Pd^0-Catalyzed Coupling Cyclization Reaction of Aryl or 1-Alkenyl Halides with 1,2-Allenyl Ketones: Scope and Mechanism. An Efficient Assembly of 2,3,4-, 2,3,5-Tri- and 2,3,4,5-Tetrasubstituted Furans

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Abstract: Described herein is the Pd^0-catalyzed coupling cyclization reaction of 1,2-allenyl ketones with organic halides leading efficiently and conveniently to not only 2,3,4- and 2,3,5-trisubstituted furans but also 2,3,4,5-tetrasubstituted furans. Furthermore, this method showed high substituent-loading capability and tolerance of various substituents. The reactions of 1,2-allenyl ketones **1e, 1p, 1q**, and deuterated [D]**1c** were performed for a mechanistic study, which demonstrated that instead of an enolization pathway, the reaction may proceed via the intermediacy of dienolate palladium and intramolecular nucleophilic attack on the π-allyl palladium intermediate by the carbonyl oxygen.

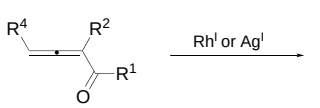
Keywords: allenes · C–C coupling · cyclization · ketones · palladium

Introduction

Furans, one of the most prominent classes of heterocyclic compounds, can be found in many naturally occurring products,[1] commercially important pharmaceuticals, and compounds with flavor and fragrance.[2] They are also considered as important synthetic intermediates for the preparation of numerous cyclic and acyclic compounds.[3] Usually, 2,3,4-, 2,3,5-trisubstituted and 2,3,4,5-tetrasubstituted furans were synthesized from either derivatization of simple furans[4] or cyclization of acyclic precursors.[5–10] Due to furans' potentials and diversity, it is desirable to develop a general methodology for their synthesis from acyclic precursors.

Marshall and co-workers reported the Rh^I- or Ag^I-catalyzed cycloisomerization of 1,2-dienyl ketones to afford substituted furans [Eq. (1)].[11] They also demonstrated the application of this reaction to the synthesis of the enantiomers of natural products such as furanocembrane rubifolide[12a] and kallolide B.[12b]

Recently, Hashmi and co-workers reported the Pd^{II}-catalyzed dimerization of terminal 1,2-allenyl ketones to afford 2,4-disubstituted furans [Eq. (2)][13] and the Au^{III}-catalyzed reaction of terminal 1,2-allenyl ketones with α,β-unsaturated ketones to afford 2,5-disubstituted furans [Eq. (3)].[14]



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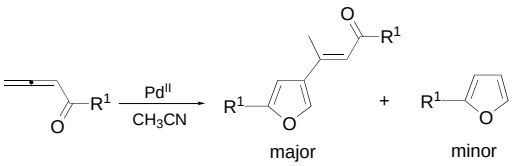

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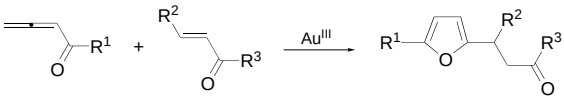

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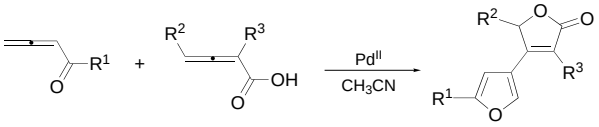
Quite recently, we developed a Pd^{II}-catalyzed cross-coupling reaction of terminal 1,2-alleny ketones with 1,2-allenic acids to afford 2,4-disubstituted furans [Eq. (4)].[15]



(4)

In spite of the excellence of Marshall's, Hashmi's, and our reactions in terms of efficiency, there is still an obvious limitation in terms of the introduction of four substituents to furans. To our knowledge, the introduction of substituents at the 3- and/or 4-position of the corresponding unsubstituted

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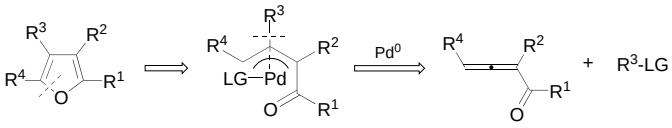
furans is difficult; thus, efficient and general methodologies for the synthesis of furans with substituents at some or all of the four positions are still of current interest.

During the course of our study on the cross-coupling cyclization reaction of functionalized allenes,[16] we noted that, due to the high substituent-loading capability and easy availability of 1,2-allenyl ketones, it would be possible to develop a general methodology for the synthesis of differently substituted furans from their coupling reaction with organic compounds containing an appropriate leaving group (Scheme 1).[17]

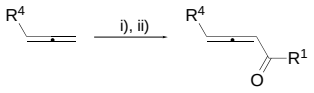


Scheme 1. Retrosynthetic analysis of polysubstituted furans.

In a previous communication,[18] we reported a palladium-catalyzed cyclization of 1,2-allenyl ketone with an organic halide to provide an efficient, general, and versatile route to polysubstituted furans with a unique assembly of substituents at the different positions of furans depending on the substitution style of both reactants. In this paper, we wish to discuss in detail the scope and mechanism of this reaction.

Results and Discussion

Synthesis of the starting 1,2-allenyl ketones: γ-Substituted 1,2-allenyl ketones **1a–e** were prepared by the treatment of 1,2-allenyl lithium (prepared by the reaction of 1,2-allene and *n*BuLi at $-50\,^{\circ}C$ for 2 h) with *N*,*N*-dimethyl organic amide at $-78\,^{\circ}C$ in THF (Scheme 2).[19] 1,2-Allenyl ketones **1f–g** were prepared by the reaction of phenyl acetyl chloride with the corresponding ylide (Scheme 3).[20]

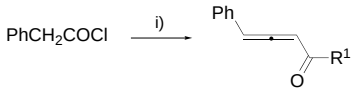


1a: $R^1 = CH_3$, $R^4 = nC_{12}H_{25}$, 40%
1b: $R^1 = CH_3$, $R^4 = nC_4H_9$, 50%
1c: $R^1 = CH_3$, $R^4 = nC_7H_{15}$, 44%
1d: R^1 = cyclohexyl, $R^4 = nC_7H_{15}$, 37%
1e: $R^1 = tC_4H_9$, $R^4 = nC_7H_{15}$, 35%

Scheme 2. Synthesis of 1,2-allenyl ketones **1a–e**. i) *n*BuLi, $-50\,^{\circ}C$, THF, 2 h; ii) R^1CONMe_2, $-78\,^{\circ}C$, THF.

Abstract in Chinese:

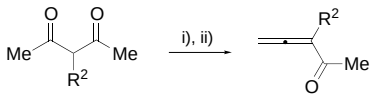
Abstract in Chinese: 通过 1，2－联烯酮与有机卤化物在钯催化下的偶联环化反应，本文发展了一种方便有效地合成 2，3，4－，2，3，5－三取代和 2，3，4，5－四取代呋喃化合物的方法。同时，该方法还具有很强的取代基装载能力和容忍度。另外通过对 1，2－联烯基酮 **1e**, **1p**, **1q** 和氘代的[D]**1c** 偶联环化反应的研究，对反应的机理有了进一步的了解。研究表明该反应可能是通过共轭二烯醇钯中间体或羰基氧进攻 π－烯丙基钯中间体进行的。



1f: $R^1 = CH_3$, 30%
1g: $R^1 = nC_3H_7$, 35%

Scheme 3. Synthesis of 1,2-allenyl ketones **1f** and **g**. i) $Ph_3P{=}CHCOR^1$, Et_3N, 0–5 °C, CH_2Cl_2.

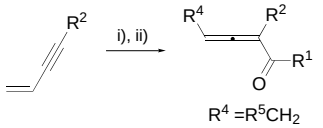
The α-substituted 1,2-allenyl ketones **1h–j** were prepared by the treatment of 3-substituted 2,4-pentadione with Ph_3PBr_2 followed by elimination of HBr in the presence of Et_3N (Scheme 4).[19]



1h: $R^2 = CH_3$, 50%
1i: $R^2 = nC_4H_9$, 76%
1j: R^2 = allyl, 60%

Scheme 4. Synthesis of 1,2-allenyl ketones **1h–j**. i) Ph_3PBr_2, CH_2Cl_2, reflux; ii) Et_3N, CH_3CN, 80 °C.

The α,γ-disubstituted 1,2-allenyl ketones **1k–p** were prepared by a one-pot stepwise reaction of an enyne with an alkyl lithium reagent followed by the addition of an *N*,*N*-dimethyl organic amide (Scheme 5).



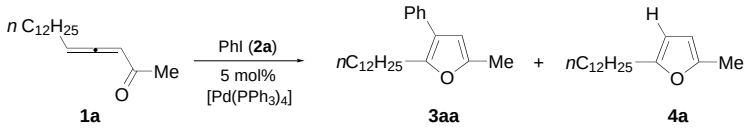
1k: $R^1 = CH_3$, $R^2 = nC_4H_9$, $R^4 = nC_5H_{11}$, 51%
1l: $R^1 = CH_3$, $R^2 = nC_5H_{11}$, $R^4 = nC_4H_9$, 66%
1m: $R^1 = CH_3$, $R^2 = nC_5H_{11}$, $R^4 = nC_5H_{11}$, 57%
1n: $R^1 = iC_3H_7$, $R^2 = nC_5H_{11}$, $R^4 = nC_4H_9$, 70%
1o: $R^1 = CH_3$, $R^2 = nC_5H_{11}$, $R^4 = CH_3CH_2CH(CH_3)CH_2$, 61%
1p: $R^1 = p\text{-}MeC_6H_4$, $R^2 = nC_4H_9$, $R^4 = nC_5H_{11}$, 74%
1q: $R^1 = p\text{-}CF_3C_6H_4$, $R^2 = nC_4H_9$, $R^4 = nC_5H_{11}$, 75%

Scheme 5. Synthesis of α,γ-disubstituted 1,2-allenyl ketones **1k–p**. i) R^5Li, -40 to 15 °C; ii) R^1CONMe_2, $-78\,^{\circ}C$.

Coupling cyclization of 1,2-allenyl ketones and organic halides

Synthesis of 2,3,5-trisubstituted furans: As a starting point, we studied the Pd^0-catalyzed cyclization reaction of heptadeca-3,4-dien-2-one **1a** with iodobenzene **2a** under different reaction conditions, the results are summarized in Table 1. From Table 1, it is clear that the major side reaction is the cycloisomerization of **1a** to afford 2-methyl-5-dodecanylfuran **4a**. Fortunately, after some screening, we found that the $Pd(PPh_3)_4$-catalyzed cyclization reaction of **1a** with PhI could afford the expected two-component coupling cyclization product **3aa** in 88% yield together with the formation of **4a** in only 8% yield by using toluene as the solvent, Et_3N-

Table 1. $Pd(PPh_3)_4$-catalyzed cyclization of heptadeca-3,4-dien-2-one with iodobenzene.



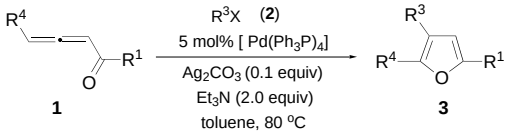
1a 3aa 4a

	PhI (equiv.)	Solvent	Base (equiv)	T [°C]	t [h]	**3aa** [%][a]	**4a** [%]
1	1.5	MeCN	Et_3N (1.5)[b]	60	15	(29)	(9)
2	1.5	THF	Et_3N (1.5)	reflux	10	54	15
3	1.2	THF	K_2CO_3 (1)	reflux	11	38	33
4	2.0	PhMe	Et_3N (1.5)	100	12	53	42
5	2.0	PhMe	iPr_2NEt (1.5)	100	12	30	67
6	2.0	MeCN	K_2CO_3 (1)[b]	80	15	33	28
7	2.0	DMF	Et_3N (2.0)[b]	80	15	39	35
8	2.0	THF	Et_3N (2.0)	reflux	12	83	15
9[c]	2.0	PhMe	Et_3N (2.0)[b]	80	12	88(75)	9

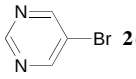
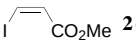
[a] NMR yield determined by using CH_2Br_2 as the internal standard. The numbers in the parenthesis are isolated yield. [b] 0.1 equivalent of Ag_2CO_3 was added. [c] Conditions A.

Ag_2CO_3 (2.0 equiv, 10 mol%) as the base (conditions A; entry 9, Table 1). By using the standard conditions A, the cyclization reaction of various 1,2-allenyl ketones bearing different R^1 and R^4 substituents with different kinds of organic halides **2** were studied. The results are summarized in Table 2.

Table 2. Efficient synthesis of 2,3,5-trisubstituted furans.[a]



1 3

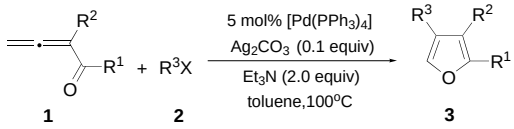
	R^1	**1** R^4	**2**	t [h]	**3** [%]
1	CH_3	$nC_{12}H_{25}$ (**1a**)	PhI (**2a**)	12	**3aa** (75)[b]
2		**1a**	p-$O_2NC_6H_4I$ (**2b**)	13	**3ab** (90)
3		**1a**	p-$MeO_2CC_6H_4I$ (**2c**)	14	**3ac** (94)[c]
4	CH_3	nC_4H_9 (**1b**)	**2a**	12	**3ba** (73)[b]
5		**1b**	**2b**	9	**3bb** (92)
6		**1b**	**2c**	9	**3bc** (85)
7		**1b**	 **2d**	11	**3bd** (71)
8		**1b**	 **2e**	11	**3be** (61)[d]
9		**1b**	p-$MeOC_6H_4I$ (**2f**)	10	**3bf** (64)
10	CH_3	nC_7H_{15} (**1c**)	**2c**	10	**3cc** (98)[c]
11		**1c**	**2f**	12	**3cf** (63)
12	cC_6H_{11}	nC_7H_{15} (**1d**)	**2a**	13	**3da** (74)
13		**1d**	**2c**	16	**3dc** (76)
14	CH_3	Ph (**1f**)	**2b**	10	**3fb** (51)
15		**1f**	**2c**	10	**3fc** (51)
16	nC_3H_7	Ph (**1g**)	**2b**	12	**3gb** (77)
17		1g	**2c**	12	**3gc** (73)

[a] Unless otherwise specified, the reaction was carried out by using 1,2-allenyl ketone (1.5 equiv), organic halide (1.0 equiv) under conditions A. [b] Two equivalents of organic halides were used. [c] Two equivalents of 1,2-allenyl ketone were used. [d] The conformation of the C=C bond was E as determined by the coupling constant between the olefinic protons (J = 15.6 Hz).

These results show that i) both aryl halides and methyl (Z)-3-iodopropenoate afforded the expected 2,3,5-trisubstituted furans **3** in moderate to excellent yields and ii) different substituents such as aryl and alkyl group could be introduced to the 2,3,5-positions of furans, depending on the structures of the 1,2-alleny ketones and organic halides.

Synthesis of 2,3,4-trisubstituted furans: After studying the Pd^0-catalyzed cyclization reaction of γ-substituted 1,2-allenyl ketones, we tried the cyclization reaction of α-substituted 1,2-allenyl ketones. As expected, the reaction occurred smoothly under conditions A giving air-sensitive[21] 2,3,4-trisubstituted furans in moderate to excellent yields (entries 1–4, Table 2). One thing that should be noted is that the allyl group in the α-position of allenyl ketones has no influence on the reaction; this showed that the reaction is highly chemoselective (entry 4, Table 3).

Table 3. Efficient synthesis of 2,3,4-trisubstituted furans.[a]



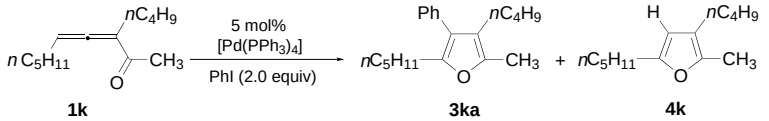
1 2 3

	1 R^1	R^2	**2**	t [h]	**3** [%]
1	Me	Me (**1h**)	**2b**	11	**3hb** (79)[b]
2		**1h**	**2c**	14	**3hc** (68)
3	Me	nC_4H_9 (**1i**)	**2d**	17	**3id** (97)
4	Me	allyl (**1j**)	**2b**	12	**3jb** (79)

[a] Unless otherwise specified, the reaction was carried out by using allenyl ketone (1.5 equiv) and organic halide (1.0 equiv) under conditions A. [b] Two equivalents of 1,2-allenyl ketone were used.

Synthesis of 2,3,4,5-tetrasubstituted furans: With the encouragement of the above results, we were very interested in the cyclization reaction of α,γ-disubstituted 1,2-allenyl ketones, since 2,3,4,5-tetrasubstituted furans[22] would be provided if the reaction succeeded. Under conditions A, we found the reaction did occur to afford the corresponding product **3ka** in 70% yield. However, the cycloisomerization product **4k** was also formed in 30% yield; this indicates that conditions A for the cross-coupling cyclization reaction of α or γ-substituted 1,2-allenyl ketones are not yet efficient enough for the highly selective coupling cyclization of α,γ-disubstituted 1,2-allenyl ketones (entry 1, Table 4). Fortunately, after several trials, we found that the Pd^0-catalyzed cyclization reaction of 1,2-allenyl ketone **1k** with PhI (**2a**) afforded the cross-coupling cyclization product **3ka** in 92% yield and the cycloisomerization product **4k** in only 8% yield using K_2CO_3 as the base and

Table 4. $Pd(PPh_3)_4$-catalyzed cyclization of 1,2-allenyl ketone **1k** with iodobenzene.



1k **3ka** **4k**

	Solvent	Base (equiv)	T [°C]	t [h]	**3ka**[a] [%]	**4k**[a] [%]
1[b]	toluene	Et_3N(2.0)	100	18	70 (57)	30 (11)
2	DME	as above	reflux	10.5	87	13
3	dioxane	as above	100	10.5	77	8
4	DMF	as above	100	10.5	90	9
5	CH_3CN	as above	reflux	14	88	11
6	DMA	as above	100	14	80	10
7	DMA	K_2CO_3(2)	100	14	92	8
8[c]	DMA	K_2CO_3(2)	100	10	90 (72)	0
9[d]	DMA	K_2CO_3(2)	100	19	29	1.3

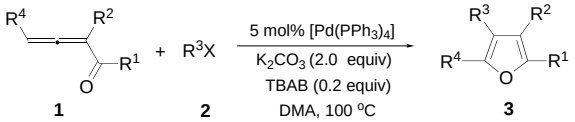
[a] NMR yield determined by using CH_2Br_2 as the internal standard. The numbers in parenthesis are isolated yields. [b] The reaction was carried out under conditions A. [c] $nBu_4N^+Br^-$ (0.2 equiv) was added (conditions B). [d] PhBr was used instead of PhI.

DMA as the solvent (entry 7, Table 4). A better result was obtained when 20 mol% of nBu_4NBr (TBAB) was added, and the reaction afforded the corresponding product **3ka** as the only product in 90% yield (isolated yield: 72%; conditions B; entry 8, Table 4). The reaction of **1k** with phenyl bromide is slow (Compare entries 8 and 9, Table 4).

By using conditions B, the reaction of various α,γ-disubstituted allenyl ketones with different organic halides afforded the corresponding 2,3,4,5-tetrasubstituted furans with different substitution patterns in moderate to excellent yields (Table 5). Considering the easy available of α,γ-disubstituted 1,2-allenyl ketones with different substituents, it is a very general, convenient, and versatile route to synthesize 2,3,4,5-tetrasubstituted furans (Scheme 6).

To our surprise, when *p*-methoxyphenyl iodide (**2f**) was used as the organic halide, the reaction afforded an unexpected furan **3ka** in 27% yield together with the normal product **3kf** (51%). The possible rational of formation of **3ka** is shown as Scheme 7. The first oxidative addition of **2f** generates the Pd^{II} intermediate **5**. Then the reductive elimination of intermediate **5** and subsequent reoxidative addition regenerates a new Pd^{II} intermediate **6**,[23] which subsequently treated with 1,2-allenyl ketone **1k** affords the unexpected product **3ka**.

Table 5. Efficient synthesis of 2,3,4,5-tetrasubstituted furans.[a]

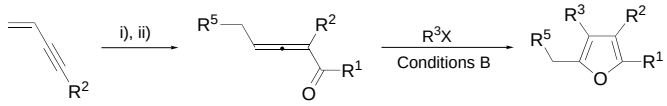


1 **2** **3**

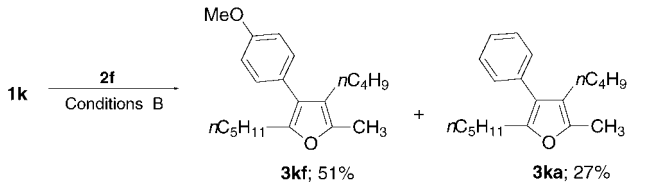
	11 R^1	R^2	R^4	**2**	t [h]	**3** [%]
1	CH_3	nC_4H_9	nC_5H_{11} (**1k**)	**2a**	14	**3ka** (72)
2		**1k**		**2c**	12	**3kc** (94)[b]
3		**1k**		**2e**	13	**3ke** (64)[c]
4		**1k**		**2f**	9	**3kf** (51)[b,d]
5	CH_3	nC_5H_{11}	nC_4H_9 (**1l**)	**2a**	10	**3la** (69)
6	CH_3	nC_5H_{11}	nC_5H_{11} (**1m**)	**2a**	10	**3ma** (59)
7	iC_3H_7	nC_5H_{11}	nC_4H_9 (**1n**)	**2a**	10	**3na** (60)
8	CH_3	nC_5H_{11}	2-methylbutyl (**1o**)	**2a**	10	**3oa** (67)

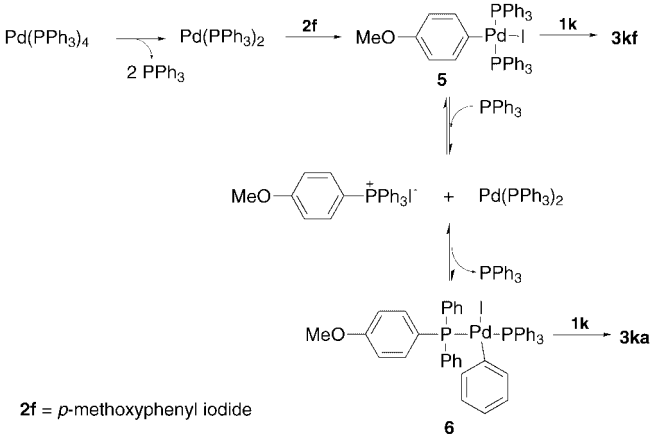
[a] Unless otherwise specified, the reaction was carried out by using allenyl ketone (1.0 equiv) and organic halide (2.0 equiv) under conditions B. [b] Two equivalents of allenyl ketone were used. [c] 1.6 equivalents of 1,2-allenyl ketone were used. [d] 0.4 equivalents of TBAB were used, unexpectedly **3ka** was also isolated in 27% yield (based on the organic halide used).

Mechanism: A plausible mechanism of this cross-coupling cyclization reaction is depicted in Scheme 8. The oxidative addition of R^3X with Pd^0 generates intermediate R^3PdX **7**. Then, carbopalladation of **7** with 1,2-allenyl ketone **1** affords the π-allyl palladium intermediate **8**, which may generate a new π-allyl palladium intermediate **9** in the presence of a base (path a). The subsequent intramolecular nucleophile attack of the intermediate **9**[16] will regenerate palladium(0) and afford the intermediate **10**, which would furnish furan **3** upon aromatization. An alternative reaction pathway of intermediate **8** is formation of palladium dienolate **11**[24] and the subsequent insertion of the C=C double bond into the oxo-palladium bond to afford intermediate **12** (path b). β-H elimination from intermediate **12** would afford the furan **3**

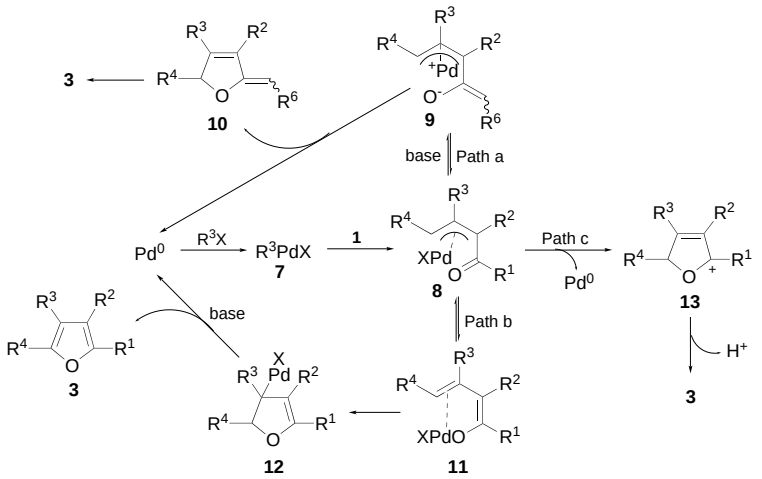


Scheme 6. Efficient and versatile route to 2,3,4,5-tetrasubstituted furans. i) R^5Li, −40 to 15 °C; ii) R^1CONMe_2, −78 °C.





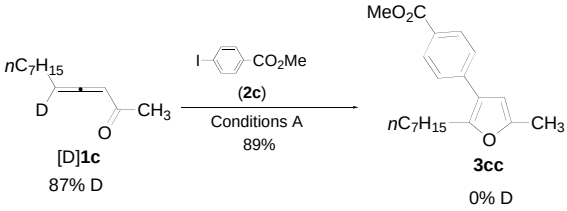
Scheme 7. The cyclization reaction of **1k** with **2f** and its plausible mechanism.



Scheme 8. Plausible mechanisms of the Pd^0-catalyzed coupling cyclization.

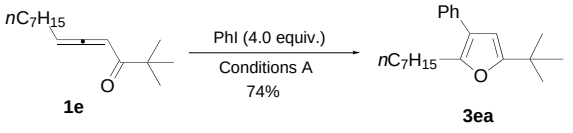
and HPdX, which would regenerate palladium(0) in the presence of a base. In addition, direct intramolecular nucleophile attack on intermediate **8** by the carbonyl oxygen atom will generate intermediate **13** and regenerate Pd^0 (path c).[25] Intermediate **13** will be deprotonated to afford **3** in the presence of a base.

In order to verify the mechanism, some control reactions were performed. The coupling cyclization of deuterated 1,2-allenyl ketone [D]**1c** with *p*-methoxycarbonylphenyl iodide (**2c**) produced non-deuterated **3cc** [Eq. (5)],



(5)

which was confirmed by ^{13}C NMR and ^{1}H NMR analysis. This rules out the possibility of path a. The cyclization results of **1e** and **1p** affording furans **3ea** and **3pc** in the absence of α'-H further support that this palladium(0)-catalyzed coupling cyclization reaction may occur via paths b or c [Eq. (6)].

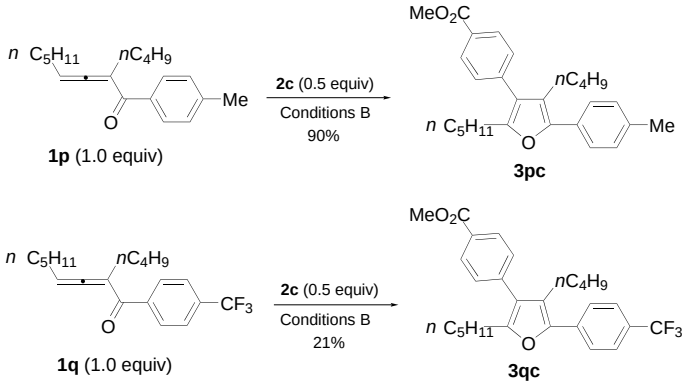


(6)

Furthermore, it is interesting to note that the cyclization of **1p** with an electron-donating methyl group on the phenyl ring afforded **3pc** in 90% yield, while the cyclization of **1q** with the electron-withdrawing trifluoromethyl group afforded **3qc** in only 21% yield. The cyclization of a 1:1 mixture of **1p** and **1q** with **2c** in a one-pot manner afforded the corresponding furans **3pc** and **3qc** in 81% and 11% yields, respectively (Scheme 9). These results further support the possibility of path c.

Conclusion

We have developed a palladium(0)-catalyzed coupling cyclization reaction of 1,2-allenyl ketones with organic halides. The advantages of this method are its generality, versatility, and efficiency not only for the synthesis of 2,3,4- and 2,3,5-trisubstituted furans but also for the synthesis of 2,3,4,5-tetrasubstituted furans. Furthermore, this methodology shows high substituent-loading capability and tolerance of various substituents. Some control reactions for mechanistic studies showed that instead of an enolization pathway, the reaction may proceed by the intermediacy of dienolate palladium and intramolecular nucleophilic attack on the π-allyl palladium intermediate by the carbonyl oxygen. Synthetic application for target molecules with potential activities is currently being carried out in our laboratory.



1p (1.0 equiv) + **1q** (1.0 equiv) —**2c** (0.5 equiv), Conditions B→ **3pc** (81%) + **3qc** (11%)

Scheme 9. The cyclization reactions of **1p** and **1q** with **2c**.

Experimental Section

The starting 1,2-alleny ketones **1b–c**,[19b] **1f**[20] and **1h–j**[19b] were prepared according to literature procedures.

Typical procedure for preparation of 1,2-allenyl ketones 1a–e: Heptadeca-3,4-dien-2-one (1a): Pentadeca-1,2-diene[26] (5.0 g, 24 mmol) was treated with *n*BuLi (2.0 M in cyclohexane, 20 mmol) in THF at −50 °C for 2 h followed by the dropwise addition of *N*,*N*-dimethylacetamide (1.7 g, 20 mmol) at −78 °C. After being stirred for 2 h at −78 °C, the resulting solution was slowly transferred into an ice-cooled aqueous HCl solution (0.1 N, 400 mL) and extracted with ether. Drying over $MgSO_4$, rotary evaporation, and column chromatography on silica gel (hexanes/ether = 100:1) afforded **1a** (2.0 g, 40%) as a liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.75–5.64$ (m, 1H; C=C=CHCO), 5.58 (q, $^{3}J(H,H) = 6.4$ Hz, 1H; HC=C=C), 2.30 (s, 3H; CH_3), 2.30–2.04 (m, 2H; CH_2), 1.70–1.50 (m, 2H; CH_2), 1.44–1.18 (m, 18H; $9CH_2$), 0.85 (t, $^{3}J(H,H) = 7.1$ Hz, 3H; CH_3); IR (neat): $\tilde{\nu} = 2926$, 2856, 1947 (C=C=C), 1686 cm^{-1}(CO); MS (70 eV): *m/z*

(%): 251 (6.29) [M^++H], 43 (100) [CH_3CO^+]; HRMS: calcd for $C_{17}H_{30}O$: 250.2297; found: 250.2285.

1-Cyclohexylundeca-2,3-dien-1-one (1d): The reaction of deca-1,2-diene (2.76 g, 20.0 mmol) with *n*BuLi (2.0 M in cyclohexane, 20 mmol) and cyclohexanecarboxylic acid *N*,*N*-dimethylamide (3.10 g, 20.0 mmol) afforded **1d** (1.84 g, 37%) as a liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.70-5.60$ (m, 1H; C=C=CHCO), 5.60–5.50 (m, 1H; CH=C=C), 2.90–2.75 (m, 1H; COCH), 2.20–2.05 (m, 2H; CH_2), 1.90–1.60 (m, 5H; 2CH_2 and CH), 1.60–1.00 (m, 15H; 7CH_2 and CH), 0.86 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 212.27$, 204.76, 96.01, 95.15, 46.67, 31.69, 29.42, 29.00, 28.98, 27.83, 25.79, 25.68, 25.61, 22.56, 14.00; IR (neat): $\tilde{\nu} =$ 1947 (C=C=C), 1676 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 248 (4.75) [M^+], 83 (100) [$C_6H_{11}^+$]; HRMS: calcd for $C_{17}H_{28}O$: 248.2140; found: 248.2143.

2,2-Dimethyltrideca-4,5-dien-3-one (1e): The reaction of deca-1,2-diene (3.4 g, 24.6 mmol) with *n*BuLi (10 mL, 2.0 M in cyclohexane, 20.0 mmol) and *N*,*N*-dimethylpivalamide (2.5 g, 19.3 mmol) afforded **1e** (1.5 g, 35%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.08-6.00$ (m, 1H; C=C=CHCO), 5.55 (q, ^3J(H,H) = ^5J(H,H) = 7.0 Hz, 1H; CH=C=C), 2.40–2.20 (m, 2H; CH_2), 1.50–1.35 (m, 2H; CH_2), 1.35–1.10 (m, 8H; 4CH_2), 1.20 (s, 9H; 3CH_3), 0.88 (t, ^3J(H,H) = 6.6 Hz, 3H; CH_3); IR (neat): $\tilde{\nu} =$ 1951 (C=C=C), 1722 (C=O), 1683 (C=C), 1670 cm^{-1}; MS (70 eV): *m/z* (%): 222 (13.23) [M^+], 207 (100) [$M^+ - CH_3$]; HRMS: calcd for $C_{15}H_{26}O$: 222.1984; found: 222.1975.

1-Phenylhepta-1,2-dien-4-one (1g): A solution of phenylacetyl chloride (3.70 g, 24 mmol) in CH_2Cl_2 was added dropwise to an ice-cooled (0 °C) solution of 1-(triphenylphosphoranylidene)pentan-2-one (6.92 g, 20 mmol) and Et_3N (3.03 g, 30 mmol) in dry CH_2Cl_2 stirred under Ar. The reaction mixture turned yellow when the reaction was complete as monitored by TLC. The reaction mixture was concentrated, and Et_2O was added to remove Ph_3PO by precipitation. Filtration, evaporation, and purification by column chromatography on silica gel (hexanes/ether = 100:1) afforded **1g** (1.30 g, 35%) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40-7.20$ (m, 5H; C_6H_5), 6.63 (d, ^5J(H,H) = 6.6 Hz, 1H; CH=C=C), 6.14 (d, ^5J(H,H) = 6.6 Hz, 1H; C=C=CHCO), 2.65–2.50 (m, 2H; CH_2), 1.68–1.55 (m, 2H; CH_2), 0.90 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 215.16$, 200.48, 131.04, 128.96, 128.13, 127.21, 100.57, 98.52, 41.27, 17.89, 13.66; IR (neat): $\tilde{\nu} =$ 1937 (C=C=C), 1683 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 186 (9.78) [M^+], 71 (100) [$C_3H_7CO^+$]; HRMS: calcd for $C_{13}H_{14}O$: 186.1045; found: 186.1052.

Typical procedure for the preparation of 1k–p: 3-Butyldeca-3,4-dien-2-one (1k): Oct-1-en-3-yne[27] (1.25 g, 11.5 mmol) was added to a solution of *n*BuLi (2 M in cyclohexane, 10 mmol) in dry THF (60 mL) stirred under Ar at −50 °C. The temperature was raised gradually to −25 °C and kept between −25 and −10 °C for 0.5 h. After the starting enyne had completely disappeared as determined by TLC, the reaction mixture was recooled to −78 °C. This was followed by the addition of a solution of *N*,*N*-dimethylacetamide (1.30 g, 15 mmol) in THF (10 mL). After being stirred for 2 h at −78 °C, the reaction mixture was poured into ice-cooled HCl (0.2 N, 100 mL), extracted with ether (3 × 50 mL), and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes/ether = 100:1) to afford **1k** (1.07 g, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 5.56–5.40 (m, 1H; CH=C=C), 2.17 (s, 3H; CH_3), 2.12–1.90 (m, 4H; 2CH_2), 1.45–1.08 (m, 10H; 5CH_2), 0.90–0.80 (m, 6H; 2CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta = 212.32$, 199.45, 109.69, 95.40, 31.33, 30.11, 28.69, 28.23, 26.88, 26.18, 22.36, 22.29, 13.96, 13.88; IR (neat): $\tilde{\nu} =$ 1944 (C=C=C), 1680 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 208 (2.77) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{14}H_{24}O$: 208.1827; found: 208.1795.

3-Pentylnona-3,4-dien-2-one (1l): The reaction of nona-1-en-3-yne[28] (2.12 g, 16.5 mmol) with *n*PrLi (1.6 M in Et_2O, 15 mmol) and *N*,*N*-dimethylacetamide (1.44 g, 16.5 mmol) afforded **1l** (2.04 g, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.56-5.40$ (m, 1H; HC=C=C), 2.20 (s, 3H; CH_3), 2.12–1.90 (m, 4H, 2CH_2), 1.45–1.08 (m, 10H; 5CH_2), 0.90–0.75 (m, 6H; 2CH_3); IR (neat): $\tilde{\nu} =$ 1944 (C=C=C), 1679 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 208 (3.85) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{14}H_{24}O$: 208.1827; found: 208.1858.

3-Pentyldeca-3,4-dien-2-one (1m): The reaction of nona-1-en-3-yne (1.34 g, 11 mmol) with *n*BuLi (2.0 M in cyclohexane, 10 mmol) and *N*,*N*-dimethylacetamide (1.04 g, 12 mmol) afforded **1m** (1.27 g 57%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.56-5.40$ (m, 1H; HC=C=C), 2.20 (s, 3H; CH_3), 2.12–1.90 (m, 4H; 2CH_2), 1.45–1.08 (m, 12H; 6CH_2), 0.90–0.75 (m, 6H; 2CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 212.71$, 199.37, 109.70, 95.37, 31.38, 31.31, 28.67, 28.21, 27.59, 26.84, 26.40, 22.42, 22.34, 13.95, 13.91; IR (neat): $\tilde{\nu} =$ 1944 (C=C=C), 1679 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 222 (1.69) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{15}H_{26}O$: 222.1984; found: 222.1949.

2-Methyl-4-pentyldeca-4,5-dien-3-one (1n): The reaction of nona-1-en-3-yne (1.34 g, 11.0 mmol) with *n*PrLi (1.6 M in Et_2O, 10.0 mmol) and *N*,*N*-dimethyl isobutyramide (1.72 g, 15.0 mmol) afforded **1n** (1.65 g, 70%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.56-5.40$ (m, 1H; HC=C=C), 3.30–2.20 (m, 1H, CH), 2.20–2.00 (m, 4H, 2CH_2), 1.50–1.10 (m, 10H; 5CH_2), 1.10–0.90 (m, 6H; 2CH_3), 0.90–0.70 (m, 6H; 2CH_3); IR (neat): $\tilde{\nu} =$ 1944 (C=C=C), 1678 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 237 (23.54) [M^++H], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{16}H_{28}O$: 236.2140; found: 236.2093.

7-Methyl-3-pentylnona-3,4-dien-2-one (1o): The reaction of nona-1-en-3-yne (1.34 g, 11 mmol) with *sec*BuLi (1.1 M in Et_2O, 10 mmol) and *N*,*N*-dimethylacetamide (1.04 g, 12 mmol) afforded **1o** (1.34 g, 61%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.56-5.40$ (m, 1H; HC=C=C), 2.20 (s, 3H; CH_3), 2.12–1.80 (m, 4H; 2CH_2), 1.45–1.08 (m, 9H, 4CH_2 and CH), 0.90–0.75 (m, 9H, 3CH_3); MS (70 eV): *m/z* (%): 222 (4.80) [M^+], 43 (100) [$C_3H_7^+$]; IR (neat): $\tilde{\nu} =$ 1944 (C=C=C), 1680 cm^{-1} (C=O); HRMS: calcd for $C_{15}H_{26}O$: 222.1984; found: 222.1961.

1-(4′-Methylphenyl)-2-butylnona-2,3-dien-1-one (1p): The reaction of oct-1-en-3-yne (2.16 g, 20 mmol) with *n*BuLi (2.0 M in cyclohexane, 20 mmol) and 4-methylbenzoic acid *N*,*N*-dimethylamide (4.08 g, 25 mmol) afforded **1p** (4.20 g, 74%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.65$ (d, ^3J(H,H) = 7.8 Hz, 2H; 2ArH), 7.16 (d, ^3J(H,H) = 7.8 Hz, 2H; 2ArH), 5.40–5.30 (m, 1H; HC=C=C), 2.44–2.30 (m, 2H; CH_2), 2.36 (s, 3H; CH_3), 2.16–2.00 (m, 2H; CH_2), 1.54–1.30 (m, 6H; 3CH_2), 1.30–1.10 (m, 4H; 2CH_2), 0.95 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3), 0.86 (t, $J = 6.9$ Hz, 3H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 212.69$, 195.08, 142.04, 136.01, 128.91, 128.24, 107.05, 94.63, 31.03, 30.10, 28.56, 28.39, 27.85, 22.27(2C), 21.36, 13.84, 13.81; IR (neat): $\tilde{\nu} =$ 1944 (C=C=C), 1651 (C=O), 1609, 1275 cm^{-1}; MS (70 eV): *m/z* (%): 284 (44.93) [M^+], 119 (100) [*p*-$CH_3C_6H_4CO^+$]; elemental analysis calcd (%) for $C_{20}H_{28}O$: C 84.45, H 9.92; found: C 84.49, H 9.91.

1-(4′-Trifluoromethylphenyl)-1-butylnona-2,3-dien-1-one (1q): The reaction of oct-1-en-3-yne (2.00 g, 18.5 mmol) with *n*BuLi (1.6 M in cyclohexane, 16 mmol) and 4-trifluoromethylbenzoic acid *N*,*N*-dimethylamide (4.00 g, 18.4 mmol) afforded **1q** (4.04 g, 75%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.1$ Hz, 2H; 2ArH), 7.54 (d, $J = 8.1$ Hz, 2H; 2ArH), 5.32 (tt, ^3J(H,H) = 9.9 Hz, ^5J(H,H) = 2.7 Hz, 1H; HC=C=C), 2.40–2.20 (m, 2H; CH_2), 2.10–1.90 (m, 2H; CH_2), 1.48–1.00 (m, 10H; 5CH_2), 0.85 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); 0.75 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 214.01$, 194.61, 142.03, 132.83 (q, ^2J(C,F) = 32.0 Hz), 128.89, 124.64 (q, ^3J(C,F) = 3.2 Hz), 123.72 (q, ^1J(C,F) = 272.3 Hz), 107.72, 95.71, 31.04, 30.10, 28.54, 28.34, 27.45, 22.31, 22.27, 13.86, 13.77; IR (neat): $\tilde{\nu} =$ 1600, 1580, 1492 cm^{-1}; MS (70 eV): *m/z* (%): 338 (3.82) [M^+], 173 (100) [*p*-$CF_3C_6H_4CO^+$]; HRMS: calcd for $C_{20}H_{25}F_3O$: 338.1857; found: 338.1850.

Typical procedure for the coupling cyclization reaction of 1,2-allenyl ketone 1a with iodobenzene: Conditions A: A mixture of $Pd(PPh_3)_4$ (23 mg, 0.002 mmol), Ag_2CO_3 (11 mg, 0.04 mmol), Et_3N (81 mg, 0.8 mmol), iodobenzene (163 mg, 0.8 mmol), **1a** (100 mg, 0.4 mmol), and toluene (5 mL) was stirred at 80 °C for 12 h under Ar. After the reaction was complete as monitored by TLC, the solvent was removed, and the residue was purified by column chromatography on silica gel (hexanes) to afford **3aa** (98 mg, 75%).

2-Dodecyl-3-phenyl-5-methylfuran (3aa): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.45-7.15$ (m, 5H; C_6H_5), 6.03 (s, 1H; CH), 2.69 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_2), 2.26 (s, 3H; CH_3), 1.72–1.58 (m, 2H; CH_2), 1.45–1.08 (m, 18H; 9CH_2), 0.85 (t, ^3J(H,H) = 6.6 Hz, 3H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 150.29$, 149.80, 134.80, 128.54, 127.66, 126.15, 121.37, 107.10, 32.01, 31.00, 29.73, 29.65, 29.45, 28.83, 27.03, 26.77, 22.78, 22.60, 14.21, 13.94, 13.55; IR (neat): $\tilde{\nu} =$ 1600, 1580, 1492 cm^{-1}; MS (70 eV): *m/z* (%): 326 (23.66) [M^+], 171 (100) [$M^+ - C_{11}H_{23}$]; HRMS: calcd for $C_{23}H_{34}O$: 326.2610; found: 326.2596.

2-Dodecyl-3-(4′-nitrophenyl)-5-methylfuran (3ab): The reaction of **1a** (75 mg, 0.3 mmol) with *p*-nitrophenyl iodide (50 mg, 0.2 mmol) afforded **3ab** (67 mg, 90%) as a yellow solid. M.p. 43–45 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.14$ (d, ^3J(H,H) = 9.0 Hz, 2H; 2ArH), 7.42 (d, ^3J(H,H) = 9.0 Hz, 2H; 2ArH), 6.04 (s, 1H, CH), 2.67 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.23 (s, 3H; CH_3), 1.73–1.54 (m, 2H; CH_2), 1.41–1.08 (m, 18H;

9 CH_2), 0.85 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 152.11, 150.70, 145.72, 141.56, 127.57, 123.87, 119.77, 106.31, 31.87, 29.62, 29.59, 29.57, 29.49, 29.31, 29.28, 29.27, 29.42, 27.21, 22.64, 14.06, 13.33; IR (neat): $\tilde{\nu}$ = 1600, 1580, 1516, 1344 cm^{-1}; MS (70 eV): *m/z* (%): 372 (6.60) [M^++H], 371 (35.85) [M^+], 216 (100) [$M^+ - C_{11}H_{23}$]; elemental analysis calcd (%) for $C_{23}H_{33}NO_3$: C 74.36, H 8.95; found: C 74.11, H 9.11.

2-Dodecyl-3-(4′-methoxycarbonylphenyl)-5-methylfuran (3ac): The reaction of **1a** (150 mg, 0.6 mmol) with *p*-methoxycarbonylphenyl iodide (79 mg, 0.3 mmol) afforded **3ac** (108 mg, 94%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, ^3J(H,H) = 8.4 Hz, 2H; 2ArH), 7.33 (d, ^3J(H,H) = 8.4 Hz, 2H; 2ArH), 6.03 (s, 1H; CH), 3.84 (s, 3H; OCH_3), 2.66 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.22 (s, 3H; CH_3), 1.68–1.52 (m, 2H; CH_2), 1.33–1.06 (m, 18H, 9 CH_2), 0.80 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 167.01, 151.28, 150.18, 139.46, 129.83, 127.53, 127.16, 120.57, 106.61, 52.00, 31.91, 29.65, 29.63, 29.61, 29.53, 29.34, 29.32, 29.31, 28.56, 27.14, 22.68, 14.10, 13.40; IR (neat): $\tilde{\nu}$ = 1726 (C=O), 1610, 1580, 1276, 1110 cm^{-1}; MS (70 eV): *m/z* (%): 384 (10.20) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{25}H_{36}O_3$: 384.2664; found: 384.2657.

2-Butyl-3-phenyl-5-methylfuran (3ba): The reaction of **1b** (69 mg, 0.5 mmol) with iodobenzene (204 mg, 1 mmol) afforded **3ba** (78 mg, 73%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.12 (m, 5H, C_6H_5), 5.98 (s, 1H; CH), 2.63 (t, J = 7.5 Hz, 2H; CH_2), 2.20 (s, 3H; CH_3), 1.65–1.50 (m, 2H; CH_2), 1.38–1.20 (m, 2H; CH_2), 0.82 (t, ^3J(H,H) = 7.5 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.15, 149.70, 134.70, 128.44, 127.57, 126.05, 121.28, 107.02, 30.90, 26.68, 22.50, 13.85, 13.44; IR (neat): $\tilde{\nu}$ = 1600, 1580, 1492 cm^{-1}; MS (70 eV): *m/z* (%): 214 (52.12) [M^+], 171 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{15}H_{18}O$: 214.1358; found: 214.1409.

2-Butyl-3-(4′-nitrophenyl)-5-methylfuran (3bb): The reaction of **1b** (207 mg, 1.5 mmol) with *p*-nitrophenyl iodide (249 mg, 1.0 mmol) afforded **3bb** (239 mg, 92%) as a yellow solid. M.p. 41–43 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, ^3J(H,H) = 8.9 Hz, 2H; 2ArH), 7.42 (d, ^3J(H,H) = 8.9 Hz, 2H; 2ArH), 6.07 (s, 1H; CH), 2.69 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_2), 2.26 (s, 3H; CH_3), 1.73–1.58 (m, 2H; CH_2), 1.46–1.30 (m, 2H; CH_2), 0.85 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 1600, 1580, 1510, 1344 cm^{-1}; MS (70 eV): *m/z* (%): 259 (28.75) [M^+], 216 (100) [$M^+ - C_3H_7$]; elemental analysis calcd (%) for $C_{15}H_{17}NO_3$: C 69.48, H 6.61, N 5.40; found: C 69 .53, H 6.77, N 5.14.

2-Butyl-3-(4′-methoxycarbonylphenyl)-5-methylfuran (3bc): The reaction of **1b** (138 mg, 1.0 mmol) with *p*-methoxycarbonylphenyl iodide (131 mg, 0.5 mmol) afforded **3bc** (115 mg, 85%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, ^3J(H,H) = 8.5 Hz, 2H; 2ArH), 7.36 (d, ^3J(H,H) = 8.5 Hz, 2H; 2ArH), 6.06 (s, 1H; CH), 3.87 (s, 3H; OCH_3), 2.69 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_2), 2.26 (s, 3H; CH_3), 1.73–1.58 (m, 2H; CH_2), 1.43–1.28 (m, 2H; CH_2), 0.85 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 167.04, 151.25, 150.21, 139.46, 129.83, 127.55, 127.17, 120.59, 106.62, 52.01, 30.70, 26.86, 22.44, 13.79, 13.40; IR (neat): $\tilde{\nu}$ = 1726 (C=O), 1610, 1580, 1276, 1110 cm^{-1}; MS (70 eV): *m/z* (%): 273 (12.76) [M^++H], 272 (41.96) [M^+], 229 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{17}H_{20}O_3$: 272.1413; found: 272.1411.

2-Butyl-3-(3′,5′-pyrimidinyl)-5-methylfuran (3bd): The reaction of **1b** (104 mg, 0.75 mmol) with 5-bromopyrimidine (80 mg, 0.5 mmol) afforded **3bd** (77 mg, 71%) as a solid. M.p. 45–48 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.06 (s, 1H; ArH), 8.71 (s, 2H; 2ArH), 6.08 (s, 1H; CH), 2.69 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_2), 2.26 (s, 3H; CH_3), 1.73–1.58 (m, 2H; CH_2), 1.43–1.34 (m, 2H; CH_2), 0.89 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 156.20, 154.88, 151.83, 151.15, 128.66, 114.53, 105.76, 30.72, 26.66, 22.36, 13.73, 13.35; IR (neat): $\tilde{\nu}$ = 1592, 1560, 1546 cm^{-1}; MS (70 eV): *m/z* (%): 217 (9.28) [M^++H], 216 (28.31) [M^+], 173 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{13}H_{16}N_2O$: 216.1263; found: 216.1255.

2-Butyl-3-(*E*-2′-methoxycarbonylethenyl)-5-methylfuran (3be): The reaction of **1b** (104 mg, 0.75 mmol) with methyl (*Z*)-3-iodopropenoate (106 mg, 0.5 mmol) afforded **3be** (68 mg, 61%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, ^3J(H,H) = 15.6 Hz, 1H; COC=CH), 6.01 (s, 1H, CH), 5.93 (d, ^3J(H,H) = 15.6 Hz, 1H; COCH=C), 3.71 (s, 3H; OCH_3), 2.62 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.20 (s, 3H; CH_3), 1.66–1.51 (m, 2H; CH_2), 1.41–1.28 (m, 2H; CH_2), 0.86 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 167.94, 157.44, 151.43, 135.64, 117.84, 114.78, 103.22, 51.38, 30.75, 25.94, 22.24, 13.72, 13.32; IR (neat): $\tilde{\nu}$ = 1720 (C=O), 1640 (C=C), 1610, 1580, 1264, 1170 cm^{-1}; MS (70 eV): *m/z* (%): 223 (15.35) [M^++H], 222 (80.64) [M^+], 179 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{13}H_{18}O_3$: 222.1256; found: 222.1249.

2-Butyl-3-(4′-methoxyphenyl)-5-methylfuran (3bf): The reaction of **1b** (104 mg, 0.75 mmol) with *p*-methoxyphenyl iodide (117 mg, 0.5 mmol) afforded **3bf** (78 mg, 64%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, ^3J(H,H) = 6.7 Hz, 2H; 2ArH), 6.92 (d, ^3J(H,H) = 6.7 Hz, 2H; 2ArH), 6.04 (s, 1H; CH), 3.83 (s, 3H; OCH_3), 2.69 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_2), 2.29 (s, 3H; CH_3), 1.70–1.60 (m, 2H; CH_2), 1.42–1.28 (m., 2H; CH_2), 0.89 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.02, 148.50, 127.63, 126.20, 119.81, 113.50, 112.90, 106.10, 54.21, 29.93, 25.61, 21.49, 12.84, 12.43; IR (neat): $\tilde{\nu}$ = 1590, 1518, 1460, 1350, 1180 cm^{-1}; MS (70 eV): *m/z* (%): 244 (44.53) [M^+], 201 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{16}H_{20}O_2$: 244.1463; found: 244.1468.

2-Heptyl-3-(4′-methoxylcarbonylphenyl)-5-methylfuran (3cc): The reaction of **1c** (108 mg, 0.6 mmol) with *p*-(methoxycarbonyl)phenyl iodide (80 mg, 0.3 mmol) afforded **3cc** (93 mg, 98%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, ^3J(H,H) = 9.0 Hz, 2H; 2ArH), 7.40 (d, ^3J(H,H) = 9.0 Hz, 2H; 2ArH), 6.11 (s, 1H; CH), 3.92 (s, 3H; OCH_3), 2.74 (t, ^3J(H,H) = 8.1 Hz, 2H; CH_2), 2.30 (s, 3H; CH_3), 1.72–1.50 (m, 2H; CH_2), 1.36–1.16 (m, 8H; 4 CH_2), 0.87 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.99, 151.26, 150.17, 139.43, 129.81, 127.50, 127.13, 120.53, 106.58, 52.00, 31.72, 29.27, 28.96, 28.56, 27.12, 22.60, 14.06, 13.40; IR (neat): $\tilde{\nu}$ = 1722 (C=O), 1609, 1578, 986, 777 cm^{-1}; MS (70 eV): *m/z* (%): 314 (32.39) [M^+], 229 (100) [$M^+ - C_6H_{13}$]; HRMS: calcd for $C_{20}H_{26}O_3$ 314.1882; found: 314.1868.

The cross coupling reaction of deuterated 1,2-allenyl ketone [D]1c with *p*-(methoxycarbonyl)phenyl iodide: The reaction of deuterated 1,2-allenyl ketone [D]**1c** (181 mg, 1.0 mmol) with **2c** (131 mg, 0.5 mmol) afforded **3cc** (140 mg, 89%).

2-Heptyl-3-(4′-methoxyphenyl)-5-methylfuran (3cf): The reaction of **1c** (135 mg, 0.75 mmol) with *p*-methoxyphenyl iodide (117 mg, 0.5 mmol) afforded **3cf** (90 mg, 63%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, ^3J(H,H) = 6.7 Hz, 2H; 2ArH), 6.92 (d, ^3J(H,H) = 6.7 Hz, 2H; 2ArH), 6.04 (s, 1H; CH), 3.83 (s, 3H; OCH_3), 2.69 (t, ^3J(H,H) = 7.8 Hz, 2H; CH_2), 2.29 (s, 3H; CH_3), 1.70–1.62 (m, 2H; CH_2), 1.34–1.23 (m, 8H; 4 CH_2), 0.89 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); IR (neat): $\tilde{\nu}$ = 1590, 1518, 1460, 1350, 1180 cm^{-1}; MS (70 eV): *m/z* (%): 287 (10.51) [M^++H], 286 (39.36) [M^+], 201 (100) [$M^+ - C_6H_{13}$]; HRMS: calcd for $C_{19}H_{26}O_2$ 286.1933; found 286.1907.

2-Heptyl-3-phenyl-5-(cyclohexyl)furan (3da): The reaction of **1d** (124 mg, 0.5 mmol) with iodobenzene (204 mg, 1.0 mmol) afforded **3da** (119 mg, 74%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50–7.20 (m, 5H; C_6H_5), 6.08 (s, 1H; CH), 2.76 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.70–2.55 (m, 1H; CH), 2.20–2.00 (m, 2H; CH_2), 1.90–1.60 (m, 6H; 3 CH_2), 1.50–1.20 (m, 12H; 6 CH_2), 0.90 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.67, 149.71, 134.87, 128.40, 127.55, 125.95, 120.78, 104.10, 37.17, 31.78, 31.53, 29.30, 29.01, 28.63, 26.96, 26.17, 25.95, 22.62, 14.07; IR (neat): $\tilde{\nu}$ = 1600, 1500 cm^{-1}; MS (70 eV): *m/z* (%): 324 (36.70) [M^+], 239 (100) [$M^+ - C_6H_{13}$]; HRMS: calcd for $C_{23}H_{32}O$: 324.2453; found: 324.2458.

2-Heptyl-3-(4′-methoxycarbonylphenyl)-5-(cyclohexyl)furan (3dc): The reaction of **1d** (186 mg, 0.75 mmol) with *p*-(methoxycarbonyl)phenyl iodide (131 mg, 0.5 mmol) afforded **3dc** (146 mg, 76%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, ^3J(H,H) = 8.7 Hz, 2H; 2ArH), 7.42 (d, ^3J(H,H) = 8.9 Hz, 2H; 2ArH), 6.09 (s, 1H; CH), 3.91 (s, 3H; OCH_3), 2.75 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.65–2.52 (m, 1H; CH), 2.15–1.95 (m, 2H; CH_2), 1.90–1.60 (m, 6H; 3 CH_2), 1.50–1.10 (m, 12H; 6 CH_2), 0.87 (t, ^3J(H,H) = 6.6 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 167.01, 159.11, 150.84, 139.63, 129.78, 127.42, 127.11, 120.09, 103.71, 51.95, 37.07, 31.73, 31.45, 29.24, 28.96, 28.45, 27.16, 26.10, 25.89, 22.58, 14.04; IR (neat): $\tilde{\nu}$ = 1724 (C=O), 1610, 1278 cm^{-1}; MS (70 eV): *m/z* (%): 382 (45.84) [M^+], 297 (100) [$M^+ - C_6H_{13}$]; HRMS: calcd for $C_{25}H_{34}O_3$: 382.2508; found: 382.2458.

2-Heptyl-3-phenyl-5-*tert*-butylfuran (3ea): The reaction of **1e** (111 mg, 0.5 mmol) with iodobenzene (408 mg, 2.0 mmol) afforded **3ea** (110 mg, 74%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 4H, 4ArH), 7.28–7.18 (m, 1H, ArH), 6.06 (s, 1H; CH), 2.75 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_2), 1.76–1.62 (m, 2H; CH_2), 1.40–1.20 (m, 8H; 4 CH_2), 1.31 (s, 9H, 3 CH_3), 0.88 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 161.83, 149.82, 134.87, 128.39, 127.54, 125.93,

120.62, 103.23, 32.47, 31.81, 29.27, 29.03, 29.02, 28.57, 26.95, 22.63, 14.09; IR (neat): $\tilde{\nu}$ = 1600, 1566, 909, 763 cm^{-1}; MS (70 eV): *m/z* (%): 298 (32.48) [M^+], 283 (100) [$M^+ - CH_3$]; HRMS: calcd for $C_{21}H_{30}O$: 298.2297; found: 298.2315.

2-Phenyl-3-(4′-nitrophenyl)-5-methylfuran (3fb): The reaction of **1f** (119 mg, 0.75 mmol) with *p*-nitrophenyl iodide (125 mg, 0.5 mmol) afforded **3fb** (71 mg, 51%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, ^3J(H,H) = 8.1 Hz, 2H; 2ArH), 7.54 (d, ^3J(H,H) = 8.1 Hz, 2H; 2ArH), 7.50–7.40 (m, 2H; 2Ar′H), 7.38–7.20 (m, 3H; 3Ar′H), 6.22 (s, 1H; CH), 2.41 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 152.31, 148.52, 146.48, 141.65, 130.63, 128.89, 128.63, 128.06, 126.57, 123.94, 120.99, 109.11, 13.53; IR (neat): $\tilde{\nu}$ = 1600, 1512, 1342, 1180 cm^{-1}; MS (70 eV): *m/z* (%): 280 (28.65) [M^++H], 279 (100) [M^+]; HRMS: calcd for $C_{17}H_{13}NO_3$: 279.08954; found: 279.08952.

2-Phenyl-3-(4′-methoxycarbonylphenyl)-5-methylfuran (3fc): The reaction of **1f** (119 mg, 0.75 mmol) with *p*-(methoxycarbonyl)phenyl iodide (131 mg, 0.5 mmol) afforded **3fc** (75 mg, 51%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, ^3J(H,H) = 8.7 Hz, 2H; 2ArH), 7.56–7.45 (m, 4H; 4Ar′H), 7.42–7.16 (m, 3H; 2ArH and Ar′H), 6.20 (s, 1H; CH), 3.92 (s, 3H; OCH_3), 2.39 (s, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.95, 151.76, 147.64, 139.50, 131.04, 129.85, 128.44, 128.42, 128.33, 127.51, 126.24, 122.10, 109.55, 52.07, 13.54; IR (neat): $\tilde{\nu}$ = 1726 (C=O), 1608, 1560, 1276, 1178, 1110 cm^{-1}; MS (70 eV): *m/z* (%): 293 (24.90) [M^++H], 292 (100) [M^+]; HRMS: calcd for $C_{19}H_{16}O_3$: 292.1100; found: 292.1114.

2-Phenyl-3-(4′-nitrophenyl)-5-propylfuran (3gb): The reaction of **1g** (140 mg, 0.75 mmol) with *p*-nitrophenyl iodide (125 mg, 0.5 mmol) afforded **3gb** (118 mg, 77%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, ^3J(H,H) = 8.9 Hz, 2H, 2ArH), 7.47 (d, ^3J(H,H) = 8.9 Hz, 2H, 2ArH), 7.42–7.37 (m, 2H, 2Ar′H), 7.26–7.16 (m, 3H; 3Ar′H), 6.15 (s, 1H; CH), 2.61 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 1.78–1.60 (m, 2H; CH_2), 0.97 (t, ^3J(H,H) = 7.5 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 156.53, 148.33, 146.40, 141.71, 130.69, 128.86, 128.57, 127.98, 126.54, 123.87, 120.75, 108.36, 29.93, 21.24, 13.78; IR (neat): $\tilde{\nu}$ = 1600, 1514, 1344 cm^{-1}; MS (70 eV): *m/z* (%): 307 (54.11) [M^+], 278 (100) [$M^+ - C_2H_5$]; HRMS: calcd for $C_{19}H_{17}NO_3$: 307.1208; found: 307.1227.

2-Phenyl-3-(4′-methoxycarbonylphenyl)-5-propylfuran (3gc): The reaction of **1g** (140 mg, 0.75 mmol) with *p*-(methoxycarbonyl)phenyl iodide (131 mg, 0.5 mmol) afforded **3gc** (116 mg, 73%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, ^3J(H,H) = 8.5 Hz, 2H; 2ArH), 7.56–7.44 (m, 4H; 2ArH and 2Ar′H), 7.35–7.20 (m, 3H; 3Ar′H), 6.22 (s, 1H; CH), 3.93 (s, 3H; OCH_3), 2.69 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 1.85–1.68 (m, 2H; CH_2), 1.05 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 66.86, 155.95, 147.43, 139.54, 131.07, 129.78, 128.35, 128.28, 127.42, 126.19, 121.82, 108.78, 108.77, 51.97, 29.93, 21.24, 13.77; IR (neat): $\tilde{\nu}$ = 1724 (C=O), 1610, 1560, 1278 cm^{-1}; MS (70 eV): *m/z* (%): 320 (65.59) [M^+], 291 (100) [$M^+ - C_2H_5$]; HRMS: calcd for $C_{21}H_{20}O_3$: 320.1413; found: 320.1411.

2,3-Dimethyl-4-(4′-nitrophenyl)furan (3hb): The reaction of **3h** (182 mg, 2.0 mmol) with *p*-nitrophenyl iodide (249 mg, 1.0 mmol) afforded **3hb** (171 mg, 79%). M.p. 91–92 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, ^3J(H,H) = 9.1 Hz, 2H; 2ArH), 7.50 (d, ^3J(H,H) = 9.1 Hz, 2H; 2ArH), 7.46 (s, 1H; CH), 2.22 (s, 3H; CH_3), 2.04 (s, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 1600, 1560, 1510, 1340, 1144 cm^{-1}; MS (70 eV): *m/z* (%): 218 (22.21) [M^++H], 217 (100) [M^+]; elemental analysis calcd (%) for $C_{12}H_{11}NO_3$: C 66.35, H 5.10, N 6.45; found: C 66.34, H 5.04, N 6.33.

2,3-Dimethyl-4-(4′-methoxycarbonylphenyl)furan (3hc): The reaction of **1h** (144 mg, 1.5 mmol) with *p*-(methoxycarbonyl)phenyl iodide (262 mg, 1.0 mmol) afforded **3hc** (156 mg, 68%). M.p. 69–71 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, ^3J(H,H) = 6.8 Hz, 2H; 2ArH), 7.42 (d, ^3J(H,H) = 6.8 Hz, 2H; 2ArH), 7.41 (s, 1H; CH), 3.82 (s, 3H; OCH_3), 2.23 (s, 3H; CH_3), 2.02 (s, 3H; CH_3); MS (70 eV): *m/z* (%): 231 (17.06) [M^++H], 230 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 1724 (C=O), 1609, 1276, 1110 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{14}O_3$: C 73.03, H 6.12; found: C 72.95, H 6.19.

2-Methyl-3-butyl-4-(3′,5′-pyrimidinyl)furan (3id): The reaction of **1i** (207 mg, 1.5 mmol) with 5-bromopyrimidine (159 mg, 1.0 mmol) afforded **3id** (209 mg, 97%). M.p. 39–40 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.10 (s, 1H; ArH), 8.70 (s, 2H; 2ArH), 7.38 (s, 1H; CH), 2.41 (t, ^3J(H,H) = 7.4 Hz, 2H; CH_2), 2.24 (s, 3H; CH_3), 1.47–1.04 (m, 4H; 2CH_2), 0.80 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.03, 155.28, 149.78, 137.87, 127.89, 120.75, 117.91, 32.58, 23.13, 22.34, 13.75, 11.77; IR (KBr): $\tilde{\nu}$ = 1550, 1410, 1140 cm^{-1}; MS (70 eV): *m/z* (%): 217 (44.11) [M^++H], 216 (63.07) [M^+], 173 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{13}H_{16}N_2O$: 216.1263; found: 216.1250.

2-Methyl-3-allyl-4-(4′-nitrophenyl)furan (3jb): The reaction of 1,2-dienyl ketone **1j** (183 mg, 1.5 mmol) with *p*-nitrophenyl iodide (249 mg, 1.0 mmol) afforded **3jb** as a yellow solid (191 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, ^3J(H,H) = 7.1 Hz, 2H; 2ArH), 7.15 (d, ^3J(H,H) = 7.1 Hz, 3H; 2ArH and CH), 5.78–5.65 (m, 1H; CH=C), 4.89 (dd, ^3J(H,H) = 10.1 Hz, ^2J(H,H) = 1.7 Hz, 1H; C=CH), 4.78 (dd, ^3J(H,H) = 7.1 Hz, ^2J(H,H) = 1.7 Hz, 1H; C=CH), 3.05 (d, ^3J(H,H) = 5.3 Hz, 2H; CH_2), 2.10 (s, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 1640 (C=C), 1600, 1510, 1340 cm^{-1}; MS (70 eV): *m/z* (%): 244 (19.31) [M^++H], 243 (100) [M^+]; elemental analysis calcd (%) for $C_{14}H_{13}NO_3$: C 69.12, H 5.39, N 5.76; found: C 69.51, H 5.52, N 5.73.

The cross-coupling reaction of 1,2-allenyl ketone 1k with iodobenzene: Conditions A: The reaction of 1,2-allenyl ketone **1k** (104 mg, 0.5 mmol) with iodobenzene (204 mg, 1 mmol) afforded **3ka** (81 mg, 57%) and **4k** (22 mg, 11%).

2-Pentyl-3-phenyl-4-butyl-5-methylfuran (3ka): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.16 (m, 5H; C_6H_5), 2.54 (t, ^3J(H,H) = 8.0 Hz, 2H; CH_2), 2.29 (t, ^3J(H,H) = 7.3 Hz, 2H; CH_2), 2.26 (s, 3H; CH_3), 1.76–1.50 (m, 2H; CH_2), 1.40–1.10 (m, 8H; 4CH_2), 0.87 (t, ^3J(H,H) = 6.7 Hz, 3H; CH_3), 0.87 (t, ^3J(H,H) = 6.7 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.95, 145.22, 134.97, 129.75, 128.42, 126.55, 122.46, 119.32, 32.70, 31.74, 28.88, 26.59, 23.50, 22.63, 22.60, 14.24, 14.03, 11.96; IR (neat): $\tilde{\nu}$ = 1608, 1585, 1495, 701 cm^{-1}; MS (70 eV): *m/z* (%): 284 (29.72) [M^+], 227 (100) [$M^+ - C_4H_9$]; HRMS: calcd for $C_{20}H_{28}O$: 284.2140; found: 284.2157.

2-Methyl-3-butyl-5-pentylfuran (4k): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (s, 1H; CH), 2.52 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.26 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_2), 2.16 (s, 3H; CH_3), 1.68–1.50 (m, 2H; CH_2), 1.50–1.40 (m, 2H; CH_2), 1.40–1.30 (m, 6H; 3CH_2), 0.91 (t, ^3J(H,H) = 7.5 Hz, 3H; CH_3), 0.90 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.53, 144.71, 119.41, 106.43, 32.62, 31.49, 28.05, 27.86, 24.56, 22.45, 22.36, 14.02, 13.94, 11.35; IR (neat): $\tilde{\nu}$ = 2958, 2929, 1578, 1467 cm^{-1}; MS (70 eV): *m/z* (%): 208 (28.69) [M^+], 151 (100) [$M^+ - C_4H_9$]; HRMS: calcd for $C_{14}H_{24}O$: 208.18272; found: 208.17948.

Typical procedure for coupling cyclization reaction of 1,2-allenyl ketone 1k with iodobenzene: Conditions B: A mixture of $Pd(PPh_3)_4$ (29 mg, 0.05 mmol), 1,2-dienyl ketone **1k** (104 mg, 1.0 mmol), K_2CO_3 (138 mg, 1.0 mmol), TBAB (32 mg, 0.1 mmol), iodobenzene (204 mg, 2.0 mmol), and DMA (2.5 mL) was stirred under Ar at 100 °C for 10 h. H_2O was added and the mixture was extracted by ether, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (hexanes) to afford **3ka** (101 mg, 72%).

2-Pentyl-3-(4′-methoxycarbonylphenyl)-4-butyl-5-methylfuran (3kc): The reaction of **1k** (208 mg, 1.0 mmol) with *p*-(methoxycarbonyl)phenyl iodide (131 mg, 0.5 mmol) afforded **3kc** (161 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, ^3J(H,H) = 8.1 Hz, 2H; 2ArH), 7.30 (d, ^3J(H,H) = 8.1 Hz, 2H; 2ArH), 3.92 (s, 3H; OCH_3), 2.52 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.30 (t, ^3J(H,H) = 6.6 Hz, 2H; CH_2), 2.23 (s, 3H; CH_3), 1.70–1.50 (m, 2H; CH_2), 1.40–1.10 (m, 8H; 4CH_2), 0.84 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3), 0.76 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 167.11, 150.19, 145.45, 139.88, 129.52, 129.22, 127.95, 121.40, 118.68, 52.02, 32.36, 31.38, 28.47, 26.34, 23.18, 22.29, 22.27, 13.93, 13.72, 11.61; IR (neat): $\tilde{\nu}$ = 1728 (C=O), 1612, 1276, 774 cm^{-1}; MS (70 eV): *m/z* (%): 342 (6.67) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{22}H_{30}O_3$: 342.2195; found: 342.2188.

2-Pentyl-3-(*E*-2′-methoxycarbonylethenyl)-4-butyl-5-methylfuran (3ke): The reaction of **1k** (166 mg, 0.8 mmol) with methyl (*E*)-3-iodopropenoate (106 mg, 0.5 mmol) afforded **3ke** (94 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, ^3J(H,H) = 16.2 Hz, 1H; COC=CH), 5.97 (d, ^3J(H,H) = 16.2 Hz, 1H; COCH=C), 3.70 (s, 3H; OCH_3), 2.60 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 2.35 (t, ^3J(H,H) = 6.9 Hz, 2H; CH_2), 2.10 (s, 3H; CH_3), 1.60–1.40 (m, 2H; CH_2), 1.40–1.10 (m, 8H; 4CH_2), 0.85 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 0.82 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 168.34, 157.36, 146.74, 136.66, 117.97, 116.25, 114.13, 51.41, 32.00, 31.73, 28.20, 26.67, 23.90, 22.39, 22.35, 13.94, 13.89, 11.20; IR (neat): $\tilde{\nu}$ = 1722 (C=O), 1640 (C=C), 1626, 1169 cm^{-1}; MS (70 eV): *m/z* (%): 292 (31.33) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{18}H_{28}O_3$: 292.2039; found: 292.2054.

2-Pentyl-3-(4′-methoxyphenyl)-4-butyl-5-methylfuran (3kf): The reaction of **1k** (208 mg, 1.0 mmol) with *p*-methoxyphenyl iodide (117 mg, 0.5 mmol) afforded **3kf** (80 mg, 51%) and **3ka** (39 mg, 27%). **3kf**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.15$ (d, $^3J(H,H) = 8.7$ Hz, 2H; 2ArH), 6.92 (d, $^3J(H,H) = 8.7$ Hz, 2H; 2ArH), 3.84 (s, 3H; OCH_3), 2.50 (t, $^3J(H,H) = 7.5$ Hz, 2H; CH_2), 2.28 (t, $^3J(H,H) = 7.5$ Hz, 2H; CH_2), 2.24 (s, 3H; CH_3), 1.60–1.50 (m, 2H; CH_2), 1.30–1.10 (m, 8H; 4CH_2), 0.86 (t, $^3J(H,H) = 6.6$ Hz, 3H; CH_3), 0.79 (t, $^3J(H,H) = 7.8$ Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 158.12$, 149.52, 144.76, 130.52, 126.93, 121.68, 119.20, 113.59, 55.16, 32.45, 31.49, 28.64, 26.33, 23.26, 22.37, 22.36, 13.99, 13.80, 11.70; IR (neat): $\tilde{\nu} = 1590$, 1512, 1246, 1174, 734 cm^{-1}; MS (70 eV): *m/z* (%): 292 (31.33) [M^+], 43 (100) [$C_3H_7^+$]; HRMS: calcd for $C_{21}H_{30}O_2$: 314.2246; found: 314.2220.

2-Butyl-3-phenyl-4-pentyl-5-methylfuran (3la): The reaction of **1l** (208 mg, 1.0 mmol) with iodobenzene (408 mg, 2.0 mmol) afforded **3la** (196 mg, 69%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42–7.16$ (m, 5H; C_6H_5), 2.54 (t, $^3J(H,H) = 8.0$ Hz, 2H; CH_2), 2.29 (t, $^3J(H,H) = 7.3$ Hz, 2H; CH_2), 2.25 (s, 3H; CH_3), 1.70–1.50 (m, 2H; CH_2), 1.40–1.10 (m, 8H; 4CH_2), 0.87 (t, $^3J(H,H) = 7.3$ Hz, 3H; CH_3), 0.87 (t, $^3J(H,H) = 6.7$ Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 149.66$, 144.95, 134.71, 129.51, 128.16, 126.30, 122.23, 119.13, 31.48, 31.09, 29.86, 26.09, 23.48, 22.38, 22.27, 13.93, 13.81, 11.69; IR (neat): $\tilde{\nu} = 2929$, 1608, 1585, 1496 cm^{-1}; MS (70 eV): *m/z* (%): 284 (53.14) [M^+], 241 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{20}H_{28}O$: 284.2140; found: 284.2180.

2,4-Dipentyl-3-phenyl-5-methylfuran (3ma): The reaction of **1m** (222 mg, 1.0 mmol) with iodobenzene (408 mg, 2.0 mmol) afforded **3ma** (176 mg, 59%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42–7.16$ (m, 5H; C_6H_5), 2.51 (t, $^3J(H,H) = 7.3$ Hz, 2H; CH_2), 2.28 (t, $^3J(H,H) = 7.3$ Hz, 2H; CH_2), 2.25 (s, 3H; CH_3), 1.70–1.50 (m, 2H; CH_2), 1.40–1.10 (m, 10H; 5CH_2), 0.84 (t, $^3J(H,H) = 6.7$ Hz, 3H; CH_3), 0.78 (t, $^3J(H,H) = 7.3$ Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 149.92$, 145.18, 134.94, 129.73 (2C), 128.38 (2C), 126.53, 122.43, 119.36, 31.71 (2C), 30.08, 30.03, 26.56, 23.71, 22.60, 22.50, 14.20, 14.17, 11.94; IR (neat): $\tilde{\nu} = 2929$, 1608, 1585, 1495, 759, 701 cm^{-1}; MS (70 eV): *m/z* (%): 298 (48.06) [M^+], 241 (100) [$M^+ - C_4H_9$]; HRMS: calcd for $C_{21}H_{30}O$: 298.2297; found: 298.2262.

2-Butyl-3-phenyl-4-pentyl-5-*iso*propylfuran (3na): The reaction of **1n** (236 mg, 1.0 mmol) with iodobenzene (408 mg, 2.0 mmol) afforded **3na** (187 mg, 60%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42–7.16$ (m, 5H; C_6H_5), 3.00 (7, $^3J(H,H) = 6.7$ Hz, 1H; CH), 2.54 (t, $^3J(H,H) = 7.3$ Hz, 2H; CH_2), 2.30 (t, $^3J(H,H) = 7.3$ Hz, 2H; CH_2), 1.70–1.56 (m, 2H; CH_2), 1.40–1.00 (m, 8H; 4CH_2), 1.28 (d, $^3J(H,H) = 6.7$ Hz, 6H; 2CH_3), 0.86 (t, $^3J(H,H) = 7.3$ Hz, 3H; CH_3), 0.78 (t, $^3J(H,H) = 6.7$ Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 153.29$, 149.39, 134.93, 129.55, 128.11, 126.21, 121.89, 117.03, 31.58, 30.95, 30.39, 26.25, 26.12, 23.30, 22.36, 22.28, 21.91, 13.91, 13.81; IR (neat): $\tilde{\nu} = 1608$, 1583, 701 cm^{-1}; MS (70 eV): *m/z* (%): 312 (41.07) [M^+], 269 (100) [$M^+ - C_3H_7$]; HRMS: calcd for $C_{22}H_{32}O$: 312.2453; found: 312.2458.

2-(2′-Methylbutyl)-3-phenyl-4-pentyl-5-methylfuran (3oa): The reaction of **1o** (222 mg, 1.0 mmol) with iodobenzene (408 mg, 2.0 mmol) afforded **3oa** (201 mg, 67%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42–7.16$ (m, 5H; C_6H_5), 2.53 (dd, $^2J(H,H) = 14.7$, $^3J(H,H) = 6.1$ Hz, 1H; CH), 2.32 (t, $^2J(H,H) = 14.7$, $^3J(H,H) = 7.9$ Hz, 1H; CH), 2.28 (t, $^3J(H,H) = 6.7$ Hz, 2H; CH_2), 2.25 (s, 3H; CH_3), 1.76–1.62 (m, 1H; CH), 1.40–1.00 (m, 8H; 4CH_2), 0.90–0.70 (m, 9H; 3CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 148.86$, 144.96, 134.81, 129.65, 128.15, 126.27, 123.24, 119.12, 34.52, 33.32, 31.48, 29.83, 29.20, 23.44, 22.27, 19.15, 13.93, 11.72, 11.38; IR (neat): $\tilde{\nu} = 1608$, 1495, 759, 701 cm^{-1}; MS (70 eV): *m/z* (%): 298 (32.58) [M^+], 241 (100) [$M^+ - C_4H_9$]; HRMS: calcd for $C_{21}H_{30}O$: 298.2297; found: 298.2254.

2-(4′-Methylphenyl)-3-butyl-4-(4″-methoxycarbonylphenyl)-5-pentylfuran (3pc): Treatment of **1p** (400 mg, 1.41 mmol) with **2c** (200 mg, 0.76 mmol) afforded **3pc** (285 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.03$ (d, $^3J(H,H) = 8.3$ Hz, 2H, 2ArH), 7.47 (d, $^3J(H,H) = 8.3$ Hz, 2H; 2ArH), 7.01 (d, $^3J(H,H) = 8.3$ Hz, 2H; 2ArH), 7.60 (d, $^3J(H,H) = 8.3$ Hz, 2H; 2ArH), 3.88 (s, 3H; OCH_3), 2.60–2.45 (m, 4H; 2CH_2), 2.32 (s, 3H; CH_3), 1.66–1.54 (m, 2H; CH_2), 1.38–1.08 (m, 8H; 4CH_2), 0.79 (t, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 0.69 (t, $^3J(H,H) = 7.2$ Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 167.06$, 151.43, 146.99, 139.33, 136.34, 129.64, 129.56, 129.17, 129.07, 128.32, 125.34, 123.32, 120.68, 52.07, 31.96, 31.35, 28.31, 26.38, 23.79, 22.53, 22.29, 21.19, 13.94, 13.64; IR (neat): $\tilde{\nu} = 1726$ (C=O), 1610, 1510 cm^{-1}; MS (70 eV): *m/z* (%): 418 (64.57) [M^+], 362 (100) [$M^+ - C_4H_8$]; HRMS: calcd for $C_{28}H_{34}O_3$: 418.2508; found: 418.2539.

2-(4′-Trifluoromethylphenyl)-3-butyl-4-(4″-methoxycarbonylphenyl)-5-pentylfuran (3qc): Treatment of **1q** (338 mg, 1.0 mmol) with **2c** (131 mg, 0.5 mmol) afforded **3qc** (50 mg, 21%) as a solid. M.p. 60–61 °C (Et_2O/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.03$ (dt, $^3J(H,H) = 8.5$ Hz, $^6J(H,H) = 1.8$ Hz, 2H; 2ArH), 7.68 (d, $^3J(H,H) = 8.2$ Hz, 2H; 2Ar′H), 7.48 (d, $^3J(H,H) = 8.2$ Hz, 2H; 2Ar′H), 7.37 (dt, $^3J(H,H) = 8.5$ Hz, $^6J(H,H) = 1.8$ Hz, 2H; 2ArH), 3.93 (s, 3H; OCH_3), 2.55 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.42 (td, $^3J(H,H) = 7.3$ Hz, $^6J(H,H) = 1.8$ Hz, 2H; CH_2), 1.60–1.30 (m, 6H; 3CH_2), 1.30–1.10 (m, 4H; 2CH_2), 0.94 (t, $^3J(H,H) = 7.0$ Hz, 3H; CH_3), 0.82 (t, $^3J(H,H) = 6.7$ Hz, 3H; CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 215.19$, 193.77, 166.63, 141.73, 139.53, 133.15 (q, $^2J(C,F) = 32.9$ Hz), 130.06, 129.25, 128.48, 127.35 (q, $^1J(C,F) = 296.3$ Hz), 126.10, 124.84 (q, $^3J(C,F) = 3.8$ Hz), 110.81, 110.06, 52.19, 31.45, 30.37, 30.18, 28.17, 27.48, 22.65, 22.35, 13.95, 13.86; IR (KBr): $\tilde{\nu} = 1724$ (C=O), 1654, 1607, 1326 cm^{-1}; MS (70 eV): *m/z* (%): 472 (9.72) [M^+], 299 (100) [$M^+ - p$-$CF_3C_6H_4CO$]; elemental analysis calcd (%) for $C_{28}H_{31}F_3O_3$: C 71.17, H 6.61; found: C 70.89, H 6.52.

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