

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

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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-allenic acids, which was obtained conveniently through chiral resolution with optically active amines, that is, cinchonidine or α -methyl benzylamine. A mechanistic

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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 Pd⁰ and protonolysis of Pd enolates formed with the in situ generated HCl.

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-allenic 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.

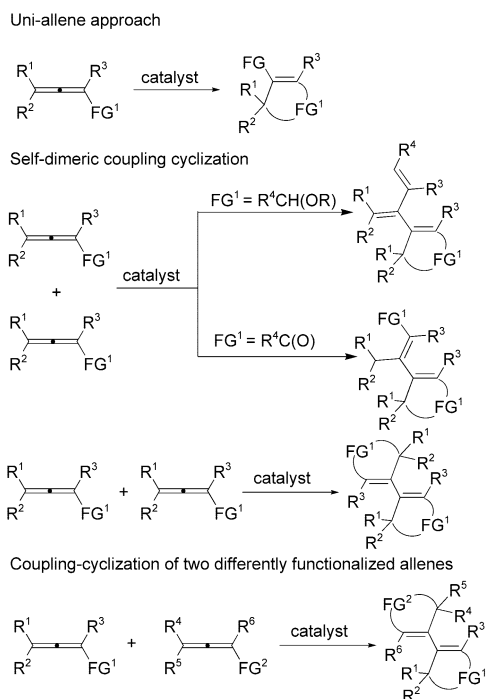
In a preliminary communication, we described a [Pd(CH₃CN)₂Cl₂]-catalyzed one step methodology for the efficient synthesis of β -(3'-furanyl)butenolides via oxidative cyclization–dimerization reaction of 2,3-allenic acids and 1,2-allenyl ketones.^[19] Here, we wish to present a detailed study on this 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-allenic 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-allenic acids and 1,2-allenyl ketones may be well matched. Under the catalysis of 5 mol % [PdCl₂(CH₃CN)₂], the cyclizative

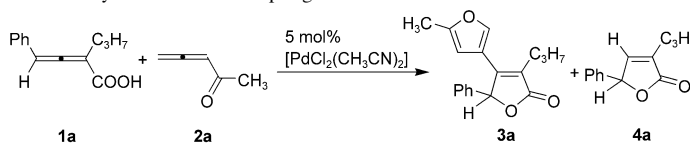
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Scheme 1. Three reaction patterns for cyclization of functionalized allenes.

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



Entry	Solvent	<i>t</i> [h]	Yield of 3a [%]	Yield of 4a [%]
1	THF	11	14	0
2	CH ₂ Cl ₂	11	23	14
3	acetone	11	40	0
4	toluene	16.5	13	18
5	DMA	17.5	76	0
6	CH ₃ CN	4	90	0
7 ^[b]	CH ₃ CN	11.5	57	12
8 ^[c]	CH ₃ CN	4	90	0
9 ^[d]	CH ₃ CN	11	0	–

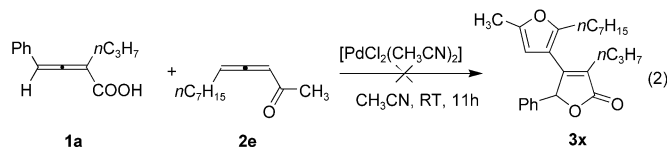
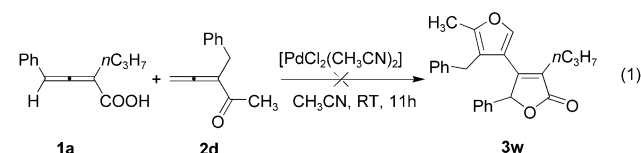
[a] The reaction was carried out in a solvent (3 mL) using **1a** (0.25 mmol), **2a** (1.25 mmol), and 5 mol % [PdCl₂(CH₃CN)₂]. [b] 3 equiv **2a** were used. [c] The reaction was carried out in an atmosphere of argon. [d] 1 equiv K₂CO₃ and 1 equiv Bu₄NBr were used.

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

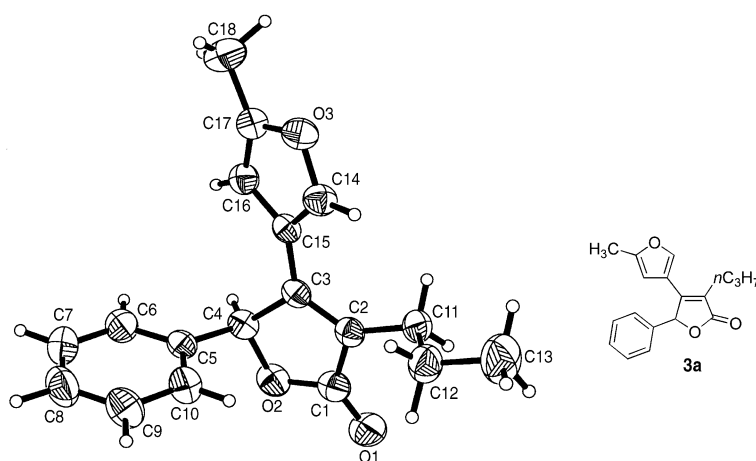
The reaction can also be carried out in CH₂Cl₂, acetone, toluene, DMA, and CH₃CN. In CH₂Cl₂ or toluene, the major by-product is the cycloisomerization product of **1a**, that is, furanone **4a** (Table 1, entries 2 and 4). The reaction in DMA afforded **3a** in 76% yield highly selectively

(Table 1, entry 5). The best results were obtained in CH₃CN (Table 1, entry 6) with 5 equiv **2a**. With less amount of 1,2-propadienyl methyl ketone **2a**, the reaction in CH₃CN 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 R¹, R² and R³ 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)].

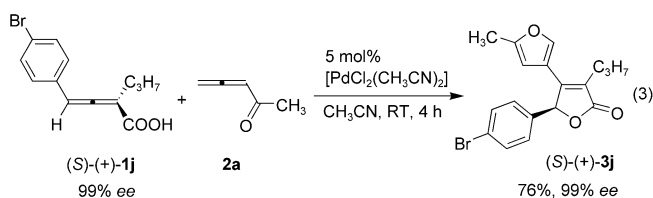


Chirality transfer: After matching the reactivities of 2,3-allenoic acids with 1,2-allenyl ketones, we turned our attention to the synthesis of the optically active β-(3'-furan-2-yl)butenolide. From our previous work, we could easily obtain the optically active 2,3-allenoic acids via chiral resolution 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)].

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	R ¹	R ²	R ³	R ⁴	3	Yield [%]
1	Ph	<i>n</i> C 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	<i>n</i> C 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	<i>n</i> C ₇ H ₁₅	H	H (1i)	CH ₃ (2a)	3i	69
10	4-Br-Ph	<i>n</i> C ₃ H ₇	H (1j)	CH ₃ (2a)	3j	70
11	Ph	<i>n</i> C ₃ H ₇	H (1a)	<i>n</i> C ₄ H ₉ (2b)	3k	84
12	Ph	CH ₃	H (1b)	<i>n</i> C ₄ H ₉ (2b)	3l	63
13	Ph	allyl	H (1d)	<i>n</i> C ₄ H ₉ (2b)	3m	66
14	α -naphthyl	CH ₃	H (1e)	<i>n</i> C ₄ H ₉ (2b)	3n	79
15	Ph	CH ₃	Et (1h)	<i>n</i> C ₄ H ₉ (2b)	3o	86
16	<i>n</i> C ₇ H ₁₅	H	H (1i)	<i>n</i> C ₄ H ₉ (2b)	3p	69
17	Ph	<i>n</i> C 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	<i>n</i> C ₇ H ₁₅	H	H (1i)	PhCH ₂ (2c)	3v	71

[a] The reaction was carried out in CH₃CN (3 mL) using **1** (0.25 mmol), **2** (1.25 mmol), and 5 mol % [PdCl₂(CH₃CN)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 stan-

dard reaction conditions. The absolute configuration of the product **3j** was determined by the X-ray single crystal diffractive 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-forming 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 K₂CO₃ (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 diffractive 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

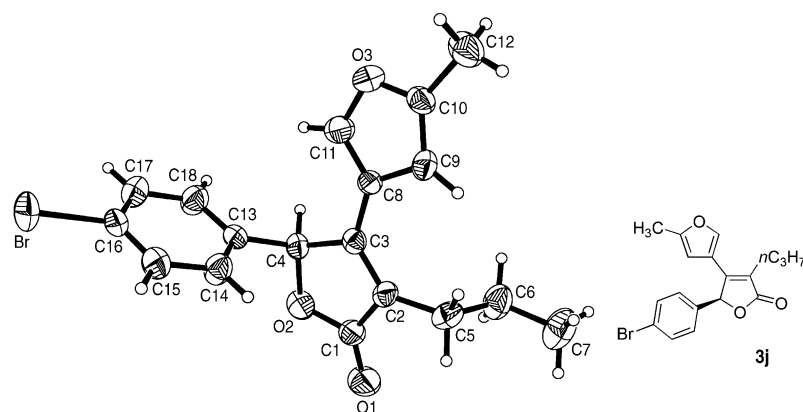
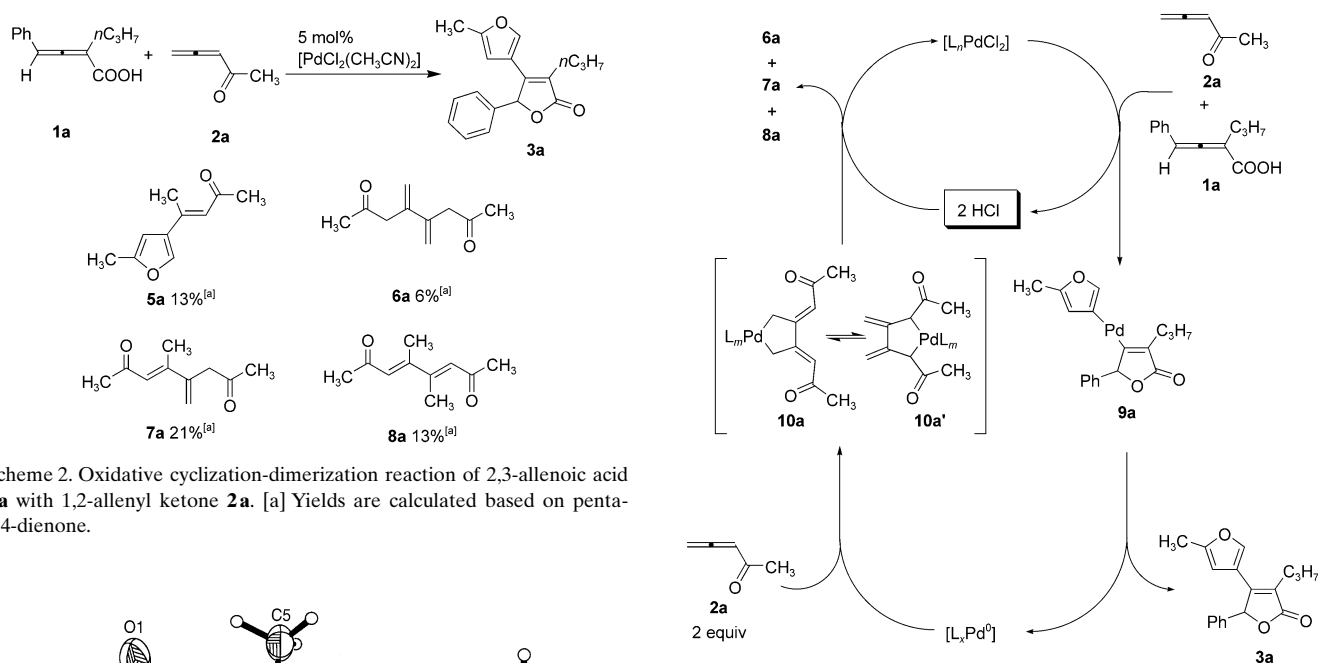


Figure 2. The X-ray structure analysis shows that compound **3j** is in *S* configuration.



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.

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

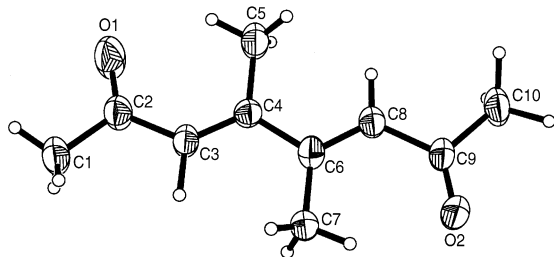


Figure 3. ORTEP drawing of compound **8a**.

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 Pd⁰ species. Then, the Pd⁰ 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_nPdCl₂ to furnish the catalytic cycle.^[26]

Conclusion

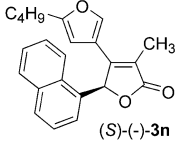
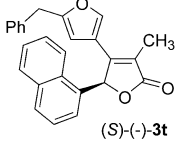
We have realized the first example of oxidative cyclization/dimerization reaction between two kinds of allenes with different functionalities providing an efficient route to polysubstituted 4-(3'-furanyl)-2(5*H*)-furanone (**3**), which are not readily available by known method. In this reaction, the 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 Pd⁰ species may be generated from the reductive elimination of palladium intermediate **9a**. Then the Pd⁰ species cyclometalated with 2 equiv alkyl-1,2-dien-3-one followed by protonation with the in situ generated HCl to regenerate [L_nPdCl₂] to furnish the catalytic

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

Reaction scheme showing the Pd^{II}-catalyzed cross coupling cyclization of 1,2-allenyl ketone **1** and 2,3-allenoic acid **2** to form product **3**. Conditions: 5 mol% [PdCl₂(CH₃CN)₂], CH₃CN, RT, 4 h.

Entry	1	2	3	Yield of 3	<i>ee</i> % of 3
1	 (<i>S</i>)-(+)- 1a (98% <i>ee</i>)	2a	 (<i>S</i>)-(+)- 3a	87	95
2	 (<i>R</i>)-(-)- 1a (97% <i>ee</i>)	2b	 (<i>R</i>)-(-)- 3k	75	> 99
3	(<i>R</i>)-(-)- 1a (97% <i>ee</i>)	2c	 (<i>R</i>)-(-)- 3q	86	> 99
4	 (<i>R</i>)-(-)- 1b (99% <i>ee</i>)	2a	 (<i>R</i>)-(-)- 3b	76	97
5	(<i>R</i>)-(-)- 1b (99% <i>ee</i>)	2b	 (<i>R</i>)-(-)- 3l	81	99
6	(<i>R</i>)-(-)- 1b (99% <i>ee</i>)	2c	 (<i>R</i>)-(-)- 3r	72	96
7	 (<i>S</i>)-(-)- 1d (98% <i>ee</i>)	2a	 (<i>S</i>)-(+)- 3d	73	97
8	(<i>S</i>)-(-)- 1d (98% <i>ee</i>)	2b	 (<i>S</i>)-(+)- 3m	67	99
9	(<i>S</i>)-(-)- 1d (98% <i>ee</i>)	2c	 (<i>S</i>)-(+)- 3s	67	98
10	 (<i>S</i>)-(+)- 1e (98% <i>ee</i>)	2a	 (<i>S</i>)-(-)- 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: Allenol acids (**1a–j**) were prepared according to the known method by treatment of the acid chlorides with ethyl 2-(triphenylphosphoranylidene) propionate and subsequent hydrolysis of 2,3-allenol esters with 1.5 equiv NaOH.^[27] The optically active 2,3-allenol acids was prepared via chiral resolution with optically active amine.^[1c]

General procedure for the synthesis of compound 3: [PdCl₂(CH₃CN)₂] (5 mol%) was added to a mixture of 2,3-allenol acids **1** (0.25 mmol), 1,2-allenyl ketones **2** (1.25 mmol) in CH₃CN (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(5H)-furanone (3a): A mixture of **1a** (50 mg, 0.248 mmol), **2a** (103 mg, 1.26 mmol) and [PdCl₂(CH₃CN)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/Et₂O 3:1) afforded **3a** as a white solid (63 mg, 90%). M.p. 84–85°C (ethyl acetate/petroleum ether); ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₈H₁₈O₃ (%): C 76.57, H 6.43; found C 76.46, H 6.45.

3-Methyl-4-(3'-(5'-methylfuranyl))-5-phenyl-2(5H)-furanone (3b): A mixture of **1b** (44 mg, 0.253 mmol), **2a** (108 mg, 1.317 mmol) and [PdCl₂(CH₃CN)₂] (3 mg, 0.012 mmol) in acetonitrile (3 mL) was stirred at room temperature for 4 h. Flash chromatography on silica gel (CH₂Cl₂, 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); ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₆H₁₄O₃ (%): C 75.57, H 5.55; found C 75.29, H 5.44.

3-Benzyl-4-(3'-(5'-methylfuranyl))-5-phenyl-2(5H)-furanone (3c): A mixture of **1c** (125 mg, 0.5 mmol), **2a** (205 mg, 2.5 mmol) and [PdCl₂(CH₃CN)₂] (6 mg, 0.023 mmol) in acetonitrile (5 mL) was stirred at room temperature for 3.5 h. Flash chromatography on silica gel (CH₂Cl₂, 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); ¹H NMR (CDCl₃, 300 MHz): δ = 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, Δ*ν* = 18 Hz, 1H), 3.91 (AB, B part of AB, *J* = 15.4 Hz, Δ*ν* = 18 Hz, 1H), 2.19 (s, 3H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₂H₁₈O₃ (%): C 79.98, H 5.49; found C 80.27, H 5.57.

3-Allyl-4-(3'-(5'-methylfuranyl))-5-phenyl-2(5H)-furanone (3d): A mixture of **1d** (50 mg, 0.25 mmol), **2a** (108 mg, 1.32 mmol) and [PdCl₂(CH₃CN)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%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₈H₁₆O₃; 280.10995; found: 280.10757.

3-Methyl-4-(3'-(5'-methylfuranyl))-5-(1-naphthyl)-2(5H)-furanone (3e): A mixture of **1e** (56 mg, 0.25 mmol), **2a** (103 mg, 1.256 mmol) and [PdCl₂(CH₃CN)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 CH₂Cl₂) afforded **3e** as a white solid (64 mg, 84%). M.p. 151–152°C (ethyl acetate/petroleum ether); ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₀H₁₆O₃ (%): C 78.93, H 5.30; found C 78.89, H 5.27.

4-(3'-(5'-Methylfuranyl))-5-(1'-naphthyl)-3-propyl-2(5H)-furanone (3f): A mixture of **1f** (126 mg, 0.5 mmol), **2a** (205 mg, 2.5 mmol) and [PdCl₂(CH₃CN)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/Et₂O 5:1) afforded **3f** as an oil (143 mg, 86%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₂H₂₀O₃; 332.14125; found 332.14557.

3-Benzyl-5-methyl-4-(3'-(5'-methylfuranyl))-2(5H)-furanone (3g): A mixture of **1g** (94 mg, 0.5 mmol), **2a** (207 mg, 2.5 mmol) and [PdCl₂(CH₃CN)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 CH₂Cl₂) afforded **3g** as an oil (120 mg,

90%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₇H₁₆O₃: 268.10995; found 268.11098.

5-Ethyl-3-methyl-4-(3'-(5'-methylfuran-2-yl))-5-phenyl-2(5H)-furanone (3h): A mixture of **1h** (101 mg, 0.5 mmol), **2a** (205 mg, 2.5 mmol) and [PdCl₂(CH₃CN)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/Et₂O 10:1) afforded **3h** as an oil (120 mg, 85%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₈H₁₈O₃: 282.12559; found 282.12471.

5-Heptyl-4-(3'-(5'-methylfuran-2-yl))-2(5H)-furanone (3i): A mixture of **1i** (91 mg, 0.5 mmol), **2a** (208 mg, 2.5 mmol) and [PdCl₂(CH₃CN)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/Et₂O 2.5:1) afforded **3i** as an oil (91 mg, 69%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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*⁺-C₂H₅], 107 (100); IR (neat): $\tilde{\nu}$ = 2954, 2927, 2856, 1751, 1635, 1606 cm⁻¹; elemental analysis calcd for C₁₆H₂₂O₃ (%): C 73.25, H 8.45; found C 73.16, H 8.49.

4-(3'-(5'-Methylfuran-2-yl))-5-(4-bromo-phenyl)-3-propyl-2(5H)-furanone (3j): A mixture of **1j** (70 mg, 0.249 mmol), **2a** (103 mg, 1.26 mmol) and [PdCl₂(CH₃CN)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/Et₂O 3:1) afforded **3j** as a white solid (63 mg, 70%). M.p. 102–103 °C (ethyl acetate/petroleum ether); ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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*⁺(⁸¹Br)], 360 (100) [*M*⁺(⁷⁹Br)]; IR (neat): $\tilde{\nu}$ = 1748, 1735, 1653 cm⁻¹; elemental analysis calcd for C₁₈H₁₇BrO₃ (%): C 59.85, H 4.74; found C 59.73, H 4.82.

4-(3'-(5'-Butylfuran-2-yl))-5-phenyl-3-propyl-2(5H)-furanone (3k): A mixture of **1a** (50 mg, 0.248 mmol), **2b** (157 mg, 1.27 mmol) and [PdCl₂(CH₃CN)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/Et₂O 3:1, then CH₂Cl₂) afforded **3k** as an oil (67 mg, 84%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₁H₂₄O₃: 324.17255; found 324.17118.

4-(3'-(5'-Butylfuran-2-yl))-3-methyl-5-phenyl-2(5H)-furanone (3l): A mixture of **1b** (44 mg, 0.253 mmol), **2b** (156 mg, 1.258 mmol) and [PdCl₂(CH₃CN)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%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₉H₂₀O₃: 296.14125; found 296.14227.

3-Allyl-4-(3'-(5'-butylfuran-2-yl))-5-phenyl-2(5H)-furanone (3m): A mixture of **1d** (50 mg, 0.25 mmol), **2b** (157 mg, 1.266 mmol) and [PdCl₂(CH₃CN)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%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₁H₂₂O₃: 322.15689; found 322.15984.

3-Methyl-4-(3'-(5'-butylfuran-2-yl))-5-(1'-naphthyl)-2(5H)-furanone (3n): A mixture of **1e** (58 mg, 0.259 mmol), **2b** (162 mg, 1.306 mmol) and [PdCl₂(CH₃CN)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%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₃H₂₂O₃: 346.15689; found 346.15762.

4-(3'-(5'-Butylfuran-2-yl))-5-ethyl-3-methyl-5-phenyl-2(5H)-furanone (3o): A mixture of **1h** (50 mg, 0.248 mmol), **2b** (153 mg, 1.23 mmol) and [PdCl₂(CH₃CN)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/Et₂O 3:1, then CH₂Cl₂) afforded **3o** (69 mg, 86%) as an oil. ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₁H₂₄O₃: 324.17255; found 324.17509.

4-(3'-(5'-Butylfuran-2-yl))-5-heptyl-2(5H)-furanone (3p): A mixture of **1i** (45 mg, 0.247 mmol), **2b** (154 mg, 1.24 mmol) and [PdCl₂(CH₃CN)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/Et₂O 3:1) afforded **3p** as an oil (52 mg, 69%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₁₉H₂₈O₃: 304.20385; found 304.20228.

4-(3'-(5'-Benzylfuran-2-yl))-5-phenyl-3-propyl-2(5H)-furanone (3q): A mixture of **1a** (50 mg, 0.248 mmol), **2c** (197 mg, 1.25 mmol) and [PdCl₂(CH₃CN)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/Et₂O 3:1) afforded **3q** as an oil (66 mg, 74%). ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 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 C₂₄H₂₂O₃: 358.15689; found 358.15212.

4-(3'-(5'-Benzylfuran-2-yl))-3-methyl-5-phenyl-2(5H)-furanone (3r): A mixture of **1b** (44 mg, 0.253 mmol), **2c** (198 mg, 1.253 mmol) and [PdCl₂(CH₃CN)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. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 7.42–7.14 (m, 11H), 6.10 (s, 1H), 5.89 (s, 1H), 3.90 (s, 2H), 2.14 (s, 3H); $^{13}\text{C NMR}$ (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 $\text{C}_{22}\text{H}_{18}\text{O}_3$: 330.12559; found 330.12942.

3-Allyl-4-(3'-(5'-benzylfuranyl))-5-phenyl-2(5H)-furanone (3s): A mixture of **1d** (31 mg, 0.155 mmol), **2c** (125 mg, 0.791 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 7.42–7.11 (m, 11H), 6.05 (s, 1H), 6.01–5.86 (m, 2H), 5.18–5.08 (m, 2H), 3.88 (s, 2H), 3.38–3.21 (m, 2H); $^{13}\text{C NMR}$ (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 $\text{C}_{24}\text{H}_{20}\text{O}_3$: 356.14125; found 356.14052.

4-(3'-(5'-Benzylfuranyl))-3-methyl-5-(1'-naphthyl)-2(5H)-furanone (3t): A mixture of **1e** (55 mg, 0.246 mmol), **2c** (199 mg, 1.259 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 8.23 (d, J = 8.40 Hz, 1H), 7.90 (t, J = 9.30 Hz, 2H), 7.66–7.51 (m, 2H), 7.39 (t, J = 7.50 Hz, 1H), 7.34–7.12 (m, 7H), 6.74 (s, 1H), 6.10 (s, 1H), 3.86 (s, 2H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (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 $\text{C}_{26}\text{H}_{20}\text{O}_3$: 380.14125; found 380.13813.

4-(3'-(5'-Benzylfuranyl))-5-ethyl-3-methyl-5-phenyl-2(5H)-furanone (3u): A mixture of **1h** (50 mg, 0.248 mmol), **2c** (195 mg, 1.24 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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_2O 2.5:1) afforded **3u** as an oil (74 mg, 84%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 7.39–7.13 (m, 11H), 6.03 (d, J = 0.9 Hz, 1H), 3.91 (s, 2H), 2.61–2.49 (m, 1H), 2.31–2.19 (m, 1H), 2.10 (s, 3H), 0.83 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (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 $\text{C}_{24}\text{H}_{22}\text{O}_3$: 358.15689; found 358.15234.

4-(3'-(5'-Benzylfuranyl))-5-heptyl-2(5H)-furanone (3v): A mixture of **1i** (45 mg, 0.247 mmol), **2c** (197 mg, 1.25 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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_2O 2.6:1, then CH_2Cl_2) afforded **3v** as an oil (59 mg, 71%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 7.57 (s, 1H), 7.38–7.22 (m, 5H), 6.18 (s, 1H), 5.98 (d, J = 1.4 Hz, 1H), 5.23–5.16 (m, 1H), 3.98 (s, 2H), 2.04–1.93 (m, 1H), 1.68–1.53 (m, 1H), 1.49–1.13 (m, 10H), 0.86 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (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 $\text{C}_{22}\text{H}_{26}\text{O}_3$: 338.18819; found 338.18783.

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

(S)-(+)-4-(3'-(5'-Methylfuranyl))-5-phenyl-3-propyl-2(5H)-furanone (3a): A mixture of **(S)-(+)-1a** (50 mg, 0.248 mmol, 98% *ee*), **2a** (103 mg, 1.26 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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_2O 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); $[\alpha]_{\text{D}}^{20}$ = +132° (c = 1.07, EtOH, T = 20°C).

(R)-(–)-3-Methyl-4-(3'-(5'-methylfuranyl))-5-phenyl-2(5H)-furanone (3b): A mixture of **(R)-(–)-1b** (44 mg, 0.253 mmol, 99% *ee*), **2a** (105 mg, 1.28 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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_2Cl_2) afforded **(R)-(–)-3b** (49 mg, 76%, 97% *ee*). (HPLC condition: AD column; rate: 0.7 mL min^{-1} ; hexane/*i*PrOH 85:15); $[\alpha]_{\text{D}}^{20}$ = –135° (c = 1.145, EtOH, T = 20°C).

(S)-(+)-3-Allyl-4-(3'-(5'-methylfuranyl))-5-phenyl-2(5H)-furanone (3d): A mixture of **(S)-(+)-1d** (50 mg, 0.25 mmol, 98% *ee*), **2a** (104 mg, 1.27 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = +70° (c = 1.045, CHCl_3 , T = 20°C).

(S)-(–)-3-Methyl-4-(3'-(5'-methylfuranyl))-5-(1'-naphthyl)-2(5H)-furanone (3e): A mixture of **(S)-(+)-1e** (56 mg, 0.25 mmol, 98% *ee*), **2a** (104 mg, 1.27 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = –34° (c = 1.635, CHCl_3 , T = 20°C).

(S)-(+)-4-(3'-(5'-Methylfuranyl))-5-(4'-bromo-phenyl)-3-propyl-2(5H)-furanone (3j): A mixture of **(S)-(+)-1j** (43 mg, 0.153 mmol, 99% *ee*), **2a** (67 mg, 0.817 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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_2O 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); $[\alpha]_{\text{D}}^{20}$ = +122° (c = 0.505, EtOH, T = 20°C).

(R)-(–)-4-(3'-(5'-Butylfuranyl))-5-phenyl-3-propyl-2(5H)-furanone (3k): A mixture of **(R)-(–)-1a** (50 mg, 0.248 mmol, 97% *ee*), **2b** (154 mg, 1.24 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = –56° (c = 1.190, CHCl_3 , T = 20°C).

(R)-(–)-4-(3'-(5'-Butylfuranyl))-3-methyl-5-phenyl-2(5H)-furanone (3l): A mixture of **(R)-(–)-1b** (44 mg, 0.253 mmol, 99% *ee*), **2b** (157 mg, 1.27 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = –42° (c = 2.540, CHCl_3 , T = 20°C).

(S)-(+)-3-Allyl-4-(3'-(5'-butylfuranyl))-5-phenyl-2(5H)-furanone (3m): A mixture of **(S)-(+)-1d** (50 mg, 0.25 mmol, 98% *ee*), **2b** (157 mg, 1.27 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = +49° (c = 1.400, CHCl_3 , T = 20°C).

(S)-(–)-3-Methyl-4-(3'-(5'-butylfuranyl))-5-(1'-naphthyl)-2(5H)-furanone (3n): A mixture of **(S)-(+)-1e** (56 mg, 0.25 mmol, 98% *ee*), **2b** (160 mg, 1.29 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = –39° (c = 3.125, CHCl_3 , T = 20°C).

(R)-(–)-4-(3'-(5'-Benzylfuranyl))-5-phenyl-3-propyl-2(5H)-furanone (3q): A mixture of **(R)-(–)-1a** (50 mg, 0.248 mmol, 97% *ee*), **2c** (198 mg, 1.25 mmol) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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); $[\alpha]_{\text{D}}^{20}$ = –44° (c = 1.785, CHCl_3 , T = 20°C).

(R)-(-)-4-(3'-(5'-Benzylfuranyl))-3-methyl-5-phenyl-2(5H)-furanone (3r): A mixture of (R)-(-)-**1b** (44 mg, 0.253 mmol, 99% *ee*), **2c** (198 mg, 1.253 mmol) and [PdCl₂(CH₃CN)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 CH₂Cl₂) afforded (R)-(-)-**3r** (60 mg, 72%, 96% *ee*). (HPLC condition: AS column; rate: 0.7 mL min⁻¹; hexane/*i*PrOH 60:40); [α]_D²⁰ = -35° (c = 2.570, CHCl₃, T = 20°C).

(S)-(+)-3-Allyl-4-(3'-(5'-benzylfuranyl))-5-phenyl-2(5H)-furanone (3s): A mixture of (S)-(-)-**1d** (31 mg, 0.155 mmol, 98% *ee*), **2c** (124 mg, 0.785 mmol) and [PdCl₂(CH₃CN)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); [α]_D²⁰ = +45° (c = 1.315, CHCl₃, T = 20°C).

(S)-(-)-3-Methyl-4-(3'-(5'-benzylfuranyl))-5-(1'-naphthyl)-2(5H)-furanone (3t): A mixture of (S)-(+)-**1e** (56 mg, 0.25 mmol, 98% *ee*), **2c** (200 mg, 1.266 mmol) and [PdCl₂(CH₃CN)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); [α]_D²⁰ = -9.7° (c = 2.675, CHCl₃, T = 20°C).

4,5-Dimethylene-2,7-octanedione (6a):^[28] ¹H NMR (CDCl₃, 300 MHz): δ = 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): ¹H NMR (CDCl₃, 300 MHz): δ = 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); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 15.59, 28.68, 32.31, 49.96, 122.44, 124.13, 142.69, 150.17, 199.40, 206.38; IR (neat): ν̄ = 1716, 1683, 1589 cm⁻¹; MS (70 eV): *m/z* (%): 166 (0.61) [M⁺], 43(100); elemental analysis calcd (%) for C₁₀H₁₄O₂: 166.09938; found 166.09793.

4,5-Dimethyl-octa-3,5-diene-2,7-dione (8a):^[29] ¹H NMR (CDCl₃, 300 MHz): δ = 6.35 (br, 2H), 2.24 (d, *J* = 1.2 Hz, 6H), 2.22 (s, 6H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 199.21, 153.85, 125.59, 32.18, 16.20; MS (70 eV): *m/z* (%): 166 (1.89) [M⁺], 123 (100); IR (KBr): ν̄ = 1678, 1582, 1418 cm⁻¹.

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