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Glucopyranoside-Functionalized NHCs-Pd(II)-PEPPSI Complexes: Anomeric Isomerism Controlled and Catalytic Activity in Aqueous Suzuki Reaction

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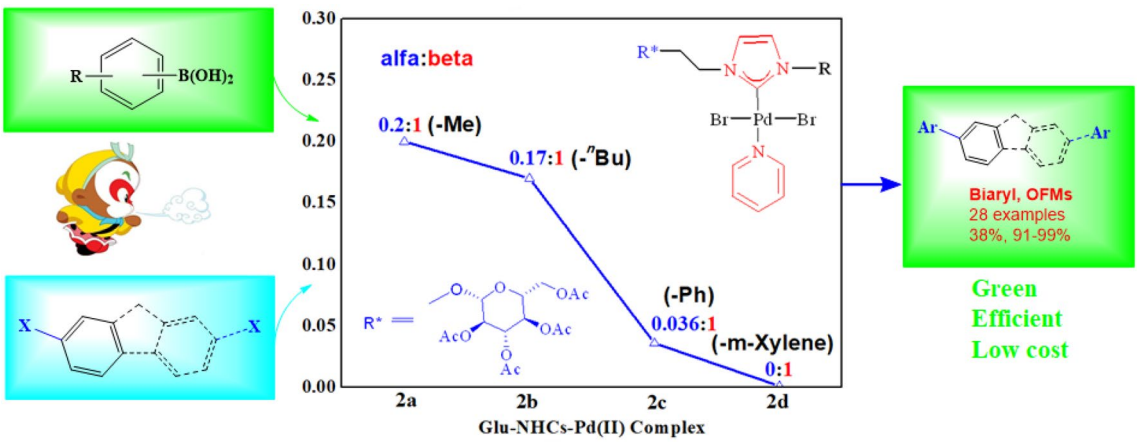
Abstract

The first system controlled anomeric isomerism of glucopyranoside-functionalized N-heterocyclic carbenes based pyridine enhanced precatalyst preparation, stabilization and initiation type palladium(II) complexes (Glu-NHCs-Pd(II)-PEPPSI, 2a–d) were prepared and fully characterized. It is interesting to note that pure β–anomer PEPPSI complex 2d was obtained, in which the Glu-substituent connects to the imidazole heterocycle ring N through ethoxy bridged anomeric carbon. In addition, the catalytic activities revealed that Glu-NHCs-Pd(II)-PEPPSI complexes 2a-d are efficient catalysts for the aqueous Suzuki reaction. Under optimized conditions, a series of fluorene-cored functional materials with different aryl-substituents were synthesized through the Suzuki reaction with excellent yields. The Glu-NHCs-Pd(II)-PEPPSI complex containing bulky and rigid 2,5-dimethylphenyl group played an important role in maintaining the β conformation and improving the catalytic activity significantly.

Graphic Abstract



Keywords Carbohydrate · N-heterocyclic carbenes · PEPPSI type catalyst · Aqueous suzuki reaction · Green chemistry

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1 Introduction

Rational catalyst design incorporating palladium N-heterocyclic carbenes (NHCs) complexes has taken center stage [1–4]. Thereby, extensive efforts have been committed to the synthesis of the biaryl fragments, including the Negishi, Hiyama, Ullmann, Kumada, Stille, and Suzuki reactions

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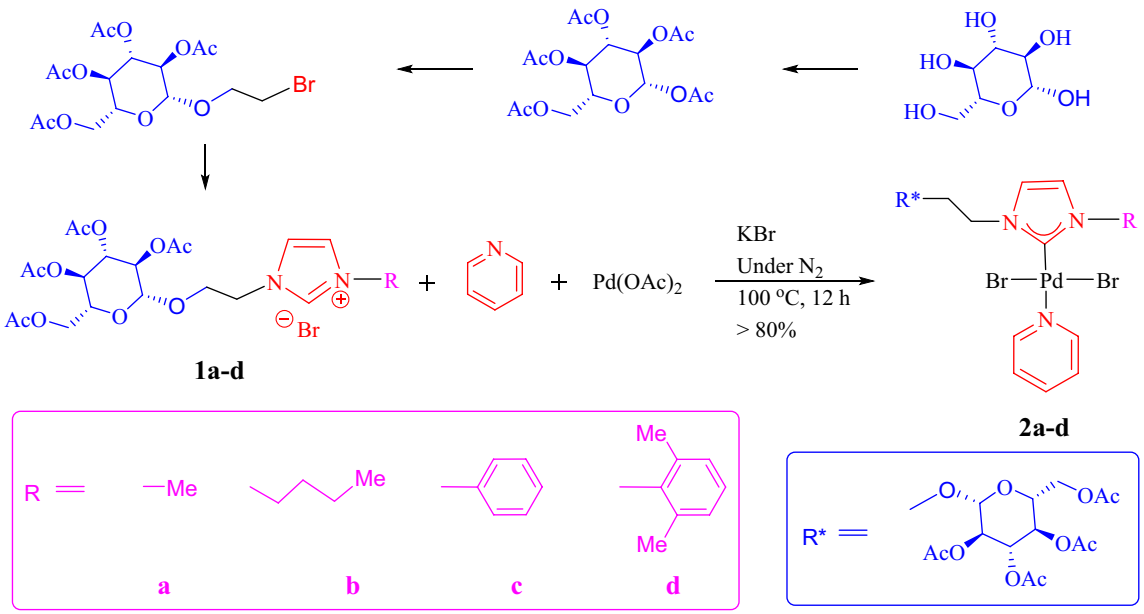
[5–8]. Among the carbon–carbon couplings, the Suzuki reaction has been recognized as one of the most workable methods for building the biaryl fragments [9–13]. A number of novel homogeneous catalysts, heterogeneous catalysts or supported palladium composites have been developed for the Suzuki reactions in recent decades [14, 15]. Conjugate organic functional small molecule and polymer materials (COFM) containing fluorene, spirofluorene, triphenylamine and carbazole substituents have attracted extensive attention in the fields of organic photovoltaic (OPV), organic light-emitting diodes (OLED), and perovskite solar cells (PVSCs), etc. [16–21]. Generally, many catalytic systems for the construction of COFM have been developed, including Pd/phosphine catalyst [22]. However, nearly all Pd/phosphine catalysts were combined with harsh reaction conditions [23–26]. The electronic donor properties of NHCs are similar to phosphines, and frequently regarded as phosphines analogues [27–31]. Generally, complexes of the metal with NHCs are kinetically robust, making NHCs potentially superior star ligands in catalysts [8, 32–34]. To accomplish high reactivity in the Suzuki reaction, numerous homogeneous Pd/NHCs catalyst has been designed. It was obviously to see the positive influence of bulky NHC ligands on the Suzuki reaction process [35, 36]. Among them, pyridine enhanced precatalyst preparation, stabilization and initiation (PEPPSI) Pd complexes were proved to be good catalyst [37–39]. Liu and Zeng found that the halogen groups on the pyridine of Pd-PEPPSI complexes were efficient for the Suzuki reaction of aryl chlorides [38, 39]. Aktas and co-workers used 2-hydroxyethyl-substituted Pd-PEPPSI complexes for the high reactivity Suzuki reaction of aryl chlorides in aqueous media [40].

Carbohydrate (Car-) is ubiquitous in nature and this of low cost and biocompatible [41]. The Car-motifs are bulky, water solubility and possess multiple chiral carbons [42]. Incorporation of Car-motifs into metal complexes affords them these superior features, which are utilized for drug delivery, catalysts, and sensors [41–43]. Only few examples dealing with Car-functionalized NHCs ligands, and Ag, Au, Ir, Ru, Rh, Ni, Pd, Pt complexes have been reported [44–52]. Related researches with Car-functionalized NHCs and NHCs-metal complexes have been reviewed [53–57]. Anchoring Car-motifs to the NHCs metal complexes via C1 carbon (anomeric carbon) could provide a bulky steric hindrance and possibly affect its steric conformation and its catalytic properties [46, 47]. However, when a C1 is connected to an imidazole heterocycle N directly, α and β-glucosides (Glu-) can be obtained, and the absolute conformation of metal complexes is difficult control with the other substituents [45]. In addition, the discipline of absolute conformation of Glu-NHCs and Glu-bridging NHCs coordination metal complexes has not been systematically studied. Our laboratory has developed a series of Car-functionalized ligand for Pd-catalyzed cross coupling over the last few years, including phosphines and NHCs ligands [58–62]. Therefore, based on our previous research, we want to systematically study anomeric isomerism of Glu-NHCs-Pd(II)-PEPPSI complexes, in which the Glu-substituent connects to the imidazole heterocycle ring nitrogen through ethoxy bridged anomeric carbon.

With this background, in this paper, four air-stable, handle-friendly Pd(II)-PEPPSI type precatalysts (2a-d) constituted by Glu-NHCs have been synthesized and characterized. Specifically, complexes 2a-d were conveniently synthesized from their respective Glu-functionalized imidazolium bromide salts by directly combined with $Pd(OAc)_2$ in pyridine. Through control the bulky and rigid of substituent carefully, it is interesting to note that pure β-anomer PEPPSI complex 2d was obtained. To the best of our knowledge, this is the first example of system controlling absolute configuration of anomeric carbon through bridging group using the steric effects of substituents. The catalytic properties of these Glu-NHCs-Pd(II)-PEPPSI complexes (2a-d) in aqueous Suzuki reaction are also described, a series of fluorene-cored functional materials (22 examples) were synthesized through the Suzuki reaction with excellent yields.

2 Results and Discussion

Herein, D-glucose was used as an initiator for the synthesis of the desired Glu-functionalized NHCs precursor 1a-d in three steps [62, 63]. Then, four Glu-NHCs-Pd(II)-PEPPSI type precatalysts 2a-d have been synthesized by direct reaction of 1a-d with $Pd(OAc)_2$ in pyridine with the isolate yields above 80% (Scheme 1). The addition of KBr will favour a complete halogen-coordinated exchange and thus to the production of a pure product. The complexes 2a-d has been characterized by electrospray mass spectrometry (ESI–MS), fourier-transform infrared spectroscopy (FT-IR), and ^{1}H and ^{13}C NMR spectroscopy. The FT-IR data evidently indicated that complexes 2a-d exhibit a characteristic $\nu_{(NCN)}$ band generally between 1360 and 1450 cm^{-1}(Figure S6). The complexes 2a-d are hygroscopic and air stable, the disappearance of the imidazole heterocycle 2-position proton (NC*H*N) ^{1}H NMR peaks in 1a-d (9.27–10.15 ppm) confirms the Glu-NHCs generated [62]. The ^{1}H NMR signals of the imidazole heterocycle 3,4-position proton (NC*H*C*H*N) of 2a-d shift about 0.6 ppm upfield compared to the chemical shifts of their corresponding imidazolium bromide salts 1a-d. The ^{13}C NMR of 2a-d showed the carbene carbon (N*C*N) bound to Pd metal (N*C*N–Pd) resonances appearing at 152.2–152.5 ppm and are comparable to that described in other reported NHC-Pd complexes (145–175 ppm) [48]. The N*C*N signal of 2a (152.2 ppm) appears around 30 ppm downfield relative to the corresponding N*C*HN signal for the



Scheme 1 Synthesis of Glu-NHCs-Pd(II)-PEPPSI complexes

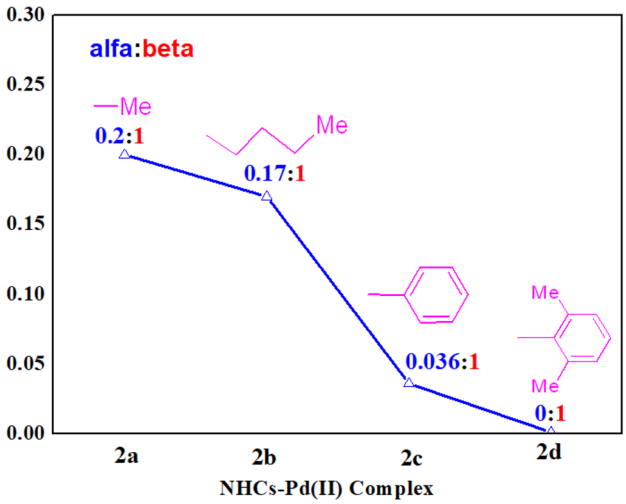


Fig. 1 The α and β isomers ratio of Glu-NHCs-Pd(II)-PEPPSI complex 2a-d in $CDCl_3$

imidazolium bromide salt 1a, and those of 2b (152.5 ppm), 2c (152.4 ppm) and 2d (152.2 ppm) shift about 30 ~ 31 ppm downfield.

Two sets of NMR signals of complex 2a-c attributed to α and β isomers are observed in $CDCl_3$ (Fig. 1, Figure S1-S4), the results were in line with the literature [48]. Since the electronic properties of the complexes 2a and 2b are quite similar, and the relative ratios of α and β isomers are 0.20:1, and 0.17:1 from the ^{1}H NMR (Figure S5). Because of the greater steric effect, smaller ratio of α and β isomers was observed (0.036:1 in 2c, Figure S5). From the results above, we found a less flexible and bulkier substituent around the Pd metal probably contributed to the formation of mixture isomers (2a, 2b and 2c). In order to further study, we choose the bulky and rigid 2,5-dimethylphenyl group next, which may restrict the rotation of the Glu-NHCs ligand around the Pd metal center. It is interesting to note that only one set of ^{1}H NMR signal of complex 2d was obtained, suggesting maintain pure β-anomer in solution (Figure S5). The crystals of complex 2a suitable for X-ray structural analysis were obtained by slow diffusion of petroleum ethers into a concentrated methanol solution.

Complex 2a crystallizes in the form of yellow rods in a monoclinical unit cell. The molecular structure of complex 2a is depicted in Fig. 2. Complex 2a adopts $P2_12_12_1$ symmetry in the solid state. The C(1)-Pd(1)-N(3) and Br(1)-Pd(1)-Br(2) angles of 178.7(2)° and 177.19(3)° for complex 2a, are in accordance with the expectation 180° for a square plane geometry. The Pd(1)-C(1) bond distances of 1.962(4) Å, and Pd(1)-N(3) bond distances of 2.102(4) Å, respectively, are consistent with those found in analogous NHCs based Pd(II)-PEPPSI based PEPPSI complexes [37–40].

Recently, the catalytic activities of NHCs-Pd(II)-PEPPSI complexes in Suzuki reactions in aqueous media have been investigated [38, 40]. In the other part of our study, we evaluated the catalytic activity of Glu-NHCs-Pd(II)-PEPPSI precatalysts 2a-d catalyst system in Suzuki reaction. We initially investigated Glu-NHCs-Pd(II)-PEPPSI complex 2a catalyzed Suzuki reaction between phenylboronic acid and 4-bromotoluene provide 4-methylbiphenyl in 80% yield after reflux in ethanol for 1 h, without the detection of dehalogenated and homo-coupling products (Table 1,

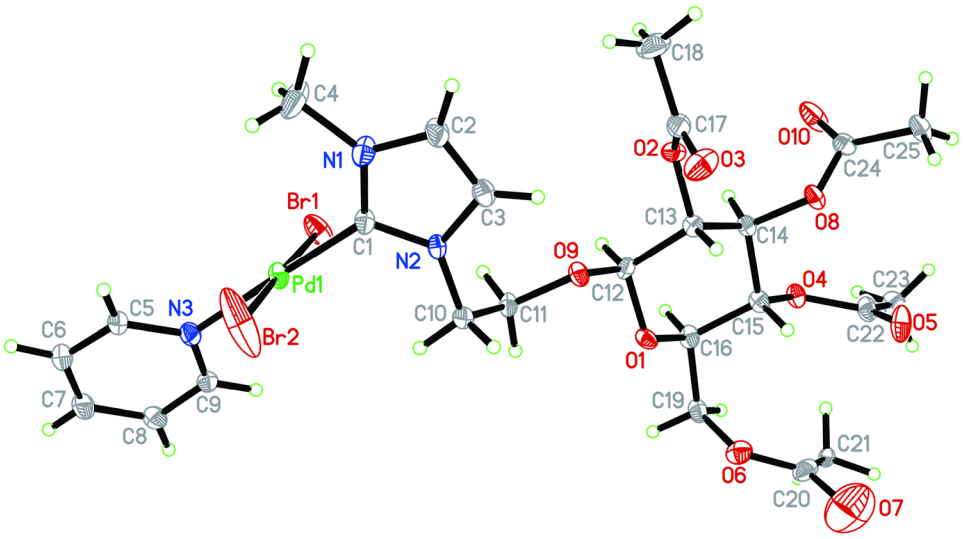
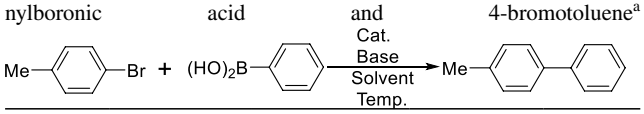


Fig. 2 The X-ray structure of Glu-NHCs-Pd(II)-PEPPSI complex 2a

Table 1 The Suzuki reaction between phenylboronic acid and 4-bromotoluene[a]



Entry	Catalyst	Amount of cat. (mol%)	Time (h)	Yield (%)[b]
1	**2a**	0.05	1	80
2	**2b**	0.05	1	85
3	**2c**	0.05	1	88
4	**2d**	0.05	1	99
5	**$PdCl_2$/1d**	1.5 (0.05)	1	75 (60)
6	**$PdCl_2$**	0.1	1	20
7	–	–	1	Trace
8	**2d**	0.03	1	94
9	**2d**	0.01	1	93
10	**2d**	0.005	3	96

[a]Reaction conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), ethanol (3.0 mL), 90 °C oil bath under N_2

[b]Isolated yield

entry 1). Encouraged by this positive result, various Glu-NHCs-Pd(II)-PEPPSI complexes 2b-d were investigated for this cross coupling. As shown in Table 1, catalyst 2d was observed to provide an excellent result with 99% yield (Table 1, entry 4), but catalyst 2b and 2c with non/smaller bulky butyl or phenyl substituents displayed inferior results (Table 1, entries 2 and 3, 85% and 88%), indicating the bulky and rigid backbone has significant influence on the catalytic activity. In the presence of 1.5 mol% of $PdCl_2$/1d (mol:mol = 1:2), 75% of 4-methylbiphenyl was obtained after 1 h, and 60% yield was obtained with 0.05 mol% of $PdCl_2$/1d (mol:mol = 1:1), the result was written in brackets (Table 1, entry 5). By contrast, only 20% yield of product was obtained in the presence of commercial $PdCl_2$ without ancillary ligand (Table 1, entry 6) and trace product was obtained without any catalyst was added (Table 1, entry 7).

Further decrease in the amount of 2d to 0.005 ~ 0.03 mol% displayed inferior results (Table 1, entries 8–10), through prolong the reflux time to 3 h, the isolated yield was improved to 96% with 0.005 mol% catalyst (Table 1, entry 10). These experiments revealed that the bulky and rigid 2,5-dimethylphenyl in Glu-NHCs-Pd(II)-PEPPSI complex 2d play important role in the elevating catalytic activity of Pd catalytic species.

Then the Suzuki reaction was carried out in a series of green solvents, including H_2O, MeOH, ^{i}PrOH, ^{n}BuOH, EtOH (95%), and EtOH/H_2O mixed solvent, resulting in good to excellent yields (Table 2, entries 1–9). Among the solvents investigated, EtOH/H_2O (v/v = 3:1) was the best choice (Table 2, entry 9), in line with the result observed by Del Zotto and co-workers [64]. Upon further evaluating the Suzuki reaction conditions via variation of the base (Table 2, entries 11–17), commonly used organic base KOBu^{t}, NaOBu^{t}, NaOMe and Et_3N were found not to be the best suitable for the Suzuki reaction herein (Table 2, entries 12–15). The inorganic weak base K_2CO_3 was confirmed as the most efficient choice and 97% yield was obtained even reduces the reaction time to 0.5 h (Table 2, entries 8 and 9). We also found that without or with other base $K_3PO_4{\cdot}7H_2O$ and Na_2CO_3 cannot afford ideal yields (Table 2, entries 11, 16 and 17). The catalytic activities of our catalytic system is only moderate among the reported NHCs-Pd(II)-PEPPSI catalysts [40].

The optimized reaction parameters were identified as follows: aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), Glu-NHCs-Pd(II)-PEPPSI complex 2d (0.01 mol%) catalyst were stirred in EtOH/H_2O (v/v = 3:1) for 0.5 h in the presence of K_2CO_3 (2.0 mmol) in 90 °C oil bath under nitrogen.

Table 2 The Suzuki reactions with different solvents and bases[a]

Entry	Base	Solvent	Yield[b]
1	K_2CO_3	H_2O	40
2	K_2CO_3	MeOH	88
3	K_2CO_3	*i*PrOH	85
4	K_2CO_3	*n*BuOH	87
5	K_2CO_3	EtOH (95%)	94
6	K_2CO_3	EtOH/H_2O = 1/1	96
7	K_2CO_3	EtOH/H_2O = 2/1	98
8	K_2CO_3	EtOH/H_2O = 3/1	99
9	K_2CO_3	EtOH/H_2O = 3/1	97[c]
10	K_2CO_3	EtOH/H_2O = 4/1	92
11	$K_3PO_4{\cdot}7H_2O$	EtOH/H_2O = 3/1	90
12	$KOBu^t$	EtOH/H_2O = 3/1	89
13	Et_3N	EtOH/H_2O = 3/1	75
14	NaOMe	EtOH/H_2O = 3/1	88
15	$NaOBu^t$	EtOH/H_2O = 3/1	91
16	Na_2CO_3	EtOH/H_2O = 3/1	83
17	–	EtOH/H_2O = 3/1	Trace

[a]Reaction conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), 2d (0.01 mol%), base (2.0 mmol), solvent (3.0 mL), 90 °C oil bath for 1.0 h under N_2

[b]Isolated yield

[c]Reaction for 0.5 h

Comparing with the best result of other reported used carbohydrate based NHCs-Pd(II) catalysts in Suzuki reaction (Table 3), our catalysts are easily synthesized, simultaneously, pure β-anomer Glu-NHCs-Pd(II)-PEPPSI complex 2d was obtained for the first time, additionally, our catalytic system with complex 2d is less time consuming, more efficient, lower catalyst loading and additive-free for the Suzuki reaction (Table 3).

With the optimal Suzuki reaction condition in hand, we set out to investigate the substrate scope of the reaction. As shown in Fig. 3, the model product 3a could be isolated in 99%, 97%, and 38% yields with 4-iodotoluene, 4-bromotoluene and 4-chlorotoluene respectively. Aryl bromides with electron-donating and electron-withdrawing substituents could afford the biaryl derivatives in excellent yields (3b-d, 95–98%, Fig. 3). To our delight, activated aryl chloride *p*-(trifluoromethyl)chlorobenzene could gave 3e without increase the amount of catalyst (3e, 93%, Fig. 3).

Since both of K_2CO_3 as base and EtOH/H_2O as solvent are highly suitable for industrial applications, the potential of Glu-NHCs-Pd(II)-PEPPSI complex 2d was further explored. COFM containing triphenylamine, fluorine and carbazole functional groups have obviously attracted attention in the field of OPV, OLED and PVSCs [20, 21, 69, 70].

The cross-couplings between 2-bromo-9*H*-fluorene, 2-chloro-9*H*-fluorene and 2,7-dibromo-9*H*-fluorene with a wide range of arylboronic acids bearing either an electron-rich or an electron-poor substituent proceeded smoothly and delivered the target products in excellent yields (3f-z, 22 examples, Fig. 3). As expected, the product 3f could be isolated in 96% yield with 2-bromo-9*H*-fluorene, and just 33% isolated yield obtained using 2-chloro-9*H*-fluorene. Subsequently, using 2-methylphenyl boronic acid, 3,5-dimethylphenyl boronic acid and 2,6-dimethylphenyl boronic acid take the place of phenyl boronic acid, the couplings were completed with yield above 91% yield (3f, 3 g, 3r, 3t and 3 s, Fig. 3). When increasing the steric hindrance of phenyl boronic acid, the yield decreased slightly. Moreover, electron-poor 3,5-difluorophenyl boronic acid, 3,4,5-trifluorophenyl boronic acid afforded the desired product with yield above 98% and 97% yield (3i, 3j, 3w and 3x, Fig. 3). Overall, we note that nearly quantitative isolate yield of products were afforded when using a series arylboronic acids as the coupling reactant herein (Fig. 3).

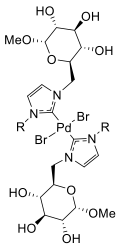
The recyclability of the best catalyst 2d (0.01 mol%) was further investigated in the coupling of 4-iodotoluene and phenylboronic acid using K_2CO_3 as base in EtOH/H_2O (v/v = 3:1). The product 4-methylbiphenyl is very easy to separate, just using petroleum ether hexane and ethyl acetate with simple extraction. The EtOH/H_2O (v/v = 3:1) polar aqueous solution, which contained catalyst 2d, was easily recycled. The catalyst 2d was retained in the aqueous solution layer, which could be recycled directly, and the results were presented in Table 3. It can be seen from the result, the catalytic activity of catalyst 2d started to slightly reduce after the third run (Table 4, entry 3). An excellent yield can be obtained after extension of reaction time (Table 4, entry 5).

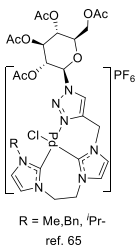
3 Conclusion

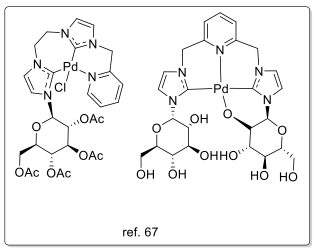
In summary, four Glu-NHCs-Pd(II)-PEPPSI complexes have been synthesized and used as effective catalysts for Suzuki reaction of aryl bromides and activated aryl chlorides in green solvent. We found a flexible and less bulkier substituent around the Pd metal contributed to the formation of α and β isomers, the 2,5-dimethylphenyl group on the NHCs heterocycle N atom provides ideal electronic properties paired with rigid and bulky surrounding of the Pd metal center restrict the rotation of the anomeric carbon, and renders the pure β-anomer. A wide range of arylboronic acids underwent the Suzuki reaction with 2-bromo-9*H*-fluorene or 2,7-dibromo-9*H*-fluorene to provide excellent yields of the corresponding products. Moreover, this EtOH/H_2O-involved protocol is in line with the idea of green chemistry and industrial application, simultaneously, is of huge interest for the preparation of conjugated organic small molecules materials.

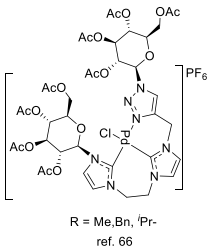
Table 3 The best result of carbohydrate based NHCs-Pd complexes catalyzed Suzuki reactions

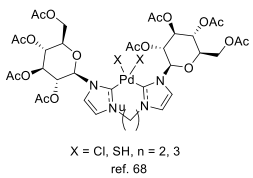
Entry	Amount cat. (mol%)	X = Br, Cl	Time (h)	Additive	Yield (%)	References
1	0.01	Br	16	/	98	[65]
2	0.5	Cl	17	TBAB	53	[65]
3	0.0001	Br	16	/	80	[66]
4	0.01	Br	16	/	98	[67]
5	0.01	Cl	16	/	10	[67]
6	0.1	Br	0.5	/	96	[68]
7	0.1	Cl	17	TBAB	57	[68]
8	0.05	Br	15	/	99	[48]
9	0.1	Cl	15	TBAB	86	[48]
10	0.005	Br	1	/	96	This work
11	0.01	Cl	6	/	93	This work











4 Experimental Section

4.1 Typical Procedure for the Synthesis of Glu-NHCs-Pd(II)-PEPPSI Themed Complexes 2a-d

The Glu-NHCs-Pd(II)-PEPPSI complexes 2a-d was synthesized according to a modified previously reported method [37]. The solution of a specific Glu-NHCs precursor 1a-d (1.0 mmol), KBr (2.0 mmol) and $Pd(OAc)_2$ (1.0 mmol) in dry pyridine (3.0 mL) was refluxed for 12 h with vigorous stirring. The resulting complexes 2a-d was purified by column chromatography (dichloromethane/methanol, 30:1 to 20:1).

4.2 [1-(2-β-D-glucopyranosyloxyethyl)-3-methyl-imidazol-ylidene]Pd(pyridine)Br_2

Yellow crystalline solid, 87%. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.95 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 4.07 (s, 3H, CH_3), 4.10 (t, J = 8.0 Hz, 1H, CH-Glu), 4.32 (m, 3H, CH-Glu and CH_2), 4.51 (d, J = 8.0 Hz, 1H, CH-Glu), 4.98 (m, 2H, CH-Glu), 5.05 (t, J = 8.0 Hz, 1H, CH-Glu), 5.15 (t, J = 8.0 Hz, 1H, CH-Glu), 6.89 (d, J = 2.0 Hz, 1H, CH-Imidazole), 6.97 (d, J = 2.0 Hz, 1H, CH-Imidazole), 7.34 (m, 2H, CH-Pyridine), 7.76 (m, 1H, CH-Pyridine), 8.99 (m, 2H, CH-Pyridine). ^{13}C NMR (101 MHz, $CDCl_3$), δ 20.5 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 38.3 (CH_3), 50.8 (CH_2-CH_2), 60.3 (CH-Glu), 61.7 (CH_2-CH_2), 68.2 (CH-Glu), 68.8 (CH-Glu), 71.1 (CH-Glu), 72.6 (CH-Glu), 100.6 (CH-Glu), 122.4 (C-Imidazole), 123.9 (C-Imidazole), 124.5 (C-Pyridine), 124.9 (C-Pyridine), 147.5 (C-Pyridine), 152.4 (NCN-Pd), 169.2 (C=O), 169.3 (C=O), 170.0 (C=O), 170.6 (C=O). FT-IR (cm^{-1}): 3475, 2965, 2872, 1757, 1602, 1471, 1445, 1375, 1235, 1159, 1067, 1055, 904, 772, 739, 685. MS (ESI): m/z (%) = 802.9 (100) $[M+1]^+$.

4.3 [1-(2-β-D-glucopyranosyloxyethyl)-3-butyl-imidazol-ylidene]Pd(pyridine)Br_2

Yellow crystalline solid, 90%. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.01 (t, J = 7.6 Hz, 3H, CH_3), 1.23 (t, J = 7.2 Hz,

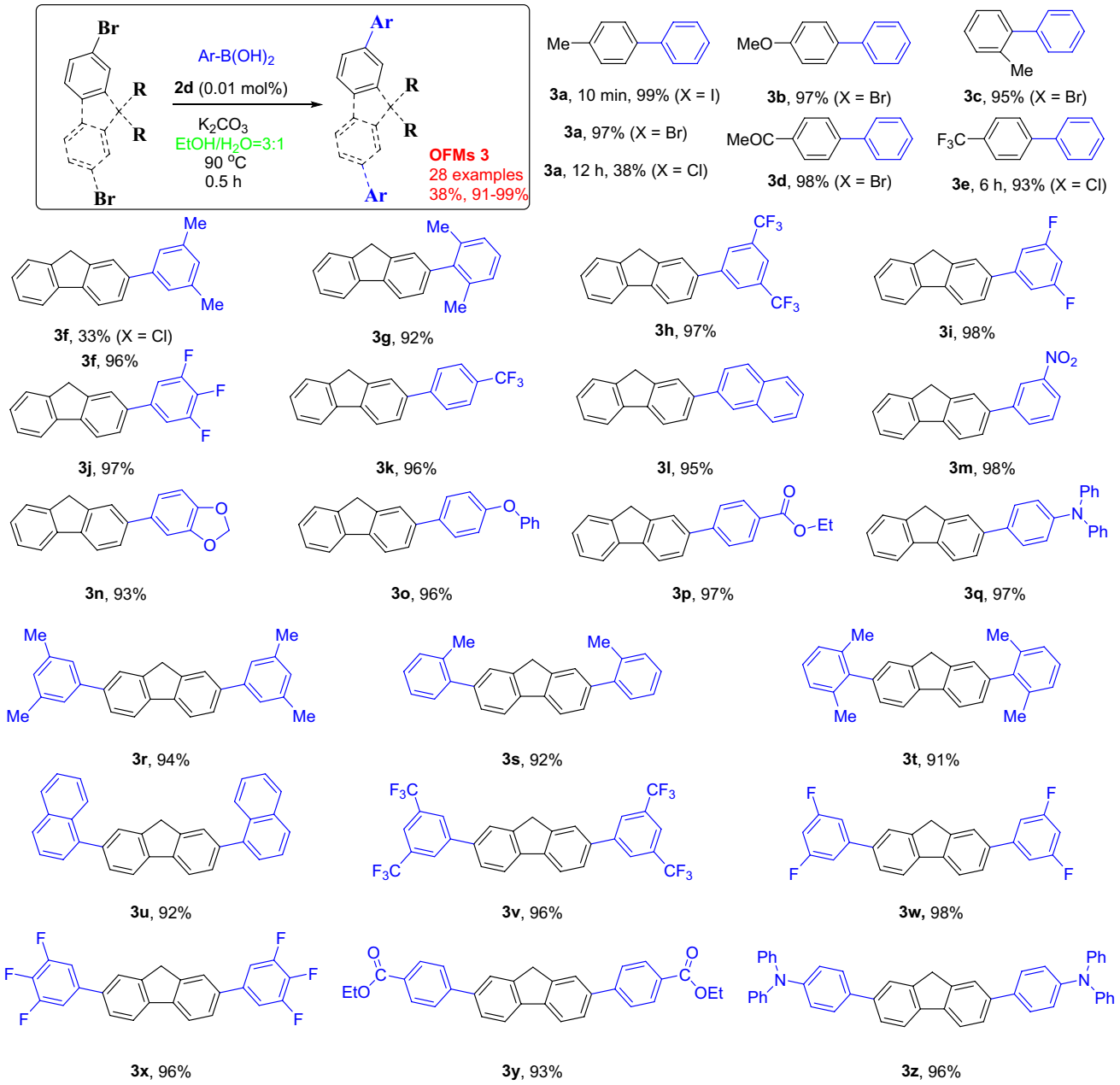


Fig. 3 The substrate scope for the synthesis of biphenyl and fluorine-cored COFMs (28 examples)

4H, CH_2), 1.46 (m, 2H, CH_2), 1.94 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 3.69 (m, 1H, CH-Glu), 4.10 (m, 2H, CH_2), 4.23 (m, 1H, CH-Glu), 4.29 (m, 1H, CH-Glu), 4.42 (m, 3H, CH-Glu and CH_2), 4.52 (m, 1H, CH-Glu), 4.98 (m, 2H, CH_2), 5.05 (t, $J = 10.0$ Hz, 1H, CH-Glu), 5.15 (t, $J = 9.2$ Hz, 1H, CH-Glu), 6.87 (d, $J = 2.0$ Hz, 1H, CH-Imidazole), 6.98 (d, $J = 2.0$ Hz, 1H, CH-Imidazole), 7.32 (m, 2H, CH-Pyridine), 7.75 (m,1H, CH-Pyridine), 8.99 (m, 2H, CH-Pyridine). ^{13}C NMR (101 MHz, $CDCl_3$), δ 13.8 (CH_3), 14.2 (CH_2), 19.9 (CH_2), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 32.1 (CH_2), 51.0 (CH_2-CH_2), 60.4 (CH-Glu), 61.8 (CH_2-CH_2), 68.9 (CH-Glu), 71.1 (CH-Glu), 71.7 (CH-Glu), 72.7 (CH-Glu), 100.7 (CH-Glu), 121.0 (C-Imidazole), 124.0 (C-Imidazole), 124.6 (CH-Pyridine), 137.9 (CH-Pyridine), 146.8 (CH-Pyridine), 152.5 (NCN-Pd), 169.3 (C = O), 169.4 (C = O), 170.1 (C = O), 170.7 (C = O). FT-IR (cm^{-1}): 3478, 2957, 2872, 1757, 1602, 1569, 1445, 1428, 1370, 1221, 1168, 1067, 1039, 907, 758, 688. MS (ESI): m/z (%) = 844.8 (100) $[M + 1]^+$.

Table 4 Reusability of the catalyst in the Suzuki reaction[a]

Run	Time (min)	Conversion[b]	Yield (%)[c]
1	10	100	98
2	10	99	98
3	10	97	95
4	10	95	93
5	30	100	99

[a]Reaction conditions: 4-iodotoluene (2.0 mmol), phenylboronic acid (3.0 mmol), catalyst **2d** (0.01 mol%), K_2CO_3 (4.0 mmol), EtOH/H_2O (v/v = 3:1, 12.0 mL), 90 °C oil bath

[b]Measured by GC–MS

[c]Isolated yield

4.4 [1-(2-β-D-glucopyranosyloxyethyl)-3-phenyl-imidazol-ylidene]Pd(pyridine)Br_2

Yellow crystalline solid, 92%. ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.00 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.72 (m, 1H, CH-Glu), 4.12 (m, 3H, CH-Glu and CH_2), 4.28 (m, 1H, CH-Glu), 4.41 (m, 1H, CH-Glu), 4.50 (m, 1H, CH-Glu), 4.60 (m, 2H, CH_2), 5.12 (m, 4H, CH-Glu and CH_2), 7.14 (d, J = 2.0 Hz, 4H, CH-Pyridine and CH-Benzene), 7.18 (d, J = 2.0 Hz, 1H, CH-Imidazole), 7.26 (m, 2H, CH-Pyridine and CH-Benzene), 7.48 (d, J = 8.0 Hz, 1H, CH-Imidazole), 7.56 (d, J = 8.0 Hz, 2H, CH-Benzene), 7.70 (m, 1H, CH-Benzene), 8.00 (m, 2H, CH-Pyridine), 8.82 (m, 2H, CH-Pyridine). ^{13}C NMR (101 MHz, $CDCl_3$), δ 20.5 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 51.3 (CH_2-CH_2), 61.8 (CH_2-CH_2), 68.3 (CH-Glu), 68.8 (CH-Glu), 71.2 (CH-Glu), 71.8 (CH-Glu), 72.7 (CH-Glu), 100.8 (CH-Glu), 122.5 (C-Imidazole), 124.5 (C-Benzene), 126.4 (C-Imidazole), 128.8 (C-Pyridine), 129.3 (C-Pyridine), 129.9 (C-Pyridine), 137.8 (C-Benzene), 139.5 (C-Benzene), 148.8 (C-Benzene), 151.9 (C-Benzene), 152.4 (NCN-Pd), 169.4 (C = O), 169.5 (C = O), 170.1 (C = O), 170.7 (C = O). FT-IR (cm^{-1}): 3394, 2920, 2850, 1754, 1647, 1602, 1560, 1499, 1428, 1367, 1224, 1168, 1065, 1039, 904, 764, 694. MS (ESI): m/z (%) = 864.7 (100) $[M+1]^+$.

4.5 [1-(2-β-D-glucopyranosyloxyethyl)-3-(2,5-dimethylphenyl)-imidazol-ylidene]Pd(pyridine)Br_2

Yellow crystalline solid, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.72 (m, 1H, CH-Glu), 4.06 (q, J = 18.0 Hz, 2H, CH_2), 4.09 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H, CH-Glu), 4.25 (dd, J_1 = 12.0 Hz, J_2 = 4.6 Hz, 1H, CH-Glu), 4.37 (m, 1H, CH-Glu), 4.48 (m, 1H, CH-Glu), 4.57 (dd, J_1 = 8.8 Hz, J_2 = 3.6 Hz, 1H, CH-Glu), 4.60 (d, J = 8.0 Hz, 2H, CH_2), 5.01–5.06 (m, 2H, CH_2), 5.22 (m, 1H, CH-Glu), 6.83 (d, J = 2.0 Hz, 1H, CH-Imidazole), 7.16 (m, 4H, CH-Pyridine and CH-Benzene), 7.19 (d, J = 2.0 Hz, 1H, CH-Imidazole), 7.27 (t, J = 8.0 Hz, 1H, CH-Pyridine), 7.60 (m, 1H, CH-Pyridine), 8.66 (m, 2H, CH-Pyridine). ^{13}C NMR (101 MHz, $CDCl_3$), δ 19.6 (CH_3), 19.7 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 20.6 (CH_3) 20.8 (CH_3), 51.4 (CH_2-CH_2), 61.5 (CH_2-CH_2), 68.0 (CH-Glu), 68.6 (CH-Glu), 71.0 (CH-Glu), 71.6 (CH-Glu), 72.5 (CH-Glu), 100.3 (CH-Glu), 123.5 (C-Imidazole), 123.7 (C-Benzene), 124.1 (C-Imidazole), 128.3 (C-Pyridine), 128.4 (C-Pyridine), 129.2 (C-Pyridine), 136.3 (C-Benzene), 136.4 (C-Benzene), 137.5 (C-Benzene), 149.4 (C-Benzene), 152.2 (NCN-Pd), 169.0 (C = O), 169.2 (C = O), 169.8 (C = O), 170.3 (C = O). FT-IR (cm^{-1}): 3495, 2920, 2868, 1754, 1644, 1602, 1446, 1428, 1367, 1224, 1171, 1064, 1036, 907, 778, 755, 694. MS (ESI): m/z (%) = 892.9 (100) $[M+1]^+$.

4.6 General procedure for the Suzuki reaction catalyzed by Glu-NHCs-Pd(II)-PEPPSI complexes 2a-d

Degassed EtOH/H_2O (v/v = 3:1, 3.0 mL) was transfer to a flask with the corresponding amount of K_2CO_3 (2.0 mmol), Glu-NHCs-Pd(II)-PEPPSI complex (0.01 mol%), then stirred for about 5 min under N_2 atmosphere, 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol) was sequentially added, the reaction solution was kept at 90 °C and stirred for the corresponding time shown in Tables 1, 2 and Fig. 2. The mixture was diluted with 3.0 mL of dichloromethane, and then washed with brine. The organic layer was collected and dried over $MgSO_4$. The organic solvent was concentrated in vacuum, and the product was purified by flash chromatograph.

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Code Availability CCDC Deposition Number 2069632 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Declarations

Conflict of interest There are no conflicts of interest to declare.

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