Supporting Information

Synchronous Double C-N Bond Formation via C-H Activation as a Novel Synthetic Route to Phenazine

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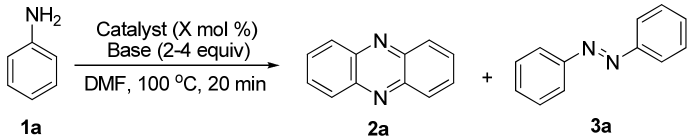
Table of Contents

I. The standardisation of various reaction parameters such as the effect of catalysts, oxidants, solvents, reaction temperature and time etc. on the self coupling of 1a to form 2a.

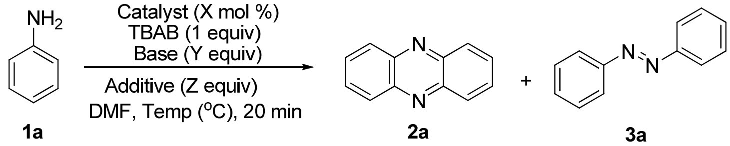
Table I-A. The effect of various Pd-compounds in the absence of stabilizer for self coupling of 1a to form 2a and 3a.[a]



Entry	Catalyst (X)	Base (equiv)	Yield (%)[b]	
			2a	**3a**
1	$[PdCl_2(PPh_3)_2]$ (10)	Ag_2CO_3 (4)	54	17
2	$[PdCl_2(PPh_3)_2]$ (5)	Ag_2CO_3 (4)	54	16
3	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (4)	52	16
4	$PdCl_2$ (1)	Ag_2CO_3 (4)	30	13
5	$Pd(OAc)_2$ (1)	Ag_2CO_3 (4)	31	11
6	$Pd(TFA)_2$ (1)	Ag_2CO_3 (4)	37	19
7	$Pd(Piv)_2$ (1)	Ag_2CO_3 (4)	22	trace
8	$Pd(acac)_2$ (1)	Ag_2CO_3 (4)	30	trace
9	$Pd(dba)_2$ (1)	Ag_2CO_3 (4)	17	trace
10	$Pd_2(dba)_3$ (1)	Ag_2CO_3 (4)	14	trace
11	$Pd(PPh_3)_4$ (1)	Ag_2CO_3 (4)	15	trace
12	Pd/C (1)	Ag_2CO_3 (4)	trace	trace
13	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	50	16
14	$[PdCl_2(PPh_3)_2]$ (1)	$Cu(OAc)_2{\cdot}H_2O$ (4)	0	0
15	$Pd(OAc)_2$ (1)	$Cu(OAc)_2{\cdot}H_2O$ (4)	0	0
16	$[PdCl_2(PPh_3)_2]$ (1)	$FeCl_3$ (4)	0	trace
17	$Pd(OAc)_2$ (1)	$FeCl_3$ (4)	0	trace

[a]Aniline **1a** (2 mmol, 2 equiv) was treated under various conditions in DMF (2 mL) at 100 °C for 20 min. [b]Isolated yield.

Table I-B. The effect of various Pd-based catalysts, bases, additives, and other reaction parameters on the self coupling of 1a to form 2a and 3a.[a]

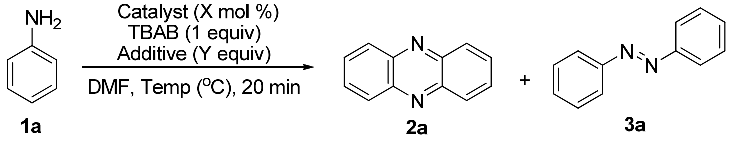


Entry	Catalyst (X)	Base (Y)	Additive (Z)	T (°C)	Yield (%)[b]	
					2a	**3a**
1	$Pd(OAc)_2$ (10)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	120	65	16
2	$Pd(OAc)_2$ (5)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	120	64	16
3	$Pd(OAc)_2$ (2.5)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	120	65	15

4	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	120	66	17
5	None	Cs_2CO_3 (2)	Ag_2CO_3 (2)	120	22	38
6	None	Cs_2CO_3 (4)	None	120	0	0
7	None	Cs_2CO_3 (4)	None	120	20	12[c]
8	None	Cs_2CO_3 (4)	None	120	20	10[d]
9	None	Cs_2CO_3 (4)	None	120	23	13[e]
10	$Pd(OAc)_2$ (1)	Cs_2CO_3 (1)	Ag_2CO_3 (2)	120	65	16
11	$Pd(OAc)_2$ (1)	Cs_2CO_3 (0.5)	Ag_2CO_3 (2)	120	64	18
12	$Pd(OAc)_2$ (1)	Cs_2CO_3 (0.5)	Ag_2CO_3 (1)	120	44	22
13	$Pd(OAc)_2$ (1)	Cs_2CO_3 (1)	Ag_2CO_3 (1)	120	43	23
14	$Pd(OAc)_2$ (1)	Cs_2CO_3 (1)	Ag_2CO_3 (0.5)	120	34	21
15	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	None	120	0	0
16	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	120	70	13
17	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (1)	Ag_2CO_3 (2)	120	66	14
18	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	40	10
19	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	AgOAc (2)	100	0	trace
20	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	AgOTf (2)	100	0	trace
21	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	$AgBF_4$ (2)	100	0	0
22	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	$AgNO_3$ (2)	100	0	trace
23	$PdCl_2$ (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	28	10
24	Na_2PdCl_4 (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	21	12
25	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	47	12
26	$Pd(acac)_2$ (1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	30	11
27	$[PdCl_2(PPh_3)_2]$ (0.5)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	41	15
28	$[PdCl_2(PPh_3)_2]$ (0.1)	Cs_2CO_3 (2)	Ag_2CO_3 (2)	100	21	12
29	$[PdCl_2(PPh_3)_2]$ (1)	K_2CO_3 (4)	None	100	0	0
30	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (4)	None	100	0	0

[a] **1a** (2 mmol, 2 equiv) was treated under various conditions in DMF (2 mL) for 20 min. [b] Isolated yield. [c] The reaction was performed for 2 h. [d] The reaction was performed for 2 h in the absence of TBAB. [e] The reaction was performed for 2 h under O_2 bubbling (10 psi).

Table I-C. The effect of various Pd-based catalysts, metal-based additives as the oxidant, and other reaction parameters on the self coupling of 1a to form 2a and 3a.[a]

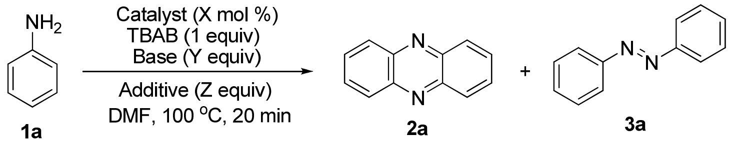


Entry	Catalyst (X)	Additive (Y)	Temp (°C)	Yield (%)[b]	
				2a	**3a**
1	$Pd(OAc)_2$ (1)	Ag_2CO_3 (2)	120	62	18
2	$Pd(OAc)_2$ (1)	Ag_2CO_3 (1)	120	17	23
3	$Pd(OAc)_2$ (1)	Ag_2CO_3 (0.5)	120	0	0
4	$Pd(OAc)_2$ (1)	None	100	0	0
5	$Pd(OAc)_2$ (1)	None	100	0	0[c]

6	$Pd(OAc)_2$ (1)	Ag_2CO_3 (3)	120	65	15
7	$Pd(OAc)_2$ (1)	Ag_2CO_3 (4)	120	71	10
8	$Pd(OAc)_2$ (1)	None	120	0	0[c]
9	$Pd(OAc)_2$ (1)	Ag_2CO_3 (4)	100	70	11
10	None	Ag_2CO_3 (4)	100	20	31
11	None	Ag_2CO_3 (4)	100	27	35[c]
12	None	Ag_2CO_3 (4)	100	28	37[d]
13	$Pd(OAc)_2$ (1)	Ag_2CO_3 (4)	80	45	19
14	$Pd(OAc)_2$ (1)	Ag_2CO_3 (4)	60	21	11
15	$Pd(OAc)_2$ (1)	AgOAc (4)	100	0	trace
16	$Pd(OAc)_2$ (1)	AgOTf (4)	100	0	0
17	$Pd(OAc)_2$ (1)	$AgBF_4$ (4)	100	0	0
18	$Pd(OAc)_2$ (1)	$AgNO_3$ (4)	100	0	trace
19	$PdCl_2$ (1)	Ag_2CO_3 (4)	100	65	11
20	$PdCl_2$ (1)	Ag_2CO_3 (4)	100	67	14[e]
21	Na_2PdCl_4 (1)	Ag_2CO_3 (4)	100	65	17
22	$Pd(PPh_3)_4$ (1)	Ag_2CO_3 (4)	100	49	16
23	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (4)	100	81	10
24	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (4)	100	80	14
25	$Pd(acac)_2$ (1)	Ag_2CO_3 (4)	100	67	19
26	$Pd(Piv)_2$ (1)	Ag_2CO_3 (4)	100	27	10
27	$Pd(TFA)_2$ (1)	Ag_2CO_3 (4)	100	43	17
28	$Pd(dba)_2$ (1)	Ag_2CO_3 (4)	100	19	trace
29	$Pd_2(dba)_3$ (1)	Ag_2CO_3 (4)	100	16	trace
30	Pd/C (1)	Ag_2CO_3 (4)	100	15	11
31	$[PdCl_2(PPh_3)_2]$ (0.5)	Ag_2CO_3 (4)	100	73	17
32	$[PdCl_2(PPh_3)_2]$ (0.1)	Ag_2CO_3 (4)	100	62	23

[a]**1a** (2 mmol, 2 equiv) was treated under various conditions in DMF (2 mL) for 20 min. [b]Isolated yield. [c]The reaction was performed for 1 h. [d]The reaction was performed for 2 h. [e]PPh_3 (2 mol %) was added externally.

Table I-D. The effect of different metal precursors, bases, metal/non-metal based additives as the oxidant on the self coupling of 1a to form 2a and 3a.[a]

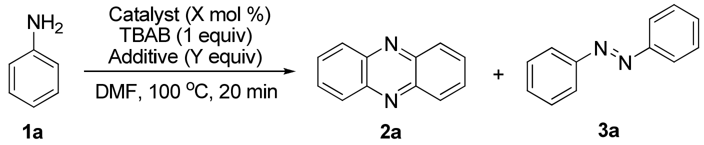


Entry	Catalyst (X)	Base (Y)	Additive (Z)	Yield (%)[b]	
				2a	**3a**
1	$Pd(OAc)_2$ (1)	None	$Cu(OAc)_2\cdot H_2O$ (4)	0	0
2	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	$Cu(OAc)_2\cdot H_2O$ (2)	0	0
3	$Pd(OAc)_2$ (1)	None	$CuCO_3\cdot Cu(OH)_2$ (4)	0	trace
4	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	$CuCO_3\cdot Cu(OH)_2$ (2)	0	trace
5	$Pd(OAc)_2$ (1)	None	CuI (4)	0	trace
6	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	CuI (2)	0	trace

7	$Pd(OAc)_2$ (1)	None	$FeCl_3$ (4)	0	trace
8	$Pd(OAc)_2$ (1)	Cs_2CO_3 (2)	$FeCl_3$ (2)	0	trace
9	$[PdCl_2(PPh_3)_2]$ (1)	None	$PhNO_2$ (4)	0	0
10	$[PdCl_2(PPh_3)_2]$ (1)	K_2CO_3 (4)	$PhNO_2$ (4)	0	0
11	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	$PhNO_2$ (2)	17	trace
12	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	$PhNO_2$ (4)	19	trace
13	$[PdCl_2(PPh_3)_2]$ (1)	None	TBHP (4)	0	0
14	$[PdCl_2(PPh_3)_2]$ (1)	None	TBHP (4)	0	0[c]
15	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	TBHP (4)	0	0
16	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	TBHP (2)	0	0[d]
17	$[PdCl_2(PPh_3)_2]$ (1)	K_2CO_3 (2)	Ag_2CO_3 (2) + $AgNO_3$ (4)	0	trace
18	$[PdCl_2(PPh_3)_2]$ (1)	K_2CO_3 (2)	Ag_2CO_3 (2) + $CuCO_3{\cdot}Cu(OH)_2$ (4)	0	trace
19	$[PdCl_2(PPh_3)_2]$ (1) + Ag_2CO_3 (10)	None	$K_2S_2O_8$ (2)	0	0
20	$[PdCl_2(PPh_3)_2]$ (1) + Ag_2CO_3 (10)	K_2CO_3 (2)	$K_2S_2O_8$ (2)	0	0
21	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	$K_2S_2O_8$ (2)	0	0[d]
22	$[PdCl_2(PPh_3)_2]$ (1) + Ag_2CO_3 (10)	None	$PhI(OAc)_2$ (2)	0	0
23	$[PdCl_2(PPh_3)_2]$ (1) + Ag_2CO_3 (10)	K_2CO_3 (2)	$PhI(OAc)_2$ (2)	0	0
24	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	$PhI(OAc)_2$ (2)	0	0[d]
25	$[PdCl_2(PPh_3)_2]$ (1) + Ag_2CO_3 (10)	None	DDQ (2)	0	0
26	$[PdCl_2(PPh_3)_2]$ (1) + Ag_2CO_3 (10)	K_2CO_3 (2)	DDQ (2)	0	0
27	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	NIS (4)	11	14[d]

[a] **1a** (2 mmol, 2 equiv) was treated under various conditions in DMF (2 mL) at 100 °C for 20 min. [b] Isolated yield. [c] The reaction was carried out under O_2 bubbling (10 psi). [d] The reaction was performed for 1 h under O_2 bubbling (10 psi). [NIS = *N*-Iodosuccinimide].

Table I-E. The effect of different metal precursors other than Pd compounds, metal-based additives as the oxidant on the self coupling of 1a to form 2a and 3a.[a]

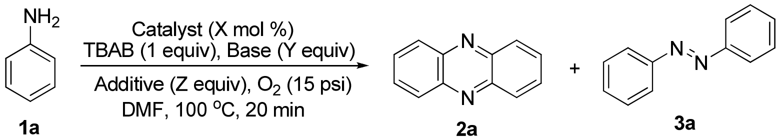


Entry	Catalyst (X)	Additive (Y)	Yield (%)[b]	
			2a	**3a**
1	$[NiCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (4)	52	14
2	$NiCl_2{\cdot}6H_2O$ (1)	Ag_2CO_3 (4)	41	12
3	$NiSO_4$ (1)	Ag_2CO_3 (4)	30	12
4	$[RuCl_2(p\text{-}cym)]_2$ (1)	Ag_2CO_3 (4)	0	trace

5	$[RuCl_2(p\text{-}cym)]_2$ (1)	$AgBF_4$ (0.1) + PivOH (0.1)	0	0[c]
6	$Ru(acac)_3$ (1)	Ag_2CO_3 (4)	0	trace
7	$Cu(OAc)_2\cdot H_2O$ (1)	Ag_2CO_3 (4)	0	18
8	$Cu(OAc)_2\cdot H_2O$ (1)	Ag_2CO_3 (2)	0	0[d]

[a] **1a** (2 mmol, 2 equiv) was treated under various conditions in DMF (2 mL) at 100 °C for 20 min. [b] Isolated yield. [c] DCE was used as solvent at reflux. [d] The reaction was carried out under O_2 bubbling (10 psi).

Table I-F. The effect of different palladium compounds, bases and metal-based additives as the oxidant on the self coupling of 1a to form 2a and 3a.[a]

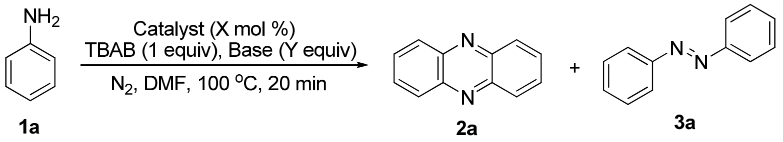


Entry	Catalyst (X)	Base (Y)	Additive (Z)	Yield (%)[b]	
				2a	**3a**
1	$[PdCl_2(PPh_3)_2]$ (1)	None	None	0	0
2	$[PdCl_2(PPh_3)_2]$ (1)	K_2CO_3 (4)	None	0	0
3	**$[PdCl_2(PPh_3)_2]$ (1)**	**Ag_2CO_3 (2)**	**None**	**83**	**12**
4	None	Ag_2CO_3 (2)	None	15	22
5	**$[PdCl_2(PPh_3)_2]$ (1)**	**Ag_2O (2)**	**None**	**81**	**14**
6	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1)	None	26	trace
7	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1)	None	50	10[c]
8	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2) + K_2CO_3 (2)	None	82	13
9	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3(1) + Cs_2CO_3 (1)	None	25	trace
10	**$[PdCl_2(PPh_3)_2]$ (1)**	**Ag_2CO_3(1) + Cs_2CO_3 (1)**	**None**	**77**	**12[c]**
11	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3(0.5) + Cs_2CO_3 (2)	None	20	trace[d]
12	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3(0.25) + Cs_2CO_3 (2)	None	0	0[d]
13	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	None	0	0[d]
14	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	None	18	trace[e]
15	**$[PdCl_2(PPh_3)_2]$ (1)**	**Ag_2CO_3 (2)**	**None**	**80**	**12[f]**
16	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	None	81	13[g]
17	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2) + KOAc (2)	None	80	12
18	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1) + KOAc (1)	None	23	trace
19	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (1)	None	28	11
20	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (1) + K_2CO_3 (1)	None	26	trace
21	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (2) + K_2CO_3 (2)	None	79	15
22	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (0.2)	None	0	0
23	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (0.2) + $Cu(OAc)_2\cdot H_2O$ (0.2)	None	0	0
24	$[PdCl_2(PPh_3)_2]$ (1)	$Cu(OAc)_2\cdot H_2O$ (0.2)	None	0	0
25	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (0.2) + $Cu(OAc)_2\cdot H_2O$ (0.2)	None	0	0
26	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (0.2) + $Cu(OAc)_2\cdot H_2O$ (0.2)	None	0	0

		+ K_2CO_3 (2)			
27	$[PdCl_2(PPh_3)_2]$ (1)	AgOAc (0.2) + TBHP (2) + Cs_2CO_3 (2)	None	0	0
28	$[PdCl_2(PPh_3)_2]$ (1)	AgOAc (0.2) + TBHP (2) + Cs_2CO_3 (2)	None	0	0[c]
29	$[PdCl_2(PPh_3)_2]$ (1)	AgOAc (0.2) + $PhI(OAc)_2$ (2) + Cs_2CO_3 (2)	None	0	0
30	$[PdCl_2(PPh_3)_2]$ (1)	AgOAc (0.2) + $PhI(OAc)_2$ (2) + Cs_2CO_3 (2)	None	0	0[c]
31	$[PdCl_2(PPh_3)_2]$ (1)	AgOAc (0.2) + $K_2S_2O_8$ (2) + Cs_2CO_3 (2)	None	0	0
32	$[PdCl_2(PPh_3)_2]$ (1)	AgOAc (0.2) + $K_2S_2O_8$ (2) + Cs_2CO_3 (2)	None	0	0[c]
33	$[PdCl_2(PPh_3)_2]$ (1)	$AgNO_3$ (2)	None	0	0
34	$[PdCl_2(PPh_3)_2]$ (1)	$AgNO_3$ (2) + K_2CO_3 (2)	None	0	trace
35	$[NiCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	None	55	11
36	$[PdCl_2(PPh_3)_2]$ (1) + $NiCl_2·6H_2O$ (1)	None	None	0	0
37	$[PdCl_2(PPh_3)_2]$ (1) + $[NiCl_2(PPh_3)_2]$ (1)	None	None	0	0
38	$[PdCl_2(PPh_3)_2]$ (1)	None	$Cu(OAc)_2·H_2O$ (2)	0	0
39	$[PdCl_2(PPh_3)_2]$ (1)	Cs_2CO_3 (2)	$Cu(OAc)_2·H_2O$ (2)	0	0
40	$PdCl_2$ (1)	Ag_2CO_3 (2)	None	68	17
41	Na_2PdCl_4 (1)	Ag_2CO_3 (2)	None	61	13
42	$PdCl_2$ (1)	Ag_2CO_3 (2)	None	74	14[g]
43	$PdCl_2$ (1)	Ag_2CO_3 (2)	None	76	11[h]
44	$PdCl_2$ (1)	Ag_2CO_3 (2)	None	80	12[i]
45	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1) + NHPI (0.2)	None	0	0[j]
46	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1) + NHPI (0.2)	None	0	0
47	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2O (0.2) + NHPI (0.2) + K_2CO_3 (2)	None	0	0

[a] **1a** (1 mmol) was treated under various conditions in DMF (2 mL) at 100 °C for 20 min under O_2 bubbling (15 psi). [b] Isolated yield. [c] The reaction was performed for 1 h. [d] The reaction was performed for 2 h. [e] The reaction was performed under O_2 balloon. [f] The reaction was performed under O_2 bubbling (10 psi). [g] The reaction was performed under O_2 bubbling (25 psi). [h] PPh_3 (2 mol %) was added externally. [i] PCy_3 (2 mol %) was added externally. [j] (biphenyl)PCy_2 (2 mol %) was added externally. [k] DCE was used as solvent under reflux. [NHPI = *N*-Hydroxy phthalimide].

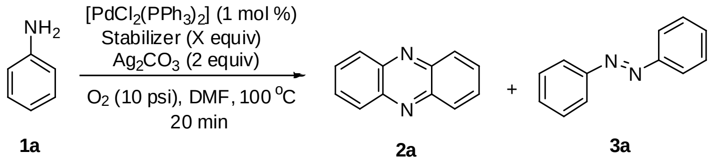
Table I-G. The effect of palladium compound, base, and the N_2 atmosphere for the self coupling of 1a to form 2a and 3a.[a]



Entry	Catalyst (X)	Base (Y)	Yield (%)[b]	
			2a	**3a**
1	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	20	16
2	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	27	18[c]
3	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2)	31	20[d]
4	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1) + Cs_2CO_3 (1)	12	trace
5	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (1) + Cs_2CO_3 (1)	16	11[c]
6	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (4)	80	13
7	$[PdCl_2(PPh_3)_2]$ (1)	Ag_2CO_3 (2) + Cs_2CO_3 (2)	21	14

[a] **1a** (1 mmol) was treated under various conditions in degassed DMF (2 mL) at 100 °C for 20 min under N_2 atmosphere. [b] Isolated yield. [c] The reaction was performed for 1 h. [d] The reaction was performed for 5 h.

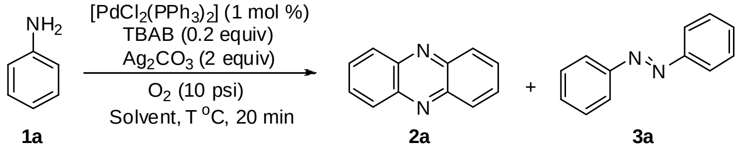
Table I-H. The effect of different stabilizers during the self coupling of 1a to form 2a and 3a.[a]



Entry	Stabilizer	X	Yield (%)[b]	
			2a	**3a**
1	Tetrabutylammonium bromide (TBAB)	1	81	10
2	TBAB	0.5	80	12
3	**TBAB**	**0.2**	**81**	**11**
4	**TBAB**	**0.2**	**79**	**13**[c]
5	TBAB	0.1	60	10
6	None	---	51	18
7	TBAF	0.2	78	12
8	TBACl	0.2	78	11
9	Tetrabutylammonium iodide (TBAI)	0.2	61	17
10	[bmim]Br	0.2	55	20
11	[bdmim]Br	0.2	53	19
12	Sodium dioctyl sulfosuccinate (SDOSS)	0.2	13	0
13	Sodium dodecyl sulfate (SDS)	0.2	trace	0
14	Tween 40	0.2	trace	0
15	Span 60	0.2	trace	0
16	Triton X 110	0.2	trace	0

[a]**1a** (2 mmol, 2 equiv) was treated in the presence of [$PdCl_2(PPh_3)_2$] (1 mol %), Ag_2CO_3 (2 equiv) in different stabilizer in DMF (2 mL) at 100 °C for 20 min under O_2 bubbling (10 psi). [b]Isolated yield. [c]Ag_2CO_3 (1 equiv) and Cs_2CO_3 (1 equiv) were used instead of Ag_2CO_3 (2 equiv) and the reaction was performed for 1 h.

Table I-I. The effect of different solvents during the self coupling of 1a to form 2a and 3a.[a]



Entry	Solvent	Temp (°C)	Yield (%)[b]	
			2a	**3a**
1	$HCONH_2$	100	0	0
2	DMF	100	81	10
3	**Diethylformamide (DEF)**	**100**	**87**	**10**
4	*N*,*N*-Dimethylacetamide (DMA)	100	86	11
5	DMPU	100	51	40
6	NMP	100	60	31
7	DMSO	100	64	20
8	1,4-Dioxane	100	54	30
9	MeCN	reflux	0	0
10	H_2O	100	0	0
11	H_2O	100	0	0[c]
12	DCE	reflux	14	trace
13	Toluene	reflux	28	17
14	THF	reflux	0	0
15	^{i}PrOH	reflux	12	10
16	PEG 400	130	0	0

[a]**1a** (2 mmol, 2 equiv) was treated in the presence of [$PdCl_2(PPh_3)_2$] (1 mol %), Ag_2CO_3 (2 equiv) and TBAB (0.2 equiv) in different solvents (2 mL) at 100 °C for 20 min under O_2 bubbling (10 psi). [b]Isolated yield. [c]SDOSS was used instead of Ag_2CO_3.

II. Evidence of NC formation during the Pd-Ag compounds catalyzed self coupling of 1a to form 2a.

Figure A. HRTEM image of Pd-Ag binary NC obtained from the reaction mixture of the [$PdCl_2(PPh_3)_2$] (7 mg, 1 mol %), Ag_2CO_3 (551 mg, 2 equiv) and TBAB (20 mol %) in DEF (2 mL) for 10 min at 100 ˚C.

Pd-Ag binary NC: (Pd particles size 3 nm – 8 nm and Ag particles size 20 nm – 40 nm)

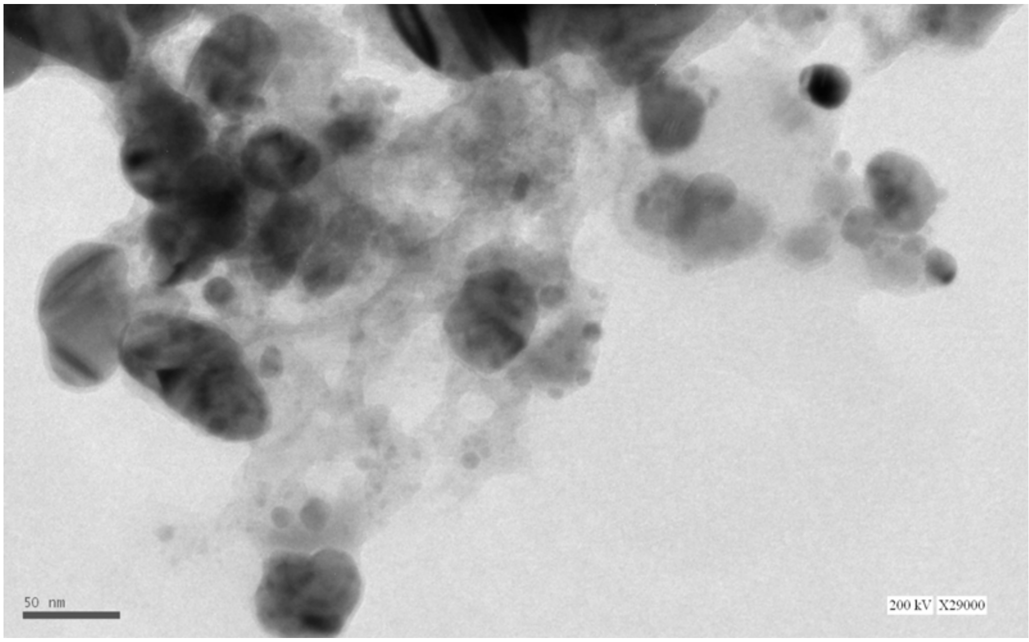


Figure B. Energy dispersive X-ray spectra of Pd-Ag binary NC (Fig. A) on carbon coated Cu grid.

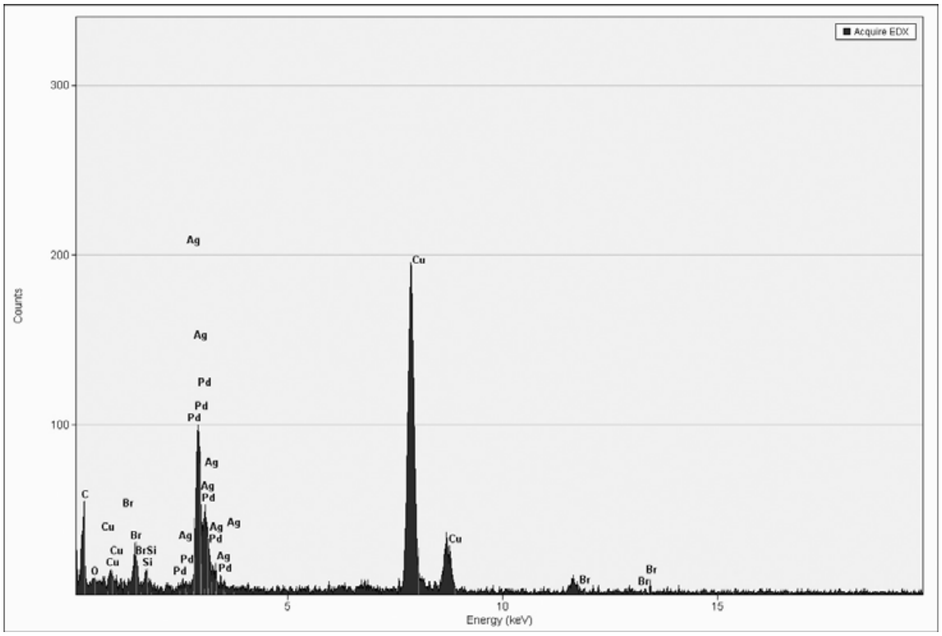


Figure C. HRTEM image of Pd-Ag binary NC obtained from the reaction mixture of the $PdCl_2$ (1.7 mg, 1 mol %), Ag_2CO_3 (551 mg, 2 equiv) and TBAB (20 mol %) in DEF (2 mL) for 10 min at 100 ˚C.

Pd-Ag binary NC: (Pd particles size 10 nm – 15 nm and Ag particles size 20 nm – 40 nm)

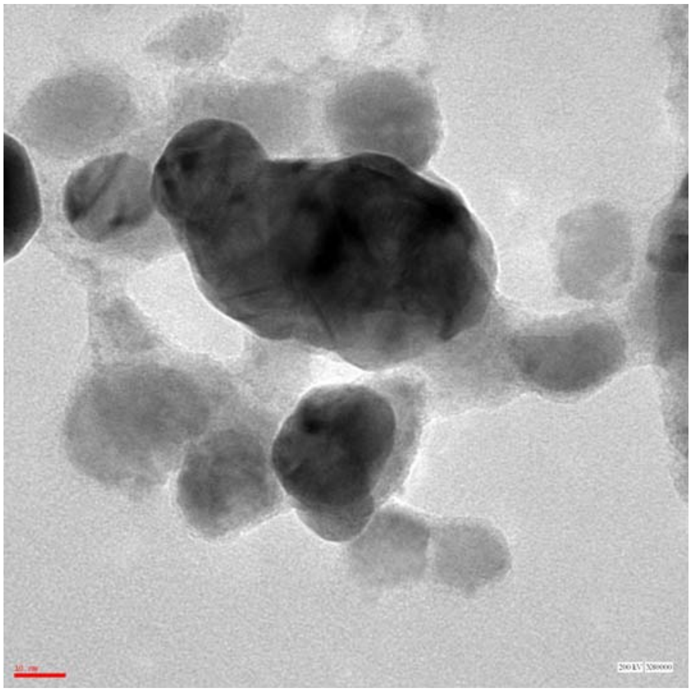
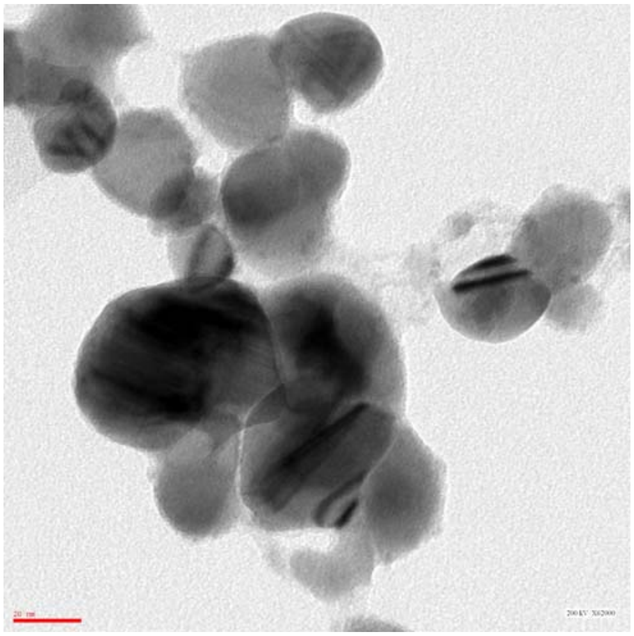


Figure D. HRTEM image of Pd-Ag binary NC obtained from the reaction mixture of the Na_2PdCl_4 (2.9 mg, 1 mol %), Ag_2CO_3 (551 mg, 2 equiv) and TBAB (20 mol %) in DEF (2 mL) for 10 min at 100 ˚C.

Pd-Ag binary NC: (Pd particles size 12 nm – 20 nm and Ag particles size 20 nm – 40 nm)

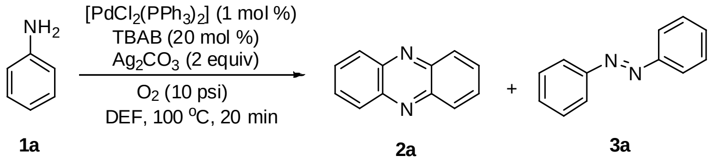


III. Experimental Procedure

General Information

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$: 7.26/77.0) using Me_4Si as an internal standard. Chemical shifts (δ) 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® silica gel respectively]. Evaporation of solvents was performed at reduced pressure, using a Bűchi 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^2-F20 instrument equipped with EDAX facility.

Typical procedure for the in-situ generated Pd-Ag NC catalyzed coupling of aniline 1a by double C-H activation to generate phenazine 2a and azobenzene 3a:-



Method A: To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %) and Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in diethylformamide, DEF (2 mL) was added aniline **1a** (186 mg, 0.18 mL, 2 mmol, 2 equiv) under O_2 bubbling (10 psi) at 100 °C. Upon completion of the reaction (20 min, monitored by TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DEF was evaporated to dryness under vacuum (10 mm Hg). The residue was passed through chromatography column (silica-gel: 100-200 mesh) and eluted with Et_3N-hexane-EtOAc solvent system to afford the phenazine[1] **2a** as brown solid, (157 mg, 87%) and azobenzene[2] **3a** as red solid, (18 mg, 10%). **2a**: mp: 172-175 °C [lit. mp: 172-176 °C]; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.83 – 7.88 (m, 4H), 8.24 – 8.28 (m, 4H); IR (KBr) ν_{max}: 2922, 1275, 1260, 1054, 1033 cm^{-1}; MS (ESI) (M^+) = 180.5. **3a**: mp: 67-70 °C [lit. mp: 65-68 °C]; TLC (Hexane:EtOAc, 98:2 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.45 – 7.54 (m, 6H), 7.91 – 7.94 (m, 4H); IR (KBr) ν_{max}: 3139, 2956, 1737, 1365, 1216 cm^{-1}; MS (ESI) (M^+) = 182.7.

Method B: To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %), Ag_2CO_3 (276 mg, 1 mmol, 1 equiv) and Cs_2CO_3 (326 mg, 1 mmol, 1 equiv) in DEF (2 mL) was added **1a** (186 mg, 0.18 mL, 2 mmol, 2 equiv) under O_2 bubbling (10 psi) at 100 °C. Upon completion of the reaction (60 min, monitored by

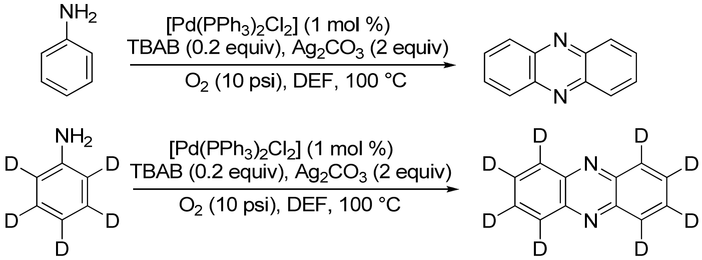
TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DEF was evaporated to dryness under vacuum (10 mm Hg). The residue was passed through chromatography column (silica-gel: 100-200 mesh) and eluted with Et_3N-hexane-EtOAc solvent system to afford the **2a**[1] as brown solid, (142 mg, 79%) and **3a**[2] as red solid, (24 mg, 13%).

Typical procedure for identification and analysis of the in-situ formed Pd-Ag binary NC: The mixture of TBAB (64.4 mg, 0.2 mmol, 20 mol %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %) and Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in DEF (2 mL) was stirred magnetically at 100 °C. An aliquot portion (3 µL) of the reaction mixture was withdrawn after 10 min, diluted and from the diluted solution, another aliquot portion (3 µL) was kept on carbon coated Cu grid (200 mesh size). The grid was air dried and was subjected to TEM analyses to identify the Pd-Ag binary NC (Pd particles 3 nm - 8 nm and Ag particles 20 nm - 40 nm).

IV. Evidences for the Proposed Mechanistic Pathway during the Self Coupling of Aniline to form Phenazine and Relevant Studies:

Scheme IV-A. Kinetic isotope effect study for the determination of k_H/k_D.

(i) Typical experimental procedure for determination ion current using (+ve) ESI-MS:



To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %), Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in DEF (2 mL) was added aniline (186 mg, 0.18 mL, 2 mmol, 2 equiv) and aniline-d_5 (196 mg, 0.18 mL, 2 mmol, 2 equiv) separately, under O_2 bubbling (10 psi) at 100 °C. At the time interval of 5 min, 10 min, 15 min and 20 min, 10 µL of the aliquot of the reaction mixture was withdrawn from the individual reaction mixture and dissolved in DCM (1 mL). From the resultant solution an aliquot amount (50 µL) was subjected to (+ve) ESI-MS in advance Thermo Scientific LTQ-XL mass spectrometer.

The total ion current corresponding to the peak area of the potassium adduct $(M + K)^+$ of the phenazine formed from aniline (m/z = 219) (Fig. E) was compared with that of the phenazine-d_5 formed from aniline-d_5 (m/z = 227) (Fig. F). In all the cases, ion current corresponding to phenazine was found to be much greater in comparison to the ion current of the corresponding phenazine-d_5. These provided direct evidences of the k_H/k_D (Table IV-A).

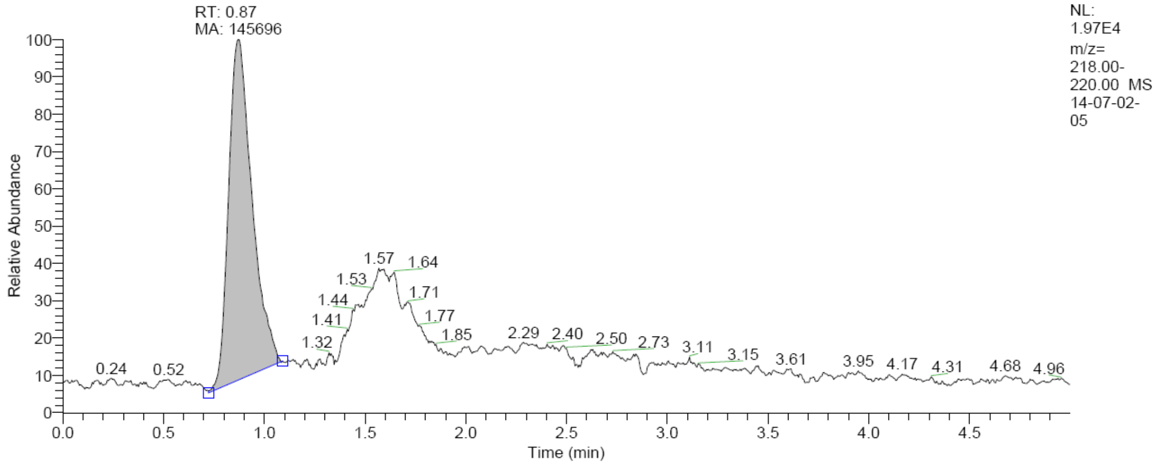
Table IV-A. The determination of k_H/k_D during phenazine formation from aniline and aniline-d_5.[a]

Entry	Time (min)	Ion current of the $(M+K^+)$ peak		
		X (R = H)[b]	Y (R = D)[b]	k_H/k_D[c]
1	5	1.45×10^5	3.30×10^4	4.39
2	10	2.03×10^5	4.69×10^4	4.33
3	15	2.36×10^5	4.75×10^4	4.98
4	20	2.50×10^5	4.84×10^4	5.18

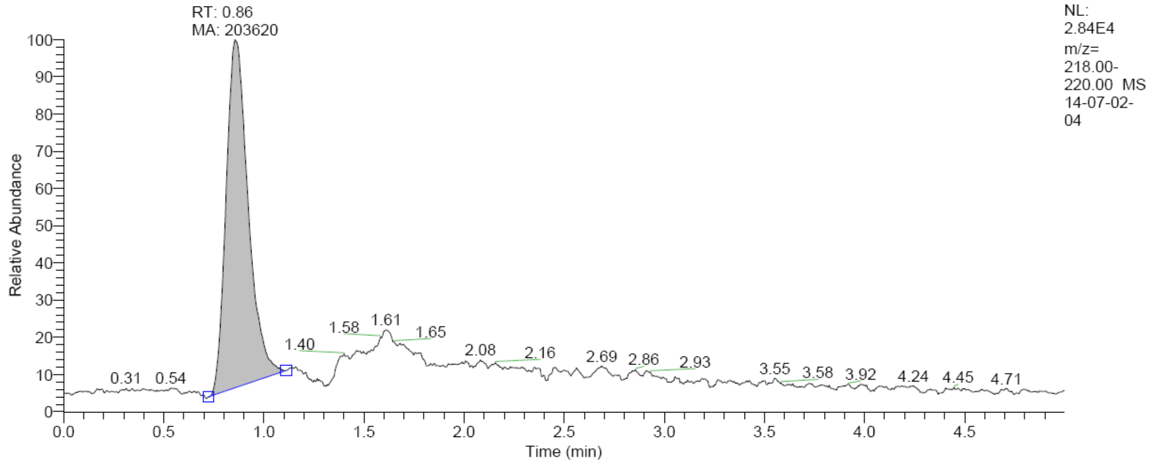
[a] Aniline (1 mmol) and aniline-d_5 (1 mmol) were separately subjected to the reaction and after the specific time interval 10 μL of the respective reaction mixture was withdrawn and subjected to ESI-MS analysis. [b] The area of the ion peak of the potassium adduct of the corresponding phenazine. [c] The relative rate (k_H/k_D) is represented by the ratio X/Y.

Figure E. The peak area of the $(M + K)^+$ of phenazine formed from aniline corresponding to the ion at $m/z = 219$:

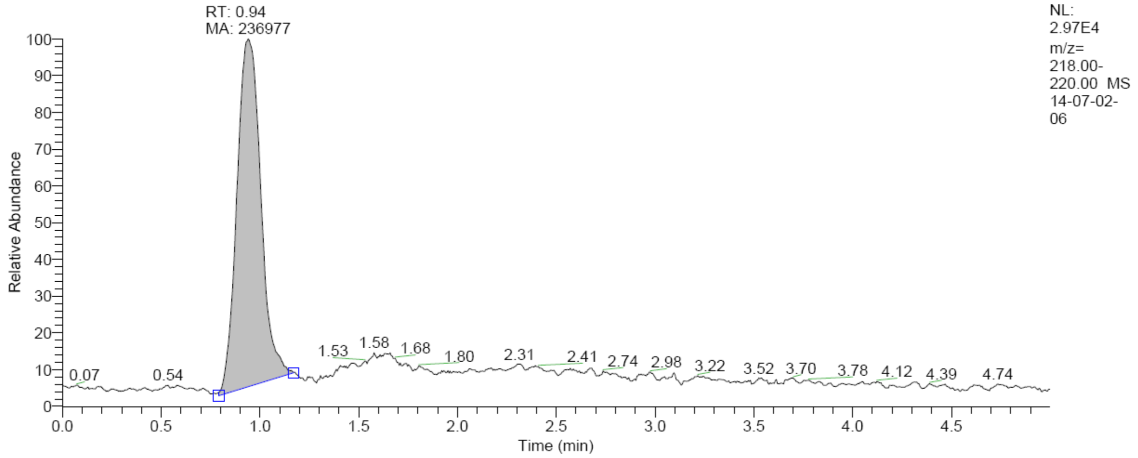
(i) At 5 min:



(ii) At 10 min:



(iii) At 15 min:



(iv) At 20 min:

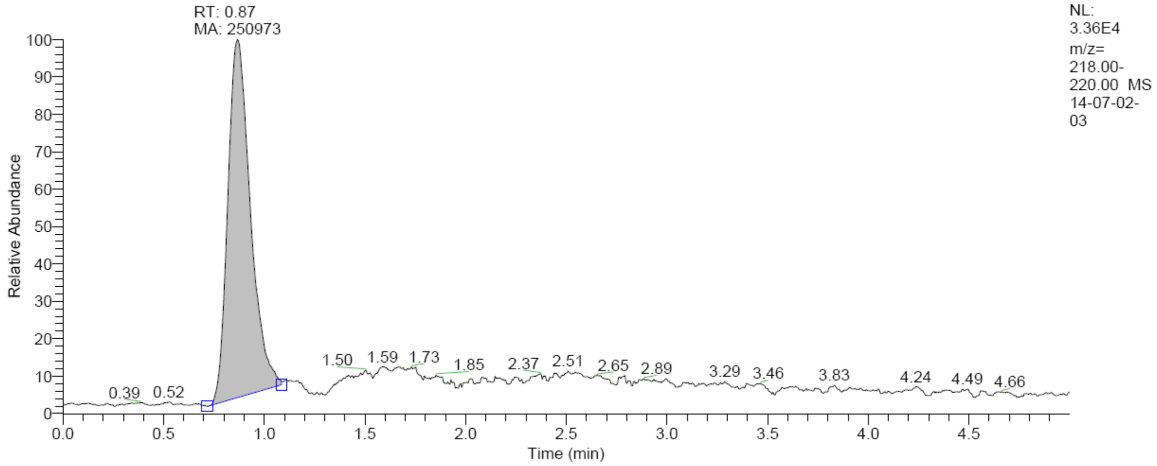
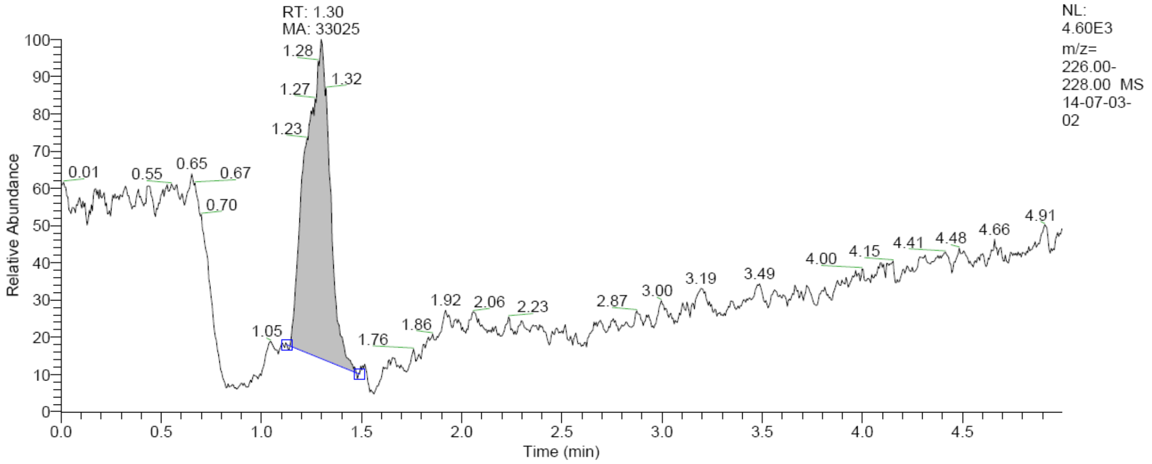
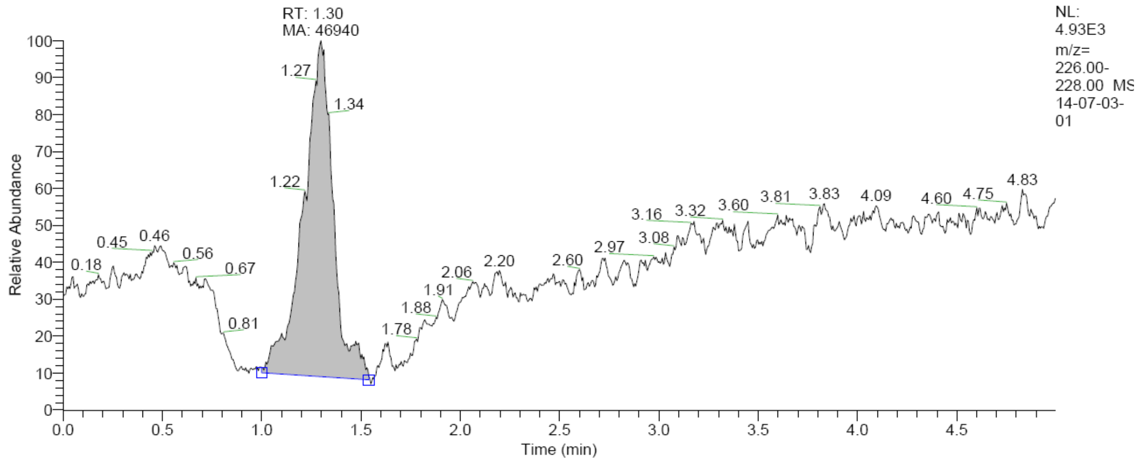


Figure F. The peak area of the $(M + K)^+$ of phenazine-d_5 formed from aniline-d_5 corresponding to the ion at m/z = 227:

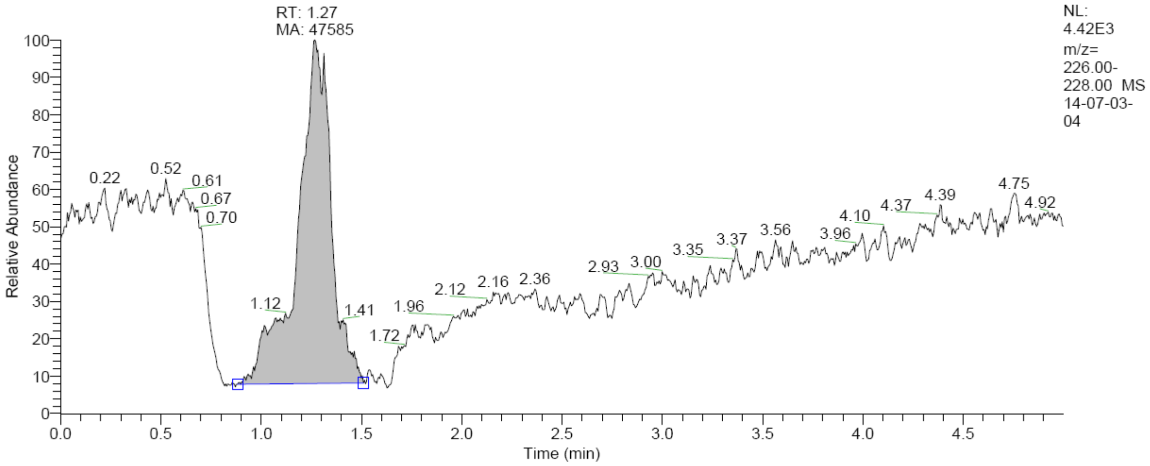
(i) At 5 min:



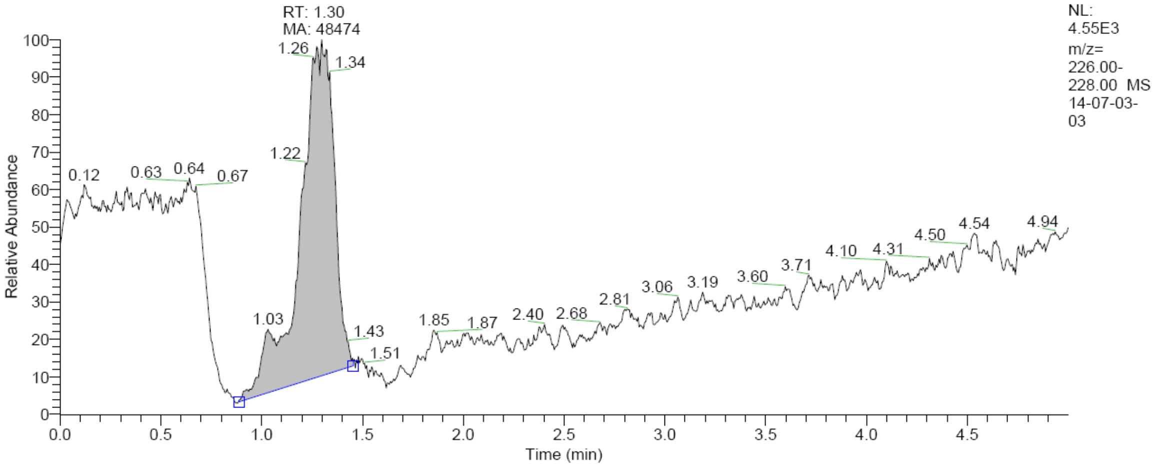
(ii) At 10 min:



(iii) At 15 min:



(iv) At 20 min:



Scheme IV-B. Plausible mechanism for the C-H activation mediated amination/cyclization/oxidation cascade of phenazine formation catalysed by Pd-Ag NC.

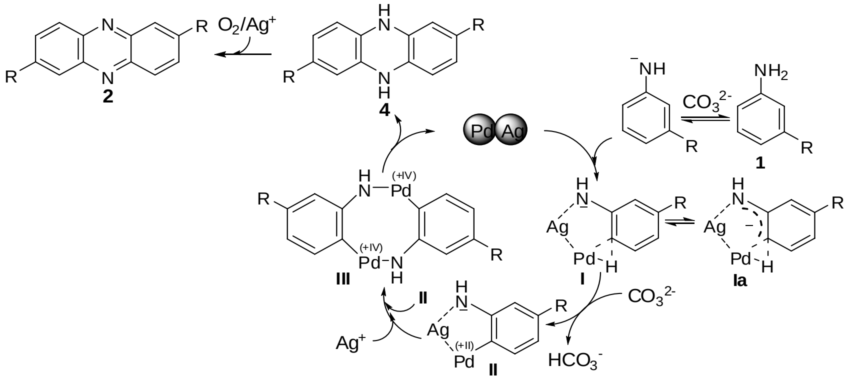
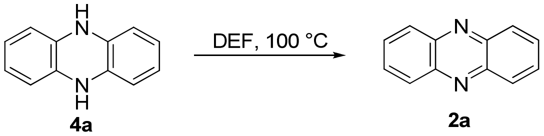


Table IV-B. The control experiments of dihydrophenazine 4a to afford the 2a.[a]

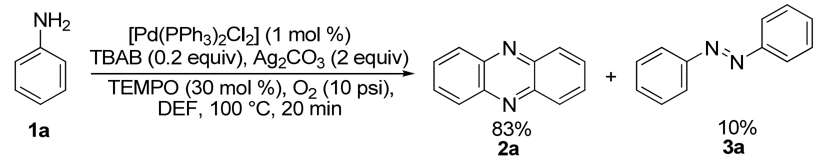


Entry	Condition	Time (min)	Yield (%)[b]
1	O_2 bubbling (10 psi)	20	96
2	Ag_2CO_3 (1 equiv)	30	94
3	O_2 bubbling (10 psi) + Ag_2CO_3 (1 equiv)	5	96
3	O_2 bubbling (10 psi) + Ag_2CO_3 (10 mol %)	20	96

[a] **4a** (1 mmol) was treated under various conditions in DEF (2 mL) at 100 °C. [b] Isolated yield of **2a**.

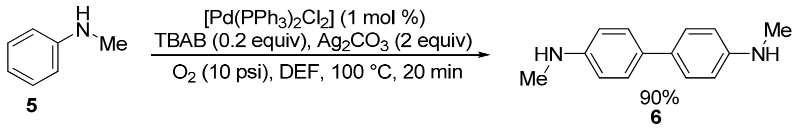
Scheme IV-C. Evidence for non-radical mechanism during the Pd-Ag NC catalyzed self coupling of aniline to form phenazine

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



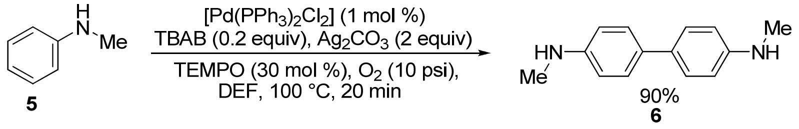
To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %) and Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in DEF (2 mL) were added TEMPO (46.9 mg, 0.3 mmol, 30 mol %) and **1a** (186 mg, 0.18 mL, 2 mmol, 2 equiv) under O_2 bubbling (10 psi) at 100 °C. Upon completion of the reaction (20 min, monitored by TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DEF was evaporated to dryness under vacuum (10 mm Hg). The residue was passed through chromatography column (silica-gel: 100-200 mesh) and eluted with Et_3N-hexane-EtOAc solvent system to afford the **2a** as brown solid (149 mg, 83%) and **3a** as red solid (18 mg, 10%).

(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 %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %) and Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in DEF (2 mL) was added *N*-methylaniline **5** (214 mg, 0.216 mL, 2 mmol, 2 equiv) under O_2 bubbling (10 psi) at 100 °C. Upon completion of the reaction (20 min, monitored by TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DEF 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*-methyl-biphenyl **6** as reddish oil, (191 mg, 90%); TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.97 (s, 6H), 6.84 – 6.78 (m, 4H), 7.26 – 7.22 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 33.9, 112.6, 118.6, 129.4, 149.0; IR (KBr) ν_{max}: 3355, 2227, 1736, 1628, 1597, 1217, 1024 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{14}H_{16}N_2Na$, 235.1211; found 235.1220.

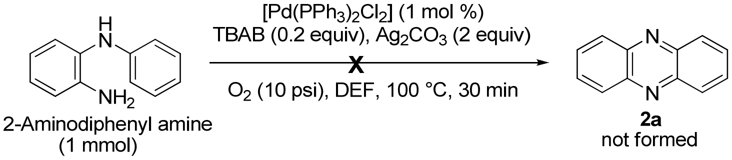
(iii) Reaction of *N*-Methylaniline 5 in the presence of radical scavenger.



To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol, 1 mol %), Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in DEF (2 mL) were added TEMPO (46.9 mg, 0.3 mmol, 30 mol %) and **5** (214 mg, 0.216 mL, 2 mmol, 2 equiv) under O_2 bubbling (10 psi) at 100 °C. Upon completion of the reaction (20 min, monitored by TLC), the reaction mixture was cooled to rt and was filtered through a short pad of celite; DEF 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 **6** as reddish oil (191 mg, 90%).

Scheme IV-D. Evidence for C-H activation and synchronous double C-N bond formation during phenazine formation.

The reaction of 2-aminodiphenyl amine



V. Characterization of compounds:

2,7-Dimethyl-phenazine[3] (entry 2, Table 1):- Yellow solid; mp: 161-163 °C. TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 2.64 (s, 6H), 7.65 (d, 2H, *J* = 8.8 Hz), 7.96 (s, 2H), 8.10 (d, 2H, *J* = 8.8 Hz); IR (KBr) ν_{max}: 2948, 1654, 1453, 1031 cm^{-1}; MS (ESI) (M + H)$^+$ = 209.3.

2,7-Bis-benzyloxy-phenazine (entry 3, Table 1):- Yellow solid; mp: 153-156 °C; TLC (Hexane:EtOAc, 25:75 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 5.27 (s, 4H), 7.35 – 7.39 (m, 2H), 7.42 – 7.45 (m, 4H), 7.49 – 7.53 (m, 6H), 7.58 (dd, 2H, *J* = 2.7 Hz, 9.4 Hz), 8.06 (d, 2H, *J* = 9.4 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 70.6, 106.1, 126.2, 127.8, 128.4, 128.7, 130.0, 136.0, 140.5, 143.4, 159.3; IR (KBr) ν_{max}: 2921, 2847, 1602, 1450, 1275 cm^{-1}; HRMS (ESI) (M + H)$^+$ Calcd. for $C_{26}H_{21}N_2O_2$, 393.1603; found 393.1590.

1,2,3,6,7,8-Hexamethoxy-phenazine (entry 4, Table 1):- Yellow solid; mp: 155-157 °C; TLC (Hexane:EtOAc, 80:20 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.06 (s, 6H), 4.13 (s, 6H), 4.23 (s, 6H), 7.37 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 56.4, 61.6, 62.2, 102.2, 135.8, 139.8, 144.6, 145.4, 155.8; IR (KBr) ν_{max}: 2923, 2850, 1602, 1406, 1048 cm^{-1}; HRMS (ESI) (M + Na)$^+$ Calcd. for $C_{18}H_{20}N_2O_6Na$, 383.1219; found 383.1221.

2,7-Dimethoxy-phenazine[4] (entry 5, Table 1):- Yellow solid; TLC (Hexane:EtOAc, 82:18 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.02 (s, 6H), 7.41 (s, 2H), 7.50 (d, 2H, *J* = 9.4 Hz), 8.04 (d, 2H, *J* = 9.4 Hz); IR (KBr) ν_{max}: 2922, 1634, 1275 cm^{-1}; MS (ESI) (M + H)$^+$ = 241.3.

2,7-Difluoro-phenazine[3] (entry 6, Table 1):- Yellow solid; mp: 252-254 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.67 – 7.72 (m, 2H), 7.84 (dd, 2H, *J* = 2.6 Hz, 9.1 Hz), 8.22 – 8.26 (m, 2H); IR (KBr) ν_{max}: 2923, 2855, 1275, 1260, 749 cm^{-1}; MS (ESI) (M + H)$^+$ = 217.2.

2,7-Bis-methylsulfanyl-phenazine (entry 7, Table 1):- Yellow solid; mp: 211-213 °C; TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 2.67 (s, 6H), 7.62 (dd, 2H, *J* = 2.1 Hz, 9.1 Hz), 7.75 (d, 2H, *J* = 2.1 Hz), 8.00 (d, 2H, *J* = 9.1 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 15.1, 121.0, 128.9, 130.7, 142.1, 142.8, 143.1; IR (KBr) ν_{max}: 2917, 2851, 1731, 1615, 1454, 1275, 1260, 1049 cm^{-1}; HRMS (ESI) (M + H)$^+$ Calcd. for $C_{14}H_{13}N_2S_2$, 273.0520; found 273.0512.

2,7-Dimethyl-phenazine[3] (entry 8, Table 1):- Yellow solid; mp: 161-163 °C. TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 2.66 (s, 6H), 7.67 (dd, 2H, *J* = 1.9 Hz, 8.9 Hz), 7.99 (s, 2H), 8.12 (d, 2H, *J* = 8.9 Hz); IR (KBr) ν_{max}: 2949, 1651, 1450, 1033 cm^{-1}; MS (ESI) (M + H)$^+$ = 209.4.

2,7-Dimethoxy-phenazine[4] (entry 9, Table 1):- Yellow solid; TLC (Hexane:EtOAc, 82:18 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.04 (s, 6H), 7.43 (d, 2H, *J* = 2.7 Hz), 7.52 (dd, 2H, *J* = 2.8 Hz, 9.4 Hz), 8.06 (d, 2H, *J* = 9.4 Hz); IR (KBr) ν_{max}: 2920, 1635, 1277 cm^{-1}; MS (ESI) (M + H)$^+$ = 241.2.

2,7-Difluoro-phenazine[3] (entry 10, Table 1):- Yellow solid; mp: 252-254 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.69 – 7.74 (m, 2H), 7.86 (dd, 2H, J = 2.7 Hz, 9.2 Hz), 8.25 – 8.28 (m, 2H); IR (KBr) ν_{max}: 2921, 2857, 1277, 1263, 751 cm^{-1}; MS (ESI) (M + H)$^+$ = 217.3.

Dibenzo[*a,h*]phenazine (entry 11, Table 1):- Light yellow solid; mp: 177 - 179 °C; TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.84 (dt, 2H, J = 1.4 Hz, 7.3 Hz), 7.90 (dt, 2H, J = 1.4 Hz, 8.4 Hz), 8.02 (d, 2H, J = 7.9 Hz), 8.09 – 8.12 (m, 4H), 9.67 (d, 2H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 125.2, 127.0, 127.7, 128.2, 129.3, 131.4, 132.4, 133.3, 140.6, 142.8; IR (KBr) ν_{max}: 2919, 2859, 1617, 1401, 1259, 1047 cm^{-1}; HRMS (ESI) [M + H]$^+$ Calcd. for $C_{20}H_{13}N_2$, 281.1079; found 281.1066.

Di-*p*-tolyl-diazene[2] (entry 2, Table 1, Footnote c):- Red solid; mp: 140-142 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.43 (s, 6H), 7.30 (s, 4H), 7.81 (s, 4H); IR (KBr) ν_{max}: 2970, 1737, 1365, 1228, 1216, 750 cm^{-1}; MS (ESI) (M + H)$^+$ = 211.3.

Bis-(4-benzyloxy-phenyl)-diazene (entry 3, Table 1, Footnote c):- Light orange solid; mp: 177-179 °C; TLC (Hexane:EtOAc, 96:4 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.15 (s, 4H), 7.06 – 7.09 (m, 4H), 7.34 – 7.37 (m, 2H), 7.39 – 7.43 (m, 4H), 7.45 – 7.47 (m, 4H), 7.86 – 7.88 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 70.2, 115.1, 124.4, 127.5, 128.1, 128.7, 136.5, 147.2, 160.8; IR (KBr) ν_{max}: 2915, 2859, 1601, 1452, 1244, 1015, 843, 733, 691 cm^{-1}; HRMS (ESI) (M + H)$^+$ Calcd. for $C_{26}H_{23}N_2O_2$, 395.1760; found 395.1757.

Bis-(3,4,5-trimethoxy-phenyl)-diazene (entry 4, Table 1, Footnote c):- Orange solid; mp: 207-209 °C; TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.94 (s, 6H), 3.98 (s, 12H), 7.25 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 56.2, 61.0, 100.3, 140.6, 148.4, 153.5; IR (KBr) ν_{max}: 2927, 2847, 1595, 1275, 1259, 1049 cm^{-1}; HRMS (ESI) (M + H)$^+$ Calcd. for $C_{18}H_{23}N_2O_6$, 363.1556; found 363.1552.

Bis-(4-methoxy-phenyl)-diazene[2] (entry 5, Table 1, Foonote c):- Orange solid; mp: 158-160 °C; TLC (Hexane:EtOAc, 92:8 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.88 (s, 6H), 7.00 (d, 4H, J = 7.6 Hz), 7.88 (d, 4H, J = 7.6 Hz); IR (KBr) ν_{max}: 2976, 1624, 1275 cm^{-1}; MS (ESI) (M + H)$^+$ = 243.4.

Bis-(4-fluoro-phenyl)-diazene[2] (entry 6, Table 1, Footnote c):- Orange solid; mp: 99-101 °C; TLC (Hexane:EtOAc, 97:3 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.16 – 7.24 (m, 4H), 7.89 – 7.97 (m, 4H); IR (KBr) ν_{max}: 2924, 2847, 1275, 1260, 764 cm^{-1}; MS (ESI) (M + H)$^+$ = 219.3.

Bis-(4-methylsulfanyl-phenyl)-diazene (entry 7, Table 1, Footnote c):- Red solid; mp: 172-174 °C; TLC (Hexane:EtOAc, 98:2 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.54 (s, 6H), 7.33 (d, 4H, J = 7.8 Hz), 7.84 (d, 4H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 15.3, 123.3, 126.0, 142.6, 150.0; IR (KBr) ν_{max}: 2918, 2851, 1584, 1555, 1434, 1404, 1086, 837 cm^{-1}; HRMS (ESI) (M + H)$^+$ Calcd. for $C_{14}H_{15}N_2S_2$, 275.0677; found 275.0684.

(*E*)-1,2-*dim*-tolyldiazene[2] (entry 8, Table 1, Footnote c):- Red solid; mp: 136-139 °C; TLC (Hexane:EtOAc, 97:3 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.50 (s, 6H), 7.01 (d, 2H, J = 7.5 Hz), 7.44 (t, 2H, J = 7.8 Hz), 7.77 (s, 4H); IR (KBr) ν_{max}: 2921, 1479, 1274, 1265 cm^{-1}; MS (ESI) (M + H)$^+$ = 211.4.

(*E*)-1,2-Bis(3-methoxyphenyl)diazene[5] (entry 9, Table 1, Footnote c):- Red solid; mp: 72-74 °C; TLC (Hexane:EtOAc, 92:8 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.93 (s, 6H), 7.01 (dd, 2H, *J* = 2.0 Hz, 8.1 Hz), 7.44 – 7.50 (m, 4H), 7.60 (m, 2H); IR (KBr) ν_{max}: 2922, 1477, 1277, 1263 cm^{-1}; MS (ESI) $(M + H)^+$ = 243.4.

(*E*)-1,2-Bis(3-fluorophenyl)diazene[6] (entry 10, Table 1, Footnote c):- Red solid; mp: 77-79 °C; TLC (Hexane:EtOAc, 94:6 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.24 (dd, 2H, *J* = 2.4 Hz, 8.2 Hz), 7.51 – 7.56 (m, 2H), 7.62 – 7.65 (m, 2H), 7.80 (d, 2H, *J* = 7.9 Hz); IR (KBr) ν_{max}: 2921, 1475, 1274, 1252 cm^{-1}; MS (ESI) $(M + H)^+$ = 219.3.

Di-naphthalen-2-yl-diazene[7] (entry 11, Table 1, Footnote c):- Orange solid; mp: 195 - 197 °C; TLC (Hexane:EtOAc, 97:3 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.58 – 7.62 (m, 4H), 7.93 – 7.98 (m, 4H), 8.06 – 8.08 (m, 2H), 8.17 (dd, 2H, *J* = 1.9 Hz, 8.8 Hz), 8.54 (d, 2H, *J* = 1.5 Hz); IR (KBr) ν_{max}: 2929, 2856, 1619, 1400, 1257, 1051 cm^{-1}; MS (ESI) $(M + H)^+$ = 283.3.

VI. Recovery and recyclability study of NC:

Typical procedure for the recovery and recyclability of Pd-Ag binary NC catalytic system for self coupling of 1a to form 2a:-

To a magnetically stirred solution of TBAB (64.4 mg, 0.2 mmol, 20 mol %), [$PdCl_2(PPh_3)_2$] (7 mg, 0.01 mmol, 1 mol %) and Ag_2CO_3 (551 mg, 2 mmol, 2 equiv) in DEF (2 mL) was added aniline **1a** (186 mg, 0.18 mL, 2 mmol, 2 equiv) under O_2 bubbling (10 psi) at 100 °C. Upon completion of the reaction (20 min, monitored by TLC), the reaction mixture was cooled to rt and was centrifuged (8000 RPM) for 10 min. DEF layer was decanted off and the remaining solid portions (contains the Pd-Ag NC) was washed with DM water (2 × 5 mL); kept in a vacuum oven for dryness (1 h) to obtain the recovered Pd-Ag NC. The recovered Pd-Ag NC was charged with DEF (2 mL), **1a** (2 mmol, 2 equiv), Ag_2CO_3 (276 mg, 1 mmol, 1 equiv) and the mixture was magnetically stirred at 100 °C under O_2 bubbling (10 psi) for 20 min to obtain **2a** in 83% 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 Pd-Ag NC after each fresh reaction to obtain **2a** in 80, 76, 71, and 63% yields.

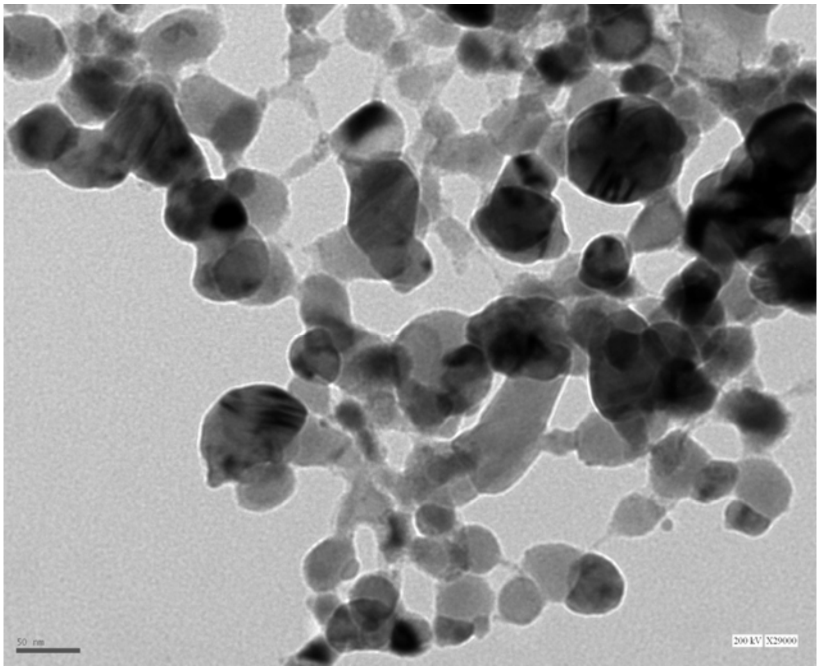
Table VI-A. Reusability of Pd-Ag binary NC system.[a]

Entry	No. of Runs	Yield (%)[b]	
		2a	**3a**
1	Fresh	87	10
2	1st reuse	83	10
3	2nd reuse	80	11
4	3rd reuse	76	10
5	4th reuse	71	trace
6	5th reuse	63	trace

[a] **1a** (2 mmol, 2 equiv) was treated in DEF (2 mL) with the recovered catalyst and Ag_2CO_3 (1 mmol, 1 equiv) for each cycle. [b] The isolated yield.

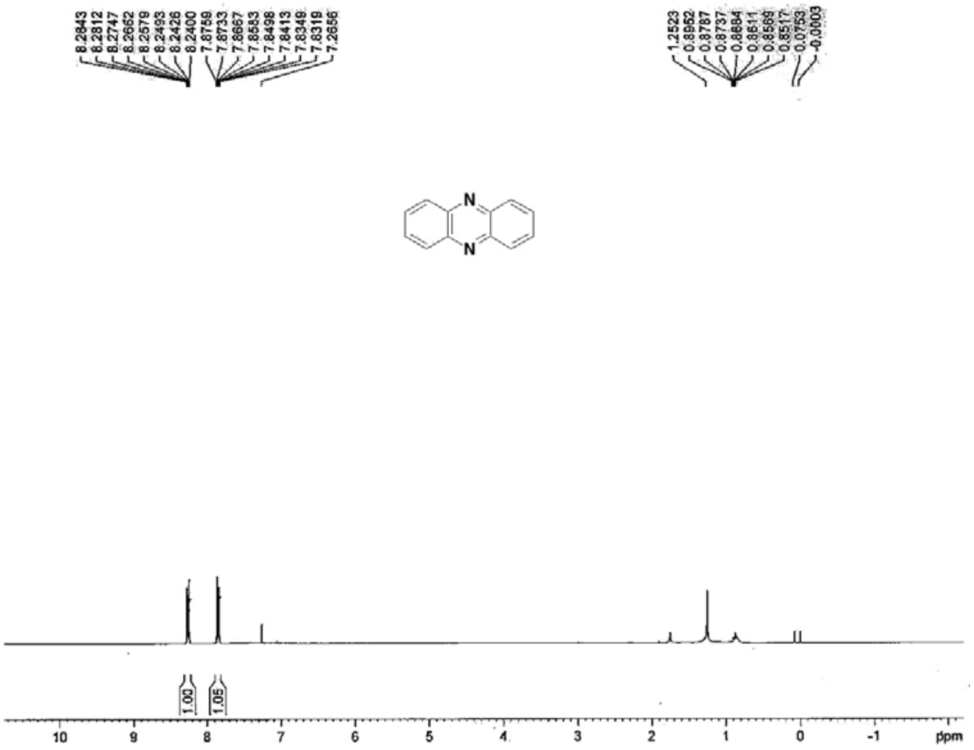
Figure G. HRTEM image of Pd-Ag binary NC in the reaction mixture at 5th cycle.

Pd-Ag binary NC: (Pd particles size 20 nm – 25 nm and Ag particles size 50 nm – 60 nm)

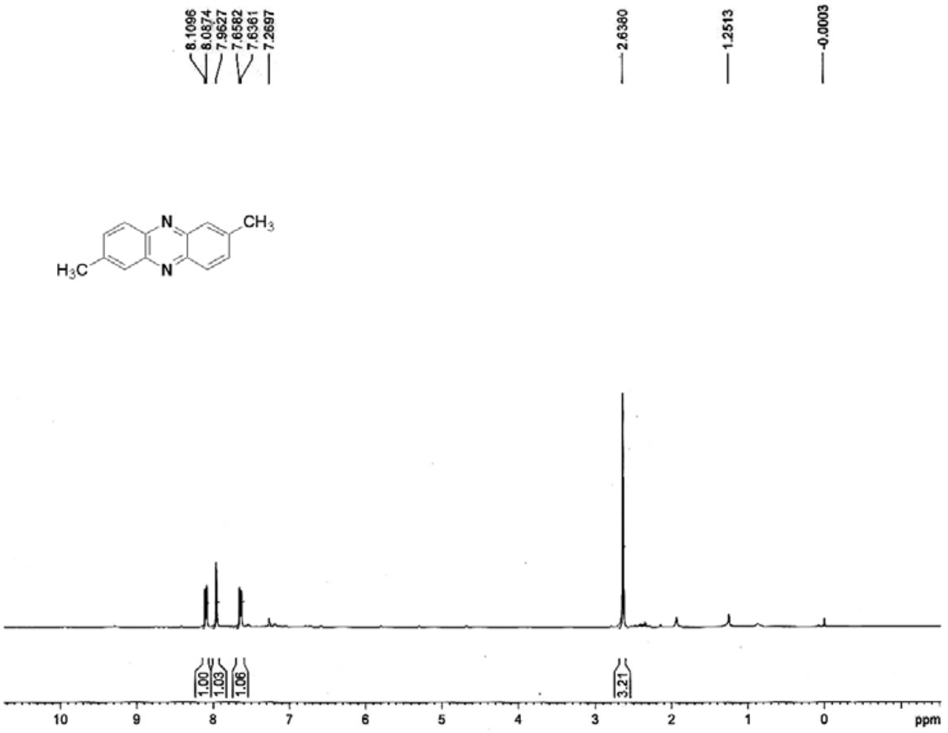


VII. Scanned NMR Spectra:

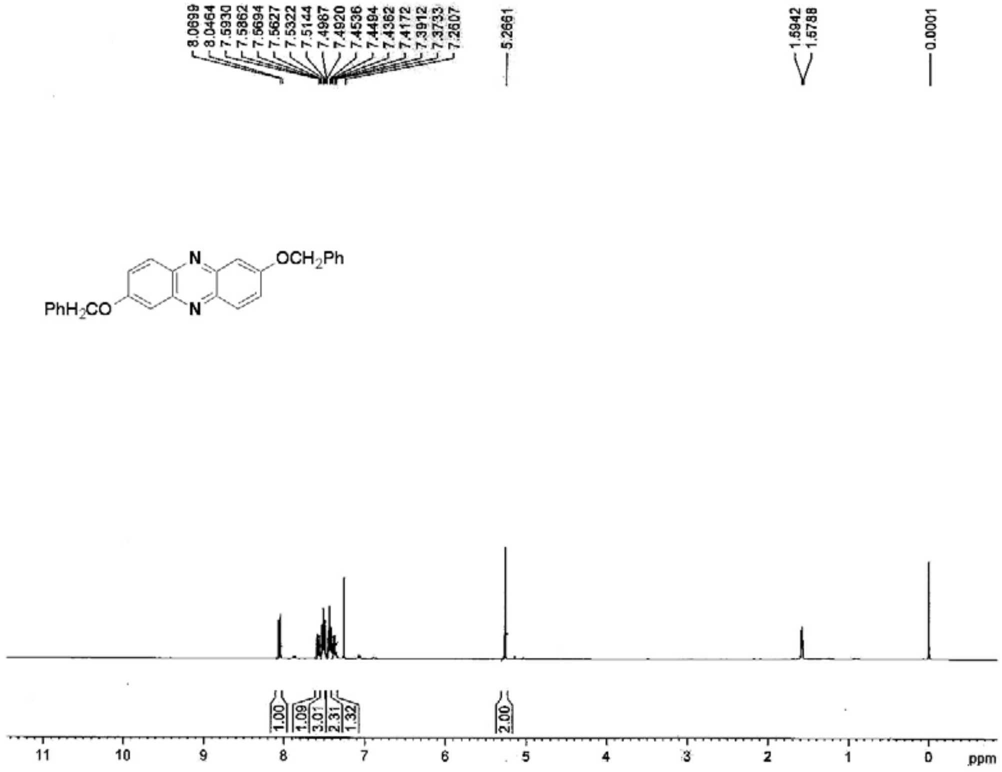
^{1}H NMR of Phenazine (entry 1, Table 1):-



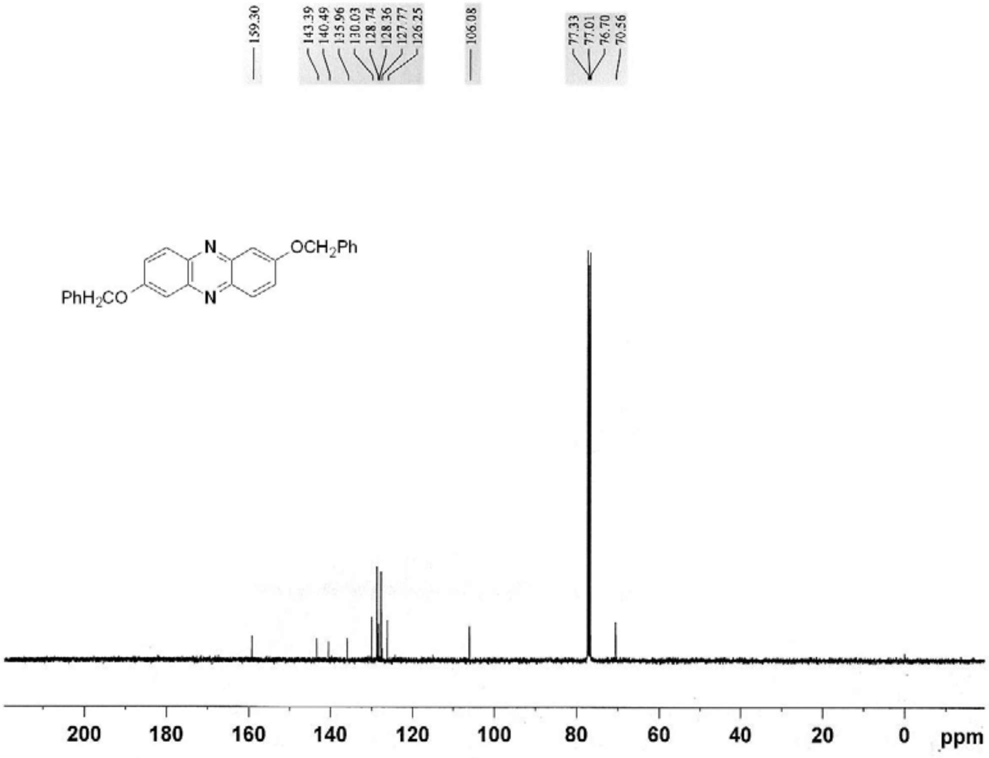
^{1}H NMR of 2,7-Dimethyl-phenazine (entry 2, Table 1):-



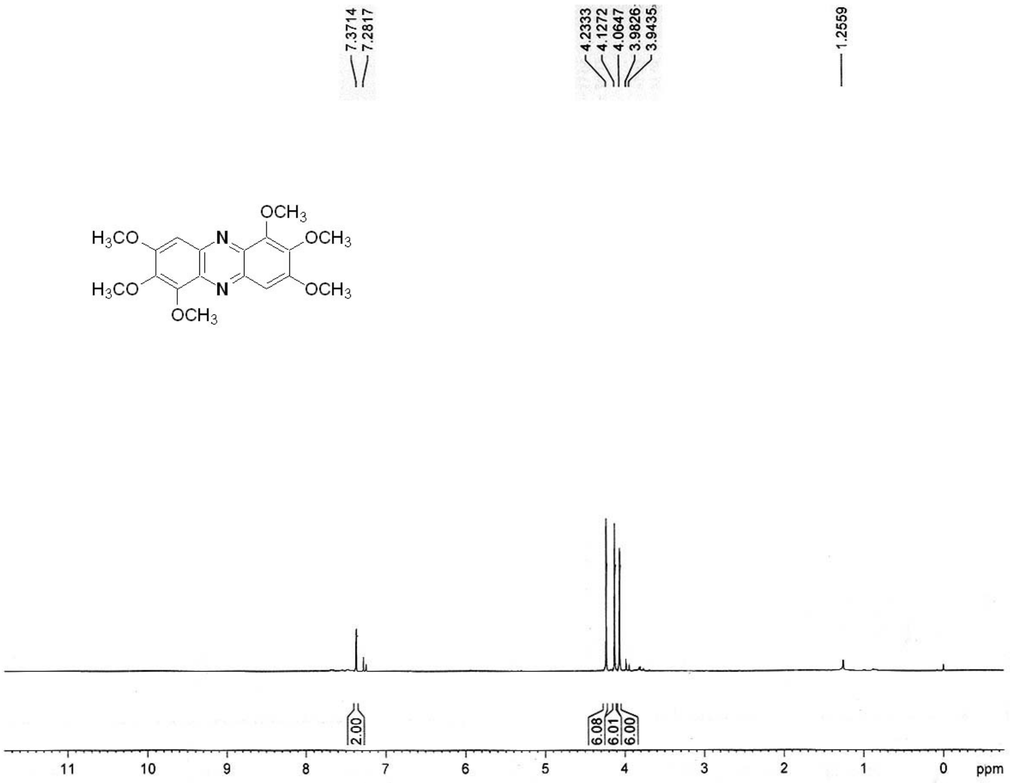
^{1}H NMR of 2,7-Bis-benzyloxy-phenazine (entry 3, Table 1):-



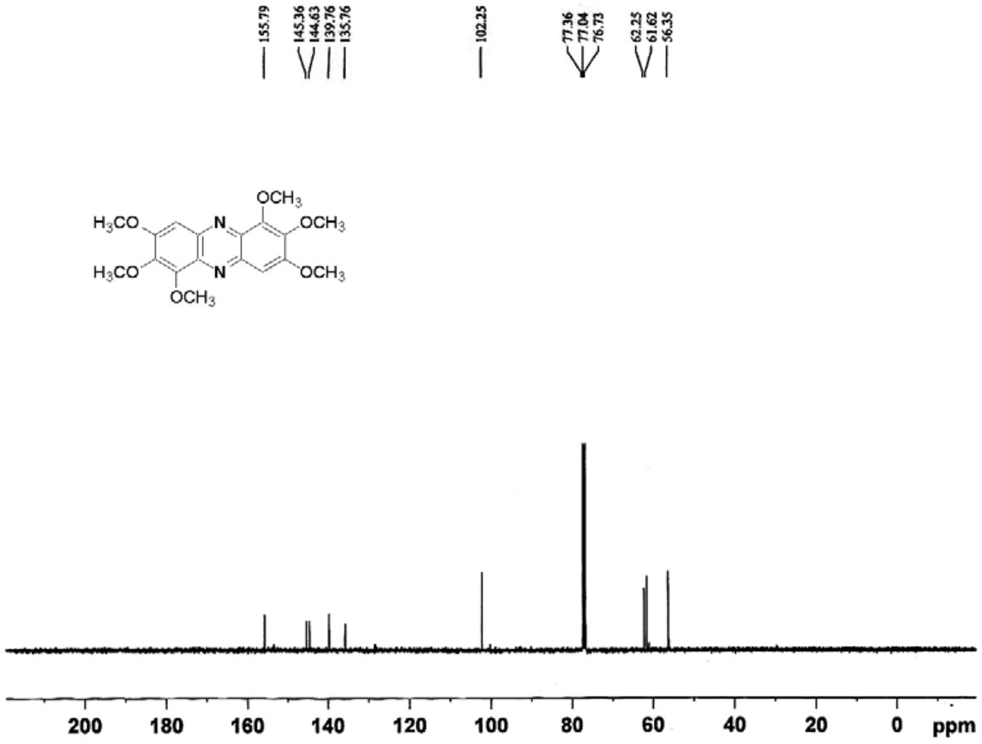
^{13}C NMR of 2,7-Bis-benzyloxy-phenazine (entry 3, Table 1):-



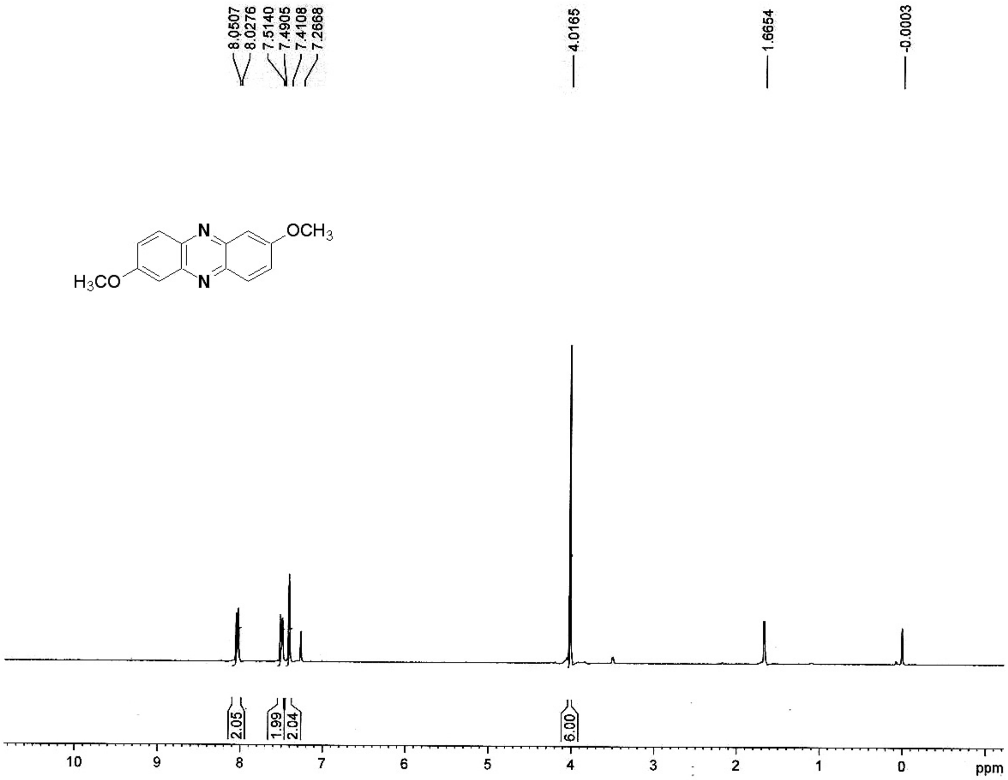
^{1}H NMR of 1,2,3,6,7,8-Hexamethoxy-phenazine (entry 4, Table 1):-



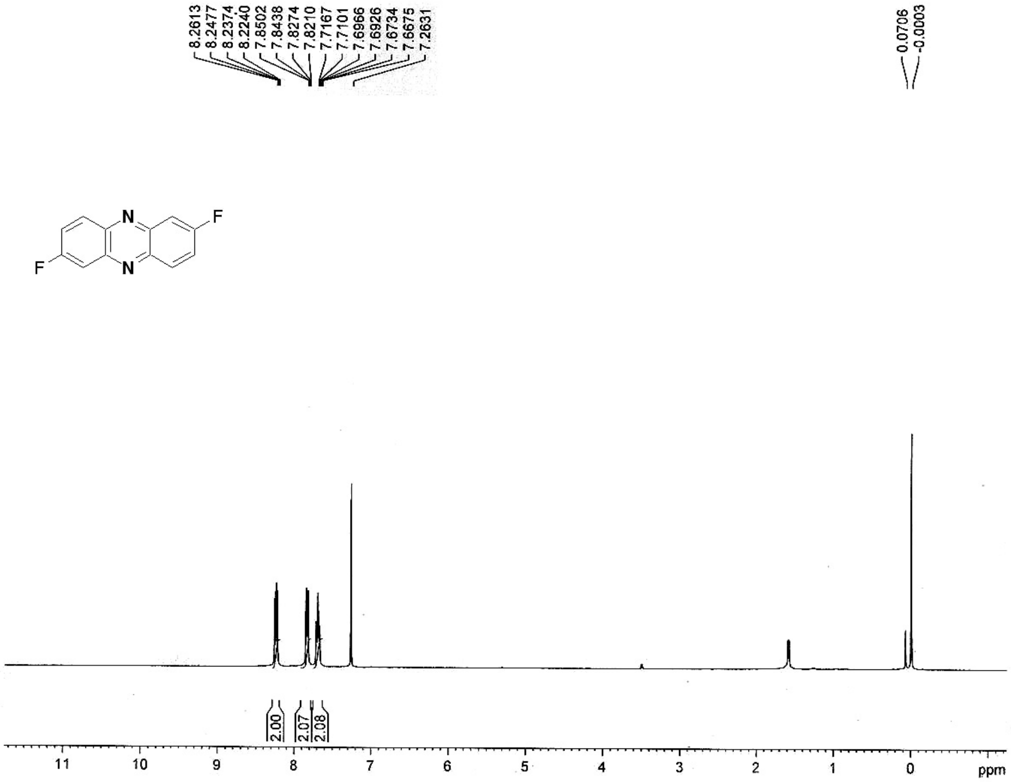
^{13}C NMR of 1,2,3,6,7,8-Hexamethoxy-phenazine (entry 4, Table 1):-



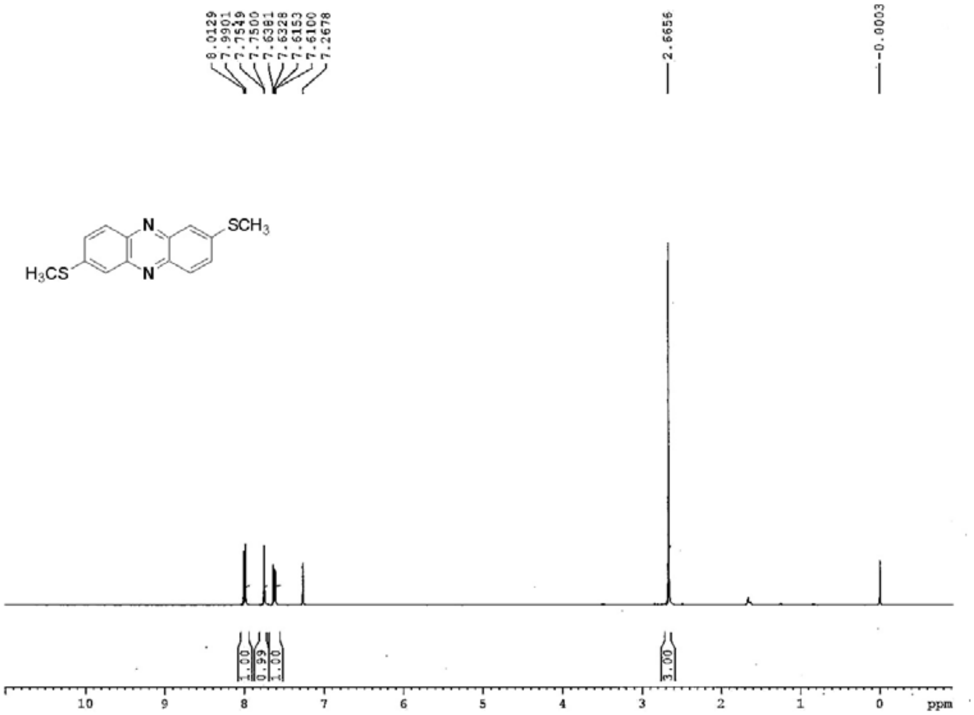
^{1}H NMR of 2,7-Dimethoxy-phenazine (entry 5, Table 1):-



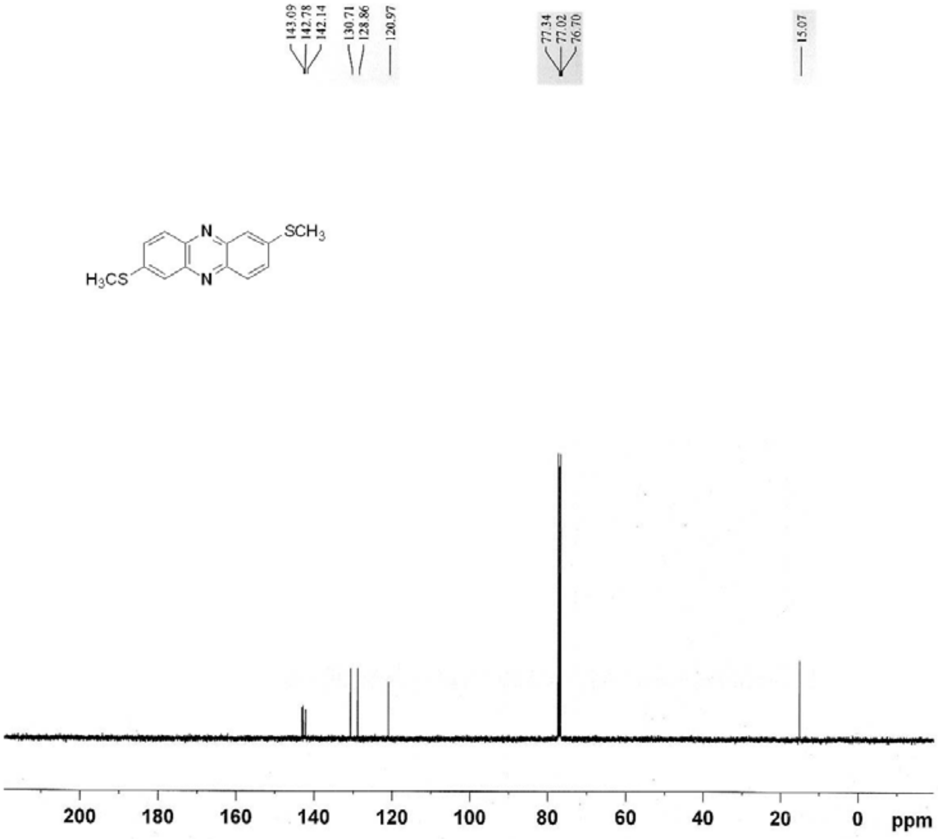
^{1}H NMR of 2,7-Difluoro-phenazine (entry 6, Table 1):-



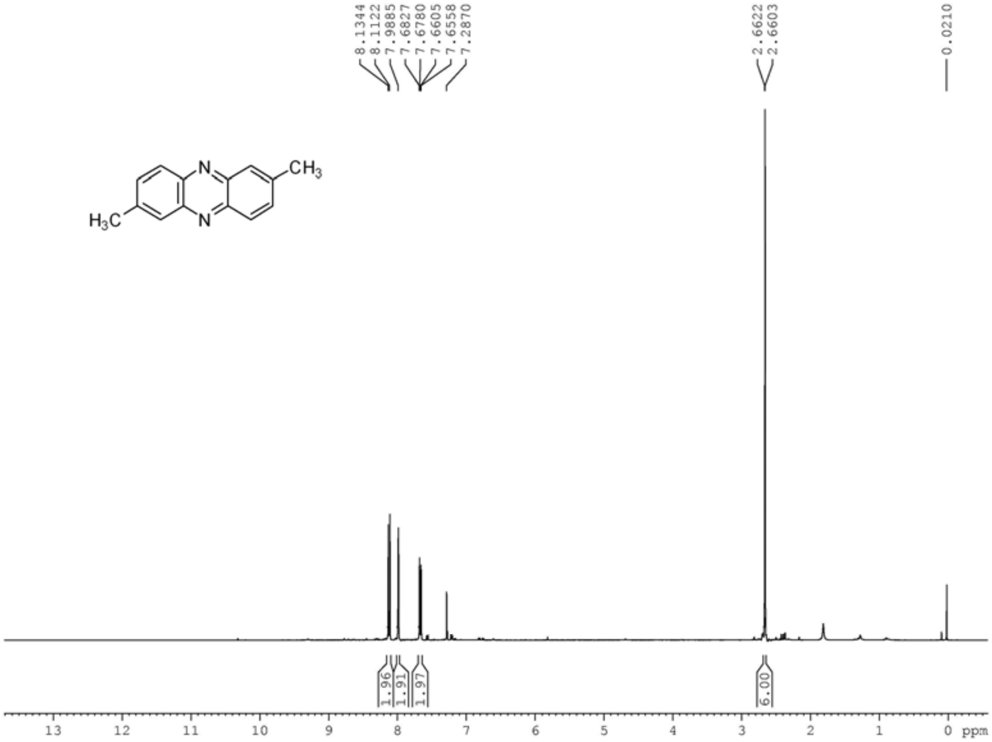
^{1}H NMR of 2,7-Bis-methylsulfanyl-phenazine (entry 7, Table 1):-



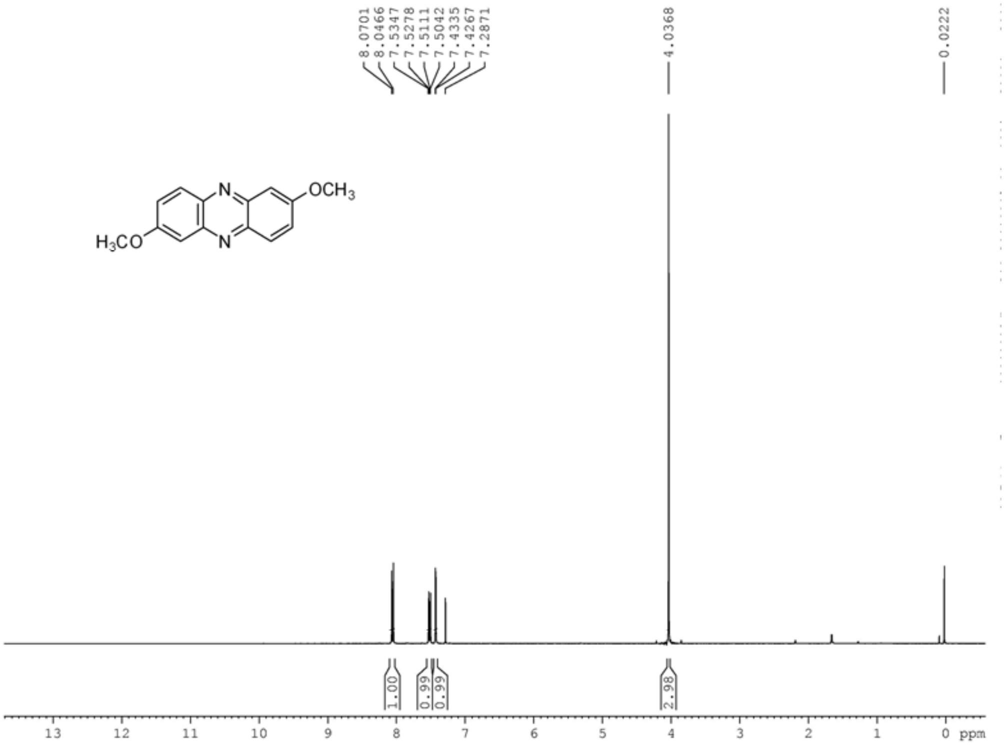
^{13}C NMR of 2,7-Bis-methylsulfanyl-phenazine (entry 7, Table 1):-



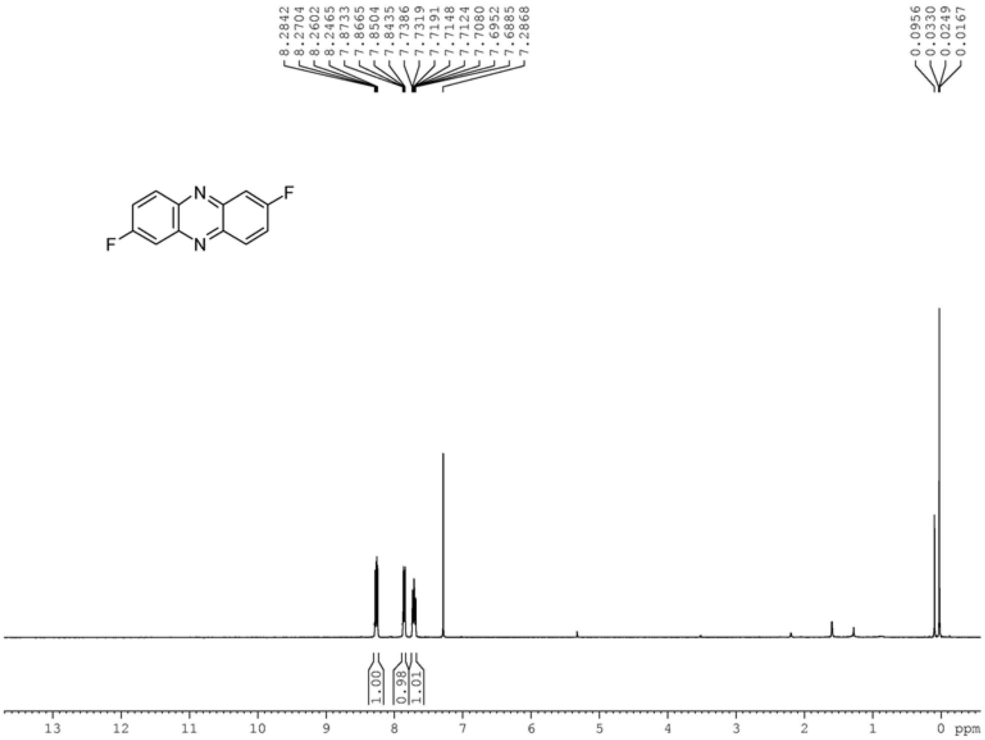
^{1}H NMR of 2,7-Dimethyl-phenazine (entry 8, Table 1):-



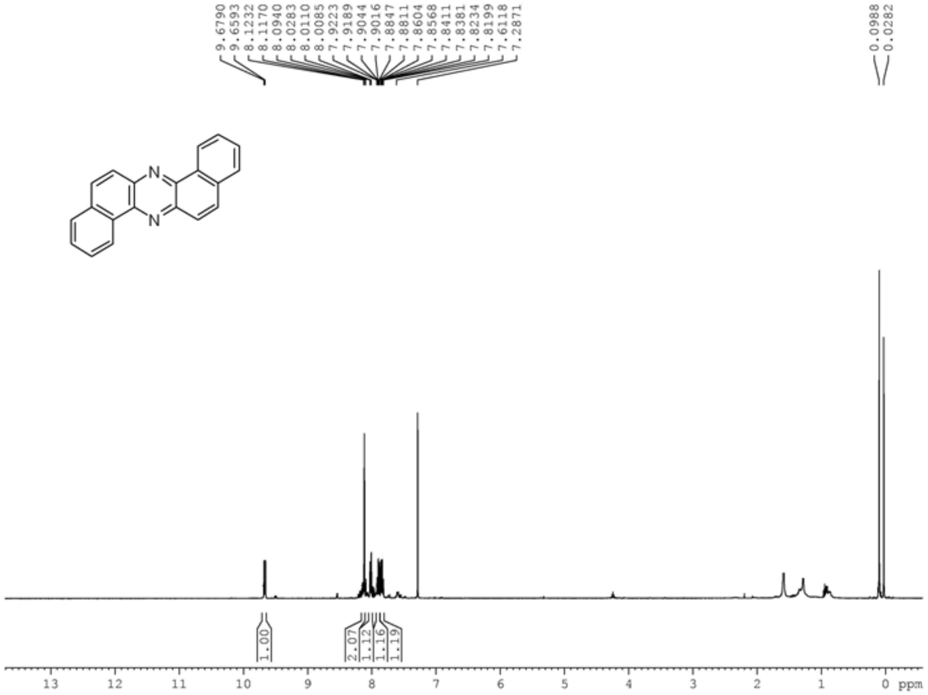
^{1}H NMR of 2,7-Dimethoxy-phenazine (entry 9, Table 1):-



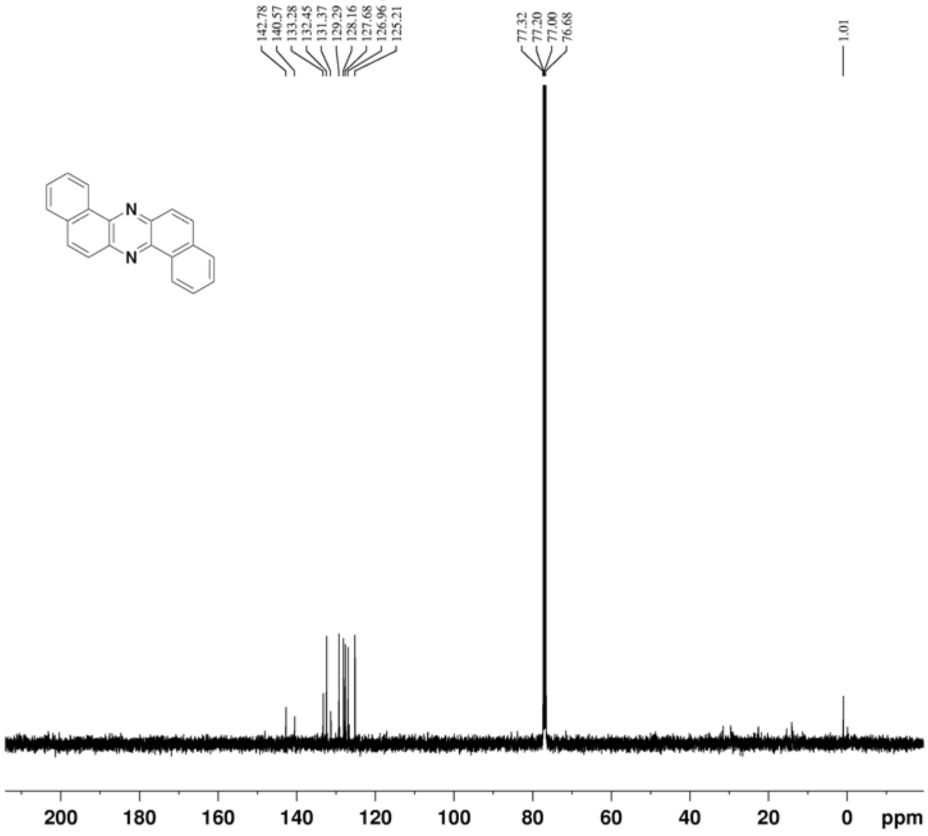
^{1}H NMR of 2,7-Difluoro-phenazine (entry 10, Table 1):-



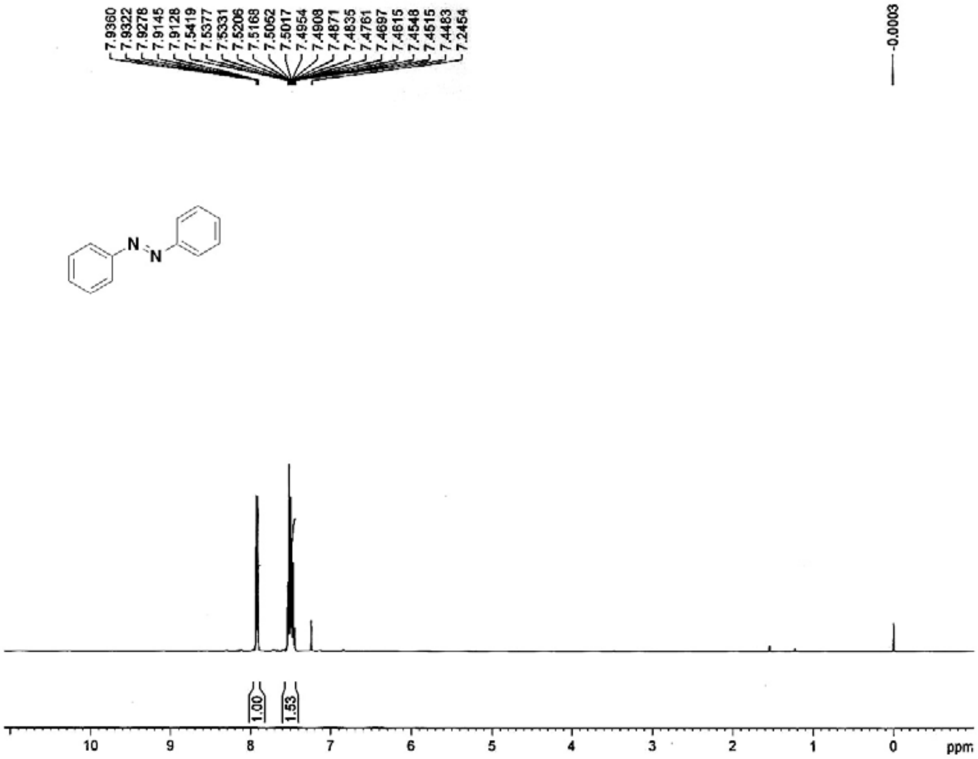
^{1}H NMR of Dibenzo[*a,h*]phenazine (entry 11, Table 1):-



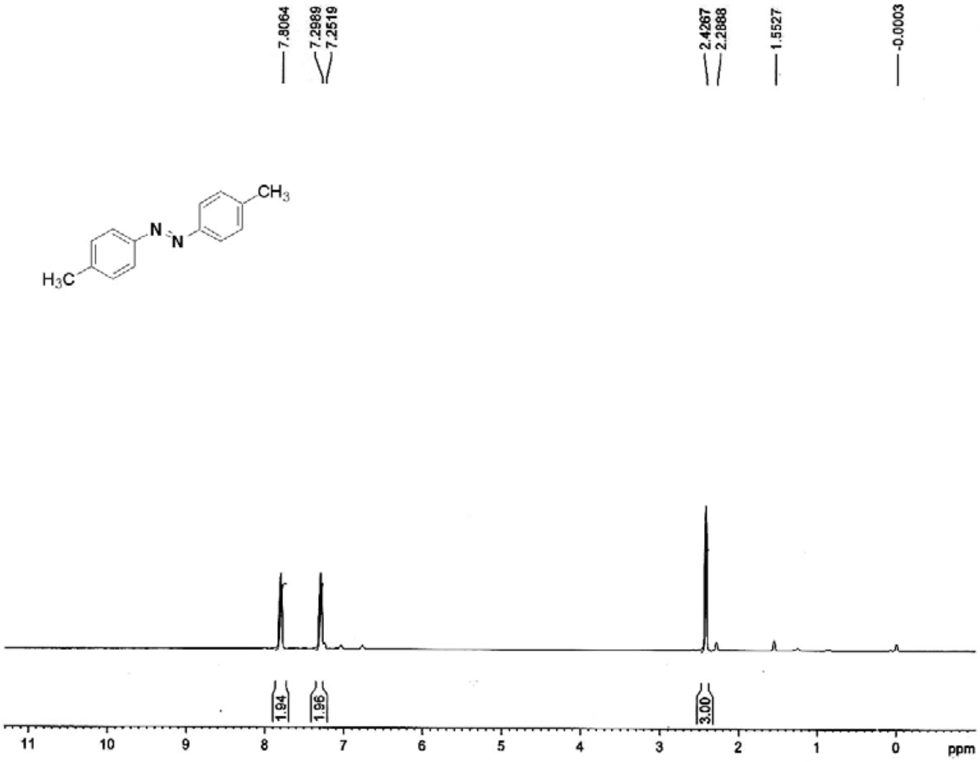
^{13}C NMR of Dibenzo[*a,h*]phenazine (entry 11, Table 1):-



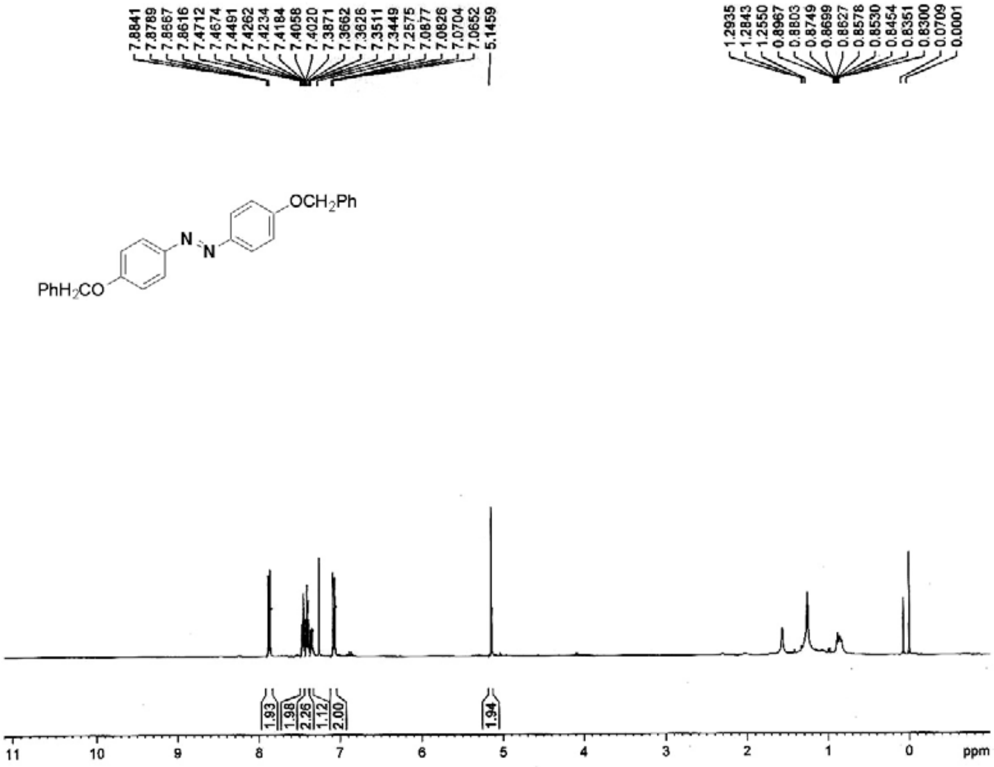
^{1}H NMR of Diphenyl-diazene (entry 1, Table 1, Footnote c):-



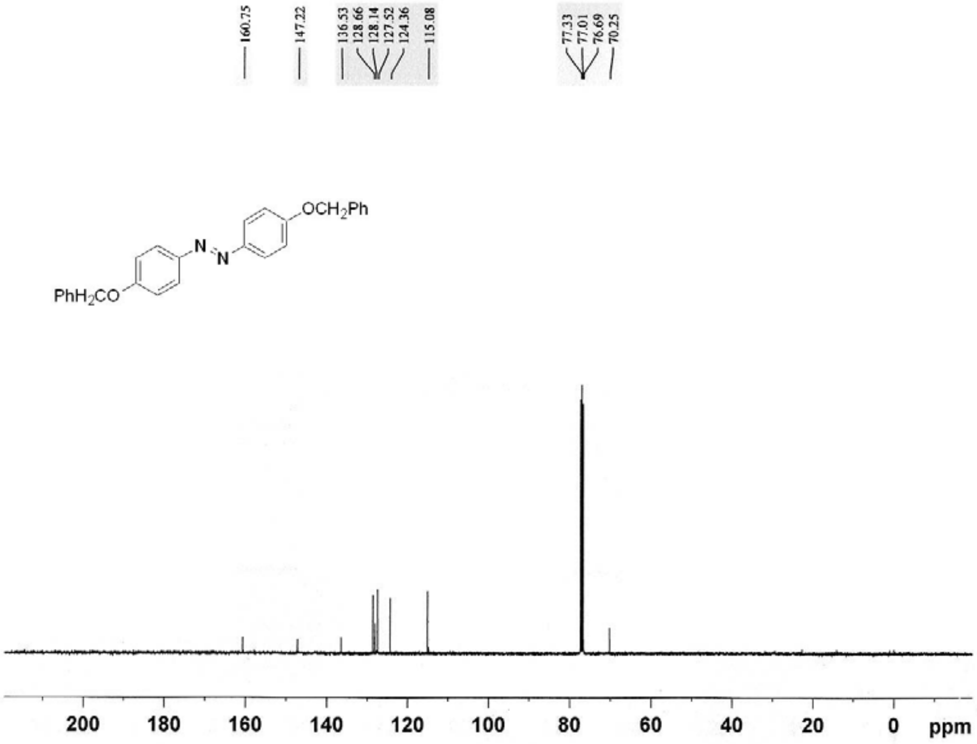
^{1}H NMR of Di-*p*-tolyl-diazene (entry 2, Table 1, Footnote c):-



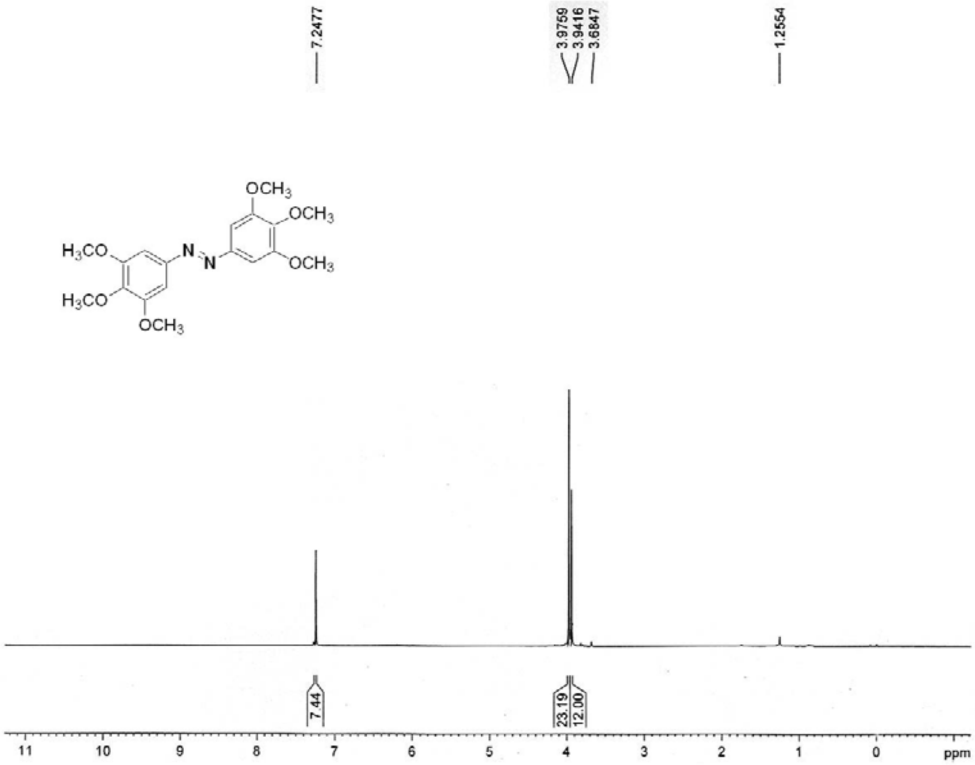
^{1}H NMR of Bis-(4-benzyloxy-phenyl)-diazene (entry 3, Table 1, Footnote c):-



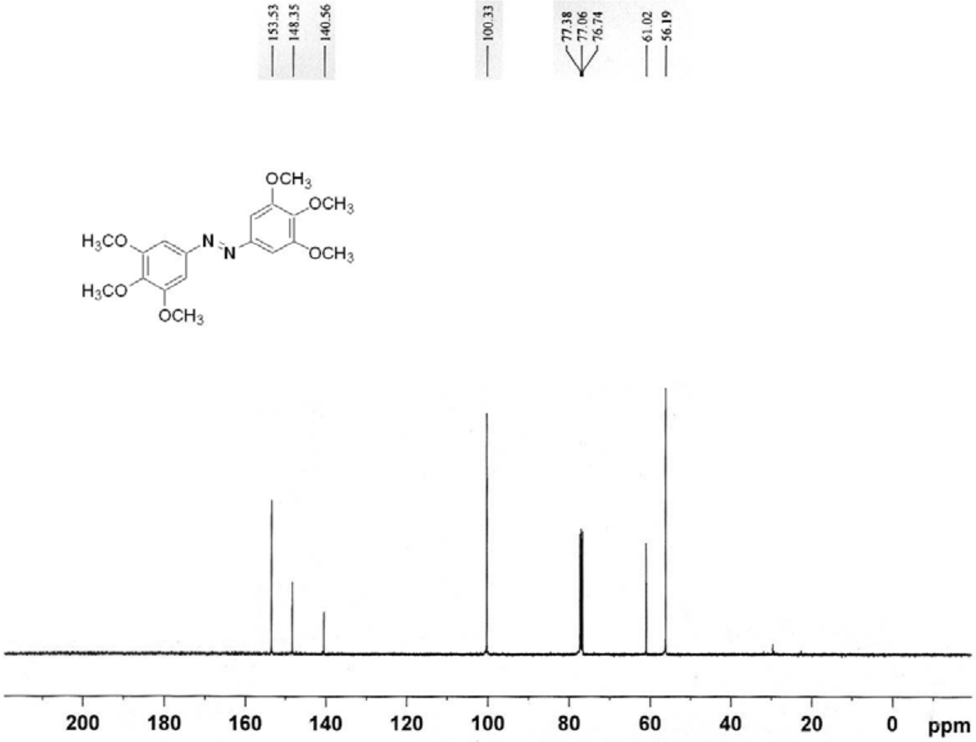
^{13}C NMR of Bis-(4-benzyloxy-phenyl)-diazene (entry 3, Table 1, Footnote c):-



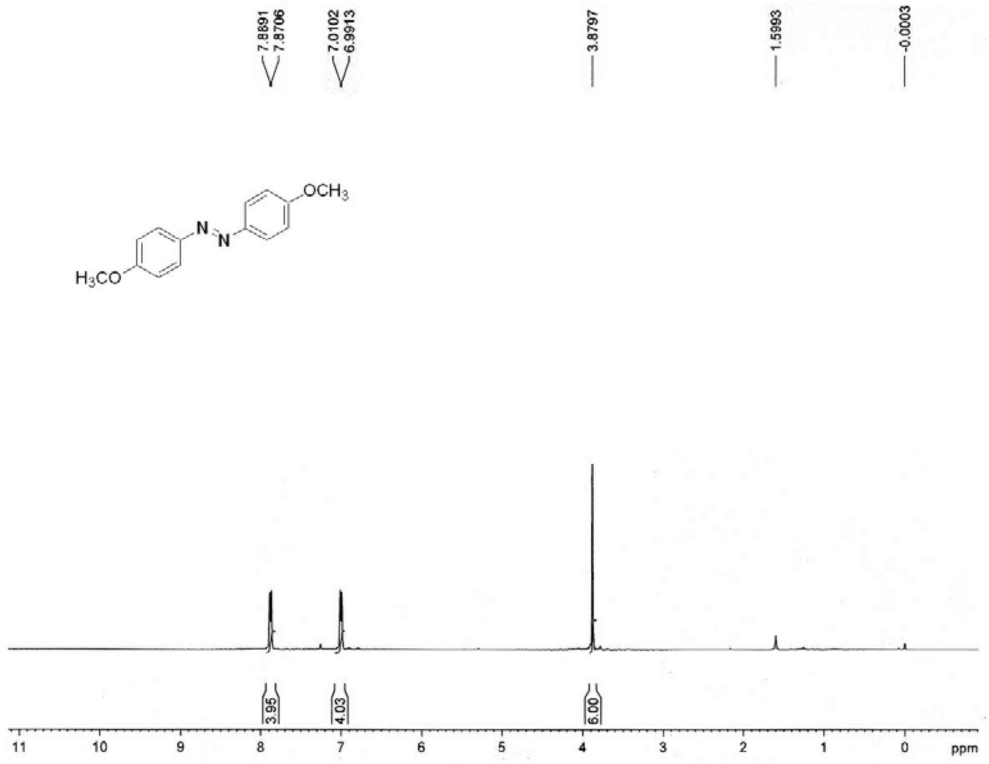
^{1}H NMR of Bis-(3,4,5-trimethoxy-phenyl)-diazene (entry 4, Table 1, Footnote c):-



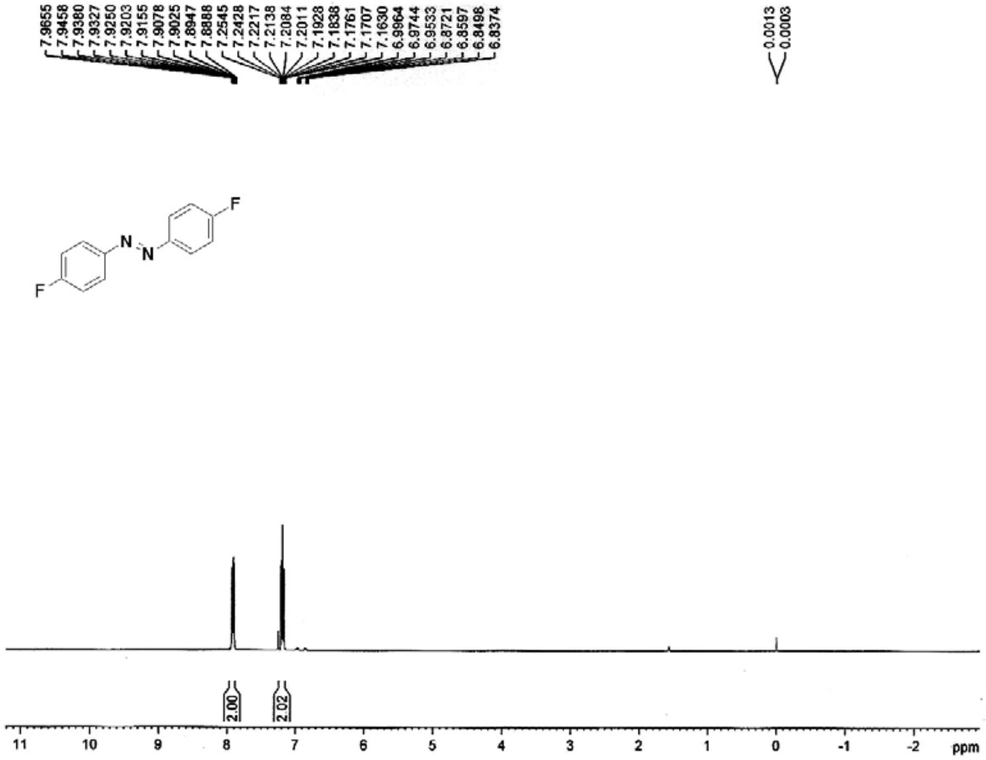
^{13}C NMR of Bis-(3,4,5-trimethoxy-phenyl)-diazene (entry 4, Table 1, Footnote c):-



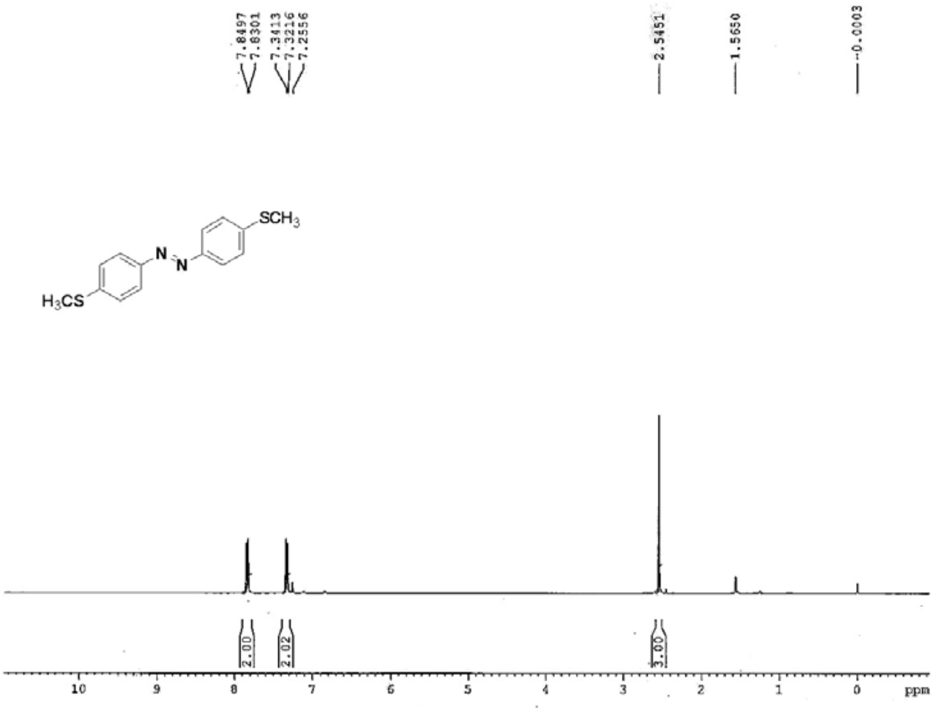
^{1}H NMR of Bis-(4-methoxy-phenyl)-diazene (entry 5, Table 1, Footnote c):-



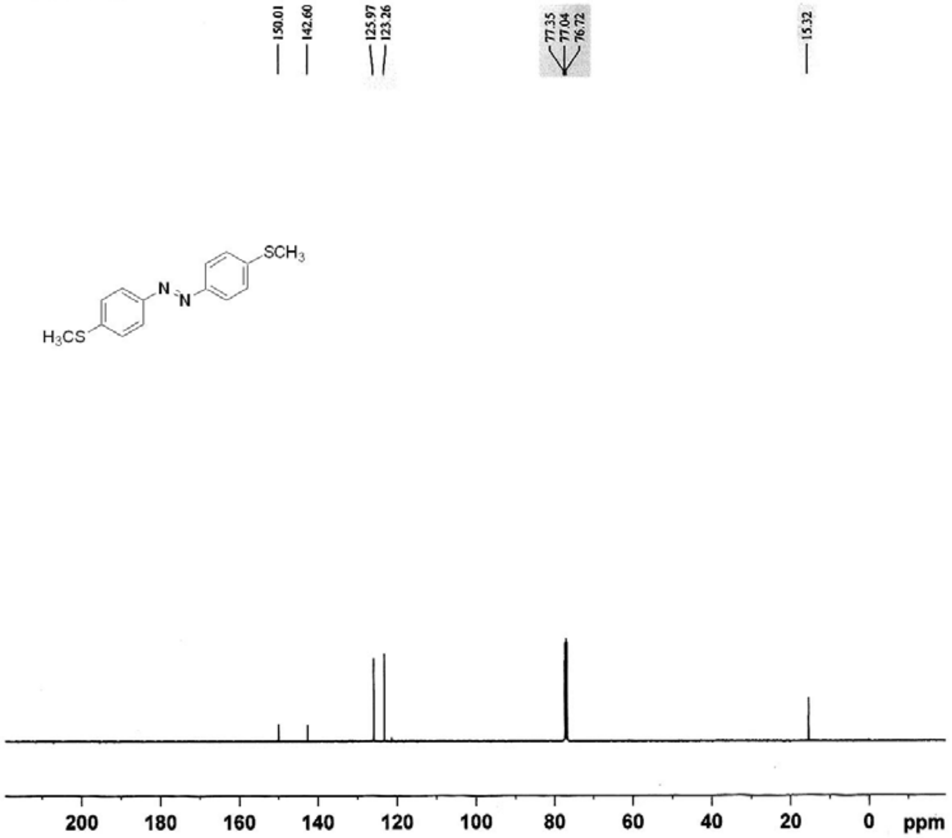
^{1}H NMR of Bis-(4-fluoro-phenyl)-diazene (entry 6, Table 1, Footnote c):-



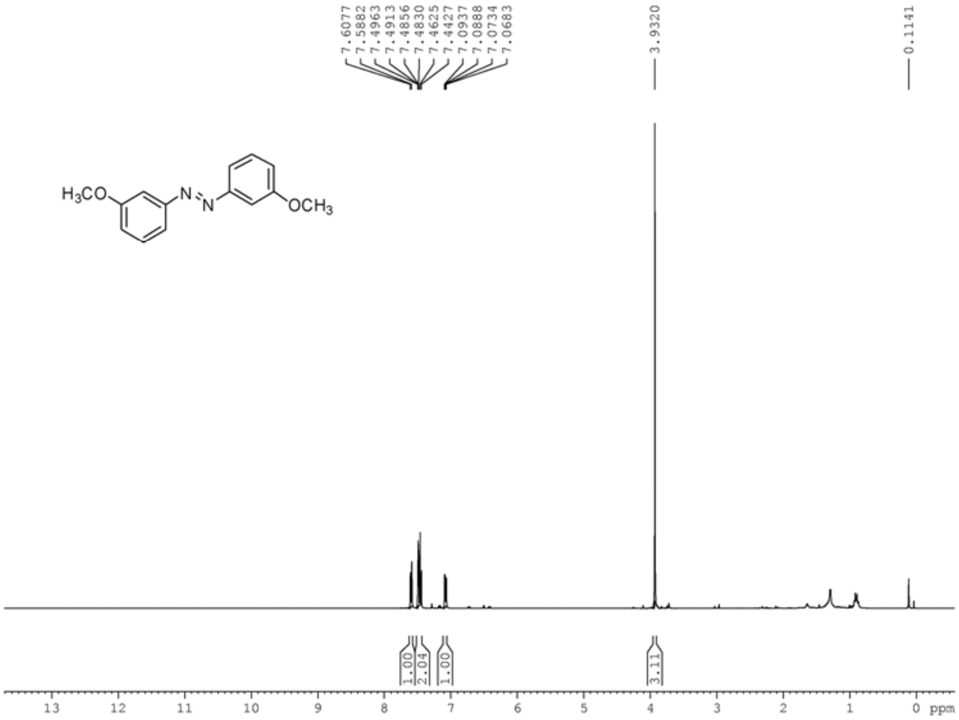
^{1}H NMR of Bis-(4-methylsulfanyl-phenyl)-diazene (entry 7, Table 1, Footnote c):-



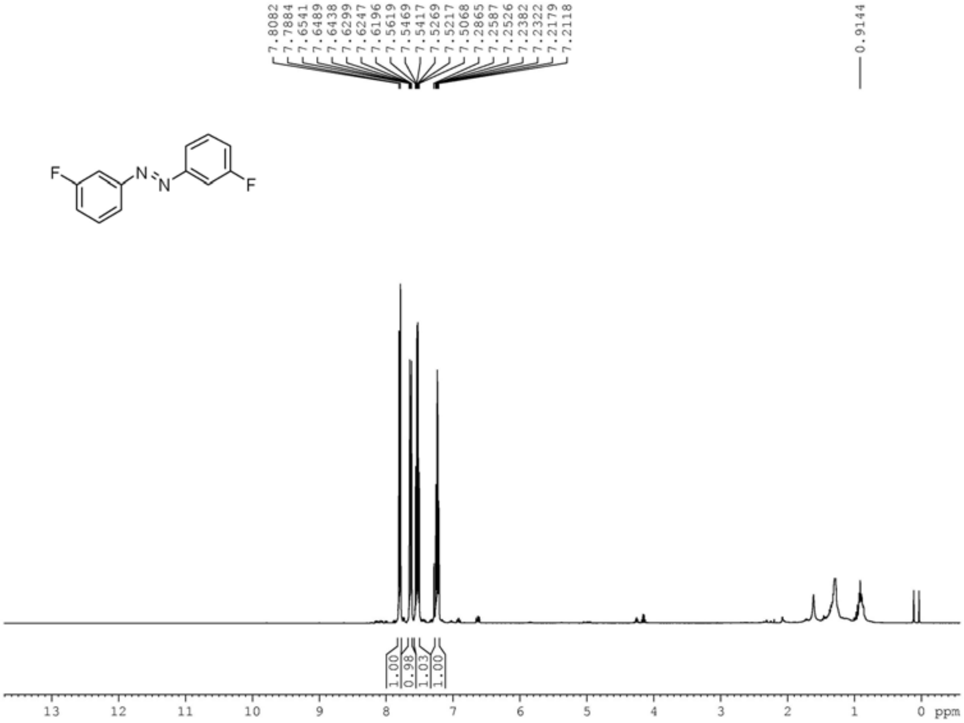
^{13}C NMR of Bis-(4-methylsulfanyl-phenyl)-diazene (entry 7, Table 1, Footnote c):-



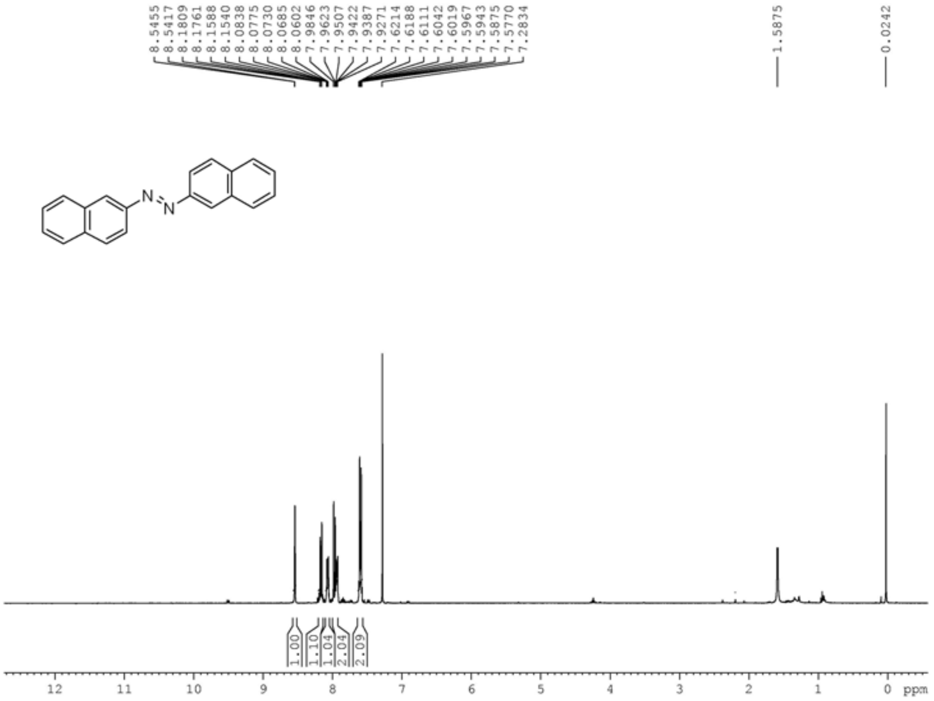
^{1}H NMR of (*E*)-1,2-Bis(3-methoxyphenyl)diazene (entry 9, Table 1, Footnote c):-



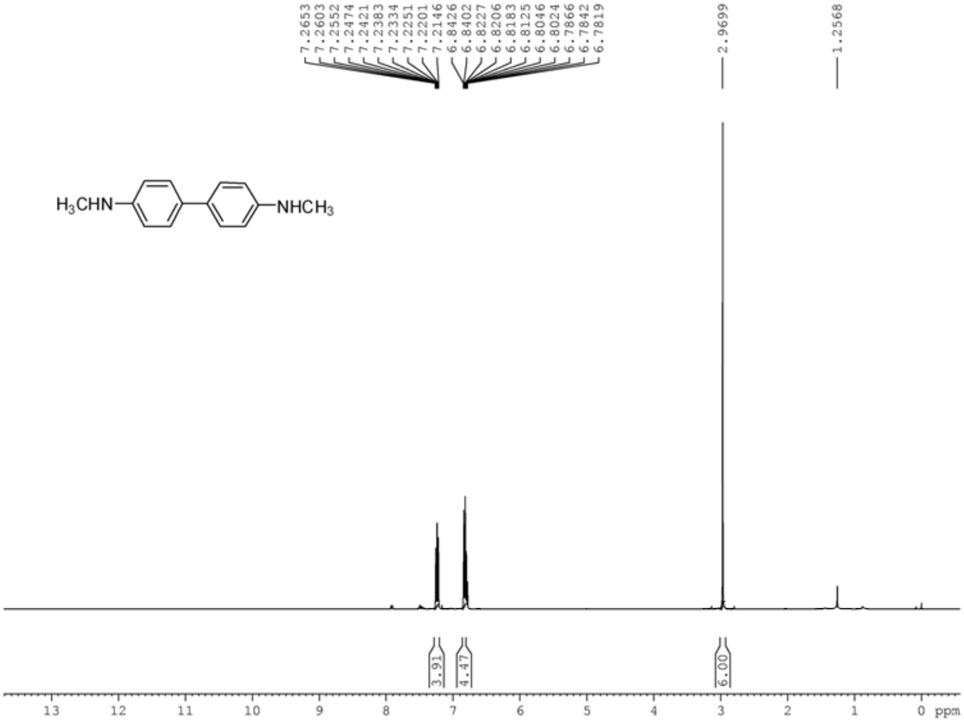
^{1}H NMR of (*E*)-1,2-Bis(3-fluorophenyl)diazene (entry 10, Table 1, Footnote c):-



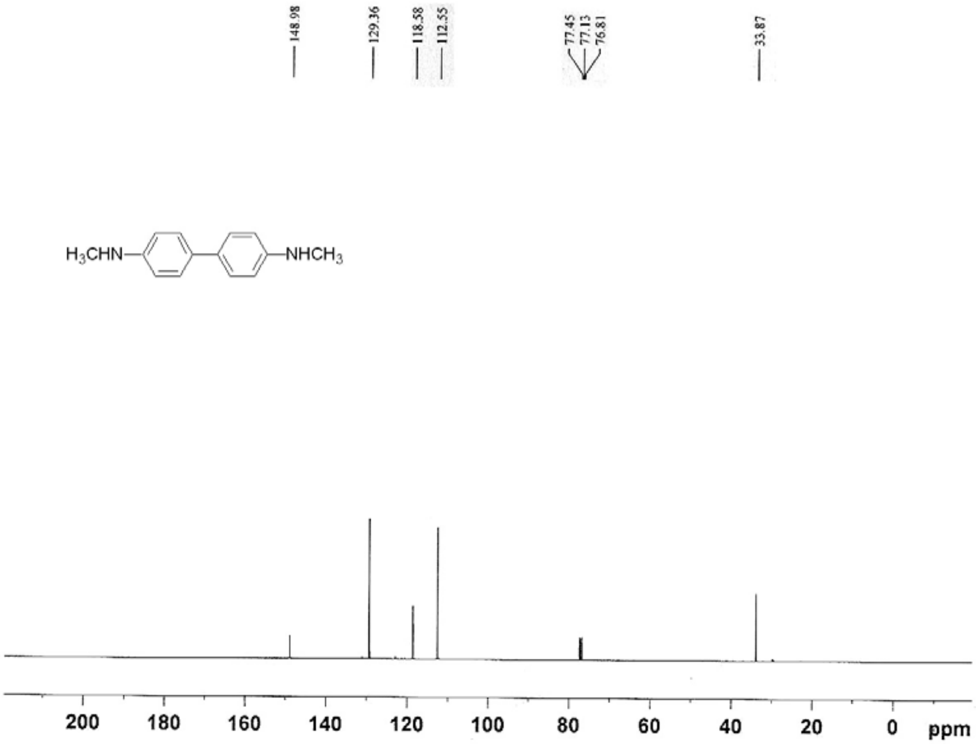
¹H NMR of Di-naphthalen-2-yl-diazene (entry 11, Table 1, Footnote c):-



^{1}H NMR of 4,4'-di-*N*-Methyl-biphenyl, 6 (*S*cheme 5):-



^{13}C NMR of 4,4'-di-*N*-Methyl-biphenyl, 6 (*S*cheme 5):-



VIII. References:

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