Advanced Synthesis of Dihydrofurans.
Effect of Formic Acid on the Mn(III)-Based Oxidation

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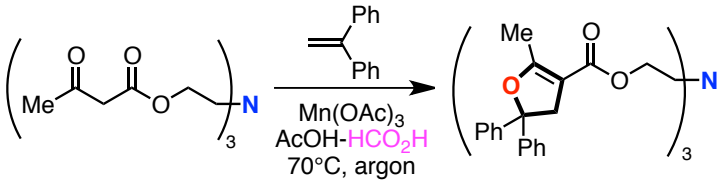
Graphical Abstract

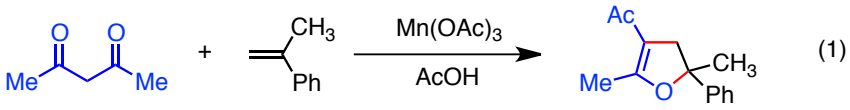


Abstract: The Mn(III)-based oxidation of a tertiary alkylamine, such as nitrilotris(ethane-2,1-diyl) tris(3-oxobutanoate) (**1**) with 1,1-diphenylethene (**2a**), effectively proceeded in an acetic acid–formic acid mixed solvent to give nitrilotris(ethane-2,1-diyl) tris(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**3**). Other typical Mn(III)-based reactions of various *β*-diketo esters **4a–e**, 2,4-pentanedione (**6a**), malonic acid (**6b**), and diethyl malonate (**6c**) with 1,1-diarylthenes **2a-d** were also investigated in a similar acetic acid–formic acid mixed solvent and it was recognized that the reaction rate was accelerated and the product yield increased.

Keywords: Oxidation; 4,5-dihydrofurans; manganese(III) acetate; alkylamine; formic acid

Introduction

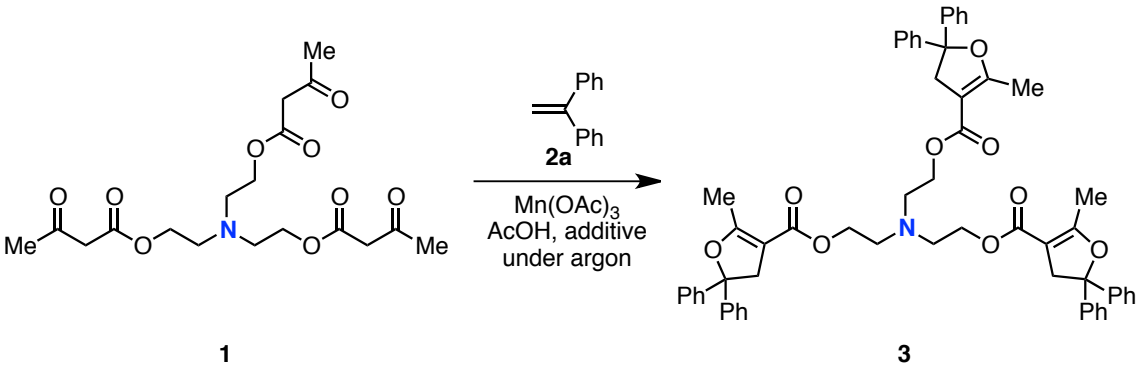
Heiba and Dessau developed the efficient synthesis of dihydrofurans using manganese(III) acetate in 1974 (eq. 1).[1] Since then, many researchers[2] and we[3] also reported similar reactions, and the Mn(III)-based oxidative radical cyclization using *β*-dicarbonyl compounds has been rapidly developing.[4] Dihydrofuran derivatives constitute the basic skeleton of many naturally occurring compounds and, therefore, are important from the viewpoint of building blocks in the total synthesis. On the other hand, the Mn(III)-mediated formation of the dihydrofuran ring is essential for the synthesis of functional macrocycles.[5] Based on this background, we embarked on synthesizing nitrogen-anchor tripodand-type tris(dihydrofuran)s. During the reaction, we found that formic acid as an additive played an important role in the production of the dihydrofurans. We now describe the characteristic reaction involving formic acid.



(1)

Results and Discussion

Nitrilotris(ethane-2,1-diyl) tris(3-oxobutanoate) (**1**)[6] was prepared by the condensation of 2,2',2"-nitrilotris(ethanol) with diketene and examined the Mn(III)-based oxidation with 1,1-diphenylethene (**2a**) under various conditions. The reaction of **1** (0.3 mmol) with **2a** (1.0 mmol) in the presence of manganese(III) acetate (1.8 mmol) was carried out in acetic acid at 100 °C under an argon atmosphere to produce the desired tris(4,5-dihydrofuran-3-carboxylate) **3** in a low yield (Table 1, Entry 1).[5] The reaction was then optimized (Entries 2–8), and the best yield of **3** was achieved for the reaction at 70 °C using the molar ratio of **1**:**2a**:$Mn(OAc)_3$ = 1:3.3:10 (Entry 7). However, the result was not acceptable from the viewpoint of the synthesis of **3**. Probably, an undesirable reaction, such as the oxidative dealkylation of **1**, occurred under the conditions at the same time.[7] In order to prevent any undesirable reaction, we next investigated the corresponding ammonium salt which might be inactive for the undesirable oxidative dealkylation. The reaction was carried out by adding various acids, such as 2M HCl, *p*-toluenesulfonic acid (*p*-TsOH), 10-camphorsulfonic acid (CSA), methanesulfonic acid (MsOH), trifluoroacetic acid (TFA), and formic acid in addition to water (Entries 9-15). Surprisingly, the reaction rate dramatically changed and, especially, the addition of TFA and formic acid was remarkable (Entries 14-18). As a result, the use of a 4:1 v/v mixture of acetic acid and formic acid led to a shorter reaction time and the production of **3** in 49% maximum yield (Entry 17).



1 **3**

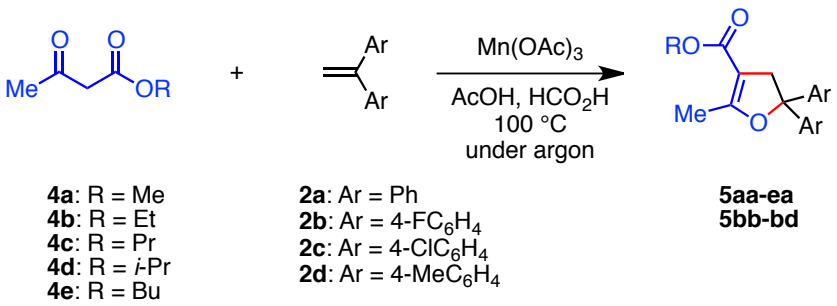
Scheme 1.

Table 1. Mn(III)-Based Reaction of Nitrilotris(ethane-2,1-diyl) Tris(3-oxobutanoate) (**1**) with 1,1-Diphenylethene (**2a**) in the Absence or Presence of Various acids[a]

Entry	**1**:**2a**:$Mn(OAc)_3$[b]	Temp/°C	AcOH/mL	Additive	Additive/mL	Time/min	**3**/Yield/%[c]
1	1:3.3:6	100	50			8	20
2	1:3.3:8	100	50			10	20
3	1:3.3:10	100	50			10	19
4	1:3.3:10	100	100			10	16
5	1:3.3:10	100	25			8	20
6	1:3.3:10	reflux	50			5	19
7	1:3.3:10	70	50			45	34
8	1:3.3:10	rt	50			1 day	6
9	1:3.3:10	70	49	H_2O	1	13	-[d]
10	1:3.3:10	70	49	2M HCl	1	5	-[d]
11	1:3.3:10	70	50	*p*-TsOH	1 eq.[e]	4	16
12	1:3.3:10	70	50	CSA	1 eq.[e]	5	26
13	1:3.3:10	70	49	MsOH	1	8	13
14	1:3.3:10	70	49	TFA	1	30	46
15	1:3.3:10	70	49	HCO_2H	1	12	41
16	1:3.3:10	70	45	HCO_2H	5	11	47
17	1:3.3:10	70	40	HCO_2H	10	7	49
18	1:3.3:10	70	35	HCO_2H	15	5	44

[a] The reaction of **1** (0.3 mmol) was carried out in acetic acid under an argon atmosphere.
[b] Molar ratio.
[c] Isolated yield based on **1**.
[d] The ethene **2a** was recovered and tris(dihydrofuran) **3** was not detected.
[e] One equivalent of *p*-toluenesulfonic acid (*p*-TsOH) and 10-camphorsulfonic acid (CSA) was added for **1**.

We were interested in the phenomena that the addition of formic acid accelerated the reaction and, then scrutinized the typical Mn(III)-based oxidative dihydrofuranation under similar conditions.[1-3] When the typical reaction of methyl 3-oxobutanoate (**4a**) with **2a** using a stoichiometric amount of manganese(III) acetate was conducted in acetic acid at 100 °C under an argon atmosphere, formic acid was added (Table 2, Entries 1-5). As a result, as the amount of formic acid increased, the reaction time decreased. Although the reaction time was the shortest using formic acid alone as the solvent (Entry 6), the yield of the product, dihydrofuranecarboxylate **5aa**, decreased, and the best yield was achieved using a 2:3 v/v mixture of acetic acid and formic acid (Entry 4). The reaction using other combination of *β*-keto esters **4b-e** and 1,1-diarylthenes **2b-d** was also examined and a similar tendency was observed except for the yield of **5bd** (R = Et, Ar = 4-MeC_6H_4) (Entry 20). In addition, the presence of manganese(II) acetate inhibited the production of the dihydrofuran **5ba** (Entries 13 and 14).



4a: R = Me
4b: R = Et
4c: R = Pr
4d: R = *i*-Pr
4e: R = Bu

2a: Ar = Ph
2b: Ar = 4-FC_6H_4
2c: Ar = 4-ClC_6H_4
2d: Ar = 4-MeC_6H_4

5aa-ea
5bb-bd

Scheme 2.

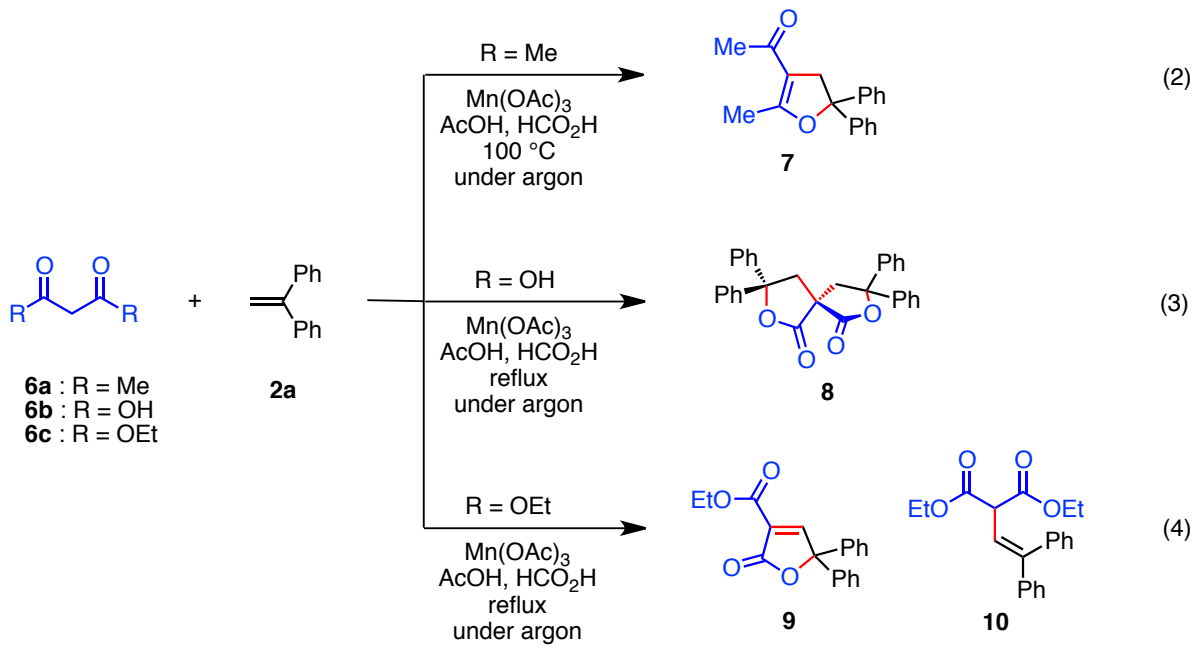
Table 2. Mn(III)-Based Dihydrofuranation Using Various *β*-Diketo Esters **4a–e**[a]

Entry	**4**/R	**2**/Ar	AcOH/mL	HCO_2H/mL	Time/sec	**5**/Yield/%[b]
1	**4a**: Me	**2a**: Ph	5	0	60	**5aa** (69)
2	**4a**: Me	**2a**: Ph	4	1	30	**5aa** (71)
3	**4a**: Me	**2a**: Ph	3	2	30	**5aa** (74)
4	**4a**: Me	**2a**: Ph	2	3	20	**5aa** (75)
5	**4a**: Me	**2a**: Ph	1	4	10	**5aa** (65)
6	**4a**: Me	**2a**: Ph	0	5	5	**5aa** (39)
7	**4b**: Et	**2a**: Ph	5	0	180	**5ba** (77)
8	**4b**: Et	**2a**: Ph	4	1	60	**5ba** (73)
9	**4b**: Et	**2a**: Ph	3	2	60	**5ba** (71)
10	**4b**: Et	**2a**: Ph	2	3	60	**5ba** (82)
11	**4b**: Et	**2a**: Ph	1	4	20	**5ba** (65)
12	**4b**: Et	**2a**: Ph	0	5	10	**5ba** (46)
13[c]	**4b**: Et	**2a**: Ph	2	3	60	**5ba** (8)
14[d]	**4b**: Et	**2a**: Ph	2	3	60	**5ba** (0)
15	**4b**: Et	**2b**: 4-FC_6H_4	5	0	90	**5bb** (55)
16	**4b**: Et	**2b**: 4-FC_6H_4	2	3	20	**5bb** (69)
17	**4b**: Et	**2c**: 4-ClC_6H_4	5	0	120	**5bc** (52)
18	**4b**: Et	**2c**: 4-ClC_6H_4	2	3	20	**5bc** (73)
19	**4b**: Et	**2d**: 4-MeC_6H_4	5	0	90	**5bd** (76)
20	**4b**: Et	**2d**: 4-MeC_6H_4	2	3	15	**5bd** (66)
21	**4c**: Pr	**2a**: Ph	5	0	180	**5ca** (67)
22	**4c**: Pr	**2a**: Ph	4	1	60	**5ca** (67)
23	**4c**: Pr	**2a**: Ph	3	2	60	**5ca** (82)
24	**4c**: Pr	**2a**: Ph	2	3	30	**5ca** (71)
25	**4c**: Pr	**2a**: Ph	1	4	10	**5ca** (61)
26	**4c**: Pr	**2a**: Ph	0	5	10	**5ca** (49)
27	**4d**: *i*-Pr	**2a**: Ph	5	0	120	**5da** (64)

28	**4d**: *i*-Pr	**2a**: Ph	4	1	30	**5da** (59)
29	**4d**: *i*-Pr	**2a**: Ph	3	2	20	**5da** (84)
30	**4d**: *i*-Pr	**2a**: Ph	2	3	20	**5da** (83)
31	**4d**: *i*-Pr	**2a**: Ph	1	4	10	**5da** (68)
32	**4d**: *i*-Pr	**2a**: Ph	0	5	10	**5da** (42)
33	**4e**: Bu	**2a**: Ph	5	0	120	**5ea** (62)
34	**4e**: Bu	**2a**: Ph	4	1	60	**5ea** (83)
35	**4e**: Bu	**2a**: Ph	3	2	60	**5ea** (74)
36	**4e**: Bu	**2a**: Ph	2	3	30	**5ea** (71)
37	**4e**: Bu	**2a**: Ph	1	4	20	**5ea** (69)
38	**4e**: Bu	**2a**: Ph	0	5	10	**5ea** (55)

[a] The reaction of butanoate **4** (0.1 mmol) using the molar ratio of **4**:**2**:$Mn(OAc)_3$ = 1:1:2 was carried out at 100 °C under an argon atmosphere.
[b] Isolated yield based on **4**.
[c] The reaction was carried out using $Mn(OAc)_3$ (0.1 mmol) in the presence of $Mn(OAc)_2$ (0.1 mmol) (**4b**:**2a**:$Mn(OAc)_3$:$Mn(OAc)_2$ = 1:1:1:1).
[d] The reaction was carried out using $Mn(OAc)_2$ (0.2 mmol) instead of $Mn(OAc)_3$ (**4b**:**2a**:$Mn(OAc)_2$ = 1:1:2).

With acceptable results in hand, we examined other typical Mn(III)-based reactions using 2,4-pentanedione (**6a**), malonic acid (**6b**), and diethyl malonate (**6c**) to produce 3-acetyl-2-methyl-4,5-dihydrofuran **7** (eq. 2 in Scheme 3),[2] spirodi-γ-lactone **8** (eq. 3),[8] and 2-oxo-2,5-dihydrofuran-3-carboxylate **9** (eq. 4),[9] respectively.



Scheme 3.

Table 3. Mn(III)-Based Reaction of Other *β*-Dicarbonyl Compounds **6a–c** with 1,1-Diphenylethene (**2a**)[a]

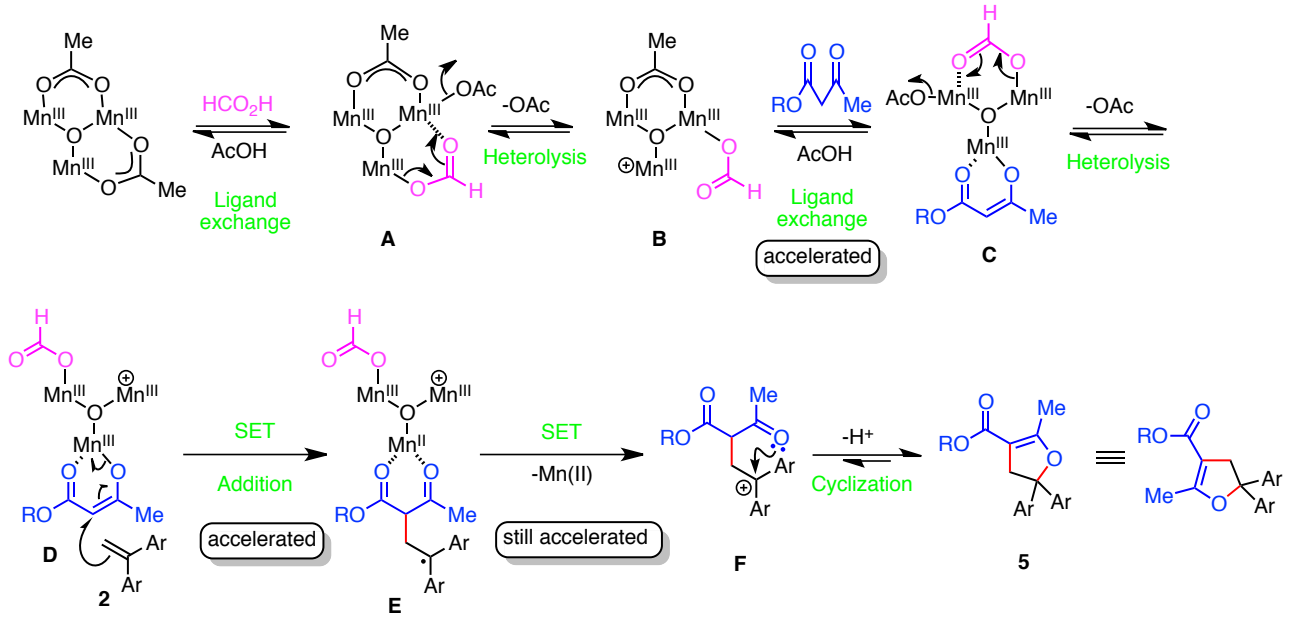
Entry	**6**/R	**6**:**2a**:$Mn(OAc)_3$[b]	Temp/°C	AcOH/mL	HCO_2H/mL	Time/min	Product Yield/%[c]
1	**6a**/Me	1:1:2	100	5	0	1	**7** (77)
2	**6a**/Me	1:1:2	100	4	1	0.5	**7** (91)
3	**6b**/OH	1:2:4	reflux	5	0	2	**8** (74)
4	**6b**/OH	1:2:4	reflux	4	1	1.5	**8** (78)
5	**6c**/OEt	1:1:2	reflux	5	0	3[d]	**9** (45), **10** (31)
6	**6c**/OEt	1:1:2	reflux	5	0	40	**9** (80)
7	**6c**/OEt	1:1:2	reflux	2	3	1	**10** (30)

[a] The reaction of **6** (0.1 mmol) was carried out in acetic acid under an argon atmosphere.
[b] Molar ratio.
[c] Isolated yield based on **6**.
[d] The reaction was quenched before the complete consumption of Mn(III).

In all cases, the presence of formic acid led to an extremely shorter reaction time (Table 3). For the reaction of the malonate **6c** with the alkene **2a** in the presence of formic acid (eq. 4 in Scheme 3), however, the oxidative addition product **9** was not obtained, but 2-ethenylmalonate **10** was isolated (Table 3, Entry 7).

The mechanism for the formation of dihydrofurans, such as **5**, is generally accepted that the acetato ligand-bridged oxo-centered trinuclear manganese(III) complex undergoes the ligand-exchange reaction with the 3-oxobutanoates to generate the manganese(III)-enolate complex, of which the production is the rate-determining step,[4g] followed by a single-electron transfer (SET) oxidation from the alkenes through the oxobutanoato ligand, giving the carbon adduct radicals. The radicals are further oxidized by Mn(III) according to the normal electron-transfer-type mechanism and subsequently cyclized to produce the dihydrofurans **5**. When formic acid was added to the reaction mixture, the ligand exchange from the bridged acetate on the manganese(III) complex into formate should readily occur as being more acidic (pK_a = 3.75) than acetic acid (pK_a = 4.76) and the 3-oxobutanoates (pK_a = 11 for **4b**) (**A** in Scheme 4).[10] Kochi reported that the manganese(III)-strong acid complexes in the oxidative decarboxylation produced both ion-pair and cationic manganese(III) species such as **B** which increased the reactivity,[11] so that the formation of the manganese(III)-oxobutanoate complex **C** should be accelerated. This was observed as considerably shorter reaction times in our experiment. Again the formato-manganese(III)-oxobutanoate complex **C** led another cationic manganese(III) species **D** that underwent SET oxidation to form adduct radicals **E**. The radicals **E** were converted into dihydrofurans **5** during a similar SET oxidation using a typical transition-metal oxidant. Formic acid itself is a reductant (CO_2 (g) + $2H^+$ + $2e^-$ = HCO_2H (aq), $E°$ (25 °C) = -0.199 V),[10] so that the oxidant $Mn(OAc)_3$ itself is reduced by the formic acid. In fact, $Mn(OAc)_3$ was completely

consumed within 2.2 minutes using acetic acid–formic acid (2:3, v/v) at 100 °C in the absence of the 1,3-dicarbonyl compound and alkene. However, it seems that the oxidative radical reaction as shown in Scheme 4 predominantly proceeded in the mixed solvent system, because all the reaction times became extremely shorter in the presence of the 1,3-dicarbonyl compound and alkene (Tables 1-3).



Scheme 4.

Conclusion

It was found that the use of an acetic acid–formic acid mixed solvent effectively accelerated the Mn(III)-based oxidation of the tertiary alkylamine **1** with 1,1-diphenylethene (**2a**) and nitrilotris(ethane-2,1-diyl) tris(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**3**) was produced in a synthetically acceptable yield. Acceleration of the reaction and increase in the product yield using a similar acetic acid–formic acid mixed solvent were also observed in other typical Mn(III)-based oxidations of various *β*-diketo esters **4a–e**, 2,4-pentanedione (**6a**), malonic acid (**6b**), and diethyl malonate (**6c**) with 1,1-diarylthenes **2a-d**. We believe that the presence of both ion-pair and cationic manganese(III) species generated in the acid-mixed solvent accelerated the oxidation reaction.

Experimental

Measurements. Melting points were taken using a Yanagimoto micromelting point apparatus and are uncorrected. The NMR spectra were recorded using a JNM ECX 500 or AL300 FT-NMR

spectrometer at 500 or 300 MHz for ^{1}H and at 125 or 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants in Hz. The following abbreviations are used for the multiplicities; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet for the ^{1}H NMR spectrum. The IR spectra were measured in $CHCl_3$ or KBr using a Shimadzu 8400 FT IR spectrometer and expressed in cm^{-1}. The EI MS spectra were obtained by a Shimadzu QP-5050A gas chromatograph-mass spectrometer at the ionizing voltage of 70 eV. The high-resolution mass spectra and the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

Materials. Manganese(II) acetate tetrahydrate, $Mn(OAc)_2 \cdot 4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared according to our modified method.[12] Nitrilotris(ethane-2,1-diyl) tris(3-oxobutanoate) (**1**) was prepared by the imidazole-catalyzed reaction of 2,2',2''-nitrilotriethanol with diketene in dry tetrahydrofuran at room temperature. The diarylethenes **2a-d** were prepared by the Grignard reaction of the corresponding arylmagnesium bromides with acetophenones followed by acid-catalyzed dehydration. Imidazole, 2,2',2''-nitrilotriethanol, diketene, propyl 3-oxobutanoate (**4c**), and butyl 3-oxobutanoate (**4e**) were purchased from Tokyo Kasei Co., Ltd., and methyl 3-oxobutanoate (**4a**), ethyl 3-oxobutanoate (**4b**), isopropyl 3-oxobutanoate (**4d**), 2,4-pentanedione (**6a**), malonic acid (**6b**), and diethyl malonate (**6c**) were from Wako Pure Chemical Ind., Ltd., and used as received. Flash column chromatography was performed on silica gel 60N (40-50 μm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 (45 μm) from Wako Pure Chemical Ind., Ltd. The solvents were commercially available first grade and used as received.

Reaction of Nitrilotris(ethane-2,1-diyl) Tris(3-oxobutanoate) (1) with 1,1-Diphenylethene (2a) in the Presence of $Mn(OAc)_3$.

A mixture of tris(3-oxobutanoate) **1** (120.8 mg; 0.3 mmol), diphenylethene **2a** (179.5 mg; 1 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (801.9 mg; 3 mmol) in glacial acetic acid (40 mL) and formic acid (10 mL) was degassed under reduced pressure for 30 min using an ultrasonicator for exchange with an argon atmosphere. The mixture was then heated at 70 °C until the brown color of Mn(III) disappeared (normally for 7 minutes). The solvent was removed in vacuo and water (25 mL) was added to the reaction mixture. The aqueous solution was then extracted three times with chloroform (25 mL). The combined extracts were washed with a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated on silica gel TLC developed with AcOEt–hexane (2:8 v/v), giving the product **3** (138.7 mg; 49%) (Table 1, entry 17). The physical data are listed below.

Nitrilotris(ethane-2,1-diyl) Tris(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (3):

Light yellow oil; R_f = 0.2 (EtOAc–hexane, 2:8); IR ($CHCl_3$) ν 1690 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.37-7.21 (10H × 3, m, arom H), 4.13 (2H × 3, t, J = 6.0 Hz, -OC$\underline{H}_2$- × 3), 3.56 (2H × 3, d, J = 1.5 Hz, C$\underline{H}_2$ × 3), 2.85 (2H × 3, t, J = 6.0 Hz, -C$\underline{H}_2$N- × 3), 2.30 (3H × 3, s, -C$\underline{H}_3$ × 3); ^{13}C NMR ($CDCl_3$) δ 166.8 ($\underline{C}$=O × 3), 165.5 (=$\underline{C}$O- × 3), 145.0 (6C) (arom C), 128.3 (12C), 127.4 (6C), 125.6 (12C) (arom CH), 101.4 (>$\underline{C}$= × 3), 91.6 (>$\underline{C}$< × 3), 61.9 (-O$\underline{C}$H$_2$- × 3), 53.5 (-N$\underline{C}$H$_2$- × 3), 43.9 (-$\underline{C}$H$_2$- × 3), 14.1 ($\underline{C}$H$_3$ × 3); FAB HRMS (acetone/NBA) calcd for $C_{60}H_{58}NO_9$ 936.4112 (M+H). Found 936.4141.

Mn(III)-Based Reaction of 1,3-Dicarbonyl Compounds 4a-e and 6a–c with 1,1-Diarylethenes 2a-d.

To a 30 mL round-bottomed flask, the 1,3-dicarbonyl compound (0.1 mmol), 1,1-diarylethene (0.1 mmol), and a mixture of acetic acid and formic acid mentioned in Tables 2 and 3 were added. After replacing air with argon in the flask, $Mn(OAc)_3$•$2H_2O$ (53.6 mg; 0.2 mmol) was added and then the mixture was heated at 100 °C until the brown color of Mn(III) disappeared (the reaction times are listed in Tables 2 and 3). After the Mn(III) oxidant was completely consumed, the solvent was removed in vacuo and 2M HCl (20 mL) was added to the residue. The aqueous solution was then extracted three times with chloroform (25 mL). The combined extracts were washed with a saturated aqueous solution of sodium hydrogencarbonate followed by water, dried over anhydrous sodium sulfate, and then concentrated to dryness. The obtained residue was separated by silica gel column chromatography eluting with AcOEt–hexane (2:8 v/v), giving dihydrofurans **5**, **7**, spirodi-γ-lactone **8**, butenolide **9**, and ethenylmalonate **10**, as shown in Schemes 2 and 3 and Tables 2 and 3. The physical data of the products are listed below.

Methyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5aa): Light yellow oil; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1693 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.39-7.24 (10H, m, arom H), 3.69 (3H, s, O-C$\underline{H}_3$), 3.60 (2H, br. q, J = 1.8 Hz, C$\underline{H}_2$), 2.35 (3H, t, J = 1.8 Hz, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 166.6 ($\underline{C}$=O), 166.2 (=$\underline{C}$O-), 145.1 (2C) (arom C), 128.3 (4C), 127.5 (2C), 125.6 (4C) (arom CH), 101.5 (>$\underline{C}$=), 91.6 (>$\underline{C}$<), 50.9 (-O$\underline{C}$H$_3$), 44.0 (-$\underline{C}$H$_2$-), 14.2 ($\underline{C}$H$_3$); FAB HRMS (acetone/NBA) calcd for $C_{19}H_{19}O_3$ 295.1334 (M+H). Found: 295.1331.

Ethyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5ba)[13]: Light yellow oil; R_f = 0.4 (EtOAc–hexane, 2:8); IR ($CHCl_3$) ν 1690 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.39-7.22 (10H, m, arom H), 4.15 (2H, q, J = 7.2 Hz, C$\underline{H}_2$-CH$_3$), 3.60 (2H, s, C$\underline{H}_2$), 2.35 (3H, s, C$\underline{H}_3$), 1.26 (3H, t, J = 7.2 Hz, CH$_2$-C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 166.2 ($\underline{C}$=O), 165.8 (=$\underline{C}$O-), 145.1 (2C) (arom C), 128.3 (4C), 127.4 (2C), 125.6 (4C) (arom CH), 101.7 (>$\underline{C}$=), 91.4 (>$\underline{C}$<), 59.5 (-O$\underline{C}$H$_2$), 44.1 (-$\underline{C}$H$_2$-), 14.4 ($\underline{C}$H$_3$), 14.2 ($\underline{C}$H$_3$); FAB HRMS (acetone/NBA) calcd for $C_{20}H_{21}O_3$ 309.1491 (M+H). Found:

309.1510.

Ethyl 5,5-Bis(4-fluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bb)[13]: Colorless liquid; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1697 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.34-7.30 (4H, m, arom H), 7.04-6.99 (4H, m, arom H), 4.16 (2H, q, J = 7.2 Hz, C$\underline{H}_2$-CH$_3$), 3.55 (2H, q, J = 1.5 Hz, C$\underline{H}_2$), 2.34 (3H, t, J = 1.5 Hz, C$\underline{H}_3$), 1.27 (3H, t, J = 7.2 Hz, CH$_2$-C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 166.0 (C=O), 165.6 (=CO-), 162.1 (2C) (arom C-F, J = 245.6 Hz) 140.8 (2C, J = 2.4 Hz, arom C-1'), 127.5 (4C, J = 7.1 Hz, arom C-2'), 115.2 (4C, J = 21.4 Hz, arom C-3'), 101.8 (>C=), 90.6 (>C<), 59.7 (-OCH$_2$), 44.3 (-CH$_2$-), 14.4 (CH$_3$), 14.2 (CH$_3$).

Ethyl 5,5-Bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bc)[14]: Colorless amorphous; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1701 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.32-7.26 (8H, m, arom H), 4.16 (2H, q, J = 7.2 Hz, C$\underline{H}_2$-CH$_3$), 3.53 (2H, br. q, J = 1.8 Hz, C$\underline{H}_2$), 2.33 (3H, t, J = 1.8 Hz, C$\underline{H}_3$), 1.27 (3H, t, J = 7.2 Hz, CH$_2$-C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 165.9 (C=O), 165.5 (=CO-), 143.2 (2C) (arom C), 133.7 (2C) (arom C), 128.6 (4C), 127.0 (4C) (arom CH), 101.8 (>C=), 90.5 (>C<), 59.7 (-OCH$_2$-), 44.0 (-CH$_2$-), 14.4 (CH$_3$), 14.2 (CH$_3$); FAB HRMS (acetone/NBA) calcd for $C_{20}H_{19}Cl_2O_3$ 377.0711 (M+H); found: 377.0692.

Ethyl 5,5-Bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bd)[13]: Light yellow oil; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1690 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.26-7.25 (4H, m, arom H), 7.13-7.12 (4H, m, arom H), 4.15 (2H, q, J = 7.2 Hz, C$\underline{H}_2$-CH$_3$), 3.60 (2H, q, J = 1.5 Hz, C$\underline{H}_2$), 2.33 (3H, t, J = 1.5 Hz, C$\underline{H}_3$), 2.32 (6H, s, C$\underline{H}_3$ × 2), 1.26 (3H, t, J = 7.2 Hz, CH$_2$-C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 166.3 (C=O), 165.9 (=CO-), 142.4 (2C) (arom C), 137.1(2C) (arom CCH$_3$), 128.9 (4C), 125.6 (4C) (arom CH), 101.7 (>C=), 91.4 (>C<), 59.5 (-OCH$_2$), 44.1 (-CH$_2$-), 21.0, 14.4, 14.2 (CH$_3$).

Propyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5ca): Light yellow oil; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1686 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.40-7.24 (10H, m, arom H), 4.06 (2H, t, J = 7.0 Hz, -OCH$_2$-), 3.60 (2H, q, J = 1.8 Hz, C$\underline{H}_2$), 2.35 (3H, t, J = 1.8 Hz, C$\underline{H}_3$), 1.65 (2H, sex, J = 7.0 Hz, -CH$_2$CH$_3$), 0.95 (3H, t, J = 7.0 Hz, CH$_2$-C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 166.2 (C=O), 165.9 (=CO-), 145.2 (2C) (arom C), 128.3 (4C), 127.5 (2C), 125.6 (4C) (arom CH), 101.8 (>C=), 91.5 (>C<), 65.2 (-OCH$_2$), 44.1 (-CH$_2$-), 22.2 (-CH$_2$CH$_3$), 14.2 (CH$_3$), 10.6 (-CH$_2$CH$_3$); FAB HRMS (acetone/NBA) calcd for $C_{21}H_{23}O_3$ 323.1647 (M+H); found 323.1679.

***i*-Propyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5da)[3e]:** Light yellow oil; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1684 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.40-7.24 (10H, m, arom H), 5.04 (1H, sep, J = 6.2 Hz, >CH-), 3.59 (2H, q, J = 1.5 Hz, C$\underline{H}_2$), 2.34 (3H, t, J = 1.5 Hz, C$\underline{H}_3$), 1.24 (6H, d, J = 6.2 Hz, -CH(C$\underline{H}_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 165.9 (C=O), 165.4 (=CO-), 145.3 (2C)

(arom C), 128.3 (4C), 127.4 (2C), 125.7 (4C) (arom CH), 102.0 (>C=), 91.3 (>C<), 66.7 (-OCH<), 44.2 (-CH_2-), 22.1 (-CH(CH_3)$_2$), 14.2 (CH_3); FAB HRMS (acetone/NBA) calcd for $C_{21}H_{23}O_3$ 323.1647 (M+H); found 323.1665.

Butyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5ea): Light yellow oil; R_f = 0.4 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1686 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.40-7.24 (10H, m, arom H), 4.10 (2H, t, J = 7.0 Hz, -OCH_2-), 3.60 (2H, q, J = 1.8 Hz, CH_2), 2.35 (3H, t, J = 1.8 Hz, CH_3), 1.62 (2H, quin, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.38 (2H, sex, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 0.93 (3H, t, J = 7.5 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 166.2 (C=O), 165.9 (=CO-), 145.2 (2C) (arom C), 128.3 (4C), 127.5 (2C), 125.6 (4C) (arom CH), 101.8 (>C=), 91.5 (>C<), 63.5 (-OCH_2-), 44.1 (-CH_2-), 30.8 (-$CH_2CH_2CH_2CH_3$), 19.3 (-$CH_2CH_2CH_2CH_3$), 14.2 (CH_3), 13.8 (-$CH_2CH_2CH_2CH_3$); FAB HRMS (acetone/NBA) calcd for $C_{22}H_{25}O_3$ 337.1804 (M+H); found 337.1828.

3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (7)[3a]: Light yellow oil; R_f = 0.3 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1667 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.39-7.25 (10H, m, arom H), 3.66 (2H, q, J = 2.0 Hz, CH_2), 2.38 (3H, t, J = 2.0 Hz, CH_3), 2.22 (3H, s, -COCH_3); ^{13}C NMR ($CDCl_3$) δ 194.1 (C=O), 165.9 (=CO-), 144.9 (2C) (arom C), 128.3 (4C), 127.6 (2C), 125.6 (4C) (arom CH), 112.2 (>C=), 91.5 (>C<), 44.8 (-CH_2-), 29.4 (-COCH_3), 15.2 (CH_3).

3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (8)[15]: Colorless microcrystals (from $CHCl_3$/hexane); mp 287-290 °C (lit, mp 284.5-285.0 °C); R_f = 0.8 ($CHCl_3$); IR ($CHCl_3$) ν 1798, 1667 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.43-7.35 (6H, m, arom H), 7.31-7.23 (14H, m, arom H), 3.01 (2H, d, J = 13.5 Hz, -CH_2-), 2.61 (2H, d, J = 13.5 Hz, -CH_2-); ^{13}C NMR ($CDCl_3$) δ 173.5 (C=O × 2), 142.1 (2C), 142.0 (2C) (arom C), 128.9 (4C), 128.6 (4C), 128.5 (2C), 128.3 (2C), 125.5 (4C), 125.4 (4C) (arom CH), 88.60 (Ph_2CO- × 2), 53.9 (>C<), 45.6 (-CH_2- × 2).

Ethyl 2-oxo-5,5-diphenyl-2,5-dihydrofuran-3-carboxylate (9)[8e,9]: Colorless microcrystals (from EtOH); mp 105-108 °C (lit, mp 107.9-109.4 °C); R_f = 0.2 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1780 (C=O), 1719 (C=O), 1267 (C-O-C); ^{1}H NMR ($CDCl_3$) δ 8.60 (1H, s, >CH-), 7.41-7.26 (10H, m, arom H), 4.36 (2H, q, J = 7.0 Hz, CH_2), 1.37 (3H, t, J = 7.0 Hz, -CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 166.5 (C=O), 164.5 (=C-), 160.1 (C=O), 138.1 (2C) (arom C), 129.0 (4C), 128.9 (2C), 126.6 (4C) (arom CH), 123.7 (>C=), 89.2 (>CPh_2), 61.89 (-CH_2CH_3), 14.1 (-CH_2CH_3).

Diethyl 2-(2,2-diphenylethenyl)malonate (10)[9,16]: Colorless liquid; R_f = 0.3 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1734 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.41-7.34 (3H, m, arom H), 7.29 (5H, s, arom H), 7.23-7.201 (2H, m, arom H), 6.33 (1H, d, J = 11.0 Hz, -CH=Ph_2), 4.21 (4H, q, J = 7.0 Hz, -CH_2CH_3 × 2), 4.19 (1H, d, J = 11.0 Hz, >CH-CO_2Et), 1.27 (6H, t, J = 7.0 Hz, -$CHCH_3$ × 2); ^{13}C NMR ($CDCl_3$) δ 168.3 (C=O × 2), 141.3 (2C) (arom C), 138.5 (-CH=CPh_2), 129.8 (2C), 128.4 (2C),

128.1 (2C), 127.8 (2C), 127.6 (2C) (arom CH), 119.7 (-<u>C</u>H=CPh$_2$), 61.5 (-<u>C</u>H$_2$CH$_3$ × 2), 53.0 (><u>C</u>H-), 14.0 (-CH$_2$<u>C</u>H$_3$ × 2).

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Supplementary Information

Measurements, materials, IR, ^{1}H and ^{13}C NMR spectra, DEPT and HRMS data including copies of ^{1}H and ^{13}C NMR spectra for **5ba**, **5bb**, **5bc**, **5bd**, **5da**, and **7-10**.

EXPERIMENTAL

Measurements

Melting points were taken using a Yanagimoto micromelting point apparatus and are uncorrected. The NMR spectra were recorded using a JNM ECX 500 or AL300 FT-NMR spectrometer at 500 or 300 MHz for ^{1}H and at 125 or 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants in Hz. The following abbreviations are used for the multiplicities; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet for the ^{1}H NMR spectrum. The IR spectra were measured in $CHCl_3$ or KBr using a Shimadzu 8400 FT IR spectrometer and expressed in cm^{-1}. The EI MS spectra were obtained by a Shimadzu QP-5050A gas chromatograph-mass spectrometer at the ionizing voltage of 70 eV. The high-resolution mass spectra and the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

Materials.

Manganese(II) acetate tetrahydrate, $Mn(OAc)_2 \cdot 4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared according to our modified method.[12] Nitrilotris(ethane-2,1-diyl) tris(3-oxobutanoate) (**1**) was prepared by the imidazole-catalyzed reaction of 2,2',2''-nitrilotriethanol with diketene in dry tetrahydrofuran at room temperature. The diarylethenes **2a-d** were prepared by the Grignard reaction of the corresponding arylmagnesium bromides with acetophenones followed by acid-catalyzed dehydration. Imidazole, 2,2',2''-nitrilotriethanol, diketene, propyl 3-oxobutanoate (**4c**), and butyl 3-oxobutanoate (**4e**) were purchased from Tokyo Kasei Co., Ltd., and methyl 3-oxobutanoate (**4a**), ethyl 3-oxobutanoate (**4b**), isopropyl 3-oxobutanoate (**4d**), 2,4-pentanedione (**6a**), malonic acid (**6b**), and diethyl malonate (**6c**) were from Wako Pure Chemical Ind., Ltd., and used as received. Flash column chromatography was performed on silica gel 60N (40-50 μm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 (45 μm) from Wako Pure Chemical Ind., Ltd. The solvents were commercially available first grade and used as received.

The physical data of the known products **5ba**, **5bb**, **5bc**, **5bd**, **5da**, and **7-10** and references are listed below.

Ethyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5ba)[13]

Light yellow oil; R_f = 0.4 (EtOAc–hexane, 2:8); IR ($CHCl_3$) ν 1690 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.39-7.22 (10H, m, arom H), 4.15 (2H, q, J = 7.2 Hz, C<u>H</u>$_2$-CH$_3$), 3.60 (2H, s, C<u>H</u>$_2$), 2.35 (3H, s, C<u>H</u>$_3$), 1.26 (3H, t, J = 7.2 Hz, CH$_2$-C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$) δ 166.2 (<u>C</u>=O), 165.8 (=<u>C</u>O-), 145.1 (2C) (arom C), 128.3 (4C), 127.4 (2C), 125.6 (4C) (arom CH), 101.7 (><u>C</u>=), 91.4 (><u>C</u><), 59.5 (-O<u>C</u>H$_2$), 44.1 (-<u>C</u>H$_2$-), 14.4 (<u>C</u>H$_3$), 14.2 (<u>C</u>H$_3$); FAB HRMS (acetone/NBA) calcd for $C_{20}H_{21}O_3$ 309.1491 (M+H). Found: 309.1510.

Ethyl 5,5-Bis(4-fluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bb)[13]

Colorless liquid; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1697 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.34-7.30 (4H, m, arom H), 7.04-6.99 (4H, m, arom H), 4.16 (2H, q, J = 7.2 Hz, C<u>H</u>$_2$-CH$_3$), 3.55 (2H, q, J = 1.5 Hz, C<u>H</u>$_2$), 2.34 (3H, t, J = 1.5 Hz, C<u>H</u>$_3$), 1.27 (3H, t, J = 7.2 Hz, CH$_2$-C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$) δ 166.0 (<u>C</u>=O), 165.6 (=<u>C</u>O-), 162.1 (2C) (arom <u>C</u>-F, J = 245.6 Hz) 140.8 (2C, J = 2.4 Hz, arom C-1'), 127.5 (4C, J = 7.1 Hz, arom C-2'), 115.2 (4C, J = 21.4 Hz,

arom C-3'), 101.8 (>C=), 90.6 (>C<), 59.7 (-OCH$_2$), 44.3 (-CH$_2$-), 14.4 (CH$_3$), 14.2 (CH$_3$).

Ethyl 5,5-Bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bc)[14]

Colorless amorphous; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1701 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.32-7.26 (8H, m, arom H), 4.16 (2H, q, J = 7.2 Hz, CH$_2$-CH$_3$), 3.53 (2H, br. q, J = 1.8 Hz, CH$_2$), 2.33 (3H, t, J = 1.8 Hz, CH$_3$), 1.27 (3H, t, J = 7.2 Hz, CH$_2$-CH$_3$); ^{13}C NMR ($CDCl_3$) δ 165.9 (C=O), 165.5 (=CO-), 143.2 (2C) (arom C), 133.7 (2C) (arom C), 128.6 (4C), 127.0 (4C) (arom CH), 101.8 (>C=), 90.5 (>C<), 59.7 (-OCH$_2$-), 44.0 (-CH$_2$-), 14.4 (CH$_3$), 14.2 (CH$_3$); FAB HRMS (acetone/NBA) calcd for $C_{20}H_{19}Cl_2O_3$ 377.0711 (M+H); found: 377.0692.

Ethyl 5,5-Bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bd)[13]

Light yellow oil; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1690 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.26-7.25 (4H, m, arom H), 7.13-7.12 (4H, m, arom H), 4.15 (2H, q, J = 7.2 Hz, CH$_2$-CH$_3$), 3.60 (2H, q, J = 1.5 Hz, CH$_2$), 2.33 (3H, t, J = 1.5 Hz, CH$_3$), 2.32 (6H, s, CH$_3$ × 2), 1.26 (3H, t, J = 7.2 Hz, CH$_2$-CH$_3$); ^{13}C NMR ($CDCl_3$) δ 166.3 (C=O), 165.9 (=CO-), 142.4 (2C) (arom C), 137.1(2C) (arom CCH$_3$), 128.9 (4C), 125.6 (4C) (arom CH), 101.7 (>C=), 91.4 (>C<), 59.5 (-OCH$_2$), 44.1 (-CH$_2$-), 21.0, 14.4, 14.2 (CH$_3$).

***i*-Propyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5da)**[3e]

Light yellow oil; R_f = 0.5 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1684 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.40-7.24 (10H, m, arom H), 5.04 (1H, sep, J = 6.2 Hz, >CH-), 3.59 (2H, q, J = 1.5 Hz, CH$_2$), 2.34 (3H, t, J = 1.5 Hz, CH$_3$), 1.24 (6H, d, J = 6.2 Hz, -CH(CH$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 165.9 (C=O), 165.4 (=CO-), 145.3 (2C) (arom C), 128.3 (4C), 127.4 (2C), 125.7 (4C) (arom CH), 102.0 (>C=), 91.3 (>C<), 66.7 (-OCH<), 44.2 (-CH$_2$-), 22.1 (-CH(CH$_3$)$_2$), 14.2 (CH$_3$); FAB HRMS (acetone/NBA) calcd for $C_{21}H_{23}O_3$ 323.1647 (M+H); found 323.1665.

3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (7)[3a]

Light yellow oil; R_f = 0.3 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1667 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.39-7.25 (10H, m, arom H), 3.66 (2H, q, J = 2.0 Hz, CH$_2$), 2.38 (3H, t, J = 2.0 Hz, CH$_3$), 2.22 (3H, s, -COCH$_3$); ^{13}C NMR ($CDCl_3$) δ 194.1 (C=O), 165.9 (=CO-), 144.9 (2C) (arom C), 128.3 (4C), 127.6 (2C), 125.6 (4C) (arom CH), 112.2 (>C=), 91.5 (>C<), 44.8 (-CH$_2$-), 29.4 (-COCH$_3$), 15.2 (CH$_3$).

3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (8)[15]

Colorless microcrystals (from $CHCl_3$/hexane); mp 287-290 °C (lit, mp 284.5-285.0 °C); R_f = 0.8 ($CHCl_3$); IR ($CHCl_3$) ν 1798, 1667 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.43-7.35 (6H, m, arom H), 7.31-7.23 (14H, m, arom H), 3.01 (2H, d, J = 13.5 Hz, -CH$_2$-), 2.61 (2H, d, J = 13.5 Hz, -CH$_2$-); ^{13}C NMR ($CDCl_3$) δ 173.5 (C=O × 2), 142.1 (2C), 142.0 (2C) (arom C), 128.9 (4C), 128.6 (4C), 128.5 (2C), 128.3 (2C), 125.5 (4C), 125.4 (4C) (arom CH), 88.60 (Ph$_2$CO- × 2), 53.9 (>C<), 45.6 (-CH$_2$- × 2).

Ethyl 2-oxo-5,5-diphenyl-2,5-dihydrofuran-3-carboxylate (9)[8e,9]

Colorless microcrystals (from EtOH); mp 105-108 °C (lit, mp 107.9-109.4 °C); R_f = 0.2 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1780 (C=O), 1719 (C=O), 1267 (C-O-C); ^{1}H NMR ($CDCl_3$) δ 8.60 (1H, s, >CH-), 7.41-7.26 (10H, m, arom H), 4.36 (2H, q, J = 7.0 Hz, CH$_2$), 1.37 (3H, t, J = 7.0 Hz, -CH$_2$CH$_3$); ^{13}C NMR ($CDCl_3$) δ 166.5 (C=O), 164.5 (=C-), 160.1 (C=O), 138.1 (2C) (arom C), 129.0 (4C), 128.9 (2C), 126.6 (4C) (arom CH), 123.7 (>C=), 89.2 (>CPh$_2$), 61.89 (-CH$_2$CH$_3$), 14.1 (-CH$_2$CH$_3$).

Diethyl 2-(2,2-diphenylethenyl)malonate (10)[9,16]

Colorless liquid; R_f = 0.3 (EtOAc–hexane, 1:9); IR ($CHCl_3$) ν 1734 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.41-7.34 (3H,

m, arom H), 7.29 (5H, s, arom H), 7.23-7.201 (2H, m, arom H), 6.33 (1H, d, J = 11.0 Hz, -C<u>H</u>=Ph_2), 4.21 (4H, q, J = 7.0 Hz, -C<u>H_2</u>CH_3 × 2), 4.19 (1H, d, J = 11.0 Hz, >C<u>H</u>-CO_2Et), 1.27 (6H, t, J = 7.0 Hz, -CHC<u>H_3</u> × 2); ^{13}C NMR ($CDCl_3$) δ 168.3 (<u>C</u>=O × 2), 141.3 (2C) (arom C), 138.5 (-CH=<u>C</u>Ph_2), 129.8 (2C), 128.4 (2C), 128.1 (2C), 127.8 (2C), 127.6 (2C) (arom CH), 119.7 (-<u>C</u>H=CPh_2), 61.5 (-<u>C</u>H_2CH_3 × 2), 53.0 (><u>C</u>H-), 14.0 (-CH_2<u>C</u>H_3 × 2).

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