

## Supporting Information

For

### Magnetically recoverable catalytic Co-Co<sub>2</sub>B nanocomposites for the chemoselective reduction of aromatic nitro compounds

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#### General Methods:

Methanol, CoCl<sub>2</sub>.6H<sub>2</sub>O, sodium borohydride and ammonium sulphate were purchased from Spectrochem, India. The purity of ammonia borane was confirmed by IR and <sup>11</sup>B NMR spectroscopy. Co-Co<sub>2</sub>B nanocomposites were characterized by TEM (Morgagni 268D). The TEM samples were prepared by sonicating the nanomaterials in methanol for 5 min before loading on the copper TEM grid. Structural characterization of the catalyst was performed by conventional X-ray Diffraction (XRD, Rigaku, Ultima IV) using the Cu K $\alpha$  radiation ( $\lambda = 1.542\text{\AA}$ ) in Bragg-Brentano ( $\theta$ - $2\theta$ ) configuration. The BET surface area measurements were carried out using SMART SORB 91 surface area analyzer. The sample was degassed at room temperature for 12h and measurements were carried out by N<sub>2</sub> adsorption at 77 K. The NMR spectra of products were obtained using AVANCE BRUKER 400 MHz NMR spectrometer. The leaching test was carried using thermoscientific S-series AAS spectrometer. Purity of compound was based on GC analysis which was done using Nucon-5765 gas chromatograph on HP-5( crosslinked 5% pH ME siloxane) capillary column with N<sub>2</sub> as carrier gas and FID detector. The kinetic studies were performed by using Perkin-Elmer UV-Vis spectrometer. The time dependent IR spectra was recorded on Bruker IR spectrometer.

#### Purification and spectroscopic data:

- Column purification effected over short pad of silica gel (60-120 mesh, *Thomas Baker*) / neutral alumina (*s. d. fine*; brockmann grade) for selected compounds. The product obtained by both the reducing methods, using hydrazine hydrate as well as sodium borohydride were in acceptable purity based on their TLC with authentic samples and spectroscopic data, which is given below.
- <sup>1</sup>H NMR spectra was immediately recorded after reduction of aromatic nitro compounds are also given below:

**Aniline (2a):** Subjection of nitrobenzene (**1a**, 2 mmol, 246 mg) to both the reducing methods, using hydrazine hydrate as well as sodium borohydride afforded aniline (**2a**) as a colorless oil (silica gel;

hexanes/ethyl acetate: 95/5). **Isolated yield:** 175 mg, (94%, by Hydrazine method) and 119 mg, (64%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.09 (t,  $J = 7.6$  Hz, 2H), 6.7 (t,  $J = 8$  Hz, 1H), 6.63 (d,  $J = 7.6$  Hz, 1H), 2.96 (2H, br). Physical data (GC analysis, TLC, boiling point) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the authentic sample.

**2-Aminotoluene (2b):** Subjection of 2-nitrotoluene (**1b**, 2 mmol, 274.3 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded 2-Aminotoluene (**2b**) as a colorless oil (silica gel; hexanes/ethyl acetate: 80/20). **Isolated yield:** 204 mg, (94%, by Hydrazine method) and 146 mg, (68%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.16 (t,  $J = 7.6$  Hz, 2H), 6.84 (t,  $J = 7.6$  Hz, 1H), 6.77 (d,  $J = 7.6$  Hz, 1H), 3.57 (s, 2H), 2.27 (s, 3H). Physical data (boiling point, TLC) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the authentic sample.

**3-Aminotoluene (2c):** Subjection of 3-nitrotoluene (**1c**, 2 mmol, 274.3 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded 3-Aminotoluene (**2c**) as a colorless oil (silica gel; hexanes/ethyl acetate: 80/20). **Isolated yield:** 197 mg, (92%, by Hydrazine method) and 148 mg, (69%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14 (t,  $J = 7.2$  Hz, 1H), 6.68 (d,  $J = 7.2$  Hz, 1H), 6.57 (d,  $J = 8$  Hz, 2H), 3.54 (s, 2H), 2.35 (s, 3H). Physical data (boiling point, TLC) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the authentic sample.

**4-Aminotoluene (2d):** Subjection of 4-nitrotoluene (**1d**, 2 mmol, 274.3 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded 4-Aminotoluene (**2d**) as a crystalline colorless solid. **Melting range (uncorrected):** 43- 45 °C (silica gel; hexanes/ethyl acetate: 80/20). **Isolated yield:** 189 mg, (88%, by Hydrazine method) and 176 mg, (82%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.89 (d,  $J = 8$  Hz, 2H), 6.53 (d,  $J = 8$  Hz, 2H), 3.26 (bs, 2H), 2.16 (s, 3H). Physical data (melting point, TLC) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the authentic sample.

**4-Chloroaniline (2e):** Subjection of 4-chloro-nitrobenzene (**1e**, 2 mmol, 315 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded 4-Chloroaniline (**2e**) as a offwhite solid. **Melting range (uncorrected):** 68- 70 °C (silica gel; hexanes/ethyl acetate: 50/50). **Isolated yield:** 240 mg, (94%, by Hydrazine method) and 222 mg, (87%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12-7.14 (m, 2H), 6.61-6.64 (m, 2H), 3.59 (bs, 2H). Physical data (melting point, TLC) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the authentic sample.

**4-Aminobenzoic acid (2g):** Subjection of 4-Nitrobenzoic acid (**1g**, 2 mmol, 334.3 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded 4-Aminobenzoic acid (**2g**) as a colorless fluffy solid. **Melting range (uncorrected):** 183- 185 °C (silica gel; hexanes/ethylacetate: 50/50). **Isolated yield:** 208 mg, (76%, by Hydrazine method) and 206 mg, (75%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (d,  $J = 8.8$  Hz, 2H), 6.62 (d,  $J = 8.4$  Hz, 2H), 4.98 (bs, 2H). Physical data (melting point, TLC) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the authentic sample.

**4-(benzyloxy)aniline (2k):** Subjection of 1-(benzyloxy)-4-nitrobenzene (**1k**, 2 mmol, 485.5 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded 4-(benzyloxy)aniline (**2k**) as a light brown thick, viscous oil (silica gel; hexanes/ethyl acetate: 80/20). **Isolated yield:** quantitative conversion based on TLC, by Hydrazine method and 359 mg, (90%, by Sodium borohydride method).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33- 7.43 (m, 5H), 6.81 (d,  $J = 8.4$  Hz, 2H), 6.64 (d,  $J = 8.4$  Hz, 2H), 4.99 (s, 2H), 3.33-3.48 (br, 2H). Physical data (TLC) and spectral data ( $^1\text{H NMR}$ , IR) were in accordance with the reported authentic sample.

**Napthalene-1-amine (2l):** Subjection of 1-nitronapthalene (**1l**, 2 mmol, 346.4 mg) to both the reducing methods, using hydrazine as well as sodium borohydride afforded Napthalene-1-amine (**2l**) as a pale

yellow solid. **Melting range (uncorrected):** 48- 50 °C (silica gel; hexanes/ethyl acetate: 50/50). **Isolated yield:** 206 mg, (72%, by Hydrazine method) and 215 mg, (75%, by Sodium borohydride method). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.79- 7.82 (m, 2H), 7.44-7.46 (m, 2H), 7.24-7.31 (m, 2H), 6.76-6.78(m, 1H), 4.09- 4.14 (br, 2H). Physical data (melting point, TLC) and spectral data (<sup>1</sup>H NMR, IR) were in accordance with the authentic sample.

**9-Aminoanthracene (2m):** Subjection of 9-nitroanthracene (**1m**, 2 mmol, 446.3 mg) to both the reducing methods, using hydrazine as well as sodiumborohydride afforded **9-Aminoanthracene (2m)** as a thick turbid oil (silica gel; hexanes/ ethylacetate: 50/50 then chloroform/ethyl acetate: 50/50). **Isolated yield:** 193 mg, (50%, by Hydrazine method) and 174 mg, (45%, by Sodium borohydride method). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.66 (d, *J* = 6.8 Hz, 1H), 7.78-8.45 (m, 2H), 7.23-7.39 (m, 6H), 4.02 (s, 2H). Green color solution of sample in CDCl<sub>3</sub> was decomposed to yellow in NMR tube itself after 30 min of isolation. Physical data (TLC) and spectral data (<sup>1</sup>H NMR, IR) were in accordance with the authentic sample.

**4-Aminobenzonitrile (2y):** Subjection of 4-nitrobenzonitrile (**1w**, 2 mmol, 296 mg) to the reducing method, using hydrazine afforded **4-Aminobenzonitrile (2y)** as a bright orange crystalline solid. **Melting range (uncorrected):** 84- 85 °C (neutral alumina; methanol/chloroform: 20/80). **Isolated yield:** 165 mg, (70%, by Hydrazine method). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.42 (d, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 7.2 Hz, 2H), 4.23 (s, 2H). Physical data (melting point, TLC) and spectral data (<sup>1</sup>H NMR, IR) were in accordance with the authentic sample.

**Reduction of 1-nitro-4-(prop-2-ene-1-yloxy) benzene (1t) (by sodium borohydride method):**

Subjection of **1-nitro-4-(prop-2-ene-1-yloxy) benzene (1t)**, 2 mmol, 358.3 mg) to reduction protocol according to general procedure afforded clear, colorless oil (silica gel; hexanes/ethyl acetate: 80/20). **Isolated yield:** 319 mg, (90%, by Sodium borohydride method). Based on <sup>1</sup>H NMR experiment (**Figure S9**, <sup>1</sup>H NMR spectrum of **2r** and **1t**.) along with trace of starting nitro compound (**1t**), selectively O-allylated terminal C-C double bond reduction took place keeping nitro group intact giving, **1-nitro-4-propoxybenzene (2r)**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21(d, *J* = 7.6 Hz, 2H), 6.95-7.0 (m, 2H), 4.03 (t, 2H), 1.85-1.9 (m, 2H), 1.08 (t, 3H).

**Reduction of 1-nitro-4-(prop-2-ene-1-yloxy) benzene (1t) (by hydrazine hydrate method):**

Subjection of **1-nitro-4-(prop-2-ene-1-yloxy) benzene (1t)**, 2 mmol, 358.3 mg) to reduction protocol according to general procedure afforded clear, colorless oil and without further purification <sup>1</sup>H NMR was recorded. **Yield:** 358 mg, (95% by Hydrazine method). Based on <sup>1</sup>H NMR experiment (**Figure S10**, <sup>1</sup>H NMR spectrum of **2p** and **2q**.) selectively nitro group was reduced under the reaction condition giving **4-(prop-2-en-1-yloxy) aniline (2p)** as major product along with **4-propoxyaniline (2q)** in (**92:8**) ratio. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.79 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.02-6.11 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 4.8 Hz, 2H) 3.47- 3.48 (br, 2H).

**Reduction of 1-nitro-4-(prop-2-ene-1-yloxy) benzene (1t) (by in situ generated equivalent amount of CoB/Sodium borohydride method) :**

Subjection of **1-nitro-4-(prop-2-ene-1-yloxy)benzene (1t)**, 2 mmol, 358.3 mg) to reduction protocol according to general procedure afforded clear, colorless oil and without further purification <sup>1</sup>H NMR was recorded. Based on <sup>1</sup>H NMR experiment (**Figure S16**, <sup>1</sup>H NMR spectrum of **2q**) no selectivity in reduction of nitro group of **1t** was observed when CoCl<sub>2</sub>/NaBH<sub>4</sub> (2:10) mixture was employed as reported and yielded only **4-propoxyaniline (2q)** as product. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.66 (d, *J* = 3.2 Hz, 2H), 6.59 (d, *J* = 3.2 Hz, 2H), 3.77 (t, 2H), 3.347- 3.438 (br, 2H), 1.65- 1.74 (m, 2H), 0.94 (t, 3H).

**Reduction of 1-nitro-4-(prop-2-ene-1-yloxy)benzene (1t) (by equivalent amount of CoB/Hydrazine hydrate method):**

After separately preparing CoB and washing it with water followed by methanol several times, the subjection of **1-nitro-4-(prop-2-ene-1-yloxy) benzene (1t)**, 2 mmol, 358.3 mg) over these CoB particles to reduction protocol according to general procedure using hydrazine as a hydrogen source afforded a clear, colorless oil and without further purification  $^1\text{H}$  NMR was recorded. Based on  $^1\text{H}$  NMR experiment (**Figure S17**,  $^1\text{H}$  NMR spectrum of **2p** when CoB/ $\text{N}_2\text{H}_4$  was employed in the reduction of **1t**) selectively nitro group was reduced under the reaction condition giving **4-(prop-2-en-1-yloxy) aniline (2p)**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.76 (d,  $J = 4.8$  Hz, 2H), 6.64 (d,  $J = 6.8$  Hz, 2H), 6- 6.09 (m, 1H), 5.41 (d,  $J = 1.6$  Hz, 1H), 5.37 (d,  $J = 1.2$  Hz, 1H), 4.46 (d,  $J = 5.6$  Hz, 2H), 3.44 (br, 2H).

**$^1\text{H}$  NMR spectrum of isolated azo intermediate, diphenyldiazene (Figure S11).**

During later part of recyclability studies, we could isolate an azo intermediate while carrying out reduction of nitrobenzene with general procedure as orange flakes. **Melting range (uncorrected):** 62-68 °c (silica gel; hexanes/ethyl acetate: 80/20).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (d,  $J = 7.2$  Hz, 2H), 7.49- 7.57 (m, 3H). **LCMS** is also given (**Figure S19**, LC-MS of azobenzene (a reaction intermediate) Peak at **m/z 182.9** corresponds to azobenzene). Physical data (melting point, TLC) and spectral data ( $^1\text{H}$  NMR, IR) were in accordance with the authentic sample.

**Reduction of p-nitroacetophenone (1u) (by hydrazine hydrate method):**

Subjection of **p-nitroacetophenone (1u)**, 2 mmol, 230.3 mg) to reduction protocol according to general procedure afforded yellow solid. **Yield:** 205 mg, (74%, by Hydrazine method). Without further purification  $^1\text{H}$  NMR was recorded. Based on  $^1\text{H}$  NMR experiment (**Figure S12**,  $^1\text{H}$  NMR spectrum of **2s** and **2u**.) under the reaction condition we obtained **1-(4-aminophenyl)ethanone (2s)** along with the adduct formed with the hydrazine (**2u**) in (**2:1**) ratio respectively.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 7.6$  Hz, 2H), 6.65 (t,  $J = 7.2$  Hz, 2H), 4.24 (bs, 2H), 2.51(s, 3H).

**Reduction of 2-nitrobenzaldehyde (1v) (by hydrazine hydrate method):**

Subjection of **2-nitrobenzaldehyde (1v)**, 2 mmol, 302 mg) to reduction protocol according to general procedure afforded solid brown flakes. **Yield:** 207 mg, (90%, by Hydrazine method). Without further purification  $^1\text{H}$  NMR was recorded. Based on  $^1\text{H}$  NMR experiment (**Figure S13**,  $^1\text{H}$  NMR spectrum of **2w**.) under the reaction condition we obtained an adduct of hydrazine, **2-(hydrazinylidinemethyl)-aniline (2w)**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.75 (s, 1H), 7.2-7.3 (m, 2H), 6.77 (t,  $J = 4.4$  Hz, 2H), 6.25 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.2, 146.2, 133.9, 131.6, 116.6, 115.8, 115.7.

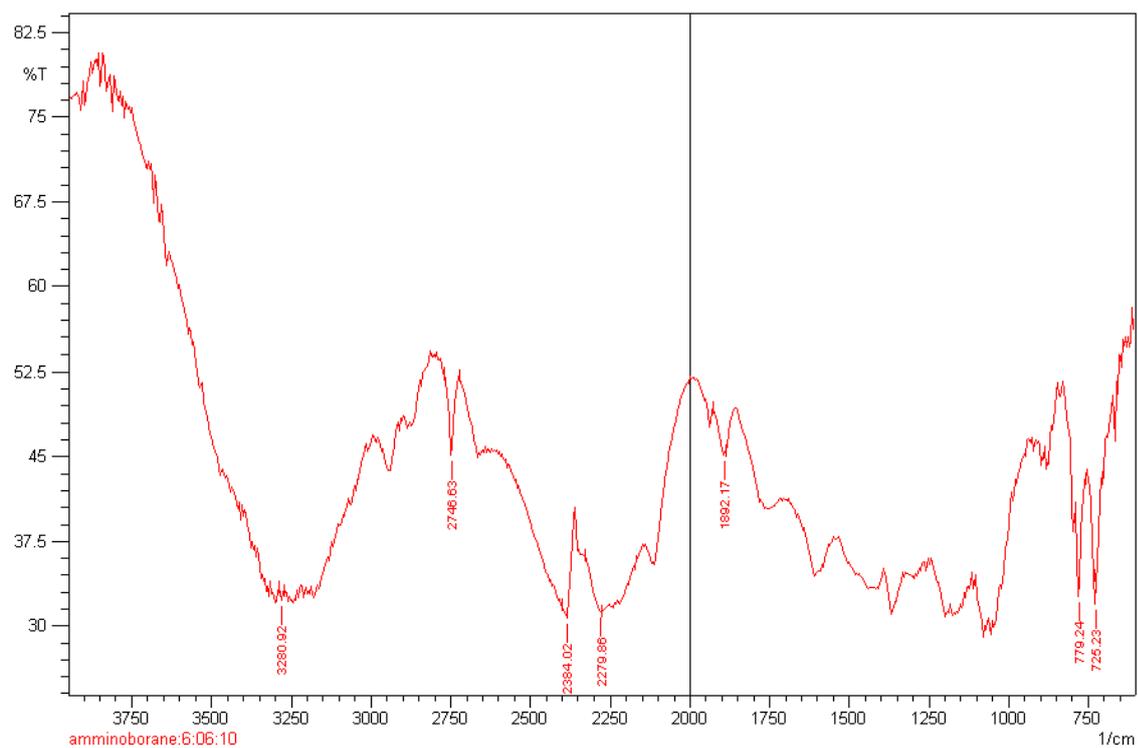


Figure S1. IR spectrum of Ammonia borane

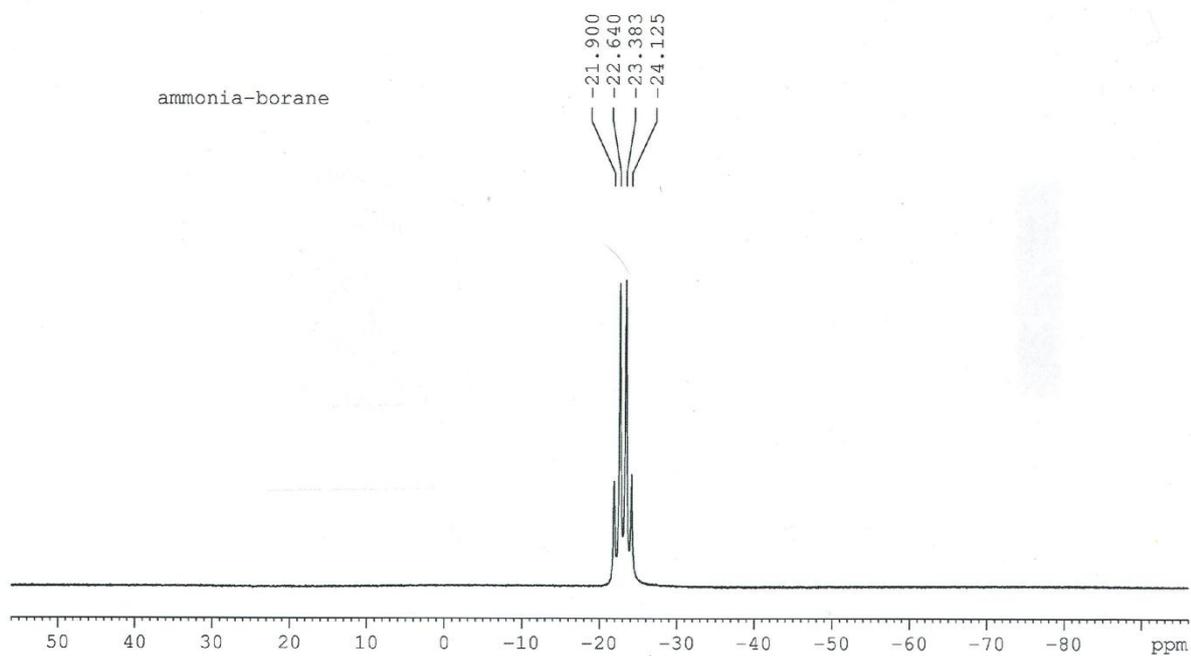
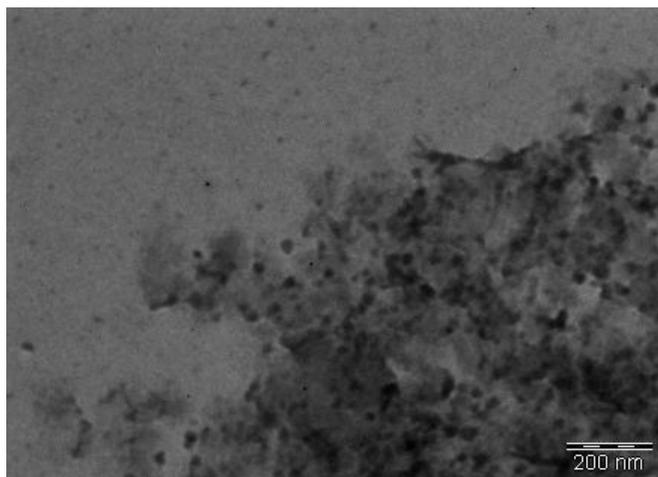
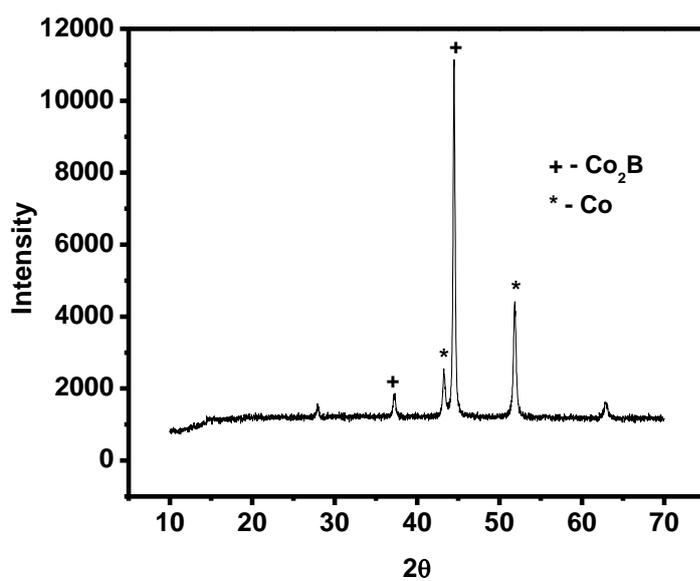


Figure S2. <sup>11</sup>B NMR spectrum of Ammonia boarne



**Figure S3.** TEM image of as prepared Co-Co<sub>2</sub>B nanocomposites (scale bar shows 200 nm).



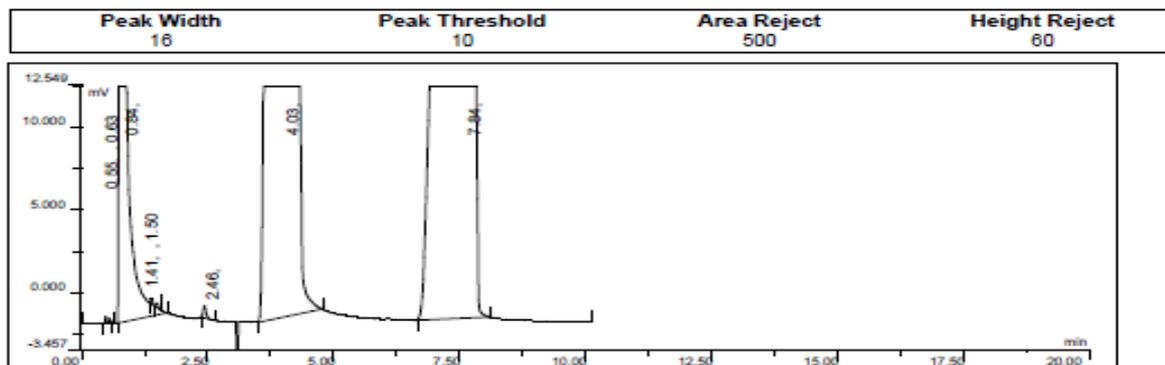
**Figure S4.** X-ray diffraction (XRD) pattern of Co-Co<sub>2</sub>B nanocomposites after annealing at 350°C for 12h in N<sub>2</sub> atmosphere.

## GC Analysis

**GC Instrument-** Nucon-5765 gas chromatogram  
**GC column-** HP-5(crosslinked 5% pH ME siloxane)  
 15m x 0.53mm x 1.5µm film thickness.  
**Carrier gas-** Nitrogen gas (N<sub>2</sub>)  
**Detector-**FID  
**Oven temperature-** 100 °c  
**Injector temperature-** 130 °c  
**Detector temperature-** 160 °c

	Retention time
Methanol	0.84
Aniline	4.03
Nitrobenzene	7.84

**Data File :** E:\sagar\0002.Dat  
**Method File :** FID.MET  
**Sample Name :** Sample1  
**Detector :** FID  
**System :** GC  
**Run Date :** 9/3/2012  
**Analysis Type :** Percent Method  
**Time :** 8:33:50 PM  
**Chan No :** Chan 1



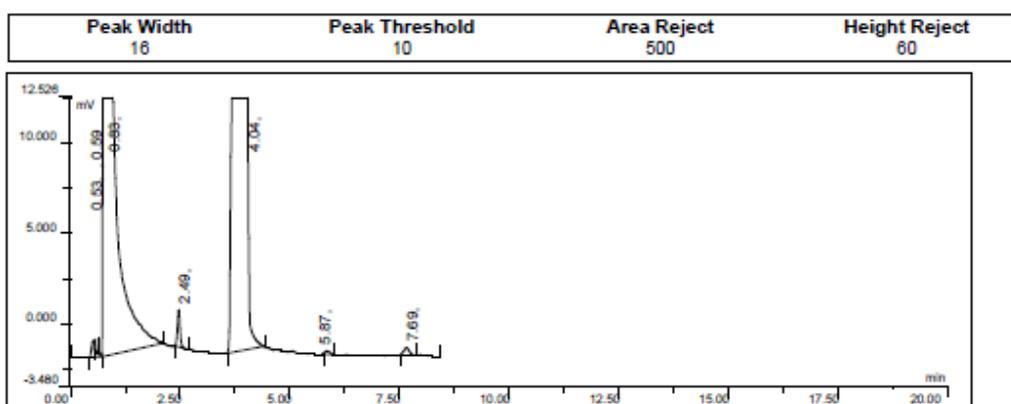
AREA%, HEIGHT %							
Sr. No.	Component Name	Ret. Time.	Area µ Volt Sec	Area %	Height µ Volt	Height %	Peak Type
1		0.55	930.9143	5.823E-03	251	0.04	BP
2		0.63	0.0000	0.00	97	0.01	PB
3		0.84	1559139.4857	9.75	285222	39.89	BB
4		1.41	980.1714	6.131E-03	348	0.05	TTP
5		1.50	706.2857	4.418E-03	234	0.03	TPT
6		2.46	3326.2857	0.02	748	0.10	BB
7		4.03	9626197.0857	60.21	284868	39.84	BB
8		7.84	4795548.2857	30.00	143177	20.03	BB
			<b>15986828.5143</b>	<b>100.00</b>	<b>714948</b>	<b>100.00</b>	

### SUMMARY

**Total Peaks :** 8  
**Multiplication Factor :** 1.0000  
**Sample Amount :** 100.0000  
**Dilution Factor :** 1.0000  
**Syssuit Standards :** IP  
**ISTD Amount :** 0.0

Gas chromatogram of authentic commercially available aniline and nitrobenzene in methanol.

Data File : E:\sagar\004.Dat  
 Method File : FID.MET  
 Sample Name : Sample1  
 Detector : FID  
 System : GC  
 Run Date : 9/3/2012  
 Analysis Type : Percent Method  
 Time : 8:59:16 PM  
 Chan No : Chan 1



AREA%, HEIGHT %

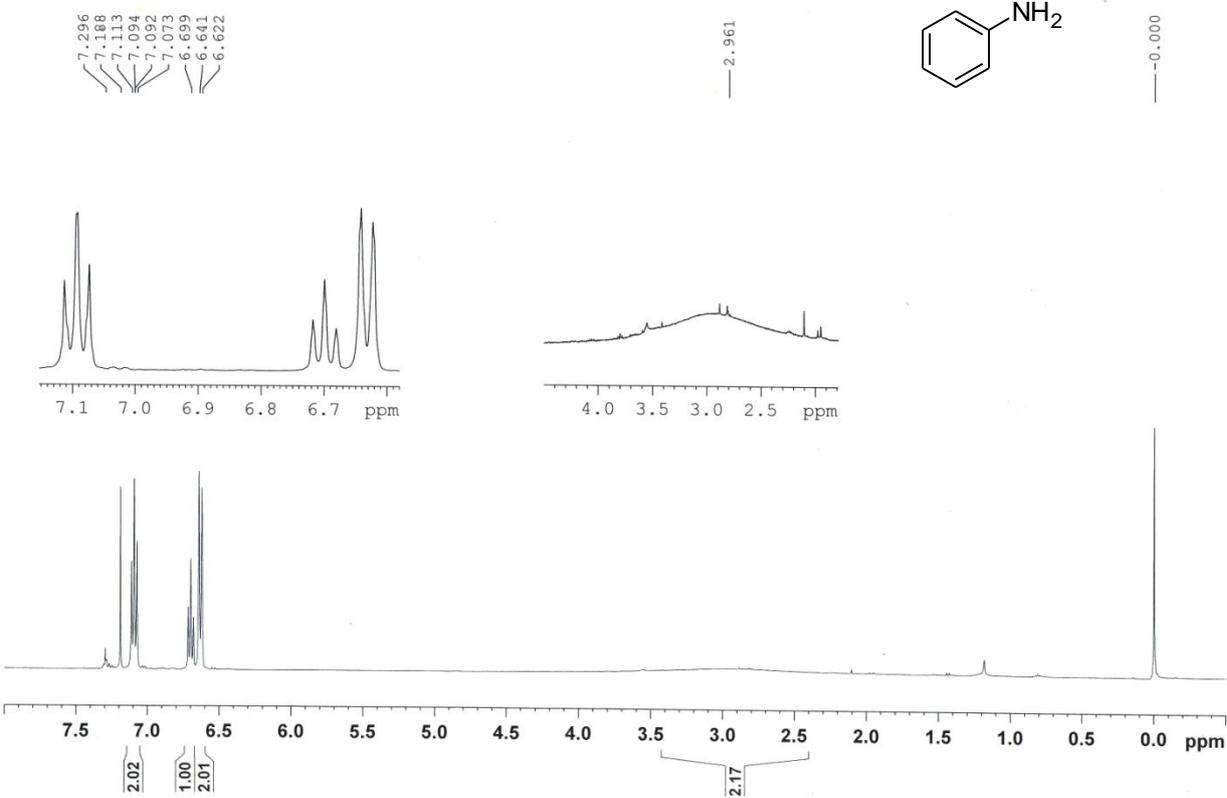
Sr. No.	Component Name	Ret. Time.	Area $\mu$ Volt Sec	Area %	Height $\mu$ Volt	Height %	Peak Type
1		0.53	4718.5143	0.08	805	0.14	BP
2		0.59	712.9143	0.01	177	0.03	TTT
3		0.83	2271076.4571	40.60	285262	50.46	PB
4		2.49	8655.4286	0.15	2057	0.36	BB
5		4.04	3303198.1714	59.05	276411	48.90	BB
6		5.87	1449.0857	0.03	188	0.03	BB
7		7.69	3825.2000	0.07	388	0.07	BB
			5593635.7714	100.00	565291	100.00	

SUMMARY

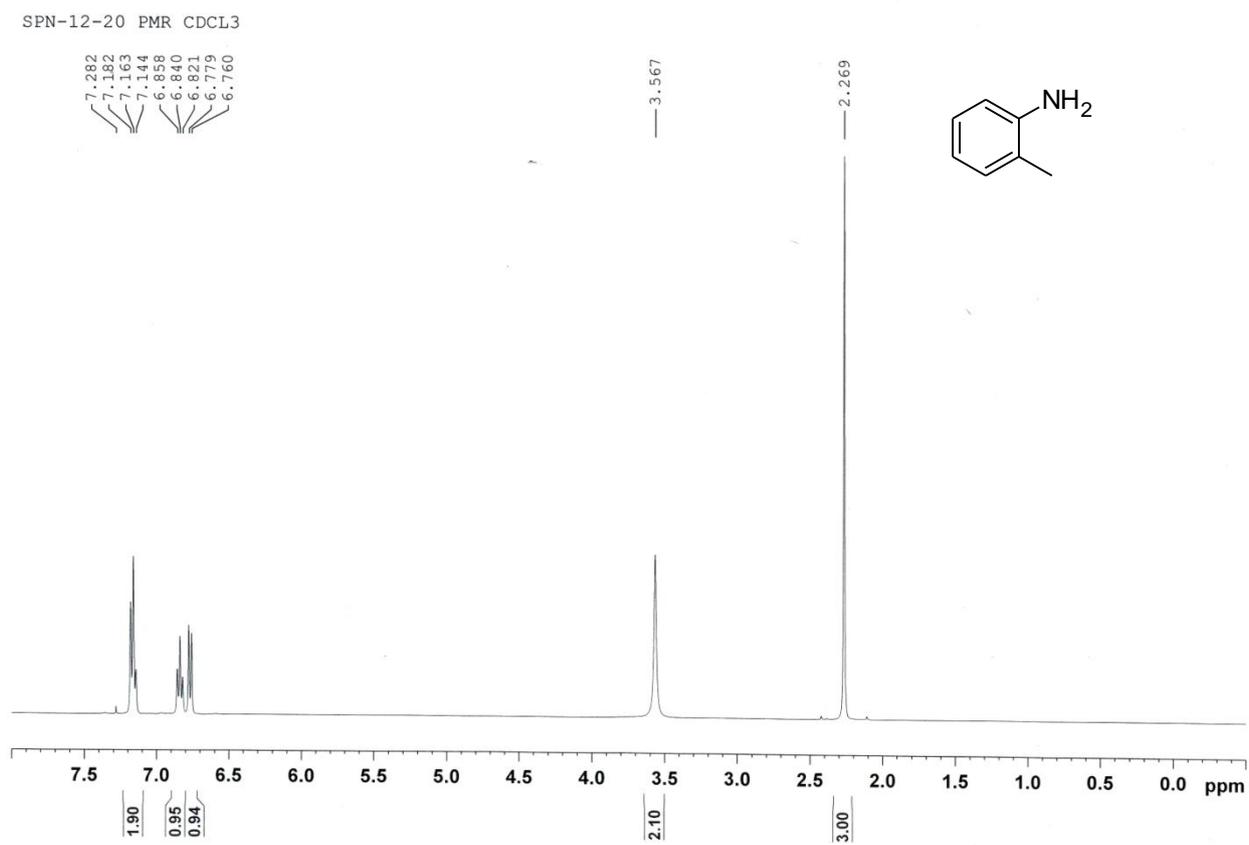
Total Peaks : 7  
 Multiplication Factor : 1.0000  
 Sample Amount : 100.0000  
 Dilution Factor : 1.0000  
 Syssuit Standards : IP  
 ISTD Amount : 0.0

Gas chromatogram of reaction mixture in methanol showing quantitative conversion of nitrobenzene to aniline with very high purity.

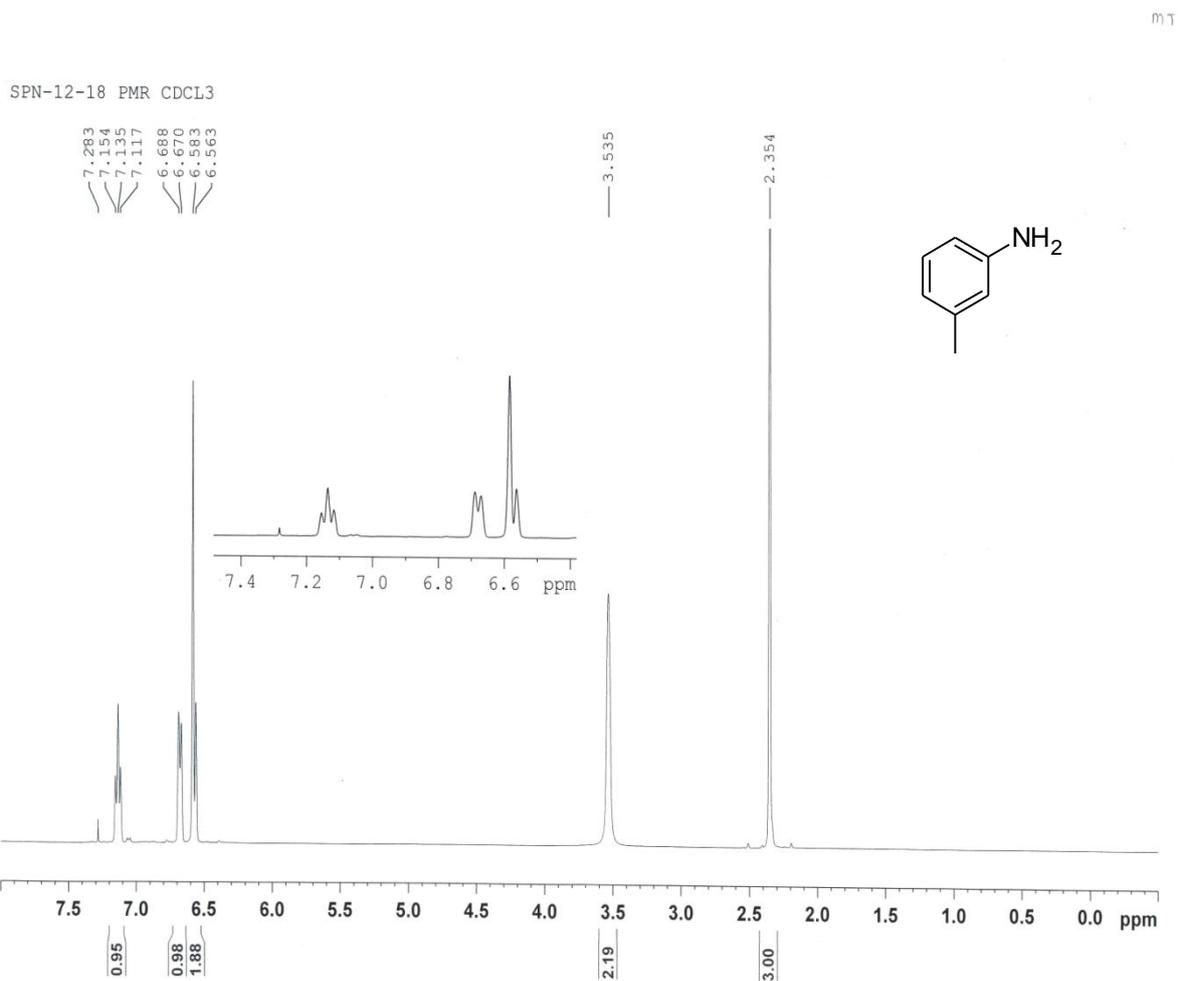
SPN-16 PMR CDCL<sub>3</sub>



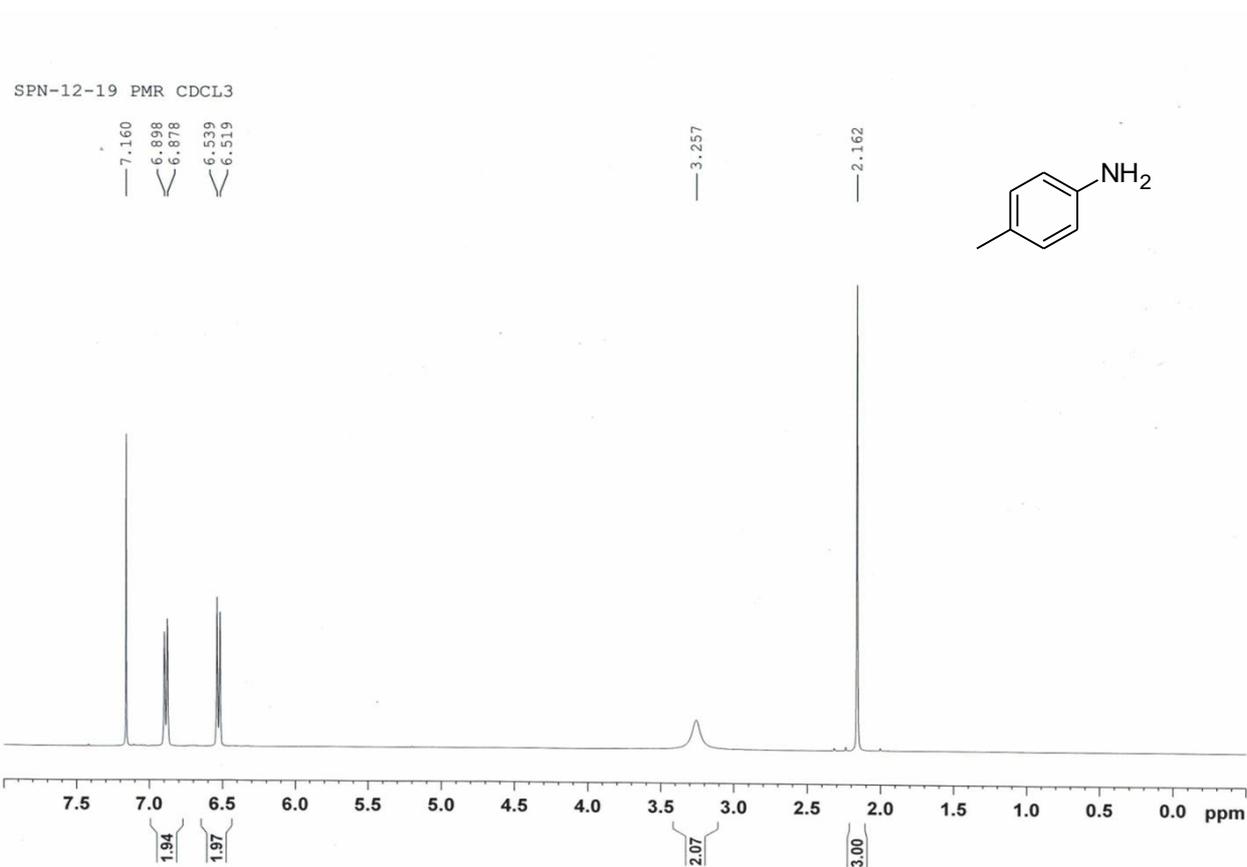
<sup>1</sup>H NMR spectrum of **2a**.



<sup>1</sup>H NMR spectrum of **2b**.



<sup>1</sup>H NMR spectrum of **2c**.



<sup>1</sup>H NMR spectrum of **2d**.

SP-12-22 CDCL3 PMR

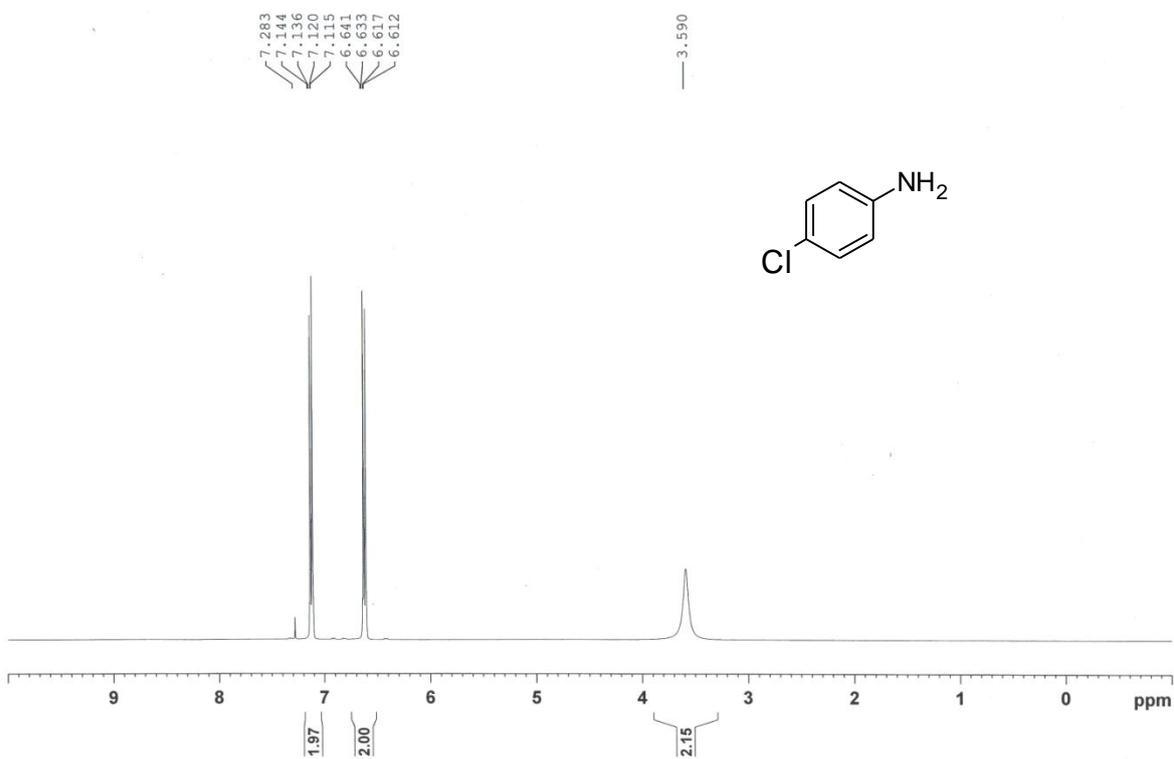


Figure S5.  $^1\text{H}$  NMR spectrum of **2e**.

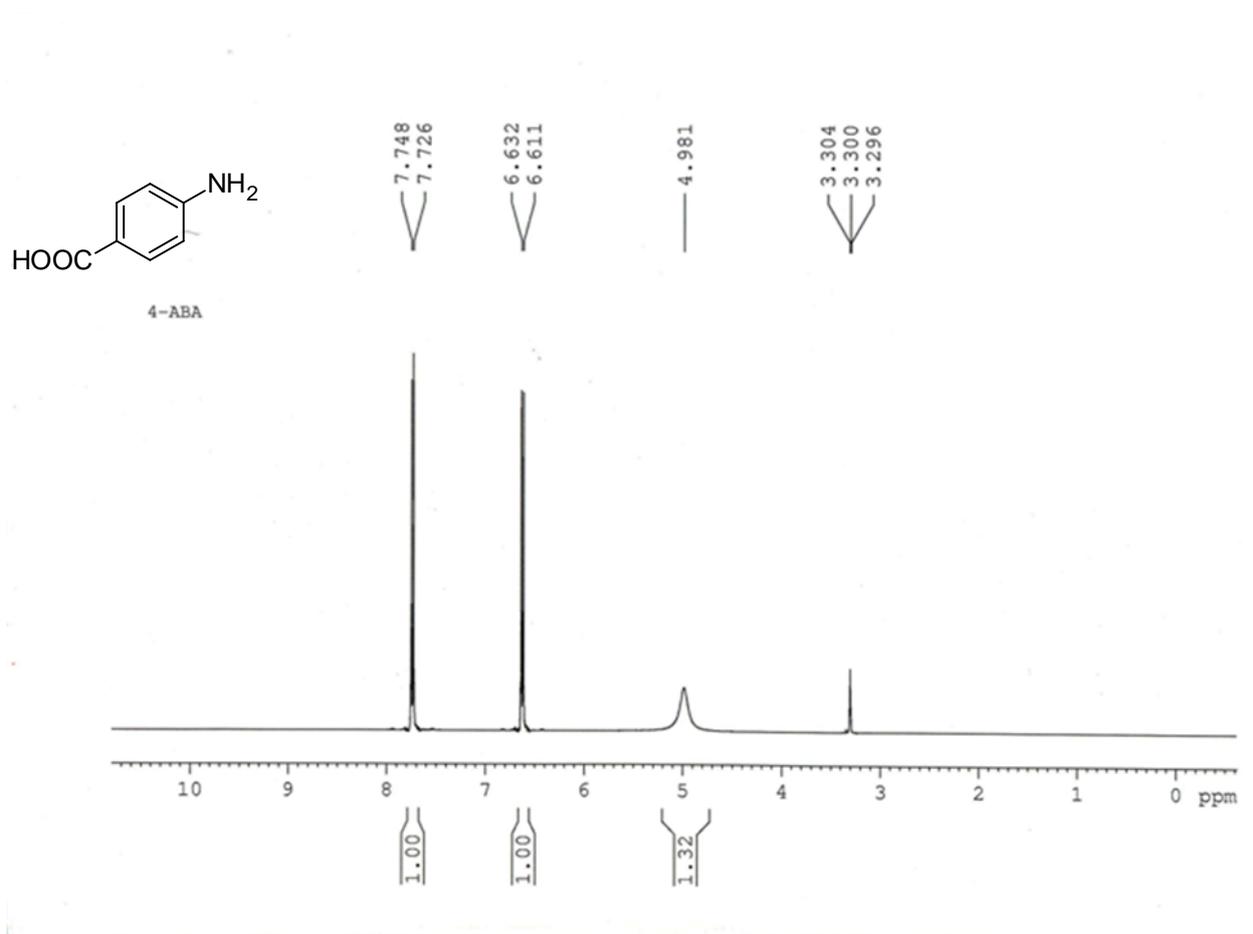


Figure S6. <sup>1</sup>H NMR spectrum of 2g.

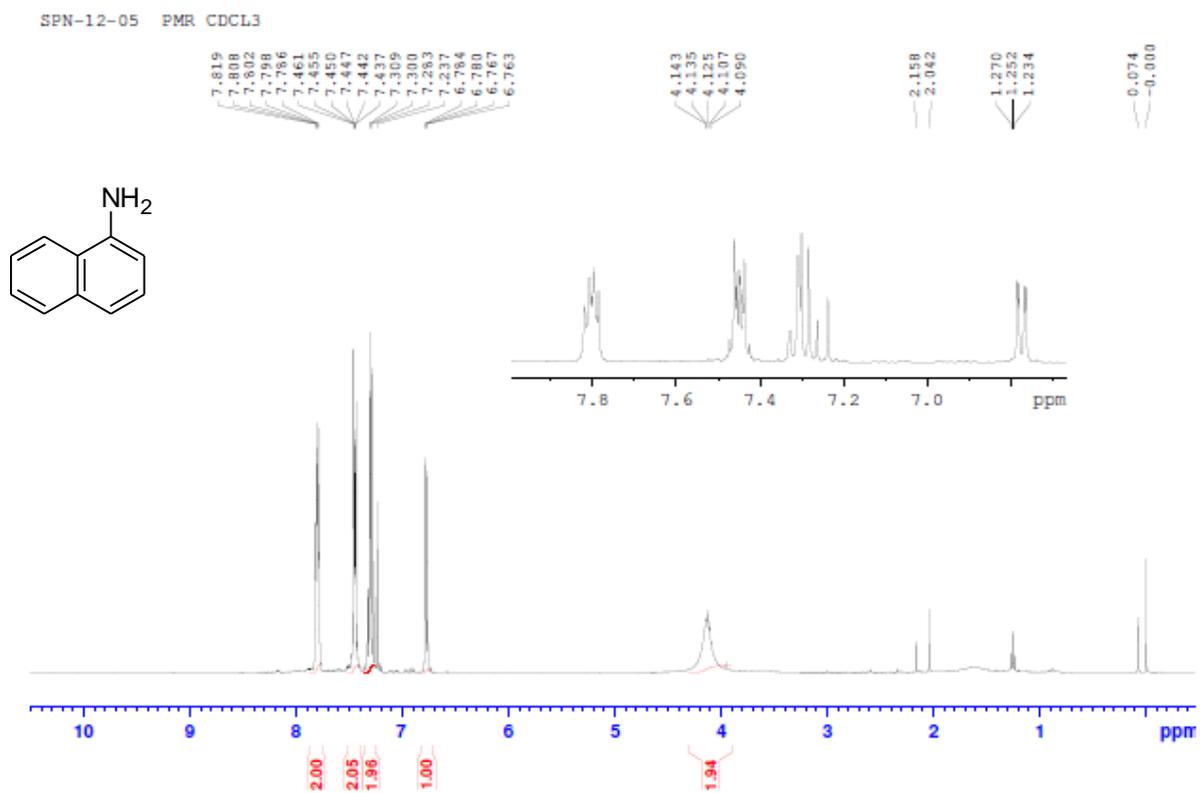


Figure S7. <sup>1</sup>H NMR spectrum of 2I.

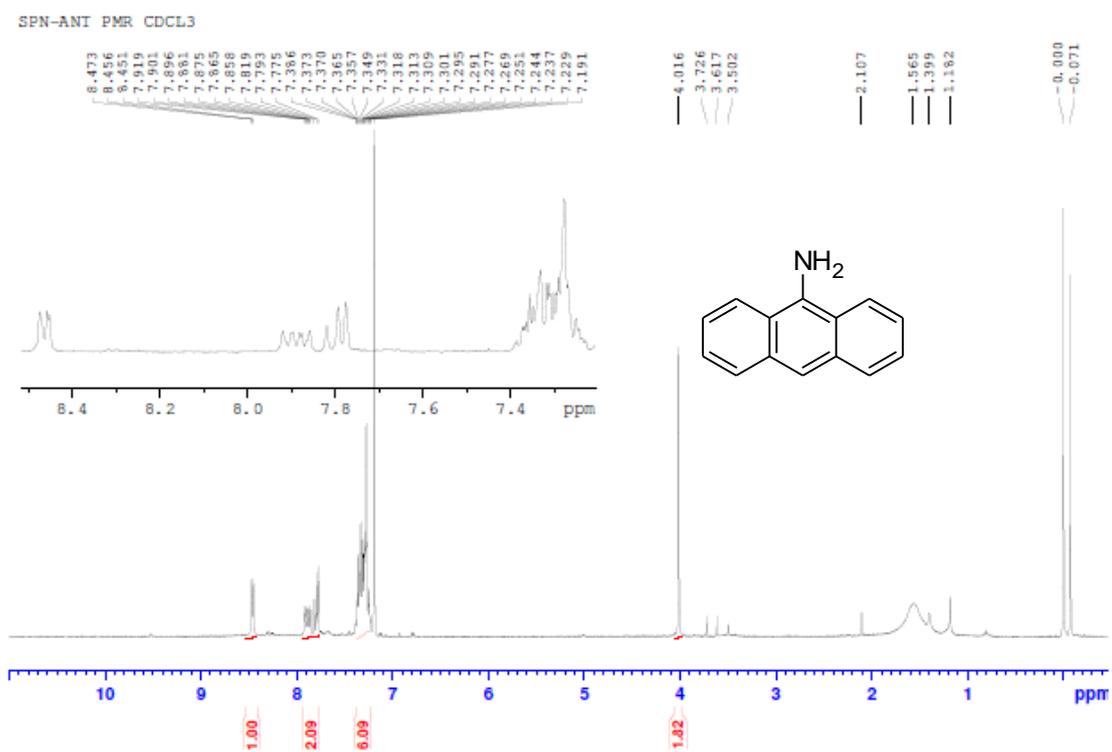


Figure S8. <sup>1</sup>H NMR spectrum of **2m**.

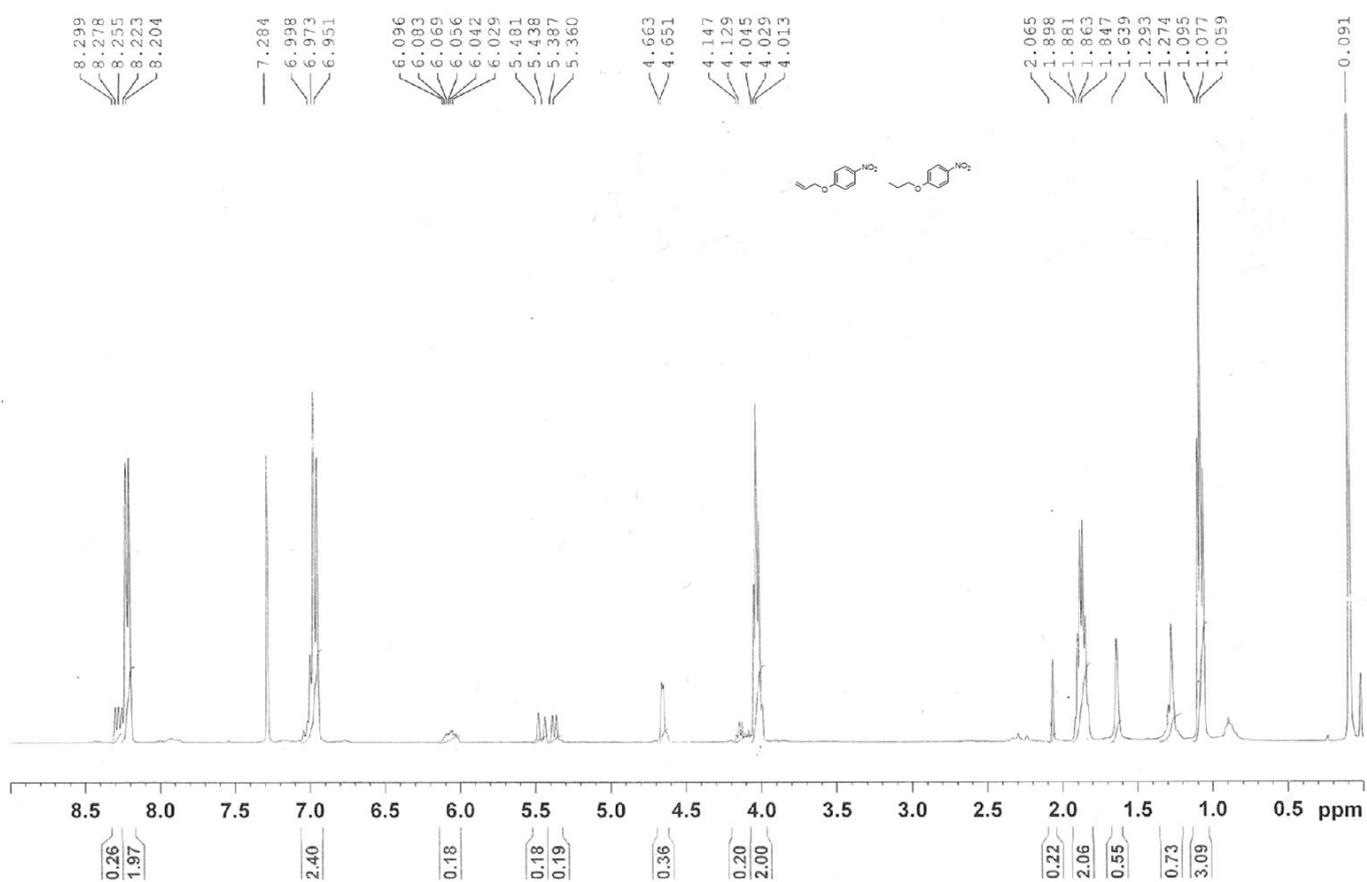


Figure S9.  $^1\text{H}$  NMR spectrum of **2r** and **1t**.

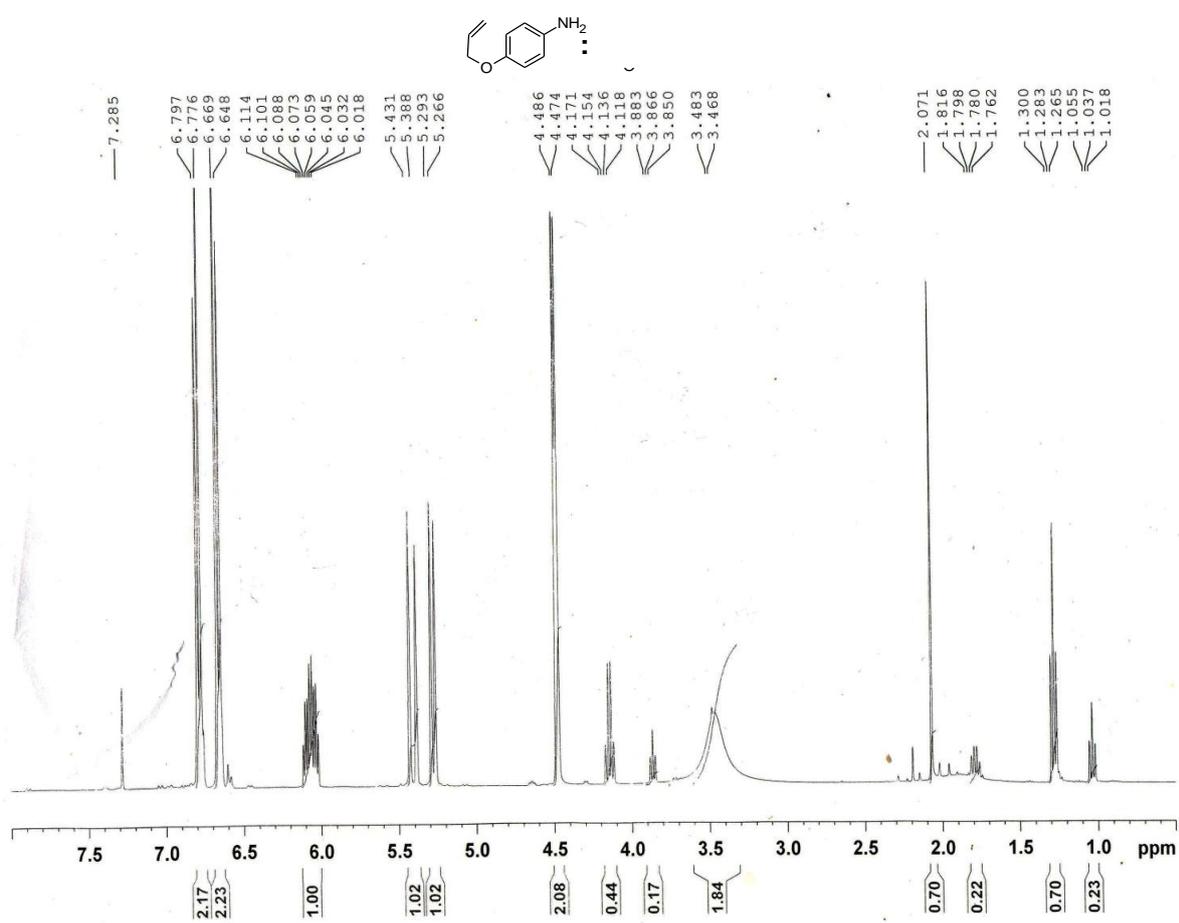
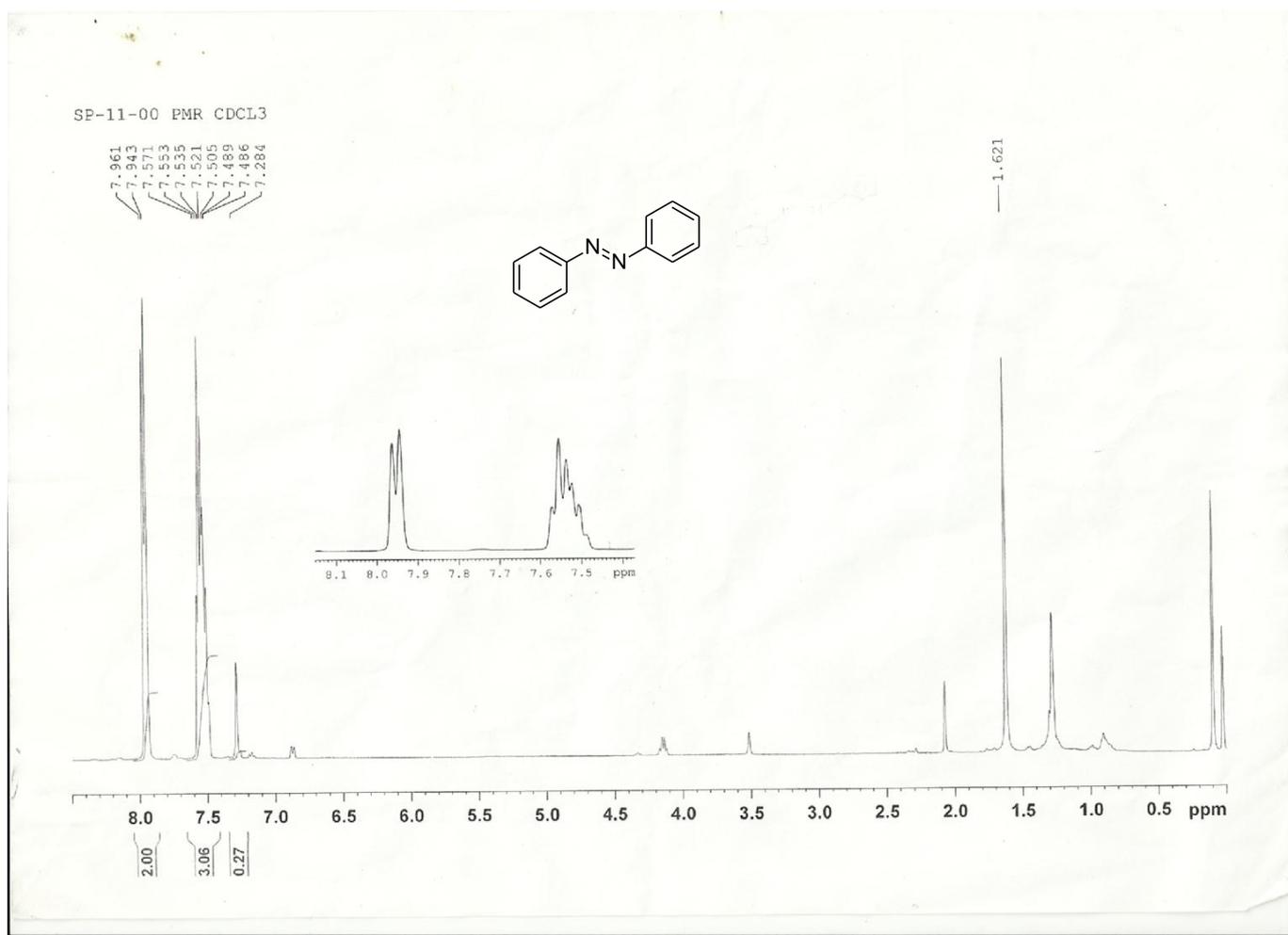
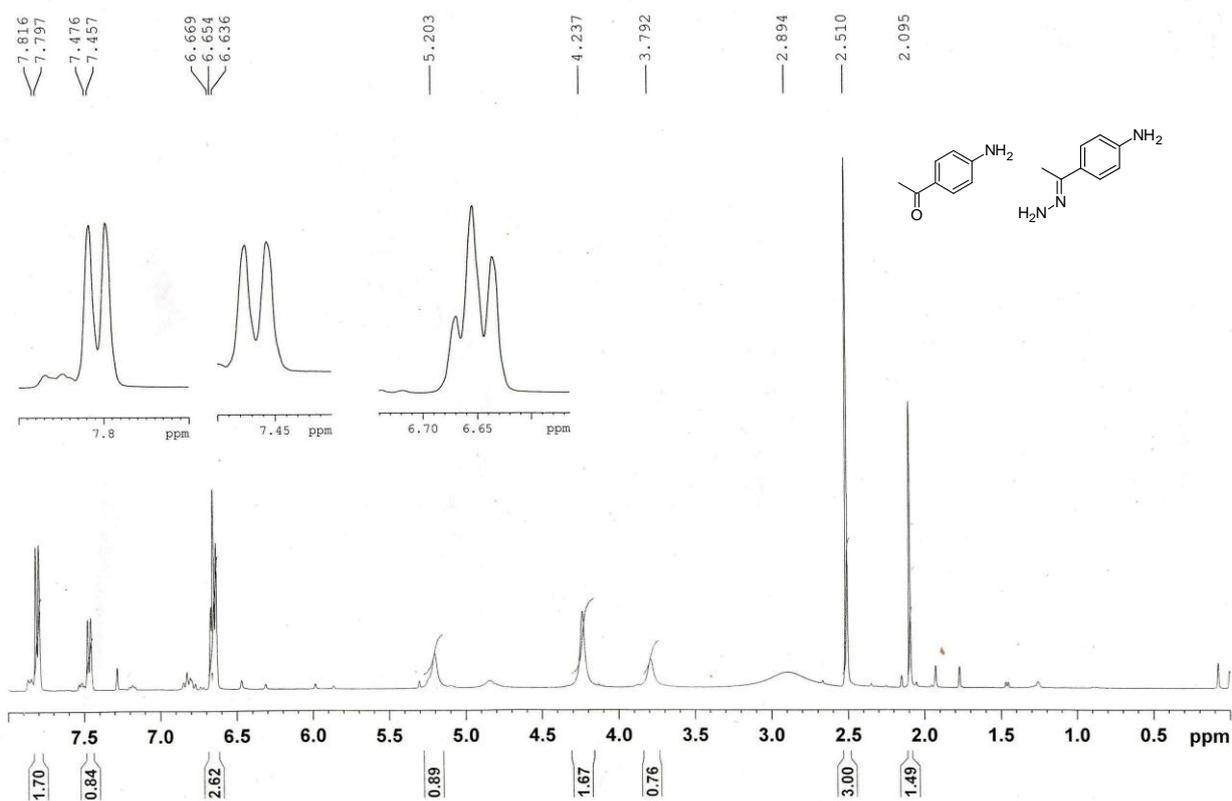


Figure S10. <sup>1</sup>H NMR spectrum of 2p and 2q.



**Figure S11.** <sup>1</sup>H NMR spectrum of isolated azo intermediate, diphenyldiazene.



**Figure S12.**  $^1\text{H}$  NMR spectrum of **2s** and **2u**.

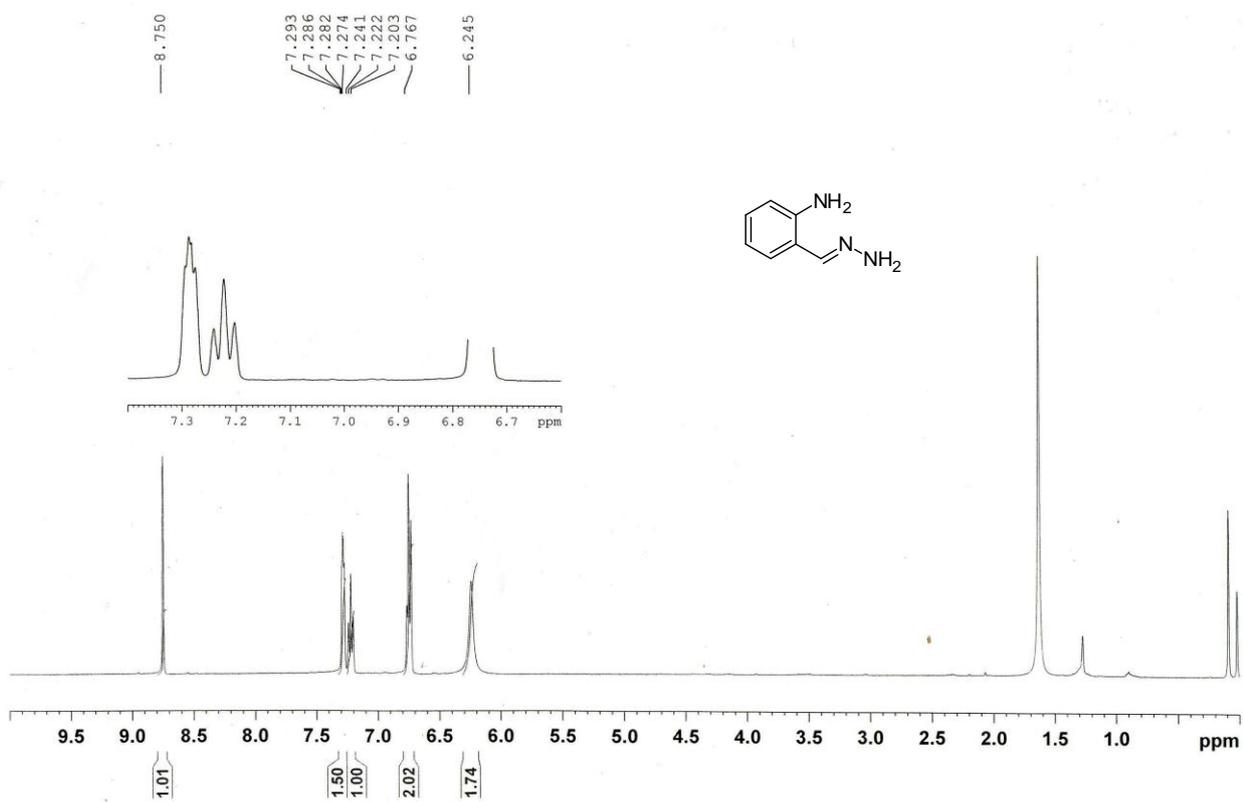


Figure S13.  $^1\text{H}$  NMR spectrum of **2w**.

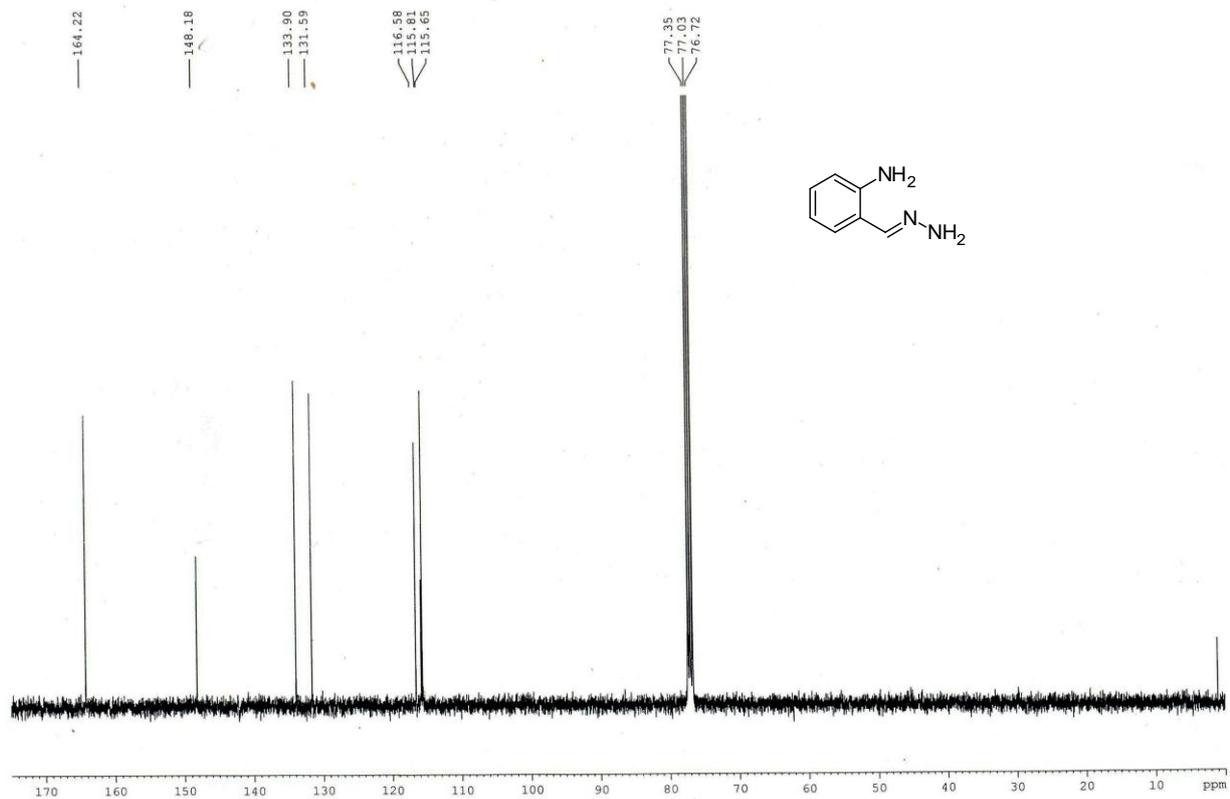


Figure S14.  $^{13}\text{C}$  NMR spectrum of 2w.

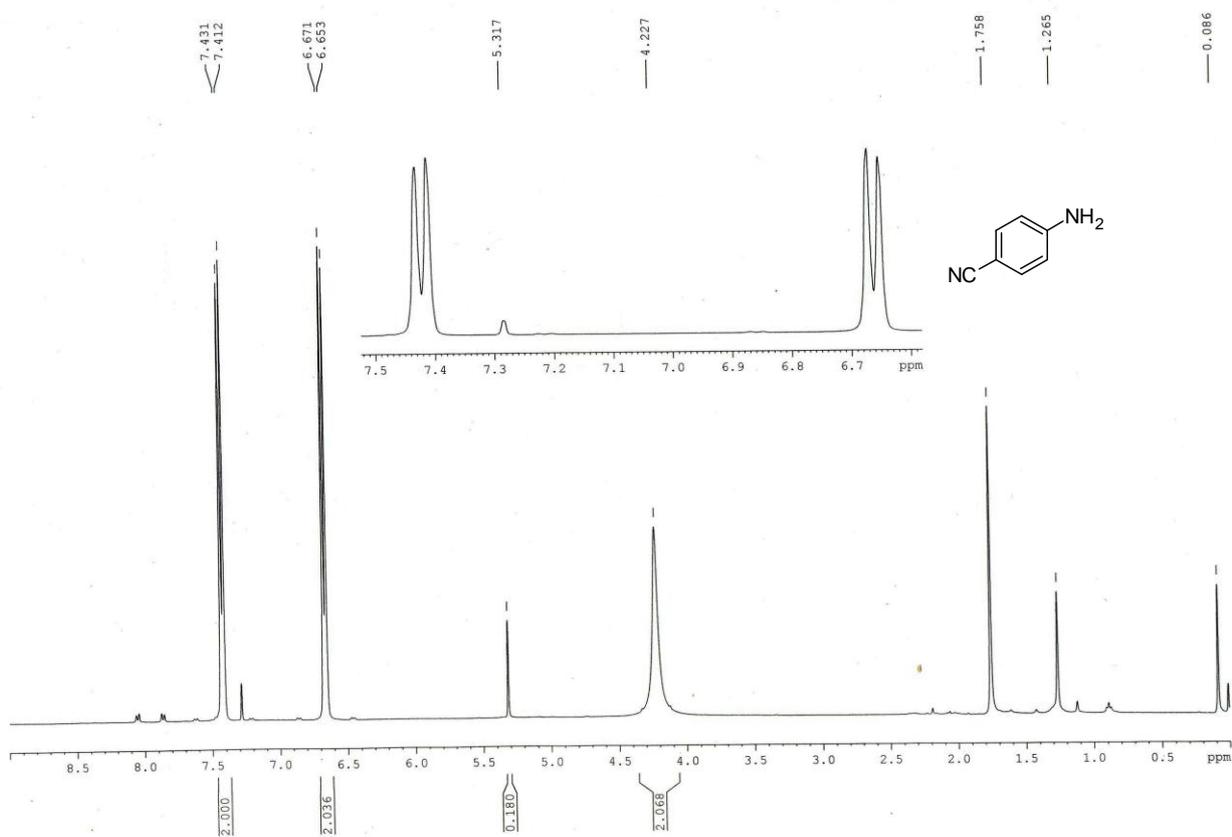
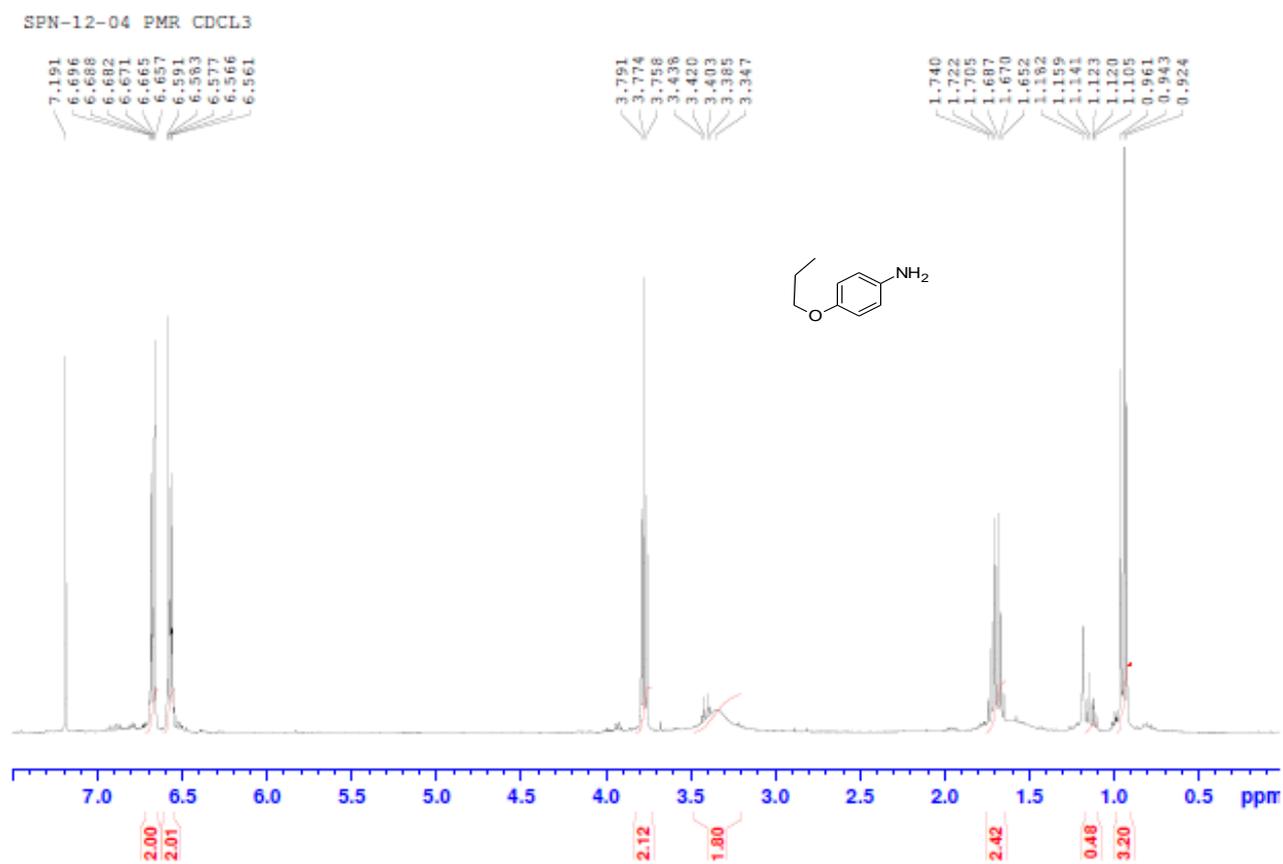


Figure S15. <sup>1</sup>H NMR spectrum of **2y** (by hydrazine method).



**Figure S16.**  $^1\text{H}$  NMR spectrum of **2q** (No selectivity in reduction of nitro group of **1t** when  $\text{CoCl}_2/\text{NaBH}_4$  (2:10) mixture was employed).

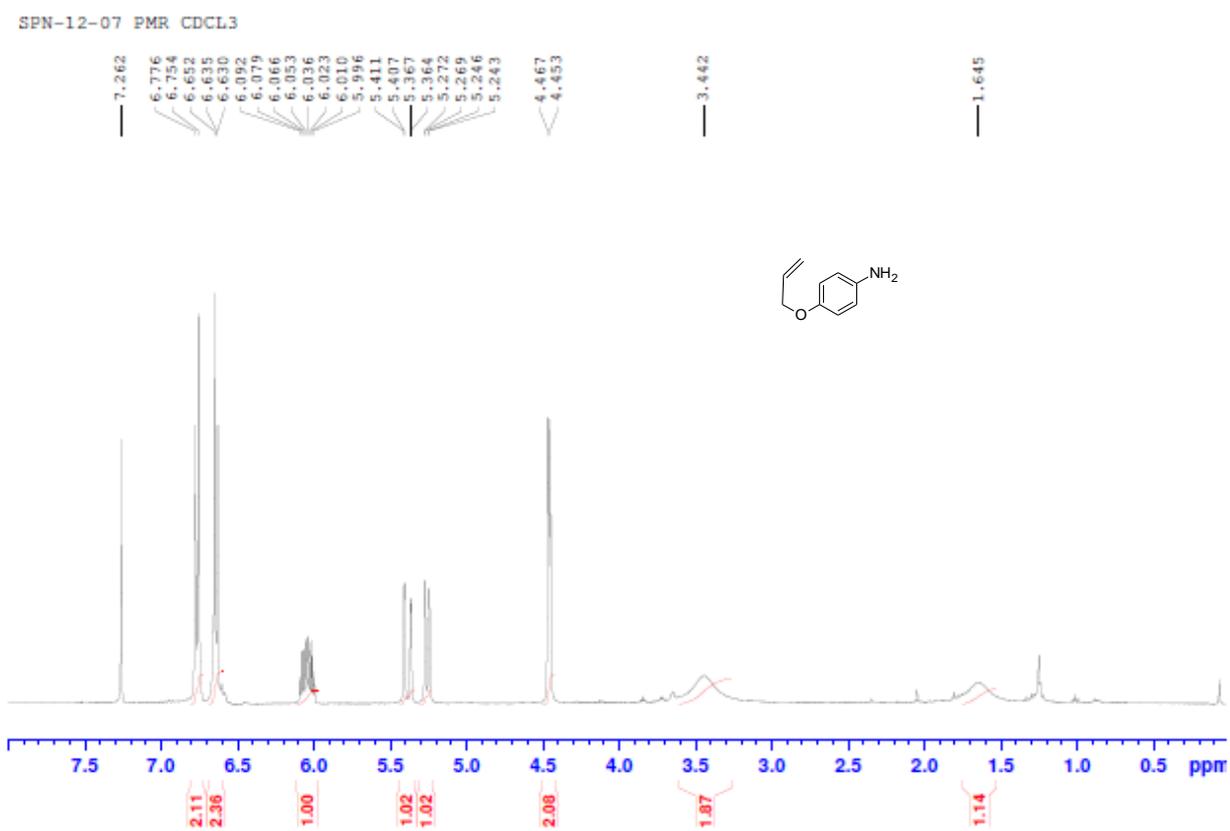


Figure S17. <sup>1</sup>H NMR spectrum of **2p** (when CoB/N<sub>2</sub>H<sub>4</sub> was employed in the reduction of **1t**).

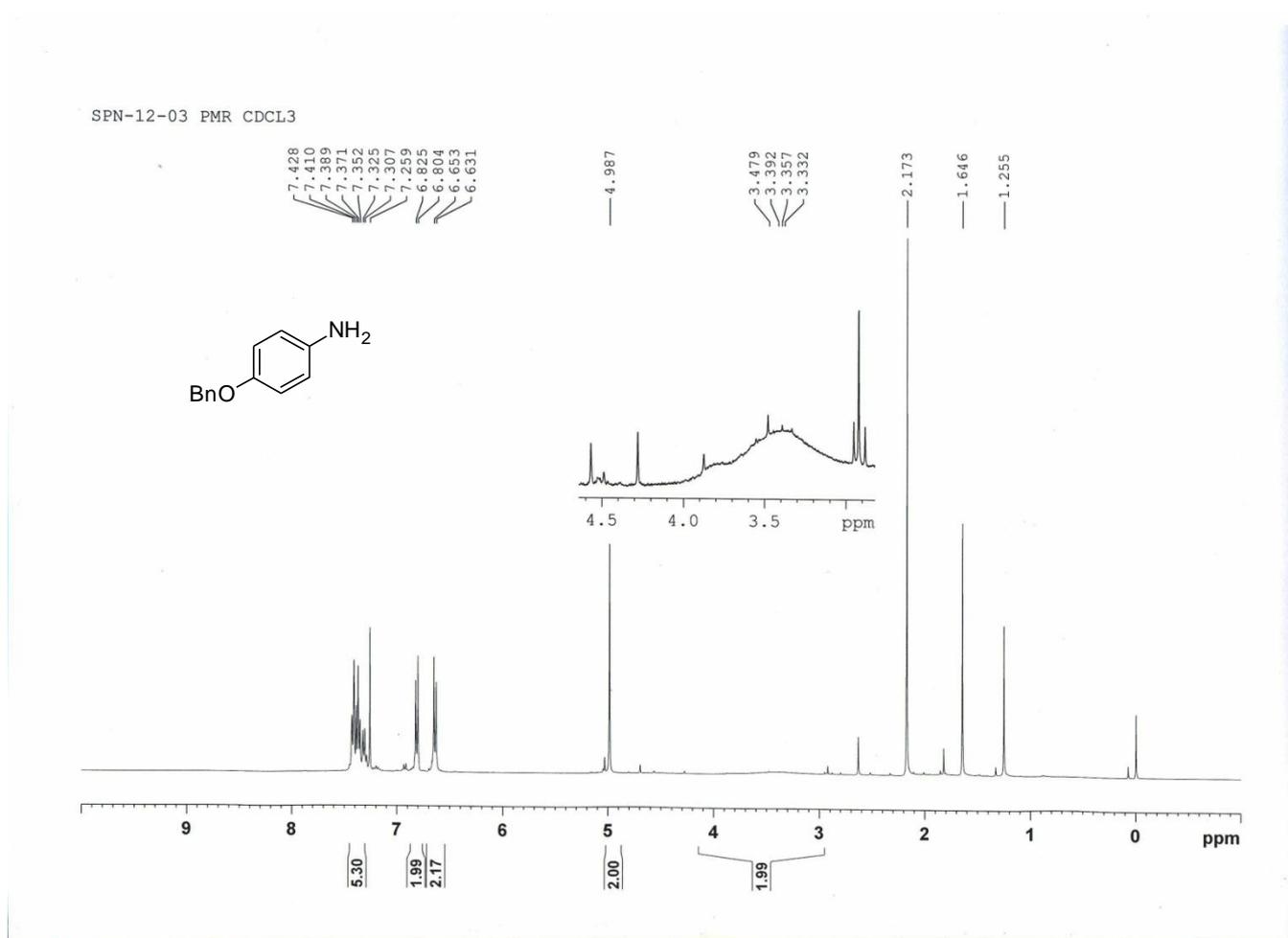


Figure S18. <sup>1</sup>H NMR spectrum of **2k** (for the reduction of **1k**).

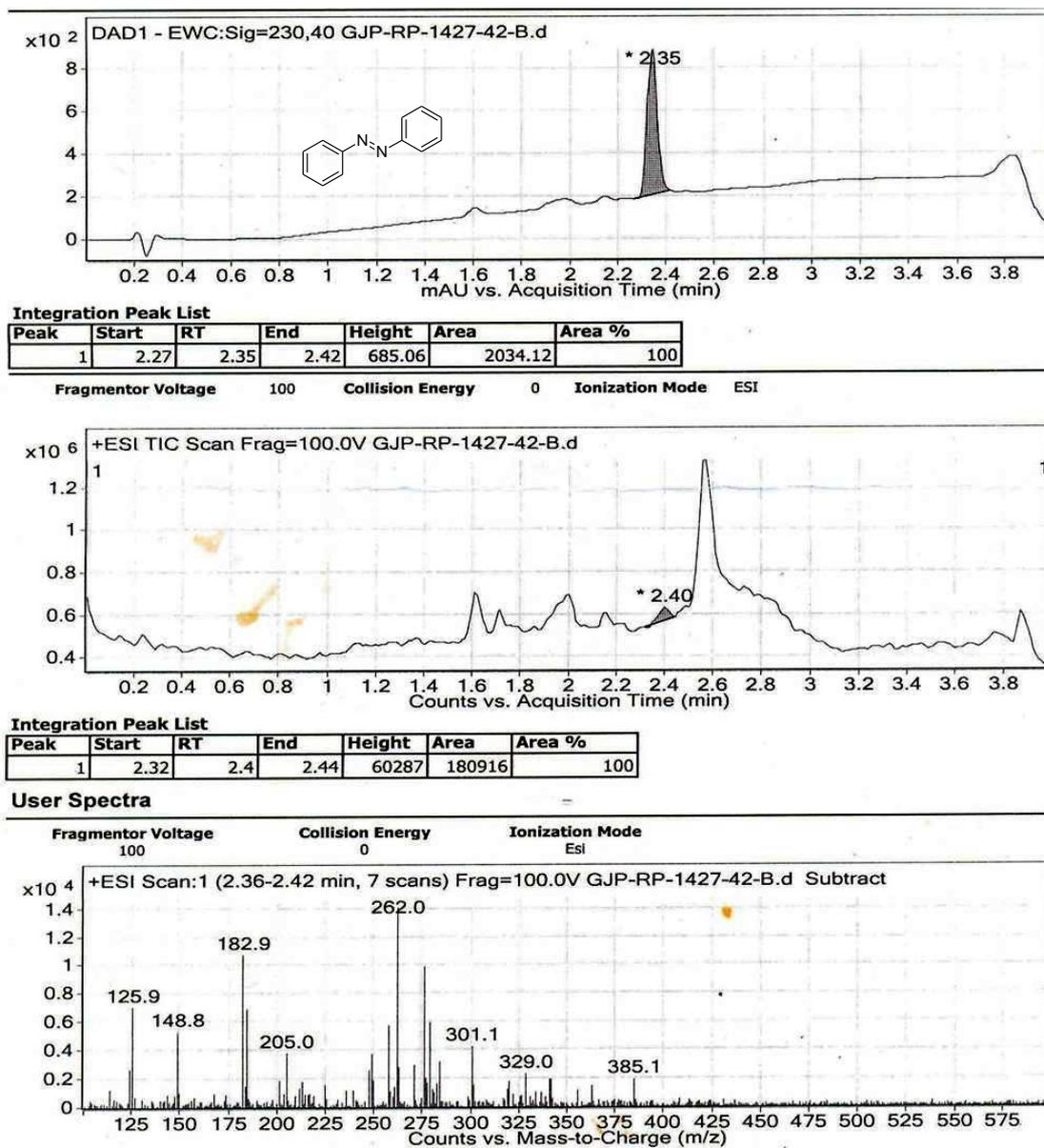
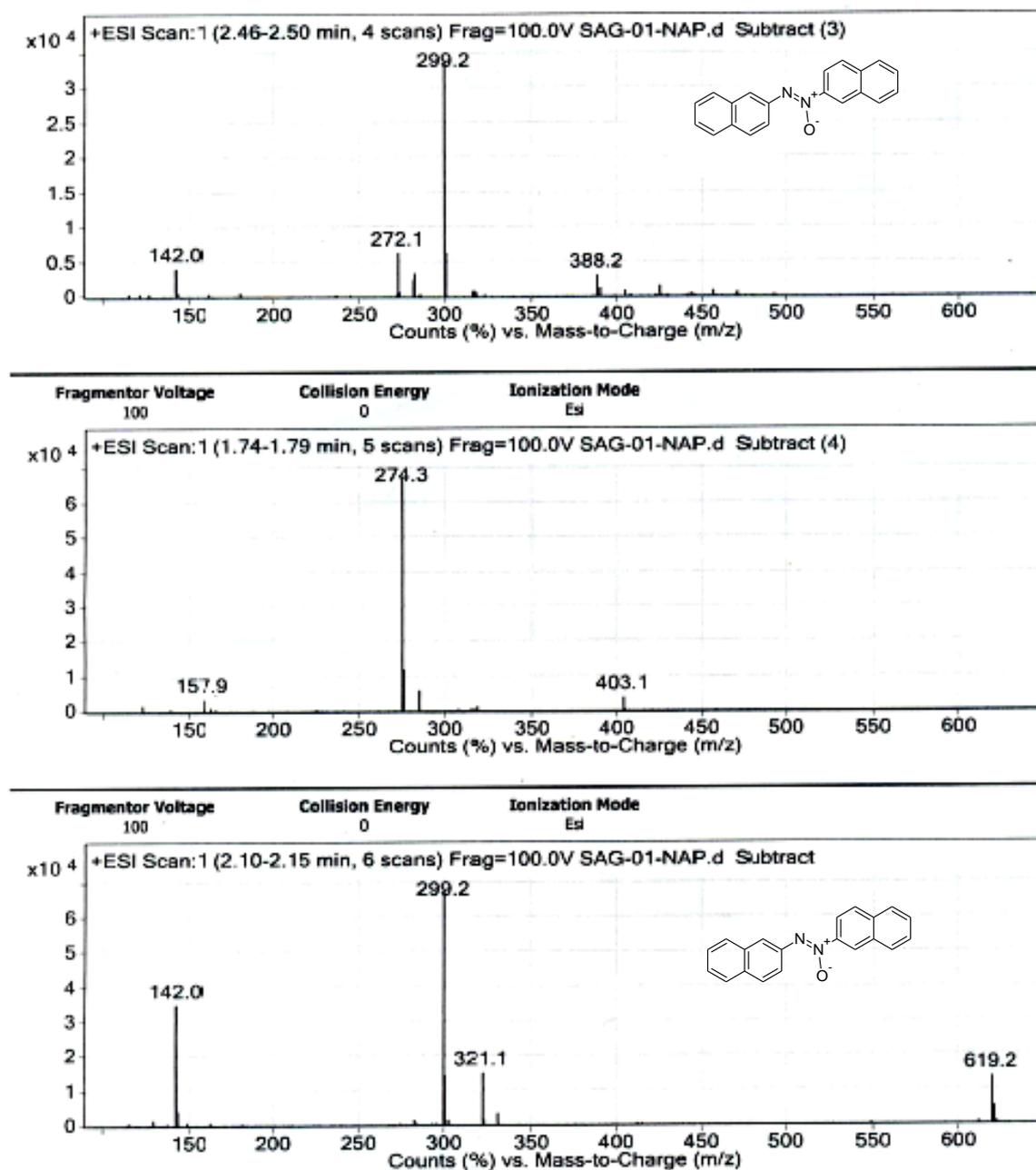
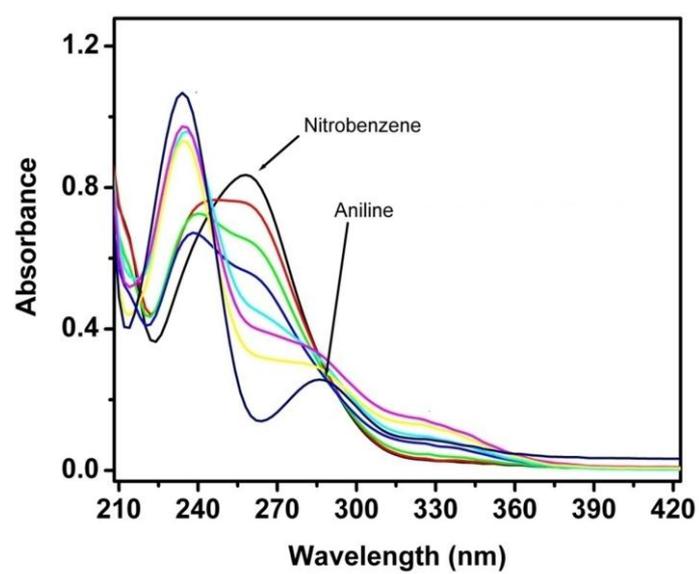


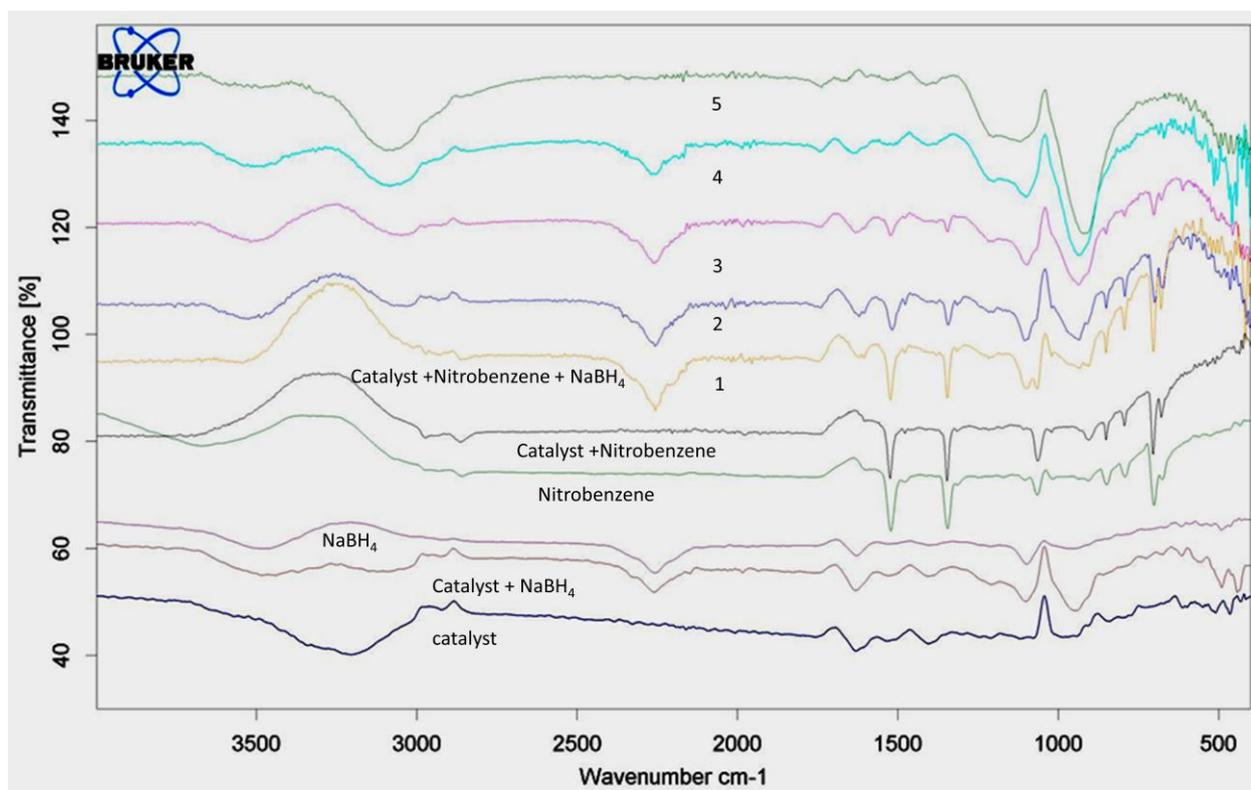
Figure S19. LC-MS of azobenzene (reaction intermediate). Peak at  $m/z$  182.9 corresponds to azobenzene.



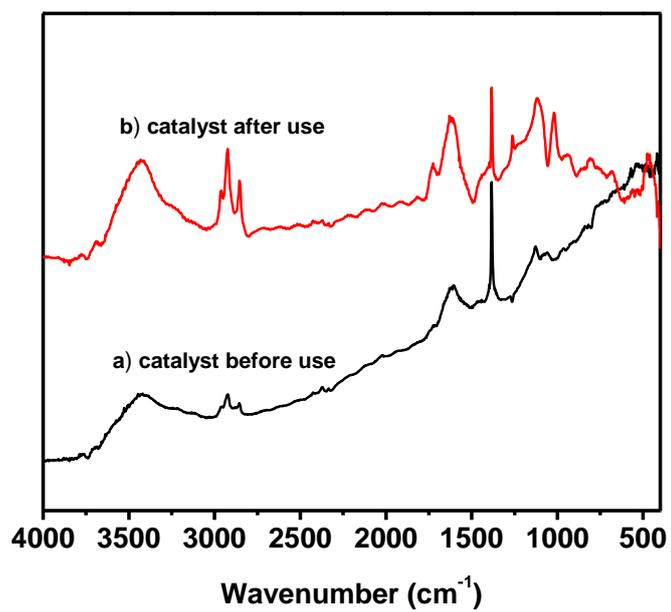
**Figure S20.** LC-MS of the reaction mixture during the reduction of **1I**. The peak at m/z 299.2 accounts for the 1-hydrox-1,2-di(naphthalen-1-yl)diazene an corresponding azoxy intermediate.



**Figure S21.** UV-Vis spectra of time dependent reduction of nitrobenzene in water/THF solvent in the presence of catalytic amount of Co-Co<sub>2</sub>B nanocomposites and sodium borohydride.



**Figure S22.** The IR spectra were recorded after every 30 sec interval after the addition of sodium borohydride to the mixture of nitrobenzene and Co-Co<sub>2</sub>B nanocomposites in water/THF solvent. Note the decrease in the bands due to N=O stretching and appearance of band due to N-H stretching vibration. **1** indicates the spectra at 0<sup>th</sup> time and then others are followed every 30 sec till the no. **5**. The control experiment spectra are also shown. The blank was corrected using water/THF solvent.



**Figure S23.** IR spectra of Co-Co<sub>2</sub>B nanocomposite before and after using in reduction process.