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Synthesis of Polysubstituted Furans Based on a Stepwise Sonogashira Coupling of (Z)-3-Iodoalk-2-en-1-ols with Terminal Propargylic Alcohols and Subsequent Au(I)- or Pd(II)-Catalyzed Cyclization−Aromatization via Elimination of H_2O

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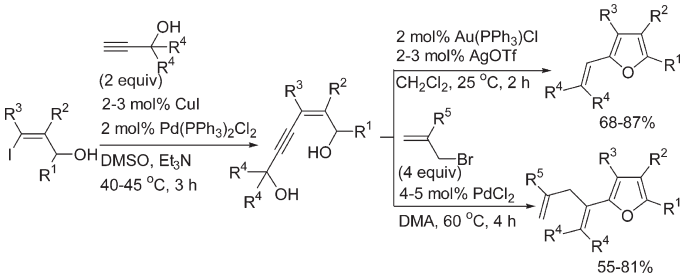

Recently, we have developed highly regio- and stereoselective carbometalation of 2-alkynols and 2,3-allenols. The organometallacyclic intermediates may be trapped with I_2 to afford 3-iodoalk-2-en-1-ols. These 3-iodoalk-2-en-1-ols may readily undergo the Sonogashira coupling with terminal propargyl alcohols to form 4-alkyn-2-ene-1,6-diols. Subsequent cycloisomerization in DMA or CH_2Cl_2 with $Au(PPh_3)Cl$ and AgOTf as the catalyst would afford polysubstituted 2-(1-alkenyl)furans; with $PdCl_2$ as the catalyst and the reaction in DMA in the presence of allylic bromides, the same substrates afforded polysubstituted 2-(1,4-alkadienyl)furans. In both types of catalyzed cyclization reactions, the elimination of H_2O promoted the aromatization to form the furan ring. Different alkyl or aryl groups could be introduced into different positions of furans due to the substituent-loading capability of 3-iodoalkenols and diversity of the terminal propargyl alcohols and allylic bromides.

Introduction

The synthesis of furans has been attracting extensive interest[1] because they are widely used as synthetic building blocks,[2] existing in numerous natural products[3] and endowed with significant pharmacological potential.[4] As we know, transition-metal-catalyzed cyclization for furan synthesis have been mostly realized under mild reaction conditions:[1c−f] Alkynyl,[5] allenyl,[5b,6] or cyclopropyl[5j,7] ketone derivatives and functionalized oxiranes[8] have been used as starting materials for such a purpose. Recently, cycloisomerization of 3-yn-2-en-1-ols has been established as an efficient approach for the assembly of the furan rings. It has been reported that *t*-BuOK-,[9a−c] Ru-,[9d−f] Pd-,[9d,g,j] Au-,[5b,9h] and IBX-catalyzed[9i] or promoted cyclization of

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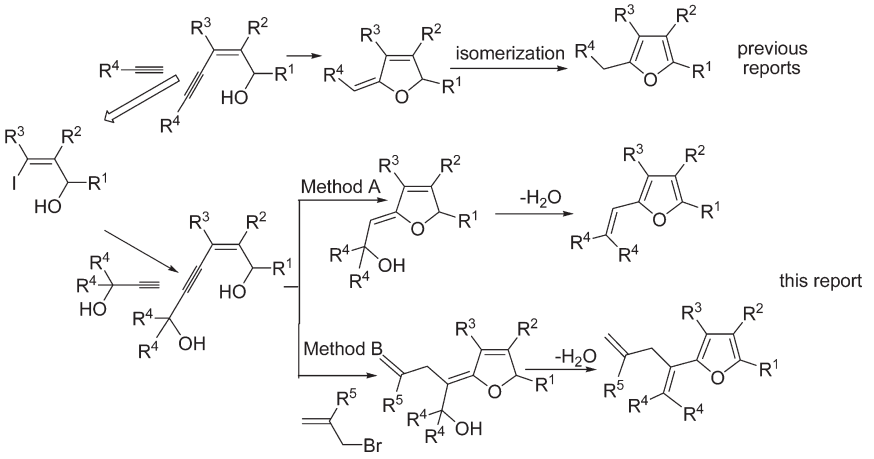
SCHEME 1



3-alkyn-2-enols afforded 2-alkylfurans. However, there are several disadvantages of the reactions; for example, a strong base[9a−c] and high temperature are required,[9d−g] and only an alkyl group (R^4CH_2-) could be introduced at the 2-position of furans[5b,9] except in a case reported by Marshall[9c] (Scheme 1). Herein, we wish to disclose a synthesis of polysubstituted furans by a Sonogashira coupling of (*Z*)-3-iodoalk-2-en-1-ols with terminal propargylic alcohols and subsequent Au(I)- or Pd(II)-catalyzed cyclization in which the hydroxyl group in the propargylic alcohols were applied to realize the aromatization via elimination of water[10] under very mild conditions.

Results and Discussion

Sonogashira coupling of (*Z*)-3-iodoalk-2-en-1-ols and terminal alkynes was developed as one of the most general procedures for the synthesis of enynols.[9a,11] Highly regio- and stereoselective carbometalation of 2-alkynols[12] and 2,3-allenols[13] followed by quenching with I_2 have been developed to afford 3-iodoalk-2-en-1-ols. We initiated our study by taking 4-iodo-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol **1a** as the starting material. First, we conducted the Sonogashira coupling reaction of **1a** with 2-methyl-3-butyn-2-ol **2a** under the modified conditions developed in our laboratory.[14] The reaction afforded the crude product, i.e., 2-methyl-6-pentyl-5-phenyl-3-yn-5(*Z*)-octen-2,7-diol **3aa**. This crude product was purified by a flash chromatography on silica gel and further treated with 4 equiv of allyl bromide **4a** in the presence of 4−5 mol % of $PdCl_2$ in DMA at room temperature. It is interesting to observe that the reaction afforded the cyclization−coupling−elimination product, 2-methyl-5-(2-methylhexa-2,5-dien-3-yl)-3-pentyl-4-phenylfuran **6aaa**, as the major product together with the cycloisomerization−elimination product, 2-methyl-5-(2-methylprop-1-enyl)-3-pentyl-4-phenylfuran **5aa**, in 64% and 0.5% yields, respectively (entry 1, Table 1). The formation of 5-(2-hydroxy-2-methylpropyl)-2-methyl-3-pentyl-4-phenylfuran **7aa** was not observed. The reaction at 60 °C afforded a higher yield of **6aaa** (81%) (entry 2, Table 1), while the reaction at 80 °C afforded the product **6aaa** in a lower yield and selectivity (entry 4, Table 1). Solvent had a remarkable influence on the reaction. DMF

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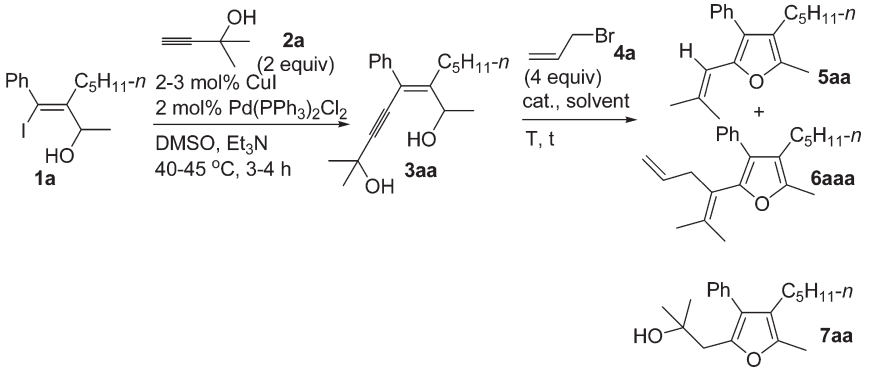
TABLE 1. Effect of Temperature, Solvent, and Catalyst on the Selective Formation of 5aa or 6aaa[a]



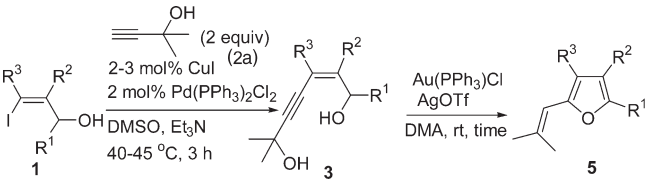
					NMR yield[b] (%)	
entry	cat. (4−5 mol %)	solvent	temp (°C)	time (h)	**5aa**	**6aaa**
1[c]	$PdCl_2$	DMA	40	14	0.5	64
2	**$PdCl_2$**	**DMA**	**60**	**4**	**0.7**	**87 (81)**
3	$PdCl_2$	DMA	60	4	1.4[d]	0
4[c]	$PdCl_2$	DMA	80	6	14	55
5	$PdCl_2$	DMF	60	4	2	71
6	$PdCl_2$	DMSO	60	4	0	0
7	$PdCl_2$	CH_3CN	60	4	11	0
8	$Pd(OAc)_2$	DMA	60	4	15	43
9[e]	$Pd(PhCN)_2Cl_2$	DMA	60	4	15	33
10	**$Au(PPh_3)Cl$[f]**	**DMA**	**rt**	**2**	**83 (77)**	**0**
11	**$Au(PPh_3)Cl$[f]**	**CH_2Cl_2**	**rt**	**2**	**81 (80)**	**0**
1[g,h]	$Au(PPh_3)Cl$	CH_2Cl_2	rt	2	0	0
13[g,i]	AgOTf	CH_2Cl_2	rt	2	8	0

[a]The first step of the reaction was conducted by using 0.25 mmol of **1a**, 2−3 mol % each of CuI and $Pd(PPh_3)_2Cl_2$, and 2 equiv of 2-methyl-3-butyn-2-ol in 1 mL each of DMSO and Et_3N; the second step of the reaction was conducted by using the product of the first step **3aa** and 1 mmol of allyl bromide in the presence of corresponding catalyst in 2 mL of solvent. [b]The numbers in the parentheses are the isolated yields. [c]The reaction time of first step was 12 h. [d]The reaction was conducted in the absence of allyl bromide, and 65% of **3aa** was recovered as determined by NMR analysis of the crude reaction product. [e]Recovery of **3aa** was 18%. [f]2 mol % of $Au(PPh_3)Cl$ was used together with 2−3 mol % of AgOTf; allyl bromide was not added. [g]2 mol % of catalyst was used; allyl bromide was not added. [h]Recovery of **3aa** was 74%. [i]Recovery of **3aa** was 78%.

offered a similar result in this reaction (entry 5, Table 1); however, neither **5aa** nor **6aaa** was formed in DMSO (entry 6, Table 1). The reaction in CH_3CN afforded **5aa** in 11% yield exclusively (entry 7, Table 1). $Pd(OAc)_2$ and $Pd(PhCN)_2Cl_2$ showed poor catalytic activities (entries 8 and 9, Table 1). With the employment of $Au(PPh_3)Cl$/AgOTf in DMA, **5aa** was afforded as a single product in 83% NMR yield (entry 10, Table 1).

We then started to study the scope of the reaction. For the synthesis of polysubstituted 2-(1-alkenyl)furans **5**, with R^3 as a Ph group, the reaction afforded **5aa** and **5da** smoothly (entries 1 and 4, Table 2). When R^3 was H or *n*-hexyl, 10 mol % of catalyst is required (entries 3, 6, and 8, Table 2). Fortunately, when the reaction was run in CH_2Cl_2, only 2 mol % of $Au(PPh_3)Cl$/AgOTf was required (entry 10, Table 1). The typical results shown in Table 3 indicated that the reaction is quite general for the synthesis of polysubstituted 2-(1-alkenyl)furans **5** and 2-(1,4-alkadienyl)furans **6**: R^1 may be hydrogen, alkyl, or aryl groups; R^2 may be alkyl or aryl groups; R^3 may be hydrogen, alkyl, or aryl groups; R^4 may be alkyl or aryl groups. We also attempted to conduct the reactions of 1.0302 g (2.99 mmol) and 1.0323 g (3.01 mmol) of 4-iodo-3-(*n*-pentyl)-4-phenyl-3(Z)-buten-2-ol **1a** under method A or B to provide 2-methyl-5-(2-methylprop-1-enyl)-3-pentyl-4-phenylfuran **5aa** in 81% yield (0.6882 g) and 2-methyl-5-(2-methylhexa-2,5-dien-3-yl)-3-pentyl-4-phenylfuran **6aaa** in 72% yield (0.6948 g), respectively (entry 12, Table 3).

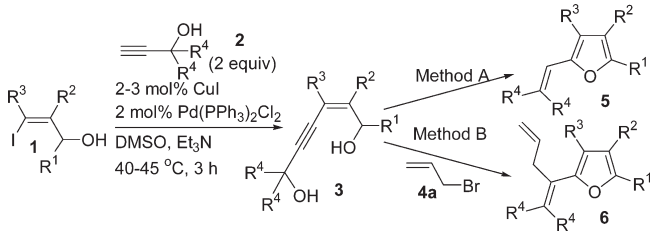
TABLE 2. Synthesis of 5 in DMA under the Reaction Conditions for Entry 9 in Table 1 with Different Loadings of the $Au(PPh_3)Cl$ and AgOTf[a]



	1			yield of
entry	$R^1/R^2/R^3$	Au^+/Ag^+ (mol %)	time (h)	**5**[b] (%)
1	Me/*n*-Pen/Ph (**1a**)	2/2	2	83 (77) (**5aa**)
2	*p*-Tol/*n*-Pen/H (**1c**)	2/2	21	20 (**5ca**)[c]
3	*p*-Tol/*n*-Pen/H (**1c**)	9/5	2	82 (78) (**5ca**)
4	Me/*i*-Pr/Ph (**1d**)	2/2	4	61 (60) (**5da**)
5	Me/*n*-Bu/*n*-Hex (**1g**)	2/2	21	53 (**5ga**)[d]
6	Me/*n*-Bu/*n*-Hex (**1g**)	10/5	2	71 (58) (**5ga**)
7	Me/*n*-Pen/H (**1h**)	2/2	22	23 (**5ha**)[e]
8	Me/*n*-Pen/H (**1h**)	9/5	2	85 (69) (**5ha**)

[a]The first step of the reaction was conducted by using 0.25 mmol of **1**, 2−3 mol % each of CuI and $Pd(PPh_3)_2Cl_2$, and 2 equiv of 2-methyl-3-butyn-2-ol in 1 mL each of DMSO and Et_3N; the second step of the reaction was conducted by using the product of the first step **3** in the presence of $Au(PPh_3)Cl$ and AgOTf in 2 mL of DMA. [b]The yield of **5** was determined by ^1H NMR analysis, and the numbers in parentheses are the isolated yields. [c]Recovery of **3ca** was 63%. [d]Recovery of **3ga** was 13%. [e]Recovery of **3ha** was 62%.

TABLE 3. Sonogashira Coupling of Various (Z)-3-Iodoalk-2-en-1-ols with Terminal Propargylic Alcohols and Subsequent Au(I)- or Pd(II)-Catalyzed Cyclization Reactions[a]



entry	1/2 $R^1/R^2/R^3/R^4/R^4$	yield of **5** (%)	yield of **6** (%)
1	Me/*n*-Pen/Ph (**1a**)/Me/Me (**2a**)	80 (**5aa**)	81 (**6aaa**)
2	H/*n*-Bu/*n*-Hex (**1b**)/Me/Me (**2a**)	72 (**5ba**)	65 (**6baa**)
3	*p*-Tol/*n*-Pen/H (**1c**)/Me/Me (**2a**)	87 (**5ca**)	72 (**6caa**)
4	Me/*i*-Pr/Ph (**1d**)/Me/Me (**2a**)	78 (**5da**)	62 (**6daa**)
5	Me/Ph/*n*-Hex (**1e**)/Me/Me (**2a**)	77 (**5ea**)	77 (**6eaa**)
6	Me/An[b]/Ph (**1f**)/Me/Me (**2a**)	75 (**5fa**)	64 (**6faa**)[c]
7	Me/*n*-Bu/*n*-Hex (**1g**)/Me/Me (**2a**)	68 (**5ga**)	76 (**6gaa**)
8	Me/*n*-Pen/H (**1h**)/Me/Me (**2a**)	83 (**5ha**)	68 (**6haa**)
9	Me/*n*-Pen/H (**1h**)/*n*-Pr/*n*-Pr (**2b**)	84 (**5hb**)	61 (**6hba**)
10	Me/*n*-Pen/H (**1h**)/$(CH_2)_5$ (**2c**)	80 (**5hc**)	71 (**6hca**)
11	Me/*n*-Pen/H (**1h**)/Ph/Ph (**2d**)	73 (**5hd**)	55 (**6hda**)[d]
12	Me/*n*-Pen/Ph (**1a**)/Me/Me (**2a**)	81 (**5aa**)[e,f]	72 (**6aaa**)[c,f]

[a]The first step of reaction was conducted by using 0.25 mmol of **1**, 2−3 mol % each of CuI and $Pd(PPh_3)_2Cl_2$, 2 equiv of **2** in 1 mL each of DMSO and Et_3N. Method A: A mixture of **3** prepared from the first step and 2−3 mol % each of $Au(PPh_3)Cl$ and AgOTf in 2 mL of CH_2Cl_2 stirred at 25 °C for 2 h. Method B: A mixture of **3** prepared from the first step, 4 equiv of allyl bromide, and 4−5 mol % $PdCl_2$ in 2 mL of DMA stirred at 60 °C for 4 h. [b]An is the abbreviation of *p*-$MeOC_6H_4$. [c]The reaction time of the first step was 4 h. [d]The reaction time of the second step was 5 h. [e]1 mol % each of $Au(PPh_3)Cl$ and AgOTf were used. [f]The reaction was conducted by using 3 mmol of **1**.

Furthermore, 2-methylallyl bromide could also be used in the reaction to afford **6aab** in 63% yield (Scheme 2). The structures of these products were further confirmed by the X-ray diffraction analysis of 2-methyl-5-(2-methylprop-1-enyl)-3-(*p*-methoxyphenyl)-4-phenylfuran **5fa** (Figure S1, Supporting Information).[15]

However, when secondary alcohol, i.e., 3-butyn-2-ol **2e**, was used, a 1:1 *Z*/*E* mixture of the expected product **5ae** was afforded with method A while a complicated mixture was formed with method B (Scheme 3, eq 1). In addition, with method A, the reaction of **1a** with 2-propyn-1-ol **2f** afforded 2-methyl-3-pentyl-4-phenyl-5-vinylfuran **5af** in very low yield (21%); with method B, the reaction is not clean: besides the cycloiosmerization−elimination product **5af**, the C=C bond migrated product **7afa** was formed in 11% yield instead of the normal product **6afa** probably due to the higher stability of the conjugated C=C double bonds. The reaction at 40 °C did produce **6afa** in 2% yield (Scheme 3, eq 2).

(15) Crystal data for **5fa**: $C_{22}H_{22}O_2$, MW = 318.40, monoclinic, space group *P*2(1)/*n*, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0436, wR2 = 0.1154, *R* indices (all data) R1 = 0.0502, wR2 = 0.1241, *a* = 9.8004(4) Å, *b* = 19.8870 (9) Å, *c* = 10.0615(4) Å, α = 90°, *β* = 113.9110(10)°, *γ* = 90°, *V* = 1792.69(13) Å^3, *T* = 296(2) K, *Z* = 4, reflections collected/unique: 20432/3146 (R_{int} = 0.0227), number of observations [$> 2\sigma(I)$] 2720, parameters 217. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 756341.

We proposed the following mechanism for this transformation (Scheme 4):[16] Au^+ may coordinate with the triple bound of **3** to afford coordination complex **8**, and then the hydroxyl group acted as a nucleophile to undergo oxymetalation forming intermediate **9**. Hydrolysis afforded dihydrofuran **10**, which subsequently underwent an H_2O-elimination-induced aromatization to afford final product **5**. On the other hand, the *exo*-oxypalladation of **11** would form vinylic palladium intermediate **12**, which is inert toward protonolysis. Carbometalation of allyl bromide with **12** would provide intermediate **13**, which would undergo subsequent debromopalladation to regenerate the catalyst Pd^{2+} and release the cross-coupling product **14**. Aromatization via elimination of H_2O would afford final product **6**.

Conclusion

In summary, we have demonstrated a synthesis of polysubstituted furans. 4-Alkyn-2-ene-1,6-diols derived from the Sonogashira coupling of different (*Z*)-3-iodoalk-2-en-1-ols with terminal propargyl alcohols undergo a cyclization−eliminaton−aromatization reaction catalyzed by $Au(PPh_3)Cl$/AgOTf to provide polysubstituted 2-(1-alkenyl)furans or a cyclization−coupling−eliminaton−aromatization reaction catalyzed by Pd(II) to provide polysubstituted 2-(1,4-alkadienyl)-furans in moderate to excellent yields. The reaction is quite general, and different alkyl and aryl groups may be introduced into the 3-, 4-, and 5-positions of the 2-(1-alkenyl)furans or 2-(1,4-alkadienyl)furans. The introduction of such substituents with C=C bond(s) to the furans will provide further opportunity for elaboration.[9c] Due to the easily availability and diversity of the starting materials and the potential of the furans, this method will be useful in organic synthesis, medicinal chemistry, and material sciences. Further studies are being pursued in our laboratory.

Experimental Section

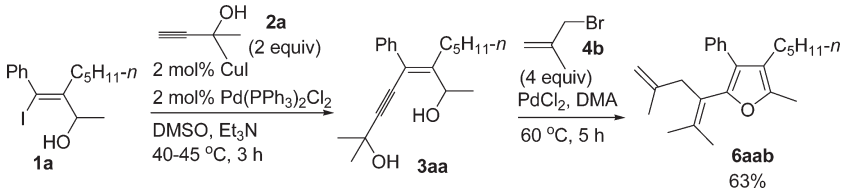
Materials. Et_3N and DMSO were distilled from KOH and CaH_2, respectively. The commercially available chemicals including $Au(PPh_3)Cl$ and AgOTf were used without additional treatment.

Starting materials **1a**,[12e] **1b**,[13] **1c**,[12c] **1d**,[12e] **1e**,[13] **1f**,[12e] **1g**,[13] and **1h**[12c] were prepared according to the published procedures.

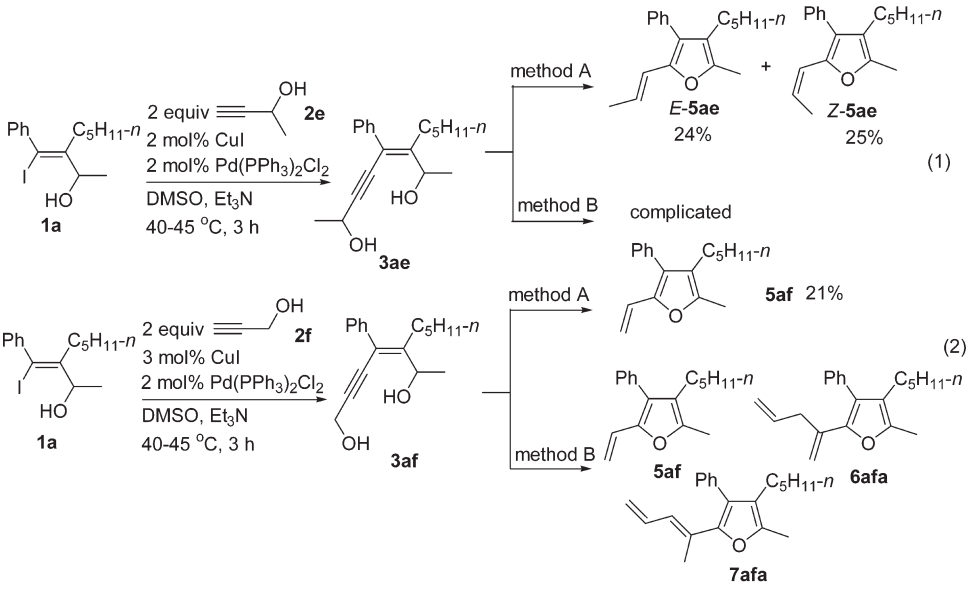
1. Experimental Details for the Results Presented in Table 2. (1) 2-Methyl-5-(2-methylpropen-1-yl)-3-pentyl-4-phenylfuran (5aa). Typical procedure: To a dry Schlenk tube were added CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.4 mg, 0.005 mmol, 2 mol %), **1a** (86.0 mg, 0.25 mmol), Et_3N (1 mL), **2a** (41.7 mg, 0.50 mmol, 2.0 equiv), and DMSO (1 mL). The resulting mixture was then heated at 40−45 °C. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with an aqueous solution of saturated NH_4Cl (5 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layer was washed sequentially with 5% HCl, satd $NaHCO_3$ (aq), and brine and then dried over anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) afforded the product **3aa** in a round-bottom flask. To this flask were added DMA (2 mL), $Au(PPh_3)Cl$ (2.6 mg, 0.005 mmol, 2 mol %), and AgOTf (1.4 mg, 0.005 mmol, 2 mol %). The resulting mixture was stirred at room temperature until complete conversion of **3aa** as monitored by TLC. The reaction

(16) Jiang, X.; Ma, X.; Zheng, Z.; Ma, S. *Chem.—Eur. J.* **2008**, *14*, 8572.

SCHEME 2



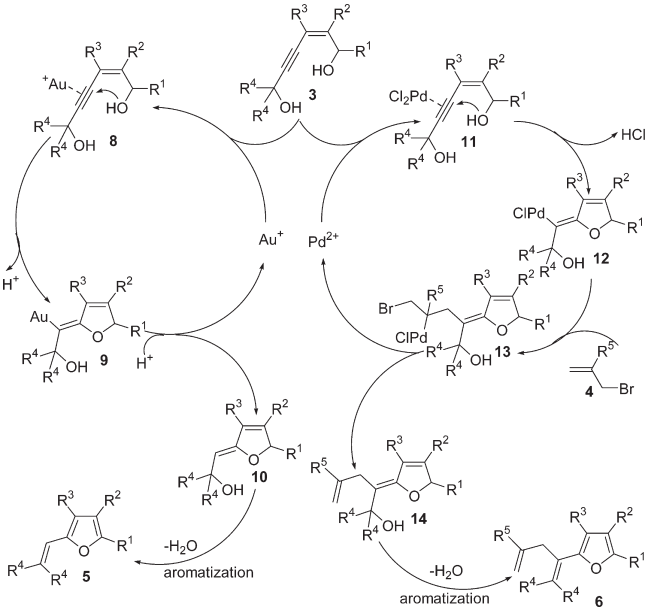
SCHEME 3



The temperature effect of method B:

1) 60 °C, 4 h, **5af**: 23%, **6afa**: 0%, **7afa**: 11%
2) 40 °C, 12 h, **5af**: 11%, **6afa**: 2%, **7afa**: 16%
3) 20 °C, 30 h, **5af**: 8%, **6afa**: 0%, **7afa**: 0%

SCHEME 4



mixture was then quenched with an aqueous solution of saturated NH_4Cl (5 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layer was sequentially washed with 5% HCl, satd $NaHCO_3$ (aq), and brine and then dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield (83%) was determined by using 1,3,5-trimethylbenzene as the internal standard (14 μL, 0.1 mmol). Chromatography on silica gel (eluent: petroleum ether) afforded the product **5aa** (54.5 mg, 77%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.34 (m, 2 H), 7.31−7.22 (m, 3 H), 5.85 (d, J = 1.2 Hz, 1 H), 2.34−2.27 (m, 5 H), 2.05 (s, 3 H), 1.80 (s, 3 H), 1.32−1.08 (m, 6 H), 0.78 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.4, 145.9, 134.4, 133.4, 129.8, 128.2, 126.4, 124.2, 119.7, 112.4, 31.4, 29.8, 27.3, 23.3, 22.3, 20.2, 14.0, 12.0; IR (neat, cm^{-1}) 3028, 2957, 2927, 2858, 1655, 1604, 1547, 1491, 1445, 1376, 1272, 1191, 1055, 1005; MS (m/z) 283 ($M^+ + 1$, 23.2), 282 (M^+, 100); HRMS calcd for $C_{20}H_{26}O$ 282.1984, found 282.1984.

(2) 2-(*p*-Methylphenyl)-5-(2-methylpropen-1-yl)-3-pentylfuran (5ca). The reaction of the first step using CuI (1.1 mg, 0.006 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.4 mg, 0.005 mmol, 2 mol %), **1c** (87.0 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.3 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3ca**. The reaction of the second step using **3ca** (from the first step)/DMA (2 mL), $Au(PPh_3)Cl$ (11.5 mg, 0.023 mmol, 9 mol %), and AgOTf (3.4 mg, 0.013 mmol, 5 mol %) afforded **5ca** (55.4 mg, 78%) (according to ^{1}H NMR analysis of the crude reaction mixture before separation, product **5ca** was formed in 82% NMR yield): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.5 Hz, 2 H), 7.19 (d, J = 7.8 Hz, 2 H), 6.13 (s, 1 H), 6.05 (s, 1 H), 2.62 (t, J = 7.8 Hz, 2 H), 2.35 (s, 3 H), 2.06 (s, 3 H), 1.91 (s, 3 H), 1.70−1.56 (m, 2 H),

1.44−1.29 (m, 4 H), 0.89 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.6, 146.5, 136.1, 134.6, 129.21, 129.17, 125.2, 122.7, 114.3, 111.5, 31.8, 29.7, 27.1, 25.9, 22.6, 21.2, 20.2, 14.1; IR (neat, cm^{-1}) 3025, 2957, 2926, 2859, 1658, 1614, 1593, 1530, 1501, 1455, 1376, 1341, 1296, 1186, 1108, 1058, 1006; MS (m/z) 283 (M^+ + 1, 21.6), 282 (M^+, 100); HRMS calcd for $C_{20}H_{26}O$ 282.1984, found 282.1983.

(3) 3-Isopropyl-2-methyl-5-(2-methylpropen-1-yl)-4-phenylfuran (5da). The reaction of the first step using CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1d** (79.2 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (41.1 mg, 0.49 mmol, 2 equiv)/DMSO (1 mL) afforded **3da**. The reaction of the second step using **3da** (from the first step)/DMA (2 mL), $Au(PPh_3)Cl$ (2.6 mg, 0.005 mmol, 2 mol %), and AgOTf (1.6 mg, 0.005 mmol, 2 mol %) afforded **5da** (37.9 mg, 60%) (according to ^{1}H NMR analysis of the crude reaction mixture before separation, product **5da** was formed in 61% NMR yield): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.34 (m, 2 H), 7.33−7.26 (m, 1 H), 7.26−7.20 (m, 2 H), 5.73 (s, 1 H), 2.73 (septet, J = 7.1 Hz, 1 H), 2.37 (s, 3 H), 2.05 (s, 3 H), 1.77 (s, 3 H), 1.13 (d, J = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.2, 144.8, 134.5, 133.1, 130.5, 128.0, 126.6, 125.3, 124.4, 112.3, 27.3, 24.1, 22.7, 20.1, 13.4; IR (neat, cm^{-1}) 3021, 2962, 2925, 1658, 1603, 1545, 1444, 1375, 1363, 1273, 1186, 1076, 1027, 1005; MS (m/z) 255 (M^++1, 20.1), 254 (M^+, 100); HRMS calcd for $C_{18}H_{22}O$ 254.1671, found 254.1671.

(4) 3-Butyl-4-hexyl-2-methyl-5-(2-methylpropen-1-yl)furan (5ga). The reaction of the first step using CuI (1.1 mg, 0.006 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1g** (85.4 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (44.7 mg, 0.53 mmol, 2 equiv)/DMSO (1 mL) afforded **3ga**. The reaction of the second step using **3ga** (from the first step)/DMA (2 mL), $Au(PPh_3)Cl$ (12.5 mg, 0.025 mmol, 10 mol %), and AgOTf (3.1 mg, 0.012 mmol, 5 mol %) afforded **5ga** (40.1 mg, 58%) (according to ^{1}H NMR analysis of the crude reaction mixture before separation, product **5ga** was formed in NMR 71% yield): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (s, 1 H), 2.33−2.22 (m, 4 H), 2.20 (s, 3 H), 2.04 (s, 3 H), 1.87 (s, 3 H), 1.48−1.24 (m, 12 H), 0.95−0.84 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.6, 145.4, 131.4, 122.4, 119.8, 112.1, 32.9, 31.7, 31.0, 29.3, 27.3, 23.7, 23.2, 22.7, 22.6, 20.0, 14.1, 14.0, 11.9; IR (neat, cm^{-1}) 2955, 2926, 2857, 2732, 1622, 1547, 1457, 1376, 1296, 1251, 1198, 1154, 1107, 1064, 1035; MS (m/z) 277 (M^+ + 1, 21.6), 276 (M^+, 100); HRMS calcd for $C_{19}H_{32}O$ 276.2453, found 276.2451.

(5) 2-Methyl-5-(2-methylpropen-1-yl)-3-pentylfuran (5ha). The reaction of the first step using CuI (1.2 mg, 0.006 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1h** (68.3 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (44.0 mg, 0.52 mmol, 2 equiv)/DMSO (1 mL) afforded **5ha**. The reaction of the second step using **3ha** (from the first step)/DMA (2 mL), $Au(PPh_3)Cl$ (11.4 mg, 0.023 mmol, 9 mol %), and AgOTf (3.0 mg, 0.012 mmol, 5 mol %) afforded **5ha** (36.4 mg, 69%) (according to ^{1}H NMR analysis of the crude reaction mixture before separation, product **5ha** was formed in 85% NMR yield): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (s, 2 H), 2.28 (t, J = 7.5, 2 H), 2.20 (s, 3 H), 1.96 (s, 3 H), 1.87 (s, 3 H), 1.55−1.44 (m, 2 H), 1.39−1.21 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.8, 145.2, 133.1, 120.6, 114.5, 109.4, 31.4, 30.1, 26.9, 24.8, 22.5, 20.0, 14.1, 11.5; IR (neat, cm^{-1}) 2958, 2926, 2857, 1662, 1624, 1542, 1450, 1376, 1340, 1295, 1241, 1200, 1158, 1060; MS (m/z) 207 (M^+ + 1, 12.4), 206 (M^+, 79.0), 150 (($M - C_4H_8)^+$, 100); HRMS calcd for $C_{14}H_{22}O$ 206.1671, found 206.1672.

2. Experimental Details for Method A (Table 3). (1) 2-Methyl-5-(2-methylpropen-1-yl)-3-pentyl-4-phenylfuran (5aa). Typical procedure for method A: To a dry Schlenk tube were added CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1a** (85.5 mg, 0.25 mmol), Et_3N (1 mL), **2a** (44.2 mg, 0.53 mmol, 2.1 equiv), and DMSO (1 mL). The resulting mixture was then heated at 40−45 °C. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with an aqueous solution of saturated NH_4Cl (5 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layer was washed sequentially with 5% HCl, satd $NaHCO_3$ (aq), and brine and then dried over anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) afforded the product **3aa** in a round-bottom flask. Then the catalyst was prepared by sequential addition of 1 mL of CH_2Cl_2, $Au(PPh_3)Cl$ (2.5 mg, 0.005 mmol, 2 mol %), and AgOTf (1.6 mg, 0.006 mmol, 2 mol %) followed by stirring at rt for 5 min. This resulting solution was then added to a solution of the above prepared **3aa** in CH_2Cl_2 (1 mL). The resulting mixture was stirred at room temperature until complete conversion of the **3aa** as monitored by TLC. The reaction mixture was then quenched with water and extracted with Et_2O (3 × 15 mL). The combined organic layer was washed with brine and then dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield (81%) was determined by using 1,3,5-trimethylbenzene as the internal standard (14 μL, 0.1 mmol). Chromatography on silica gel (eluent: petroleum ether) afforded the product **5aa** (56.2 mg, 80%). The data of the compound are the same as listed above.

(2) 2-Methyl-5-(2-methylpropen-1-yl)-3-pentyl-4-phenylfuran (5aa). Following method A, the reaction of the first step using CuI (11.0 mg, 0.058 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (42.7 mg, 0.061 mmol, 2 mol %), **1a** (1030.2 mg, 3.0 mmol)/Et_3N (12 mL), and **2a** (504.4 mg, 6.0 mmol, 2 equiv)/DMSO (12 mL) afforded **3aa**. The reaction of the second step using **3aa** (from the first step)/CH_2Cl_2 (12 mL) and $Au(PPh_3)Cl$ (14.7 mg, 0.03 mmol, 1 mol %)/AgOTf (8.0 mg, 0.03 mmol, 1 mol %)/CH_2Cl_2 (12 mL) afforded **5aa** (688.2 mg, 81%). The data of the compound are the same as those listed above.

(3) 4-Butyl-3-hexyl-2-(2-methylpropen-1-yl)furan (5ba). Following method A, the reaction of the first step using CuI (1.1 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1b** (80.0 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (43.3 mg, 0.52 mmol, 2 equiv)/DMSO (1 mL) afforded **3ba**. The reaction of the second step using **3ba** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.4 mg, 0.005 mmol, 2 mol %)/AgOTf (1.9 mg, 0.007 mmol, 3 mol %)/CH_2Cl_2 (1 mL) afforded **5ba** (46.5 mg, 72%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 1 H), 5.91 (s, 1 H), 2.36−2.28 (m, 4 H), 2.04 (s, 3 H), 1.88 (s, 3 H), 1.59−1.24 (m, 12 H), 0.98−0.84 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.3, 136.6, 133.2, 126.0, 121.5, 112.2, 31.7, 31.6, 30.6, 29.2, 27.3, 23.5, 23.4, 22.7, 22.6, 20.0, 14.1, 13.9; IR (neat, cm^{-1}) 2957, 2927, 2858, 2732, 1662, 1534, 1465, 1376, 1344, 1284, 1233, 1202, 1136, 1099, 1059, 1020; MS (m/z) 263 (M^+ + 1, 14.3), 262 (M^+, 65.5), 205 (100); HRMS calcd for $C_{18}H_{30}O$ 262.2297, found 262.2296.

(4) 2-(*p*-Methylphenyl)-5-(2-methylpropen-1-yl)-4-pentylfuran (5ca). Following method A, the reaction of the first step using CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1c** (85.2 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (45.1 mg, 0.54 mmol, 2 equiv)/DMSO (1 mL) afforded **3ca**. The reaction of the second step using **3ca** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.4 mg, 0.005 mmol, 2 mol %)/AgOTf (1.4 mg, 0.005 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5ca** (61.1 mg, 87%). The data of the compound are the same as those listed above.

(5) 3-Isopropyl-2-methyl-5-(2-methylpropen-1-yl)-4-phenylfuran (5da). Following method A, the reaction of the first step using CuI (1.1 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.3 mg, 0.005 mmol, 2 mol %), **1d** (79.1 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (41.4 mg, 0.49 mmol, 2 equiv)/DMSO (1 mL) afforded **3da**. The reaction of the second step using **3da** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.5 mg, 0.005 mmol, 2 mol %)/AgOTf (1.4 mg, 0.005 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5da** (49.5 mg, 78%). The data of the compound are the same as those listed above.

(**6**) **4-Hexyl-2-methyl-5-(2-methylpropen-1-yl)-3-phenylfuran (5ea).** Following method A, the reaction of the first step using CuI (1.4 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 0.005 mmol, 2 mol %), **1e** (88.5 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (44.0 mg, 0.52 mmol, 2 equiv)/DMSO (1 mL) afforded **3ea**. The reaction of the second step using **3ea** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.5 mg, 0.005 mmol, 2 mol %)/AgOTf (1.7 mg, 0.007 mmol, 3 mol %)/CH_2Cl_2 (1 mL) afforded **5ea** (56.3 mg, 77%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.34 (m, 2 H), 7.32−7.21 (m, 3 H), 5.96 (s, 1 H), 2.36 (t, J = 7.5 Hz, 2 H), 2.26 (s, 3 H), 2.09 (s, 3 H), 1.91 (s, 3 H), 1.33−1.08 (m, 8 H), 0.81 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.1, 146.3, 134.3, 132.7, 129.4, 128.2, 126.4, 122.8, 121.8, 111.9, 31.4, 30.4, 29.0, 27.4, 23.5, 22.5, 20.1, 14.0, 12.4; IR (neat, cm^{-1}) 2926, 2857, 1621, 1599, 1549, 1495, 1444, 1376, 1309, 1250, 1202, 1109, 1069, 1011; MS (m/z) 297 (M^+ + 1, 22.7), 296 (M^+, 100); HRMS calcd for $C_{21}H_{28}O$ 296.2140, found 296.2141.

(**7**) **2-Methyl-3-(methoxylpheyl)-5-(2-methylpropen-1-yl)-4-phenylfuran (5fa).** Following method A, the reaction of the first step using CuI (1.3 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1f** (95.1 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (43.3 mg, 0.52 mmol, 2 equiv)/DMSO (1 mL) afforded **3fa**. The reaction of the second step using **3fa** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.4 mg, 0.005 mmol, 2 mol %)/AgOTf (1.5 mg, 0.006 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5fa** (59.4 mg, 75%) (petroleum ether/ethyl acetate = 100/1): solid; mp 111.4−111.8 °C (hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.16 (m, 3 H), 7.13−7.06 (m, 2 H), 7.01−6.94 (m, 2 H), 6.83−6.76 (m, 2 H), 5.99 (s, 1 H), 3.78 (s, 3 H), 2.37 (s, 3 H), 2.09 (s, 3 H), 1.85 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.0, 147.8, 146.6, 134.9, 133.5, 130.7, 130.1, 127.9, 126.2, 125.6, 123.0, 121.4, 113.5, 112.4, 55.1, 27.3, 20.3, 12.6; IR (KBr, cm^{-1}) 3035, 2914, 2835, 1655, 1602, 1573, 1549, 1511, 1443, 1376, 1321, 1288, 1246, 1176, 1106, 1041, 1021; MS (m/z) 319 (M^+ + 1, 24.2), 318 (M^+, 100). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.82; H, 6.91.

(**8**) **3-Butyl-4-hexyl-2-methyl-5-(2-methylpropen-1-yl)furan (5ga).** Following method A, the reaction of the first step using CuI (1.3 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1g** (84.2 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (43.0 mg, 0.51 mmol, 2 equiv)/DMSO (1 mL) afforded **3ga**. The reaction of the second step using **3ga** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.6 mg, 0.005 mmol, 2 mol %)/AgOTf (1.8 mg, 0.006 mmol, 3 mol %)/CH_2Cl_2 (1 mL) afforded **5ga** (46.9 mg, 68%). The data of the compound are the same as those listed above.

(**9**) **2-Methyl-5-(2-methylpropen-1-yl)-3-pentylfuran (5ha).** Following method A, the reaction of the first step using CuI (1.2 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 2 mol %), **1h** (67.1 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.2 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3ha**. The reaction of the second step using **3ha** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.6 mg, 0.005 mmol, 2 mol %)/AgOTf (1.6 mg, 0.006 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5ha** (42.6 mg, 83%). The data of the compound are the same as those listed above.

(**10**) **2-Methyl-3-pentyl-5-(2-propyl-1-penten-1-yl)furan (5hb).** Following method A, the reaction of the first step using CuI (1.1 mg, 0.006 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 2 mol %), **1h** (66.1 mg, 0.25 mmol)/Et_3N (1 mL), and **2b** (71.7 mg, 0.51 mmol, 2 equiv)/DMSO (1 mL) afforded **3hb**. The reaction of the second step using **3hb** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.3 mg, 0.005 mmol, 2 mol %)/AgOTf (1.6 mg, 0.006 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5hb** (54.6 mg, 84%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (s, 1 H), 5.94 (s, 1 H), 2.36−2.24 (m, 4 H), 2.20 (s, 3 H), 2.09 (t, J = 7.2 Hz, 2 H), 1.57−1.41 (m, 6 H), 1.38−1.22 (m, 4 H), 1.01−0.84 (m, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.6, 145.2, 141.4, 120.6, 113.9, 109.3, 40.3, 34.1, 31.5, 30.1, 24.7, 22.5, 21.36, 21.34, 14.4, 14.1, 13.9, 11.5; IR (neat, cm^{-1}) 2958, 2929, 2871, 1651, 1623, 1540, 1465, 1378, 1338, 1296, 1211, 1102; MS (m/z) 263 (M^++1, 14.3), 262 (M^+, 76.3), 233 (M-C_2H_5)$^+$, 100); HRMS calcd for $C_{18}H_{30}O$ 262.2297, found 262.2296.

(**11**) **5-Cyclohexylidenemethyl-2-methyl-3-pentylfuran (5hc).** Following method A, the reaction of the first step using CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.4 mg, 0.005 mmol, 2 mol %), **1h** (66.5 mg, 0.25 mmol)/Et_3N (1 mL), and **2c** (58.2 mg, 0.47 mmol, 2 equiv)/DMSO (1 mL) afforded **3hc**. The reaction of the second step using **3hc** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.5 mg, 0.005 mmol, 2 mol %)/AgOTf (1.3 mg, 0.005 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5hc** (48.8 mg, 80%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (s, 1 H), 5.87 (s, 1 H), 2.61−2.54 (m, 2 H), 2.27 (t, J = 7.5 Hz, 2 H), 2.22−2.16 (m, 5 H), 1.64−1.54 (m, 6 H), 1.54−1.42 (m, 2 H), 1.38−1.22 (m, 4 H), 0.88 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.4, 145.3, 141.4, 120.5, 111.2, 109.9, 37.6, 31.4, 30.1, 30.0, 28.6, 27.5, 26.5, 24.7, 22.5, 14.1, 11.5; IR (neat, cm^{-1}) 2927, 2854, 1659, 1624, 1543, 1447, 1378, 1342, 1296, 1233, 1213, 1002; MS (m/z) 247 (M^+ + 1, 18.9), 246 (M^+, 100); HRMS calcd for $C_{17}H_{26}O$ 246.1984, found 246.1986.

(**12**) **5-(2,2-Diphenylvinyl)-2-methyl-3-pentylfuran (5hd).** Following method A, the reaction of the first step using CuI (1.3 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 0.005 mmol, 2 mol %), **1h** (67.3 mg, 0.25 mmol)/Et_3N (1 mL), and **2d** (101.1 mg, 0.49 mmol, 2 equiv)/DMSO (1 mL) afforded **3hd**. The reaction of the second step using **3hd** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.4 mg, 0.005 mmol, 2 mol %)/AgOTf (1.7 mg, 0.007 mmol, 3 mol %)/CH_2Cl_2 (1 mL) afforded **5hd** (60.6 mg, 73%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.35 (m, 3 H), 7.34−7.18 (m, 7 H), 6.89 (s, 1 H), 5.23 (s, 1 H), 2.16−2.09 (m, 5 H), 1.37−1.10 (m, 6 H), 0.86 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.2, 146.6, 141.9, 140.5, 137.9, 129.7, 128.8, 128.2, 127.4, 127.0, 126.6, 121.5, 116.3, 111.5, 31.2, 29.8, 24.5, 22.4, 14.1, 11.5; IR (neat, cm^{-1}) 3057, 2956, 2927, 2856, 1593, 1531, 1491, 1444, 1375, 1277, 1186, 1145, 1073, 1031, 1001; MS (m/z) 331 (M^+ + 1, 26.2), 330 (M^+, 100); HRMS calcd for $C_{24}H_{26}O$ 330.1984, found 330.1974.

(**13**) (*E*)**-2-Methyl-3-pentyl-4-phenyl-5-propenylfuran (*E*-5ae) and (*Z*)-2-methyl-3-pentyl-4-phenyl-5-propenylfuran (*Z*-5ae).** Following method A, the reaction of the first step using CuI (1.3 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 0.005 mmol, 2 mol %), **1a** (83.0 mg, 0.24 mmol)/Et_3N (1 mL), and **2e** (37.3 mg, 0.53 mmol, 2 equiv)/DMSO (1 mL) afforded **3ae**. The reaction of the second step using **3ae** (from the first step)/CH_2Cl_2 (1 mL) and $Au(PPh_3)Cl$ (2.5 mg, 0.005 mmol, 2 mol %)/AgOTf (1.6 mg, 0.007 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded *E*-**5ae** (11.9 mg, 18%, purity: 95%) and *Z*-**5ae** (11.2 mg, 17%). According to ^{1}H NMR analysis of the crude reaction mixture before separation, product *E*-**5ae** was formed in 24% yield together with 25% of the *Z*-**5ae**. *E*-**5ae**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.34 (m, 2 H), 7.32−7.22 (m, 3 H), 6.00 (dq, J = 11.7 and 1.7 Hz, 1 H), 5.53−5.40 (m, 1 H), 2.35−2.26 (m, 5 H), 2.06 (dd, J = 7.5 and 1.7 Hz, 3 H), 1.33−1.10 (m, 6 H), 0.78 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6, 146.7, 134.1, 129.7, 128.2, 126.6, 125.9, 123.5, 119.8, 116.5, 31.4, 29.8, 23.2, 22.3, 15.3, 13.9, 12.0; IR (neat, cm^{-1}) 3030, 2956, 2929, 2858, 1673, 1604, 1491, 1445, 1296, 1005; MS (m/z) 268 (M^+, 34.61), 43 (100); HRMS calcd for $C_{19}H_{24}O$ (M^+) 268.1827, found 268.1828. *Z*-**5ae**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.35 (m, 2 H), 7.33−7.23 (m, 3 H), 6.16−6.10 (m, 2 H), 2.34−2.26 (m, 5 H), 1.82−1.78 (m, 3 H), 1.31−1.08 (m, 6 H), 0.78 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.6, 146.3, 133.9, 129.6, 128.2, 126.6, 123.4, 123.0, 120.2, 118.6, 31.4, 29.7, 23.3, 22.3, 18.4, 14.0, 11.8; IR (neat, cm^{-1}) 3032, 2956, 2929, 2858, 1673, 1604, 1493, 1445, 1377, 1283, 1008; MS (m/z) 268 (M^+, 68.34), 43 (100); HRMS calcd for $C_{19}H_{24}O$ (M^+) 268.1827, found 268.1829.

(14) 2-Methyl-3-pentyl-4-phenyl-5-vinylfuran (5af). Following method A, the reaction of the first step using CuI (1.2 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1a** (85.9 mg, 0.25 mmol)/Et_3N (1 mL), and **2f** (29.5 mg, 0.53 mmol, 2 equiv)/DMSO (1 mL) afforded **3af**. The reaction of the second step using **3af** (from the first step)/CH_2Cl_2 (1 mL), $Au(PPh_3)Cl$ (2.6 mg, 0.005 mmol, 2 mol %)/AgOTf (1.4 mg, 0.005 mmol, 2 mol %)/CH_2Cl_2 (1 mL) afforded **5af** (10.9 mg, 17%): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43−7.35 (m, 2 H), 7.34−7.23 (m, 3 H), 6.41 (dd, J = 17.6 and 11.3 Hz, 1 H), 5.60 (dd, J = 17.4 and 1.8 Hz, 1 H), 5.02 (dd, J = 11.3 and 1.7 Hz, 1 H), 2.35−2.28 (m, 5 H), 1.32−1.08 (m, 6 H), 0.78 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.3, 146.6, 133.5, 129.6, 128.3, 126.9, 125.8, 123.9, 120.5, 110.2, 31.4, 29.7, 23.2, 22.3, 14.0, 11.9; IR (neat, cm^{-1}) 2955, 2929, 2859, 1672, 1605, 1545, 1493, 1445, 1377, 1289, 1266, 1156, 1037; MS (m/z) 254 (M^+, 26.4), 43 (100); HRMS calcd for $C_{18}H_{22}O$ (M^+) 254.1671, found 256.1679.

3. Experimental Details for Method B (Table 3). (1) 2-Methyl-5-(2-methylhexa-2,5-dien-3-yl)-3-pentyl-4-phenylfuran (6aaa). Typical procedure for method B: To a dry Schlenk tube were added CuI (1.5 mg, 0.008 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 0.005 mmol, 2 mol %), **1a** (88.0 mg, 0.26 mmol), Et_3N (1 mL), **2a** (44.8 mg, 0.53 mmol, 2.1 equiv), and DMSO (1 mL). The resulting mixture was then heated at 40−45 °C. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with an aqueous solution of saturated NH_4Cl (5 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layer was washed sequentially with 5% HCl, satd $NaHCO_3$ (aq), and brine and then dried over anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) afforded the product **3aa** in a round-bottom flask. Then DMA (1 mL), **4a** (122.0 mmg, 1.0 mmol, 4.0 equiv), DMA (1 mL), and $PdCl_2$ (2.3 mg, 0.013 mmol, 5 mol %) were added into this flask. The resulting mixture was then heated at 60 °C until complete conversion of **3aa** as monitored by TLC. The reaction mixture was then quenched with an aqueous solution of saturated NH_4Cl (5 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layer was washed sequentially with 5% HCl, satd $NaHCO_3$ (aq), and brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield (87%) was determined by using 1,3,5-trimethylbenzene as the internal standard (14 μL, 0.1 mmol). Chromatography on silica gel (eluent: petroleum ether) afforded the product **6aaa** (67.0 mg, 81%): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−7.26 (m, 2 H), 7.25−7.17 (m, 3 H), 5.82−5.67 (m, 1 H), 5.02−4.88 (m, 2 H), 3.00 (d, J = 6.6 Hz, 2 H), 2.33 (t, J = 7.7 Hz, 2 H), 2.25 (s, 3 H), 1.69 (s, 3 H), 1.37 (s, 3 H), 1.35−1.10 (m, 6 H), 0.79 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.4, 145.8, 136.2, 135.2, 134.5, 129.0, 128.1, 126.1, 123.8, 122.5, 119.1, 114.7, 36.6, 31.5, 29.9, 23.5, 22.7, 22.3, 20.2, 14.0, 11.9; IR (neat, cm^{-1}) 3077, 3031, 2956, 2928, 2858, 1637, 1605, 1566, 1492, 1445, 1378, 1255, 1225, 1175, 1128, 1044, 1026; MS (m/z) 323 (M^+ + 1, 24.7), 322 (M^+, 100); HRMS calcd for $C_{23}H_{30}O$ 322.2291, found 322.2302.

(2) 2-Methyl-5-(2-methylhexa-2,5-dien-3-yl)-3-pentyl-4-phenylfuran (6aaa). Following method B, the reaction of the first step using CuI (11.5 mg, 0.061 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (42.0 mg, 0.060 mmol, 2 mol %), **1a** (1035.3 mg, 3.0 mmol)/Et_3N (12 mL), and **2a** (501.3 mg, 6.0 mmol, 2 equiv)/DMSO (12 mL) afforded **3aa**. The reaction of the second step using **3aa** (from the first step)/DMA (12 mL), **4a** (1447.2 mg, 12.0 mmol, 4.0 equiv)/DMA(12 mL), and $PdCl_2$ (21.4 mg, 0.12 mmol, 5 mol %) afforded **6aaa** (694.8 mg, 72%). The data of the compound are the same as those listed above.

(3) 4-Butyl-3-hexyl-2-(2-methylhexa-2,5-dien-3-yl)furan (6baa). Following method B, the reaction of the first step using CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1b** (80.1 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.5 mg, 0.51 mmol, 2 equiv)/DMSO (1 mL) afforded **3ba**. The reaction of the second step using **3ba** (from the first step)/DMA (1 mL), **4a** (121.7 mg, 1.0 mmol, 4.0 equiv)/DMA (1 mL), and $PdCl_2$ (1.7 mg, 0.01 mmol, 4 mol %) afforded **6baa** (48.7 mg, 65%): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 1 H), 5.80−5.65 (m, 1 H), 5.03−4.88 (m, 2 H), 3.04 (d, J = 6.3 Hz, 2 H), 2.35 (td, J = 7.8 and 1.2 Hz, 2 H), 2.25−2.17 (m, 2 H), 1.81 (s, 3 H), 1.63 (s, 3 H), 1.60−1.48 (m, 2 H), 1.46−1.34 (m, 4 H), 1.30−1.22 (m, 6 H), 0.94 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.7, 136.8, 136.1, 135.2, 125.7, 123.1, 120.5, 114.5, 36.8, 31.7, 31.3, 29.6, 29.5, 24.2, 23.9, 22.72, 22.69, 22.6, 22.0, 14.1, 14.0; IR (neat, cm^{-1}) 3076, 2956, 2927, 2858, 1637, 1549, 1458, 1378, 1278, 1261, 1218, 1137, 1100, 1038; MS (m/z) 303 (M^+ + 1, 19.8), 302 (M^+, 83.1), 259 (100); HRMS calcd for $C_{21}H_{34}O$ 302.2610, found 302.2609.

(4) 5-(2-Methylhexa-2,5-dien-3-yl)-2-(*p*-methylphenyl)-3-pentylfuran (6caa). Following method B, the reaction of the first step using CuI (1.5 mg, 0.008 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1c** (86.0 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.1 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3ca**. The reaction of the second step using **3ca** (from the first step)/DMA (1 mL), **4a** (124.1 mg, 1.0 mmol, 4.1 equiv)/DMA (1 mL), and $PdCl_2$ (2.0 mg, 0.011 mmol, 5 mol %) afforded **6caa** (57.8 mg, 72%): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 2 H), 7.19 (d, J = 7.8 Hz, 2 H), 6.18 (s, 1 H), 5.93−5.77 (m, 1 H), 5.12−4.93 (m, 2 H), 3.20 (d, J = 5.7 Hz, 2 H), 2.63 (t, J = 7.7 Hz, 2 H), 2.35 (s, 3 H), 2.07 (s, 3 H), 1.87 (s, 3 H), 1.70−1.56 (m, 2 H), 1.44−1.26 (m, 4 H), 1.00−0.90 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.0, 146.3, 136.3, 136.0, 131.8, 129.3, 129.1, 125.1, 122.3, 122.0, 114.6, 112.0, 35.5, 31.8, 29.6, 26.0, 23.1, 22.5, 21.9, 21.2, 14.1; IR (neat, cm^{-1}) 2955, 2927, 2859, 1637, 1524, 1501, 1454, 1377, 1184, 1109, 1037; MS (m/z) 323 (M^+ + 1, 24.2), 322 (M^+, 100); HRMS calcd for $C_{23}H_{30}O$ 322.2297, found 322.2299.

(5) 3-Isopropyl-2-methyl-5-(2-methylhexa-2,5-dien-3-yl)-4-phenylfuran (6daa). Following method B, the reaction of the first step using CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 2 mol %), **1d** (78.6 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.3 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3da**. The reaction of the second step using **3da** (from the first step)/DMA (1 mL), **4a** (123.1 mg, 1.0 mmol, 4.1 equiv)/DMA (1 mL), and $PdCl_2$ (1.9 mg, 0.011 mmol, 4 mol %) afforded **6daa** (45.5 mg, 62%): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.27 (m, 2 H), 7.26−7.21 (m, 1 H), 7.20−7.14 (m, 2 H), 5.80−5.65 (m, 1 H), 5.00−4.85 (m, 2 H), 2.96 (d, J = 6.6 Hz, 2 H), 2.76 (septet, J = 7.1 Hz, 1 H), 2.33 (s, 3 H), 1.66 (s, 3 H), 1.37 (s, 3 H), 1.15 (d, J = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.0, 144.6, 136.2, 135.2, 134.6, 129.9, 127.9, 126.2, 124.6, 123.9, 122.4, 114.6, 36.6, 24.0, 22.8, 22.7, 20.2, 13.4; IR (neat, cm^{-1}) 3077, 3029, 2961, 2927, 2872, 1637, 1604, 1561, 1491, 1444, 1363, 1255, 1214, 1185, 1163, 1127, 1109, 1073, 1037, 1021; MS (m/z) 295 (M^+ + 1, 21.6), 294 (M^+, 100); HRMS calcd for $C_{21}H_{26}O$ 294.1984, found 294.1983.

(6) 4-Hexyl-2-methyl-5-(2-methylhexa-2,5-dien-3-yl)-3-phenylfuran (6eaa). Following method B, the reaction of the first step using CuI (1.3 mg, 0.007 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 2 mol %), **1e** (90.1 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (43.4 mg, 0.52 mmol, 2 equiv)/DMSO (1 mL) afforded **3ea**. The reaction of the second step using **3ea** (from the first step)/DMA (1 mL), **4a** (126.1 mg, 1.0 mmol, 4.2 equiv)/DMA (1 mL), and $PdCl_2$ (1.7 mg, 0.01 mmol, 4 mol %) afforded **6eaa** (65.1 mg, 77%) (petroleum ether/ethyl acetate = 200 mL/6 drops): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.33 (m, 2 H), 7.30−7.22 (m, 3 H), 5.86−5.70 (m, 1 H), 5.07−4.90 (m, 2 H), 3.11 (d, J = 6.3 Hz, 2 H), 2.30−2.22 (m, 5 H), 1.83 (s, 3 H), 1.73 (s, 3 H), 1.18−1.00 (m, 8 H), 0.78 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.5, 146.2, 136.1, 135.1, 134.8, 129.2, 128.2, 126.2, 122.9, 122.0, 120.8, 114.5, 36.8, 31.4, 29.2, 28.9,

24.4, 22.8, 22.4, 20.1, 14.0, 12.3; IR (neat, cm^{-1}) 3078, 3057, 3031, 2954, 2925, 2857, 1637, 1602, 1574, 1495, 1443, 1377, 1246, 1112, 1070, 1018; MS (*m*/*z*) 337 ($M^+ + 1$, 22.8), 336 (M^+, 71.8), 293 (100); HRMS calcd for $C_{24}H_{32}O$ 336.2448, found 336.2443.

(**7**) **2-Methyl-3-(methoxylpheyl)-5-(2-methylhexa-2,5-dien-3-yl)-4-phenylfuran (6faa).** Following method B, the reaction of the first step using CuI (1.1 mg, 0.006 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1f** (95.8 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (41.7 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3fa**. The reaction of the second step using **3fa** (from the first step)/DMA (1 mL), **4a** (121.7 mg, 1.0 mmol, 4.0 equiv)/DMA (1 mL), and $PdCl_2$ (1.7 mg, 0.01 mmol, 4 mol %) afforded **6faa** (57.7 mg, 64%) (petroleum ether/ethyl acetate = 100/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21−7.10 (m, 3 H), 7.04−6.97 (m, 4 H), 6.84−6.78 (m, 2 H), 5.88−5.74 (m, 1 H), 5.06−4.93 (m, 2 H), 3.79 (s, 3 H), 3.05 (d, J = 6.6 Hz, 2 H), 2.33 (s, 3 H), 1.74 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.9, 149.1, 146.6, 136.1, 135.4, 134.1, 130.8, 129.3, 127.8, 125.90, 125.87, 122.7, 122.3, 114.9, 113.4, 55.1, 36.6, 22.7, 20.3, 12.5; IR (neat, cm^{-1}) 3034, 2919, 2854, 1636, 1603, 1574, 1511, 1444, 1374, 1329, 1287, 1245, 1175, 1107, 1072, 1042, 1021, 1006; MS (*m*/*z*) 359 ($M^+ + 1$, 27.4), 358 (M^+, 100); HRMS calcd for $C_{25}H_{26}O_2$ 358.1933, found 358.1925.

(**8**) **3-Butyl-4-hexyl-2-methyl-5-(2-methylhexa-2,5-dien-3-yl)-furan (6gaa).** Following method B, the reaction of the first step using CuI (1.1 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1g** (84.3 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.1 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3ga**. The reaction of the second step using **3ga** (from the first step)/DMA (1 mL), **4a** (123.2 mg, 1.1 mmol, 4.2 equiv)/DMA (1 mL), and $PdCl_2$ (2.3 mg, 0.01 mmol, 5 mol %) afforded **6faa** (60.1 mg, 76%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.65 (m, 1 H), 5.03−4.87 (m, 2 H), 3.04 (d, J = 6.6 Hz, 2 H), 2.28 (t, J = 7.7 Hz, 2 H), 2.20−2.12 (m, 5 H), 1.80 (s, 3 H), 1.65 (s, 3 H), 1.49−1.20 (m, 12 H), 0.96−0.84 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.7, 145.2, 136.3, 134.4, 123.4, 121.2, 119.3, 114.3, 36.9, 32.7, 31.7, 29.8, 29.6, 24.5, 23.7, 22.8, 22.6, 20.0, 14.1, 14.0, 11.8; IR (neat, cm^{-1}) 2956, 2928, 2858, 2729, 1637, 1575, 1456, 1378, 1246, 1211, 1115; MS (*m*/*z*) 317 (M^++1, 19.9), 316 (M^+, 85.7), 273 (100); HRMS calcd for $C_{22}H_{36}O$ 316.2761, found 316.2767.

(**9**) **2-Methyl-5-(2-methylhexa-2,5-dien-3-yl)-3-pentylfuran (6haa).** Following method B, the reaction of the first step using CuI (1.4 mg, 0.007 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (4.0 mg, 0.006 mmol, 2 mol %), **1h** (67.7 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (45.3 mg, 0.54 mmol, 2 equiv)/DMSO (1 mL) afforded **3ha**. The reaction of the second step using **3ha** (from the first step)/DMA (1 mL), **4a** (127.4 mg, 1.1 mmol, 4.2 equiv)/DMA (1 mL), and $PdCl_2$ (2.4 mg, 0.014 mmol, 5 mol %) afforded **6haa** (42.5 mg, 68%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98 (s, 1 H), 5.88−5.73 (m, 1 H), 5.06−4.90 (m, 2 H), 3.13 (d, J = 6.0 Hz, 2 H), 2.28 (t, J = 7.7 Hz, 2 H), 2.19 (s, 3 H), 1.96 (s, 3 H), 1.82 (s, 3 H), 1.56−1.40 (m, 2 H), 1.39−1.20 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.1, 144.9, 136.4, 130.7, 122.3, 120.1, 114.3, 110.1, 35.5, 31.5, 30.1, 24.8, 22.9, 22.5, 21.6, 14.1, 11.5; IR (neat, cm^{-1}) 2957, 2927, 2857, 1637, 1456, 1377, 1215, 1128, 1034; MS (*m*/*z*) 247 ($M^+ + 1$, 19.1), 246 (M^+, 100); HRMS calcd for $C_{17}H_{26}O$ 246.1978, found 246.1981.

(**10**) **2-Methyl-3-pentyl-5-(5-propylocta-1,4-dien-4-yl)furan (6hba).** Following method B, the reaction of the first step using CuI (1.4 mg, 0.007 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1h** (68.2 mg, 0.25 mmol)/Et_3N (1 mL), and **2b** (71.2 mg, 0.51 mmol, 2 equiv)/DMSO (1 mL) afforded **3hb**. The reaction of the second step using **3hb** (from the first step)/DMA (1 mL), **4a** (126.4 mg, 1.0 mmol, 4.2 equiv)/DMA (1 mL), and $PdCl_2$ (2.1 mg, 0.012 mmol, 5 mol %) afforded **6hba** (47.2 mg, 61%) (chromatography twice on silica gel): liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (s, 1 H), 5.87−5.76 (m, 1 H), 5.03 (dq, J = 16.8 and 1.7 Hz, 1 H), 4.95 (dq, J = 10.0 and 1.6 Hz, 1 H), 3.12 (d, J = 5.6 Hz, 2 H), 2.33−2.25 (m, 4 H), 2.21 (s, 3 H), 2.14−2.09 (m, 2 H), 1.56−1.42 (m, 6 H), 1.39−1.26 (m, 4 H), 0.96 (t, J = 7.2 Hz, 6 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 145.0, 140.1, 137.1, 122.4, 120.0, 114.4, 109.6, 35.9, 35.25, 35.19, 31.5, 30.1, 24.8, 22.5, 22.4, 22.0, 14.5, 14.4, 14.1, 11.5; IR (neat, cm^{-1}) 3077, 2958, 2928, 2870, 1637, 1466, 1377, 1210, 1132, 1078; MS (*m*/*z*) 303 ($M^+ + 1$, 21.3), 302 (M^+, 92.9), 273 (100); HRMS calcd for $C_{21}H_{34}O$ 302.2604, found 302.2604.

(**11**) **5-(1-Cyclohexylidenebut-3-en-1-yl)-2-methyl-3-pentylfuran (6hca).** Following method B, the reaction of the first step using CuI (1.5 mg, 0.008 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1h** (66.8 mg, 0.25 mmol)/Et_3N (1 mL), and **2c** (61.3 mg, 0.49 mmol, 2 equiv)/DMSO (1 mL) afforded **3hc**. The reaction of the second step using **3hc** (from the first step)/DMA (1 mL), **4a** (122.1 mg, 1.0 mmol, 4.0 equiv)/DMA (1 mL), and $PdCl_2$ (1.9 mg, 0.01 mmol, 4 mol %) afforded **6hca** (50.8 mg, 71%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (s, 1 H), 5.87−5.72 (m, 1 H), 5.01 (dq, J = 16.8 and 1.8 Hz, 1 H), 4.93 (dq, J = 10.2 and 1.7 Hz, 1 H), 3.11 (d, J = 6.0 Hz, 2 H), 2.50−2.41 (m, 2 H), 2.32−2.20 (m, 4 H), 2.19 (s, 3 H), 1.62−1.43 (m, 8 H), 1.38−1.22 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.9, 145.0, 140.1, 136.8, 119.9, 119.4, 114.3, 110.0, 35.3, 32.2, 31.5, 31.3, 30.1, 28.3, 28.2, 26.8, 24.8, 22.5, 14.1, 11.6; IR (neat, cm^{-1}) 2926, 2854, 1637, 1552, 1448, 1377, 1216; MS (*m*/*z*) 287 ($M^+ + 1$, 21.4), 286 (M^+, 100); HRMS calcd for $C_{20}H_{30}O$ 286.2291, found 286.2294.

(**12**) **5-(1,1-Diphenylpenta-1,4-dien-2-yl)-2-methyl-3-pentylfuran (6hda).** Following method B, the reaction of the first step using CuI (1.1 mg, 0.006 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol, 2 mol %), **1h** (66.3 mg, 0.25 mmol)/Et_3N (1 mL), and **2d** (103.6 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3hb**. The reaction of the second step using **3hb** (from the first step)/DMA (1 mL), **4a** (122.1 mg, 1.0 mmol, 4.0 equiv)/DMA (1 mL), and $PdCl_2$ (1.8 mg, 0.01 mmol, 4 mol %) afforded **6hda** (50.3 mg, 55%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.16 (m, 8 H), 7.13−7.08 (m, 2 H), 6.00−5.84 (m, 1 H), 5.52 (s, 1 H), 5.08−4.97 (m, 2 H), 3.23 (d, J = 6.0 Hz, 2 H), 2.14 (t, J = 7.2 Hz, 2 H), 2.02 (s, 3 H), 1.38−1.08 (m, 6 H), 0.86 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.0, 145.7, 144.0, 142.9, 138.7, 137.3, 129.6, 129.4, 127.94, 127.91, 126.9, 126.7, 126.4, 120.7, 115.3, 112.6, 36.4, 31.2, 29.8, 24.5, 22.5, 14.1, 11.4; IR (neat, cm^{-1}) 3077, 3057, 3019, 2956, 2927, 2856, 1637, 1598, 1530, 1490, 1442, 1377, 1270, 1204, 1139, 1074, 1030; MS (*m*/*z*) 371 ($M^+ + 1$, 22.2), 370 (M^+, 75.5), 329 (($M^+ - C_3H_5$), 100); HRMS calcd for $C_{27}H_{30}O$: 370.2291, found 370.2283.

(**13**) **5-(2,2-Dimethylhexa-2,5-dien-3-yl)-2-methyl-3-pentyl-4-phenylfuran (6aab).** Following method B, the reaction of the first step using CuI (1.0 mg, 0.005 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol, 2 mol %), **1a** (86.5 mg, 0.25 mmol)/Et_3N (1 mL), and **2a** (42.0 mg, 0.50 mmol, 2 equiv)/DMSO (1 mL) afforded **3aa**. The reaction of the second step using **3aa** (from the first step)/DMA (1 mL), **4b** (132.0 mg, 1.0 mmol, 3.9 equiv)/DMA (1 mL), and $PdCl_2$ (1.7 mg, 0.01 mmol, 4 mol %) afforded **6aab** (53.3 mg, 63%): liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.26 (m, 2 H), 7.25−7.16 (m, 3 H), 4.66 (s, 1 H), 4.60 (s, 1 H), 2.89 (s, 2 H), 2.31 (t, J = 7.5 Hz, 2 H), 2.25 (s, 3 H), 1.70 (s, 3 H), 1.62 (s, 3 H), 1.45 (s, 3 H), 1.38−1.08 (m, 6 H), 0.78 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100z) δ 148.6, 145.5, 143.8, 135.3, 135.1, 129.1, 128.0, 126.1, 123.6, 122.8, 119.2, 110.8, 40.0, 31.4, 29.8, 23.5, 22.8, 22.6, 22.3, 20.6, 14.0, 11.9; IR (neat, cm^{-1}) 3075, 3030, 2956, 2928, 2858, 1651, 1606, 1564, 1491, 1445, 1373, 1253, 1225, 1170, 1089, 1070, 1051, 1028; MS (*m*/*z*) 337 ($M^+ + 1$, 26.1), 336 (M^+, 100); HRMS calcd for $C_{24}H_{32}O$ 336.2453, found 336.2456.

(**14**) (*E*)-**(2-Methyl-5-(penta-2,4-dien-2-yl)-3-pentyl-4-phenylfuran (7afa).** Following method B, the reaction of the first step

using CuI (1.2 mg, 0.006 mmol, 3 mol %), $Pd(PPh_3)_2Cl_2$ (3.4 mg, 0.005 mmol, 2 mol %), 1a (83.7 mg, 0.24 mmol)/Et_3N (1 mL), and **2f** (28.8 mg, 0.51 mmol, 2 equiv)/DMSO (1 mL) afforded **3af**. The reaction of the second step using **3af** (from the first step)/DMA (1 mL), **4a** (121.7 mg, 1.0 mmol, 4.0 equiv)/DMA (1 mL), and $PdCl_2$ (2.2 mg, 0.01 mmol, 5 mol %) afforded **5af** (12.8 mg, 21%) and **7afa** (6.2 mg, 9%). According to ^{1}H NMR analysis of the crude reaction mixture before separation, product **7afa** was formed in 11% yield together with 23% of the **5af**. **7afa**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.29 (m, 3 H), 7.25−7.20 (m, 2 H), 6.69−6.55 (m, 1 H), 6.48−6.40 (m, 1 H), 5.18−5.02 (m, 2 H), 2.28 (s, 3 H), 2.16 (t, J = 7.4 Hz, 2 H), 1.71 (d, J = 1.2 Hz, 3 H), 1.26−1.06 (m, 6 H), 0.77 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.1, 146.1, 135.1, 132.9, 130.1, 128.0, 127.3, 126.9, 125.3, 125.0, 122.0, 116.7, 31.3, 29.8, 23.2, 22.2, 14.4, 13.9, 11.9; IR (neat, cm^{-1}) 2956, 2928, 2858, 1655, 1606, 1489, 1444, 1378, 1249, 1071; MS (m/z) 294 (M^+, 100); HRMS calcd for $C_{21}H_{26}O$ 294.1984, found 294.1981.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all compounds and an ORTEP drawing of **5fa**. This material is available free of charge via the Internet at http://pubs.acs.org.