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Palladium-catalyzed synthesis of 1,3,4-alkatrien-2-yldihydrofurans from 2,3-allenylacetylacetates and propargylic carbonates and their application to synthesize polysubstituted dihydrofurylcyclopentenones

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ABSTRACT

An efficient route to 1,3,4-alkatrien-2-yldihydrofurans via a highly chemo- and regioselective palladium(0)-catalyzed coupling–cyclization reaction of 2-(2′,3′-allenyl)acetylacetates with propargylic carbonates was reported. The reaction proceeded smoothly under neutral conditions, affording the O-attacked five-membered products with a 1,3,4-trienyl substituent exclusively in good to excellent yields. The products can be efficiently applied to the synthesis of polysubstituted 2-(dihydrofuryl)cyclopentenone derivatives via a catalytic Pauson–Khand reaction under ambient conditions.

1. Introduction

Recently, much attention has been paid to the chemistry of allenes, demonstrating their potential in organic synthesis.[1,2] Thus, synthesis of allenes has started to become and will continue to be a hot research topic in organic synthesis.[3,4] For the synthesis of allenes, the palladium-catalyzed reaction of propargylic alcohol derivatives should be one of the most straight forward procedures.[5,6] On the other hand, dihydrofurans are also widely existed in biologically active compounds,[7,8] thus, many new methods have been developed for the efficient synthesis of dihydrofurans.[9,10] To the best of our knowledge, the synthesis of molecules with such two important structural cores has not been nicely explored.[11] As a part of our research program toward the synthesis[12] and the transition-metal-catalyzed coupling cyclization of functionalized allenes,[1f,k] we wish to report an efficient construction of 1,3,4-alkatrien-2-yldihydrofuran derivatives from palladium-catalyzed coupling cyclization of 2,3-allenylacetylacetates and propargylic carbonates with exclusive chemo- and regioselectivity.

2. Results and discussion

On the basis of our previous work on the palladium-catalyzed reaction of (2,3-allenyl)malonates with propargylic carbonates forming 1,3,4-alkatrien-2-ylcyclopropane derivatives exclusively,[13] we envisioned that Pd(0)-catalyzed cyclization of propargylic carbonates with (2,3-allenyl)acetylacetates may form 1,3,4-alkatrien-2-yl 4,5-dihydrofurans, 2,5-dihydroxepines, cyclopropanes, or cyclopentenes via the intramolecular attack of the enolate intermediate (Scheme 1).

We started our investigation with the reaction employing **1a** and **2a** catalyzed by 5 mol % $Pd(PPh_3)_4$ and 10 mol % TBAI in CH_3CN at 80 °C. To our delight, 1,3,4-alkatrien-2-yldihydrofuran **3aa** was obtained in 87% yield as the only product through highly chemo- and regioselective O-attacked at the π-allylic species (entry 1, Table 1). The formation of O-attacked seven-membered product **4aa** and the *C*-attacked products **5aa** and **6aa** were not observed. Further investigation on the solvent effect revealed that the reaction proceeded smoothly to afford the desired product **3aa** within a short period of time in all the tested aprotic solvents (entries 1, 2 and 4–8, Table 1) except DCE (entry 3, Table 1): THF gave the best result, affording the product **3aa** in 95% isolated yield (entry 4, Table 1). The reaction only gave complicated results in protic solvents such as MeOH or HOAc (entries 9 and 10, Table 1).

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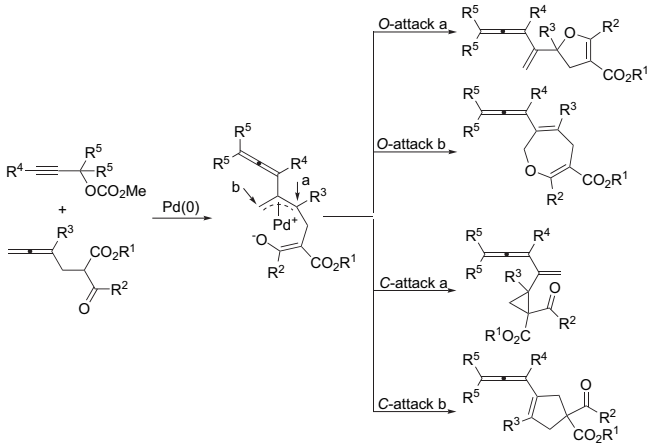
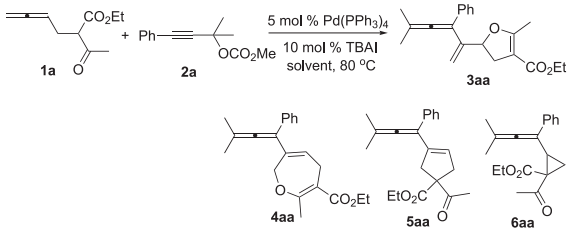


Scheme 1.

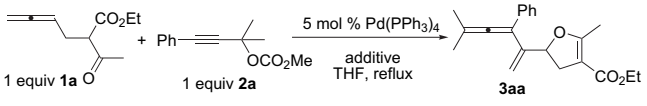
Table 1
Solvent effect on the reaction of ethyl 2-acetyl-4,5-hexadienoate **1a** and propargylic carbonate **2a**[a]



Entry	Solvent	Time (h)	Isolated yield of **3aa** (%)
1	CH_3CN	0.6	87
2	Toluene	1	65
3	DCE	1.5	38[b]
4	THF	1.5	95
5	DMSO	1	66
6	DMF	1	66
7	CH_3NO_2	1	68
8	Dioxane	1.5	84
9	MeOH	1.5	Complicated[c]
10	HOAc	1.5	Complicated[c]

[a] The reaction was carried out with 0.2 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % $Pd(PPh_3)_4$, and 10 mol % TBAI in 2 mL of indicated solvent. TBAI=tetrabutylammonium iodide.
[b] The yield was determined by ^1H NMR analysis using dibromomethane as the internal standard, and 45% of the starting material remained.
[c] The starting materials were completely consumed.

Next, we tested the effect of tetrabutylammonium halides by using THF as the solvent. As shown in Scheme 2, the reaction is also operative in the absence of a tetrabutylammonium halide, affording **3aa** in a relatively lower yield (76%) after 2.5 h. TBAB and TBAC are



PTC	time (h)	yield of **3aa**[a]
10 mol % TBAI	1.5	95%
10 mol % TBAB[b]	2	71%
10 mol % TBAC[b]	2	66%
none	2.5	76%

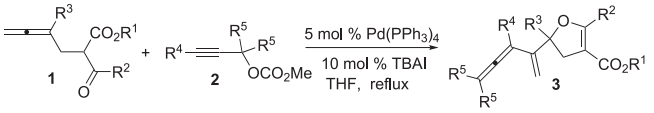
[a] The reaction was carried out in 0.2 mmol scale.
[b] TBAB = tetrabutylammonium bromide. TBAC = tetrabutylammonium chloride.

Scheme 2. Effect of tetrabutylammonium halide on the reaction of **1a** with **2a**.

not very effective for this transformation. Thus, we defined the reaction of 1 equiv of **1** and 1 equiv of **2** catalyzed by 5 mol % $Pd(PPh_3)_4$ and 10 mol % TBAI in refluxing THF as the standard conditions.

With the optimized conditions in hand, we examined the scope of the substrates. To our delight, various different substituted 2,3-allenylacetylacetates and terminal or non-terminal propargylic carbonates worked well under the standard conditions, affording the five-membered products **3** in good to excellent yields (Table 2).

Table 2
Palladium(0)-catalyzed coupling–cyclization reaction of **1** with **2**[a]



Entry	**1**				**2**	Time (min)	Isolated yield of **3** (%)
	R^1	R^2	R^3	R^4	R^5		
1	Et	Me	H (**1a**)	Ph	Me (**2a**)	100	95 (**3aa**)
2	Et	Me	H (**1a**)	H	Me (**2b**)	43	82 (**3ab**)
3	Et	Me	H (**1a**)	H	$-C_5H_{10}-$ (**2c**)	43	75 (**3ac**)
4	Et	Me	H (**1a**)	H	Et (**2d**)	65	96 (**3ad**)
5	Me	*i*-Pr	H (**1b**)	H	$-C_5H_{10}-$ (**2c**)	40	79 (**3bc**)
6	Et	Me	H (**1a**)	CO_2Me	Me (**2e**)	50	74 (**3ae**)
7	Et	Me	H (**1a**)	*n*-Bu	Me (**2f**)	54	85 (**3af**)
8	Et	Me	H (**1a**)	$CH_2OTBDMS$	Me (**2g**)	70	89 (**3ag**)
9	Me	*i*-Pr	H (**1b**)	*n*-Bu	Me (**2f**)	60	92 (**3bf**)
10	Me	*i*-Pr	H (**1b**)	H	Me (**2b**)	28	65 (**3bb**)
11	Me	*i*-Pr	Bn (**1c**)	H	Et (**2d**)	50	80 (**3cd**)
12	Me	*i*-Pr	Bn (**1c**)	H	$-C_5H_{10}-$ (**2c**)	75	75 (**3cc**)
13	Me	Me	H (**1d**)	H	Et (**2d**)	43	83 (**3dd**)

[a] The reaction was carried out using 0.2 mmol of **1**, 0.2 mmol of **2**, 5 mol % $Pd(PPh_3)_4$, and 10 mol % of TBAI in 2 mL of THF.

The γ position of the propargylic carbonates does not have an obvious influence against this reaction (entries 6 and 7, Table 2). It is noteworthy that $TBDMSOCH_2$ (TBDMS=*tert*-butyldimethylsilyl) is also compatible in this coupling–cyclization process (entry 8, Table 2). Besides the normal 2,3-allenylacetylacetates, a substituent R^3 can also be introduced onto the allene moiety to afford the same type of product with a quaternary carbon center in good yields (entries 11 and 12, Table 2). It should be noted that the formation of all-carbon quaternary centers is not easy since the process requires the creation of a new C–C bond at a sterically hindered carbon center.[14] The structure of **3** was confirmed by the X-ray study of **3bb** (Fig. 1).[15]

A plausible rationale for this reaction is shown in Scheme 3. Oxidative addition of propargylic carbonate **2** with Pd(0) would afford allenylpalladium intermediate **M1**, which underwent intermolecular carbopalladation with the allene moiety of **1** to generate π-allylpalladium intermediate **M2**. In the presence of TBAI, the π-allylpalladium intermediate would prefer *syn* configuration, i.e., *syn*-**M2**.[16] The acetylacetate moiety in **M2** would be deprotonated by the methoxy anion generated in situ in the oxidative addition step to yield the intermediate **M3**, which would isomerize to the enolate intermediate **M4**. **M4** underwent regioselective intramolecular allylation to afford the final product **3** and regenerate the catalytically active species Pd(0).

When the 1,3,4-alkatrien-2-yldihydrofurans **3** were exposed to the catalytic Pauson–Khand reaction conditions catalyzed by $[RhCl(CO)_2]_2$ under 1 atm of carbon monoxide,[13,17] various polysubstituted dihydrofurylcyclopententone derivatives were obtained in good yields (Table 3), which are structural motifs extensively existing in natural products and bioactive molecules.[18]

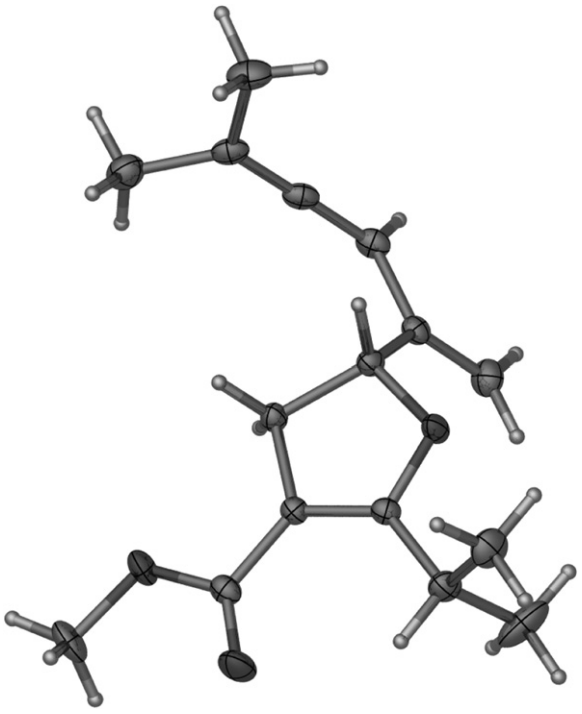
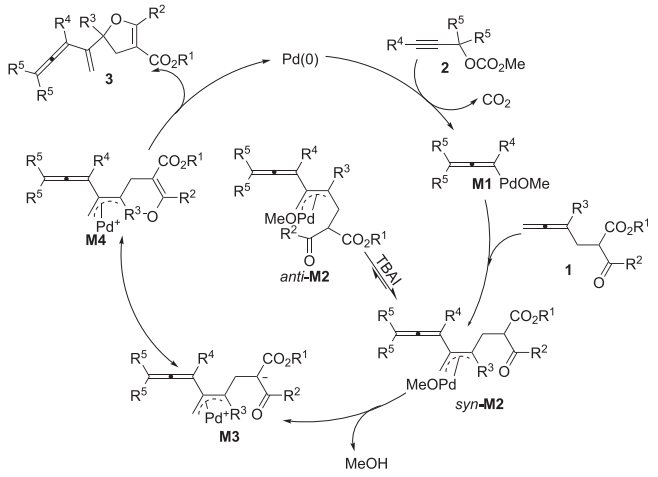
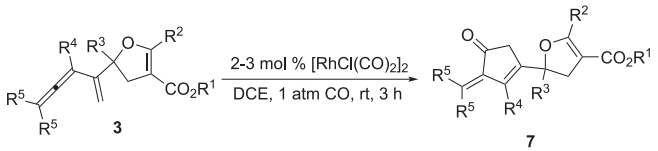


Figure 1. ORTEP representation of **3bb**.



Scheme 3. Plausible mechanism for the palladium-catalyzed reaction of **1** with **2**.

Table 3
The Pauson–Khand reaction of 1,3,4-alkatrien-2-yldihydrofurans **3**[a]



Entry	R^1	R^2	R^3	R^4	R^5 (**3**)	Yield of **7**[b] (%)
1	Me	*i*-Pr	H	H	Me (**3bb**)	90 (**7a**)
2	Me	*i*-Pr	Bn	H	Et (**3cd**)	89 (**7b**)
3[c]	Me	*i*-Pr	Bn	H	$-C_5H_{10}-$ (**3cc**)	96 (**7c**)
4	Et	Me	H	H	Et (**3ad**)	84 (**7d**)
5[d]	Et	Me	H	*n*-Bu	Me (**3af**)	71 (**7e**)
6[d]	Et	Me	H	Ph	Me (**3aa**)	81 (**7f**)
7	Me	Me	H	H	Et (**3dd**)	88 (**7g**)

[a] The reaction was carried out with 0.1–0.2 mmol of **3** in 2 mL of dichloroethane.
[b] Isolated yield.
[c] The reaction finished within 1 h.
[d] The reaction was complete within 48 h.

3. Conclusion

We have demonstrated an efficient and direct route for the preparation of functionalized vinyl allene with a dihyrofuryl substituent. This reaction proceeded smoothly under neutral conditions with an exclusive selectivity. The dihydrofurylvinyl allenes can be successfully applied to the preparation of polysubstituted dihydrofurylcyclopentenones under ambient conditions. Further study in this area and synthetic application of the products including the cyclization between dihydrofuran ring and the allene moiety is ongoing in our laboratory.

4. Experimental section

4.1. General remarks

NMR spectra were taken with a Varian Mercury-300 spectrometer (300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR) or Varian Mercury-400 spectrometer (400 MHz for ^{1}H NMR, 100.5 MHz for ^{13}C NMR) in $CDCl_3$. Chemical shifts were recorded in parts per million (ppm) relative to internal standard $CDCl_3$ and coupling constants were reported in hertz (Hz). The high-resolution mass spectra were recorded with a Finnigan MAT 8430 spectrometer. Other mass spectra were obtained on a Shimadzu GCMS-2010 or Shimadzu LCMS-2010 spectrometer. IR studies were carried out on a Perkin–Elmer 983 spectrometer. X-ray intensity data were measured at 173 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a fine-focus Mo-target X-ray tube (λ=0.71073 Å) operated at 1500 W. The detector was placed at a distance of 6.042 cm from the crystal. The frames were integrated with the SAINT software package (Bruker, Billerica, MA) by using a narrow-frame integration algorithm. All reactions were carried out in an oven dried Schlenk tube under argon atmosphere. All solvents were distilled from the indicated drying reagents right before use: toluene and THF (Na, benzophenone), DCE, MeCN, $MeNO_2$, DMSO, dioxane, DMF (CaH_2). Purification by column chromatography was performed using Huanghai (Shandong, China) silica gel (10–40 μ).

4.2. Synthesis of 1,3,4-alkatrien-2-yldihydrofurans 3

*4.2.1. 3-(Ethoxycarbonyl)-2-methyl-5-(5-methyl-3-phenyl-1,3,4-hexatrien-2-yl)-4,5-dihydrofuran (**3aa**).* To a flame-dried Schlenk tube were added TBAI (7 mg, 0.019 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), **1a** (35 mg, 0.19 mmol), **2a** (45 mg, 0.21 mmol), and 2 mL of THF sequentially under argon. The resulting mixture was stirred under reflux. When the reaction was completed in 100 min, the solvent was evaporated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate=15:1 (precooled in the refrigerator at −20 °C)) to afford 59 mg (95%) of **3aa** as a viscous oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.20 (m, 5H), 5.29–5.20 (m, 2H), 4.97 (s, 1H), 4.17 (q, J=7.2 Hz, 2H), 3.18–3.08 (m, 1H), 2.85–2.76 (m, 1H), 2.25 (s, 3H), 1.79 (s, 6H), 1.28 (t, J=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 202.8, 167.6, 166.2, 144.5, 137.3, 129.0, 128.1, 126.9, 111.9, 104.7, 101.7, 98.4, 82.2, 59.4, 36.6, 20.3, 14.4, 14.1; MS (EI) m/z (%) 324 (M^+, 5.77), 43 (100); IR (neat) 1947, 1701, 1651, 1598, 1491, 1445, 1383, 1340, 1324, 1257, 1224, 1171, 1142, 1125, 1083 cm^{-1}; HRMS calcd for $C_{21}H_{24}O_3$ (M^+): 324.1725. Found: 324.1711.

*4.2.2. 3-(Ethoxycarbonyl)-2-methyl-5-(5-methyl-1,3,4-hexatrien-2-yl)-4,5-dihydrofuran (**3ab**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1a** (33 mg, 0.18 mmol), and **2b** (28 mg, 0.20 mmol) in 2 mL of THF afforded 37 mg (82%) of **3ab** as an oil (eluent: petroleum ether/ethyl acetate=20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73–5.68 (m, 1H), 5.08 (dd, J=10.8, 8.7 Hz, 1H),

5.02 (s, 1H), 4.99 (s, 1H), 4.15 (q, J=7.2 Hz, 2H), 3.08–2.98 (m, 1H), 2.74–2.64 (m, 1H), 2.22 (t, J=1.5 Hz, 3H), 1.71 (d, J=3.0 Hz, 3H), 1.68 (d, J=3.0 Hz, 3H), 1.26 (t, J=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 202.9, 167.6, 166.2, 143.5, 111.2, 101.9, 98.3, 90.7, 81.9, 59.4, 36.2, 20.2, 20.1, 14.4, 14.0; MS (EI) m/z (%) 248 (M^+, 2.40), 43 (100); IR (neat) 1954, 1701, 1651, 1447, 1385, 1375, 1341, 1325, 1260, 1224, 1171, 1142, 1126, 1084, 1017 cm^{-1}; HRMS calcd for $C_{15}H_{20}O_3$ (M^+): 248.1412. Found: 248.1402.

*4.2.3. 3-(Ethoxycarbonyl)-2-methyl-5-(5,5-pentamethylene-1,3,4-pentatrien-2-yl)-4,5-dihydrofuran (**3ac**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1a** (33 mg, 0.18 mmol), and **2c** (34 mg, 0.19 mmol) in 2 mL of THF afforded 39 mg (75%) of **3ac** as an oil (eluent: petroleum ether/ethyl acetate=10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (s, 1H), 5.09 (dd, J=11.1, 8.7 Hz, 1H), 5.01 (s, 1H), 4.98 (s, 1H), 4.15 (q, J=7.2 Hz, 2H), 3.11–3.01 (m, 1H), 2.72–2.63 (m, 1H), 2.26–2.21 (m, 3H), 2.17–2.08 (m, 4H), 1.72–1.45 (m, 6H), 1.25 (t, J=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 199.5, 167.6, 166.2, 143.7, 110.5, 105.3, 101.9, 90.7, 81.6, 59.3, 36.3, 31.1, 31.0, 27.0, 25.8, 14.4, 14.0; MS (EI) m/z (%) 288 (M^+, 1.74), 43 (100); IR (neat) 1949, 1702, 1651, 1624, 1446, 1381, 1340, 1324, 1253, 1222, 1170, 1141, 1126, 1084 cm^{-1}; HRMS calcd for $C_{18}H_{24}O_3$ (M^+): 288.1725. Found: 288.1733.

*4.2.4. 3-(Ethoxycarbonyl)-5-(5-ethyl-1,3,4-heptatrien-2-yl)-2-methyl-4,5-dihydrofuran (**3ad**).* The reaction of $Pd(PPh_3)_4$ (13 mg, 0.011 mmol), TBAI (9 mg, 0.024 mmol), **1a** (31 mg, 0.17 mmol), and **2d** (31 mg, 0.18 mmol) in 2 mL of THF at 80 °C afforded 45 mg (96%) of **3ad** as an oil (petroleum ether/ethyl acetate=20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96–5.90 (m, 1H), 5.08 (dd, J=11.1, 8.7 Hz, 1H), 5.02–4.98 (m, 2H), 4.15 (q, J=6.9 Hz, 2H), 3.09–2.98 (m, 1H), 2.74–2.64 (m, 1H), 2.22 (t, J=1.2 Hz, 3H), 2.14–1.91 (m, 4H), 1.26 (t, J=6.9 Hz, 3H), 1.03 (t, J=7.2 Hz, 3H), 1.00 (t, J=7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.4, 167.6, 166.2, 143.9, 111.2, 110.2, 101.8, 94.8, 81.4, 59.4, 36.6, 25.7, 25.6, 14.4, 14.0, 12.2, 12.1; MS (EI) m/z (%) 276 (M^+, 1.55), 43 (100); IR (neat) 1945, 1703, 1652, 1625, 1458, 1382, 1341, 1324, 1250, 1223, 1171, 1142, 1126, 1084 cm^{-1}; HRMS calcd for $C_{17}H_{24}O_3$ (M^+): 276.1725. Found: 276.1721.

*4.2.5. 2-Isopropyl-3-(methoxycarbonyl)-5-(5,5-pentamethylene-1,3,4-pentatrien-2-yl)-4,5-dihydrofuran (**3bc**).* The reaction of $Pd(PPh_3)_4$ (13 mg, 0.011 mmol), TBAI (9 mg, 0.024 mmol), **1b** (41 mg, 0.21 mmol), and **2c** (43 mg, 0.24 mmol) in 2 mL of THF afforded 50 mg (79%) of **3bc** as an oil (petroleum ether/ethyl acetate=20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74–5.72 (m, 1H), 5.09 (dd, J=11.1, 7.8 Hz, 1H), 4.99 (s, 1H), 4.95 (s, 1H), 3.69–3.60 (m, 4H), 3.08 (dd, J=14.7, 11.4 Hz, 1H), 2.61 (dd, J=14.7, 7.8 Hz, 1H), 2.22–2.07 (m, 4H), 1.72–1.43 (m, 6H), 1.18 (d, J=6.6 Hz, 3H), 1.15 (d, J=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 199.6, 175.6, 166.4, 144.2, 109.1, 105.6, 99.1, 91.1, 80.4, 50.7, 36.7, 31.3, 31.1, 27.20, 27.16, 26.8, 25.9, 19.7, 19.6; MS (EI) m/z (%) 302 (M^+, 2.15), 43 (100); IR (neat) 1949, 1758, 1705, 1642, 1469, 1437, 1387, 1349, 1231, 1189, 1118, 1068, 1048 cm^{-1}; HRMS calcd for $C_{19}H_{26}O_3$ (M^+): 302.1882. Found: 302.1876.

*4.2.6. 3-(Ethoxycarbonyl)-2-methyl-5-(3-(methoxycarbonyl)-5-methyl-1,3,4-hexatrien-2-yl)-4,5-dihydrofuran (**3ae**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (8 mg, 0.022 mmol), **1a** (36 mg, 0.20 mmol), and **2e** (40 mg, 0.20 mmol) in 2 mL of THF afforded 45 mg (74%) of **3ae** as an oil (petroleum ether/ethyl acetate=10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (s, 1H), 5.33 (s, 1H), 5.11 (dd, J=10.8, 8.7 Hz, 1H), 4.13 (q, J=6.9 Hz, 2H), 3.72 (s, 3H), 3.05–2.95 (m, 1H), 2.71–2.62 (m, 1H), 2.20 (s, 3H), 1.80 (s, 3H), 1.78 (s, 3H), 1.24 (t, J=6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 208.1, 167.5, 166.5, 166.0, 139.6, 114.1, 101.7, 101.2, 97.5, 82.2, 59.4, 52.1, 36.0, 19.44, 19.41, 14.4, 14.0; MS (EI) m/z (%) 306 (M^+, 11.14), 43 (100); IR (neat) 1948, 1758, 1723, 1703, 1651, 1436, 1384, 1320, 1283, 1261, 1224, 1171, 1143, 1085 cm^{-1}; HRMS calcd for $C_{17}H_{22}O_5$ (M^+): 306.1467. Found: 306.1463.

*4.2.7. 5-(3-Butyl-5-methyl-1,3,4-hexatrien-2-yl)-3-(ethoxycarbonyl)-2-methyl-4,5-dihydrofuran (**3af**).* The reaction of $Pd(PPh_3)_4$ (13 mg, 0.011 mmol), TBAI (7 mg, 0.019 mmol), **1a** (36 mg, 0.20 mmol), and **2f** (42 mg, 0.21 mmol) in 2 mL of THF afforded 51 mg (85%) of **3af** as an oil (petroleum ether/ethyl acetate=20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.12 (dd, J=10.8, 8.1 Hz, 1H), 5.06 (s, 1H), 5.02 (s, 1H), 4.15 (q, J=7.2 Hz, 2H), 3.08–2.98 (m, 1H), 2.60 (dd, J=14.4, 8.1 Hz, 1H), 2.23 (s, 3H), 2.15 (t, J=7.2 Hz, 2H), 1.71 (s, 3H), 1.68 (s, 3H), 1.50–1.26 (m, 4H), 1.26 (t, J=7.2 Hz, 3H), 0.90 (t, J=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.6, 167.6, 166.2, 145.3, 107.3, 101.7, 100.9, 98.1, 82.3, 59.3, 37.1, 29.7, 29.2, 22.4, 20.3, 20.2, 14.4, 14.1, 14.0; MS (EI) m/z (%) 304 (M^+, 3.89), 43 (100); IR (neat) 1948, 1703, 1651, 1620, 1446, 1384, 1324, 1254, 1223, 1170, 1142, 1125, 1084 cm^{-1}; HRMS calcd for $C_{19}H_{28}O_3$ (M^+): 304.2038. Found: 304.2042.

*4.2.8. 3-(Ethoxycarbonyl)-2-methyl-5-(5-methyl-3-(tert-butyl-dimethylsilyloxy)-methyl-1,3,4-hexatrien-2-yl)-4,5-dihydrofuran (**3ag**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (8 mg, 0.022 mmol), **1a** (35 mg, 0.19 mmol), and **2g** (56 mg, 0.20 mmol) in 2 mL of THF afforded 67 mg (89%) of **3ag** as an oil (petroleum ether/ethyl acetate=20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (s, 1H), 5.11–5.05 (m, 2H), 4.35 (d, J=12.0 Hz, 1H), 4.31 (d, J=12.0 Hz, 1H), 4.15 (qd, J=7.2, 1.2 Hz, 2H), 3.06–2.97 (m, 1H), 2.68–2.60 (m, 1H), 2.22 (t, J=1.2 Hz, 3H), 1.73 (s, 3H), 1.70 (s, 3H), 1.25 (t, J=7.2 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.5, 167.6, 166.2, 143.0, 108.6, 101.8, 101.6, 99.1, 82.4, 62.5, 59.3, 36.7, 25.7, 20.2, 20.1, 18.1, 14.4, 14.0, −5.3; MS (EI) m/z (%) 392 (M^+, 3.17), 75 (100); IR (neat) 1952, 1703, 1651, 1622, 1471, 1463, 1446, 1384, 1341, 1325, 1255, 1224, 1170, 1139, 1084, 1006 cm^{-1}; HRMS calcd for $C_{22}H_{36}O_4Si$ (M^+): 392.2383. Found: 392.2388.

*4.2.9. 5-(3-Butyl-5-methyl-1,3,4-hexatrien-2-yl)-2-isopropyl-3-(methoxycarbonyl)-4,5-dihydrofuran (**3bf**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1b** (38 mg, 0.19 mmol), and **2f** (40 mg, 0.20 mmol) in 2 mL of THF afforded 57 mg (92%) of **3bf** as an oil (petroleum ether/ethyl acetate=20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (dd, J=11.6, 7.6 Hz, 1H), 5.05 (s, 1H), 5.00 (s, 1H), 3.74–3.63 (m, 4H), 3.05 (dd, J=14.4, 11.6 Hz, 1H), 2.53 (dd, J=14.4, 7.6 Hz, 1H), 2.20–2.08 (m, 2H), 1.74 (s, 3H), 1.71 (s, 3H), 1.46–1.25 (m, 4H), 1.20 (d, J=6.8 Hz, 3H), 1.15 (d, J=6.8 Hz, 3H), 0.90 (t, J=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.7, 175.6, 166.5, 145.8, 105.9, 101.3, 98.9, 98.2, 81.1, 50.6, 37.5, 29.8, 29.1, 26.8, 22.4, 20.4, 20.3, 19.7, 14.0; MS (EI) m/z (%) 318 (M^+, 8.28), 43 (100); IR (neat) 1947, 1707, 1642, 1468, 1436, 1361, 1348, 1300, 1257, 1230, 1189, 1118, 1067, 1050 cm^{-1}; HRMS calcd for $C_{20}H_{30}O_3$ (M^+): 318.2195. Found: 318.2202.

*4.2.10. 2-Isopropyl-3-(methoxycarbonyl)-5-(5-methyl-1,3,4-hexatrien-2-yl)-4,5-dihydrofuran (**3bb**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1b** (37 mg, 0.19 mmol), and **2b** (27 mg, 0.19 mmol) in 2 mL of THF afforded 32 mg (65%) of **3bb** as an oil (petroleum ether/ethyl acetate=20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75–5.69 (m, 1H), 5.06 (dd, J=10.8, 8.4 Hz, 1H), 5.01 (s, 1H), 4.96 (s, 1H), 3.73–3.61 (m, 4H), 3.04 (dd, J=14.0, 10.8 Hz, 1H), 2.61 (dd, J=14.0, 8.4 Hz, 1H), 1.74 (d, J=2.8 Hz, 3H), 1.71 (d, J=2.4 Hz, 3H), 1.18 (d, J=6.8 Hz, 3H), 1.15 (d, J=7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 203.0, 175.7, 166.4, 144.1, 109.5, 99.1, 98.6, 91.3, 80.6, 50.7, 36.6, 26.8, 20.3, 20.2, 19.7, 19.6; MS

(EI) *m*/*z* (%) 262 (M^+, 19.53), 43 (100); IR (neat) 1951, 1705, 1641, 1469, 1436, 1349, 1300, 1230, 1189, 1118, 1068, 1050 cm^{-1}; HRMS calcd for $C_{16}H_{22}O_3$ (M^+): 262.1569. Found: 262.1572.

*4.2.11. 5-Benzyl-2-isopropyl-5-(5-ethyl-1,3,4-heptatrien-2-yl)-3-(methoxycarbonyl)-4,5-dihydrofuran (**3cd**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1c** (59 mg, 0.21 mmol), and **2d** (35 mg, 0.21 mmol) in 2 mL of THF afforded 59 mg (80%) of **3cd** as an oil (petroleum ether/ethyl acetate=20:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.19–7.08 (m, 5H), 5.84–5.81 (m, 1H), 4.87 (s, 2H), 3.59–3.48 (m, 4H), 3.03 (d, *J*=14.0 Hz, 1H), 2.98 (d, *J*=14.0 Hz, 1H), 2.93 (d, *J*=14.8 Hz, 1H), 2.73 (d, *J*=14.8 Hz, 1H), 2.18–1.95 (m, 4H), 1.09 (d, *J*=6.8 Hz, 3H), 1.06–0.99 (m, 9H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 201.8, 173.7, 166.3, 145.9, 136.3, 130.7, 127.6, 126.4, 112.0, 109.9, 99.1, 94.2, 89.8, 50.6, 44.6, 40.3, 26.8, 25.63, 25.60, 19.9, 19.7, 12.3, 12.0; MS (EI) *m*/*z* (%) 380 (M^+, 5.80), 43 (100); IR (neat) 1944, 1706, 1643, 1612, 1496, 1468, 1455, 1435, 1351, 1280, 1242, 1188, 1125, 1103, 1067, 1046 cm^{-1}; HRMS calcd for $C_{25}H_{32}O_3$ (M^+): 380.2351. Found: 380.2340.

*4.2.12. 5-Benzyl-2-isopropyl-3-(methoxycarbonyl)-5-(5,5-pentamethylene-1,3,4-pentatrien-2-yl)-4,5-dihydrofuran (**3cc**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1c** (61 mg, 0.21 mmol), and **2c** (37 mg, 0.20 mmol) in 2 mL of THF afforded 60 mg (75%) of **3cc** as an oil (petroleum ether/ethyl acetate=20:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.18 (m, 5H), 5.75 (s, 1H), 4.92 (s, 1H), 4.88 (s, 1H), 3.68–3.57 (m, 4H), 3.14 (d, *J*=13.6 Hz, 1H), 3.06 (d, *J*=13.6 Hz, 1H), 3.00 (d, *J*=14.8 Hz, 1H), 2.86 (d, *J*=14.8 Hz, 1H), 2.37–2.18 (m, 4H), 1.75–1.51 (m, 6H), 1.20 (d, *J*=6.8 Hz, 3H), 1.13 (d, *J*=7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 200.1, 173.6, 166.4, 145.6, 136.5, 130.5, 127.5, 126.3, 112.5, 104.4, 99.1, 91.2, 89.8, 50.7, 44.7, 40.9, 31.1, 31.0, 26.9, 26.8, 26.6, 25.9, 19.9, 19.7; MS (EI) *m*/*z* (%) 392 (M^+, 11.58), 43 (100); IR (neat) 1949, 1705, 1643, 1612, 1496, 1468, 1435, 1385, 1351, 1279, 1241, 1188, 1124, 1101, 1067, 1046 cm^{-1}; HRMS calcd for $C_{26}H_{32}O_3$ (M^+): 392.2351. Found: 392.2368.

*4.2.13. 5-(5-Ethyl-1,3,4-heptatrien-2-yl)-2-methyl-3-(methoxycarbonyl)-4,5-dihydrofuran (**3dd**).* The reaction of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), TBAI (7 mg, 0.019 mmol), **1d** (37 mg, 0.22 mmol), and **2d** (38 mg, 0.22 mmol) in 2 mL of THF afforded 48 mg (83%) of **3dd** as an oil (petroleum ether/ethyl acetate=20:1): ^1H NMR (300 MHz, $CDCl_3$) δ 5.95–5.90 (m, 1H), 5.08 (dd, *J*=10.2, 8.4 Hz, 1H), 4.99 (s, 2H), 3.68 (s, 3H), 3.03 (dd, *J*=14.1, 10.2 Hz, 1H), 2.67 (dd, *J*=14.1, 8.4 Hz, 1H), 2.22 (s, 3H), 2.17–1.89 (m, 4H), 1.06–0.95 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.4, 168.0, 166.5, 143.8, 111.2, 110.1, 101.5, 94.8, 81.4, 50.8, 36.5, 25.7, 25.5, 14.0, 12.2, 12.1; MS (EI) *m*/*z* (%) 262 (M^+, 18.12), 43 (100); IR (neat) 1944, 1708, 1651, 1625, 1437, 1384, 1360, 1329, 1250, 1223, 1189, 1140, 1089 cm^{-1}; HRMS calcd for $C_{16}H_{22}O_3$ (M^+): 262.1569. Found: 262.1560.

4.3. The Pauson–Khand reaction of 3

*4.3.1. 4-(2-Isopropyl-3-(methoxycarbonyl)-4,5-dihydrofuran-5-yl)-2-(isopropylidene)cyclopent-3-enone (**7a**).* To a flame-dried Schlenk tube containing $[RhCl(CO)_2]_2$ (1 mg, 0.0026 mmol) were added **3bb** (26 mg, 0.099 mmol) and 2 mL of DCE sequentially under the atmosphere of CO. The resulting mixture was stirred at room temperature with CO (1 atm) being introduced via the installation of a CO balloon. When the reaction was completed as monitored by TLC in 3 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) to afford 26 mg (90%) of **7a** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 6.68–6.66 (m, 1H), 5.27 (dd, *J*=10.8, 7.6 Hz, 1H), 3.69 (s, 3H), 3.64 (heptet, *J*=6.8 Hz, 1H), 3.08 (dd, *J*=14.4, 10.8 Hz, 1H), 2.91–2.89 (m, 2H), 2.74 (dd, *J*=14.4, 7.6 Hz, 1H), 2.24 (s, 3H), 1.95 (s, 3H), 1.12 (d, *J*=6.8 Hz, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 203.9, 175.4, 166.0, 145.2, 138.5, 133.1, 127.9, 99.1, 80.1, 50.8, 41.7, 34.3, 26.8, 23.6, 20.2, 19.6, 19.5; MS (EI) *m*/*z* (%) 290 (M^+, 38.58), 187 (100); IR (neat) 1718, 1634, 1469, 1436, 1349, 1299, 1232, 1190, 1168, 1118, 1064, 1041 cm^{-1}; HRMS calcd for $C_{17}H_{22}O_4$ (M^+): 290.1518. Found: 290.1507.

*4.3.2. 4-(5-Benzyl-2-isopropyl-3-(methoxycarbonyl)-4,5-dihydrofuran-5-yl)-2-(1-ethylpropylidene)cyclopent-3-enone (**7b**).* The reaction of $[RhCl(CO)_2]_2$ (1 mg, 0.0026 mmol) and **3cd** (46 mg, 0.12 mmol) in 2 mL of DCE under carbon monoxide atmosphere afforded 44 mg (89%) of **7b** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–7.08 (m, 5H), 6.46–6.44 (m, 1H), 3.57 (s, 3H), 3.52 (heptet, *J*=6.8 Hz, 1H), 3.04 (d, *J*=14.0 Hz, 1H), 2.98 (d, *J*=14.0 Hz, 1H), 2.90–2.84 (m, 3H), 2.78 (d, *J*=14.8 Hz, 1H), 2.62 (q, *J*=7.2 Hz, 2H), 2.19–2.08 (m, 2H), 1.08 (d, *J*=6.8 Hz, 3H), 1.07 (d, *J*=6.8 Hz, 3H), 0.96 (t, *J*=7.6 Hz, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 203.8, 174.3, 166.0, 156.3, 142.4, 135.3, 132.1, 130.6, 128.0, 126.8, 126.4, 98.9, 88.4, 50.7, 44.5, 42.8, 38.7, 27.8, 26.8, 24.1, 19.8, 19.6, 12.84, 12.76; MS (EI) *m*/*z* (%) 408 (M^+, 1.70), 317 (100); IR (neat) 1715, 1640, 1496, 1455, 1436, 1396, 1360, 1285, 1242, 1189, 1119, 1065, 1016 cm^{-1}; HRMS calcd for $C_{26}H_{32}O_4$ (M^+): 408.2301. Found: 408.2300.

*4.3.3. 4-(5-Benzyl-2-isopropyl-3-(methoxycarbonyl)-4,5-dihydrofuran-5-yl)-2-(1-cyclohexylidene)cyclopent-3-enone (**7c**).* The reaction of $[RhCl(CO)_2]_2$ (1 mg, 0.0026 mmol) and **3cc** (36 mg, 0.092 mmol) in 2 mL of DCE under carbon monoxide atmosphere afforded 37 mg (96%) of **7c** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.22–7.08 (m, 5H), 6.53–6.51 (m, 1H), 3.57 (s, 3H), 3.51 (heptet, *J*=6.8 Hz, 1H), 3.05 (d, *J*=14.0 Hz, 1H), 2.97 (d, *J*=14.0 Hz, 1H), 2.92–2.80 (m, 5H), 2.78 (d, *J*=14.4 Hz, 1H), 2.23–2.19 (m, 2H), 1.62–1.51 (m, 6H), 1.07 (t, *J*=6.6 Hz, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 204.8, 174.3, 166.0, 153.0, 141.7, 135.4, 130.6, 130.4, 128.0, 126.8, 126.2, 98.9, 88.3, 50.7, 44.5, 43.2, 38.7, 33.1, 28.6, 28.3, 28.1, 26.8, 26.2, 19.8, 19.7; MS (EI) *m*/*z* (%) 420 (M^+, 2.12), 329 (100); IR (neat) 1714, 1639, 1496, 1468, 1437, 1387, 1352, 1286, 1243, 1188, 1121, 1065, 1016 cm^{-1}; HRMS calcd for $C_{27}H_{32}O_4$ (M^+): 420.2301. Found: 420.2310.

*4.3.4. 4-(3-(Ethoxycarbonyl)-2-methyl-4,5-dihydrofuran-5-yl)-2-(1-ethylpropylidene)cyclopent-3-enone (**7d**).* The reaction of $[RhCl(CO)_2]_2$ (1 mg, 0.0026 mmol) and **3ad** (28 mg, 0.10 mmol) in 2 mL of DCE under carbon monoxide atmosphere afforded 26 mg (84%) of **7d** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 5.27 (t, *J*=6.9 Hz, 1H), 4.16 (q, *J*=7.2 Hz, 2H), 3.11–3.03 (m, 1H), 2.95 (d, *J*=17.1 Hz, 1H), 2.89 (d, *J*=17.1 Hz, 1H), 2.82–2.74 (m, 1H), 2.70 (q, *J*=7.6 Hz, 2H), 2.26 (q, *J*=7.2 Hz, 2H), 2.21 (s, 3H), 1.27 (t, *J*=7.2 Hz, 3H), 1.08 (t, *J*=7.6 Hz, 3H), 1.03 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 203.8, 167.4, 165.9, 157.0, 138.6, 132.0, 128.0, 101.8, 80.5, 59.6, 42.0, 34.2, 27.9, 24.1, 14.4, 14.0, 12.9, 12.8; MS (EI) *m*/*z* (%) 305 (M^++1, 12.15), 304 (M^+, 51.56), 43 (100); IR (neat) 1716, 1650, 1619, 1461, 1383, 1319, 1256, 1222, 1167, 1126, 1082 cm^{-1}; HRMS calcd for $C_{18}H_{24}O_4$ (M^+): 304.1675. Found: 304.1677.

*4.3.5. 3-Butyl-4-(3-(ethoxycarbonyl)-2-methyl-4,5-dihydrofuran-5-yl)-2-(isopropylidene)cyclopent-3-enone (**7e**).* The reaction of $[RhCl(CO)_2]_2$ (1 mg, 0.0026 mmol) and **3af** (44 mg, 0.14 mmol) in 2 mL of DCE under carbon monoxide atmosphere afforded 34 mg (71%) of **7e** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 5.63 (dd, *J*=10.8, 8.4 Hz, 1H), 4.15 (q, *J*=7.2 Hz, 2H), 3.10–3.02 (m, 1H), 2.83 (s, 2H), 2.71–2.64 (m, 1H), 2.49 (t, *J*=7.2 Hz, 2H), 2.28 (s, 3H), 2.17 (t, *J*=1.6 Hz, 3H), 2.08 (s, 3H), 1.53–1.29 (m, 4H), 1.26 (t, *J*=7.2 Hz, 3H), 0.92 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 205.0, 167.6, 165.8, 145.7, 142.2, 134.0, 133.4, 101.9, 77.4, 59.5, 39.9, 34.9, 31.9, 27.4, 23.5, 22.6, 14.4, 13.92, 13.85; MS (EI) *m*/*z* (%) 333 (M^++1,

12.58), 332 (M^+, 46.43), 43 (100); IR (neat) 1704, 1649, 1604, 1463, 1382, 1322, 1256, 1221, 1143, 1125, 1082 cm^{-1}; HRMS calcd for $C_{20}H_{28}O_4$ (M^+): 332.1988. Found: 332.1975.

*4.3.6. 4-(3-(Ethoxycarbonyl)-2-methyl-4,5-dihydrofuran-5-yl)-2-(isopropylidene)-3-phenylcyclopent-3-enone (**7f**).* The reaction of $[RhCl(CO)_2]_2$ (1 mg, 0.0026 mmol) and **3aa** (32 mg, 0.10 mmol) in 2 mL of DCE under carbon monoxide atmosphere afforded 28 mg (81%) of **7f** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (m, 3H), 7.26–7.03 (m, 2H), 5.14 (dd, J=10.4, 8.4 Hz, 1H), 4.14 (q, J=7.0 Hz, 2H), 3.02 (s, 2H), 2.97–2.89 (m, 1H), 2.78–2.71 (m, 1H), 2.26 (s, 3H), 2.14 (s, 3H), 1.36 (s, 3H), 1.25 (t, J=7.0 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 204.0, 167.6, 165.8, 148.1, 143.3, 136.8, 135.4, 133.8, 128.5, 127.6, 101.8, 77.9, 59.5, 40.0, 34.9, 24.1, 22.6, 14.4, 13.9; MS (EI) m/z (%) 353 (M^++1, 13.97), 352 (M^+, 60.25), 263 (100); IR (neat) 1717, 1698, 1649, 1608, 1494, 1443, 1382, 1321, 1257, 1218, 1170, 1122, 1082 cm^{-1}; HRMS calcd for $C_{22}H_{24}O_4$ (M^+): 352.1675. Found: 352.1690.

*4.3.7. 2-(1-Ethylpropylidene)-4-(2-methyl-3-(methoxycarbonyl)-4,5-dihydrofuran-5-yl)-cyclopent-3-enone (**7g**).* The reaction of $[RhCl(CO)_2]_2$ (2 mg, 0.0051 mmol) and **3dd** (45 mg, 0.17 mmol) in 2 mL of DCE under carbon monoxide atmosphere afforded 44 mg (88%) of **7g** as an oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.26 (t, J=9.6 Hz, 1H), 3.68 (s, 3H), 3.10–2.97 (m, 1H), 2.90 (s, 2H), 2.82–2.63 (m, 3H), 2.24 (q, J=7.5 Hz, 2H), 2.19 (s, 3H), 1.06 (t, J=7.5 Hz, 3H), 1.01 (t, J=7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 203.7, 167.7, 166.2, 157.0, 138.4, 131.9, 128.1, 101.5, 80.6, 50.8, 41.9, 34.0, 27.8, 24.0, 13.9, 12.81, 12.79; MS (EI) m/z (%) 291 (M^++1, 11.20), 290 (M^+, 72.90), 43 (100); IR (neat) 1713, 1649, 1618, 1438, 1384, 1360, 1327, 1258, 1223, 1189, 1166, 1132, 1087 cm^{-1}; HRMS calcd for $C_{17}H_{22}O_4$ (M^+): 290.1518. Found: 290.1509.

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Supplementary data

$^1H/^{13}C$ NMR spectra of all new compounds. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.02.030.

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