

Supporting Information

Catalyst-free Electrochemical Decarboxylative Cross-Coupling of *N*-Hydroxyphthalimide Esters and *N*-Heteroarenes towards C(sp³)-C(sp²) Bond Formation

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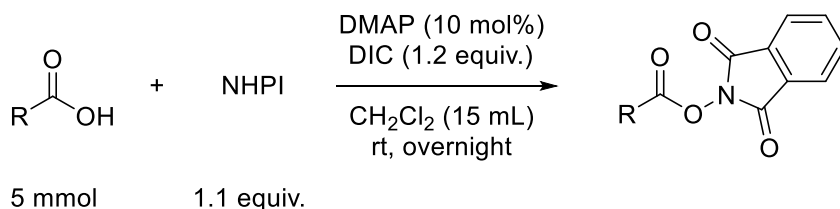
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General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. DMA was purchased from Sinopharm. *p*-TsOH was purchased from Innochem, the other compounds, such as quinoline derivatives, acid derivatives, NHPI and DIC were purchased from Heowns. ⁿBu₄NBF₄ was purchased from J&K. The NHP esters (1a-1l) were prepared according to literature report. Graphite felt was purchased from Hitechcarbon Co., Ltd. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. GC yields were recorded with a Shimadzu GC-2014. GC-MS was recorded by Shimadzu GCMS-QP2010 SE. All new compounds were characterized by ¹H NMR, ¹³C NMR, ¹⁹F NMR and HRMS. The known compounds were characterized by ¹H NMR, ¹³C NMR and ¹⁹F NMR. ¹H and ¹³C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ¹H), and CDCl₃ (77.16 ppm for ¹³C) respectively. High resolution mass spectra (HRMS) were measured with Orbitrap Velos Pro, Thermo Scientific or Waters Micromass GCT Premier, accurate masses were reported for the molecular ion + proton ([M+H]⁺) or molecular ion + Na⁺ ([M+Na]⁺).

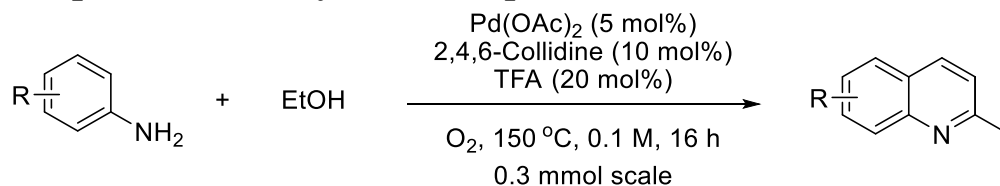
Experimental section

1) General procedure for synthesis of redox-active esters (1a-1l)¹

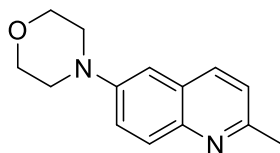


General procedure: To a solution of the corresponding acid (5 mmol, 1.0 equiv.), 4-dimethylaminopyridine (61 mg, 0.5 mmol, 10 mol%) and *N,N*-diisopropylcarbodiimide (756 mg, 0.6 mmol, 1.2 equiv.) in CH₂Cl₂ (15 mL) was stirred under air at room temperature for 5 min. Then, the NHPI (897 mg, 5.5 mmol, 1.1 equiv.) was added into the solution, and stirred overnight at room temperature. After reaction, the solution was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluted with petroleum/ethyl acetate to afford the desired product. The compound **1a-1l** was previously reported.

2) General procedure for synthesis of quinlines (3c and 3e)²

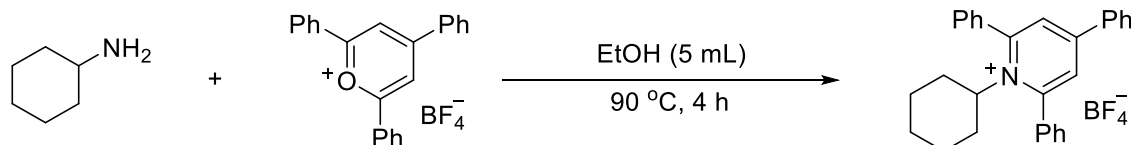


General procedure: Anilines 1 (0.3 mmol), Pd(OAc)_2 (5 mol%), 2,4,6-collidine (10 mol%), and TFA (20 mol%) were added to a Schlenk tube charged with a magnetic stir bar in 3.0 mL of ethanol. The resulting suspension was stirred at 150 °C under O_2 for 16 h. After reaction, the solution was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with petroleum/ethyl acetate to afford the desired product.



4-(2-methylquinolin-6-yl)morpholine (3e). ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.90 (m, 2H), 7.45 (dd, J = 9.6, 2.8 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 2.8 Hz, 1H), 3.93 – 3.91 (m, 4H), 3.28 – 3.26 (m, 4H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.39, 148.84, 143.65, 135.19, 129.48, 127.49, 122.45, 122.14, 109.36, 67.02, 49.75, 25.20.

3) General procedure for synthesis of *N*-cyclohexylpyridinium salt (6)³



General procedure: A Schlenk tube equipped with a magnetic stirrer bar was charged with triphenylpyrylium tetrafluoroborate (5 mmol, 1.0 equiv.) and the cyclohexylamine (6 mmol, 1.2 equiv.). Ethanol (5 mL) was added to the reaction vessel and the tube was sealed. The reaction mixture was heated to 90 °C and after 4 h cooled to ambient temperature. The solid was collected by filtration and washed with ethanol and diethyl ether. After the operations required the solids were dried under reduced pressure to obtain the analytically pure pyridinium salts.

4) Procedures and analytical data of compounds for alkylated product

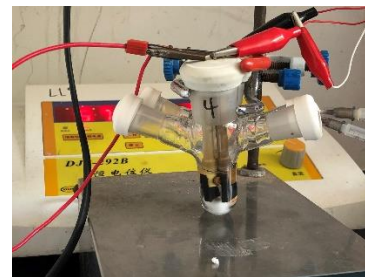
Graphical guide for the set-up: As experiment set-up, a piece of graphite felt (15 mm×10 mm×3 mm) was fixed on electrode for anode, and another piece of graphite felt (15 mm×10 mm×3 mm) was fixed on electrode for cathode. Rubber plugs, magneton, an undivided three-necked bottle and a dual display potentiostat (HJS-292B) (made in China) were used.



A) graphite felt anode and cathode



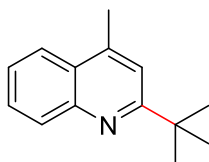
B) Assembly of electrochemical cell



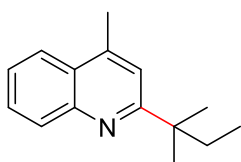
C) Current control electrolysis

General conditions: An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped a graphite felt (15 mm×10 mm×3 mm) electrode as the anode and another graphite felt (15 mm×10 mm×3 mm) electrode as the cathode. The corresponding ester (0.4 mmol, if it was solid), the quinoline derivate (0.2 mmol, if it was solid) and $n\text{Bu}_4\text{NBF}_4$ (82.3mg, 0.25 mmol, 0.05 M) was added into the undivided cell. And then the cell was charged with argon gas by glove box. $p\text{-TsOH}$ (51.6mg, 0.3 mmol, 1.5 equiv.) was added in the glove box. After leaving glove box, the cell was charged with nitrogen. Finally, DMA (5 mL) were added. If any substrate was liquid, it would be added by using microsyringe before adding the solvent. The reaction mixture was stirred and electrolyzed at a constant current of 7.5 mA under room temperature for 2.5 h. The reaction was quenched with saturated sodium carbonate (aq.). The organic layer was extracted with EtOAc, dried with anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

Analytical data of compounds:

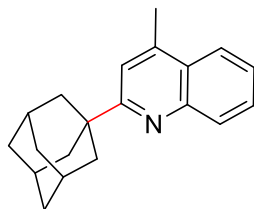


2-(tert-butyl)-4-methylquinoline (3aa). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 50:1) to give **3aa** in 82% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ 1H), 7.93 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.67-7.63 (m, 1H), 7.50-7.46 (m, 1H), 7.35 (d, $J = 0.8$ Hz, 1H), 2.68 (d, $J = 0.8$ Hz, 3H), 1.46 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.04, 147.38, 143.73, 130.04, 128.82, 126.65, 125.50, 123.51, 119.04, 38.04, 30.26, 19.12.

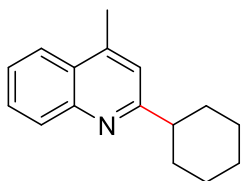


4-methyl-2-(tert-pentyl)quinoline (3ba) Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 50:1) to give **3ba** in 83% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.93 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.67-7.63 (m, 1H), 7.50-7.46 (m, 1H), 7.29 (s, 1H), 2.67 (d, $J = 0.4$ Hz, 3H), 1.83

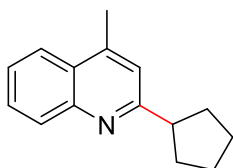
(q, $J = 7.6$ Hz, 2H), 1.42 (s, 6H), 0.73 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.17, 147.47, 143.47, 130.08, 128.73, 126.59, 125.46, 123.52, 119.52, 41.31, 35.97, 27.48, 19.12, 9.40.



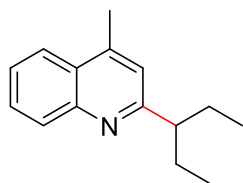
2-((1s,3s)-adamantan-1-yl)-4-methylquinoline (3ca). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3ca** in 67% yield as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$, 1H), 7.93 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.67-7.63 (m, 1H), 7.50-7.46 (m, 1H), 7.32 (d, $J = 0.8$ Hz, 1H), 2.68 (m, $J = 0.8$ Hz, 3H), 2.15-2.10 (s, 9H), 1.82 (t, $J = 2.8$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.82, 147.60, 143.70, 130.03, 128.76, 126.82, 125.45, 123.56, 118.67, 41.91, 39.66, 37.01, 28.95, 19.15.



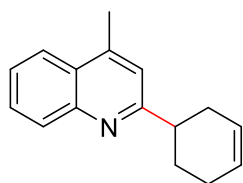
2-cyclohexyl-4-methylquinoline (3da). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3da** in 91% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.93 (dd, $J = 8.4$, 0.8 Hz, 1H), 7.68-7.63 (m, 1H), 7.50-7.46 (m, 1H), 7.16 (s, 1H), 2.87 (tt, $J = 12.0$, 3.2 Hz, 1H), 2.67 (s, 3H), 2.01 (dd, $J = 13.2$, 1.6 Hz, 2H), 1.91 – 1.86 (dt, $J = 12.8$, 3.2 Hz, 2H), 1.81 – 1.77 (m, 1H), 1.62 (qd, $J = 12.4$, 3.2 Hz, 2H), 1.46 (qt, $J = 12.8$, 3.2 Hz, 2H), 1.34 (tt, $J = 12.4$, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.62, 147.70, 144.32, 129.57, 129.02, 127.12, 125.45, 123.66, 120.33, 47.74, 32.94, 26.67, 26.23, 18.96.



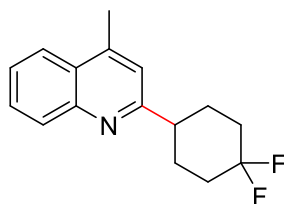
2-cyclopentyl-4-methylquinoline (3ea). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3ea** in 63% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.89 – 7.87 (m, 1H), 7.65-7.61 (m, 1H), 7.47-7.43 (m, 1H), 7.14 (s, 1H), 3.36 – 3.28 (m, 1H), 2.61 (d, $J = 7.2$ Hz, 3H), 2.18 – 2.12 (m, 2H), 1.91 – 1.70 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.88, 147.52, 144.06, 129.46, 128.90, 126.95, 125.33, 123.53, 120.64, 48.84, 33.60, 26.06, 18.82.



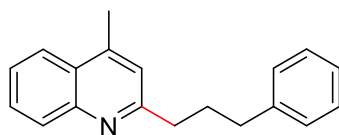
4-methyl-2-(pentan-3-yl)quinoline (3fa). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3fa** in 66% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.95 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.69-7.64 (m, 1H), 7.52-7.48 (m, 1H), 7.10 (d, $J = 0.4$ Hz, 1H), 2.77-2.68 (m, 4H), 1.82-1.74 (m, 4H), 0.83 (t, $J = 7.6$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.75, 147.74, 144.07, 129.66, 128.94, 127.16, 125.44, 123.70, 120.79, 52.34, 28.39, 19.01, 12.39.



2-(cyclohex-3-en-1-yl)-4-methylquinoline (3ga). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3ga** in 72% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.95 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.69-7.65 (m, 1H), 7.52-7.48 (m, 1H), 7.18 (s, 1H), 5.87 – 5.75 (m, 2H), 3.18 – 3.10 (m, 1H), 2.68 (s, 3H), 2.44-2.40 (m, 2H), 2.24– 2.21 (m, 2H), 2.09 – 2.05 (m, 1H), 1.97-1.87 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.04, 147.71, 144.51, 129.60, 129.12, 127.14, 127.02, 126.52, 125.58, 123.70, 120.50, 43.26, 31.49, 28.70, 25.78, 18.99.

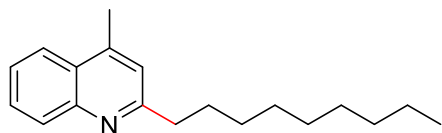


2-(4,4-difluorocyclohexyl)-4-methylquinoline (3ha). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to give **3ha** in 50% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.96 (dd, $J = 7.2, 0.8$ Hz, 1H), 7.71-7.67 (m, 1H), 7.54-7.50 (m, 1H), 7.17 (s, 1H), 2.97 (tt, $J = 11.2, 3.6$ Hz, 1H), 2.70 (d, $J = 0.8$ Hz, 3H), 2.30-2.22 (m, 2H), 2.11-1.84 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.00, 147.66, 144.91, 129.60, 129.35, 127.25, 125.89, 123.77, 123.77, 123.39 (dd, $J = 243.2, 240.3$ Hz), 119.89, 45.29, 33.87 (dd, $J = 25.6, 22.8$ Hz), 28.86 (d, $J = 9.8$ Hz), 19.02. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -91.60 (d, $J = 236.0$ Hz), -101.54 (d, $J = 236.4$ Hz).

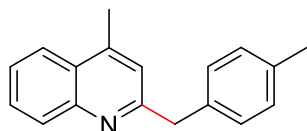


4-methyl-2-(3-phenylpropyl)quinoline (3ia) Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 15:1) to give **3ia** in 49% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.94 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.69-7.65 (m, 1H), 7.51-7.47 (m, 1H), 7.30-7.16 (m, 6H), 2.99-2.95 (m, 2H),

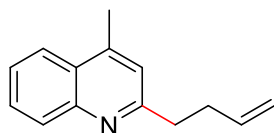
2.76-2.65 (m, 5H), 2.18 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.28, 147.80, 144.38, 142.26, 129.41, 129.18, 128.60, 128.42, 126.89, 125.89, 125.58, 123.71, 122.16, 38.86, 35.87, 31.77, 18.81.



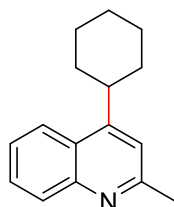
4-methyl-2-nonylquinoline (3ja). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3ja** in 52% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.51-7.47 (m, 1H), 7.14 (s, 1H), 2.93-2.89 (m, 2H), 2.67 (s, 3H), 1.83-1.75 (m, 2H), 1.44-1.26 (m, 12H), 0.89-0.85 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.93, 147.81, 144.23, 129.43, 129.10, 126.87, 125.47, 123.69, 122.18, 39.47, 32.01, 30.28, 29.76, 29.68, 29.65, 29.44, 22.81, 18.84, 14.26. **HR-MS (ESI):** m/z calculated for $[\text{C}_{19}\text{H}_{28}\text{N}]^+$, $[\text{M}+\text{H}]^+$: 270.2216, measured: 270.2225



4-methyl-2-(4-methylbenzyl)quinoline (3ka). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to give **3ka** in 36% yield as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 0.8 Hz, 1H), 7.70-7.66 (m, 1H), 7.52-7.48 (m, 1H), 7.16 (dd, J = 38.0, 8.0 Hz, 2H), 7.05 (s, 1H), 4.25 (s, 2H), 2.59 (d, J = 0.4 Hz, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.23, 147.67, 144.69, 136.38, 136.09, 129.57, 129.41, 129.25, 129.19, 126.97, 125.80, 123.73, 122.25, 45.20, 21.18, 18.84.

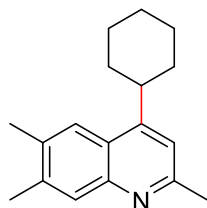


2-(but-3-en-1-yl)-4-methylquinoline (3la). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 15:1) to give **3la** in 21% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.4, 0.8 Hz, 1H), 7.70-7.66 (m, 1H), 7.53-7.49 (m, 1H), 7.15 (s, 1H), 5.98-5.88 (m, 1H), 5.12-5.07 (m, 1H), 5.02-4.98 (m, 1H), 3.03 (dd, J = 9.6, 8 Hz, 2H), 2.68 (d, J = 0.8 Hz, 3H), 2.61-2.55 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.80, 147.75, 144.53, 137.91, 129.39, 129.26, 126.95, 125.68, 123.76, 122.26, 115.30, 38.54, 34.02, 18.89.

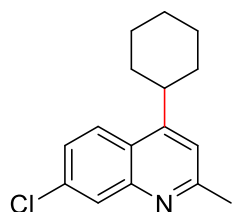


4-cyclohexyl-2-methylquinoline (3ab). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 15:1) to give **3ab** in 90% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.8 Hz, 2H), 7.67-7.63 (m, 1H), 7.51-7.47 (m, 1H), 7.17 (s, 1H), 3.31-3.26 (m, 1H), 2.72 (s, 3H), 2.02-1.84 (m, 5H), 1.60-

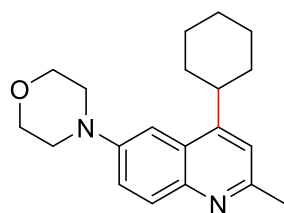
1.48 (m, 4H), 1.39-1.31 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.92, 153.43, 148.20, 129.59, 128.91, 125.38, 125.25, 122.96, 118.44, 38.88, 33.67, 27.05, 26.44, 25.67.



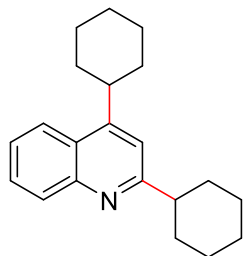
4-cyclohexyl-2,6,7-trimethylquinoline (3ac). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to give **3ac** in 89% yield as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.73 (s, 1H), 7.08 (s, 1H), 3.28-3.22 (m, 1H), 2.68 (s, 3H), 2.45 (d, J = 6.0 Hz, 6H), 1.99-1.84 (m, 5H), 1.58 – 1.47 (m, 4H), 1.38-1.29 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.83, 152.62, 147.26, 138.90, 134.96, 129.04, 123.66, 122.30, 117.65, 38.77, 33.68, 27.08, 26.48, 25.52, 20.55, 20.38. **HR-MS (ESI):** m/z calculated for $[\text{C}_{18}\text{H}_{24}\text{N}]^+$, $[\text{M}+\text{H}]^+$: 254.1903, measured: 254.1900.



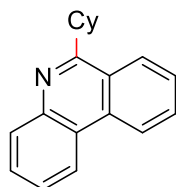
7-chloro-4-cyclohexyl-2-methylquinoline (3ad). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to give **3ad** in 90% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 2.0 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.41 (dd, J = 8.8, 2.0 Hz, 1H), 7.15 (s, 1H), 3.24-3.18 (m, 1H), 2.70 (s, 3H), 1.97-1.83 (m, 5H), 1.59-1.45 (m, 4H), 1.36-1.27 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.18, 153.44, 148.74, 134.60, 128.53, 126.19, 124.38, 123.66, 118.61, 38.93, 33.59, 26.93, 26.31, 25.62.



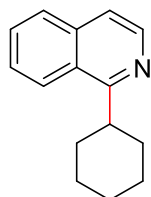
4-(4-cyclohexyl-2-methylquinolin-6-yl)morpholine (3ae). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) to give a mixture of **3ae** and **3e**, the NMR yield was 48% and **3ae** was a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 9.2 Hz, 1H), 7.42 (dd, J = 9.2, 2.8 Hz, 1H), 7.23 (d, J = 2.4 Hz, 1H), 7.11 (s, 1H), 3.94 (t, J = 4.4 Hz, 4H), 3.28 (t, J = 4.8 Hz, 4H), 3.20-3.16 (m, 1H), 2.67 (s, 3H), 2.02-1.84 (m, 5H), 1.63 – 1.47 (m, 4H), 1.39-1.32 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.27, 151.94, 148.65, 143.86, 130.36, 125.85, 121.51, 118.69, 105.27, 67.07, 49.94, 39.01, 33.45, 27.12, 26.47, 25.32. **HR-MS (ESI):** m/z calculated for $[\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}]^+$, $[\text{M}+\text{H}]^+$: 311.2118, measured: 311.2109



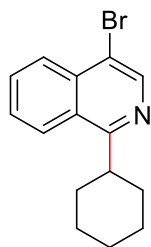
2,4-dicyclohexylquinoline (3af). Prepared according to general condition, but 4 equiv. of NHP ester (0.8 mmol) was used and the time was expanded to 5 hours. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give **3af** in 64% yield as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07-8.02 (m, 2H), 7.66-6.62 (m, 1H), 7.49-7.45 (m, 1H), 7.20 (s, 1H), 3.32-3.27 (m, 1H), 2.88 (tt, $J = 12.0, 3.2$ Hz, 1H), 2.03-1.77 (m, 10H), 1.69-1.29 (m, 10H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.73, 153.45, 148.14, 129.98, 128.68, 125.74, 125.29, 122.90, 115.84, 47.97, 39.06, 33.73, 33.00, 27.07, 26.70, 26.45, 26.23.



6-cyclohexylphenanthridine (3ag). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 50:1) to give **3ag** in 97% yield as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (d, $J = 8.0$ Hz, 1H), 8.47 (d, $J = 8.0$ Hz, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 8.13 (d, $J = 7.6$ Hz, 1H), 7.75-7.53 (m, 4H), 3.58 (tt, $J = 11.6, 2.8$ Hz, 1H), 2.08-1.81 (m, 7H), 1.60-1.36 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.33, 143.93, 133.03, 129.99, 129.96, 128.44, 127.11, 126.18, 125.65, 124.76, 123.40, 122.61, 121.89, 42.05, 32.38, 26.97, 26.42.

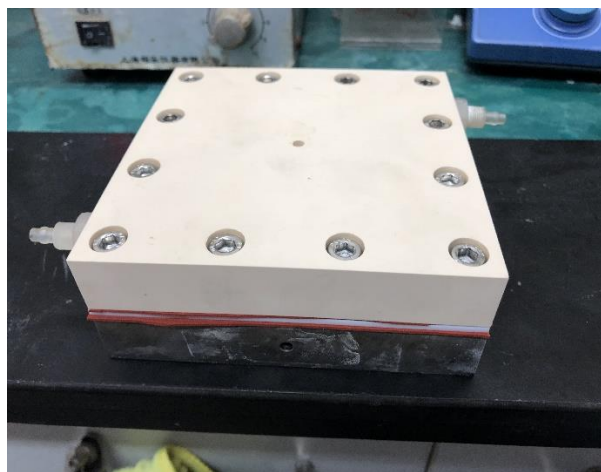


1-cyclohexylisoquinoline (3ah). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 15:1) to give **3ah** in 35% yield as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.48 (d, $J = 5.6$ Hz, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.63-7.54 (m, 2H), 7.45 (d, $J = 5.6$ Hz, 1H), 3.55 (tt, $J = 9.6, 3.2$ Hz, 1H), 2.00-1.79 (m, 7H), 1.52 (qt, $J = 12.4, 3.2$ Hz, 2H), 1.40 (tt, $J = 12.4, 3.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.71, 141.95, 136.38, 129.56, 127.57, 126.84, 126.29, 124.74, 118.92, 41.55, 32.63, 26.93, 26.30.



4-bromo-1-cyclohexylisoquinoline (3ai). Prepared according to general condition, after work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to give **3ai** in 65% yield as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.65 (s, 1H), 8.20 (dd, J = 13.2, 8.4 Hz, 2H), 7.78-7.74 (m, 1H), 7.66-7.62 (m, 1H), 3.51 (tt, J = 11.6, 2.8 Hz, 1H), 1.98-1.91 (m, 4H), 1.84- 1.74 (m, 3H), 1.52 (qt, J = 13.2, 3.6 Hz, 2H), 1.39 (tt, J = 12.4, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.44, 143.68, 134.96, 130.89, 127.83, 127.69, 126.94, 125.16, 117.63, 41.56, 32.63, 26.88, 26.26.

5) The gram scale reaction in continue-flow system



A The undivided electrolytic cell by using two pieces of carbon paper



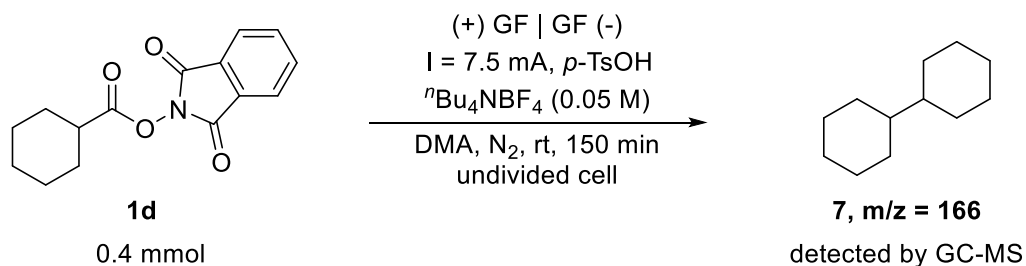
B The continuous-flow reactor

A 200 mL Schlenk tube equipped with a magnetic stirrer bar was charged with **1d** (4.10 g, 15 mmol, 2 equiv.) and $^t\text{Bu}_4\text{NBF}_4$ (1.64 g, 5 mmol, 0.05M). And then the tube was charged with argon gas by glove box. *p*-TsOH (1.94 g, 11.25 mmol, 1.5 equiv.) was added in the glove box. After leaving glove box, the cell was charged with nitrogen. Finally, **2a** (1.07 g, 7.5 mmol, 1 equiv.) and DMA (100 mL) were added. After stirring for 10 min, the pump was started and electrolyzed at a constant current of 10 mA under room temperature for 45 h. The reaction was quenched with saturated sodium carbonate (aq.). The organic layer was extracted with EtOAc, dried with anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel to give 71% of isolated yield (1.2 g).

For more details of the continue-flow device please check our previous work⁴.

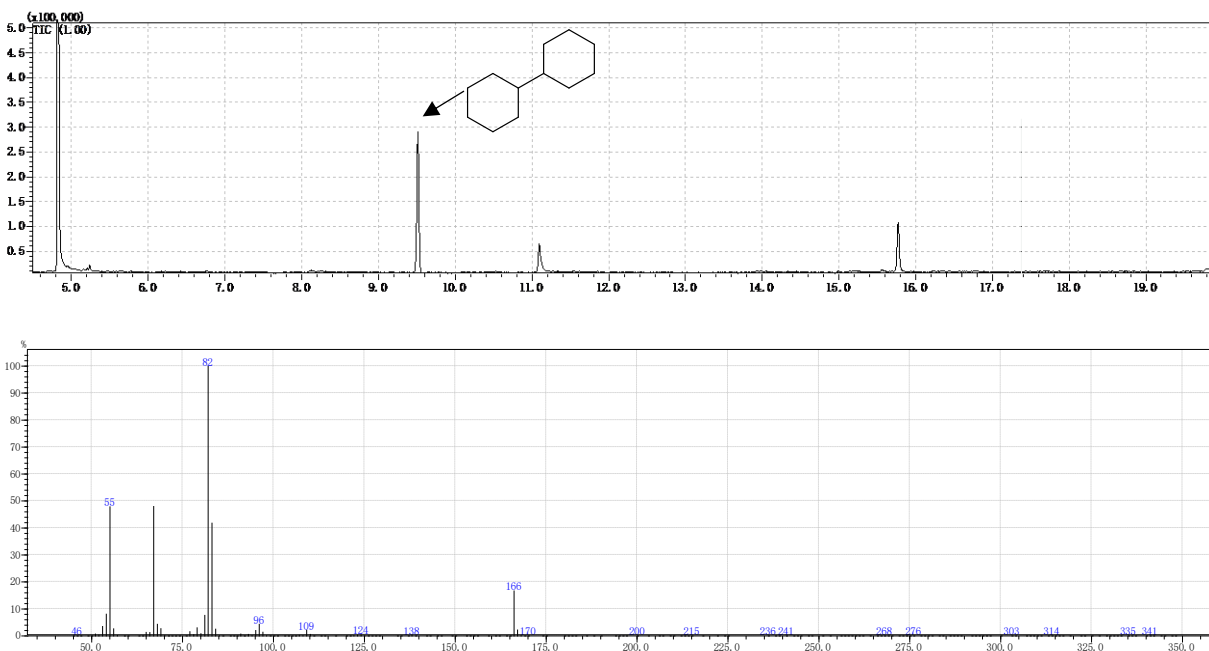
6) Control experiments

A: Home-coupling product

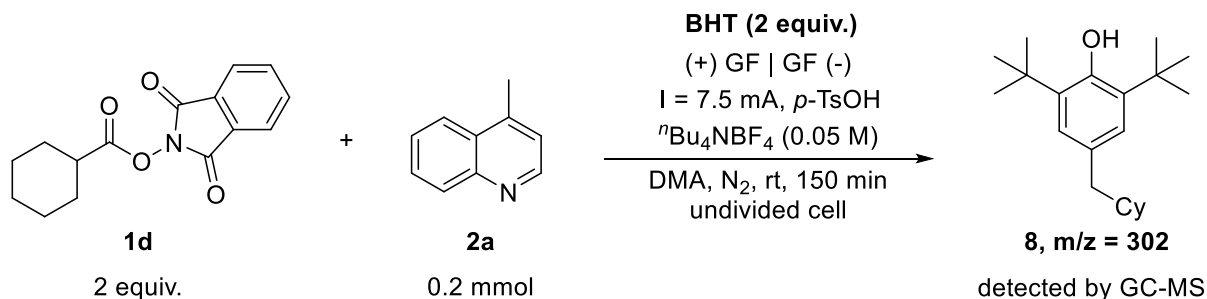


An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped a graphite felt (15 mm×10 mm×3 mm) electrode as the anode and another graphite felt (15 mm×10 mm×3 mm) electrode as the cathode. The **1d** (109.2 mg, 0.4 mmol), *n*Bu₄NBF₄ (82.3mg, 0.25 mmol, 0.05 M) was added in to the undivided cell. And then the cell was charged with argon gas by glove box. *p*-TsOH (51.6mg, 0.3 mmol, 1.5 equiv.) was added in the glove box. After leaving glove box, the cell was charged with nitrogen. Finally, DMA (5 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 7.5 mA under room temperature for 2.5 h. The reaction was quenched with saturated sodium carbonate (aq.). The organic layer was extracted with EtOAc (10 mL). Take a drop from the reaction solution and use the “plug” to filter it. Finally, dilute to 10 µL/ mL in a vial and do the GC-MS test.

GC-MS data

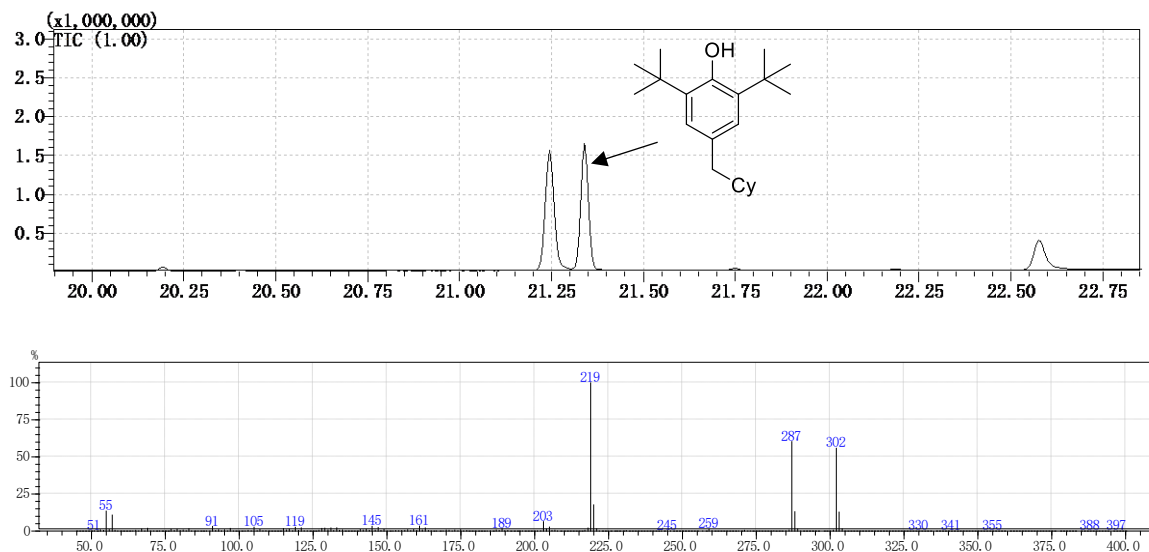


B: The radical trapping experiment

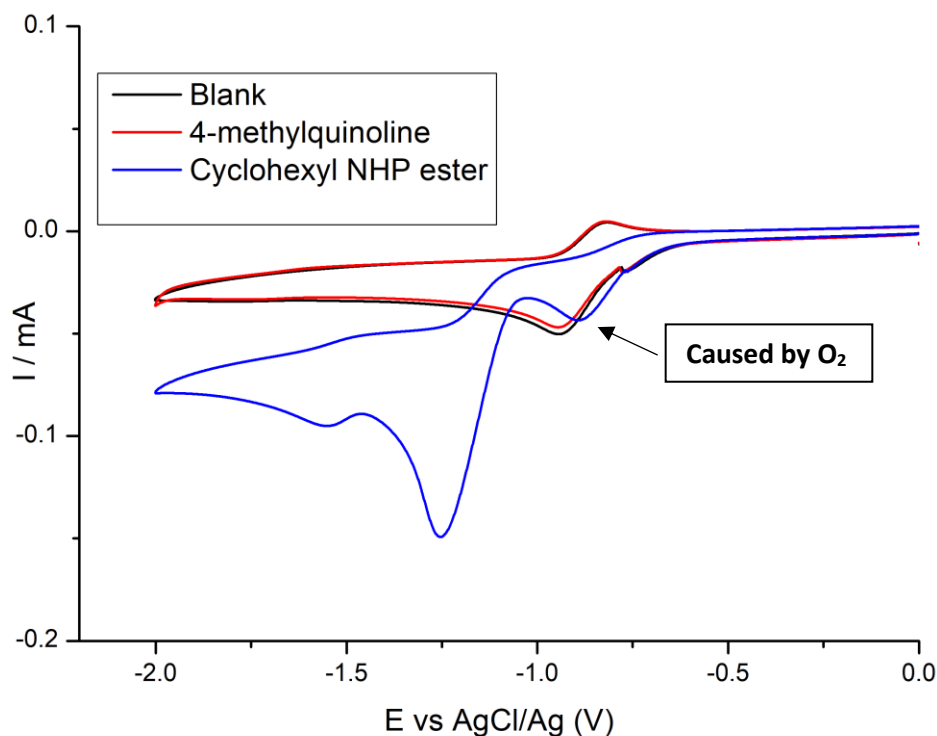


An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped a graphite felt (15 mm×10 mm×3 mm) electrode as the anode and another graphite felt (15 mm×10 mm×3 mm) electrode as the cathode. The ester **1d** (109.2 mg, 0.4 mmol), BHT (butylated hydroxytoluene, 44.0 mg, 0.4 equiv.) and $n\text{Bu}_4\text{NBF}_4$ (82.3mg, 0.25 mmol, 0.05 M) was added into the undivided cell. And then the cell was charged with argon gas by glove box. $p\text{-TsOH}$ (51.6mg, 0.3 mmol, 1.5 equiv.) was added in the glove box. After leaving glove box, the cell was charged with nitrogen. Finally, the quinoline **2a** (24 μL , 0.2 mmol) and DMA (5 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 7.5 mA under room temperature for 2.5 h. The reaction was quenched with saturated sodium carbonate (aq.). The organic layer was extracted with EtOAc (10 mL). Take a drop from the reaction solution and use the “plug” to filter it. Finally, dilute it to 10 μL / mL in a vial and do the GC-MS test.

GC-MS data



7) Cyclic voltammetry (CV) tests



CV test conditions: Study of the reduction potential during the electrolysis. A cyclic voltammograms in DMA (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and AgCl/Ag as the reference electrode. The scan rate was 100 mV/s.

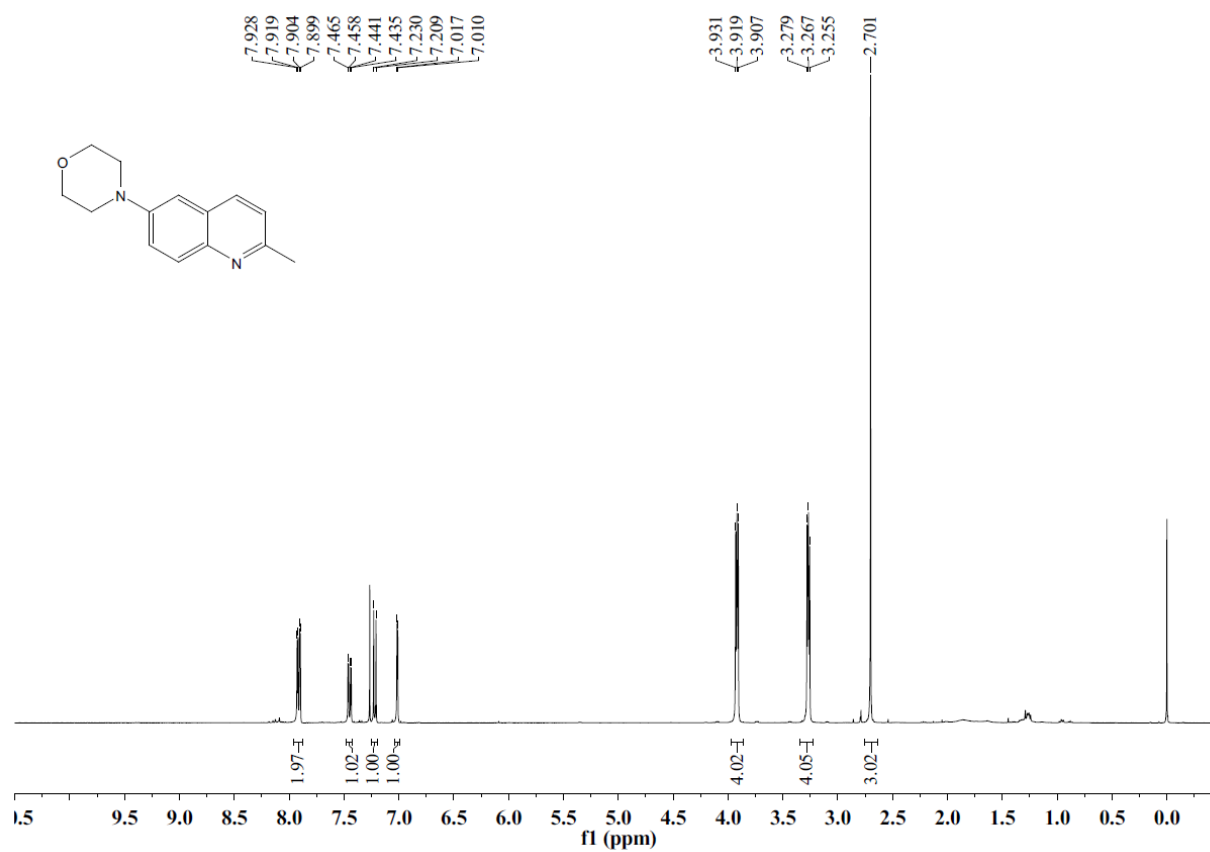
black line: 0.05 M ⁿBu₄NBF₄ in DMA (10 mA) under air; **red line:** 4-methylquinoline (**2a**, 0.1 mmol), 0.05 M ⁿBu₄NBF₄ in DMA (10 mA) under air; **blue line:** Cyclohexyl NHP ester (**1d**, 0.1 mmol), 0.05 M ⁿBu₄NBF₄ in DMA (10 mA) under air.

References

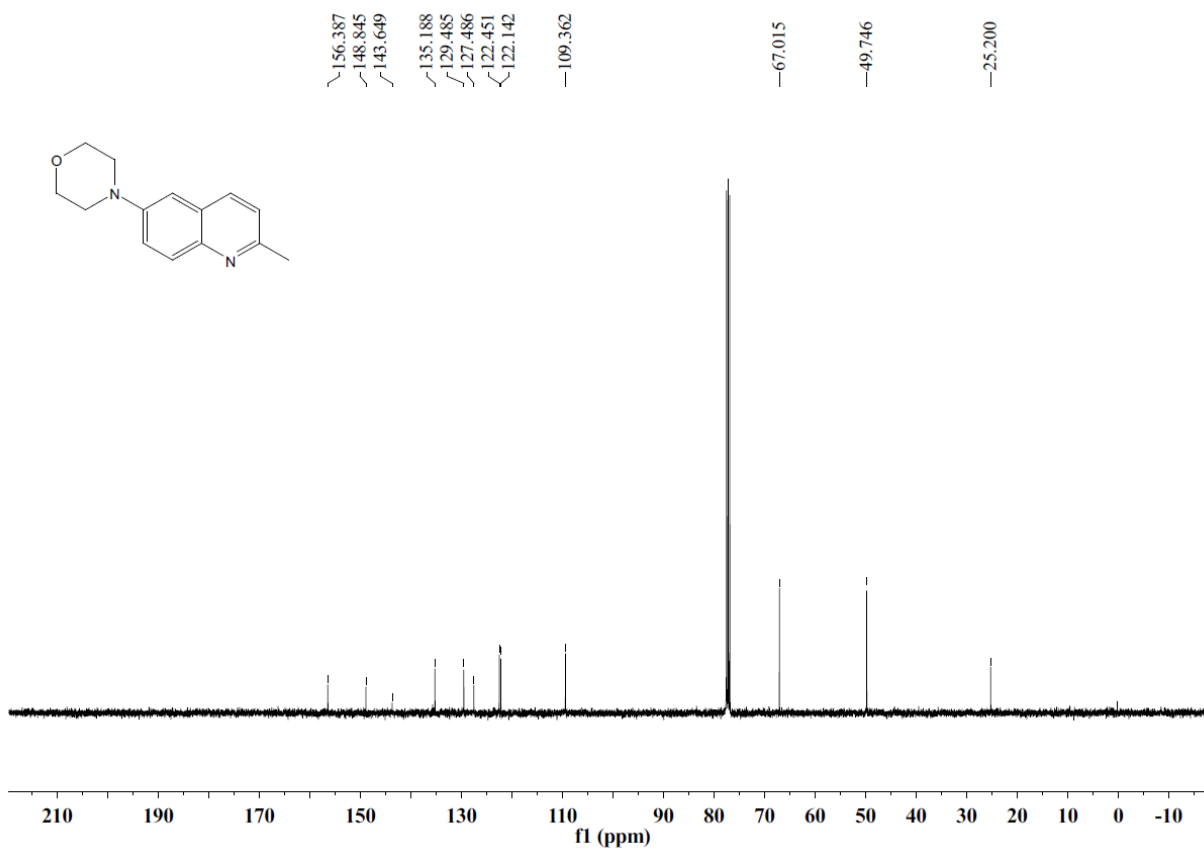
1. A. Tlahuext-Aca, R. Garza-Sanchez, and F. Glorius, *Angew. Chem. Int. Ed.*, 2017, **56**, 3708-3711.
2. J. Li, J. Zhang, H. Yang, and G. Jiang, *J. Org. Chem.*, 2017, **82**, 3284-3290.
3. F. Klauck, M. James, and F. Glorius, *Angew. Chem. Int. Ed.*, 2017, **56**, 12336-12339.
4. D. Wang, P. Wang, S. Wang, Y. Chen, H. Zhang and A. Lei, *Nature Commun.*, 2019, **10**, 2796

NMR Spectra of Products

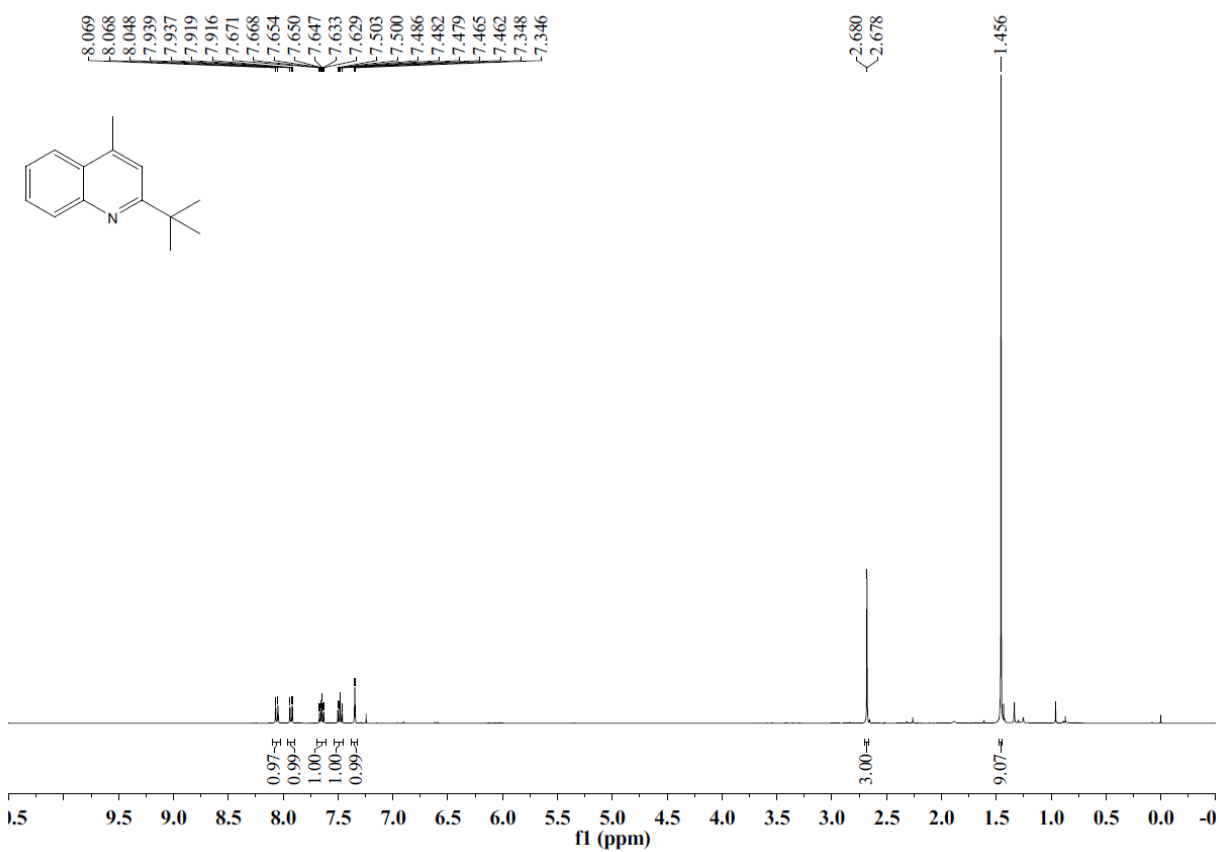
3e ¹H NMR



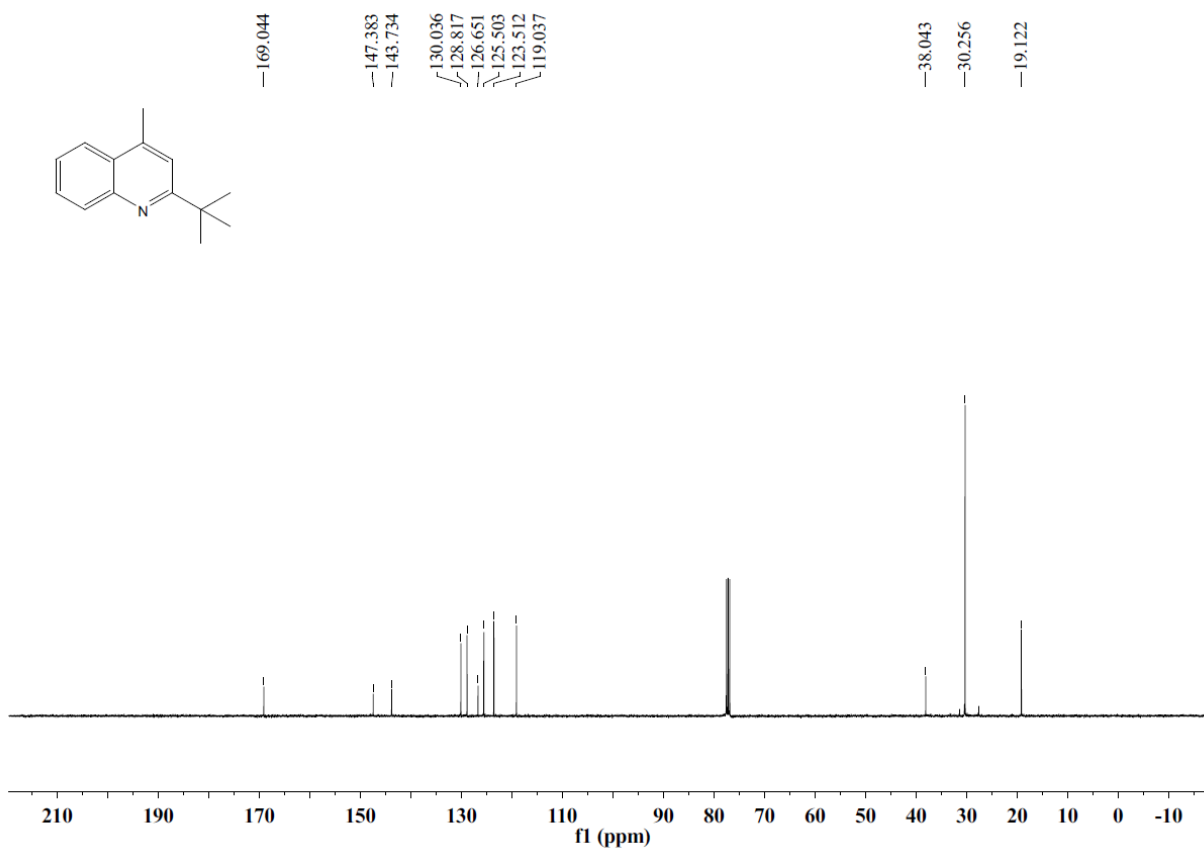
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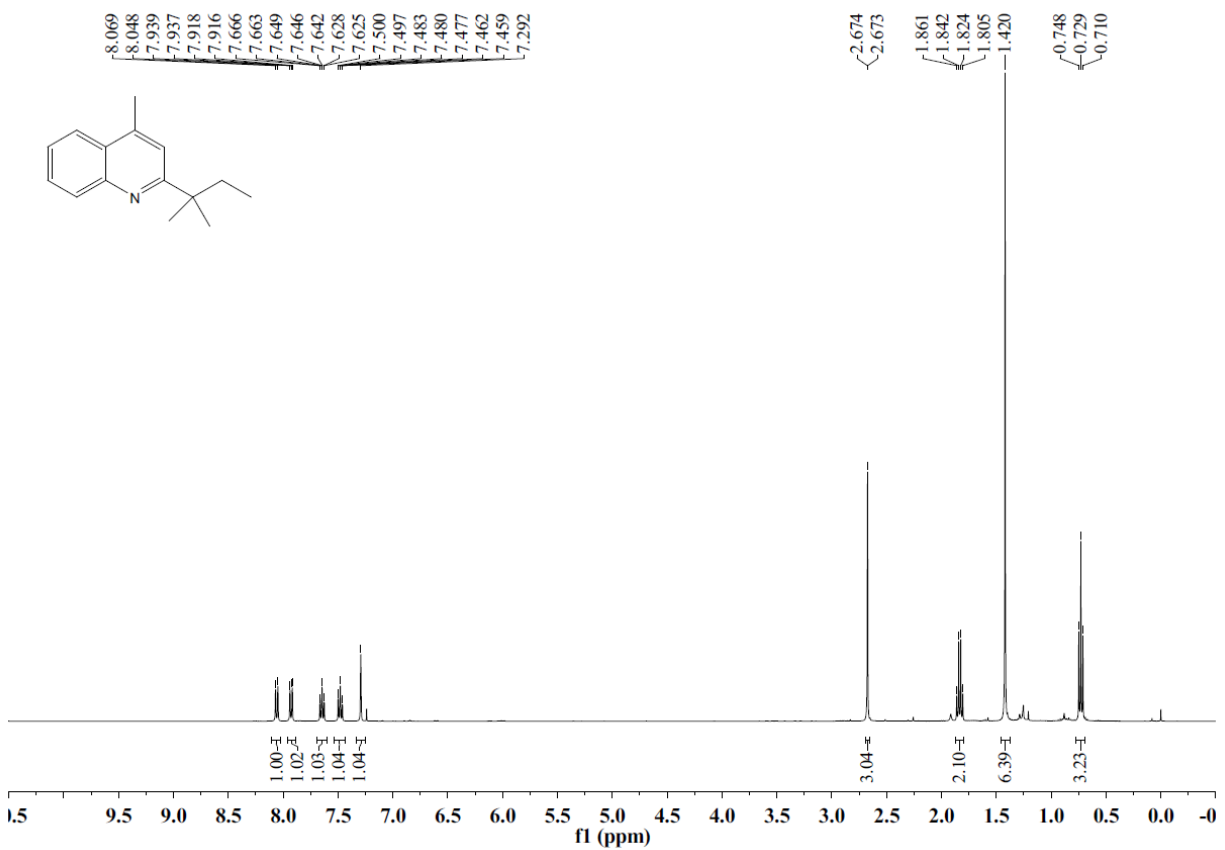
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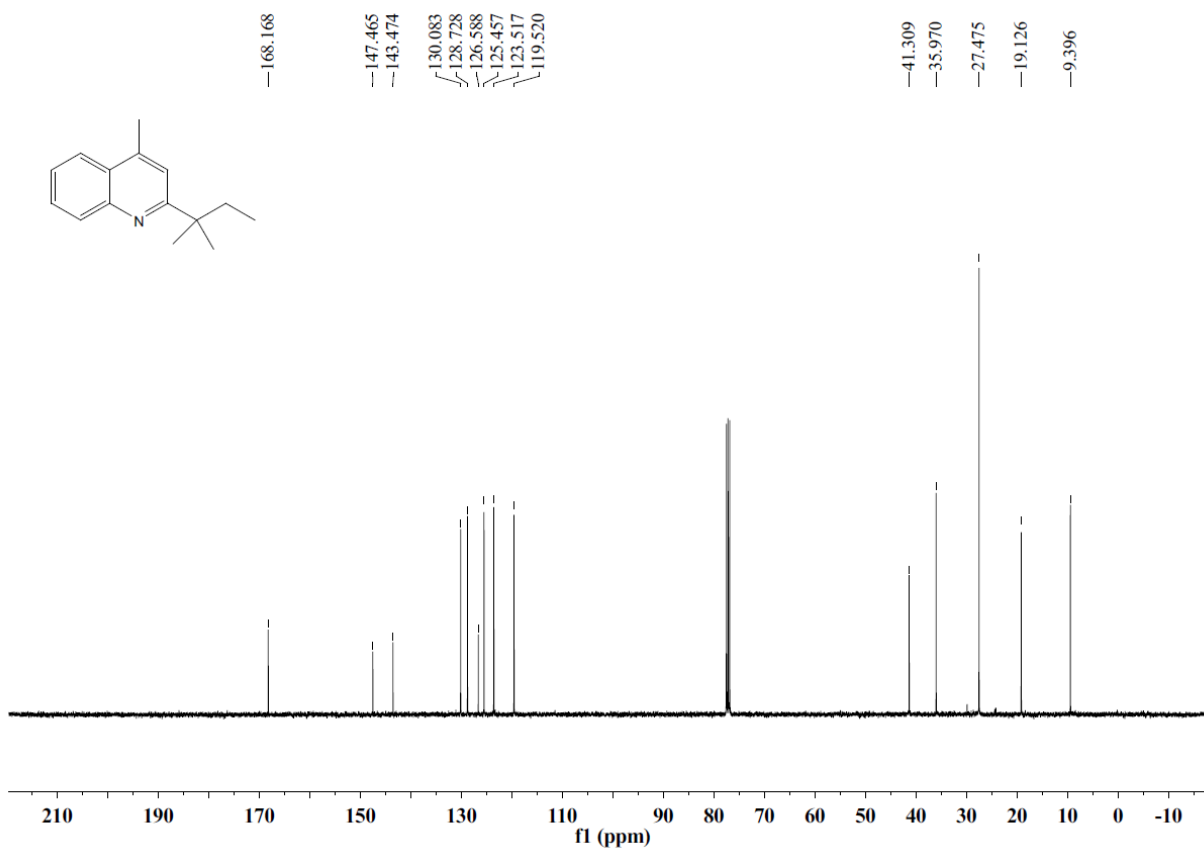
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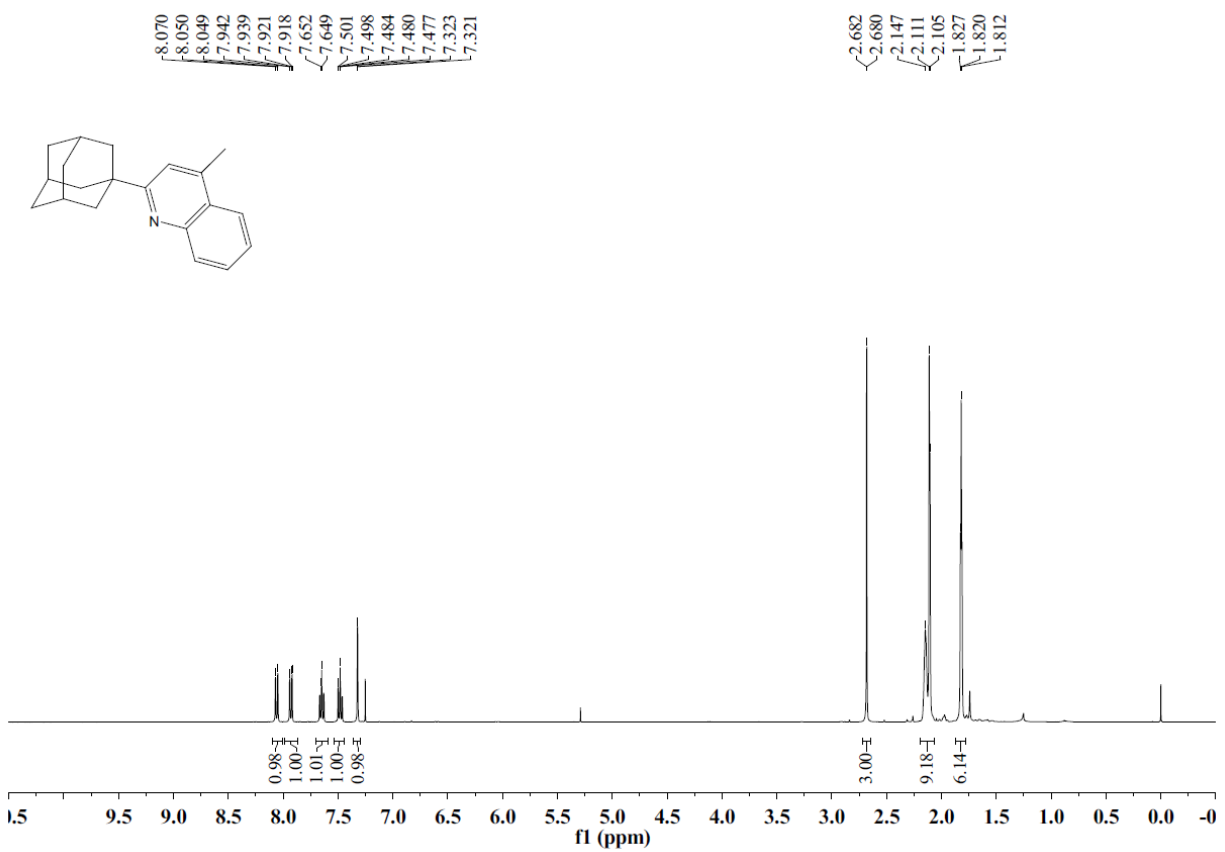
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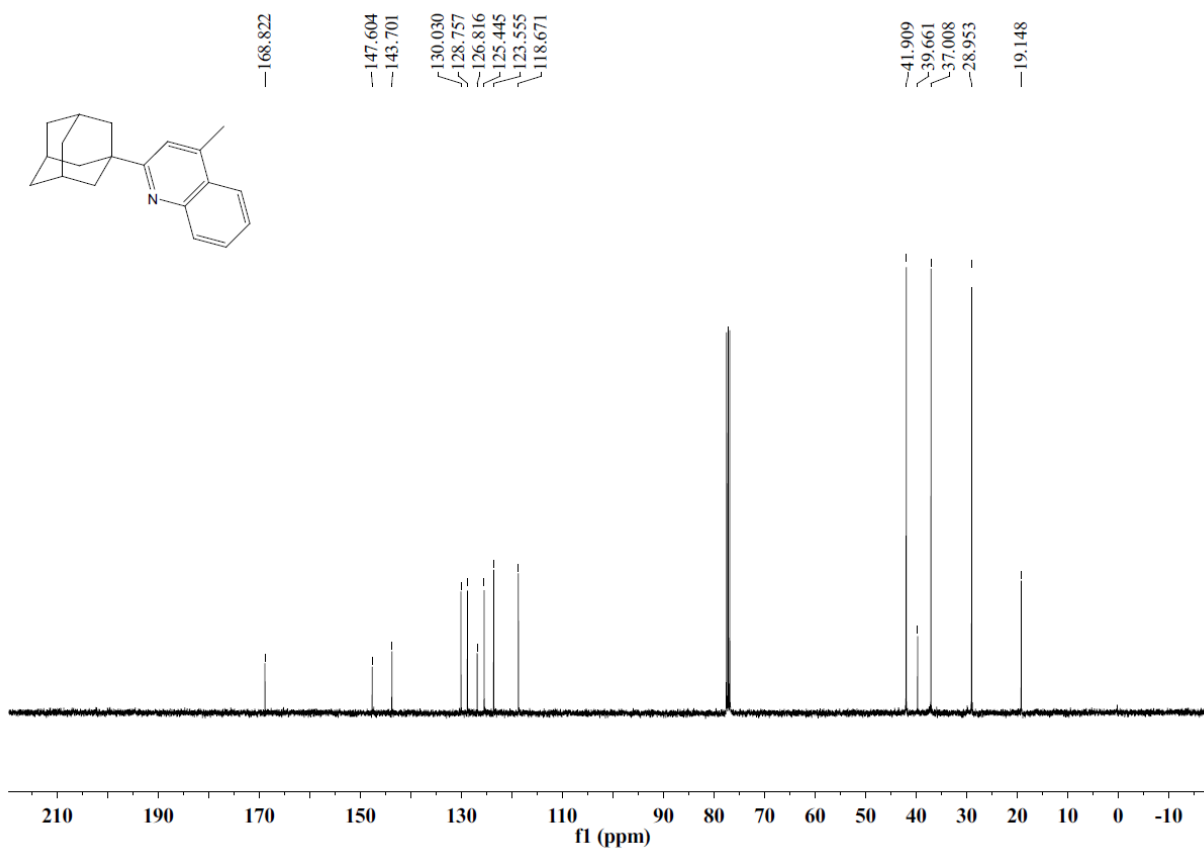
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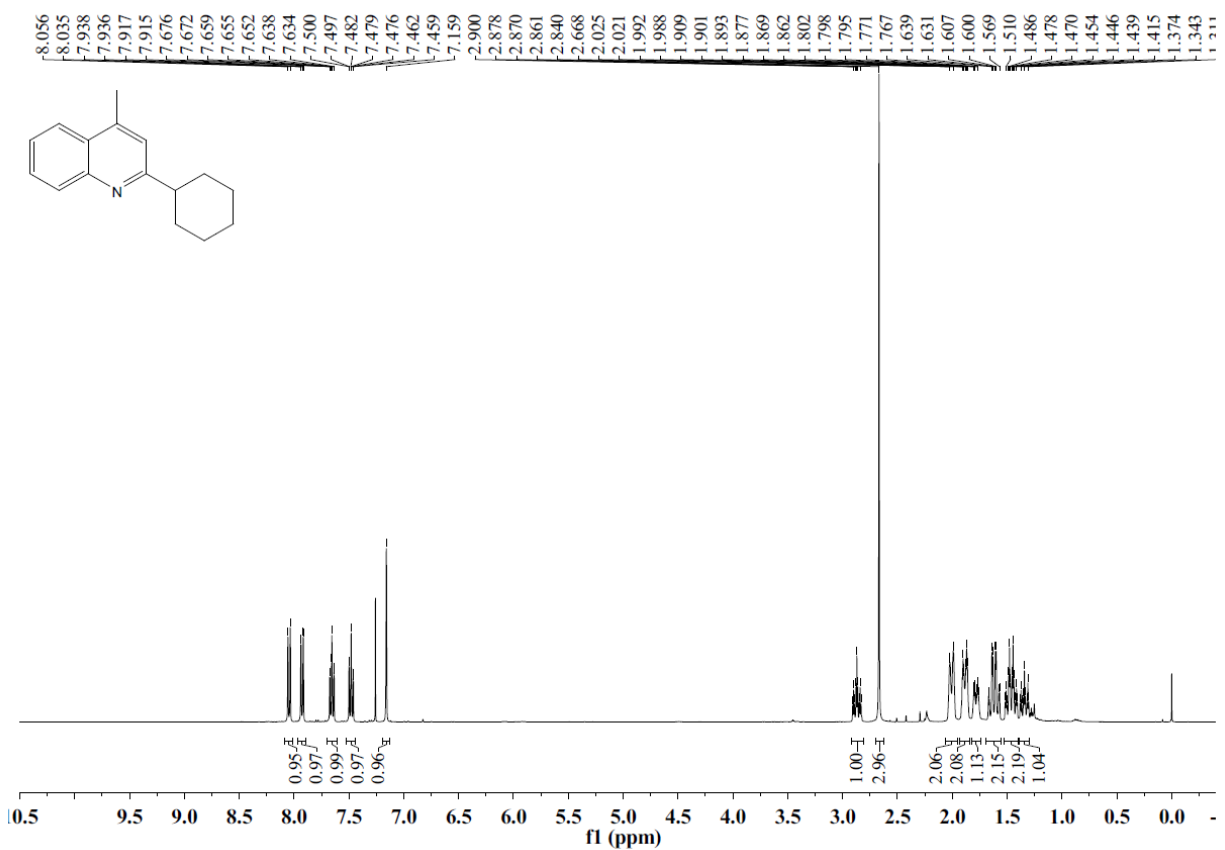
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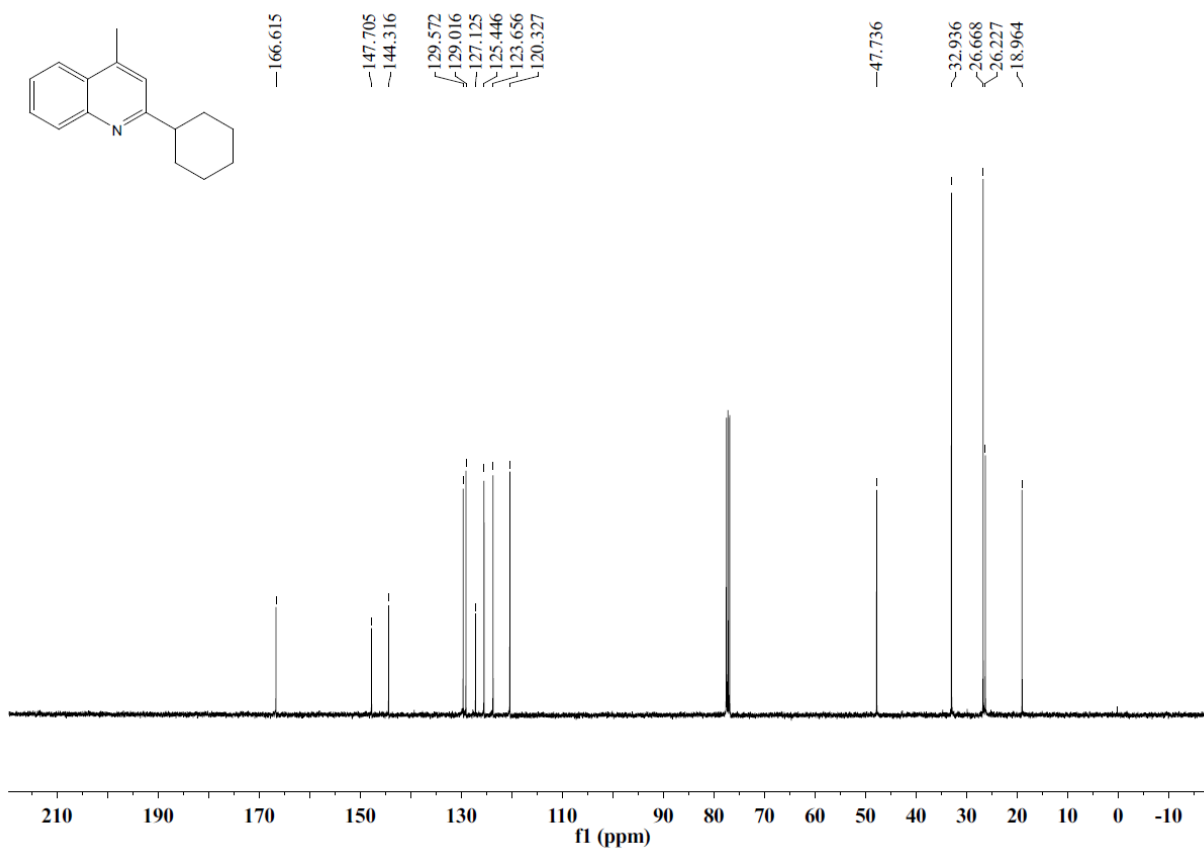
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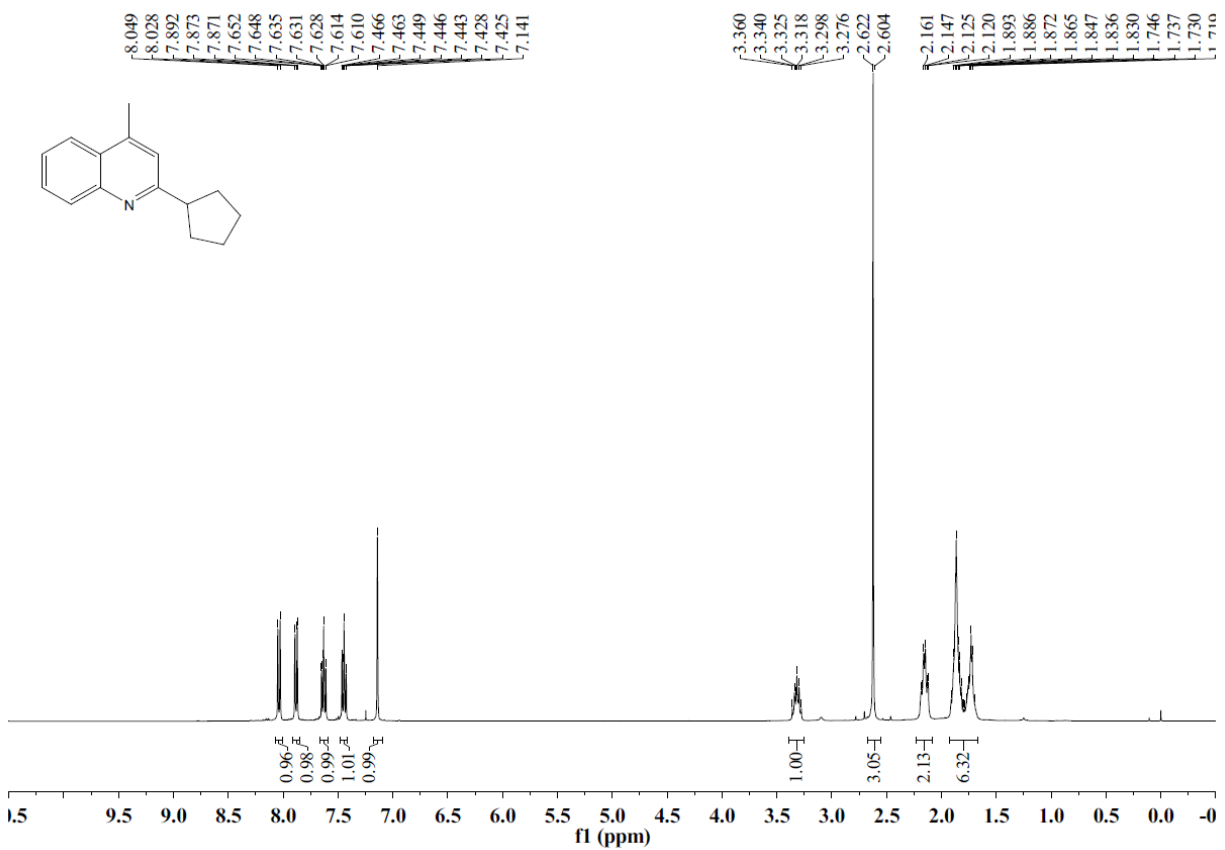
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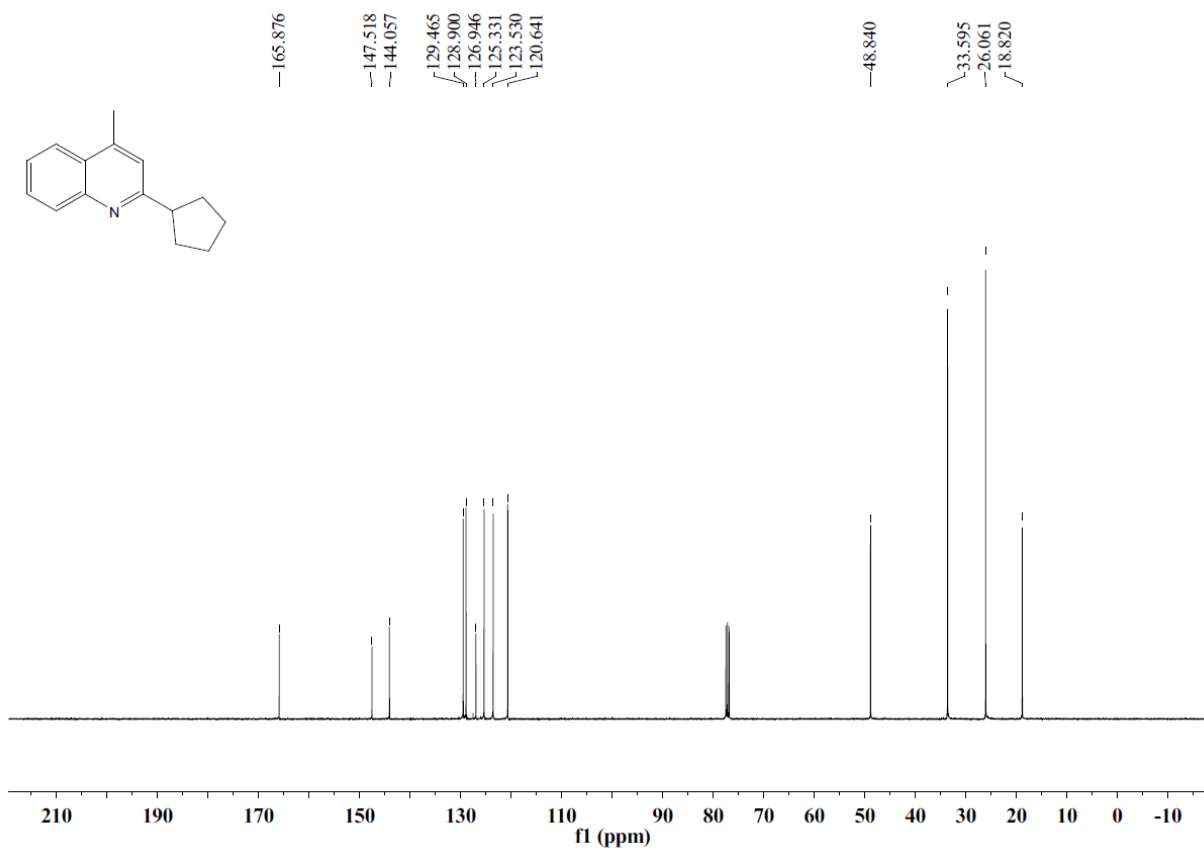
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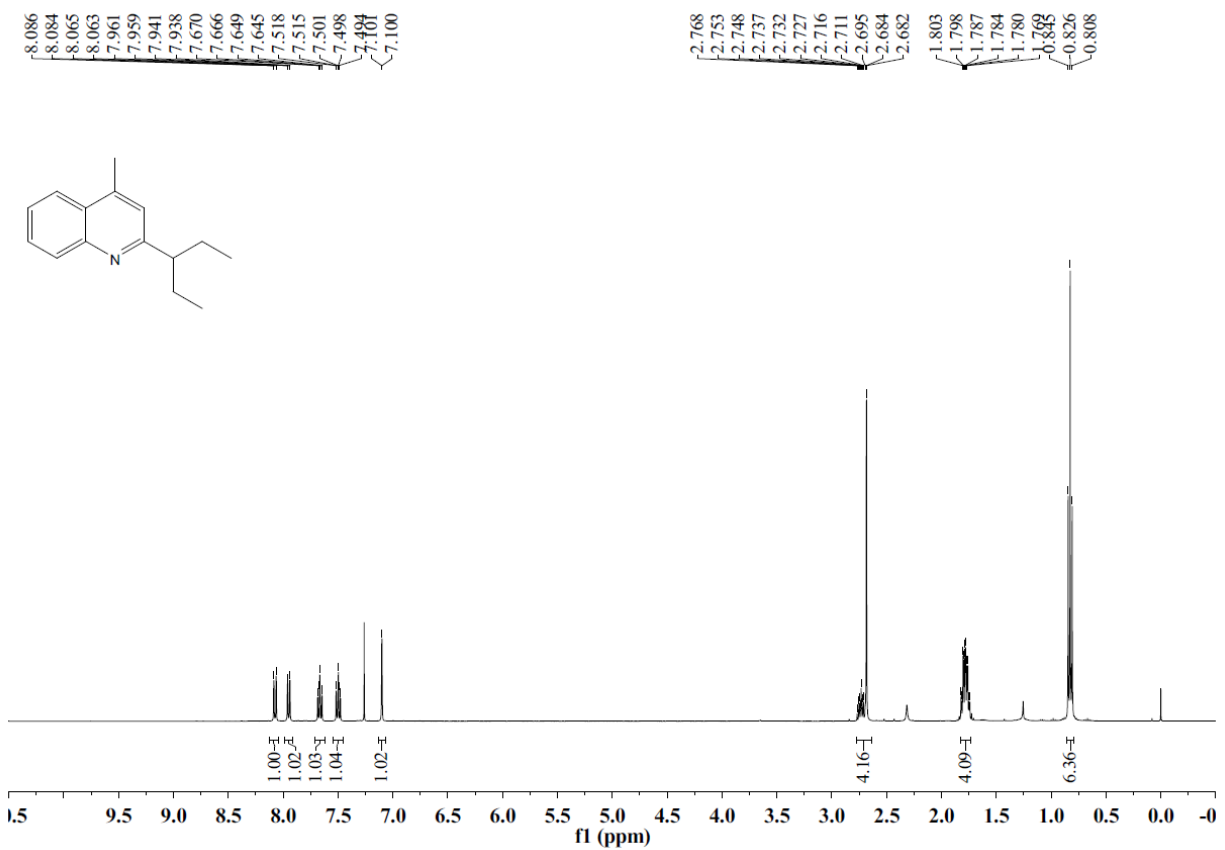
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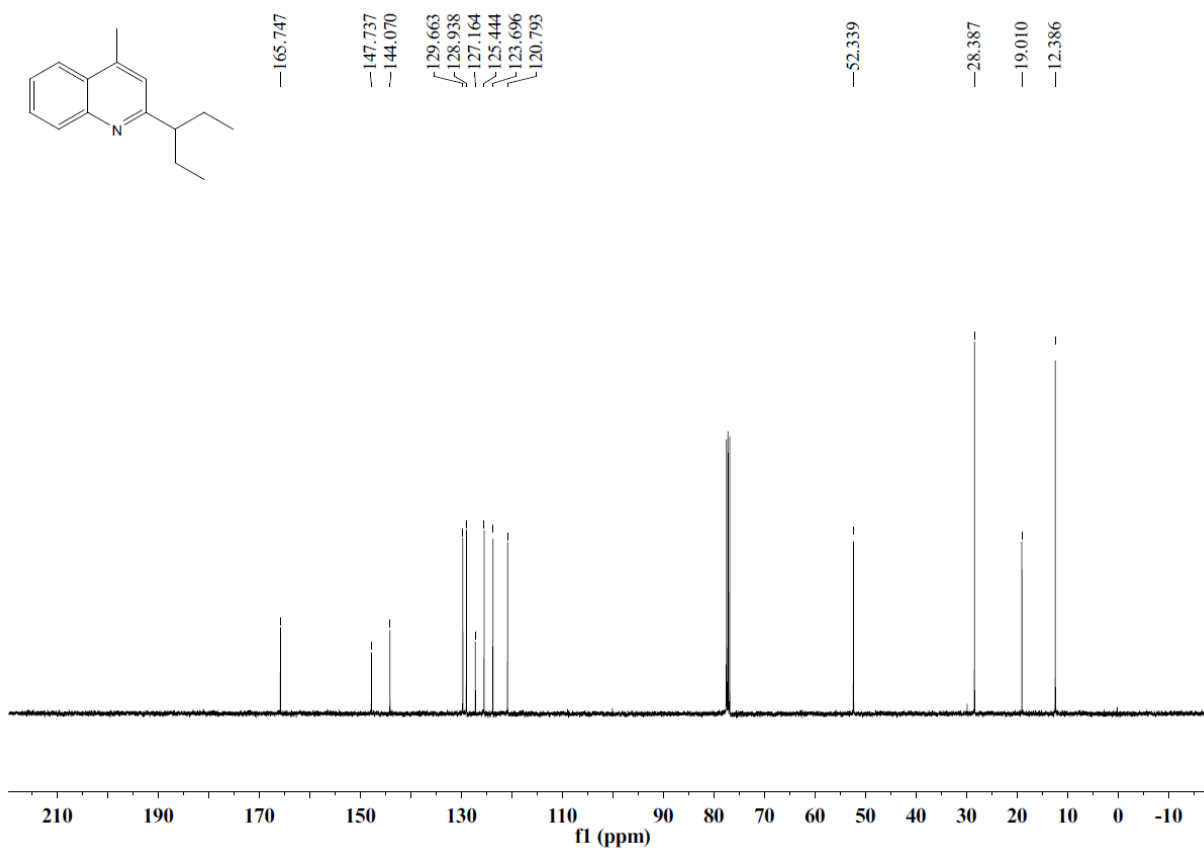
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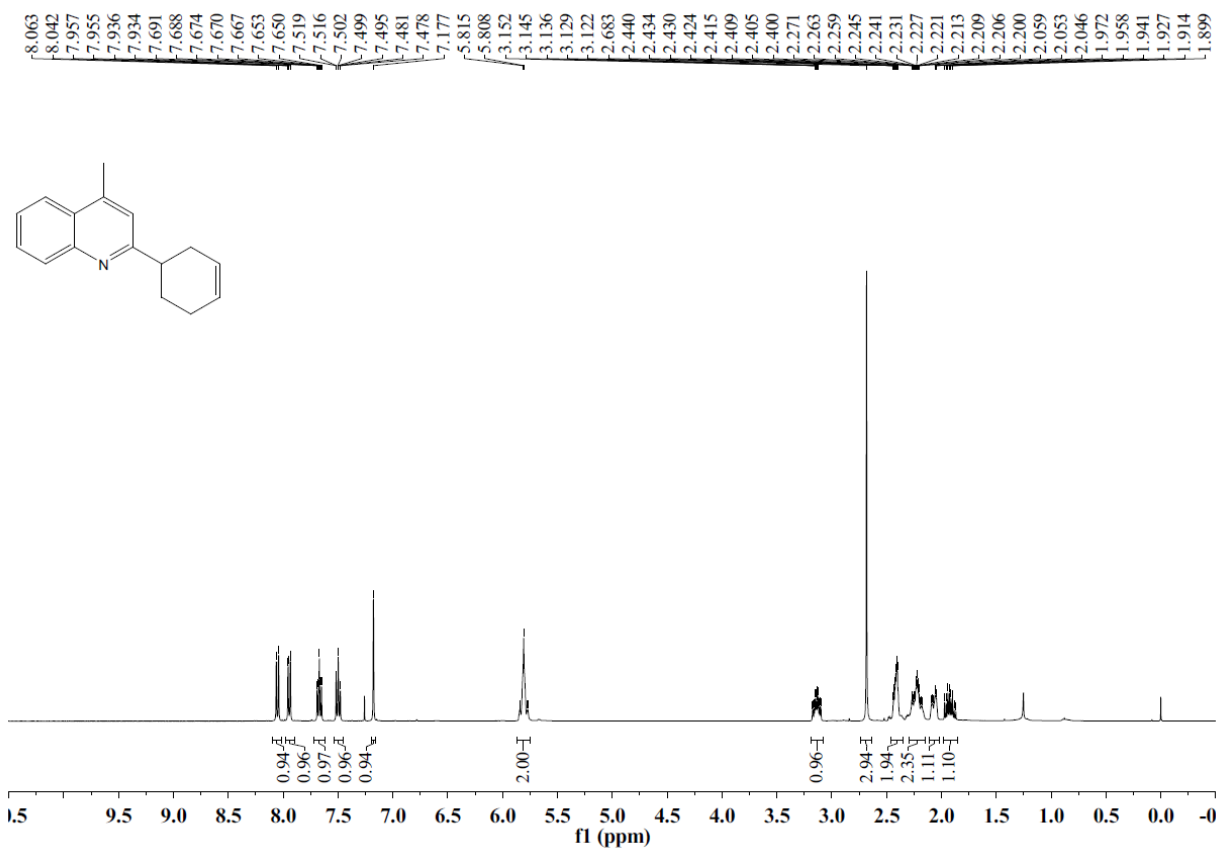
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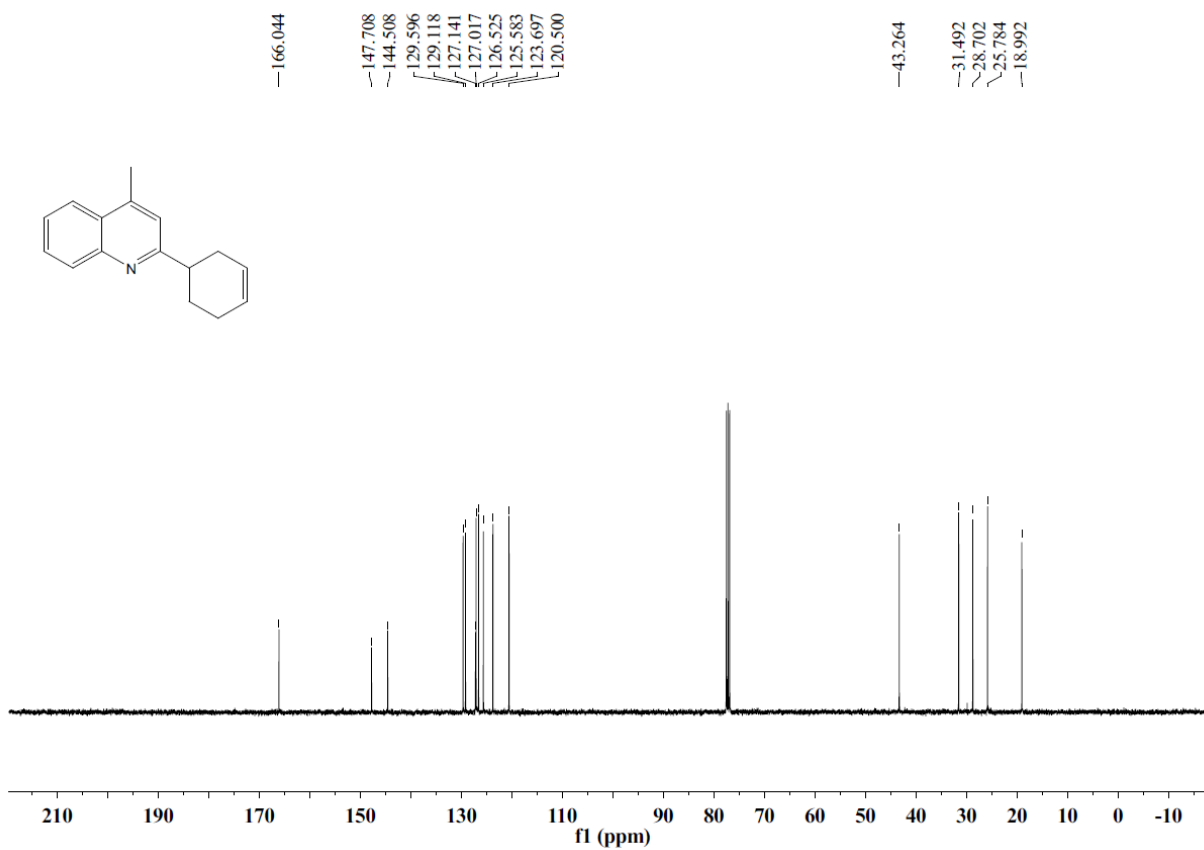
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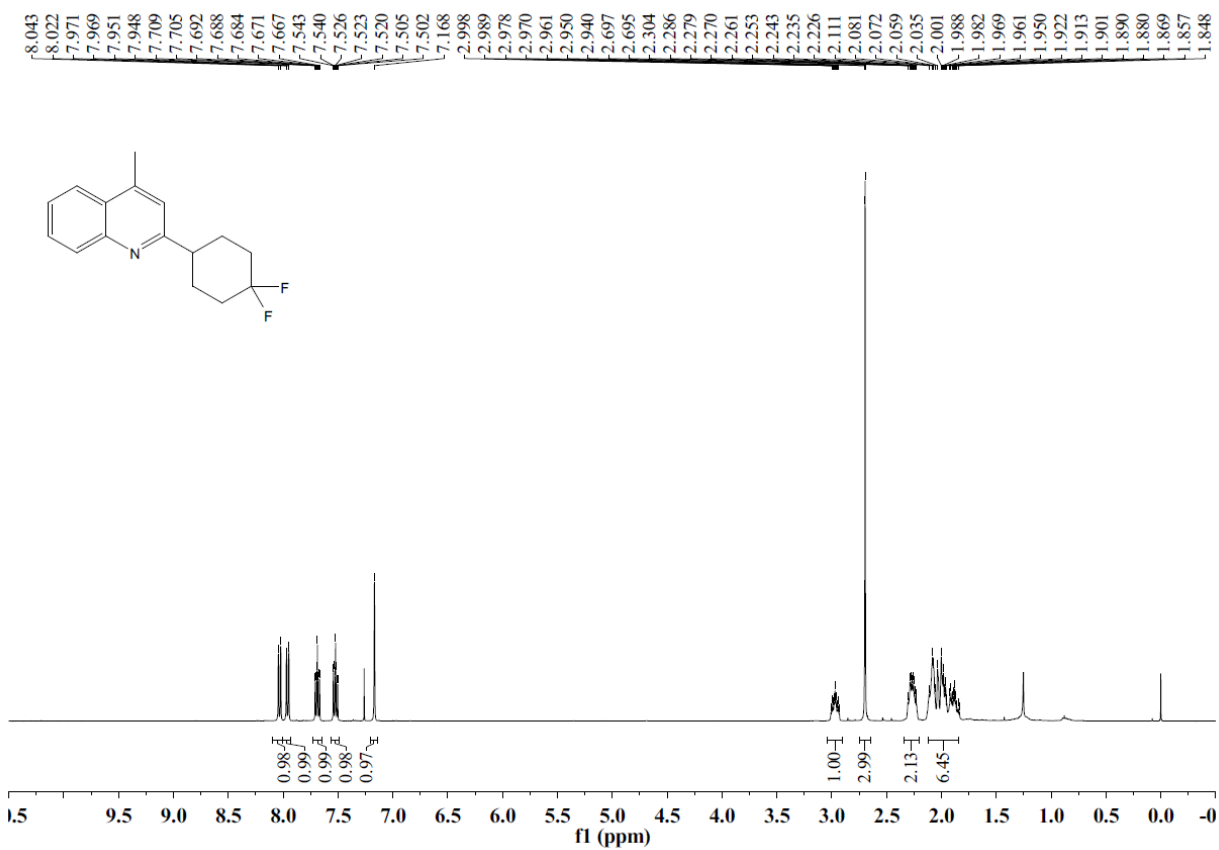
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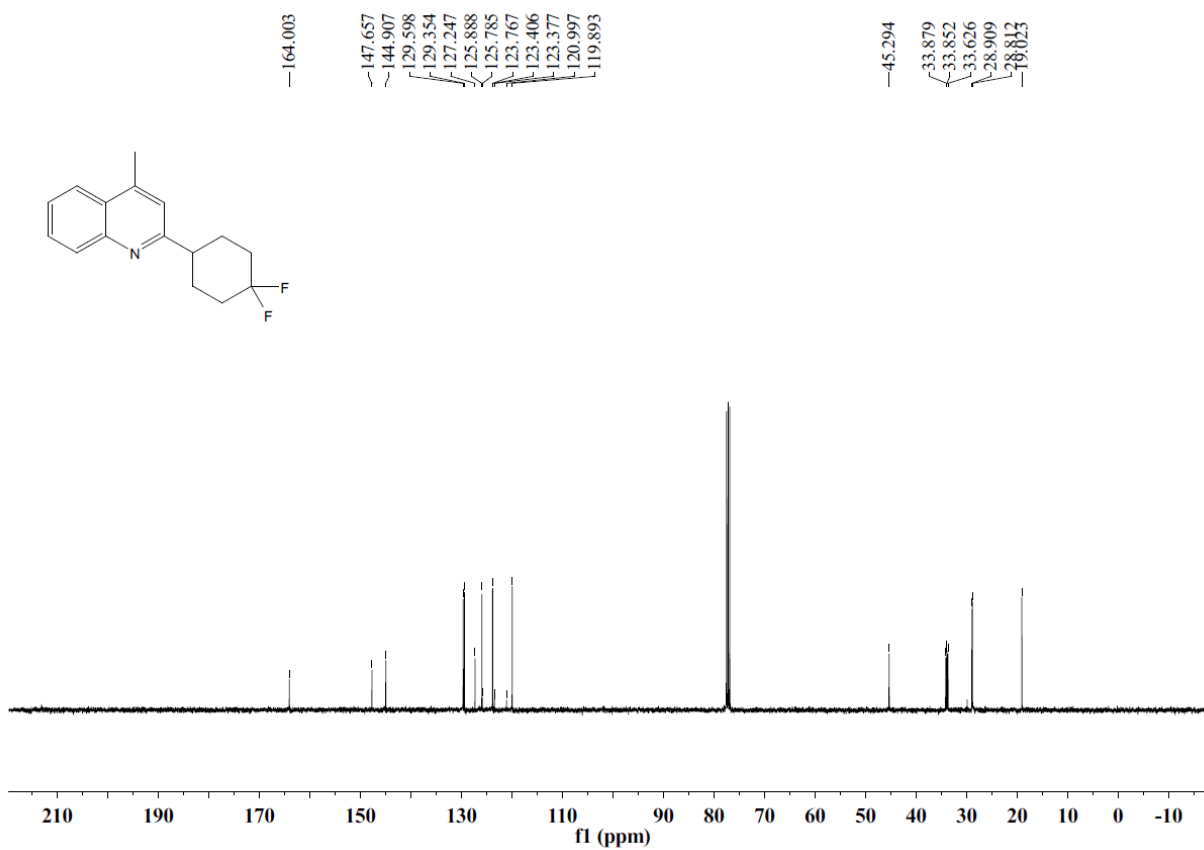
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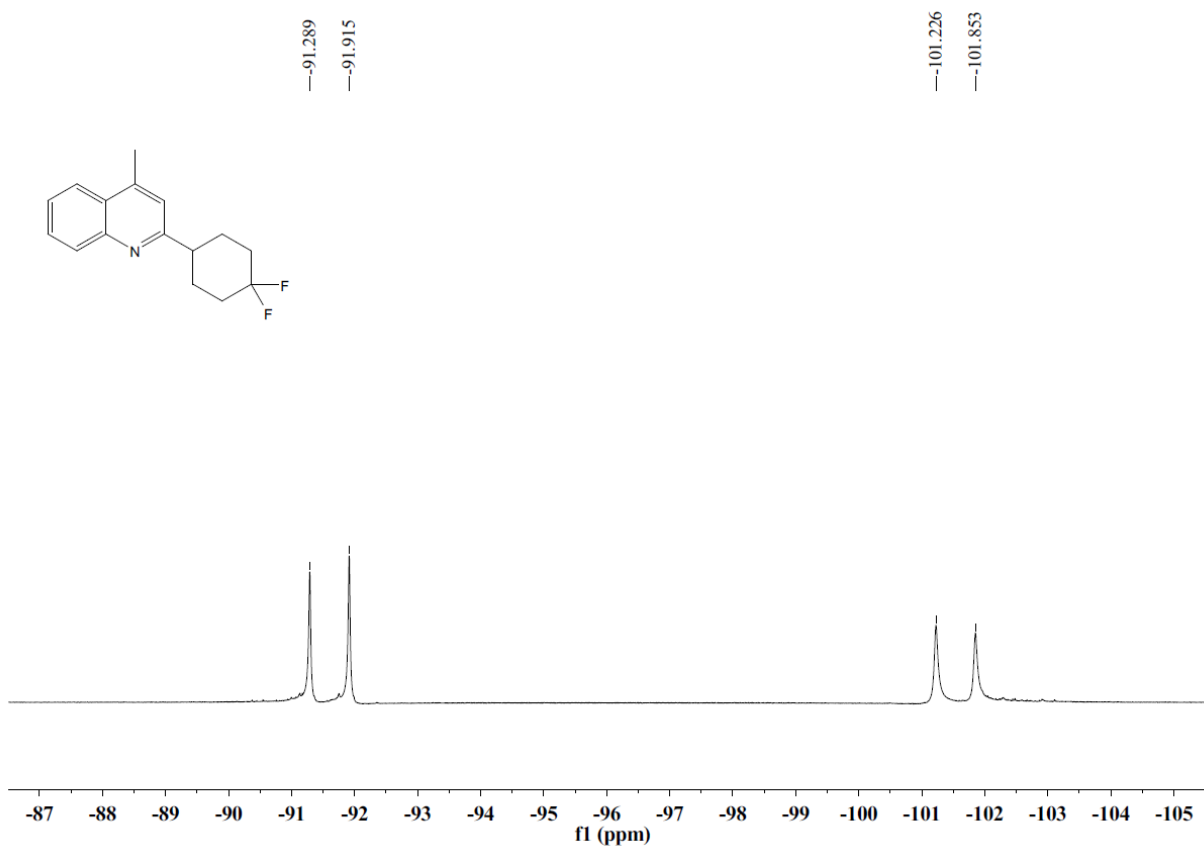
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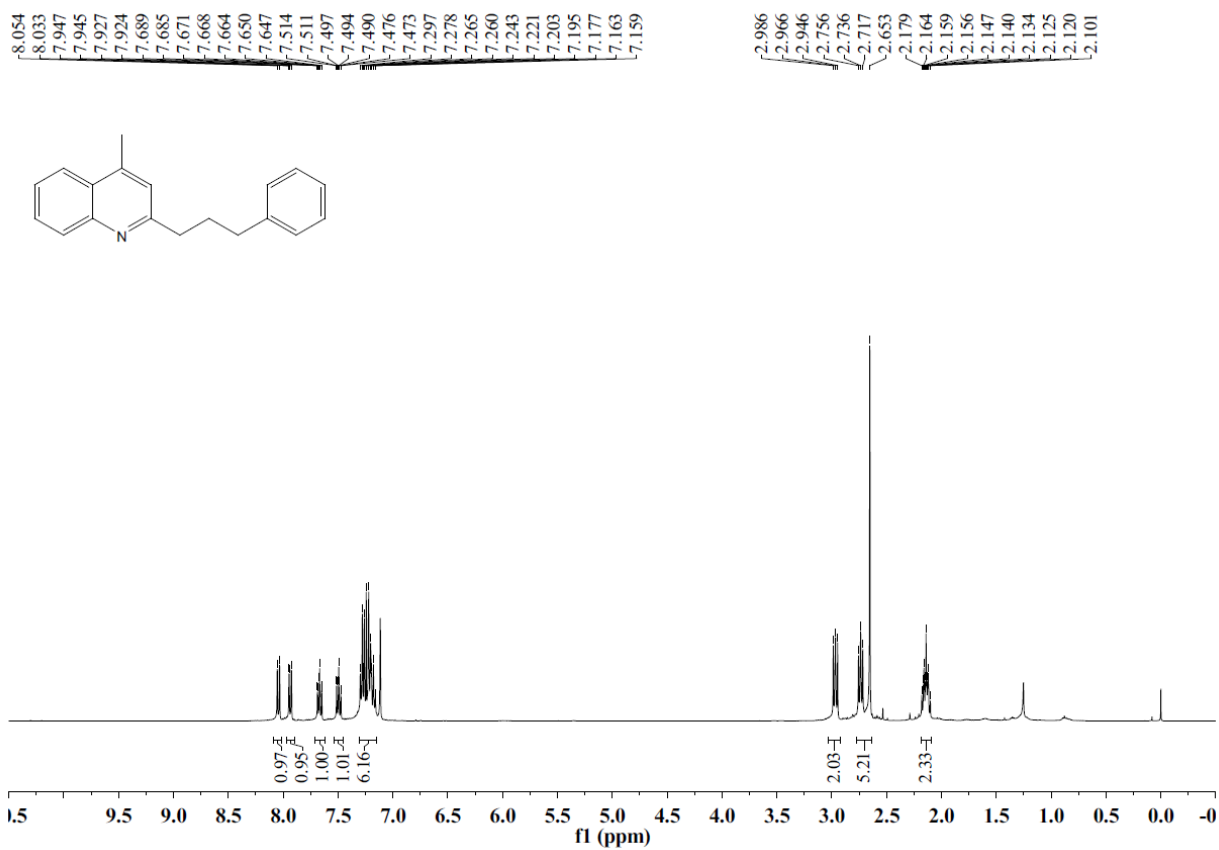
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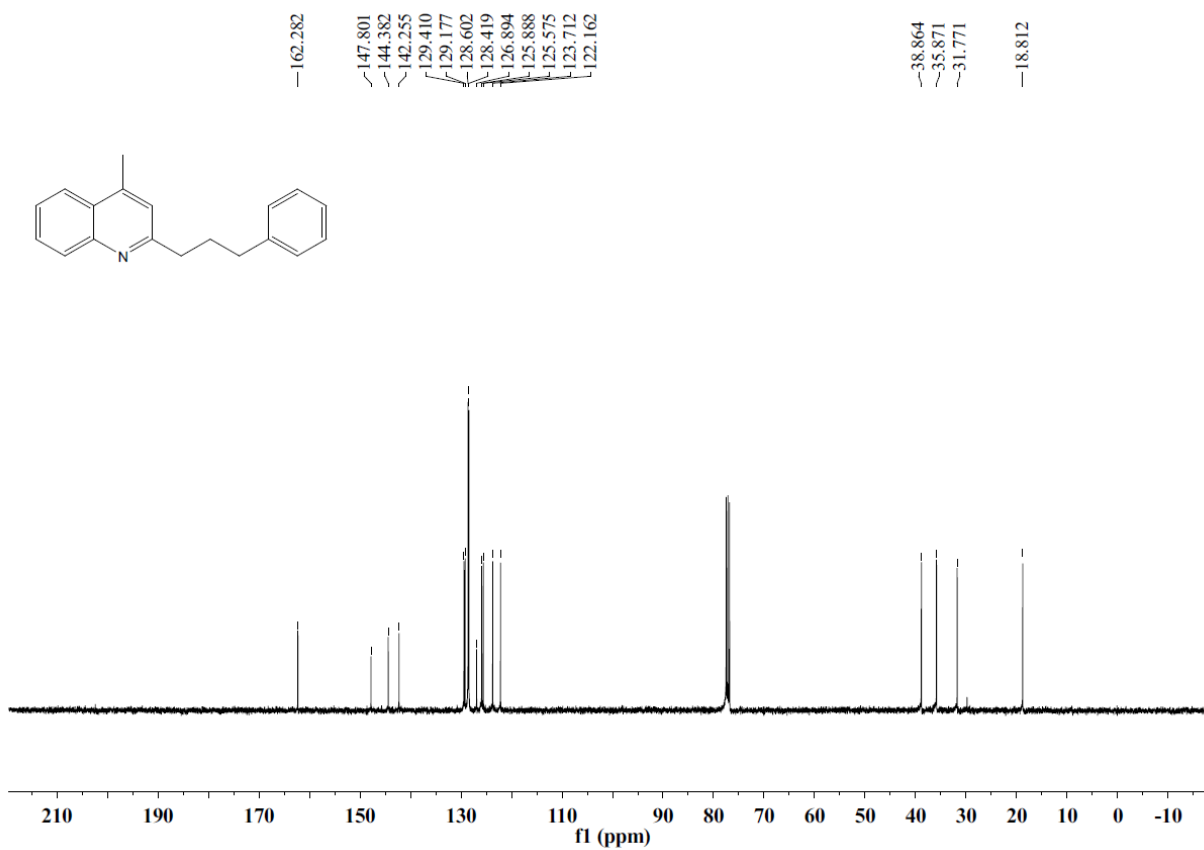
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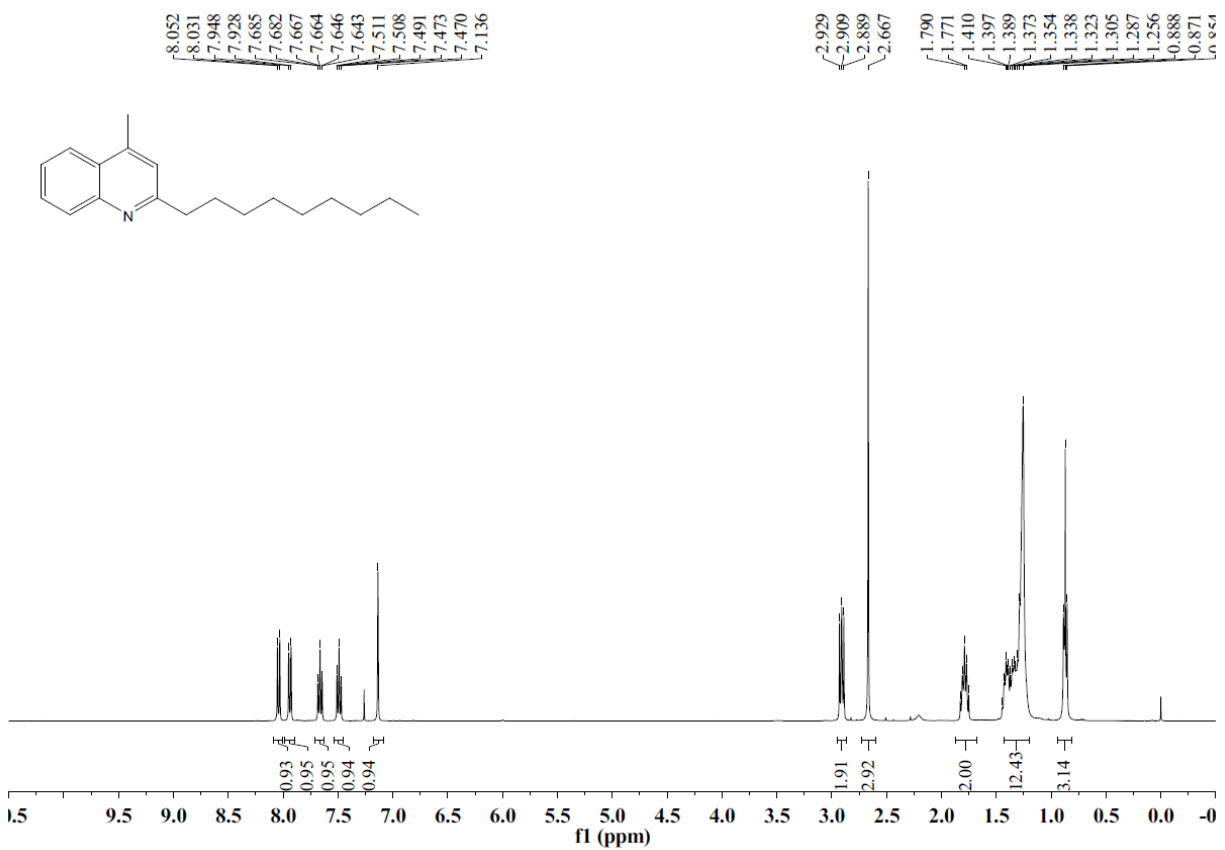
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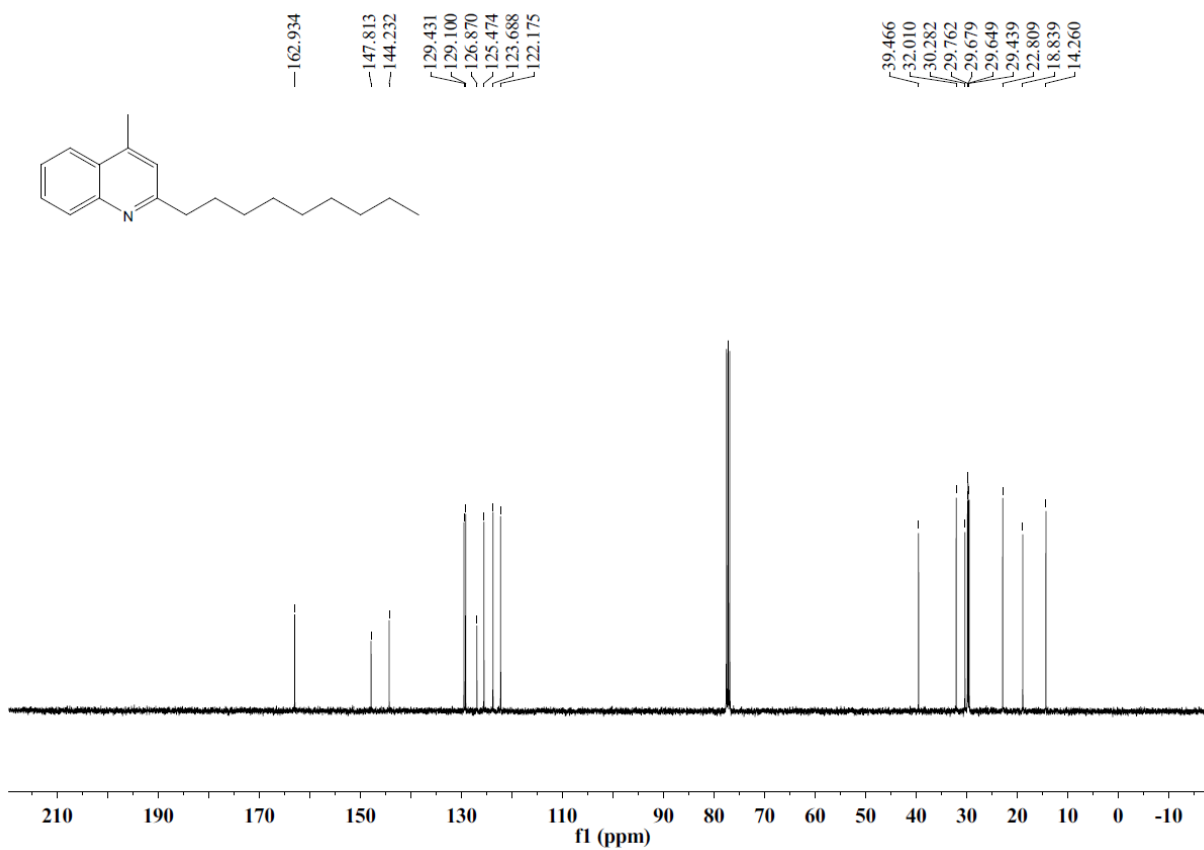
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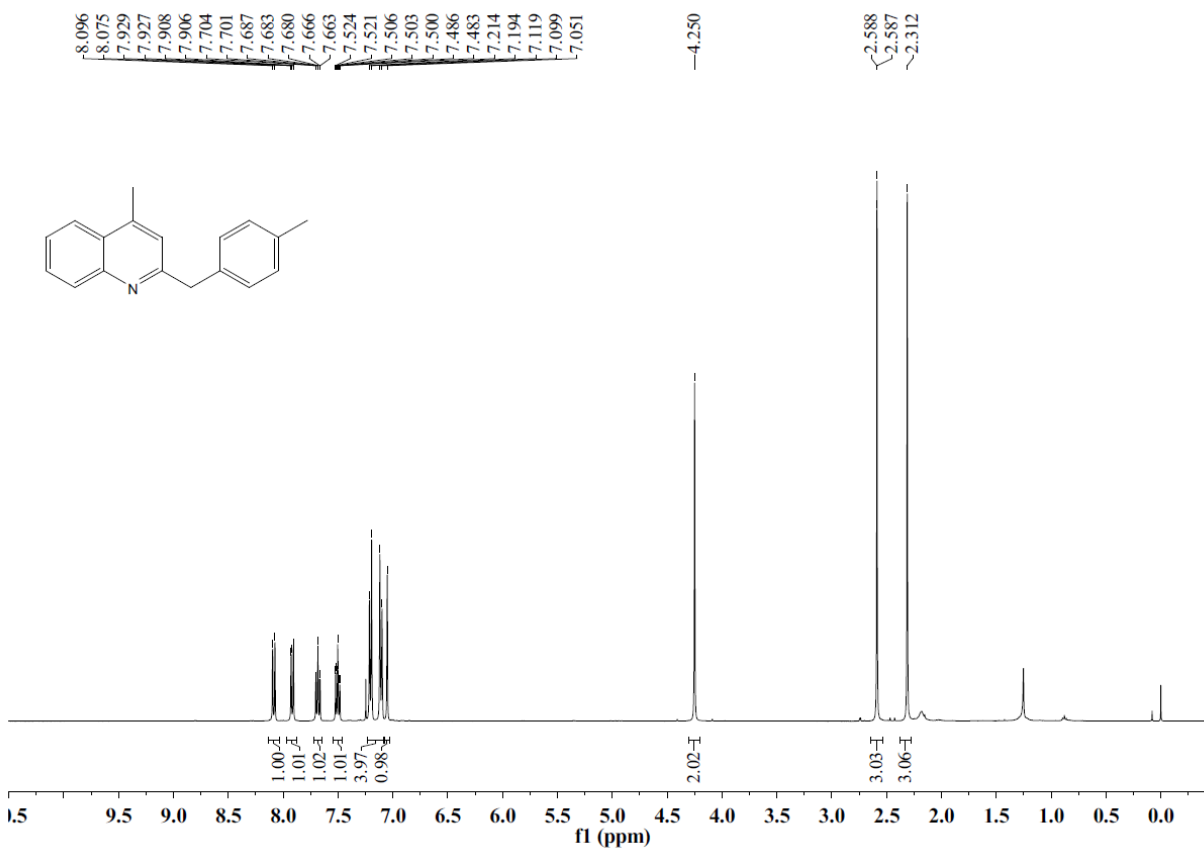
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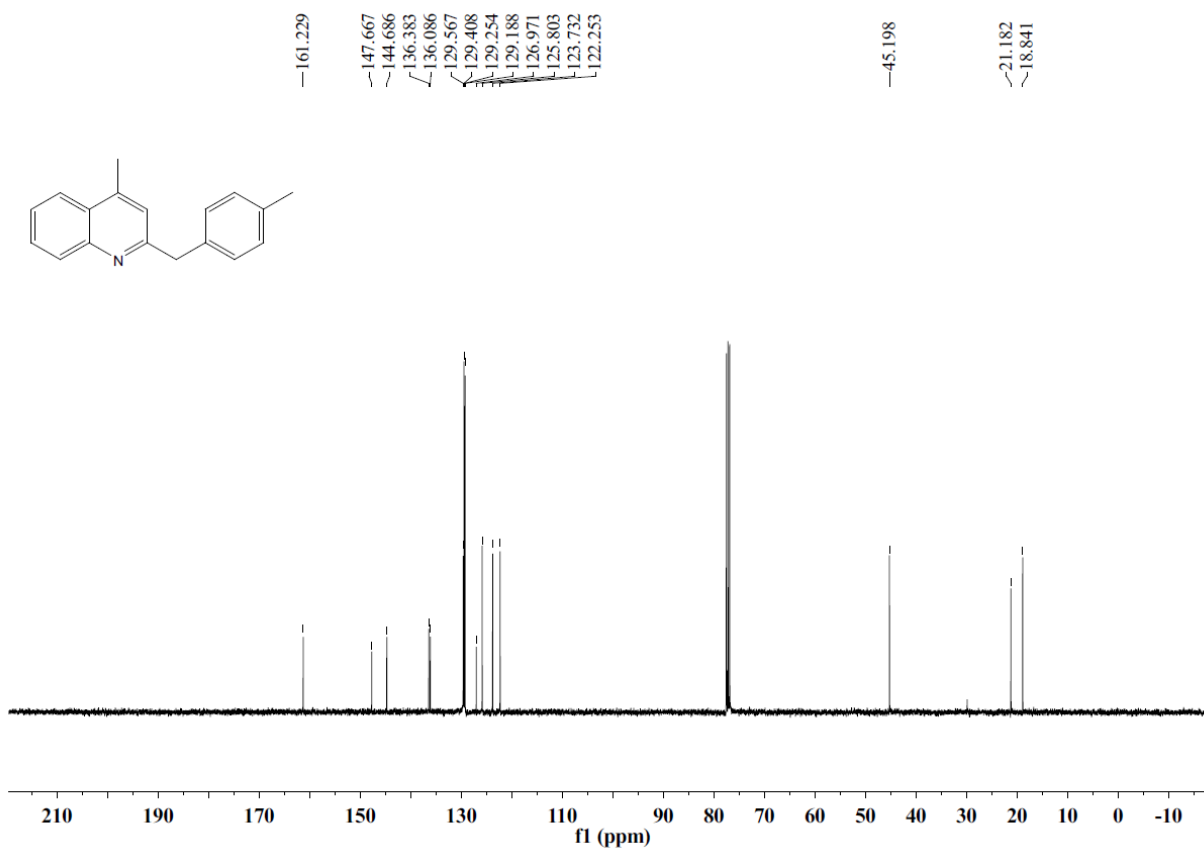
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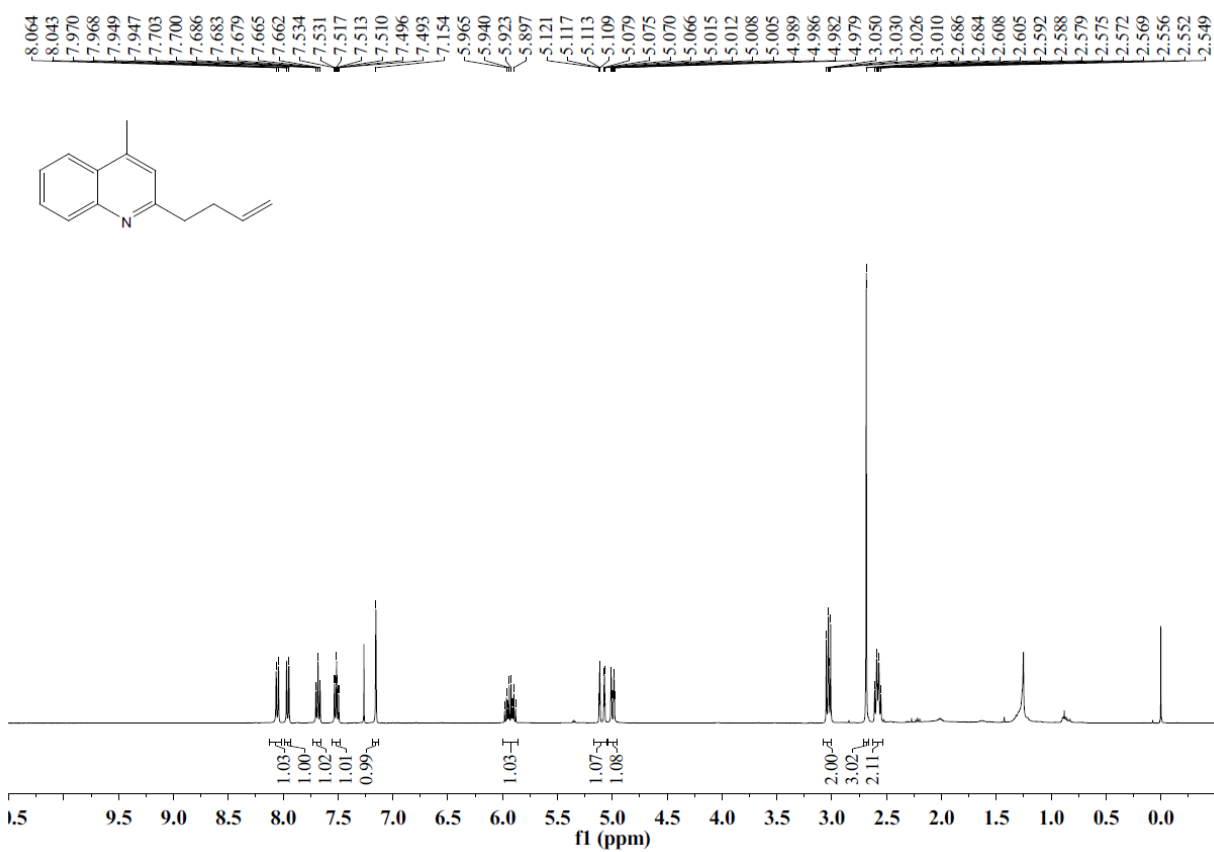
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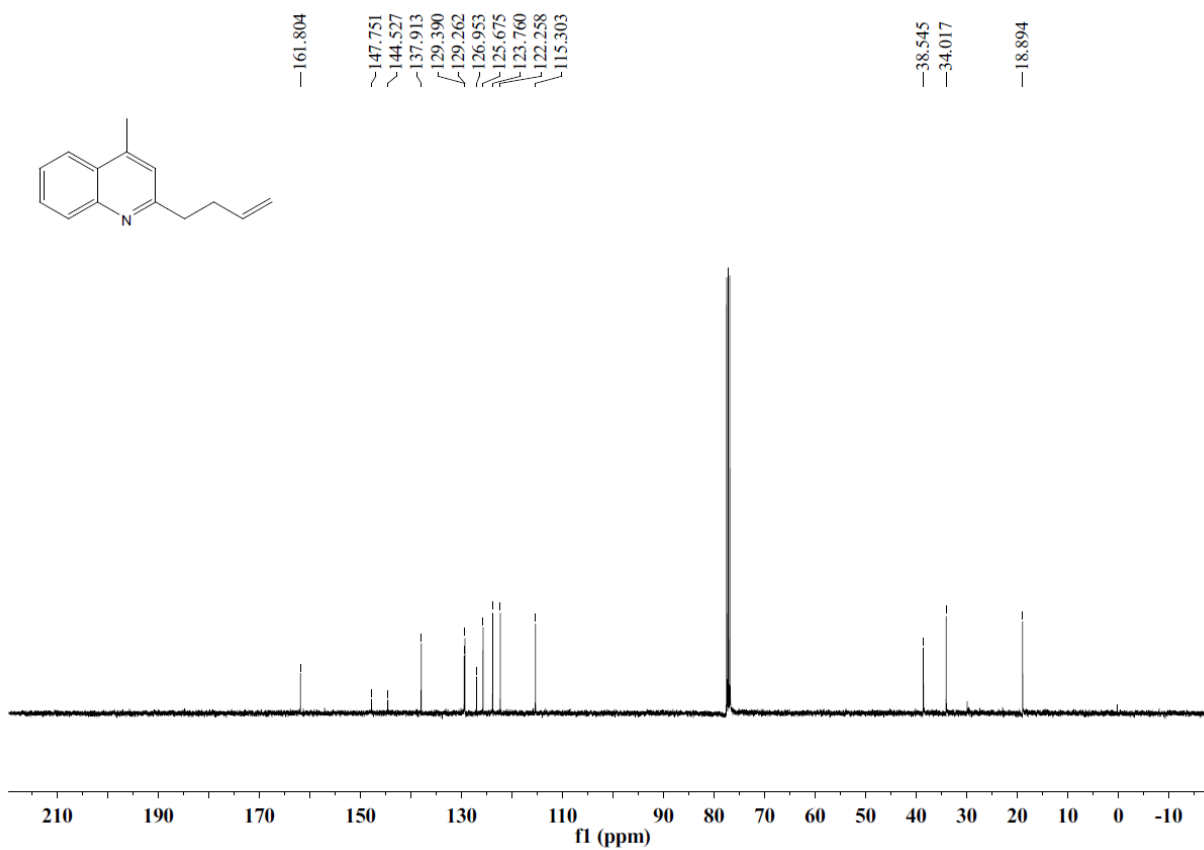
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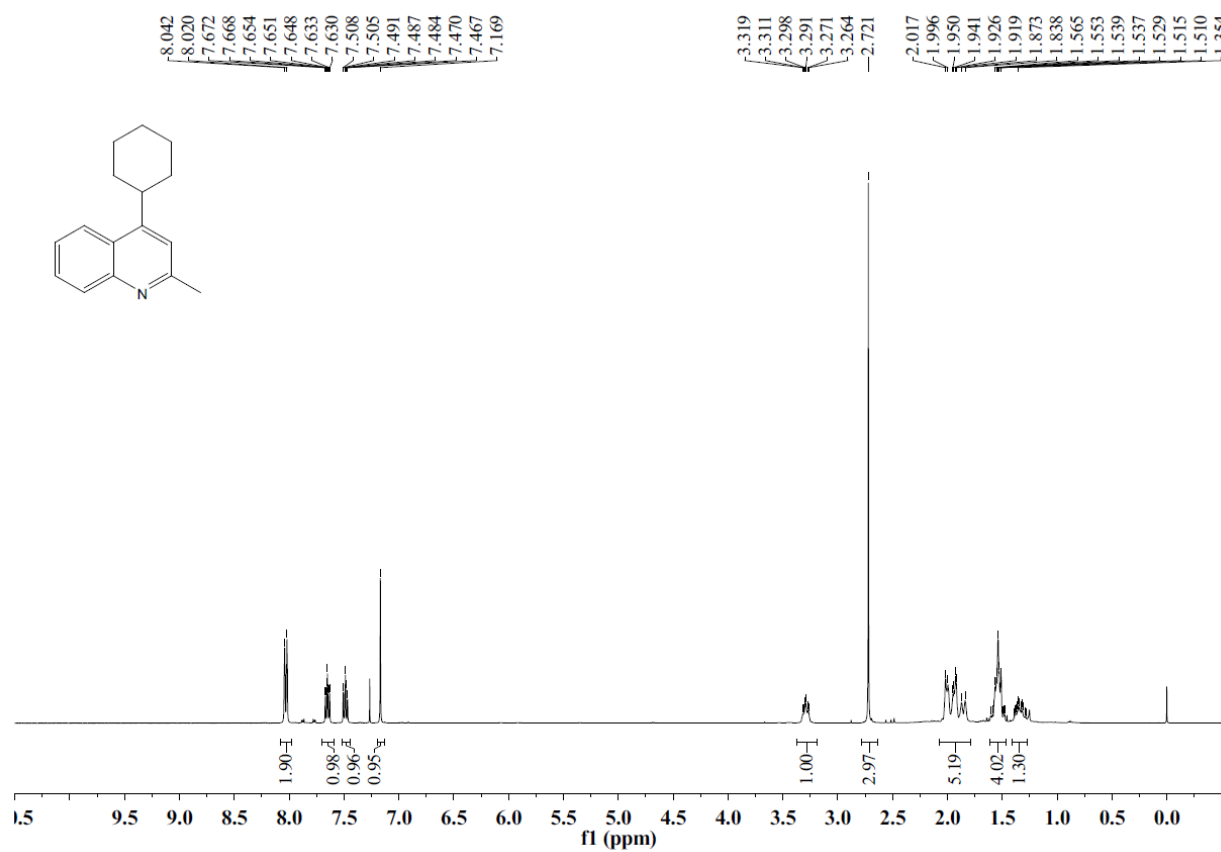
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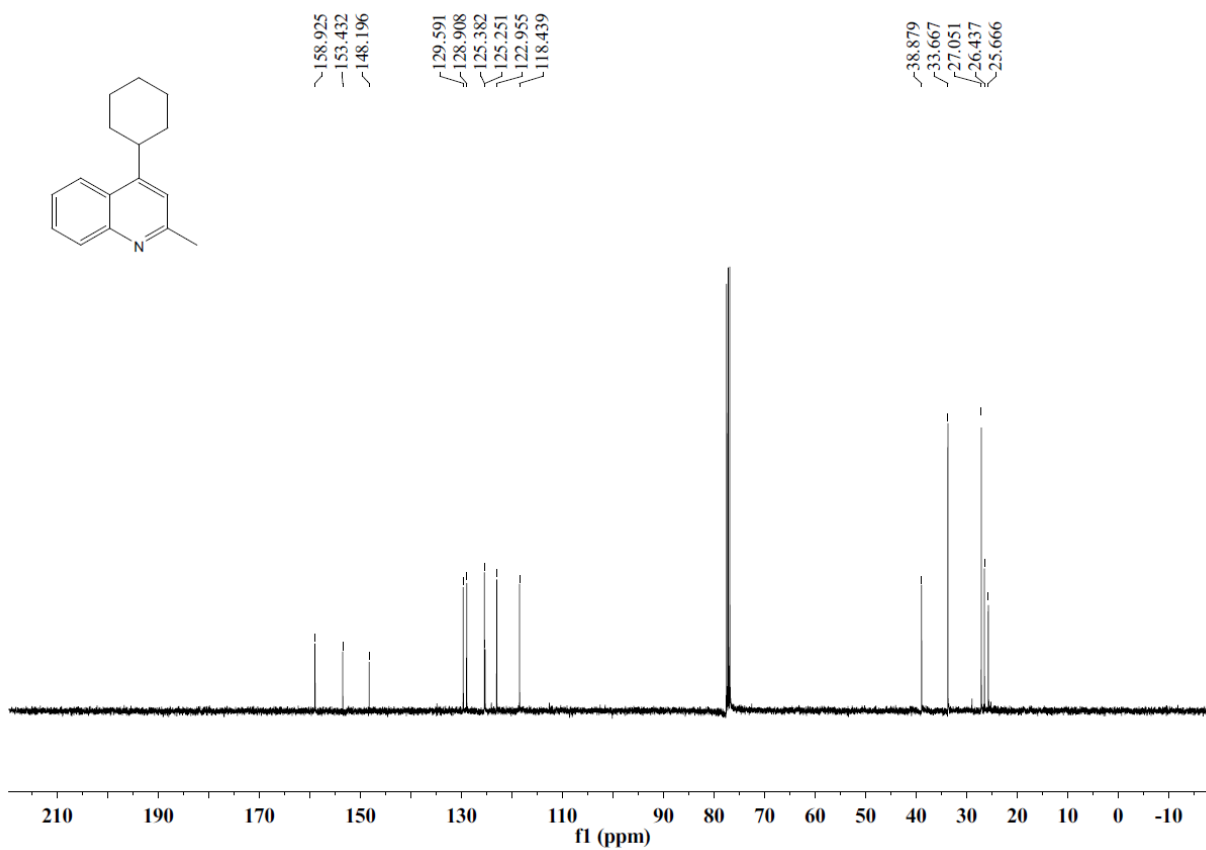
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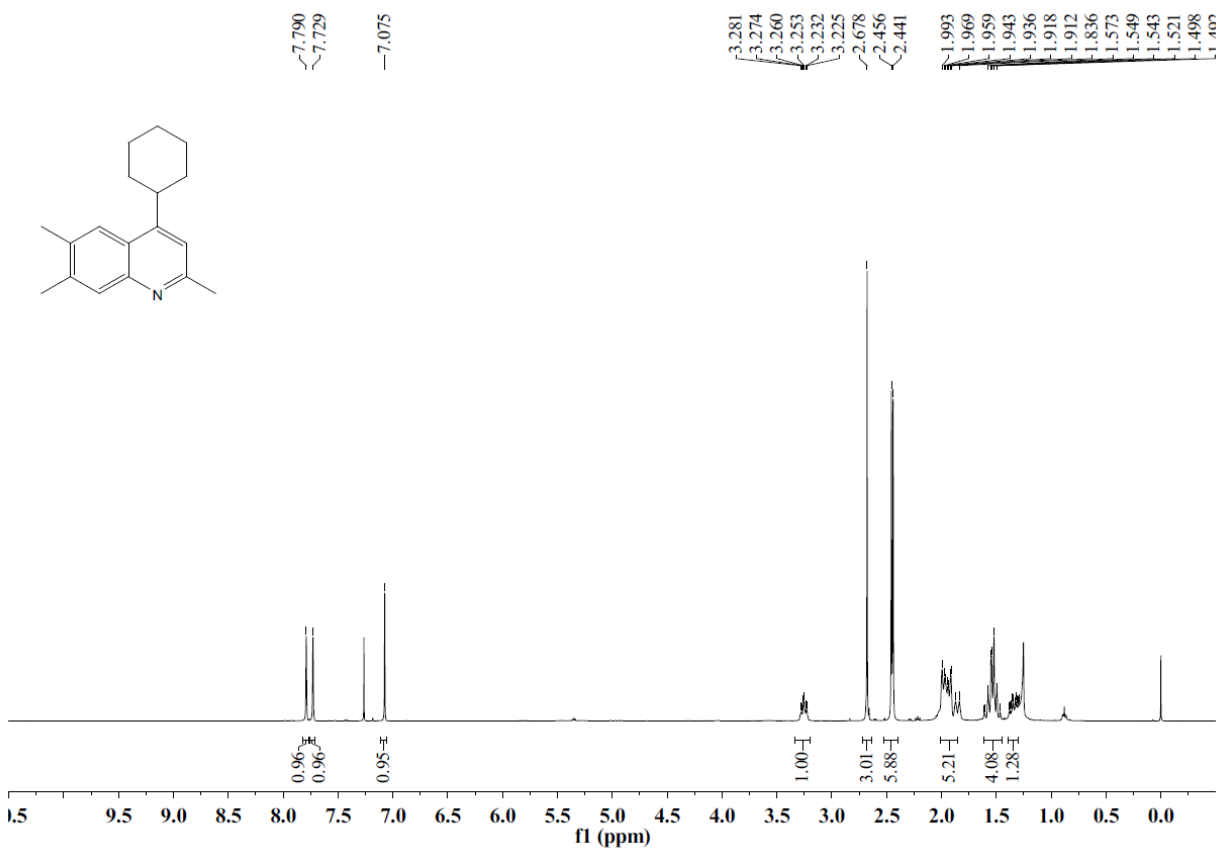
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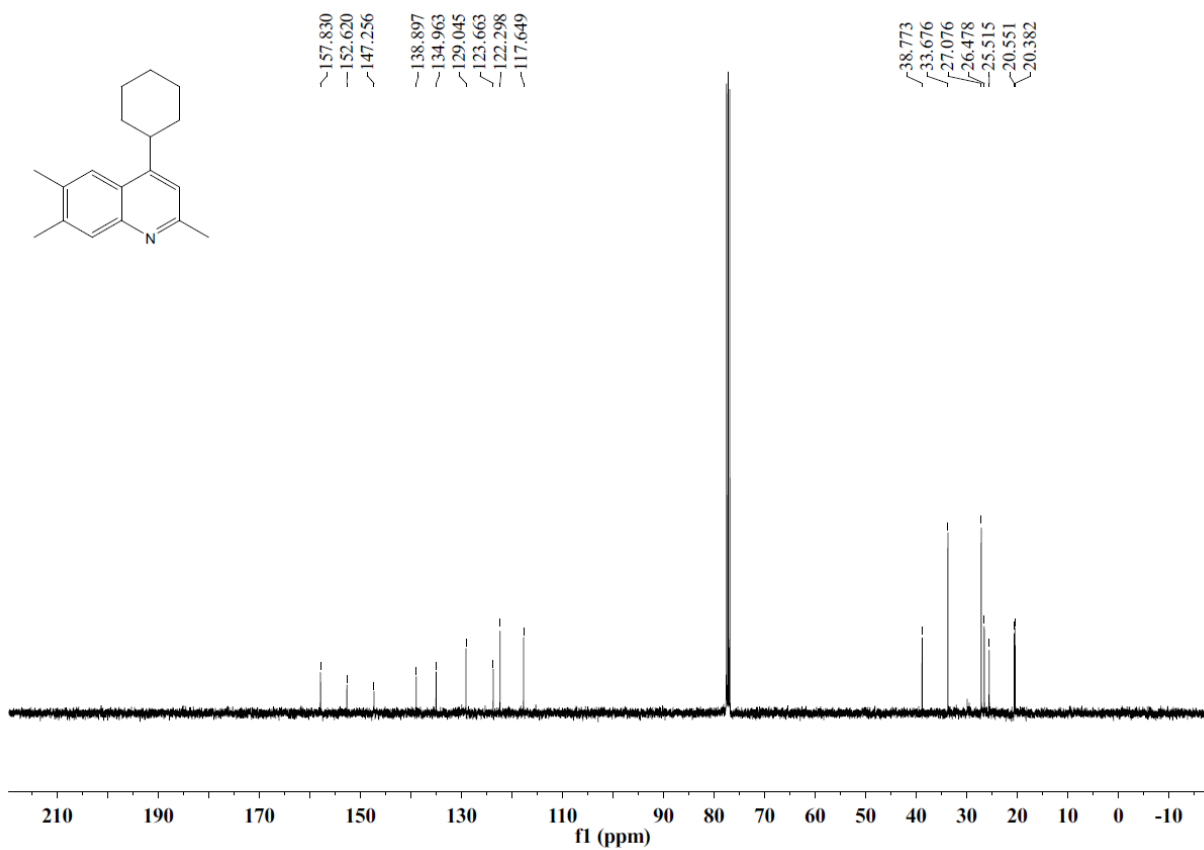
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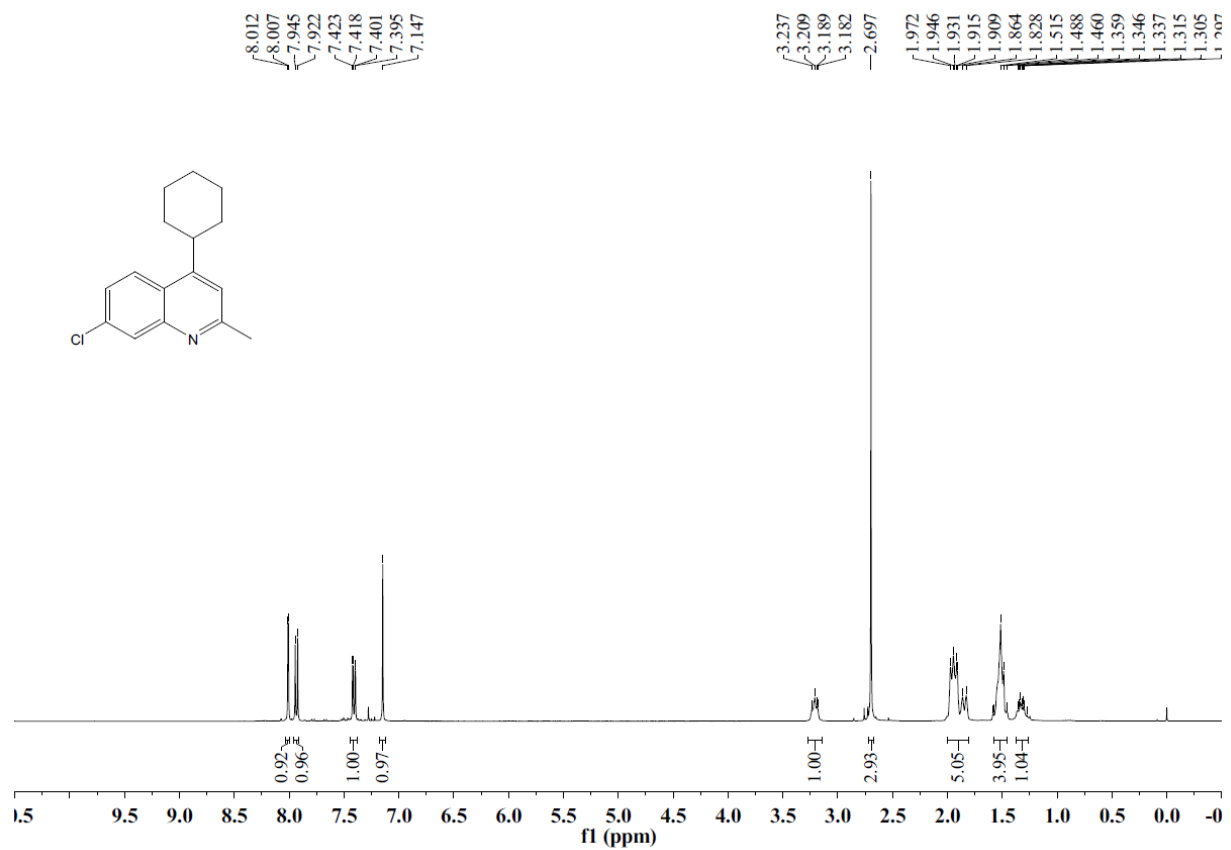
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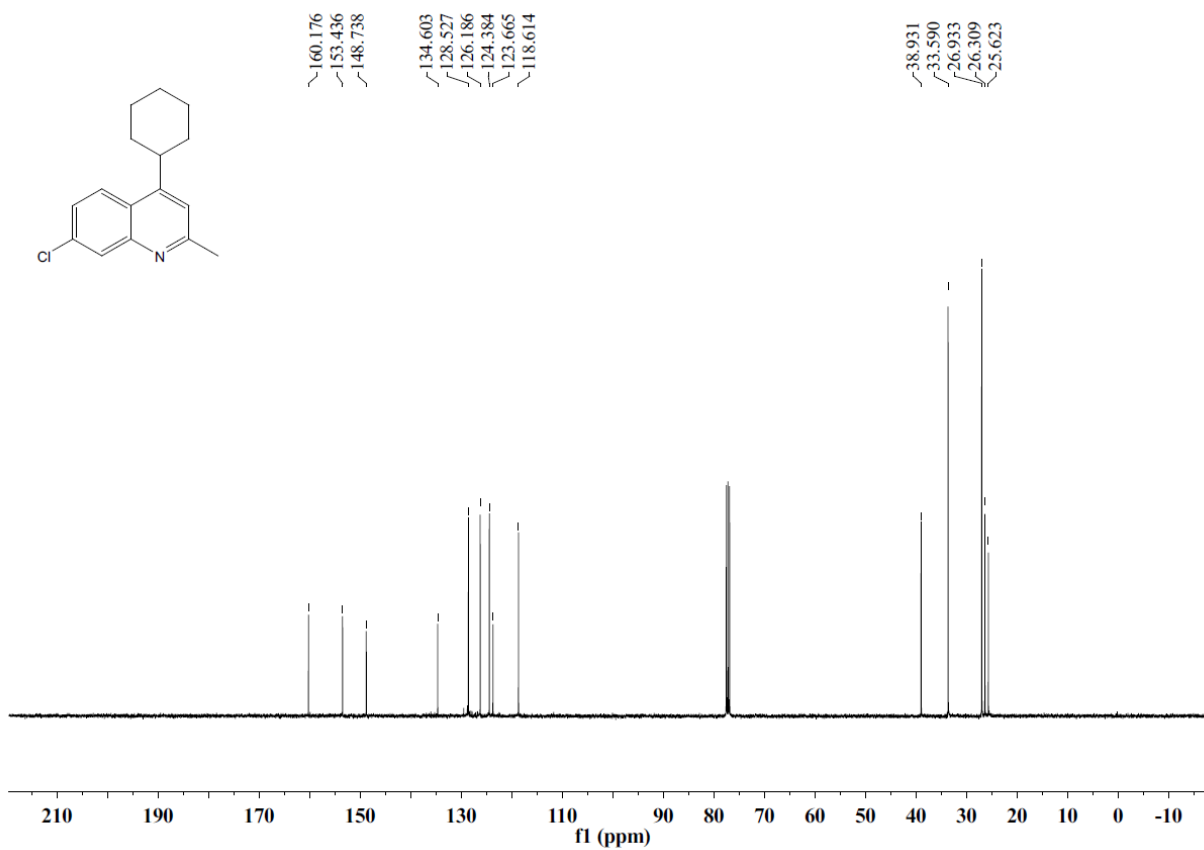
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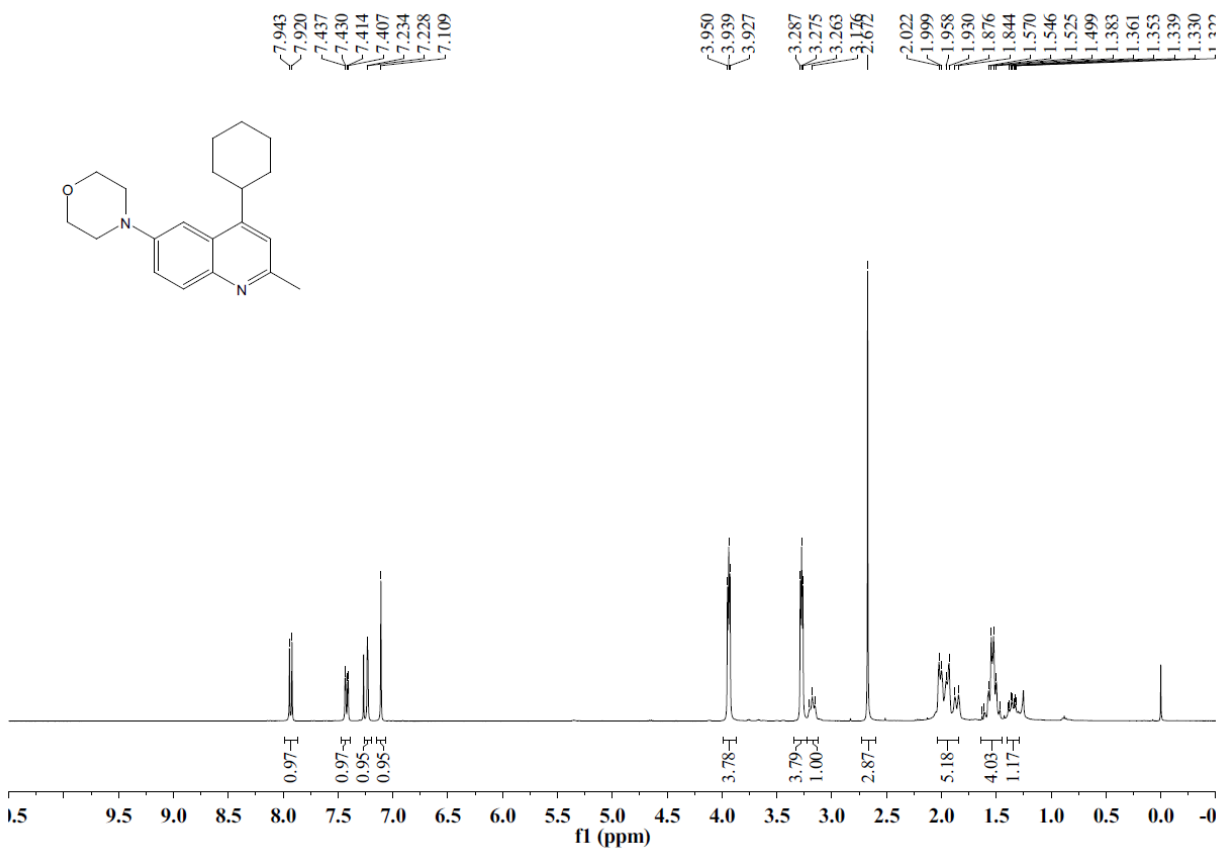
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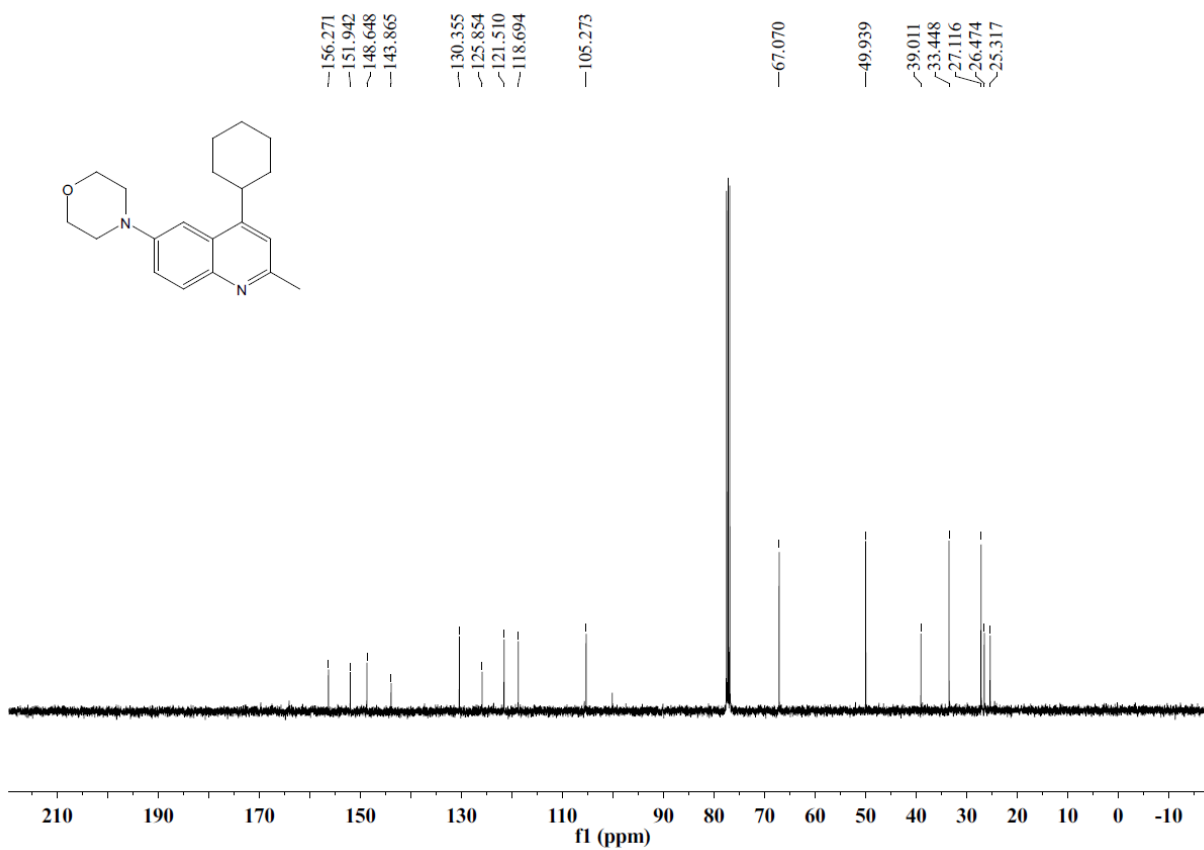
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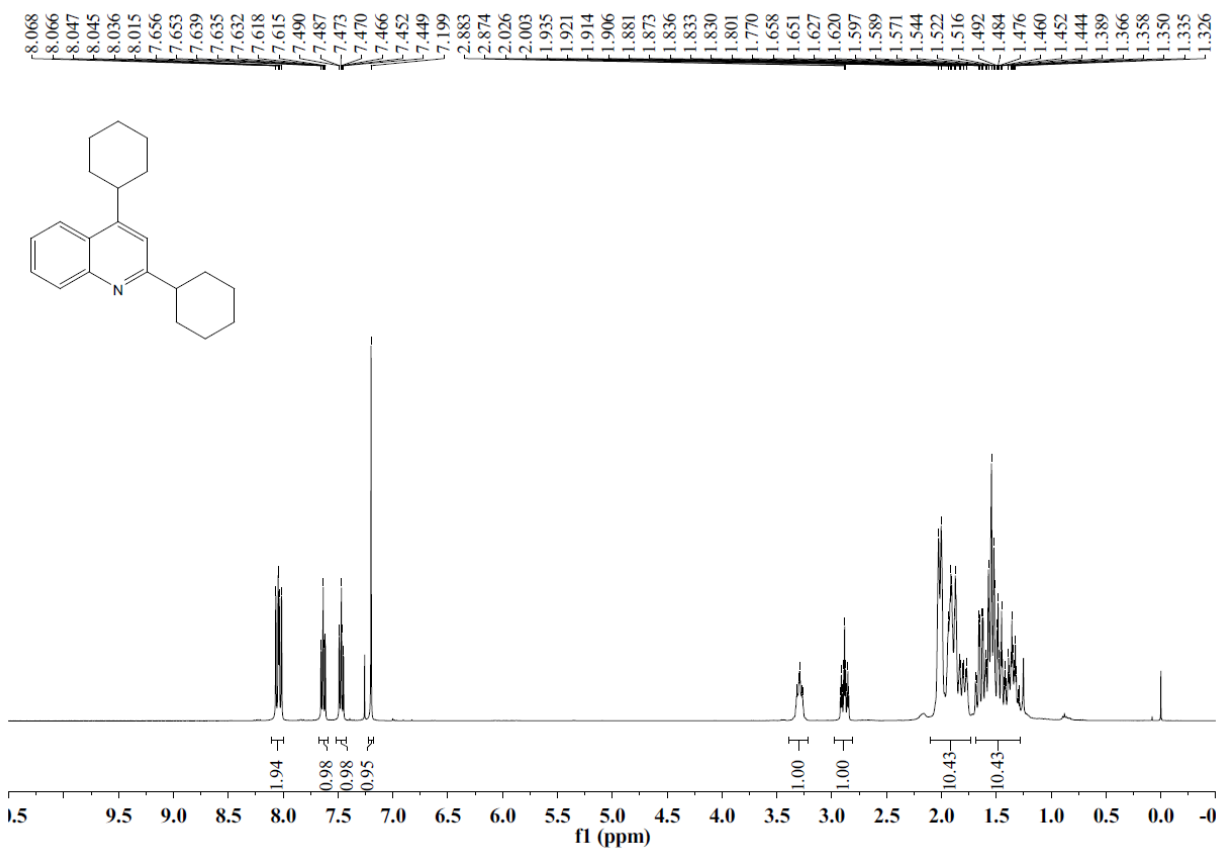
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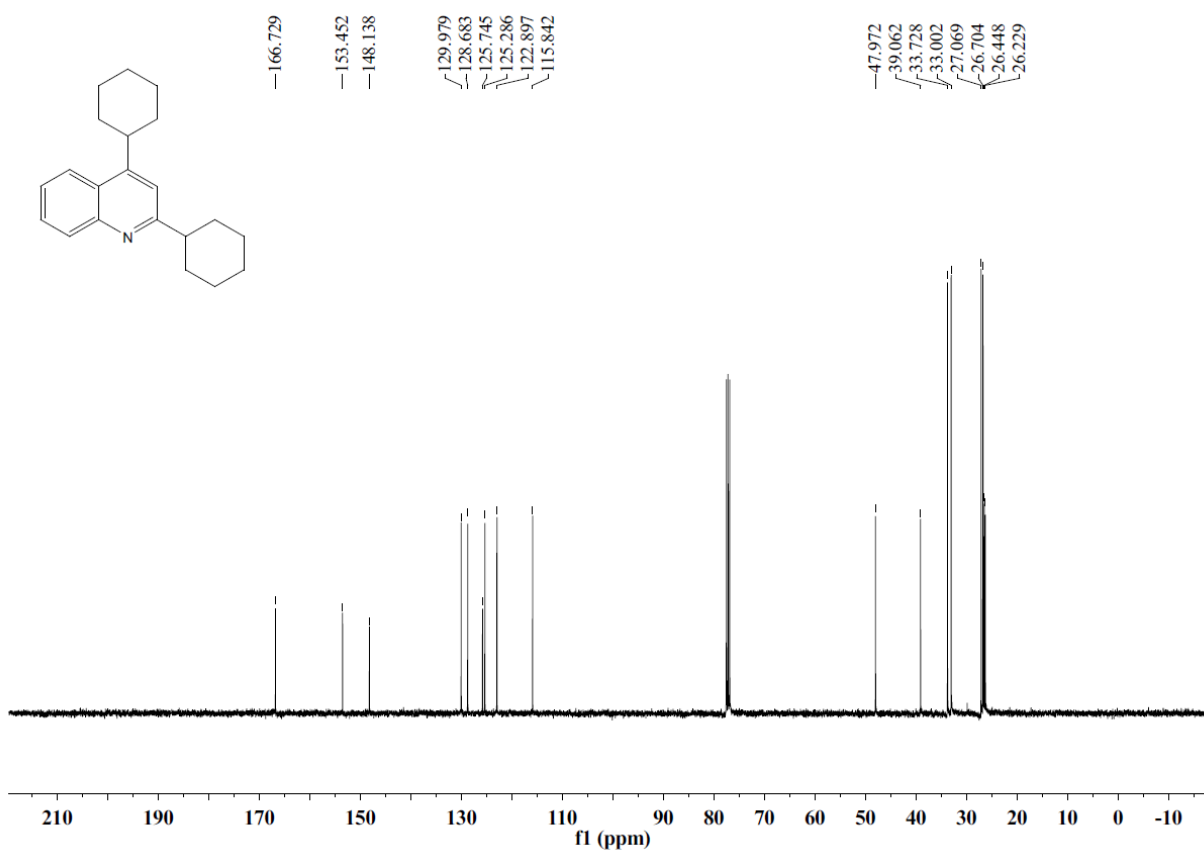
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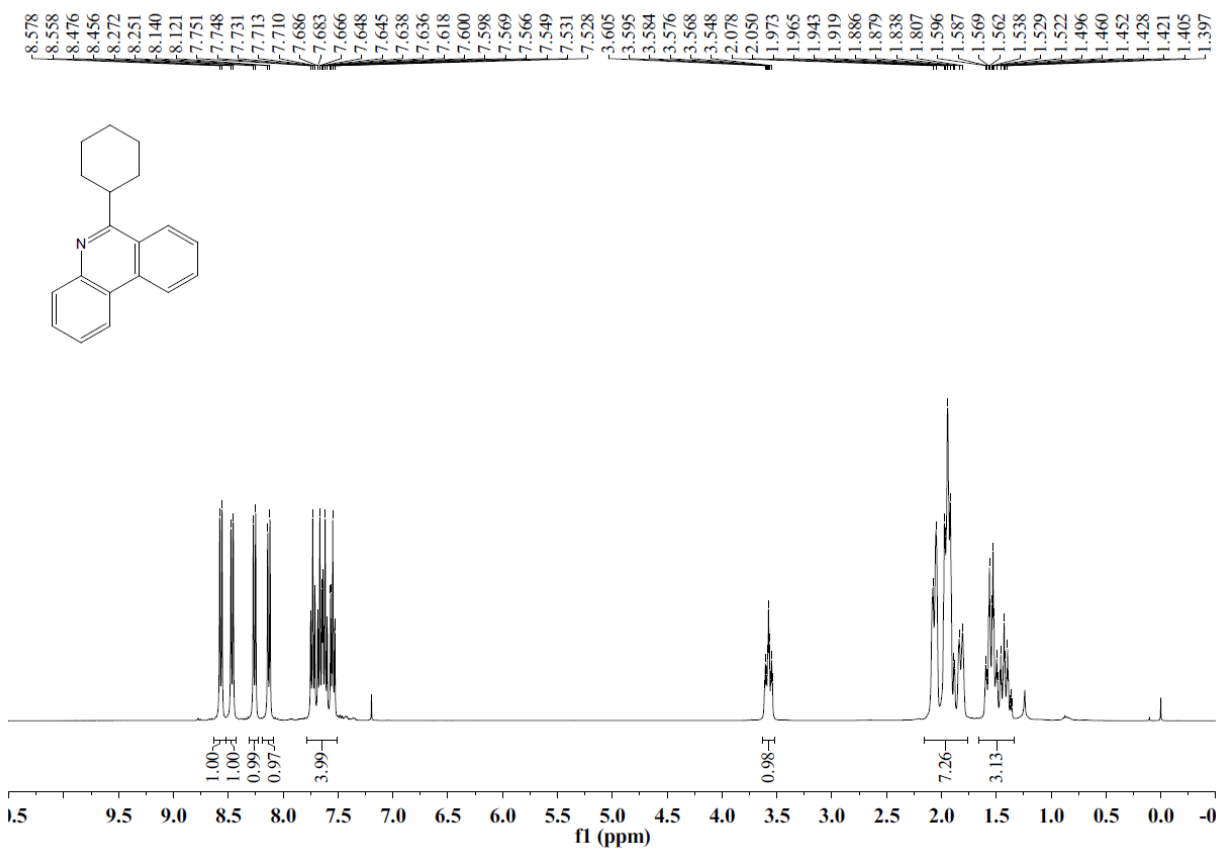
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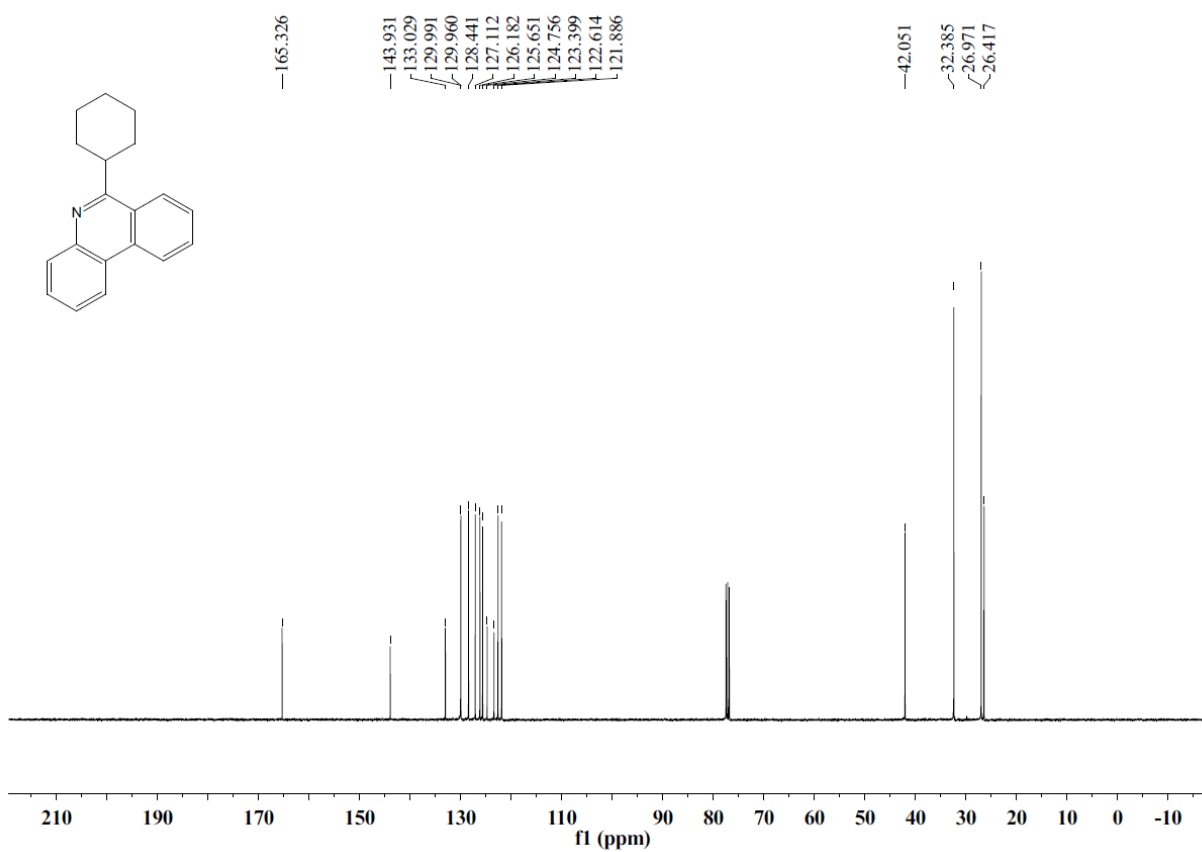
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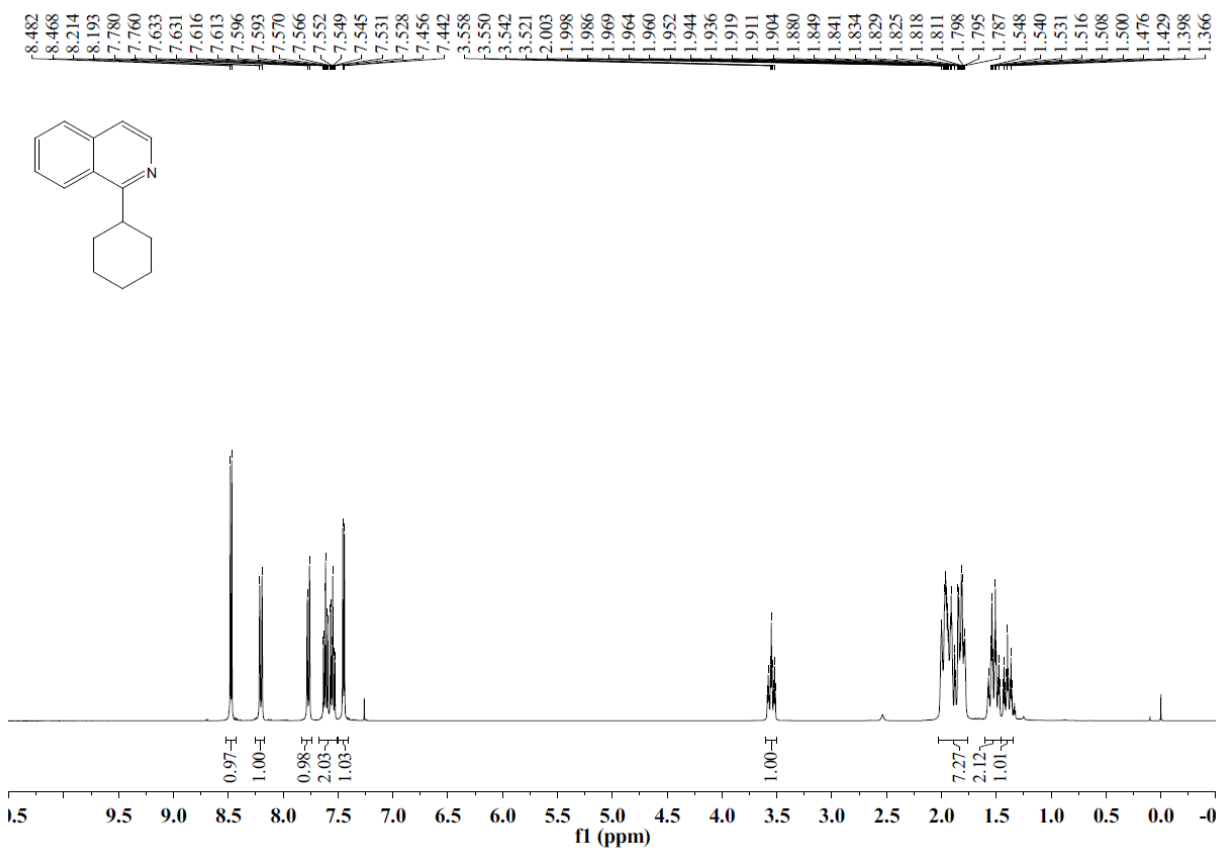
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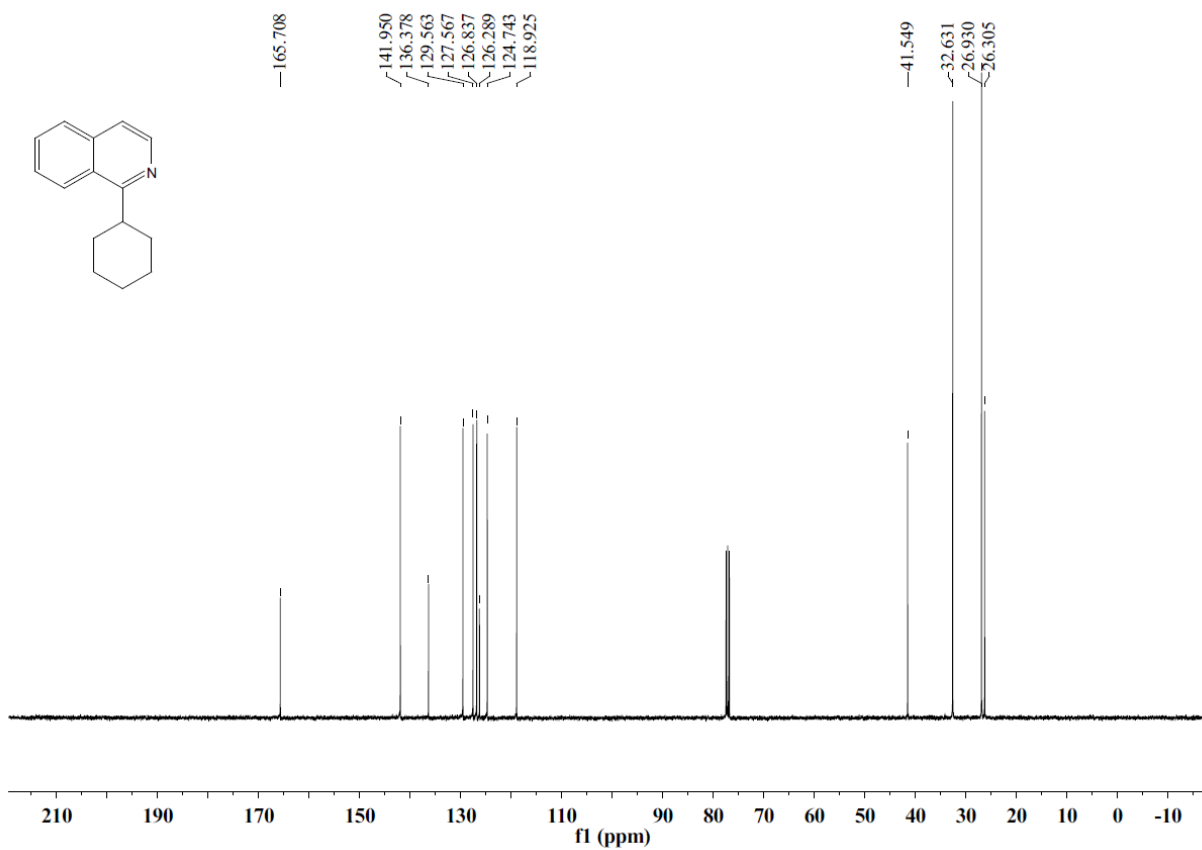
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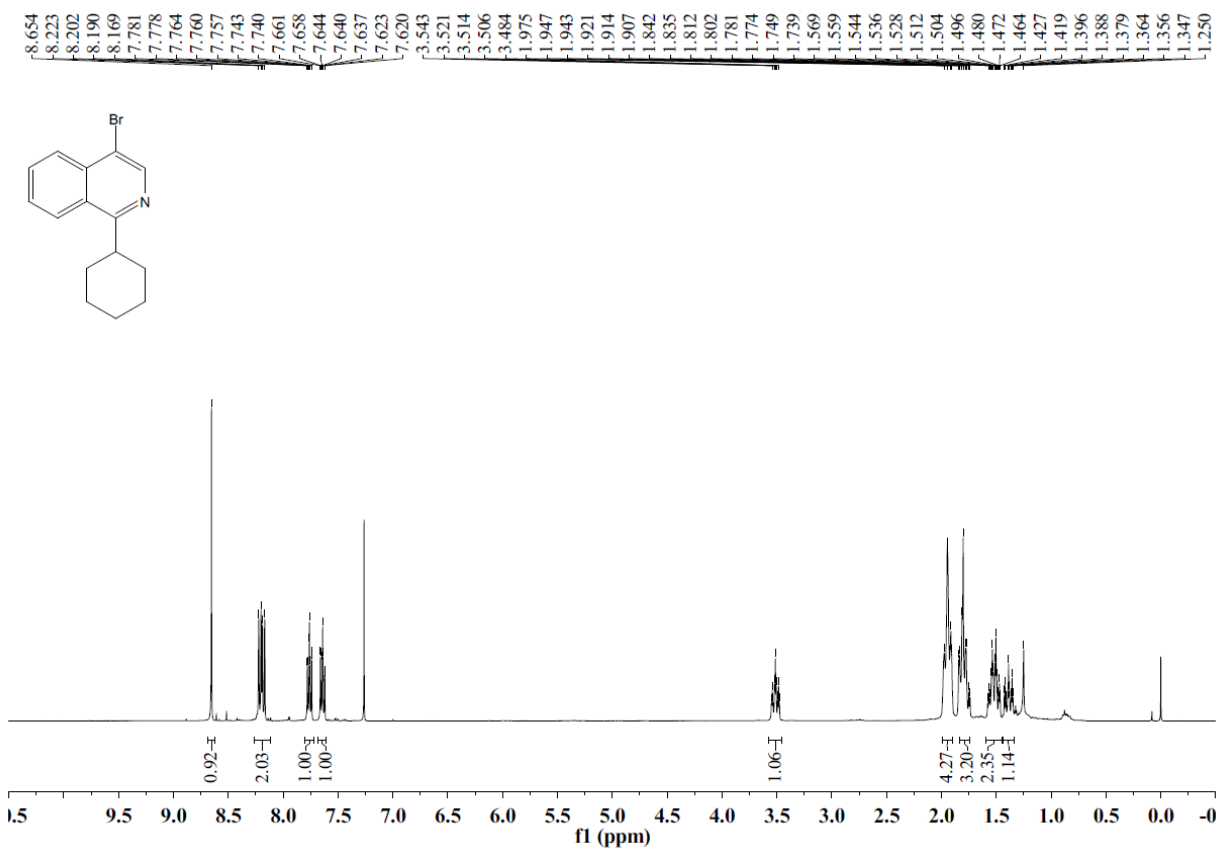
3ah 1H NMR



3ah ¹³C NMR



3ai ¹H NMR



3ai ¹³C NMR

