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Supporting Information

The Salt-Based Catalytic Enhancement of CO_2 Absorption by a Tertiary Amine Medium

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Contents

Synthesis of catalysts

Synthesis of intermediate A: To a solution of N1-(2-aminoethyl)-N1-methylethane-1,2-diamine (2.00 g, 17.0 mmol) in EtOH, 3-nitrobenzaldehdye (5.15 g, 34.1 mmol) was added under N_2 atmosphere and heated at 60 ^oC for 12 h. After cooling to room temperature, resulting yellow crystals were filtered and dried. Yield = 5.12 g, 92 %. To a solution of imine(4.00 g, 10.4 mmol) in MeOH, $NaBH_4$ (1.57 g, 41.7 mmol) was added and stirred at RT for 12 h under N_2 atmosphere. After completion of the reaction, monitored by TLC, MeOH was reduced under reduced pressure and it was diluted with CH_2Cl_2 and DM water. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. It afforded yellow sticky mass which was dried under high vacuum. Yield = 3.99 g, 99%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 2H), 8.14 – 8.00 (m, 2H), 7.66 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 3.91 (s,4H),, 2.72 (dd, *J* = 6.5, 5.3 Hz, 4H), 2.54 (dd, *J* = 6.4, 5.4 Hz, 4H), 2.21 (s, 3H), 2.06 (s, 4H).

Synthesis of intermediate B: To a solution of intermediate **A** (4.50 g, 11.2 mmol) in CH_3CN (120 mL) and acetic acid(30 mL), formaldehyde solution (16.6 mL) was added and stirred for 2 h. $NaBH_4$ (2.49 g, 67.0 mmol) was added pinch by pinch at 0 ^oC and this temperature was maintained for 2 h and continued the stirring at RT for 12 h. The white precipitate was filtered and the filtrate was concentrated under vacuum. The filtrate pH was adjusted to basic with NaOH solution and the yellow solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Yield = 4.00 g, 83%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (t, *J* = 1.9 Hz, 2H), 8.09 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 2H), 7.66 (ddd, *J* = 7.7, 1.8, 1.0 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 3.61 (s, 4H), 2.55 (q, *J* = 2.8 Hz, 8H), 2.24 (s, 3H), 2.23 (s, 6H).

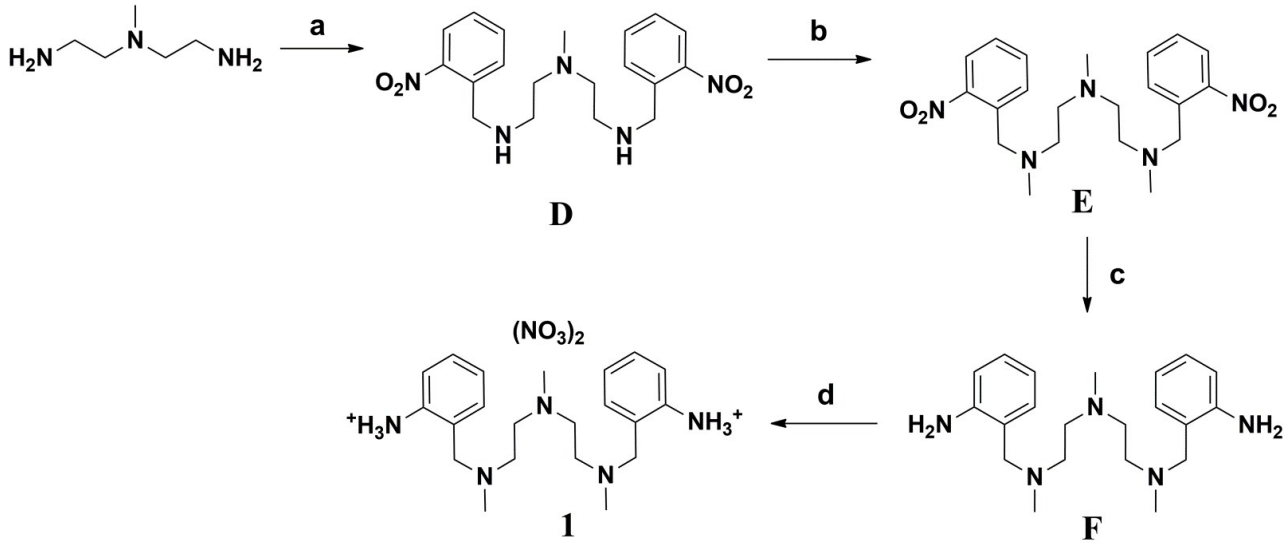
Synthesis of intermediate C: To a mixture of Pd/C (0.274 g) and B (2.74 g, 93.1 mmol) in EtOH (55 mL), hydrazine hydrate (30.0 mL) was added under N_2 atmosphere. Then mixture temperature was slowly increased to 60 ^oC at this temperature stirred for 8 h. After cooling to RT, the mixture was filtered using celite bed and concentrated under vacuum. Resulting colorless liquid was extracted with CH_2Cl_2 and dried over Na_2SO_4 and concentrated. Yield = 1.20 g, 45%. ESI-Mass: (M+1= 356.02). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.04 (m, 2H), 6.73 – 6.65 (m, 4H), 6.60 – 6.55 (m, 2H), 3.43 (s, 4H), 2.65 – 2.46 (m, 8H), 2.25 (s, 3H), 2.22 (s, 6H).

Synthesis of 2: To a solution of C (0.300 g,) in EtOH (15 mL) 0.1 M HNO_3 solution was added and stiireed for 12 h. The solvents were rmoved under reduced pressure and resulting light yello solution was triturated with diethylether to get as light yellow solid. Yield = 0.289 g, 71%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.00 (t, *J* = 7.6 Hz, 2H), 6.57 – 6.46 (m, 6H), 5.15 (s, 4H), 3.57 (s, 4H), 2.98 (m, 4H), 2.73 (s, 2H), 2.53 – 2.43 (m, 2H), 2.29 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 147.25, 129.37, 118.02, 117.36, 115.42, 113.85, 51.92, 46.50, 42.88, 41.93, 36.24.

Synthesis of 1: Similar synthetic procedure of **2** was followed to synthesis **1** from 2-nitrobenzaldehyde. Scheme S1 (Amine) Yield = 0.221 g, 47%. ESI-Mass: (M+Na = 378.02) ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.97 (td, *J* = 7.6, 1.6 Hz, 2H), 6.90 (dd, *J* = 7.4, 1.6 Hz, 2H), 6.60 (dd, *J* = 7.9, 1.2 Hz, 2H), 6.48 (td, *J* = 7.3, 1.2 Hz, 2H), 5.29 (s, 4H), 3.33 (s, 4H), 2.55 – 2.33 (m, 8H), 2.12 (d, *J* = 2.4 Hz, 3H), 2.06 (s, 6H). (Amine salt - **1**): Yield = 0.350 g, 86%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 3.9 Hz, 2H), 6.98 (dt, *J* = 7.5, 2.0 Hz, 2H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.62 – 6.43 (m, 2H), 3.37 (s, 4H), 2.47 – 2.34 (m, 8H), 2.15 – 2.00 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.05, 135.93, 129.06, 122.90, 116.37, 62.17, 54.88, 41.94, 36.64, 33.75.

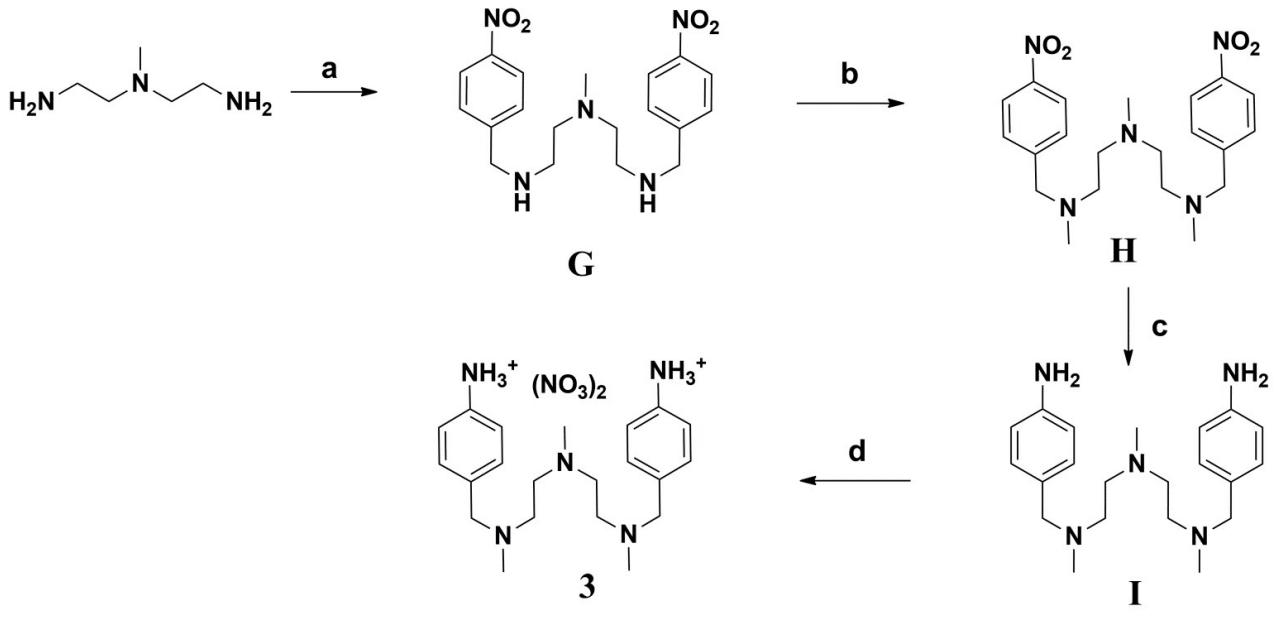
Synthesis of 3 : Similar synthetic procedure of **2** was followed to synthesis the ligand from 4-nitrobenzaldehyde. Scheme S2 (Amine) Yield =0.363 g, 87%. ESI-Mass: (M+Na = 378.02). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.00 (d, *J* = 8.0 Hz, 4H), 6.55 (d, *J* = 8.3 Hz, 4H), 3.60 (s, 4H), 2.42 (td, *J* = 6.4, 2.7 Hz, 8H), 2.13 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.33, 128.35, 115.97, 113.95, 99.98, 77.49, 65.02, 55.59, 46.59, 41.59, 34.06. (Amine salt – **3**): Yield = 0.387 g, 95 %. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.10 – 6.92 (m, 4H), 6.54 (dd, *J* = 17.8, 9.7 Hz, 4H), 5.11 (s, 4H), 3.89 (s, 4H), 2.99 (m, 4H), 2.68 (m, 4H), 2.39 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (75 MHz, DMSO) δ 148.99, 131.45, 130.05, 121.51, 118.99, 115.73, 66.08, 56.64, 51.25, 44.90, 36.14.

Scheme S1: Synthesis of **1**



Reagents: a. 2-nitrobenzaldehyde, EtOH, $NaBH_4$, MeOH b. HCHO, $NaBH_4$, CH_3CN/AcOH c. Pd/C, Hydrazine hydrate d. 0.1 M HNO_3

Scheme S2: Synthesis of **3**



Reagents: a. 4-nitrobenzaldehyde, EtOH, $NaBH_4$, MeOH b. HCHO, $NaBH_4$, CH_3CN/AcOH c. Pd/C, Hydrazine hydrate d. 0.1 M HNO_3

Table 1. Crystal data and structure refinement for **2**

CCDC number	1454963	
Empirical formula	C21 H35 N7 O6	
Formula weight	481.56	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 14.3139(5) Å	α= 90°
	b = 16.8590(5) Å	β= 90°
	c = 10.2559(4) Å	γ = 90°
Volume	2474.93(15) $Å^3$	
Z	4	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	1032	
Crystal size	0.17 x 0.14 x 0.11 mm^3	
Theta range for data collection	2.73 to 27.94°.	
Index ranges	-18<=h<=18, -21<=k<=22, -13<=l<=13	
Reflections collected	52356	
Independent reflections	5894 [R(int) = 0.0340]	
Completeness to theta = 27.94°	99.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5894 / 1 / 312	
Goodness-of-fit on F^2	0.755	
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0998	
R indices (all data)	R1 = 0.0450, wR2 = 0.1074	
Absolute structure parameter	0.2(8)	
Largest diff. peak and hole	0.504 and -0.432 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **2**

Bond lengths [Å]		Bond angles [°]	
N(1)-C(2)	1.463(2)	C(2)-N(1)-C(3)	109.47(12)
N(1)-C(3)	1.468(2)	C(2)-N(1)-C(1)	111.20(13)
N(1)-C(1)	1.464(2)	C(3)-N(1)-C(1)	111.39(13)
N(7)-O(4)	1.237(2)	O(4)-N(7)-O(6)	120.89(14)
N(7)-O(6)	1.248(2)	O(4)-N(7)-O(5)	120.40(15)
N(7)-O(5)	1.2567(19)	O(6)-N(7)-O(5)	118.70(15)
N(6)-O(2)	1.231(2)	O(2)-N(6)-O(1)	122.05(16)
N(6)-O(1)	1.241(2)	O(2)-N(6)-O(3)	119.12(15)
N(6)-O(3)	1.2775(19)	O(1)-N(6)-O(3)	118.83(15)
N(2)-C(6)	1.492(2)	C(6)-N(2)-C(4)	111.07(14)
N(2)-C(4)	1.506(2)	C(6)-N(2)-C(8)	110.22(13)
N(2)-C(8)	1.519(2)	C(4)-N(2)-C(8)	111.78(13)
N(3)-C(7)	1.499(2)	C(7)-N(3)-C(5)	111.15(13)
N(3)-C(5)	1.506(2)	C(7)-N(3)-C(15)	108.74(13)
N(3)-C(15)	1.522(2)	C(5)-N(3)-C(15)	113.25(13)
N(4)-C(13)	1.373(2)	N(1)-C(3)-C(5)	111.97(13)
N(5)-C(20)	1.380(2)	N(1)-C(2)-C(4)	112.10(13)
C(3)-C(5)	1.519(2)	C(9)-C(8)-N(2)	111.64(13)
C(2)-C(4)	1.522(2)	N(2)-C(4)-C(2)	111.78(13)
C(8)-C(9)	1.510(2)	N(3)-C(5)-C(3)	111.47(13)
C(9)-C(14)	1.390(2)	C(14)-C(9)-C(10)	120.32(16)
C(9)-C(10)	1.394(3)	C(14)-C(9)-C(8)	119.91(16)
C(14)-C(13)	1.404(2)	C(10)-C(9)-C(8)	119.76(16)
C(13)-C(12)	1.405(3)	C(9)-C(14)-C(13)	120.92(17)
C(12)-C(11)	1.386(3)	N(4)-C(13)-C(12)	121.37(16)
C(10)-C(11)	1.390(3)	N(4)-C(13)-C(14)	120.19(16)
C(16)-C(21)	1.387(2)	C(12)-C(13)-C(14)	118.33(16)
C(16)-C(17)	1.397(2)	C(11)-C(12)-C(13)	120.13(17)
C(16)-C(15)	1.502(2)	C(11)-C(10)-C(9)	118.90(17)
C(21)-C(20)	1.396(2)	C(10)-C(11)-C(12)	121.37(17)
C(20)-C(19)	1.405(2)	C(21)-C(16)-C(17)	119.79(16)
C(17)-C(18)	1.392(3)	C(21)-C(16)-C(15)	119.49(15)

C(18)-C(19)	1.386(3)	C(17)-C(16)-C(15)	120.70(16)
N(1)-C(2)	1.463(2)	C(16)-C(21)-C(20)	121.64(15)
N(1)-C(3)	1.468(2)	N(5)-C(20)-C(21)	120.18(16)
N(1)-C(1)	1.464(2)	N(5)-C(20)-C(19)	121.48(16)
N(7)-O(4)	1.237(2)	C(21)-C(20)-C(19)	118.32(16)
N(7)-O(6)	1.248(2)	C(16)-C(17)-C(18)	118.85(17)
N(7)-O(5)	1.2567(19)	C(16)-C(15)-N(3)	113.21(14)
N(6)-O(2)	1.231(2)	C(19)-C(18)-C(17)	121.48(17)
N(6)-O(1)	1.241(2)	C(18)-C(19)-C(20)	119.89(17)
N(6)-O(3)	1.2775(19)	C(2)-N(1)-C(3)	109.47(12)
N(2)-C(6)	1.492(2)	C(2)-N(1)-C(1)	111.20(13)
N(2)-C(4)	1.506(2)	C(3)-N(1)-C(1)	111.39(13)
N(2)-C(8)	1.519(2)	O(4)-N(7)-O(6)	120.89(14)
N(3)-C(7)	1.499(2)	O(4)-N(7)-O(5)	120.40(15)
N(3)-C(5)	1.506(2)	O(6)-N(7)-O(5)	118.70(15)
N(3)-C(15)	1.522(2)	O(2)-N(6)-O(1)	122.05(16)
N(4)-C(13)	1.373(2)	O(2)-N(6)-O(3)	119.12(15)
N(5)-C(20)	1.380(2)	O(1)-N(6)-O(3)	118.83(15)
C(3)-C(5)	1.519(2)	C(6)-N(2)-C(4)	111.07(14)
C(2)-C(4)	1.522(2)	C(6)-N(2)-C(8)	110.22(13)
C(8)-C(9)	1.510(2)	C(4)-N(2)-C(8)	111.78(13)
C(9)-C(14)	1.390(2)	C(7)-N(3)-C(5)	111.15(13)
C(9)-C(10)	1.394(3)	C(7)-N(3)-C(15)	108.74(13)
C(14)-C(13)	1.404(2)	C(5)-N(3)-C(15)	113.25(13)
C(13)-C(12)	1.405(3)	N(1)-C(3)-C(5)	111.97(13)
C(12)-C(11)	1.386(3)	N(1)-C(2)-C(4)	112.10(13)
C(10)-C(11)	1.390(3)	C(9)-C(8)-N(2)	111.64(13)
C(16)-C(21)	1.387(2)	N(2)-C(4)-C(2)	111.78(13)
C(16)-C(17)	1.397(2)	N(3)-C(5)-C(3)	111.47(13)
C(16)-C(15)	1.502(2)	C(14)-C(9)-C(10)	120.32(16)
C(21)-C(20)	1.396(2)	C(14)-C(9)-C(8)	119.91(16)
C(20)-C(19)	1.405(2)	C(10)-C(9)-C(8)	119.76(16)
C(17)-C(18)	1.392(3)	C(9)-C(14)-C(13)	120.92(17)
C(18)-C(19)	1.386(3)	N(4)-C(13)-C(12)	121.37(16)

Symmetry transformations used to generate equivalent atoms:

Fig. S1. Single crystal X-ray structure of **1** with weak hydrogen bonding between the nitrate anion and protonated amine

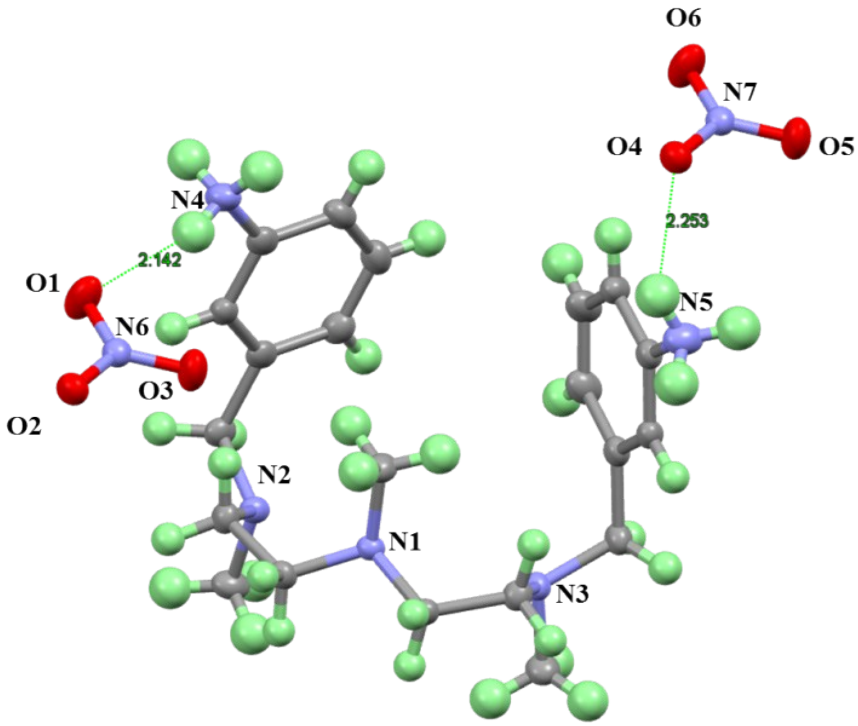


Fig. S2. FT-IR spectra of catalysts **1-3.** Top (**1**), middle (**2**) and bottom (**3**)

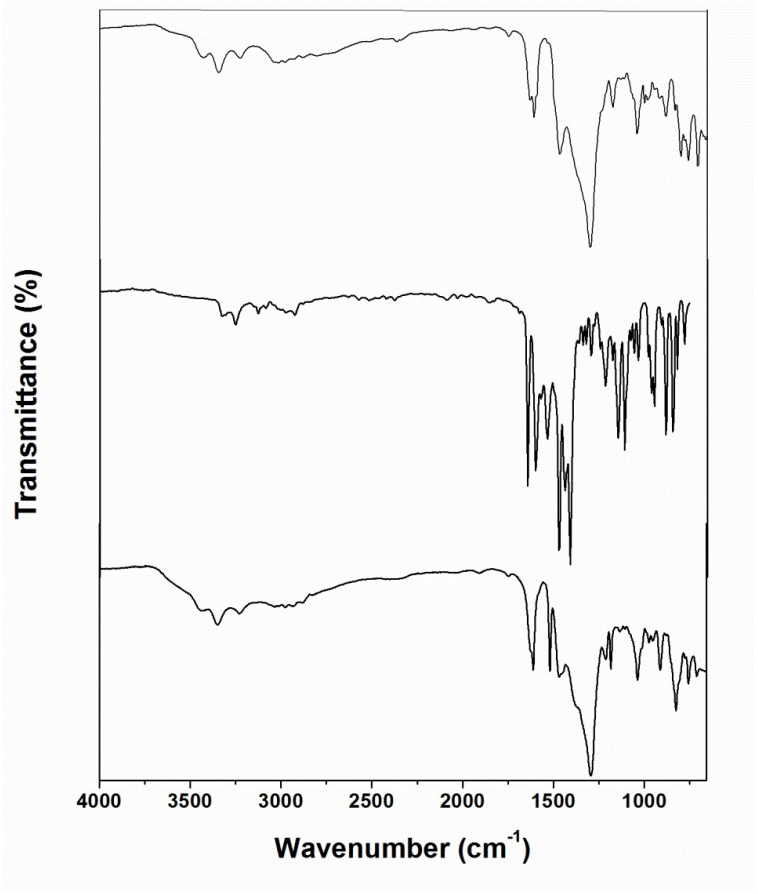


Fig. S3. ^{13}C NMR spectra of MDEA, MDEA with CO_2, and MDEA with **1** and CO_2 in D_2O

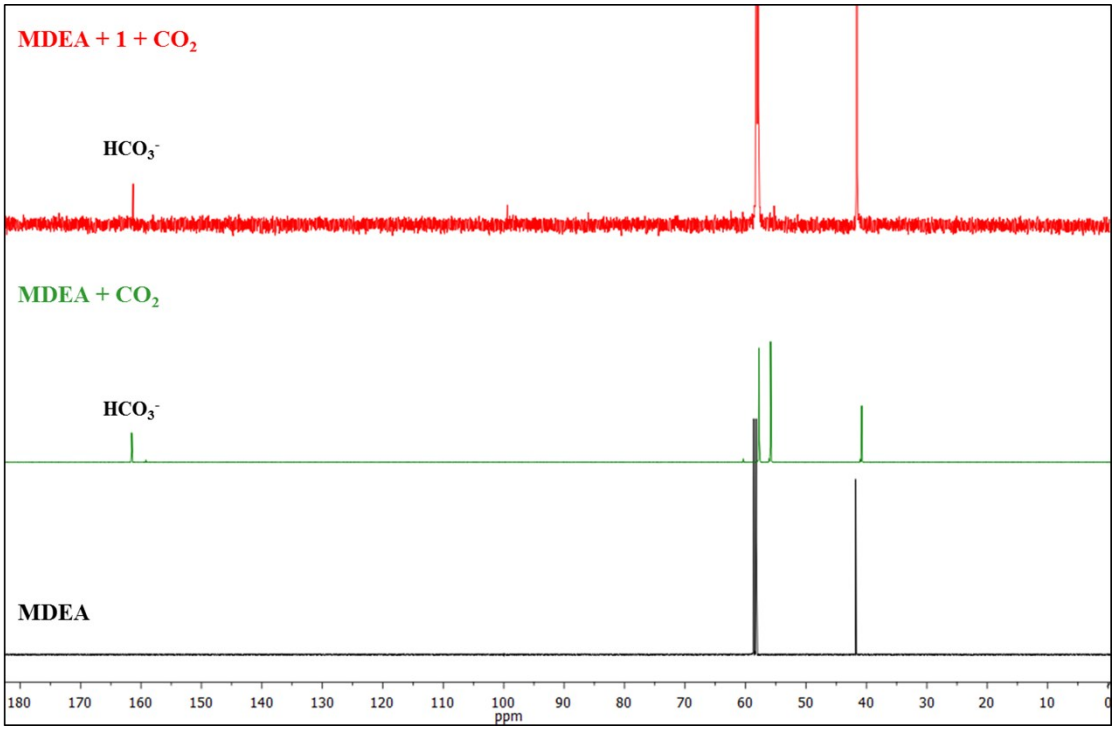


Fig S4: ^{1}H NMR spectrum of A

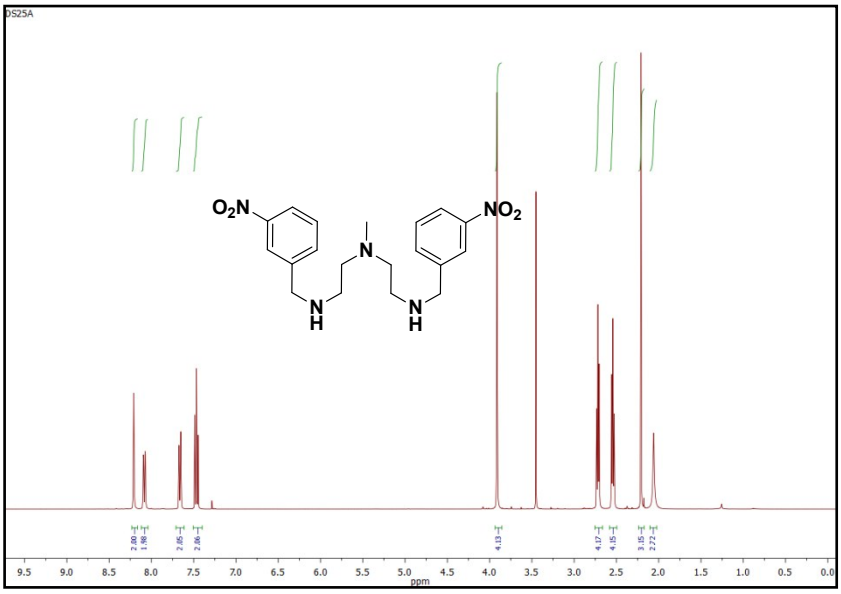


Fig. S5: ^{1}H NMR spectrum of B

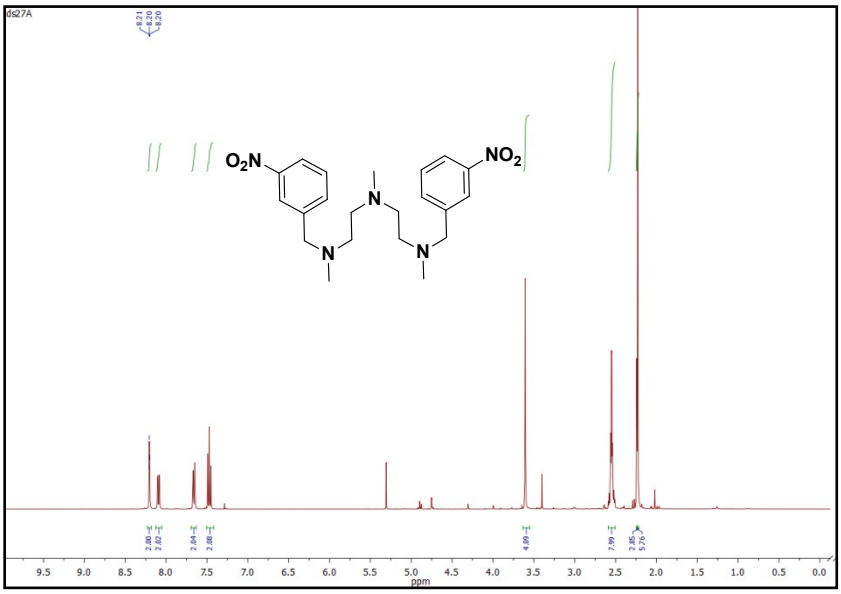


Fig. S6. ^{1}H NMR spectrum of C

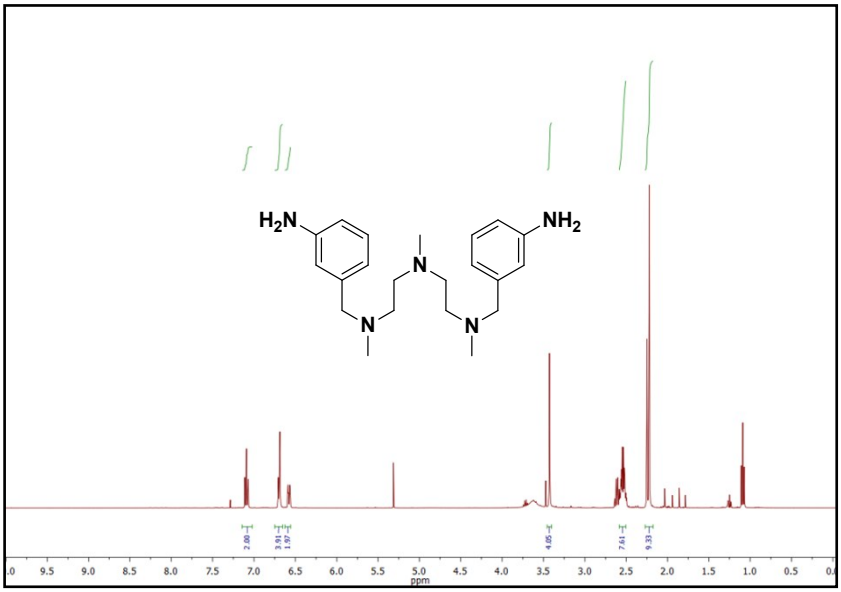


Fig. S7. ^{1}H NMR spectrum of **2**, (diethyl ether(δ 1.11 & 3.41) and ethyl alcohol (δ 1.11 & 3.41) in DMSO-d6)

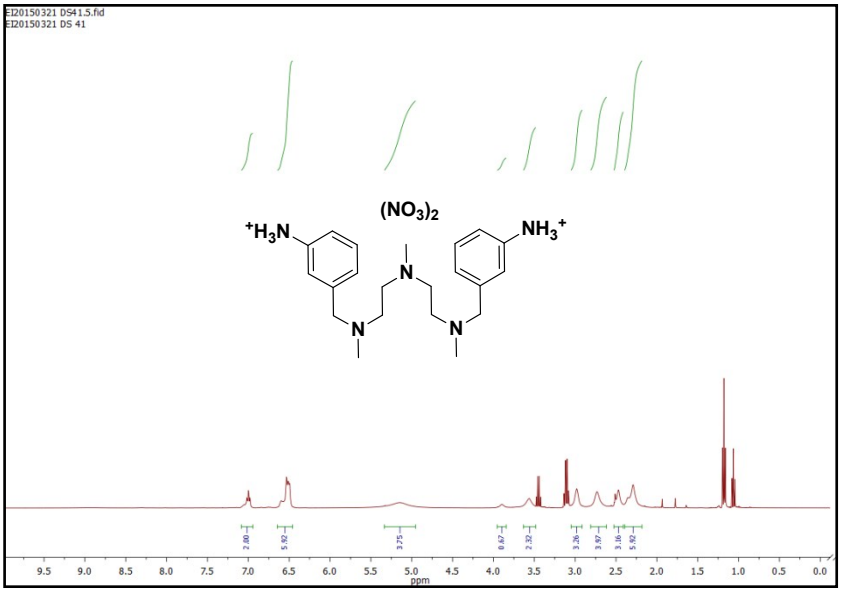


Fig. S8. ^{1}H NMR spectrum of D

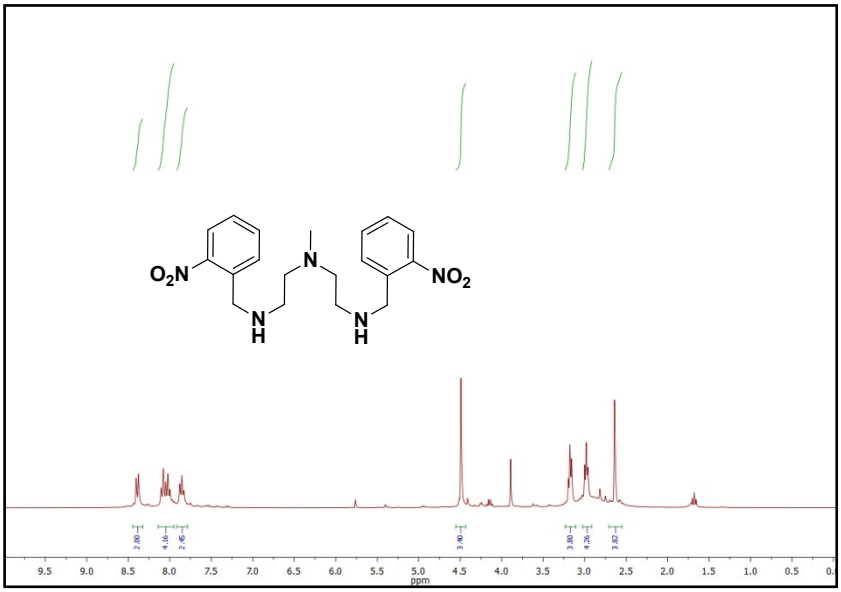


Fig. S9. ^{1}H NMR spectrum of E

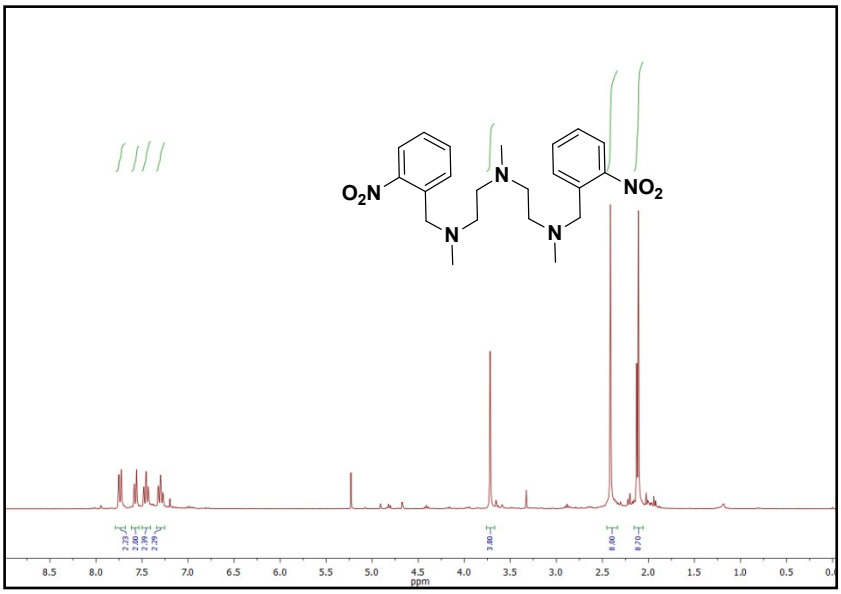


Fig. S10. ^{1}H NMR spectrum of F

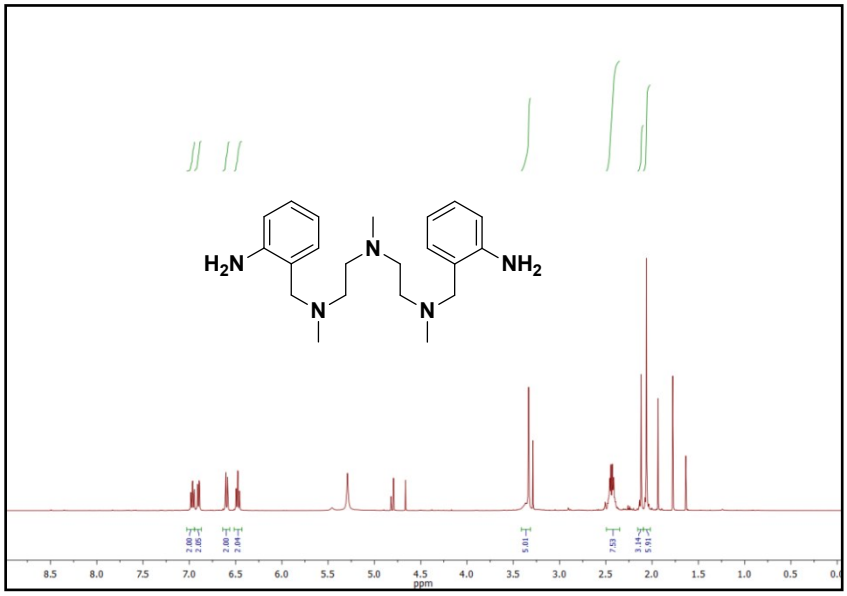


Fig. S11. ^{1}H NMR spectrum of **1**

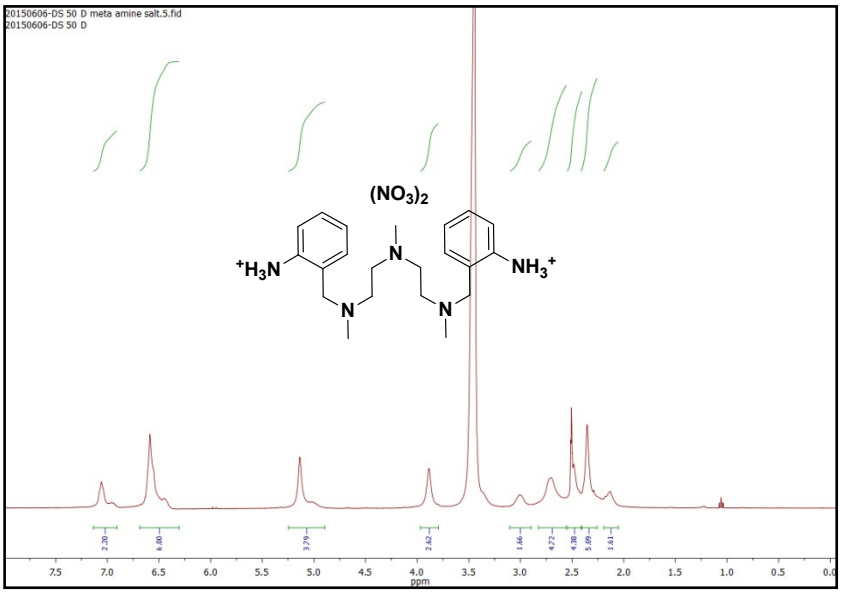


Fig. S12. ^{1}H NMR spectrum of G

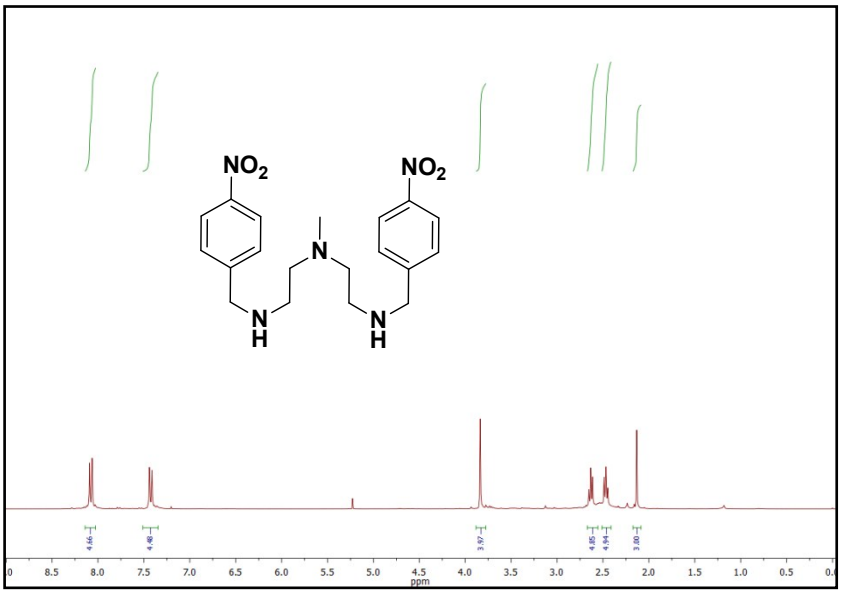


Fig. S13. ^{1}H NMR spectrum of H

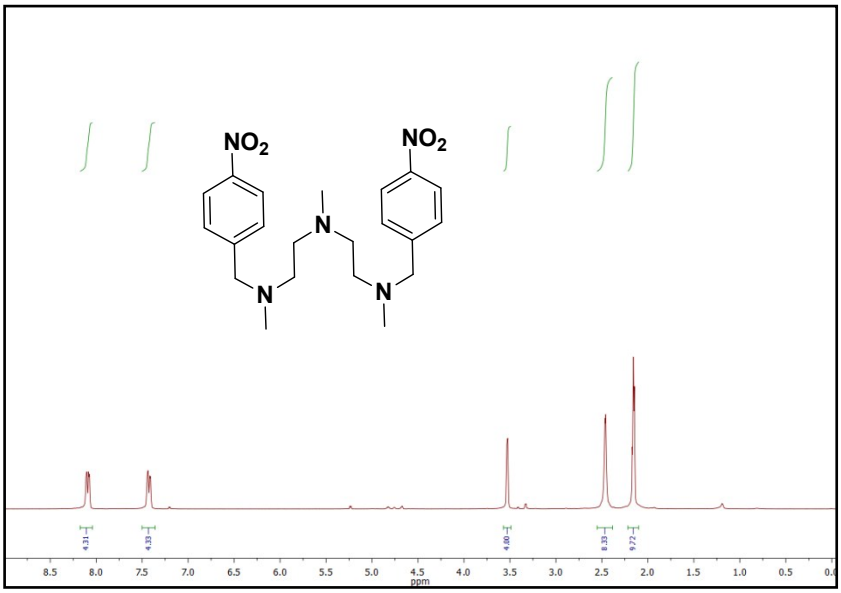


Fig. S14. ^{1}H NMR spectrum of I

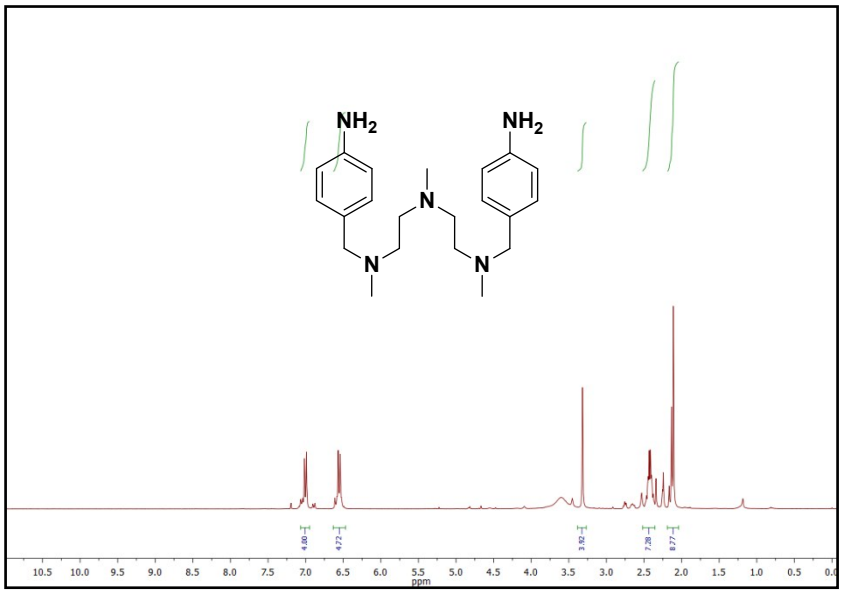


Fig. S15. ^{1}H NMR spectrum of **3 (**diethyl ether(δ 1.11 & 3.41) in DMSO-d6)