Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

For the Manuscript Entitled

Trinuclear $\{Co^{2+}\text{-}M^{3+}\text{-}Co^{2+}\}$ Complexes Catalyze Reduction of Nitro Compounds

By

Sumit Srivastava, Manvender S Dagur, Afsar Ali,

and Rajeev Gupta*

Index

Tables:

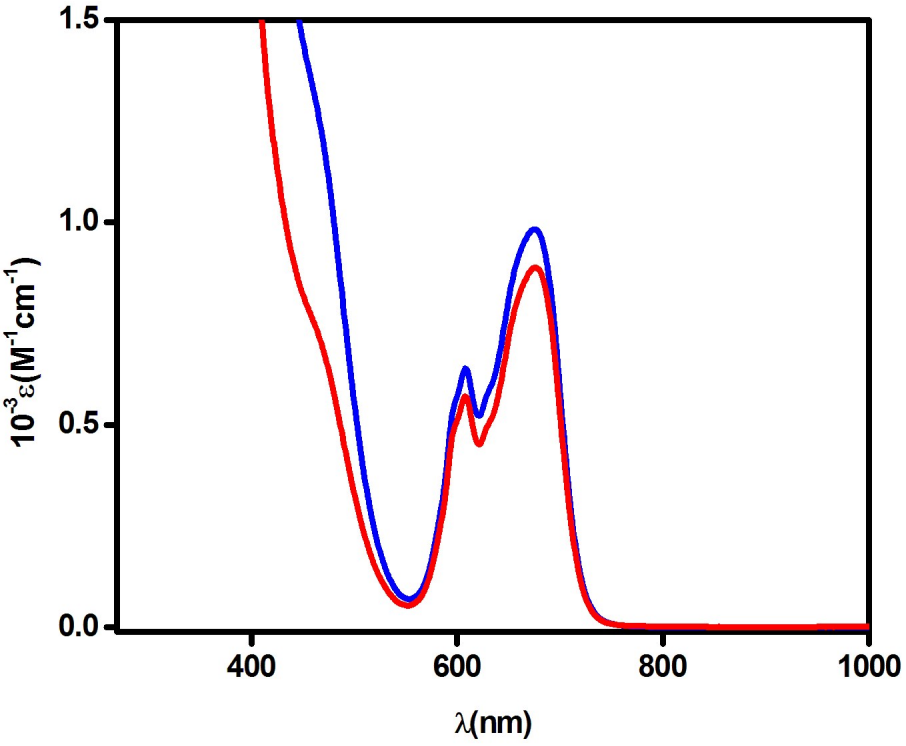


Figure S1. Absorption spectrum of complexes **3** (blue trace) and **4** (red trace) recorded in DMF.

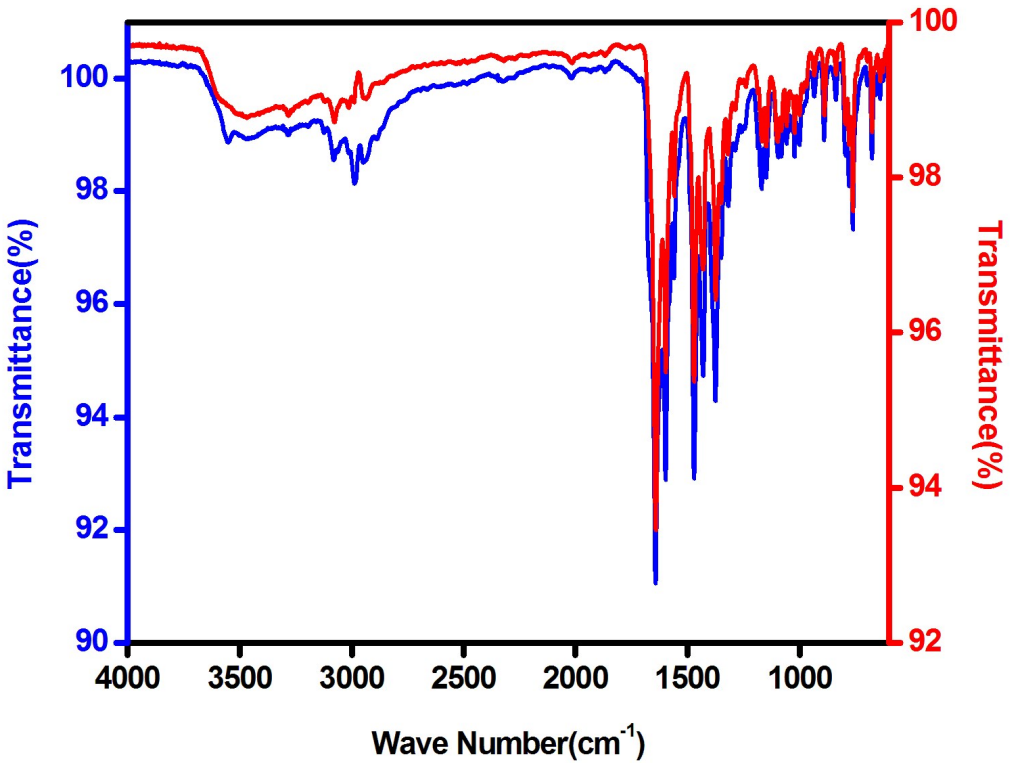


Figure S2. FTIR spectra for complexes **3** (blue trace) and **4** (red trace).

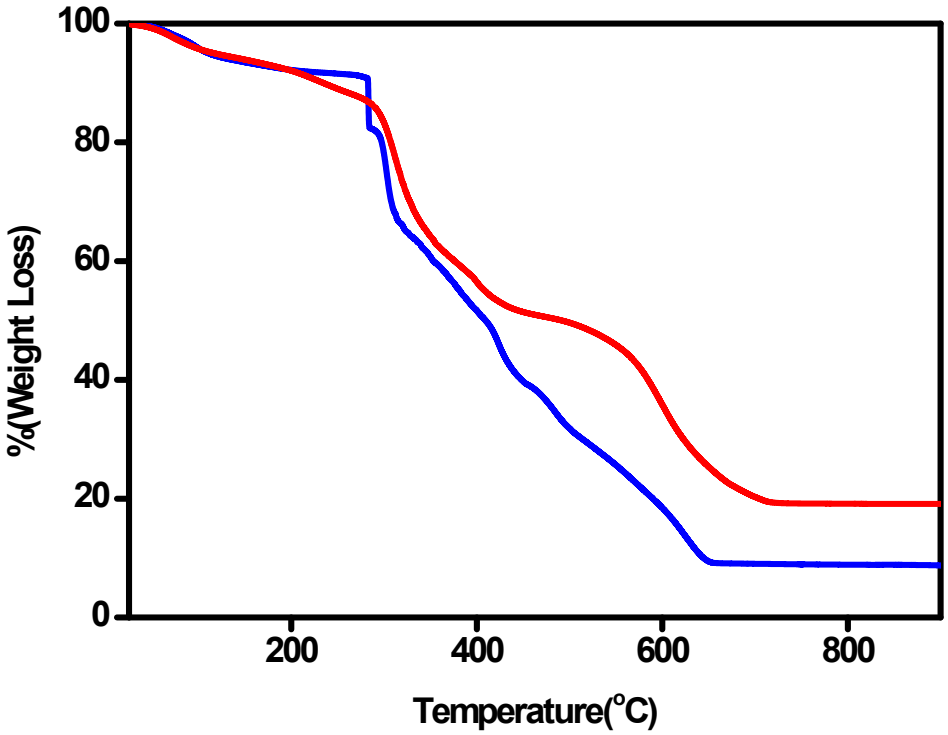


Figure S3. TGA plots for complexes **3** (blue trace) and **4** (red trace).

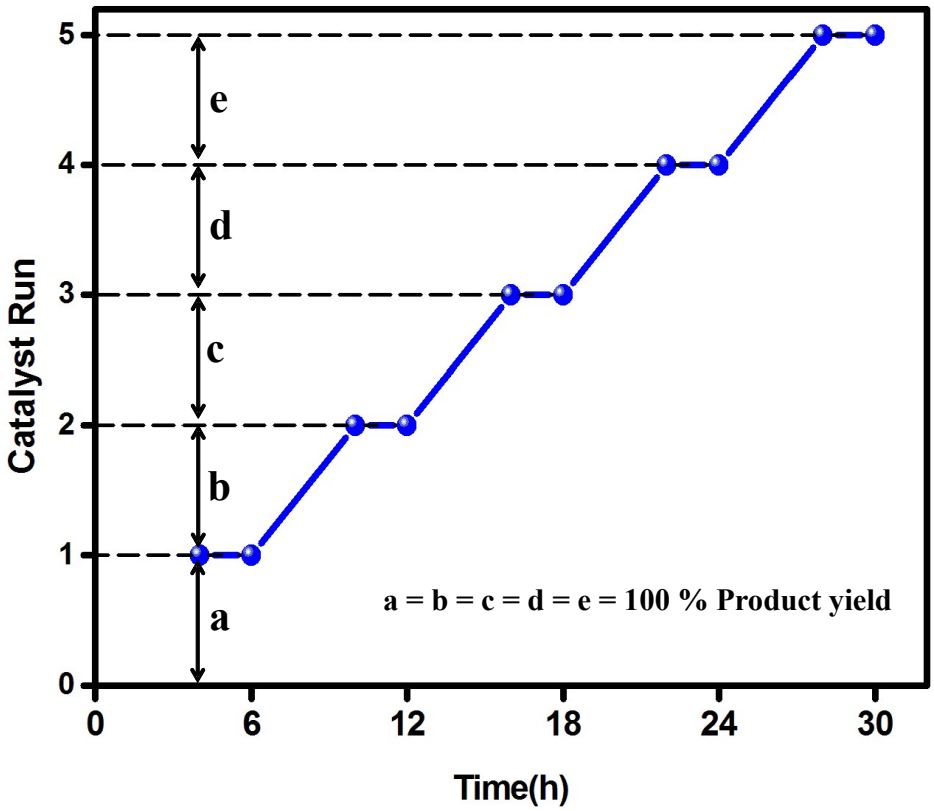


Figure S4. Catalytic performance of catalyst **3** in the reduction of nitrobenzene to aniline displaying identical performances during successive addition of five batches of nitrobenzene (a – e); a = b = c = d = e = 100% aniline formation. The yields were calculated using gas chromatograph.

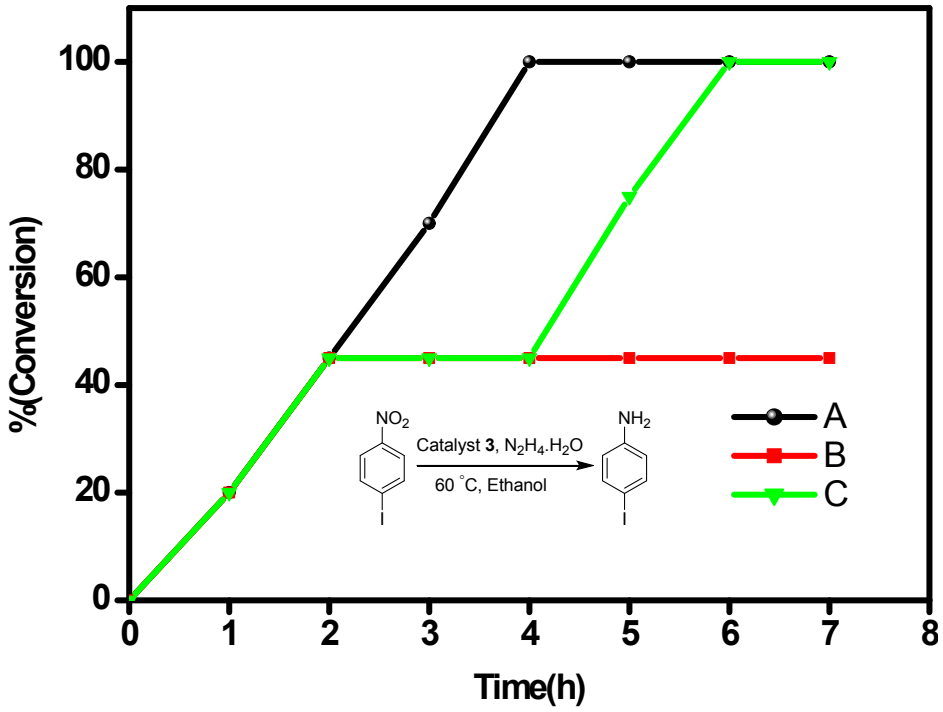


Figure S5. (A) Reduction of 1-iodo-4-nitrobenzene with hydrazine in the presence of complex **3** showing maximum reduction at 4 h. (B) Catalyst was filtered after 2 h and as a result the reduction was stopped. (C) Catalyst was re-added after a gap of 2 h, and maximum reduction was observed after 2 h. In all cases, the yield was calculated using gas chromatograph.

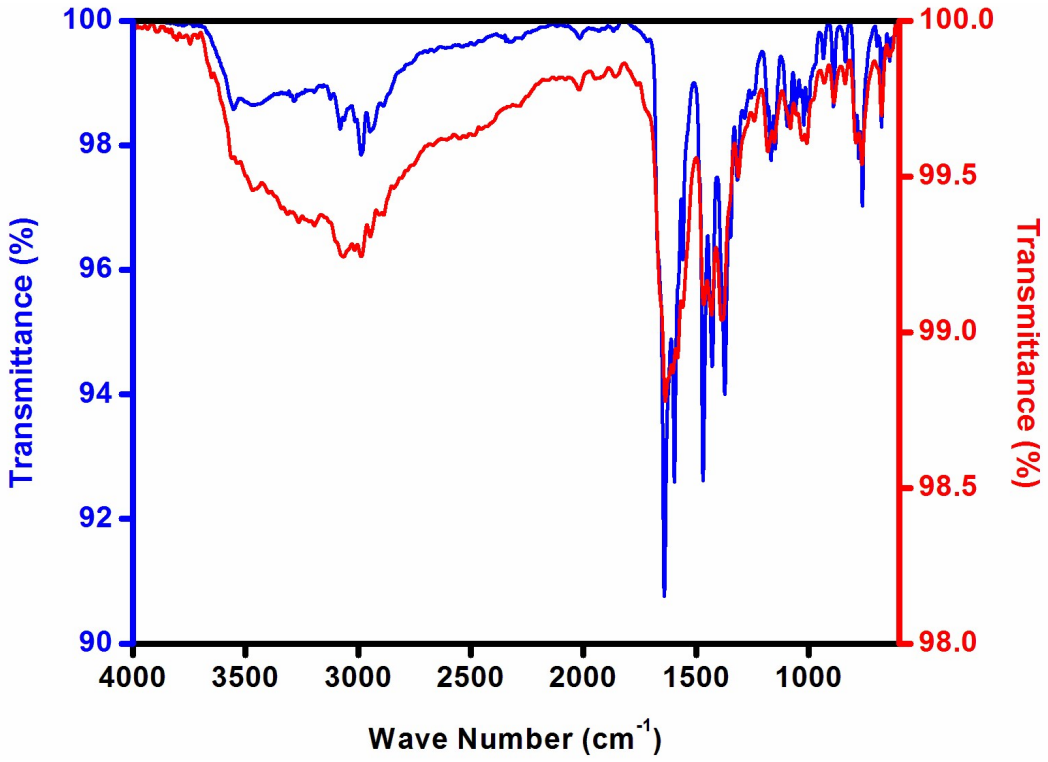


Figure S6. FTIR spectra of complex **3** before (blue trace) and after (red trace) the reduction of nitrobenzene to aniline.

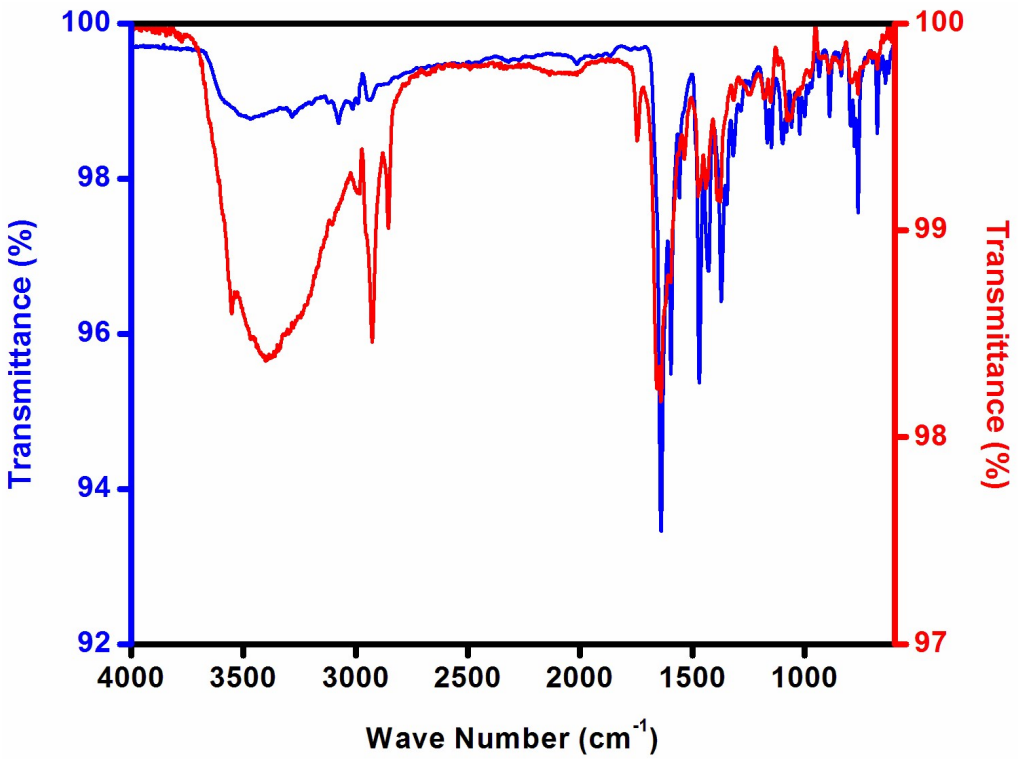


Figure S7. FTIR spectra of complex **4** before (blue trace) and after (red trace) the reduction of nitrobenzene to aniline.

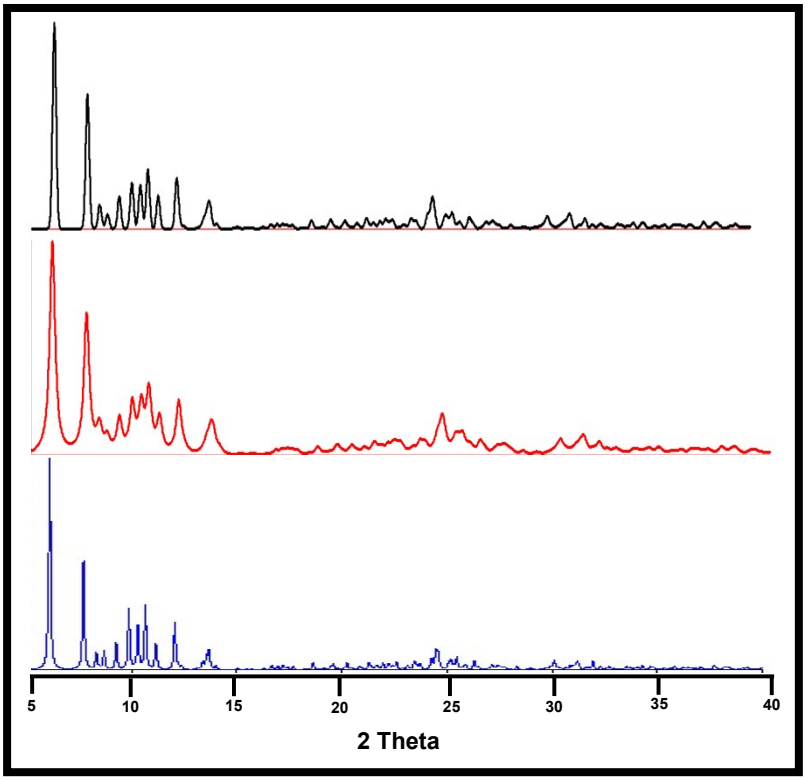


Figure S8. X-ray powder diffraction patterns for complex **3** simulated by the Mercury 3.0 using single crystal data (blue trace), as-synthesized (red trace) and after the reduction of nitrobenzene to aniline (black trace).

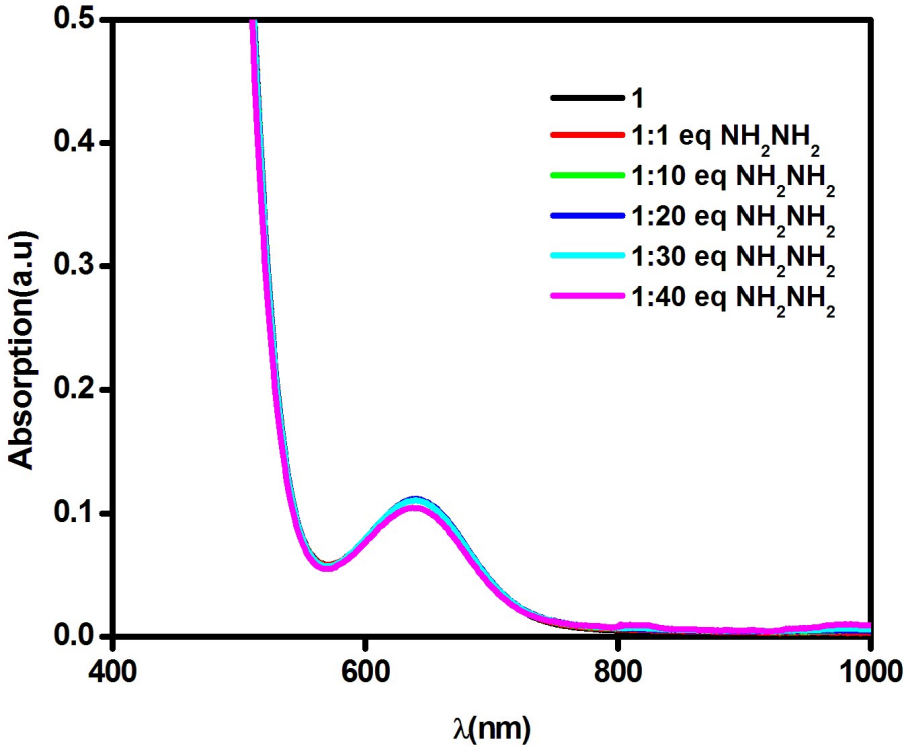


Figure S9. UV/Vis spectral titration of complex **1** with varying amounts of hydrazine (1 equiv. – 40 equiv.) displaying no change in the spectral features.

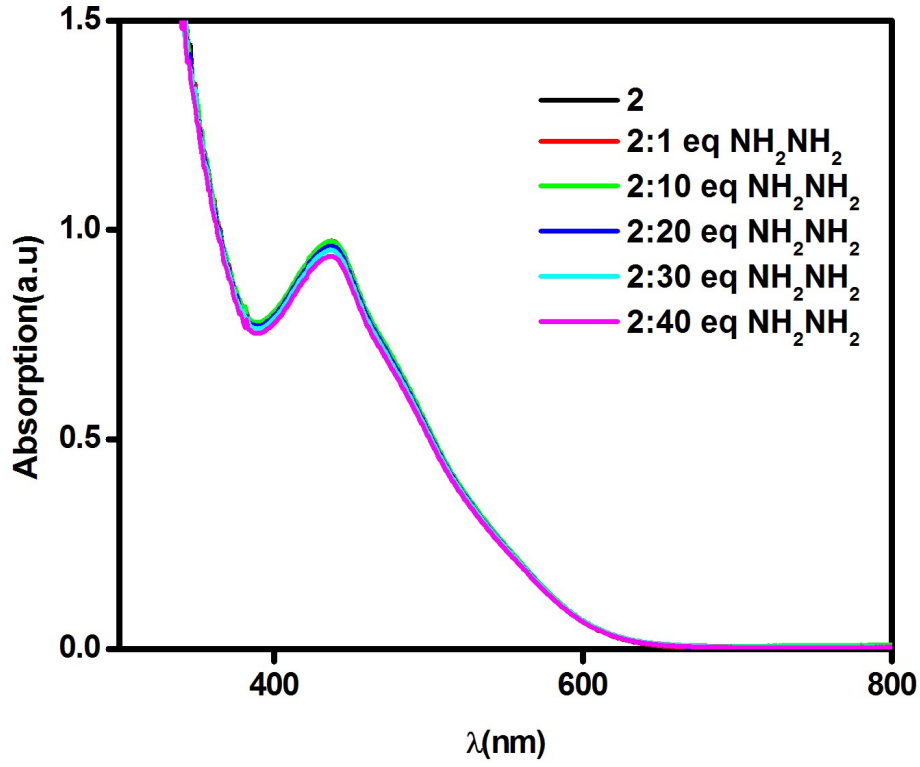


Figure S10. UV/Vis spectral titration of complex **2** with varying amounts of hydrazine (1 equiv. – 40 equiv.) displaying no change in the spectral features.

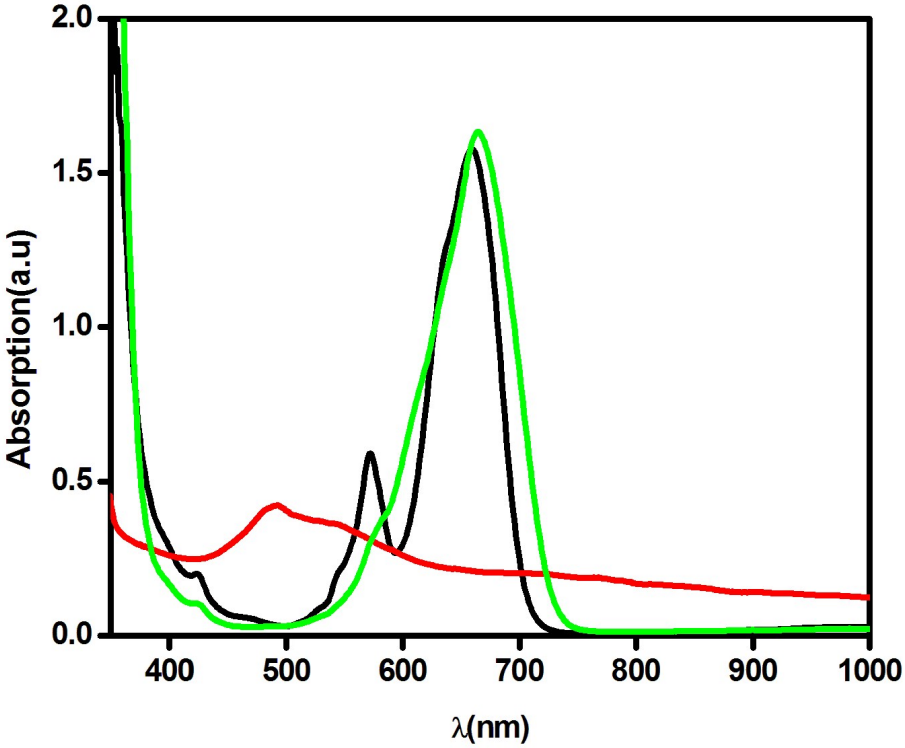


Figure S11. UV/Vis spectrum of complex **7** (black trace); complex **7** after the addition of 0.25 equivalent of hydrazine (red trace); after the addition of 0.5 equivalent of bromine (green trace).

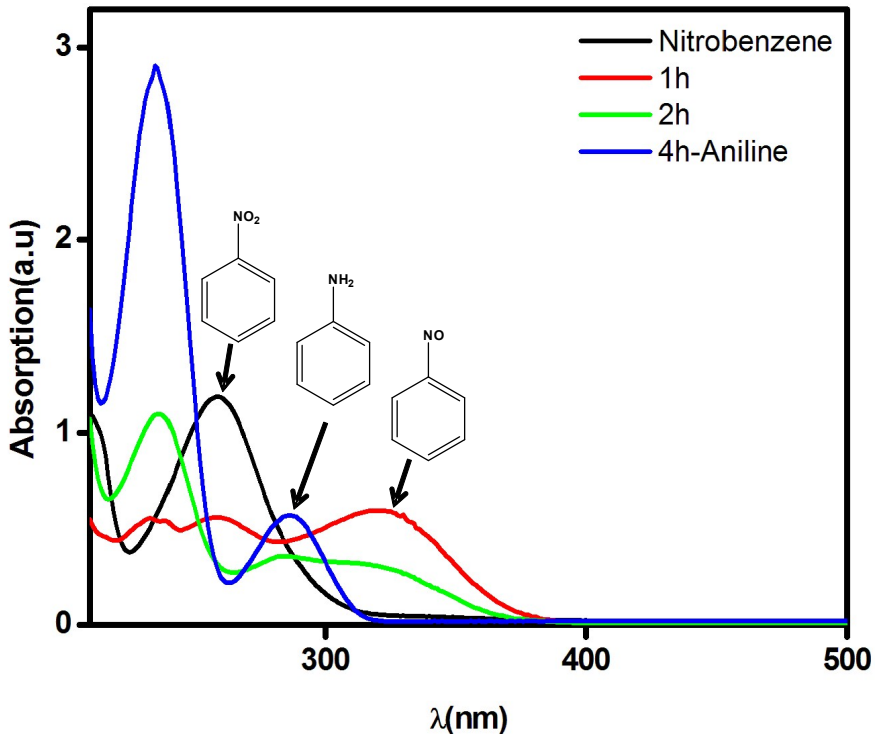


Figure S12. UV/Vis spectral monitoring for the reduction of nitrobenzene to aniline with respect to time using complex **3** and hydrazine in EtOH.

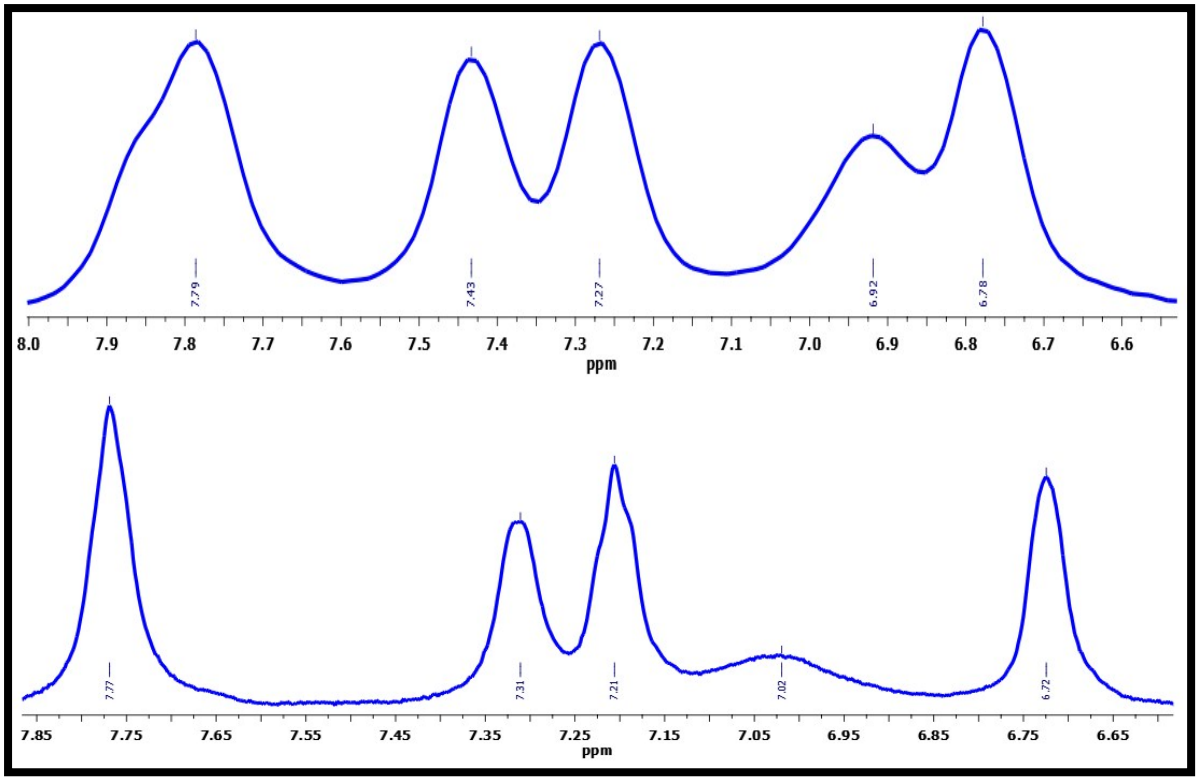


Figure S13. Selected portion of the ^{1}H NMR spectra recorded in D_2O of complex **3** before (lower trace) and after the addition of 0.5 equiv. of hydrazine (upper trace).

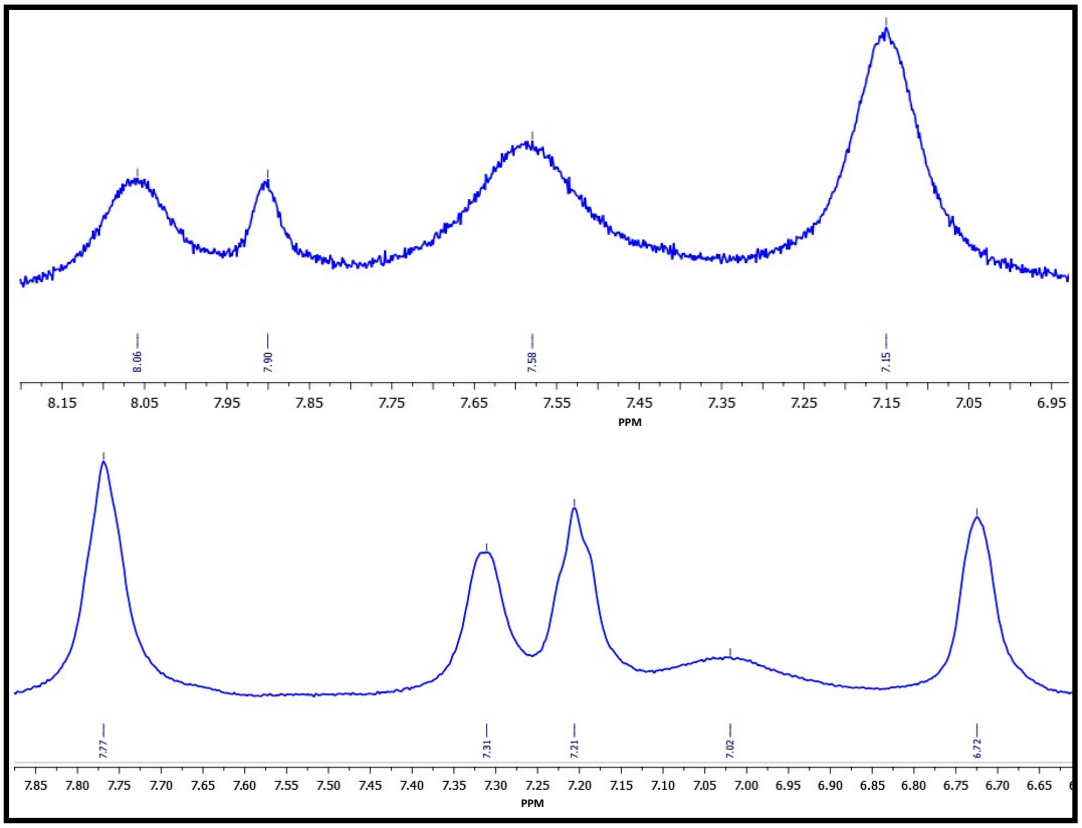


Figure S14. Selected portion of the ^{1}H NMR spectra recorded in D_2O of complex **4** before (lower trace) and after the addition of 0.5 equiv. of hydrazine (upper trace).

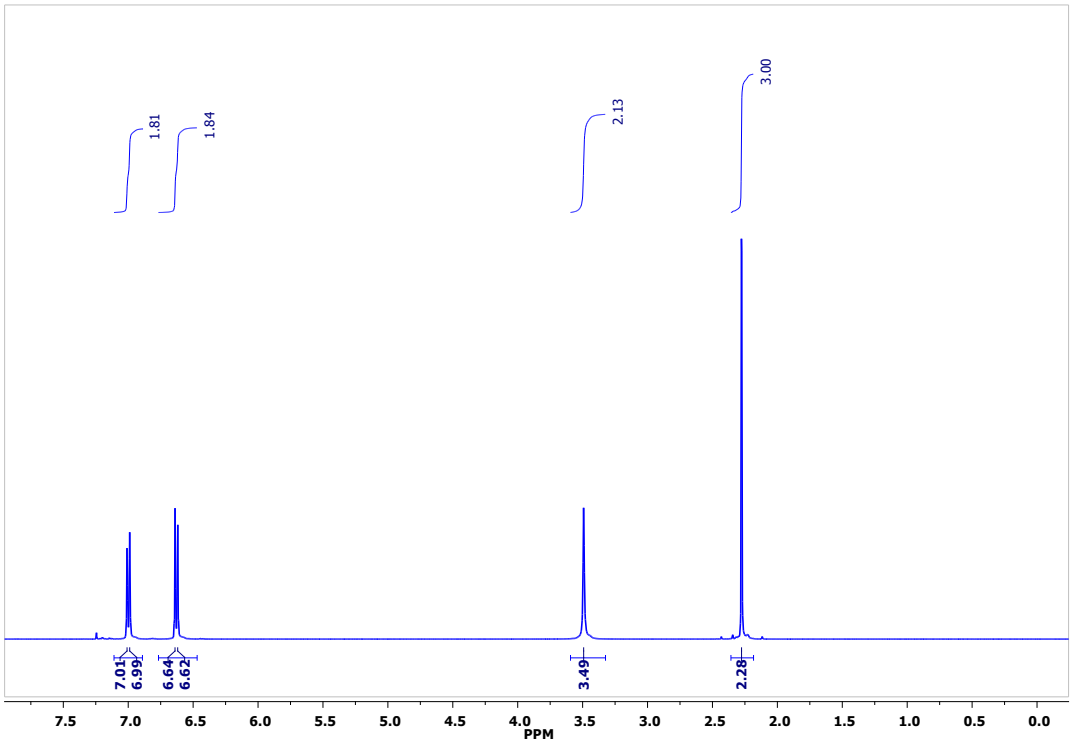


Figure S15. ^{1}H NMR spectrum of 4-aminotoluene (**1b**) in $CDCl_3$.

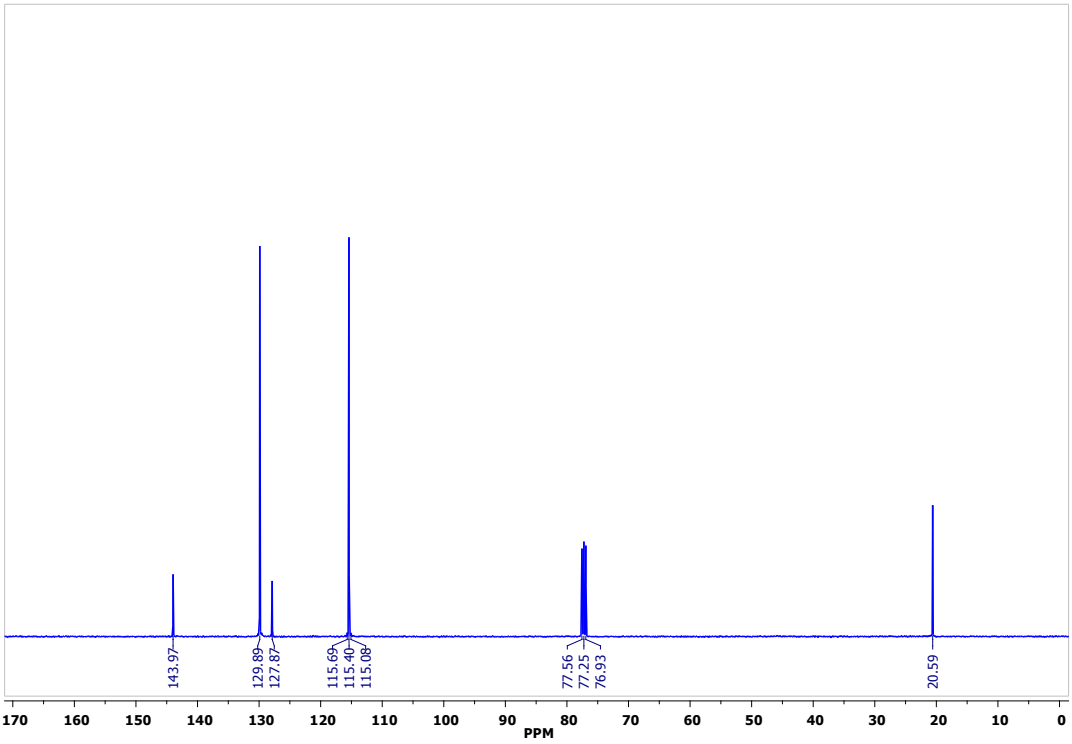


Figure S16. ^{13}C NMR spectrum of 4-aminotoluene (**1b**) in $CDCl_3$.

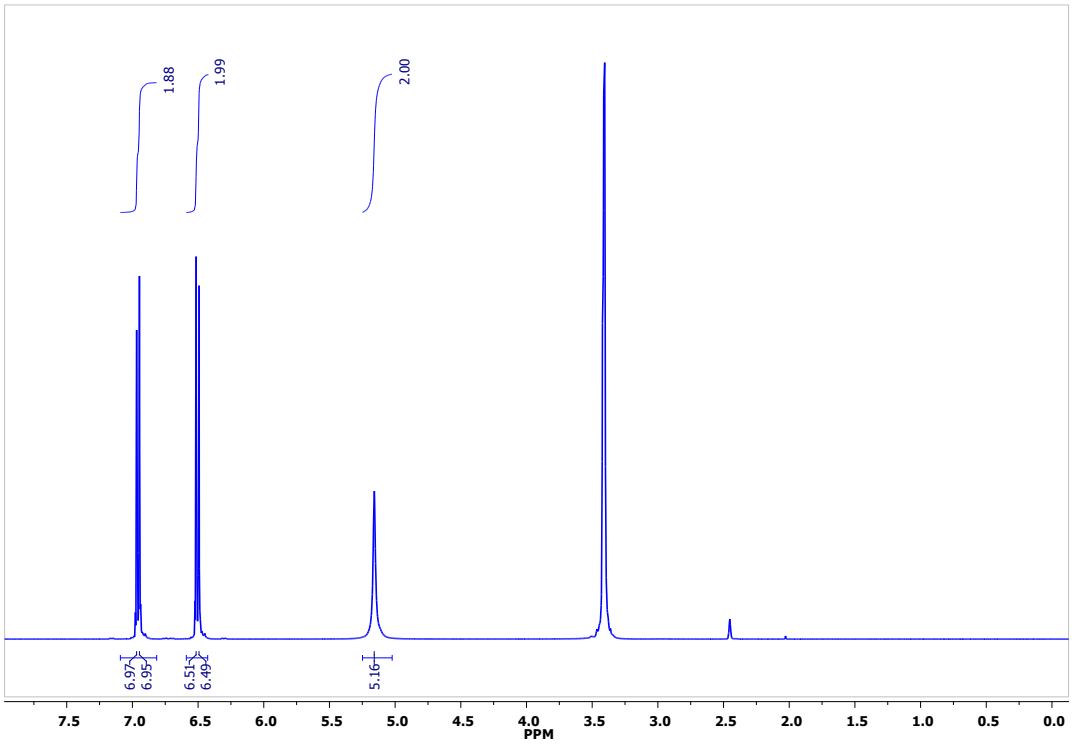


Figure S17. ^{1}H NMR spectrum of 4-chloroaniline (**1i**) in DMSO-d_6.

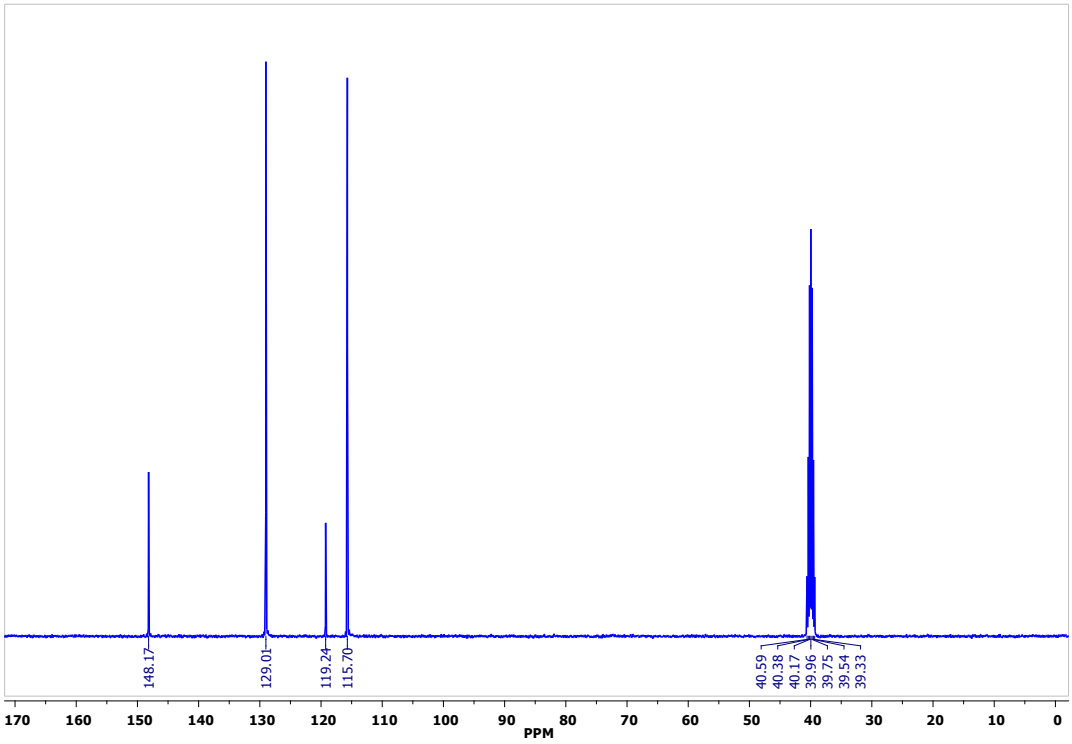


Figure S18. ^{13}C NMR spectrum of 4-chloroaniline (**1i**) in DMSO-d_6.

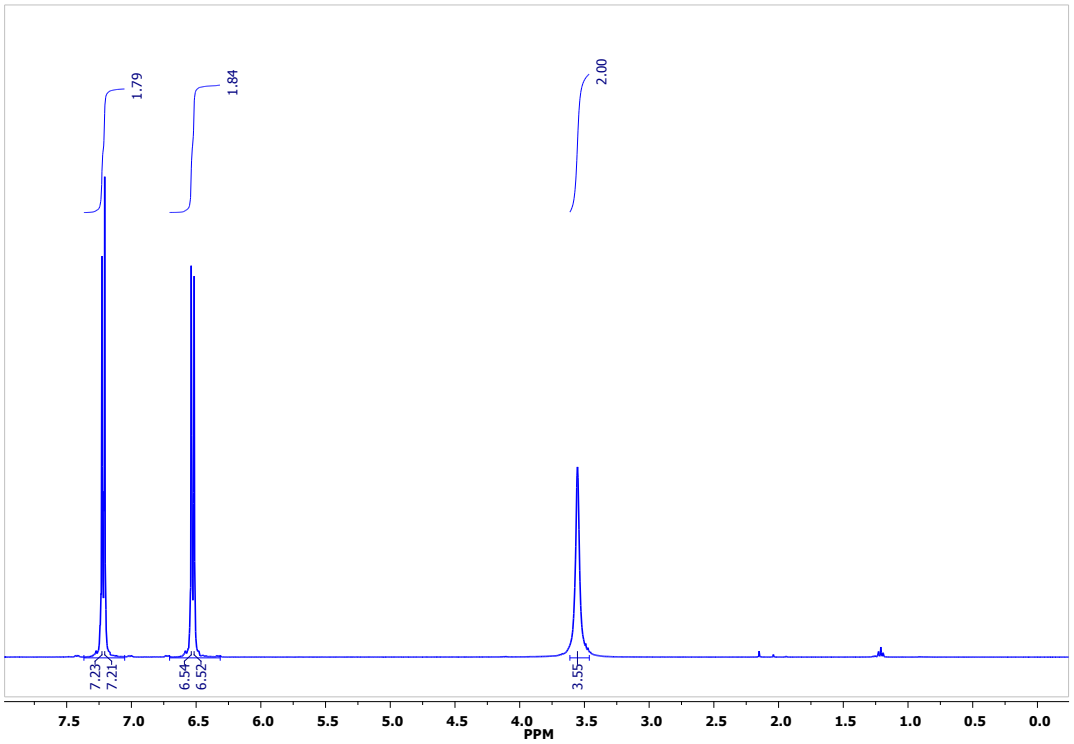


Figure S19. ^{1}H NMR spectrum of 4-aminobenzonitrile (**1o**) in $CDCl_3$.

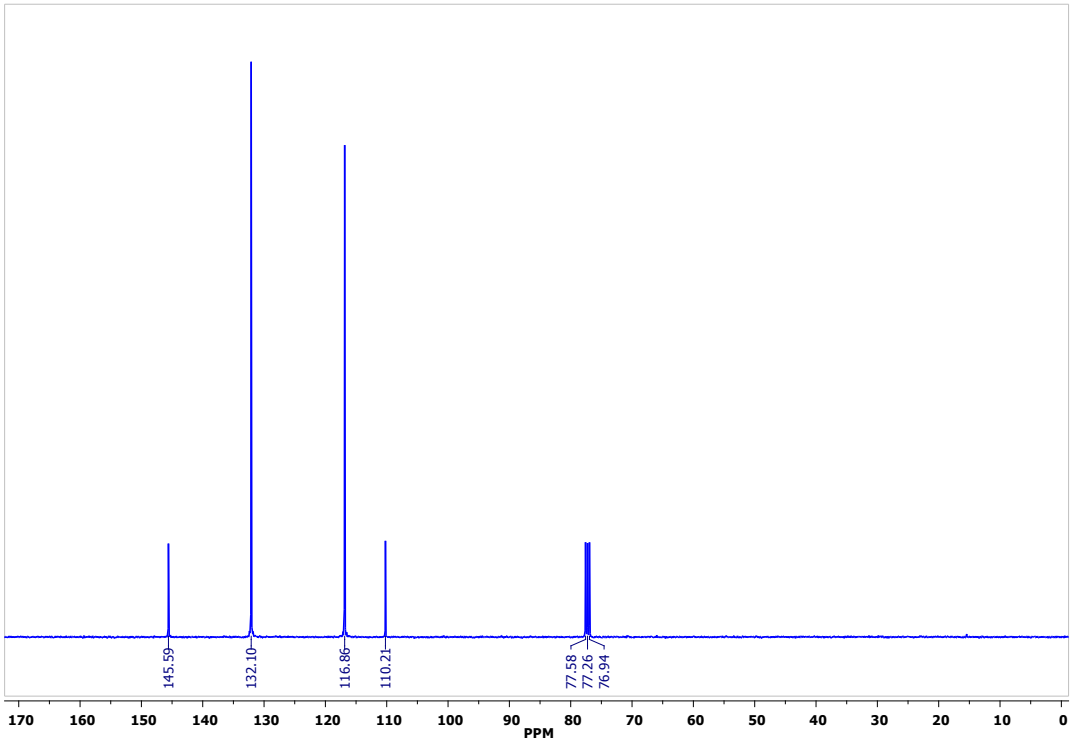


Figure S20. ^{13}C NMR spectrum of 4-aminobenzonitrile (**1o**) in $CDCl_3$.

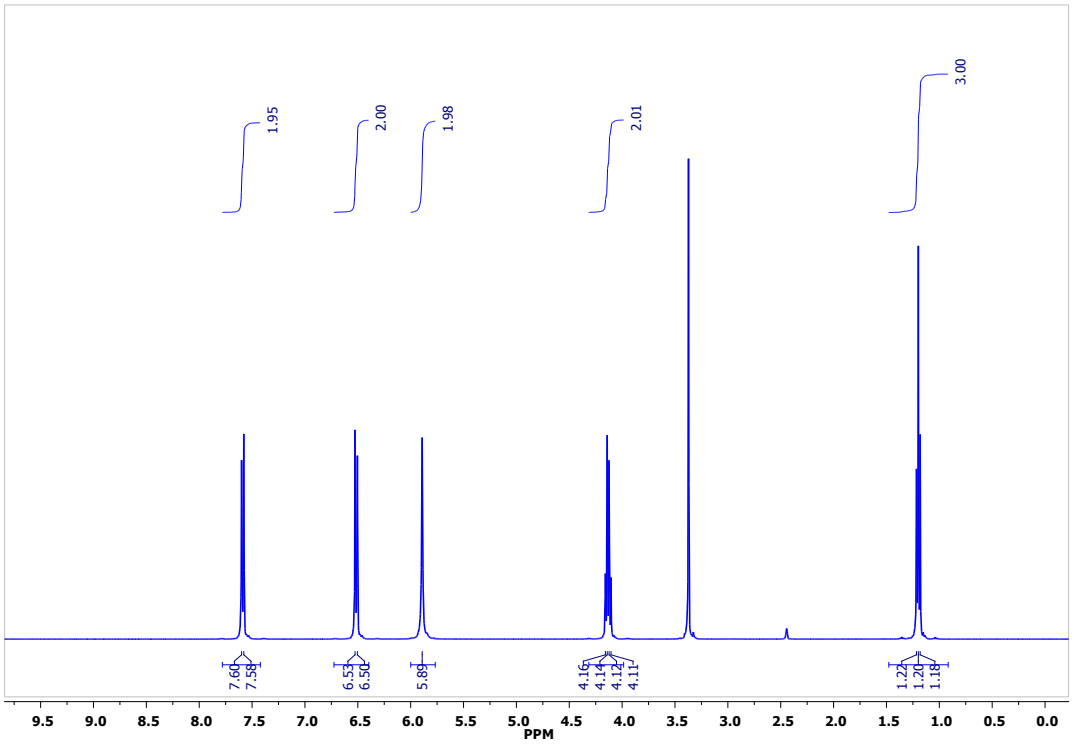


Figure S21. ^{1}H NMR spectrum of ethyl-4-aminobenzoate (**1q**) in DMSO-d_6.

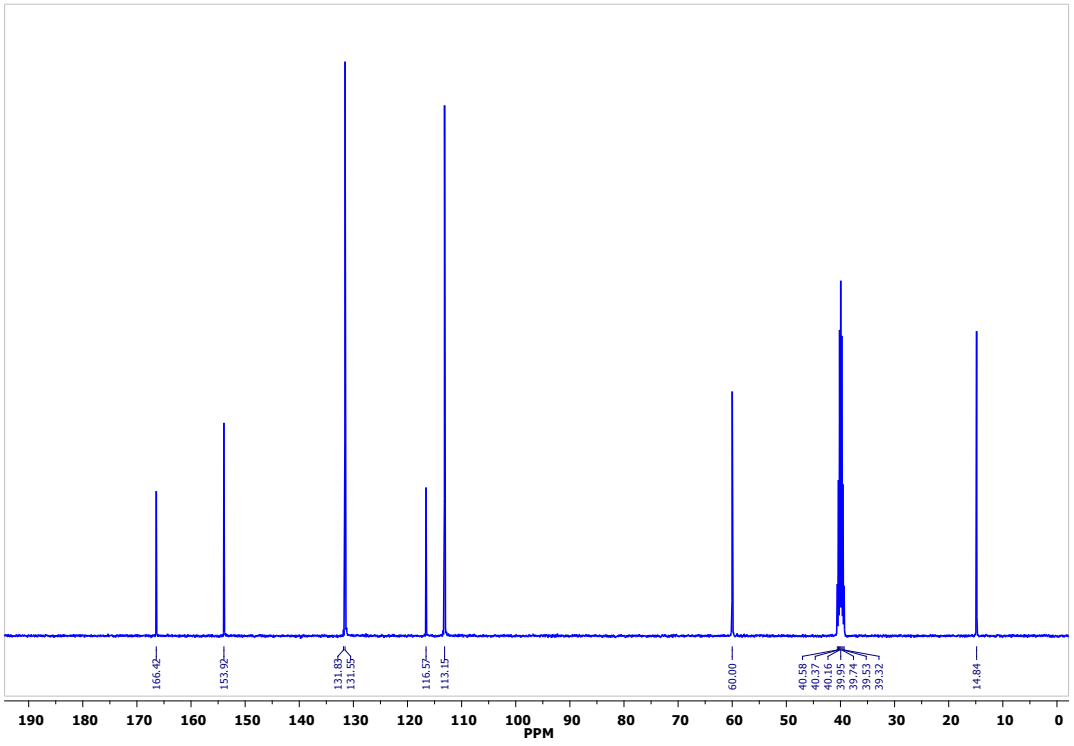


Figure S22. ^{13}C NMR spectrum of ethyl-4-aminobenzoate (**1q**) in DMSO-d_6.

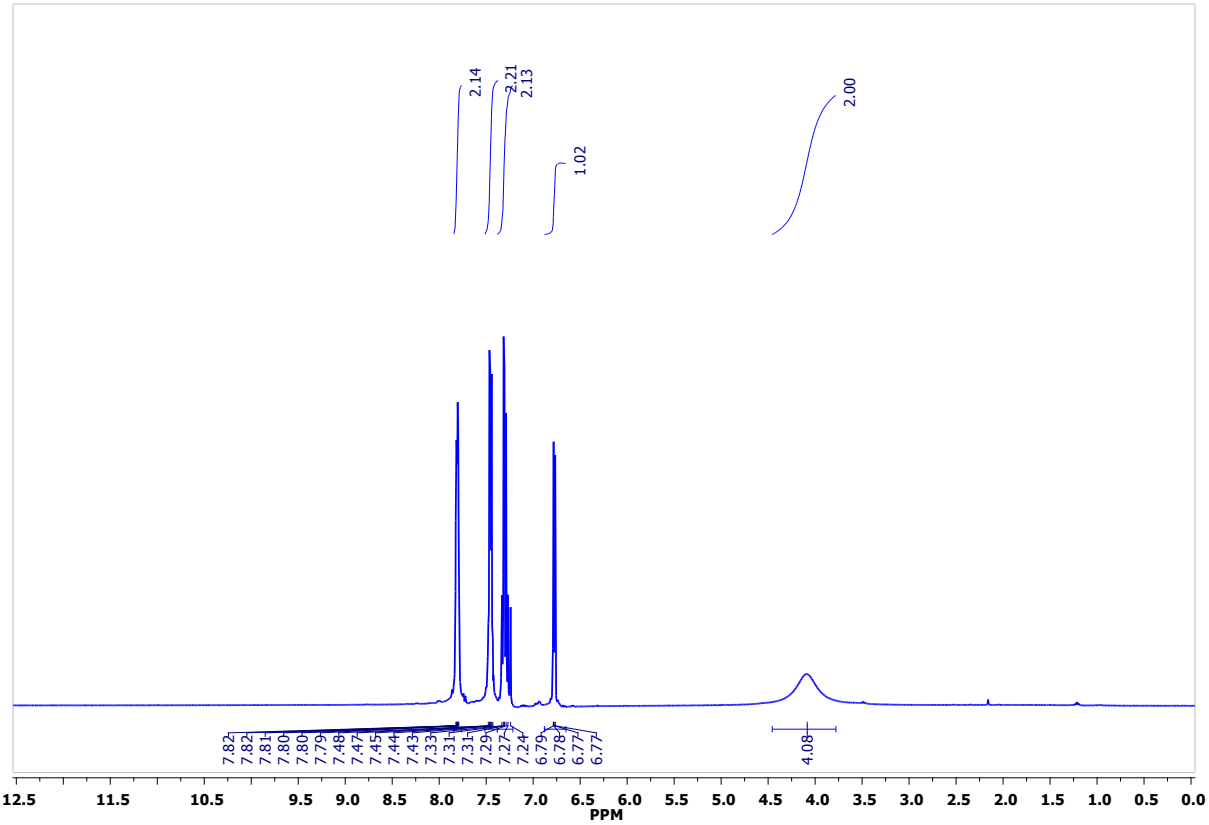


Figure S23. ^{1}H NMR spectrum of 1-napthylamine (**1r**) in $CDCl_3$.

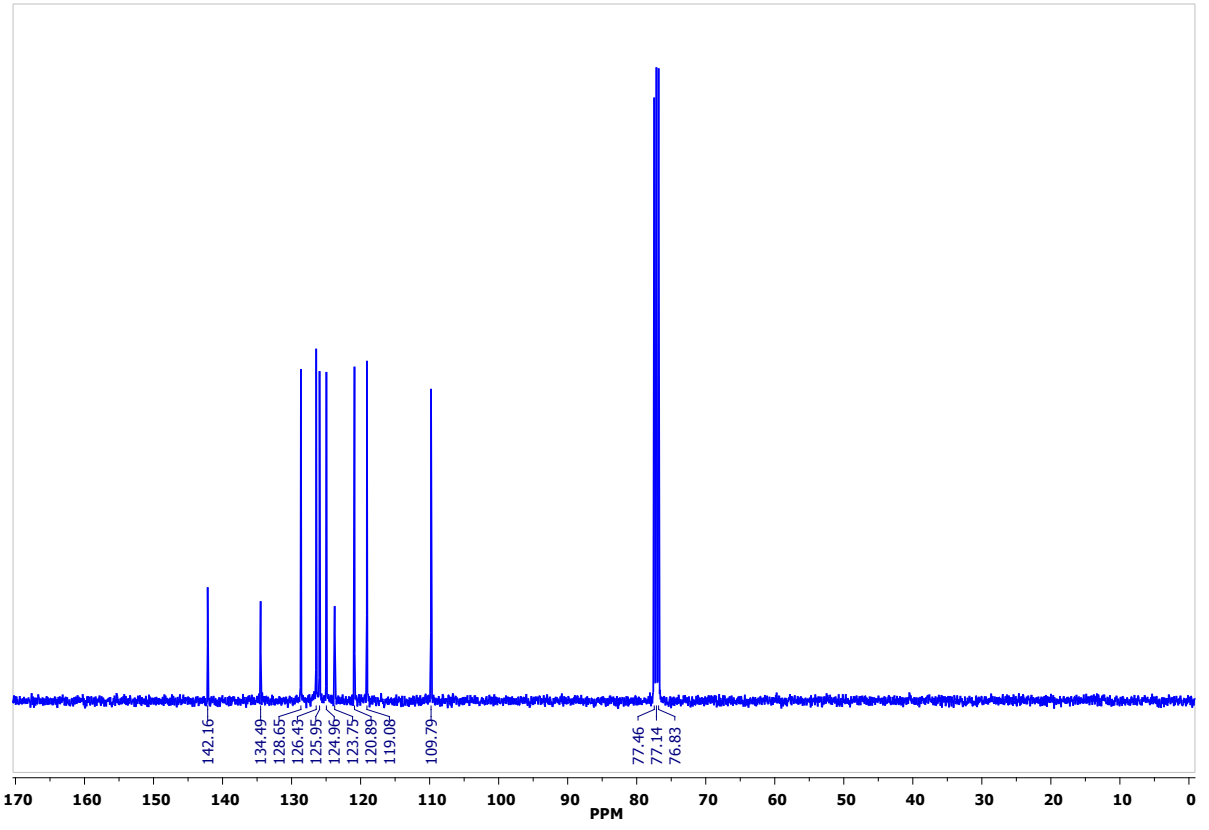


Figure S24. ^{13}C NMR spectrum of 1-napthylamine (**1r**) in $CDCl_3$.

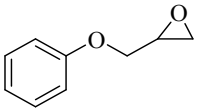
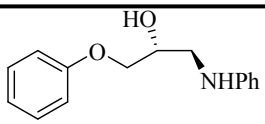
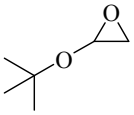
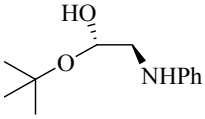
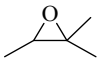
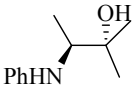
Table S1. X-ray crystallographic data collection and structure refinement parameters for complexes **3** and **4**.

	Complex **3**	Complex **4**
CCDC No.	**1058484**	**1058485**
Molecular formula	$C_{42}H_{42}Cl_4Co_3N_{11}O_4$	$C_{42}H_{42}Cl_4Co_2FeN_{11}O_4.4H_2O$
Fw	1083.46	1144.38
T(K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	*P -1*	*P -1*
a	12.048(3)	12.0632(8)
b	14.749(4)	14.8156(9)
c	15.152(4)	15.2289(12)
α	89.745(4)	89.271(5)
β	72.994(4)	73.261(6)
γ	84.012(5)	84.058(5)
V (Å^3)	2559.7(12)	2592.0(3)
Z	2	2
d (g cm^{-3})	1.406	1.466
F (000)	1104	1166
Goodness of fit (F^2)	1.068	0.881
R_1, wR_2 [I >2 (*I*)]	0.0765, 0.1956	0.0611, 0.1387
R_1, w$_{R2}$ [all data][a]	0.1210, 0.2195	0.1394, 0.1555
[a]$R_1 = \Sigma\|\|Fo\| - \|Fc\|\|/\Sigma\|Fo\|$; $wR_2 = \{\Sigma[w(/Fo/^2 - /Fc/^2)^2]/\Sigma[wFo^4]\}^{1/2}$		

Table S2. Selected bond lengths [Å] and bond angles [°] around the central Co^{3+} and Fe^{3+}; and peripheral Co^{2+} metal ions for complexes **3** and **4**.

Complex **3**		Complex **4**	
Bond lengths		**Bond lengths**	
Co(1)-N(1)	1.974(6)	Fe(1)-N(1)	1.952(5)
Co(1)-N(2)	1.946(6)	Fe(1)-N(2)	1.958(5)
Co(1)-N(3)	1.967(6)	Fe(1)-N(3)	1.949(6)
Co(1)-N(4)	1.954(6)	Fe(1)-N(4)	1.962(5)
Co(1)-N(5)	1.870(6)	Fe(1)-N(5)	1.864(4)
Co(1)-N(6)	1.861(6)	Fe(1)-N(6)	1.862(4)
Co(2)-N(7)	2.042(8)	Co(1)-N(7)	2.039(5)
Co(2)-N(8)	2.055(6)	Co(1)-N(8)	2.052(5)
Co(2)-Cl(1)	2.246(3)	Co(1)-Cl(1)	2.240(2)
Co(2)-Cl(2)	2.248(3)	Co(1)-Cl(2)	2.246(3)
Co(3)-N(9)	2.047(6)	Co(2)-N(9)	2.060(6)
Co(3)-N(10)	2.048(6)	Co(2)-N(10)	2.052(6)
Co(3)-Cl(3)	2.246(3)	Co(2)-Cl(3)	2.233(3)
Co(3)-Cl(4)	2.253(2)	Co(2)-Cl(4)	2.254(3)
Bond angles		**Bond angles**	
N(5)-Co(1)-N(6)	176.8(3)	N(5)- Fe(1)-N(6)	176.4(2)
N(1)- Co(1)-N(3)	92.0(2)	N(1)- Fe(1)-N(3)	91.2(2)
N(3)- Co(1)-N(2)	90.6(3)	N(3)- Fe(1)-N(2)	92.4(2)
N(1)- Co(1)-N(2)	161.0(3)	N(1)- Fe(1)-N(2)	161.6(2)
N(4)- Co(1)-N(3)	161.5(3)	N(4)- Fe(1)-N(3)	161.1(2)
N(1)- Co(1)-N(4)	90.7(3)	N(1)- Fe(1)-N(4)	91.4(2)
N(4)- Co(1)-N(2)	92.8(3)	N(4)- Fe(1)-N(2)	90.9(2)
N(8)-Co(2)-N(7)	127.4(3)	N(8)-Co(1)-N(7)	126.7(2)
Cl(2)-Co(2)-Cl(1)	113.4(1)	Cl(2)-Co(1)-Cl(1)	114.88(9)
N(9)-Co(3)-N(10)	126.9(2)	N(9)-Co(2)-N(10)	126.3(2)
Cl(4)-Co(3)-Cl(3)	115.56(9)	Cl(4)-Co(2)-Cl(3)	112.3(1)

Table S3. Un-optimized ring-opening reactions of a few epoxides using aniline as the nucleophile with complex **7** as the catalyst.

Entry[a]	Epoxide	Product	Yield[b] Catalyst 7
1			35
2			55
3			40

[a]Conditions: catalyst: 5-mol%; 12 h stirring at room temperature (25 °C). [b]Yields were calculated from the gas chromatograph.