Electronic Supplementary Material

Electron Transport Chain-Inspired Coordination Polymer for Macroscopic Spatiotemporal Scales of Charge Separation and Transport in Photocatalysis

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1. Materials and Methods.

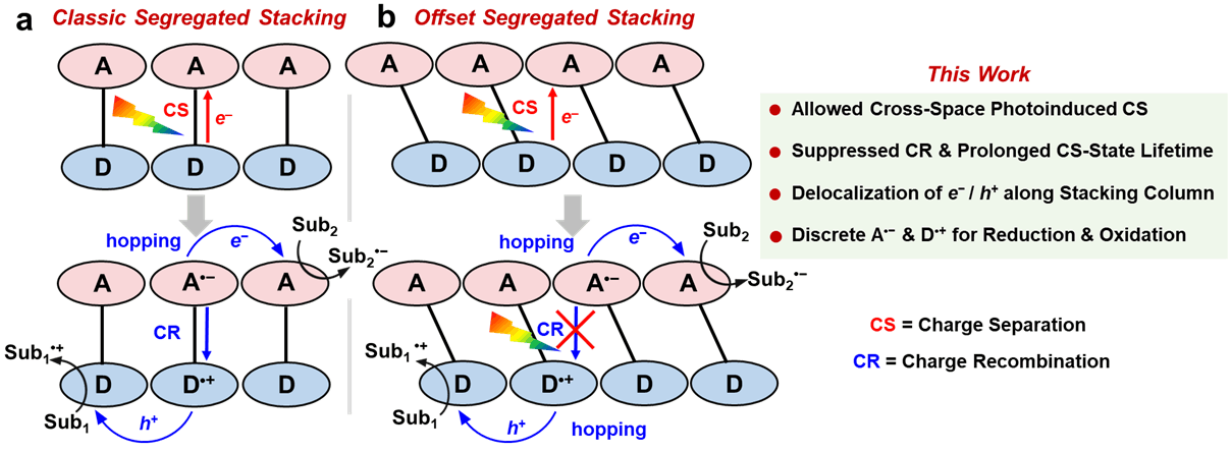
All materials were used as received from commercial sources without further purification unless otherwise noted. 2,5-di(pyridin-4-yl)thiazolo[5,4-*d*]thiazole was synthesized according to literature.[1] The white LEDs were purchased from Philips. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance NEO 600M NMR Spectroscopy, and chemical shifts were recorded in parts per million (ppm, δ). Chemical shifts were referenced to residual solvent peaks. The powder X-ray diffraction (PXRD) diffractograms were obtained on a Rigaku Smart Lab XRD instrument with Cu Kα radiation (λ = 1.54056 Å). FTIR spectra were recorded from KBr pellets on JASCO FT/IR-430. Thermogravimetric analyses (TGA) were performed at a ramp rate of 10 °C/min up to 800 °C in a nitrogen flow with Mettler-Toledo TGA/SDTA851 instrument. Scanning electron microscopy (SEM) images were taken using a Plus Field Emission Scanning Electron Microscopy 7610. Solid UV-vis spectra were recorded on Hitachi U-4100 UV-vis-NIR spectrophotometer. Fluorescent spectra and photoluminescence decay profiles were recorded on Edinburgh FLS 920 stable/transient fluorescence spectrometer.

Photoelectrochemical Measurements: Solid-state cyclic voltammogram (CV) tests and electrochemical impedance spectroscopy (EIS) measurements were carried out on a ZAHNER ENNIUM Electrochemical Workstation. Transient photocurrent tests were performed on a CHI 650E electrochemical workstation. Typically, 2 mg catalysts were added into ethanol/H_2O (0.2 mL/0.2 mL) and 10 µL 5 wt% Nafion mixed solution. The fluoride-tin oxide (FTO) glass plate coated 1 cm^2 mixed solution was utilized as working electrodes. The Ag/AgCl electrode is used as the reference electrode and a platinum plate as a counter electrode. 1.0 M KCl solution was used as the electrolyte. The three-electrode system was used for all electrochemical tests. The Mott-Schottky measurements were performed at frequencies of 500 Hz, 1000 Hz, and 1500 Hz.

Fs-TA Measurements: The fs-TA measurements were performed in a Helios Fire spectrometer (Ultrafast Systems LLC) with pump and probe beams derived from an amplified Ti: sapphire laser system (Coherent Astrella, 800 nm, 5.5 mJ pulse^{-1}, 35 fs, and 1 kHz repetition rate) at room temperature. A custom-designed fibre-coupled alignment-free spectrometer with a 1024-pixel CMOS sensor (spectral response: 200−1000 nm) was used as the vis/UV−vis detector. Spectral acquisition rate up to 2400 spectra·s^{-1}. ADC resolution was 16-bit. Preparation of the sample: Cd-**TzBDP** was finely ground and dispersed in DMSO, the suspension was transferred into a quartz cuvette and its UV-visible absorbance was adjusted to 0.5 before further characterization.

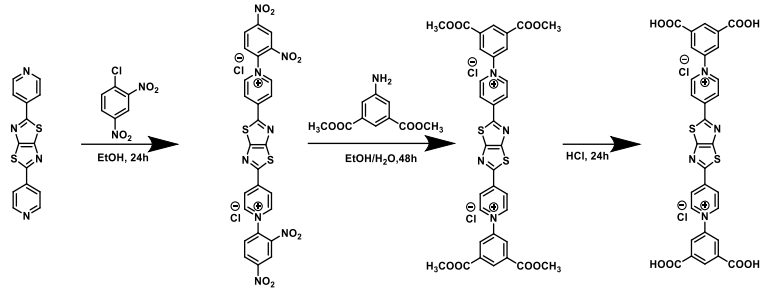
EPR Detection: Electron paramagnetic resonance (EPR) measurements were performed on Bruker E500. To verify the viologen radical, we have tested the spectra of Cd−**TzBDP** under the irradiation of a Xenon lamp and without light, respectively. The ROS generated by radiated Cd−**TzBDP** has been detected by EPR in the presence of DMPO. ESR measurements were carried out during the light irradiation with a 300 W Xenon lamp (λ >400 nm) under air conditions.

2. Supplementary Demonstration of the Segregated D-A Stacking in Photocatalysis.



Scheme S1. Schematic demonstration of the segregated stacking for photocatalysis. (a) Classic segregated stacking and (b) offset segregated stacking in this work.

3. Preparation of Materials.

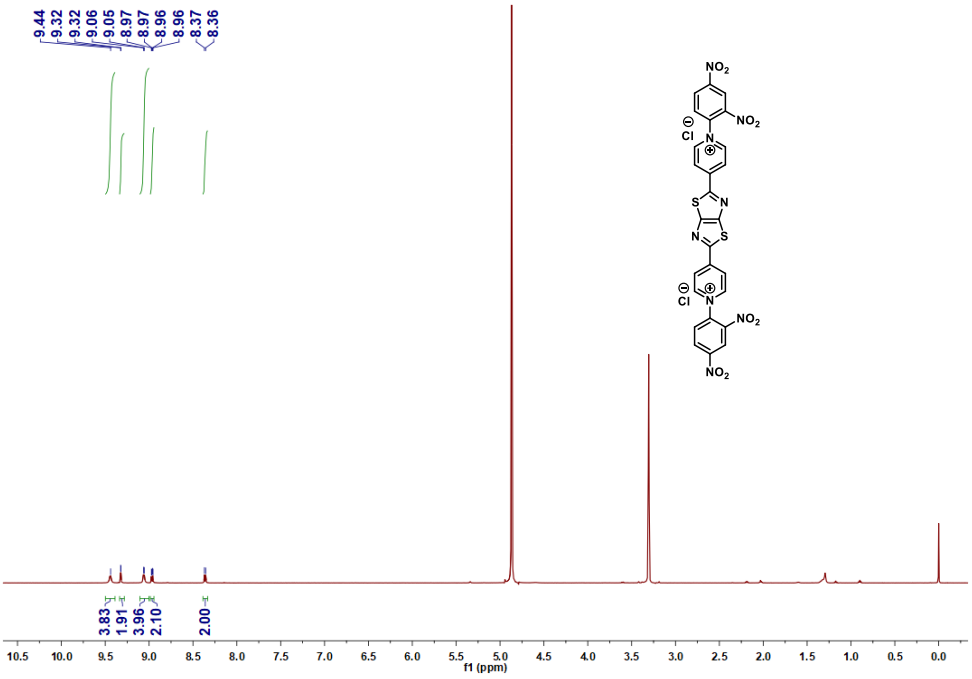


Scheme S2. Synthetic steps of ligand **TzBDP**.

Synthesis of Ligand

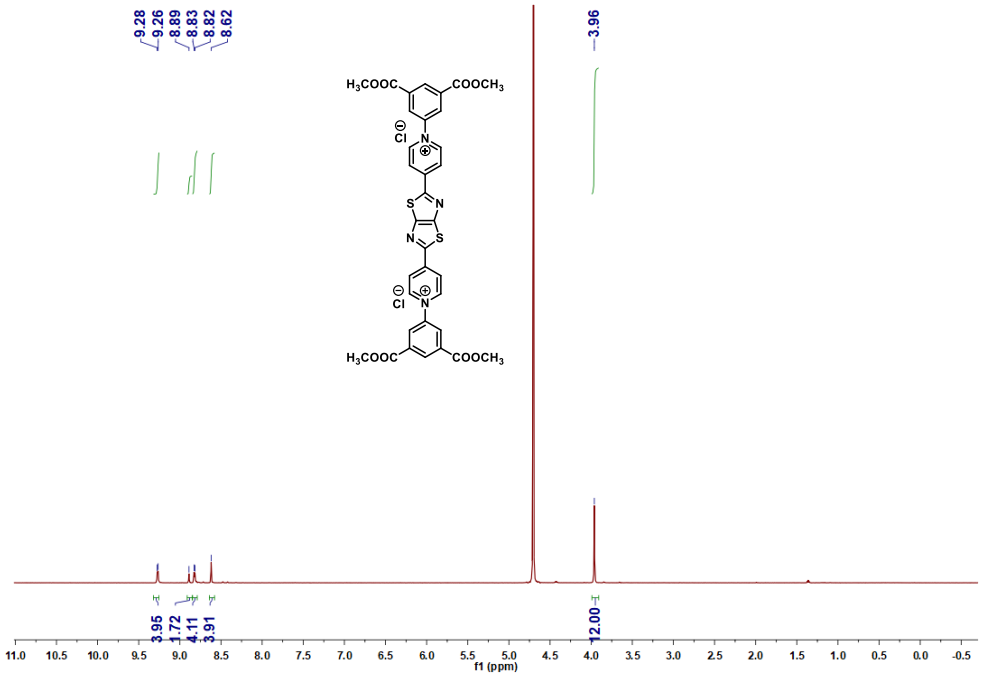
Synthesis of 4,4'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(1-(2,4-dinitrophenyl)pyridin-1-ium) chloride

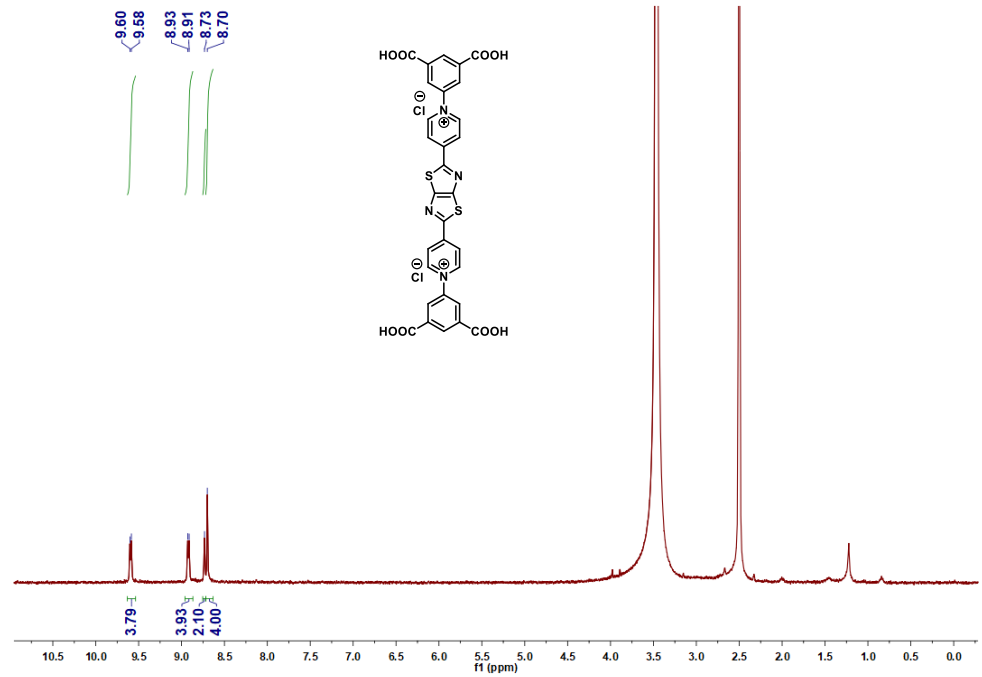
This compound was synthesized according to the previously reported literature with slight modifications.[1] 2,5-di(pyridin-4-yl)thiazolo[5,4-*d*]thiazole (2 mmol, 0.59 g) and 1-chloro-2,4-dinitrobenzene (8 mmol, 1.61 g) were added into a 250 mL flask containing 100 mL ethanol. The solution was reflux for 24 h. After cooling to room temperature, the solution was evaporated. The resulting residue was dissolved in CH_3CN (100 mL) and the precipitate was filtered off, then washed with ethyl acetate and dried in a vacuum oven. Yield: 65%. ^{1}H NMR (600 MHz, d_4-MeOH) δ 9.44 (s, 4H), 9.32 (d, J = 2.3 Hz, 2H), 9.06 (d, J = 5.4 Hz, 4H), 8.96 (dd, J = 8.6, 2.4 Hz, 2H), 8.36 (d, J = 8.6 Hz, 2H). The NMR data were inconsistent with the reported data.[1]



Synthesis of 4,4'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(1-(3,5-dicarboxyphenyl)pyridin-1-ium) chloride

The syntheses of these compounds were similar to the literature-reported procedure.[1] A mixture of 4,4'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(1-(2,4-dinitrophenyl)pyridin-1-ium) chloride (2 mmol, 1.40 g) and dimethyl 5-aminoisophthalate (12 mmol, 2.5 g) in 200 mL ethanol/H_2O (v:v 2/1) were reflux for 48 h. The mother liquor was evaporated and the residue was dissolved in ethyl acetate. The precipitate was filtered off, then washed with diethyl ether and dried. Yield: 80%. ^{1}H NMR (600 MHz, D_2O) δ 9.27 (d, J = 6.8 Hz, 4H), 8.89 (s, 2H), 8.82 (d, J = 6.7 Hz, 4H), 8.62 (s, 4H), 3.96 (s, 12H). Furthermore, the 4,4'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(1-(3,5-bis(methoxycarbonyl)phenyl)pyridin-1-ium) chloride was hydrolyzed by hydrochloric acid to produce the ligand **TzBDP**. Yield: 55%. ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.59 (d, J = 6.5 Hz, 4H), 8.92 (d, J = 6.6 Hz, 4H), 8.73 (s, 2H), 8.70 (s, 4H).





Synthesis of Cd–TzBDP

$Cd(NO_3)_2{\cdot}4H_2O$ (0.05 mmol) and ligand **TzBDP** (0.012 mmol) were dissolved in a mixed solution of CH_3CN/H_2O (2.0 mL/1.0 mL), and then 20 μL of HCl was added. The resulting solution was transferred to a Teflon-lined Parr bomb and heated at 130 ºC for 48 hours. After cooling to room temperature slowly, brown crystals of Cd–**TzBDP** were obtained. Further purification was carried out by washing the crystals with CH_3CN three times and the product was dried in a vacuum overnight. Yield: 80% (based on metal salt).

4. Single Crystal X-Ray Analyses.

Single-crystal X-ray diffraction data of Cd−**TzBDP** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation source using the SMART and SAINT programs.[2-3] All structures were solved by the direct method and refined with full-matrix least squares on F^2 using the SHELXTL-2014 program package.[4] All host-framework non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically. The PLATON SQUEEZE treatment[5] was applied to Cd−**TzBDP**. Crystallographic data and refinement parameters were provided in Table S1.

Table S1. Crystal data and structure refinement for Cd−**TzBDP**.

Compound	Cd−**TzBDP**
Empirical formula	$C_{15}H_7CdN_3O_7S$
Formula weight	485.68
Temperature/K	260(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	7.7436(17)
b/Å	9.132(2)
c/Å	12.604(3)
α/°	108.398(4)
β/°	91.815(4)
γ/°	108.545(4)
Volume/Å^3	793.1(3)
Z	2
ρ_{calc}g/cm^3	2.034
μ/mm^{-1}	1.557
F(000)	476.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.01 to 61.802
Reflections collected	4977
Data/restraints/parameters	4977/4/251
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0513, wR_2 = 0.1016
Final R indexes [all data]	R_1 = 0.0755, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	1.83/-1.36
CCDC number	2355405

5. Characterization of Coordination Polymer.

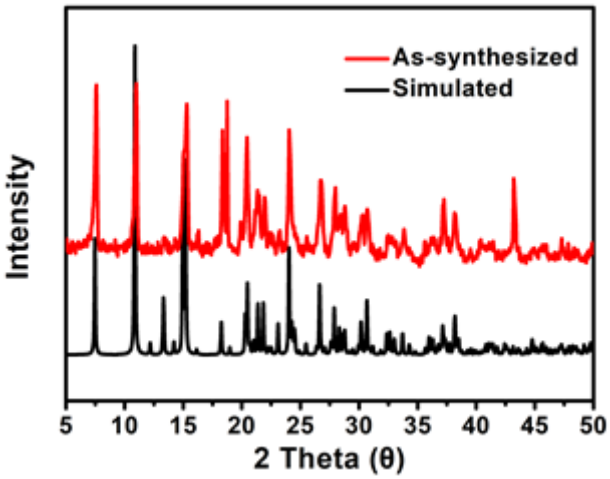


Fig. S1 PXRD patterns of simulated and as-synthesized Cd–**TzBDP**.

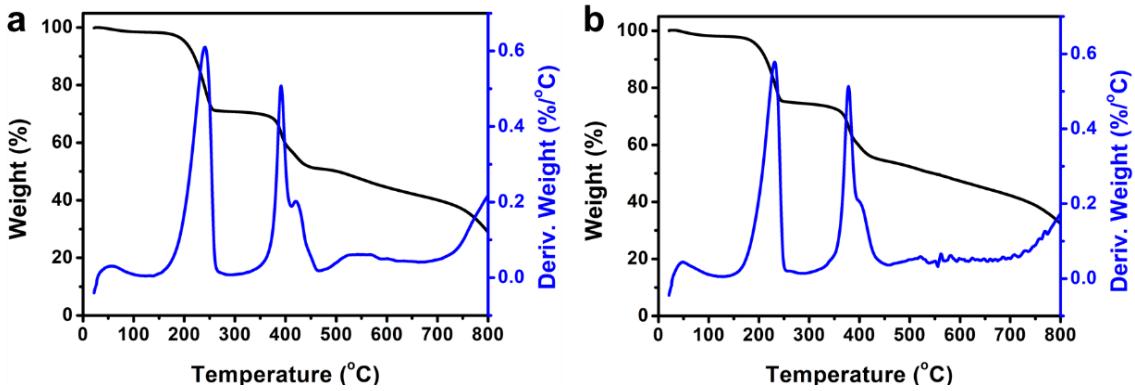


Fig. S2 Thermogravimetric analyses (TGA) of the as-synthesized (a) and recovered (b) Cd–**TzBDP**.

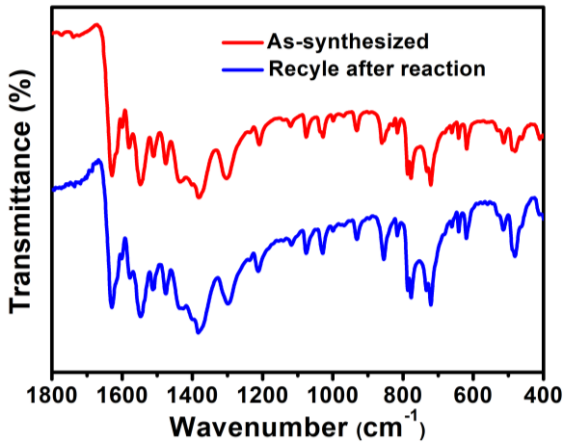


Fig. S3 IR spectra of the as-synthesized and recovered Cd–**TzBDP**.

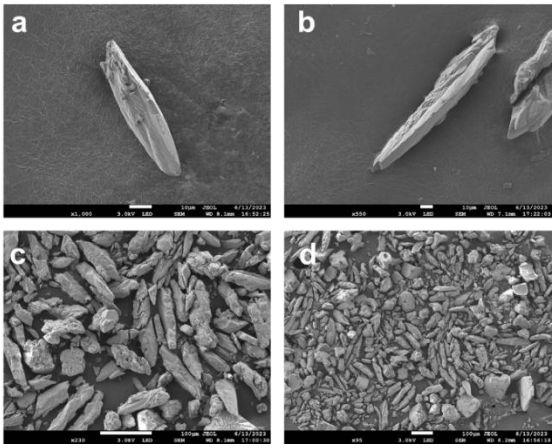


Fig. S4 Scanning electron microscopy (SEM) images of Cd−**TzBDP**.

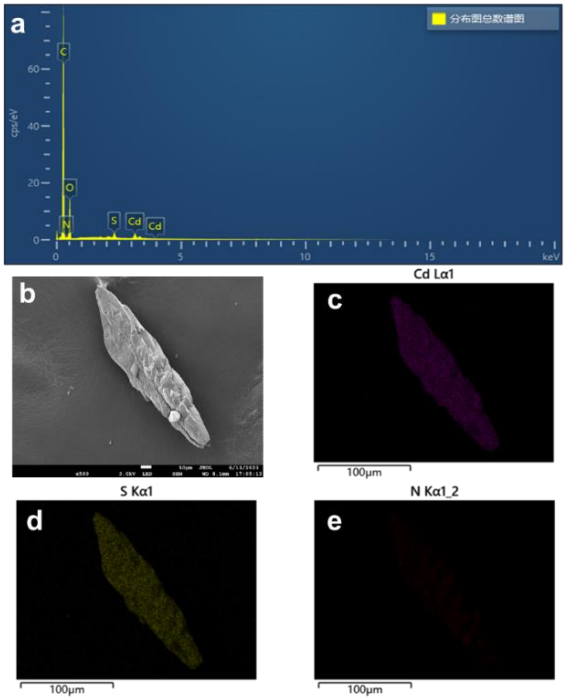


Fig. S5 The EDS (a) and SEM images (b) of Cd−**TzBDP** and elemental mapping images of the block crystal for Cd (c), S (d), and N (e) elements.

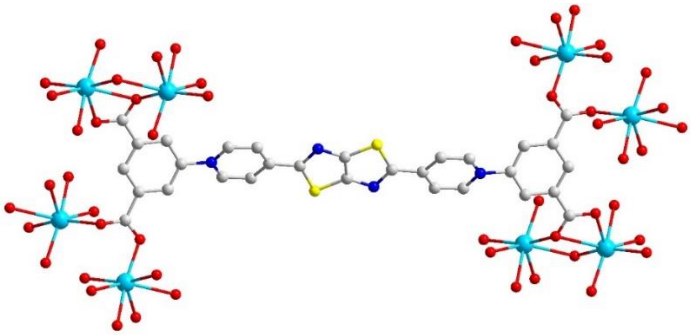


Fig. S6 The coordination environment of Cd−**TzBDP**.

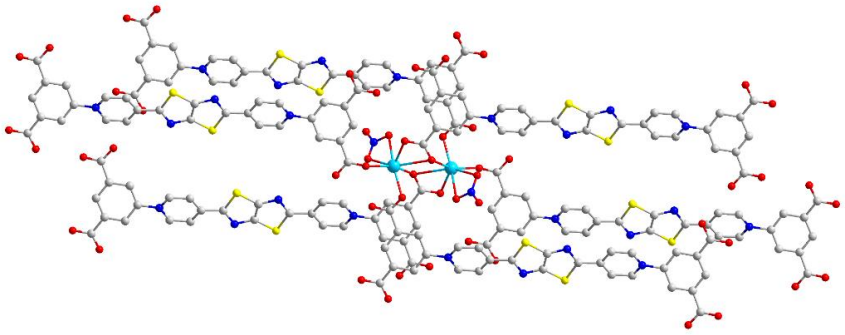


Fig. S7 The dinuclear motif of Cd−**TzBDP**.

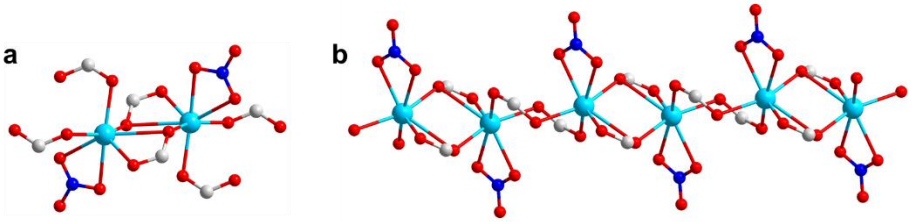


Fig. S8 (a) A dinuclear metallic cluster $Cd_2(O_2C)_6(O_3N)_2$ (Cd_2). (b) The coordinated environments of a one-dimensional Cd−O−Cd chain.

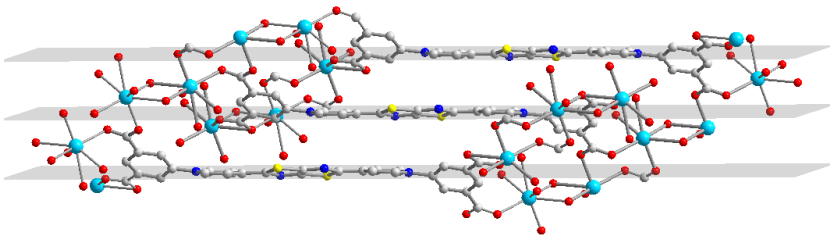


Fig. S9 The close aromatic stacking of ligand moieties and the distance between two adjacent planes (grey planes) is 3.4 Å.

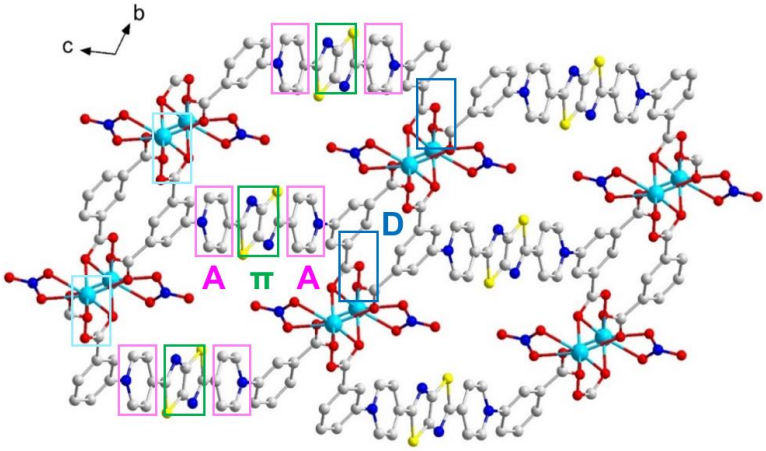


Fig. S10 Windows in the Cd−**TzBDP**. The blue, purple, and green boxes represent the stacking columns of **D**, **A**, and π.

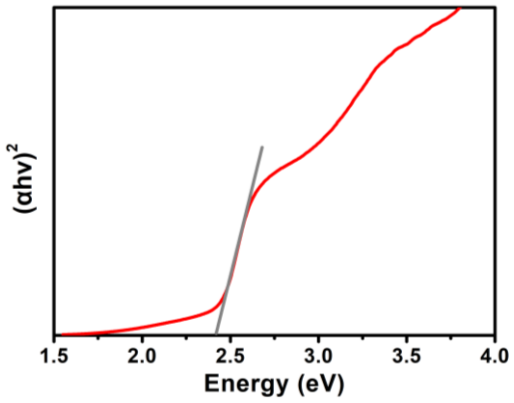


Fig. S11 Tauc plot of Cd–**TzBDP**.

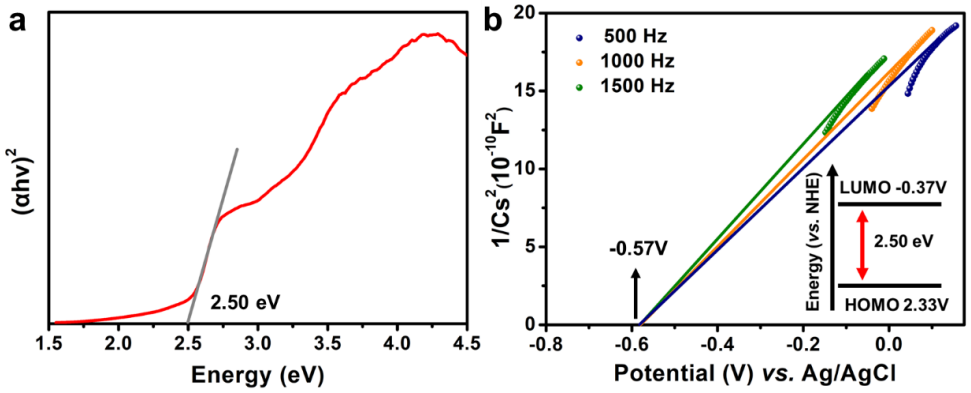


Fig. S12 Tauc plot and Mott–Schottky plots of **TzBDP**.

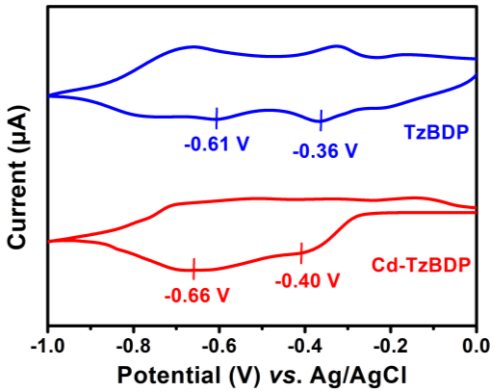


Fig. S13 Solid-state cyclic voltammetry curves of **TzBDP** and Cd–**TzBDP**

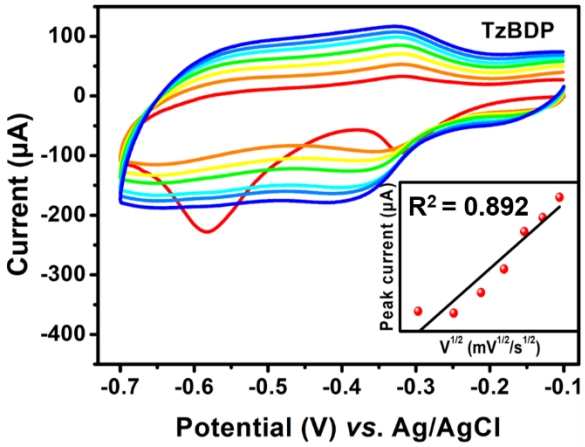


Fig. S14 Cyclic voltammetry curves for **TzBDP** in the negative potential range with varying scan rates: 10, 20, 30, 40, 50, 60, and 70 $mV \cdot s^{-1}$. The inset shows the plot of peak current density *vs*. the square roots of the scan rate $(\upsilon)^{1/2}$.

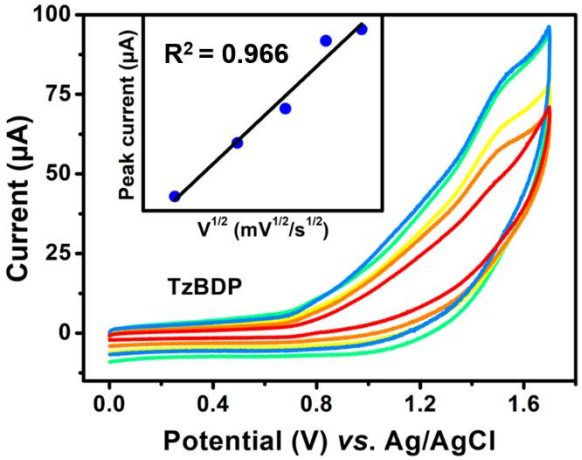


Fig. S15 Cyclic voltammetry curves for **TzBDP** in the positive potential range with varying scan rates: 10, 20, 30, 40, and 50 $mV \cdot s^{-1}$. The inset shows the plot of peak current density *vs*. the square roots of the scan rate $(\upsilon)^{1/2}$.

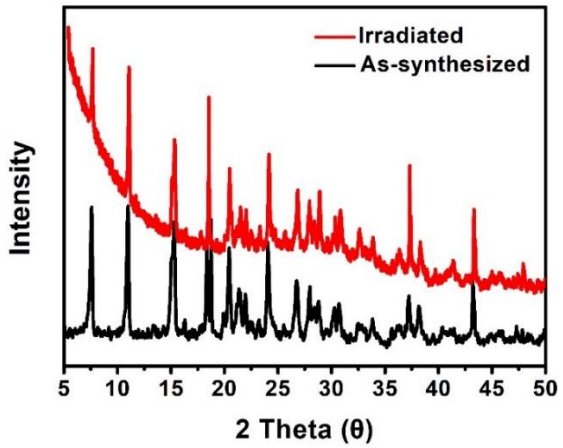


Fig. S16 The PXRD patterns of Cd–**TzBDP** before and after irradiation.

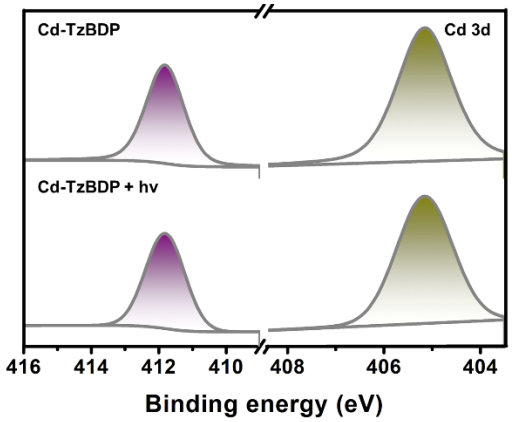


Fig. S17 Cd 3d core-level spectra of Cd−**TzBDP** before and after irradiation.

6. Photocatalytic Details.

General Procedure for Photocatalytic α-Cyanation of Tertiary Amine

A glass tube was filled with a magnetic stir bar, *N*,*N*-dimethylaniline **1** (1 equiv., 0.2 mmol), trimethylsilyl cyanide (0.6 mmol), Cd−**TzBDP** (5 mol% based on ligand moiety, 0.01 mmol), DMF/CH_3CN (2 mL /1 mL). The resulting mixture was stirred and irradiated with white LEDs in air condition for 24 hours (with circulating water to keep the reaction at room temperature). After the reaction finished, Cd−**TzBDP** was filtered and the filtrate was concentrated. Further purification of the crude product was achieved to give the target product **2** by flash chromatography on silica gel.

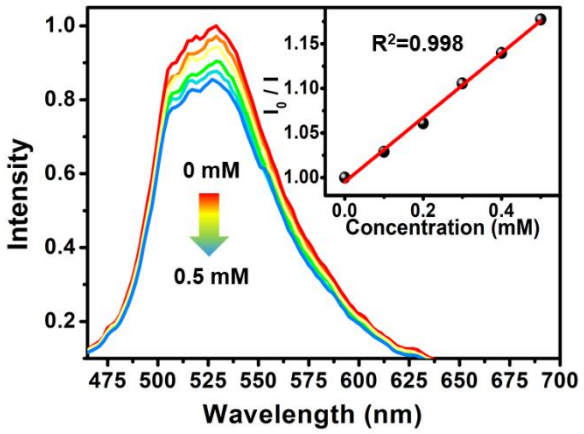


Fig.S18 Luminescence quenching spectra of Cd−**TzBDP** suspension upon addition of *N*,*N*-dimethylaniline **1a**.

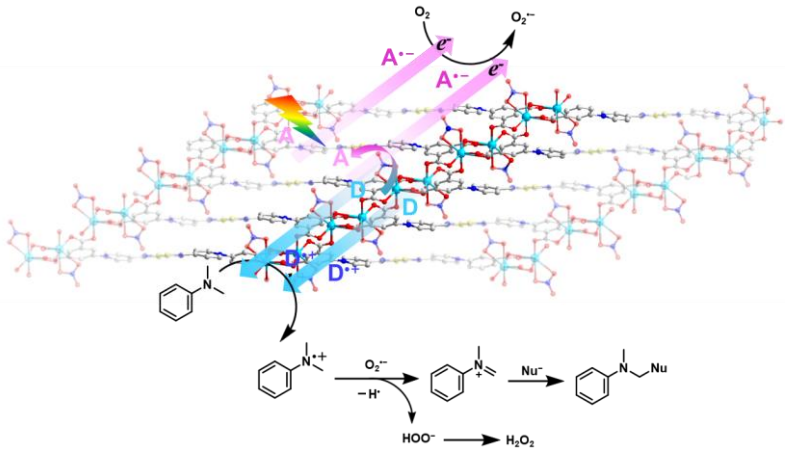
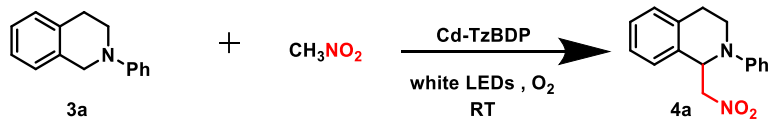


Fig. S19 Plausible mechanism for the photocatalytic α-C-H activation of tertiary amine **1** *via* Cd−**TzBDP**.

General Procedure for Photocatalytic α-Functionalization of Tertiary Amine

A glass tube was filled with a magnetic stir bar, *N*-aryl-tetrahydroisoquinoline **3** (1 equiv., 0.2 mmol), Cd−**TzBDP** (5 mol% based on ligand moiety, 0.01 mmol), nitroalkane (1.0 mL) or other specified nucleophile (2 mmol), and CH_3OH (1 mL). The resulting mixture was stirred and irradiated with a white LED in the air for 24 hours (with circulating water to keep the reaction at room temperature). Cd−**TzBDP** was filtered after the reaction was finished. The filtrate was concentrated and further purified by silica gel column chromatography to obtain the target product **4**.

Table S2. The photocatalytic α-functionalization of *N*-phenyl-tetrahydroisoquinoline **3a** under different conditions.



Entry	Variation from the standard	Yield (%)
1[a]	None	94
2[b]	$Cd(NO_3)_2{\cdot}4H_2O$	trace
3[c]	**TzBDP**	40
4	$Cd(NO_3)_2{\cdot}4H_2O$ and **TzBDP**	39
5	No light	N.R.
6	No Catalyst	N.R.

[a] Standard conditions: substrate (1 equiv., 0.2 mmol), nitromethane (1 mL), Cd−**TzBDP** (5 mol% based on ligand moiety), CH_3OH (1 mL), irradiation by white LEDs for 24 h. Isolated yields. [b] $Cd(NO_3)_2{\cdot}4H_2O$ (0.02 mmol) or [c] **TzBDP** (0.01 mol) was used in the amount equivalent to the corresponding component of Cd−**TzBDP**. N.R.= no reaction.

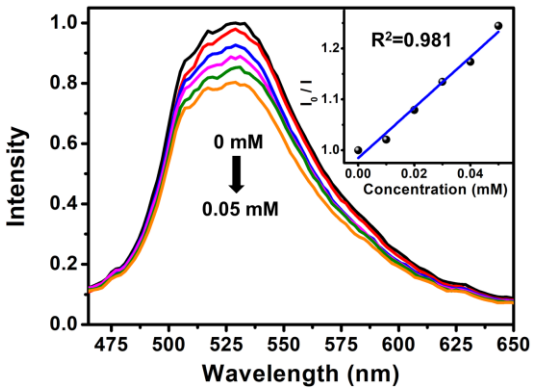


Fig. S20 Fluorescence quenching spectra of Cd−**TzBDP** upon the addition of *N*-phenyl-tetrahydroisoquinoline **3a**.

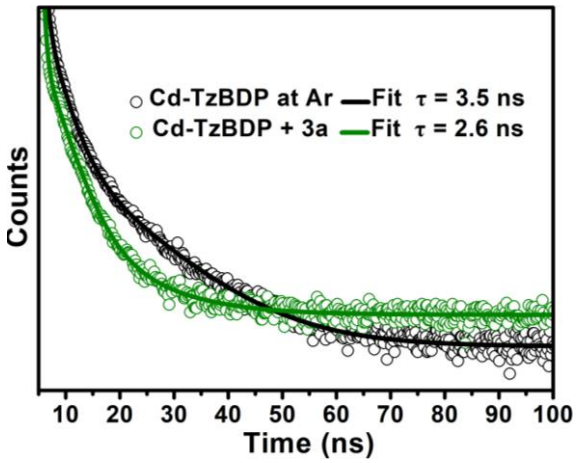


Fig. S21 Time-resolved fluorescence emission decay spectra of Cd–**TzBDP** suspension before and after the addition of *N*-phenyl tetrahydroisoquinoline.

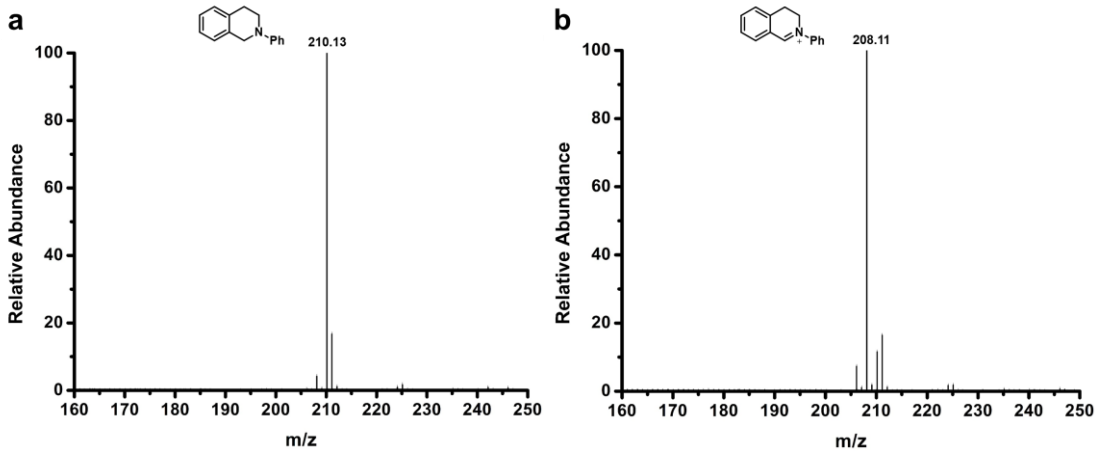


Fig. S22 The EIS-MS of the reaction mixture of *N*-phenyl-tetrahydroisoquinoline **3a** under the standard reaction condition (Table S2, entry 1) except the absence of any nucleophiles, sampling (a) before and (b) after white LED irradiation for 3 hours.

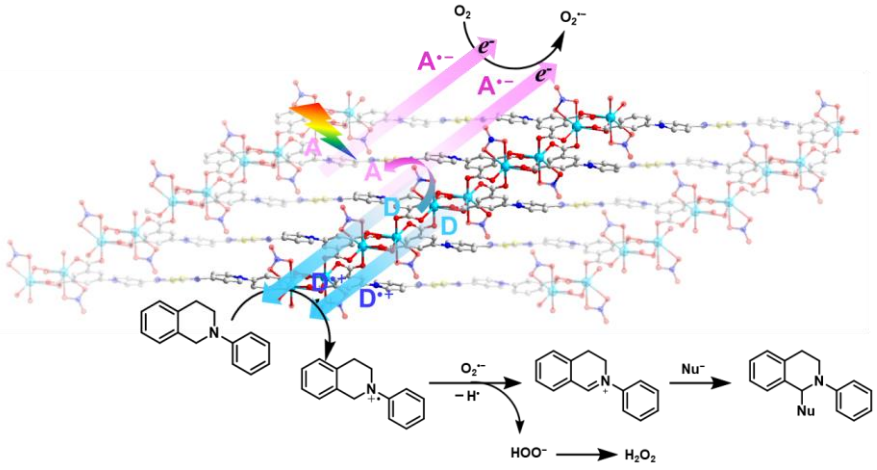
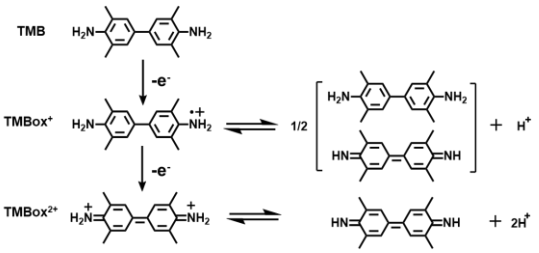


Fig. S23 Proposed mechanism of photocatalytic α-functionalization of tertiary amine **3** by using Cd–**TzBDP** as the photocatalyst.

Table S3. Comparison of the catalytic performances in the oxidative α-functionalizations of tertiary amines.

Catalyst	Reaction Conditions	Yields (%)	Gram-Scale Synthesis	Reaction Scopes	Value-Added Applications	Ref.
EY@UiO−66-NH_2	10 mg catalyst, visible household light, MeOH, 4 h, air	63~96		22 examples		6
In−TPBD-20	0.005 mmol catalyst, 455 nm LED, CH_3CN, 12 h, O_2	53~98		28 examples		7
TiO_2−DHMIQ NPs	2.5 mg catalyst, 462 nm LED, CH_3CN, 3/16/24 h, O_2	85~97		8 examples	cyano-gramine, cyano-nicotine, cyano-atropine	8
$AuClPPh_3$	10 mol% catalyst, MeOH, 5 h, ^tBuOOH	92~98		9 examples		9
Cd−TzBDP	**5 mol% catalyst, White LED DMF-CH_3CN/MeOH, 24 h, O_2**	**70~99**	**Yes**	**24 examples**	**cyano corydaline, cyano gramine, nitromethyl corydaline**	**This work**

7. Biomimicking ETC-mediated Electron Leak by Photocatalytic Membrane Reactor.



Scheme S3. Reaction scheme for the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB).

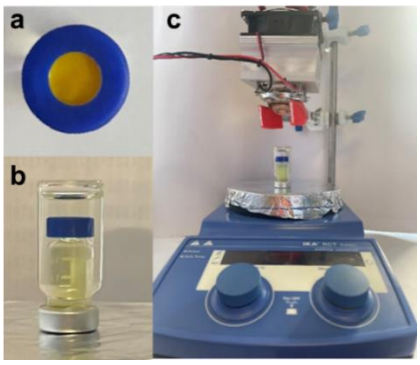


Fig. S24 Illustration of the photocatalytic reactions over Cd−**TzBDP**@Nafion membrane. (a) Cap of the vial inlaid with Cd−**TzBDP**@Nafion membrane. The original Nafion membrane was placed in 2 mL ethanol for 30 minutes, then cut into a circle with a diameter of *ca*. 6 mm. The Cd−**TzBDP** (10 mg) was added to a mixed solution with 0.5 mL of 5 wt% Nafion and 0.5 mL of ethanol. Then one-quarter of the slurry was added to a piece of swelling circular Nafion membrane by drop-casting and drying in air. (b) A nested double-layered photoreactor consisting of an interior vial (with a degassed 1.5 mL CH_3CN solution of 0.015 mmol TMB) and an outer sealed ampoule (with an air-saturated 4.0 mL CH_3CN). (c) Diagram of the reaction setup for membrane reactor with a 405 nm LED.

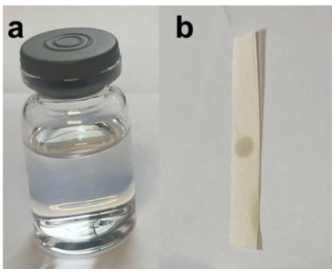


Fig. S25 (a) Diagram of the reaction mixture in the outer sealed ampoule (containing the normoxic CH_3CN with ROS-like peroxides), the interior vial was taken out after photoirradiation. (b) Detecting H_2O_2 from the reaction mixture of the outer ampoule bottle by KI/Starch testing paper after photocatalysis over Cd−**TzBDP**@Nafion membrane.

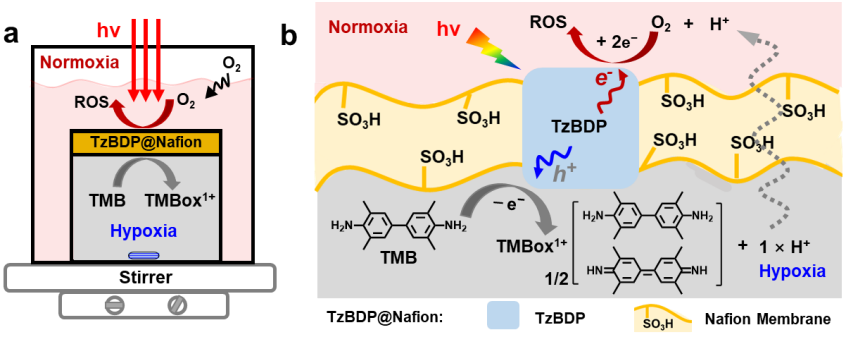
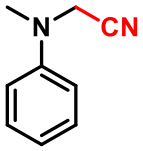


Fig. S26 Schematic illustration of (a) the setup for photocatalytic membrane reactor, and (b) the transfer of electrons and protons across **TzBDP**@Nafion membrane and the distal photooxidation and photoreduction in different compartments.

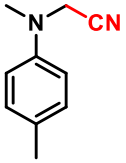
8. NMR Data of the Isolated Compounds

N-Methyl-*N*-phenylaminoacetonitrile (**2a**)



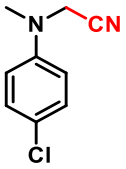
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.9 Hz, 2H), 6.94 – 6.71 (m, 3H), 4.10 (s, 2H), 2.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 129.5, 120.3, 115.5, 114.9, 42.3, 39.3. This compound has been reported by literature, and our spectra were consistent with the literature.[10]

N-Methyl-*N*-(4-methylphenyl)aminoacetonitrile (**2b**)



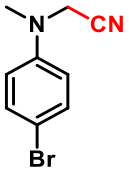
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.14 (s, 2H), 2.97 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 130.0, 129.9, 115.50 (overlapped), 115.47 (overlapped), 42.9, 39.5, 20.4. This compound has been reported by literature, and our spectra were consistent with the literature.[11]

2-((4-Chlorophenyl)(methyl)amino)acetonitrile (**2c**)



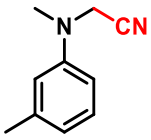
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 4.15 (s, 2H), 2.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 132.3, 116.5, 115. 1, 112.6, 42.2, 39.4. This compound has been reported by literature, and our spectra were consistent with the literature.[10]

2-((4-Bromophenyl)(methyl)amino)acetonitrile (**2d**)



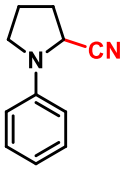
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.08 (m, 2H), 6.72 (d, J = 9.0 Hz, 2H), 4.08 (s, 2H), 2.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 129.4, 125.4, 116.2, 115.2, 42.4, 39.4. This compound has been reported by literature, and our spectra were consistent with the literature.[12]

N-Methyl-*N*-(3-methylphenyl)aminoacetonitrile (**2e**)



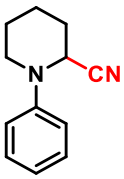
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 1H), 6.75 (d, J = 7.4 Hz, 1H), 6.72 – 6.55 (m, 2H), 4.17 (s, 2H), 2.99 (d, J = 11.8 Hz, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 139.3, 129.3, 121.2, 115.7, 115.5, 112.1, 42.4, 39.3, 21.8. This compound has been reported by literature, and our spectra were consistent with the literature.[11]

1-Phenylpyrrolidine-2-carbonitrile (**2f**)



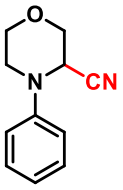
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 7.9 Hz, 2H), 4.53 – 4.36 (m, 1H), 3.47 (td, J = 8.3, 2.8 Hz, 1H), 3.38 (dd, J = 15.7, 8.4 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.36 – 2.16 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 129.5, 119.3, 118.3, 112.7, 49.1, 47.5, 31.6, 24.0. This compound has been reported by literature, and our spectra were consistent with the literature.[12]

1-Phenylpiperidine-2-carbonitrile (**2g**)



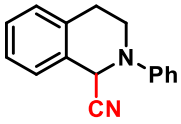
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 2H), 7.00 (t, J = 8.1 Hz, 3H), 4.63 (d, J = 3.3 Hz, 1H), 3.45 (d, J = 12.1 Hz, 1H), 3.04 (ddd, J = 12.1, 9.5, 2.5 Hz, 1H), 2.03 (d, J = 3.5 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.75 – 1.65 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 129.4, 122.2, 118.3, 117.2, 52.0, 46.6, 29.3, 25.2, 20.2. This compound has been reported by literature, and our spectra were consistent with the literature.[12]

4-Phenylmorpholine-3-carbonitrile (**2h**)



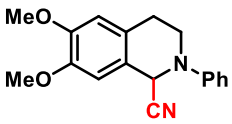
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 7.4 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H), 4.44 (s, 1H), 4.19 (d, J = 11.5 Hz, 1H), 4.12 (d, J = 11.4 Hz, 1H), 3.94 (d, J = 11.5 Hz, 1H), 3.84 – 3.63 (m, 1H), 3.32 (d, J = 7.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 129.6, 122.7, 117.3, 116.0, 68.1, 66.9, 51.1, 45.5. This compound has been reported by literature, and our spectra were consistent with the literature.[7]

2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**2i**)



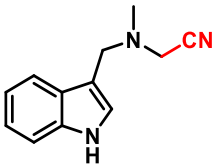
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 6H), 7.07 (d, J = 7.9 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 5.50 (s, 1H), 3.74 (ddd, J = 5.8, 2.9, 0.9 Hz, 1H), 3.47 (ddd, J = 12.4, 10.8, 4.1 Hz, 1H), 3.14 (ddd, J = 16.5, 10.7, 6.0 Hz, 1H), 2.95 (dt, J = 16.3, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 134.7, 129.6, 129.6, 129.4, 128.8, 127.1, 126. 9, 121.9, 117.8, 117.6, 53.2, 44.2, 28.6. This compound has been reported by literature, and our spectra were consistent with the literature.[9]

6,7-Dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**2j**)



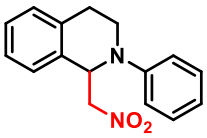
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.5, 7.5 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 7.02 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 25.3 Hz, 2H), 5.44 (s, 1H), 3.894 (s, 3H) (overlapped), 3.892 (s, 3H) (overlapped), 3.84 – 3.73 (m, 1H), 3.54 – 3.33 (m, 1H), 3.09 (ddd, J = 16.7, 11.1, 5.9 Hz, 1H), 2.94 – 2.78 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.5, 148.1, 129.6, 126.9, 122.0, 121.1, 117.9, 117.8, 111.6, 109.3, 56.1, 56.0, 53.1, 44.2, 28.1. This compound has been reported by literature, and our spectra were consistent with the literature.[13]

2-(((1*H*-indol-3-yl)methyl)(methyl)amino)acetonitrile (**2k**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.17 – 6.97 (m, 3H), 3.69 (d, *J* = 4.0 Hz, 2H), 3.33 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 127.2, 124.2, 122.4, 119.8, 119.4, 114.9, 111.6, 111.3, 51.2, 43.6, 42.4. This compound has been reported by literature, and our spectra were consistent with the literature.[8]

1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**4a**)

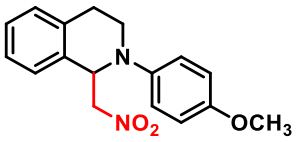


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 13.6, 6.1 Hz, 3H), 7.20 (dd, *J* = 15.9, 7.6 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 5.55 (t, *J* = 7.2 Hz, 1H), 4.87 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.56 (dd, *J* = 11.9, 6.7 Hz, 1H), 3.69 – 3.57 (m, 2H), 3.13 – 3.05 (m, 1H), 2.79 (dt, *J* = 16.3, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 135.3, 132.9, 129.5, 129.2, 128.1, 127.0, 126.7, 119.5, 115.1, 78.8, 58.2, 42.1, 26.5. This compound has been reported by literature, and our spectra were consistent with the literature.[14]

1-(Nitromethyl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (**4b**)

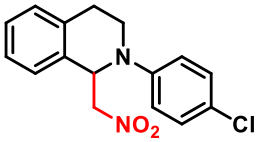
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 6.96 (m, 6H), 6.87 (d, *J* = 7.9 Hz, 2H), 5.48 (t, *J* = 6.9 Hz, 1H), 4.82 (dd, *J* = 11.3, 8.4 Hz, 1H), 4.53 (dd, *J* = 11.6, 6.3 Hz, 1H), 3.71 – 3.44 (m, 2H), 3.03 (d, *J* = 6.8 Hz, 1H), 2.73 (d, *J* = 16.3 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 135.4, 133.0, 130.0, 129.3, 129.1, 128.0, 127.0, 126.8, 115.9, 78.9, 58.4, 42.3, 26.2, 20.4. This compound has been reported by literature, and our spectra were consistent with the literature.[14]

2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4c**)



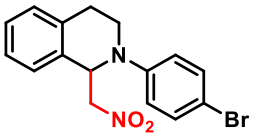
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.13 (m, 4H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.42 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.86 (dd, *J* = 11.9, 8.7 Hz, 1H), 4.59 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.78 (s, 3H), 3.65 – 3.56 (m, 2H), 3.05 (ddd, *J* = 16.2, 9.1, 6.9 Hz, 1H), 2.72 (dt, *J* = 16.5, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 143.1, 135.5, 132.9, 129.5, 127.9, 126.9, 126.6, 118.9, 114.7, 79.0, 58.9, 55.6, 43.1, 25.8. This compound has been reported by literature, and our spectra were consistent with the literature.[15]

2-(4-Chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4d**)



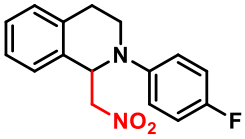
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.00 (m, 6H), 6.86 – 6.72 (m, 2H), 5.40 (dd, J = 14.8, 7.5 Hz, 1H), 4.76 (dd, J = 12.0, 8.2 Hz, 1H), 4.49 (dd, J = 12.0, 6.3 Hz, 1H), 3.60 – 3.43 (m, 2H), 3.04 – 2.91 (m, 1H), 2.70 (dt, J = 16.4, 4.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 135.1, 132.5, 129.34 (two peaks overlapped), 128.3, 127.0, 126.8, 124.4, 116.5, 78.7, 58.2, 42.2, 26.2. This compound has been reported by literature, and our spectra were consistent with the literature.[16]

2-(4-Bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4e**)



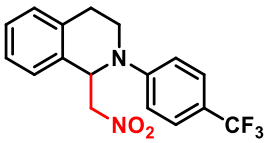
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.9 Hz, 2H), 7.30 – 7.12 (m, 4H), 6.87 (d, J = 8.9 Hz, 2H), 5.51 (t, J = 7.2 Hz, 1H), 4.87 (dd, J = 11.9, 8.1 Hz, 1H), 4.59 (dd, J = 11.9, 6.4 Hz, 1H), 3.64 (dd, J = 8.8, 4.1 Hz, 2H), 3.19 – 3.01 (m, 1H), 2.81 (dt, J = 16.4, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 135.1, 132.5, 132.2, 129.3, 128.3, 127.0, 126.9, 116.8, 111.6, 78.6, 58.1, 42.1, 26.2. This compound has been reported by literature, and our spectra were consistent with the literature.[16]

2-(4-Fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4f**)



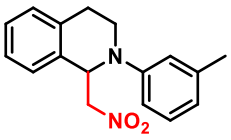
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.02 (m, 4H), 6.91 – 6.69 (m, 4H), 5.35 (dd, J = 8.4, 6.1 Hz, 1H), 4.75 (dd, J = 12.0, 8.7 Hz, 1H), 4.49 (dd, J = 12.0, 5.9 Hz, 1H), 3.58 – 3.38 (m, 2H), 2.95 (ddd, J = 16.0, 9.1, 6.5 Hz, 1H), 2.64 (dt, J = 16.5, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (d, J = 239.2 Hz), 145.3 (d, J = 2.3 Hz), 135.3, 132.6, 129.5, 128.1, 127.0, 126.8, 117.95 (d, J = 7.7 Hz), 115.89 (d, J = 22.1 Hz), 78.9, 58.7, 42.8, 25.8. This compound has been reported by literature, and our spectra were consistent with the literature.[14]

1-(Nitromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (**4g**)



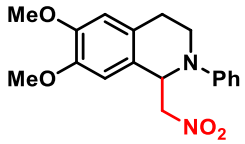
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 8.7 Hz, 2H), 7.16 (ddd, J = 19.4, 13.4, 7.3 Hz, 3H), 7.06 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 5.53 (t, J = 7.2 Hz, 1H), 4.78 (dd, J = 12.0, 7.7 Hz, 1H), 4.51 (dd, J = 12.0, 6.8 Hz, 1H), 3.66 – 3.41 (m, 2H), 3.09 – 2.95 (m, 1H), 2.78 (dt, J = 16.2, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 134.9, 132.4, 129.2, 128.5, 127.05 (overlapped), 127.00 (overlapped), 126.9 (q, J = 3.6 Hz), 124.7 (q, J = 270.8 Hz), 113.4 (two peaks overlapped), 78.5, 57.8, 41.8, 26.6. This compound has been reported by literature, and our spectra were consistent with the literature.[16]

1-(Nitromethyl)-2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline (**4h**)



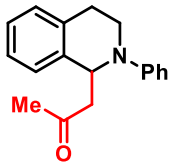
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (ddt, J = 31.3, 15.5, 7.3 Hz, 5H), 6.70 (d, J = 9.3 Hz, 2H), 6.59 (d, J = 7.4 Hz, 1H), 5.45 (t, J = 7.2 Hz, 1H), 4.77 (dd, J = 11.8, 7.8 Hz, 1H), 4.46 (dd, J = 11.8, 6.7 Hz, 1H), 3.61 – 3.41 (m, 2H), 3.04 – 2.91 (m, 1H), 2.69 (dt, J = 16.3, 4.9 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 139.3, 135.4, 133.0, 129.4, 129.2, 128.1, 127.0, 126.7, 120.4, 115.9, 112.2, 78.8, 58.2, 42.1, 26.6, 21.9. This compound has been reported by literature, and our spectra were consistent with the literature.[14]

6,7-Dimethoxy-1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**4i**)



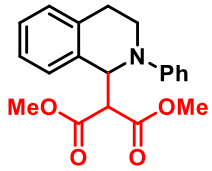
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J = 9.2, 6.4 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 17.8 Hz, 2H), 5.46 (t, J = 7.1 Hz, 1H), 4.85 (dd, J = 11.7, 8.0 Hz, 1H), 4.56 (dd, J = 11.8, 6.4 Hz, 1H), 3.856 (s, 3H, overlapped), 3.849 (s, 3H, overlapped), 3.67 (dt, J = 10.0, 4.9 Hz, 1H), 3.62 – 3.47 (m, 1H), 3.10 – 2.92 (m, 1H), 2.67 (dt, J = 16.1, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 148.6, 147.7, 129.5, 127.4, 124.6, 119.6, 115.5, 111.7, 109.6, 78.8, 58.0, 56.1, 55.9, 42.1, 25.8. This compound has been reported by literature, and our spectra were consistent with the literature.[17]

1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (**4j**)



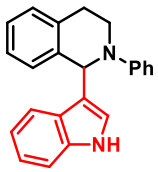
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 6H), 6.93 (d, J = 8.2 Hz, 2H), 6.77 (t, J = 7.4 Hz, 1H), 5.40 (t, J = 6.3 Hz, 1H), 3.69 – 3.61 (m, 1H), 3.57 – 3.48 (m, 1H), 3.10 – 3.00 (m, 2H), 2.87 – 2.77 (m, 2H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 148.9, 138.3, 134.4, 129.4, 129.3, 128.7, 126.9, 126.8, 126.3, 118.3, 114.8, 54.8, 50.2, 42.1, 31.1, 27.2. This compound has been reported by literature, and our spectra were consistent with the literature.[15]

Dimethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (**4k**)



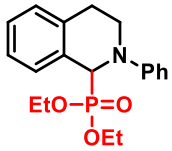
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.05 (m, 6H), 6.97 (t, J = 10.8 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 5.70 (d, J = 9.4 Hz, 1H), 3.96 (t, J = 9.4 Hz, 1H), 3.78 – 3.59 (m, 5H), 3.55 (s, 3H), 3.07 (ddd, J = 15.6, 8.9, 6.4 Hz, 1H), 2.87 (dt, J = 16.5, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 167.4, 148.8, 135.7, 134.8, 129.1, 129.0, 127.6, 127.1, 126.0, 118.6, 115.2, 59.1, 58.2, 52.5, 42.2, 29.7, 26.1. This compound has been reported by literature, and our spectra were consistent with the literature.[16]

1-(1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**4l**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.46 (dd, J = 15.5, 5.6 Hz, 1H), 7.23 – 7.07 (m, 7H), 6.95 (dd, J = 7.5, 4.6 Hz, 3H), 6.70 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 1.7 Hz, 1H), 6.10 (s, 1H), 3.55 (dd, J = 7.6, 4.6 Hz, 2H), 2.99 (dt, J = 15.6, 7.7 Hz, 1H), 2.73 (dt, J = 16.2, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 137.4, 136.6, 135.6, 129.2, 128.8, 128.1, 126.7, 126.5, 125.7, 124.2, 122.1, 120.1, 119.7, 119.3, 118.1, 115.8, 111.0, 56.7, 42.3, 26.6. This compound has been reported by literature, and our spectra were consistent with the literature.[18]

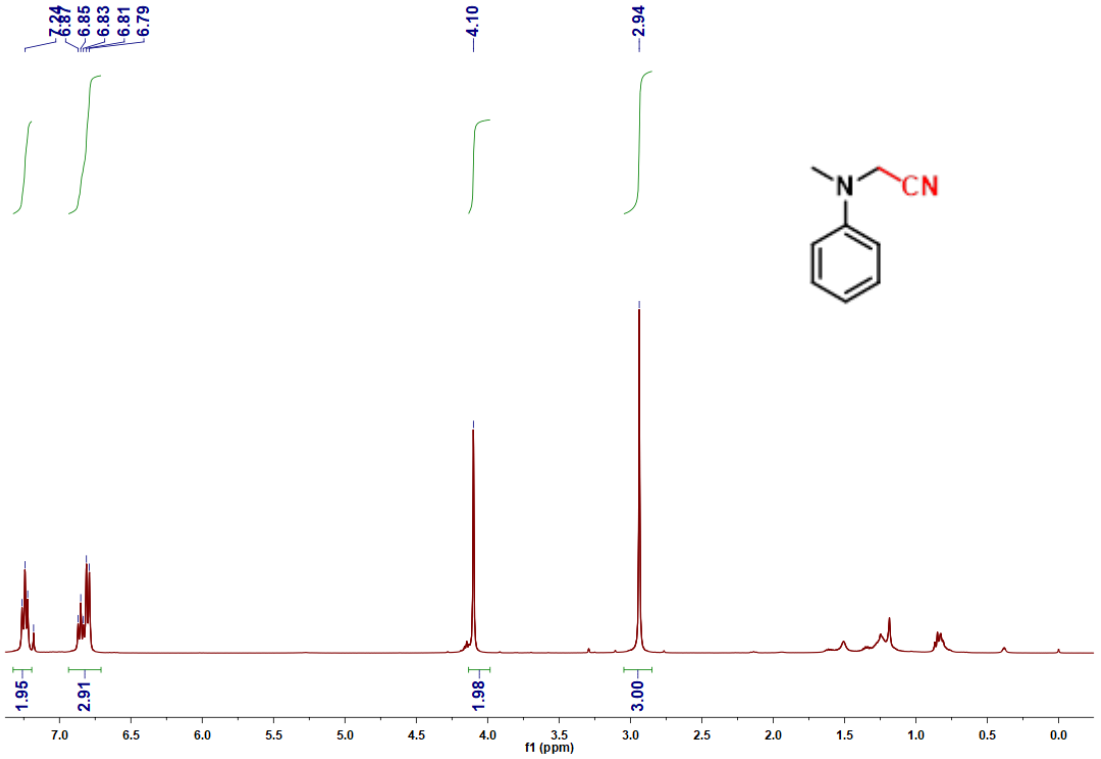
Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-yl) phosphonate (**4m**)

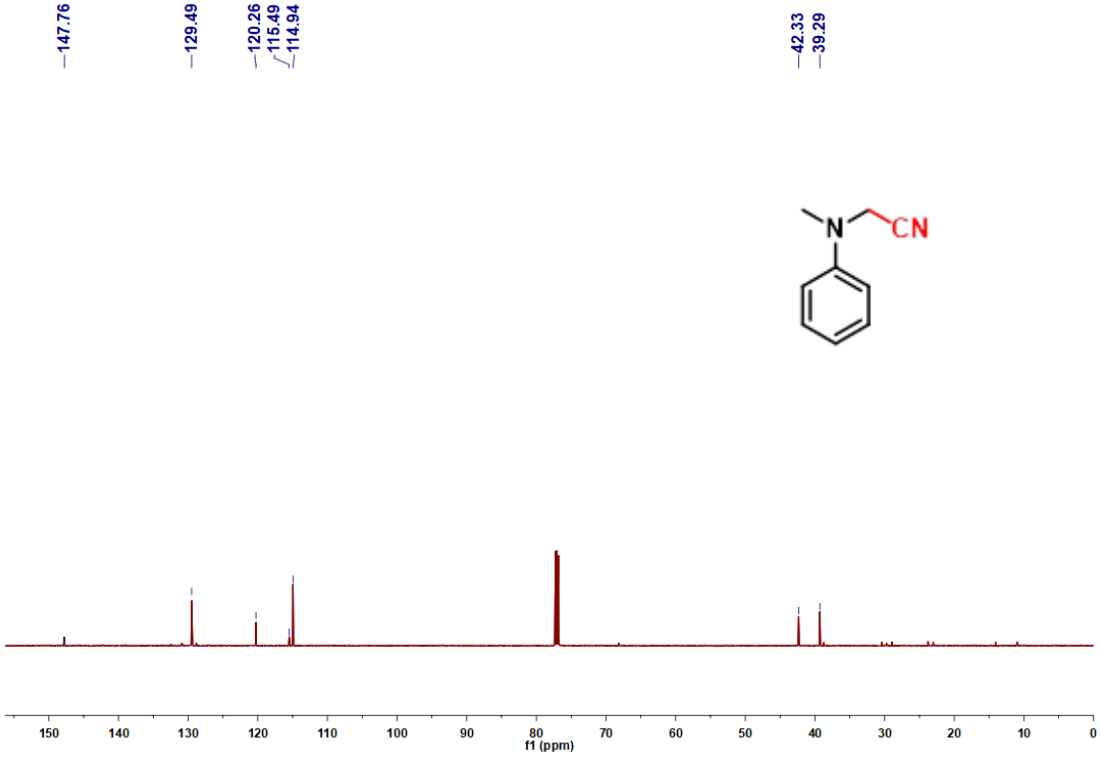


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 1H), 7.30 – 7.09 (m, 5H), 6.97 (d, J = 8.3 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 5.18 (d, J = 20.0 Hz, 1H), 4.16 – 3.85 (m, 5H), 3.62 (dt, J = 11.9, 6.0 Hz, 1H), 3.18 – 2.92 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4 (d, J = 6.0 Hz), 136.5 (d, J = 5.5 Hz), 130.7, 129.2, 128.8 (d, J = 2.1 Hz), 128.2 (d, J = 4.6 Hz), 127.4 (d, J = 3.4 Hz), 125.9 (d, J = 2.7 Hz), 118.5, 114.8, 63.3 (d, J = 7.3 Hz), 62.4 (d, J = 7.6 Hz), 58.8 (d, J = 159.1 Hz), 43.5, 26.8, 16.5 (d, J = 5.4 Hz), 16.4 (d, J = 5.6 Hz). This compound has been reported by literature, and our spectra were consistent with the literature.[16]

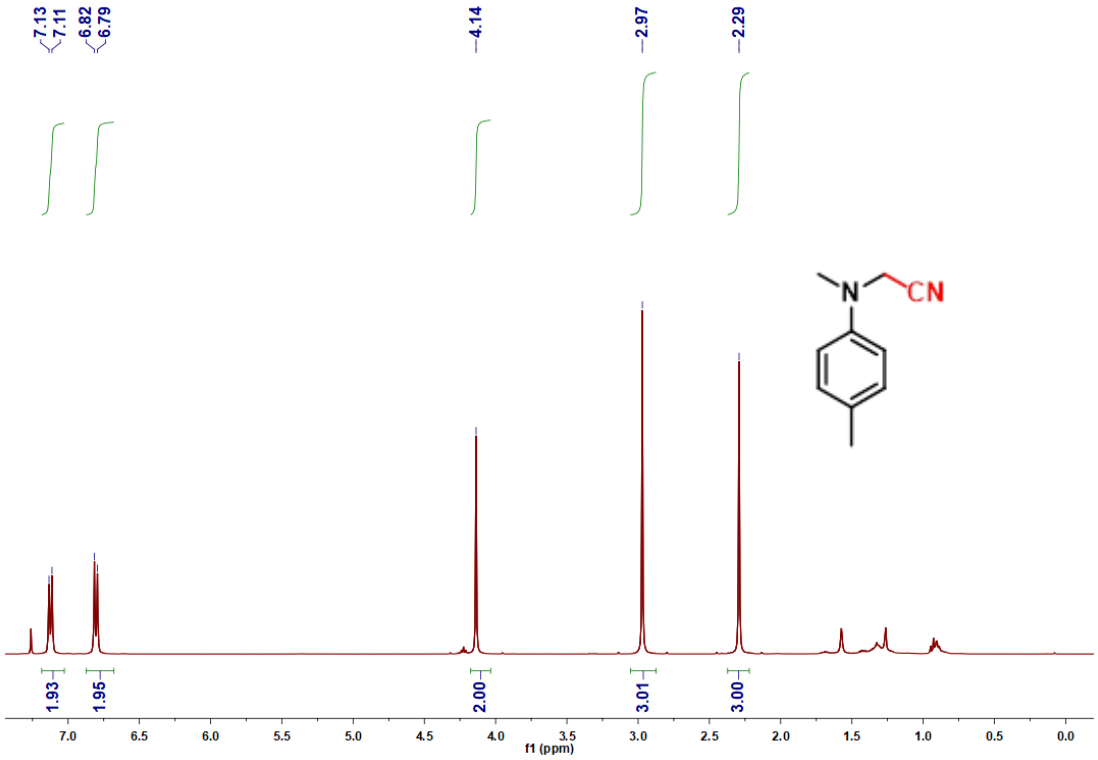
9. NMR Spectra of the Isolated Compounds.

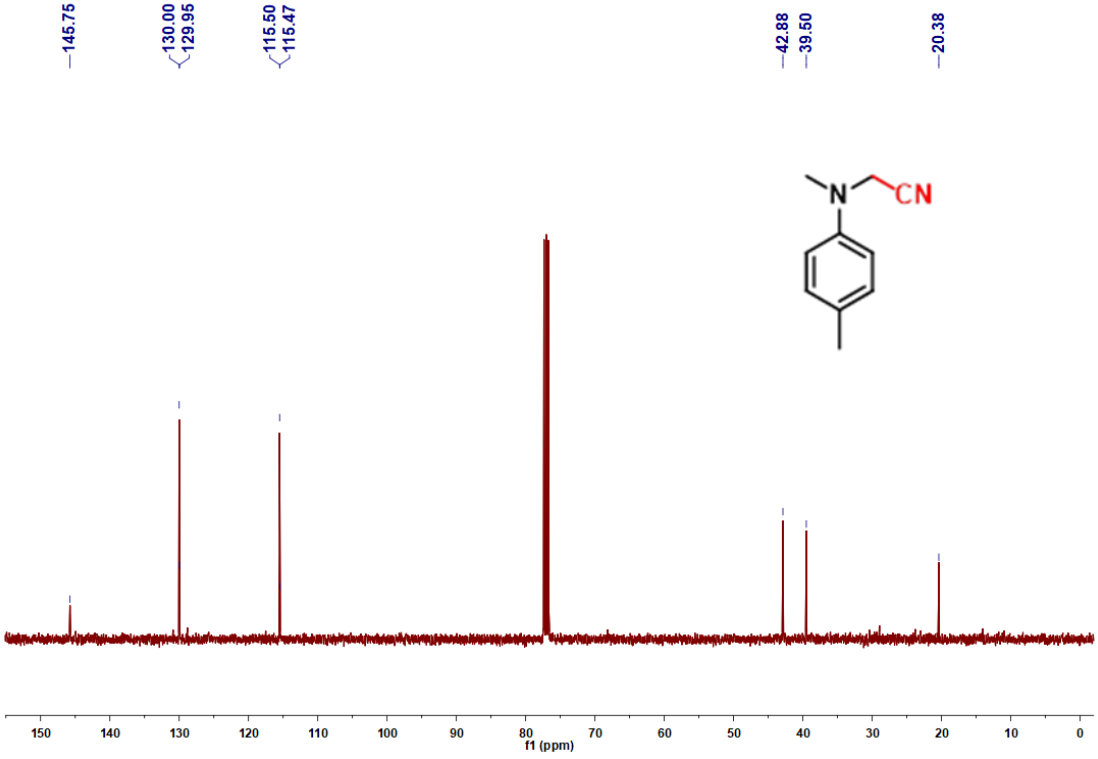
^{1}H and ^{13}C NMR Spectra of *N*-Methyl-*N*-phenylaminoacetonitrile (**2a**)



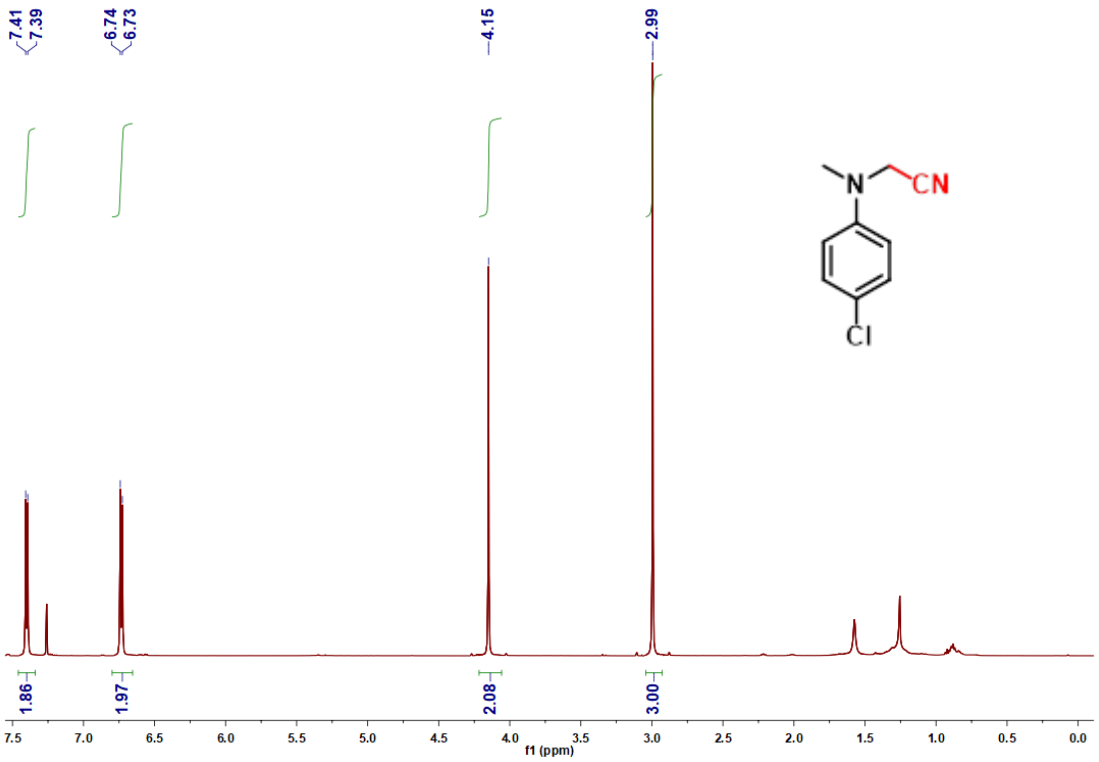


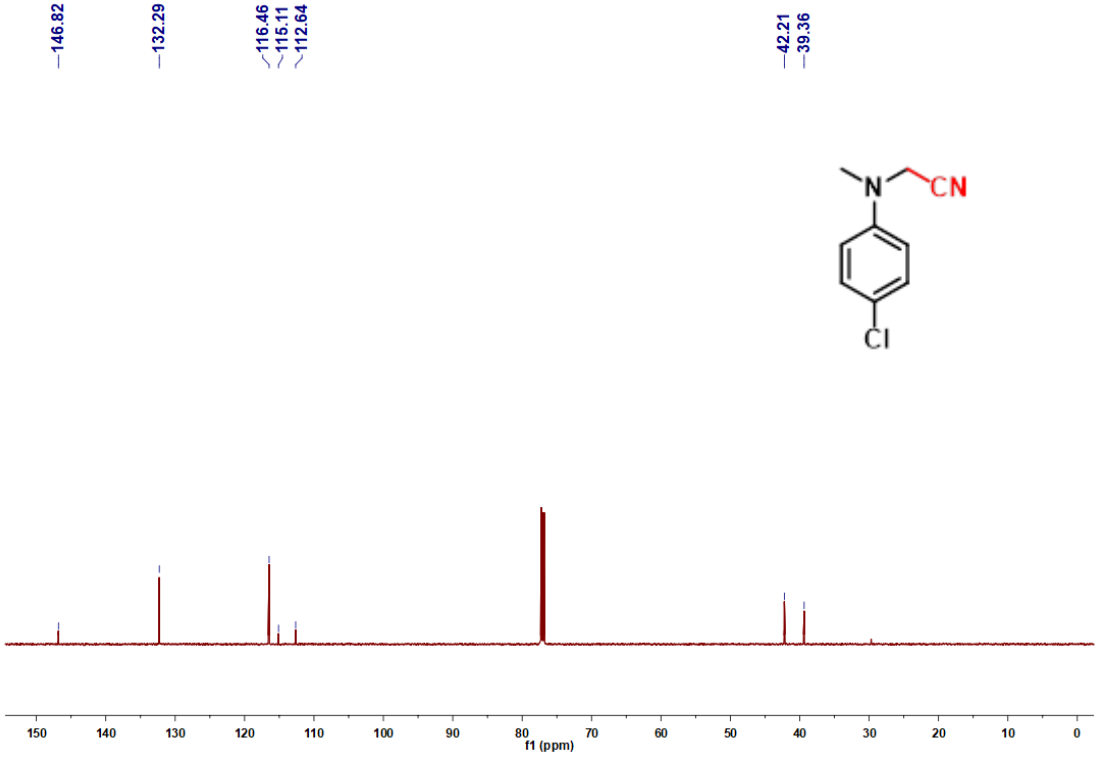
^{1}H and ^{13}C NMR Spectra of *N*-Methyl-*N*-(4-methylphenyl)aminoacetonitrile (**2b**)



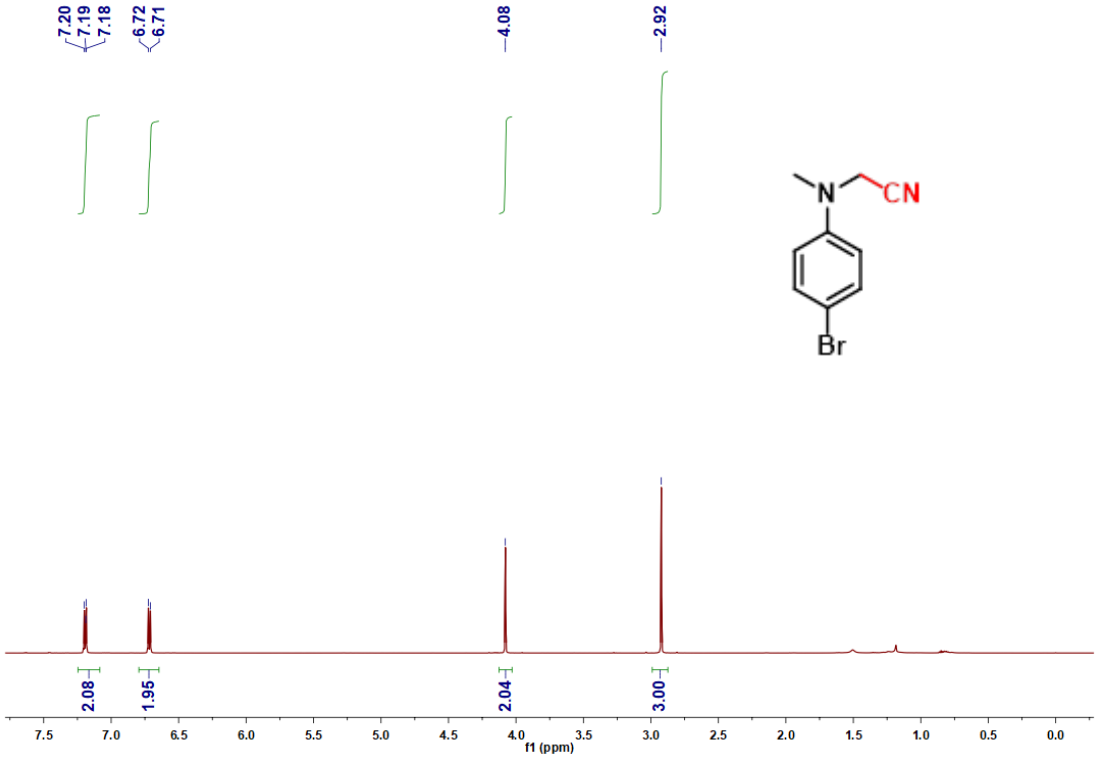


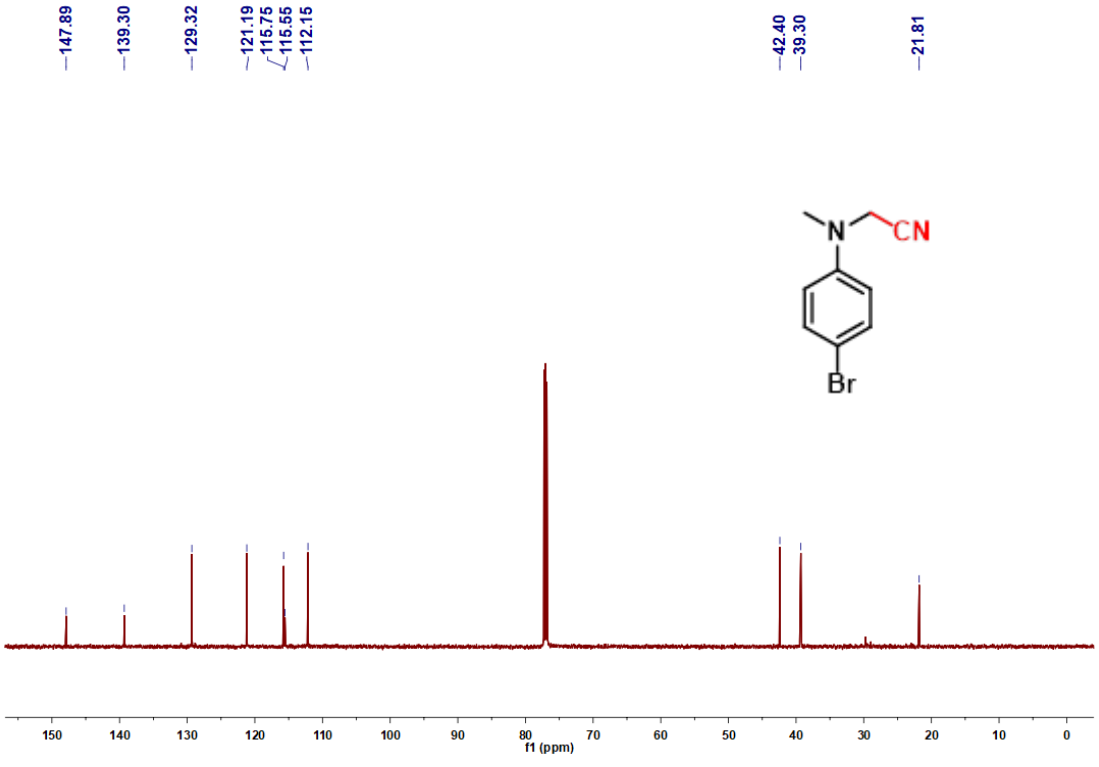
^{1}H and ^{13}C NMR Spectra of 2-((4-Chlorophenyl)(methyl)amino)acetonitrile (**2c**)



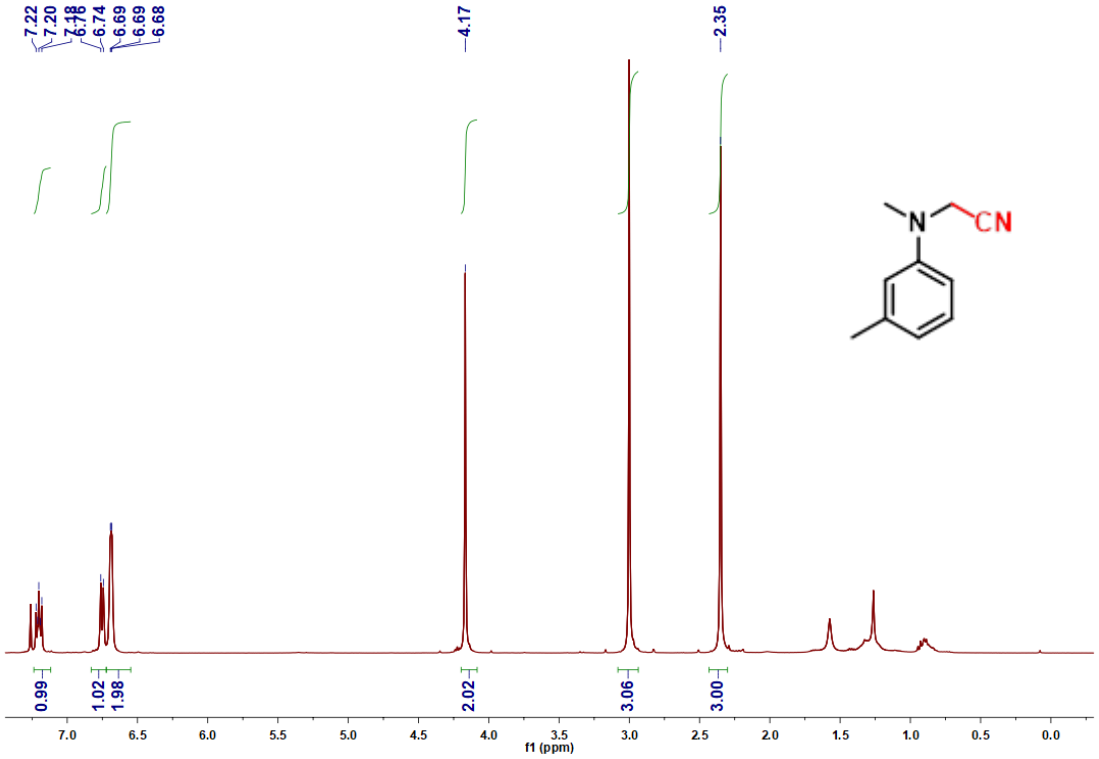


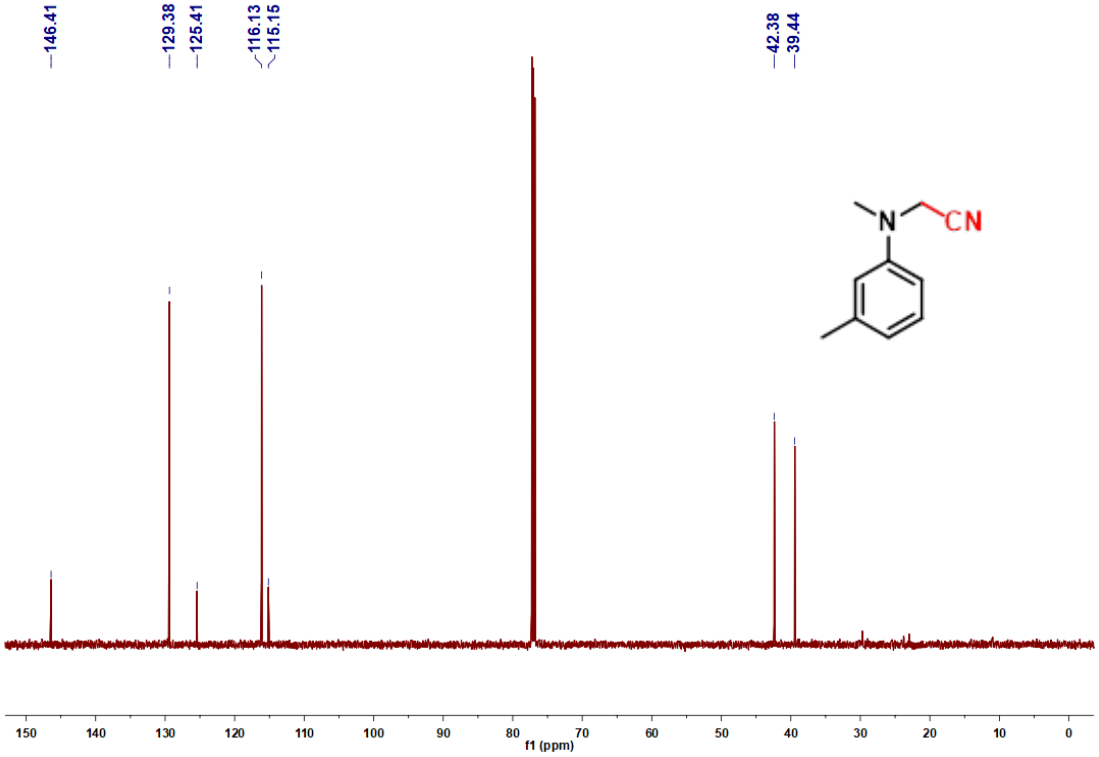
^{1}H and ^{13}C NMR Spectra of 2-((4-Bromophenyl)(methyl)amino)acetonitrile (**2d**)



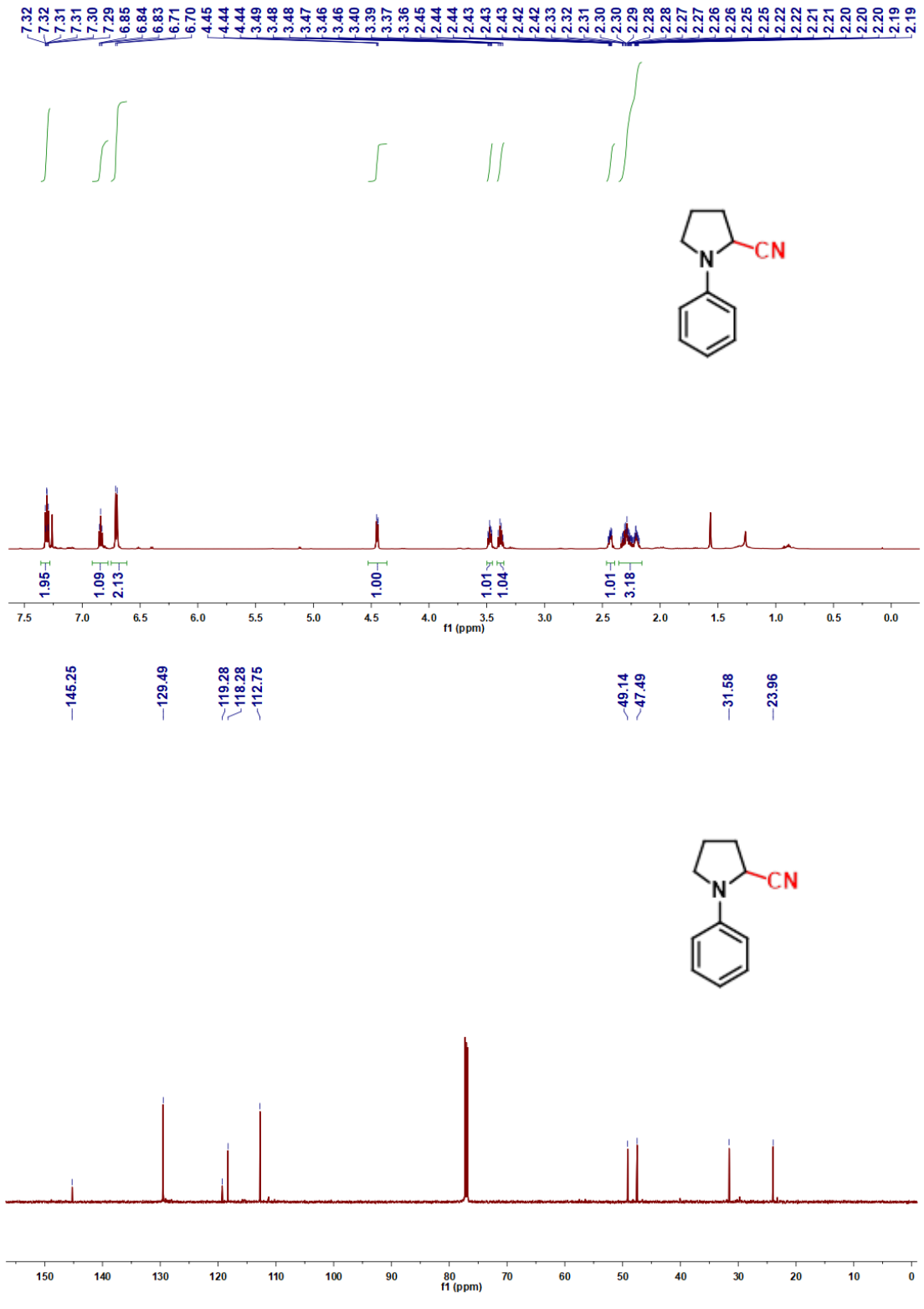


^{1}H and ^{13}C NMR Spectra of *N*-Methyl-*N*-(3-methylphenyl)aminoacetonitrile (**2e**)





^{1}H and ^{13}C NMR Spectra of 1-Phenylpyrrolidine-2-carbonitrile (**2f**)



^{1}H and ^{13}C NMR Spectra of 1-Phenylpiperidine-2-carbonitrile (**2g**)

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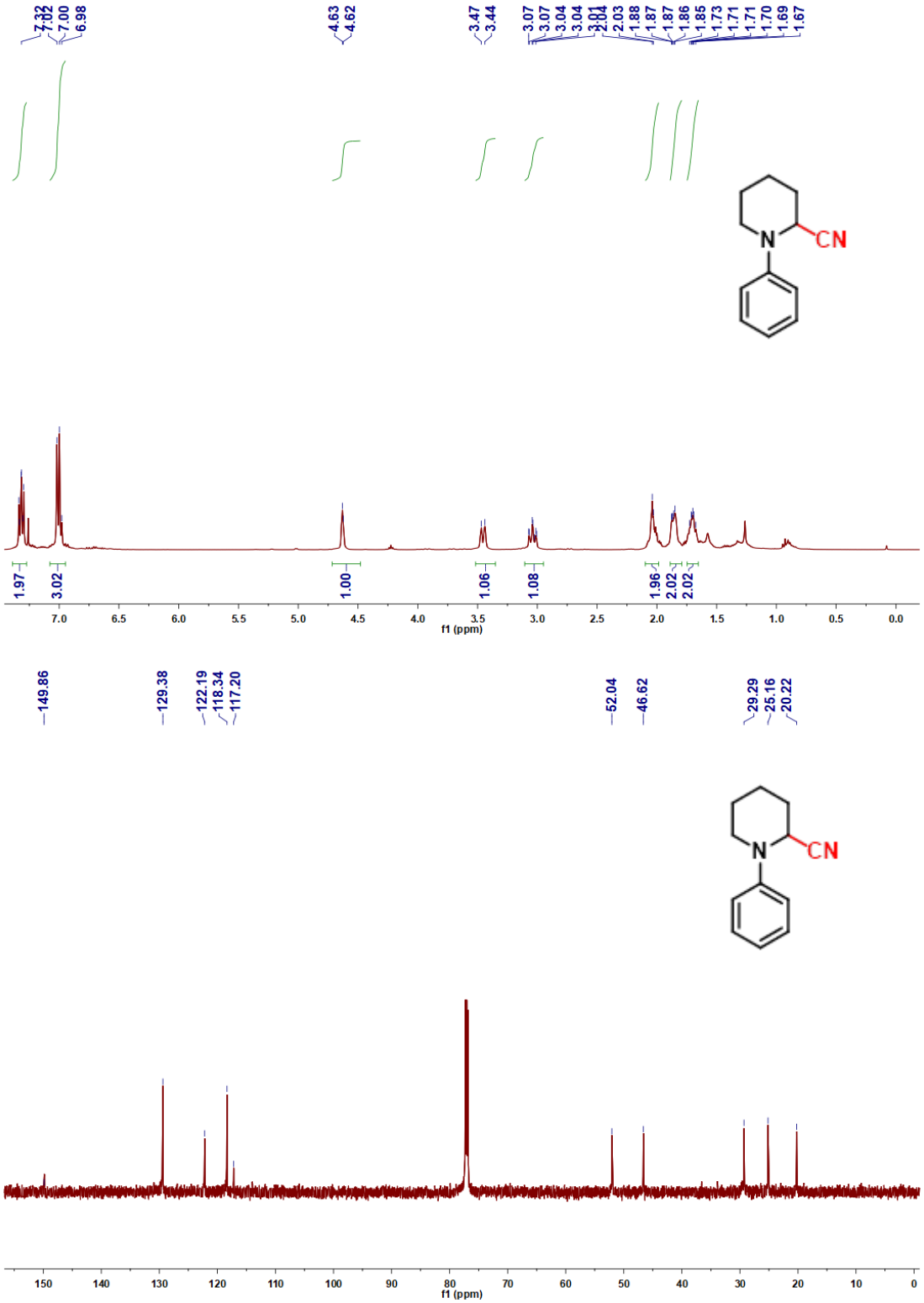
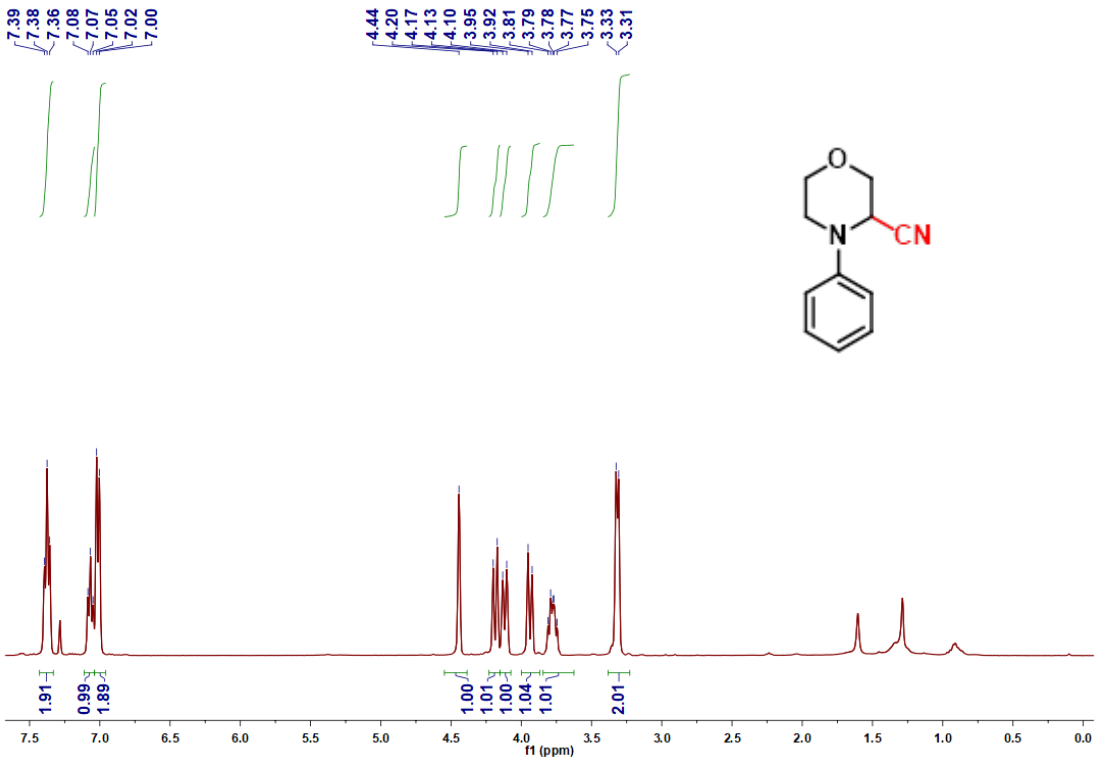
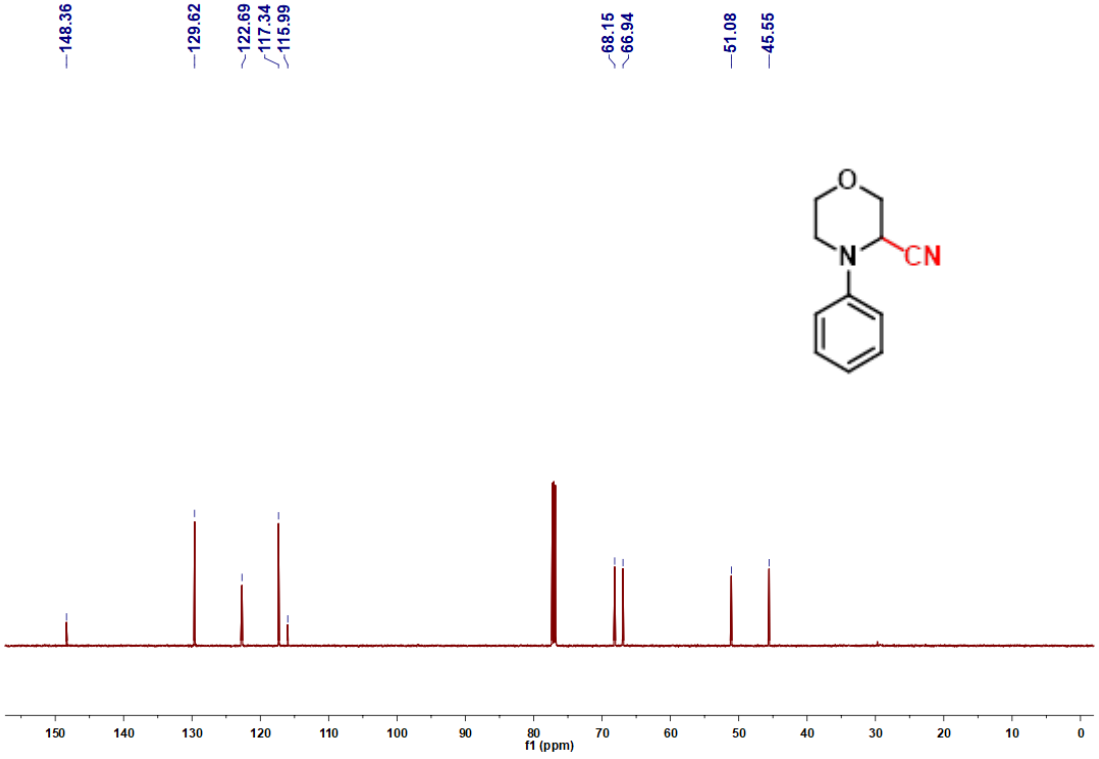
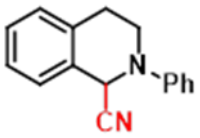


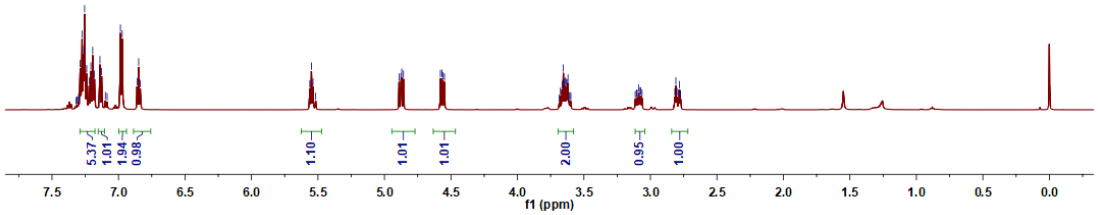
^{1}H and ^{13}C NMR Spectra of 4-Phenylmorpholine-3-carbonitrile (**2h**)

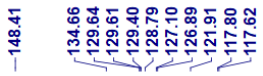


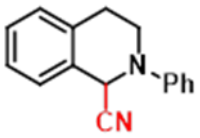


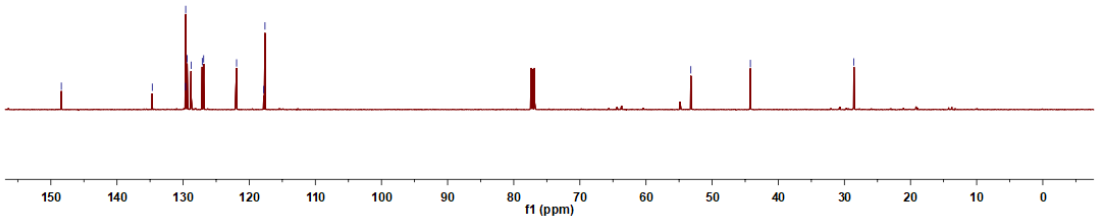
^{1}H and ^{13}C NMR Spectra of 2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**2i**)



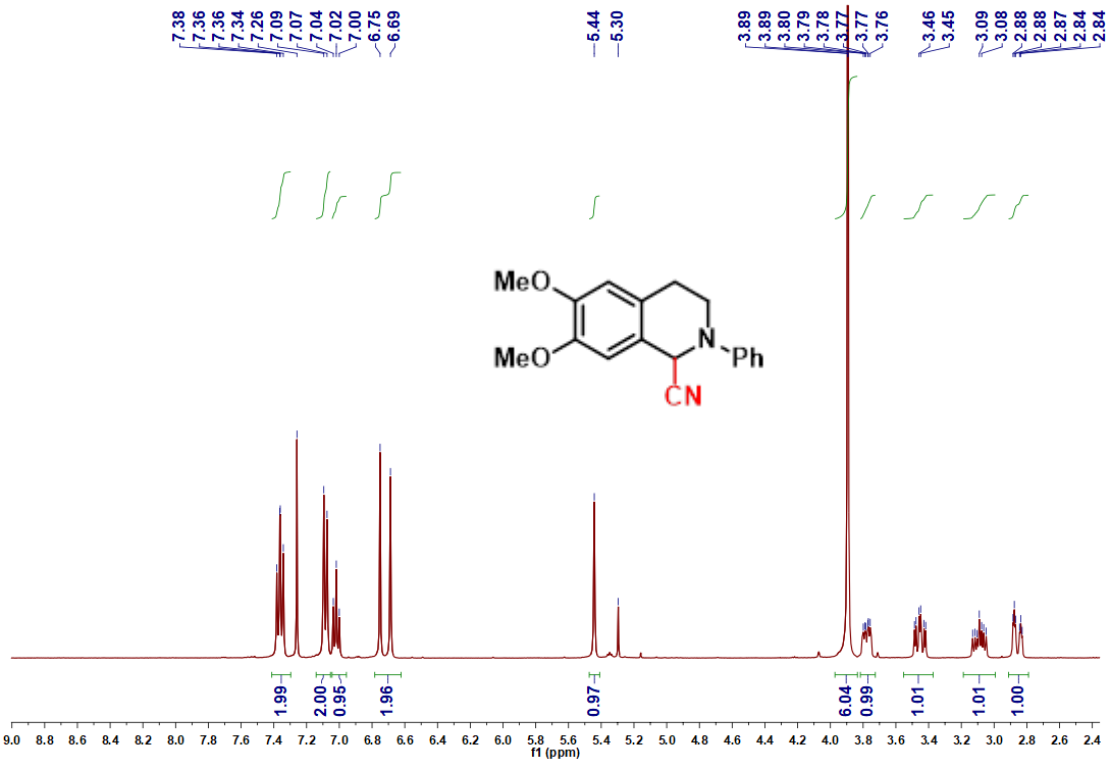


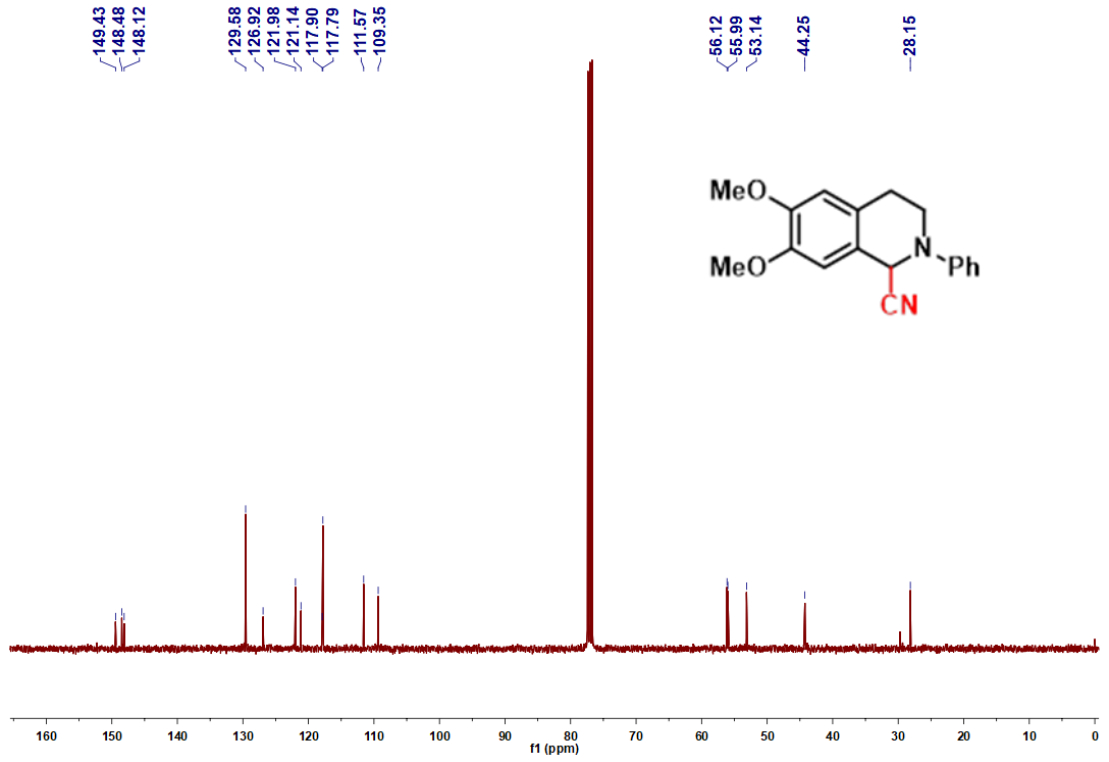




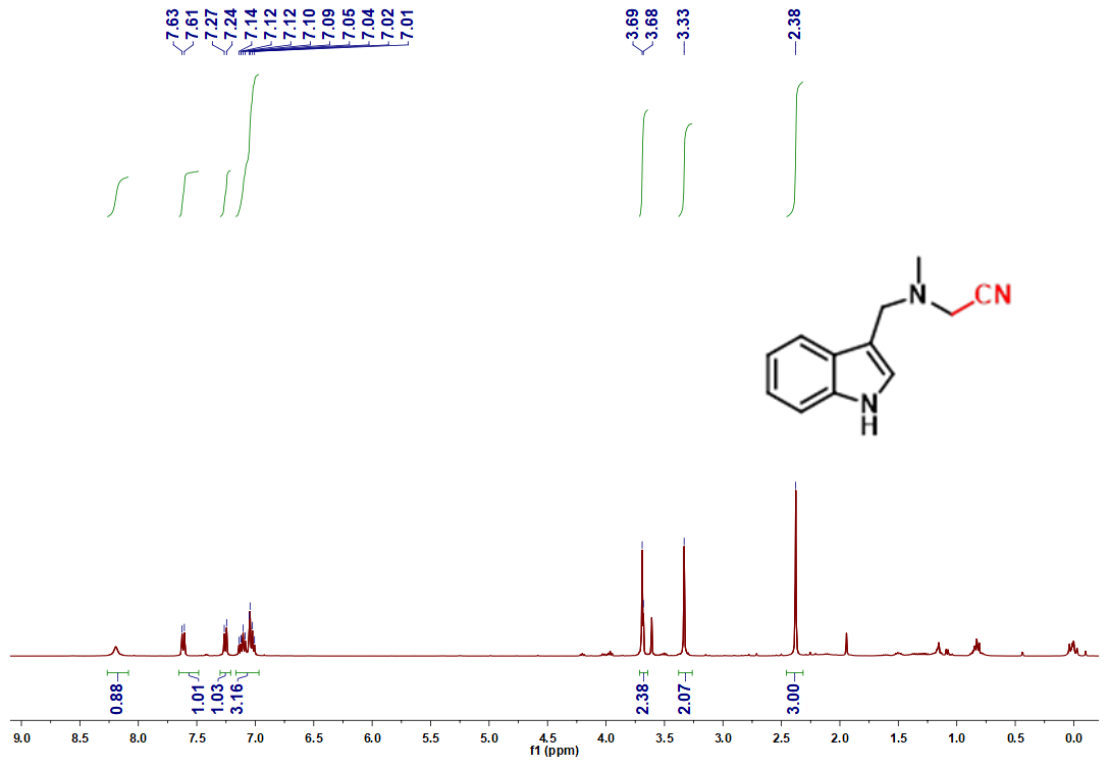


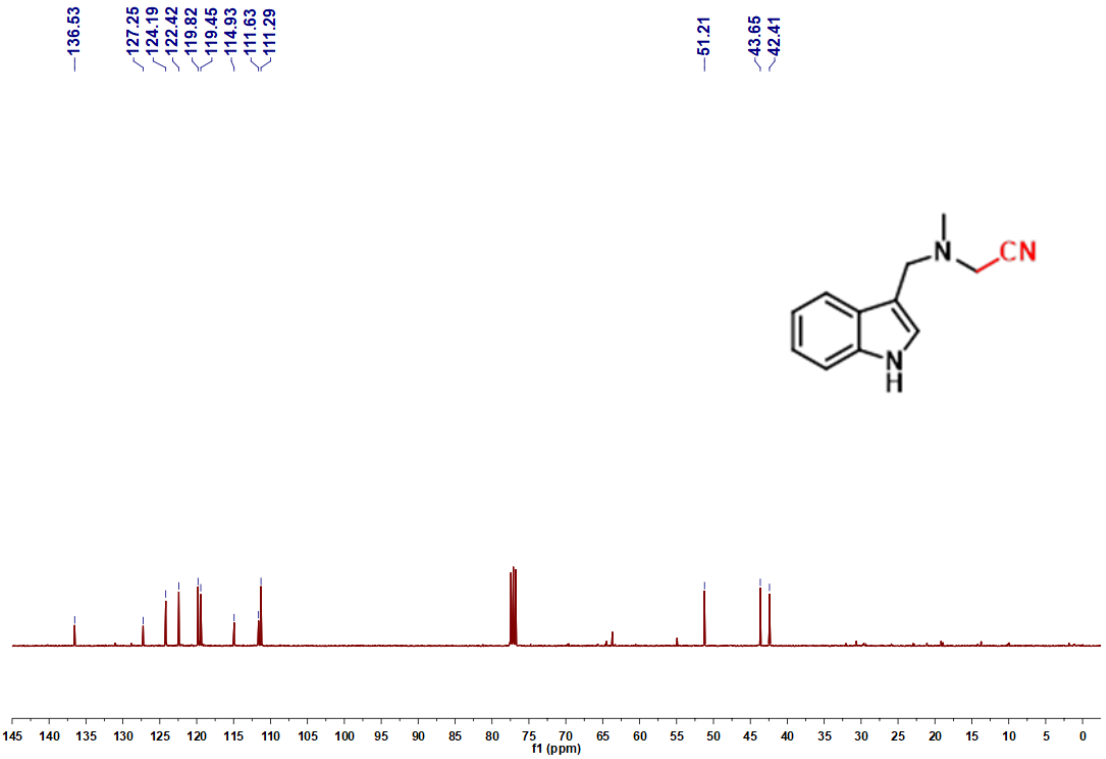
^{1}H and ^{13}C NMR Spectra of 6,7-Dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**2j**)



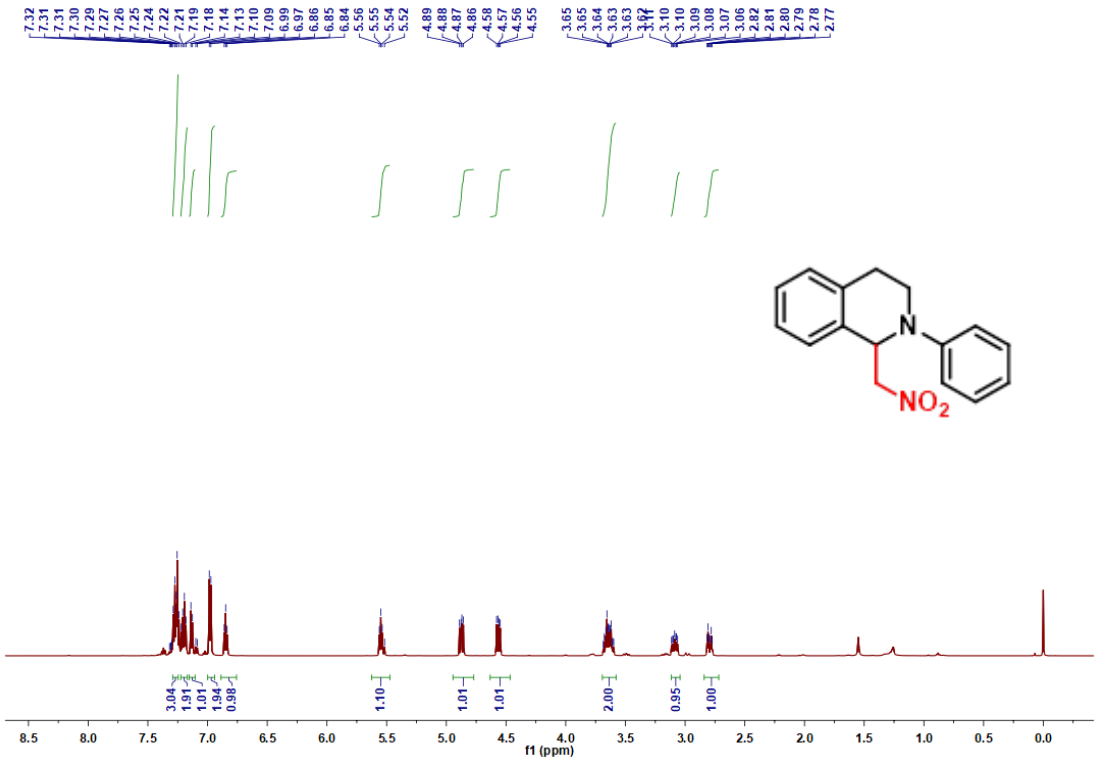


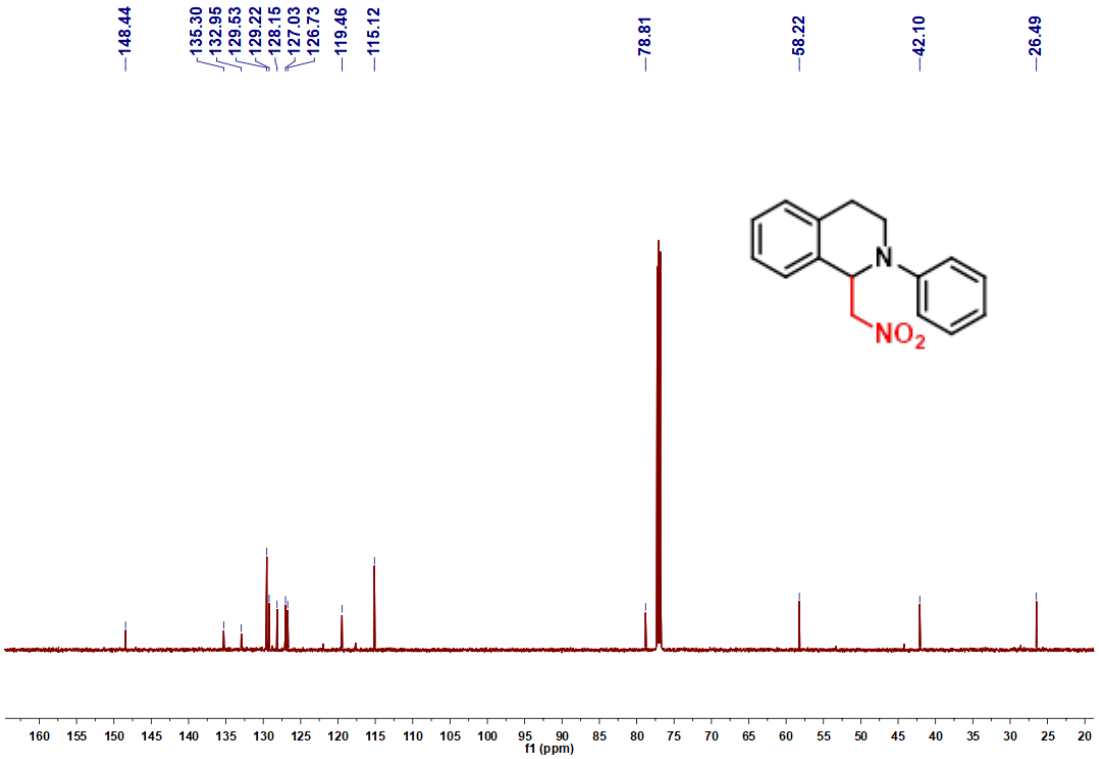
^{1}H and ^{13}C NMR Spectra of 2-(((1*H*-indol-3-yl)methyl)(methyl)amino)acetonitrile (**2k**)



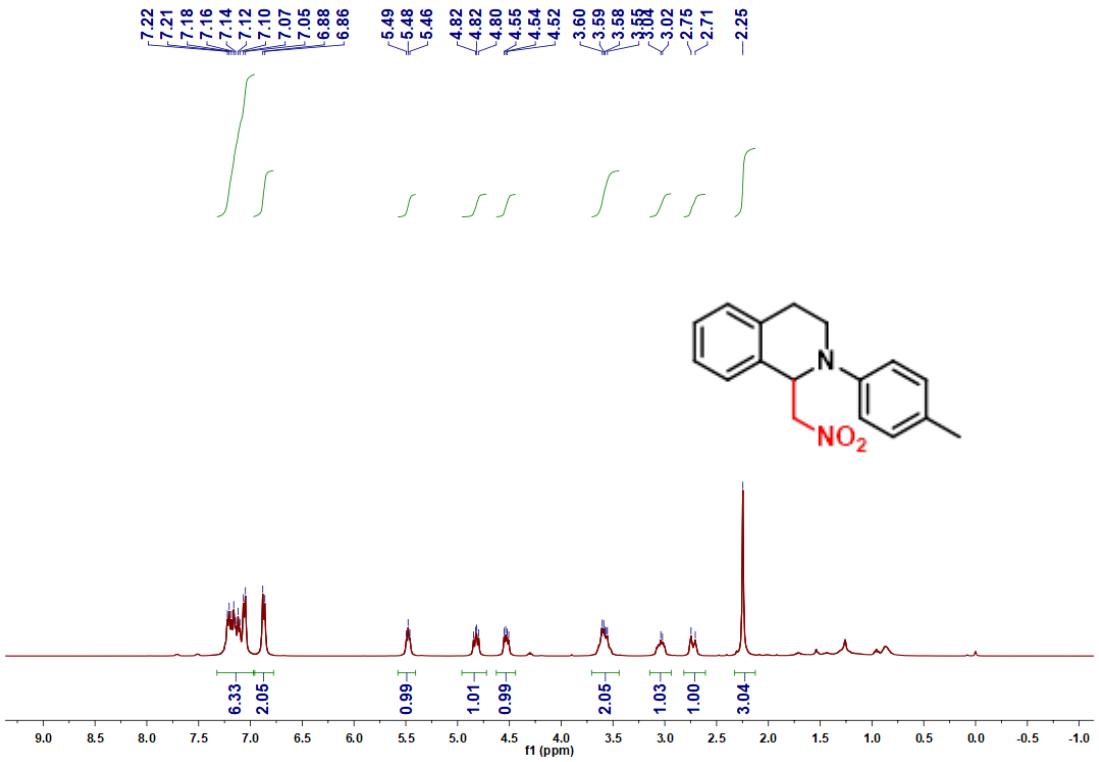


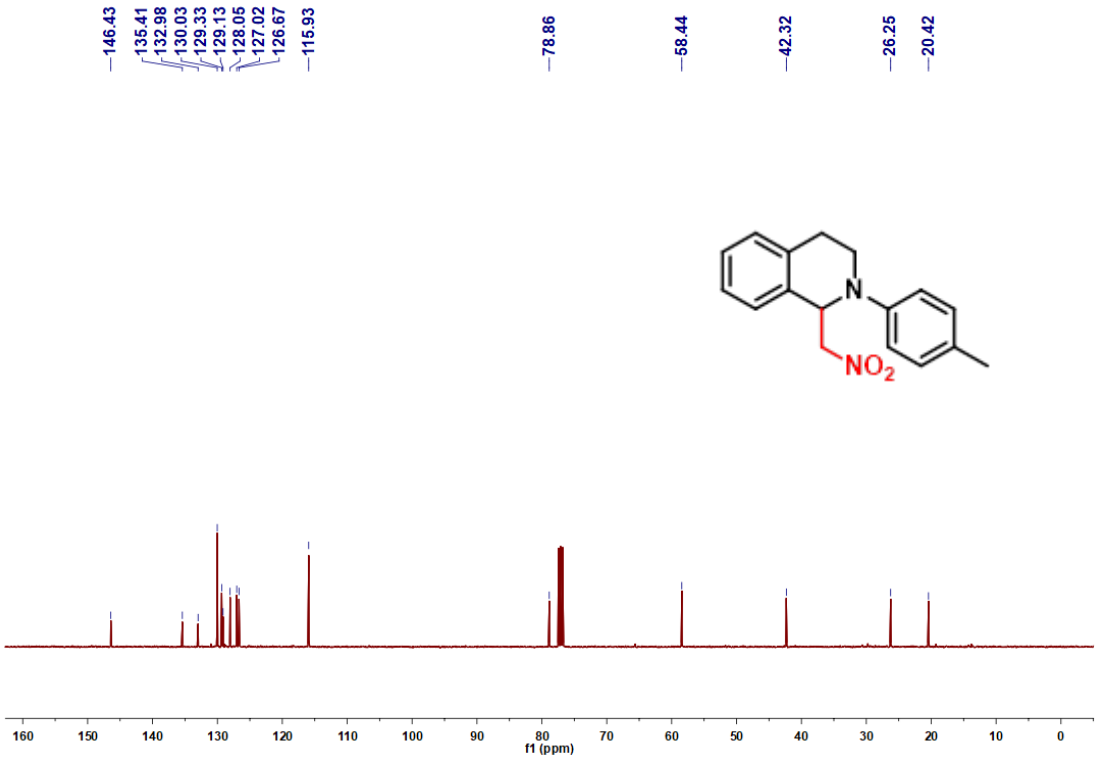
^{1}H and ^{13}C NMR Spectra of 1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**4a**)



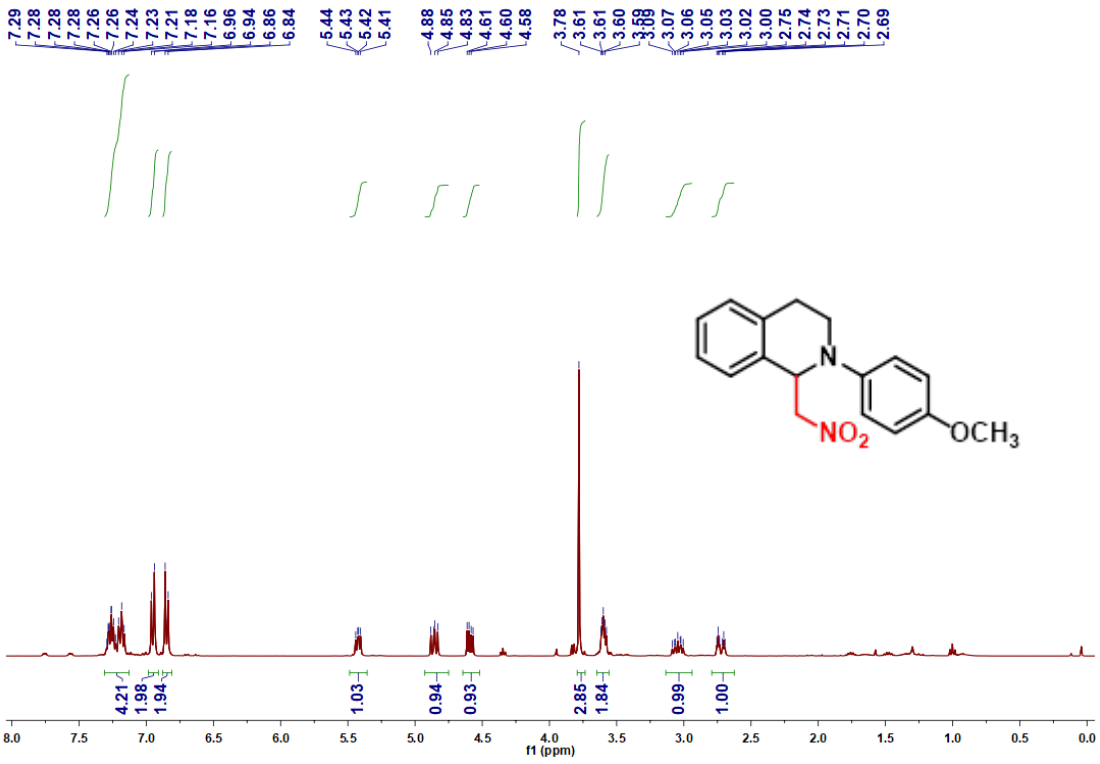


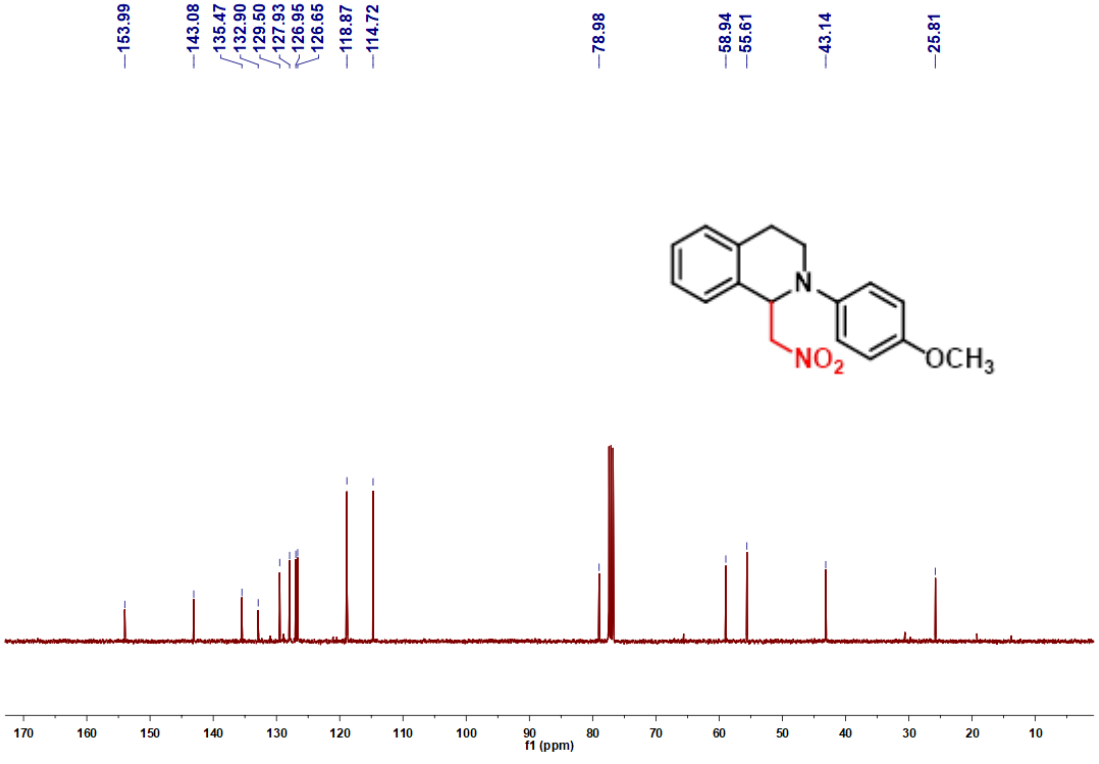
^{1}H and ^{13}C NMR Spectra of 1-(Nitromethyl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (**4b**)



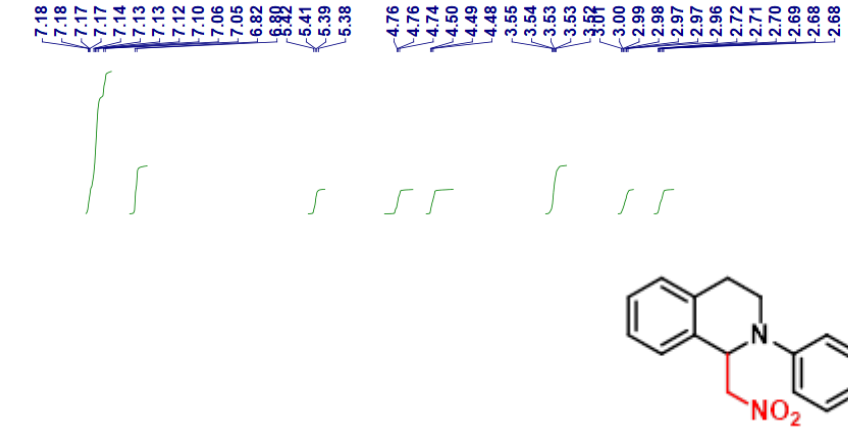


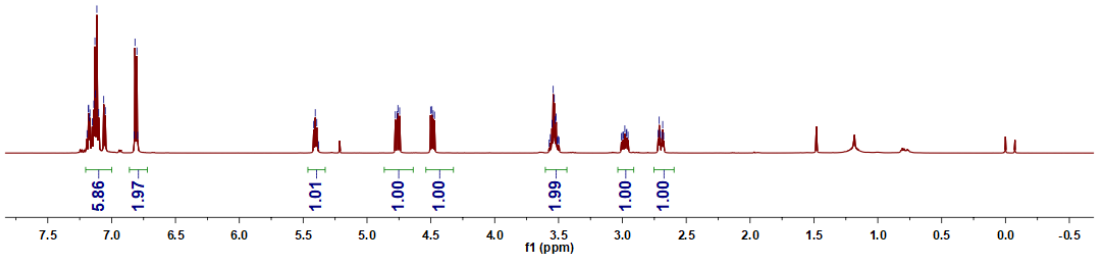
^{1}H and ^{13}C NMR Spectra of 2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4c**)

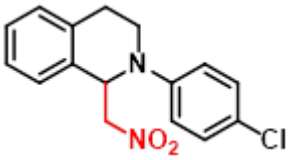


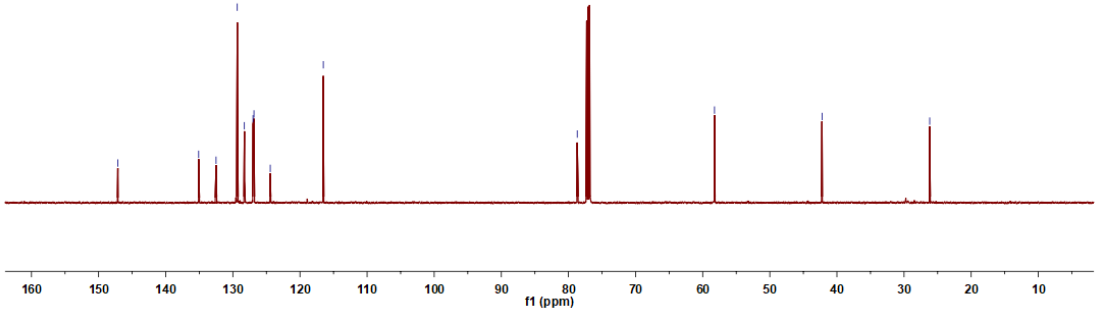


^{1}H and ^{13}C NMR Spectra of 2-(4-Chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4d**)

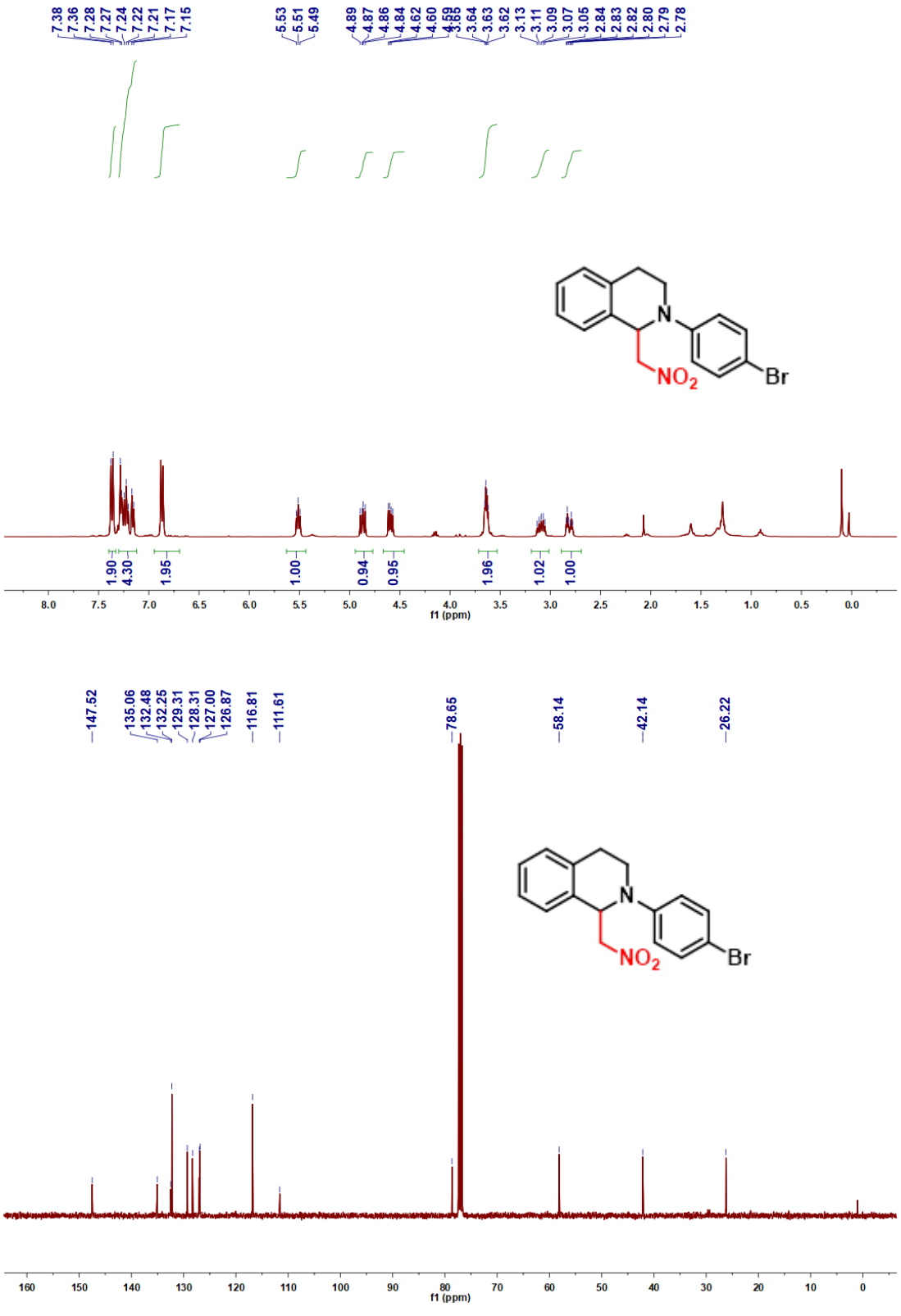




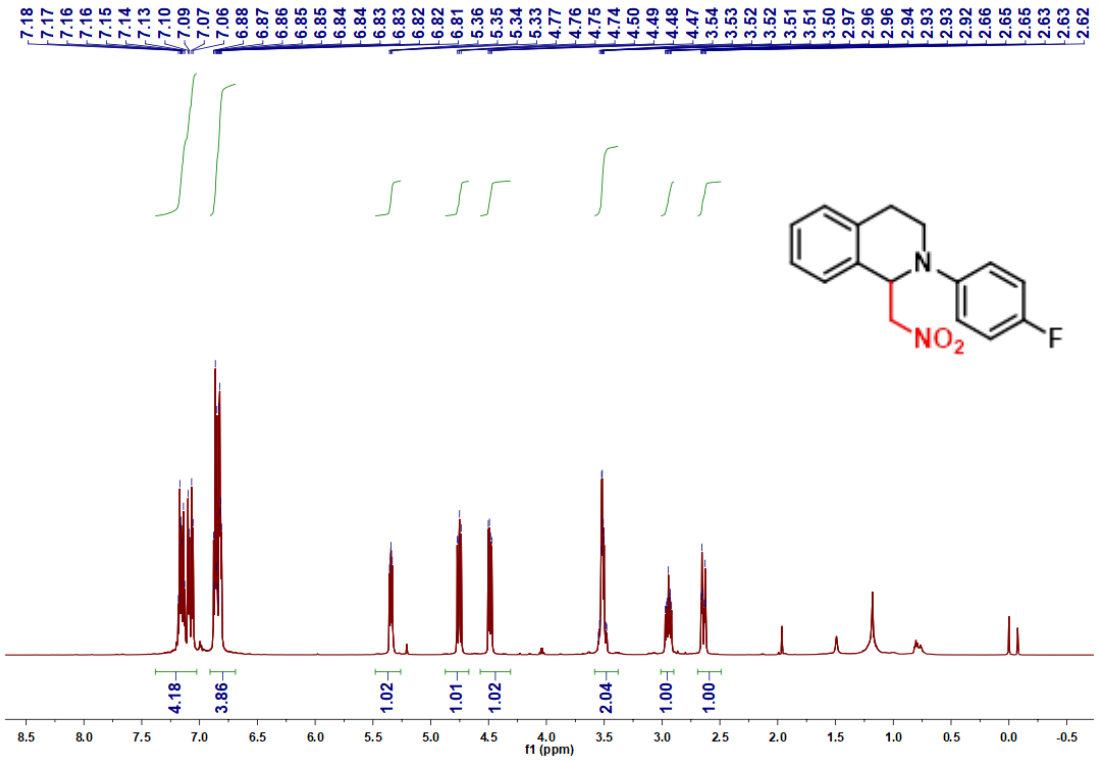


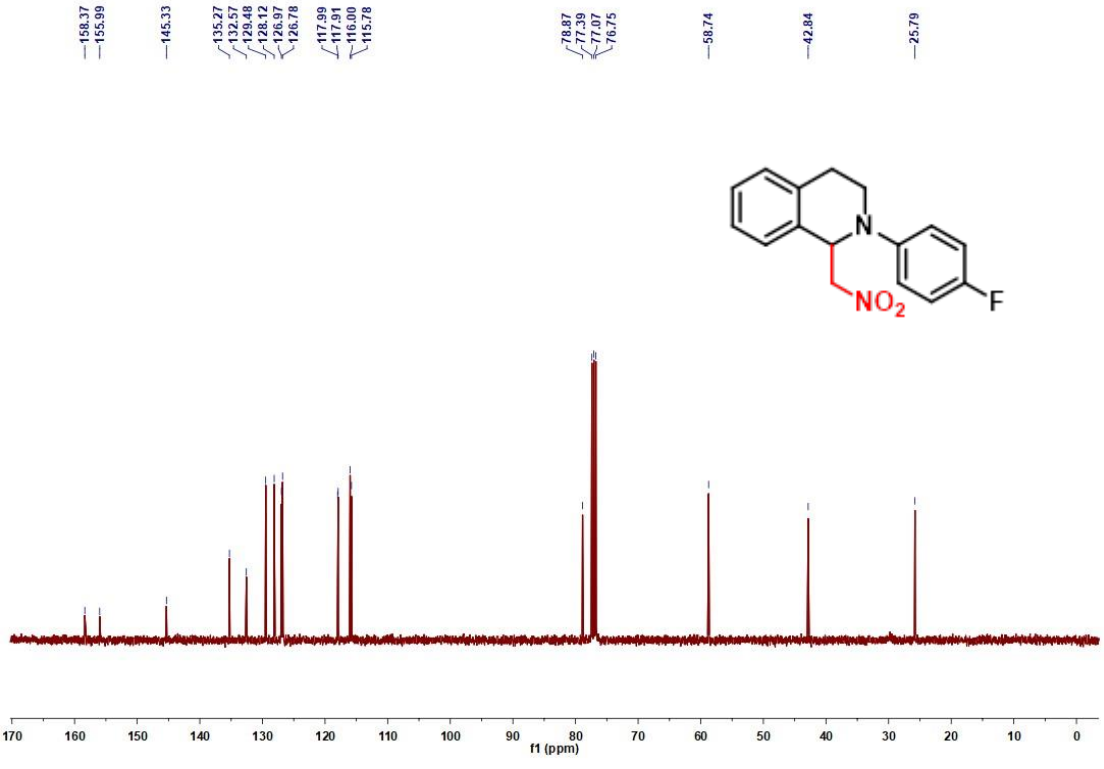


^{1}H and ^{13}C NMR Spectra of 2-(4-Bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4e**)

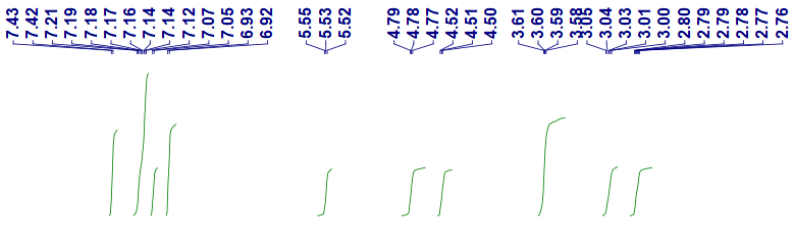


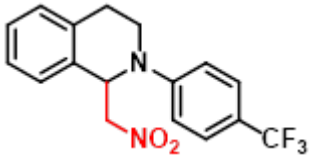
^{1}H and ^{13}C NMR Spectra of 2-(4-Fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**4f**)

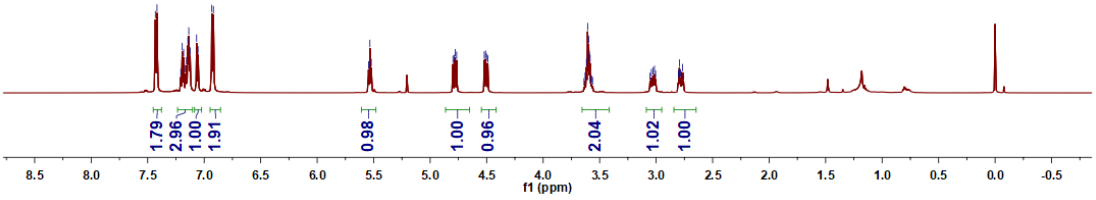


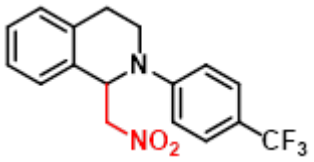


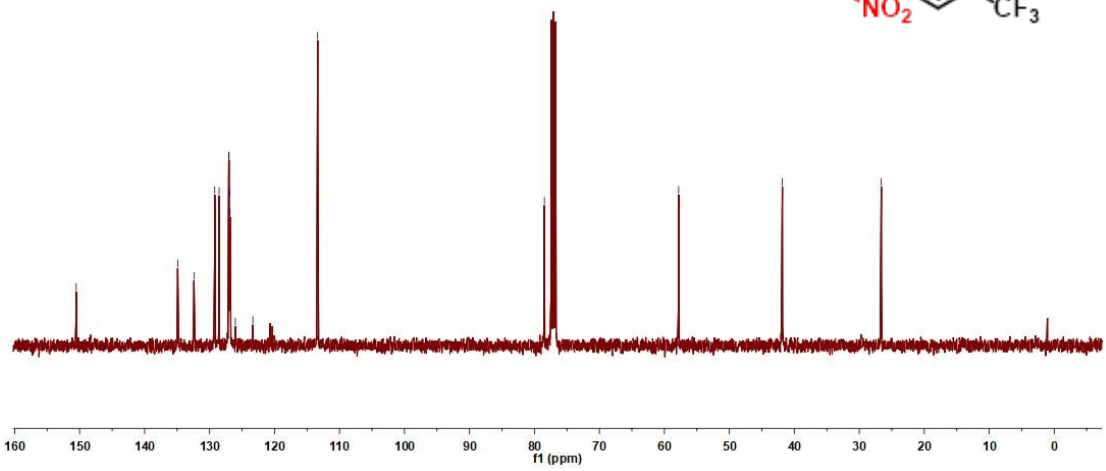
^{1}H and ^{13}C NMR Spectra of 1-(Nitromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (**4g**)



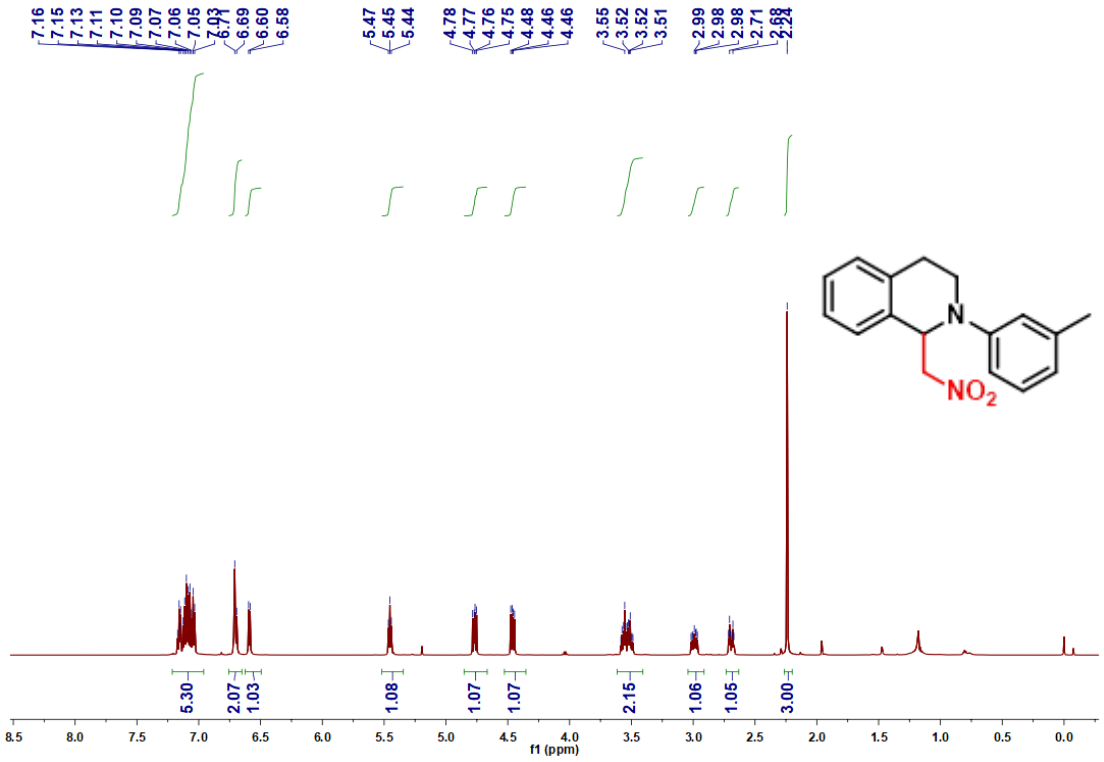


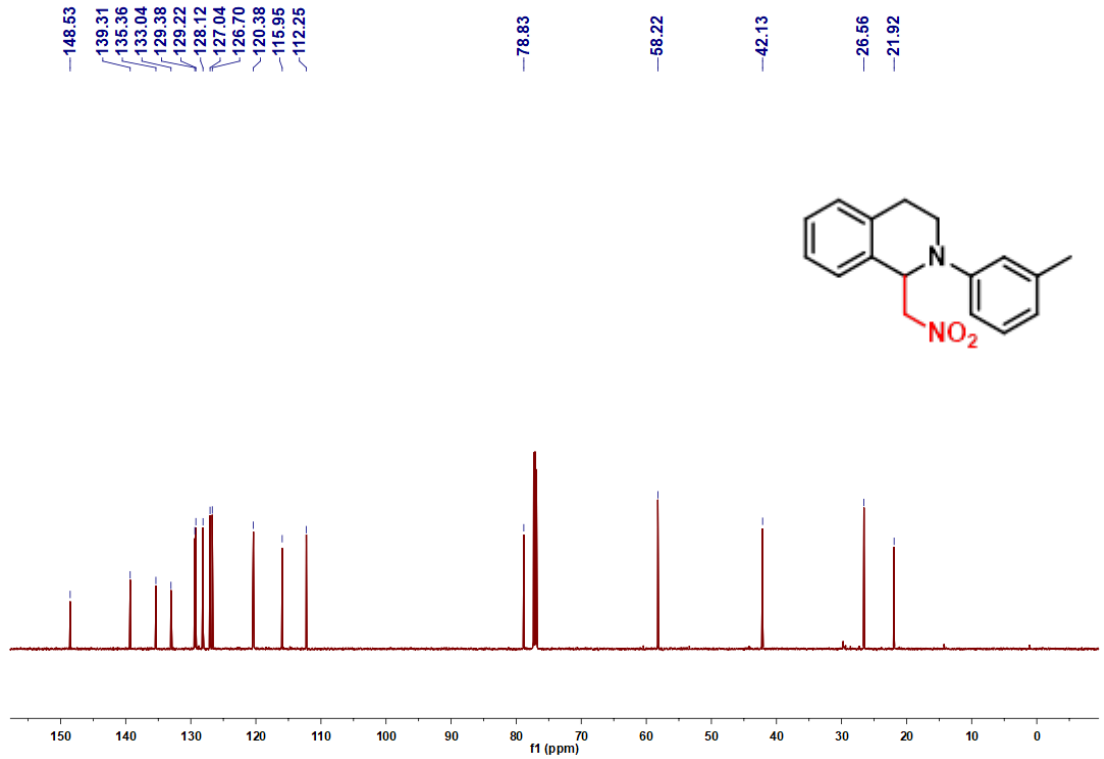




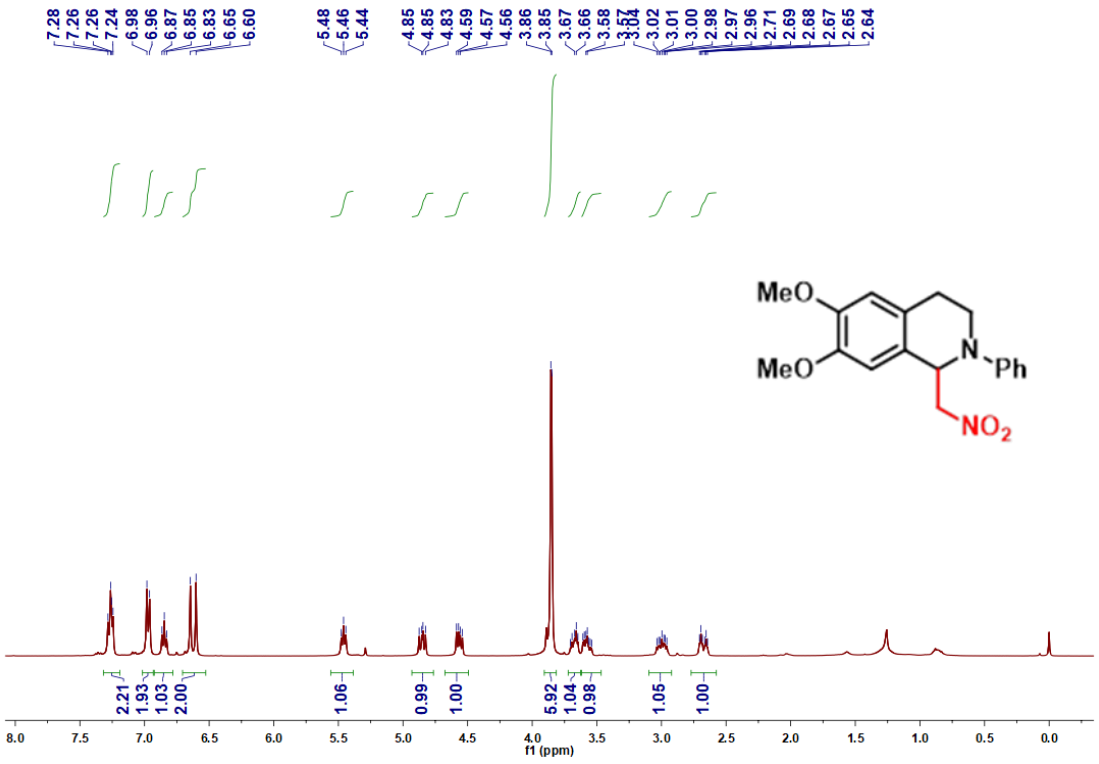


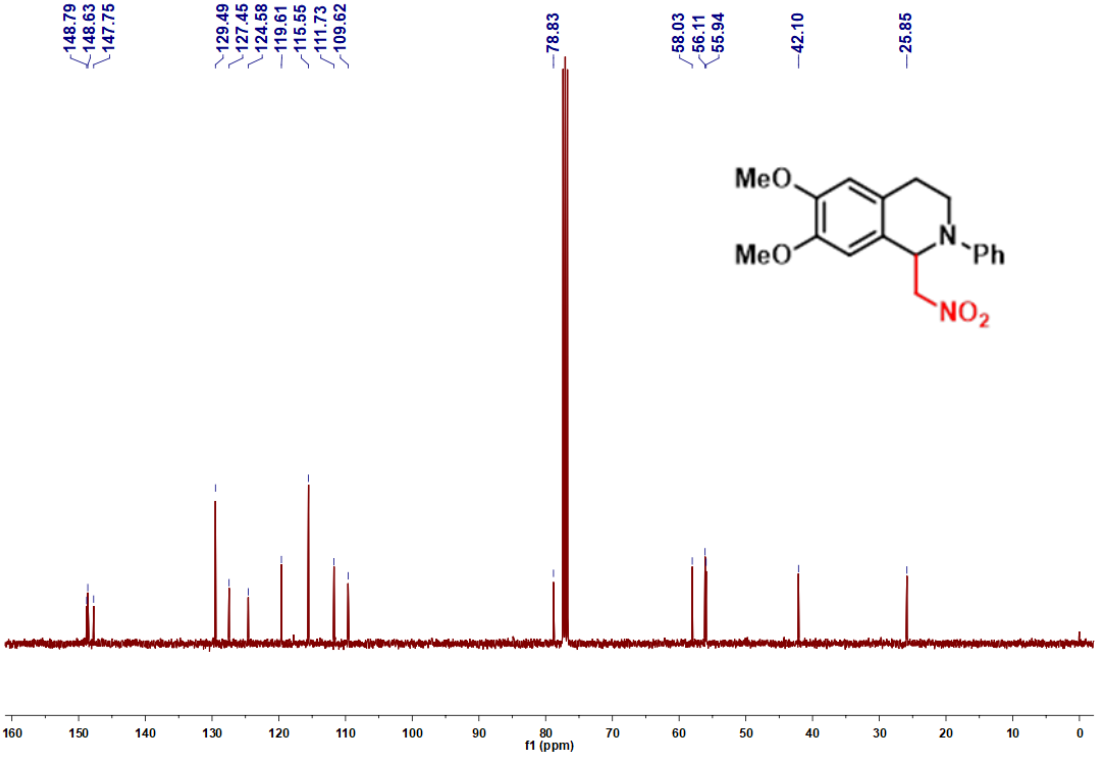
^{1}H and ^{13}C NMR Spectra of 1-(Nitromethyl)-2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline (**4h**)



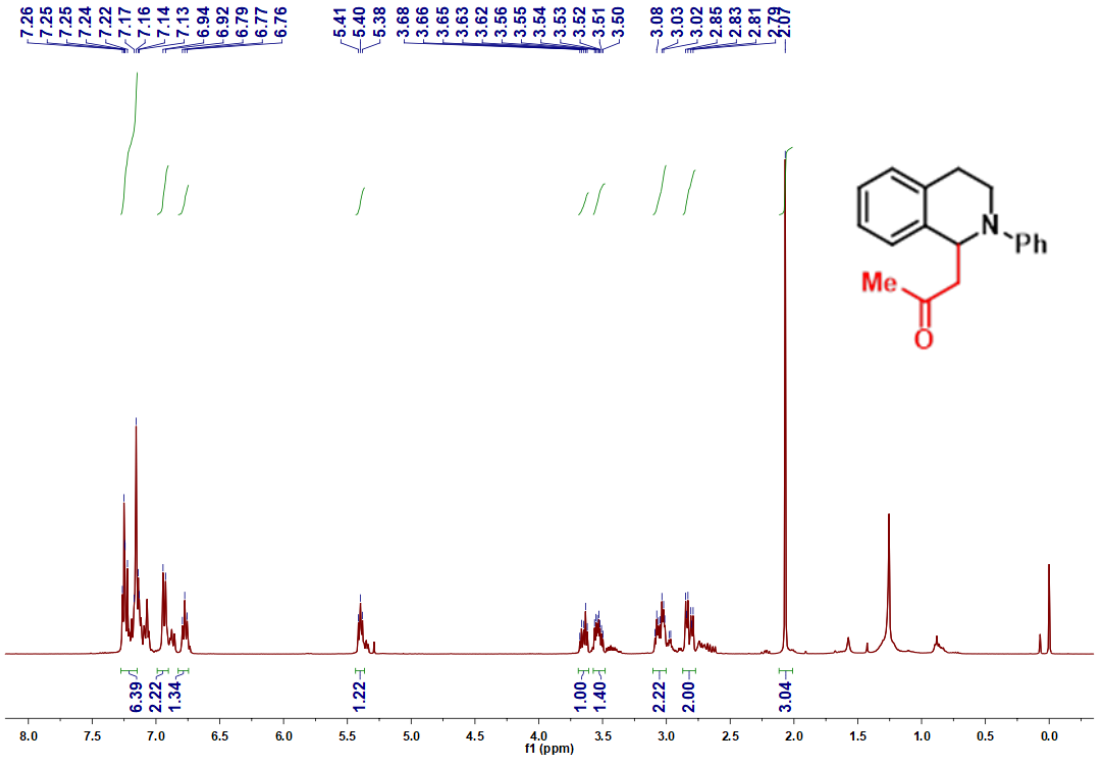


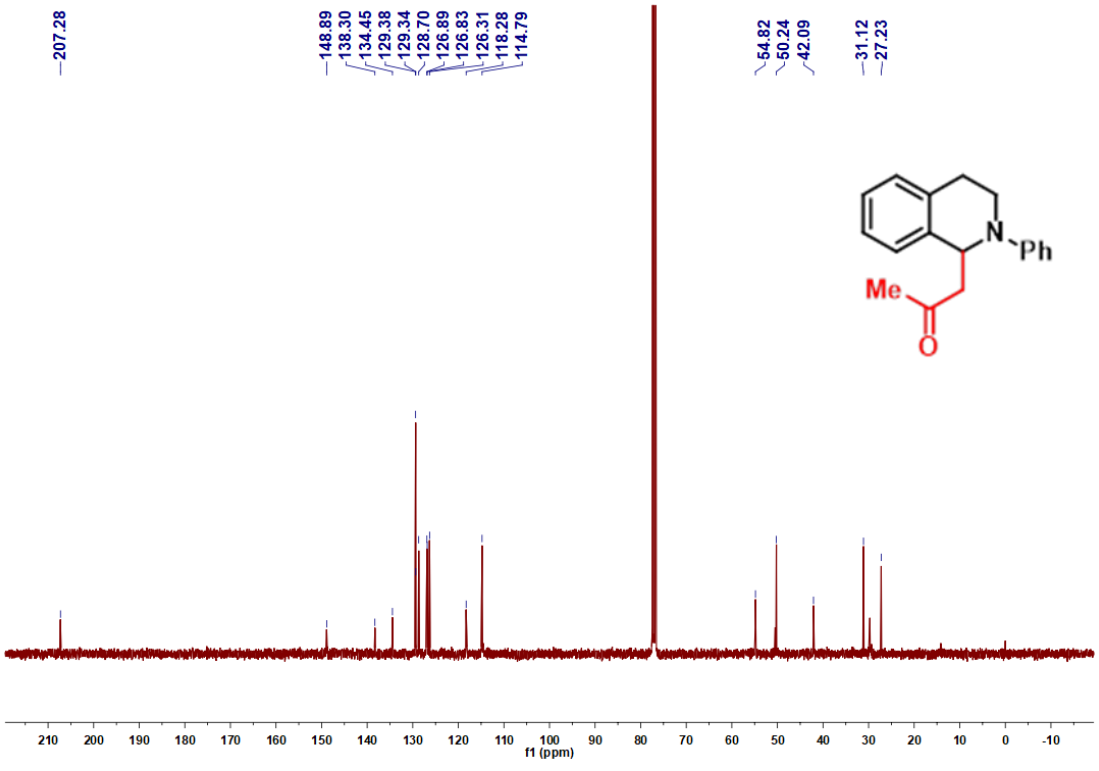
^{1}H and ^{13}C NMR Spectra of 6,7-Dimethoxy-1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**4i**)



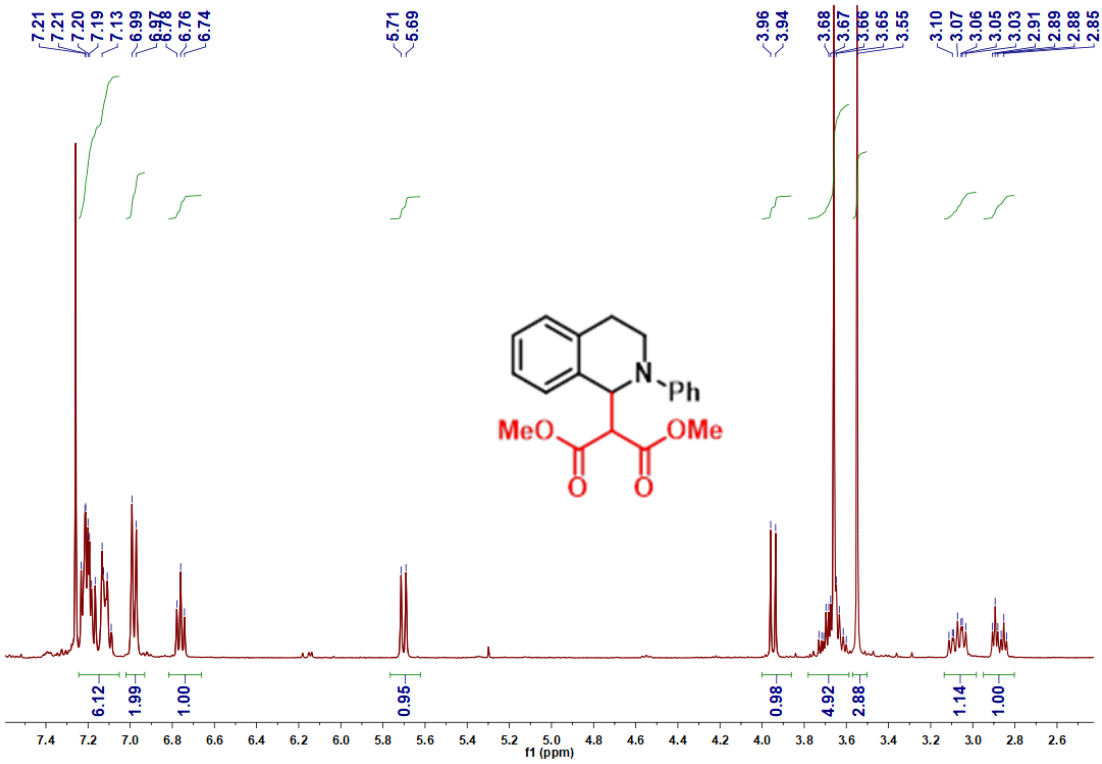


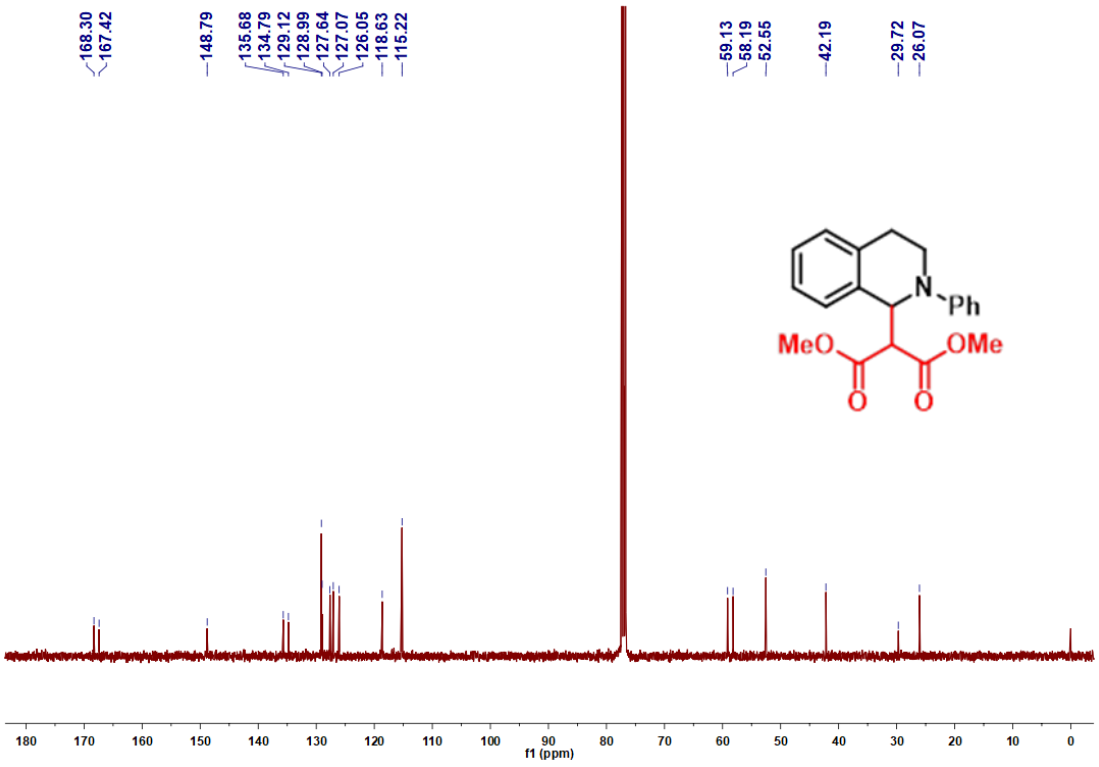
^{1}H and ^{13}C NMR Spectra of 1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (**4j**)



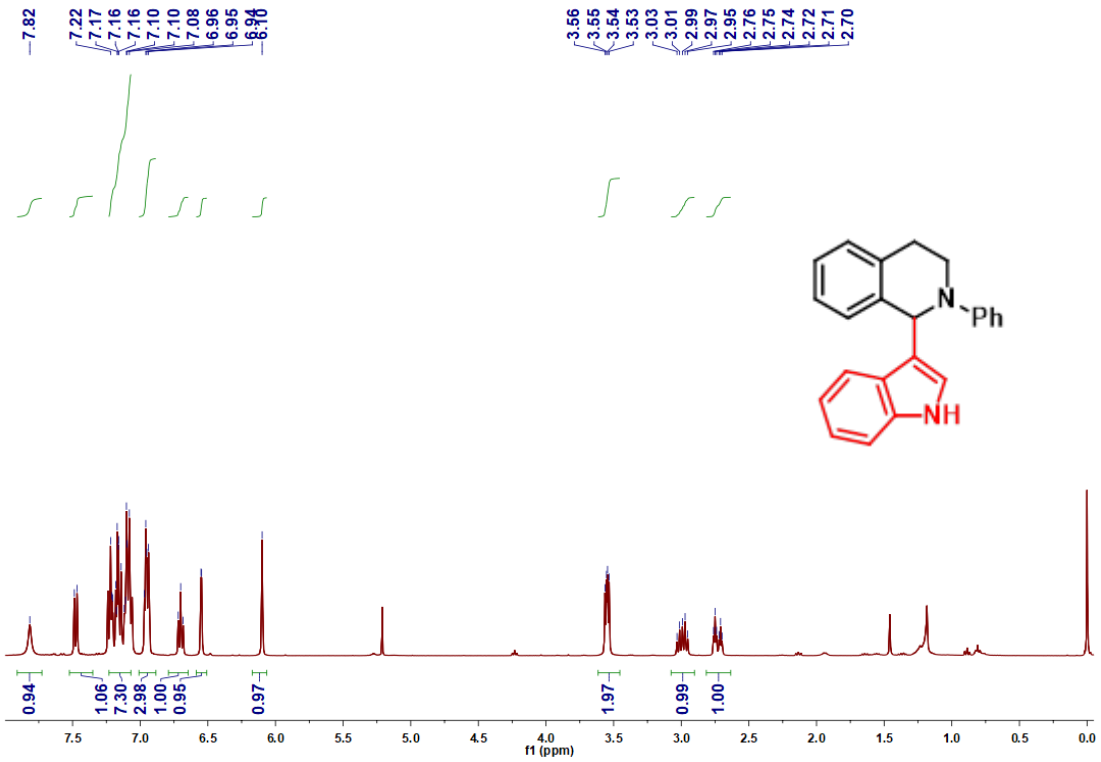


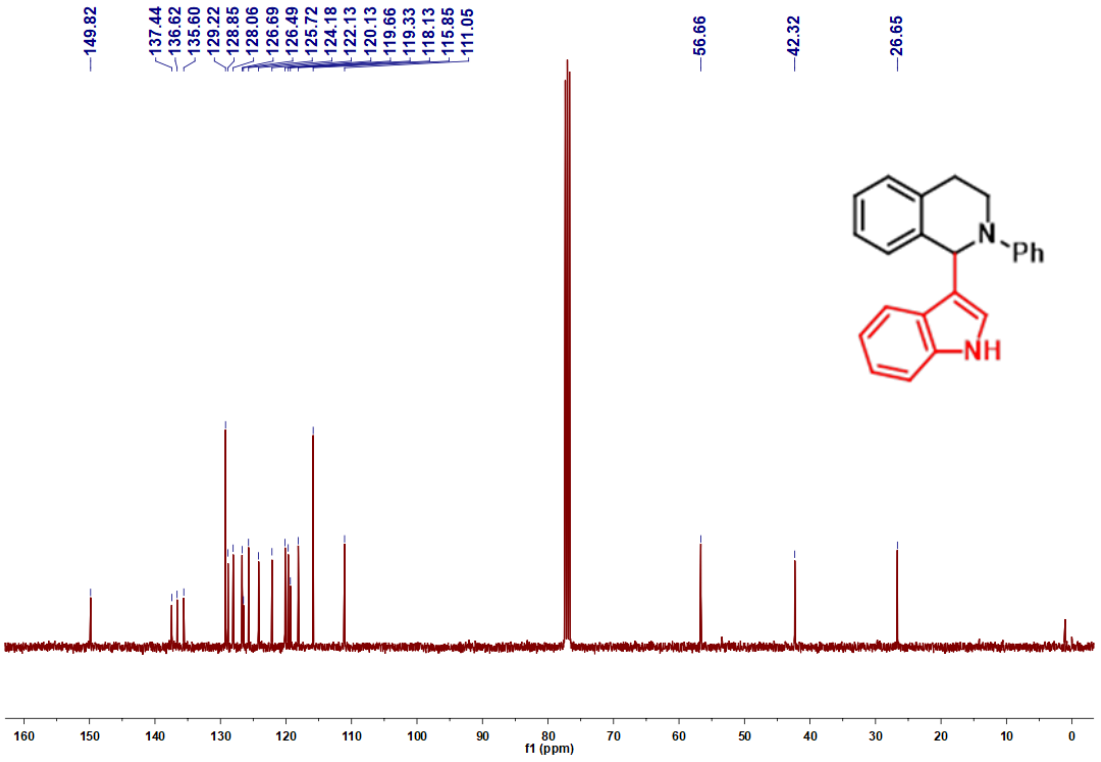
^{1}H and ^{13}C NMR Spectra of Dimethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (**4k**)



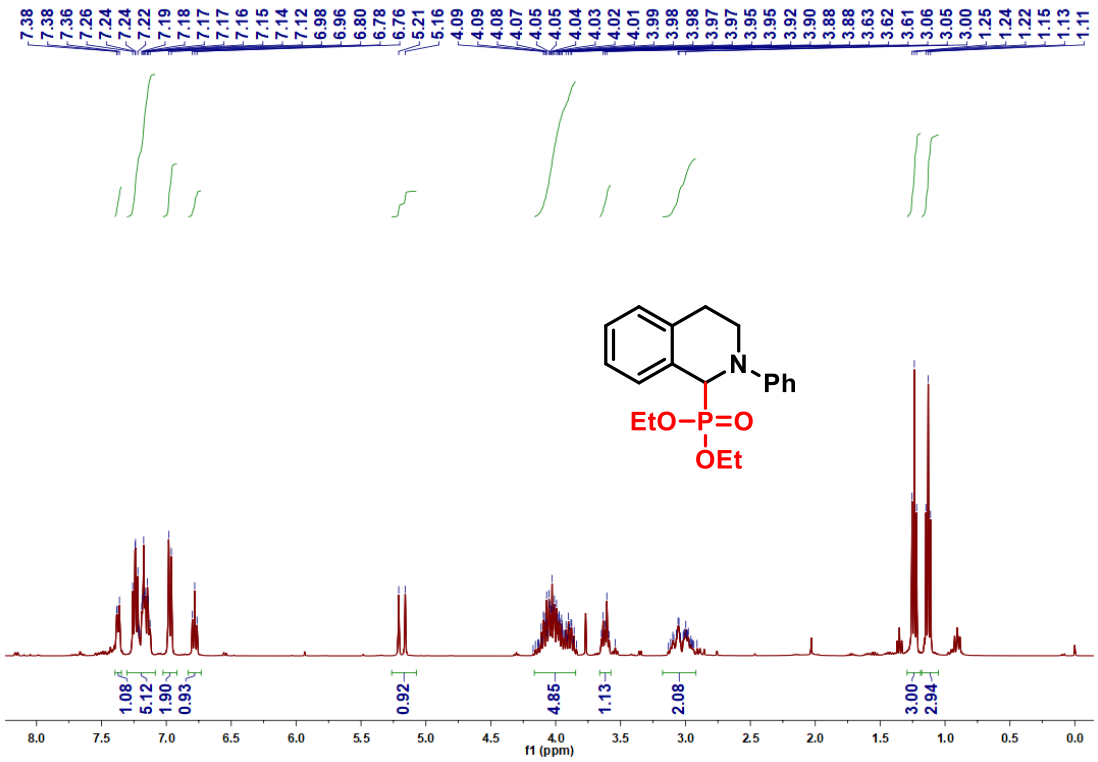


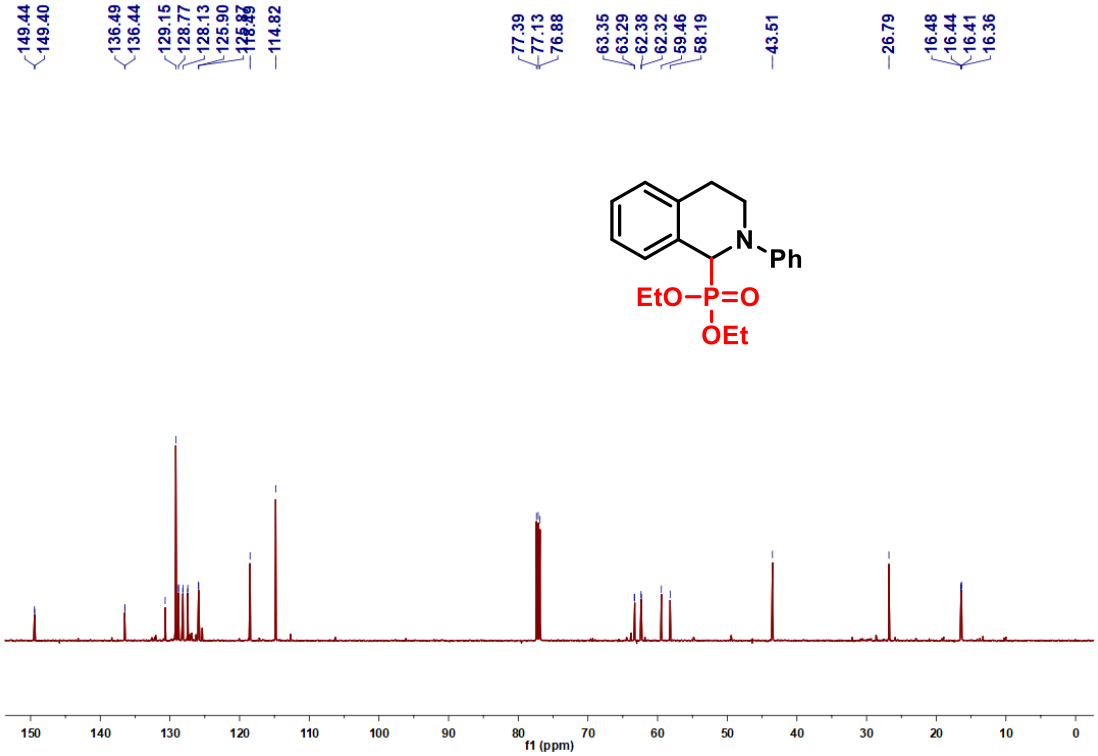
^{1}H and ^{13}C NMR Spectra of 1-(1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**4l**)





^{1}H and ^{13}C NMR Spectra of Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) phosphonate (**4m**)





References

1 (a) A. N. Woodward, J. M. Kolesar, S. R. Hall, N.-A. Saleh, D. S. Jones, M. G. Walter, *J. Am. Chem. Soc.,* 2017, **139**, 8467-8473; (b) C. Zhang, Y. Liu, L. Sun, H. Shi, C. Shi, Z. Liang, J. Li, *Chem.-Eur. J.,* 2018, **24**, 2718-2724; (c) Y. Luo, J. P. Liu, L. K. Li, S. Q. Zang, *Inorg. Chem*., 2023, **62**, 14385-14392.

2 SMART, Data collection software (version 5.629) (Bruker AXS Inc.; Madison, WI, 2003).

3 SAINT, Data reduction software (version 6.45) (Bruker AXS Inc.; Madison, WI, 2003).

4 G. M. Sheldrick, SHELXTL97, Program for Crystal Structure Solution (University of Göttingen: Göttingen, Germany, 1997).

5 A. L. Spek, *J. Appl. Cryst.,* 2003, **36**, 7−13.

6 G. Kumar, P. Solanki, M. Nazish, S. Neogi, R. I. Kureshy and N.-u. H. Khan, *J. Catal.*, 2019, **371**, 298-304.

7 L. Hou, X. Jing, H. Huang, C. Duan, *J. Mater. Chem. A*, 2022,**10**, 24320-24330.

8 A. M. Nauth, E. Schechtel, R. Dören, W. Tremel, T. Opatz, *J. Am. Chem. Soc*., 2018, **140**, 14169-14177.

9 Y. Zhang, H. Peng, M. Zhang, Y. X.Cheng, C. J. Zhu, *Chem. Commun*., 2011, **47**, 2354-2356.

10 N. Sakai, A. Mutsuro, R. Ikeda, T. Konakahara, *Synlett*, 2013; **24**, 1283-1285

11 O. Yilmaz, C. Dengiz, M. H. Emmert, *J. Org. Chem.,* 2021, **86**, 2489-2498.

12 K. T. V. Rao, B. Haribabu, P. S. S. Prasad, N. Lingaiah, *ChemCatChem*., 2012, **4**, 1173-1178.

13 B. Ullah, Y. Zhou, J. Chen, Z. Bao, Y. Yang, Q. Yang, Q. Ren, Z. Zhang, *Tetrahedron Lett*., 2019, **60**, 348-351.

14 S. Zhang, L. Ma, W. Ma, L. Chen, K. Gao, S. Yu, M. Zhang, L. Zhang, G. He, *Angew. Chem. Int. Ed.,* 2022, **61**, e202209054.

15 Y. Zhi, S. Ma, H. Xia, Y. Zhang, Z. Shi, Y. Mu, X. Liu, *Appl. Catal. B Environ*., 2019, **244**, 36-44.

16 S.-S. Zhu, Y. Liu, X. L. Chen, L. B. Qu, B. Yu, *ACS Catal*., 2021, **12**, 126-134.

17 W. Liang, T. Zhang, Y. Liu, Y. Huang, Z. Liu, Y. Liu, B. Yang, X. Zhou, J. Zhang, *ChemSusChem,* 2018, **11**, 3586.

18 E. Boess, C. Schmitz, M. Klussmann, *J. Am. Chem. Soc*., 2012, **134**, 5317-5325.