Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Copper-Catalysed Dehydrogenative α-C(sp^3)−H Amination of Tetrahydroquinolines with *O*–benzoyl hydroxylamines

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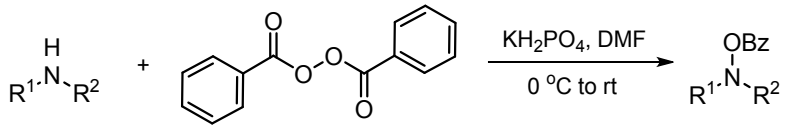
Part 1. Experimental procedures and spectra data

General Methods

The NMR spectra were recorded on Bruker spectrometers (^{1}H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts (δ) were given in ppm with reference to solvent signals [^{1}H NMR: $CHCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.02)]. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, br t = broad triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254). All reactions sensitive to air or moisture were conducted under nitrogen atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Anhydrous THF was distilled over sodium benzophenone ketyl under nitrogen atmosphere. All other solvents and reagents were used as obtained from commercial sources without further purification. X-Ray diffraction data of one these crystals were collected on a Bruker SMART diffractometer. And the structures were solved by direct methods SHELXS-2014.

Synthesis of O-Benzoyl Hydroxylamines

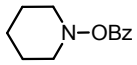
All starting materials were prepared according to the previously reported procedure.[1]



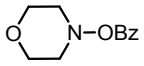
General Procedure: Under nitrogen atmosphere and 0 °C, to a 50 mL flask equipped with a stir bar and a rubber septum was charged with benzoyl peroxide (70% purity, 1 equiv), dipotassium hydrogen phosphate (2 equiv), and N,N-dimethylformamide. Amine starting material (1.5 equiv) was added dropwise. The suspension was stirred at ambient temperature for the indicated reaction time. The reaction was quenched with deionized water (10 mL) and the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was extracted with dichloromethane (3 × 30 mL). The organic phase was collected and washed with two

25 mL portions of saturated aq. $NaHCO_3$ solution, 25 mL of brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel to give desired product O-benzoyl hydroxylamine.

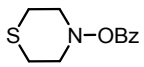
Characterization Data for *O*–benzoyl hydroxylamines



Compound **2a** was prepared according to General Procedure using piperidine with stirring for 1 h to yield 1-benzoyloxy-piperidine (70% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.60 – 7.53 (m, 1H), 7.48 – 7.40 (m, 2H), 3.53 (br s, 2H), 2.89 (br s, 2H), 1.93 – 1.79 (m, 4H), 1.68 (br s, 1H), 1.32 – 1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 132.9, 129.7, 129.4, 128.3, 57.5, 24.9, 23.3.

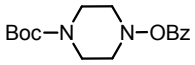


Compound **2b** was prepared according to General Procedure using morpholine with stirring for 1 h to yield 4-benzoyloxy-morpholine (75% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.72 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.50 – 7.40 (m, 2H), 4.06 – 3.80 (m, 4H), 3.46 (br d, J = 7.40 Hz, 2H), 3.15 – 2.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 133.2, 129.4, 129.2, 128.4, 65.8, 57.0.

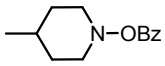


Compound **2c** was prepared according to General Procedure using thiomorpholine with stirring for 1 h to yield 4-benzoyloxy-thiomorpholine (65% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.62 –

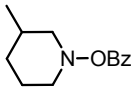
7.54 (m, 1H), 7.50 – 7.40 (m, 2H), 3.89 – 3.15 (m, 4H), 3.10 – 2.70 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 133.2, 129.5, 129.2, 128.5, 57.7, 26.6.



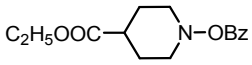
Compound **2d** was prepared according to General Procedure using tert-butyl piperazine-1-carboxylate with stirring for 1 h to yield tert-butyl 4-(benzoyloxy) piperazine-1-carboxylate (75% yield) as a white solid after flash chromatography with 20% ethyl acetate : petroleum ether. Analytical data for the compound **2d**: ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.06– 8.00 (m, 2H), 7.63 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 4.05 (br s, 2H), 3.60 – 3.22 (m, 4H), 2.94 (br s, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 154.4, 133.2, 129.4, 129.1, 128.5, 80.2, 55.9, 28.4.



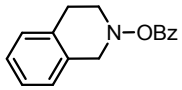
Compound **2e** was prepared according to General Procedure using 4-methylpiperidine with stirring for 2 h to yield 1-benzoyloxy-4-methylpiperidine (70% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 3.61 – 3.43 (m, 2H), 2.84 – 2.54 (m, 2H), 1.85– 1.69 (m, 2H), 1.67– 1.44 (m, 3H),1.03-0.91 (br d, J = 5.64 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 132.9, 129.7, 129.4, 128.3, 57.3, 33.7, 30.2, 21.3.



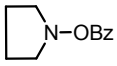
Compound **2f** was prepared according to General Procedure using 3-methylpiperidine with stirring for 2 h to yield 1-benzoyloxy-3-methylpiperidine (70% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 3.55 (br s, 2H), 2.69 – 2.55 (m, 1H), 2.47 – 2.26 (m, 1H), 2.19 – 1.55 (m, 5H), 0.95 (d, J = 6.72 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 132.9, 129.7, 129.4, 128.3, 64.8, 57.1, 32.0, 31.4, 24.7, 19.5.



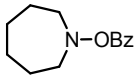
Compound **2g** was prepared according to General Procedure using ethyl piperidine-4-carboxylate with stirring for 1 h to yield ethyl 1-(benzoyloxy)piperidine- 4-carboxylate (70% yield) as a white solid after flash chromatography with 20% ethyl acetate : petroleum ether. Analytical data for the compound **2g**: ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.51 – 7.45 (m, 1H), 7.38 – 7.32 (m, 2H), 4.19 – 4.00 (m, 2H), 3.61 – 2.63 (m, 4H), 2.36 – 1.88 (m, 5H), 1.26-1.06 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 164.7, 133.0, 130.0, 129.4, 128.4, 60.6, 56.2, 40.4, 27.6, 14.2.



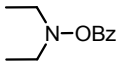
Compound **2h** was prepared according to General Procedure using 1,2,3,4-tetrahydroisoquinoline with stirring for 5 h to yield 3,4-dihydroisoquinolin- 2(1H)-yl benzoate (50% yield) as a white solid after flash chromatography with 20% ethyl acetate : petroleum ether. Analytical data for the compound **2h**: ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.03– 7.97 (m, 2H), 7.60 – 7.52 (m, 1H), 7.46 – 7.39 (m, 2H), 7.23 – 7.13 (m, 3H), 7.09 – 7.03 (m, 1H), 4.43 (s, 2H), 3.55 (br s, 2H), 3.12 (t, J_1 = 6.12 Hz, J_2 = 12.20 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 133.1, 132.9, 132.3, 129.5, 129.3, 128.4, 128.3, 126.9, 126.8, 126.2, 58.1, 53.4, 26.7.



Compound **2i** was prepared according to General Procedure using pyrrolidine with stirring for 1 h to yield pyrrolidin-1-yl benzoate (60% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.40 (m, 2H), 3.40 – 3.20 (m, 4H), 1.97 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 132.9, 129.6, 129.4, 128.3, 57.7, 22.2.



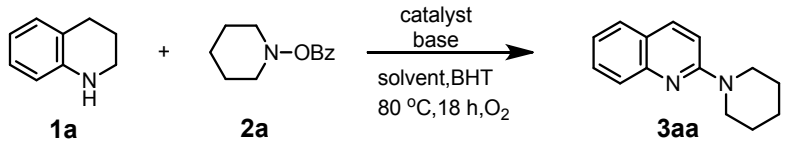
Compound **2j** was prepared according to General Procedure using azepane with stirring for 1 h to yield 1-benzoyloxy-azepane (65% yield) as a white solid after flash chromatography with 15% ethyl acetate : petroleum ether. Analytical data for the compound **2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.60 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 3.39 – 3.30 (m, 4H), 1.89 – 1.77 (m, 4H), 1.73 – 1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 132.9, 129.8, 129.4, 128.4, 59.5, 26.4, 24.2.



Compound **2k** was prepared according to General Procedure using diethylamine with stirring for 3 h to yield *O*-benzoyl-N,N-diethylhydroxylamine (65% yield) as a yellow oil after flash chromatography with 10% ethyl acetate : petroleum ether. Analytical data for the compound **2k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.60 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 3.10 – 3.00 (q, 4H), 1.18 (t, J_1 = 7.04 Hz, J_2 = 14.08 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 132.9, 129.4, 129.2, 128.3, 53.4, 11.8.

Detailed Optimization Studies

Table S1 Optimization of reaction conditions[a]



entry	Additive (equiv)	Base (equiv)	Solvent	Yieid of **3aa** (%)[b]
1	BHT (0.05)	KOH (1.5)/K_2CO_3 (1.5)	THF	57
2	BHT (0.1)	KOH (1.5)/K_2CO_3 (1.5)	THF	35
3	BHT (0.2)	KOH (1.5)/K_2CO_3 (1.5)	THF	24
4	BHT (0.3)	KOH (1.5)/K_2CO_3 (1.5)	THF	15
5	BHT (0.4)	KOH (1.5)/K_2CO_3 (1.5)	THF	10
6	BHT (0.5)	KOH (1.5)/K_2CO_3 (1.5)	THF	3.5
7	BHT (1.0)	KOH (1.5)/K_2CO_3 (1.5)	THF	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), CuI (40 mol%), THF (3 mL), 80 °C, 18 h, O_2.

[b]GC yields (%). BHT = 2,6-di-tert-butyl-4-methylphenol.

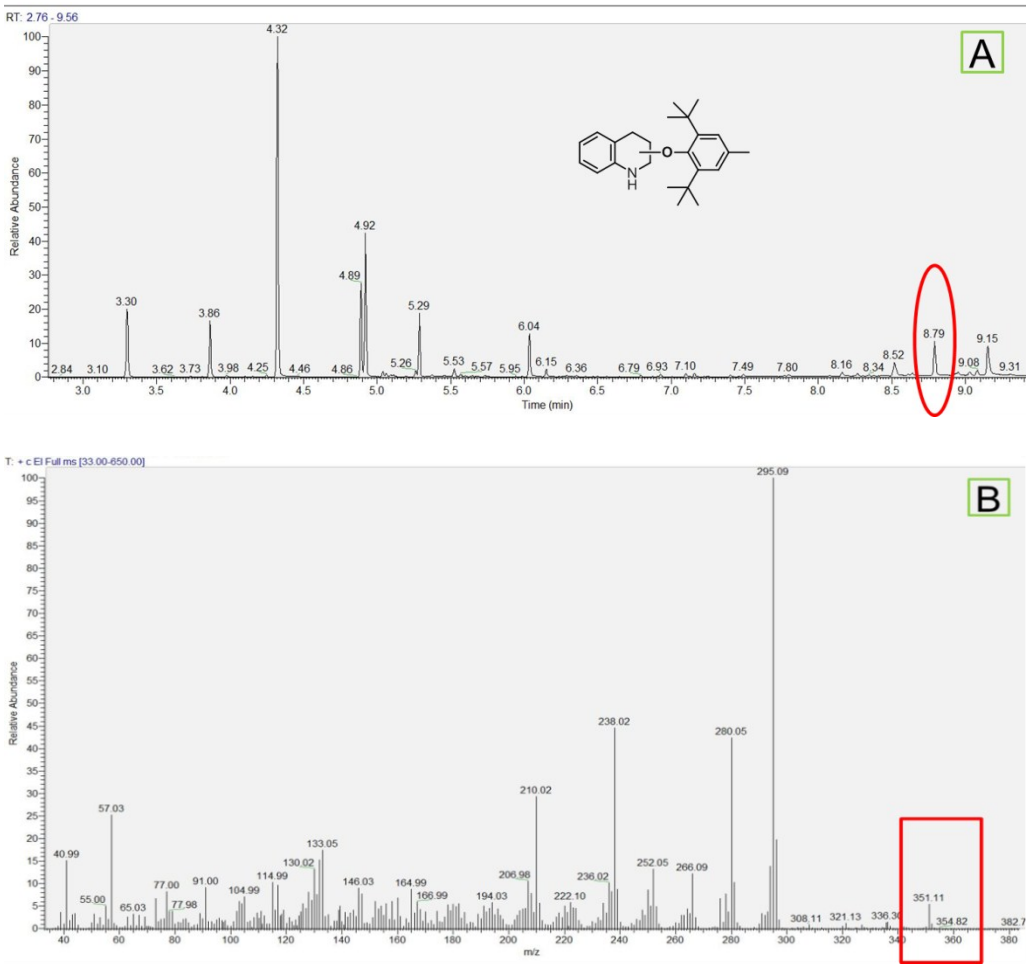
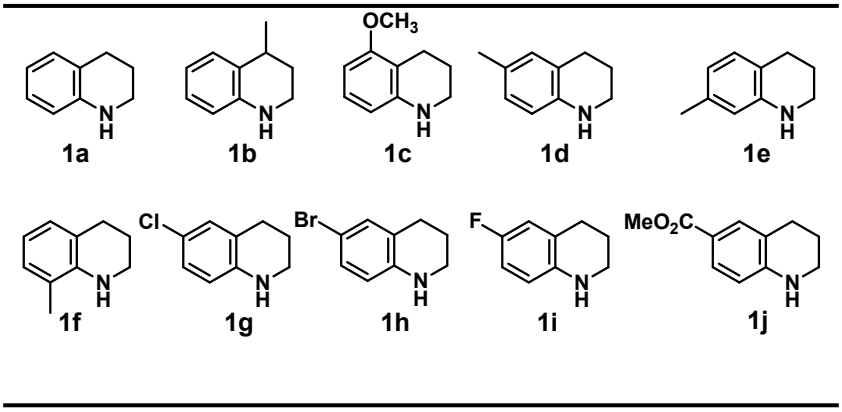


Figure S1. GC-MS spectra of the 1,2,3,4-tetrahydroquinoline combined with BHT.

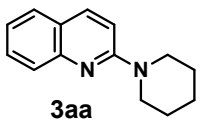
Typical procedure for the synthesis of 3:

Under oxygen atmosphere, a mixture of tetrahydroquinoline **1** (0.2 mmol), *O*-benzoyl hydroxylamine **2** (0.6 mmol), CuI (0.08 mmol), KOH (0.3 mmol), K_2CO_3 (0.3 mmol), BHT (0.45 mol %) and 3 mL distill THF was stirred at 80 ^oC for 18 h. The mixture was extracted with EtOAc three times, and the combined organic extracts were washed with aq. NaCl three times and dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the desired product.

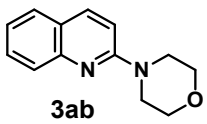
Scheme S1. Substrates employed for tetrahydroquinoline



Characterization Data for Products

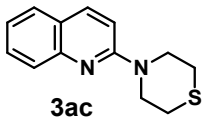


Known compound, yellow oil, 90% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.80 Hz, 1H), 7.74 – 7.66 (m, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.23 – 7.15 (m, 1H), 6.97 (d, J = 9.2 Hz, 1H), 3.78 – 3.67 (m, 4H), 1.72 – 1.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 148.1, 137.2, 129.4, 127.1,126.5, 122.8, 122.0, 109.9, 46.3, 25.8, 24.9; IR (neat): v = 2930, 2849, 1610, 1505, 1431, 1349, 1228, 1121, 1019, 808, 752 cm^{-1}; MS (EI): m/z 212.1 $[M]^+$.



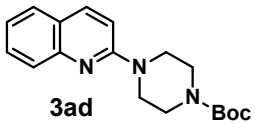
Known compound, pale yellow solid, 92% yield, m.p.: 86.5 – 86.6 ^oC; ^1H NMR (400

MHz, $CDCl_3$) δ 7.91 (d, J = 9.2 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.57 – 7.52 (m, 1H), 7.27 – 7.22 (m, 1H), 6.95 (d, J = 9.2 Hz, 1H), 3.85 (t, J_1 = 4.8 Hz, J_2 = 9.6 Hz, 4H), 3.71 (t, J_1 = 5.2 Hz, J_2 = 9.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 137.6, 129.7, 129.5, 127.2, 126.7, 123.3, 122.7, 66.9, 45.7; IR (neat): v = 3051, 2957, 2922, 2851, 1609, 1556, 1428, 1390, 1260, 1229, 1058, 926, 808, 753 cm^{-1}; MS (EI): m/z 214.1 $[M]^+$.



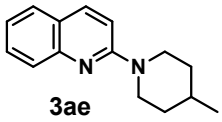
3ac

Known compound, pale yellow solid, 80% yield, m.p.: 72.5 – 72.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 9.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.53 (t, J_1 = 7.6 Hz, J_2 = 15.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.91 (d, J = 9.2 Hz, 1H), 4.11 (t, J_1 = 5.0 Hz, J_2 = 10.0 Hz, 4H), 2.70 (t, J_1 = 5.1 Hz, J_2 = 10.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 147.9, 137.7, 129.6, 127.2, 126.6, 122.9, 122.5, 109.7, 48.0, 26.6; IR (neat): v = 2986, 2857, 1607, 1553, 1502, 1426, 1391, 950, 806, 753 cm^{-1}; MS (EI): m/z 230.0 $[M]^+$.



3ad

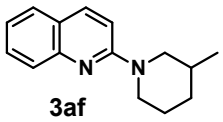
Known compound, white solid, 84% yield, m.p.: 127.2 – 127.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.2 Hz, 1H), 7.72 (d, J = 7.2 Hz,1H), 7.61 (d, J = 7.6 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.26 – 7.20 (m, 1H), 6.97 (d, J = 9.2 Hz, 1H), 3.78 – 3.70 (m, 4H), 3.62 – 3.55 (m, 4H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.9, 147.7, 137.7, 129.7, 127.2, 126.6, 123.2, 122.7, 109.6, 80.0, 45.1, 28.5; IR (neat): v = 2977, 2858, 1691, 1611, 1551, 1509, 1409, 1238, 1167, 1121, 862, 807, 758 cm^{-1}; MS (EI): m/z 313.1 $[M]^+$.



3ae

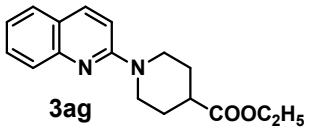
Known compound, dark red solid, 70% yield, m.p.: 45.6 – 45.7 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.45 (m, 2H), 7.23 – 7.13 (m, 1H), 6.77 (d, *J* = 9.2 Hz, 1H), 4.51 (d, *J* = 13.2 Hz, 2H), 3.00 – 2.87 (m, 2H), 1.79 – 1.71 (m, 2H), 1.69 – 1.58 (m, 1H), 1.30 – 1.20 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 148.1, 137.3, 129.4, 127.1, 126.5, 122.8, 122.0, 109.9, 53.0, 45.7, 34.1, 31.3, 22.0; IR (neat): *v* = 2921, 1611, 1547, 1510, 1428, 1388, 1017, 803 cm^{-1}; MS (EI): m/z 226.1 $[M]^+$.



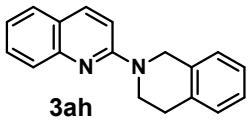
3af

Unknown compound, pink solid, 44% yield, m.p.: 67.5 – 67.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.52 – 7.46 (m, 1H), 7.21 – 7.14 (m, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 4.48 – 4.36 (m, 2H), 2.96 – 2.86 (m, 1H), 2.62 – 2.53 (m, 1H), 1.80 – 1.66 (m, 2H), 1.64 – 1.53 (m, 1H), 1.35 – 1.11 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 148.1, 137.2, 129.4, 127.1, 126.5, 122.8, 121.9, 109.9, 53.0, 45.7, 31.0, 25.3, 19.4; IR (neat): *v* = 2924, 2856, 1610, 1552, 1505, 1432, 1394, 1231, 806, 751 cm^{-1}; MS (EI): m/z 226.1 $[M]^+$, HRMS (ESI) Calcd. For : 227.1543 $[M+H]^+$; Found: m/z 227.1547.



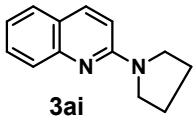
3ag

Known compound, white solid, 80% yield, m.p.: 43.8 – 43.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.2 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.61 – 7.49 (m, 2H), 7.24 – 7.17 (m, 1H), 6.99 (d, *J* = 9.2 Hz, 1H), 4.50 – 4.40 (m, 2H), 4.19 – 4.12 (m, 2H), 3.15 – 3.06 (m, 2H), 2.63 – 2.52 (m, 1H), 2.07 – 1.96 (m, 2H), 1.87 – 1.73 (m, 2H), 1.27 (t, J_1 = 6.8 Hz, J_2 = 14.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 157.3, 147.9, 137.4, 129.5, 127.2, 126.6, 123.0, 122.3, 109.8, 60.5, 44.9, 41.5, 27.9, 14.3; IR (neat): *v* = 2928, 1740, 1727, 1611, 1548, 1510, 1429, 1386, 1316, 1244, 1168, 1045, 807, 753, 615; cm^{-1}; MS (EI): m/z 284.1 $[M]^+$.



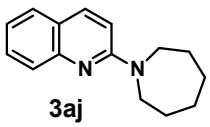
3ah

Known compound, white solid, 46% yield, m.p.: 114.1 – 114.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.2 Hz, 1H), 7.80 (br s, 1H), 7.63 – 7.51 (m, 2H), 7.26 – 7.16 (m, 5H), 7.03 (d, J = 9.2 Hz, 1H), 4.92 (s, 2H), 4.02 (t, J_1 = 5.6 Hz, J_2 = 11.6 Hz, 2H), 3.02 (t, J_1 = 6.0 Hz, J_2 = 11.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 137.7, 135.3, 134.3, 129.7, 128.4, 127.3, 126.6, 126.5, 126.3, 122.8, 122.3, 109.6, 47.4, 43.0, 29.2; IR (neat): v = 3054, 2992, 2954, 2924, 2852, 1618, 1603, 1557, 1540, 1504, 1252, 1043, 811, 760 cm^{-1}; MS (EI): m/z 260.1 $[M]^+$.



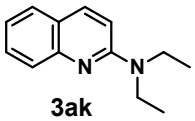
3ai

Known compound, white solid, 40% yield, m.p.: 86.1 – 86.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 9.2 Hz, 1H), 7.72 (d, J = 9.4 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.53 – 7.48 (m, 1H), 7.19 – 7.13 (m, 1H), 6.71 (d, J = 8.8 Hz, 1H), 3.62 (t, J_1 = 6.8 Hz, J_2 = 13.2 Hz, 4H), 2.06 – 2.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 137.0, 129.4, 127.4, 126.0, 122.6, 121.2, 110.3, 46.9, 25.6; IR (neat): v = 3053, 2957, 2924, 2857, 1606, 1553, 1511, 1482, 1430, 1401, 1157, 1118, 869, 807, 752; MS (EI): m/z 198.1 $[M]^+$.



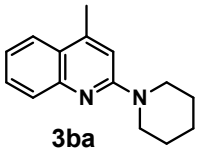
3aj

Known compound, yellow oil, 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.53 – 7.48 (m, 1H), 4.92 (s, 2H), 7.19 – 7.13 (m, 1H), 6.86 (d, J = 9.2 Hz, 1H), 3.79 (t, J_1 = 6.0 Hz, J_2 = 12.0 Hz, 4H), 1.85 (br s, 4H), 1.60 – 1.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 148.5, 137.1, 129.3, 127.2, 126.3, 122.4, 121.3, 109.0, 47.8, 28.1, 27.1; IR (neat): v = 2927, 1748,1613, 1553, 1510, 1373, 1244, 1051, 810 cm^{-1}; MS (EI): m/z 226.1 $[M]^+$.



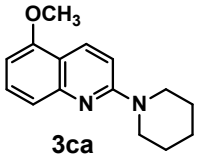
3ak

Known compound, yellow oil, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 9.2 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.19 – 7.10 (m, 1H), 6.82 (d, J = 8.8 Hz, 1H), 3.72 – 3.59 (m, 4H), 1.24 (t, J_1 = 7.2 Hz, J_2 = 14.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.5, 137.0, 129.2, 127.1, 126.3, 122.3, 121.2, 109.1, 42.4, 13.3; IR (neat): v = 3053, 2968, 2924, 1606, 1553, 1510, 1430, 1078, 1019, 809, 752 cm^{-1}; MS (EI): m/z 200.1 $[M]^+$.



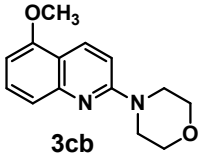
3ba

Known compound, yellow oil, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 2H), 7.50 (t, J_1 = 7.2 Hz, J_2 = 15.2 Hz, 1H), 7.21 (t, J_1 = 7.6 Hz, J_2 = 15.2 Hz, 1H), 6.84 (s, 1H), 3.71 (s, 4H), 2.57 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 147.9, 144.9, 129.2, 126.9, 123.4, 123.2, 121.8, 110.2, 46.3, 25.9, 24.9, 19.3; IR (neat): v = 3060, 2929, 2852, 1609, 1551, 1483, 1414, 1271, 1216, 1122, 1025, 843, 753 cm^{-1}; MS (EI): m/z 226.2 $[M]^+$.



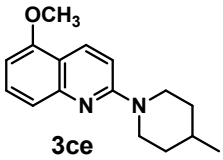
3ca

Unknown compound, yellow solid, 90% yield, m.p.: 89.1 – 89.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 9.2 Hz, 1H), 7.41 (t, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 1H), 7.32 – 7.25 (m, 1H), 6.92 (d, J = 9.6 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.71 (s, 4H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 155.4, 149.1, 131.9, 129.3, 119.2, 114.4, 108.5, 100.9, 55.5, 46.2, 25.8, 24.9; IR (neat): v = 2927, 2850, 1602, 1559, 1511, 1420, 1319, 1247, 1175, 1097, 1026, 978, 797, 784 cm^{-1}; MS (EI): m/z 242.1 $[M]^+$, HRMS (ESI) Calcd. For : 243.1497 $[M+H]^+$; Found: m/z 243.1496.



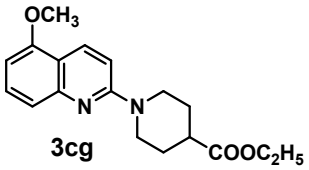
3cb

Unknown compound, yellow solid, 93% yield, m.p.: 167.3 – 167.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 9.6 Hz, 1H), 7.45 (t, J_1 = 8.0 Hz, J_2 = 16.4 Hz, 1H), 7.32 (d, J = 8.4 Hz,1H), 6.90 (d, J = 9.6 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 3.95 (s, 3H), 3.85 (t, J_1 = 4.4 Hz, J_2 = 9.6 Hz, 4H), 3.71 (t, J_1 = 5.2 Hz, J_2 = 9.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.4, 148.7, 132.3, 129.6, 119.3, 115.1, 107.9, 101.4, 66.9, 55.5, 45.5; IR (neat): v = 2923, 1607, 1555, 1421, 1255, 1110, 797, 753 cm^{-1}; MS (EI): m/z 244.1 $[M]^+$, HRMS (ESI) Calcd. For : 245.1285 $[M+H]^+$; Found: m/z 245.1289.



3ce

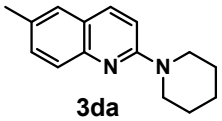
Unknown compound, yellow solid, 60% yield, m.p.: 74.6 – 74.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 9.2 Hz, 1H), 7.41 (t, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 1H), 7.30 (br s, 1H), 6.94 (d, J = 9.6 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.52 (d, J = 12.8 Hz, 2H), 3.94 (s, 3H), 2.93 (t, J_1 = 12.0 Hz, J_2 = 24.8 Hz, 2H), 1.75 (d, J = 13.2 Hz, 2H), 1.70 – 1.57 (m, 1H), 1.33 – 1.18 (m, 2H), 0.97 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.4, 149.1, 131.9, 129.3, 119.2, 114.4, 108.5, 100.9, 55.5, 45.6, 34.1, 31.3, 21.9; IR (neat): v = 3062, 2921, 2844, 1603, 1561, 1511, 1419, 1375, 1321, 1232, 1175, 1140, 1094, 1051, 968, 867, 796, 748 cm^{-1}; MS (EI): m/z 256.1 $[M]^+$, HRMS (ESI) Calcd. For : 257.1648 $[M+H]^+$; Found: m/z 257.1653.



3cg

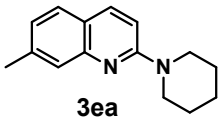
Unknown compound, white solid, 85% yield, m.p.: 80.4 – 80.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.4 Hz, 1H), 7.42 (t, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 9.2 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 4.45 (d, J =

12.8 Hz, 2H), 4.23 – 4.05 (m, 2H), 3.93 (s, 3H), 3.08 (t, J_1 = 12.0 Hz, J_2 = 24.0 Hz, 2H), 2.57 (br s, 1H), 2.02 (d, J = 12.0 Hz, 2H), 1.87 – 1.71 (m, 2H), 1.26 (t, J_1 = 6.8 Hz, J_2 = 13.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 157.6, 155.4, 148.9, 132.1, 129.5, 119.2, 114.6, 108.5, 101.2, 60.5, 55.5, 44.8, 41.5, 27.9, 14.2; IR (neat): v = 2923, 2852, 1600, 1563, 1511, 1448, 1420, 1373, 1316, 1257, 1224, 1169, 1096, 1037, 973, 796, 751 cm^{-1}; MS (EI): m/z 314.1 $[M]^+$, HRMS (ESI) Calcd. For : 315.1703 $[M+H]^+$; Found: m/z 315.1707.



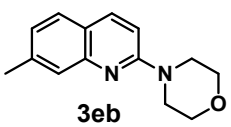
3da

Known compound, yellow oil, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 9.2 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.39 – 7.30 (m, 2H), 6.94 (d, J = 9.2 Hz, 1H), 3.68 (s, 4H), 2.43 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 146.4, 136.7, 131.4, 131.3, 126.3, 126.2, 122.8, 109.9, 46.4, 25.8, 24.9, 21.2; IR (neat): v = 2928, 2854, 1606, 1553, 1496, 1400, 1321, 1229, 1121, 1021, 958, 882, 818 cm^{-1}; MS (EI): m/z 226.2 $[M]^+$.



3ea

Unknown compound, yellow oil, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 9.2 Hz, 1H), 7.49 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H),, 6.90 (d, J = 9.2 Hz, 1H), 3.70 (s, 4H), 2.46 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.2, 139.5, 136.9, 126.8, 125.9, 124.0, 120.8, 108.9, 46.35, 25.8, 24.9, 21.8; IR (neat): v = 2929, 2852, 1612, 1550, 1514, 1450, 1389, 1370, 1231, 1124, 1022, 963, 887, 822, 777 cm^{-1}; MS (EI): m/z 226.2 $[M]^+$, HRMS (ESI) Calcd. For : 227.1543 $[M+H]^+$; Found: m/z 227.1546.



3eb

Unknown compound, yellow solid, 70% yield, m.p.: 86.4 – 86.5 ^{o}C; ^{1}H NMR (400

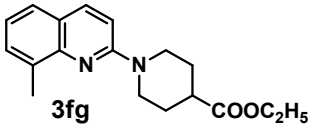
MHz, $CDCl_3$) δ 7.86 (d, J = 9.2 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 9.2 Hz, 1H), 3.84 (t, J_1 = 4.4 Hz, J_2 = 9.6 Hz, 4H), 3.68 (t, J_1 = 5.2 Hz, J_2 = 9.6 Hz, 4H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 147.8, 139.8, 137.3, 126.9, 126.1, 124.8, 121.3, 108.4, 66.9, 45.7, 21.9; IR (neat): v = 2927, 1612, 1511, 1446, 1384, 1229, 1118, 818 cm^{-1}; MS (EI): m/z 228.1 $[M]^+$, HRMS (ESI) Calcd. For : 229.1335 $[M+H]^+$; Found: m/z 229.1339.

3fa

Unknown compound, yellow oil, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.08 (t, J_1 = 7.6 Hz, J_2 = 14.8 Hz, 1H), 6.95 (d, J = 9.2 Hz, 1H), 3.71 (s, 4H), 2.65 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 146.8, 137.5, 134.3, 129.5, 125.0, 122.4, 121.6, 109.4, 46.4, 25.7, 25.0, 17.9; IR (neat): v = 3047, 2930, 2853, 1612, 1564, 1505, 1437, 1383, 1324, 1238, 1127, 1024, 956, 815, 755, 708 cm^{-1}; MS (EI): m/z 226.1 $[M]^+$, HRMS (ESI) Calcd. For : 227.1543 $[M+H]^+$; Found: m/z 227.1546.

3fb

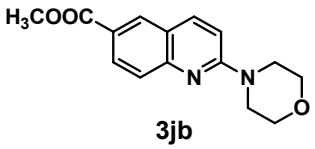
Known compound, yellow oil, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.2 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.15 (t, J_1 = 7.6 Hz, J_2 = 14.8 Hz, 1H), 6.94 (d, J = 9.2 Hz, 1H), 3.87 (t, J_1 = 4.4 Hz, J_2 = 9.2 Hz, 4H), 3.71 (t, J_1 = 4.8 Hz, J_2 = 9.2 Hz, 4H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 146.4, 137.9, 134.6, 129.8, 125.1, 123.0, 122.4, 108.8, 66.9, 45.7, 17.8; IR (neat): v = 3047, 2961, 2916, 2849, 1611, 1567, 1505, 1434, 1375, 1324, 1233, 1152, 1117, 1067, 968, 863, 819, 758, 707, 603 cm^{-1}; MS (EI): m/z 228.0 $[M]^+$.



3fg

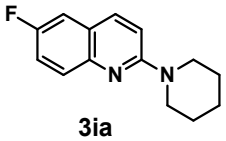
Known compound, brown oil, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J =

9.2 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.12 (t, J_1 = 7.6 Hz, J_2 = 15.2 Hz, 1H), 6.99 (d, J = 9.2 Hz, 1H), 4.48 (d, J = 13.6 Hz, 2H), 4.21 – 4.10 (m, 2H), 3.10 (t, J_1 = 4.4 Hz, J_2 = 9.2 Hz, 2H), 2.65 (s, 3H), 2.07 – 2.00 (m, 2H), 1.86 – 1.77 (m, 2H), 1.30 – 1.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 156.4, 146.6, 137.9, 134.4, 129.6, 125.1, 122.6, 122.0, 109.4, 60.5, 44.9, 41.7, 27.8, 17.9, 14.3; IR (neat): v = 2935, 1609, 1568, 1504, 1438, 1383, 1322, 1256, 1175, 1103, 1041, 958, 859, 817, 759 cm^{-1}; MS (EI): m/z 298.1 $[M]^+$.



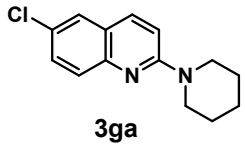
3jb

Unknown compound, white solid, 40% yield, m.p.: 147.8 – 147.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 9.2 Hz, 1H), 3.94(s, 3H), 3.84 (s, 4H), 3.77 (br d, J = 2.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 158.2, 138.7, 130.4, 129.7, 126.5, 123.9, 122.1, 109.7, 100, 66.8, 52.1, 45.3; IR (neat): v = 2924, 1613, 1548, 1498, 1397, 1276, 1228, 1192, 1105, 971, 800, 754 cm^{-1}; MS (EI): m/z 272.1 $[M]^+$, HRMS (ESI) Calcd. For : 273.1234 $[M+H]^+$; Found: m/z 273.1237.



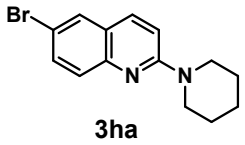
3ia

Unknown compound, yellow solid, 47% yield, m.p. : 59.4 – 59.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 9.2 Hz, 1H), 7.67 (s, 1H), 7.31 – 7.24 (m, 1H), 7.23 – 7.17 (m, 1H), 7.01 (d, J = 9.2 Hz, 1H), 3.70 (s, 4H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 156.8, 136.5, 128.3, 122.8, 122.7, 118.9, 118.6, 110.8, 110.5, 110.3, 46.4, 25.8, 24.8; IR (neat): v = 2929, 2854, 1611, 1552, 1502, 1403, 1318, 1231, 1117, 1021, 958, 857, 816, 749 cm^{-1}; MS (EI): m/z 230.1 $[M]^+$, HRMS (ESI) Calcd. For : 231.1292 $[M+H]^+$; Found: m/z 231.1296.



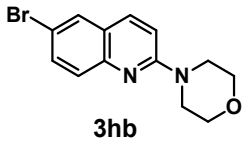
3ga

Unknown compound, yellow solid, 43% yield, m.p. : 74.0 – 74.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H), 7.45 – 7.38 (m, 1H), 6.96 (d, J = 9.2 Hz, 1H), 3.70 (br d, J = 5.6 Hz, 4H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 146.6, 136.3, 129.9, 128.0, 126.9, 125.9, 123.3, 110.6. 46.2, 25.8, 24.8; IR (neat): v = 2926, 2856, 1610, 1552, 1504, 1459, 1399, 1318, 1228, 1025, 805, 709 cm^{-1}; MS (EI): m/z 246.0 $[M]^+$, HRMS (ESI) Calcd. For : 247.09997 $[M+H]^+$; Found: m/z 247.0999.



3ha

Known compound, yellow solid, 43% yield, m.p. : 73.9– 74.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 9.2 Hz, 1H), 7.68 (s, 1H), 7.55 (s, 2H), 6.97 (d, J = 9.2 Hz, 1H), 3.71 (s, 4H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 146.9, 136.2, 132.5, 129.1, 128.2, 123.9, 114.6, 110.6. 46.2, 25.8, 24.8; IR (neat): v = 2929, 2851, 1610, 1547, 1503, 1458, 1395, 1312, 1230, 1122, 1021, 961, 929, 819 cm^{-1}; MS (EI): m/z 290.1 $[M]^+$.

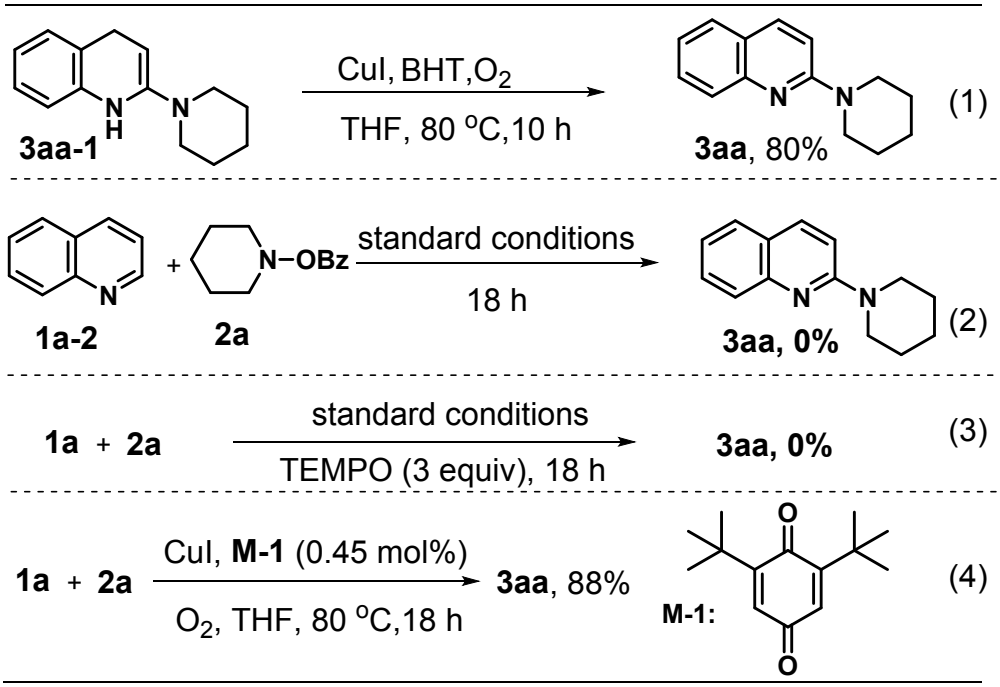


3hb

Known compound, yellow solid, 46% yield, m.p. : 152.8– 152.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 1H), 7.74 (s, 1H), 7.63 – 7.53 (m, 2H), 6.95 (d, J = 9.2 Hz, 1H), 3.84 (t, J_1 = 4.4 Hz, J_2 = 8.8 Hz, 4H), 3.70 (t, J_1 = 4.4 Hz, J_2 = 8.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 146.5, 136.6, 132.8, 129.3, 128.4, 124.4, 115.5, 110.0. 66.8, 45.4; IR (neat): v = 2967, 2848, 1646, 1609, 1546, 1533, 1496, 1460, 1388, 1311, 1263, 1222, 1187, 1115, 1058, 972, 927, 870, 816, 740, 613 cm^{-1}; MS (EI): m/z 292.0 $[M]^+$.

(1) Berman, A. M.; Johnson, J. S. *J. Org. Chem.* **2006,** *71*, 219-224.

Scheme S2. The control experiments



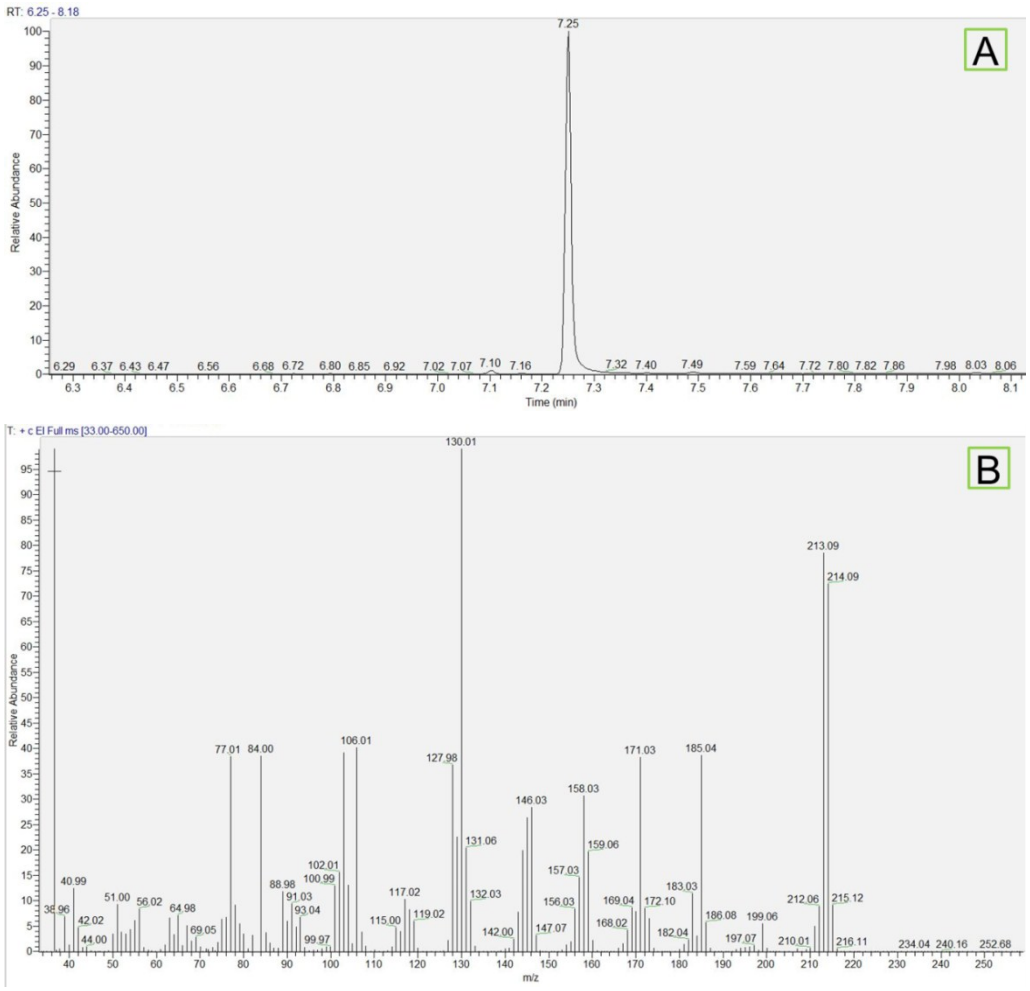


Figure S2. Detection of **3aa-1** by means of GC-MS analysis

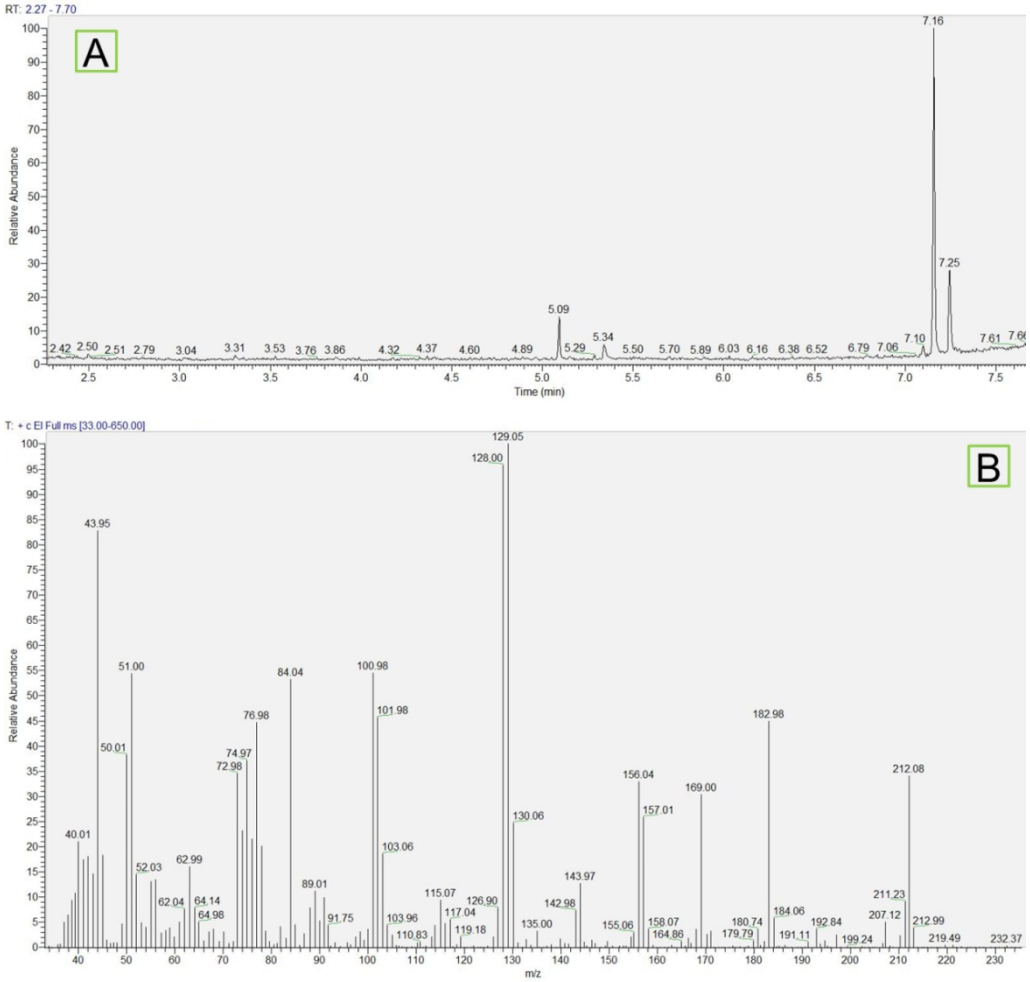
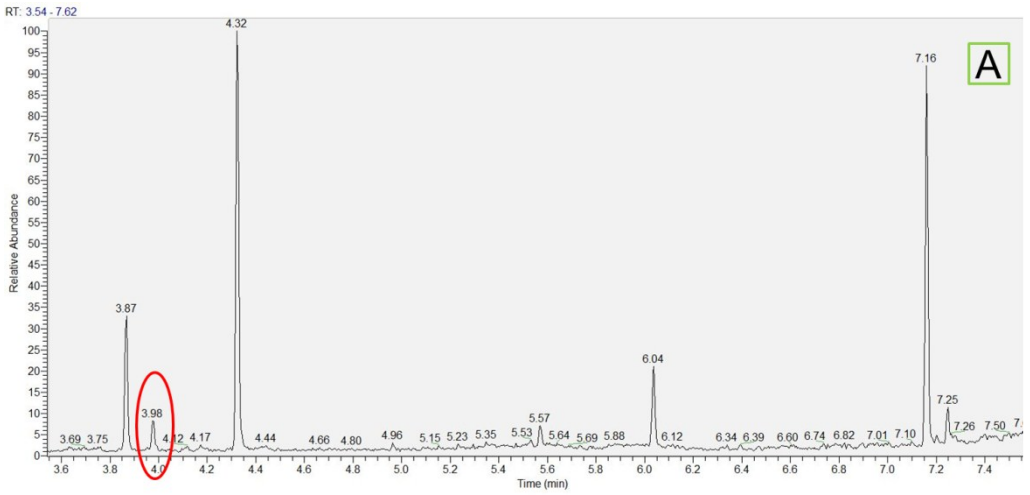


Figure S3. GC-MS detection for the conversion of **3aa-1** into **3aa**



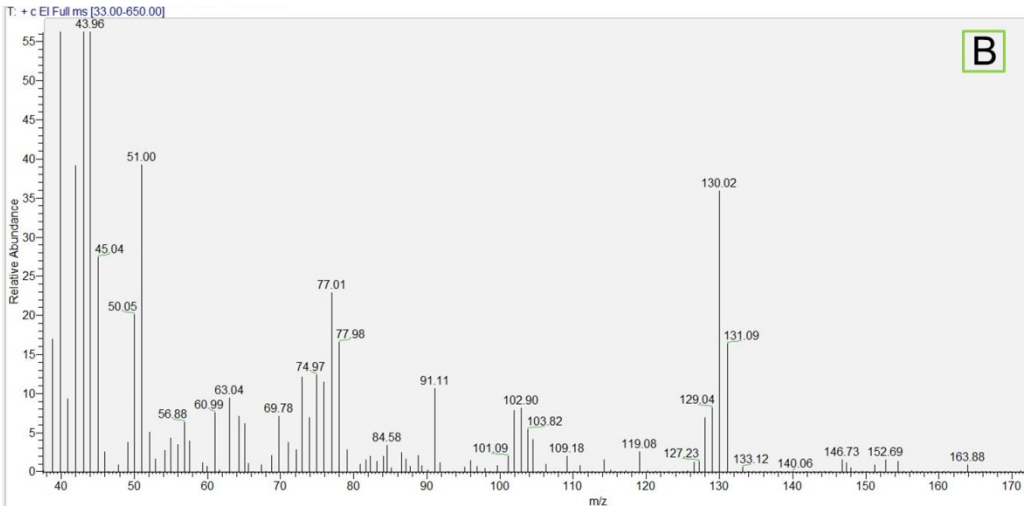


Figure S4. Detection of **1a-1** by means of GC-MS analysis

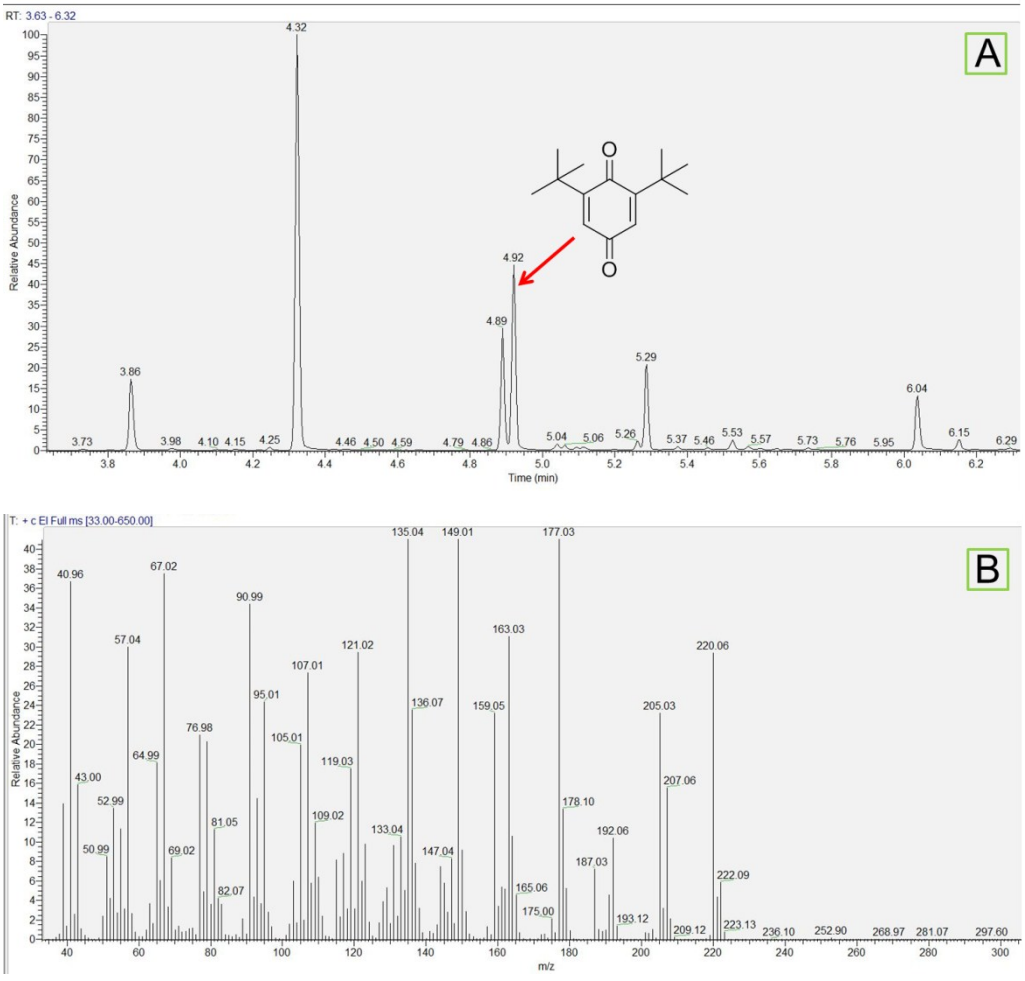


Figure S5. Detection of **M-1** by means of GC-MS analysis

Part 2. Single crystal X-ray diffraction data of 3hb

Yellow and transparent block-like single crystals of 3hb were grown by layering a dichlormethane solution with n-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a Bruker SMART diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 A). Data were collected at 296 K, using the ω- and φ- scans to a maximum θ value of 25.027°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.

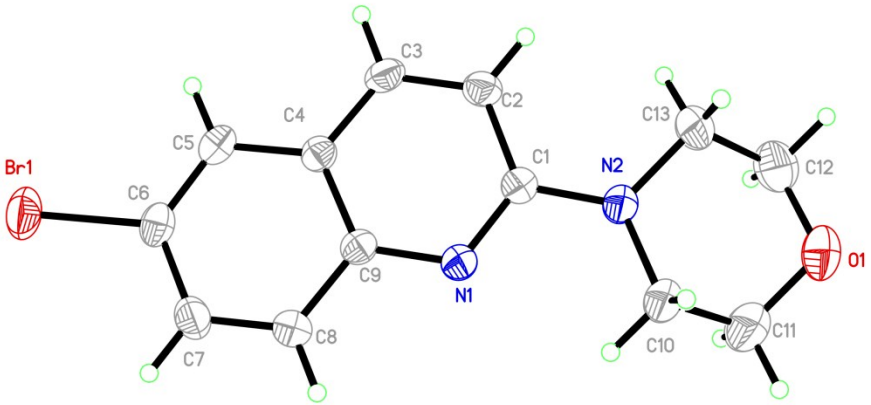


Figure S6. ORTEP drawing of 3hb with the numbering scheme.

Table S1 Crystal data and structure refinement for 3hb.

Identification code	3hb	
Empirical formula	C13 H13 Br N2 O	
Formula weight	293.16	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.6730(7) Å	α= 90°.
	b = 11.9750(8) Å	β= 96.144(2)°.
	c = 10.6305(8) Å	γ = 90°.
Volume	1224.30(15) $Å^3$	
Z	4	
Density (calculated)	1.590 Mg/m^3	
Absorption coefficient	3.342 mm^{-1}	
F(000)	592	
Crystal size	0.21 x 0.2 x 0.19 mm^3	
Theta range for data collection	2.570 to 25.027°.	
Index ranges	-11<=h<=8, -14<=k<=14, -11<=l<=12	
Reflections collected	7785	
Independent reflections	2162 [R(int) = 0.0498]	
Completeness to theta = 25.242°	97.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2162 / 0 / 154	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0891	
R indices (all data)	R1 = 0.0725, wR2 = 0.1042	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.402 and -0.372 $e.Å^{-3}$	

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3hb. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	6913(1)	5369(1)	300(1)	73(1)
O(1)	15453(3)	7070(3)	7556(3)	84(1)
N(1)	11746(3)	5771(2)	4385(3)	41(1)
N(2)	12891(3)	6648(3)	6122(3)	55(1)
C(1)	11698(3)	6503(3)	5313(3)	41(1)
C(2)	10479(4)	7139(3)	5461(4)	48(1)
C(3)	9367(4)	7045(3)	4594(4)	48(1)
C(4)	9395(3)	6321(3)	3560(3)	40(1)
C(5)	8280(4)	6219(3)	2590(4)	47(1)
C(6)	8386(4)	5480(3)	1632(4)	49(1)
C(7)	9567(4)	4813(3)	1589(4)	54(1)
C(8)	10648(4)	4912(3)	2513(4)	50(1)
C(9)	10612(3)	5675(3)	3514(3)	39(1)
C(10)	14056(4)	5888(3)	6107(4)	63(1)
C(11)	15383(5)	6457(5)	6417(5)	94(2)
C(12)	14363(5)	7842(4)	7496(5)	88(2)
C(13)	12982(4)	7369(3)	7224(4)	72(1)

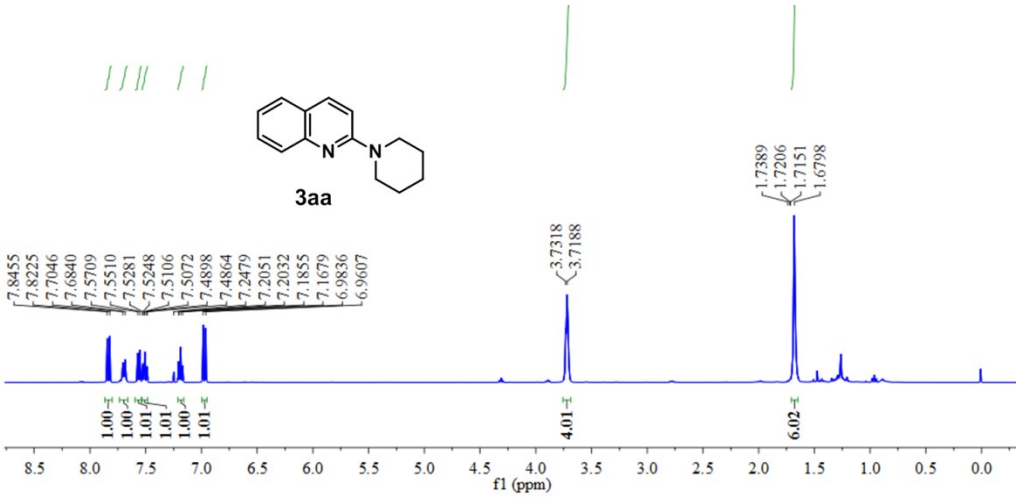
Table S3 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3hb. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

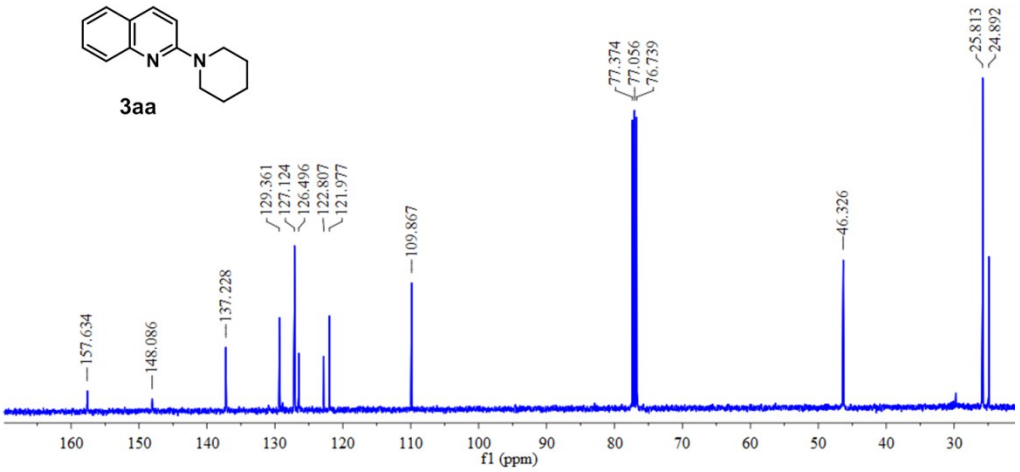
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	55(1)	99(1)	62(1)	-5(1)	-13(1)	-13(1)
O(1)	62(2)	102(2)	82(3)	-16(2)	-19(2)	-9(2)
N(1)	40(2)	41(2)	43(2)	-1(1)	3(1)	3(1)
N(2)	44(2)	59(2)	59(2)	-17(2)	-7(2)	8(2)
C(1)	41(2)	40(2)	41(2)	2(2)	5(2)	0(2)
C(2)	48(2)	43(2)	53(3)	-9(2)	9(2)	3(2)
C(3)	36(2)	46(2)	62(3)	-2(2)	8(2)	8(2)
C(4)	37(2)	39(2)	44(2)	2(2)	6(2)	-3(2)
C(5)	35(2)	50(2)	56(3)	6(2)	4(2)	-1(2)
C(6)	41(2)	52(2)	52(3)	7(2)	0(2)	-10(2)
C(7)	55(2)	57(2)	48(2)	-10(2)	2(2)	-9(2)
C(8)	49(2)	51(2)	51(3)	-8(2)	6(2)	3(2)
C(9)	37(2)	40(2)	40(2)	4(2)	7(2)	-1(2)
C(10)	47(2)	69(3)	68(3)	-14(2)	-8(2)	6(2)
C(11)	54(3)	112(4)	110(5)	-29(4)	-8(3)	7(3)
C(12)	76(3)	91(4)	94(4)	-38(3)	-5(3)	-16(3)
C(13)	65(3)	78(3)	70(3)	-33(2)	-9(2)	5(2)

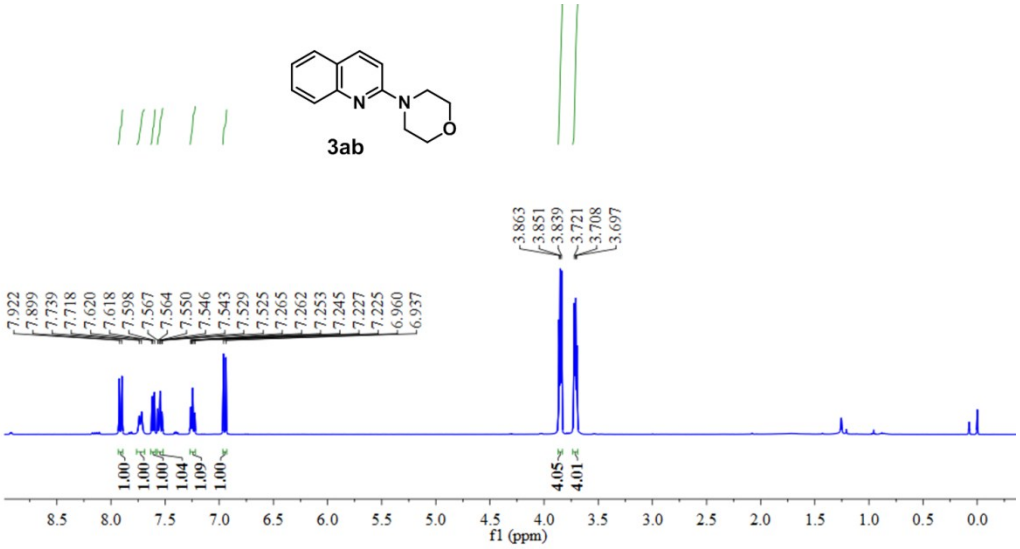
Table S4 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 3hb.

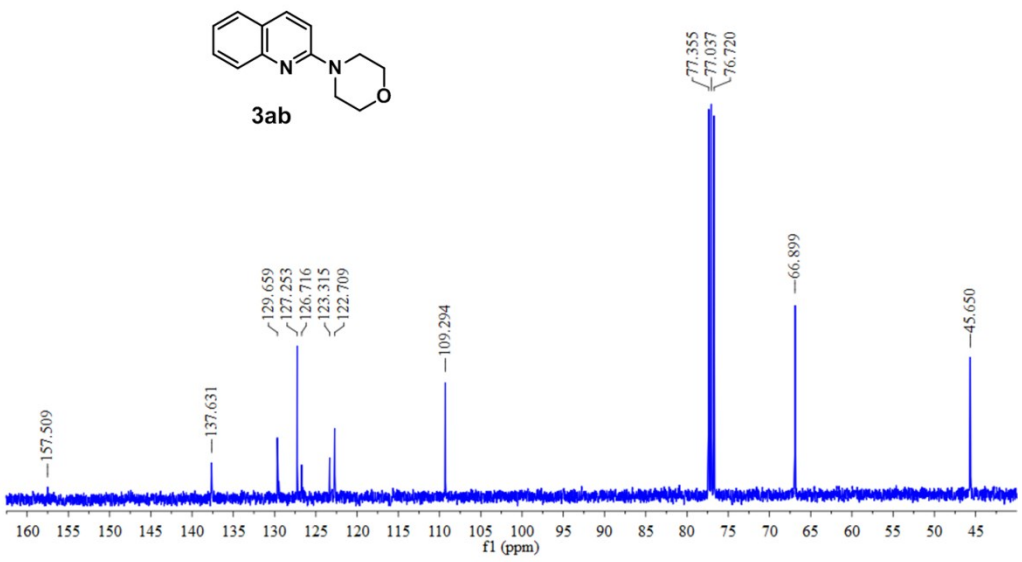
	x	y	z	U(eq)
H(2A)	10454	7613	6151	57
H(3A)	8573	7463	4680	58
H(5A)	7484	6651	2607	57
H(7A)	9613	4305	932	65
H(8A)	11429	4463	2482	60
H(10A)	14036	5553	5274	75
H(10B)	13968	5293	6713	75
H(11A)	16123	5907	6484	112
H(11B)	15538	6961	5732	112
H(12A)	14502	8389	6848	106
H(12B)	14407	8234	8298	106
H(13A)	12309	7968	7079	87
H(13B)	12753	6943	7950	87

Part 3. ^{1}H and ^{13}C NMR Spectra for Products





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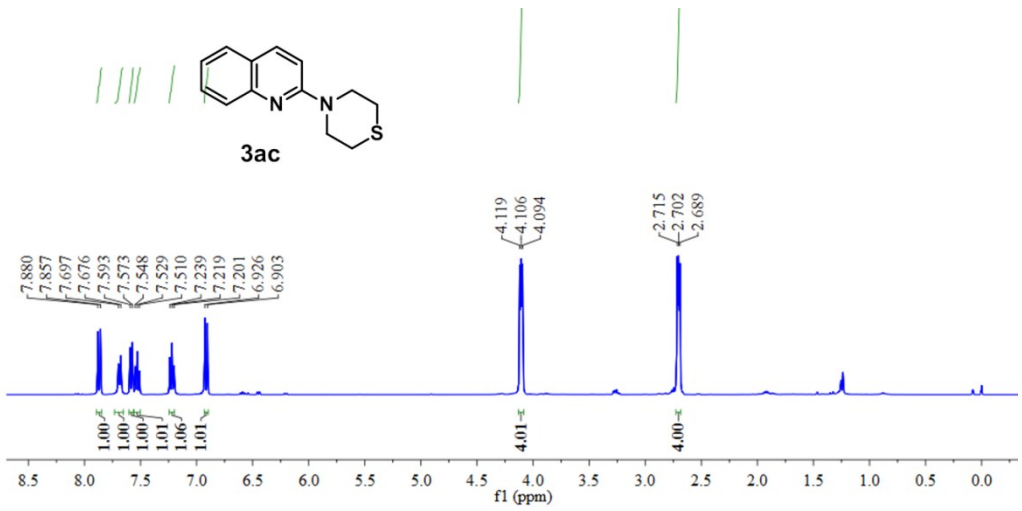
77.037
76.720
66.899
45.650
129.659
127.253
126.716
123.315
122.709
109.294
137.631
157.509
f1 (ppm)


3ac
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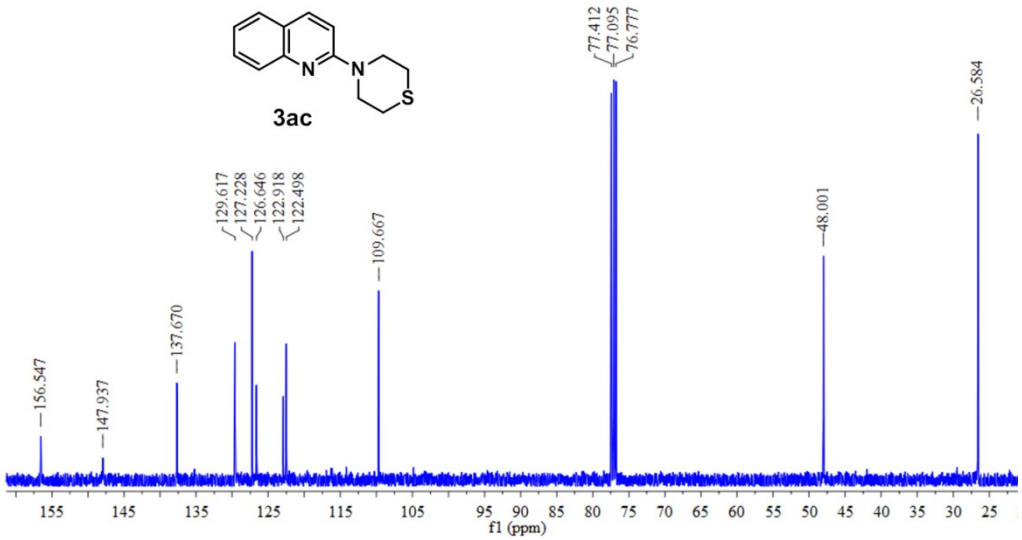
4.106
4.094
2.715
2.702
2.689
7.880
7.857
7.697
7.676
7.593
7.573
7.548
7.529
7.510
7.239
7.219
7.201
6.926
6.903
1.00
1.00
1.00
1.01
1.06
1.01
4.01
4.00
f1 (ppm)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76.777
26.584
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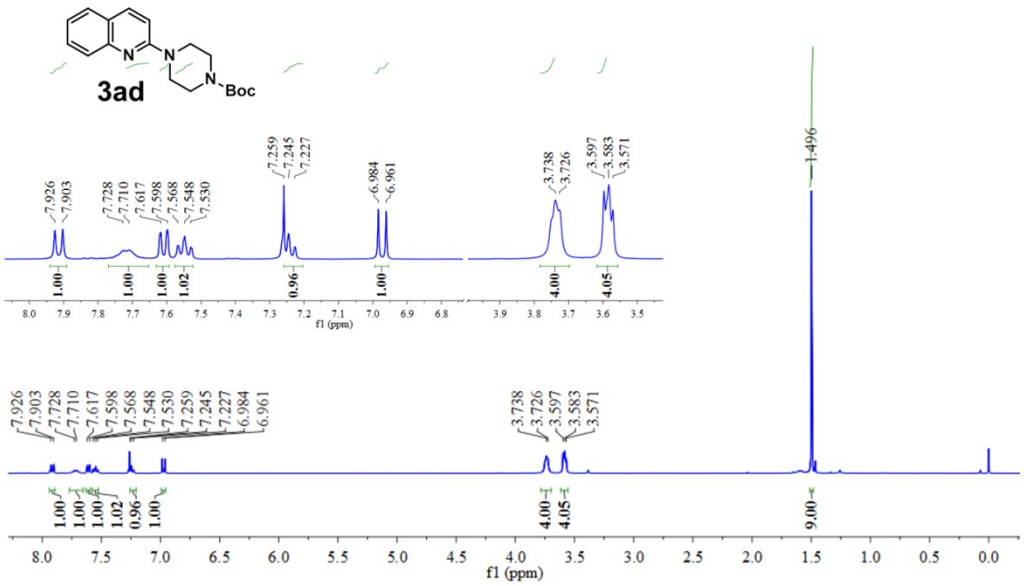
147.937
156.547
f1 (ppm)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Boc
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7.903
7.728
7.710
7.617
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7.568
7.548
7.530
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6.961
3.738
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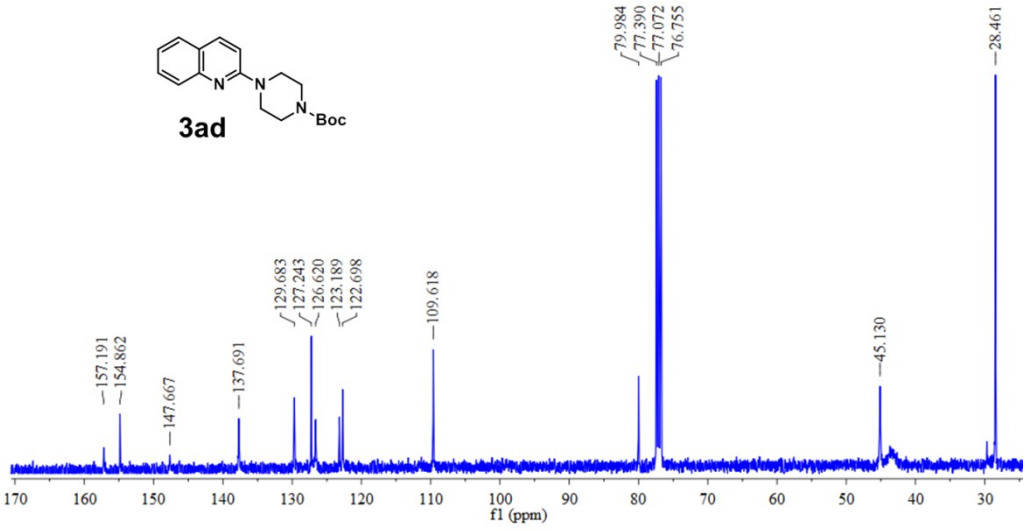
3.597
3.583
3.571
1.496
f1 (ppm)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Boc
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77.072
76.755
28.461
157.191
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147.667
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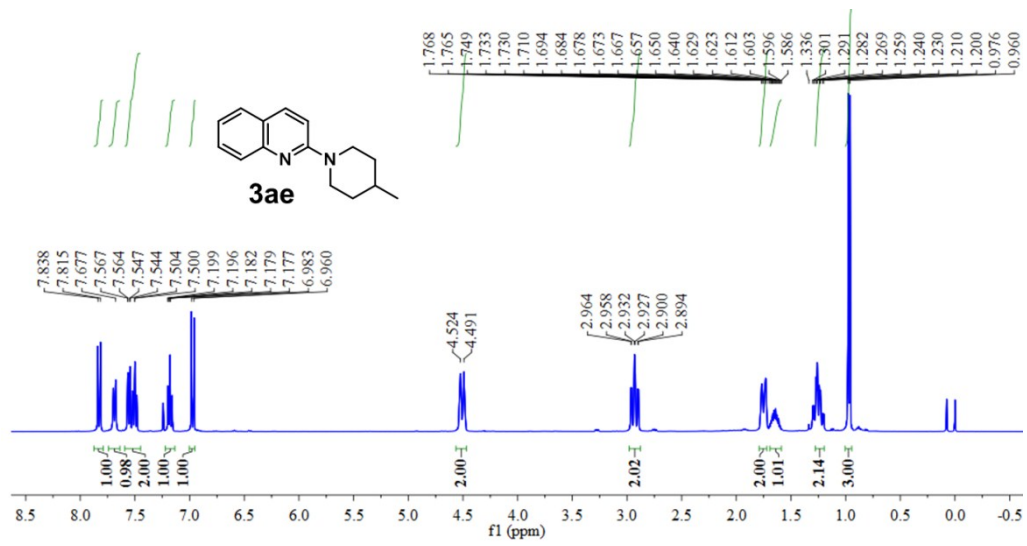
109.618
45.130
f1 (ppm)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1.733
1.730
1.710
1.694
1.684
1.678
1.673
1.667
1.657
1.650
1.640
1.629
1.623
1.612
1.603
1.596
1.586
1.336
1.301
1.291
1.282
1.269
1.259
1.240
1.230
1.210
1.200
0.976
0.960
7.838
7.815
7.677
7.567
7.564
7.547
7.544
7.504
7.500
7.199
7.196
7.182
7.179
7.177
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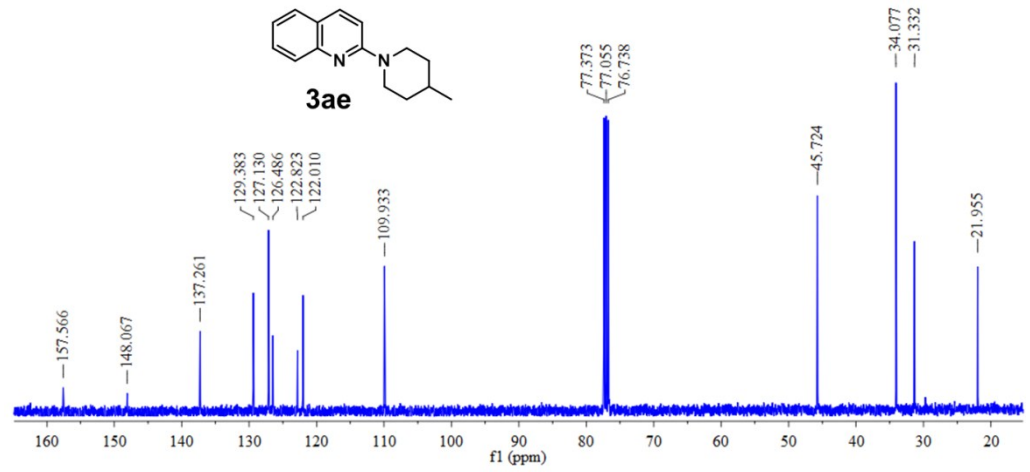
2.932
2.927
2.900
2.894
f1 (ppm)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129.383
127.130
126.486
122.823
122.010
109.933
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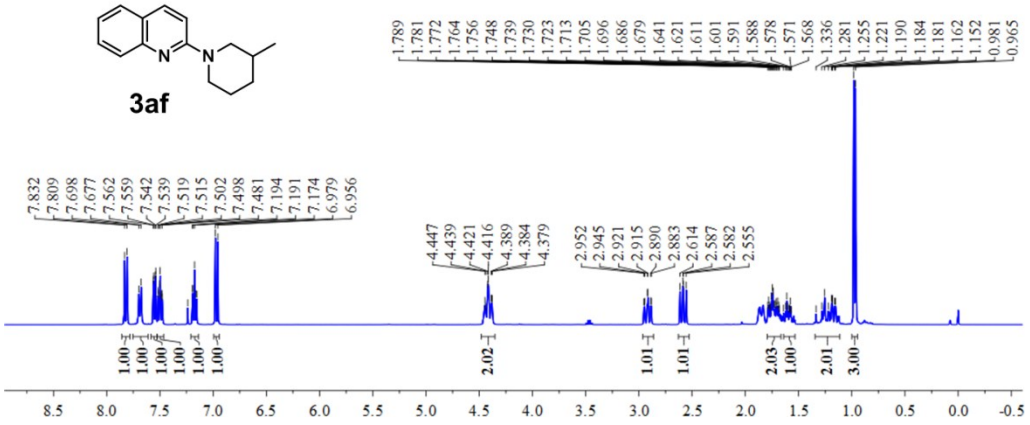
45.724
34.077
31.332
21.955
f1 (ppm)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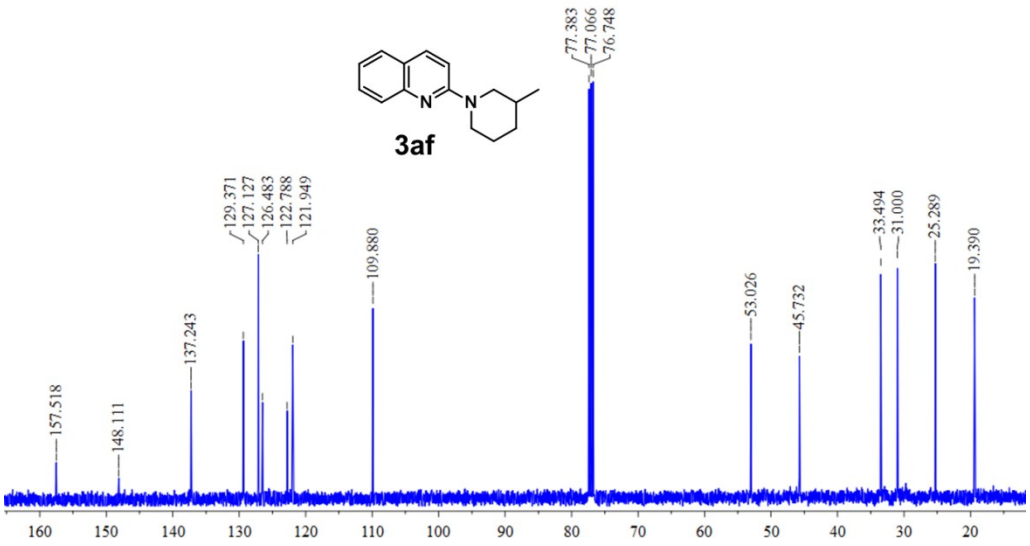
1.00
1.00
1.00
2.02
1.01
1.01
2.03
1.00
2.01
3.00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129.371
127.127
126.483
122.788
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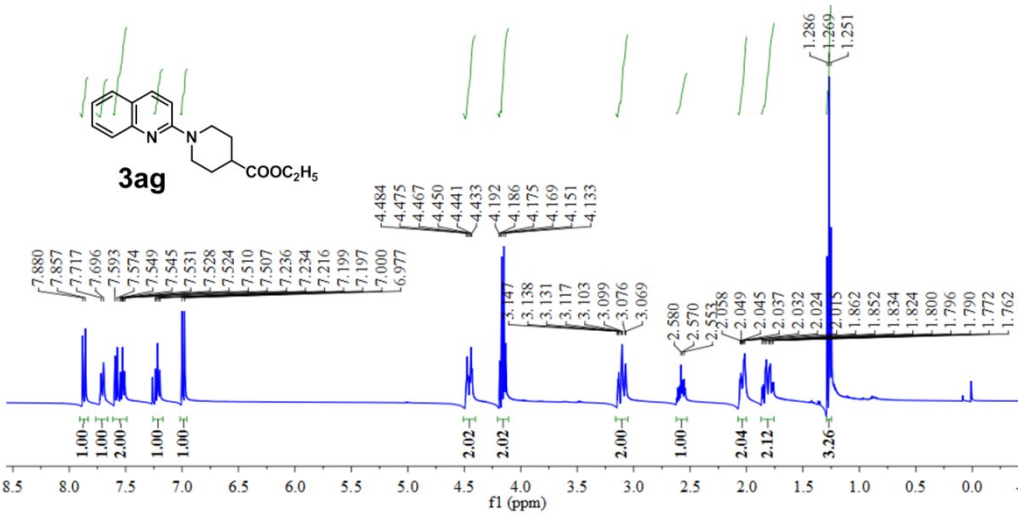
53.026
45.732
33.494
31.000
25.289
19.390


3ag
COOC2H5
7.880
7.857
7.717
7.696
7.593
7.574
7.549
7.545
7.531
7.528
7.524
7.510
7.507
7.236
7.234
7.216
7.199
7.197
7.000
6.977
4.484
4.475
4.467
4.450
4.441
4.433
4.192
4.186
4.175
4.169
4.151
4.133
3.147
3.138
3.131
3.117
3.103
3.099
3.076
3.069
2.580
2.570
2.553
2.538
2.049
2.045
2.037
2.032
2.024
2.015
1.862
1.852
1.834
1.824
1.800
1.796
1.790
1.772
1.762
1.286
1.269
1.251
1.00
1.00
2.00
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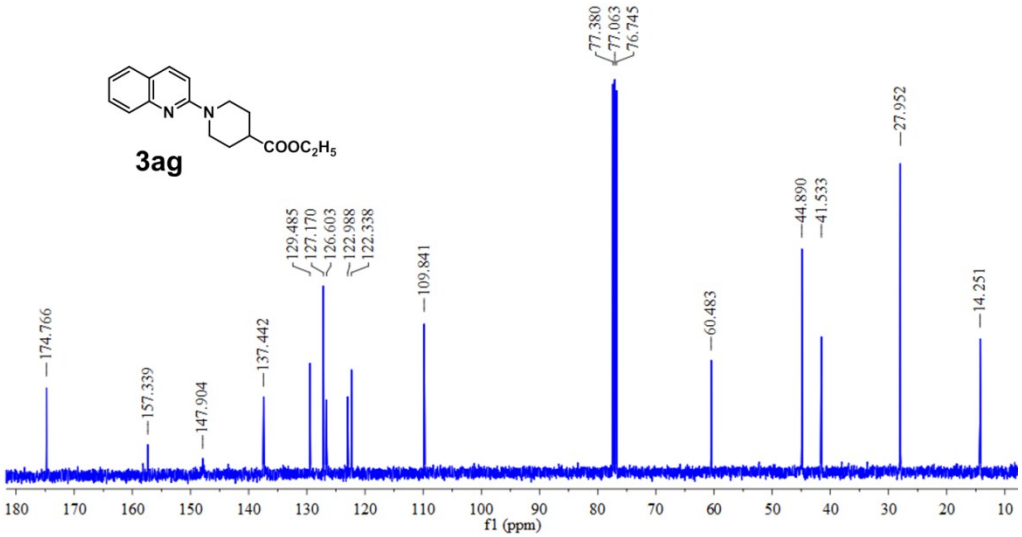
1.00
2.02
2.02
2.00
1.00
2.04
2.12
3.26
f1 (ppm)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COOC2H5
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77.063
76.745
174.766
157.339
147.904
137.442
129.485
127.170
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122.988
122.338
109.841
60.483
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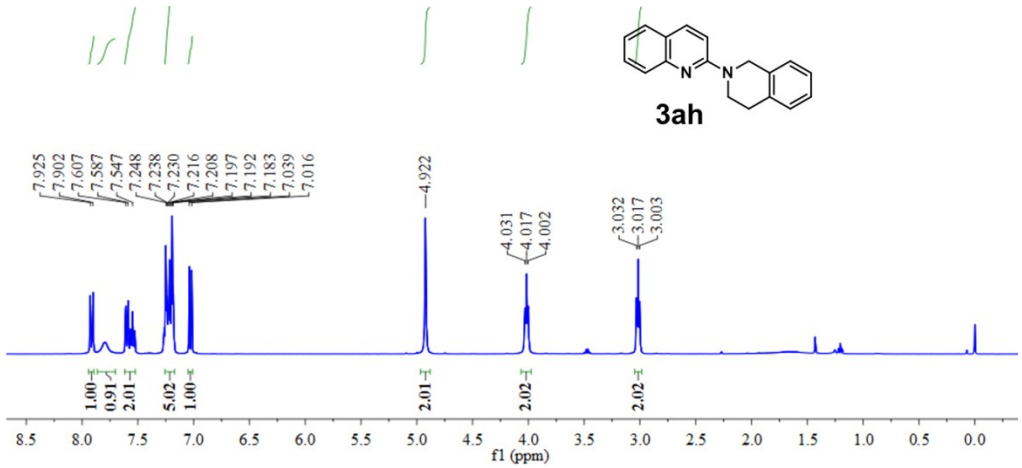
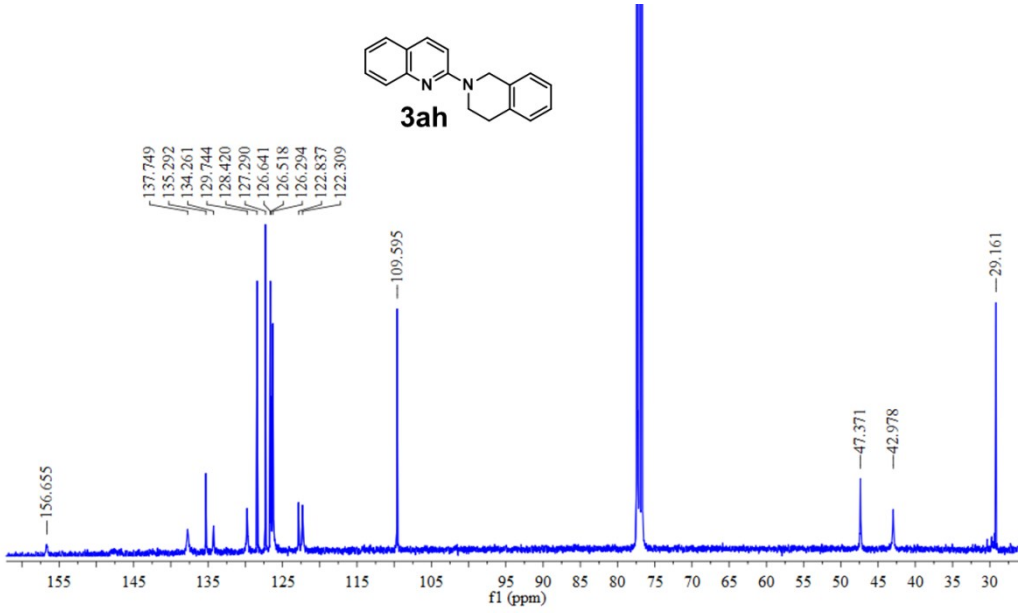
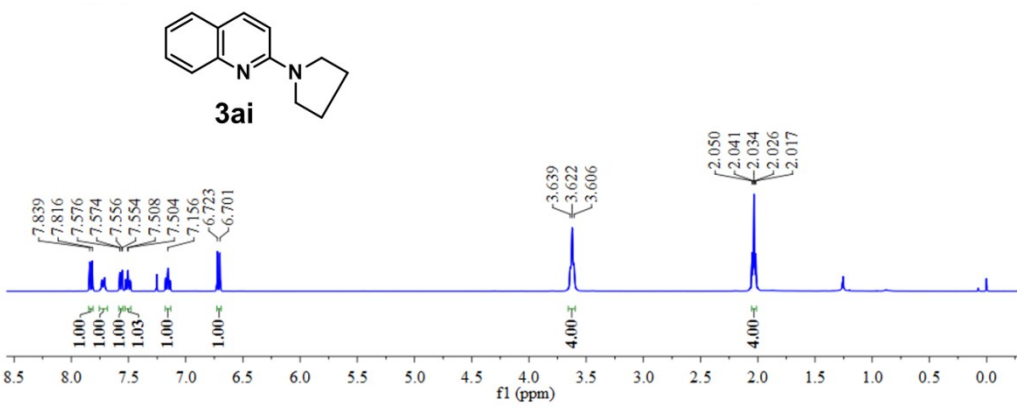
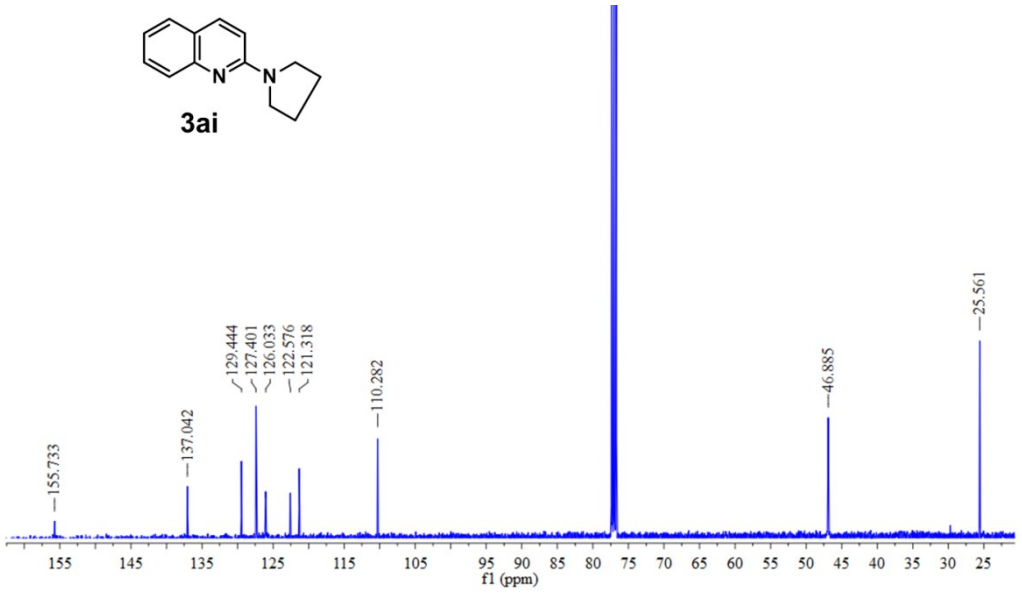
41.533
27.952
14.251
f1 (ppm)


3ah
7.925
7.902
7.607
7.587
7.547
7.248
7.238
7.230
7.216
7.208
7.197
7.192
7.183
7.039
7.016
4.922
4.031
4.017
4.002
3.032
3.017
3.003
1.00
0.91
2.01
5.02
1.00
2.01
2.02
2.02
f1 (ppm)


3ah
137.749
135.292
134.261
129.744
128.420
127.290
126.641
126.518
126.294
122.837
122.309
109.595
29.161
47.371
42.978
156.655
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)


3ai
7.839
7.816
7.576
7.574
7.556
7.554
7.508
7.504
7.156
6.723
6.701
3.639
3.622
3.606
2.050
2.041
2.034
2.026
2.017
1.00
1.00
1.00
1.03
1.00
1.00
4.00
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3ai
155.733
137.042
129.444
127.401
126.033
122.576
121.318
110.282
46.885
25.561
155
145
135
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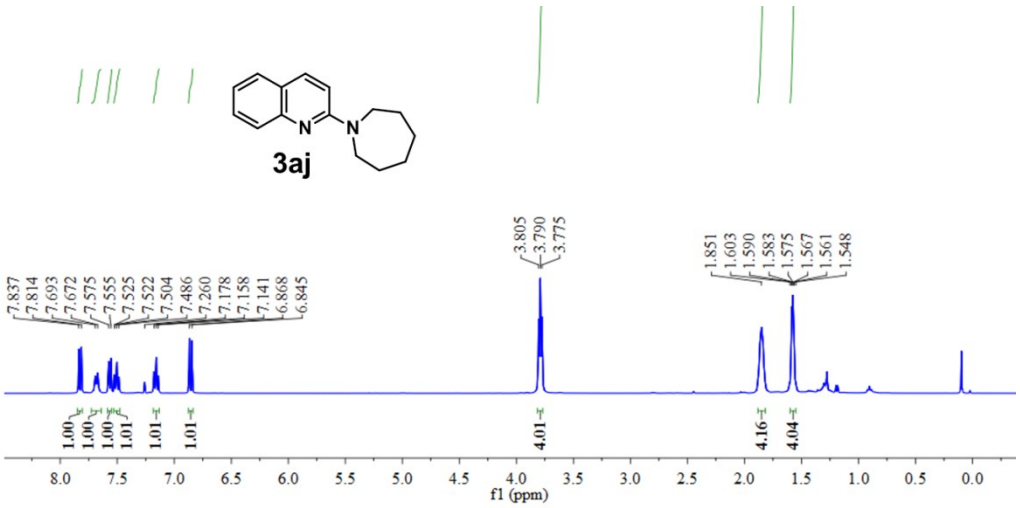
55
50
45
40
35
30
25
f1 (ppm)


3aj
7.837
7.814
7.693
7.672
7.575
7.555
7.525
7.522
7.504
7.486
7.260
7.178
7.158
7.141
6.868
6.845
3.805
3.790
3.775
1.851
1.603
1.590
1.583
1.575
1.567
1.561
1.548
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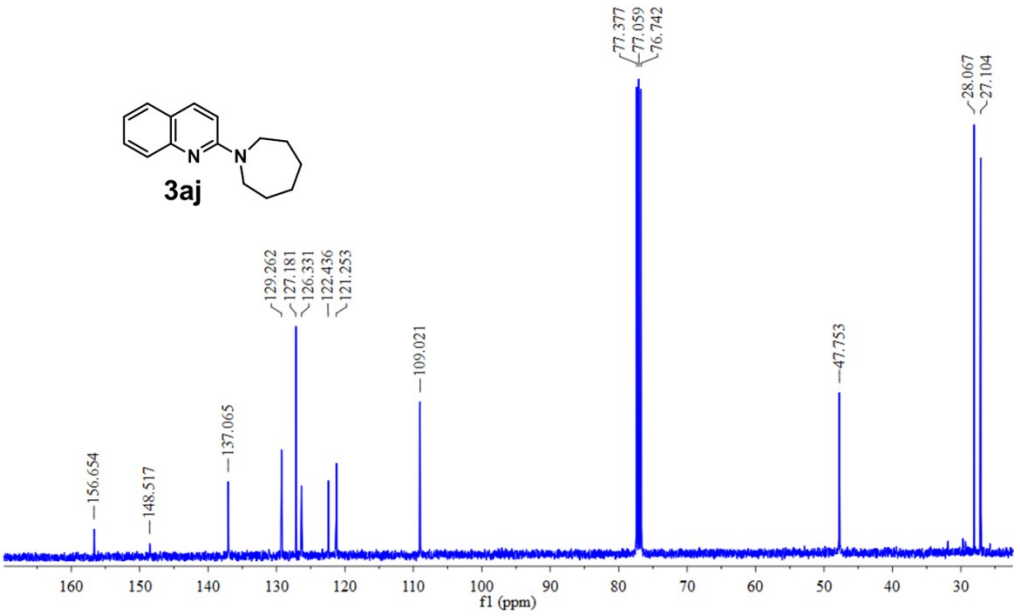
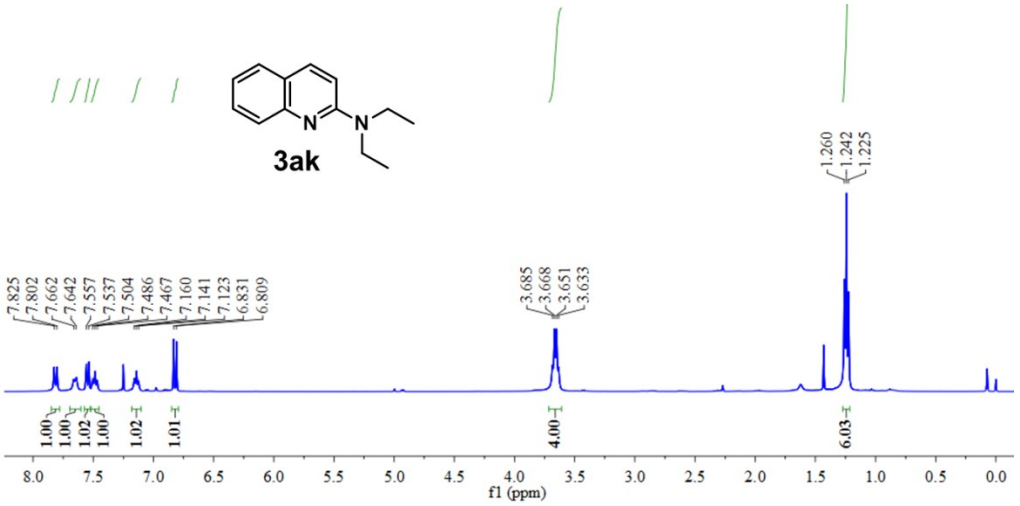
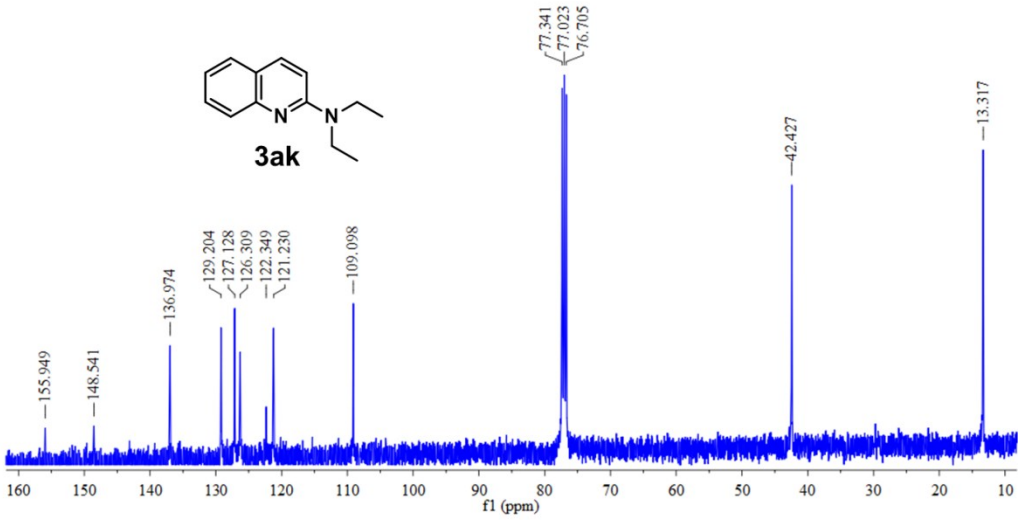
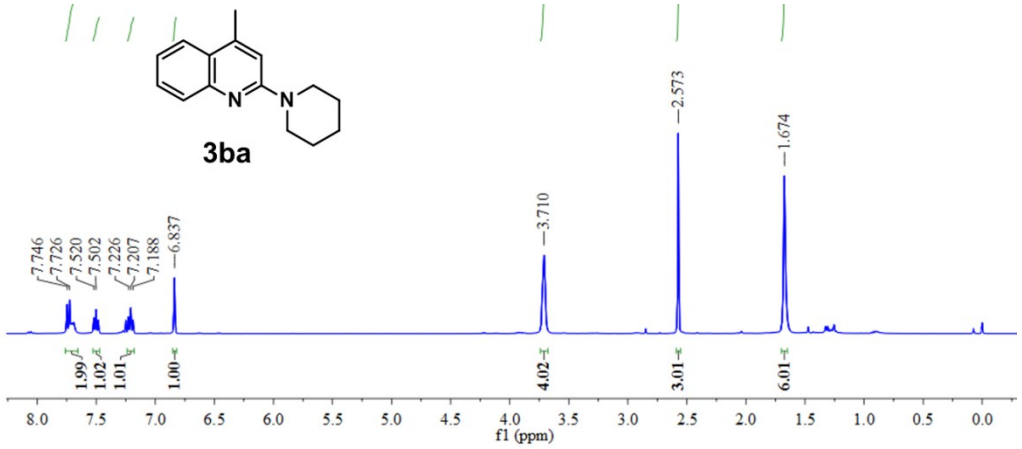
1.00
1.00
1.01
1.01
1.01
4.01
4.16
4.04
f1 (ppm)


3aj
77.377
77.059
76.742
28.067
27.104
129.262
127.181
126.331
122.436
121.253
109.021
47.753
156.654
148.517
137.065
f1 (ppm)


3ak
7.825
7.802
7.662
7.642
7.557
7.537
7.504
7.486
7.467
7.160
7.141
7.123
6.831
6.809
3.685
3.668
3.651
3.633
1.260
1.242
1.225
1.00
1.00
1.02
1.00
1.02
1.01
4.00
6.03
f1 (ppm)


3ak
77.341
77.023
76.705
42.427
13.317
129.204
127.128
126.309
122.349
121.230
109.098
136.974
155.949
148.541
f1 (ppm)


3ba
2.573
1.674
3.710
7.746
7.726
7.520
7.502
7.226
7.207
7.188
6.837
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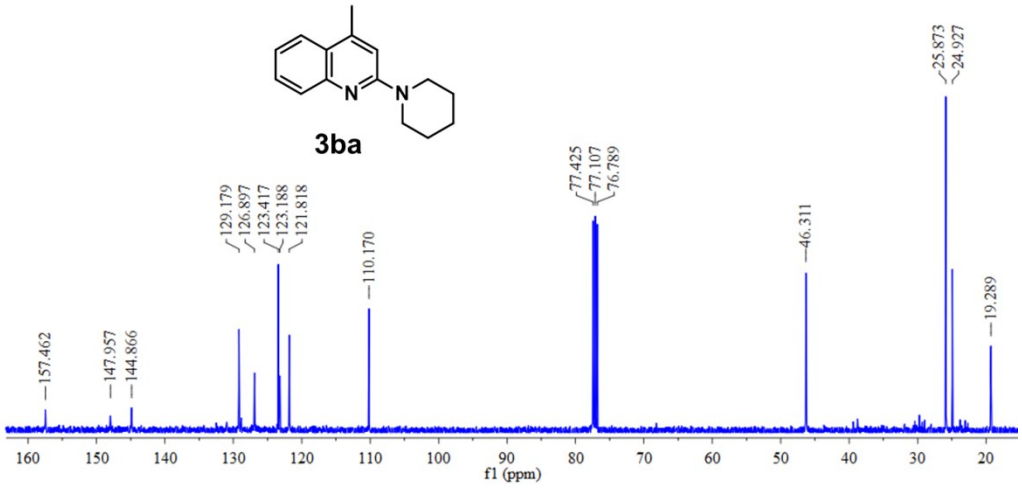
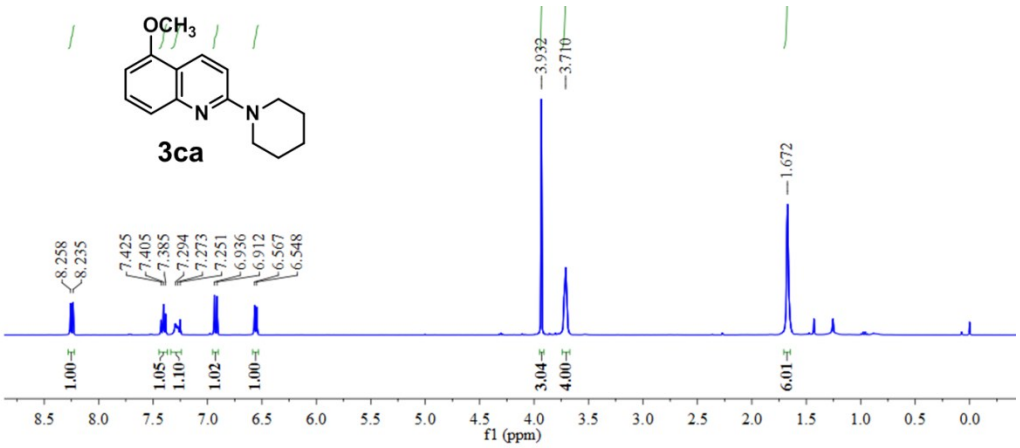
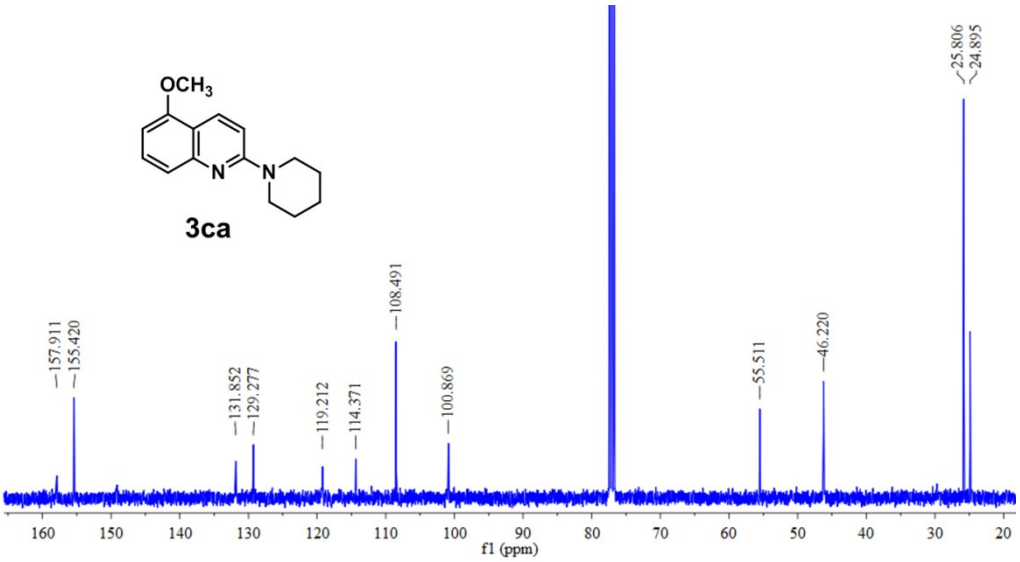
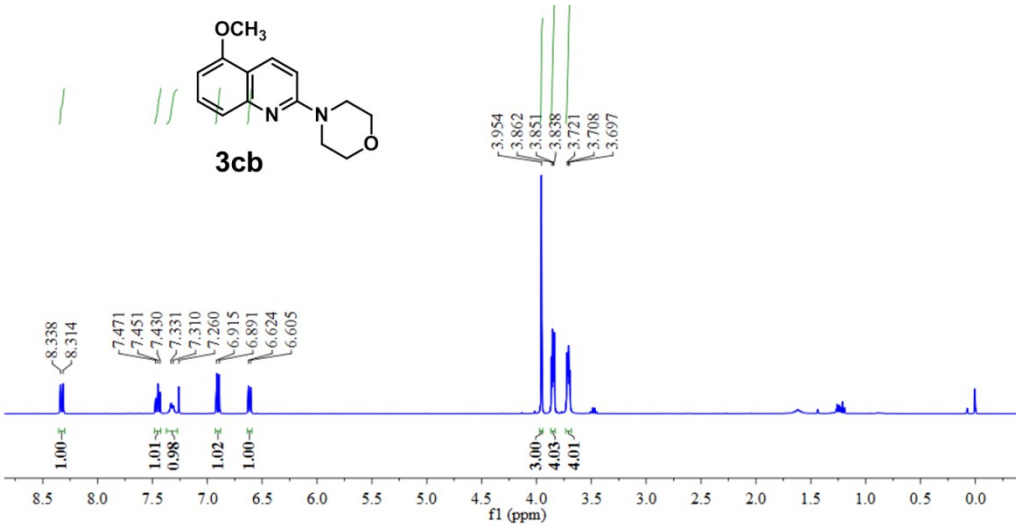
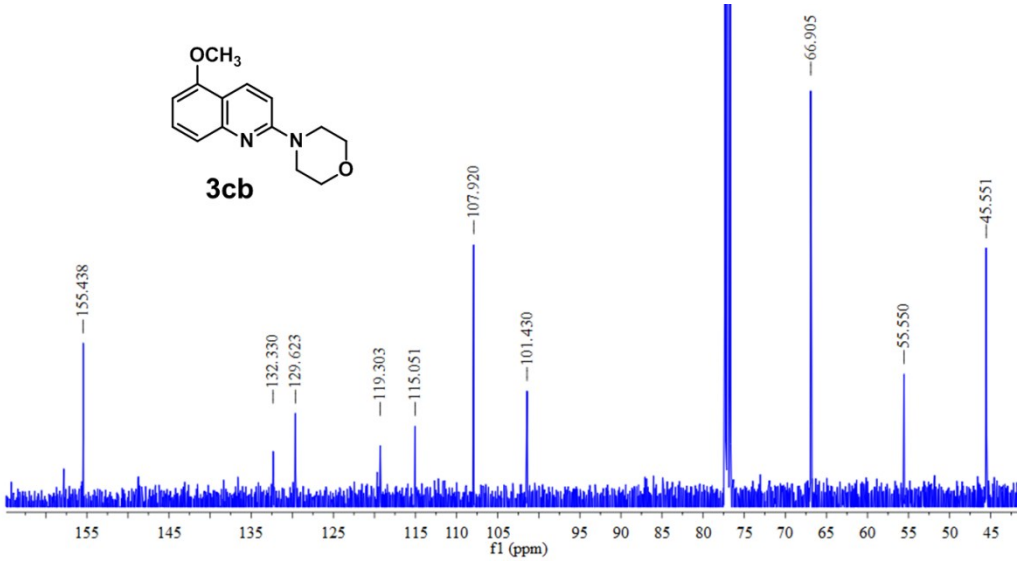
1.02
1.01
1.00
4.02
3.01
6.01
f1 (ppm)

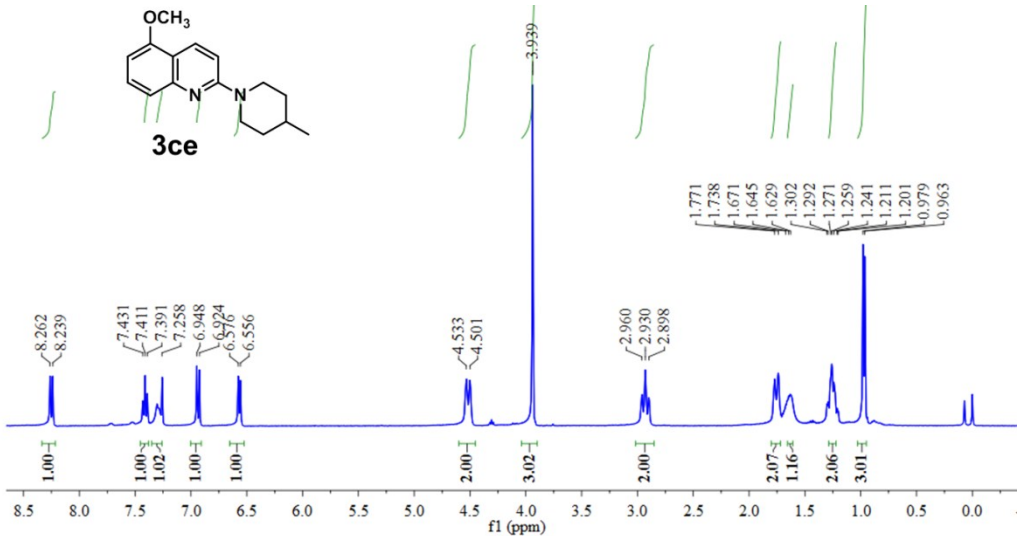

3ba
25.873
24.927
77.425
77.107
76.789
46.311
19.289
129.179
126.897
123.417
123.188
121.818
110.170
157.462
147.957
144.866
f1 (ppm)


OCH3
N
N
3ca
8.258
8.235
7.425
7.405
7.385
7.294
7.273
7.251
6.936
6.912
6.567
6.548
3.932
3.710
1.672
1.00
1.05
1.10
1.02
1.00
3.04
4.00
6.01
f1 (ppm)


OCH3
N
N
3ca
157.911
155.420
131.852
129.277
119.212
114.371
108.491
100.869
55.511
46.220
25.806
24.895
f1 (ppm)


OCH3
N
O
3cb
8.338
8.314
7.471
7.451
7.430
7.331
7.310
7.260
6.915
6.891
6.624
6.605
3.954
3.862
3.851
3.838
3.721
3.708
3.697
1.00
1.01
0.98
1.02
1.00
3.00
4.03
4.01
f1 (ppm)


OCH3
N
N
O
3cb
155.438
132.330
129.623
119.303
115.051
107.920
101.430
66.905
55.550
45.551
155
145
135
125
115
110
105
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)


OCH3
N
N
3ce
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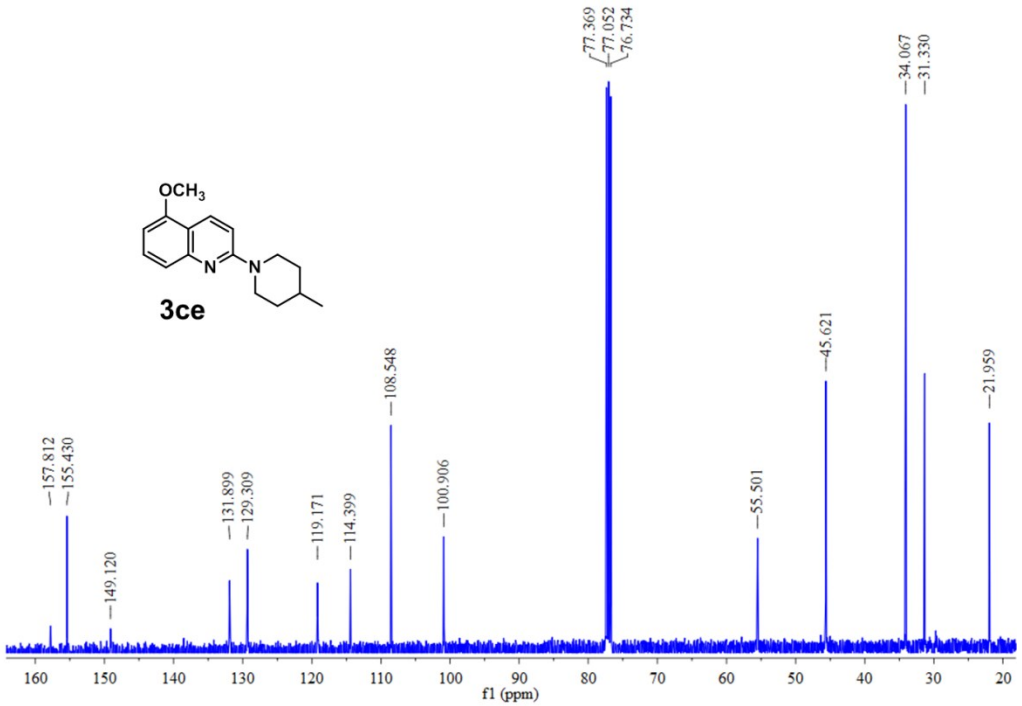
1.771
1.738
1.671
1.645
1.629
1.302
1.292
1.271
1.259
1.241
1.211
1.201
0.979
0.963
8.262
8.239
7.431
7.411
7.391
7.258
6.948
6.924
6.576
6.556
4.533
4.501
2.960
2.930
2.898
1.00
1.00
1.02
1.00
1.00
2.00
3.02
2.00
2.07
1.16
2.06
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OCH3
N
N
3ce
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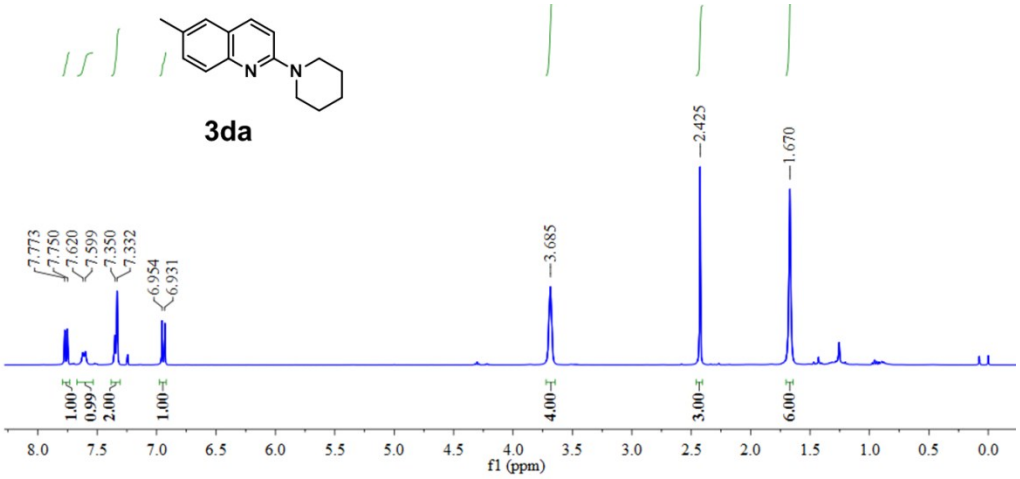
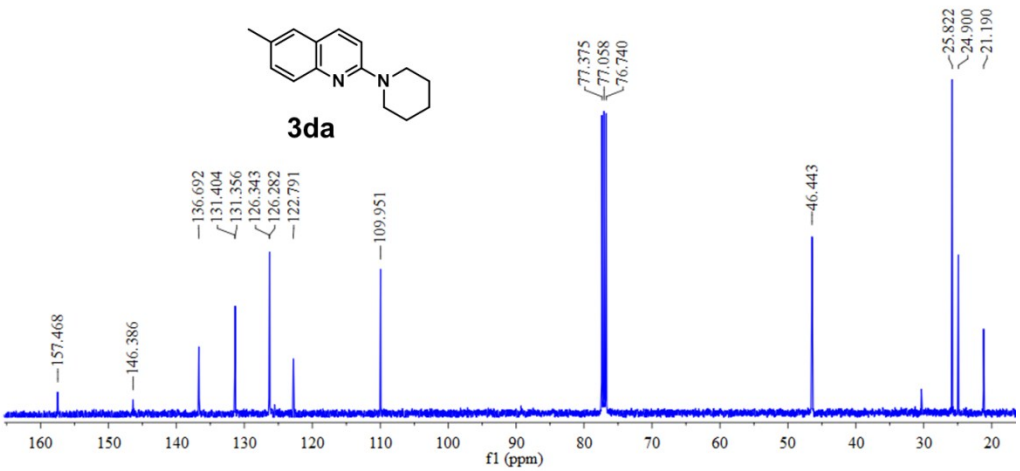
77.052
76.734
34.067
31.330
157.812
155.430
149.120
131.899
129.309
119.171
114.399
108.548
100.906
55.501
45.621
21.959
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


3da
7.773
7.750
7.620
7.599
7.350
7.332
6.954
6.931
3.685
2.425
1.670
1.00
0.99
2.00
1.00
4.00
3.00
6.00
f1 (ppm)


3da
157.468
146.386
136.692
131.404
131.356
126.343
126.282
122.791
109.951
77.375
77.058
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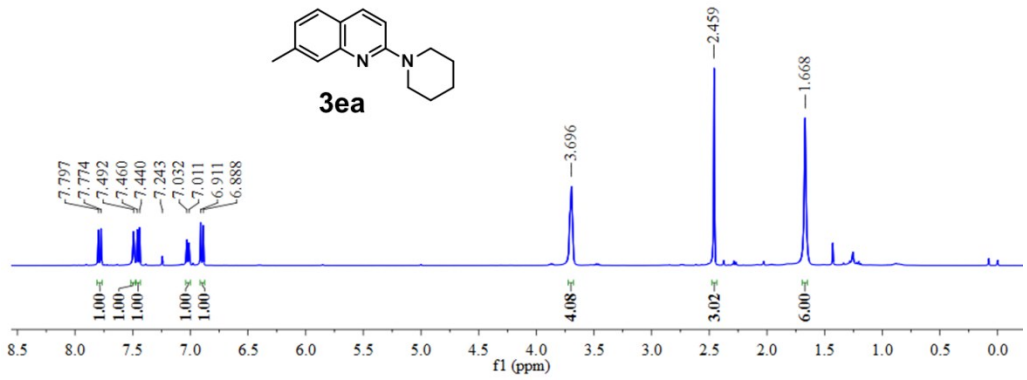
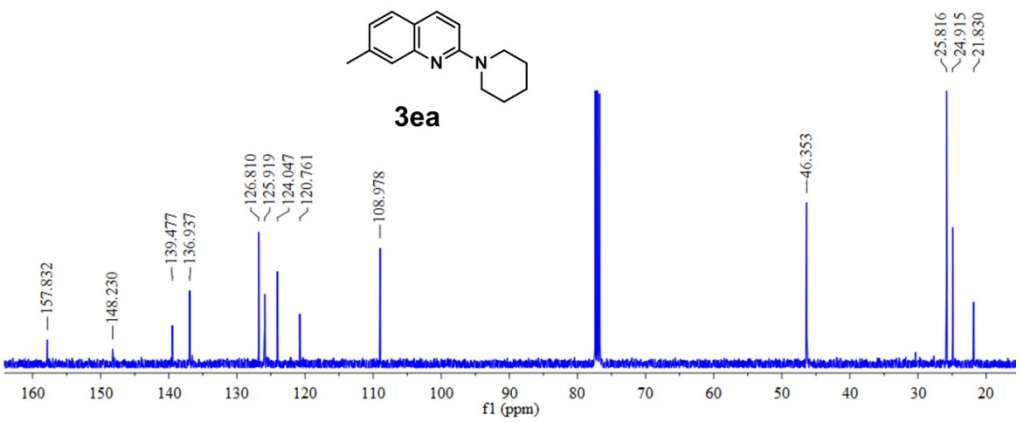
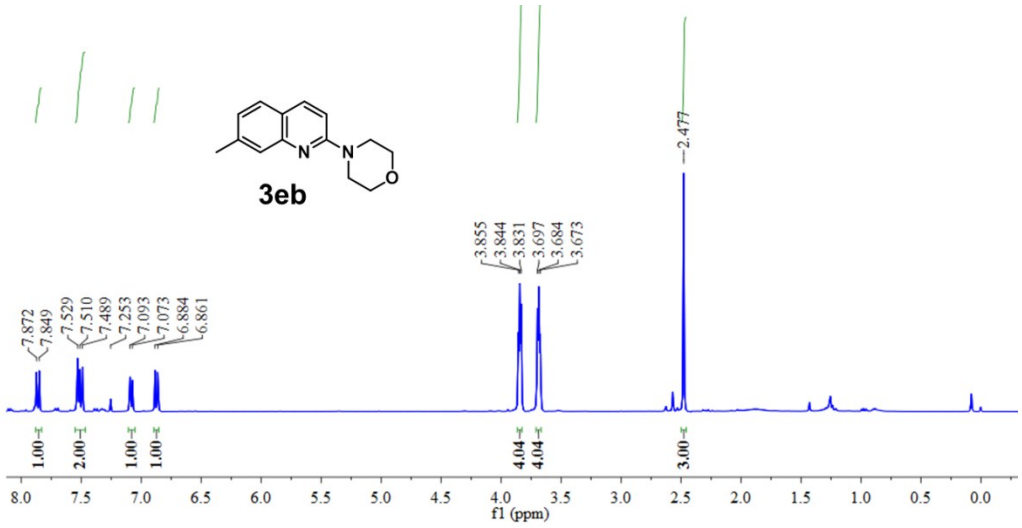
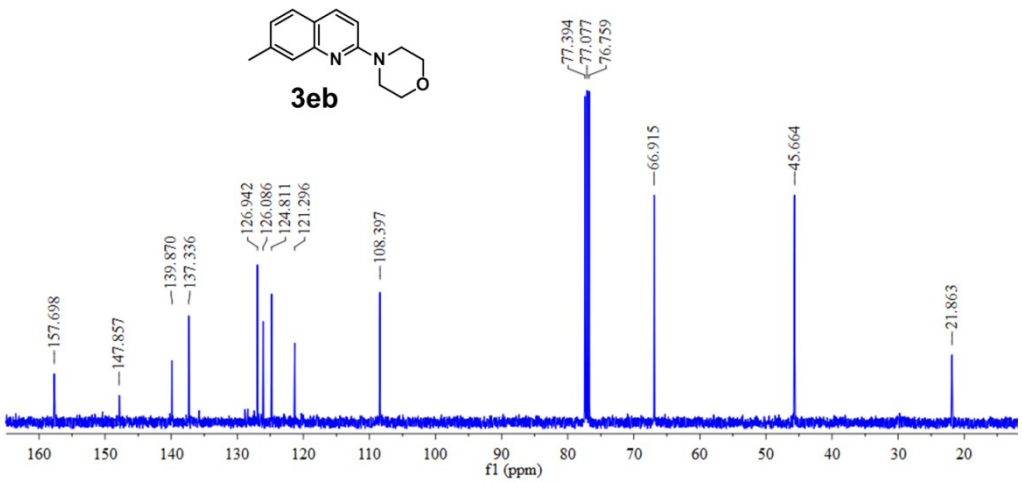
46.443
25.822
24.900
21.190
f1 (ppm)


3ea
7.797
7.774
7.492
7.460
7.440
7.243
7.032
7.011
6.911
6.888
3.696
2.459
1.668
1.00
1.00
1.00
1.00
1.00
4.08
3.02
6.00
f1 (ppm)


3ea
157.832
148.230
139.477
136.937
126.810
125.919
124.047
120.761
108.978
46.353
25.816
24.915
21.830
f1 (ppm)


3eb
7.872
7.849
7.529
7.510
7.489
7.253
7.093
7.073
6.884
6.861
3.855
3.844
3.831
3.697
3.684
3.673
2.477
1.00
2.00
1.00
1.00
4.04
4.04
3.00
f1 (ppm)


3eb
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76.759
66.915
45.664
157.698
147.857
139.870
137.336
126.942
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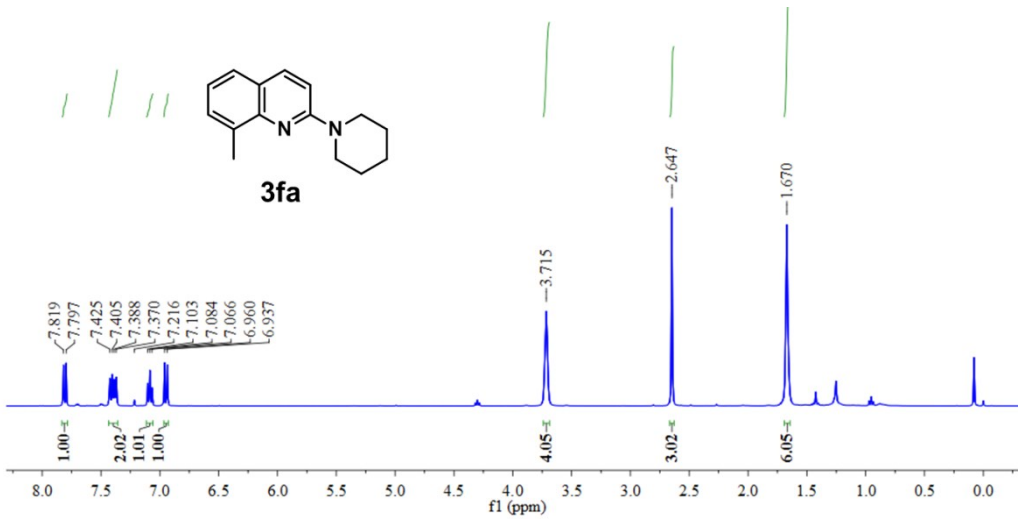
124.811
121.296
108.397
21.863
f1 (ppm)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7.819
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7.425
7.405
7.388
7.370
7.216
7.103
7.084
7.066
6.960
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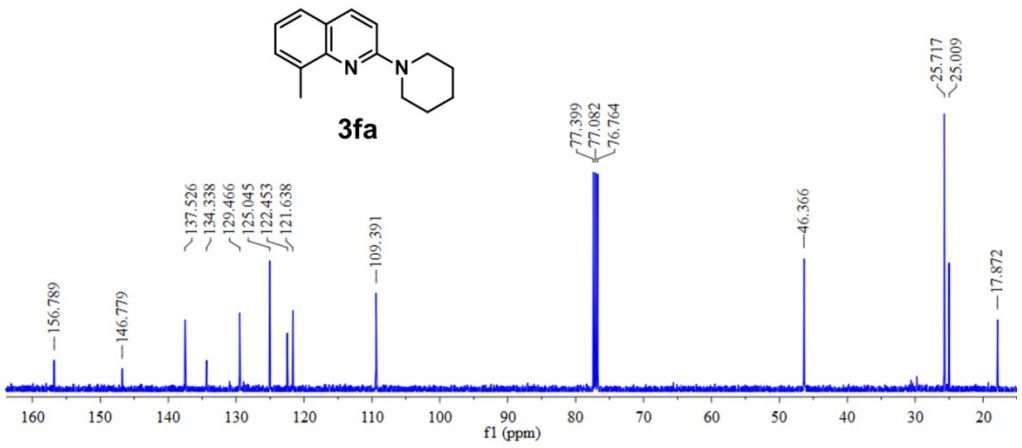
1.00
4.05
3.02
6.05
f1 (ppm)


3fa
156.789
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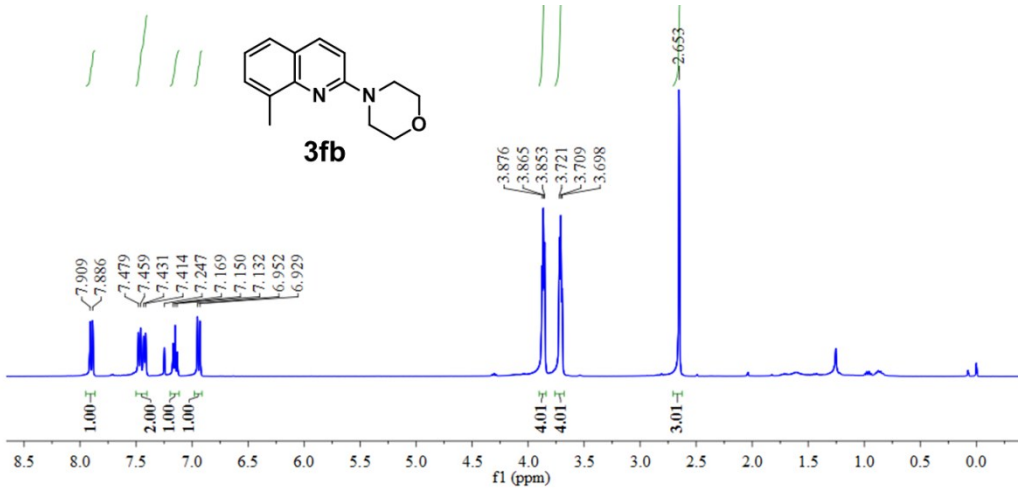
137.526
134.338
129.466
125.045
122.453
121.638
109.391
77.399
77.082
76.764
46.366
25.717
25.009
17.872
f1 (ppm)


3fb
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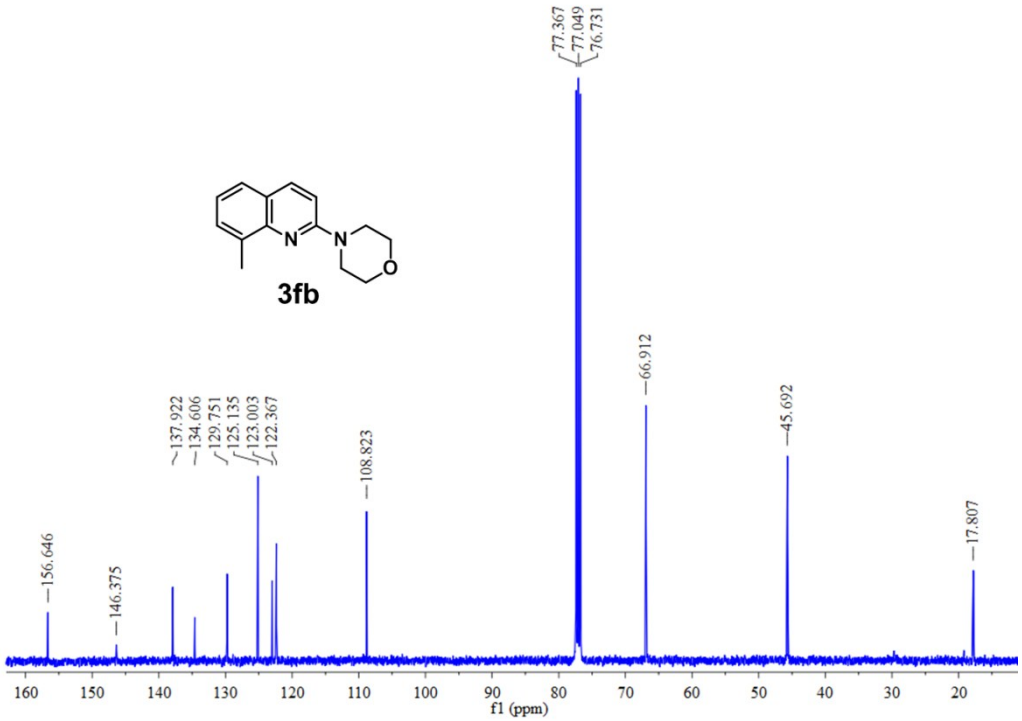
7.886
7.479
7.459
7.431
7.414
7.247
7.169
7.150
7.132
6.952
6.929
3.876
3.865
3.853
3.721
3.709
3.698
2.653
1.00
2.00
1.00
1.00
4.01
4.01
3.01
f1 (ppm)


3fb
156.646
146.375
137.922
134.606
129.751
125.135
123.003
122.367
108.823
77.367
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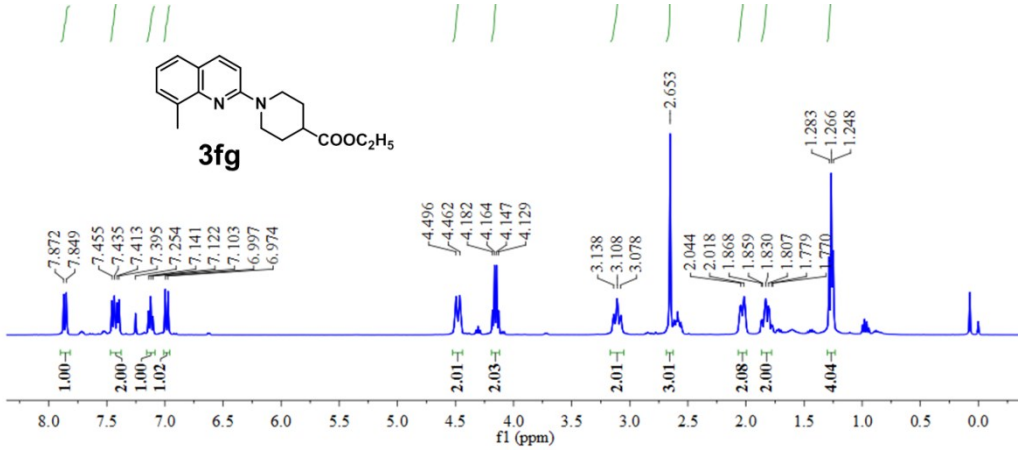
76.731
66.912
45.692
17.807
f1 (ppm)


3fg
COOC2H5
7.872
7.849
7.455
7.435
7.413
7.395
7.254
7.141
7.122
7.103
6.997
6.974
4.496
4.462
4.182
4.164
4.147
4.129
3.138
3.108
3.078
2.653
2.044
2.018
1.868
1.859
1.830
1.807
1.779
1.770
1.283
1.266
1.248
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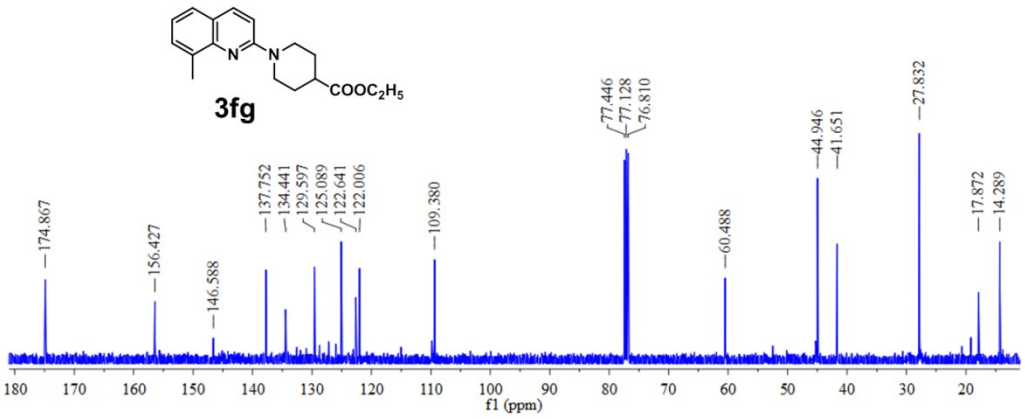
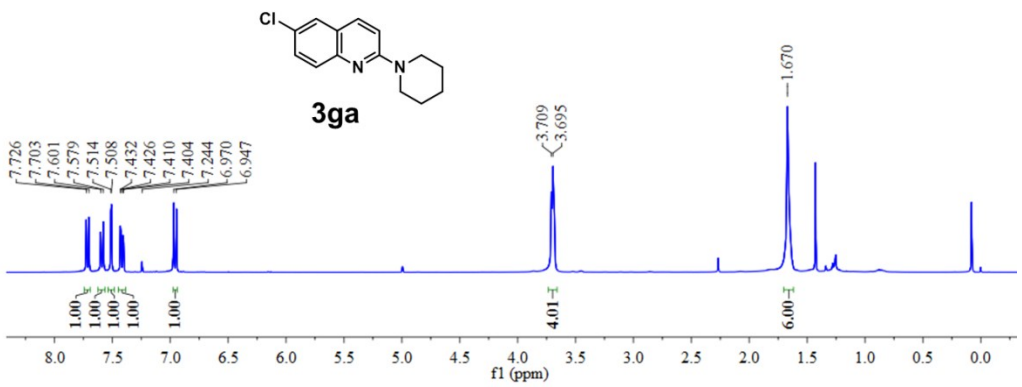
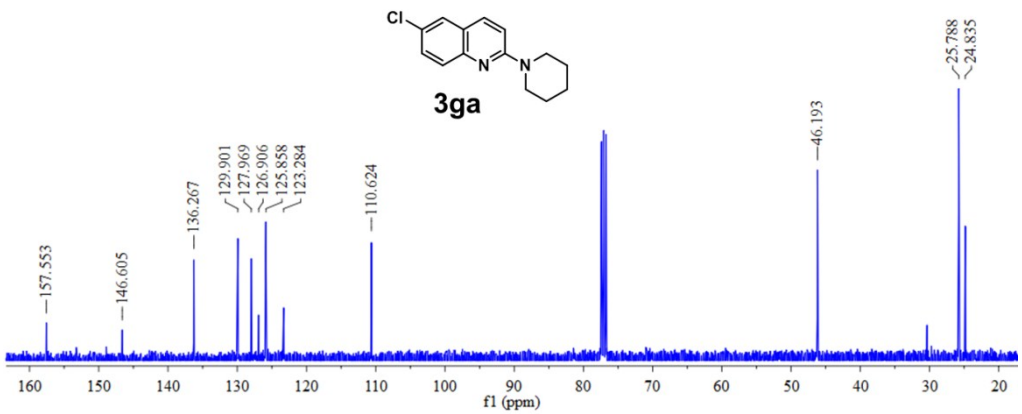
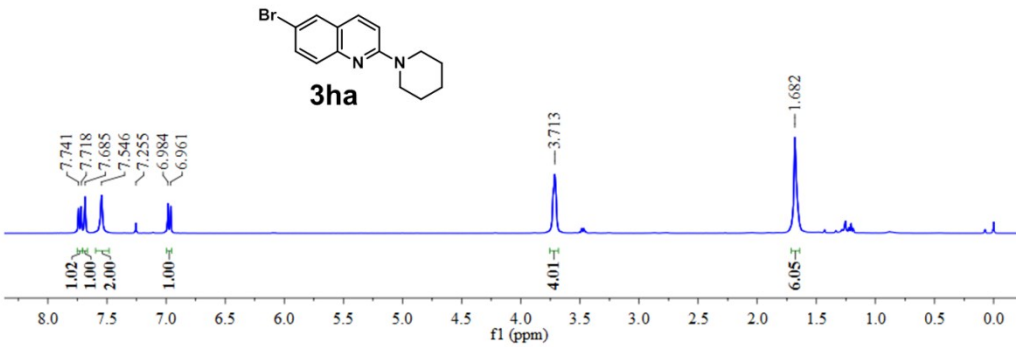
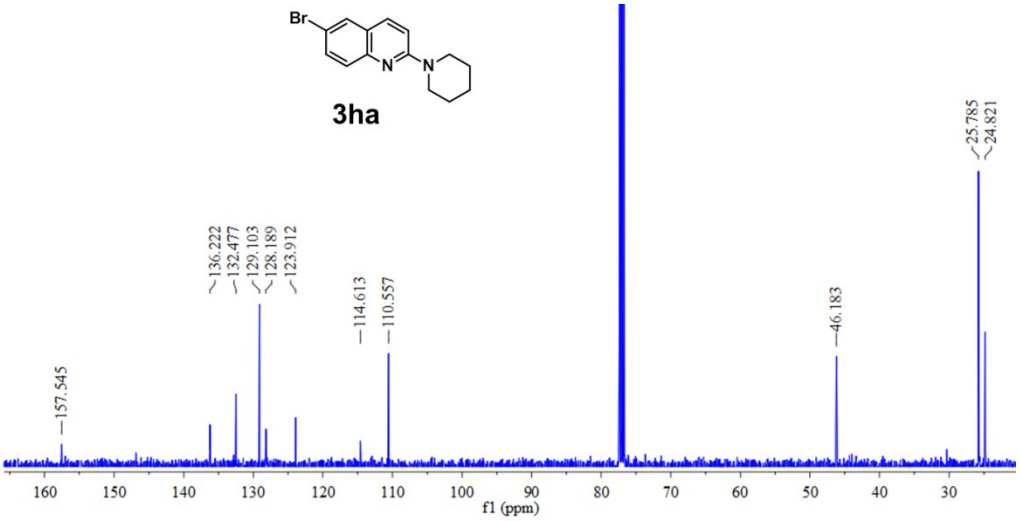
3.01
2.08
2.00
4.04
f1 (ppm)

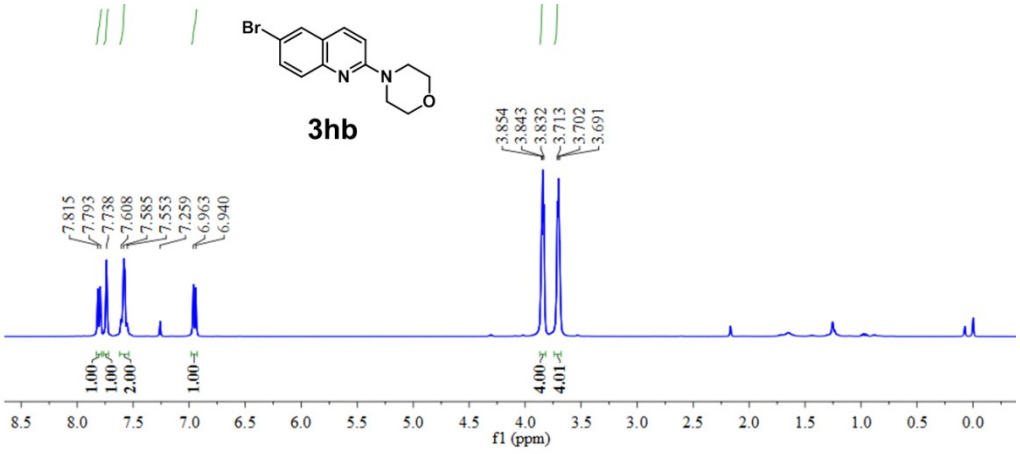

3fg
COOC2H5
174.867
156.427
146.588
137.752
134.441
129.597
125.089
122.641
122.006
109.380
77.446
77.128
76.810
60.488
44.946
41.651
27.832
17.872
14.289
f1 (ppm)

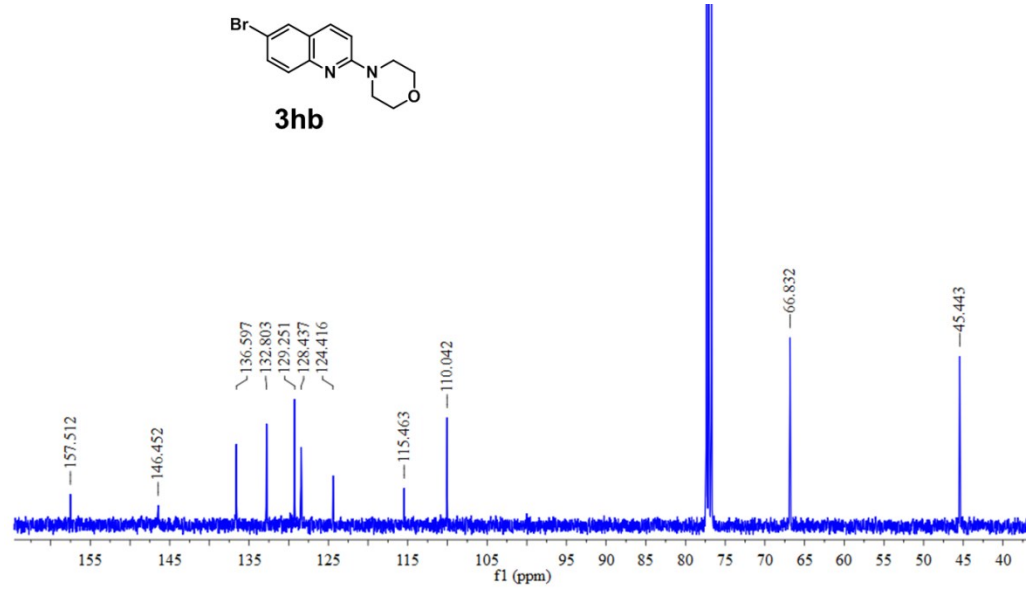

Cl
3ga
7.726
7.703
7.601
7.579
7.514
7.508
7.432
7.426
7.410
7.404
7.244
6.970
6.947
3.709
3.695
1.670
1.00
1.00
1.00
1.00
1.00
4.01
6.00
f1 (ppm)

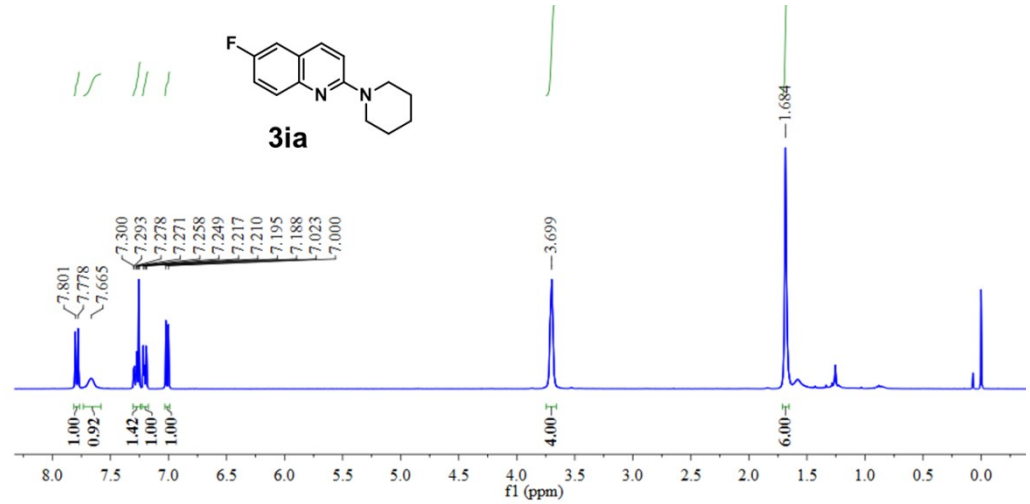

Cl
3ga
157.553
146.605
136.267
129.901
127.969
126.906
125.858
123.284
110.624
46.193
25.788
24.835
f1 (ppm)

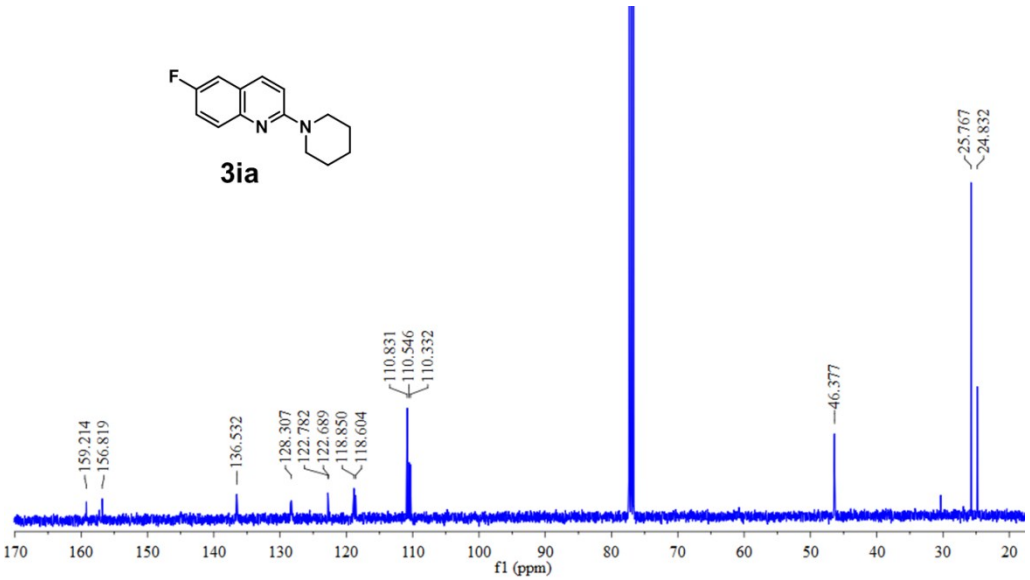

Br
N
N
3ha
7.741
7.718
7.685
7.546
7.255
6.984
6.961
3.713
1.682
1.02
1.00
2.00
1.00
4.01
6.05
f1 (ppm)

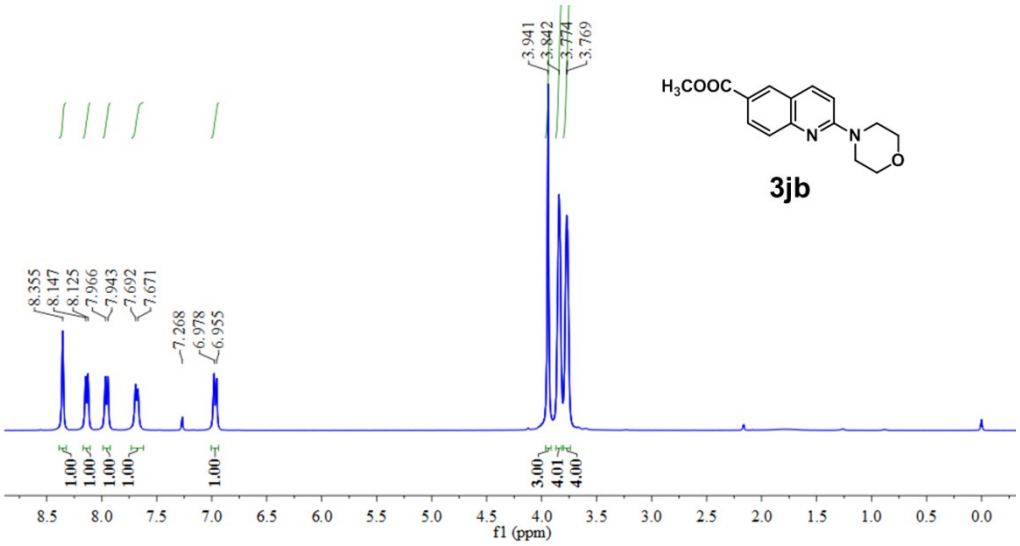

Br
N
N
3ha
157.545
136.222
132.477
129.103
128.189
123.912
114.613
110.557
46.183
25.785
24.821
f1 (ppm)

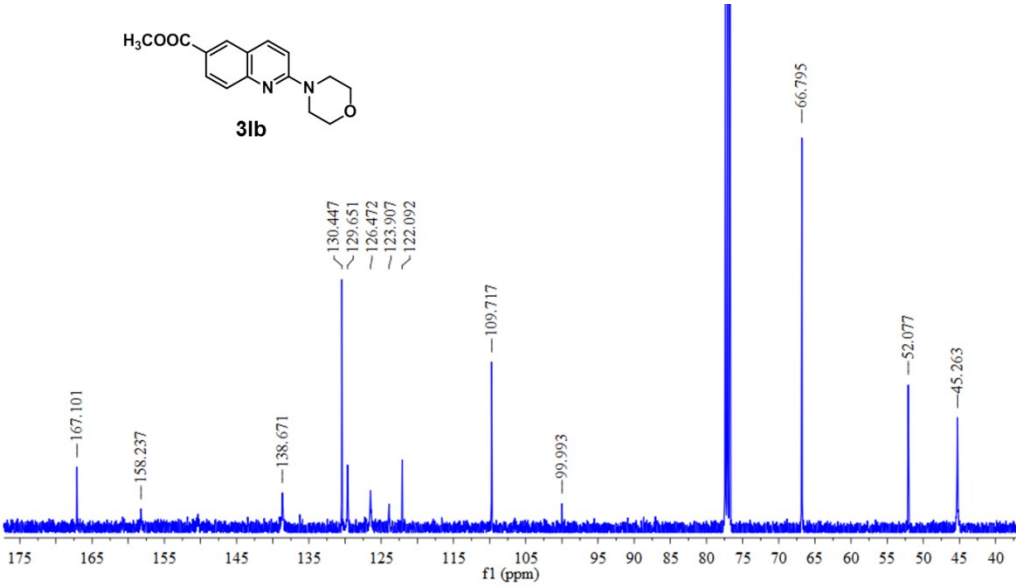

Br
N
O
3hb
7.815
7.793
7.738
7.608
7.585
7.553
7.259
6.963
6.940
3.854
3.843
3.832
3.713
3.702
3.691
1.00
1.00
2.00
1.00
4.00
4.01
f1 (ppm)


Br
N
N
O
3hb
157.512
146.452
136.597
132.803
129.251
128.437
124.416
115.463
110.042
66.832
45.443
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
f1 (ppm)


F
N
N
3ia
7.801
7.778
7.665
7.300
7.293
7.278
7.271
7.258
7.249
7.217
7.210
7.195
7.188
7.023
7.000
3.699
1.684
1.00
0.92
1.42
1.00
1.00
4.00
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
N
N
3ia
159.214
156.819
136.532
128.307
122.782
122.689
118.850
118.604
110.831
110.546
110.332
46.377
25.767
24.832
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


3.941
3.842
3.774
3.769
H3COOC
N
O
3jb
8.355
8.147
8.125
7.966
7.943
7.692
7.671
7.268
6.978
6.955
1.00
1.00
1.00
1.00
1.00
3.00
4.01
4.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3COOC
N
O
3lb
66.795
130.447
129.651
126.472
123.907
122.092
109.717
52.077
45.263
167.101
158.237
138.671
99.993
175 165 155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)