JOC The Journal of Organic Chemistry

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Rhodium-Catalyzed Decarboxylative and Dehydrogenative Coupling of Maleic Acids with Alkynes and Alkenes

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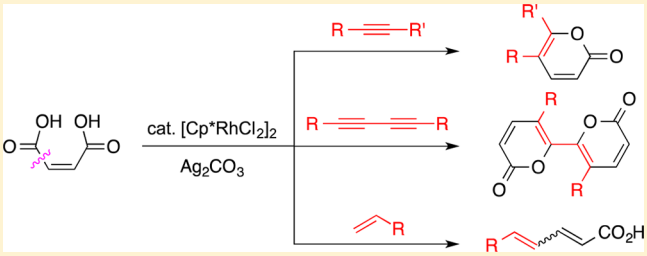
Supporting Information

ABSTRACT: The dehydrogenative coupling of maleic acids with alkynes proceeds smoothly accompanied by decarboxylation under rhodium catalysis to produce variously substituted α-pyrone derivatives. The catalyst system is also applicable to the coupling with 1,3-diynes and alkenes.



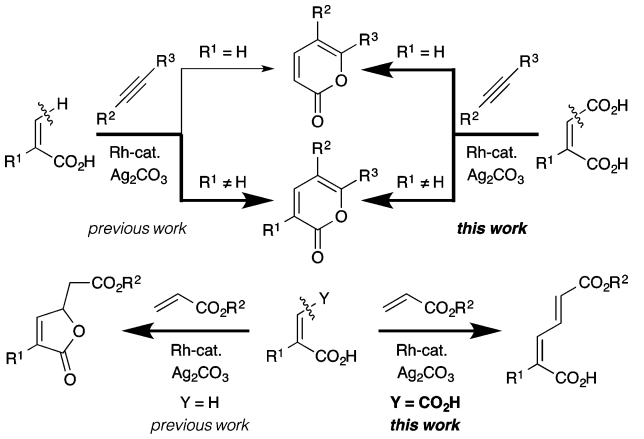
INTRODUCTION

α-Pyrones with various substitution patterns are found in a wide range of natural products and in a number of pharmacologically active compounds.[1] Therefore, development of methods for the selective syntheses of the family of α-pyrones has attracted much attention. As one of the step-economical synthetic routes to them, we developed the rhodium-catalyzed dehydrogenative coupling of substituted acrylic acids with internal alkynes.[2] Thus, 2-substituted acrylic acids such as methacrylic acid underwent the coupling smoothly to produce 3,5,6-trisubstituted α-pyrones. However, the reaction of acrylic acid itself did not proceed efficiently even with an increased rhodium loading, giving the corresponding 5,6-disubstituted α-pyrone in a moderate yield. Such 5,6-disubstituted[3] as well as 6-monosubstituted α-pyrones[4] are of particular importance because of their androgen-like and antifungal activities, respectively. In the context of our studies on the rhodium-catalyzed dehydrogenative coupling of carboxylic acids,[5,6] we found that the 3-unsubstituted α-pyrones can be synthesized in good yields by using maleic acid in place of acrylic acid (Scheme 1). Since maleic acids are comparably cheap, readily available build blocks,[7] we investigated their decarboxylative coupling[8] further. Consequently, it was found that the couplings of acrylate esters and relevant alkenes selectively give acyclic products, dienoic acids, rather than cyclic butenolides, which are obtained in the reaction of 2-substituted acrylic acids.[2] The results obtained with respect to these reactions are described herein.

RESULTS AND DISCUSSION

Under similar conditions to those for the reaction of methacrylic acid with alkynes in our previous work using 1 mol % of $[Cp^*RhCl_2]_2$ and 1 equiv of Ag_2CO_3 in DMF at 120 °C,[2] the reaction of acrylic acid (**1a**) (0.5 mmol) with diphenylacetylene (**2a**) (0.5 mmol) was sluggish to produce

Scheme 1. Dehydrogenative Coupling of Acrylic and Maleic Acids with Alkynes and Alkenes



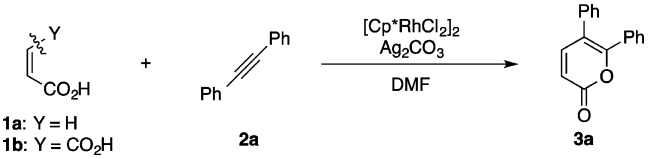
5,6-diphenyl-2*H*-pyran-2-one (**3a**) in a moderate yield (entry 1 in Table 1). In contrast, maleic acid (**1b**) reacted with **2a** efficiently accompanied by decarboxylation to afford **3a** almost quantitatively (entry 2). At 100 °C, both the reaction rate and the product yield decreased considerably (entry 3). In the presence of $Cu(OAc)_2 \cdot H_2O$ (1 mmol) as an oxidant in place of Ag_2CO_3, the yield of **3a** was low (entry 4).

Next, we examined the reactions of **1b** with various alkynes **2**. Under the conditions employed for entry 2 in Table 1, **1b** coupled with *para*-substituted diphenylacetylene **2b**–**d** to form the corresponding pyrones **3b**–**d** in 84–96% yields (entries 1–3 in Table 2). The reactions with di(2-thienyl)acetylene (**2e**), 4-octyne (**2f**), and 8-hexadecyne (**2g**) also proceeded smoothly to give 5,6-dithienyl- (**3e**) and 5,6-dialkyl-α-pyrones **3f**,**g** in

Received: September 9, 2013
Published: October 15, 2013

   dx.doi.org/10.1021/jo401992d | J. Org. Chem. 2013, 78, 11427–11432

Table 1. Reaction of Acrylic- or Maleic Acid 1 with Diphenylacetylene (2a)[a]

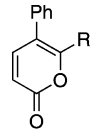


1a: Y = H
1b: Y = CO_2H
2a
3a

entry	1	temp (°C)	time (h)	yield of 3a (%)
1	**1a**	120	4	39 (44)[b]
2	**1b**	120	2	97 (98)[b]
3	**1b**	100	10	(70)[b]
4[c]	**1b**	160	6	(29)[b]

[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), Ag_2CO_3 (0.5 mmol), DMF (2.5 mL) under N_2. [b]GC yield. [c]$Cu(OAc)_2·H_2O$ (1 mmol) was used in place of Ag_2CO_3.

good yields (entries 4–6). Unsymmetrical alkylphenylacetylenes **2h** and **2i** coupled with **1b** to form 5-alkyl-6-phenyl-α-pyrones **3h** and **3i** predominantly, along with minor amounts of separable regioisomers **3h′** and **3i′** (entries 7 and 8). The reaction of ethyl phenylpropiolate (**2j**) required a higher temperature (140 °C), which resulted in a lower regioselectivity (entry 9). In contrast, the reaction with 2-methyl-4-phenylbut-3-yn-2-ol (**2k**) gave **3k** exclusively, with no other isomer being detected by GC and GC-MS (entry 10). In the reaction of 2-methylmaleic acid (**1c**) with **2a**, regioselective decarboxylation took place efficiently to afford **3l** in 90% yield (entry 11). 2-Phenylmaleic acid (**1d**) also reacted with a series of diarylacetylenes **2a,c-f** to selectively produce 3,5,6-triaryl-α-pyrones **3m–q** in 78–98% yields (entries 12–16). The electron-withdrawing groups in **2** tend to retard the reaction.

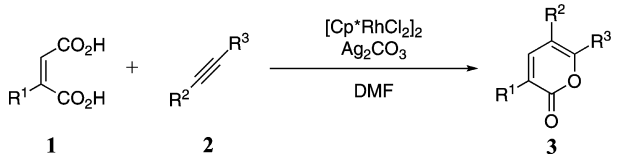


3′

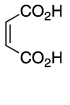
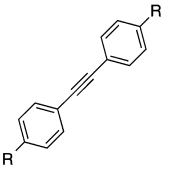
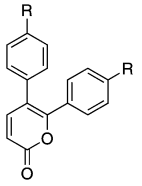
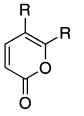
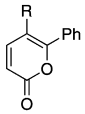
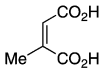
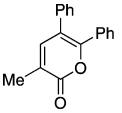
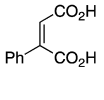
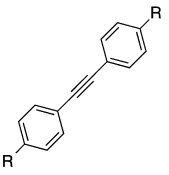
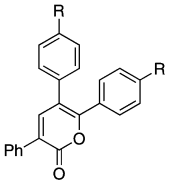
A possible mechanism for the coupling of maleic acids **1** with **2** is illustrated in Scheme 2, in which neutral ligands are omitted. Coordination of the carboxyl oxygen atoms of **1** to a $Cp^*Rh(III)X_2$ species gives a rhodium(III) dicarboxylate **A**. Subsequent decarboxylation to form a five-membered rhodacycle **B**, alkyne insertion to give **C**, and reductive elimination take place to produce **3**. The resulting $Cp^*Rh(I)$ species may be oxidized in the presence of Ag_2CO_3 to regenerate $Cp^*Rh(III)X_2$. In the cases using 2-substituted maleic acids, the decarboxylation takes place at the C3-position to selectively form **B** rather than **B′**. The reason for the facile formation of **B** is not clear at the present stage. In addition, it is possible that the decarboxylation is induced by the silver salt rather than Rh.[9] However, it was confirmed that the decarboxylation of **1d** (R^1 = Ph) did not proceed at all by treatment with Ag_2CO_3 in the absence of $[Cp^*RhCl_2]_2$. Thus, under conditions using 1 equiv of Ag_2CO_3 in DMF at 120 °C, **1d** was quantitatively recovered.

In contrast to reactive internal alkynes **2**, terminal alkynes could not be employed for the reaction.[10] Actually, treatment of **1b** with phenylacetylene did not give desired 6-phenyl-α-pyrone at all. However, the monosubstituted α-pyrone could be prepared via (1) the coupling of **1b** with **2k** and (2) the palladium-catalyzed deprotection (Scheme 3).[11] Thus, treatment of **3k** (0.2 mmol), formed in entry 10 in Table 2, by using

Table 2. Reaction of Acid 1 with Alkynes 2[a]



1 **2** **3**

entry	1	2	product(s), % yield
			
1	**1b**	**2b**: R = Me	**3b**: R = Me, 87
2		**2c**: R = OMe	**3c**: R = OMe, 96
3		**2d**: R = Cl	**3d**: R = Cl, 84
			
4	**1b**	**2e**: R = 2-thienyl	**3e**: R = 2-thienyl, 83
5		**2f**: R = *n*-Pr	**3f**: R = *n*-Pr, 85
6		**2g**: R = *n*-C_7H_{15}	**3g**: R = *n*-C_7H_{15}, 89
			
7	**1b**	**2h**: R = Me	**3h**: R = Me, 73[b]
8		**2i**: R = *n*-Bu	**3i**: R = *n*-Bu, 75[c]
9[d]		**2j**: R = CO_2Et	**3j**: R = CO_2Et, 40[e]
10		**2k**: R = C(OH)Me_2	**3k**: R = C(OH)Me_2, 58
			
11	**1c**	**2a**	**3l**, 90
			
12[f]	**1d**	**2a**: R = H	**3m**: R = H, 95
13[g]		**2c**: R = OMe	**3n**: R = OMe, 96
14[h]		**2d**: R = Cl	**3o**: R = Cl, 95
15[g]		**2e**: R = *t*-Bu	**3p**: R = *t*-Bu, 98
16[i]		**2f**: R = CF_3	**3q**: R = CF_3, 78

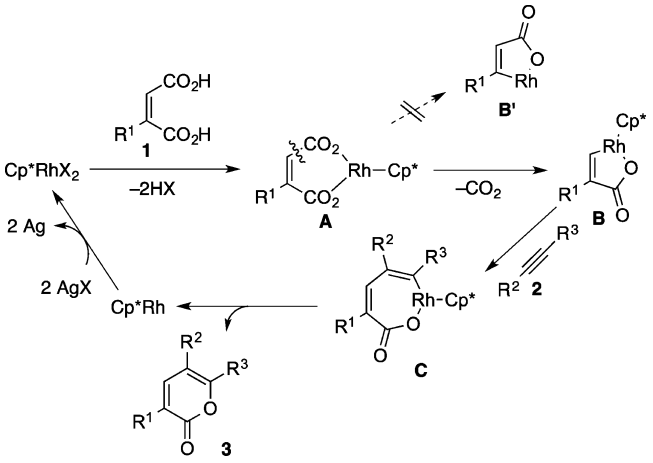
[a]Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), Ag_2CO_3 (0.5 mmol) in DMF (2.5 mL) at 120 °C under N_2 for 2 h. [b]An isomer **3h′** (1%) was also formed. [c]An isomer **3i′** (7%) was also formed. [d]At 140 °C for 4 h. [e]Isomer **3j′** (10%) was also formed. [f]For 8 h. [g]For 4 h. [h]For 24 h. [i]For 72 h.

$Pd(OAc)_2$ (10 mol %), P(1-naphthyl)$_3$ (20 mol %), bromobenzene (20 mol %), and Cs_2CO_3 (20 mol %) in refluxing *o*-xylene for 16 h gave 6-phenyl-α-pyrone (**4**) in 80% yield.

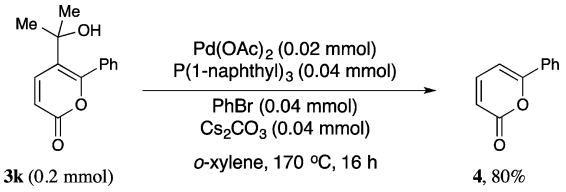
It was found that not only monoynes **2** but also 1,3-diynes **5** react with **1b** to furnish *6H,6′H*-[2,2′-bipyran]-6,6′-dione frameworks. Under the standard conditions, **1b** coupled with octa-3,5-diyne (**5a**) in a 2:1 manner to form **6a** in 54% yield (Scheme 4). At 140 °C, the reaction was completed within 2 h

dx.doi.org/10.1021/jo401992d | J. Org. Chem. 2013, 78, 11427–11432

Scheme 2. Possible Mechanism for the Reaction of 1a with 2

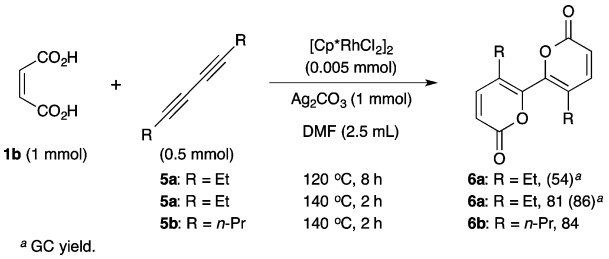


Scheme 3. Deprotection of 3k



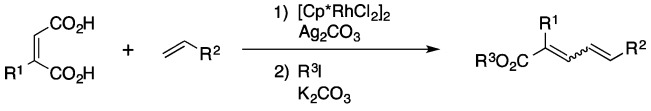
and the yield of **6a** was enhanced to 86% yield. Similarly, the reaction with deca-4,6-diyne (**5b**) gave **6b** in 84% yield.

Scheme 4. Reaction of 1b with 1,3-Diynes 5



Finally, we examined the decarboxylative coupling of maleic acids **1** with alkenes **7**. First, **1b** (0.5 mmol) was treated with butyl acrylate (**7a**) (1 mmol) in the presence of $[Cp^*RhCl_2]_2$ (1 mol %) and Ag_2CO_3 (1 equiv) in DMF at 140 °C. After 1 h, GC and GC-MS analyses of the resulting mixture did not show any coupling/cyclization product including a butenolide, which was formed in the reaction of 2-substituted acrylic acids with **7a** (Scheme 1).[2] Instead, after esterification using MeI (5 equiv) and K_2CO_3 (3 equiv) at rt for 3 h for quantification, 1-*n*-butyl 6-methyl hexa-2,4-dienedioate (**8a**) was obtained as a mixture of two geometric isomers in 57% yield (entry 1 in Table 3). At the present stage, however, the reason the acyclic product was selectively formed involving partial 2*E*−2*Z* isomerization is obscure. Increasing the Rh-catalyst loading (2 mol %) somewhat improved the yield of **8a** (entry 2). The ratio of geometric isomers was determined to be (2*E*,4*E*):(2*Z*,4*E*) = 1.1:1. Similarly, a di-*n*-butyl ester **8b** was obtained by using *n*-BuI in the esterification step after the coupling (entry 3). The coupling of **1b** with ethyl acrylate (**7b**) and subsequent esterification with EtI gave diethyl ester **8c** in 71% yield (entry 4). Cyclohexyl (**7c**) and *t*-butyl acrylate (**7d**) also underwent

Table 3. Reaction of Maleic Acids 1 with Alkenes 2[a]



entry	1	7	R^3I	product(s), % yield
1[b]	**1b**	**7a**: R' = *n*-Bu	MeI	**8a**: R' = *n*-Bu, R^3 = Me, 57 [(2*E*,4*E*): (2*Z*,4*E*) = ND]
2		**7a**: R' = *n*-Bu	MeI	**8a**: R' = *n*-Bu, R^3 = Me, 68 [(2*E*,4*E*): (2*Z*,4*E*) = 1.1:1]
3		**7a**: R' = *n*-Bu	*n*-BuI	**8b**: R' = R^3 = *n*-Bu, 71 [(2*E*,4*E*): (2*Z*,4*E*) = 1.1:1]
4		**7b**: R' = Et	EtI	**8c**: R' = R^3 = Et, 71 [(2*E*,4*E*): (2*Z*,4*E*) = 1.4:1]
5		**7c**: R' = Cy[c]	MeI	**8d**: R' = Cy, R^3 = Me, 80 [(2*E*,4*E*): (2*Z*,4*E*) = 1.5:1]
6		**7d**: R' = *t*-Bu	MeI	**8e**: R' = *t*-Bu, R^3 = Me, 77 [(2*E*,4*E*): (2*Z*,4*E*) = 1.8:1]
7	**1b**	**7e**	MeI	**8f**, 51 [(2*E*,4*E*): (2*Z*,4*E*) = 1.3:1]
8[d]	**1b**	**7f**: Ar = Ph	MeI	**8g**: Ar = Ph, 37 [(2*E*,4*E*): (2*Z*,4*E*) = 5:1]
9[d]		**7g**: Ar = 2-Nap[e]	MeI	**8h**: Ar = 2-Nap, 37 [(2*E*,4*E*): (2*Z*,4*E*) = 6:1]
10	**1c**	**7a**	MeI	**8i**, 53 [(2*Z*,4*E*): (2*E*,4*E*) = 19:1]

[a]Reaction conditions: (1) **1** (0.5 mmol), **7** (1 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), Ag_2CO_3 (0.5 mmol) in DMF (2.5 mL) under N_2 at 140 °C under N_2 for 1 h; (2) with the addition of R^3I (2.5 mmol) and K_2CO_3 (1.5 mmol) at rt for 3 h. [b]With $[Cp^*RhCl_2]_2$ (0.005 mmol) for 6 h. [c]Cy = cyclohexyl. [d]With **7** (2.5 mmol) for 2 h. [e]Nap = naphthyl.

the reaction to produce the corresponding hexadienedioates **8d** and **8e** in 80% and 77% yields, respectively (entries 5 and 6). Not only acrylates but also *N*-*t*-butylacrylamide (**7e**), styrene (**7f**), and 2-vinylnaphthalene (**7g**) coupled with **1b** (entries 7−9). The reaction of **1c** with **7a** gave the corresponding (2*Z*,4*E*)-hexa-2,4-dienedioate **8i** almost exclusively (entry 10). The methyl group in **1c** seems to suppress 2*E*−2*Z* isomerization because of steric reasons.

CONCLUSIONS

We have demonstrated that the decarboxylative and dehydrogenative coupling of maleic acids with alkynes and alkenes can be performed efficiently under rhodium catalysis. The procedure provides simple synthetic routes to α-pyrones and dienoic acid derivatives.

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS data were obtained by EI using a

dx.doi.org/10.1021/jo401992d | J. Org. Chem. 2013, 78, 11427−11432

double focusing mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC-MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **2b-e** were prepared according to published procedures.[12] All starting materials and reagents were commercially available.

General Procedure for the Reaction of Maleic Acids with Alkynes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added maleic acid **1** (0.5 mmol), alkyne **2** (0.5 mmol), [(Cp*RhCl$_2$)$_2$] (0.005 mmol, 3 mg), Ag_2CO_3 (0.5 mmol, 138 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and DMF (2.5 mL). Then, the resulting mixture was stirred under nitrogen at 120 °C for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by water (100 mL, three times), and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **3** was isolated by column chromatography on silica gel using hexane−ethyl acetate (10:1, v/v) as eluant.

General Procedure for the Reaction of Maleic Acids with Alkenes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added maleic acid **1** (0.5 mmol), alkene **7** (1−2.5 mmol), [(Cp*RhCl$_2$)$_2$] (0.01 mmol, 6 mg), Ag_2CO_3 (0.5 mmol, 138 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and DMF (2.5 mL). Then, the resulting mixture was stirred under nitrogen at 140 °C for 1−2 h. After cooling, alkyliodide (2.5 mmol) and K_2CO_3 (1.5 mmol, 207 mg) were added and the resulting mixture was stirred under air at room temperature for 3 h. GC and GC-MS analyses of the mixtures confirmed formation of **8**. Then, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **8** was isolated by column chromatography on silica gel using hexane−ethyl acetate (10:1, v/v) as eluant.

*5,6-Diphenyl-2(2H)-pyran-2-one (**3a**).*[2] Mp 85−88 °C (yellow solid), 120 mg (97%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (d, J = 9.6 Hz, 1H), 7.15−7.38 (m, 10H), 7.46 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.0, 117.8, 127.9, 128.1, 128.9, 129.1, 129.2, 129.9, 132.0, 136.2, 147.8, 158.0, 161.7; HRMS m/z Calcd for $C_{17}H_{12}O_2$ (M^+) 248.0837, found 248.0840.

*5,6-Bis(4-methylphenyl)-2(2H)-pyran-2-one (**3b**).* Mp 113−115 °C (pale yellow solid), 120 mg (87%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.35 (s, 3H), 6.32 (d, J = 9.2 Hz, 1H), 7.03−7.07 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.4, 113.6, 117.4, 128.9, 129.0, 129.1, 129.3, 129.7, 133.4, 137.7, 140.2, 148.1, 158.1, 162.0; MS m/z 276 (M^+). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.36; H, 5.91.

*5,6-Bis(4-methoxyphenyl)-2(2H)-pyran-2-one (**3c**).* Mp 135−136 °C (yellow solid), 148 mg (96%); hexane−ethyl acetate 85:15 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.82 (s, 3H), 6.29 (d, J = 9.2 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 9.2 Hz, 2H), 7.41 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3 (overlapped), 113.0, 113.6, 114.5, 116.5, 124.6, 128.7, 130.3, 130.7, 148.3, 157.8, 159.2, 160.7, 162.1; MS m/z 308 (M^+). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.87; H, 5.16.

*5,6-Bis(4-chlorophenyl)-2(2H)-pyran-2-one (**3d**).* Mp 133−136 °C (yellow solid), 133 mg (84%); hexane−ethyl acetate 85:15 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 9.5 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 7.24−7.33 (m, 6H), 7.41 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.6, 116.9, 128.7, 129.4, 130.2, 130.4, 130.5, 134.3, 134.4, 136.4, 147.2, 157.0, 161.2; MS m/z 316, 318, 320 (M^+). Anal. Calcd for $C_{17}H_{10}Cl_2O_2$: C, 64.38; H, 3.18; Cl, 22.36. Found: C, 64.36; H, 3.25; Cl, 22.10.

*5,6-Di(2-thienyl)-2(2H)-pyran-2-one (**3e**).* Mp 152−155 °C (brown solid), 108 mg (83%); purified by recrystallization with hexane−ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (d, J = 9.2 Hz, 1H), 6.98 (dd, J = 3.9, 5.0 Hz, 1H), 7.08 (dd, J = 1.3, 3.5 Hz, 1H), 7.14 (dd, J = 3.6, 5.1 Hz, 1H), 7.34 (d, J = 9.5 Hz, 1H), 7.37 (dd, J = 1.1, 5.1 Hz, 1H), 7.41 (dd, J = 1.3, 3.9 Hz, 1H), 7.50 (dd, J = 1.3, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.9, 112.3, 127.3, 128.0, 128.1, 129.1, 130.5, 130.7, 133.8, 135.9, 147.9, 154.6, 160.6; MS m/z 260 (M^+). Anal. Calcd for $C_{13}H_8O_2S_2$: C, 59.98; H, 3.10. Found: C, 59.93; H, 3.10.

*5,6-Di(n-propyl)-2(2H)-pyran-2-one (**3f**).*[13] Oil, 77 mg (85%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93−0.99 (m, 6H), 1.46−1.56 (m, 2H), 1.65−1.75 (m, 2H), 2.28 (t, J = 7.7 Hz, 2H), 2.48 (t, J = 7.5 Hz, 2H), 6.14 (d, J = 9.5 Hz, 1H), 7.17 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 13.7, 21.0, 23.3, 31.1, 32.5, 113.3, 115.0, 147.0, 161.8, 162.9; HRMS m/z Calcd for $C_{11}H_{16}O_2$ (M^+) 180.1150, found 180.1157.

*5,6-Di(n-heptyl)-2(2H)-pyran-2-one (**3g**).* Oil, 130 mg (89%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87−0.91 (m, 6H), 1.28−1.32 (m, 16H), 1.44−1.48 (m, 2H), 1.60−1.67 (m, 2H), 2.28 (t, J = 7.7 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 6.14 (d, J = 9.2 Hz, 1H), 7.16 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (overlapped), 22.6 (overlapped), 27.6, 29.0, 29.06, 29.09, 29.2, 29.3, 30.2, 30.8, 31.67, 31.72, 113.3, 115.1, 147.0, 161.9, 163.0; MS m/z 292 (M^+). Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03. Found: C, 77.82; H, 10.74.

*5-Methyl-6-phenyl-2(2H)-pyran-2-one (**3h**).*[14] Mp 102−108 °C (white solid), 68 mg (73%); hexane−ethyl acetate 85:15 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 6.28 (d, J = 9.5 Hz, 1H), 7.30 (d, J = 9.5 Hz, 1H), 7.44−7.48 (m, 3H), 7.57−7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 111.2, 114.4, 128.3, 128.7, 129.8, 132.5, 148.4, 157.6, 162.2; HRMS m/z Calcd for $C_{12}H_{10}O_2$ (M^+) 186.0681, found 186.0685.

*6-Methyl-5-phenyl-2(2H)-pyran-2-one (**3h′**).*[15] Oil, 1.3 mg (1%); hexane−ethyl acetate 85:15 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.25 (d, J = 9.2 Hz, 1H), 7.24−7.26 (m, 2H), 7.34 (d, J = 9.5 Hz, 1H), 7.35−7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 113.2, 117.9, 127.9, 128.8 (overlapped), 135.8, 146.7, 159.5, 162.2; HRMS m/z Calcd for $C_{12}H_{10}O_2$ (M^+) 186.0681, found 186.0685.

*5-(n-Butyl)-6-phenyl-2(2H)-pyran-2-one (**3i**).*[3a] Oil, 86 mg (75%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.4 Hz, 3H), 1.27−1.36 (m, 2H), 1.48−1.56 (m, 2H), 2.43 (t, J = 7.9 Hz, 2H), 6.31 (d, J = 9.6 Hz, 1H), 7.35 (d, J = 9.5 Hz, 1H), 7.44−7.46 (m, 3H), 7.51−7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.2, 29.1, 32.2, 114.7, 116.2, 128.4, 128.7, 129.8, 132.5, 147.0, 158.0, 162.2; HRMS m/z Calcd for $C_{15}H_{16}O_2$ (M^+) 228.1150, found 228.1153.

*6-(n-Butyl)-5-phenyl-2(2H)-pyran-2-one (**3i′**).* Oil, 8.4 mg (7%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 7.4 Hz, 3H), 1.24−1.33 (m, 2H), 1.63−1.70 (m, 2H), 2.51 (t, J = 7.7 Hz, 2H), 6.23 (d, J = 9.2 Hz, 1H), 7.22−7.25 (m, 2H), 7.30 (d, J = 9.6 Hz, 1H), 7.35−7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 22.3, 29.7, 31.2, 113.0, 117.9, 127.9, 128.8, 128.9, 136.0, 146.9, 162.5, 163.2; HRMS m/z Calcd for $C_{15}H_{16}O_2$ (M^+) 228.1150, found 228.1152.

*Ethyl 2-Oxo-6-phenyl-2H-pyran-5-calboxylate (**3j**).* Oil, 49 mg (40%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, J = 7.1 Hz, 3H), 4.15 (q, J = 7.1 Hz, 2H), 6.33 (d, J = 9.9 Hz, 1H), 7.43−7.56 (m, 5H), 7.85 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 61.5, 109.9, 113.3, 128.0, 129.0, 131.1, 132.3, 144.2, 160.3, 164.6, 167.2; MS m/z 244 (M^+). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.57; H, 4.97.

*Ethyl 2-Oxo-5-phenyl-2H-pyran-6-calboxylate (**3j′**).* Oil, 12 mg (10%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J = 7.1 Hz, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.55 (d, J = 9.5 Hz, 1H), 7.25−7.27 (m, 2H), 7.38 (d, J = 9.5 Hz, 1H), 7.41−7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 62.2, 119.2, 123.9, 128.3, 128.5, 128.6, 134.7, 146.50, 146.54, 159.3, 159.9; HRMS m/z Calcd for $C_{14}H_{12}O_4$ (M^+) 244.0736, found 244.0742.

*5-(2-Hydroxypropan-2-yl)-6-phenyl-2(2H)-pyran-2-one (**3k**).* Mp 83−84 °C (white solid), 67 mg (58%); hexane−ethyl acetate 50:50

dx.doi.org/10.1021/jo401992d | J. Org. Chem. 2013, 78, 11427−11432

(v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 6H), 2.25 (s, 1H), 6.29 (d, J = 10.0 Hz, 1H), 7.37−7.46 (m, 5H), 7.80 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 70.6, 114.4, 124.2, 128.1, 129.1, 129.8, 134.2, 145.2, 157.8, 161.9; HRMS m/z Calcd for $C_{14}H_{14}O_3$ (M^+) 230.0943, found 230.0942.

3-Methyl-5,6-diphenyl-2(2H)-pyran-2-one (**3l**).[2] Mp 127−128 °C (yellow solid), 118 mg (90%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (d, J = 1.1 Hz, 3H), 7.16−7.35 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 117.9, 123.7, 127.7, 128.0, 128.8, 129.0, 129.2, 129.5, 132.2, 136.5, 143.9, 155.3, 163.0; HRMS m/z Calcd for $C_{18}H_{14}O_2$ (M^+) 262.0994, found 262.0990.

3,5,6-Triphenyl-2(2H)-pyran-2-one (**3m**).[2] Mp 141−143 °C (yellow solid), 154 mg (95%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.42 (m, 13H), 7.59 (s, 1H), 7.75 (d, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5, 125.4, 127.9, 128.06, 128.13, 128.4, 128.5, 128.9, 129.07, 129.14, 129.8, 131.8, 134.3, 136.3, 144.2, 156.6, 161.1; HRMS m/z Calcd for $C_{23}H_{16}O_2$ (M^+) 324.1150, found 324.1149.

5,6-Bis(4-methoxyphenyl)-3-phenyl-2(2H)-pyran-2-one (**3n**). Mp 157−158 °C (yellow solid), 184 mg (96%); hexane−ethyl acetate 75:25 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.80 (s, 3H), 6.75 (d, J = 9.2 Hz, 2H) 6.88 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 7.34−7.42 (m, 5H), 7.56 (s, 1H), 7.74 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2 (overlapped), 113.5, 114.4, 117.1, 124.29, 124.33, 128.1, 128.29, 128.34, 128.8, 130.3, 130.6, 134.5, 144.9, 156.4, 159.1, 160.6, 161.4; HRMS m/z Calcd for $C_{25}H_{20}O_4$ (M^+) 384.1362, found 384.1360.

5,6-Bis(4-chlorophenyl)-3-phenyl-2(2H)-pyran-2-one (**3o**). Mp 150−151 °C (yellow solid), 186 mg (95%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.36−7.44 (m, 3H), 7.53 (s, 1H), 7.72 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.6, 126.0, 128.1, 128.5, 128.6, 128.8, 129.4, 129.9, 130.3, 130.4, 134.0, 134.2, 134.4, 136.2, 143.5, 155.5, 160.7; HRMS m/z Calcd for $C_{23}H_{14}Cl_2O_2$ (M^+) 392.0371, found 392.0369.

5,6-Bis[4-(tert-butyl)phenyl]-3-phenyl-2(2H)-pyran-2-one (**3p**). Mp 185−186 °C (yellow solid), 214 mg (98%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 9H), 1.34 (s, 9H), 7.19 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.34−7.41 (m, 7H), 7.58 (s, 1H), 7.74 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0, 31.2, 34.6, 34.7, 118.0, 124.8, 125.0, 125.9, 128.1, 128.36, 128.38, 128.7, 128.8, 129.0, 133.5, 134.5, 144.9, 150.9, 153.2, 156.6, 161.3; HRMS m/z Calcd for $C_{31}H_{32}O_2$ (M^+) 436.2402, found 436.2404.

3-Phenyl-5,6-bis[4-(trifluoromethyl)phenyl]-2(2H)-pyran-2-one (**3q**). Mp 65−66 °C (yellow solid), 179 mg (78%); hexane−ethyl acetate 85:15 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.47 (m, 5H), 7.51 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.58 (s, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.75 (dd, J = 1.4, 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.3, 123.5 (q, J = 272.2 Hz), 123.8 (q, J = 272.2 Hz), 125.4 (q, J = 3.8 Hz), 126.2 (q, J = 3.8 Hz), 127.0, 128.2, 128.6, 129.1, 129.5, 129.6, 130.5 (q, J = 32.6 Hz), 131.9 (q, J = 32.6 Hz), 133.8, 134.8, 139.5, 143.0, 155.3, 160.4; HRMS m/z Calcd for $C_{25}H_{14}F_6O_2$ (M^+) 460.0898, found 460.0901.

6-Phenyl-2(2H)-pyran-2-one (**4**).[15] Mp 66−67 °C (yellow solid), 27 mg (80%); hexane−ethyl acetate 75:25 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (dd, J = 0.9, 9.2 Hz, 1H), 6.67 (dd, J = 0.9, 6.9 Hz, 1H), 7.41−7.47 (m, 4H), 7.80−7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.0, 114.0, 125.6, 128.9, 130.9, 131.3, 143.7, 161.1, 162.0; HRMS m/z Calcd for $C_{11}H_8O_2$ (M^+) 172.0524, found 172.0523.

3,3′-Diethyl-6H,6′H-[2,2′-bipyran]-6,6′-dione (**6a**). Mp 111−113 °C (yellow solid), 100 mg (81%); hexane−ethyl acetate 50:50 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 7.8 Hz, 6H), 2.39 (q, J = 7.8 Hz, 4H), 6.43 (d, J = 9.6 Hz, 2H), 7.37 (d, J = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.6, 117.9, 122.0, 145.7, 148.0, 160.3; HRMS m/z Calcd for $C_{14}H_{14}O_4$ (M^+) 246.0892, found 246.0893.

3,3′-Dipropyl-6H,6′H-[2,2′-bipyran]-6,6′-dione (**6b**). Mp 59−60 °C (yellow solid), 115 mg (84%); hexane−ethyl acetate 50:50 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 6H), 1.59 (tq, J = 7.3, 7.3 Hz, 4H), 2.34 (t, J = 7.3 Hz, 4H), 6.41 (d, J = 9.6 Hz, 2H), 7.35 (d, J = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 22.5, 31.1, 117.7, 120.6, 146.0, 148.4, 160.3; HRMS m/z Calcd for $C_{16}H_{18}O_4$ (M^+) 274.1205, found 274.1206.

1-(n-Butyl) 6-Methyl hexa-2,4-dienedioate [(2E,4E):(2Z,4E) = 1.1:1] (**8a**). 72 mg (68%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96−1.01 (m, 3H), 1.41−1.50 (m, 2H), 1.68−1.74 (m, 2H), 3.82 (s, 3H), 4.21−4.24 (m, 2H), 6.01 (d, J = 10.5 Hz, 1H, 2Z,4E), 6.15 (d, J = 15.6 Hz, 1H, 2Z,4E), 6.23−6.26 (m, 2H, 2E,4E), 6.69 (t, J = 11.5 Hz, 1H, 2Z,4E), 7.32−7.37 (m, 2H, 2E,4E), 8.41 (dd, J = 11.9, 15.6 Hz, 1H, 2Z,4E); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 13.7, 19.07, 19.12, 30.57, 30.59, 51.6, 51.9, 64.6, 64.7, 124.1, 127.8, 128.6, 129.2, 138.3, 140.6, 140.7, 141.0, 165.7, 165.9, 166.1, 166.3; HRMS m/z Calcd for $C_{11}H_{16}O_4$ (M^+) 212.1049, found 212.1050.

Di(n-Butyl) Hexa-2,4-dienedioate [(2E,4E):(2Z,4E) = 1.1:1] (**8b**).[16] 90 mg (71%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93−0.98 (m, 6H), 1.37−1.46 (m, 4H), 1.63−1.71 (m, 4H), 4.17−4.20 (m, 4H), 5.96 (d, J = 11.5 Hz, 1H, 2Z,4E), 6.11 (d, J = 15.6 Hz, 1H, 2Z,4E), 6.21 (dd, J = 3.2, 11.5 Hz, 2H, 2E,4E), 6.64 (t, J = 11.5 Hz, 1H, 2Z,4E), 7.31 (dd, J = 3.2, 11.5 Hz, 2H, 2E,4E), 8.39 (dd, J = 11.5, 15.6 Hz, 1H, 2Z,4E); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (2E,4E, 2Z,4E), 19.05 (2E,4E), 19.09 (2Z,4E), 30.51 (2Z,4E), 30.54 (2E,4E), 30.6 (2Z,4E), 64.5 (2Z,4E), 64.6 (2Z,4E), 64.7 (2E,4E), 124.6 (2Z,4E), 128.3 (2E,4E), 129.0 (2Z,4E), 138.4 (2Z,4E), 140.3 (2Z,4E), 140.7 (2E,4E), 165.4 (2Z,4E), 166.0 (2E,4E), 166.1 (2Z,4E); HRMS m/z Calcd for $C_{14}H_{22}O_4$ (M^+) 254.1518, found 254.1517.

Diethyl Hexa-2,4-dienedioate [(2E,4E):(2Z,4E) = 1.4:1] (**8c**).[17] 70 mg (71%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30−1.35 (m, 6H), 4.22−4.27 (m, 4H), 5.96 (d, J = 11.5 Hz, 1H, 2Z,4E), 6.10 (d, J = 15.6 Hz, 1H, 2Z,4E), 6.20 (dd, J = 3.2, 11.5 Hz, 2H, 2E,4E), 6.64 (t, J = 11.5 Hz, 1H, 2Z,4E), 7.32 (dd, J = 3.2, 11.5 Hz, 2H, 2E,4E), 8.40 (dd, J = 11.5, 15.6 Hz, 1H, 2Z,4E); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (2E,4E), 14.2 (2Z,4E), 60.6 (2Z,4E), 60.7 (2Z,4E), 60.8 (2E,4E), 124.6 (2Z,4E), 128.3 (2E,4E), 129.0 (2Z,4E), 138.4 (2Z,4E), 140.4 (2Z,4E), 140.7 (2E,4E), 165.3 (2Z,4E), 165.9 (2E,4E), 166.0 (2Z,4E); HRMS m/z Calcd for $C_{10}H_{14}O_4$ (M^+) 198.0892, found 198.0891.

1-Cyclohexyl 6-Methyl Hexa-2,4-dienedioate [(2E,4E):(2Z,4E) = 1.5:1] (**8d**). 95 mg (80%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26−1.55 (m, 6H), 1.75−1.89 (m, 4H), 3.78 (s, 3H, 2Z,4E), 3.79 (s, 3H, 2E,4E), 4.83−4.88 (m, 1H), 5.96 (d, J = 11.5 Hz, 1H, 2Z,4E), 6.11 (d, J = 15.6 Hz, 1H, 2Z,4E), 6.16−6.24 (m, 2H, 2E,4E), 6.65 (t, J = 11.5 Hz, 1H, 2Z,4E), 7.26−7.36 (m, 2H, 2E,4E), 8.36 (dd, J = 11.5, 15.6 Hz, 1H, 2Z,4E); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (2Z,4E), 23.7 (2E,4E), 25.25 (2E,4E), 25.29 (2Z,4E), 31.50 (2Z,4E), 31.52 (2E,4E), 51.6 (2Z,4E), 51.9 (2E,4E), 73.0 (2Z,4E), 73.2 (2E,4E), 123.9 (2Z,4E), 127.6 (2E,4E), 129.2 (2E,4E), 129.8 (2Z,4E), 138.0 (2Z,4E), 140.3 (2E,4E), 140.8 (2Z,4E), 141.1 (2E,4E), 165.3 (2E,4E), 165.4 (2Z,4E), 165.7 (2Z,4E), 166.3 (2E,4E); HRMS m/z Calcd for $C_{13}H_{18}O_4$ (M^+) 238.1205, found 238.1203.

1-(tert-Butyl) 6-Methyl Hexa-2,4-dienedioate [(2E,4E):(2Z,4E) = 1.8:1] (**8e**).[18] 82 mg (77%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 9H, 2E,4E), 1.51 (s, 9H, 2Z,4E), 3.77 (s, 3H, 2Z,4E), 3.78 (s, 3H, 2E,4E), 5.94 (d, J = 11.5 Hz, 1H, 2Z,4E), 6.04 (d, J = 15.6 Hz, 1H, 2Z,4E), 6.11−6.20 (m, 2H, 2E,4E), 6.63 (t, J = 11.5 Hz, 1H, 2Z,4E), 7.18−7.35 (m, 2H, 2E,4E), 8.28 (dd, J = 11.5, 15.6 Hz, 1H, 2Z,4E); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0 (2E,4E), 28.1 (2Z,4E), 51.6 (2Z,4E), 51.9 (2E,4E), 80.9 (2Z,4E), 81.1 (2E,4E), 123.6 (2Z,4E), 127.3 (2E,4E), 130.6 (2E,4E), 131.2 (2Z,4E), 137.5 (2Z,4E), 139.7 (2E,4E), 140.9 (2Z,4E), 141.3 (2E,4E), 165.1 (2E,4E), 165.3 (2Z,4E), 165.8 (2Z,4E), 166.4 (2E,4E); HRMS m/z Calcd for $C_{11}H_{16}O_4$ (M^+) 212.1049, found 212.1051.

Methyl 6-(tert-Butylamino)-6-oxohexa-2,4-dienoate [(2E,4E):(2Z,4E) = 1.3:1] (**8f**). 54 mg (51%); hexane−ethyl acetate 50:50 (v/

dx.doi.org/10.1021/jo401992d | J. Org. Chem. 2013, 78, 11427−11432

v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.400 (s, 9H, 2*Z*,4*E*), 1.402 (s, 9H, 2*E*,4*E*), 3.76 (s, 3H, 2*Z*,4*E*), 3.77 (s, 3H, 2*E*,4*E*), 5.85 (s, 1H, 2*Z*,4*E*), 5.88 (d, *J* = 11.5 Hz, 1H, 2*Z*,4*E*), 5.95 (s, 1H, 2*E*,4*E*), 6.09−9.22 (m, 2H, 2*E*,4*E*), 6.20 (d, *J* = 15.3 Hz, 1H, 2*Z*,4*E*), 6.60 (t, *J* = 11.5 Hz, 1H, 2*Z*,4*E*), 7.18−7.32 (m, 2H, 2*E*,4*E*), 8.15 (dd, *J* = 11.5, 15.3 Hz, 1H, 2*Z*,4*E*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.61, 28.64, 51.5, 51.6, 51.7, 122.7, 126.2, 132.7, 133.72, 133.74, 136.3, 140.9, 141.6, 164.0, 164.5, 165.9, 166.7; HRMS *m*/*z* Calcd for $C_{11}H_{18}NO_3$ ($M+H^+$) 212.1287, found 212.1282.

*Methyl (2E,4E)-5-Phenylpenta-2,4-dienoate [(2E,4E):(2Z,4E) = 5:1] (**8g**).*[18] 35 mg (37%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 6.00 (d, *J* = 15.4 Hz, 1H), 6.88−6.90 (m, 2H), 7.31−7.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 120.8, 126.2, 127.2, 128.8, 129.1, 135.9, 140.5, 144.8, 167.5; HRMS *m*/*z* Calcd for $C_{12}H_{12}O_2$ (M^+) 188.0837, found 188.0838.

*Methyl (2E,4E)-5-(Naphthalen-2-yl)penta-2,4-dienoate [(2E,4E):(2Z,4E) = 6:1] (**8h**).*[19] 44 mg (37%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.03 (d, *J* = 15.3 Hz, 1H), 6.94−7.07 (m, 2H), 7.44−7.83 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 120.8, 123.3, 126.5, 126.6, 126.7, 127.7, 128.2, 128.3, 128.5, 133.4, 133.5, 133.6, 140.7, 144.9, 167.5; HRMS *m*/*z* Calcd for $C_{16}H_{14}O_2$ (M^+) 238.0994, found 238.0993.

*6-(n-Butyl) 1-Methyl (2Z,4E)-2-Methylhexa-2,4-dienedioate [(2Z,4E):(2E,4E) = 19:1] (**8i**).* 60 mg (53%); hexane−ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.39−1.44 (m, 2H), 1.63−1.70 (m, 2H), 2.06 (s, 3H), 3.82 (s, 3H), 4.17 (t, *J* = 6.9 Hz, 2H), 5.98 (d, *J* = 15.6 Hz, 1H), 6.48 (d, *J* = 11.9 Hz, 1H), 8.10 (dd, *J* = 11.9, 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.1, 21.2, 30.6, 51.9, 64.4, 125.9, 134.5, 135.7, 139.9, 166.6, 167.2; HRMS *m*/*z* Calcd for $C_{12}H_{18}O_4$ (M^+) 226.1205, found 226.1207.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid from MEXT, JSPS, and JST, Japan.

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