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Palladium-catalyzed carbon dioxide elimination–fixation reaction of 6-methoxycarbonyloxy-2,4-hexadien-1-ols

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Abstract—Cyclic carbonates substituted with 1,3-butadienyl moiety were synthesized by a palladium-catalyzed reaction of dienylic carbonates including a carbon dioxide elimination–fixation process. The reaction proceeded via a migration–isomerization of the resulting π-allylpalladium intermediates to afford *trans*-1,3-dienyl-substituted cyclic carbonates in a selective manner.

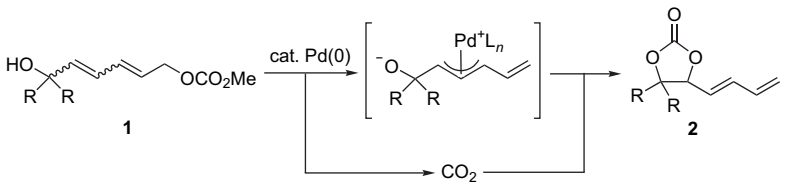
1. Introduction

Fixation of carbon dioxide into organic substances represents an attractive area of study in both organic and green chemistry.[1] Palladium-catalyzed reactions are one of the common methods to fix external carbon dioxide into organic compounds.[2] Recently, we have developed a novel type of palladium-catalyzed reaction using propargylic carbonates with phenols, which involves a CO_2-recycling process.[3] The reaction proceeds via a carbon dioxide elimination–fixation step to afford phenoxy-substituted cyclic carbonates.[3a–3c] This process can be successfully applied to a palladium-catalyzed reaction using allylic carbonates.[3d] In these reactions, the formation of π-allylpalladium intermediate followed by fixation of CO_2 is a key step. We sought to determine whether a CO_2-recycling process could apply for conjugated dienylic carbonates. Although there are many examples about the reaction of allylic compounds by palladium catalyst,[4] only a few examples have been reported about the reactivity for conjugated dienylic compounds.[5] We report here a palladium-catalyzed reaction of 6-methoxycarbonyloxy-2,4-hexadien-1-ols **1** to produce 1,3-dienyl-substituted cyclic carbonates **2** via a CO_2-recycling process (Scheme 1).

2. Results and discussion

The dienylic carbonates **1** for the palladium-catalyzed reactions were synthesized as follows (Scheme 2). The ketones **3a–d** were subjected to the nucleophilic addition of siloxy enyne (*E*)-**4**[6] in the presence of BuLi leading to the corresponding acetylenic alcohols, which were desilylated with TBAF to afford diols (*E*)-**5a–d**. *trans*-Selective reduction of the alkyne moiety using $LiAlH_4$ followed by treatment with methyl chloroformate to produce the dienylic carbonates (*E*,*E*)-**1a–d**. Similarly, dienylic benzoate (*E*,*E*)-**6** was prepared from **5a** in two steps.

We also prepared geometric isomers of (*E*,*E*)-**1a** possessing (*E*,*Z*)-, (*Z*,*E*)-, and (*Z*,*Z*)-olefinic moieties (Scheme 3). Addition of siloxy enyne (*Z*)-**4**, which was easily prepared from



Scheme 1.

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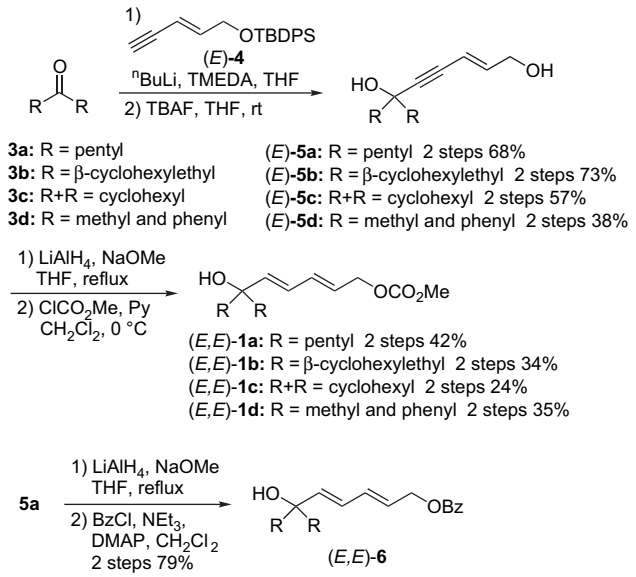
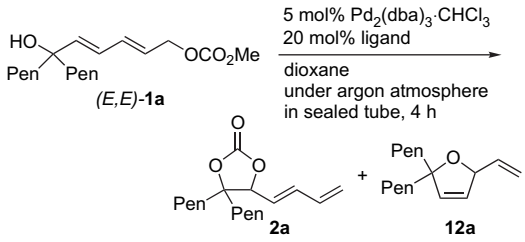


Scheme 2.

Table 1. Initial attempts for the reaction of (*E*,*E*)-**1a**[a]

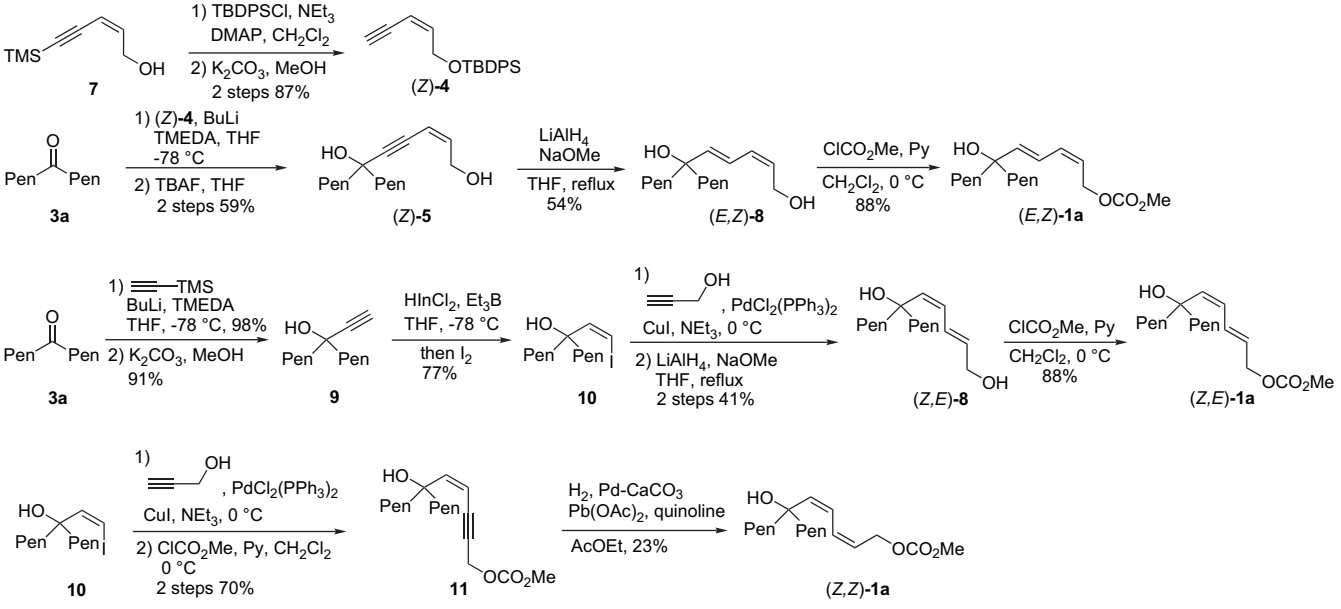


Entry	Ligand	Temp (°C)	Product's yield (%)	
			2a	**12a**
1	dppe	50	57	—
2	dppp	50	15	—
3	dppf	50	15	—
4	dppm	50	7	60
5[b]	PPh_3	50	4	56
6	dppv	50	58	27
7	dppv	80	28	58
8	dppv	100	22	74

[a] Pen=pentyl.
[b] Ligand (40 mol %) was used.

known enyne **7**,[7] to dipentylketone (**3a**) followed by desilylation yielded the diol (*Z*)-**5**. Conversion of (*Z*)-**5** by the same procedure described for (*E*)-**5a** gave dienylic carbonate (*E*,*Z*)-**1a** in a stereoselective manner. Isomers (*Z*,*E*)-**1a** and (*Z*,*Z*)-**1a** were prepared from (*Z*)-iodoalkene **10**. After the formation of propargylic alcohol **9** from **3a**, **10** was prepared by regio- and stereoselective hydroindation–iodolysis.[8] The compound **10** was then subjected to Sonogashira reaction with propargyl alcohol followed by $LiAlH_4$ reduction to provide the coupled product (*Z*,*E*)-**8**, which was transformed to dienylic carbonate (*Z*,*E*)-**1a**. The substrate (*Z*,*Z*)-**1a** was obtained by Lindlar reduction of a propargylic carbonate **11**, derived from **10** in two steps.

Our initial attempt at palladium-catalyzed reaction of dienylic carbonate begins with (*E*,*E*)-**1a** (Table 1). When (*E*,*E*)-**1a** was subjected to the reaction, treated with 5 mol % $Pd_2(dba)_3\cdot CHCl_3$ and 20 mol % 1,2-bis(diphenylphosphino)ethane (dppe) in dioxane at 50 °C under an argon atmosphere in a sealed tube, cyclic carbonate **2a** having a (*E*)-1,3-dienyl group was produced in 57% yield (entry 1). The yield of **2a** was decreased to 15% on the reaction in the presence of 1,3-bis(diphenylphosphino)propane (dppp) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) (entries 2 and 3). Interestingly, vinyl-substituted dihydrofuran **12a** was predominantly yielded when bis(diphenylphosphino)-methane (dppm) and triphenylphosphine were used as a ligand (entries 4 and 5). The best result was obtained by carrying out the reaction in the presence of 1,2-bis(diphenylphosphino)ethylene (dppv) (58% yield for **2a**, 27% yield for **12a**) (entry 6). It was also found that the ratio of **2a** to **12a** was changed by altering the reaction temperature (entries 7 and 8). Accordingly, the yield of **2a** decreased to 22%, and that of **12a** increased to 74% by the reaction at 100 °C (entry 8).

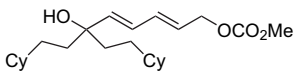
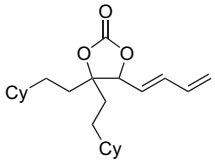
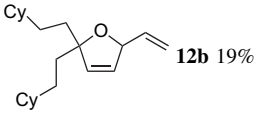
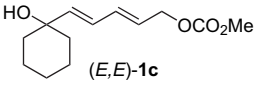
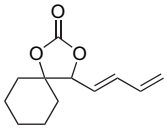
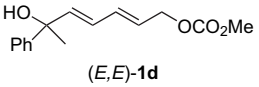
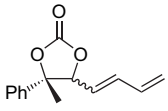
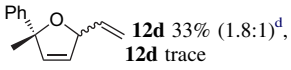
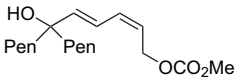
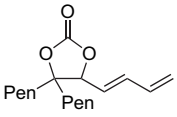
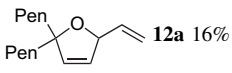
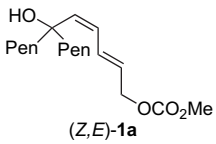
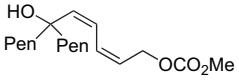


Scheme 3.

Dienylic carbonates having various substituents were next subjected to the palladium-catalyzed reaction conditions described above (Table 2). Substrate (*E*,*E*)-**1b** with dicyclohexylethyl substitution underwent the reaction to give cyclic carbonate **2b** in 50% yield along with dihydrofuran **12b** in 19% yield (entry 1). Reaction of substrate (*E*,*E*)-**1c** containing a cyclohexanol moiety provided the corresponding product **2c** in 68% yield (entry 2). Dienylic carbonate (*E*,*E*)-**1d**, which has unsymmetric substituents, was transformed to cyclic carbonates **2d** (1.8:1 mixture, 34% total yields) and dihydrofurans **12d** (1.8:1 mixture, 33% total yields) as the diastereomeric mixture (entry 3). Although the conversion of (*E*,*E*)-**1d** to **2d** was unsatisfied, the yield could be improved to 72% (3.5:1 mixture) when the process was conducted under a CO_2 atmosphere (entry 4). Substrate (*E*,*Z*)-**1a**, which is a geometric isomer of (*E*,*E*)-**1a**, also reacted with palladium catalyst to give cyclic carbonate **2a** in 70% yield with dihydrofuran **12a** (entry 5). Similarly, reactions using other isomers (*Z*,*E*)-**1a** and (*Z*,*Z*)-**1a** resulted in the production of **2a** along with **12a** in moderate yields, respectively (entries 6 and 7). In these reactions, the olefinic stereochemistries in the resulting cyclic carbonates **2a**–**d** are all *E*, and the results indicate that the reaction proceeds via a thermodynamically favorable common intermediate.

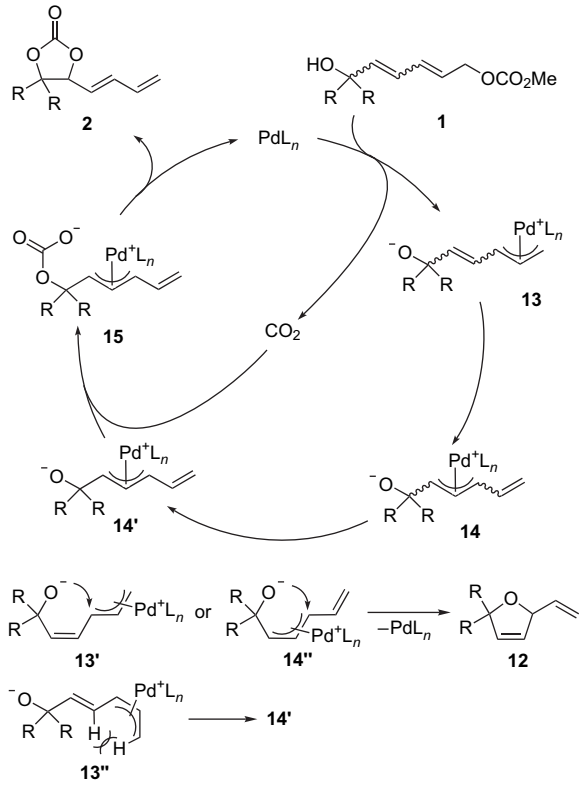
A plausible mechanism for the formation of cyclic carbonates **2** and dihydrofurans **12** is shown in Scheme 4. In this process, the palladium catalyst initially promotes decarboxylation of the conjugated dienylic carbonate **1** to generate the π-allylpalladium complex **13** and CO_2. The complex **13** would be equilibrated to the intermediates **14**, in which the π-allylpalladium is migrated to the internal allylic position. The intermediates **14** would be further transformed to the most thermodynamically favorable *syn*-configurated isomer **14′** via the π–σ–π isomerization process.[4] Finally, fixation of CO_2 followed by cyclization of the resulting intermediate **15** produces the cyclic carbonates **2**. The selective formation of (*E*)-1,3-dienyl-substituted cyclic carbonate **2a** regardless of the olefinic geometry of the substrate **1a** supports that all the reactions have occurred via the common intermediate **14′**. On the other hand, dihydrofurans **12** would be yielded from the direct cyclization of *anti*-configurated π-allyl isomer **13′** or **14″**. At higher reaction temperatures, it is expected that the direct cyclization would proceed prior to the fixation of CO_2 resulting in the selective formation of dihydrofurans **12** (entries 7 and 8 in Table 1).[9] The best yield for **2** was observed from the substrate (*E*,*Z*)-**1a** (entry 5 in Table 2). For this reason, the initially formed π-allylintermediate **13″** from (*E*,*Z*)-**1a** would be relatively unstable

Table 2. Reactions using various substituted dienylic carbonates[a]

Entry	Dienylic carbonate **1**	Product's yield	
		2	**12**
1[b]	 (*E*,*E*)-**1b**	 **2b** 50%	 **12b** 19%
2[b]	 (*E*,*E*)-**1c**	 **2c** 68%	
3[b] 4[c,e]	 (*E*,*E*)-**1d**	 **2d** 34% (1.8:1)[d], **2d** 72% (3.5:1)[d]	 **12d** 33% (1.8:1)[d], **12d** trace
5[c]	 (*E*,*Z*)-**1a**	 **2a** 70%	 **12a** 16%
6[c]	 (*Z*,*E*)-**1a**	**2a** 53%	**12a** 31%
7[c]	 (*Z*,*Z*)-**1a**	**2a** 47%	**12a** 26%

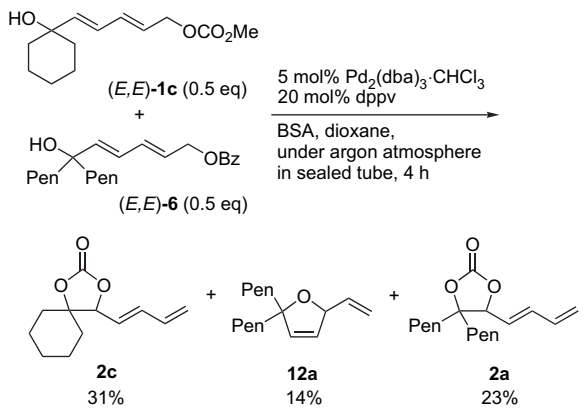
[a] All reactions were carried out with 5 mol % $Pd_2(dba)_3 \cdot CHCl_3$ and 20 mol % ligand in dioxane at 50 °C for 4–12 h.
[b] dppe was used as a ligand.
[c] dppv was used as a ligand.
[d] The stereochemistries of each product are not determined.
[e] The reaction was carried out under CO_2 atmosphere.

because of the allylic strain, which would cause the fast conversion to the intermediate **14′** resulting in the efficient production of cyclic carbonates **2**. The increased yield of **12** from the reaction of (*Z*,*E*)-**1a** (entry 6 in Table 2) indicates that initially formed π-allyl intermediate **13′** or **14″** from this substrate would facilitate the direct cyclization to give **12**. Although the reason for the observed specificity for the production of **2** and **12** depending on the ligand is not clear, it is proposed that this CO_2 elimination–fixation process is sensitive for the steric and electronic property of the phosphine ligand.



Scheme 4. Proposed reaction mechanism for the production of **2** and **12**.

To examine whether CO_2 dissociates from the substrate in the reaction, a crossover experiment with allylic carbonate (*E*,*E*)-**1c** and allylic benzoate (*E*,*E*)-**6** was next performed (Scheme 5). Reaction of an equimolar mixture of (*E*,*E*)-**1c** and (*E*,*E*)-**6** with palladium catalysis in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[10] gave cyclic carbonate **2a** in 23% yield, which was derived from (*E*,*E*)-**6**, along with the formation of (*E*,*E*)-**1c**-derived cyclic carbonate **2c** and (*E*,*E*)-**6**-derived dihydrofuran **12a** in 31% and 14% yield, respectively. It has been clear that **2a** arises by reaction of in situ generated CO_2 formed by decarboxylation of (*E*,*E*)-**1c**.



Scheme 5. Crossover experiment using carbonate (*E*,*E*)-**1c** and benzoate (*E*,*E*)-**6**.

3. Conclusion

In conclusion, we have developed a methodology for the synthesis of 1,3-dienyl-substituted cyclic carbonates by a CO_2-recycling reaction of dienylic carbonates with a palladium catalyst. This reaction proceeded via a successive migration–isomerization of the resulting π-allylpalladium intermediate as well as CO_2 elimination–fixation process. Cyclic carbonates are attractive and important compounds in a variety of chemical research fields, and this reaction would provide a new protocol for the synthesis of cyclic carbonates having a 1,3-dienyl substituent. Synthetic applications of the obtained products and further studies about this type of reactions are now in progress.

4. Experimental

4.1. General

All nonaqueous reactions were carried out under a positive atmosphere of argon and nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. The phrase ‘residue upon workup’ refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure.

4.1.1. (*E*)-6-Hydroxy-1,1-dipentyl-4-hexen-2-yn-1-ol [(*E*)-5a]. To a stirred solution of siloxy enyne (*E*)-**4** (1.5 g, 4.7 mmol) and TMEDA (1.1 mL, 7.05 mmol) in THF (25 mL) was added dropwise a 1.60 M solution of BuLi in hexane (4.4 mL, 7.05 mmol) at −78 °C. After stirring was continued for 2 h at −78 °C, a solution of the 6-undecanone (**3a**) (1.4 mL, 7.05 mmol) in THF (5 mL) was added dropwise to this solution, and stirring was continued for 4 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give the alcohol. To a stirred solution of alcohol in THF (30 mL) was added dropwise a 1.0 M TBAF in THF (9.6 mL, 9.6 mmol) at rt. After stirring was continued for 24 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (80:20 v/v) as eluent to give diol (*E*)-**5a** [814 mg, 68% from (*E*)-**4**] as a yellow oil; IR (neat) 3304, 2934, 2860 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$)

δ 0.96 (6H, t, J=6.6 Hz), 1.31–1.68 (17H, m), 1.90 (1H, s), 4.22 (2H, dd, J=3.6 and 6.4 Hz), 5.78 (1H, td, J=3.6 and 15.9 Hz), 6.23 (1H, td, J=6.4 and 15.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.4, 23.7, 31.8, 41.8, 62.4, 71.5, 82.0, 92.9, 109.9, 141.8; MS m/z 181 [$M^+-71(C_5H_{11})$]; HRMS m/z calcd for $C_{11}H_{17}O_2$ [$M^+-71(C_5H_{11})$]: 181.1228, found 181.1221.

4.1.2. (*E*)-6-Hydroxy-1,1-bis(2-cyclohexylethyl)-4-hexen-2-yn-1-ol [(*E*)-5b]. Yield 73% (for two steps); colorless oil; IR (neat) 3329, 2920, 2851 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84–0.96 (4H, m), 1.11–1.24 (10H, m), 1.33–1.41 (4H, m), 1.63–1.74 (14H, m), 4.18–4.26 (2H, m), 5.78 (1H, d, J=15.1 Hz), 6.23 (1H, td, J=5.1 and 15.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 26.5, 31.6, 33.2, 37.8, 39.2, 62.6, 71.7, 82.0, 93.1, 110.0, 141.7; MS m/z 301 [$M^+-31(CH_2OH)$]; HRMS m/z calcd for $C_{21}H_{33}O$ [$M^+-31(CH_2OH)$]: 301.2531, found 301.2525.

4.1.3. 1-{(*E*)-(5-Hydroxy-3-hexen-1-yl)}-cyclohexanol [(*E*)-5c]. Yield 57% (for two steps); yellow oil; IR (neat) 3461, 2931, 2856 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19–1.94 (10H, m), 2.51 (1H, br s), 2.68 (1H, s), 4.20 (2H, dd, J=1.5 and 4.8 Hz), 5.79 (1H, dt, J=1.5 and 15.9 Hz), 6.24 (1H, dt, J=4.8 and 15.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 25.0, 39.8, 62.3, 62.6, 69.0, 82.1, 93.5, 109.9, 141.9; MS m/z 180 (M^+); HRMS m/z calcd for $C_{11}H_{16}O_2$ (M^+): 180.1151, found 180.1150.

4.1.4. 6-Hydroxy-1-methyl-1-phenyl-4-hexen-2-yn-1-ol [(*E*)-5d]. Yield 38% (for two steps); yellow oil; IR (neat) 3287, 2984, 2927, 2862 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (3H, s), 1.43 (1H, s), 2.33 (1H, s), 4.23 (2H, dd, J=1.8 and 5.1 Hz), 5.84 (1H, td, J=1.8 and 15.9 Hz), 6.31 (1H, td, J=5.1 and 15.9 Hz), 7.27–7.40 (3H, m), 7.64–7.67 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.2, 62.8, 70.3, 82.7, 93.2, 109.7, 124.9, 127.7, 128.3, 142.3, 145.5; MS m/z 187 [$M^+-15(CH_3)$]; HRMS m/z calcd for $C_{12}H_{11}O_2$ [$M^+-15(CH_3)$]: 187.0759, found 187.0747.

4.1.5. (2*E*,4*E*)-1,1-Dipentyl-6-methoxycarbonyloxy-2,4-hexadien-1-ol [(*E*,*E*)-1a]. To a stirred suspension of LAH (30.4 mg, 0.8 mmol) and NaOMe (86.4 mg, 1.6 mmol) in THF (20 mL) was added dropwise the solution of diol (*E*)-**5a** (100.0 mg, 0.4 mmol) in THF (5 mL) at 0 °C. After refluxing for 3 h, the reaction mixture was treated with the minimum amount of cold water, and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give the dienylic alcohol. To a stirred solution of this dienylic alcohol and pyridine (97.1 μL, 1.2 mmol) in CH_2Cl_2 (20 mL) was added dropwise methyl chloroformate (34.0 μL, 0.44 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give dienylic carbonate (*E*,*E*)-**1a** [52.6 mg, 42% from (*E*)-**5a**] as a colorless oil; IR (neat) 3477, 2932, 2858, 1732 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, J=6.9 Hz), 1.25–1.51 (17H, m), 3.79 (3H, s), 4.66 (2H, d, J=6.6 Hz), 5.70 (1H, d, J=15.0 Hz), 5.74 (1H, td, J=6.6 and 14.7 Hz), 6.23 (1H, dd J=10.2 and 15.0 Hz), 6.34 (1H, dd, J=14.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.1, 32.2, 41.0, 54.7, 68.1, 75.2, 124.9, 126.7, 134.8, 142.0, 155.8; MS m/z 241 [$M^+-71(C_5H_{11})$]; HRMS m/z calcd for $C_{13}H_{21}O_4$ [$M^+-71(C_5H_{11})$]: 241.1440, found 241.1432.

4.1.6. (2*E*,4*E*)-1,1-Bis(2-cyclohexylethyl)-6-methoxycarbonyloxy-2,4-hexadien-1-ol [(*E*,*E*)-1b]. Yield 34% (for two steps); yellow oil; IR (neat) 3479, 2922, 2851, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.87 (4H, m), 1.11–1.24 (10H, m), 1.45–1.50 (4H, m), 1.51–1.69 (13H, m), 3.79 (3H, s), 4.66 (2H, d, J=6.6 Hz), 5.71 (1H, d, J=15.1 Hz), 5.78 (1H, dd, J=6.6 and 14.9 Hz), 6.20 (1H, dd, J=10.5 and 15.1 Hz), 6.32 (1H, dd, J=10.5 and 14.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 26.5, 30.8, 33.2, 33.3, 38.0, 38.3, 54.6, 68.1, 75.1, 124.8, 126.8, 134.8, 142.0, 155.7; MS m/z 374 [$M^+-18(H_2O)$]; HRMS m/z calcd for $C_{24}H_{38}O_2$ [$M^+-18(H_2O)$]: 374.2821, found 374.2818.

4.1.7. 1-{(1*E*,3*E*)-(5-Methoxycarbonyloxy-1,3-hexadienyl)}-cyclohexanol [(*E*,*E*)-1c]. Yield 24% (for two steps); yellow oil; IR (neat) 3400, 2932, 2856, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25–1.32 (2H, m), 1.49–1.68 (9H, m), 3.78 (3H, s), 4.65 (2H, dd, J=0.96 and 6.6 Hz), 5.76 (1H, td, J=6.6 and 14.6 Hz), 5.87 (1H, d, J=14.6 Hz), 6.24–6.35 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 25.2, 37.5, 54.6, 67.9, 71.2, 125.2, 125.9, 134.8, 143.3, 155.6; MS m/z 240 (M^+); HRMS m/z calcd for $C_{13}H_{20}O_4$ (M^+): 240.1361, found 240.1347.

4.1.8. (2*E*,4*E*)-6-Methoxycarbonyloxy-1-methyl-1-phenyl-2,4-hexadien-1-ol [(*E*,*E*)-1d]. Yield 35% (for two steps); yellow oil; IR (neat) 3443, 2976, 2956, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (3H, s), 1.90 (1H, s), 3.78 (3H, s), 4.69 (2H, dd, J=1.0 and 6.8 Hz), 5.79 (1H, dt, J=6.8 and 14.9 Hz), 6.04 (1H, d, J=14.7 Hz), 6.27 (1H, dd, J=10.4 and 14.7 Hz), 6.34 (1H, t, J=10.4 Hz), 7.23–7.27 (1H, m), 7.32–7.36 (2H, m), 7.42–7.46 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.5, 54.7, 67.9, 74.3, 125.2, 126.3, 126.7, 127.2, 128.4, 134.3, 142.0, 146.4, 155.7; MS m/z 247 [$M^+-15(CH_3)$]; HRMS m/z calcd for $C_{14}H_{15}O_4$ [$M^+-15(CH_3)$]: 247.0970, found 247.0953.

4.1.9. (2*E*,4*E*)-1,1-Dipentyl-6-benzoyloxy-2,4-hexadien-1-ol [(*E*,*E*)-6]. To a stirred suspension of LAH (96.4 mg, 2.54 mmol) and NaOMe (274 mg, 5.08 mmol) in THF (25 mL) was added dropwise the solution of diol (*E*)-**5a** (257 mg, 1.27 mmol) in THF (5 mL) at 0 °C. After refluxing for 3 h, the reaction mixture was treated with the minimum amount of cold water, and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give the dienylic alcohol. To a stirred solution of the resulting dienylic alcohol, triethylamine (0.35 mL, 2.54 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (20 mL) was added dropwise benzoyl chloride (0.15 mL, 1.27 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined

extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (80:20 v/v) as eluent to give dienyl allylic benzoate (*E*,*E*)-**6** [358 mg, 79% from (*E*)-**5a**] as a colorless oil; IR (neat) 3416, 2932, 2860, 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, J=6.6 Hz), 1.27–1.63 (16H, m), 4.86 (2H, d, J=6.3 Hz), 5.75 (2H, d, J=15.3 Hz), 5.87 (1H, td, J=6.6 and 14.7 Hz), 6.26 (1H, dd, J=10.5 and 14.7 Hz), 6.39 (1H, dd, J=10.5 and 15.3 Hz), 7.41–7.47 (2H, m), 7.53–7.59 (1H, m), 8.05–8.08 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.1, 32.2, 41.1, 65.2, 75.2, 125.8, 126.9, 128.4, 129.7, 130.3, 133.0, 134.1, 141.6, 166.5; MS *m*/*z* 340 [$M^+-18(H_2O)$]; HRMS *m*/*z* calcd for $C_{23}H_{32}O_2$ [$M^+-18(H_2O)$]: 340.2402, found 340.2383.

4.1.10. (*Z*)-5-*tert*-Butyldiphenylsilyloxy-3-penten-1-yne [(*Z*)-4]. To a stirred solution of (*Z*)-allylic alcohol **7** (308 mg, 2.0 mmol), triethylamine (0.56 mL, 4.0 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (20 mL) was added TBDPSCl (0.627 mL, 2.4 mmol) at 0 °C, and stirring was continued for 1 h at rt. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give TBDPS ether. To a stirred solution of the formed TBDPS ether in methanol (20 mL) was added K_2CO_3 (332 mg, 2.4 mmol) at rt. After stirring was continued for 5 h at rt, the reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give silyl ether (*Z*)-**4** (559.7 mg, 87% from **7**) as a colorless oil; IR (neat) 3294, 2932, 2856 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s), 3.00 (1H, s), 4.49 (2H, dd, J=1.6 and 6.0 Hz), 5.45 (1H, ddd, J=1.6, 3.6 and 10.8 Hz), 6.17 (1H, dt, J=6.0 and 10.8 Hz), 7.53–7.44 (6H, m), 7.64–17.69 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.9, 62.4, 79.3, 82.8, 108.0, 127.6, 129.6, 133.5, 135.5, 144.4; MS *m*/*z* 320 (M^+); HRMS *m*/*z* calcd for $C_{21}H_{24}OSi$ (M^+): 320.1596, found 320.1578.

4.1.11. (*Z*)-6-Hydroxy-1,1-dipentyl-4-hexen-2-yn-1-ol [(*Z*)-5]. To a stirred solution of silyl ether (*Z*)-**4** (352 mg, 1.1 mmol) and TMEDA (0.25 mL, 1.65 mmol) in THF (20 mL) was added dropwise a 1.60 M solution of BuLi in hexane (1.0 mL, 1.65 mmol) at −78 °C. After stirring was continued for 2 h at −78 °C, a solution of the 6-undecanone (**3a**) (0.34 mL, 1.65 mmol) in THF (5 mL) was added dropwise to this solution, and stirring was continued for 4 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give propargylic alcohol. To a stirred solution of the formed propargylic alcohol in THF (30 mL) was added dropwise a 1.0 M TBAF in THF (2.2 mL, 2.2 mmol) at rt. After stirring was continued for 24 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with AcOEt–hexane (20:80 v/v) as eluent to give diol (*Z*)-**5** (162 mg, 59% from (*Z*)-**4**) as a yellow oil; IR (neat) 3333, 2934, 2860 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (6H, t, J=6.9 Hz), 1.26–1.69 (16H, m), 1.94 (1H, s), 2.05 (1H, s), 4.40 (2H, dd, J=1.5 and 5.7 Hz), 5.64 (1H, td, J=1.5 and 10.8 Hz), 6.08 (1H, td, J=5.7 and 10.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.8, 31.8, 41.8, 60.8, 71.7, 79.8, 98.6, 110.4, 141.4; MS *m*/*z* 181 [$M^+-71(C_5H_{11})$]; HRMS *m*/*z* calcd for $C_{11}H_{17}O_2$ [$M^+-71(C_5H_{11})$]: 181.1229, found 181.1229.

4.1.12. (2*E*,4*Z*)-6-Hydroxy-1,1-dipropyl-2,4-hexadien-1-ol [(*E*,*Z*)-8]. To a stirred suspension of LAH (22.8 mg, 0.60 mmol) and NaOMe (64.8 mg, 1.20 mmol) in THF (15 mL) was added dropwise the solution of diol (*Z*)-**5** (75.7 mg, 0.30 mmol) in THF (5 mL) at 0 °C. After refluxing for 3 h, the reaction mixture was treated with the minimum amount of cold water, and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give dienylic alcohol (*E*,*Z*)-**8** (41.5 mg, 54%) as a colorless oil; IR (neat) 3360, 2955, 2860 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, J=6.6 Hz), 1.26–1.33 (12H, m), 1.49–1.55 (4H, m), 1.78 (1H, s), 2.08 (1H, s), 4.33 (2H, d, J=6.9 Hz), 5.35 (1H, td, J=6.9 and 11.1 Hz), 5.73 (1H, d, J=15.0 Hz), 6.10 (1H, t, J=11.1 Hz), 6.51 (1H, dd, J=11.1 and 15.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.1, 32.2, 41.0, 58.6, 75.3, 122.5, 128.8, 130.4, 142.1; MS *m*/*z* 183 [$M^+-71(C_5H_{11})$]; HRMS *m*/*z* calcd for $C_{11}H_{19}O_2$ [$M^+-71(C_5H_{11})$]: 183.1385, found 183.1366.

4.1.13. (2*E*,4*Z*)-1,1-Dipentyl-6-methoxycarbonyloxy-2,4-hexadien-1-ol [(*E*,*Z*)-1a]. To a stirred solution of dienylic alcohol (*E*,*Z*)-**8** (40.7 mg, 0.16 mmol) and pyridine (38.8 μL, 0.48 mmol) in CH_2Cl_2 (5 mL) was added dropwise methyl chloroformate (13.6 μL, 0.18 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (80:20 v/v) as eluent to give dienylic carbonate (*E*,*Z*)-**1a** (44.0 mg, 88%) as a colorless oil; IR (neat) 3485, 2931, 2860, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, J=7.2 Hz), 1.27–1.34 (11H, m), 1.45–1.54 (6H, m), 3.79 (3H, s), 4.83 (2H, d, J=7.2 Hz), 5.52 (1H, td, J=7.2 and 10.2 Hz), 5.78 (1H, d, J=15.0 Hz), 6.21 (1H, dd, J=10.2 and 11.2 Hz), 6.51 (1H, dd, J=11.2 and 15.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.1, 32.2, 41.0, 54.7, 63.8, 75.3, 122.1, 122.7, 133.0, 143.5, 155.9; MS *m*/*z* 237 [$M^+-75(OCO_2CH_3)$]; HRMS *m*/*z* calcd for $C_{16}H_{29}O$ [$M^+-75(OCO_2CH_3)$]: 237.2218, found 237.2208.

4.1.14. 3-Pentyl-1-octyn-3-ol (9). To a stirred solution of trimethylsilyl acetylene (7.1 mL, 50.0 mmol) and TMEDA (7.5 mL, 50.0 mmol) in THF (225 mL) was added dropwise a 1.60 M BuLi in hexane (31.3 mL, 50.0 mmol) at −78 °C. After stirring was continued for 2 h at −78 °C, a solution of the 6-undecanone (**3a**) (5.1 mL, 25.0 mmol) in THF (25.0 mL) was added dropwise to this solution, and stirring was continued for 4 h at the same temperature. The reaction

mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give propargylic alcohol (6.58 g, 98%) as a colorless oil. To a stirred solution of the above propargylic alcohol (3.30 g, 12.3 mmol) in methanol (120 mL) was added K_2CO_3 (2.04 g, 14.8 mmol) at rt. After stirring was continued for 5 h at rt, the reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give alkyne **9** (2.20 g, 91%) as a colorless oil; IR (neat) 3400, 3310, 2935, 3862 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (6H, t, J=6.8 Hz), 1.26–1.39 (8H, m), 1.46–1.54 (4H, m), 1.61–1.69 (4H, m), 1.88 (1H, s), 2.43 (1H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 22.5, 23.7, 31.9, 41.7, 71.0, 72.0, 87.0; MS m/z 125 [$M^+-71(C_5H_{11})$]; HRMS calcd for $C_8H_{13}O$ [$M^+-71(C_5H_{11})$]: 125.1004, found 125.0985.

4.1.15. (*Z*)-1,1-Dipentyl-3-iode-2-propen-1-ol (10). To a stirred suspension of anhydrous indium trichloride (747 mg, 3.4 mmol) in THF (25 mL) was added dropwise DIBAL (1.0 M hexane solution, 3.3 mL, 3.3 mmol) at −78 °C. After stirring was continued for 30 min at −78 °C, a solution of alkyne **9** (491 mg, 2.5 mmol) in THF (5 mL) and triethylborane (1.0 M hexane solution 0.5 mL, 0.5 mmol) were added to this suspension, and stirring was continued for 2.5 h at the same temperature. Iodine (1.9 g, 7.5 mmol) was then added to the reaction mixture, and the mixture was continuously stirred for 30 min at −78 °C. The reaction mixture was poured into saturated $NaHCO_3$ solution and sodium thiosulfate solution was added. The product was extracted with Et_2O, and the combined extracts were washed with saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give alkenyl iodide **10** (577 mg, 77%) as a colorless oil; IR (neat) 3467, 2930, 2954 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (6H, t, J=6.8 Hz), 1.24–1.43 (12H, m), 1.54–1.71 (4H, m), 2.12 (1H, s), 6.25 (1H, d, J=8.5 Hz), 6.49 (1H, d, J=8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.2, 32.3, 40.6, 75.5, 77.3, 144.4; MS m/z 253 [$M^+-71(C_5H_{11})$]; HRMS m/z calcd for $C_8H_{14}OI$ [$M^+-71(C_5H_{11})$]: 253.0089, found 253.0074.

4.1.16. (2*Z*,4*E*)-6-Hydroxy-1,1-dipropyl-2,4-hexadien-1-ol [(*Z*,*E*)-8]. To a suspension of CuI (16.2 mg, 85.0 μmol), $PdCl_2(PPh_3)_2$ (59.7 mg, 85.0 μmol) in triethylamine (20 mL) was added propargyl alcohol (0.14 mL, 1.7 mmol) at 0 °C. After stirring was continued for 30 min at 0 °C, a solution of alkenyl iodide **10** (551 mg, 1.7 mmol) in triethylamine (5 mL) was added to this solution, and stirring was continued for 1 h at the same temperature. The reaction mixture was poured into saturated NH_4Cl solution and extracted with AcOEt. The combined extracts were washed with saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give enyne. To a stirred suspension of LAH (129 mg, 3.4 mmol) and NaOMe (367 mg, 6.8 mmol) in THF (20 mL) was added dropwise the solution of the produced enyne in THF (5 mL) at 0 °C. After refluxing for 3 h, the reaction mixture was treated with the minimum amount of cold water, and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with toluene–AcOEt (90:10 v/v) as eluent to give dienylic alcohol (*Z*,*E*)-**8** (165.9 mg, 41% from **10**) as a yellow oil; IR (neat) 3360, 2955, 2860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, t, J=7.1 Hz), 1.22–1.30 (10H, m), 1.43–1.57 (8H, m), 4.20 (2H, d, J=6.1 Hz), 5.30 (1H, d, J=11.7 Hz), 5.77 (1H, td, J=6.1 and 15.2 Hz), 6.01 (1H, t, J=11.7 Hz), 7.14 (1H, dd, J=11.5 and 15.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.5, 32.4, 42.4, 63.6, 77.5, 128.3, 128.7, 133.4, 136.3; MS m/z 183 [$M^+-71(C_5H_{11})$]; HRMS m/z calcd for $C_{11}H_{19}O_2$ [$M^+-71(C_5H_{11})$]: 183.1385, found 183.1373.

4.1.17. (2*Z*,4*E*)-1,1-Dipentyl-6-methoxycarbonyloxy-2,4-hexadien-1-ol [(*Z*,*E*)-1a]. To a stirred solution of dienylic alcohol (*Z*,*E*)-**8** (166 mg, 0.65 mmol) and pyridine (0.16 mL, 1.95 mmol) in CH_2Cl_2 (10 mL) was added dropwise methyl chloroformate (60.2 μL, 0.78 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give dienylic carbonate (*Z*,*E*)-**1a** (178 mg, 88%) as a yellow oil; IR (neat) 3520, 2932, 2860, 1747 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.43 (6H, t, J=6.8 Hz), 0.71–0.95 (17H, m), 2.86 (3H, s), 4.08 (2H, dd, J=1.2 and 6.6 Hz), 4.66 (1H, d, J=12.0 Hz), 5.13 (1H, dt, J=6.6 and 15.4 Hz), 5.45 (1H, t, J=11.7 Hz), 7.07 (1H, ddd, J=1.2, 11.7 and 15.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.2, 32.2, 42.3, 54.7, 68.4, 77.6, 127.1, 128.4, 132.1, 137.9, 155.8; MS m/z 237 [$M^+-75(OCO_2CH_3)$]; HRMS m/z calcd for $C_{16}H_{29}OI$ [$M^+-75(OCO_2CH_3)$]: 237.2219, found 237.2231.

4.1.18. (*Z*)-1,1-Dipentyl-6-methoxycarbonyloxy-2-hexen-4-yn-1-ol (11). To a suspension of CuI (13.8 mg, 72.5 μmol) and $PdCl_2(PPh_3)_4$ (50.9 mg, 72.5 μmol) in triethylamine (10 mL) was added propargyl alcohol (0.12 mL, 1.45 mmol) at 0 °C. After stirring was continued for 30 min at 0 °C, a solution of alkenyl iodide **10** (471 mg, 1.45 mmol) in triethylamine (5 mL) was added to this solution, and stirring was continued for 1 h at the same temperature. The reaction mixture was poured into saturated NH_4Cl solution and extracted with AcOEt. The combined extracts were washed with saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give enyne. To a stirred solution of the formed enyne and pyridine (0.35 mL, 4.35 mmol) in CH_2Cl_2 (20 mL) was added dropwise methyl chloroformate (0.11 mL, 1.45 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (85:15 v/v) as eluent to give propargylic carbonate **11** (315 mg, 70% from **10**) as a yellow oil; IR (neat) 3562, 2932, 2860, 1747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, J=6.9 Hz), 1.24–1.41 (12H, m), 1.43–1.56 (4H, m), 2.82 (1H, s), 3.81 (3H, s),

4.86 (2H, d, J=2.4 Hz), 5.56 (1H, td, J=2.4 and 12.0 Hz), 5.93 (1H, d, J=12.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.4, 23.0, 32.1, 41.0, 54.9, 55.9, 76.4, 83.5, 88.8, 105.8, 150.6, 155.0; MS m/z 310 (M^+); HRMS m/z calcd for $C_{18}H_{30}O_4$ (M^+): 310.2144, found 310.02115.

4.1.19. (2*Z*,4*E*)-1,1-Dipentyl-6-methoxycarbonyloxy-2,4-hexadien-1-ol [(*Z*,*Z*)-1a]. To a stirred solution of propargylic carbonate **11** (79.1 mg, 0.23 mmol) in AcOEt (2.6 mL) was added Pd/$CaCO_3$ (14.0 mg) poisoned with lead and quinoline (5.6 μL) at rt. The reaction flask was purged with H_2. After stirring was continued for 4 h at same temperature. The reaction mixture was filtered through a short pad of Celite. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give dienylic carbonate (*Z*,*Z*)-**3a** (16.0 mg, 23%) as a yellow oil; IR (neat) 3498, 2955, 2860, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, t, J=6.8 Hz), 1.21–1.34 (11H, m), 1.54–1.58 (6H, m), 3.79 (3H, s), 4.81 (2H, dd, J=1.5 and 7.1 Hz), 5.44 (1H, d, J=12.0 Hz), 5.58 (1H, td, J=7.1 and 12.0 Hz), 6.27 (1H, t, J=12.0 Hz), 7.13 (1H, tt, J=1.5 and 12.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.4, 32.3, 42.4, 54.8, 63.2, 77.6, 123.1, 124.0, 129.3, 138.9, 155.6; MS m/z 294 [$M^+-18(H_2O)$]; HRMS m/z calcd for $C1_8H_{30}O_3$ [$M^+-18(H_2O)$]: 294.2195, found 294.2179.

4.2. General procedure for the palladium-catalyzed reaction of dienylic carbonate 1. Reaction of (*E*,*E*)-1a (entry 6 in Table 1)

To a stirred solution of dienylic carbonate [(*E*,*E*)-**1a**] (34.3 mg, 0.11 mmol) in dioxane (1.1 mL) were added $Pd_2(dba)_3\cdot CHCl_3$ (5.7 mg, 5.5 μmol) and dppv (8.7 mg, 22.0 μmol) in a sealed tube at rt. After stirring was continued for 4 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give cyclic carbonate **2a** (17.8 mg, 58%) and dihydrofuran **12a** (7.0 mg, 27%) as a colorless oil, respectively.

4.2.1. (3*E*)-1,2-Carbonyldioxy-1,1-dipentyl-hexadiene (2a). Yield 58%; colorless oil; IR (neat) 2931, 2870, 1790 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (6H, t, J=6.8 Hz), 1.26–1.75 (16H, m), 4.80 (1H, d, J=7.6 Hz), 5.27 (1H, d, J=9.2 Hz), 5.35 (1H, d, J=14.7 Hz), 5.67 (1H, dd, J=7.6 and 14.4 Hz), 6.33–6.41 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.3, 22.5, 22.5, 31.8, 31.8, 33.2, 36.3, 84.5, 88.3, 120.9, 124.3, 135.1, 136.8, 154.2; MS m/z 236 [$M^+-44(CO_2)$]; HRMS m/z calcd for $C_{16}H_{28}O$ [$M^+-44(CO_2)$]: 236.2140, found 236.2134.

4.2.2. 2,2-Dipentyl-5-vinyl-2,5-dihydrofuran (12a). Yield 27%; yellow oil; IR (neat) 2930, 2860, 1468 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, J=6.9 Hz), 1.26–1.37 (12H, m), 1.50–1.61 (4H, m), 5.09 (1H, dd, J=1.2 and 10.2 Hz), 5.16 (1H, dd, J=1.8 and 7.2 Hz), 5.25 (1H, dd, J=1.2 and 17.1 Hz), 5.60 (1H, dd, J=1.8 and 6.0 Hz), 5.61 (1H, d, J=6.0 Hz), 5.80 (1H, ddd, J=7.2, 10.2 and 17.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 22.6, 23.6, 24.0, 32.3, 32.3, 39.8, 40.1, 87.1, 93.5, 115.7, 128.4, 133.4, 139.1; MS m/z 236 (M^+); HRMS m/z calcd for $C_{16}H_{28}O$ (M^+): 236.2140, found 236.2133.

4.2.3. (3*E*)-1,2-Carbonyldioxy-bis(2-cyclohexylethyl)-hexadiene (2b). Yield 50%; yellow oil; IR (neat) 2922, 2851, 1801 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87–0.94 (4H, m), 1.11–1.33 (12H, m), 1.62–1.78 (14H, m), 4.77 (1H, d, J=7.6 Hz), 5.28 (1H, d, J=9.5 Hz), 5.36 (1H, d, J=14.9 Hz), 5.64 (1H, dd, J=7.6 and 14.9 Hz), 6.32–6.42 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1, 26.4, 30.2, 30.2, 30.6, 33.0, 33.0, 33.1, 33.2, 33.8, 37.7, 37.8, 84.5, 88.5, 120.8, 124.4, 135.1, 136.7, 154.2; MS m/z 360 (M^+); HRMS m/z calcd for $C_{23}H_{36}O_3$ (M^+): 360.2655, found 360.2642.

4.2.4. 2,2-Bis-(2-cyclohexyl-ethyl)-5-vinyl-2,5-dihydrofuran (12b). Yield 19%; colorless oil; IR (neat) 2922, 2851, 1448 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78–0.81 (4H, m), 1.07–1.22 (12H, m), 1.41–1.63 (14H, m), 5.02 (1H, dd, J=1.2 and 10.2 Hz), 5.07 (1H, dd, J=1.0 and 7.3 Hz), 5.17 (1H, dd, J=1.2 and 17.4 Hz), 5.58 (1H, dd, J=2.0 and 6.1 Hz), 5.61 (1H, d, J=6.1 Hz), 5.72 (1H, ddd, J=7.3, 10.2, and 17.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 26.4, 26.7, 31.5, 32.0, 33.4, 33.4, 33.5, 37.1, 37.6, 38.2, 38.2, 87.1, 93.5, 115.5, 128.3, 133.4, 139.0; MS m/z 316 (M^+); HRMS m/z calcd for $C_{22}H_{36}O$ (M^+): 316.2767, found 316.2758.

4.2.5. (3*E*)-1,2-Carbonyldioxy-(1-spirocyclohexyl)-3,5-hexadiene (2c). Yield 68%; yellow oil; IR (neat) 3026, 2928, 1800 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21–1.30 (1H, m), 1.39–1.46 (1H, m), 1.55–1.58 (6H, m), 1.60–1.92 (2H, m), 4.64 (1H, d, J=7.8 Hz), 5.27 (1H, d, J=5.6 and 9.3 Hz), 5.35 (1H, d, J=5.6 and 15.6 Hz), 5.65 (1H, dd, J=7.8 and 14.2 Hz), 6.31–6.42 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.1, 24.7, 31.5, 35.4, 85.7, 85.7, 120.1, 123.9, 134.9, 136.6, 153.9; MS m/z 208 (M^+); HRMS m/z calcd for $C_{12}H_{16}O_3$ (M^+): 208.1100, found 208.1061.

4.2.6. Carbonyldioxy-1-methyl-1-phenyl-(3*E*)-hexadiene (2d). Yield 34% (1.8:1 diastereomeric mixture); major product: yellow oil; IR (neat) 2983, 2930, 1798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (3H, s), 4.96 (1H, d, J=7.8 Hz), 5.33 (1H, d, J=9.5 Hz), 5.39 (1H, d, J=15.8 Hz), 5.80 (1H, dd, J=8.0 and 14.4 Hz), 6.37–6.48 (2H, m), 7.32–7.44 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 86.4, 86.7, 121.5, 122.8, 123.8, 128.9, 129.0, 134.8, 137.9, 140.9, 153.4; MS m/z 230 (M^+); HRMS m/z calcd for $C_{14}H_{14}O_3$ (M^+): 230.0943, found 230.0936. Minor product: yield 12%; yellow oil; IR (neat) 2982, 2927, 1798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (3H, s), 4.93 (1H, dd, J=8.5 and 18.1 Hz), 4.96 (1H, d, J=8.5 Hz), 5.16 (1H, dd, J=1.2 and 10.4 Hz), 5.28 (1H, dd, J=1.2 and 17.1 Hz), 6.08 (1H, td, J=10.4 and 17.1 Hz), 6.29 (1H, dd, J=10.4 and 18.1 Hz), 7.20–7.24 (2H, m), 7.32–7.41 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 86.7, 87.2, 120.9, 124.9, 125.1, 128.4, 128.5, 134.7, 136.9, 137.6, 153.9; MS m/z 230 (M^+); HRMS m/z calcd for $C_{14}H_{14}O_3$ (M^+): 230.0943, found 230.0936.

4.2.7. 2-Methyl-2-phenyl-5-vinyl-2,5-dihydrofuran (12d). Yield 33% (1.8:1 diastereomeric mixture); colorless oil; IR (neat) 2923, 2852, 1462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (1.92H, s), 1.69 (1.08H, s), 5.10 (0.64H, dt, J=1.2 and 10.2 Hz), 5.17 (0.36H, dt, J=1.2 and 10.2 Hz),

5.26 (1H, m), 5.31–5.37 (1H, m), 5.72 (1H, m), 5.80 (0.64H, ddd, J=7.3, 10.0 and 17.3 Hz), 5.90 (0.36H, ddd, J=7.0, 9.5 and 17.3 Hz), 6.04 (1H, m), 7.23 (1H, m), 7.30–7.34 (2H, m), 7.40–7.45 (2H, m); MS m/z 186 (M^+); HRMS m/z calcd for $C_{13}H_{14}O$ (M^+): 186.1044, found 186.1040.

4.3. Crossover experiment of (*E*,*E*)-1a and (*E*,*E*)-6

To a stirred solution of dienylic carbonate (*E*,*E*)-**1c** (35.4 mg, 0.15 mmol) and dienylic benzoate (*E*,*E*)-**6** (53.7 mg, 0.15 mmol) in dioxane (3.0 mL) were added $Pd_2(dba)_3 \cdot CHCl_3$ (15.5 mg, 15.0 μmol), dppv (23.8 mg, 0.06 mmol), and BSA (55.6 μL, 0.23 mmol) in a sealed tube at rt. After stirring was continued for 4 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give **2a** (9.5 mg, 23%), **2c** (9.6 mg, 31%), and dihydrofuran **12a** (5.0 mg, 14%) as a colorless oil, respectively.

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References and notes

1. Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R. *Chem. Rev.* **2001**, *101*, 953.
2. Examples about palladium-catalyzed CO_2 fixation reactions to give cyclic carbonates: (a) Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.; Sakai, S. *Chem. Lett.* **1985**, 199; (b) Trost, B. M.; Angle, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 6123; (c) Trost, B. M.; Lynch, J. K.; Angle, S. R. *Tetrahedron Lett.* **1987**, *28*, 375; (d) Wershofen, S.; Scharf, H. D. *Synthesis* **1988**, 854; (e) Suzuki, S.; Fujita, Y.; Kobayashi, Y.; Sato, F. *Tetrahedron Lett.* **1989**, *30*, 3487; Uemura, K.; Shiraishi, D.; Noziri, M.; Inoue, Y. *Bull. Chem. Soc.* **1999**, *72*, 1063.
3. (a) Yoshida, M.; Ihara, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 616; (b) Yoshida, M.; Fujita, M.; Ishii, T.; Ihara, M. *J. Am. Chem. Soc.* **2003**, *125*, 4874; (c) Yoshida, M.; Fujita, M.; Ihara, M. *Org. Lett.* **2003**, *5*, 3325; (d) Yoshida, M.; Ohsawa, Y.; Ihara, M. *J. Org. Chem.* **2004**, *69*, 1590; (e) Yoshida, M.; Ihara, M. *Chem.—Eur. J.* **2004**, 2886.
4. For reviews about palladium-catalyzed reactions of allylic compounds: (a) Tsuji, J. *Acc. Chem. Res.* **1969**, *2*, 144; (b) Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197; (c) Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281; (d) Tsuji, J. *Tetrahedron* **1986**, *42*, 4261; (e) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140; (f) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.
5. (a) Trost, B. M.; Lautens, M.; Hung, M.-H.; Carmichael, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 7641; (b) Ishii, Y.; Gao, C.; Xu, W.-X.; Iwasaki, M.; Hidai, M. *J. Org. Chem.* **1993**, *58*, 6818; (c) Kang, S.-K.; Park, D.-C.; Jeon, J.-H.; Rho, H.-S.; Yu, C.-M. *Tetrahedron Lett.* **1994**, *35*, 2357; (d) Kang, S.-K.; Park, D.-C.; Rho, H.-S.; Yu, C.-M.; Hong, J.-H. *Synth. Commun.* **1995**, *25*, 203.
6. Pearson, W. H.; Hines, J. V. *J. Org. Chem.* **2000**, *65*, 5785.
7. Hartung, I. V.; Eggert, U.; Haustedt, L. O.; Niess, B.; Schäfer, P. M.; Hoffmann, H. M. R. *Synthesis* **2003**, 1844.
8. Takami, K.; Mikami, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **2003**, *68*, 6627.
9. As another possibility for the production of **12**, reversible ring opening of **2** by palladium followed by the direct cyclization from the π-allyl complex **13′** or **14″** would be occurred (see Refs. 5c and 5d). However, no reaction has occurred from a reaction of the isolated cyclic carbonate **2a** with palladium catalyst. The result implies that cyclic carbonate **2** is produced irreversibly.
10. For a review on BSA: El Gihani, M. T.; Heaney, H. *Synthesis* **1998**, 357.