Efficient Synthesis of 4-(3′-Furanyl)butenolide Derivatives via Pd^{II}-Catalyzed Oxidative Heterodimeric Cyclization Reaction of 2,3-Allenoic Acids and 1,2-Allenyl Ketones

Shengming Ma* and Zhanqian Yu[a]

Abstract: The oxidative cyclization/dimerization reaction between two classes of allenes with different functionalities was reported to provide an efficient route to polysubstituted 4-(3′-furanyl)-2(5*H*)-furanones, which are not readily available from the known methods. The highly optically active butenolides could be easily formed from the optically active 2,3-allenoic acids, which was obtained conveniently through chiral resolution with optically active amines, that is, cinchonidine or α-methyl benzylamine. A mechanistic study showed that the reaction proceeded via a matched double oxypalladation–reductive elimination process. The Pd^{II} species may be regenerated via the subsequent cyclometallation of two equivalents of 1,2-allenyl ketones with Pd^0 and protonlysis of Pd enolates formed with the in situ generated HCl.

Keywords: allenes • chirality • cyclization • furans • lactones

Introduction

Allenes are a class of compounds with a 1,2-diene functionality possessing two perpendicular π-orbitals showing unique reactivities due to the presence of the axial chirality as well as the substituent-loading capability.[1] At present, a series of preparative useful methodologies are available to access substituted allenes,[2] which can serve as potential precursors for the synthesis of highly complex and strained target molecules of biological and industrial importance.[3,4]

Three reaction patterns were established in the cyclization reactions of functionalized allenes (Scheme 1). One is the uniallene reaction. We[5–6] and others[7–14] have established the transition-metal-catalyzed or mediated cyclization reaction of functionalized allenes for the formation of carbon−carbon bonds as well as carbon−heteroatom bonds leading to cyclic products. The second pattern is the self-dimerization cyclization reactions of functionalized allenes. In this area, three reaction pathways were observed. In the dimeric reactions leading to monocyclic products,[15] the catalyst was regenerated by β-heteroatom elimination for the reactions with allenols, while the dimeric reactions of 1,2-allenyl ketones regenerated the catalyst via protonation.[16,17] Recently, we reported the oxidative self-dimeric cyclization reaction of 2,3-allenoic acids,[18] producing bicyclic bibutenolides, in which the catalyst was regenerated with alkyl iodide and oxygen. The more attractive pattern is dimeric cyclization reaction between two differently functionalized allenes to give interesting compounds with two different cycles in a single step. The formidable challenges are to match the reactivities of two different allenes and regenerate the catalyst. More significantly, optically active products may be formed via the efficient transfer of chirality of allenes.

In a preliminary communication, we described a [Pd(CH$_3$CN)$_2$Cl$_2$]-catalyzed one step methodology for the efficient synthesis of β-(3′-furanyl)butenolides via oxidative cyclization–dimerization reaction of 2,3-allenoic acids and 1,2-allenyl ketones.[19] Here, we wish to present a detailed study on this reaction: the scope of the reaction, mechanism, and the highly efficient chirality transfer leading to optically active butenolides.

Results and Discussion

Optimization of reaction conditions for oxidative dimeric coupling reaction: We studied the Pd^{II}-catalyzed oxidative dimerization cyclization reaction of 2,3-allenoic acid **1a** and 1,2-allenyl ketone **2a** under different reaction conditions. The results are summarized in Table 1 showing that the oxidative dimeric coupling reaction occurred smoothly. These phenomena elucidate that the reactivities of 2,3-allenoic acids and 1,2-allenyl ketones may be well matched. Under the catalysis of 5 mol% [PdCl$_2$(CH$_3$CN)$_2$], the cyclizative

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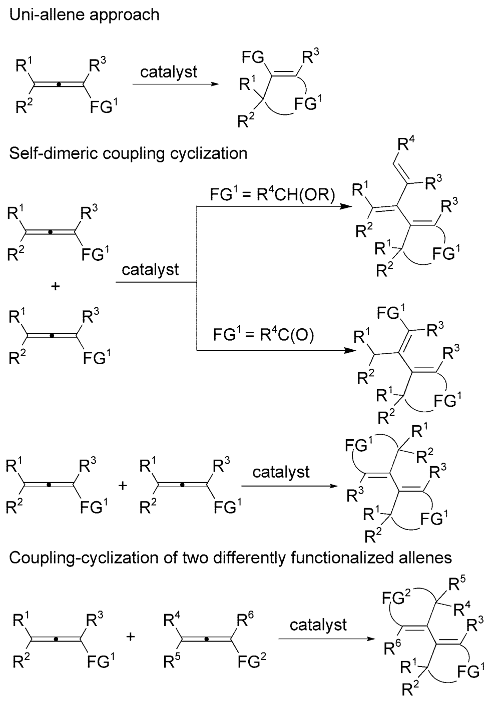
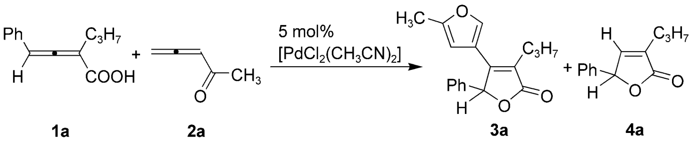


Scheme 1. Three reaction patterns for cyclization of functionalized allenes.

Table 1. Cyclizative cross coupling reaction of **1a** and **2a**.[a]



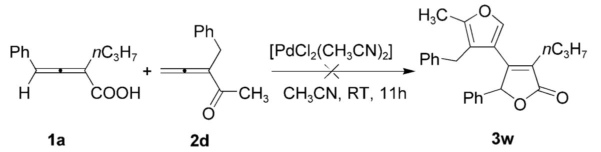
Entry	Solvent	*t* [h]	Yield of **3a** [%]	Yield of **4a** [%]
1	THF	11	14	0
2	CH_2Cl_2	11	23	14
3	acetone	11	40	0
4	toluene	16.5	13	18
5	DMA	17.5	76	0
6	CH_3CN	4	90	0
7[b]	CH_3CN	11.5	57	12
8[c]	CH_3CN	4	90	0
9[d]	CH_3CN	11	0	–

[a] The reaction was carried out in a solvent (3 mL) using **1a** (0.25 mmol), **2a** (1.25 mmol), and 5 mol% $[PdCl_2(CH_3CN)_2]$. [b] 3 equiv **2a** were used. [c] The reaction was carried out in an atmosphere of argon. [d] 1 equiv K_2CO_3 and 1 equiv Bu_4NBr were used.

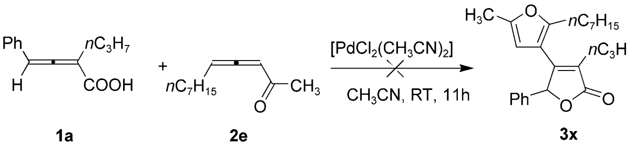
cross coupling reaction of 3-(*n*-propyl)-4-phenyl-2,3-butadienoic acid (**1a**) with five equivalents of 1,2-propdienyl methyl ketone (**2a**) in THF afforded a 14% yield of 3-(*n*-propyl)-4-(3′-(5′-methyl)furanyl)-5-phenyl-2(5*H*)-furanone (**3a**) (Table 1, entry 1). The structure of compound **3a** was confirmed by the X-ray single crystal diffractional analysis (Figure 1).[20]

The reaction can also be carried out in CH_2Cl_2, acetone, toluene, DMA, and CH_3CN. In CH_2Cl_2 or toluene, the major by-product is the cycloisomerization product of **1a**, that is, furanone **4a** (Table 1, entries 2 and 4). The reaction in DMA afforded **3a** in 76% yield highly selectively (Table 1, entry 5). The best results were obtained in CH_3CN (Table 1, entry 6) with 5 equiv **2a**. With less amount of 1,2-propdienyl methyl ketone **2a**, the reaction in CH_3CN also afforded **4a** as the by-product (Table 1, entry 7).

Oxidative dimeric cyclization reaction of 2,3-allenoic acids and 1,2-allenyl ketones: Using these standard conditions, the oxidative dimerization cyclization reaction of various 2,3-allenoic acids bearing different R^1, R^2 and R^3 substituents with different 1,2-allenyl ketones were studied. From the results summarized in Table 2, we observed that the reaction can be furnished under mild conditions (RT, 4 h) and the yields are from moderate to fairly good. It should be noted that this is the first example of oxidative sequential cyclizative cross coupling reaction of two differently functionalized allenes to give interesting bicyclic compounds in a single step. In this reaction, differently substituted 2,3-allenoic acids could be used: monosubstituted 2,3-allenoic acids reacted with the 1,2-allenyl ketones smoothly to give the corresponding products (Table 2, entries 9, 16 and 22); disubstituted 2,3-allenoic acids are more popularly used in this reaction. The substituents of 2,3-allenoic acids could be aryl, alkyl, benzyl and allyl. As a result of the allyl group, further elaboration of the C=C bond may provide an efficient access to other butenolide derivatives (Table 2, entries 4, 13 and 19); with the fully substituted 2,3-allenoic acids, the reaction also afforded the products in fairly good yields (Table 2, entries 8, 15 and 21). Furthermore, the substituent of 1,2-allenyl ketones could be an alkyl or benzyl group. The polysubstituted 1,2-allenyl ketones, however, could not be used to yield the corresponding products probably due to the low reactivity towards oxypalladation [Eqs. (1) and (2)].

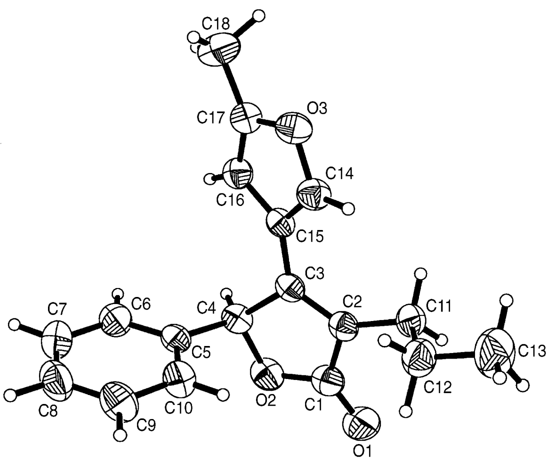


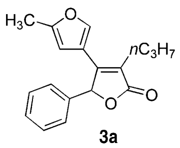
(1)



(2)

Chirality transfer: After matching the reactivities of 2,3-allenoic acids with 1,2-allenyl ketones, we turned our attention to the synthesis of the optically active β-(3′-furanyl)butenolide. From our previous work, we could easily obtain the optically active 2,3-allenoic acids via chiral resolution of 2,3-allenoic acids with optically active amines.[1d] With the optically active (*S*)-(+)-2,3-allenoic acid (**1j**) (99% *ee*) in hand, we examined the oxidative coupling cyclization reaction of 1,2-pentadien-3-one **2a** with **1j** under the standard reaction conditions [Eq. (3)].

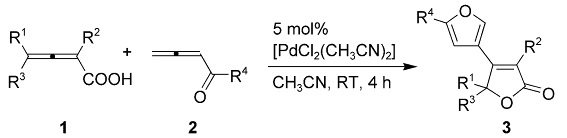




3a

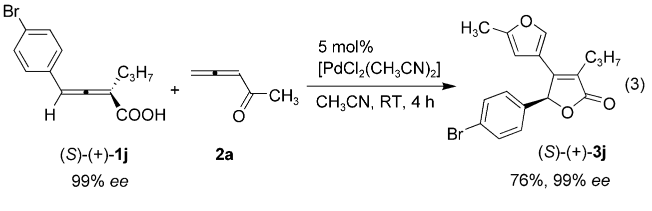
Figure 1. The X-ray structure of compound **3a**.

Table 2. Pd^{II}-Catalyzed cyclizative cross coupling reaction of 2,3-allenoic acids and 1,2-allenyl ketones.[a]



Entry	1			2	3	Yield [%]
	R^1	R^2	R^3	R^4		
1	Ph	nC$_3$H$_7$	H (**1a**)	CH$_3$ (**2a**)	**3a**	90
2	Ph	CH$_3$	H (**1b**)	CH$_3$ (**2a**)	**3b**	73
3	Ph	PhCH$_2$	H (**1c**)	CH$_3$ (**2a**)	**3c**	92
4	Ph	allyl	H (**1d**)	CH$_3$ (**2a**)	**3d**	86
5	α-naphthyl	CH$_3$	H (**1e**)	CH$_3$ (**2a**)	**3e**	84
6	α-naphthyl	nC$_3$H$_7$	H (**1f**)	CH$_3$ (**2a**)	**3f**	86
7	CH$_3$	PhCH$_2$	H (**1g**)	CH$_3$ (**2a**)	**3g**	90
8	Ph	CH$_3$	Et (**1h**)	CH$_3$ (**2a**)	**3h**	85
9	nC$_7$H$_{15}$	H	H (**1i**)	CH$_3$ (**2a**)	**3i**	69
10	4-Br-Ph	nC$_3$H$_7$	H (**1j**)	CH$_3$ (**2a**)	**3j**	70
11	Ph	nC$_3$H$_7$	H (**1a**)	nC$_4$H$_9$ (**2b**)	**3k**	84
12	Ph	CH$_3$	H (**1b**)	nC$_4$H$_9$ (**2b**)	**3l**	63
13	Ph	allyl	H (**1d**)	nC$_4$H$_9$ (**2b**)	**3m**	66
14	α-naphthyl	CH$_3$	H (**1e**)	nC$_4$H$_9$ (**2b**)	**3n**	79
15	Ph	CH$_3$	Et (**1h**)	nC$_4$H$_9$ (**2b**)	**3o**	86
16	nC$_7$H$_{15}$	H	H (**1i**)	nC$_4$H$_9$ (**2b**)	**3p**	69
17	Ph	nC$_3$H$_7$	H (**1a**)	PhCH$_2$ (**2c**)	**3q**	74
18	Ph	CH$_3$	H (**1b**)	PhCH$_2$ (**2c**)	**3r**	86
19	Ph	allyl	H (**1d**)	PhCH$_2$ (**2c**)	**3s**	82
20	α-naphthyl	CH$_3$	H (**1e**)	PhCH$_2$ (**2c**)	**3t**	90
21	Ph	CH$_3$	Et (**1h**)	PhCH$_2$ (**2c**)	**3u**	84
22	nC$_7$H$_{15}$	H	H (**1i**)	PhCH$_2$ (**2c**)	**3v**	71

[a] The reaction was carried out in CH$_3$CN (3 mL) using **1** (0.25 mmol), **2** (1.25 mmol), and 5 mol% [PdCl$_2$(CH$_3$CN)$_2$].



We found that the reaction occurred smoothly to give the product **3j** in a 76% yield and 99% *ee*. This result elucidated that chirality transfer is highly efficient under the standard reaction conditions. The absolute configuration of the product **3j** was determined by the X-ray single crystal diffractional analysis (Figure 2).[21] From (*S*)-(+)-2,3-allenoic acids **1j**, the product **3j** was obtained in *S* configuration, which indicates that the reaction may proceed via the Pd^{II}-mediated oxypalladation rather than the π-allyl Pd-formating carbopalladation mechanism.[23]

Some other typical results are listed in Table 3; the yields ranged from moderate to excellent. The chirality of 2,3-allenoic acids was completely transferred into the products. The absolute configurations of other products were assigned based on the absolute configuration of 2,3-allenoic acids according to the oxypalladation result of (*S*)-**1j** [Eq. (3)].

Mechanism of oxidative dimeric cyclization reaction: Comparing the products with starting materials, we observed that two hydrogen atoms were lost after the reaction. Where had they gone? Two control experiments were conducted to answer this question. In an atmosphere of argon, the reaction occurred smoothly to afford **3a** in 90% yield (Table 1, entry 8), indicating that oxygen does not participate the catalytic cycle. Another interesting point is that the reaction did not yield **3a** in the presence of 1 equiv K$_2$CO$_3$ (Table 1, entry 9), indicating that H$^+$ may be formed from the loss of two protons from both starting materials and plays an important role in this reaction.

Further study shows that the reaction also afforded the homodimerization product of **2a**, (i.e., furan **5a**), 4,5-dimethyleneocta-2,7-dione (**6a**) and its C=C double bond isomers **7a**, and **8a** as the by-products (Scheme 2). The structures of **6a**, **7a** and **8a** were established by the X-ray single crystal diffractional analysis of **8a** (Figure 3),[22] indicating that the missing hydrogens were transferred from starting materials into 2,4-dien-1,6-diketones **6a**, **7a** and **8a**.

Based on these facts, a plausible mechanism is proposed for this reaction (Scheme 3). Firstly, the intermediate **9a** is

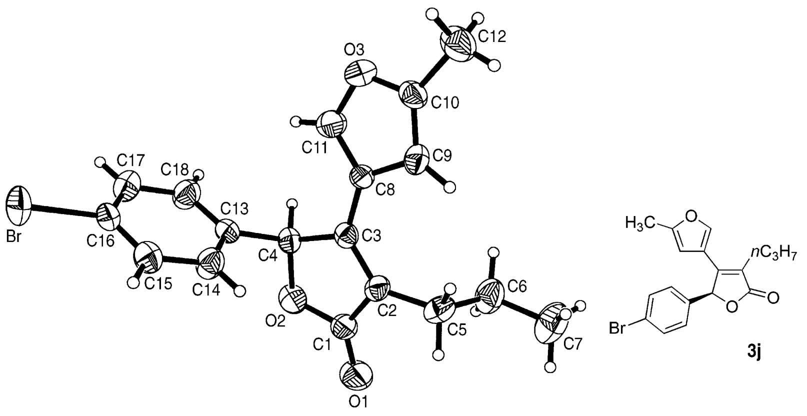
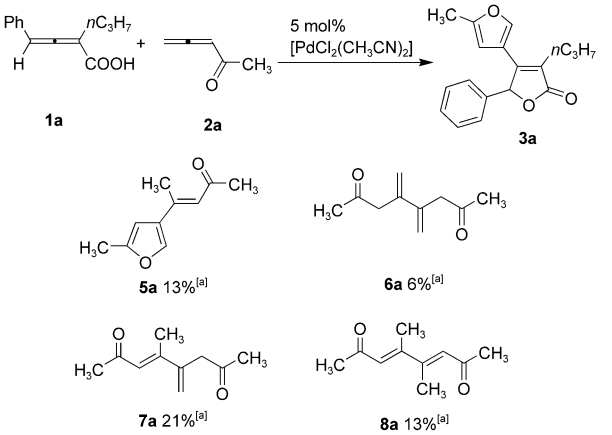


Figure 2. The X-ray structure analysis shows that compound **3j** is in *S* configuration.



Scheme 2. Oxidative cyclization-dimerization reaction of 2,3-allenoic acid **1a** with 1,2-allenyl ketone **2a**. [a] Yields are calculated based on penta-3,4-dienone.

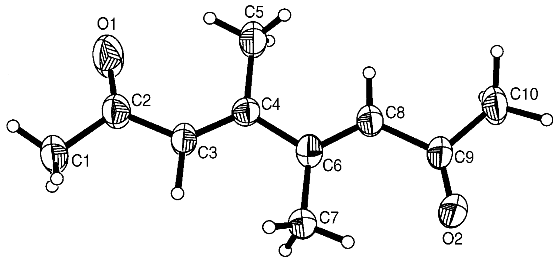
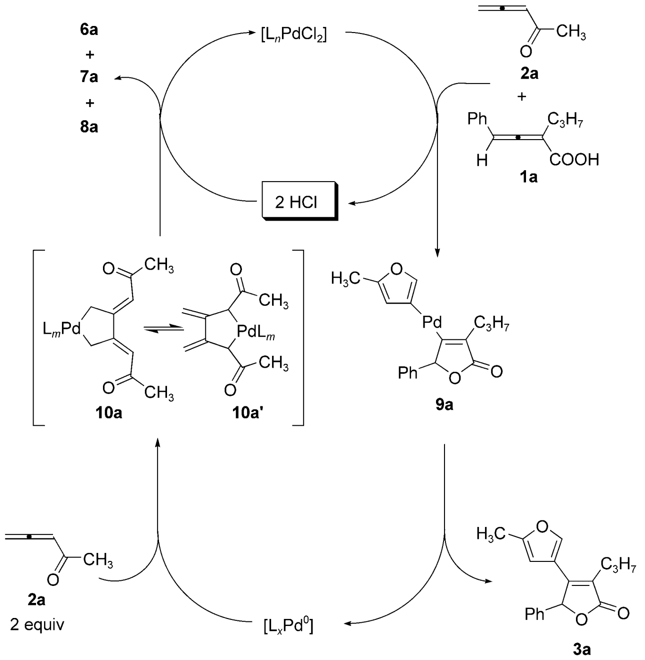


Figure 3. ORTEP drawing of compound **8a**.

formed from the 1,2-allenoic ketone and 2,3-allenoic acids via double oxypalladation, which is further supported by the highly efficient chirality transfer. In our previous work, we observed that the chirality transfer is not efficient in a carbopalladation pathway but very efficient in an oxypalladation pathway.[24] After the reductive elimination of **9a**, the product **3a** is formed along with the Pd^0 species. Then, the Pd^0 species cyclometalate with 2 equiv of penta-3,4-dien-2-one to form the cyclic Pd intermediate **10a** and/or **10a′**,[25] which may be protonated with the in situ generated HCl (2 equiv) to form **6a**, **7a** and **8a** and regenerate L_nPdCl_2 to furnish the catalytic cycle.[26]

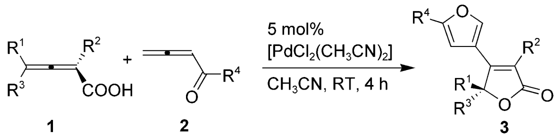


Scheme 3. Proposed catalytic cycle for the oxidative cyclization–dimerization reaction.

Conclusion

We have realized the first example of oxidative cyclization/dimerization reaction between two kinds of allenes with different functionalities providing an efficient route to polysubstituted 4-(3′-furanyl)-2(5*H*)-furanone (**3**), which are not readily available by known method. In this reaction, the chirality transfer was highly efficient. The highly optical active butenolides could be easily formed from the optically active 2,3-allenoic acids, which can be prepared conveniently through chiral resolution of racemic 2,3-allenoic acids with optically active amines. The control experiment showed that the product **3** along with the Pd^0 species may be generated from the reductive elimination of palladium intermediate **9a**. Then the Pd^0 species cyclometalated with 2 equiv alka-1,2-dien-3-one followed by protonation with the in situ generated HCl to regenerate $[L_nPdCl_2]$ to furnish the catalytic

Table 3. Pd^{II}-Catalyzed cross coupling cyclizations of 1,2-allenyl ketones with optically active 2,3-allenoic acids.



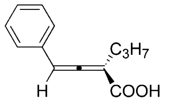
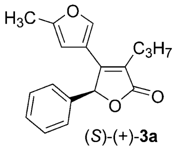
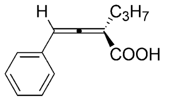
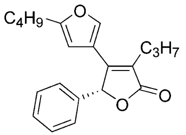
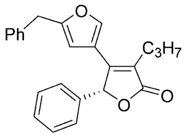
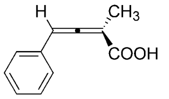
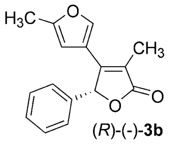
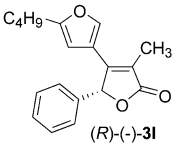
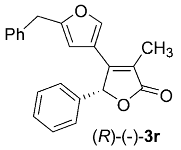
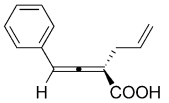
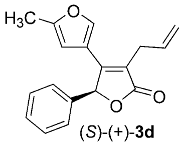
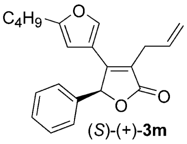
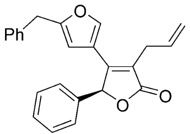
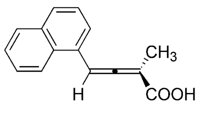
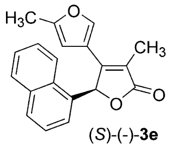
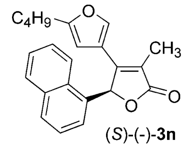
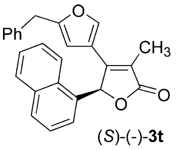
Entry	**1**	**2**	**3**	Yield of **3**	*ee*% of **3**
1	 (*S*)-(+)-**1a** (98% *ee*)	**2a**	 (*S*)-(+)-**3a**	87	95
2	 (*R*)-(−)-**1a** (97% *ee*)	**2b**	 (*R*)-(-)-**3k**	75	>99
3	(*R*)-(−)-**1a** (97% *ee*)	**2c**	 (*R*)-(-)-**3q**	86	>99
4	 (*R*)-(−)-**1b** (99% *ee*)	**2a**	 (*R*)-(-)-**3b**	76	97
5	(*R*)-(−)-**1b** (99% *ee*)	**2b**	 (*R*)-(-)-**3l**	81	99
6	(*R*)-(−)-**1b** (99% *ee*)	**2c**	 (*R*)-(-)-**3r**	72	96
7	 (*S*)-(−)-**1d** (98% *ee*)	**2a**	 (*S*)-(+)-**3d**	73	97
8	(*S*)-(−)-**1d** (98% *ee*)	**2b**	 (*S*)-(+)-**3m**	67	99
9	(*S*)-(−)-**1d** (98% *ee*)	**2c**	 (*S*)-(+)-**3s**	67	98
10	 (*S*)-(+)-**1e** (98% *ee*)	**2a**	 (*S*)-(-)-**3e**	74	97

Table 3. (Continued)

Entry	1	2	3	Yield of **3**	*ee*% of **3**
11	(*S*)-(+)-**1e** (98% *ee*)	**2b**	 (*S*)-(-)-**3n**	76	99
12	(*S*)-(+)-**1e** (98% *ee*)	**2c**	 (*S*)-(-)-**3t**	87	>99

cycle. Synthetic application for target molecules with potential bioactivities is currently being carried out in our laboratory.

Experimental Section

Synthesis of starting materials: Allenoic acids (**1a–j**) were prepared according to the known method by treatment of the acid chlorides with ethyl 2-(triphenylphoranylidene) propionate and subsequent hydrolysis of 2,3-allenoic esters with 1.5 equiv NaOH.[27] The optically active 2,3-allenoic acids was prepared via chiral resolution with optically active amine.[1c]

General procedure for the synthesis of compound 3: [$PdCl_2(CH_3CN)_2$] (5 mol%) was added to a mixture of 2,3-allenoic acids **1** (0.25 mmol), 1,2-allenyl ketones **2** (1.25 mmol) in CH_3CN (3 mL). Then the mixture was stirred at room temperature for 4 h. After evaporation, the residue was purified on a silica gel column to give pure compound **3**.

4-(3′-(5′-Methylfuranyl))-5-phenyl-3-propyl-2(5*H*)-furanone (3a): A mixture of **1a** (50 mg, 0.248 mmol), **2a** (103 mg, 1.26 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 3:1) afforded **3a** as a white solid (63 mg, 90%). M.p. 84–85 °C (ethyl acetate/petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41$–7.21 (m, 5H), 7.18 (s, 1H), 6.04 (s, 1H), 5.89 (s, 1H), 2.55 (t, $J = 8.26$ Hz, 2H), 2.24 (s, 3H), 1.78–1.63 (m, 2H), 1.06 (t, $J = 7.33$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 13.30$, 14.14, 21.39, 26.51, 82.99, 104.77, 118.09, 126.24, 127.86, 129.04, 129.55, 135.85, 141.42, 150.37, 153.82, 174.30; MS (70 eV): *m/z* (%): 283 (28.39) [M^++H], 282 (100) [M^+]; IR (neat): $\tilde{\nu} =$ 2960, 2920, 1732, 1654, 1603 cm^{-1}; elemental analysis calcd for $C_{18}H_{18}O_3$ (%): C 76.57, H 6.43; found C 76.46, H 6.45.

3-Methyl-4-(3′-(5′-methylfuranyl))-5-phenyl-2(5*H*)-furanone (3b): A mixture of **1b** (44 mg, 0.253 mmol), **2a** (108 mg, 1.317 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (CH_2Cl_2, then ethyl acetate/petroleum ether 1:2) afforded **3b** as a white solid (47 mg, 73%). M.p. 112–113 °C (ethyl acetate/petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40$–7.35 (m, 3H), 7.30–7.23 (m, 2H), 7.22 (s, 1H), 6.03 (s, 1H), 5.89 (s, 1H), 2.23 (s, 3H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 10.23$, 13.25, 82.99, 104.61, 118.32, 121.50, 127.86, 128.96, 129.54, 135.54, 141.44, 150.37, 153.67, 174.48; MS (70 eV): *m/z* (%): 254 (100) [M^+]; IR (neat): $\tilde{\nu} = 1735$, 1658, 1550, 1498 cm^{-1}; elemental analysis calcd for $C_{16}H_{14}O_3$ (%): C 75.57, H 5.55; found C 75.29, H 5.44.

3-Benzyl-4-(3′-(5′-methylfuranyl))-5-phenyl-2(5*H*)-furanone (3c): A mixture of **1c** (125 mg, 0.5 mmol), **2a** (205 mg, 2.5 mmol) and [$PdCl_2(CH_3CN)_2$] (6 mg, 0.023 mmol) in acetonitrile (5 mL) was stirred at room temperature for 3.5 h. Flash chromatography on silica gel (CH_2Cl_2, then petroleum ether/ethyl acetate 15:1) afforded **3c** as a white solid (151 mg, 92%). M.p. 122–123 °C (petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41$–7.20 (m, 10H), 7.17 (s, 1H), 5.99 (s, 2H), 3.97 (AB, A part of AB, $J = 15.4$ Hz, $\Delta\tilde{\nu} = 18$ Hz, 1H), 3.91 (AB, B part of AB, $J = 15.4$ Hz, $\Delta\tilde{\nu} = 18$ Hz, 1H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 13.16$, 30.10, 83.10, 104.60, 117.77, 124.24, 126.52, 127.76, 127.96, 128.68, 128.96, 129.49, 135.51, 137.51, 141.80, 151.84, 153.81, 174.02; MS (70 eV): *m/z* (%): 331 (28.96) [M^++H], 330 (100) [M^+]; IR (neat): $\tilde{\nu} = 1743$, 1648, 1601, 1585, 1538 cm^{-1}; elemental analysis calcd for $C_{22}H_{18}O_3$ (%): C 79.98, H 5.49; found C 80.27, H 5.57.

3-Allyl-4-(3′-(5′-methylfuranyl))-5-phenyl-2(5*H*)-furanone (3d): A mixture of **1d** (50 mg, 0.25 mmol), **2a** (108 mg, 1.32 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 6 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded **3d** as an oil (60 mg, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40$–7.25 (m, 5H), 7.22 (s, 1H), 6.03–5.90 (m, 3H), 5.22–5.14 (m, 2H), 3.36–3.30 (m, 2H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 13.20$, 28.33, 83.00, 104.68, 116.47, 117.69, 123.06, 127.74, 128.93, 129.49, 132.74, 135.43, 141.70, 151.73, 153.73, 173.76; MS (70 eV): *m/z* (%): 281 (11.13) [M^++H], 280 (79.49) [M^+], 146 (100); IR (neat): $\tilde{\nu} = 1751$, 1655, 1605, 1540, 1455 cm^{-1}; HRMS: *m/z*: calcd for $C_{18}H_{16}O_3$: 280.10995; found: 280.10757.

3-Methyl-4-(3′-(5′-methylfuranyl))-5-(1′-naphthyl)-2(5*H*)-furanone (3e): A mixture of **1e** (56 mg, 0.25 mmol), **2a** (103 mg, 1.256 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 4:1, then CH_2Cl_2) afforded **3e** as a white solid (64 mg, 84%). M.p. 151–152 °C (ethyl acetate/petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.17$ (d, $J = 8.40$ Hz, 1H), 7.81 (t, $J = 9.30$ Hz, 2H), 7.58–7.42 (m, 2H), 7.30 (t, $J = 7.50$ Hz, 1H), 7.19–7.10 (m, 2H), 6.66 (s, 1H), 5.93 (s, 1H), 2.16 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 10.51$, 13.18, 78.86, 104.64, 118.72, 122.32, 122.66, 125.15, 126.06, 126.37, 127.03, 128.89, 130.15, 131.21, 131.92, 133.77, 141.61, 150.20, 153.70, 174.27; MS (70 eV): *m/z* (%): 304 (100) [M^+]; IR (neat): $\tilde{\nu} = 1736$, 1653, 1607, 1600 cm^{-1}; elemental analysis calcd for $C_{20}H_{16}O_3$ (%): C 78.93, H 5.30; found C 78.89, H 5.27.

4-(3′-(5′-Methylfuranyl))-5-(1′-naphthyl)-3-propyl-2(5*H*)-furanone (3f): A mixture of **1f** (126 mg, 0.5 mmol), **2a** (205 mg, 2.5 mmol) and [$PdCl_2(CH_3CN)_2$] (6 mg, 0.023 mmol) in acetonitrile (5 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 5:1) afforded **3f** as an oil (143 mg, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.25$ (d, $J = 8.56$ Hz, 1H), 7.89 (t, $J = 9.17$ Hz, 2H), 7.64–7.50 (m, 2H), 7.38 (t, $J = 7.95$ Hz, 1H), 7.22 (d, $J = 7.33$ Hz, 1H), 7.17 (s, 1H), 6.74 (s, 1H), 6.03 (s, 1H), 2.68–2.58 (m, 2H), 2.20 (s, 3H), 1.81–1.67 (m, 2H), 1.10 (t, $J = 7.33$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta =$ 13.22, 14.15, 21.23, 26.68, 78.76, 104.60, 118.33, 122.63, 125.17, 126.05, 126.26, 126.98, 127.01, 128.88, 130.09, 131.37, 131.89, 133.74, 141.50, 149.98, 153.76, 174.06; MS (70 eV): *m/z* (%): 333 (15.13) [M^++H], 332 (62.66) [M^+], 84 (100); IR (neat): $\tilde{\nu} = 2960$, 1747, 1651, 1538, 1511 cm^{-1}; HRMS: *m/z*: calcd for $C_{22}H_{20}O_3$: 332.14125; found 332.14557.

3-Benzyl-5-methyl-4-(3′-(5′-methylfuranyl))-2(5*H*)-furanone (3g): A mixture of **1g** (94 mg, 0.5 mmol), **2a** (207 mg, 2.5 mmol) and [$PdCl_2(CH_3CN)_2$] (6 mg, 0.023 mmol) in acetonitrile (5 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1, then CH_2Cl_2) afforded **3g** as an oil (120 mg, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.46$ (s, 1H), 7.35–7.16 (m, 5H), 6.13 (s, 1H), 5.22 (q, $J=6.42$ Hz, 1H), 3.90 (d, $J=15.27$ Hz, 1H), 3.71 (d, $J=15.28$ Hz, 1H), 2.30 (s, 3H), 1.52 (d, $J=6.42$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=13.63$, 20.68, 30.19, 77.96, 104.93, 117.95, 123.35, 126.80, 128.22, 128.98, 137.84, 141.58, 154.69, 155.19, 174.48; MS (70 eV): m/z (%): 269 (2.49) [M^++H], 268 (12.51) [M^+], 43 (100); IR (neat): $\tilde{\nu}=$ 2986, 2934, 1754, 1653, 1603 cm^{-1}; HRMS: m/z: calcd for $C_{17}H_{16}O_3$: 268.10995; found 268.11098.

5-Ethyl-3-methyl-4-(3′-(5′-methylfuranyl))-5-phenyl-2(5*H*)-furanone (3h): A mixture of **1h** (101 mg, 0.5 mmol), **2a** (205 mg, 2.5 mmol) and [$PdCl_2(CH_3CN)_2$] (6 mg, 0.023 mmol) in acetonitrile (5 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 10:1) afforded **3h** as an oil (120 mg, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.33$ (s, 5H), 7.13 (s, 1H), 5.94 (d, $J=1.22$ Hz, 1H), 2.61–2.49 (m, 1H), 2.33–2.19 (m, 4H), 2.11 (s, 3H), 0.81 (t, $J=7.33$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=7.47$, 10.46, 13.53, 28.34, 89.83, 105.34, 118.12, 122.80, 126.53, 128.92, 129.00, 138.74, 141.56, 153.77, 154.53, 174.71; MS (70 eV): m/z (%): 283 (1.68) [M^++H], 282 (11.89) [M^+], 253 (100); IR (neat): $\tilde{\nu}=2977$, 2938, 2879, 1759 cm^{-1}; HRMS: m/z: calcd for $C_{18}H_{18}O_3$: 282.12559; found 282.12471.

5-Heptyl-4-(3′-(5′-methylfuranyl))-2(5*H*)-furanone (3i): A mixture of **1i** (91 mg, 0.5 mmol), **2a** (208 mg, 2.5 mmol) and [$PdCl_2(CH_3CN)_2$] (6 mg, 0.023 mmol) in acetonitrile (5 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 2.5:1) afforded **3i** as an oil (91 mg, 69%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.52$ (s, 1H), 6.15 (d, $J=2.0$ Hz, 1H), 5.96 (d, $J=1.0$ Hz, 1H), 5.18 (dt, $J=7.5$ and 2.2 Hz, 1H), 2.29 (d, $J=1.0$ Hz, 3H), 2.06–1.92 (m, 1H), 1.64–1.51 (m, 1H), 1.42–1.13 (m, 10H), 0.81 (t, $J=7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=13.57$, 14.27, 22.79, 24.32, 29.25, 29.42, 31.88, 34.50, 82.32, 104.79, 112.68, 118.38, 140.96, 154.90, 160.37, 173.47; MS (70 eV): m/z (%): 233 (9.00) [$M^+-C_2H_5$], 107 (100); IR (neat): $\tilde{\nu}=2954$, 2927, 2856, 1751, 1635, 1606 cm^{-1}; elemental analysis calcd for $C_{16}H_{22}O_3$ (%): C 73.25, H 8.45; found C 73.16, H 8.49.

4-(3′-(5′-Methylfuranyl))-5-(4′-bromo-phenyl)-3-propyl-2(5*H*)-furanone (3j): A mixture of **1j** (70 mg, 0.249 mmol), **2a** (103 mg, 1.26 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4.5 h. Flash chromatography on silica gel (petroleum ether/Et_2O 3:1) afforded **3j** as an white solid (63 mg, 70%). M.p. 102–103 °C (ethyl acetate/petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.48$ (d, $J=7.35$ Hz, 2H), 7.20 (s, 1H), 7.12 (d, $J=7.35$ Hz, 2H), 6.01 (s, 1H), 5.85 (s, 1H), 2.58–2.47 (m, 2H), 2.23 (s, 3H), 1.72–1.58 (m, 2H), 1.03 (t, $J=7.20$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=13.30$, 14.10, 21.28, 26.45, 81.98, 104.56, 117.78, 123.60, 126.44, 129.41, 132.18, 134.82, 141.21, 149.80, 153.96, 173.91; MS (70 eV): m/z (%): 362 (99.04) [M^+(^{81}Br)], 360 (100) [M^+(^{79}Br)]; IR (neat): $\tilde{\nu}=1748$, 1735, 1653 cm^{-1}; elemental analysis calcd for $C_{18}H_{17}BrO_3$ (%): C 59.85, H 4.74; found C 59.73, H 4.82.

4-(3′-(5′-Butylfuranyl))-5-phenyl-3-propyl-2(5*H*)-furanone (3k): A mixture of **1a** (50 mg, 0.248 mmol), **2b** (157 mg, 1.27 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 3:1, then CH_2Cl_2) afforded **3k** as an oil (67 mg, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.38$–7.14 (m, 5H), 7.16 (d, $J=1.0$ Hz, 1H), 6.03 (s, 1H), 5.89 (s, 1H), 2.59–2.50 (m, 4H), 1.74–1.63 (m, 2H), 1.58–1.48 (m, 2H), 1.37–1.22 (m, 2H), 1.04 (t, $J=7.4$ Hz, 3H), 0.88 (t, $J=7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=13.65$, 14.08, 21.32, 22.04, 26.43, 27.31, 29.66, 82.93, 103.78, 117.75, 126.10, 127.79, 128.94, 129.46, 135.68, 141.24, 150.30, 158.05, 174.27; MS (70 eV): m/z (%): 324 (4.43) [M^+], 197 (100); IR (neat): $\tilde{\nu}=2959$, 2931, 2872, 1754, 1653, 1600 cm^{-1}; HRMS: m/z: calcd for $C_{21}H_{24}O_3$: 324.17255; found 324.17118.

4-(3′-(5′-Butylfuranyl))-3-methyl-5-phenyl-2(5*H*)-furanone (3l): A mixture of **1b** (44 mg, 0.253 mmol), **2b** (156 mg, 1.258 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (ethyl acetate/petroleum ether 1:5) afforded **3l** as an oil (47 mg, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.42$–7.34 (m, 3H), 7.32–7.22 (m, 2H), 7.20 (s, 1H), 6.04 (s, 1H), 5.90 (s, 1H), 2.53 (t, $J=7.65$ Hz, 2H), 2.15 (s, 3H), 1.60–1.48 (m, 2H), 1.37–1.22 (m, 2H), 0.88 (t, $J=7.20$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=10.25$, 13.65, 22.04, 27.32, 29.67, 83.02, 103.78, 118.11, 121.44, 127.88, 128.95, 129.52, 135.57, 141.38, 150.47, 158.04, 174.51; MS (70 eV): m/z (%): 296 (100) [M^+]; IR (neat): $\tilde{\nu}=1757$, 1656, 1601 cm^{-1}; HRMS: m/z: calcd for $C_{19}H_{20}O_3$: 296.14125; found 296.14227.

3-Allyl-4-(3′-(5′-butylfuranyl))-5-phenyl-2(5*H*)-furanone (3m): A mixture of **1d** (50 mg, 0.25 mmol), **2b** (157 mg, 1.266 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 6:1) afforded **3m** as an oil (53 mg, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.35$–7.19 (m, 5H), 7.16 (s, 1H), 5.99–5.83 (m, 3H), 5.16–5.04 (m, 2H), 3.36–3.18 (m, 2H), 2.47 (t, $J=7.50$ Hz, 2H), 1.53–1.41 (m, 2H), 1.30–1.16 (m, 2H), 0.82 (t, $J=7.20$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=13.65$, 22.03, 27.31, 28.42, 29.65, 83.15, 103.92, 116.57, 117.56, 123.10, 127.83, 129.00, 129.58, 132.84, 135.46, 141.71, 151.93, 158.17, 173.94; MS (70 eV): m/z (%): 322 (9.87) [M^+], 84 (100); IR (neat): $\tilde{\nu}=1755$, 1655, 1600 cm^{-1}; HRMS: m/z: calcd for $C_{21}H_{22}O_3$: 322.15689; found 322.15984.

3-Methyl-4-(3′-(5′-butylfuranyl))-5-(1′-naphthyl)-2(5*H*)-furanone (3n): A mixture of **1e** (58 mg, 0.259 mmol), **2b** (162 mg, 1.306 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded **3n** as an oil (71 mg, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.25$ (d, $J=7.80$ Hz, 1H), 7.90 (t, $J=9.30$ Hz, 2H), 7.66–7.51 (m, 2H), 7.38 (t, $J=7.65$ Hz, 1H), 7.27–7.20 (m, 2H), 6.75 (s, 1H), 6.02 (s, 1H), 2.51 (t, $J=7.50$ Hz, 2H), 2.24 (s, 3H), 1.57–1.45 (m, 2H), 1.34–1.20 (m, 2H), 0.86 (t, $J=7.20$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=10.53$, 13.62, 22.00, 27.27, 29.63, 78.90, 103.83, 118.53, 122.27, 122.71, 125.15, 126.07, 126.39, 127.02, 128.90, 130.15, 131.26, 131.94, 133.79, 141.58, 150.31, 158.09, 174.33; MS (70 eV): m/z (%): 346 (100) [M^+]; IR (neat): $\tilde{\nu}=1751$, 1656, 1598 cm^{-1}; HRMS: m/z: calcd for $C_{23}H_{22}O_3$: 346.15689; found 346.15762.

4-(3′-(5′-Butylfuranyl))-5-ethyl-3-methyl-5-phenyl-2(5*H*)-furanone (3o): A mixture of **1h** (50 mg, 0.248 mmol), **2b** (153 mg, 1.23 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 3:1, then CH_2Cl_2) afforded **3o** (69 mg, 86%) as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.38$–7.29 (m, 5H), 7.13 (s, 1H), 5.96 (s, 1H), 2.60–2.47 (m, 3H), 2.31–2.19 (m, 1H), 2.11 (s, 3H), 1.61–1.50 (m, 2H), 1.38–1.24 (m, 2H), 0.89 (t, $J=7.2$ Hz, 3H), 0.81 (t, $J=7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=7.53$, 10.52, 13.99, 22.42, 27.68, 28.43, 30.00, 89.75, 104.49, 117.91, 122.80, 126.56, 128.88, 128.96, 138.83, 141.41, 154.51, 158.11, 174.65; MS (70 eV): m/z (%): 325 (6.02) [M^++H], 324 (22.46) [M^+], 295 (100); IR (neat): $\tilde{\nu}=2895$, 2932, 2872, 1751, 1650 cm^{-1}; HRMS: m/z: calcd for $C_{21}H_{24}O_3$: 324.17255; found 324.17509.

4-(3′-(5′-Butylfuranyl))-5-heptyl-2(5*H*)-furanone (3p): A mixture of **1i** (45 mg, 0.247 mmol), **2b** (154 mg, 1.24 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 3:1) afforded **3p** as an oil (52 mg, 69%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.53$ (s, 1H), 6.14 (d, $J=0.7$ Hz, 1H), 5.97 (d, $J=1.4$ Hz, 1H), 5.21–5.15 (m, 1H), 2.60 (t, $J=7.5$ Hz, 2H), 2.07–1.90 (m, 1H), 1.67–1.53 (m, 3H), 1.45–1.14 (m, 12H), 0.9 (t, $J=7.3$ Hz, 3H), 0.82 (t, $J=6.6$ Hz, 3H); ^{13}C NMR ($CDCL_3$, 75.4 MHz): $\delta=13.65$, 13.95, 22.06, 22.48, 24.04, 27.34, 28.92, 29.10, 29.62, 31.57, 34.23, 82.01, 103.59, 112.28, 117.84, 140.54, 158.95, 160.11, 173.16; MS (70 eV): m/z (%): 304 (61.56) [M^+], 206 (100); IR (neat): $\tilde{\nu}=2956$, 2928, 2858, 1751, 1635, 1600 cm^{-1}; HRMS: m/z: calcd for $C_{19}H_{28}O_3$: 304.20385; found 304.20228.

4-(3′-(5′-Benzylfuranyl))-5-phenyl-3-propyl-2(5*H*)-furanone (3q): A mixture of **1a** (50 mg, 0.248 mmol), **2c** (197 mg, 1.25 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et_2O 3:1) afforded **3q** as an oil (66 mg, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.40$–7.15 (m, 11H), 6.08 (d, $J=0.9$ Hz, 1H), 5.88 (s, 1H), 3.90 (s, 2H), 2.53 (t, $J=8.4$ Hz, 2H), 1.73–1.61 (m, 2H), 1.03 (t, $J=7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta=14.36$, 21.61, 26.76, 34.48, 83.26, 105.68, 118.26, 126.79, 127.08, 128.11, 128.86, 129.31, 129.84, 135.92, 137.22, 142.24, 150.41, 156.47, 174.49; MS (70 eV): m/z (%): 358 (5.85) [M^+], 91 (100); IR (neat): $\tilde{\nu}=2961$, 1750, 1653, 1495, 1455 cm^{-1}; HRMS: m/z: calcd for $C_{24}H_{22}O_3$: 358.15689; found 358.15212.

4-(3′-(5′-Benzylfuranyl))-3-methyl-5-phenyl-2(5*H*)-furanone (3r): A mixture of **1b** (44 mg, 0.253 mmol), **2c** (198 mg, 1.253 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (ethyl acetate/petroleum ether 1:5) afforded **3r** (72 mg, 86 %) as an oil. ^{1}H NMR (CDCl$_3$, 300 MHz): δ=7.42–7.14 (m, 11 H), 6.10 (s, 1 H), 5.89 (s, 1 H), 3.90 (s, 2 H), 2.14 (s, 3 H); ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ=10.27, 34.12, 82.99, 105.24, 118.23, 121.72, 126.76, 127.86, 128.53, 128.55, 128.97, 129.58, 135.41, 136.88, 142.06, 150.19, 156.06, 174.43; MS (70 eV): *m/z* (%): 330 (100) [M^+]; IR (neat): $\tilde{\nu}$=1752, 1657, 1601 cm^{-1}; HRMS: *m/z*: calcd for $C_{22}H_{18}O_3$: 330.12559; found 330.12942.

3-Allyl-4-(3′-(5′-benzylfuranyl))-5-phenyl-2(5*H*)-furanone (3s): A mixture of **1d** (31 mg, 0.155 mmol), **2c** (125 mg, 0.791 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (2 mg, 0.0077 mmol) in acetonitrile (2 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded **3s** as an oil (45 mg, 82 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=7.42–7.11 (m, 11 H), 6.05 (s, 1 H), 6.01–5.86 (m, 2 H), 5.18–5.08 (m, 2 H), 3.88 (s, 2 H), 3.38–3.21 (m, 2 H); ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ=28.47, 34.15, 83.10, 105.50, 116.63, 117.74, 123.49, 126.79, 127.83, 128.56, 129.03, 129.61, 132.80, 135.37, 136.87, 142.37, 151.58, 156.20, 173.75; MS (70 eV): *m/z* (%): 356 (83.18) [M^+], 91 (100); IR (neat): $\tilde{\nu}$=1752, 1655, 1601 cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{20}O_3$: 356.14125; found 356.14052.

4-(3′-(5′-Benzylfuranyl))-3-methyl-5-(1′-naphthyl)-2(5*H*)-furanone (3t): A mixture of **1e** (55 mg, 0.246 mmol), **2c** (199 mg, 1.259 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded **3t** as an oil (84 mg, 90 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=8.23 (d, *J*=8.40 Hz, 1 H), 7.90 (t, *J*=9.30 Hz, 2 H), 7.66–7.51 (m, 2 H), 7.39 (t, *J*=7.50 Hz, 1 H), 7.34–7.12 (m, 7 H), 6.74 (s, 1 H), 6.10 (s, 1 H), 3.86 (s, 2 H), 2.23 (s, 3 H); ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ=10.48, 34.03, 78.87, 105.24, 118.63, 122.52, 122.62, 125.14, 126.07, 126.35, 126.68, 127.04, 128.46, 128.49, 128.91, 130.16, 131.14, 131.87, 133.79, 136.84, 142.22, 150.08, 156.09, 174.21; MS (70 eV): *m/z* (%): 380 (100) [M^+]; IR (neat): $\tilde{\nu}$=1749, 1657, 1598 cm^{-1}; HRMS: *m/z*: calcd for $C_{26}H_{20}O_3$: 380.14125; found 380.13813.

4-(3′-(5′-Benzylfuranyl))-5-ethyl-3-methyl-5-phenyl-2(5*H*)-furanone (3u): A mixture of **1h** (50 mg, 0.248 mmol), **2c** (195 mg, 1.24 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et$_2$O 2.5:1) afforded **3u** as an oil (74 mg, 84 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=7.39–7.13 (m, 11 H), 6.03 (d, *J*=0.9 Hz, 1 H), 3.91 (s, 2 H), 2.61–2.49 (m, 1 H), 2.31–2.19 (m, 1 H), 2.10 (s, 3 H), 0.83 (t, *J*=7.2 Hz, 3 H); ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ=7.58, 10.53, 28.42, 34.50, 89.72, 105.98, 118.07, 123.09, 126.56, 127.10, 128.89, 128.91, 128.94, 129.02, 137.27, 138.73, 142.13, 154.27, 156.14, 174.57; MS (70 eV): *m/z* (%): 359 (13.54) [M^++H], 358 (15.81) [M^+], 91 (100); IR (neat): $\tilde{\nu}$=2975, 2937, 1748, 1650, 1599 cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{22}O_3$: 358.15689; found 358.15234.

4-(3′-(5′-Benzylfuranyl))-5-heptyl-2(5*H*)-furanone (3v): A mixture of **1i** (45 mg, 0.247 mmol), **2c** (197 mg, 1.25 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et$_2$O 2.6:1, then CH$_2$Cl$_2$) afforded **3v** as an oil (59 mg, 71 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=7.57 (s, 1 H), 7.38–7.22 (m, 5 H), 6.18 (s, 1 H), 5.98 (d, *J*=1.4 Hz, 1 H), 5.23–5.16 (m, 1 H), 3.98 (s, 2 H), 2.04–1.93 (m, 1 H), 1.68–1.53 (m, 1 H), 1.49–1.13 (m, 10 H), 0.86 (t, *J*=7.1 Hz, 3 H); ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ=14.29, 22.82, 24.41, 29.25, 29.43, 31.91, 34.56, 82.31, 105.42, 113.05, 118.41, 127.20, 128.96, 137.01, 141.45, 157.51, 160.13, 173.34; MS (70 eV): *m/z* (%): 339 (5.52) [M^++H], 338 (23.68) [M^+], 91 (100); IR (neat): $\tilde{\nu}$=2953, 2926, 2856, 1750, 1636, 1597 cm^{-1}; HRMS: *m/z*: calcd for $C_{22}H_{26}O_3$: 338.18819; found 338.18783.

Preparation of optically active 4-(3′-furanyl)-2(5*H*)-furanone 3

(*S*)-(+)-4-(3′-(5′-Methylfuranyl))-5-phenyl-3-propyl-2(5*H*)-furanone (3a): A mixture of (*S*)-(+)-**1a** (50 mg, 0.248 mmol, 98 % *ee*), **2a** (103 mg, 1.26 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et$_2$O 5:1) afforded (*S*)-(+)-**3a** (61 mg, 87 %, 95 % *ee*). (HPLC condition: AD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 80:20); $[\alpha]_{\mathrm{D}}^{20}=+132^{\circ}$ (*c*=1.07, EtOH, *T*=20 °C).

(*R*)-(−)-3-Methyl-4-(3′-(5′-methylfuranyl))-5-phenyl-2(5*H*)-furanone (3b): A mixture of (*R*)-(−)-**1b** (44 mg, 0.253 mmol, 99 % *ee*), **2a** (105 mg, 1.28 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (ethyl acetate/petroleum ether 1:2, then CH$_2$Cl$_2$) afforded (*R*)-(−)-**3b** (49 mg, 76 %, 97 % *ee*). (HPLC condition: AD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 85:15); $[\alpha]_{\mathrm{D}}^{20}=-135^{\circ}$ (*c*=1.145, EtOH, *T*=20 °C).

(*S*)-(+)-3-Allyl-4-(3′-(5′-methylfuranyl))-5-phenyl-2(5*H*)-furanone (3d): A mixture of (*S*)-(−)-**1d** (50 mg, 0.25 mmol, 98 % *ee*), **2a** (104 mg, 1.27 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 6 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded (*S*)-(+)-**3d** (51 mg, 73 %, 97 % *ee*). (HPLC condition: OD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 80:20); $[\alpha]_{\mathrm{D}}^{20}=+70^{\circ}$ (*c*=1.045, CHCl$_3$, *T*=20 °C).

(*S*)-(−)-3-Methyl-4-(3′-(5′-methylfuranyl))-5-(1′-naphthyl)-2(5*H*)-furanone (3e): A mixture of (*S*)-(+)-**1e** (56 mg, 0.25 mmol, 98 % *ee*), **2a** (104 mg, 1.27 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1) afforded (*S*)-(−)-**3e** (56 mg, 74 %, 97 % *ee*). (HPLC condition: OD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 60:40); $[\alpha]_{\mathrm{D}}^{20}=-34^{\circ}$ (*c*=1.635, CHCl$_3$, *T*=20 °C).

(*S*)-(+)-4-(3′-(5′-Methylfuranyl))-5-(4′-bromo-phenyl)-3-propyl-2(5*H*)-furanone (3j): A mixture of (*S*)-(+)-**1j** (43 mg, 0.153 mmol, 99 % *ee*), **2a** (67 mg, 0.817 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (2 mg, 0.0077 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/Et$_2$O 3:1) afforded (*S*)-(+)-**3j** (42 mg, 76 %, 99 % *ee*). (HPLC condition: AD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 95:5); $[\alpha]_{\mathrm{D}}^{20}=+122^{\circ}$ (*c*=0.505, EtOH, *T*=20 °C).

(*R*)-(−)-4-(3′-(5′-Butylfuranyl))-5-phenyl-3-propyl-2(5*H*)-furanone (3k): A mixture of (*R*)-(−)-**1a** (50 mg, 0.248 mmol, 97 % *ee*), **2b** (154 mg, 1.24 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1) afforded (*R*)-(−)-**3k** (60 mg, 75 %, >99 % *ee*). (HPLC condition: OD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH=70/30),$[\alpha]_{\mathrm{D}}^{20}=-56^{\circ}$ (*c*=1.190, CHCl$_3$, *T*=20 °C).

(*R*)-(−)-4-(3′-(5′-Butylfuranyl))-3-methyl-5-phenyl-2(5*H*)-furanone (3l): A mixture of (*R*)-(−)-**1b** (44 mg, 0.253 mmol, 99 % *ee*), **2b** (157 mg, 1.27 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (ethyl acetate/petroleum ether 1:5) afforded (*R*)-(−)-**3l** (61 mg, 81 %, 99 % *ee*). (HPLC condition: OD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 90:10); $[\alpha]_{\mathrm{D}}^{20}=-42^{\circ}$ (*c*=2.540, CHCl$_3$, *T*=20 °C).

(*S*)-(+)-3-Allyl-4-(3′-(5′-butylfuranyl))-5-phenyl-2(5*H*)-furanone (3m): A mixture of (*S*)-(−)-**1d** (50 mg, 0.25 mmol, 98 % *ee*), **2b** (157 mg, 1.27 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 6:1) afforded (*S*)-(+)-**3m** (54 mg, 67 %, 99 % *ee*). (HPLC condition: OD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 90:10); $[\alpha]_{\mathrm{D}}^{20}=+49^{\circ}$ (*c*=1.400, CHCl$_3$, *T*=20 °C).

(*S*)-(−)-3-Methyl-4-(3′-(5′-butylfuranyl))-5-(1′-naphthyl)-2(5*H*)-furanone (3n): A mixture of (*S*)-(+)-**1e** (56 mg, 0.25 mmol, 98 % *ee*), **2b** (160 mg, 1.29 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded (*S*)-(−)-**3n** (66 mg, 76 %, 99 % *ee*). (HPLC condition: AS column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 80:20); $[\alpha]_{\mathrm{D}}^{20}=-39^{\circ}$ (*c*=3.125, CHCl$_3$, *T*=20 °C).

(*R*)-(−)-4-(3′-(5′-Benzylfuranyl))-5-phenyl-3-propyl-2(5*H*)-furanone (3q): A mixture of (*R*)-(−)-**1a** (50 mg, 0.248 mmol, 97 % *ee*), **2c** (198 mg, 1.25 mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 8:1) afforded (*R*)-(−)-**3q** (76 mg, 86 %, >99 % *ee*). (HPLC condition: OD column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 60:40); $[\alpha]_{\mathrm{D}}^{20}=-44^{\circ}$ (*c*=1.785, CHCl$_3$, *T*=20 °C).

(*R*)-(−)-4-(3′-(5′-Benzylfuranyl))-3-methyl-5-phenyl-2(5*H*)-furanone (3r): A mixture of (*R*)-(−)-**1b** (44 mg, 0.253 mmol, 99% *ee*), **2c** (198 mg, 1.253 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (ethyl acetate/petroleum ether 1:3, then CH_2Cl_2) afforded (*R*)-(−)-**3r** (60 mg, 72%, 96% *ee*). (HPLC condition: AS column; rate: 0.7 mL min^{-1}; hexane/*i*PrOH 60:40); $[\alpha]_D^{20} = -35°$ ($c = 2.570$, $CHCl_3$, $T = 20°C$).

(*S*)-(+)-3-Allyl-4-(3′-(5′-benzylfuranyl))-5-phenyl-2(5*H*)-furanone (3s): A mixture of (*S*)-(−)-**1d** (31 mg, 0.155 mmol, 98% *ee*), **2c** (124 mg, 0.785 mmol) and [$PdCl_2(CH_3CN)_2$] (2 mg, 0.0077 mmol) in acetonitrile (2 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded (*S*)-(+)-**3s** (37 mg, 67%, 99% *ee*). (HPLC condition: AS column; rate: 0.7 mL min^{-1};hexane/*i*PrOH 60:40); $[\alpha]_D^{20} = +45°$ ($c = 1.315$, $CHCl_3$, $T = 20°C$).

(*S*)-(−)-3-Methyl-4-(3′-(5′-benzylfuranyl))-5-(1′-naphthyl)-2(5*H*)-furanone (3t): A mixture of (*S*)-(+)-**1e** (56 mg, 0.25 mmol, 98% *ee*), **2c** (200 mg, 1.266 mmol) and [$PdCl_2(CH_3CN)_2$] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded (*S*)-(−)-**3t** (83 mg, 87%, >99% *ee*). (HPLC condition: AS column; rate: 0.7 mL min^{-1}; eluent: hexane/*i*PrOH 60:40); $[\alpha]_D^{20} = -9.7°$ ($c = 2.675$, $CHCl_3$, $T = 20°C$).

4,5-Dimethylene-2,7-octanedione (6a):[28] ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.23$ (s, 2H), 5.15 (s, 2H), 3.40 (s, 4H), 2.16 (s, 6H).

4-Methyl-5-methylene-3-octene-2,7-dione (7a): ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.13$ (s, 1H), 5.69 (s, 1H), 5.38 (s, 1H), 3.37 (s, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta =$ 15.59, 28.68, 32.31, 49.96, 122.44, 124.13, 142.69, 150.17, 199.40, 206.38; IR (neat): $\tilde{\nu} = 1716$, 1683, 1589 cm^{-1}; MS (70 eV): *m*/*z* (%): 166 (0.61) [M^+], 43(100); elemental analysis calcd (%) for $C_{10}H_{14}O_2$: 166.09938; found 166.09793.

4,5-Dimethyl-octa-3,5-diene-2,7-dione (8a):[29] ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.35$ (br, 2H), 2.24 (d, $J = 1.2$ Hz, 6H), 2.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 199.21$, 153.85, 125.59, 32.18, 16.20; MS (70 eV): *m*/*z* (%): 166 (1.89) [M^+], 123 (100); IR (KBr): $\tilde{\nu} = 1678$, 1582, 1418 cm^{-1}.

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[1] For some typical examples of axial chirality transfer, see: a) G. Kresze, L. Kloimstein, W. Runge, *Justus Liebigs Ann. Chem.* **1976**, *64*, 979; b) S. Musierowicz, A. E. Wroblewski, *Tetrahedron* **1978**, *34*, 461; c) S. Ma, S. Wu, *Chem. Commun.* **2001**, 441.

[2] a) B. M. Trost, A. B. Pinkerton, M. Seidel, *J. Am. Chem. Soc.* **2001**, *123*, 12466; b) H. Ohno, K. Miyamura, T. Tanaka, S. Oishi, A. Toda, Y. Takemoto, N. Fujii, T. Ibuka, *J. Org. Chem.* **2002**, *67*, 1359; c) *The Chemistry of the Allenes, Vol. 1* (Ed.: S. R. Landor), Academic, London, **1982**; d) *Allenes in Organic Synthesis* (Eds.: H. F. Schuter, G. M. Coppola), Wiley, New York, **1984**.

[3] a) R. W. Bates, V. Satcharoen, *Chem. Soc. Rev.* **2002**, *31*, 12; b) R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067; c) Y. Yamamoto, U. Radhakrishnan, *Chem. Soc. Rev.* **1999**, *28*, 199.

[4] a) *The Chemistry of Ketenes, Allenes and Related Compounds* (Ed.: S. Patai), Wiley, Chichester, **1980**; b) *The Chemistry of the Allenes, Vol. 2* (Ed.: S. R. Landor), Academic, London, **1982**.

[5] For the recent synthesis of butenolides from 2,3-allenoic acids, see: a) S. Ma, Z. Yu, *Angew. Chem.* **2003**, *115*, 1999; *Angew. Chem. Int. Ed.* **2003**, *42*, 1955; b) S. Ma, Z. Shi, S. Wu, *Tetrahedron: Asymmetry* **2001**, *12*, 193; c) S. Ma, Z. Yu, S. Wu, *Tetrahedron* **2001**, *57*, 1585; for the synthesis of 4-halopyrrol-2(5*H*)-ones, see: d) S. Ma, H. Xie, *Org. Lett.* **2000**, *2*, 3801.

[6] For the cyclization coupling reaction of 2,3-allenols with halides, see: a) S. Ma, S. Zhao, *J. Am. Chem. Soc.* **1999**, *121*, 7943; S. Ma, W. Gao, *Tetrahedron Lett.* **2000**, *41*, 8933; b) for the synthesis of carbocycles, see: S. Ma, S. Zhao, *Org. Lett.* **2000**, *2*, 2495; for the synthesis of polysubstituted furans from 1,2-allenyl ketones, see: c) S. Ma, J. Zhang, *Chem. Commun.* **2000**, 117; S. Ma, L. Li, *Org. Lett.* **2000**, *2*, 941; S. Ma, J. Zhang, L. Lu, *Chem. Eur. J.* **2003**, *9*, 2447.

[7] For catalytic cycloisomerization of allenols, see: a) J. A. Marshall, X. Wang, *J. Org. Chem.* **1990**, *55*, 2995; b) J. A. Marshall, X. Wang, *J. Org. Chem.* **1991**, *56*, 960; c) L. I. Olsson, A. Claesson, *Synthesis* **1979**, 743; d) S. S. Nikam, K. H. Chu, K. K. Wang, *J. Org. Chem.* **1986**, *51*, 745; e) R. Gelin, S. Gelin, M. Albrand, *Bull. Soc. Chim. Fr.* **1972**, 1946; f) J. A. Marshall, C. A. Sehon, *J. Org. Chem.* **1995**, *60*, 5966; g) A. Hoffmann-Roder, N. Krause, *Org. Lett.* **2001**, *3*, 2537.

[8] For catalytic cycloisomerization of 2,3-allenoic acids, see: J. A. Marshall, M. A. Wolf, E. M. Wallace, *J. Org. Chem.* **1997**, *62*, 367.

[9] For the Pd^0-catalyzed coupling-cyclization reaction of allenols with aryl or vinyl halides, see: a) K. Uemura, D. Shiraishi, M. Noziri, Y. Inoue, *Bull. Chem. Soc. Jpn.* **1999**, 1063; b) S.-K. Kang, T.-G. Baik, A. N. Kulak, *Synlett* **1999**, 324; c) S.-K. Kang, T. Yamaguchi, S.-J. Pyun, Y.-T. Lee, T.-G. Baik, *Tetrahedron Lett.* **1998**, *39*, 2127.

[10] For the Ru-catalyzed cyclization reaction of allenols, see: a) E. Yoneda, T. Kaneko, S.-W. Zhang, K. Onitsuka, S. Takahashi, *Org. Lett.* **2000**, *2*, 441; b) B. M. Trost, A. B. Pinkerton, *J. Am. Chem. Soc.* **1999**, *121*, 10842.

[11] For the Pd^0-catalyzed coupling-cyclization reaction of allenic amides with aryl or vinyl halides, see: a) H. Ohno, M. Anzai, A. Toda, S. Ohishi, N. Fujii, T. Tanaka, Y. Takemoto, T. Ibuka, *J. Org. Chem.* **2001**, *66*, 4904; b) S.-K. Kang, K.-J. Kim, *Org. Lett.* **2001**, *3*, 511; c) M. Anzai, A. Toda, H. Ohno, Y. Takemoto, N. Fujii, T. Ibuka, *Tetrahedron Lett.* **1999**, *40*, 7393; d) F. P. J. T. Rutjes, K. C. M. F. Tjen, L. B. Wolf, W. F. J. Karstens, H. E. Schoemaker, H. Hiemstra, *Org. Lett.* **1999**, *1*, 717; e) H. Ohno, A. Toda, Y. Miwa, T. Taga, E. Osawa, Y. Yamaoka, N. Fujii, T. Ibuka, *J. Org. Chem.* **1999**, *64*, 2992.

[12] For the Pd-catalyzed coupling-cyclization reaction of allenic amides with allylic halides, see: a) W. F. J. Karstens, D. Klomp, F. P. J. T. Rutjes, H. Hiemstra, *Tetrahedron* **2001**, *57*, 5123; b) M. Kimura, K. Fugami, S. Tanaka, Y. Tamaru, *J. Org. Chem.* **1992**, *57*, 6377.

[13] For Ag$^+$-catalyzed cycloisomerization of aminoallenes, see: a) M. O. Amombo, A. Hausherr, H.-U. Reissig, *Synlett* **1999**, 1871; b) I. W. Davies, T. Gallagher, R. B. Lamont, D. I. C. Scopes, *J. Chem. Soc. Chem. Commun.* **1992**, 335; c) D. N. A. Fox, D. Lathbury, M. F. Mahon, K. C. Molloy, T. Gallagher, *J. Chem. Soc. Chem. Commun.* **1989**, 1073; d) J. S. Prasad, L. S. Liebeskind, *Tetrahedron Lett.* **1988**, *29*, 4253; e) R. Kinsman, D. Lathbury, P. Vernon, T. Gallagher, *J. Chem. Soc. Chem. Commun.* **1987**, 243.

[14] For Pd-catalyzed cycloisomerization of 2-(allenyl)malonates, see: a) S. Kamijo, Y. Yamamoto, *Tetrahedron Lett.* **1999**, *40*, 1747; M. Meguro, Y. Yamamoto, *J. Org. Chem.* **1999**, *64*, 694; M. Meguro, S. Kamijo, Y. Yamamoto, *Tetrahedron Lett.* **1996**, *37*, 7453; for Pd-catalyzed coupling cyclization of 2-(allenyl)malonates with organic halides, see: b) L. Besson, J. Bazin, J. Gore, B. Cazes, *Tetrahedron Lett.* **1994**, *35*, 2881; M. Ahmar, B. Cazes, J. Gore, *Tetrahedron Lett.* **1985**, *26*, 3795.

[15] a) M. Kimura, S. Tanaka, Y. Tamaru, *J. Org. Chem.* **1995**, *60*, 3764; b) S. Ma, W. Gao, *J. Org. Chem.* **2002**, *67*, 6104.

[16] For dimerization of 1,2-allenyl ketones, see: a) A. S. K. Hashmi, J.-H. Choi, J. W. Bats, *J. Prakt. Chem.* **1999**, *341*, 342; b) A. S. K. Hashmi, T. L. Ruppert, T. Knöfel, J. W. Bats, *J. Org. Chem.* **1997**, *62*, 7295; c) A. S. K. Hashmi, *Angew. Chem.* **1995**, *107*, 1749; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1581; d) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285.

[17] For a recent highlight, see: A. S. K. Hashmi, *Angew. Chem.* **2000**, *112*, 3737; *Angew. Chem. Int. Ed.* **2000**, *39*, 3590.

[18] S. Ma, Z. Yu, *Org. Lett.* **2003**, *5*, 1507.

[19] S. Ma, Z. Yu, *Angew. Chem.* **2002**, *114*, 1853; *Angew. Chem. Int. Ed.* **2002**, *41*, 1775.

[20] X-ray crystal data for compound **3a**: $C_{18}H_{18}O_3$, $M_W = 282.32$, Monoclinic, space group $P2(1)/c$, $Mo_{K\alpha}$, final R indices $[I > 2\sigma(I)]$, $R1 = 0.0433$, $wR2 = 0.1145$, $a = 8.0816(6)$, $b = 11.2728(8)$, $c = 17.3410(12)$ Å, $\alpha = 90$, $\beta = 103.1590\ (10)$, $\gamma = 90°$, $V = 1538.32(19)$ Å^3, $T = 293(2)$ K, $Z = 4$, reflections collected/unique: 9159/3553 ($R_{int} = 0.0324$), no observation $[I > 2\sigma(I)]$ 2456, parameters 262.
CCDC-210552 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[21] X-ray crystal data for compound (*S*)-(+)-**3j**: $C_{18}H_{17}BrO_3$, $M_W = 361.23$, monoclinic, space group $P2(1)$, $Mo_{K\alpha}$, final R indices $[I > 2\sigma(I)]$, $R1 = 0.0593$, $wR2 = 0.1449$, $a = 5.0626(9)$, $b = 13.984(3)$, $c = 11.860(2)$ Å, $\alpha = 90$, $\beta = 92.835(4)$, $\gamma = 90°$, $V = 838.6(3)$ Å^3, $T = 293(2)$ K, $Z = 2$, reflections collected/unique: 5033/3558 ($R_{int} = 0.1186$), no observation $[I > 2\sigma(I)]$ 1617, parameters 205.
CCDC-210551 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[22] X-ray crystal data for compound **8a**: $C_{10}H_{14}O_2$, $M_W = 166.21$, monoclinic, space group $C2/c$, $Mo_{K\alpha}$, final R indices $[I > 2\sigma(I)]$, $R1 = 0.0697$, $wR2 = 0.1869$, $a = 14.336(4)$, $b = 12.844(4)$, $c = 10.683(3)$ Å, $\alpha = 90$, $\beta = 90.999(7)$, $\gamma = 90°$, $V = 1966.8(9)$ Å^3, $T = 293(2)$ K, $Z = 8$, reflections collected/unique: 5830/2222 ($R_{int} = 0.1917$), no observation $[I > 2\sigma(I)]$ 567, parameters 133.
CCDC-210550 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[23] S. Ma, W. Gao, *Synlett* **2002**, 65.

[24] S. Ma, Z. Shi, *Chem. Commun.* **2002**, 540.

[25] For the Pd^0 species cyclometallate with two allenes to form the cyclic Pd intermediate, see: a) C. H. Oh, H. S. Yoo, S. H. Jung, *Chem. Lett.* **2001**, 1288; b) M. Arisawa, T. Sugihara, M. Yamaguchi, *Chem. Commun.* **1998**, 2615; c) R. Grigg, N. Kongkathip, B. Kongkathip, S. Luangkamin, H. A. Dondas, *Tetrahedron* **2001**, *57*, 7965.

[26] For protonolysis of Pd enolate to regenerate divalent palladium, see: a) Z. Wang, X. Lu, *J. Org. Chem.* **1996**, *61*, 2254; b) G. Liu, X. Lu, *Org. Lett.* **2001**, *3*, 3879; c) A. Lei, X. Lu, *Org. Lett.* **2000**, *2*, 2699; d) X. Xie, X. Lu, *Synlett* **2000**, 707; e) H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2003**, *125*, 2056.

[27] For the synthesis of allenoic acids, see: H. J. Bestmann, H. Hartung, *Chem. Ber.* **1966**, *99*, 1198.

[28] L. S. Hegedus, R. J. Perry, *J. Org. Chem.* **1985**, *50*, 4955.

[29] M. Franck-Neumann, M. Sedrati, M. Mokhi, *Angew. Chem.* **1986**, *98*, 1138; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1131.

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