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Palladium Nanoparticles in Water: A Reusable Catalytic System for the Cycloetherification or Benzannulation of α-Allenols

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Abstract: A convenient ligand-free catalytic system has been developed for the chemoselective cyclization reaction of various α-allenol derivatives by palladium nanoparticles (PdNPs) in an aqueous reaction medium.

Keywords: allenes; cyclization; environmental chemistry; heterogeneous catalysis; palladium

Allenes, a class of compounds with two cumulative carbon-carbon double bonds, are versatile synthetic intermediates in organic synthesis.[1] Metal nanoparticles (NPs) have recently received considerable attention in organic synthesis because of their efficient catalytic activity.[2] In contrast, there is lack of information about the reactivity of the allene moiety in the presence of metal NPs. Among the different metallic nanocatalysts, palladium nanoparticles (PdNPs) have generated a huge interest.[3] Traditional Pd-catalyzed reactions often require the use of expensive and unstable ligands. Thus, the use of ligand-free heterogeneous Pd catalysts is highly desirable. Besides, the use of heterogeneous catalysts considerably reduces the residual metal impurities in the products. The solvent used for the catalytic reaction is very important from the perspective of preservation of the integrity of the nanocatalytic species. Water has gained a lot of attention in the recent times because of the appealing properties of organic reactions in aqueous media from both the economical and "green chemistry" points of view.[4]

The dihydrofuran motif has attracted much interest because of both the biological activity of naturally occurring representatives as well as its synthetic versatility as a building block.[5] Transition metal-catalyzed cycloetherification of allenols is one of the most rapid and convenient methods for the preparation of oxacycles.[6] The synthesis of the relevant carbazole nucleus[7] has also been accomplished through precious metal-catalyzed carbocyclization/dehydration of allenols.[8] However, the expensiveness of gold and platinum catalysts makes their use often impractical in larger scale synthesis. Besides, the previously reported methods are homogeneous which circumvents the noble metal catalyst recycling, thus diminishing their applications. It has been reported for classical C–C bond-forming reactions that the use of water instead of organic solvents improved the catalytic activity of PdNPs, because palladium clusters which could be stabilized in water were found to be the catalytically active species for ligand-free palladium-catalyzed cross-coupling reactions.[9] We envisioned that the oxycyclization or benzannulation of the allenol moiety might be achieved utilizing a reusable metal catalyst in water. Herein, we present a convenient cyclization of allenols towards the preparation of dihydrofurans and carbazoles catalyzed by PdNPs.[10]

To test the reactivity of the α-allenol moiety, several sets of conditions were screened. Allene **1a** was chosen as a model substrate for the PdNPs-catalyzed oxycyclization reaction. There are several key experimental parameters that determine the formation of PdNPs including reducing agent, solvent, surfactant, and temperature. There are also two different approaches for the preparation of PdNPs, namely, *in situ* and precatalytic generation. In our typical optimized

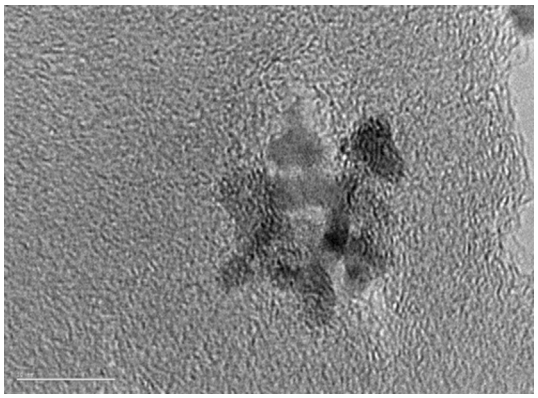
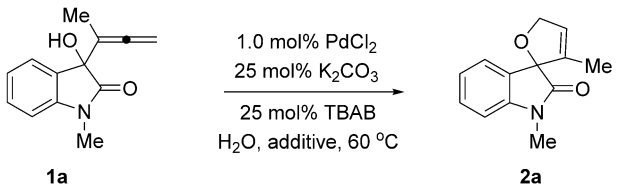


Figure 1. TEM image (JEOL-JEM-2100) of the pre-generated PdNPs (magnification = 600000).

generation of PdNPs, $PdCl_2$ was used as the Pd precursor, K_2CO_3 was selected as the reducing agent, water was used as the solvent, and TBAB (tetrabutylammonium bromide) as the surfactant. The solution of $PdCl_2$ turns into a black heterogeneous mixture due the presence of both K_2CO_3 and TBAB, which implied the formation of PdNPs as checked by using transmission electron microscopy (TEM) as analytical technique (Figure 1). Disappointingly, the reaction of allenol **1a** in the presence of PdNPs did not occur, recovering unaltered the starting material. Happily, the addition of a stoichiometric amount of phenol to the reaction system, results in an unanticipated benefit for the cycloetherification reaction. While PdNPs generated *in situ* in the presence of phenol could catalyze the cycloetherification reaction of **1a** to 2,5-dihydrofuran **2a** in a very poor 3% yield, the pre-generated PdNPs in the presence of phenol gave the desired product **2a** in a more promising 10% yield (Table 1, entry 1). Among the different phenol derivatives tested, 4-bromophenol was encountered as the better performance, rendering **2a** in an 80% yield (Table 1, entry 4). 4-Bromophenol was recovered unaltered as stoichiometric product at the end of the reaction. No phenol derivative was identified as a side reaction product. The palladium source $PdCl_2$ was used in 1.0 mol%. The conversion of α-allenol **1a** to oxacycle **2a** at 20 °C is less than 5%, but it can reach up to 80% at 60 °C (reaction time 1 h, additive: 4-bromophenol). Consequently, it may be inferred that higher temperature is beneficial to the catalytic activity of the PdNPs.

Table 1. PdNPs-catalyzed oxycyclization reaction of α-allenol **1a**.[a]



1a **2a**

Entry	Additive	Time [h]	Yield [%][b]
1	phenol	3.5	10
2	4-nitrophenol	24	11
3	4-methoxyphenol	4	39
4	4-bromophenol	3	80

[a] A precatalytic approach was used for the generation of the palladium nanoparticles.

[b] Yield of pure, isolated product **2a** after silica gel chromatography with correct analytical and spectral data.

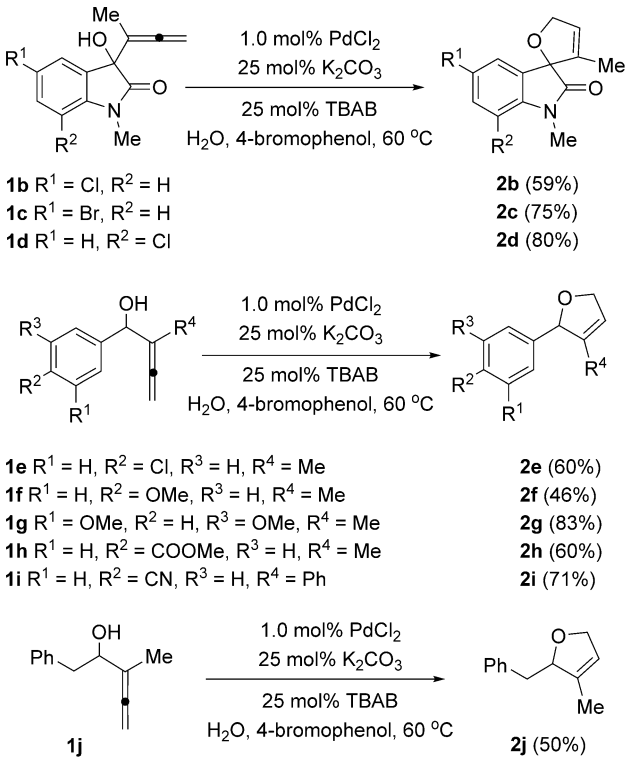
Under the present study it appears that the K_2CO_3 should act as the reducing agent to form the PdNPs from the pre-catalyst $PdCl_2$.[11] To prove this, the cyclization reaction of α-allenol **1a** was performed in the absence of K_2CO_3 under otherwise identical conditions. In the event, just 5% yield of the desired product **2a** was isolated after 3 h of reaction. The PdNPs were not formed in the absence of K_2CO_3 as in this case no visual formation (non-existence of blackening at the reaction mixture) was observed and little reaction took place.

In the absence of 4-bromophenol the reaction of allenol **1a** in the presence of PdNPs did not occur, thus highlighting the crucial role of this additive in our catalytic system. This result suggests that the phenol acts as a ligand to the palladium active species. The proposed charge transfer interaction between PdNPs and the aromatic ring of 4-bromophenol has been invoked based on previous literature reports on cation-π interaction.[12]

It is well known that the use of a stabilizer is essential to prevent agglomeration of the metal NPs.[13] Tetraalkylammonium stabilizers act through electrostatic and steric interactions. Taking into account the poor results in the absence of TBAB, it should impart electrosteric (combination of steric and electrostatic) stabilization.

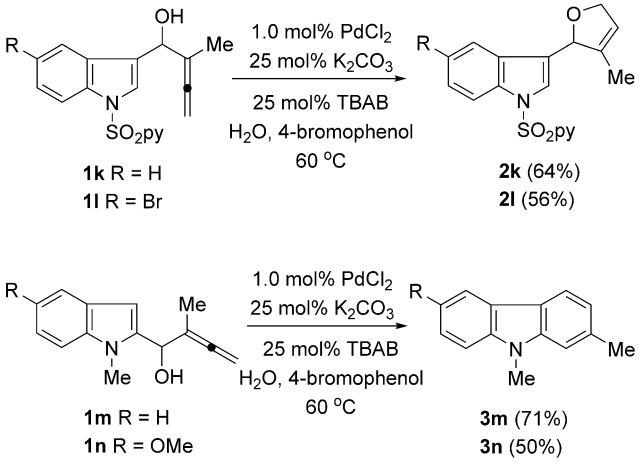
With the optimized reaction conditions in hand we then examined the scope and generality of the PdNPs-catalyzed method. Various alkyl- and aryl-substituted α-allenols **1b–j** were reacted to give a range of 2,5-dihydrofurans **2b–j**, serving the above process as a general approach to 2,5-dihydrofurans (Scheme 1). Both electron-donating (OMe) and electron-withdrawing substituents (Cl, Br, COOMe, CN) on the aromatic rings were tolerated. The above observation points to the great activity under mild conditions of nanosized palladium particles as heterogeneous catalyst in aqueous environment.

Next, the challenging α-hydroxyallenyl-tethered indoles **1k–n** were selected as systems to explore the catalytic activity of PdNPs. α-Hydroxyallenyl C-3 tethered indoles **1k** and **1l** reacted to afford cycloetherification products **2k** and **2l** in reasonable yields



Scheme 1. Synthesis of 2,5-dihydrofurans **2b–i** through PdNPs-catalyzed oxycyclization reaction of α-allenols **1b–i**, **2b**: 1.5 h; **2c**: 3 h; **2d**: 2 h; **2e**: 3.5 h; **2f**: 4 h; **2g**: 6 h; **2h**: 8 h; **2i**: 2 h; **2j**: 3 h.

(Scheme 2). The above transformation (Scheme 1 and Scheme 2) tolerates precursors that contain Cl- and Br-substituted aryl rings (**1b–e** and **1l**), which could suffer a Heck-type reaction with the allene moiety. Interestingly, when α-hydroxyallenyl C-2 tethered in-



Scheme 2. Synthesis of 2,5-dihydrofurans **2k**, **l** and carbazoles **3m**, **n** through PdNPs-catalyzed cyclization reaction of α-allenols **1k–n**, **2k**: 24 h; **2l**: 24 h; **3m**: 3.5 h; **3n**: 5 h; py = 2-pyridyl.

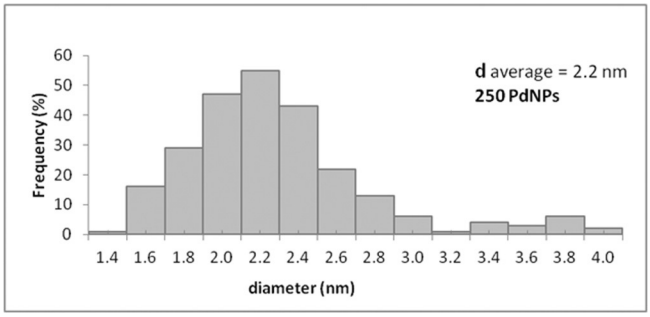


Figure 2. Histogram of the pre-generated PdNPs.

doles **1m** and **1n** were employed as substrates, the reaction failed to afford 2,5-dihydrofuran products, and carbazoles **3m** and **3n** were obtained instead (Scheme 2). For thoses cases, C-cyclization was favoured over O-cyclization. Besides, the PdNPs-catalyzed oxy- or carbocyclization reactions of indole precursors **1** occurred without harming the sensitive indole ring. As a consequence of the high surface area of nanoparticles, the required catalyst concentration is lower. Thus, the cyclization of α-allenols **1** can be achieved using just 1.0 mol% of one of the most economical sources of palladium, $PdCl_2$.

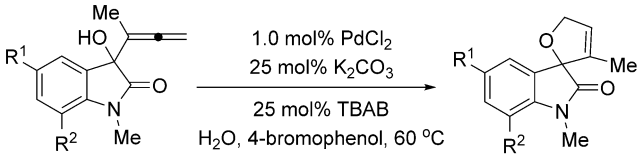
The characterization of PdNPs was carried out by using transmission electron microscopy (TEM) as analytical technique. Thus, it was shown that the obtained Pd(0) particles are in the nano region with an average size of 2.2 nm (Figure 1 and Figure 2).[14] The electron dispersive X-ray (EDX) spectrum confirmed that the metal component of our nanoparticles is palladium (Figure S1, Supporting Information).

To study the recyclability of the PdNPs, when the reaction of α-allenols **1a** and **1b** has gone to completion, the mixture was allowed to cool to room temperature and the catalyst was recovered by centrifugation. Then, the solid was washed with water and acetone, dried under reduced pressure and reused for further oxycyclization reactions. A high level of catalytic activity was retained in the PdNPs at least after four cycles, because 2,5-dihydrofurans **2a** and **2b** were obtained in similar yields even in the fourth recycling as shown in Table 2.

The above results point to a good retention factor of palladium in the cyclization reactions, because catalyst leaching should be accompanied by diminished catalytic activity after recycling. The experiments using **1a** and **1b** proved the ability of the PdNPs to be recycled because the cyclization reaction was iteratively repeated using the same batch of catalyst. TEM studies of fresh and reused catalysts after the fourth cycle point to the unchanged nanoparticle size before and after the cyclization reaction (Figures S2–S7, Supporting Information).

Micro-Raman spectroscopy was used to analyze the possible presence of embedded TBAB in the PdNPs.

Table 2. Catalyst recovery from the PdNPs-catalyzed oxycyclization reaction of α-allenols **1**.[a]



1a R^1 = H, R^2 = H
1b R^1 = Cl, R^2 = H

2a
2b

Cycle	Product	Yield [%][b]	Catalyst Recovery [%]
native[a]	**2a**	80	96
1	**2a**	78	91[c]
2	**2a**	75	88[c]
3	**2a**	71	80[c]
native[a]	**2b**	59	95
1	**2b**	58	90[c]
2	**2b**	56	86[c]
3	**2b**	53	80[c]

[a] PdNPs were generated through a precatalytic approach.
[b] Yield of pure, isolated product **2** after silica gel chromatography with correct analytical and spectral data.
[c] With recovered catalyst.

Raman spectra were obtained using two excitation wavelengths (532 and 633 nm) and making power scans of 2.5 mW and 25 mW, respectively, to select the best conditions of register for each wavelength. Figure 3 shows Raman spectra of TBAB (red line), allenol **1a** (black line), precatalytic generated PdNPs (sky blue line), recycled (one cycle) PdNPs washed with water and acetone (cobalt blue line), recycled (one cycle) PdNPs without washing with water and acetone (green line). In the light regions, no TBAB was detected in the spectra of the PdNP samples, indicating the absence of TBAB in the metallic catalyst.

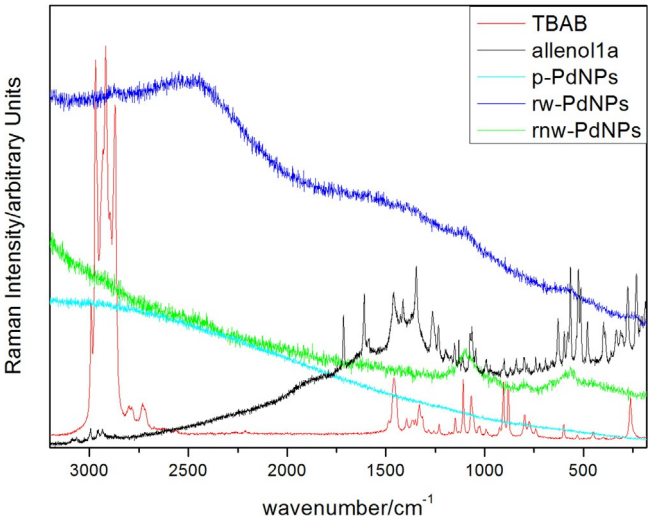


Figure 3. Raman spectra recorded using a wavelength of 532 nm (except for allenol **1a** which required 633 nm). All the Raman spectra were normalized to the maximun intensity.

For the oxycyclization reaction of allenol **1a**, we detected that the dihydrofuran formation catalyzed by PdNPs was faster than that catalyzed by homogeneous $PdCl_2$. Thus, the turnover frequency (TOF) of the catalyst for the heterogeneous C–O bond formation was 155-fold higher than that for the homogeneous catalyst.[15] These results demonstrate improved efficiency of PdNPs over homogeneous catalysis in this particular reaction. By contrast, it was observed that cyclization/coupling reaction sequences of allenols **1** with unsaturated halides were not feasible. The mixture of allenol **1a** either with allyl bromide or iodobenzene under PdNPs-catalyzed conditions was nonproductive for the oxycyclization/cross-coupling adduct formation.

In conclusion, the activity of palladium nanoparticles (PdNPs) as a convenient catalyst for the chemoselective cyclization reaction of various α-allenol derivatives in water under ligandless conditions has been disclosed. The heterogeneous catalyst also offers the advantages of recyclability, ease of removal, and high turnover frequency than the homogeneous catalyst.

Experimental Section

General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-500, Bruker Avance-300, or Varian VRX-300S. NMR spectra were recorded in $CDCl_3$ solutions, except where otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{13}C, 77.0 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. The transmission electron microscopy (TEM) analysis was performed on a JEOL-JEM-2010 microscope using a 200 kV voltage. Dispersive Raman spectra at 633 and 532 nm were recorded in a RM 1000 Renishaw Raman Microscope System. The Raman spectrometer is equipped with a Leica microscope and an electrically refrigerated CCD camera. The spectra were obtained with ×50 magnification objective lenses. The final spectra were the result of 10 accumulations to improve the signal-to-noise ratio and the integration time was 10 s. The software employed for data acquisition and analysis was Wire for Windows and Galactic Industries GRAMS/32TM. Five scans were recorded to improve the signal-to-noise ratio. The Raman shift was calibrated before the measurements according to the silicon peak at 520 cm^{-1}. The 633 nm line had a laser power from 0.25 to 25 mW and finally, the 532 nm line had a laser power from 0.0005 to 5 mW. The measurements were done directly in the sample (*in situ*), the sample preparation is not necessary. All com-

mercially available compounds were used without further purification.

Typical Procedure for Cyclization of Allenols using *in situ* Generated PdNPs

To a magnetically stirred solution of tetrabutylammonium bromide (TBAB) (0.25 mmol), $PdCl_2$ (0.01 mmol) and K_2CO_3 (0.25 mmol) in H_2O (4 mL) were added the corresponding allenol **1** (1 mmol) and 4-bromophenol (1 mmol) at 60 °C. Upon completion of the reaction (monitored by TLC), the reaction mixture was allowed to cool to room temperature, was diluted with ethyl acetate (3×5 mL), and the ethyl acetate layer was separated from the aqueous layer. The organic extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate mixtures gave analytically pure compounds.

Typical Procedure for Cyclization of Allenols using Precatalytic Generation of PdNPs

A solution of tetrabutylammonium bromide (TBAB) (0.25 mmol), $PdCl_2$ (0.01 mmol) and K_2CO_3 (0.25 mmol,) in H_2O (4 mL) was stirred for fifteen minutes at 60 °C. Then, the corresponding allenol **1** (1 mmol) and 4-bromophenol (1 mmol) were added. The reaction mixture was stirred at 60 °C until the starting material disappeared as indicated by TLC. The reaction mixture was allowed to cool to room temperature, was diluted with ethyl acetate (3×5 mL), and the ethyl acetate layer was separated from the aqueous layer. The organic extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds **2** and **3** follow.

Dihydrofuran (2a): From 40 mg (0.18 mmol) of allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent, gave compound **2a** as a colorless oil; yield: 31 mg (80%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.32 (td, J = 7.7, 1.2 Hz, 1H), 7.20 (d, J = 6.3 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 5.96 (q, J = 1.5 Hz, 1H), 5.01 and 4.90 (dt, J = 12.4, 1.9 Hz, each 1H), 3.20 (s, 3H), 1.42 (m, 3H), ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 175.6, 144.0, 135.8, 130.0, 128.3, 124.9, 124.4, 123.1, 108.2, 92.4,76.3, 26.3, 11.1; IR ($CHCl_3$): ν = 1715 cm^{-1}; HR-MS (ES): m/z = 215.0956, calcd. for $C_{13}H_{13}NO_2$ $[M]^+$: 215.0946.

Dihydrofuran (2b): From 57 mg (0.23 mmol) of allenol **1b**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent, gave compound **2b** as a yellow oil; yield: 34 mg (59%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30 (dd, J = 8.3, 2.1 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 5.98 (m, 1H), 5.00 and 4.90 (dt, J = 12.4, 2.0 Hz, each 1H), 3.18 (s, 3H), 1.44 (q, J = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 175.1, 142.5, 135.2, 130.0, 129.9, 128.6, 125.3, 124.9, 109.2, 92.3, 76.5, 26.4, 11.1; IR ($CHCl_3$): ν = 1729, 1487 cm^{-1}; HR-MS (ES): m/z = 250.0612, calcd. for $C_{13}H_{13}ClNO_2$ $[M+H]^+$: 250.0635.

Dihydrofuran (2c): From 75 mg (0.25 mmol) of allenol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, gave compound **2c** as a yellow oil; yield: 55 mg (75%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.44 (dd, J = 8.3, 1.8 Hz, 1H), 7.30 (d, J = 1.8 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 5.97 (d, J = 1.3 Hz, 1H), 4.99 and 4.89 (m, each 1H), 3.17 (s, 3H), 1.43 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 175.0, 142.9, 135.2, 132.8, 130.3, 127.6, 125.3, 115.8, 109.7, 92.2, 76.5, 26.3, 11.1; IR ($CHCl_3$): ν = 1730, 1468 cm^{-1}; HR-MS (ES): m/z = 293.0053, calcd. for $C_{13}H_{12}BrNO_2$ $[M]^+$: 293.0051.

Dihydrofuran (2d): From 40 mg (0.16 mmol) of allenol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, gave compound **2d** as a yellow solid; yield: 32 mg (80%); mp 81–83 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.24 (dd, J = 8.1, 1.2 Hz, 1H), 7.08 (dd, J = 7.3, 1.2 Hz, 1H), 6.98 (t, J = 7.7 Hz, 1H), 5.97 (m, 1H), 4.99 and 4.89 (dt, J = 12.4, 1.9 Hz, each 1H), 3.56 (s, 3H), 1.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 175.9, 139.7, 135.5, 132.2, 131.2, 125.1, 123.9, 123.0, 115.7, 91.8, 76.5, 29.7, 11.1; IR ($CHCl_3$): ν = 1734, 1461 cm^{-1}; HR-MS (ES): m/z = 249.0551, calcd. for $C_{13}H_{12}ClNO_2$ $[M]^+$: 249.0557.

Dihydrofuran (2e): From 43 mg (0.22 mmol) of allenol **1e**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **2e** as a colorless oil; yield: 26 mg (60%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.32 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 5.65 (m, 1H), 5.46 (m, 1H), 4.84 and 4.71 (m, each 1H), 1.55 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 140.0, 138.1, 133.5, 128.6 (2C), 128.2 (2C), 121.0, 89.8, 75.5, 12.4; IR ($CHCl_3$): ν = 1730, 1684, 1091 cm^{-1}; HR-MS (ES): m/z = 194.0506, calcd. for $C_{11}H_{11}ClO$ $[M]^+$: 194.0498.

Dihydrofuran (2f): From 47 mg (0.25 mmol) of allenol **1f**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **2f** as a yellow oil; yield: 22 mg (46%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.05 (t, J = 2.5 Hz, 1H), 4.92 (m, 2H), 3.81 (s, 3H), 1.55 (t, J = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.3, 138.5, 133.5, 128.2 (2C), 120.6, 113.8 (2C), 90.1, 75.1, 55.2, 12.5; IR ($CHCl_3$): ν = 1609, 1511, 1248 cm^{-1}; HR-MS (ES): m/z = 191.1067, calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072.

Dihydrofuran (2g): From 47 mg (0.21 mmol) of allenol **1g**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent, gave compound **2g** as a colorless oil; yield: 38 mg (83%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.44 (d, J = 2.2 Hz, 2H), 6.40 (m, 1H), 5.63 (m, 1H), 5.41 (m, 1H), 4.84 and 4.70 (m, each 1H), 3.79 (s, 6H), 1.58 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.9 (2C), 143.9, 138.4, 120.8, 104.7 (2C), 99.8, 90.5, 75.4, 55.3 (2C), 12.5; IR ($CHCl_3$): ν = 1596, 1153 cm^{-1}; HR-MS (ES): m/z = 221.1175, calcd. for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1178.

Dihydrofuran (2h): From 45 mg (0.20 mmol) of allenol **1h**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, gave compound **2h** as a colorless oil; yield: 26 mg (60%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.16 (d, J = 8.4 Hz, 2H), 7.17 (m, 2H), 5.38 (m, 1H), 5.13 (q, J = 1.6 Hz, 1H), 4.61 (m, 2H) 3.50 (s, 3H), 1.23 (t, J = 1.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 137.0, 147.9, 138.8, 130.7, 130.5, 127.3, 121.7, 90.5, 76.1, 51.9, 12.6; IR ($CHCl_3$): ν = 1723, 1281, 1112 cm^{-1}; HR-MS (ES): m/z = 218.0938, calcd. for $C_{13}H_{14}O_3$ $[M]^+$: 218.0943.

Dihydrofuran (2i): From 40 mg (0.16 mmol) of allenol **1i**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **2i** as a colorless oil;

yield: 28 mg (71%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35 (s, 4H), 7.14 (m, 3H), 7.09 (d, J = 3.0 Hz, 2H), 6.05 (td, J = 4.6, 1.8 Hz, 1H), 5.98 (q, J = 1.9 Hz, 1H), 4.76 (d, J = 1.9 Hz, 1H), 4.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 146.7, 141.3, 133.0, 132.7, 129.0, 128.6, 128.5, 127.2, 124.2, 119.0, 112.8, 87.9, 76.1; IR ($CHCl_3$): ν = 2230, 1758, 843 cm^{-1}; HR-MS (ES): m/z = 247.1005, calcd. for $C_{17}H_{13}NO$ $[M]^+$: 247.0997.

Dihydrofuran (2j): From 47 mg (0.27 mmol) of allenol **1j**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **2j** as a colorless oil; yield: 24 mg (50%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25 (m, 5H), 5.44 (q, J = 1.6 Hz, 1H), 4.88 (m, 1H), 4.46 (m, 2H), 3.01 (dd, J = 14.1, 3.9 Hz, 1H), 2.72 (dd, J = 14.1, 6.8 Hz, 1H), 1.74 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 138.2, 137.5, 129.4 (2C), 128.0 (2C), 126.0, 121.3, 88.1, 74.4, 40.4, 12.7; IR ($CHCl_3$): ν = 1759, 1081, 1027 cm^{-1}; HR-MS (ES): m/z = 174.1041, calcd. for $C_{12}H_{14}O$ $[M]^+$: 174.1045.

Dihydrofuran (2k): From 40 mg (0.12 mmol) of allene **1k**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **2k** as a pale yellow oil; yield: 26 mg (64%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.50 (m, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.78 (td, J = 7.7, 1.7 Hz, 1H), 7.57 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36 (ddd, J = 7.7, 4.7, 1.0 Hz, 1H), 7.18 (m, 2H), 5.66 (m, 2H), 4.76 and 4.71 (m, each 1H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.3, 150.5, 138.1, 137.1, 136.0, 129.1, 127.6, 125.8, 124.8, 123.5, 122.3, 121.8, 121.6, 120.2, 113.9, 83.5, 75.2, 15.5; IR ($CHCl_3$): ν = 2850, 1377, 1188 cm^{-1}; HR-MS (ES): m/z = 341.0954, calcd. for $C_{18}H_{17}N_2O_3S$ $[M+H]^+$: 341.0960.

Dihydrofuran (2l): From 40 mg (0.09 mmol) of allene **1l**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **2l** as a pale yellow oil; yield: 21 mg (56%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.58 (m, 1H), 8.09 (dt, J = 7.9, 0.9 Hz, 1H), 7.89 (m, 2H), 7.63 (s, 1H), 7.62 (d, J = 1.7 Hz, 1H), 7.47 (ddd, J = 7.7, 4.7, 1.1 Hz, 1H), 7.38 (dd, J = 8.8, 1.9 Hz, 1H), 5.74 (m, 2H), 4.85 and 4.75 (m, each 1H), 1.59 (t, J = 1.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.0, 150.5, 138.2, 136.6, 134.7, 130.7, 127.7, 127.6, 126.8, 122.9, 122.2, 121.8, 121.0, 117.1, 115.4, 83.2, 75.2, 12.4; IR ($CHCl_3$): ν = 2992, 1381, 1188 cm^{-1}; HR-MS (ES): m/z = 417.9971, calcd. for $C_{18}H_{15}BrN_2O_3S$ $[M]^+$: 417.9986.

Carbazole (3m): From 40 mg (0.18 mmol) of allenol **1m**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **3m** as a colorless solid; yield: 25 mg 71%); mp 92–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.96 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.36 (m, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.13 (m, 2H), 6.97 (dd, J = 8.0, 0.8 Hz, 1H), 3.72 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 142.0, 141.4, 136.3, 125.5, 123.8, 120.9, 120.8, 120.4 (2C), 119.1, 109.1, 108.7, 29.4, 22.7; IR ($CHCl_3$,): ν = 1469, 1249, 701 cm^{-1}; HR-MS (ES): m/z = 195.1040, calcd. for $C_{14}H_{13}N$ $[M]^+$: 195.1048.

Carbazole (3n): From 40 mg (0.16 mmol) of allenol **1n**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **3n** as a colorless solid; yield: 20 mg (50%); mp 94–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.92 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.29 (s, 1H), 7.16 (s, 1H), 7.08 (dd, J = 8.8, 2.5 Hz, 1H), 7.03 (d, J = 7.9 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.5, 141.9, 136.0, 135.8, 123.0, 120.2, 119.8 (2C), 114.0, 108.9, 108.7, 103.2, 56.1, 29.0, 22.2; IR ($CHCl_3$): ν = 1486, 1287 cm^{-1}; HR-MS (ES): m/z = 225.1153, calcd. for $C_{15}H_{15}NO$ $[M]^+$: 225.1154.

Typical Procedure for the Recovery and Recyclability of PdNPs

Upon completion of the reaction (monitored by TLC) of the appropriate allenol (1 mmol), the reaction mixture was allowed to cool to room temperature and was diluted with ethyl acetate (2 × 5 mL). The aqueous layer which contains the Pd nanoparticles, was separated from the organic layer. The particles were collected by centrifugation and redispersed again in water. Then, the corresponding allenol **1** (1 mmol) and 4-bromophenol (1 mmol) were added. The reaction mixture was stirred at 60 °C until the starting material disappeared as indicated by TLC. The mixture was diluted with ethyl acetate (3 × 5 mL) and the ethyl acetate layer was separated from the aqueous layer. The organic extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate mixtures gave analytically pure compounds. The process was repeated for four consecutive times.

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