

## Supporting Information

### The Palladium and Copper Contrast: A Twist to Product of Different Chemotype and Altered Mechanistic Pathway

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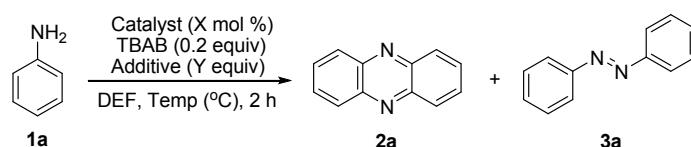
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**I. The standardisation of various reaction parameters such as the effect of catalysts, oxidants, solvents, reaction temperature and time etc. on the oxidative N-N self coupling of 1a to form 3a.**

**Table I-A. The effect of various Cu and Au catalysts, metal-based additives as the oxidant, and other reaction parameters for the N-N self coupling of 1a to form 2a and 3a.<sup>a</sup>**



Entry	Catalyst (X)	Additive (Y)	Temp (°C)	Yield (%) <sup>b</sup>	
				<b>2a</b>	<b>3a</b>
1	CuI (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	11	66
2	CuCl (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	13	24
3	CuBr (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	12	43
4	CuCl <sub>2</sub> ·2H <sub>2</sub> O (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	20	21
5	CuSO <sub>4</sub> ·5H <sub>2</sub> O (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	10	57
6	Cu(BF <sub>4</sub> ) <sub>2</sub> ·xH <sub>2</sub> O (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	15	24
7	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	11	83
8	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	22	44
9	Cu metal (10)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	19	31
10	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (5)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	11	81
11	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	12	81
12	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (1)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	13	51
13	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (0.5)	Ag <sub>2</sub> CO <sub>3</sub> (4)	100	23	21
14	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (3)	100	13	82
15	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (2)	100	15	72
16	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (1)	100	26	40
17	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	100	0	0
18	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	100	15	82
19	None	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	100	19	13
20	Cu(acac) <sub>2</sub> (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	100	10	70
21	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	AgOTf (2.5)	100	10	0
22	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	AgBF <sub>4</sub> (2.5)	100	0	0
23	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	AgOAc (2.5)	100	12	30
24	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	AgNO <sub>3</sub> (2.5)	100	15	32
<b>25</b>	<b>Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (2.5)</b>	<b>Ag<sub>2</sub>CO<sub>3</sub> (2.5)</b>	<b>80</b>	<b>14</b>	<b>81</b>
26	HAuCl <sub>4</sub> (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	80	10	57
27	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	60	14	31
28	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	40	0	0
29	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	80	0	0
30	None	Ag <sub>2</sub> CO <sub>3</sub> (2.5)	80	10	11
31	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	80	15	33

32  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (2.5)  $\text{Ag}_2\text{CO}_3$  (1) 80 trace 14

<sup>a</sup>Aniline **1a** (2 mmol, 2 equiv) was treated in the presence of TBAB (20 mol %) under various conditions in diethylformamide, DEF (2 mL) for 2 h. <sup>b</sup>Isolated yield.

**Table I-B. The effect of various Cu and Ag catalysts, bases, metal-based additives as the oxidant, and other reaction parameters for the N-N self coupling of 1a to form 2a and 3a.<sup>a</sup>**

Entry	Catalyst (X)	Base (Y)	Additive (Z)	T (°C)	Yield (%) <sup>b</sup>	
					2a	3a
1	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{K}_2\text{CO}_3$ (2.5)	$\text{AgOTf}$ (2.5)	100	10	0
2	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{K}_2\text{CO}_3$ (2.5)	$\text{AgBF}_4$ (2.5)	100	0	0
3	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{K}_2\text{CO}_3$ (2.5)	$\text{AgOAc}$ (2.5)	100	14	27
4	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{K}_2\text{CO}_3$ (2.5)	$\text{AgNO}_3$ (2.5)	100	11	29
5	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{K}_2\text{CO}_3$ (2.5)	$\text{Ag}_2\text{CO}_3$ (1.5)	80	0	13
6	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{KOAc}$ (1)	$\text{Ag}_2\text{CO}_3$ (1.5)	80	0	17
7	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	None	$\text{Ag}_2\text{CO}_3$ (1.5) + $\text{O}_2$ (10 psi)	80	0	--- <sup>c</sup>
8	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{K}_2\text{CO}_3$ (1)	$\text{Ag}_2\text{CO}_3$ (1.5) + $\text{O}_2$ (10 psi)	80	0	--- <sup>c</sup>
9	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	$\text{KOH}$ (1)	None	80	0	0
		+ $\text{Ag}_2\text{CO}_3$ (10)				
10	$\text{Ag}_2\text{CO}_3$ (10)	$\text{KOH}$ (1)	None	80	0	0
11	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	None	$\text{Ag}_2\text{CO}_3$ (1) + $\text{O}_2$ (10 psi) + $\text{NHPI}$ (0.02)	80	0	--- <sup>c</sup>
12	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	None	$\text{Ag}_2\text{CO}_3$ (1) + $\text{O}_2$ (10 psi) + $\text{NHPI}$ (0.02)	80	0	--- <sup>c,d</sup>
13	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (5)	None	$\text{NHPI}$ (0.02) + $\text{O}_2$ (10 psi)	80	0	0
14	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (5)	$\text{K}_2\text{CO}_3$ (2.5)	$\text{NHPI}$ (0.02) + $\text{O}_2$ (10 psi)	80	0	trace
15	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (5)	None	$\text{Ag}_2\text{CO}_3$ (1) + $\text{NHPI}$ (0.02)	80	trace	17

<sup>a</sup>**1a** (2 mmol, 2 equiv) was treated in the presence of TBAB (20 mol %) under various conditions in DEF (2 mL) for 2 h. <sup>b</sup>Isolated yield. <sup>c</sup>Complex reaction mixture. <sup>d</sup>DCE was used as solvent.

**Table I-C. The effect of various Cu catalysts, bases, non-metal based additives as the oxidant, and other reaction parameters for the N-N self coupling of 1a to form 2a and 3a.<sup>a</sup>**

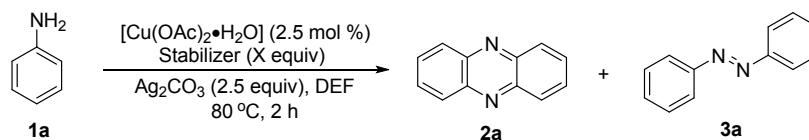
Entry	Catalyst (X)	Base (Y)	Additive (Z)	Temp (°C)	Yield (%) <sup>b</sup>	
					2a	3a
1	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.5)	None	$\text{PhNO}_2$ (2.5)	100	0	0

2	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	K <sub>2</sub> CO <sub>3</sub> (2.5)	PhNO <sub>2</sub> (2.5)	100	0	0
3	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	PhNO <sub>2</sub> (1.5)	100	0	trace <sup>c</sup>
4	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	PhNO <sub>2</sub> (2.5)	100	0	trace <sup>c</sup>
5	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	TBHP (2.5)	100	0	0
6	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	K <sub>2</sub> CO <sub>3</sub> (2.5)	TBHP (2.5)	100	0	0
7	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	TBHP (1.5)	100	0	trace <sup>c</sup>
8	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	TBHP (2.5)	100	0	trace <sup>c</sup>
9	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	None	O <sub>2</sub> (10 psi)	80	0	0
10	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.5)	K <sub>2</sub> CO <sub>3</sub> (2.5)	O <sub>2</sub> (10 psi)	80	0	0
11	CuI (5)	None	TBHP (3)	80	0	0 <sup>d</sup>

<sup>a</sup>1a (2 mmol, 2 equiv) was treated in the presence of TBAB (20 mol %) under various conditions in DEF (2 mL).

<sup>b</sup>Isolated yield. <sup>c</sup>Ag<sub>2</sub>CO<sub>3</sub> (1 equiv) was used. <sup>d</sup>1,10-Phenanthroline (15 mol %) was added externally as ligand.

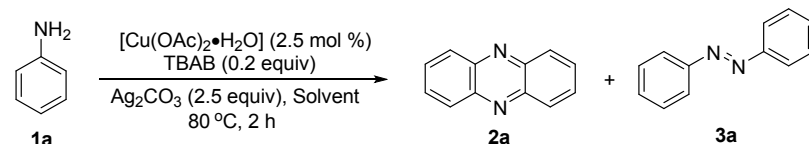
**Table I-D. The effect of different stabilizers during the N-N self coupling of 1a to form 2a and 3a.<sup>a</sup>**



Entry	Stabilizer	X	Yield (%) <sup>b</sup>	
			2a	3a
1	Tetrabutylammonium bromide (TBAB)	1	13	82
2	TBAB	0.5	13	82
3	<b>TBAB</b>	<b>0.2</b>	<b>14</b>	<b>81</b>
4	TBAB	0.1	31	60
5	None	---	22	46
6	TBAF	0.2	0	0
7	TBACl	0.2	11	32
8	Tetrabutylammonium iodide (TBAI)	0.2	15	39
9	[bmim]Br	0.2	13	56
10	[bdmim]Br	0.2	16	52

<sup>a</sup>1a (2 mmol, 2 equiv) was treated in the presence of Cu(OAc)<sub>2</sub>·OH<sub>2</sub> (2.5 mol %) and Ag<sub>2</sub>CO<sub>3</sub> (2.5 equiv) in different stabilizers in DEF (2 mL) at 80 °C for 2 h. <sup>b</sup>Isolated yield.

**Table I-E. The effect of different solvents during the N-N self coupling of 1a to form 2a and 3a.<sup>a</sup>**



Entry	Solvent	Yield (%) <sup>b</sup>	
		2a	3a
1	HCONH <sub>2</sub>	30	trace



2	<i>N,N</i> -Dimethylformamide (DMF)	12	83
3	<i>N,N</i> -Diethylformamide (DEF)	10	83
4	<i>N,N</i> -Dimethylacetamide DMA	14	81
5	NMP	24	51
6	DMPU	27	trace
7	DMSO	23	55
8	DMF	trace	47 <sup>c</sup>
9	1,4-Dioxane	19	32
10	THF <sup>d</sup>	11	62
11	MeCN <sup>d</sup>	15	48
12	H <sub>2</sub> O	0	22
13	H <sub>2</sub> O	0	0 <sup>e</sup>
14	DCE	trace	13
15	Toluene	12	31
16	<sup>i</sup> PrOH	0	19
17	Polyethylene glycol 400 (PEG 400)	0	0

<sup>a</sup>**1a** (2 mmol, 2 equiv) was treated in the presence of Cu(OAc)<sub>2</sub>·OH<sub>2</sub> (2.5 mol %), Ag<sub>2</sub>CO<sub>3</sub> (2.5 equiv) and TBAB (0.2 equiv) in different solvents (2 mL) at 80 °C for 2 h. <sup>b</sup>Isolated yield. <sup>c</sup>The reaction was performed with pre-formed isolated Cu-Ag binary NC. <sup>d</sup>Reflux temperature. <sup>e</sup>SDOSS was used instead of Ag<sub>2</sub>CO<sub>3</sub>.

#### Calculation of turn over number (TON):

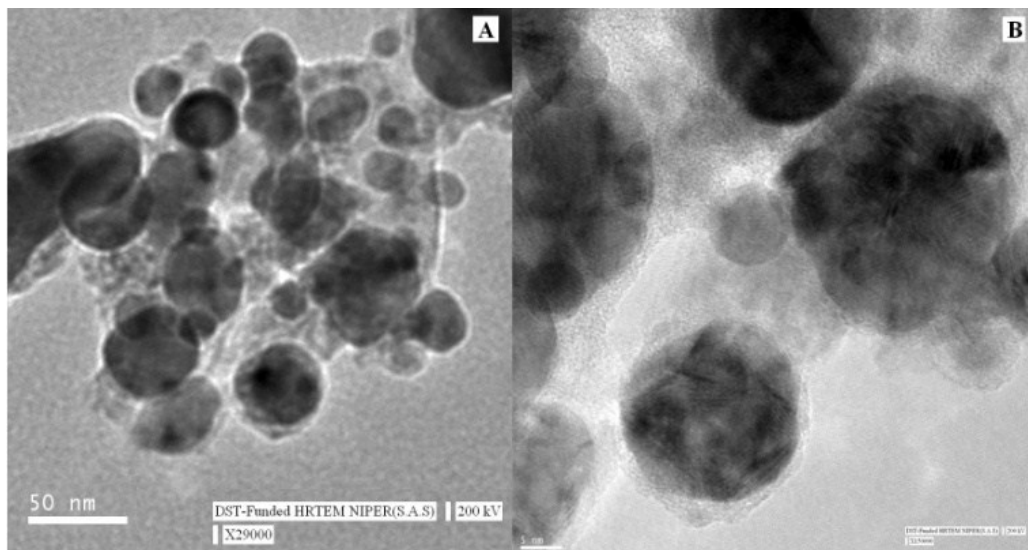
Since the NCs were prepared in-situ and the nanoparticles are poly-dispersed in nature, the TON has been calculated based on the catalytic amount [*Angew. Chem. Int. Ed.*, 2001, **40**, 3408] of palladium or copper used.

$$\text{TON} = \frac{\text{moles of reactant}}{\text{moles of catalyst}} \times \% \text{ yield}$$

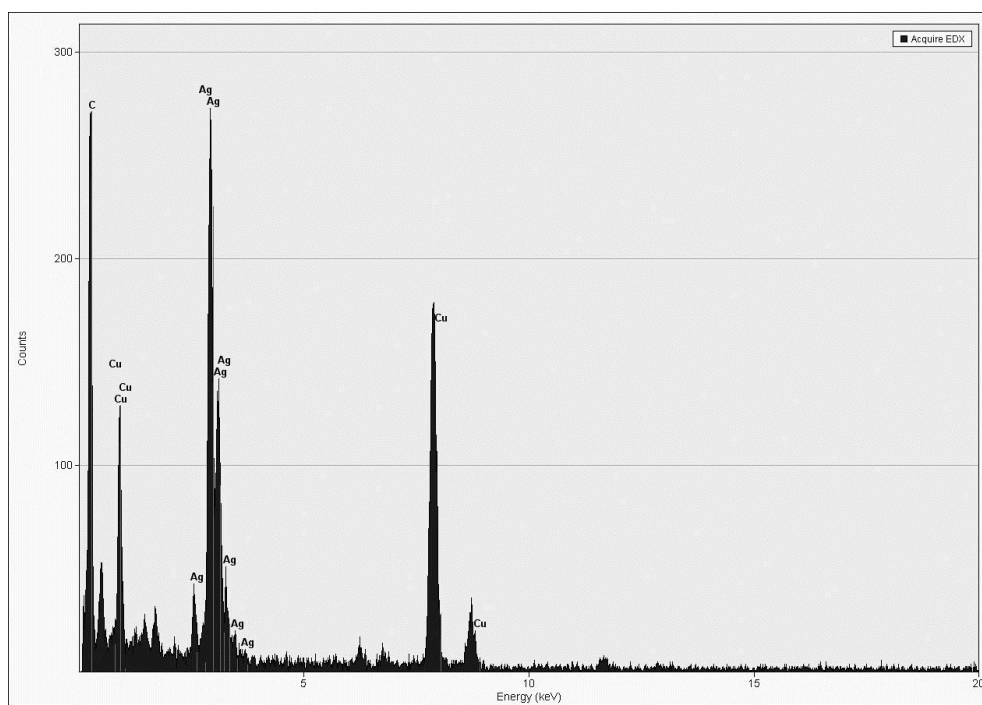
## II. Evidence of NC formation during the N-N coupling of 1a to form 3a.

**Figure A. HRTEM image of Cu-Ag binary NC obtained from the reaction mixture of the [Cu(OAc)<sub>2</sub>·OH<sub>2</sub>] (5 mg, 2.5 mol %), Ag<sub>2</sub>CO<sub>3</sub> (689 mg, 2.5 equiv) and TBAB (20 mol %) in DMF (2 mL) for 10 min at 80 °C.**

Cu-Ag binary NC: (Cu particles size 8 nm – 15 nm and Ag particles size 20 nm – 30 nm)

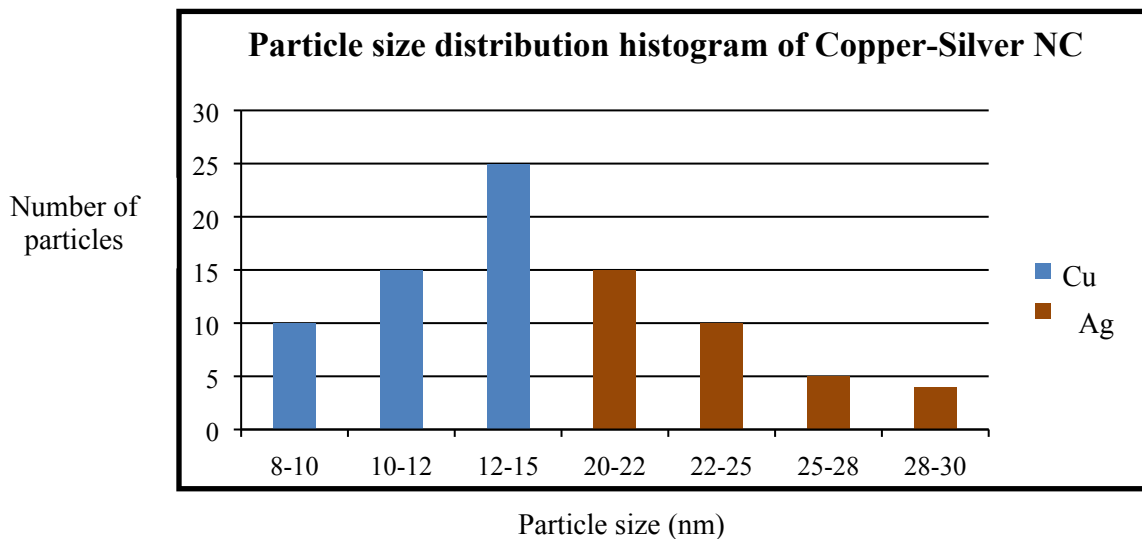


**Figure B. Energy dispersive X-ray spectra of Cu-Ag binary NC (Fig. A) on carbon coated Cu grid.**

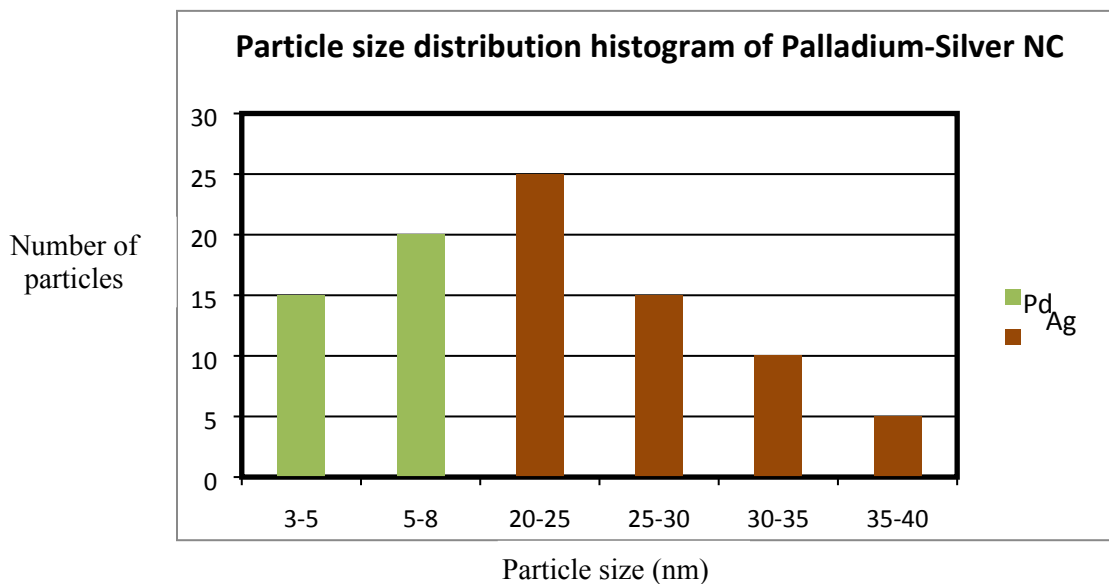


**Figure C. Particles size distribution histogram.**

**(i) Histogram of Cu-Ag NC:**

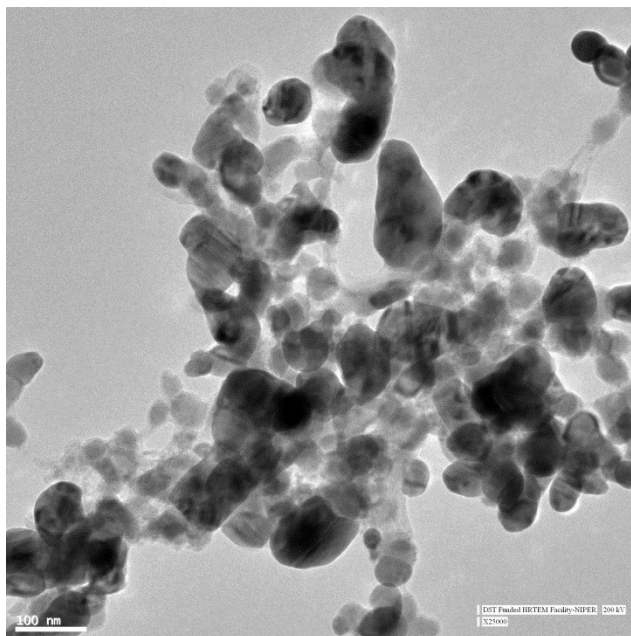


**(ii) Histogram of Pd-Ag NC:**



**Figure D. HRTEM image of pre-formed Cu-Ag binary NC obtained from  $[\text{Cu}(\text{OAc})_2 \cdot \text{OH}_2]$  (5 mg, 2.5 mol %),  $\text{Ag}_2\text{CO}_3$  (689 mg, 2.5 equiv) and TBAB (20 mol %) in DMF (2 mL) at 80 °C.**

Cu-Ag binary NC: (Cu particles size 40 nm – 50 nm and Ag particles size 80 nm – 100 nm)



**Figure E. HRTEM image of pre-formed Pd-Ag binary NC obtained from  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (7 mg, 1 mol %),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2 equiv) and TBAB (20 mol %) in DEF (2 mL) at 100 °C.**

Pd-Ag binary NC: (Pd particles size 25 nm – 40 nm and Ag particles size 90 nm – 100 nm)

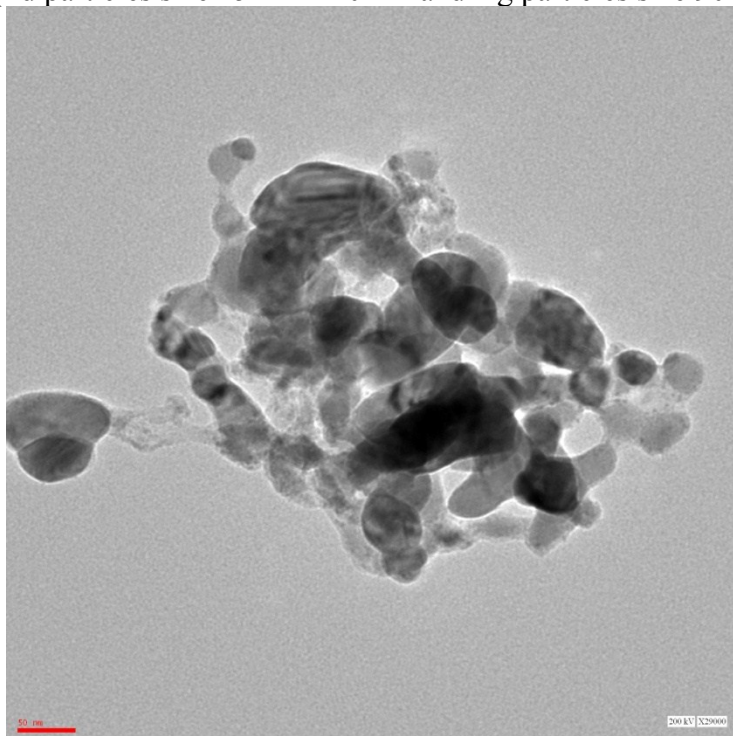


Figure F. XRD spectra of the Cu-Ag binary NC.

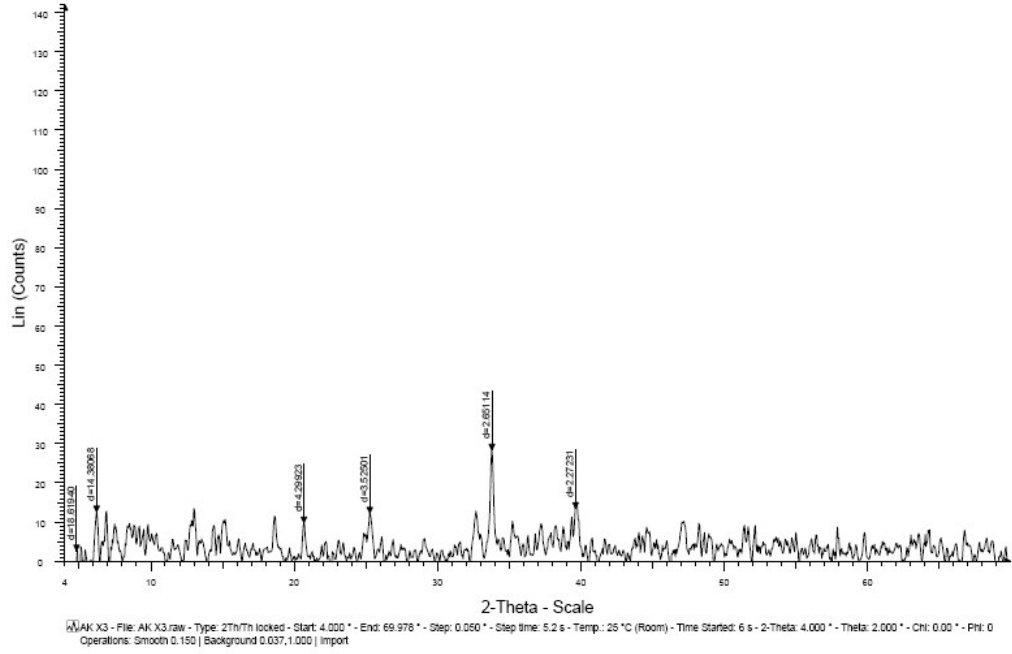
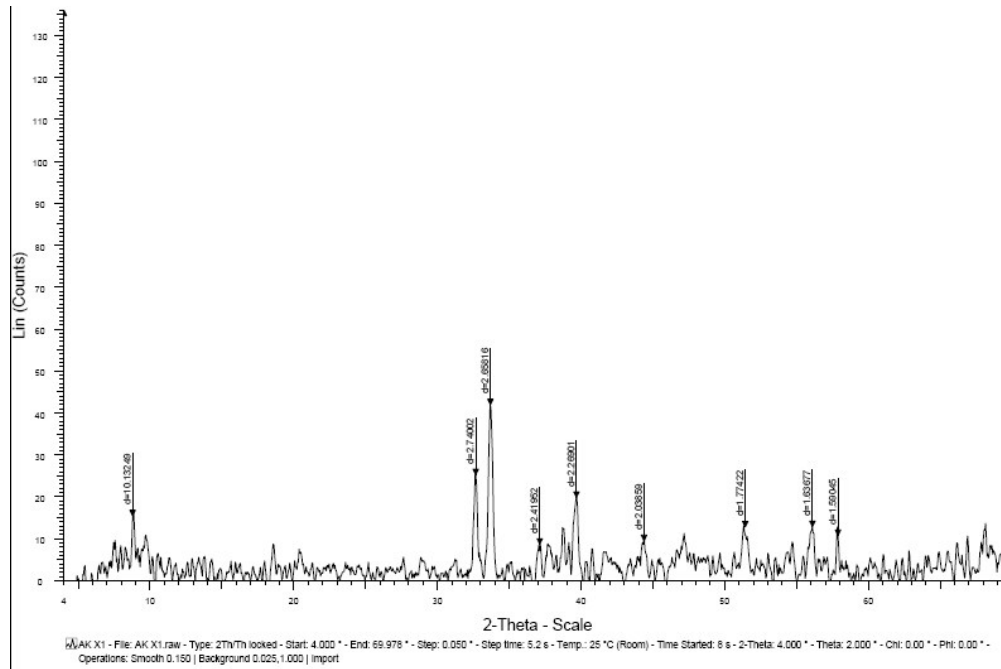


Figure G. XRD spectra of the Pd-Ag binary NC.

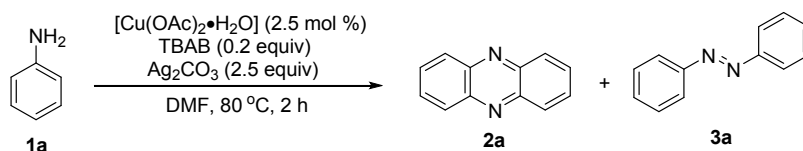


### III. Experimental procedure

#### General Information

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer in  $\text{CDCl}_3$  with residual undeuterated solvent ( $\text{CDCl}_3$  : 7.26/77.0) using  $\text{Me}_4\text{Si}$  as an internal standard. Chemical shifts ( $\delta$ ) are given in ppm and  $J$  values are given in Hz. The IR spectra were recorded either on KBr pellets (for solids) or neat (for liquids) on a Nicolet Impact 410 FTIR spectrometer. The HRMS spectra were obtained with a Bruker Maxis instrument. Melting points were measured with Gupta scientific, India melting point apparatus. Column chromatography, thin layer chromatography (TLC) was performed on Silica gel [Fisher Scientific silica gel 100-200 mesh or 60-120 mesh, F254 and Merck<sup>®</sup> silica gel respectively]. Evaporation of solvents was performed at reduced pressure, using a Büchi rotary evaporator. All chemicals were purchased from Aldrich, Lancaster, Alfa Aesar, Fluka Chemicals and Loba Chemie and used as received. All the HRTEM images were taken on carbon coated Cu grids in FEI-TECHNAI-G<sup>2</sup>-F20 instrument equipped with EDAX facility.

#### Typical procedure for the in-situ generated Cu-Ag NC catalyzed N-N self coupling of 1a to generate 2a and 3a:



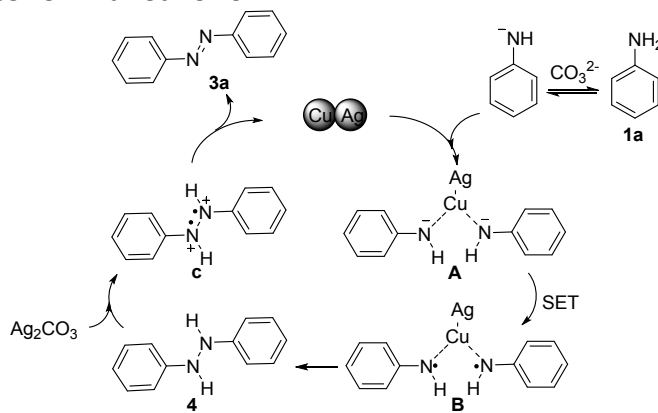
To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %),  $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$  (5 mg, 0.025 mmol, 2.5 mol %) and  $\text{Ag}_2\text{CO}_3$  (689 mg, 2.5 mmol, 2.5 equiv) in DMF (2 mL) was added aniline **1a** (186 mg, 0.18 mL, 2 mmol, 2 equiv) at 80 °C. Upon completion of the reaction (2 h, monitored by TLC), the reaction mixture was filtered through a short pad of celite; DMF was evaporated to dryness under vacuum (10 mm Hg). The residue was passed through chromatography column (silica-gel: 60-120 mesh) and eluted with hexane/EtOAc solvent system to afford the phenazine<sup>1</sup> **2a** as brown solid, (22 mg, 12%) and azobenzene<sup>2</sup> **3a** as red solid, (151 mg, 83%). **2a**: mp: 172-175 °C [lit. mp: 172-176 °C]; TLC (Hexane:EtOAc, 95:5 v/v):  $R_f \approx 0.5$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.85 – 7.89 (m, 4H), 8.26 – 8.30 (m, 4H); IR (KBr)  $\nu_{\text{max}}$ : 2920, 1276, 1261, 1055, 1031  $\text{cm}^{-1}$ ; MS (ESI) ( $\text{M}^+$ ) = 180.4. **3a**: mp: 67-70 °C [lit. mp: 65-68 °C]; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.48 – 7.58 (m, 6H), 7.94 – 7.97 (m, 4H); IR (KBr)  $\nu_{\text{max}}$ : 3138, 2957, 1735, 1366, 1212  $\text{cm}^{-1}$ ; MS (ESI) ( $\text{M}^+$ ) = 182.6.

**Typical procedure for identification and analysis of the in-situ formed Cu-Ag binary NC:** The mixture of TBAB (64.4 mg, 0.2 mmol, 20 mol %),  $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$  (5 mg, 0.025 mmol, 2.5 mol %) and  $\text{Ag}_2\text{CO}_3$  (689 mg, 2.5 mmol, 2.5 equiv) in DMF (2 mL) was stirred magnetically at 80 °C. An aliquot portion (3  $\mu\text{L}$ ) of the reaction mixture was withdrawn after 10 min, diluted and from the diluted solution, another aliquot portion (3  $\mu\text{L}$ ) was kept on carbon

coated Cu grid (200 mesh size). The grid was air dried and was subjected to TEM analyses to identify the Cu-Ag binary NC (Cu particles 8 nm - 15 nm and Ag particles 20 nm - 30 nm).

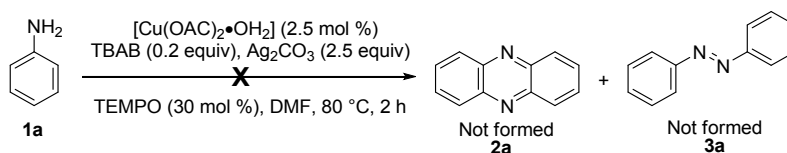
#### IV. Evidences for the proposed mechanistic pathway during the oxidative N-N self coupling of aniline to form azoarene and relevant studies:

##### Scheme IV-A. Plausible mechanism for the Cu-Ag NC catalyzed oxidative N-N self coupling of aniline to form azoarene.

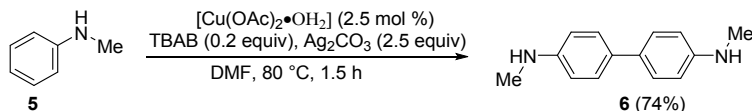


##### Scheme IV-B. Evidence for radical mechanism involving oxidative N-N coupling during the Cu-Ag NC catalyzed formation of azoarene

###### (i) Reaction of aniline in the presence of radical scavenger.



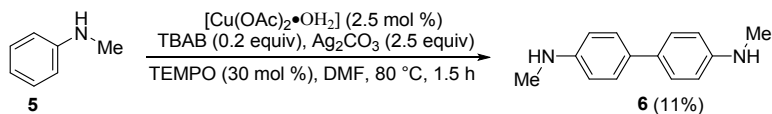
###### (ii) Reaction of *N*-Methylaniline **5** in the absence of radical scavenger.



To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), [Cu(OAc)<sub>2</sub>·H<sub>2</sub>O] (5 mg, 0.025 mmol, 2.5 mol %) and Ag<sub>2</sub>CO<sub>3</sub> (689 mg, 2.5 mmol, 2.5 equiv) in DMF (2 mL) was added *N*-methylaniline **5** (214 mg, 0.216 mL, 2 mmol, 2 equiv) at 80 °C. Upon completion of the reaction (1.5 h, monitored by TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DMF was evaporated to dryness under vacuum (10 mm Hg). The residue was passed through chromatography column (silica-gel: 60-120 mesh) and eluted with hexane-EtOAc solvent system to afford the 4,4'-di-*N*-methylbiphenyl<sup>13b</sup> **6** as reddish oil (157 mg, 74%); TLC (Hexane:EtOAc, 95:5 v/v): *R*<sub>f</sub> ≈ 0.5; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 3.07 (s, 6H), 6.89 –

6.94 (m, 4H), 7.32 – 7.37 (m, 4H); IR (KBr)  $\nu_{\text{max}}$ : 3354, 2229, 1737, 1626, 1599, 1218, 1020  $\text{cm}^{-1}$ ; MS (ESI)  $(\text{M} + \text{H})^+ = 213.4$ .

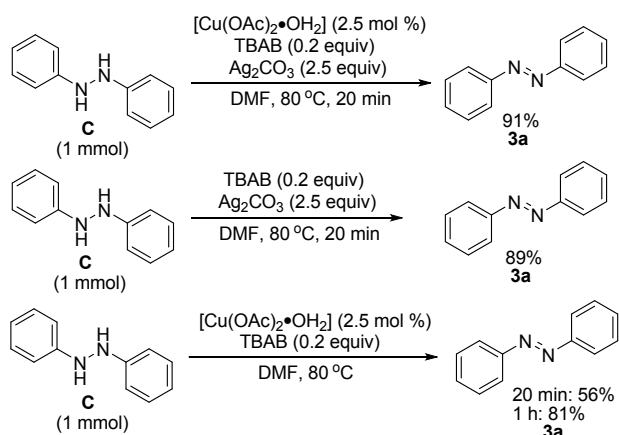
### (iii) Reaction of **5** in the presence of radical scavenger.



To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %),  $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$  (5 mg, 0.025 mmol, 2.5 mol %),  $\text{Ag}_2\text{CO}_3$  (689 mg, 2.5 mmol, 2.5 equiv) in DMF (2 mL) were added TEMPO (30 mol %) and **5** (214 mg, 0.216 mL, 2 mmol, 2 equiv) at 80 °C. Upon completion of the reaction (1.5 h, monitored by TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DMF was evaporated to dryness under vacuum (10 mm Hg). The residue was passed through chromatography column (silica-gel: 60-120 mesh) and eluted with hexane-EtOAc solvent system to afford the **6**<sup>b</sup> as reddish oil (23 mg, 11%).

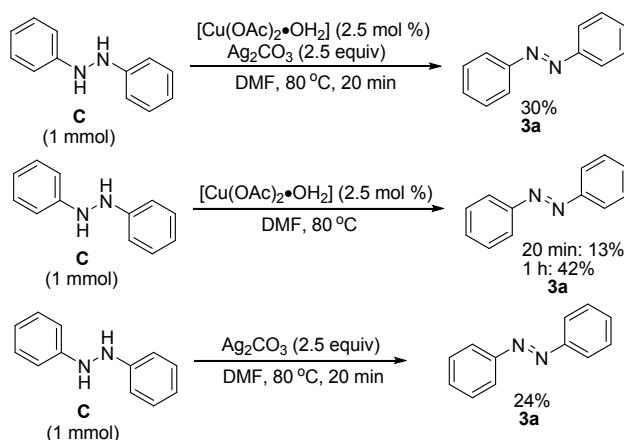
### Scheme IV-C. Relevance/importance of the formation of the phenyl hydrazine intermediate 'C' through oxidative N-N coupling during the Cu-Ag NC catalyzed formation of azoarene.

#### (i) Reactions with pre-formed phenyl hydrazine in the presence of stabilizer, TBAB:

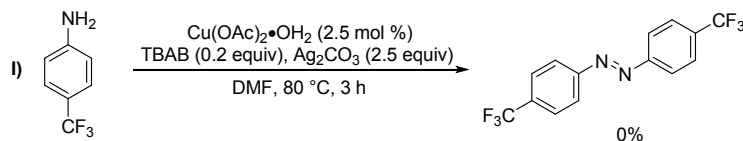




**(ii) Reactions with pre-formed phenyl hydrazine in the absence of stabilizer, TBAB:**



**Scheme IV-D. The influence of electron deficiency of anilines during the Cu-Ag NC catalyzed synthesis of azoarene.**



**V. The comparison of Cu-Ag NC catalyzed azoarene formation under the present study with those of few literature reports as well as with some modifications in some of these literature protocols:**

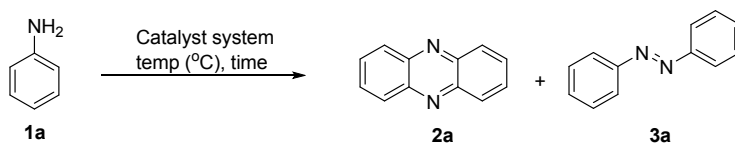
**Table V-A. The oxidative N-N coupling of aniline under the reported conditions as well as with different variations of solvent/temperature.<sup>a</sup>**

Entry	Catalyst system	Condition	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>	
					2a	3a
<b>A) Jiao's catalyst/condition</b>						
1	CuBr (6 mol %), Pyridine (18 mol %), THF, air (1 atm)	originally reported <sup>c</sup>	60	20	---	96
2	CuBr (6 mol %), Pyridine (18 mol %), THF, air (1 atm)	modified	60	2	---	---
3	CuBr (6 mol %), Pyridine (18 mol %), DMF, air (1 atm)	modified	60	2	0	0 <sup>d</sup>
4	$[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$ (2.5 mol %), TBAB (20 mol %), $\text{Ag}_2\text{CO}_3$ (2.5 equiv), DMF	modified	60	2	14	31 <sup>d</sup>
5	$[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$ (2.5 mol %),	modified	60	20	16	50 <sup>d</sup>

6	TBAB (20 mol %), Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), DMF [Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] (2.5 mol %), TBAB (20 mol %), Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), DMF	this work	80	2	12	83 <sup>d</sup>
<b>B) Li's catalyst/condition</b>						
7	Ag/C (6 mol %), KOH (1 equiv), DMSO, air (1 atm)	originally reported <sup>e</sup>	60	24	---	97
8	[Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] (2.5 mol %), TBAB (20 mol %), Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), DMSO	modified	60	2	12	26 <sup>d</sup>
9	[Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] (2.5 mol %), TBAB (20 mol %), Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), DMSO	modified	60	24	18	32 <sup>d</sup>
10	[Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] (2.5 mol %), TBAB (20 mol %), Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), DMF	this work	80	2	12	83 <sup>d</sup>

<sup>a</sup>1a (2 mmol, 2 equiv) was treated under various conditions. <sup>b</sup>Isolated yield. <sup>c</sup>Data as per reported literature procedure (*Angew. Chem. Int. Ed.*, 2010, **49**, 6174). <sup>d</sup>Experiment performed under present study. <sup>e</sup>Data as per reported literature procedure (*ACS Catal.*, 2013, **3**, 478).

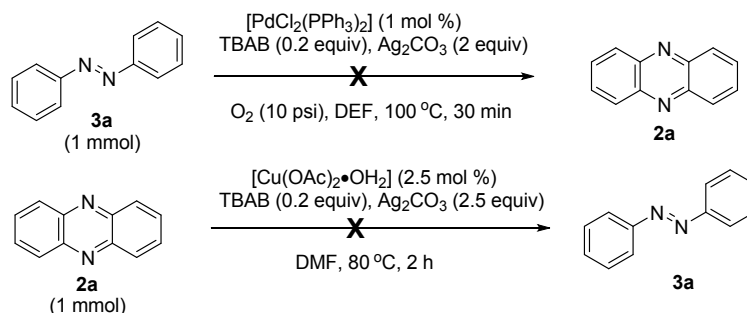
**Table V-B. The oxidative N-N coupling of aniline under the reported conditions as well as with individual Cu and Ag NPs.<sup>a</sup>**



Entry	Catalyst system	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>	
				2a	3a
1	Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), TBAB (20 mol %), DMF	80	2	14	11
2	[Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] (2.5 mol %), TBAB (20 mol %), DMF	80	2	0	0
3	[Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] (2.5 mol %), TBAB (20 mol %), Ag <sub>2</sub> CO <sub>3</sub> (2.5 equiv), DMF	80	2	12	83

<sup>a</sup>1a (2 mmol, 2 equiv) was treated under various conditions. <sup>b</sup>Isolated yield.

**VI. Evidence to support that the Pd-Ag NC catalyzed phenazine formation does not proceed through the intermediacy of azoarene and Cu-Ag NC catalyzed azoarene formation does not proceed through the intermediacy of phenazine:**



## VII. Characterization of compounds:

### Phenazines:

**2,7-Dimethyl-phenazine<sup>3</sup> (entry 4, Table 1):**- Yellow solid; mp: 161-163 °C. TLC (Hexane:EtOAc, 85:15 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.66 (s, 6H), 7.65 – 7.67 (m, 2H), 7.98 (s, 2H), 8.12 (d, 2H,  $J = 8.9$  Hz); IR (KBr)  $\nu_{\text{max}}$ : 2949, 1655, 1455, 1030 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 209.4.

**2,7-Bis-benzyloxy-phenazine<sup>3b</sup> (entry 6, Table 1):**- Yellow solid; mp: 153-156 °C; TLC (Hexane:EtOAc, 25:75 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 5.17 (s, 4H), 7.40 – 7.48 (m, 6H), 7.52 – 7.62 (m, 8H), 8.08 (d, 2H,  $J = 9.4$  Hz); IR (KBr)  $\nu_{\text{max}}$ : 2922, 2849, 1600, 1451, 1277 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 393.5.

**1,2,3,6,7,8-Hexamethoxy-phenazine<sup>3b</sup> (entry 8, Table 1):**- Yellow solid; mp: 155-157 °C; TLC (Hexane:EtOAc, 80:20 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 4.07 (s, 6H), 4.13 (s, 6H), 4.24 (s, 6H), 7.37 (s, 2H); IR (KBr)  $\nu_{\text{max}}$ : 2926, 2851, 1601, 1408, 1049 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 361.5.

**2,7-Dimethoxy-phenazine<sup>4</sup> (entry 10, Table 1):**- Yellow solid; TLC (Hexane:EtOAc, 82:18 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 4.03 (s, 6H), 7.42 (d, 2H,  $J = 2.7$  Hz), 7.50 – 7.53 (m, 2H), 8.05 (d, 2H,  $J = 9.4$  Hz); IR (KBr)  $\nu_{\text{max}}$ : 2920, 1635, 1277 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 241.4.

**2,7-Bis-methylsulfanyl-phenazine<sup>3b</sup> (entry 14, Table 1):**- Yellow solid; mp: 211-213 °C; TLC (Hexane:EtOAc, 90:10 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.69 (s, 6H), 7.65 (dd, 2H,  $J = 2.1$  Hz, 9.1 Hz), 7.78 (d, 2H,  $J = 2.1$  Hz), 8.03 (d, 2H,  $J = 9.1$  Hz); IR (KBr)  $\nu_{\text{max}}$ : 2919, 2850, 1733, 1616, 1455, 1277, 1261, 1048 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 273.4.

### Azoarenes:

**Di-*p*-tolyl-diazene<sup>2</sup> (entry 4, Table 1):**- Red solid; mp: 140-142 °C; TLC (Hexane:EtOAc, 95:5 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.46 (s, 6H), 7.33 (d, 4H,  $J = 8.3$  Hz), 7.84 (d, 4H,  $J = 8.3$  Hz); IR (KBr)  $\nu_{\text{max}}$ : 2972, 1738, 1366, 1227, 1215, 752 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 211.4.

**Bis-(4-benzyloxy-phenyl)-diazene<sup>3b</sup> (entry 6, Table 1):**- Light orange solid; mp: 177-179 °C; TLC (Hexane:EtOAc, 96:4 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 5.18 (s, 4H), 7.09 – 7.12 (m, 4H), 7.37 – 7.50 (m, 10H), 7.89 – 7.91 (m, 4H); IR (KBr)  $\nu_{\text{max}}$ : 2917, 2858, 1602, 1451, 1245, 1017, 840, 730 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 395.5.

**Bis-(3,4,5-trimethoxy-phenyl)-diazene<sup>3b</sup> (entry 8, Table 1):**- Orange solid; mp: 207-209 °C; TLC (Hexane:EtOAc, 90:10 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 3.96 (s, 6H), 4.00 (s, 12H), 7.27 (s, 4H); IR (KBr)  $\nu_{\max}$ : 2929, 2849, 1597, 1277, 1261, 1048 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 363.4.

**Bis-(4-methoxy-phenyl)-diazene<sup>2</sup> (entry 10, Table 1):**- Orange solid; mp: 158-160 °C; TLC (Hexane:EtOAc, 92:8 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 3.91 (s, 6H), 7.02 – 7.04 (m, 4H), 7.90 – 7.92 (m, 4H); IR (KBr)  $\nu_{\max}$ : 2978, 1625, 1277 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 243.4.

**Bis-(4-fluorophenyl)diazene<sup>2</sup> (entry 12, Table 1 & entry 1, Table 2):**- Red solid; mp: 77-79 °C; TLC (Hexane:EtOAc, 94:6 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.19 – 7.25 (m, 4H), 7.93 – 7.98 (m, 4H); IR (KBr)  $\nu_{\max}$ : 2923, 1477, 1273, 1250 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 219.5.

**Bis-(4-methylsulfanyl-phenyl)-diazene<sup>3b</sup> (entry 14, Table 1):**- Red solid; mp: 172-174 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.58 (s, 6H), 7.35 – 7.38 (m, 4H), 7.86 – 7.88 (m, 4H); IR (KBr)  $\nu_{\max}$ : 2919, 2853, 1586, 1559, 1431, 1403, 1083 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 275.5.

**(E)-1,2-dim-tolyldiazene<sup>2</sup> (entry 16, Table 1 & entry 6, Table 2):**- Red solid; mp: 136-139 °C; TLC (Hexane:EtOAc, 97:3 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.50 (s, 6H), 7.33 (d, 2H,  $J = 7.5$  Hz), 7.45 (t, 2H,  $J = 7.6$  Hz), 7.78 (d, 4H,  $J = 6.3$  Hz); IR (KBr)  $\nu_{\max}$ : 2922, 1478, 1277, 1266 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 211.6.

**(E)-1,2-Bis(3-methoxyphenyl)diazene<sup>5</sup> (entry 18, Table 1 & entry 7, Table 2):**- Red solid; mp: 72-74 °C; TLC (Hexane:EtOAc, 92:8 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 3.93 (s, 6H), 7.09 (d, 2H,  $J = 2.5$  Hz), 7.44 – 7.50 (m, 4H), 7.59 – 7.61 (m, 2H); IR (KBr)  $\nu_{\max}$ : 2921, 1479, 1279, 1265 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 243.3.

**(E)-1,2-Bis(3-fluorophenyl)diazene<sup>6</sup> (entry 20, Table 1 & entry 4, Table 2):**- Red solid; mp: 77-79 °C; TLC (Hexane:EtOAc, 94:6 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.10 – 7.17 (m, 2H), 7.39 – 7.44 (m, 2H), 7.50 – 7.54 (m, 2H), 7.68 (d, 2H,  $J = 7.9$  Hz); IR (KBr)  $\nu_{\max}$ : 2925, 1478, 1275, 1251 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 219.3.

**Di-naphthalen-2-yl-diazene<sup>7</sup> (entry 22, Table 1):**- Orange solid; mp: 195-197 °C; TLC (Hexane:EtOAc, 97:3 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.59 – 7.62 (m, 4H), 7.93 – 7.99 (m, 4H), 8.06 – 8.08 (m, 2H), 8.09 – 8.18 (m, 2H), 8.54 (d, 2H,  $J = 1.4$  Hz); IR (KBr)  $\nu_{\max}$ : 2928, 2859, 1617, 1403, 1259, 1050 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 283.4.

**Bis-(4-chloro-phenyl)-diazene<sup>2</sup> (entry 2, Table 2):**- Orange solid; mp: 185-187 °C; TLC (Hexane:EtOAc, 97:3 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.49 – 7.52 (m, 4H), 7.86 – 7.89 (m, 4H); IR (KBr)  $\nu_{\max}$ : 2924, 1275, 1260, 1084, 750 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 252.3.

**Bis-(4-bromo-phenyl)-diazene<sup>2</sup> (entry 3, Table 2):**- Orange solid; mp: 205-207 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.63 – 7.67 (m, 4H), 7.77 – 7.81 (m, 4H); IR (KBr)  $\nu_{\max}$ : 2920, 1273, 1260, 1089, 750 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 341.2.

**(E)-1,2-Bis-(3-chlorophenyl)diazene<sup>8</sup> (entry 5, Table 2):**- Yellow solid; mp: 99-101 °C; TLC (Hexane:EtOAc, 97:3 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.47 – 7.50 (m, 4H), 7.83 – 7.87 (m, 2H), 7.91 – 7.92 (m, 2H); IR (KBr)  $\nu_{\max}$ : 2919, 1471, 1276, 1261 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 252.3.

**(E)-1,2-Di-*o*-tolylidiazene<sup>8</sup> (entry 8, Table 2):**- Red solid; mp: 52-54 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.74 (s, 6H), 7.24 – 7.28 (m, 2H), 7.33 – 7.37 (m, 4H), 7.61 – 7.63 (m, 2H); IR (KBr)  $\nu_{\max}$ : 2922, 1587, 1487, 1275, 1241, 1156 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 211.1.

**(E)-1,2-Bis-(2-methoxyphenyl)diazene<sup>7</sup> (entry 9, Table 2):**- Red solid; mp: 152-154 °C; TLC (Hexane:EtOAc, 94:6 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 4.01 (s, 6H), 7.00 (dt, 2H,  $J = 1.3$  Hz, 8.1 Hz), 7.07 (d, 2H,  $J = 8.2$  Hz), 7.38 – 7.44 (m, 2H), 7.63 (dd, 2H,  $J = 1.3$  Hz, 8.1 Hz); IR (KBr)  $\nu_{\max}$ : 2922, 1589, 1486, 1276, 1242, 1157, 1023 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 243.1.

**(E)-1,2-Bis-(2-fluorophenyl)diazene<sup>6</sup> (entry 10, Table 2):**- Red solid; mp: 102-104 °C; TLC (Hexane:EtOAc, 97:3 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.20 – 7.29 (m, 4H), 7.44 – 7.50 (m, 2H), 7.79 (dt, 2H,  $J = 1.7$  Hz, 7.8 Hz); IR (KBr)  $\nu_{\max}$ : 2923, 1589, 1484, 1263, 1217, 1111 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 219.3.

**(E)-1,2-Bis-(2-chlorophenyl)diazene<sup>9</sup> (entry 11, Table 2):**- Red solid; mp: 114-116 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.40 (dt, 2H,  $J = 1.5$  Hz, 8.0 Hz), 7.45 (dt, 2H,  $J = 1.7$  Hz, 7.8 Hz), 7.60 (dd, 2H,  $J = 1.4$  Hz, 8.0 Hz), 7.80 (dd, 2H,  $J = 1.8$  Hz, 7.9 Hz); IR (KBr)  $\nu_{\max}$ : 2919, 1589, 1470, 1274, 1260 cm<sup>-1</sup>; MS (ESI) (M)<sup>+</sup> = 251.09.

**(E)-1,2-Bis-(2-bromophenyl)diazene<sup>10</sup> (entry 12, Table 2):**- Red solid; mp: 127-129 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.37 (dt, 2H,  $J = 1.8$  Hz, 7.8 Hz), 7.44 (dt, 2H,  $J = 1.3$  Hz, 7.4 Hz), 7.78 – 7.81 (m, 4H); IR (KBr)  $\nu_{\max}$ : 3006, 1582, 1461, 1275, 1260 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 340.9.

**(E)-1,2-Bis-(2-iodophenyl)diazene<sup>11</sup> (entry 13, Table 2):**- Red solid; mp: 143-145 °C; TLC (Hexane:EtOAc, 99:1 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.19 (dt, 2H,  $J = 1.6$  Hz, 7.6 Hz), 7.46 (dt, 2H,  $J = 1.2$  Hz, 8.1 Hz), 7.76 (dd, 2H,  $J = 1.6$  Hz, 8.1 Hz), 8.04 (dd, 2H,  $J = 1.2$  Hz, 8.0 Hz); IR (KBr)  $\nu_{\max}$ : 2917, 1472, 1275, 1260 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 434.9.

**(E)-1,2-Bis-(3-chloro-4-fluorophenyl)diazene (entry 14, Table 2):**- Yellow solid; mp: 106-108 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.21 (t, 2H,  $J = 8.6$  Hz), 7.73 – 7.77 (m, 2H), 7.88 (dd, 2H,  $J = 2.4$  Hz, 6.9 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 116.9, 117.1, 122.2, 122.4, 124.1, 124.3, 124.0, 148.7, 148.7, 158.6, 161.1; IR (KBr)  $\nu_{\max}$ : 2919, 1476, 1270, 1261, 1110 cm<sup>-1</sup>; HRMS (ESI) (M + H)<sup>+</sup> Calcd. for C<sub>12</sub>H<sub>7</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>, 286.9954; found 286.9947.

**(E)-1,2-Bis-(2,6-dimethylphenyl)diazene<sup>10</sup> (entry 15, Table 2):**- Red solid; mp: 50-52 °C; TLC (Hexane:EtOAc, 98:2 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.32 (s, 12H), 7.04 – 7.06 (m, 6H); IR (KBr)  $\nu_{\max}$ : 2959, 2925, 1727, 1465, 1273, 1122, 1072, 770 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 239.4.

**(E)-1,2-Bis-(2,6-diisopropylphenyl)diazene<sup>12</sup> (entry 16, Table 2):**- Red solid; mp: 157-159 °C; TLC (Hexane:EtOAc, 99:1 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 1.22 – 1.24 (m, 24H), 3.25 – 3.32 (m, 4H), 7.31 – 7.37 (m, 6H); IR (KBr)  $\nu_{\max}$ : 2923, 1610, 1453, 1161, 1049 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 351.6.

**Di-naphthalen-1-yl-diazene<sup>9</sup> (entry 17, Table 2):**- Orange solid; mp: 186-188 °C; TLC (Hexane:EtOAc, 99:1 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.61 – 7.72 (m, 6H), 7.97 – 8.05 (m, 6H), 9.08 (d, 2H,  $J = 8.4$  Hz); IR (KBr)  $\nu_{\max}$ : 2927, 2855, 1617, 1403, 1262, 1049 cm<sup>-1</sup>; MS (ESI) (M + H)<sup>+</sup> = 283.5.

**(E)-9-Ethyl-2-((9-ethyl-9H-carbazol-3-yl)diazenyl)-9H-carbazole (entry 18, Table 2):**- Red solid; mp: 195-198 °C; TLC (Hexane:EtOAc, 92:8 v/v):  $R_f \approx 0.5$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 1.53 (t, 6H,  $J = 7.2$  Hz), 4.46 (q, 4H,  $J = 7.2$  Hz), 7.33 (t, 2H,  $J = 7.4$  Hz), 7.48 (d, 2H,  $J = 8.1$  Hz), 7.56 (d, 4H,  $J = 8.6$  Hz), 8.22 - 8.26 (m, 4H), 8.78 (d, 2H,  $J = 1.7$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 13.9, 37.9, 108.6, 108.9, 116.1, 119.6, 120.8, 120.9, 123.4, 123.7, 126.1, 140.7, 141.3, 146.6; IR (KBr)  $\nu_{\max}$ : 2917, 1472, 1278, 1260, 1113 cm<sup>-1</sup>; HRMS (ESI) (M + Na)<sup>+</sup> Calcd. for C<sub>28</sub>H<sub>24</sub>N<sub>4</sub>Na 439.1899; found 439.1873.

## VIII. Recovery and recyclability study of NC:

### Typical procedure for the recovery and recyclability of Cu-Ag binary NC catalytic system for oxidative N-N coupling of **1a** to form **3a**:-

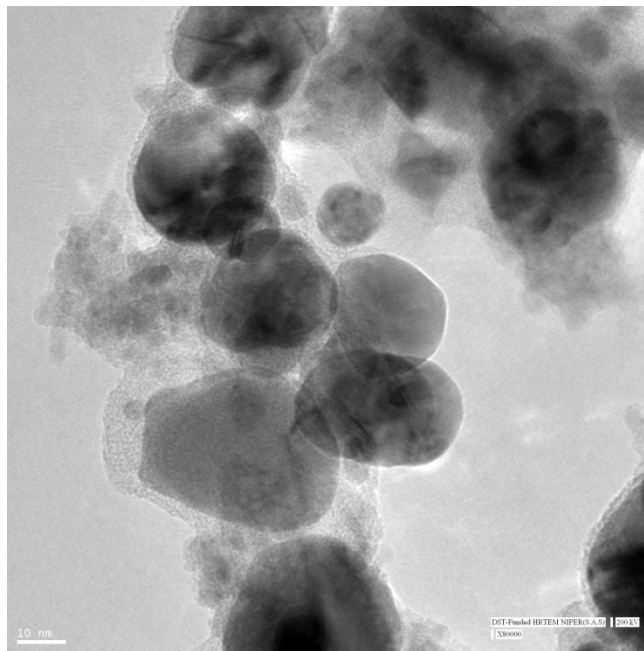
To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), [Cu(OAc)<sub>2</sub>·OH<sub>2</sub>] (5 mg, 0.025 mmol, 2.5 mol %) and Ag<sub>2</sub>CO<sub>3</sub> (689 mg, 2.5 mmol, 2.5 equiv) in DMF (2 mL) was added **1a** (186 mg, 0.18 mL, 2 mmol, 2 equiv) at 80 °C. Upon completion of the reaction (2 h, monitored by TLC), the reaction mixture was cooled to rt and was centrifuged (8000 RPM) for 10 min. DMF layer was decanted off and the remaining solid portions (contains the Cu-Ag NC) was washed with DM water (2 × 5 mL); kept in a vacuum oven for dryness (1 h) to obtain the recovered Cu-Ag NC. The recovered Cu-Ag NC was charged with DMF (2 mL), **1a** (2 mmol, 2 equiv), Ag<sub>2</sub>CO<sub>3</sub> (276 mg, 1 mmol, 1 equiv) and the mixture was magnetically stirred at 80 °C for 2 h to obtain **3a** in 82% yield after usual workup and purification. The fresh batches of reaction involving **1a** (2 mmol, 2 equiv) were repeated for four consecutive times with the recovered Cu-Ag NC after each fresh reaction to obtain the **3a** in 80, 77, 72, and 67% yields.

**Table VIII-A. Reusability of Cu-Ag binary NC system.<sup>a</sup>**

Entry	No. of Runs	Yield (%) <sup>b</sup>	
		<b>2a</b>	<b>3a</b>
1	Fresh	12	83
2	1 <sup>st</sup> reuse	10	82
3	2 <sup>nd</sup> reuse	10	80
4	3 <sup>rd</sup> reuse	12	77
5	4 <sup>th</sup> reuse	12	72
6	5 <sup>th</sup> reuse	trace	67

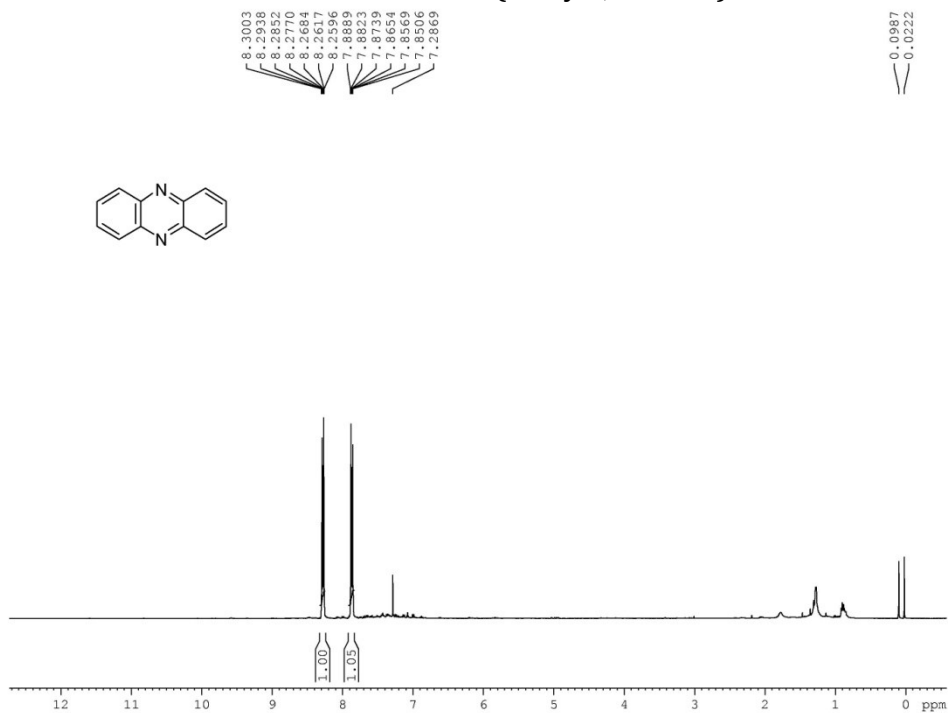
<sup>a</sup>**1a** (2 mmol, 2 equiv) was treated in DMF (2 mL) with the recovered catalyst and Ag<sub>2</sub>CO<sub>3</sub> (1 mmol, 1 equiv) for each cycle. <sup>b</sup>The isolated yield.

**Figure H. HRTEM image of Cu-Ag binary NC in the reaction mixture at 5<sup>th</sup> cycle.**  
Cu-Ag binary NC: (Cu particles size 15 nm – 25 nm and Ag particles size 40 nm – 50 nm)

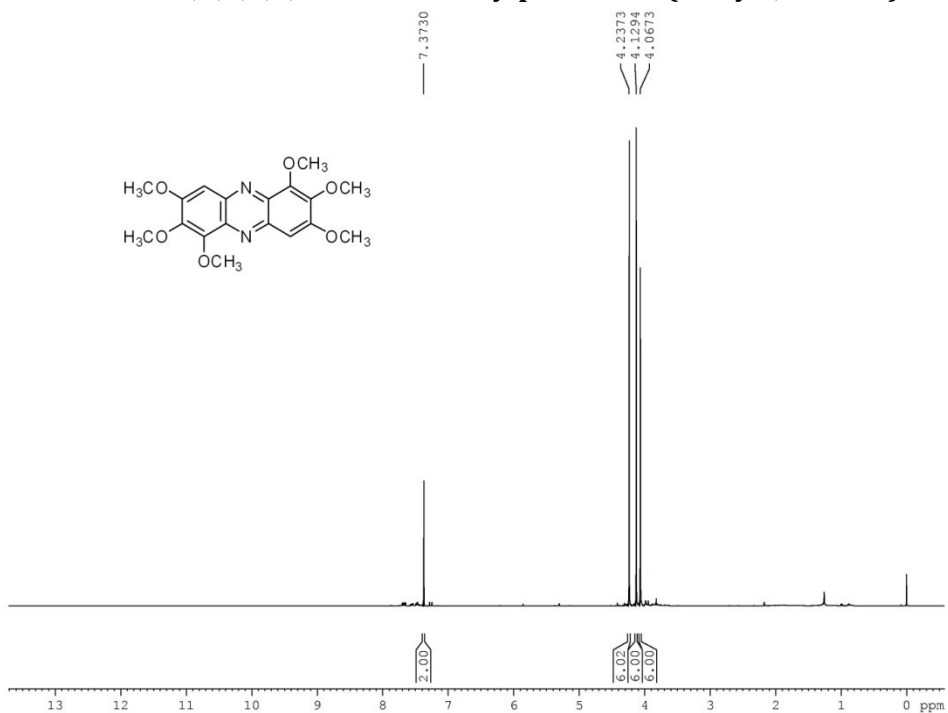


## IX. Scanned NMR Spectra:

### <sup>1</sup>H NMR of Phenazine (entry 2, Table 1):-

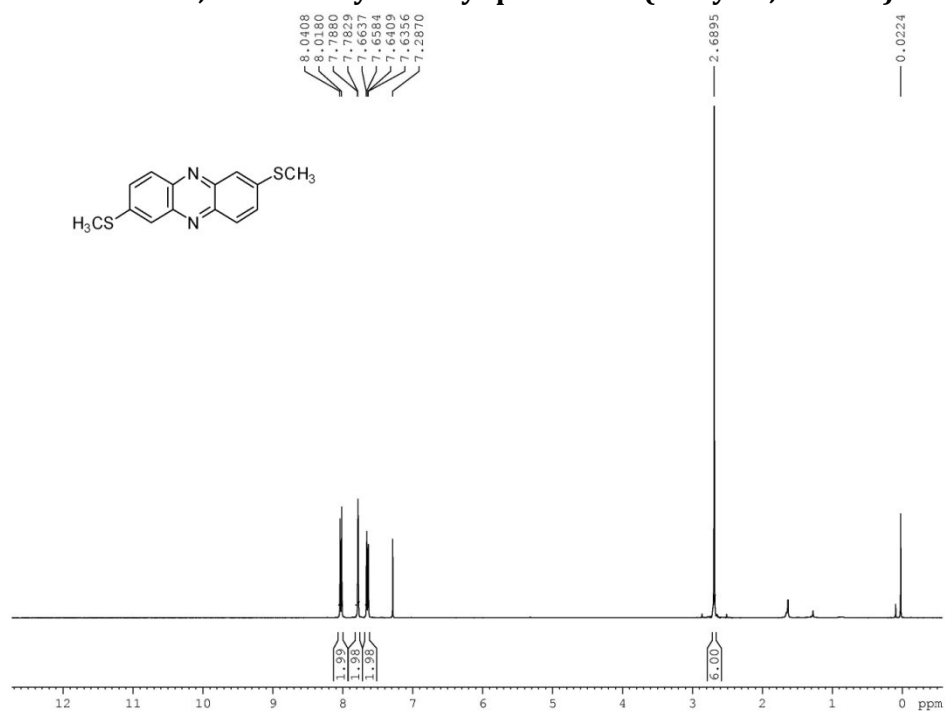


### <sup>1</sup>H NMR of 1,2,3,6,7,8-Hexamethoxy-phenazine (entry 8, Table 1):-

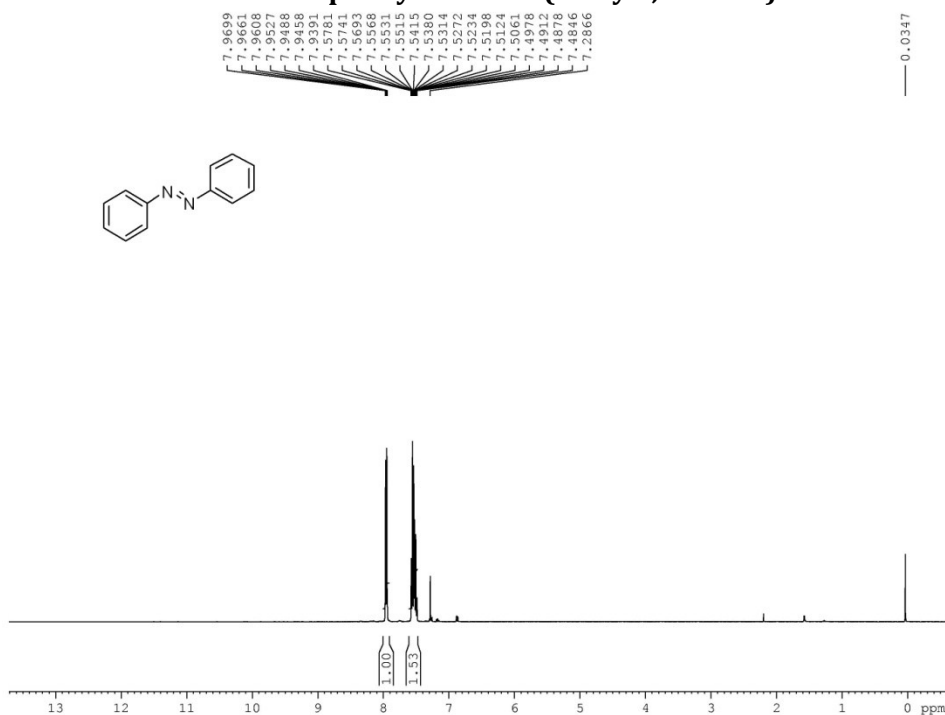




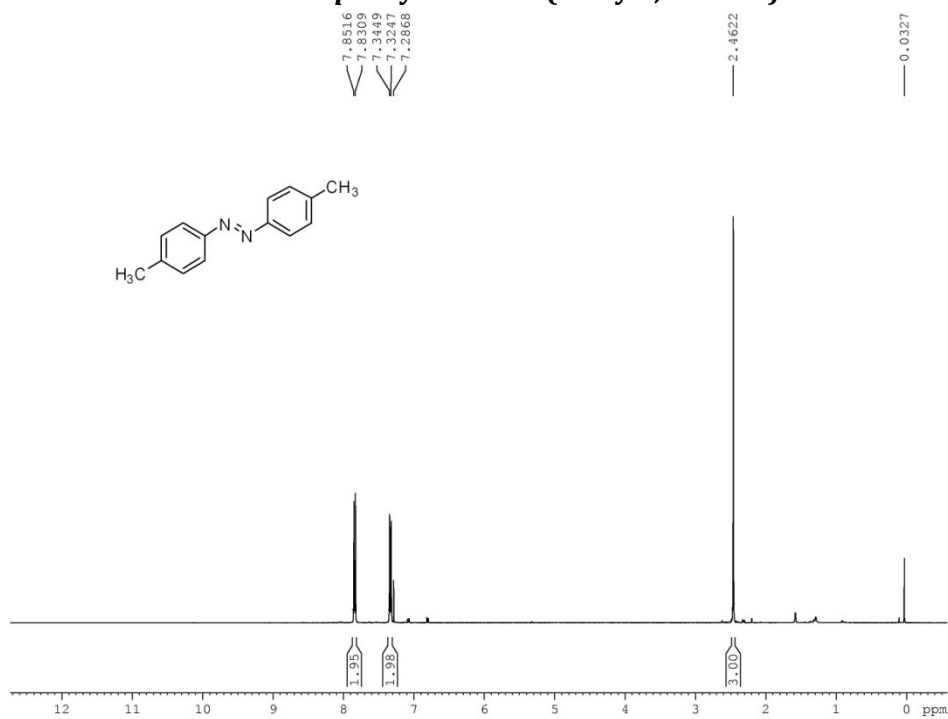
**<sup>1</sup>H NMR of 2,7-Bis-methylsulfanyl-phenazine (entry 14, Table 1):-**



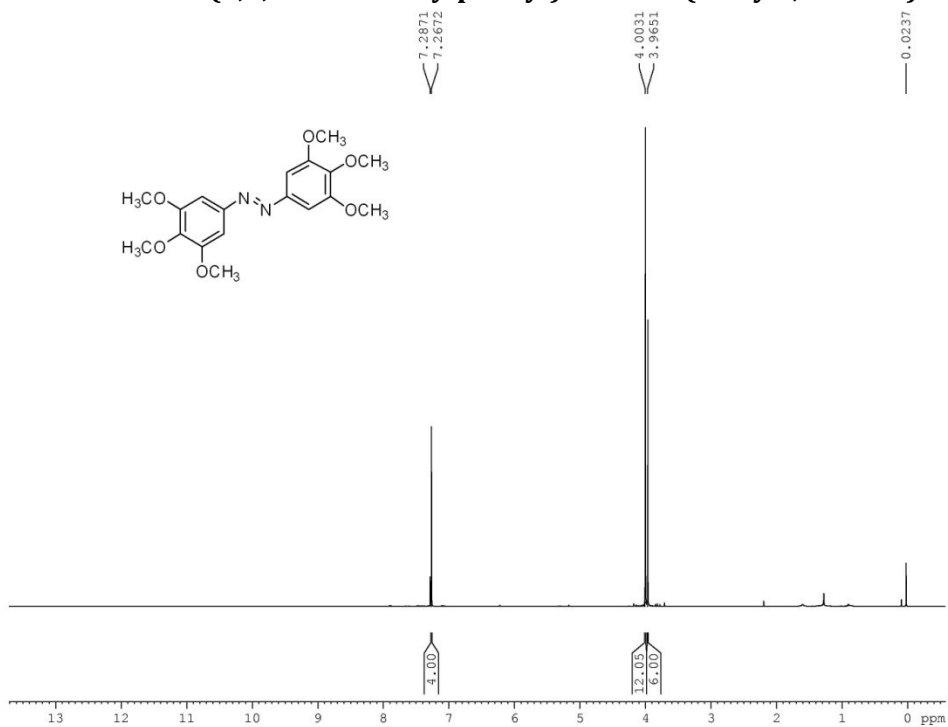
**<sup>1</sup>H NMR of Diphenyl-diazene (entry 2, Table 1):-**



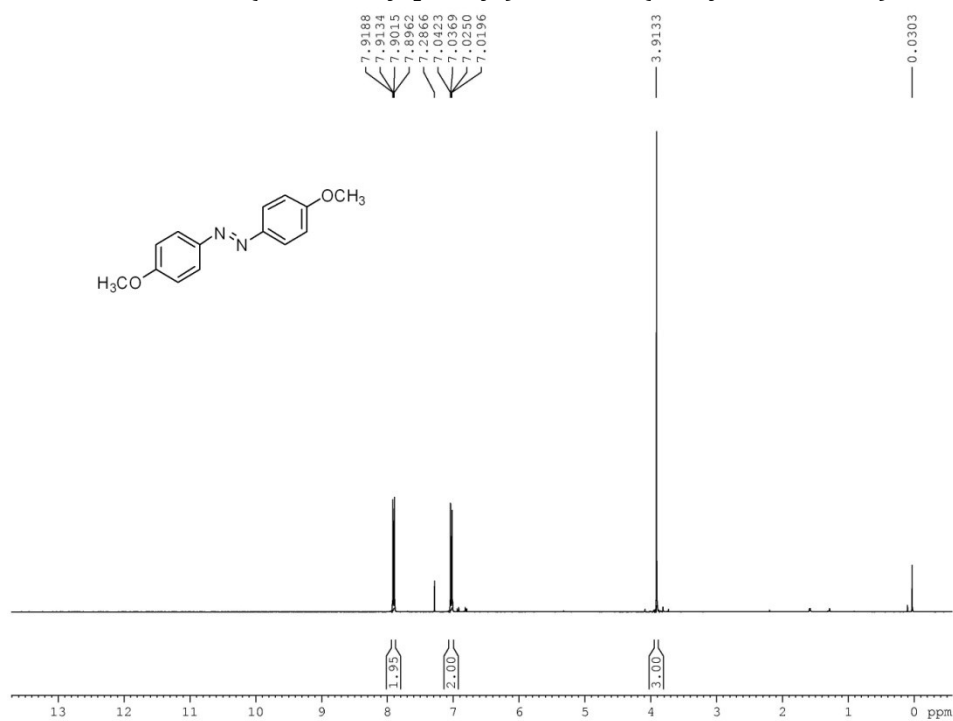
**<sup>1</sup>H NMR of Di-*p*-tolyl-diazene (entry 4, Table 1):-**



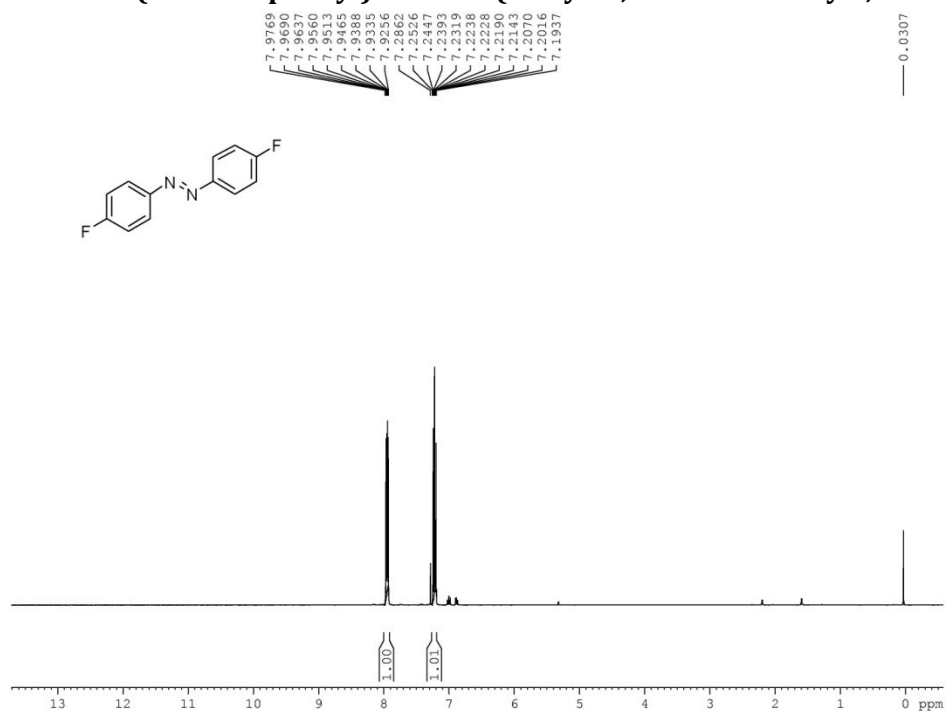
**<sup>1</sup>H NMR of Bis-(3,4,5-trimethoxy-phenyl)-diazene (entry 8, Table 1):-**



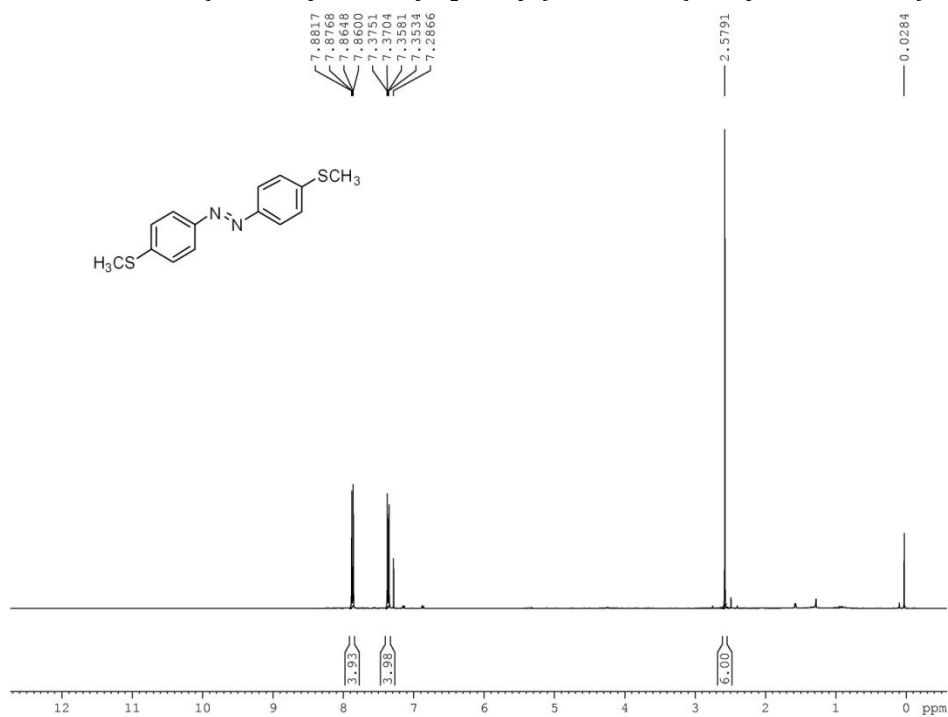
**<sup>1</sup>H NMR of Bis-(4-methoxy-phenyl)-diazene (entry 10, Table 1):-**



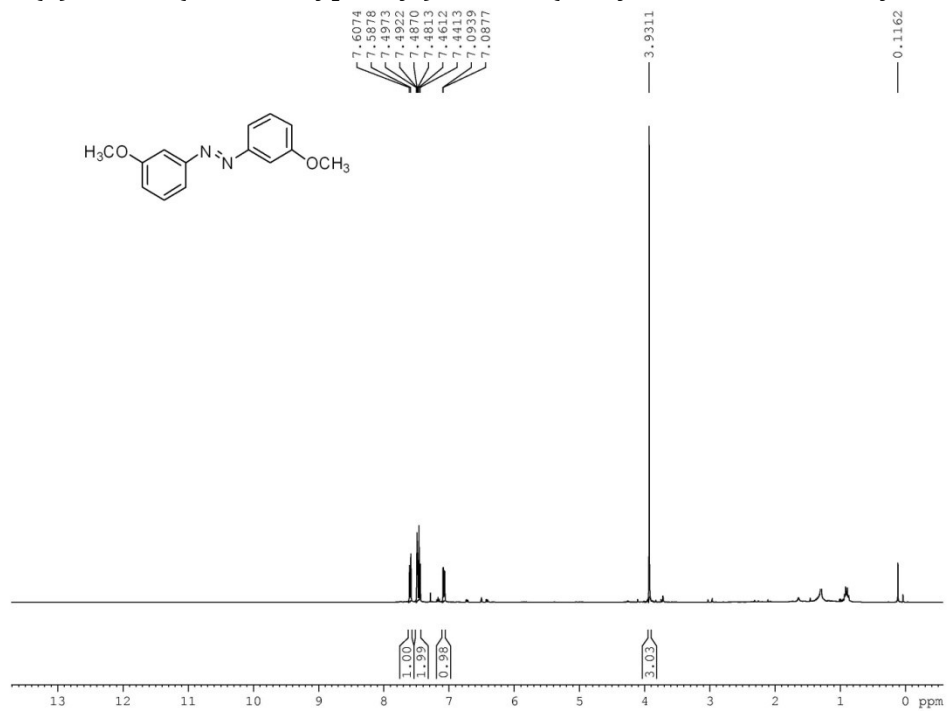
**<sup>1</sup>H NMR of Bis-(4-fluoro-phenyl)-diazene (entry 12, Table 1 & entry 1, Table 2):-**



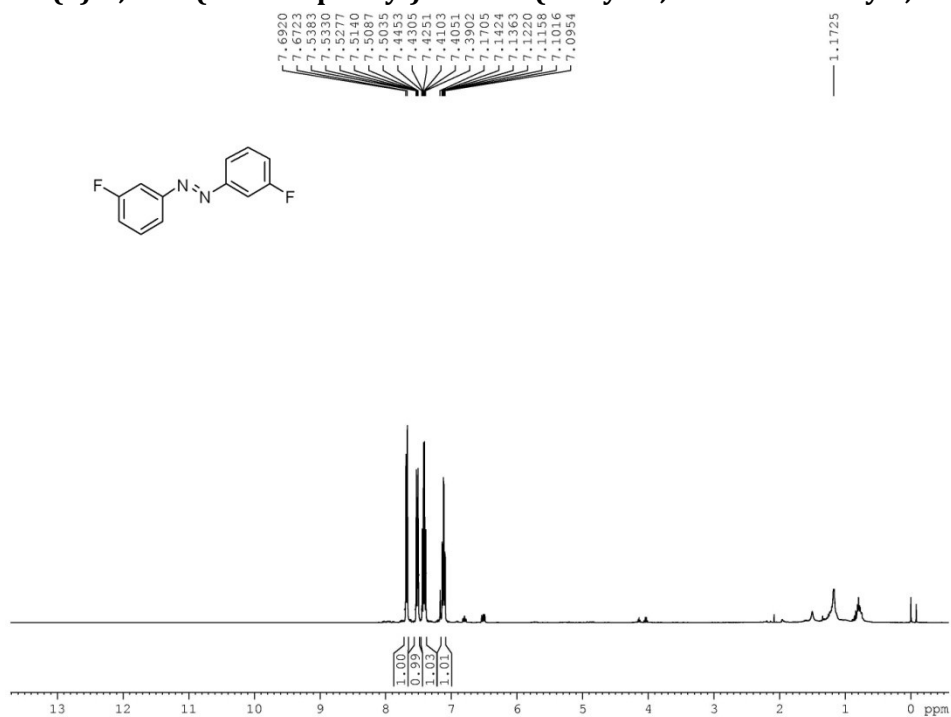
**<sup>1</sup>H NMR of Bis-(4-methylsulfonyl-phenyl)-diazene (entry 14, Table 1):-**



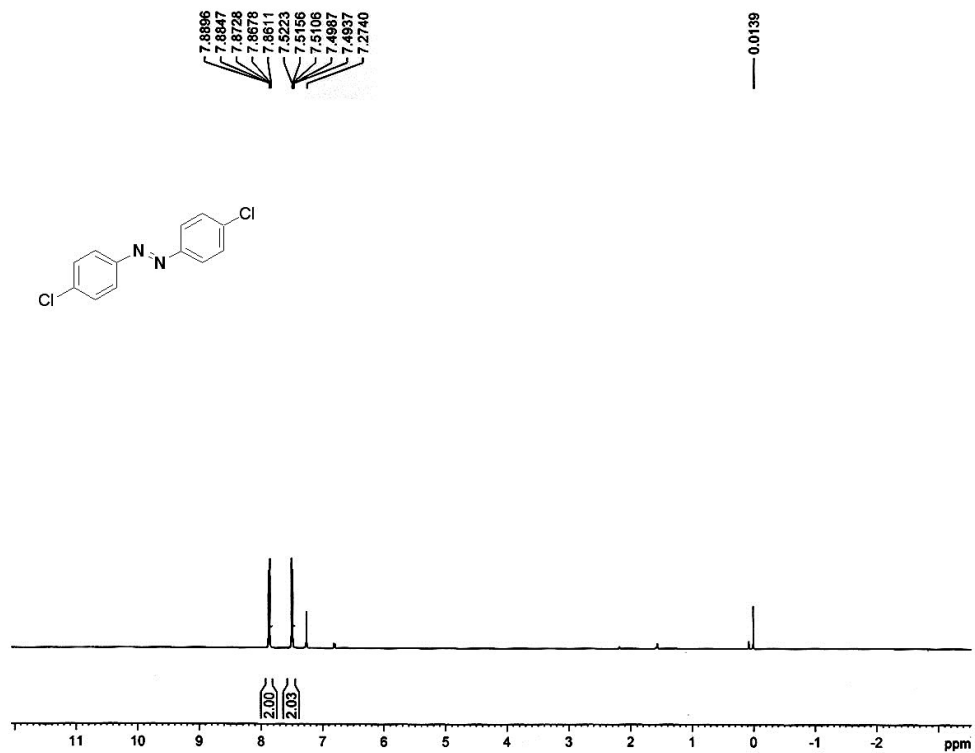
**<sup>1</sup>H NMR of (*E*)-1,2-Bis(3-methoxyphenyl)diazene (entry 18, Table 1 & entry 7, Table 2):-**



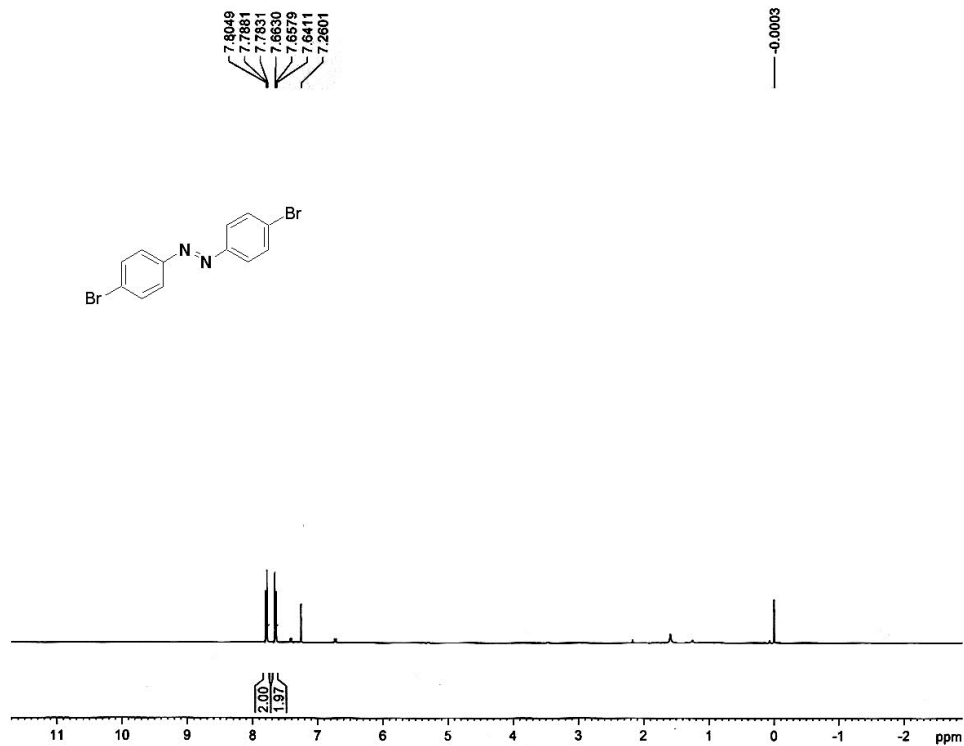
**<sup>1</sup>H NMR of (E)-1,2-Bis(3-fluorophenyl)diazene (entry 20, Table 1 & entry 4, Table 2):-**



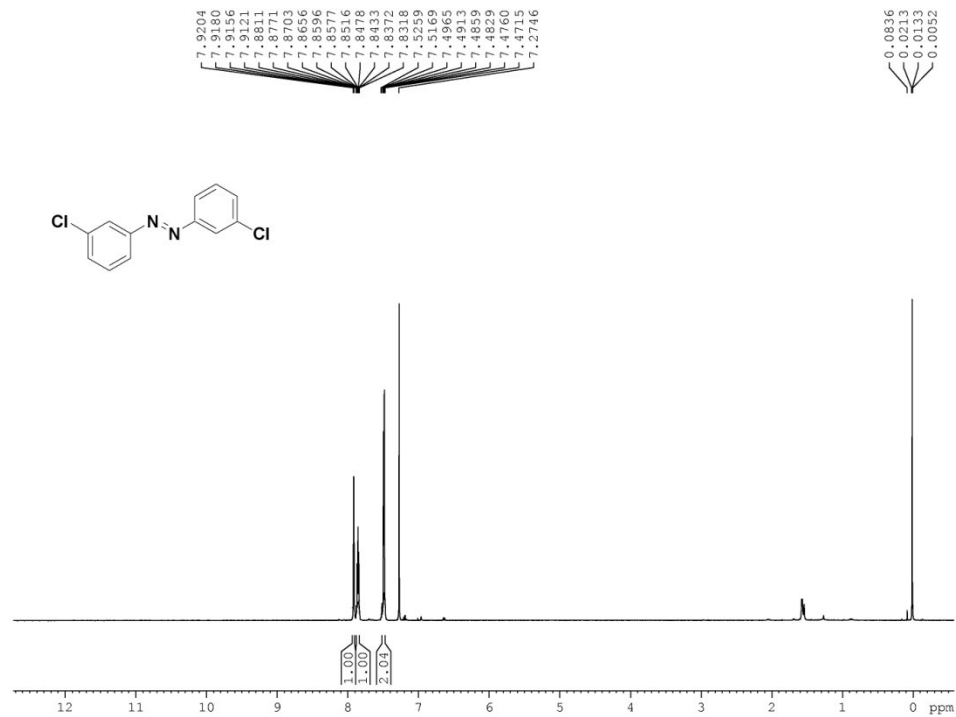
**<sup>1</sup>H NMR of Bis-(4-chloro-phenyl)-diazene (entry 2, Table 2):-**



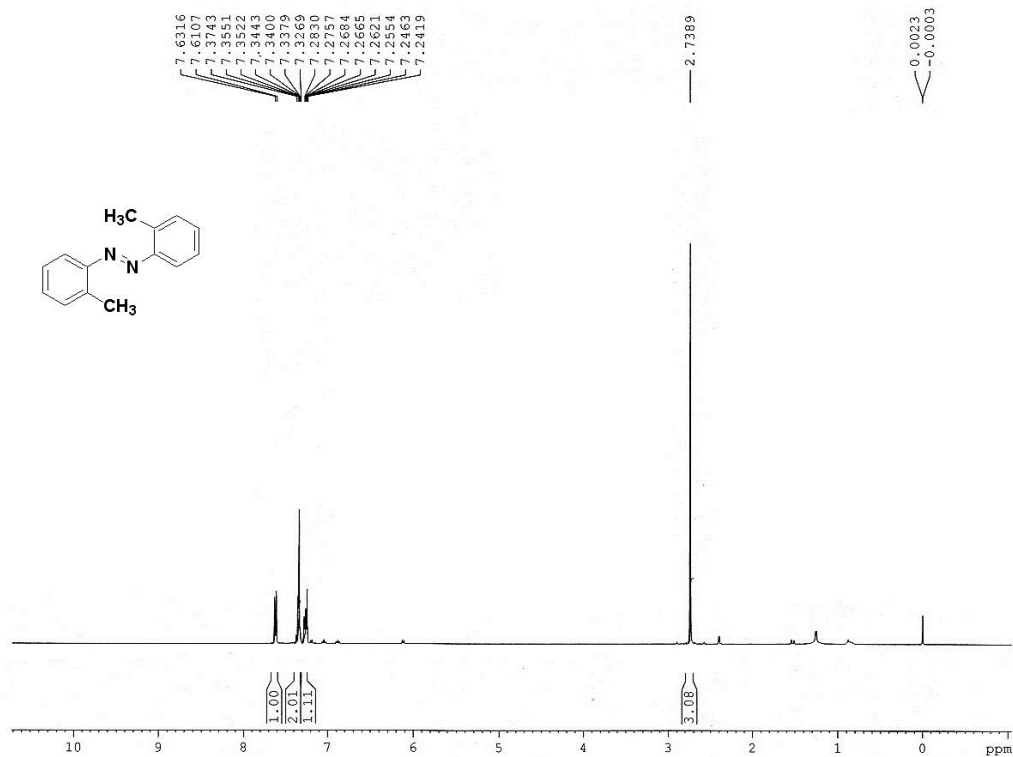
**<sup>1</sup>H NMR of Bis-(4-bromo-phenyl)-diazene (entry 3, Table 2):-**



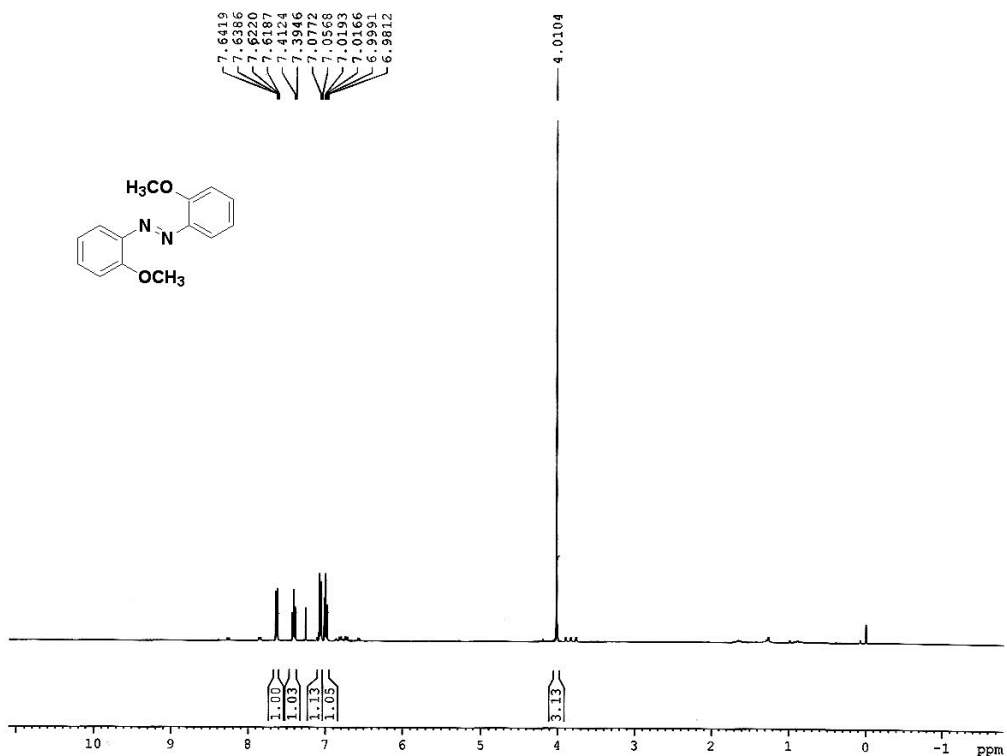
**<sup>1</sup>H NMR of (*E*)-1,2-Bis(3-chlorophenyl)diazene (entry 5, Table 2):-**



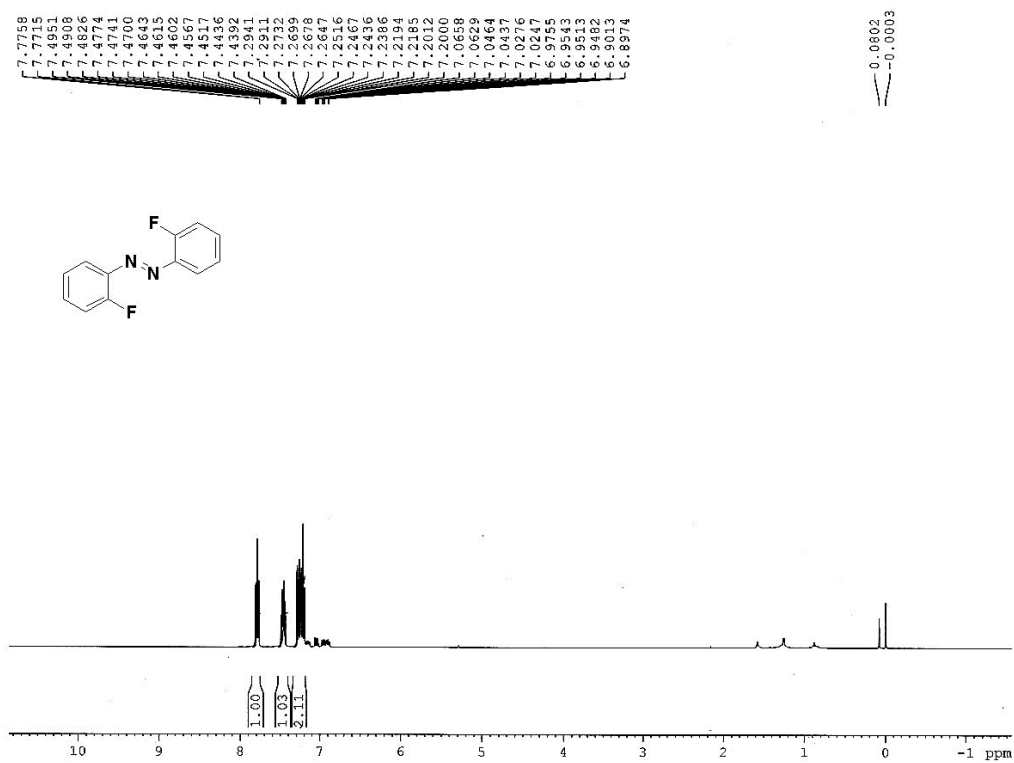
**<sup>1</sup>H NMR of (*E*)-1,2-Di-*o*-tolylidiazene (entry 8, Table 2):-**



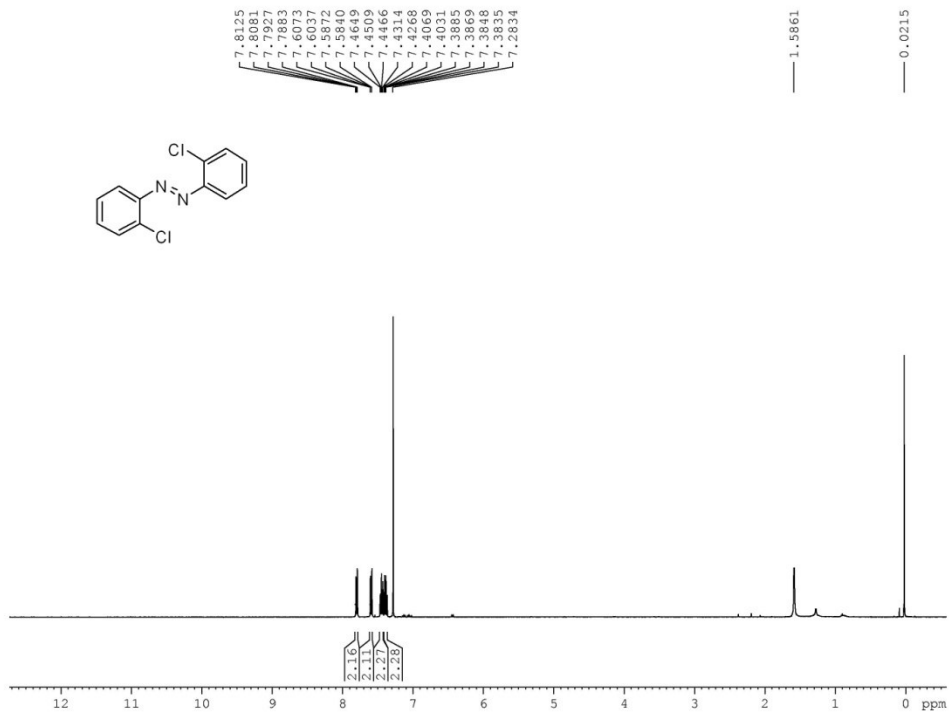
**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2-methoxyphenyl)diazene (entry 9, Table 2):-**



**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2-fluorophenyl)diazene (entry 10, Table 2):-**

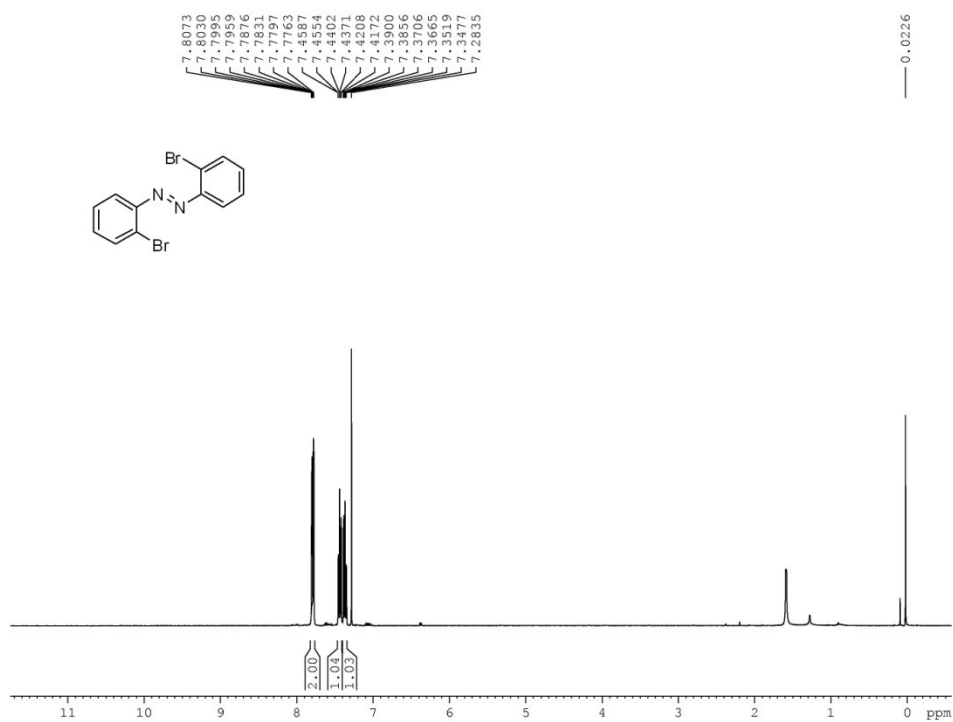


**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2-chlorophenyl)diazene (entry 11, Table 2):-**

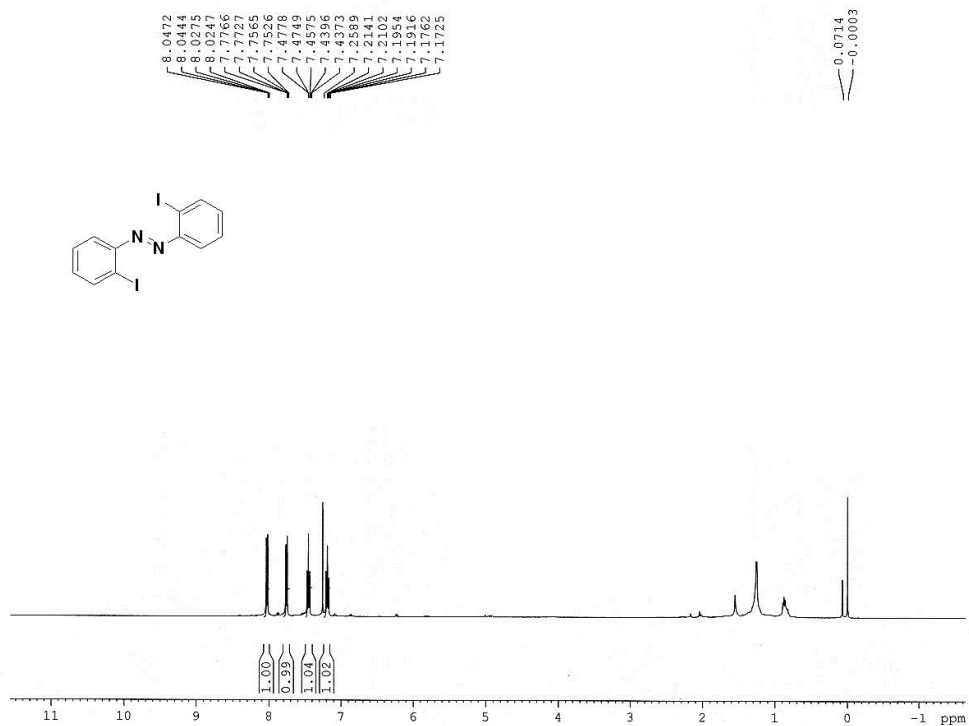




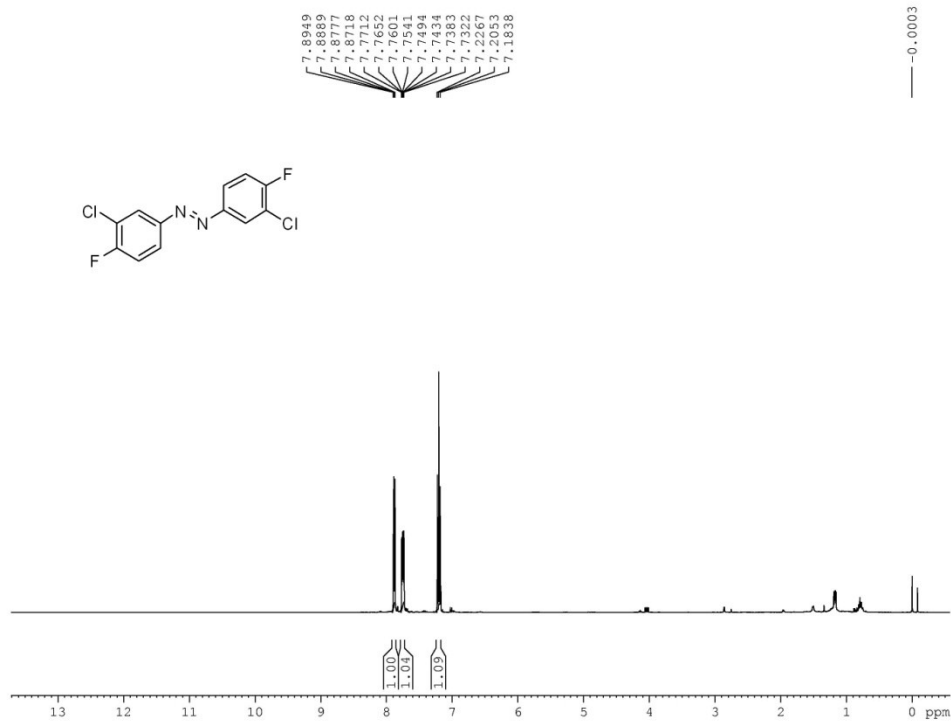
**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2-bromophenyl)diazene (entry 12, Table 2):-**



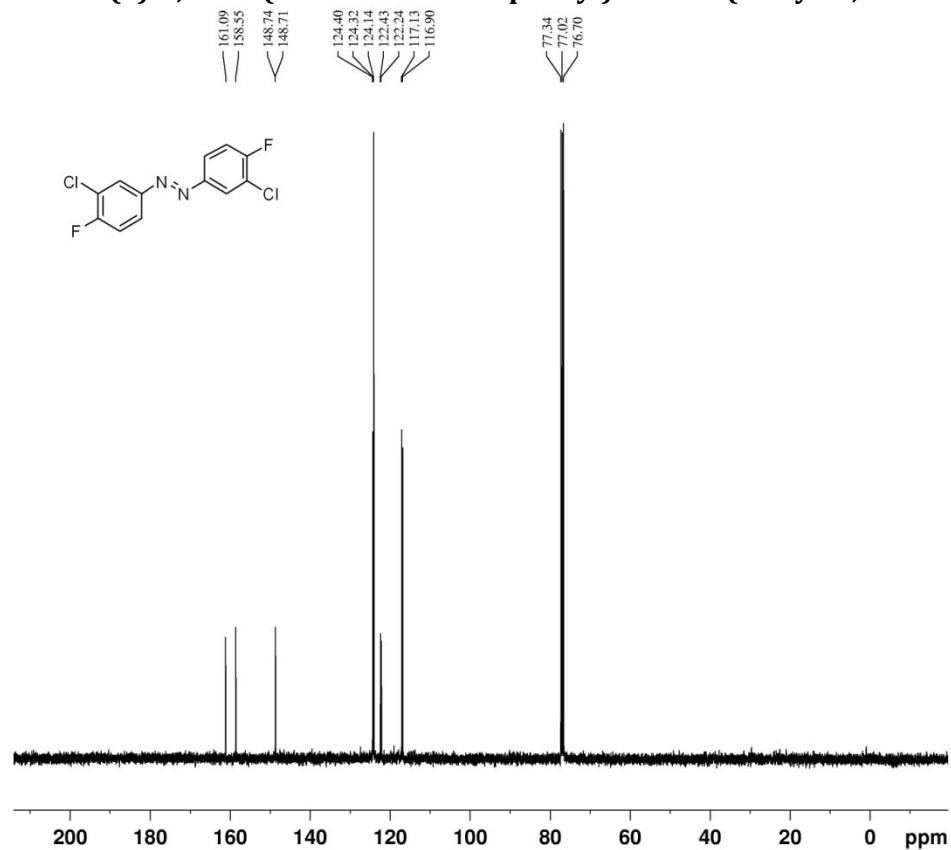
**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2-iodophenyl)diazene (entry 13, Table 2):-**



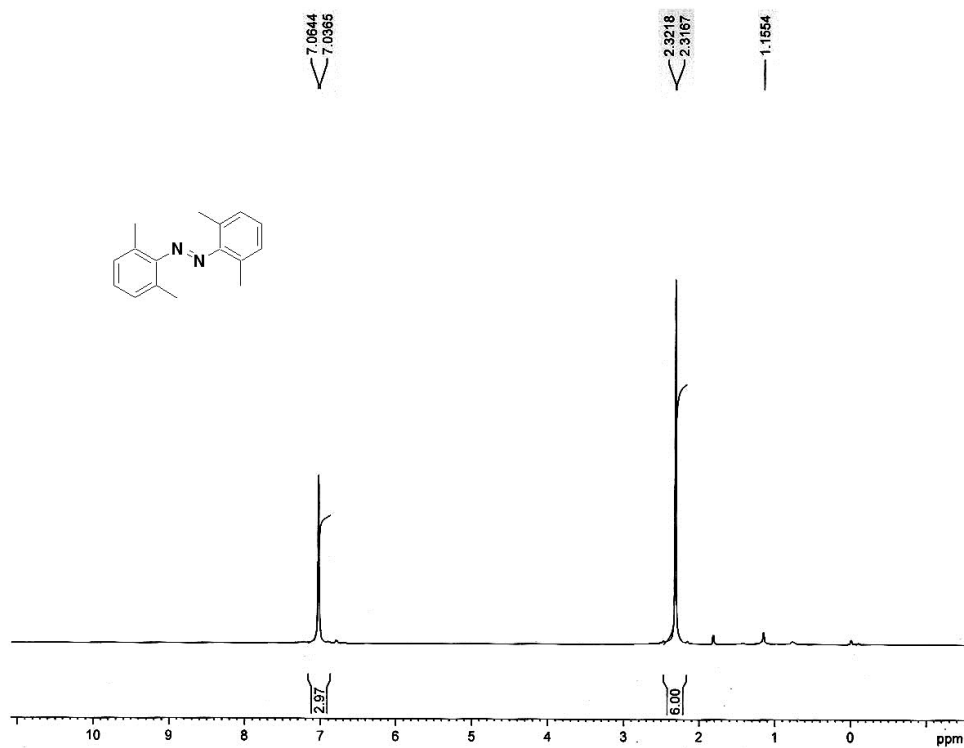
**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(3-chloro-4-fluorophenyl)diazene (entry 14, Table 2):-**



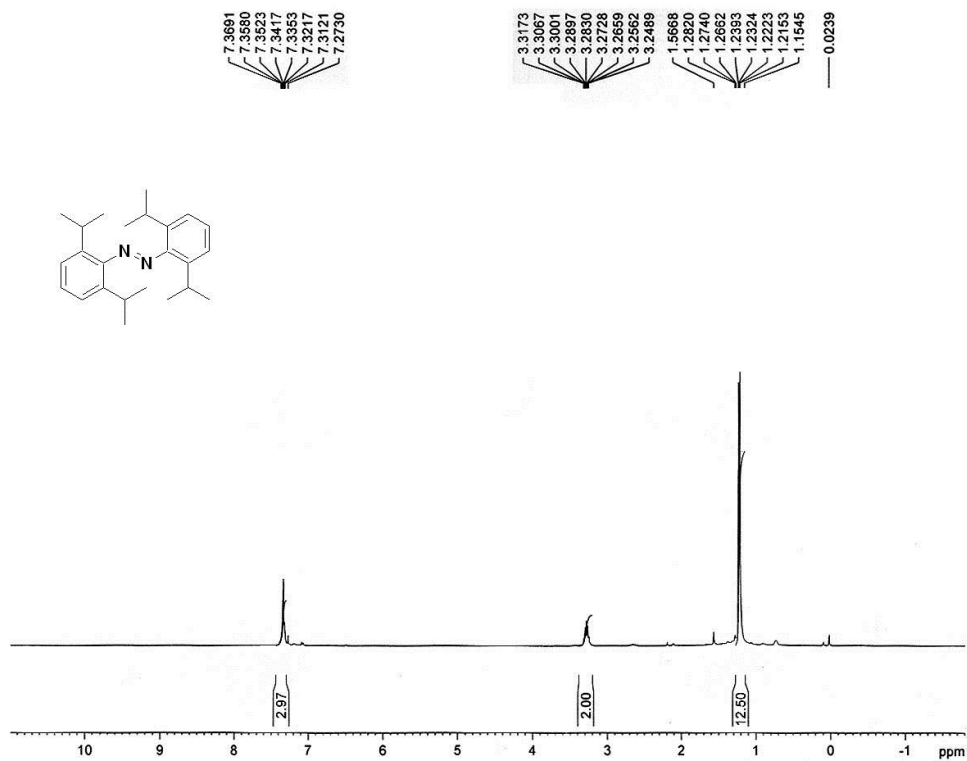
**<sup>13</sup>C NMR of (*E*)-1,2-Bis-(3-chloro-4-fluorophenyl)diazene (entry 14, Table 2):-**



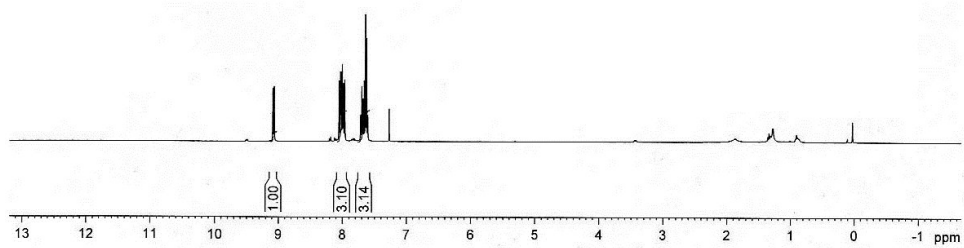
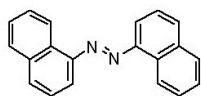
**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2,6-dimethylphenyl)diazene (entry 15, Table 2):-**



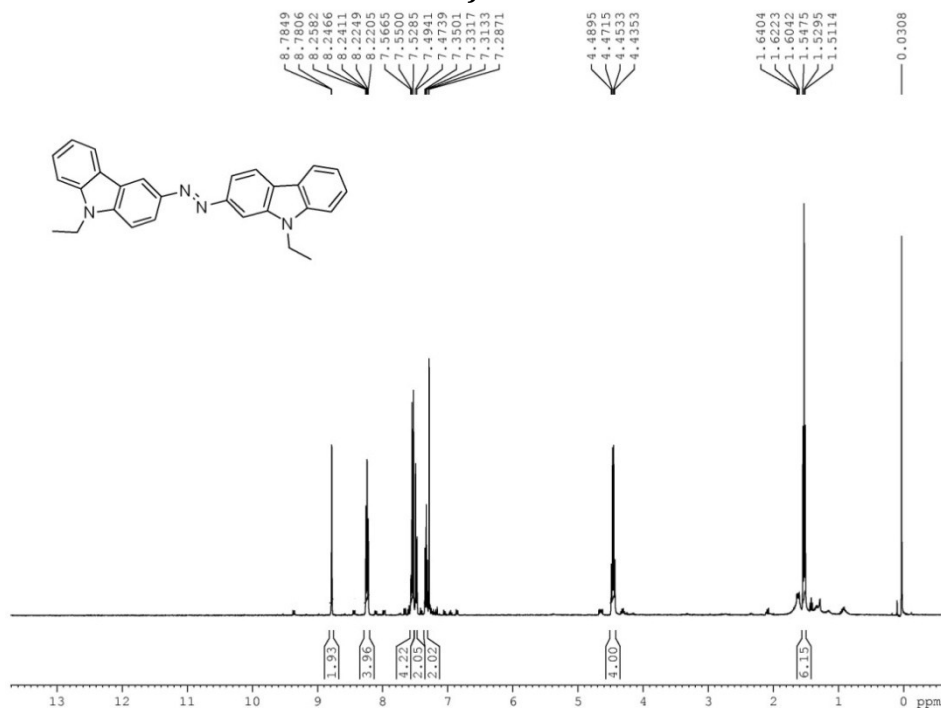
**<sup>1</sup>H NMR of (*E*)-1,2-Bis-(2,6-diisopropylphenyl)diazene (entry 16, Table 2):-**



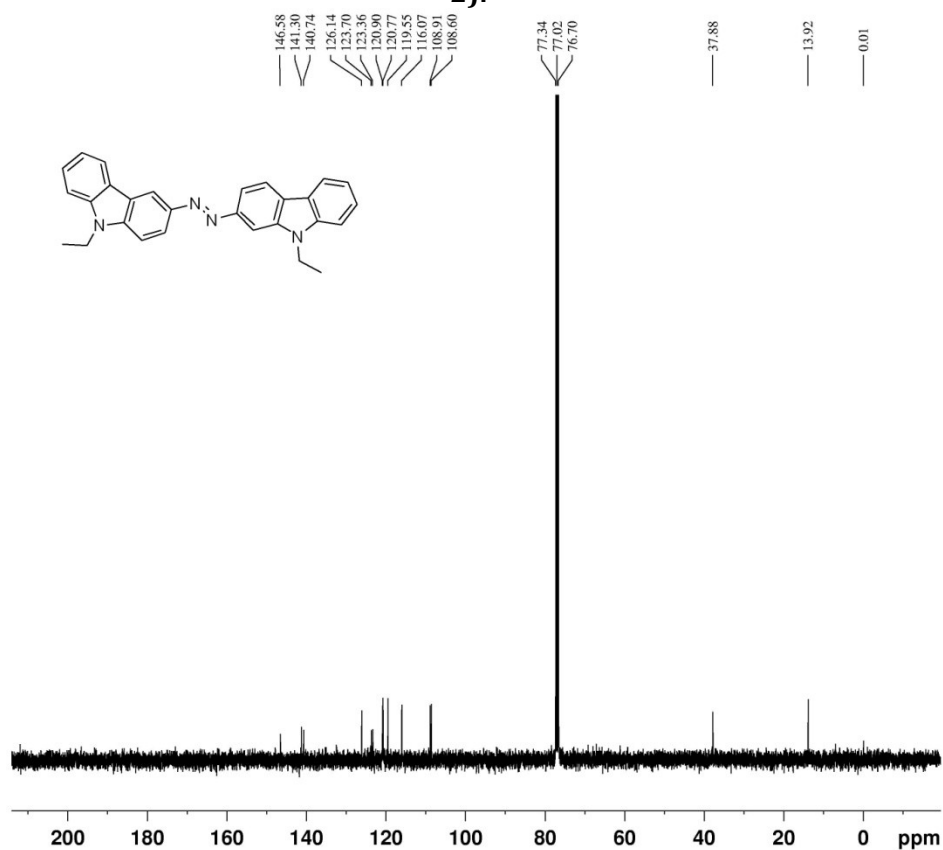
**<sup>1</sup>H NMR of Di-naphthalen-1-yl-diazenide (entry 17, Table 2):-**



**<sup>1</sup>H NMR of (*E*)-9-Ethyl-2-((9-ethyl-9H-carbazol-3-yl)diazenyl)-9H-carbazole (entry 18, Table 2):-**



**<sup>13</sup>C NMR of (*E*)-9-Ethyl-2-((9-ethyl-9H-carbazol-3-yl)diazenyl)-9H-carbazole (entry 18, Table 2):-**



## X. References:

1. (a) J. K. Laha, K. S. S. Tummalapalli and A. Gupta, *Eur. J. Org. Chem.*, 2014, 4773; (b) J. K. Laha, K. S. S. Tummalapalli and A. Gupta, *Org. Lett.*, 2014, **16**, 4392.
2. C. Zhang and N. Jiao, *Angew. Chem. Int. Ed.*, 2010, **49**, 6174.
3. (a) L. Yu, X. Zhou, D. Wu and H. Xiang, *J. Organometallic Chem.*, 2012, **705**, 75; (b) K. Seth, S. Raha Roy and A. K. Chakraborti, *Chem. Commun.*, 2016, **52**, 922.
4. J. D. Winkler, B. M. Twenter and T. Gendrineau, *Heterocycles*, 2012, **84**, 1345.
5. R. Thorwirth, F. Bernhardt, A. Stolle, B. Ondruschka and J. Asghari, *Chem. Eur. J.*, 2010, **16**, 13236.
6. A. V. Biradar, T. V. Kotbagi, M. K. Dongare and S. B. Umbarkar, *Tetrahedron Lett.*, 2008, **49**, 3616.
7. W. Lu and C. Xi, *Tetrahedron Lett.*, 2008, **49**, 4011.
8. Y. Zhu and Y. Shi, *Org. Lett.*, 2013, **15**, 1942.
9. G. R. Srinivasa, K. Abiraj and D. C. Gowda, *Tetrahedron Lett.*, 2003, **44**, 5835.
10. R. K. Sharma and Y. Monga, *Applied Catal. A: Gen.*, 2013, **454**, 1.
11. R. Thorwirth, F. Bernhardt, A. Stolle, B. Ondruschka and J. Asghari, *Chem. Eur. J.*, 2010, **16**, 13236.
12. M. I. Lipschutz and T. D. Tilley, *Chem. Commun.*, 2012, **48**, 7146.