SUPPORTING INFORMATION

Pd@BTL-Cd core-shell nanoparticles as plasmonic photocatalyst for the reductive amination of furfural in water

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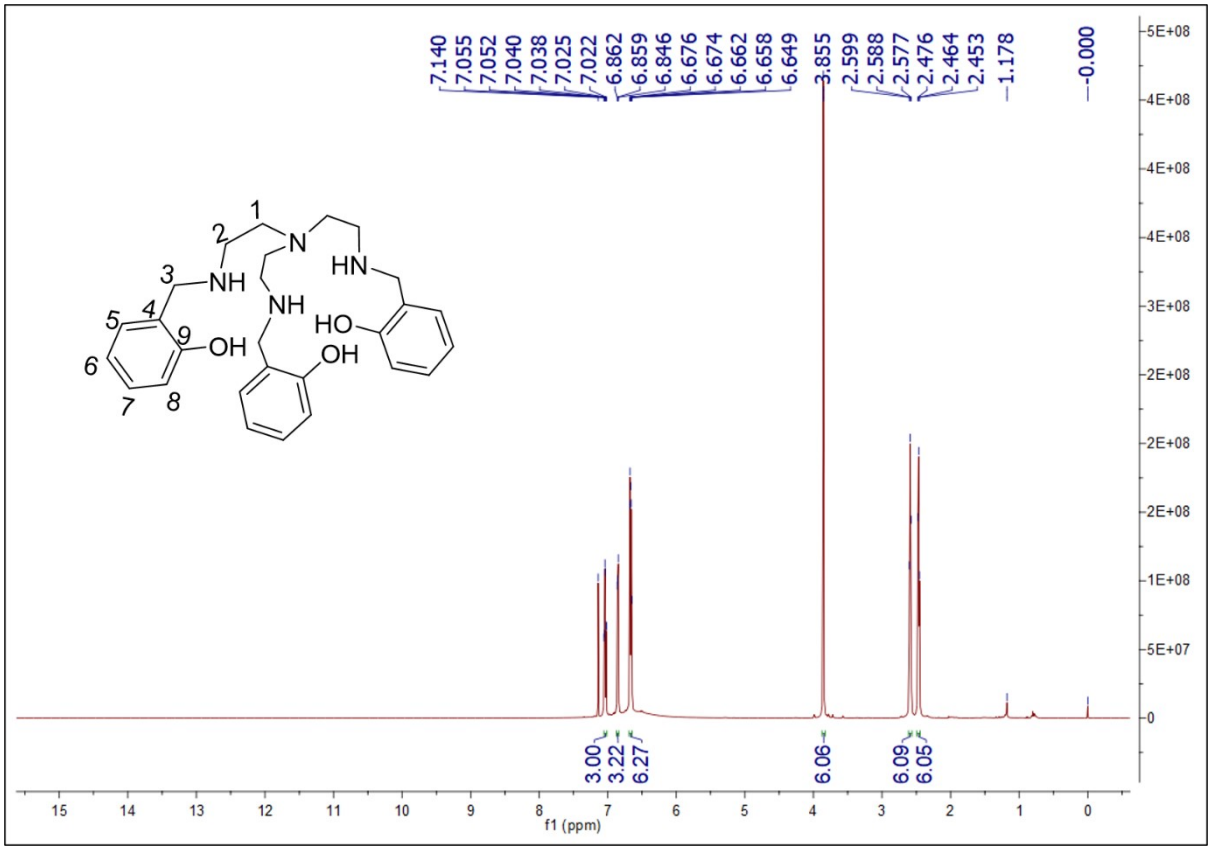

Fig. S1 ^{1}H NMR spectrum of tripodal ligand BTL

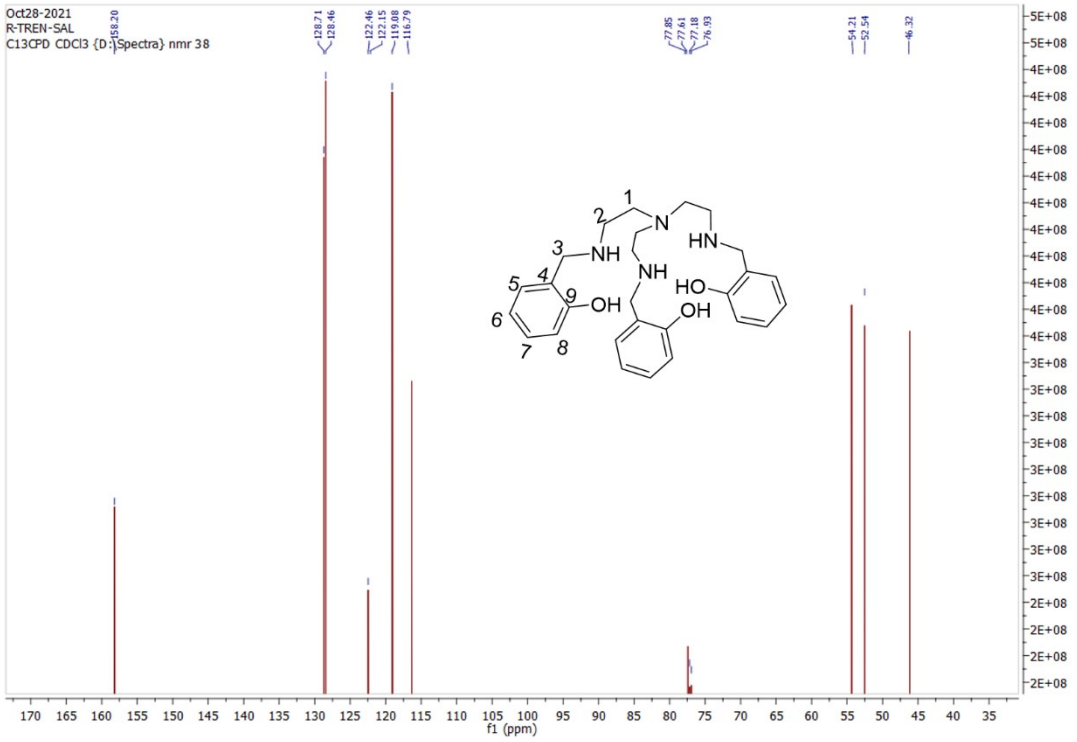

Fig. S2 ^{13}C NMR spectrum of tripodal ligand BTL

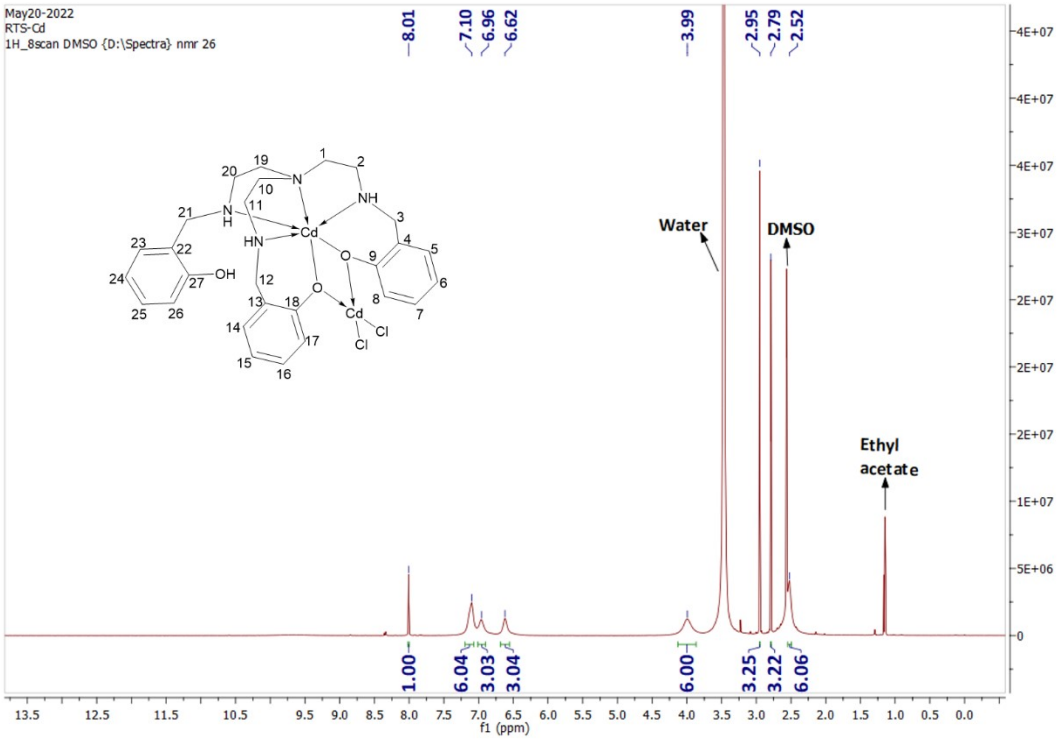

Fig. S3 ^{1}H NMR spectrum of metal complex BTL-Cd

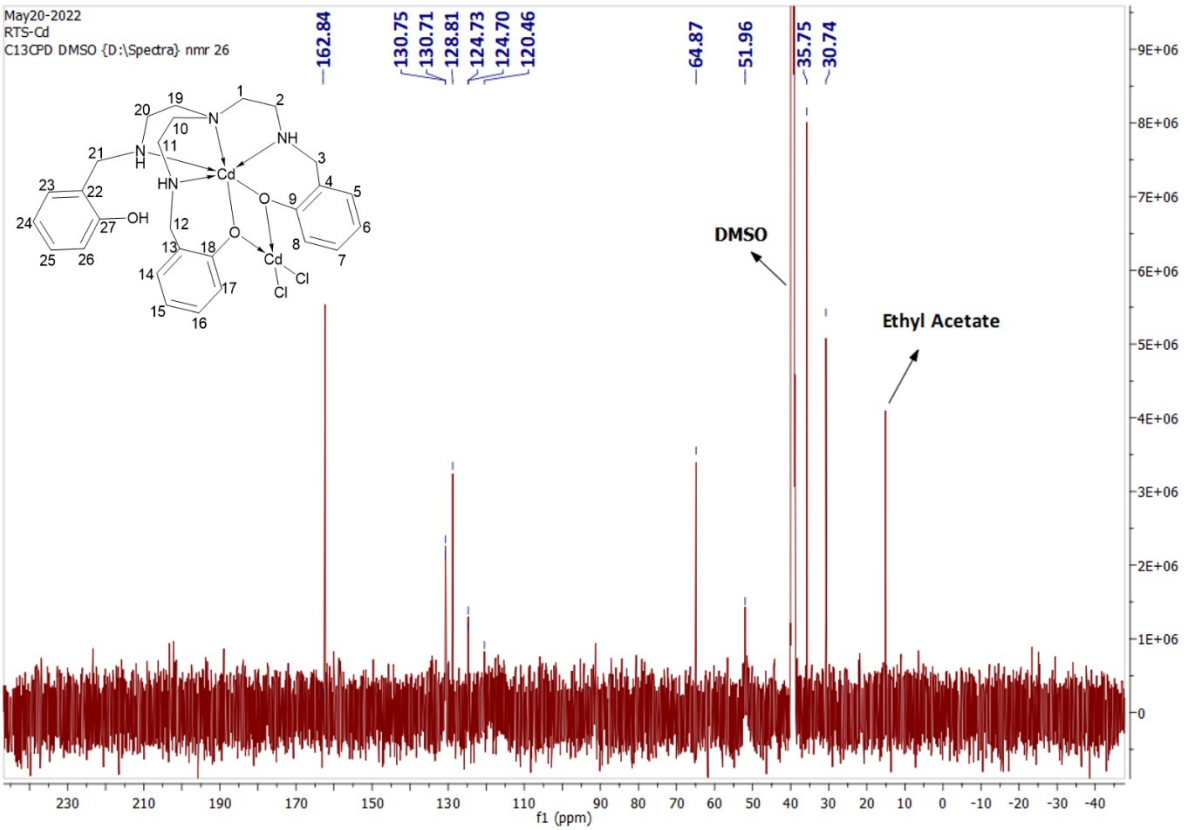

Fig. S4 ^{13}C NMR spectrum of metal complex BTL-Cd

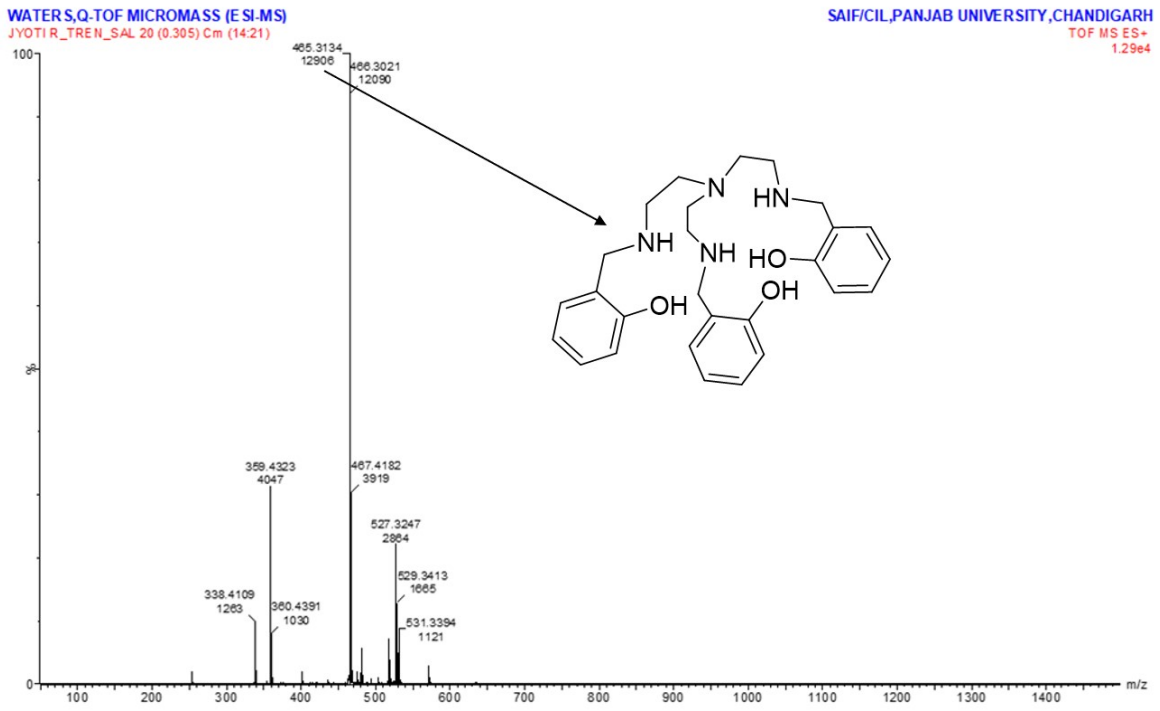

Fig. S5 ESI-MS spectrum of tripodal ligand BTL

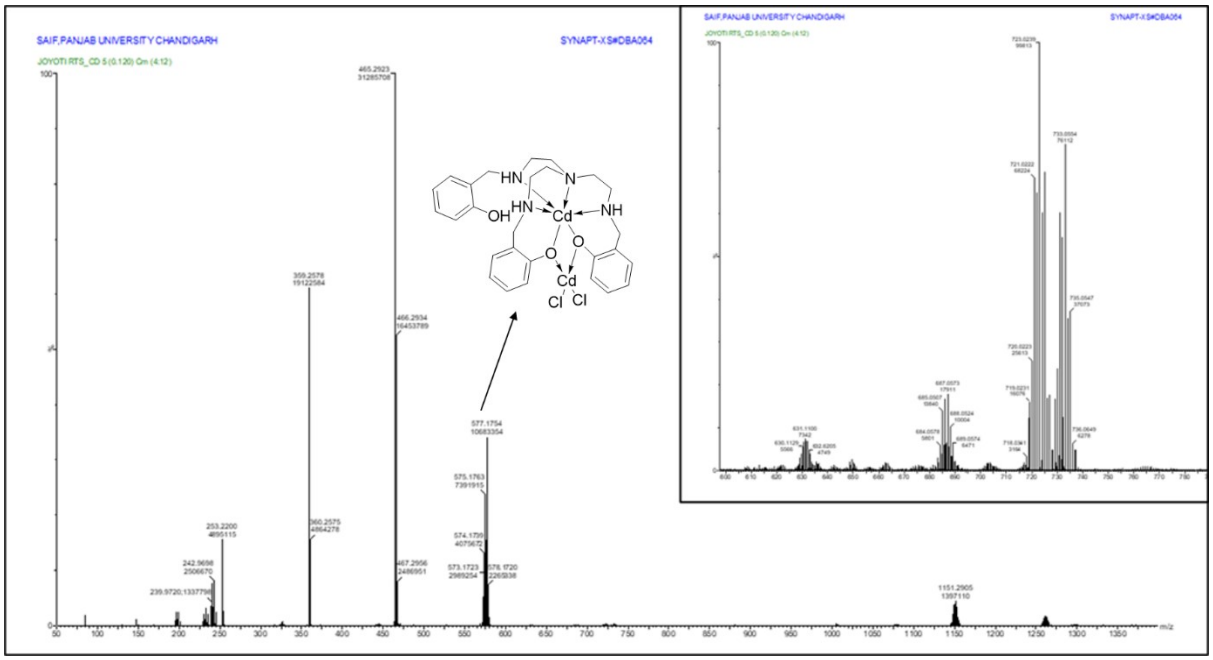

Fig. S6 ESI-MS spectrum of BTL-Cd metal complex

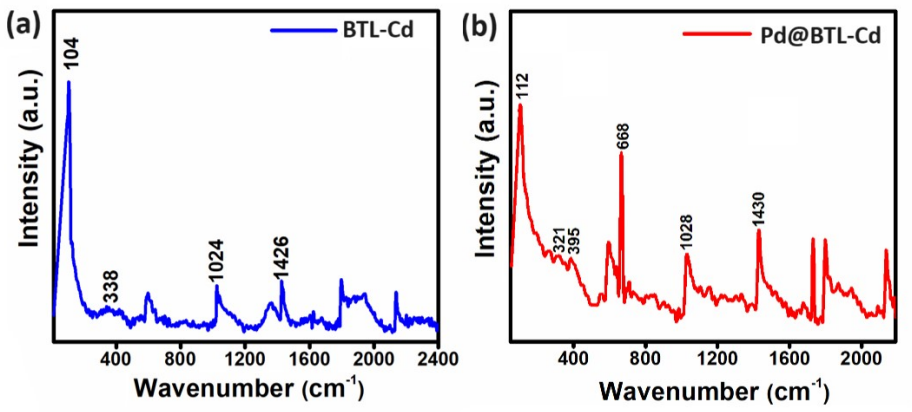

Fig. S7 Raman spectra of (a) BTL-Cd, and (b) Pd@BTL-Cd

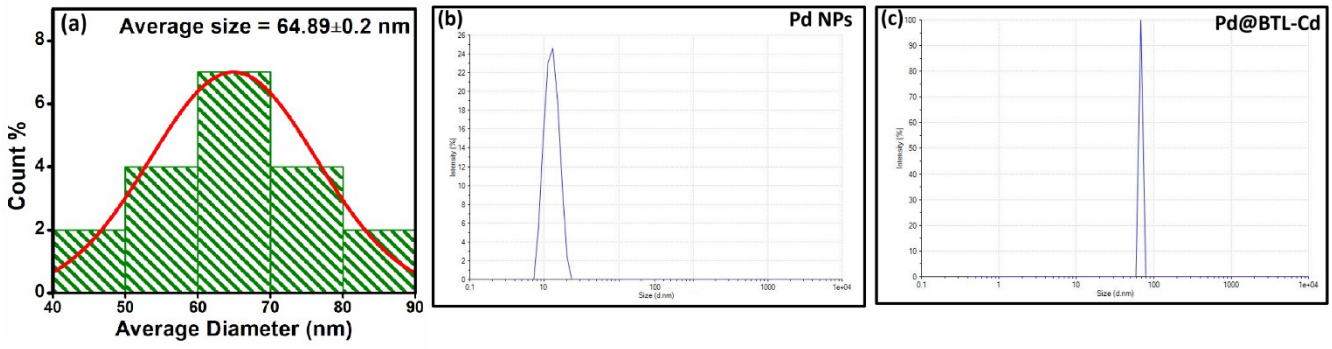

Fig. S8 (a) Particle size histogram of Pd@BTL-Cd core shell nanoparticle, DLS of (b) Pd NPs, and (c) Pd@BTL-Cd

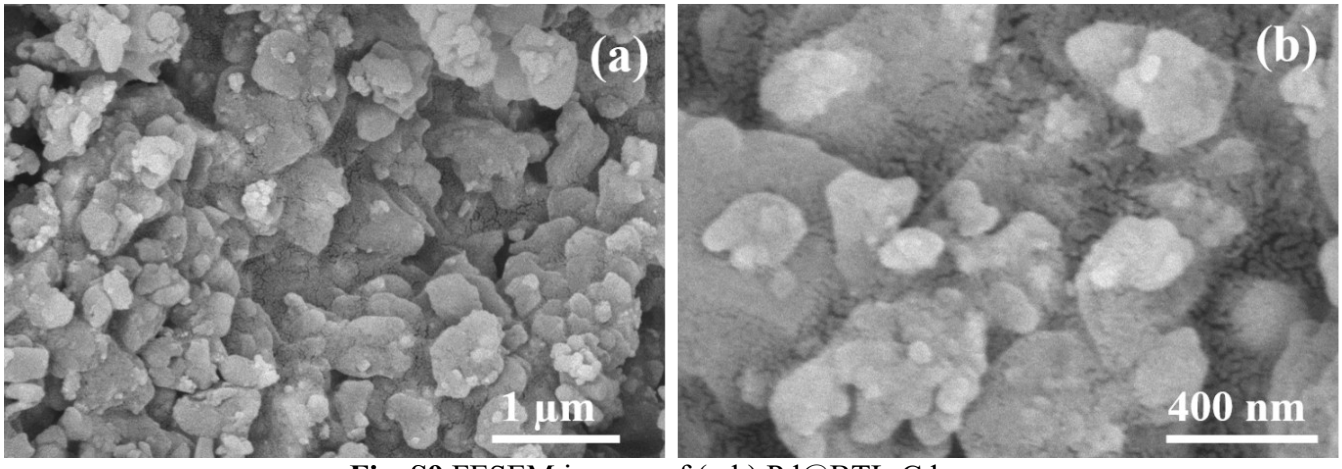

Fig. S9 FESEM images of (a-b) Pd@BTL-Cd

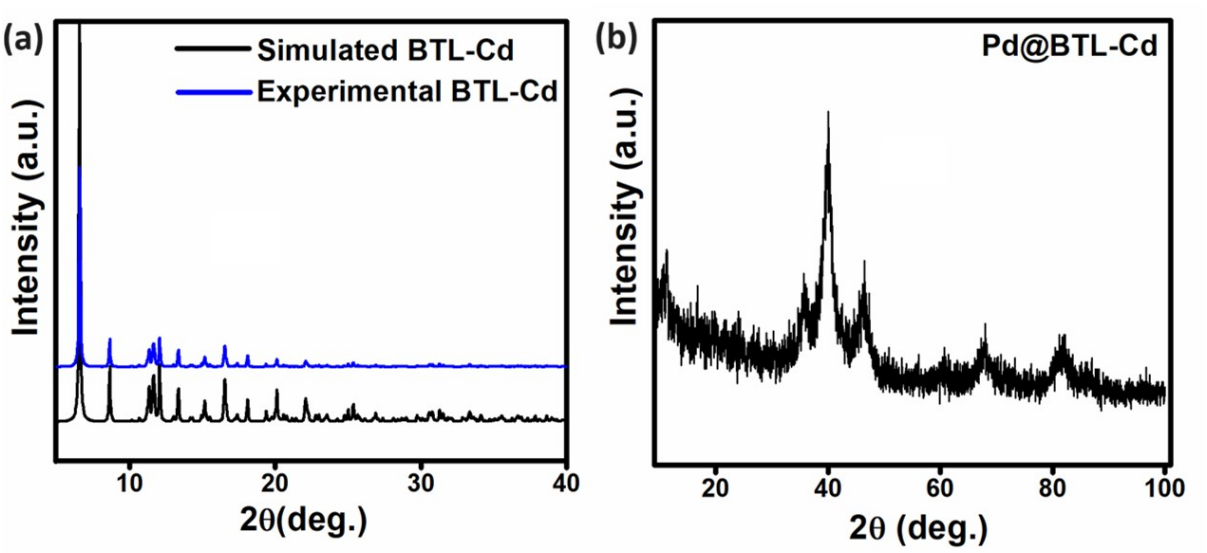

Fig. S10 (a) PXRD pattern of BTL-Cd showing a comparison of both experimental and simulated data, (b) PXRD pattern of Pd@BTL-Cd

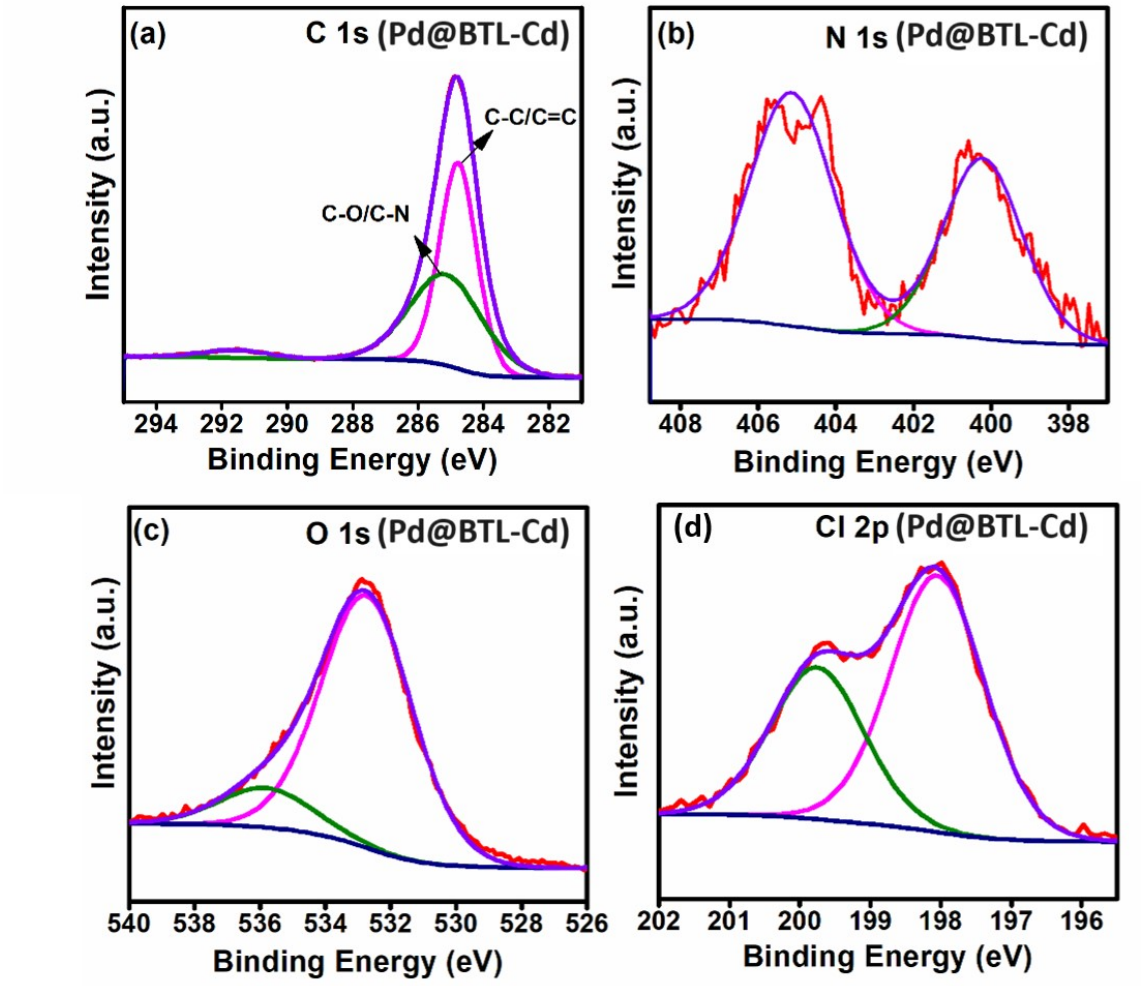

Fig. S11 XPS plots of (a) C 1s (Pd@BTL-Cd), (b) N 1s (Pd@BTL-Cd), (c) O 1s (Pd@BTL-Cd), (d) Cl 2p (Pd@BTL-Cd)

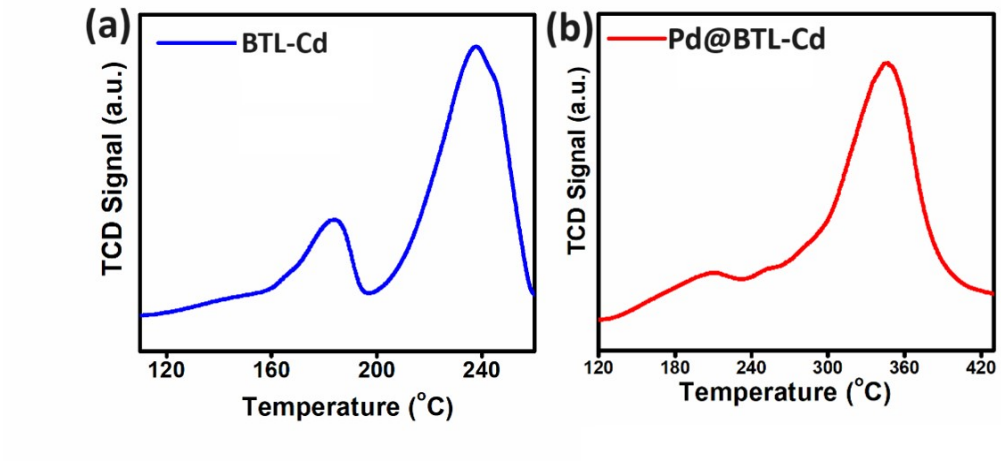

Fig. S12 NH_3-TPD spectra of (a) BTL-Cd, (b) Pd@BTL-Cd

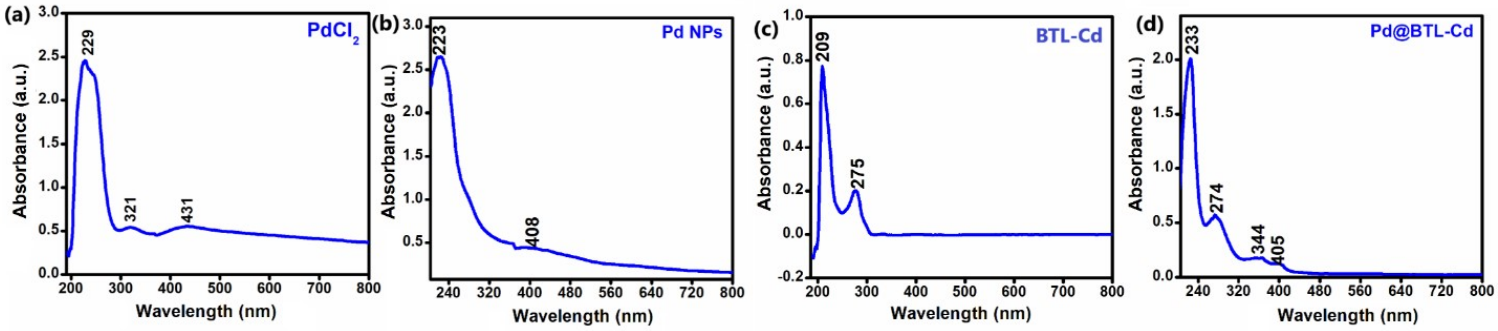

Fig. S13 UV absorption spectrum of (a) $PdCl_2$, (b) Pd NPs, (c) BTL-Cd, and (d) Pd@BTL-Cd

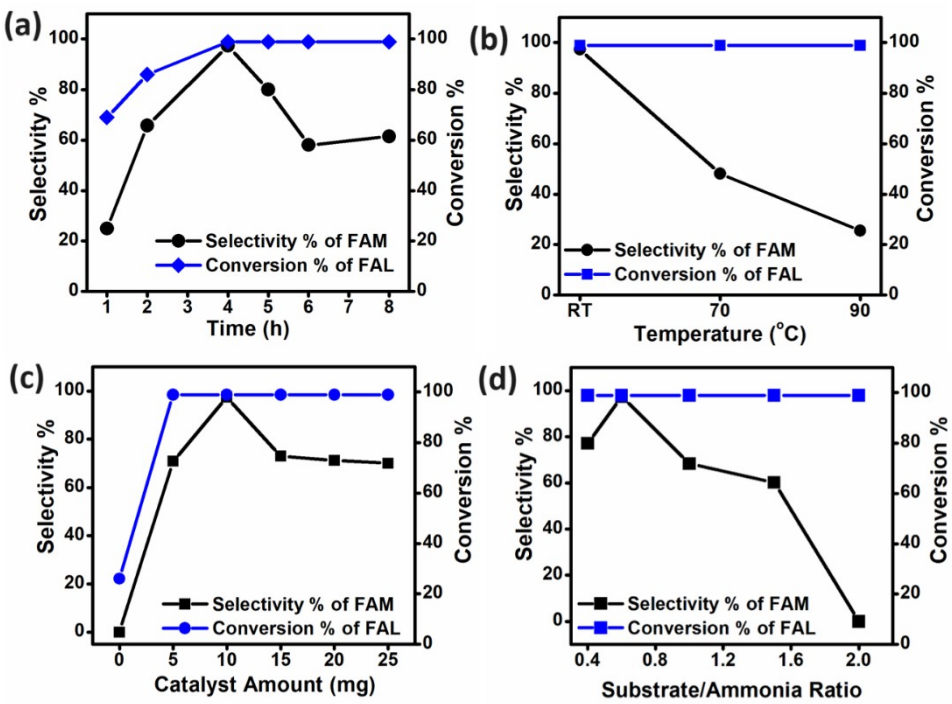

Fig. S14 Kinetics curve of conversion of furfural to furfuryl amine to show the influence of reaction time, Reaction Conditions: Distilled water (15 ml), Room Temperature, 0.6 substrate/ammonia ratio, Catalyst amount =10 mg, (b) Kinetics curve of conversion of furfural to furfuryl amine to show the influence of temperature, Reaction Conditions: Distilled water (15 ml), 4 h, 0.6 substrate/ammonia ratio, Catalyst amount = 10 mg, (c) Kinetics curve of conversion of furfural to furfuryl amine to show the influence of catalyst amount, Reaction Conditions: Distilled water (15 ml), Room Temperature, 0.6 substrate/ammonia ratio 3 h, (d) Kinetics curve of conversion of furfural to furfuryl amine to show the influence of substrate/Ammonia ratio, Reaction conditions: Distilled water (15 ml), Room Temperature, 3 h, Catalyst amount =10 mg.

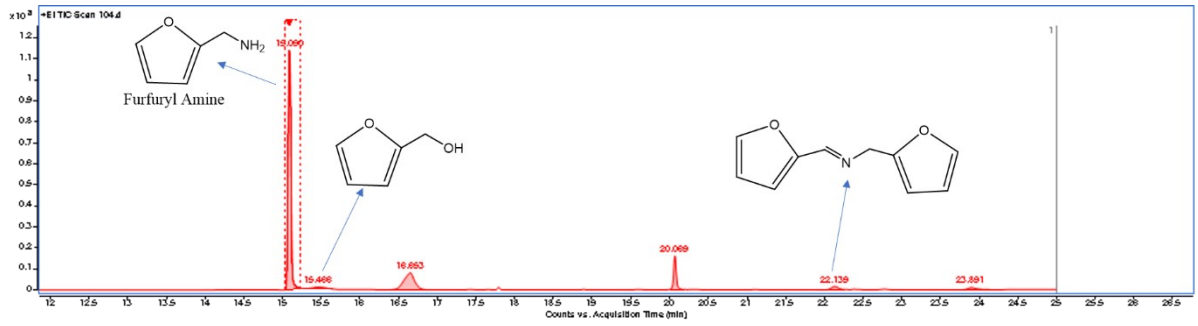

Fig. S15 GC spectrum of the typical reaction mixture. Reaction conditions: 10 mg (Pd@BTL-Cd), 10 mmol (Furfural), 15 mmol (Aqueous ammonia), xenon light, 4 h

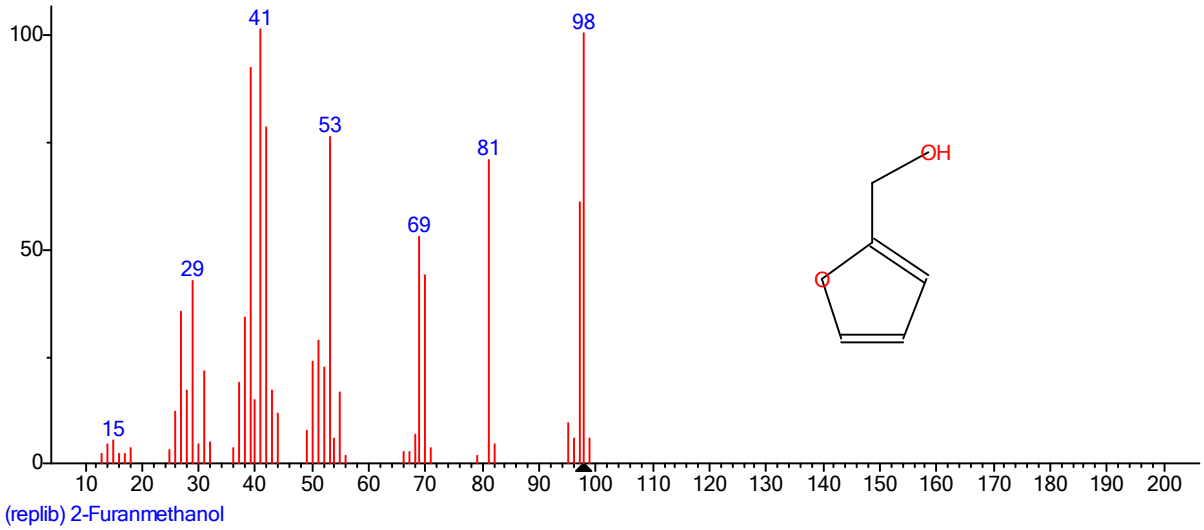

Fig. S16 The MS spectrum of furfuryl alcohol.

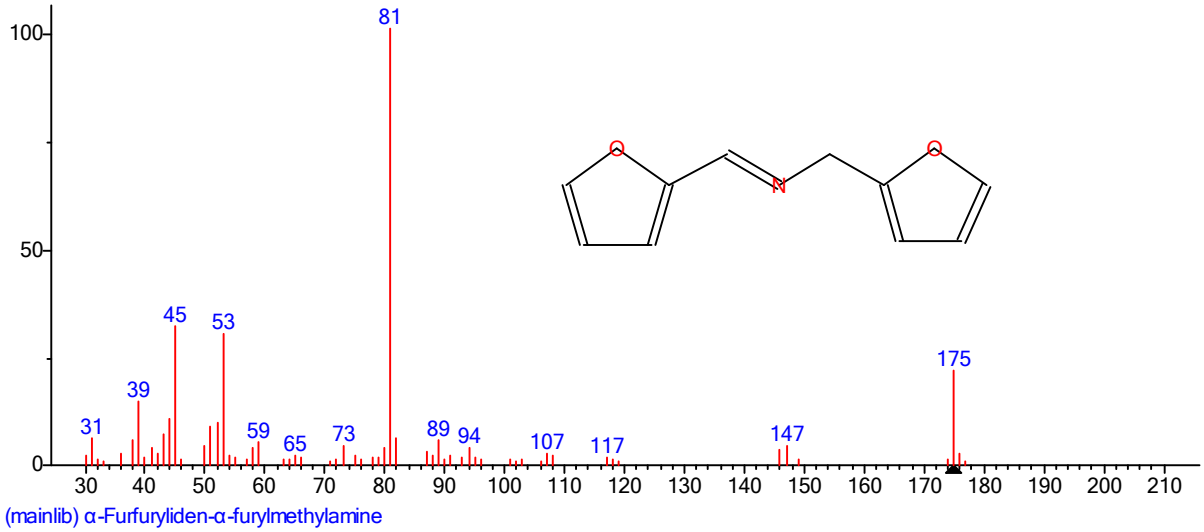

Fig. S17 The MS spectrum of Schiff base intermediate.

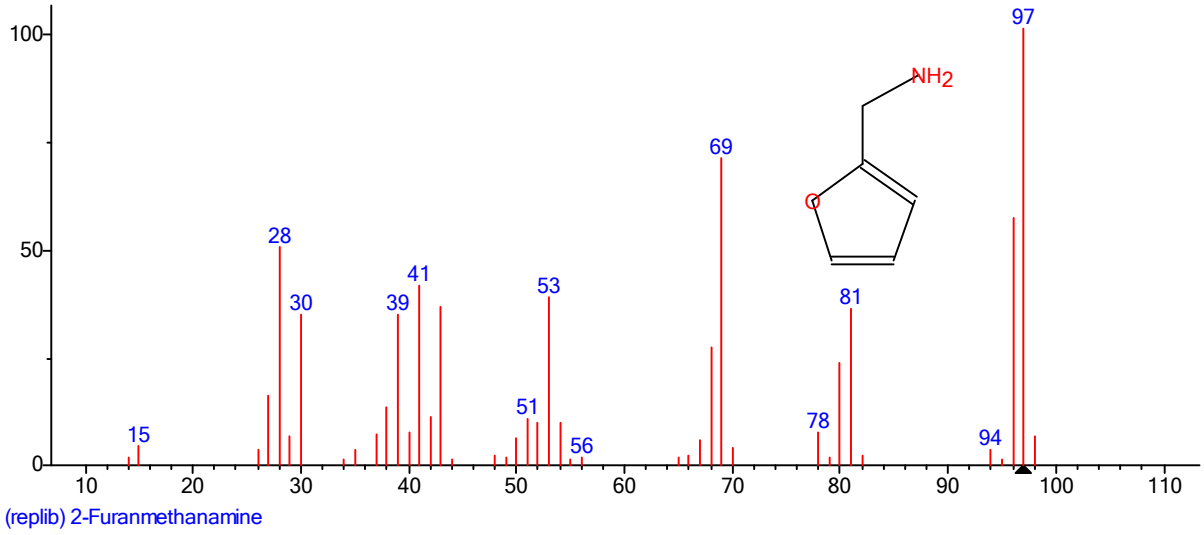

Fig. S18 The MS spectrum of furfuryl amine

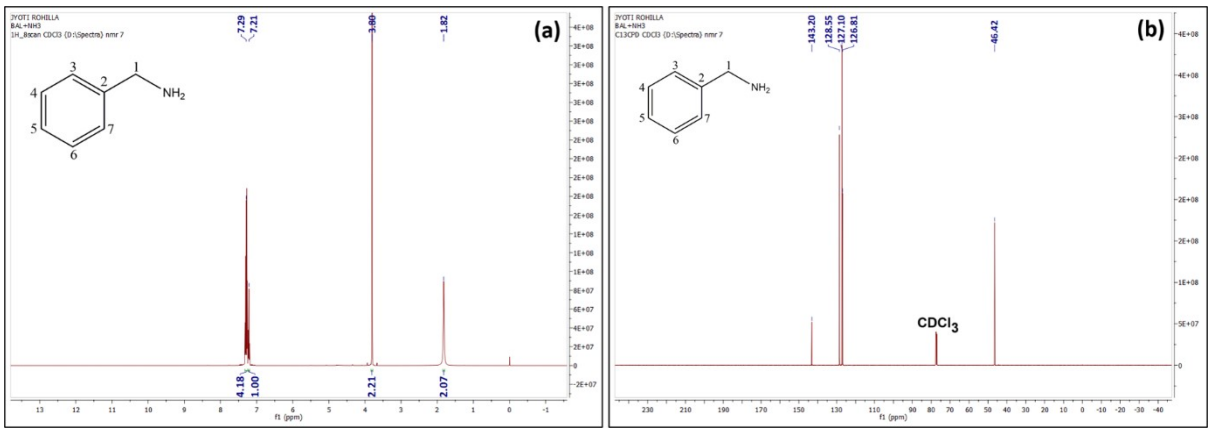

Fig. S19 ^{1}H and ^{13}C nmr of benzyl amine [^{1}H NMR ($CDCl_3$, 500 MHz): 1.82 (s, 2H, -NH_2), 3.80 (s, 2H, H^1), 7.21 (t, 1H, 3 J = 10 Hz, H^5), 7.29 (m, 4H, 3 J = 10 Hz, $H^{3,4,6,7}$). ^{13}C NMR ($CDCl_3$, 125 MHz): (46.42, C^1), (126.81, C^5), (127.10, C^3,C^7), (128.55, C^4,C^6), (143.19, C^2)].

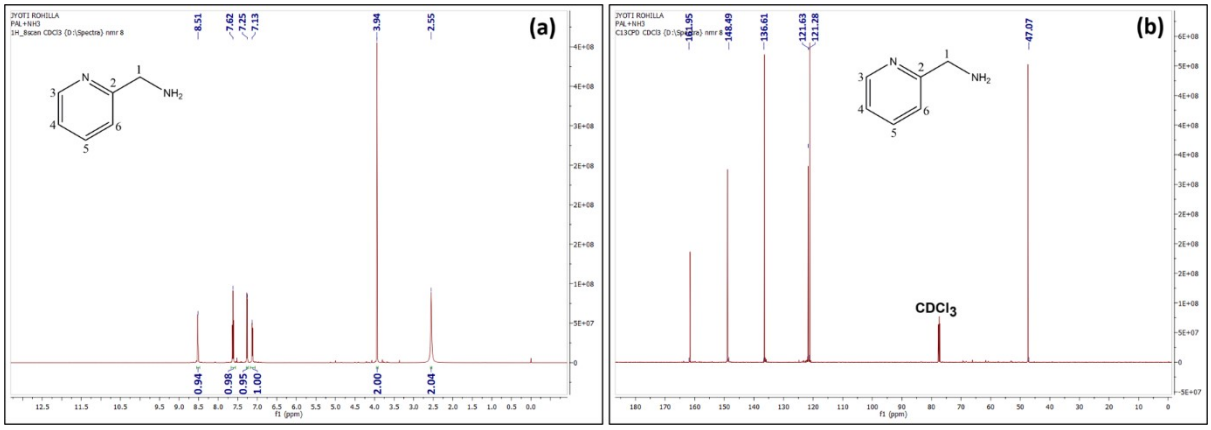

Fig. S20 ^{1}H and ^{13}C spectra of 2-pyridine methanamine [^{1}H NMR ($CDCl_3$, 500 MHz): 2.55 (s, 2H, -NH_2), 3.90 (s, 2H, H^1), 7.12 (dt, 1H, 3 J = 5 Hz, H^4), 7.25 (d, 1H, 3 J = 10 Hz, H^6), 7.62 (dt, 1H, 3J= 5 Hz, H^5), 8.51 (d, 1H, 3J= 5 Hz, H^3). ^{13}C NMR ($CDCl_3$, 125 MHz): (47.07, C^1), (121.08, C^4), (121.63, C^6), (136.04, C^5), (148.49, C^3), (161.02, C^2)].

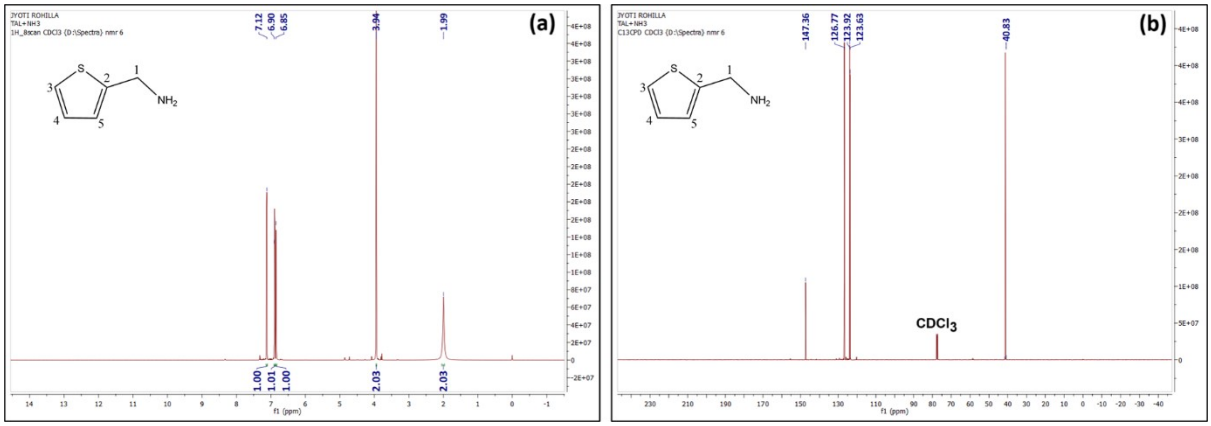

Fig. S21 ^{1}H and ^{13}C spectra of 2-thiophene methanamine [^{1}H NMR ($CDCl_3$, 500 MHz): 1.99 (s, 2H, -NH_2), 3.94 (s, 2H, H^1), 6.847 (m, 1H, 3 J = 5 Hz, H^4), 6.891 (dd, 1H, 3 J = 5 Hz, H^5), 7.125 (dd, 1H, 3J= 5 Hz, H^3). ^{13}C NMR ($CDCl_3$, 125 MHz): (41.21, C^1), (123.63, C^3), (123.92, C^5), (126.77, C^4), (147.35, C^2)]

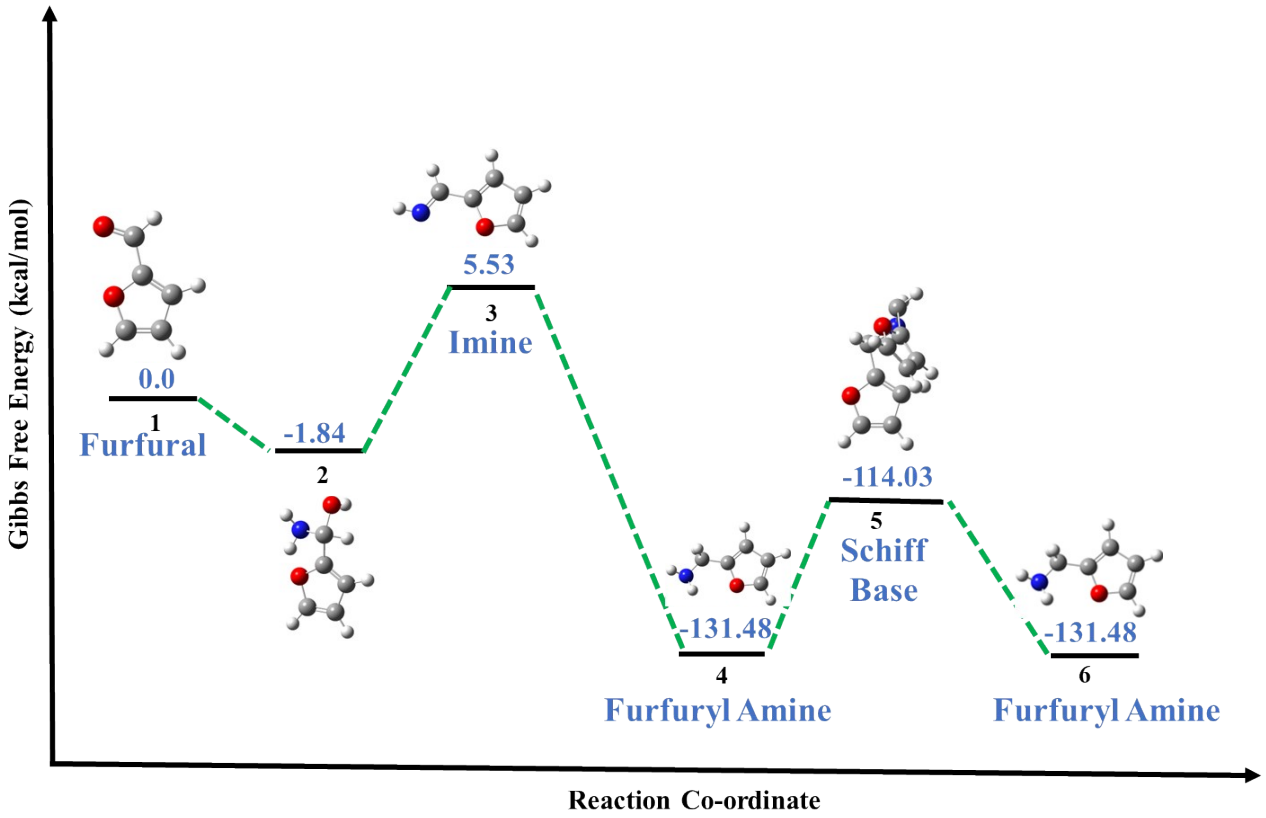

Fig. S22 Energy profile diagram of catalytic conversion of furfural to furfuryl amine.

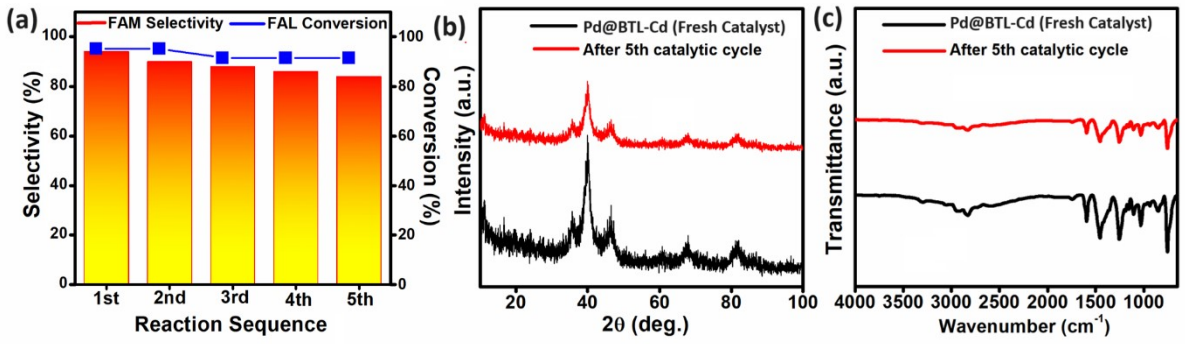

Fig. S23 (a) Recyclability study of Pd@BTL-Cd, (b) PXRD pattern of Pd@BTL-Cd fresh catalyst and after 5th catalytic cycles, (c) FTIR spectra of Pd@BTL-Cd fresh catalyst and after 5th catalytic cycles.

Table S1 Crystallographic data and structural parameters for ligand BTL and BTL-Cd

Parameters	**BTL**	**BTL-Cd**
Empirical formula	$C_{27}H_{39}Cl_3N_4O_3$	$C_{27}H_{34}Cd_2Cl_2N_4O_3$
Formula weight	573.97	758.28
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12$
a/Å	10.0304(10)	26.9155(6)
b/Å	19.479(3)	15.7883(3)
c/Å	17.5363(18)	8.7097(2)
α/°	90	90
β/°	97.579(12)	90
γ/°	90	90
Volume/Å^3	3396.3(7)	3701.19(14)
Z	4	4
ρ_{calc}g/cm^3	1.123	1.361
μ/mm^{-1}	0.300	1.321
F(000)	1216.0	1512.0
Crystal size/mm^3	0.8 × 0.6 × 0.2	0.7 × 0.4 × 0.2
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.282 to 57.472	6.52 to 54.884
Index ranges	-12 ≤ h ≤ 12, -24 ≤ k ≤ 23, -22 ≤ l ≤ 20	-33 ≤ h ≤ 34, -20 ≤ k ≤ 13, -11 ≤ l ≤ 10
Reflections collected	25032	31122
Independent reflections	7133 [R_{int} = 0.1827, R_{sigma} = 0.1471]	7869 [R_{int} = 0.0386, R_{sigma} = 0.0408]
Data/restraints/parameters	7133/0/337	7869/1/308
Goodness-of-fit on F^2	0.904	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0925, wR_2 = 0.2654	R_1 = 0.0346, wR_2 = 0.0678
Final R indexes [all data]	R_1 = 0.1874, wR_2 = 0.3455	R_1 = 0.0486, wR_2 = 0.0719
Largest diff. peak/hole / e Å^{-3}	0.49/-0.42	0.28/-0.31

Table S2 Selected bond length (Å) and bond angle (º) for BTL

Bond length (Å)			
BTL		**BTL-Cd**	
O1-C5	1.358(7)	Cd01-O3	2.289(3)
O2-C14	1.367(6)	Cd01-O2	2.303(4)
O3-C23	1.379(7)	Cd01-N4	2.359(4)
N1-C7	1.506(6)	Cd02-Cl1	2.414(13)
N2-C27	1.508(6)	Cd02-O3	2.184(4)
N2-C11	1.484(7)	Cd01-N2	2.331(4)
C13-C18	1.373(7)	Cd01-N1	2.461(4)
C5-C4	1.391(7)	Cd01-N3	2.367(4)
C10-C11	1.523(7)	Cd02-Cl2	2.421(17)
C22-C23	1.399(7)	Cd03-O2	2.148(3)

Bond angle (º)			
BTL		**BTL-Cd**	
C7-N1-C8	115.3(4)	O3-Cd01-N2	112.18(13)
C11-N2-C27	115.2(4)	O3-Cd01-N1	153.81(15)
C9-N4-C10	110.2(4)	O3-Cd01-N3	118.92(15)
C19-N4-C10	110.2(4)	N2-Cd01-N4	111.09(17)
C19-N4-C9	110.4(4)	O2-Cd01-N2	83.25(15)
C21-N3-C20	113.7(4)	O2-Cd01-N4	152.31(14)
O2-C14-C13	117.7(4)	N4-Cd01-N1	74.42(16)
C4-C3-C2	121.9(5)	N3-Cd01-N1	73.99(15)
C3-C4-C5	120.5(6)	O3-Cd02-Cl1	116.95(11)
C6-C7-N1	112.3(4)	O2-Cd02-Cl1	114.51(11)
C6-C1-C2	120.8(6)	O2-Cd02-O3	78.12(13)
C24-C25C26	120.0(6)	C18-O3-Cd01	131.6(3)
N3-C20-C19	111.3(5)	C8-N2-Cd01	110.9(3)
C16-C15-C14	119.8(5)	Cd02-O2-Cd01	104.78(14)
BTL-Cd		C10-N1-Cd01	106.8(3)
N4-Cd01-N3	109.76(16)	C19-N1-C10	111.8(4)
Cl1-Cd02-Cl2	112.43(6)	O3-Cd01-O2	72.96(12)
O3-Cd02-Cl2	114.63(11)	O3-Cd01-N4	79.60(14)
O2-Cd02-Cl2	116.26(12)	N2-Cd01-N1	75.07(13)
Cd02-O3-Cd01	104.05(14)	N2-Cd01-N3	118.44(15)
C18-O3-Cd02	124.2(3)	O2-Cd01-N1	133.17(14)
C7-N2-Cd01	114.3(3)	O2-Cd01-N3	81.15(15)
C23-O2-Cd01	121.2(2)	C9-N1-Cd01	105.5(3)
C19-N1-Cd01	109.3(3)	C12-N4-Cd01	110.8(4)

Table S3 Previous reported Palladium based catalytic systems for reductive amination of furfural

S. N.	Catalyst	Hydrogen Source	Substrate (mmol)	Solvent	NH_3 (mmol)	Temp. (°C)	Time (h)	Yield of FAM	Ref.
1.	Pd/CNT	Formic Acid	1	Methanol	-	120	6	>99	50
2.	Pd/SiO_2	H_2 gas	1	Dioxane/water	5	120	10	10	16
3.	Pd/HZSM-5(46)	H_2 gas	2	Methanol	7 M	100	15 min	44	3
4.	Ru/Nb_2O_5	H_2 gas	0.5	MeOH	8	90	4	89	51
5.	Co@NC-800	H_2 gas	1	EtOH	28	130	12	82	52
6.	Ru NPs	H_2 gas	0.5	MeOH	8	90	2	90	53
7.	Ru/TiO_2	H_2 gas	0.5	MeOH	8	90	4	72	51
8.	Fe_3O_4@SiO_2-Ni	H_2 gas	1	EtOH	750 µL	120	2	73	54
9.	Raney Ni	H_2 gas	5	MeOH	NH_3 (g) (0.1 MPa)	120	2	65	55
10.	Ru/BNC	H_2 gas	0.12	MeOH	$N_2H_4.2H_2O$ (0.48)	80	16	95	56
11.	0.5% Ru/P25	Ethanol	0.5	EtOH	8	rt	6	69	19
12.	$Ni/CaCO_3$	Water/Zn	5	Water	20	80	10	91	17
13.	**Pd@BTL-Cd**	**Water**	**5**	**Water**	**8**	**RT**	**4**	**97**	**This Work**

Table S4 Optimization of different aldehyde sources for the catalytic activity of Pd@BTL-Cd

S.No.	Substrate	Product	Product Yield (%)
1.	Benzaldehyde	Benzyl Amine	79
2.	2-Thiophene Carboxaldehyde	2-Thiophene methylamine	83
3.	2-Pyridine Carboxaldehyde	2-pyridyl methyl amine	80

Section S1

Detailed calculation of acidic active sites of Pd@BTL-Cd:

Calibration Factor (counts/mmol) = 35,890,228

Weight of catalyst = 0.0588 g

Area (count) at 209.7 ℃ = 5,34,351

Area (count) at 237.6 ℃ = 43,89,992

Total area (counts) = 49,24,343

NH_3 desorbed (mmol) = $\frac{Total\ area\ (counts)}{Calibration\ Factor\ (counts/mmol)} = \frac{49,24,343}{35,890,228}$ = 0.1372 mmol

Acidic Sites (mmol) = $\frac{NH3\ desorbed\ (mmol)}{Catalyst\ weight\ (g)} = \frac{0.1372}{0.0588}$ = 2.33 mmol/g

Section S2

Detailed calculation of Turnover Number:

In a heterogeneous catalytic reaction, active sites refer to the specific sites capable of facilitating a particular reaction. The no. of acidic site available in the catalyst was calculated through TPD studies. The available acidic sites act as catalytic active sites for the reaction.

The available acidic sites present in Pd@BTL-Cd = 2.333 $mmolg^{-1}$

According to TPD studies,

1 g of Pd@BTL-Cd contain active sites = 2.333 mmol g^{-1}

10 mg of Pd@BTL-Cd contain active sites = 2.33×10^{-2} mmol g^{-1}

The effectiveness of the catalyst in a reaction system is typically expressed as the turnover number (TON), which quantifies the number of reactions occurring per active site. The TON value can be calculated as follows:

TON = $\frac{\%\ yield\ \times No.\ of\ moles\ of\ reactant}{No.\ of\ moles\ of\ catalyst}$

For the catalytic reaction,

$$\% \text{ yield} = \frac{Selectivity\% \times Conversion\%}{100}$$

$= 98 \times 99/100$

$= 97.02\ \%$

$$\text{TON} = \frac{97.02 \times 5}{2.33 \times 10^{-2}}$$

$= 20819\ \text{mmolg}^{-1}$

$$\text{Mol \%} = \frac{Moles\ of\ catalyst \times 100}{Moles\ of\ reactant}$$

$$= \frac{2.33 \times 10^{-2}\ mmol \times 100}{5\ mmol}$$

$= 0.5\%$