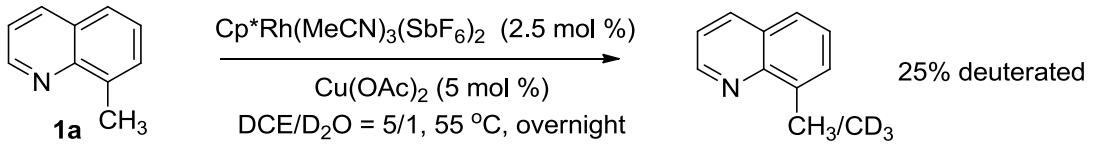
Compound **3a**': 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.93 (m, 1H), 6.90 – 6.84 (m, 2H), 3.72 – 3.69 (m, 2H), 3.64 (s, 2H), 2.82 – 2.71 (m, 2H), 2.60 (t, J = 6.4 Hz, 2H), 2.42 – 2.31 (m, 2H), 2.09 – 1.96 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.1, 155.7, 135.9, 127.3, 127.0, 124.7, 123.8, 122.7, 106.5, 45.7, 35.8, 27.6, 26.3, 24.4, 22.2, 21.6; HRMS (ESI): Calcd for $C_{16}H_{18}NO$: $[M+H]^+$ 240.1382, sFound: m/z 240.1379.



Compound **3v**': 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, J = 7.2 Hz, 1H), 6.81 (d, J = 7.2 Hz, 1H), 6.52 (t, J = 7.2 Hz, 1H), 3.79 – 3.68 (m, 4H), 3.39 – 3.29 (m, 1H), 3.21 – 2.99 (m, 3H), 2.90 – 2.69 (m, 3H), 2.05 – 1.91 (m, 2H), 1.01 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 140.4, 127.3, 121.7, 118.7, 115.5, 54.0, 51.8, 48.2, 42.1, 27.9, 24.9, 22.0, 11.9; HRMS (ESI): Calcd for $C_{15}H_{20}NO_2$ $[M+H]^+$ 246.1490, Found: m/z 246.1488.

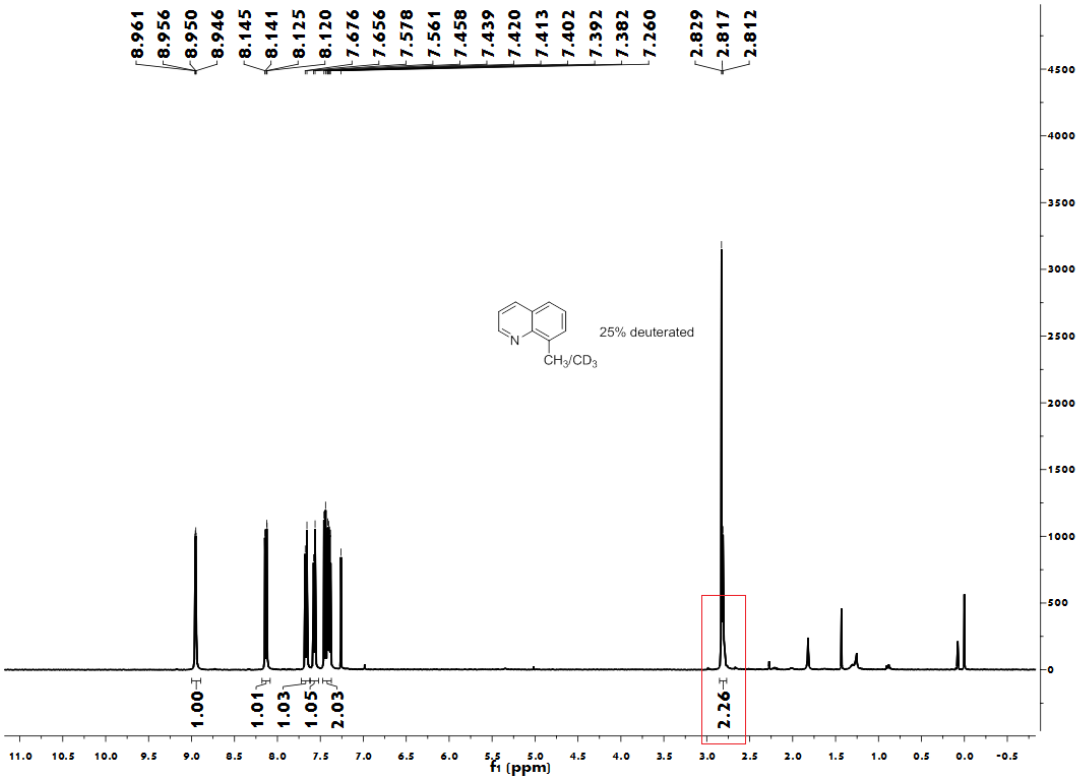
c) Mechanistic study

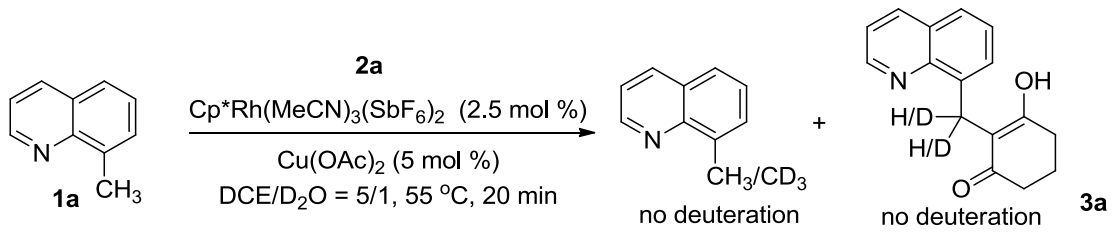
(1) Hydrogen-deuterium exchange experiment



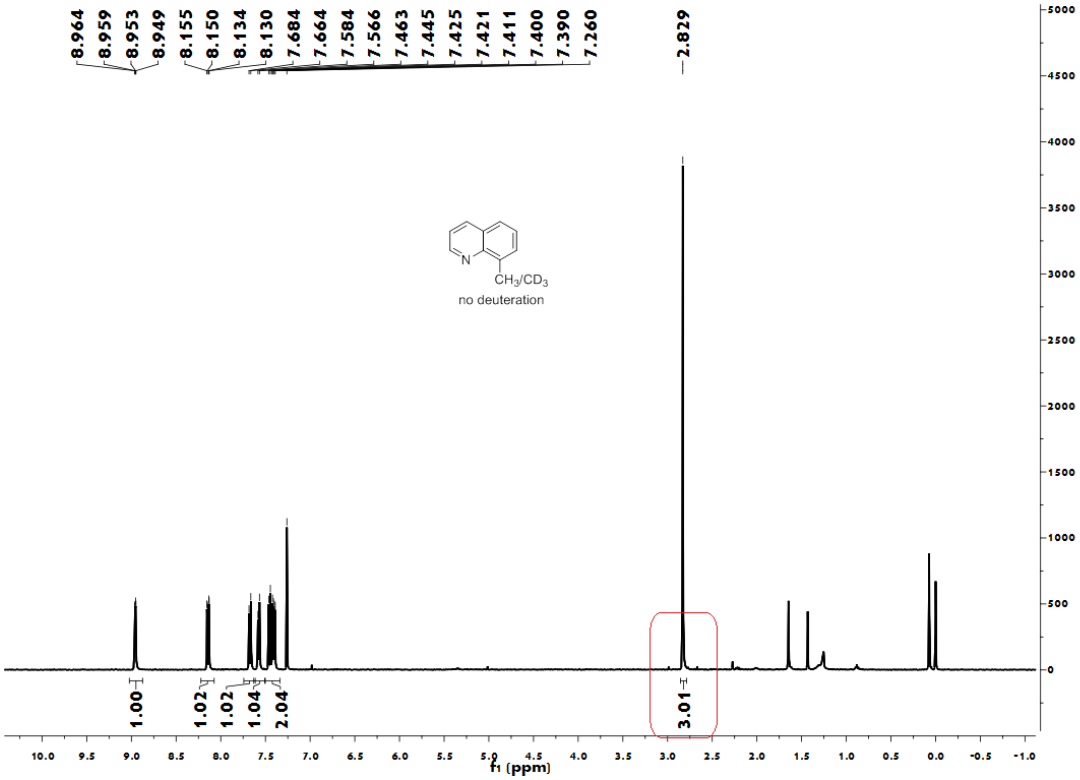
$Cp^*Rh(MeCN)_3(SbF_6)_2$ (2.5 mol %), $Cu(OAc)_2$ (5 mol %), 8-methylquinoline **1a** (0.2 mmol) and DCE:D_2O (2 mL, 5:1) were added to a test tube. The reaction mixture was stirred at 55 ^{o}C overnight. The solution was filtered through a celite pad and washed with dichloromethane. Then, the solvent was removed under reduced pressure and the

residue was purified by silica gel chromatography using PE/EA to provide **1a**-*dn*. ^{1}H NMR analysis showed that 25% hydrogen at the C8-position methyl of quinolone was deuterated.





$Cp^*Rh(MeCN)_3(SbF_6)_2$ (2.5 mol %), $Cu(OAc)_2$ (5 mol %), 8-methylquinoline **1a** (0.2 mmol), diazo compound **2a** (0.3 mmol) and DCE:D_2O (2 mL, 5:1) were added to a test tube. The reaction mixture was stirred at 55 ^{o}C for 20 min. The solution was filtered through a celite pad and washed with dichloromethane. Then, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to provide **1a**-*dn* and **3a**-*dn*. No deuteration was observed at the C8-position methyl of quinolone.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8.949
8.155
8.150
8.134
8.130
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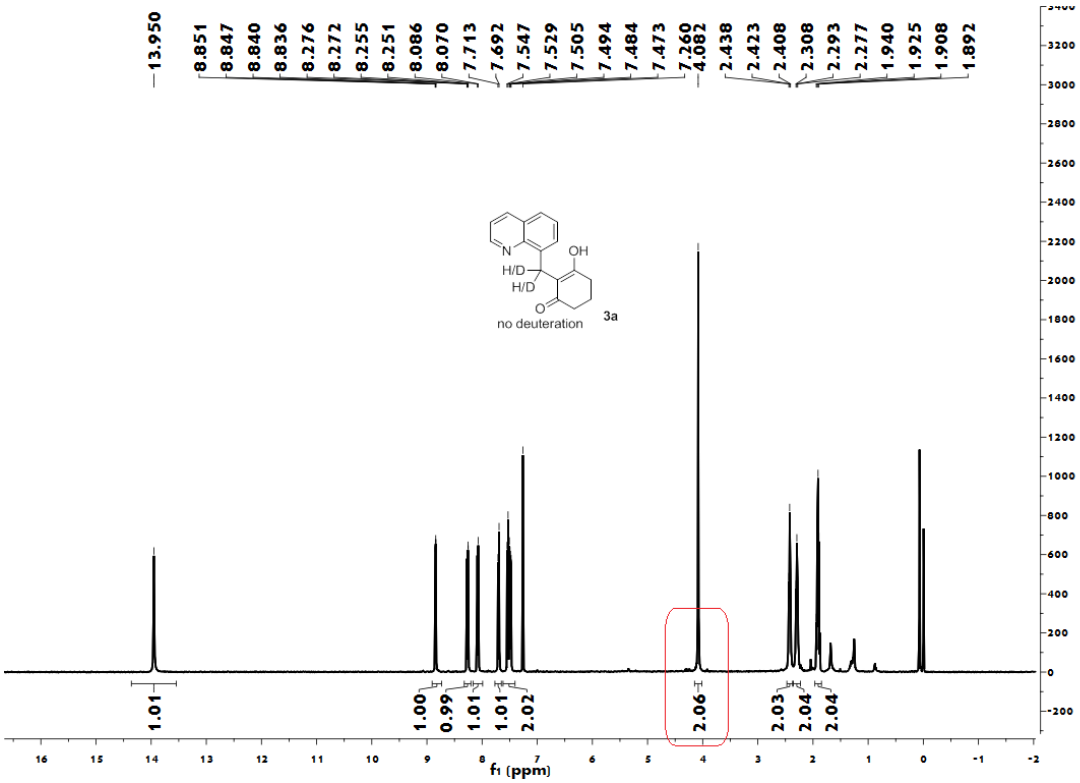
7.664
7.584
7.566
7.463
7.445
7.425
7.421
7.411
7.400
7.390
7.260
2.829
CH3/CD3
no deuteration
1.00
1.02
1.02
1.04
2.04
3.01
f1 (ppm)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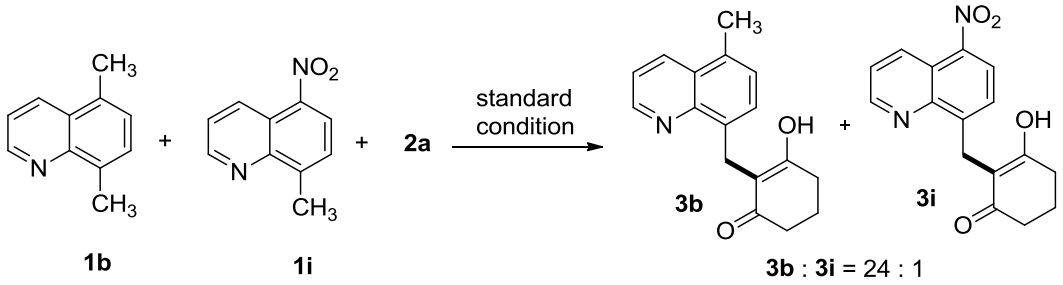
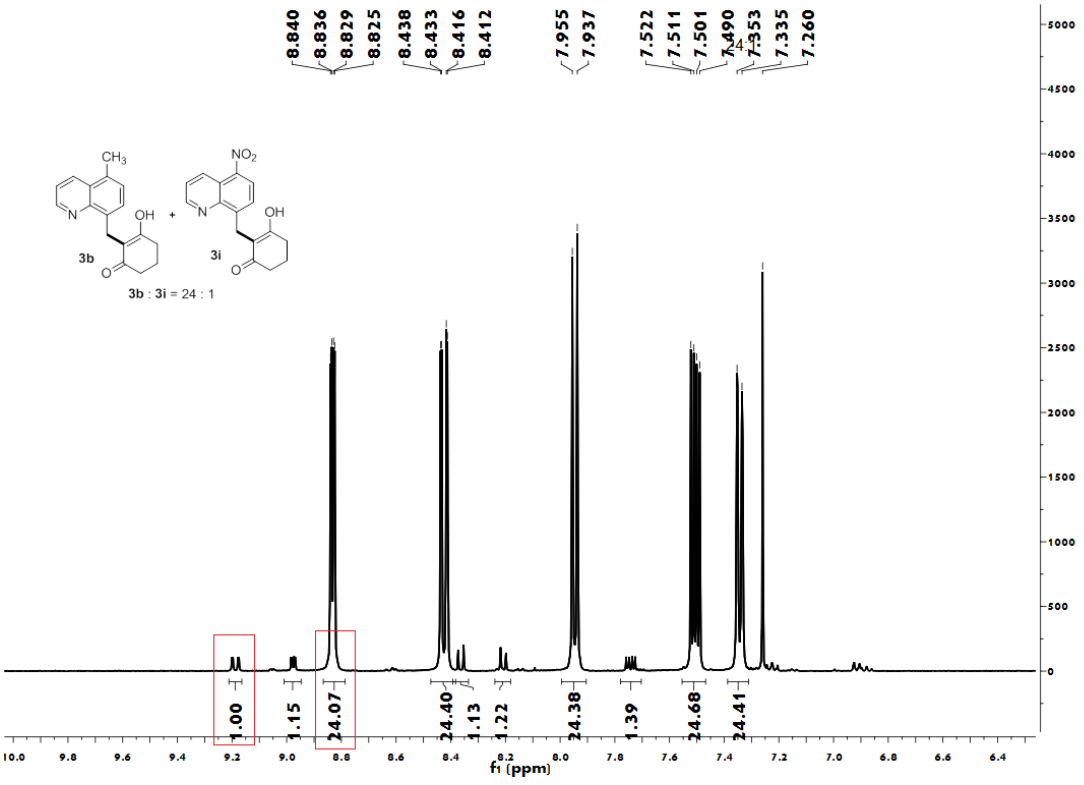
2.408
2.308
2.293
2.277
1.940
1.925
1.908
1.892
OH
H/D
H/D
O
no deuteration
3a
1.01
1.00
0.99
1.01
1.01
2.02
2.06
2.03
2.04
2.04
f1 (ppm)

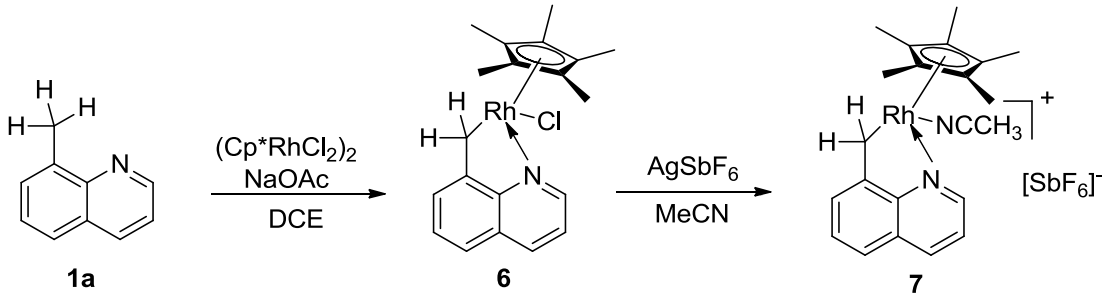
(2) Competitive Reaction



A mixture of **1b** (0.1 mmol), **1i** (0.1 mmol), Cp*Rh(MeCN)$_3$(SbF$_6$)$_2$ (2.5 mol %), Cu(OAc)$_2$ (5 mol %), diazo compound **2a** (0.1 mmol) and DCE (1 mL) were added to a test tube. The reaction mixture was stirred at 55 ^{o}C for 3 h. The solution was filtered through a celite pad and washed with dichloromethane. Then, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford compounds **3b** and **3i** as a mixture, which was characterized by ^{1}H NMR spectroscopy.

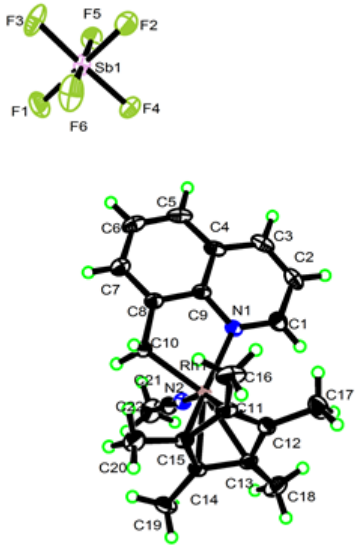


(3) Synthesis of cyclometalated Rh(III) complex



Rh(III) complex **6** was prepared according to the literature procedures.[S3] A mixture of substituted 8-methyl-quinoline (0.6 mmol), $[Cp^*RhCl_2]_2$ (5.0 mol %), NaOAc (0.3 mmol) and MeOH (1 mL) were weighted in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 80 ℃ overnight, concentrated under vacuum. The product was purified by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1: 2, 20% yield).

To the suspension of Rh(III) complex **6** (0.23 mmol) in dried CH_3CN (1.5 mL), the solution of $AgSbF_6$ (1 mmol) in dried CH_3CN (2 mL) was added in 2 min. Then the white solid precipitated immediately. The reaction was stirred at rt for another 3 h. Then the solid was removed by filtration on celite and washed with CH_3CN. The filtrate was evaporated in vacuo and then Et_2O was added dropwise and the brown solid precipitated. The solid was collected by filtration, washed with EtOAc and Et_2O, dried in vacuo to afford Rh(III) complex **7** (50% yield). The structure of Rh(III) complex **9** was unambiguously confirmed by X-ray analysis (CCDC 1049041).



Reference:

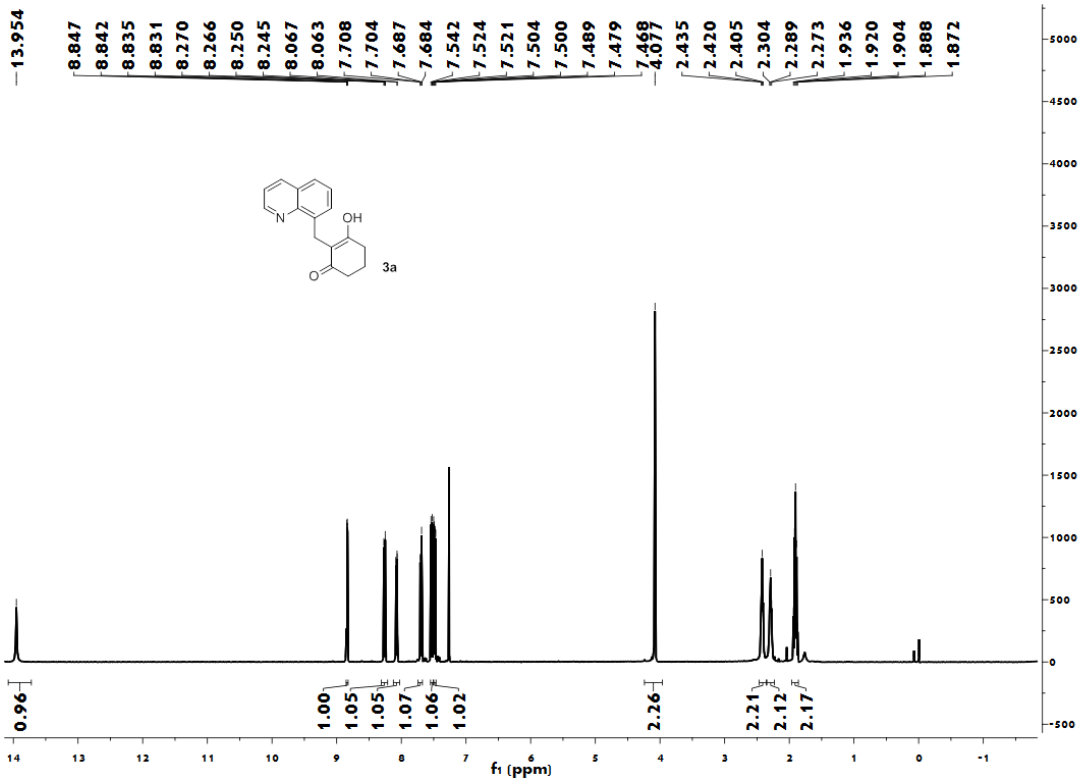
S1: K. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, *Org. Lett.* **2004**, *6*, 2785.

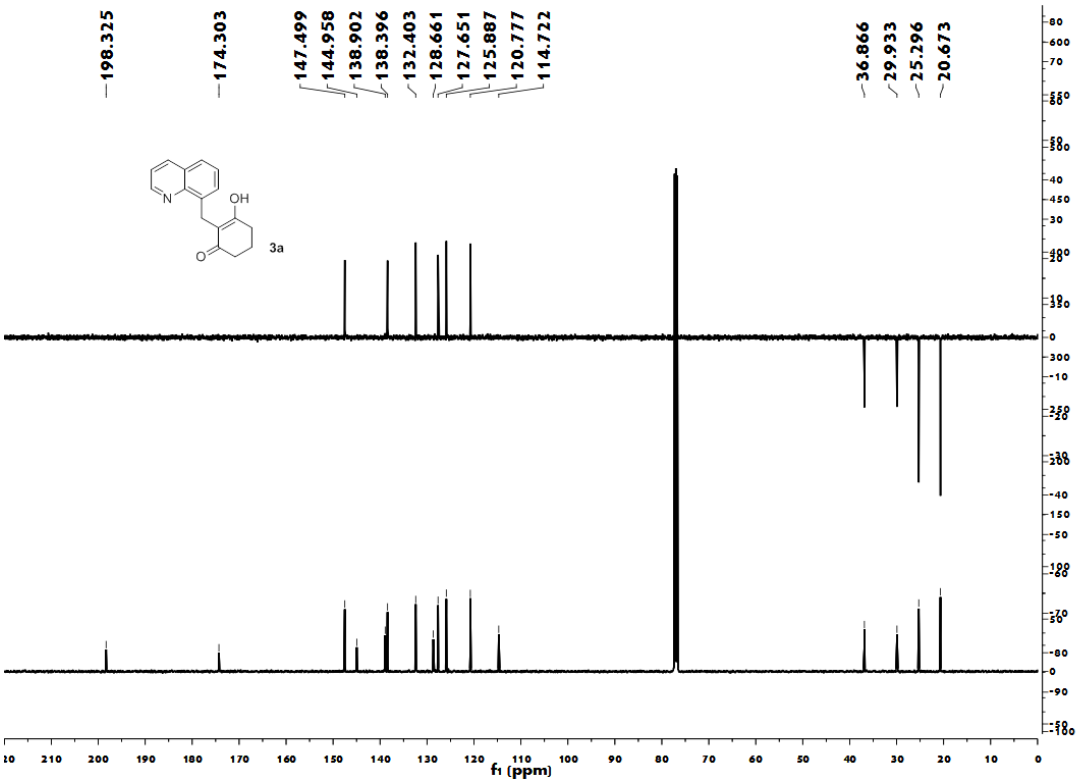
S2: Yang Li, Bi-Jie Li, Wen-Hua Wang, Wei-Ping Huang, Xi-Sha Zhang, Kang Chen, Zhang-Jie Shi, *Angew. Chem. Int. Ed.*, **2011**, *50*, 2115.

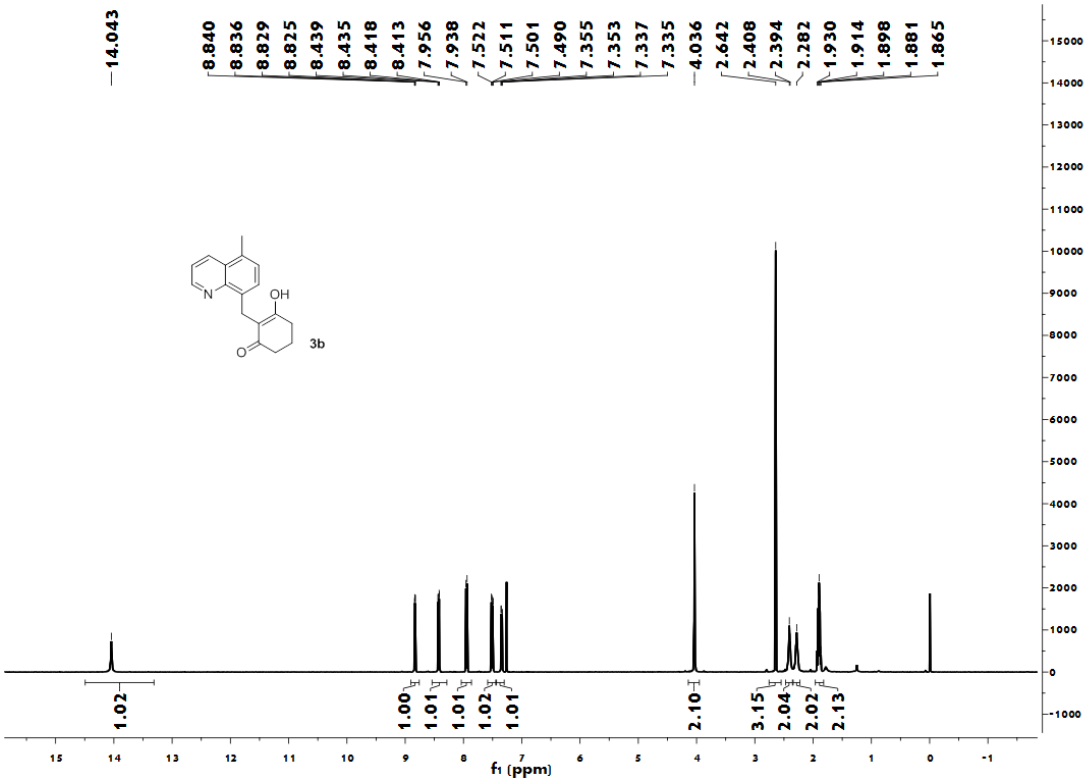
S3: Bingxian Liu, Tao Zhou, Bin Li, Shansheng Xu, Haibin Song, and Baiquan Wang, *Angew. Chem. Int. Ed*., **2014**, *53*, 4191.

S4: (a) M. P. Doyle, M. McKervey, T. Ye, Modern, Catalytic Methods for Organic Synthesis with Diazo Compounds, John Wiley & Sons Inc: New York, **1998**, Ch. 1, p.10; (b) Z. M. Jászay, T. S. Pham, K. Gönczi, I. Petneházy, L. Tőke, *Synthetic Communications*, **2010**, *40*, 1574.

^{1}H and ^{13}C NMR Spectra of Compounds



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7.511
7.501
7.490
7.355
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7.337
7.335
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2.408
2.394
2.282
1.930
1.914
1.898
1.881
1.865
OH
O
N
3b
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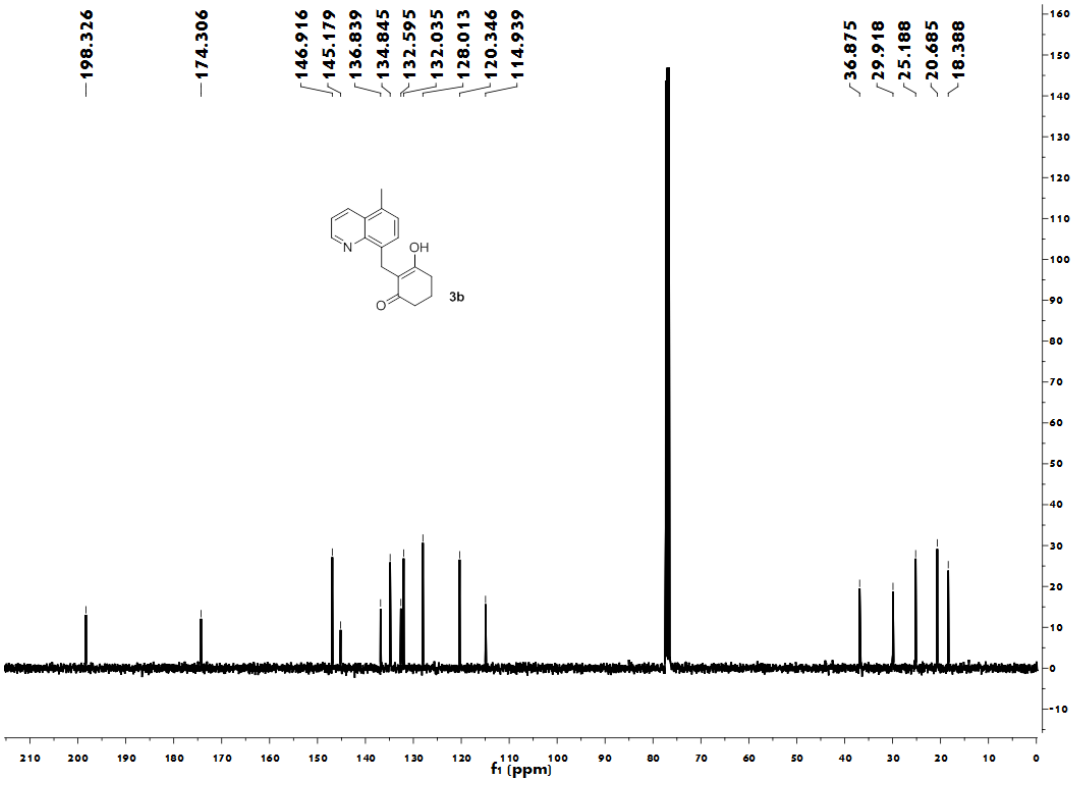
2.13
f1 (ppm)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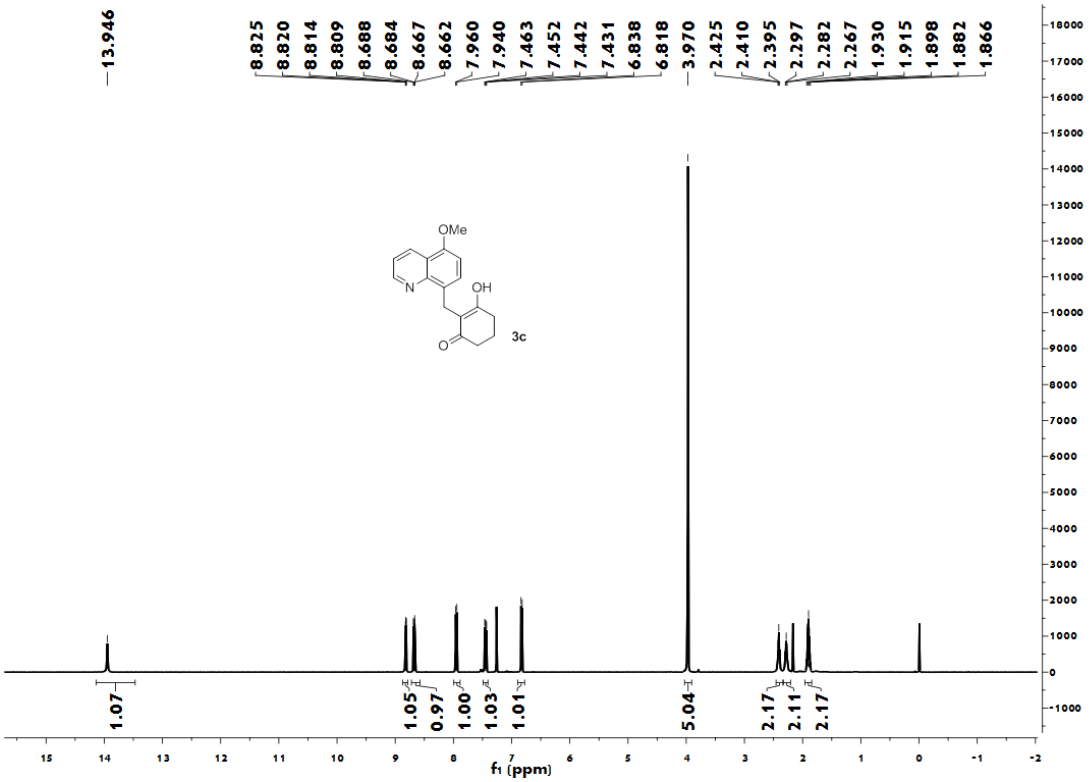
N
3b
f1 (ppm)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7.431
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6.818
3.970
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2.410
2.395
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2.282
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1.915
1.898
1.882
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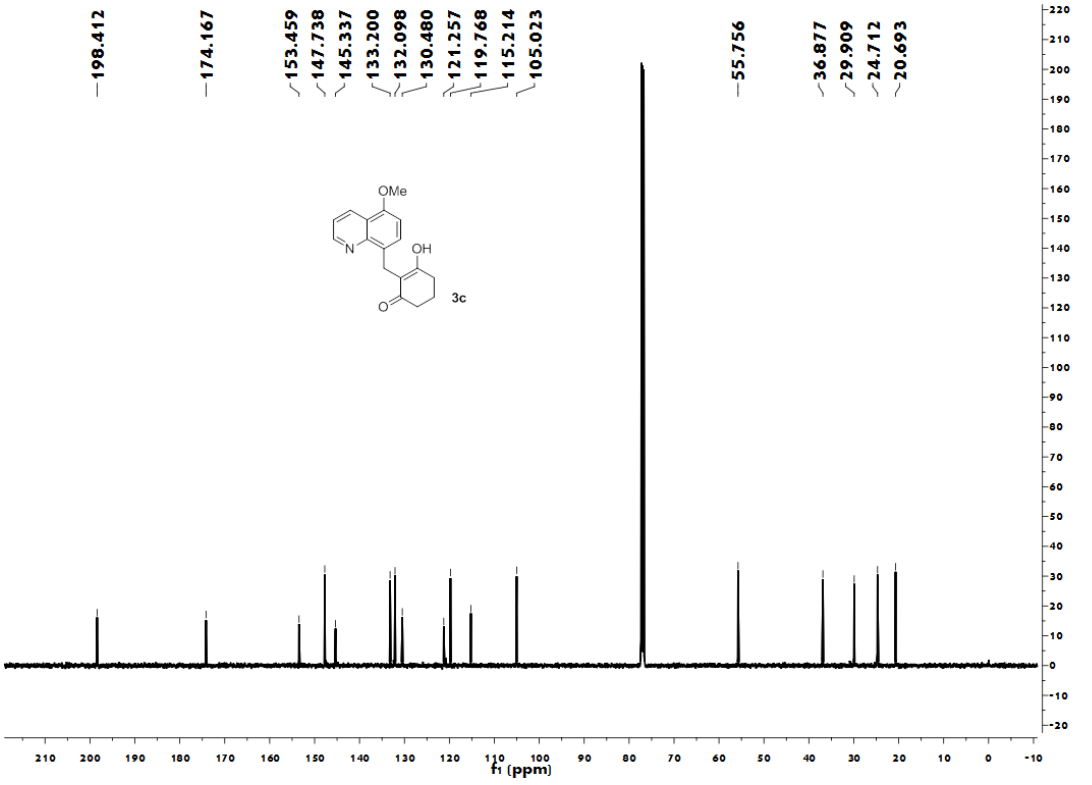
f1 (ppm)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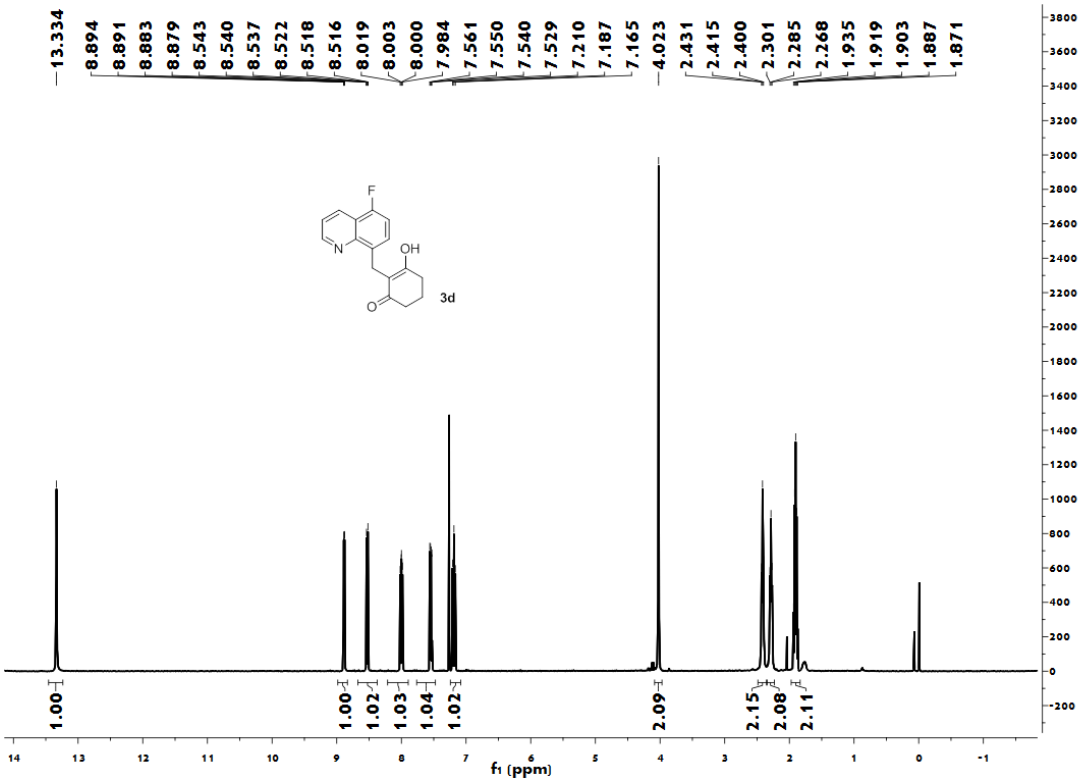
OMe
OH
N
O
3c
f1 (ppm)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8.000
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7.561
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OH
O
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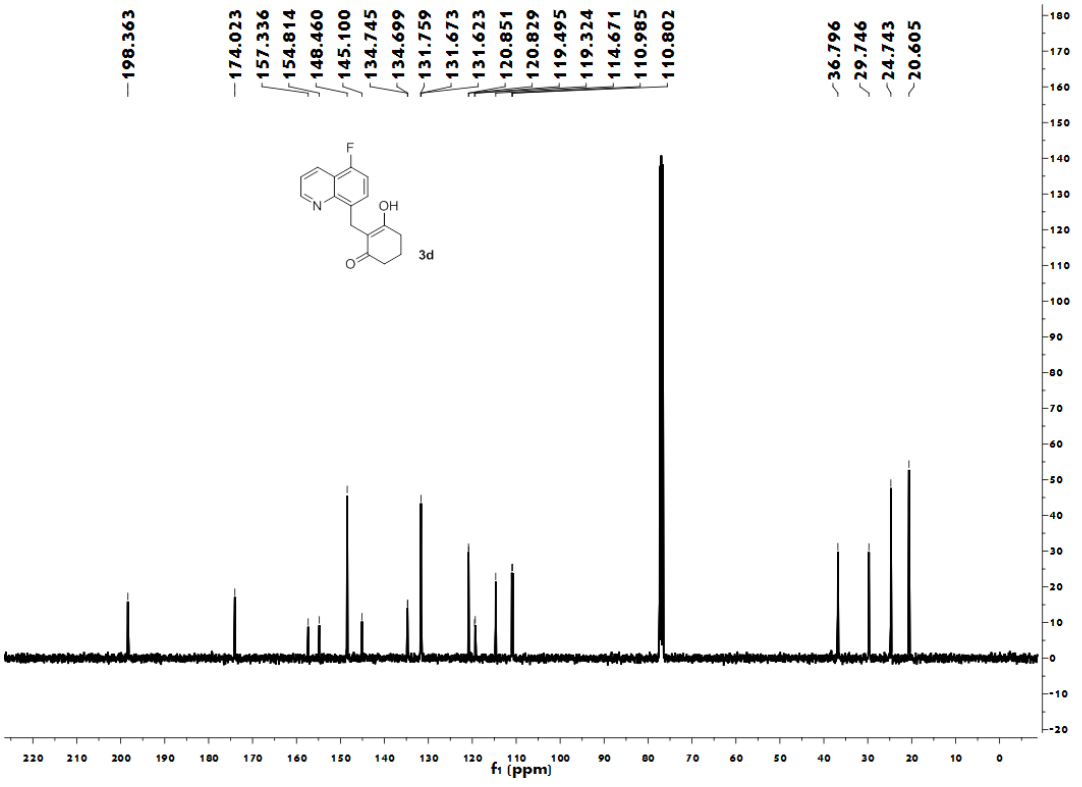
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O
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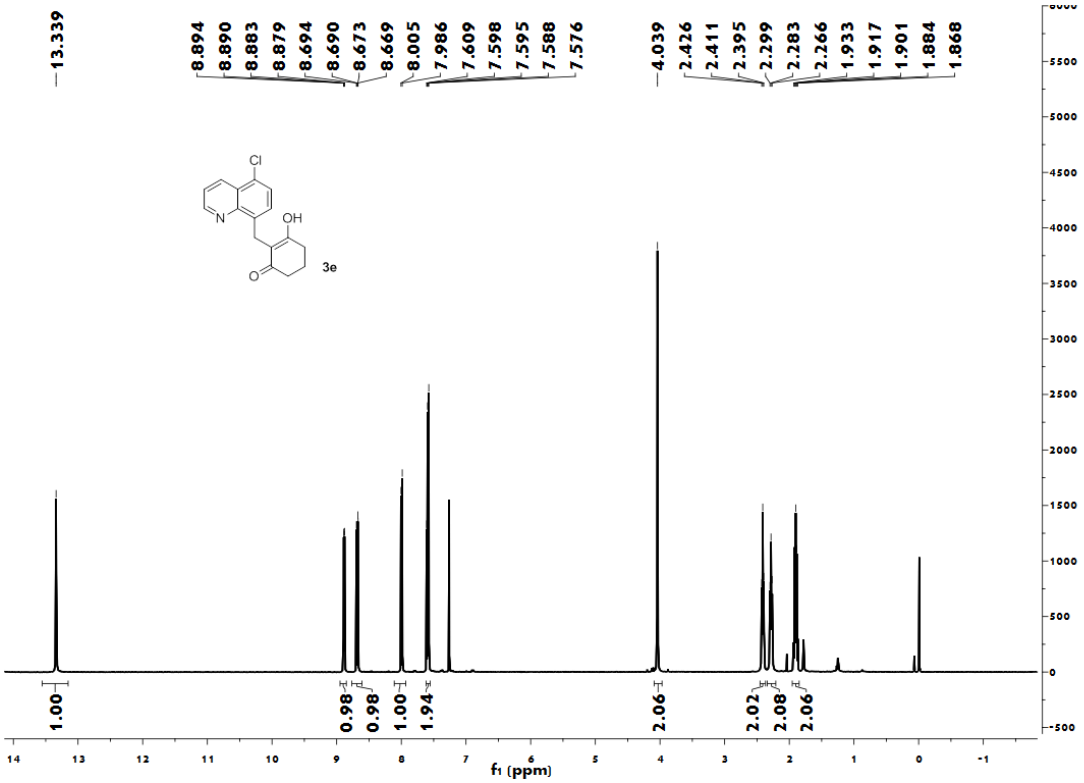
f1 (ppm)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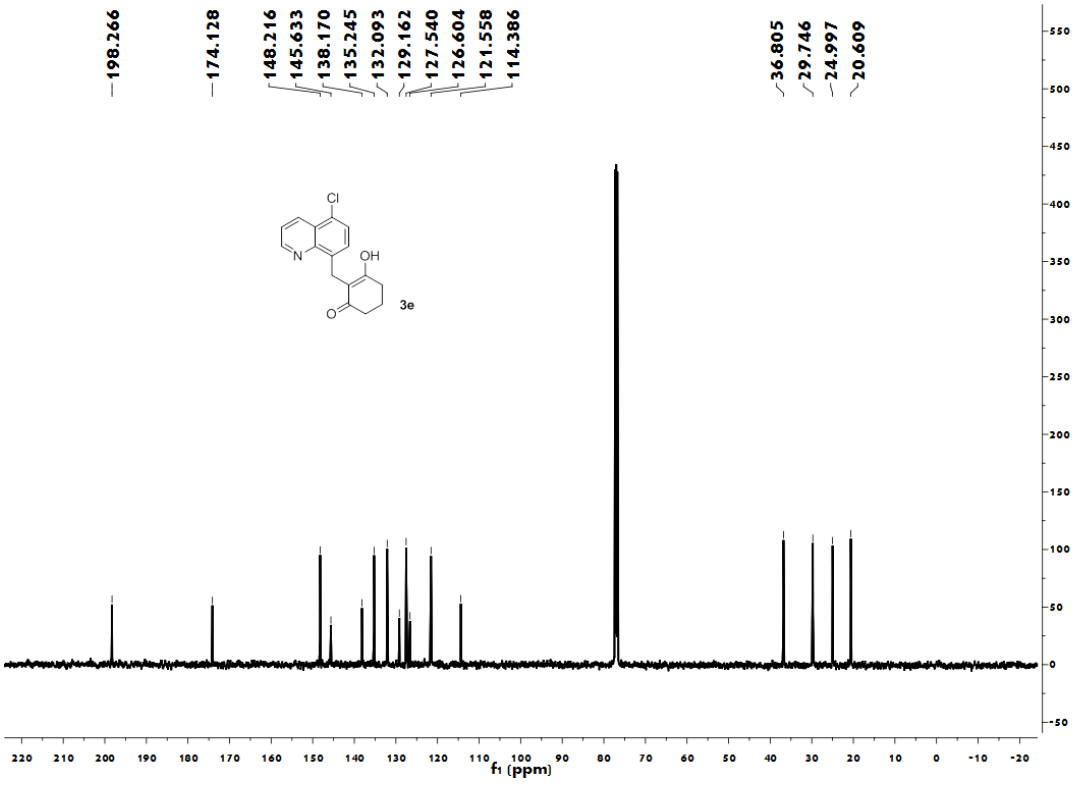
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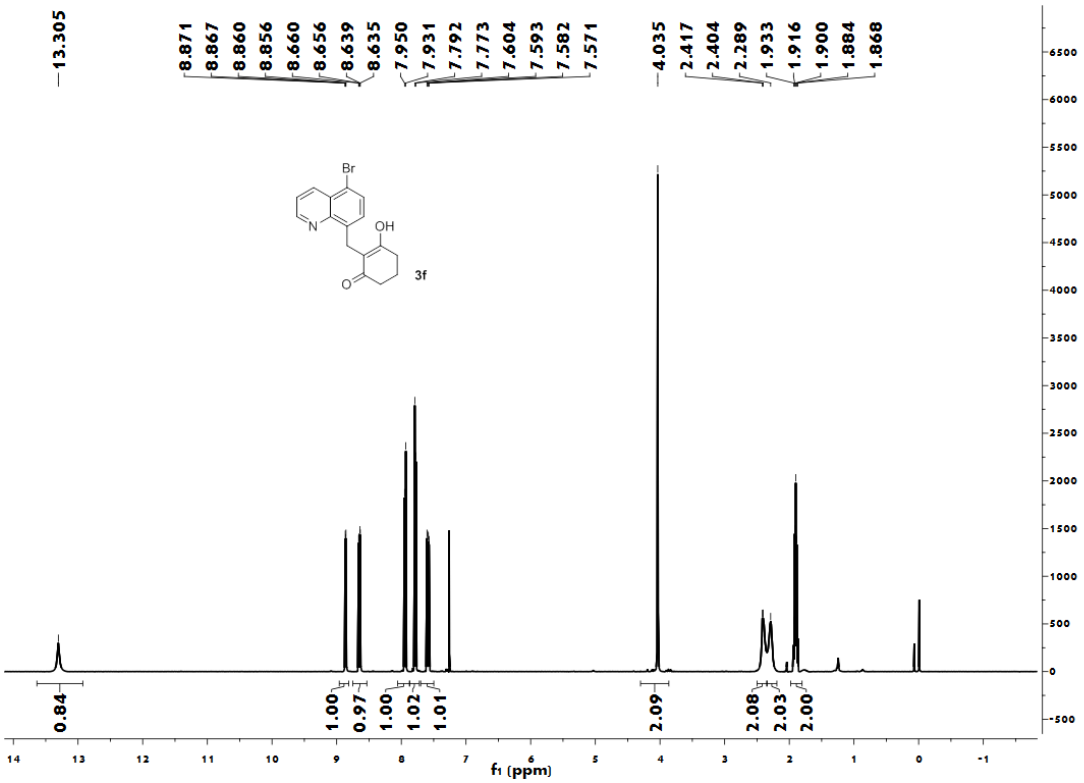
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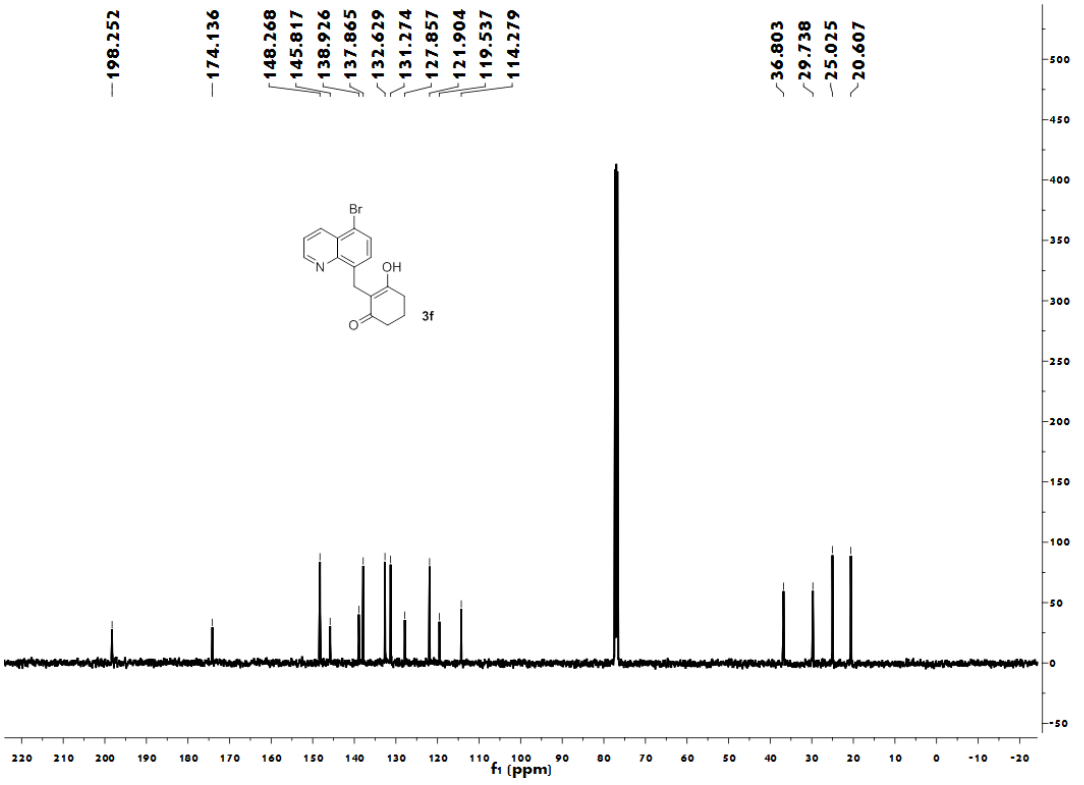
f1 (ppm)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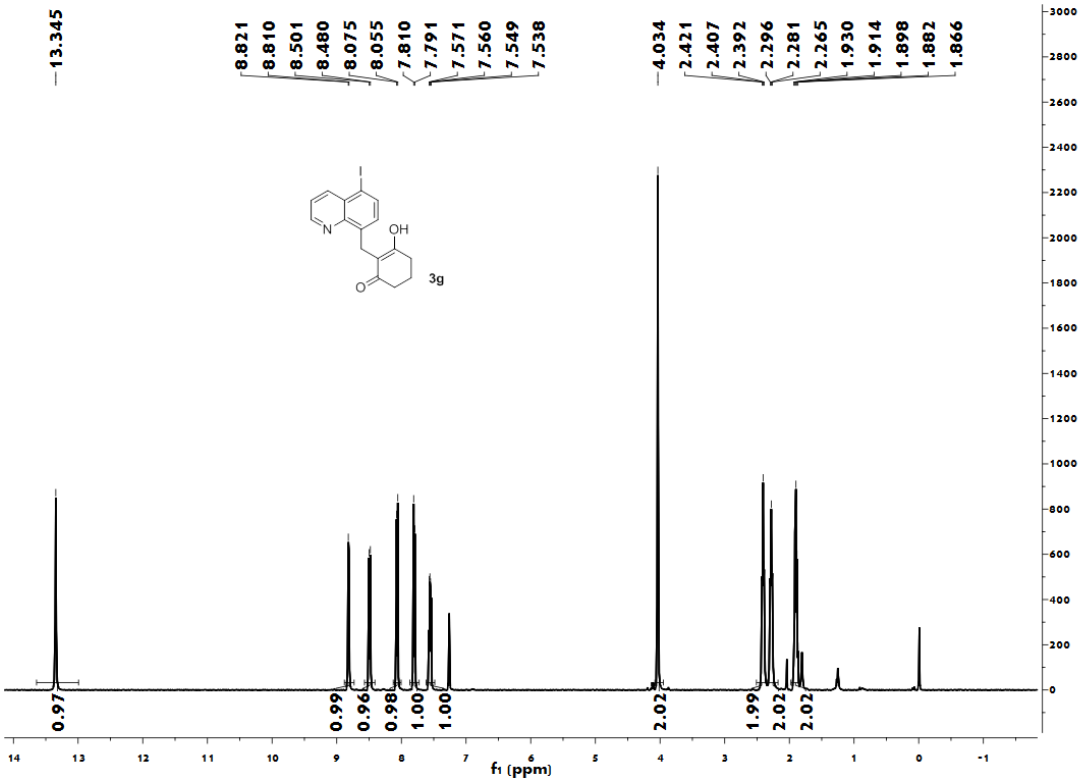
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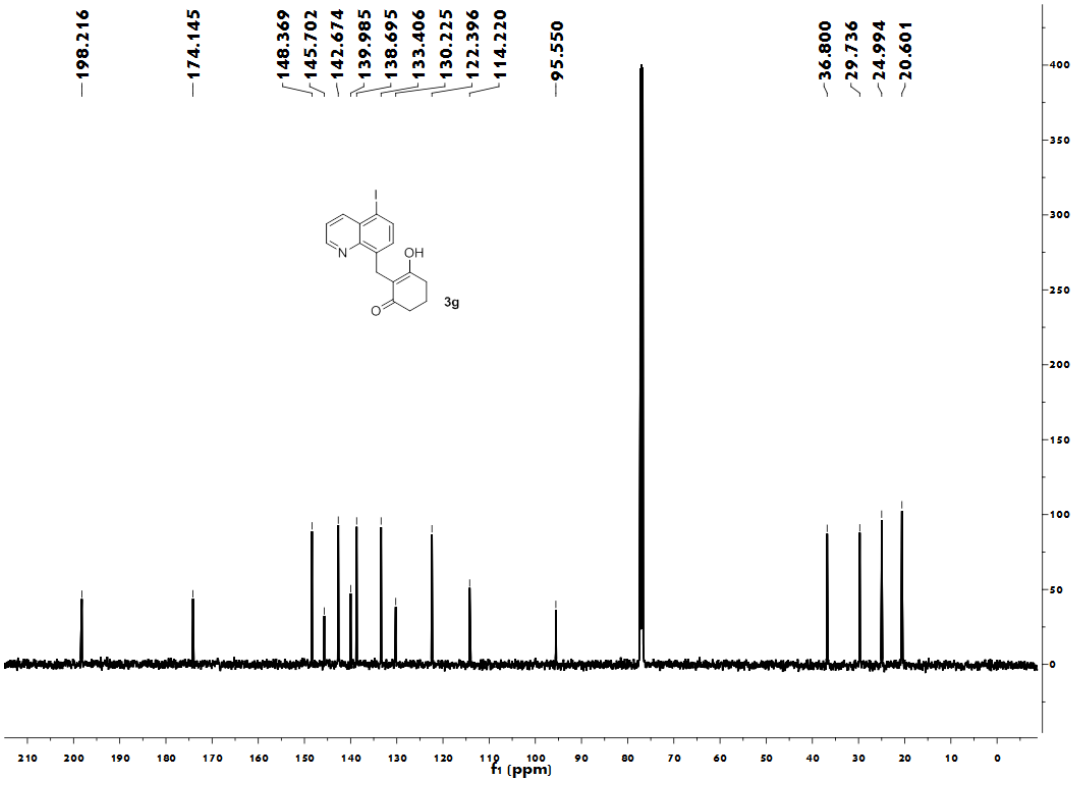
f1 (ppm)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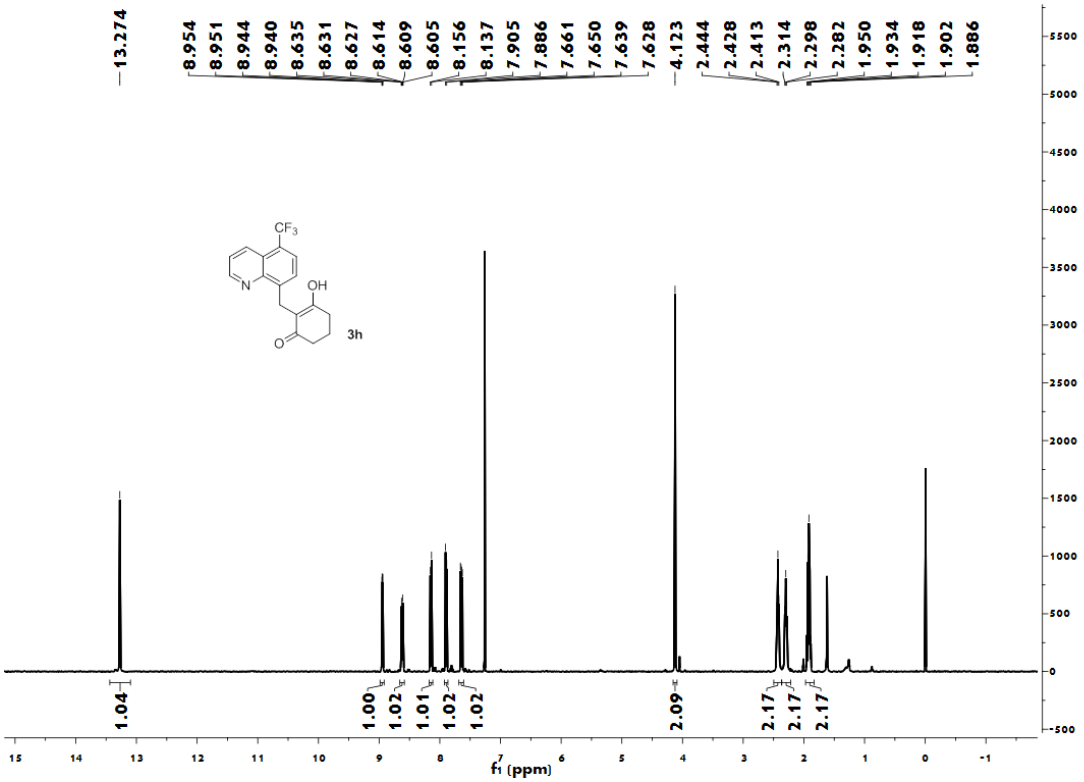
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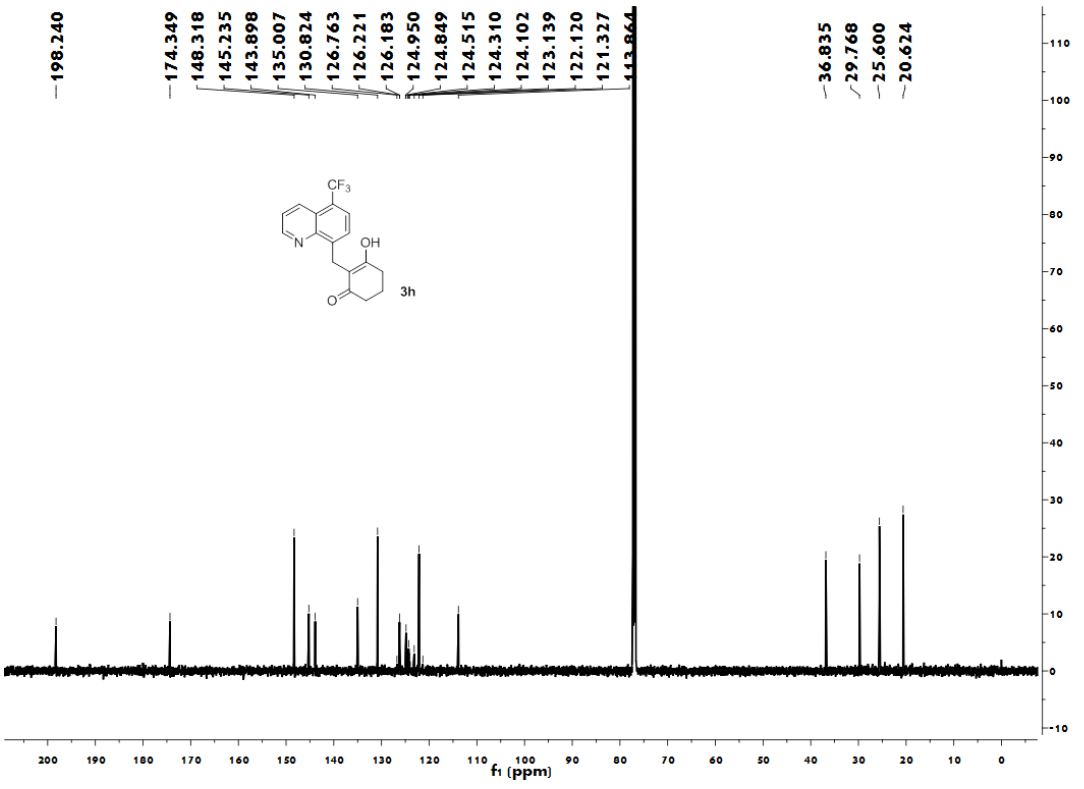
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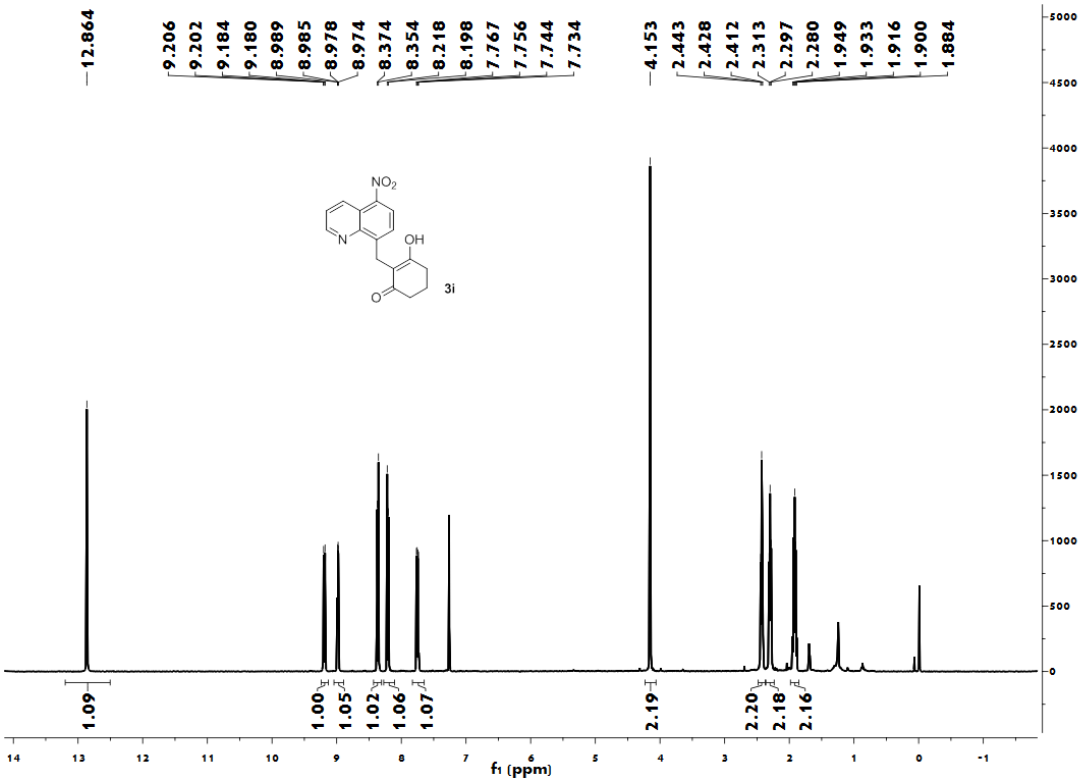
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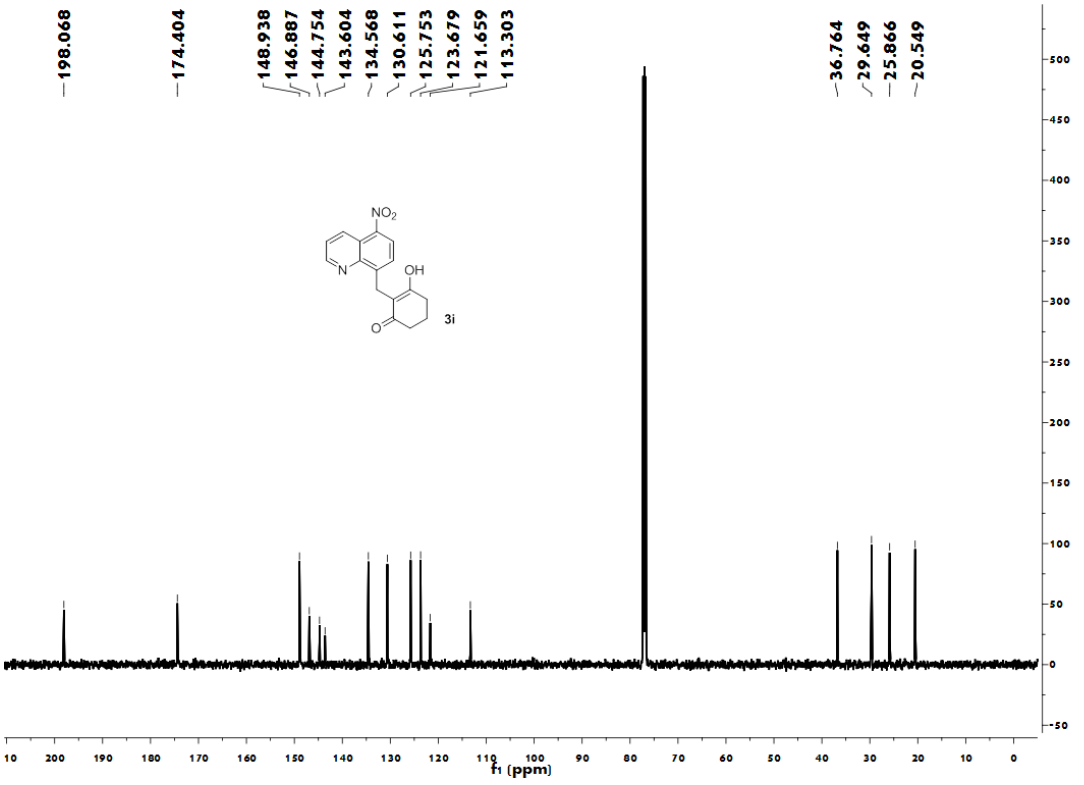
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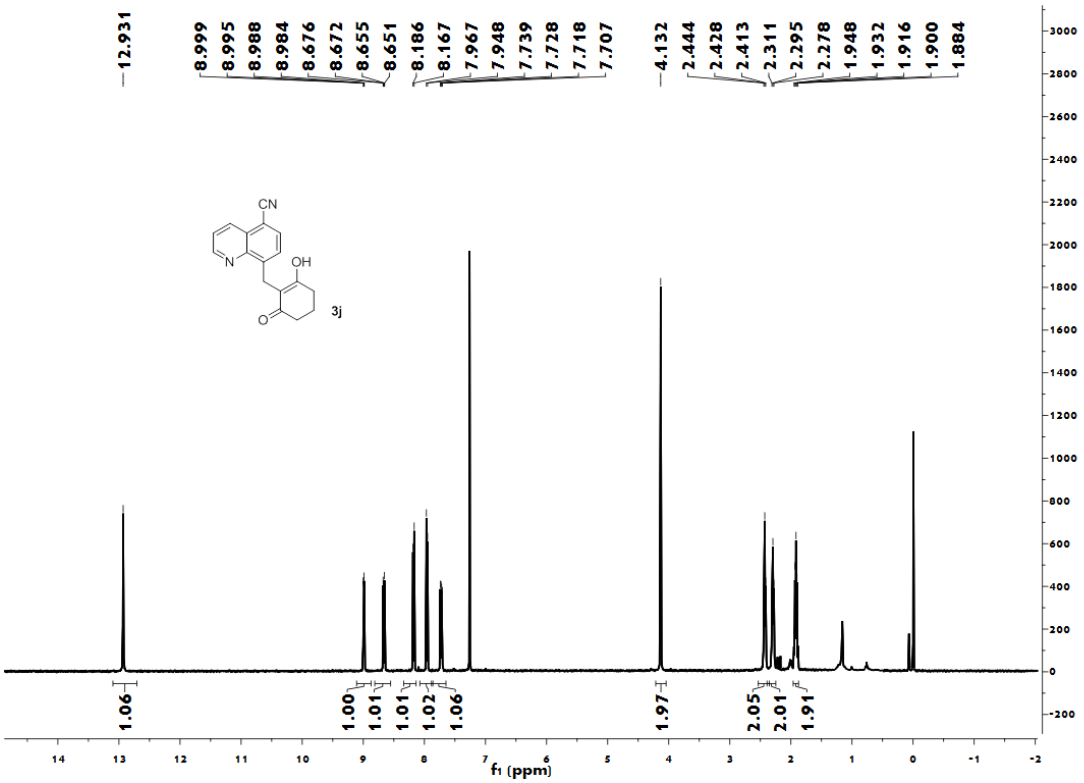
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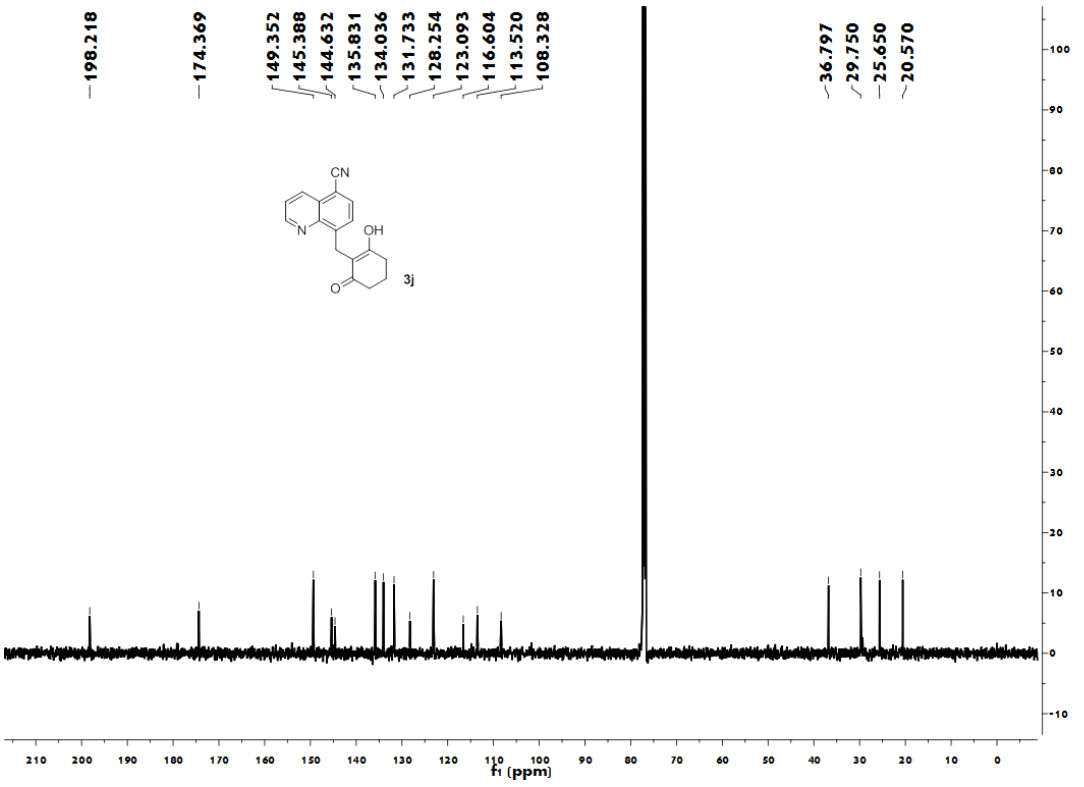
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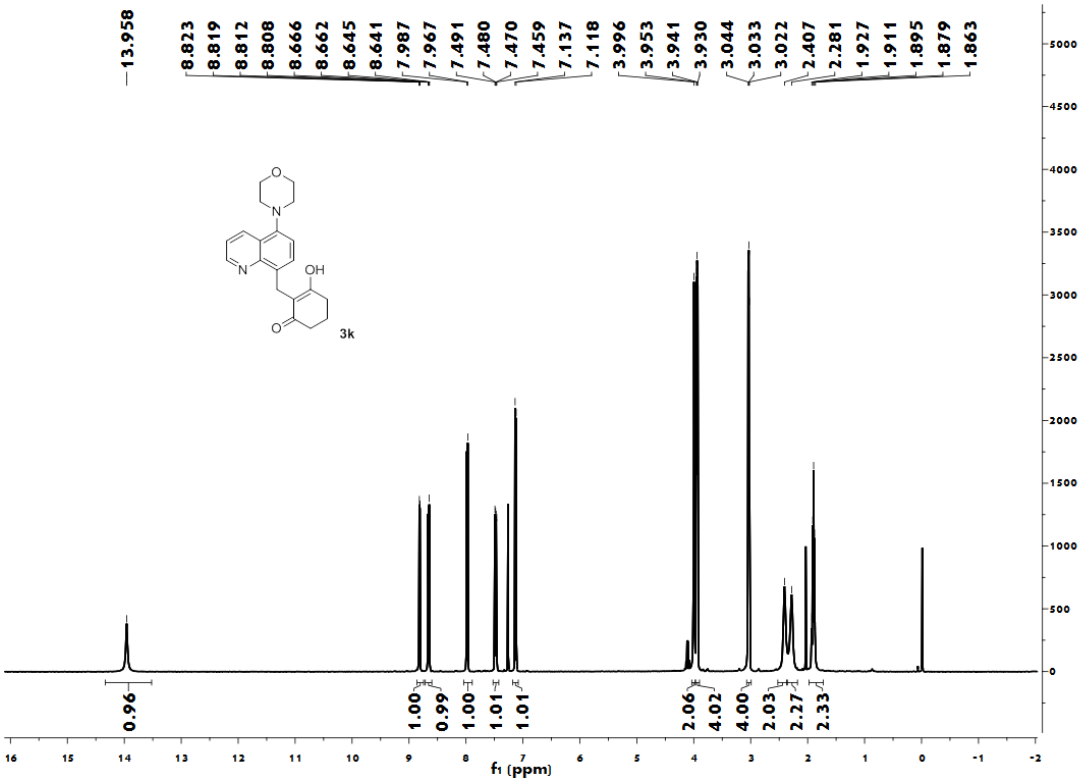
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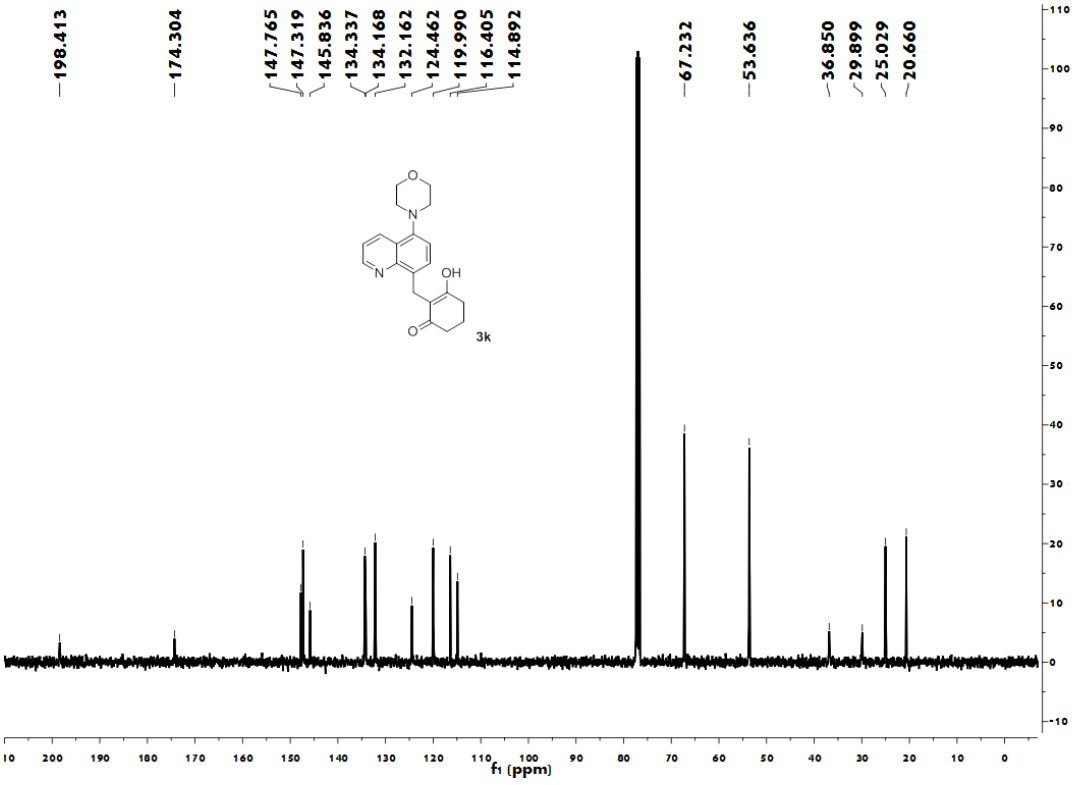
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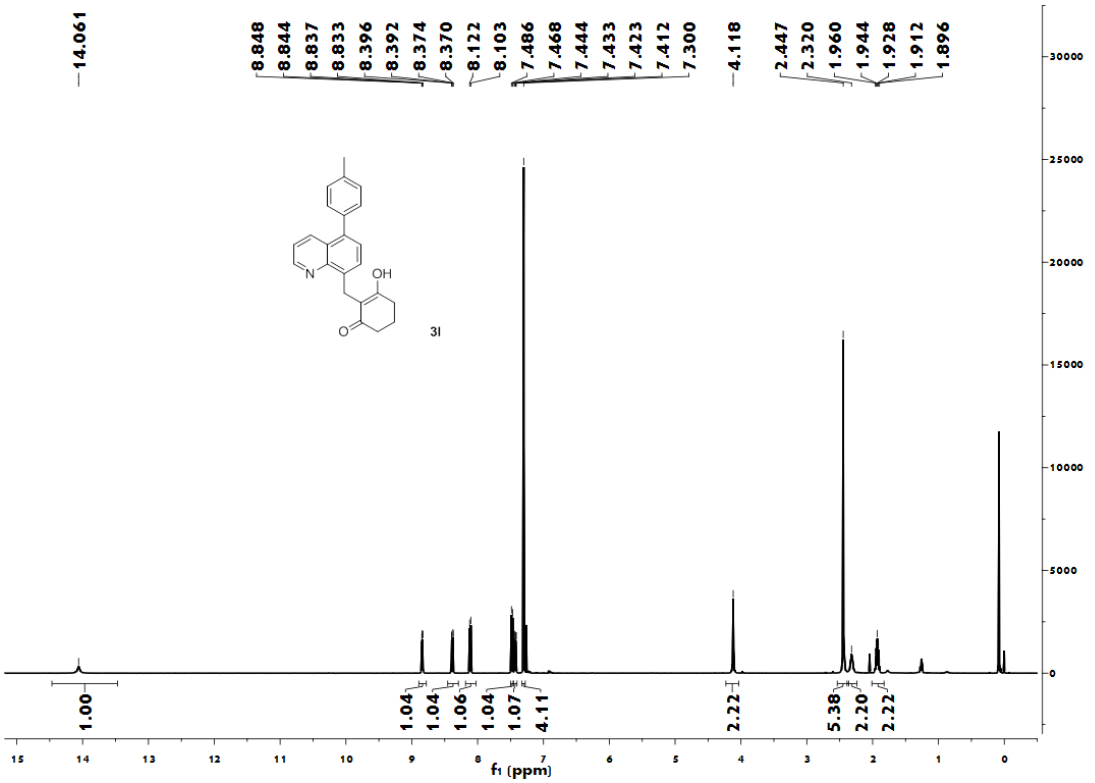
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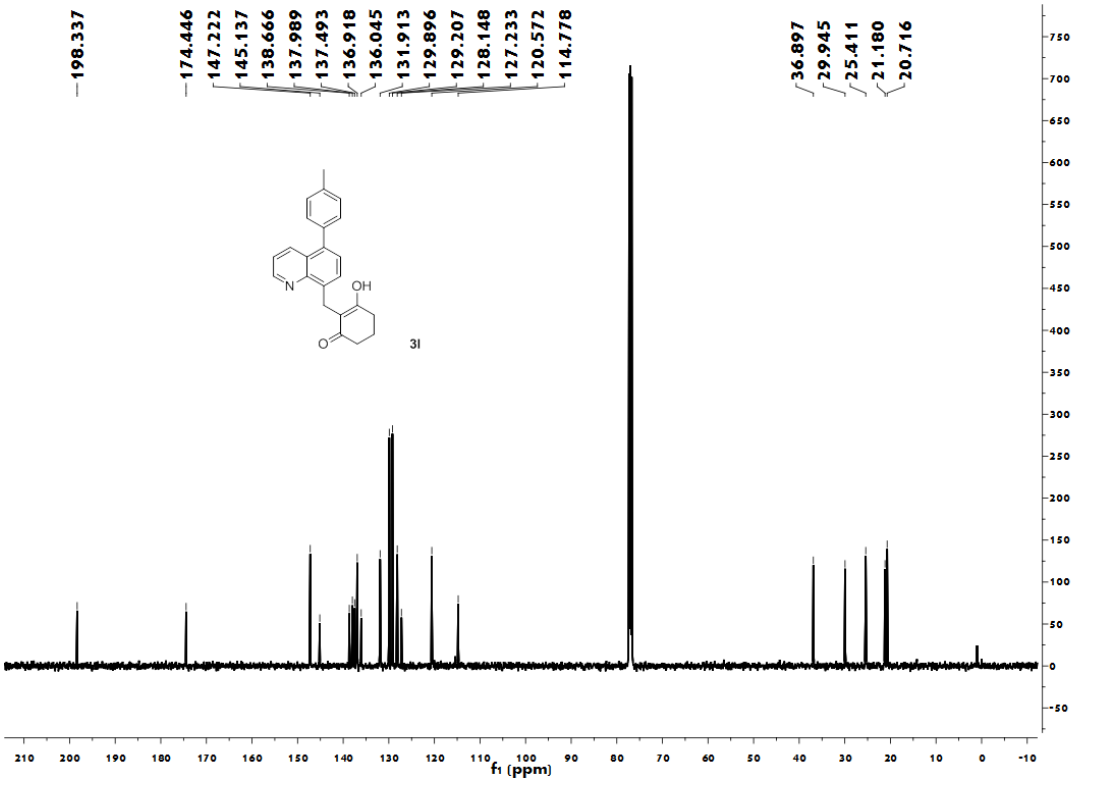
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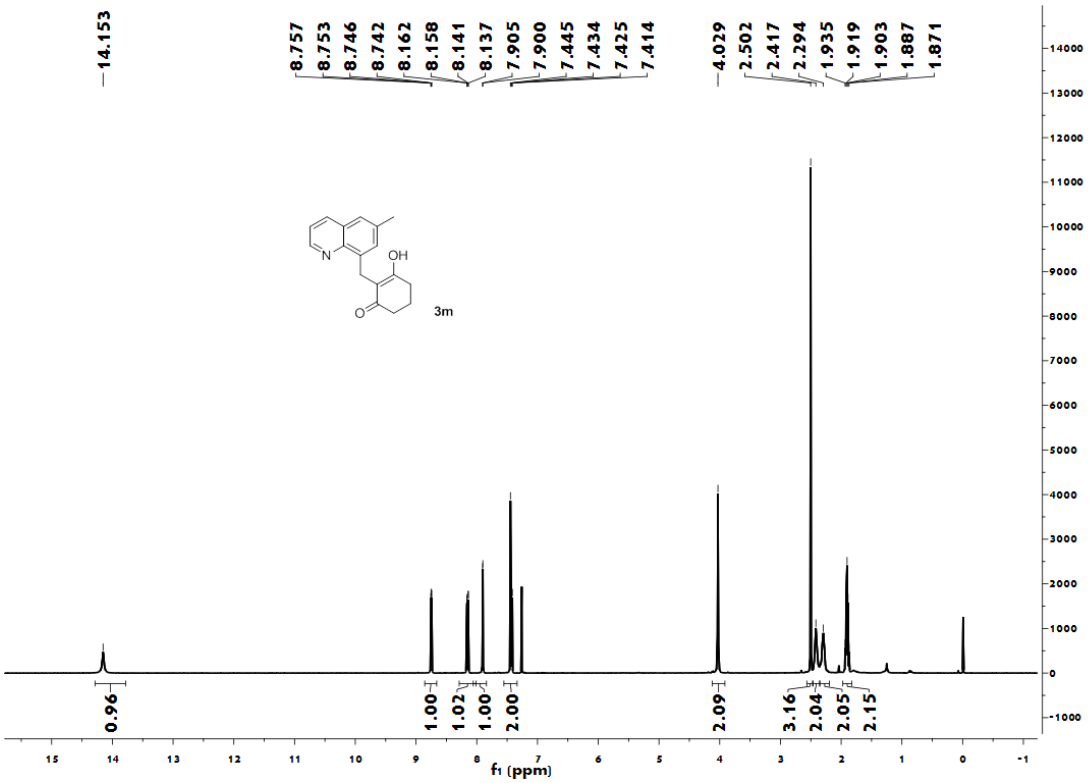
25.411
21.180
20.716
OH
O
N
3l
f1 (ppm)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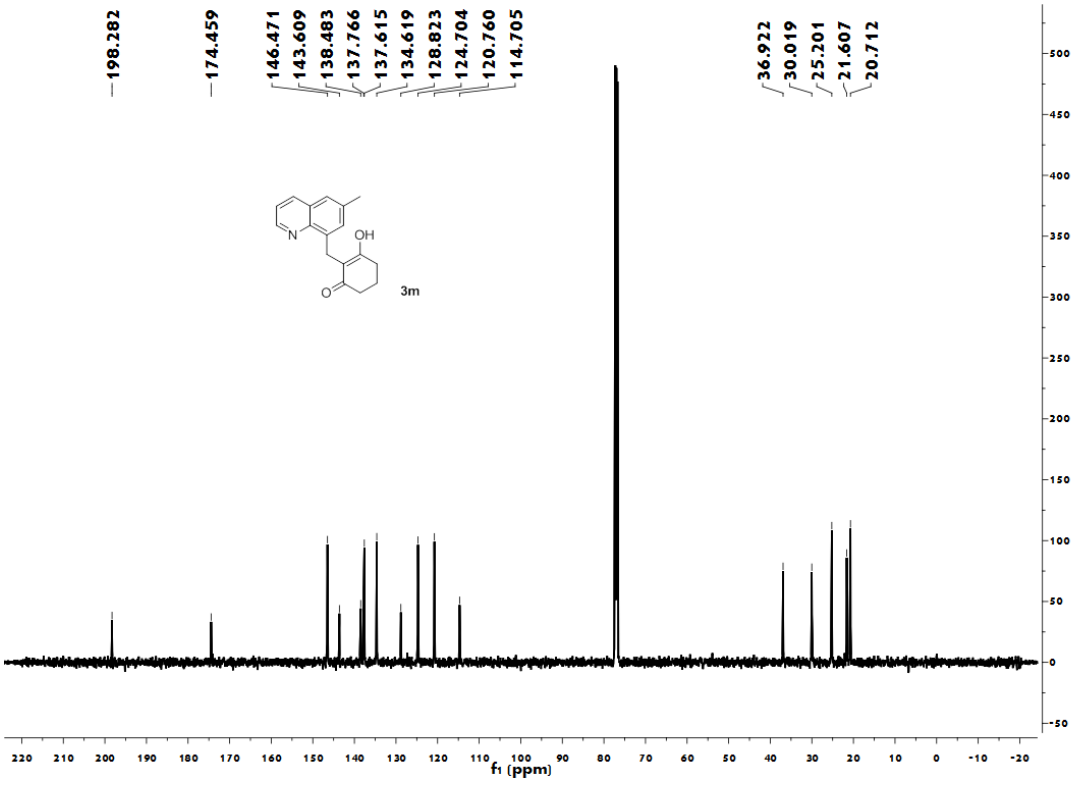
8.753
8.746
8.742
8.162
8.158
8.141
8.137
7.905
7.900
7.445
7.434
7.425
7.414
4.029
2.502
2.417
2.294
1.935
1.919
1.903
1.887
1.871
OH
N
O
3m
0.96
1.00
1.02
1.00
2.00
2.09
3.16
2.04
2.05
2.15
f1 (ppm)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146.471
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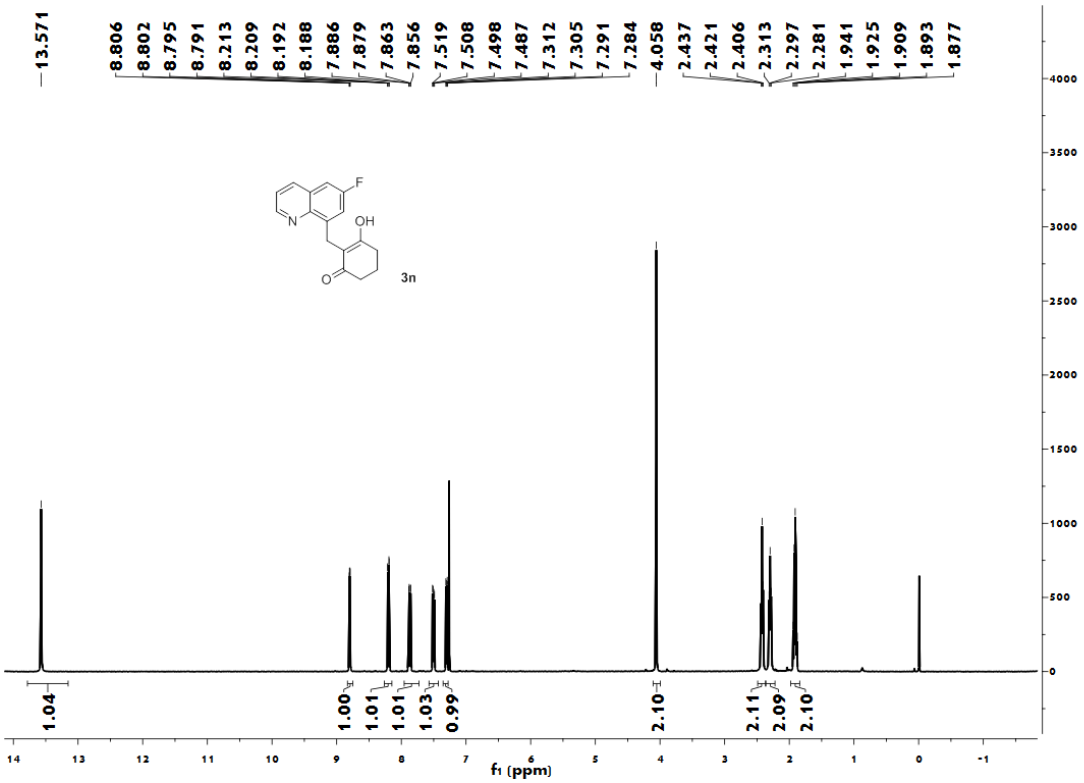
138.483
137.766
137.615
134.619
128.823
124.704
120.760
114.705
36.922
30.019
25.201
21.607
20.712
OH
N
O
3m
f1 (ppm)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8.802
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8.213
8.209
8.192
8.188
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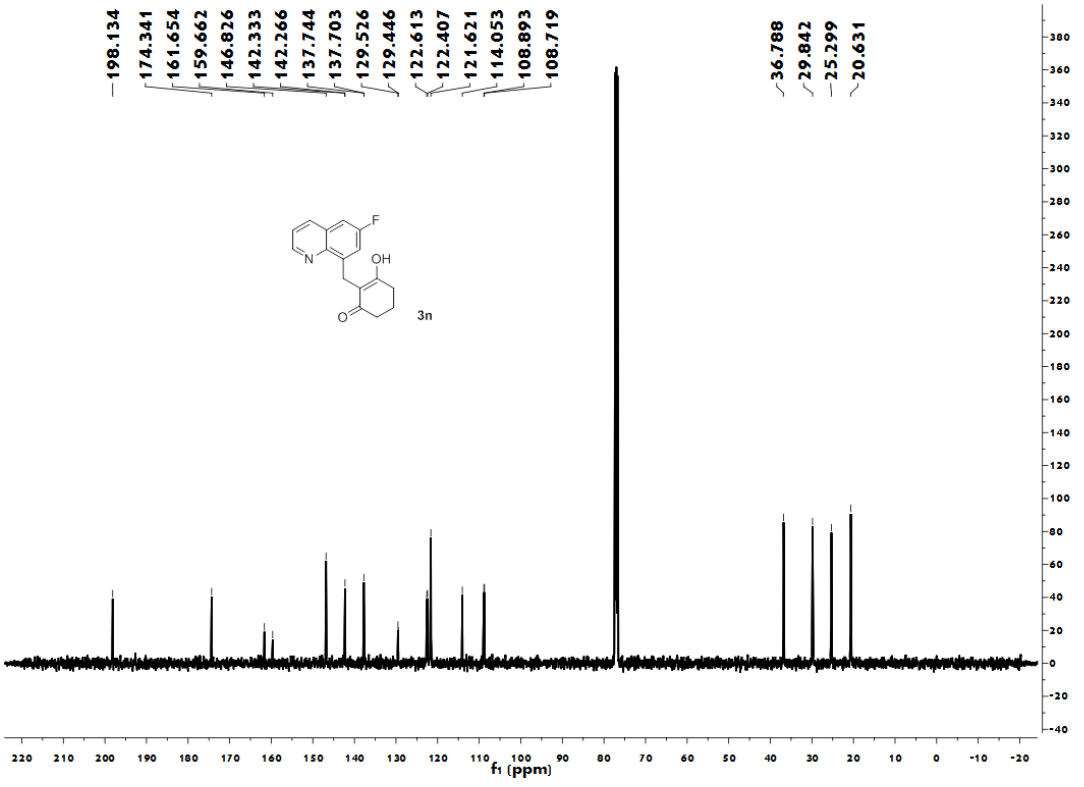
7.879
7.863
7.856
7.519
7.508
7.498
7.487
7.312
7.305
7.291
7.284
4.058
2.437
2.421
2.406
2.313
2.297
2.281
1.941
1.925
1.909
1.893
1.877
F
N
OH
O
3n
1.04
1.00
1.01
1.01
1.03
0.99
2.10
2.11
2.09
2.10
f1 (ppm)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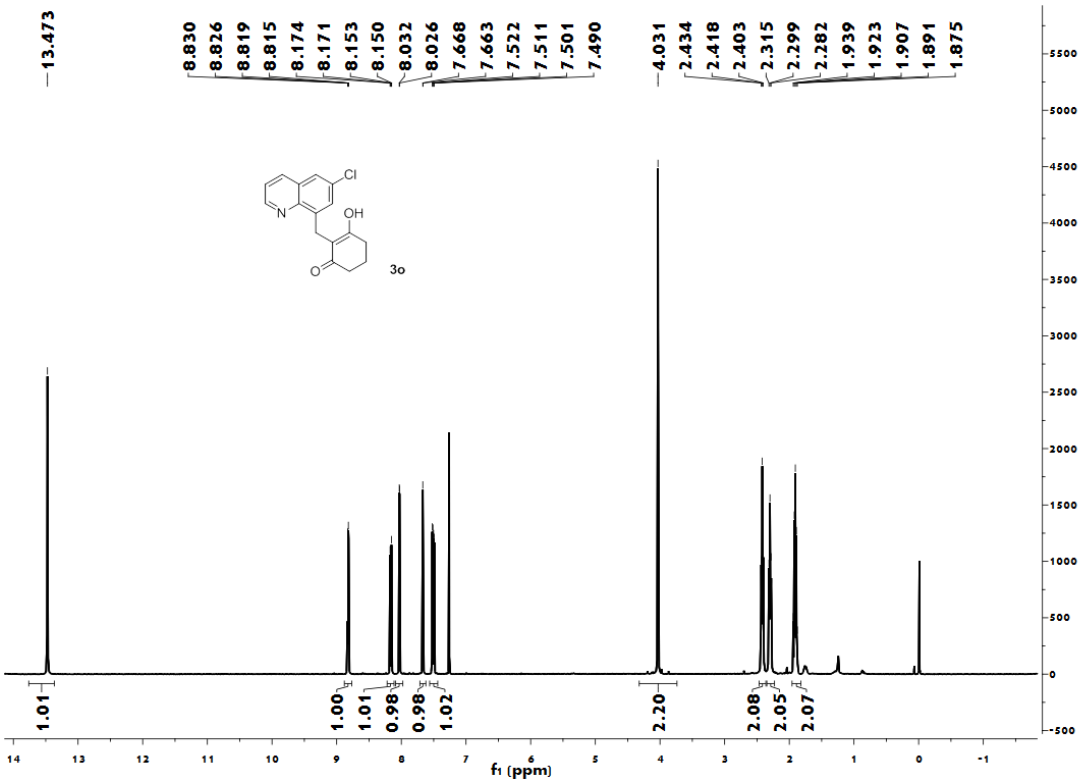
142.266
137.744
137.703
129.526
129.446
122.613
122.407
121.621
114.053
108.893
108.719
36.788
29.842
25.299
20.631
F
N
OH
O
3n
f1 (ppm)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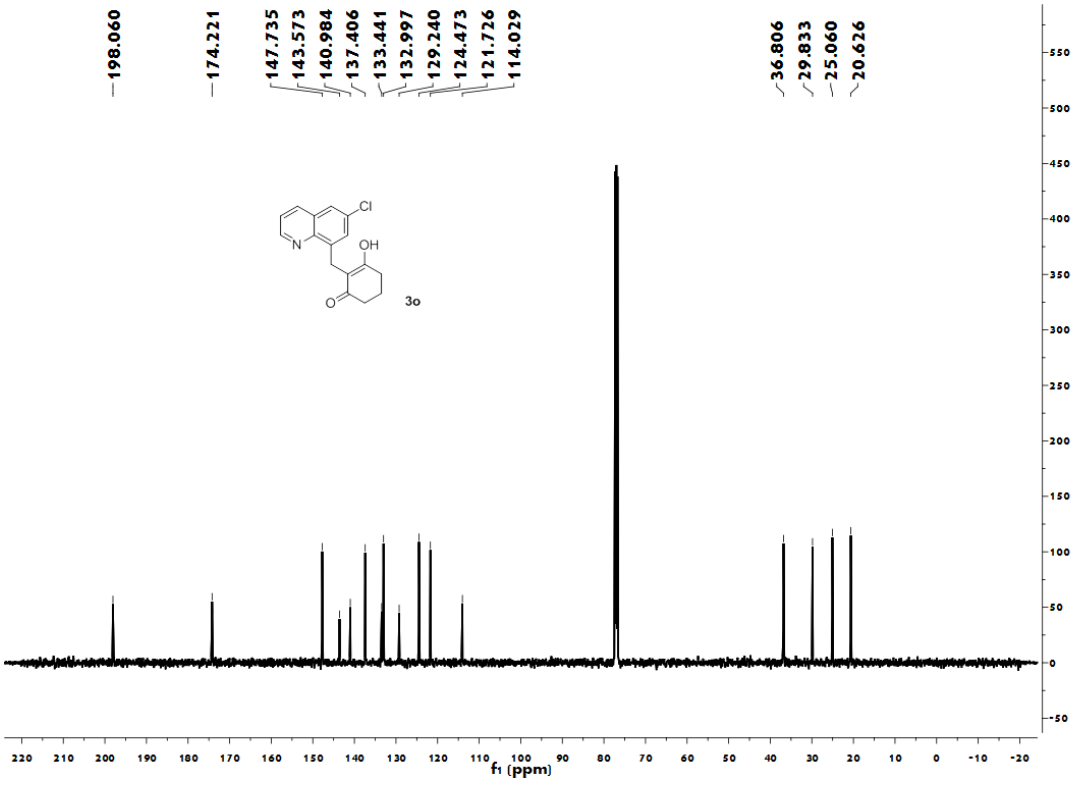
8.826
8.819
8.815
8.174
8.171
8.153
8.150
8.032
8.026
7.668
7.663
7.522
7.511
7.501
7.490
4.031
2.434
2.418
2.403
2.315
2.299
2.282
1.939
1.923
1.907
1.891
1.875
Cl
N
OH
O
3o
1.01
1.00
1.01
0.98
0.98
1.02
2.20
2.08
2.05
2.07
f1 (ppm)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143.573
140.984
137.406
133.441
132.997
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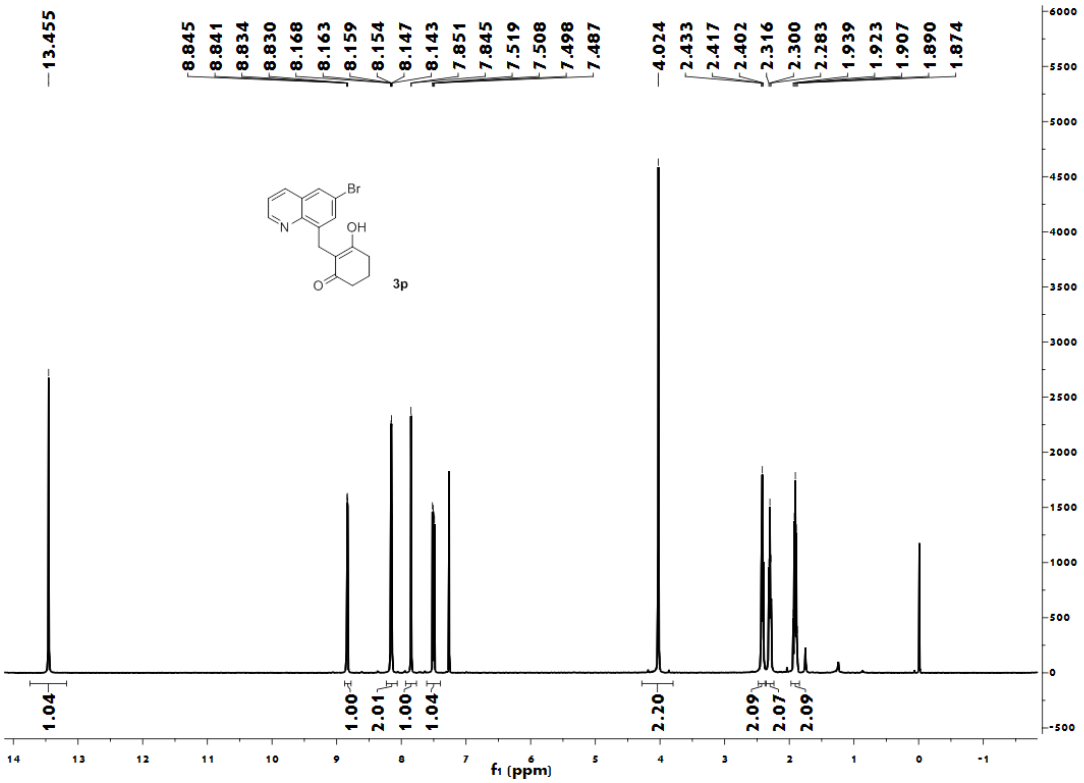
121.726
114.029
36.806
29.833
25.060
20.626
Cl
N
OH
O
3o
f1 (ppm)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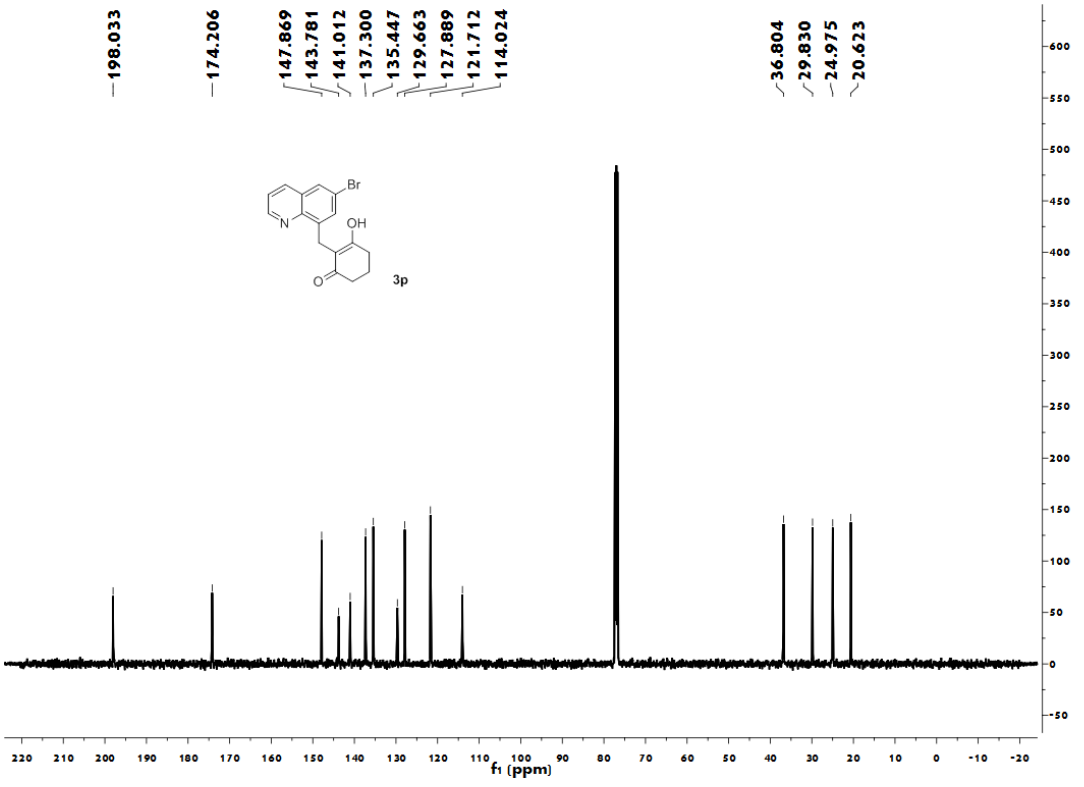
8.841
8.834
8.830
8.168
8.163
8.159
8.154
8.147
8.143
7.851
7.845
7.519
7.508
7.498
7.487
4.024
2.433
2.417
2.402
2.316
2.300
2.283
1.939
1.923
1.907
1.890
1.874
Br
OH
N
O
3p
1.04
1.00
2.01
1.00
1.04
2.20
2.09
2.07
2.09
f1 (ppm)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147.869
143.781
141.012
137.300
135.447
129.663
127.889
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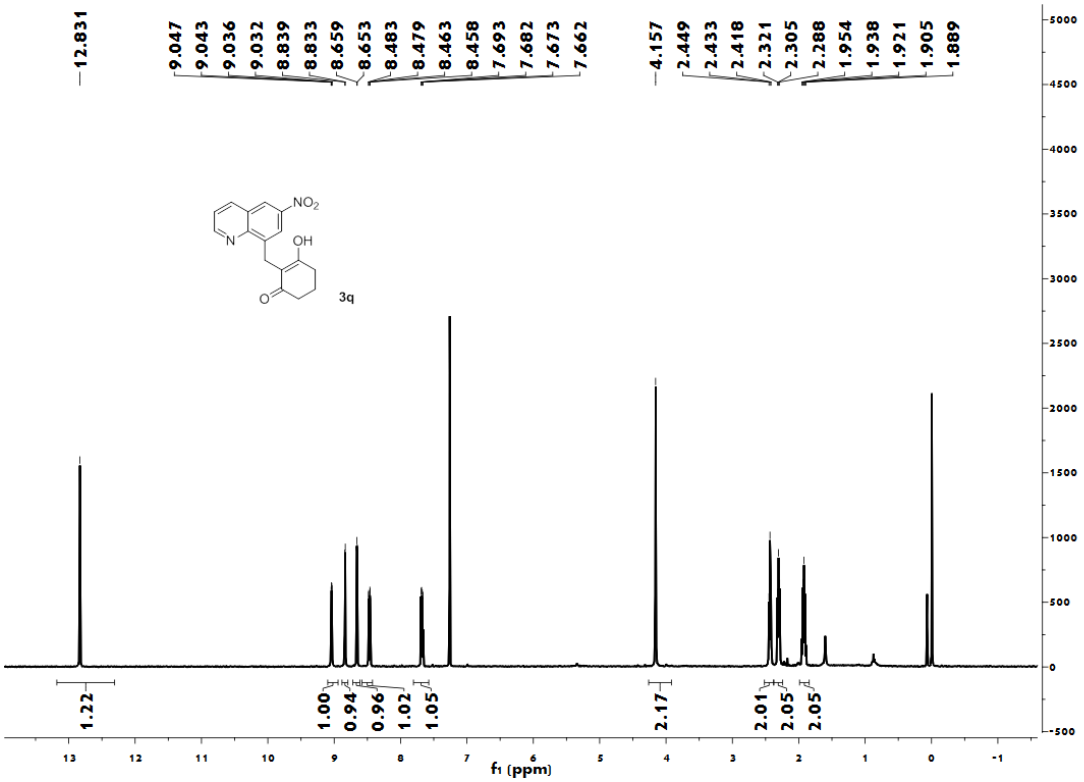
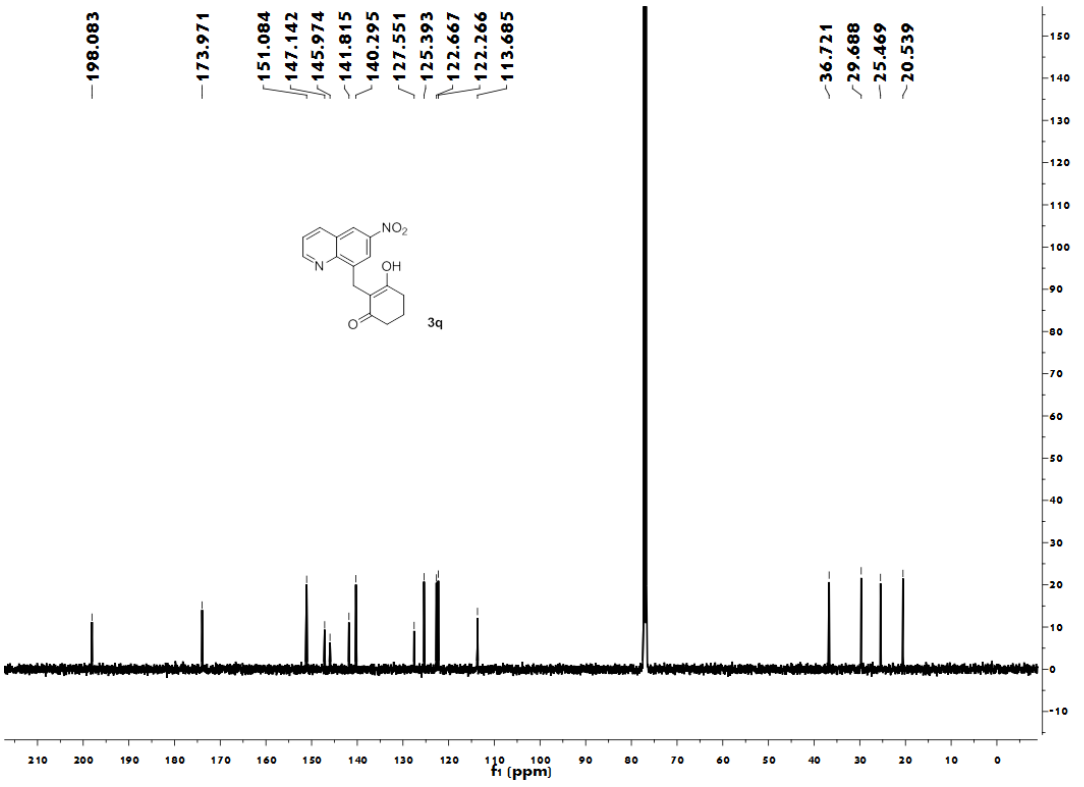
114.024
36.804
29.830
24.975
20.623
Br
OH
N
O
3p
f1 (ppm)


12.831
9.047
9.043
9.036
9.032
8.839
8.833
8.659
8.653
8.483
8.479
8.463
8.458
7.693
7.682
7.673
7.662
4.157
2.449
2.433
2.418
2.321
2.305
2.288
1.954
1.938
1.921
1.905
1.889
NO2
OH
N
O
3q
1.22
1.00
0.94
0.96
1.02
1.05
2.17
2.01
2.05
2.05
f1 (ppm)


198.083
173.971
151.084
147.142
145.974
141.815
140.295
127.551
125.393
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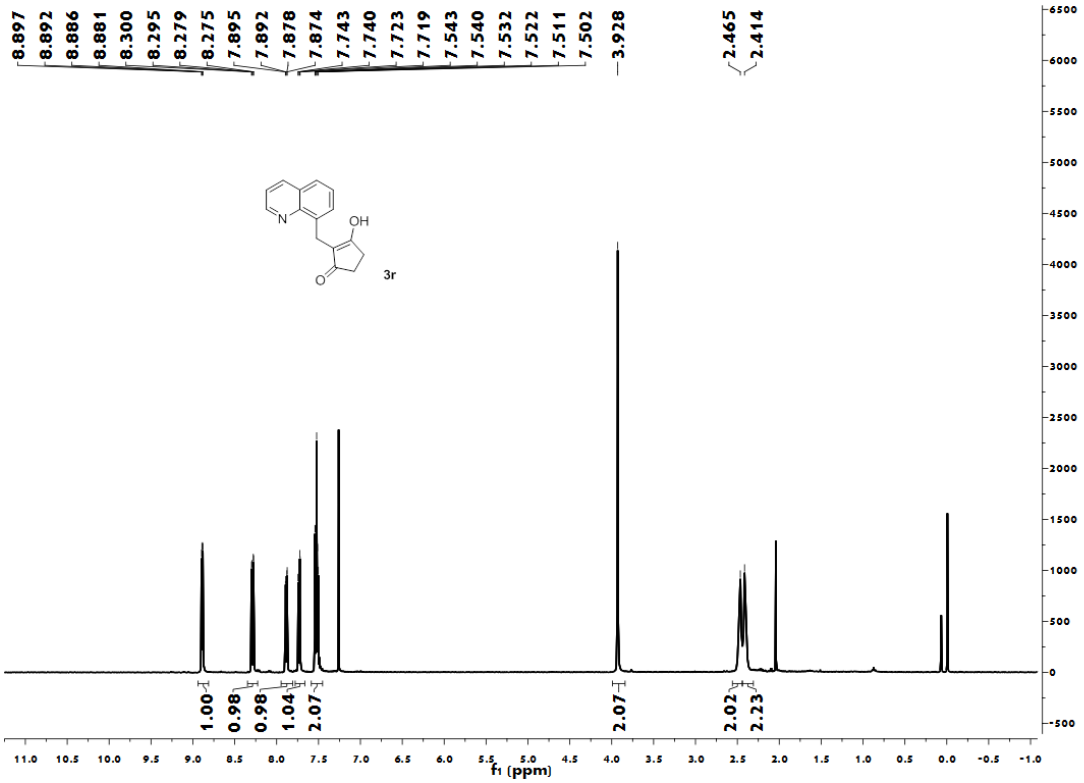
122.266
113.685
36.721
29.688
25.469
20.539
NO2
OH
N
O
3q
f1 (ppm)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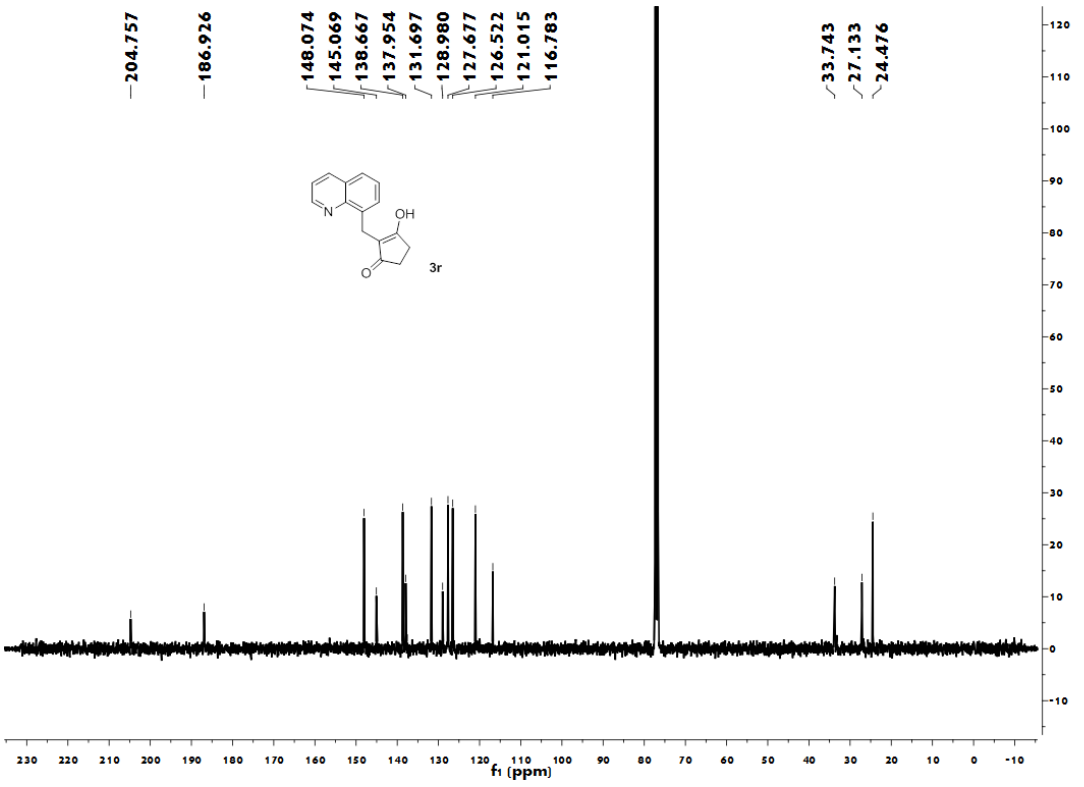
8.892
8.886
8.881
8.300
8.295
8.279
8.275
7.895
7.892
7.878
7.874
7.743
7.740
7.723
7.719
7.543
7.540
7.532
7.522
7.511
7.502
3.928
2.465
2.414
OH
O
3r
1.00
0.98
0.98
1.04
2.07
2.07
2.02
2.23
f1 (ppm)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186.926
148.074
145.069
138.667
137.954
131.697
128.980
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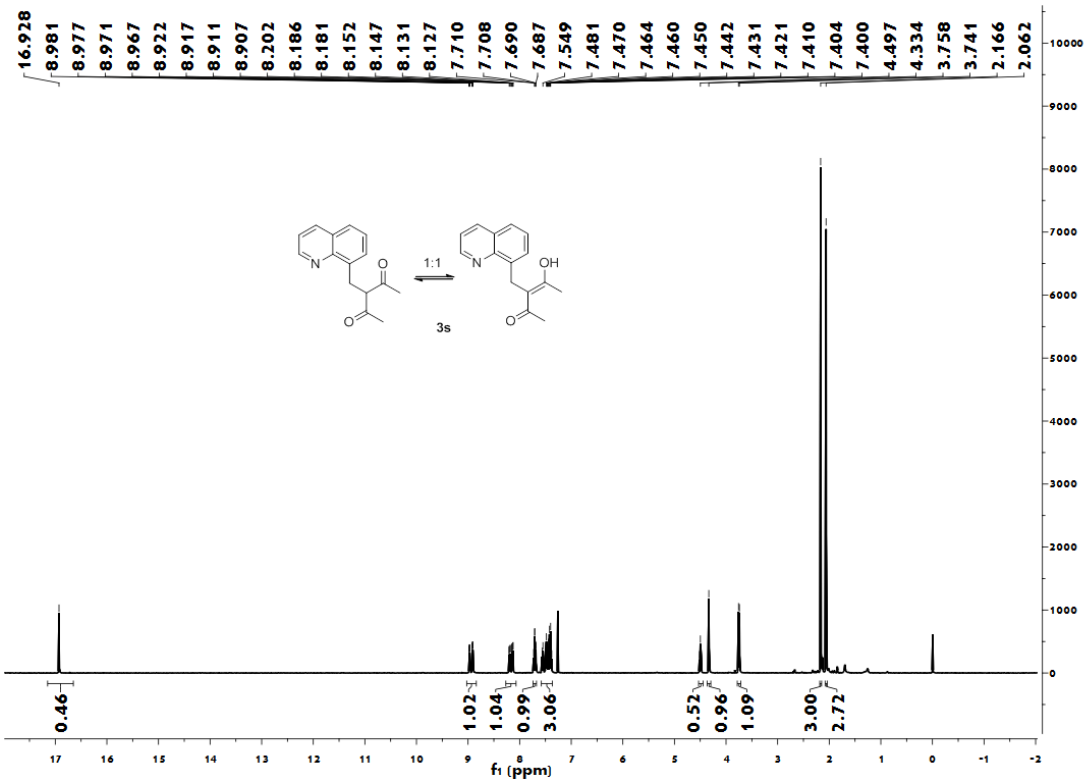
121.015
116.783
33.743
27.133
24.476
OH
O
3r
f1 (ppm)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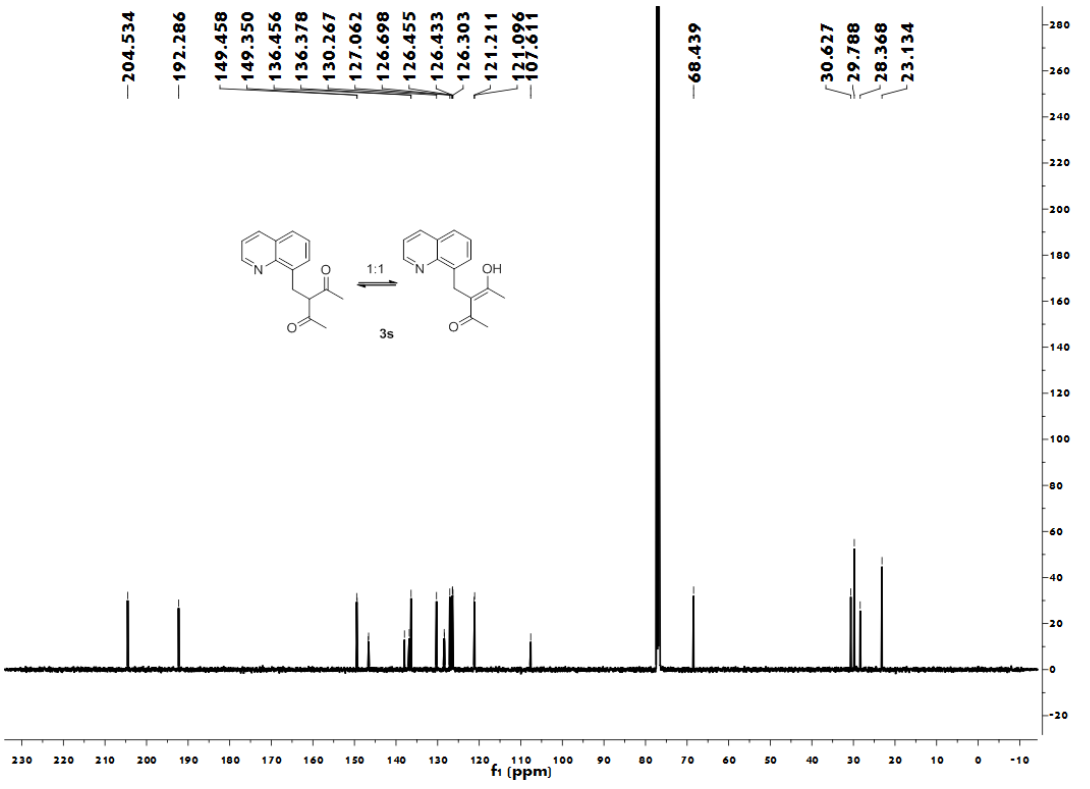
8.977
8.971
8.967
8.922
8.917
8.911
8.907
8.202
8.186
8.181
8.152
8.147
8.131
8.127
7.710
7.708
7.690
7.687
7.549
7.481
7.470
7.464
7.460
7.450
7.442
7.431
7.421
7.410
7.404
7.400
4.497
4.334
3.758
3.741
2.166
2.062
1:1
OH
3s
0.46
1.02
1.04
0.99
3.06
0.52
0.96
1.09
3.00
2.72
f1 (ppm)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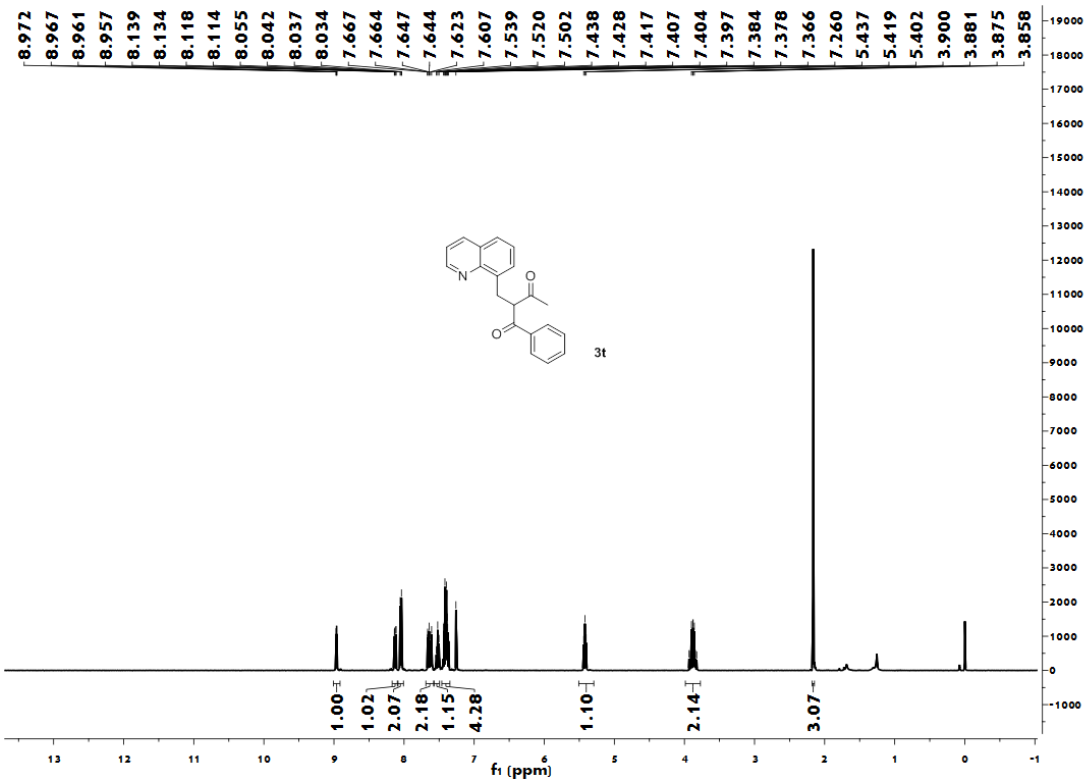
149.458
149.350
136.456
136.378
130.267
127.062
126.698
126.455
126.433
126.303
121.211
121.096
107.611
68.439
30.627
29.788
28.368
23.134
1:1
OH
3s
f1 (ppm)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8.957
8.139
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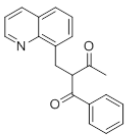
8.118
8.114
8.055
8.042
8.037
8.034
7.667
7.664
7.647
7.644
7.623
7.607
7.539
7.520
7.502
7.438
7.428
7.417
7.407
7.404
7.397
7.384
7.378
7.366
7.260
5.437
5.419
5.402
3.900
3.881
3.875
3.858
1.00
1.02
2.07
2.18
1.15
4.28
1.10
2.14
3.07
f1 (ppm)


3t

204.001
197.022
149.324
146.753
136.867
136.551
136.439
133.406
130.917
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128.575
128.364
126.955
126.330
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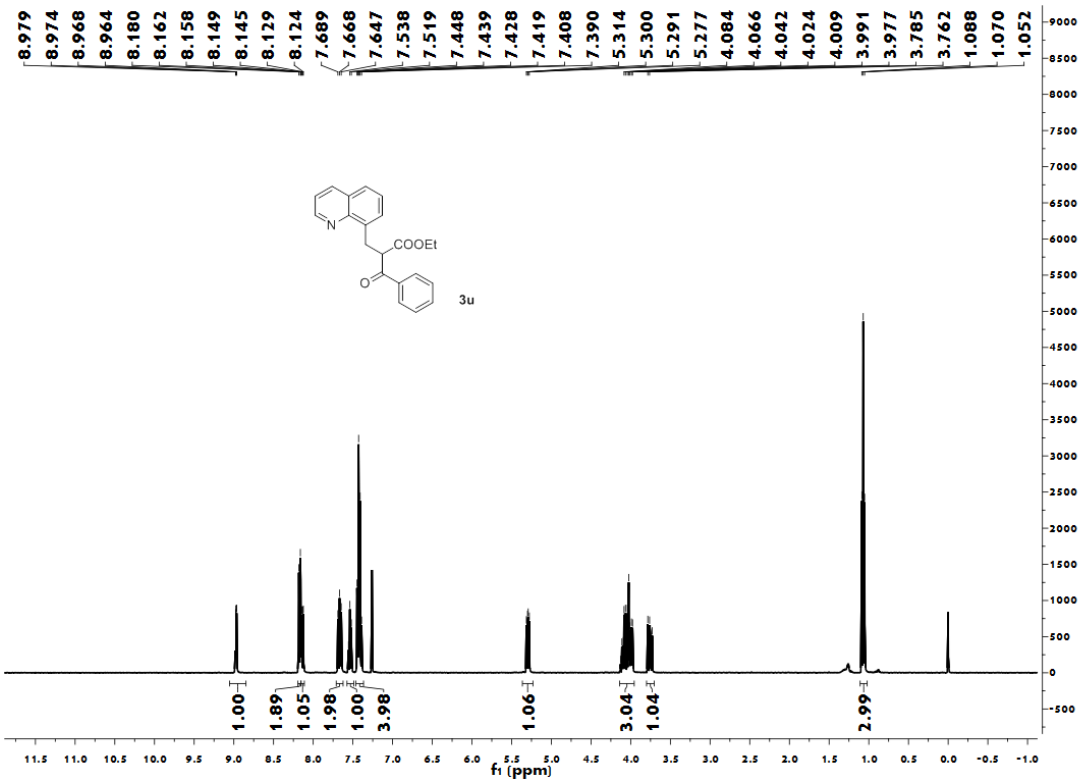
31.856
29.224
f1 (ppm)

3t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8.149
8.145
8.129
8.124
7.689
7.668
7.647
7.538
7.519
7.448
7.439
7.428
7.419
7.408
7.390
5.314
5.300
5.291
5.277
4.084
4.066
4.042
4.024
4.009
3.991
3.977
3.785
3.762
1.088
1.070
1.052
COOEt
O
N
3u
1.00
1.89
1.05
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1.00
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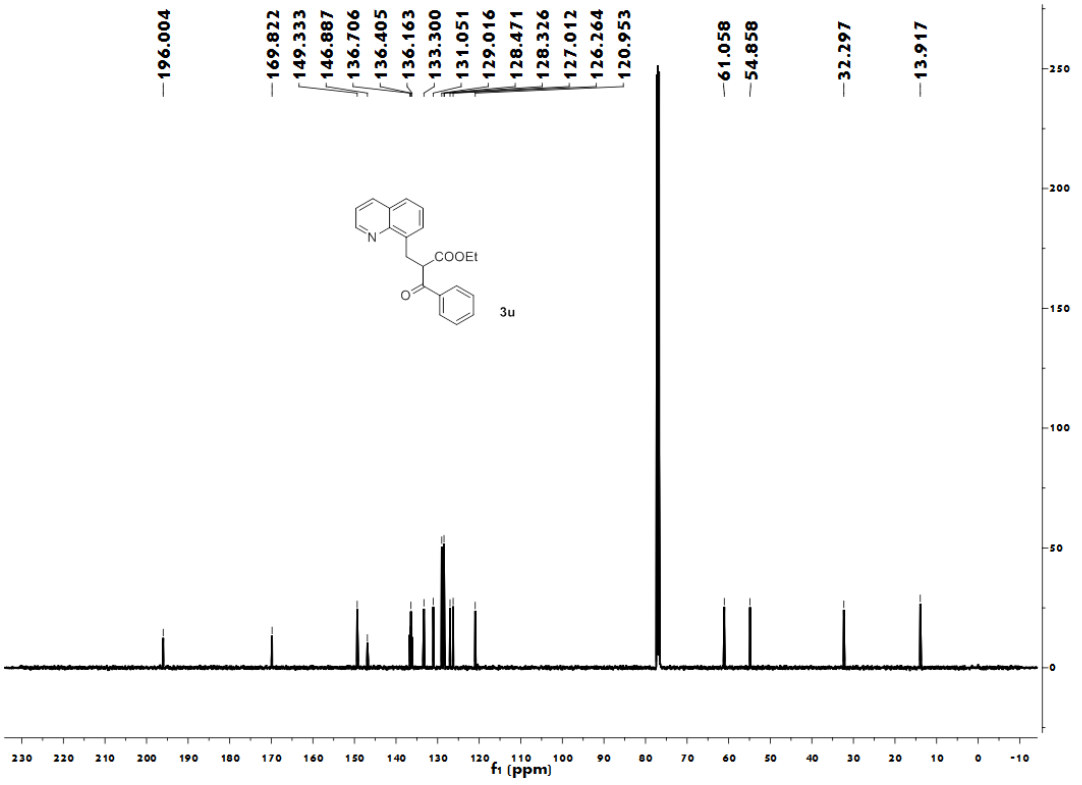
1.06
3.04
1.04
2.99
f1 (ppm)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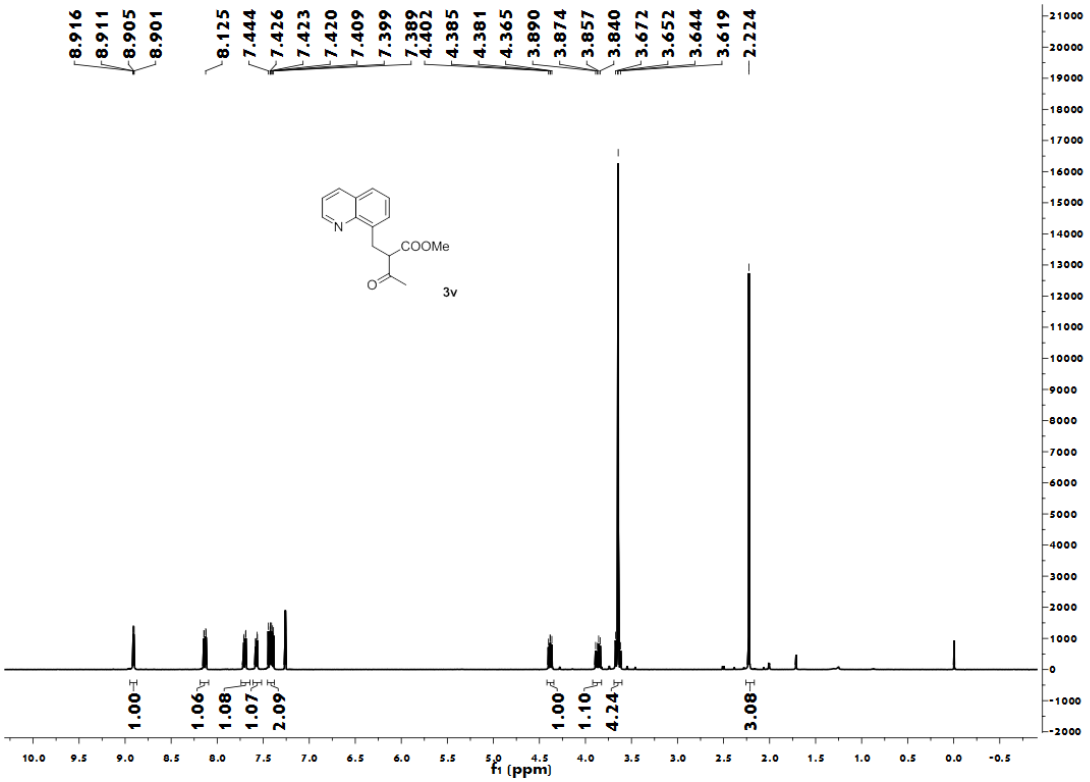
120.953
61.058
54.858
32.297
13.917
COOEt
O
N
3u
f1 (ppm)


8.916
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7.426
7.423
7.420
7.409
7.399
7.389
4.402
4.385
4.381
4.365
3.890
3.874
3.857
3.840
3.672
3.652
3.644
3.619
2.224
COOMe
3v
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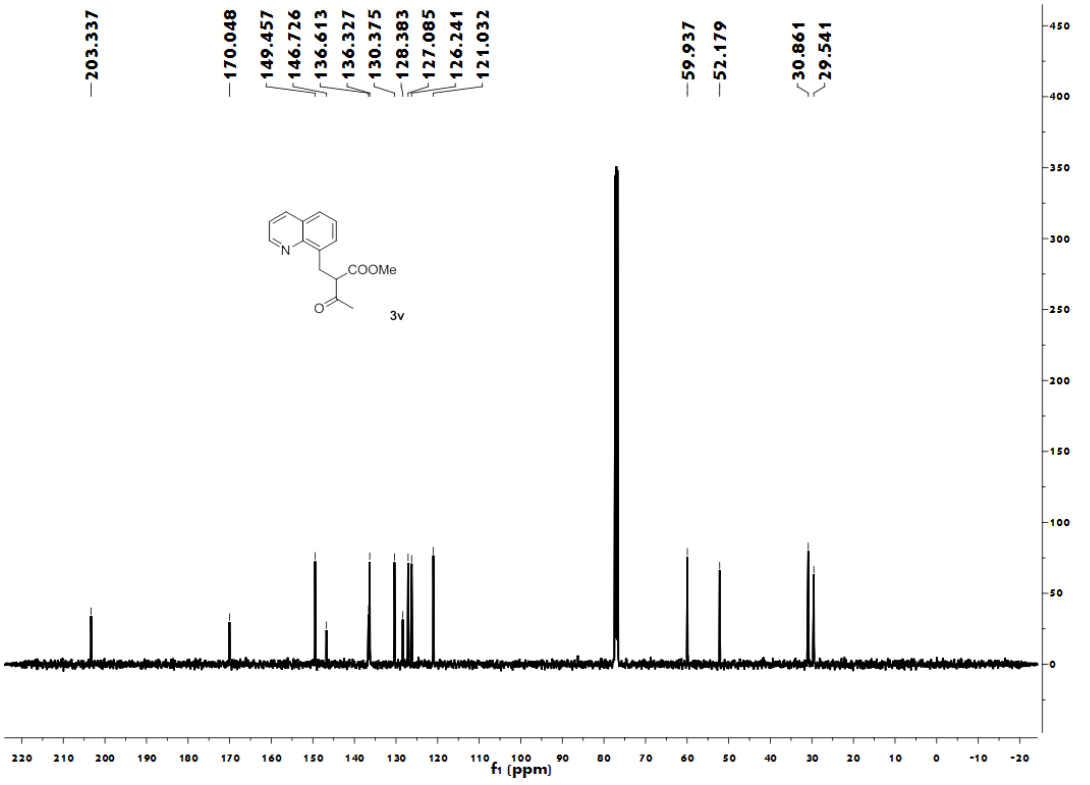
1.06
1.08
1.07
2.09
1.00
1.10
4.24
3.08
f1 (ppm)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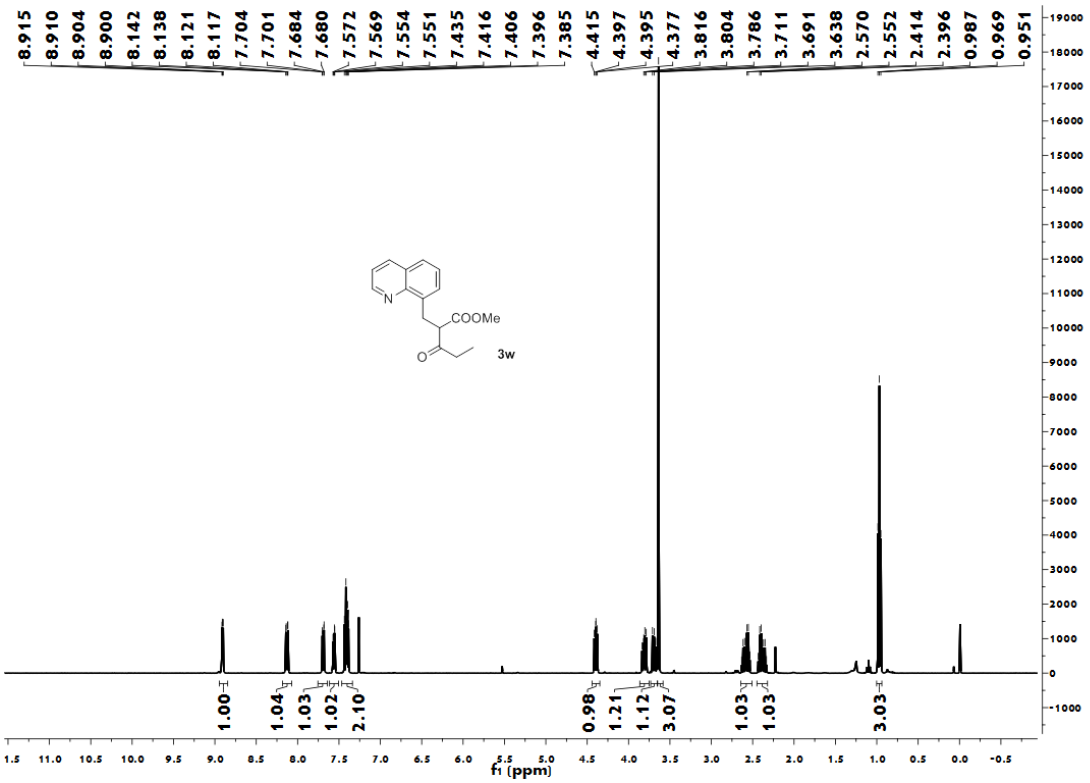
29.541
COOMe
3v
f1 (ppm)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8.900
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8.117
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7.572
7.569
7.554
7.551
7.435
7.416
7.406
7.396
7.385
4.415
4.397
4.395
4.377
3.816
3.804
3.786
3.711
3.691
3.638
2.570
2.552
2.414
2.396
0.987
0.969
0.951
COOMe
3w
1.00
1.04
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1.12
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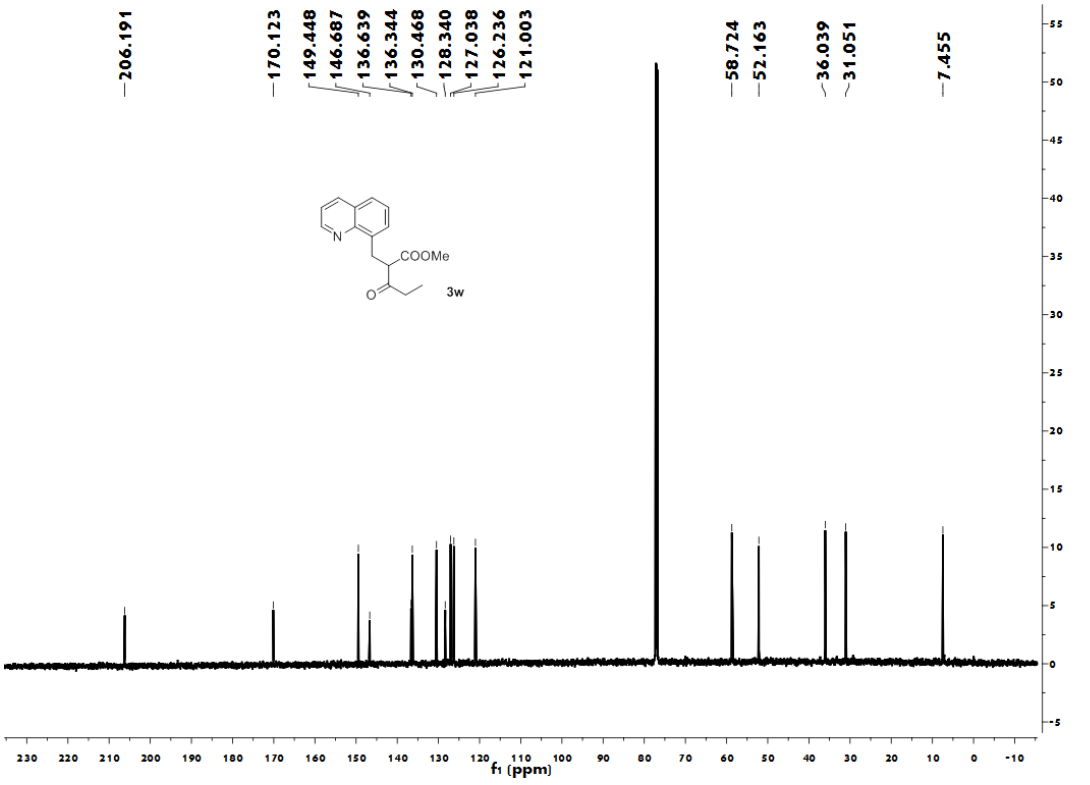
1.03
1.03
3.03
f1 (ppm)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121.003
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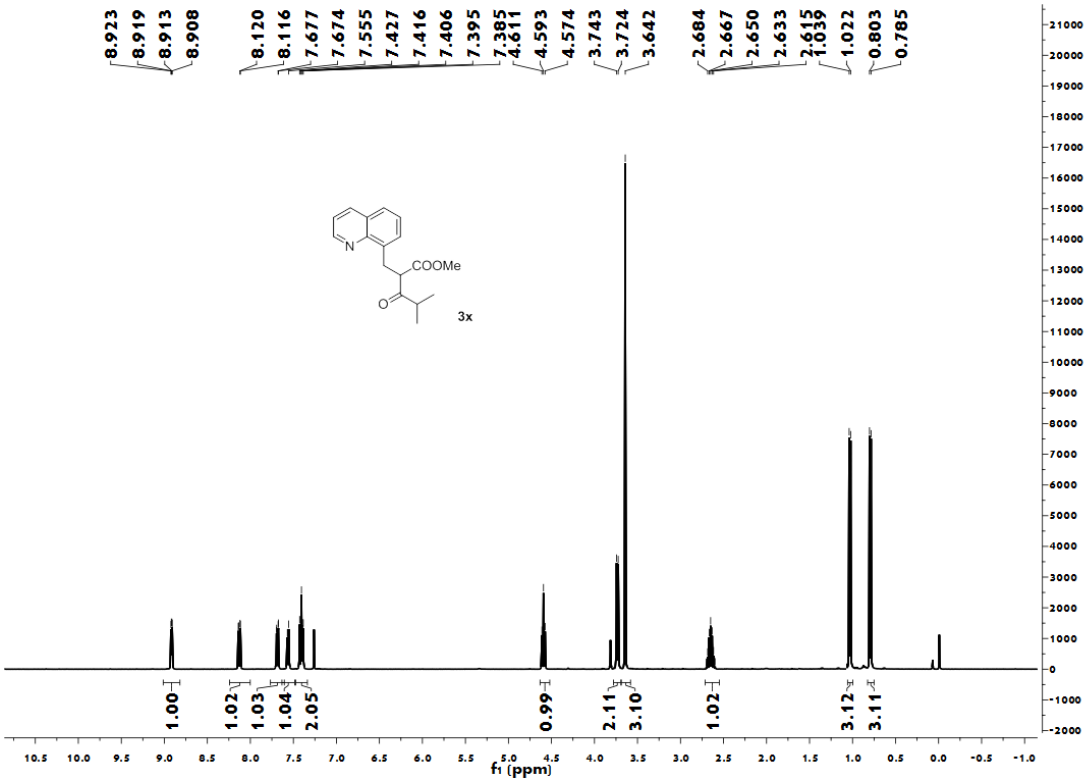
52.163
36.039
31.051
7.455
COOMe
3w
f1 (ppm)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7.674
7.555
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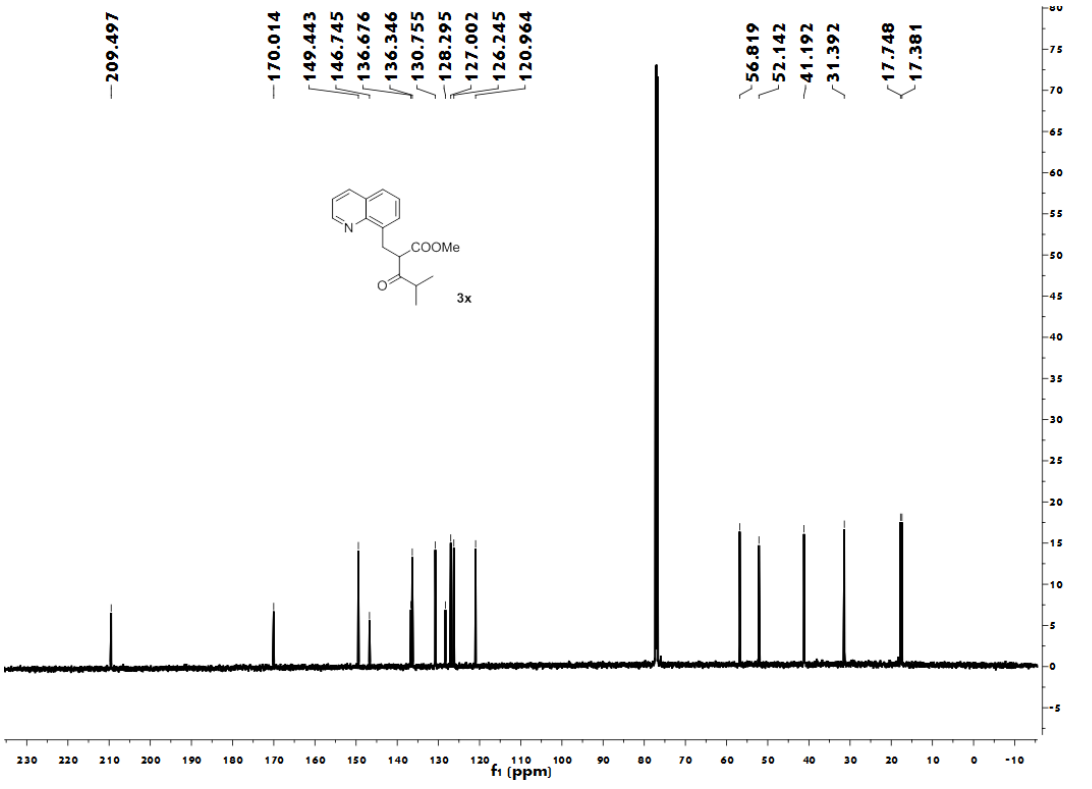
7.416
7.406
7.395
7.385
4.611
4.593
4.574
3.743
3.724
3.642
2.684
2.667
2.650
2.633
2.615
1.039
1.022
0.803
0.785
COOMe
O
3x
1.00
1.02
1.03
1.04
2.05
0.99
2.11
3.10
1.02
3.12
3.11
f1 (ppm)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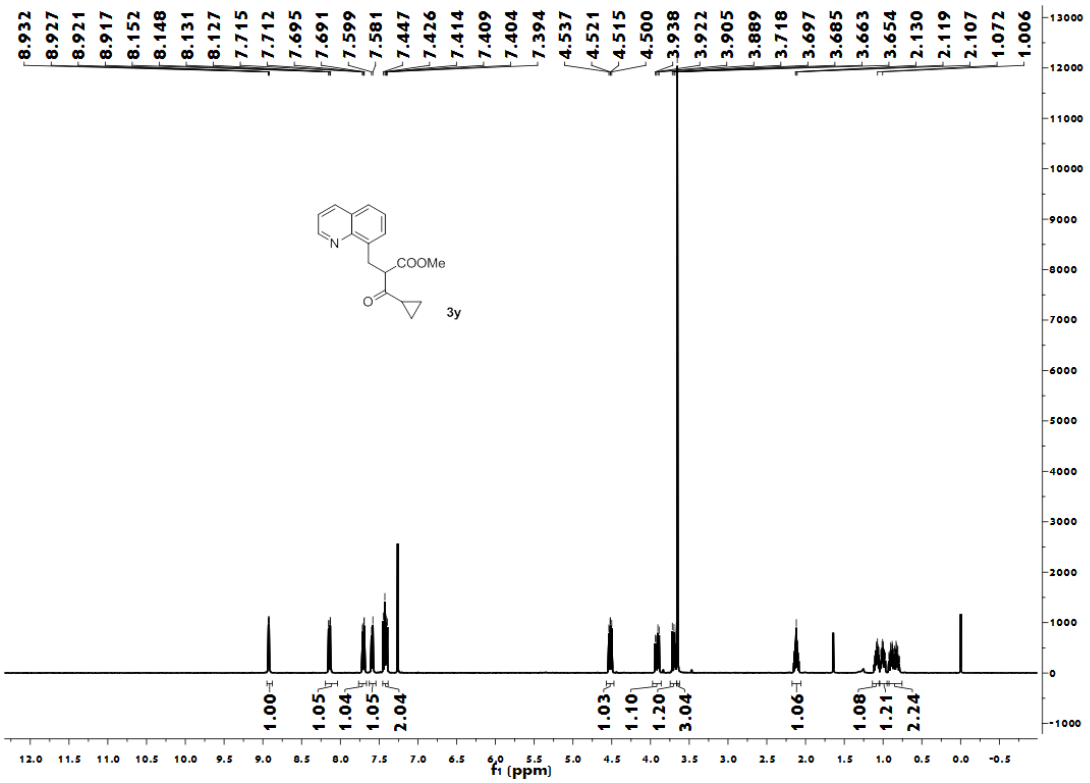
17.748
17.381
COOMe
O
3x
f1 (ppm)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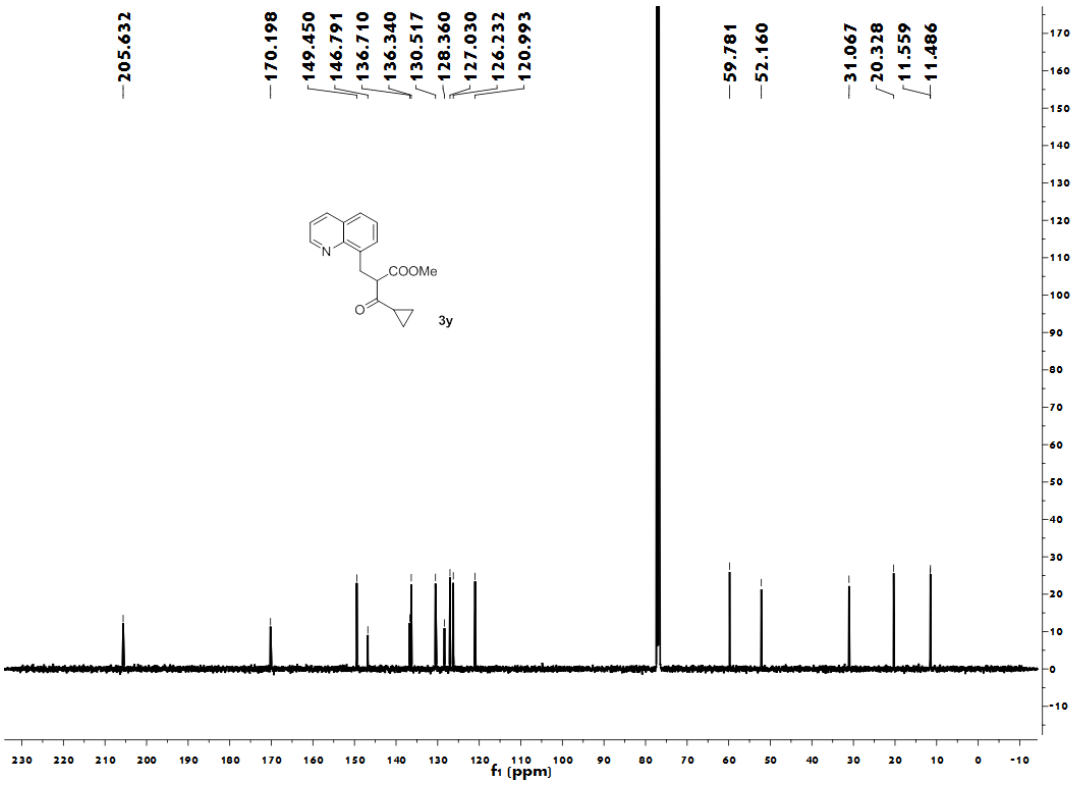
7.691
7.599
7.581
7.447
7.426
7.414
7.409
7.404
7.394
4.537
4.521
4.515
4.500
3.938
3.922
3.905
3.889
3.718
3.697
3.685
3.663
3.654
2.130
2.119
2.107
1.072
1.006
COOMe
O
3y
1.00
1.05
1.04
1.05
2.04
1.03
1.10
1.20
3.04
1.06
1.08
1.21
2.24
f1 (ppm)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136.340
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128.360
127.030
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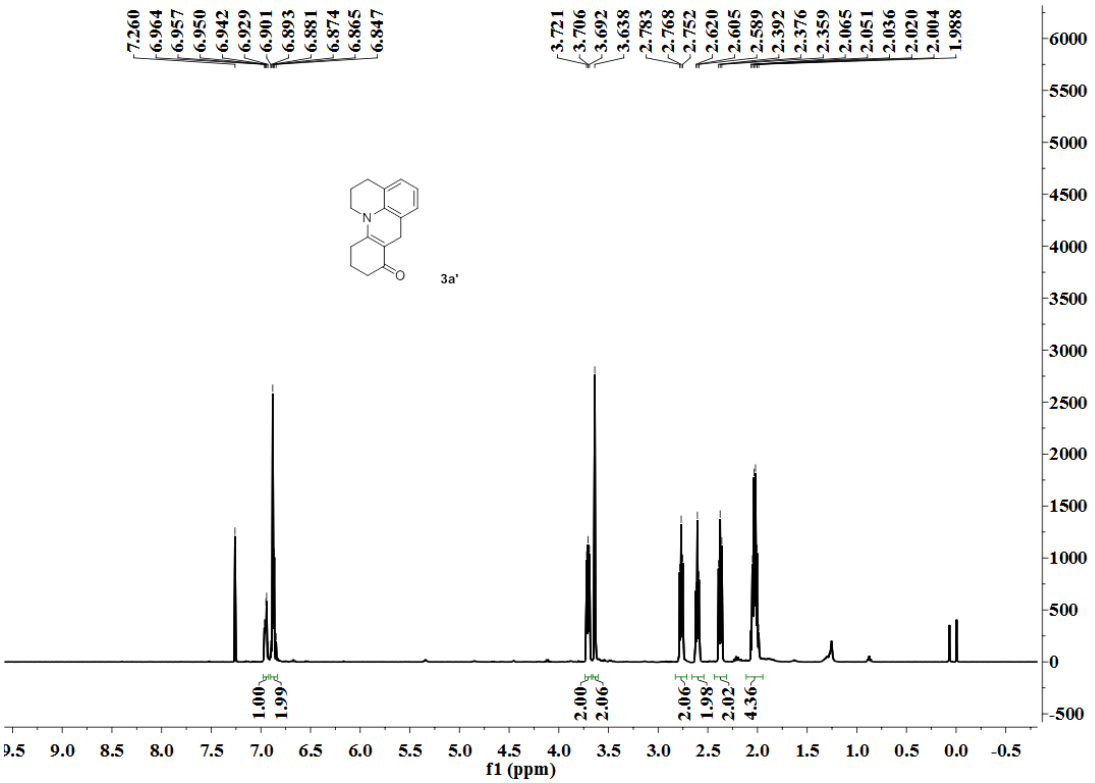
52.160
31.067
20.328
11.559
11.486
COOMe
O
3y
f1 (ppm)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6.942
6.929
6.901
6.893
6.881
6.874
6.865
6.847
3.721
3.706
3.692
3.638
2.783
2.768
2.752
2.620
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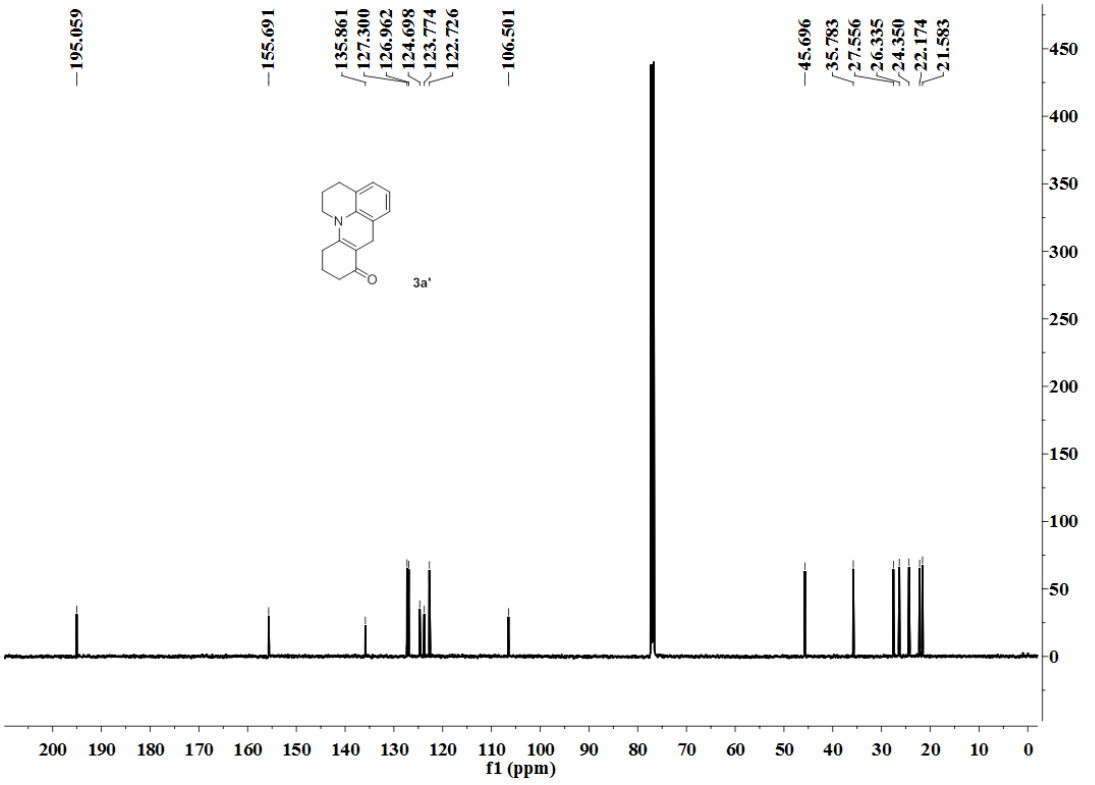
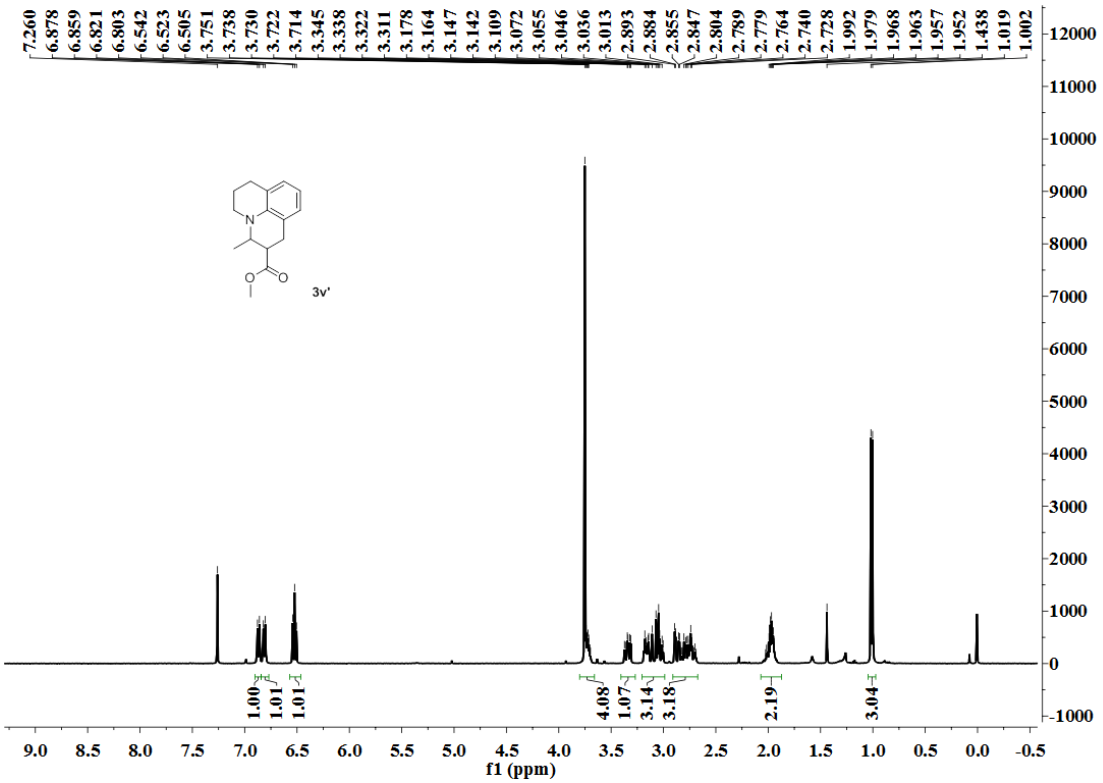
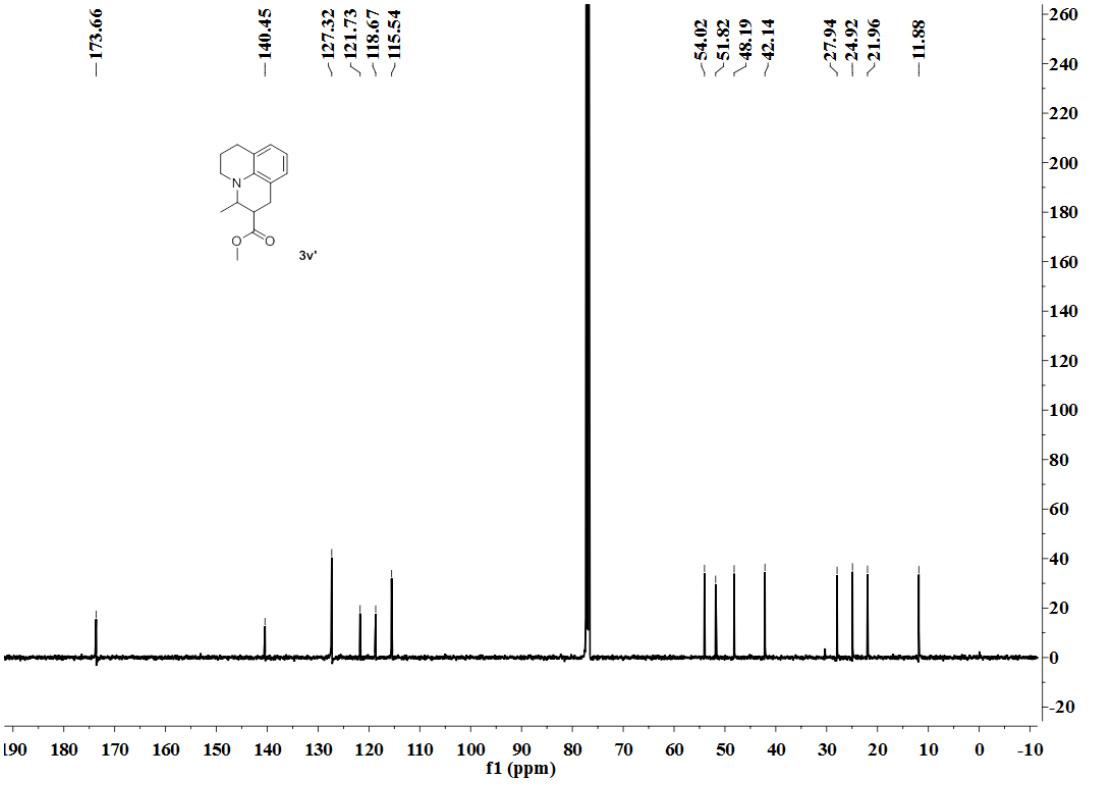
2.589
2.392
2.376
2.359
2.065
2.051
2.036
2.020
2.004
1.988
3a'
1.00
1.99
2.00
2.06
2.06
1.98
2.02
4.36
f1 (ppm)


195.059
155.691
135.861
127.300
126.962
124.698
123.774
122.726
106.501
45.696
35.783
27.556
26.335
24.350
22.174
21.583
3a'
f1 (ppm)


7.260
6.878
6.859
6.821
6.803
6.542
6.523
6.505
3.751
3.738
3.730
3.722
3.714
3.345
3.338
3.322
3.311
3.178
3.164
3.147
3.142
3.109
3.072
3.055
3.046
3.036
3.013
2.893
2.884
2.855
2.847
2.804
2.789
2.779
2.764
2.740
2.728
1.992
1.979
1.968
1.963
1.957
1.952
1.438
1.019
1.002
3v'
1.00
1.01
1.01
4.08
1.07
3.14
3.18
2.19
3.04
f1 (ppm)


173.66
140.45
127.32
121.73
118.67
115.54
54.02
51.82
48.19
42.14
27.94
24.92
21.96
11.88
3v'
f1 (ppm)