Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Minisci C-H Alkylation of N-Heteroarene with Aliphatic Alcohol via β-Scission of Alkoxy Radical

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Content

1. Reagents

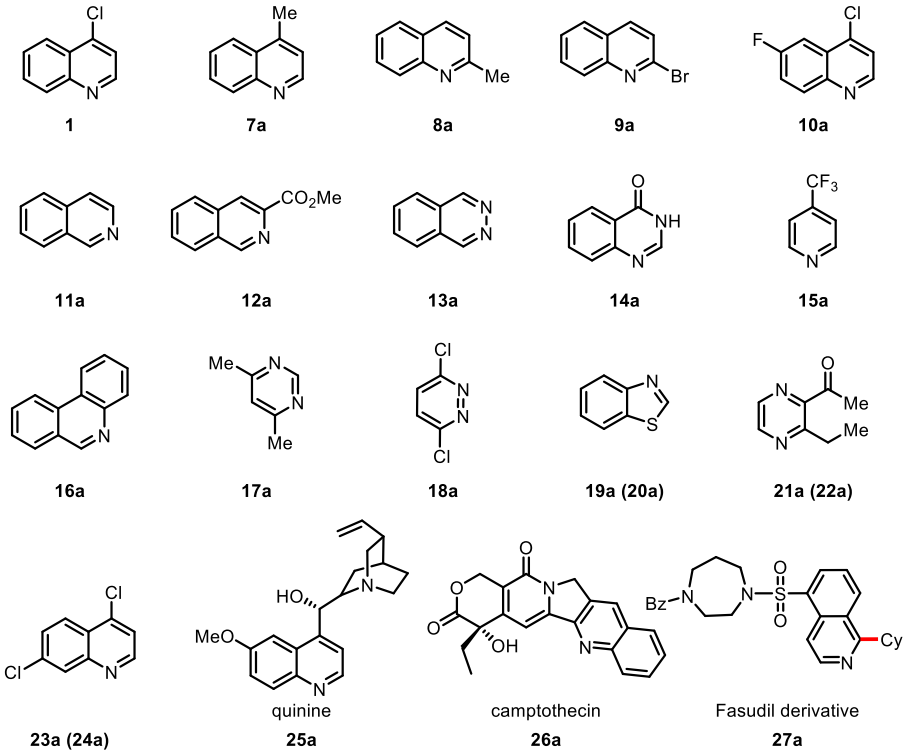
All commercial materials were used as received without further purification unless otherwise noted. The alcohol starting material was either purchased from TCI or simply synthesized according to the reported procedure. Perfluorohydroxylbenziodoxole (PFBI-OH),[1] hydroxylbenziodoxole (BI-OH),[2] acetoxybenziodoxole (BI-OAc), [2] were synthesized according to reported procedures and used as freshly prepared. $[Ru(bpy)_3]Cl_2$ (98%, Ru＞15.75%, Energy Chemical) and HFIP (99.0%, ACS grade, J&K Chemical) were used as received unless otherwise noted. Analytical thin layer chromatography (TLC) were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λmax = 254 nm). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China.

2. Instruments

All reactions were carried out in a 4 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with a PTFE cap on bench top. 23 W CFL was used for visible-light promoted reactions. NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference ($CDCl_3$, δ 7.26 for ^1H and δ 77.16 for ^{13}C. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br s = broad singlet, m = multiplet.) High resolution ESI mass experiments were operated on a Waters LCT Premier instrument.

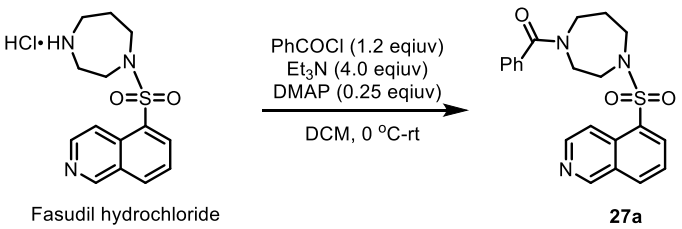
3. Synthesis of substrates

3.1 N-Heteroaromatic substrates



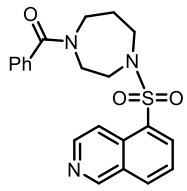
Scheme S1. List of N-Heteroaromatic substrates used in this study

Except the substrate **27a**, all N-heteroaromatics substrated were commercial available and used as received.



Scheme S2. Synthesis of compound 27a

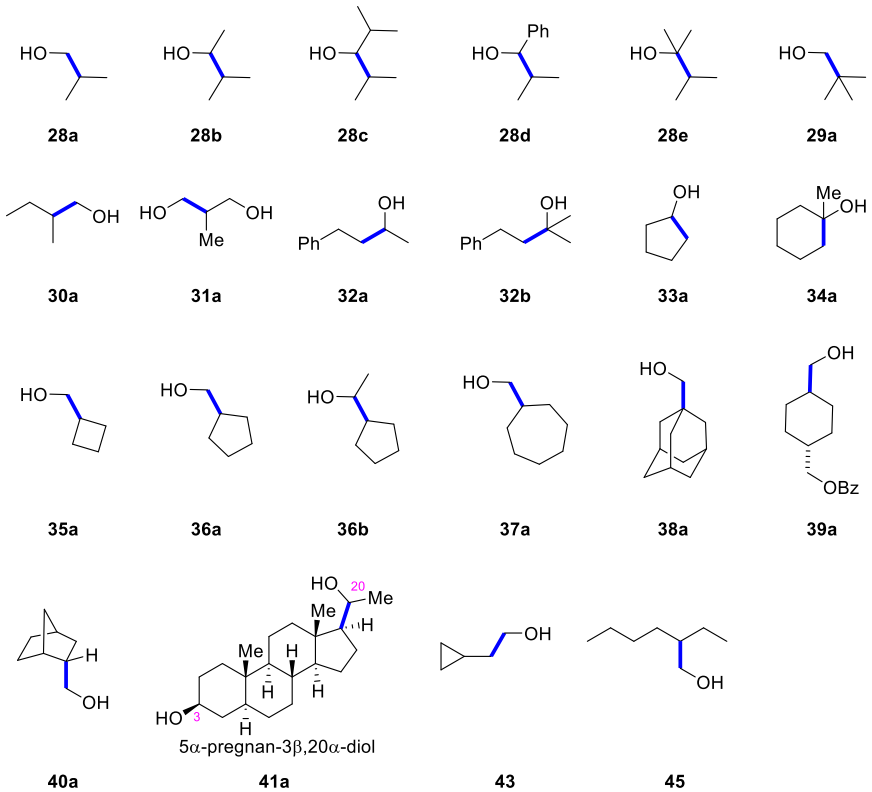
To a solution of Fasudil hydrochloride (500.0 mg, 1.7 mmol, 1.0 equiv), DMAP (52.5 mg, 0.4 mmol, 0.25 equiv) and Et_3N (1.0 mL, 6.9 mmol, 4.0 equiv) in CH_2Cl_2 (10 mL) at 0 °C was added benzoyl chloride (485.0 mg, 3.4 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 10 hours. H_2O (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with dichloromethane/ methanol (v/v 20:1)) to give compound **27a** as a white solid in 82% yield (550.0 mg), R_f = 0.5 (5% Methanol/Dichloromethane).



27a

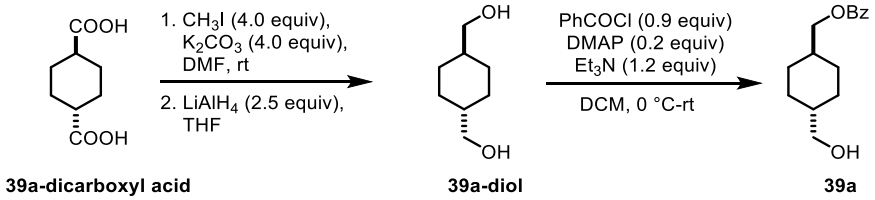
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.70 (t, *J* = 7.3 Hz, 1H), 8.46–8.28 (m, 2H), 8.21 (t, *J* = 6.8 Hz, 1H), 7.76–7.63 (m, 1H), 7.45-7.28 (m, 5H), 3.92–3.80 (m, 2H), 3.63–3.54 (m, 2H), 3.54–3.43 (m, 3H), 3.40–3.31 (m, 1H), 2.16-2.09 (m, 1H), 1.86-1.76 (m, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 153.5, 145.4, 136.1, 133.8, 133.3, 131.6, 129.8, 129.3, 128.7, 126.6, 126.5, 126.0, 117.5, 51.9, 50.6, 48.7, 48.4, 48.3, 48.0, 46.7, 45.1, 31.1, 29.9, 27.7. HRMS (ESI) calcd for $C_{21}H_{22}N_3O_3S^+$ $[M+H]^+$ 396.1376, found 396.1376.

3.2 Alcohol substrates



Scheme S3. List of Alcohols used in this study

Except the substrate **39a**, alcohol substrates were commercial available and used as received.



Scheme S4. Synthesis of compound 39a

Compound trans-1,4-cyclohexanedicarboxylic acid (1.5 g, 8.7 mmol, 1.0 equiv) was dissolved in DMF (35 mL), then K_2CO_3 (4.81 g, 34.9 mmol, 4.0 equiv) and CH_3I (4.95g, 34.9 mmol, 4.0 equiv) were added at room temperature. The reaction mixture was stirred at room temperature for 12 hours. Ethyl acetate (150 mL) was added, then the mixture was washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. The crude product was dissolved in anhydrous THF (45 mL), and the resulting solution was added slowly to a mixture of $LiAlH_4$ (860.0 mg, 22.6 mmol, 2.5 equiv) in anhydrous THF (30 mL) at 0 °C. The reaction mixture was heated at reflux for 12 hours. After being cooled to room temperature, the reaction mixture was quenched with 2 M NaOH (aq) to precipitate the inorganic salts. The precipitate was removed by filtration through a pad of celite. The filtrate was concentrated *in vacuo* and the crude product was used for the next step without further purification.

To a solution of the corresponding alcohol made above (551.6 mg, 3.8 mmol, 1.0 equiv), DMAP (93.5 mg, 0.8 mmol, 0.2 equiv) and Et_3N (0.5 mL, 4.6 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL) was added benzoyl chloride (486.1 mg, 3.5 mmol, 0.9 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 14 hours. H_2O (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluted with hexane/EtOAc (v/v 1:1)) to give compound **39a** as a colorless oil in 73% yield (1.580 g), R_f = 0.6 (50% Ethyl acetate in Hexanes).

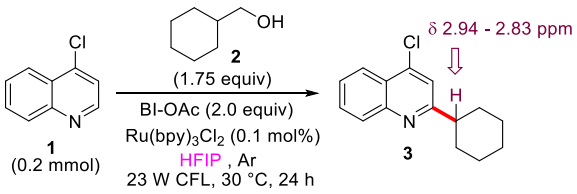
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.15 (d, *J* = 6.5 Hz, 2H), 3.47 (d, *J* = 6.0 Hz, 2H), 1.98-1.82 (m, 4H), 1.82-1.70 (m, 1H), 1.64-1.41 (m, 2H), 1.19-0.93 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 133.0, 130.5, 129.7, 128.5, 70.0, 68.6, 40.5, 37.5, 29.2, 28.9. HRMS (ESI) calcd for $C_{15}H_{21}O_3^+$ $[M+H]^+$ 249.1485, found 249.1485.

4. Optimization of reaction conditions

All screening reactions were carried out at a 0.2 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2). The reaction vials were purged with Ar for 1 min and sealed with PTEF cap and stirred on bench top. Stock solution of $Ru(bpy)_3Cl_2$ in HFIP was used if necessary. A 23 W Compact Fluorescent Lamps (CFL) bulb was positioned 10 cm aside from the reaction vials.

4-Chloroquinoline **1** (32.6 mg, 0.2 mmol, 1.0 equiv), Cyclohexylmethanol **2** and other specified

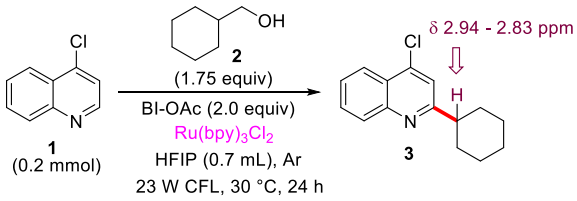
reagents were dispersed in 0.7 mL of solvent containing photocatalyst. The mixture was stirred at 30 ℃ under 23w CFL irradiation for 24 h. After removal of the solvent in vacuo, the residue was dissolved in 1 mL of $CDCl_3$ along with K_2CO_3 solid (approximate 200 mg) and the resulting mixture was vigorously stirred for 10 min. To the solution was added $Cl_2CHCHCl_2$ (20 μL) as an internal standard for ^1H NMR analysis. The crude yield of target product were calculated based on the integration of the peaks at 2.94-2.83 (m, 1H) for compound **3**.



Entry	HFIP (mL)	Yield (%, NMR)
1	1.5	37
2	1.3	49
3	1.1	61
4	0.9	73
5	0.7	85(80)[a]
6	0.5	76
7	0.3	60

[a]Isolated yield.

Table S1. Evaluation of the loading of solvent of reaction

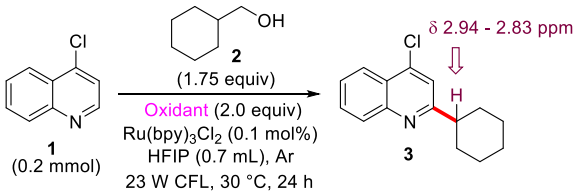


Entry	$Ru(bpy)_3Cl_2$ (mol%)	Yield (%, NMR)
1	0	<2
2	0.05	67
3	0.1	85(80)[a]
4	0.2	77
5	0.5	73
6	1.0	69

[a]Isolated yield.

Table S2. Evaluation of the loading of Photocatalysts

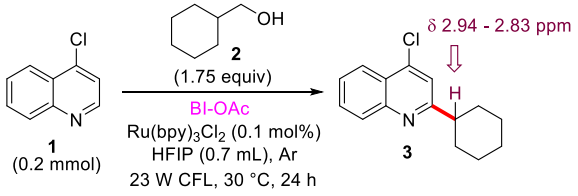
此处修改了，Ru*量为 0 时，由< 1% 修改为 < 2%



Entry	Oxidant	Yield (%, NMR)
1	BI-OH	61
2	BI-OAc	85(80)[a]
3	PFBI-OH	51
4	PIDA	42
5	PIFA	18
6	BI-CF_3	<5

[a]Isolated yield.

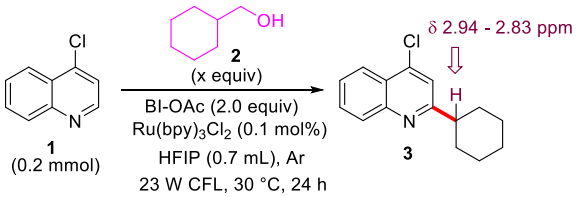
Table S3. Evaluation of Oxidants



Entry	BI-OAc (equiv)	Yield (%, NMR)
1	1.0	41
2	1.5	70
3	2.0	85(80)[a]
4	2.5	78
5	3.0	55

[a]Isolated yield.

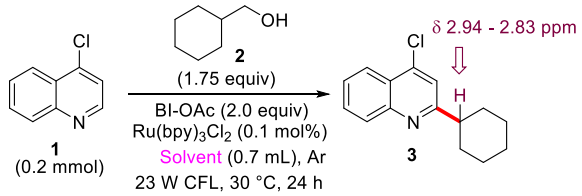
Table S4. Evaluation of the loading of BI-OAc



Entry	Alcohol (equiv)	Yield (%, NMR)
1	1.0	48
2	1.25	59
3	1.5	75
4	1.75	85(80)[a]
5	2.0	86
6	2.25	86
7	2.5	86

[a]Isolated yield.

Table S5. Evaluation of the loading of Alcohol



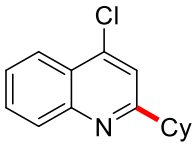
Entry	Solvent	Yield (%, NMR)
1	HFIP	85(80)[a]
2	DCM	<5
3	CH_3CN	<5
4	DMF	<5
5	EA	<5
6	THF	<5

[a]Isolated yield.

Table S6. Evaluation of Solvents

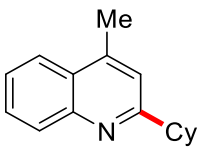
5. General procedure and substrate scope

General Procedure: *N*-heteroaromatic substrate (0.2 mmol, 1.0 equiv), alcohols (0.35 mmol, 1.75 equiv) and BI-OAc **6** (0.4 mmol, 2.0 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (0.0002 mmol, 0.1 mol%) in HFIP (0.7 mL). The reaction vial was purged with Ar for 1 min and sealed with PTFE cap, then the mixture was stirred at 30 ℃ under the Compact Fluorescent Lamps irradiation (23 W) for 24 h. The solvent was removed in vacuo and the residue was dissolved in DCM (1 mL). To the solution was added K_2CO_3 (approximate 150 mg), and the resulting mixture was vigorously stirred for 10 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.



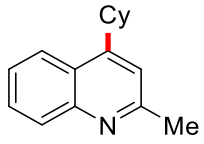
3

Compound **3** was isolated in 80% yield (39.4 mg) as a colorless oil, following the general procedure. R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.79-7.67 (m, 1H), 7.62-7.52 (m, 1H), 7.42 (s, 1H), 2.94-2.83 (m, 1H), 2.09-1.97 (m, 2H), 1.96-1.85 (m, 2H), 1.84-1.69 (m, 2H), 1.68-1.54 (m, 2H), 1.54-1.39 (m, 2H), 1.39-1.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 148.8, 142.8, 130.3, 129.4, 126.7, 125.3, 124.0, 119.9, 47.6, 32.8, 26.6, 26.1; The Spectra data consistent with those reported in the literature.[3]



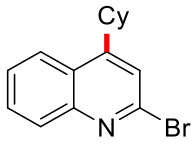
7

Compound **7** was isolated in 86% yield (38.8 mg) as a colorless oil, following the general procedure. R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 2.94-2.80 (m, 1H), 2.68 (s, 3H), 2.07-1.95 (m, 2H), 1.95-1.84 (m, 2H), 1.84-1.73 (m, 1H), 1.71-1.55 (m, 2H), 1.54-1.40 (m, 2H), 1.40-1.25 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 147.8, 144.4, 129.6, 129.1, 127.2, 125.5, 123.7, 120.4, 47.8, 33.00, 26.7, 26.3, 19.0; The Spectra data consistent with those reported in the literature.[4]



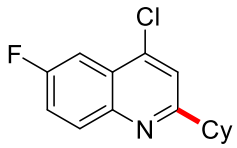
8

Compound **8** was isolated in 81% yield (34.5 mg) as a colorless oil, following the general procedure. R_f = 0.5 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 3.35-3.23 (m, 1H), 2.72 (s, 3H), 2.04-1.92 (m, 4H), 1.87-1.80 (m, 1H), 1.62-1.46 (m, 4H), 1.41-1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 147.8, 144.4, 129.6, 129.1, 127.2, 125.5, 123.7, 120.4, 47.8, 33.0, 27.0, 26.3, 19.0; The Spectra data consistent with those reported in the literature.[5]



9

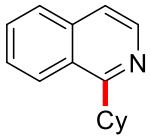
Compound **9** was isolated in 60% yield (34.8 mg) as a colorless oil, following the general procedure. R_f = 0.6 (10% EtOAc/hexanes) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.4 Hz, 2H), 7.71-7.67 (m, 1H), 7.59-7.55 (m, 1H), 7.39 (s, 1H), 3.35-3.22 (m, 1H), 2.09-1.90 (m, 4H), 1.90-1.80 (m, 1H), 1.70-1.43 (m, 5H), 1.42-1.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 149.0, 142.7, 130.0, 129.7, 126.8, 125.9, 123.4, 122.3, 39.2, 33.5, 26.9, 26.3; HRMS (ESI) calcd for $C_{15}H_{17}BrN^+$ $[M+H]^+$ 290.0539, found 290.0537.



10

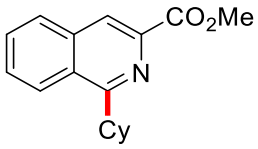
Compound **10** was isolated in 80% yield (42.2 mg) as a colorless oil, following the general procedure. R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 9.2, 5.3 Hz, 1H), 7.78 (dd, *J* = 9.4, 2.8 Hz, 1H), 7.52-7.45 (m, 1H), 7.43 (s, 1H), 2.92-2.81 (m, 1H), 2.07-1.95 (m, 2H), 1.95- 1.84 (m, 2H), 1.84-1.73 (m, 1H), 1.68-1.53 (m, 2H), 1.53-1.38 (m, 2H), 1.38-1.23 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ166.27 (d, *J* = 2.7 Hz), 160.80 (d, *J* = 248.1 Hz), 145.9, 141.91 (d, *J* = 5.6 Hz), 132.1 (d, *J* = 9.1 Hz), 126.08 (d, *J* = 10.2 Hz), 120.6, 120.40 (d, *J* = 25.7

Hz), 107.81 (d, J = 24.3 Hz), 47.4, 32.8, 26.6, 26.1; HRMS (ESI) calcd for $C_{15}H_{16}ClFN^+$ $[M+H]^+$ 264.0950, found 264.0948.



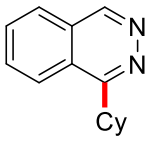
11

Compound **11** was isolated in 62% yield (26.2 mg) as a colorless oil, following the general procedure. R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51-8.46 (m, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.69-7.54 (m, 2H), 7.50-7.45 (m, 1H), 3.63-3.48 (m, 1H), 2.04-1.92 (m, 4H), 1.88-1.77 (m, 3H), 1.61-1.47 (m, 2H), 1.46-1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 142.1, 136.5, 129.7, 127.7, 126.9, 126.4, 124.9, 119.0, 41.7, 32.7, 27.0, 26.4; The Spectra data consistent with those reported in the literature.[5]



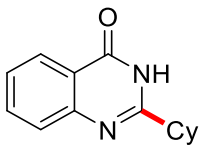
12

Compound **12** was isolated in 73% yield (39.4 mg) as a colorless oil, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.31-8.24 (m, 1H), 7.98-7.91 (m, 1H), 7.76-7.67 (m, 2H), 4.03 (s, 3H), 3.63-3.51 (m, 1H), 2.07-1.87 (m, 7H), 1.86-1.76 (m, 1H), 1.62-1.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.3, 140.8, 136.1, 130.2, 129.2, 129.2, 127.9, 125.1, 122.6, 52.8, 42.2, 32.4, 26.9, 26.2; HRMS (ESI) calcd for $C_{17}H_{20}NO_2^+$ $[M+H]^+$ 270.1489, found 270.1486.



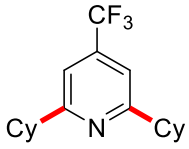
13

Compound **13** was isolated in 57% yield (24.2 mg) as a colorless oil, following the general procedure. R_f = 0.4 (40% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.20-8.14 (m, 1H), 7.96 -7.83 (m, 3H), 3.57-3.42 (m, 1H), 2.10-1.89 (m, 6H), 1.88-1.78 (m, 1H), 1.61-1.32 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 150.3, 132.4, 131.8, 127.3, 126.8, 125.2, 123.6, 40.9, 32.5, 27.0, 26.3; HRMS (ESI) calcd for $C_{14}H_{17}N_2^+$ $[M+H]^+$ 213.1386, found 213.1386.



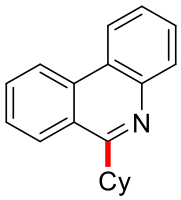
14

Compound **14** was isolated in 41% yield (18.7 mg) as a white solid, following the general procedure. R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.82-7.65 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 2.78-2.66 (m, 1H), 2.13-1.99 (m, 2H), 1.99-1.86 (m, 2H), 1.86-1.64 (m, 4H), 1.56-1.29 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 160.2, 149.7, 134.8, 127.5, 126.4, 126.4, 121.0, 45.0, 30.7, 26.1, 25.9; HRMS (ESI) calcd for $C_{14}H_{17}N_2O^+$ $[M+H]^+$ 229.1335, found 229.1332.



15

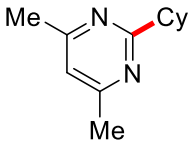
Compound **15a** (29.4 mg, 0.2 mmol, 1.0 equiv), Cyclohexylmethanol **2** (80.0 mg, 0.7 mmol, 3.5 equiv) and BI-OAc **6** (244.8 mg, 0.8 mmol, 4.0 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (0.128 mg, 0.0002 mmol, 0.1 mol%) in HFIP (0.7 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 24 h. The solvent was removed in vacuo and the residue was dissolved in DCM (2 mL). To the solution was added K_2CO_3 (approximate 300 mg), the mixture was vigorously stirred for 10 min. After that, the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel to afford compound **15** as a colorless oil (35.0 mg, 56% yield). R_f = 0.9 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 2.86-2.68 (m, 2H), 2.05-1.94 (m, 4H), 1.94-1.83 (m, 4H), 1.82-1.74 (m, 2H), 1.61-1.40 (m, 8H), 1.37-1.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.32, 138.84 (q, *J* = 32.9 Hz), 123.54 (q, *J* = 273.3 Hz), 113.66 (dd, *J* = 7.0, 3.4 Hz), 46.73, 32.99, 26.59, 26.17; The Spectra data consistent with those reported in the literature.[3]



16

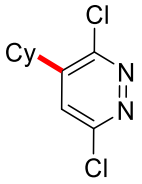
Compound **16** was isolated in 80% yield (41.8 mg) as a colorless oil, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 8.3 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.70 (q, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 3.68-3.57 (m, 1H), 2.17-2.04 (m, 2H), 2.04-1.91 (m, 4H), 1.89-1.81 (m, 1H), 1.66-1.51 (m, 2H), 1.51-1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

165.4, 144.1, 133.2, 130.1, 130.0, 128.5, 127.2, 126.2, 125.7, 124.9, 123.5, 122.7, 121.9, 42.1, 32.5, 27.0, 26.5; HRMS (ESI) calcd for $C_{19}H_{20}N^+$ $[M+H]^+$ 262.1590, found 262.1586.



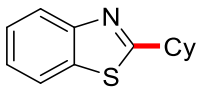
17

Compound **17** was isolated in 62% yield (23.7 mg) as a colorless oil, following the general procedure. R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 2.84-2.72 (m, 1H), 2.43 (s, 6H), 1.98-1.88 (m, 2H), 1.88-1.77 (m, 2H), 1.75-1.58 (m, 3H), 1.44-1.24 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 166.5, 117.5, 47.8, 32.1, 26.4, 26.1, 24.2; The Spectra data consistent with those reported in the literature.[6]



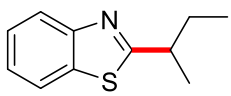
18

Compound **18** was isolated in 50% yield (23.2 mg) as a colorless solid, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 2.93-2.80 (m, 1H), 1.99-1.87 (m, 4H), 1.86-1.77 (m, 1H), 1.52-1.39 (m, 2H), 1.37-1.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 156.4, 148.8, 127.2, 40.3, 31.9, 26.3, 25.8; The Spectra data consistent with those reported in the literature.[7]



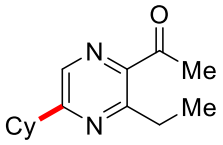
19

Compound **19** was isolated in 71% yield (30.9 mg) as a colorless oil, following the general procedure. R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.47-7.40 (m, 1H), 7.36-7.30 (m, 1H), 3.11 (tt, *J* = 11.7, 3.6 Hz, 1H), 2.26-2.16 (m, 2H), 1.94-1.84 (m, 2H), 1.81-1.73 (m, 1H), 1.71-1.58 (m, 2H), 1.52-1.38 (m, 2H), 1.38-1.25 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 153.3, 134.7, 125.9, 124.6, 122.7, 121.7, 43.6, 33.6, 26.2, 25.9; The Spectra data consistent with those reported in the literature.[8]



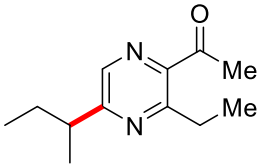
20

Compound **20** was isolated in 64% yield (24.5 mg) as a colorless oil, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.1, 0.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.48-7.42 (m, 1H), 7.37-7.31 (m, 1H), 3.27-3.16 (m, 1H), 1.98-1.86 (m, 1H), 1.84-1.71 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ178.1, 153.2, 134.8, 125.9, 124.7, 122.7, 121.7, 41.2, 30.8, 20.9, 12.0; HRMS (ESI) calcd for $C_{11}H_{14}NS^+$ $[M+H]^+$ 192.0841, found 192.0840.



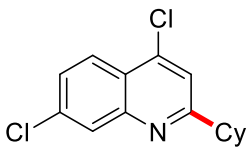
21

Compound **21** was isolated in 66% yield (30.7 mg) as a colorless oil, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 3.13 (q, *J* = 7.5 Hz, 2H), 2.83-2.73 (m, 1H), 2.67 (s, 3H), 2.00-1.82 (m, 4H), 1.81-1.71 (m, 1H), 1.65-1.53 (m, 2H), 1.50-1.37 (m, 2H), 1.37-1.29 (m, 1H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 163.3, 158.0, 144.4, 138.8, 44.4, 32.4, 29.1, 28.2, 26.4, 26.0, 13.4; HRMS (ESI) calcd for $C_{14}H_{21}N_2O^+$ $[M+H]^+$ 233.1648, found 233.1647.



22

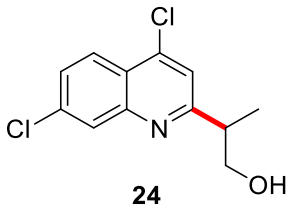
Compound **22** was isolated in 53% yield (21.9 mg) as a colorless oil, following the general procedure. R_f = 0.9 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 3.14 (q, *J* = 7.5 Hz, 2H), 2.93–2.82 (m, 1H), 2.69 (s, 3H), 1.88–1.74 (m, 1H), 1.73–1.60 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.27 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ201.6, 163.5, 158.2, 144.4, 139.3, 41.5, 29.6, 29.1, 28.3, 19.9, 13.4, 12.1; HRMS (ESI) calcd for $C_{12}H_{19}N_2O^+$ $[M+H]^+$ 207.1492, found 207.1490.



23

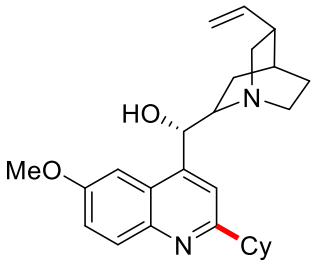
Compound **23** was isolated in 90% yield (50.4 mg) as a colorless oil, following the general procedure. R_f = 0.7 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.04 (m, 2H), 7.53-7.49 (m, 1H), 7.40 (s, 1H), 2.91-2.80 (m, 1H), 2.07-1.95 (m, 2H), 1.95-1.84 (m, 2H), 1.84-1.74 (m, 1H), 1.68-1.53 (m, 2H), 1.53-1.38 (m, 2H), 1.37-1.26 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

168.2, 149.2, 142.7, 136.3, 128.5, 127.7, 125.4, 123.8, 120.3, 47.5, 32.7, 26.5, 26.1; The Spectra data consistent with those reported in the literature.[5]



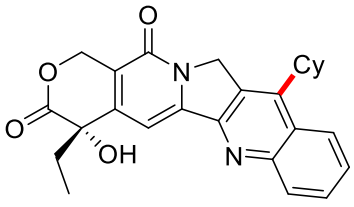
24

Compound **24** was isolated in 35% yield (17.8 mg) as a colorless oil, following the general procedure. R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 1H), 8.06 (d, *J* = 1.6 Hz, 1H), 7.59–7.53 (m, 1H), 7.43 (s, 1H), 4.09–3.92 (m, 2H), 3.30–3.17 (m, 1H), 1.40 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 148.3, 143.5, 137.0, 128.3, 128.2, 125.6, 123.8, 121.2, 66.5, 42.8, 17.2; HRMS (ESI) calcd for $C_{12}H_{12}Cl_2NO^+$ $[M+H]^+$ 256.0290, found 256.0289.



25

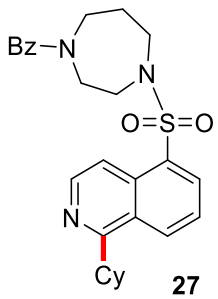
Compound **25** was isolated in 56% yield (45.7 mg) as a light yellow solid, following the general procedure. R_f = 0.5 (5% Methanol/Dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 1H), 7.49 (s, 1H), 7.22 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.14 (s, 1H), 5.81-5.57 (m, 2H), 4.93 (t, *J* = 14.5 Hz, 2H), 3.79 (s, 3H), 3.70 (s, 1H), 3.19-3.03 (m, 2H), 2.85-2.61 (m, 3H), 2.42-2.25 (m, 1H), 1.97-1.87 (m, 2H), 1.86-1.72 (m, 6H), 1.53-1.21 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 157.4, 147.2, 143.9, 141.1, 125.0, 121.3, 116.9, 115.1, 101.2, 71.1, 60.0, 56.8, 56.0, 47.5, 43.6, 39.6, 33.0, 31.0, 27.9, 27.1, 26.6, 26.2, 20.7; HRMS (ESI) calcd for $C_{26}H_{35}N_2O_2^+$ $[M+H]^+$ 407.2693, found 407.2688. The Spectra data consistent with those reported in the literature.[3]



26

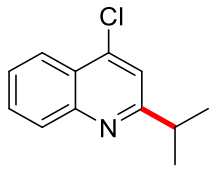
Compound **26** was isolated in 67% yield (57.7 mg) as a light yellow solid following the general procedure. R_f = 0.5 (5% Methanol/Dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.16 (m, 2H), 7.83-7.74 (m, 1H), 7.71-7.61 (m, 2H), 5.76 (d, *J* = 16.3 Hz, 1H), 5.41 (s, 2H), 5.31 (d, *J* = 16.2

Hz, 1H), 3.79 (s, 1H), 3.65 (s, 1H), 2.09-1.83 (m, 9H), 1.62-1.45 (m, 3H), 1.04 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 157.7, 152.5, 150.4, 149.5, 148.7, 146.7, 131.0, 130.0, 127.8, 127.1, 123.8, 118.4, 97.8, 72.9, 66.5, 50.8, 31.9, 31.9, 31.7, 31.1, 27.1, 26.1, 8.0; HRMS (ESI) calcd for $C_{26}H_{27}N_2O_4^+$ $[M+H]^+$ 431.1965, found 431.1965. The Spectra data consistent with those reported in the literature.[9]



27

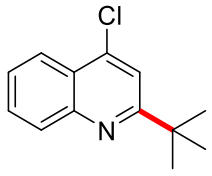
Compound **27** was obtained as a mixture of rotamers in 91% yield (86.9 mg). Light yellow solid, R_f = 0.4 (5% Methanol/Dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (t, J = 7.5 Hz, 1H), 8.49 (t, J = 6.6 Hz, 1H), 8.37-8.14 (m, 2H), 7.70-7.60 (m, 1H), 7.45-7.27 (m, 5H), 3.94-3.79 (m, 2H), 3.62-3.41 (m, 6H), 3.39-3.33 (m, 1H), 2.16-2.01 (m, 1H), 2.00-1.93 (m, 3H), 1.88-1.81 (m, 3H), 1.73-1.64 (m, 1H), 1.62-1.47 (m, 2H), 1.45-1.30 (m, 1H), 1.24-0.86 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 166.9, 144.2, 136.1, 134.8, 132.8, 132.3, 130.8, 129.8, 128.7, 127.1, 126.6, 126.4, 125.4, 115.4 , 68.8, 52.0, 50.6, 48.8, 48.3, 48.2, 48.1, 46.6, 45.1, 42.2, 40.6, 32.8, 31.0, 29.9, 29.7, 27.7, 26.9, 26.7, 26.2, 25.9; HRMS (ESI) calcd for $C_{27}H_{32}N_3O_3S^+$ $[M+H]^+$ 478.2159, found 478.2159.



28

77%, 31.8 mg (from **28a**)
85%, 35.0 mg (from **28b**)
55%, 22.6 mg (from **28c**)
90%, 37.0 mg (from **28d**)
74%, 30.4 mg (from **28e**)

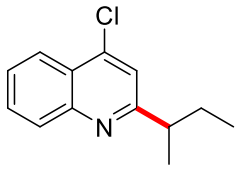
Compound **28** was isolated as a colorless oil, following the general procedure. R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.77-7.69 (m, 1H), 7.61-7.53 (m, 1H), 7.43 (s, 1H), 3.31-3.16 (m, 1H), 1.39 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 148.8, 142.8, 130.3, 129.5, 126.8, 125.3, 124.0, 119.5, 37.3, 22.5; The Spectra data consistent with those reported in the literature.[10]



29

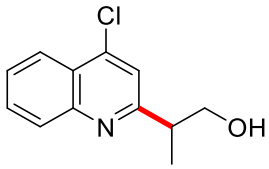
Compound **29** was isolated in 57% yield (25.0 mg) as a colorless oil, following the general procedure. R_f = 0.8 (10% EtOAc/hexanes) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.3 Hz, 1H),

8.08 (d, J = 8.4 Hz, 1H), 7.76-7.69 (m, 1H), 7.63-7.54 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 148.3, 142.3, 130.0, 129.8, 126.6, 124.7, 123.7, 118.5, 38.3, 30.0; HRMS (ESI) calcd for $C_{13}H_{15}ClN^+$ $[M+H]^+$ 220.0888, found 220.0887.



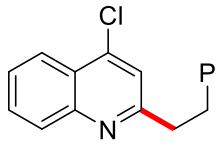
30

Compound **30** was isolated in 77% yield (33.8 mg) as a colorless oil, following the general procedure. R_f = 0.8 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.4, 1.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.77-7.69 (m, 1H), 7.61-7.53 (m, 1H), 7.39 (s, 1H), 3.03-2.92 (m, 1H), 1.92-1.77 (m, 1H), 1.77-1.64 (m, 1H), 1.36 (d, J = 7.0 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 148.8, 142.7, 130.3, 129.5, 126.7, 125.3, 124.0, 119.9, 44.6, 30.0, 20.4, 12.3; HRMS (ESI) calcd for $C_{13}H_{15}ClN^+$ $[M+H]^+$ 220.0888, found 220.0887.



31

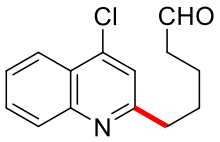
Compound **31** was isolated in 43% yield (19.2 mg) as a colorless oil, following the general procedure. R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.78-7.71 (m, 1H), 7.64-7.57 (m, 1H), 7.43 (s, 1H), 4.34 (s, 1H), 4.11-4.02 (m, 1H), 4.02-3.91 (m, 1H), 3.28-3.13 (m, 1H), 1.41 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 148.1, 143.3, 130.7, 129.4, 127.2, 125.3, 124.1, 121.0, 66.6, 42.6, 17.4; HRMS (ESI) calcd for $C_{12}H_{13}ClNO^+$ $[M+H]^+$ 222.0680, found 222.0680.



41%, 22.0 mg (from **32a**)
63%, 33.7 mg (from **32b**)

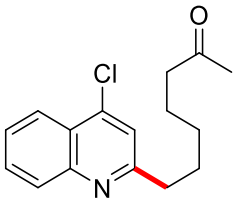
32

Compound **32** was isolated as a colorless oil, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.71-7.64 (m, 1H), 7.55-7.47 (m, 1H), 7.25-7.10 (m, 6H), 3.21-3.12 (m, 2H), 3.12-3.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 148.9, 142.7, 141.3, 130.5 129.4, 128.6, 126.9, 126.3, 125.1, 124.1, 121.9, 40.9, 35.8; HRMS (ESI) calcd for $C_{17}H_{15}ClN^+$ $[M+H]^+$ 268.0888, found 268.0888.



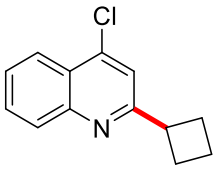
33

Compound **33** was isolated in 20% yield (9.9 mg) as a colorless oil, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.79-7.71 (m, 1H), 7.65-7.55 (m, 1H), 7.40 (s, 1H), 3.04-2.93 (m, 2H), 2.56-2.46 (m, 2H), 1.95-1.82 (m, 2H), 1.81-1.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 162.2, 148.9, 142.9, 130.5, 129.3, 127.0, 125.2, 124.1, 121.4, 43.8, 38.7, 29.1, 22.0; HRMS (ESI) calcd for $C_{14}H_{15}ClNO^+$ $[M+H]^+$ 248.0837, found 248.0834.



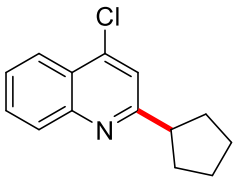
34

Compound **34** was isolated in 18% yield (10.0 mg) as a colorless oil, following the general procedure. R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.77-7.69 (m, 1H), 7.62-7.54 (m, 1H), 7.39 (s, 1H), 2.98-2.90 (m, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 1.86-1.79 (m, 2H), 1.69-1.59 (m, 2H), 1.46-1.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 162.8, 148.9, 142.7, 130.4, 129.3, 126.8, 125.1, 124.1, 121.5, 43.7, 39.0, 30.0, 29.6, 29.1, 23.7; HRMS (ESI) calcd for $C_{16}H_{19}ClNO^+$ $[M+H]^+$ 276.1150, found 276.1149.



35

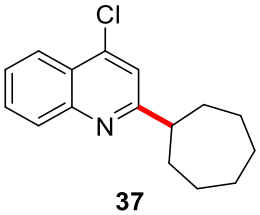
Compound **35** was isolated in 52% yield (22.6 mg) as a colorless oil, following the general procedure. R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.76-7.70 (m, 1H), 7.60-7.54 (m, 1H), 7.43 (s, 1H), 3.89-3.77 (m, 1H), 2.49-2.40 (m, 4H), 2.19-2.06 (m, 1H), 2.02-1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 148.8, 142.7, 130.3, 129.5, 126.8, 125.1, 124.0, 119.9, 42.6, 28.3, 18.4; The Spectra data consistent with those reported in the literature.[4]



36

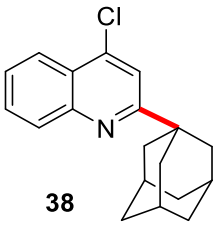
71%, 32.9 mg (from **36a**)
75%, 34.8 mg (from **36b**)

Compound **36** was isolated as a colorless oil, following the general procedure. R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.76-7.68 (m, 1H), 7.60-7.52 (m, 1H), 7.43 (s, 1H), 3.42-3.28 (m, 1H), 2.24-2.11 (m, 2H), 1.95-1.81 (m, 4H), 1.81-1.69 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 148.7, 142.6, 130.3, 129.5, 126.7, 125.2, 124.0, 120.4, 48.8, 33.6, 26.1; The Spectra data consistent with those reported in the literature.[3]



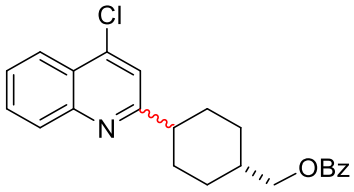
37

Compound **37** was isolated in 73% yield (37.9 mg) as a colorless oil, following the general procedure. R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.76-7.68 (m, 1H), 7.60-7.52 (m, 1H), 7.39 (s, 1H), 3.14-2.97 (m, 1H), 2.10-1.97 (m, 2H), 1.90-1.57 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 148.6, 142.7, 130.3, 129.4, 126.6, 125.1, 124.0, 120.0, 49.5, 35.0, 28.1, 27.4; HRMS (ESI) calcd for $C_{16}H_{19}ClN^+$ $[M+H]^+$ 260.1201, found 260.1200.



38

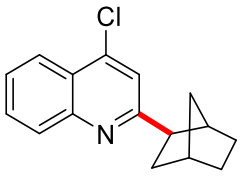
Compound **38** was isolated in 20% yield (11.9 mg) as a white solid, following the general procedure. R_f = 0.8 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.75-7.68 (m, 1H), 7.60-7.53 (m, 2H), 2.16 (br s, 3H), 2.10 (br s, 6H), 1.83 (br s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 148.7, 142.5, 130.0, 129.9, 126.7, 125.0, 123.9, 118.3, 41.9, 40.1, 36.9, 28.9; HRMS (ESI) calcd for $C_{19}H_{21}ClN^+$ $[M+H]^+$ 298.1357, found 298.1355.



39
(2.5:1 dr)

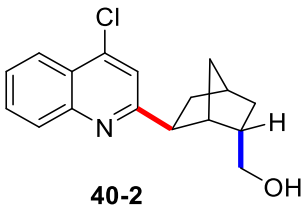
Compound **39-major** was isolated in 53% yield (40.1 mg) as a white solid, following the general procedure. R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 0.7 Hz, 1H), 8.12-8.01 (m, 3H), 7.79-7.69 (m, 1H), 7.64-7.53 (m, 2H), 7.50-7.40 (m, 3H), 4.24 (d, *J* = 6.3 Hz, 2H), 2.97-2.86 (m, 1H), 2.20-2.02 (m, 4H), 2.01-1.89 (m, 1H), 1.79-1.65 (m, 2H), 1.44-1.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 166.2, 148.8, 142.9, 133.0, 130.6, 130.4, 129.7, 129.5, 128.5, 126.9, 125.3, 124.1, 119.9, 69.9, 47.2, 37.0, 32.0, 29.7; HRMS (ESI) calcd for $C_{23}H_{23}ClNO_2^+$ $[M+H]^+$ 380.1412, found 380.1409.

Compound **39-minor** was isolated in 21% yield (16.7 mg) as a white solid, following the general procedure. R_f = 0.8 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, 0.6 Hz, 1H), 8.08-8.03 (m, 3H), 7.79-7.69 (m, 1H), 7.62-7.54 (m, 2H), 7.50-7.40 (m, 3H), 4.41 (d, *J* = 7.4 Hz, 1H), 4.17 (d, *J* = 6.4 Hz, 1H), 3.13-2.95 (m, 1H), 2.3-2.14 (m, 1H), 2.09-1.86 (m, 5H), 1.84-1.74 (m, 2H), 1.23-1.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 165.8, 148.8, 142.8, 133.0, 130.6, 130.3, 129.7, 129.6, 128.5, 126.9, 124.7, 124.0, 120.1, 67.0, 33.3, 29.1, 27.8, 26.7; HRMS (ESI) calcd for $C_{23}H_{23}ClNO_2^+$ $[M+H]^+$ 380.1412, found 380.1409.



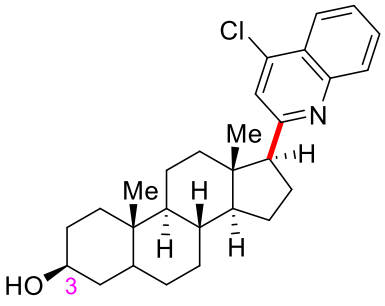
40-1

Compound **40-1** was isolated in 27% yield (13.9 mg) as a white solid, following the general procedure. R_f = 0.9 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.77-7.67 (m, 1H), 7.60-7.51 (m, 1H), 7.43 (s, 1H), 3.06-2.94 (m, 1H), 2.60-2.53 (m, 1H), 2.47-2.37 (m, 1H), 2.29-2.19 (m, 1H), 1.79-1.70 (m, 1H), 1.69-1.57 (m, 3H), 1.51-1.42 (m, 1H), 1.38-1.29 (m, 1H), 1.23-1.16 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 148.6, 142.3 130.1, 129.7, 126.6, 125.0, 123.9, 121.2, 50.2, 43.2, 36.9, 36.4, 36.1, 30.6, 29.3; HRMS (ESI) calcd for $C_{16}H_{17}ClN^+$ $[M+H]^+$ 258.1044, found 258.1044.



40-2

Compound **40-2** was isolated in 39% yield (22.4 mg) as a white solid, following the general procedure. R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.75-7.68 (m, 1H), 7.59-7.52 (m, 1H), 7.39 (s, 1H), 3.87-3.73 (m, 2H), 3.39-3.30 (m, 1H), 2.66 (br s, 1H), 2.40 (br s, 1H), 2.36-2.21 (m, 2H), 1.86-1.74 (m, 1H), 1.71-1.57 (m, 2H), 1.35-1.22 (m, 1H), 0.80-0.69 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 148.3, 142.6, 130.3, 129.2, 126.7, 124.9, 124.0, 121.1, 63.8, 44.7, 43.2, 42.1, 37.2, 37.1, 36.0, 32.9; HRMS (ESI) calcd for $C_{17}H_{19}ClNO^+$ $[M+H]^+$ 288.1150, found 288.1146.

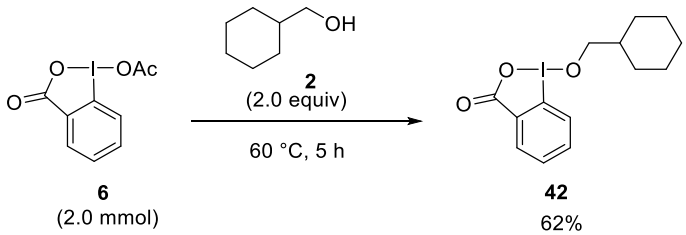


41

Compound **41** was isolated in 37% yield (32.5 mg) as a colorless oil, following the general procedure. Only one diastereomer was obtained, the configration was assigned as shown above without further confirmation. R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.76-7.68 (m, 1H), 7.60-7.52 (m, 1H), 7.29 (s, 1H), 3.57-3.45 (m, 1H), 3.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.33-2.16 (m, 2H), 2.08-1.95 (m, 1H), 1.87-1.66 (m, 3H), 1.58-1.49 (m, 3H), 1.47-1.37 (m, 4H), 1.35-1.28 (m, 3H), 1.26-1.19 (m, 3H), 1.07-1.03 (m, 1H), 1.02 (s, 3H), 0.84-0.79 (m, 1H), 0.77 (s, 3H), 0.51-0.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 148.5, 141.4, 130.0, 129.8, 126.6, 124.9, 123.9, 122.3, 71.4, 58.0, 53.8, 50.6, 46.6, 44.9, 38.3, 37.0, 36.1, 35.5, 32.7, 31.6, 29.4, 28.9, 27.2, 26.5, 21.6, 21.1, 12.4; DEPT 90 (101 MHz, $CDCl_3$) δ 130.04, 129.84, 126.59, 123.93, 122.33, 71.39, 57.98, 53.84, 50.56, 44.85, 36.09; HRMS (ESI) calcd for $C_{28}H_{37}ClNO^+$ $[M+H]^+$ 438.2558, found 438.2555.

6. Mechanism studies

6.1 Alcoholysis of BI-OAc for preparation of compound 42.

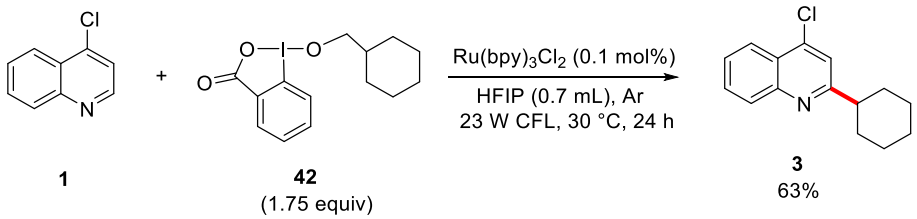


Scheme S5

A mixture of BI-OAc (612.2 mg, 2.0 mmol, 1.0 equiv) and Cyclohexylmethanol (456.8 mg, 4.0 mmol, 2.0 equiv) was stirred at 60 ° C for 5 h. Then it was diluted with anhydrous diethyl ether (15 mL) to give a white solid, which was filtered and washed repeatedly with diethyl ether. The resulting

solid is dried under dry air and gave the desired compound **42** in 62% yield (446.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 4.06 (d, *J* = 6.4 Hz, 2H), 1.87–1.68 (m, 5H), 1.35–1.26 (m, 2H), 1.2–1.14 (m, 2H), 1.09–0.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 135.2, 133.0, 131.1, 130.8, 126.1, 119.1, 80.3, 41.7, 29.9, 26.6, 25.9. HRMS (ESI) calcd for $C_{14}H_{18}IO_3^+$ $[M+H]^+$ 361.0295, found 361.0292.

6.2 Minisci alkylation reaction using compound 42.



1 **42** (1.75 equiv) **3** 63%

Scheme S6

4-Chloroquinoline **1** (32.6 mg, 0.2 mmol, 1.0 equiv) and compound **42** (126.1mg, 0.35 mmol, 1.75 equiv) were added to a solution of $Ru(bpy_3Cl_2$ (0.128 mg, 0.0001 mmol, 0.1 mol%) in HFIP (0.7 mL). The reaction vial was purged with Ar for 1 min and sealed with PTFE cap, then the mixture was stirred at 30 ℃ under the fluorescent light irradiation (23 W CFL) for 24 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (1 mL). To the solution was added K_2CO_3 (approximate 120 mg), and the resulting mixture was vigorously stirred for 10 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography (10% EtOAc/hexanes, R_f 0.5) to afford compound **3** in 63% yield (31.1 mg).

6.3 ^{1}H NMR analysised alcoholysis procedure of BIOAc with alcohol.

The solution of Cyclohexylmethanol **2** (11.4 mg, 0.1 mmol, 1.0 equiv) and BI-OAc **6** (30.7 mg, 0.1 mmol, 1.0equiv) in $CDCl_3$ (2.0 mL) was added into a NMR tube. The tube was kept at 30 ℃ for 10 h, then the mixture was analysised by ^{1}H NMR. The results indicated that compound **42** formed in 50% yield**.** When Cyclohexylmethanol **2** (11.4 mg, 0.1 mmol, 1.0 equiv) and BI-OAc **6** (30.7 mg, 0.1 mmol, 1.0equiv) was mixed in HFIP at 30 ℃, compound **42** can be observed in 41% yield analysised by ^{1}H NMR spectra after 2 hours.

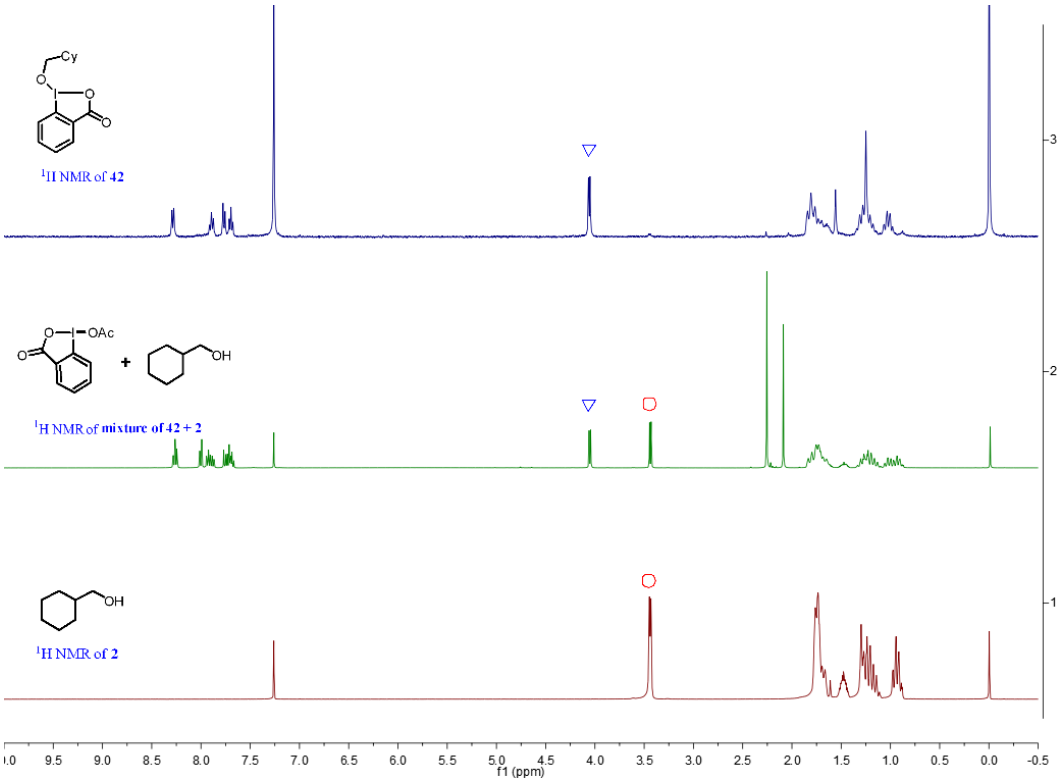
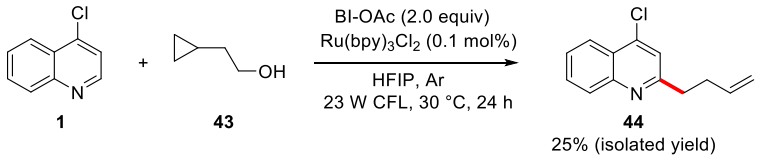


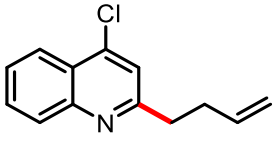
Figure S1

6.4 Radical clock experiment



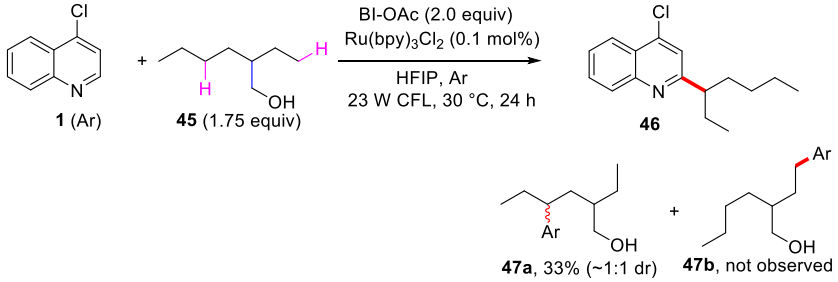
Scheme S6

4-chloroquinoline **1** (32.7 mg, 0.2 mmol, 1.0 equiv), 2-cyclopropylethan-1-ol **43** (30.1mg, 0.35 mmol, 1.75 equiv) and BI-OAc **6** (122.4 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (0.128 mg, 0.0002 mmol, 0.1 mol%) in HFIP (0.7 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 ℃ under the Compact Fluorescent Lamps irradiation (23 W) for 24 h. The solvent was removed in vacuo and the residue was dissolved in DCM (1 mL). To the solution was added K_2CO_3 (approximate 150 mg), and the resulting mixture was vigorously stirred for 10 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford compound **44** (11.0 mg, 25%) as a colorless oil.



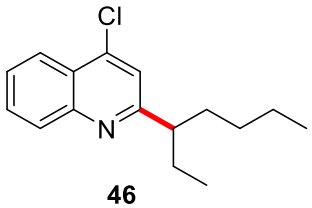
R_f = 0.7 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, CDCl3) δ 8.19 (d, J = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.79-7.71 (m, 1H), 7.63-7.55 (m, 1H), 7.41 (s, 1H), 5.99-5.85 (m, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 5.01 (d, *J* = 10.2 Hz, 1H), 3.10-2.99 (m, 2H), 2.59 (dd, *J* = 14.8, 7.2 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 162.1, 149.0, 142.7, 137.5, 130.5, 129.4, 126.9, 125.2, 124.1, 121.6, 115.7, 38.4, 33.6; HRMS (ESI) calcd for C13H13ClN+ [M+H]+ 218.0731, found 218.0731.

6.5 Competitive experiment



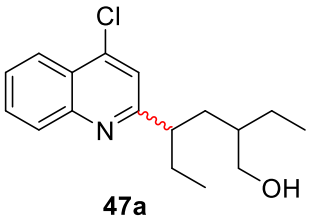
Scheme S7

4-chloroquinoline **1** (32.7 mg, 0.2 mmol, 1.0 equiv), 2-ethylhexan-1-ol **45** (45.6 mg, 0.35 mmol, 1.75 equiv) and BI-OAc **6** (122.4 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (0.128 mg, 0.0002 mmol, 0.1 mol%) in HFIP (0.7 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 ℃ under the Compact Fluorescent Lamps irradiation (23 W) for 24 h. The solvent was removed in vacuo and the residue was dissolved in DCM (1 mL). To the solution was added K_2CO_3 (approximate 150 mg), and the resulting mixture was vigorously stirred for 10 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford compounds **46** (11.0 mg, 25%) as a colorless oil, compounds **47a-1** (10.5 mg, 18%) as a colorless oil, and compounds **47a-2** (9.0 mg, 15%) as a colorless oil. No compound **47b** was observed.



46

Compound **46** was isolated in 45% yield (23.5 mg) as a colorless oil, following the general procedure. R_f = 0.9 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ8.19 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.08 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.78-7.69 (m, 1H), 7.62-7.54 (m, 1H), 7.36 (s, 1H), 2.89-2.74 (m, 1H), 1.84-1.67 (m, 4H), 1.35-1.21 (m, 3H), 1.17-1.05 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ166.4, 148.9, 142.6, 130.2, 129.6, 126.7, 125.3, 124.1, 120.4, 50.7, 35.2, 30.0, 28.7, 23.0, 14.1, 12.3; HRMS (ESI) calcd for $C_{16}H_{21}ClN^+$ $[M+H]^+$ 262.1357, found 262.1355.



47a
(~1:1 dr)

Compound **47a-1** was isolated in 18% yield (10.5 mg) as a colorless oil, following the general procedure. R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.78-7.70 (m, 1H), 7.63-7.56 (m, 1H), 7.41 (s, 1H), 3.52-3.34 (m, 2H), 3.03-2.94 (m, 1H), 2.19-2.08 (m, 1H), 1.84-1.71 (m, 2H), 1.65-1.56 (m, 1H), 1.45-1.36 (m, 2H), 1.34-1.26 (m, 1H), 0.92-0.83 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 148.4, 143.0, 130.6, 129.2, 127.0, 125.3, 124.1, 121.3, 65.4, 47.9, 41.0, 35.1, 30.0, 24.5, 11.9, 11.4; HRMS (ESI) calcd for $C_{17}H_{23}ClNO^+$ $[M+H]^+$ 292.1463, found 292.1460.

Compound **47a-2** was isolated in 15% yield (9.0 mg) as a colorless oil, following the general procedure. R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.78-7.70 (m, 1H), 7.64-7.56 (m, 1H), 7.40 (s, 1H), 3.62-3.51 (m, 1H), 3.50–3.42 (m, 1H), 3.15–3.00 (m, 1H), 1.93–1.82 (m, 1H), 1.82-1.69 (m, 2H), 1.38–1.33 (m, 1H), 1.30–1.19 (m, 3H), 0.93–0.75 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 148.3, 143.3, 130.6, 129.2, 127.0, 125.3, 124.1, 120.1, 65.7, 47.3, 40.0, 37.2, 29.3, 24.8, 12.3, 11.4; HRMS (ESI) calcd for $C_{17}H_{23}ClNO^+$ $[M+H]^+$ 292.1463, found 292.1460.

7. References

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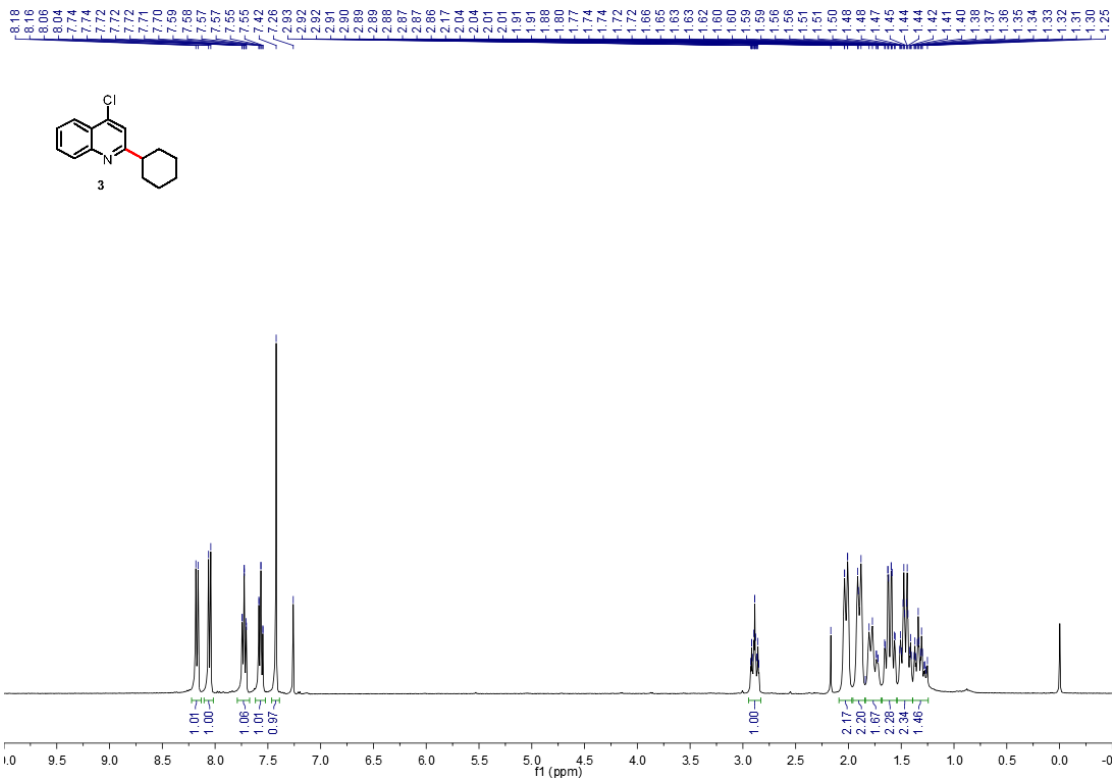
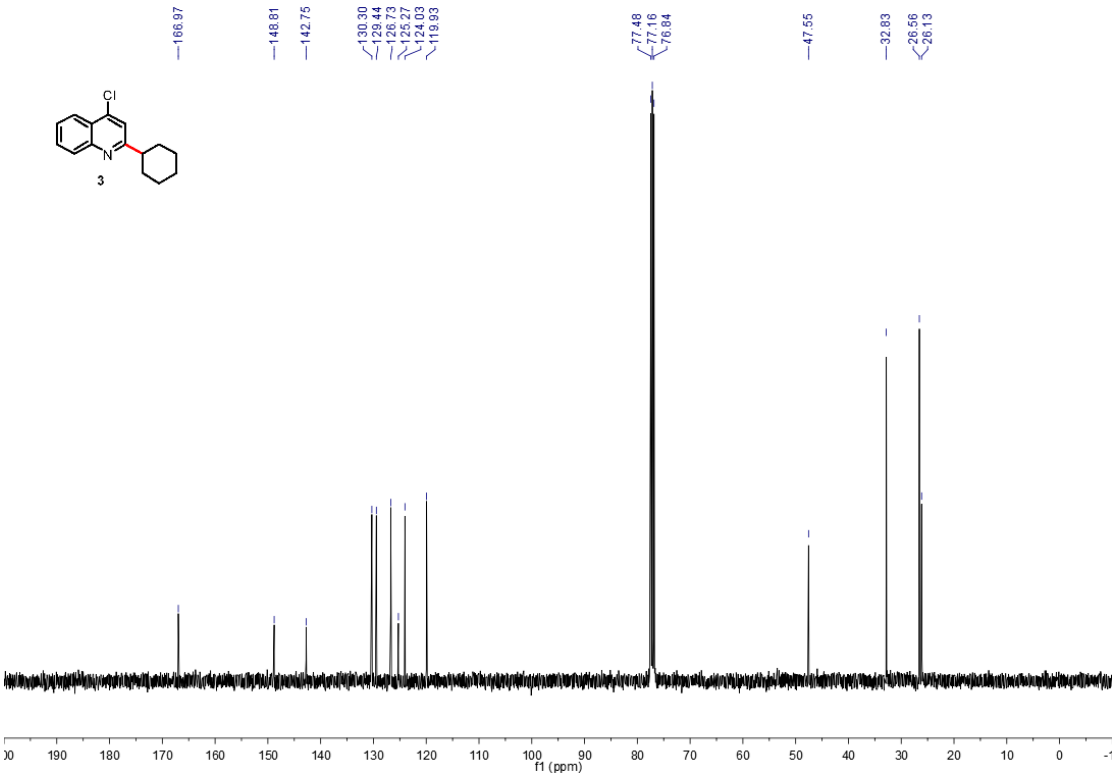
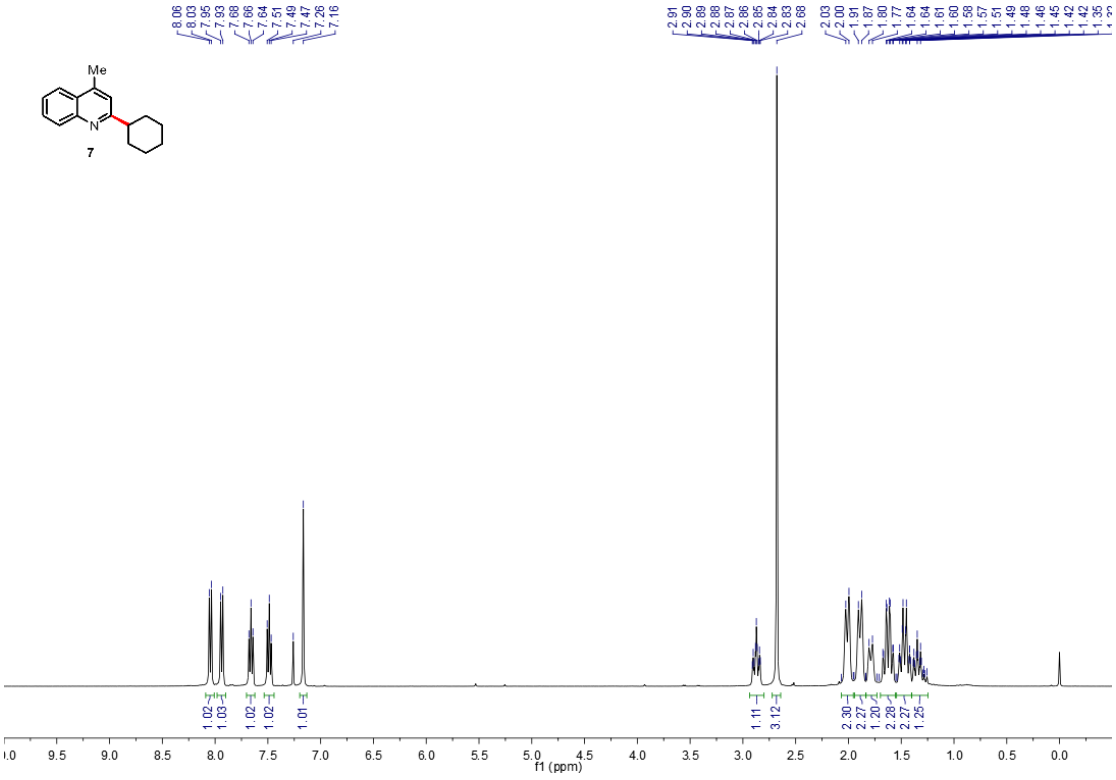
8. ^{1}H and ^{13}C NMR Spectra



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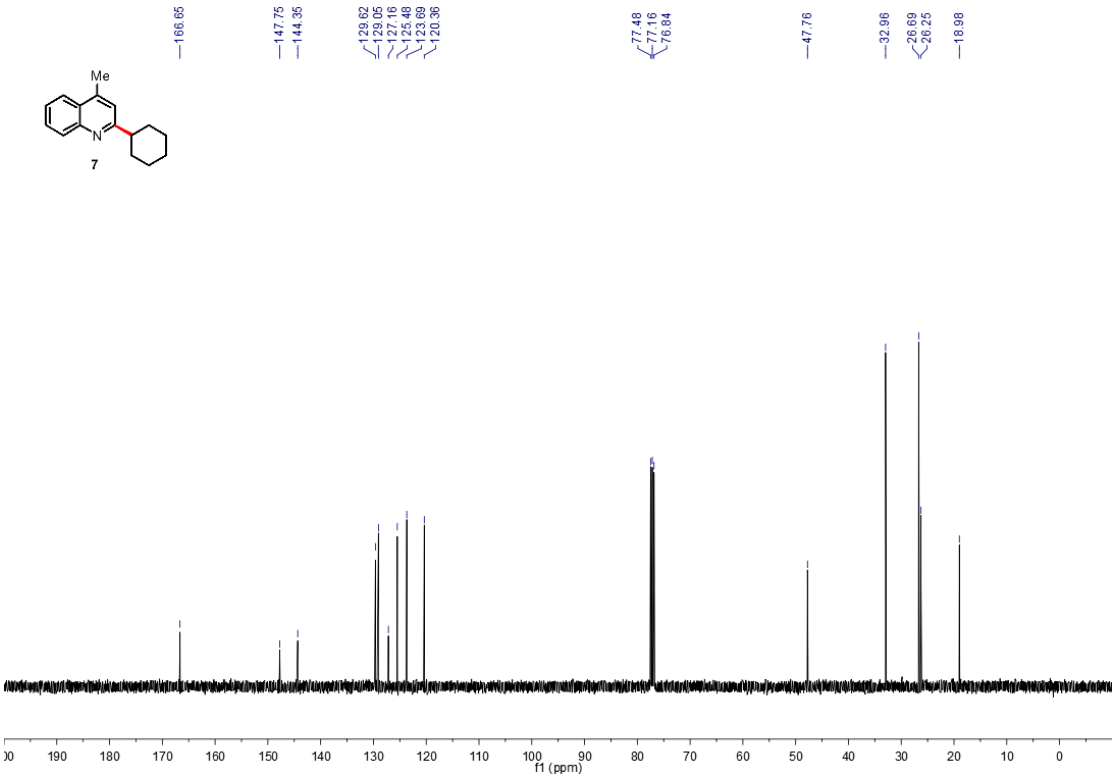
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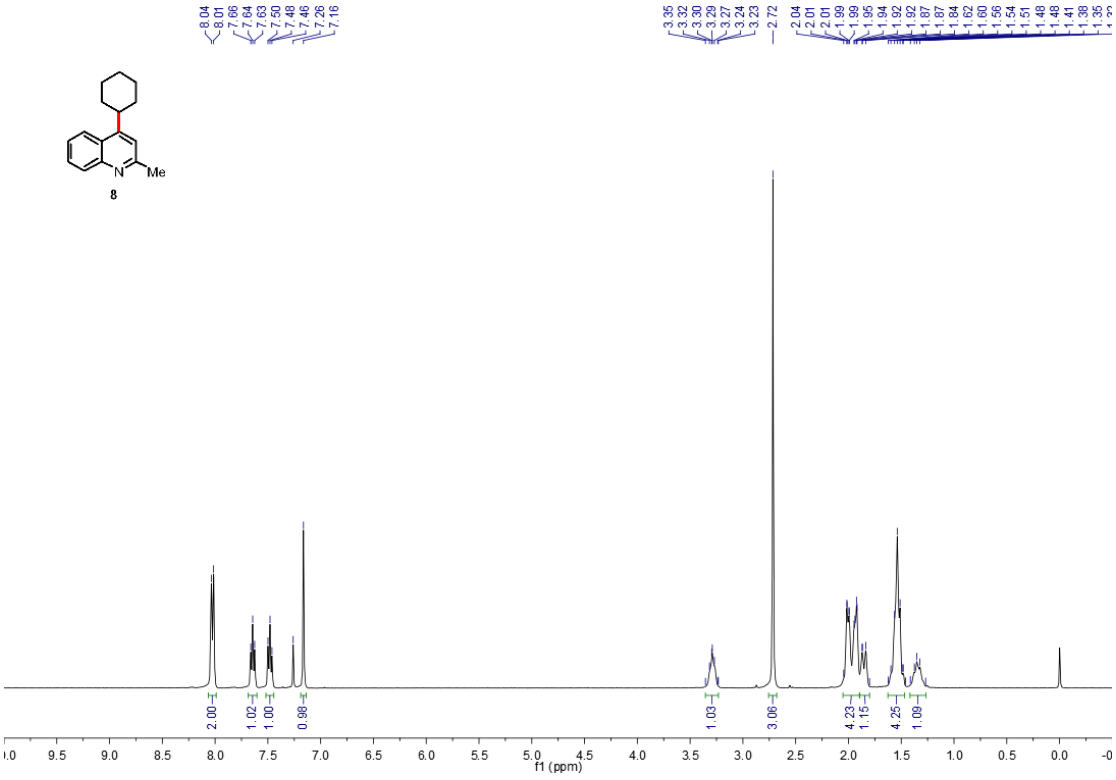
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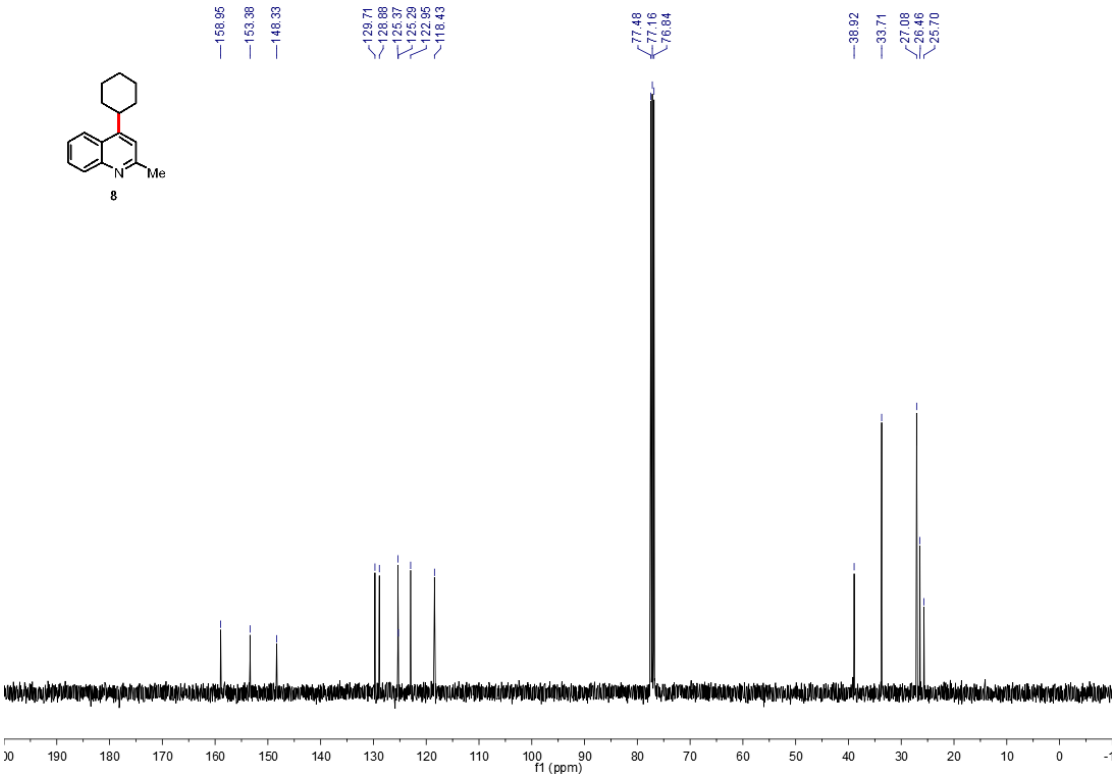
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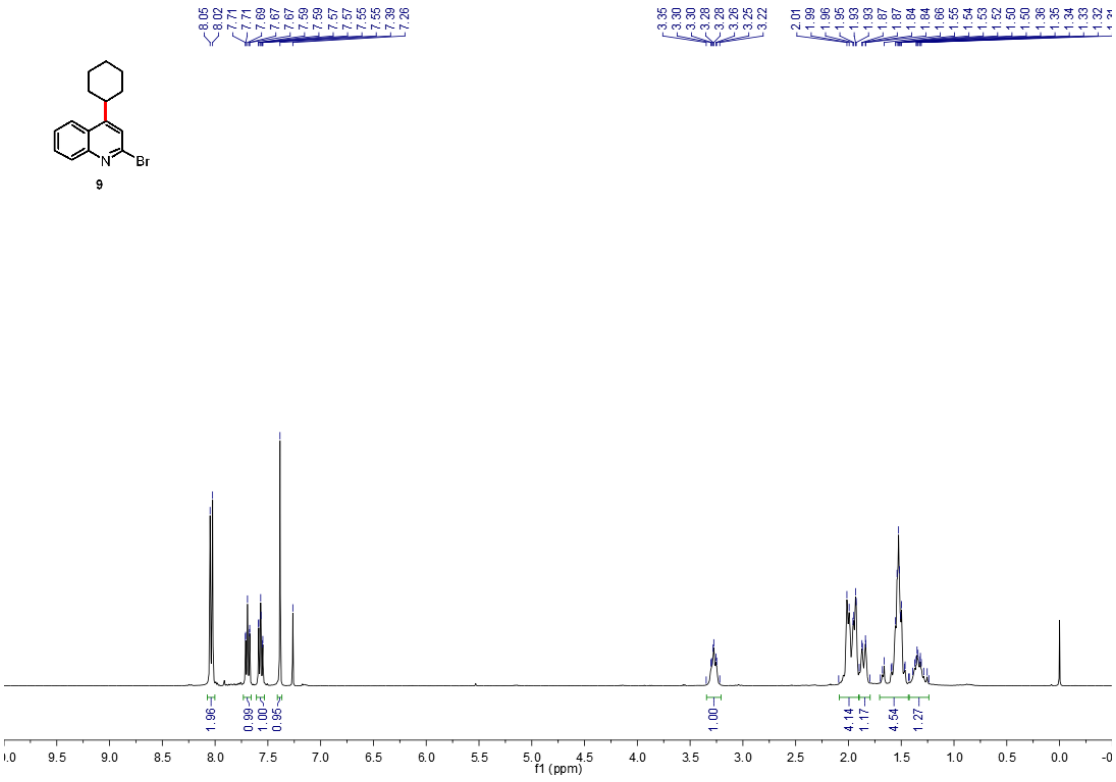
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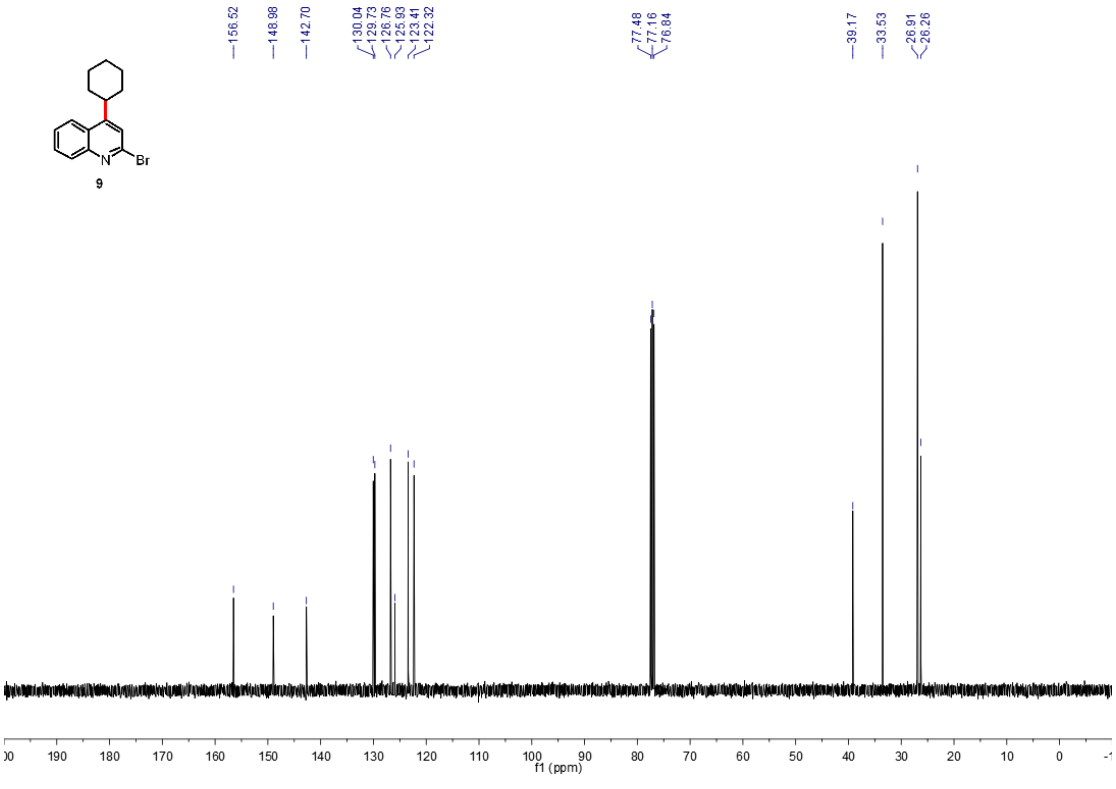
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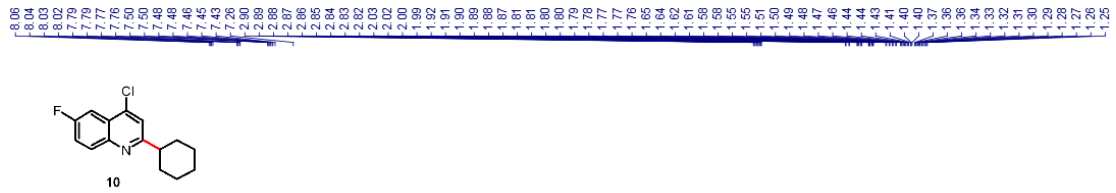

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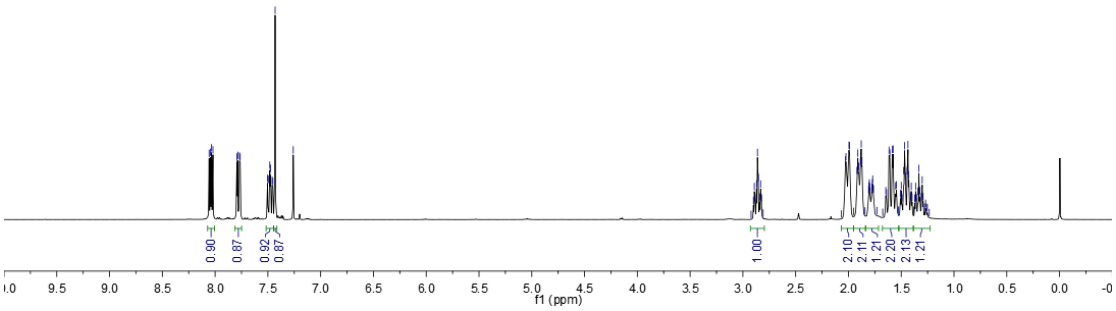

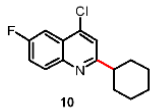

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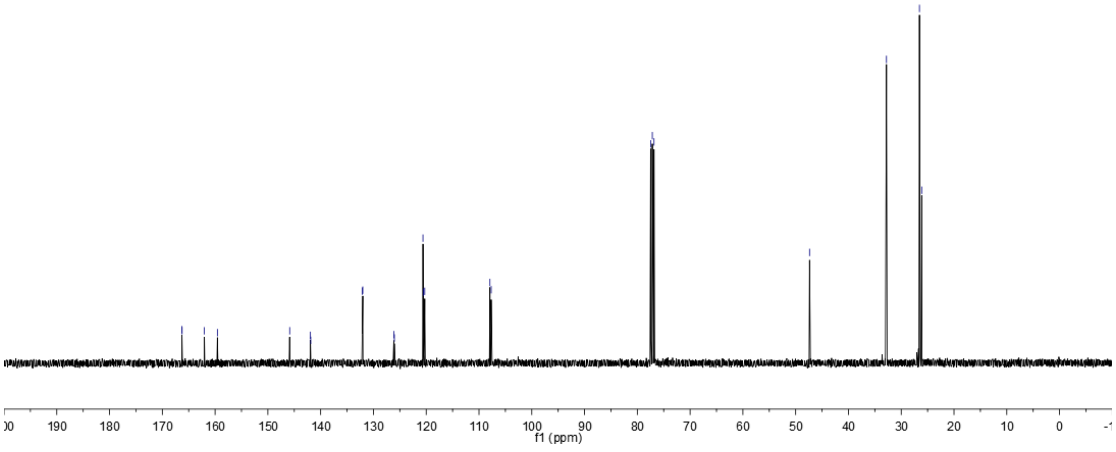


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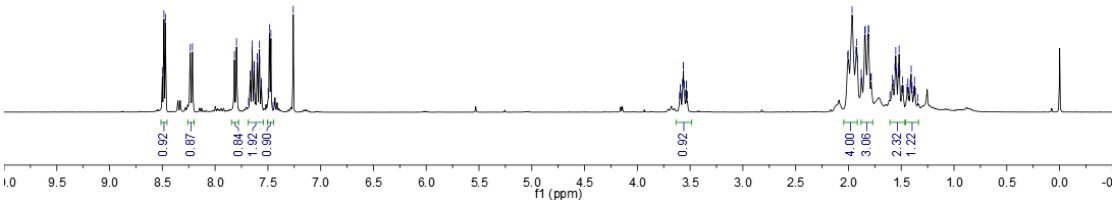
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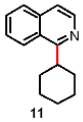
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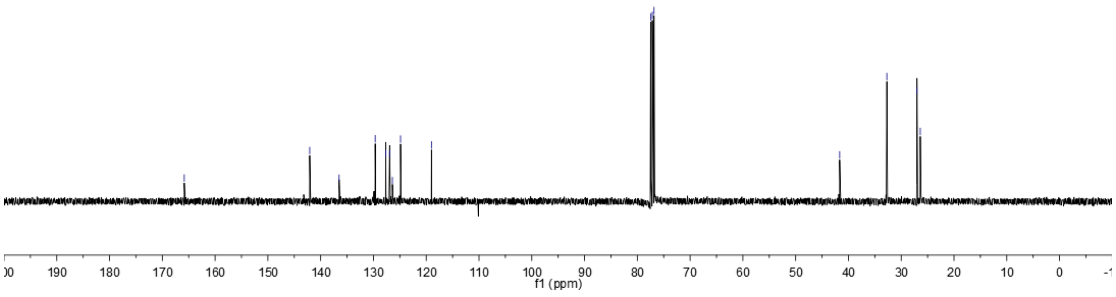
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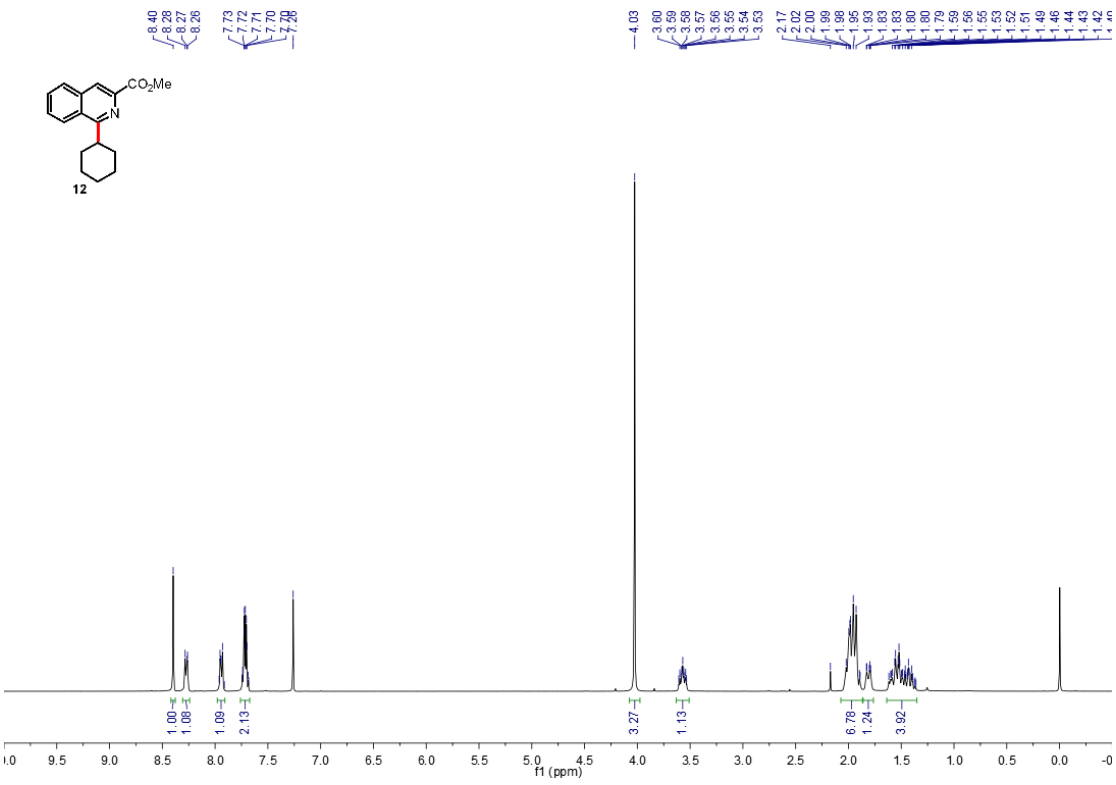
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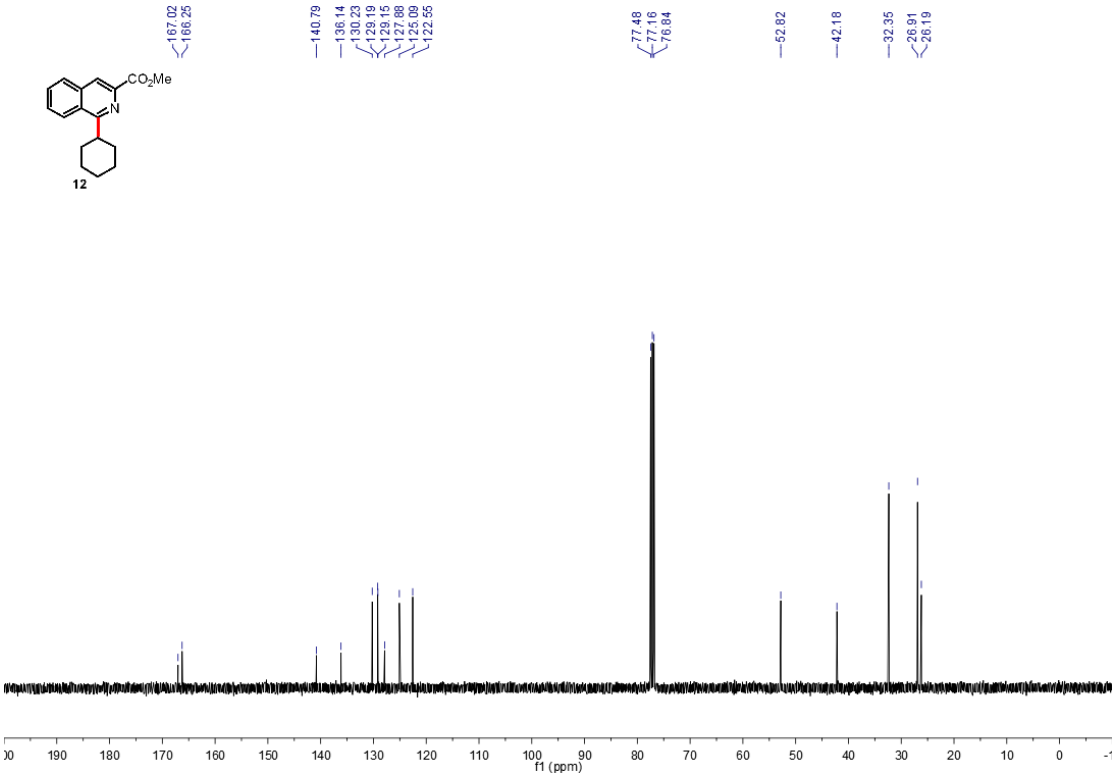
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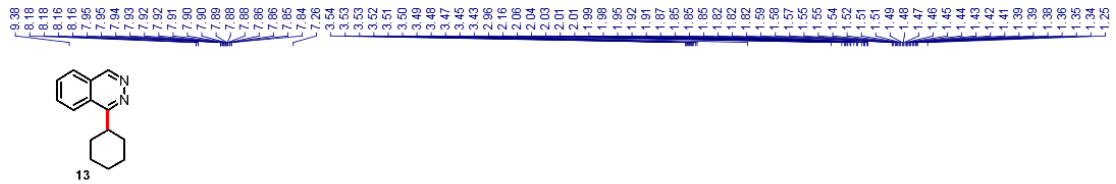

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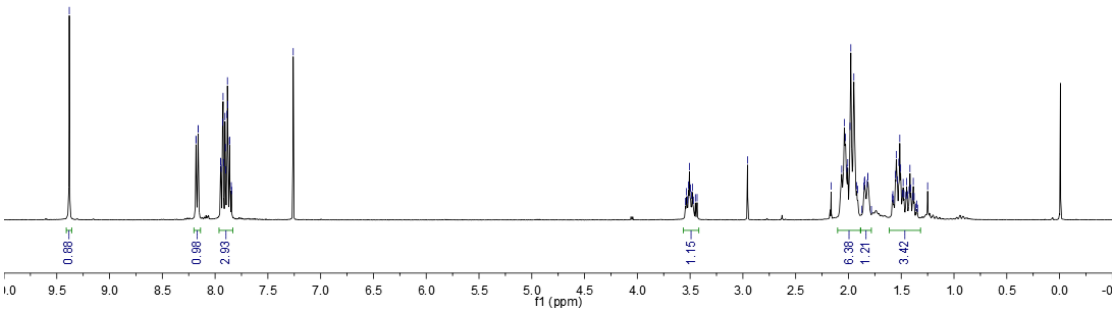
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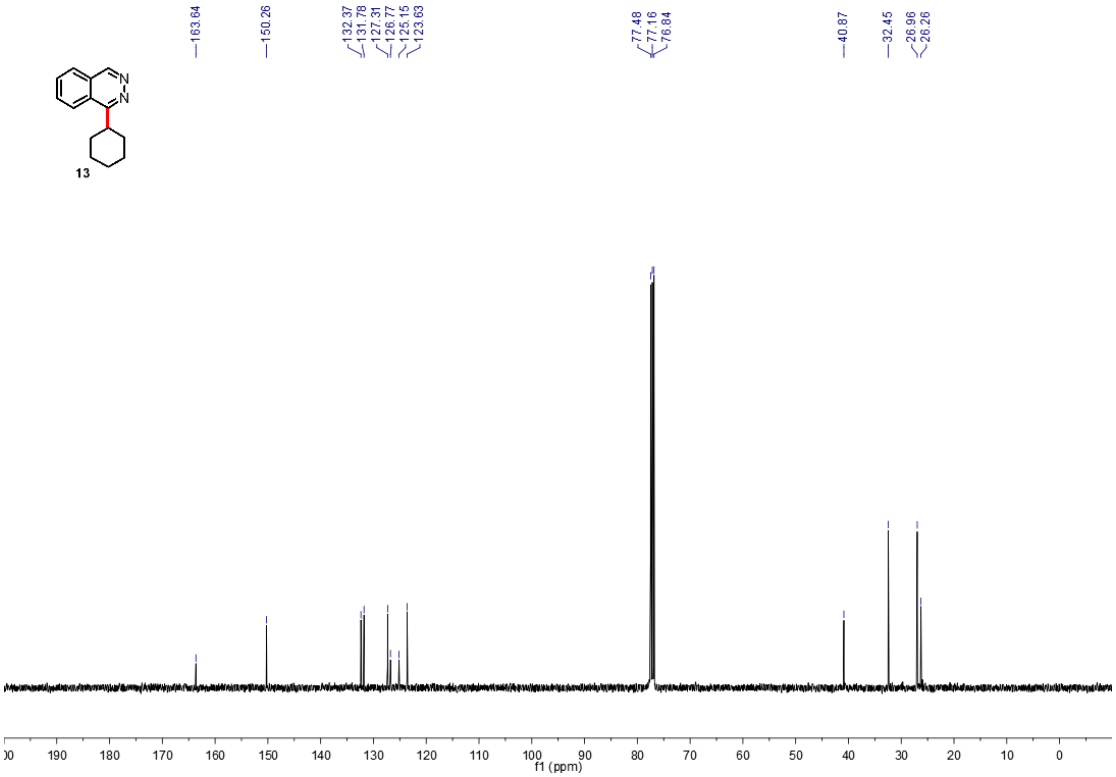
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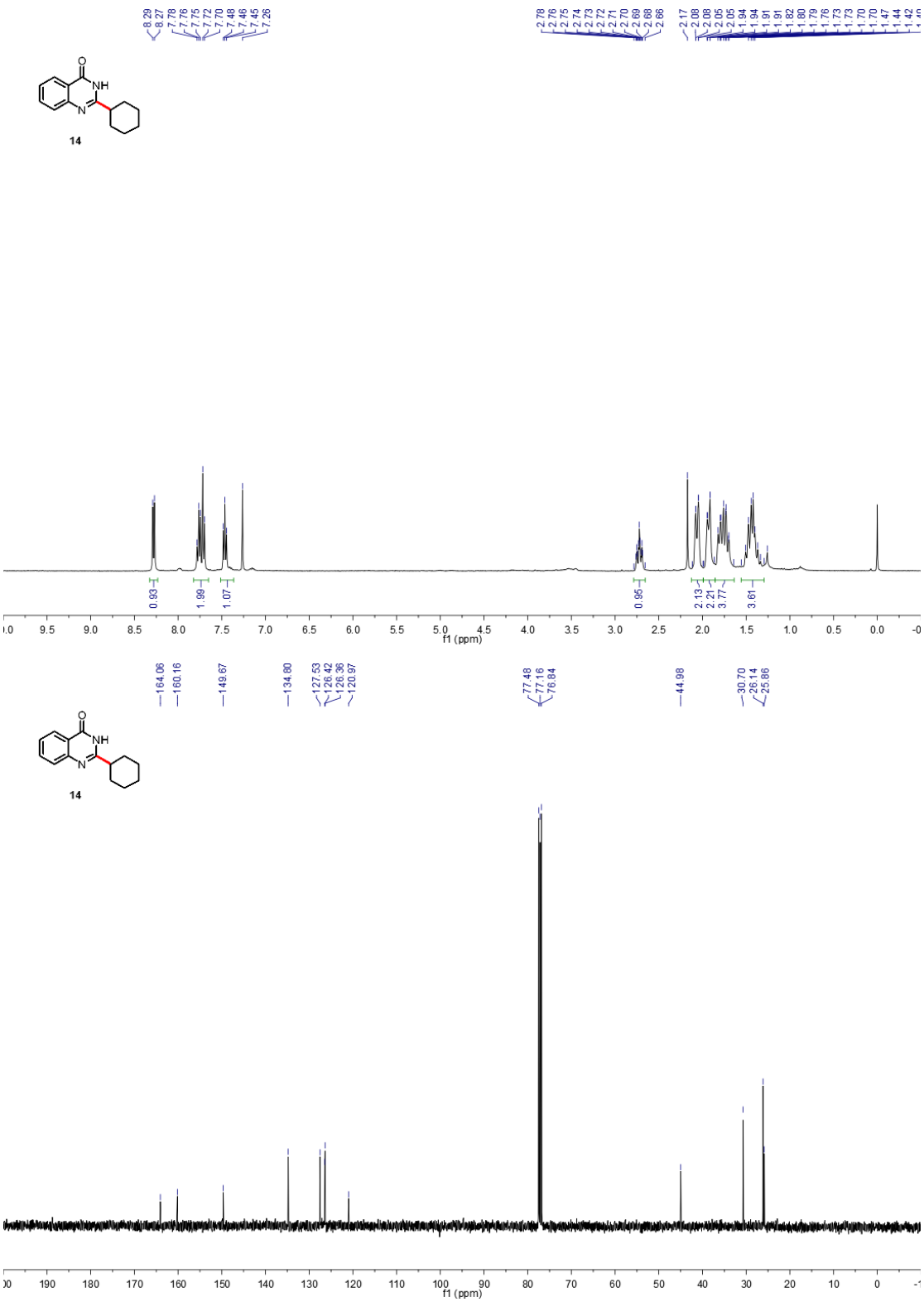
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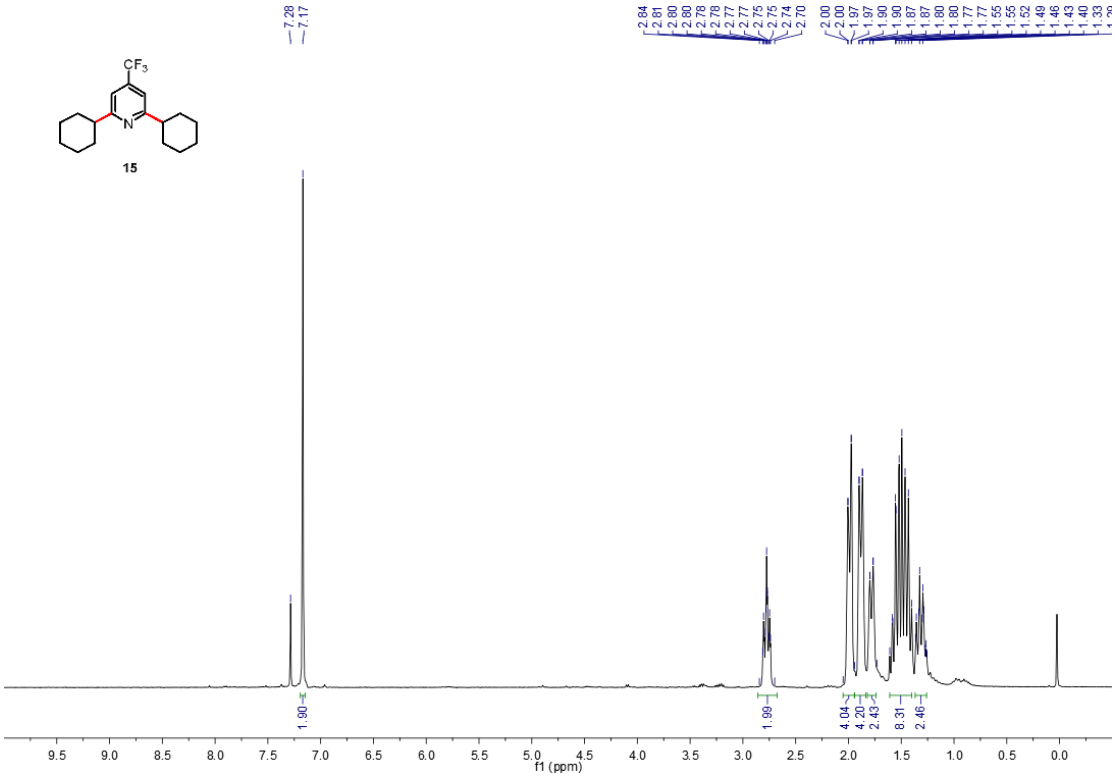
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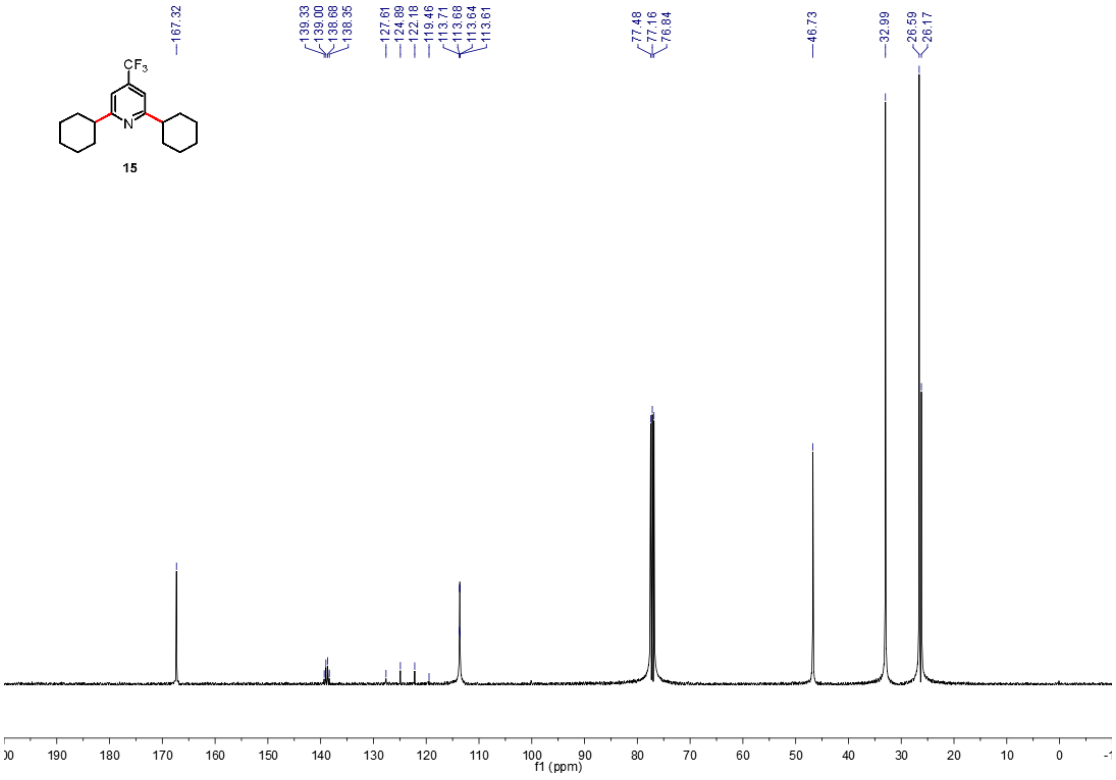
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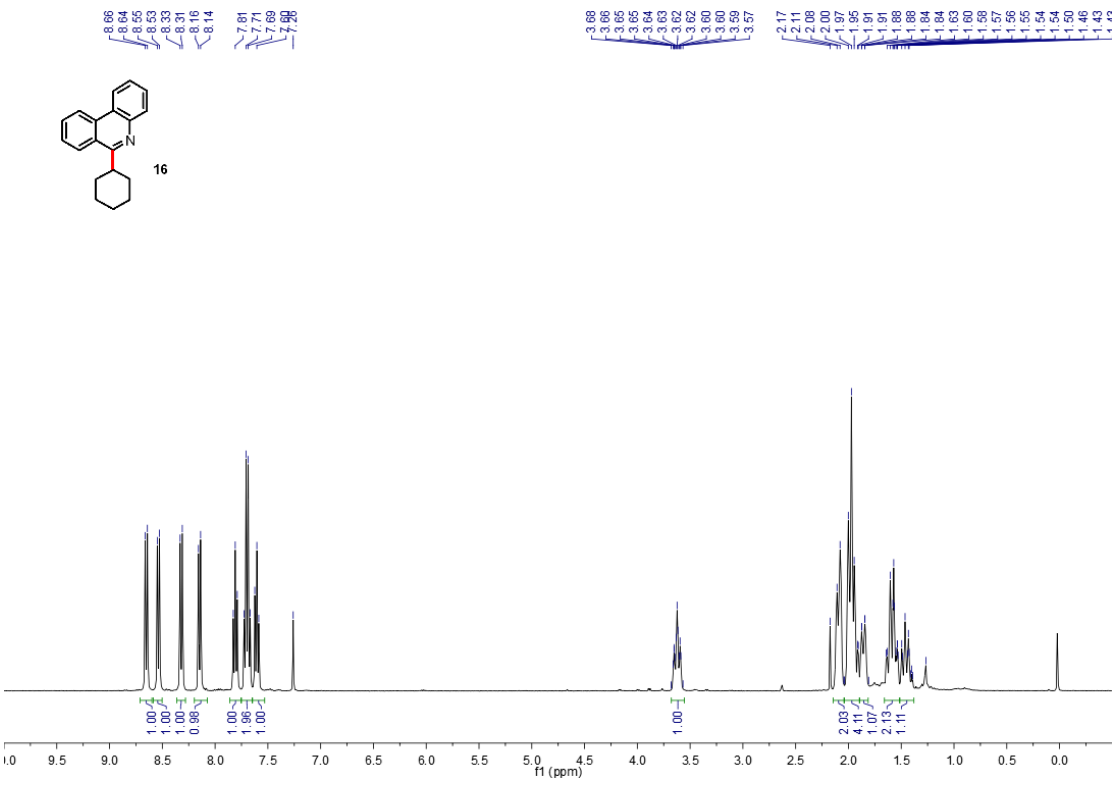
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3.63
3.62
3.62
3.60
3.60
3.59
3.57
2.17
2.11
2.08
2.00
1.97
1.95
1.91
1.91
1.88
1.88
1.84
1.84
1.63
1.60
1.58
1.57
1.56
1.55
1.54
1.54
1.50
1.46
1.43
16
1.00
1.00
1.00
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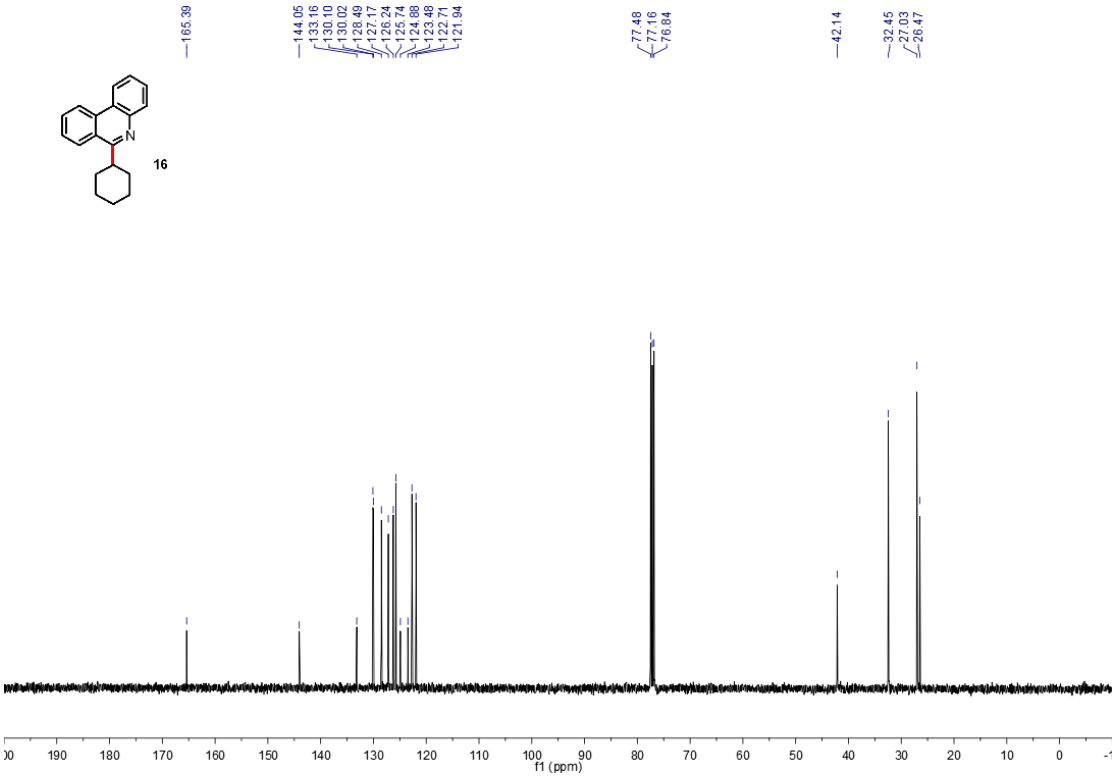
1.96
1.00
1.00
2.03
4.11
1.07
2.13
1.11
f1 (ppm)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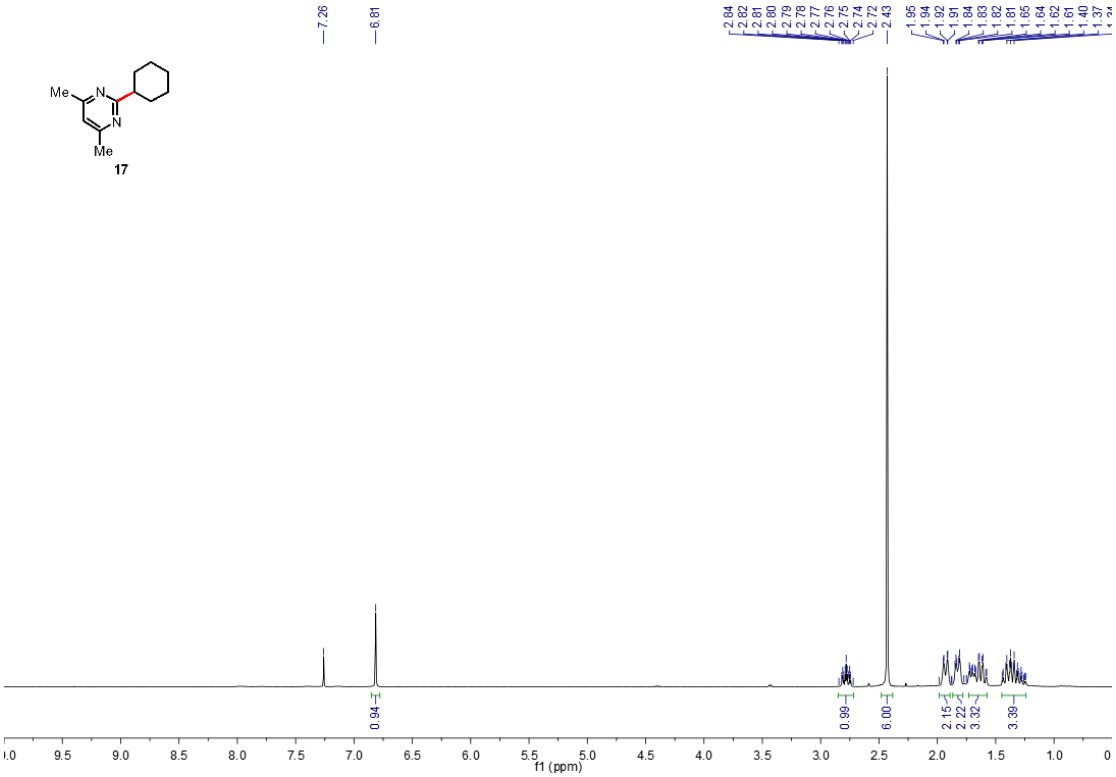
130.02
128.49
127.17
126.24
125.74
124.88
123.48
122.71
121.94
77.48
77.16
76.84
42.14
32.45
27.03
26.47
16
f1 (ppm)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6.81
2.84
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2.80
2.79
2.78
2.77
2.76
2.75
2.74
2.72
2.43
1.95
1.94
1.92
1.91
1.84
1.83
1.82
1.81
1.65
1.64
1.62
1.61
1.40
1.37
Me
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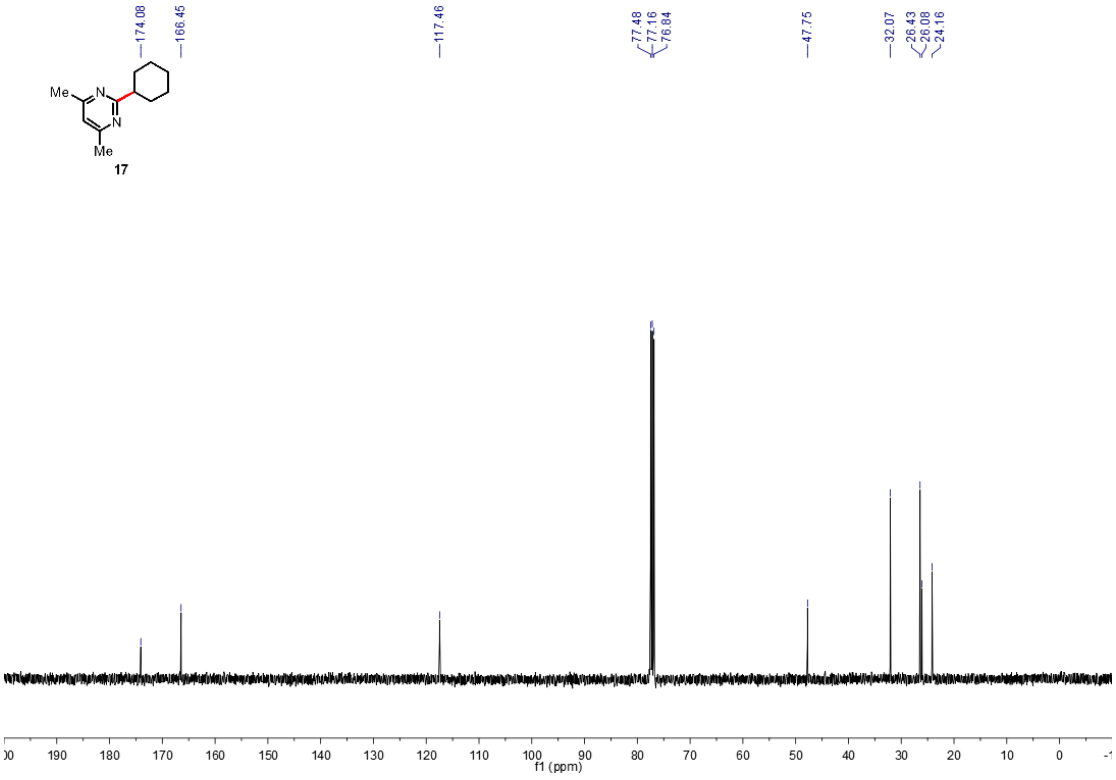
Me
17
0.94
0.99
6.00
2.15
2.22
3.32
3.39
f1 (ppm)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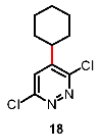
166.45
117.46
77.48
77.16
76.84
47.75
32.07
26.43
26.08
24.16
Me
N
N
Me
17
f1 (ppm)


Cl
Cl
N
N

18

7.34
7.26
2.92
2.91
2.90
2.89
2.89
2.87
2.86
2.86
2.84
2.83
2.83
2.81
2.80
1.97
1.97
1.97
1.93
1.89
1.47
1.46
1.45
1.44
1.43
1.41
1.36
1.35
1.33
1.32
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1.30
1.29
1.28
0.97
1.00
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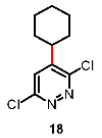
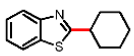
1.11
2.17
3.25
f1 (ppm)


Cl
Cl
N
N

18

156.82
156.42
148.84
127.20
77.48
77.16
76.84
40.26
31.89
26.31
25.79
f1 (ppm)



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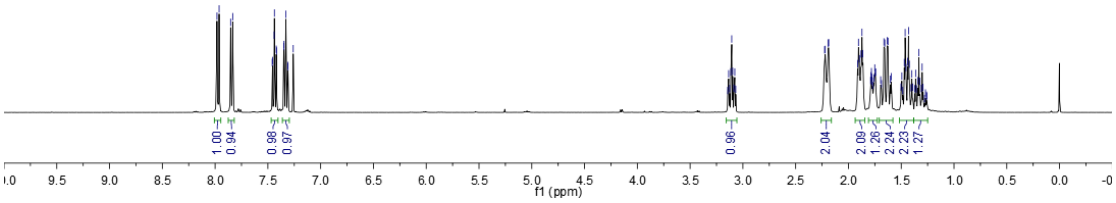

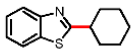

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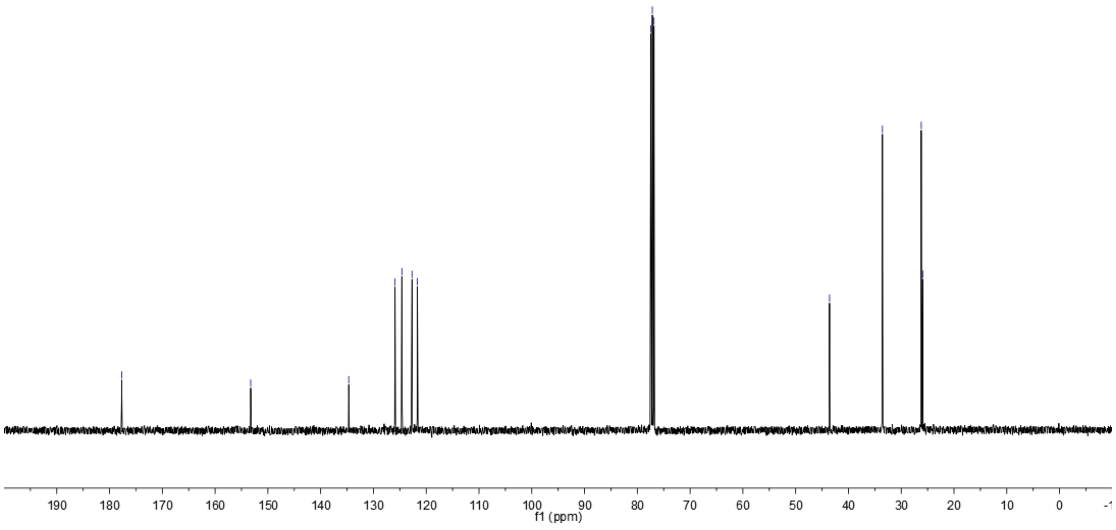

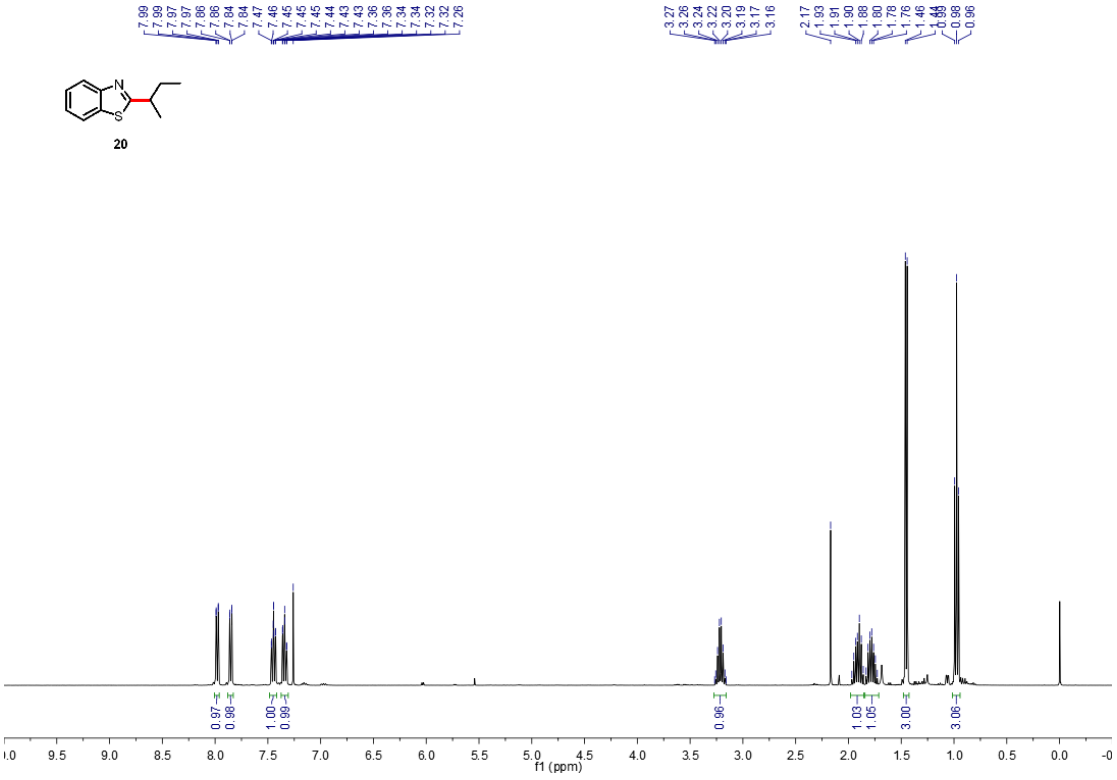
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7.97
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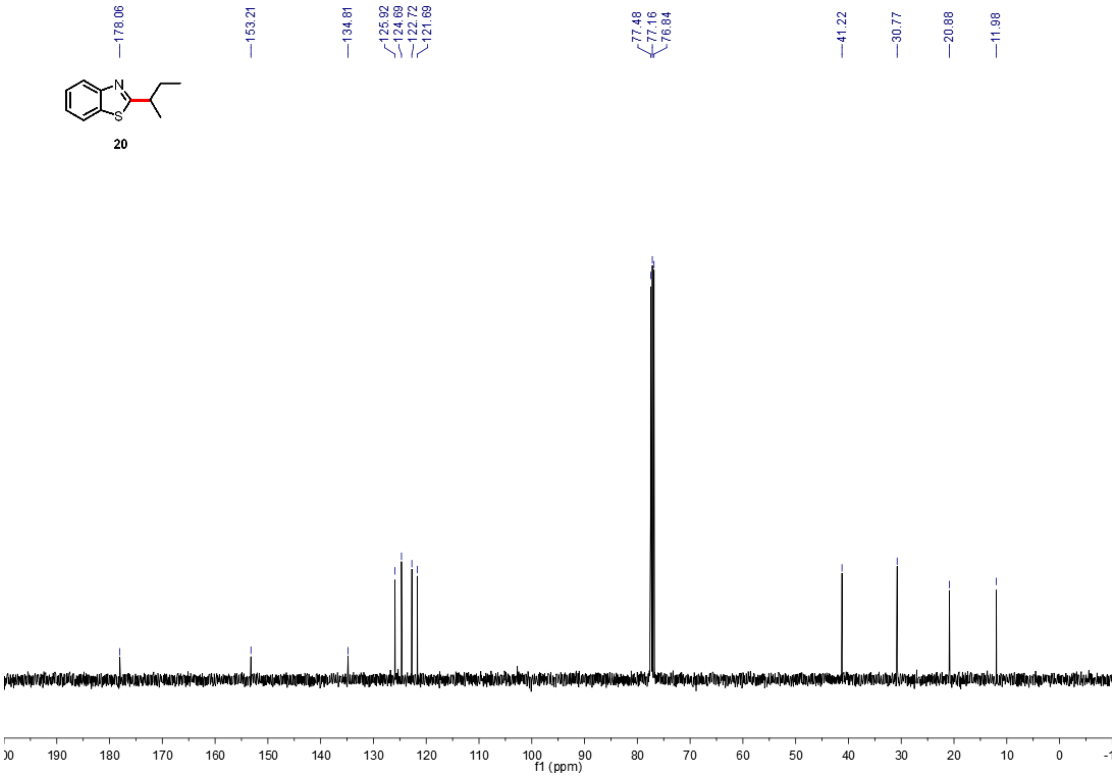
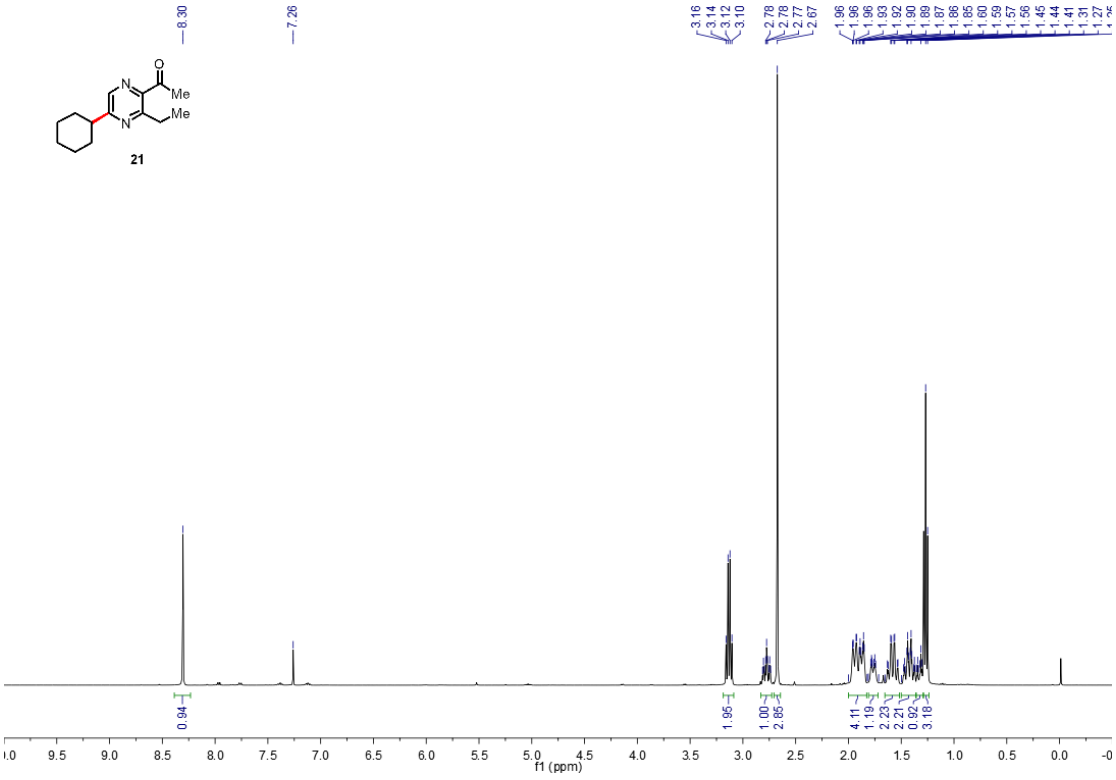
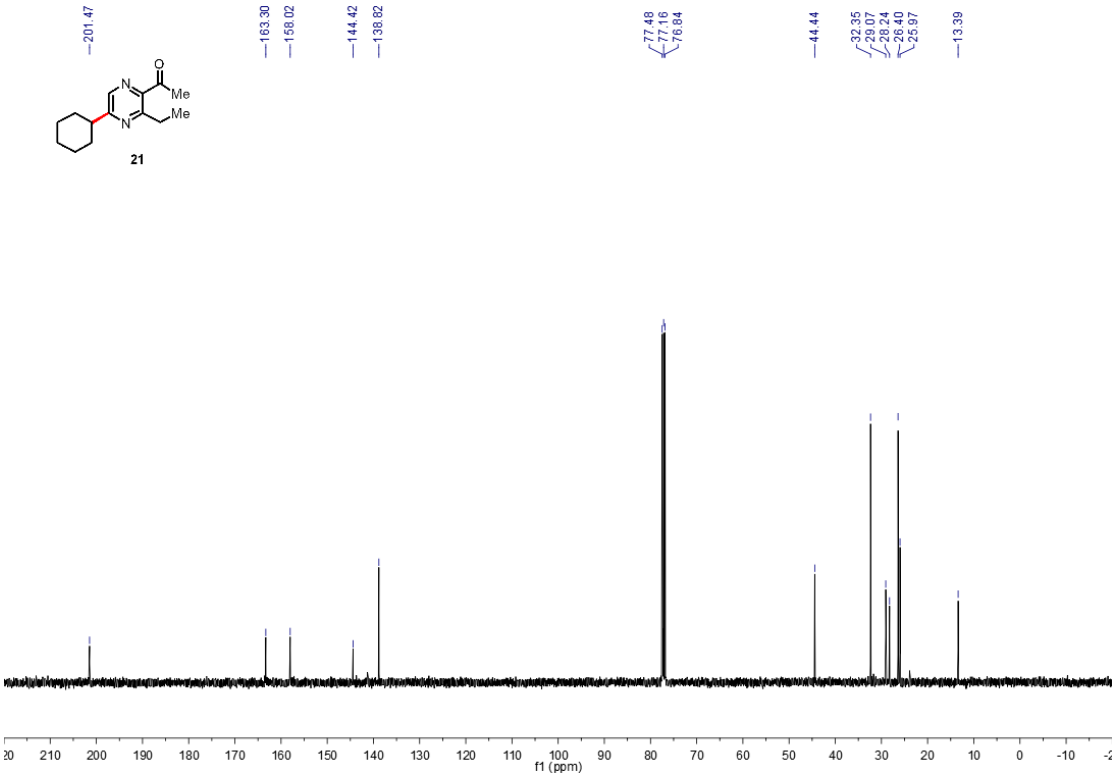
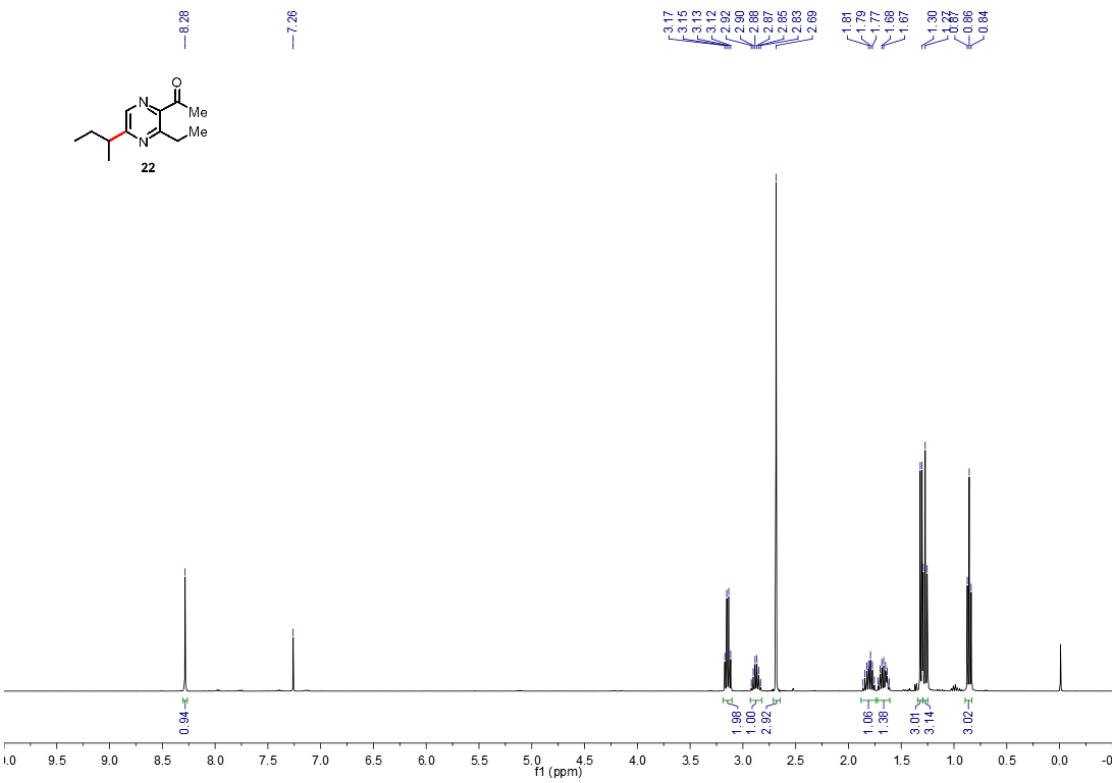
7.86
7.84
7.84
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.36
7.36
7.34
7.34
7.32
7.32
7.26
3.27
3.26
3.24
3.22
3.20
3.19
3.17
3.16
2.17
1.93
1.91
1.90
1.88
1.80
1.78
1.76
1.46
1.44
0.99
0.98
0.96
N
S
20
0.97
0.98
1.00
0.99
0.96
1.03
1.05
3.00
3.06
f1 (ppm)


178.06
153.21
134.81
125.92
124.69
122.72
121.69
77.48
77.16
76.84
41.22
30.77
20.88
11.98
N
S
20
f1 (ppm)


8.30
7.26
3.16
3.14
3.12
3.10
2.78
2.78
2.77
2.67
1.96
1.96
1.96
1.93
1.92
1.90
1.89
1.87
1.86
1.85
1.60
1.59
1.57
1.56
1.45
1.44
1.41
1.31
1.27
Me
Me
21
0.94
1.95
1.00
2.85
4.11
1.19
2.23
2.21
0.92
3.18
f1 (ppm)


201.47
163.30
158.02
144.42
138.82
77.48
77.16
76.84
44.44
32.35
29.07
28.24
26.40
25.97
13.39
Me
Me
21
f1 (ppm)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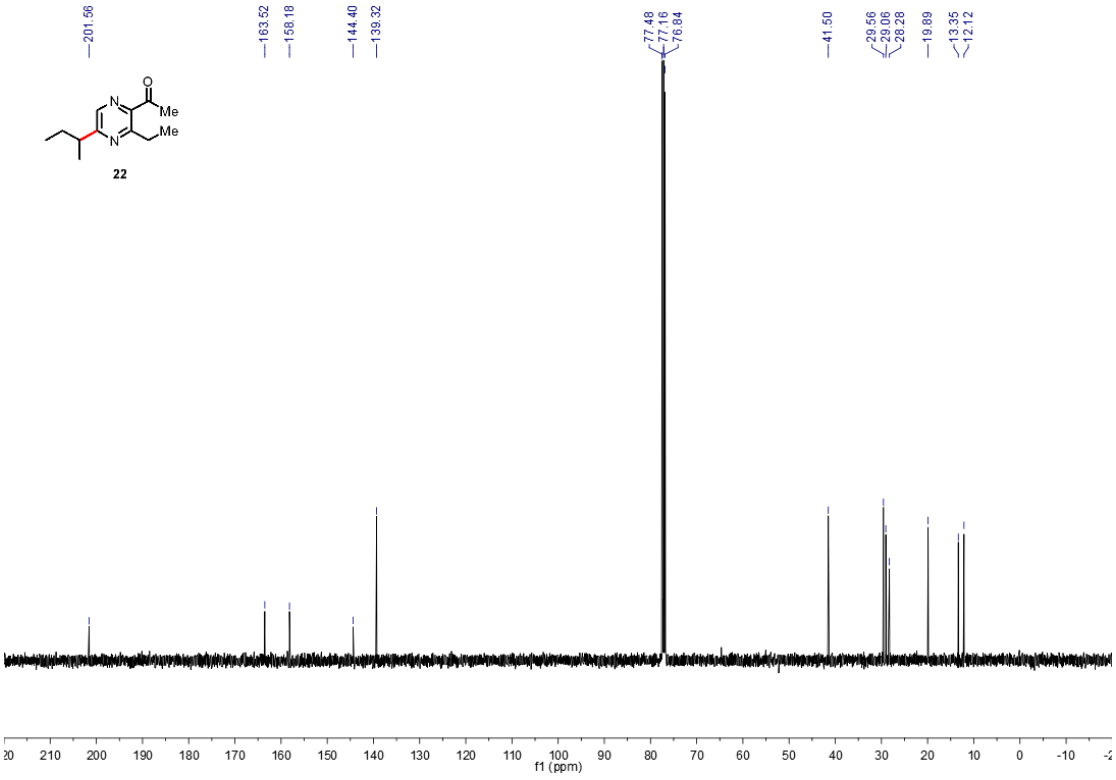
7.26
3.17
3.15
3.13
3.12
2.92
2.90
2.88
2.87
2.85
2.83
2.69
1.81
1.79
1.77
1.68
1.67
1.30
1.27
0.87
0.86
0.84
O
N
N
Me
Me
22
0.94
1.98
1.00
2.92
1.06
1.38
3.01
3.14
3.02
f1 (ppm)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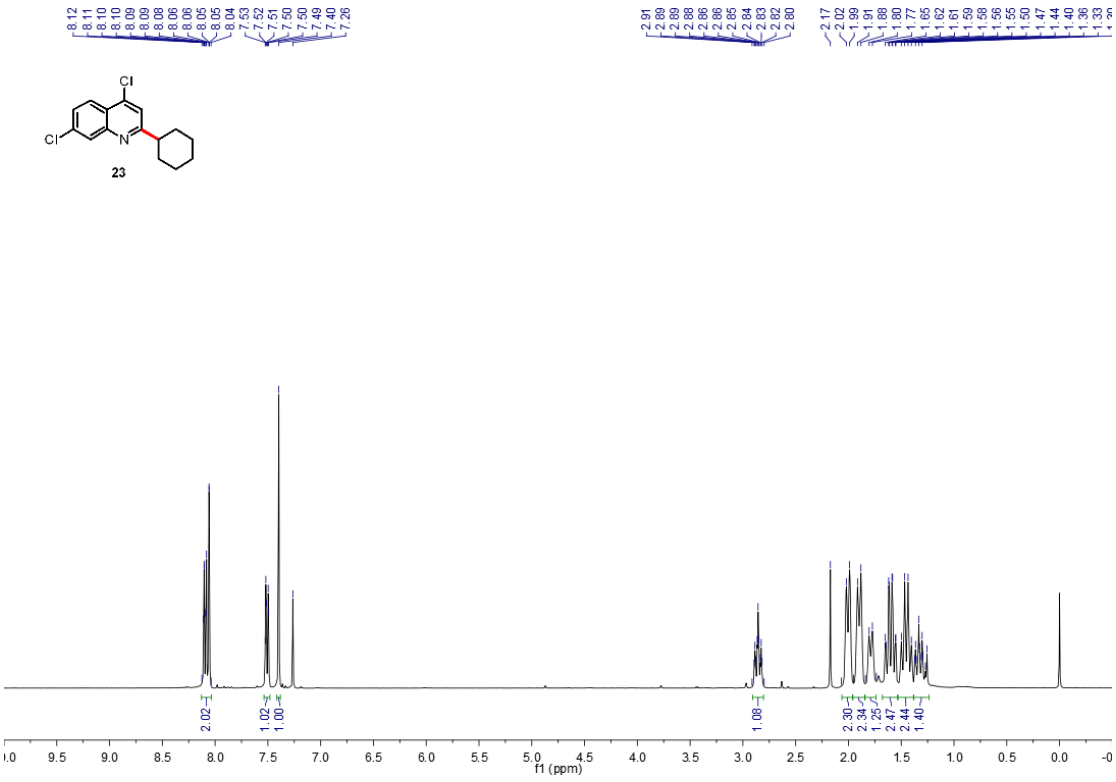
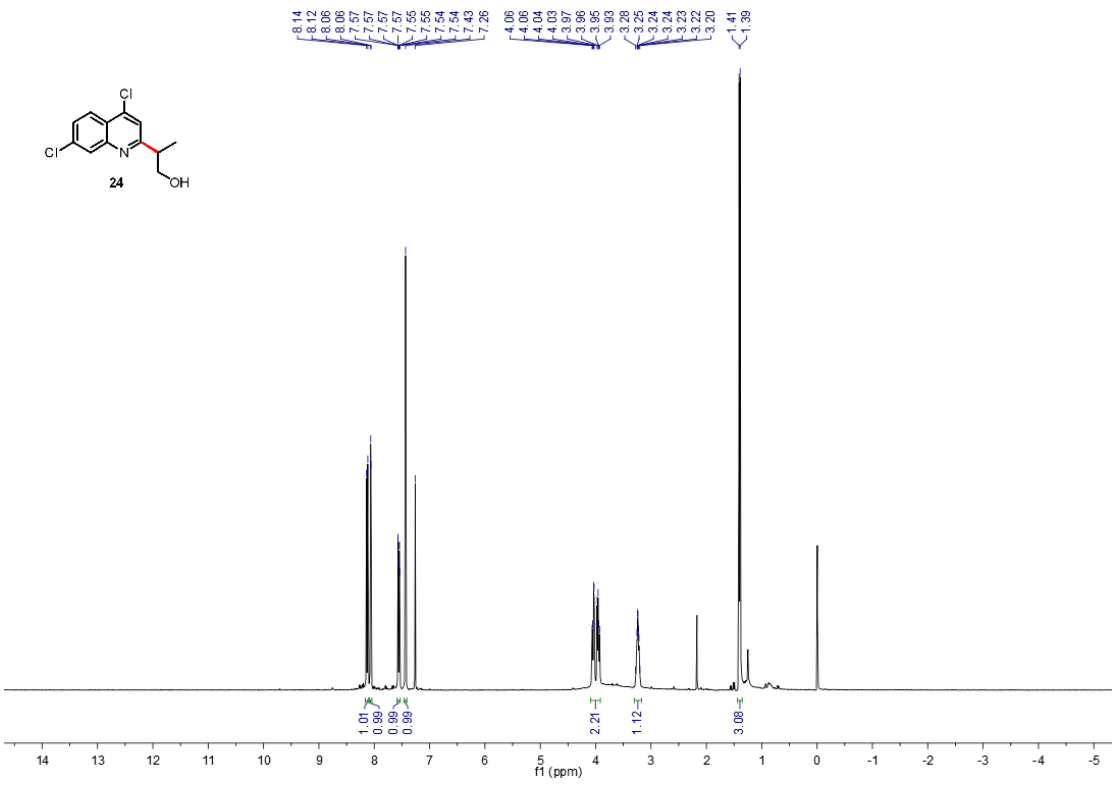
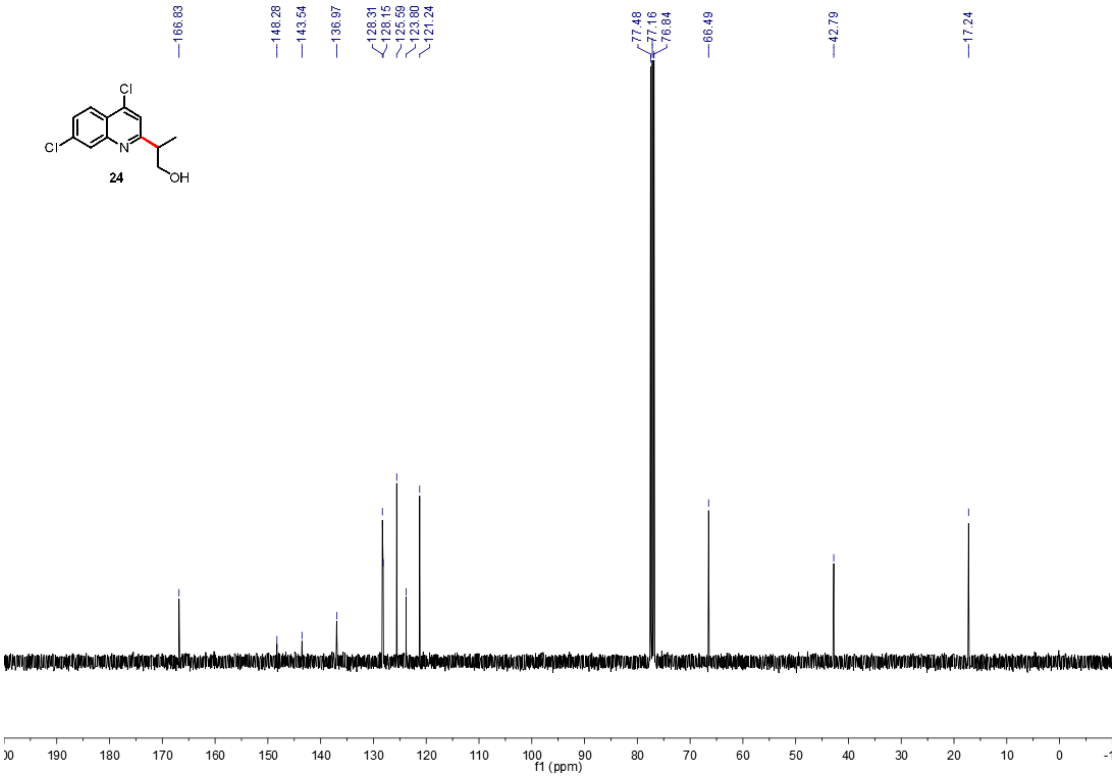
163.52
158.18
144.40
139.32
77.48
77.16
76.84
41.50
29.56
29.06
28.28
19.89
13.35
12.12
O
N
N
Me
Me
22
f1 (ppm)


8.12 8.11 8.10 8.10 8.09 8.09 8.08 8.06 8.06 8.05 8.05 8.04 7.53 7.52 7.51 7.50 7.50 7.49 7.40 7.26
2.91 2.89 2.89 2.88 2.86 2.86 2.85 2.84 2.83 2.82 2.80
2.17 2.02 1.99 1.91 1.88 1.80 1.77 1.65 1.62 1.61 1.59 1.58 1.56 1.55 1.50 1.47 1.44 1.40 1.36 1.33
Cl
Cl
N
23
2.02 1.02 1.00 1.08 2.30 2.34 1.25 2.47 2.44 1.40
f1 (ppm)
168.27 149.21 142.65 136.32 128.48 127.66 125.44 123.75 120.27 77.48 77.16 76.84 47.45 32.69 26.51 26.09
Cl
Cl
N
23
f1 (ppm)


8.14
8.12
8.06
8.06
7.57
7.57
7.57
7.57
7.55
7.55
7.54
7.54
7.43
7.26
4.06
4.06
4.04
4.03
3.97
3.96
3.95
3.93
3.28
3.25
3.24
3.24
3.23
3.22
3.20
1.41
1.39
Cl
Cl
N
OH
24
1.01
0.99
0.99
0.99
2.21
1.12
3.08
f1 (ppm)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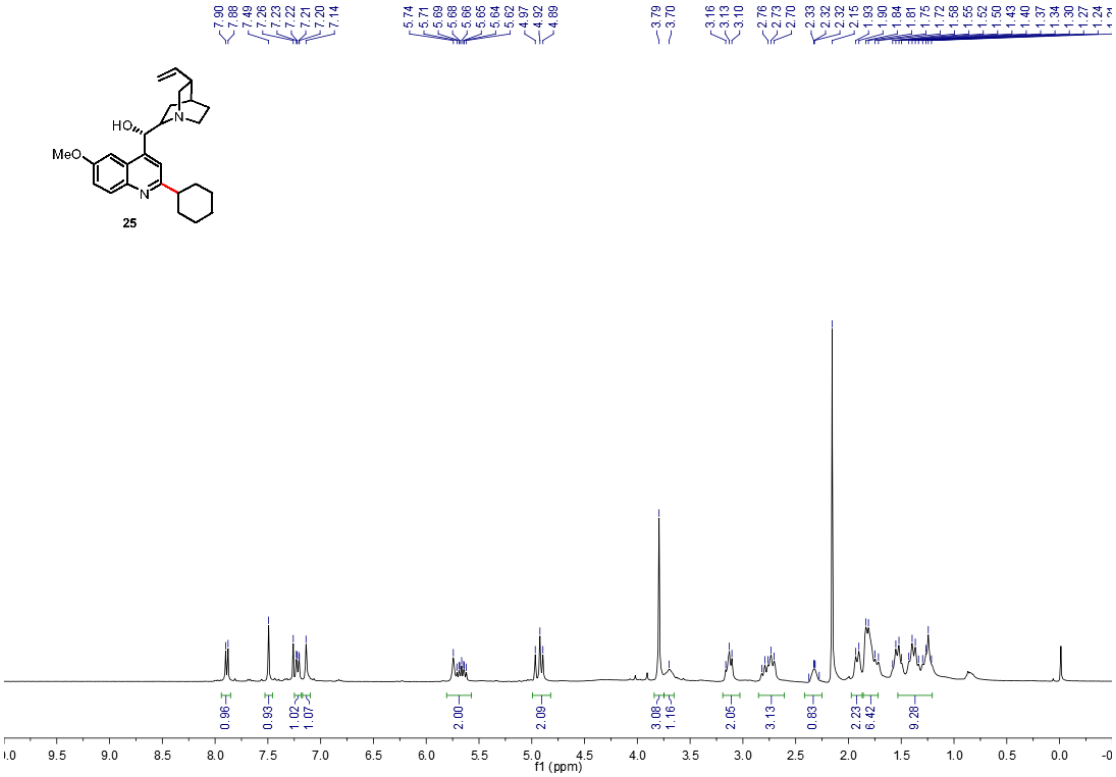
148.28
143.54
136.97
128.31
128.15
125.59
123.80
121.24
77.48
77.16
76.84
66.49
42.79
17.24
Cl
Cl
N
OH
24
f1 (ppm)


7.90
7.88
7.49
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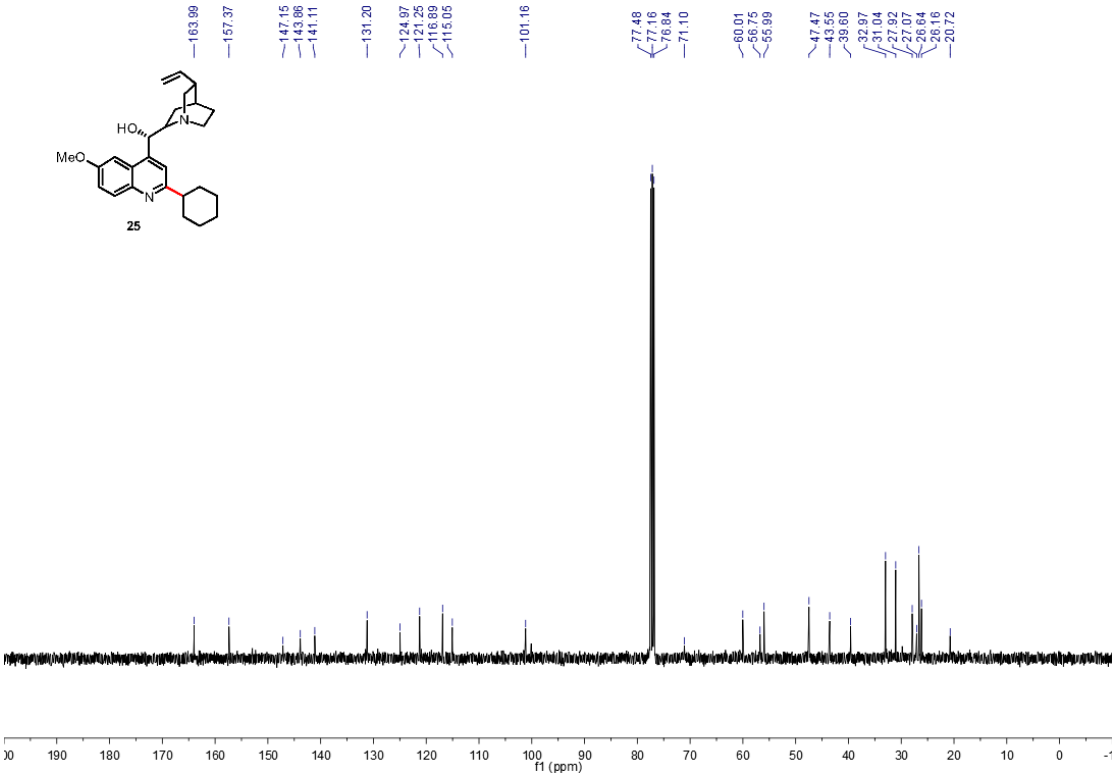
7.22
7.21
7.20
7.14
5.74
5.71
5.69
5.68
5.66
5.65
5.64
5.62
4.97
4.92
4.89
3.79
3.70
3.16
3.13
3.10
2.76
2.73
2.70
2.33
2.32
2.32
2.15
1.93
1.90
1.84
1.81
1.75
1.72
1.68
1.55
1.52
1.50
1.43
1.40
1.37
1.34
1.30
1.27
1.24
HO
MeO
N
N
25
0.96
0.93
1.02
1.07
2.00
2.09
3.08
1.16
2.05
3.13
0.83
2.23
6.42
9.28
f1 (ppm)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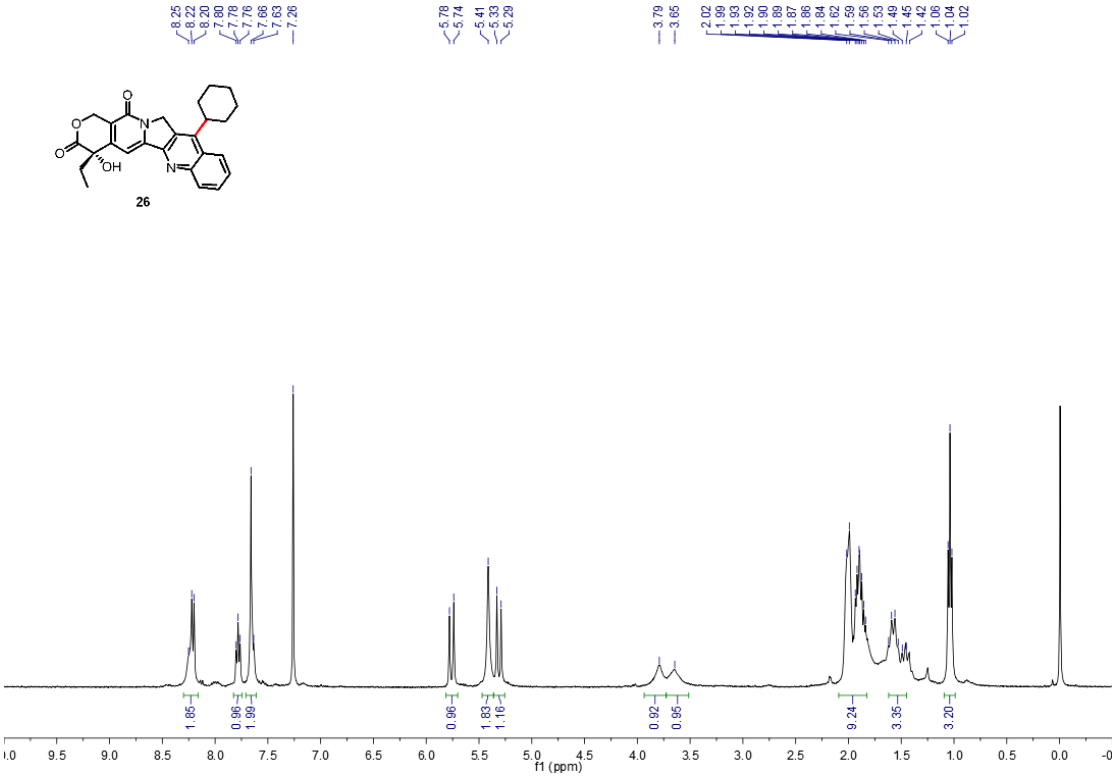
131.20
124.97
121.25
116.89
115.05
101.16
77.48
77.16
76.84
71.10
60.01
56.75
55.99
47.47
43.55
39.60
32.97
31.04
27.92
27.07
26.64
26.16
20.72
HO
MeO
N
N
25
f1 (ppm)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8.22
8.20
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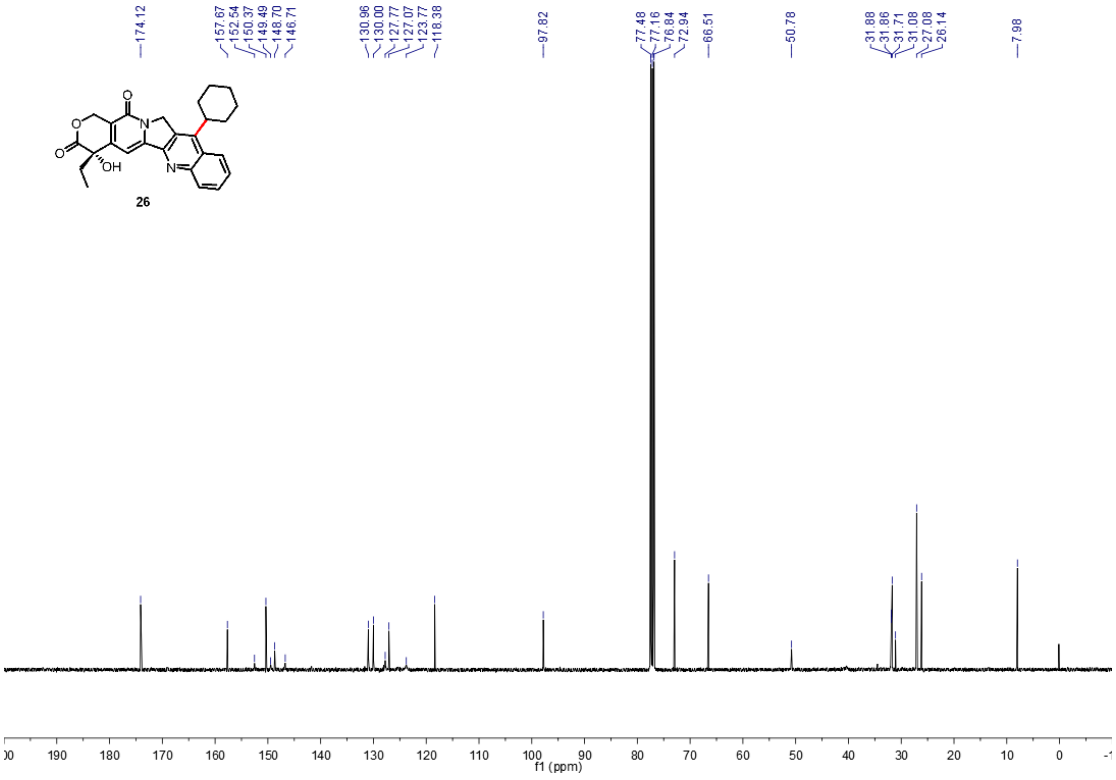
7.76
7.66
7.63
7.26
5.79
5.74
5.41
5.33
5.29
3.79
3.65
2.02
1.99
1.93
1.92
1.90
1.89
1.87
1.86
1.84
1.62
1.59
1.56
1.53
1.49
1.45
1.42
1.06
1.04
1.02
O
N
O
OH
N
26
1.85
0.96
1.99
0.96
1.83
1.16
0.92
0.95
9.24
3.35
3.20
f1 (ppm)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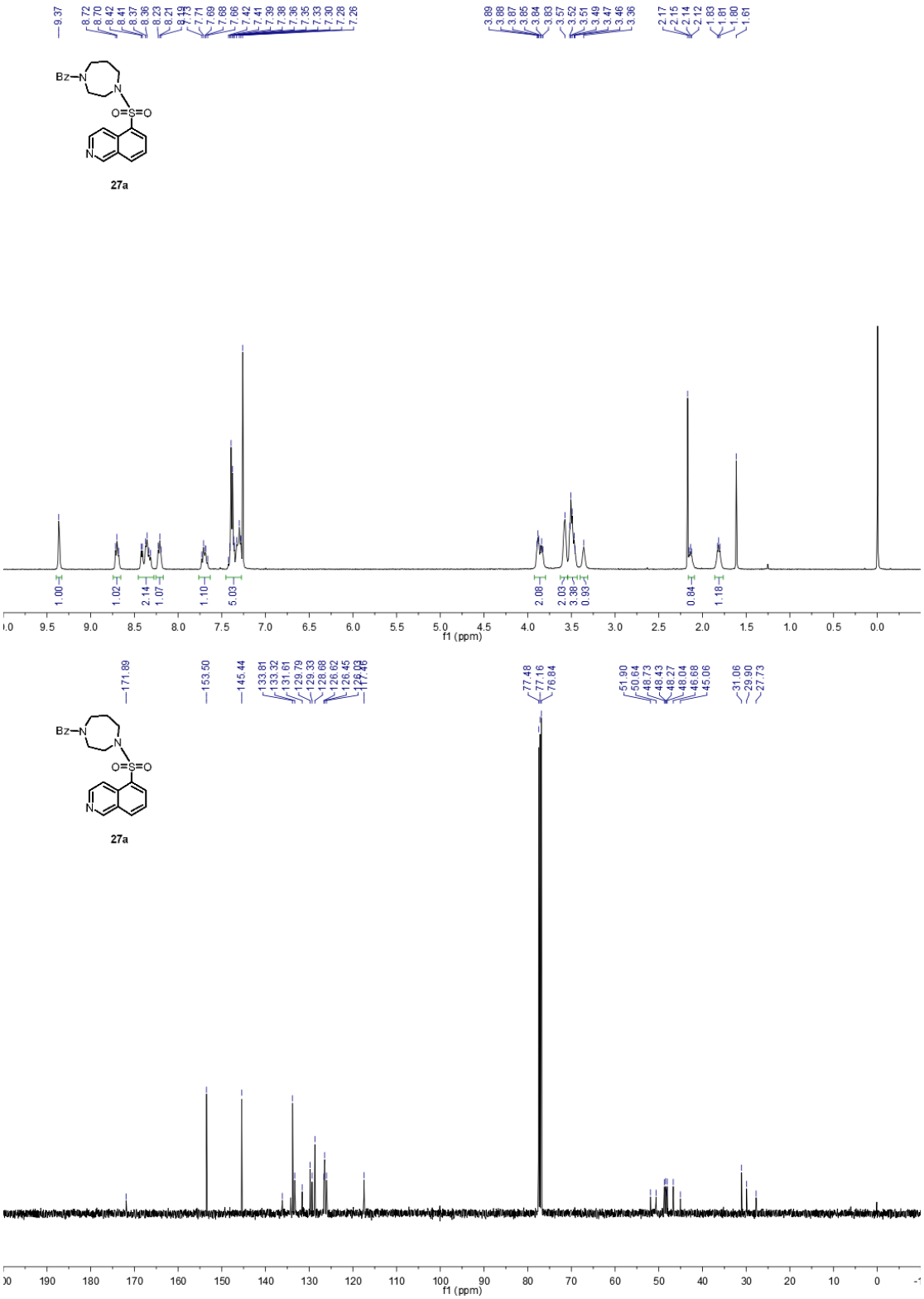
150.37
149.49
148.70
146.71
130.96
130.00
127.77
127.07
123.77
118.38
97.82
77.48
77.16
76.84
72.94
66.51
50.78
31.88
31.86
31.71
31.08
27.08
26.14
7.98
O
N
O
OH
N
26
f1 (ppm)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8.70
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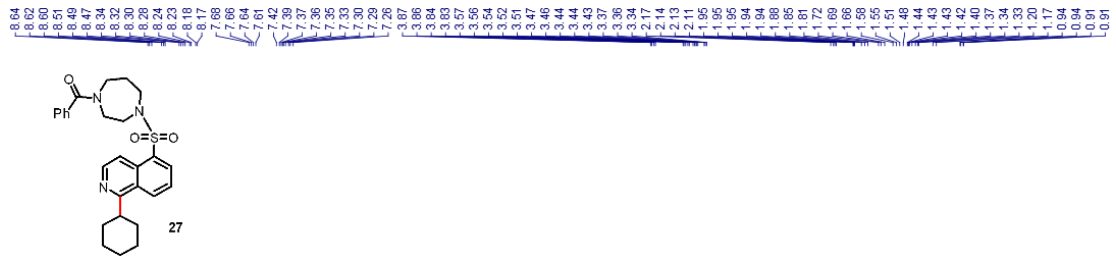
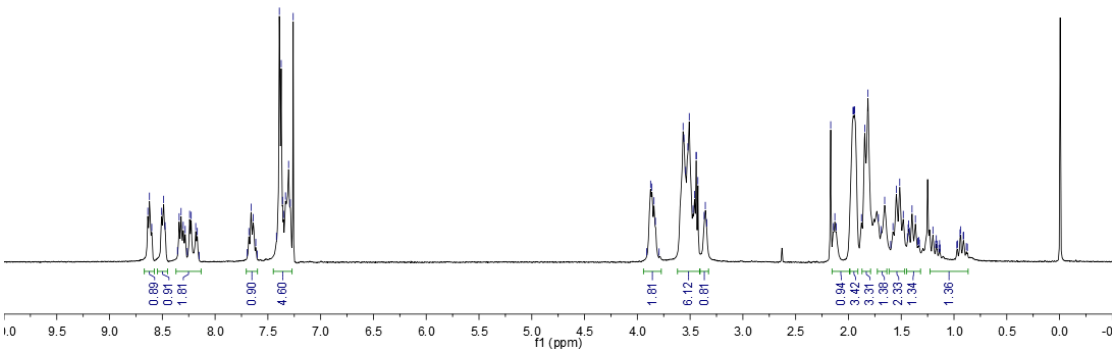
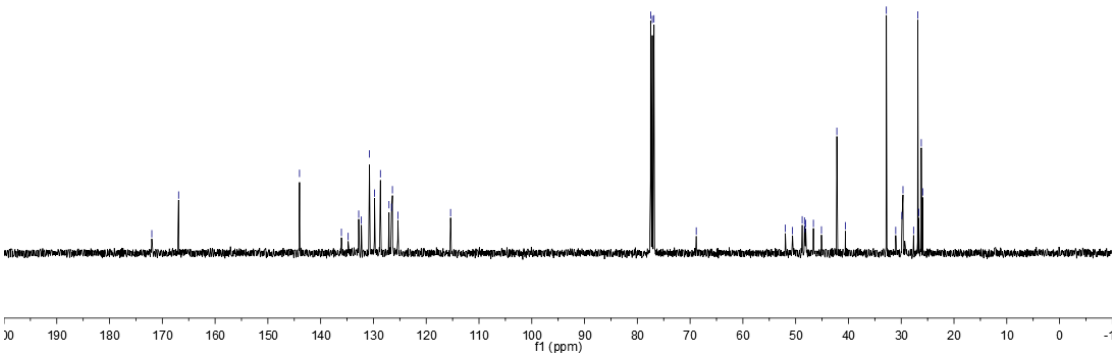
8.41
8.37
8.36
8.23
8.21
7.73
7.71
7.69
7.68
7.66
7.42
7.41
7.39
7.38
7.36
7.35
7.33
7.30
7.28
7.26
3.89
3.88
3.87
3.85
3.84
3.83
3.57
3.52
3.51
3.49
3.47
3.46
3.36
2.17
2.15
2.14
2.12
1.83
1.81
1.80
1.61
Bz
N
O=S=O
N
27a
1.00
1.02
2.14
1.07
1.10
5.03
2.08
2.03
3.38
0.93
0.84
1.18
f1 (ppm)
171.89
153.50
145.44
133.81
133.32
131.61
129.79
129.33
128.88
126.62
126.45
77.48
77.16
76.84
51.90
50.64
48.73
48.43
48.27
48.04
46.68
45.06
31.06
29.90
27.73
Bz
N
O=S=O
N
27a
f1 (ppm)

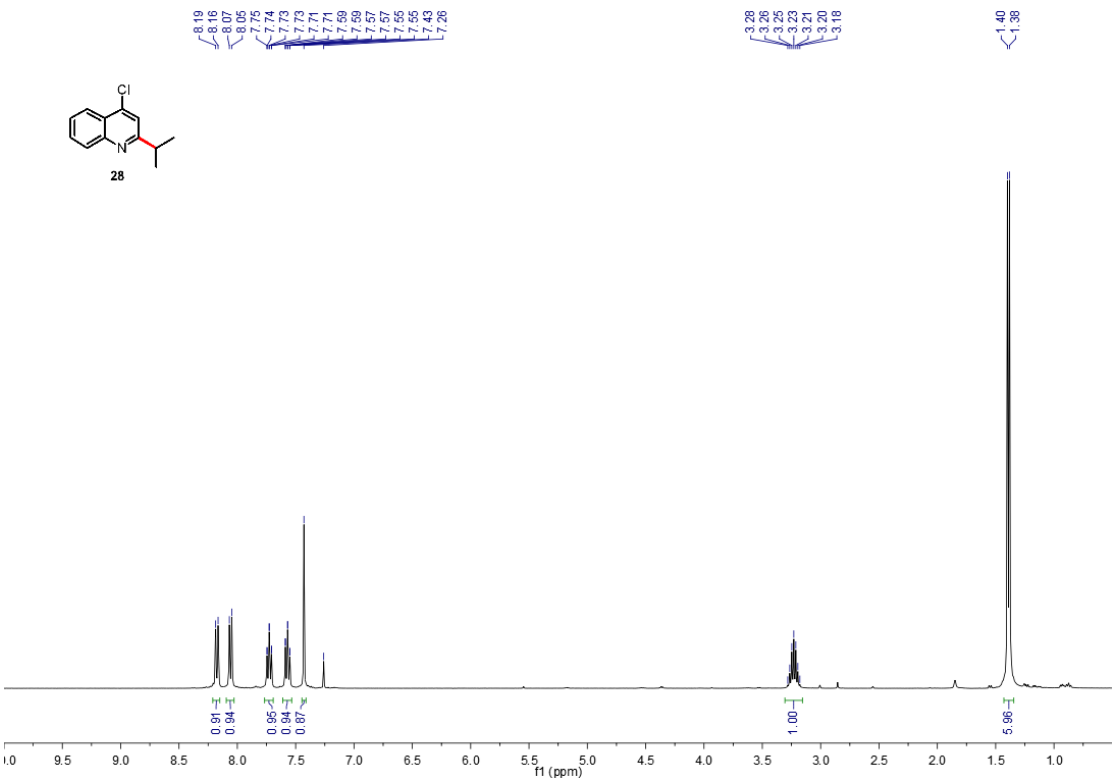


27



27

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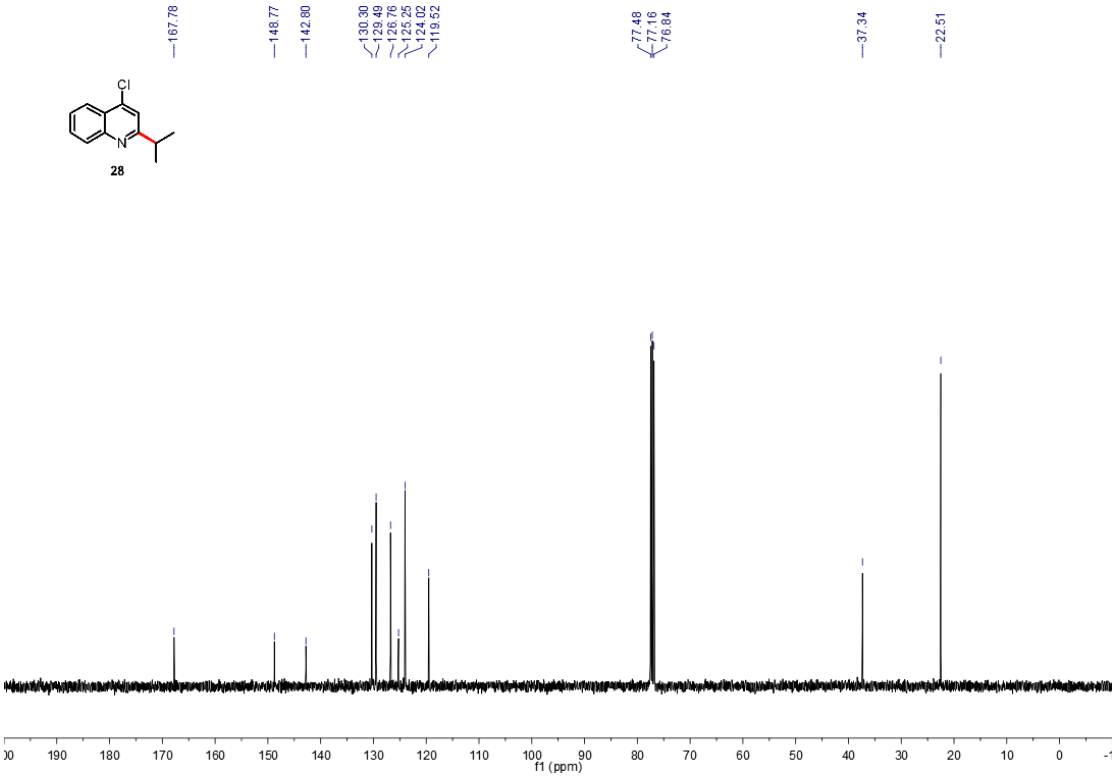
8.07
8.05
7.75
7.74
7.73
7.73
7.71
7.71
7.59
7.59
7.57
7.57
7.55
7.55
7.43
7.26
3.28
3.26
3.25
3.23
3.21
3.20
3.18
1.40
1.38
Cl
N
28
0.91
0.94
0.95
0.94
0.87
1.00
5.96
f1 (ppm)


167.78
148.77
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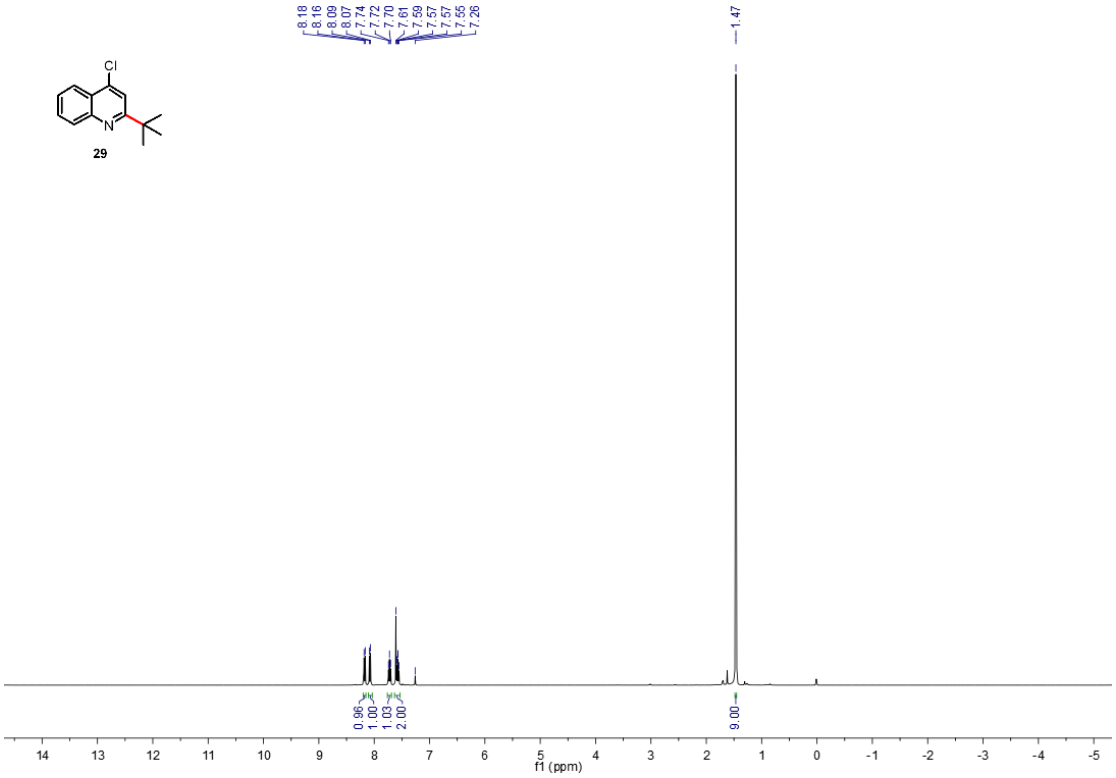
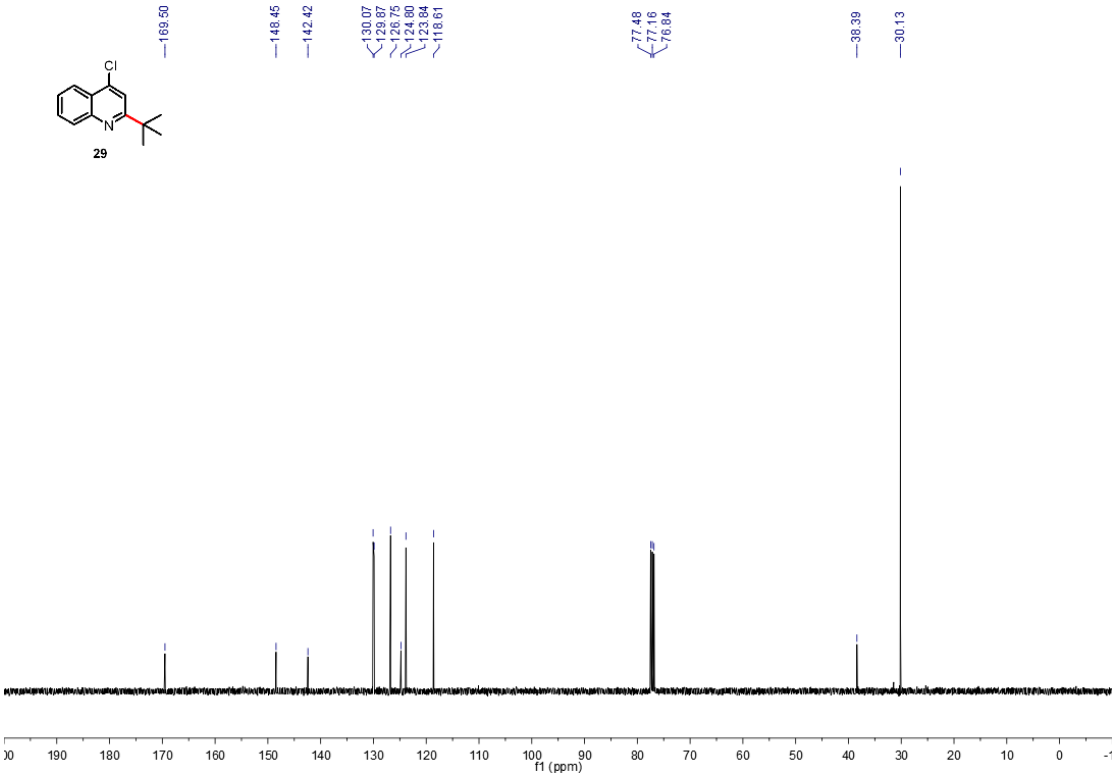
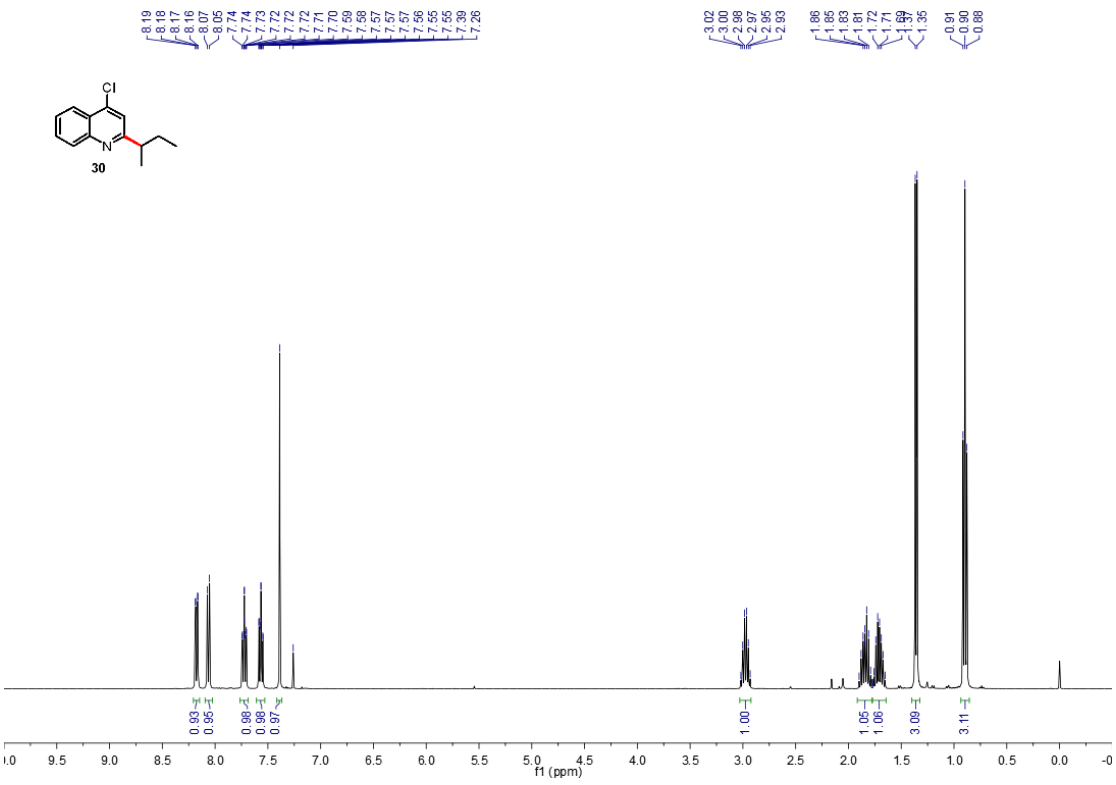
130.30
129.49
128.76
125.25
124.02
119.52
77.48
77.16
76.84
37.34
22.51
Cl
N
28
f1 (ppm)


8.18
8.16
8.09
8.07
7.74
7.72
7.70
7.61
7.59
7.57
7.57
7.55
7.26
1.47
Cl
N
29
0.96
1.00
1.03
2.00
9.00
f1 (ppm)


169.50
148.45
142.42
130.07
129.87
126.75
124.80
123.84
118.61
77.48
77.16
76.84
38.39
30.13
Cl
N
29
f1 (ppm)


8.19
8.18
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8.16
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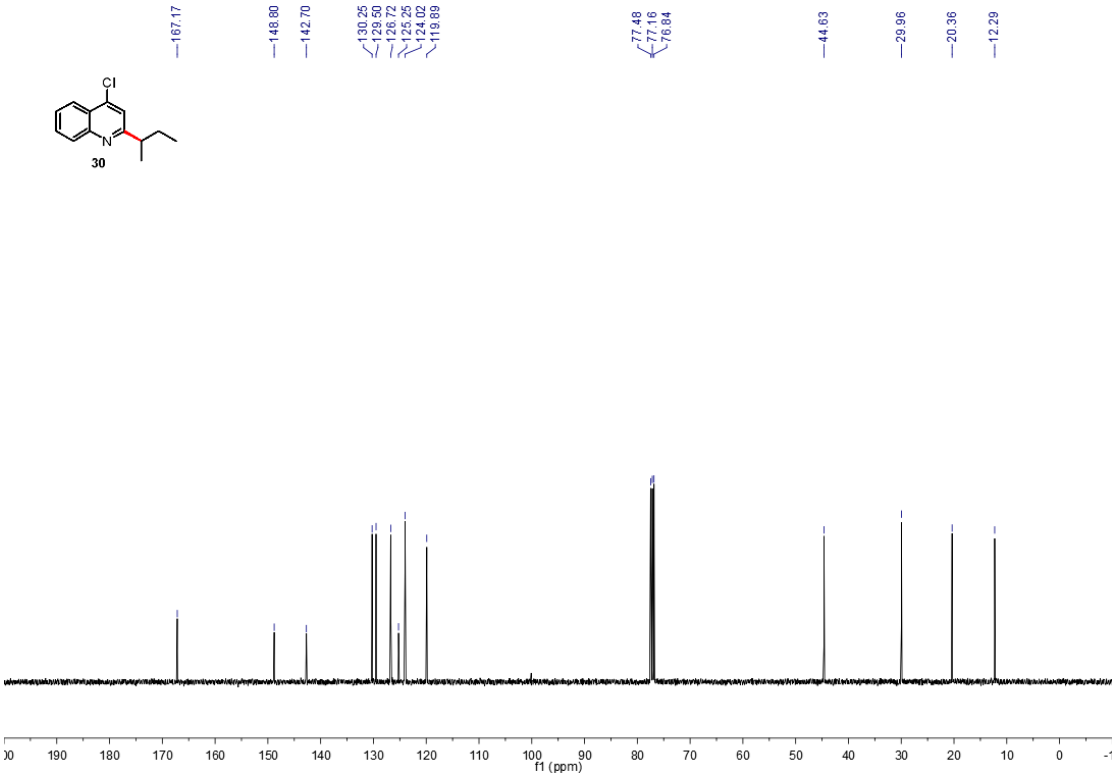
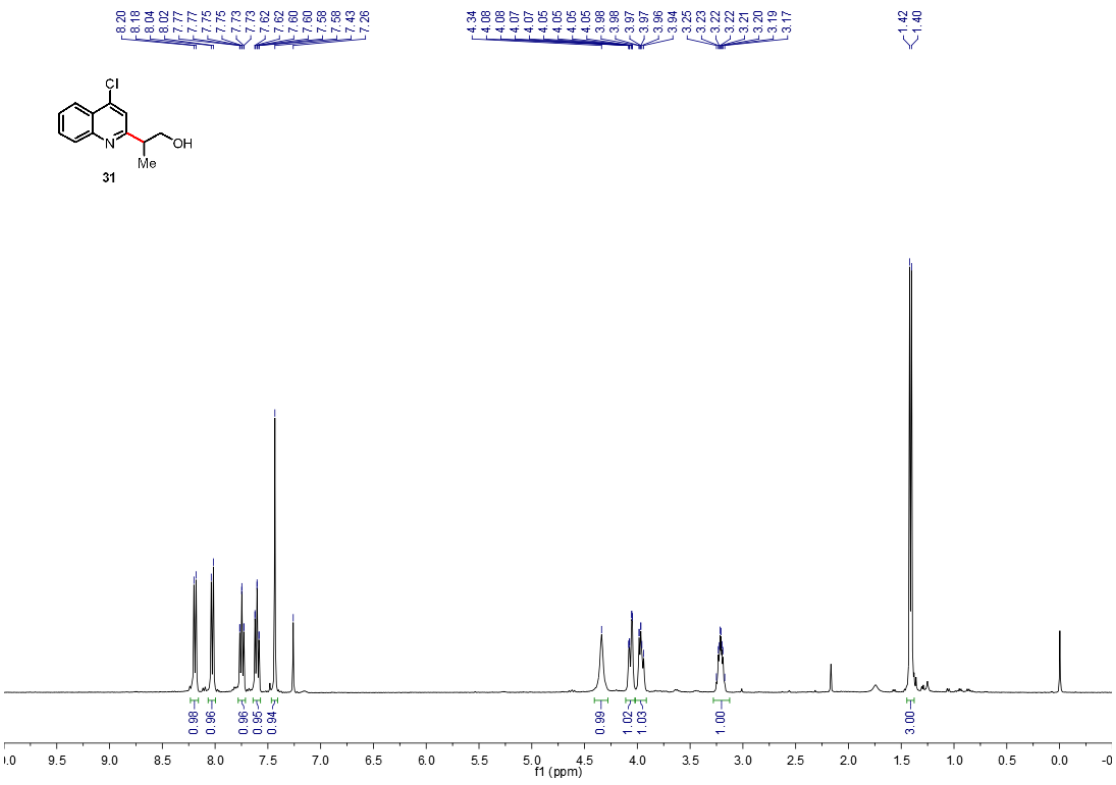
8.05
7.74
7.73
7.72
7.72
7.72
7.71
7.70
7.69
7.68
7.57
7.57
7.57
7.56
7.55
7.39
7.26
3.02
3.00
2.98
2.97
2.95
2.93
1.86
1.85
1.83
1.81
1.72
1.71
1.69
1.37
1.35
0.91
0.90
0.88
Cl
N
30
0.93
0.95
0.98
0.98
0.97
1.00
1.05
1.06
3.09
3.11
f1 (ppm)


167.17
148.80
142.70
130.25
129.50
128.72
125.25
124.02
119.89
77.48
77.16
76.84
44.63
29.96
20.36
12.29
Cl
N
30
f1 (ppm)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8.02
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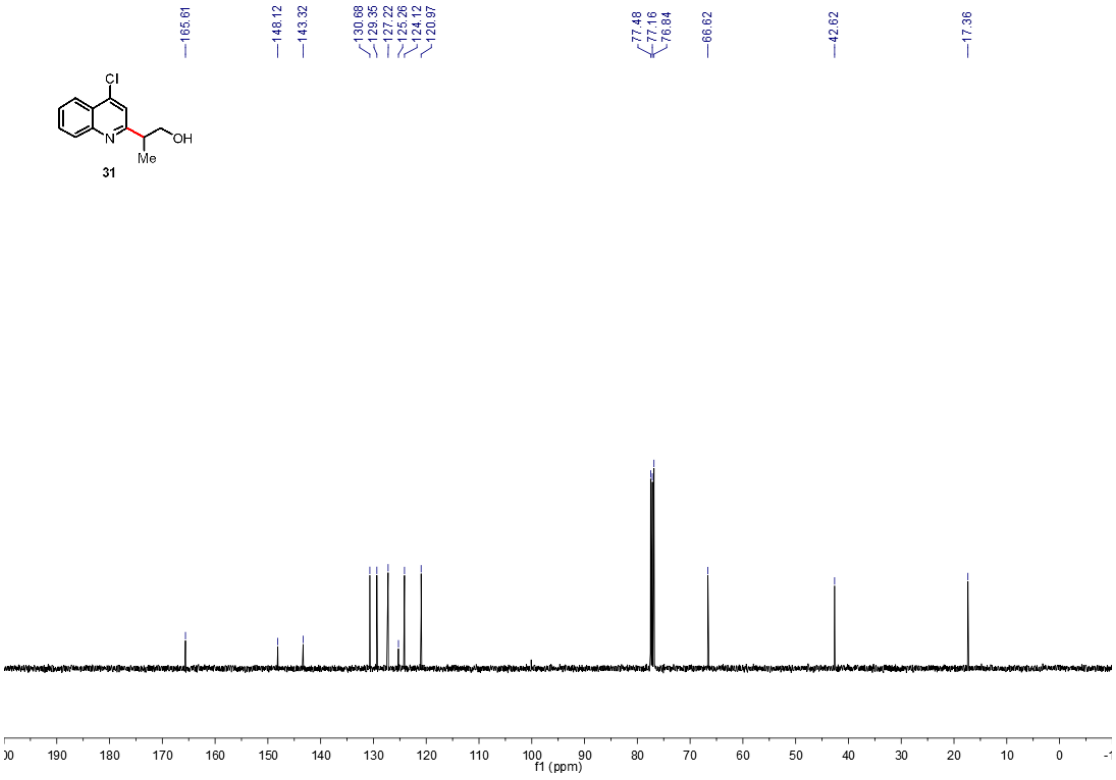
7.75
7.73
7.62
7.60
7.58
7.43
7.26
4.34
4.08
4.07
4.05
3.98
3.97
3.96
3.94
3.25
3.23
3.22
3.21
3.20
3.19
3.17
1.42
1.40
Cl
N
OH
Me
31
0.98
0.96
0.96
0.95
0.94
0.99
1.02
1.03
1.00
3.00
f1 (ppm)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148.12
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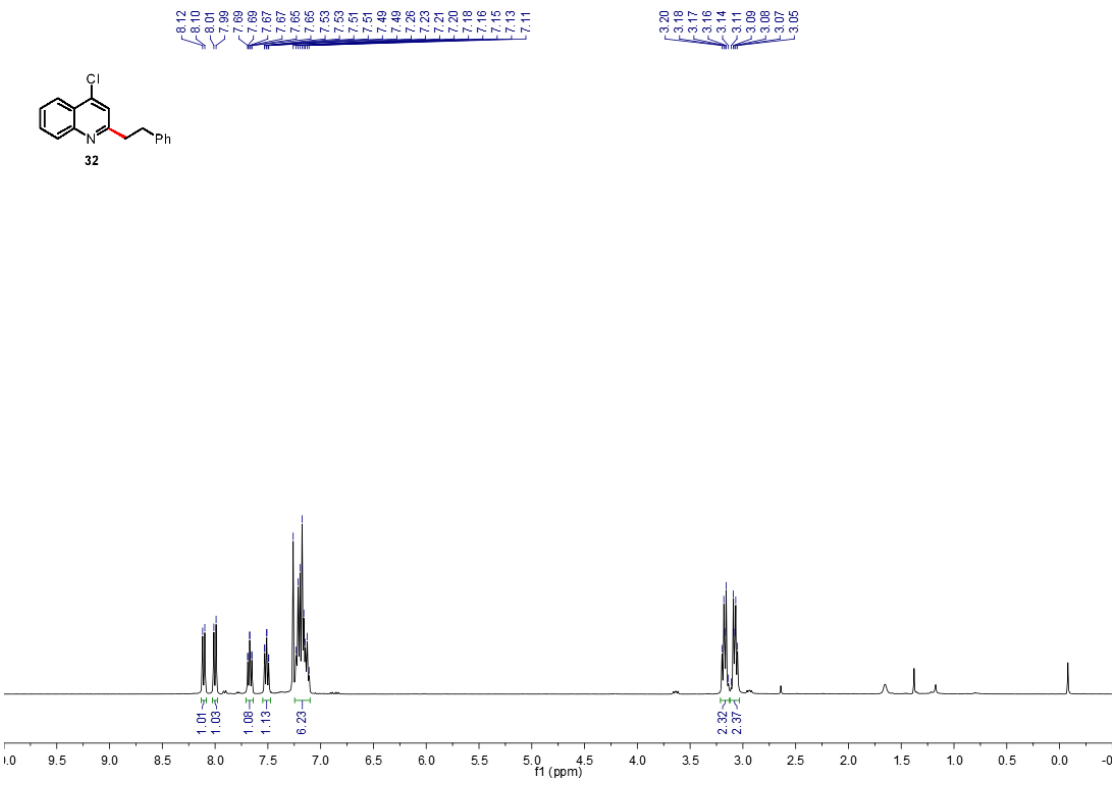
129.35
127.22
125.26
124.12
120.97
77.48
77.16
76.84
66.62
42.62
17.36
Cl
N
OH
Me
31
f1 (ppm)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7.69
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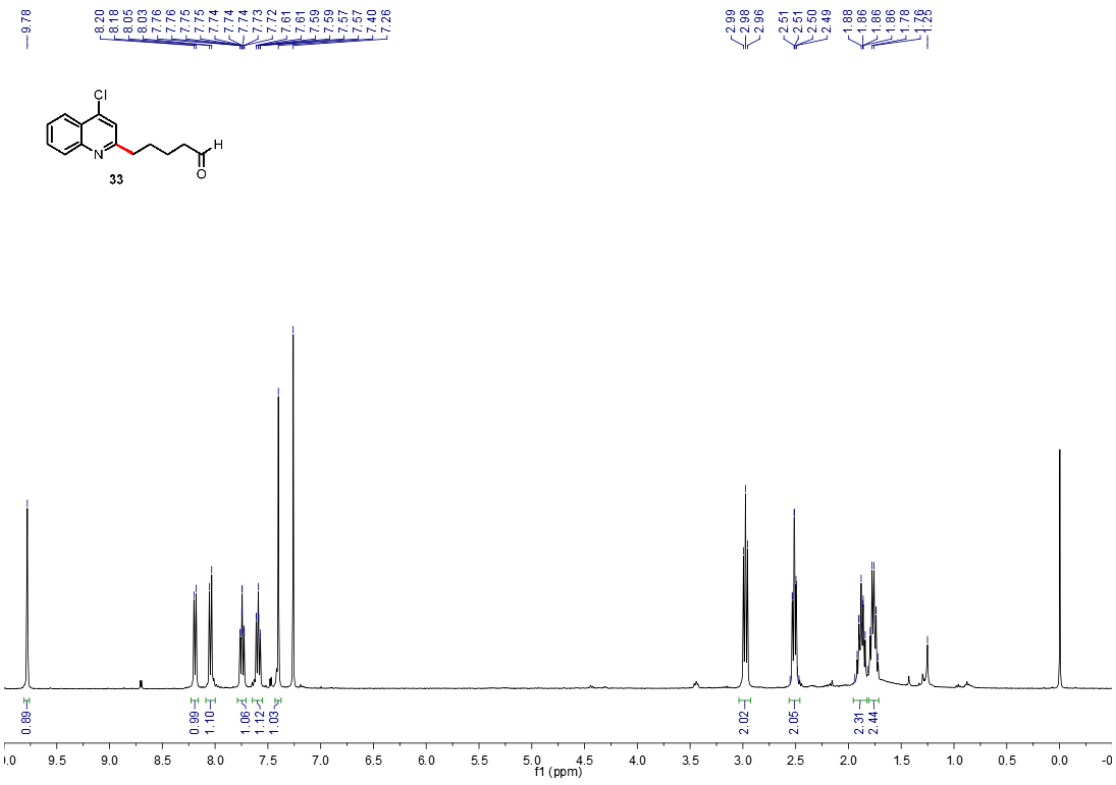
7.67
7.65
7.65
7.53
7.53
7.51
7.51
7.49
7.49
7.26
7.23
7.21
7.20
7.18
7.16
7.15
7.13
7.11
3.20
3.18
3.17
3.16
3.14
3.11
3.09
3.08
3.07
3.05
Cl
N
Ph
32
1.01
1.03
1.08
1.13
6.23
2.32
2.37
f1 (ppm)
161.85
148.93
142.67
141.29
130.48
129.35
128.61
126.93
126.27
125.14
124.10
121.68
77.48
77.16
76.84
40.87
35.76
Cl
N
Ph
32
f1 (ppm)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8.20
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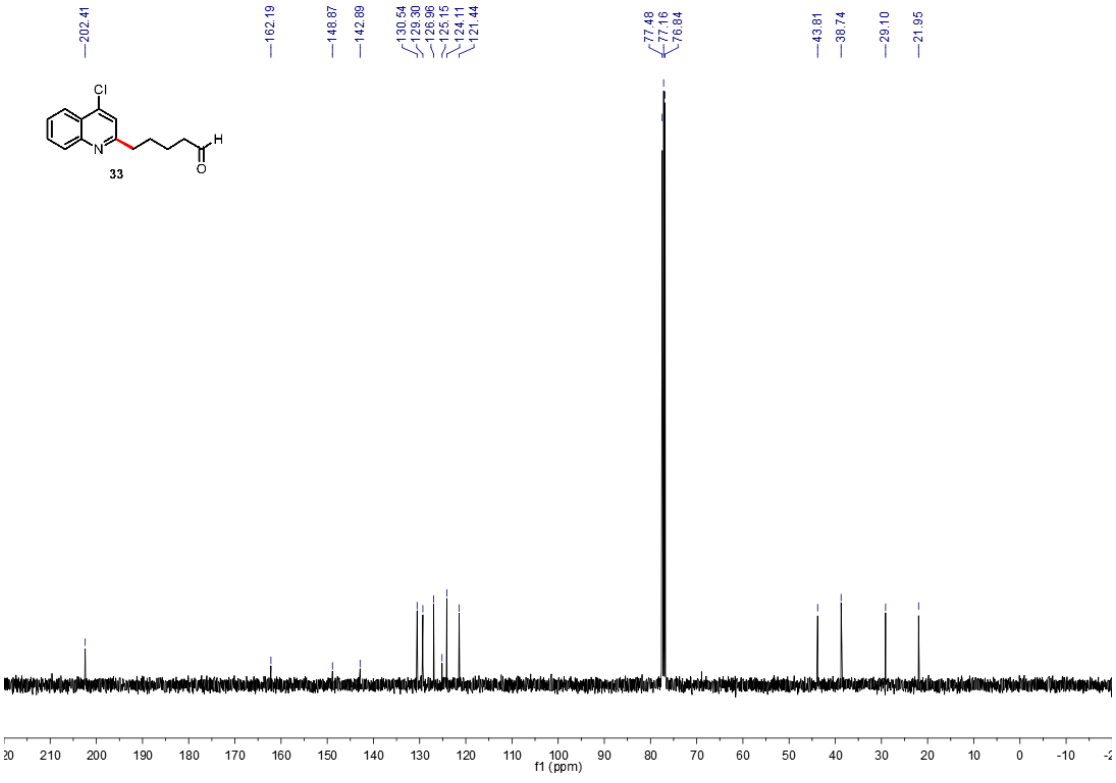
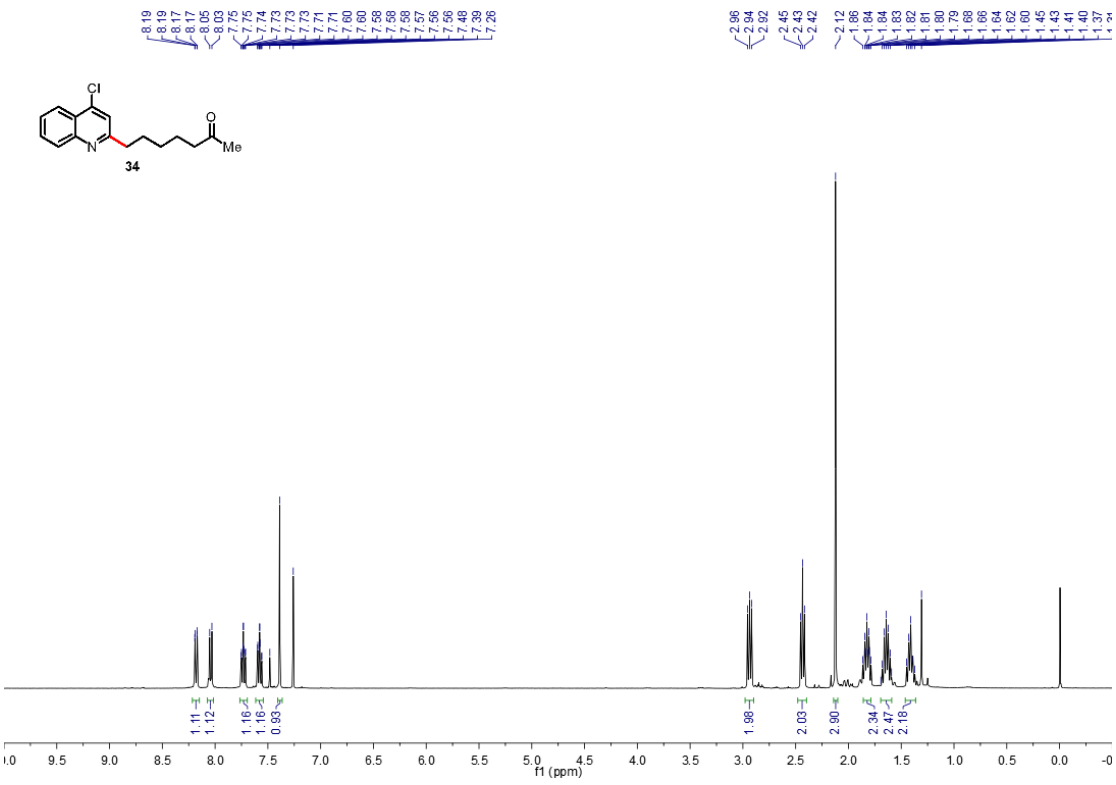
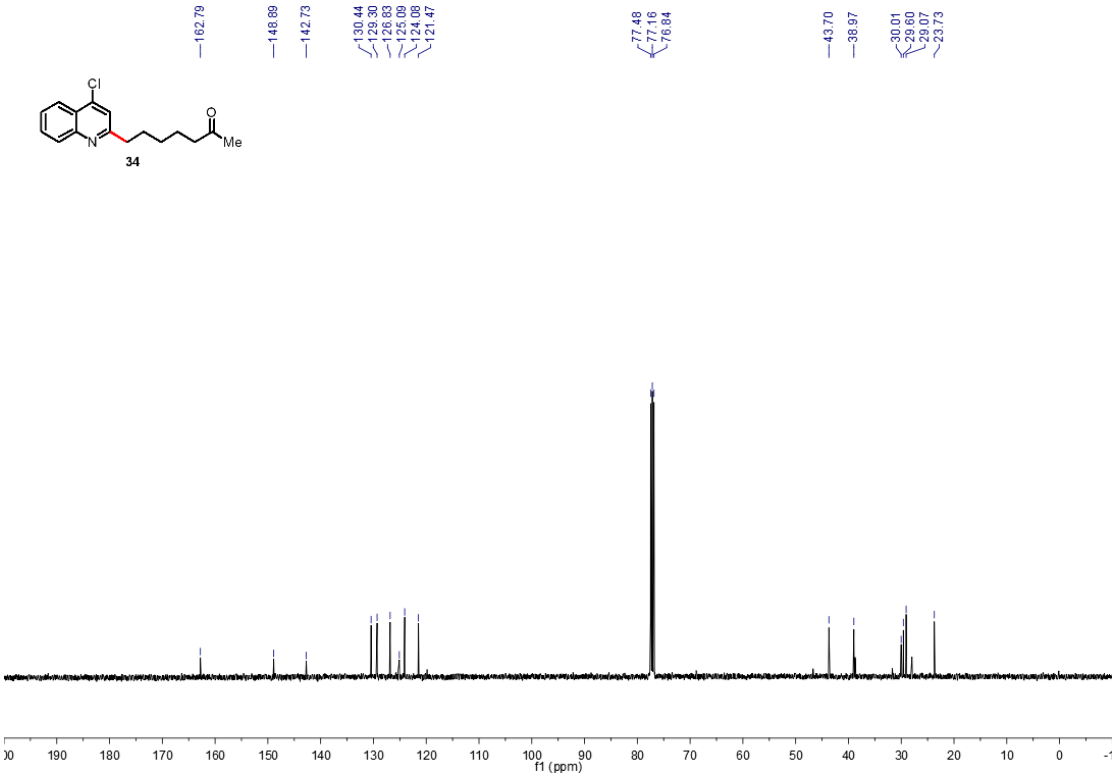
8.05
8.03
7.76
7.76
7.75
7.75
7.74
7.74
7.73
7.72
7.61
7.61
7.59
7.59
7.57
7.57
7.40
7.26
2.99
2.98
2.96
2.51
2.51
2.50
2.49
1.88
1.86
1.86
1.86
1.78
1.25
Cl
N
H
O
33
0.89
0.99
1.10
1.06
1.12
1.03
2.02
2.05
2.31
2.44
f1 (ppm)


202.41
162.19
148.87
142.89
130.54
129.30
126.96
125.15
124.11
121.44
77.48
77.16
76.84
43.81
38.74
29.10
21.95
Cl
N
H
O
33
f1 (ppm)

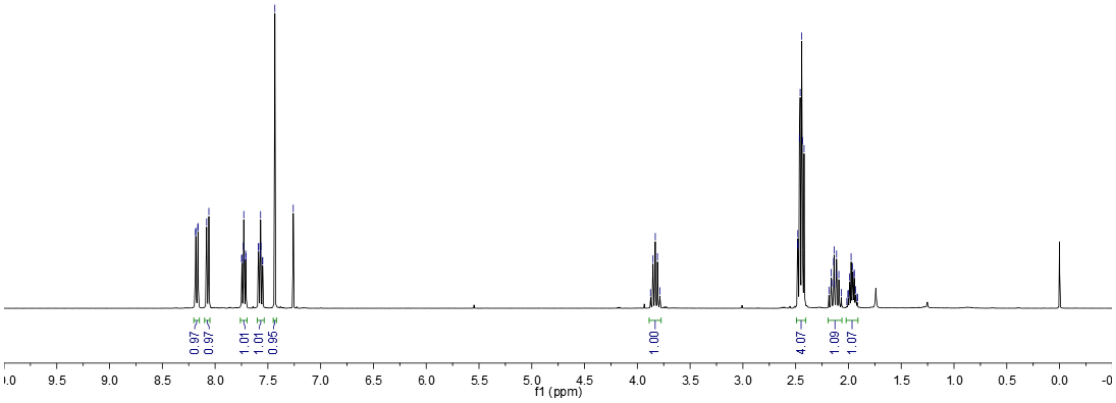

8.19
8.19
8.17
8.17
8.05
8.03
7.75
7.75
7.74
7.73
7.73
7.73
7.71
7.71
7.60
7.60
7.58
7.58
7.58
7.57
7.56
7.56
7.48
7.39
7.26
2.96
2.94
2.92
2.45
2.43
2.42
2.12
1.86
1.84
1.84
1.83
1.82
1.81
1.80
1.79
1.68
1.66
1.64
1.62
1.60
1.45
1.43
1.41
1.40
1.37
Cl
N
O
Me
34
1.11
1.12
1.16
1.16
0.93
1.98
2.03
2.90
2.34
2.47
2.18
f1 (ppm)


162.79
148.89
142.73
130.44
129.30
126.83
125.09
124.08
121.47
77.48
77.16
76.84
43.70
38.97
30.01
29.60
29.07
23.73
Cl
N
O
Me
34
f1 (ppm)


8.19
8.18
8.16
8.16
8.08
8.06
7.75
7.75
7.73
7.73
7.72
7.71
7.71
7.59
7.59
7.57
7.57
7.57
7.55
7.43
7.26
3.88
3.85
3.83
3.81
3.79
2.48
2.48
2.46
2.46
2.44
2.44
2.42
2.18
2.16
2.16
2.14
2.14
2.13
2.12
2.11
2.09
2.07
2.02
2.00
2.00
1.99
1.97
1.96
1.95
1.94
1.93
1.92
1.91

Cl
N

35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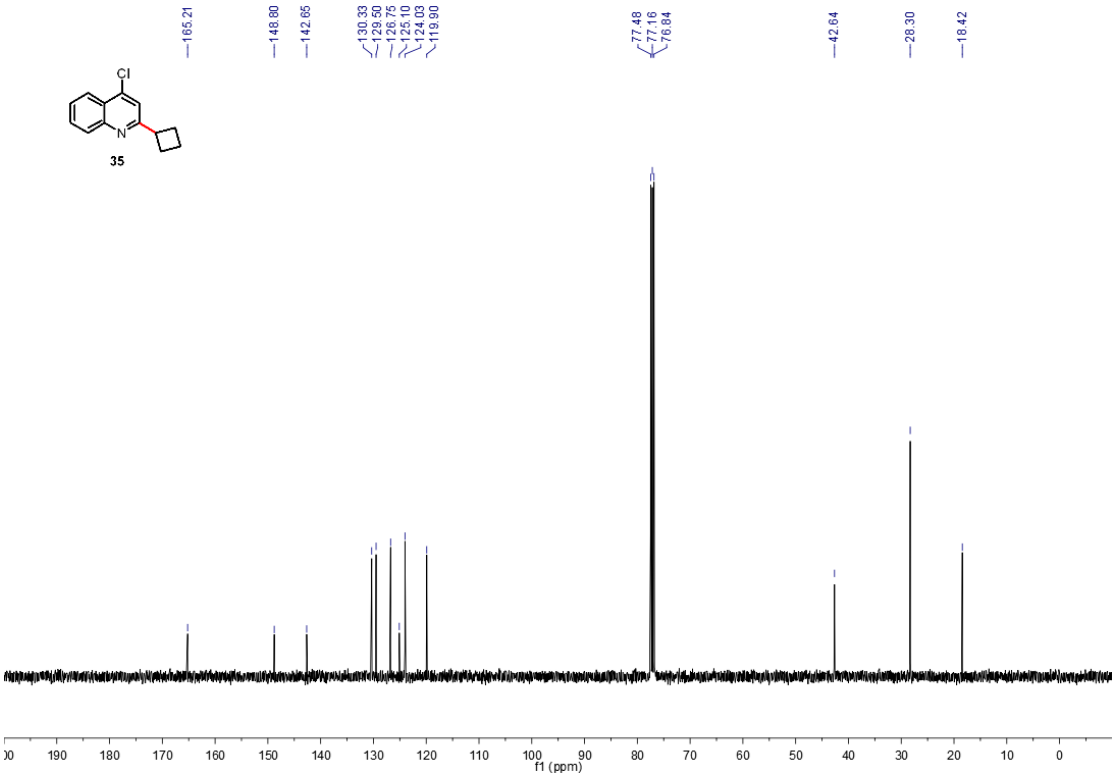
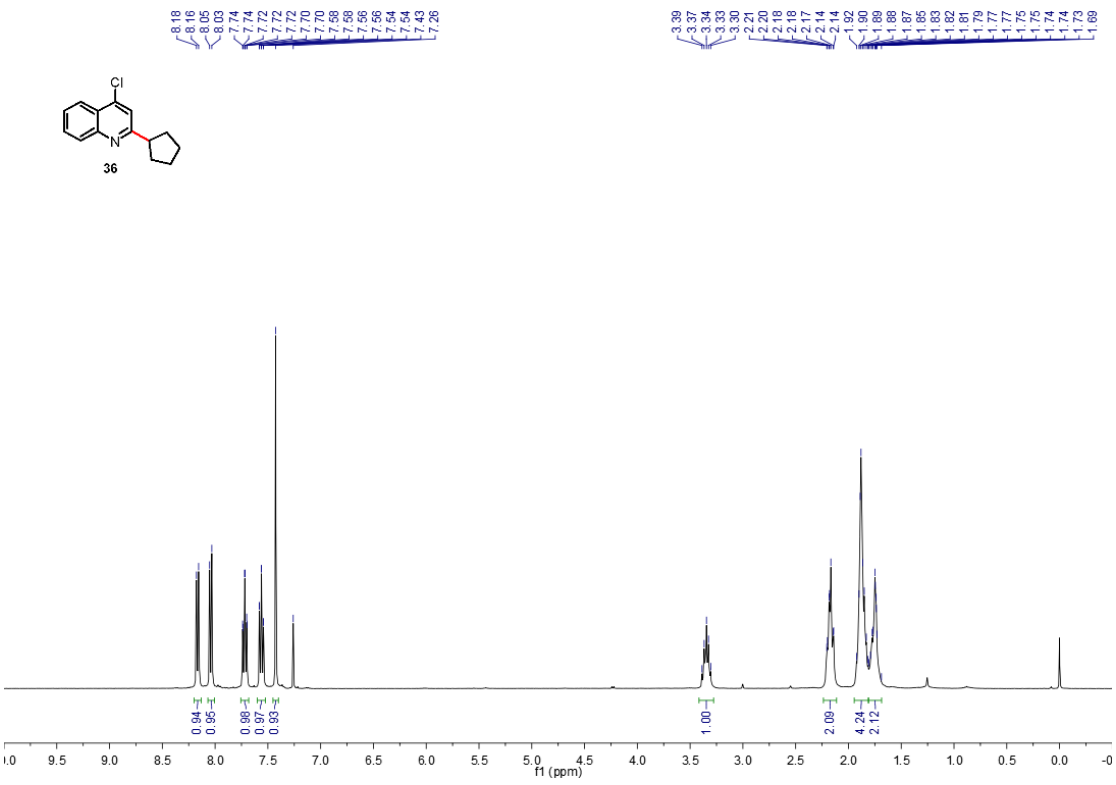
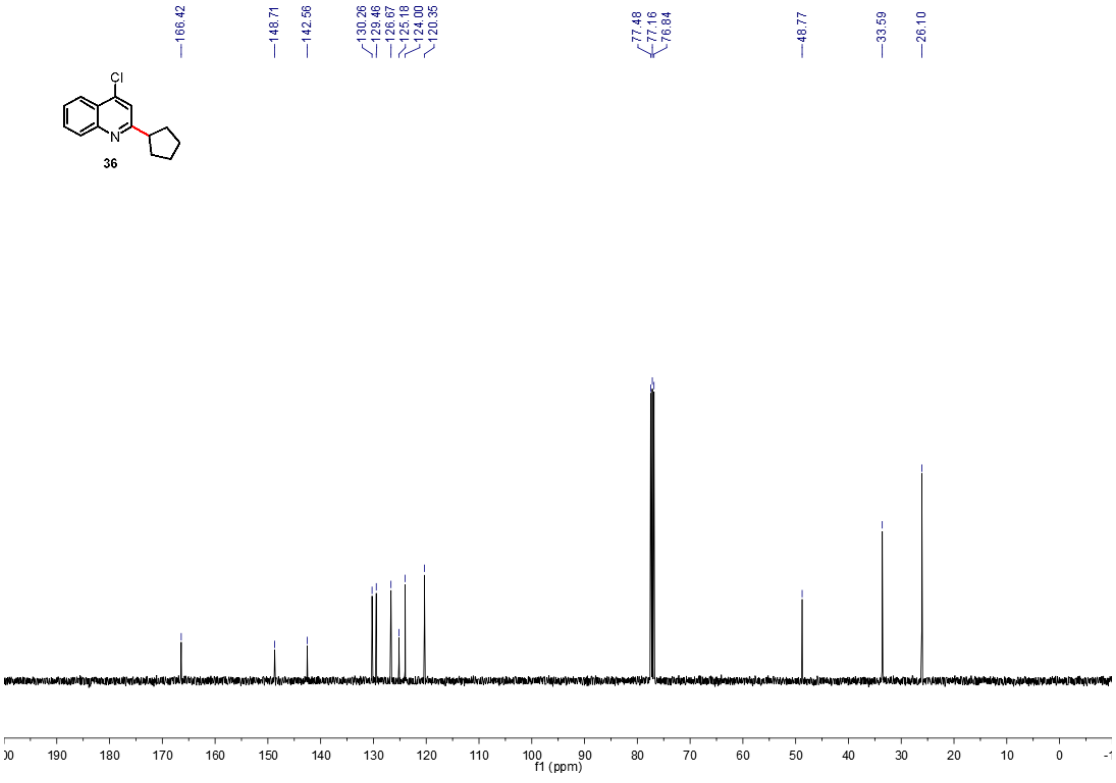
0.97
1.01
1.01
0.95
1.00
4.07
1.09
1.07
f1 (ppm)


165.21
148.80
142.65
130.33
129.50
128.75
125.10
124.03
119.90
77.48
77.16
76.84
42.64
28.30
18.42
Cl
N
f1 (ppm)

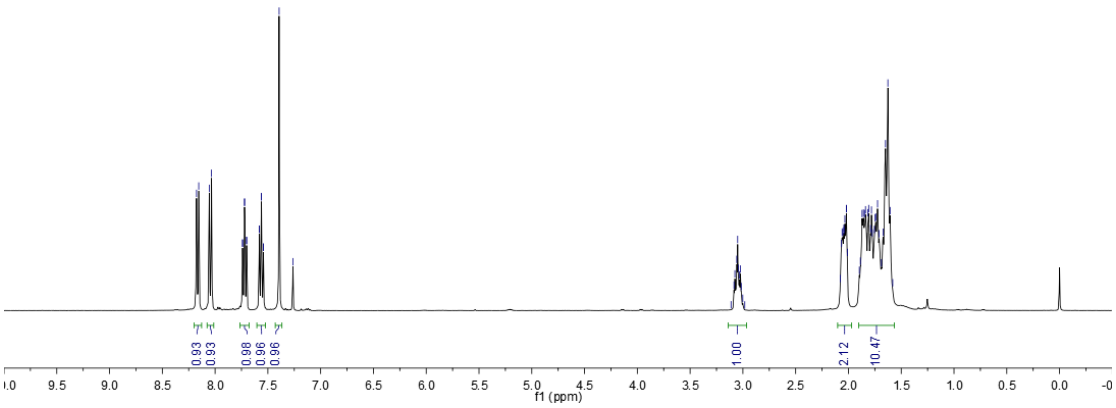
35


8.18
8.16
8.05
8.03
7.74
7.74
7.72
7.72
7.72
7.70
7.70
7.68
7.68
7.66
7.66
7.54
7.54
7.43
7.26
3.39
3.37
3.34
3.33
3.30
2.21
2.20
2.18
2.18
2.17
2.14
2.14
1.92
1.90
1.89
1.88
1.87
1.85
1.83
1.82
1.81
1.79
1.77
1.77
1.75
1.75
1.74
1.74
1.73
1.69
Cl
N
36
0.94
0.95
0.98
0.97
0.93
1.00
2.09
4.24
2.12
f1 (ppm)

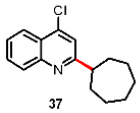

166.42
148.71
142.56
130.26
129.46
126.67
125.18
124.00
120.35
77.48
77.16
76.84
48.77
33.59
26.10
Cl
N
36
f1 (ppm)

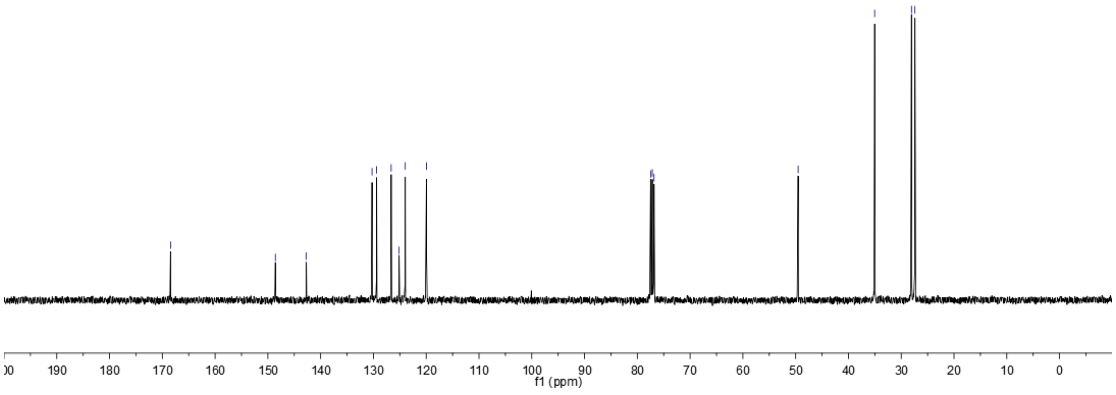

8.18
8.16
8.06
8.03
7.74
7.72
7.72
7.70
7.70
7.68
7.68
7.66
7.66
7.54
7.54
7.39
7.26
3.11
3.08
3.08
3.06
3.06
3.05
3.04
3.03
3.02
3.02
3.00
2.98
2.05
2.04
2.04
2.03
2.02
2.02
1.87
1.86
1.85
1.84
1.82
1.81
1.79
1.78
1.75
1.75
1.74
1.72
1.67
1.65
1.63

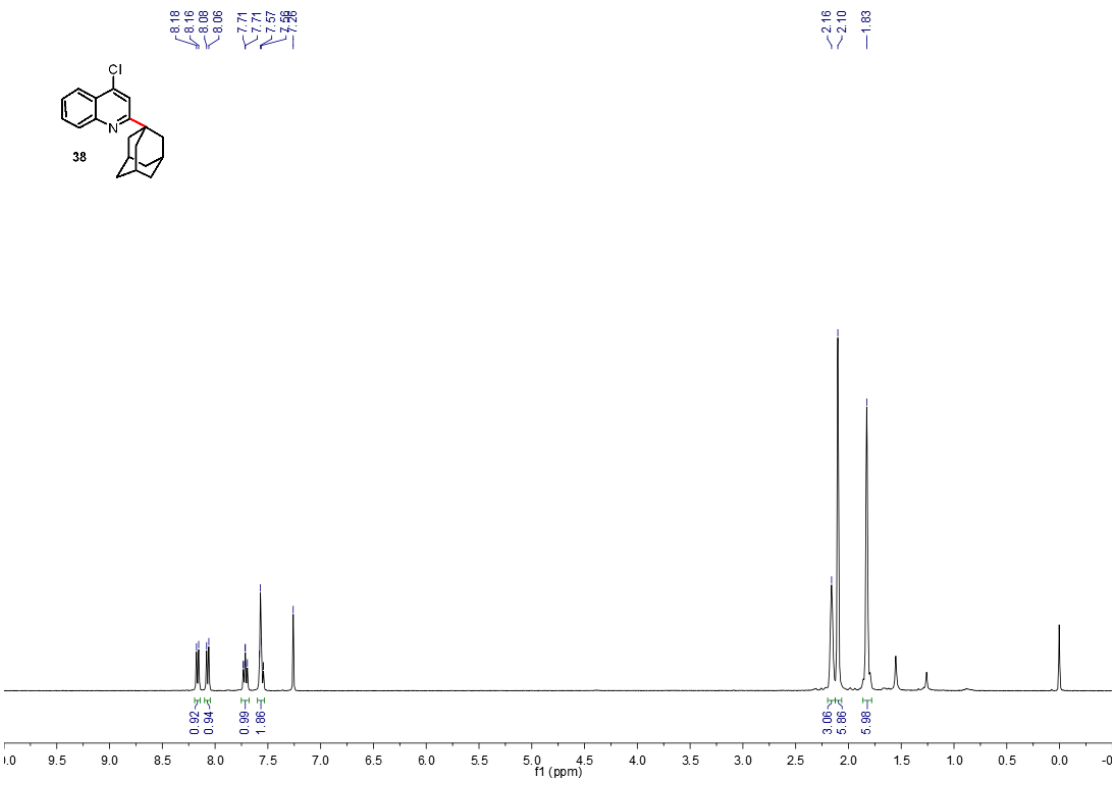
Cl
N
37

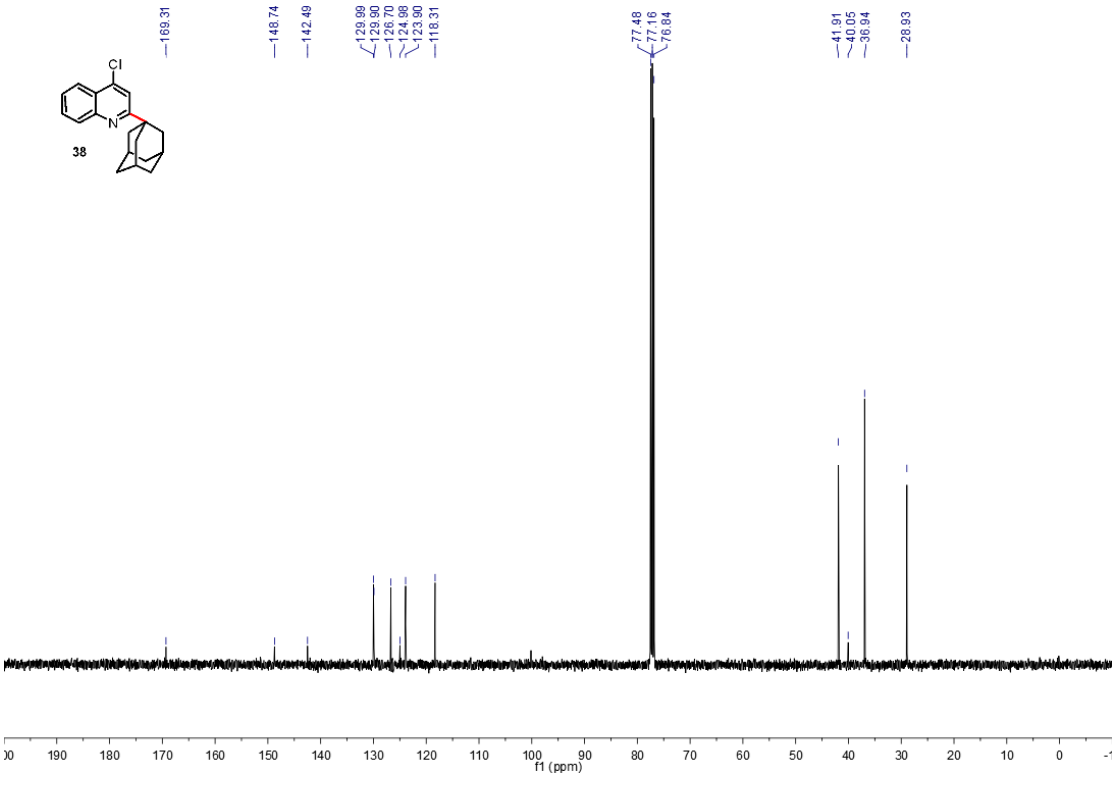

0.93
0.93
0.98
0.96
0.96
1.00
2.12
10.47
f1 (ppm)


168.45
148.58
142.71
130.26
129.40
126.64
125.14
123.97
119.96
77.48
77.16
76.84
49.53
35.03
28.05
27.41


Cl
N
37


f1 (ppm)


8.18
8.16
8.08
8.06
7.71
7.71
7.57
2.16
2.10
1.83
Cl
N
38
0.92
0.94
0.99
1.86
3.06
5.86
5.98
f1 (ppm)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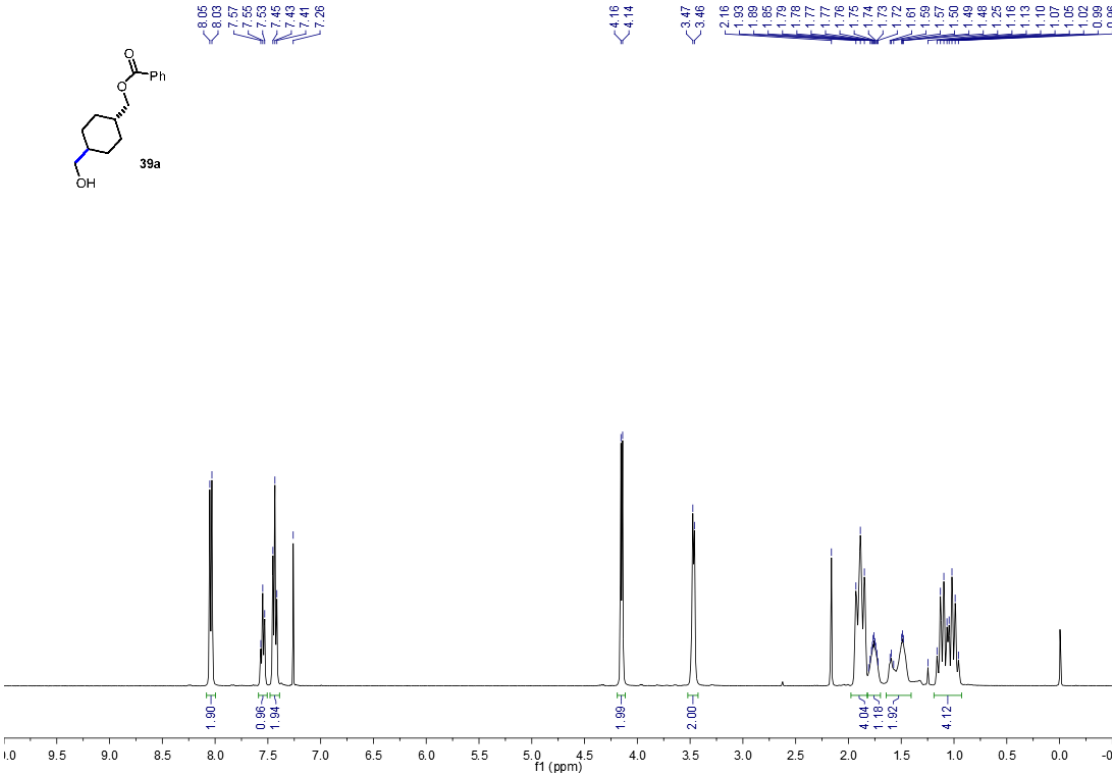
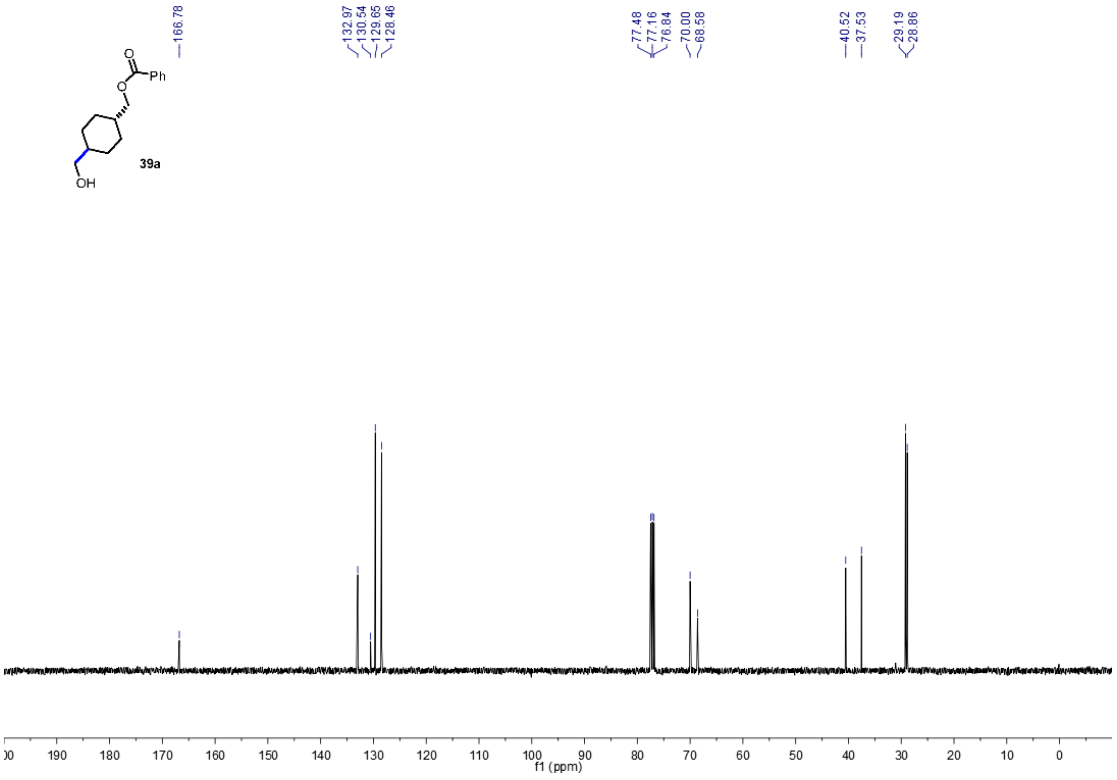
148.74
142.49
129.99
129.90
126.70
124.98
123.90
118.31
77.48
77.16
76.84
41.91
40.05
36.94
28.93
Cl
N
38
f1 (ppm)


8.05
8.03
7.57
7.55
7.53
7.45
7.43
7.41
7.26
4.16
4.14
3.47
3.46
2.16
1.93
1.89
1.85
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.72
1.61
1.59
1.57
1.50
1.49
1.48
1.25
1.16
1.13
1.10
1.07
1.05
1.02
0.99
O
Ph
O
OH
39a
1.90
0.96
1.94
1.99
2.00
4.04
1.18
1.92
4.12
f1 (ppm)


166.78
132.97
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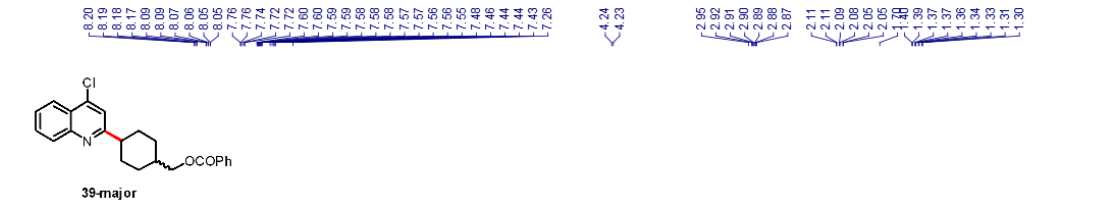
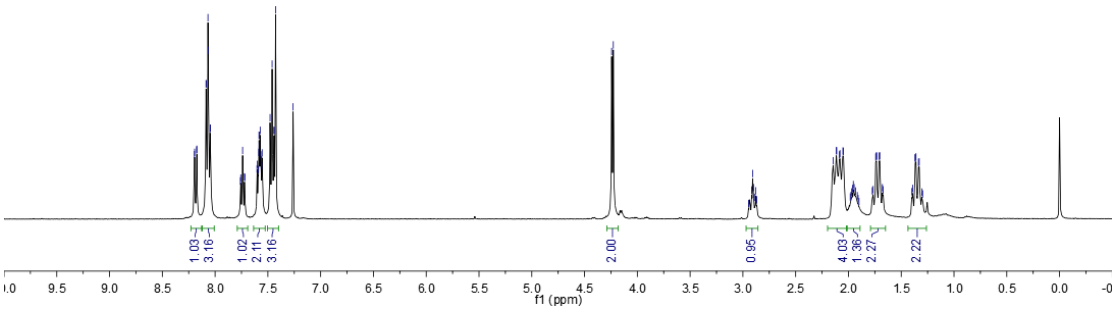
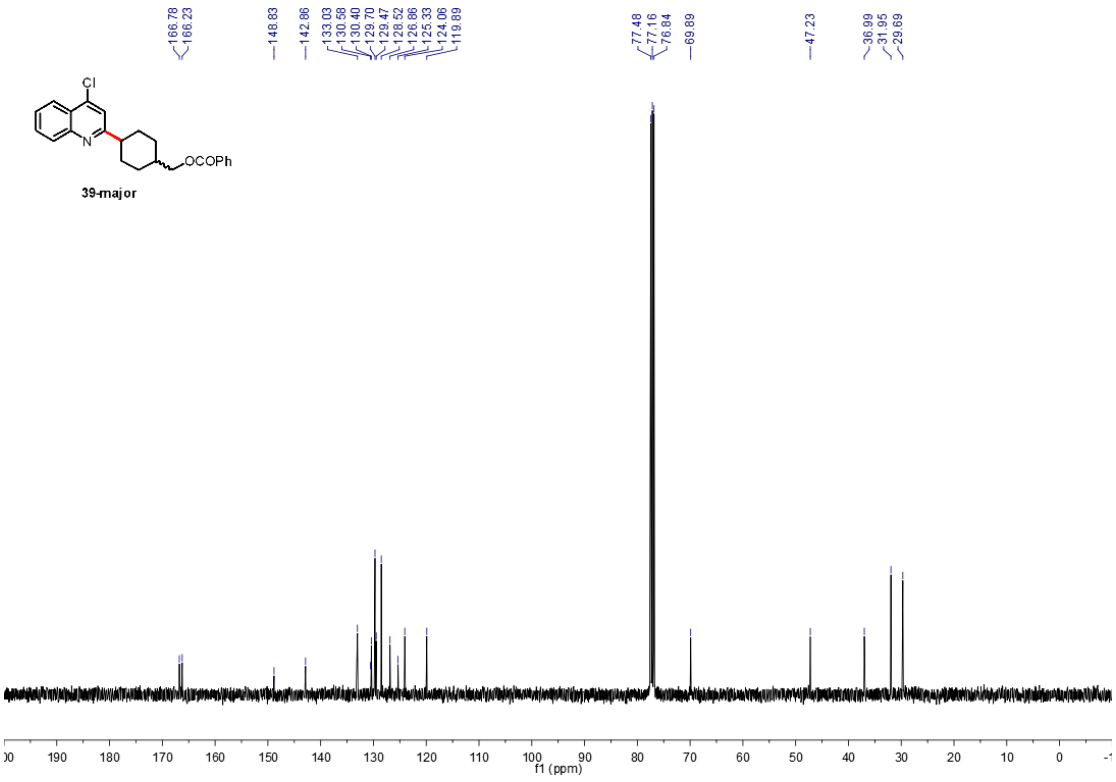
129.65
128.46
77.48
77.16
76.84
70.00
68.58
40.52
37.53
29.19
28.86
O
Ph
O
OH
39a
f1 (ppm)

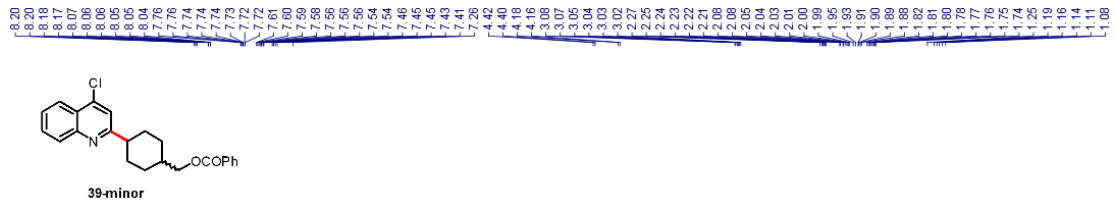


39-major

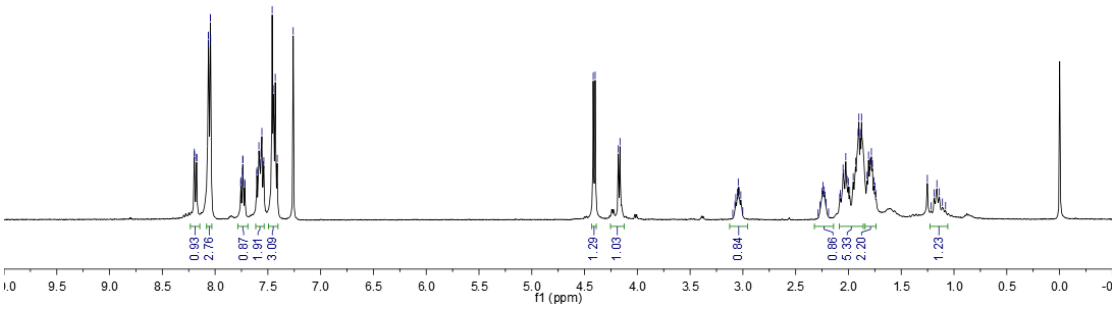


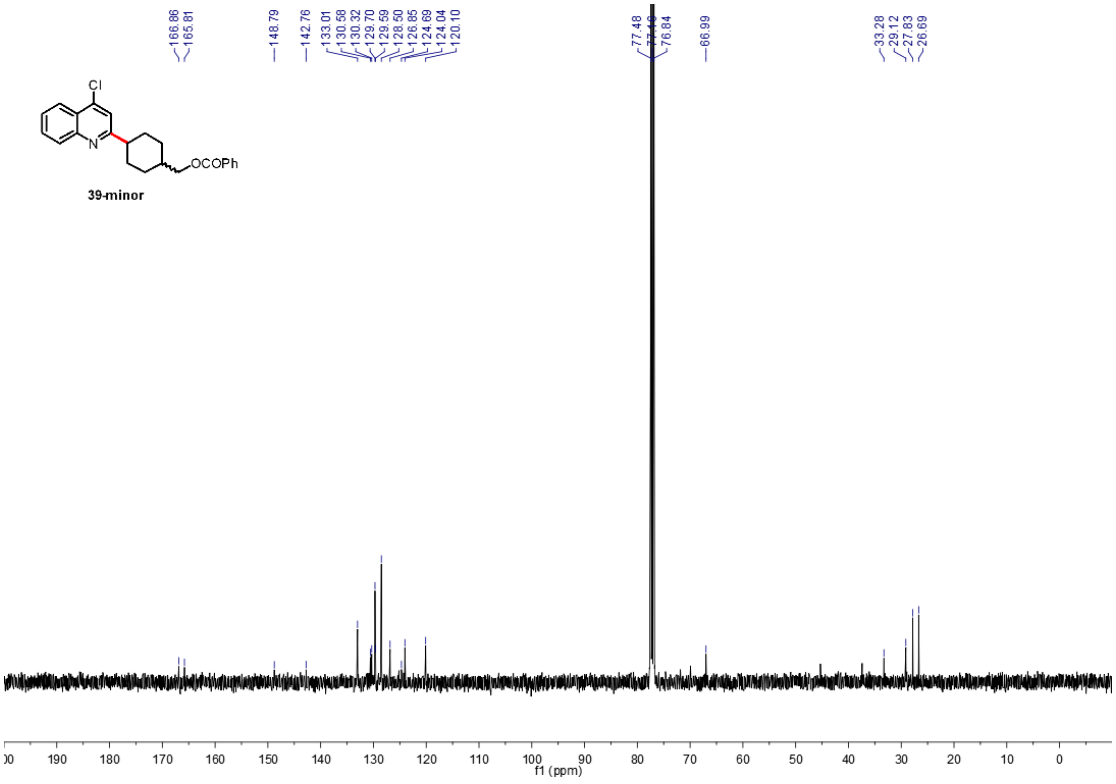


39-major

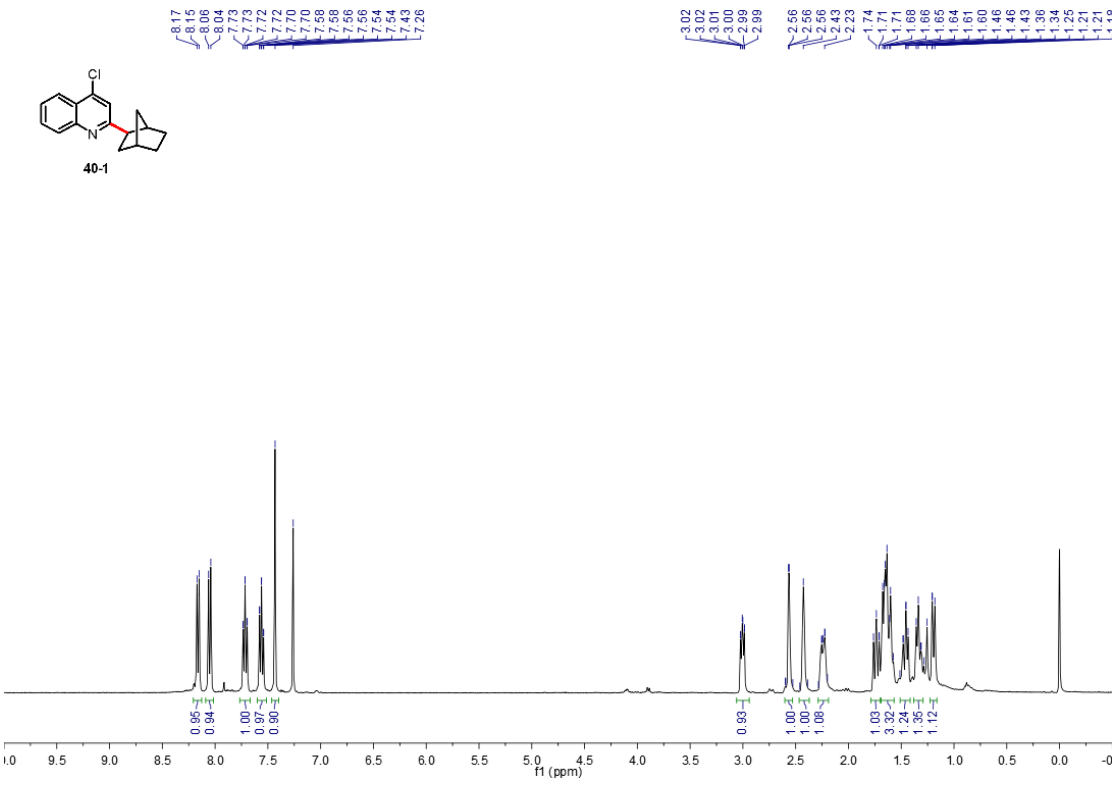


39-minor





39-minor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8.06
8.04
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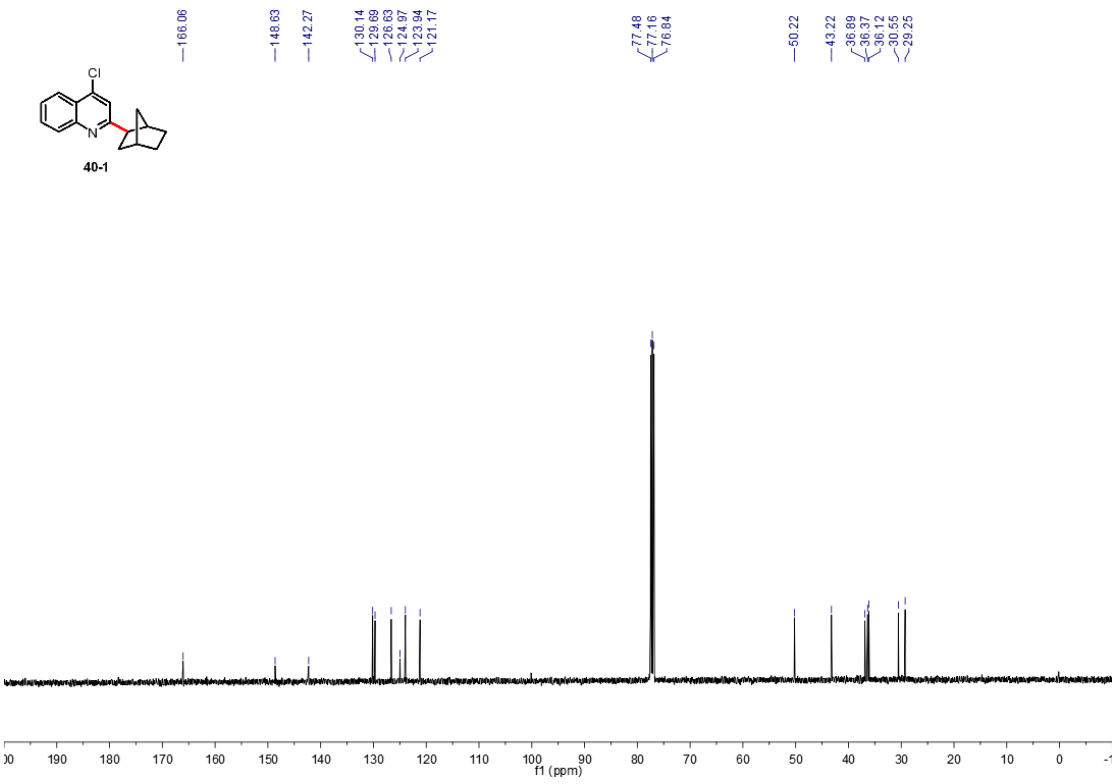
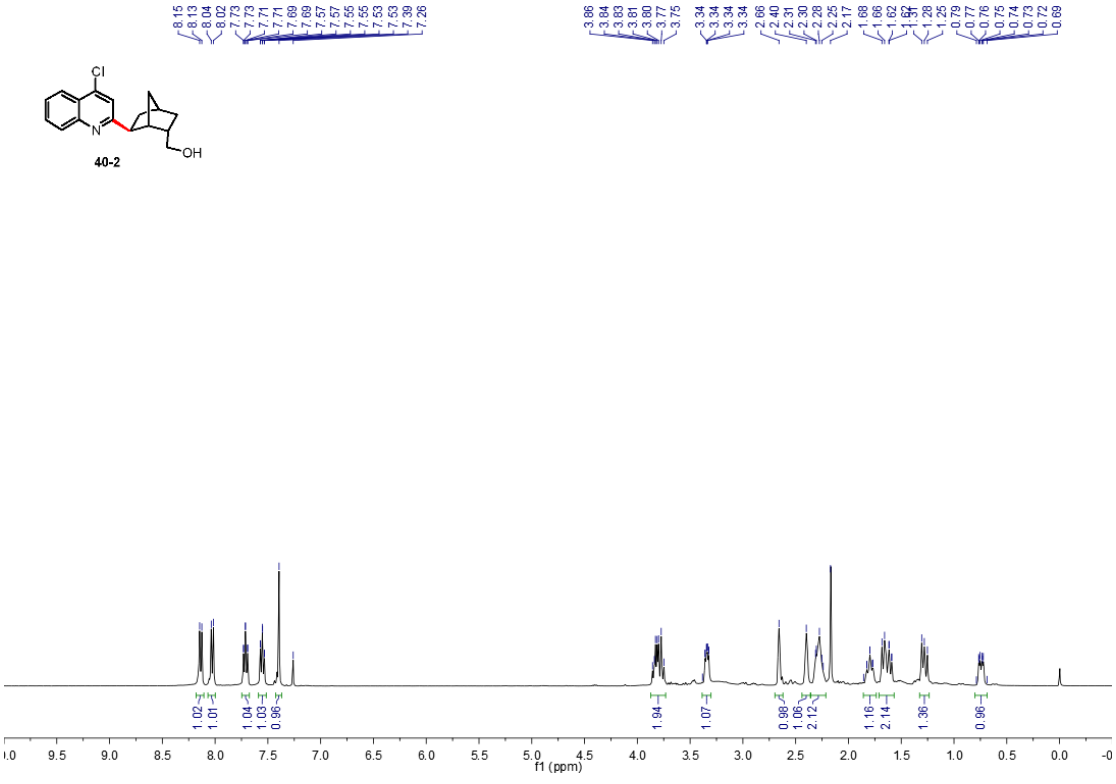
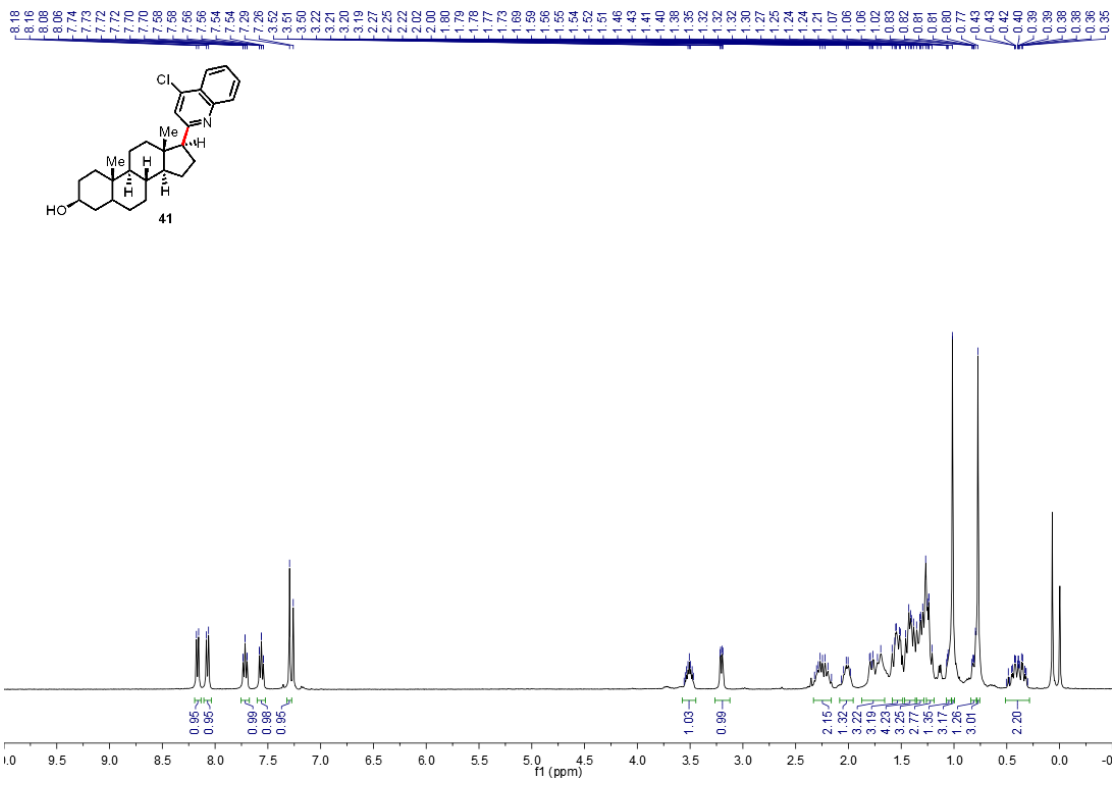
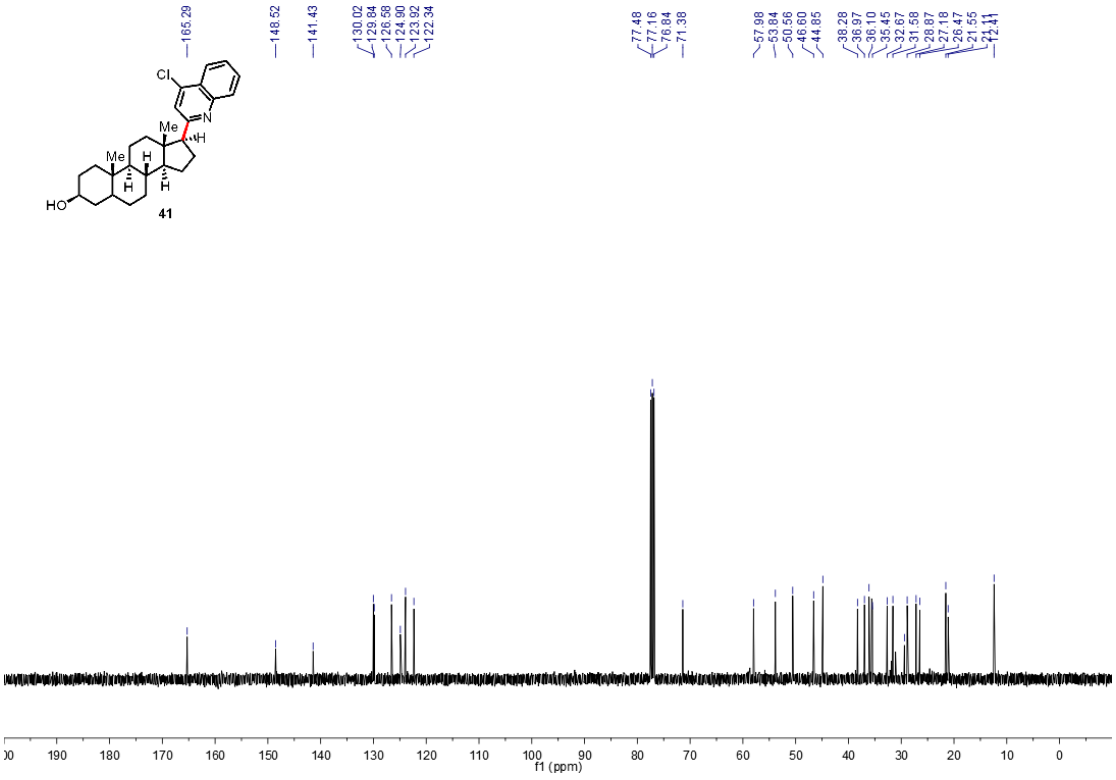
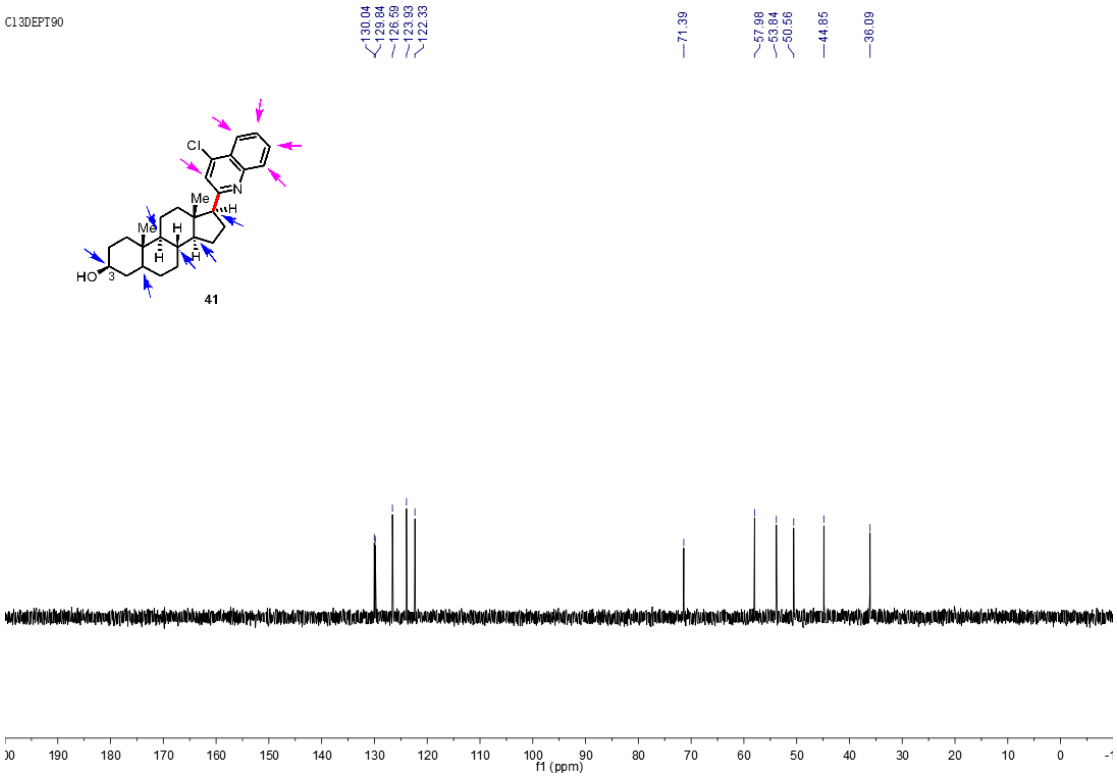
7.72
7.72
7.70
7.70
7.58
7.58
7.56
7.56
7.54
7.54
7.43
7.26
3.02
3.02
3.01
3.00
2.99
2.99
2.56
2.56
2.56
2.43
2.23
1.74
1.71
1.71
1.68
1.66
1.65
1.64
1.61
1.60
1.46
1.46
1.43
1.36
1.34
1.25
1.21
1.21
Cl
N
40-1
0.95
0.94
1.00
0.97
0.90
0.93
1.00
1.00
1.08
1.03
3.32
1.24
1.35
1.12
f1 (ppm)

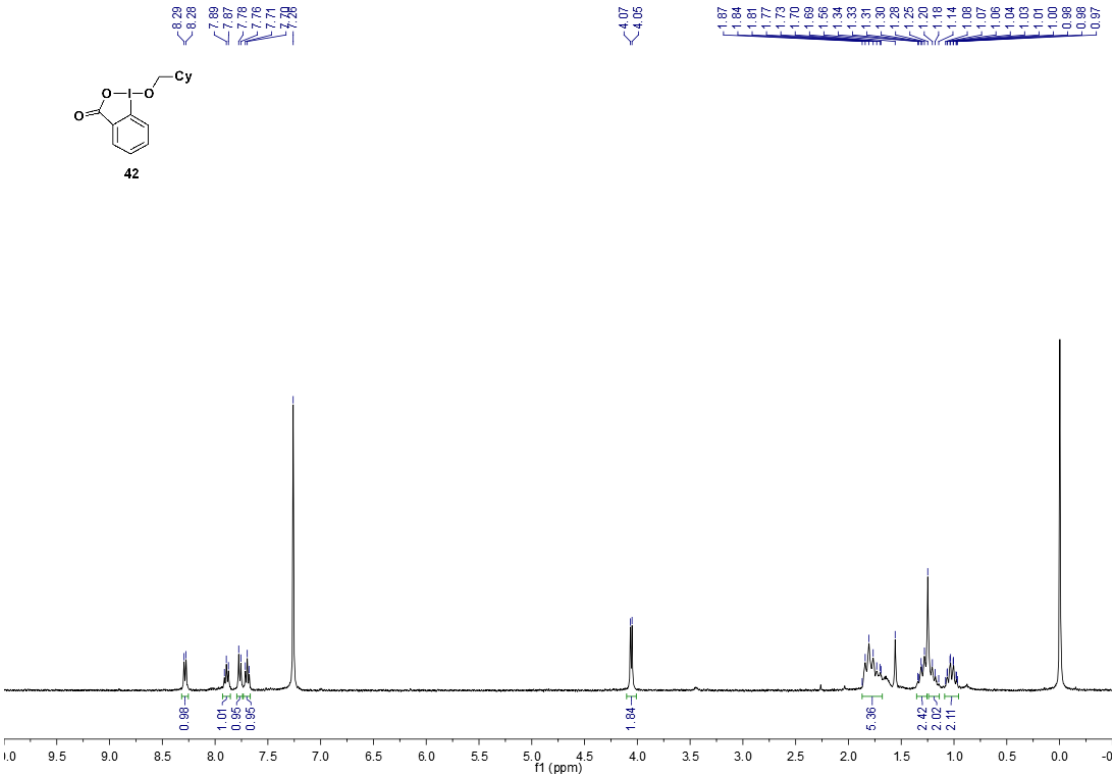

166.06
148.63
142.27
130.14
129.89
126.63
124.97
123.94
121.17
77.48
77.16
76.84
50.22
43.22
36.89
36.37
36.12
30.55
29.25
Cl
N
40-1
f1 (ppm)

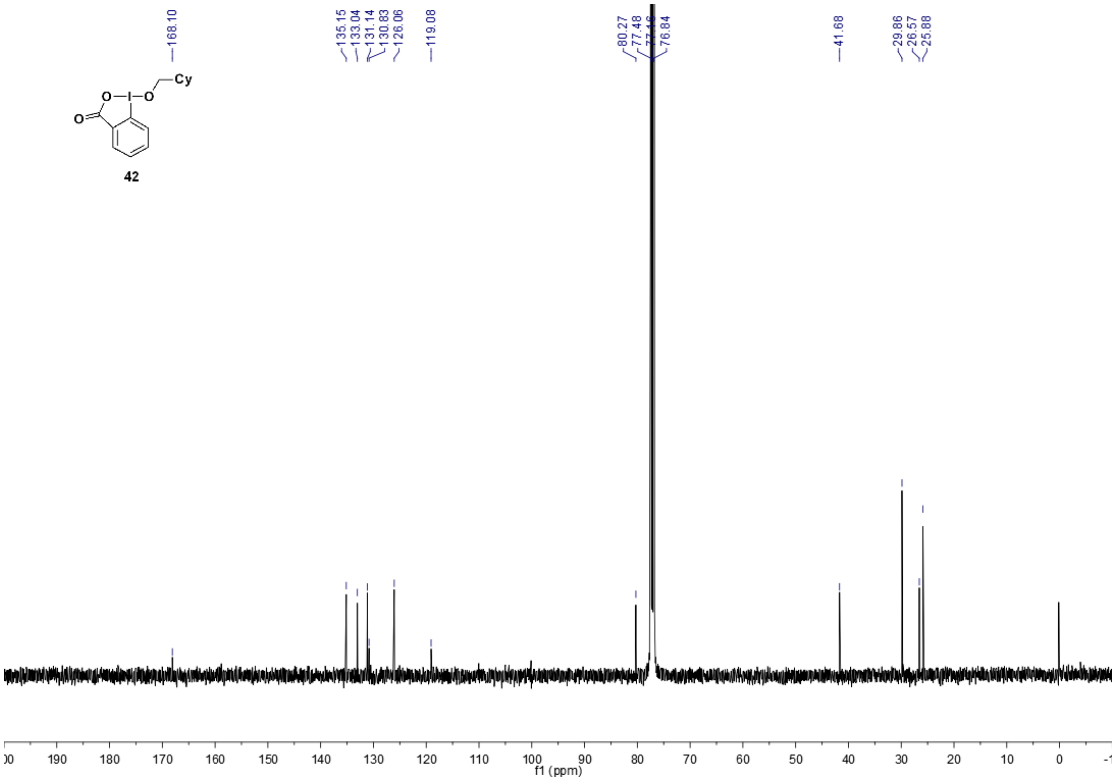

8.15
8.13
8.04
8.02
7.73
7.71
7.71
7.69
7.69
7.57
7.57
7.55
7.55
7.53
7.53
7.39
7.26
3.86
3.84
3.83
3.81
3.80
3.77
3.75
3.34
3.34
3.34
3.34
2.66
2.40
2.31
2.30
2.28
2.25
2.17
1.68
1.66
1.62
1.62
1.31
1.28
1.25
0.79
0.77
0.76
0.75
0.74
0.73
0.72
0.69
Cl
N
OH
40-2
1.02
1.01
1.04
1.03
0.96
1.94
1.07
0.98
1.06
2.12
1.16
2.14
1.36
0.96
f1 (ppm)
165.81
148.28
142.55
130.32
129.22
126.74
124.91
123.99
121.05
77.48
77.16
76.84
63.83
44.74
43.18
42.12
37.17
37.14
35.96
32.90
Cl
N
OH
40-2
f1 (ppm)

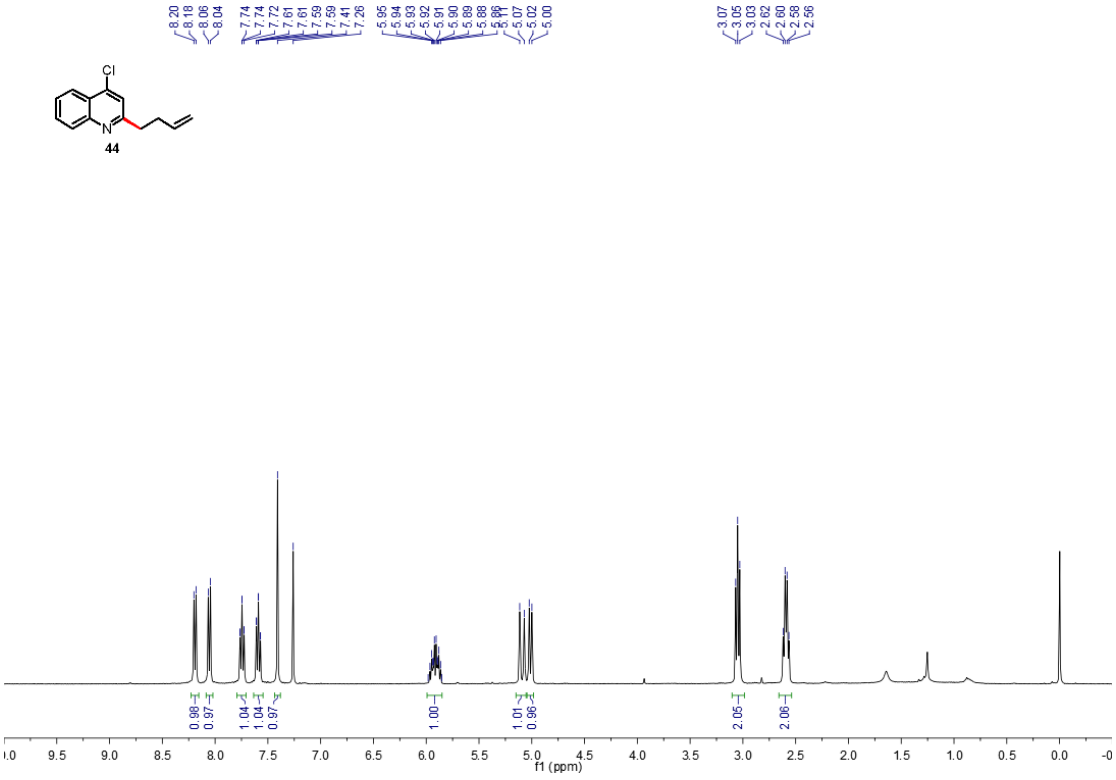

Cl
N
Me
H
Me
H
H
HO
41
f1 (ppm)

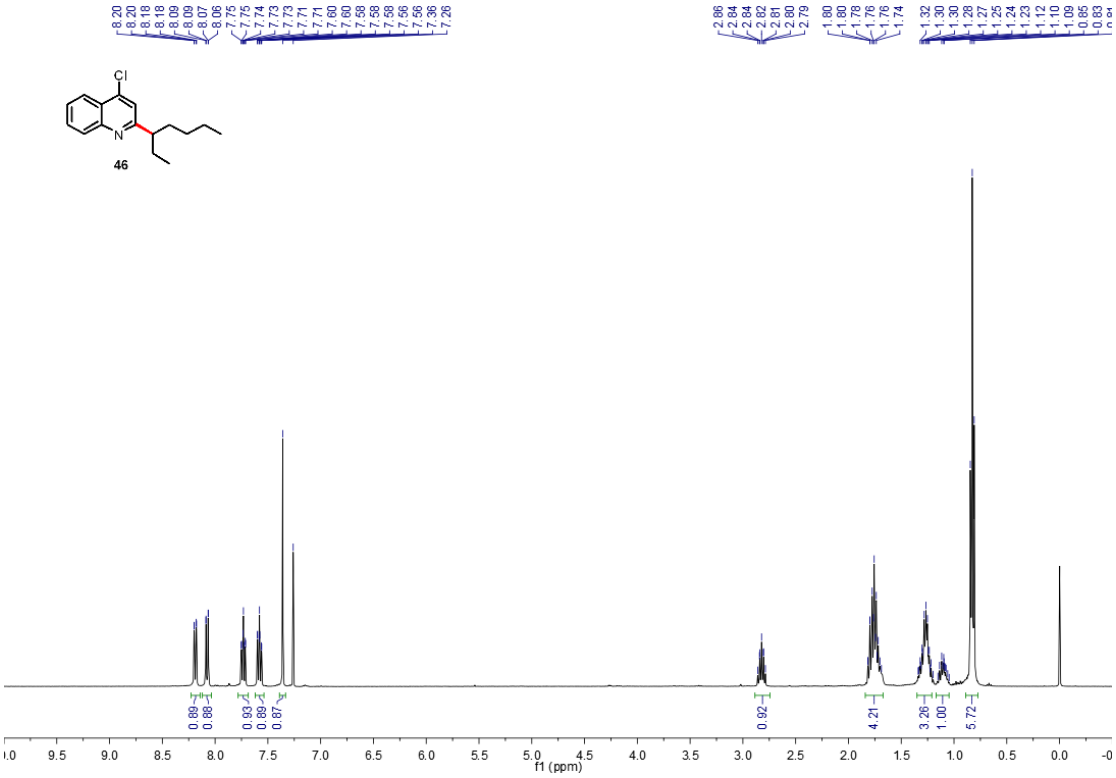

Cl
N
Me
H
Me
H
H
HO
41
f1 (ppm)

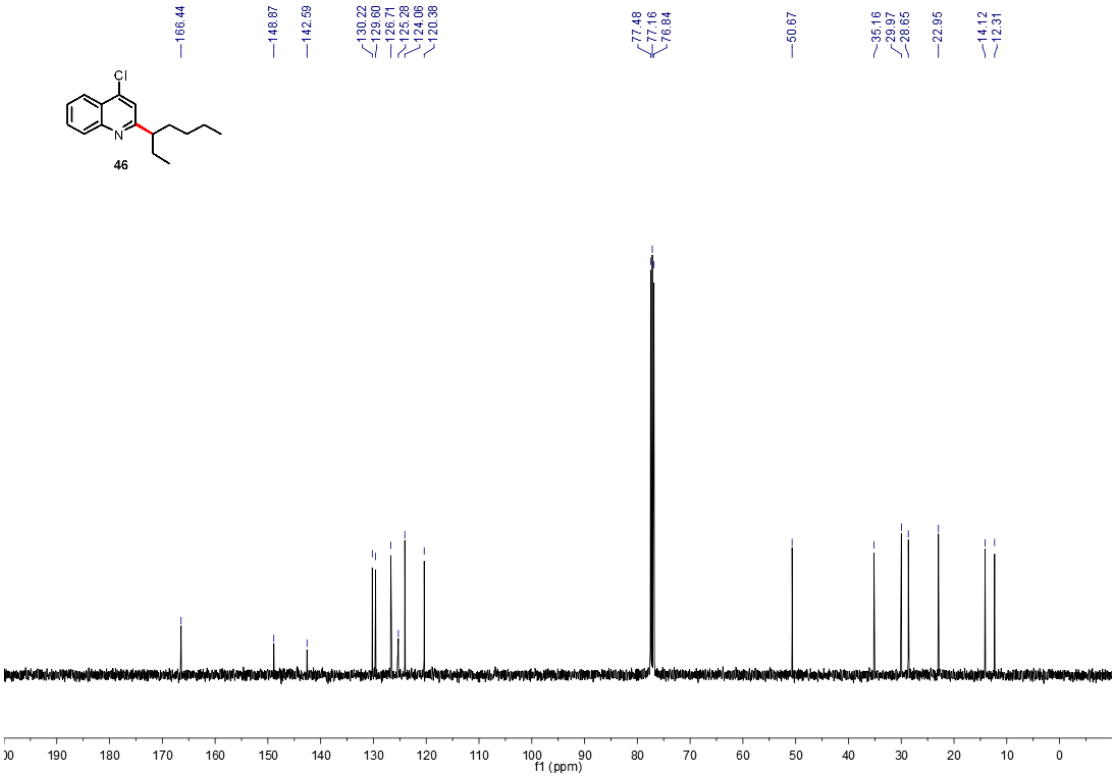

C13DEPT90
130.04
129.84
126.59
123.93
122.33
71.39
57.98
53.84
50.56
44.85
36.09
Cl
N
Me
H
Me
H
H
HO
3
41
f1 (ppm)

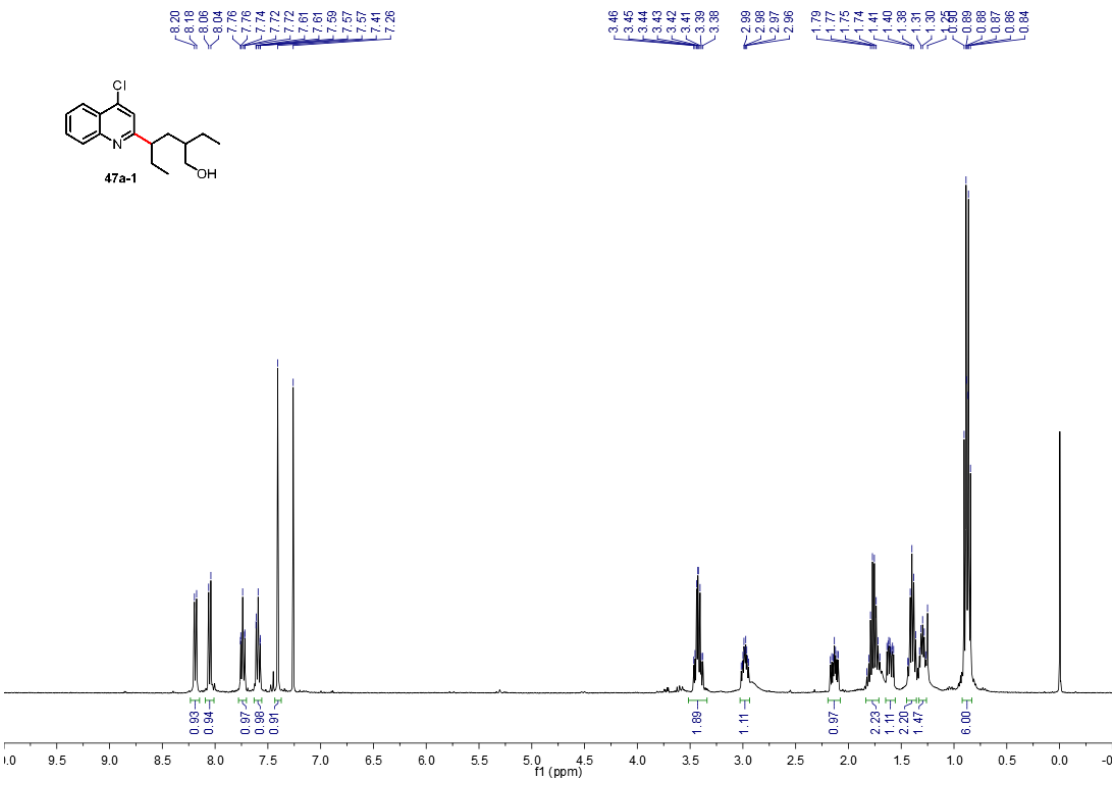

8.29
8.28
7.89
7.87
7.78
7.76
7.71
4.07
4.05
1.87
1.84
1.81
1.77
1.73
1.70
1.69
1.66
1.34
1.33
1.31
1.30
1.28
1.25
1.20
1.18
1.14
1.08
1.07
1.06
1.04
1.03
1.01
1.00
0.98
0.98
0.97
Cy
O
I
O
O
42
0.98
1.01
0.95
0.95
1.84
5.36
2.42
2.02
2.11
f1 (ppm)

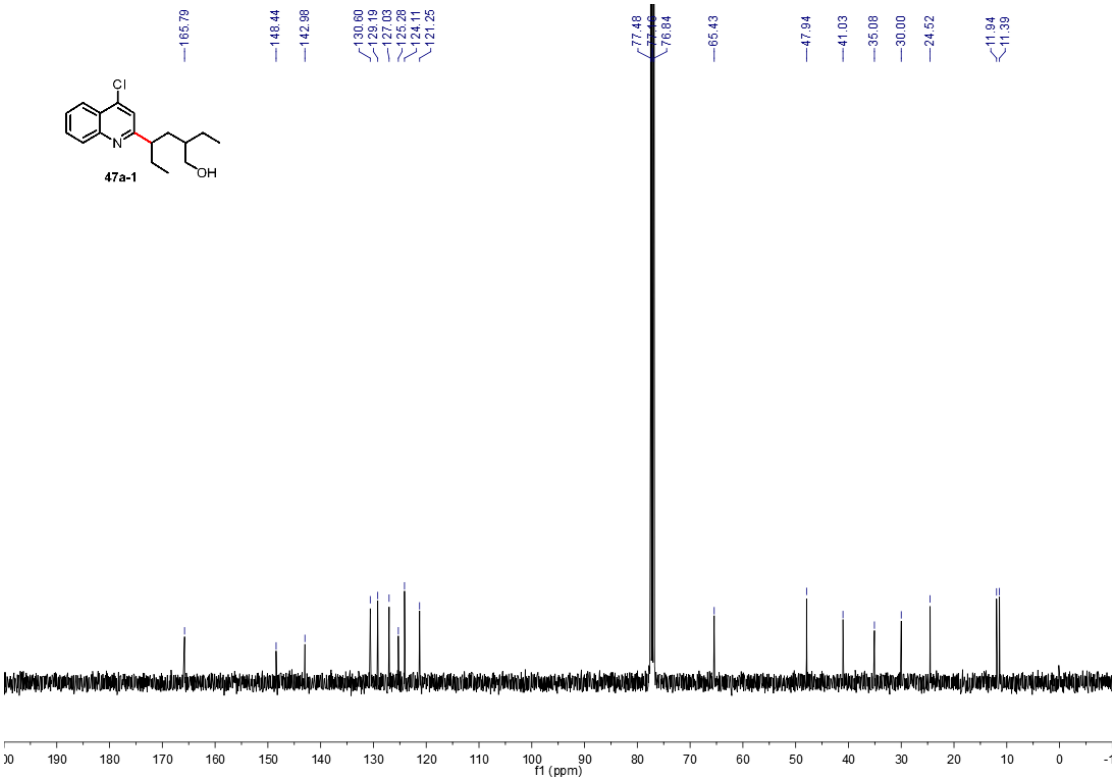

168.10
135.15
133.04
131.14
130.83
126.06
119.08
80.27
77.48
76.84
41.68
29.86
26.57
25.88
Cy
O
I
O
O
42
f1 (ppm)

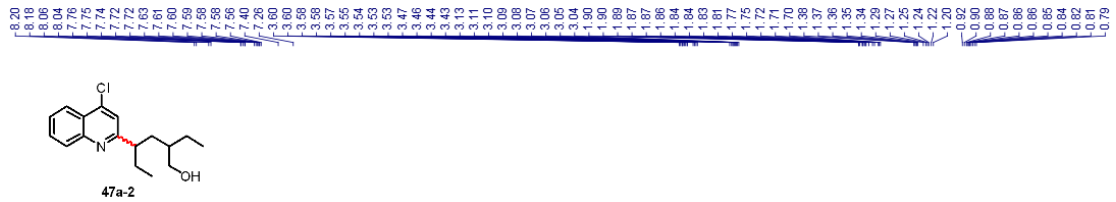

8.20
8.18
8.06
8.04
7.74
7.74
7.72
7.61
7.61
7.59
7.59
7.41
7.26
5.95
5.94
5.93
5.92
5.91
5.90
5.89
5.88
5.07
5.02
5.00
3.07
3.05
3.03
2.62
2.60
2.59
2.56
Cl
N
44
0.98
0.97
1.04
1.04
0.97
1.00
1.01
0.96
2.05
2.06
f1 (ppm)
162.10
148.95
142.69
137.47
130.46
129.38
126.89
125.15
124.09
121.57
115.67
77.48
77.16
76.84
38.42
33.62
Cl
N
44
f1 (ppm)


8.20
8.20
8.18
8.18
8.09
8.09
8.07
8.06
7.75
7.74
7.73
7.73
7.71
7.71
7.60
7.60
7.59
7.59
7.56
7.56
7.36
7.26
2.86
2.84
2.84
2.82
2.81
2.80
2.79
1.80
1.80
1.78
1.76
1.76
1.74
1.32
1.30
1.30
1.28
1.27
1.25
1.24
1.23
1.12
1.10
1.09
0.85
0.83
Cl
N
46
0.89
0.88
0.93
0.89
0.87
0.92
4.21
3.26
1.00
5.72
f1 (ppm)


166.44
148.87
142.59
130.22
129.60
126.71
125.28
124.06
120.38
77.48
77.16
76.84
50.67
35.16
29.97
28.65
22.95
14.12
12.31
Cl
N
46
f1 (ppm)

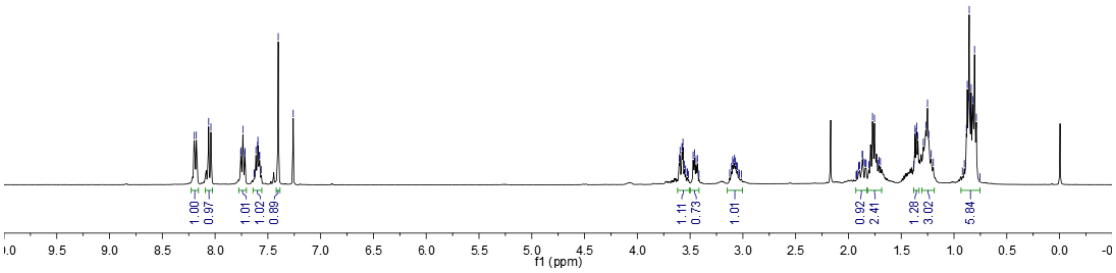

8.20
8.18
8.06
8.04
7.76
7.76
7.74
7.72
7.72
7.61
7.61
7.59
7.57
7.57
7.41
7.26
3.46
3.45
3.44
3.43
3.42
3.41
3.39
3.38
2.99
2.98
2.97
2.96
1.79
1.77
1.75
1.74
1.41
1.40
1.38
1.31
1.30
0.90
0.89
0.88
0.87
0.86
0.84
Cl
N
OH
47a-1
0.93
0.94
0.97
0.98
0.91
1.89
1.11
0.97
2.23
1.11
2.20
1.47
6.00
f1 (ppm)


165.79
148.44
142.98
130.60
129.19
127.03
125.28
124.11
121.25
77.48
77.16
76.84
65.43
47.94
41.03
35.08
30.00
24.52
11.94
11.39
Cl
N
OH
47a-1
f1 (ppm)

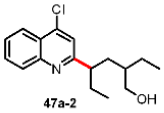

8.20
8.18
8.06
8.04
7.76
7.75
7.74
7.72
7.72
7.63
7.61
7.60
7.59
7.58
7.58
7.56
7.40
7.26
3.60
3.60
3.58
3.58
3.57
3.55
3.54
3.53
3.53
3.47
3.46
3.44
3.43
3.13
3.11
3.10
3.09
3.08
3.07
3.06
3.05
3.04
1.90
1.90
1.89
1.87
1.87
1.86
1.84
1.84
1.83
1.81
1.77
1.75
1.72
1.71
1.70
1.38
1.37
1.36
1.35
1.34
1.29
1.27
1.25
1.24
1.22
1.20
0.92
0.90
0.88
0.87
0.86
0.86
0.85
0.84
0.82
0.81
0.79

Cl
N
OH

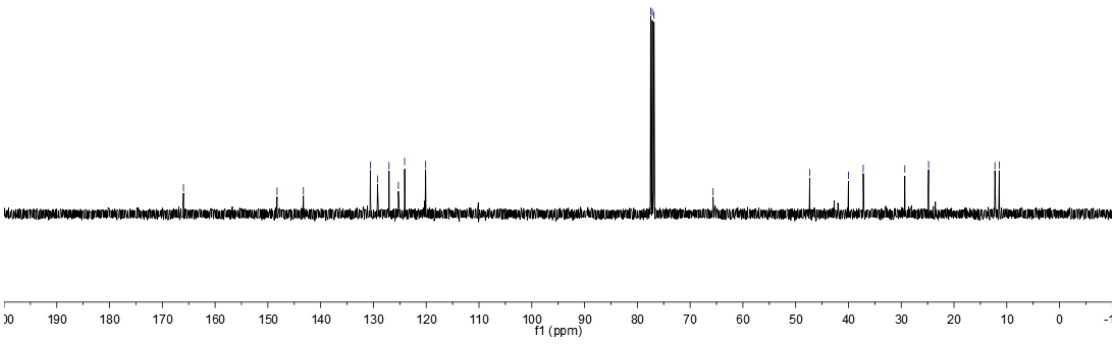
47a-2


1.00
0.97
1.01
1.02
0.89
1.11
0.73
1.01
0.92
2.41
1.28
3.02
5.84
f1 (ppm)


166.00
148.26
143.27
130.58
129.22
127.04
125.27
124.09
120.11
77.48
77.16
76.84
65.65
47.34
40.01
37.20
29.32
24.82
12.25
11.43


Cl
N
OH

47a-2


f1 (ppm)