Supporting information

N-heterocyclic Carbene(Cu) Synergistic Photothermal Hydrogen Release Involving Double Hydrogen Transfer Catalyzed by Porphyrin(Cu)-Based Conjugated Microporous Polymers for Efficient Quinoline Hydrogenation

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Section 1. Chemicals and Instrumentation.

Unless otherwise stated, all chemicals are purchased from commercial sources and can be used without further purification. The water used in all experiments is deionized water.

Fourier transform infrared (FT-IR) spectra were obtained using FTIR-650 spectrometer (frequency range from 4000 to 400 cm^{-1}) with KBr pellet. The PXRD pattern was measured with a Cu target tube at 40 kV and 30 mA on Rigaku MiniFlex 600 diffractometer. The morphology analysis of the as-prepared samples were conducted on a scanning electron microscope (SEM, S4800, Hitachi Co., Japan). The UV–vis spectra of the samples were measured on a TU-1901 Ultraviolet spectrometer at room temperature and $BaSO_4$ was used as the reflectance standard reference. X-ray photoelectron spectroscopy (XPS) was performed on Thermo SCIENTIFICTM ESCALAB 250Xi spectrometer with K-Alpha+ X-ray source. Energy (BE) is calibrated by setting the measured BE of C 1s to 284.8 eV. Thermo gravimetric analysis (TGA) was carried out on Shanghai Yinnuo 1000 B in N_2 atmosphere at a heating rate of 10 ℃ min^{-1}. ^{1}H-NMR, ^{13}C-NMR data were recorded on Bruker Avance III DM 600 MHz. Solid-state ^{13}C CP-MAS NMR spectra were conducted on a Bruker Avance-600 spectrometer. GC-MS analyses were obtained on a Shimadzu QP-2020. The adsorption-desorption isotherms of N_2 were measured at 77 K using ASPS 2020 gas sorption analyzer. Inductively coupled plasma (ICP) analysis was performed on a PerkinElmer Optima 8000 ICP-OES instrument. High resolution mass spectra data were recorded on Bruker IMPACT II. Photoluminescence spectra and fluorescence lifetimes test were conducted on Edinburgh FLS920 Fluorescence Spectrometer.

All products were isolated by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluents. Products are known compounds and are characterized by comparison of their ^{1}H NMR, ^{13}C NMR spectra data and mass data with those reported in the literatures. 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 ^{1}H) and $CDCl_3$ (77.16 ppm for ^{13}C), respectively.

Electrochemical measurements: the photoelectrochemical measurements were carried out in CHI-660 electrochemical station (Chenhua instrument, Shanghai, China) using a common three electrode configuration with Pt foil as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. Na_2SO_4 (0.2 M) solution was used as the electrolyte and Xe lamp (300W, $\lambda \geqslant 420$ nm, CEL-HXE 300, Beijing China Education Au-light Technology Co., Ltd). The working electrodes were prepared by the

following steps: 5 mg of photocatalyst was well dispersed in 0.5 mL ethanol containing 10 μL nafion and sonicated for 10 min. Next, 250 μL above suspension was dispersed dropwise onto the surface of a clear ITO glass with exposed 1 × 1 cm^2 area. After drying overnight in oven, the loading mass was about 0.4 mg/cm^2. The photocurrent response was measured at + 0.4 V bias voltage under chopped light and the Mott-Schottky plots were tested in the dark at 300/500/1000 Hz. The electrochemical impedance spectroscopy (EIS) measurement was performed in the frequency range from 10^{-2} to 10^6 Hz with a bias potential of 0.4 V.

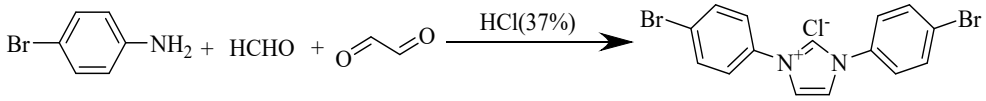
Cyclic voltammetry (CV) experiments were measured on a CHI 660E in a three-electrode electrochemical cell and a scan rate of 50 mV s^{-1} . The experiments were conducted in anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.The reference electrode was based on the Ag/Ag^+ couple. The working electrode was a glassy carbon electrode.The auxiliary electrode was a platinum flakelet.

All computational studies were conducted using the Gaussian 16 software package[1]. The DFT calculations were performed with the Becke's three-parameter hybrid method with the Lee, Yang, and Parr (B3LYP) gradient-corrected correlation functional.[2] The all-electron basis set 6-31+G(d,p) was adopted for all atoms.

Section 2. The preparation of monomers and ploymers.

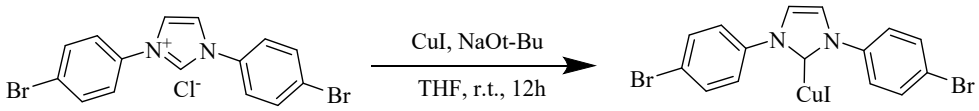
1. Monomer Synthesis

1.1 Synthesis of 1,3-bis(4-bromophenyl)-1H-imidazol-3-ium chloride (Im)[3]

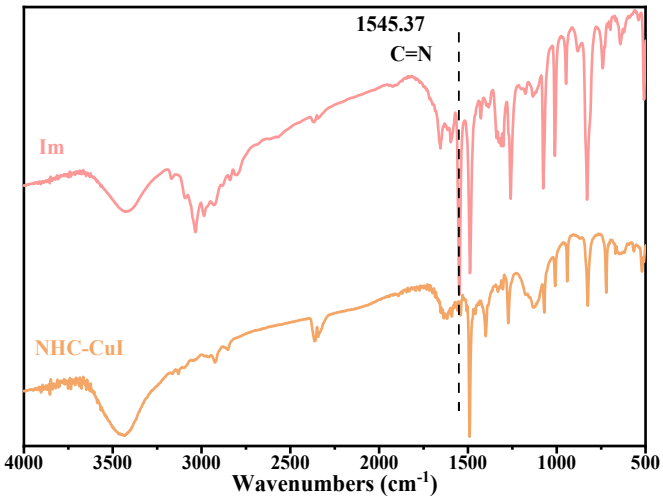


Formaldehyde polymer (98 mg, 3.3 mmol) was introduced into a 50 mL round-bottom flask, followed by the addition of 10 mL of toluene. A mixture of p-bromoaniline (1.0 g, 6.0 mmol) and a 40% (v/v) aqueous solution of glyoxal (4.0 g, 3.0 mmol) in 5 mL of toluene was prepared separately and then slowly added to the reaction mixture. Subsequently, HCl [37% (v/v), 0.3 mL, 3 mmol] was added dropwise to the above mixture. The reaction mixture was refluxed at 140°C using a Dean-Stark apparatus until no further increase in collected water volume was observed. The solvent was removed under reduced pressure by rotary evaporation, and the residue was dissolved in acetonitrile followed by filtration to remove insoluble impurities. After removal of the solvent by rotary evaporation, a light brown powder was obtained. The product was subsequently characterized by ^{1}H NMR spectroscopy.

1.2 Synthesis of NHC(Cu)[4]

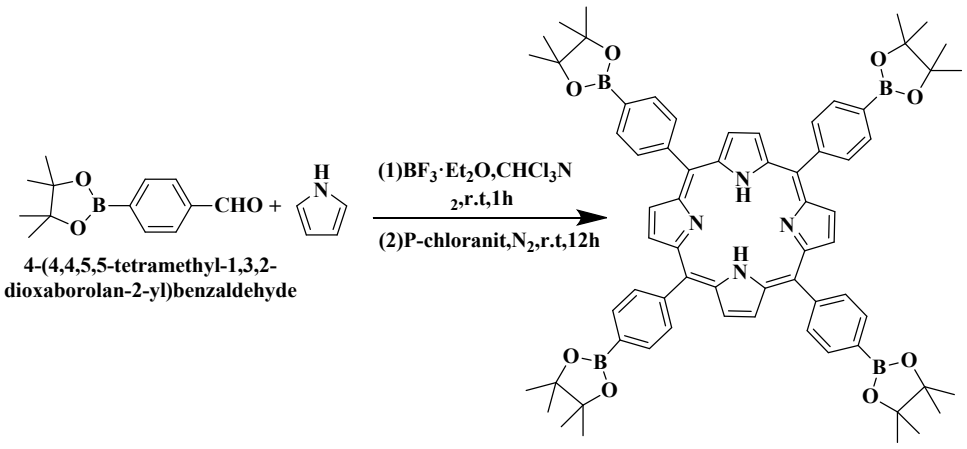


In a 50 mL round-bottom flask, the imidazole monomer **Im** (1.0 equiv, 0.04 mmol, 15 mg), sodium tert-butoxide (1.0 equiv, 0.08 mmol, 7.69 mg), and copper(I) iodide (1.0 equiv, 0.04 mmol, 7.6 mg) were added sequentially, followed by the addition of 2 mL of anhydrous tetrahydrofuran under inert atmosphere. The reaction was conducted under a nitrogen atmosphere at room temperature for 12 hours. Upon completion, 6 mL of deionized water was added, and the resulting mixture was stirred thoroughly to ensure complete phase separation. Centrifugation yielded a brown solid, which was subsequently washed with a mixed solvent system (isopropyl alcohol: petroleum ether = 1 : 3) until the filtrate became colorless. The product was then subjected to vacuum drying to afford the target carbene monomer, whose successful formation was confirmed by infrared spectroscopy.



1.3 Synthesis of 5,10,15,20-Tetrakis (4-boronic acid pinacol esterylphenyl) porphyrin (Por) [5,6]

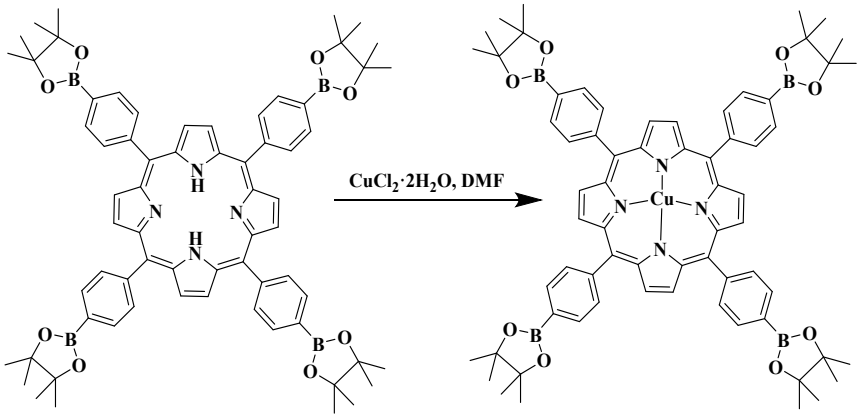
Referring to literature, the monomer **Por** was successfully synthesized. In a 500 mL flask, 4 -(4,4,5, 5-tetramethyl-1,3,2-dioxaboran-2-yl) benzaldehyde (0.232 g, 1 mmol) and pyrrole (0.07 mL, 1 mmol) were dissolved in 125 mL chloroform solvent, and the mixed solution was quickly frozen in a liquid nitrogen bath and filled with nitrogen. At room temperature, boron trifluoride ether complex ($BF_3{\cdot}Et_2O$, 20 μL) was dissolved in 5 mL $CHCl_3$ and added to the system. After stirring for 1 h, tetrachlorobenzophenone (0.37 g, 1.5 mmol) was added to the reaction bottle in N_2 atmosphere. The reaction mixture was stirred at room temperature for 16 h. After rotational evaporation, the crude product was purified by column chromatography on silica gel to give as a purple powder.



1.4 Synthesis of Por(Cu) [5,6]

Por (200 mg, 0.19 mmol)and $CuCl_2{\cdot}2H_2O$ (358 mg, 2.1 mmol) in 50 mL of DMF was refluxed for 16 h. When the mixture was cooled down to room temperature, H_2O was added until all solids are

precipitated. The mixture was filtered, the system was extracted with trichloromethane and saturated sodium chloride aqueous solution three times. The combined organic layer was dried over $MgSO_4$ and then evaporated to dryness to get red solid **Por(Cu)**.



2. Synthesis of Im-PCMP

A mixture of 1,3-bis(4-bromophenyl)-1H-imidazol-3-ium chloride (**Im**, 103.63 mg, 0.25 mmol), 5,10,15,20-Tetrakis (4-boronic acid pinacol esterylphenyl) porphyrin (**Por**, 139.83 mg, 0.125 mmol), tetrakis-(triphenylphosphine)palladium (0) (28 mg, 0.025 mmol), and K_2CO_3 (86.4 mg, 0.625 mmol) were degassed in a 50 mL flask. After that, a mixture solution of 28 mL N, N-dimethylformamide (DMF) and 2 mL H_2O was successively injected into the flask (**Scheme 1**, for details see the Supporting Information). The mixture solution was stirred at 100 ℃ for 3 days under a nitrogen atmosphere. After cooling to room temperature, the precipitate was centrifuged and washed three times with DMF, dichloromethane, methanol, and H_2O to remove unreacted monomer or residual catalysts, respectively. The black-purple powder was further purified by Soxhlet extraction from methanol and dichloromethane for 48 h. The obtained products were dried under vacuum at 80 ℃ for 12 h.

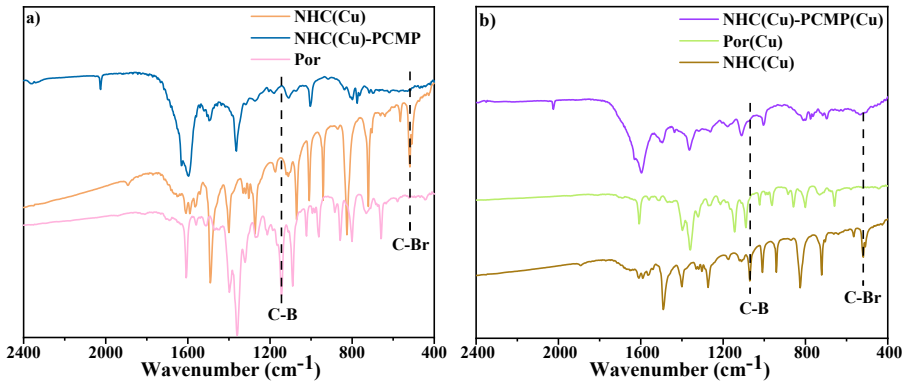
3. Synthesis of NHC(Cu)-PCMP and **NHC(Cu)-PCMP(Cu)**[7]

The synthesis method of **NHC(Cu)-PCMP** is similar to that of material **Im-PCMP**, simply replace the monomer **Im** with the monomer **NHC(Cu)** (142.38 mg, 0.25 mmol). The final product is brown powder in 58% isolation yield.

The synthesis method of **NHC(Cu)-PCMP(Cu)** is similar to that of material **NHC(Cu)-PCMP**, simply replace the monomer **Por** with the monomer **Por(Cu)** (147.52 mg, 0.125 mmol). The final product is dark brown powder in 60% isolation yield.

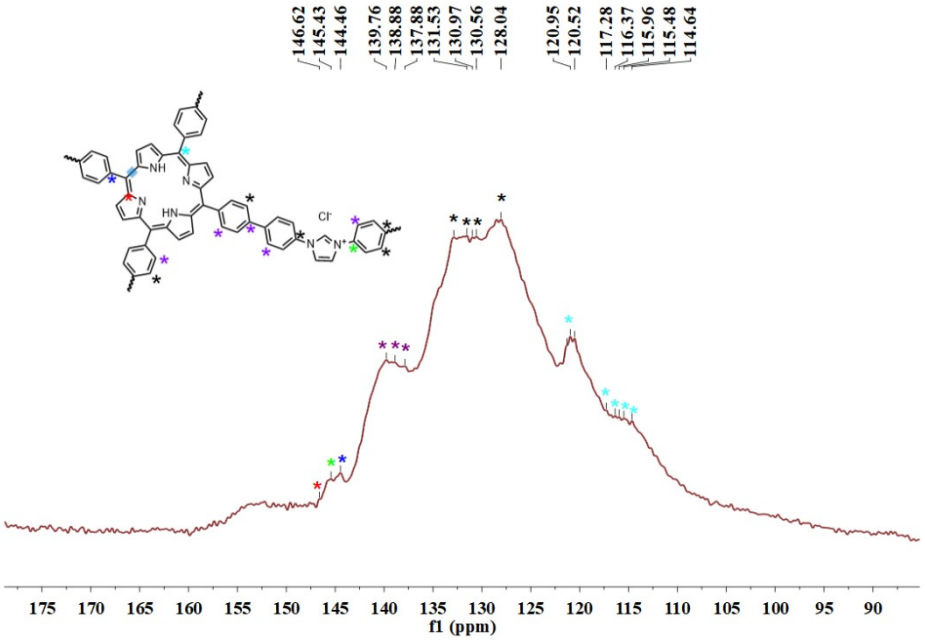
Section 3. The characterization of ploymers.

1. FT-IR spectra of the monomers and NHC(Cu)-PCMP, NHC(Cu)-PCMP(Cu). (Figure. S1)

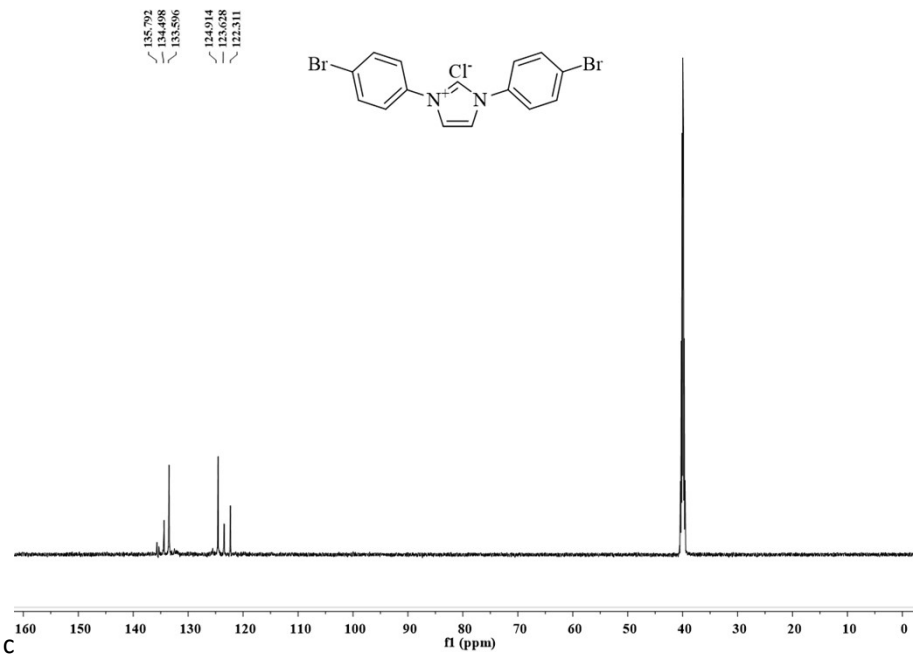


2. The solid-state ^{13}C-MAS NMR spectrum of Im-PCMP. (Figure. S2)

a)

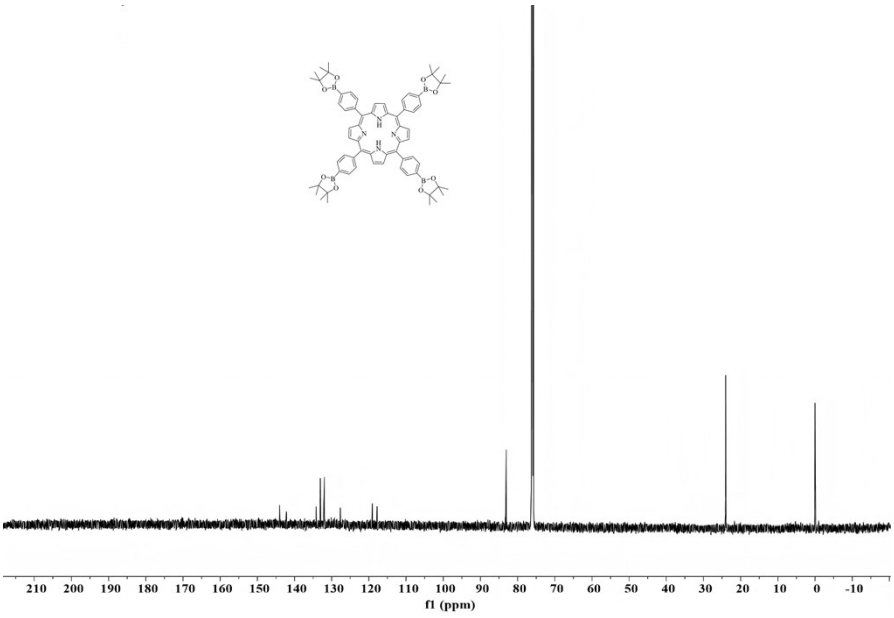


b)

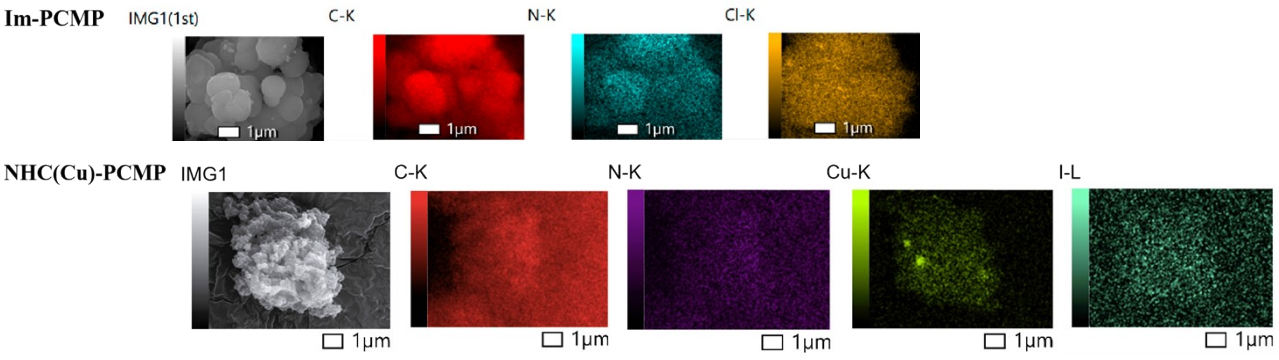


c

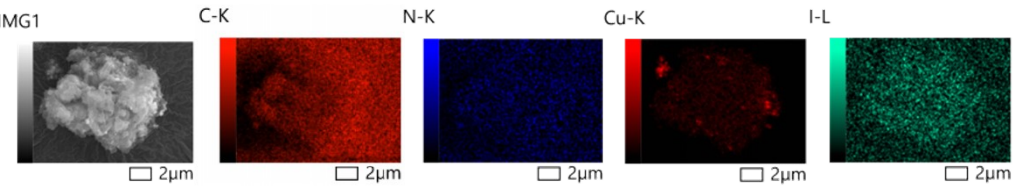
c)



3. SEM images and corresponding elemental mapping images of Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu). (Figure S3)



NHC(Cu)-PCMP(Cu)



Im-PCMP

Element	Line	Mass%	Atom%
C	K	74.30±0.03	78.82±0.03
N	K	21.69±0.10	19.73±0.09
Cl	K	4.01±0.01	1.44±0.00
Total		100.00	100.00
Map_003_wholespectrum			Fitting ratio 0.0970

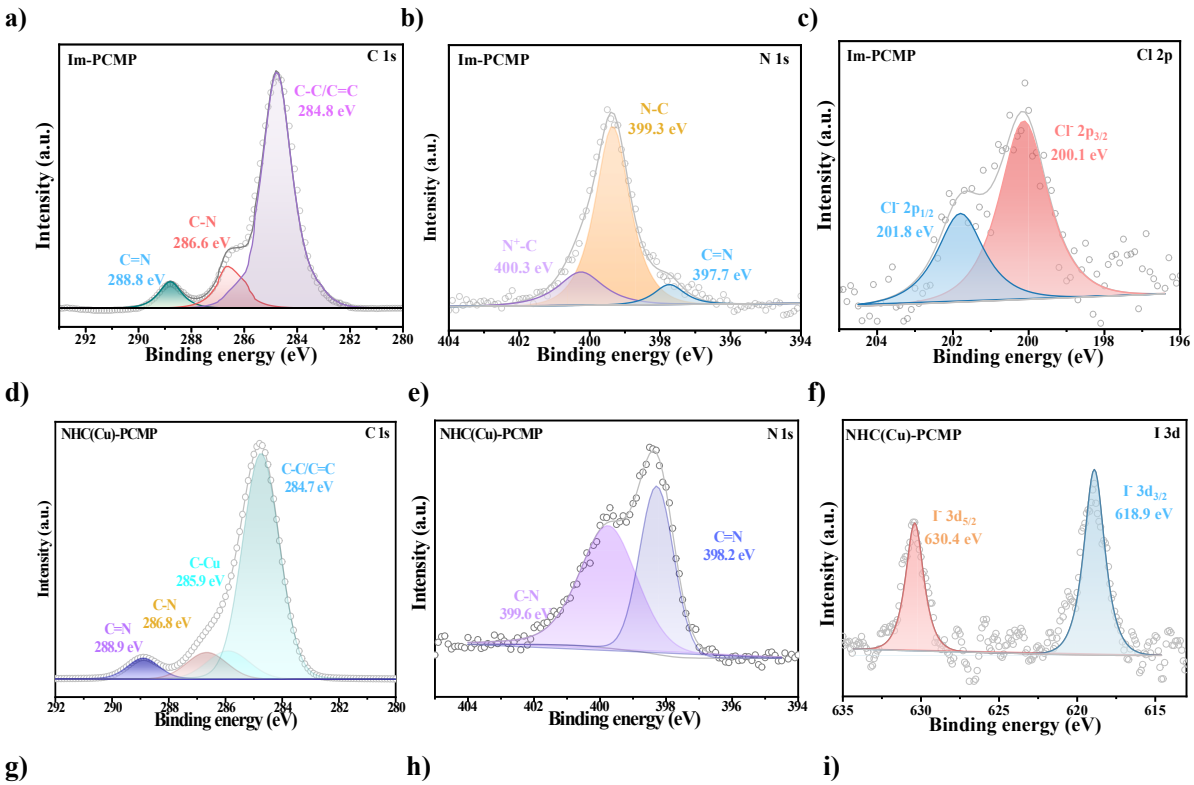
NHC(Cu)-PCMP

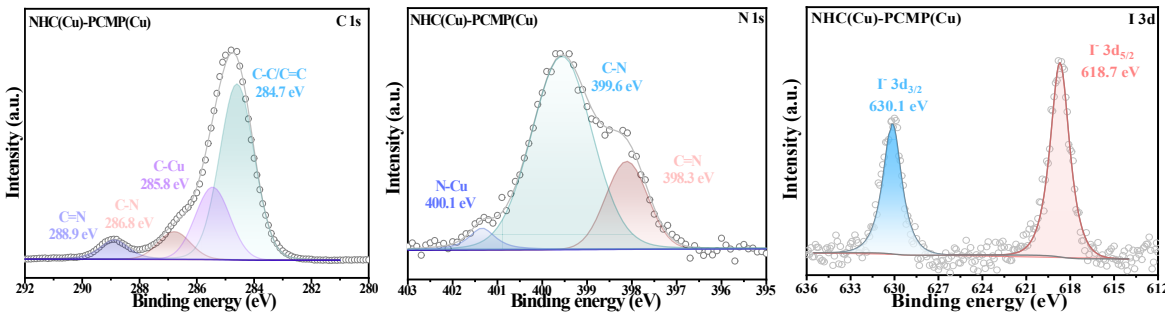
Element	Line	Mass%	Atom%
C	K	85.29±0.03	89.86±0.03
N	K	10.27±0.09	9.28±0.08
Cu	K	4.23±0.03	0.84±0.01
I	L	0.21±0.01	0.02±0.00
Total		100.00	100.00
Map_001_wholespectrum			Fitting ratio 0.0693

NHC(Cu)-PCMP(Cu)

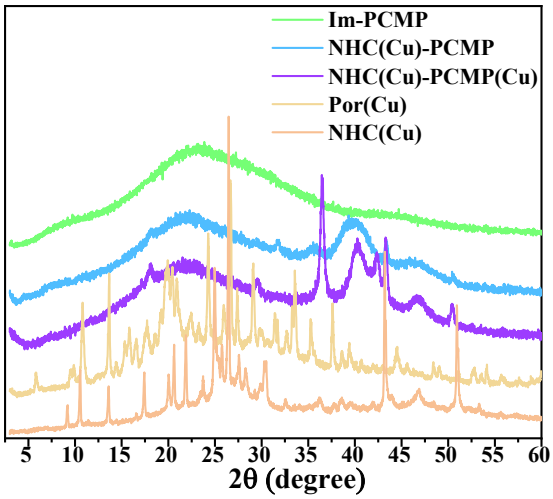
Element	Line	Mass%	Atom%
C	K	90.16±0.06	98.03±0.06
N	K	nd	nd
Cu	K	9.36±0.05	1.92±0.01
I	L	0.48±0.02	0.05±0.00
Total		100.00	100.00
Map_003_wholespectrum			Fitting ratio 0.3216

4. The high-resolution XPS spectra of C 1s, N 1s, Cl 2p/I 3d of Im-PCMP, NHC(Cu)- PCMP and NHC(Cu)-PCMP(Cu); (Figure S4)

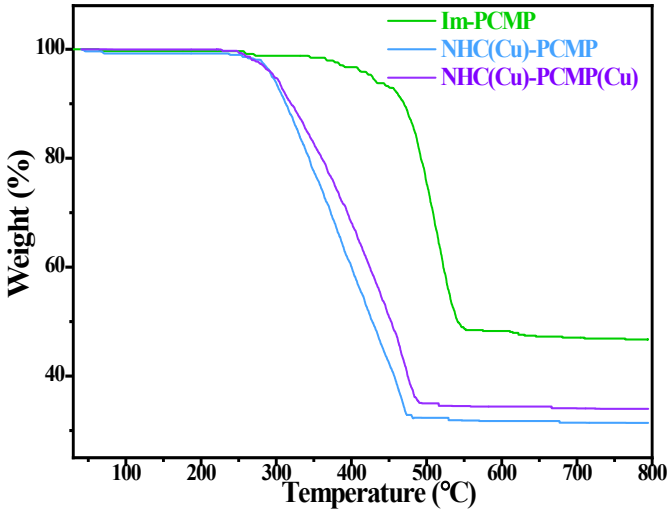




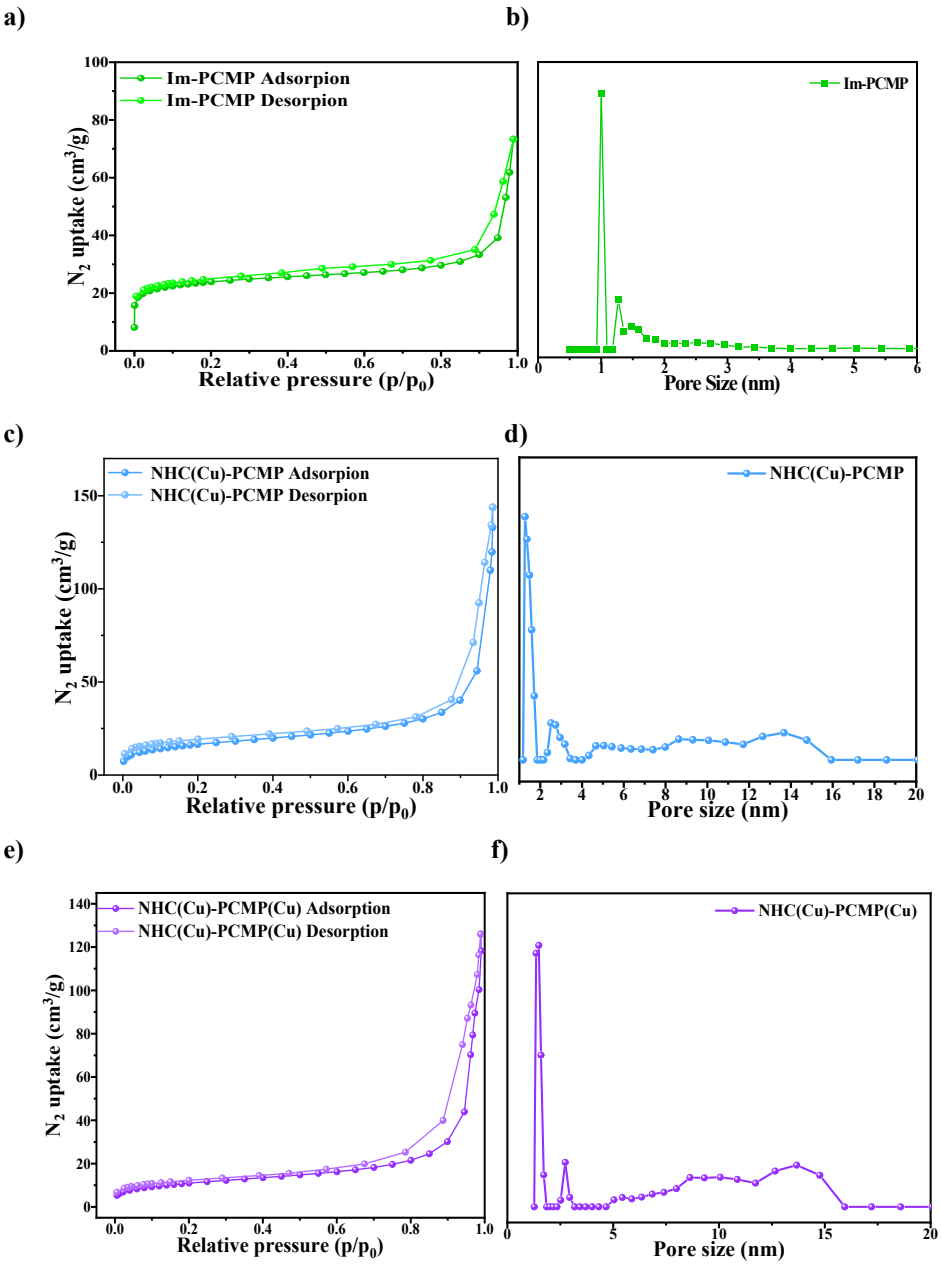
5. **The PXRD spectra of Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu) samples and Por(Cu) and NHC(Cu). (Figure S5)**



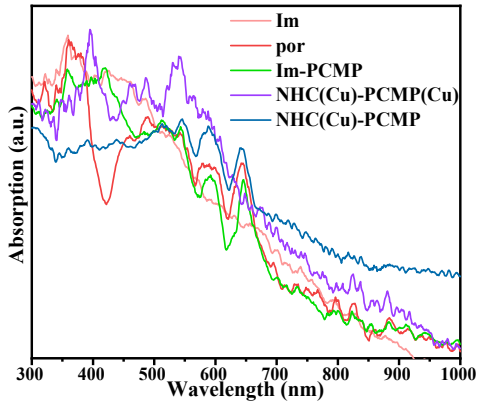
6. **Thermogravimetric analysis curves of Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu) samples. (Figure S6)**



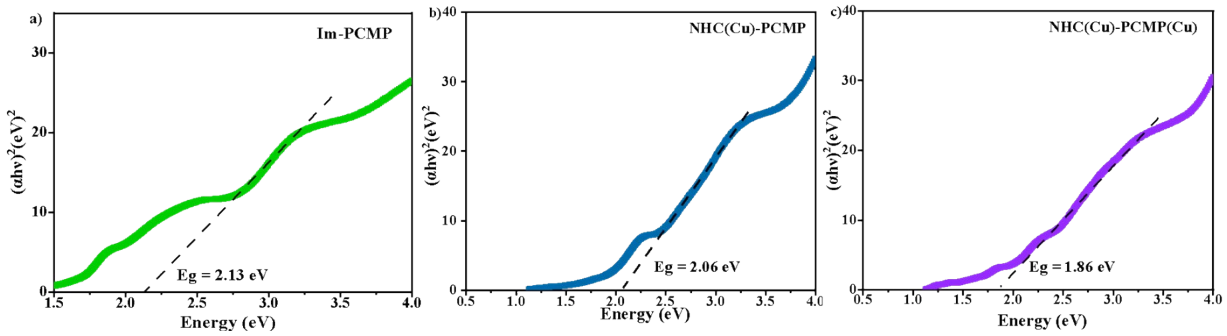
7. **N_2 adsorption isotherms and pore size distributions Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu) samples. (Figure S7)**



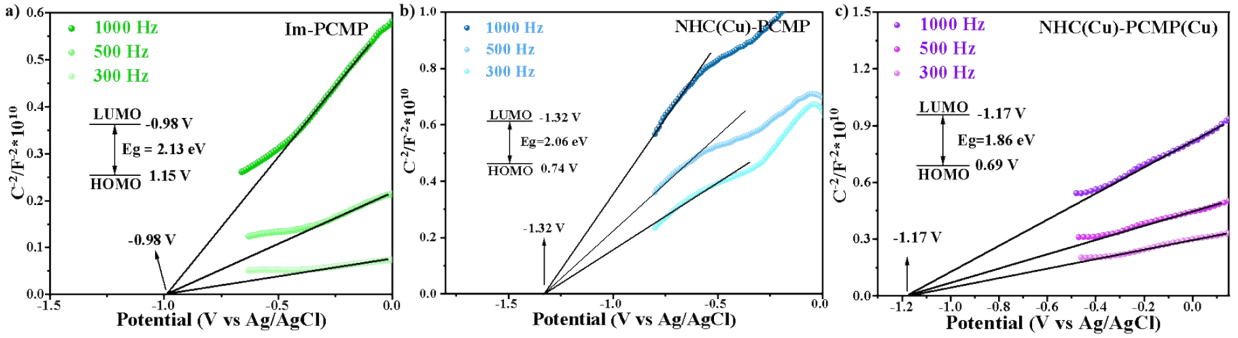
8. The UV-vis diffuse reflectance spectra of Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu) samples. (Figure S8)



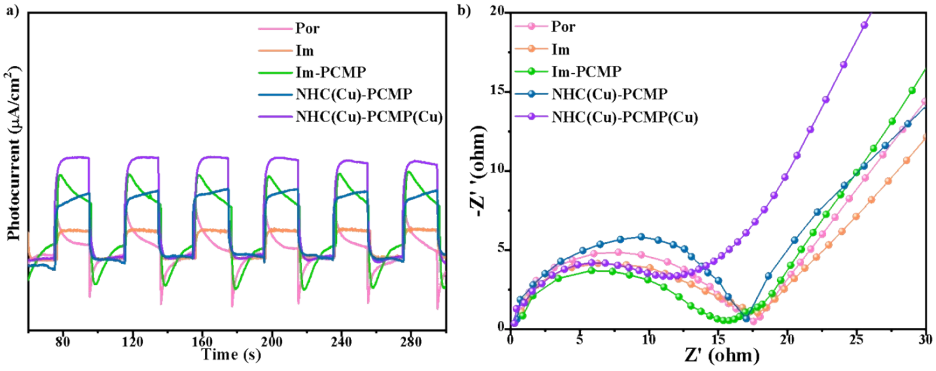
9. **The corresponding tauc plots for the calculation of band gaps of a) Im-PCMP; b) NHC(Cu)-PCMP and c) NHC(Cu)-PCMP(Cu). (Figure S9)**



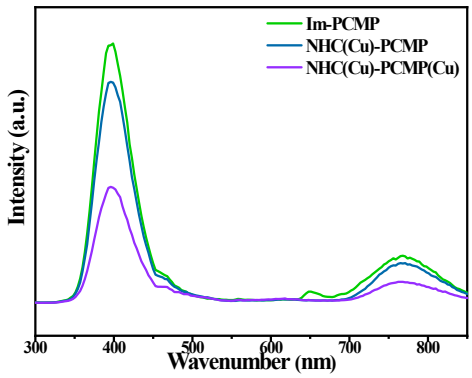
10. **Mott–Schottky plot in 0.2 M Na_2SO_4 aqueous solution: a) Im-PCMP; b) NHC(Cu)-PCMP and c) NHC(Cu)-PCMP(Cu). (Figure S10)**



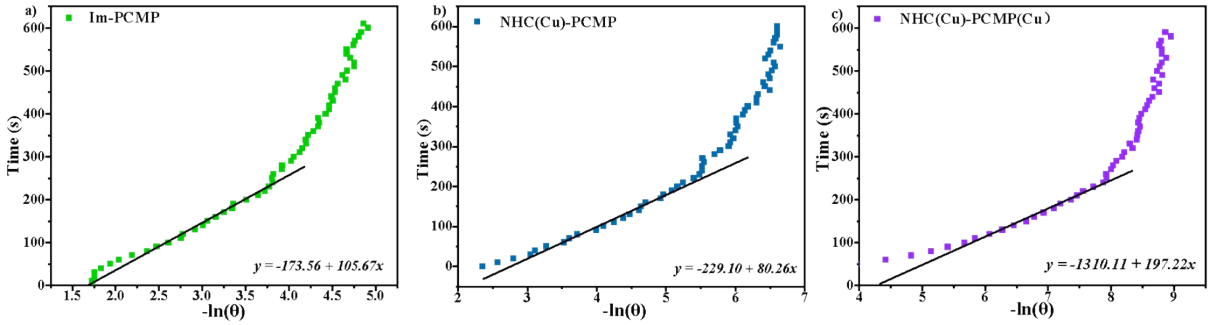
11. **Transient photocurrent response and electrochemical impedance spectra of monomers and polymers. (Figure S11)**



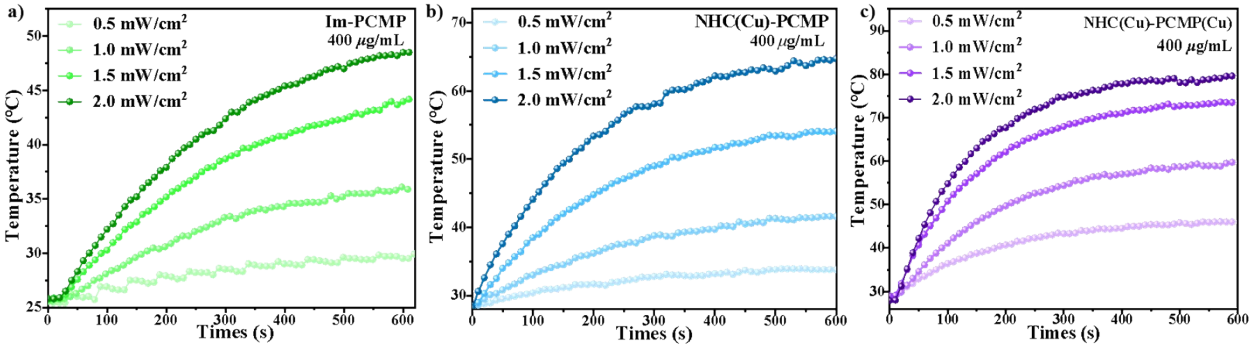
12. **Photoluminescence spectra of Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu). (Figure S12)**



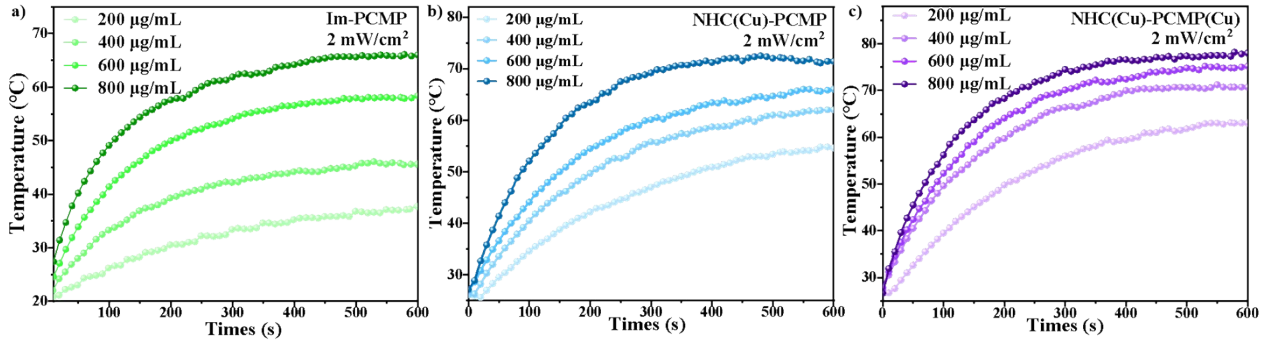
13. **Linear fitting of Im-PCMP, NHC(Cu)-PCMP and NHC(Cu)-PCMP(Cu) to calculate the photothermal conversion efficiency. (Figure S13)**



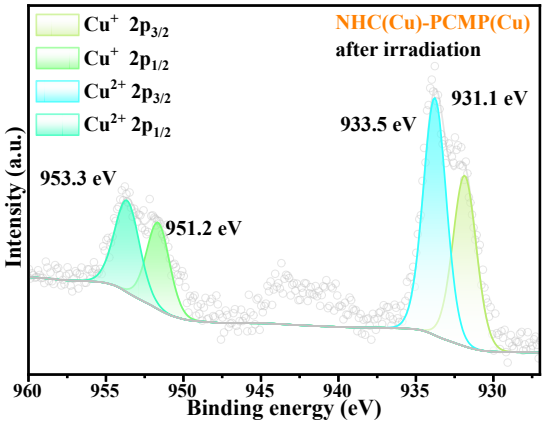
14. **Temperature variation curves with different laser power densities under 808 nm laser irradiation (400 μg mL^{-1}). (Figure S14)**



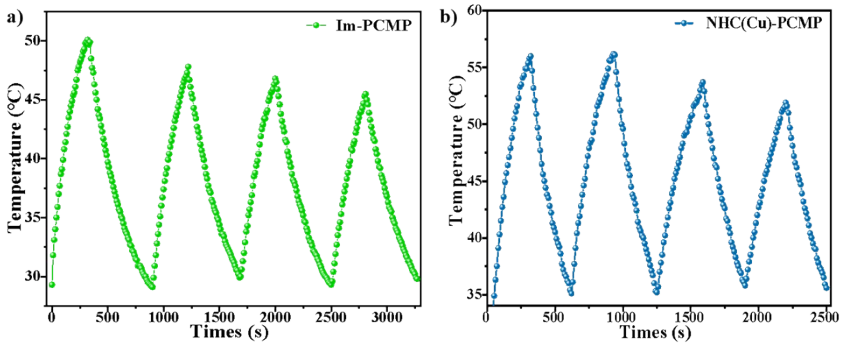
15. **Temperature variation curves with different concentrations under 808 nm laser irradiation (2.0 W cm^{-2}). (Figure S15)**



16. **The Cu 2p XPS spectra of NHC(Cu)-PCMP(Cu) after irradiation. (Figure S16)**



17. **Laser on/off heating and cooling cycle of Im-PCMP, NHC(Cu)-PCMP for photostability tests (2.0 W cm^{-2}). (Figure S17)**

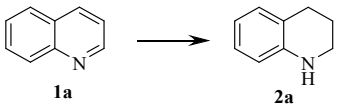


Section 4. Catalysis

1. Photocatalytic experiment

In a 5 mL branched Schlenk, **NHC(Cu)-PCMP(Cu)** (10 mg) was added in a mixture of toluene (1 mL), quinoline (**1a**, 0.2 mmol) and t-$BuNH_2BH_3$ (4eq., 0.8 mmol). The reaction was conducted under gentle stirring and irradiated with a 300 W Xe lamp ($\lambda \geq 420$ nm), while being monitored by GC-MS. Upon completion of the reaction, the catalyst was separated via centrifugation, extensively washed with methanol, and subsequently reused in further reaction cycles. The organic layers were quenched with 10 mL of saturated NaCl solution and subsequently extracted with dichloromethane (3 × 10 mL). The combined organic layers were concentrated under vacuum, and the residue was purified by flash column chromatography to afford product **2a**.

2. Condition optimization for transfer hydrogenation reaction of quinoline. (Table S1) [a,b]



1a 2a

Entry	Catalyst	Hydride [equiv.]	Sol.	Light	Time	Conv. [%]	Sel.[%]
1	NHC(Cu)-PCMP(Cu) (10 mg)	NH_3BH_3 (3）	toluene	Xe	12 h	12%	60%
2	NHC(Cu)-PCMP(Cu) (10mg)	$PhEt_2NBH_3$ (3）	toluene	Xe	12 h	32%	90%
3	NHC(Cu)-PCMP(Cu) (10 mg)	$tBuNH_2BH_3$ (3)	toluene	Xe	12 h	85%	100%
4	NHC(Cu)-PCMP(Cu) (10mg)	H_2 (1 atm)	toluene	Xe	5 h	-	-
5	***NHC(Cu)-PCMP(Cu) (10mg)***	***$tBuNH_2BH_3$ (4)***	***toluene***	***Xe***	***5 h***	***94%***	***100%***
6	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	EtOH	Xe	5 h	30%	100%
7	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	MeCN	Xe	5 h	41%	100%
8	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	Dry toluene	Xe	5 h	94%	100%
9	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	94%	100%
10	NHC(Cu)-PCMP (10 mg)	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	71%	100%
11	Im-PCMP (10 mg)	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	28%	100%
12[c]	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	R.t.	5 h	29%	100%
13 [c]	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	80℃	5 h	99%	100%
14 [c]	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	75℃	5 h	85%	100%
15 [c]	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	50℃	5 h	29%	100%
16[d]	NHC(Cu)-PCMP(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	R.t.	5 h	28%	100%
17	NHC(Cu) (10 mg)	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	-	-
18	Por(Cu) (10mg)	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	-	-
19	---	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	-	-
20	$Pd(PPh_3)_4$ (2 mg)	$tBuNH_2BH_3$ (4)	toluene	Xe	5 h	-	-

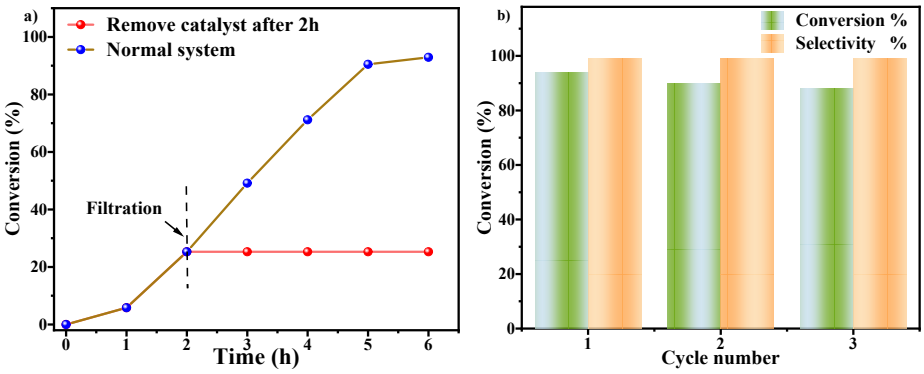
[a] Reaction condition: **1a** (0.2 mmol), Hydride, solvent (2 mL), 300 W Xe lamp ($\lambda > 420$nm), N_2 ball;

[b] Conversion and selectivity determined by GC-MS, the selectivity was reflected in parentheses;

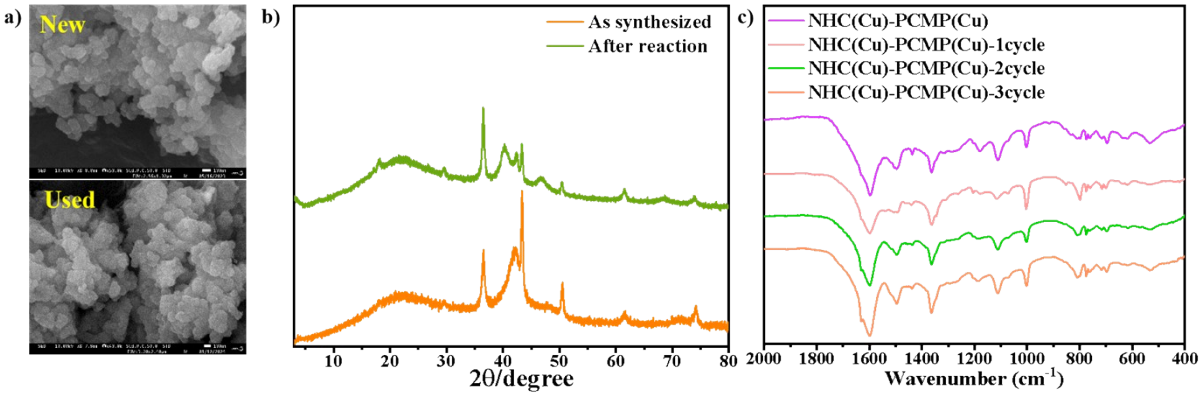
[c] Dark conditions;

[d] 300 W Xe lamp (λ > 420nm), maintaining room temperature with condensate water.

3. Hot filtration experiment and recycling experiments. (Figure S18)



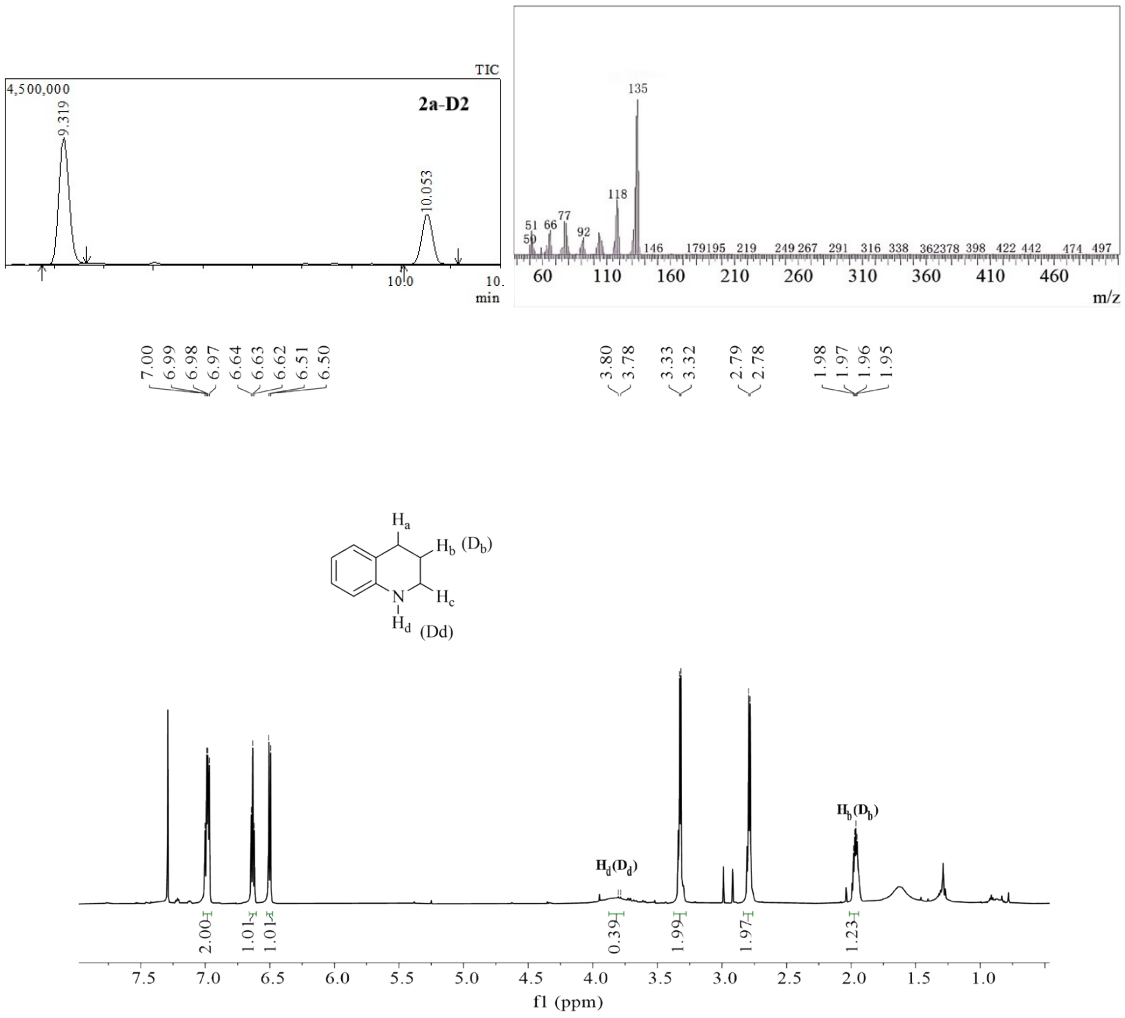
4. The SEM images, PXRD and IR spectra for NHC(Cu)-PCMP(Cu) of the as-synthesized sample and after the 3th runs of the transfer hydrogenation reactions. (Figure S19)



5. Comparison of the photo-thermal reduction with previous reports. (Table S2)

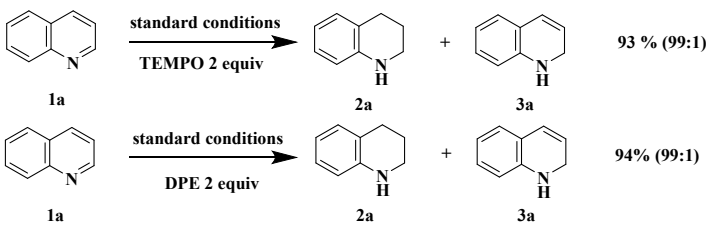
Entry	Catalyst	Condition	Conversion	Ref.
1	Co_3Cu_1Ox	H_2, 4 MPa	>99%	8
2	$2Ir_n$/SC	100 °C, 2 MPa H_2	>99%	9
3	$Fe_4Ni_6Cu_5$/MCM-41	H_2, 4 MPa, 50-80°C	>90%	10
4	ZCT-3 (Cu_3@Zn-TiO_2)	H_2 balloon, 125W halogen lamp	87%	11
5	Pd@ompg-C_3N_4	H_2 1 bar ,100 °C	>99%	12
6	Ni-bipy-COF	NH_3BH_3 (5.0 eq.), 90°C	62-98%	13
7	***NHC(Cu)-PCMP(Cu)***	***t-NH_2BH_3 (4 eq.), 300 W Xe lamp***	***65-100%***	***This work***

6. The GC-MS and ^{1}H NMR spectra for 2a-D2 in deuterium-labeled experiments. (Figure S20)

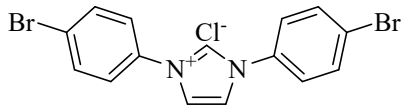


7. Free radical experiments

In a typical reaction, **NHC(Cu)-PCMP(Cu)** (10 mg) was used as catalyst, **1a** (0.2 mmol) and t-$BuNH_2BH_3$ (0.8 mmol) and TEMPO / DPE (0.4 mmol) were dispersed in toluene (2.0 mL) in 5 mL branched Schlenk tube, which were irradiated with a 300W Xe lamp for 5 hours under N_2 atmosphere. After the reaction was finished, the yield was determined by GC-MS.

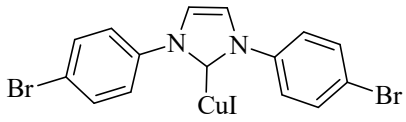


Section 5. NMR data of monomer and products



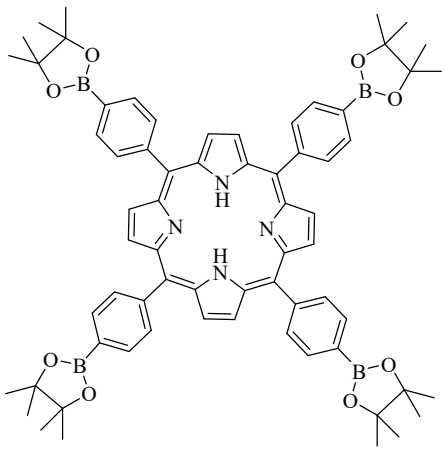
1,3-Bis(4-bromophenyl)-1H-imidazol-3-chloride (Im)

^{1}H NMR (600 MHz, DMSO) δ 10.43 (s, 1H), 8.60 (s, 2H), 7.97 (d, J = 9.0 Hz, 4H), 7.90 (d, J = 9.0 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.8, 134.5, 133.6, 124.9, 123.6, 122.3.



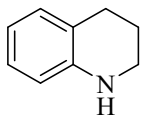
(1,3-bis(4-bromophenyl)-2,3-dihydro-2-yl)copper(I) iodide (NHC(Cu))

^{1}H NMR (600 MHz, DMSO) δ 8.05 (s, 2H), 7.86 (s, 4H), 7.73 (s, 4H). ^{13}C NMR (151 MHz, DMSO) δ 139.2, 133.6, 132.8, 132.4, 125.8, 124.6, 123.5, 122.7, 121.7. HRMS (ESI): calculated for $C_{15}H_{11}Br_2CuIN_2$ (M + H^+) requires 566.7630, found: 566.7639 Anal. Calcd for $C_{15}H_{10}Br_2CuIN_2$ (Mr-565.7551): C, 31.69%; H, 1.77%; N. 4.93%; Cu, 11.18%; I, 22.32%; Br, 28.11%. Found: C, 31.95%; H, 1.63%; N. 4.93%; Cu, 11.68%; I, 22.02%; Br, 27.79%.



5,10,15,20-Tetras(4-borate pinnal phenyl)porphyrin (Por)

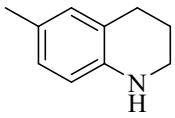
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s, 8H), 8.22 (d, J = 7.8 Hz, 8H), 8.18 (d, J = 7.8 Hz, 8H), 1.50 (s, 48H).



1,2,3,4-tetrahydroquinoline (2a) [14]

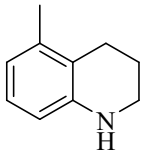
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 – 6.95 (m, 2H), 6.65 (d, J = 7.3 Hz, 1H), 6.51 (d, J = 7.9 Hz, 1H), 3.85 (s, 1H), 3.37

– 3.31 (m, 2H), 2.80 (t, J = 6.4 Hz, 2H), 2.03 – 1.95 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 129.5, 126.7, 121.4, 116.9, 114.1, 41.9, 26.9, 22.1. HRMS (ESI) m/z calculated for $C_9H_{12}N$ ([M + H]$^+$): 134.0964, found 134.0965.



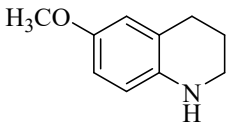
6-methyl-1,2,3,4-tetrahydroquinoline (2b) [14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, J = 6.0 Hz, 2H), 6.52 – 6.50 (t, J = 8.4 Hz, J = 5.4 Hz,1H), 3.78 (s, 1H), 3.38 – 3.36 (t, J = 10.8 Hz, J = 5.4 Hz, 2H), 2.84 – 2.83 (t, J = 13.2 Hz, J = 6.6 Hz, 2H), 2.31 (s, 3H), 2.04 – 2.02 (t, J = 10.4 Hz, J = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 130.0, 127.2, 126.2, 121.6, 114.4, 42.1, 26.9, 22.4, 20.4. HRMS (ESI) m/z calculated for $C_{10}H_{14}N$ ([M + H]$^+$): 148.1121, found148.1121.



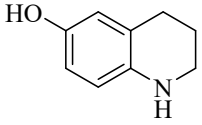
5-methyl-1,2,3,4-tetrahydroquinoline (2c)[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (s, 1H), 6.91 – 6.88 (m, 1H), 6.53 (d, J = 7.2 Hz, 1H), 6.38 (d, J = 7.5 Hz, 1H), 3.28 – 3.25 (t, J = 11.4 Hz, J = 5.4 Hz, 2H), 2.66 – 2.64 (t, J = 13.2 Hz, J = 6.6 Hz, 2H), 2.19 (s, 3H), 2.01 – 1.99 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 137.2, 126.1, 120.2, 118.9, 112.4, 41.5, 24.0, 22.5, 19.3. HRMS (ESI) m/z calculated for $C_{10}H_{14}N$ ([M + H]$^+$): 148.1121, found148.1123.



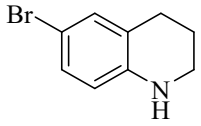
6-methoxy-1,2,3,4-tetrahydroquinoline (2d)[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.60 – 6.56 (m, 2H), 6.46 (d, J = 8.4 Hz, 1H), 3.73 (s, 3H), 3.27 – 3.25 (t, J = 10.8 Hz, J = 5.4 Hz, 2H), 2.76 (t, J = 12.0 Hz, J = 6.0 Hz, 2H), 1.95 – 1.91 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 138.7, 122.9, 115.6, 114.9, 112.9, 55.8, 42.3, 27.1, 22.4. HRMS (ESI) m/z calculated for $C_{10}H_{14}NO$ ([M + H]$^+$): 164.1070, found 164.1070.



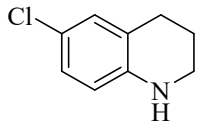
6-methoxy-1,2,3,4-tetrahydroquinoline (2e) [14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.50 (d, J = 10.2 Hz, 2H), 6.40 (d, J = 8.4 Hz, 1H), 3.26 – 3.24 (t, J = 10.2 Hz, J = 5.4 Hz, 2H), 2.73 – 2.72 (t, J = 12.0 Hz, J = 6.0 Hz, 2H), 1.93 – 1.91 (t, J = 11.4 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 147.8, 138.1, 121.2, 115.5, 114.8, 113.5, 41.3, 26.7, 22.1. HRMS (ESI) m/z calculated for $C_9H_{12}NO$ ($[M + H]^+$): 150.0913, found 150.0914.



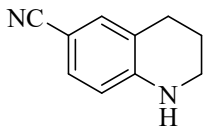
6-bromo-1,2,3,4-tetrahydroquinoline (2f) [14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 2H), 6.34 (d, J = 8.4 Hz, 1H), 3.83 (s, 1H), 3.29 – 3.27 (t, J = 10.8 Hz, J = 5.4 Hz, 2H), 2.74 – 2.71 (t, J = 12.0 Hz, J = 6.0 Hz, 2H), 1.92 – 1.90 (t, J = 12.0 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 131.8, 129.3, 123.4, 115.5, 108.2, 41.8, 26.8, 21.7. HRMS (ESI) m/z calculated for $C_9H_{11}NBr$ ($[M + H]^+$): 212.0069, found 212.0070.



6-chloro-1,2,3,4-tetrahydroquinoline (2g) [14]

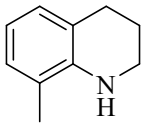
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (d, J = 10.8 Hz, 2H), 6.38 (d, J = 8.4 Hz, 1H), 3.82 (s, 1H), 3.29 – 3.27 (t, J = 10.8 Hz, J = 5.4 Hz, 2H), 2.74 – 2.71 (t, J = 12.0 Hz, J = 6.0 Hz, 2H), 1.92 – 1.90 (t, J = 12.0 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 129.0, 126.5, 122.8, 121.1, 115.0, 41.8, 26.8, 21.7. HRMS (ESI) m/z calculated for $C_9H_{11}NCl$ ($[M + H]^+$): 168.0575, found 168.0578.



6-carbonitrile-1,2,3,4-tetrahydroquinoline (2h) [14]

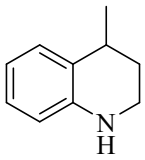
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 2H), 6.41 (d, J = 8.4 Hz, 1H), 4.46 (s, 1H), 3.38 (t, J = 9.6 Hz, J = 4.8 Hz, 2H), 2.74 (t, J = 12.6 Hz, J = 6.6 Hz, 2H), 1.95 – 1.91 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 133.1 (d), 131.2 (d), 120.9, 113.3 (m), 97.6, 41.6 (t), 26.7 (t), 21.0 (t). HRMS (ESI) m/z calculated for $C_{10}H_{11}N_2$ ($[M + H]^+$):

159.0917, found 159.0920.



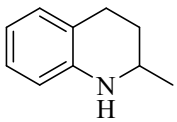
8-methyl-1,2,3,4-tetrahydroquinoline (2i)[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, J = 7.8 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.66 – 6.64 (m, 1H), 3.87 (s, 1H), 3.46 (t, J = 9.6 Hz, J = 4.8 Hz, 2H), 2.88 (t, J = 12.0 Hz, J = 6.0 Hz, 2H), 2.17 (s, 3H), 2.05 – 2.01 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 127.9 (d), 127.4 (d), 121.2 (d), 120.9 (d), 116.3 (d), 42.4 (t), 27.4, 22.2 (t), 17.1 (m). HRMS (ESI) m/z calculated for $C_{10}H_{14}N$ ($[M + H]^+$): 148.1121, found 148.1123.



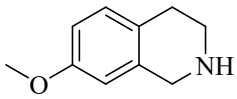
4-methyl-1,2,3,4-tetrahydroquinoline (2j) [14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, J = 17.4 Hz, J = 9.0 Hz, 1H), 7.02 (t, J = 16.8 Hz, J = 9.0 Hz, 1H), 6.72 – 6.68 (m, 1H), 6.55 – 6.52 (m, 1H), 3.49 (s, 1H), 3.39 – 3.31 (m, 2H), 2.98 (t, J = 10.8 Hz, J = 6.0 Hz, 1H), 2.05 (t, J = 7.2 Hz, J = 3.6 Hz, 1H), 1.74 (t, J = 10.2 Hz, J = 3.6 Hz, 1H), 1.36 (dd, J = 10.8 Hz, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 128.5 (t), 126.7 (t), 117.1, 116.9, 114.2 (t), 39.1 (t), 30.3 (t), 29.9, 22.8 (d). HRMS (ESI) m/z calculated for $C_{10}H_{14}N$ ($[M + H]^+$): 148.1121, found 148.1122.



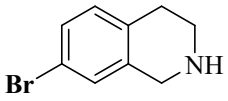
2-methyl-1,2,3,4-tetrahydroquinoline (2k) [14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 – 6.99 (m, 2H), 6.65 (t, J = 13.2 Hz, J = 6.0 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 3.74 (s, 1H), 3.43 (m, 1H), 2.86 (m, 1H), 2.78 (m, 1H), 1.96 (m, 1H), 1.63 (m, 1H), 1.25 (d, J = 6.6, J = 4.2, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 129.3 (d), 126.7 (d),121.1 (d), 117.0 (d), 113.7 (d), 47.3 (d), 30.1 (d), 26.7, 22.7 (d). HRMS (ESI) m/z calculated for $C_{10}H_{14}N$ ($[M + H]^+$): 148.1121, found 148.1121.



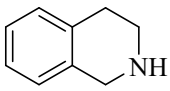
7-methoxy-1,2,3,4-tetrahydroisoquinoline (2l)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.51 (s, 1H), 3.92 (s, 2H), 3.72 (s, 3H), 3.05 (t, J = 12.0 Hz, J = 6.0 Hz, 2H), 2.67 (t, J = 12.0 Hz, J = 5.4 Hz, 2H), 2.38 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 136.8, 130.1(d), 126.7, 112.4 (d), 110.8 (t), 55.2 (m), 48.4 (t), 44.0, 28.3 (m). HRMS (ESI) m/z calculated for $C_{10}H_{14}NO$ ($[M + H]^+$): 164.1070, found 164.1073.



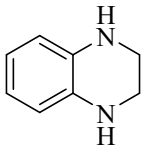
7-bromo-1,2,3,4-tetrahydroisoquinoline (2m)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.23 (dd, J = 7.8, 1.8 Hz, 1H), 7.16 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 3.97 (s, 2H), 3.11 (t, J = 11.4 Hz, J = 6.0 Hz, 2H), 2.73 (t, J = 11.4 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.1, 133.8, 131.0, 129.0, 119.2, 48.0, 43.6, 28.7. HRMS (ESI) m/z calculated for $C_9H_{10}NBr$ ($[M + H]^+$): 212.0069, found 212.0070.



1,2,3,4-tetrahydroisoquinoline (2n)

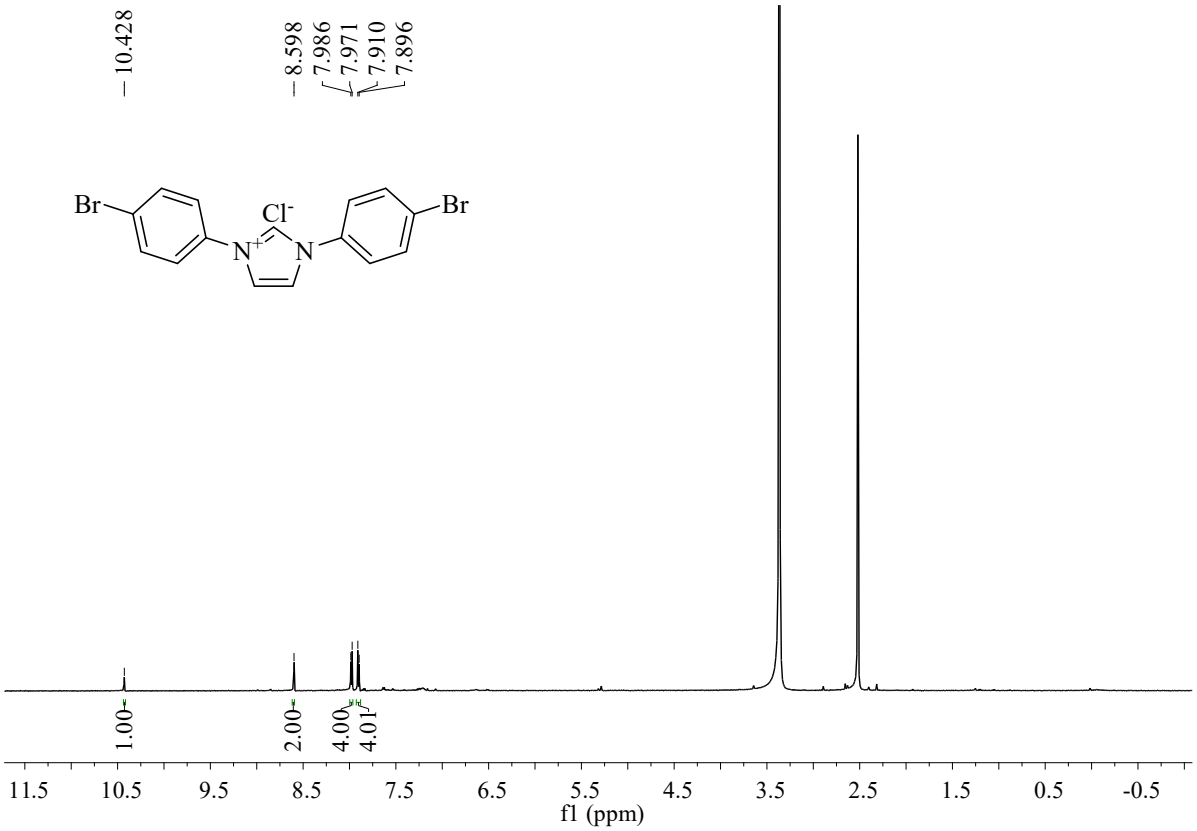
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.23 (dd, J = 7.8, 1.8 Hz, 1H), 7.16 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 3.97 (s, 2H), 3.11 (t, J = 11.4 Hz, J = 6.0 Hz, 2H), 2.73 (t, J = 11.4 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 134.8, 129.3, 126.2, 126.0, 125.7, 48.3 (t), 43.9, 29.2. HRMS (ESI) m/z calculated for $C_9H_{12}N$ ($[M + H]^+$): 134.0964, found 134.0960.

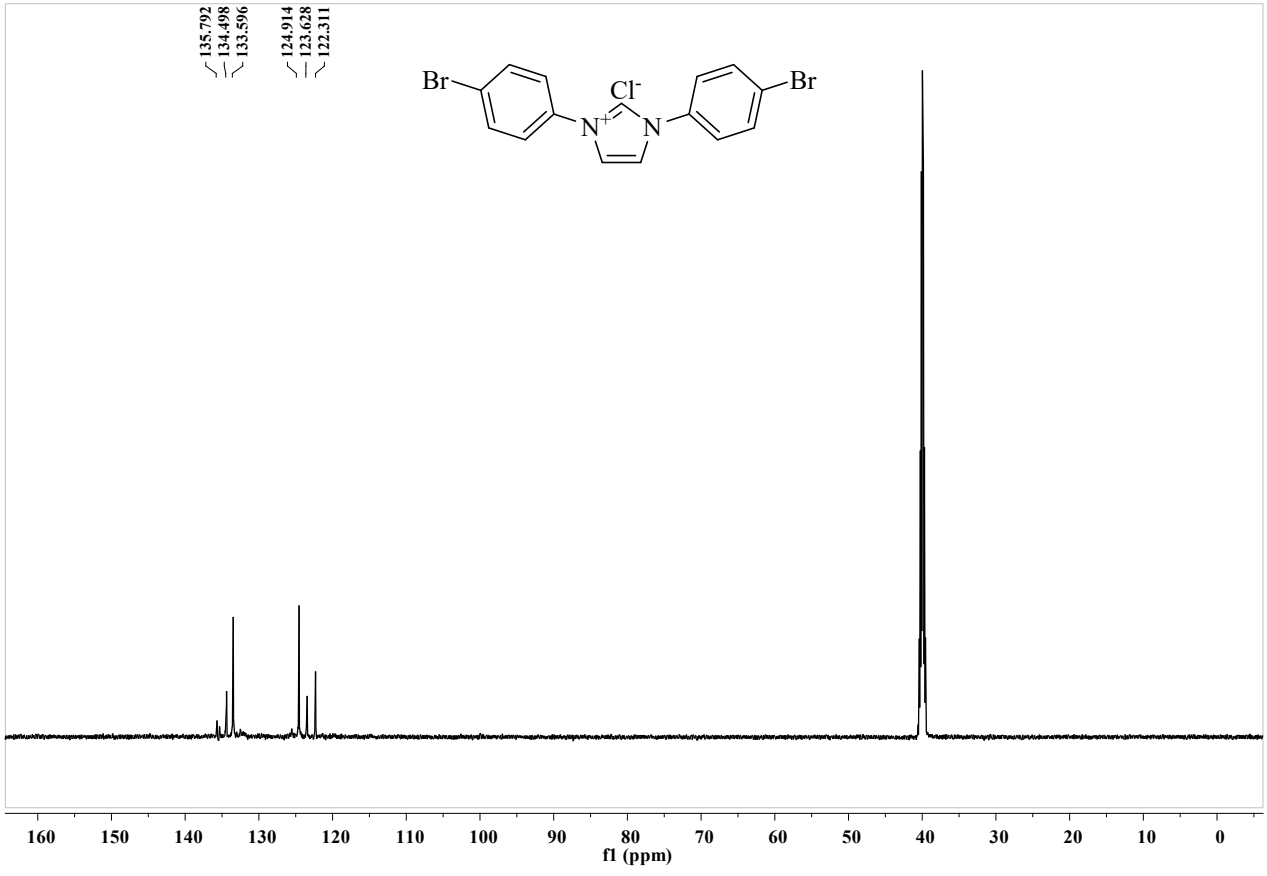


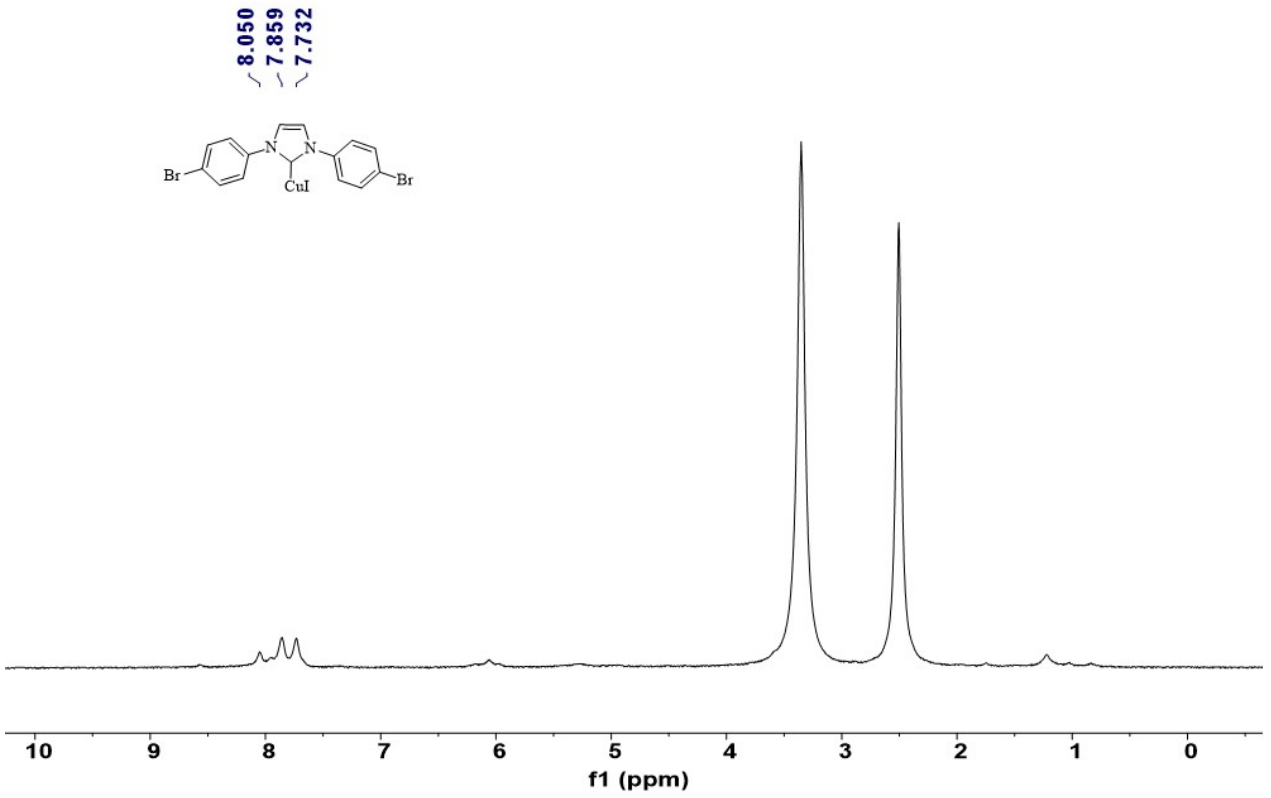
1,2,3,4-tetrahydroquinoxaline (2o)

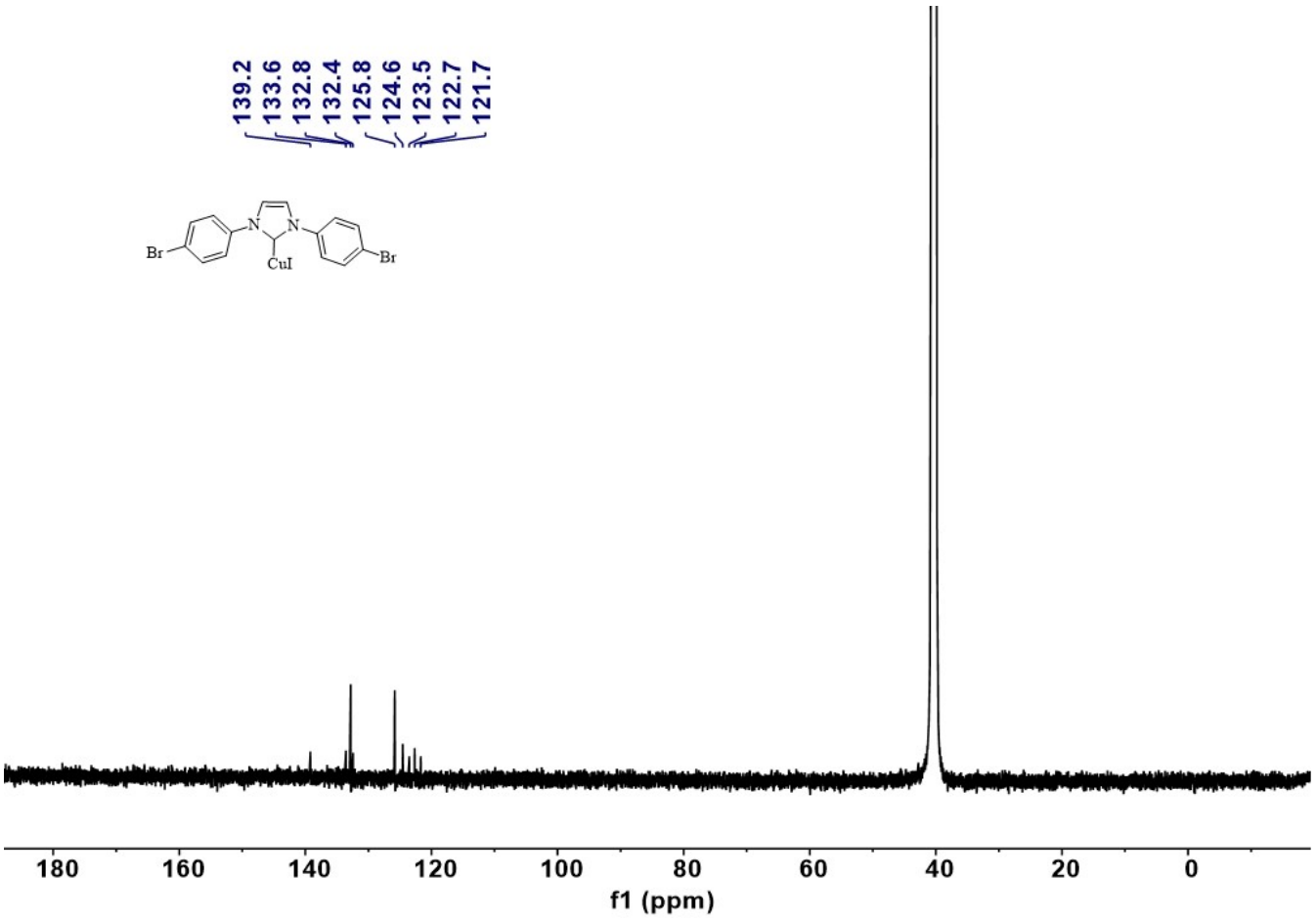
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 – 6.58 (m, 2H), 6.52 – 6.49 (m, 2H), 3.64 (s, 2H), 3.42 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.7, 118.8, 118.7, 115.1, 114.7, 114.4, 41.7, 41.4. HRMS (ESI) m/z calculated for $C_9H_{12}N$ ($[M + H]^+$): 135.0917, found 135.0920.

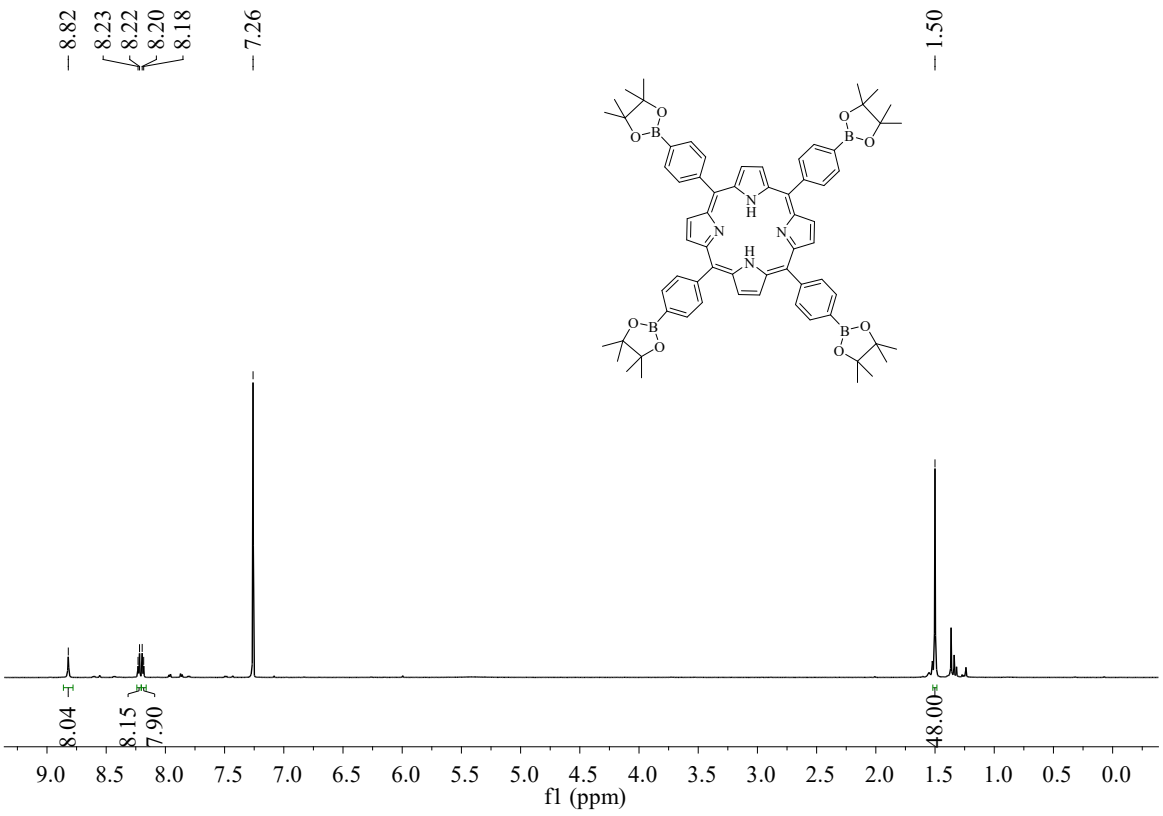
Section 6. NMR spectra of products

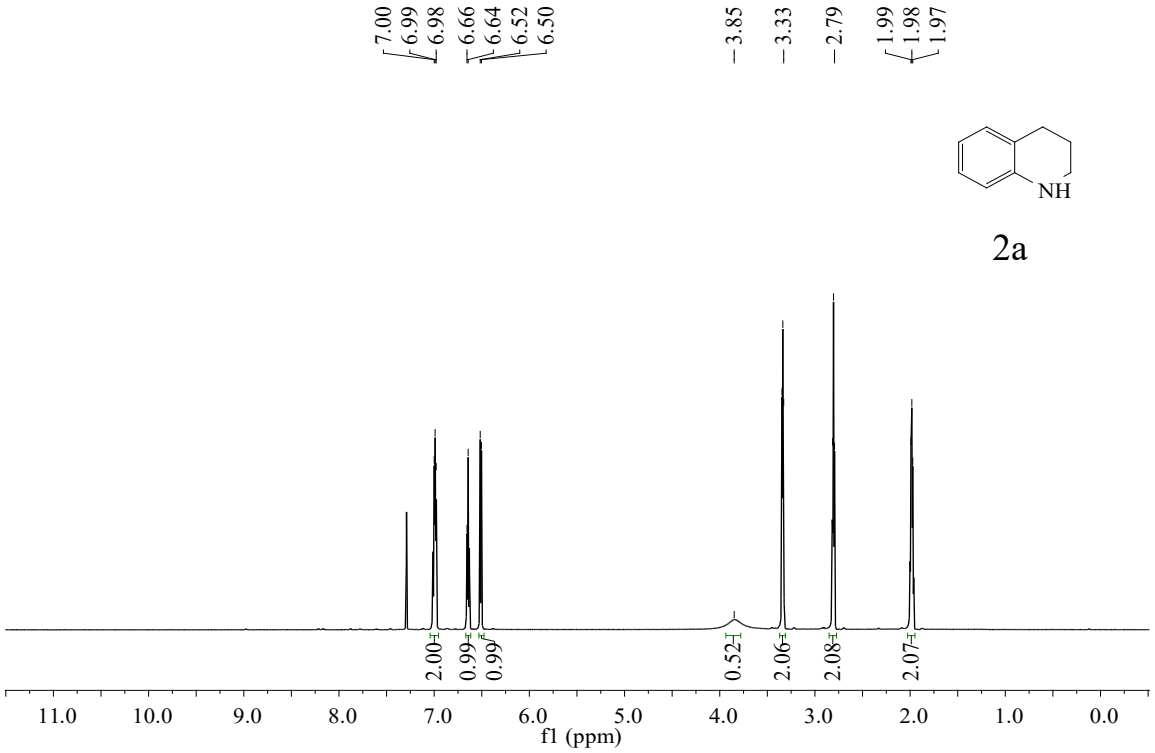

10.428
8.598
7.986
7.971
7.910
7.896
Br
Cl-
N+
N
Br
1.00
2.00
4.00
4.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

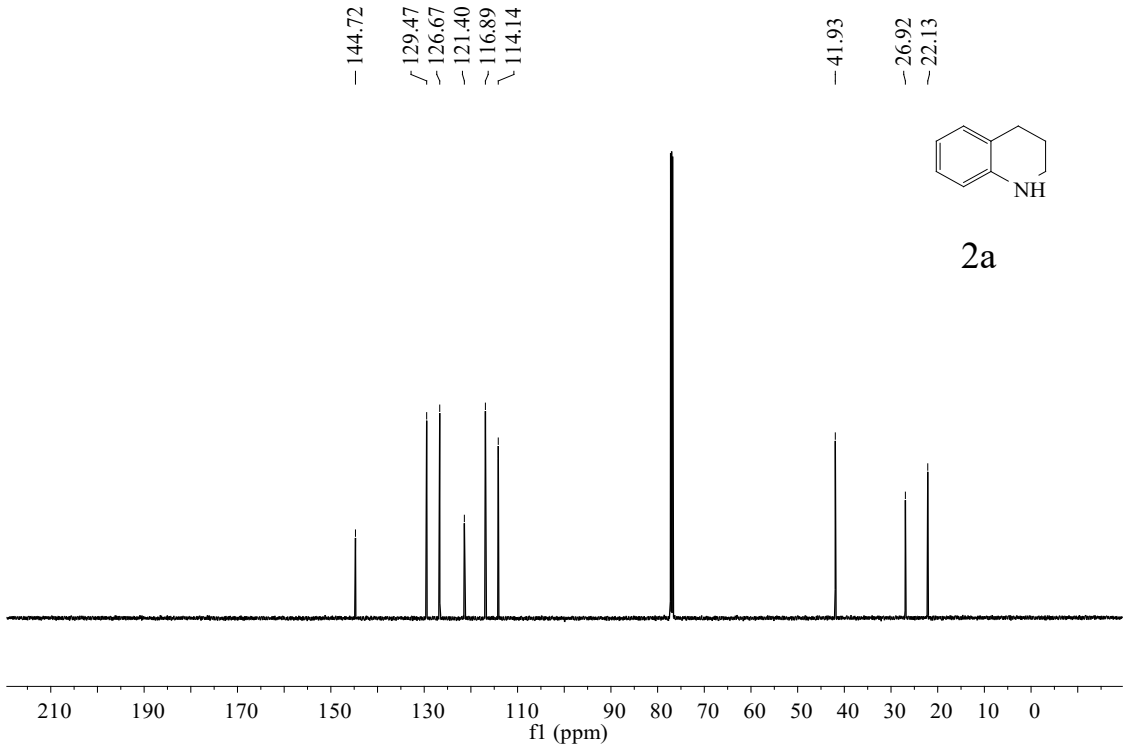

135.792
134.498
133.596
124.914
123.628
122.311
Br
Cl-
N+
N
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

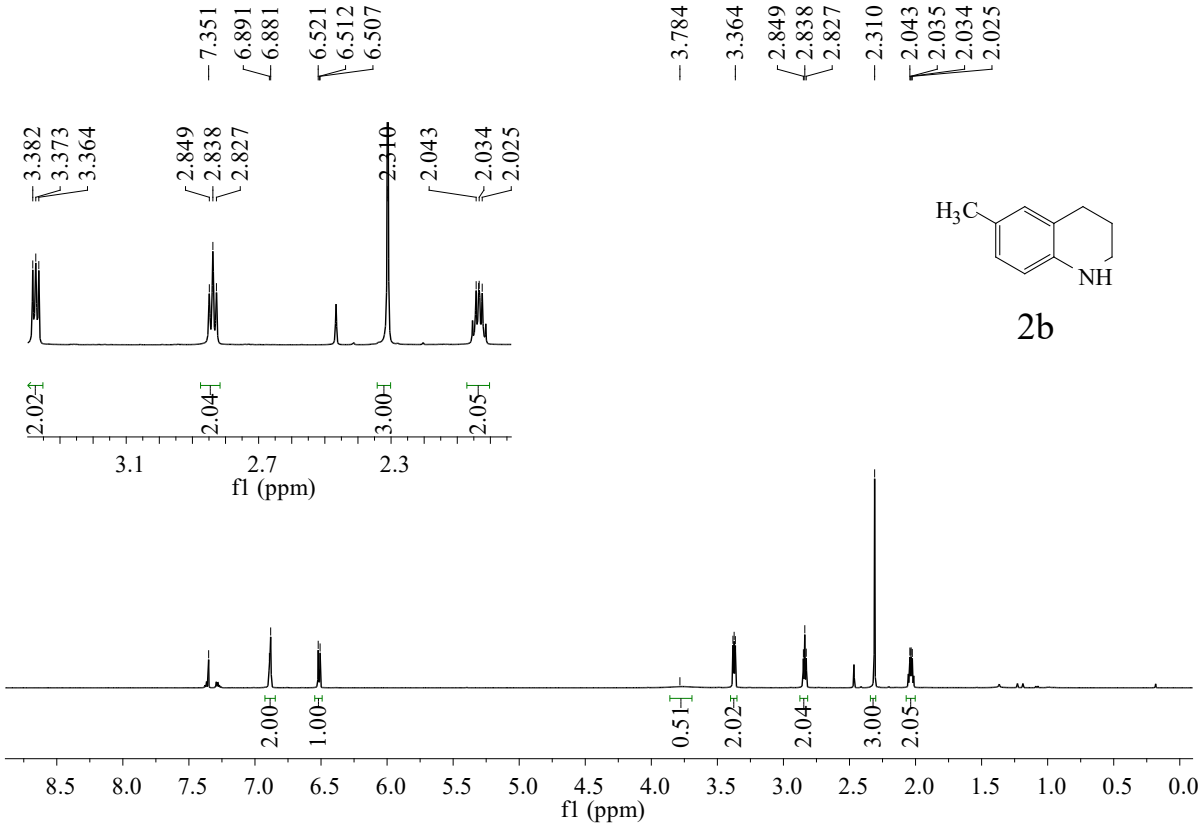

8.050
7.859
7.732
Br
N
N
CuI
Br
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


139.2
133.6
132.8
132.4
125.8
124.6
123.5
122.7
121.7
Br
N
N
CuI
Br
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.82
8.23
8.22
8.20
8.18
7.26
1.50
8.04
8.15
7.90
48.00
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)

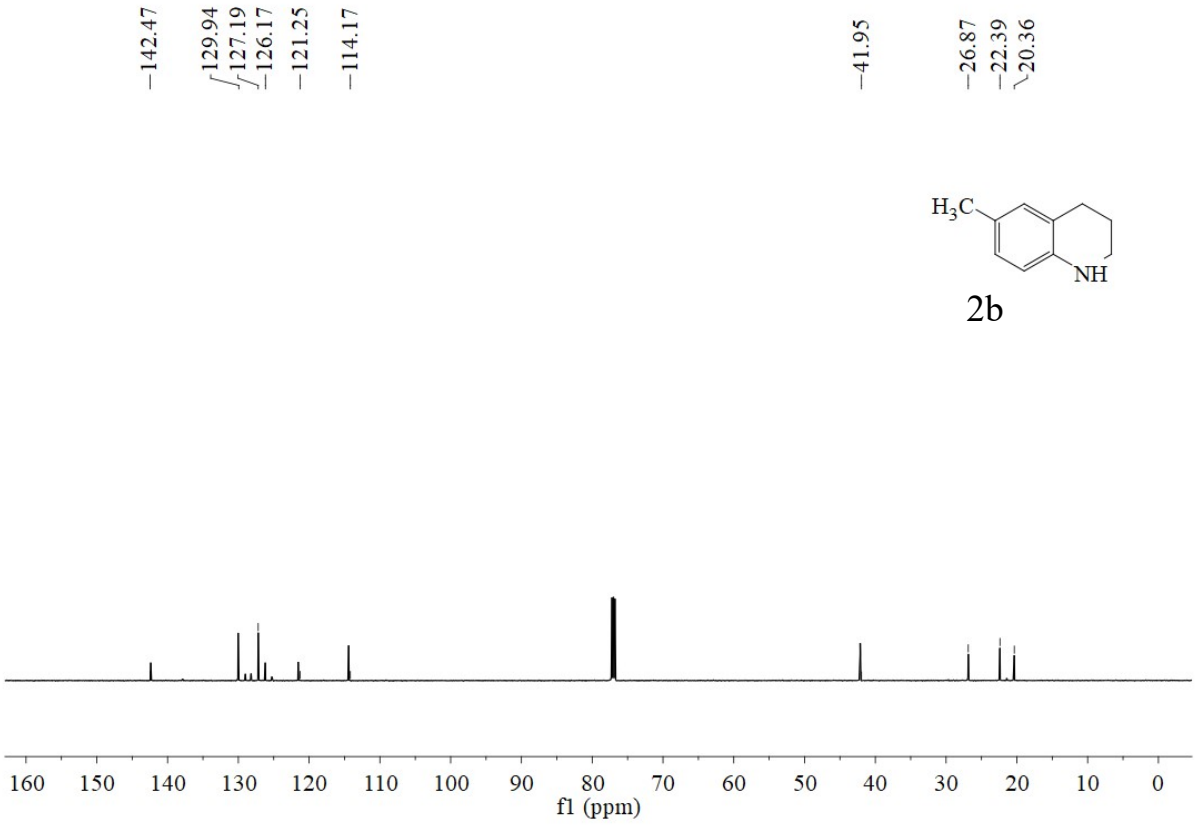

7.00
6.99
6.98
6.66
6.64
6.52
6.50
3.85
3.33
2.79
1.99
1.98
1.97
NH
2a
2.00
0.99
0.99
0.52
2.06
2.08
2.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


144.72
129.47
126.67
121.40
116.89
114.14
41.93
26.92
22.13
NH
2a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.351
6.891
6.881
6.521
6.512
6.507
3.784
3.364
2.849
2.838
2.827
2.310
2.043
2.035
2.034
2.025
3.382
3.373
3.364
2.849
2.838
2.827
2.310
2.043
2.034
2.025
2.02
2.04
3.00
2.05
3.1
2.7
2.3
f1 (ppm)
2.00
1.00
0.51
2.02
2.04
3.00
2.05
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)

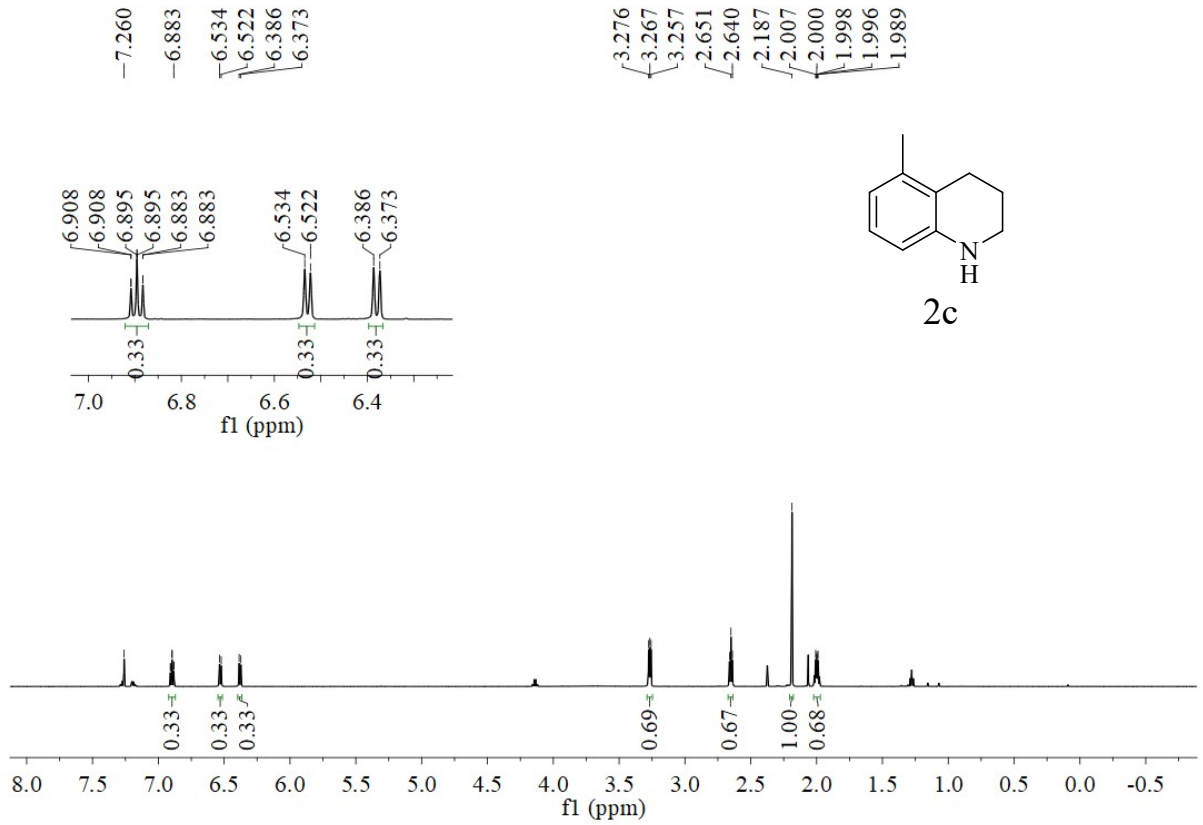
H3C
NH

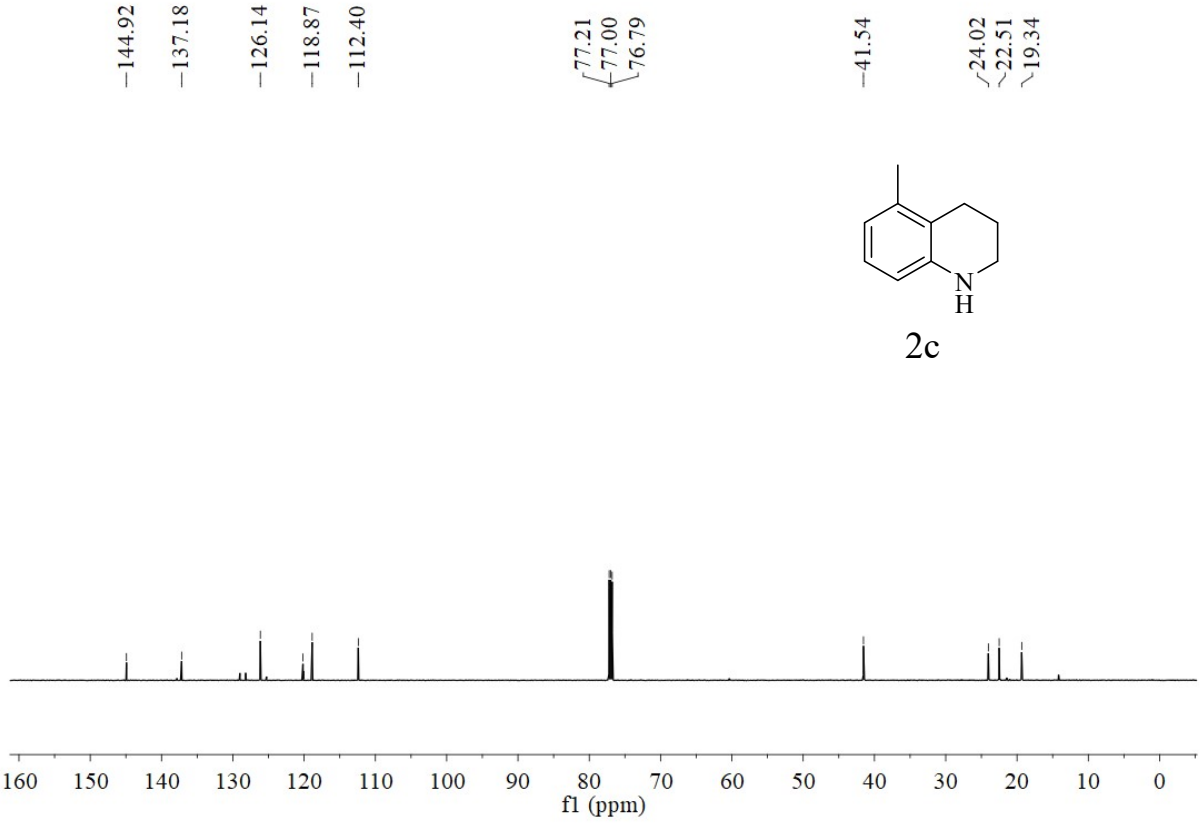
2b

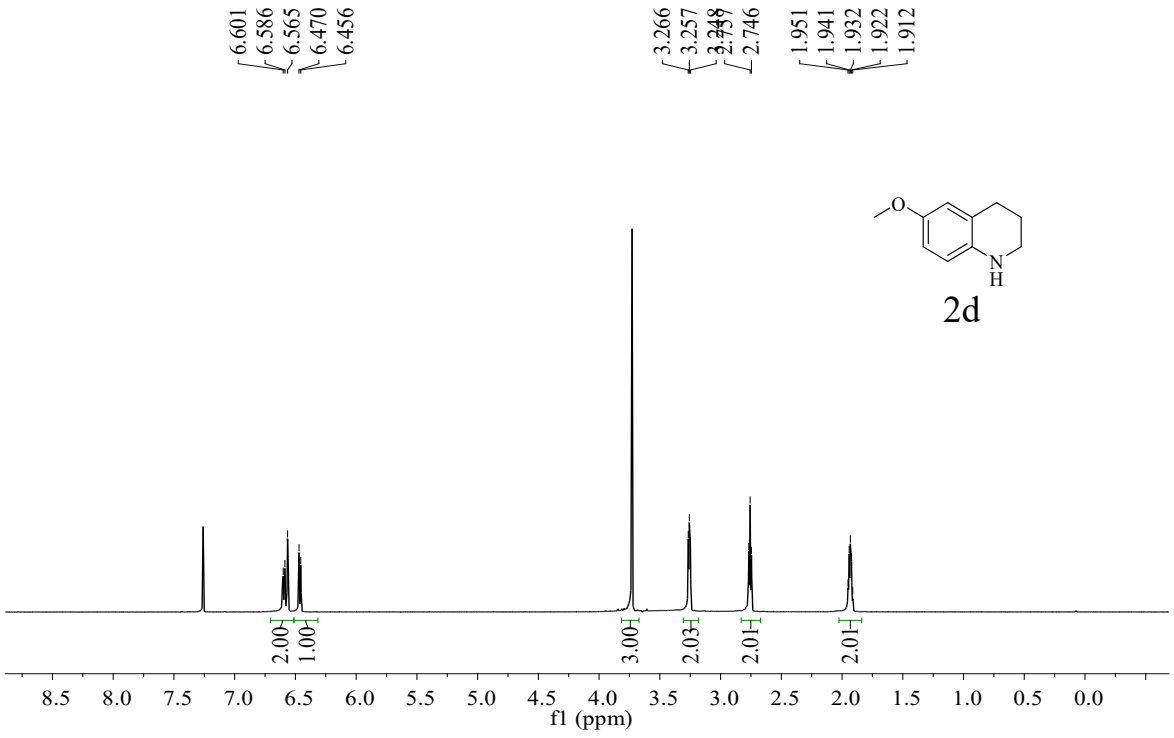

142.47
129.94
127.19
126.17
121.25
114.17
41.95
26.87
22.39
20.36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

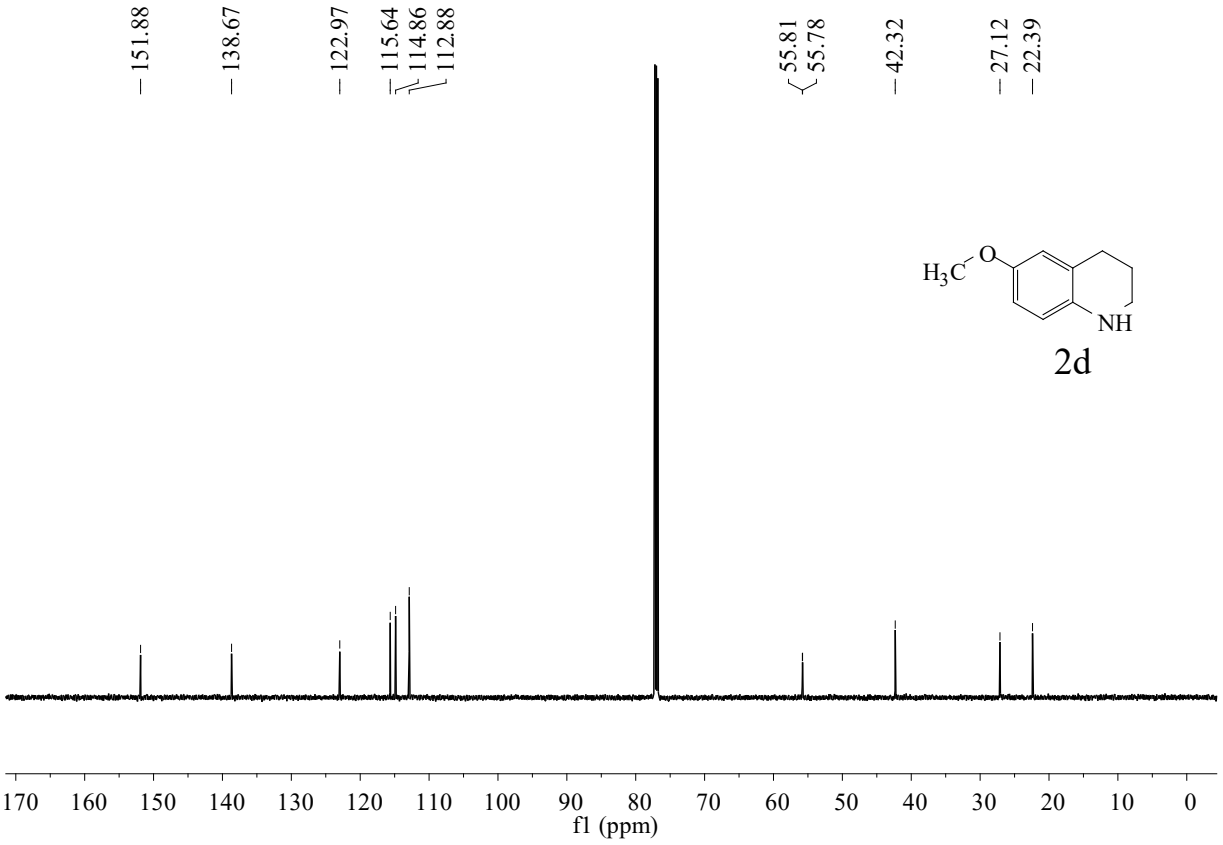
H3C
NH

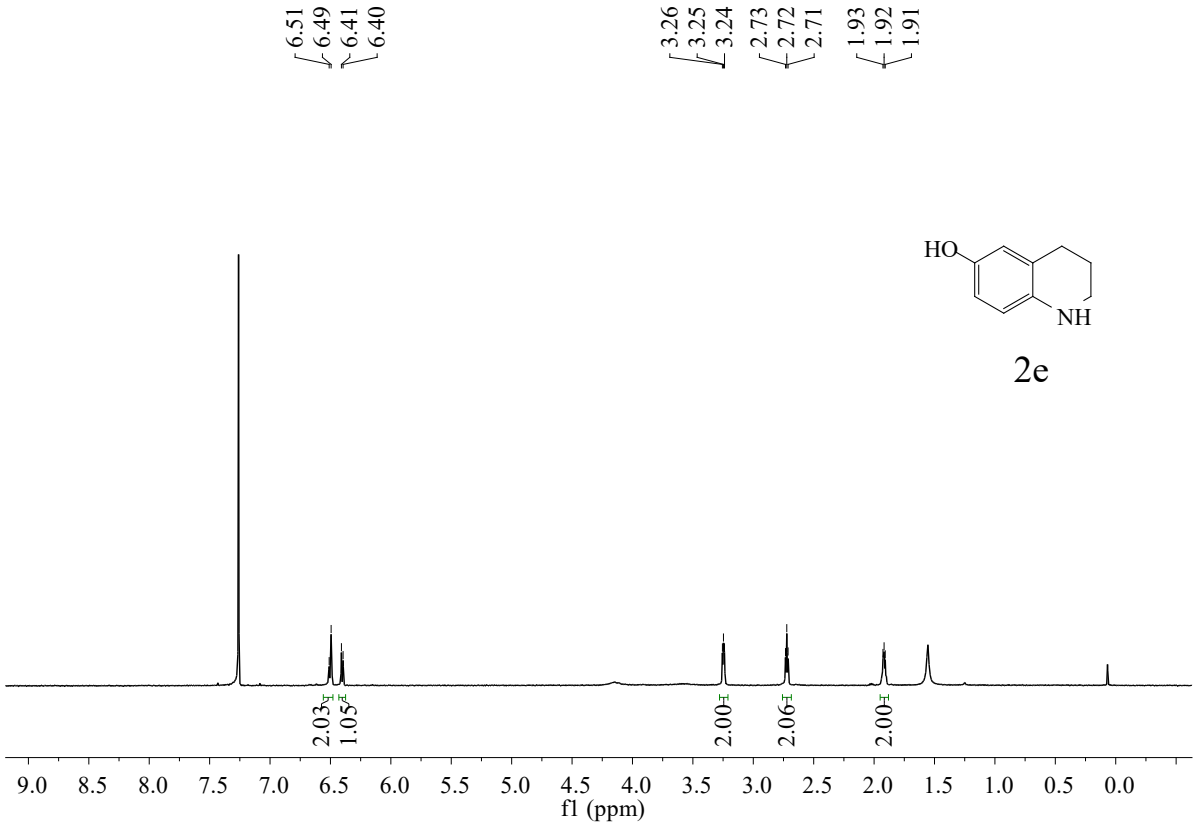
2b

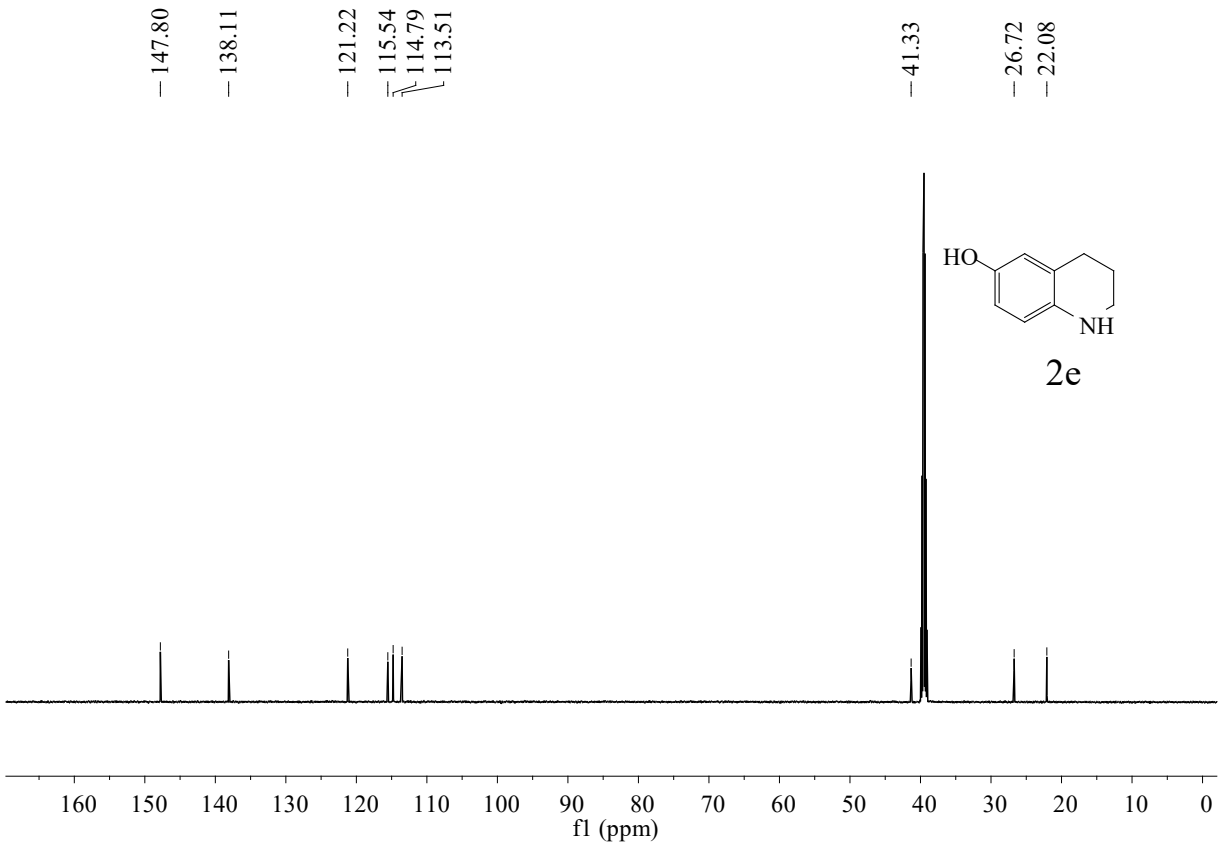

7.260
6.883
6.534
6.522
6.386
6.373
3.276
3.267
3.257
2.651
2.640
2.187
2.007
2.000
1.998
1.996
1.989
6.908
6.908
6.895
6.895
6.883
6.883
6.534
6.522
6.386
6.373
0.33
0.33
0.33
7.0
6.8
6.6
6.4
f1 (ppm)
N
H
2c
0.33
0.33
0.33
0.69
0.67
1.00
0.68
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

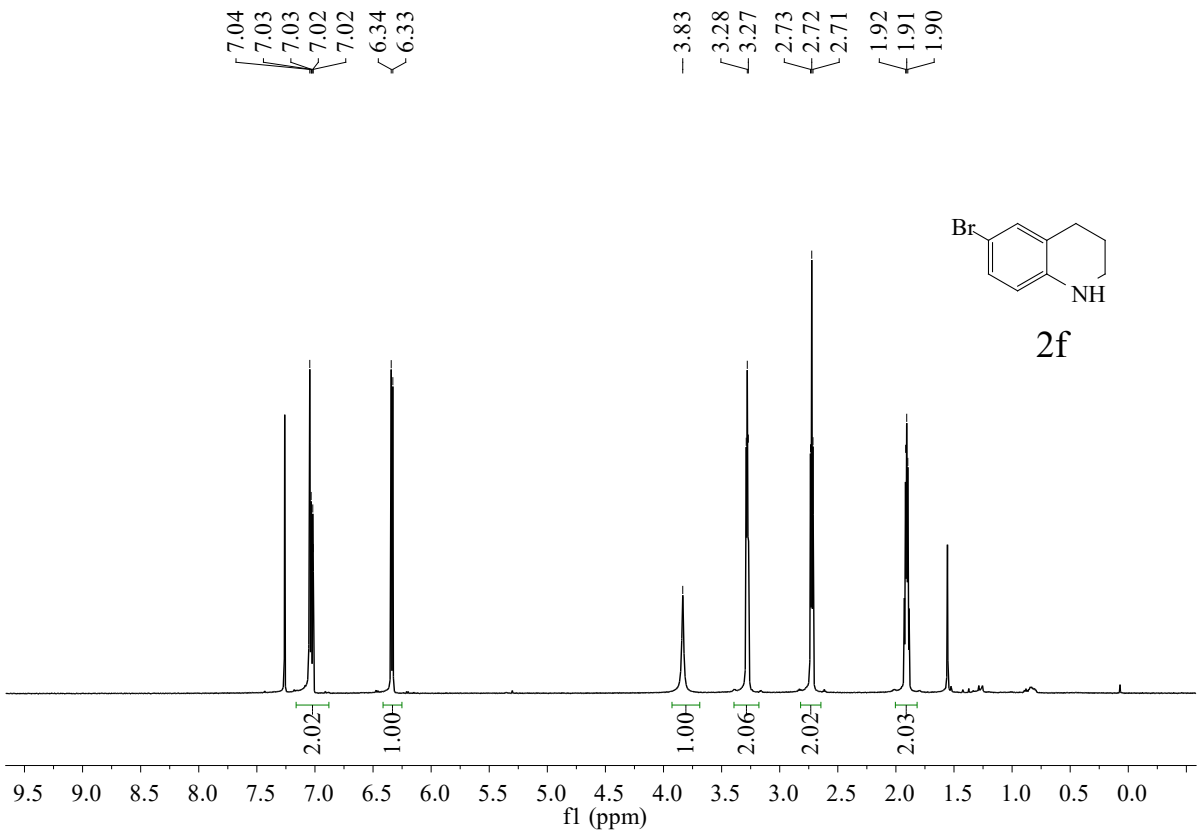

144.92
137.18
126.14
118.87
112.40
77.21
77.00
76.79
41.54
24.02
22.51
19.34
N
H
2c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

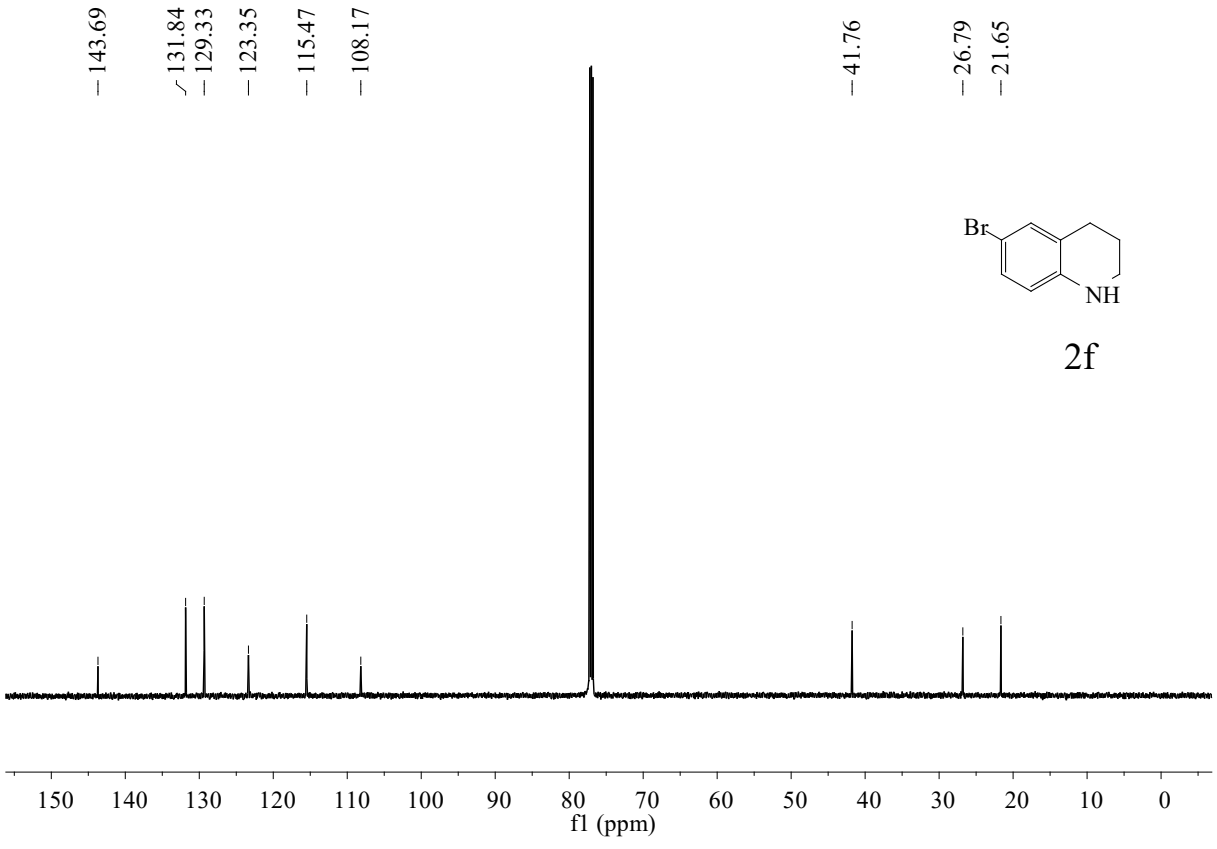

6.601
6.586
6.565
6.470
6.456
3.266
3.257
2.746
1.951
1.941
1.932
1.922
1.912
O
N
H
2d
2.00
1.00
3.00
2.03
2.01
2.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

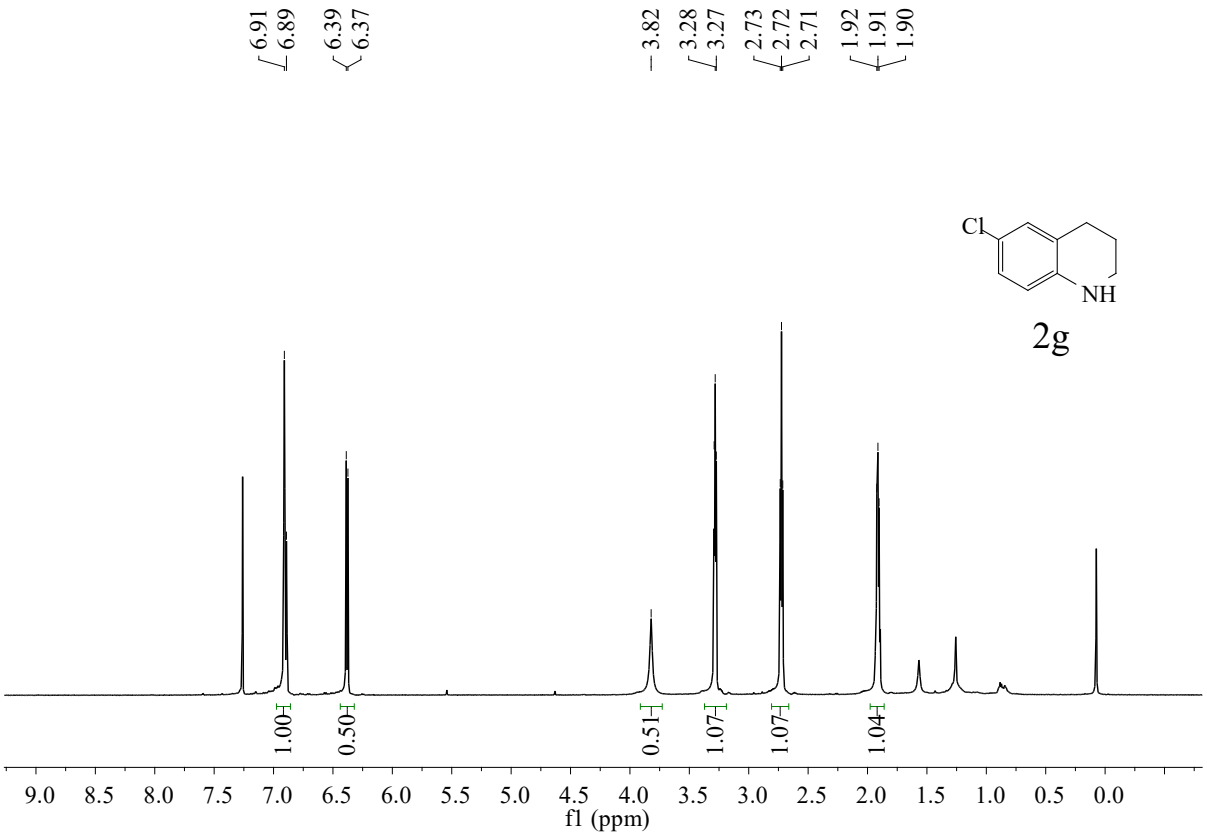

151.88
138.67
122.97
115.64
114.86
112.88
55.81
55.78
42.32
27.12
22.39
H3C
O
NH
2d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

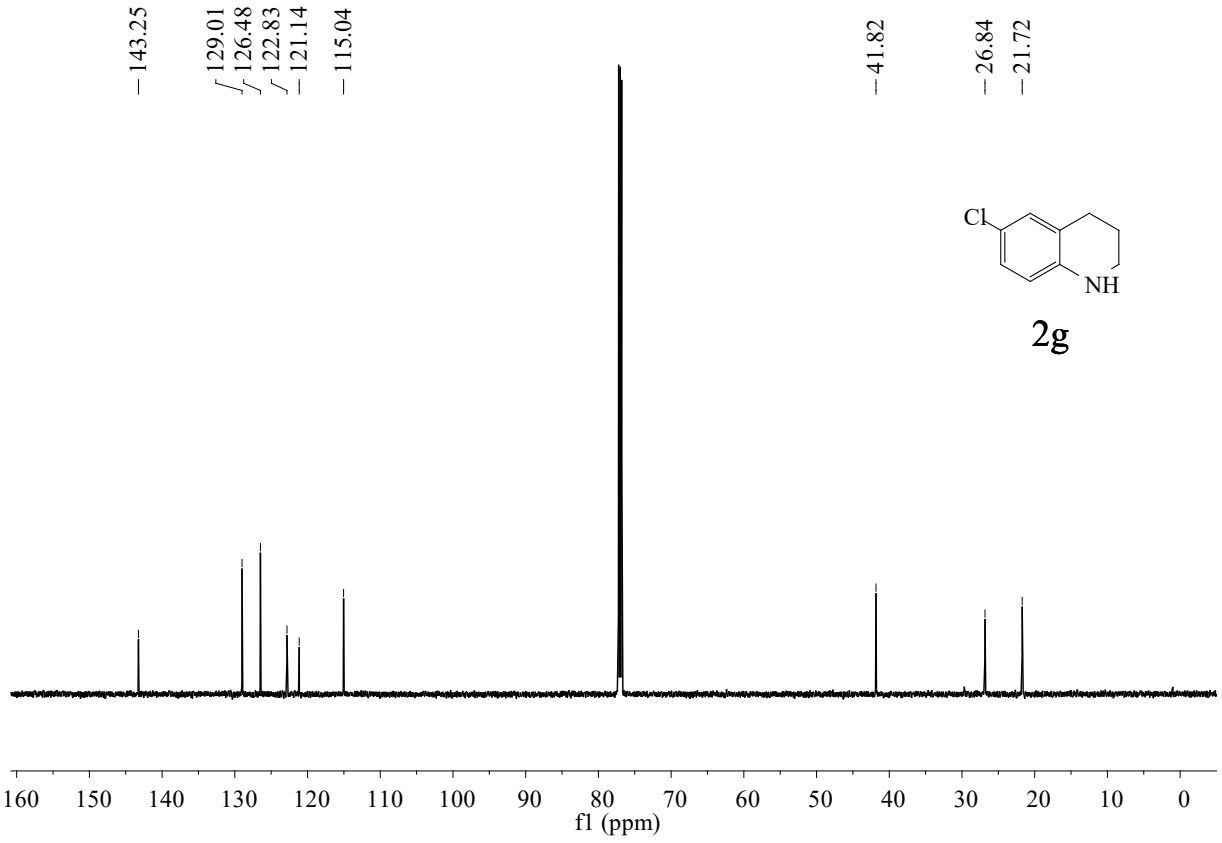

6.51
6.49
6.41
6.40
3.26
3.25
3.24
2.73
2.72
2.71
1.93
1.92
1.91
HO
NH
2e
2.03
1.05
2.00
2.06
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

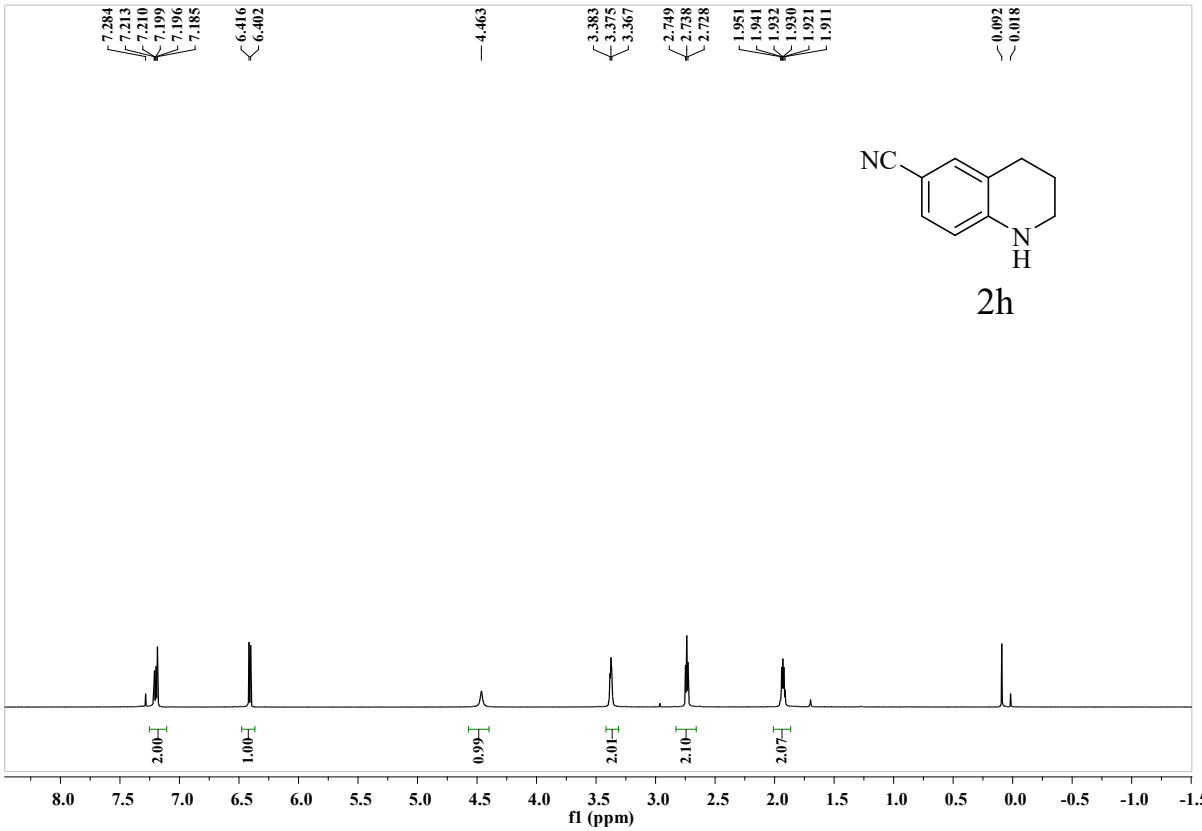

147.80
138.11
121.22
115.54
114.79
113.51
41.33
26.72
22.08
HO
NH
2e
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

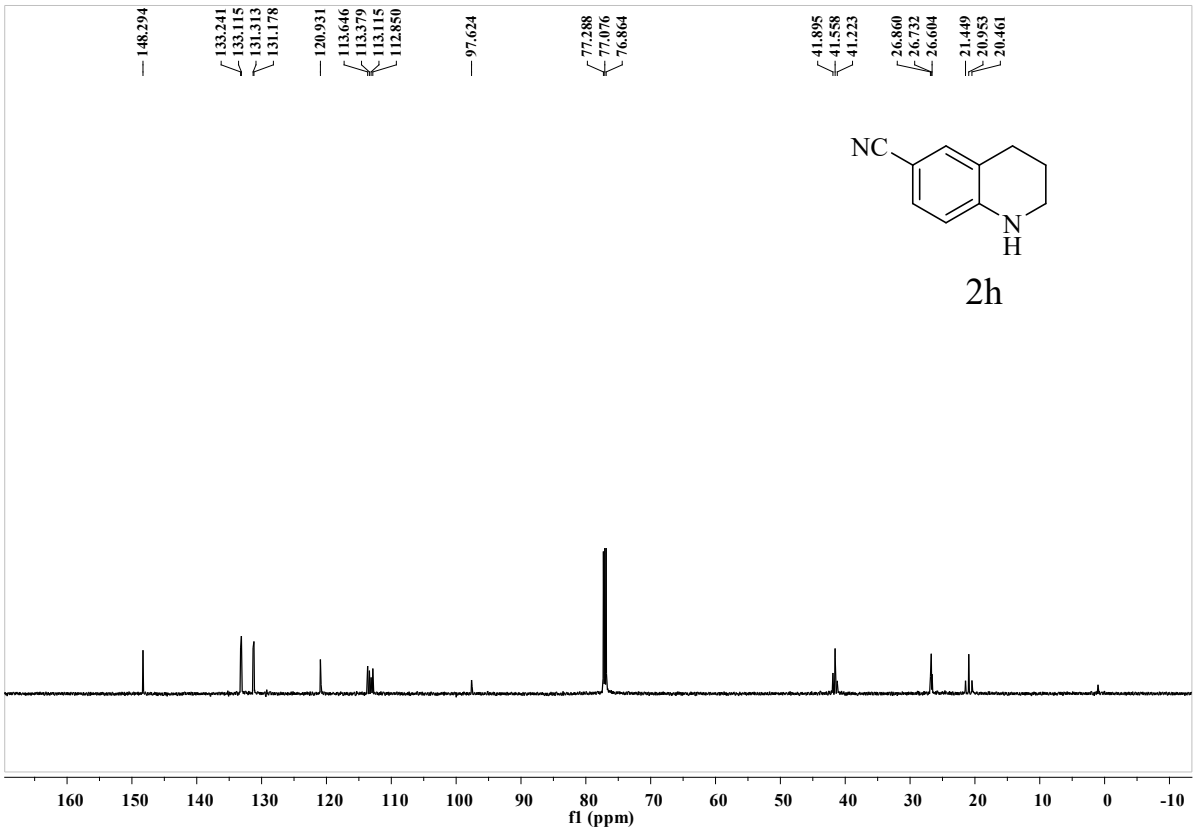

7.04
7.03
7.03
7.02
7.02
6.34
6.33
3.83
3.28
3.27
2.73
2.72
2.71
1.92
1.91
1.90
Br
NH
2f
2.02
1.00
1.00
2.06
2.02
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

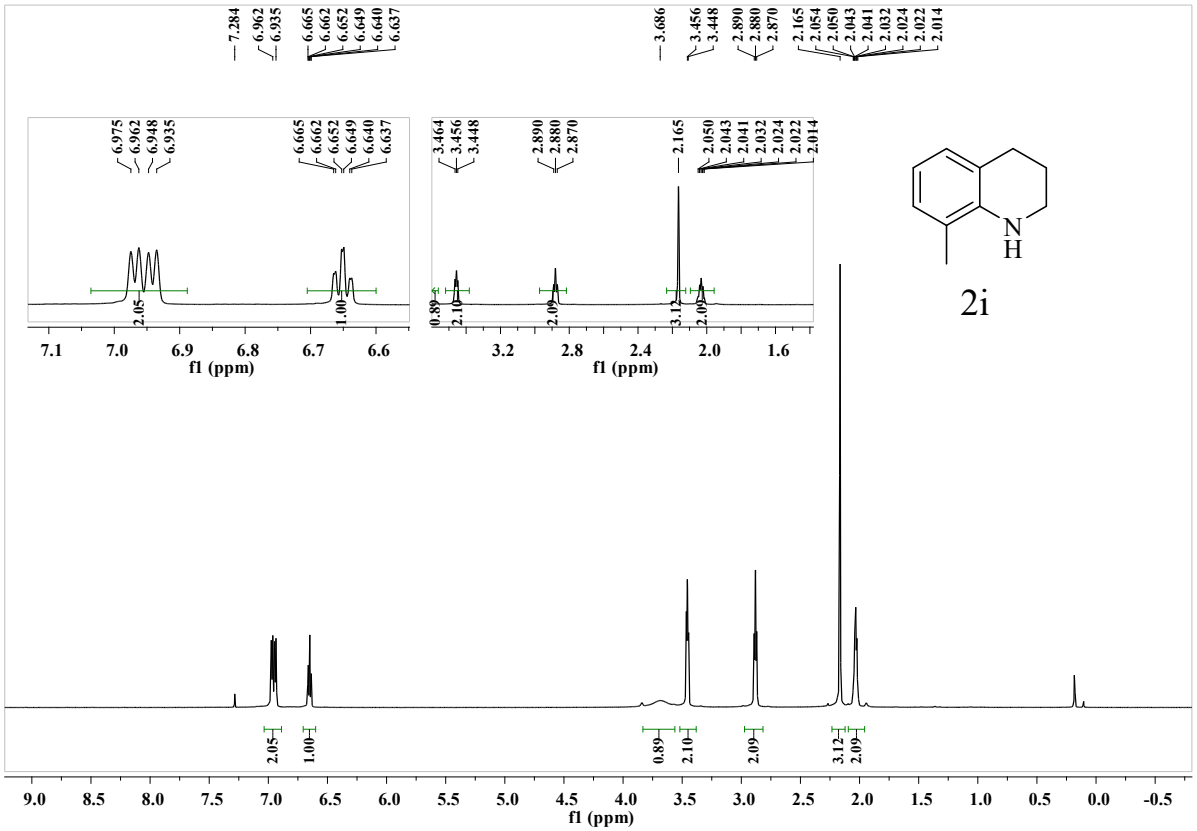

143.69
131.84
129.33
123.35
115.47
108.17
41.76
26.79
21.65
Br
NH
2f
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

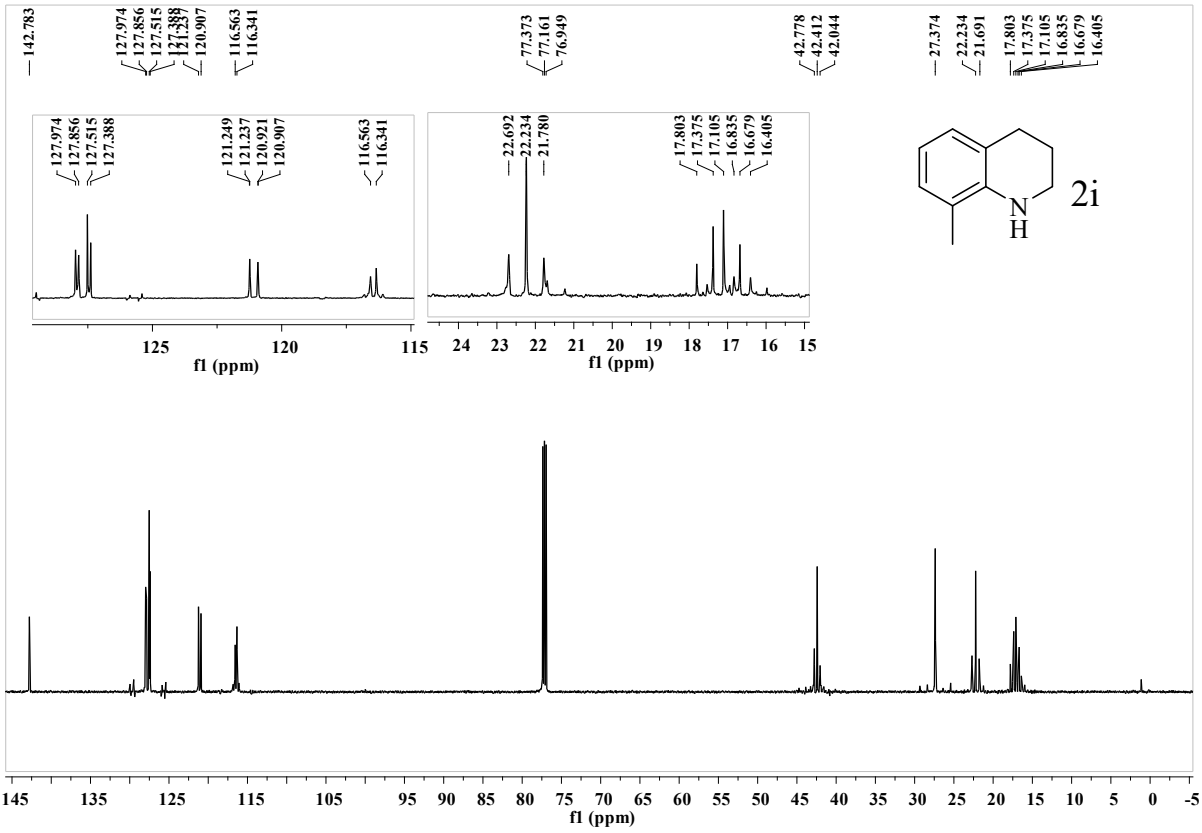

6.91
6.89
6.39
6.37
3.82
3.28
3.27
2.73
2.72
2.71
1.92
1.91
1.90
Cl
NH
2g
1.00
0.50
0.51
1.07
1.07
1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

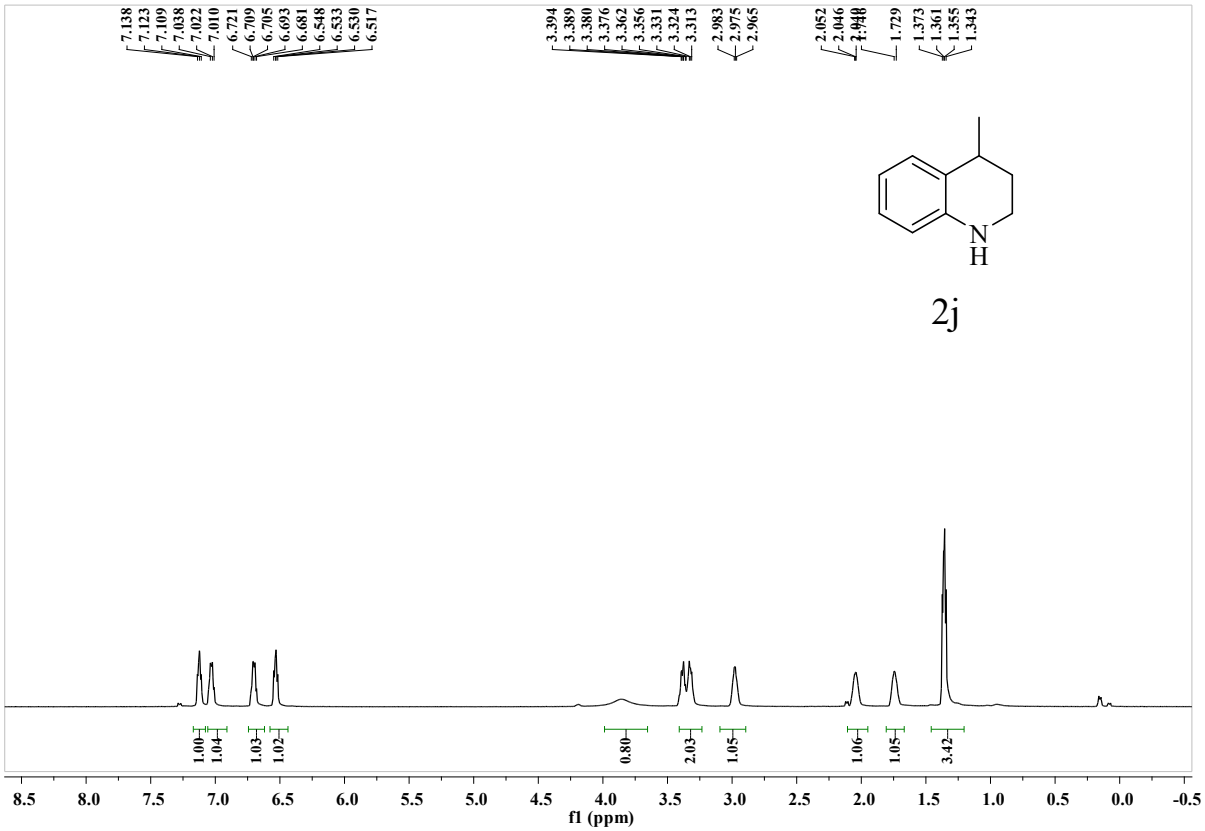

143.25
129.01
126.48
122.83
121.14
115.04
41.82
26.84
21.72
Cl
NH
2g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

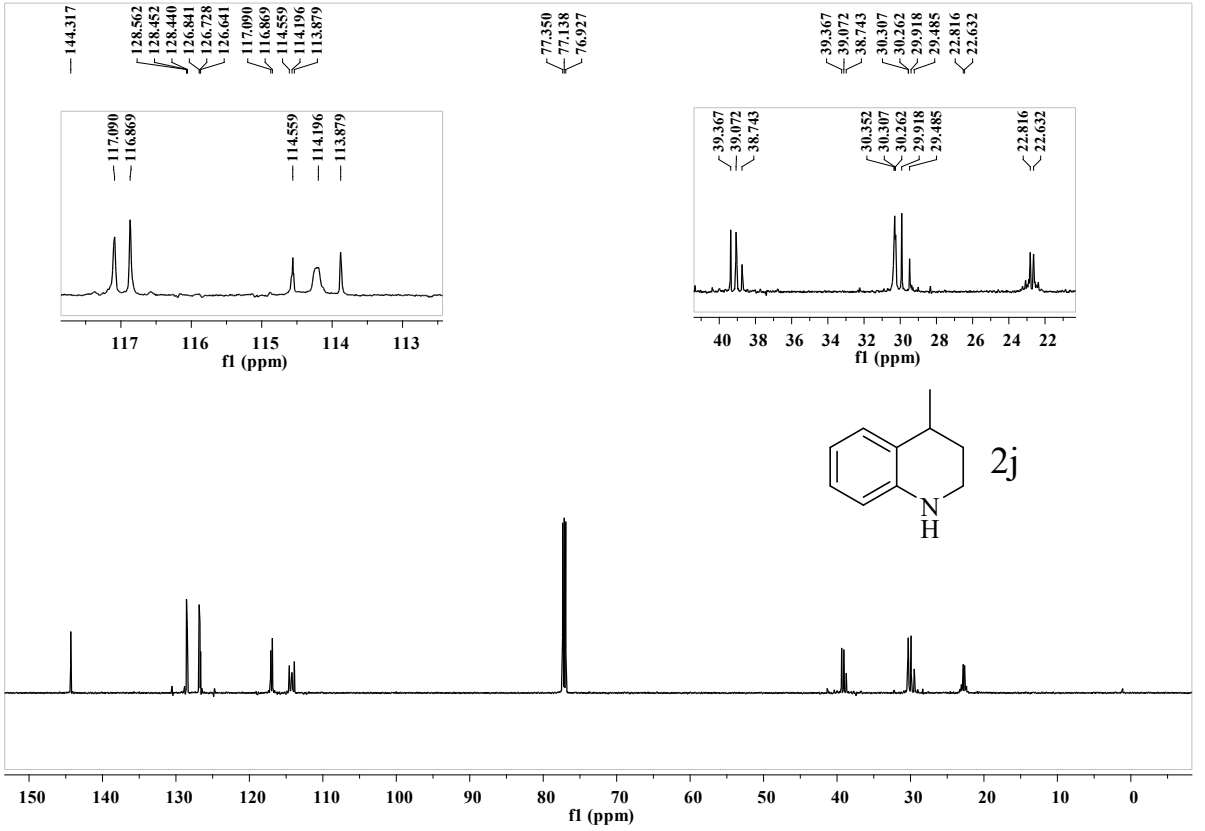

7.284
7.213
7.210
7.199
7.196
7.185
6.416
6.402
4.463
3.383
3.375
3.367
2.749
2.738
2.728
1.951
1.941
1.932
1.930
1.921
1.911
0.092
0.018
NC
N
H
2h
2.00
1.00
0.99
2.01
2.10
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

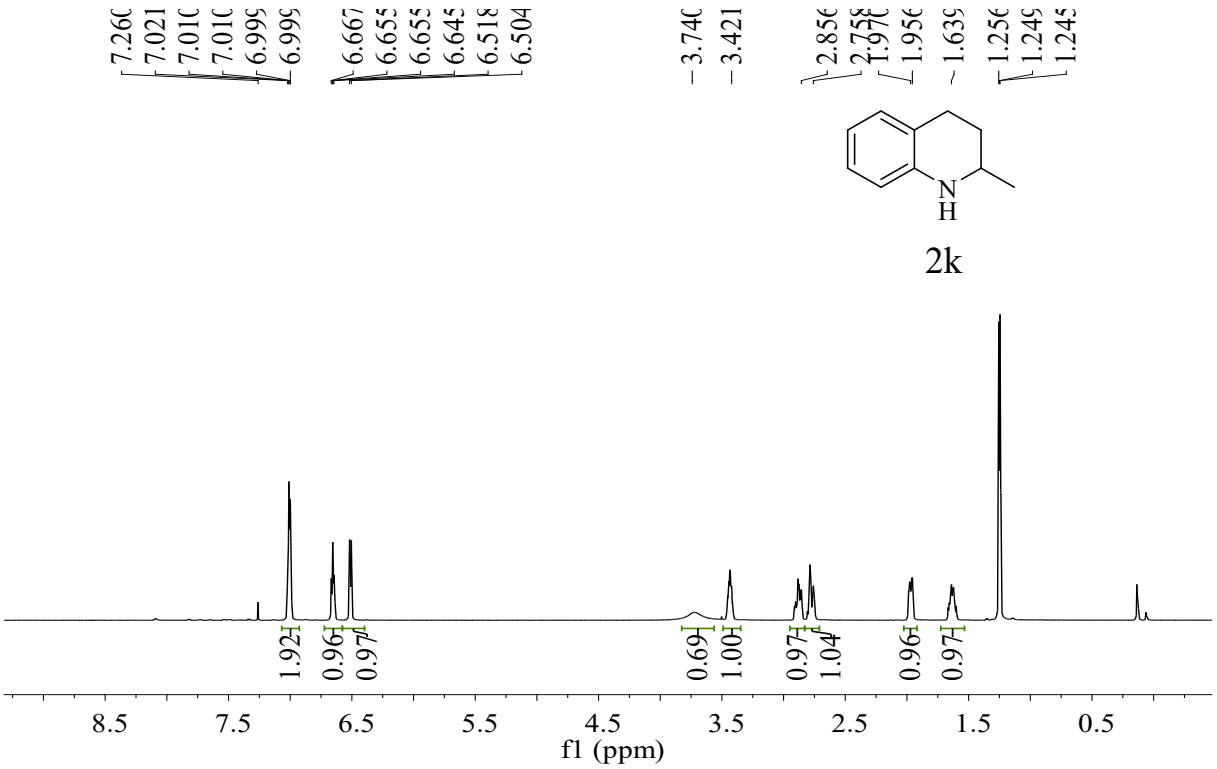

148.294
133.241
133.115
131.313
131.178
120.931
113.646
113.379
113.115
112.850
97.624
77.288
77.076
76.864
41.895
41.558
41.223
26.860
26.732
26.604
21.449
20.953
20.461
NC
N
H
2h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.284
6.962
6.935
6.665
6.662
6.652
6.649
6.640
6.637
3.686
3.456
3.448
2.890
2.880
2.870
2.165
2.054
2.050
2.043
2.041
2.032
2.024
2.022
2.014
2.05
1.00
0.89
2.10
2.09
3.12
2.09
f1 (ppm)
N
H
2i

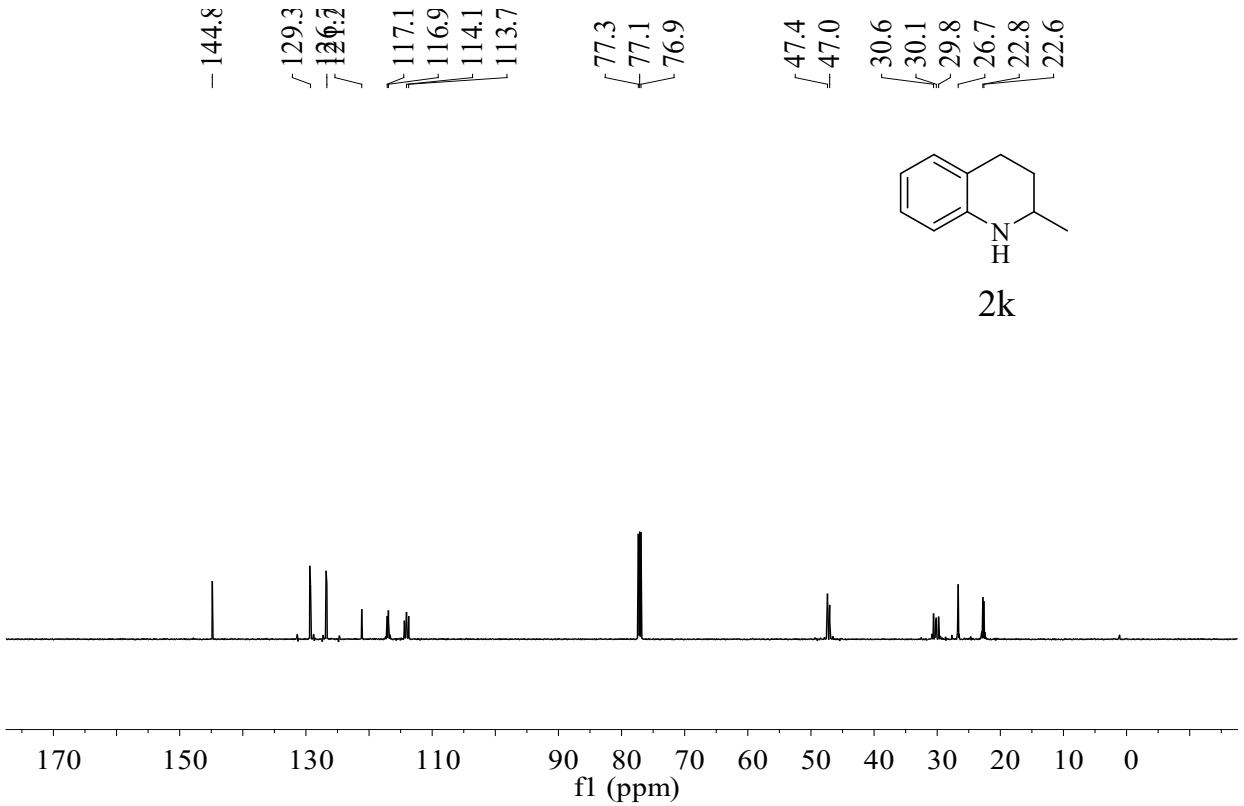

142.783
127.974
127.856
127.515
127.388
121.249
121.237
120.921
120.907
116.563
116.341
77.373
77.161
76.949
42.778
42.412
42.044
27.374
22.692
22.234
21.780
17.803
17.375
17.105
16.835
16.679
16.405
f1 (ppm)
N
H
2i


7.138
7.123
7.109
7.038
7.022
7.010
6.721
6.709
6.705
6.693
6.681
6.548
6.533
6.530
6.517
3.394
3.389
3.380
3.376
3.362
3.356
3.331
3.324
3.313
2.983
2.975
2.965
2.052
2.046
1.729
1.373
1.361
1.355
1.343
N
H
2j
1.00
1.04
1.03
1.02
0.80
2.03
1.05
1.06
1.05
3.42
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)

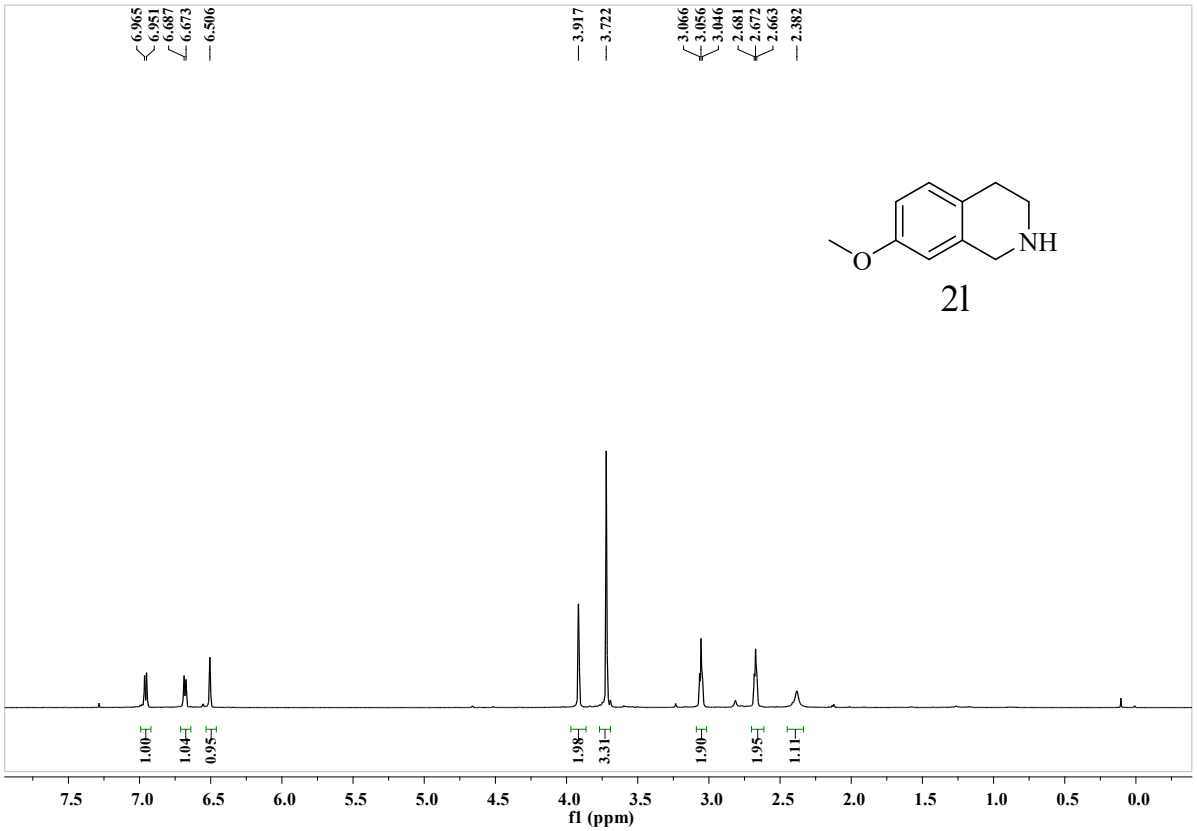

144.317
128.562
128.452
128.440
126.841
126.728
126.641
117.090
116.869
114.559
114.196
113.879
77.350
77.138
76.927
39.367
39.072
38.743
30.307
30.262
29.918
29.485
22.816
22.632
117 116 115 114 113
f1 (ppm)
40 38 36 34 32 30 28 26 24 22
f1 (ppm)
N
H
2j
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260
7.021
7.010
7.010
6.995
6.995
6.667
6.655
6.655
6.645
6.518
6.504
3.740
3.421
2.856
2.758
1.976
1.956
1.635
1.256
1.245
1.245
N
H
1.92
0.96
0.97
0.69
1.00
0.97
1.04
0.96
0.97
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

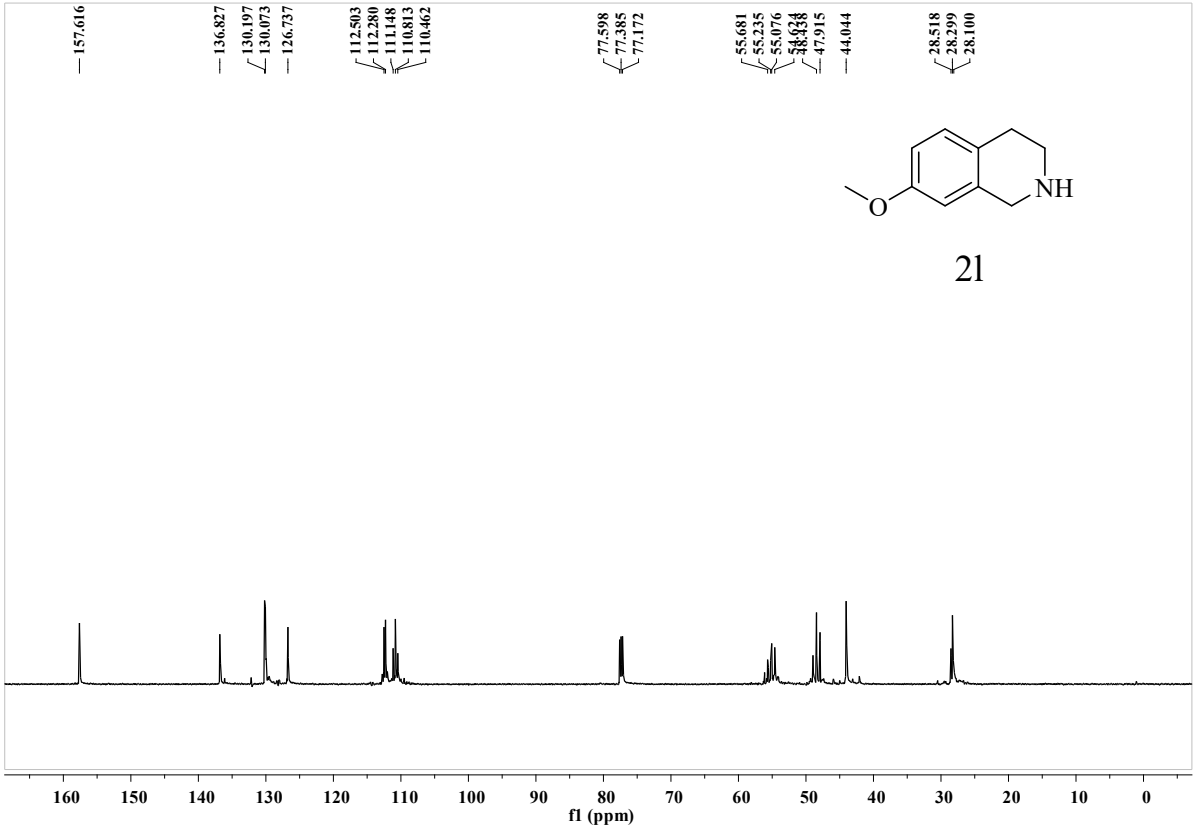
2k


144.8
129.3
117.1
116.9
114.1
113.7
77.3
77.1
76.9
47.4
47.0
30.6
30.1
29.8
26.7
22.8
22.6
N
H
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

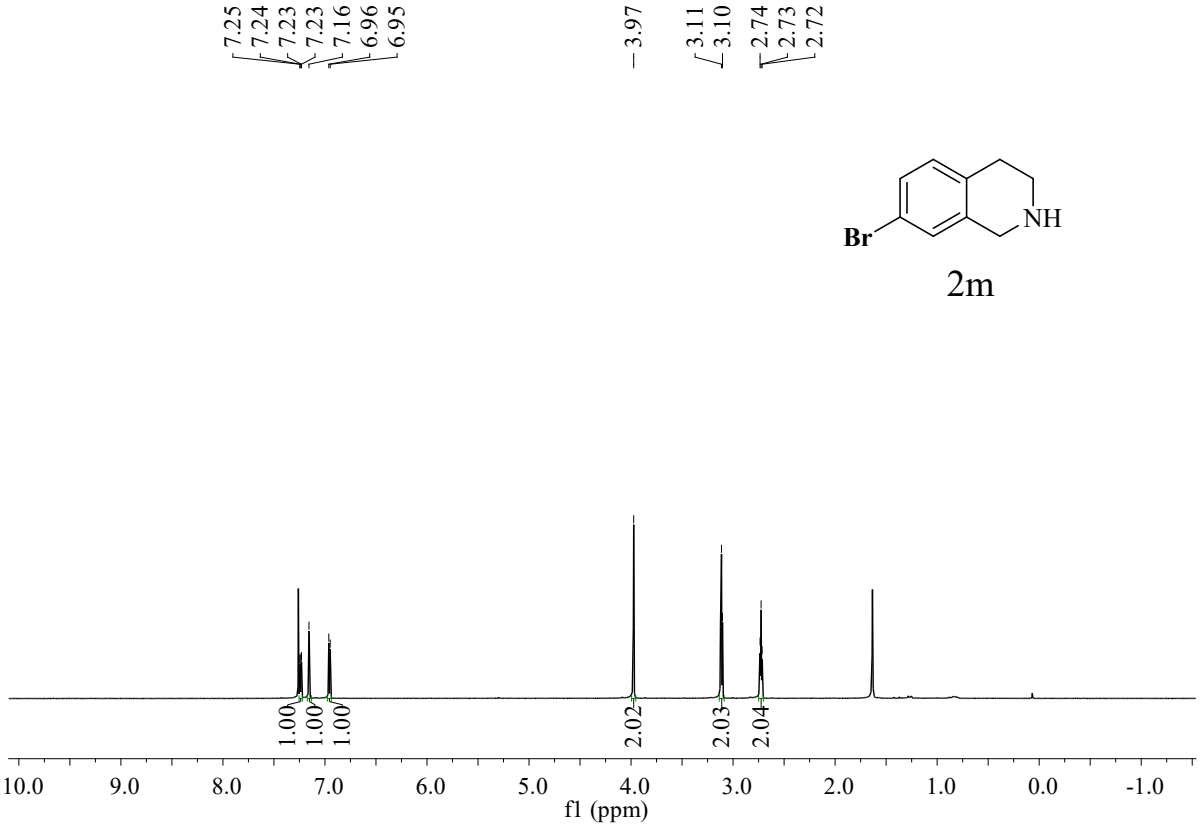
2k


6.965
6.951
6.687
6.673
6.506
3.917
3.722
3.066
3.056
3.046
2.681
2.672
2.663
2.382
NH
O
1.00
1.04
0.95
1.98
3.31
1.90
1.95
1.11
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)

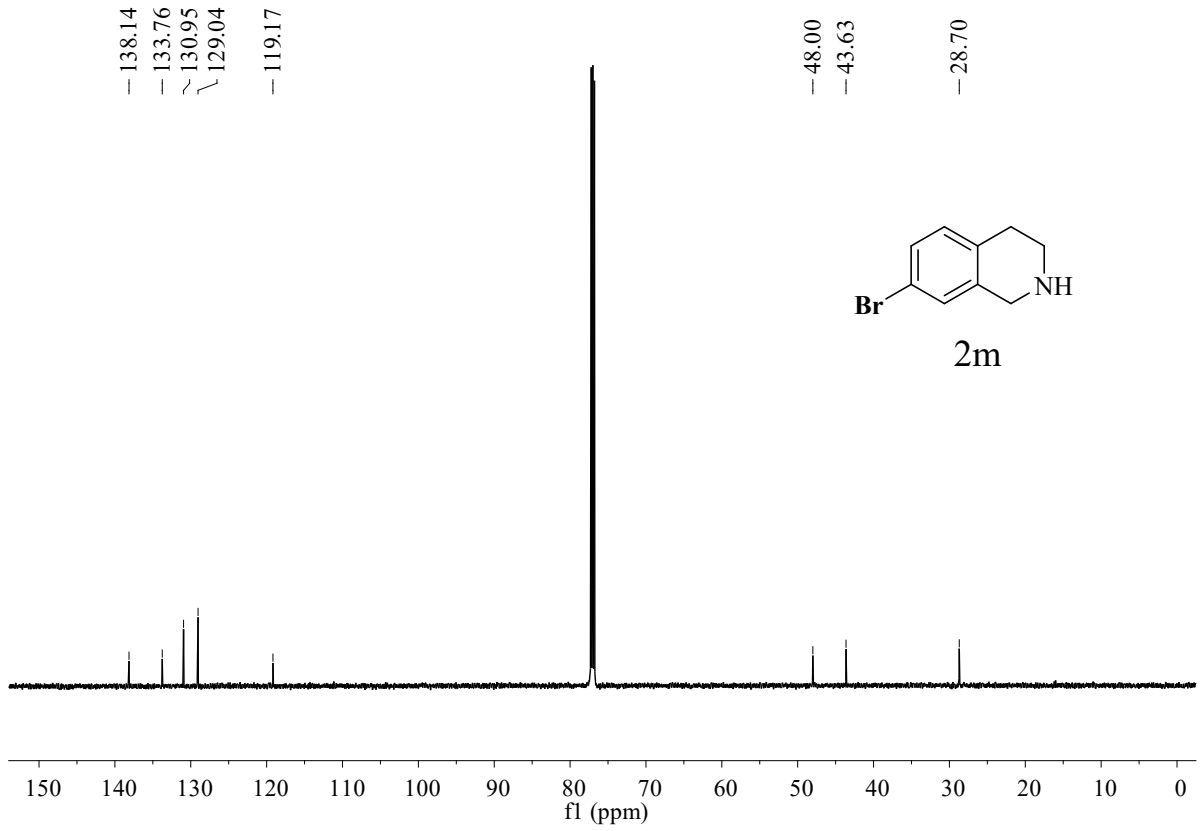
21


157.616
136.827
130.197
130.073
126.737
112.503
112.280
111.148
110.813
110.462
77.598
77.385
77.172
55.681
55.235
55.076
47.915
44.044
28.518
28.299
28.100
NH
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

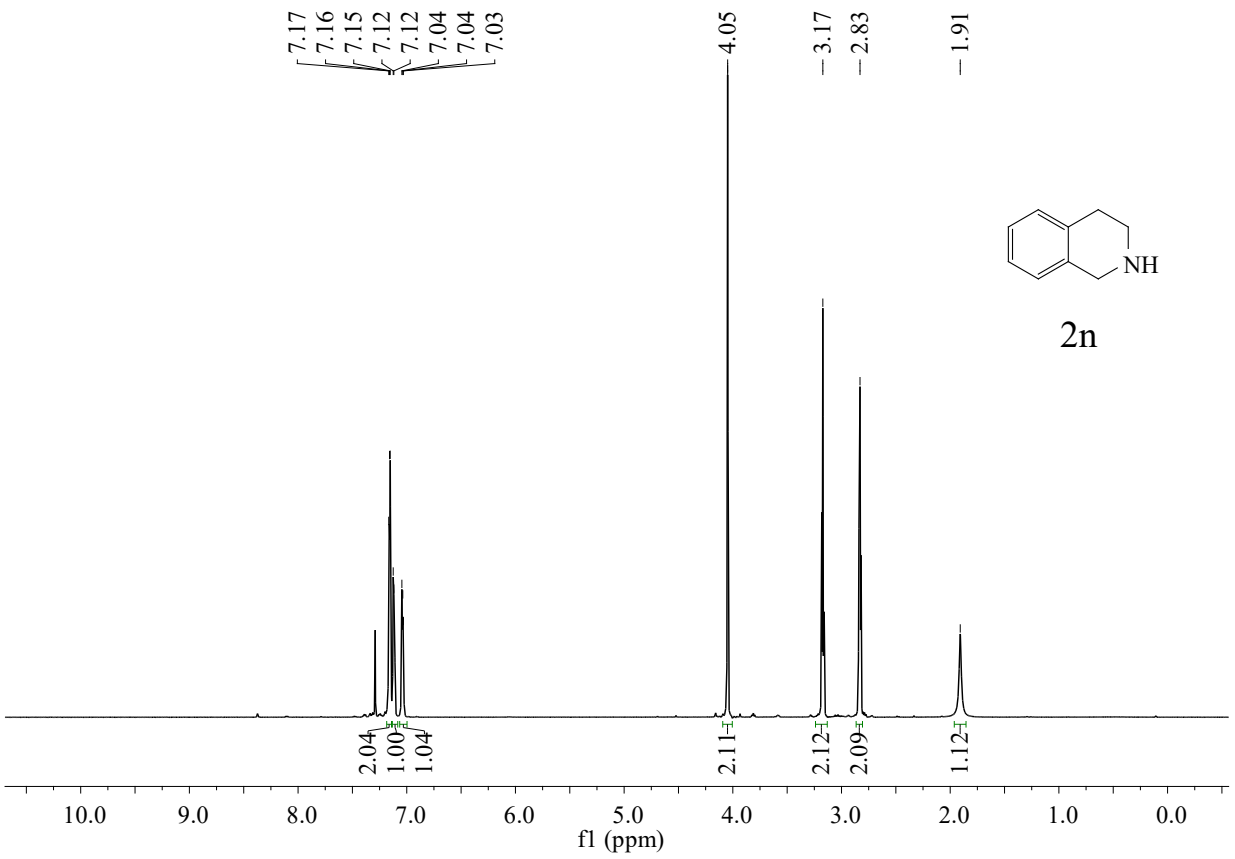
21

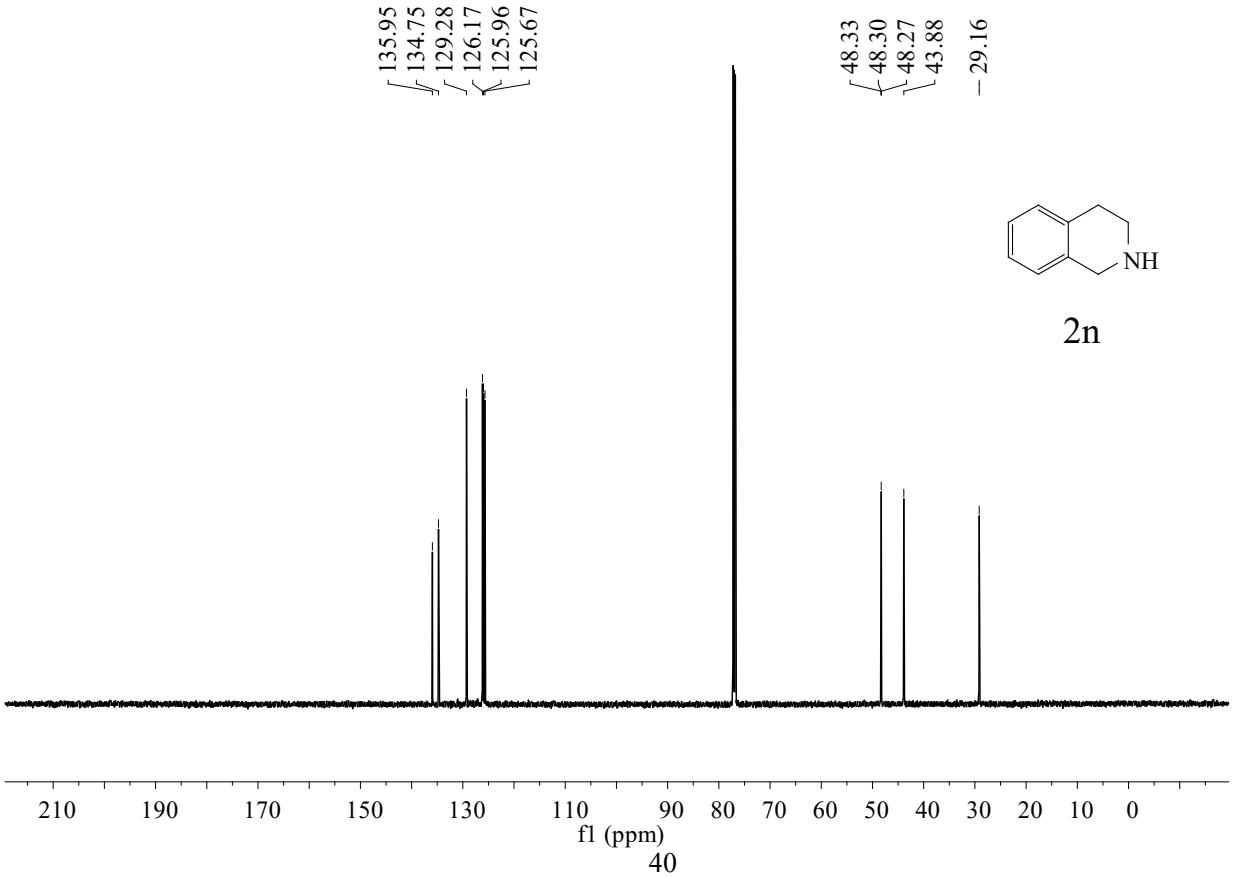

7.25
7.24
7.23
7.23
7.16
6.96
6.95
3.97
3.11
3.10
2.74
2.73
2.72
Br
NH
1.00
1.00
1.00
2.02
2.03
2.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

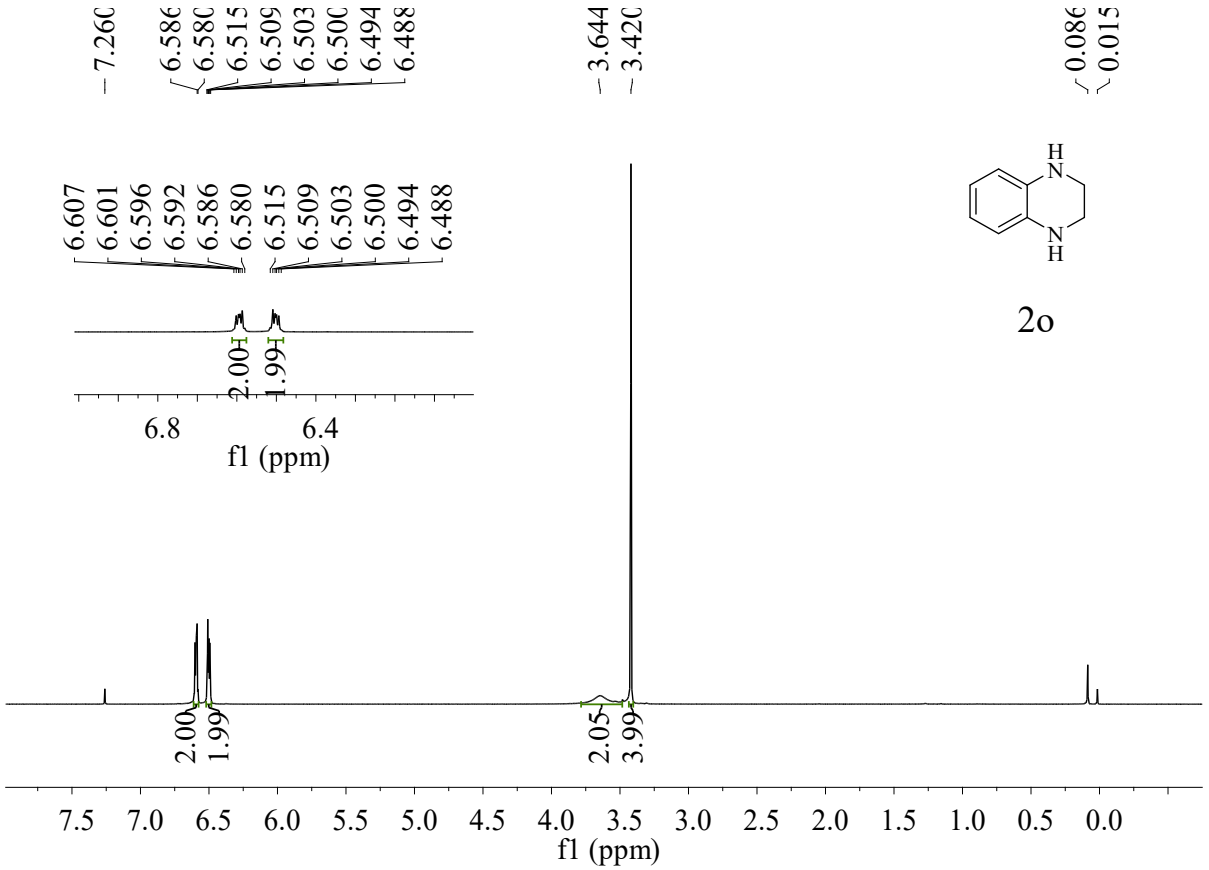
2m


138.14
133.76
130.95
129.04
119.17
48.00
43.63
28.70
Br
NH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

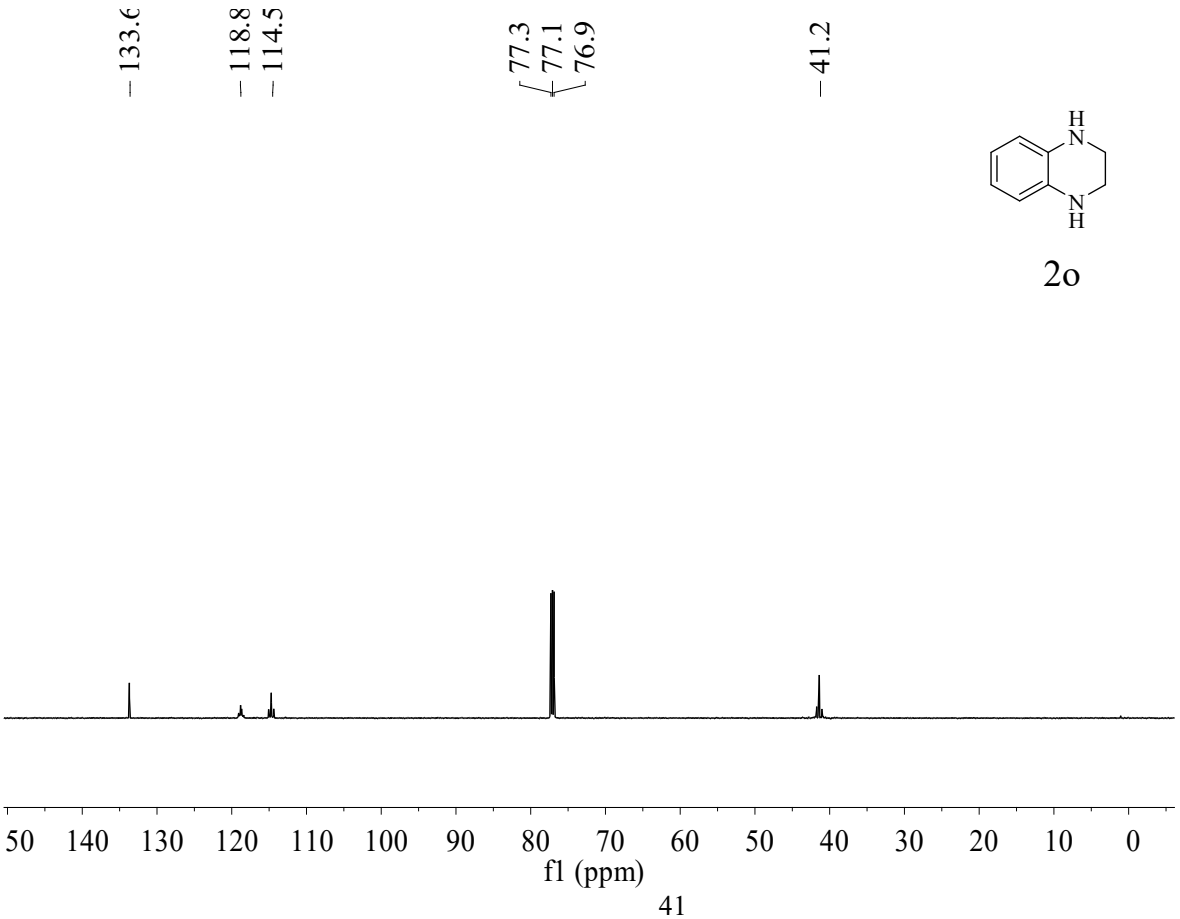
2m


7.17
7.16
7.15
7.12
7.12
7.04
7.04
7.03
4.05
3.17
2.83
1.91
NH
2n
2.04
1.00
1.04
2.11
2.12
2.09
1.12
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


135.95
134.75
129.28
126.17
125.96
125.67
48.33
48.30
48.27
43.88
29.16
NH
2n
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
6.586
6.580
6.515
6.509
6.503
6.500
6.494
6.488
3.644
3.420
0.086
0.015
6.607
6.601
6.596
6.592
6.586
6.580
6.515
6.509
6.503
6.500
6.494
6.488
2.00
1.99
6.8
6.4
f1 (ppm)
2.00
1.99
2.05
3.99
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)

2o


133.6
118.8
114.5
77.3
77.1
76.9
41.2
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2o

Section 7. References.

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