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A general approach to arylated furans, pyrroles, and thiophenes

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ABSTRACT

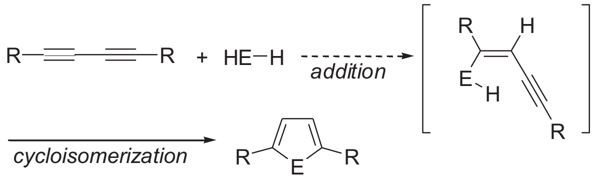
A general and practical synthetic method for aryl-substituted five-membered heterocycles has been developed. In the presence of KOH (30%), 1,4-diaryl-1,3-butadiynes undergo the cyclocondensation reaction with water, primary amines, and $Na_2S\cdot 9H_2O$ in DMSO at 80 °C to afford 2,5-diarylfurans, 1,2,5-trisubstituted pyrroles, and 2,5-diarylthiophenes in good to high yields. Further studies have disclosed that aryl-substituted five-membered heterocycles can be also synthesized by a one-pot, two-step strategy from the terminal alkynes in DMSO firstly catalyzed by CuCl, and then via addition of KOH to promote the cyclocondensation of 1,3-butadiynes generated in situ.

1. Introduction

Cyclocondensation of alkynes represent one of the most powerful methods for the synthesis of cyclic compounds with the significant advantages of high-atom efficiency and easy availability of starting materials, which has been well applied in the synthesis of highly functionalized cyclic compounds.[1] Development of efficient and practical synthetic methods to synthesize functionalized five-membered heterocycles of furans, pyrroles, and thiophenes is one of important research topics in synthetic chemistry, since they have interesting biological and physiological activities, and versatile applications in the synthesis of other heterocycles. On the other hand, 1,3-butadiyne derivatives have been applied as important building blocks for the synthesis of various carbo- and heterocyclic compounds, and recently, a number of reports on the transition metal-catalyzed synthesis of naphthalenes,[2] furans,[3] thiophenes,[3d,4] pyrroles,[3b,5] and other cyclic compounds[6] using 1,3-butadiyne derivatives as starting materials have appeared in the literature. Encouraged by our previous success in the preparation of pyrroles,[5c] furans,[3e] and benzo[*f*]quinazolines[7] via the cycloaddition of 1,3-butadiynes with primary amines, water, and nitriles, respectively, we investigated the possibility in this paper to establish a general procedure for the synthesis of five-membered heterocycles using 1,4-disubstituted 1,3-butadiynes as one of the reactants and without use of transition metal complex as catalyst.

2. Results and discussion

As depicted in Scheme 1, the five-membered heterocycles are expected to form via the cycloaddition of 1,3-butadiynes with E–H bond (E=O, S, and N). The challenging work is to optimize a general catalytic system, which can promote both intermolecular addition and intramolecular cycloaddition of E–H bond across C–C triple bonds. On the basis of the previous reports, it seems that the presence of basic additives is one of the crucial factors to promote the transformation of 1,3-butadiynes to furan derivatives in the presence of Cu[3d] and Pd.[3e] Therefore we examined the reaction of 1,4-diphenyl-1,3-butadiyne (**1a**) with water in presence of a variety of basic compounds without the use of transition metal catalyst to investigate the possibility to synthesize 2,5-diarylfuran (**2a**).



Scheme 1. Formation of five-membered heterocycles via the cyclocondensation of 1,3-butadiyne.

As concluded in Table 1, it proved possible to obtain the desirable **2a** in high isolated yield when 30% of KOH was used as catalyst in DMSO at 80 °C for 4 h (entry 7), although other inorganic bases, such as $NaHCO_3$, Na_2CO_3, K_2CO_3, K_3PO_4, Cs_2CO_3 (entries 1–5), and organic bases such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene),

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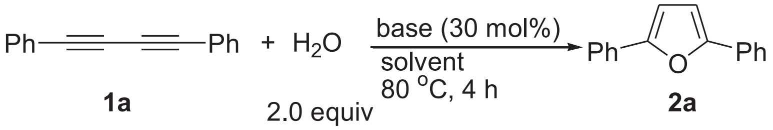
Table 1
Formation of 2,5-diphenylfuran from the cyclocondensation of 1,4-diphenyl-1,3-butadiyne with water under different conditions[a]



Entry	Base	Solvent	Yield[b] (%)
1	$NaHCO_3$	DMSO	0
2	Na_2CO_3	DMSO	0
3	K_2CO_3	DMSO	0
4	K_3PO_4	DMSO	0
5	CS_2CO_3	DMSO	<5
6	NaOH	DMSO	67
7	KOH	DMSO	96 (92)
8	KOH	DMF	37
9	KOH	THF	13
10	KOH	CH_3CN	<5
11	KOH	1,4-Dioxane	0
12	KOH	1,2-DCE	0
13	DBU	DMSO	<5
14	NEt_3	DMSO	0
15	DABCO	DMSO	0
16[c]	KOH	DMSO	88
17[d]	KOH	DMSO	72
18	—	DMSO	0

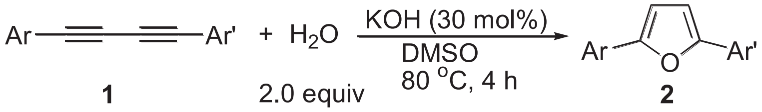
[a] Reaction conditions: **1a** (1.0 mmol), H_2O (2.0 mmol), and base (0.3 mmol) in solvent (2.0 mL) at 80 °C for 4 h.
[b] GC yield of **2a**, and isolated yield in parenthesis.
[c] KOH of 20 mol % was used.
[d] KOH of 10 mol % was used.

Et_3N, and DABCO (1,4-diazabicyclo[2.2.2]octane) (entries 13–15) showed no catalytic activity at all. It was also found that NaOH in DMSO showed moderate catalytic activity (entry 6), and the catalytic activity of KOH greatly depended on the nature of solvents. When DMF, THF, and CH_3CN were used as solvents, KOH showed fair and low catalytic activity (entries 8–10), and in 1,4-dioxane and 1,2-DCE, no catalytic activity was observed (entries 11 and 12). Decrease of the amount of KOH resulted in the considerable decrease of yields (entries 16 and 17). In addition, it was confirmed that no **2a** was formed in the absence of KOH (entry 18).

In fact, KOH/DMSO as the superbasic medium showing versatile diverse catalytic activity has been well applied in a variety of organic transformation reported by Trofimov,[8] Bolm,[9] and other groups.[10]

The results shown in Table 2 verify the scope and generality for the formation of 2,5-diarylfurans using KOH/DMSO catalyst system.

Table 2
Synthesis of 2,5-diarylfurans from the reaction of 1,4-diaryl-1,3-butadiyne with water[a]



Entry	Ar, Ar′		Yield of **2**[b] (%)	
1	Ar=Ar′=*p*-tolyl	**1b**	**2b**	92
2	Ar=Ar′=*o*-tolyl	**1c**	**2c**	83
3	Ar=Ar′=*m*-tolyl	**1d**	**2d**	90
4	Ar=Ar′=*p*-EtC$_6$H$_4$	**1e**	**2e**	90
5	Ar=Ar′=*p*-^{n}PrC$_6$H$_4$	**1f**	**2f**	87
6	Ar=Ar′=*p*-^{n}BuC$_6$H$_4$	**1g**	**2g**	89
7	Ar=Ar′=*p*-^{n}C$_5$H$_{11}$C$_6$H$_4$	**1h**	**2h**	86
8	Ar=Ar′=*p*-MeOC$_6$H$_4$	**1i**	**2i**	91
9	Ar=Ar′=3,5-Me$_2$C$_6$H$_3$	**1j**	**2j**	87
10	Ar=Ar′=2-naphthyl	**1k**	**2k**	87
11	Ar=Ar′=*p*-ClC$_6$H$_4$	**1l**	**2l**	90
12	Ar=Ar′=*p*-FC$_6$H$_4$	**1m**	**2m**	88
13	Ar=Ar′=*p*-CF$_3$C$_6$H$_4$	**1n**	**2n**	85
14	Ar=Ar′=2-thienyl	**1o**	**2o**	90
15	Ar=Ph Ar′=*p*-EtOC$_6$H$_4$	**1p**	**2p**	91
16	Ar=Ph Ar′=2-Naphthyl	**1q**	**2q**	86
17	Ar=*p*-^{n}PrC$_6$H$_4$ Ar′=*p*-EtOC$_6$H$_4$	**1r**	**2r**	90

[a] Unless otherwise noted, the reactions were carried out using **1** (1.0 mmol), H_2O (2.0 mmol), and KOH (0.3 mmol) in DMSO (2.0 mL) at 80 °C for 4 h.
[b] Isolated yield.

It was found that both electron-donating and electron-withdrawing groups on the benzene rings were insensitive to the formation of furans, all of the reactions afforded the corresponding furan derivatives in high yields. The cyclocondensation of 1,4-bis(2-thienyl)-1,3-butadiyne (**1o**) with H_2O gave the high yield of the expected five-membered heterocyclic trimer (**2o**), which has interesting electrical and/or optical properties.[11]

In addition, in order to verify the practicality of the present procedure, a 15-fold scale-up reaction of **1a** was also performed. As shown in Eq. 1, the expected product **2a** was obtained on a gram-level with a similar yield as shown in entry 7 of Table 1.

$$\begin{array}{cccc} \mathbf{1a} & + \quad H_2O & \xrightarrow[\substack{\text{DMSO}\\ 80\,^{\circ}\text{C, 4 h}}]{\text{KOH (30 mol\%)}} & \mathbf{2a} \\ \substack{15.0\text{ mmol}\\(3.03\text{ g})} & 2.0\text{ equiv} & & 2.94\text{ g (97\%)} \end{array} \qquad (1)$$

The simplicity of the KOH-catalyzed formation of furan derivatives (**2**) makes the procedure highly attractive as a preparative method, and it can probably be considered efficient in the synthesis of other five-membered heterocycles. Therefore the reaction conditions indicated in entry 7 of Table 1 were applied as the standard conditions in the transformation of 1,3-butadiynes into pyrroles and thiophenes.

As summarized in Table 3, aniline (**3a**), *n*-propylamine (**3b**), *p*-methoxyaniline (**3c**), and *p*-fluoroaniline (**3d**) underwent the cyclocondensation smoothly to afford the corresponding 1,2,3-triaryl pyrroles in high isolated yields.

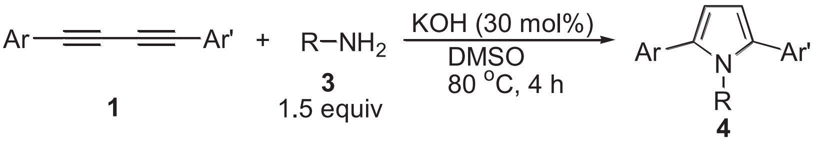
In addition, under the similar conditions, the corresponding 2,5-diarylthiophenes could be also obtained in high yields by the reaction of 1,3-butadiynes with 2.0 equiv of $Na_2S\cdot 9H_2O$ as shown in Table 4.

It should be noted that although there have been several reports on the formation of 2,5-diarylthiophenes via the cyclocondensation of 1,4-diaryl-1,3-butadiynes using different sulfur sources under different conditions (e.g., H_2S gas/NaOH in methanol,[12] $Na_2S\cdot 9H_2O$ in DMF[13]), the present transformation provides an alternative and practical procedure for the synthesis of 2,5-diarylthiophenes, particularly for the formation of terthiophene (**5d**) efficiently under mild conditions.

In our previous work, we developed an efficient oxidative homocoupling reaction of terminal alkynes to form 1,4-disubstituted 1,3-diyne (**1**) catalyzed by CuCl/piperidine,[14] we then investigated the possibility to develop a one-pot, two-step strategy for the synthesis of five-membered heterocycles directly using terminal alkynes as one of the reaction partners. Therefore we re-optimized the reaction conditions for the formation of **1**, and fortunately found that in DMSO, CuCl could efficiently catalyze the formation of **1** from terminal alkynes at 80 °C without use of any additive. As shown in Table 5, 2,5-diarylfurans could be synthesized from aromatic terminal alkynes as starting materials by a one-pot, two-step sequential procedure involving the formation of 1,4-diaryl-1,3-butadiynes in situ and cyclocondensation with water by addition catalytic amount of KOH. The yields of the desired furan derivatives in this manner are comparable to those achieved by the reaction of 1,4-diaryl-1,3-butadiynes with water as shown in Table 2.

In addition, as exampled in Eqs. 2 and 3, the present sequential CuCl and KOH-catalyzed one-pot strategy could be successfully

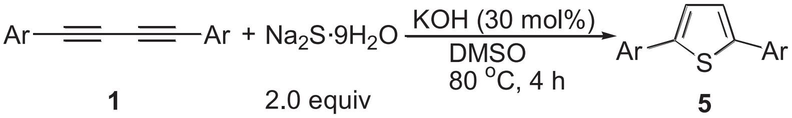
Table 3
Synthesis of 1,2,5-triarylpyrroles[a]



Entry	Ar, Ar′		R		Yield of **4**[b] (%)	
1	Ar=Ar′=Ph	**1a**	Ph	**3a**	**4a**	84
2	Ar=Ar′=Ph	**1a**	n-C$_3$H$_7$	**3b**	**4b**	82
3	Ar=Ar′=Ph	**1a**	p-MeOC$_6$H$_4$	**3c**	**4c**	87
4	Ar=Ar′=p-EtC$_6$H^4	**1e**	p-FC$_6$H$_4$	**3d**	**4d**	91
5	Ar=Ar′=p-MeOC$_6$H$_4$	**1i**	Ph	**3a**	**4e**	84
6	Ar=Ar′=2-thienyl	**1o**	Ph	**3a**	**4f**	85
7	Ar=Ph Ar′=2-naphthyl	**1q**	Ph	**3a**	**4g**	87

[a] Unless otherwise noted, the reactions were carried out using **1** (1.0 mmol), amine **3** (1.5 mmol), and KOH (0.3 mmol) in DMSO (2.0 mL) at 80 °C for 4 h.
[b] Isolated yield.

Table 4
Synthesis of 2,5-diarylthiophenes[a]

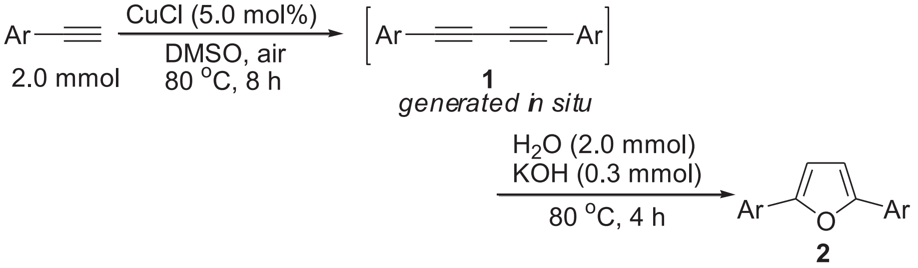


Entry	Ar		Yield of **5**[b] (%)	
1	Ph	**1a**	**5a**	97
2	p-^{n}BuC$_6$H$_4$	**1g**	**5b**	92
3	p-FC$_6$H$_4$	**1n**	**5c**	93
4	2-Thienyl	**1o**	**5d**	93

[a] Unless otherwise noted, the reactions were carried out using **1** (1.0 mmol), H_2O (2.0 mmol), and KOH (0.3 mmol) in DMSO (2.0 mL) at 80 °C for 4 h.
[b] Isolated yield.

Table 5

One-pot synthesis of 2,5-diarylfurans from the reaction of terminal alkynes with water[a]

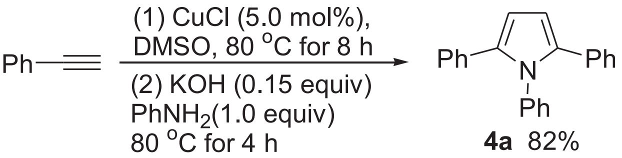


Entry	Ar	Diyne **1**	Yield of **2**[b] (%)	
1	Ar=Ph	**1a**	**2a**	90
2	Ar=*m*-tolyl	**1d**	**2d**	86
3	Ar=*p*-$^nPrC_6H_4$	**1f**	**2f**	84
4	Ar=*p*-$MeOC_6H_4$	**1i**	**2i**	86
5	Ar=*p*-FC_6H_4	**1n**	**2n**	87
6	Ar=2-thienyl	**1o**	**2o**	82

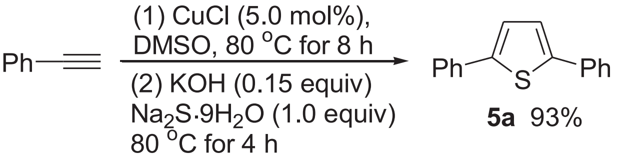
[a] Reaction conditions for first step: terminal alkyne (2.0 mmol) and CuCl (5 mol %, 10.0 mg) in DMSO (2.0 mL) in air was heated with stirring at 80 °C for 8 h; second step: H_2O (2.0 mmol) and KOH (0.3 mmol, 16.8 mg) were added to the reaction mixture of the first step, and then heated at 80 °C for 4 h.

[b] Isolated yield.

applied to the synthesis of 1,3,5-triphenylpyrrole (**4a**) and 2,5-diphenylthiophene (**5a**) in high yields by the reactions of phenylacetylene with aniline and $Na_2S\cdot 9H_2O$, respectively.



(2)



(3)

It has been well-known that carbon–carbon triple bond of alkynes easily undergoes the nucleophilic addition and then cycloisomerization to afford cyclic compounds. On the basis of the proposed route for the formation of five-membered heterocycles as shown in Scheme 1, the present formation of five-membered heterocycles is reasonably considered to be resulted from the nucleophilic addition of 1,3-butadiynes with nucleophilic species such as HO^-, RNH^- or HS^- under basic conditions, and subsequent protonation and cycloisomerization.

3. Conclusion

We have developed a general synthetic method for the formation of 2,5-diarylfurans, 1,2,5-triarylpyrroles or 2,5-diarylpyrroles, and 2,5-diarylthiophenes by the cyclocondensation of 1,4-diaryl-1,3-butadiynes with water, primary amines, and sodium sulfide nonahydrate, respectively, in the presence of KOH in DMSO at 80 °C. The present procedure provides a promising protocol using simple and cheap catalytic system for the construction of five-membered heterocycles bearing a variety of electron-rich and electron-deficient aryl groups in good to high yields. Interestingly, the five-membered heterocycles can be also obtained by a one-pot, two-step procedure from terminal alkynes sequentially catalyzed by CuCl and KOH in DMSO. Compared to the known procedures for the synthesis of five-membered heterocycles, the present procedures have the merits of easily available starting materials and one-pot reaction with high-atom efficiency.

4. Experimental section

4.1. General method

All organic starting materials are analytically pure and used without further purification. 1,4-Diaryl-1,3-butadiynes were prepared by an oxidative homocoupling reaction of terminal alkynes according to a known catalytic system.[14] The purity of KOH is 99.99%. ^1H NMR (300 MHz) chemical shifts (δ) were referenced to TMS and ^{13}C NMR (75 MHz) chemical shifts (δ) were referenced to internal solvent resonance. GC analyses of organic compounds were performed on a GC instrument with a 30 M capillary column. Mass spectra were obtained on a low-resolution GC–MS spectrometer, and high-resolution mass spectra (ESI) were obtained with a micro TOF mass spectrometer.

4.2. General procedure for the synthesis of 2,5-diaryl-substituted furans, pyrroles, and thiophenes from the reaction of 1,4-diaryl-1,3-butadiyne with water, primary amines or sodium sulfide nonahydrate

A solution of 1,4-diaryl-1,3-butadiynes (**1**) (1.0 mmol), KOH (0.3 mmol), and H_2O (2.0 mmol), or RNH_2 (1.5 mmol), or $Na_2S\cdot 9H_2O$ (2.0 mmol) in DMSO (2.0 mL) was heated at 80 °C with stirring for 4 h. The reaction mixture was then cooled to room temperature, and the volatiles were removed under reduced pressure. The obtained residue was subjected to silica gel column chromatography (eluting with CH_2Cl_2/petroleum ether: 0:1 to 1:10) to give 2,5-diaryl-substituted five-membered heterocycles.

4.3. A typical procedure for the synthesis of 2,5-phenylfuran (2a) from phenylacetylene (Table 5, entry 1)

A mixture of phenylacetylene (204.0 mg, 2.0 mmol) and CuCl (10.0 mg, 0.1 mmol) in DMSO (2.0 mL) in an atmosphere of air was heated with stirring at 80 °C for 8 h, and then the reaction mixture was cooled to room temperature, and KOH (16.8 mg, 0.3 mmol) was added. The obtained mixture was further heated at 80 °C for 4 h.

After work-up and isolation as mentioned-above, **2a** (198.0 mg, 0.90 mmol, 90%) was obtained as colorless solid.

4.4. Characterization data of new products

Compounds **2c**, **2f**, **2g**, **2h**, and **2j** are new compounds and characterized by ^{1}H, ^{13}C NMR, mass spectrum, and HRMS (ESI). Other products are known compounds, which were characterized by ^{1}H, ^{13}C NMR and mass spectra, see Supplementary data.

*4.4.1. 2,5-Bis(o-tolyl)furan (**2c**).* White solid, mp 81–83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, 2H, J=7.6 Hz), 7.29–7.21 (m, 6H), 6.67 (s, 2H), 2.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 134.6, 131.4, 130.2, 127.5, 126.9, 126.2, 110.6, 22.3; GC–MS m/z (% rel inten.) 248 (M^+, 100), 233 (2), 205 (9), 129 (24), 119 (14), 91 (4), 65 (7); HRMS (ESI) calcd for $C_{18}H_{17}O$ $[M+H]^+$: 249.1273, found 249.1274.

*4.4.2. 2,5-Bis(p-n-propylphenyl)furan (**2f**).* White solid, mp 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 4H, J=7.9 Hz), 7.19 (d, 4H, J=7.9 Hz), 6.65 (s, 2H), 2.59 (t, 4H, J=7.2 Hz), 1.72–1.59 (m, 4H), 0.95 (t, 6H, J=7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.0, 128.9, 128.6, 123.8, 106.6, 37.9, 24.6, 13.9; GC–MS m/z (% rel inten.) 304 (M^+, 86), 275 (100), 259 (4), 246 (48), 202 (8), 152 (4), 123 (18), 110 (9), 90 (9), 77 (5); HRMS (ESI) calcd for $C_{22}H_{25}O$ $[M+H]^+$: 305.1899, found 305.1903.

*4.4.3. 2,5-Bis(p-n-butylphenyl)furan (**2g**).* White solid, mp 87–88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, 4H, J=8.3 Hz), 7.22 (d, 4H, J=8.3 Hz), 6.67 (s, 2H), 2.64 (t, 4H, J=7.6 Hz), 1.68–1.54 (m, 4H), 1.45–1.27 (m, 4H), 0.95 (t, 6H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.3, 128.9, 128.6, 123.8, 106.6, 35.6, 33.7, 22.5, 14.1; GC–MS m/z (% rel inten.) 332 (M^+, 99), 289 (100), 246 (54), 202 (7), 128 (6), 115 (5), 103 (4), 90 (8), 77 (4); HRMS (ESI) calcd for $C_{24}H_{29}O$ $[M+H]^+$: 333.2212, found 333.2208.

*4.4.4. 2,5-Bis(p-n-pentylphenyl)furan (**2h**).* White solid, mp 90–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 3H, J=8.3 Hz), 7.54 (d, 1H, J=8.3 Hz), 7.25–7.18 (m, 4H), 6.67 (s, 2H), 2.63 (t, 4H, J=7.6 Hz), 1.69–1.55 (m, 6H), 1.36–1.26 (m, 6H), 0.91 (t, 6H, J=7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.3, 129.1, 128.9, 123.8, 106.6, 35.9, 31.6, 31.2, 22.7, 14.2; GC–MS m/z (% rel inten.) 360 (M^+, 99), 303 (100), 259 (9), 246 (50), 233 (4), 215 (4), 159 (5), 128 (5), 90 (8), 77 (4); HRMS (ESI) calcd for $C_{26}H_{33}O$ $[M+H]^+$: 361.2525, found 361.2528.

*4.4.5. 2,5-Bis(3,5-dimethylphenyl)furan (**2j**).* White solid, mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 4H), 6.93 (s, 2H), 6.70 (s, 2H), 2.39 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 138.3, 130.9, 129.2, 121.7, 107.1, 21.5; GC–MS m/z (% rel inten.) 276 (M^+, 100), 233 (5), 218 (4), 203 (3), 143 (14), 138 (13), 123 (11), 105 (10), 91 (2), 77(8); HRMS m/z calcd for $C_{20}H_{21}O$ $[M+H]^+$: 277.1586, found 277.1585.

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Supplementary data

General method, characterization data of known products, and copies of ^{1}H, ^{13}C NMR charts of all products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.09.025.

References and notes

1. Selected reviews, see: (a) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901; (b) Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787; (c) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127; (d) Hua, R.; Abrenica, M. V. A.; Wang, P. *Curr. Org. Chem.* **2011**, *15*, 712.
2. (a) Sun, H.; Wu, X.; Hua, R. *Tetrahedron Lett.* **2011**, *52*, 4408; (b) Singha, R.; Nandi, S.; Ray, J. K. *Tetrahedron Lett.* **2012**, *53*, 6531.
3. (a) Pridmore, S. J.; Slatford, P. A.; Williams, J. M. J. *Tetrahedron Lett.* **2007**, *48*, 5111; (b) Kramer, S.; Madsen, J. L. H.; Rottländer, M.; Skrydstrup, T. *Org. Lett.* **2010**, *12*, 2758; (c) Nun, P.; Dupuy, S.; Gaillard, S.; Poater, A.; Cavallod, L.; Nolan, S. P. *Catal. Sci. Technol.* **2011**, *1*, 58; (d) Jiang, H.; Zeng, W.; Li, Y.; Wu, W.; Huang, L.; Fu, W. *J. Org. Chem.* **2012**, *77*, 5179; (e) Zheng, Q.; Hua, R.; Yin, T. *Curr. Org. Synth.* **2013**, *10*, 161.
4. Beny, J.-P.; Dhawan, S. N.; Kagan, J.; Sundlass, S. *J. Org. Chem.* **1982**, *47*, 2201.
5. (a) Pridmore, S. J.; Slatford, P. A.; Daniel, A.; Whittlesey, M. K.; Williams, J. M. J. *Tetrahedron Lett.* **2007**, *48*, 5115; (b) Lavallo, V.; Frey, G. D.; Donnadieu, B.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5224; (c) Zheng, Q.; Hua, R. *Tetrahedron Lett.* **2010**, *51*, 4512.
6. (a) Mandadapu, A. K.; Sharma, S. K.; Gupta, S.; Krishna, D. G. V.; Kundu, B. *Org. Lett.* **2011**, *13*, 3162; (b) Mandadapu, A. K.; Dathi, M. D.; Arigela, R. K.; Kundu, B. *Tetrahedron* **2012**, *68*, 8207; (c) Wang, L.; Yu, X.; Feng, X.; Bao, M. *Org. Lett.* **2012**, *14*, 2418.
7. Yang, L.; Hua, R. *Chem. Lett.* **2013**, *42*, 769.
8. Selected reports, see: (a) Trofimov, B. A. *Sulfur Rep.* **1992**, *11*, 207; (b) Trofimov, B. A.; Vasil'tsov, A. M.; Schmidt, E. Y.; Zaitsev, A. B.; Mikhaleva, A. I.; Afonin, A. V. *Synthesis* **2000**, 1521; (c) Trofimov, B. A.; Malysheva, S. F.; Gusarova, N. K.; Kuimov, V. A.; Belogorlova, N. A.; Sukhov, B. G. *Tetrahedron Lett.* **2008**, *49*, 3480; (d) Trofimov, B. A.; Vasil'tsov, A. M.; Mikhaleva, A. I.; Ivanov, A. V.; Skital'tseva, E. V.; Schmidt, E. Y.; Senotrusova, E. Y.; Ushakov, I. A.; Petrushenko, K. B. *Tetrahedron Lett.* **2009**, *50*, 97; (e) Trofimov, B. A.; Schmidt, E. Y.; Ushakov, I. A.; Zorina, N. V.; Skital'tseva, E. V.; Protsuk, N. I.; Mikhaleva, A. I. *Chem.—Eur. J.* **2010**, *16*, 8516; (f) Schmidt, E. Y.; Zorina, N. V.; Skitaltseva, E. V.; Ushakov, I. A.; Mikhaleva, A. I.; Trofimov, B. A. *Tetrahedron Lett.* **2011**, *52*, 3772; (g) Trofimov, B. A.; Schmidt, E. Y.; Bidusenko, I. A.; Ushakov, I. A.; Protsuk, N. I.; Zorina, N. V.; Mikhaleva, A. I. *Tetrahedron* **2012**, *68*, 1241.
9. (a) Yuan, Y.; Thomé, I.; Kim, S. H.; Chen, D.; Beyer, A.; Bonnamour, J.; Zuidema, E.; Chang, S.; Bolm, C. *Adv. Synth. Catal.* **2010**, *352*, 2892; (b) Beyer, A.; Reucher, C. M. M.; Bolm, C. *Org. Lett.* **2011**, *13*, 2876.
10. (a) Bernard, M. K. *Tetrahedron* **2000**, *56*, 7273; (b) Cano, R.; Ramón, D. J.; Yus, M. *J. Org. Chem.* **2011**, *76*, 654.
11. Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.
12. Potts, K. T.; Nye, S. A.; Smith, K. A. *J. Org. Chem.* **1992**, *57*, 3895.
13. Tang, J.; Zhao, X. *RSC Adv.* **2012**, *2*, 5488.
14. Zheng, Q.; Hua, R.; Wan, Y. *Appl. Organomet. Chem.* **2010**, *24*, 314.