Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Reduction of selective polyaromatic nitrotriptycene *via* azoxytriptycene intermediate under ambient conditions using cobalt/cobalt oxide nanocomposite (CoNC)

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Table of Contents Page No.

1. XRD and SEM-EDX of CoNC

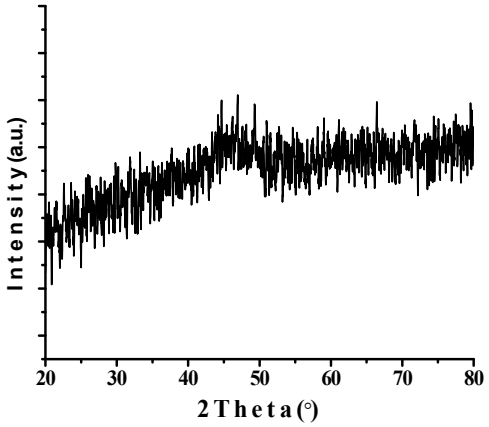
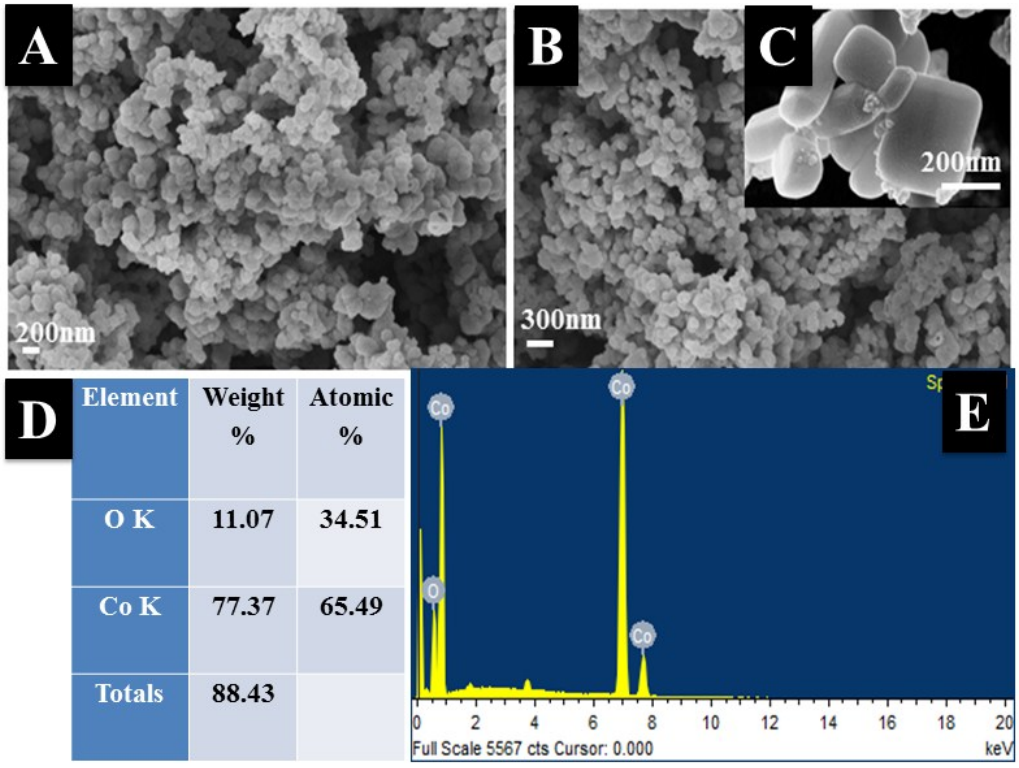


Fig.S1 Powder XRD pattern of **CoNC**.

SEM EDAX of the fresh catalyst



Element	Weight %	Atomic %
O K	11.07	34.51
Co K	77.37	65.49
Totals	88.43	

Fig.S2SEM images of as synthesized **CoNC**; (A) 200 nm; (B) 300 nm; (C) incent picture showing capsule like structure of **CoNC**; (D) EDAX table; (E) EDAX analysis

2. Time dependent ^{1}H NMR spectra for the catalytic reduction of M1 and M2

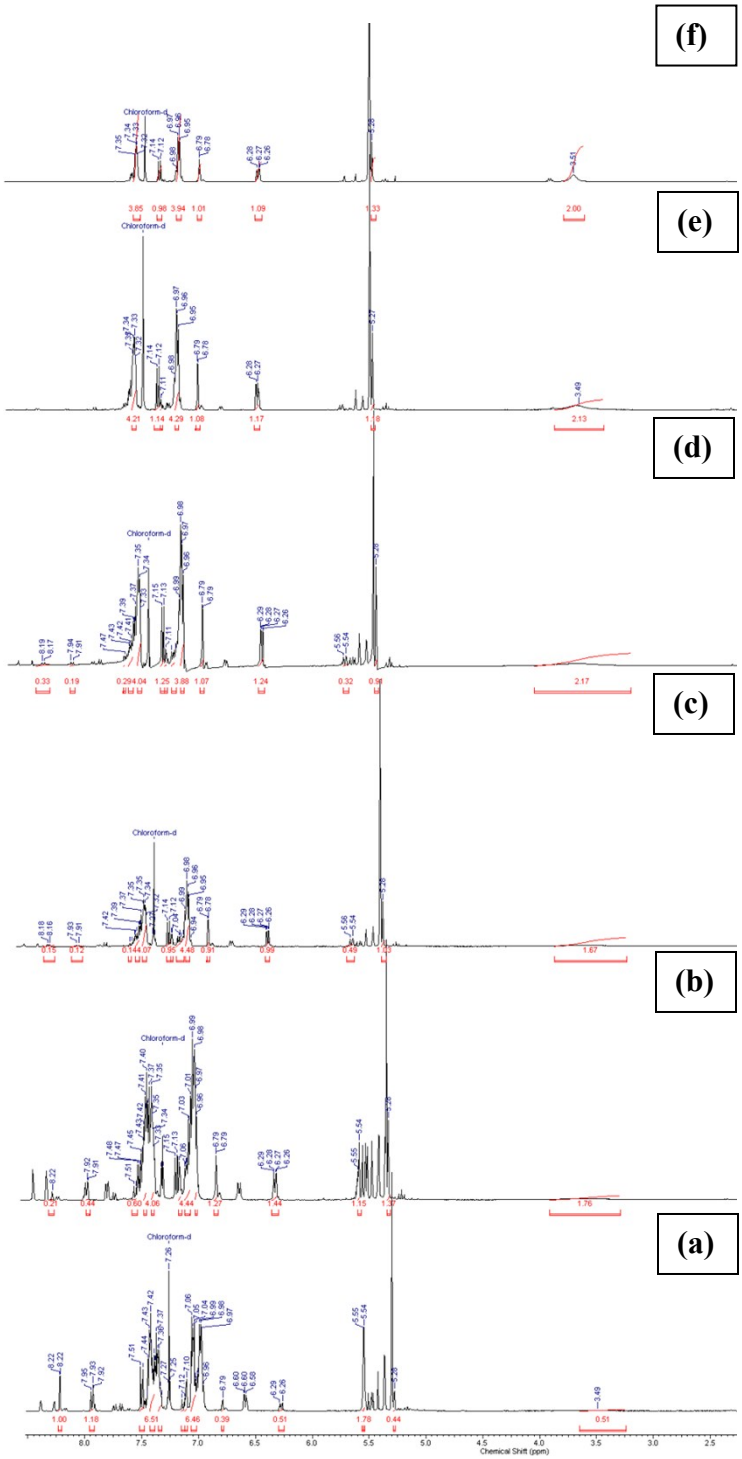


Fig. S3 Time dependent ^{1}H NMR spectra for the catalytic reduction of mononitrotriptycene (**M1**) at **(a)** 10 min, **(b)** 20 min, **(c)** 30 min, **(d)** 40 min, **(e)** 50 min, **(f)** 60 min

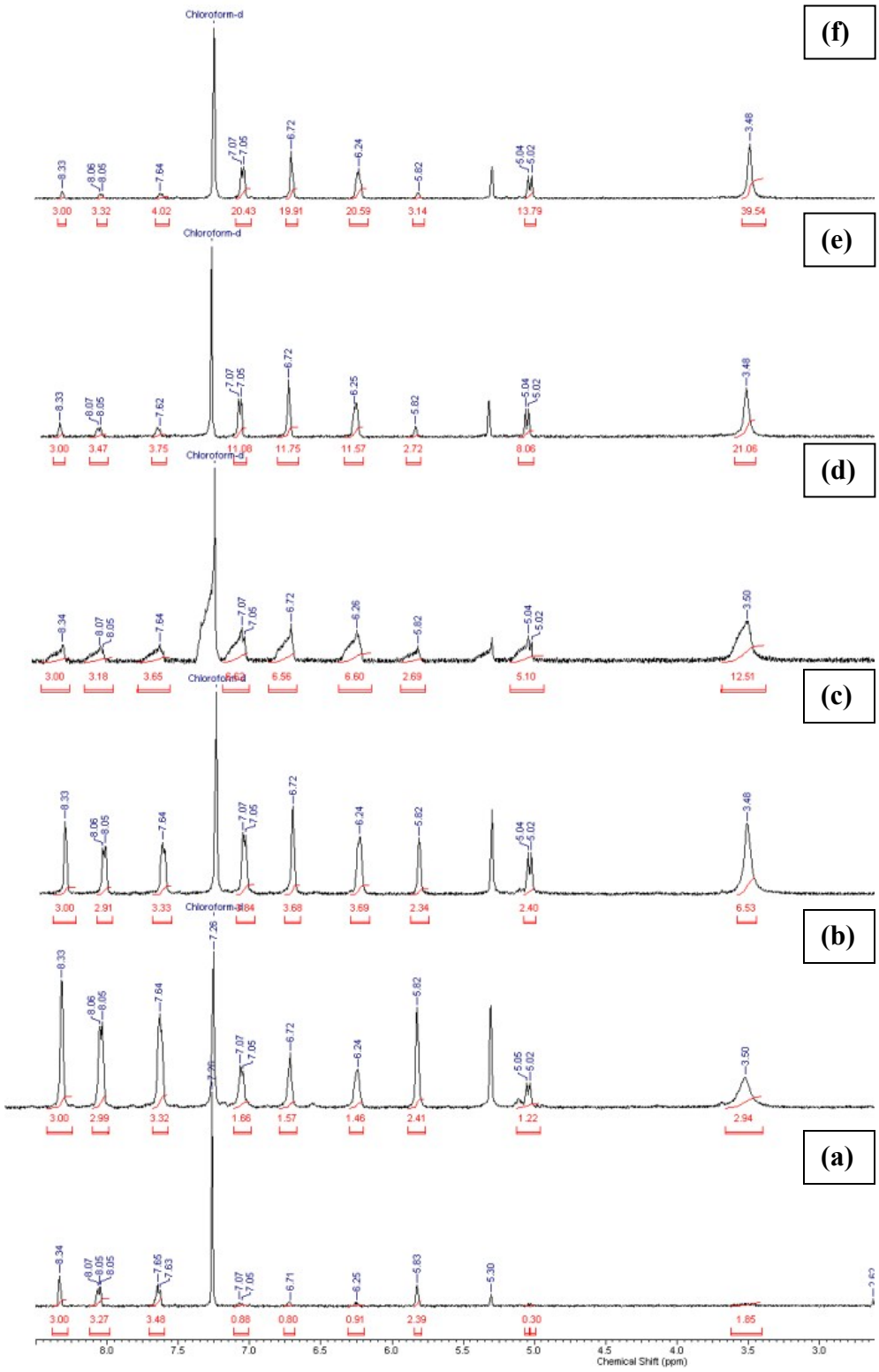


Fig. S4 Time dependent ^{1}H NMR spectra for the catalytic reduction of trinitrotriptycene (**M2**) at **(a)** 5 min, **(b)** 10 min, **(c)** 15 min, **(d)** 20 min, **(e)** 25 min, **(f)** 30 min

3. XPS of CoNC

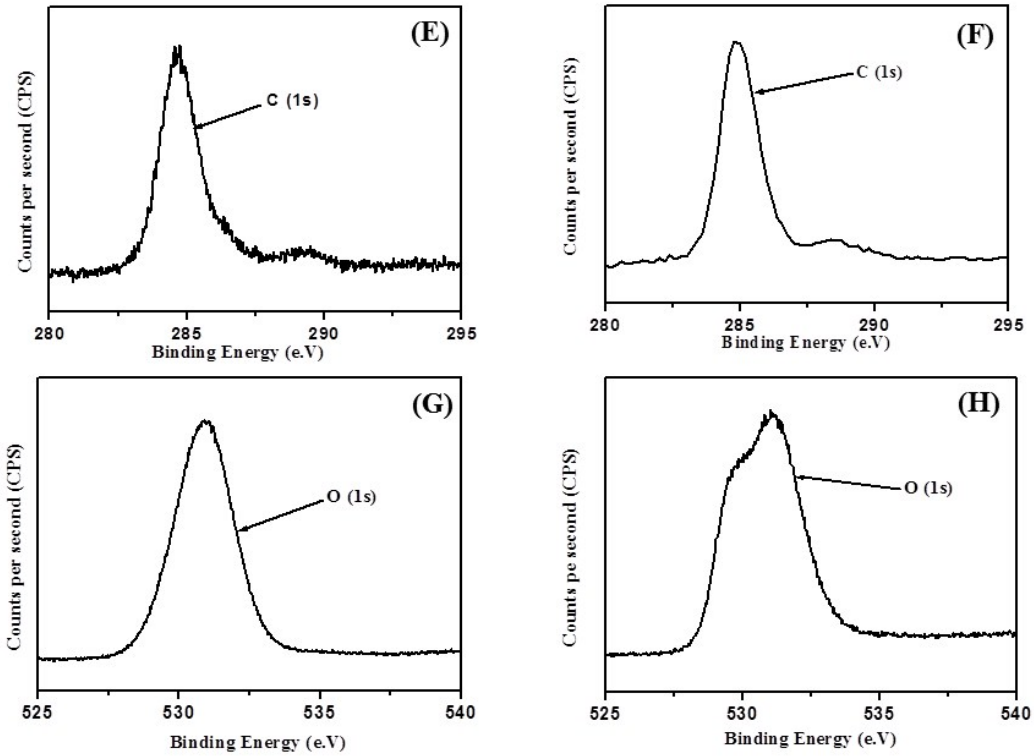


Fig.S5XPS spectra; (E) C correction for fresh **CoNC**; (F) O present in **CoNC**; (G) spent **CoNC**; (H) Co present in **CoNC**

4. SEM-EDAX of spent CoNC

After each cycle, catalyst was separated by the external magnet, dried and reused (Video attached).

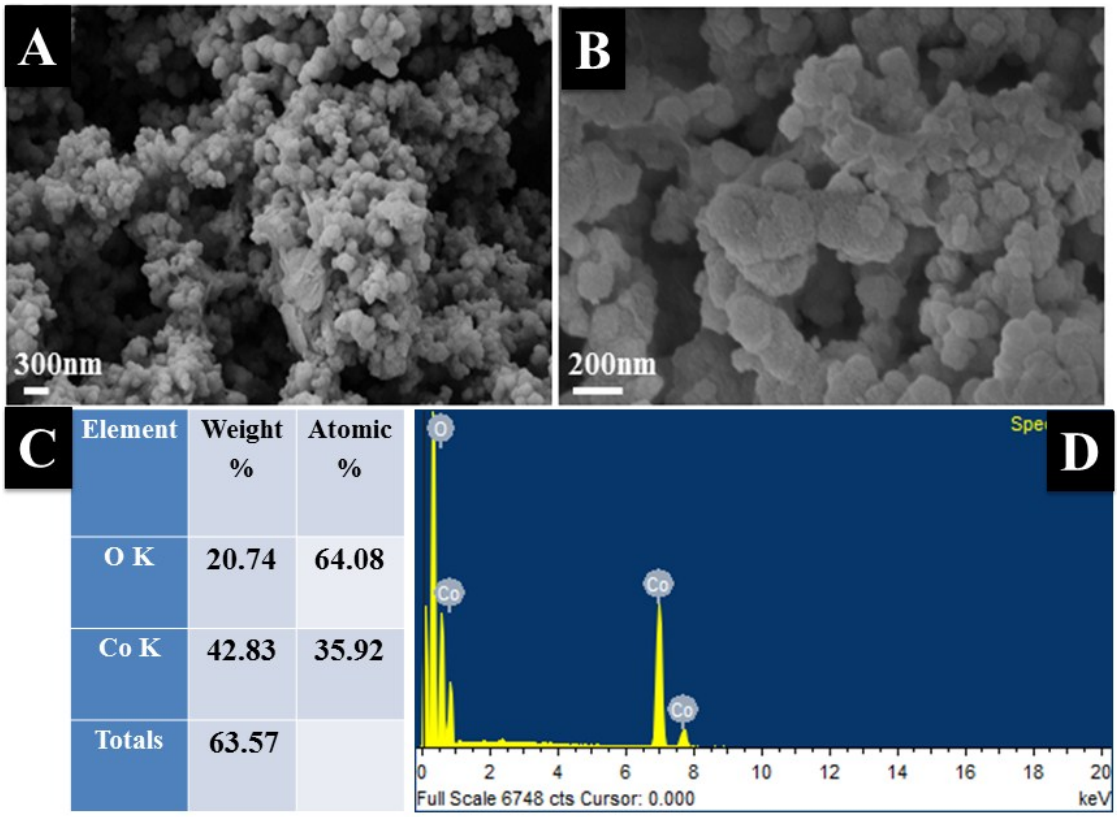


Fig.S6SEM images of recycled **CoNC**; (A) 300 nm; (B) 200 nm; (C) EDAX table; (D) EDAX analysis

5. Mechanistic confirmation of intermediates and product (1)

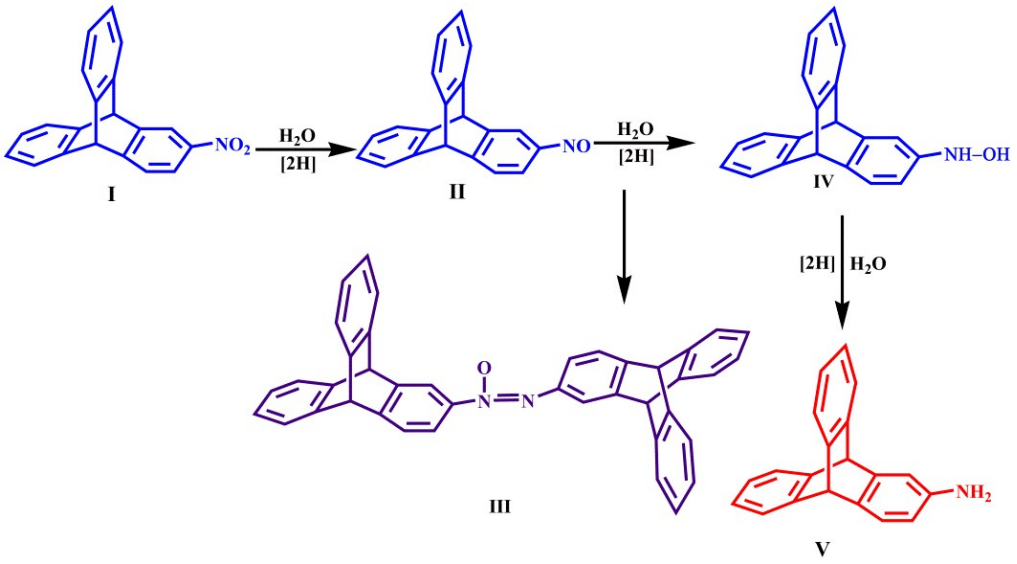
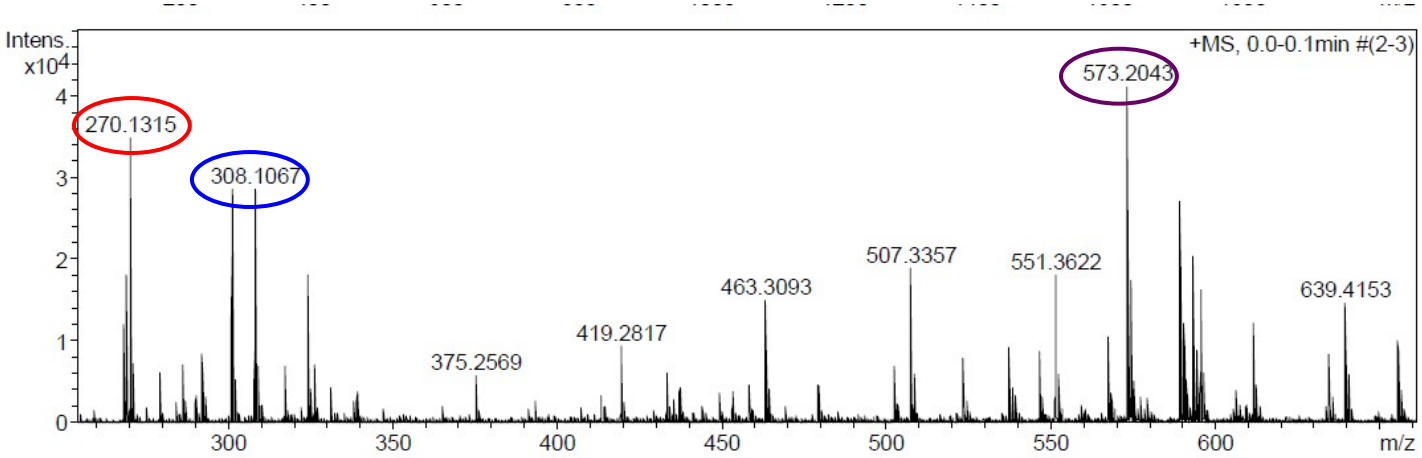
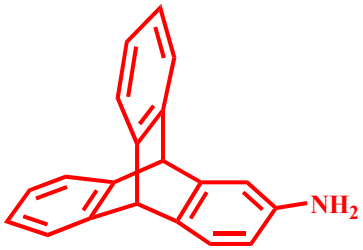
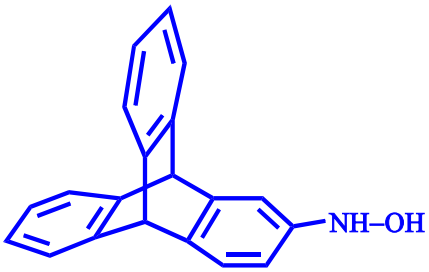


Fig.S7 Plausible mechanism for the catalytic reduction of **M1**.

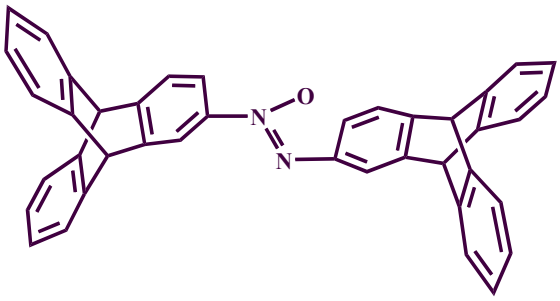




270[M+1]



308[M+23]



573[M]

Fig. S8 Mechanistic confirmation of intermediates and product **(1)**

6. H-bonded 2D-network of 2

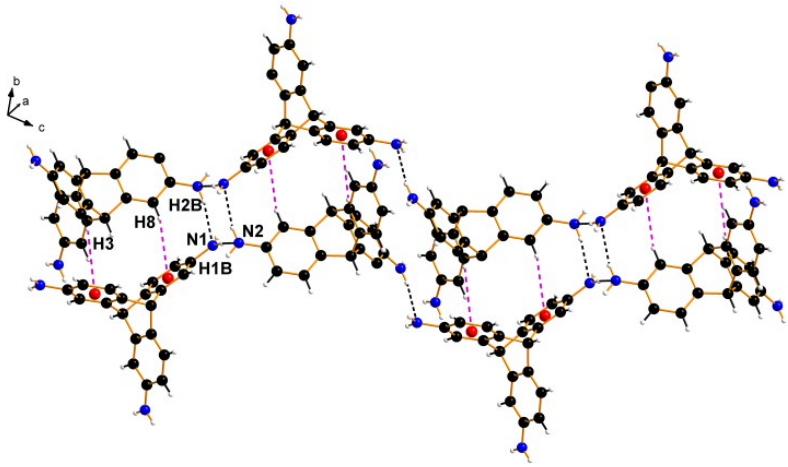
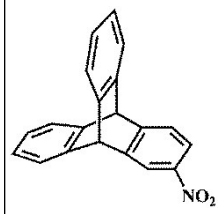
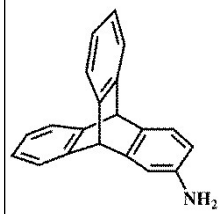
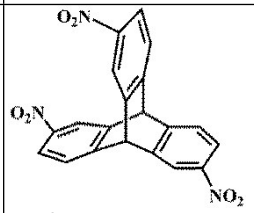
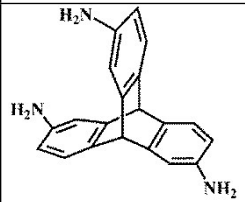
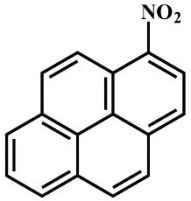
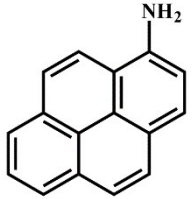
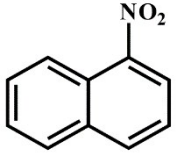
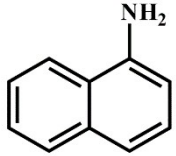
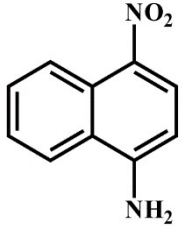
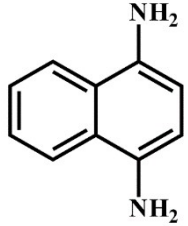


Fig. S9 Packing of **2** showing H-bonded 2D-network

The packing of 2 reveals presence of intermolecular H-bonding (N-H···N) between N-atom of one of the amine group and H-atom of another amine from neighboring unit leading to the formation of 1D polymeric chain. Furthermore, the 1D-polymeric chains extend via same N-H···N and C–H···π interactions along the *a*-axis leading to the formation of a 2D-network.

7. **Table S1.Reduction of polyaromatic nitro compounds in different solvents**

Entry No.	Substrate	Product	Conversion / Selectivity(%) / time				
			DCM	**Ethyl acetate**	**Ether**	**Water**	**Methanol**
	 **M1**	 **1**	95/99/60min	73/68 /70min	61/52/70min	30/37/240min	Sparingly soluble
	 **M2**	 **2**	95/99/30min	82/99/70min	90/99/70min	66/99/180min	Sparingly soluble
3			86/87/60min	70/71/70min	8/99/70min	6/99/300min	99/99/70min
4			61/90/60min	43/54/70min	63/93/70min	95/98/120min	95/99/70min
5			99/99/60min	44/95/70min	95/99/70min	16/99/240min	99/99/70min

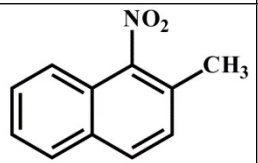
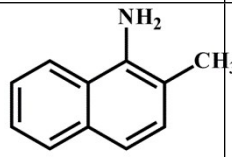
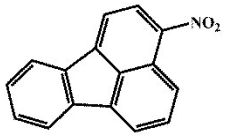
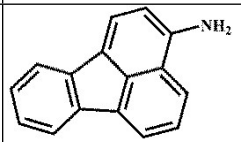
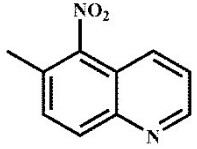
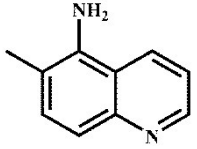
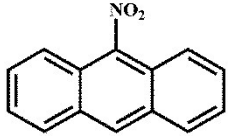
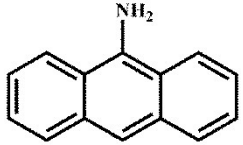
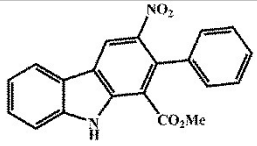
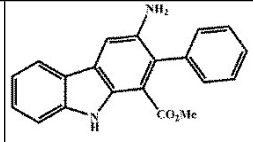
6			Low yield (<3%)	Low yield (<2%)	10/99/70min	8.5/99/300min	98/99/70min
7			98/99/60min	90/90/70min	90/90/70min	12/99/300min	95/99/70min
8			13/99/60min	60/99/70min	99/99/70min	56/99/180min	99/99/70min
9			70/83/60min	27/25/70min	35/30/70min	49/51/180min	Low yield (<2%)
10			75/99/60min	In this case reactions were performed only for optimized solvents (DCM and MeOH).			11/99/70min

Table S2. Crystallographic details for 2 and III

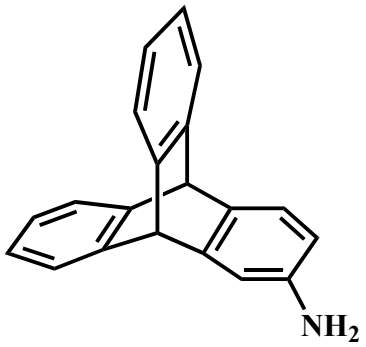
Identification code	**2**	**III**
Empirical formula	$C_{21}H_{19}Cl_2N_3$	$C_{40}H_{26}N_2O$
Formula weight	384.29	550.63
Temperature	293(2) K	293(2) K
Wavelength (Å)	1.54184	1.5418
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, Å	12.084(6)	10.6315(7)
b, Å	9.0350(12)	11.8390(9)
c, Å	17.401(6)	12.1481(8)
α, deg	90	87.279(6)
β, deg	100.28(3)	68.228(6)
γ, deg	90	86.725(6)
Volume, A^3	1869.3(11)	1417.08(18)
Z	4	2
D_{calcd}, mg/m^3	1.366	1.290
μ, mm^{-1}	3.188	0.602
F(000)	800	576
Crystal size, mm^3	0.330 x 0.260 x 0.210	0.210 x 0.170 x 0.130
θ range, deg	4.893 to 39.994	3.741 to 71.277
Index ranges	-10<=h<=9, -7<=k<=6, -14<=l<=14	-12<=h<=12, -14<=k<=14, -14<=l<=11

Reflections collected/unique	3830 / 1132 [R(int) = 0.0352]	9377 / 5357 [R(int) = 0.0223]
Max. and min. transmission	1.00000 and 0.50552	1.00000 and 0.90865
Data/restraints/parameters	1132 / 0 / 235	5357 / 101 / 464
GOF, F^2	1.076	1.027
R_1, wR_2 [$I>2\sigma(I)$]	R1 = 0.0812, wR2 = 0.2345	R1 = 0.0527, wR2 = 0.1382
R_1, wR2 (all data)	R1 = 0.0850, wR2 = 0.2400	R1 = 0.0699, wR2 = 0.1545
Largest diff. peak and hole, e. $Å^{-3}$	1.065 and -0.617	0.185 and -0.239
CCDC No.	**1422762**	**1422763**

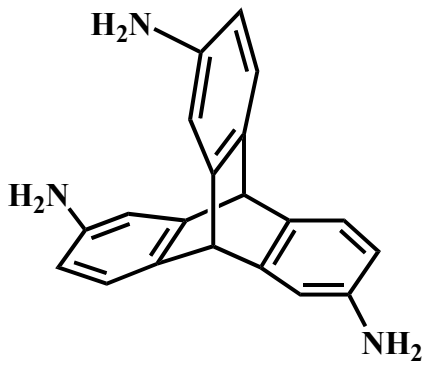
Table S3. Hydrogen bonding parameters for**2[Å** and **(º)]**

D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
N2-H2B**...**N1 (3)	0.860(1)	2.361(1)	3.130(1)	149.05(1)
Equivalent positions: (3) -x+1/2,+y-1/2,-z+1/2+2				

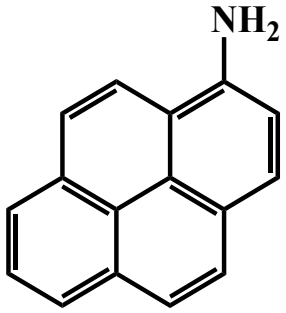
8. ^{1}H NMR data and spectra for the compounds



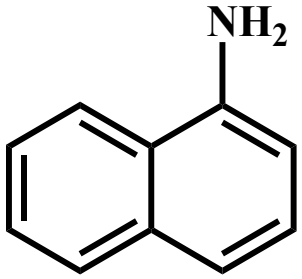
Monoaminotriptycene (1)^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) = 7.32-7.35 (m, 4H, Ph) 7.12(d 1H, J= 8 Hz Ph), 6.95-6.98 (m 4H, Ph) 6.78(d, J= 2 Hz 1H), 6.26(d of d J = 2 Hz, 8 Hz 1H, Ph). 5.29 (s 1H, bridgehead), 3.51(brs, 2H, NH_2).



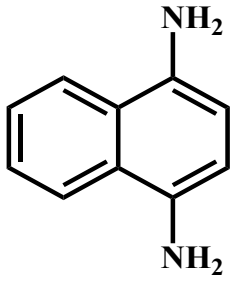
Triaminotriptycene (2)^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) = 7.04 (d, 3H, 8Hz Ph) 6.72 (s 3H, Ph), 6.23(m 3H, Ph) 5.04(s, 1H, bridgehead), 5.02(s 1H, bridgehead), 3.48(brs, 6H, NH2).



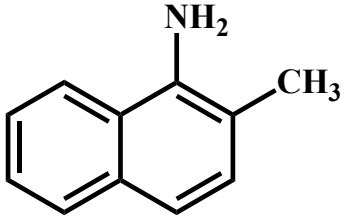
1-aminopyrene (3) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) 7.90-8.06 (m, 7H), 7.80(d, 1H, J=8.8 Hz), 7.37 (d, 1H J= 8 Hz), 4.49 (brs, 2H, NH_2).



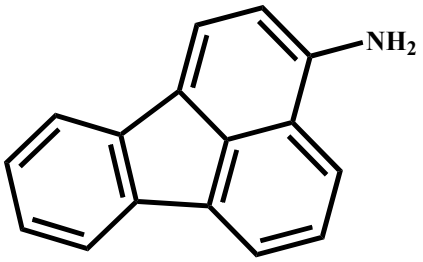
1-aminonaphthelene (4) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) 7.78-7.82 (m, 2H) 7.43-7.45 (m, 2H), 7.24-7.30 (m, 2H), 6.76 (d, 1H, J= 6.4Hz), 4.13 (brs, 2H NH_2).



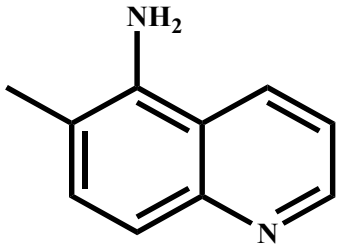
1,4-diaminonaphthelene (5) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) 7.84-7.87 (m, 2H), 7.46-7.52 (m, 2H), 6.68 (s, 2H), 3.79 (brs, 4H, NH_2)



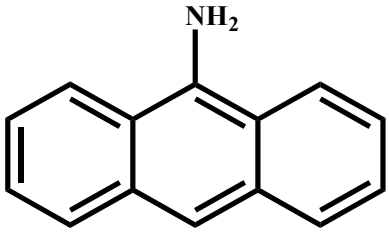
2-methyl-1-aminonaphthelene (6) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) 7.76-7.81 (m, 2H), 7.38-7.46 (m, 2H), 7.21-7.28 (m, 2H), 4.10 (brs 2H, NH_2), 2.36 (s, 3H, CH_3).



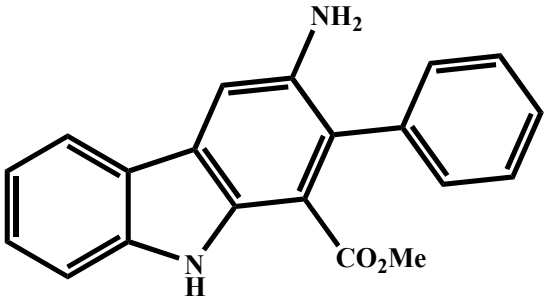
1-aminoflourenthene (7) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm), 7.93-7.95 (d, 1H, J= 6.8 Hz), 7.86-7.88 (d, 1H, J= 11.2 Hz), 7.75-7.80 (m, 2H), 7.69-7.71(d,1H, J= 7.52 Hz) 7.55-7.59 (m, 1H), 7.31-7.34 (m, 1H), 7.24-7.27 (m, 1H), 6.73(d, 1H, J = 7.28 Hz), 4.42(brs, 2H, NH_2).



6-methyl-5-aminoquinoline (8)^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) , 8.83(m, 1H) 8.14(d, 1H, J= 8.2 Hz,), 7.50-7.53(d, 1H, 8.2 Hz),7.43-7.45 (d, 1H, J.=. 8.2 Hz), 7.31-7.33(m, 1H), 4.14(brs, 2H, NH_2), 2.35(s, 3H, CH_3)



9-aminoanthracene (9) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm) ,7.92 (m, 4H), 7.88 (s, 1H), 7.42 (m, 4H), 4.86 (brs, 2H, NH_2)



1-methoxycarbonyl-2-phenyl-3-nitro-9H-carbazole (10) ^{1}H-NMR (400MHz, $CDCl_3$) δ(ppm), 9.51(s, 1H), 8.00 (d, 1H, J = 6.8 Hz), 7.67 (s, 1H), 7.40-7.46 (m, 2H), 7.19-7.22 (m, 1H), 6.53(s, 1H), 3.65 (brs, 2H, NH_2), 3.52 (s, 3H, CH_3)

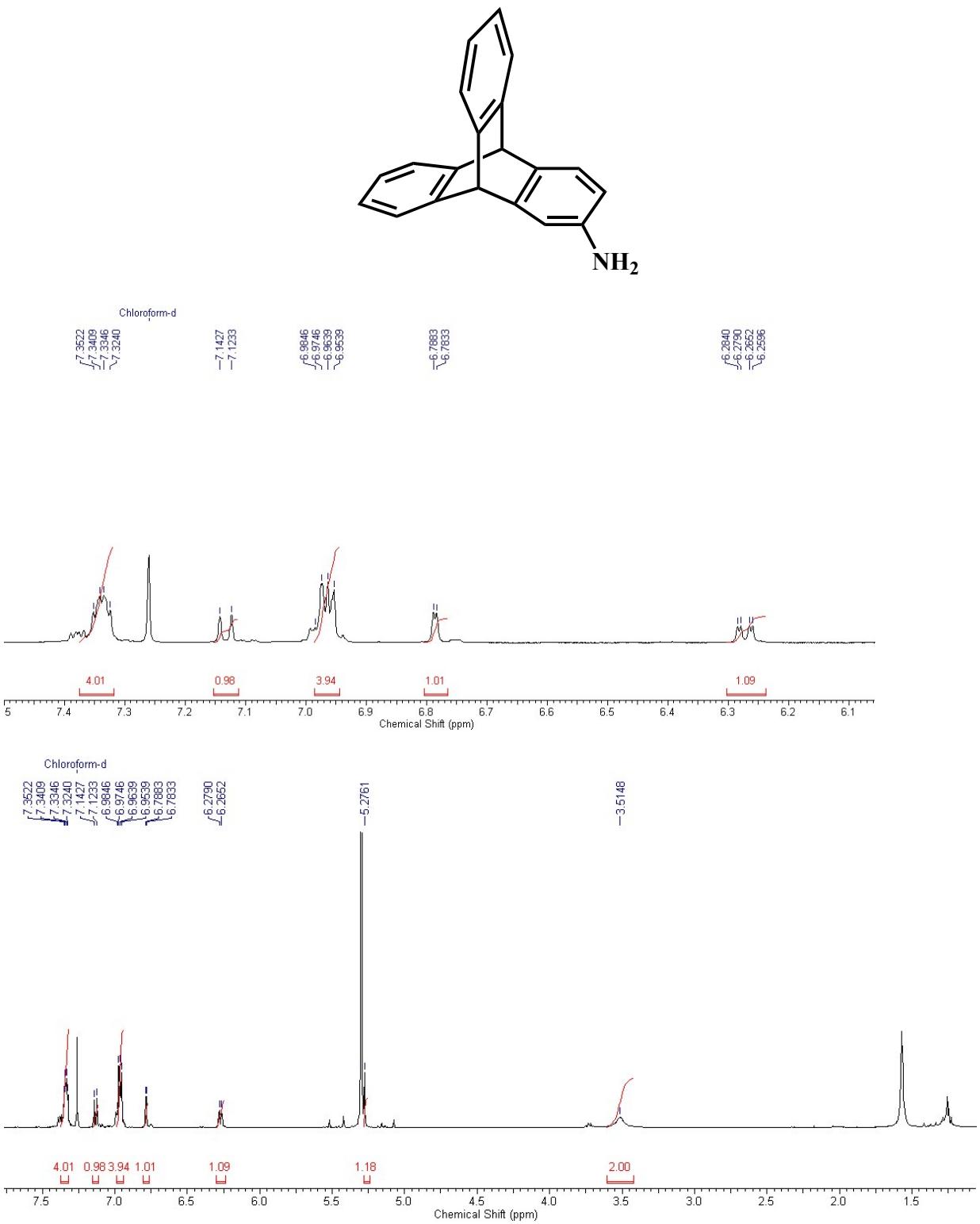


Fig.S10^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**.

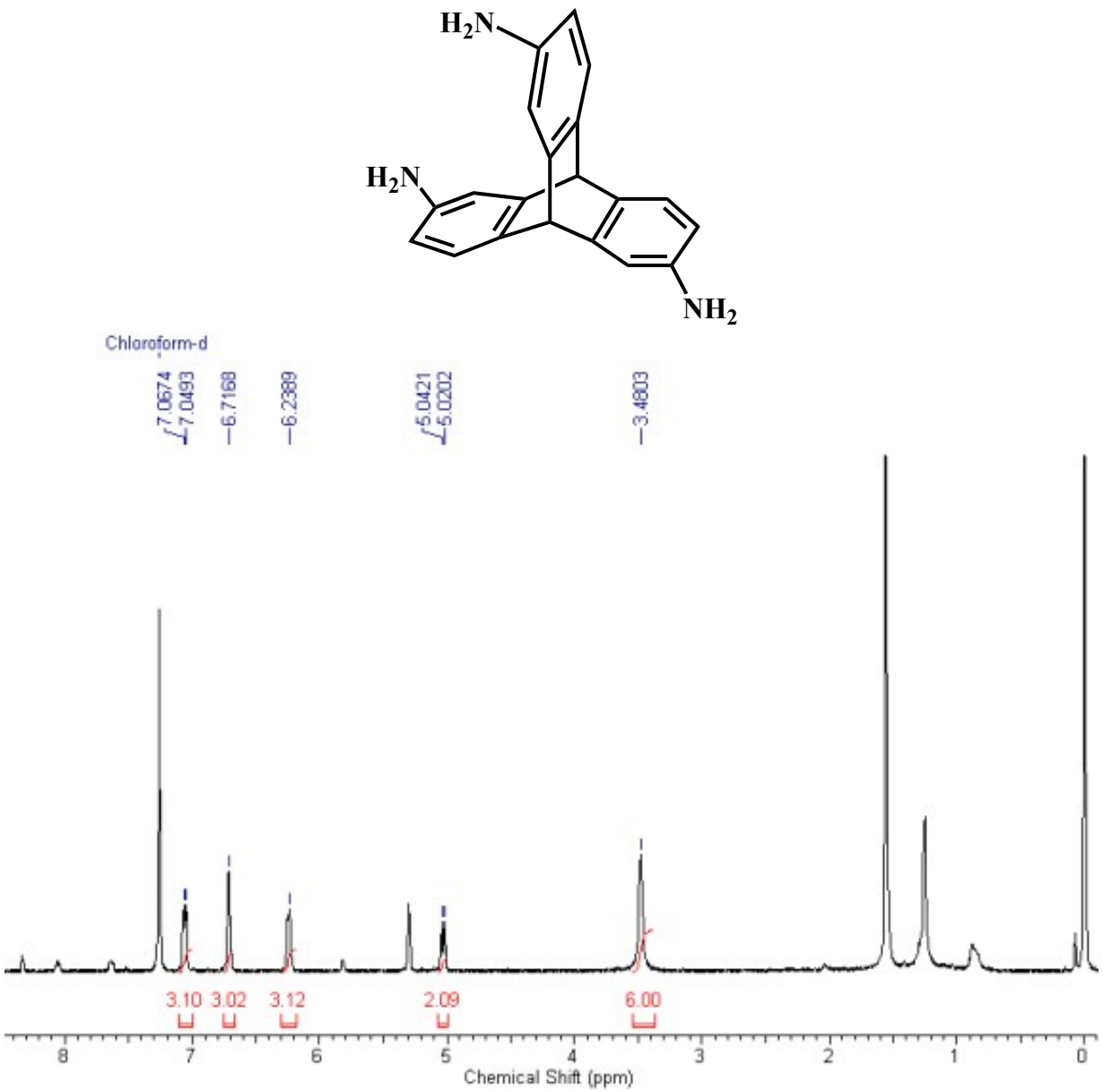


Fig. S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**.

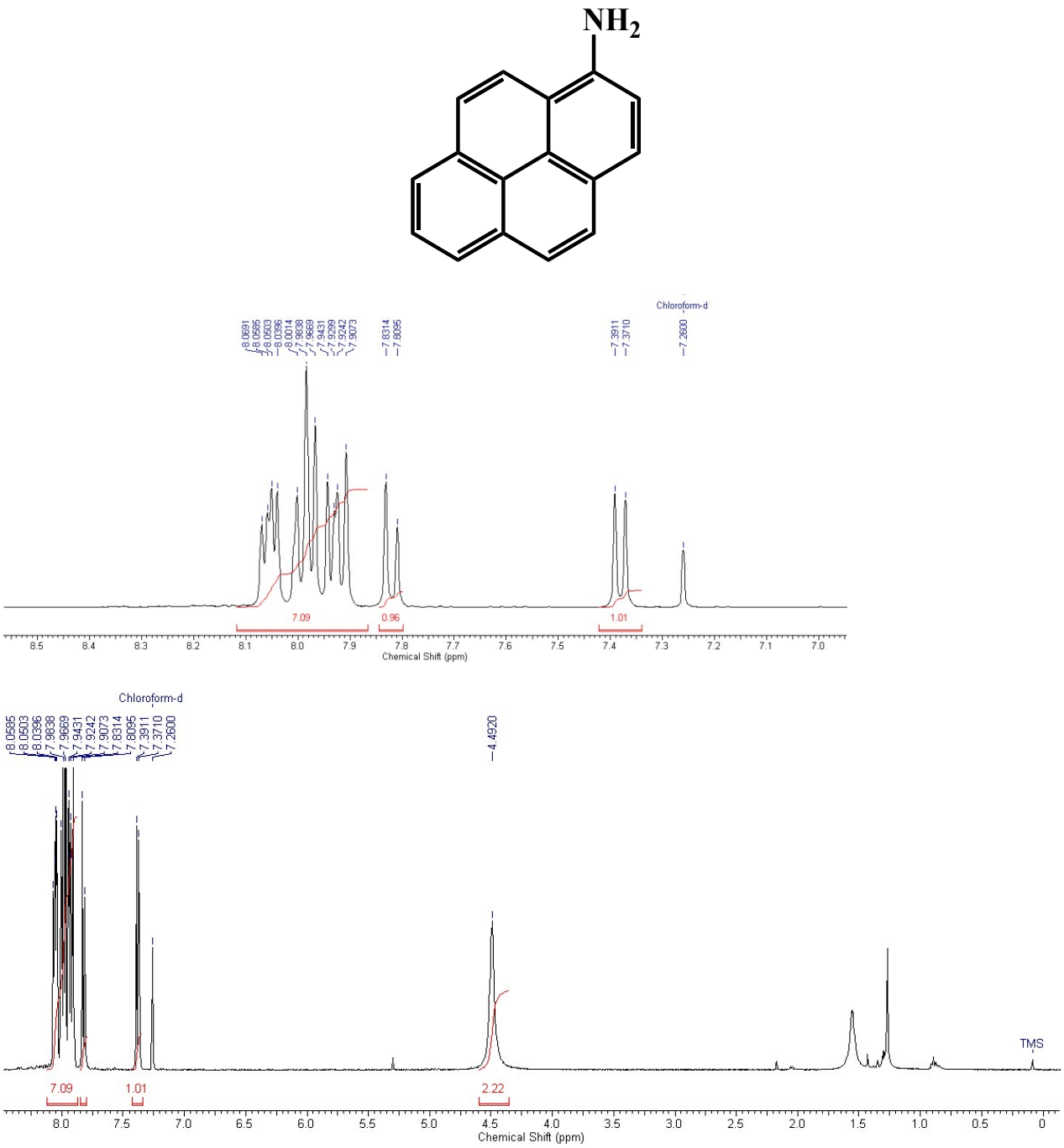


Fig. S12[1]H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

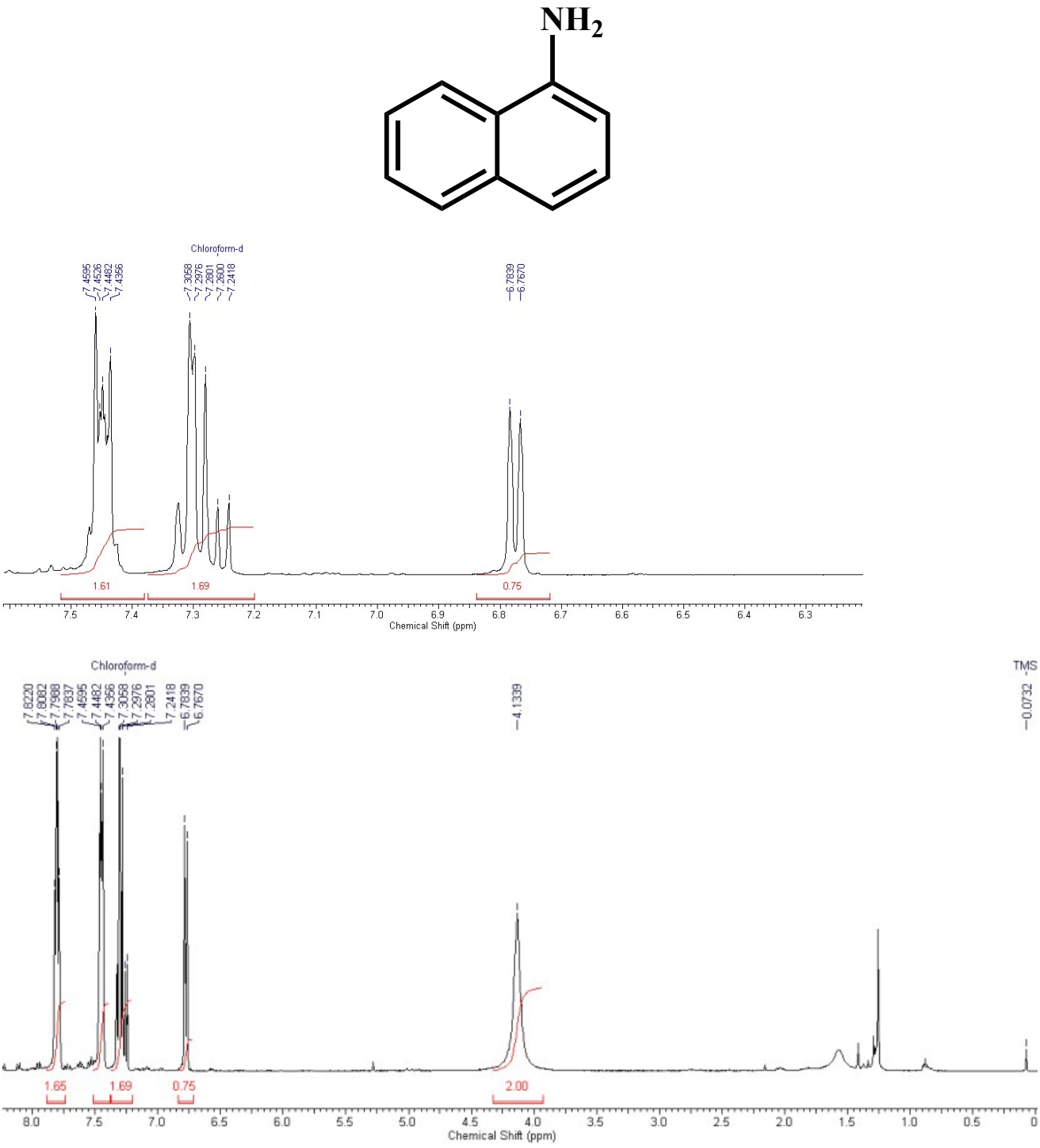


Fig. S13 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

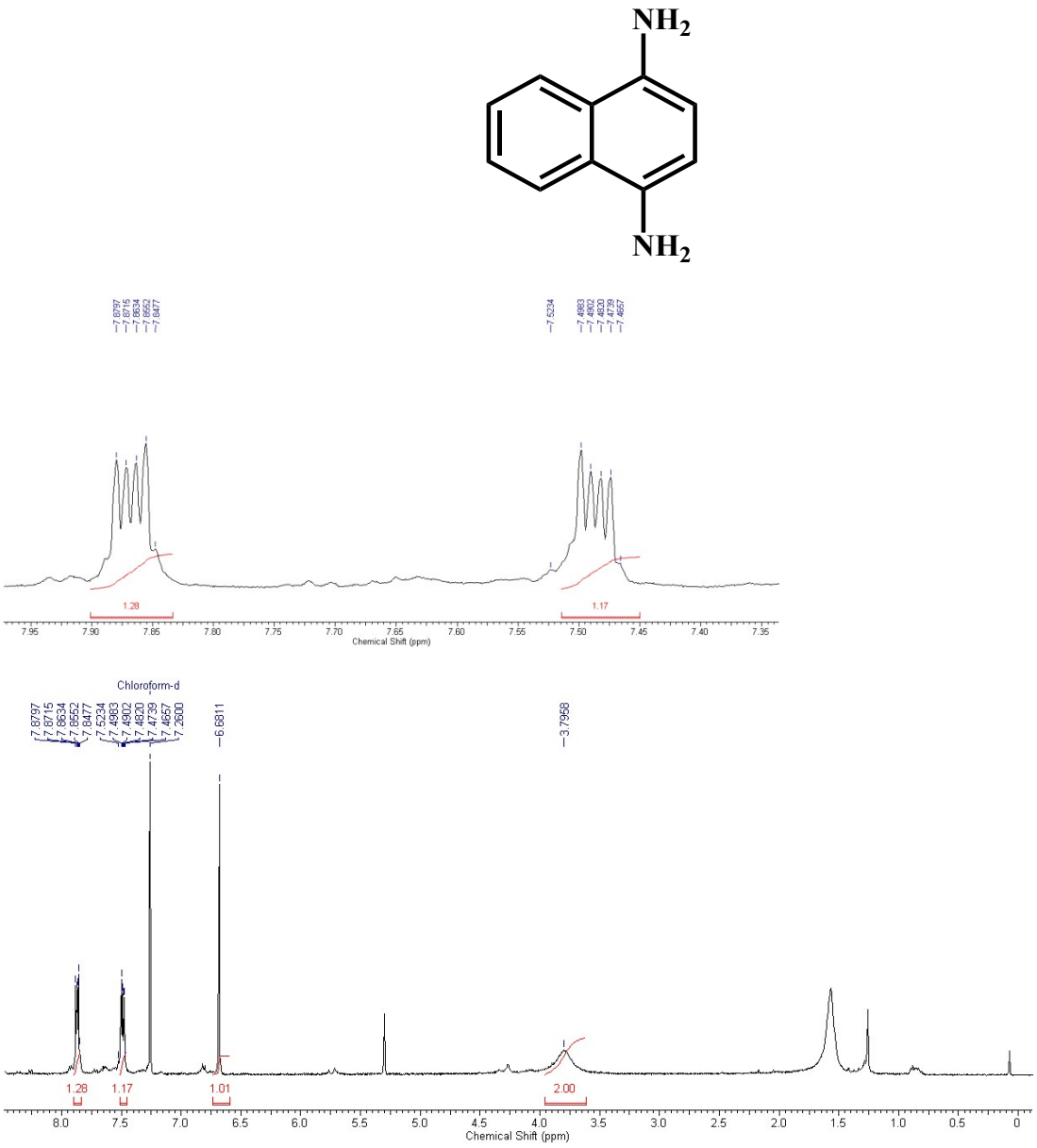


Fig. S14^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**.

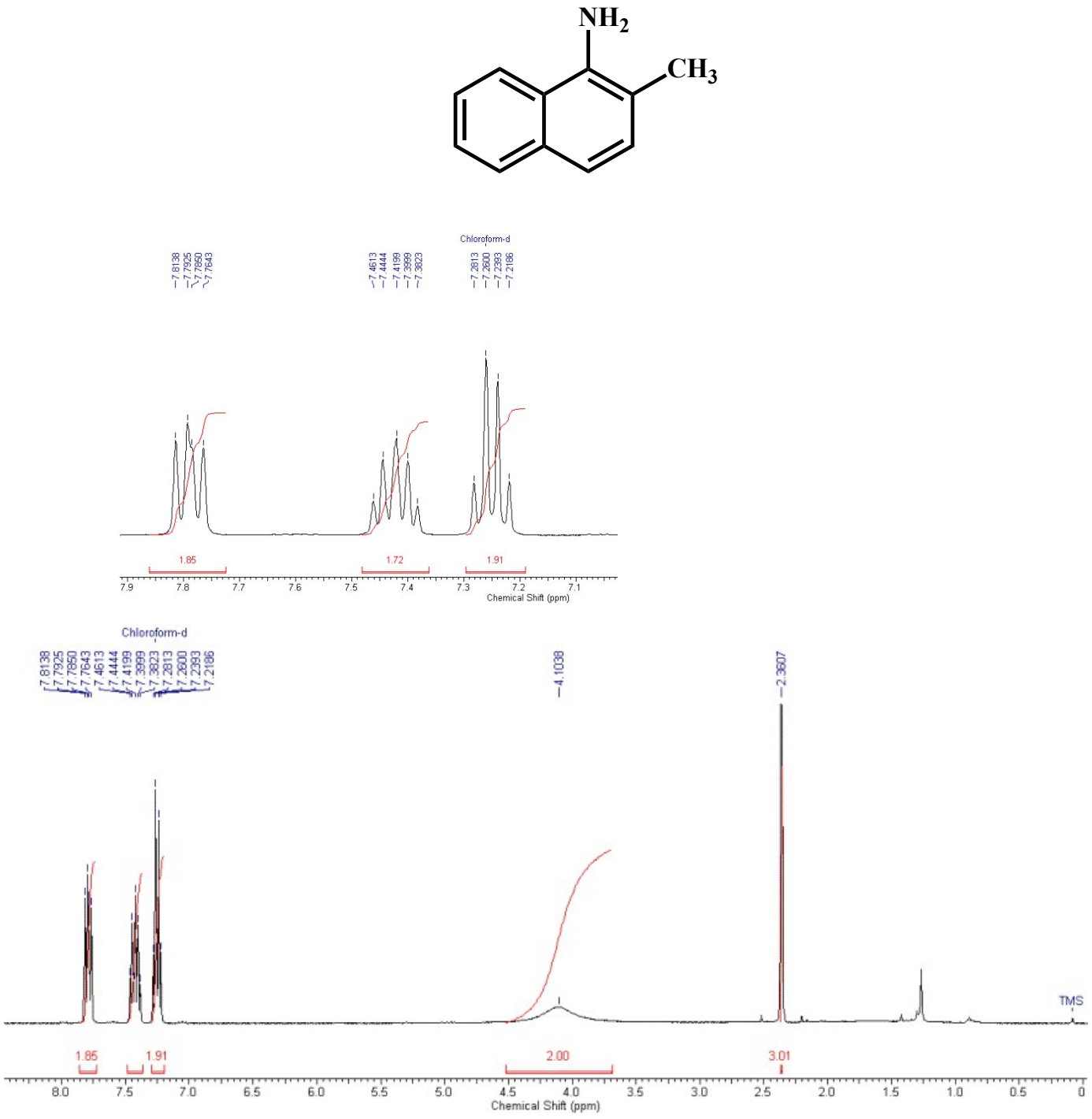


Fig. S15^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**.

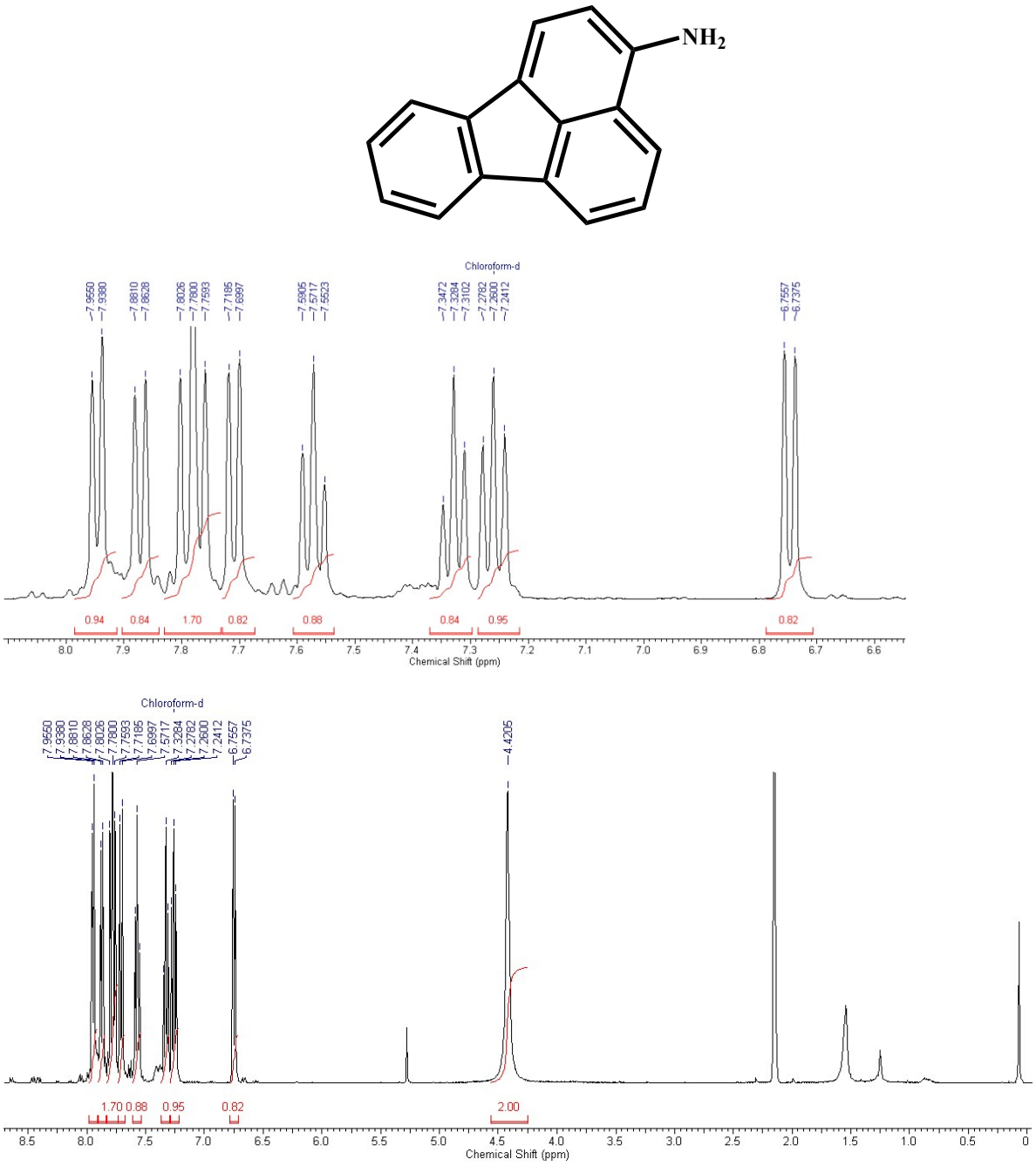


Fig. S16^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7**.

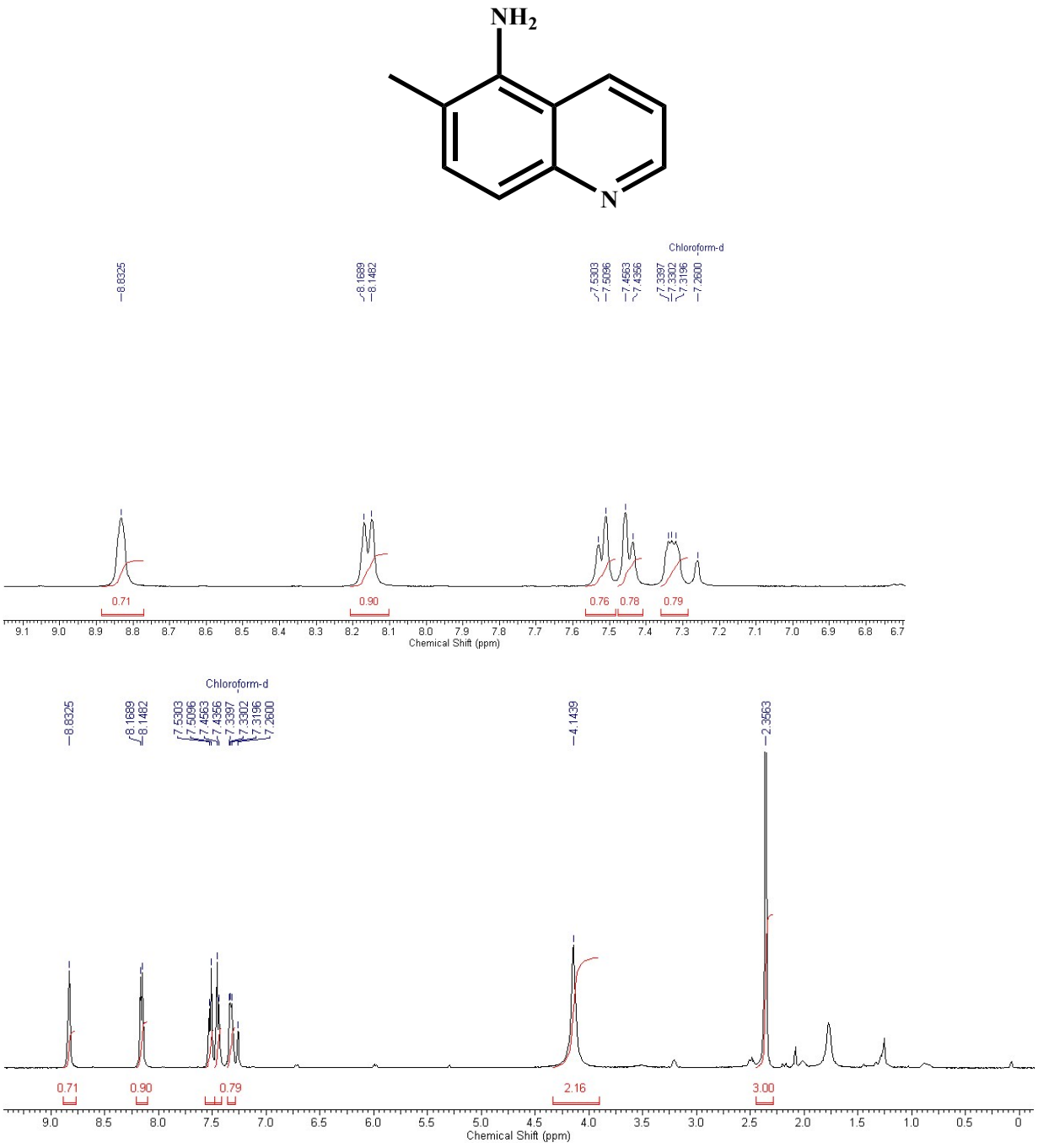


Fig.S17[1]H NMR spectrum (400 MHz, $CDCl_3$) of **8**.