Electronic Supplementary Information

Pd@L-Asparagine-EDTA-Chitosan: A highly effective and reusable bio-based and biodegradable catalyst for Heck Cross-Coupling Reaction under mild conditions

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Graphical Abstract

Pd@L-Asparagine-EDTA-Chitosan: A highly effective and reusable bio-based and biodegradable catalyst for Heck Cross-Coupling Reaction under mild conditions

Mohammad Dohendou [a], Mohammad G. Dekamin[a*], Danial Namaki[a]

A novel supramolecular Pd(II) catalyst supported on chitosan grafted by L-asparagine, and EDTA linker named Pd@ASP-EDTA-CS was prepared and characterized by applicable spectroscopic and analytical techniques. The heterogeneous low-loaded Pd catalyst was successfully employed in the Heck cross-coupling reaction (HCR) in good to excellent yields with proper reusability.

Model Reaction:

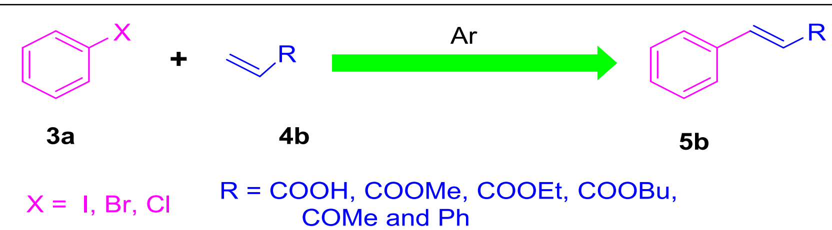
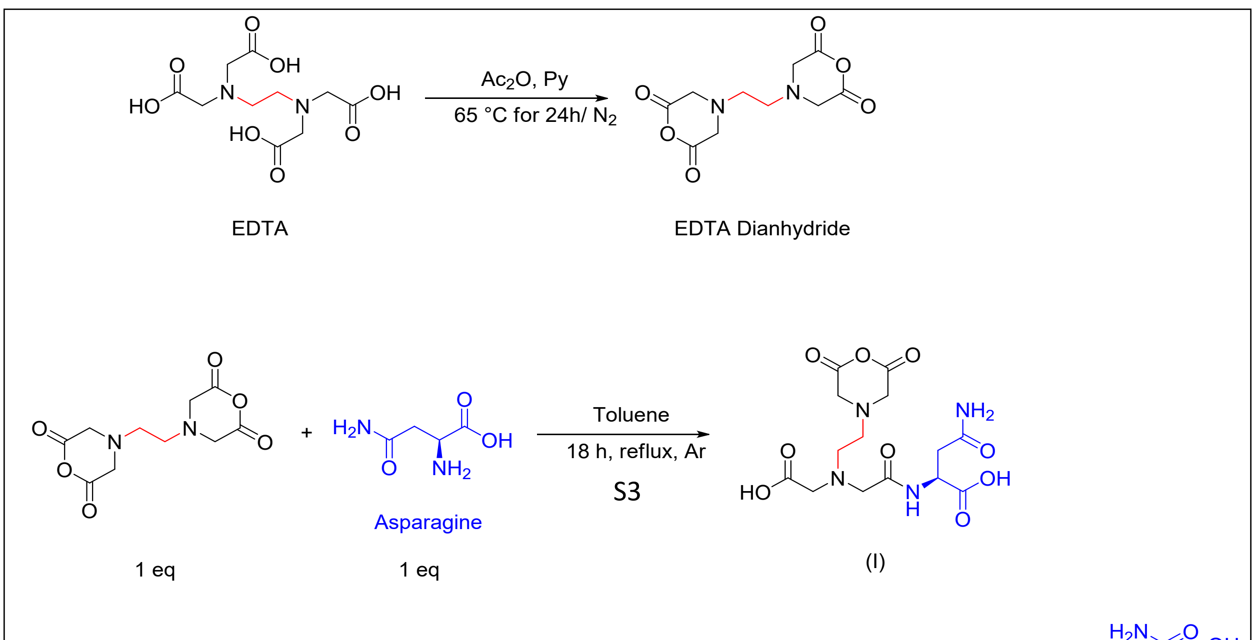


Fig S1 The model reaction for HCR catalyzed by catalyst **1**.

Catalyst Preparation:

The graphical procedure for the synthesis of the catalyst is shown in Scheme S1.



Scheme 1 Schematic representation of (Pd@ASP-EDTA-CS) catalyst (1) preparation steps.

FTIR Spectra:

The FTIR spectra of the catalyst **1** components are illustrated in (**Fig. S2**).

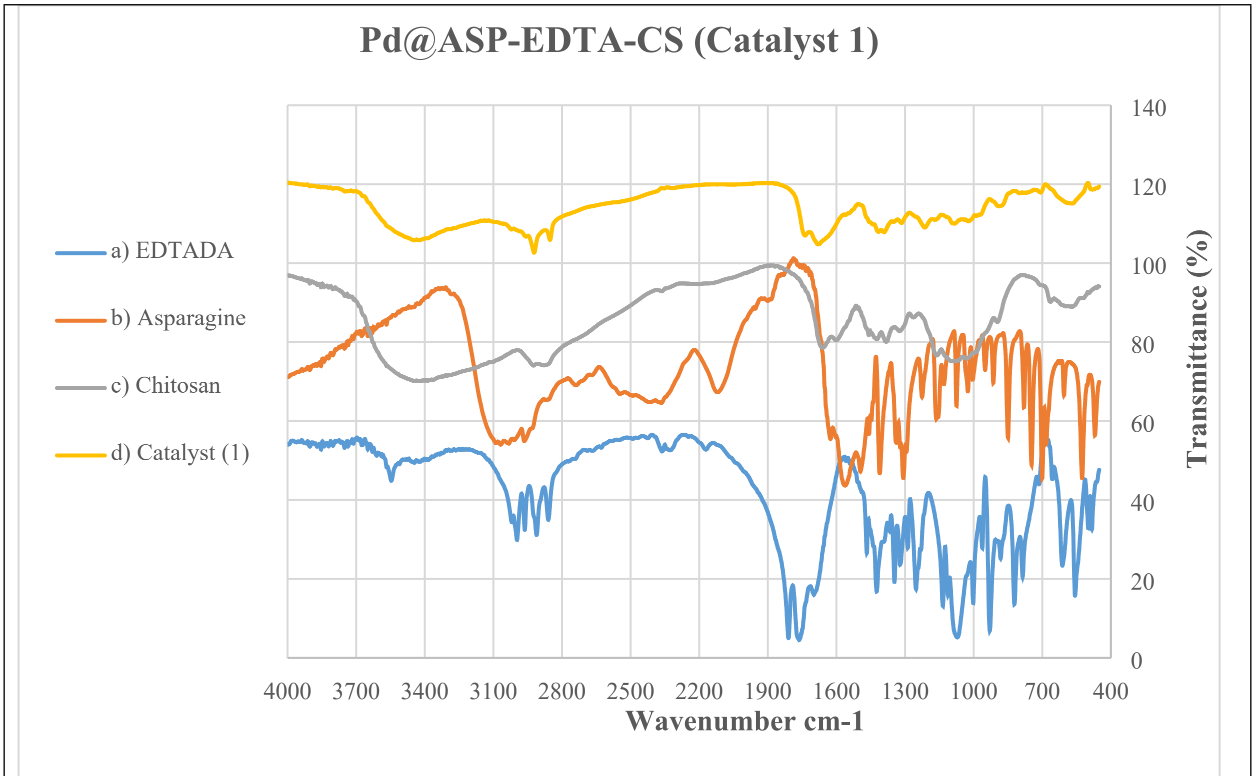


Fig. S2 Mixed FTIR spectrums of catalyst **1** from initial section.

The observed bands at 3400-3600 are attributed to hydroxyl and amine groups, the vibration double bands of C=O groups in EDTA dianhydride stand in 1810 and 1760 respectively which are displaced by amidic and acidic groups during the processes at 1675 cm^{-1} and 1733 cm^{-1}. The SP^3 C–H bands are shown at 2900-3000 cm^{-1} and peaks at 1200-1400 cm^{-1} are assigned to the bending of –NH groups. The C-O stretching band is located at about 1100 cm^{-1} .

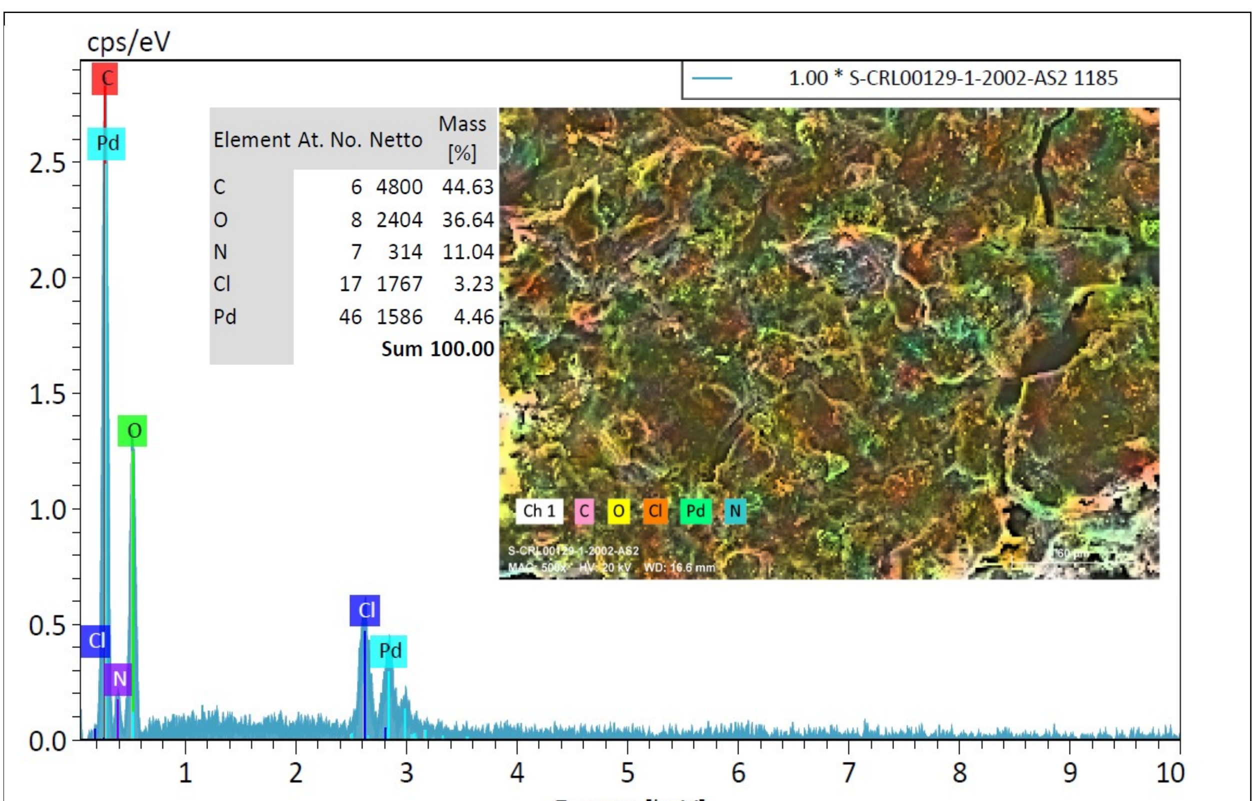
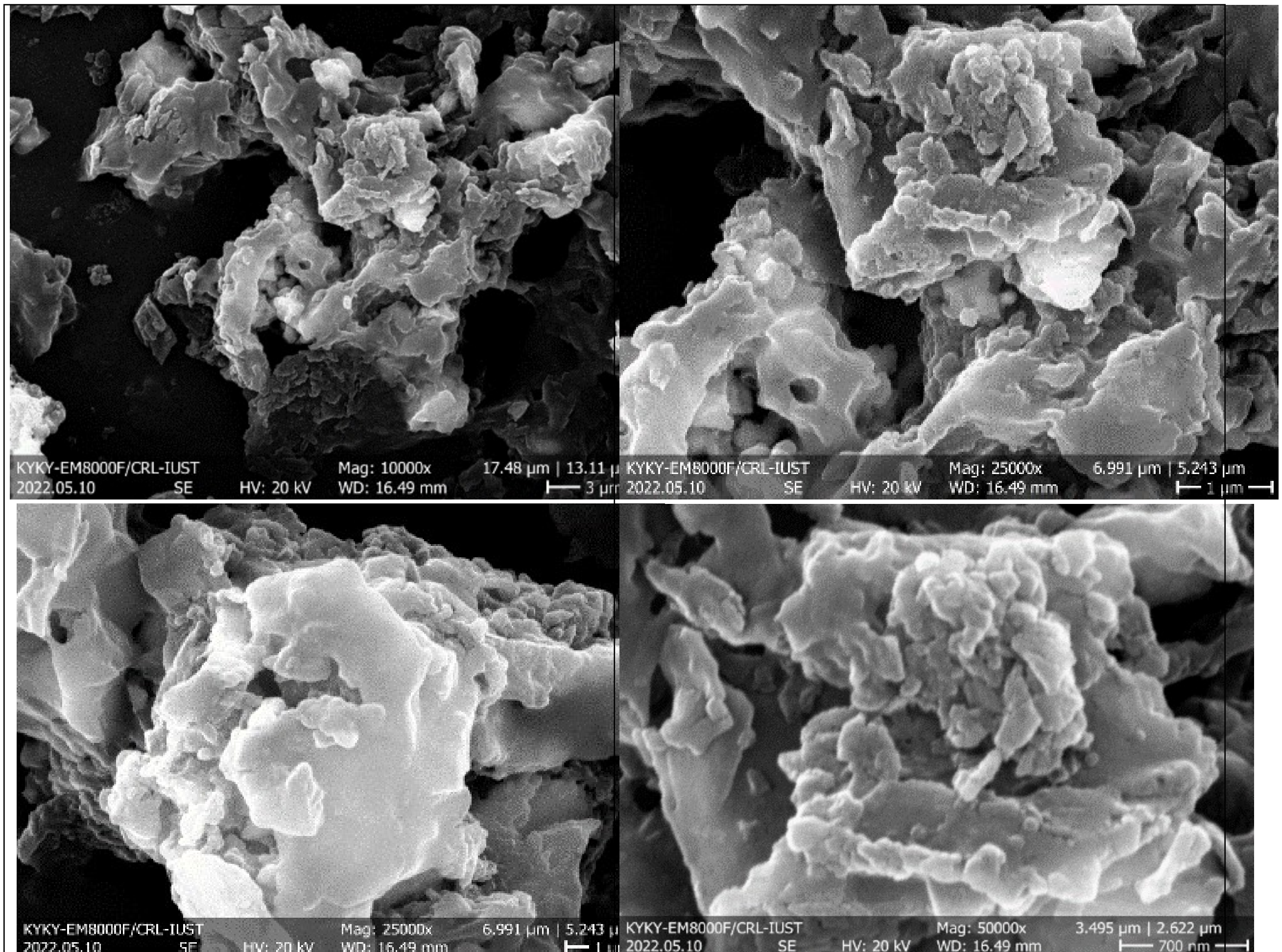


Fig. S3 EDS spectrum of Pd@ASP-EDTA-CS organocatalyst (**1**).



The Iranian legend of Rostam and Sohrab.

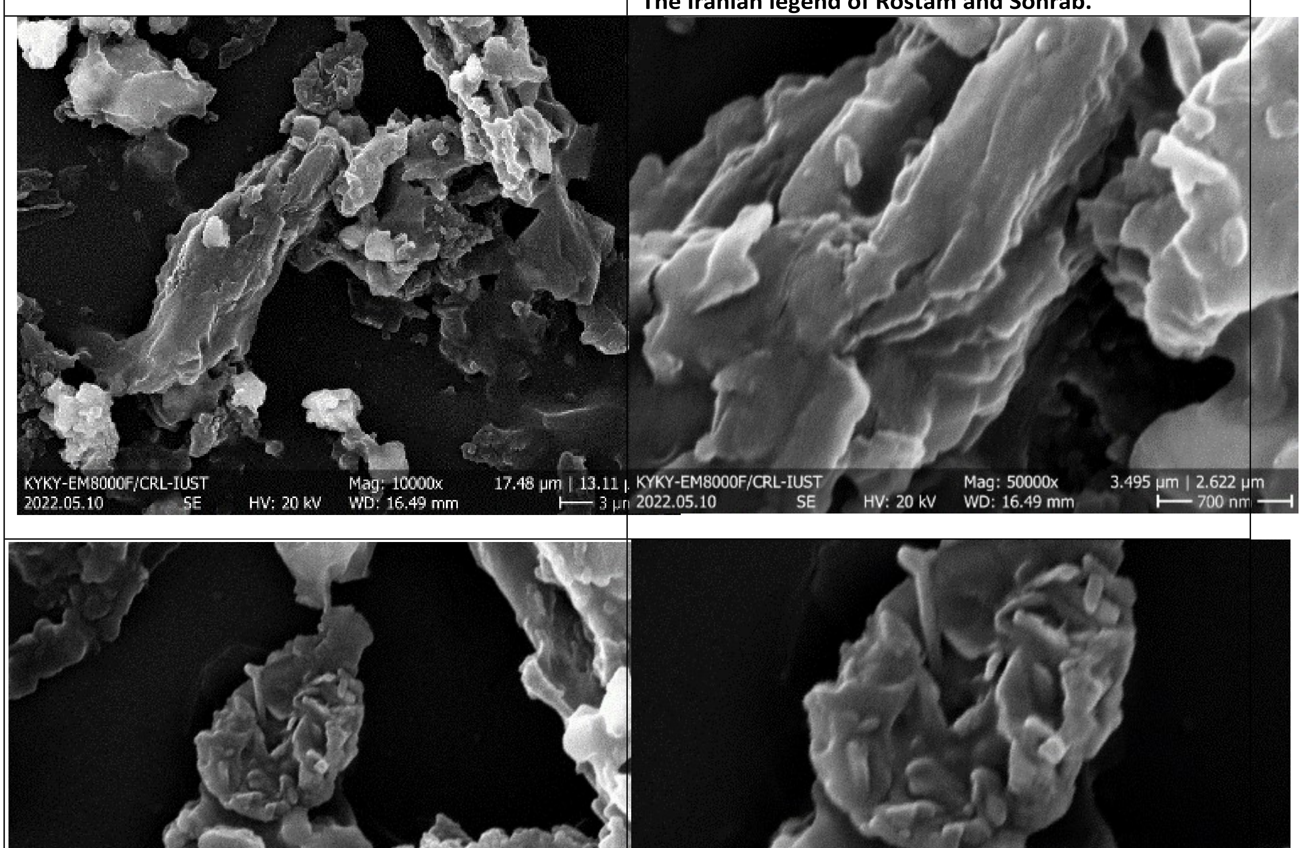


Fig. S4 FESEM images of Pd@ASP-EDTA-CS catalyst (**1**).

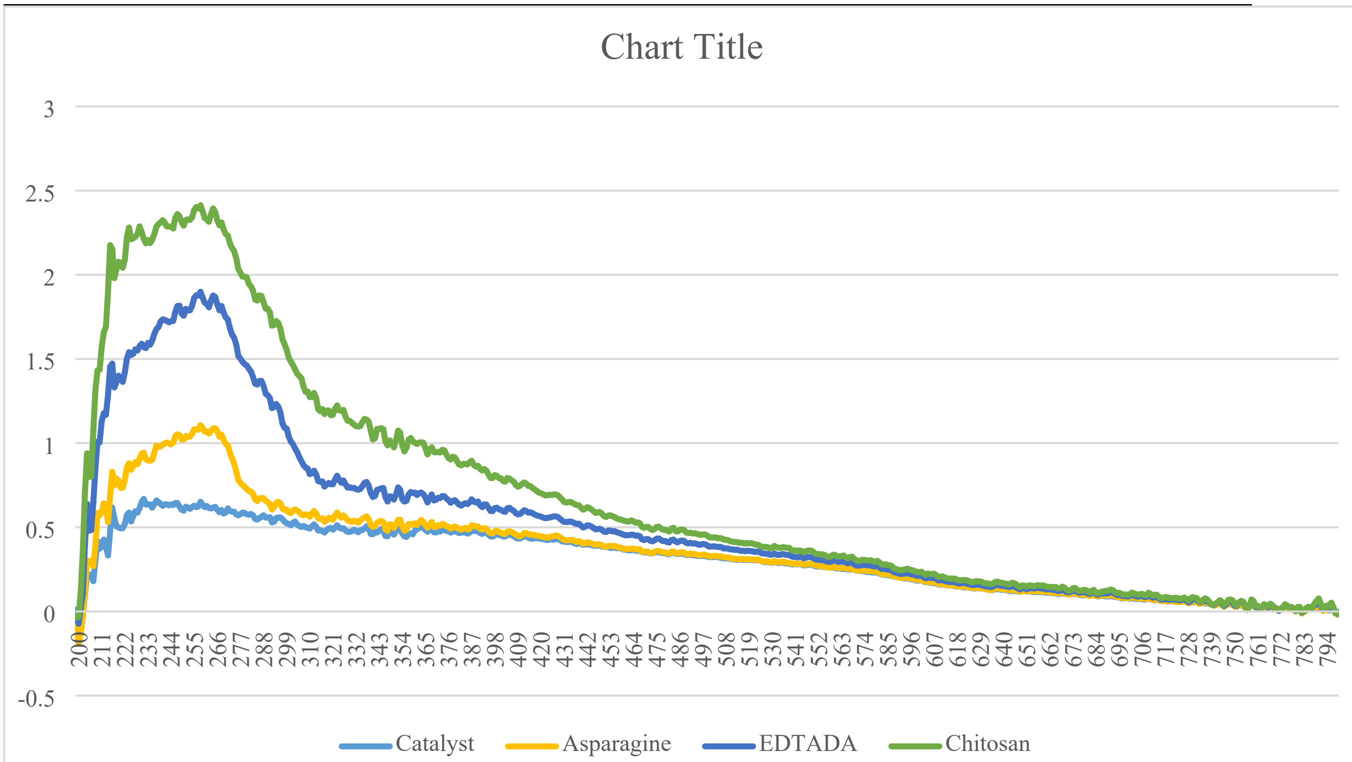


Fig. S5a DRS pattern of Pd@ASP-EDTA-CS catalyst (**1**).

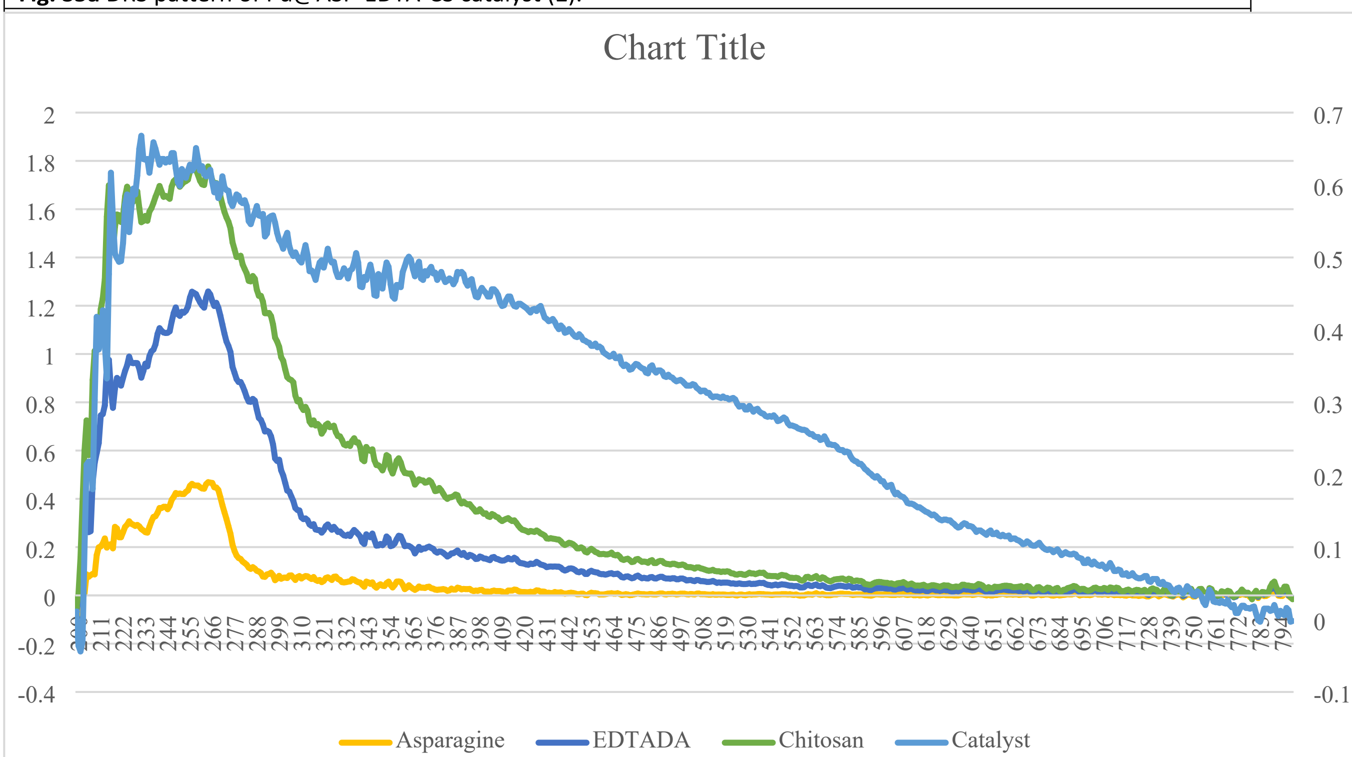


Fig. S5b DRS pattern of Pd@ASP-EDTA-CS in second axis for catalyst (**1**).

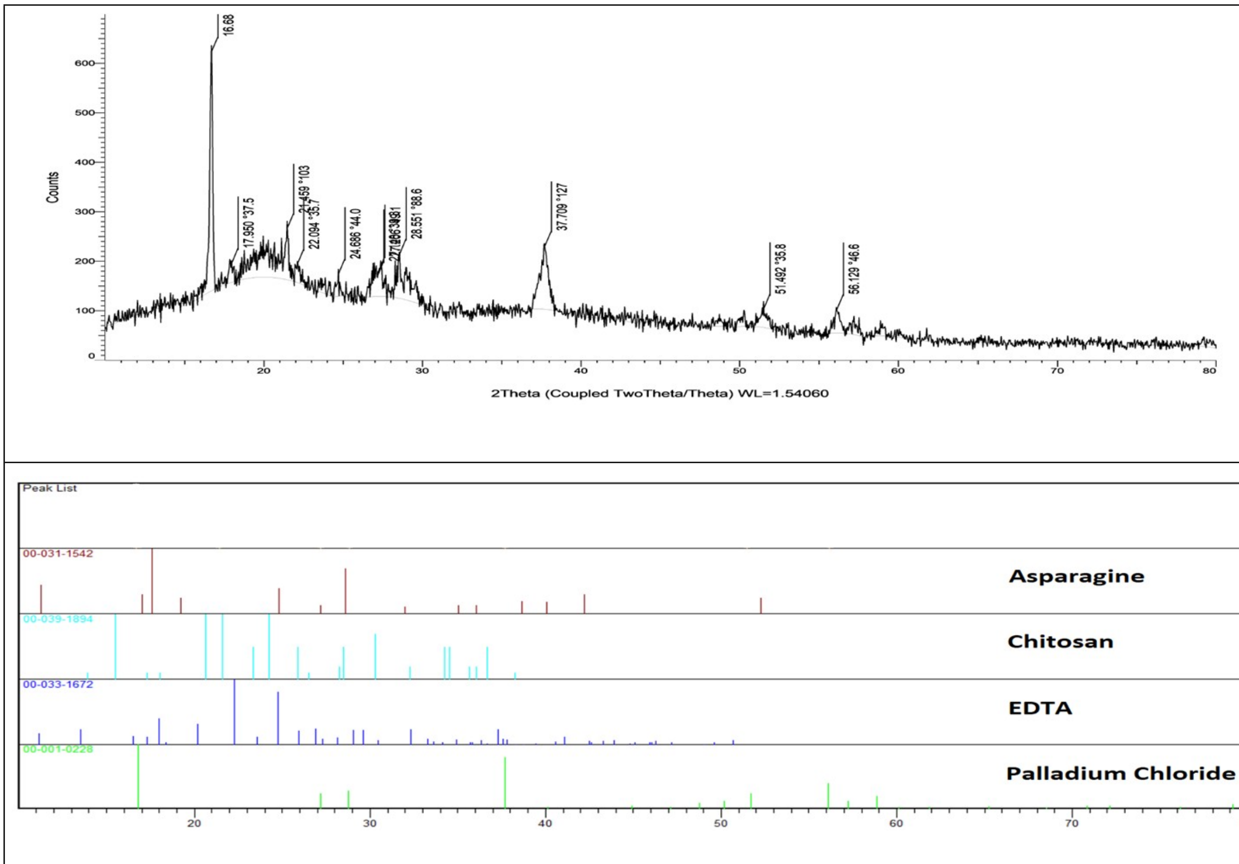
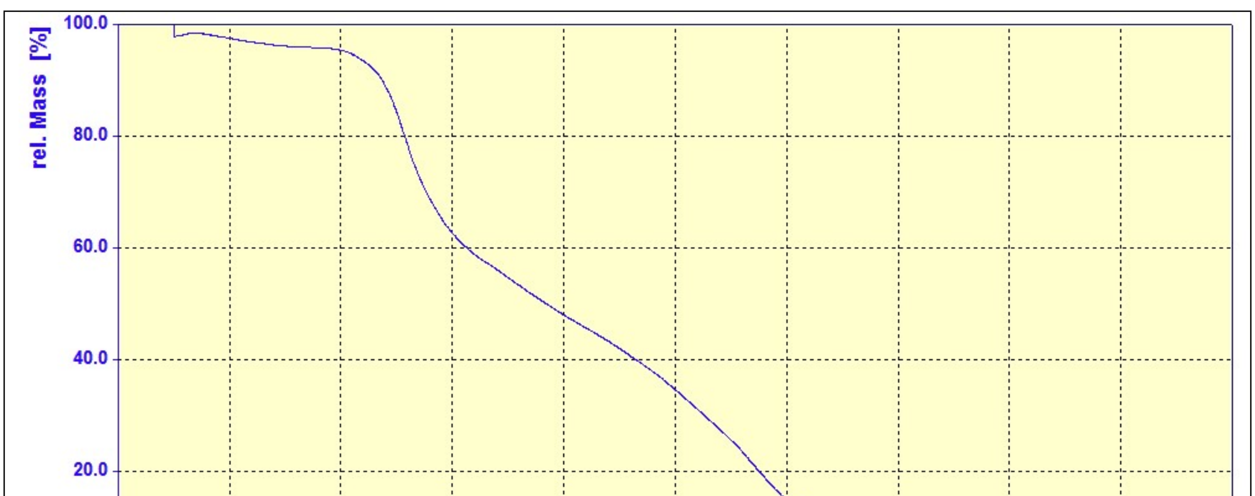


Fig. S6 XRD pattern of Pd@ASP-EDTA-CS catalyst (**1**).



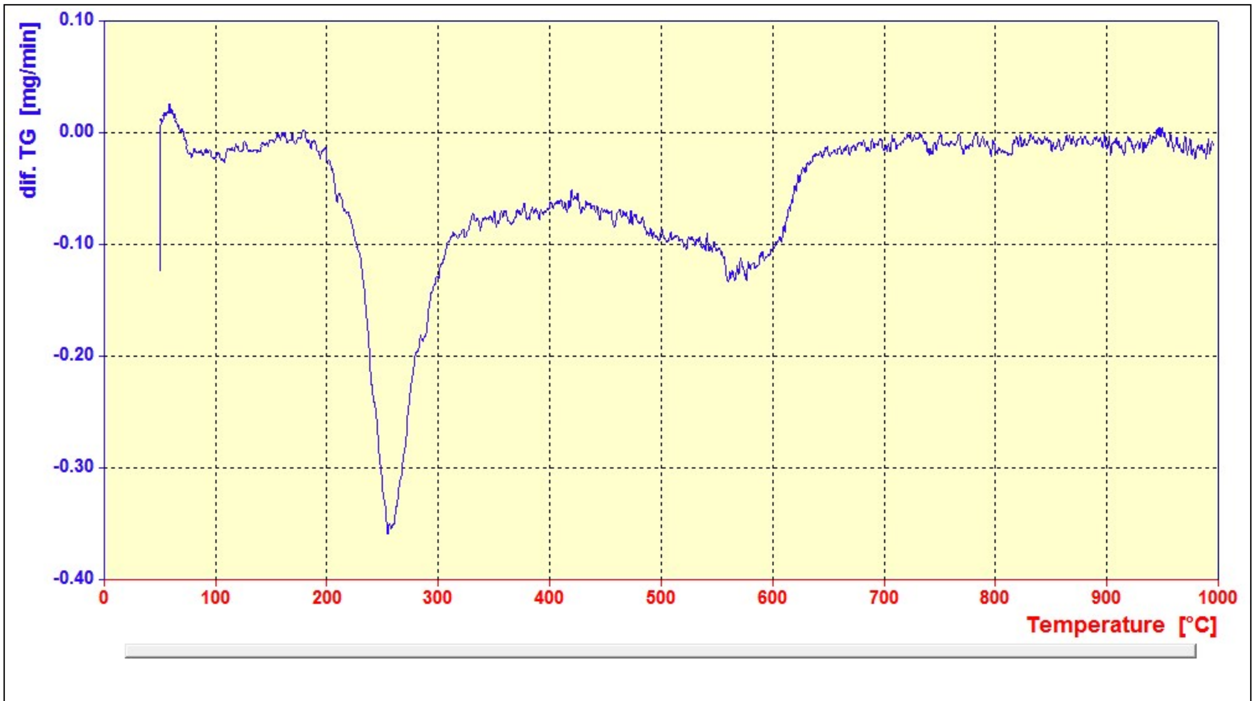


Fig. S7 TGA and diff. TGA Curves of the catalyst (**1**).

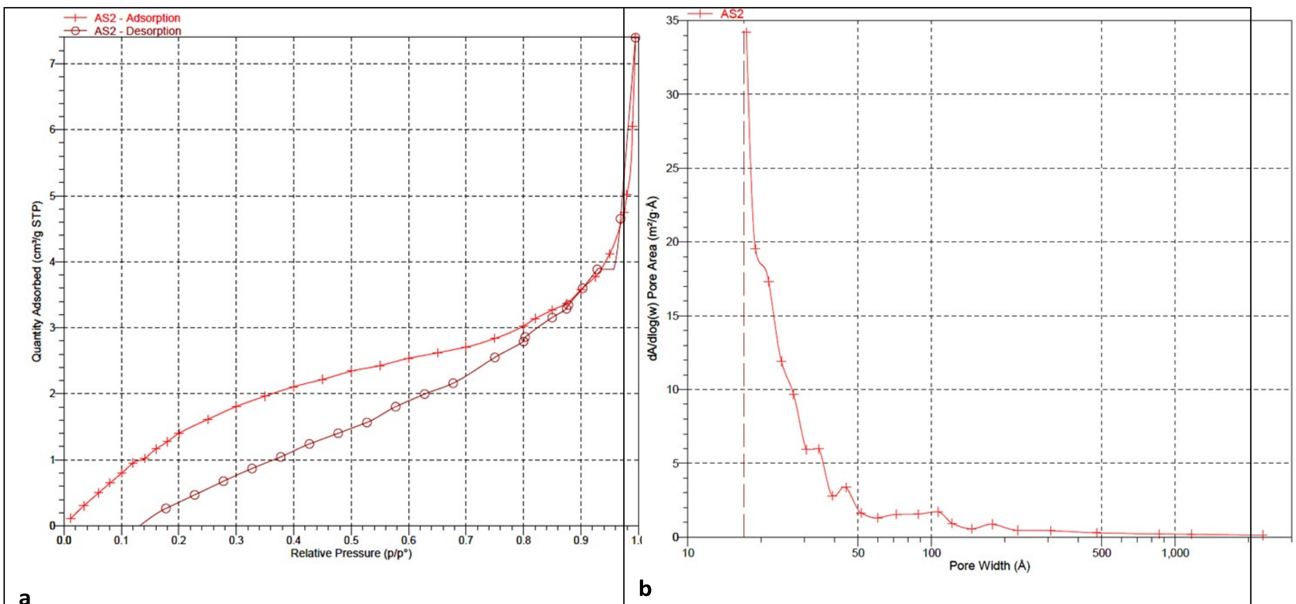


Fig. S8 The N2 adsorption–desorption isotherm of catalyst (1).

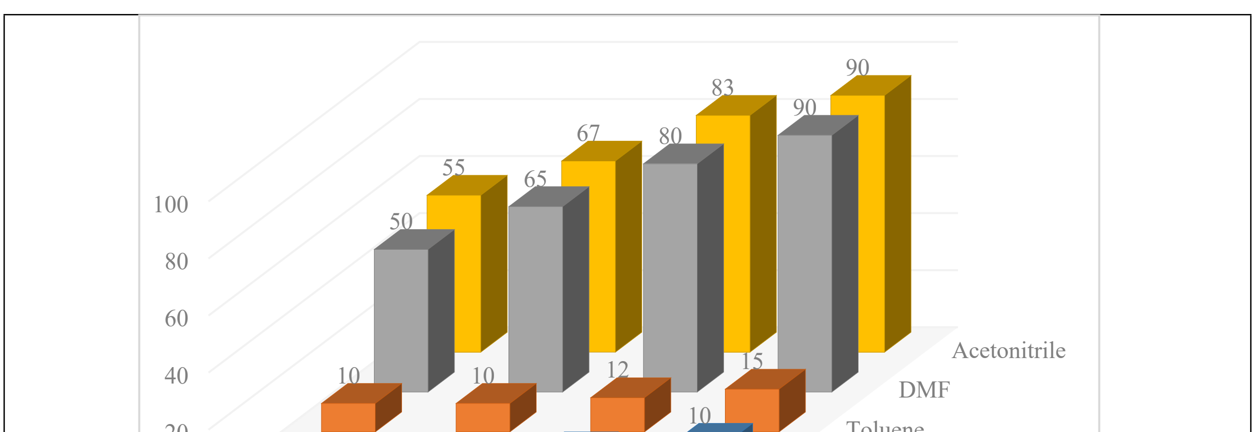


Fig. S9 Investigation of the optimized amount of catalyst **1** in different solvents for HCR.

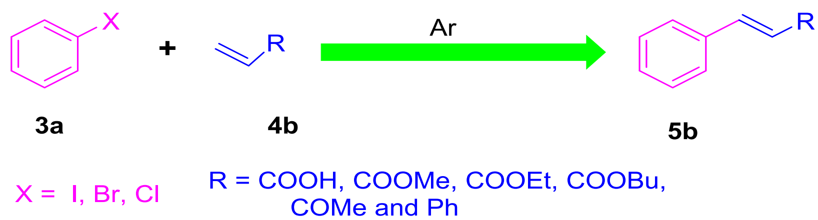
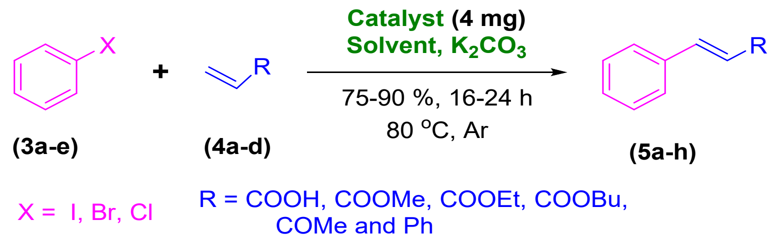


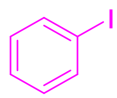
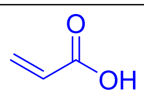
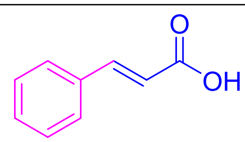
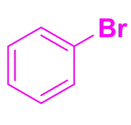
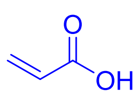
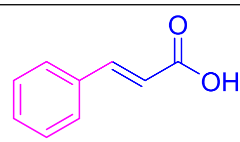
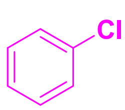
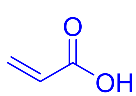
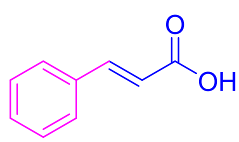
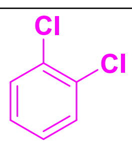
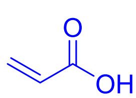
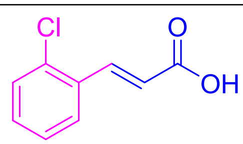
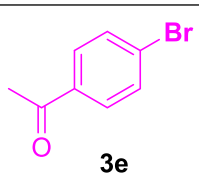
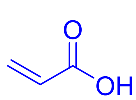
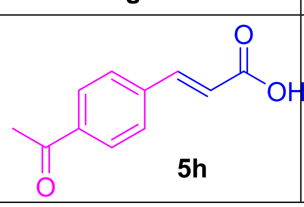
Table S1. Optimization of the conditions for HCR in the model reaction of Iodobenzene (**3a**), methyl acrylate (**4b**) to afford **5b** under different conditions in the presence of catalyst (**1**).[a]

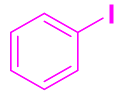
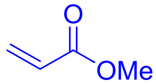
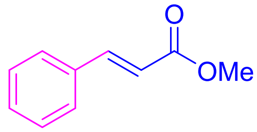
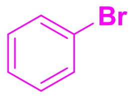
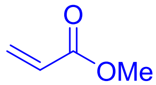
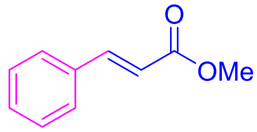
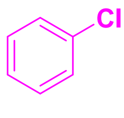
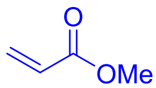
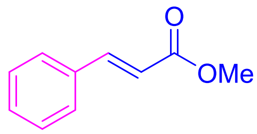
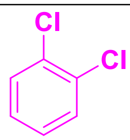
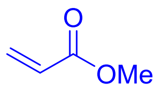
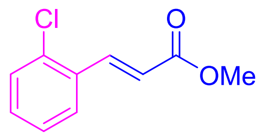
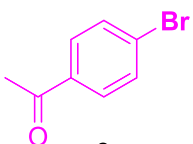
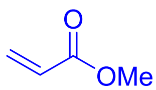
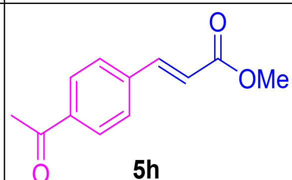
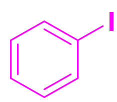
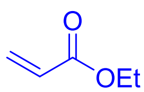
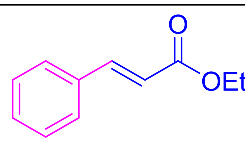
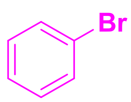
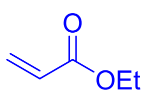
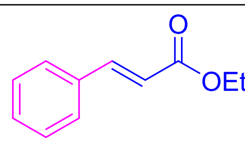
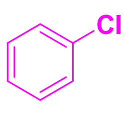
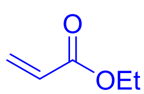
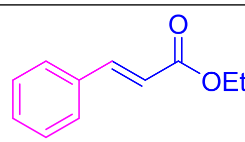
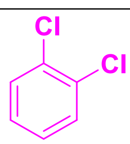
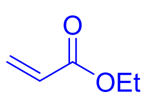
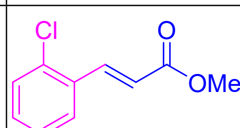
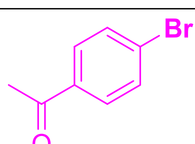
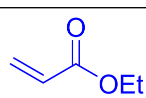
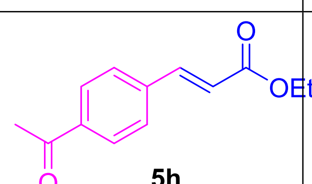
Entry	Catalyst	Base	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	-	K_2CO_3	DMF	r.t	48	N.R
2	-	K_2CO_3	DMF	Reflux	48	N.R
3	Pd@ASP-ETDA-CS	-	DMF	Reflux	48	N.R
4	Pd@ASP-ETDA-CS	-	ACN	Reflux	48	N.R
5	Pd@ASP-ETDA-CS	-	Solvent-free	80	24	trace
6	Pd@ASP-ETDA-CS	K_2CO_3	**DMF**	**90**	**14-20**	**78-90**
7	Pd@ASP-ETDA-CS	K_2CO_3	**ACN**	**80**	**16-20**	**75-90**
8	Pd@ASP-ETDA-CS	K_2CO_3	Toluene	105	36	Trace
9	Pd@ASP-ETDA-CS	K_2CO_3	H_2O	105	36	Trace
10	ASP-ETDA	K_2CO_3	DMF	130	36	N.R
11	ASP-ETDA-CS	K_2CO_3	DMF	130	36	N.R
12	ASP-ETDA	K_2CO_3	ACN	80	36	N.R
13	ASP-ETDA-CS	K_2CO_3	ACN	80	36	N.R
14	Asparagine	K_2CO_3	DMF	130	36	N.R
15	EDTA	K_2CO_3	DMF	130	36	N.R

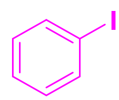
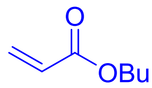
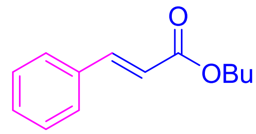
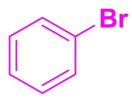
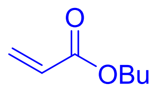
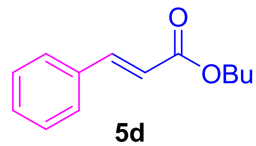
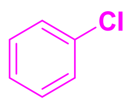
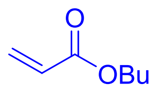
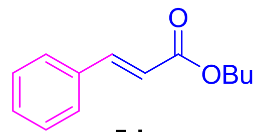
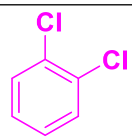
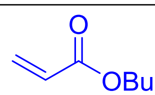
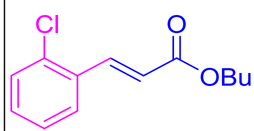
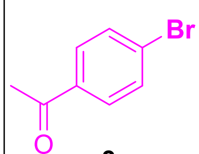
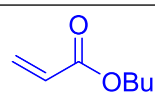
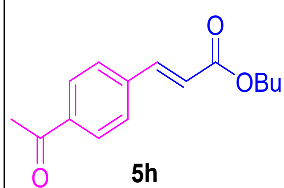
[a]Reaction conditions: aryl halide (**3 a-d**, 2 mmol), alkene (**4 a-f,** 3 mmol), K_2CO_3 (2 mmol), [Pd@ASP-EDTA-CS (**1**) (4 mg) and solvent (3 ml). [b]Isolated yield.

Table 2 Investigation of the synthesis of desired derivatives of cinnamic acid (**5a–h)** through HCR catalyzed by catalyst **1** under the optimized conditions. [a]



Entry	Ar-X	Alkene	Product	Time (h)	Temp. (°C)	Yield [b] (%)	m.p. (°C)	m.p. (°C) (Lit.)
1	 **3a**	 **4a**	 **5a**	**14**	**80**	**85**	**131-132**	**133**[116]
2	 **3b**	 **4a**	 **5a**	**20**	**80**	**75**	**131-132**	**133**
3	 **3c**	 **4a**	 **5a**	**40**	**80**	**20**	**--**	**133**
4	 **3d**	 **4a**	 **5g**	**48**	**80**	**trace**	**--**	**212**
5	 **3e**	 **4a**	 **5h**	**48**	**80**	**trace**	**--**	**224-226**[117]

6	 3a	 4b	 5b	17	80	90	33-35	34-38[118]
7	 3b	 4b	 5b	19	80	80	33-35	34-38
8	 3c	 4b	 5b	36	80	20	33-35	34-38
9	 3d	 4b	 5g	48	80	trace	--	34-38
10	 3e	 4b	 5h	48	80	trace	--	34-38
11	 3a	 4c	 5c	14	80	85	liquid	(6.5-7.5)[119]
12	 3b	 4c	 5c	20	80	76	liquid	6.5-7.5
13	 3c	 4c	 5c	36	80	20	liquid	6.5-7.5
14	 3d	 4c	 5g	48	80	Trace	-	-
15	 3e	 4c	 5h	48	80	Trace	-	-

16	 **3a**	 **4d**	 **5d**	**16**	**80**	**85**	**liquid**[99]	**B.P.: 271**
17	 **3b**	 **4d**	 **5d**	**20**	**80**	**80**	**liquid**	**B.P.: 271**
18	 **3c**	 **4d**	 **5d**	**36**	**80**	**20**	**liquid**	**B.P.: 271**
19	 **3d**	 **4d**	 **5g**	**48**	**80**	**Trace**	-	-
20	 **3e**	 **4d**	 **5h**	**48**	**80**	**Trace**	-	-

[a] Reaction conditions: aryl halide (**3a-d**, 2 mmol), alkene (**4a-d**, 3 mmol), K_2CO_3 (2 mmol), Pd@ASP-EDTA-CS (**1**, 4mg) and solvent (3 ml). [b] Isolated yield.

Table S3 The comparison of the obtained results for HCR using catalyst **1** and other catalysts.

Entry	Catalyst	Reaction Conditions	Catalyst Amount	Time (h)	Yield (%)	Reference
1	Trifunctional N,N,O-terdentate amido/pyridyl carboxylate Pd(II) complexes	DMF / 145 °C / Base	0.01 mol %	20	3-92	116
2	Trifunctional N,N,O-terdentate amido/pyridyl carboxylate Pd(II) complexes	DMF / 145 °C / Na_2CO_3	0.01 mol %	20	92	116
3	$Pd(OAc)_2$	NMP / 135 °C / NaOAc	0.05 mol %		12	
4	CMH-Pd (0)	DMF / 120 °C / Et_3N	50 mg	6	90	124
5	NHC-Pd/ IL@SiO_2	NMP / 140 °C / NaOAc	0.01 mol %	24	94	117
6	Pd(quinoline-8-carboxylate)$_2$	DMF / 130 °C / K_2CO_3	0.01 mol %	30	39-94	118
7	OCMCS-Pd	DMF / 140 °C / Et_3N	0.02 mmol	12	89-98	125
8	**Pd@ASP-EDTA-CS**	DMF / 90 °C / K_2CO_3	**4 mg**	**16**	**90**	**This work**
9	**Pd@ASP-EDTA-CS**	ACN / 80 °C / K_2CO_3	**4 mg**	**18**	**90**	**This work**

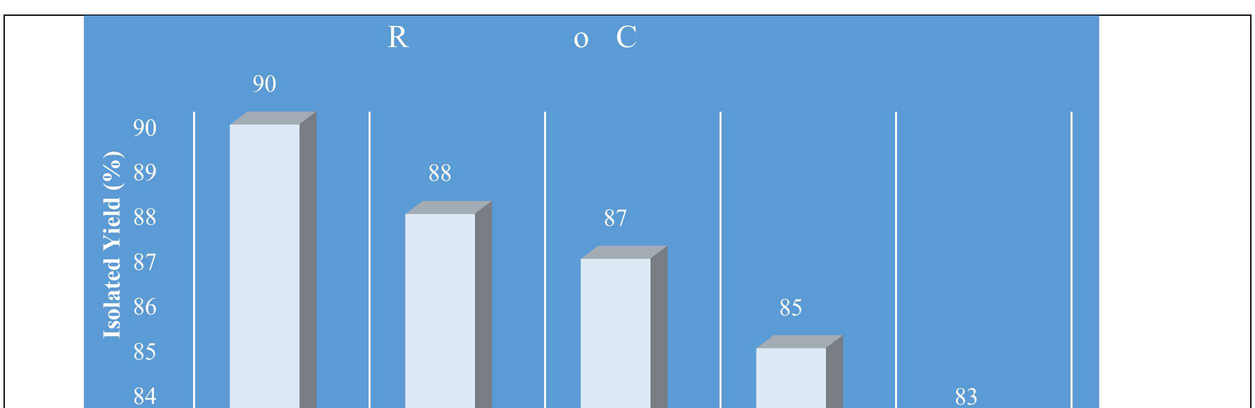
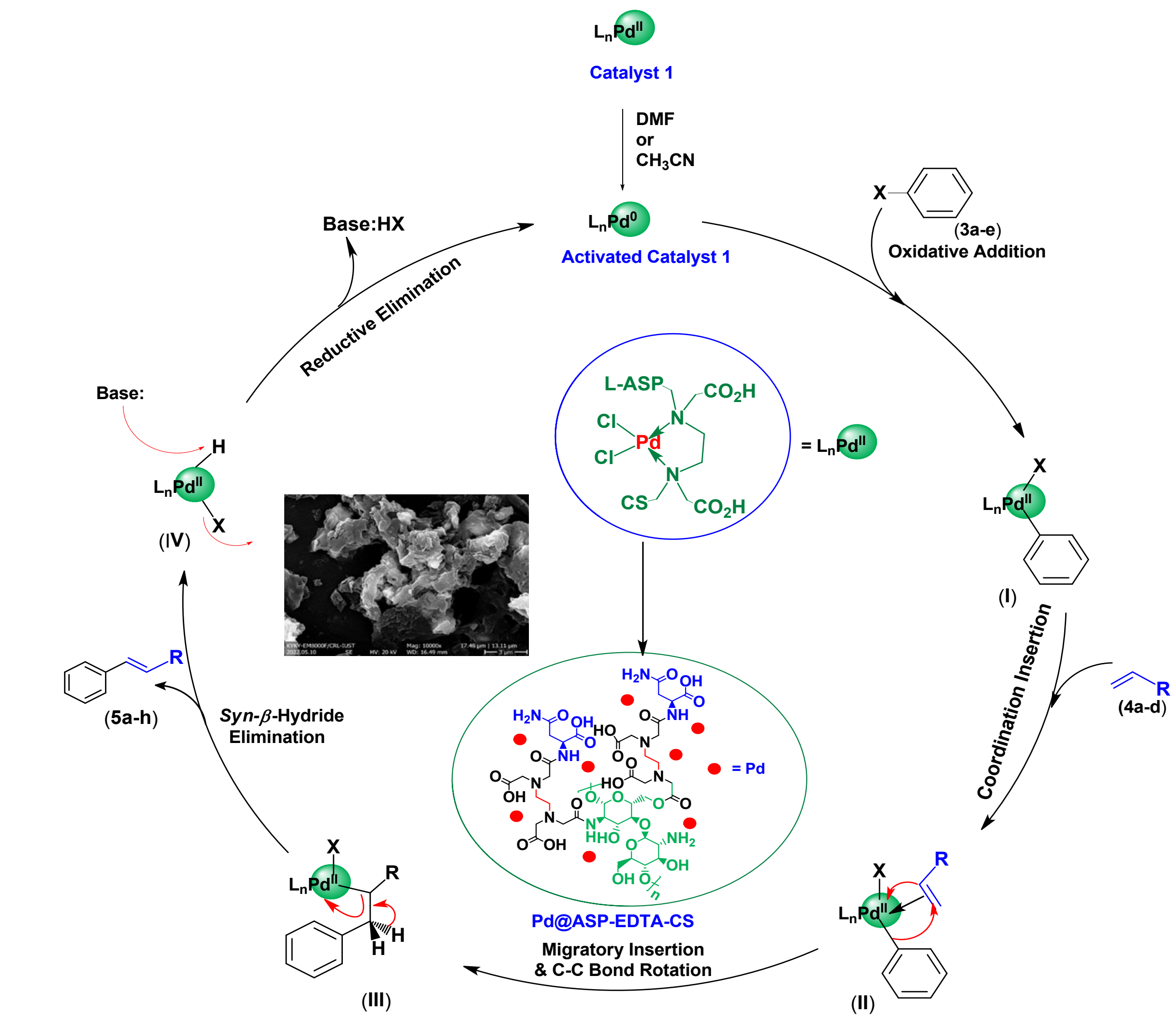


Fig. S10 Reusability of the Catalyst **1** in the model reaction to afford **5b.**



Scheme 2 The proposed mechanism for the synthesis cinnamic acid derivatives using aryl halides and active alkenes in the presence of catalyst **1**.

Spectral data of the selected products

Cinnamic acid (**5c**):

White crystals, m.p. = 132-133 °C; FTIR (KBr, cm^{-1}) v = 3410, 2945, 1718, 1640, 1580, 1452; ^1H NMR (500MHz, DMSO–d6) δ (ppm) = 12.40 (S, 1H), 7.59 (d, J = 16.0 Hz, 1H), 7.71-7.63 (m, 2H), 7.44-7.32 (m, 3H), 6.52 (d, J = 16.0 Hz, 1H) ppm.

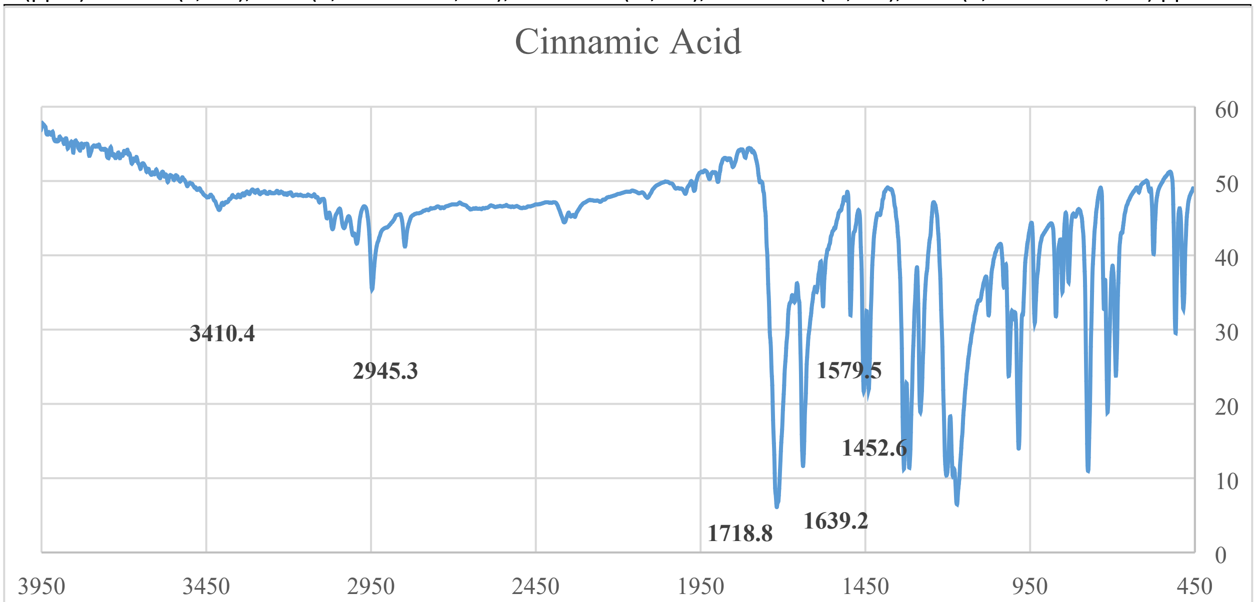


Fig. S11 FTIR spectrum of cinnamic acid.

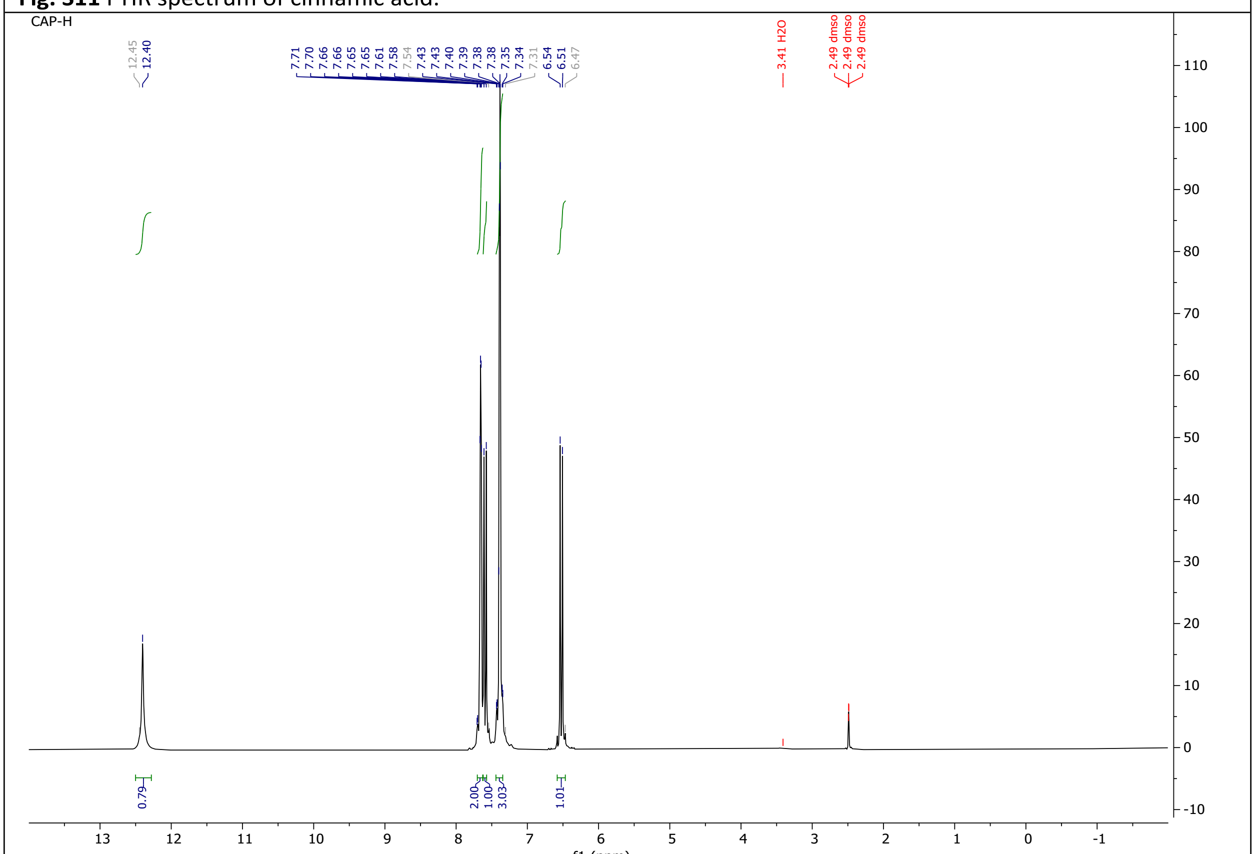


Fig. S12 ^1H NMR of cinnamic acid.

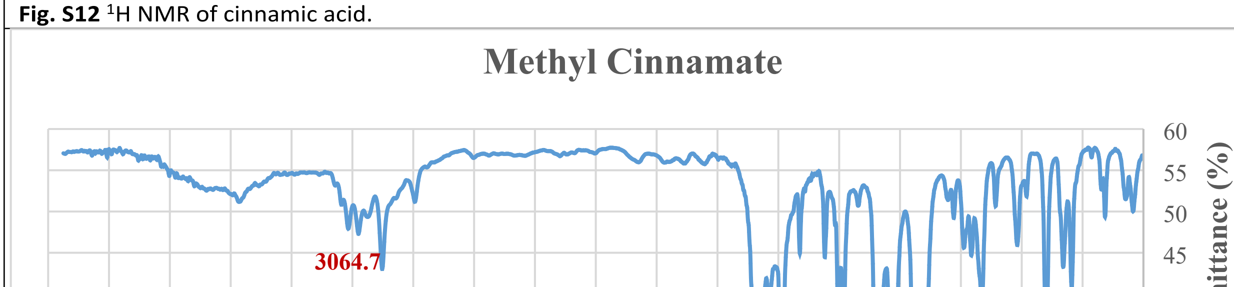


Fig. S13 FTIR spectrum of Methyl Cinnamate.

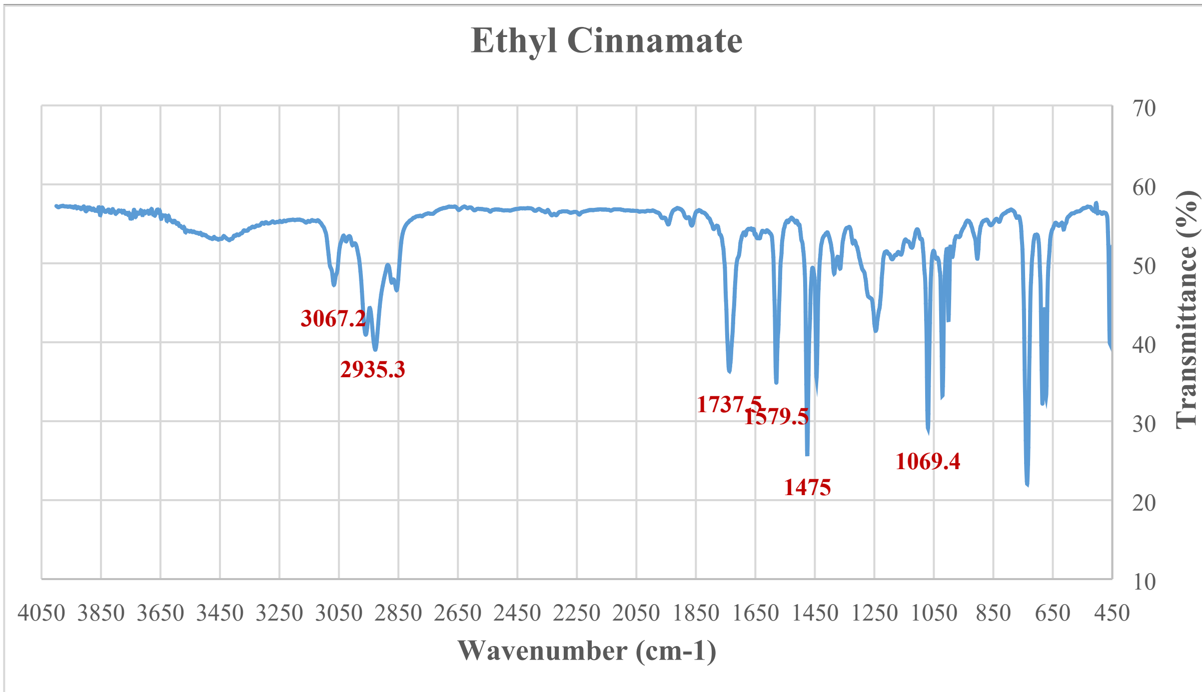


Fig. S14 FTIR spectrum of Ethyl Cinnamate.

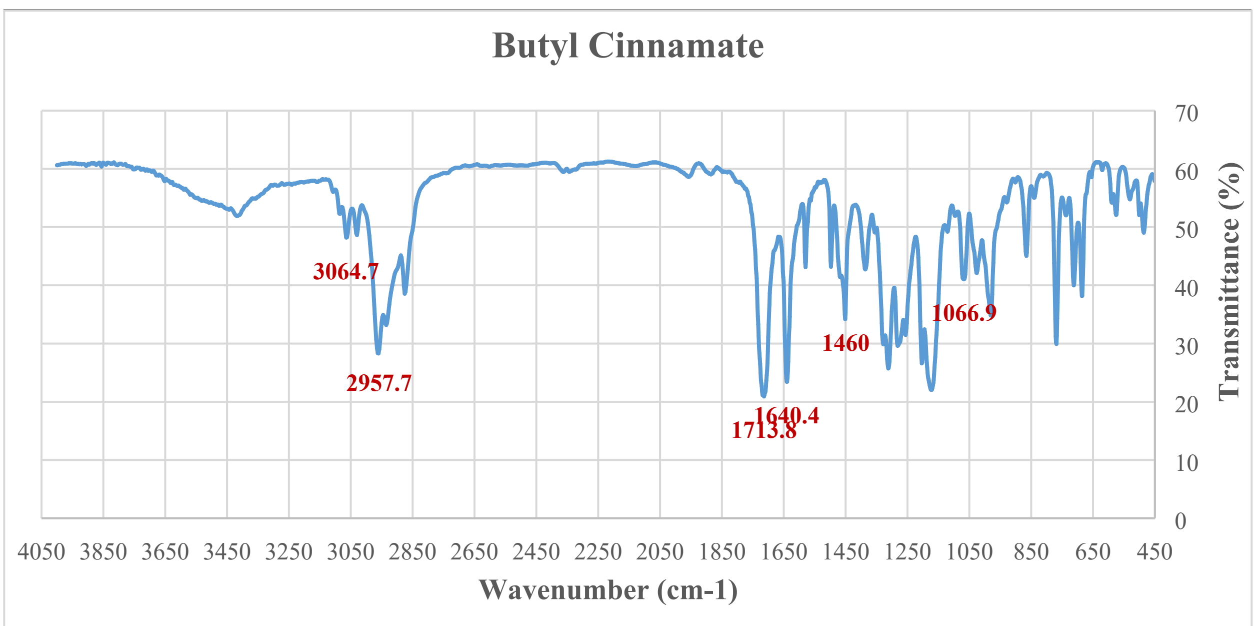


Fig. S15 FTIR spectrum of Butyl Cinnamate.

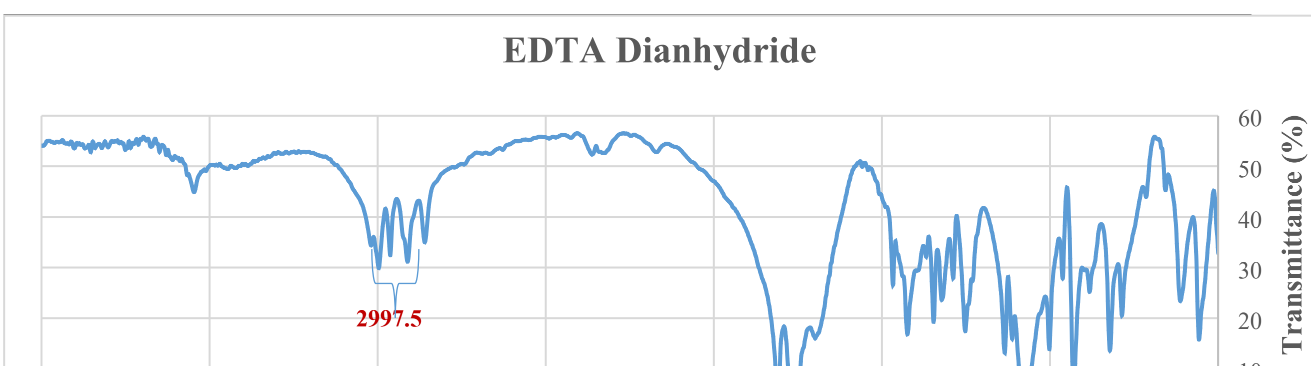


Fig. S16 FTIR spectrum of EDTA Dianhydride.

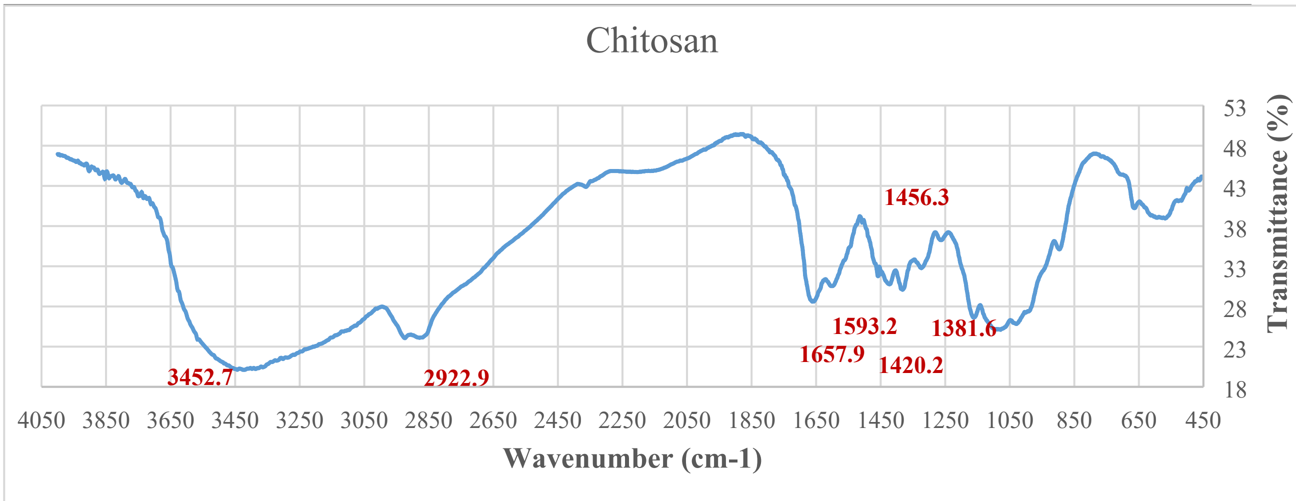


Fig. S17 FTIR spectrum of Chitosan.

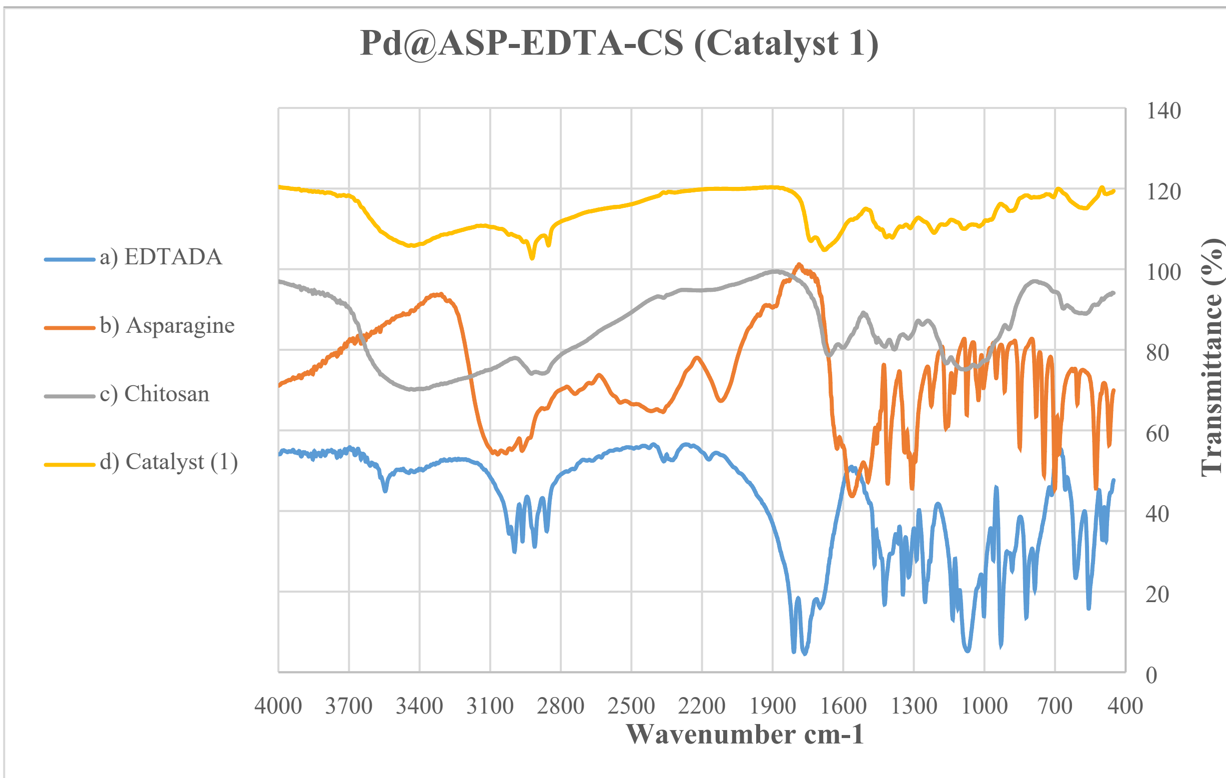


Fig. S18 FTIR spectra of the Pd@ASP-EDTA-CS catalyst (**1**).