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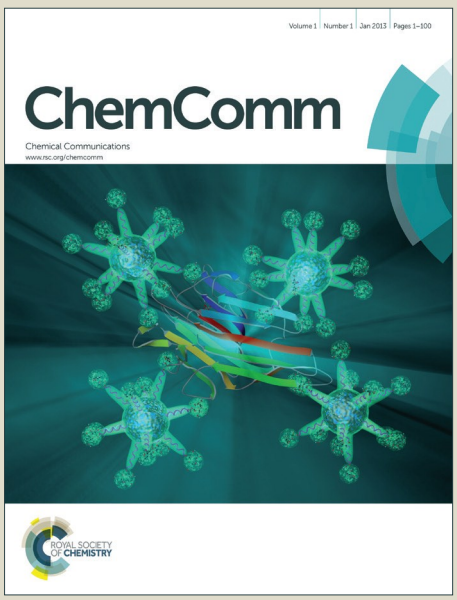

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Synthesis of diversely substituted 2-(furan-3-yl)acetates from allenols through cascade carbonylations

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

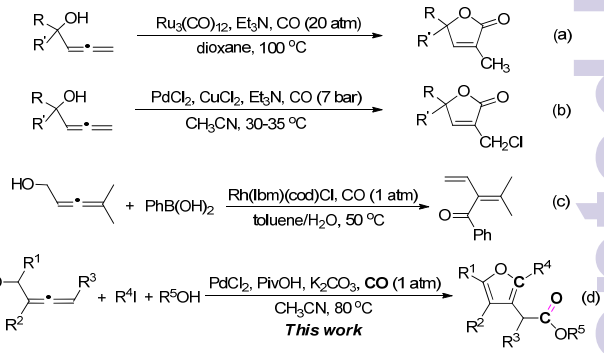
DOI: 10.1039/b000000x

A novel synthesis of diversely substituted 2-(furan-3-yl) acetates via palladium-catalyzed one-pot multi-component reactions of allenols, aryl iodides, alcohols, and carbon monoxide has been developed. Notably, the formation of the title compounds features a cascade process combining carbonylation of aryl iodide, alcohoxyl carbonylation of the in situ formed allyl palladium complex, and intramolecular condensation of the α-hydroxyl enone intermediate. Moreover, the 2-(furan-3-yl)acetates obtained herein were found to be ready intermediates for the construction of the biologically significant naphtho[1,2-*b*]furan-5-ol scaffold.

Furan derivatives have attracted tremendous attention due to their wide presence in numerous natural products, pharmaceuticals, and functional materials.[1] Moreover, furan and its analogs have also been routinely utilized as building blocks in synthetic chemistry.[2] Owing to their importance, a number of strategies for the preparation of furan derivatives have been developed.[3-9] While these literature methods are generally efficient and reliable, there is still an urgent demand to develop more general and practical methods that can produce functionalized furans through simplified procedures and from easily obtainable or commercially available starting materials.

Meanwhile, efficient construction of the library of compounds with biological and synthetic interests has relied heavily on multi-component reactions (MCRs) since this kind of reactions allow rapid generation of complex and structurally diverse products in a one-pot manner by using simple substrates.[10] In this aspect, carbon monoxide as an inexpensive and atom-economy C1 source has been frequently utilized in various MCRs.[11]

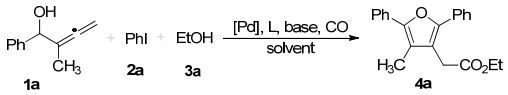
On the other hand, allene derivatives are indispensable intermediates in the synthesis of a myriad of organic compounds owing to their diverse reactivity.[12] In previous studies, Takahashi has disclosed that allenyl alcohols could undergo cyclo-carbonylation in the presence of a ruthenium catalyst to give five-membered lactones in high yields with 100% atom economy (Scheme 1, (a)).[13a] Ma developed a mild and efficient method for the synthesis of 3-chloromethyl-2(5*H*)-furanones via $PdCl_2$-catalyzed chlorocyclocarbonylation of allenols in the presence of $CuCl_2$ (Scheme 1, (b)).[13b] Choi recently reported a NHC-rhodium-catalyzed carbonylative C-C bond formation of allenyl alcohols with arylboronic acids under carbon monoxide (Scheme 1, (c)).[13c] Inspired by those pioneering studies and as a continuation of our recent efforts in developing novel synthetic methodologies by using allene derivatives as key substrates,[14] we herein report a novel and convenient synthesis of 2-(furan-3-yl)acetates through Pd-catalyzed one-pot MCRs of allenols, aryl iodides, alcohols and CO (Scheme 1, (d)). To the best of our knowledge, this is the first example in which two cascade carbonylations to introduce one C to construct the furan scaffold and another C to form the carboxyl unit are involved in the preparation of functionalized furans.



Scheme 1 Carbonylation of allenic alcohols under different conditions

Our studies were initiated by treating 2-methyl-1-phenylbuta-2,3-dien-1-ol (**1a**, 0.3 mmol), obtained from the reaction of 1-bromobut-2-yne with benzaldehyde,[15] with iodobenzene (**2a**, 0.6 mmol) and ethanol (**3a**, 3 mmol) in the presence of $Pd(OAc)_2$ (0.03 mmol), P(2-furyl)$_3$ (0.12 mmol), and K_2CO_3 (0.3 mmol) under an atmosphere of CO in CH_3CN at 80 °C for 8 h. From this reaction, the desired ethyl 2-(4-methyl-2,5-diphenylfuran-3-yl)acetate (**4a**) was obtained in 24% yield (Table 1, entry 1). To improve the efficiency, different catalysts were tried, and $PdCl_2$ was found to be more effective than $Pd(PPh_3)_2Cl_2$, $Pd_2(dba)_3$, $Pd(PPh_3)_4$, and $Pd(OAc)_2$ (entries 1-5). Next, various ligands such as PPh_3, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos), 2-dicyclohexylphosphino-2′,4′,6′-dimethoxylbiphenyl (SPhos), tri-*tert*-butylphosphonium tetrafluoroborate (^{t}Bu$_3$P·BF$_4$), tricyclohexylphosphine (PCy_3), 1,10-phenanthroline (1,10-phen), *N*,*N*′-dimethylethylenediamine (DMEDA), *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA), *L*-proline, and pivalic acid (PivOH) were also tested (entries 6-15). To our delight, the presence of *L*-proline or PivOH could improve the yield of **4a** to 45% or 63%, respectively (entries 14 and 15). Following studies on the effect of different bases on this reaction showed that K_2CO_3 gave the best yield of **4a** (entries 15-18). Finally, we found that changing CH_3CN to ethanol, toluene, DCE, 1-methyl-2-pyrrolidinone (NMP), 1,4-dioxane, or DMF as the reaction medium resulted in decreased efficiency (entries 19-24 vs 15).

Table 1 Optimization studies for the formation of **4a** [a]

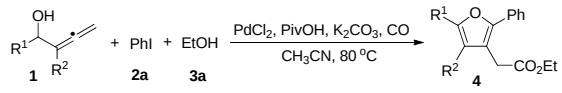


Entry	Pd source	Ligand	Solvent	Base	Yield (%) [b]
1	$Pd(OAc)_2$	P(2-furyl)$_3$	CH_3CN	K_2CO_3	24
2	$PdCl_2$	P(2-furyl)$_3$	CH_3CN	K_2CO_3	30
3	$Pd(PPh_3)_2Cl_2$	P(2-furyl)$_3$	CH_3CN	K_2CO_3	-
4	$Pd_2(dba)_3$	P(2-furyl)$_3$	CH_3CN	K_2CO_3	-
5	$Pd(PPh_3)_4$	P(2-furyl)$_3$	CH_3CN	K_2CO_3	trace
6	$PdCl_2$	PPh_3	CH_3CN	K_2CO_3	41
7	$PdCl_2$	XPhos	CH_3CN	K_2CO_3	38
8	$PdCl_2$	SPhos	CH_3CN	K_2CO_3	27
9	$PdCl_2$	$^tBu_3P{\cdot}BF_4$	CH_3CN	K_2CO_3	35
10	$PdCl_2$	PCy_3	CH_3CN	K_2CO_3	trace
11	$PdCl_2$	1,10-Phen	CH_3CN	K_2CO_3	32
12	$PdCl_2$	DMEDA	CH_3CN	K_2CO_3	20
13	$PdCl_2$	TMEDA	CH_3CN	K_2CO_3)	trace
14	$PdCl_2$	L-Proline	CH_3CN	K_2CO_3	45
15	**$PdCl_2$**	**PivOH**	**CH_3CN**	**K_2CO_3**	**63**
16	$PdCl_2$	PivOH	CH_3CN	Et_3N	32
17	$PdCl_2$	PivOH	CH_3CN	Cs_2CO_3	45
18	$PdCl_2$	PivOH	CH_3CN	NaOH	43
19	$PdCl_2$	PivOH	ethanol	K_2CO_3	51
20	$PdCl_2$	PivOH	toluene	K_2CO_3	40
21	$PdCl_2$	PivOH	DCE	K_2CO_3	31
22	$PdCl_2$	PivOH	NMP	K_2CO_3	29
23	$PdCl_2$	PivOH	1,4-dioxane	K_2CO_3	48
24	$PdCl_2$	PivOH	DMF	K_2CO_3	49

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), **3a** (3 mmol), catalyst (0.03 mmol), ligand (0.12 mmo), base (0.3 mmol), solvent (2 mL), 80 °C, CO (1 atm), 8 h; [b] Isolated yield.

With the optimized reaction conditions in hand (Table 1, entry 15), the scope of this Pd-catalyzed double carbonylation protocol leading to 2-(furan-3-yl)acetates (**4**) was explored. Firstly, the suitability of various allenic alcohols (**1**) was studied by using **2a** and **3a** as model substrates. The results listed in Table 2 showed that this method was effective for phenyl substituted allenic alcohols bearing different substituents on the phenyl ring to afford the desired 2-(furan-3-yl)acetates **4a-4f** in moderate to good yields (entries 1-6). Various functional groups, from the electron-donating methoxy to the electron-withdrawing trifluoromethyl, were well compatible and the electronic nature of the aromatic ring did not show obvious effect on the yield of **4**. Moreover, naphthyl and thienyl substituted allenols underwent

Table 2 Substrate scope for the synthesis of **4** (I) [a]



Entry	R^1	R^2	**4**	Yield (%) [b]
1	Ph	CH_3	**4a**	63
2	2-$CH_3C_6H_4$	CH_3	**4b**	50
3	3-BrC_6H_4	CH_3	**4c**	68
4	3-FC_6H_4	CH_3	**4d**	64
5	4-$F_3CC_6H_4$	CH_3	**4e**	54
6	3,4-di-$CH_3OC_6H_3$	CH_3	**4f**	57
7	2-naphthyl	CH_3	**4g**	48
8	2-thienyl	CH_3	**4h**	57
9	PhCH=CH	CH_3	**4i**	62
10	Bn	CH_3	**4j**	52
11	$PhCH_2CH_2$	CH_3	**4k**	55
12	4-$CH_3C_6H_4$	C_2H_5	**4l**	58
13	2-naphthyl	C_2H_5	**4m**	48

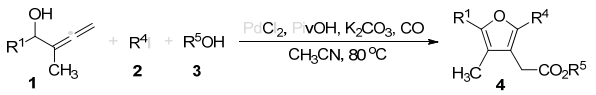
[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.6 mmol), **3a** (3 mmol), $PdCl_2$ (0.03 mmol), PivOH (0.12 mmol), K_2CO_3 (0.3 mmol), CH_3CN (2 mL), 80 °C, CO (1 atm), 8 h; [b] Isolated yield.

this cascade reaction to give **4g** and **4h** in 48% and 57% yields (entries 7-8). In addition to aryl unit, cinnamenyl and alkyl substituted allenol substrates took part in this procedure smoothly to afford **4i**, **4j** and **4k** in 62%, 52% and 55% yields, respectively (entries 9-11). As a further aspect, reactions of allenols bearing an ethyl group on the internal position of the allenic moiety also proceeded effectively (entries 12 and 13).

Next, the scope of the aryl iodide substrates (**2**) was studied. Gratifyingly, reactions with different **2** took place smoothly to afford a series of 2-(furan-3-yl)acetates with good yields (Table 2, entries 1-4). It was also found that aryl iodide bearing an electron-donating group (EDG) was less favorable than those with electron-withdrawing groups (EWGs) (entry 1 *vs* entries 2-4). Moreover, the position of the substituent on the aromatic ring had no obvious effect on this transformation. Notably, a di(thiophen-2-yl)furan derivative (**4r**) with unique fluorescent properties was conveniently prepared by using this method (entry 5).[16] To explore the generality of the alcohol substrates (**3**), different alcohols were tested (entries 6-11). While all of them could take part in this reaction, tertiary alcohol was less effective than primary alcohols, most likely due to steric hindrance.

It was then noticed that all the 2-(furan-3-yl)acetates obtained so far had a tetra-substituted furan moiety. To get tri-substituted furan derivatives (**6**), a series of allenol substrates without substituent attached on the internal position of the allenic moiety (**5**), prepared through CuI and dicyclohexylamine promoted reaction of 1-phenylprop-2-yn-1-ols with paraformaldehyde,[17] were subjected to the standard conditions as shown in Table 1. The results listed in Table 4 showed that 1-phenyl substituted allenols (**5**) with EDG or EWG on the phenyl ring underwent this

Table 3 Substrate scope for the synthesis of **4** (II) [a]

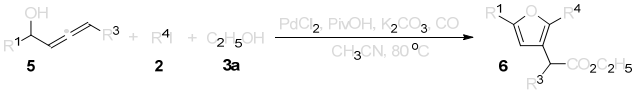


Entry	R^1	R^4	R^5	4	Yield (%) [b]
1	Ph	4-$CH_3OC_6H_4$	C_2H_5	**4n**	50
2	Ph	2-Br-4-FC_6H_3	C_2H_5	**4o**	78
3	3,4-di-$CH_3OC_6H_3$	2-$F_3CC_6H_4$	C_2H_5	**4p**	82
4	3,4-di-$CH_3OC_6H_3$	4-FC_6H_4	C_2H_5	**4q**	70
5	2-thienyl	2-thienyl	C_2H_5	**4r**	48
6	Ph	Ph	CH_3	**4s**	62
7	Ph	Ph	^{n}Bu	**4t**	42
8	Ph	Ph	^{n}Hex	**4u**	40
9	Ph	Ph	Bn	**4v**	50
10	Ph	Ph	allyl	**4w**	40
11	3,4-di-$CH_3OC_6H_3$	2-$F_3CC_6H_4$	^{t}Bu	**4x**	28

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), **3** (3 mmol), $PdCl_2$ (0.03 mmol), PivOH (0.12 mmol), K_2CO_3 (0.3 mmol), CH_3CN (2 mL), 80 °C, CO (1 atm), 8 h; [b] Isolated yield.

cascade process smoothly to give **6** in moderate to good yields and the electronic nature of substrates had no obvious influence on this reaction (entries 1-5). Apart from 1-phenyl allenols, 1-naphthyl and 1-thienyl substituted allenols were well compatible (entries 6, 7). Then, different aryl iodides (**2**) were also tested. Among them, aryl iodide with an EWG (entry 9) was more favourable than that with an EDG (entry 8). Finally, allenol bearing a phenyl group on the terminal position of the allenic moiety could also take part in this cascade reaction smoothly (entry 10).

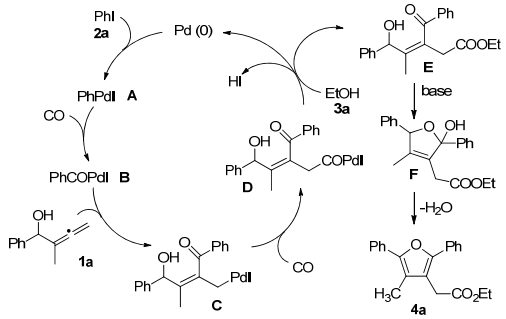
Table 4 Substrate scope for the synthesis of **6** [a]



Entry	R^1	R^3	R^4	6	Yield (%)[b]
1	Ph	H	Ph	**6a**	60
2	2-$CH_3C_6H_4$	H	Ph	**6b**	44
3	2-FC_6H_4	H	Ph	**6c**	40
4	4-$CH_3C_6H_4$	H	Ph	**6d**	55
5	4-ClC_6H_4	H	Ph	**6e**	50
6	2-naphthyl	H	Ph	**6f**	65
7	2-thienyl	H	Ph	**6g**	63
8	Ph	H	4-$CH_3OC_6H_4$	**6h**	50
9	Ph	H	4-ClC_6H_4	**6i**	62
10	Ph	Ph	Ph	**6j**	48

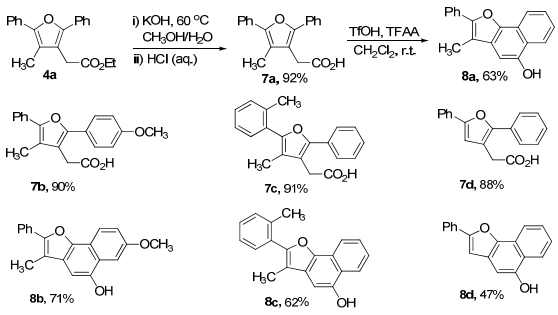
[a] Reaction conditions: **5** (0.3 mmol), **2** (0.6 mmol), **3a** (3 mmol), $PdCl_2$ (0.03 mmol), PivOH (0.12 mmol), K_2CO_3 (0.3 mmol), CH_3CN (2 mL), 80 °C, CO (1 atm), 8 h; [b] Isolated yield.

Based on the above observations and previous reports,[13, 18] a plausible pathway to account for the formation of **4a** is proposed in Scheme 2. Initially, oxidative addition of Pd(0) into **2a** forms intermediate **A**, which then undergoes carbonylation to afford an acylpalladium complex **B**. The following alkene coordination and insertion into the Pd-C(O)Ph bond gives an allyl palladium intermediate **C**. Carbonylation of **C** affords acylpalladium complex **D**. The following nucleophilic displacement of **D** with **3a** affords **E** and regenerates Pd(0). In the final stage of this cascade process, **E** undergoes an intramolecular nucleophilic addition followed by tautomerization and dehydration giving the final product **4a**.



Scheme 2 Plausible mechanism for the formation of **4a**

Having established a simple and efficient synthesis of 2-(furan-3-yl)acetates, we were then interested in exploring their synthetic applications by taking advantage of their unique structural characteristics. For this purpose, **4a** was firstly treated with KOH in aqueous methanol followed by acidification with aqueous HCl to afford 2-(4-methyl-2,5-diphenylfuran-3-yl)acetic acid (**7a**, 92%). Next, **7a** was subjected to a mixture of TfOH and TFAA to undergo an intramolecular Friedel-Crafts reaction to afford 3-methyl-2-phenylnaphtho[1,2-*b*]furan-5-ol (**8a**) in 63% yield (Scheme 3). It has been well recognized that naphtho[1,2-*b*]furan is a key structural unit in numerous compounds displaying significant medicinal and biological activities.[19] In particular, compounds bearing a naphtho[1,2-*b*]furan-5-ol unit are found to be efficient agents to alter the lifespan of eukaryotic organisms.[20] To explore the generality of this novel method for the synthesis of naphtho[1,2-*b*]furan-5-ol, some other 2-(furan-3-yl)acetates were tried. It turned out that all of them were suitable substrates to give the corresponding naphtha[1,2-*b*]furan-5-ols (**8b**-**8d**) with good efficiency (Scheme 3).



Scheme 3 Synthesis of naphtho[1,2-*b*]furan-ols (**8**) from **4** or **7**.

In summary, we have developed a novel strategy for the preparation of diversely substituted 2-(furan-3-yl)acetates from the one-pot cascade reactions of allenols with aryl iodides, alcohols, and carbon monoxide. This cascade procedure combines two palladium-catalyzed carbonylations, and tolerates various functional groups to give products with high structural diversity. Moreover, the usefulness of the 2-(furan-3-yl)acetates

obtained herein as valuable synthetic intermediates was showcased by their facile and efficient transformation into the biologically promising naphtha[1,2-*b*]furan-5-ol scaffold. Further exploitation of MCRs based on the dicarbonylation of allenols to achieve unprecedented organic transformations is underway in our laboratory.

This work was financially supported by the National Natural Science Foundation of China (NSFC) (grant numbers 21272058, 21172057), Program for Innovative Research Team in Science and Technology in University of Henan Province (15IRTSTHN 003), Program for Science and Technology Innovation Talents in Universities of Henan Province (15HASTIT005), and the Fostering Foundation of Henan Normal University for the National Excellent Doctorial Dissertation (01333900013).

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterisation data and NMR spectra. See DOI: 10.1039/b000000x/

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