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Abstract:
An oxidant- and metal-free photoelectrocatalytic C–H alkylation reaction of heteroarenes with alkyl oxalates has been developed. Several classes of heteroaromatics such as quinoline, isoquinoline, pyridine, and phenanthridine are alkylated with tertiary and secondary alkyl oxalates. The photoelectrochemical synthesis employs 4CzIPN as a molecular catalyst and allows the oxidative transformations to proceed through H₂ evolution without need for sacrificial chemical oxidants.

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C-H Alkylation of Heteroarenes with Alkyl Oxalates by Molecular Photoelectrocatalysis

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Note: If an author has relocated from where the research was carried out, this is indicated with the next available reference number (usually 1); the new address should be added as that reference in the reference section.

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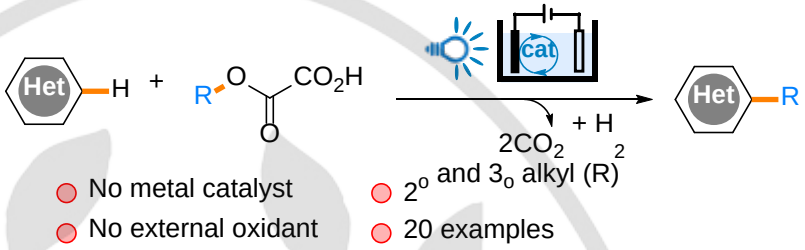
Dedicated to Prof. Ilhyong Ryu on the occasion of his 70th birthday.



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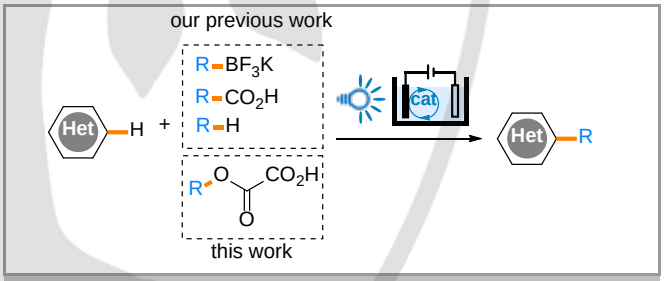
Abstract An oxidant- and metal-free photoelectrocatalytic C–H alkylation reaction of heteroarenes with alkyl oxalates has been developed. Several classes of heteroaromatics such as quinoline, isoquinoline, pyridine, and phenanthridine are alkylated with tertiary and secondary alkyl oxalates. The photoelectrochemical synthesis employs 4CzIPN as a molecular catalyst and allows the oxidative transformations to proceed through H_2 evolution without need for sacrificial chemical oxidants.

Key words Synthetic photoelectrochemistry, molecular photoelectrocatalysis, C-H functionalization, alkyl oxalates, heterocycles

Organic electrochemistry[1] and molecular photochemistry[2] are two promising synthetic tools that have been attracting renewed interests. Electrochemistry, due to the ability of the counter electrode to self-adjust its potential to achieve electron flow, can often employs benign and abundant electron acceptors or donors (such as protons or solvent molecules) to achieve oxidation or reduction processes. As a result, electrochemical dehydrogenative reactions do not require external electron and proton acceptors and generate H_2 as the sole theoretical byproduct. While both photoredox catalysis and organic electrochemistry are powerful in promoting single electron transfer (SET) processes, one relies on transient excited states, the other uses electrodes as an electron reservoir or sink. These differences allow the two technologies to achieve different selectivities. For example, electron-rich alkyl radicals generated through SET oxidation by an excited photocatalyst rarely undergo further oxidation to carbocations because the transient nature of the excited state catalyst and the radical species makes additional SET between them difficult. On the other hand, electron-rich carbon radicals generated electrochemically are frequently oxidized further to carbocations due to their low oxidation potentials.[3,4]

Molecular photoelectrochemistry, which combines the methods of electrochemistry and molecular photochemistry and shares the advantages of both technologies, is emerging as a powerful tool for the development of sustainable synthetic methods.[5,6] Although research in this direction dates back in 1980s,[7] synthetic applications of molecular photoelectrochemistry remained unexplored until very recently by us[8] and others.[9] In this context, we have reported photoelectrochemical alkylation reactions of heteroarenes with organotrifluoroborates, carboxylic acids or alkanes as alkylation agents (Scheme 1, top).[8] In these reactions, the alkylation agents are converted to alkyl radicals, which undergo radical addition to the heteroarenes to forge the key C–C bond.



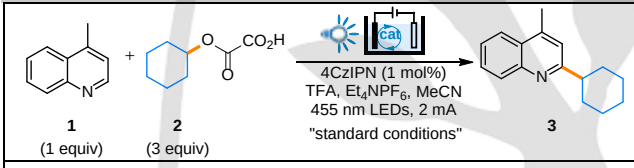
Scheme 1 Photoelectrochemical C-H alkylation of heteroarenes

Alkyl oxalates, which are prepared from alcohols, have been shown by Macmillan and Overman to be viable precursors for alkyl radicals under visible light photoredox conditions.[10] The Overman group reported latter a C–H alkylation reaction of heteroarenes with tertiary alkyl oxalates in the presence of a Ir-based photocatalyst and a stoichiometric $(NH_4)_2S_2O_8$ as terminal oxidant.[11a] The authors found that secondary oxalates were much less efficient than tertiary ones probably due to slower decarboxylation of the former.[10] It has been suggested that decarboxylative radical reactions of oxalates are difficult to achieve under electrochemical conditions.[12] We thus envision a photoelectrochemical approach to achieve decarboxylative cross coupling reactions of oxalates. We report herein metal- and oxidant-free photoelectrocatalytic C-H alkylation reaction of

heteroarenes with secondary and tertiary alkyl oxalates employing an organic molecular catalyst (Scheme 1, bottom).

We chose the alkylation of lepidine (**1**) with secondary oxalate **2** as a model reaction for optimization of conditions.[13] The photoelectrocatalytic reaction was conducted with a constant current of 2 mA in an undivided cell that was exposed to blue LEDs (455 nm) and equipped with a reticulated vitreous carbon (RVC) anode and Pt plate cathode. The solution contained MeCN as solvent, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as the catalyst,[14] trifluoroacetic acid (TFA) as an additive, and Et_4NPF_6 as the supporting electrolyte. Under these conditions, the desired product **3** was obtained in an optimal yield of 76%. Control experiments showed that the catalyst (entry 2), electricity (entry 3), light irradiation (entry 4), TFA (entry 5), and supporting electrolyte Et_4NPF_6 (entry 6) were all needed to obtain optimal results. Residual oxygen was probably served as the terminal oxidant in the absence of electricity to promote the formation of **3**. The use of other salts such as Et_4NOTs (entry 7) or nBu$_4$NPF$_6$ (entry 8) or other electrode materials such as Ni cathode (entry 9) or graphite anode (entry 10) resulted in inferior results.

Table 1 Optimization of reaction conditions.[a]

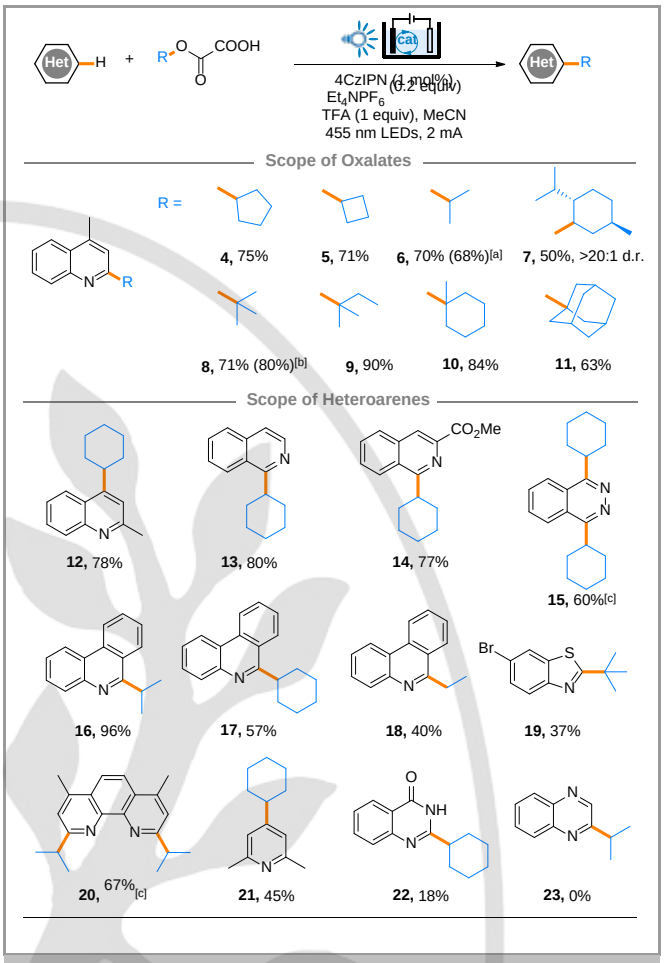


1 (1 equiv) **2** (3 equiv) **3**

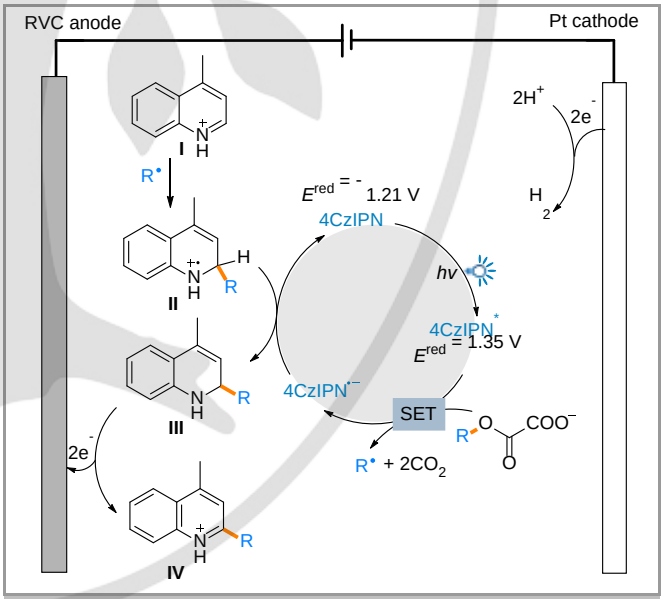
Entry	Deviation from standard conditions	Yield [%][b]
1	None	76[c]
2	No 4CzIPN	11 (74)
3	No electricity	46 (43)
4	No LEDs	<5 (11)
5	No TFA	37 (47)
6	No Et_4NPF_6	60 (27)
7	Et_4NOTs	55 (29)
8	nBu$_4$NPF$_6$	32 (35)
9	Ni plate as cathode	10 (16)
10	graphite plate as anode	11 (57)

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), 4CzIPN (0.002 mmol), TFA (0.2 mmol), Et_4NPF_6 (0.04 mmol), MeCN (6 mL), RVC anode, Pt cathode, 2 mA, 11.5 h (4.3 F mol^{-1}). [b] Yield determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. Unreacted **1** was shown in parenthesis. [c] Isolated yield.

The scope of the photoelectrocatalytic C–H alkylation reaction was explored (Scheme 2).[15] Several secondary (**3**–**7**)[16] and tertiary (**8**–**11**) oxalates reacted efficiently with lepidine to give the desired alkylated products. Primary alkyl oxalates were inefficient alkylation reagents under these conditions, although ethyl oxalate reacted with phenanthridine in 40% yield (**18**). Viable heteroaromatic scaffolds included 2-substituted quinoline (**12**), isoquinoline (**13**, **14**), phthalazine (**15**), phenanthridine (**16**-**18**), benzothiazole (**19**), 1,10-phenanthroline (**20**),[17] and pyridine (**21**).[18] While quinazolinone (**22**) afforded low yield of the alkylation product, quinoxaline (**23**) failed completely. Note that secondary and tertiary a-keto acids are also viable alkylation agents under the photoelectrochemical conditions as demonstrated for the synthesis of compounds **6** and **8**.



Scheme 2 Reaction scope. [a] *i*PrCOCOOH as alkylation agent. [b] *t*BuCOCOOH as alkylation agent. [a] Reaction with 6 equiv of oxalate.



Scheme 3 Proposed mechanism

While alkyl oxalates are attractive radical precursors because of the ease availability of alcohols, alkyl hydrogen oxalates, particularly tertiary ones, undergo disproportionation to give oxalic acid and dialkyl oxalates on storage and during the photoelectrochemical reaction.[10] Although the cesium oxalate salts are more stable on storage and easy to handle, they are less

effective than the hydrogen oxalates for the present photoelectrocatalytic alkylation reactions. In addition, disproportionation cannot be avoided under the acidic conditions, which are essential for the C–H alkylation of heteroarenes. The stability issues associated with oxalates hampered the further development of photoelectrocatalytic C–H alkylation reactions with these agents.

A possible mechanism was proposed for the photoelectrocatalytic C–H alkylation reaction based on literature reports[10] and our previous work (Scheme 3).[8] Single electron transfer (SET) oxidation of the alkyl oxalate (E_p^{ox} = 1.28 V vs SCE for *t*BuOCOCO$_2$Cs)[10] by the photoexcited catalyst 4CZIPN* (E^{red} = 1.35 V vs SCE) generates persistent radical anion 4CzIPN$^{\bullet-}$ and alkyl radical R$^\bullet$ after double decarboxylation. Addition of R$^\bullet$ onto protonated heterocycle **I** generates radical cation **II**, which undergoes highly exothermic SET reduction with 4CzIPN$^{\bullet-}$ to afford 1,2-dihydroquinoline **III** with concomitant regeneration of the ground state catalyst 4CzIPN (E^{red} = -1.21 V vs SCE). **II** ($E_{p/2}^{ox}$ = 0.47 V vs SCE for R = *n*Bu) is then oxidized at the anode through electron and proton loss to furnish the final alkylated heterocycle **IV**.[8b] Protons are reduced at the cathode to generate hydrogen gas, obviating the need for sacrificial electron and proton acceptors.

In summary, an oxidant- and metal-free C–H alkylation reaction of heteroarenes with alkyl oxalates have been achieved by molecular photoelectrocatalysis with an organocatalyst. Secondary and tertiary hydrogen oxalates undergo successful decarboxylative alkylation with several types of N-heteroaromatics and proceed through H_2 evolution.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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(15) **General procedure for the photoelectrochemical alkylation reactions**: A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), oxalate (0.6 mmol, 3.0 equiv), 4CzIPN (0.002 mmol, 1 mol%), Et_4NPF_6 (0.04 mmol, 0.2 equiv) and MeCN (6 mL). The Schlenk tube was equipped with a reticulated vitreous carbon (100 PPI)

anode (0.5 cm x 1.5 cm x 1.2 cm) and a platinum plate (1 cm x 1 cm) cathode. The reaction mixture was bubbled with argon for 15 min. TFA (0.2 mmol, 1 equiv) was added. 455 nm LEDs (20 W) were placed 2 cm to the side of the reactor. The reaction was carried out using a constant current of 2 mA at about 50 °C (internal temperature) until complete consumption of the substrate (detected by TLC or ^{1}H NMR). The reaction was quenched with saturated $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product.

(16) Spectra data for compound **3**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.74–7.65 (m, 1H), 7.57–7.46 (m, 1H), 7.18 (s, 1H), 2.90 (td, *J* = 12.1, 3.4 Hz, 1H), 2.69 (s, 3H), 2.08–2.01 (m, 2H), 1.95–1.88 (m, 2H), 1.84–1.78 (m, 1H), 1.70–1.61 (m, 2H), 1.53–1.44 (m, 2H), 1.40–1.33 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 147.7, 144.4, 129.6, 129.0, 127.1, 125.5, 123.7, 120.4, 47.7, 32.9, 26.7, 26.2, 19.0.

(17) Spectra data for compound **20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.37 (s, 2H), 3.52 (hept, *J* = 6.9 Hz, 2H), 2.74 (s, 6H), 1.47 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 145.4, 144.2, 126.7, 121.1, 121.0, 37.3, 23.0, 19.5.

(18) Spectra data for compound **21**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.51 (s, 6H), 2.43 (tt, *J* = 12.0, 4.8 Hz, 1H), 1.92–1.73 (m, 6H), 1.48–1.35 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 157.4, 119.1, 44.0, 33.7, 26.8, 26.2, 24.6.

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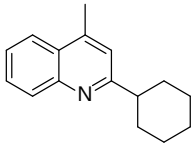
1. General Information

Anhydrous MeCN were purchased from Aldrich and used directly. Et_4NPF_6 were purchased from TCI and used directly. Flash column chromatography was performed with silica gel (200–300 mesh) which was purchased from Adamas. NMR spectra were recorded on Bruker AV-400, Bruker AV-500, and Bruker AV-600 instruments. ^1H NMR spectra are reported in parts per million (ppm) downfield relative to TMS (0.00 ppm) and all ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.2 ppm) unless stated otherwise. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The electrodes used for the preparative electrolysis were the same as those previously reported.

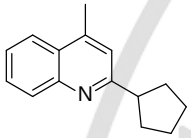
2. General Procedure for the Electrophotocatalytic Reactions

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), oxalate (0.6 mmol, 3.0 equiv), 4CzIPN (0.002 mmol, 1 mol%), Et_4NPF_6 (0.04 mmol, 0.2 equiv) and MeCN (6 mL). The Schlenk tube was equipped with a reticulated vitreous carbon (100 PPI) anode (0.5 cm x 1.5 cm x 1.2 cm) and a platinum plate (1 cm x 1 cm) cathode. The reaction mixture was bubbled with argon for 15 min. TFA (0.2 mmol, 1 equiv) was added. 455 nm LEDs (20 W) were placed 2 cm to the side of the reactor. The reaction was carried out using a constant current of 2 mA at about 50 °C (internal temperature) until complete consumption of the substrate (detected by TLC or ^1H NMR). The reaction was quenched with saturated $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product.

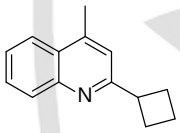
3. Characterization Data



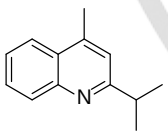
2-Cyclohexyl-4-methylquinoline[1] **(3).** Colorless oil; Yield = 76%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.74–7.65 (m, 1H), 7.57–7.46 (m, 1H), 7.18 (s, 1H), 2.90 (td, *J* = 12.1, 3.4 Hz, 1H), 2.69 (s, 3H), 2.08–2.01 (m, 2H), 1.95–1.88 (m, 2H), 1.84–1.78 (m, 1H), 1.70–1.61 (m, 2H), 1.53–1.44 (m, 2H), 1.40–1.33 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 147.7, 144.4, 129.6, 129.0, 127.1, 125.5, 123.7, 120.4, 47.7, 32.9, 26.7, 26.2, 19.0.



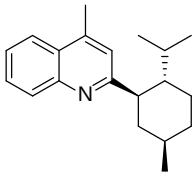
2-Cyclopentyl-4-methylquinoline[1] **(4)**. Colorless oil; Yield = 75%; Electricity = 4.4 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.28 (s, 1H), 3.52 (p, *J* = 8.3 Hz, 1H), 2.76 (s, 3H), 2.46–2.20 (m, 2H), 2.05–1.67 (m, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 147.4, 145.0, 130.4, 127.6, 127.0, 126.5, 123.8, 120.6, 47.5, 34.0, 26.2, 19.3.



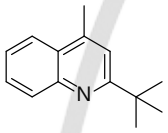
2-Cyclobutyl-4-methylquinoline[1] **(5).** Colorless oil; Yield = 71%; Electricity = 4.4 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.70 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.24 (s, 1H), 3.88 (p, *J* = 8.8 Hz, 1H), 2.72 (s, 3H), 2.47 (td, *J* = 9.0, 6.0 Hz, 4H), 2.20–2.11 (m, 1H), 2.02–1.94 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 147.7, 144.3, 129.7, 129.1, 127.0, 125.5, 123.7, 120.4, 42.8, 28.4, 18.9, 18.5.



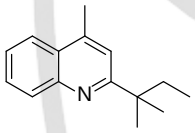
2-Isopropyl-4-methylquinoline[1] **(6)**. Colorless oil; Yield = 70%; Electricity = 4.4 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.21 (s, 1H), 3.26 (hept, *J* = 6.9 Hz, 1H), 2.72 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 147.3, 144.9, 129.4, 129.3, 127.1, 125.7, 123.7, 119.9, 37.2, 22.7, 19.0.



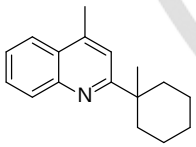
2-((2S,5R)-2-Isopropyl-5-methylcyclohexyl)-4-methylquinoline[1] **(7)**. Colorless oil; Yield = 50%; Electricity = 4.2 F mol^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.94 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.12 (s, 1H), 2.87 (td, *J* = 11.7, 3.5 Hz, 1H), 2.68 (s, 3H), 1.91–1.86 (m, 2H), 1.84–1.77 (m, 2H), 1.75–1.66 (m, 1H), 1.56 (ddd, *J* = 11.6, 6.0, 3.0 Hz, 1H), 1.39–1.33 (m, 1H), 1.29–1.23 (m, 1H), 1.10 (dd, *J* = 11.9, 3.3 Hz, 1H), 0.92–0.90 (m, 3H), 0.82 (d, *J* = 6.9 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H).



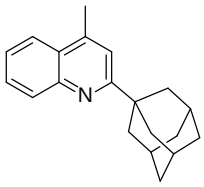
2-(*tert*-Butyl)-4-methylquinoline[1] **(8).** Colorless oil; Yield = 71%; Electricity = 4.1 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.71–7.66 (m, 1H), 7.54–7.49 (m, 1H), 7.38 (s, 1H), 2.72 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 147.4, 143.7, 130.1, 128.8, 126.7, 125.5, 123.5, 119.0, 38.1, 30.3, 19.1.



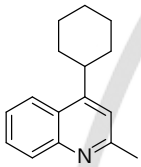
4-Methyl-2-(*tert*-pentyl)quinoline[1] **(9).** Colorless oil; Yield = 90%; Electricity = 4.5 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.68 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.33 (s, 1H), 2.71 (d, *J* = 1.0 Hz, 3H), 1.87 (q, *J* = 7.5 Hz, 2H), 1.46 (s, 6H), 0.77 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 147.5, 143.5, 130.1, 128.7, 126.6, 125.5, 123.5, 119.5, 41.3, 36.0, 27.5, 19.1, 9.4.



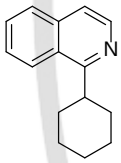
4-Methyl-2-(1-methylcyclohexyl)quinoline[2] **(10).** Colorless oil; Yield = 84%; Electricity = 4.4 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.32 (s, 1H), 2.68 (s, 3H), 2.42–2.30 (m, 2H), 1.66–1.56 (m, 4H), 1.50–1.41 (m, 4H), 1.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 147.7, 143.6, 130.1, 128.7, 126.6, 125.4, 123.5, 119.5, 41.4, 37.3, 26.5, 23.1, 19.1.



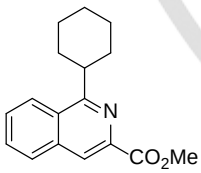
2-((1*s*,3*s*)-Adamantan-1-yl)-4-methylquinoline[1] **(11).** White solid; Yield: 63%; Electricity = 4.2 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.72–7.66 (m, 1H), 7.60–7.49 (m, 1H), 7.36 (s, 1H), 2.72 (s, 3H), 2.22–2.12 (m, 9H), 1.96–1.83 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 147.6, 143.7, 130.1, 128.7, 126.8, 125.4, 123.5, 118.6, 41.9, 39.7, 37.0, 29.0, 19.1.



4-Cyclohexyl-2-methylquinoline[3] **(12).** Colorless oil; Yield = 78%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10–7.98 (m, 2H), 7.66 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.18 (s, 1H), 3.39–3.22 (m, 1H), 2.73 (s, 3H), 2.05–1.99 (m, 2H), 1.97–1.91 (m, 2H), 1.90–1.83 (m, 1H), 1.56 (m, 4H), 1.41–1.30 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 153.4, 148.2, 129.6, 128.9, 125.4, 125.2, 122.9, 118.4, 38.9, 33.7, 27.0, 26.4, 25.6.

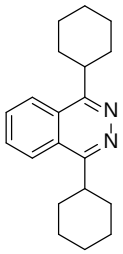


1-Cyclohexylisoquinoline[4] **(13)**. Colorless oil; Yield = 80%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.6 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.68–7.64 (m, 1H), 7.60 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 7.49 (d, *J* = 5.7 Hz, 1H), 3.58 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.05–1.78 (m, 7H), 1.56 (qt, *J* = 13.0, 3.5 Hz, 2H), 1.42 (qt, *J* = 12.9, 3.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 142.0, 136.5, 129.6, 127.6, 126.9, 126.4, 124.8, 119.0, 41.6, 32.7, 27.0, 26.4.

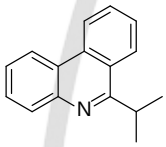


Methyl 1-cyclohexylisoquinoline-3-carboxylate[5] **(14).** Light yellow solid; Yield = 77%; Electricity = 4.4 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.34–8.26 (m, 1H), 8.02–7.92 (m, 1H), 7.77–7.70 (m, 2H), 4.04 (s, 3H), 3.59 (tt, *J* = 11.3, 3.6 Hz, 1H), 2.05–1.91 (m, 6H), 1.87–1.80 (m, 1H), 1.61–1.52 (m, 2H), 1.48–1.41 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 166.3, 140.8, 136.1, 130.2, 129.2, 129.2, 127.9, 125.1,

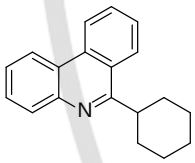
122.5, 52.8, 42.2, 32.4, 26.9, 26.2.



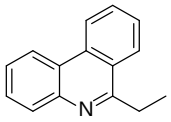
1,4-Dicyclohexylphthalazine[1] **(15).** Reaction under general procedure but with 6 equiv of oxalates. Colorless oil; Yield = 60%; Electricity = 6.2 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.84 (dd, *J* = 6.3, 3.3 Hz, 2H), 3.46 (tt, *J* = 11.6, 3.5 Hz, 2H), 2.08–1.93 (m, 11H), 1.84–1.79 (m, 3H), 1.52 (qt, *J* = 12.8, 3.4 Hz, 4H), 1.38 (qt, *J* = 12.9, 3.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 131.2, 125.1, 124.3, 40.6, 32.5, 27.0, 26.4.



6-Isopropylphenanthridine[6] **(16).** Light yellow oil; Yield = 96%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.92–7.81 (m, 1H), 7.79–7.68 (m, 2H), 7.66–7.61 (m, 1H), 4.03 (hept, *J* = 6.8 Hz, 1H), 1.56 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 143.9, 133.2, 130.1, 128.5, 127.2, 126.3, 125.8, 124.9, 123.5, 122.7, 121.9, 31.6, 22.1.

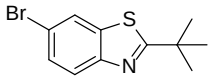


6-Cyclohexylphenanthridine[3] **(17)**. Colorless oil; Yield = 57%; Electricity = 4.0 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.81–7.75 (m, 1H), 7.72–7.63 (m, 2H), 7.60–7.55 (m, 1H), 3.60 (tt, *J* = 11.4, 3.2 Hz, 1H), 2.13–2.03 (m, 2H), 2.00–1.88 (m, 4H), 1.87–1.81 (m, 1H), 1.63–1.51 (m, 2H), 1.49–1.38 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 144.0, 133.1, 130.0, 130.0, 128.5, 127.2, 126.2, 125.7, 124.8, 123.5, 122.7, 121.9, 42.1, 32.4, 27.0, 26.5.

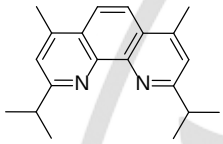


6-Ethylphenanthridine[7] **(18).** Colorless oil; Yield = 40%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.55 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.84 (ddd, *J* = 8.3, 7.0, 1.3 Hz,

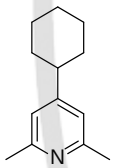
1H), 7.71 (dddd, *J* = 8.3, 6.9, 5.3, 1.3 Hz, 2H), 7.62 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 3.42 (q, *J* = 7.6 Hz, 2H), 1.52 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 143.9, 133.1, 130.5, 129.7, 128.7, 127.4, 126.5, 126.4, 125.2, 123.8, 122.7, 122.1, 29.5, 13.8.



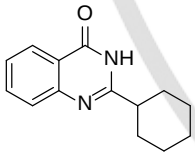
6-Bromo-2-cyclohexylbenzo[*d*]thiazole[6] **(19).** Colorless oil; Yield = 37%; Electricity = 4.4 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.54 (dd, *J* = 8.7, 1.9 Hz, 1H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 182.6, 152.3, 136.8, 129.3, 124.1, 123.9, 118.1, 38.6, 30.8.



2,9-Diisopropyl-4,7-dimethyl-1,10-phenanthroline (20). Reaction under general procedure but with 6 equiv of oxalates. Light yellow solid; Yield = 67%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.37 (s, 2H), 3.52 (hept, *J* = 6.9 Hz, 2H), 2.74 (s, 6H), 1.47 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 145.4, 144.2, 126.7, 121.1, 121.0, 37.3, 23.0, 19.5. IR (neat, cm^{-1}): 2958, 2924, 2867, 1549, 1455, 1089, 750. ESI HRMS *m/z* $(M+H)^+$ calcd 293.2012, obsd 293.2007.



4-Cyclohexyl-2,6-dimethylpyridine[3] **(21).** Colorless oil; Yield = 45%; Electricity = 4.3 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.51 (s, 6H), 2.43 (tt, *J* = 12.0, 4.8 Hz, 1H), 1.92–1.73 (m, 6H), 1.48–1.35 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 157.4, 119.1, 44.0, 33.7, 26.8, 26.2, 24.6.



2-Cyclohexylquinazolin-4(3*H*)-one[3] **(22).** Light yellow solid; Yield = 18%; Electricity = 6.2 F mol^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.01 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.79–7.74 (m, 1H), 7.73–7.69 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 2.71 (tt, *J* = 12.2, 3.7 Hz, 1H), 2.12–2.02 (m, 2H), 1.98–1.89 (m, 2H), 1.84–1.78 (m, 1H), 1.76–1.68 (m, 2H), 1.50–1.34 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 160.0, 149.6, 134.8, 127.5, 126.5, 126.4, 121.0, 45.0, 30.7, 26.1, 25.8.

4. Procedures for the Synthesis of Oxalates

To a solution of alcohol (1.0 equiv.) in DCM (0.1 M) was added oxalyl chloride (1.2 equiv.) at 0 °C under argon. The mixture was warmed to rt gradually and stirred overnight. H_2O was added. The resulting mixture was stirred for 30 min at rt before extraction with $CHCl_3$. The aqueous layer was washed with $CHCl_3$. The combined organic phase was dried over Na_2SO_4, filtered and concentrated to afford the oxalate, which was used without further purification.

5. References

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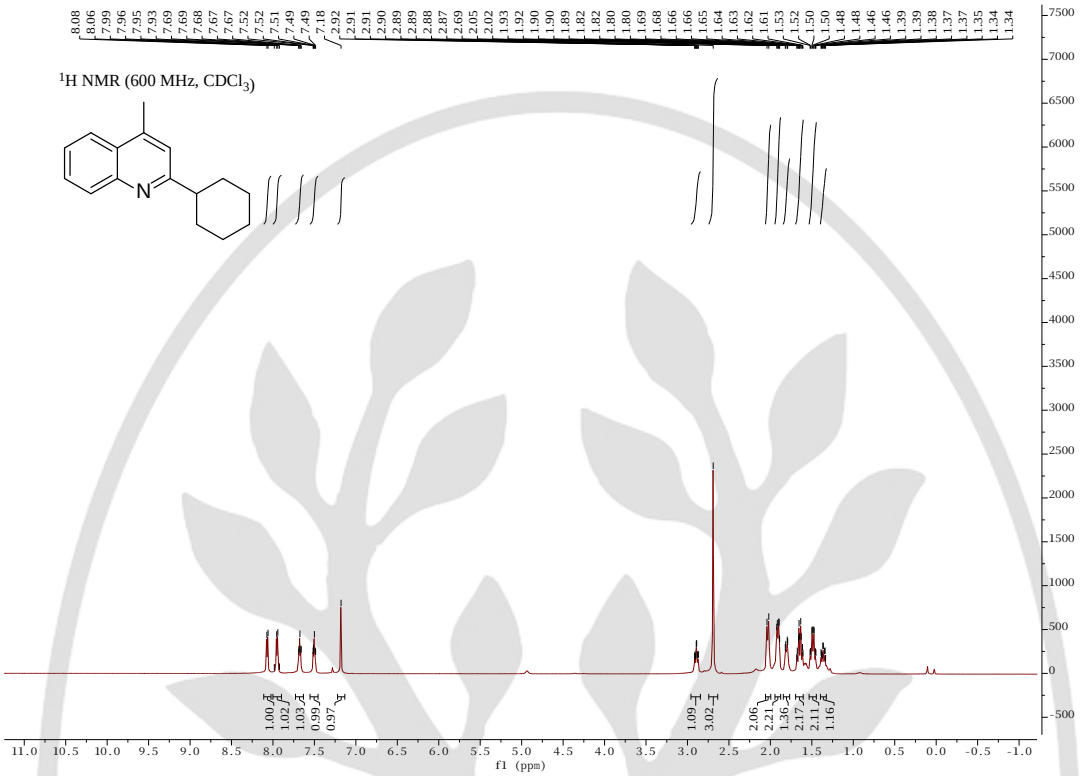
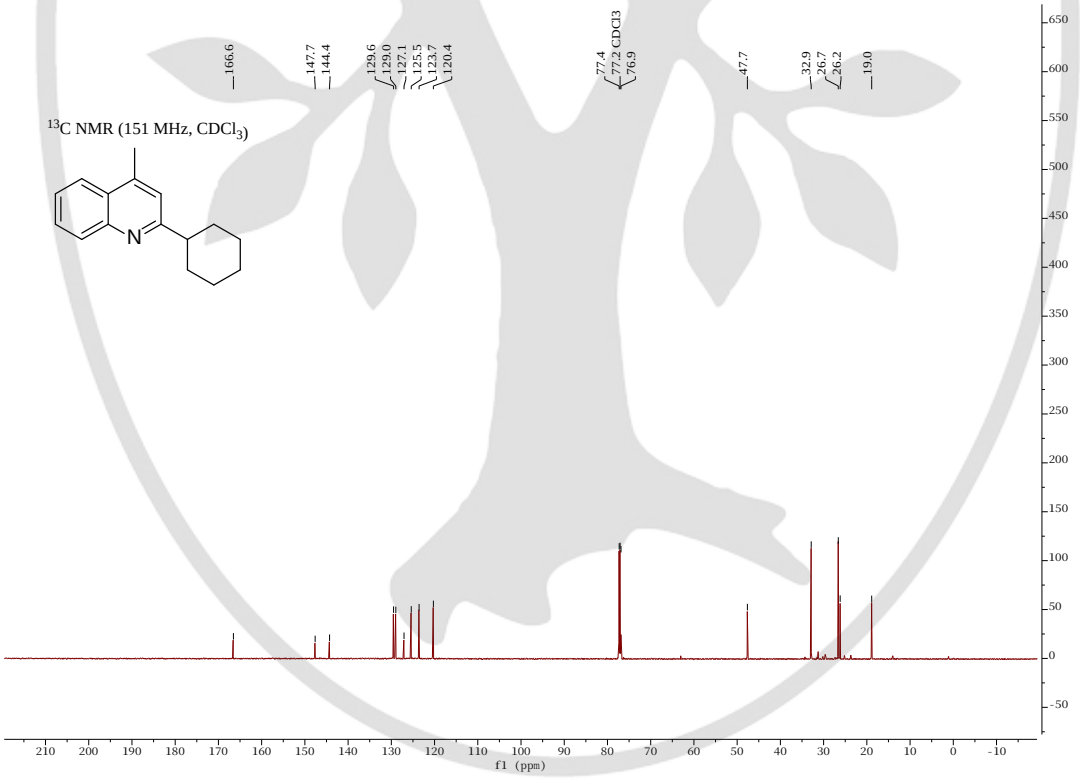
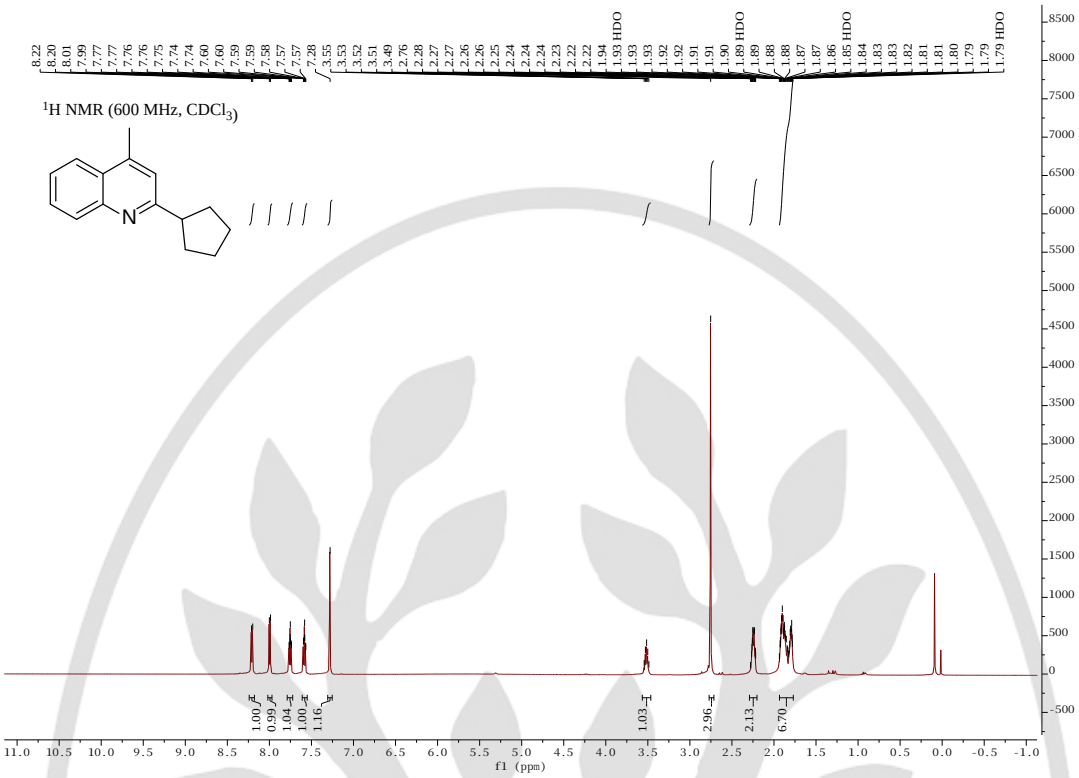
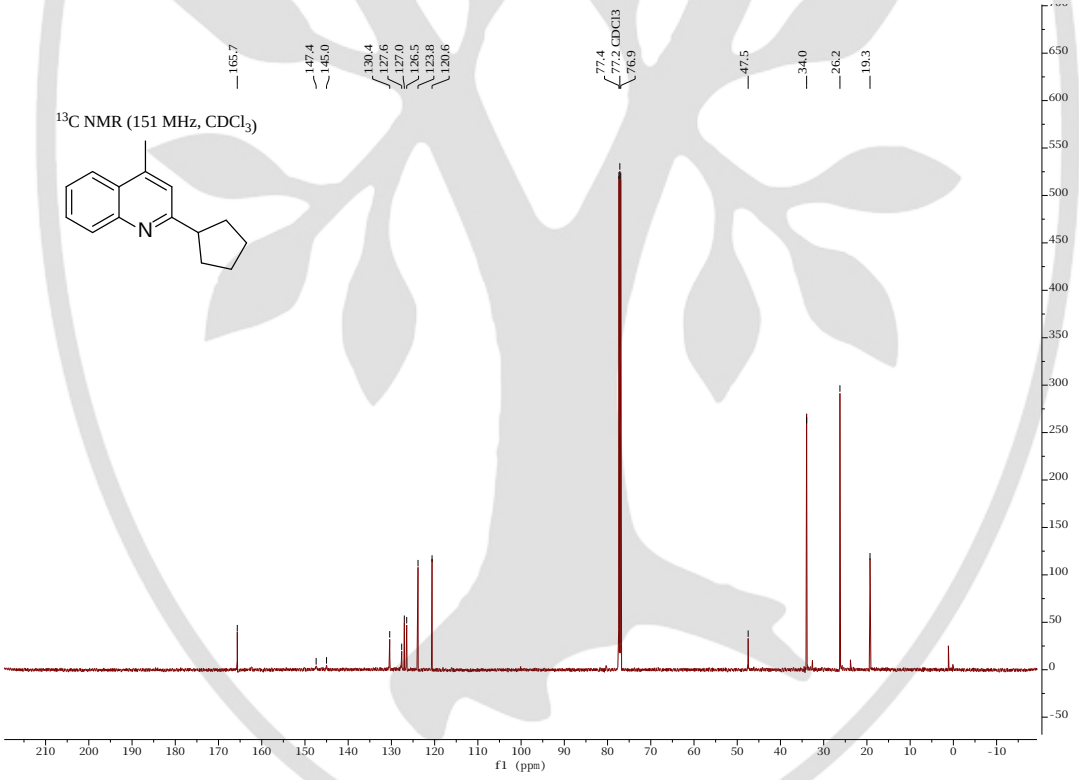
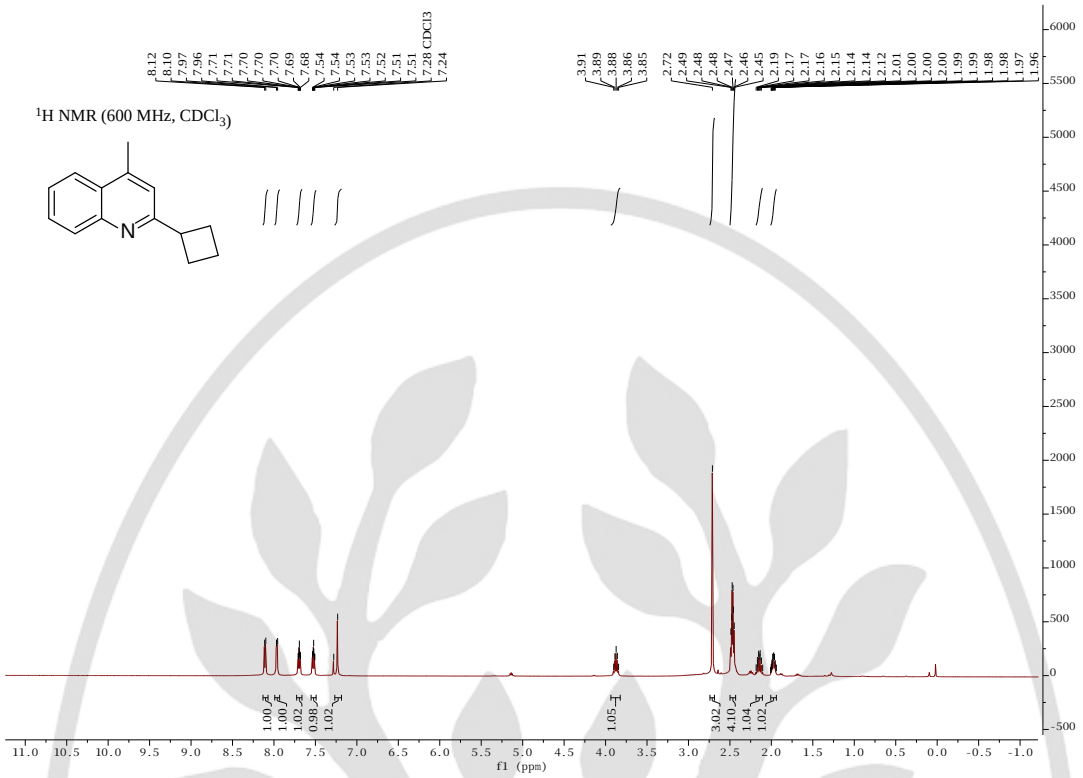
6. NMR Spectra

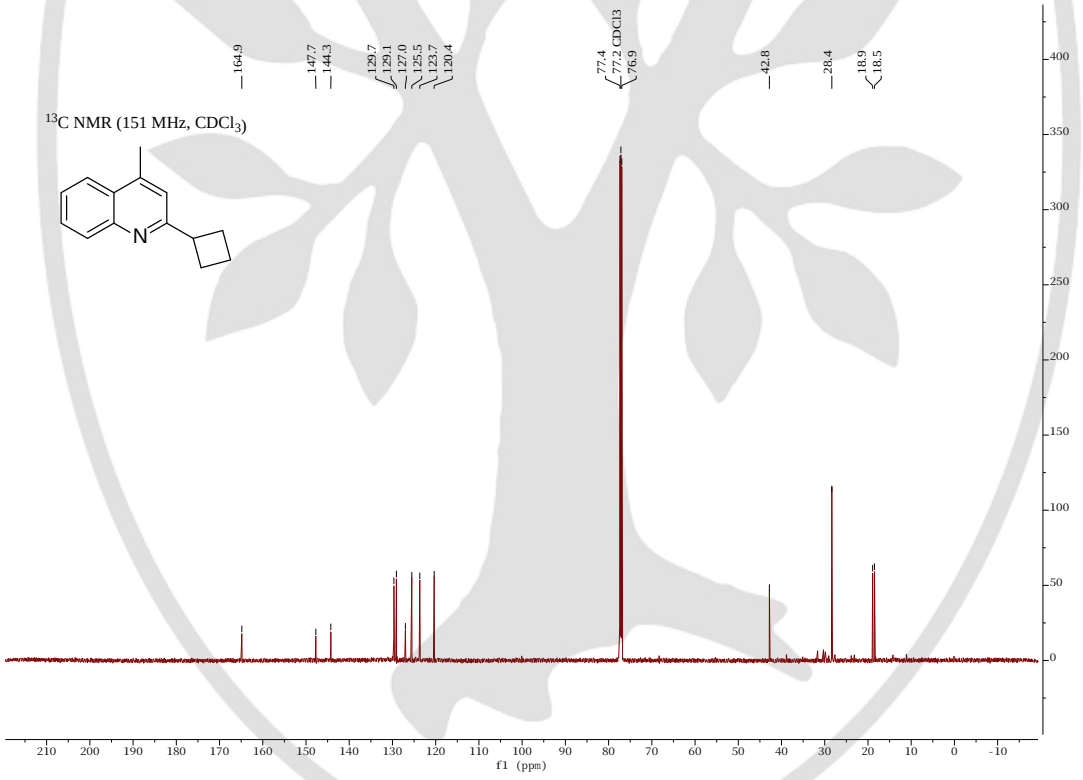


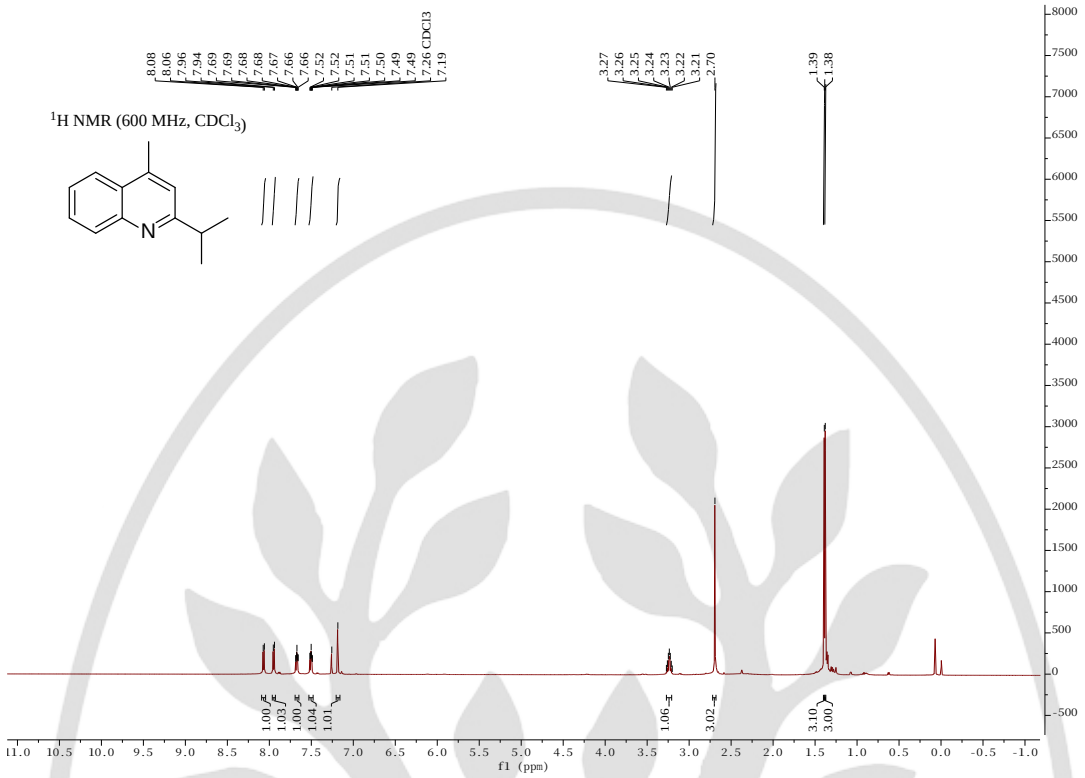


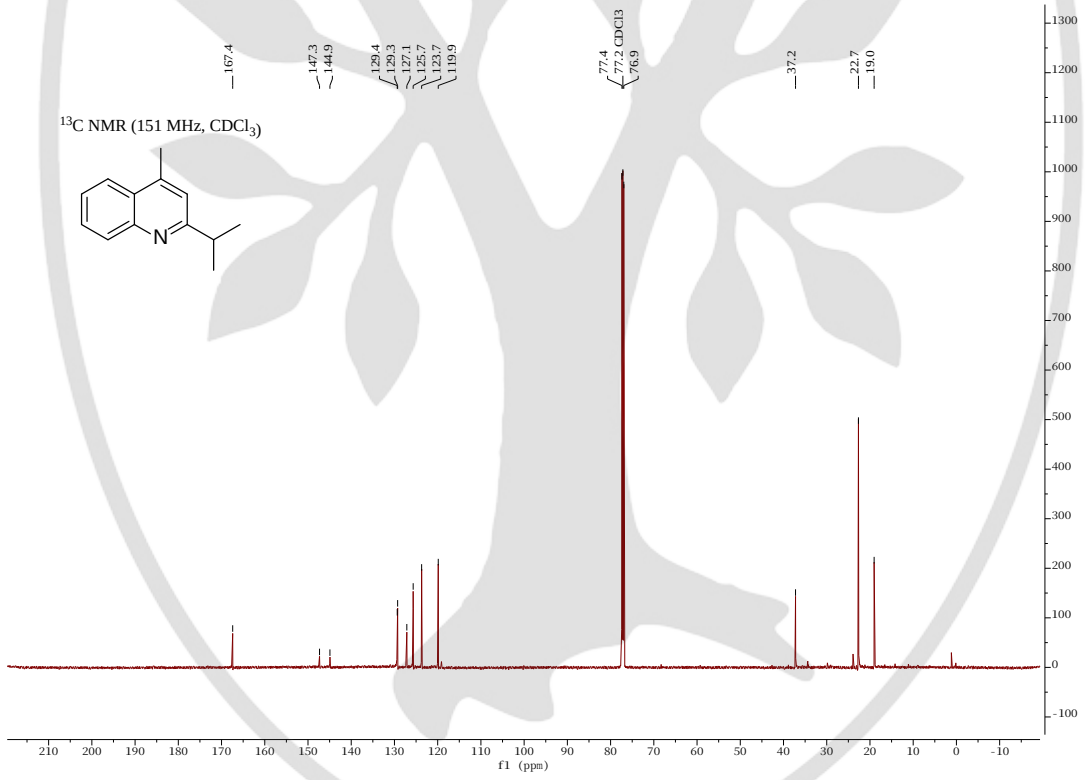


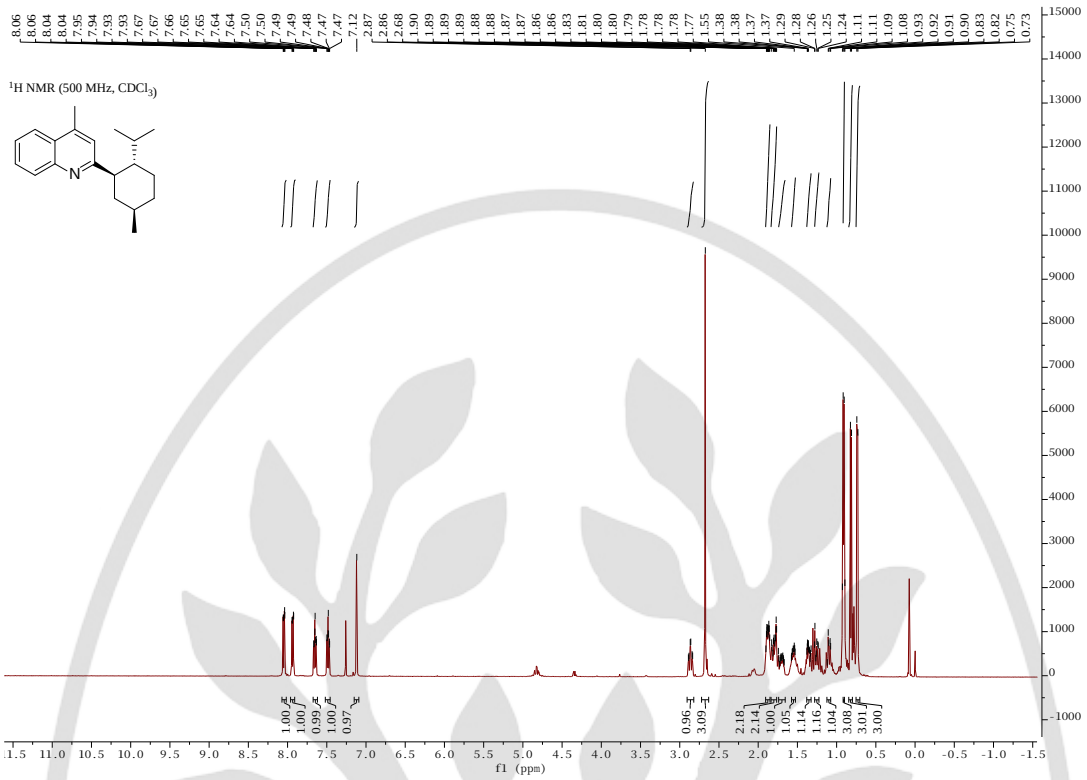


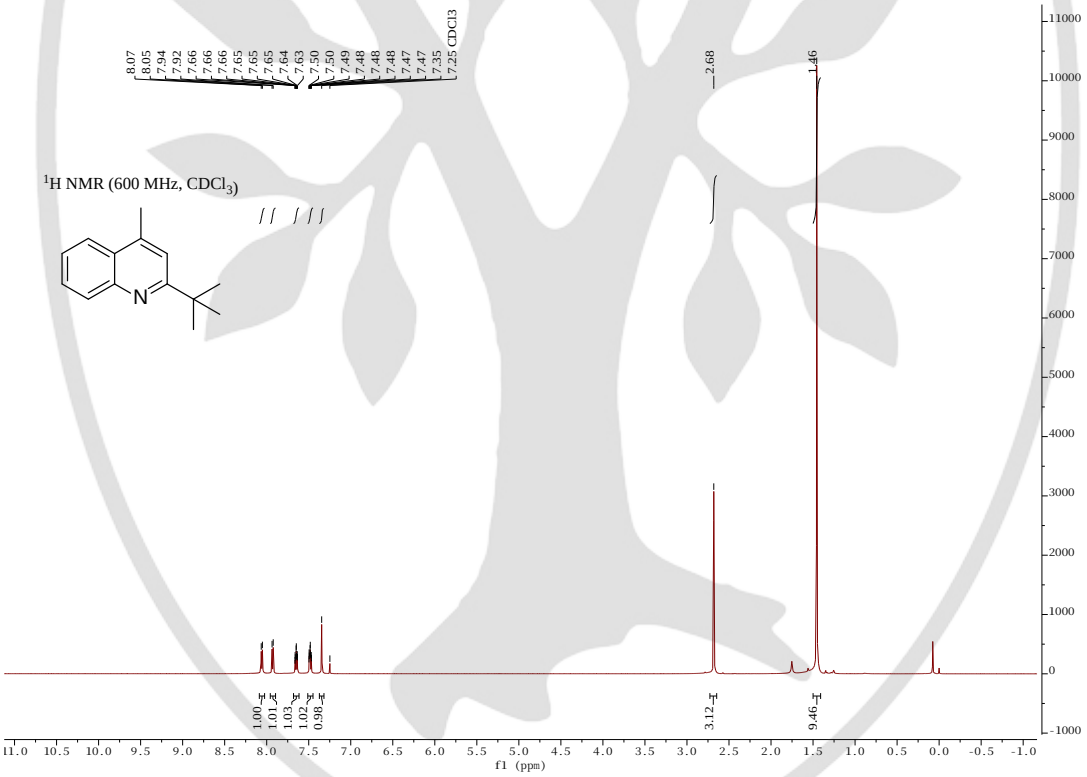


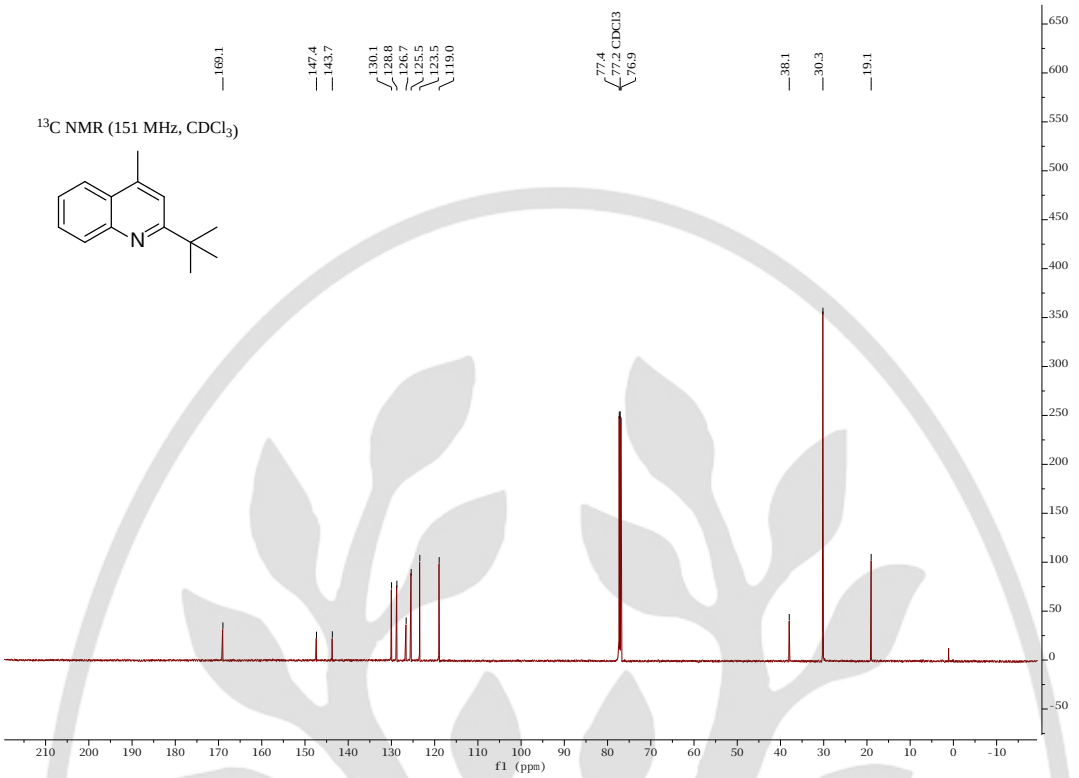


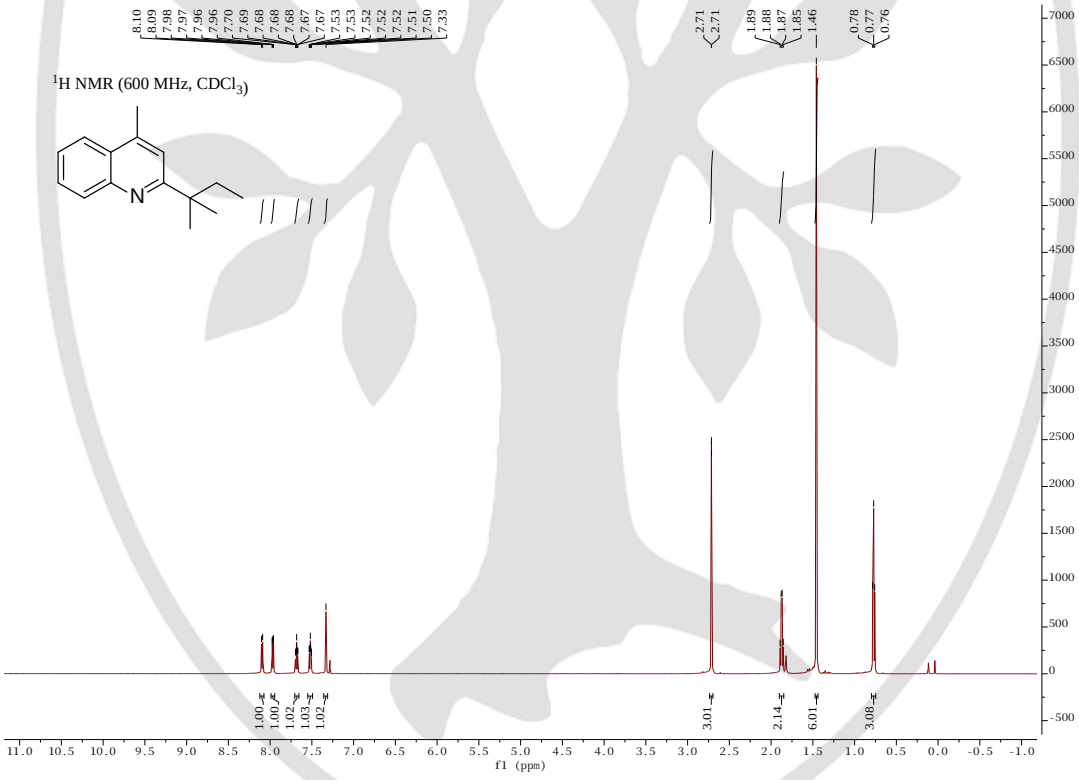


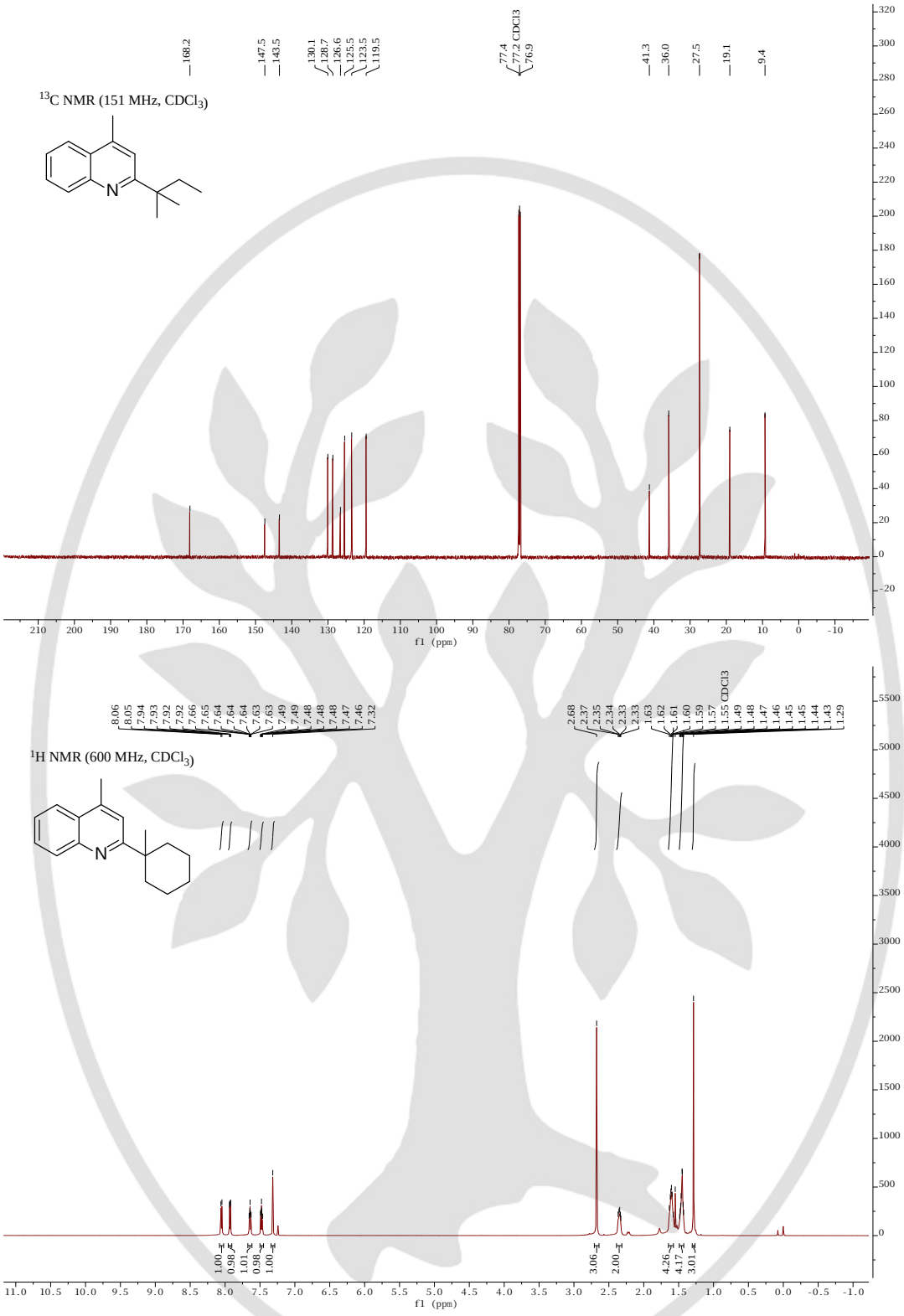


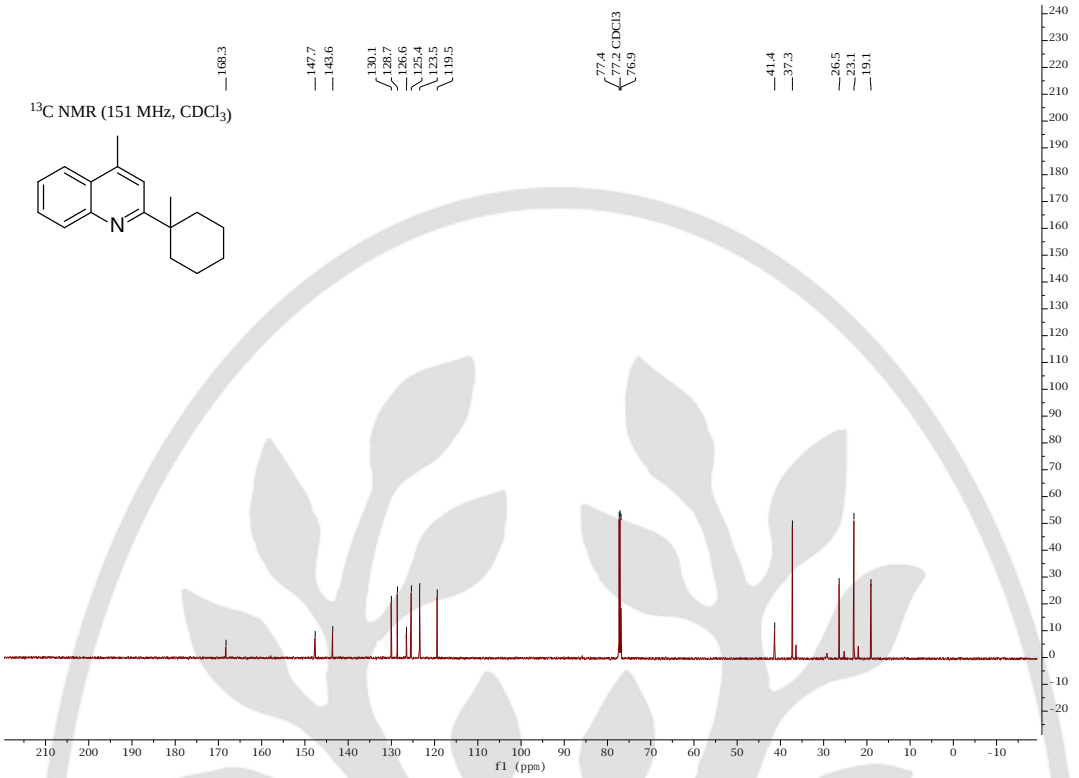




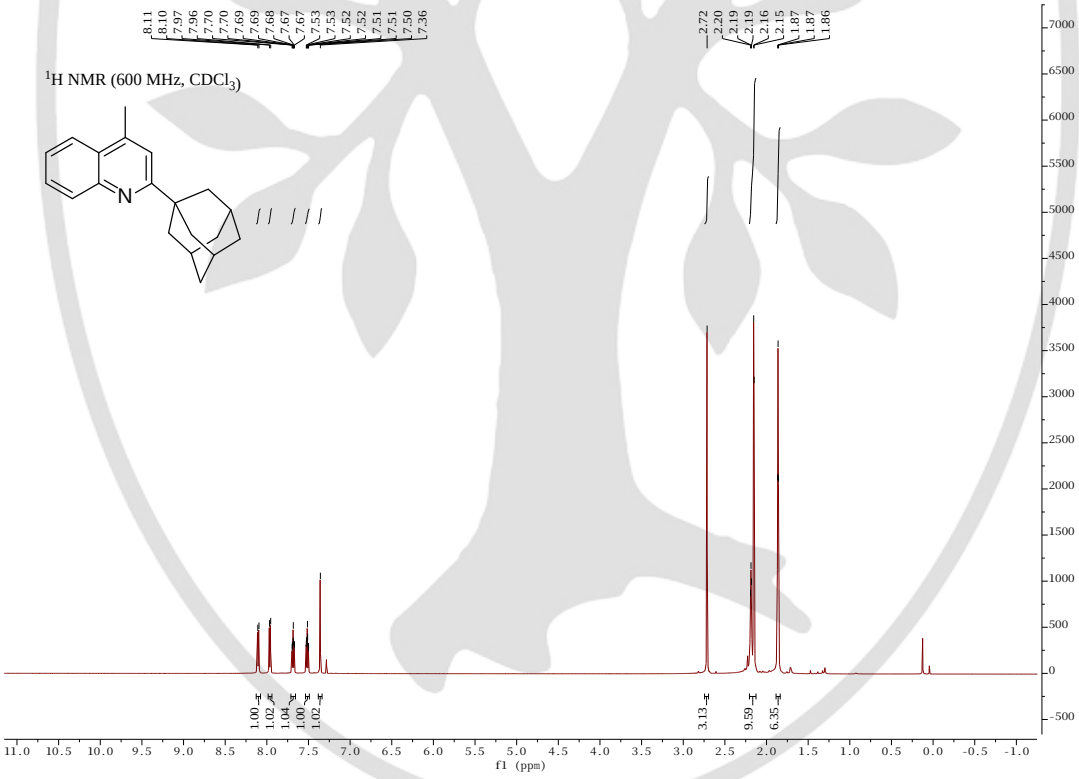








^{13}C NMR (151 MHz, $CDCl_3$)



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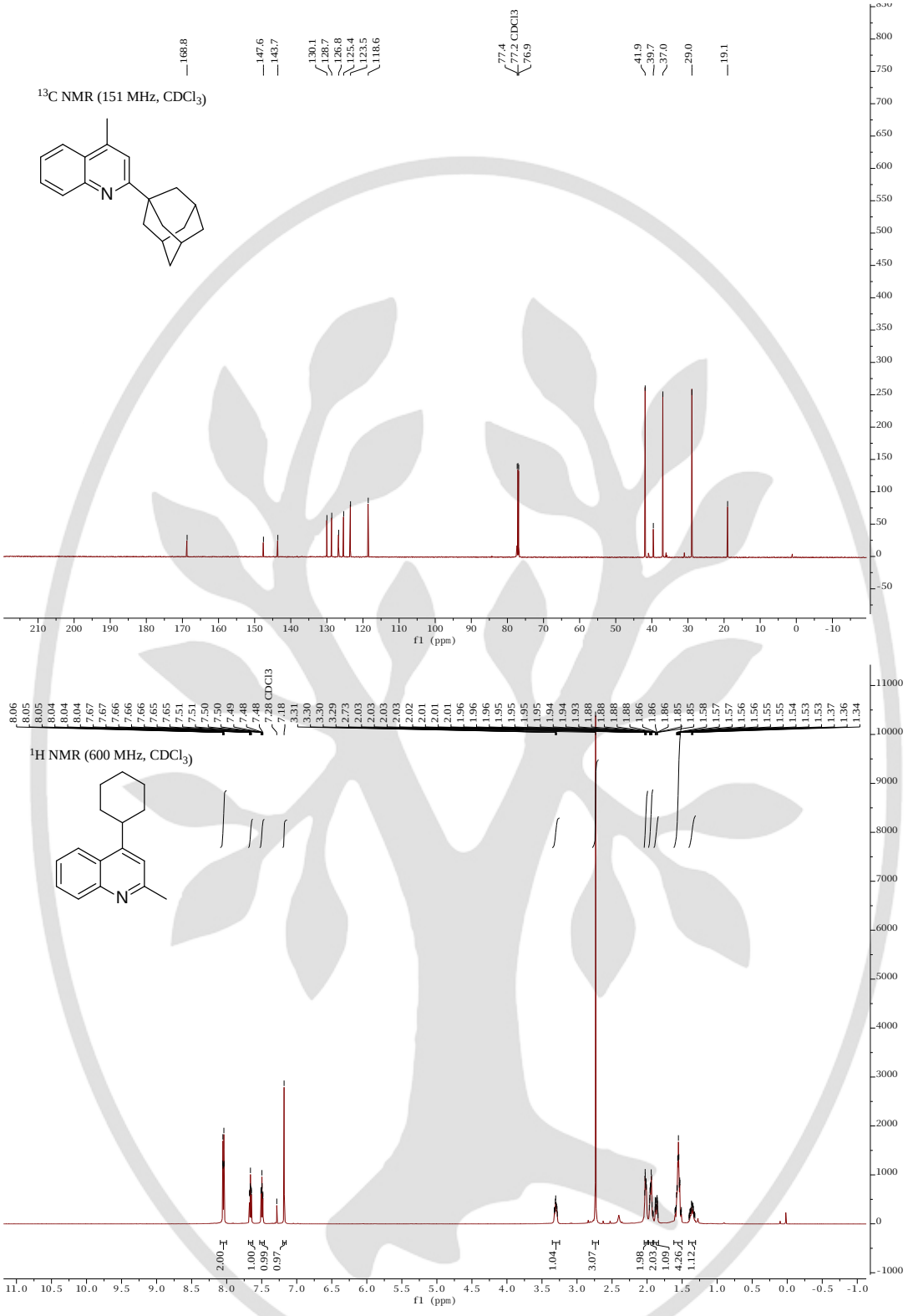

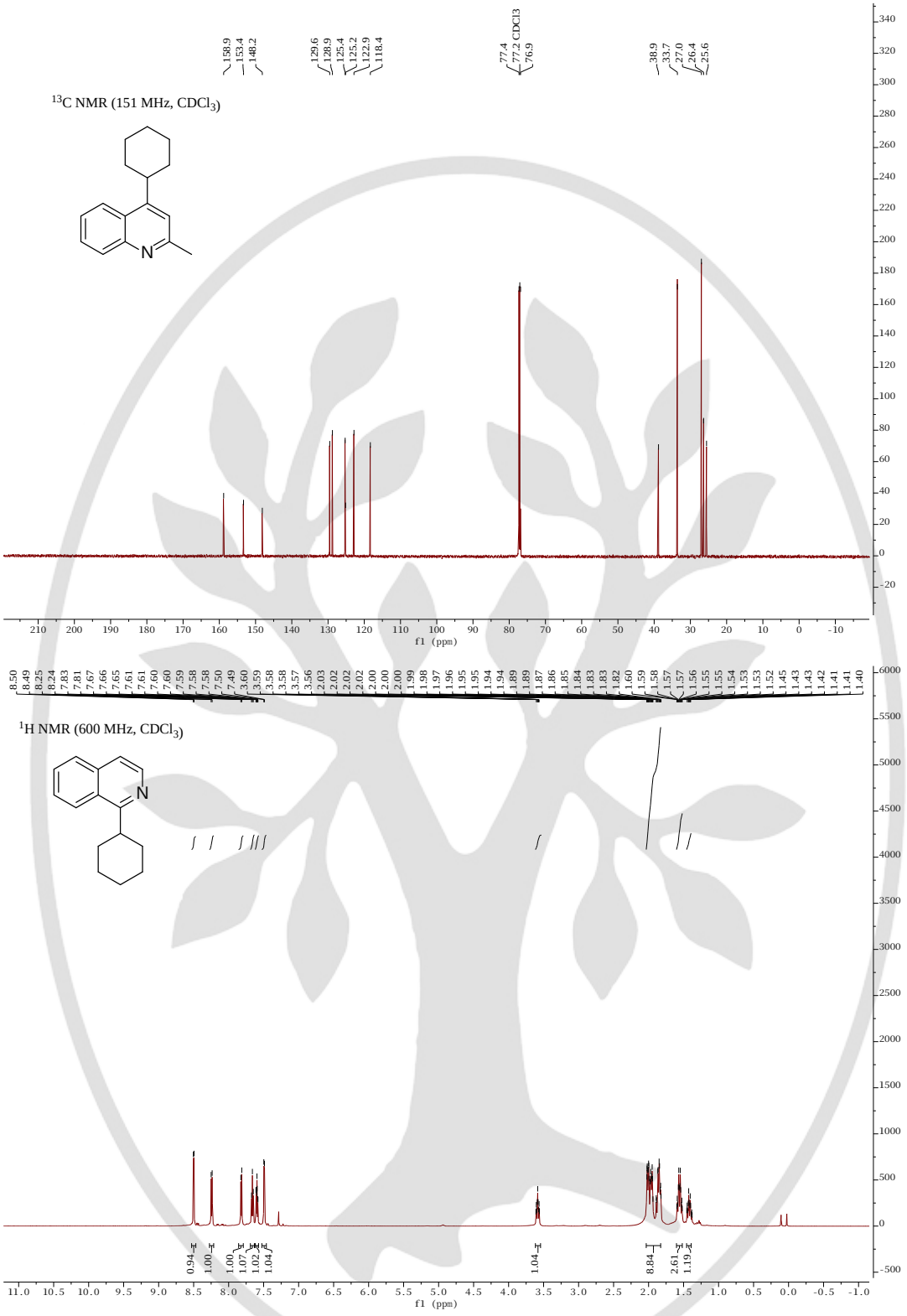

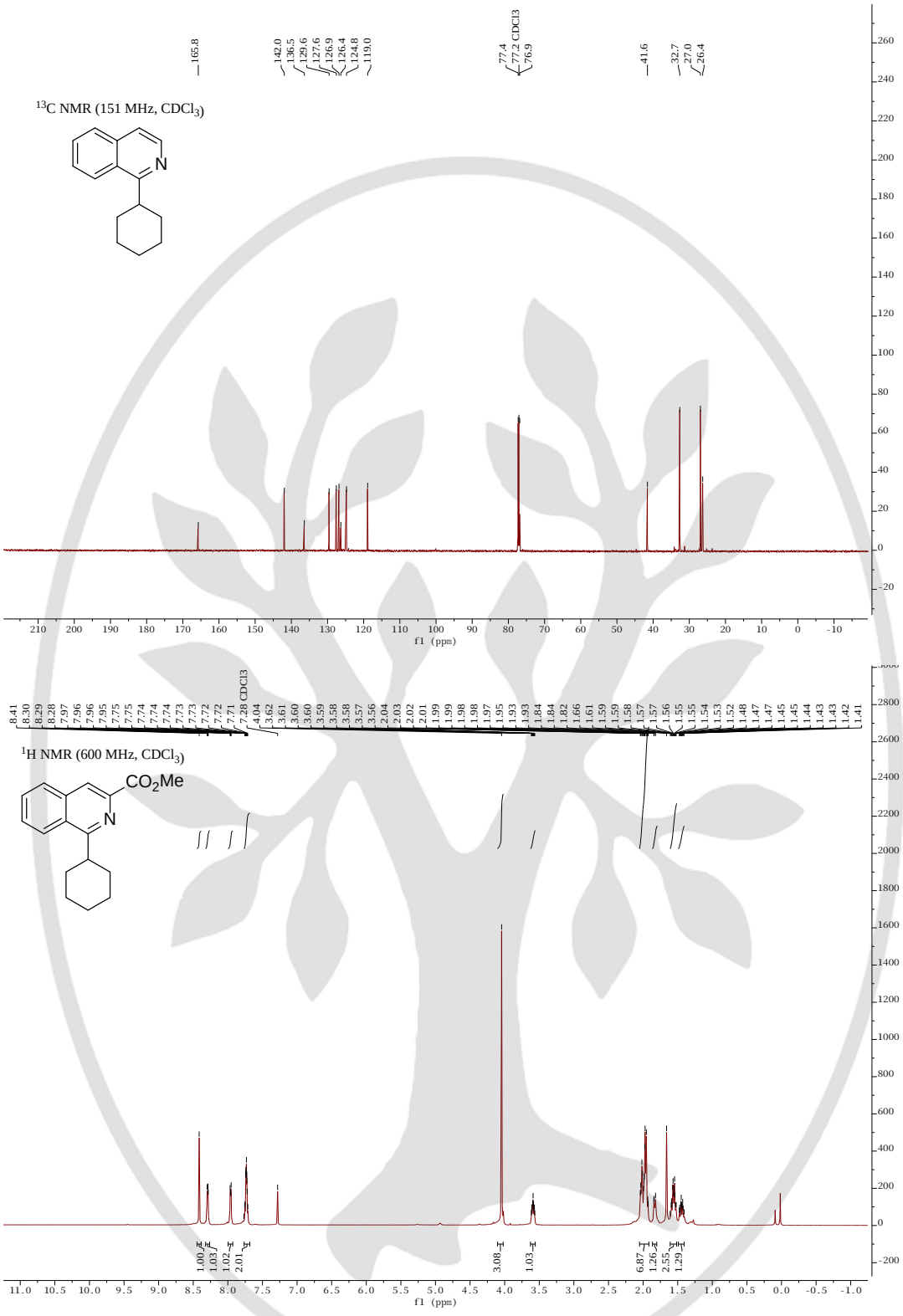

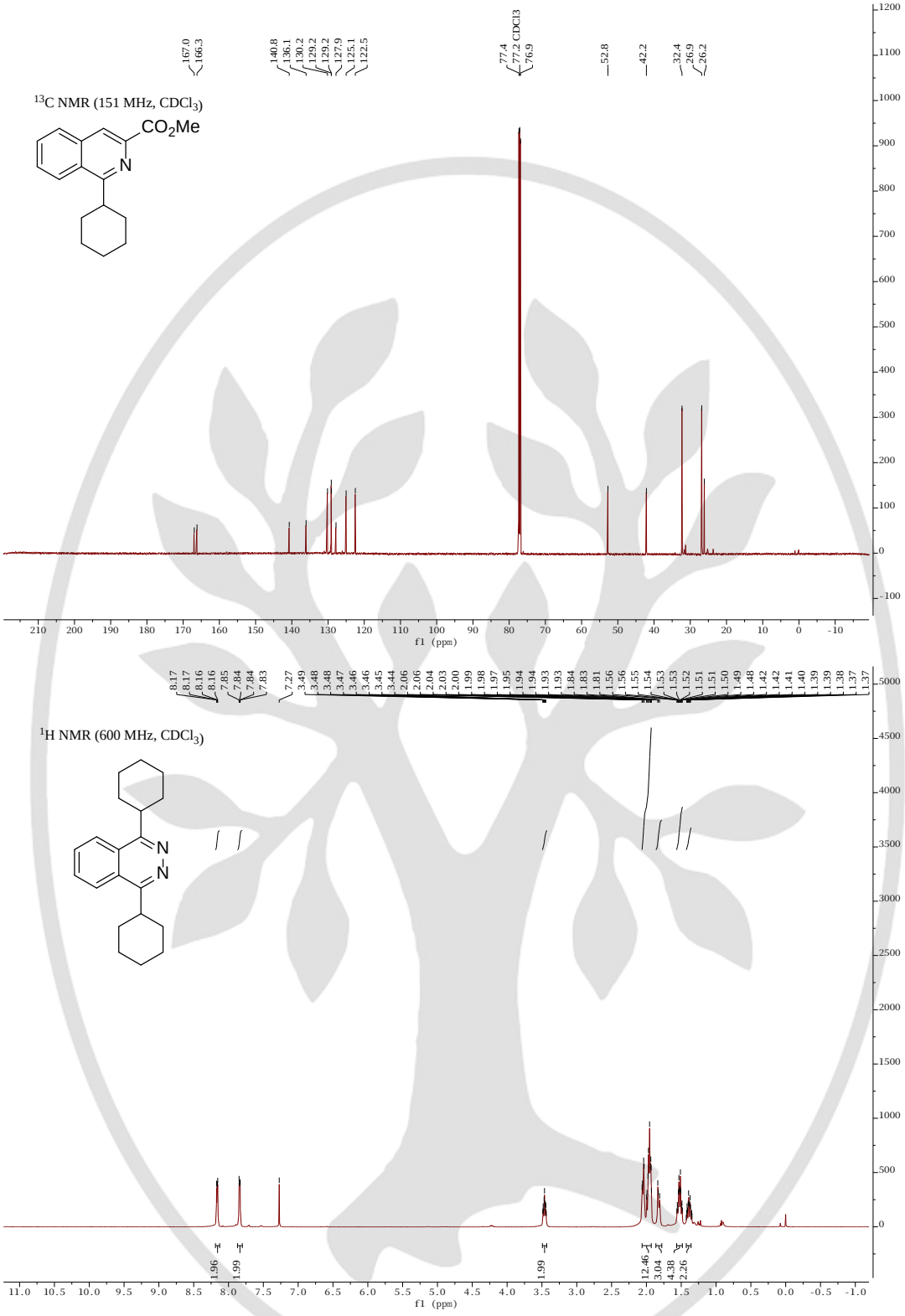

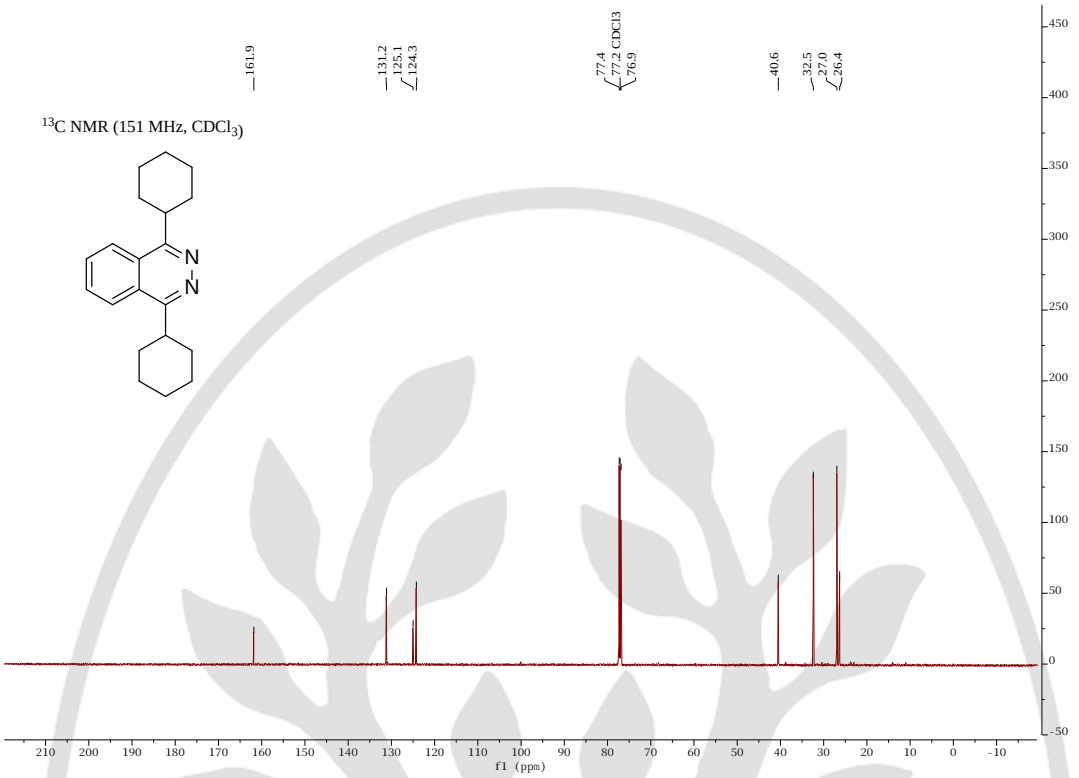

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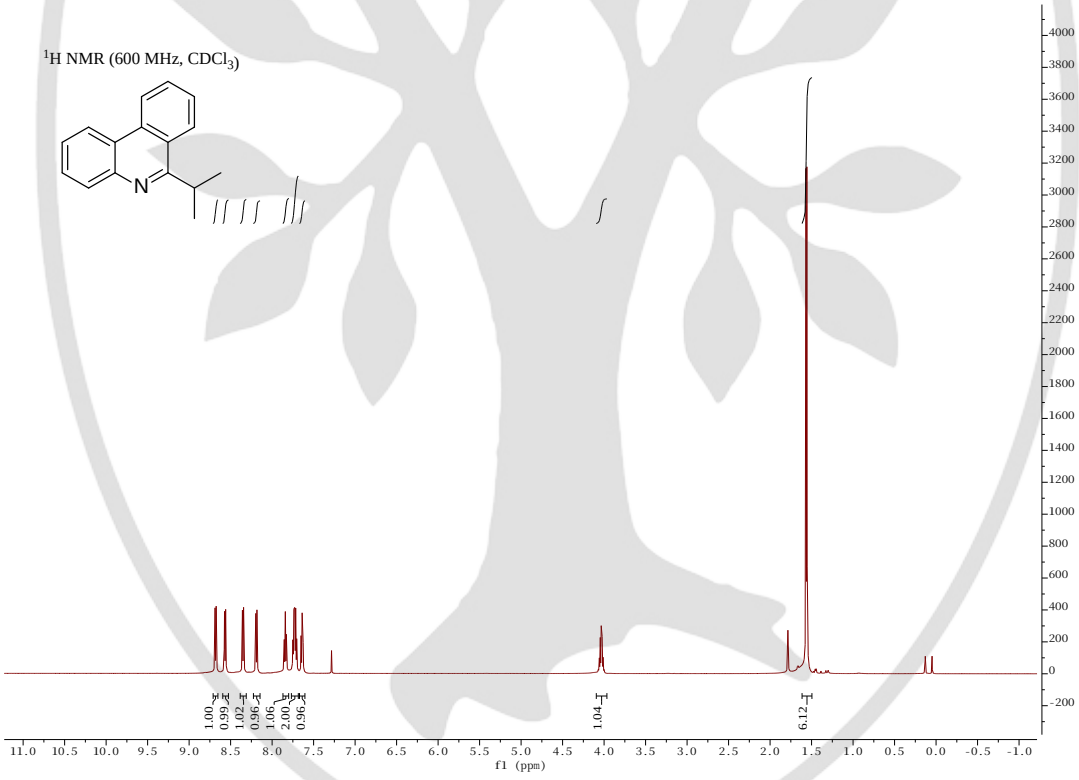

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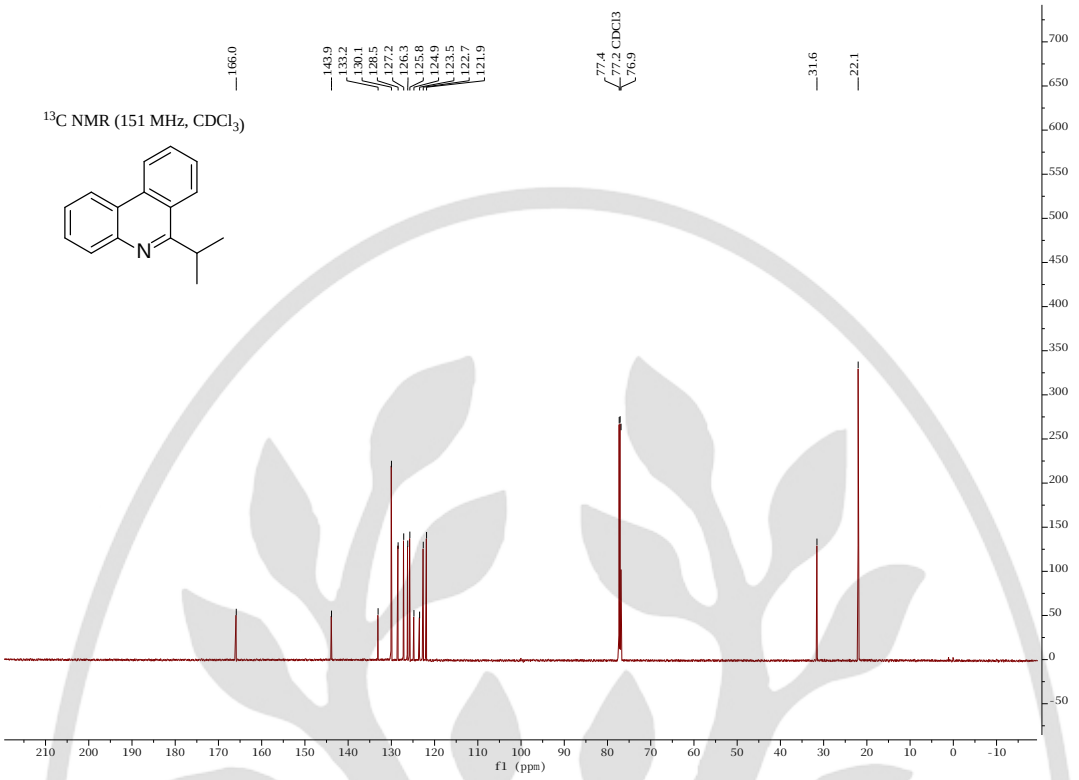

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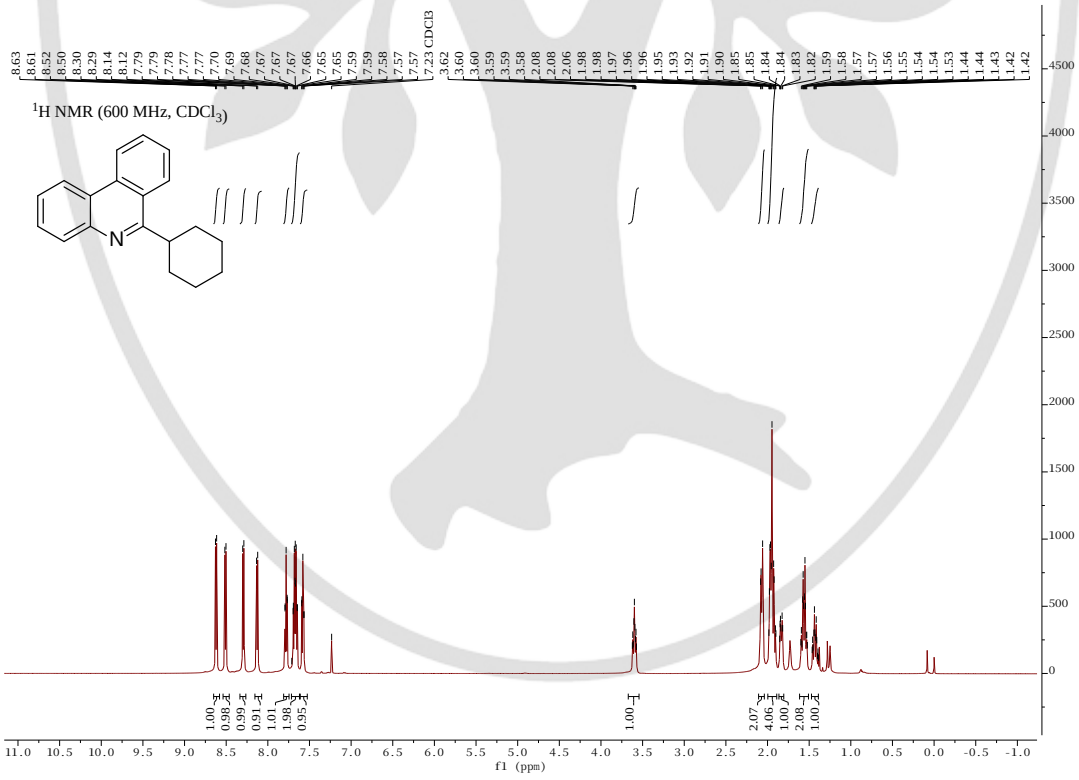

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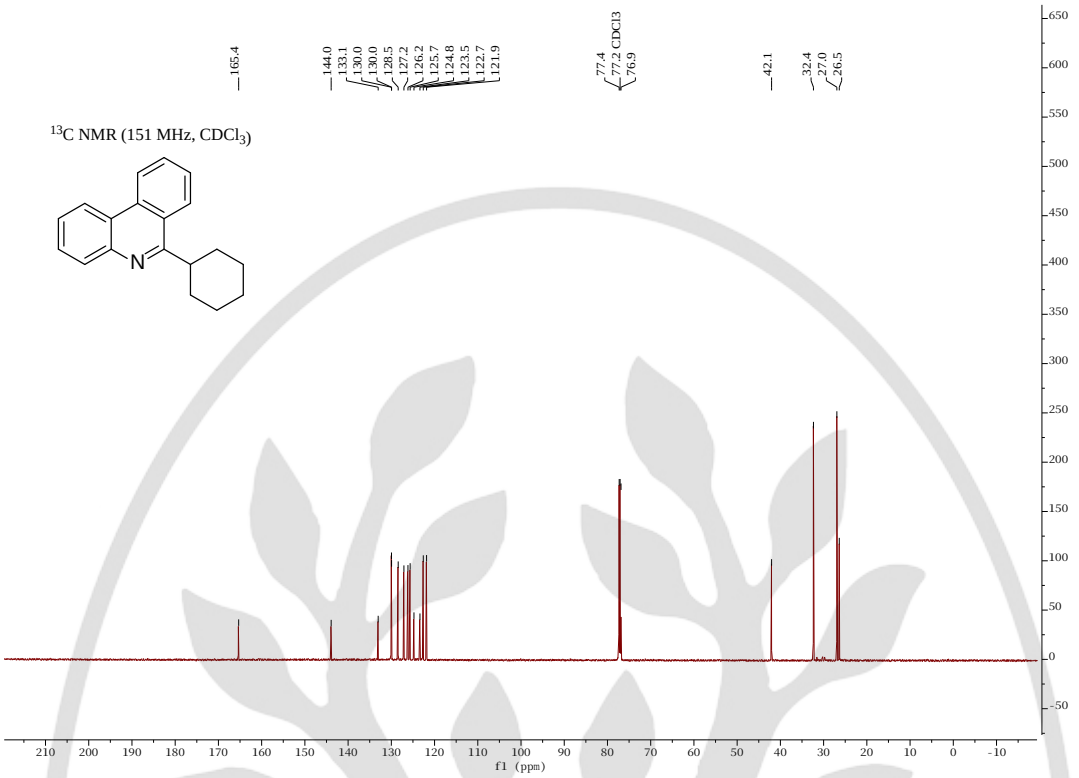

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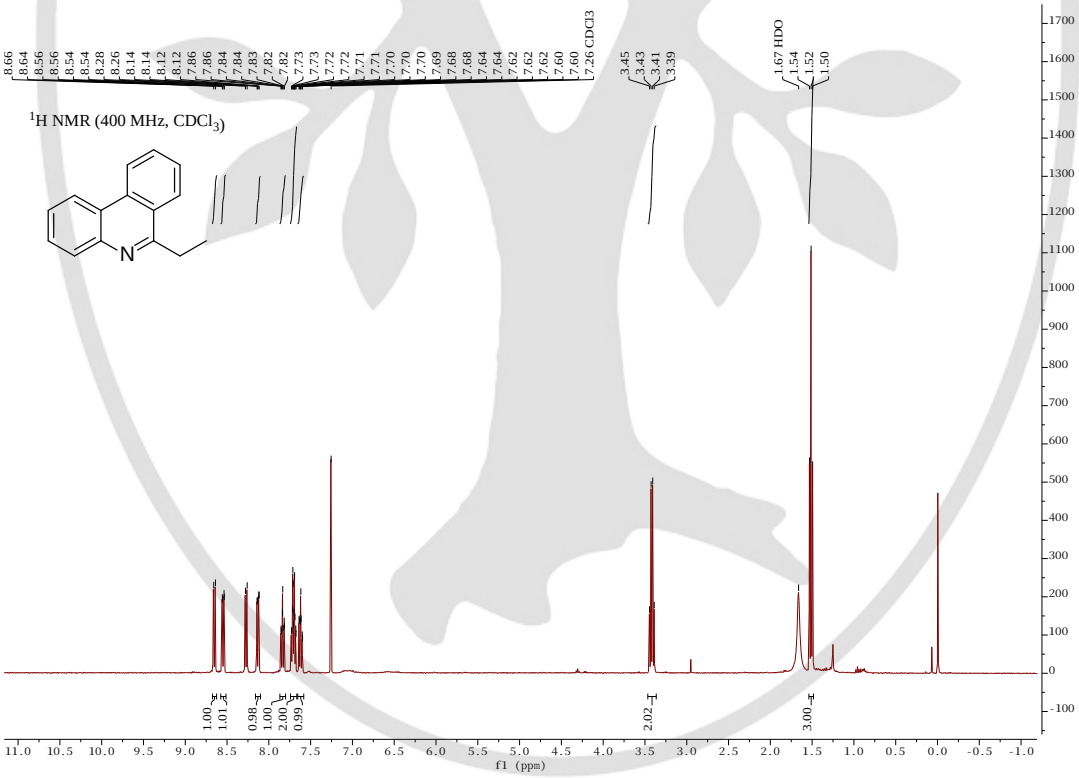

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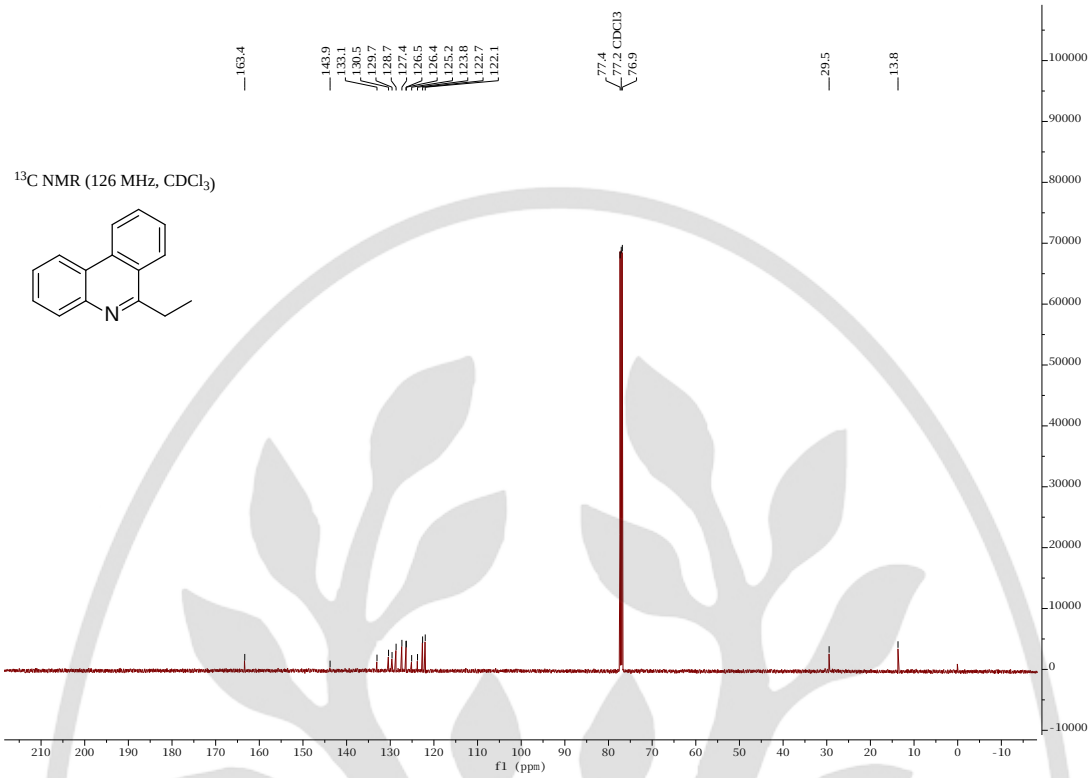

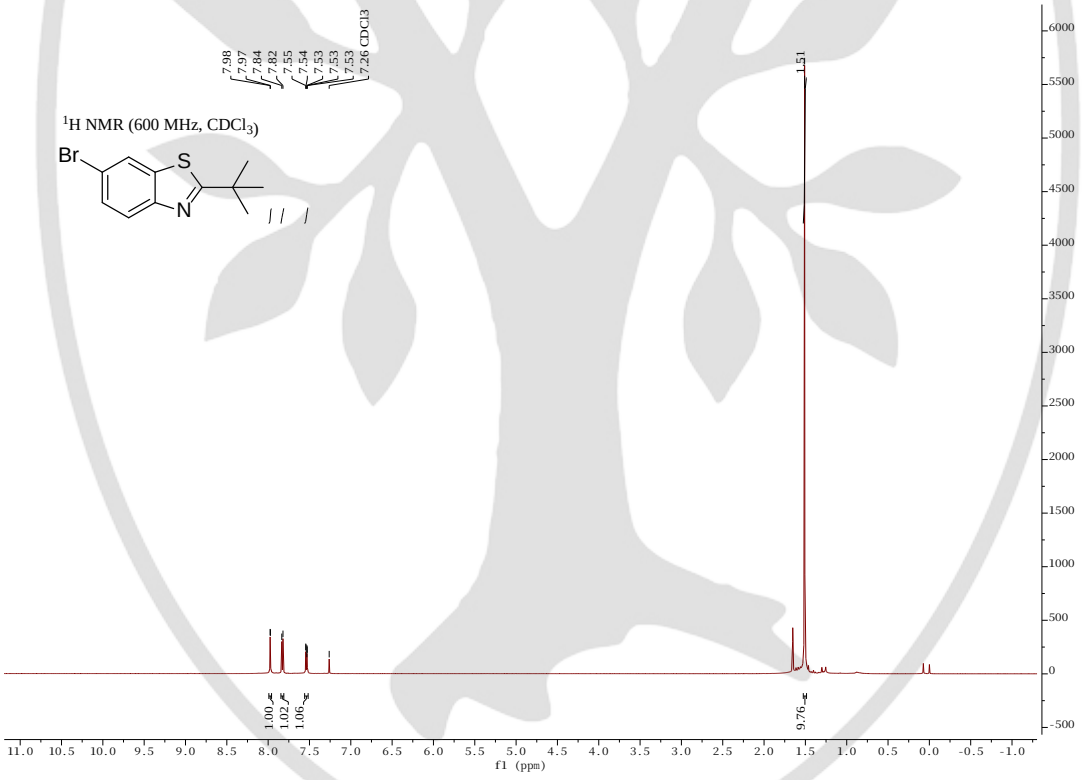

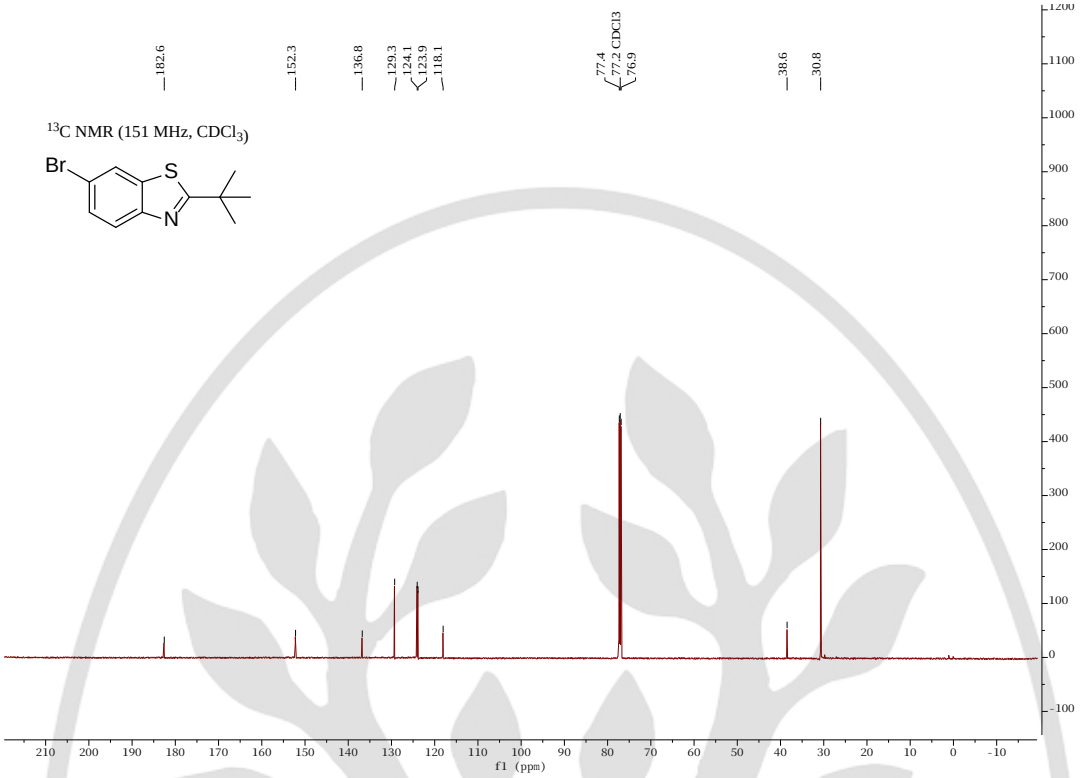

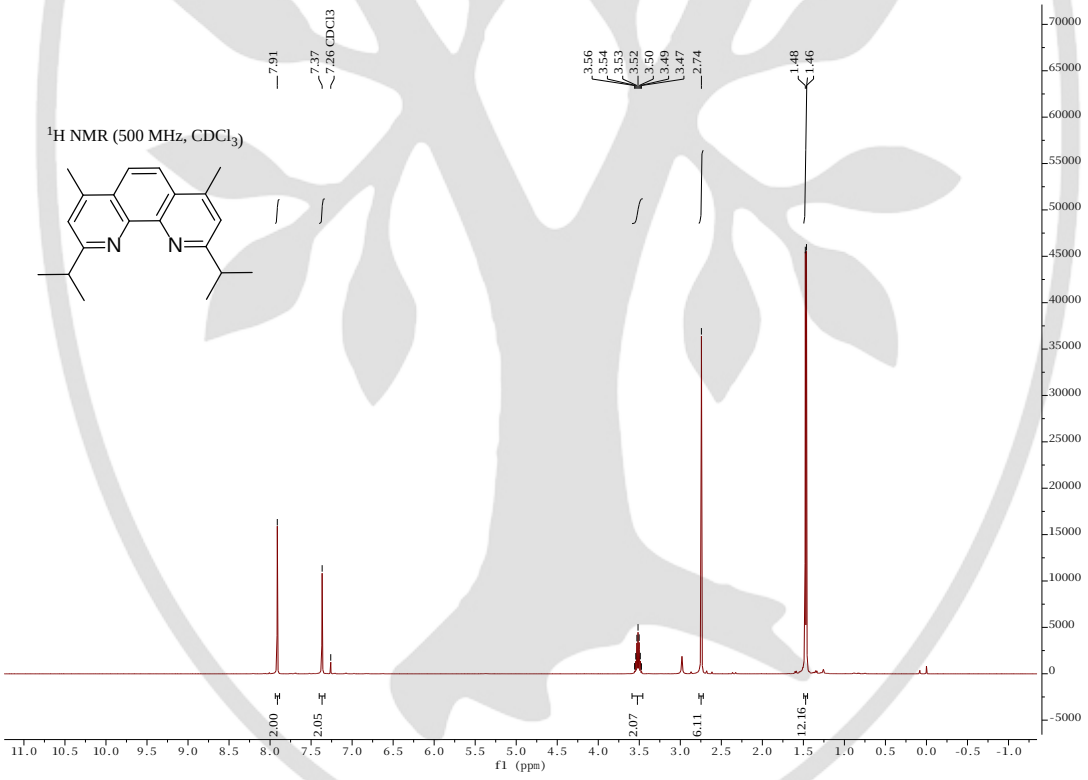

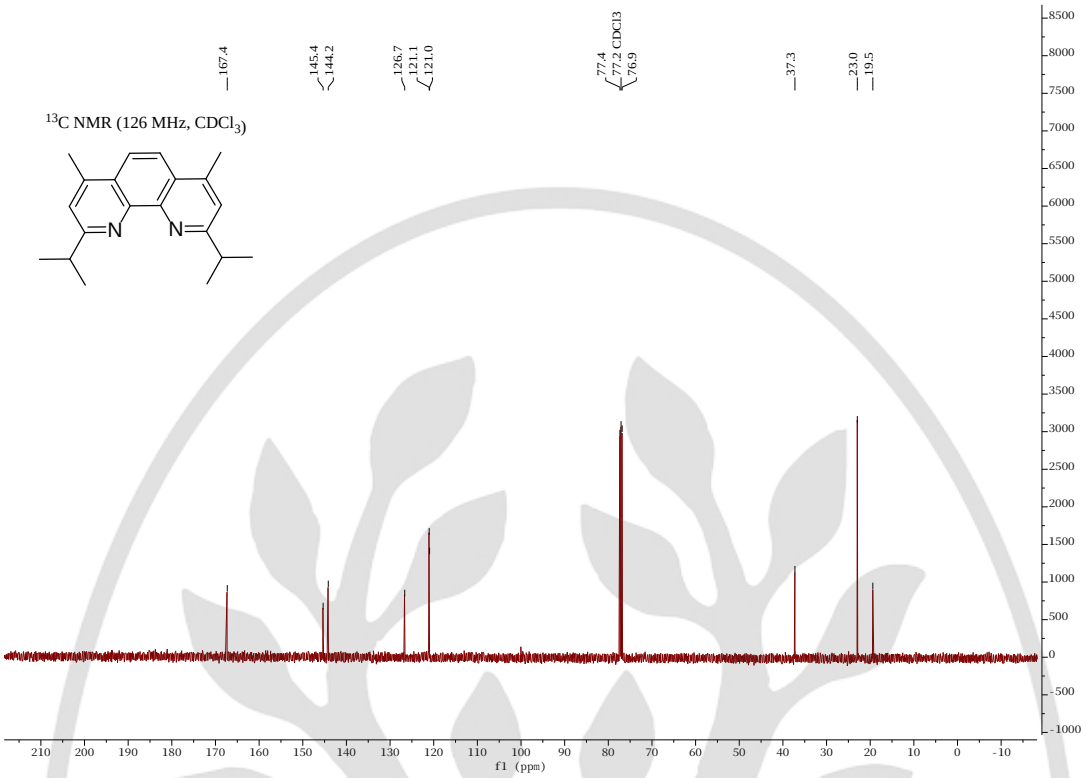

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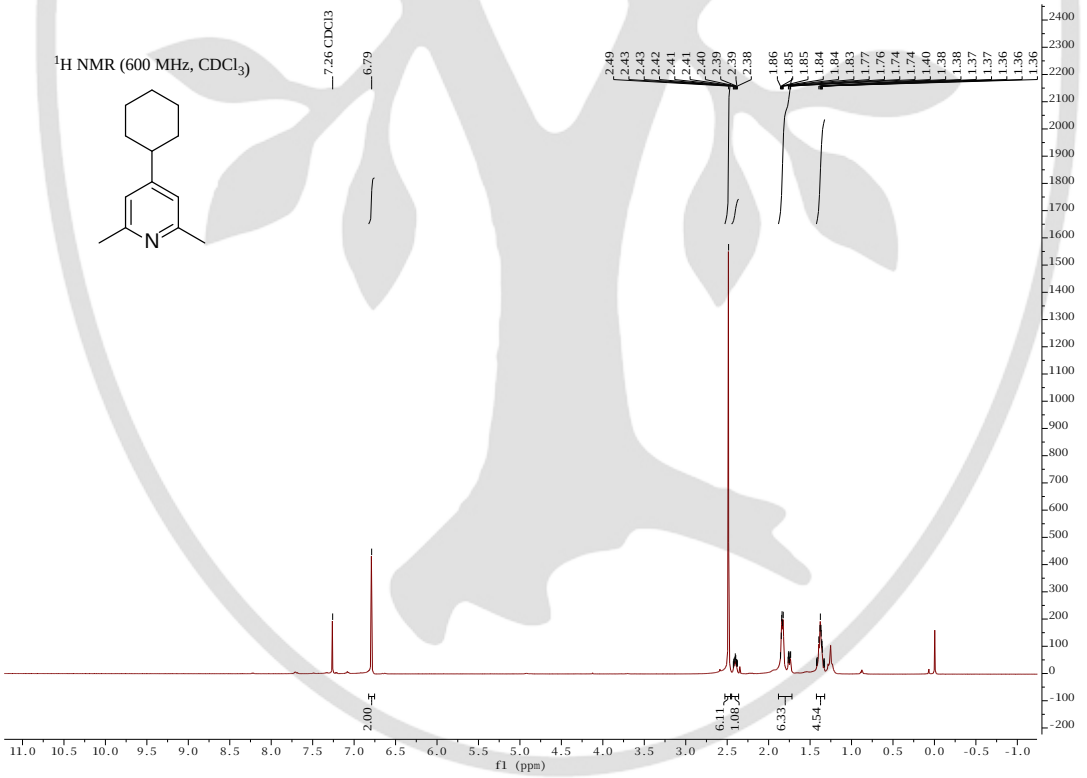

^{1}H NMR (600 MHz, $CDCl_3$)