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Electronic Supplementary Information

Supramolecular Pd@Methioine-EDTA-Chitosan nanocomposite: an effective and recyclable bio-based and eco-friendly catalyst for the green Heck cross-coupling reaction under mild conditions

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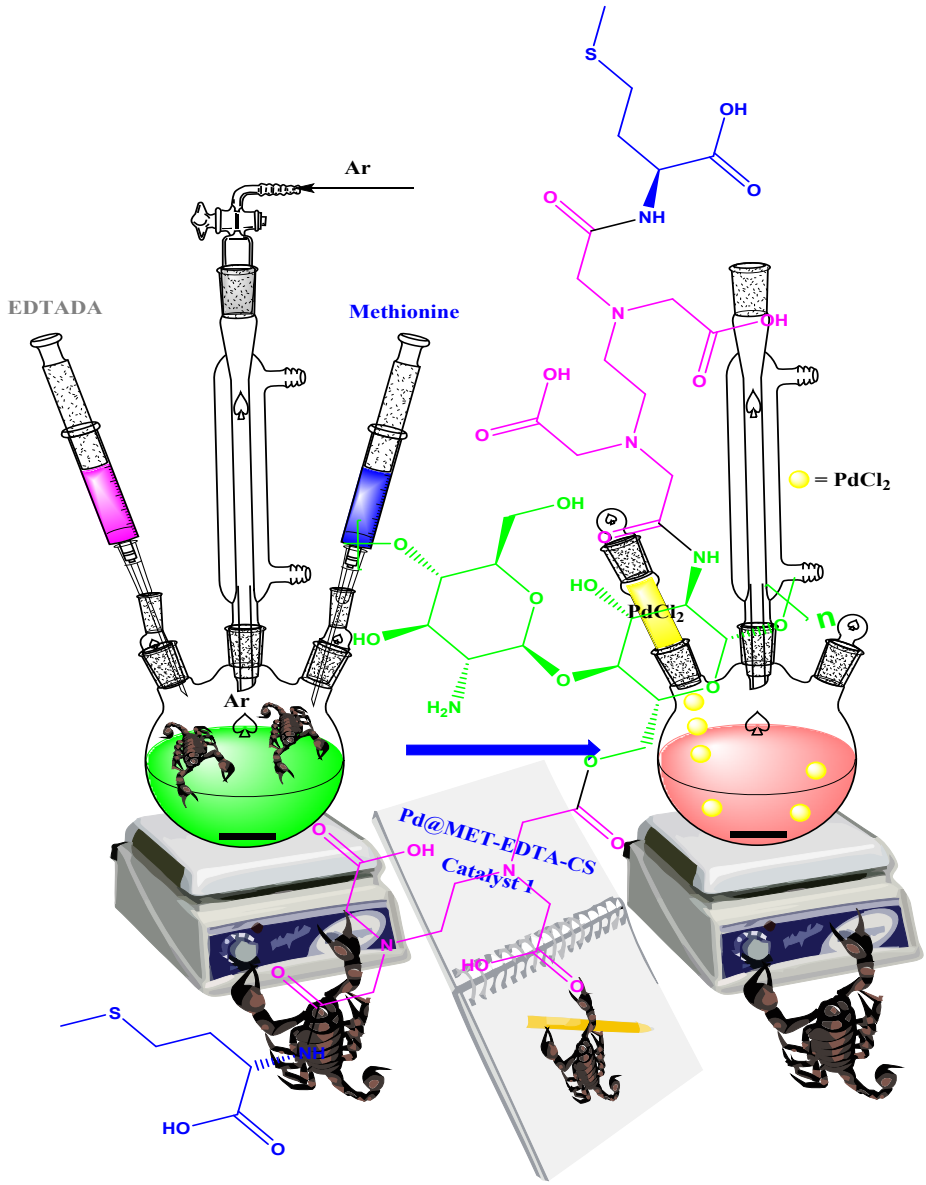
Graphical Abstract

Supramolecular Pd@Methioine-EDTA-Chitosan: An effective and recyclable bio-based and eco-friendly catalyst for the green Heck cross-coupling reaction under mild conditions

Mohammad Dohendou, Mohammad G. Dekamin*, Danial Namaki

A new supramolecular Pd(II) supported on the modified chitosan by DL-methionine using EDTA linker was prepared and characterized. The obtained low loaded Pd(II) catalyst effectively promotes the HCR in good to excellent yields and proper reusability.



Model Reaction:

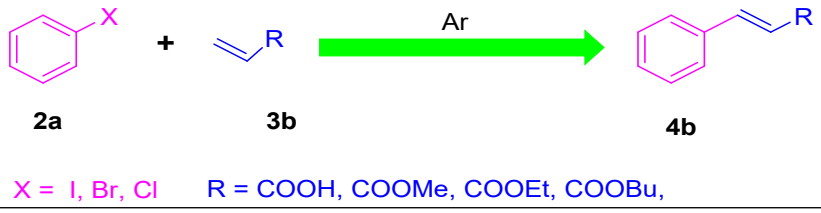
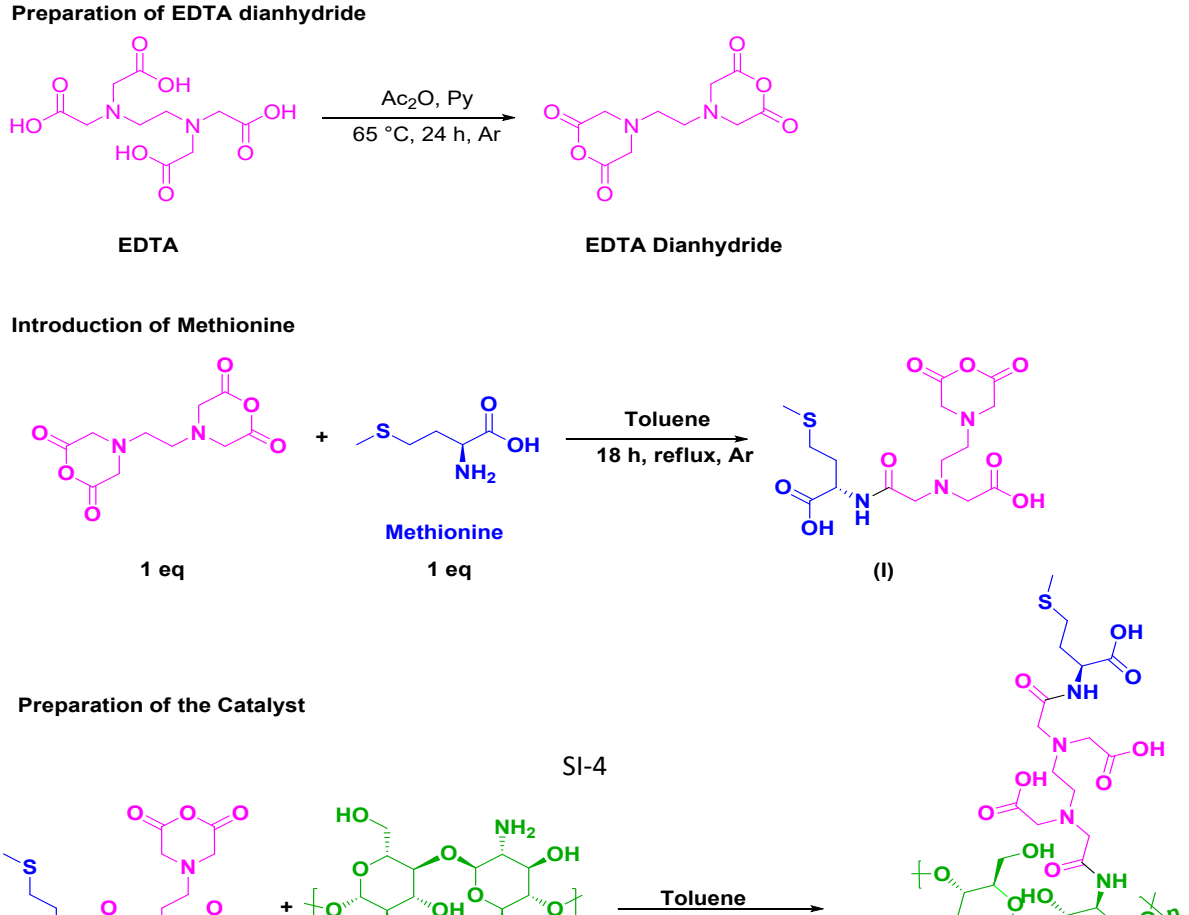


Fig S1. The model reaction for HCR catalyzed by catalyst **1**.

Catalyst Preparation:

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



Scheme S1. Schematic representation for the preparation of Pd@MET−EDTA−CS nanocatalyst (**1**).

FTIR Spectrums:

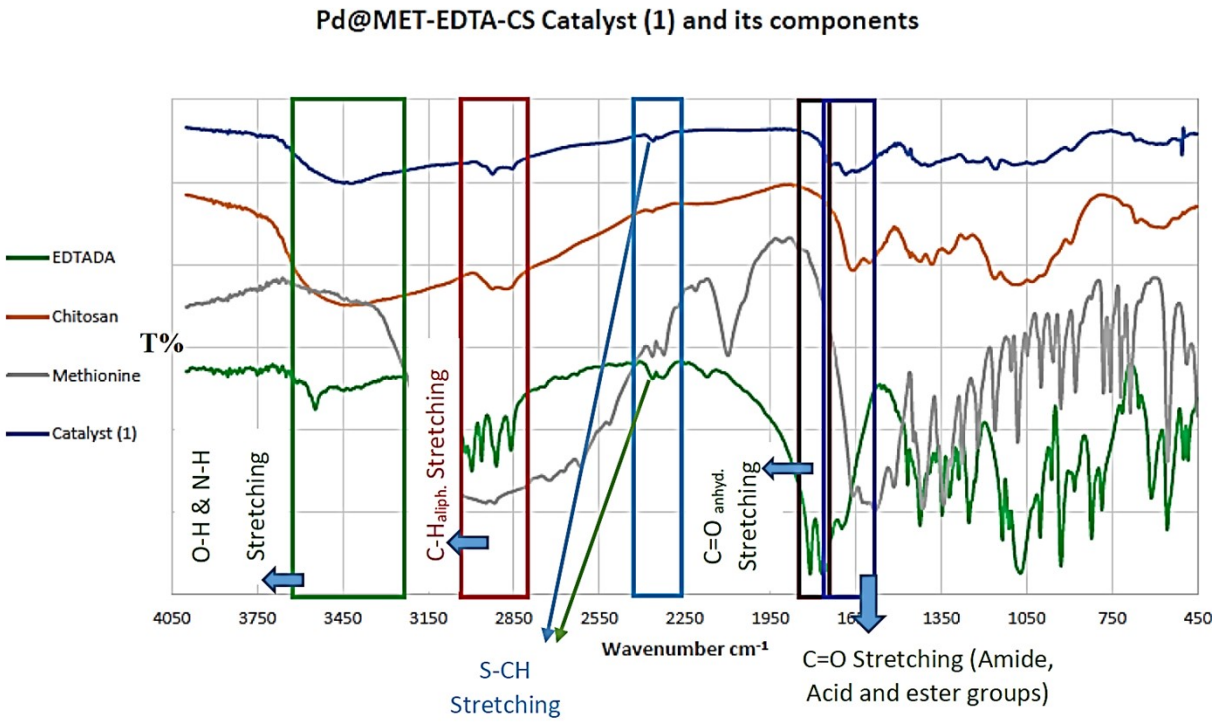


Fig. S2. FTIR spectra of the Pd@MET-EDTA-CS catalyst (**1**) and its components.

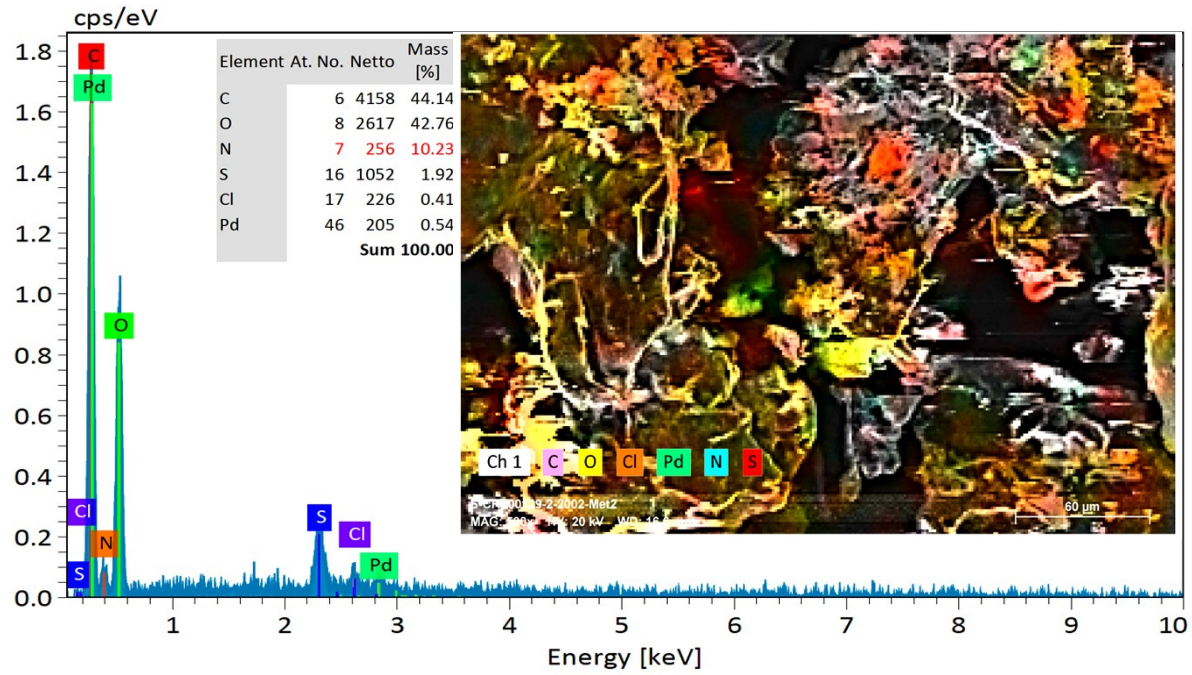


Fig. S3a. EDS spectrum of the Pd@MET-EDTA-CS nanocatalyst (**1**).

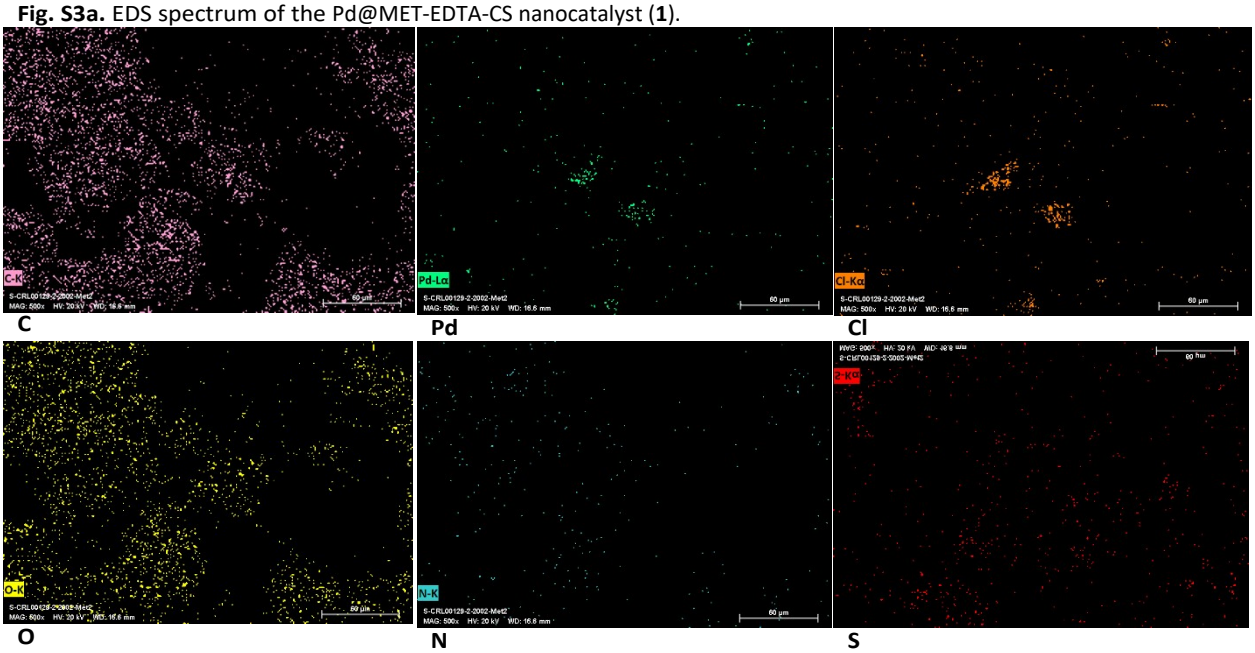
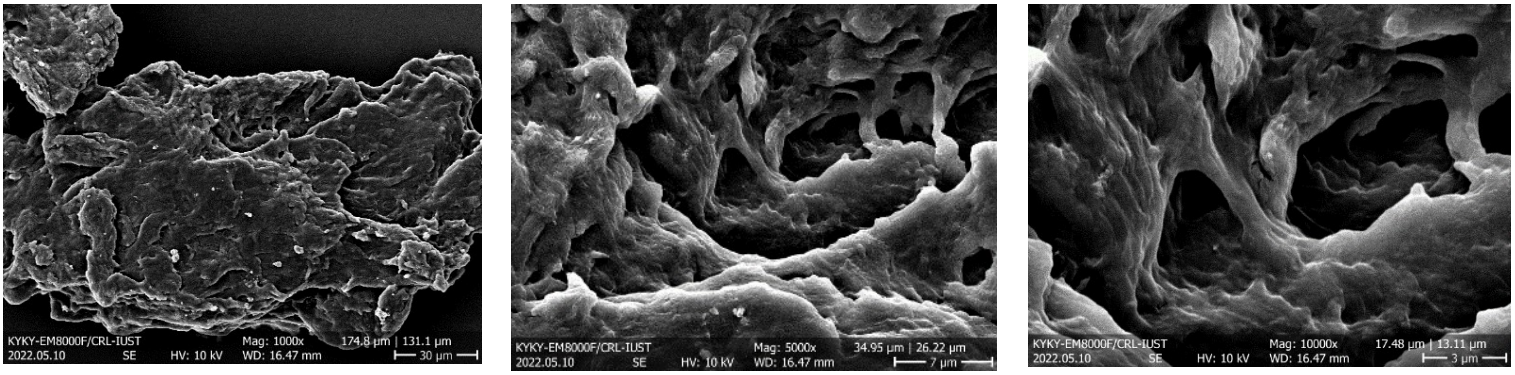


Fig. S3b. The mapping images of Pd, C, N, O, Cl and S in the Pd@MET-EDTA-CS nanocatalyst (**1**).



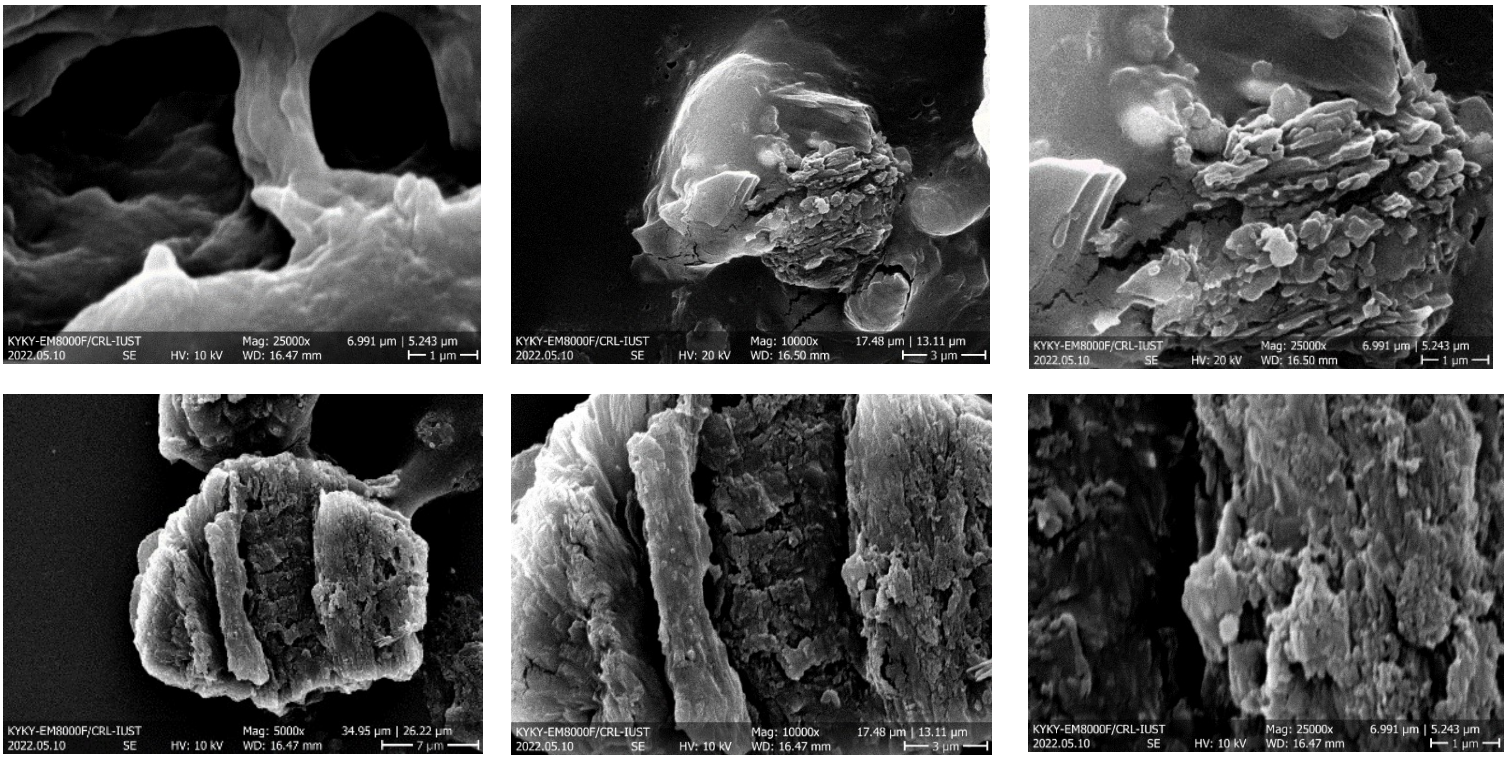


Fig. S4. FESEM images of the Pd@MET-EDTA-CS nanocatalyst (**1**).

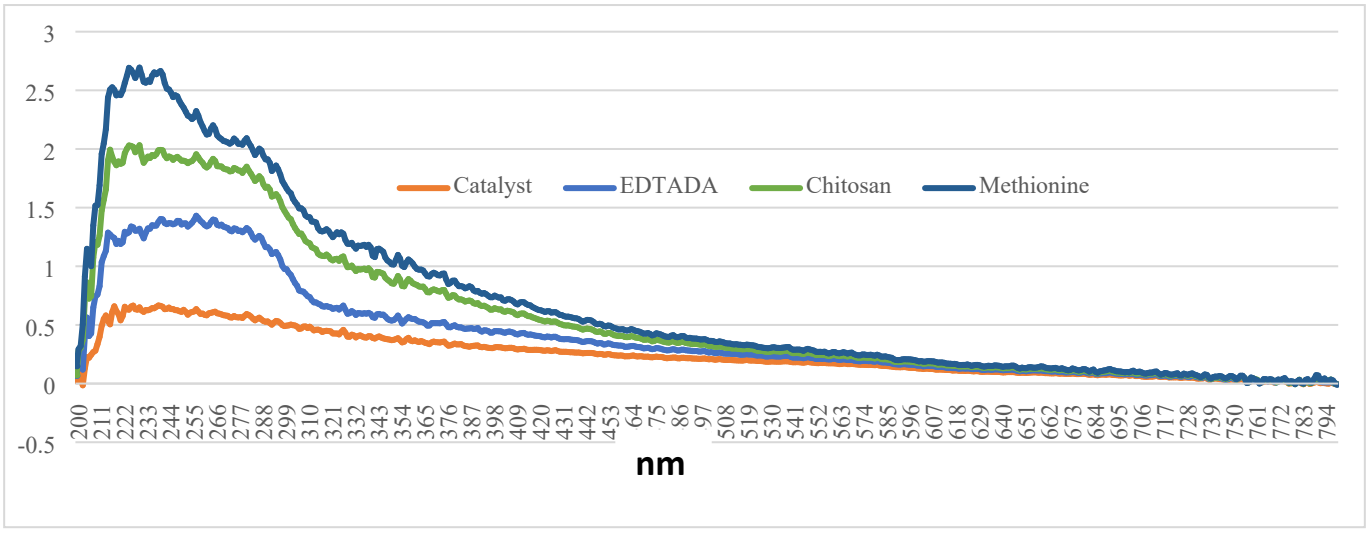


Fig. 4a DRS of the Pd@MET-EDTA-CS catalyst (**1**) and its components.

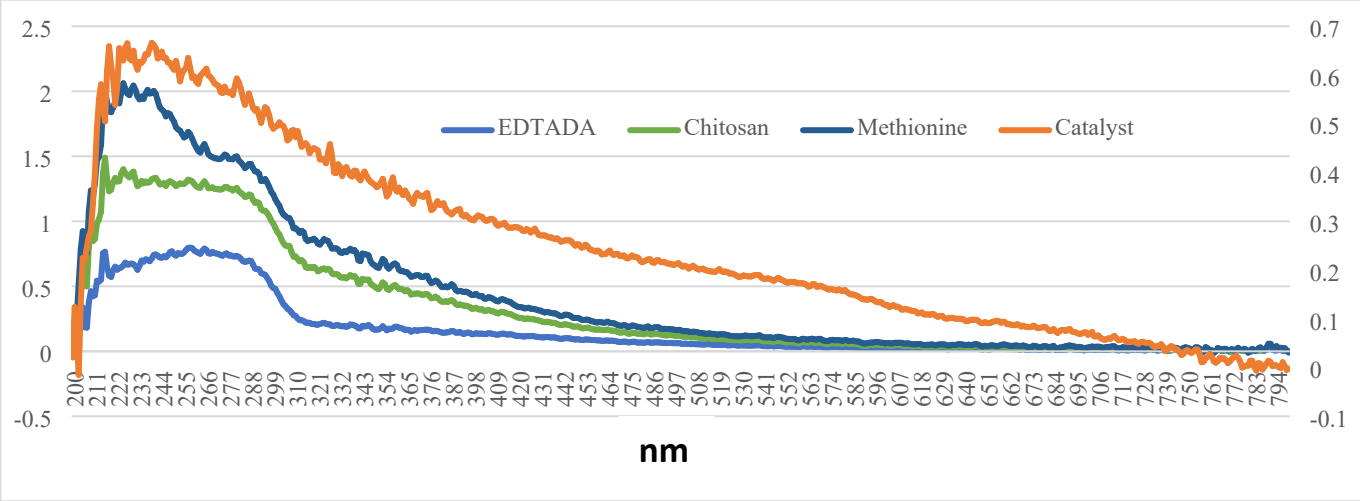


Fig. 4b Intensified DRS of the Pd@MET-EDTA-CS catalyst (**1**).

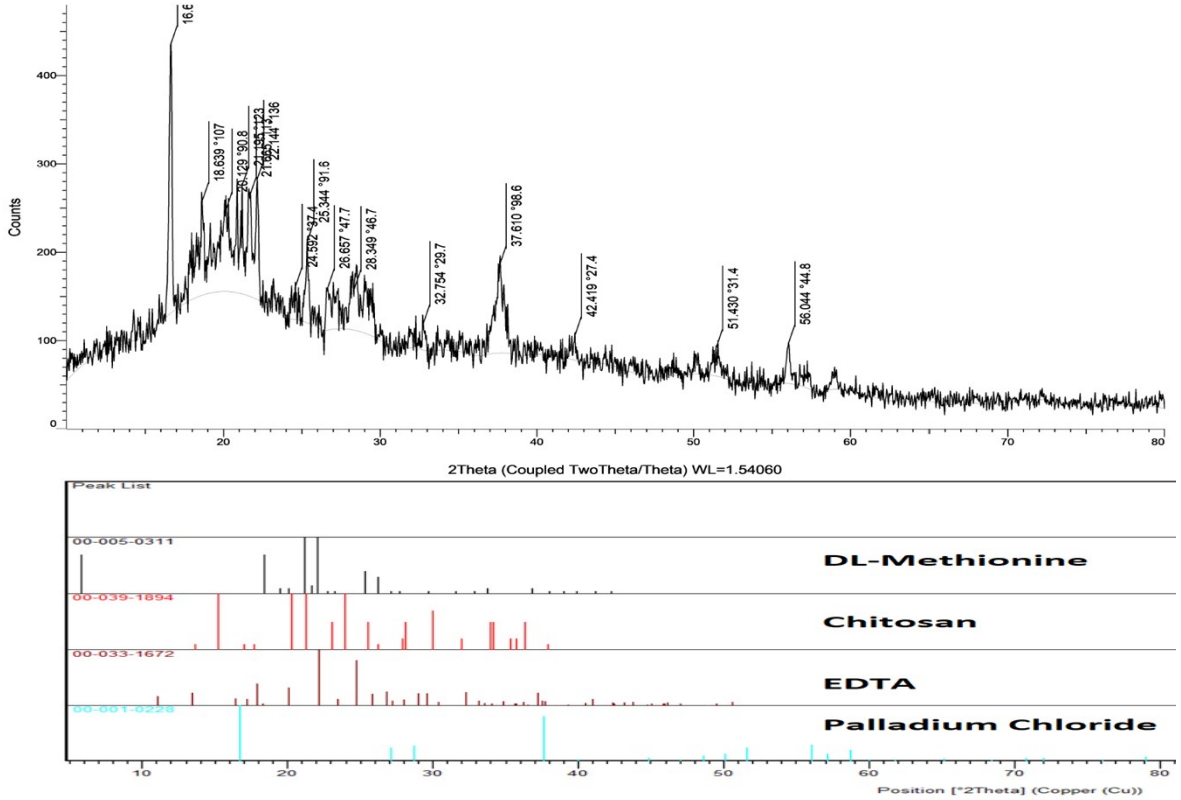
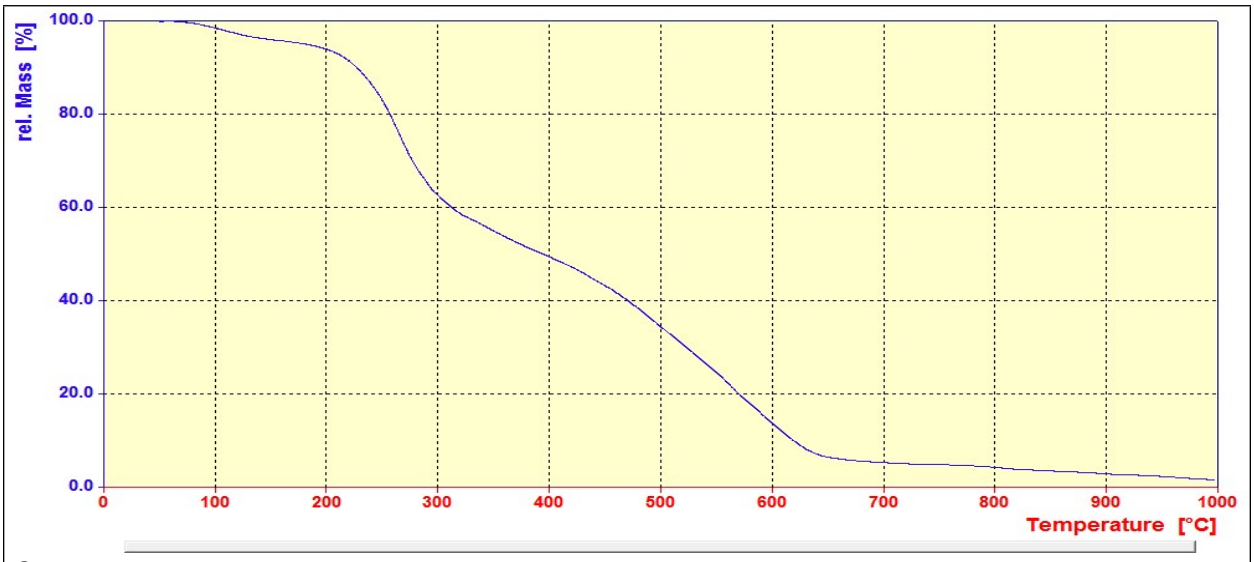
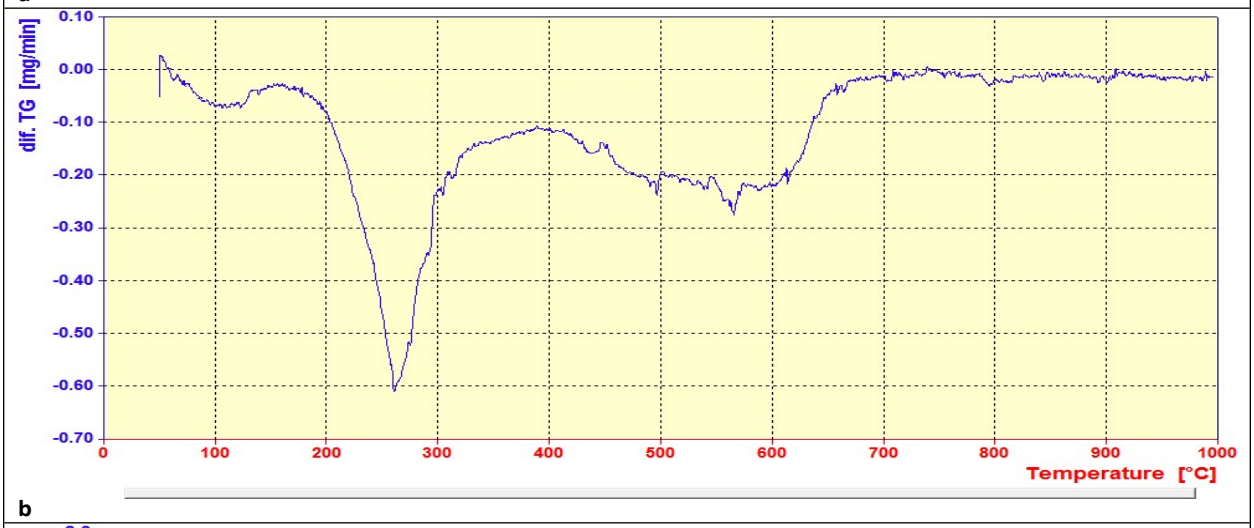


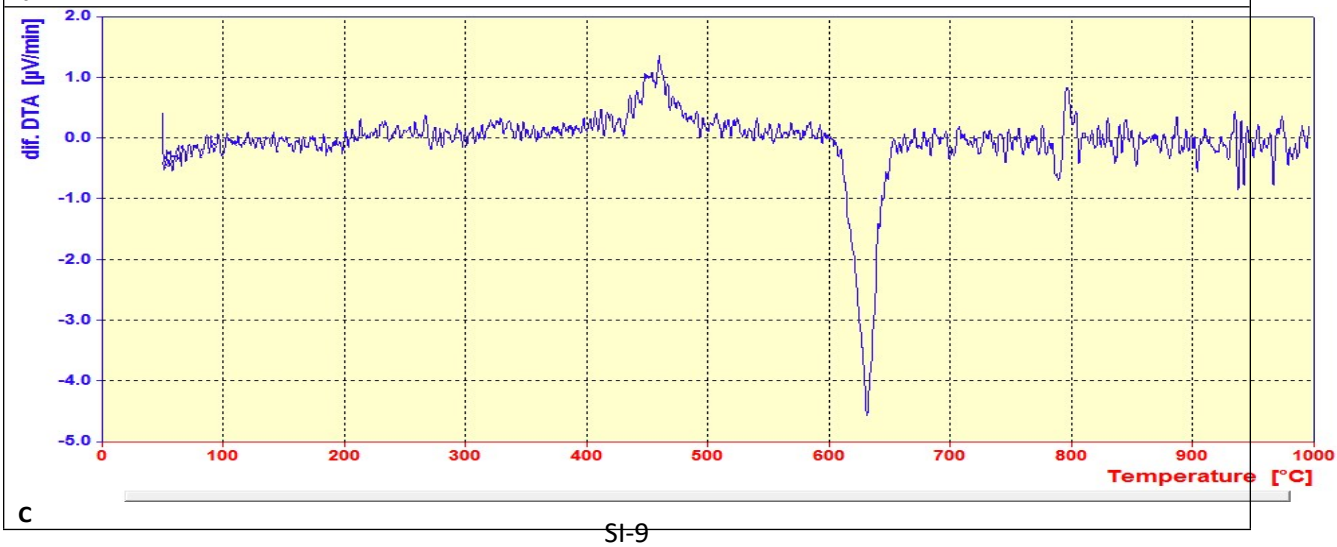
Fig. S6. XRD pattern of the Pd@MET-EDTA-CS catalyst (**1**).


rel. Mass [%]
100.0
80.0
60.0
40.0
20.0
0.0
0
100
200
300
400
500
600
700
800
900
1000
Temperature [°C]

a


dif. TG [mg/min]
0.10
0.00
-0.10
-0.20
-0.30
-0.40
-0.50
-0.60
-0.70
0
100
200
300
400
500
600
700
800
900
1000
Temperature [°C]

b


dif. DTA [µV/min]
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0
100
200
300
400
500
600
700
800
900
1000
Temperature [°C]

C

Fig. S7. (a) TGA, (b) diff. TGA and (c) diff. DTA Curves of the Pd@MET-EDTA-CS catalyst (**1**).

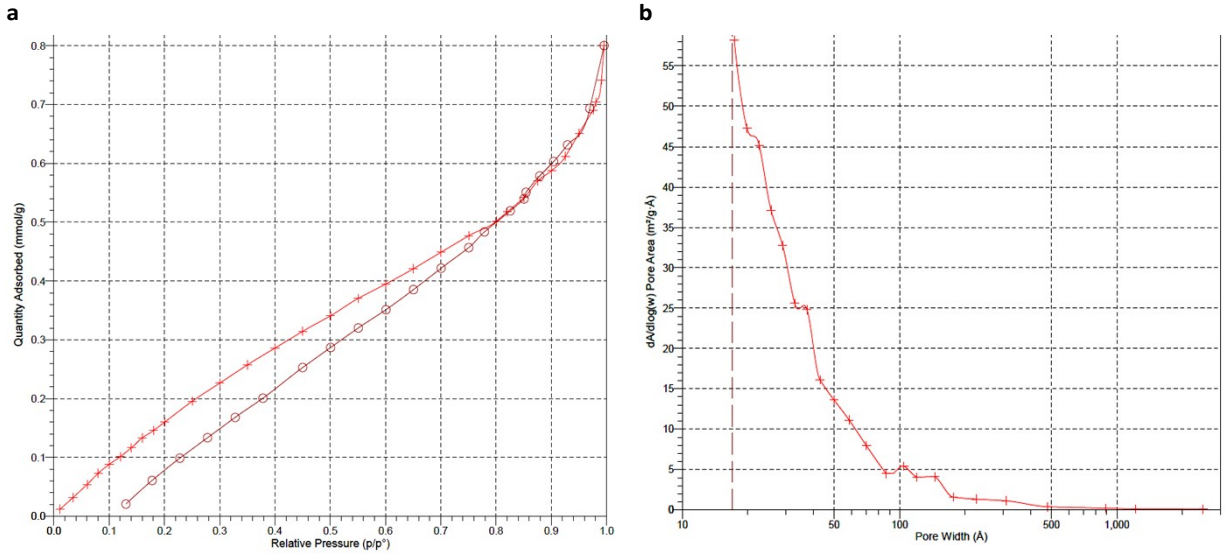


Fig. S8. (a)The N2 adsorption–desorption isotherm of Pd@MET-EDTA-CS catalyst (**1**), and (b) its pore width.

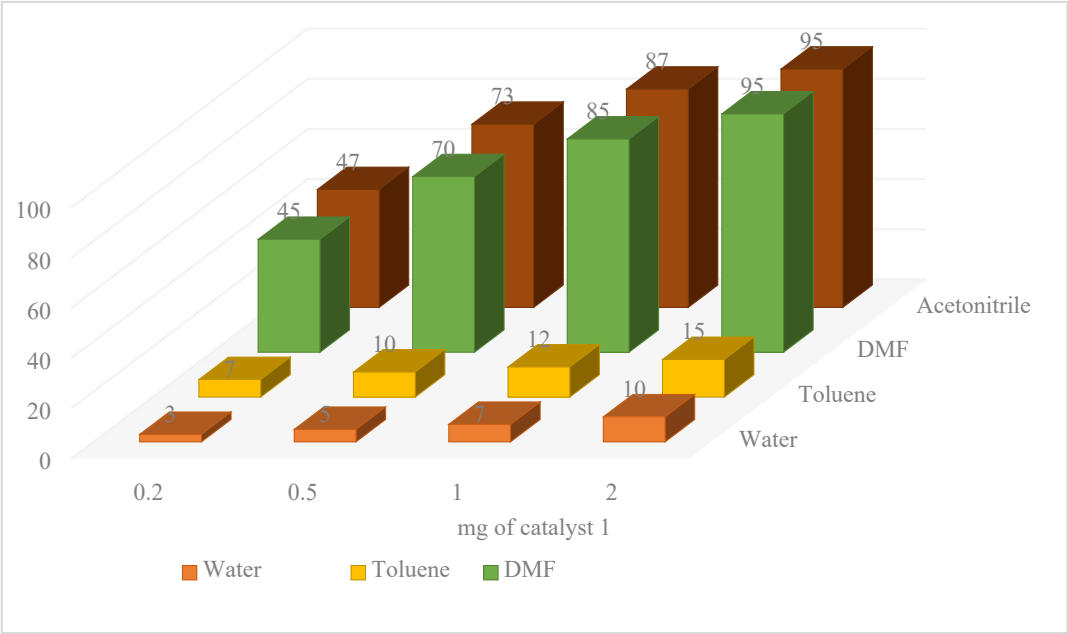


Fig. S9. Investigation of the optimized loading of the Pd@MET−EDTA−CS catalyst (**1**) in different solvents for the HCR to afford **5b**.

Table S1. Optimization of the conditions for the HCR in the model reaction of Iodobenzene (**3a**) and methyl acrylate (**4b**) to afford methy cinnamate (**5b**) under different conditions in the presence of Pd@MET–EDTA–CS catalyst (**1**) (0.0027 mol %).[a]

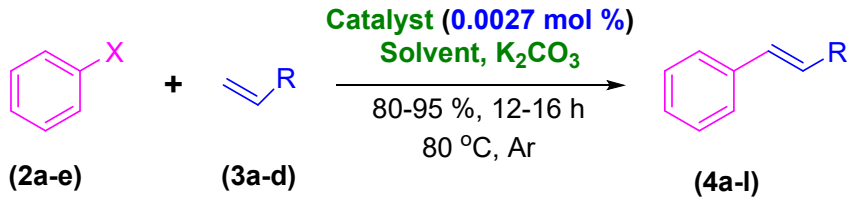
2a **3b** **4b**

X = I, Br, Cl R = COOH, COOMe, COOEt, COOBu

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@MET-ETDA-CS	-	DMF	Reflux	48	N.R
4	Pd@MET-ETDA-CS	-	ACN	Reflux	48	N.R
5	Pd@MET-ETDA-CS	-	Solvent-free	80	24	Trace
6	Pd@MET-ETDA-CS	K_2CO_3	**DMF**	**90**	**12-16**	**80-95**
7	Pd@MET-ETDA-CS	K_2CO_3	**ACN**	**80**	**13-19**	**80-95**
8	Pd@MET-ETDA-CS	K_2CO_3	Toluene	105	36	Trace
9	Pd@MET-ETDA-CS	K_2CO_3	H_2O	105	36	Trace
10	MET-ETDA	K_2CO_3	DMF	130	36	N.R
11	MET-ETDA-CS	K_2CO_3	DMF	130	36	N.R
12	MET-ETDA	K_2CO_3	ACN	80	36	N.R
13	MET-ETDA-CS	K_2CO_3	ACN	80	36	N.R
14	DL-methionine	K_2CO_3	DMF	130	36	N.R
15	EDTA	K_2CO_3	DMF	130	36	N.R

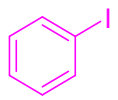
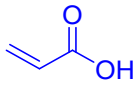
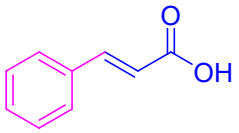
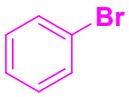
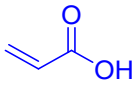
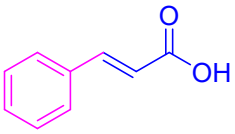
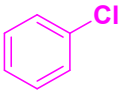
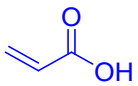
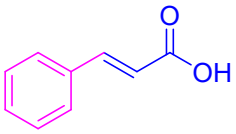
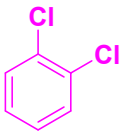
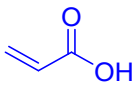
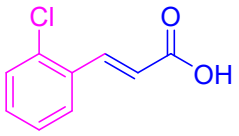
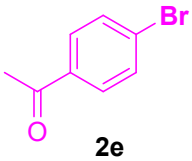
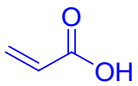
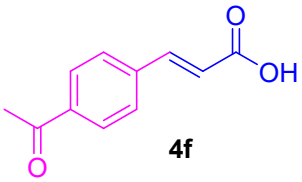
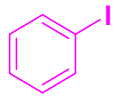
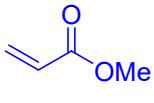
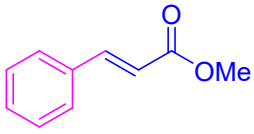
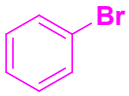
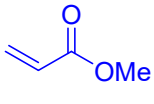
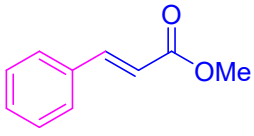
[a]Reaction conditions: aryl halide (**2a**, 2.0 mmol), alkene (**3b,** 3.0 mmol), K_2CO_3 (2.0 mmol), Pd@MET-EDTA-CS (**1**) (2.0 mg, 0.0027 mol %) and solvent (3.0 mL), under the Ar atmosphere. [b]Isolated yields.

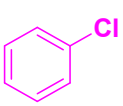
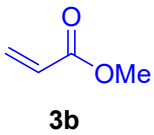
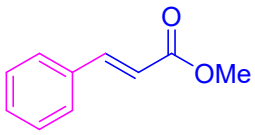
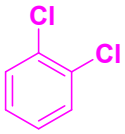
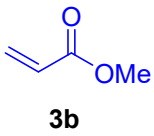
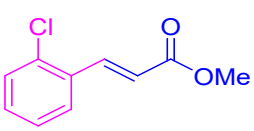
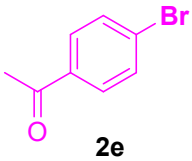
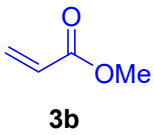
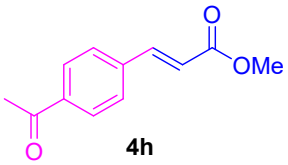
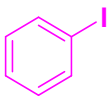
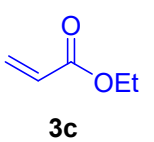
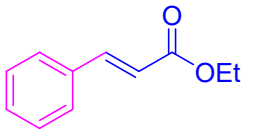
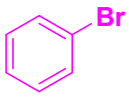
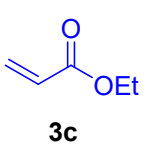
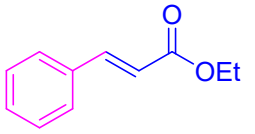
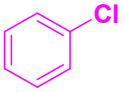
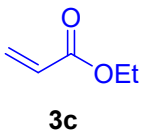
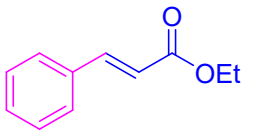
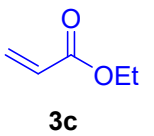
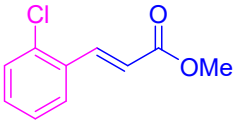
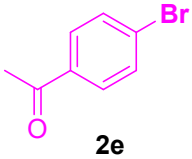
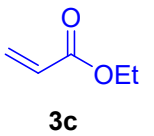
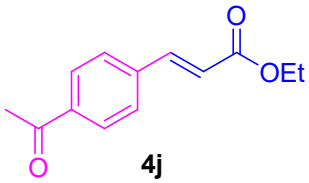
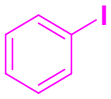
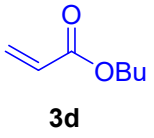
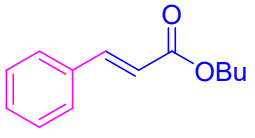
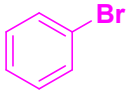
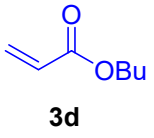
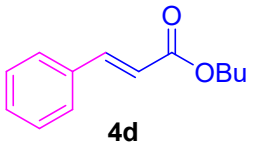
Table S2 Synthesis of different derivatives of cinnamic acid (**4a–l)** through the HCR catalyzed by Pd@MET–EDTA–CS catalyst (**1**) under the optimized conditions.[a]

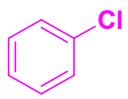
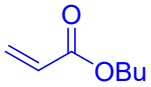
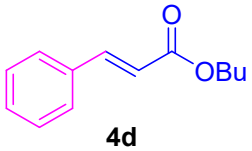
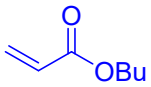
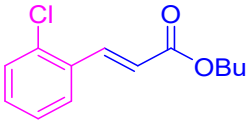
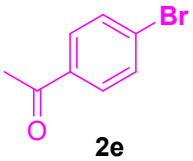
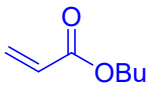
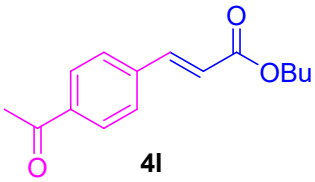


(2a-e) **(3a-d)** **(4a-l)**

X = I, Br, Cl R = COOH, COOMe, COOEt, COOBu

Entry	Ar-X	Alkene	Product	Time (h)	Temp. (°C)	Yield [b] (%)	TON	TOF (h^{-1})	m.p. (°C)	m.p. (°C) (Lit.)
1	 **2a**	 **3a**	 **4a**	12	80	90	33330	2778	131-132	133[135]
2	 **2b**	 **3a**	 **4a**	14	80	80	29630	2116	131-132	133
3	 **2c**	 **3a**	 **4a**	40	80	20	7407	185	131-132	133
4	 **2d**	 **3a**	 **4e**	48	80	trace	NA	NA	------	212
5	 **2e**	 **3a**	 **4f**	48	80	trace	NA	NA	------	224-226[136]
6	 **2a**	 **3b**	 **4b**	13	80	95	35185	2706	33-35	34-38[137]
7	 **2b**	 **3b**	 **4b**	15	80	85	31481	2099	33-35	34-38

8	 2c	 3b	 4b	36	80	20	7407	206	--	34-38
9	 2d	 3b	 4g	48	80	trace	NA	NA	------	34-38
10	 2e	 3b	 4h	48	80	trace	NA	NA	------	34-38
11	 2a	 3c	 4c	13	80	90	33330	2564	liquid	(6.5-7.5)[138]
12	 2b	 3c	 4c	16	80	80	29630	1852	liquid	6.5-7.5
13	 2c	 3c	 4c	36	80	20	7407	206	liquid	6.5-7.5
14	 2d	 3c	 4i	48	80	Trace	NA	NA	------	------
15	 2e	 3c	 4j	48	80	Trace	NA	NA	------	------
16	 2a	 3d	 4d	15	80	90	33330	2222	liquid[139]	b.p.: 271
17	 2b	 3d	 4d	16	80	85	31481	1968	liquid	b.p.: 271

18	 2c	 3d	 4d	**36**	**80**	**20**	**7407**	**206**	**liquid**	**b.p.: 271**
19	 2d	 3d	 4k	**48**	**80**	**Trace**	**NA**	**NA**	**------**	**------**
20	 2e	 3d	 4l	**48**	**80**	**Trace**	**NA**	**NA**	**------**	**------**

[a] Reaction conditions: aryl halide (**2a-e**, 2.0 mmol), alkene (**3a-d**, 3.0 mmol), K_2CO_3 (2.0 mmol), Pd@MET-EDTA-CS (**1**, 2.0 mg, 0.0027 mol %) and solvent (3.0 mL), under the Ar. [b] Isolated yields.

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

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 / Na_2CO_3	0.01 mol %	20	92	[131]
2	$Pd(OAc)_2$	NMP / 135 °C / NaOAc / UV – VIS	0.05 mol %	44	80	[132]
3	CMH-Pd (0)	DMF / 120 °C / Et_3N	50 mg	6	90	[133]
4	NHC-Pd/ IL@SiO_2	NMP / 140 °C / NaOAc	0.01 mol %	24	94	[134]
5	Pd(quinoline-8-carboxylate)$_2$	DMF / 130 °C / K_2CO_3	0.01 mol %	30	39-94	[135]
6	OCMCS-Pd	DMF / 140 °C / Et_3N	0.02 mmol	12	89-98	[136]
7	**Pd@MET–EDTA–CS**	**DMF / 90 °C / K_2CO_3**	0.0027 mol %	**16**	**95**	**This work**
8	**Pd@MET–EDTA–CS**	**CH_3CN / 80 °C / K_2CO_3**	0.0027 mol %	**18**	**95**	**This work**

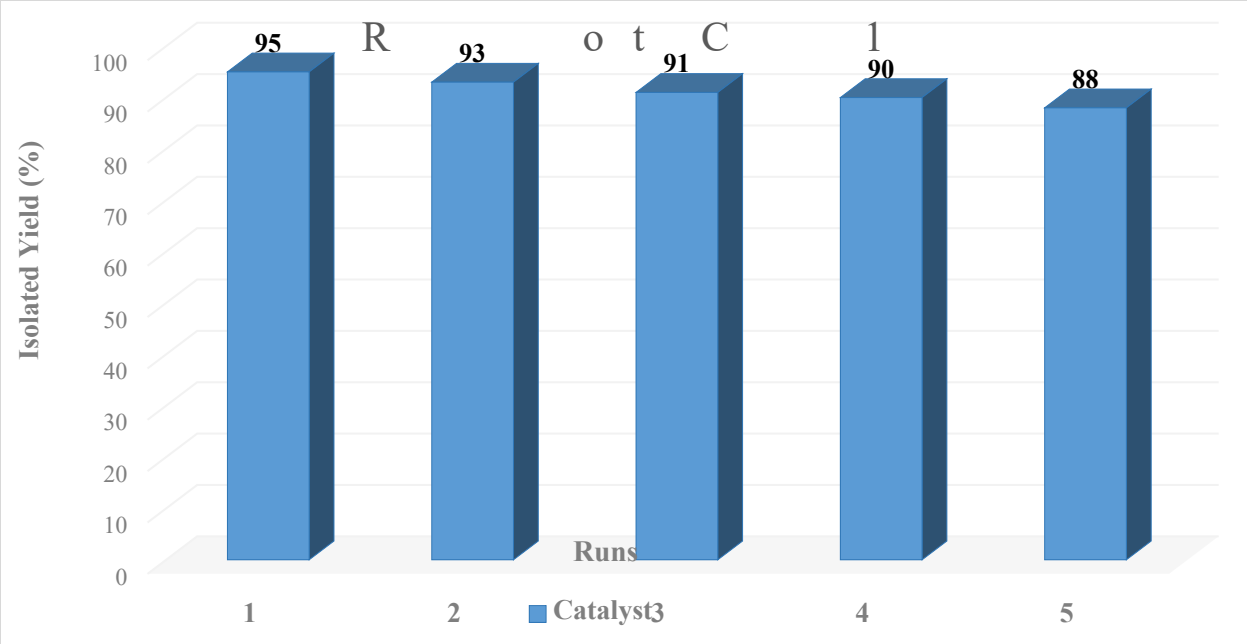
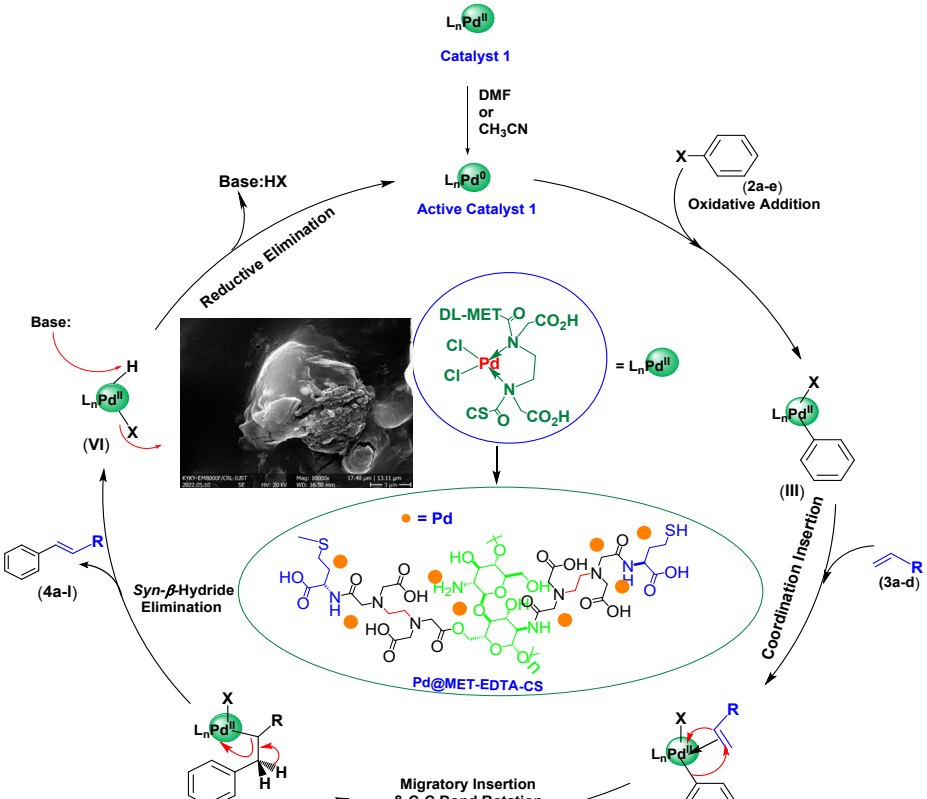


Fig. S10. Reusability of the Pd@MET−EDTA−CS Catalyst (**1**) in the model reaction to afford methyl cinnamate (**4b**).

Table S4. The result of AAS for the percentage of Pd species in catalyst **1.**

Supplier	Materials and Energy Research Center (MERC)
Device Model	GBC 932 plus (Atomic Absorption Spectrometer) Made by GBC Co., Australia
Pd Content (wt %)	0.286
Sample Code	02022000301AAA1
Date of Analysis	May 10, 2023



Scheme S2. The proposed mechanism for the synthesis cinnamic acid derivatives **4** using aryl halides and active alkenes in the presence of catalyst **1**.

Spectral data of the selected products

Methyl Cinnamate (**4b**):White crystals, M.P. = 34 - 38 °C; FT-IR (KBr, cm^{-1}) *v* = 3324, 3087, 2955, 1689, 1622, 1567,1453, 1218, 1082; ^{1}H NMR (500 MHz, DMSO–d_6) δ (ppm) = 3.7 (s, 3H, OCH_3), 6.6 (1H, d, *J* = 16.0 Hz, MeOCCH=), 7.4 (3H, m, Ar-H), 7.7 (2H, m, Ar-H), 7.64 (1H, d, *J* = 16.0 Hz, ArCH=) (**Fig. S11-12**).

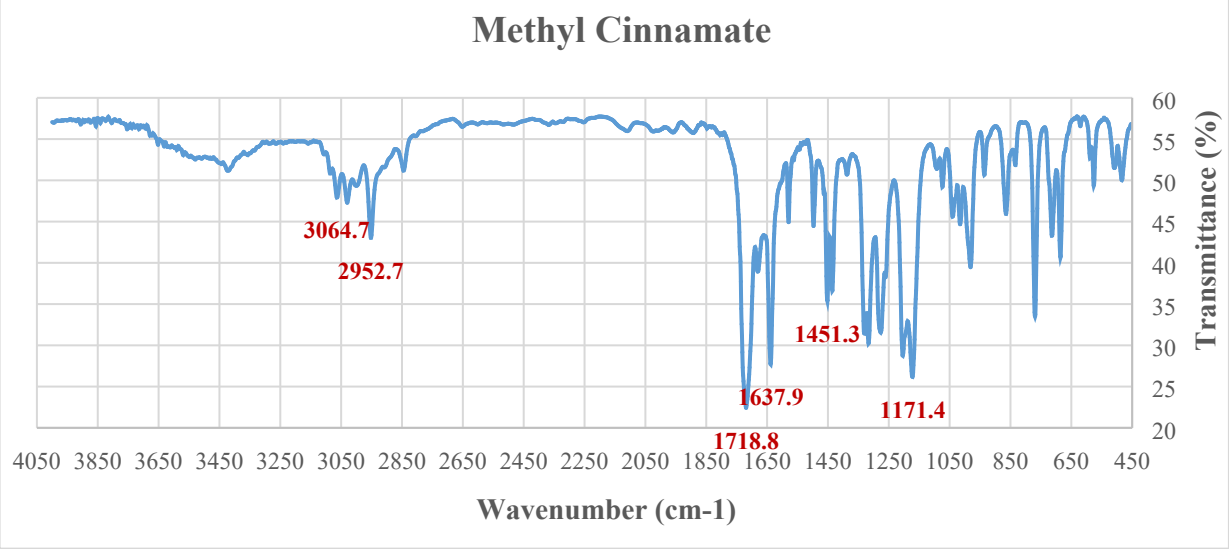


Fig. S11. FTIR of methyl cinnamate.

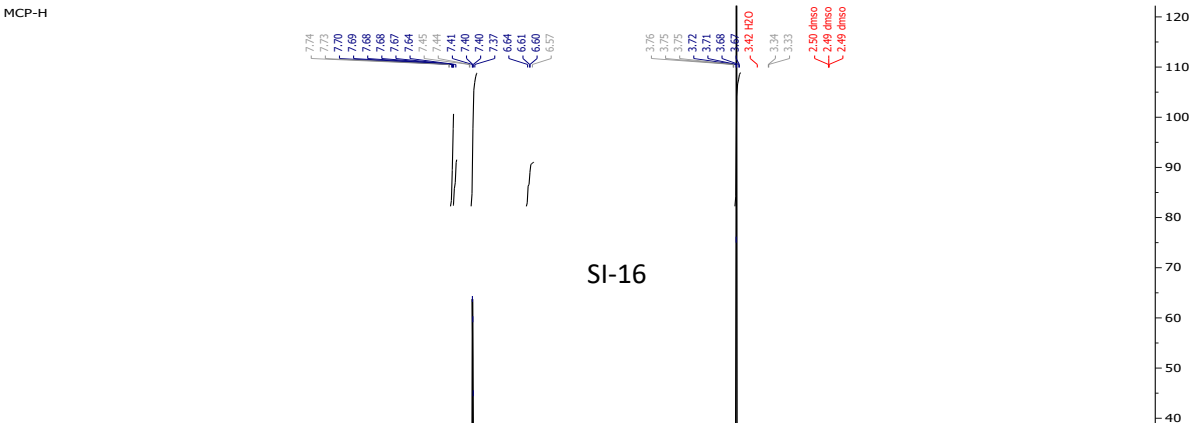


Fig. S12 [1]H NMR of methyl cinnamate.

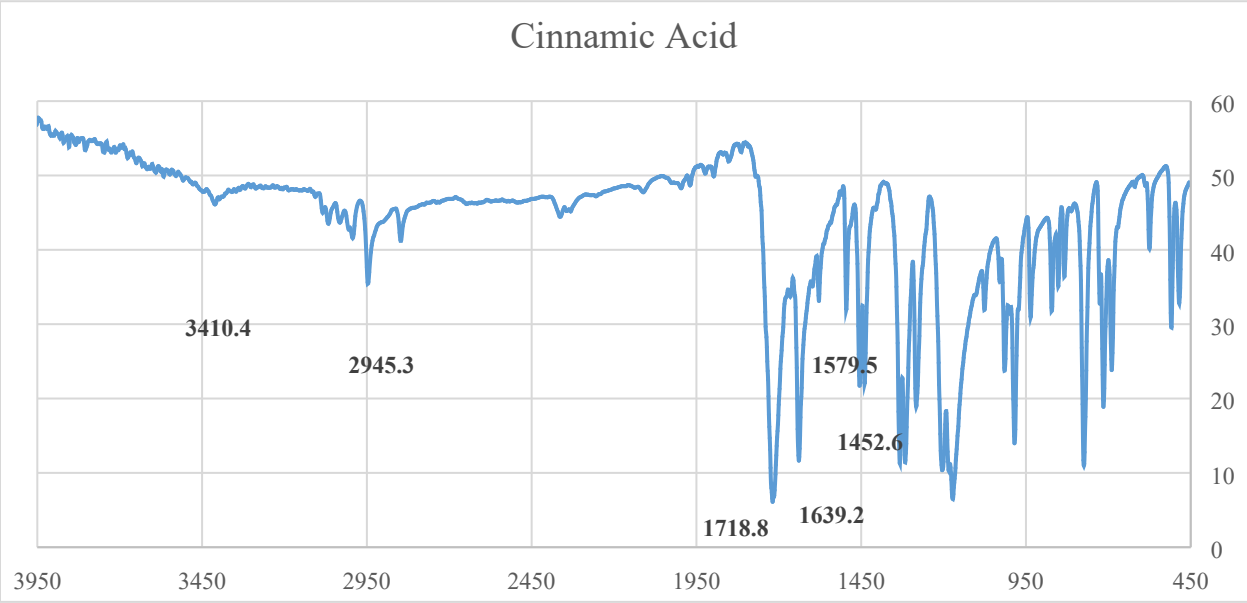


Fig. S13. FTIR of cinnamic acid.

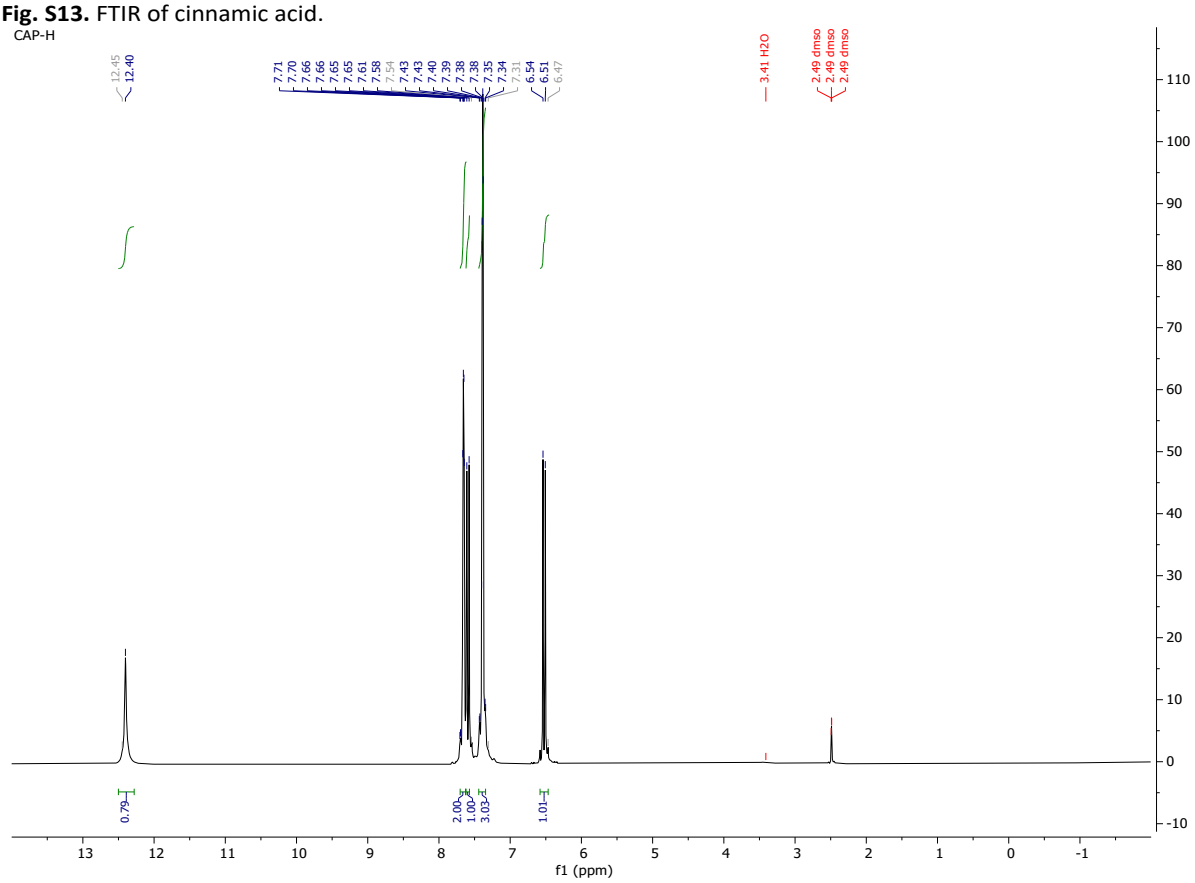


Fig. S14. [1]H NMR of cinnamic acid.

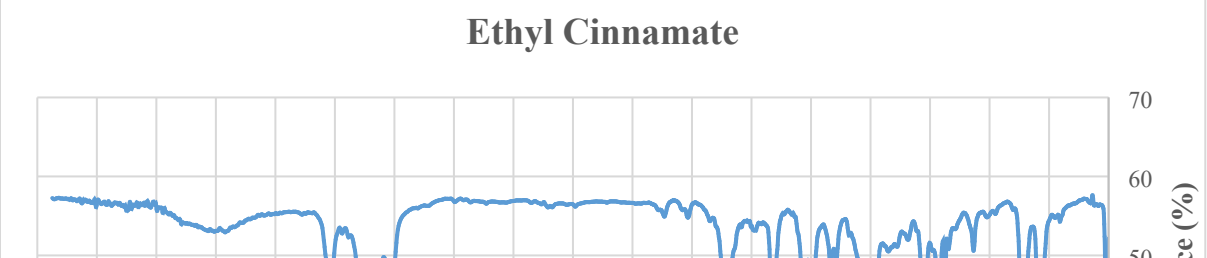


Fig. S15. FTIR of Ethyl Cinnamate.

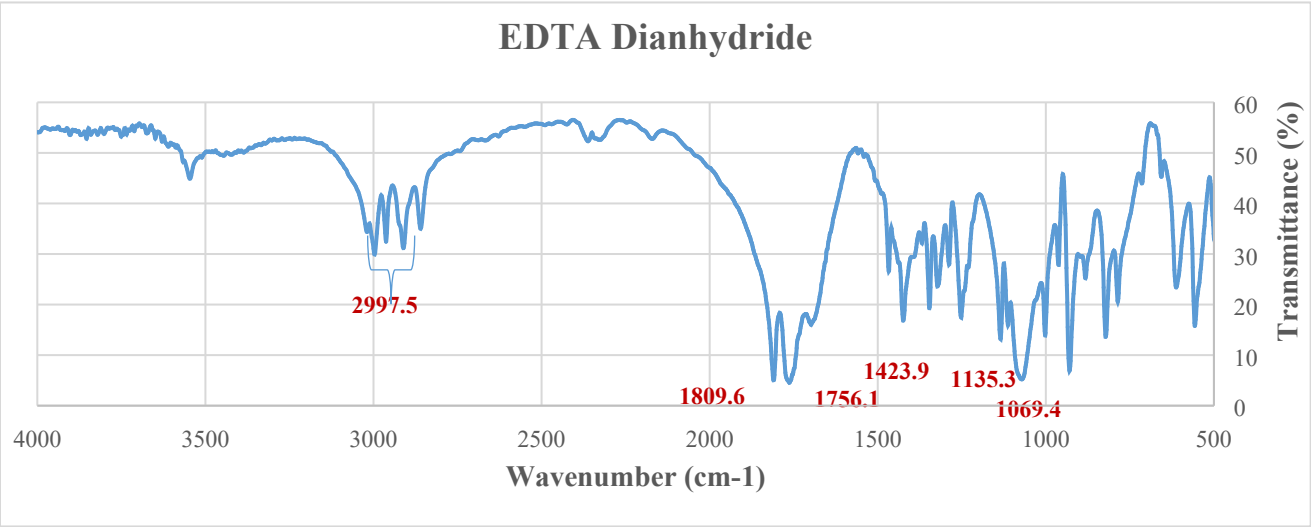


Fig. S16. FTIR of EDTA Dianhydride.

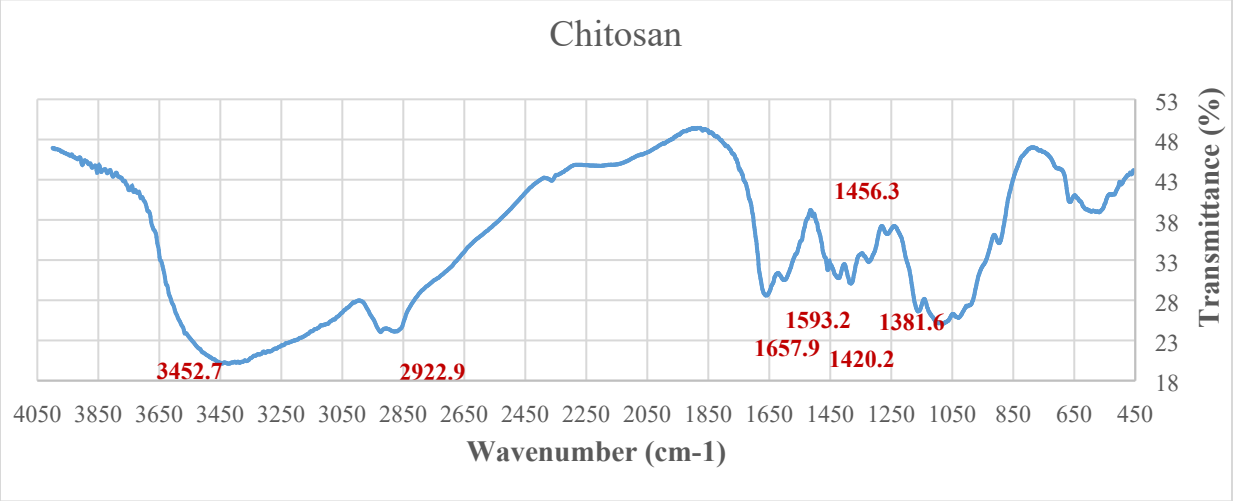


Fig. S17. FTIR of Chitosan.

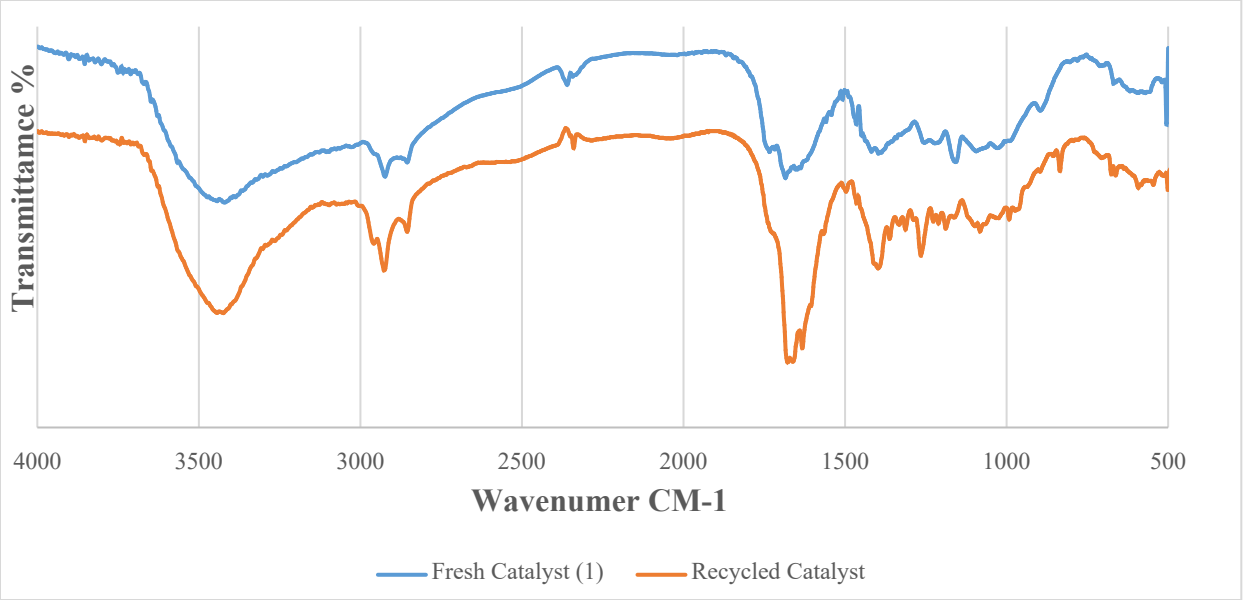
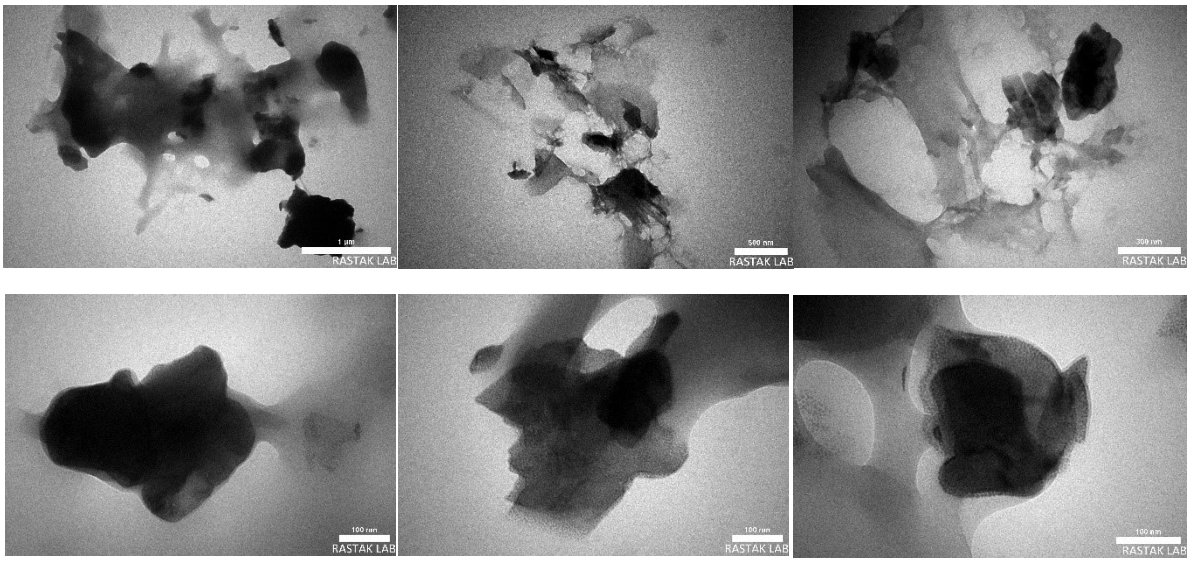


Fig. S18. The FTIR of fresh (blue) and recycled (orange) Pd@MET–EDTA–CS nanocatalyst (**1**)



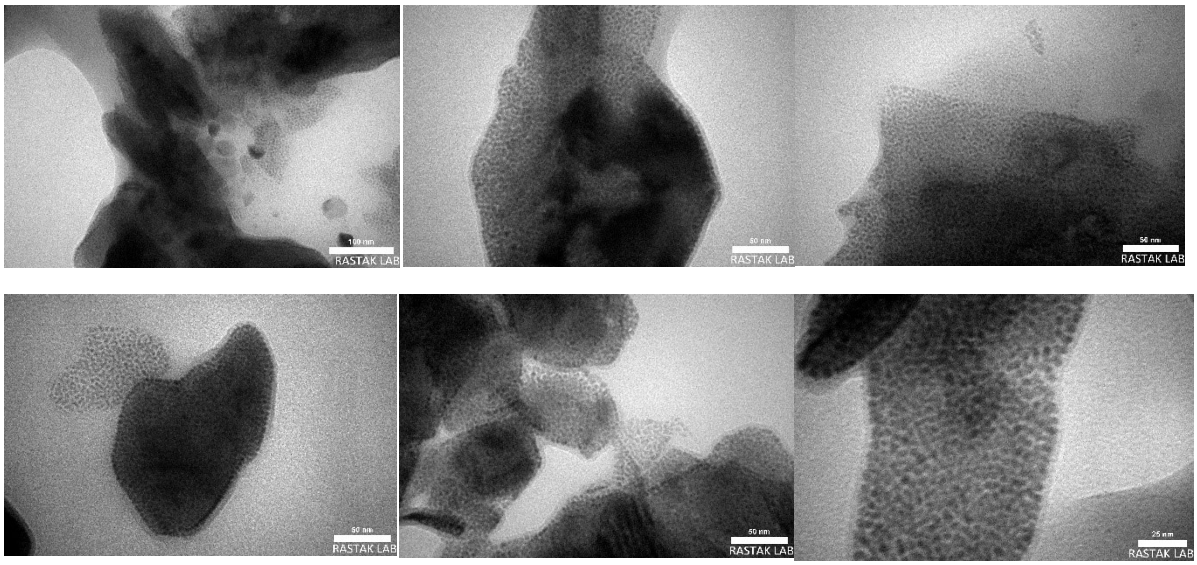


Fig. S19. The TEM images of Pd@MET-EDTA-CS nanocatalyst (**1**)

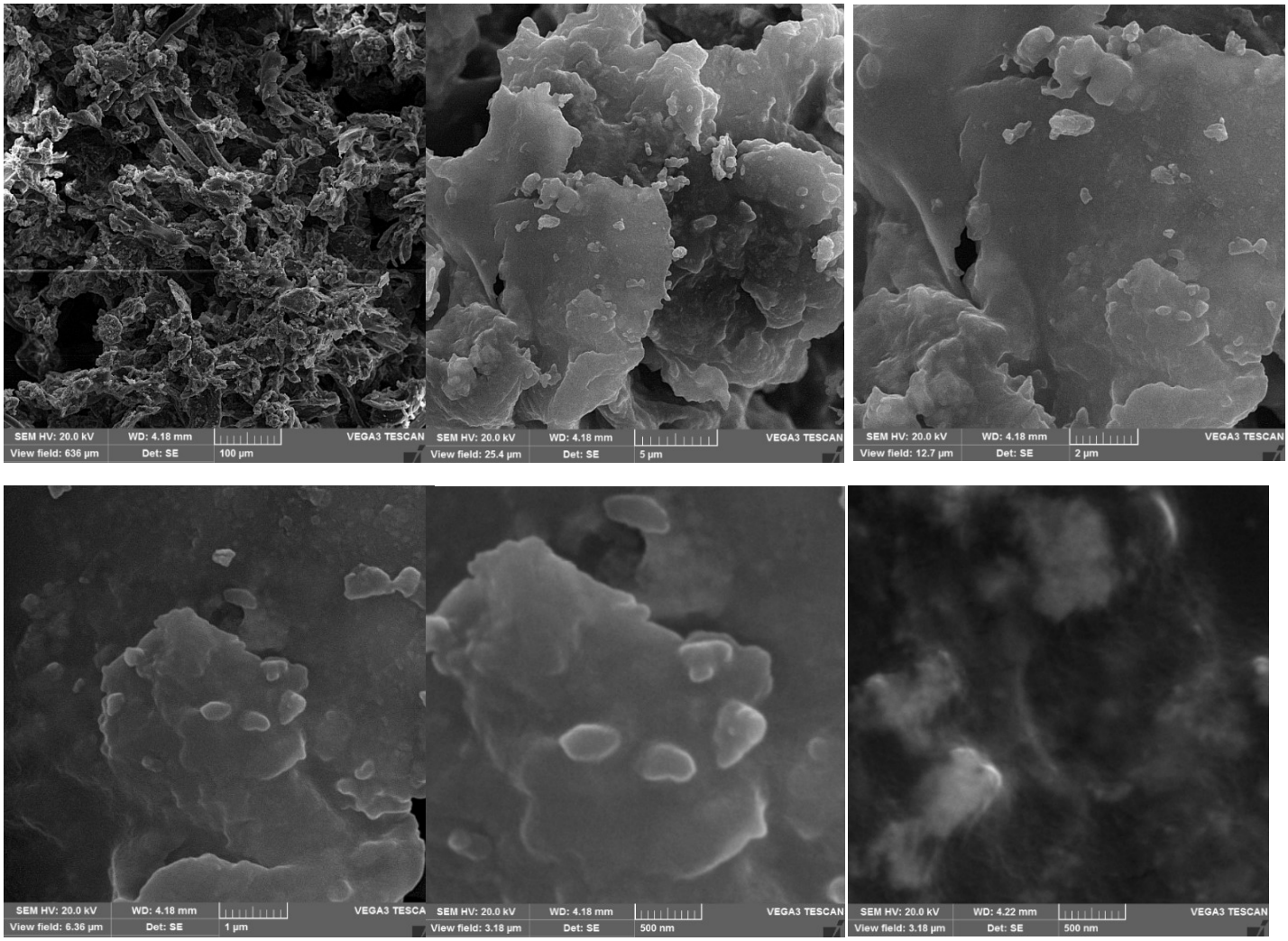


Fig. S20. The FESEM images of the recycled nanocatalyst (**1**)

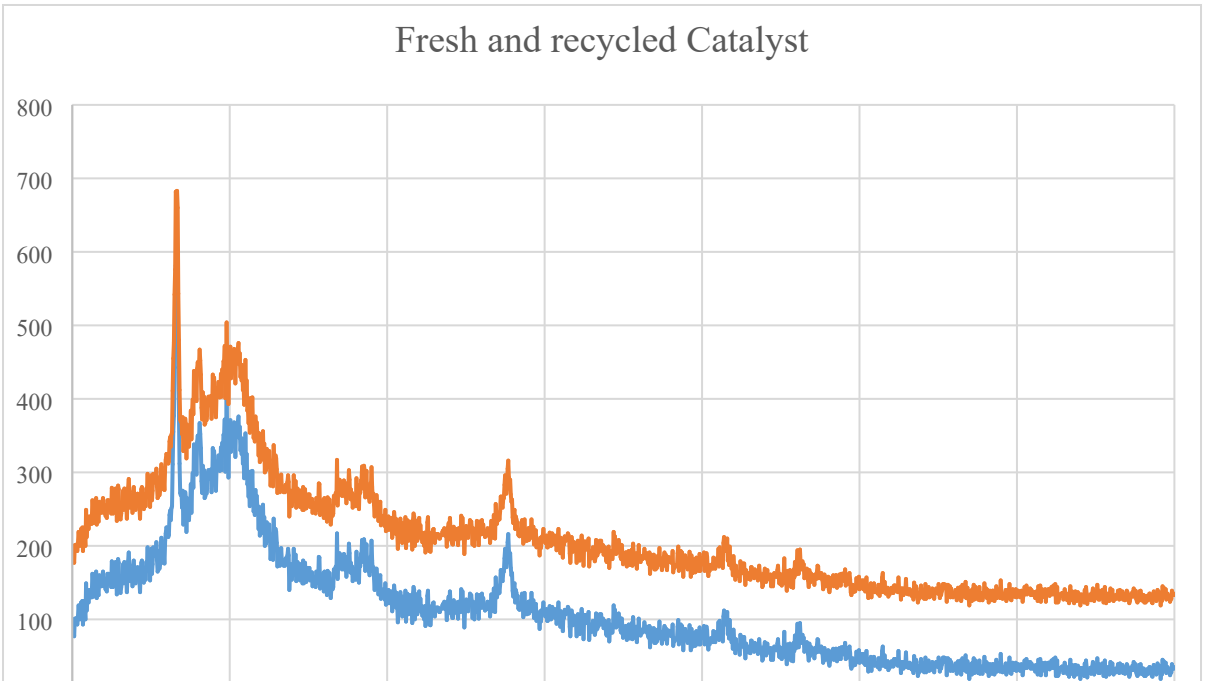


Fig. S21. The XRD pattern of the fresh (orange) and recycled (blue) Pd@MET−EDTA−CS nanocatalyst (**1**)