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Visible-Light Mediated Photocatalytic Aerobic Dehydrogenation of *N*-Heterocycles by Surface Grafted TiO_2 and 4-Amino-TEMPO

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1. Materials and chemicals:

Commercial TiO_2 Evonik Aeroxide P25 powder with 20% rutile and 80% anatase crystal phase and 50 m^2/g specific surface area and TiO_2 Hombikat UV 100 with 100% anatase crystal phase and ~ 320 m^2/g specific surface areas were kindly provided by Evonik and Venator (GmbH), respectively. All other reagents for the organic synthesis namely 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), 4-Hydroxy-TEMPO, 4-Oxo-TEMPO, 4-Amino-TEMPO, 1,2,3,4-tetra-hydroquinoline, 6-methoxy-1,2,3,4-tetrahydroquinoline, 2-methyl-1,2,3,4-tetrahydro-quinoline, 6-chloro-1,2,3,4-tetrahydroquinoline, 6-methyl-1,2,3,4-tetrahydroquinoline, 2-methyl-quinoline-8-carboxylic acid, 1,2,3,4-tetrahydroiso-quinoline, 1-methyl-1,2,3,4-tetrahydroiso-quinoline, 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline, 1-phenyl-1,2,3,4-tetrahydroisoquinoline, 1,2,3,4-tetrahydroquinoxaline, 2-phenyl-4,5-dihydro-1H-imidazole, indoline, and 2-methyl indoline were purchased from Combi-Blocks, Inc. and Sigma-Aldrich, respectively (≥96%). The other employed metal-oxide powders namely ZnO, WO_3, SiO_2, Al_2O_3 were purchased from Sigma-Aldrich. The employed solvents, i.e., methanol, ethanol, 2-propanol, acetonitrile, hexanes, ethyl acetate, dichloromethane with the highest purity (>99.9%) were purchased from Carl-Roth. For the preparation of co-catalysts as a precursor appropriate metal salts, namely nickel(II) nitrate hexahydrate $Ni(NO_3)_2{\bullet}6H_2O$, copper(II) chloride dihydrate $CuCl_2{\bullet}2H_2O$, iron(III) chloride

hexahydrate $FeCl_3$•$6H_2O$, cobalt(II) chloride hexahydrate $CoCl_2$•$6H_2O$, niobium(V) chloride $NbCl_5$, chloroplatinic acid H_2PtCl_6•$6H_2O$, palladium (II) acetate $Pd(OAc)_2$, rhodium-acetate dimer $Rh_2(OAc)_4$ were purchased from Sigma-Aldrich. The deionized water (18.2 MΩ cm) was obtained from a Sartorius Arium 611 apparatus. Unless stated otherwise, all chemicals were used without any purification.

Thin-layer chromatography (TLC) was carried out for determining the appropriate eluent before doing column chromatography on a commercial glass covered with 0.25 mm layer of Merck Silica gel 60F254 or Aluminum oxide 60F254 (EMD, Inc.). The separation of the reaction mixture was visualized under fluorescence UV light with 254 nm wavelength. A mobile phase eluent was determined for each substrate separately with a solvent mixture of hexanes and ethyl acetate or dichloromethane (CH_2Cl_2) and acetone. Afterward, column chromatography was carried out for all reaction samples with the determined eluent mixture, and 230-400 mesh silica gel (SiO_2) or Alumina Neutral flash grade was used as a stationary phase.

The nuclear magnetic resonance (NMR) characterization of all the obtained isolated compounds was done using Bruker Avance DPX-400 spectrometer. ^{1}H NMR and ^{13}C NMR measurements were recorded in chemical shifts (δ) with parts per million (ppm) relative to residual signals in deuterated chloroform $CDCl_3$ (7.26 ppm for ^{1}H; 77.23 ppm for ^{13}C) at room temperature. Abbreviations used in the NMR experiments are: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet.

Synthesis of substrate TBSO-1,2,3,4-tetrahydroquinoline (1b)[1]

To an oven-dried 10 mL, round bottom flask with a magnetic stirring bar was added 7-hydroxy-1,2,3,4-tetrahydroquinoline **1b** (298 mg, 2 mmol), triethylamine (0.82 mL, 5.9 mmol) and 0.5 mL of anhydrous dichloromethane (CH_2Cl_2) as a solvent.[2] After cooling to 0 °C in an ice bath, TBDMSCl (543 mg, 3.6 mmol) was added. The reaction mixture was purged with nitrogen and kept in the inert atmosphere during the reaction for 12 h. Afterward, the organic mixture was separated by adding saturated aqueous sodium chloride (brine). The brine layer was extracted with CH_2Cl_2 three times. The organic layers were combined, dried over $MgSO_4$, and filtered. After concentrating by a rotavapor, the residue was purified by column chromatography using silica gel (5:1 Hex/EtOAc). 368 mg (70%) of TBSO-THQ was isolated.

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2. Analytical methods

Gas chromatography-flame ionization detector (GC-FID) measurements: To optimize the reaction, quantitative analysis was performed to determine the concentrations of the substrates and desired products by employing GC-FID and an Rtx-5 (d = 0.25 mm) capillary column. The operating temperature was as following: injection temperature 250 °C, column temperature 100 °C (hold 2 min), from 100 °C to 300 °C at the rate of 10 °C/min, in splitless mode. Injection volume was 1.0 µl with nitrogen as the carrier gas. The concentrations of the substrate as well as of the products were determined derived from linear calibration curves prepared with commercial organic reactant and product purchased from Sigma-Aldrich (95-99.8% purity). 50 mol% benzyl alcohol purchased from Sigma-Aldrich with the highest (99.9%) purity was used as an internal standard.

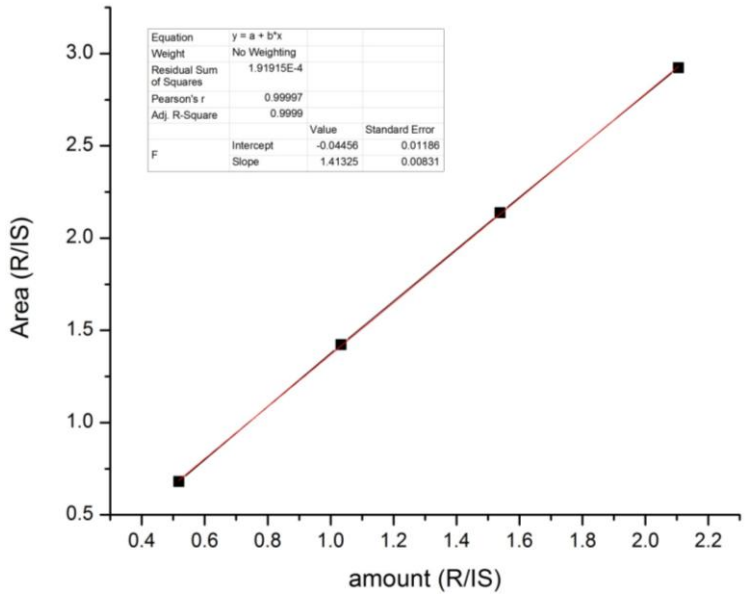

Fig S1 (a). Calibration curves for the reactant (R) 1,2,3,4-tetrahydroquinoline (THQ) obtained from the GC device with the presence of 50 mol% benzyl alcohol as an internal standard (IS).

$$n_R = \text{slope} \times n_{R(\text{calibration})} \frac{n_{IS(\text{measurement})}}{n_{IS(\text{calibration})}}$$

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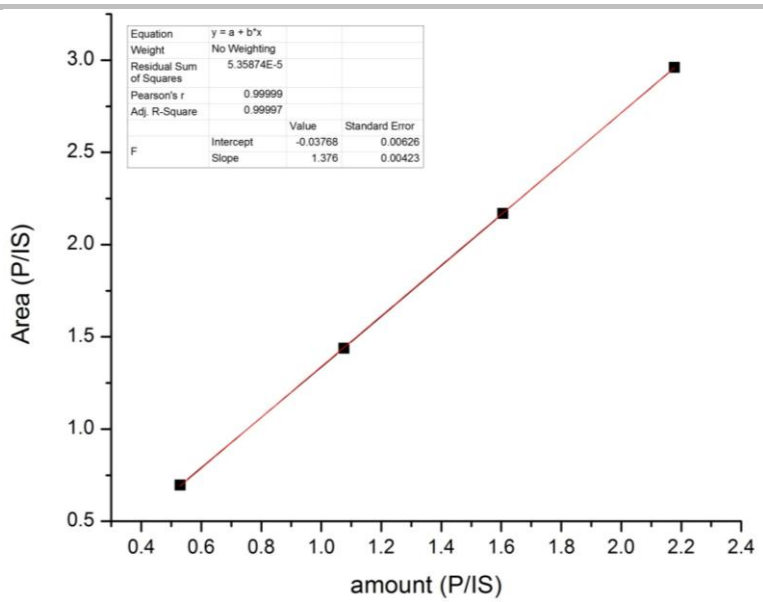

Fig S1 (b). Calibration curves for the product (P) quinoline obtained from the GC device with the presence of 50 mol% benzyl alcohol as an internal standard (IS).

$$n_P = \text{slope} \times n_{P(\text{calibration})} \frac{n_{IS(\text{measurement})}}{n_{IS(\text{calibration})}}$$

X-ray powder diffraction (XRD) analysis of photocatalysts.

Experimental: The X-ray powder diffractograms of TiO_2 (UV-100), 0.1 wt% Ni/TiO_2 before and after the reaction, were obtained by the Burker D8-advance X-ray diffractometer (Operating current: 40 mA, Operating Voltage: 40 kV) with Cu-Kα radiation (λ = 0.15406 nm) at room temperature in a scanning 2θ over the angular range of 10° – 80° with a step size of 0.05°. The diffraction data were analyzed using TOPAS 4.2 (Bruker-AXS) software by comparison with reference patterns in the database.

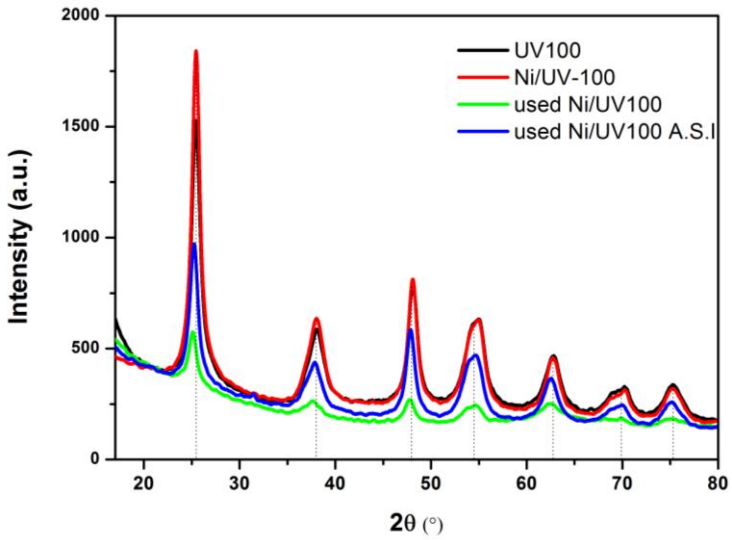

Figure S2. Polycrystalline X-ray diffraction patterns of the TiO_2 (UV-100) (black line), 0.1 wt% Ni/UV-100 (red line), used 0.1 wt% Ni/UV-100 (green line) and used 0.1 wt% Ni/UV-100 cleaned upon illumination with solar light for 2 h (blue line)

Transmission electron microscopy (TEM)

Experimental: The morphology of 0.1 wt% Ni grafted TiO_2 was measured using transmission electron microscopy (TEM), the Tecnai G2 F20 TMP from FEI at 200 kV field-effect FEG. The samples were sonicated in ethanol for 15 min before the TEM analysis, and the alcoholic solution was dropped on a 300 mesh carbon-coated copper TEM grid, purchased from Quantifoil, and the images were taken in a bright field mode.

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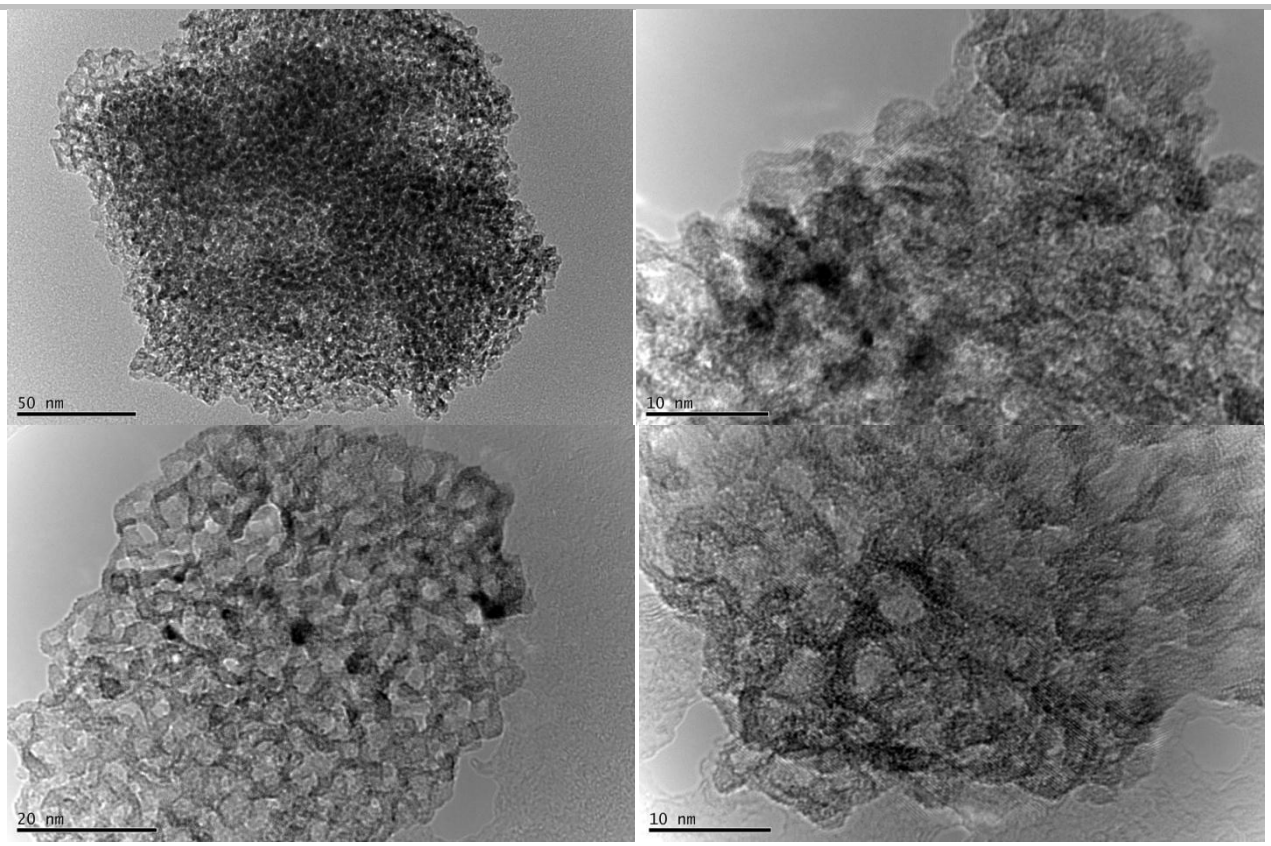

Figure S3. TEM images of 0.1 wt% Ni(II) grafted TiO_2 (UV-100)

UV−visible diffuse reflectance spectroscopy (DRS)

Experimental: Diffuse reflectance spectra (DRS) of powders were recorded in wavelength range from 190 to 800 nm using a Varian Spectrophotometer Cary-100 Bio from Agilent. Barium sulfate was used as a 100% reflectance reference for powder measurement. The F(R) and band gap energy were calculated according to the Kubelka Munk equation and Tauc plot, respectively.

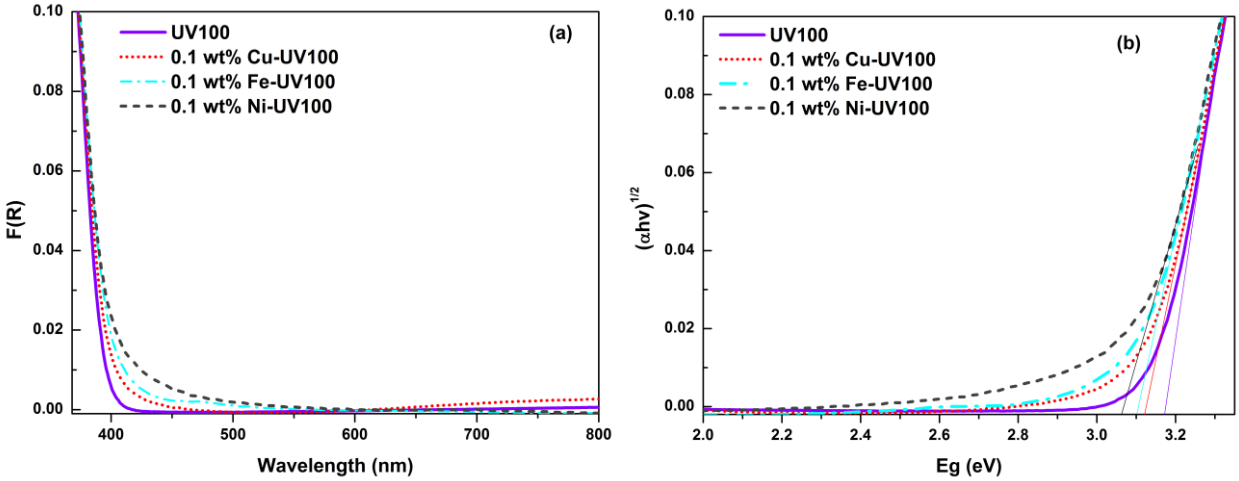

Figure S4. Absorption spectra calculated according to the Kubelka-Munk equation (a) and bandgap (Eg) calculation of Tauc plot (b) of photocatalyst powders used in the present study: UV-100 (TiO_2), Cu(II)-grafted UV-100, Fe(III)-grafted UV-100, and Ni(II)-grafted UV-100.

UV-Vis absorption spectra of the suspended samples in 2-propanol were recorded in wavelength range from 190 to 800 nm using a Varian Spectrophotometer Cary-100 Bio from Agilent.

In Figure S11, the absorption spectra of different metal ions grafted TiO_2 and 1,2,3,4-tetrahydroquinoline mixtures are shown.

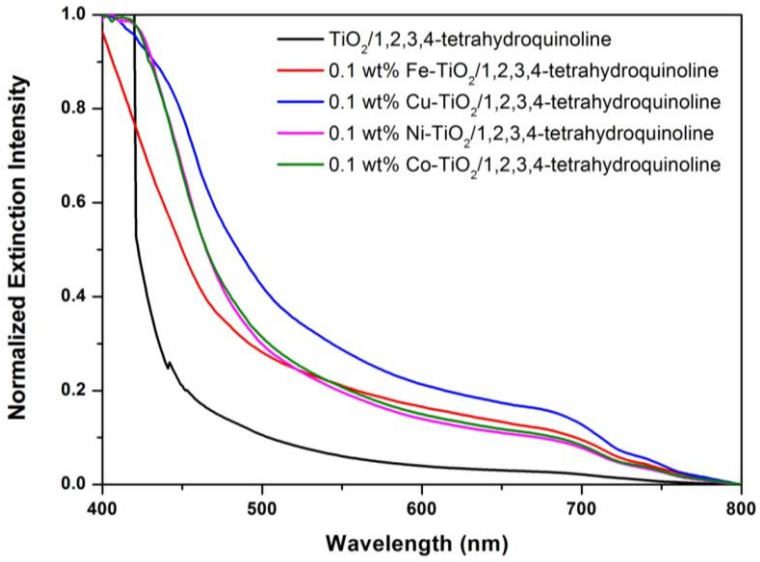

Figure S5. Normalized extinction spectra of Metal ions / TiO_2 and 1,2,3,4-tetrahydroquinoline.

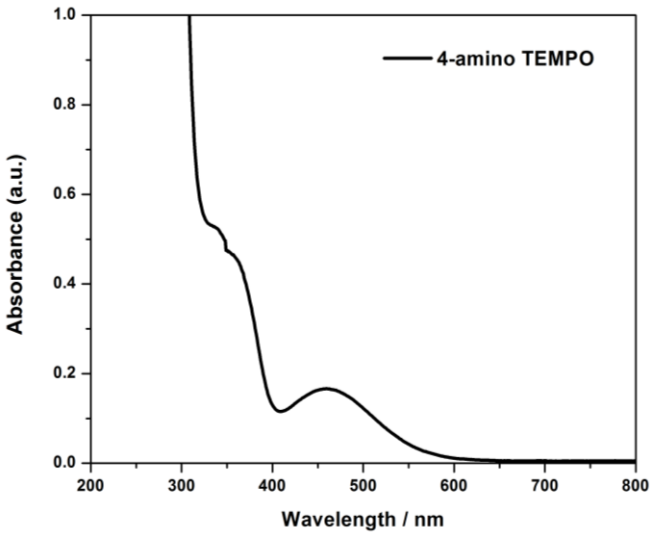

Figure S6. Absorption spectra of 4-amino TEMPO

The absorption spectra of bare TiO_2 (UV-100) and UV-100/H_2O_2 were measured and shown in Figure S7. Since the mixture of hydrogen-peroxide and titania formed a surface complex, the suspension color turned brown, which absorbed light in the visible region.

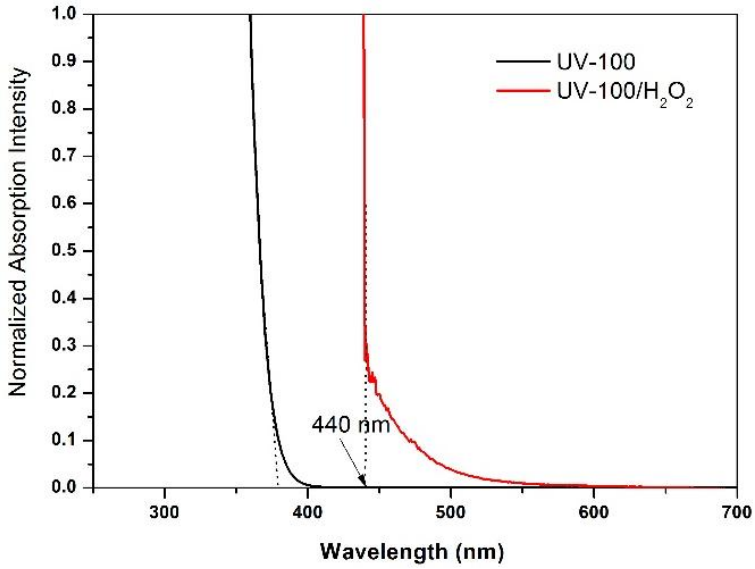

Figure S7. Absorption spectra of TiO_2 (UV-100) (black line) and UV-100/ H_2O_2 adsorbed onto a TiO_2 surface (red line)

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Nitrogen physisorption measurements

Experimental: The specific surface area and nitrogen adsorption-desorption isotherms of samples before and after the photocatalytic reaction were measured with the Quantachrome Autosorb-3 instrument at liquid nitrogen temperature (77 K). The samples were firstly degassed under vacuum at 80 °C for 24 h before measurement. The specific surface area was obtained by applying the Brunauer-Emmett-Teller (BET) method. Barrett-Joyner-Halenda (BJH) equation was used for the calculation of the pore size distribution. The total pore volume was estimated using the single point method at p/p0 = 0.99.

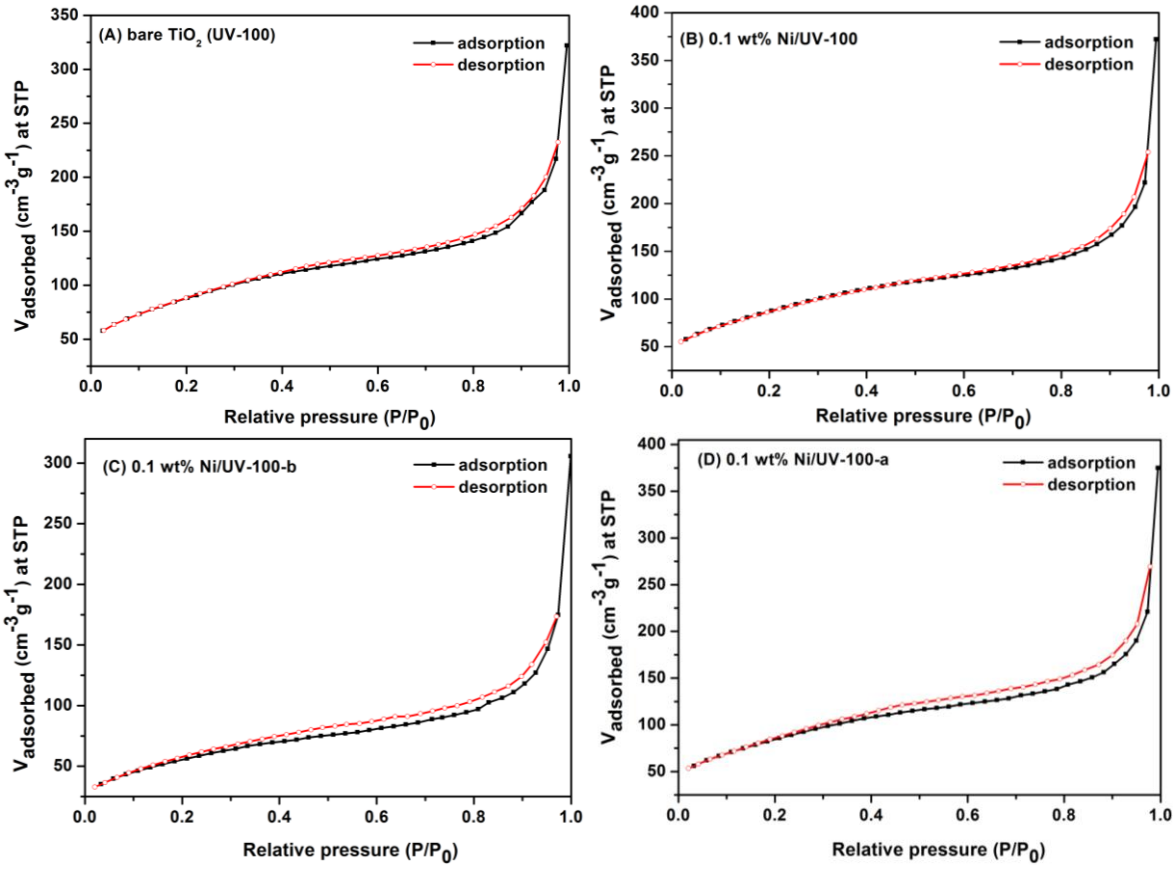

Figure S8. Nitrogen physisorption isotherms for (A) bare TiO_2 (UV-100); (B) surface grafted 0.1 wt% Ni/UV-100 before reaction, (C) surface grafted 0.1 wt% Ni/UV-100 after 4th cycle reaction cleaned by washing 3 times with acetone, (D) surface grafted 0.1 wt% Ni/UV-100 after 4th cycle reaction cleaned by illumination with solar simulator (500 W) for 2 hours.

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Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement

Experimental: The content of Ni ions grafted onto TiO_2 surface before and after the reaction was determined by using the Varian 715-ES from VARIAN optical emission spectrometer with radial inductively coupled plasma as excitation source ICP-OES and a patented VistaChip CCD simultaneous detector with echelle grating. The samples were digested in an aqua regia (1 : 3 nitric acid and hydrochloric acid mixture) at 150 °C for 3 h before measurement and elemental analysis were carried out in a 3% HNO_3 solution as well as by coupling to a femtosecond laser.

Electron paramagnetic resonance (EPR) spectroscopy measurement

Experimental: Powder bare UV100 (TiO_2) and 0.1 wt% Ni(II) grafted UV100 were conducted in order to detect the paramagnetic sites existed in darkness and generated under illumination. MiniScope MS 400 X-band EPR spectrometer were employed and experiments were carried out at 77 K liquid nitrogen temperature. During the measurement the input parameters were as following: the microwave frequency 9.54 GHz, microwave power 5 mW, modulation frequency 100 kHz, modulation amplitude 0.15 mT. The experiment was carried out under irradiation with UV-vis light (Xe lamp from Hamamatsu, LC 8) with the wavelength of λ=300-450 nm and 200 W power. The g values were calculated with the Equation: $g = h\nu/\beta B_0$ (B_0 – external magnetic field, β – Bohr magneton, g – Lande g-factor).

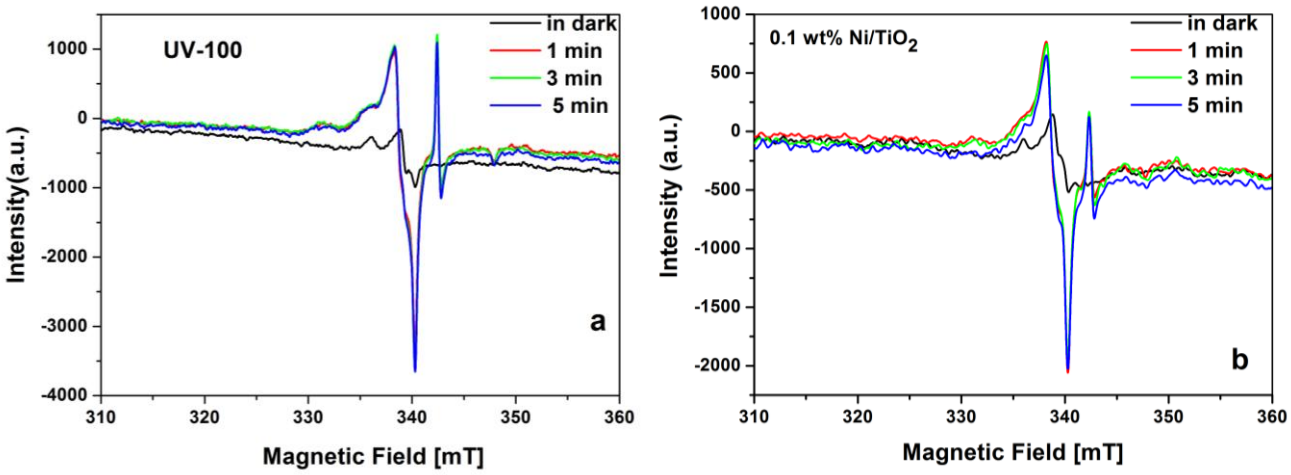

Figure S9. In situ EPR spectra at 77K of bare TiO_2 (UV-100) (a) with the magnetic field, and 0.1 wt% Ni/TiO_2 (UV-100) (b) with the magnetic field

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The EPR spectra obtained from liquid measurement using capillary tube recorded at room temperature (Figure S10). 2 mM 4-amino-TEMPO was dissolved in *i*-PrOH. During the measurement the input parameters were as following: the microwave frequency 9.42 GHz, microwave power 5 mW, modulation frequency 100 kHz, modulation amplitude 0.15 mT. LED blue light has been used as a light source (λ=453).

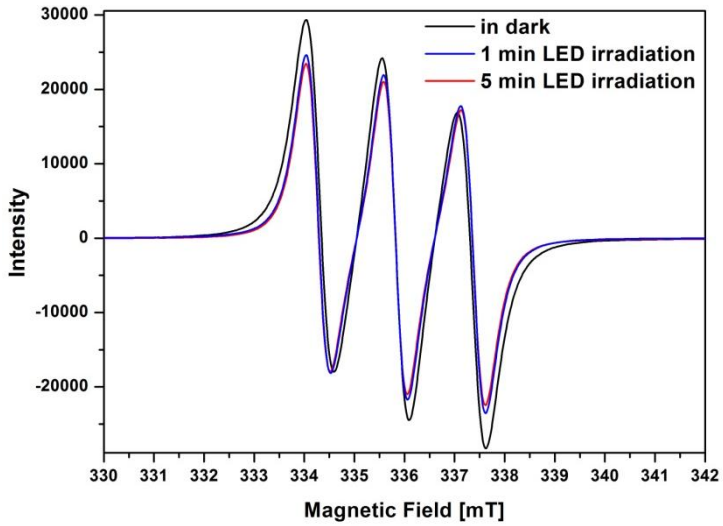

Figure S10. The EPR spectra of 4-amino-TEMPO in dark (black line), during 1 min visible light (λ= 453 nm) irradiation (blue line) and 5 min visible light (λ= 453 nm) irradiation (red line) in i-PrOH solvent.

ATR-FTIR spectroscopy measurement

Experimental: In order to confirm the formation of the surface-complex of photocatalyst with the amine, attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectra were recorded using ATR-FTIR spectrometer IFS 66 BRUKER equipped with an internal reflection element 45° ZnSe crystal and a deuterated triglycine sulfate (DTGS) detector. The spectra were recorded from acetonitrile and TiO_2 suspension mixed with 1,2,3,4-THQ, with 300 scans at 4 cm^{-1} resolution, and the OPUS version 6.5 software was used for analyzing data. The background was subtracted with a baseline correction spectrum in order to reduce the slight shift as a result of device unsteadiness.

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FT-IR spectroscopy measurement

Experimental: Tensor 27 from Bruker, which has a Pike Miracle single-bounce attenuated total reflectance (ATR) cell equipped with a ZnSe single crystal, was used for the powder measurement of TiO_2, 0.1 wt% Ni grafted TiO_2 before and after the photocatalytic experiment. The device was equipped with a room temperature DTGS detector, a KBr beamsplitter, and, a mid-IR source (4000 to 650 cm^{-1}) with the resolution of 1 cm^{-1}. The OPUS 5.0 program (Optical User Software) from Bruker was employed for data collection and analysis.

3. Control reactions

Additionally, comparative results of different solvents were carried out for 24 h in the same reaction ambient and showed at Table S1.

Table S1. Control reactions

Entry	Catalysts	Solvent	Condition	Y (%)	S (%)
1	UV-100	MeOH	4-amino TEMPO	12	13
2	UV-100	EtOH	4-amino TEMPO	32	37
3	UV-100	i-PrOH	4-amino TEMPO	81	82
4	UV-100	CH_3CN	4-amino TEMPO	79	81
5[a]	UV-100	i-PrOH	4-amino TEMPO	N.D.	N.D.
6[a]	Ni/UV-100	i-PrOH	4-amino TEMPO	N.D.	N.D.
7[b]	UV-100	i-PrOH	-	4	86
8[b]	UV-100	i-PrOH	4-amino TEMPO	6	83

Reaction condition: 10 mg UV-100, 0.4 mmol 1, 2, 3, 4-tetrahydroquinoline, 0.08 mmol 4-amino TEMPO, 24 h, room temperature, 1 atm O_2, 453 LED lamp, 4 mL solvent: methanol (entry 1), ethanol (entry 2), 2-propanol (entry 3), acetonitrile (entry 4). [a]in the absence of O_2, [b] 505 LED lamp

Table S2. Some control reactions over different metal-oxides.

Entry	Catalysts	Solvent	Y (%)	S (%)
1	ZnO	i-PrOH	3	96
2	WO_3	i-PrOH	5	97
3	Al_2O_3	i-PrOH	<2	97
4	SiO_2	i-PrOH	No reaction	-

Reaction condition: 10 mg metal-oxide, 0.4 mmol 1, 2, 3, 4-tetrahydroquinoline, 24 h, room temperature, 1 atm O_2, 453 LED lamp, 4 mL solvent: i-PrOH

4. Catalyst recycling experiments

In an oven-dried 20 mL glass vial equipped with a magnetic stirring bar, 10 mg TiO_2 (0.03 $mol \cdot L^{-1}$), 4 mL 2-propanol (as the solvent), and 0.08 mmol 4-amino-TEMPO (13.7 mg), and 0.4 mmol 1,2,3,4-THQ were added. The reaction mixture was sonicated for 5 min until the TiO_2 catalyst was dispersed. After tightly sealing the reactor, the reaction was carried out at 1 atm O_2 environment upon visible light irradiation for 24 h. After completion of the reaction, the catalyst was separated by centrifugation and benzyl alcohol (50 mol%, 20.6 µl, 0.2 mmol) was added to the reaction mixture as an internal standard. The yield was analyzed by GC-FID chromatography. The collected catalyst was washed three times with acetone, dried at 70 °C for 12h, and used without further purification for the next run. Although the photocatalytic activity and selectivity of the catalyst did not decrease significantly, the specific surface area of the catalyst decreased up to ~206 m^2/g presumably because the absorption of some organic molecules, as well as H_2O_2 on the surface of titania, led to the occupation of some mesoporous cavities. However, irradiating of the water dispersed used catalyst for 2 h in air atmosphere upon solar simulator light (500 W) resulted in complete recovery of the specific surface area.

5. Detection of hydrogen peroxide (H_2O_2) after dehydrogenation reaction of 1,2,3,4-tetrahydroquinoline in the presence and in the absence of 4-amino-TEMPO

The formation of H_2O_2 in the reaction mixture was detected with KI as reported by Balaraman et al. with slightly changing in the method,[3] and the pictures were shown in Fig S11.

H_2O_2 oxidized iodide ion to iodine in the presence of an acid and molybdate catalyst. The liberated iodine was detected using a starch solution as the indicator.

$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O$

Note: This method was suitable for the determination of the low concentration of **H_2O_2 (**0.1-5%) with minimal interference from organic compounds.

Used reagents for the H_2O_2 analysis:

All reagents were analytical reagent grade, and only deionized water (Milli-Q 18.2 mΩ•cm) was used.

1. Potassium Iodide (KI): 10 g of KI was dissolved in 100 mL of water (0.6 M).

2. Ammonium molybdate [$(NH_4)_6$ Mo_7O_{24}•$4H_2O$]: 0.018 g of $(NH_4)_6$ Mo_7O_{24}•$4H_2O$ was dissolved in 75 mL of water (2×10^{-3} M). While stirring, 30 mL of 98% concentrated H_2SO_4 was slowly added.

3. Potassium Iodate (KIO_3): 0.357g of KIO_3 was weighed and transferred to a 100 mL volumetric flask, and 40 mL of deionized water, 0.2 g of sodium hydroxide, and 2 g of potassium iodide were added. The mixture was agitated until complete dissolving and diluted to the volume to make 1.7 M solution.

4. Starch Solution (10 g/L): 10 g of soluble starch was added into a 150 mL beaker. While stirring, about 5 mL of water was gradually added until a paste was formed. The paste was then added to 100 mL of boiling water, and the resulting solution was cooled at room temperature. 5 g of KI was added to the solution and stirred until complete dissolution.

Procedure:

After 24 h photocatalytic dehydrogenation of 1, 2, 3, 4-tetrahydroquinoline to quinoline, the photocatalyst was separated by centrifugation from the reaction mixture. The clear reaction solution was diluted with DI water to 15 mL **(A1 and B1)**. To a 20 mL scintillation vial, 2 mL from the diluted reaction mixture **(A1 and B1)** was added and additionally diluted with 5 mL of Milli-Q water with stirring in order to get a lighter-colored solution **(A2 and B2).** 3 mL of **Ammonium molybdate and H_2SO_4** solution was added which turned the color of the solution to the pale yellow (**A3 and B3**). To these solution 6 mL 10% KI solution was added. The color of the solution changed to darker yellow **(A4 and B4)** due to the formation of molecular iodine. As shown from the pictures, the color was more yellowish at **A3**. At the last step, to the solution, 2 mL of freshly prepared starch solution was added and the color changes to dark blue-black (**A5 and B5**). The color of the **B5** solution was lighter in comparison with **A5** solution. This observation supported the role of 4-amino-TEMPO to reduce hydrogen peroxide. When 2 mL of the dark blue solution was diluted with 10 mL of DI water, a more visible difference was

observed **(A6 and B6).** The lighter color confirmed the presence of less amount of H_2O_2 in the reaction mixture with 4-amino-TEMPO.

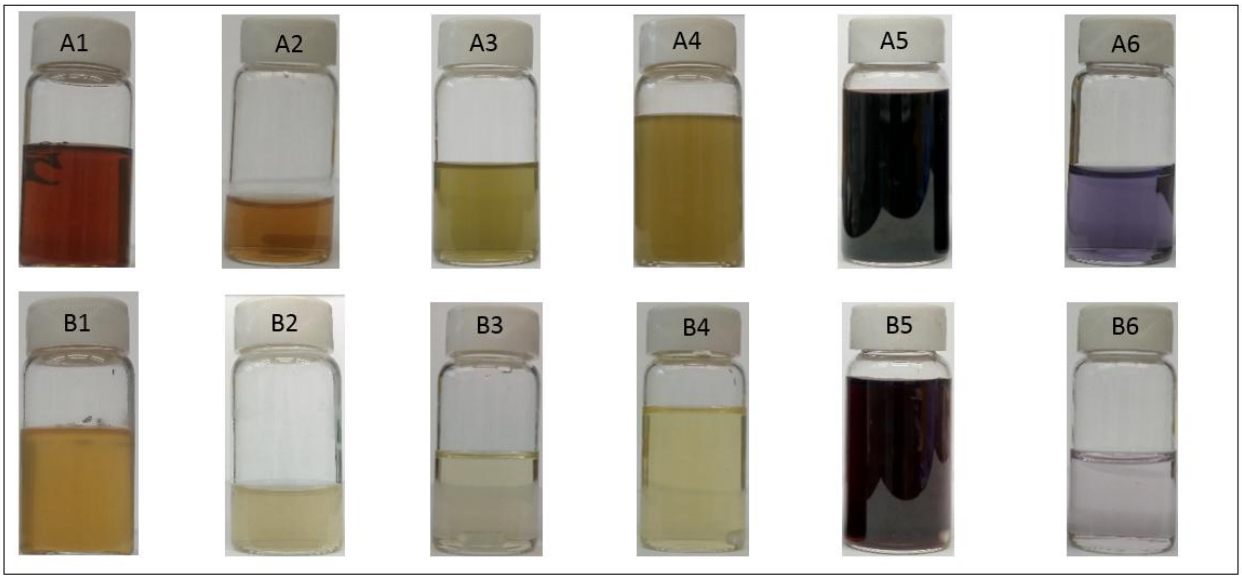
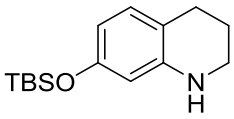
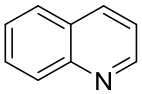


Figure S11. The solution obtained after dehydrogenation reaction of 1,2,3,4-tetrahydroquinoline using UV-100 as a photocatalyst **(A1)** The solution obtained after dehydrogenation reaction of 1,2,3,4-tetrahydroquinoline using UV-100 as a photocatalyst and 4-amino-TEMPO **(B1)**

6. Characterization Data

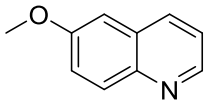


(1b) The white powder product **TBSO-1,2,3,4-tetrahydroquinoline** was isolated with flash column using silica gel (5:1 Hex/EtOAc) (368 mg, 70%) of TBSO-THQ was isolated. Characterization data matched with those reported.[1] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.76 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.11 (dd, *J* = 8.1, 2.4 Hz, 1H), 5.98 (d, *J* = 2.4 Hz, 1H), 3.30 – 3.21 (m, 2H), 2.68 (t, *J* = 6.6 Hz, 2H), 1.95 – 1.87 (m, 2H), 0.96 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.03, 144.95, 129.44, 114.15, 108.57, 105.09, 76.87, 76.55, 76.23, 41.43, 25.85, 25.28, 21.99, 17.73, -4.84.

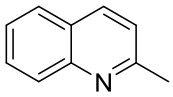


(2a) Following the representative procedure, **quinoline 2a** was synthesized from 0.4 mmol **1,2,3,4-tetrahydroquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The transparent (colorless) product was isolated with flash column using silica gel (3:2 Hex/EtOAc)

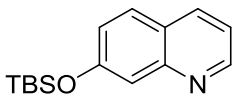
(43.6 mg, 91%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-d) δ 8.93 (dd, J = 4.3, 1.8 Hz, 1H), 8.17 (t, J = 8.7, 8.4 Hz, 1.2 Hz, 2H), 7.83 (dd, J = 8.2, 1.5 Hz, 1H), 7.73 (t, J = 8.4, 6.9, 1.5 Hz, 1H), 7.55 (t, J = 8.1, 6.8, 1.2 Hz, 1H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.96, 147.86, 135.57, 129.03, 127.83, 127.32, 126.28, 126.07, 120.61.



(2b) Following the representative procedure, **6-methoxy-quinoline 2b** was synthesized from 0.4 mmol **6-methoxy- 1,2,3,4-tetrahydroquinoline (**upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The white-beige product was isolated with flash column using silica gel (2:1 Hex/EtOAc) (60 mg, 94%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 – 8.71 (m, 1H), 8.07 – 7.96 (m, 2H), 7.40 – 7.30 (m, 2H), 7.06 (dd, *J* = 3.0, 1.6 Hz, 1H), 3.96 – 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.71, 147.87, 144.36, 134.81, 131.07, 129.29, 122.28, 121.35, 105.12, 55.51.

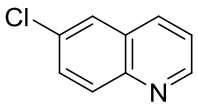


(2c) Following the representative procedure, **quinaldine 2c** was synthesized from 0.4 mmol **1,2,3,4-tetrahydroqunaldine** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of acetonitrile in 1 atm O_2 (balloon) condition. The colorless product was isolated with flash column using silica gel (3:2 Hex/EtOAc) (55.2 mg, 92%). Characterization data matched with those reported by AIST.[8] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (ddd, *J* = 8.6, 2.6, 0.9 Hz, 2H), 7.75 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.67 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.32 – 7.22 (m, 1H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.97, 147.87, 136.13, 129.39, 128.63, 127.47, 126.47, 125.64, 121.97, 25.38.

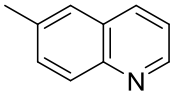


(2d) Following the representative procedure, 7-**TBSO-quinoline 2d** was synthesized from 0.4 mmol 7-**TBSO- 1,2,3,4-tetrahydroquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The pale white product was isolated with flash column using silica gel (5:1 Hex/EtOAc) (86 mg, 83 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.06 (ddd, *J* = 8.2, 1.8, 0.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.47 (dt, *J* = 2.5, 0.6 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 1.03 (s, 9H), 0.29 (s, 6H). ^{13}C NMR (101 MHz,

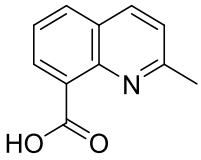
$CDCl_3$) δ 156.36, 150.13, 149.25, 135.18, 128.37, 123.39, 122.55, 122.52, 118.62, 115.69, 25.27, 25.26, 25.22, 17.83, -4.55, -4.83, -5.12.



(2e) Following the representative procedure, **6-Chloroquinoline 2e** was synthesized from 0.4 mmol **6-chloro - 1,2,3,4-tetrahydroquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The product was isolated with flash column using silica gel (3:1 Hex/EtOAc) (62.2 mg, 92%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-d) δ 8.89 (dd, J = 4.2, 1.7 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.77 (d, J = 2.3 Hz, 1H), 7.62 (dd, J = 9.0, 2.3 Hz, 1H), 7.39 (dd, J = 8.4, 4.2 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 150.59, 146.64, 135.08, 132.27, 131.12, 130.39, 128.82, 126.40, 121.90.

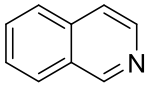


(2f) Following the representative procedure, **6-methylquinoline 2f** was synthesized from 0.4 mmol **6-methyl - 1,2,3,4-tetrahydroquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The product was isolated with flash column using silica gel (3:1 Hex/EtOAc) (33.3 mg, 74%). Characterization data matched with those reported by Sigma Aldrich.[5] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.34 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.54, 146.93, 136.37, 135.29, 131.73, 129.10, 128.32, 126.58, 121.06, 21.54.

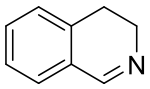


(2g) Following the representative procedure, **2-methylquinoline-8-carboxylic acid 2g** was synthesized from 0.4 mmol **2-methyl-8-carboxylic acid - 1,2,3,4-tetrahydroquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The product was isolated with flash column using silica gel (1:2 Hex/EtOAc) (69.7 mg, 93%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.02 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.36, 158.52, 144.53, 138.47, 134.62, 132.63, 126.18, 126.10, 123.59, 122.64, 24.59.

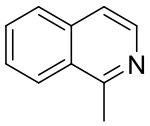
SUPPORTING INFORMATION



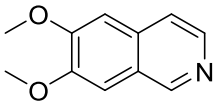
(2h) Following the representative procedure, **isoquinoline 2h** was synthesized from 0.4 mmol **1,2,3,4-tetrahydroisoquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The colorless product was isolated with flash column using alumina gel (3:1 Hex/EtOAc) (22.1 mg, 43%). Characterization data matched with those reported by Sigma Aldrich.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.26 (t, *J* = 1.0 Hz, 1H), 8.53 (d, *J* = 5.7 Hz, 1H), 7.97 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.82 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.73 – 7.57 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.18, 142.67, 135.41, 129.94, 128.32, 127.24, 126.85, 126.09, 120.05.



(2h*) Following the representative procedure, **3,4-dihydroisoquinoline 2h*** was synthesized from 0.4 mmol **1,2,3,4-tetrahydroisoquinoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition as a second main product. The pale yellow product was isolated with flash column using alumina gel (3:1 Hex/EtOAc) (27.2 mg, 52%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.37 (td, *J* = 7.1, 2.1 Hz, 1H), 7.35 – 7.21 (m, 2H), 7.24 – 7.11 (m, 1H), 3.79 (ddd, *J* = 9.9, 6.2, 2.2 Hz, 2H), 2.83 – 2.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.99, 135.98, 131.81, 130.69, 127.06, 126.85, 126.72, 47.02, 24.68.

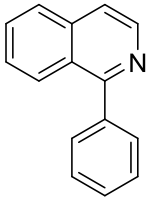


(2i) Following the representative procedure, **1-methyl isoquinoline 2i** was synthesized from 0.4 mmol **1-methyl-1,2,3,4-tetrahydroisoquinoline** upon 24 h LED blue light illumination, at 47°C temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The pale yellow product was isolated with flash column using silica gel (2:1 Hex/EtOAc) (43.1 mg, 75%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 5.8 Hz, 1H), 8.12 (dq, *J* = 8.3, 1.0 Hz, 1H), 7.80 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.59 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.50 (d, *J* = 5.8 Hz, 1H), 2.97 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 158.13, 141.37, 135.44, 129.45, 127.06, 126.74, 126.55, 125.16, 118.79, 21.96.

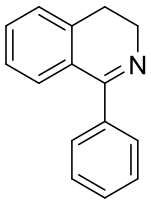


(2j) Following the representative procedure, **6,7-dimethoxy-isoquinoline 2j** was synthesized from 0.4 mmol **6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline** upon 24 h LED blue light illumination, at room temperature, in a

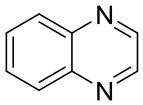
solvent of 2 mL of CH_2Cl_2 (dichloromethane) and 2 mL of 2-propanol in 1 atm O_2 (balloon) condition. The pale yellow product was isolated with flash column using silica gel (10:1 DCM/acetone) (61.5 mg, 81%). Characterization data matched with those reported.[6,7] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.05 (s, 1H), 8.39 (d, *J* = 5.7 Hz, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.21 (s, 1H), 7.07 (s, 1H), 4.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.64, 149.95, 149.54, 141.58, 132.15, 124.38, 118.85, 104.93, 104.17, 55.70, 55.66.



(2k) Following the representative procedure, **1-phenyl isoquinoline 2k** was synthesized from 0.4 mmol **1-phenyl-1,2,3,4-tetrahydroisoquinoline** upon 24 h LED blue light illumination, at 47°C temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The white powder product was isolated with flash column using silica gel (3:1 Hex/EtOAc) (27.0 mg, 33%). Characterization data matched with those reported.[7] NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 5.7 Hz, 1H), 8.11 (dq, *J* = 8.6, 1.0 Hz, 1H), 7.89 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.73 – 7.67 (m, 3H), 7.65 (dd, *J* = 5.7, 0.9 Hz, 1H), 7.57 – – 7.47 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.41, 141.89, 139.26, 136.51, 129.64, 129.56, 128.22, 127.99, 127.24, 126.80, 126.63, 126.38, 119.93.

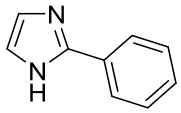


(2k*) Following the representative procedure, **1-phenyl-3,4-dihydroisoquinoline 2k*** was synthesized from 0.4 mmol **1-phenyl-1,2,3,4-tetrahydroisoquinoline** upon 24 h LED blue light illumination, at 47°C temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition as a second main product. The product was isolated with flash column using silica gel (3:1 Hex/EtOAc) (43.9 mg, 54%). Characterization data matched with those reported.[7] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.54 (m, 2H), 7.49 – 7.33 (m, 4H), 7.31 – 7.21 (m, 3H), 3.89 – 3.83 (m, 2H), 2.84 – 2.78 (m, 2H).) ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.22, 138.98, 138.80, 130.61, 129.24, 128.79, 128.74, 128.09, 127.87, 127.35, 126.51, 47.62, 26.28.

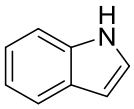


(2l) Following the representative procedure, **quinoxaline 2l** was synthesized from 0.4 mmol **1,2,3,4-tetrahydroquinoxaline (**upon 24 h LED blue light illumination, at room temperature, 4 mL of 2-propanol in 1 atm O_2 (O_2 purging) condition. The white crystal product was isolated with flash column using alumina gel (5:1 Hex/EtOAc) (43.3 mg, 83%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz,

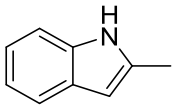
Chloroform-*d*) δ 8.86 (d, *J* = 6.7 Hz, 2H), 8.12 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.79 (dd, *J* = 6.5, 3.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.52, 142.61, 129.61, 129.08.



(2m) Following the representative procedure, **2-phenylimidazole 2m** was synthesized from 0.4 mmol 2-phenyl-2-imidazoline upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in 1 atm O_2 (balloon) condition. The product was isolated with flash column using silica gel (5:1 Hex/EtOAc) (53.2 mg, 93%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.38 – 7.28 (m, 3H), 7.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.16, 130.37, 128.87, 128.59, 125.52, 123.06.



(2n) Following the representative procedure, **indole 2n** was synthesized from 0.4 mmol **indoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4 mL of 2-propanol in air (needle poked through septum). The colorless product was isolated with flash column using silica gel (12:1 Hex/EtOAc) (39.4 mg, 84%). Characterization data matched with those reported by Sigma Aldrich.[4] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.16 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.59 (ddd, *J* = 3.1, 2.1, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.33, 127.41, 123.66, 121.54, 120.29, 119.37, 110.56, 102.19.



(2o) Following the representative procedure, **2-methyl indole 2o** was synthesized from 0.4 mmol **2-methyl indoline** upon 24 h LED blue light illumination, at room temperature, in a solvent of 4ml of 2-propanol in 1atm O_2 (O_2 purging) condition. The colorless product was isolated with flash column using silica gel (13:1 Hex/EtOAc) (43.2 mg, a mixture of 7% starting material and 76% product). Notably, because the starting material and the product had the same R_f value, the unconverted starting material could not be separated from the product. Characterization data matched with those reported by AIST.[8] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.55 (dq, *J* = 7.5, 0.9 Hz, 1H), 7.28 (dq, *J* = 8.1, 0.9 Hz, 1H), 7.18 – 7.06 (m, 2H), 6.24 (dp, *J* = 2.0, 1.0 Hz, 1H), 2.44 (s, *J* = 1.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.61, 134.60, 128.63, 124.31, 120.48, 119.18, 109.77, 99.95, 13.25.

7. References

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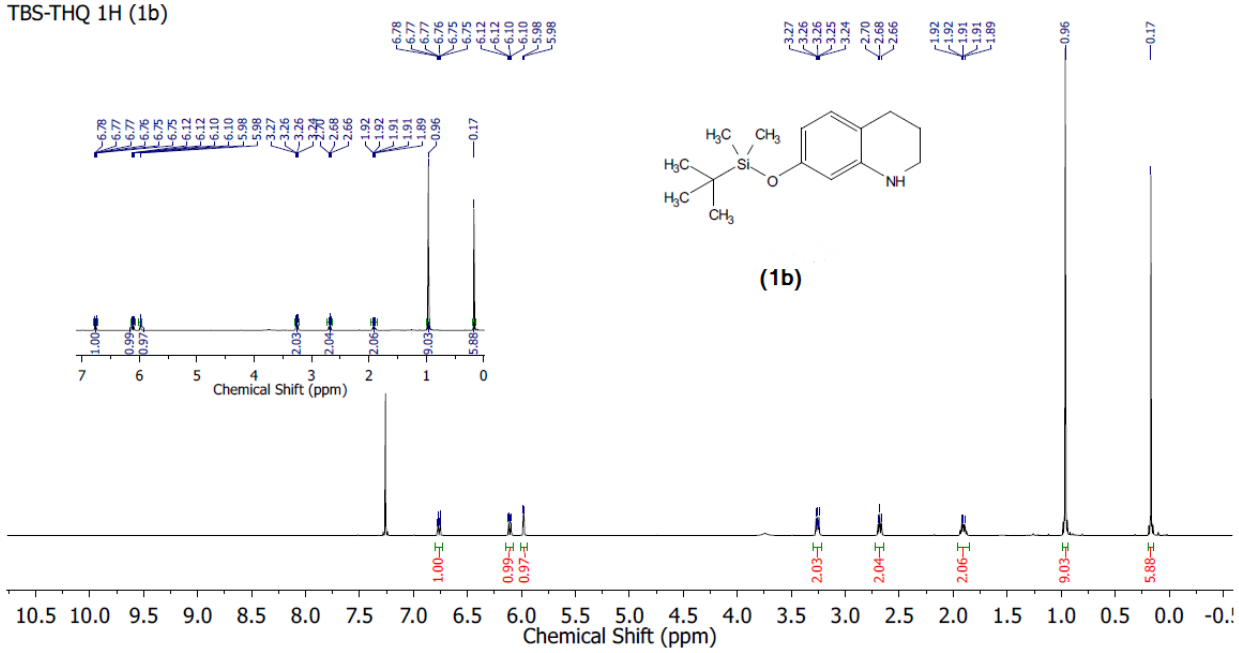
(8) https.//sdbs.db.aist.go.jp

SUPPORTING INFORMATION

8. Copy of 1H and 13C Spectra

TBS-THQ 1H (1b)



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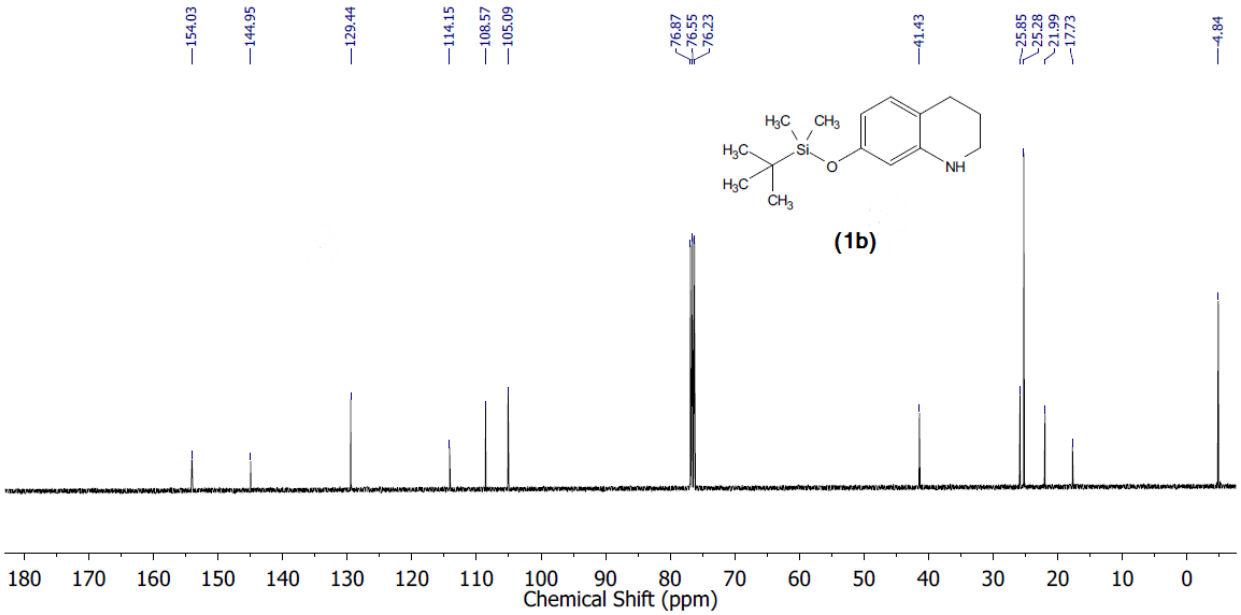
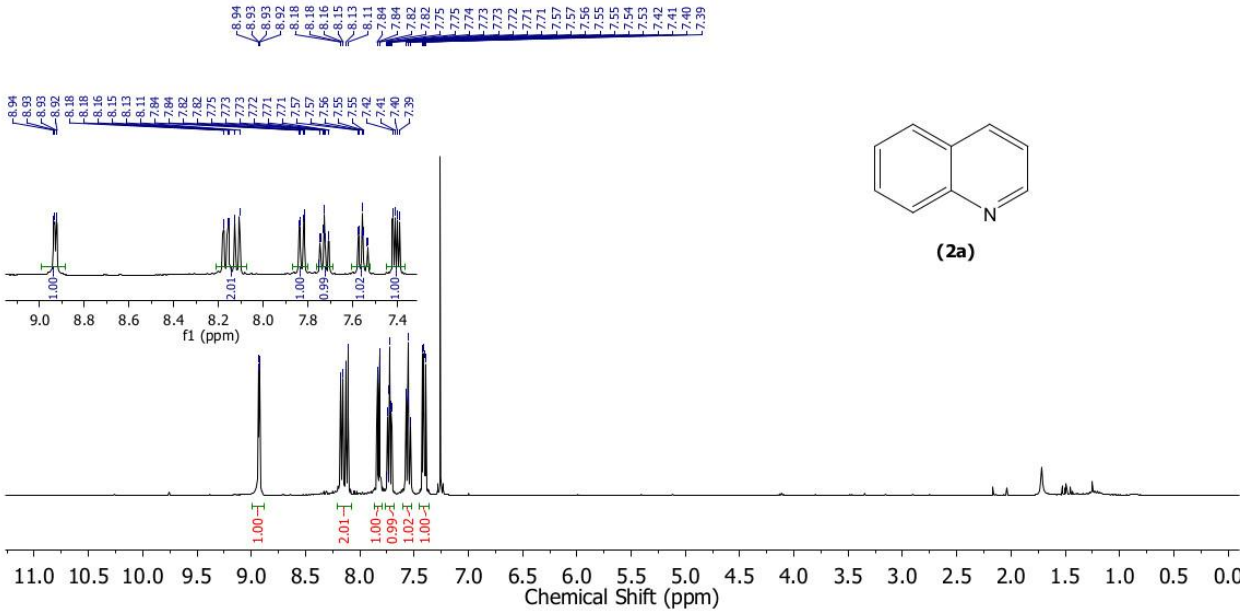
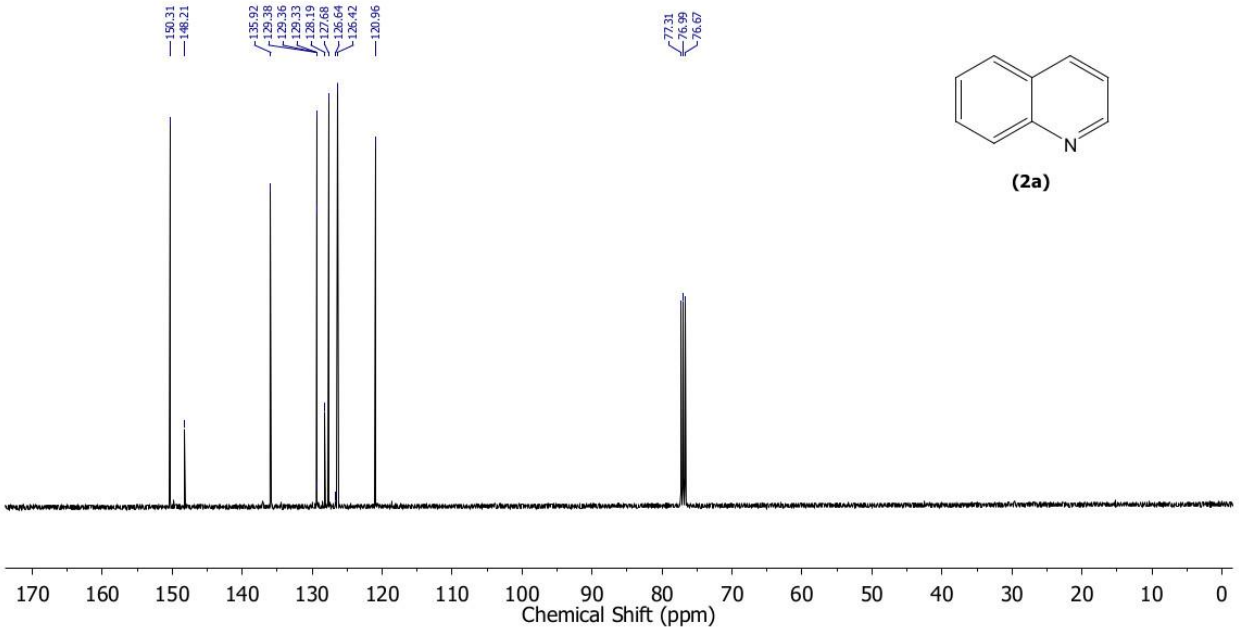


SUPPORTING INFORMATION

NMR Quinoline 1H of (2a)

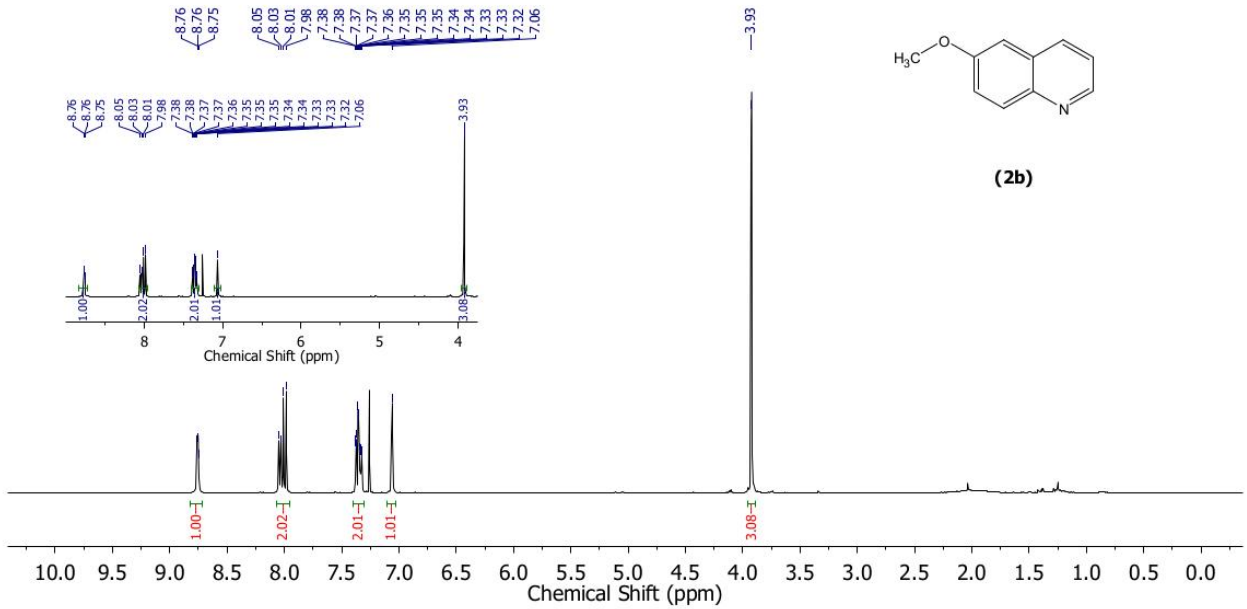


Quinoline C13 (2a)

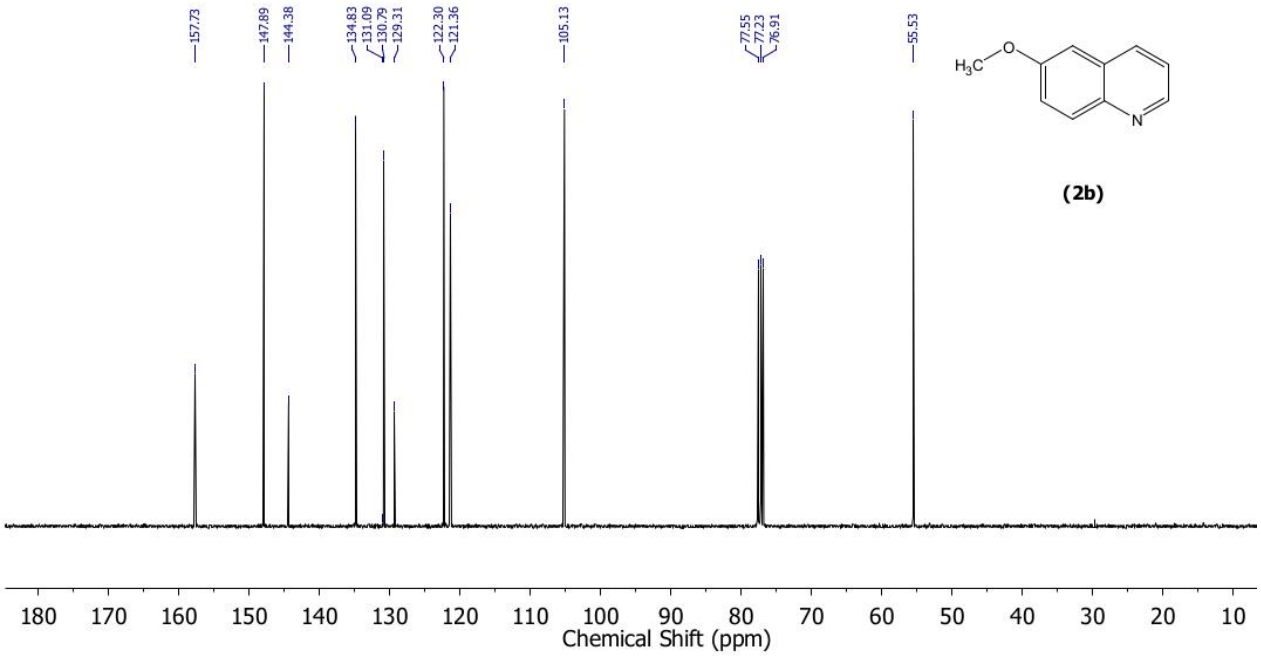


SUPPORTING INFORMATION

6-methoxy-quinoline 1H (2b)

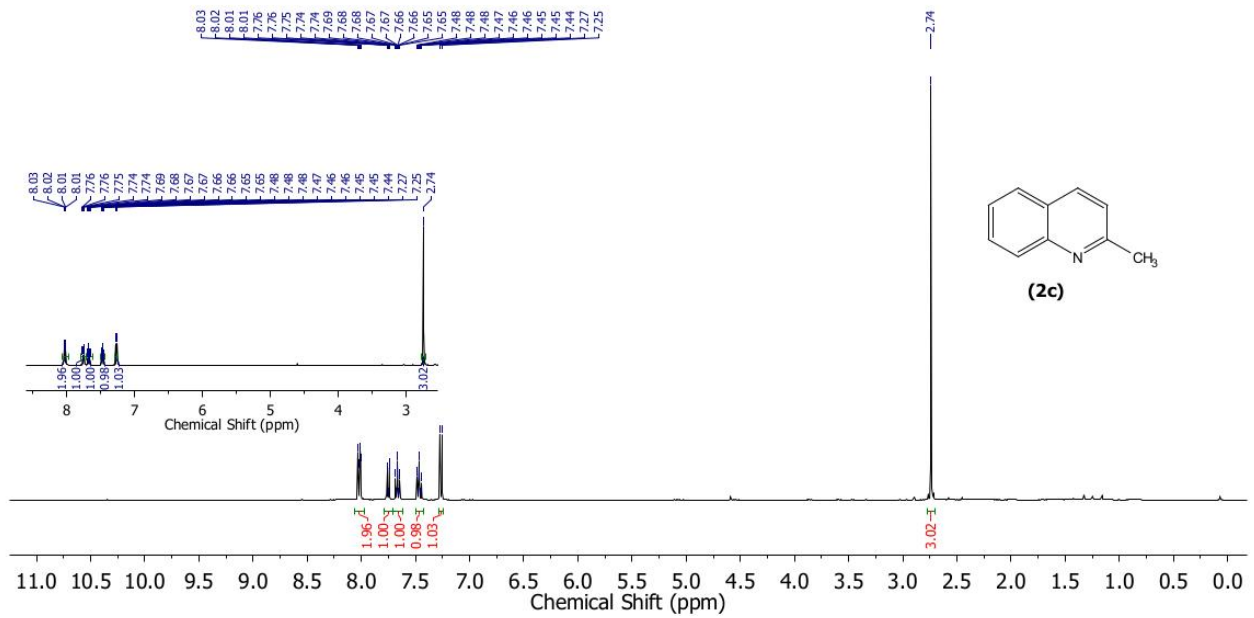


6-methoxy-quinoline 13C (2b)

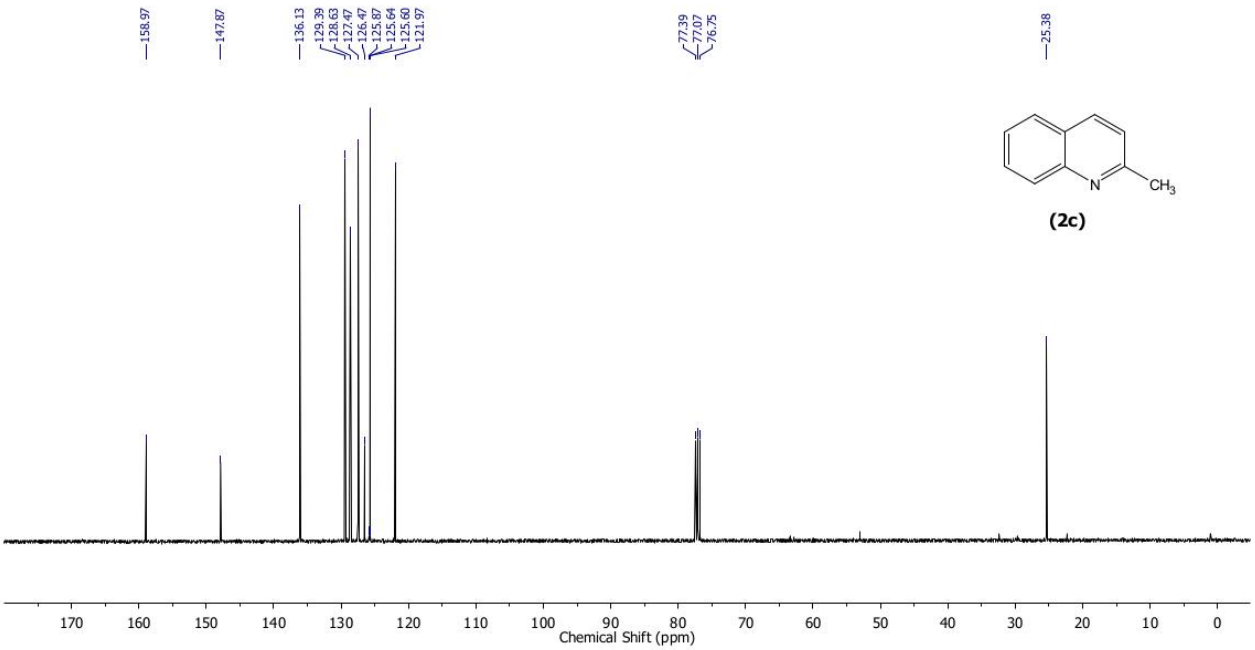


SUPPORTING INFORMATION

Quinaldine 1H (2c)

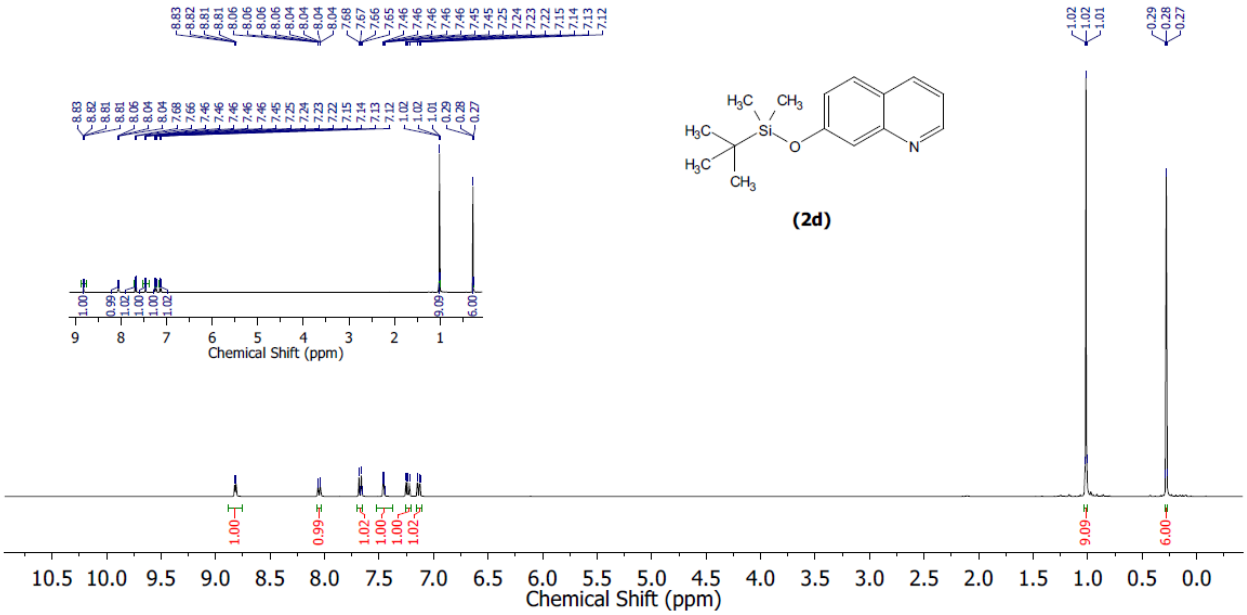


Quinaldine 13C NMR (2c)

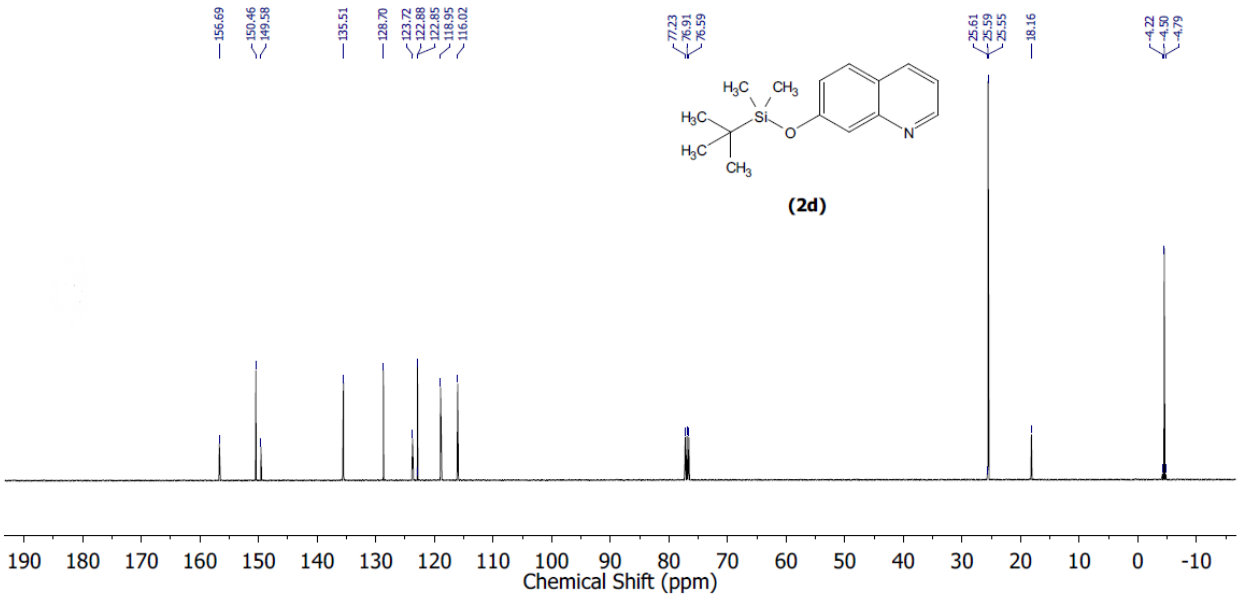


SUPPORTING INFORMATION

TBSO-Quinoline 1H (2d)

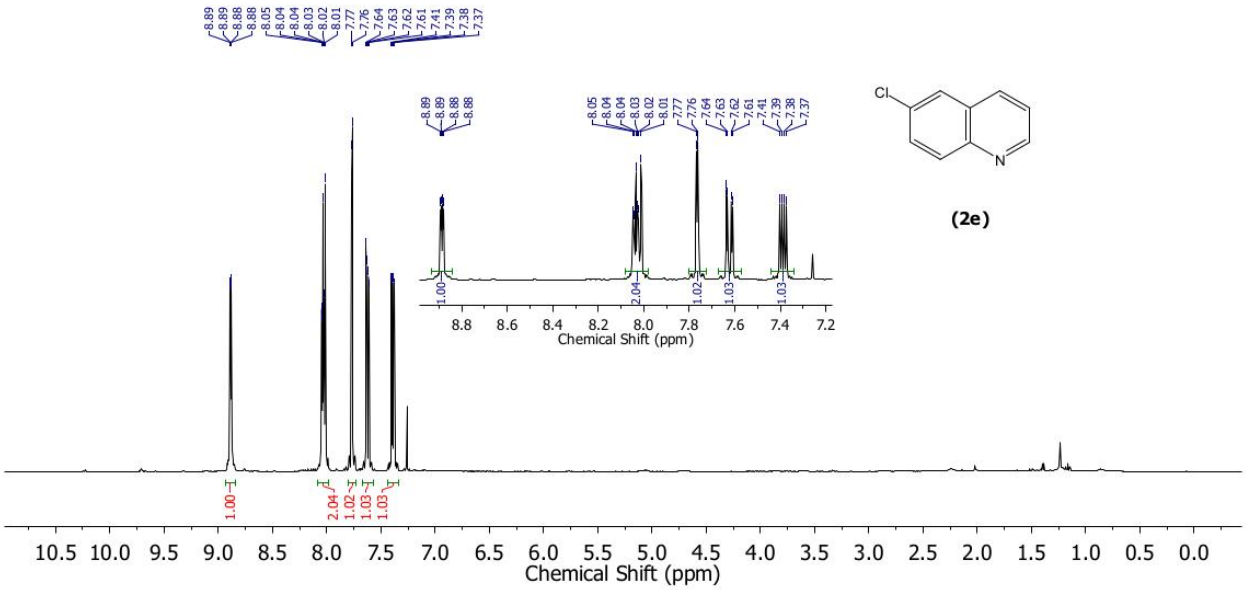


TBS-quinoline C13 (2d)

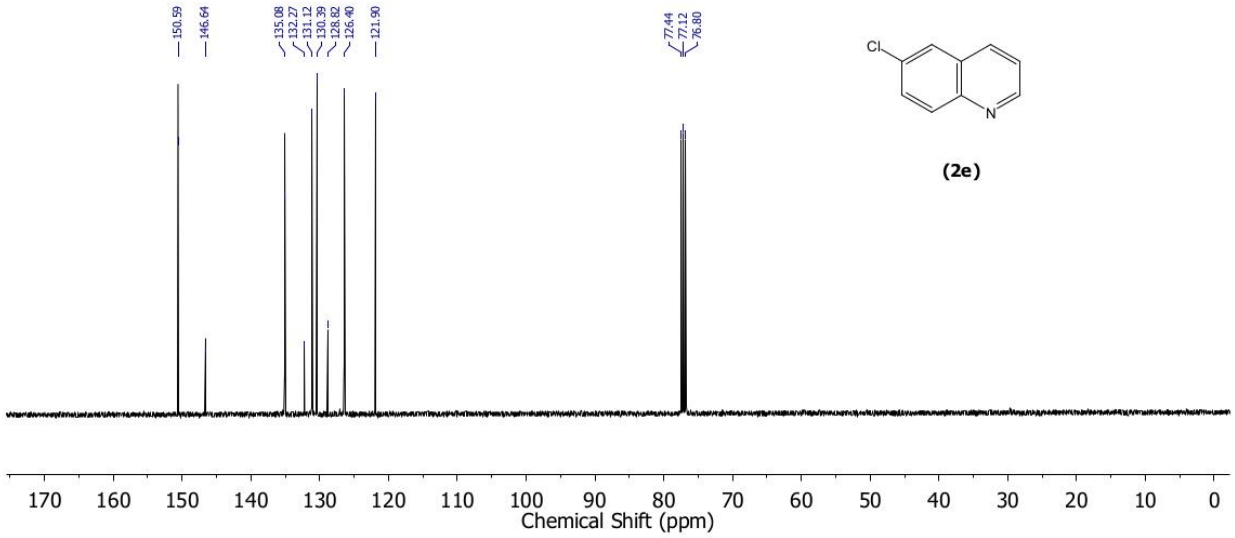


SUPPORTING INFORMATION

6-Chloroquinoline 1H (2e)

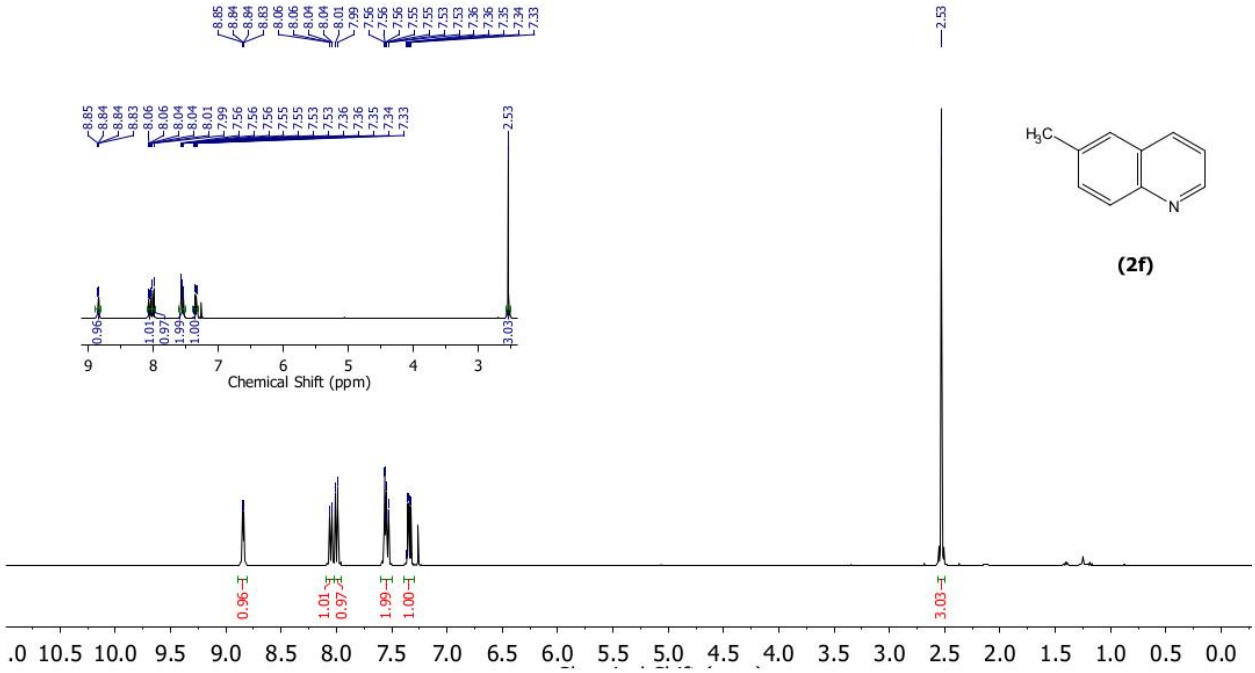


6-Chloroquinoline 13C (2e)

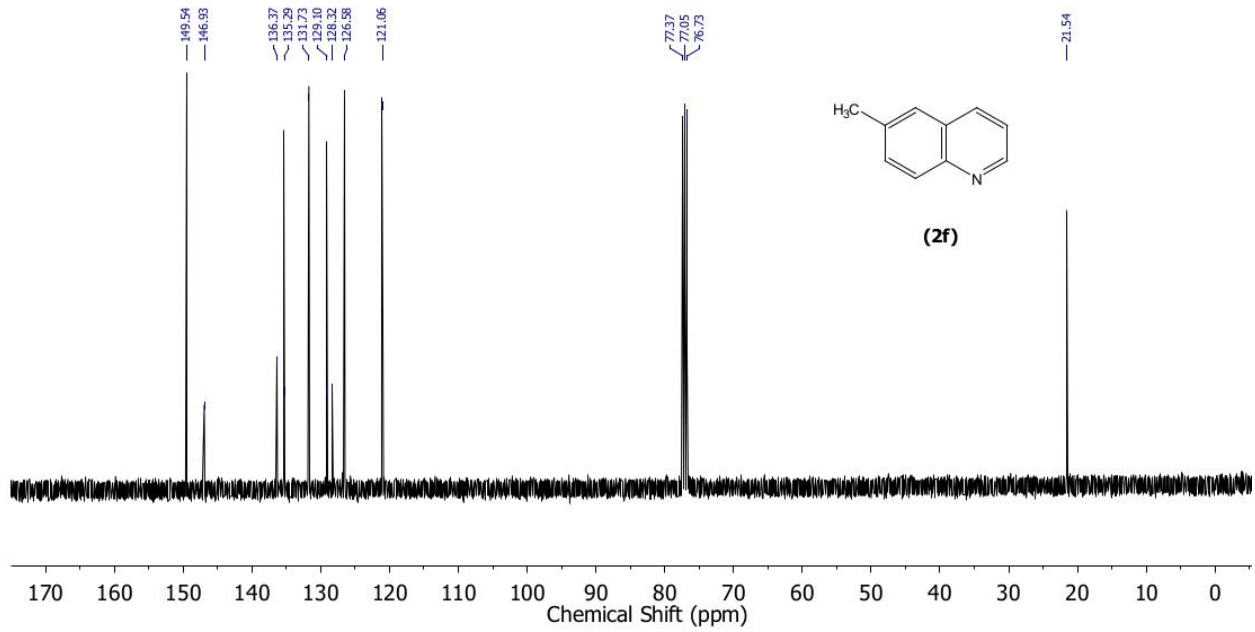


SUPPORTING INFORMATION

6-methylquinoline 1H (2f)

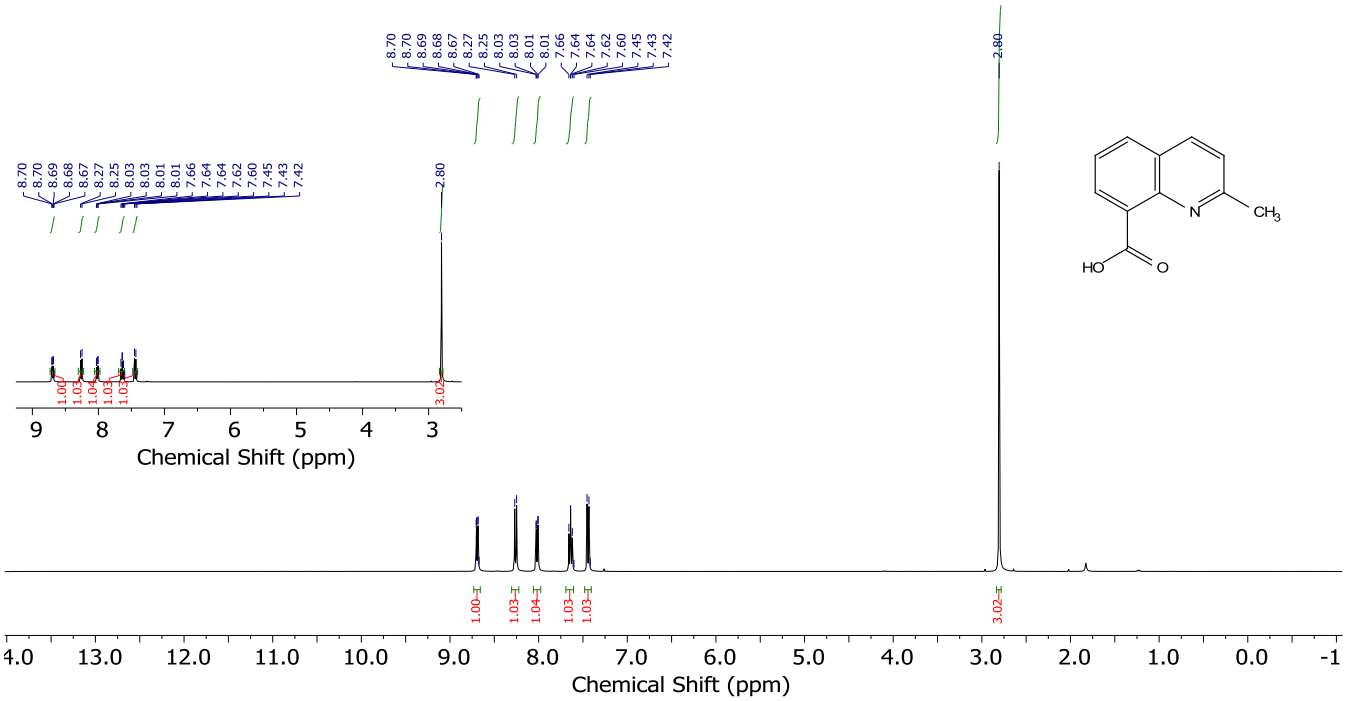


6-methylquinoline C13 (2f)

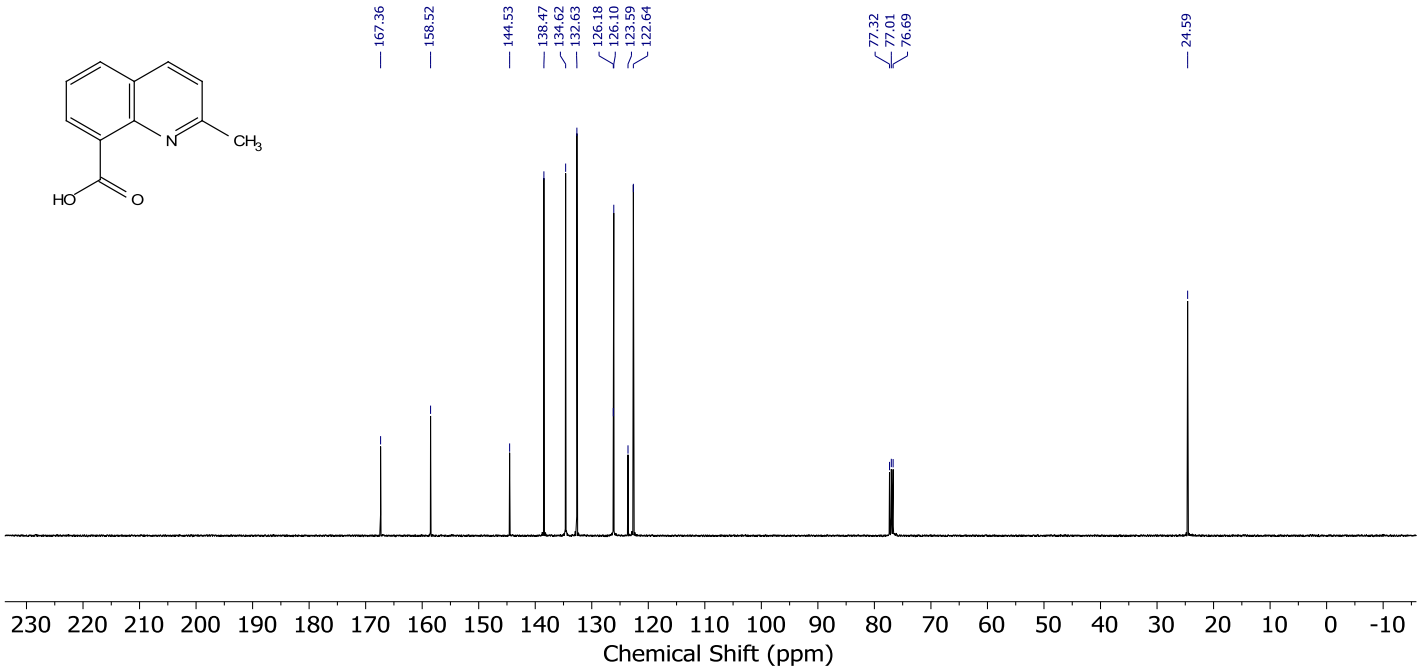


SUPPORTING INFORMATION

2-methylquinoline-8-carboxylic acid 1H (2g)

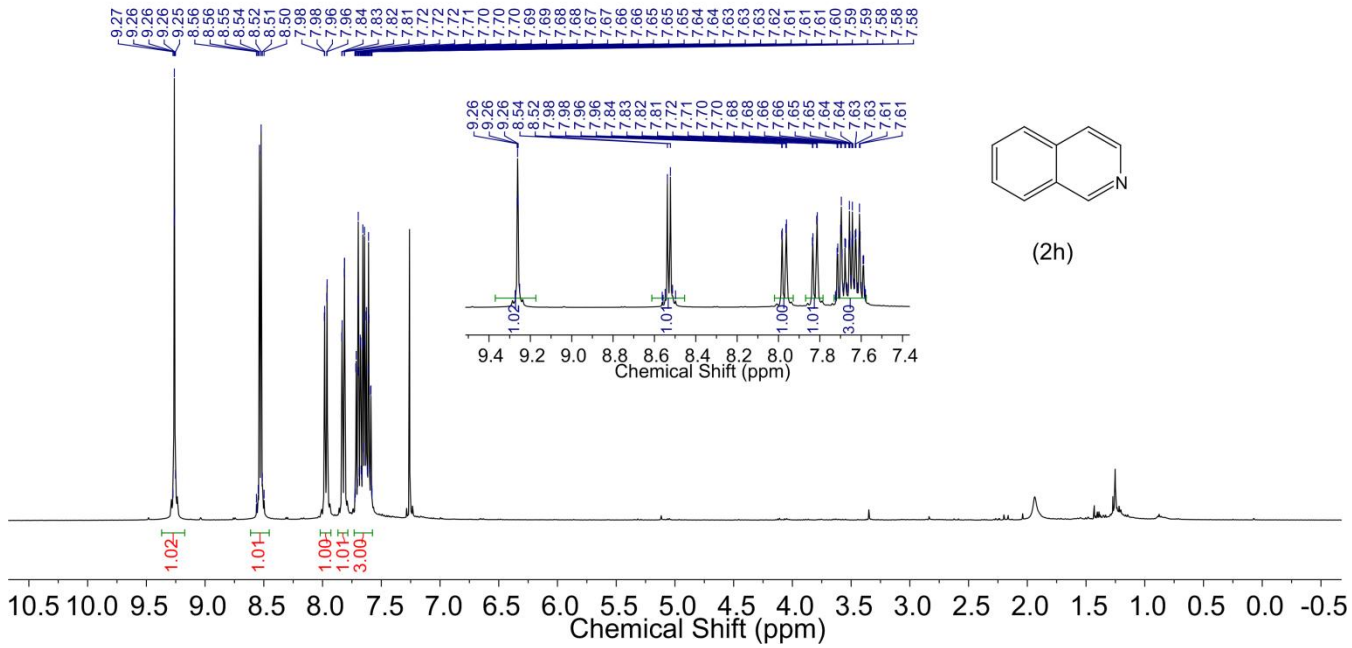


2-methylquinoline-8-carboxylic acid 13C (2g)

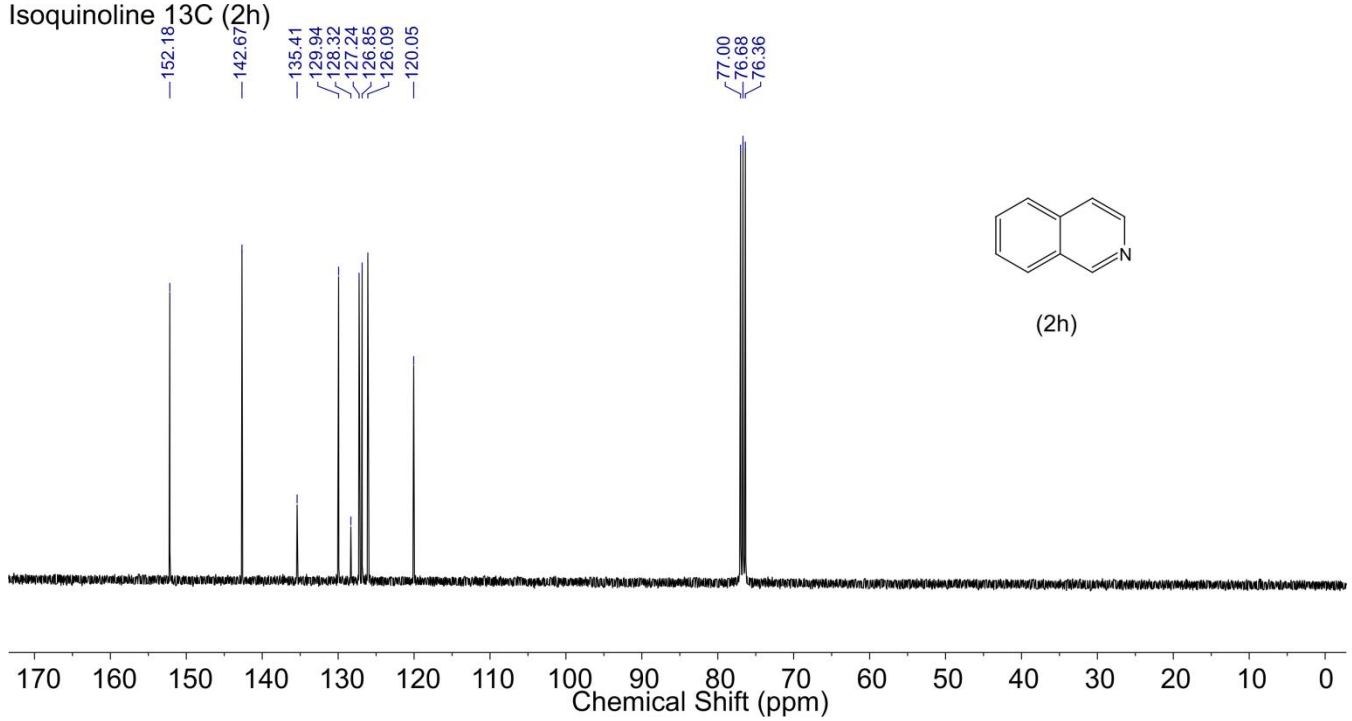


SUPPORTING INFORMATION

Isoquinoline 1H (2h)

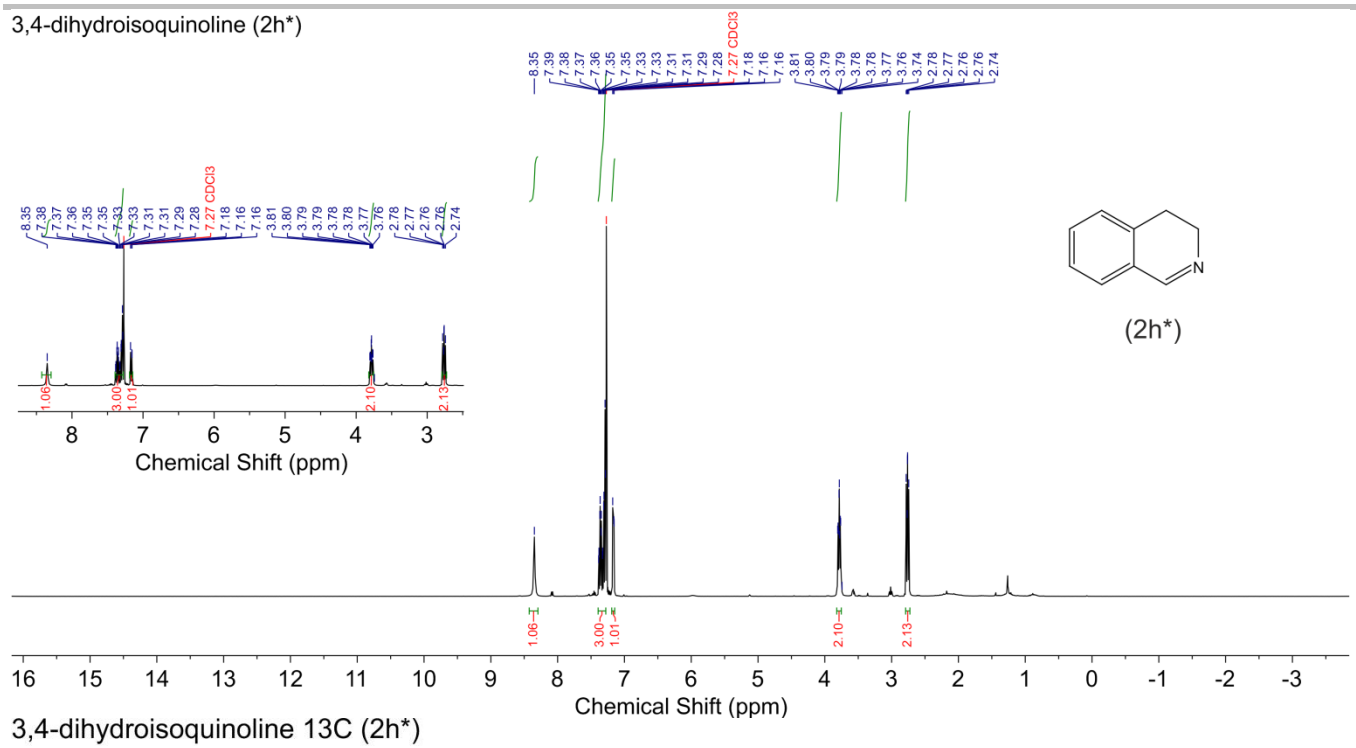


Isoquinoline 13C (2h)

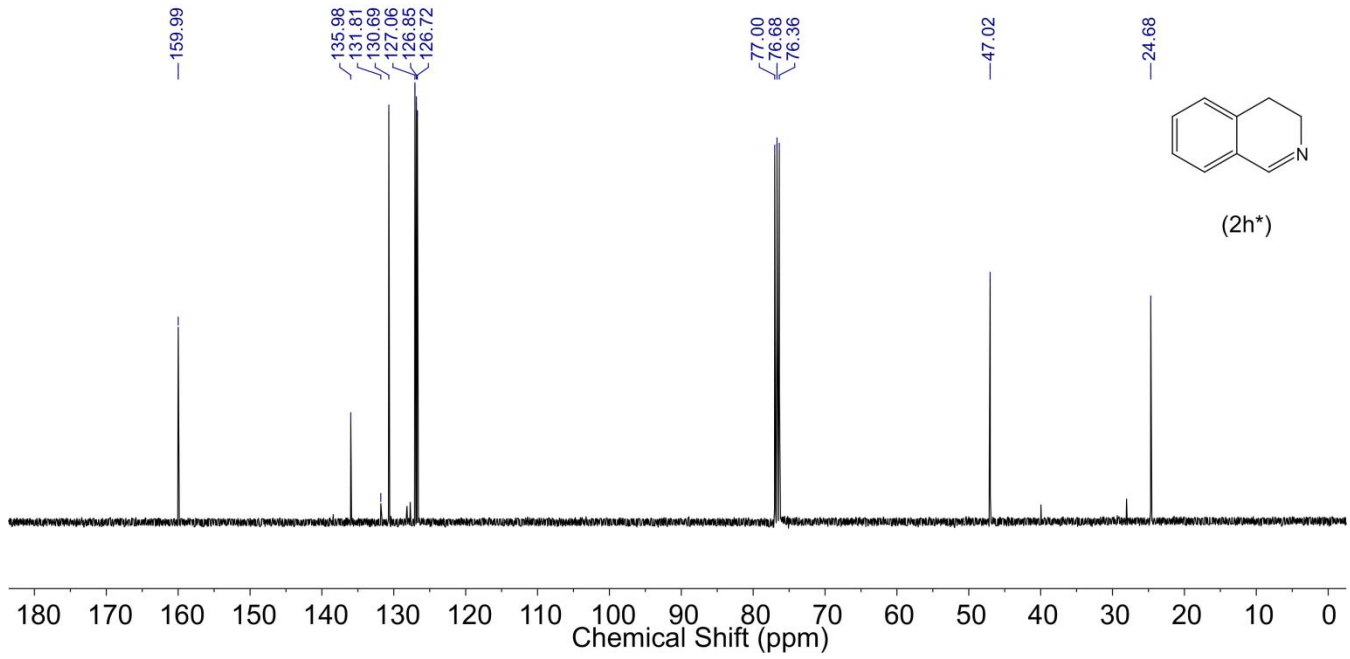


SUPPORTING INFORMATION

3,4-dihydroisoquinoline (2h*)

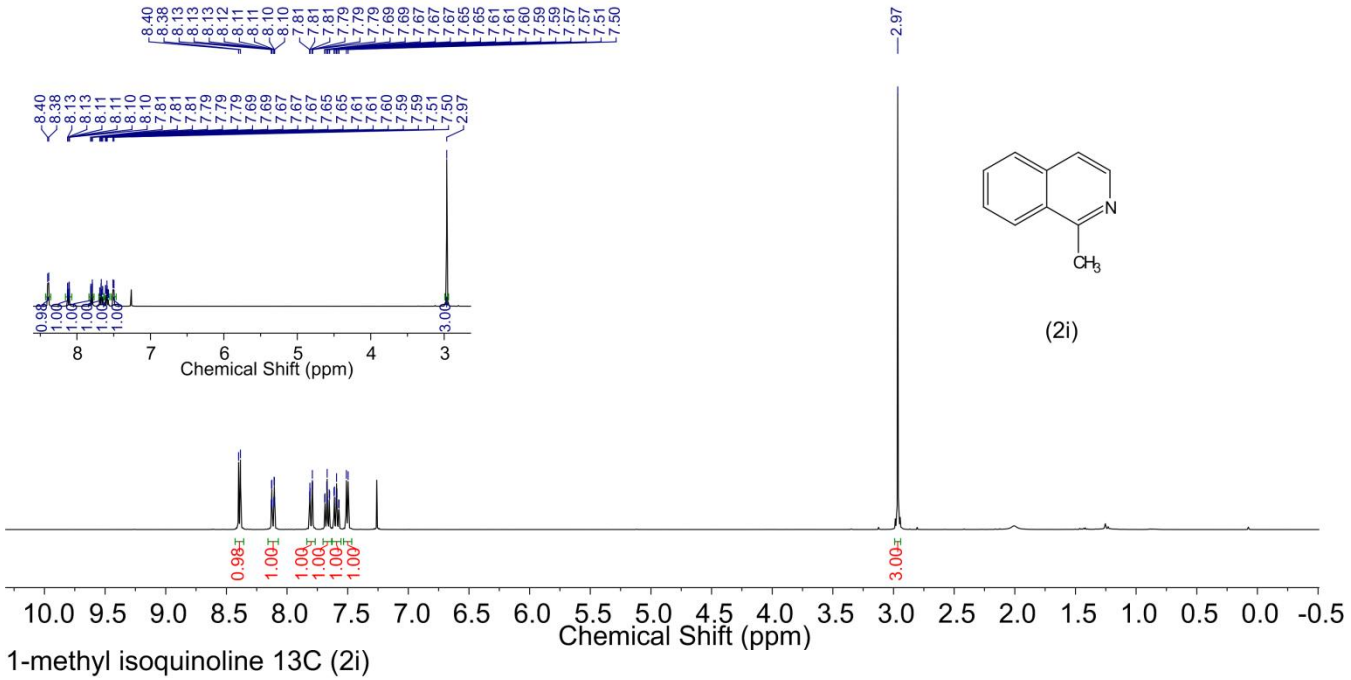


3,4-dihydroisoquinoline 13C (2h*)

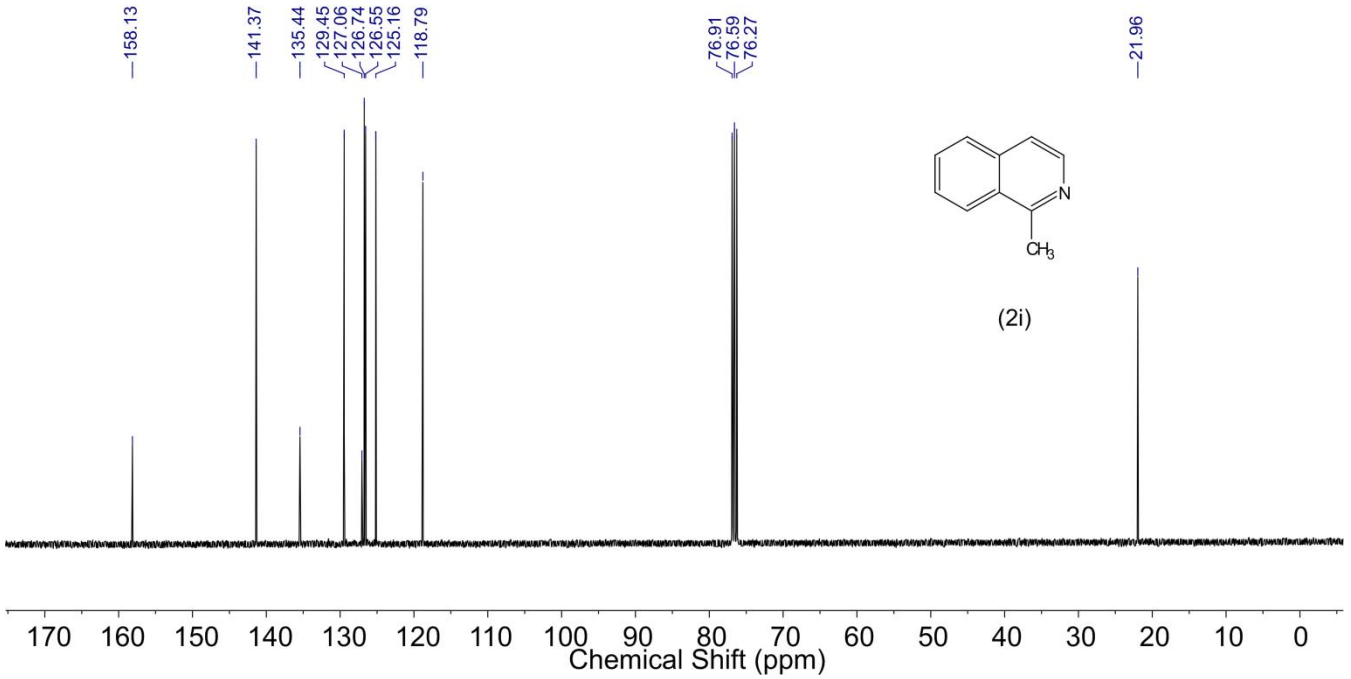


SUPPORTING INFORMATION

1-methyl isoquinoline 1H (2i)

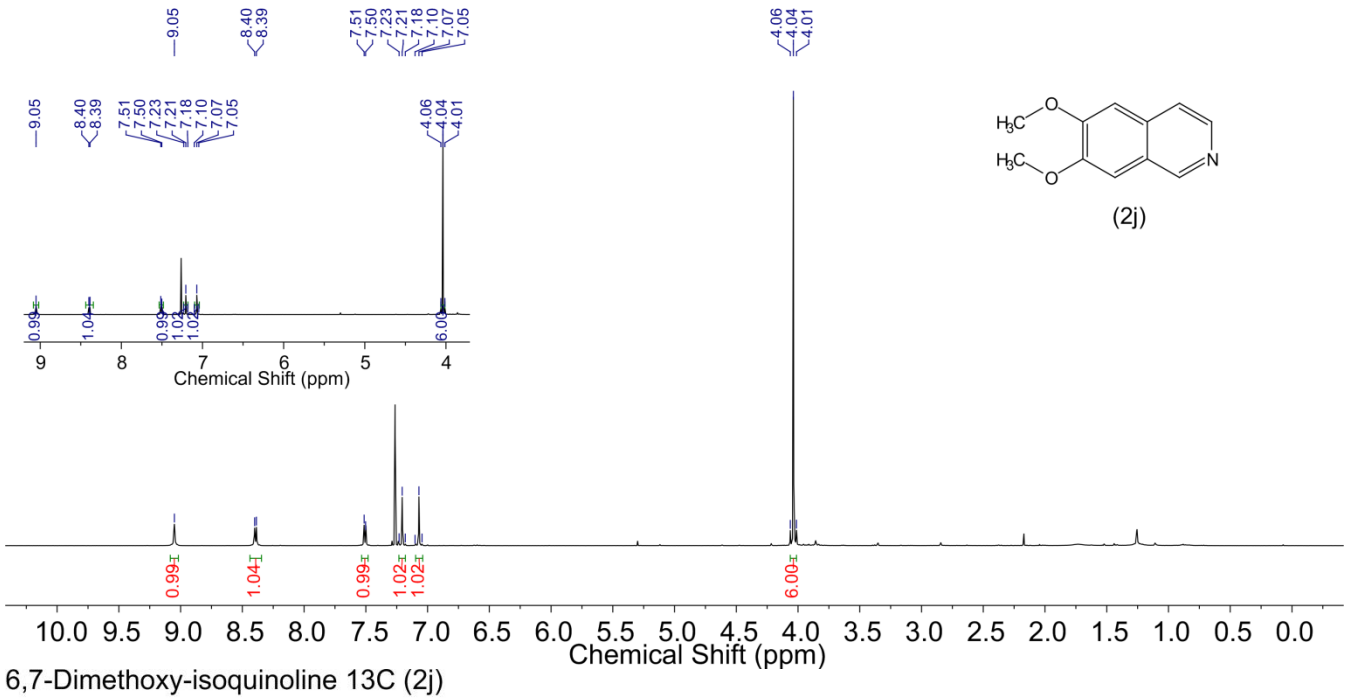


1-methyl isoquinoline 13C (2i)

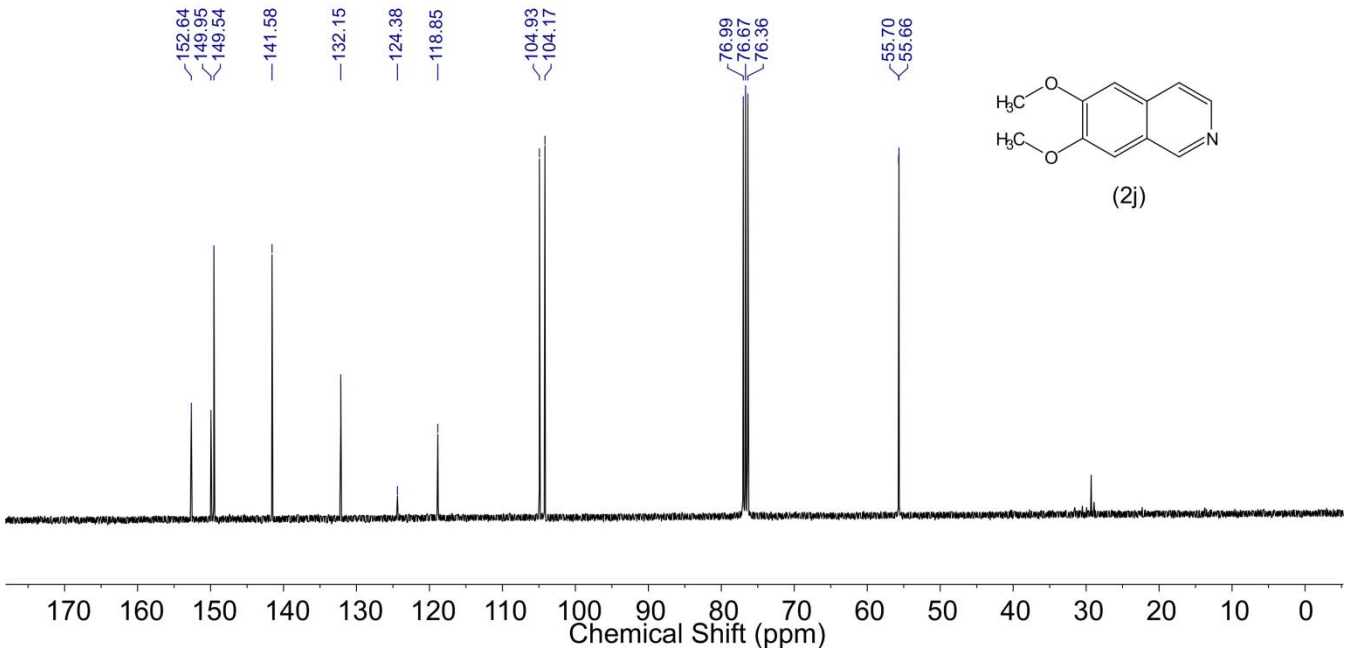


SUPPORTING INFORMATION

6,7-Dimethoxy-isoquinoline 1H (2j)

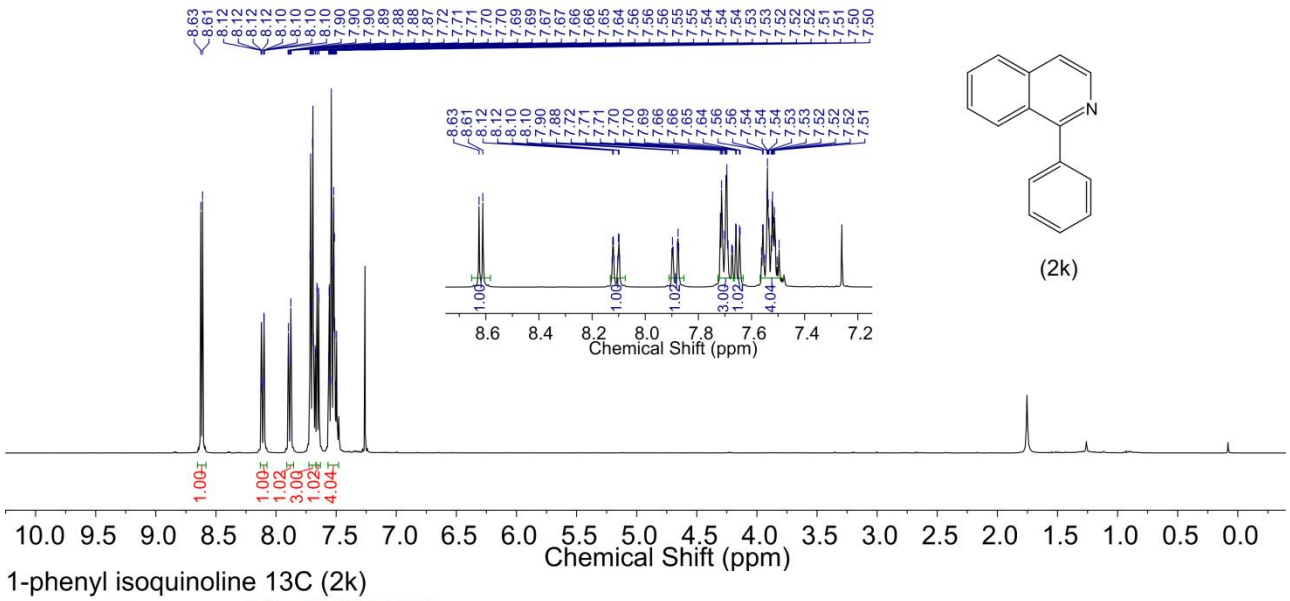


6,7-Dimethoxy-isoquinoline 13C (2j)

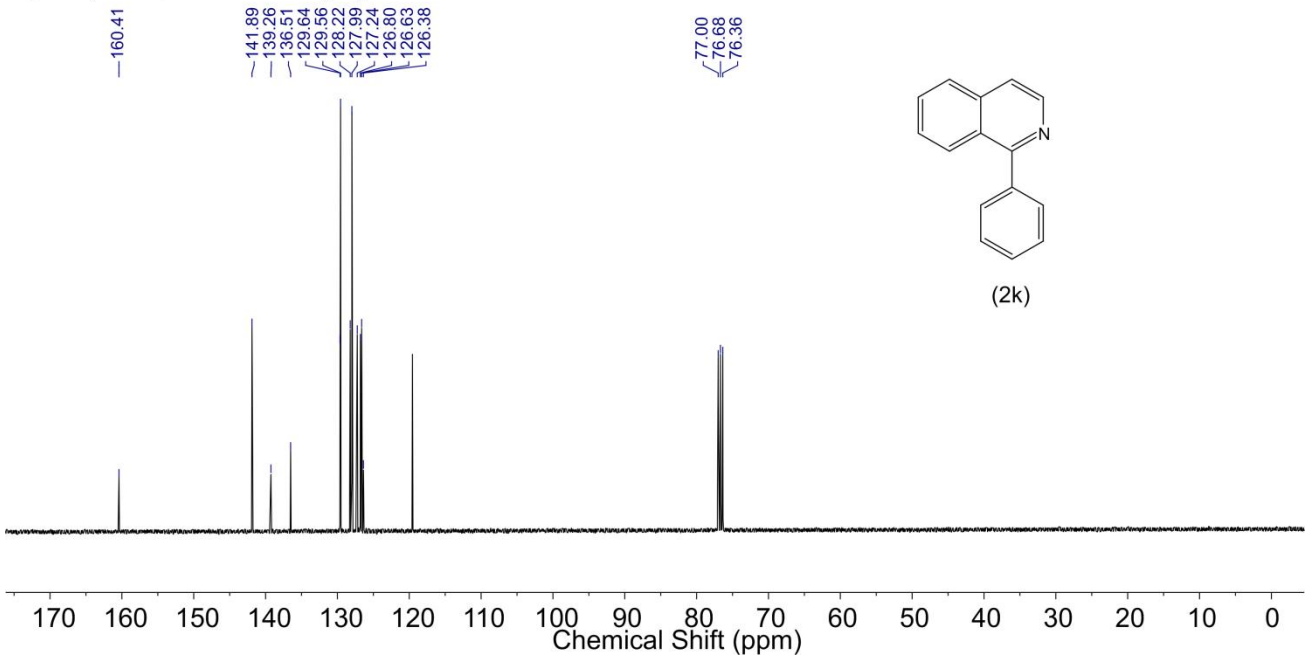


SUPPORTING INFORMATION

1-phenyl isoquinoline 1H (2k)

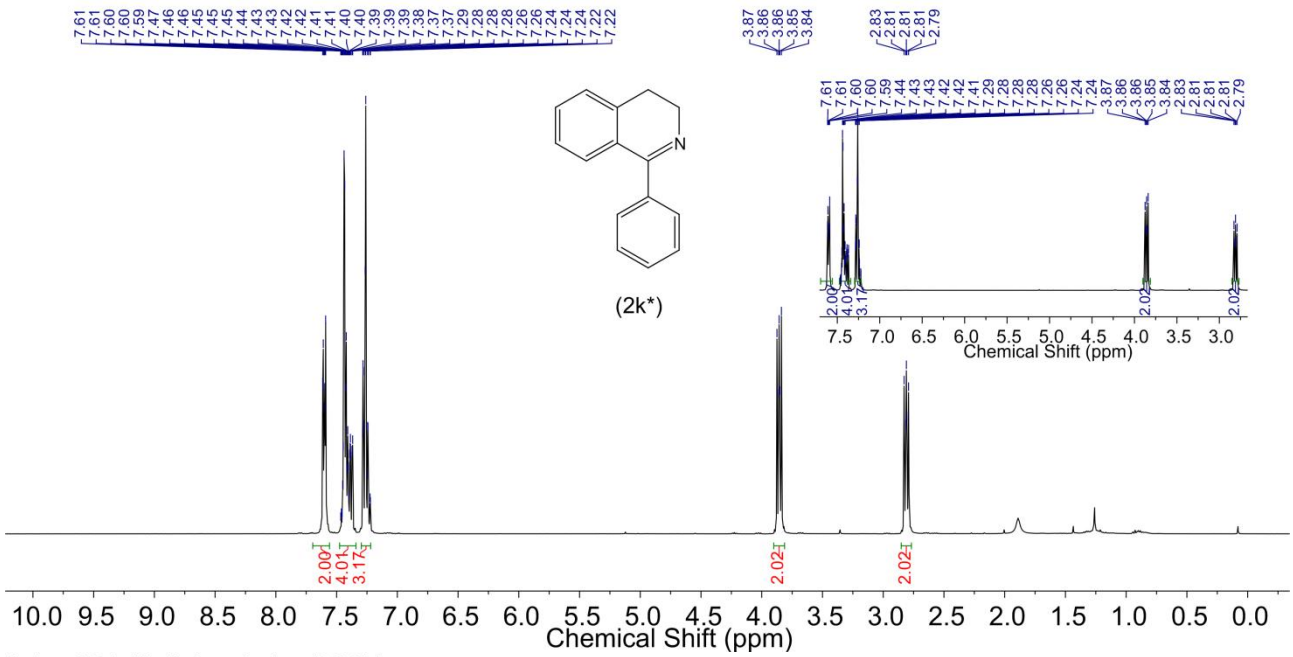


1-phenyl isoquinoline 13C (2k)

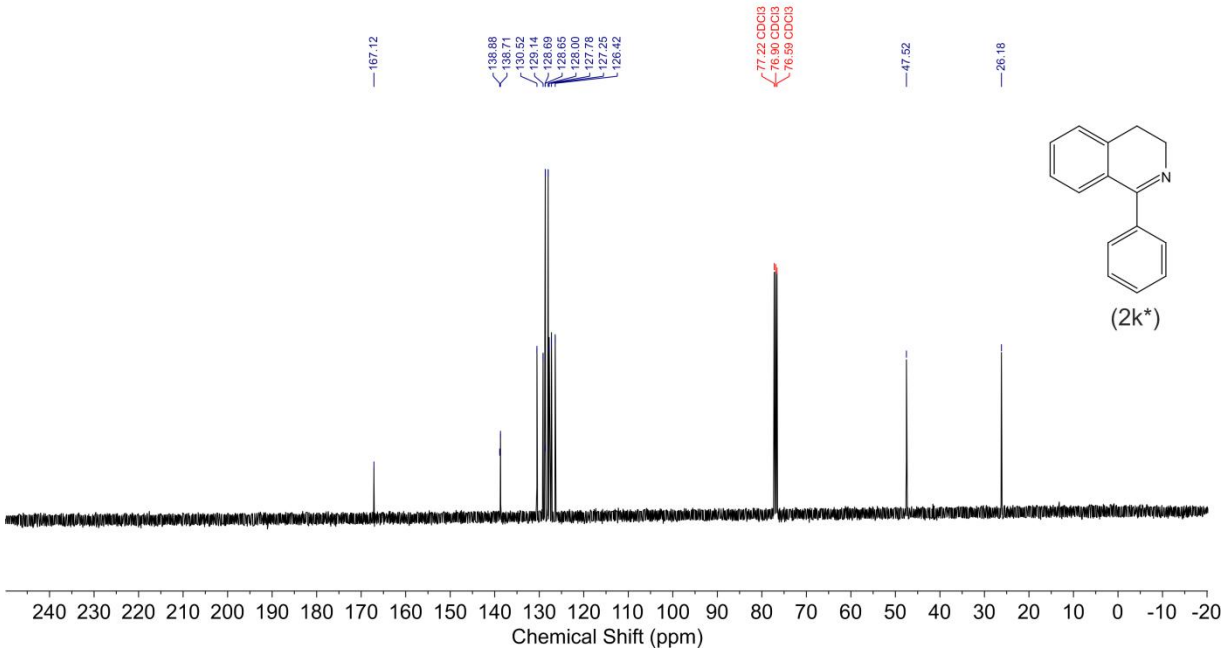


SUPPORTING INFORMATION

1-phenyl-3,4-dihydroisoquinoline 1H (2k*)

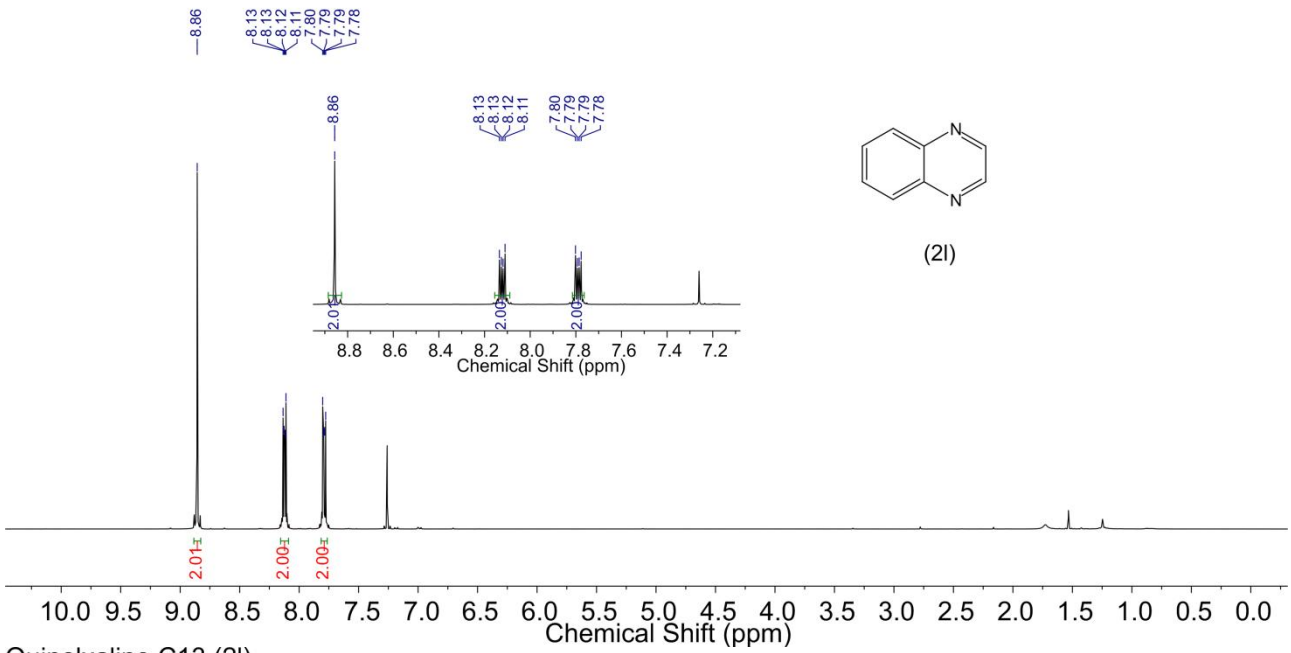


1-phenyl-3,4-dihydroisoquinoline 13C 2k*



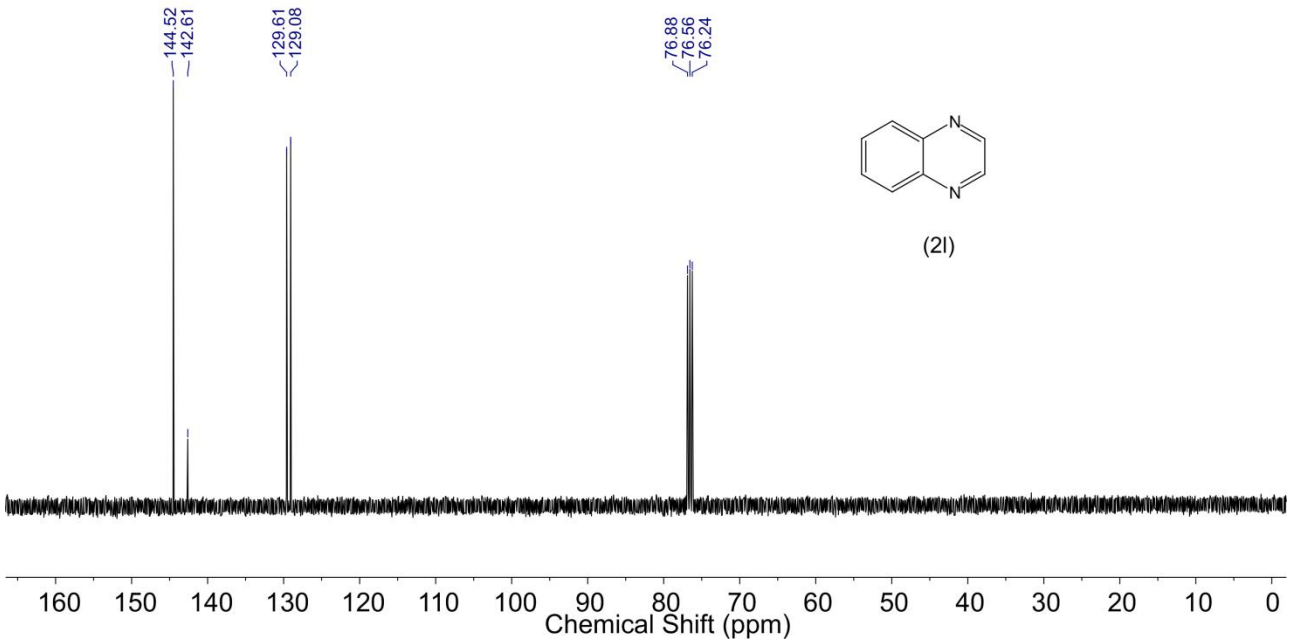
SUPPORTING INFORMATION

Quinoxaline 1H (2l)



(2l)

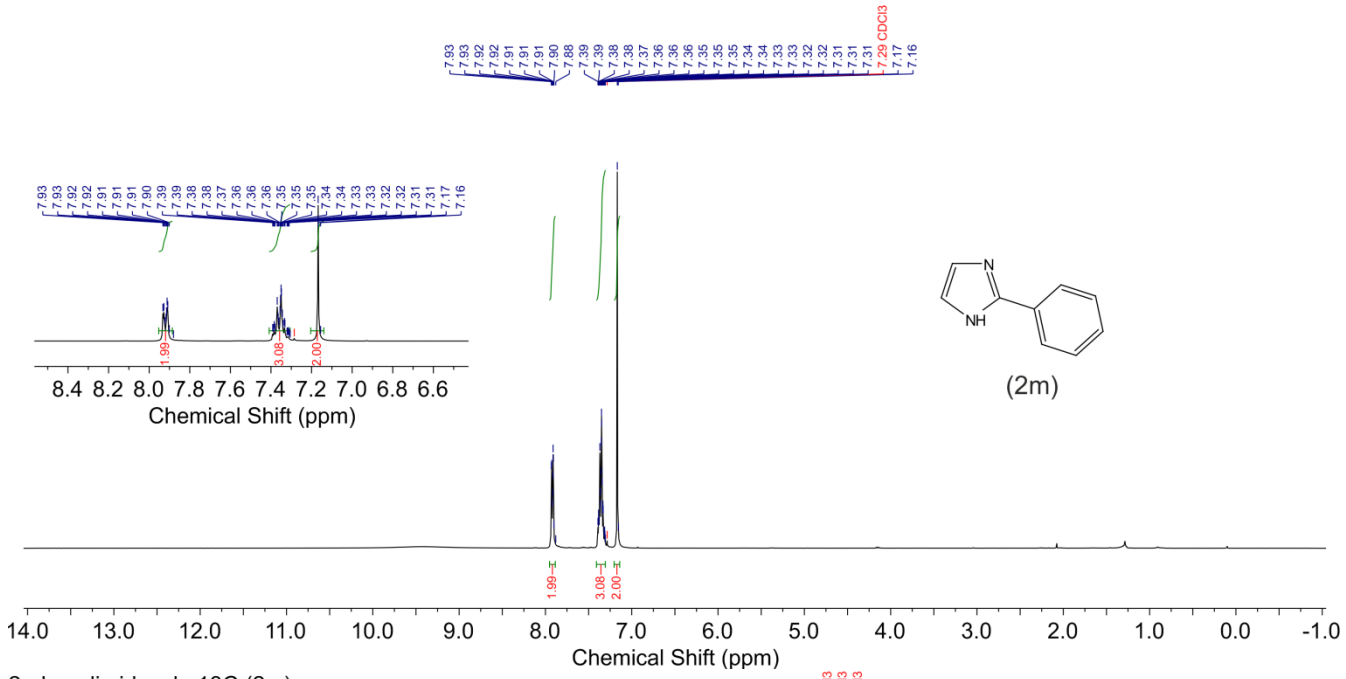
Quinolxaline C13 (2l)



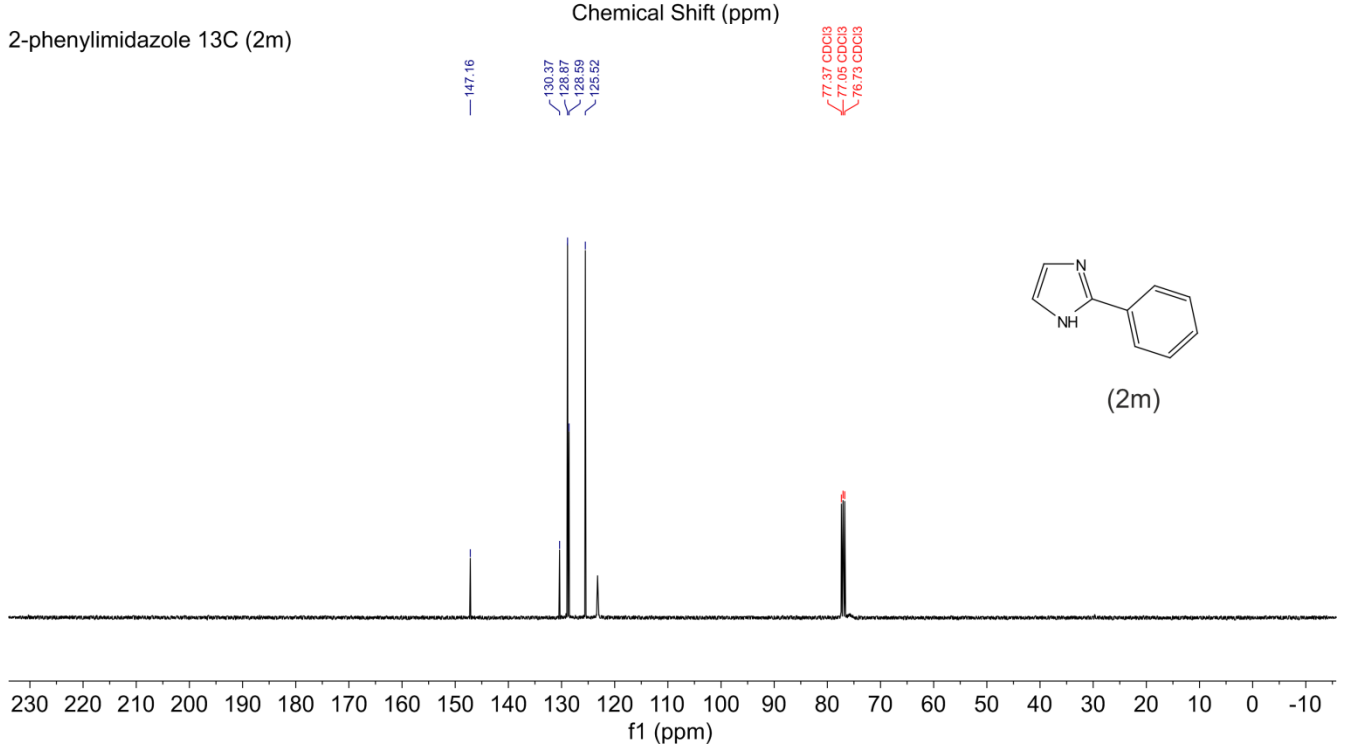
(2l)

SUPPORTING INFORMATION

2-phenylimidazole 1H (2m)

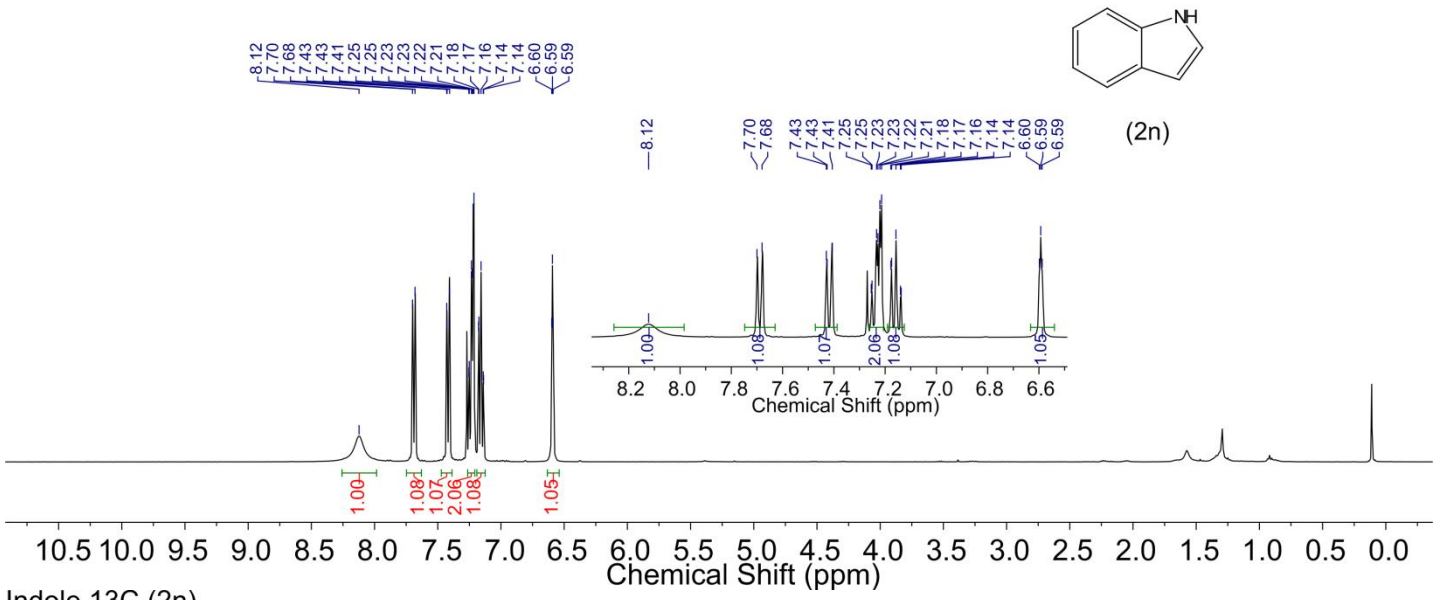


2-phenylimidazole 13C (2m)

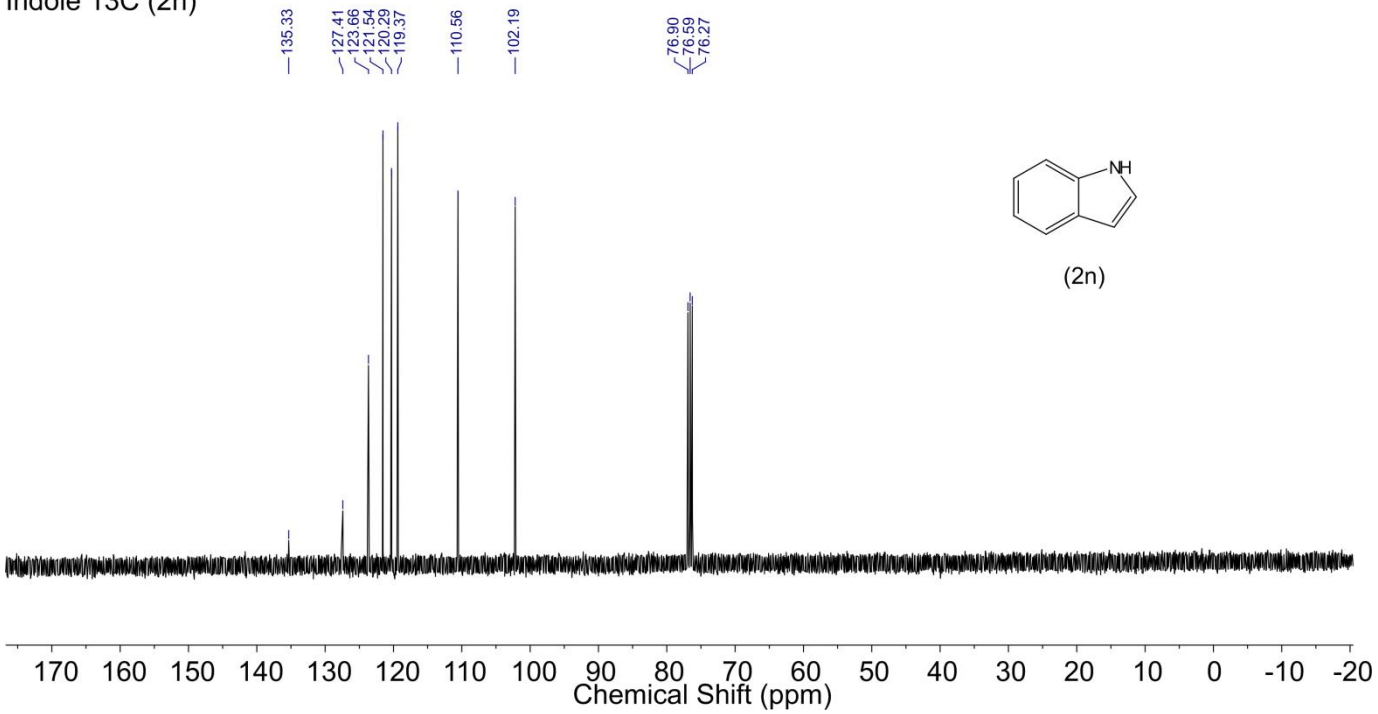


SUPPORTING INFORMATION

Indole 1H (2n)

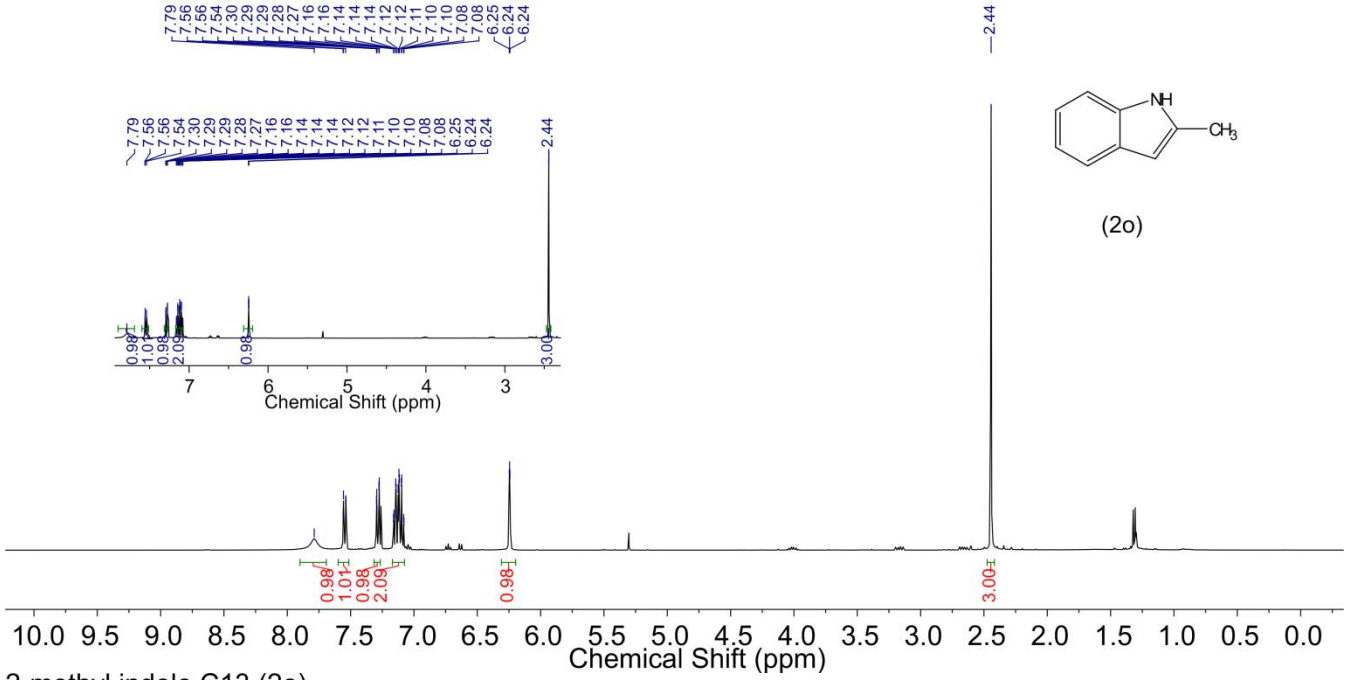


Indole 13C (2n)



SUPPORTING INFORMATION

2-methyl indole 1H (2o)



2-methyl indole C13 (2o)