Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cobalt Complex Catalyzed Atom-Economical Synthesis of Quinoxaline, Quinoline and 2-Alkylaminoquinoline Derivatives

Sujan Shee, Kasturi Ganguli, Kalipada Jana and Sabuj Kundu*

Department of Chemistry, Indian Institute of Technology, Kanpur, Kanpur-208016, India

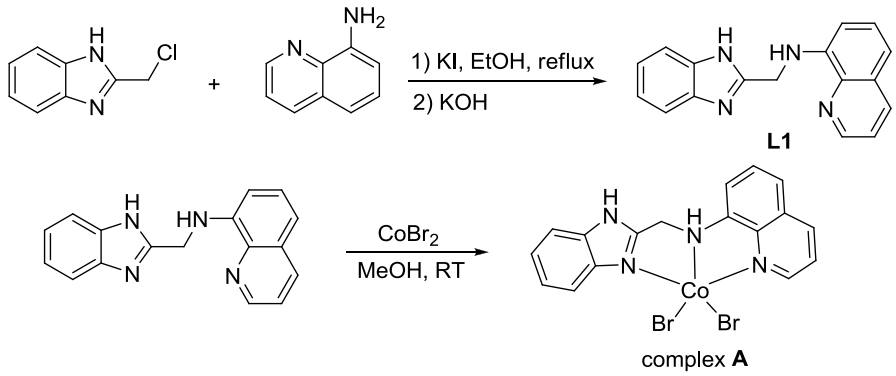
Email: sabuj@iitk.ac.in

Content

1. General Consideration

All the experiments were carried out under argon atmosphere either inside the argon filled glove box or using standard Schlenk line technique unless otherwise stated. Glasswares were oven dried prior to use. Solvents were distilled under argon atmosphere according to literature procedures and deoxygenated prior to use. All the commercial reagents and metal precursors were purchased from Sigma-aldrich, Alfa-aesar, Spectrochem, Avra, SD-fine chemical and Arora Matthey, India. 2-(Chloromethyl)benzimidazole was synthesized following the literature report.[1] All the ^{1}H and ^{13}C spectra were recorded with $CDCl_3$, DMSO-D_6 in JEOL Spectrometer. ESI-MS were recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. UV spectra was recorded on Shimadzu UV spectrophotometer (UV-1800). All the GC analysis were performed using Perkein Elmer Clarus 600 and Agilent 7890 B Gas Chromatograph, where as GC-MS were measured using Agilent 7890 A Gas Chromatograph equipped with Agilent 5890 triple-quadrupole mass system. FT-IR spectra were recorded using PerkinElmer FT-IR spectrometer. Crystallized complex **A** was powdered, washed several times with dry diethyl ether and dried under vaccum prior to use for elemental analysis. This technique was carried out on a Thermoquest EA1110 CHNS/O analyser.

2. Ligand and Metal Complex Synthesis



2.1 N-((1H-Benzo[d]imidazol-2-yl)methyl)quinolin-8-amine (L1)

A mixture of 2-(chloromethyl)benzimidazole (600 mg, 3.60 mmol), 8-aminoquinoline (519 mg, 3.60 mmol) and potassium iodide (598 mg, 3.60 mmol) were taken in a 100 mL round bottom flask equipped with a magnetic pellet. Next 30 mL ethanol was added to the mixture and refluxed for 8 h under argon atmosphere. After that the reaction mixture was cooled under inert atmosphere and 202 mg of KOH (3.60 mmol) was added. The reaction mixture was again refluxed for 3 h. After completion 20 mL cold water was poured into the reaction mixture and the organic part was extracted with ethyl acetate (3 x 12 mL), dried over anhydrous Na_2SO_4. Solvent was evaporated in reduced pressure and final product was separated by silica gel column chromatography using ethyl acetate/hexane as eluent. A yellow coloured solid was obtained. Yield (690 mg, 70%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 10.12 (brs, 1H), 8.69 (dd, $J_{H,H}$ = 4.20, 1.68 Hz, 1H), 8.05 (dd, $J_{H,H}$ = 8.36, 1.64 Hz, 1H), 7.66 (brs, 1H), 7.37 (q, $J_{H,H}$ = 4.24 Hz, 1H), 7.26 (t, $J_{H,H}$ = 7.88 Hz, 2H overlap with $CDCl_3$), 7.21 (q, $J_{H,H}$ = 3.01 Hz, 2H), 7.11 (d, $J_{H,H}$ = 7.68 Hz, 1H), 6.80 (t, $J_{H,H}$ = 5.60 Hz, 1H), 6.62 (d, $J_{H,H}$ = 7.88 Hz, 1H), 4.83 (d, $J_{H,H}$ = 5.72 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 153.42, 147.52, 144.02, 138.35,

136.39, 128.68, 127.87, 122.59, 121.85, 116.12, 106.30, 43.14. **IR (KBr)**: 3398, 3046, 2854, 2924, 1574, 1513, 1416, 1321, 1269, 817, 743 cm^{-1}. **HRMS (ESI):** *m/z*: calcd. for $C_{17}H_{15}N_4$ $[M+H]^+$: 275.1297; found: 275.1298.

2.2 Cobalt(II) Complex Synthesis

A methanolic solution (15 mL) of ligand **L1** (150 mg, 0.54 mmol) was added dropwise into a 10 mL methanolic solution of anhydrous $CoBr_2$ (118 mg, 0.54 mmol) in stirring condition under argon atmosphere. Then the reaction mixture was allowed to stir for 12 h in room temperature. After that solvent was evaporated under reduced pressure. The resulting solid was washed two times with diethyl ether and dried under vacuum. A dark yellow colour paramagnetic cobalt complex was obtained. Suitable crystal was obtained from MeOH/DCM solvent mixture for the single crystal X-ray diffraction.

Yield: 237 mg (89%).

Elemental Analysis: Anal. Calcd for $C_{17}H_{14}Br_2CoN_4$: C 41.41; H 2.86; N 11.36 Found: C 41.48; H 2.79; N 11.45.

IR (KBr): 3429, 3187, 3064, 2924, 1593, 1503, 1454, 1383, 1326, 1274, 831, 748 cm^{-1}.

HRMS (ESI): *m/z*: 411.9733 ($[M-Br]^+$).

UV-vis: The UV-visible spectra of complex **A** in methanol showed absorption at 371 and 468 nm (346 nm for **L1**).

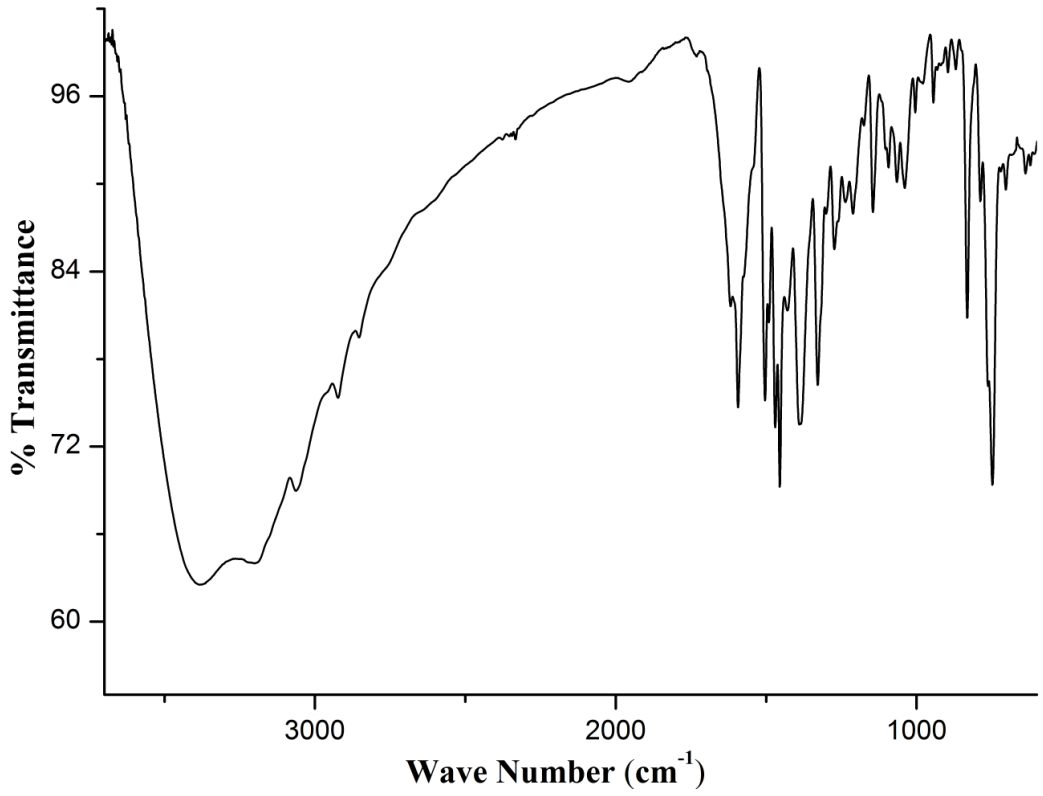


Fig. S1 FT-IR spectra of complex **A**.

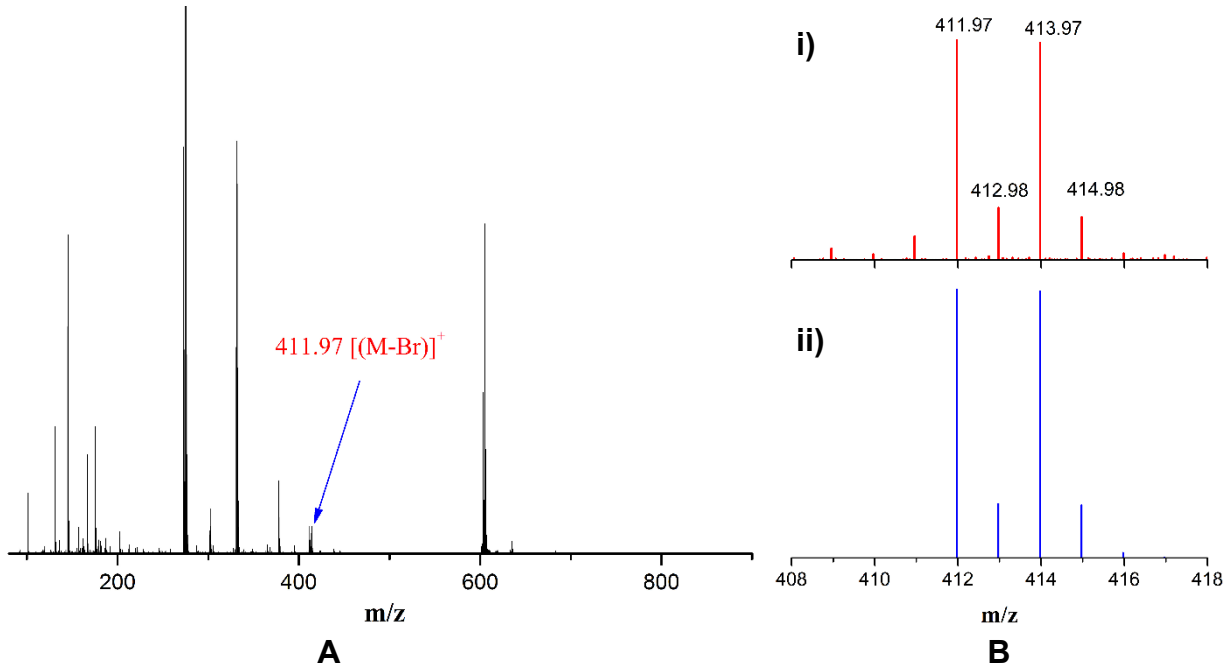


Fig. S2 A) Full ESI-MS spectra of complex **A**; B) ESI-MS pattern of complex **A** i) experimental ii) simulated.

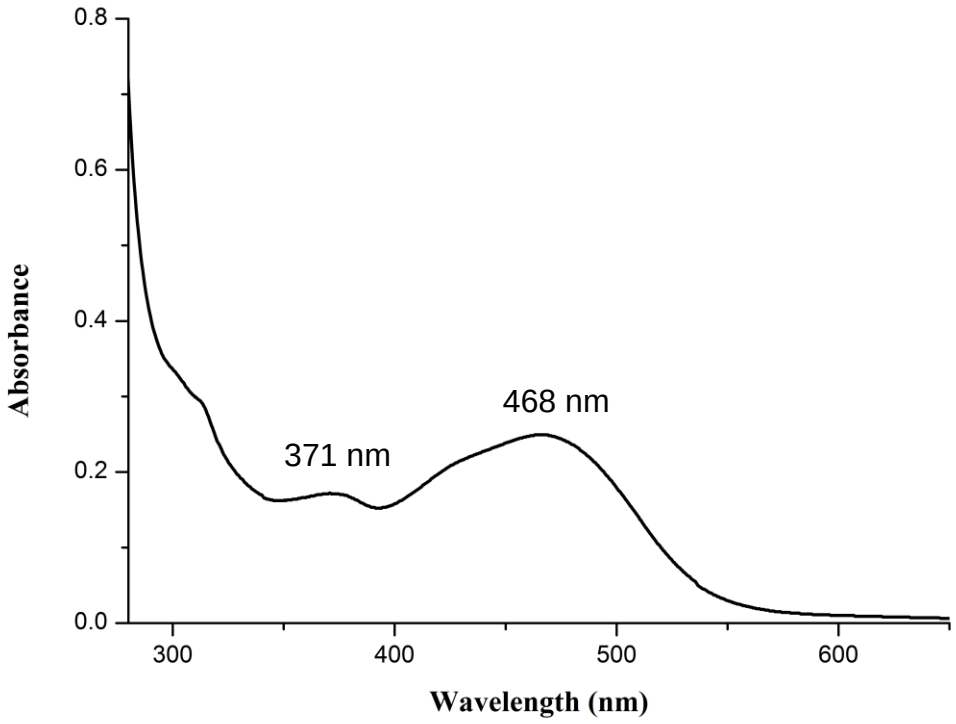
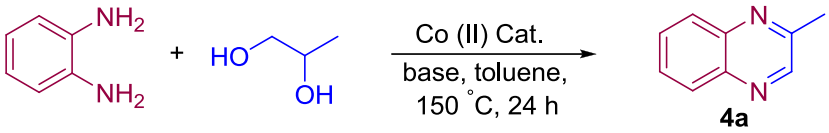


Fig. S3 UV-vis spectra of complex **A**.

3. Optimization Details

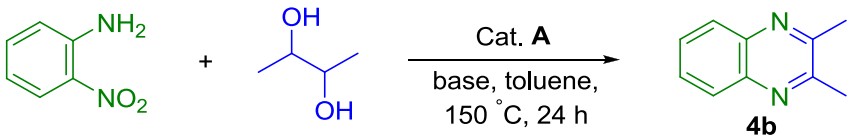
3.1 Table S1. Optimization of Reaction Parameters for Quinoxaline Synthesis from *o*-Phenylenediamine.[a]



Entry	Co (II) Cat.	Base (equiv.)	Yield of **4a** (%)
1	$CoBr_2$	KO^{t}Bu (1.2)	25
2	A	KO^{t}Bu (1.2)	88
3[b]	A	KO^{t}Bu (1.2)	82
4[c]	A	KO^{t}Bu (1.2)	15
5	-	KO^{t}Bu (1.2)	2
6	A	NaO^{i}Pr (1.2)	73
7	A	KOH (1.2)	75
8	A	$CsOH.H_2O$ (1.2)	96
9	A	$CsOH.H_2O$ (1.0)	80
10[d]	A	$CsOH.H_2O$ (1.2)	70
11[e]	A	$CsOH.H_2O$ (1.2)	75

[a]Reaction conditions: *o*-phenylenediamine (0.5 mmol), 1,2-propanediol (2.5 mmol), Cat. **A** (5 mol%), base, toluene (2 mL), heated at 150 °C for 24 h under closed condition; GC yield (using *n*-dodecane as internal standard). [b]*m*-xylene solvent, [c]dioxane solvent, [d]heated at 140 °C; [e]amine : alcohol = 1:3.

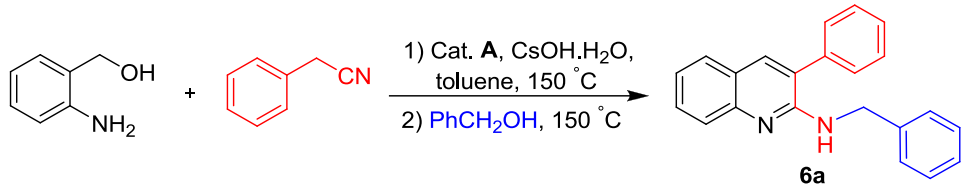
3.2 Table S2. Optimization of Reaction Parameters for Quinoxaline Synthesis from 2-Nitroaniline.[a]



Entry	Amount of Cat. **A** (mol%)	Base (equiv.)	Conversion (%)	Yield of **4b** (%)
1	5	KO^{t}Bu (1)	100	99
2	0.2	KO^{t}Bu (0.5)	80	76
3	0.2	NaO^{i}Pr (0.5)	70	60
4	0.2	KOH (0.5)	85	82
5	0.2	Cs_2CO_3 (0.5)	40	38
6	0.2	$CsOH.H_2O$ (0.5)	99	98
7	0.2	$CsOH.H_2O$ (0.25)	62	60
6[b]	0.2	$CsOH.H_2O$ (0.5)	76	72

[a]Reaction conditions: 2-nitroaniline (0.5 mmol), 2,3-butanediol (1.5 mmol), Cat. **A**, base, toluene (2 mL), heated at 150 °C for 24 h under closed condition; GC yields (using *n*-dodecane as internal standard). [b]heated at 140 °C.

3.3 Table S3. Optimization of Reaction Parameters for 2-Alkylaminoquinoline Synthesis.[a]



6a

Entry	Cat. **A** (mol%)	Base (equiv.)	Yield of **6a** (%)
1	5	1	32
2[b]	5	1	23
3[c]	5	2	47
4[d]	10	2	88
5[e]	5+5	1+1	98

[a]Reaction conditions: 1st step: 2-aminobenzyl alcohol (0.5 mmol), phenyl acetonitrile (0.5 mmol), Cat. **A** (5 mol%), $CsOH.H_2O$ (0.5 mmol), toluene (2 mL), heated at 150 °C for 12 h under closed condition; 2nd step: benzyl alcohol (2.5 mmol), refluxed for 24 h; GC yield (using *n*-dodecane as internal standard). [b]benzyl alcohol (1.0 mmol). [c]$CsOH.H_2O$ (1.0 mmol). [d]Cat. **A** (10 mol%), $CsOH.H_2O$ (1.0 mmol). [e]1st step: Cat. **A** (5 mol%) and $CsOH.H_2O$ (0.5 mmol), heated at 150 °C for 12 h; 2nd step: Cat. **A** (5 mol%), $CsOH.H_2O$ (0.5 mmol) and benzyl alcohol (2.5 mmol) heated at 150 °C for 24 h.

4. General Procedures

4.1 Synthesis of Quinoxaline from Diamines

Diamine (0.5 mmol), vicinal diol (2.5 mmol), Cat. **A** (5 mol%), $CsOH.H_2O$ (0.6 mmol) and 2 mL toluene were taken in a 9 mL ace pressure tube and it was sealed under argon atmosphere. Then the tube was placed in a preheated oil bath (150 °C) and refluxed for 24 h. Next the reaction mixture was cooled and 6 mL water was added. The organic part was extracted with ethyl acetate (3 x 8 mL) and the solvent was evaporated under reduced pressure after drying over anhydrous Na_2SO_4. Final product was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

4.2 Synthesis of Quinoxaline from 2-Nitroanilines

2-Nitroarylamine (0.5 mmol), vicinal diol (1.5 mmol), Cat. **A** (0.2 mol%), $CsOH.H_2O$ (0.25 mmol) and 2 mL toluene were taken in a 9 mL ace pressure tube. It was sealed under argon atmosphere and heated in preheated oil bath (150 °C) for 24 h. The reaction mixture was cooled and 6 mL water was added. The organic part was extracted with ethyl acetate (3 x 8 mL). The combined organic part was dried over anhydrous Na_2SO_4 and solvent was evaporated under reduced pressure. Final product was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

4.3 Synthesis of Quinolines

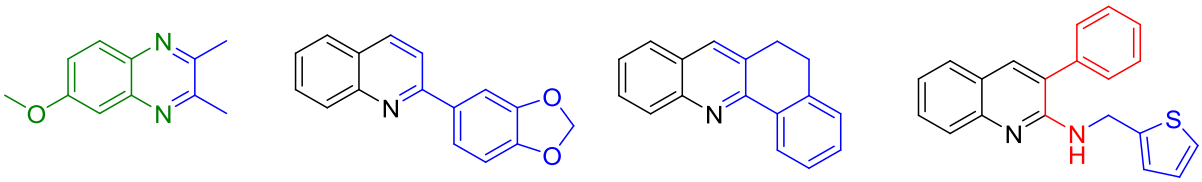
2-aminoaryl alcohol (0.5 mmol), secondary alcohol (0.6 mmol), Cat. **A** (5 mol%) and $CsOH.H_2O$ (0.5 mmol) were taken in a 9 mL ace pressure tube. After addition of 2 mL toluene the tube was sealed under argon atmosphere. Next, the tube was dipped in the preheated oil bath (150 °C) and heated for 6 h. After cooling to room temperature the reaction mixture was diluted with 6 mL water and the organic part was extracted with ethyl acetate (3 x 8 mL). The

combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The quinoline products were isolated through silica gel column chromatography using ethyl acetate/hexane as eluent. The final products were authenticated by NMR, GC-MS analysis.

4.4 One-pot Synthesis of 2-Alkylaminoquinolines

2-aminoaryl alcohol (0.5 mmol), nitrile (0.5 mmol), Cat. **A** (5 mol%), $CsOH.H_2O$ (0.5 mmol) and 2 mL toluene were taken in a 9 mL ace pressure tube. The tube was sealed under argon atmosphere and refluxed at 150 °C in preheated oil bath for 12 h. After that, the tube was immediately taken inside the glove box and cooled to room temperature. Next, another portion of Cat. **A** (5 mol%), $CsOH.H_2O$ (0.5 mmol) and primary alcohol (2.5 mmol) were added. Then the tube was sealed under argon atmosphere and heated at 150 °C for 24 h. The reaction mixture was cooled and 6 mL water was added. The organic part was extracted with ethyl acetate (3 x 8 mL). The combined organic part was dried over anhydrous Na_2SO_4 and solvent was evaporated under reduced pressure. 2-Alkylaminoquinolines were purified through silica gel column chromatography using ethyl acetate/hexane as eluent. The final products were authenticated by NMR, GC-MS and ESI-MS analysis.

5. Preparative Scale Reactions



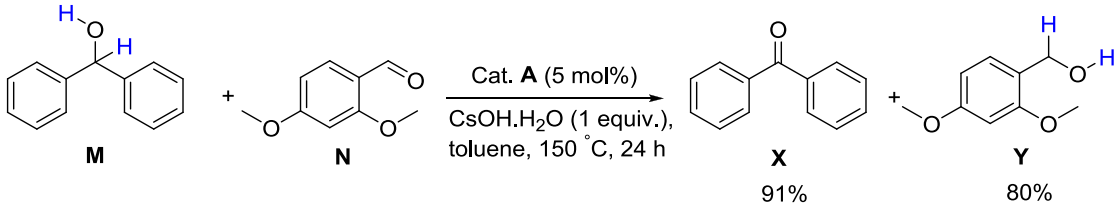
4m, **1.10 g** (81%) **5h**, **1.30 g** (80%) **5i**, **1.26 g** (84%) **6f**, **1.10 g** (68%)

Scheme S1. Gram scale reaction of quinoxaline, quinoline and 2-alkylaminoquinoline. All the compounds were synthesized following the standard reaction conditions (SI 4.2, 4.3 and 4.4) taking proportionate amount of substrates and solvent.

6. Controlled Experiments

6.1 Intermolecular Hydrogen Transfer during Dehydrogenation of Alcohols

Diphenylmethanol (0.2 mmol), 2,4-dimethoxybenzaldehyde (0.2 mmol), Cat. **A** (5 mol%), $CsOH.H_2O$ (0.2 mmol) and 2 mL toluene were taken in a 9 mL ace pressure tube under argon atmosphere. The reaction mixture was refluxed at 150 °C for 24 h. After cooling to room temperature 20 μL reaction mixture was syringed out for GC analysis and the conversion and yield of the products were calculated using *n*-dodecane as internal standard. In this reaction 80% 2,4-dimethoxybenzyl alcohol (**Y**) and 91% benzophenone (**X**) were produced respectively based on the GC analysis.



Scheme S2. Hydrogen transfer during dehydrogenation of alcohol.

6.2 Cobalt(I) Complex Catalyzed Quinoxaline Synthesis

Complex **A** (5 mol%) and 2 mL toluene were taken in a 9 mL ace pressure tube inside the glove box. Then, 1.1 equiv. $LiBEt_3H$ (1M in THF, 5.5 mol%) solution was added dropwise to the solution under stirring condition. During this process gradually complex became soluble and the solution colour changed from light yellow to dark pink. After stirring for 20 minutes, *o*-phenylenediamine (0.5 mmol), 1,2-propanediol (2.5 mmol) and $CsOH.H_2O$ (8 mol%) were added to the mixture and the tube was sealed under argon condition. Next, the tube was placed in a preheated oil bath (150 °C) and refluxed for 24 h. After cooling 4 mL ethyl acetate was added and 20 μL solution was syringed out for GC analysis (*n*-dodecane as internal standard). Yield of 2-methylquinoxaline was 95% based on GC (91% isolated).

7. Hg^0 Poisoning Experiment

Cat. **A** (0.2 mol%), $CsOH.H_2O$ (0.25 mmol) and 2 mL toluene were taken in a 9 mL ace pressure tube under argon atmosphere. Then 2,3-butanediol (1.5 mmol), 2-nitroaniline (0.5 mmol) and mercury (50 equiv.) were added and the tube was sealed under argon atmosphere. Then the tube was heated at 150 °C in preheated oil bath for 24 h. The reaction mixture was cooled and 20 μL reaction mixture was syringed out for GC analysis (*n*-dodecane was used as internal standard). The conversion of 2-nitroaniline was 96% with the yield of quinoxaline (**4b**) 94%. Next rest of the reaction mixture was diluted with 5 mL water. The organic part was extracted with ethyl acetate (3 x 5 mL). The combined organic part was dried over anhydrous Na_2SO_4. Next solvent was evaporated under reduced pressure. Final product was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

8. X-ray Crystallographic Studies

Single crystal X-ray data of the complex A was collected by using a Bruker SMART APEX II CCD diffractometer and Bruker D8 Quest Single Crystal diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). All the data were collected at 100 K temperature. The frames were indexed, integrated and scaled using SMART and SAINT software package[2] and the data were corrected for absorption using the SADABS program.[3] The structures were solved and refined using WINGX, Olex2 and SHELX programs.[2, 4] The crystallographic figures have been generated using Diamond 3 software10 (30% probability thermal ellipsoids).[5] The CCDC number of the complexes **A** is 1828731.

Crystallographic data and pertinent refinement parameters and molecular structure for complex **A** was shown below.

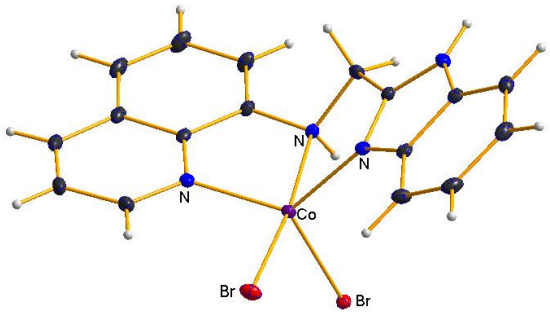


Fig. S4 Molecular structure of complex **A** (30% thermal ellipsoids).

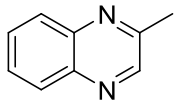
Table S4. Crystal data and structure refinement parameters for complex A.

Identification code	complex A
Empirical formula	$C_{17}H_{16}Br_2CoN_4O$
Formula weight	511.08
Temperature/K	99.99
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.8812(4)
b/Å	17.0462(7)
c/Å	11.8893(5)
α/°	90
β/°	96.1423(13)
γ/°	90
Volume/Å^3	1789.60(13)
Z	4
ρ_{calc}g/cm^3	1.8968
μ/mm^{-1}	5.437
F(000)	1003.6
Crystal size/mm^3	0.01 × 0.009 × 0.005
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.9 to 56.6
Index ranges	-11 ≤ h ≤ 11, -22 ≤ k ≤ 22, -15 ≤ l ≤ 15
Reflections collected	28576
Independent reflections	4441 [R_{int} = 0.0295, R_{sigma} = 0.0182]
Data/restraints/parameters	4441/0/232
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0197, wR_2 = 0.0448
Final R indexes [all data]	R_1 = 0.0228, wR_2 = 0.0460
Largest diff. peak/hole / e Å^{-3}	0.53/-0.54

9. Characterization of Products

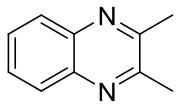
9.1 Characterization of Quinoxaline Derivatives

2-Methylquinoxaline (**4a**):[6]



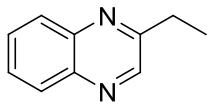
67 mg; 93% isolated yield from diamine and 54 mg; 75% isolated yield from nitroamine; yellow liquid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.71 (s, 1H), 8.05 (d, $J_{H,H}$ = 8.56 Hz, 1H), 7.99 (d, $J_{H,H}$ = 7.64 Hz, 1H), 7.73-7.65 (m, 2H), 2.75 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 153.97, 146.21, 142.25, 141.15, 130.20, 129.36, 129.12, 128.85, 22.79. **GC-MS (M^+)**: 144.0.

2,3-Dimethylquinoxaline (**4b**):[6]



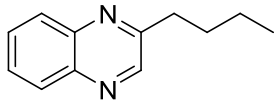
61 mg; 77% isolated yield from diamine and 76 mg; 96% isolated yield from nitroamine; yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.96 (dd, $J_{H,H}$ = 6.24, 3.36 Hz, 2H), 7.65 (dd, $J_{H,H}$ = 6.48, 3.52 Hz, 2H), 2.72 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 153.70, 141.27, 129.06, 128.50, 23.41. **GC-MS (M^+)**: 158.0.

2-Ethylquinoxaline (**4c**):[6]



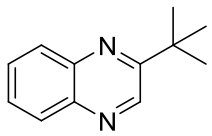
72 mg; 92% isolated yield from diamine and 54 mg; 69% isolated yield from nitroamine; yellow liquid: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 8.75 (s, 1H), 8.07-8.02 (m, 2H), 7.74-7.67 (m, 2H), 3.05 (q, $J_{H,H}$ = 7.60 Hz, 2H), 1.42 (t, $J_{H,H}$ = 7.65 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 158.70, 145.76, 142.39, 141.44, 130.13, 129.36, 129.12, 129.08, 29.84, 13.61. **GC-MS (M^+)**: 158.1.

2-Butylquinoxaline (**4d**):[6]



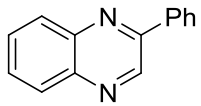
75 mg; 81% isolated yield from diamine and 61 mg; 66% isolated yield from nitroamine; dense yellow liquid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.72 (s, 1H), 8.07-8.01 (m, 2H), 7.74-7.66 (m, 2H), 3.00 (t, $J_{H,H}$ = 7.80 Hz, 2H), 1.86-1.78 (m, 2H), 1.49-1.40 (m, 2H), 0.96 (t, $J_{H,H}$ = 7.36 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 157.91, 146.05, 142.39, 141.38, 130.12, 129.36, 129.11, 129.04, 36.47, 31.87, 22.79, 14.11. **GC-MS (M^+)**: 186.1.

2-tert-Butylquinoxaline (**4e**):[6]



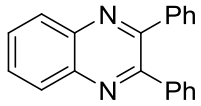
67 mg; 72% isolated yield from diamine and 58 mg; 62% isolated yield from nitroamine; dense yellow liquid: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 8.97 (s, 1H), 8.05-8.03 (m, 2H), 7.72-7.66 (m, 2H), 1.50 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 163.90, 143.63, 141.83, 141.00, 129.84, 129.50, 129.11, 129.07, 37.46, 29.96. **GC-MS (M^+)**: 186.1.

2-Phenylquinoxaline (**4f**):[7]



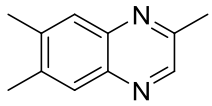
87 mg; 85% isolated yield; yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 9.32 (s, 1H), 8.20-8.10 (m, 4H), 7.80-7.72 (m, 2H), 7.59-7.50 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 152.09, 143.61, 1742.52, 141.79, 137.00, 130.52, 130.42, 129.84, 129.78, 129.39, 129.34, 127.78. **GC-MS (M^+)**: 206.0.

2,3-Diphenylquinoxaline (**4g**):[8]



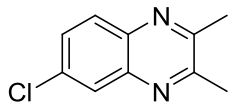
115 mg; 82% isolated yield from diamine and 129 mg; 92% isolated yield from nitroamine; white solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.18 (dd, $J_{H,H}$ = 6.48, 3.48 Hz, 2H), 7.77 (dd, $J_{H,H}$ = 6.52, 3.52 Hz, 2H), 7.53-7.50 (m, 4H), 7.36-7.31 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 153.69, 141.45, 139.30, 130.16, 130.05, 129.42, 129.01, 128.47. **GC-MS (M^+)**: 282.1.

2,6,7-Trimethylquinoxaline (**4h**):[9]



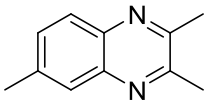
68 mg; 80% isolated yield from diamine and 61 mg; 71% isolated yield from nitroamine; pale yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.62 (s, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 2.72 (s, 3H), 2.47 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 152.92, 145.24, 141.21, 140.73, 140.11, 139.53, 128.40, 127.95, 22.92, 20.62, 20.46. **GC-MS (M^+)**: 172.1.

6-Chloro-2,3-dimethylquinoxaline (**4i**):[9]



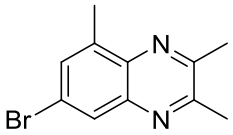
74 mg; 77% isolated yield from diamine and 91 mg; 95% isolated yield from nitroamine; yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.94 (d, $J_{H,H}$ = 2.20 Hz, 1H). 7.88 (d, $J_{H,H}$ = 8.96 Hz, 1H), 7.58 (dd, $J_{H,H}$ = 8.76, 2.20 Hz, 1H), 2.69 (s, 6H).). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 154.76, 153.96, 141.56, 139.74, 134.58, 129.96, 129.75, 127.55, 23.41. **GC-MS (M^+)**: 192.0.

2,3,6-Trimethylquinoxaline (**4j**):[10]



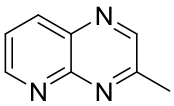
64 mg; 75% isolated yield; light yellow solid: **^{1}H NMR (400 MHz, DMSO-D$_6$)**: δ = 7.79 (d, $J_{H,H}$ = 8.48 Hz, 1H), 7.67 (s, 1H), 7.50 (dd, $J_{H,H}$ = 8.52, 1.84 Hz, 1H), 3.52 (s, 3H), 2.58 (s, 6H). **^{13}C NMR (100 MHz, DMSO-D$_6$)**: δ = 154.34, 153.48, 140.89, 139.27, 131.39, 128.05, 127.32, 23.21, 23.09, 21.69. **GC-MS (M$^+$)**: 172.1.

7-Bromo-2,3,5-trimethylquinoxaline (**4k**):



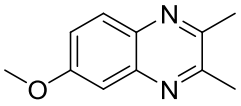
87 mg; 70% isolated yield from diamine and 116 mg; 93% isolated yield from nitroamine; yellow solid: **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.96 (s, 1H), 7.57 (s, 1H), 2.71 (s, 3H), 2.69 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)**: δ = 154.14, 152.79, 141.95, 139.29, 138.90, 132.24, 128.65, 122.28, 23.56, 23.30, 17.11. **HRMS (ESI):** calcd. for $C_{11}H_{12}BrN_2$ $[M+H]^+$: 251.0184; found: 251.0183.

3-Methylpyrido[2,3-b]pyrazine (**4l**):[11]



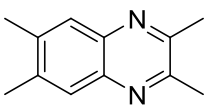
49 mg; 68% isolated yield; yellow solid: **^{1}H NMR (500 MHz, CDCl$_3$)**: δ = 9.11 (d, $J_{H,H}$ = 3.95 Hz, 1H), 8.81 (s, 1H), 8.42 (dd, $J_{H,H}$ = 8.30, 1.80 Hz, 1H), 7.66 (dd, $J_{H,H}$ = 8.30, 4.200 Hz, 1H), 2.84 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 157.88, 154.14, 150.98, 147.35, 138.40, 136.18, 124.64, 23.04. **GC-MS (M$^+$)**: 145.0.

6-Methoxy-2,3-dimethylquinoxaline (**4m**):[12]



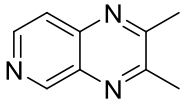
84 mg; 90% isolated yield; yellow solid: **^{1}H NMR (400 MHz, CDCl$_3$)**: δ = 7.84 (d, $J_{H,H}$ = 8.90 Hz, 1H), 7.29-7.26 (m, 2H), 3.91 (s, 3H), 2.67 (s, 3H), 2.66 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)**: δ = 160.12, 153.55, 150.82, 142.62, 137.16, 129.42, 121.86, 106.31, 55.86, 23.31, 23.00. **GC-MS (M$^+$):** 188.1.

2,3,6,7-Tetramethylquinoxaline (**4n**):[9]



86 mg; 93% isolated yield; light yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.70 (s, 2H), 2.67 (s, 6H), 2.43 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 152.53, 140.16, 139.24, 127.67, 23.29, 20.48. **GC-MS (M^+):** 186.1.

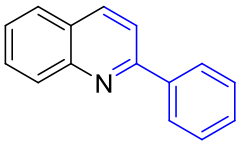
2,3-Dimethylpyrido[3,4-b]pyrazine (**4o**):[13]



38 mg; 48% isolated yield; yellow solid: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 9.39 (s, 1H), 8.72 (d, $J_{H,H}$ = 5.70 Hz, 1H), 7.80 (d, $J_{H,H}$ = 5.70 Hz, 1H), 2.76 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.03, 155.94, 153.58, 146.86, 143.95, 136.67, 121.09, 23.94, 23.57. **GC-MS (M^+)**: 159.0.

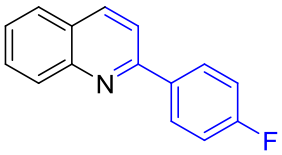
9.2 Characterization of Quinoline Derivatives

2-Phenylquinoline (**5a**):[14]



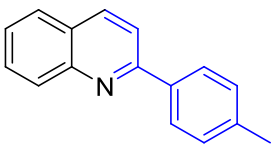
95 mg; 93% isolated yield; white solid: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 8.22-8.15 (m, 4H), 7.88 (d, $J_{H,H}$ = 8.56 Hz, 1H), 7.83 (d, $J_{H,H}$ = 7.96 Hz, 1H), 7.74-7.70 (m, 1H), 7.55-7.44 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 157.57, 148.48, 139.89, 136.98, 129.94, 129.86, 129.52, 129.05, 127.78, 127.66, 127.38, 126.48, 119.22. **GC-MS (M^+)**: 205.1.

2-(4-Fluorophenyl)quinoline (**5b**):[15]



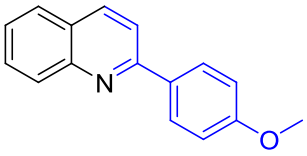
97 mg; 87% isolated yield; white solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.22 (d, $J_{H,H}$ = 8.60 Hz, 1H), 8.17-8.13 (m, 1H), 7.83 (d, $J_{H,H}$ = 8.60 Hz, 1H), 7.74-7.70 (m, 1H), 7.54-7.50 (m, 1H), 7.23-7.17 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 165.25, 162.77, 156.44, 148.38, 137.16, 135.99, 130.03, 129.81, 129.67, 129.58, 127.69, 127.28, 126.57, 118.85, 116.10, 115.88. **GC-MS (M^+)**: 223.0.

2-(4-Methylphenyl)quinoline (**5c**):[15]



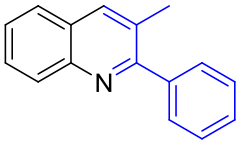
98 mg; 90% isolated yield; light yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.19-8.16 (m, 2H), 8.08 (d, $J_{H,H}$ = 8.20 Hz, 2H), 7.85 (d, $J_{H,H}$ = 8.65 Hz, 1H), 7.80 (d, $J_{H,H}$ = 8.00 Hz, 1H), 7.72-7.70 (m, 1H), 7.52-7.48 (m, 1H), 7.34 (d, $J_{H,H}$ = 7.90 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 152.49, 143.44, 134.56, 132.02, 131.83, 124.79, 124.74, 122.61, 122.26, 121.24, 114.03, 16.52. **GC-MS (M^+)**: 219.1.

2-(4-Methoxyphenyl)quinoline (**5d**):[14]



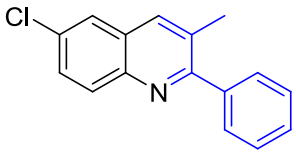
103 mg; 88% isolated yield; light yellow solid: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 8.17 (d, $J_{H,H}$ = 8.60 Hz, 1H), 8.15-8.12 (m, 3H), 7.83 (d, $J_{H,H}$ = 8.60 Hz, 1H), 7.80 (d, $J_{H,H}$ = 8.05 Hz, 1H), 7.71 (m, 1H), 7.50 (t, $J_{H,H}$ = 7.45 Hz, 1H), 7.05 (d, $J_{H,H}$ = 8.75 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 156.02, 152.15, 143.49, 131.86, 127.48, 124.80, 124.71, 124.11, 122.65, 122.12, 121.13, 113.80, 109.44, 50.62. **GC-MS (M^+)**: 235.1.

3-Methyl-2-phenylquinoline (**5e**):[14]



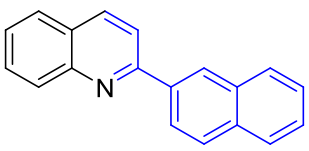
85 mg; 78% isolated yield; yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.15 (d, $J_{H,H}$ = 8.60 Hz, 1H), 7.98 (s, 1H), 7.76 (d, $J_{H,H}$ = 8.24 Hz, 1H), 7.67-7.63 (m, 1H), 7.60-7.58 (m, 2H), 7.52-7.42 (m, 4H), 2.45 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 160.64, 146.74, 140.97, 136.87, 129.39, 129.33, 128.98, 128.88, 128.42, 128.31, 127.73, 126.84, 126.53, 20.74. **GC-MS (M^+)**: 219.1.

6-Chloro-3-methyl-2-phenylquinoline (**5f**):[16]



91 mg; 72% isolated yield; white solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.05 (d, $J_{H,H}$ = 9.04 Hz, 1H), 7.92 (s, 1H), 7.75 (d, $J_{H,H}$ = 2.32 Hz, 1H), 7.59-7.56 (m, 3H), 7.50-7.43 (m, 3H), 2.45 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 160.93, 145.04, 140.47, 136.12, 132.32, 131.03, 130.59, 129.96, 129.02, 128.66, 128.58, 128.37, 125.56, 20.87. **GC-MS (M^+)**: 253.0

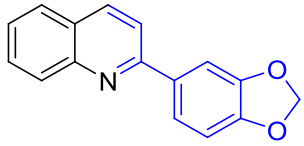
2-(Naphthalen-2-yl)quinoline (**5g**):[17]



114 mg; 90% isolated yield; white solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.61 (s, 1H), 8.38 (dd, $J_{H,H}$ = 8.64, 1.80 Hz, 1H), 8.25 (t, $J_{H,H}$ = 8.56 Hz, 2H), 8.03-7.98 (m, 3H), 7.90-7.87 (m,

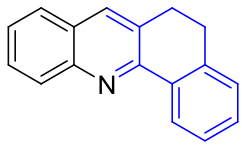
1H), 7.85 (d, $J_{H,H}$ = 7.64 Hz, 1H), 7.77-7.72 (m, 1H), 7.55-7.51 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 157.37, 148.57, 137.16, 137.02, 134.05, 133.70, 129.94, 129.03, 128.79, 127.93, 127.71, 127.43, 127.35, 126.92, 126.54, 125.27, 119.37. **GC-MS (M^+)**: 255.1.

2-(Benzo[d][1,3]dioxol-5-yl)quinoline (**5h**):[18]



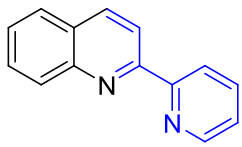
109 mg, 88% isolated yield, white solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.17 (d, $J_{H,H}$ = 8.60 Hz, 1H), 8.12 (d, $J_{H,H}$ = 8.55 Hz, 1H), 7.80-7.77 (m, 2H), 7.74 (d, $J_{H,H}$ = 1.65 Hz, 1H), 7.71-7.68 (m, 1H), 7.66 (dd, $J_{H,H}$ = 8.05, 1.65 Hz, 1H), 7.50-7.47 (m, 1H), 6.94 (d, $J_{H,H}$ = 8.15 Hz, 1H), 6.03 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 156.89, 149.04, 148.61, 148.40, 136.90, 134.35, 129.86, 129.76, 127.63, 127.21, 126.28, 121.96, 118.83, 108.70, 108.14, 101.58. **GC-MS (M^+)**: 249.0.

5,6-Dihydrobenzo[c]acridine (**5i**):[19]



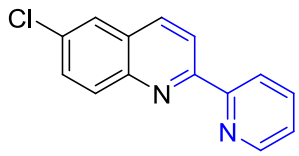
106 mg; 92% isolated yield; light yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.61 (d, $J_{H,H}$ = 7.72 Hz, 1H), 8.17 (d, $J_{H,H}$ = 8.28 Hz, 1H), 7.88 (s, 1H), 7.73 (d, $J_{H,H}$ = 8.20 Hz, 1H), 7.67-7.63 (m, 1H), 7.48-7.42 (m, 2H), 7.39 (td, $J_{H,H}$ = 7.56, 1.56 Hz, 1H), 7.28 (d, $J_{H,H}$ = 7.80 Hz, 1H), 3.11-3.07 (m, 2H), 3.02-2.97 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 153.55, 147.80, 139.58, 134.88, 133.86, 130.74, 129.85, 129.57, 128.81, 128.12, 128.04, 127.49, 127.10, 126.24, 126.22, 28.99, 28.56. **GC-MS (M^+)**: 231.1.

2-(Pyridin-2-yl)quinoline (**5j**):[20]



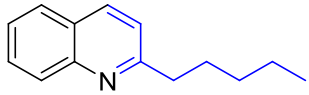
93 mg; 90% isolated yield; light yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.73 (d, $J_{H,H}$ = 4.60 Hz, 1H), 8.65 (d, $J_{H,H}$ = 7.96 Hz, 1H), 8.56 (d, $J_{H,H}$ = 8.60 Hz, 1H), 8.28 (d, $J_{H,H}$ = 8.60 Hz, 1H), 8.18 (d, $J_{H,H}$ = 8.48 Hz, 1H), 7.88-7.82 (m, 2H), 7.74 (t, $J_{H,H}$ = 7.92 Hz, 1H), 7.55 (t, $J_{H,H}$ = 7.56 Hz, 1H), 7.34 (dd, $J_{H,H}$ = 7.32, 4.48 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 156.51, 156.33, 149.36, 148.10, 137.16, 137.02, 130.00, 129.76, 128.44, 127.82, 126.96, 124.23, 122.04, 119.15. **GC-MS (M^+)**: 206.0.

6-Chloro-2-(pyridin-2-yl)quinoline (**5k**):



102 mg; 85% isolated yield; light yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.72 (d, $J_{H,H}$ = 4.32 Hz, 1H), 8.61 (d, $J_{H,H}$ = 7.96 Hz, 1H), 8.56 (d, $J_{H,H}$ = 8.64 Hz, 1H), 8.16 (d, $J_{H,H}$ = 8.68 Hz, 1H), 8.09 (d, $J_{H,H}$ = 9.00 Hz, 1H), 7.86 (td, $J_{H,H}$ = 7.60, 1.44 Hz, 1H), 7.80 (d, $J_{H,H}$ = 2.04 Hz, 1H), 7.65 (dd, $J_{H,H}$ = 9.00, 2.24 Hz, 1H), 7.35-7.32 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 156.57, 156.06, 149.40, 146.44, 137.17, 136.02, 132.60, 131.55, 130.66, 128.95, 126.48, 124.40, 121.97, 120.00. **GC-MS (M^+)**: 240.0.

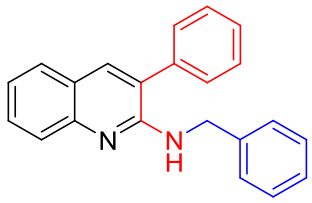
2-Pentylquinoline (**5l**):[21]



54 mg; 55% isolated yield; light yellow dense oil: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.05 (d, $J_{H,H}$ = 8.36 Hz, 2H), 7.76 (d, $J_{H,H}$ = 8.00 Hz, 1H), 7.68-7.64 (m, 1H), 7.48-7.44 (m, 1H), 7.29 (d, $J_{H,H}$ = 8.52 Hz, 1H), 2.97 (t, $J_{H,H}$ = 7.84 Hz, 2H), 1.84-1.77 (m, 2H), 1.39-1.35 (m, 4H), 0.91 (T, $J_{H,H}$ = 6.88 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 163.34, 148.09, 136.38, 129.52, 129.02, 127.68, 126.91, 125.83, 121.58, 39.57, 31.97, 30.01, 22.79, 14.24. **GC-MS (M^+)**: 199.1.

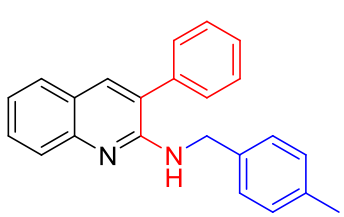
9.3 Characterization of 2-Alkylaminoquinoline Derivatives

N-Benzyl-3-phenylquinolin-2-amine (**6a**):[17]



145 mg; 93% isolated yield; yellow gel: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.77 (d, $J_{H,H}$ = 8.35 Hz, 1H), 7.68 (s, 1H), 7.61 (d, $J_{H,H}$ = 7.95 Hz, 1H), 7.53 (t, $J_{H,H}$ = 7.40 Hz, 1H), 7.47-7.44 (m, 4H), 7.41-7.34 (m, 3H), 7.29 (t, $J_{H,H}$ = 7.40 Hz, 2H), 7.22 (t, $J_{H,H}$ = 7.20 Hz, 2H), 5.09 (s, 1H - NH), 4.82 (d, $J_{H,H}$ = 5.50 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 154.43, 147.79, 140.10, 137.70, 136.63, 129.55, 129.47, 129.30, 128.73, 128.44, 127.96, 127.59, 127.25, 126.49, 125.81, 123.91, 122.51, 45.68. **HRMS (ESI)**: *m/z*: Calcd. for $C_{22}H_{19}N_2$ $[M+H]^+$ = 311.1548; found: 311.1548.

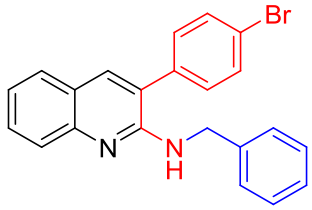
N-(4-Methylbenzyl)-3-phenylquinolin-2-amine (**6b**):[17]



149 mg; 92% isolated yield; yellow gel: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.78 (d, $J_{H,H}$ = 8.35 Hz, 1H), 7.69 (s, 1H), 7.62 (d, $J_{H,H}$ = 7.85 Hz, 1H), 7.55 (t, $J_{H,H}$ = 7.00 Hz, 1H), 7.47-7.45 (m, 4H), 7.40-7.38 (m, 1H), 7.26-7.22 (m, 3H overlap with $CDCl_3$ peak), 7.12 (d, $J_{H,H}$ = 7.70 Hz,

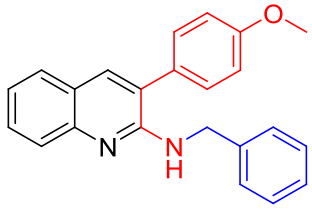
2H), 5.07 (s, 1H -NH), 4.78 (d, $J_{H,H}$ = 5.40 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)**: δ = 154.45, 147.80, 137.69, 136.94, 136.88, 136.57, 129.51, 129.43, 129.39, 129.27, 128.39, 127.97, 127.58, 126.45, 125.81, 123.86, 122.43, 45.47, 21.29. **HRMS (ESI)**: *m/z*: Calcd. for $C_{23}H_{21}N_2$ $[M+H]^+$ = 325.1705; found: 325.1705.

N-Benzyl-3-(4-bromophenyl)quinolin-2-amine (**6c**):[22]



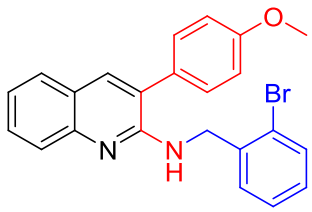
157 mg; 81% isolated yield; yellow solid: **^{1}H NMR (400 MHz, CDCl$_3$)**: δ = 7.77 (d, $J_{H,H}$ = 8.36 Hz, 1H), 7.66 (s, 1H), 7.61-7.53 (m, 4H), 7.36-7.29 (m, 6H), 7.23 (t, $J_{H,H}$ = 7.56 Hz, 2H), 4.96 (s, 1H -NH), 4.80 (d, $J_{H,H}$ = 5.48 Hz, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)**: δ = 154.02, 147.82, 139.86, 136.75, 136.54, 132.65, 130.97, 129.81, 128.78, 128.02, 127.61, 127.37, 126.52. 124.51, 123.72, 122.68, 45.75. **HRMS (ESI)**: *m/z*: Calcd. for $C_{22}H_{18}BrN_2$ $[M+H]^+$ = 389.0653; found: 389.0651.

N-Benzyl-3-(4-methoxyphenyl)quinolin-2-amine (**6d**):



148 mg; 87% isolated yield; yellow solid: **^{1}H NMR (500 MHz, CDCl$_3$)**: δ = 7.78 (d, $J_{H,H}$ = 8.25 Hz, 1H), 7.67 (s, 1H), 7.61 (d, $J_{H,H}$ = 7.95 Hz, 1H), 7.54 (t, $J_{H,H}$ = 7.00 Hz, 1H), 7.42-7.36 (m, 4H), 7.31 (t, $J_{H,H}$ = 8.20 Hz, 2H), 7.26-7.21 (m, 2H overlap with $CDCl_3$ peak), 7.01 (d, $J_{H,H}$ = 8.60 Hz, 2H), 5.12 (s, 1H -NH), 4.83 (d, $J_{H,H}$ = 5.45 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)**: δ = 159.78, 154.74, 147.67, 136.41, 130.47, 129.34, 128.71, 127.97, 127.48, 127.22, 126.46, 122.41, 114.90, 55.55, 45.71. **HRMS (ESI)**: *m/z*: Calcd. for $C_{23}H_{21}N_2O$ $[M+H]^+$ = 341.1654; found: 341.1653.

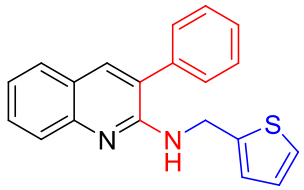
N-(2-Bromobenzyl)-3-(4-methoxyphenyl)quinolin-2-amine (**6e**):



131 mg; 63% isolated yield; yellow solid: **^{1}H NMR (500 MHz, CDCl$_3$)**: δ = 7.75 (d, $J_{H,H}$ = 8.40 Hz, 1H), 7.64 (s, 1H), 7.58-7.49 (m, 5H), 7.41 (d, $J_{H,H}$ = 8.60 Hz, 2H), 7.23-7.19 (m, 2H), 7.08 (t, $J_{H,H}$ = 7.60 Hz, 1H), 7.01 (d, $J_{H,H}$ = 8.60 Hz, 2H), 5.36 (s, 1H -NH), 4.84 (d, $J_{H,H}$ = 6.00 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)**: δ = 159.82, 154.39, 147.58, 139.09,

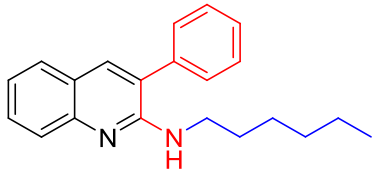
136.39, 132.88, 130.95, 130.95, 130.54, 129.75, 129.31, 128.84, 127.56, 127.47, 126.54, 125.58, 124.14, 124.02, 122.46, 114.90, 55.59, 45.86. **HRMS (ESI)**: *m/z*: Calcd. for $C_{23}H_{20}BrN_2O$ $[M+H]^+$ = 419.0759; found: 419.0757.

3-Phenyl-N-(thiophen-2-ylmethyl)quinolin-2-amine (**6f**):



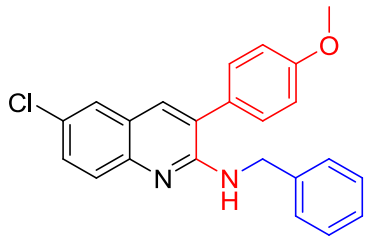
126 mg; 80% isolated yield; yellow gel: **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.82 (d, $J_{H,H}$ = 8.40 Hz, 1H), 7.70 (s, 1H), 7.63 (d, $J_{H,H}$ = 7.90 Hz, 1H), 7.57 (t, $J_{H,H}$ = 7.05 Hz, 1H), 7.48 (d, $J_{H,H}$ = 4.50 Hz, 4H), 7.43-7.39 (m, 1H), 7.25 (t, $J_{H,H}$ = 7.05 Hz, 1H), 7.17 (d, $J_{H,H}$ = 5.10 Hz, 1H), 7.00 (d, $J_{H,H}$ = 3.40 Hz, 1H), 6.92 (dd, $J_{H,H}$ = 5.00, 3.50 Hz, 1H), 5.15 (s, 1H -NH), 4.78 (d, $J_{H,H}$ = 5.60 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 153.82, 147.56, 143.09, 137.51, 136.68, 129.58, 129.42, 129.30, 128.43, 127.62, 126.72, 126.52, 125.76, 125.59, 124.91, 124.00, 122.67, 40.65. **HRMS (ESI)**: *m/z*: Calcd. for $C_{20}H_{17}N_2S$ $[M+H]^+$ = 317.1112; found: 317.1111.

N-Hexyl-3-phenylquinolin-2-amine (**6g**):



84 mg; 55% isolated yield; yellow gel: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.74 (d, $J_{H,H}$ = 8.35 Hz, 1H), 7.62 (s, 1H), 7.52 (d, $J_{H,H}$ = 7.95 Hz, 1H), 7.53-7.40 (m, 6H), 7.19 (t, $J_{H,H}$ = 7.70 Hz, 1H), 4.74 (s, 1H -NH), 3.55 (q, $J_{H,H}$ = 6.55 Hz, 2H), 1.57-1.54 (m, 2H), 1.35-1.28 (m, 6H), 0.87 (t, $J_{H,H}$ = 6.15 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 154.78, 143.14, 136.31, 129.43, 125.43, 129.31, 128.40, 127.58, 126.32, 125.92, 123.62, 122.20, 41.77, 31.77, 29.67, 26.98, 22.79, 14.21. **HRMS (ESI)**: *m/z*: Calcd. for $C_{21}H_{25}N_2$ $[M+H]^+$ = 305.2018; found: 305.2017.

N-Benzyl-6-chloro-3-(4-methoxyphenyl)quinolin-2-amine (**6h**):[22]

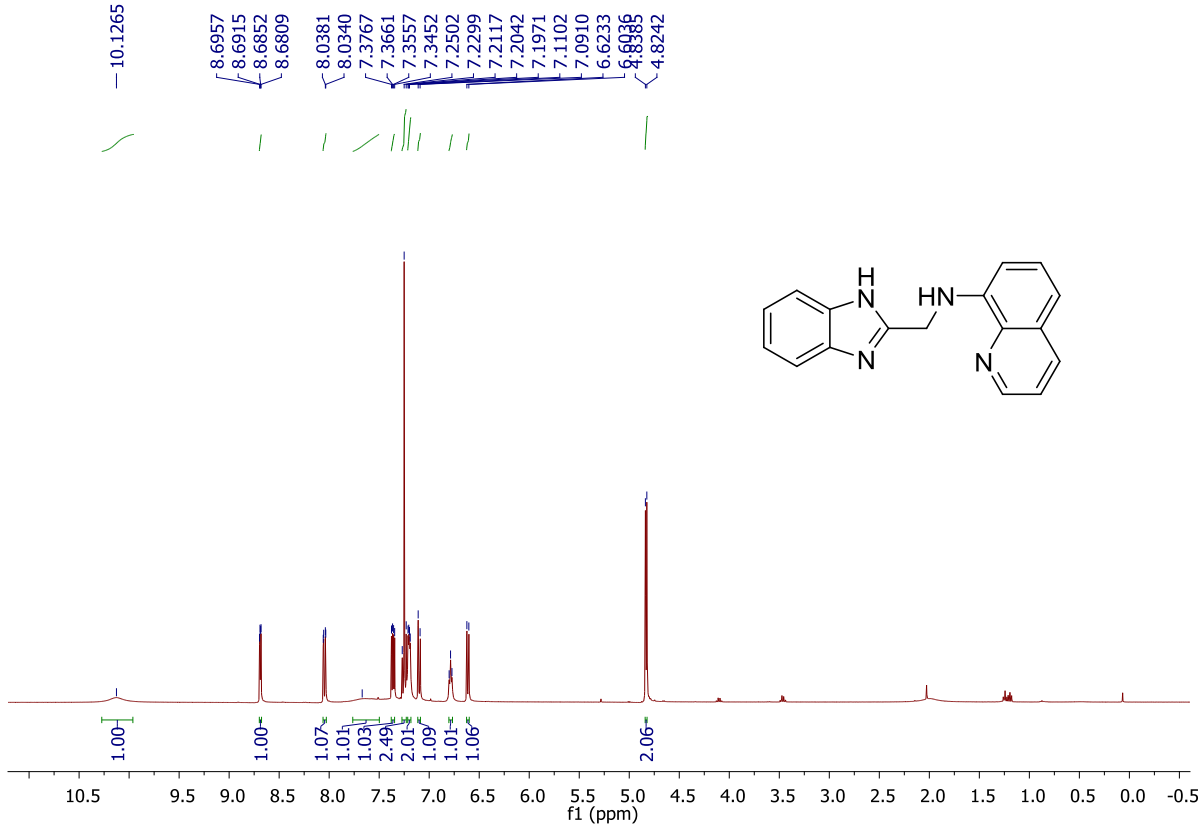


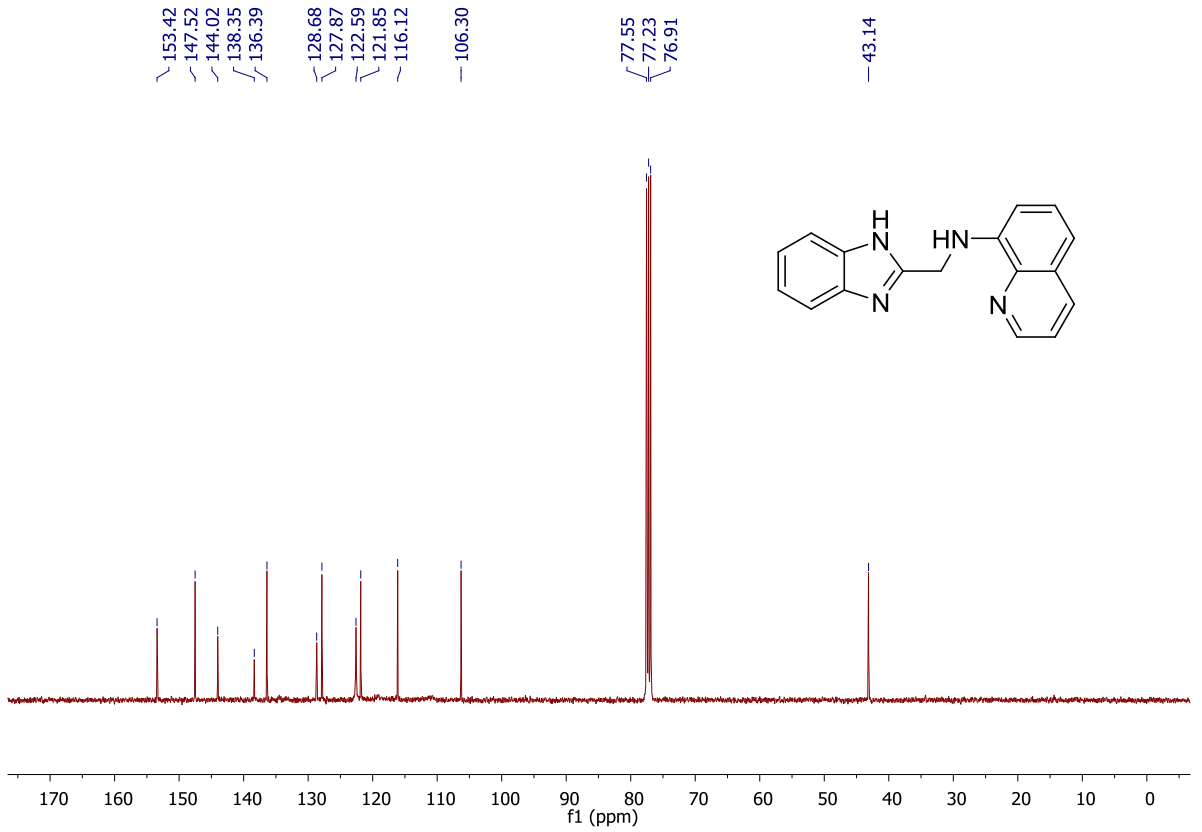
157 mg; 84% isolated yield; yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.67 (d, $J_{H,H}$ = 8.90 Hz, 1H), 7.55-7.54 (m, 2H), 7.45 (dd, $J_{H,H}$ = 8.80, 2.35 Hz, 1H), 7.37-7.29 (m, 6H), 7.23-7.21 (m, 1H), 6.99-6.97 (m, 2H), 5.14 (s, 1H -NH), 4.78 (d, $J_{H,H}$ = 5.50 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 154.91, 149.84, 134.81, 130.39, 125.38, 124.87, 124.17, 123.97, 122.95, 122.89, 122.39, 122.34, 121.43, 121.20, 109.96, 50.58, 40.68. **HRMS (ESI)**: *m/z*: Calcd. for $C_{23}H_{20}ClN_2O$ $[M+H]^+$: 375.1264; found: 375.1262.

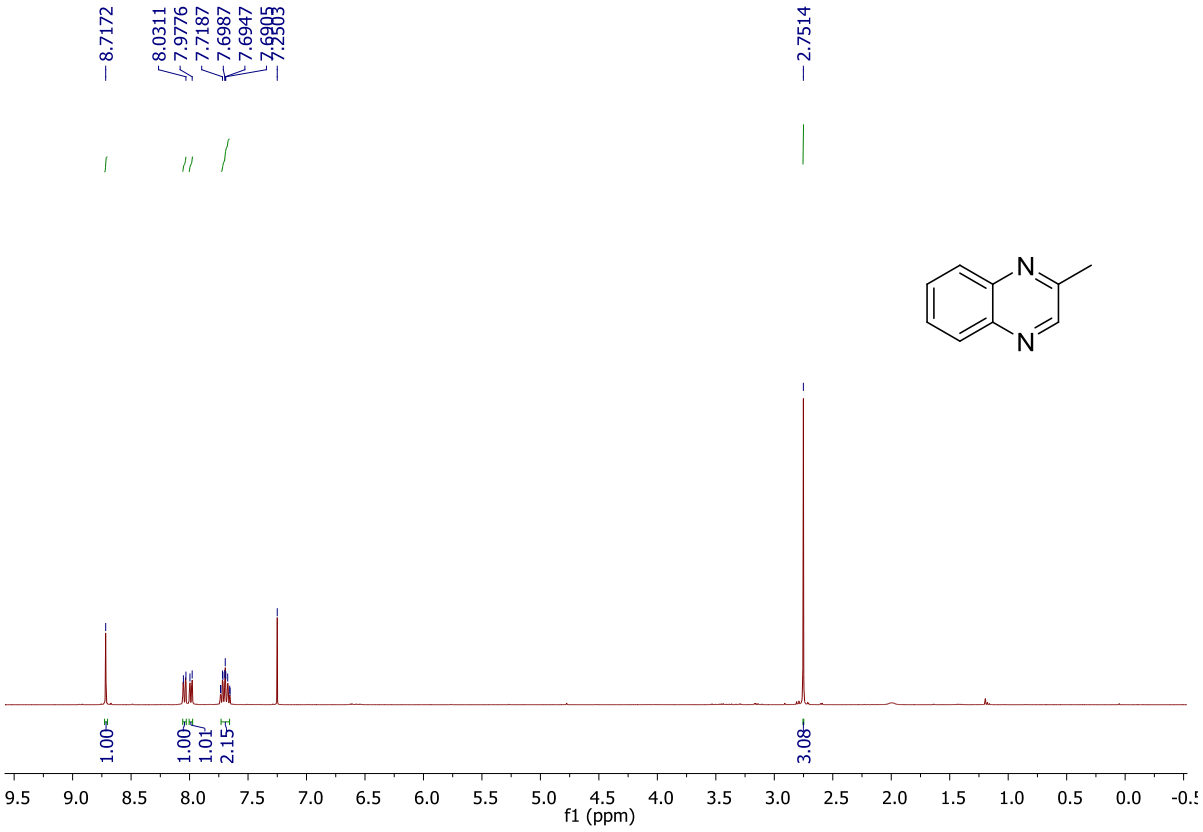
10. References:

1. I. I. Sahay and P. S. Ghalsasi, *Synth. Commun.*, 2017, **47**, 825-834.
2. SAINT+ Software for CCD Difractometers, Bruker AXS, Madison, WI, 2000.
3. M. G. Sheldrick, SADABS Program for Correction of Area Detector Data, University of Gottingen, Gottingen, Germany, 1999.
4. M. G. Sheldrick, SHELXS-86 and SHELXL-97, University of Gottingen, Gottingen, Germany, 1997.
5. K. Bradenburg, Diamond, version 3.1e; Crystal Impact GbR: Bonn, Germany, 2005.
6. T. Hille, T. Irrgang and R. Kempe, *Chem. Eur. J.*, 2014, **20**, 5569.
7. K. Padmavathy, G. Nagendrappa and K. V. Geetha, *Tetrahedron Lett.*, 2011, **52**, 544.
8. M. Darabantu, L. Boully, A. Turck and N. Plé, *Tetrahedron*, 2005, **61**, 2897.
9. J. K. Lanquist and G. J. Stacey, *J. Chem. Soc.*, 1953, 2822.
10. Z. T. Bhutia, G. Prasannakumar, A. Das, M. Biswas, A. Chatterjee and M. Banerjee, *ChemistrySelect*, 2017, **2**, 1183.
11. S. A. Raw, C. D. Wilfred and R. J. K. Taylor, *Org. Biomol. Chem.*, 2004, **2**, 788.
12. R. W. Bost and E. E. Towell, *J. Am. Chem. Soc.*, 1948, **70**, 903.
13. F. Xie, M. Zhang, H. Jiang, M. Chen, W. Lv, A. Zheng and X. Jian, *Green Chem.*, 2015, **17**, 279.
14. L.-Y. Xi, R.-Y. Zhang, L. Zhang, S.-Y. Chen and X.-Q. Yu, *Org. Biomol. Chem.*, 2015, **13**, 3924.
15. C. S. Cho, B. T. Kim, H.-J. Choi, T.-J. Kim and S. C. Shim, *Tetrahedron*, 2003, **59**, 7997.
16. J. Jacob and W. D. Jones, *J. Org. Chem.*, 2003, **68**, 3563.
17. W. Lv, B. Xiong, H. Jiang and M. Zhang, *Adv. Synth. Catal.*, 2017, **359**, 1202.
18. T. Rodrigues, D. Reker, J. Kunze, P. Schneider and G. Schneider, *Angew. Chem. Int. Ed.*, 2015, **54**, 10516.
19. R. Martínez, D. J. Ramón and M. Yus, *J. Org. Chem.*, 2008, **73**, 9778.
20. R. Wang, H. Fan, W. Zhao and F. Li, *Org. Lett.*, 2016, **18**, 3558.
21. Y.-F. Liang, X.-F. Zhou, S.-Y. Tang, Y.-B. Huang, Y.-S. Feng and H.-J. Xu, *RSC Adv.*, 2013, **3**, 7739.
22. M. Maji, K. Chakrabarti, B. Paul, B. C. Roy and S. Kundu, *Adv. Synth. Catal.*, 2018, **360**, 722.

11. Copies of ^{1}H and ^{13}C NMR Spectra



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7.9776
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7.6987
7.6947
7.2503
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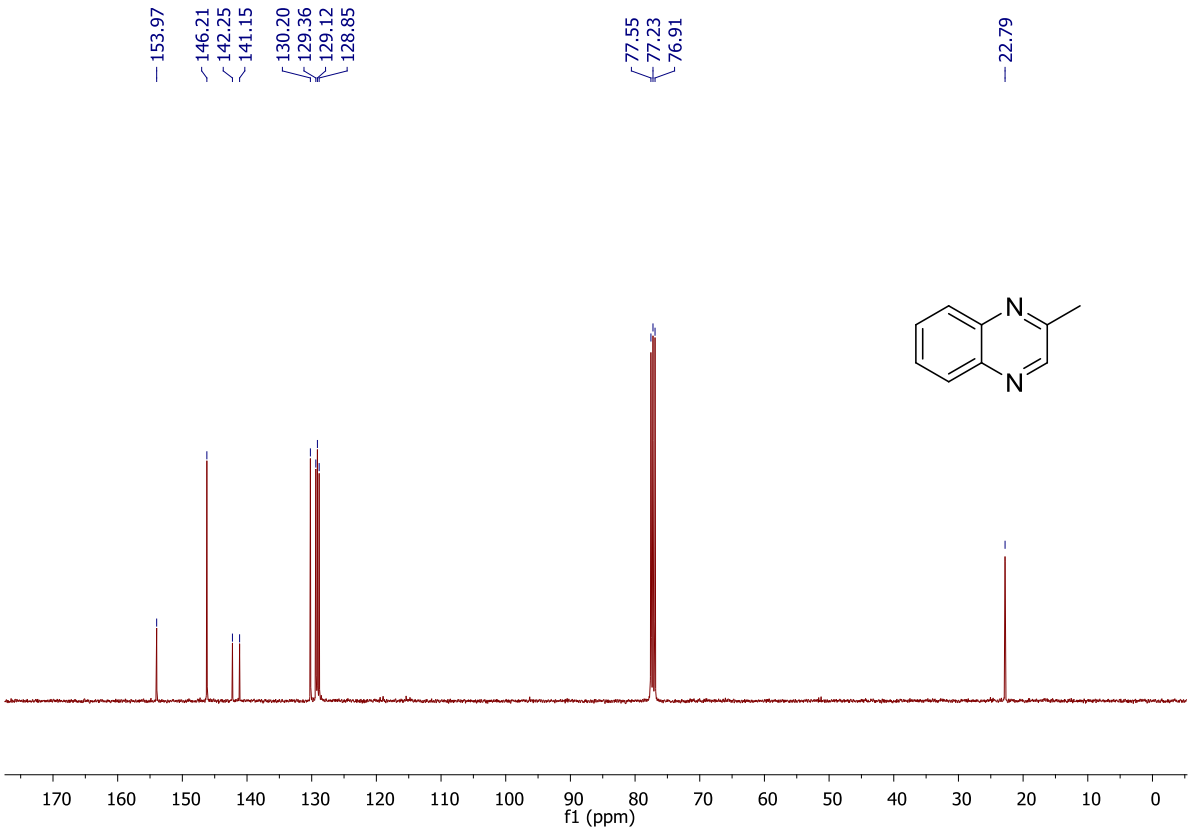
1.00
1.00
1.01
2.15
3.08
f1 (ppm)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130.20
129.36
129.12
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77.55
77.23
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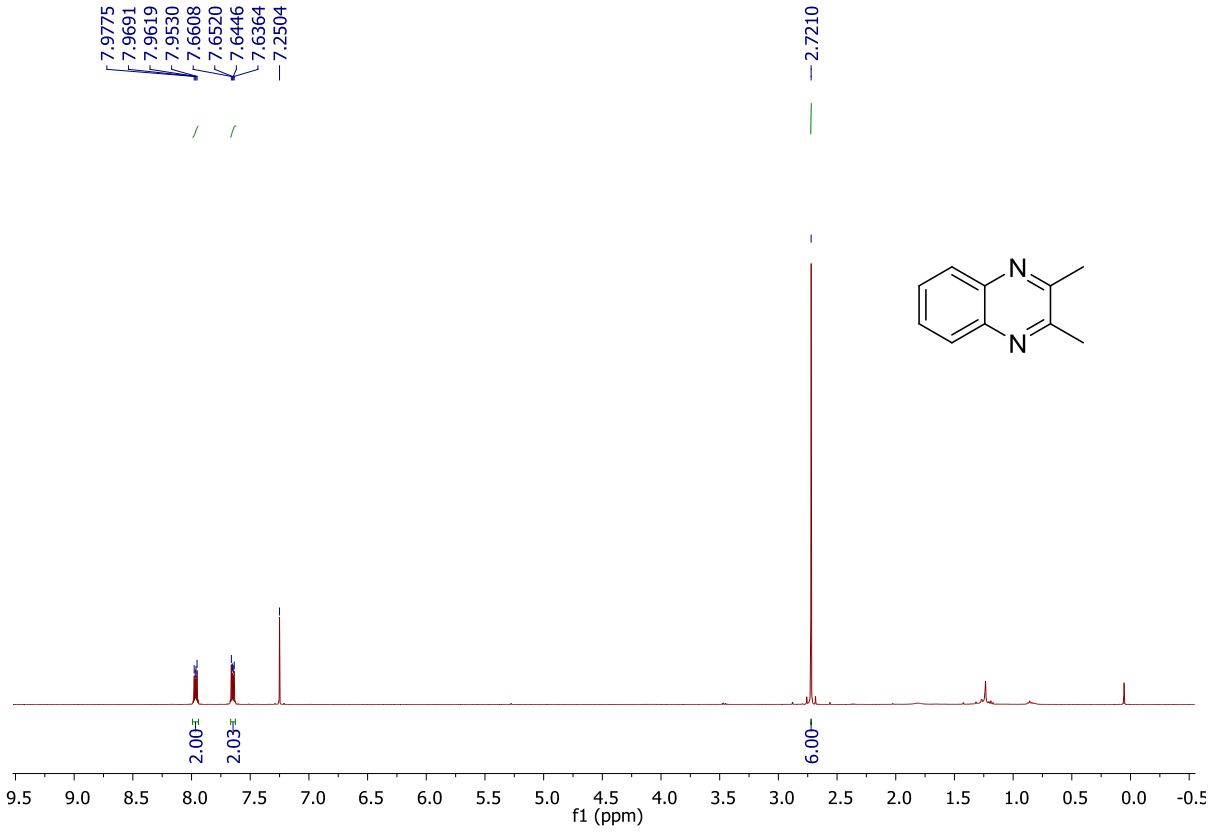
22.79
f1 (ppm)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7.9530
7.6608
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7.6446
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N
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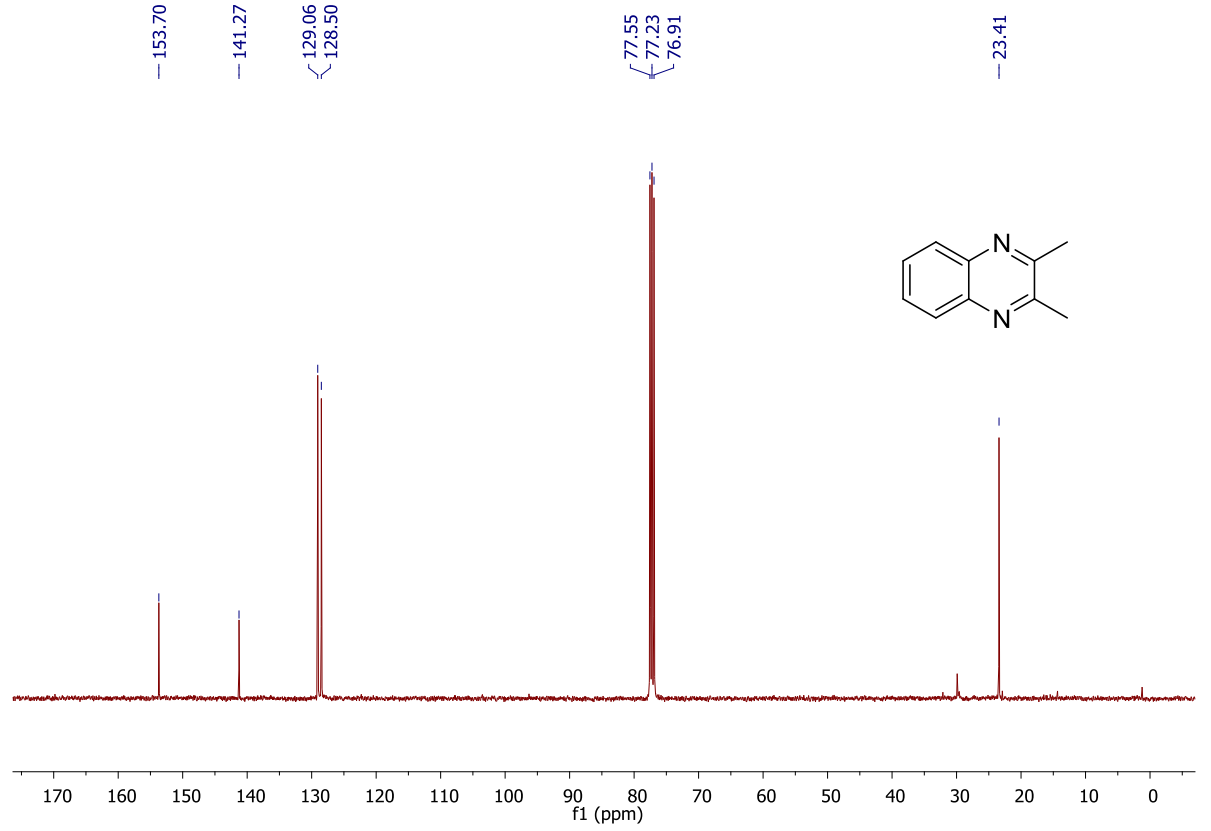
2.03
6.00
f1 (ppm)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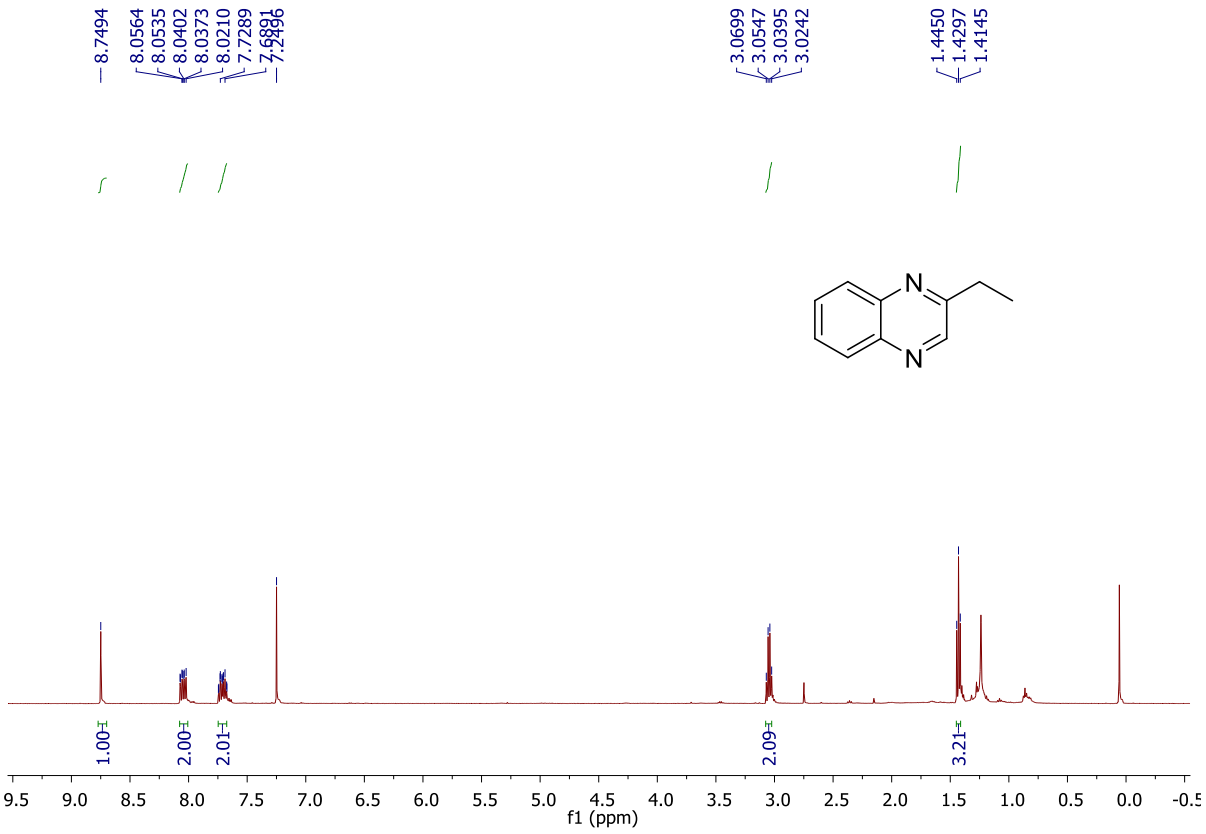
f1 (ppm)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N
N
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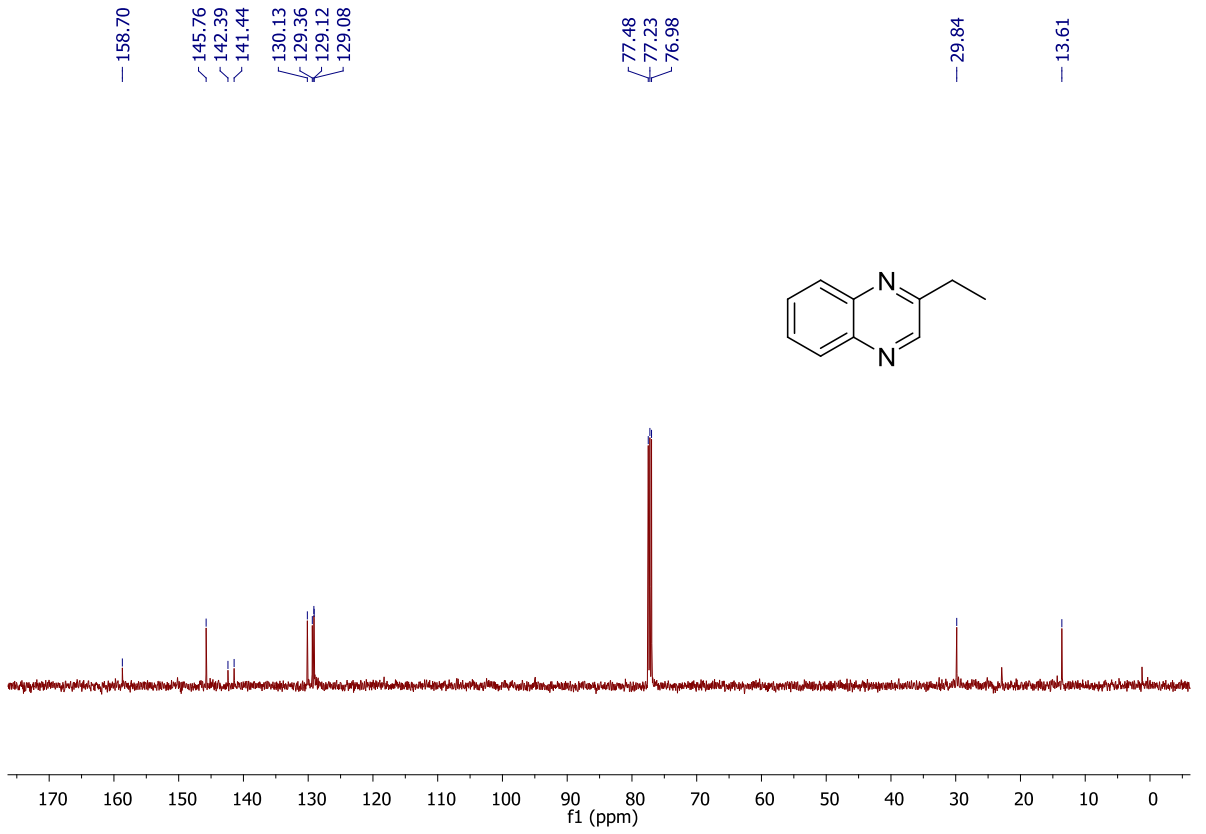
2.00
2.01
2.09
3.21
f1 (ppm)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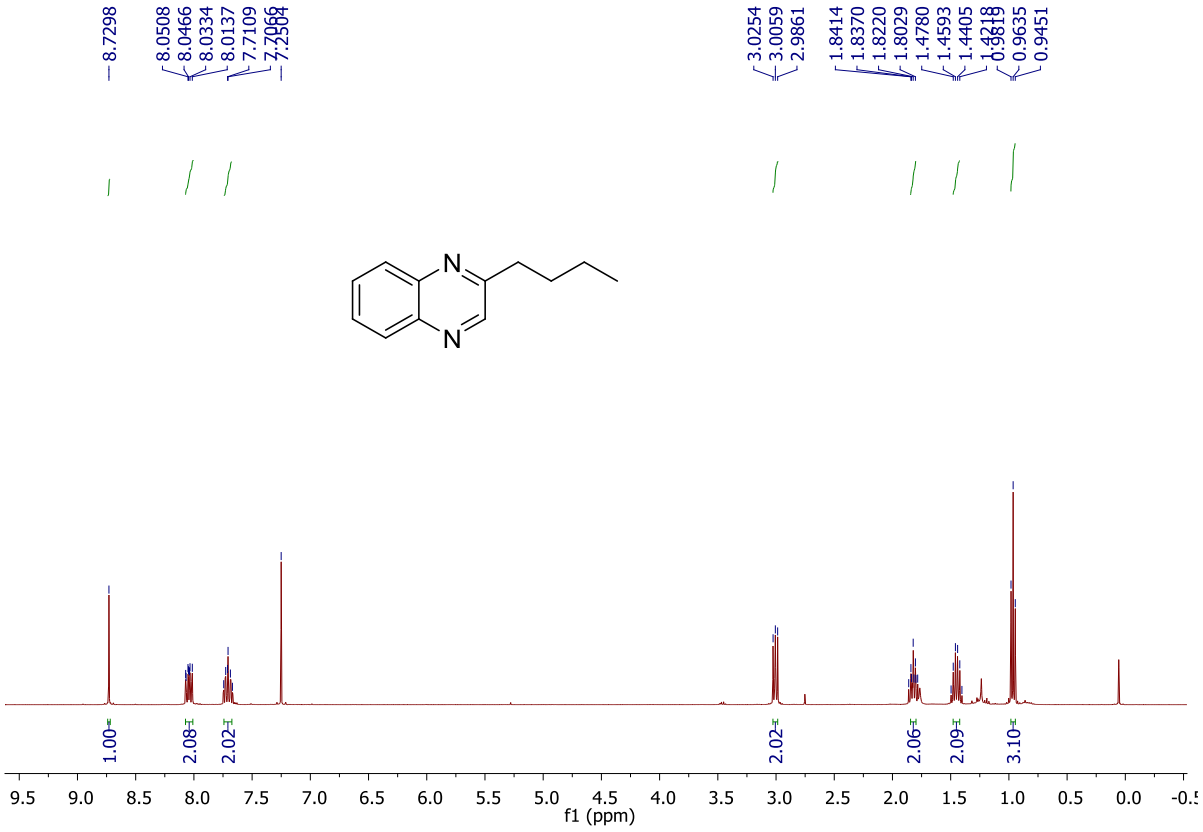
N
f1 (ppm)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1.8220
1.8029
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2.02
2.02
2.06
2.09
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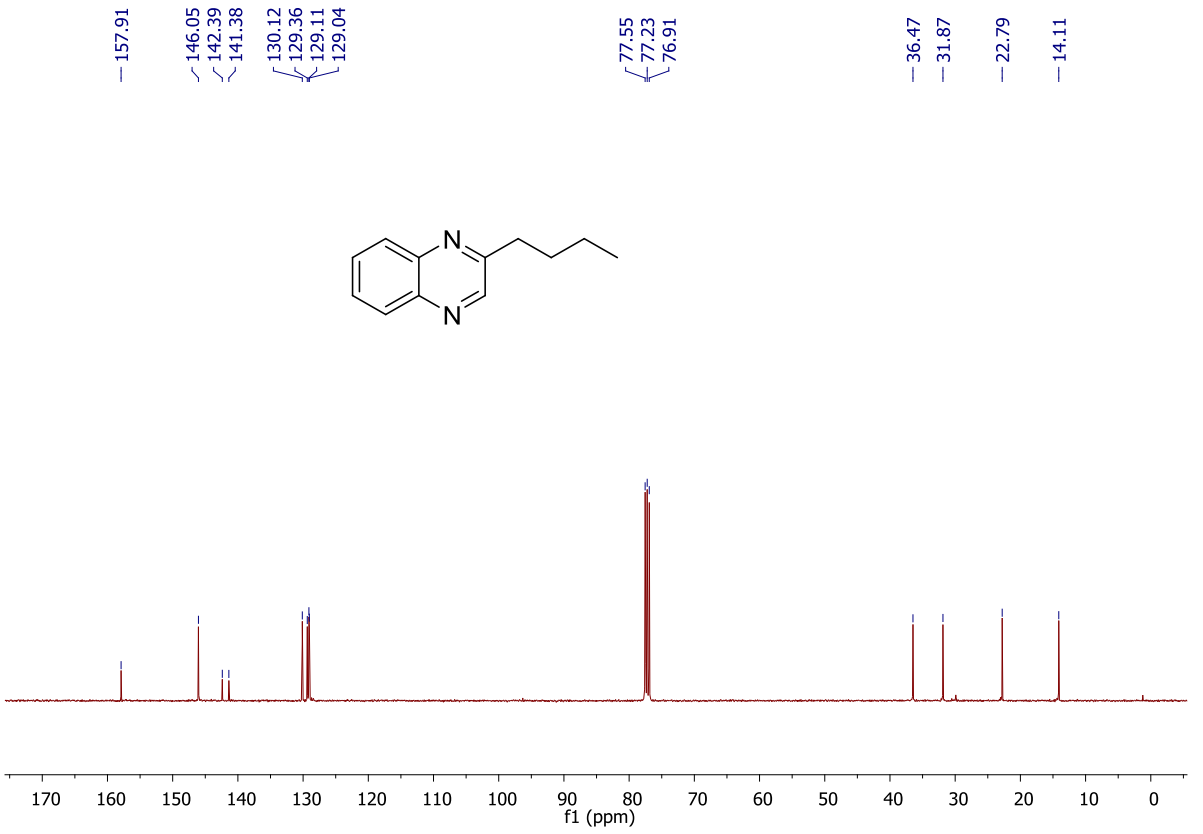
f1 (ppm)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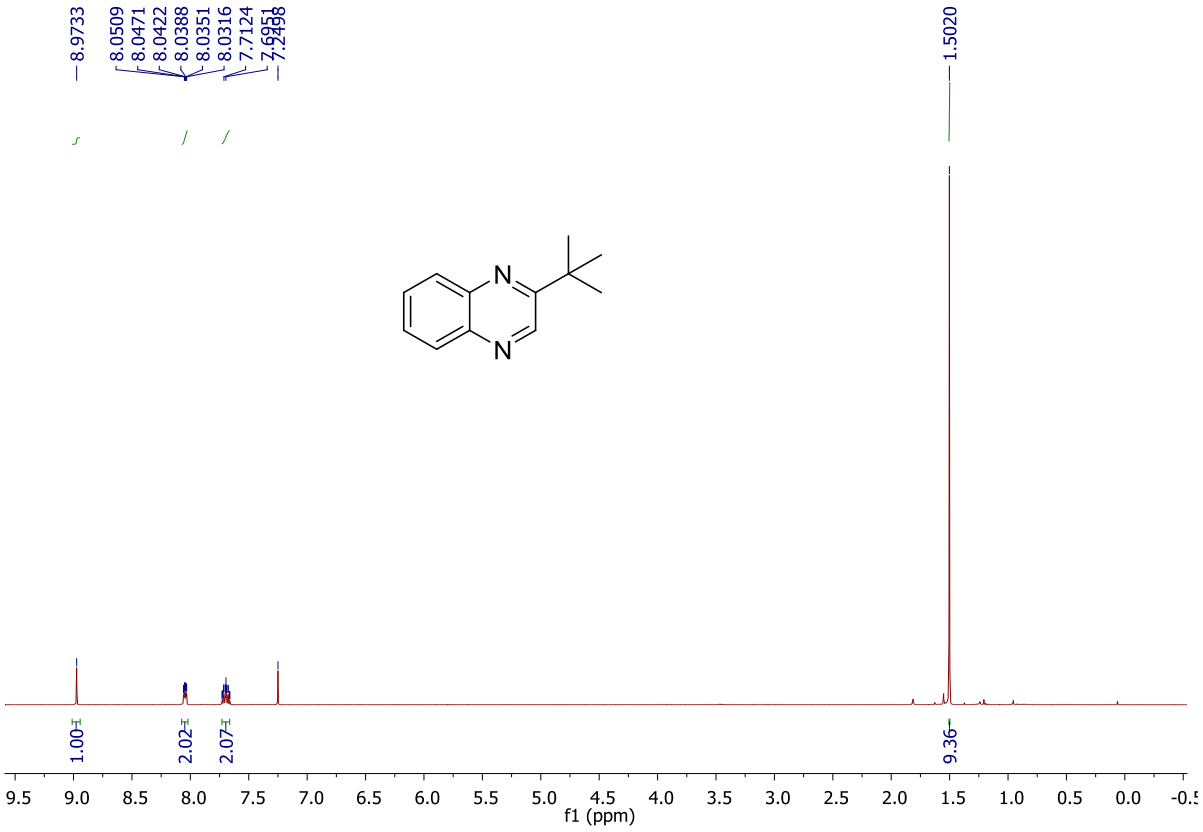
14.11
f1 (ppm)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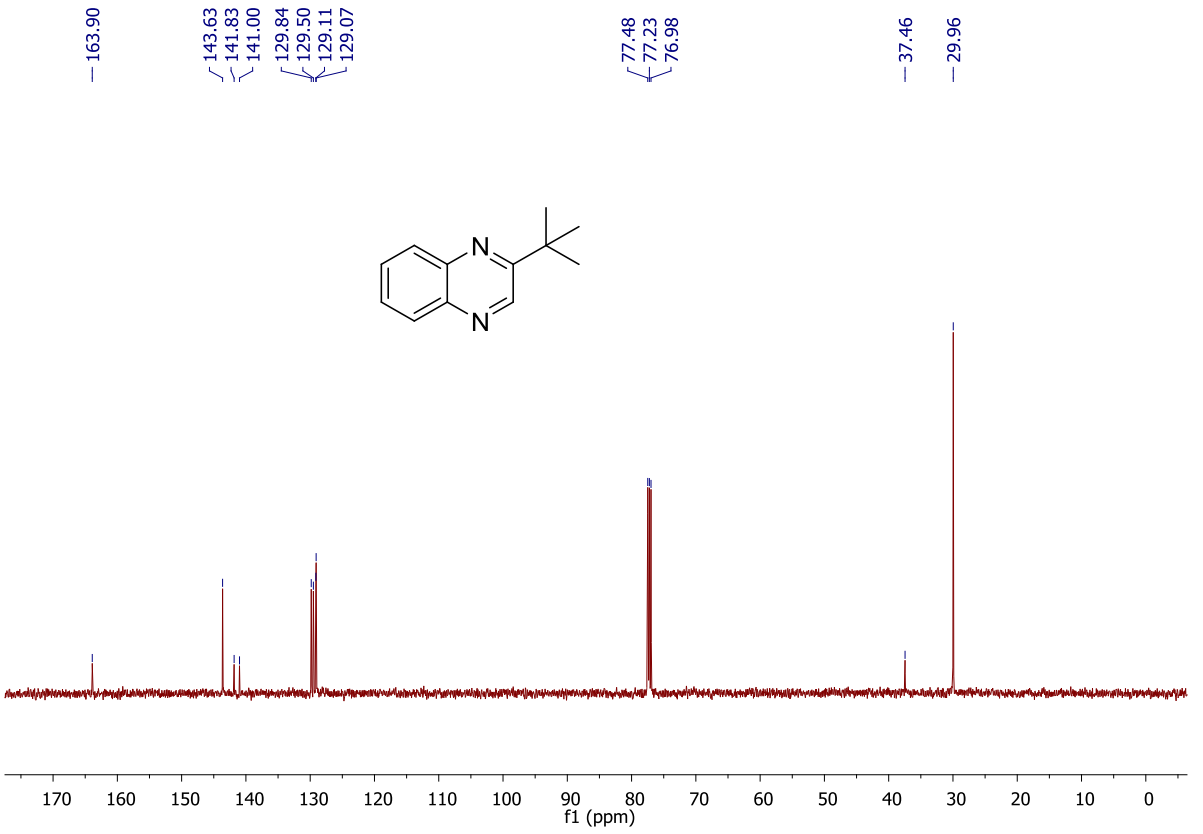
9.36
f1 (ppm)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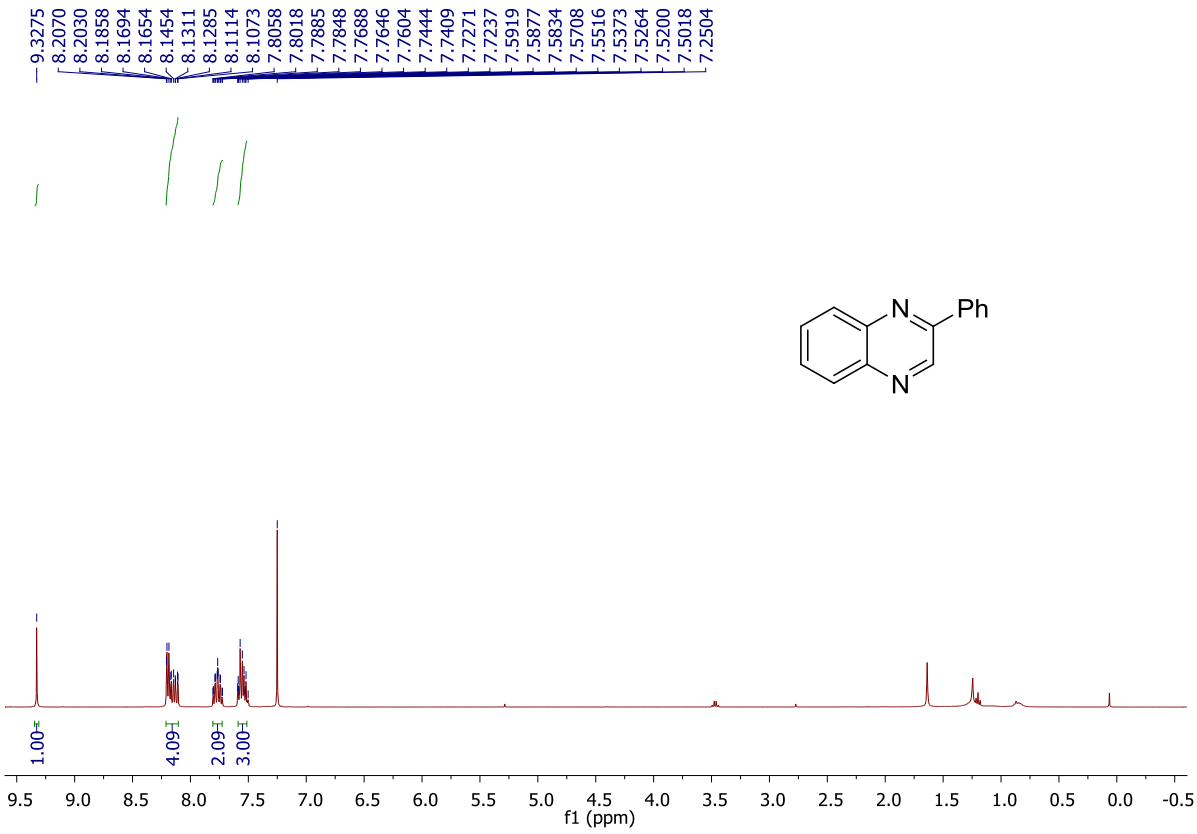
f1 (ppm)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7.5264
7.5200
7.5018
7.2504
N
Ph
N
1.00
4.09
2.09
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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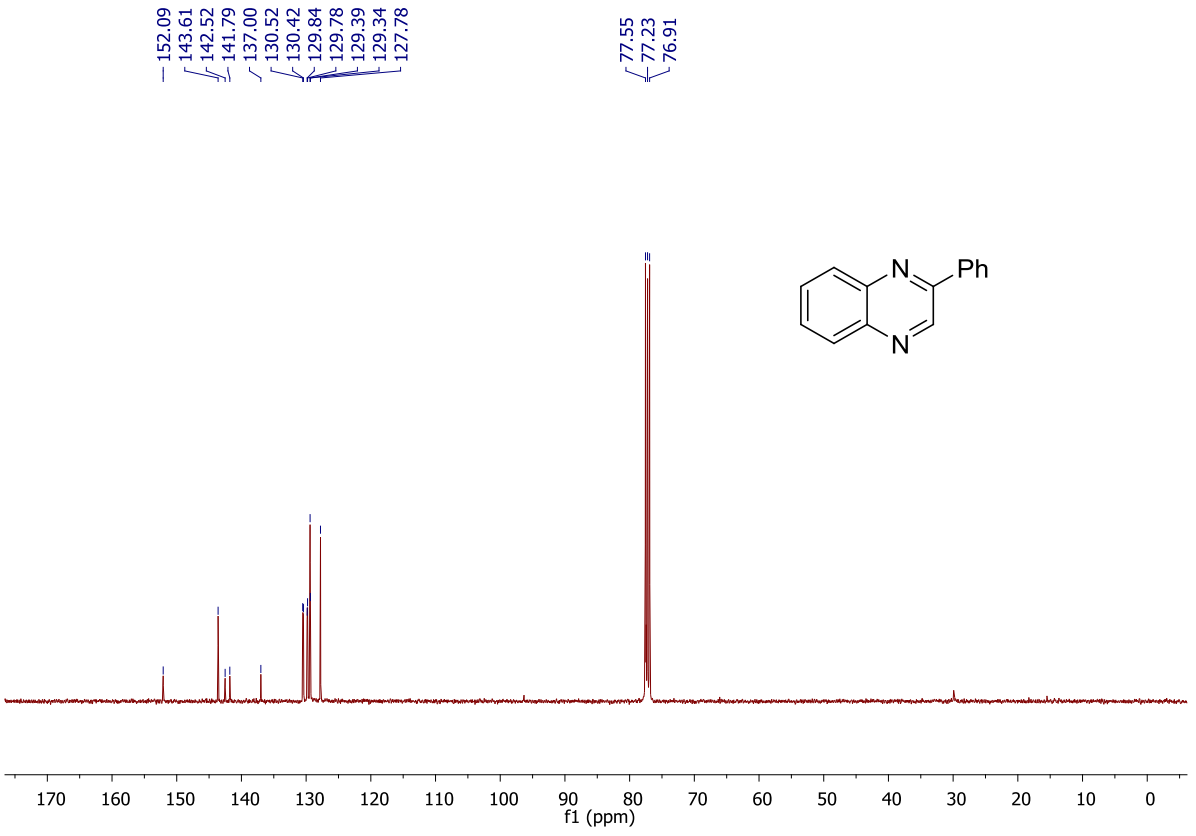
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129.84
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129.39
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77.23
76.91
N
Ph
N
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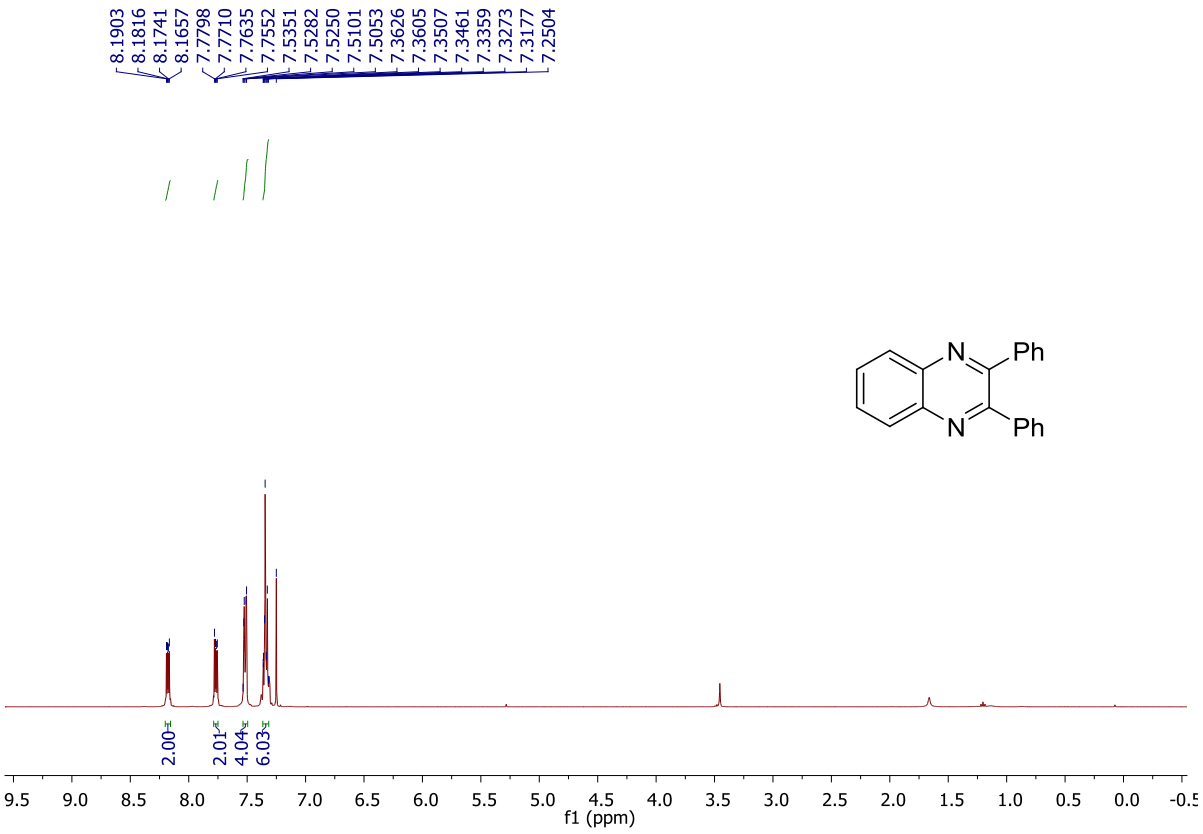
f1 (ppm)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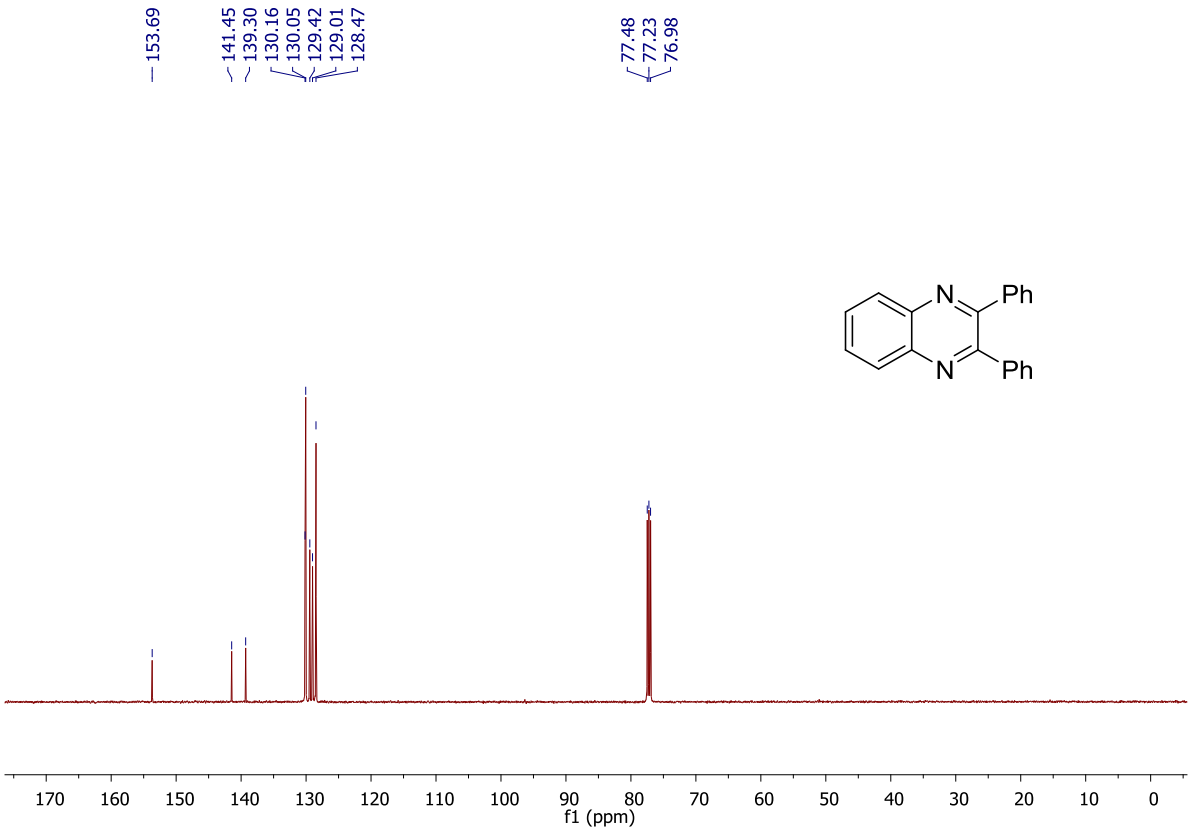
7.5250
7.5101
7.5053
7.3626
7.3605
7.3507
7.3461
7.3359
7.3273
7.3177
7.2504
N
Ph
N
Ph
2.00
2.01
4.04
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.01
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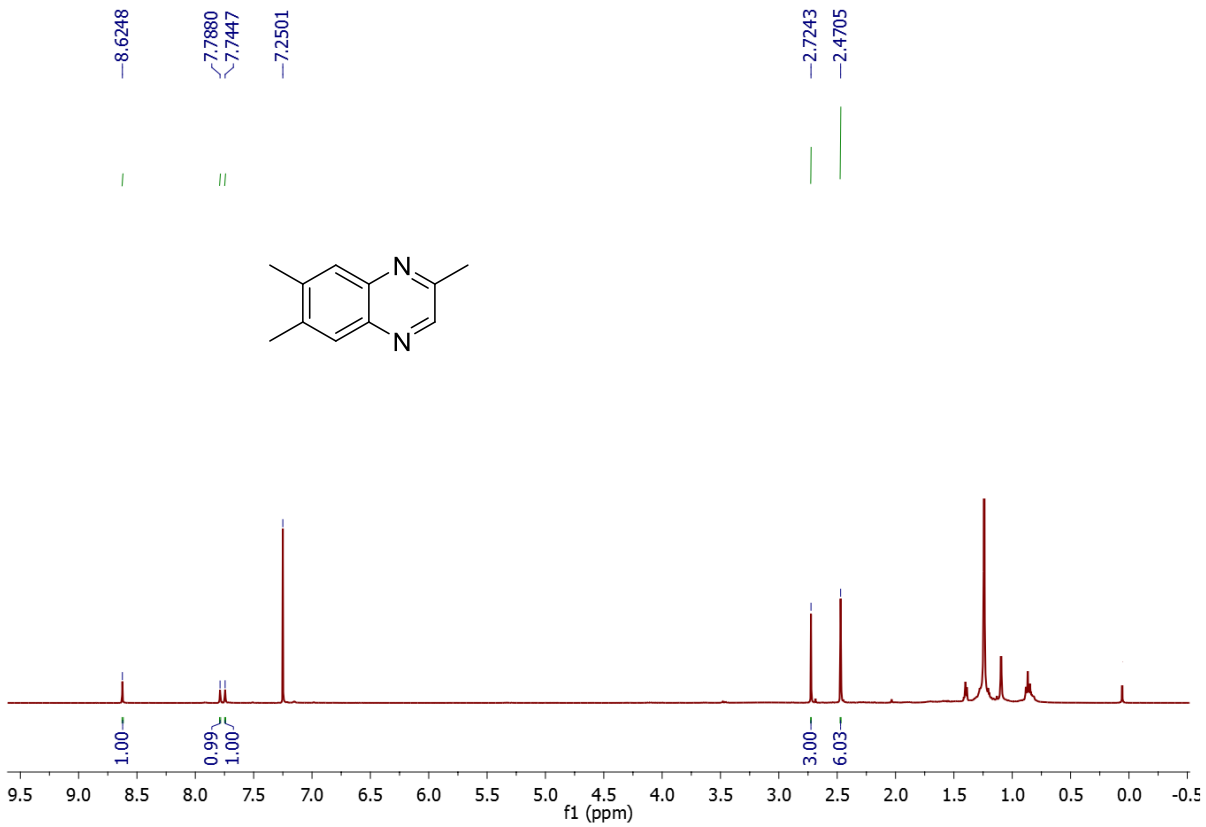
77.23
76.98
N
Ph
N
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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2.7243
2.4705
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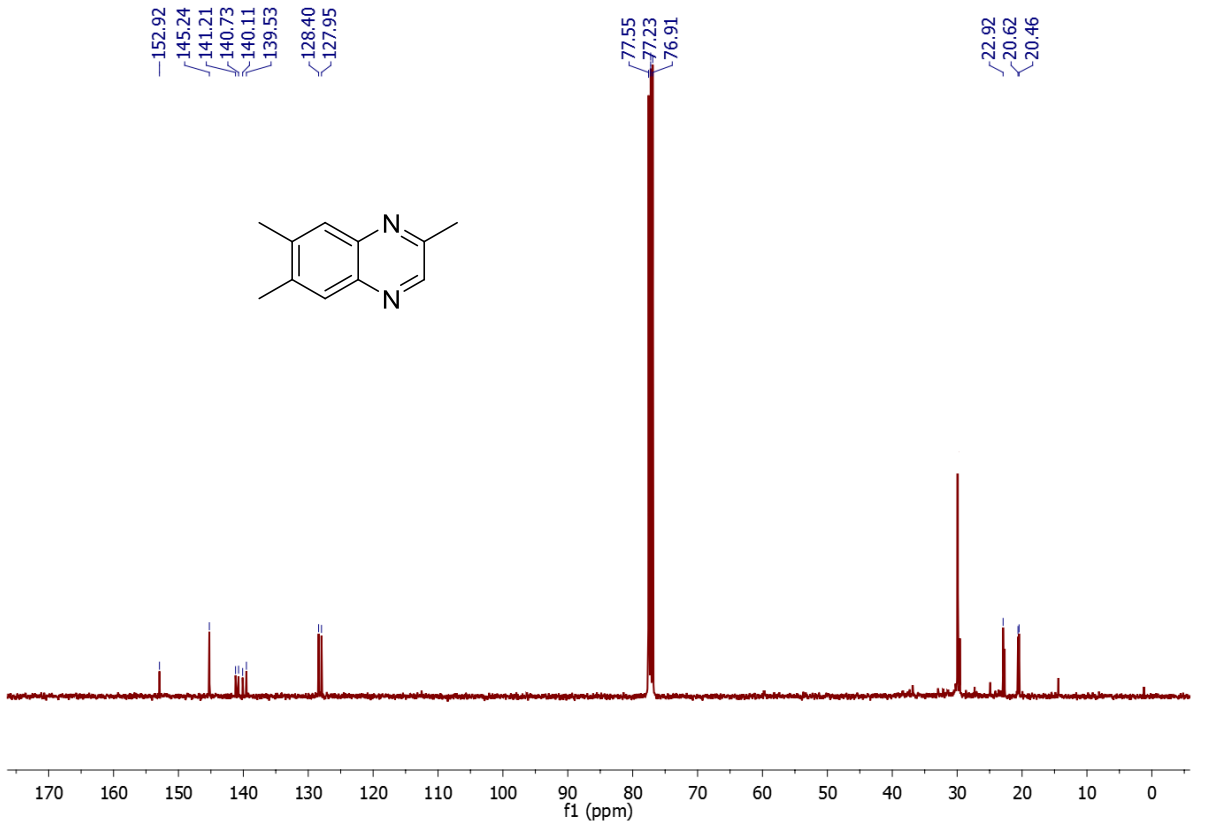
0.99
1.00
3.00
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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22.92
20.62
20.46
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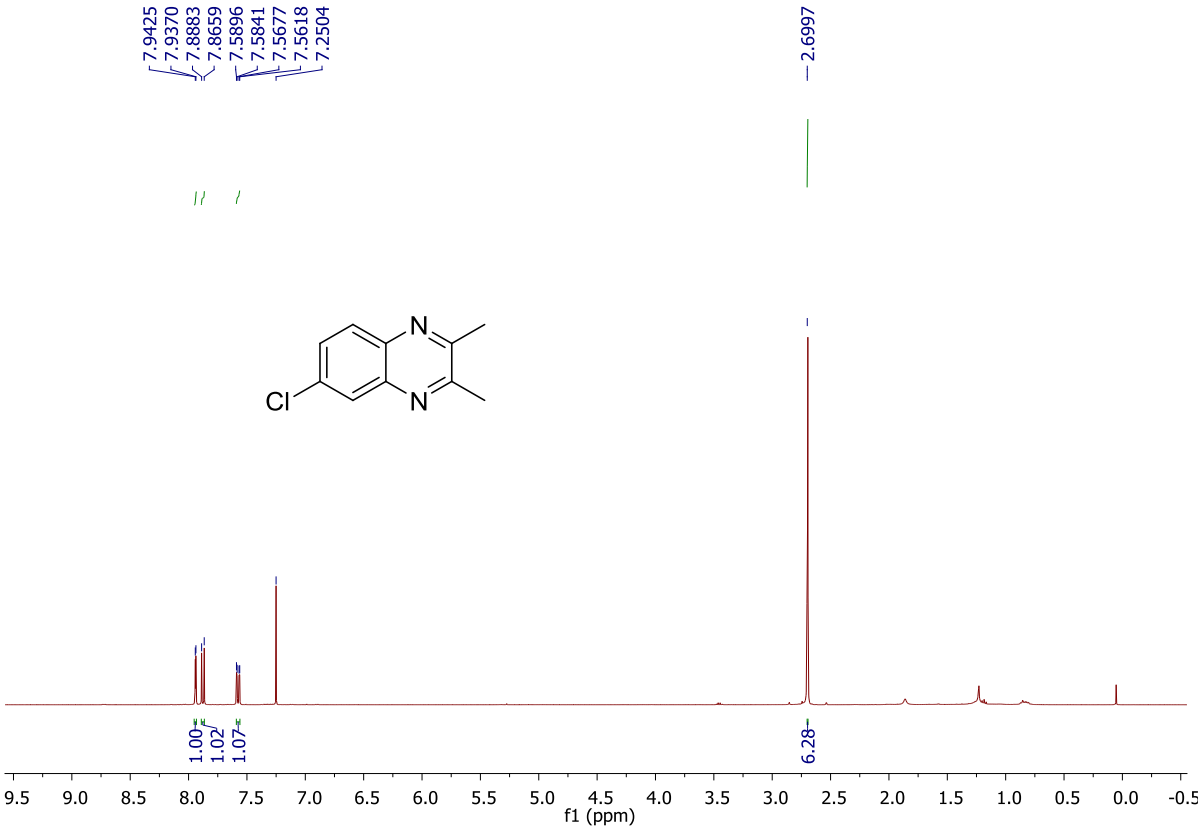
f1 (ppm)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7.8883
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7.5896
7.5841
7.5677
7.5618
7.2504
2.6997
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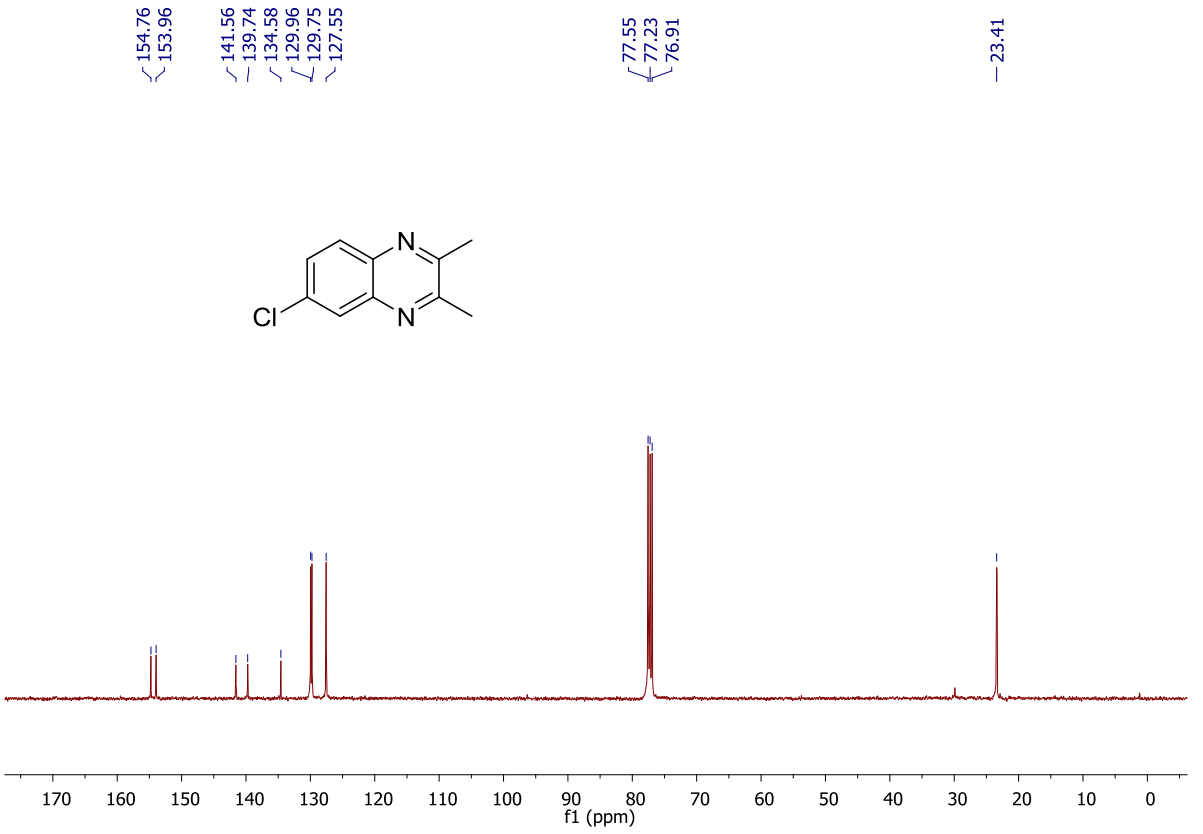
1.00
1.02
1.07
6.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.96
129.75
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76.91
23.41
Cl
N
N
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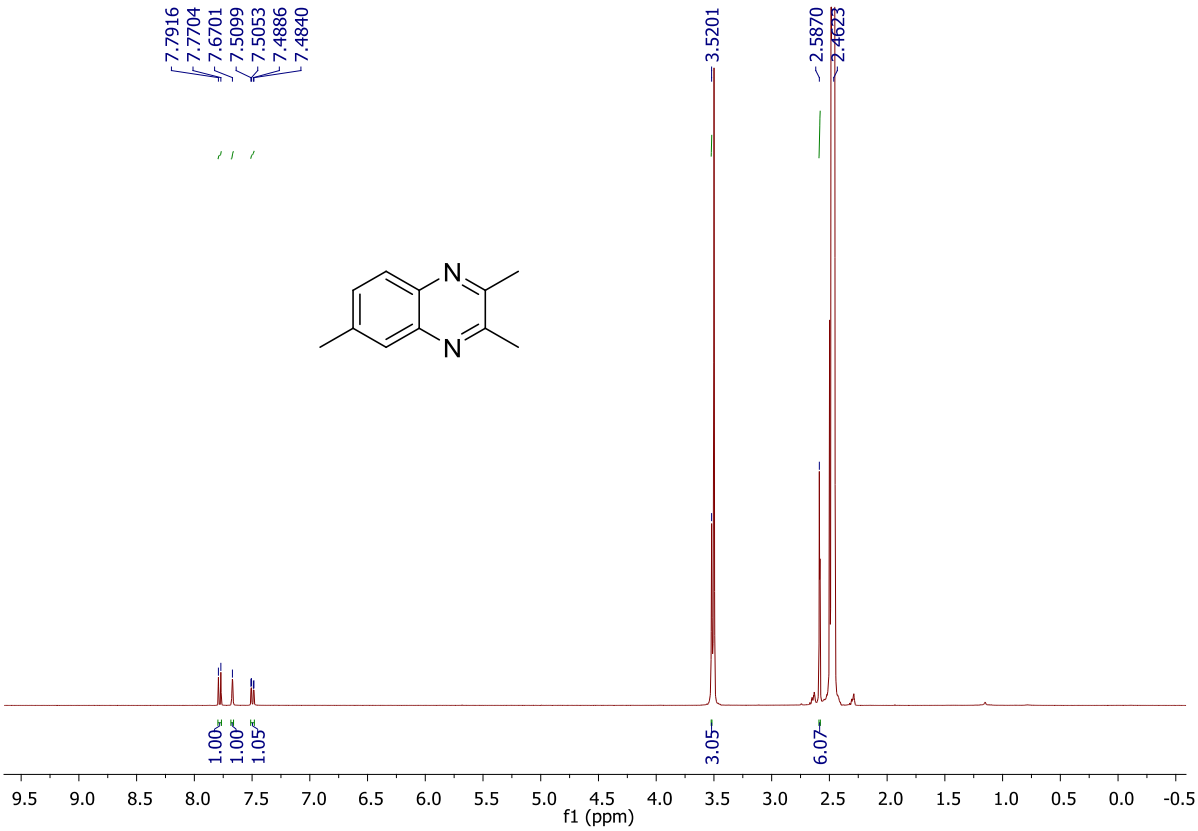
f1 (ppm)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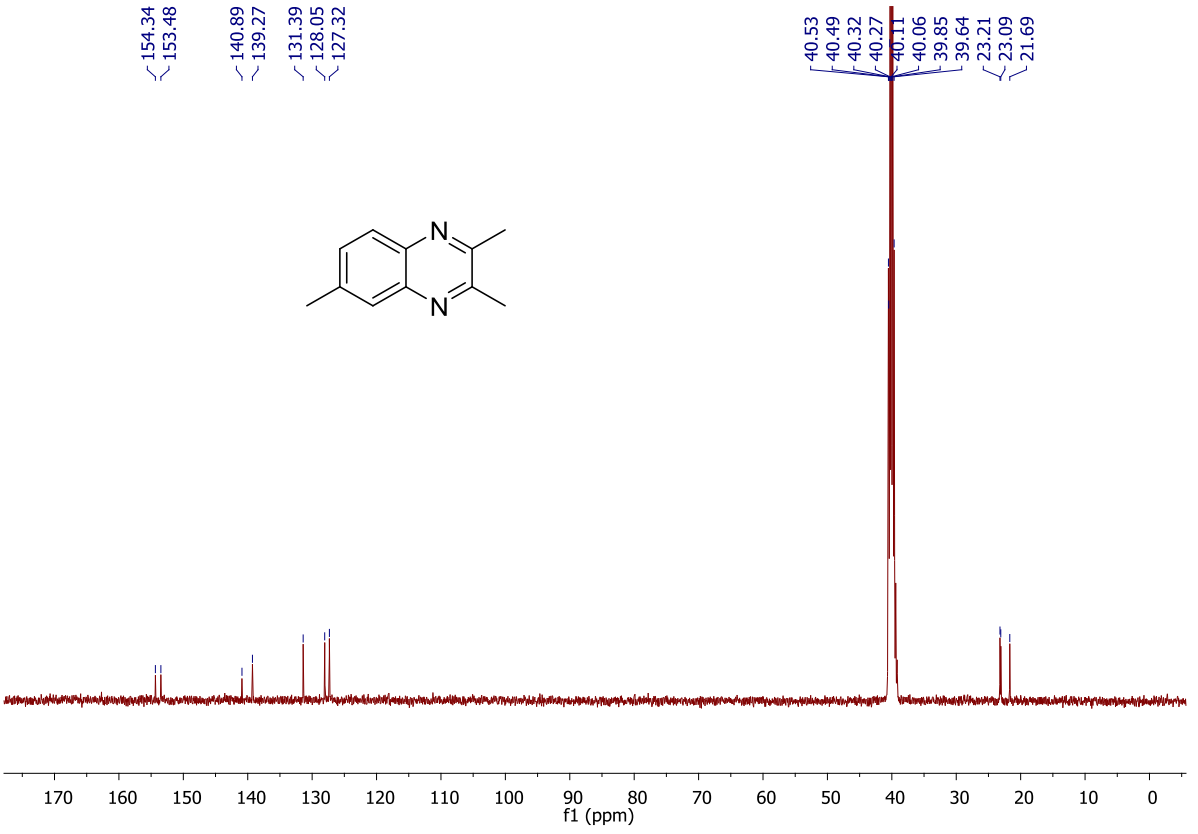
7.4886
7.4840
3.5201
2.5870
2.4623
N
N
1.00
1.00
1.05
3.05
6.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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140.89
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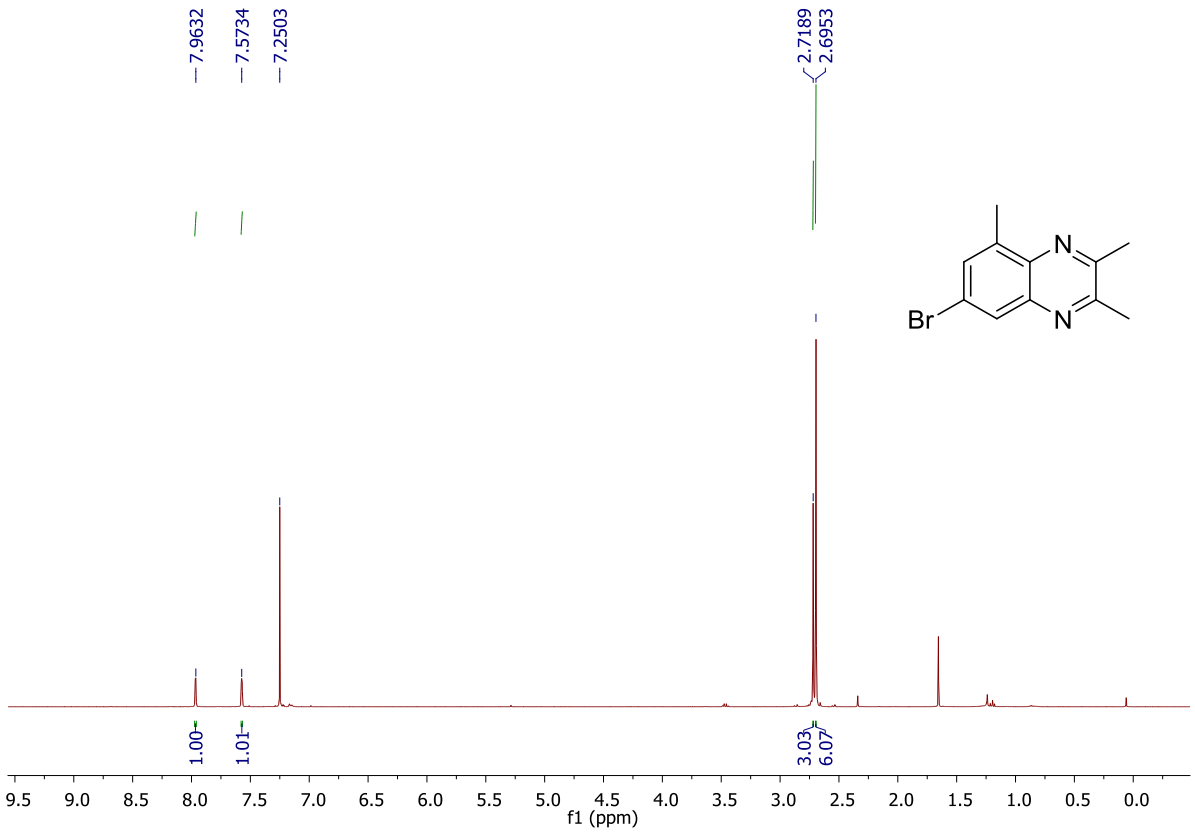
131.39
128.05
127.32
40.53
40.49
40.32
40.27
40.11
40.06
39.85
39.64
23.21
23.09
21.69
N
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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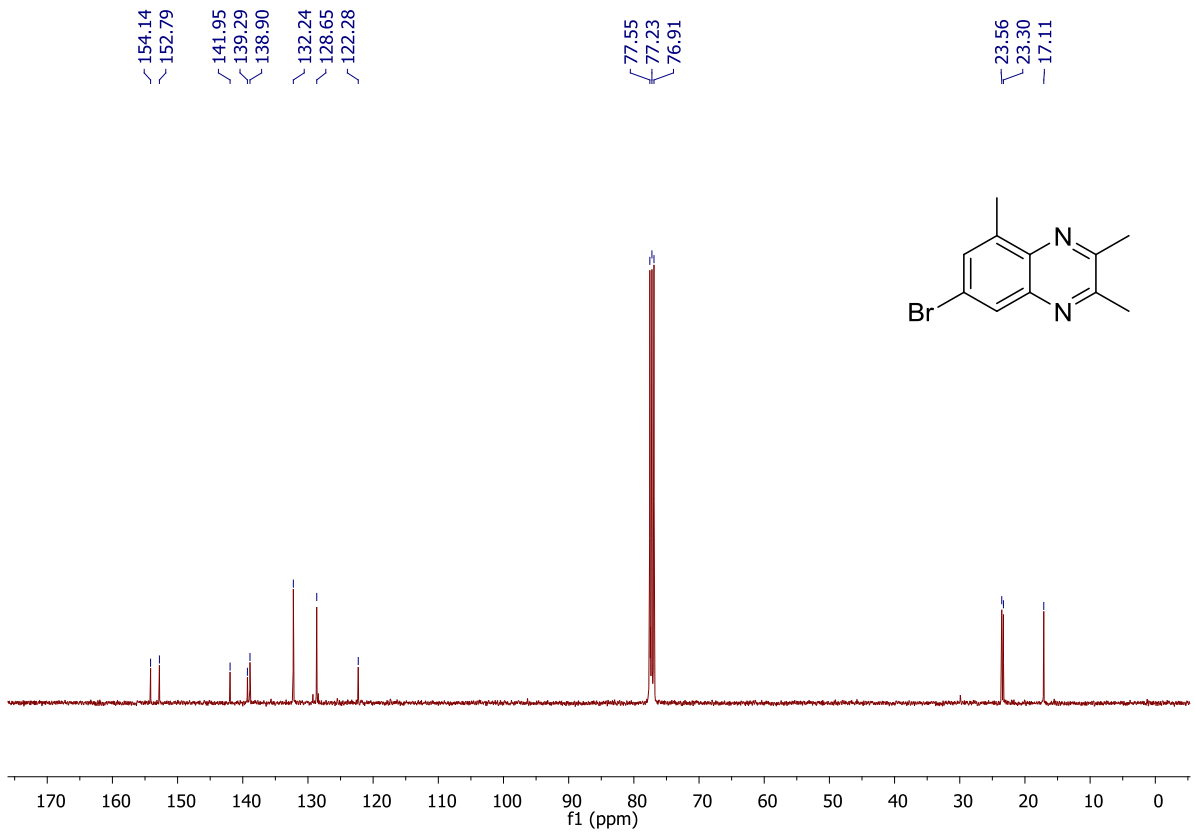
7.5734
7.2503
2.7189
2.6953
1.00
1.01
3.03
6.07
Br
N
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.79
141.95
139.29
138.90
132.24
128.65
122.28
77.55
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76.91
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23.30
17.11
Br
N
N
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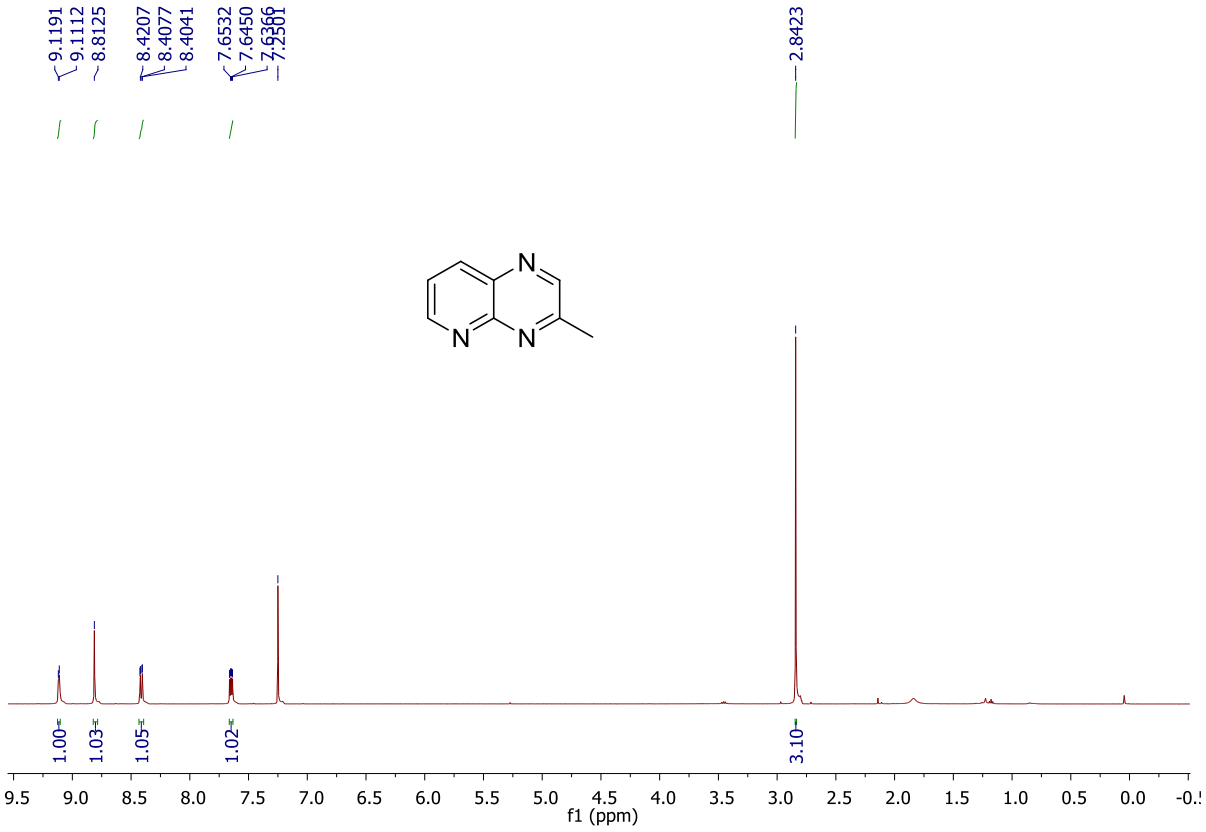
f1 (ppm)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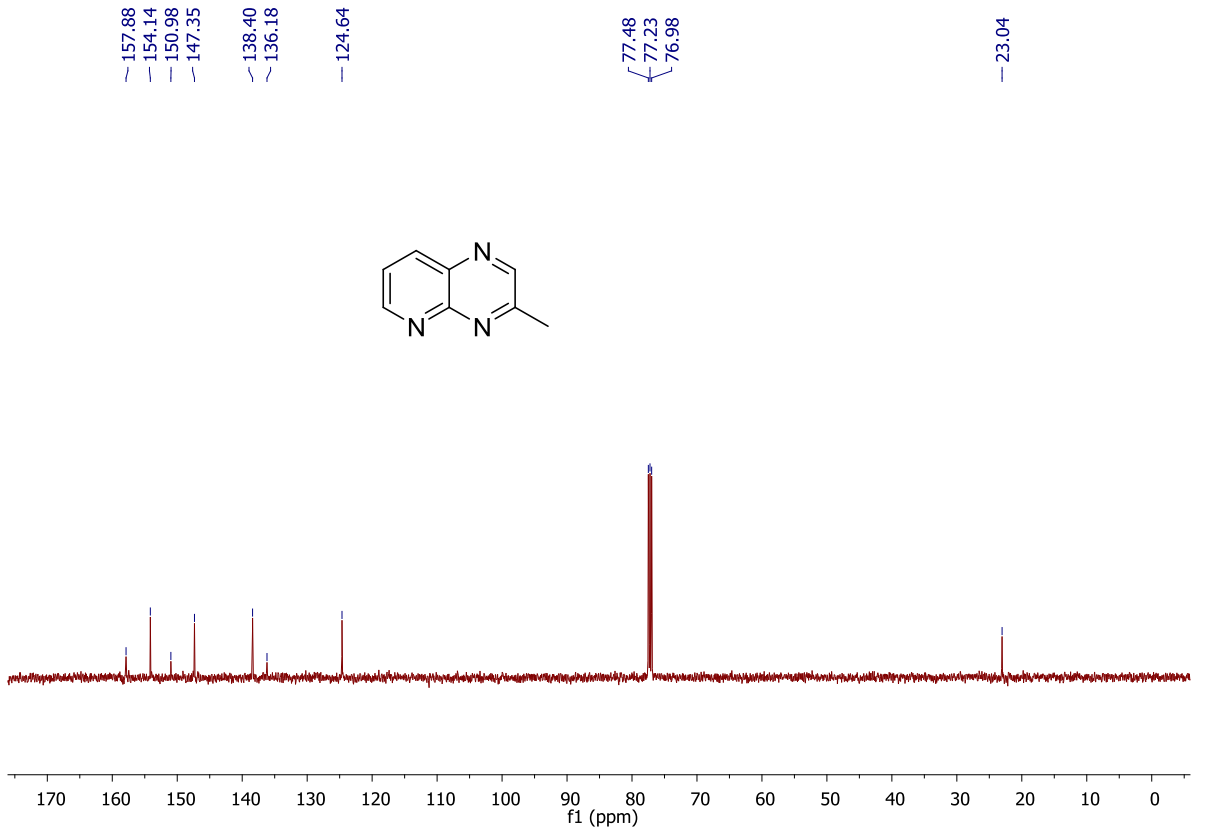
8.8125
8.4207
8.4077
8.4041
7.6532
7.6450
2.8423
1.00
1.03
1.05
1.02
3.10
f1 (ppm)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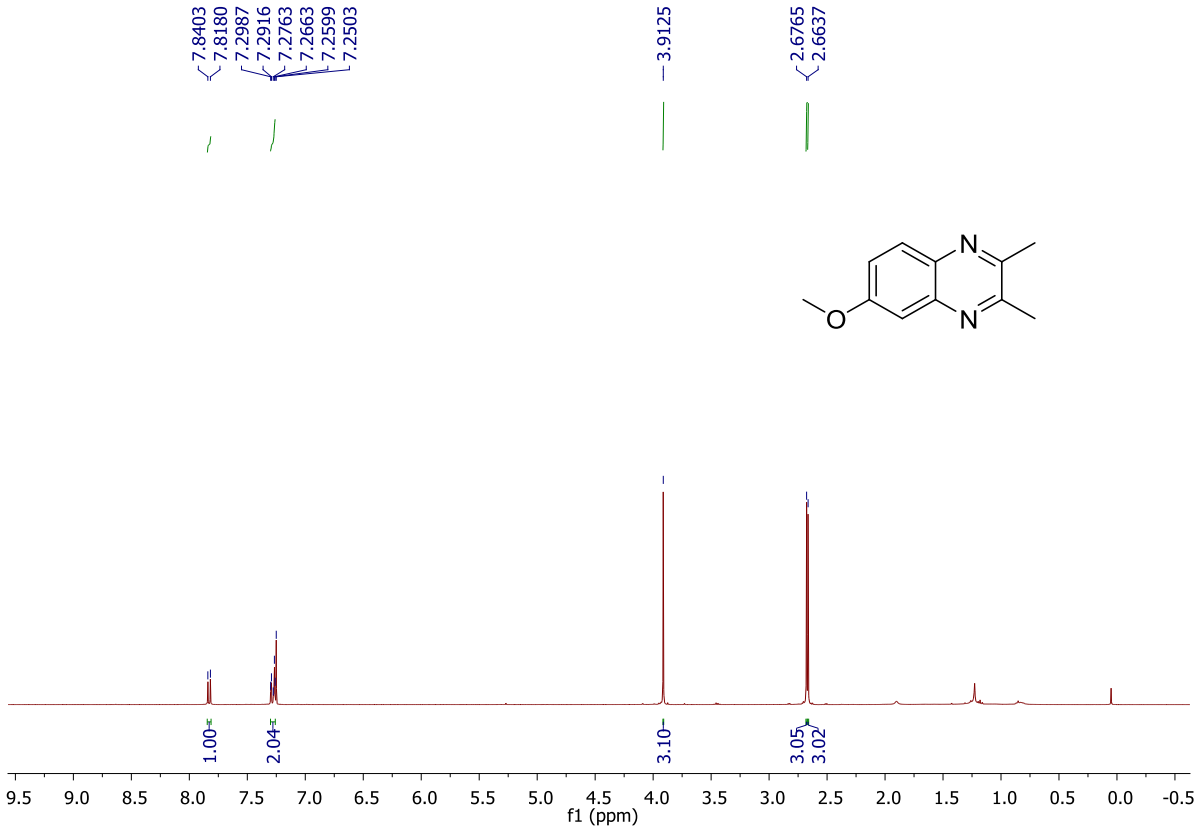
77.48
77.23
76.98
23.04
f1 (ppm)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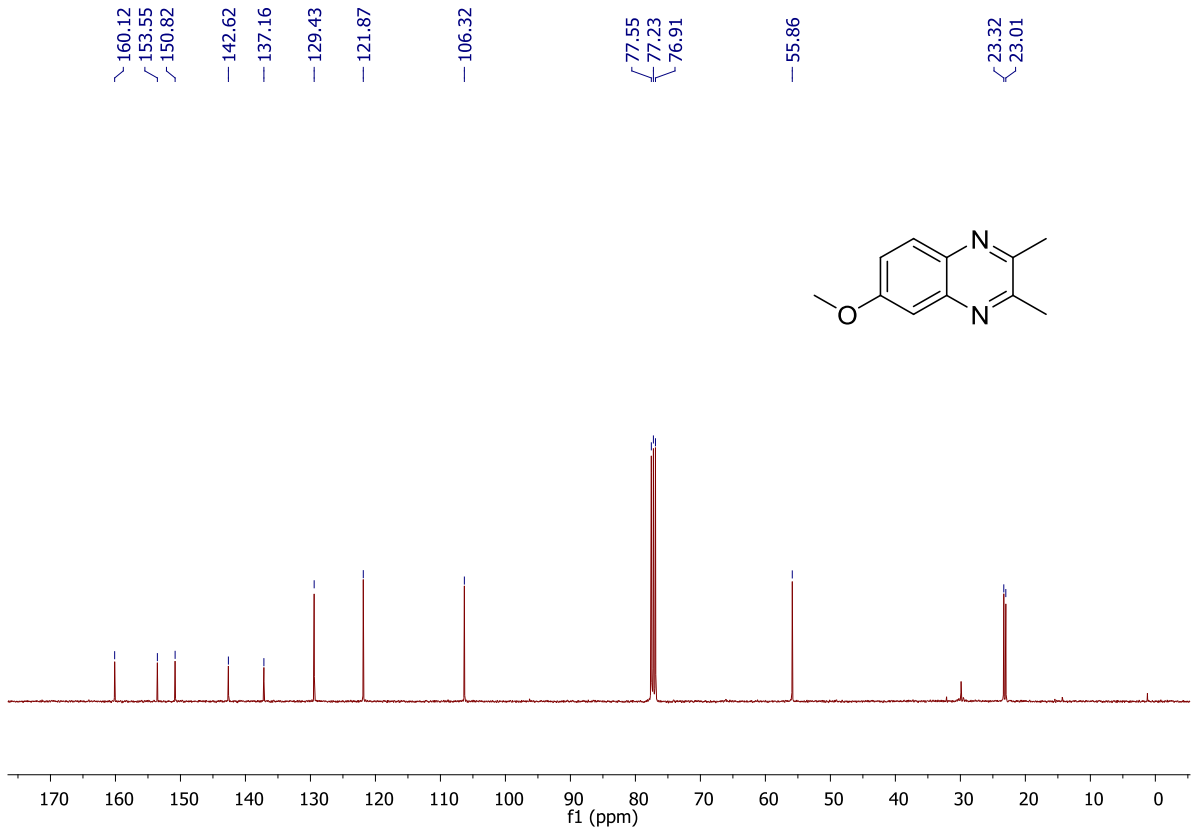
7.2763
7.2663
7.2599
7.2503
3.9125
2.6765
2.6637
N
O
N
1.00
2.04
3.10
3.05
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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106.32
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76.91
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23.32
23.01
N
O
N
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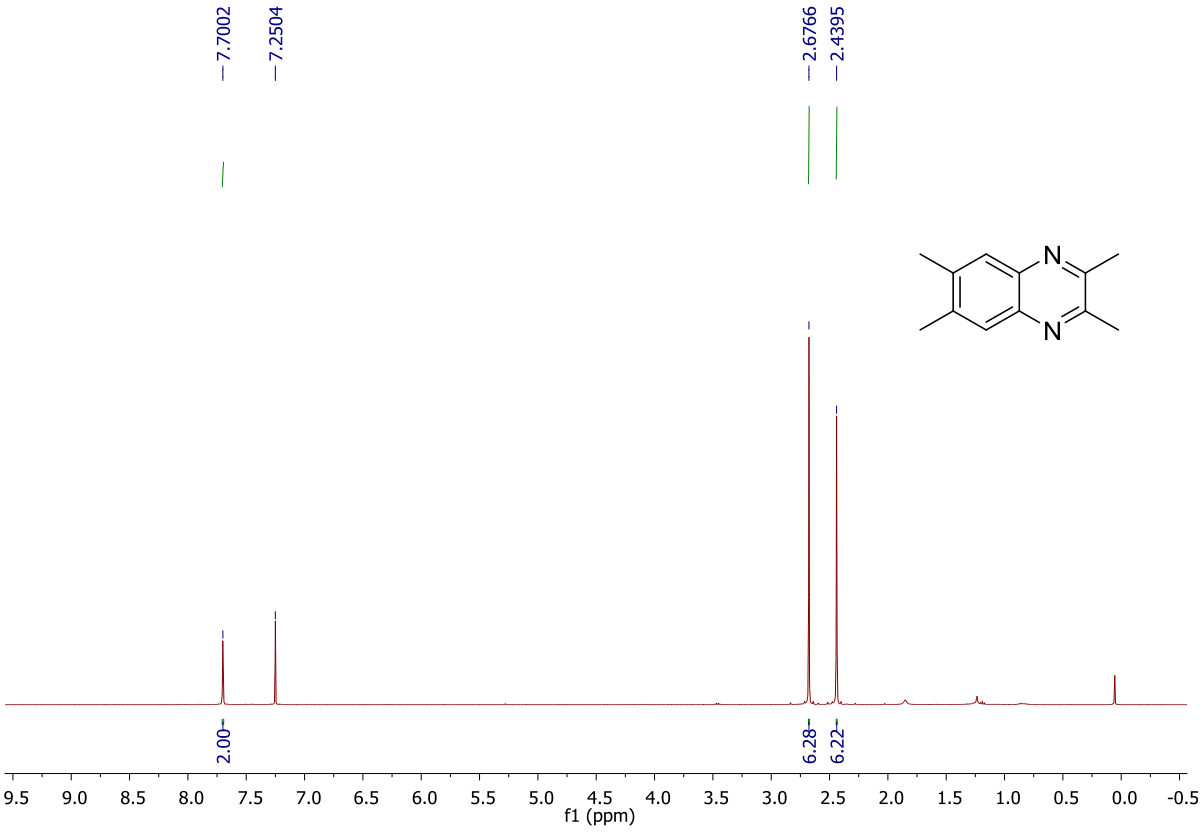
f1 (ppm)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2.6766
2.4395
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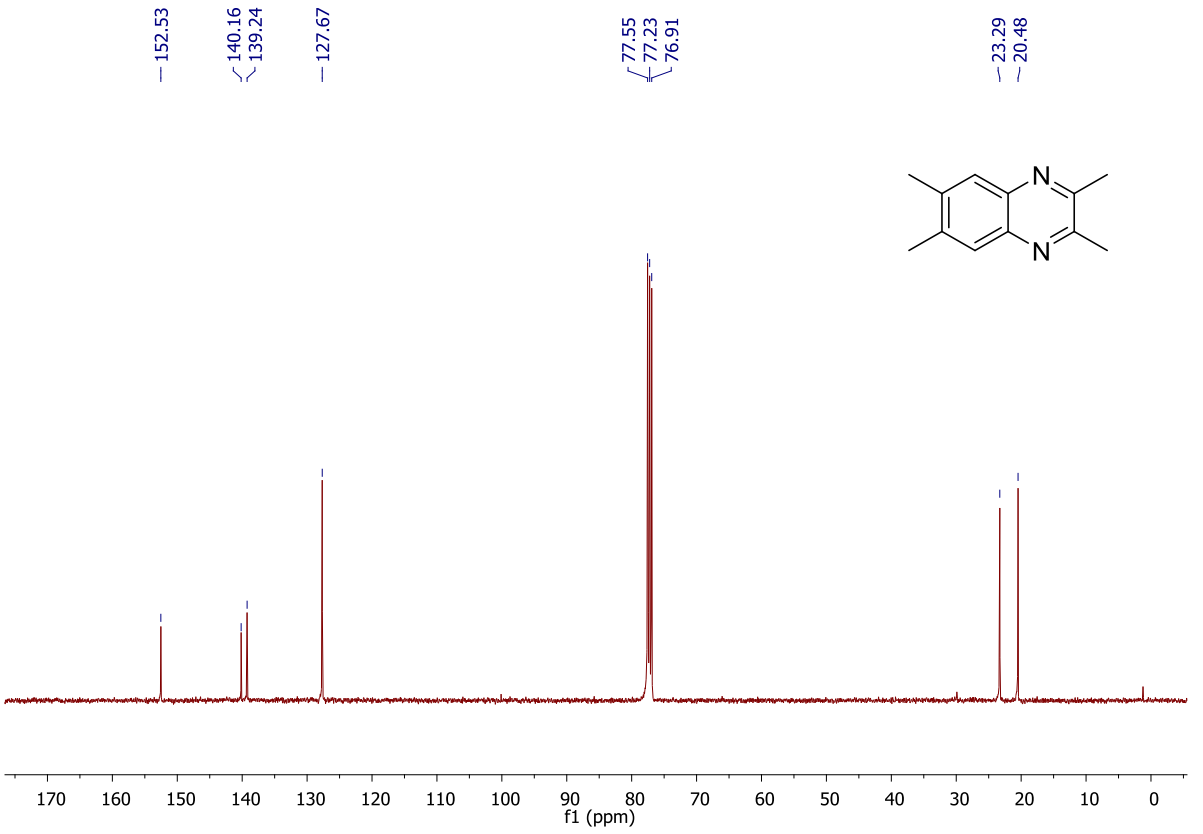
2.00
6.28
6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.23
76.91
23.29
20.48
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N
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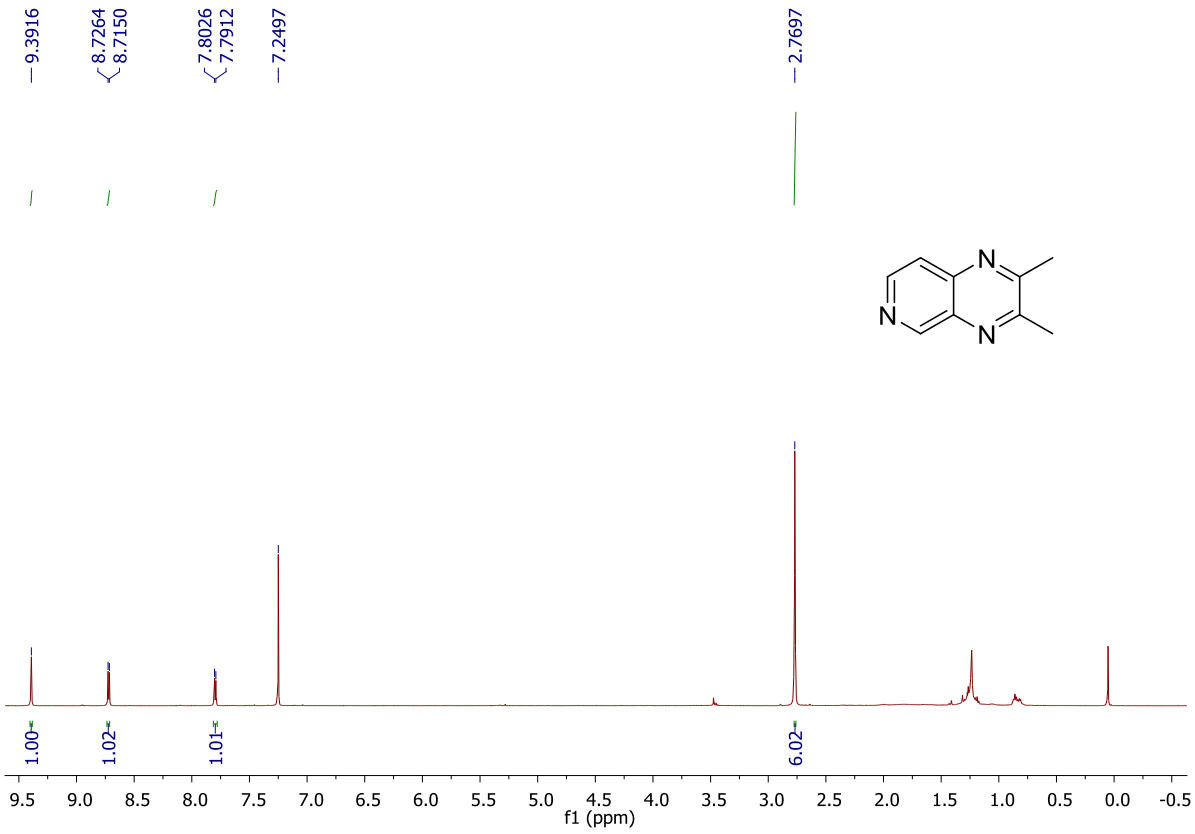
f1 (ppm)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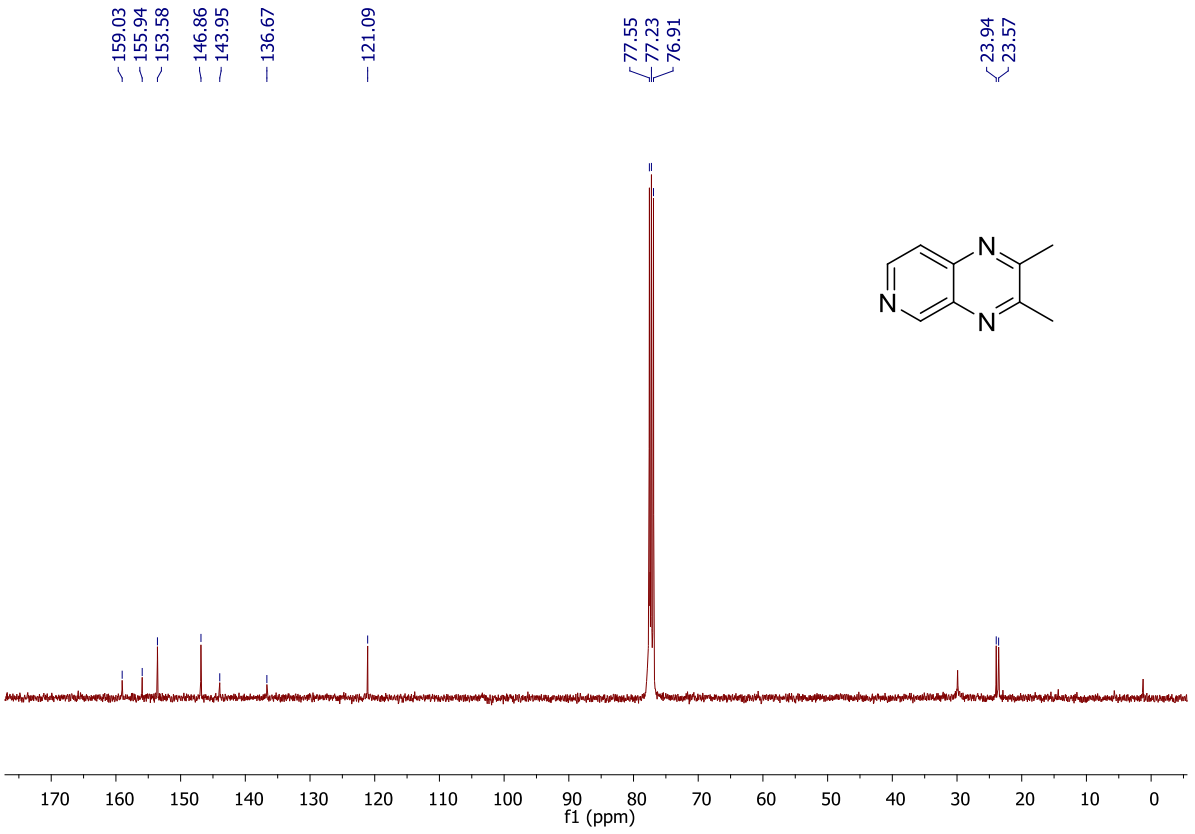
7.7912
7.2497
2.7697
1.00
1.02
1.01
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.23
76.91
23.94
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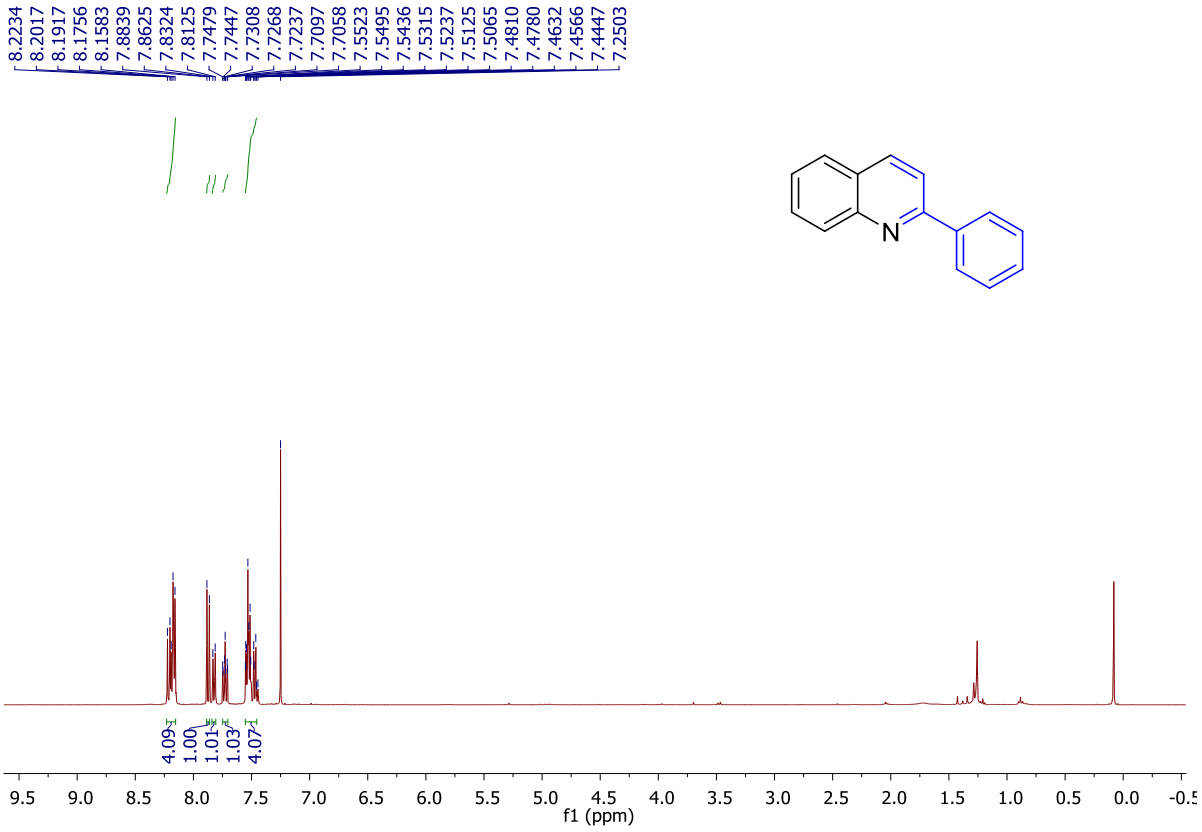
f1 (ppm)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7.5436
7.5315
7.5237
7.5125
7.5065
7.4810
7.4780
7.4632
7.4566
7.4447
7.2503
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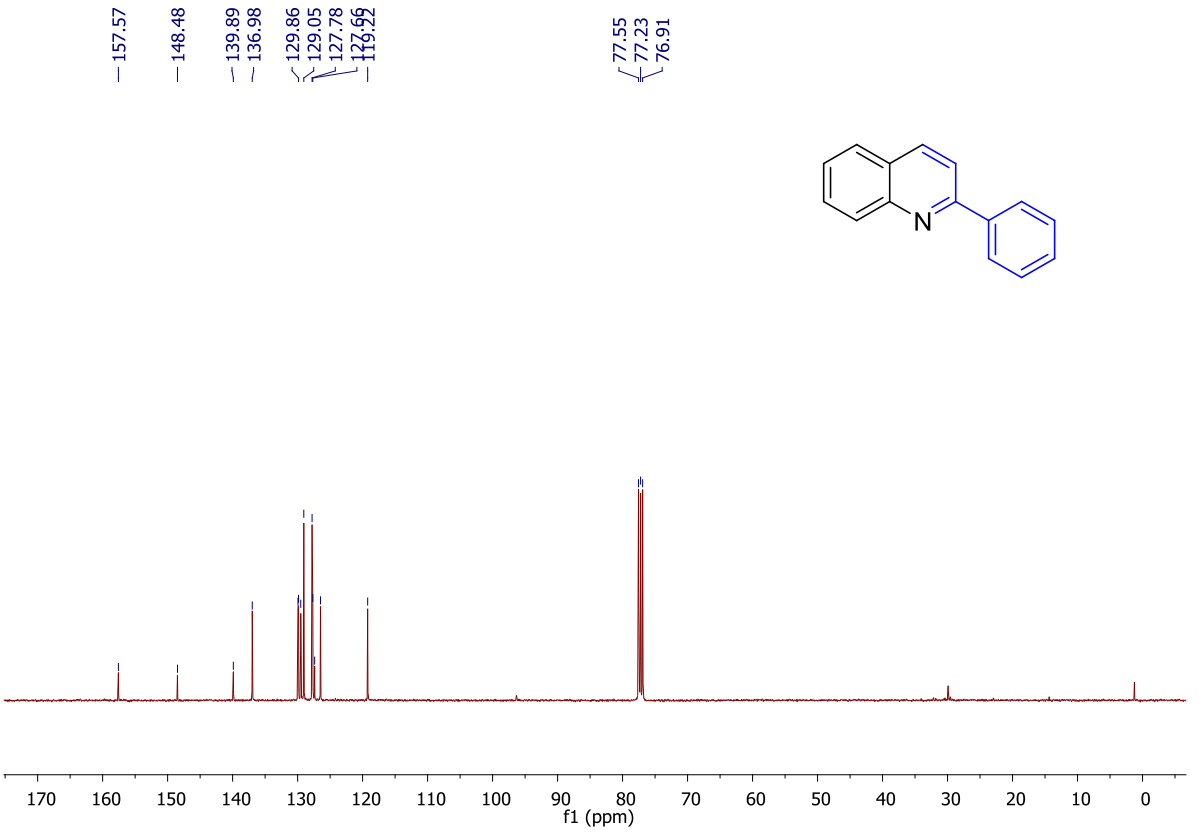
1.00
1.01
1.03
4.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.23
76.91
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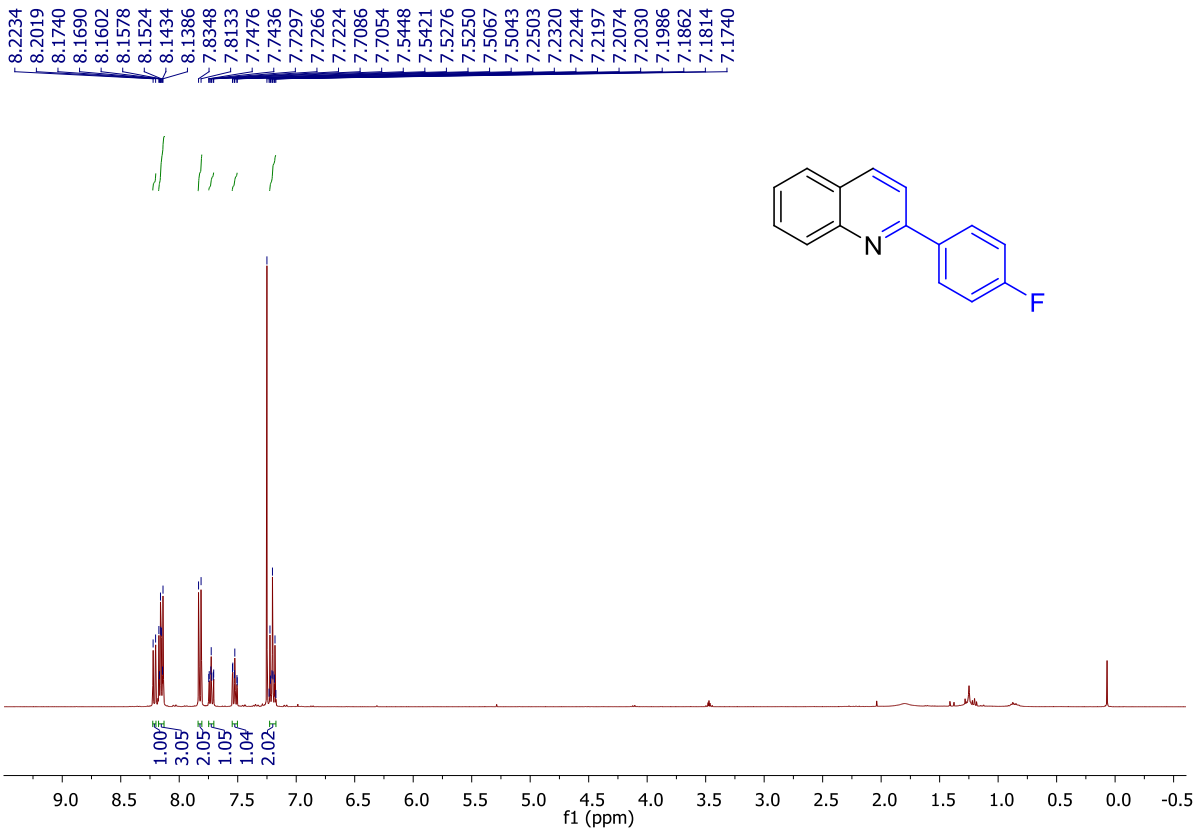
f1 (ppm)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7.2244
7.2197
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7.1986
7.1862
7.1814
7.1740
N
F
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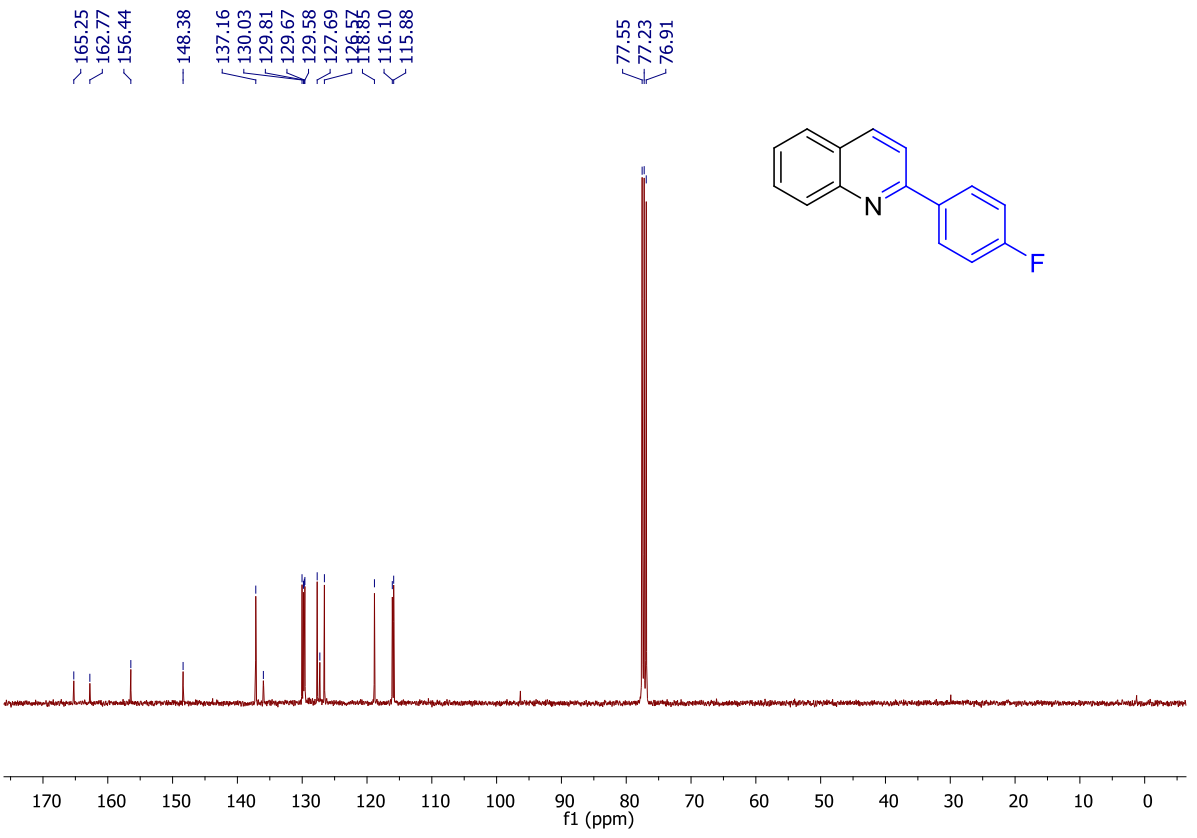
3.05
2.05
1.05
1.04
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.55
77.23
76.91
N
F
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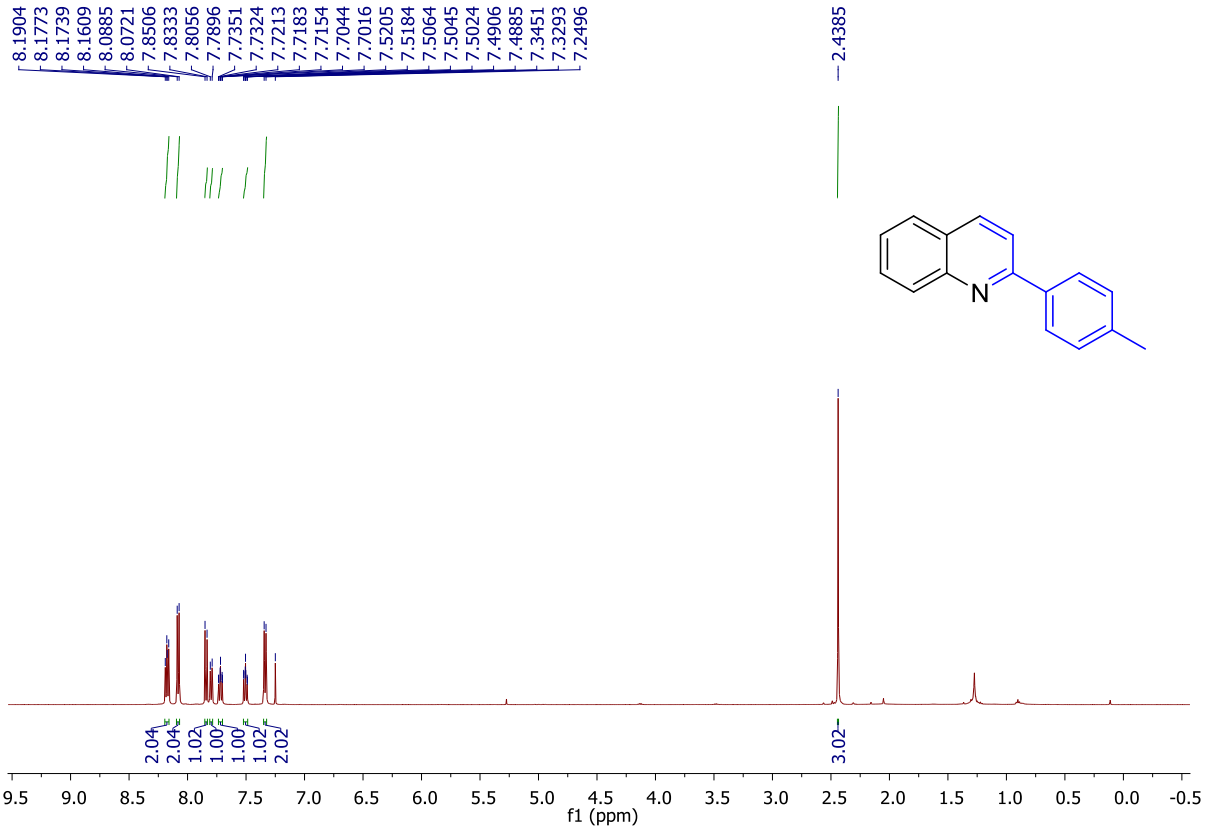
f1 (ppm)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2.04
1.02
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1.00
1.02
2.02
3.02
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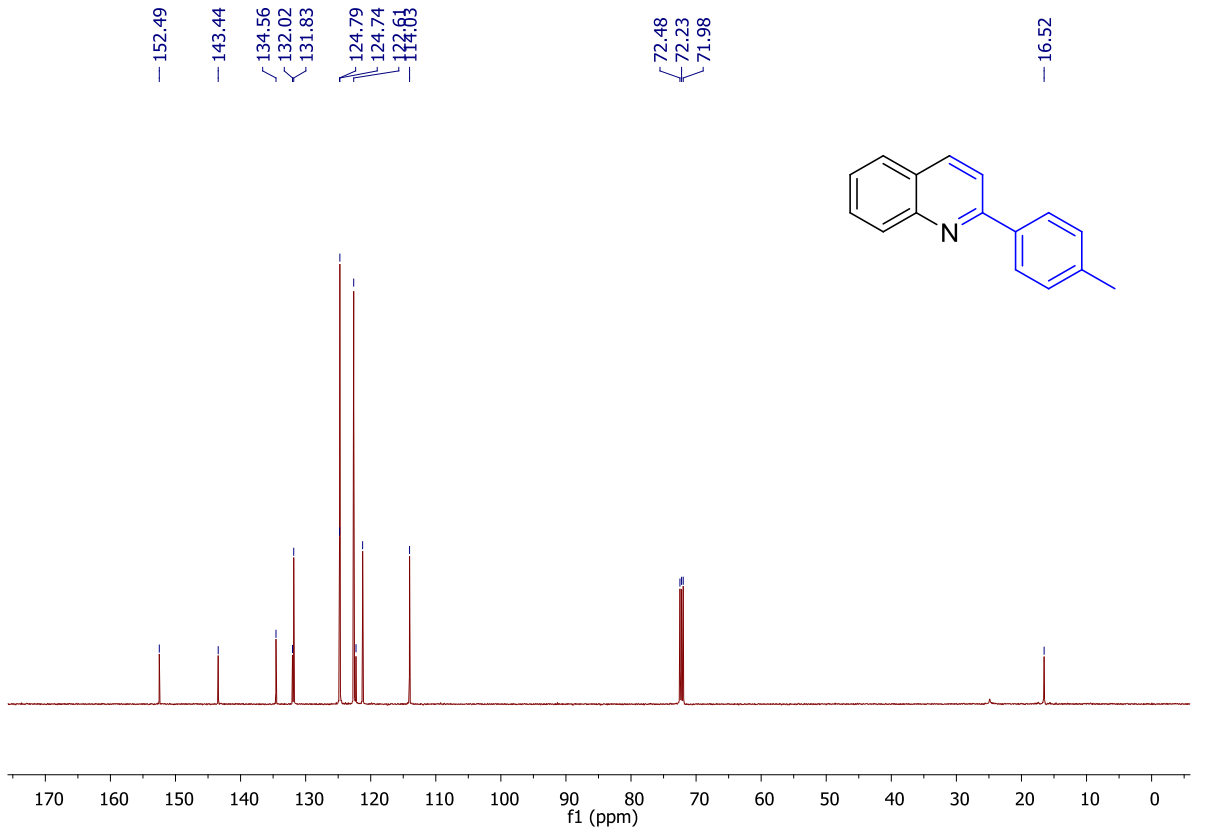
f1 (ppm)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72.23
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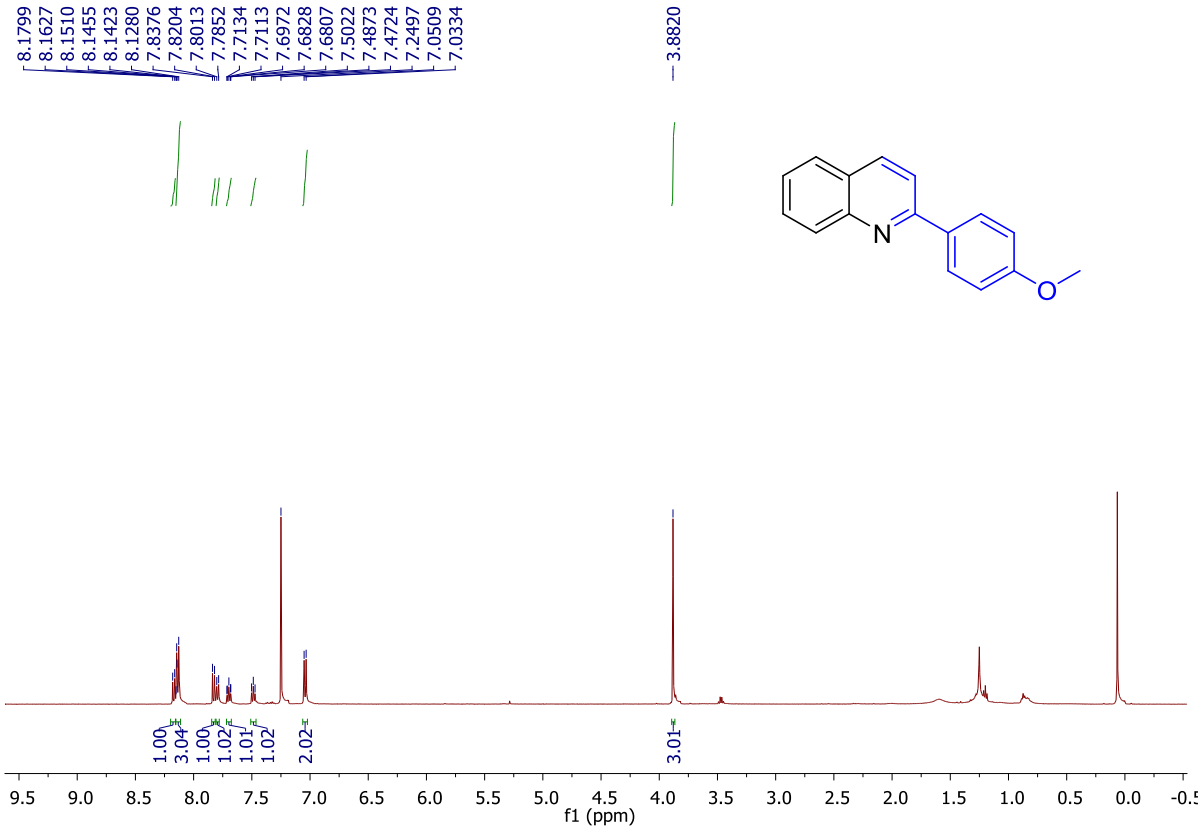
f1 (ppm)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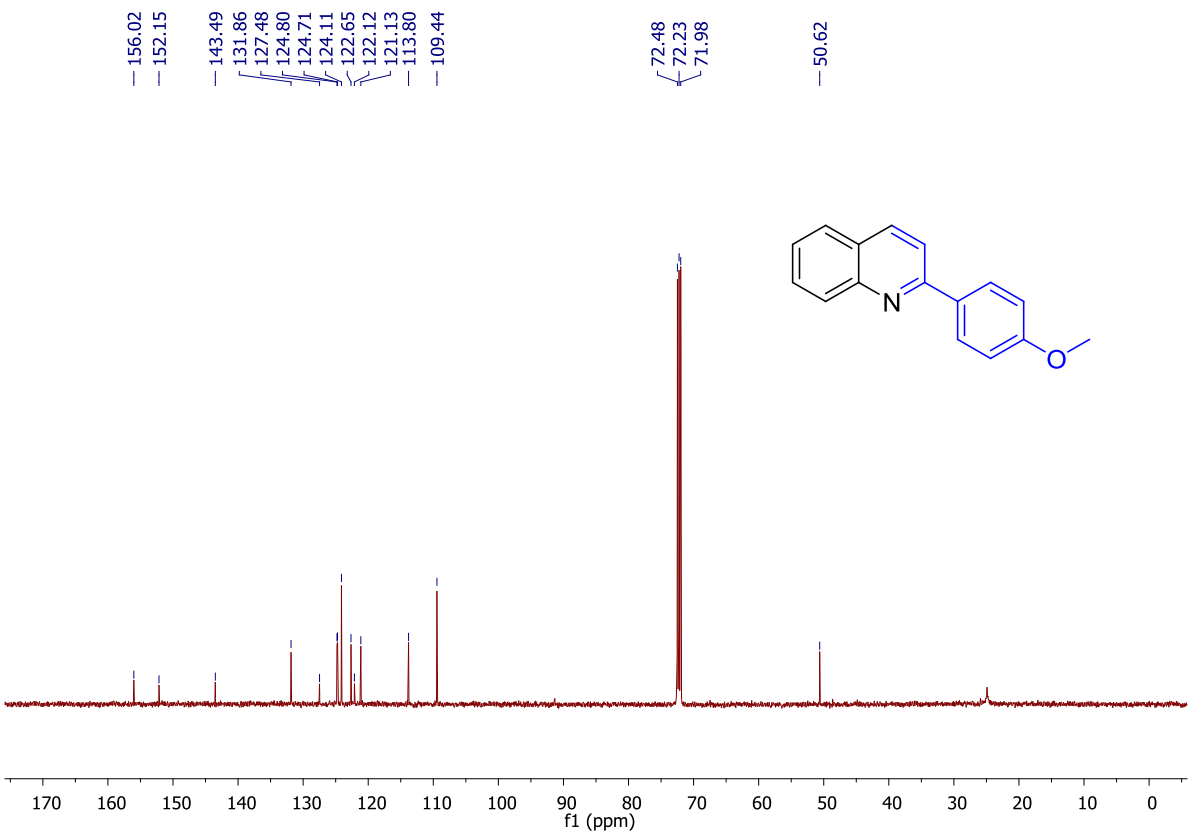
1.00
1.02
1.01
1.02
2.02
3.01
f1 (ppm)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71.98
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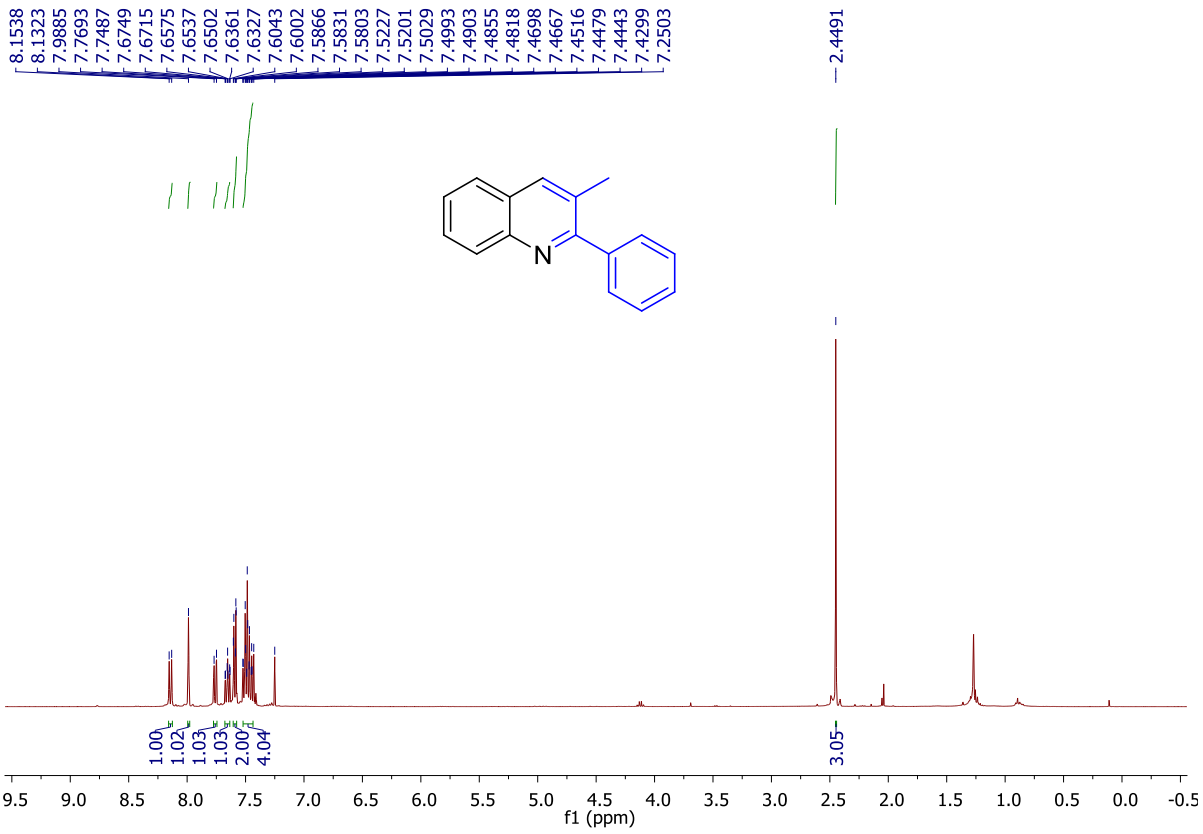
N
O
f1 (ppm)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2.00
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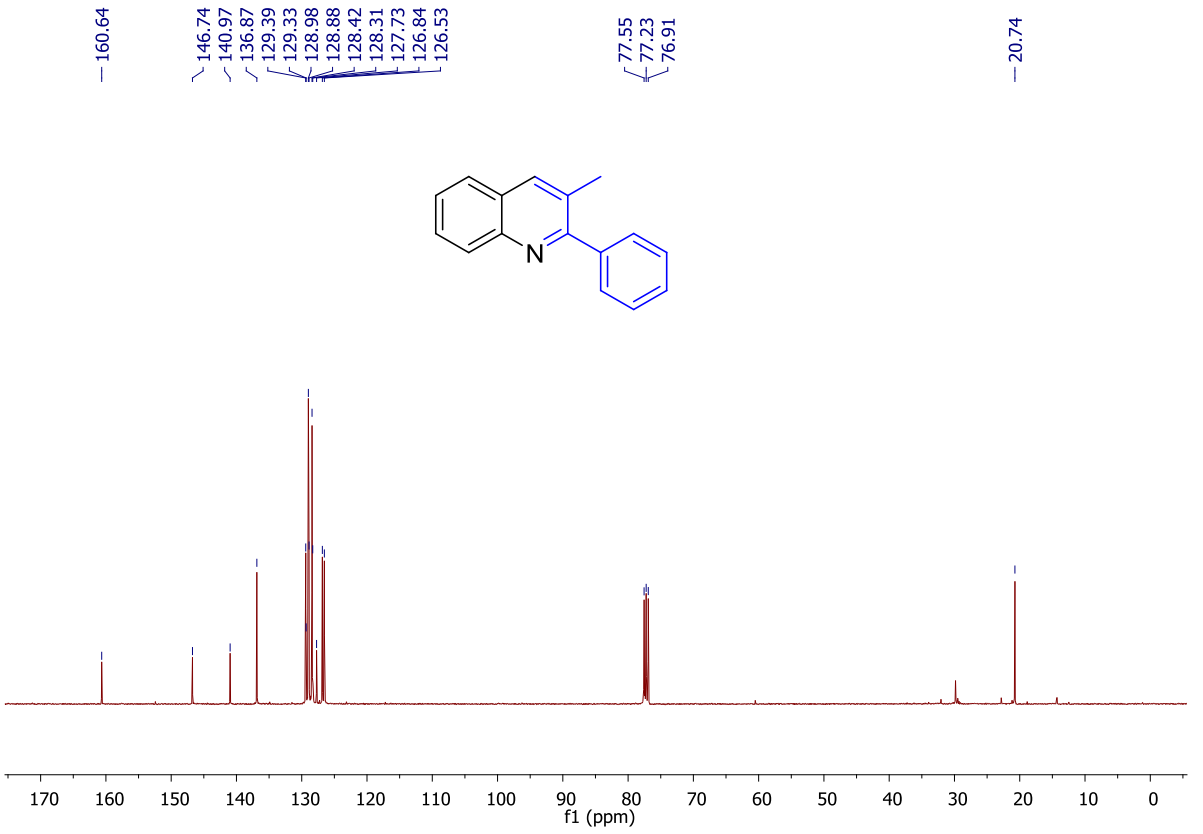
3.05
f1 (ppm)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77.23
76.91
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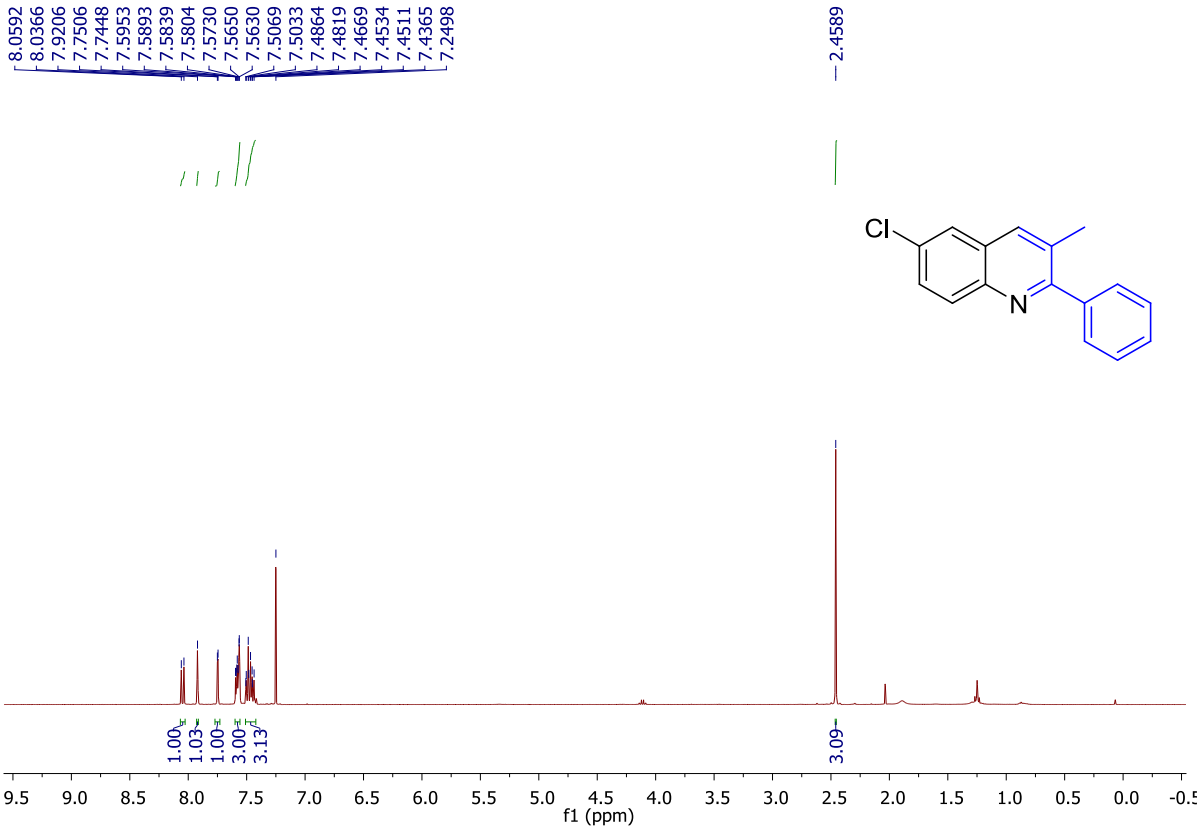
N
f1 (ppm)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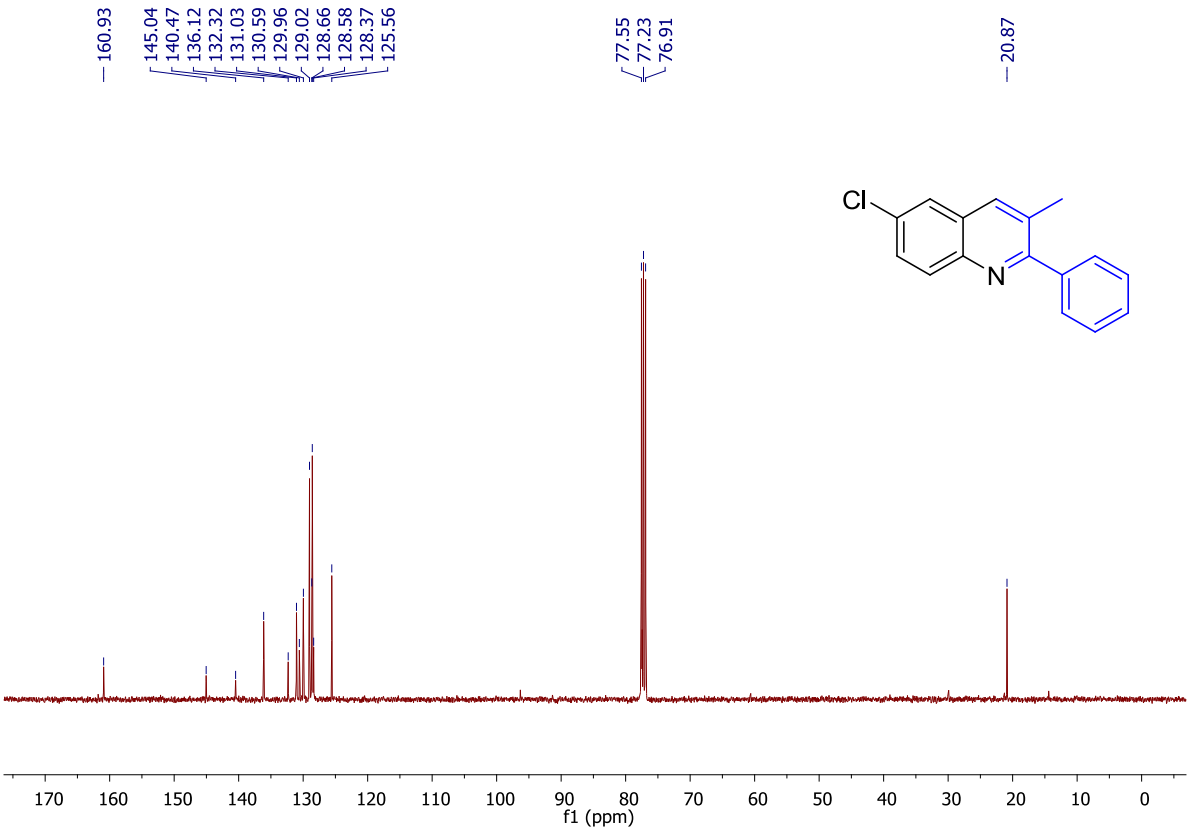
7.7506
7.7448
7.5953
7.5893
7.5839
7.5804
7.5730
7.5650
7.5630
7.5069
7.5033
7.4864
7.4819
7.4669
7.4534
7.4511
7.4365
7.2498
2.4589
Cl
N
1.00
1.03
1.00
3.00
3.13
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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145.04
140.47
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132.32
131.03
130.59
129.96
129.02
128.66
128.58
128.37
125.56
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77.23
76.91
20.87
Cl
N
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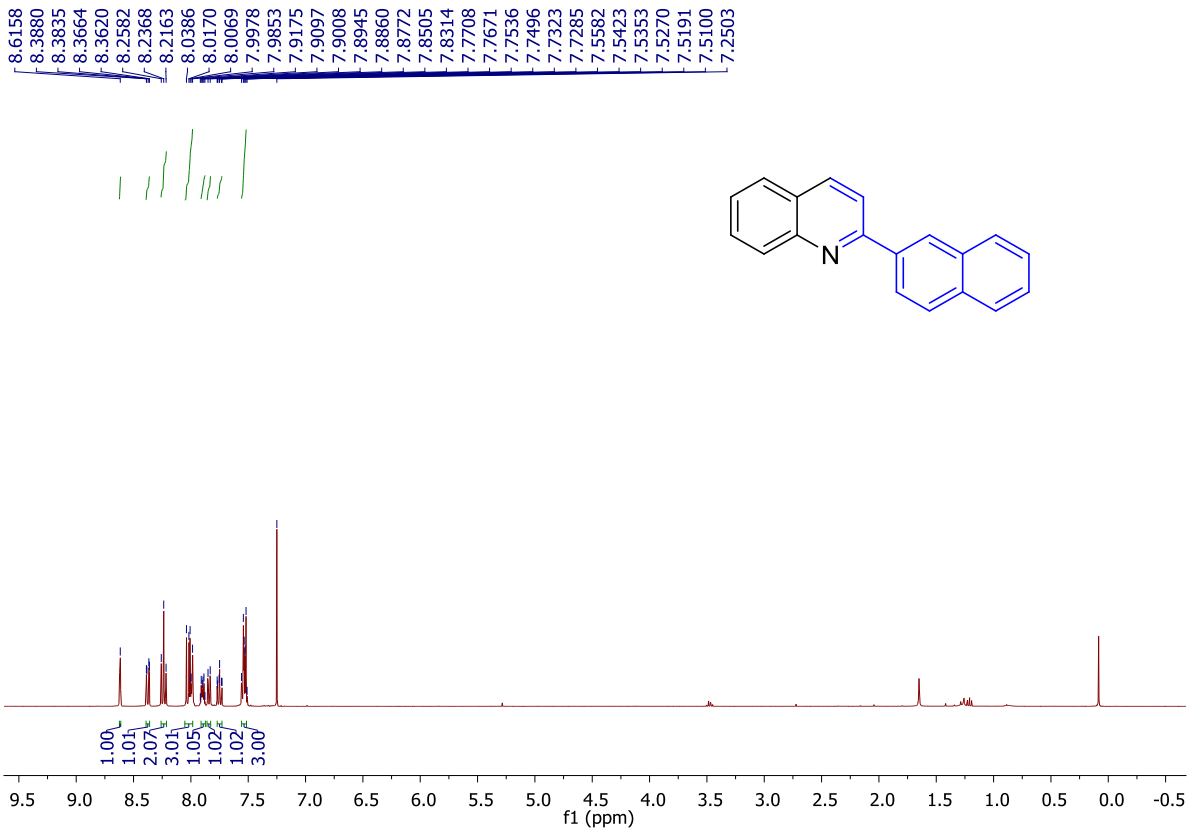
f1 (ppm)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8.3620
8.2582
8.2368
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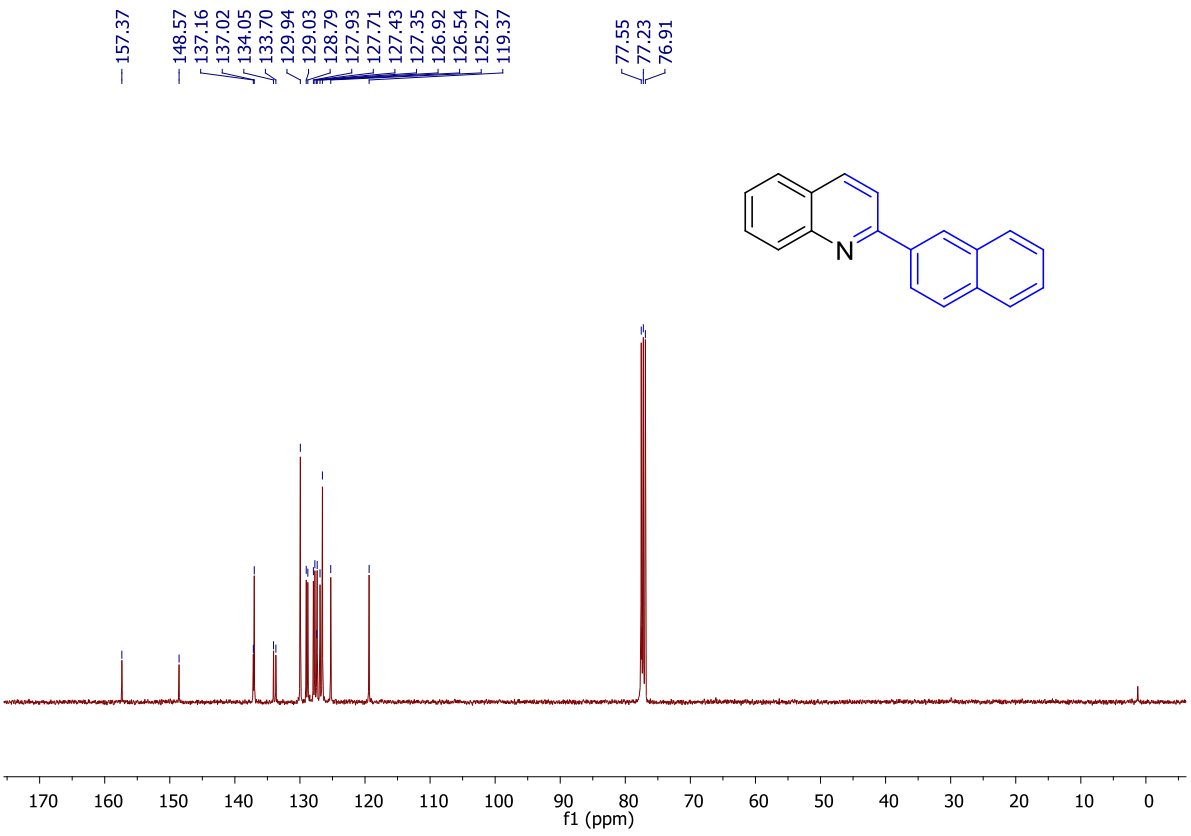
8.0386
8.0170
8.0069
7.9978
7.9853
7.9175
7.9097
7.9008
7.8945
7.8860
7.8772
7.8505
7.8314
7.7708
7.7671
7.7536
7.7496
7.7323
7.7285
7.5582
7.5423
7.5353
7.5270
7.5191
7.5100
7.2503
N
1.00
1.01
2.07
3.01
1.05
1.02
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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148.57
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137.02
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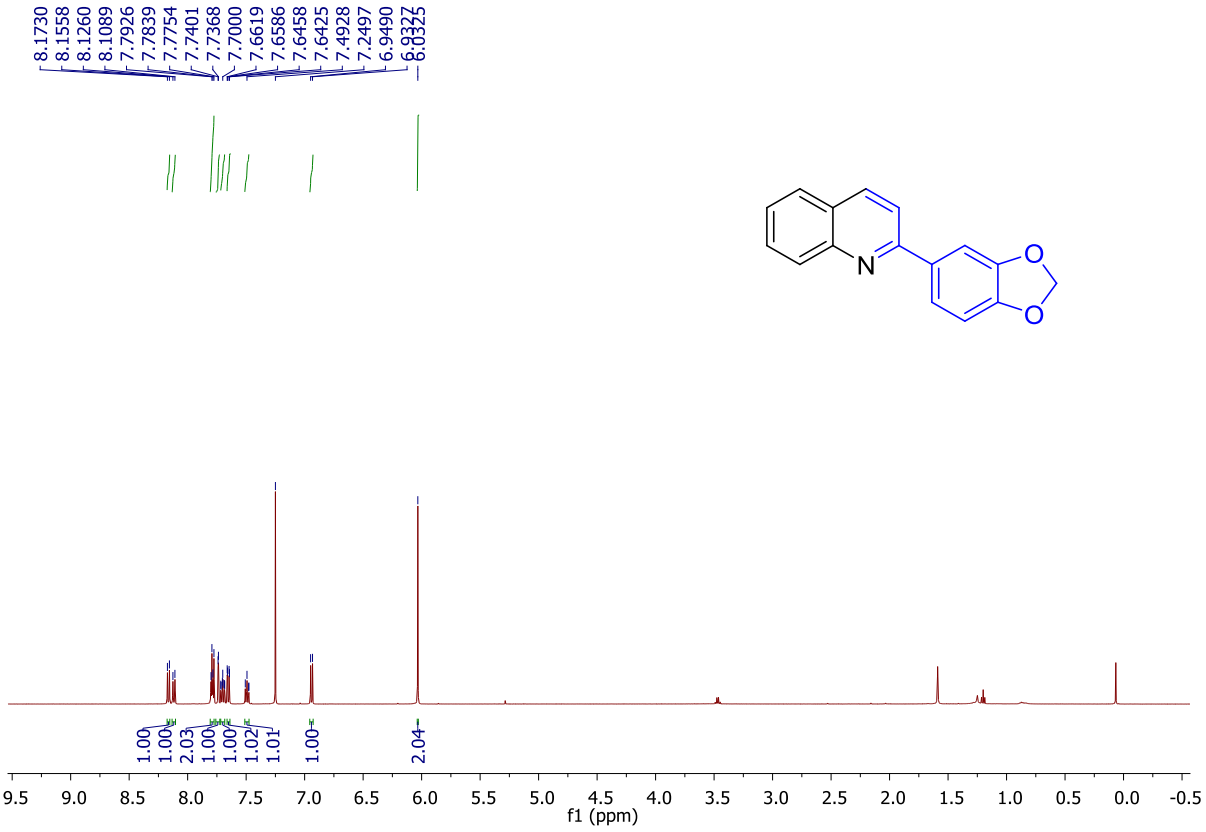
133.70
129.94
129.03
128.79
127.93
127.71
127.43
127.35
126.92
126.54
125.27
119.37
77.55
77.23
76.91
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.1260
8.1089
7.7926
7.7839
7.7754
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7.7368
7.7000
7.6619
7.6586
7.6458
7.6425
7.4928
7.2497
6.9490
6.0325
O
O
N
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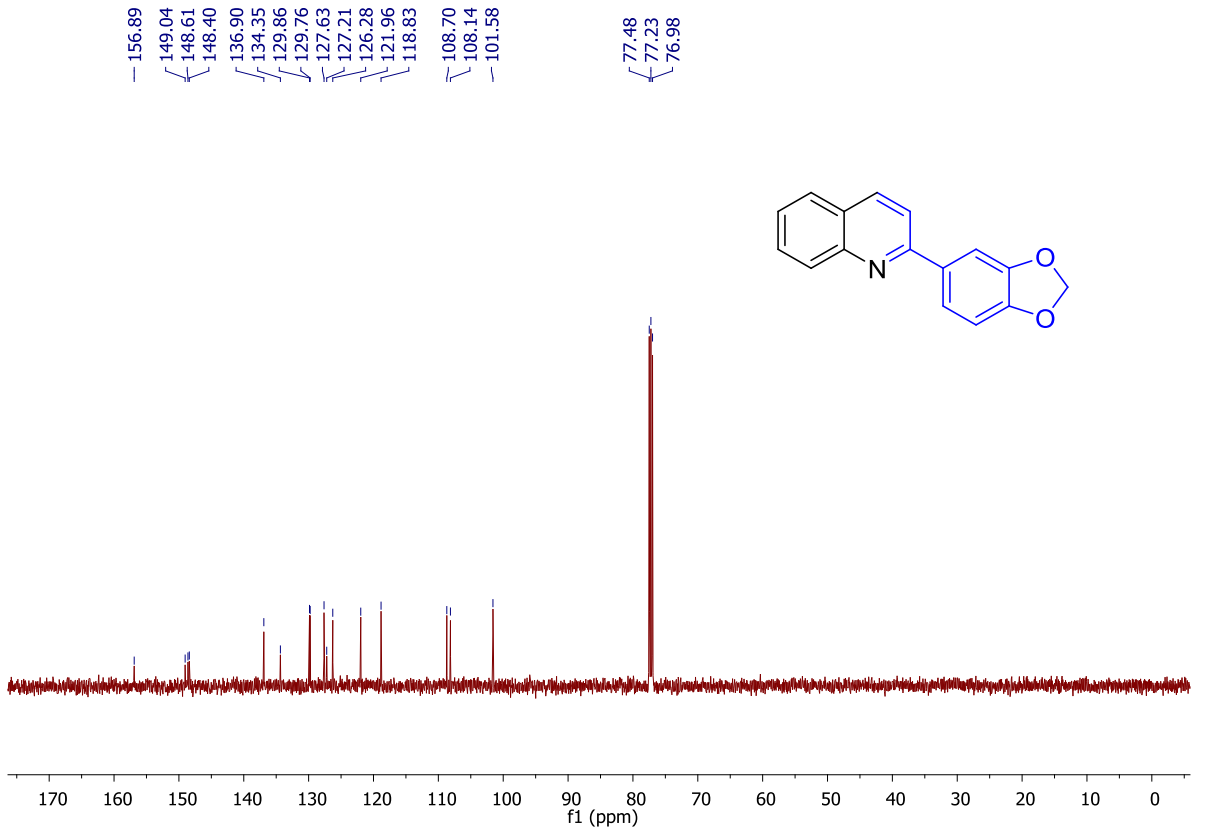
1.00
2.03
1.00
1.00
1.02
1.01
1.00
2.04
f1 (ppm)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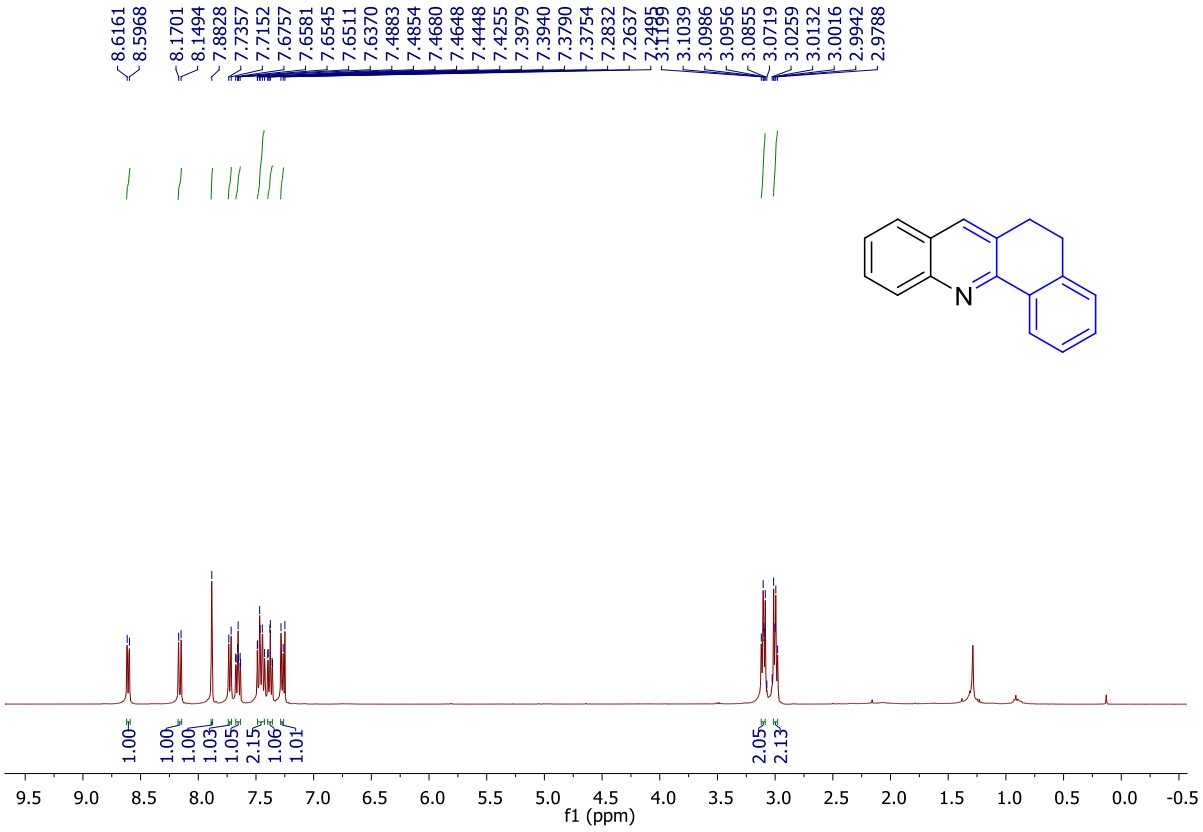
148.61
148.40
136.90
134.35
129.86
129.76
127.63
127.21
126.28
121.96
118.83
108.70
108.14
101.58
77.48
77.23
76.98
O
O
N
f1 (ppm)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7.6370
7.4883
7.4854
7.4680
7.4648
7.4448
7.4255
7.3979
7.3940
7.3790
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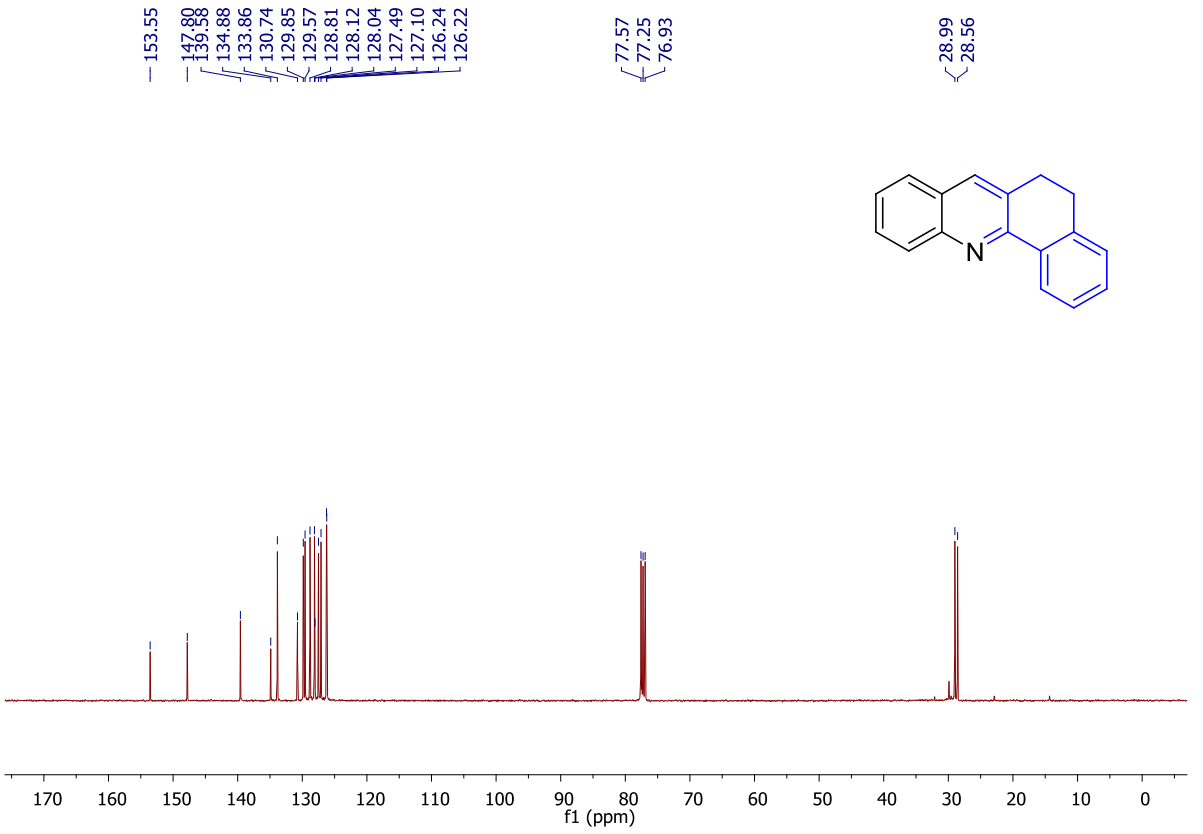
7.2832
7.2637
3.1039
3.0986
3.0956
3.0855
3.0719
3.0259
3.0132
3.0016
2.9942
2.9788
N
1.00
1.00
1.00
1.03
1.05
2.15
1.06
1.01
2.05
2.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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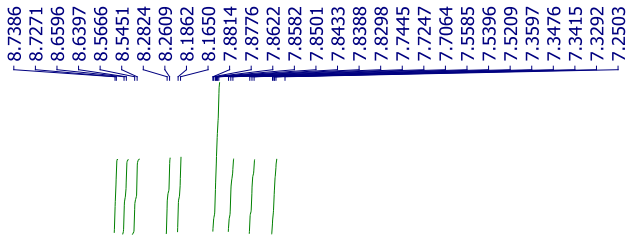
139.58
134.88
133.86
130.74
129.85
129.57
128.81
128.12
128.04
127.49
127.10
126.24
126.22
77.57
77.25
76.93
28.99
28.56
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.6596
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8.5666
8.5451
8.2824
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8.1862
8.1650
7.8814
7.8776
7.8622
7.8582
7.8501
7.8433
7.8388
7.8298
7.7445
7.7247
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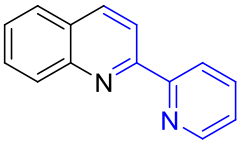
7.5585
7.5396
7.5209
7.3597
7.3476
7.3415
7.3292
7.2503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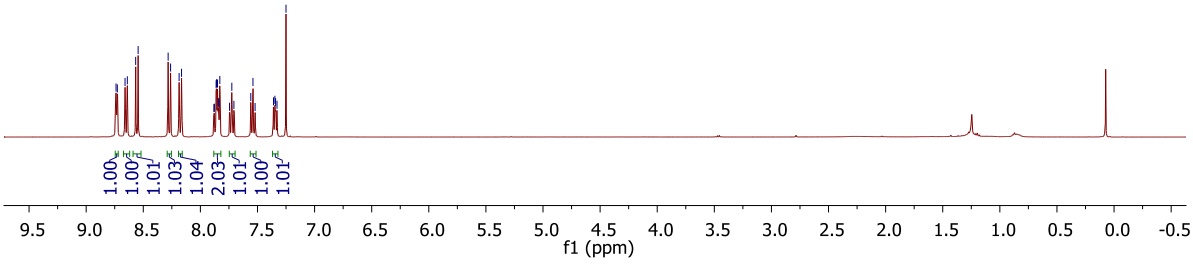
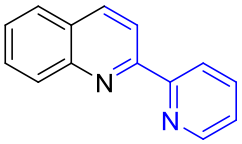
N


1.00
1.00
1.01
1.03
1.04
2.03
1.01
1.00
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


156.51
156.33
149.36
148.10
137.16
137.02
130.00
129.76
128.44
127.82
126.96
124.23
122.04
119.15
77.55
77.23
76.91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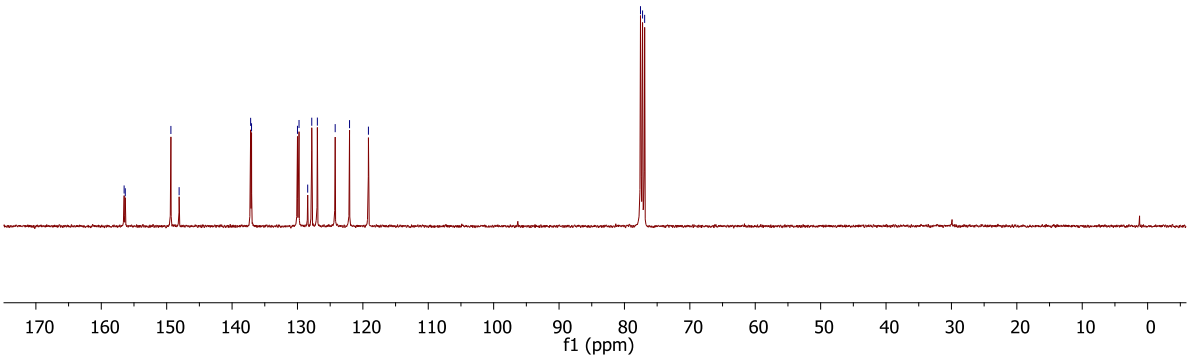
N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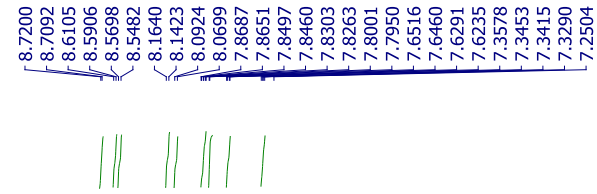
f1 (ppm)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8.5698
8.5482
8.1640
8.1423
8.0924
8.0699
7.8687
7.8651
7.8497
7.8460
7.8303
7.8263
7.8001
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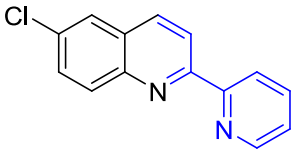
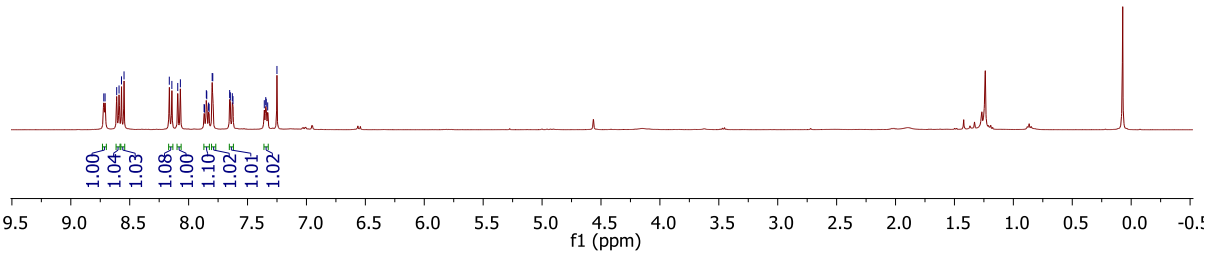
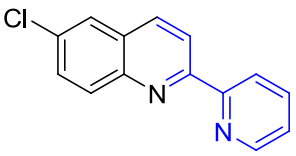
7.3578
7.3453
7.3415
7.3290
7.2504

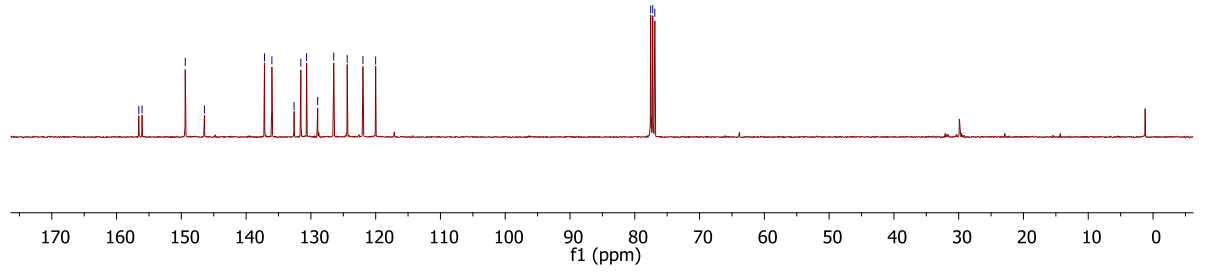

Cl
N
N


1.00
1.04
1.03
1.08
1.00
1.10
1.02
1.01
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.57
156.06
149.40
146.44
137.17
136.02
132.60
131.55
130.66
128.95
126.48
124.40
121.97
120.00


77.55
77.23
76.91


Cl
N
N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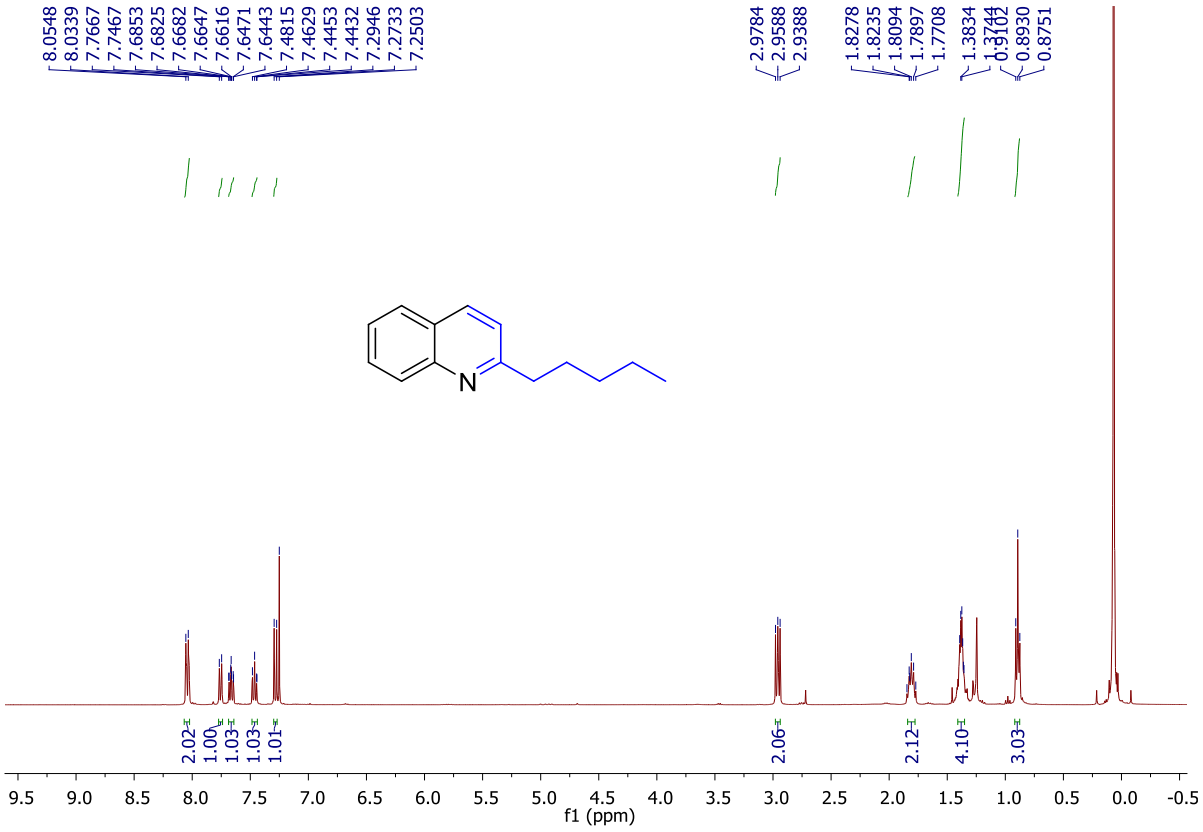
f1 (ppm)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7.6471
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7.4815
7.4629
7.4453
7.4432
7.2946
7.2733
7.2503
2.9784
2.9588
2.9388
1.8278
1.8235
1.8094
1.7897
1.7708
1.3834
0.8930
0.8751
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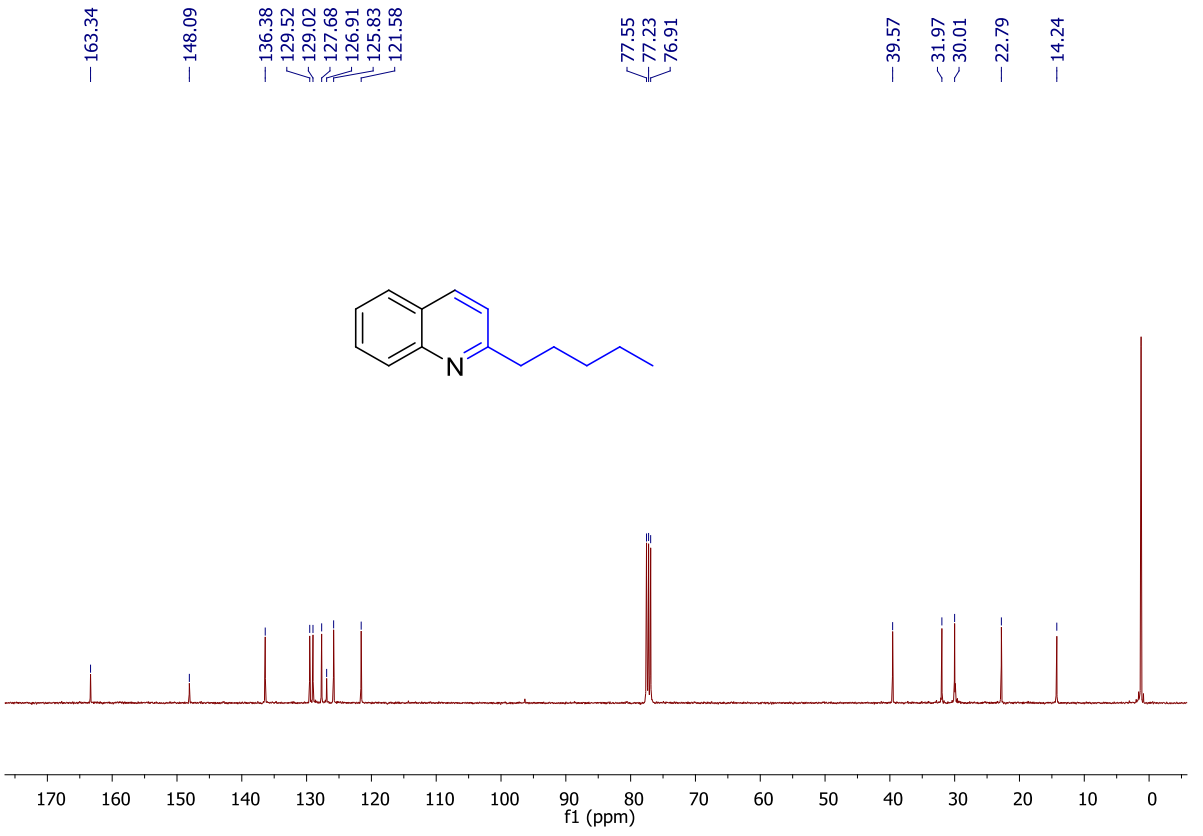
1.03
1.03
1.01
2.06
2.12
4.10
3.03
f1 (ppm)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136.38
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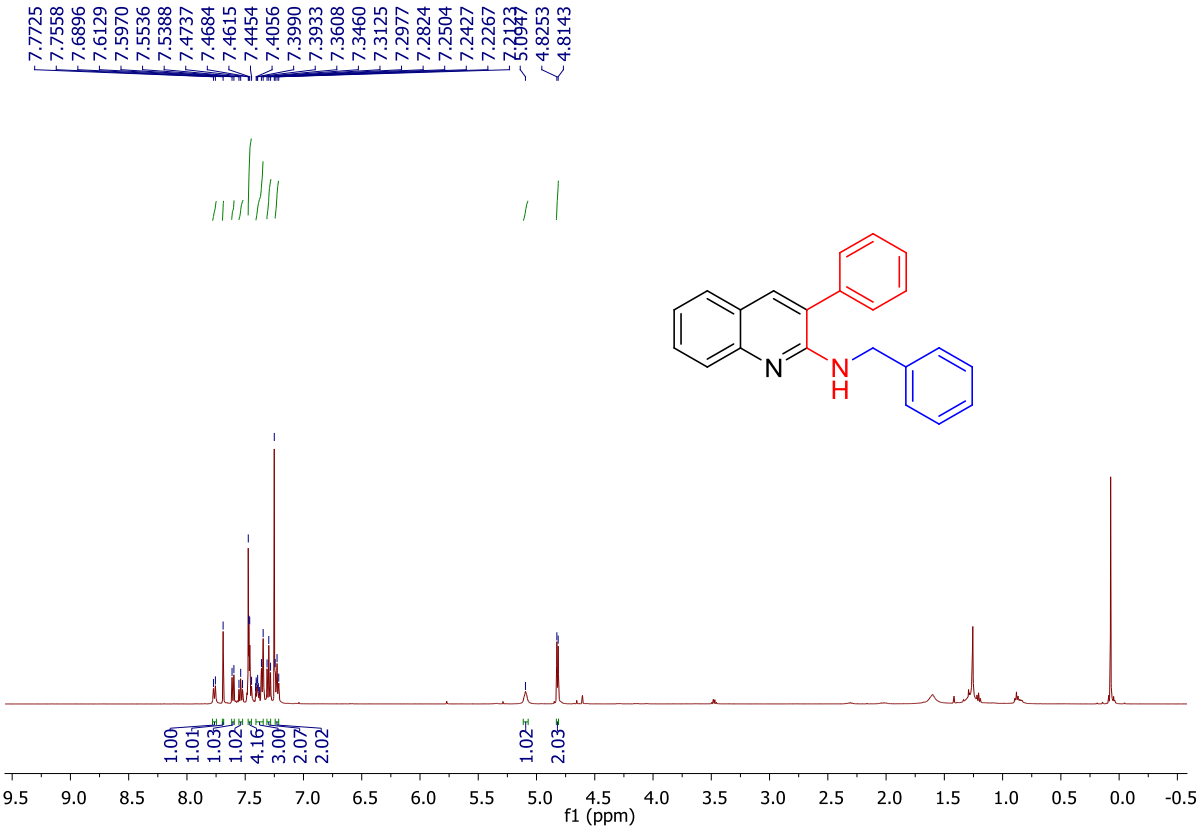
129.02
127.68
126.91
125.83
121.58
77.55
77.23
76.91
39.57
31.97
30.01
22.79
14.24
N
f1 (ppm)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7.4684
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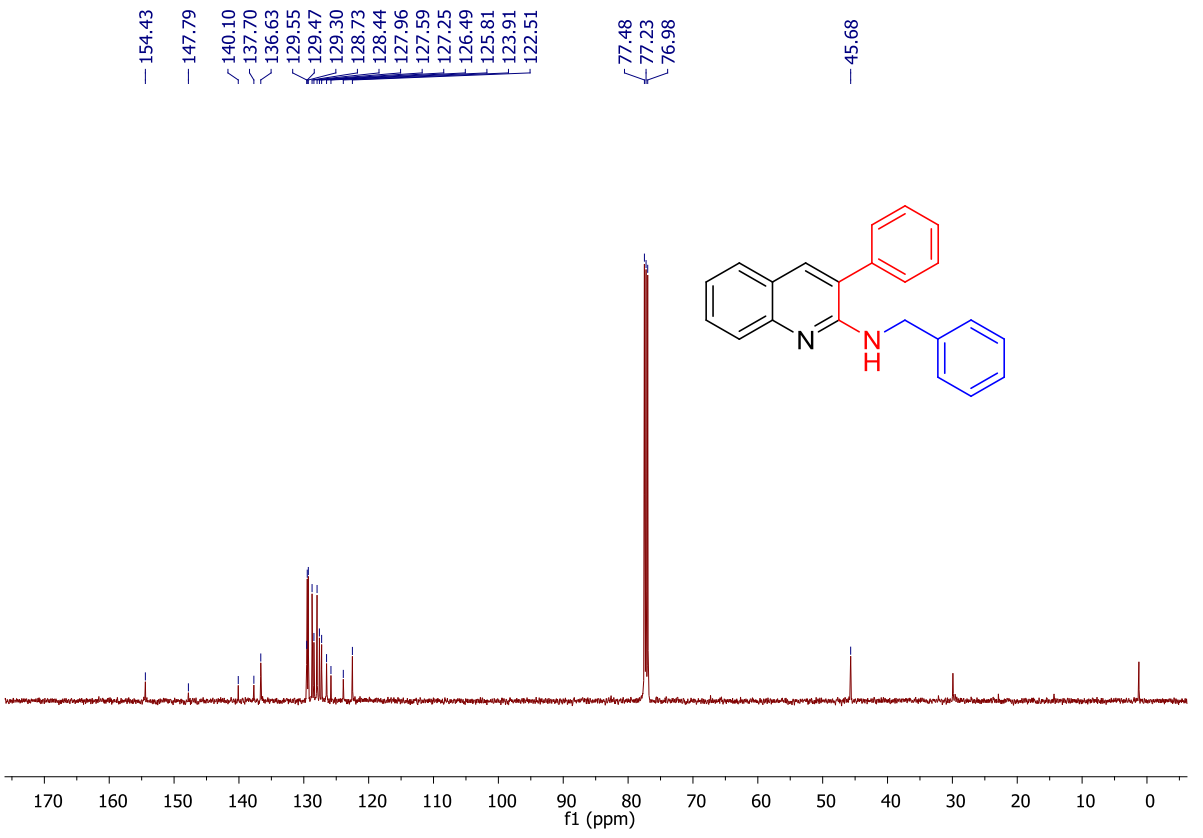
7.4454
7.4056
7.3990
7.3933
7.3608
7.3460
7.3125
7.2977
7.2824
7.2504
7.2427
7.2267
5.0947
4.8253
4.8143
1.00
1.01
1.03
1.02
4.16
3.00
2.07
2.02
1.02
2.03
N
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.55
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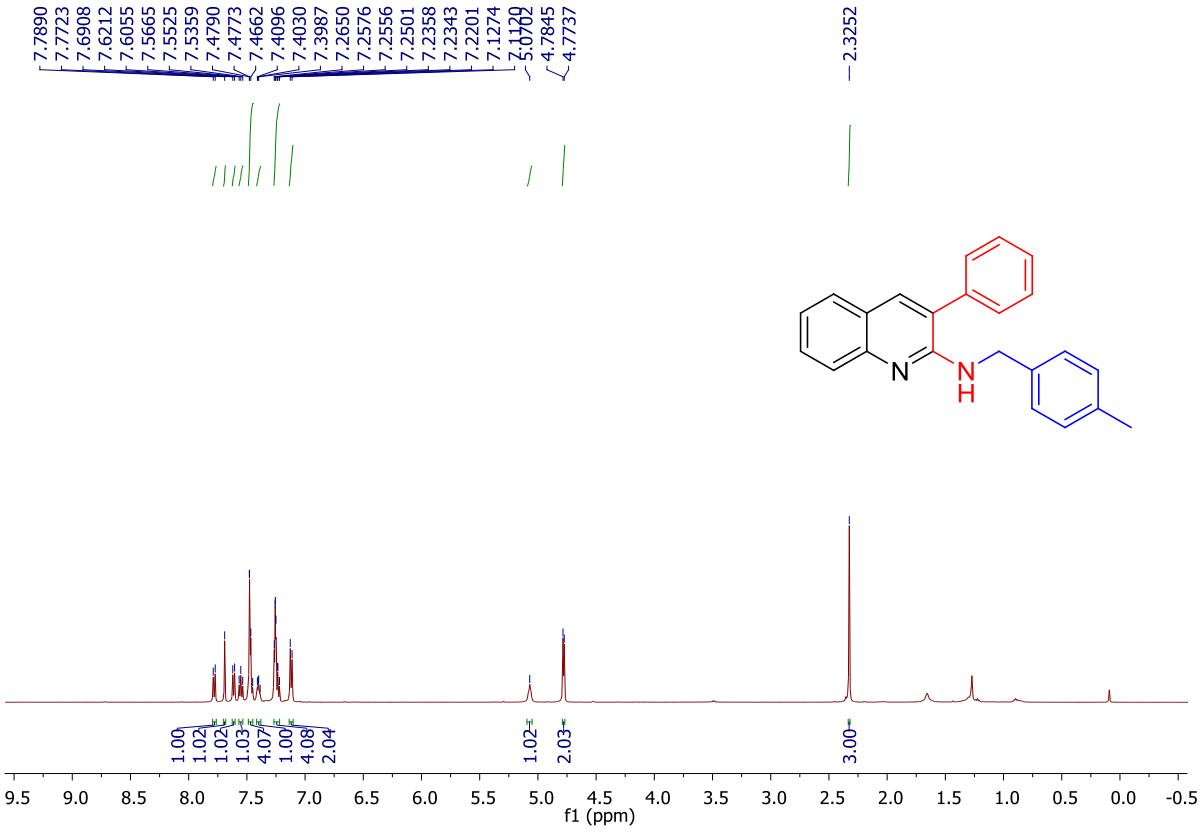
129.30
128.73
128.44
127.96
127.59
127.25
126.49
125.81
123.91
122.51
77.48
77.23
76.98
45.68
N
H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5525
7.5359
7.4790
7.4773
7.4662
7.4096
7.4030
7.3987
7.2650
7.2576
7.2556
7.2501
7.2358
7.2343
7.2201
7.1274
7.1120
5.0762
4.7845
4.7737
2.3252
N
H
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1.02
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1.03
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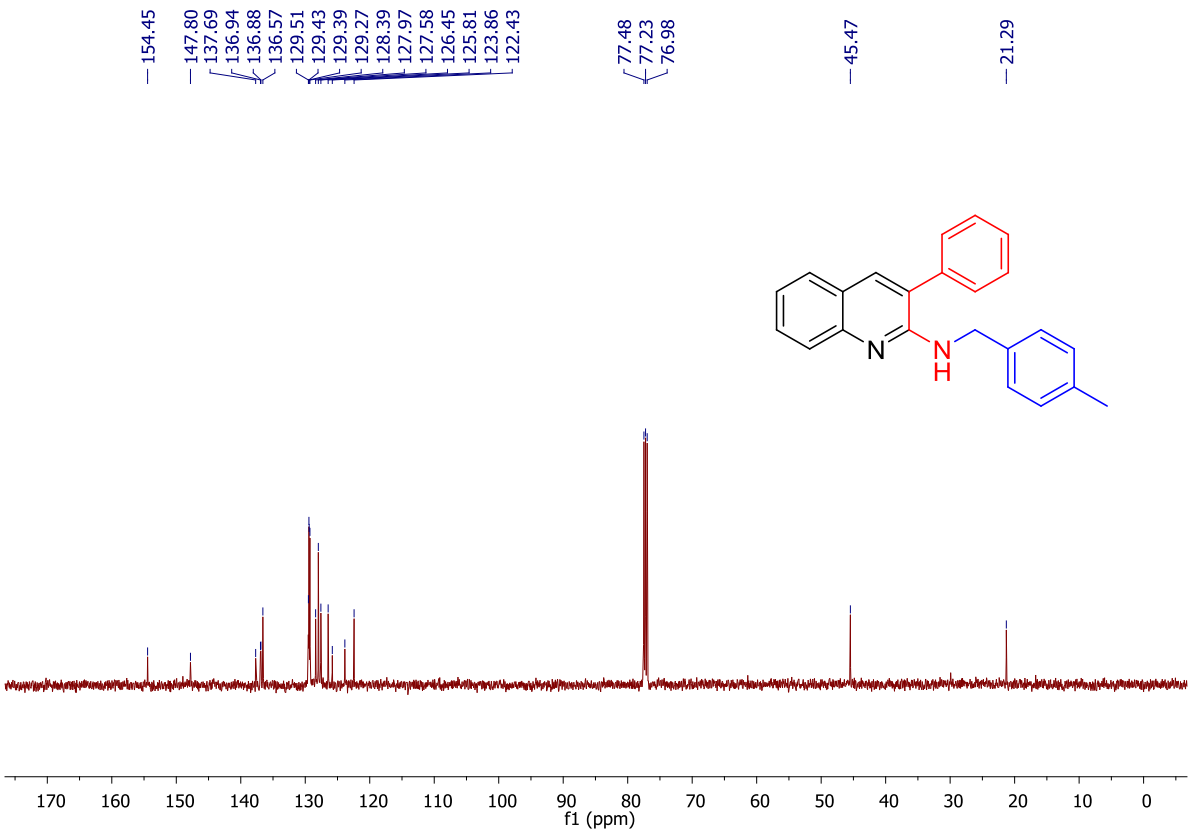
4.08
2.04
1.02
2.03
3.00
f1 (ppm)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129.27
128.39
127.97
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126.45
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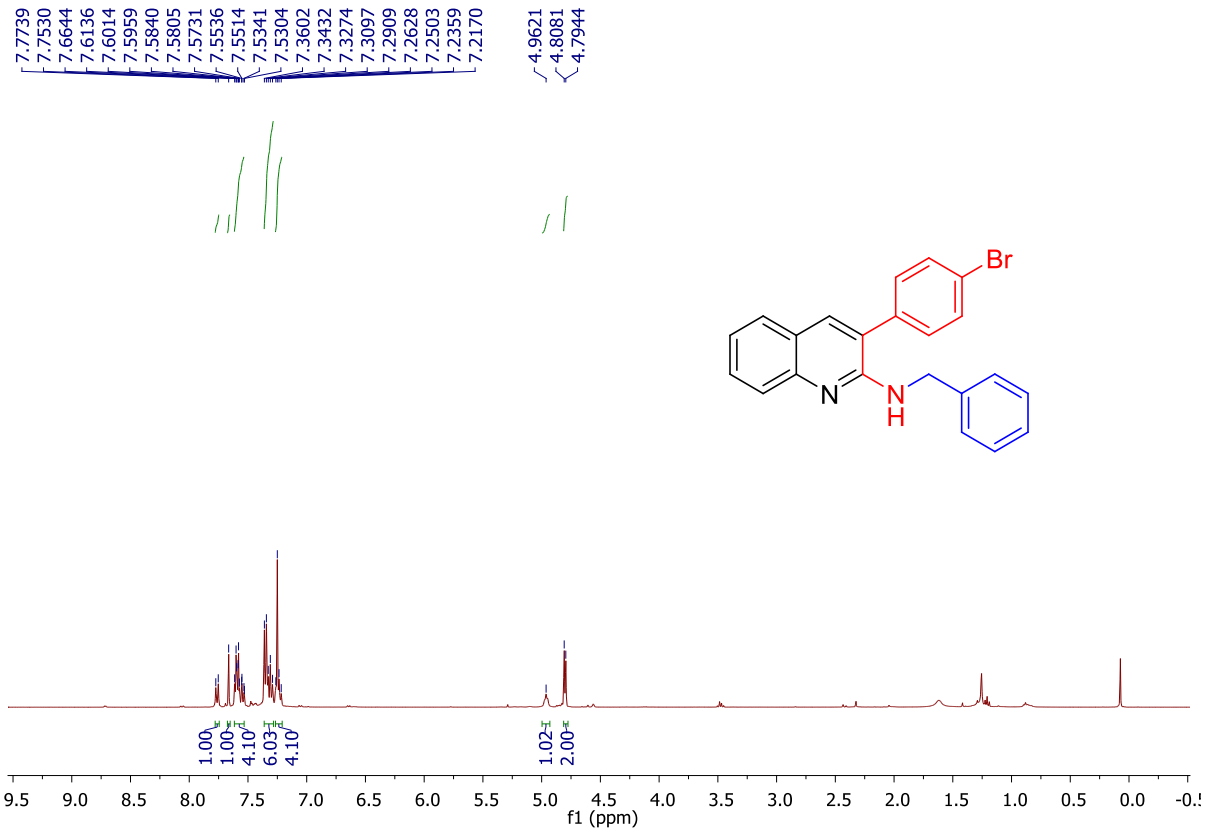
123.86
122.43
77.48
77.23
76.98
45.47
21.29
N
H
f1 (ppm)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7.5304
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7.3274
7.3097
7.2909
7.2628
7.2503
7.2359
7.2170
4.9621
4.8081
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N
H
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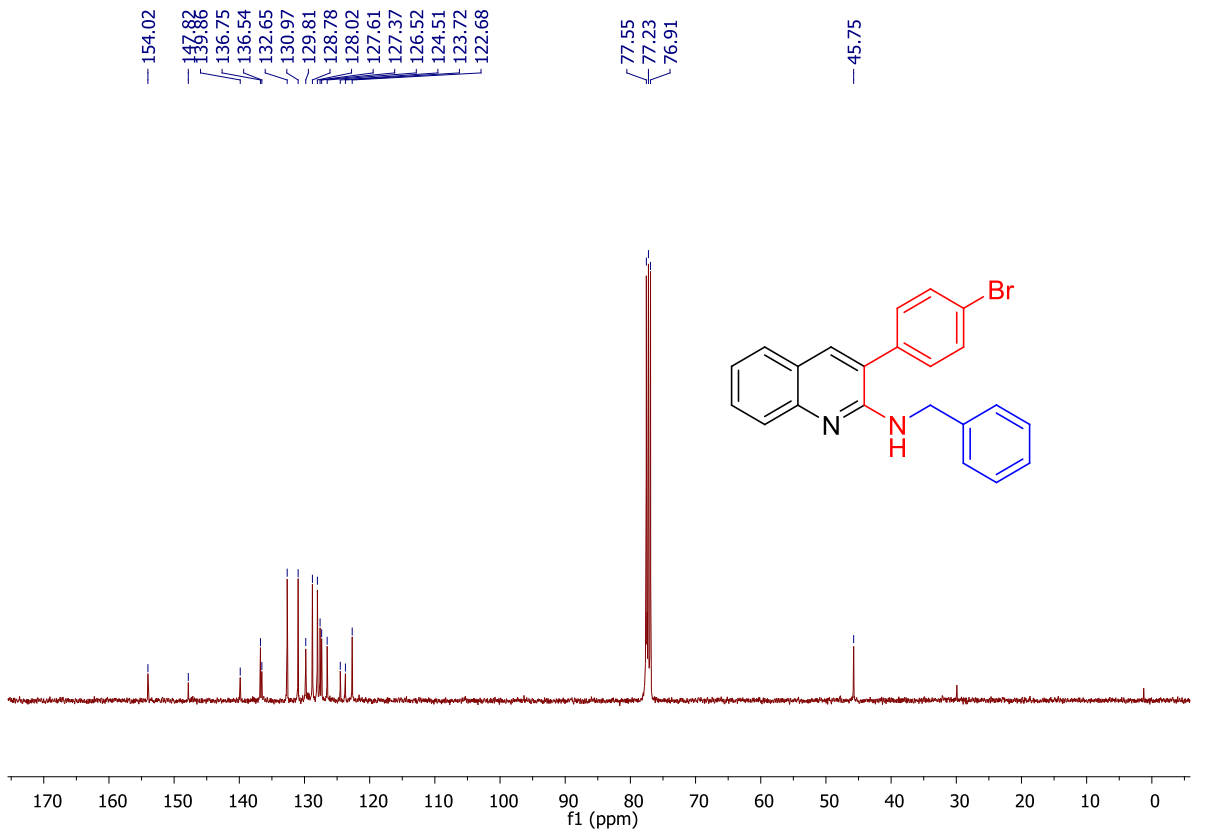
1.00
4.10
6.03
4.10
1.02
2.00
f1 (ppm)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128.02
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127.37
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123.72
122.68
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77.23
76.91
45.75
Br
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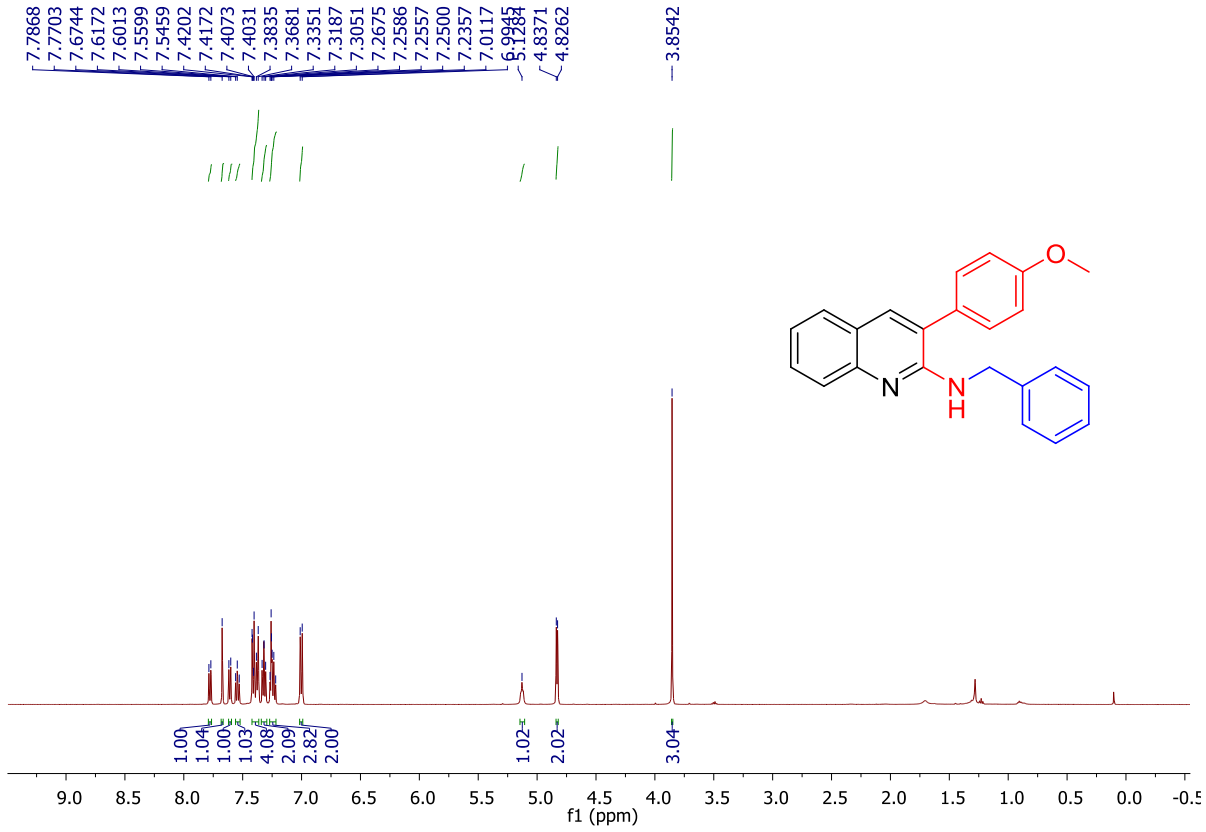
N
H
f1 (ppm)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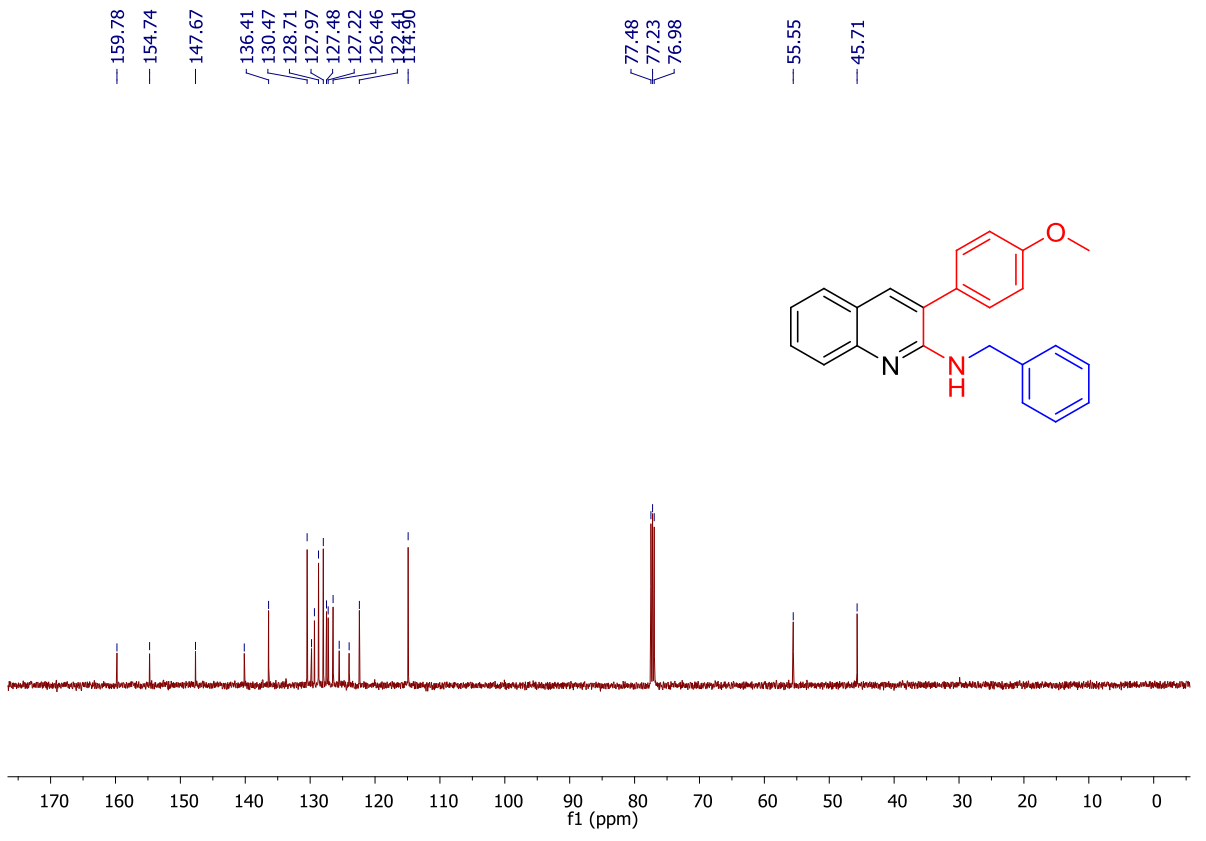
7.2557
7.2500
7.2357
7.0117
5.1284
4.8371
4.8262
3.8542
O
N
N
H
1.00
1.04
1.00
1.03
4.08
2.09
2.82
2.00
1.02
2.02
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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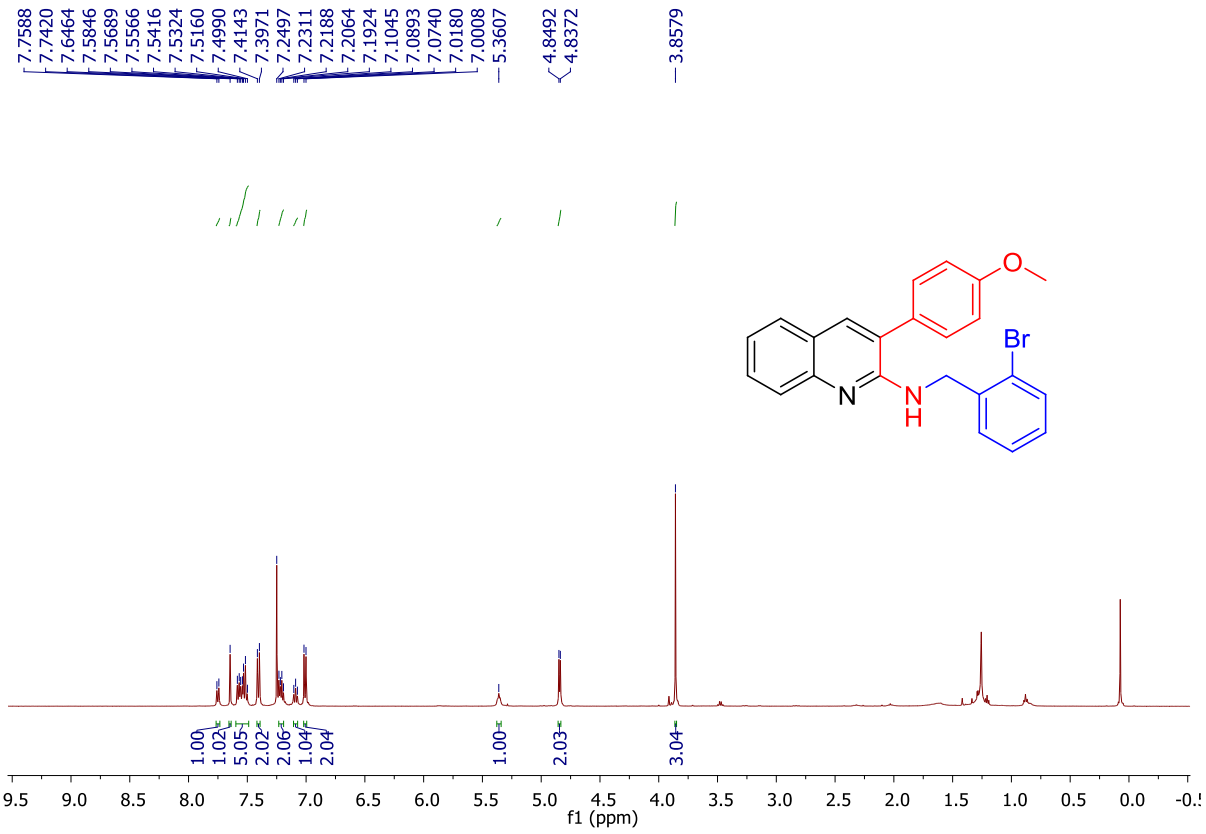
130.47
128.71
127.97
127.48
127.22
126.46
77.48
77.23
76.98
55.55
45.71
O
N
N
H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5689
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7.5416
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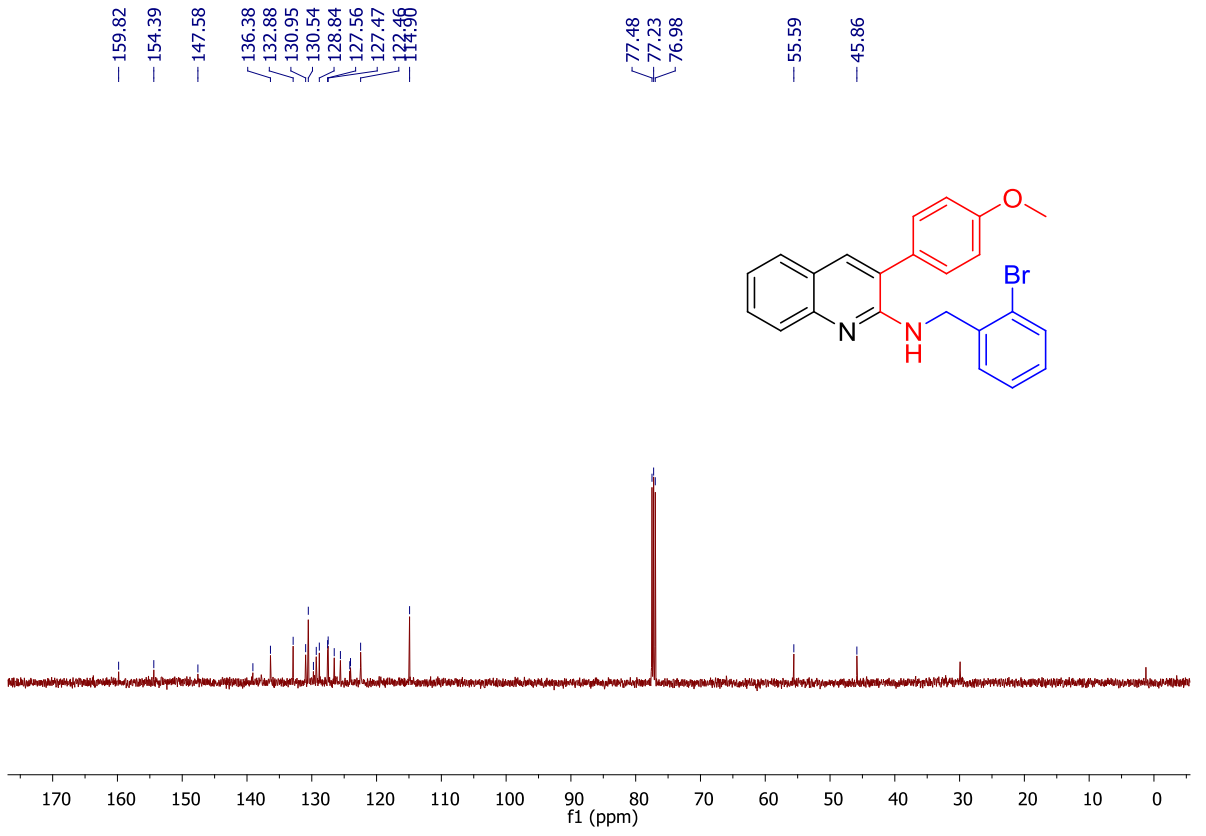
7.5160
7.4990
7.4143
7.3971
7.2497
7.2311
7.2188
7.2064
7.1924
7.1045
7.0893
7.0740
7.0180
7.0008
5.3607
4.8492
4.8372
3.8579
O
Br
N
N
H
1.00
1.02
5.05
2.02
2.06
1.04
2.04
1.00
2.03
3.04
f1 (ppm)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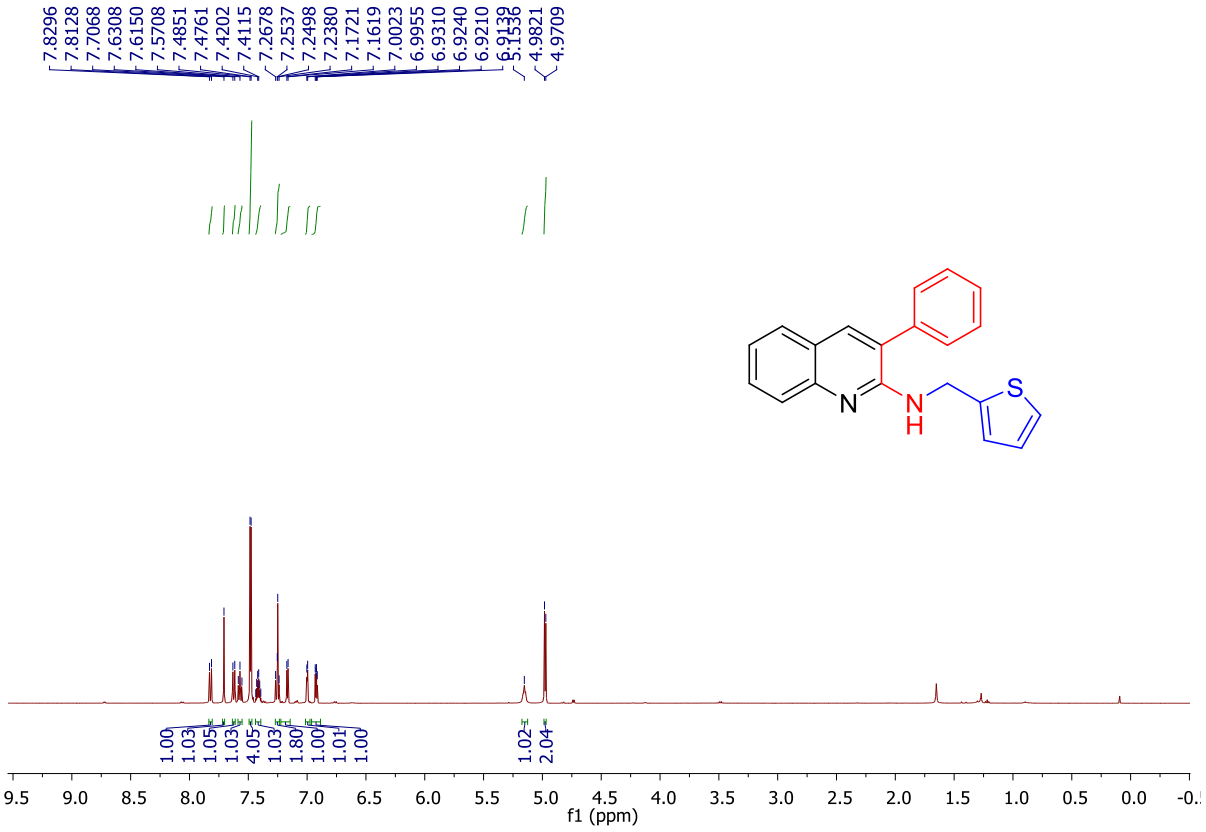
154.39
147.58
136.38
132.88
130.95
130.54
128.84
127.56
127.47
77.48
77.23
76.98
55.59
45.86
O
Br
N
N
H
f1 (ppm)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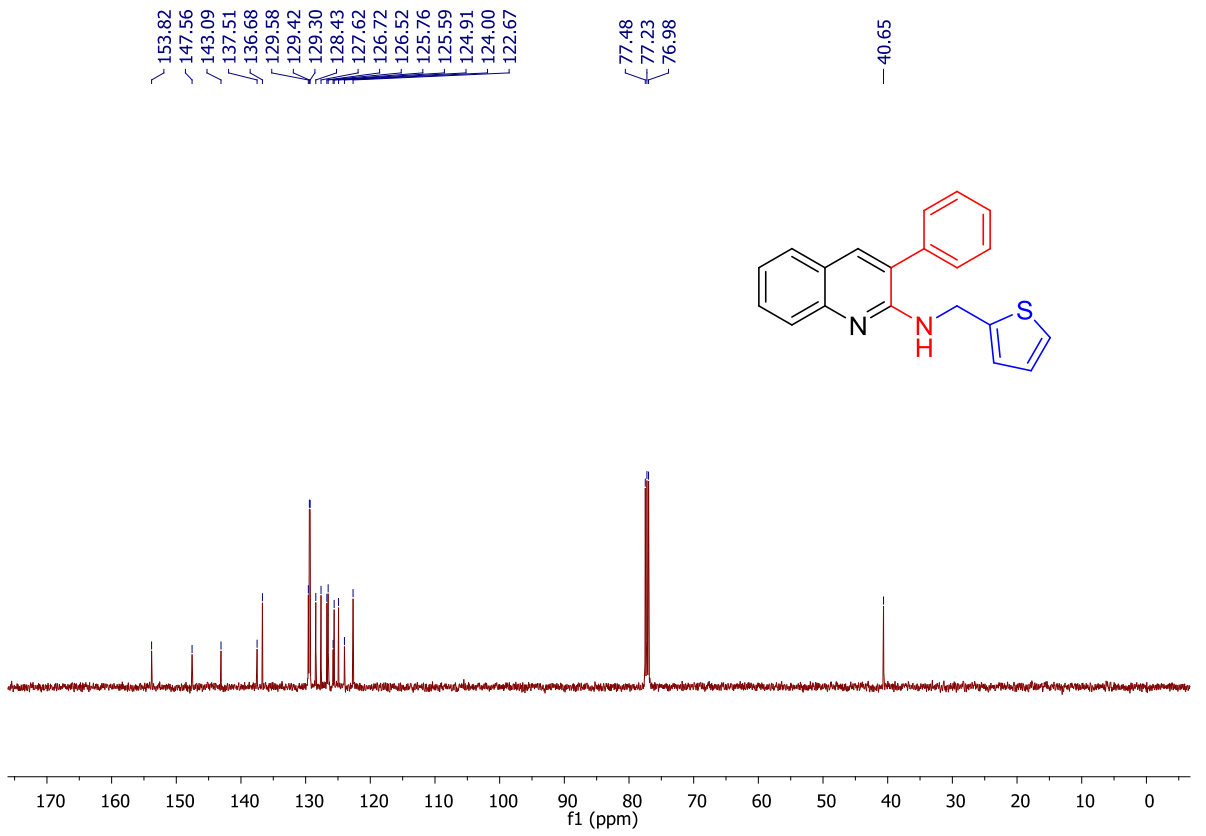
7.4115
7.2678
7.2537
7.2498
7.2380
7.1721
7.1619
7.0023
6.9955
6.9310
6.9240
6.9210
6.9139
5.1538
4.9821
4.9709
N
N
H
S
1.00
1.03
1.05
1.03
4.05
1.03
1.80
1.00
1.01
1.00
1.02
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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147.56
143.09
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136.68
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129.30
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126.72
126.52
125.76
125.59
124.91
124.00
122.67
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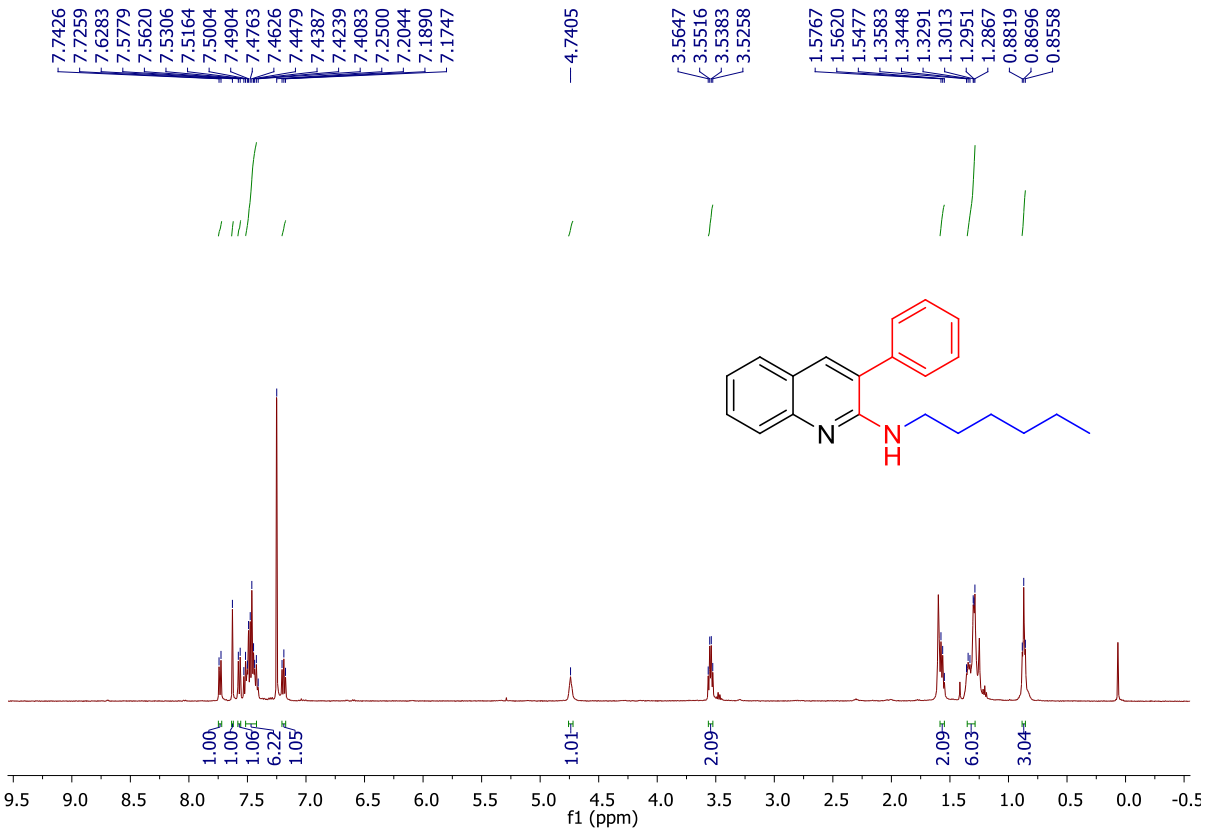
77.23
76.98
40.65
N
N
H
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.4479
7.4387
7.4239
7.4083
7.2500
7.2044
7.1890
7.1747
4.7405
3.5647
3.5516
3.5383
3.5258
1.5767
1.5620
1.5477
1.3583
1.3448
1.3291
1.3013
1.2951
1.2867
0.8819
0.8696
0.8558
N
N
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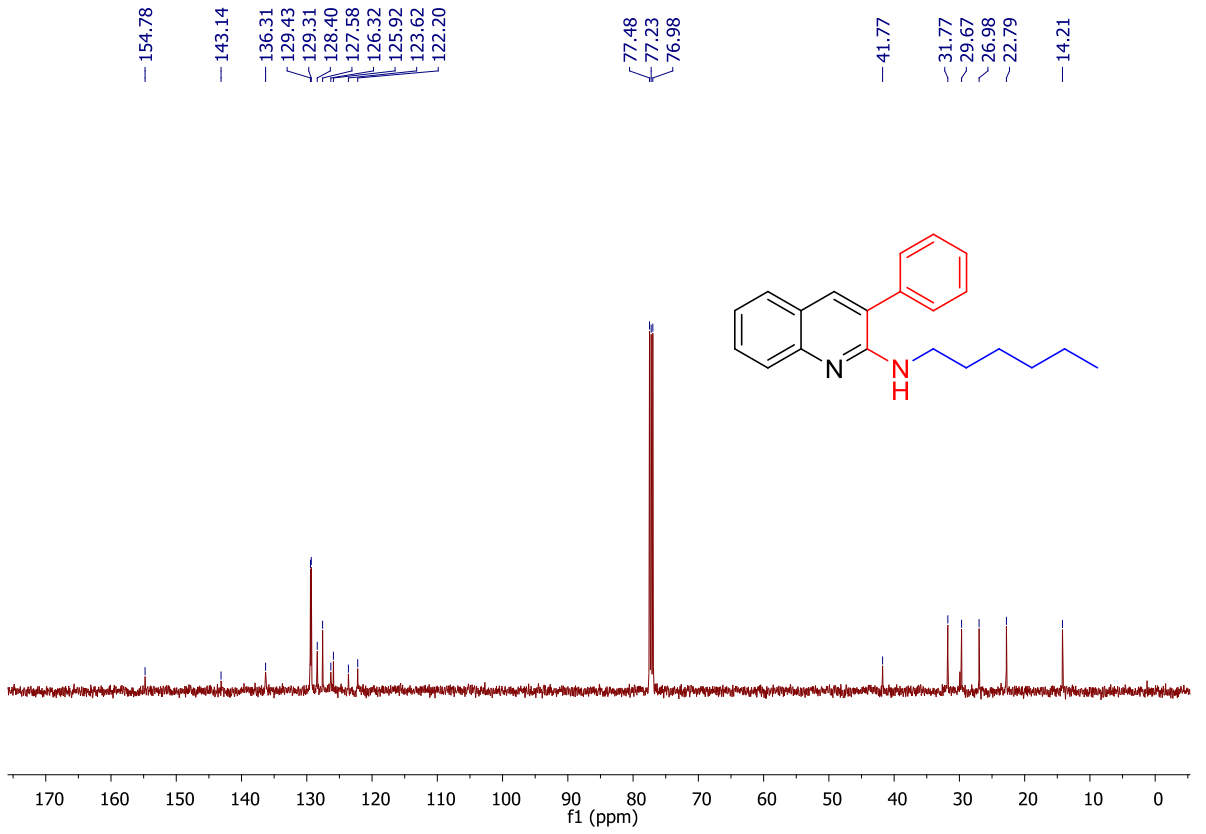
1.06
6.22
1.05
1.01
2.09
2.09
6.03
3.04
f1 (ppm)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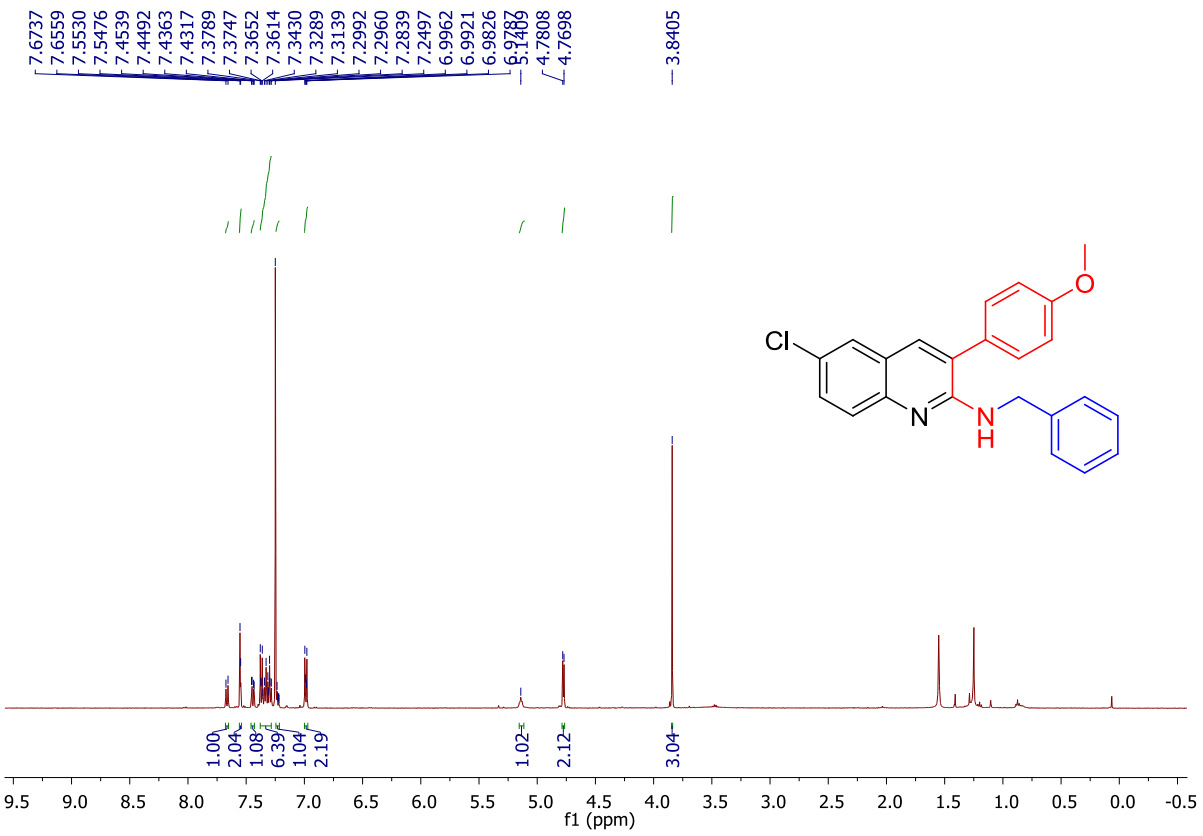
128.40
127.58
126.32
125.92
123.62
122.20
77.48
77.23
76.98
41.77
31.77
29.67
26.98
22.79
14.21
N
N
H
f1 (ppm)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7.4539
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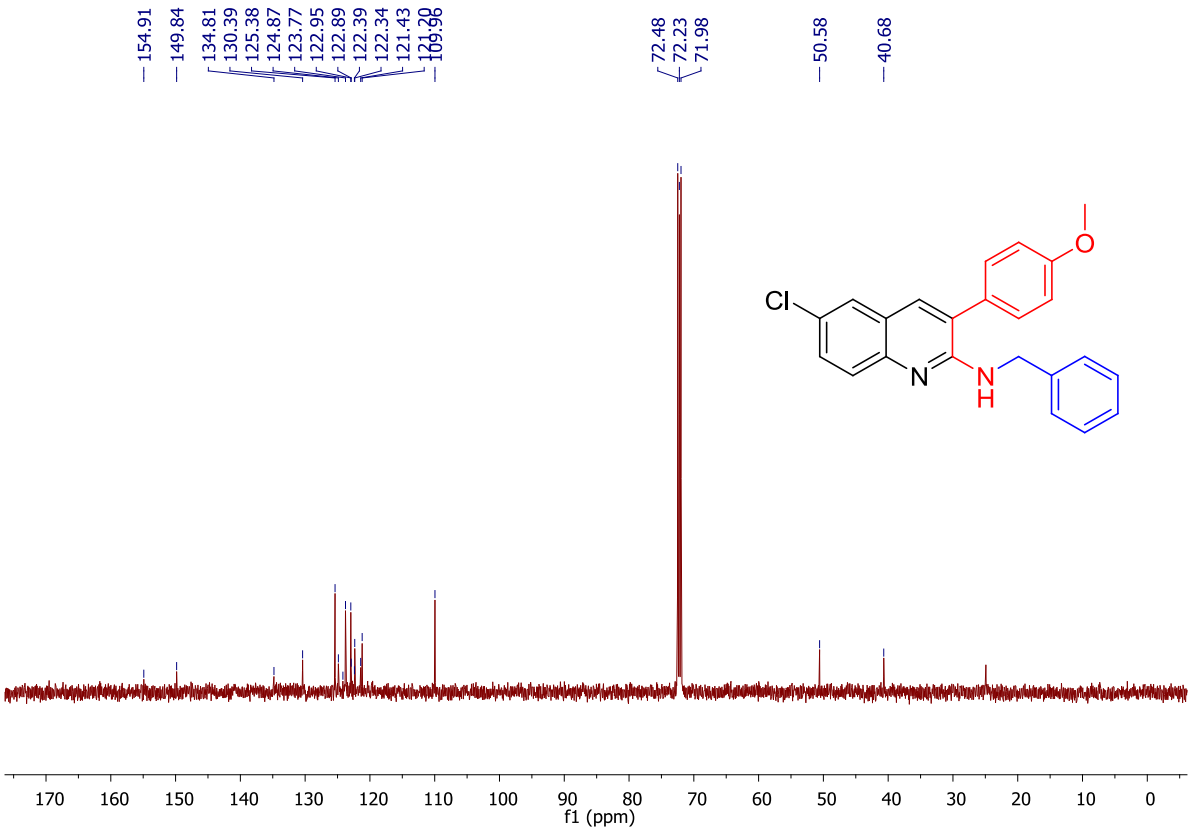
7.4363
7.4317
7.3789
7.3747
7.3652
7.3614
7.3430
7.3289
7.3139
7.2992
7.2960
7.2839
7.2497
6.9962
6.9921
6.9826
5.1489
4.7808
4.7698
3.8405
1.00
2.04
1.08
6.39
1.04
2.19
1.02
2.12
3.04
Cl
O
N
N
H
f1 (ppm)


154.91
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134.81
130.39
125.38
124.87
123.77
122.95
122.89
122.39
122.34
121.43
72.48
72.23
71.98
50.58
40.68
Cl
O
N
N
H
f1 (ppm)