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SHORT COMMUNICATION

Amino acid-modified cyclodextrins as ligands for Heck reaction in water

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Abstract Three novel amino-acid modified β-cyclodextrins were synthesized, which were used as supramolecular hosts and promoters for the Pd-catalyzed Heck reactions of aryl iodides with styrene in aqueous solution to give the corresponding adducts with high yields (up to 95 %). The catalyst can be recovered and reused.

Keywords Heck reactions · Amino acid-modified · Cyclodextrin · Aqueous reactions

Introduction

Transition metal-catalyzed carbon–carbon cross-coupling reactions have attracted considerable attention recently [1–3]. These reactions are widely utilized in producing fine chemicals including pharmaceuticals. Among the different types of known methodologies, Heck reaction is one of the most important, which involves the coupling of unsaturated aryl halides with alkenes in the presence of a palladium catalyst system [4–9]. Heck reaction shows advantages including high selectivity, mild reaction conditions and wide substrate tolerance, but suffers from several key limitations such as the use of poisonous phosphane ligands and high boiling point organic solvents.

Some phosphine-free systems for Heck reactions have been explored, including amino acids, *N*-heterocyclic, amido/pyridyl carboxylate, hydrazone, sulfoxide and bis-imidazole [10–18]. Among them the amino acids as ligands are especially interesting, because they are inexpensive, conveniently available, environmentally benign, and structurally diverse. Previously, we have reported that amino acid ligands could promote several types of reactions [19–21]. To avoid the use of the organic solvent, much attention has been focused on looking for Heck reaction in aqueous solutions. It has been reported that Heck reaction can be carried out in mixture of organic-solvents/water bi-phase system or with bulk surfactants [22–24].

We were interested in finding better catalyst systems for Heck reaction in water. Cyclodextrin (CD) is a good option to be involved in aqueous and reusable reaction. CD is a widely used host molecule capable of guest molecules in water with binding constants in the $10^{0.5}$–10^{5} M^{-1} range [25, 26]. CDs have been extensively used as catalysts in aqueous phase because of their ability to solubilize the hydrophobic compounds and their ability to recognize different molecules [27–32]. In our previous work, we have synthesized an array of modified CDs for construction of various supramolecular systems [33–38]. Herein, we report a novel Pd-catalyzed Heck reaction using amino-acid modified β-CD as ligand in aqueous solution.

Experimental methods

Materials and methods

All solvents were reagent grade, purchased from commercial sources, and used without further purification, except DMSO, which was dried over CaH_2 under N_2, filtered and distilled under reduced pressure. Iodobenzene,

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PPh_3, $Pd(Ac)_2$, β-CD, amino acid and *p*-toluenesulfonyl acid (TSA) were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received. ^{1}H NMR spectra were recorded on a 400 MHz Bruker ARX400 spectrometer at 20 °C. Chemical shifts were referenced to the residual protonated solvent peak.

Synthesis of 6-O-p-toluenesulfonyl-β-cyclodextrin (OTs-β-CD) and mono-6-iodine-6-deoxy-β-cyclodextrin (I-β-CD)

OTs-β-CD and I-β-CD were prepared according to our previously reports [34–38].

*Synthesis of ligand **2**, **3** and **4***

General procedure of amino acid-β-CDs synthesis: A mixture of dried β-CD-I (5.5 g, 4.5 mmol) and commercial amino acid (22.5 mmol) in the solution of anhydrous DMF (50 mL) and Et_3N (6.25 mL) is stirred at 80 °C for overnight. Then the solution is precipitated by 500 mL acetone. The precipitate was filtered, and dissolved in DMF and precipitated in acetone for 3 times.

Yield of ligand **2**, 90 %. Positive ion MALDI–TOF mass *m/z*: 1370.4 ($M + Na^+ = 1{,}228$). ^{1}H NMR (500 MHz. DMSO–d_6): δ(ppm) 5.88–5.57 (m, 14H, O(2) and O(3) of β-CD), 4.94–4.79 (m, 7H, C(1) of β-CD), 4.57–4.41 (m, O(6) and C(6′) of β-CD), 3.80–3.56 (m, 28H, C(6)H, C(3)H and C(5) of β-CD), 3.40–3.18 (m, overlaps, with HOD, C(4)H and C(2) of β-CD), 1.07–1.34 (m, 3H, CH_3 of alanine). ^{13}C NMR(DMSO–d_6, 300 MHz): δ(ppm) 171.9 (C of –CO–), 102.3 (C(1) of β-CD), 81.9 (C(4) of β-CD), 73.5 (C(3) of β-CD), 72.8 (C(2) of β-CD), 72.5 (C(5) of β-CD), 64.7 (C of $–CH_2–CO$), 60.4 (C(6) of β-CD), 56.6 (C(6′) of β-CD), 31.3, (C of CH_3).

Yield of ligand **3**, 86 %. Positive ion MALDI–TOF mass *m/z*: 1370.4 ($M + Na^+ = 1{,}304$). ^{1}H NMR (500 MHz. DMSO–d_6): δ(ppm) 6.8–8.0 (m, 5H, phenyl), 5.85–5.65 (m, 14H, O(2) and O(3) of β-CD), 4.87–4.76 (m, 7H, C(1) of β-CD), 4.64–4.40 (m, O(6) and C(6′) of β-CD), 3.83–3.54 (m, 28H, C(6)H, C(3)H and C(5) of β-CD), 3.43–3.15 (m, overlaps with HOD, C(4)H and C(2) of β-CD), 1.86–2.15 (m, 2H, CH_2 of phenylalanine). ^{13}C NMR(DMSO–d_6, 300 MHz): δ(ppm) 171.8 (C of –CO–), 129.8, 129.7, 128.8, 128.3, (C of phenyl), 102.4 (C(1) of β-CD), 81.9 (C(4) of β-CD), 73.5 (C(3) of β-CD), 72.8 (C(2) of β-CD), 72.5 (C(5) of β-CD), 64.6 (C of $–CH_2–CO$), 60.4 (C(6) of β-CD), 56.6 (C(6′) of β-CD), 18.8 (C of $–CH_2–$).

Yield of ligand **4**, 85 %. Positive ion MALDI–TOF mass *m/z*: 1370.4 ($M + Na^+ = 1{,}254$). ^{1}H NMR (500 MHz. DMSO–d_6): δ(ppm) 5.85–5.67 (m, 14H, O(2) and O(3) of β-CD), 4.85–4.79 (m, 7H, C(1) of β-CD), 4.63–4.41 (m, O(6) and C(6′) of β-CD), 3.81–3.56 (m, 28H, C(6)H, C(3)H and C(5) of β-CD), 3.45–3.20 (m, overlaps with HOD, C(4)H and C(2) of β-CD), 2.41–1.01 (m, 6H, $(CH_2)_3$ of proline). ^{13}C NMR (300 MHz. DMSO–d_6): δ(ppm) 172.0 (C of –CO–), 102.5 (C(1) of β-CD), 81.9 (C(4) of β-CD), 73.5 (C(3) of β-CD), 72.8 (C(2) of β-CD), 72.5 (C(5) of β-CD), 61.0 (C of $–CH_2–CO$), 60.4 (C(6) of β-CD), 58.6 (C(6′) of β-CD), 47.2, 31.1, 23.1 (CH_2 of proline).

General procedure of amino acid-β-CDs/Pd Heck reaction

General procedure of amino acid-β-CDs/Pd Heck reaction: A mixture of aryl halide (0.5 mmol), styrene (0.75 mmol), $Pd(OAc)_2$ (0.1 mol%), β-CD–phenylalanine (10 mol%), Li_2CO_3 (20 mmol) in 1 mL saturated β-CD aqueous solution is stirred under argon at 100 °C for 10 h. After the mixture is cooled, extracted by ether and evaporated, the residue is purified by chromatography to afford pure product.

(E)-4-(t-Bu)-Flourostilbene (entry 4, Table 3)

White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.47 (t, $J = 8.4$ Hz, 4H), 7.41 (d, $J = 8.6$, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.07 (d, $J = 16.3$ Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (300 MHz. $CDCl_3$): δ(ppm) 150.9, 136.7, 134.5, 128.4, 127.9, 126.8, 126.3, 126.0, 125.7, 125.5, 34.7, 31.4. MS (EI): *m/z* (relative intensity): 254 (100).

(E)-4-(t-Bu)-Chlorostilbene (entry 7, Table 3)

^{1}H NMR (500 MHz, $CDCl_3$): δ7.44 (t, $J = 8.3$ Hz, 4H), 7.39 (d, $J = 8.5$, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.04 (d, $J = 16.3$ Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (300 MHz. $CDCl_3$): δ(ppm)151.1, 136.1, 134.3, 129.9, 128.9, 127.6, 126.6, 126.4, 125.7, 125.7, 34.7, 31.4. MS (EI): *m/z* (relative intensity): 270 (100).

Results and discussion

Our strategy of Heck reaction involves a supramolecular system to build amino acid modified β-CD as ligand. Therefore, novel CD-derivative **2**, **3** and **4** have been synthesized from commercial amino acids that were reacted with iodo-β-CD. The amino acids are used as metal ligand parts, whereas CD is used as the host molecule. Three kinds of amino acids were chosen, including alkylic D-alanine, aromatic L-phenylalanine, and cyclic L-proline, to be linked at the 6-position of CD to give **2**, **3** and **4**, respectively (Fig. 1).

In the first stage of the study we focused on the coupling between iodobenzene and styrene using amino acid

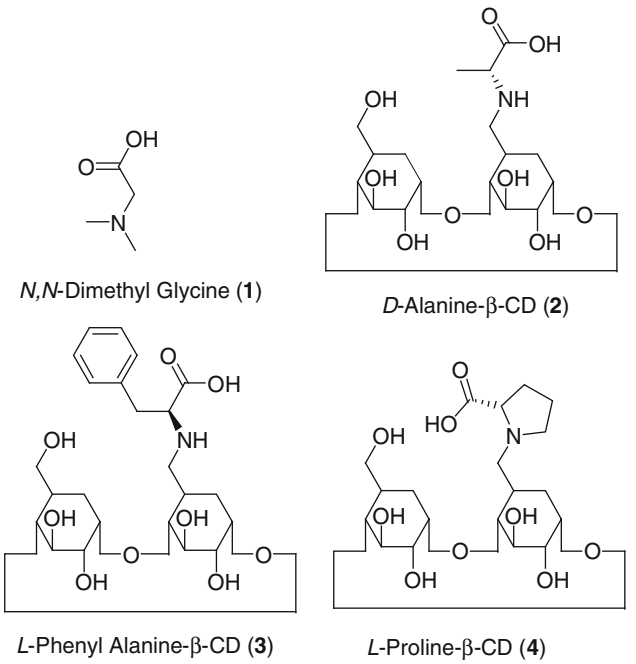
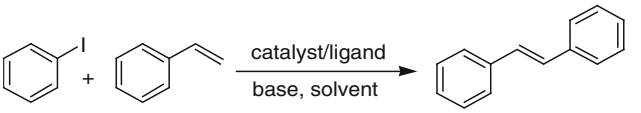


Fig. 1 Structures of ligands **1–4**

derivatives as the ligands. We examined the effects of various copper salts, bases, solvents, reaction temperatures, and reaction times on the yields of the coupling. The detailed results are listed in Table 1.

A preliminary trial using amino acid ligands in organic solvent NMP at 130 °C afforded the coupling products with similar yields for all the four ligands (Table 1, entry 1–4). After the change of the solvent to water, the yields decreased due to the poor solubility of iodobenzene and styrene in water (Table 1, entry 5, 6). To increases the reactant solubility, saturated β-CD solution was used instead of water, and ligand **3** gave much better results (73 %) than **2** (25 %) and **4** (58 %). It should be noted that the CD's concentration is important due to the binding constants of iodobenzene and styrene with β-CD around 10^2 M^{-1}. Also, 10 % ligand under saturated β-CD gave the comparable yields to saturated ligand. Therefore, the former strategy was used to save the amino acid modified CDs. We then explored the reaction in various bases, and found that the yield is highly dependent on the base. Inorganic bases were much better than the organic bases such as NEt_3 and DIEA, and Li_2CO_3 showed the best yield (90 %). In addition to $Pd(OAc)_2$, we also used CuI and $PdCl_2$ as the catalyst. However, the yields with the latter are much lower than the yield with CuI. A control experiment without ligand **3** showed yield as low as 40 %, indicating that the amino acid modified CD played an important role. Therefore, we conclude the reaction conditions in entry 10 were optimal for further investigation on the scope reactions.

Table 1 Optimization of reaction conditions for Heck reaction



Entry[a]	Catalyst	Ligand	Solvent	Base	Yield (%)[d]
1	$Pd(OAc)_2$	**1**	NMP[c]	K_2CO_3	72
2	$Pd(OAc)_2$	**2**	NMP[c]	K_2CO_3	70
c	$Pd(OAc)_2$	**3**	NMP[c]	K_2CO_3	84
4	$Pd(OAc)_2$	**4**	NMP[c]	K_2CO_3	74
5	$Pd(OAc)_2$	**3**	H_2O	K_2CO_3	54
6	$Pd(OAc)_2$	**3**	H_2O	Li_2CO_3	56
7	$Pd(OAc)_2$	**2**	β-CD/H_2O	K_2CO_3	25
8	$Pd(OAc)_2$	**3**	β-CD/H_2O	K_2CO_3	73
9	$Pd(OAc)_2$	**4**	β-CD/H_2O	K_2CO_3	58
10	**$Pd(OAc)_2$**	**3**	**β-CD/H_2O**	**Li_2CO_3**	**90**
11	$Pd(OAc)_2$	**3**	β-CD/H_2O	Li_2CO_3	95[e]
12	$Pd(OAc)_2$	**3**	β-CD/H_2O	K_2HPO_4	84
13	$Pd(OAc)_2$	**3**	β-CD/H_2O	K_3PO_4	87
14	$Pd(OAc)_2$	**3**	β-CD/H_2O	Et_3N	19
15	$Pd(OAc)_2$	**3**	β-CD/H_2O	DIEA	15
16	$Pd(OAc)_2$[b]	**3**	β-CD/H_2O	Li_2CO_3	27
17	CuI	**3**	β-CD/H_2O	Li_2CO_3	Trace
18	$PdCl_2$	**3**	β-CD/H_2O	Li_2CO_3	<10
19	$Pd(OAc)_2$	None	β-CD/H_2O	Li_2CO_3	40

Bold values emphasize the used reaction conditions in the Tables 2 and 3

[a] Reaction conditions: iodobenzene (0.5 mmol), styrene (0.75 mmol), catalyst (0. 1 mol%), ligand (10 mol%) in 1 mL solvent at 100 °C for 10 h

[b] Catalyst is 0.01 mol%

[c] Under 130°

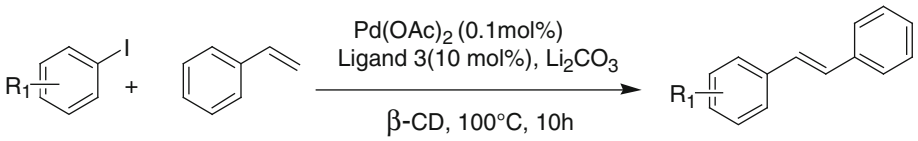
[d] GC-mass yield with a internal standard

[e] Reaction time is 24 h

With the conditions in entry 10 Table 1, we first set out to carry out the reactions of styrene with various iodobenzene substrates, as shown in Table 2. For iodobenzene substrates, electron-withdrawing substitutions, such as NO_2 and CN, dramatically reduced the yields, while fluoro gave the yield high to 95 %. Bromo substitutions showed almost equivalent mono- and di-arylation compounds due to the similar activity of bromo and iodo, leading to low yields (Table 2, entry 3, 4). To our disappointment, carboxylic acid groups failed to give the corresponding product (Table 2, entry 8, 9). The reason should be that the acid substitution is difficult to enter CD cavity to form a supramolecular complex, which was detected by H NMR spectrum [39]. Notably, esterified carboxylic acid substrates could be phenylated in good yields (Table 2, entry 10, 11).

Furthermore, the reactions between three kinds of iodobenzene with various styrenes were also investigated

Table 2 Scope of iodobenzene for Heck-reaction



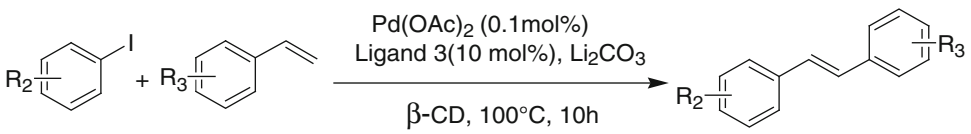
Entry[a]	R_1	Ligand	Yield (%)[b]
1	4-F	**3**	95 (87)[c]
2	4-Cl	**3**	95 (85)[c]
3	4-Br	**3**	29
4	2-Br	**3**	36
5	4-OCH_3	**3**	77
6	4-NO_2	**3**	Trace
7	3-CN	**3**	44
8	4-COOH	**3**	Trace
9	2-COOH	**3**	Trace
10	4-COOEt	**3**	55
11	2-$COOCH_3$	**3**	42

[a] General conditions: 0.1 mol% $Pd(OAc)_2$, 10 mol% ligand, 1 mL β-CD/H_2O solvent, 0.5 mmol Ph–I, 0.75 mmol styrene, 12.5 mmol Li_2CO_3, temperature = 100 °C, reaction time = 10 h

[b] GC-mass yield with an internal standard

[c] Isolated yield under 10 times scale

Table 3 Heck-type reaction facilitated by ligand **3**



Entry[a]	R_2	R_3	Yield (%)[b]
1	H	4-*t*-Bu	37
2	H	4-OMe	51
3	H	2,3,4,5,6-Pentafluoro	57
4	4-F	4-*t*-Bu	77
5	4-F	4-OMe	69
6	4-F	2,3,4,5,6-Pentafluoro	87
7	4-Cl	4-*t*-Bu	95
8	4-Cl	4-OMe	50
9	4-Cl	2,3,4,5,6-Pentafluoro	93

[a] General conditions: 0.1 mol% $Pd(OAc)_2$, 10 mol% ligand, 1 mL β-CD/H_2O solvent, 0.5 mmol Ph–I, 0.75 mmol styrene, 20 mmol Li_2CO_3, temperature = 100 °C, reaction time = 10 h

[b] GC-mass yield with an internal standard

under identical conditions (Table 3). To our delight, most substituted triarylphosphines were well tolerated under the optimized conditions, leading to the desired products in moderate to good yields. Interestingly, 2,3,4,5,6-pentafluoro groups gave the best yields, which might provide an opportunity for fluoro compounds synthesis. Moreover, in all the amino acid modified CD-mediated Heck reactions, the percentage of 2-coupling compounds is no more than 10 % as detected by GC/MS.

In addition, the recycle of our catalyst system were tested. After each reaction was finished, all the products were extracted out using ether, and the remaining water

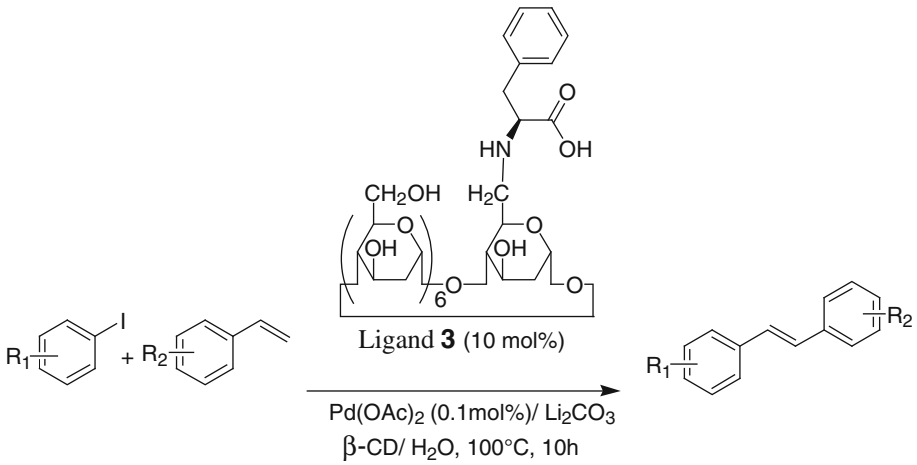


Fig. 2 Amino acid-modified CD as ligand catalyzes Heck reaction

layer was used to initiate a new round of Heck reaction. Unfortunately, the yield decreased to half and failed to catalyze this reaction after five runs. The reason is possibly due to the loss of $Pd(OAc)_2$ in large quantities at the ether extraction. Therefore, supplying half quality of $Pd(OAc)_2$ after reaction, the yield give a slight increase (92 %).

Conclusion

Novel mild conditions have been found for the Pd-catalyzed Heck coupling reactions of aryl iodides with styrenes with amino acids modified CD as ligands in water (Fig. 2). The coupling yields are high to 95 % and the catalyst is recovered and reused. We are working now on this Heck coupling reactions using aryl bromides and chlorides as reactants. Another challenge is how to catalyze enantioselective reactions by the system.

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