

## Unleashing the photo catalytic potential of noble-metal-free heteroleptic copper complex-based nanomaterial for enhanced aza-Henry reaction

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### Abstract

In this work, we have fabricated a versatile and noble metal free copper based heterogeneous photocatalyst to represent a green shift from precious group metals such as Ir, Ru, Pt which have been widely utilized as photocatalysts. The successfully synthesized and characterized copper photocatalyst was employed to establish a Cross dehydrogenative coupling via C–H activation between tertiary amines and carbon nucleophiles. The highly efficient copper based photocatalyst has been characterized by numerous physico-chemical techniques, which advocate the successful formation as well as its high activity. Inductively coupled plasma (ICP-OES) analysis revealed that the composite Cu@Xantphos@ASMNPs has very high loading of 0.423 mmol/g of copper. The magnetic Cu@Xantphos@ASMNPs have been utilized as potential heterogeneous photocatalyst for very facile and regioselective conversion of aryl tetrahydroquinoline to respective nitroalkyl aryl tetrahydroisoquinoline in high yield using air as an oxidant and methanol as green solvent over irradiation with visible light under mild reaction conditions. Additionally, the catalyst shows exceptional chemical stability and reusability without any agglomeration even after several cycles of use are one of the key features of this material and strive as a potential candidate from economic and environmental perspectives.

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## General Information

**Material Synthesis.** Unless otherwise indicated, all the chemicals were purchased from commercial source and were utilized without further purifications. Ferric sulphate hydrate and ferrous sulphate heptahydrate were obtained from Central Drug house and Thomas Bakers, respectively. The commercially unavailable tetrahydroisoquinoline derivatives were prepared in the lab by utilizing the previously reported procedure.<sup>1</sup> All the photochemical reactions were carried out in inert atmosphere, unless otherwise indicated. Double distilled water was used throughout for the synthetic procedures of materials.

**Material Characterization.** The various physiochemical techniques such as Fourier transform-infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), UV-Vis spectroscopy, high resolution-transmission electron microscopy (HR-TEM), vibrating sample magnetometry (VSM), inductively coupled-plasma optical emission spectrometry (ICP-OES), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), energy-dispersive X-ray fluorescence (ED-XRF), and nuclear magnetic resonance spectroscopy (NMR) were utilized to characterise the fabricated Cu@Xantphos@ASMNPs catalyst. The Fourier transform-infrared spectra were investigated in the range of 4000 to 400  $\text{cm}^{-1}$  by employing PerkinElmer Spectrum 2000 using KBr pellet method. PXRD patterns were recorded to determine the phase, purity and crystalline nature on a Rigaku Cu ( $K_{\alpha}$ ) diffractogram at a scan rate of 4 degree per min and  $2\theta$  range of 4-80 degree. UV-Vis spectrum of Cu@Xantphos@ASMNPs has been investigated on a Thermo Scientific absorption spectrophotometer within the wavelength range of 250-800 nm. FEI TECHNAI G2 T20 transmission electron microscope was utilized to capture the TEM images of the nanoparticles at 200 KV. The TEM samples of MNPs, SMNPs, Cu@Xantphos@ASMNPs were prepared by drop casting method where the desired nanoparticles were drop cast over a carbon coated copper grid. Elemental analysis of the catalyst was acquired using an Ametek EDAX system. Copper loading/content of the Cu@Xantphos@ASMNPs catalyst was quantitatively analysed by Perkin Elmer Avio 200 ICP-OES System. Magnetization of the nanoparticles were recorded using a vibrating sample magnetometer (EV-9, Microsense, ADE) in the range of -10000 Oe to 10000 Oe.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a JEOL JNM-EXCP 400 and data are reported in terms of chemical shift related to  $\text{CDCl}_3$  (7.26 ppm) or with tetramethylsilane (TMS,  $\delta$  0.00 ppm) as the internal standard, abbreviation used to indicate the multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of

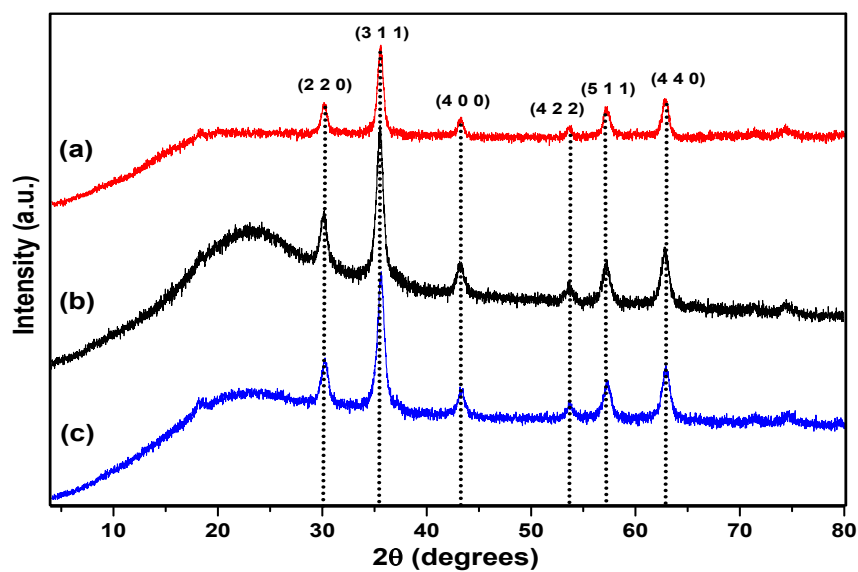
doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet), coupling constant (Hz), integration. Thin-layer chromatography (TLC) was performed by utilizing Merck silica gel plates 60 F<sub>254</sub> to check the course of reactions and visualised under UV light.

Light Source: 20 W Philips white LED bulbs, Quantity of light source: Two

**Figure S1.** Photocatalytic reaction setup.

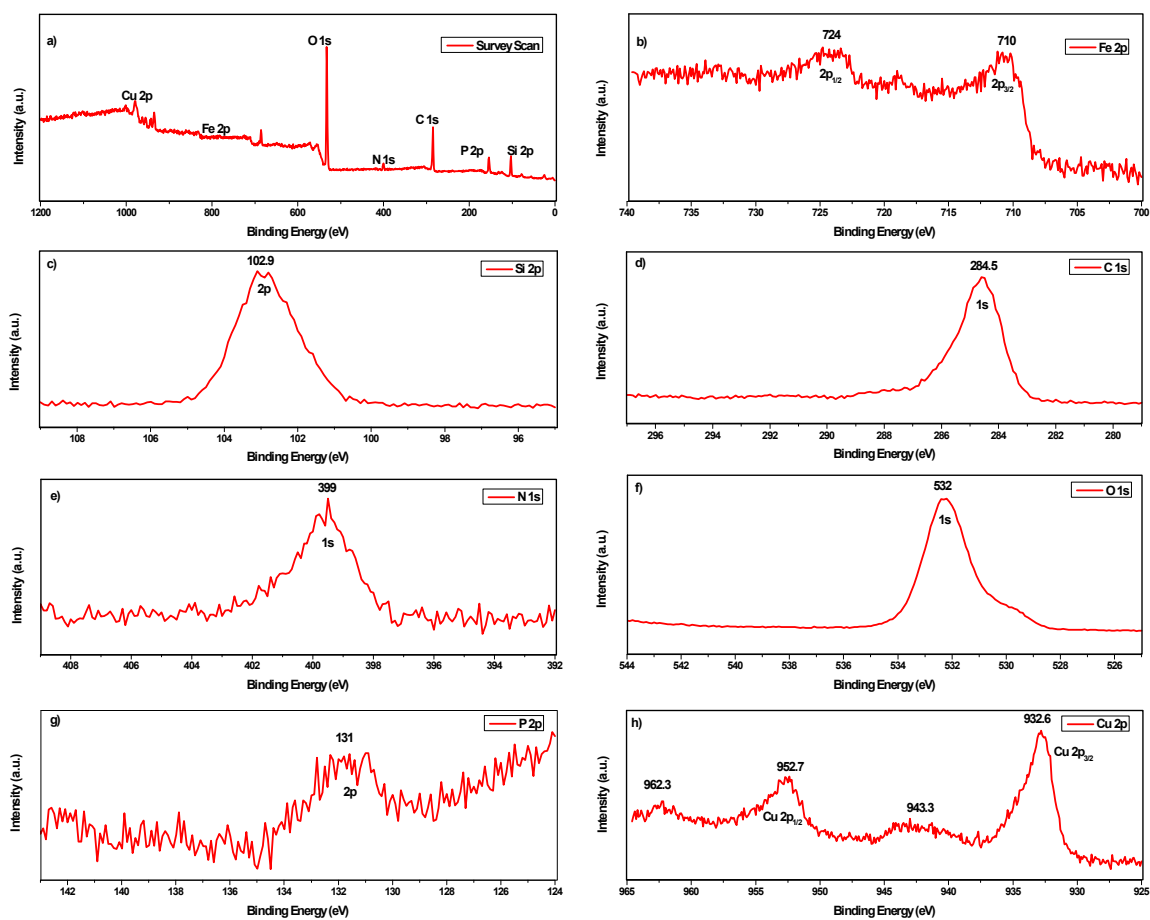
## RESULT AND DISCUSSION

### XRD



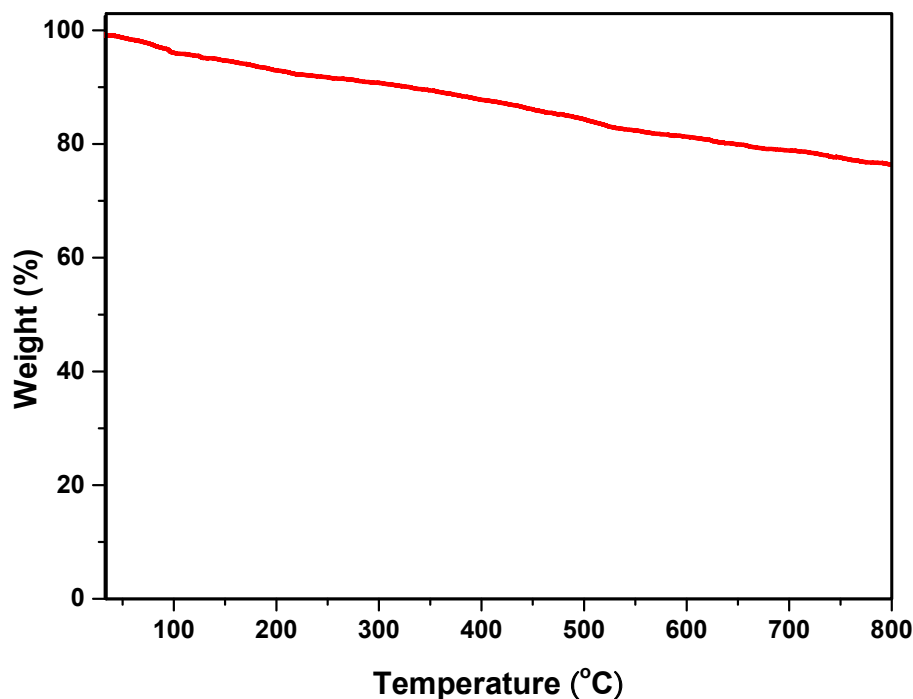
**Figure S2.** PXRD pattern of a) MNPs, b) SMNPs and c) Cu@Xantphos@SMNPs.

## XPS



**Figure S3.** a) XPS survey spectra of Cu@Xantphos@ASMNPs catalyst and detailed XPS spectra of b) Fe 2p, c) Si 2p, d) C 1s, e) N 1s, (f) O 1s, (g) P 2p and (h) Cu 2p.

## TGA

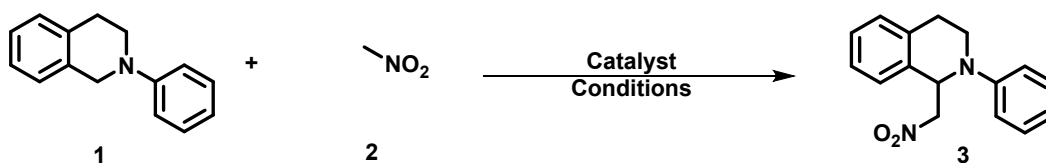


**Figure S4.** TGA analysis of Cu@Xantphos@ASMNPs photocatalyst.

## COMPARISON WITH LITERATURE PRECEDENTS

Comprehensive literature survey suggests the predominance of earth abundant, cheap and non-toxic Cu@Xantphos@ASMNPs over the previously reported catalysts in terms of mild reaction conditions, lower reaction time, high yield, facile magnetic recoverability and recyclability (Table S1). Moreover, the catalytic reaction showed high selectivity, with no over oxidised product formation. The Cu@Xantphos@ASMNPs photoredox nanocatalyst also showed promising results in terms of mild reaction condition in comparison with the literature precedents (Table S1).

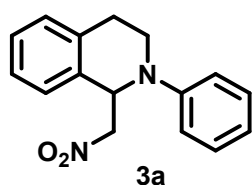
**Table S1.** Comparison of the catalytic activity of the fabricated photocatalyst with the earlier reported heterogeneous photocatalysts for cross-dehydrogenative coupling.



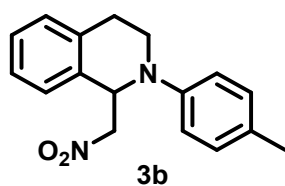
S. No.	Catalyst	Conditions	Light source	Recyclability	Yield (%)	Ref.
i	2 mol % Cot-RB Catalyst	20 mol% pyrrolidine/TFA, acetone, RT, 24 h	12 W green LEDs	6	93	2
ii	10 mg EY-POP-1	RT, air, 24 h	14 W household bulb	12	98	3
iii	1 equiv of TiO <sub>2</sub> (P25)	EtOH	11 W fluorescent lamp	5	75	4
iv	MNPs-eosin Y (0.25 mmol)	DMSO, RT, air, 12 h	3 W green LEDs	8	92	5
v	Cu <sub>2</sub> O–MoS <sub>2</sub> / graphene (CMG) composite	O <sub>2</sub> , RT, 8 h	24 W compact fluorescent bulb	6	79	6
vi	UiO-68-mtpdc/etpdc	Air, 12 h	blue LEDs ( $\lambda_{\max}$ = 450 nm)	5	88	7
vii	OH-TFP-TTA	MeOH, 6 h, 25 °C	460 nm LED	4	76	8
viii	15 mg mpg-C <sub>3</sub> N <sub>4</sub>	22-34 h, 1 bar O <sub>2</sub>	60 W energy-saving bulb,		92	9
ix	2 mg LP-Cu <sub>2</sub> O	O <sub>2</sub> balloon, 8 h	4 W blue LEDs	5	90	10
x	TFB-COF catalyst (30 mg, 30 mol%)	RT, O <sub>2</sub> (1 atm),	45 W energy-saving lamp	4	76	11
xi	Au <sub>4</sub> @MOF1	RT, 3.5 h, O <sub>2</sub>	$\lambda_{\max} > 370$ nm	5	86	12
xii	ZIF-9 (10 wt%)	6 h, 40 °C	Solar simulator with a 515 nm longpass filter	4	84	13
xiii	10 mg EY@UiO-66-NH <sub>2</sub>	MeOH, 8 h, RT	16 W visible household light	10	82	14
xiv	Cu-TPA (3 mol%)	30 h	26 W fluorescent lamp	3	79	15
xv	Phosphorescent cross-linked polymers 1 derivatives of Ru(bpy) <sub>3</sub> <sup>2+</sup> (0.2 mol% ratio)	8 h	26 W fluorescent lamp	4	89	16
xvi	In <sub>2</sub> S <sub>3</sub> /MoS <sub>2</sub> composite	O <sub>2</sub> , RT, 24 h	20 W LED bulb	6	74	17
xvii	PCN-808-BDBR		450 nm LED lamp	6	99	18
xviii	Ir-PCP (1 mol%) /Ru-PCP (0.2 mol%)	8 h	Visible Light	4	94/90	19
xix	CdS	MeCN, 24 h	h $\nu$ 440 nm		97	20
xx	RuL <sub>3</sub> @InBTB		20 W fluorescent lamp	9	80	21
xxi	1 mol% MOF-5/MOF-6 catalyst	12 h	26 W fluorescent lamp	59/86	3	22
xxii	2 mg PAF-BT(Ph) <sub>2</sub>	RT, air	23 W lamp	97	5	23
xxiii	ZJU-56-0.2	32 h, 323 K	660 nm LEDs	54	3	24

S. No.	Catalyst	Conditions	Light source	Recyclability	Yield (%)	Ref.
xiv	RB-CMP1	RT, air, 15 h	60 W household bulb	95	10	<sup>25</sup>
xv	Cu@Xantphos@ASMNPs (35 mg)	1 mL MeOH, RT, air, 18 h.	20 × 2 W white LEDs as light source	5	90	<b>Present work</b>

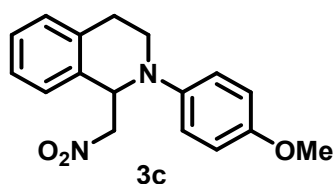
## <sup>1</sup>H AND <sup>13</sup>C NMR DATA OF THE CORRESPONDING PRODUCTS



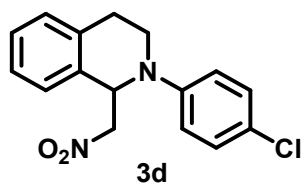
**1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a).**<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.21 (m, 5H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.59 (t, *J* = 7.1 Hz, 1H), 4.90 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.60 (dd, *J* = 11.8, 6.8 Hz, 1H), 3.74-3.62 (m, 2H), 3.16-3.08 (m, 1H), 2.83 (dt, *J* = 16.3, 4.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.5, 135.3, 133.0, 129.5, 129.2, 128.1, 127.0, 126.7, 119.5, 115.2, 78.8, 58.2, 42.1, 26.5.



**1-(nitromethyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3b).**<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26-7.06 (m, 6H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.49 (t, *J* = 7.2 Hz, 1H), 4.85 (dd, *J* = 11.8, 8.1 Hz, 1H), 4.55 (dd, *J* = 11.8, 6.3 Hz, 1H), 3.67-3.54 (m, 2H), 3.10-3.02 (m, 1H), 2.74 (dt, *J* = 16.4, 4.5 Hz, 1H), 2.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.5, 135.5, 133.0, 130.1, 129.4, 129.2, 128.1, 127.1, 126.7, 116.0, 76.8, 58.5, 42.4, 26.3, 20.5.



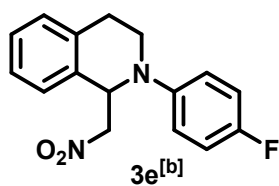
**2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3c).**<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.17 (m, 4H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.43 (dd, *J* = 8.4, 6.1 Hz, 1H), 4.86 (dd, *J* = 11.8, 8.8 Hz, 1H), 4.59 (q, *J* = 5.9 Hz, 1H), 3.78 (s, 3H), 3.61-3.58 (m, 2H), 3.09-3.00 (m, 1H), 2.72 (dt, *J* = 16.5, 3.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.0, 143.0, 135.5, 132.9, 129.5, 127.9, 126.9, 126.6, 118.8, 114.7, 79.0, 58.9, 55.6, 43.1, 25.8.



**2-(4-chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3d).**<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.31-7.16 (m, 6H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.52 (t, *J* = 7.3 Hz, 1H), 4.87 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.59 (dd, *J* = 11.9, 6.4 Hz, 1H), 3.70-3.62 (m, 2H), 3.13-



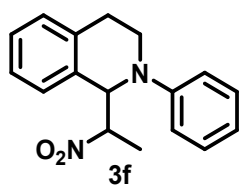
3.05 (m, 1H), 2.81 (dt,  $J = 16.3, 4.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 135.1, 132.5, 129.3, 128.2, 127.0, 126.8, 124.4, 116.5, 78.7, 58.2, 42.2, 26.2.



**2-(4-fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline**

**(3e).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-6.89 (m, 9H), 5.43 (dd,  $J = 8.7, 5.9$  Hz, 1H), 4.83 (dd,  $J = 12.0, 8.7$  Hz, 1H), 4.57 (q,  $J = 6.0$  Hz, 1H), 3.59 (q,  $J = 4.5$  Hz, 2H), 3.07-2.99 (m, 1H), 2.72 (dt,  $J = 16.5, 4.2$

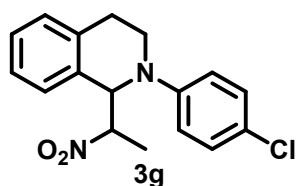
Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 156.0, 145.4, 135.4, 132.6, 129.6, 128.2, 127.1, 118.0, 116.1, 115.8, 78.9, 58.8, 42.9, 25.8.



**1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f).**<sup>26</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12-7.33 (m, 6H), 7.02 (d,  $J = 8.5$  Hz, 2H), 6.82-6.87 (m, 1H), 5.27 (t,  $J = 8.8$  Hz, 1H), [5.04-5.11 (m), 4.88-4.95 (m), 1H], [3.83-3.90 (m), 3.62 (dd,  $J = 15.1, 5.9$  Hz), 2H], [3.05-3.12 (m),

2.87-2.98 (m), 2H], [1.73 (d,  $J = 6.8$  Hz), 1.57 (d,  $J = 6.8$  Hz), 3H];  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 148.9, 135.6, 134.8, 133.8, 132.0, 129.4, 129.3, 129.1, 128.7, 128.4, 128.2, 127.3, 126.6, 126.1, (119.3, 118.8), (115.4, 114.5), (89.0, 85.4), (62.8, 61.2), (43.6, 42.7), (26.8, 26.4), (17.4, 16.4).



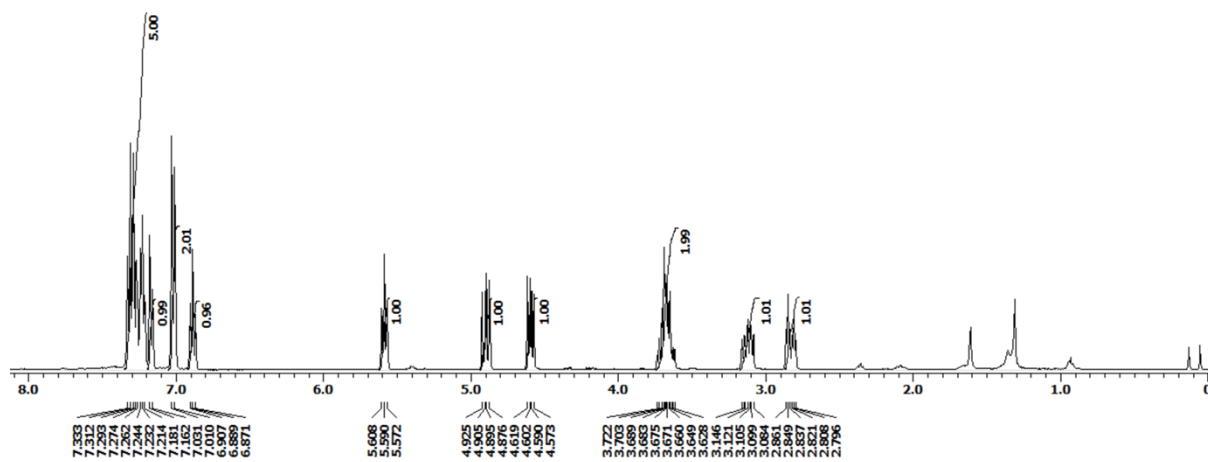
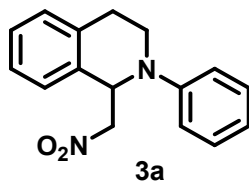
**2-(4-Chlorophenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydro-**

**isoquinoline (3g).**<sup>26</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.09 (m, 6H), 6.91-6.85 (2H), 5.15 (dd,  $J = 22.9, 8.7$  Hz, 1 H), [5.03-4.96 (m), 4.86 (dt,  $J = 15.6, 6.9$  Hz), 1 H], [3.84-3.76 (m), 3.59-3.47 (m), 2H],

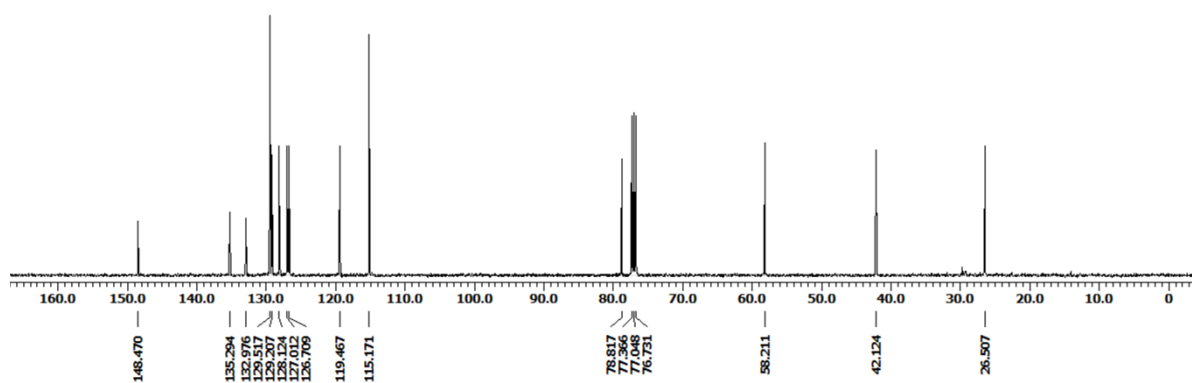
[3.07-2.99 (m), 2.94-2.83 (m), 2H], [1.66 (d,  $J = 6.7$  Hz), 1.54 (d,  $J = 6.6$  Hz), 3H];  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 147.6, 135.4, 134.6, 133.6, 131.8, 129.3, 129.3, 129.2, 128.8, 128.5, 127.2, 126.8, 126.3, (116.7, 115.8), (88.9, 85.5), (62.9, 61.2), (43.9, 42.9), (26.7, 26.2), (17.4, 16.7).

## NMR SPECTRA

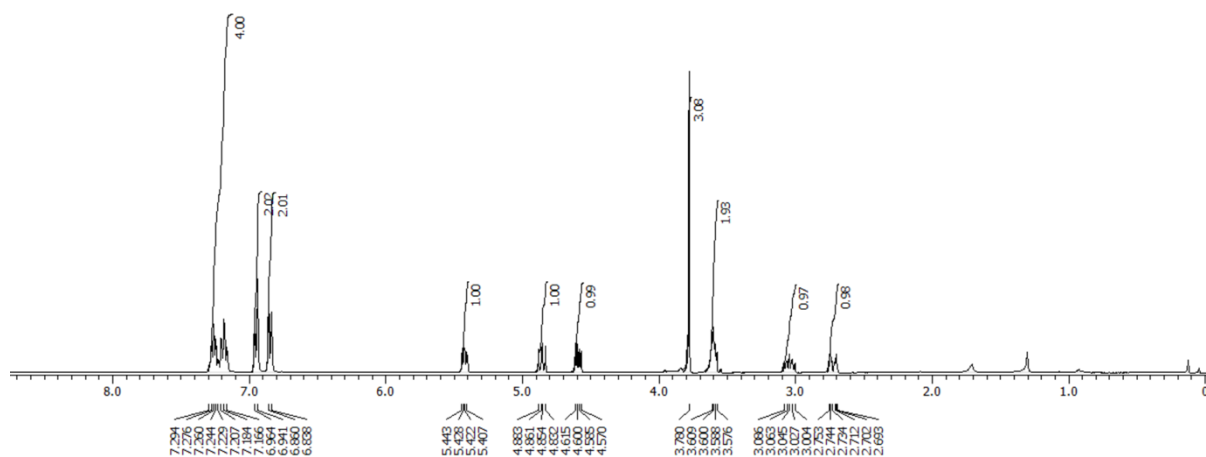
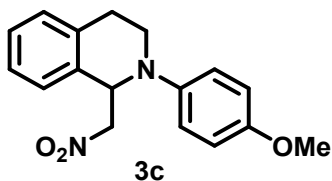
### <sup>1</sup>H NMR Spectra of 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



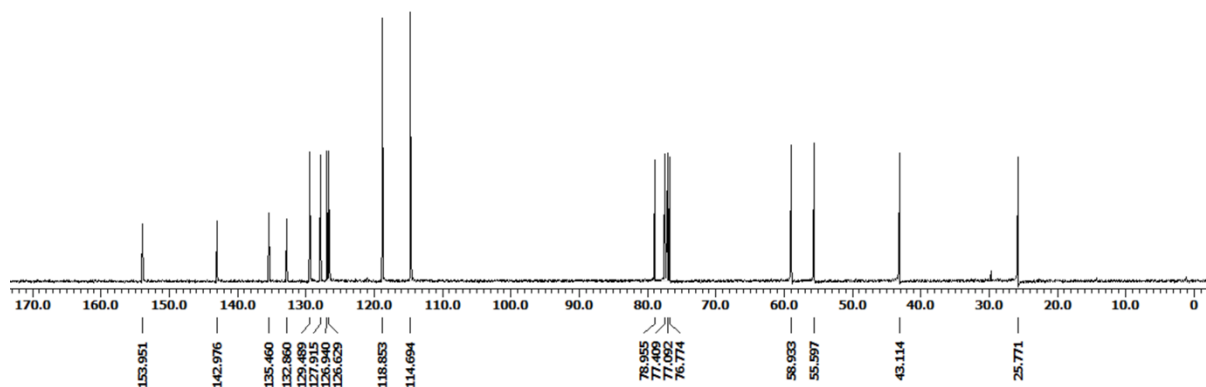
### <sup>13</sup>C NMR Spectra of 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



## <sup>1</sup>H NMR Spectra of 2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydro isoquinoline



## <sup>13</sup>C NMR Spectra of 2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydro isoquinoline



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