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Synthesis of trisubstituted furans via Ag-catalyzed cascade heterocyclization of 2-(1-alkynyl)-2-alken-1-ones with aryl-amines

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Abstract A silver(I)-catalyzed cascade heterocyclization of 2-(1-alkynyl)-2-alken-1-ones with aryl-amines is described to synthesize trisubstituted furans in moderate to good yields. Tertiary amine is also efficient in this reaction. This transformation proceeds smoothly with the formation of C–N or C–C bonds in one-pot with good functional group tolerance under mild conditions.

Graphical Abstract



Keywords Silver catalyzed · Trisubstituted furans · Cascade reaction · Cyclization · Aryl-amine

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Introduction

Transition metal-catalyzed cyclization reactions of carboncarbon and carbon-heteroatom bond formation have proven to be an efficient and straightforward methodology for the synthesis of cyclic compounds (Patil and Yamamoto 2008; Weibel et al. 2008; Harmata 2010; Yamamoto 2012; Zeni and Larock 2004; Rubin et al. 2003; Cornil et al. 2015). Generally, silver complexes are considered to have similar efficiency compared with other late transition metal catalysts and recent studies have shown that silver species exhibited interesting catalytic activities for C–C, C–N, C– O, C–P, C–S bond formation (Liu et al. 2015; Hu et al. 2014; Wang et al. 2014; Ji et al. 2009; Hu et al. 2017).

Polysubstituted furans, which is one of the most important heterocyclic compounds, are not only key structural units in natural products and pharmaceuticals (Keay and Dibble 1996; Meegan 1984; Nakanishi 1974) but also useful intermediates in total syntheses (Wong et al. 1999; Lee et al. 2005). Many efforts have been made to obtain furan derivatives. (Blanc et al. 2016; Gulevich et al. 2013) Transition metal-catalyzed cyclization of 2-(1-alkynyl)-2-alken-1-ones with nucleophiles is one of the typical approaches to obtain polysubstituted furans since Larock (Yao et al. 2004) and co-works first report in 2004. Although the cyclization of 2-(1-alkynyl)-2-alken-1-ones with alcohols (Yao et al. 2004, 2005; Patil et al. 2005), nitrones (Liu et al. 2009, 2010), alkenes (Liu and Zhang 2011; He et al. 2013a, b; Wang et al. 2015), alkynes (Gao and Zhang 2012; Zhou et al. 2014), etc. (Xiao and Zhang 2008, 2009; Zhao and Zhang 2010; Li and Zhang 2010; Gao et al. 2010a, b, 2011; Ghosh et al. 2016) have proven to be available, the reaction of amines, especially secondary amines with this envnone was rarely reported (Oh et al. 2006; Chen et al. 2011).

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Herein, we report an efficient silver-catalyzed cascade heterocyclization of 2-(1-alkynyl)-2-alken-1-ones with aryl-amines to construct trisubstituted furans with an arylamino-group function.

Results and discussion

Our initial research focused on the reaction of (E)-2-benzylidene-1,4-diphenylbut-3-yn-1-one 1a and N-methylaniline 2a (1.5 equiv.) in the presence of AgNO₃ (5 mol %) in tetrahydrofuran (THF) at room temperature (Table 1, entry 1). We were pleased to find that the desired product rac-N-((2,5-diphenylfuran-3-yl)(phenyl)methyl)-N-methylaniline 3aa was isolated in 78% yield after 4 h. Further survey showed that, when dichloromethane was used as solvent, the reaction proceeded to provide 3aa in 95% yield after 1 h (Table 1, entry 2), whereas no reaction occurred in acetonitrile (Table 1, entry 3). Other catalysts, such as AgOTf, Ag₂CO₃, and Cu(OAc)₂ could not afford better results (Table 1, entries 4–6). Herein, the optimum reaction conditions for the synthesis of 3aa were found to be 1.0 equiv. of 1a, 1.5 equiv. of 2a and 5 mol % of AgNO₃ in dichloromethane at room temperature.

With the optimum conditions in hand, the scope of this cascade cyclization reaction of various ketones 1 with *N*-methylaniline **2a** was investigated (Table 2). A substrate with *para*-bromo-phenyl group in alkene substituent R^1 gave the desired product **3ba** in the yield of 78% (Table 2, entry 2). The alkyne substituents R^2 and ketone substituents R^3 could be both electron-deficient and electron-

Table 1 Optimization of reaction conditions

	Ph + Ph N	catalyst solvent, rt.	Ph N Ph
	la 2a		3aa
Entry	Catalyst(5 mol%)	Solvent(conditions)	Yield ^{b,c} (%)
1	AgNO ₃	THF(4h)	78
2	AgNO ₃	CH ₂ Cl ₂ (1h)	95
3	AgNO ₃	CH ₃ CN(24h)	nr^d
4	AgOTf	CH ₂ Cl ₂ (1h)	80
5	Ag ₂ CO ₃	$CH_2Cl_2(24h)$	nr^d
6	Cu(OAc) ₂	$CH_2Cl_2(24h)$	nr^d

Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol) with **2a** (1.5 equiv) in solvent (2 mL) at room temperature under air atmosphere

nr no reaction

^aYield of the isolated product

^bThe product is racemate

Table 2 Silver-catalyzed cascade reactions of various ketones 1 andN-methylaniline 2a

		B^{1} B^{2}	+ H Ph ^{-N}	$\begin{array}{c} 5 \text{ mol% AgNO}_3 \\ \hline CH_2CI_2, \text{ rt.} \end{array} \qquad \begin{array}{c} 0 \\ R^2 \\ R^2 \\ R^1 \end{array}$	`Ph	
		1	2a	3		
Entry	1	R^1	R^2	R ³	3^{b}	Yield ^c (%)
1	1a	Ph	Ph	Ph	3aa	95
2	1b	p-Br-C ₆ H ₄	Ph	Ph	3ba	78
3	1c	Ph	p-Me-C ₆ H ₄	Ph	3ca	96 ^d
4	1d	Ph	p-Cl-C ₆ H ₄	Ph	3da	94 ^d
5	1e	Ph	Ph	p-F-C ₆ H ₄	3ea	66 ^e
6	1f	Ph	Ph	3,5-Dimethyl-4-OMe-C ₆ H ₄	3fa	95
7	1g		Č	Ph	3ga	82

Unless otherwise noted, all reactions were carried out with 1 (0.2 mmol), 1.5 equiv. 2a and 0.05 equiv. of $AgNO_3$ in 2 mL CH_2Cl_2 at room temperature under air atmosphere for 1 h

^aThe products are racemates

^bYield of the isolated product

^cReactions run at rt for 2 h

^dReactions run at rt for 4 h

rich groups to afford the corresponding furan products **3ca**–**3fa** in good to excellent yields (Table 2, entry 3–6). The electron-donating group showed a higher yield than the electron-withdrawing group in \mathbb{R}^3 in this reaction (**3ea**–**3fa**). The structure of **3fa** was confirmed by an X-ray crystal structure analysis (see ESI[†]; CCDC 1019024 2017). To our delight, the cyclic substrate (*Z*)-2-(phenylethynyl)-cyclohex-2-enone **1g** also afforded the desired product **3ga** in 82% yield under the standard reaction conditions (Table 2, entry 7).

We next investigated the scope of the cascade cyclization of (*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-one **1a** and various aryl-amines **2** under the optimized conditions (Table 3). The primary amines with electron-withdrawing and electron-donating-substituted groups afforded the desired products **3ab** and **3ac** in moderate to good yields (Table 3, entries 1, 2). Comparing **3ab** with **3ac**, the electron-rich group was more efficient in this reaction. The reaction also proceeded smoothly with various secondary amines, such as 2-fluoro-*N*-methylaniline diphenylamine and 4-methyl-*N*-phenylaniline (**3ad–3af**, entries 3–5).

To our surprise, tertiary amine could also react with (*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-one **1a** to afford the corresponding furan product (Table 4). When **1a** and *N*,*N*dimethylaniline **2g** were employed in the above reaction, we were pleased to find that the reaction resulted in 92% yield of the product rac-4-((2,5-diphenylfuran-3-yl)(phenyl)methyl)-*N*,*N*-dimethylaniline **4ag** (entry 1).Other tertiary amines, such as *N*,*N*-diethylaniline and *N*,*N*-3-

O Ph	-Ph	+	5 mol% AgNO ₃	Ph-	Ph Ar ¹ N. Ph
1a		2		3	
Entry	2	Ar ¹	R^4	3^{b}	Yield ^c (%)
1	2b	<i>p</i> -Me-C ₆ H ₄	Н	3ab	71^d
2	2c	p-Cl-C ₆ H ₄	Н	3ac	85 ^d
3	2d	o-F-C ₆ H ₄	Me	3ad	70
4	2e	Ph	Ph	3ae	56
5	2f	<i>p</i> -Me-C ₆ H ₄	Ph	3af	72^c

Table 3 Silver-catalyzed cascade reactions of ketone 1a and various aryl-amines 2

Unless otherwise noted, all reactions were carried out with 1a (0.2 mmol), 1.5 equiv. 2 and 0.05 equiv. of AgNO₃ in 2 mL CH₂Cl₂ at room temperature under air atmosphere for 1 h

^aThe products are racemates

^bYield of the isolated product

^cReactions run at 60 °C for 2 h

 Table 4
 Silver-catalyzed cascade reactions of ketone 1a and various tertiary amines 2

C (P	Ph Ph	+ Ph	$\overset{R^4}{\underset{R^5}{}} \xrightarrow{\overset{5\%}{\underset{R^6}{}} AgNO_3} \underbrace{\overset{5}{\underset{R^6}{}} CH_2CI_2}$		$Ph \xrightarrow{Ph}_{R^6} R^4$		
	1a		2		4		
Entry	2	R^4	\mathbb{R}^5	\mathbb{R}^{6}	4 ^b	Yield ^c (%)	
1	2g	Me	Me	Н	4ag	92	
2	2h	Et	Et	Н	4ah	68	
3	2i	Me	Me	<i>m</i> -Me	4ai	86 ^d	

Unless otherwise noted, all reactions were carried out with 1a (0.2 mmol), 1.5 equiv. 2 and 0.05 equiv. of AgNO₃ in 2 mL CH₂Cl₂ at room temperature under air atmosphere for 1 h

^aThe products are racemates

^bYield of the isolated product

^cReactions run at rt for 4 h

trimethylaniline could also give the desired product **4ah** and **4ai** in moderate to excellent yields (entries 2–3).

With the above experimental results in hand, a plausible mechanism is proposed (Scheme 1). In this process, the silver-coordinated alkyne **M** is attacked by the oxygen of the carbonyl group to form an oxonium ion intermediate, which isomerizes to a furan carbocation **N** subsequently. This would be followed by the nucleophilic attack by

amines 2 to give an intermediate O, which undergoes protonation to generate the desired furan products 3 or 4.

Conclusion

In summary, we have described an efficient method for the synthesis of trisubstituted furans with an arylamino-group function via silver-catalyzed cascade heterocyclization of 2-(1-alkynyl)-2-alken-1-ones with aryl-amines. The N–H bond will be activated when primary amine and secondary amine are used as nucleophile, while C–H bond of benzene ring is activated when tertiary amine is used. The reaction showed moderate to excellent yields under mild conditions. Further studies into the scope and mechanism of this reaction are being conducted in our laboratory.

Experimental

General remarks

Column chromatography was carried out on silica gel. Unless noted, ¹H NMR spectra were recorded on 400 MHz and ¹³C NMR spectra were recorded on 100 MHz in CDCl₃ using TMS as internal standard. All new compounds were further characterized by (ESI)HRMS, HRMS was obtained using a Q-TOF instrument equipped with APCI. Copies of their ¹H NMR and ¹³C NMR spectra are provided. Commercially available reagents and solvents were used without further purification. THF was distilled from Na/benzophenone and used immediately.

Preparation of (*E*)-2-benzylidene-1,4-diphenylbut-3yn-1-ol

In a three-necked round flask, 1 mmol (*E*)-2-benzylidene-4-phenylbut-3-ynal was dissolved in 20 mL THF under N₂. Then, 1.5 mmol Grignard reagent (phenylmagnesium bromide) in THF was added via syringe, the mixture was stirred at room temperature for 15 min, and monitored by TLC. The mixture was quenched by adding NH₄Cl solution. The product was extracted with ethyl acetate, and the combined extracts were evaporated in vacuo. The product was isolated by the chromatography on silica gel.

Preparation of (*E*)-2-benzylidene-1,4-diphenylbut-3yn-1-one 1a

1 mmol (*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-ol was dissolved in 100 mL of THF under stirring, then 50 mmol





of MnO_2 was added. The mixture was stirred at room temperature for 24 h and monitored by TLC. The mixture was filtered and evaporated in vacuo. The residue was purified by chromatography on silica gel to obtain (*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-one **1a**.

General produce for the synthesis of trisubstituted furans 3aa

To a solution of $AgNO_3$ (1.7 mg, 0.01 mmol) in 2.0 mL of anhydrous dichloromethane were added **1a** (61.6 mg, 0.2 mmol) and **2a** (32.1 mg, 0.3 mmol). The mixture was stirred at room temperature for 1 h. The solvent was evaporated in vacuo. The residue was purified by chromatography on silica gel to afford **3aa**.

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References

- Blanc A, Bénéteau V, Weibel J-M, Pale P (2016) Silver & goldcatalyzed routes to furans and benzofurans. Org Biomol Chem 14:9184–9205. doi:10.1039/c6ob01468b
- CCDC 1019024 (2017) (**3fa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif
- Chen WL, Li J, Zhu YH, Ye LT, Hu W, Mo WM (2011) AgOTfcatalyzed cyclization of enynals or enynones with amines: an efficient synthesis of 1,2,4-trisubstituted pyrroles and 2,3,5trisubstituted Furans. ARKIVOC 9:381–392

- Cornil J, Gonnard L, Bensoussan C, Serra-Muns A, Gnamm C, Commandeur C, Commandeur M, Reymond S, Guérinot A, Cossy J (2015) Iron- and indium-catalyzed reactions toward nitrogen- and oxygen-containing saturated heterocycles. Acc Chem Res 48:761–773. doi:10.1021/ar5004412
- Gao HY, Zhang JL (2012) Cationic rhodium(I)-catalyzed regioselective tandem heterocyclization/[3+2] cycloaddition of 2-(1alkynyl)-2-alken-1-ones with alkynes. Chem Eur J 18:2777–2782. doi:10.1002/chem.201103924
- Gao HY, Wu XX, Zhang JL (2010a) Exo/endo selectivity-control in Lewis-acid catalyzed tandem heterocyclization/formal [4+3] cycloaddition: synthesis of polyheterocycles from 2-(1-alkynyl)-2-alken-1-ones and 1,3-diphenylisobenzofuran. Chem Commun 46:8764–8766. doi:10.1039/C0CC02778B
- Gao HY, Zhao XL, Yu YH, Zhang JL (2010b) Highly substituted furo[3,4-c]azepines by gold(I)-catalyzed diastereoselective tandem double heterocyclizations and 1,2-alkyl migration. Chem Eur J 16:456–459. doi:10.1002/chem.200901813
- Gao HY, Wu XX, Zhang JL (2011) Gold(I)-catalyzed, highly diastereoselective, tandem heterocyclizations/[3+2] cycloadditions: synthesis of highly substituted cyclopenta[c]furans. Chem Eur J 17:2838–2841. doi:10.1002/chem.201003363
- Ghosh J, Biswas P, Sarkar T, Drew MGB, Bandyopadhyay C (2016) 5-Aryl-2-(2-hydroxyphenyl)furan-3-carbaldehyde: synthesis and study on its ring-chain tautomerism. Tetrahedron Lett 57:3354–3357. doi:10.1016/j.tetlet.2016.06.069
- Gulevich AV, Dudnik AS, Chernyak N, Gevorgyan V (2013) Transition metal-mediated synthesis of monocyclic aromatic heterocycles. Chem Rev 113:3084–3213. doi:10.1021/cr300333u
- Harmata M (2010) Silver-catalyzed cycloisomerization reactions. In: Belmont P (ed) Silver in organic chemistry, vol 5. John Wiley & Sons Inc, Hoboken, pp 143–162
- He T, Gao P, Zhao SC, Shi YD, Liu XY, Liang YM (2013a) Platinum(IV)-catalyzed regioselective synthesis of highly substituted 4H-cyclopenta[b]furans via cascade hetero-cyclization of 2-(1-alkynyl)-3-aryl-2-propenals with arylethenes. Adv Synth Catal 355:365–369. doi:10.1002/adsc.201200597
- He T, Gao P, Qiu YF, Yan XB, Liu XY, Liang YM (2013b) Goldcatalyzed intermolecular reaction of 2-(1-alkynyl)-2-alken-1ones with diarylethenes to construct polysubstituted cyclopenta[c]furans through a cascade heterocyclization/[3+2] cycloaddition sequence. RSC Adv 3:19913–19916. doi:10.1039/ C3RA44467H
- Hu F, Shao XX, Zhu DH, Lu L, Shen QL (2014) Silver-catalyzed decarboxylative trifluoromethylthiolation of aliphatic carboxylic acids in aqueous emulsion. Angew Chem Int Ed 53:6105–6109. doi:10.1002/anie.201402573
- Hu Z, Dong J, Men Y, Lin Z, Cai J, Xu X (2017) Silver-catalyzed chemoselective [4+2] annulation of two isocyanides: a general route to pyridone-fused carbo- and heterocycles. Angew Chem Int Ed 56:1805–1809. doi:10.1002/anie.201611024
- Ji KG, Shu XZ, Zhao SC, Zhu HT, Niu YN, Liu XY, Liang YM (2009) Novel carbon–carbon bond formation from propargylic alcohols and olefin toward five-membered heterocyclic rings catalyzed by $AgSbF_{6}$. Org Lett 11:3206–3209. doi:10.1021/ ol901270b
- Keay BA, Dibble PW (1996) Furans and their Benzo derivatives: applications. In: Katritzky AR, Donnelly C, Rees W, Scriven EFV (eds) Comprehensive heterocyclic chemistry II, vol 2. Pergamon Press, Oxford, pp 395–436
- Lee HK, Chan KF, Hui CW, Yim HK, Wu XW, Wong HNC (2005) Use of furans in synthesis of bioactive compounds. Pure Appl Chem 77:139–143
- Li WB, Zhang JL (2010) Tetrasubstituted furans by PdII/CuIcocatalyzed three-component domino reactions of 2-(1-alkynyl)-

2-alken-1-ones, nucleophiles and diaryliodonium salts. Chem Commun 46:8839–8841. doi:10.1039/c0cc03450a

- Liu RR, Zhang JL (2011) Polyheterocycles by palladium(II)-catalyzed oxidative domino reactions involving direct C–H functionalization. Adv Synth Catal 353:36–40. doi:10.1002/adsc. 201000670
- Liu F, Yu YH, Zhang JL (2009) Highly substituted furo[3,4d][1,2]oxazines: gold-catalyzed regiospecific and diastereoselective 1,3-dipolar cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with nitrones. Angew Chem Int Ed 48:5505–5508. doi:10.1002/ anie.200901299
- Liu F, Qian DY, Li L, Zhao XL, Zhang JL (2010) Diastereo- and enantioselective gold(I)-catalyzed intermolecular tandem cyclization/[3+3]cycloadditions of 2-(1-alkynyl)-2-alken-1-ones with nitrones. Angew Chem Int Ed 49:6669–6672. doi:10.1002/ anie.201003136
- Liu JQ, Liu ZH, Liao PQ, Zhang L, Tu T, Bi XH (2015) Silvercatalyzed cross-coupling of isocyanides and active methylene compounds by a radical process. Angew Chem Int Ed 54:10618–10622. doi:10.1002/anie.201504254
- Meegan DMXMJ (1984) Furans and their Benzo derivatives: (iii) synthesis and applications. In: Katritzky AR, Rees CW (eds) Comprehensive heterocyclic chemistry, vol 4. Pergamon, Oxford, pp 657–712
- Nakanishi K (1974) Natural Products Chemistry. Kodansha, Toyko, p 392
- Oh CH, Reddy VR, Kim A, Rhim CY (2006) Nucleophile-assisted Ptcatalyzed cyclization of enynones: an access to synthesis of highly substituted furans. Tetrahedron Lett 47:5307–5310. doi:10.1016/j.tetlet.2006.05.119
- Patil NT, Yamamoto Y (2008) Coinage metal-assisted synthesis of heterocycles. Chem Rev 108:3395–3442. doi:10.1021/ cr050041j
- Patil NT, Wu H, Yamamoto Y (2005) Cu(I) catalyst in DMF: an efficient catalytic system for the synthesis of furans from 2-(1-alkynyl)-2-alken-1-ones. J Org Chem 70:4531–4534. doi:10. 1021/jo050191u
- Rubin M, Sromek AW, Gevorgyan V (2003) New advances in selected transition metal-catalyzed annulations. Synlett 15:2265–2291. doi:10.1055/s-2003-43334
- Wang H, Guo LN, Duan XH (2014) Silver-catalyzed decarboxylative acylfluorination of styrenes in aqueous media. Chem Commun 50:7382–7384. doi:10.1039/C4CC02800G
- Wang YD, Zhang PC, Qian DY, Zhang JL (2015) Highly regio-, diastereo-, and enantioselective gold(I)-catalyzed intermolecular annulations with *N*-allenamides at the proximal C=C bond. Angew Chem Int Ed 54:14849–14852. doi:10.1002/anie. 201507165
- Weibel JM, Blanc A, Pale P (2008) Ag-mediated reactions: coupling and heterocyclization reactions. Chem Rev 108:3149–3173. doi:10.1021/cr078365q
- Wong HNC, Yu P, Yick CY (1999) The use of furans in natural product syntheses. Pure Appl Chem 71:1041–1044
- Xiao YJ, Zhang JL (2008) Tetrasubstituted furans by a PdII-catalyzed three-component michael addition/cyclization/cross-coupling reaction. Angew Chem Int Ed 47:1903–1906. doi:10.1002/anie. 200704531
- Xiao YJ, Zhang JL (2009) Palladium(II)-catalyzed domino reaction of 2-(1-alkynyl)-2-alken-1-ones with nucleophiles: scope, mechanism and synthetic application in the synthesis of 3,4-fused bicyclic tetrasubstituted furans. Adv Synth Catal 351:617–629. doi:10.1002/adsc.200800715
- Yamamoto Y (2012) Transition-metal-catalyzed cycloisomerizations of α, ω-dienes. Chem Rev 112:4736–4769. doi:10.1021/ cr300050n

- Yao TL, Zhang XX, Larock RC (2004) AuCl₃-catalyzed synthesis of highly substituted furans from 2-(1-alkynyl)-2-alken-1-ones. J Am Chem Soc 126:11164–11165. doi:10.1021/ja0466964
- Yao TL, Zhang XX, Larock RC (2005) Synthesis of highly substituted furans by the electrophile-induced coupling of 2-(1-alkynyl)-2-alken-1-ones and nucleophiles. J Org Chem 70:7679–7685. doi:10.1021/jo0510585
- Zeni G, Larock RC (2004) Synthesis of heterocycles via palladium πolefin and π-alkyne chemistry. Chem Rev 104:2285–2310. doi:10.1021/cr020085h
- Zhao WX, Zhang JL (2010) Rhodium-catalyzed domino heterocyclization and [(3+2)+2] : construction of fused tricycloheptadienes. Chem Commun 46:7816–7818. doi:10.1039/C0CC02382
- Zhou LJ, Zhang MR, Li WB, Zhang JL (2014) Furan-based *o*quinodimethanes by gold-catalyzed dehydrogenative heterocyclization of 2-(1-alkynyl)-2-alken-1-ones: a modular entry to 2,3-furan fused carbocycles. Angew Chem Int Ed 53:6542–6545. doi:10.1002/anie.201403709