

Article

Pd-HPW/SiO₂ Bi-Functional Catalyst: Sonochemical Synthesis, Characterization, and Effect on Octahydroquinazolinone Synthesis

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Abstract: A Palladium-doped silica-supported heteropoly acid (HPW) (1%Pd-HPW/SiO₂) bi-functional catalyst was produced using ultrasonic and conventional procedures. Both forms of catalyst were characterized with distinct analytical approaches in order to access the advantages of each one. The presence of the required functional groups in the catalyst was confirmed using FT-IR. The crystallinity of ultrasonically generated 1%Pd-HPW/SiO₂ was confirmed with XRD. The existence of necessary elements in the catalyst was also suggested by XPS and EDX data. BET was used to calculate the surface area of the ultrasonically synthesized catalyst (395 m² g⁻¹), and it was found to be greater than that of the non-ultrasonic synthesized catalyst (382 m² g⁻¹). The N₂ adsorption-desorption isotherm indicated mesoporous structures. The SEM morphology at a similar magnification exhibited quite different shapes. In comparison to traditional methods, ultrasonic approaches produce higher yields in less time and use less energy. Furthermore, the effect of the preparation method of the 1%Pd-HPW/SiO₂ catalyst was extensively studied with respect to the synthesis of octahydroquinazolinones. Excellent product yields, a fast reaction time, and simple work-up methods are some peculiarities associated with the ultrasonically synthesized catalyst. The recycling study was also investigated and found suitable for up to four reaction cycles.

Keywords: 1%Pd-HPW/SiO₂ catalyst; ultrasonic; non-ultrasonic; octahydroquinazolinone



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1. Introduction

The properties and applications of catalysts are mainly correlated with the preparation process, so an adequate variety of preparation techniques can essentially determine the efficiency of the catalysts [1]. Scientists have developed varieties of synthetic techniques to prepare materials/catalysts [2]. The synthetic processes that have been used for catalyst preparation so far are the gas-phase, liquid-phase, and mixed-phase methods [3]. These methods often entail harsh reaction conditions due to the organic solvents, surfactants, and potent reducing agents, which generate plenty of harmful waste [4,5]. Additionally, the conventional techniques are also very expensive. Hence, to bypass these hazardous approaches, a greener and more cost-effective alternative method is desirable for adequate catalyst preparation.

The ultrasound-assisted method is the most valuable synthetic tool for preparing nano-sized materials; for example, Cu/Zn substitution in Malachite–Rosasite [6] and SBA-

15@ADMPT/H₅PW₁₀V₂O₄₀ were reported recently [7]. The cavitation effect was produced during the sonochemical production of a Cu/ZnO-based catalyst for methanol synthesis [8]. Ultrasound was applied to co-precipitation and the ageing phase of precipitation during preparation of a Cu/ZnO/Al₂O₃ catalyst for a water-gas shift reaction [9]. In the fabrication of the Zirconia catalyst, a high ultrasonic frequency generates the vibration of ions in a solution, rapid collisions, and spontaneous particle movement, and it eventually regulates the size of the catalyst [10].

Polyoxometalates that have been used as catalysts in various applications [11,12] are inherently multifunctional compounds of substantial structural mobility [1,2]. Heteropoly acids of Keggin form Hn [XM₁₂O₄₀] (HPA), where the most common polyoxometalates are X = Si⁴⁺, P⁵⁺ and M = Mo⁶⁺, W⁶⁺, V⁵⁺, etc. These are strong Brønsted acids and efficient redox agents. Their acid and redox properties can be tuned by varying their polyanion composition, whereas the molecular (primary) structure of HPA remains unchanged. Solid HPA causes a large change in their texture in a regulated way (secondary structure), and it can be chemically changed to add a metal function, Lewis acidity, basicity, and so on [11,12]. As multifunctional catalysts, the ability of polyoxometalates has long been recognized. Heteropoly acid (HPA) is more active than traditional solid acids, such as SiO₂, Zeolites, Al₂O₃ [13], and especially H₃PW₁₂O₄₀ (PW) or H₄SiW₁₂O₄₀ (SiW). The regeneration of HPA, however, restricts it to having a limited use as a catalyst [14]. In SiO₂ or Al₂O₃ [15], regeneration can be easily managed by heating up to 500 °C. Due to its poor thermal stability, such a regeneration technique is not feasible for HPA [16]. The efficient use of HPA as a heterogeneous catalyst could be made possible by adding certain transition metals, such as Pd or Pt, to increase its regeneration capacity [15,16]. Efficient bi-functional catalysts for alkane isomerization were thus found to be solid HPA doped with Pd and Pt [17]. A Pd-doped HPA catalyst was developed with the Showa-Denko process to produce ethane-oxidizing acetic acid [18]. The difficulty in extracting a catalyst from a product has led to economic and environmental issues, which is problematic in continuous production. Any acidic or neutral supports, such as SiO₂ [18,19], TiO₂ [20,21], ZrO₂ [22], acidic ion exchange resin, or active carbon resin, are impregnated with HPA to solve these problems [18].

The use of multicomponent reactions to synthesize octahydroquinazolinone derivatives has gained popularity due to its easy synthetic procedure, economic efficiency, and good selectivity [23]. Octahydroquinazolinone derivatives also have well-known moiety for the top medicinal agents. They have been used for antimicrobial [24], anti-inflammatory analgesic [25], anticancer [26], and antiviral [27] purposes. Pietro Biginelli first achieved the synthesis of MCRs through acid-catalyzed cyclo-condensation of aldehyde, ethyl acetoacetate, and urea, and these reactions are known as the Biginelli reactions [28]. Biginelli reactions preferably use β-diketone rather than open-chain dicarbonyl compounds to synthesize octahydroquinazolinone [29]. Much of the literature has shown the synthesis of octahydroquinazolinone using different catalysts or chemical agents, such as Conc. HCl [30], Conc. H₂SO₄ [29], trimethylsilyl chloride (TMCl) [31], SOCl₂ [32], and Lewis acids (La(OTf)₃, L₂O₃, ZrCl₄) [29,33]. However, these chemicals are associated with one or more of the following disadvantages: generation of side reactions, harsh reaction conditions, handling difficulties, and expensive costs [34–36]. In other way, heterogeneous catalysts, such as silica sulfuric acid [37] or vanadium n-propyl amino phosphate, are used because of their non-toxic nature and ability to promote selective reactions for octahydroquinazolinone synthesis [38]. In many multicomponent organic reactions, the catalysts that are needed must have the qualities of numerous active sites, nano range size, and a large surface area. To improve these qualities, materials can be subjected to an ultrasound technique. In fact, the synthesis of inorganic nanomaterials (used as catalysts) with ultrasound effects can produce abundant active sites. Since polyoxymetalate-type metal-based catalysts are made by sonochemically reducing metal ions like Pd(II), Pt(IV), Ni(II), and others [39], as a result overall morphology can be controlled. Meanwhile, solid supports and the heterogeneous

metal-based catalysts produced with sonochemical effects can provide a highly selective surface by increasing the surface area [40,41].

This study concerns the synthesis of a 1%Pd-HPW/SiO₂ catalyst with the ultrasound technique and the traditional method in order to improve the catalysts' performance in octahydroquinazoline synthesis. The performance of the catalysts was compared according to the characteristics of each methods of preparation. Both forms of catalysts were well characterized. Furthermore, the effects of the catalysts were checked with respect to the synthesis of some octahydroquinazolinone derivatives.

2. Results and Discussion

2.1. Characterization of the Pd-HPW/SiO₂ Bi-Functional Catalyst

2.1.1. FT-IR Spectroscopy

The ultrasonically and non-ultrasonically synthesized catalysts had peaks at 1066 and 1077 cm⁻¹ and at 792 and 796 cm⁻¹ in the FT-IR spectrum (Figure 1) for 1% Pd-HPW/SiO₂ with silica. In both cases, vibrations at 981 and 982 appeared at the usual positions with unchanged relative intensity due to the W=O band. The peak at 792 and 796 cm⁻¹ corresponded to the corner sharing band of W-O-W. This suggests that, regardless of the preparation process, the HPW retained the Keggin structure, which was already confirmed by our previous efforts [42,43]. The peak assigned at 1066 and 1077 cm⁻¹ may have been due to Si-O-Si stretching vibrations [42]. Some other peaks for SiO and SiO₂ may not have been visible due to the overlapping of HPW as result of impregnation with the SiO₂ support [42]. However, a band above 1600 cm⁻¹ was not observed due to the reduction of heteropoly acid after Pd loading, which is consistent with other work [44]. Furthermore, Pd does not substantially change the primary structure of heteropoly acid [44].

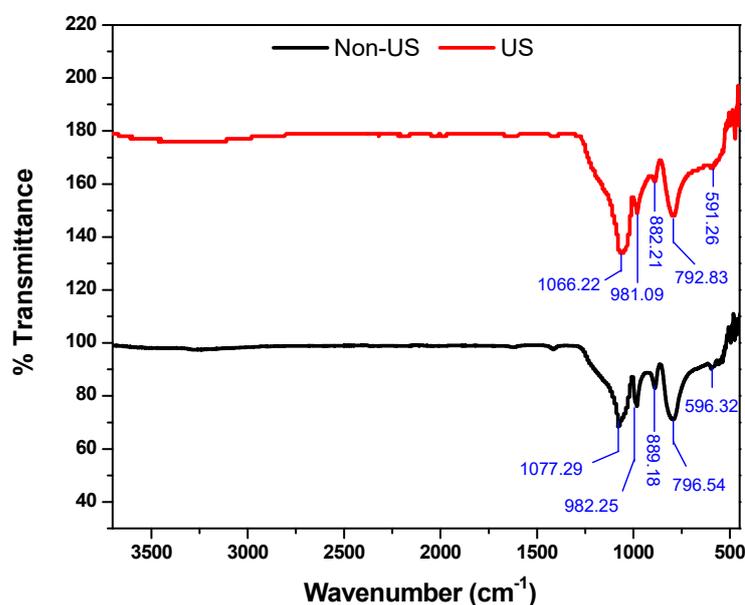


Figure 1. FT-IR analysis of the ultrasonically and non-ultrasonically synthesized 1%Pd-HPW/SiO₂ bi-functional catalysts.

2.1.2. XRD Patterns

Figure 2 delineates the XRD patterns of the ultrasonically and non-ultrasonically synthesized catalysts. It can be seen that some sharp peaks punctuated a broad peak at $2\theta \approx 13^\circ$ – 35° , which was related to amorphous silica, whereas the sharp peaks were ascribed to HPW phases. With caution, a peak at around $2\theta \approx 38^\circ$ suggested a distinct metallic palladium phase of the fcc structure and was aligned with the HPW peak, which matched with JCPDS No. 46-1043 for Pd. It may be concluded that this peak could be attributed to palladium or HPW, or that there was an overlap of the peaks. It was reported

that when the content of Pd increased from 1% to any higher level, the crystallinity of the peak became more apparent and prominent [45]. In the present case, the Pd loading was only 1 wt.%, revealing a relatively weak XRD signal. The other XRD diffractogram postulated the presence of heteropoly anions of HPW that were distributed over the SiO₂ [46]. The XRD band at $2\theta \approx 26^\circ$ could be attributed to SiO₂, which matches with JCPDS No. 41-1413 and was confirmed by our earlier work [42]. Moreover, the XRD pattern of the ultrasonically synthesized catalyst showed a somewhat higher intensity of its peaks than the non-ultrasonically synthesized catalyst, indicating that it was slightly more crystalline than the other. This was further confirmed by the FWHM values of 0.370 (25 nm) and 0.350 (22 nm) for the non-ultrasonically and ultrasonically synthesized catalysts, respectively.

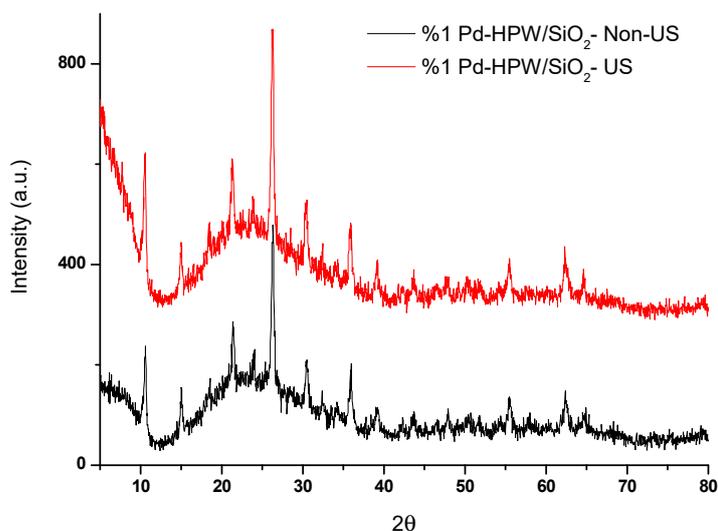


Figure 2. XRD analysis of the ultrasonically and non-ultrasonically synthesized Pd-HPW/SiO₂.

2.1.3. N₂ Adsorption-Desorption Isotherm

Figure 3 displays the nitrogen adsorption–desorption isotherm for the synthesized 1%Pd-HPW/SiO₂ (US) and 1%Pd-HPW/SiO₂ (non-US) catalysts. Both catalysts demonstrated isotherm type IV with an H₁ hysteresis loop, thus representing a mesoporous solid with non-uniform shape and size. This isotherm resembled the isotherm of silica. Since the current catalyst contained more than 90% of silica, the nature of the adsorption-desorption isotherm was justified [42,47].

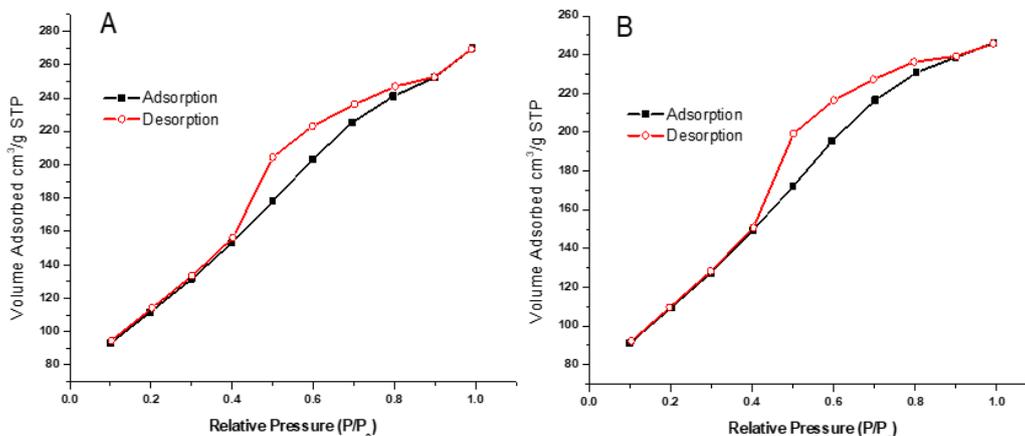


Figure 3. N₂ adsorption–desorption isotherm of the ultrasonically (A) and non-ultrasonically (B) prepared 1%Pd-HPW/SiO₂ bi-functional catalysts.

Additionally, the steep increase in nitrogen adsorption in the low-pressure region indicated the existence of micropores and mesopores in the catalysts.

The Measurements of the BET Surface Area

The BET catalyst surface was analyzed based on multiple points. It was found that the surface area of the non-ultrasonically synthesized Pd-HPW/SiO₂ was 382 m² g⁻¹, whereas it was 395 m² g⁻¹ for the ultrasonically synthesized catalyst (Table 1). Despite the slight increase in surface area of the ultrasonically synthesized catalyst, it seems that the ultra-sonication treatment did not play a significant role in the increment in the catalyst surface area.

Table 1. The texture and Pd dispersion of the catalysts studied.

Catalyst	S_{BET}^a m ² g ⁻¹	Pore volume ^b cm ³ g ⁻¹	Pore Size ^c Å
1%Pd-HPW/SiO ₂ (US)	395	0.27	18.13
1%Pd-HPW/SiO ₂ (Non US)	382	0.23	18.18

^a BET surface area. ^b Multipoint total pore volume. ^c Average BET pore diameter.

2.1.4. XPS and EDX Analysis of Non-US Pd-HPW/SiO₂ Catalyst

The XPS and EDX spectra of the non-US catalyst are shown in Figures 4 and 5, respectively. As reported in the literature [48], there are usually no substantial variations depending on the preparation method, hence the spectra of the non-US catalyst are only presented.

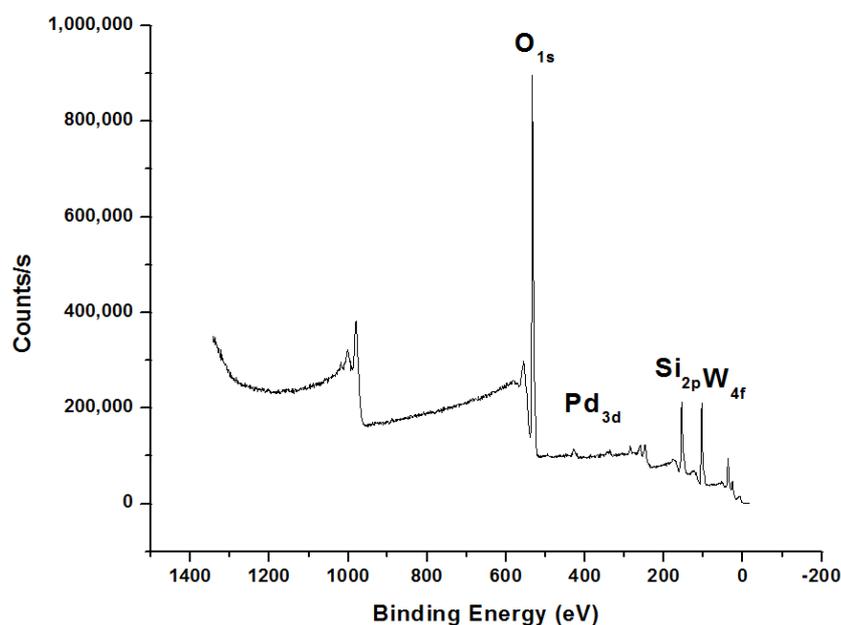


Figure 4. XPS spectra of the 1%Pd-HPW/SiO₂ bi-functional catalyst.

Both analyses identified W, Si, Pd, and all of the elements present in their stoichiometric amounts.

The chemical composition of the 1%Pd-HPW/SiO₂ catalyst was further investigated with X-ray photoelectron spectroscopy (XPS). The surveyed XPS spectrum of the 1%Pd-HPW/SiO₂ catalyst is shown in Figure 4. The spectrum was dominated by characteristic peaks of W 4f, Si 2p, Pd 3d, and O 1s, corresponding to the elements of tungsten, silicon, palladium and oxygen O 1s, respectively. The absence of other elements indicated the high purity of the examined 1%Pd-HPW/SiO₂ catalyst. Further, the EDX analysis shown in Figure 5 indicates that Pd reacted well with HPW-SiO₂. The quantitative surface composi-

tion was found to be O = 62.36%, W = 0.29%, Si = 31.59%, and Pd = 0.03%. The high percentage ratio of the O 1s peak reflects the high oxidation state of the 1%Pd-HPW/SiO₂ catalyst.

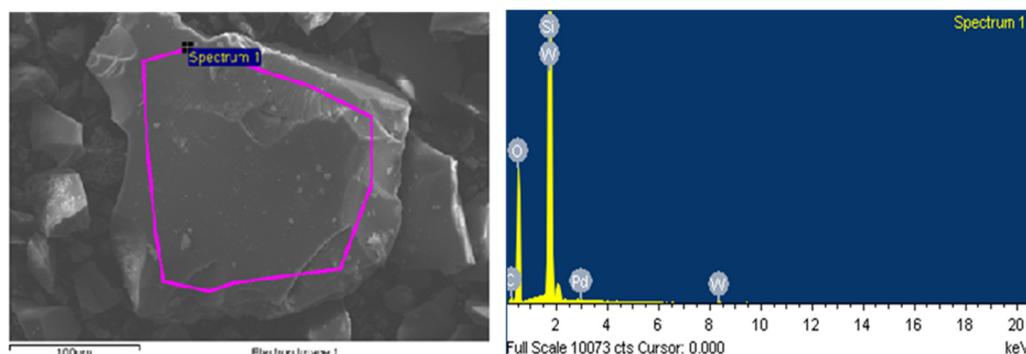


Figure 5. EDX analysis of the 1%Pd-HPW/SiO₂ bi-functional catalyst.

2.1.5. SEM Images of Pd-HPW/SiO₂

Figure 6A,B presents the SEM images for ultrasonically and non-ultrasonically synthesized Pd-HPW/SiO₂. From the images, the morphologies of the two samples were slightly different. Generally, both samples revealed an irregularly shaped aggregate and diverse particles of different sizes and shapes. In addition, it is worth noting that the particle size of 1%Pd-HPW/SiO₂ (US) was smaller than that of 1%Pd-HPW/SiO₂ (non-US). Despite the different sizes of the particles in the two samples, their surface areas were very close (Table 1). A portion of the 1%Pd-HPW/SiO₂ (US) catalyst's particles had a smaller size, which played a role in the fact that the surface area of the catalyst was close to that of the other sample of 1%Pd-HPW/SiO₂ (non-US).

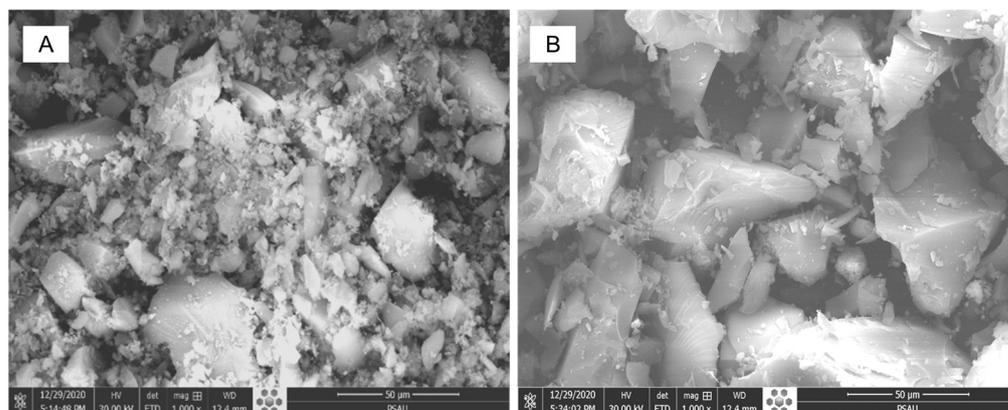


Figure 6. SEM images of the ultrasonically (A) and non-ultrasonically (B) prepared 1%Pd-HPW/SiO₂ bi-functional catalysts.

2.2. Study of the Attributes of Ultrasound Effects Significant to the Preparation of 1%Pd-HPW/SiO₂

The 1%Pd-HPW/SiO₂ catalysts were prepared with the conventional (with stirring) and ultrasonic methods. It took 1 h to prepare the desired catalyst with the non-ultrasonic method with an obtained yield of 80%. On the contrary, the preparation of the same catalyst with the ultrasonic method resulted in a high yield of 95% at the expense of only 20 min (Table 2).

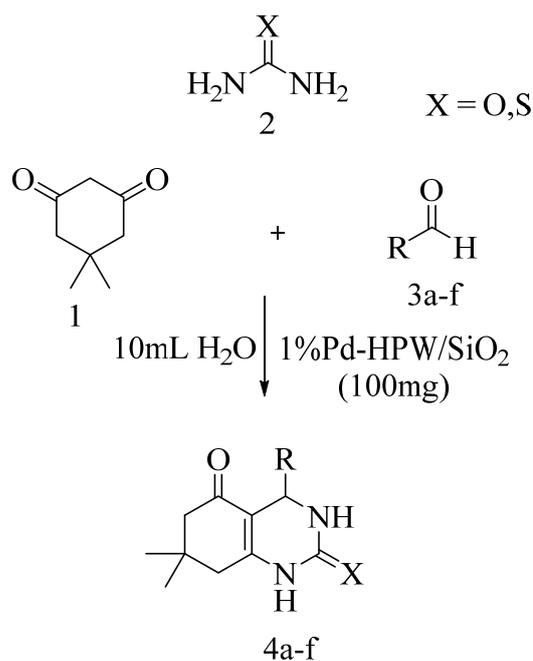
Table 2. Synthesis of 1%Pd-HPW/SiO₂ with the non-ultrasonic (non-US) and ultrasonic (US) methods.

Entry	Reaction Time		Yield (%)		Energy Utilized (kJ/g)		Energy Saved (%)
	NUS	US	NUS	US	NUS	US	
1	1 h	20 min	80	95	1.64	0.92	44

The superiority of one of the two methods was further validated by the energy measurements, as shown in Table 2. In the non-ultrasonic method, the total energy consumption was found to be 1.64 kJ/g, while only 0.92 kJ/g was used for the ultrasonic method. Thus, by using an ultrasonic procedure, a total of 44% of the energy was saved. (Yield and energy calculations are available in Supplementary Materials from page no S20–S22). The ultrasonic method's excellent yield and energy efficiency were attributed to the extreme microscopic conditions created by rapid bombardment and material collapse, which eventually formed small particles within the reaction system [49].

2.3. Catalytic Activity

In a multicomponent reaction, the catalytic activity of the ultrasonically and non-ultrasonically prepared 1% Pd-HPW/SiO₂ was assessed for the synthesis of octahydroquinazolinone (4a–f) from dimedone (1 mmol), urea/thiourea (1.5 mmol), and aldehydes (1 mmol) (Scheme 1).

**Scheme 1.** 1%Pd-HPW/SiO₂ catalyzed Octahydroquinazolinone synthesis.

Initially, the hit and trial method was adopted in order to obtain the compound with the highest yield with both catalyst forms. The compound containing 4-fluorobenzaldehyde was chosen as the model compound since it produced the maximum yield when utilizing the ultrasonically generated catalyst.

The effects of the ultrasonically and non-ultrasonically synthesized catalysts are presented in Table 3 for the synthesis of model compound 4a in aqueous conditions.

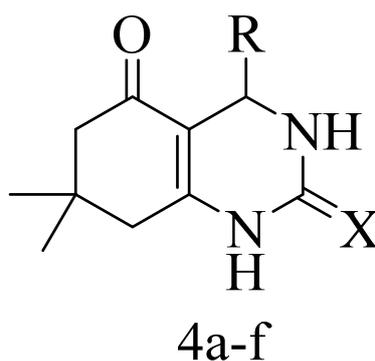
Table 3. Effects of the 1%Pd-HPW/SiO₂ catalyst for the synthesis of the octahydroquinazolinone model (4a) ^a.

Entry	Catalyst (mg)	(US)	Yield (%) ^b (NON-US)	Time (Minute)
1	-	Trace	Trace	120
2	50	72	67	60
3	70	78	70	40
4	80	90	85	30
5	100	97	93	20
6	120	92	89	20

^a Dimedone (1 mmol), 4-fluoro benzaldehyde (1 mmol), and urea (1.5 mmol) with 100 mg of 1%Pd-HPW/SiO₂ as a catalyst in 10 mL of distilled water at 100 °C. ^b Yield of isolated products.

In the absence of catalysts, trace amounts of the target model-octahydroquinazolinone produced by reacting dimedone (1 mmol), urea (1.5 mmol), and 4-fluorobenzaldehyde (1 mmol)—were produced for up to 2 h. (Table 3, entry 1). The conversion of the desired model compound was achieved by increasing order of the catalyst load (Table 3, entries 2–5). A maximum yield was found with the model compound when utilizing 100 mg of the catalyst for with only 20 min of reaction time (Table 3, entry 5). It also discovered that with a further rise in the catalyst load (120 mg), no improvement in the yield was observed when using the ultrasonically (US) and non-ultrasonically synthesized 1%Pd-HPW/SiO₂ (entry 6, Table 3). Therefore, it was assumed that 100 mg would be the optimal quantity with which to obtain the target octahydroquinazolinone.

The use of different aldehydes and urea/thiourea with dimedone in a typical multi-component reaction to obtain a series of octahydroquinazolinones (4a-f) was investigated (Table 4, entries 1–6). In general, the yield was better under the influence of the ultrasonically synthesized catalyst than with the non-ultrasonic form for all of the products listed (Table 4, entries 1–6). The better performance of the ultrasonically synthesized catalyst could be attributed to the moderately elevated BET surface area (Table 1) and small particle size compared to the non-ultrasonically prepared catalyst (Figure 6).

Table 4. The synthesis of octahydroquinazolinones (4a-f) derivatives catalyzed with 1%Pd-HPW/SiO₂.

Entry	R	X	Product	Time (min)	Yield (%) ^{a,b}		M.P (°C)		Ref. No.
					US	Non-US	Observed	Reported	
1	4-(F)-C ₆ H ₄	O	4a	20	97	94	268–270	274–75	[50]
2	3,4,5-(CH ₃ O)-C ₆ H ₂	O	4b	25	95	92	135–137	139–140	[51]
3	2-(CH ₃)-C ₆ H ₄	O	4c	25	93	91	238–240	240–241	[51]
4	4-(F)-C ₆ H ₄	S	4d	20	91	90	261–263	260–262	[33]
5	3,4,5-(CH ₃ O)-C ₆ H ₂	S	4e	30	89	86	132–134	134–136	[52]
6	2-(CH ₃)-C ₆ H ₄	S	4f	25	86	84	156–158	-	-

^a All reactions were performed with 100 mg of 1%Pd-HPW/SiO₂ as a catalyst in a stoichiometric ratio of each reacting species in 10 mL of distilled water. ^b Isolated yields.

Under optimized conditions, the investigation scrutinized the substrate selection (aldehydes, urea, and thiourea). The compound with a monosubstituted electron-withdrawing group (**4a**, **4d**) displayed the highest yield in just 20 min (Table 4, entry 1) compared to the compound with an electron-donating substitution (Table 4, entries 2, 3 and 5, 6). In addition, the compounds with urea components gave a higher yield than their thiourea counterparts. Interestingly, the catalyst's performance was superior in terms of the yield and reaction time for all of the compounds studied [33,50,51].

The significance of the catalyst (1%Pd-HPW/SiO₂) was further evaluated by comparing it with tungstophosphoric acid (HPW) and silica-supported tungstophosphoric acid (HPW/SiO₂) with respect to the synthesis of the model compound. When the reaction was performed and triggered with HPW and HPW/SiO₂, the yield was found to be 71 and 88%, respectively, at the expense of 3 and 1.5 h (Table 5, entries 1,2). However, the yield abruptly increased with the introduction of 1% Pd, and the reaction was completed in just 20 min (Table 5, entry 3). The improvement in the results observed with 1%Pd-HPW/SiO₂ could be attributed to the active sites of the catalyst being exposed to the reactant more uniformly, resulting in a higher product yield.

Table 5. Catalyst optimization for the synthesis of the model octahydroquinazolinone **4a** ^a.

Entry	Catalyst	Time	Yield ^b
1	HPW	3 h	71
2	HPW/SiO ₂	1.5 h	88
3	1%Pd-HPW/SiO ₂	20 min	97

^a Dimedone (1 mmol), 4-fluoro benzaldehyde (1 mmol), and urea (1.5 mmol) with 100 mg of 1%Pd-HPW/SiO₂ as a catalyst in 10 mL of distilled water at 100 °C. ^b Yield of isolated products.

2.4. Catalyst Reusability

The reusability of the sonochemically synthesized catalyst (1% Pd-HPW/SiO₂) in the model reaction under identical reaction conditions was checked in four runs. In each cycle, the catalyst was dried in an oven before being reused in the subsequent reaction.

The compound yield was marginally reduced after each run owing to the decrease in the amount of catalyst after every reaction (Table 6).

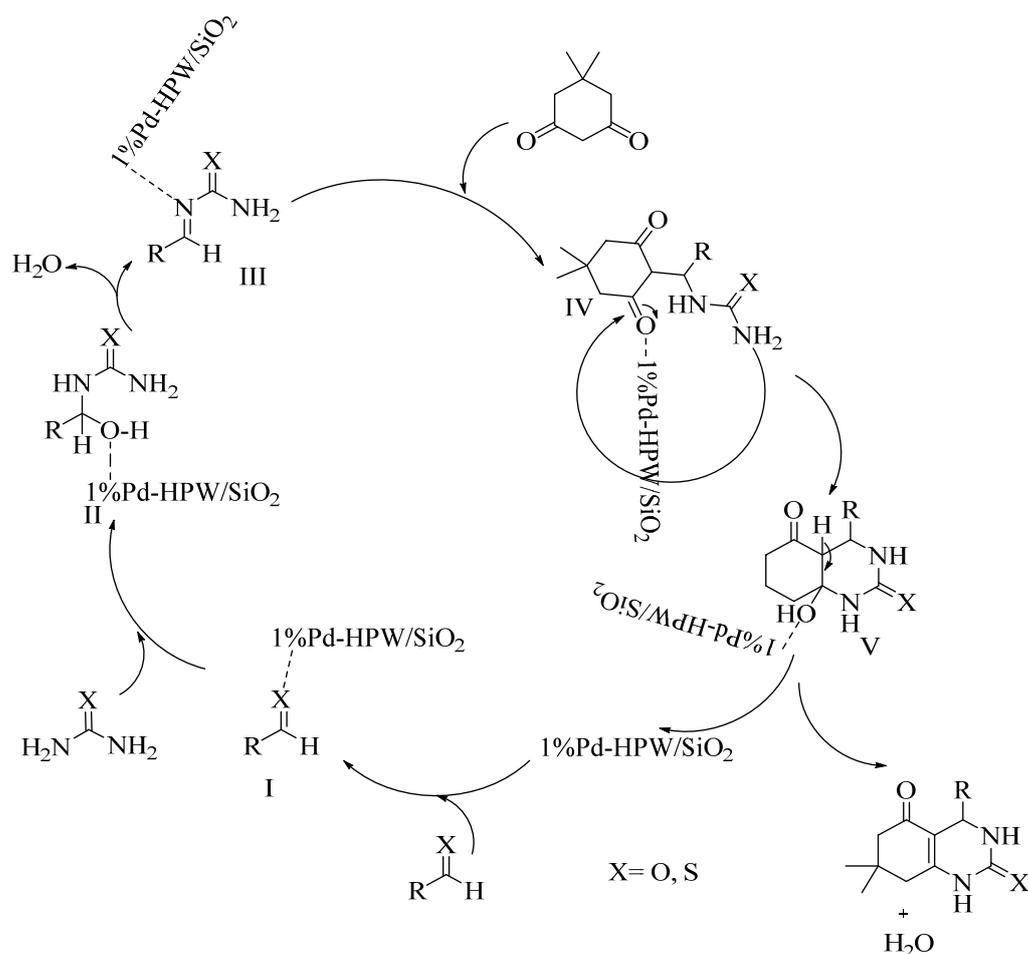
Table 6. Reusability studies of the 1%Pd-HPW/SiO₂ catalyst ^a.

Run	Time (min)	Yield (%)	Catalyst Amount (mg)
1	20	97	100
2	20	96	90
3	20	95	83
4	20	93	77

^a Reactions performed under optimized conditions reactions in a stoichiometric ratio of each reacting species with 100 mg of 1%Pd-HPW/SiO₂ as a catalyst.

2.5. Probable Mechanism

A predicted mechanism that was verified by the 1% Pd-HPW/SiO₂-catalyzed octahydroquinazolinone synthesis is shown in Scheme 2. The mechanism begins with the catalyst activating the carbonyl group of an aldehyde to form intermediate I, followed by condensation with urea/thiourea to form iminium intermediate (III) by removing the water molecule, and finally, it reacts with dimedone to form another intermediate (IV). The removal of another water molecule and the subsequent cyclization result in the desired octahydroquinazolinone.



Scheme 2. Proposed mechanism for octahydroquinazolinone synthesis.

3. Materials and Methods

3.1. Materials and Instrumentations

The Thermo Science iD5 ATR diamond Nicolet iS 5 FT-IR Spectrometer was used to record the FT-IR spectra for the catalyst. The data spacing with a single beam with the DOMINIC software was 0.482 cm⁻¹. The catalyst XRD diffractogram was defined by using an X-ray diffractometer from ULTIMA NR, Tokyo, Japan. A scanning electron microscope (Business (FEI), Model: Quanta FEG 250, GH Eindhoven, Holland) was used to assess the morphological attributes of the catalyst. The specially designed Thermocraft built-in tube furnace was used for catalyst calcination. Catalyst synthesis was carried out using the UP 20Ht (serial no. 351219415), a Hielscher ultrasonic processor with a 26 kHz frequency and a 200 W ultrasonic probe (dimensions = 300 mm 190 mm 90 mm), which was produced in Germany. The BET surface area of the catalyst was assessed with QuantachromeASiQwin, version 5.2., BOYNTON BEACH, FL, USA. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Waltham, MA, USA) was performed by using a flood gun for charge compensation. The analysis of the XPS spectra and data was performed with the Thermo Avantage software (version 5.932). Energy-dispersive X-ray spectroscopy (EDX) was used for an elemental analysis of the prepared catalyst (Jeol, Tokyo, Japan, Model, ASEM-6360A). The ¹H-NMR and ¹³C spectra of the synthesized octahydroquinazolinones were recorded with a Bruker-Plus (400 MHz) NMR instrument, with tetramethylsilane as an internal standard. All of the chemicals used in this study were bought from Sigma Aldrich in the United States (Burlington, MA, USA). These compounds were employed in the studies without being purified beforehand.

3.2. Preparation of the 1%Pd-HPW/SiO₂ Bi-Functional Catalyst

A magnetic stirrer was used for the non-ultrasonic method and a 26 kHz ultrasonic reactor was used for the ultrasonic method to prepare the catalyst. In the non-ultrasonic method, a 200 mL beaker and 2.96 g of 25% HPW/SiO₂ powder with a 0.02 M Pd(OAc)₂ solution in benzene (14 mL) were stirred at room temperature for 1 h in a magnetic stirrer, followed by gradual evaporation of the benzene in a rotary evaporator. The procedure was repeated for 20 min in a specially built jacketed flask using an ultrasonic reactor. The catalyst was calcined under vacuum at 150 °C/0.1 kPa after drying and then reduced in an oven for 2 h with a hydrogen flow at 250 °C.

3.3. General Procedure for the Synthesis of Octahydroquinazoline Derivatives (4a–f)

In a 100 mL round-bottom flask, a mixture of dimedone (1) (1 mmol), urea/thiourea (2) (1.5 mmol), and different aldehydes (3) (1 mmol) was stirred in the presence of an optimized amount (100 mg) of 1%Pd-HPW/SiO₂ catalyst in 10 mL of water at 100 °C. In a solvent system of ethyl acetate and acetone (3:7), the progress of the reaction was continuously monitored.

4-(4-Fluorophenyl)-7,7-dimethyl-1,2,3,4,5,6,7,8-octahydroquinazoline-2,5-dione (4a). White solid; FT-IR (cm⁻¹, ATR); 3433 and 3336 (NH), 1594 (C=O, ring), 1461 (C=O, urea), 1372 (C=C); ¹H NMR (DMSO-*d*₆, 400 MHz): 11.88 (s, 1H, NH), 9.96 (s, 1H, NH), 8.08–8.08 (d, 1H, *J* = 2.84 Hz, Ar-H), 7.90 (s, 1H, Ar-H), 7.25–6.94 (m, 2H, Ar-H), 5.49 (1H, s, CH), 2.40–2.37 (d, 2H, *J* = 13.88 Hz, CH₂), 2.28–2.21 (d, 2H, *J* = 25.48 Hz, CH₂), 1.07 (s, 6H, 2 × CH₃); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 195.55 (C=O), 190.55 (NC=O), 162.44 (C-F), 159.79 (NC=C), 133.65, 133.62, 128.30, 115.52, (ArC), 101.41 (OC-C=C), 64.31 (C-NH), 50.66 (1C, CH₂), 42.94 (1C, CH₂), 31.40 (1C, CH), 28.25 (2CH₃); ¹³C-DEPT-135 NMR (DMSO-*d*₆, MHz, δ ppm) 130.32, 128.51, 115.10, 114.90, −50.46, −47.01, 31.11, 30.78, 29.09, 28.23, 26.96.

4-(3,4,5-Trimethoxy)-7,7-dimethyl-1,2,3,4,5,6,7,8-octahydroquinazoline-2,5-dione (4b). Light yellow solid; FT-IR (cm⁻¹, ATR); 3305 and 2948 (NH), 1658 (C=O, ring), 1457 (C=O, urea), 1361 (C=C); ¹H-NMR (DMSO-*d*₆, 400 MHz): 9.86 (s, 1H, NH), 7.24 (s, 1H, NH), 6.60 (s, 1H, Ar-H), 6.40 (s, 1H, Ar-H), 4.46 (1H, s, CH), 3.68 (s, 9H, 3 × OCH₃), 2.55–2.51 (d, 2H, *J* = 12.56 Hz, CH₂), 2.29–2.25 (d, 2H, *J* = 16.25 Hz, CH₂), 2.12–2.08 (d, 2H, *J* = 16.28 Hz, CH₂), 1.03–0.92 (s, 6H, 2 × CH₃); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 197.10 (C=O), 163.76 (NC=O), 152.76 (C-OCH₃), 140.39 (NC=C), 136.27, 114.67 (ArC), 105.80 (OC-C=C), 60.41 (3C, 3 × OCH₃), 56.19 (1C, CH), 50.46 (1C, CH₂), 32.28 (1C, CH₂), 29.15 (1C, CH), 26.66 (2CH₃); ¹³C-DEPT-135 NMR (DMSO *d*₆, MHz, δ ppm) 105.80, 60.41, −50.46, −40.09, 31.66, 29.15, 26.66.

4-(*o*-Tolyl)-7,7-dimethyl-1,2,3,4,5,6,7,8-octahydroquinazoline-2,5-dione (4c). Light yellow solid; FT-IR (cm⁻¹, ATR); 3299 and 2966 (NH), 1628 (C=O, ring), 1547 (C=O, urea), 1480 (C=C); ¹H-NMR (DMSO-*d*₆, 400 MHz): 10.22 (s, 1H, NH), 9.33 (s, 1H, NH), 7.92 (s, 1H, Ar-H), 7.03–6.86 (m, 3H, Ar-H), 4.59 (1H, s, CH), 2.68–2.41 (s, 2H, CH₂), 2.31–2.03 (s, 2H, CH₂), 1.99 (3H, s, CH₃), 1.02–0.85 (s, 6H, 2 × CH₃); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 197.19 (C=O), 163.36 (NC=O), 143.91 (NC=C), 136.78, 130.04, 126.46, 126.22, 116.07, 114.91 (ArC), 101.48 (OC-C=C), 60.49 (1C, CH), 50.47 (1C, CH₂), 47.33 (1C, CH₂), 32.29 (1C, CH₂), 29.16 (1C, CH), 26.63 (2CH₃), 19.82 (1C, CH₃); ¹³C-DEPT-135 NMR (DMSO-*d*₆, MHz, δ ppm) 130.04, 127.99, 126.46, 60.49, −50.47, −47.19, 27.62, 26.63, 19.82.

4-(4-Fluoro)-7,7-dimethyl-5-oxo-1,2,3,4,5,6,7,8-octahydroquinazoline-2-thione (4d). White solid; FT-IR (cm⁻¹, ATR); 3383 and 2952 (NH), 1647 (C=O, ring), 1511 (C=S, thiourea), 1456 (C=C); ¹H-NMR (DMSO-*d*₆, 400 MHz): 8.01 (s, 1H, NH), 7.19 (s, 1H, NH), 7.17–6.96 (m, 4H, Ar-H), 5.92 (1H, s, CH), 2.337–2.331 (s, 4H, 2 × CH₂), 1.03–0.90 (s, 6H, 2 × CH₃); ¹³C-NMR (DMSO-*d*₆, 100 MHz): δ 196.57 (C=O), 187.69 (NC=S), 163.44 (NC=C), 140.91, 137.39, 128.59, 128.52, 115.10 (Ar C), 114.93 (OC-C=C), 59.31 (1C, CH), 50.46 (1C, CH₂), 47.01 (1C, CH₂), 32.34 (1C, CH₂), 31.77 (1C, CH), 28.24, 26.96 (2CH₃); ¹³C-DEPT-135 NMR (DMSO-*d*₆, MHz, δ ppm) 130.32, 128.51, −50.46, −47.01, 31.11, 30.78, 29.09, 28.23, 26.96.

4-(3,4,5-Trimethoxy)-7,7-dimethyl-5-oxo-1,2,3,4,5,6,7,8-octahydroquinazoline-2-thione (4e). Light yellow solid; FT-IR (cm⁻¹, ATR); 3313 and 2944 (NH), 1660 (C=O, ring), 1509 (C=S,

thiourea), 1455 (C=C); $^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz): 8.12 (s, 1H, NH), 7.29 (s, 1H, NH), 6.99–6.83 (m, 1H, Ar-H), 6.22 (s, 1H, Ar-H), 5.84 (1H, s, CH), 2.51–2.50 (t, 2H, $J = 3.44$ Hz, CH_2), 2.32 (s, 2H, CH_2), 1.10–0.82 (s, 6H, $2 \times \text{CH}_3$); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 197.09 (C=O), 188.25 (NC=S), 152.81 (NC=C), 137.13, 135.39, 114.88, 114.68, 105.81 (ArC), 104.19 (OC-C=C), 60.45 (1C, CH), 56.00 (3C, OCH_3), 46.95 (1C, CH_2), 31.74 (1C, CH_2), 28.13 (1C, CH), 26.67 (2CH_3); $^{13}\text{C-DEPT-135 NMR}$ (DMSO- d_6 , MHz, δ ppm) 105.81, 104.19, 60.46, 56.00, -50.46 , -46.96 , 31.40, 28.13, 26.13.

4-(*o*-Tolyl)-7,7-dimethyl-5-oxo-1,2,3,4,5,6,7,8-octahydroquinazoline-2-thione (**4f**). Light yellow solid; FT-IR (cm^{-1} , ATR); 3348 and 2954 (NH), 1657 (C=O, ring), 1614 (C=S, thiourea), 1460 (C=C); $^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz): 10.22 (s, 1H, NH), 9.54 (s, 1H, NH), 7.04–6.86 (m, 4H, Ar-H), 5.83 (1H, s, CH), 2.68–2.51 (m, 2H, CH_2), 2.26–2.03 (m, 2H, CH_2), 1.02–0.85 (s, 6H, $2 \times \text{CH}_3$); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 197.22 (C=O), 186.87 (NC=S), 163.38 (NC=C), 143.91, 138.79, 136.78, 135.00, 130.05, 125.53, 116.07 (Ar C), 101.48 (OC-C=C), 60.49 (1C, H), 50.47 (1C, CH_2), 47.09 (1C, CH_2), 32.29, 28.14, 26.62, 19.81 (1C, CH_3); $^{13}\text{C-DEPT-135 NMR}$ (DMSO- d_6 , MHz, δ ppm) 130.05, 127.99, 125.53, 124.99, 60.50, -50.47 , -47.09 , 29.16, 28.14, 26.62, 20.51.

Details of spectroscopic data are available from Figure S1–Figure S18 in Supplementary Materials.

4. Conclusions

In conclusion, 1%Pd-HPW/SiO₂ catalysts were prepared with both ultrasonic and non-ultrasonic methods. Both catalysts were analyzed in order to determine their qualitative characteristics. The ultrasonic method was found to be a moderately superior, more cost-effective, less time-consuming, high-yielding, and energy-saving process. The synthesis of octahydroquinazolinone derivatives was investigated and compared when using both of the catalysts. The ultrasonic methodology presented here offers attractive features in terms of product yield, reaction time, and recyclability when compared with non-ultrasonic catalysts, as well as with other catalysts that have a wide scope in organic synthesis. Moreover, this is a simple procedure that involves aqueous conditions combined with easy recovery of the catalyst, which makes this method economically and environmentally safe. In future research, the bi-functional properties of Pd doping on heteropoly acid with silica support could be used in various organic syntheses.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111273/s1>. Figure S1: **4a** $^1\text{H-NMR}$, Figure S2: **4a** $^{13}\text{C-NMR}$, Figure S3: **4a** $^{13}\text{C-DEPT 135 NMR}$, Figure S4: **4b** $^1\text{H-NMR}$, Figure S5: **4b** $^{13}\text{C-NMR}$, Figure S6: **4b** $^{13}\text{C-DEPT 135 NMR}$, Figure S7: **4c** $^1\text{H-NMR}$, Figure S8: **4c** $^{13}\text{C-NMR}$, Figure S9: **4c** $^{13}\text{C-DEPT 135 NMR}$, Figure S10: **4d** $^1\text{H-NMR}$, Figure S11: **4d** $^{13}\text{C-NMR}$, Figure S12: **4d** $^{13}\text{C-DEPT 135 NMR}$, Figure S13: **4e** $^1\text{H-NMR}$, Figure S14: **4e** $^{13}\text{C-NMR}$, Figure S15: **4e** $^{13}\text{C-DEPT 135 NMR}$, Figure S16: **4f** $^1\text{H-NMR}$, Figure S17: **4f** $^{13}\text{C-NMR}$, Figure S18: $^{13}\text{C-DEPT 135 NMR}$.

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