Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Green Synthesis of Silver and Palladium Nanocomposites: A Study of Catalytic Activity towards Etherification Reaction

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Section I

Table S1 Few reports on the biosynthesis of silver and palladium nanocomposites

Entry	Biomaterial	Condition of synthesis	Reactants	Particle size (nm)	Ref
Silver Nanocomposite	Guar gum (GG)	GG was dissolved in 10 mL of water (pH 6). After complete dissolution, the temperature was increased to 70 ºC and then reactant was added	$AgNO_3$ solution	4-12	1
	Latex from *Jatropha Curcas* plant	3% latex solution was formed by diluting with water and the same amount of reactant was mixed	$AgNO_3$ solution	~20-35	2
	Carboxymethyl cellulose sodium (CMS)	10 mL of reactant was mixed with certain volume of 0.1% CMS with continuous stirring	$AgNO_3$ solution	~15	3
	Terminalia Chebula fruit	Aqueous extract of fruit was treated with reactant solution	$AgNO_3$ solution	25	4
	Leaf extract of *Mimusops elengi*	The crude extract was first filtered and then mixed with a reactant	$AgNO_3$ solution	55-83	5
	Glucose	NH_3 was added slowly to the reactant solution to get $AgOH/Ag_2O$ ppt. Then the $Ag(NH_3)_2OH$ solution was mixed with graphene oxide (GO) and glucose-containing solution	$AgNO_3$ solution	--	6

	Montmorillonite (MMT)	The reactant was dissolved in chitosan solution under constant stirring, then it was added to MMT suspension and vigorously stirred for 4 h at room temperature	$AgNO_3$ solution	10.97 ± 5.60	7
Palladium Nanocomposite	Poly(3,4-ethylenedioxythiophene) (PEDOT)	The entire process was done in a round-bottom flask equipped with a magnetic stirrer. 3,4-ethylenedioxythiophene (EDOT) alcoholic solution was rapidly added into reactant under vigorous stirring for 3 h	H_2PdCl_4 solution	~4.5	8
	Reduced graphene oxide (rGO)-carbon nanotube (CNT)	rGO-CNT was dipped into an aqueous solution of reactant maintained in a vial under vigorous stirring for 30 min in an ice bath	K_2PdCl_4 aqueous solution	4	9
	Fruits of *Piper Longum*	Aqueous extract of fruits of *piper longum* was added to reactant and natrolite zeolite was added and stirred for 15 h at 100 ºC	$PdCl_2$ solution	–	10
	Theobroma cacao L. seeds extract	Cocoa seed aqueous extract was added dropwise to a well-mixed solution of the reactant with constant stirring at 50 °C for 2 h	$PdCl_2$ solution	~40	11

	Extract of marine alga, *Sargassum bovinum*	Aqueous extract of the reactant was mixed with crude extract of marine alga. The whole mixture was put into a rotary shaker at 60 °C (160 rpm) for 24 h and maintained in the dark	$PdCl_2$ solution	~5	12
	g-C_3N_4	g-C_3N_4 was dispersed in isopropyl alcohol with sonication in a low power sonic-bath for 30 min. Then it was stirred, and reactant solution (1 M) was added under continuous stirring for 2 h at room temperature	$Pd(NO_3)_2$ solution	--	13
Ag, Pd and Ag-Pd nanocomposite	Rutin	Different pH solutions of rutin were treated with same concentration of reactant solution(s). For Ag@rutin, the nanocomposite was obtained within 5 to 10 mins. For the formation of Pd@rutin and Ag-Pd@rutin, around 72 h reaction time was required at 40 °C	$AgNO_3$ and $PdCl_2$	~50 nm for Ag@rutin, ~10 nm for Pd@rutin and ~80 nm for Ag-Pd@rutin	This Work

Section II

Spectral Study:

i) The visual color change of rutin solution adjusted at different pHs with the gradual addition of $PdCl_2$, $AgNO_3$ and $PdCl_2$-$AgNO_3$ mixture

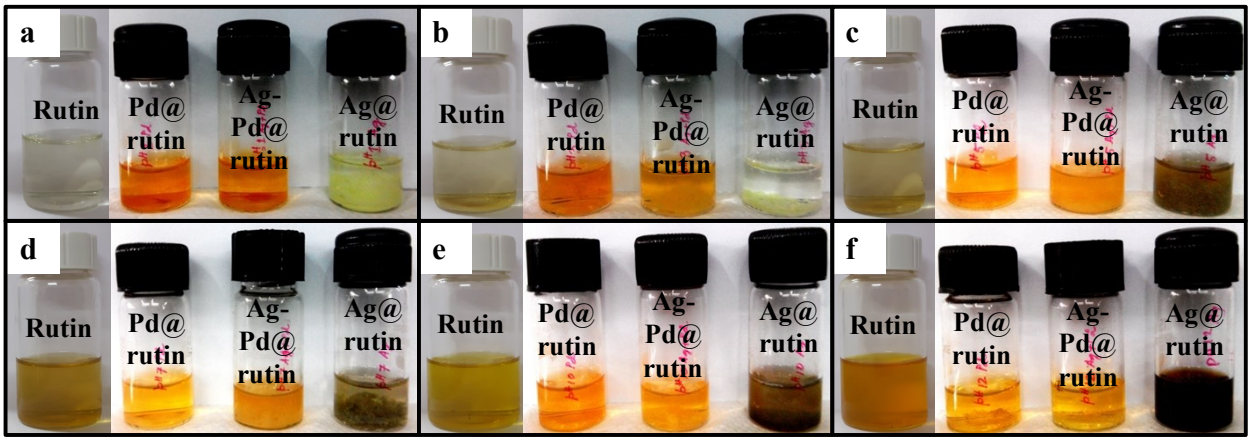


Fig. S1 Pictorial presentation of pristine rutin, Pd@rutin, Ag-Pd@rutin and Ag@rutin prepared in (a) pH1; (b) pH 3; (c) pH 5; (d) pH 7; (e) pH 9; (f) pH 12.

Table S2 Feed composition and yield of the prepared nanocomposites

Nanocomposites	Feed Composition	Yield (g)
Ag@rutin	5 mL 10 mM rutin solution of pH 12 + 5 mL 10 mM $AgNO_3$ solution	0.0392
Pd@rutin	5 mL 10 mM rutin solution of pH 1 (Solution A) + 5 mL 10 mM $PdCl_2$ solution	0.0258
Ag-Pd@rutin	Solution A + 2.5 mL 10 mM $AgNO_3$ solution + 2.5 mL 10 mM $PdCl_2$ solution	0.0228

ii) The absorption spectra of $AgNO_3$, $PdCl_2$ and $AgNO_3$-$PdCl_2$ mixture in respective pHs.

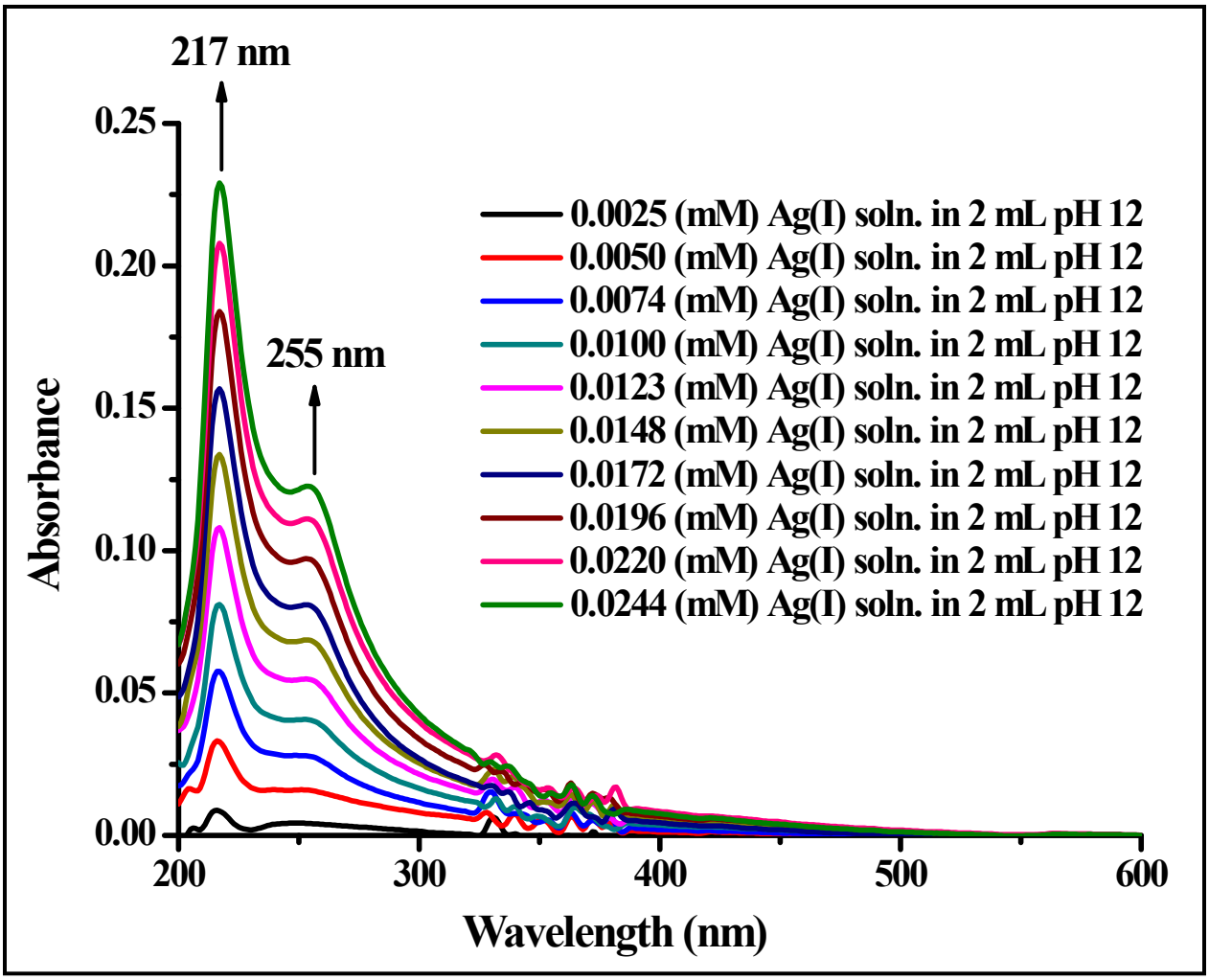


Fig. S2 Absorption spectra of silver in pH 12.

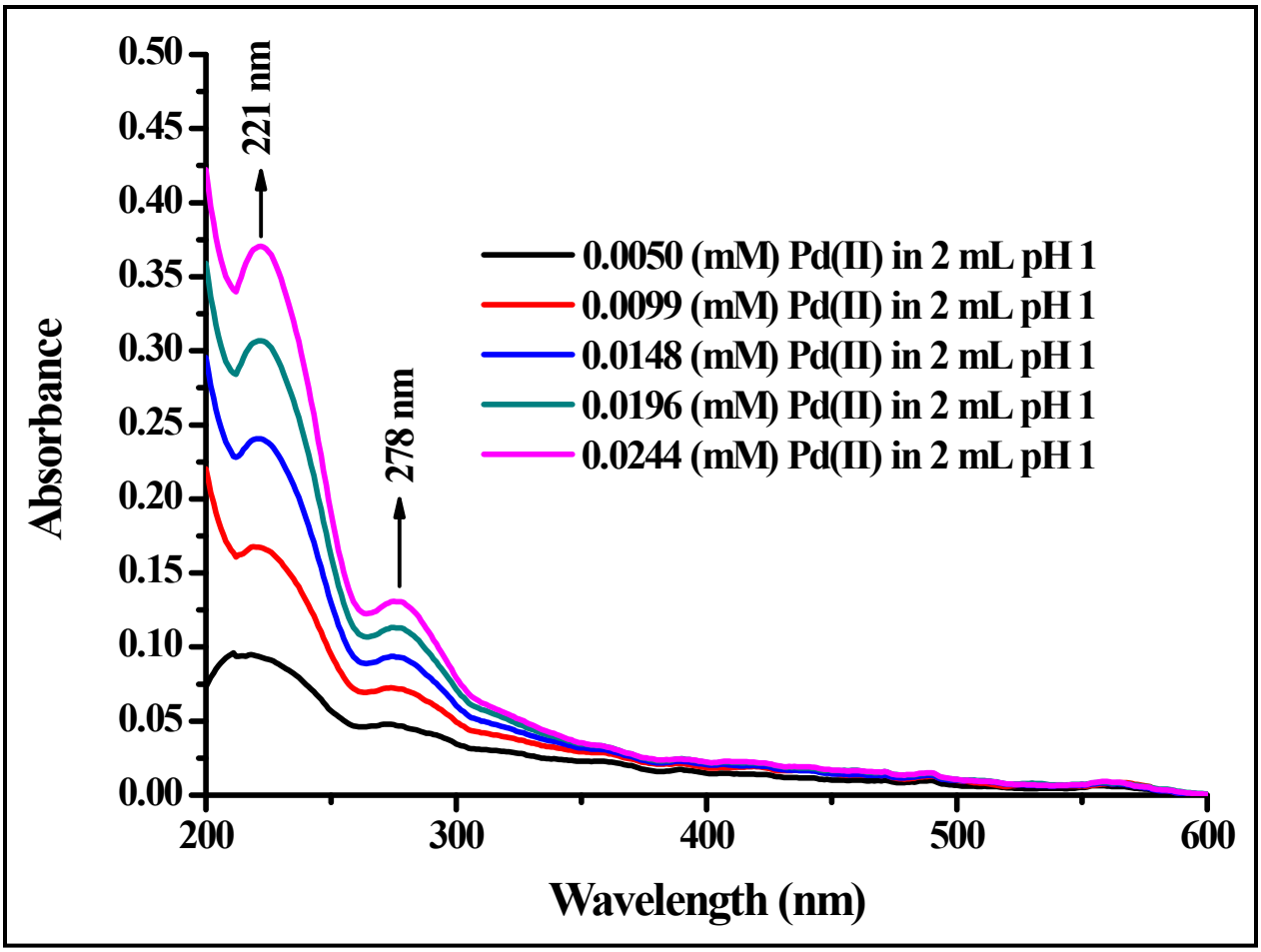


Fig. S3 Absorption spectra of palladium in pH 1 at 40 °C.

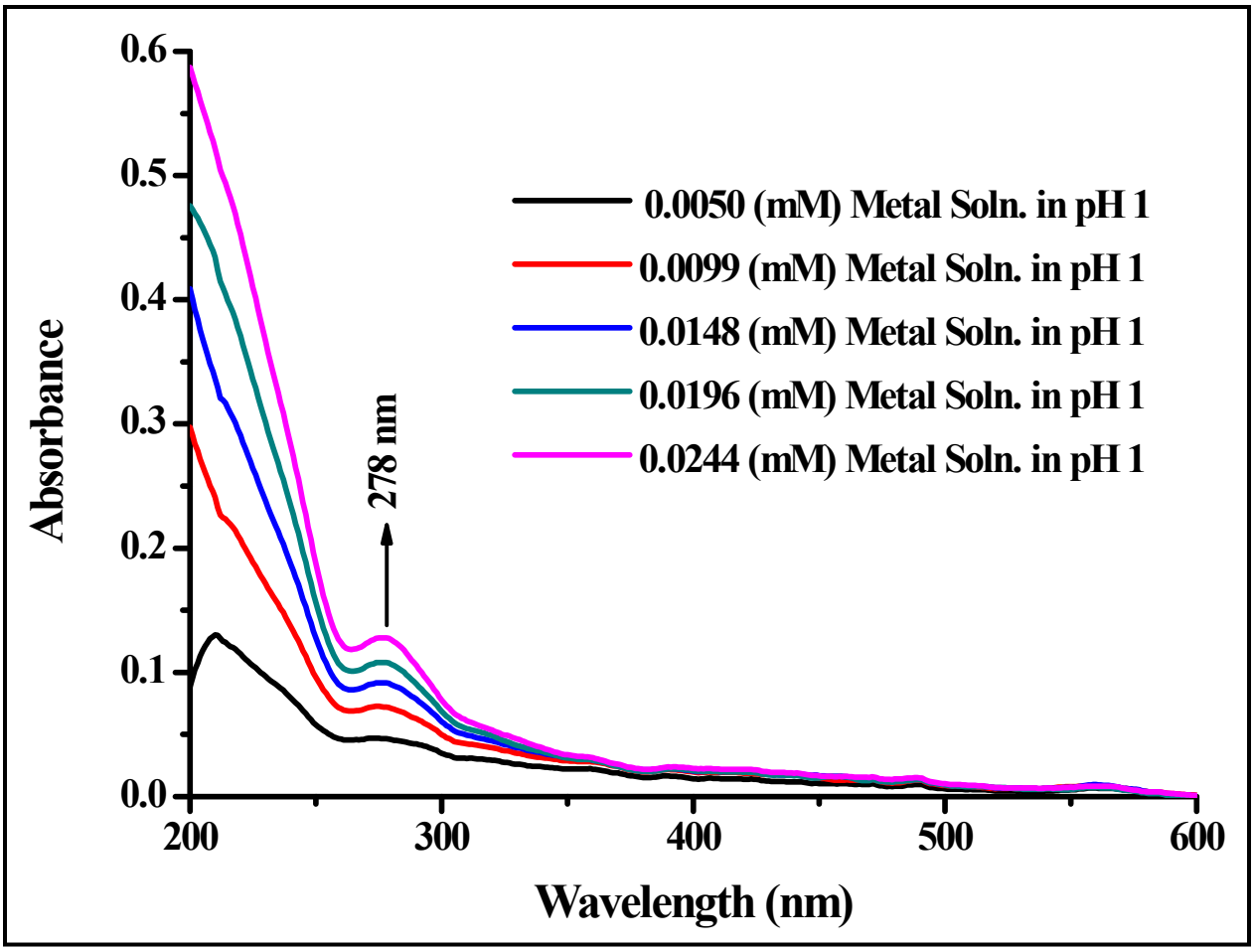


Fig. S4 Absorption spectra of the silver-palladium bimetallic solution in pH 1 at 40 °C.

Section III

XPS figures:

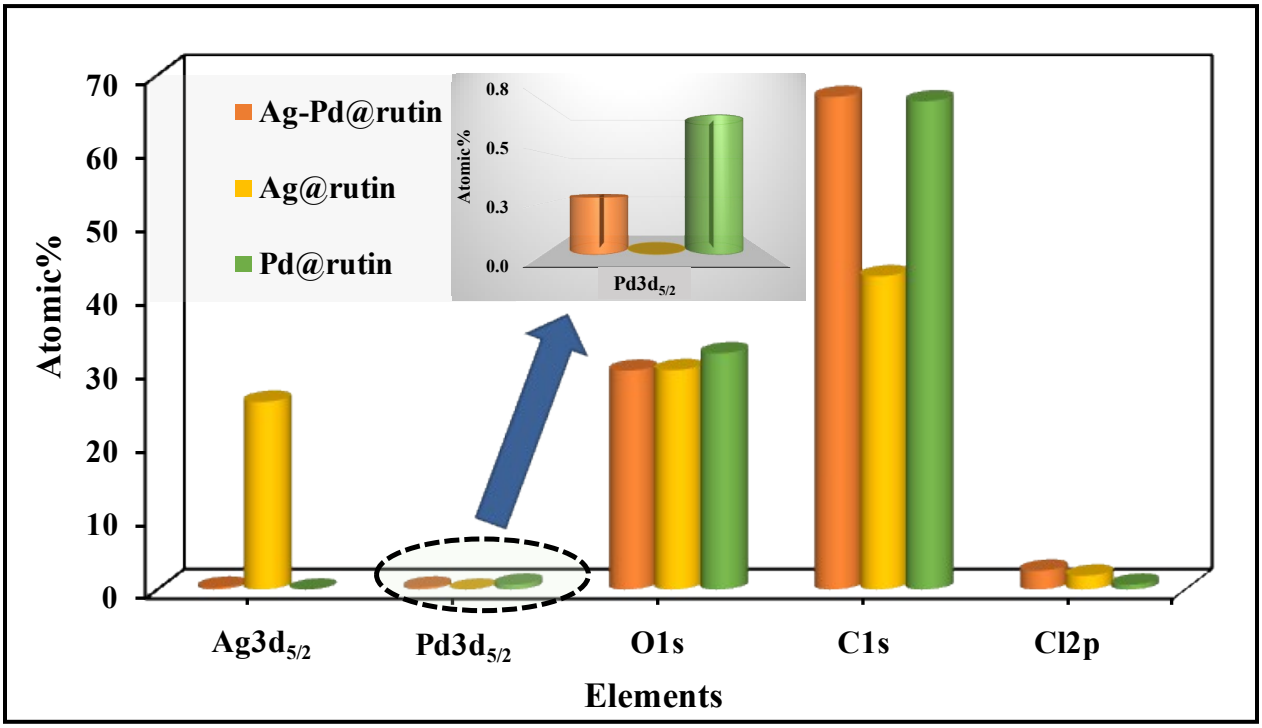


Fig. S5 Survey scan data of Ag-Pd@rutin, Ag@rutin, and Pd@rutin NC samples with Pd atomic% data zoomed in the inset. Minimum three areas from each sample were acquired and average data is shown above.

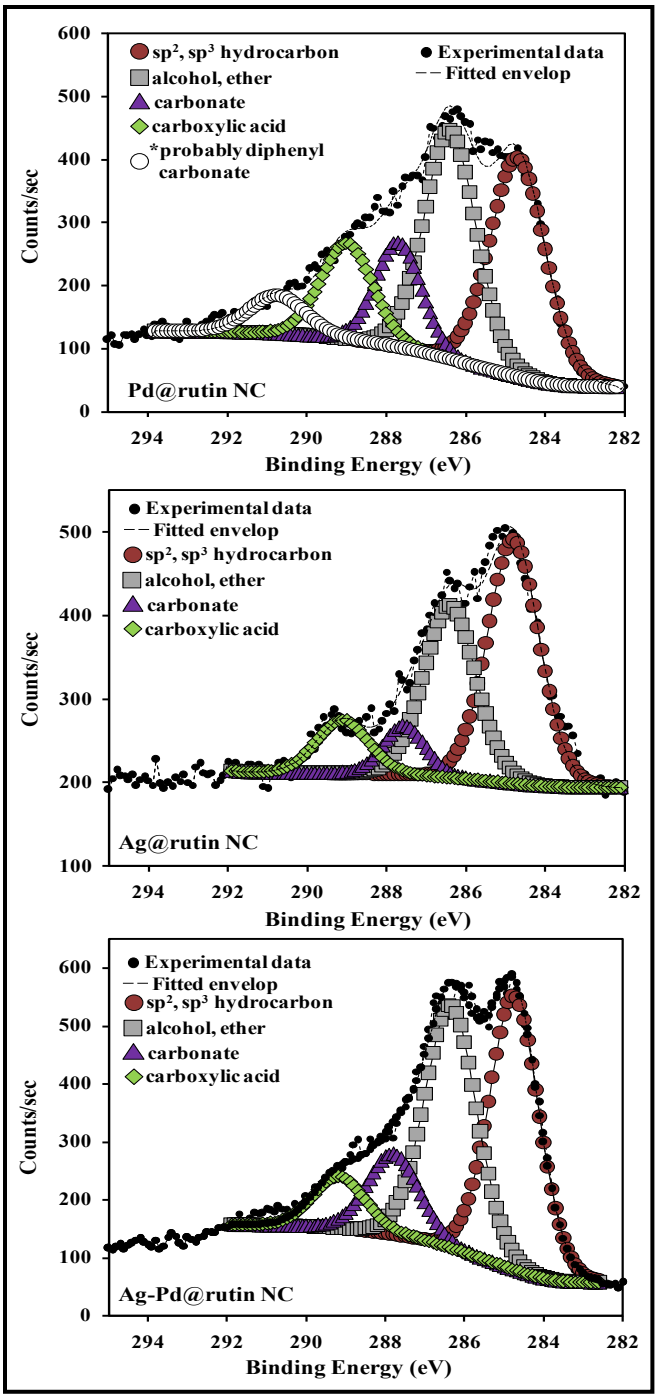


Fig. S6 Representative C1s narrow scan spectra of NCs of Pd@rutin, Ag@rutin, and Ag-Pd@rutin. The deconvolution of the narrow scan data is carried out with a constraint of mixed sp^2 and sp^3 C1s hydrocarbon peak fixed at 284.75 eV. Necessary post data acquisition peak shifts due to charging are carried out keeping this mixed hydrocarbon peak fixed, which is a standard practice in XPS analysis.

Section IV

Reaction Optimization:

Reaction optimization data using Ag@rutin and Ag-Pd@rutin catalyst.

Table S3 Standardization of reaction conditions using Ag@rutin catalyst[a]

Entry	Solvent	Base	Temp. (ºC)	Time (h)	Yield[b] (%)
1	DMF	$NaHCO_3$	120	18	40
2	Toluene	$NaHCO_3$	110	18	27
3	Acetonitrile	$NaHCO_3$	78	18	12
4	**Water**	**$NaHCO_3$**	**100**	**18**	**75**
5	Water	K_2CO_3	100	18	72
6	Water	Cs_2CO_3	100	18	32
7	Water	$NaHCO_3$	60	18	43
8	Water	$NaHCO_3$	rt	30	-
9	Water	$NaHCO_3$	100	10	34
10	Water	$NaHCO_3$	100	22	75

[a]Condition: Cinnamyl acetate (1 mmol), *p*-cresol (1 mmol), base (2 mmol), Ag@rutin (1.7 mg, 0.00027 mol%), solvent, temp., time; [b]Yields refer to those of isolated products.

Table S4 Standardization of reaction conditions using Ag-Pd@rutin catalyst[a]

Entry	Solvent	Base	Temp. (°C)	Time (h)	Yield[b] (%)
1	DMF	$NaHCO_3$	120	18	36
2	Toluene	$NaHCO_3$	110	18	8
3	Acetonitrile	$NaHCO_3$	78	18	<5
4	**Water**	**$NaHCO_3$**	**100**	**18**	**72**
5	Water	K_2CO_3	100	18	67
6	Water	Cs_2CO_3	100	18	22
7	Water	$NaHCO_3$	60	18	39
8	Water	$NaHCO_3$	rt	30	-
9	Water	$NaHCO_3$	100	10	30
10	Water	$NaHCO_3$	100	22	73

[a]Condition: Cinnamyl acetate (1 mmol), *p*-cresol (1 mmol), base (2 mmol), Ag-Pd@rutin (14.6 mg, 0.00027 mol% of Ag and 0.000027 mol% of Pd), solvent, temp., time; [b]Yields refer to those of isolated products.

Section V

Comparison of the work:

The comparison between different palladium-catalyzed etherification reaction and this work

Table S5 Few reports on palladium-catalyzed etherification reactions

Entry	Catalyst	Reaction Conditions	Yield (%)	Reusability of the catalyst	Reference
1	Pd(II)-PS-Ala	Cinnamyl acetate and *p*-cresol, water, K_2CO_3, 16 h, reflux	90	5	14
2	Fe_3O_4–dopamine–Pd	Cinnamyl acetate and *p*-cresol, water, $NaHCO_3$, 5h, reflux	85	5	15
3	Fe_3O_4@SiO_2Pd	Cinnamyl acetate and *p*-cresol, water, $NaHCO_3$, 6h, reflux	85	4	16
4	$Pd(PPh_3)_4$	Allylic acetate and aliphatic alcohol, THF, Et_2Zn, 25 °C, 2 to 6 h	70	---	17
5	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1,3-diphenylpropenyl acetate, benzyl alcohol, CH_3CN, Cs_2CO_3, 10 °C, 24 h under argon atmosphere	98	---	18
6	polystyrene–poly(ethylene glycol) copolymer resin supported by Pd–imidazoindolephosphine complex	Allylic ester, phenol, water, K_2CO_3, 25 °C, 12 h under N_2 atmosphere	94	2	19
7	$PdCl_2$	2-iodophenol, phenylboronic acid, methylene chloride, DMF, Cs_2CO_3, 100 °C, 12 h	74	---	20
8	$Pd(CH_3CN)_2Cl_2$	1,3-diphenylallyl acetate, benzyl alcohol, CH_3CN, Cs_2CO_3, 20 °C, 4 h	86	3	21
9	$Pd(dba)_2$	Sodium 4-methoxyphenolate, 1-bromo-2-methylbenzene, toluene, 80 °C, 12 h	85	---	22
10	$Pd(OAc)_2$	Allyl alcohol, *p*-cresol, benzene, PPh_3, 50 °C, 4 -20 h	91	---	23

11	$Pd(OAc)_2$	3-(2-bromo-phenyl)propan-1-ol, toluene, $Ca2CO_3$, 50 °C, 21 h	85	---	24
12	Pd@rutin	Cinnamyl acetate and *p*-cresol, water, K_2CO_3, 18 h, reflux	88	4	This work

Section VI

^{1}H and ^{13}C NMR spectra of synthesized products

1-(cinnamyloxy)-4-methylbenzene (Table 8, 3a): ^{1}H NMR 300 MHz, $CDCl_3$ δ 7.34-6.31 (m, 11H), 4.60-4.58 (d, 2H), 2.21 (bs, 3H); ^{13}C NMR 75 MHz, $CDCl_3$ δ 156.55, 130, 114.70, 77.08, 68.76, 20.89.

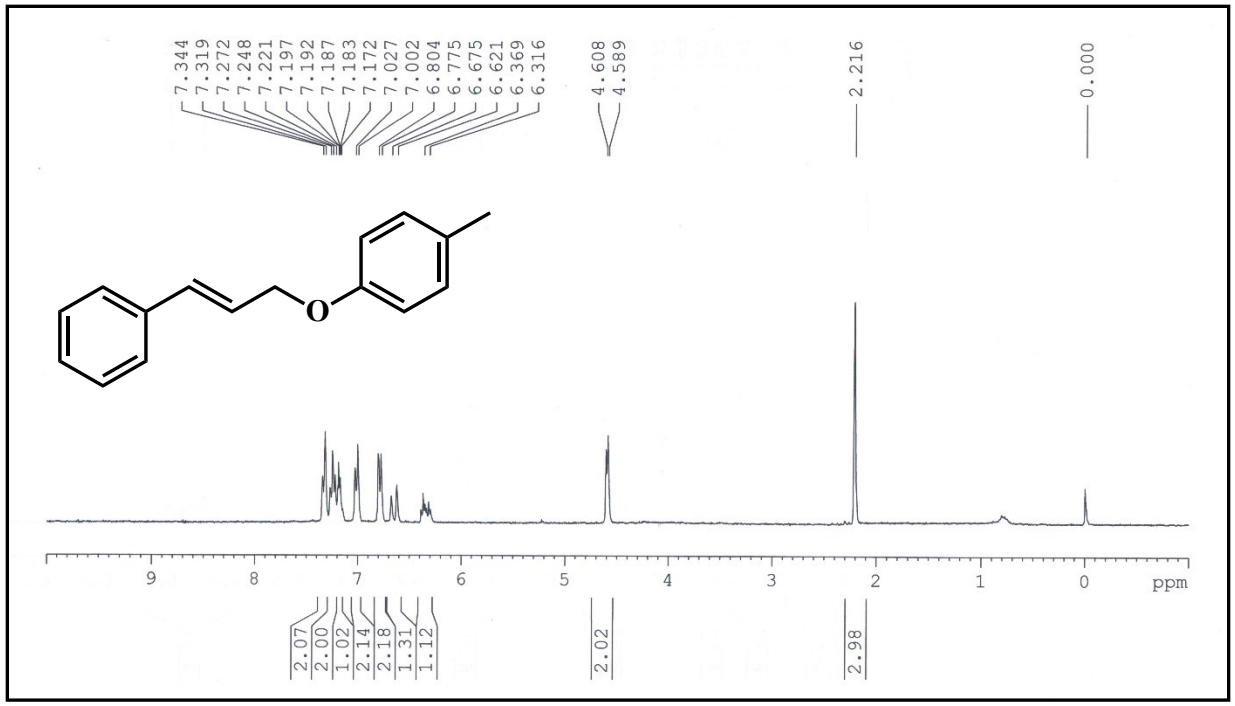
1-bromo-4-(cinnamyloxy)benzene (Table 8, 3b): ^{1}H NMR 300 MHz, $CDCl_3$ δ 7.34-7.16 (m, 7H), 6.79-6.61 (m, 3H), 6.35-6.26 (m, 1H), 4.60-4.58 (q, 2H); ^{13}C NMR 75 MHz, $CDCl_3$ δ 157.69, 130, 116.58, 113.02, 77.10, 68.81.

(E)-1-bromo-4-((3-(p-tolyl)allyl)oxy)benzene (Table 8, 3c): ^{1}H NMR 300 MHz, $CDCl_3$ δ 7.32-6.23 (m, 10H), 4.59-4.57 (d, 2H), 2.27 (bs, 3H); ^{13}C NMR 75 MHz, $CDCl_3$ δ 158.19, 136.42, 134.04, 132.63, 128.35, 127.85, 126.65, 124.19, 117.08, 113.45, 117.08, 113.45, 69.05, 20.59.

(E)-1-bromo-4-((3-(4-methoxyphenyl)allyl)oxy)-benzene (Table 8, 3d): ^{1}H NMR 300 MHz, $CDCl_3$ δ 7.27-6.17 (m, 10H), 4.55 (bs, 2H), 3.75 (bs, 3H); ^{13}C NMR 75 MHz, $CDCl_3$ δ 158, 133, 128, 121.61, 116.66, 114.05, 76.8, 69.13, 55.29.

(E)-1-methoxy-4-(3-(p-tolyloxy)prop-1-en-1-yl)-benzene (Table 8, 3e): ^{1}H NMR 300 MHz, $CDCl_3$ δ 7.41-6.16 (m, 10H), 4.58-4.56 (d, 2H), 3.73 (bs, 3H), 2.20 (bs, 3H); ^{13}C NMR 75 MHz, $CDCl_3$ δ 159.5, 129.82, 121, 114, 76.80, 68.92, 55.22, 20.19.

Fig. S5 ^{1}H and ^{13}C-NMR spectra of 1-(cinnamyloxy)-4-methylbenzene (3a)**.**



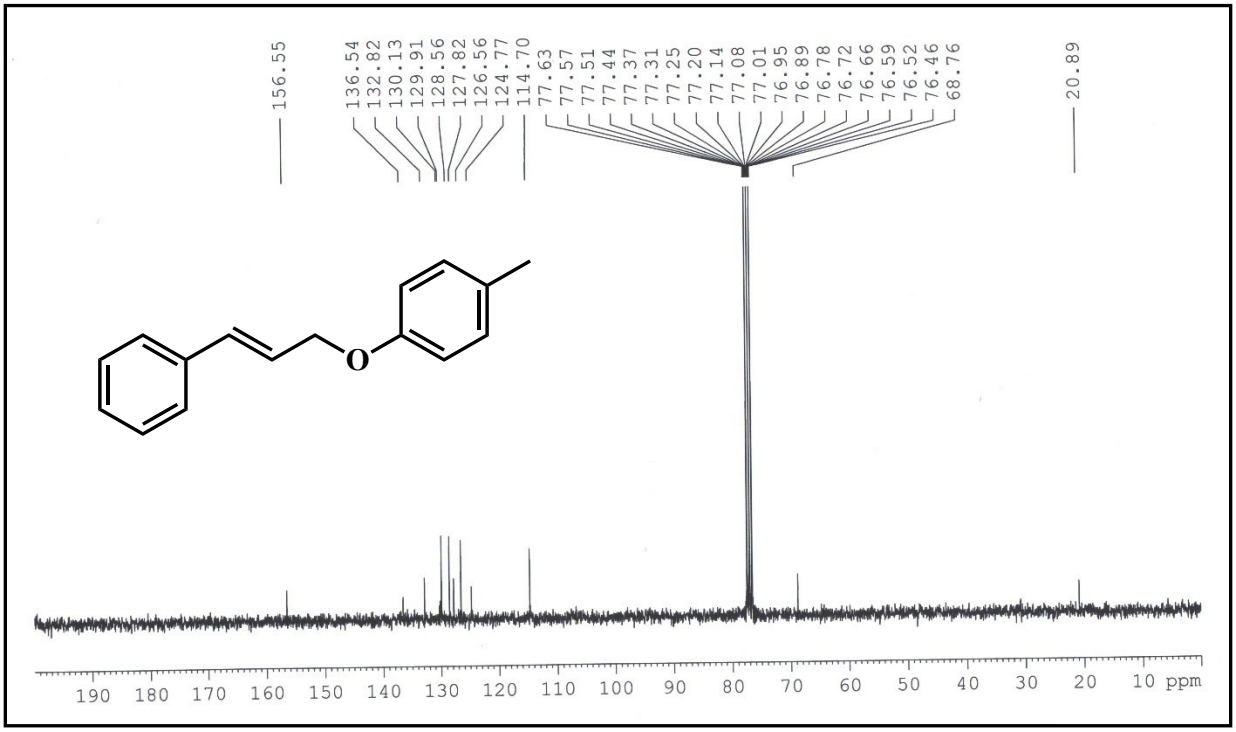
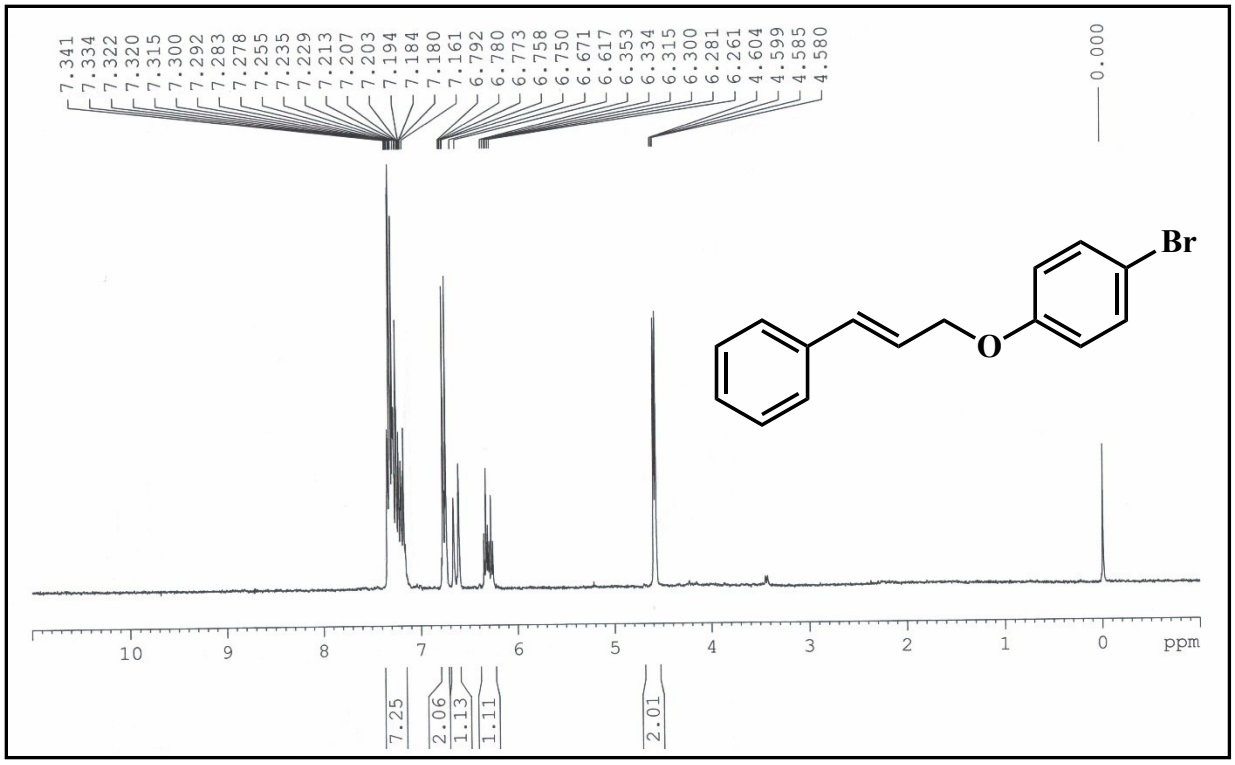


Fig. S6 ^{1}H and ^{13}C-NMR spectra of 1-bromo-4-(cinnamyloxy)benzene (3b)**.**



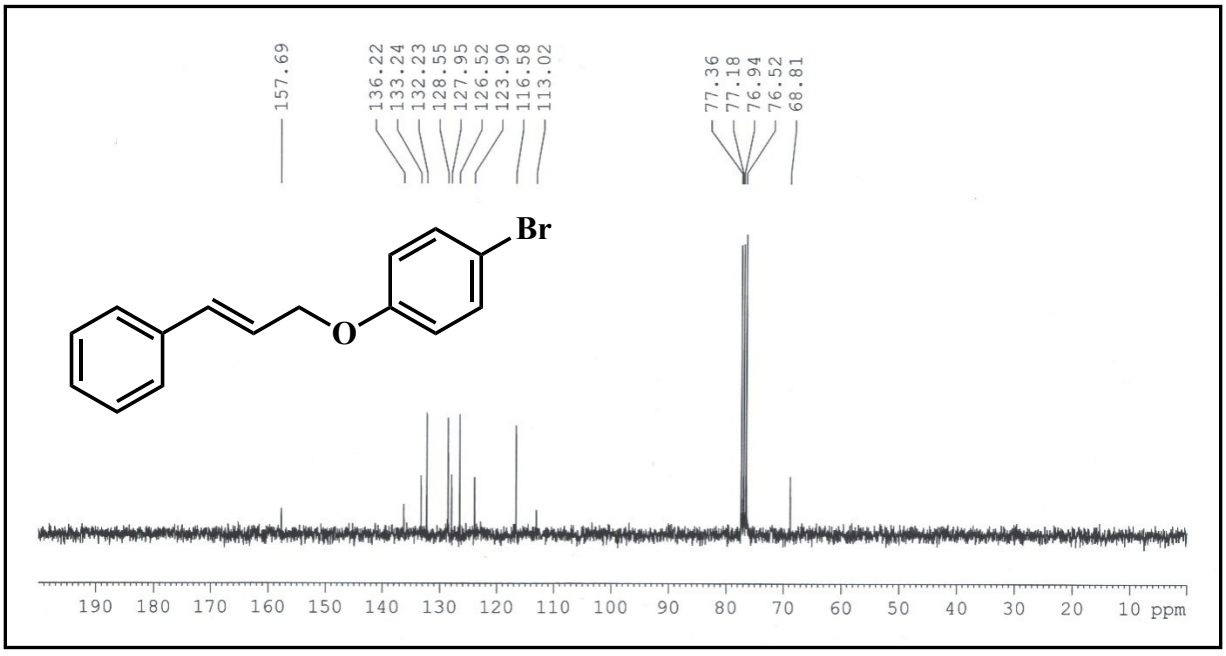
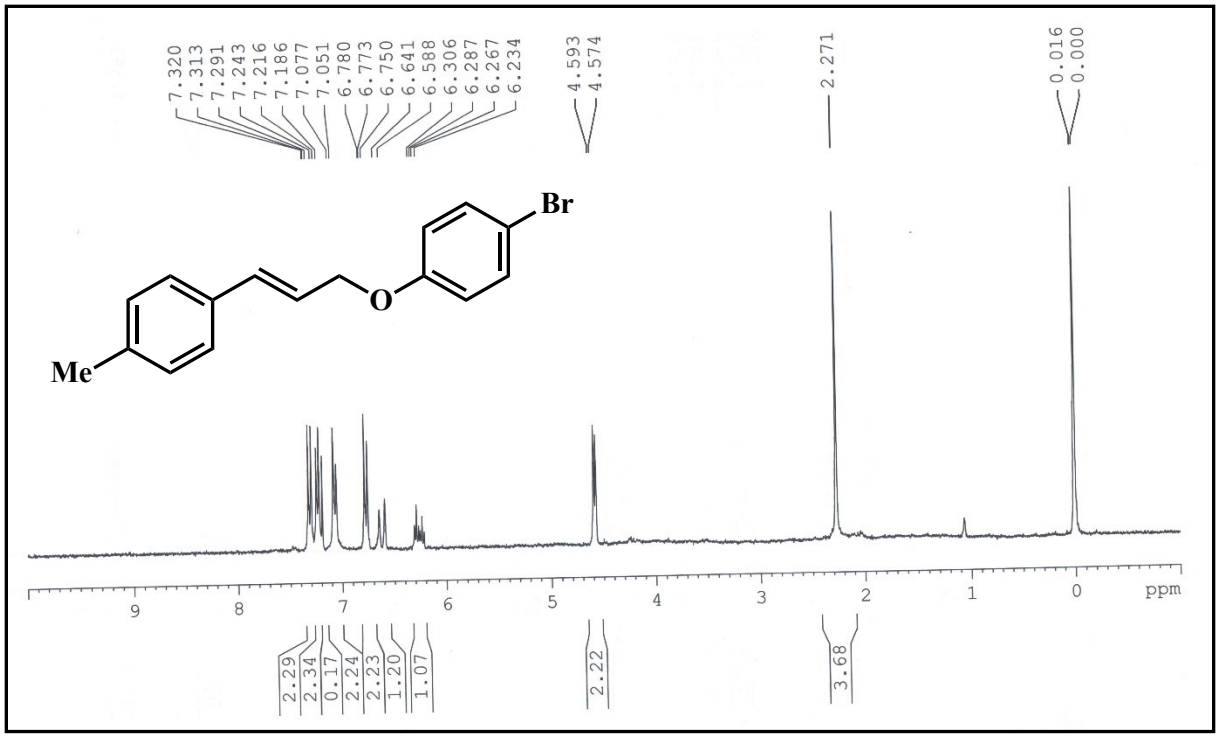


Fig. S7 ^{1}H and ^{13}C-NMR spectrum of (E)-1-bromo-4-((3-(p-tolyl)allyl)oxy)benzene (3c)**.**



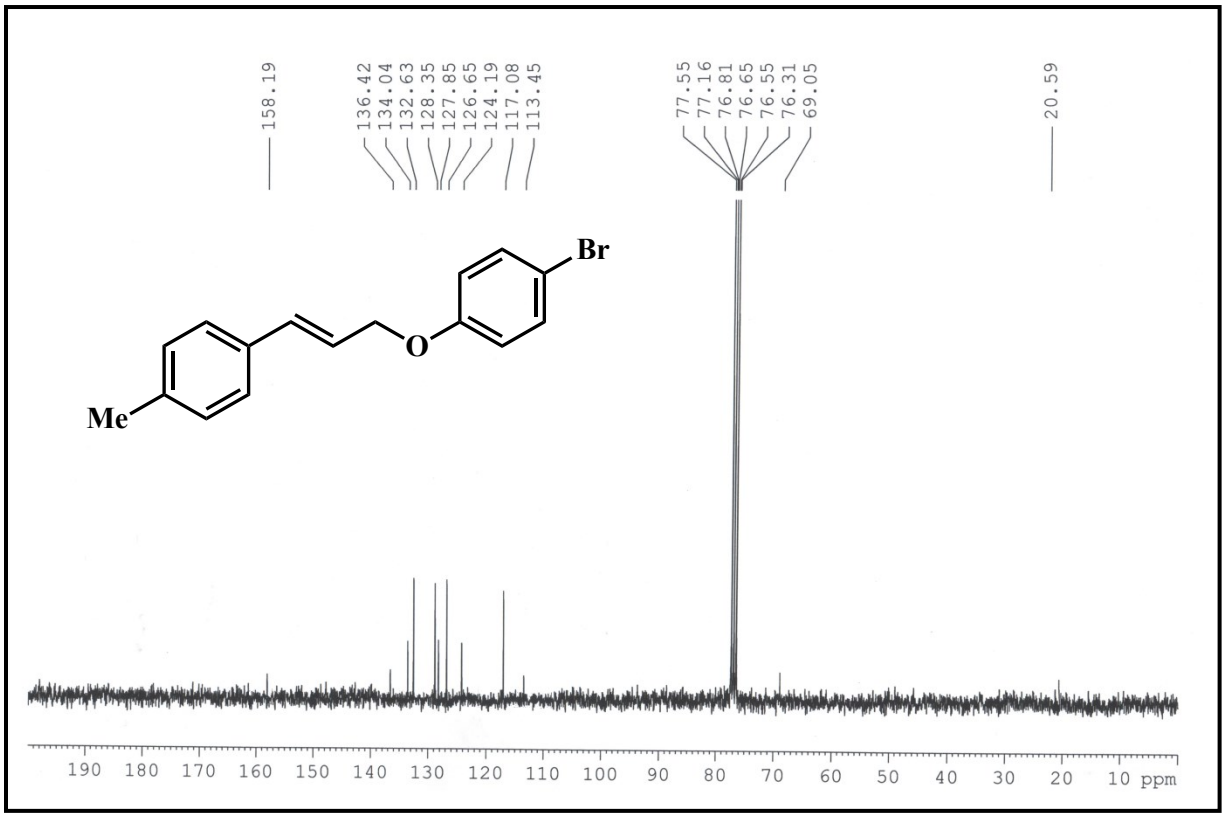
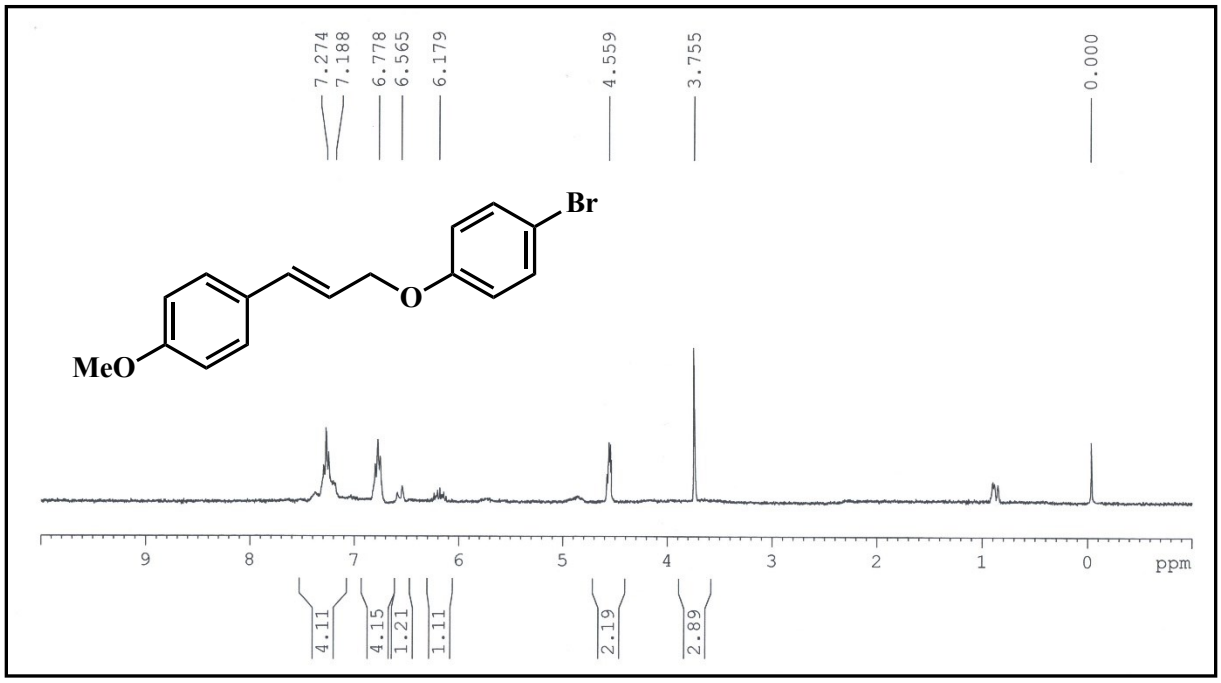


Fig. S8 ^{1}H and ^{13}C-NMR spectra of (E)-1-bromo-4-((3-(4-methoxyphenyl)allyl)oxy)-benzene (3d)**.**



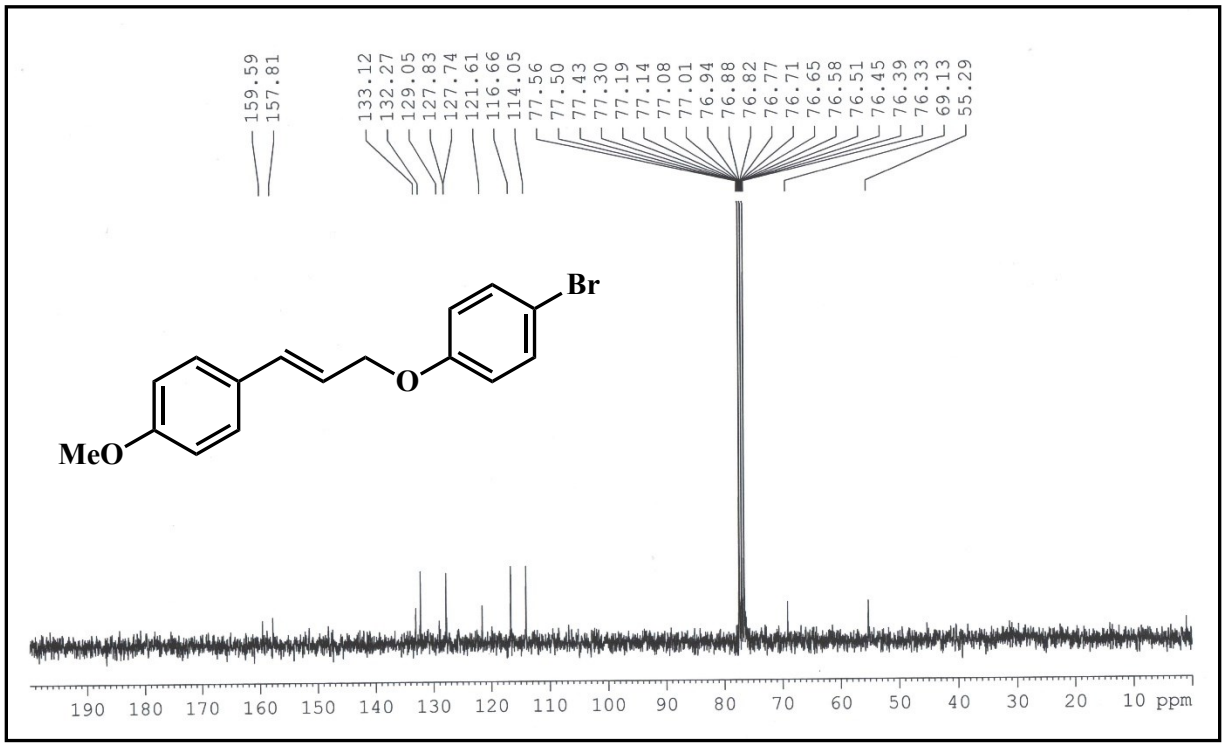
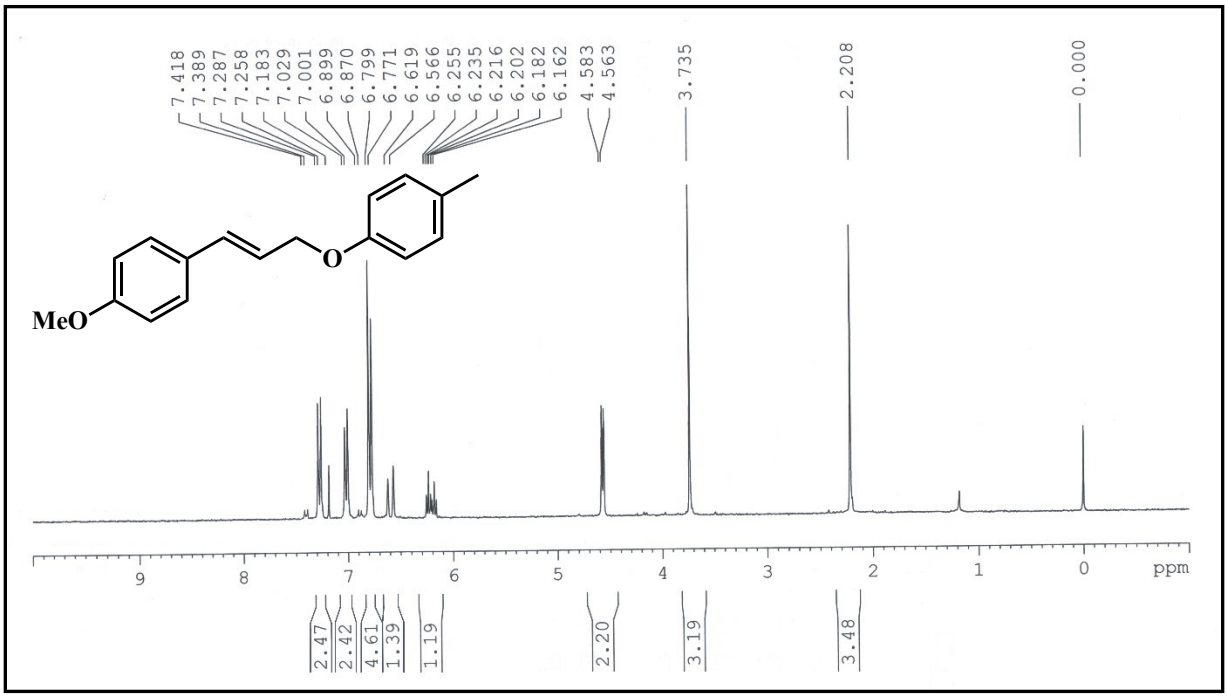
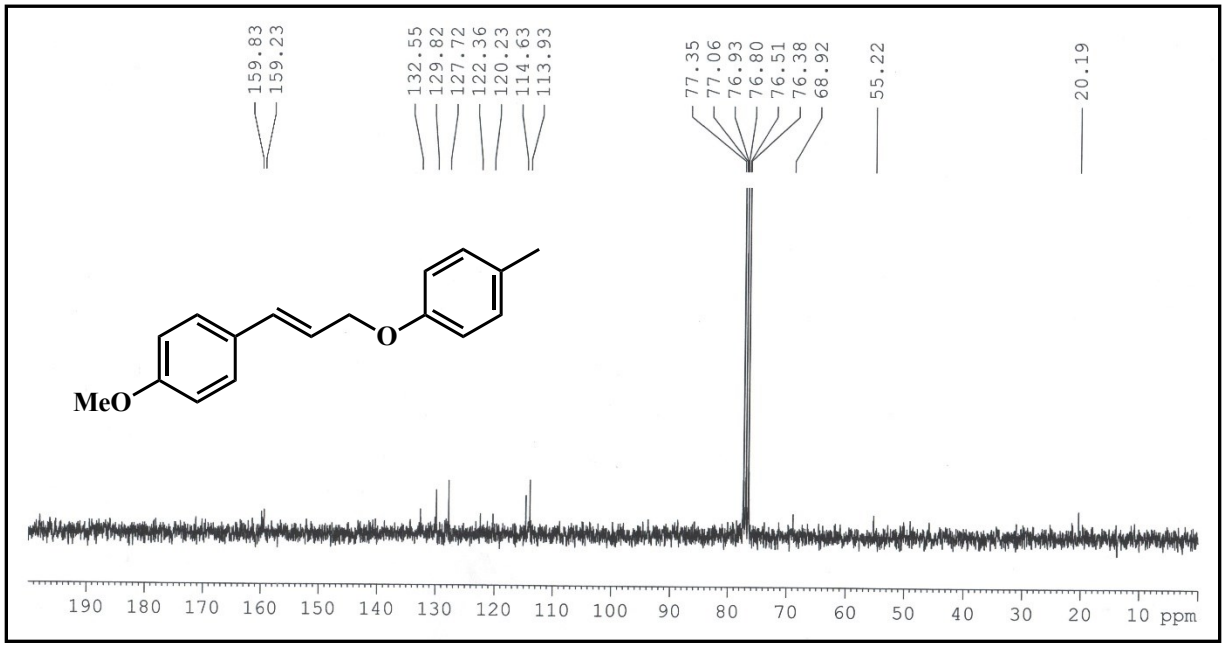


Fig. S9 ^{1}H and ^{13}C-NMR spectra of (E)-1-methoxy-4-(3-(p-tolyloxy)prop-1-en-1-yl)-benzene (3e)**.**





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