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ARTICLE TYPE

Novel glycosyl pyridyl-triazole@palladium nanoparticles: efficient and recoverable catalysts for C-C cross-couplings

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We report the development of a series of glycosyl pyridyl-triazole@palladium nanoparticles (GPT-Pd) which were synthesized by reaction of azidoglycosides with 2-ethynyl-pyridine *via* a click chemistry. These palladium nanoparticles were obtained in high yields and were fully characterized by ^{1}H and ^{13}C NMR, elemental analysis, transmission electron microscopy, and thermogravimetric analysis. The single crystal structure of GPT-Pd catalyst **5c** was determined to show that the glycosyl pyridyl-triazoles coordinated with palladium in bidentate (N,N) coordination mode. Their use in the palladium-catalyzed C-C coupling such as Suzuki-Miyaura coupling, Heck reaction and Sonogashira reaction achieved a quantitative production under mild conditions. Furthermore, the catalysts can be easily separated from the reaction mixture and the catalytic activity remained unchanged even after 8 successive catalytic cycles.

Introduction

The C-C cross-coupling reactions are among the most useful and most widely studied synthetic transformations.[1-3] The three most important processes, the Suzuki-Miyaura coupling, the Heck reaction and the Sonogashira reaction typically catalyzed by palladium catalysts, have been widely studied in recent decades.[4-6] Such reactions are key steps in the total synthesis of a large number of natural products, biologically active compounds, and many organic building blocks.[7] Transition metal-based homogenous catalysts has attracted a great deal of attention and showed remarkable activity and selectivity in these couplings. However, the difficulty of separating the homogeneous catalysts from reaction medium restricts their applications in the pharmaceutical industry.[8] Alternatively, metal catalysts anchored on a heterogeneous support have received tremendous attention recently in C-C cross-coupling.[9] The heterogeneous processes have advantages such as ease of separation of the product, reusability of the catalyst, better steric control of the reaction intermediate and so on .[10] However, the activities of heterogeneous catalysts are generally lower than those of their homogeneous counterparts, due to the lower dimensionality of the interaction between the substrates and the catalyst surface. In contrast, metal nanoparticle catalysts are advantageous over their homogeneous and heterogeneous counterparts in terms of high activity, high stability, and efficient recovery.[11] There has been considerable recent interest in the rational design and synthesis of high active and recoverable catalysts.[12] Nano-catalysts can be isolated and recovered by filtration or centrifugation methods, whereas the inconvenience and inefficiency of these tedious methods caused by the nano size of the catalyst particles hamper the sustainability and economics of the nanocatalytic strategy. Therefore, based on the concerns of economic and green chemistry, the development of mild, simple and efficient procedures using low catalyst loading, cheaper, environmentally friendly nanocatalysts is still a topic of considerable interest to organic synthesis and industry.[13]

Recently, green chemistry methods utilizing the biomass sources such as chitosan, starch, cellulose and lignin have generated significant interest in the synthesis of nanoparticles owing to its green and essential roles in nanocatalysts catalyzed reactions.[14] The biomass-based nanoparticles are of great interest due to their extremely small size and large surface to volume ratio, and they exhibited utterly novel characteristics compared to the large particles of bulk material.[15] Following our interest in carbohydrates as inexpensive and highly modular green sources for catalytic reaction,[16-20] we herein report a series of novel carbohydrate-derived pyridyl-triazole@palladium nanoparticles which were synthesized by reaction of azidoglycosides with 2-ethynylpyridine *via* a click chemistry. These nanoparticles were fully characterized by ^{1}H and ^{13}C NMR, elemental analysis, transmission electron microscopy (TEM) and thermogravimetric analysis (TG). Their use in the palladium-catalyzed C-C coupling

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR spectra, ^{13}C NMR spectrum, GC/MS profile, HRMS profile. See DOI: 10.1039/b000000x/

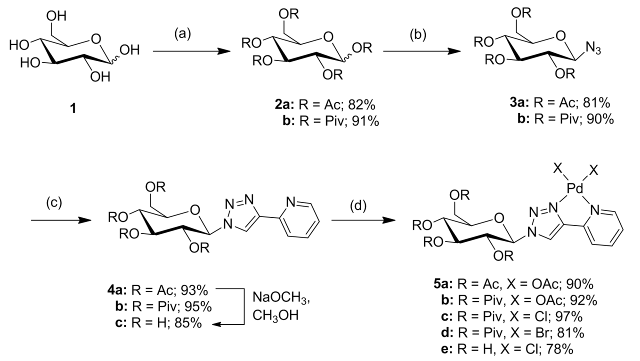
‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

such as Suzuki-Miyaura coupling, Heck reaction and Sonogashira reaction achieved a quantitative production in water. Furthermore, the catalyst can be easily separated from the reaction mixture and reused eight times without significant loss of its activity and it does not leave any detectable Pd metal impurity in the organic solvent as confirmed by ICP-AES measurement.

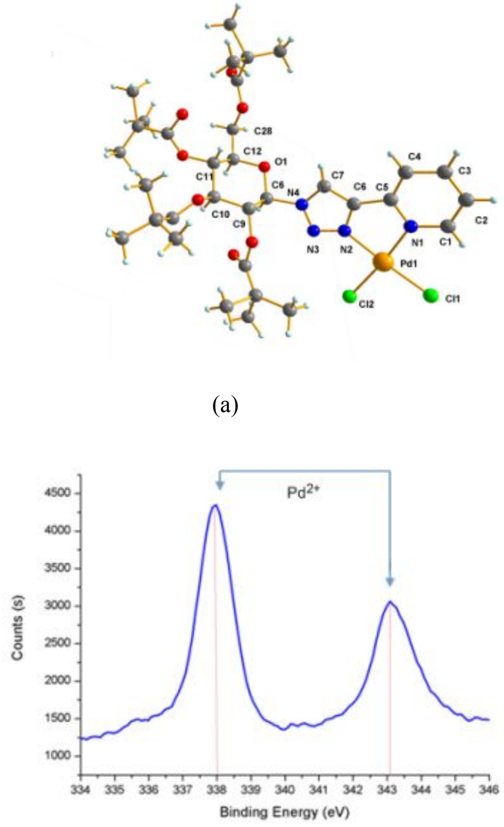
Results and discussion

The palladium nanoparticles were prepared from D-glucose as follows (Scheme 1): the free OH of D-glucose were protected by acetyl or pivaloyl group to afford sugar substrate **2a-b** and the azide group was introduced into **2** through a simple procedure to produce the glycosyl azide **3**.[21] Then azide **3** underwent a click process with commercially available 2-ethynylpyridine in the presence of copper sulfate and sodium ascorbate in *tert*-butanol to give glycosyl triazoles **4a-b** in high yields.[22] The resulting triazoles **4a-b** were further treated with $Pd(OAc)_2$, $PdCl_2$ and $PdBr_2$ in anhydrous toluene to provide the desired catalysts **5a-d** in high yield. In addition, **5e** was obtained from **4c** which was deprotected from **4a** in $NaOCH_3/CH_3OH$ condition. The GPT-Pd catalysts are air- and moisture-stable in the solid state and even in solution.

Their structures were confirmed by ^1H NMR, ^{13}C NMR, elemental analysis, TEM, and TG. All catalysts were in good agreement with the results by NMR. It was clear that the proton signals on pyridine and triazole rings of Pd salts in general were shifted downfield apparently, which indicated that the palladium ion was coordinated with the units of glycosyl triazoles. Meanwhile, because the triazole ligand could bind with the palladium ion through either N2 or N3 atom,[23-24] the spectra of catalysts showed two sets of proton signals (^1H NMR of **5a-e**. ESI†; the proton signal trizole ring are in the range δ 9.2-9.8) and the GPT-Pd catalysts had the different ratioes. For example, the ratio of proton signals was around 1:5 in **5a**, 1:3.5 in **5b** respectively. Hence the formation of five-membered chelate rings by binding with the N3 atom and the nitrogen atom of pyridine was considered to be the predominant structure. Importantly, in **5c**, **5d** and **5e,** there was only one proton signal for the trizole. The 2D ROESY NMR spectrum was conducted to check the the potential spatial proximities among the different protons of catalysts(Figure S1. ESI†). No contacts were observed among the aromatic protons of the sugar ring protons and the triazole-pyridine from the spectrum, showing that the functional group was not embraced in the sugar ring. In addition to the NMR analysis, we have performed a detailed X-ray crystallography measurement to gain more insight into such bonding interactions between the Pd ion with triazole rings.



Scheme 1 Synthesis of glycosyl pyridyl triazole@palladium nanoparticles (GPT-Pd) **5a-e**. Reaction conditions: (a) Ac_2O/pyridine, 24 h or PivCl/ pyridine, 60 h; (b) $TMSN_3$, $SnCl_4$, CH_2Cl_2, 12 h; (c) 2-ethynylpyridine, $CuSO_4$/NaASc, *tert*-butanol, rt, 12h; (d) PdX_2 [X = OAc, Cl, Br], toluene, rt, 6 h.



(a)

(b)

Figure 1 a) ORTEP diagram of GPT-Pd catalyst **5c** showing atom-labelling scheme. Hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 30% probability; b) XPS analysis of GPT-Pd catalyst **5c.**

A single crystal of **5c** was obtained from acetonitrile/ dichloromethane. Its crystal structure (Figure 1a) exhibited that the synthesis of such a palladium(II) complex wih the triazole ligand bind with the palladium metal through N2 atom entirely. The crystal data, refinement parameter, bond lengths and bond angles are given in Supplementary Information (Table S1, ESI†). The elemental composition of the as-prepared GPT-Pd catalyst **5c** was determined by XPS. The Pd (3d5/2) and Pd (3d3/2) peaks were observed at 337.98 and 343.08 eV respectively, which are the characteristic values for Pd metal (Figure 1b). Pd3d XPS of Pd nanoparticles suggested the formation of two-valent Pd species. Then the thermal stability of GPT-Pd catalysts **5a-e** was proved by TG analysis. The TG shows that **5a-d** are stable up to 200 °C, suggesting that their high thermal stability allows them to be compatible with most organic reactions. In addition, GPT-Pd catalysts **5c-d** displayed good thermal stability with respect to **5a-b** and a sharp decrease in weight was observed in 200- 400 °C for all of these catalysts **5a-d** (Figure 2).

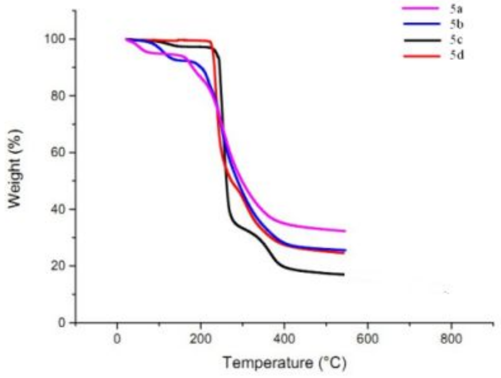


Figure 2. Thermo-gravimetric analysis graphs of GPT-Pd catalysts **5a-d**

Nextly, the surface morphology and crystal structure of the synthesized catalysts were characterized by TEM. The results showed that the average diameter of the GPT-Pd catalysts' diameter was about 2-6 nm and the dispersion of the Pd particles was very well (Figure 3a-d). The TEM images also suggested that no palladium clusters were formed during the preparation.

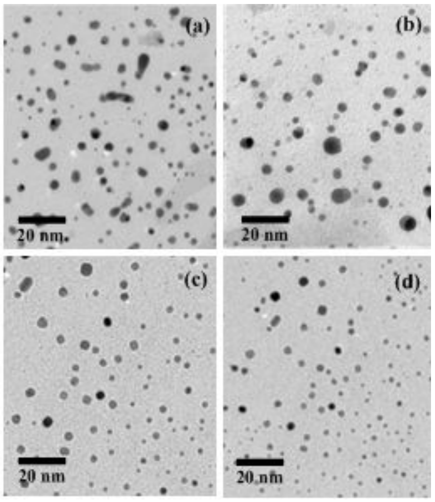
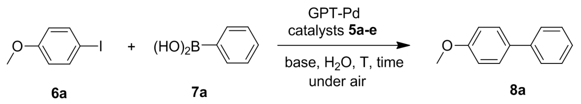


Figure 3. TEM images of (a) GPT-Pd catalyst **5a**, (b) GPT-Pd catalyst **5b**, (c) GPT-Pd catalyst **5c** and (d) GPT-Pd catalyst **5d**.

With the characterized catalysts the in hand, we then applied catalysts **5a-e** to the Suzuki-Miyaura reaction firstly. The Suzuki-Miyaura reaction is among the most important coupling reactions for synthetic organic and process chemistry including pharmaceuticals, agricultural chemicals and sophisticated materials.[25-30] The coupling reaction of 4-iodoanisole with phenlyboronic acid was used as a model reaction to optimize the reaction conditions, including catalyst, base, and solvent. As shown in Table 1, different amounts of catalyst **5a** between 0.01-0.1 mol% were investigated firstly for this reaction, and 0.025 mol% loading of Pd was found to be optimal. For the higher amounts of catalyst, the desired product was obtained in a nearly quantitative yield (Table 1, entries 1-2). However, the yield of the reaction was lower in 0.01 mol% Pd dosage (Table 1, entry 3). The coligands, including AcO$^-$, Br$^-$ and Cl$^-$ and have some influence on the catalytic results (Table 1, entries 4-7). The GPT-Pd **5a-b** with AcO afforded the products in 90% and 88%, respectively and showed that the protected group on glucose did no influence on the catalytic results (Table 1, entry 4 and entry 5). The GPT-Pd **5c-d** with halide coligands (Cl, Br) were found to give the good results, with 99% and 96% yield (Table 1, entry 6 and entry 7). GPT-Pd catalysts **5e** revealed low activity for this model reaction (Table 1, entry 8). A possible reason for this is that the hydroxyl groups of sugar ring were deprotonated with potassium carbonate, leading to the formation of a stable palladium complex and the possibility of the hydrogen bonding interaction in different sugar molecule which maybe case catalyst clusters cannot be excluded. The best result was obtained after 6 h at 80 °C using 0.025 mol% of GPT-Pd catalyst **5c** and K_2CO_3 as base.

Table 1 Optimization of Reaction Conditions.[a]

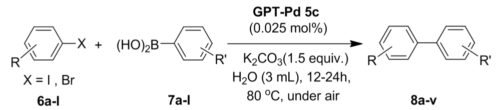


Entry	Catalyst (mol%)	Base	Temp. [°C]	Time (h)	Yield (%)[b]
1	**5a**(0.1)	K_2CO_3	80	6	96
2	**5a**(0.05)	K_2CO_3	80	6	94
3	**5a**(0.025)	K_2CO_3	80	6	90
4	**5a**(0.01)	K_2CO_3	80	12	65
5	**5b**(0.025)	K_2CO_3	80	6	88
6	**5c(0.025)**	$\mathbf{K_2CO_3}$	**80**	**6**	**99(95)**[c]
7	**5d**(0.025)	K_2CO_3	80	6	96
8	**5e**(0.025)	K_2CO_3	80	6	51
9	**5c**(0.025)	KOH	80	6	92
10	**5c**(0.025)	Na_2CO_3	80	6	97
11	**5c**(0.025)	Cs_2CO_3	80	12	54
12	**5c**(0.025)	K_3PO_4	80	24	83
13	**5c**(0.025)	NaOH	80	12	92
14	**5c** (0.025)	Et_3N	80	24	83
15	**5c** (0.01)	K_2CO_3	80	6	85
16	**5c** (0.025)	K_2CO_3	50	6	90
17	**5c** (0.025)	K_2CO_3	rt	6	45

[a]Reaction was carried out with 4-iodoanisole **6a** (1 mmol), phenylboronic acid **7a** (1.5 mmol), catalysts (0.01-0.025 mol%), base (1.5 mmol) and in water (3 mL) under air. [b]GC-MS yield(using *n*-dodecane as an internal standard). [c]Isolated yield in parentheses.

The scope of the Pd catalyst was further examined by the coupling reactions between various types of iodo-, bromo-, and chloroaryl derivatives and aryl boronic acids in the presence of **5c** (Table 2). The effect of varying aryl iodides was initially investigated by using phenylboronic acid as a substrate. The reactions of electron-deficient and electron-rich aryl iodoes with phenylboronic acid provide the desirable products in excellent yields (Table 2, entries 1–10). Generally, the catalytic system possesses a good tolerance to various functional groups, such as -OH, -CF_3, -NO_2, and -Cl. Interestingly, the *ortho*-, *meta*- and *para*- substituted iodotoluene produce the corresponding coupling products in excellent yields. These results suggest the steric and electronic characters of aryl iodides have no obvious effect on the coupling reactions under the reaction conditions.

Table 2 Suzuki-Miyaura Reactions with GPT-Pd **5c**.[a]



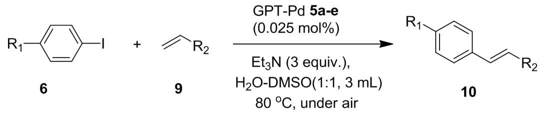
Entry	R	X	R'	Yield[b](%)
1	4-CH_3O	I	Ph	95(**8a**)
2	4-CH_3	I	Ph	96(**8b**)
3	4-Cl	I	Ph	83(**8c**)
4	4-OH	I	Ph	93(**8d**)
5	4-NO_2	I	Ph	96(**8e**)
6	4-CF_3	I	Ph	96(**8f**)
7	4-Ph	I	Ph	90(**8g**)
8	H	I	Ph	95(**8h**)
9	3-NO_2	I	Ph	96(**8i**)[c]
10	2-CH_3	I	Ph	91(**8j**)
11	4-CH_3O	Br	Ph	83(**8a**)
12	4-CH_3	Br	Ph	85(**8b**)
13	4-CH_3O	Cl	Ph	61(**8a**)[c,d]
14	4-CH_3O	I	*p*-OCF_3-C6H_4	86(**8k**)
15	4-CH_3O	I	*p*-OCH_3-C_6H_4	94(**8l**)
16	4-CH_3O	I	*p*-CH_3-C_6H_4	88(**8m**)
17	4-CH_3O	I	*o*-OCH_3-C_6H_4	85(**8n**)
18	4-CH_3O	I	*p*-F-C_6H_4	87(**8o**)
19	4-CH_3O	I	*p*-$C(CH_3)_3$-C_6H_4	92(**8p**)
20	4-CH_3O	I	*p*-OH-C_6H_4	85(**8q**)
21	4-CH_3O	I	*m*-CH_3,*p*-NH_2-C_6H_4	81(**8r**)
22	4-CH_3O	I	thiophene	82(**8s**)
23	4-$COCH_3$	I	*p*-F C_6H_4	90(**8t**)
24	4-NO_2	I	*p*-$C(CH_3)_3C_6H_4$	92(**8u**)
25	4-NO_2	I	*p*-$C(CH_3)_3C_6H_4$	92(**8u**)
26	2-NH2	I	*p*-CH_3O C_6H_4	92(**8v**)
27	4-F	Br	thiophene	85(**8w**)[e]

[a]Reaction conditions: aryl halides **6** (1.0 mmol), ary- boronic acids **7** (1.5 mmol), 1.5 mmol K_2CO_3, 0.025 mol% of **5c**, 3 mL H_2O at 80 °C, under air. [b] Isolated yield. [c] 24 h. [d] 100 °C.

Thus, we examined the efficiency of our system for Suzuki reaction of aryl bromides or chlorides with boronic acids. As can be seen in entry 11 and entry 12 of Table 2, our condition was quite effective for cross-coupling reaction of aryl bromides with boronic acids in good yields. However, when aryl chlorides was used as coupling partner only moderate yields were obtained. The cross-coupling reactions using activated and deactivated aryl boronic acids were also performed, the corresponding biaryl products were obtained in good yields. Also, electron-rich aryl boronic acids such as those bearing OMe, OH or NH_2 groups at *para*- or *meta*- position, which are classified as highly challenging coupling partners, selectively furnished the corresponding products in good yields. Remarkably, no product arising from homocoupling of aryl boronic acids or cross-coupling with OH and NH_2 functional groups were detected in this substrates. Then, we focused our investigation for Suzuki reaction of aryl iodides and heteroaryl boronic acid and interestingly it was found that the system was effective for the synthesis of heteroaryl compounds using as low as 0.025 mol% of the catalyst at 80 °C as exemplified by entry 22 in Table 2.

The catalytic activity of GPT-Pd catalysts are not limited to Suzuki reactions. It can be readily extended to other coupling reactions such as Heck reactions[31] and Sonogashira reaction[32]. Selected results for GPT-Pd-catalyzed Heck reactions are summarized in Table 3. The low yields was obtained due to that both Pd catalysts and organic substrates have poor solubility in water (Table 3, entry 1). To conquer this drawback, a mixture of H_2O:DMSO(1:1) was used as solvent and the reaction of an iodobenzene with a styrene in the presence of the **5c** exhibits stereoselectivity with a high conversion (95%) for trans-coupling (Table 3, entry 4). Electron-rich and electron-deficient aromatic iodides were readily converted to the corresponding products with 86-95% yield, respectively (entries 7-11). The coupling of iodobenzene and methyl acrylate also proceeded smoothly to give the corresponding methyl cinnamate with 93% yield. Aryliodides were also used as substrates for Sonogashira reactions with phenylacetylene and 2-ethynylpyridine (See Table S2).

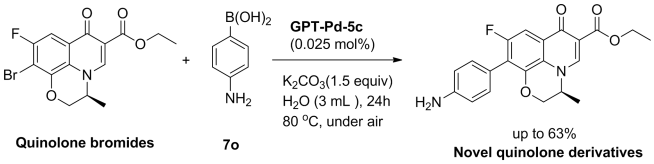
Table 3. Mizoroki-Heck Reaction with GPT-Pd **5**[a]



Entry	catalyst	R_1	R_2	Yield[b](%)
1	**5a**	H	Ph	53[c](**10a**)
2	**5a**	H	Ph	80(**10a**)
3	**5b**	H	Ph	85(**10a**)
4	**5c**	H	Ph	95(**10a**)
5	**5d**	H	Ph	93(**10a**)
6	**5e**	H	Ph	81(**10a**)
7	**5c**	CH_3	Ph	92(**10b**)
8	**5c**	NO_2	Ph	95(**10c**)
9	**5c**	Cl	Ph	94(**10d**)
10	**5c**	OH	Ph	86(**10e**)
11	**5c**	CH_3CO	Ph	88(**10f**)
12	**5c**	H	CO_2Me	93(**10g**)

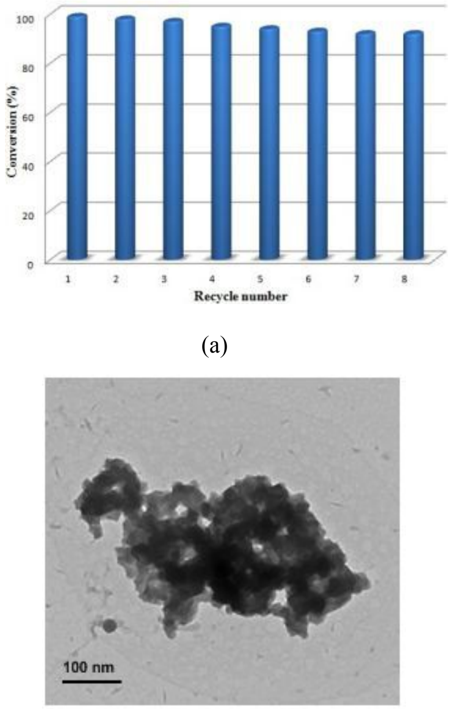
[a]Reaction conditions: aryl iodides **6** (0.5 mmol), olefins **9** (0.6 mmol), Et_3N (1.5 mmol), 0.025 mol% of **5a-e,** 3 mL of H_2O : DMSO (1:1) at 80 °C under air. [b] Isolated yield. [c]3 mL H_2O were used as solvent.

Encouraged by the initial success of the Suzuki-Miyaura reaction for a wide variety of substrates containing a variety of functional groups (Tables 2), we applied our newly developed GPT-Pd **5c**-catalyzed cross-coupling strategy to synthesize the novel fluoroquinolone derivatives. The reaction of quinolone bromides[33] and (4-aminophenyl) boronic acid **7o** was investigated. The reaction could afford the novel fluoroquinolone derivatives in up to 63% yield after recrystallization (Scheme 2). Therefore, this protocol could be used as a practical method to synthesize the precursors of some important bioactive molecules. More importantly, the ICP-AES studies detected no palladium contamination in reaction solvent (residual Pd content < 20 ppm).



Scheme 2 Application of **5c**-catalyzed Suzuki-Miyaura coupling in synthesis of novel fluoroquinolone derivatives.

For practical applications of catalytic systems, the lifetime of the catalyst and its level of reusability are significant factors. To clarify this issue, the feasibility of recycling the catalyst was then examined. After the reaction, the catalyst was simply recovered by filtration and washed with H_2O and ether twice. GPT-Pd **5c** was reused eight times in the reaction of 4-iodoanisole and phenylboronic acid and the results were shown in Figure 4. In the recycling experiment, the separated **5c** was recharged with fresh substrate for the next run under the same reaction conditions. It was notable that the catalyst still remained catalytically active after being reused eight times. The Suzuki-Miyaura reaction at the 7th and 8th runs gave the desired product in 94% and 92% yields (Figure 4a). From the TEM images, it was found that the size of the impregnated palladium catalysts inside the beads had increased from 2-6 nm to 20-30 nm after 8th run (Figure 4b). Metal leaching, as measured by ICP-AES analysis showed that no Pd metal was detected in the reaction solvent after completion of the reaction, which confirms the fact that **5c** was stable and minimizing deterioration, preventing metal leaching, and enabling efficient catalyst recycling. The recycling of the novel catalyst was better than other catalysts. The sustained catalytic activity of the present catalyst was attributed to a strong bonding interaction between the glycosyl pyridyl-triazoles and palladium ion, which holds the palladium nanoparticles from leaching during catalysis. Then the Hg poisoning experiment was carried out. A mercury droplet was added to the reaction mixture and an immediate suppression of activity was observed which shown the heterogeneous nature of the present system[34] (See Supporting Information). Additionally, the XPS analysis of Pd catalyst after catalylic reaction showed that there was no significant change in the Pd 3d XPS peaks before and after the reaction(Figure S3, ESI†).



(a)

(b)

Figure 4 (a) Catalyst recycling for Suzuki-Miyaura reaction. Reaction conditions: see Table 1, Entry 10. The catalyst **5c** was recovered by simple filtration after reaction; (b) TEM image of the recycled GPT-Pd **5c** after 8th reaction run.

Conclusions

In conclusion, we have prepared a series of novel glycosyl pyridyl-tria-zole@ palladium nanoparticles (GPT-Pd) *via* a "click" route and the obtained catalysts have demonstrated a promising catalytic activity for the Suzuki-Miyaura coupling, the Heck reaction and the Sonogashira reaction under mild conditions. Furthermore, the catalysts can be easily separated from the reaction mixture and the catalytic activity remained unchanged even after 8 successive recyling experiments. The study also indicated a strong chemical interaction of the different coligands and glycosyl pyridyl-triazoles present in the palladium centers, which is primarily responsible for such sustained catalytic activity during the consecutive C-C couplings. We believe that the simplicity of the design of these palladium nanoparticles, in combination with their great catalytic performance and recyclability, may inspire future research in the pharmaceutical field and practical applications.

Experimental section

General information

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ^{o}C) and ethyl acetate. Melting points were determined on an X-5 Data microscopic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature with $CDCl_3$ or DMSO-d_6 as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard. Mass spectra (GC-MS) were acquired on an Agilent 5975 spectrometer. Transmission electron microscopy (TEM) images were taken on FEI T20 microscope. ICP-AES metal determinations were carried out on a Perkin-Elmer Optima 3100 XL inductively coupled plasma atomic emission spectrometer equipped with an axial torch, segmented array charge-coupled device detector, and Babington-type nebulizer with cyclonic spray chamber for sample introduction. The small-angle X-ray diffraction (SAXRD) data were taken on a German Bruker D4 X-ray diffractometer with Niltered Cu Ka radiation (40 kV, 40 mA). Thermogravi metric analyses (TG) were performed with a SII Nano Technology EXTAR TG/DTA7220 thermal analyzer at 10 °C/min in nitrogen atmosphere (10 ml/min). 5 mg of each sample in an alumina pan was analyzed in the 40-900 °C temperature range. The sugar substrates were prepared according to our previous reports.[21-22] All compounds were characterized by ^{1}H NMR and mass spectroscopy, which are consistent with those reported in the literature (See Supporting Information).

General Procedure for synthesis of glycosyl pyridyl-triazole @palladium nanoparticles 5a-e.

Synthesis of GPT-Pd catalyst **5**: PdX_2(X = OAc, Cl, Br) (0.50 mmol) was dissolved in anhydrous toluene (20.0 mL) and **4a-c** (0.60 mmol) was added. The solid-liquid mixture was stirred for

6 h at room temperature, after which the solid was filtered, washed thoroughly with large volume of acetone in order to remove any adsorbed palladium and finally dried at 30 °C under vacuum. The glycosyl pyridyl-triazole@palladium nanoparticles were obtained as light yellow powder.

General procedure for Suzuki-Miyaura coupling reaction between aryl halides and arylboronic acids.
The Suzuki reaction was performed in a 10 mL round-bottomed flask, aryl halides (1.0 mmol), arylboronic acids (1.5 mmol), GPT-Pd catalysts **5** (0.025 mol% respect to aryl halides), K_2CO_3 (1.5 mmol) and water (3 mL) were charged and stirred at 80 to 100 °C under air. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was allowed to cool to room temperature. Then the aqueous phase was extracted with CH_2Cl_2 for 3 times (3×2 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography (*n*-hexane/ethyl acetate 10:1) to afford the desired product.

General procedure for Heck reaction between aryl halides and olefins.
The Heck reaction was performed in a 10 mL round- bottomed flask, aryl halides (0.5 mmol), olefins (0.6 mmol), GPT-Pd catalyst **5** (0.025 mol% respect to aryl halides), Et_3N (3.0 mmol) and a mixture of water and DMSO (1:1, 3 mL) was charged and stirred at 80 to 100 °C under air. Monitoring of the reaction, workup procedure, and purification of the Heck-coupled products were performed as described for the Suzuki-Miyaura coupling reactions.

General procedure for the catalyst recycling experiment.
4-iodoanisole **6a** (1 mmol), phenylboronic acid **7a** (1.5 mmol), GPT-Pd catalyst **5c** (0.025 mol%) and K_2CO_3 (1.5 mmol) was added to 3 mL water and was heated under air in an oil bath at 80 °C. After completion of the reaction under the optimal conditions reaction, a simple filtration was sufficient to separate the catalyst solution from the products when the reaction was cool down. The catalyst was washed with H_2O twice and ether twice and the catalyst was dried for 12 h at 50 °C. Then the separated catalyst was recharged with fresh substrate for the next run under the same reaction conditions.

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