DOI: 10.1002/ejoc.201201194

Mechanism and Scope of the Mn^{III}-Initiated Oxidation of β-Ketocarbonyl Compounds: Furan Synthesis

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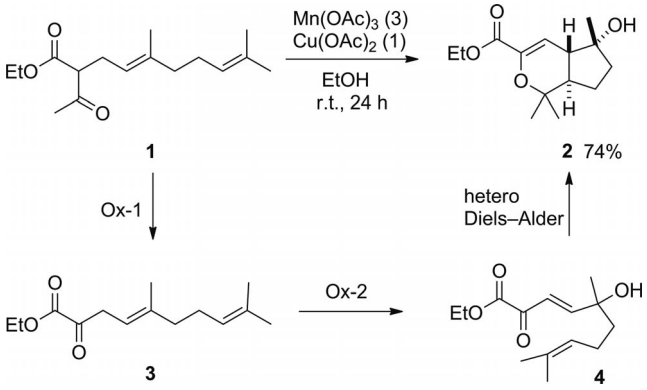
Dedication to Professor Masato Koreeda on the occasion of his 70th birthday

Keywords: Reaction mechanisms / Cyclization / Oxygen heterocycles / Radicals / Manganese / Oxidation

Unless the Mn^{III}-produced carbon-radical from β-ketocarbonyl compounds undergoes smooth intramolecular addition to alkenes, it traps molecular oxygen in the reaction medium to produce a peroxy radical, which reacts with the neighbouring carbonyl group to form 1,2-dioxetane. Thermal decomposition of 1,2-dioxetane completes the oxidation to produce α-oxo ester. This oxidation seems to be general at 50 °C under aerobic conditions, and can be catalytic for Mn^{III} in AcOH with ultrasonic irradiation. Thus, the development of a new synthetic method for diversely substituted furans has been accomplished based on a couple of the Mn^{III}-initiated domino oxidation of β-ketocarbonyl compounds with a suitable α-allylic substitution.

Introduction

The Mn^{III}-initiated radical cyclisation of β-keto esters containing a suitably substituted alkenyl chain has proven to be a useful method for the construction of five- or six-membered ring structures.[1] The cascade cyclisation is especially suitable for the synthesis of cyclic isoprenoids.[2] We recently reported the unusual Mn^{III}-initiated oxidation of β-keto ester **1** containing a geranyl group at the α-position. The δ-hydroxy β,γ-unsaturated α-oxo ester **4** was conceived to be formed after two consecutive oxidations through **3** and to undergo the intramolecular hetero Diels–Alder reaction to produce the bicyclic dihydropyran **2** in 74% yield (Scheme 1).[3] We also demonstrated that this type of reaction is general for β-keto esters with a similar substitution pattern.



Scheme 1. Mn^{III}-initiated oxidation/hetero-Diels–Alder reaction of α-geranyl-β-keto ester **1**.

Several questions consequently arose: Is this oxidation truly general for β-keto esters and would other substitution patterns lead to other useful structures? What is the controlling factor for the reaction pathway either to the carbon-radical cyclisation or to the oxidation? What is the mechanism of this unusual oxidation? Why are three equivalents of $Mn(OAc)_3$ required for the oxidation? Can it be catalytic? To address these questions, we prepared a diverse set of β-keto esters and extensively studied the Mn^{III}-initiated oxidation reaction under various conditions. The results are disclosed in this work.

Results and Discussion

The β-keto ester **5**, containing an alkenyl chain with different methyl substitution patterns, was first prepared to check the generality of the above oxidation, more specifically in the hope of producing a furan derivative. No carbon-radical cyclisation was observed under conditions involving $Mn(OAc)_3{\cdot}2H_2O$ and $Cu(OAc)_2{\cdot}H_2O$ in EtOH at room temperature for 6 h, and the δ-hydroxy β,γ-unsatu-

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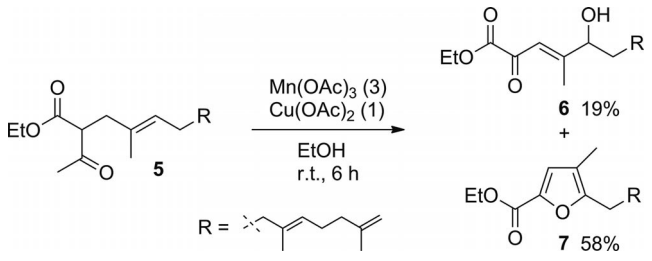
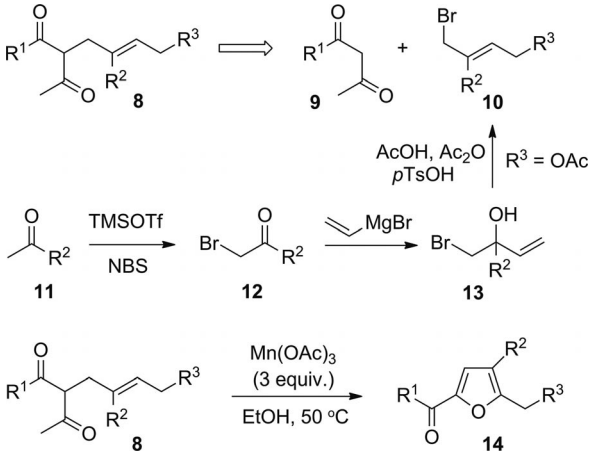
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201194.

rated α-oxo ester **6** and the furan **7** were obtained in 19 and 58% yields, respectively (Scheme 2). It is clear that the Mn^{III}-initiated oxidation of β-keto ester **5** produced the α-oxo ester **6**, containing the secondary δ-hydroxy group, which then underwent heterocyclisation to produce furan **7**. Inspired by this finding, we decided to examine the generality of this furan synthesis by the Mn^{III}-initiated oxidation and heterocyclisation strategy.



Scheme 2. Mn^{III}-initiated oxidation/heterocyclisation of β-keto ester **5**.

The general structure **8** was proposed for the furan synthesis, which can be prepared by coupling between β-ketocarbonyl compounds **9** and allylic bromides **10** (Scheme 3). Allylic bromides **10**, containing various R^2 substituents, were efficiently synthesized from readily available methyl ketones **11** following the sequence of bromination (*N*-bromosuccinimide (NBS), cat. TMS·OTf),[4] vinylmagnesium bromide addition, and acetylation/allylic migration (cat. *p*TsOH, AcOH/Ac_2O for R^3 = OAc).[5] A mixture of *E*- and *Z*-isomers was obtained in the alkenyl chain, which did not affect the oxidation or cyclisation.



Scheme 3. Preparation and Mn^{III}-initiated furan synthesis of β-keto esters **8**.

The best conditions {3 equiv. $Mn(OAc)_3·2H_2O$ in 94% EtOH (6% water content) at 50 °C for 5 h in the air (see below)} were applied to produce the diversely substituted furans **14** in moderate to good yields (Table 1). Our furan synthesis allows a carbonyl group (ketone, ester, and amide) to be located at the 2-position, which is complementary to the Feist–Benary method, which provides a carbonyl group at the 3-position.[6] Various alkyl, cycloalkyl, and aryl R^2 groups can be attached at the 4-position. We mostly utilised OAc as R^3 for the sake of synthetic convenience, which can be replaced by other functional groups for further manipulations.

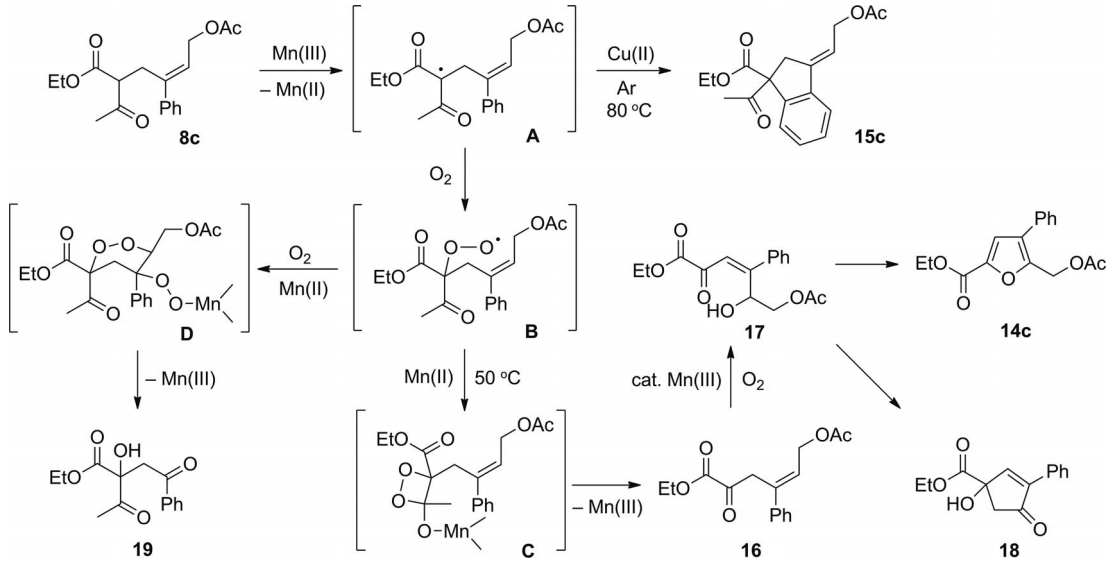
Table 1. Mn^{III}-initiated furan synthesis of β-keto esters **8** according to Scheme 3.

Entry	**8**	R^1	R^2	R^3	Yield **14** [%]
1	**a**	OEt	Me	OAc	57
2	**b**	OEt	Me	OMe	60
3	**c**	OEt	Ph	OAc	74
4	**d**	Me	Ph	OAc	47
5	**e**	NEt_2	Ph	OAc	41
6	**f**	OEt	*p*-Cl-C_6H_4	OAc	65
7	**g**	OEt	*p*-MeO-C_6H_4	OAc	52
8	**h**	OEt	2-naphthyl	OAc	64
9	**i**	OEt	cyclopropyl	OAc	63
10	**j**	OEt	cyclohexyl	OAc	55

The β-keto ester **8c** containing a phenyl group as R^2 was selected as a model case to elucidate the full mechanistic details of the Mn^{III}-initiated oxidation, in which the competitive carbon-radical cyclisation to the phenyl ring would possibly produce indane **15c** (Scheme 4). The products and their yields of the Mn^{III}-initiated reaction of **8c** are summarized, together with the reaction conditions, in Table 2, and detailed mechanisms are proposed in Scheme 4. Our initial concern was to develop the possibility of controlling the reaction pathway by directing the reaction towards either oxidation to the furan **14c** or carbon-radical cyclisation to indane **15c**.

Application of the initial conditions {3 equiv. $Mn(OAc)_3·2H_2O$, 1 equiv. $Cu(OAc)_2·H_2O$ in 94% EtOH at 15 °C for 24 h in the air} produced furan **14c** in 39% yield (Table 2, entry 1). We found an interesting temperature effect on the reaction pathway; furan formation was optimised at 50 °C, whereas radical cyclisation was the major pathway at 80 °C in the presence of Cu^{II} salt, which partly indicated the importance of O_2 solubility in the reaction medium depending on the temperature (Table 2, entries 2 and 3). The formation of indane **15c** in up to 53% yield was optimised in anhydrous EtOH (Table 2, entry 4) under an argon atmosphere after careful degassing (Table 2, entry 5). The Cu^{II} salt is necessary for oxidative aromatisation of the cyclohexadienyl radical. Indane **15c** was not observed in the absence of Cu^{II} salt, instead, cyclopentenone **18** (39%) was obtained together with furan **14c** (15%) at 80 °C under aerobic conditions (Table 2, entry 6). The water content (less than 6%) in EtOH does not make any difference to furan formation (Table 2, entries 2 and 7), but the Cu^{II} salt reduces the yield by 10% at 50 °C (Table 2, entries 2 and 8). The optimised yield of **14c** (74%) was obtained when $Mn(OAc)_3·2H_2O$ (3 equiv.) was used in 94% EtOH at 50 °C for 5 h in the air (Table 2, entry 8).

It is clear that one-electron oxidation of the manganese(III) enolate of β-keto ester **8c** produces the α-carbon-radical **A** in the first step (Scheme 4).[7] The α-peroxy radical **B** is then postulated to be formed from **A** by trapping O_2, which is dissolved in the solvent.[8] This scenario was



Scheme 4. Products and the mechanism of the Mn^{III}-initiated reaction of β-keto ester **8c**.

Table 2. The products and yields of the Mn^{III}-initiated reaction of β-keto ester **8c** (see Scheme 4).[a]

Entry	Mn^{II} (equiv.)	Cu^{II} (equiv.)	Solvent	*T*/*t* [°C/h]	Product yield [%] **8c**	**14c**	**15c**
1	3	1	EtOH[b]	15/24	–	39	–
2	3	1	EtOH[b]	50/5	–	64	–
3	3	1	EtOH[b]	80/5	–	6	16
4	3	1	EtOH[c]	80/5	–	–	34
5	3	1	EtOH[c] Ar[d]	80/5	–	–	53
6[e]	3	0	EtOH[b]	80/5	–	15	–
7	3	1	EtOH[c]	50/5	–	62	–
8	3	0	EtOH[b]	50/5	–	74	–
9	3	0	EtOH[b] Ar[d]	50/5	50	2	–
10[f]	3	0	EtOH[b] O_2[g]	15/24	–	31	–
11	3	0	MeCN	50/5	57	13	–
12	3	0	AcOH	50/5	–	53	–
13	2	0	EtOH[b]	50/5	–	57	–
14	1	0	EtOH[b]	50/11	–	35	–
15	1	0	AcOH[h]	15/1	–	53	29
16	1	0	AcOH[h]	50/1	–	47	26
17	0.3	0	AcOH[h]	15/1	–	39	18
18	0.1	0	AcOH[h]	15/1	8	40	9
19[i]	0.1	0	AcOH[h] O_2[g]	15/1	6	35	–
20	0.3	0	AcOH[j]	15/1	4	57	–

[a] The reaction was carried out in the air unless otherwise noted. [b] 94% EtOH (6% H_2O). [c] 99.9% EtOH (anhydrous). [d] The reaction mixture was degassed by the freeze-thaw method before argon was added. [e] **18** was also obtained in 39% yield. [f] **19** was also obtained in 16% yield. [g] A balloon filled with O_2 was attached to the reaction flask. [h] Ultrasonic irradiation with 20% intensity of maximum 130 W, 20 KHz power was continuously applied. [i] **19** was also obtained in 12% yield. [j] Ultrasonic irradiation with the intensity given in footnote [h] for 60 sec and then 10 sec pause were repeatedly applied.

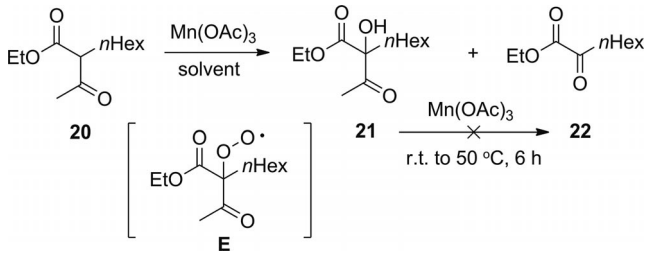
supported by the fact that **8c** (50%) was recovered with only 2% yield of the furan product **14c** under the optimised condition but in the absence of O_2 (Table 2, entry 9). The first oxidation may be completed through the formation and fragmentation of 1,2-dioxetane **C** to produce α-oxo ester **16**. Thermal decomposition of 1,2-dioxetanes to carbonyl compounds is known in the literature.[9] The second oxidation of **16** to **17** may proceed in a similar way. One-electron oxidation of the Mn^{III} enolate of α-oxo ester **16**, O_2 trapping of the resulting δ-carbon-radical, and reduction of the peroxy radical to peroxide and then to the hydroxy group produces δ-hydroxy β,γ-unsaturated α-oxo ester **17**. Under these conditions, EtOH and Mn^{II} can act as a reducing agent in the above reduction.[10] Finally, δ-hydroxy β,γ-unsaturated α-oxo ester **17** cyclised and aromatised to give furan **14c**.

The 1,2-dioxetane formation/fragmentation and the final cyclisation seemed to be favourable at 50 °C (the optimum temperature for furan formation). On the other hand, the formation of cyclopentenone **18** (39%) was the major process at 80 °C in the air (Table 2, entry 6), which presumably proceeds through Mn^{III}-mediated deacetylation and intramolecular aldol reaction from **17**. Considering the importance of O_2 in the oxidation, the reaction was carried out under a positive pressure of O_2 at 15 °C (Table 2, entry 10). Tricarbonyl compound **19** (16%) was obtained, presumably via 1,2-diperoxide intermediate **D**, together with furan **14c** (31%). The stable tertiary benzylic radical generated from the peroxy radical intermediate **B** would trap extra O_2 in the reaction medium to produce 1,2-diperoxide intermediate **D**, which would undergo fragmentation to provide tricarbonyl compound **19**. The solvent effect on the oxidation reaction was then checked. Acetonitrile was not a good solvent for the oxidation; under these conditions most **8c** (57%) was recovered, and only 13% of the furan product **14c** was produced (Table 2, entry 11). A little inferior but almost comparable yield of **14c** (53%) was obtained in AcOH under the above optimised conditions (Table 2, entry 12).

The oxidation can be catalytic for Mn^{III} because Mn^{II} may be oxidised back during the formation of **C** (Scheme 4). Thermal decomposition of **C** would regenerate $Mn(OAc)_3$. Furthermore, in the second oxidation Mn^{II} can be converted into Mn^{III} during the reduction of the peroxy radical. The yield of the furan product **14c** was, however, decreased as the amount of Mn^{III} was reduced (Table 2, entries 13 and 14). Because, under these conditions, EtOH is a good reducing agent, it may compete with Mn^{II} in reducing the oxy radical of 1,2-dioxetane to the corresponding hemiacetal and/or the peroxy radical to the corresponding peroxide, which requires another equivalent of Mn^{III} for the oxidation of the resulting α-hydroxyethyl radical to acetaldehyde.[9] This explains the requirement for three equivalents of Mn^{III} in the optimised conditions in EtOH.

With the above considerations in mind, we replaced the solvent with AcOH, which is a much weaker hydrogen donor, to develop a catalytic version of the oxidative furan synthesis of β-keto ester **8c**. We were able to reduce the amount of Mn^{III} from three to one equivalent in AcOH (at 15 °C for 1 h, ultrasonic irradiation) without decreasing the yield of furan **14c** (Table 2, entry 15).[11] The formation of indane **15c** (29%) was also observed in this case, which could be explained by the activation (or possibly degassing) effect of ultrasonic irradiation. Raising the reaction temperature to 50 °C under ultrasonication did not provide any positive effect (Table 2, entry 16). The amount of Mn^{III} could be reduced to even 0.3 or 0.1 equiv. to produce ca. 40% yield of furan **14c** in AcOH under ultrasonication (Table 2, entries 17 and 18). The catalytic reaction under a positive O_2 pressure may reduce the amount of carbon-radical cyclisation product **15c**, however, tricarbonyl compound **19** (12%) was obtained instead (Table 2, entry 19). An improved yield of furan **14c** (57%) under catalytic conditions was obtained by the programmed application of ultrasonic irradiation (on for 60 sec and off for 10 sec) for 1 h to alleviate the activation of the carbon-radical cyclisation (Table 2, entry 20).

The Mn^{III}-promoted oxidation of simple β-keto ester **20**, containing a α-hexyl group, was reinvestigated to gain a better understanding of the temperature and the solvent effects (Scheme 5 and Table 3). α-Hydroxy β-keto ester **21** and α-oxo ester **22** were obtained in 21 and 27% yields, respectively, when one equivalent of Mn^{III} was used in 94% EtOH at 15 °C for 6 h. The reaction was not complete, presumably because of the role of EtOH in the reduction of the intermediate peroxy and oxy radicals, which required Mn^{III} for the oxidation of the resulting α-hydroxyethyl radical to acetaldehyde, and thus 17% of the β-keto ester **20** was recovered (Table 3, entry 1).



Scheme 5. Mn^{III}-promoted oxidation of β-keto ester **20** with α-hexyl substitution.

Table 3. The products and yields of the Mn^{III}-promoted oxidation of β-keto ester **20**.[a]

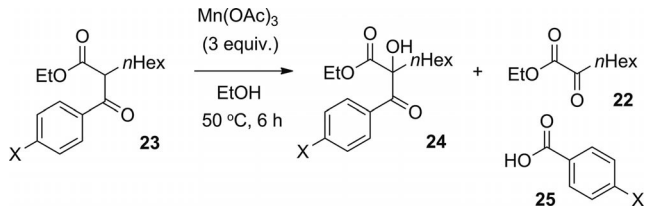
Entry	Mn^{III} [equiv.]	Solvent	*T*/*t* [°C/h]	Product [%] **20**	**21**	**22**	Ratio **22/21**
1	1.0	EtOH[b]	15/6	17	21	27	1.3
2	1.0	EtOH[b]	50/6	–	16	46	2.9
3	0.3	EtOH[b]	15/6	44	14	13	0.9
4	0.3	EtOH[b]	50/6	26	12	30	2.5
5	0.1	EtOH[b]	15/24	70	11	11	1.0
6	0.1	EtOH[b]	50/6	37	10	28	2.8
7	1.0	AcOH	15/6	30	–	34	**22** only
8	0.3	AcOH	15/6	35	–	8	**22** only
9	0.1	AcOH	15/6	56	–	6	**22** only
10	0.1	AcOH	50/6	30	–	21	**22** only
11	0.1	AcOH[c]	15/1	–	–	63	**22** only

[a] The reaction was carried out in the air. [b] 94% EtOH (6% H_2O). [c] Ultrasonic irradiation with 20% intensity of maximum 130 W, 20 KHz power was applied.

The assumption that α-hydroxy β-keto ester **21** might be a precursor of α-oxo ester **22** was ruled out because **21** did not produce **22** upon treatment with 2 equiv. Mn^{III} even at 50 °C for 6 h. Ester **21** and α-oxo ester **22** must be produced from the peroxy radical intermediate **E** by either direct reduction or through the formation of 1,2-dioxetane. We observed that conducting the reaction at a temperature of 50 °C again favoured formation of the α-oxo ester **22**. The yield of **22** was increased to 46% and **20** was not observed at 50 °C when one equivalent of Mn^{III} was used in EtOH (Table 3, entry 2). We confirmed that this temperature effect was also apparent under the catalytic conditions of Mn^{III} in EtOH; under these conditions ca. 1:1 yield ratio of **22/21** was obtained at 15 °C, whereas the ratio changed to ca. 2.8:1 in favour of **22** at 50 °C (Table 3, entries 3–6). Thus, 1,2-dioxetane formation and decomposition from the peroxy radical **E** is favoured at 50 °C to produce α-oxo ester **22**.

No α-hydroxy β-keto ester **21** was observed under any conditions when AcOH was used as solvent (Table 3, entries 7–11); in these cases, Mn^{II} might be the main reducing agent for the intermediate peroxy radical **E**. The peroxy radical **E** presumably led to 1,2-dioxetane formation and fragmentation in AcOH instead of direct reduction mediated by Mn^{II}. However, the reaction was still not catalytic for Mn^{III}, and an appreciable amount of β-keto ester **20** was recovered even at 50 °C (Table 3, entries 7–10). Activation by ultrasonic irradiation was necessary to induce the formation and fragmentation of 1,2-dioxetane to produce α-oxo ester **22**. Finally, 63% yield of α-oxo ester **22** was obtained when 0.1 equiv. Mn^{III} was used for the oxidation in AcOH under ultrasonication (Table 3, entry 11).

A series of α-benzoyl esters **23a**–**d** containing the aromatic *para*-substituent X (Cl, H, Me, and OMe) of a different electronic nature was prepared to support the 1,2-dioxetane mechanism for the oxidation to α-oxo ester **22** (Scheme 6 and Table 4). The oxidation was carried out using 3 equiv. Mn^{III} in 94% EtOH at 50 °C for 6 h. We anticipated that the electron-deficient benzoyl group would facilitate intramolecular 1,2-dioxetane formation for the intermediate peroxy radical to produce **22** rather than reduction to **24**. This idea was confirmed by the observed increasing ratio of the yields of **22** over **24** as the electron-withdrawing efficiency of X increased. The corresponding benzoic acid derivatives **25a**–**d** were also obtained in slightly lower yield, presumably due to adsorption by silica gel during the purification process.



Scheme 6. Mn^{III}-promoted oxidation of α-benzoyl ester **23**.

Table 4. Products and yields of the Mn^{III}-promoted oxidation of α-benzoyl ester **23**.

Entry	**23** (X)	Yield **24** [%]	Yield **22** [%]	Yield **25** [%]	Ratio **22/24**
1	**a** (Cl)	11	32	24	2.90
2	**b** (H)	12	21	14	1.75
3	**c** (Me)	31	27	12	0.87
4[a]	**d** (OMe)	14	6	5	0.43

[a] The reaction of **23d** was slow compared to the other cases and required 16 h.

Conclusions

We developed a new method for furan synthesis by Mn^{III}-initiated oxidations and heterocyclisation of β-keto esters containing α-allylic substitution. We established the controlling factors for the reaction pathway leading to either oxidation or to carbon-radical cyclisation. Rigorous exclusion of O_2 as well as a suitable disposition of alkenyl groups relative to the radical centre are prerequisites for smooth carbon-radical cyclisation, together with the assistance of the Cu^{II} salt. Otherwise, oxidation of the α-carbon radicals is the general pathway. Molecular oxygen is trapped to give the α-peroxy radical, which could either be directly reduced to a hydroxy group or undergo 1,2-dioxetane formation and fragmentation (favoured at 50 °C) to produce α-oxo esters. This oxidation can be catalytic in AcOH under ultrasonication. Further work on extending this oxidation and cyclisation to the synthesis of polycyclic compounds is underway.

Experimental Section

General Experimental: ^1H and ^{13}C NMR spectra were recorded with a Varian 400-MR spectrometer at 400 and 100 MHz NMR frequencies, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. Solvents for extraction and chromatography were reagent grade and used as received. Column chromatography was performed by the method of Still with silica gel 60, 70–230 mesh ASTM supplied by Merck, using a gradient mixture of EtOAc/hexanes. Reactions were performed in a flask open to the air unless noted otherwise. The reaction mixture under argon atmosphere was prepared by the freeze-thaw method to remove O_2 completely, and the reagents were added in a glove box filled with argon. Reactions under positive pressure of O_2 were performed by using a balloon filled with O_2. Ultrasonic irradiation was applied for a designated time period with 20% intensity of maximum 130 W, 20 KHz power.

Ethyl 2-Acetyl-4,8,12-trimethyltrideca-4,8,12-trienoate (5): To a stirred solution of 2,6,10-trimethylundeca-2,6,10-trien-1-ol (0.50 g, 2.41 mmol) in Et_2O (25 mL), was added PBr_3 (0.27 g, 0.96 mmol) at 0 °C. The mixture was stirred for 30 min, diluted with Et_2O, washed with H_2O, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give 11-bromo-2,6,10-trimethylundeca-1,5,9-triene as a light-yellow oil.

To a stirred solution of ethyl acetoacetate (0.32 g, 2.41 mmol) in THF (20 mL) was added 60% NaH (0.20 g, 4.82 mmol) at 0 °C. The mixture was stirred for 1 h, and the above crude bromination product was added to the mixture. The reaction mixture was stirred at room temperature for 12 h, diluted with EtOAc, washed with 1 M HCl solution, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give **5** (0.33 g, 0.11 mmol, 43%) as a clear oil. ^1H NMR: δ = 1.26 (t, J = 7.2 Hz, 3 H), 1.59 (s, 3 H), 1.61 (s, 3 H), 1.73 (s, 3 H), 1.93–1.97 (m, 2 H), 2.01–2.08 (m, 4 H), 2.08–2.16 (m, 2 H), 2.21 (s, 3 H), 2.46–2.58 (m, 2 H), 3.61 (t, J = 8.0 Hz, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 4.68 (s, 1 H), 4.71 (s, 1 H), 5.11 (dt, J_d = 1.2, J_t = 6.8 Hz, 1 H), 5.16 (dt, J_d = 1.2, J_t = 7.2 Hz, 1 H) ppm. ^{13}C NMR: δ = 14.1, 15.8, 15.9, 22.5, 26.2, 26.6, 28.8, 37.8, 38.0, 39.4, 58.5, 61.3, 109.8, 124.2, 127.2, 130.9, 134.8, 145.9, 169.6, 203.0 ppm. IR (KBr): $\tilde{\nu}$ = 3074, 2967, 2925, 2856, 1741, 1717, 1650, 1446, 1368, 1358, 1331, 1298, 1262, 1214, 1174, 1150, 1098, 1046, 1025, 886 cm^{-1}. HRMS (CI^+): calcd. for $C_{20}H_{33}O_3$ 321.2430; found 321.2431.

Ethyl 5-Hydroxy-4,8,12-trimethyl-2-oxotrideca-3,8,12-trienoate (6) and Ethyl 5-(3,7-Dimethylocta-3,7-dienyl)-4-methylfuran-2-carboxylate (7): To a stirred solution of β-keto ester **5** (0.86 g, 2.68 mmol) in 94% EtOH (10 mL), were added $Mn(OAc)_3{\cdot}2H_2O$ (2.24 g, 8.03 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.47 g, 2.68 mmol). The reaction mixture was stirred at 20 °C for 6 h, then the resulting mixture was diluted with CH_2Cl_2, washed with 1 M HCl solution, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give **6** (0.16 g, 0.50 mmol, 19%) and **7** (0.45 g, 1.55 mmol, 58%) as light-yellow oils.

Compound 6: ^1H NMR: δ = 1.38 (t, J = 7.2 Hz, 3 H), 1.64 (s, 3 H), 1.72 (s, 3 H), 1.72–1.83 (m, 2 H), 2.00–2.08 (m, 2 H), 2.08–2.17 (m, 4 H), 2.18 (s, 3 H), 4.17 (dd, J = 7.8, 4.0 Hz, 1 H), 4.33 (q, J = 7.2 Hz, 2 H), 4.68 (s, 1 H), 4.71 (s, 1 H), 5.20 (t, J = 6.4 Hz, 1 H), 7.02 (s, 1 H) ppm. ^{13}C NMR: δ = 14.0, 15.8, 16.9, 22.4, 26.0, 33.1, 35.6, 37.5, 62.3, 76.2, 109.9, 116.7, 125.4, 134.3, 145.6, 162.2, 162.7, 182.8 ppm. IR (KBr): $\tilde{\nu}$ = 3477, 3074, 2978, 2934, 1728, 1537, 1447, 1371, 1315, 1261, 1192, 1095, 1022 cm^{-1}. HRMS (CI^+): calcd. for $C_{18}H_{29}O_4$ 309.2066; found 309.2071.

Compound 7: ^{1}H NMR: δ = 1.35 (t, J = 7.2 Hz,3 H), 1.63 (s, 3 H), 1.71 (s, 3 H), 1.97 (s, 3 H), 1.99 (t, J = 8.4 Hz, 2 H), 2.10 (q, J = 7.2 Hz, 2 H), 2.30 (t, J = 7.6 Hz, 2 H), 2.72 (t, J = 8.0 Hz, 2 H), 4.33 (q, J = 7.2 Hz, 2 H), 4.65 (s, 1 H), 4.69 (s, 1 H), 5.12 (t, J = 6.8 Hz, 3 H), 6.95 (s, 1 H) ppm. ^{13}C NMR: δ = 9.7, 14.4, 15.9, 22.4, 25.4, 26.1, 37.6, 37.9, 60.5, 109.8, 116.8, 121.1, 125.1, 133.7, 145.7, 156.5, 159.0 ppm. IR (KBr): $\tilde{\nu}$ = 2966, 2928, 1726, 1655, 1535, 1448, 1369, 1313, 1192 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{18}H_{27}O_3$ 291.1960; found 291.1967.

(*E*)-Ethyl 6-Acetoxy-2-acetyl-4-phenyl-4-hexenoate (8c): To a stirred solution of ethyl acetoacetate (0.51 g, 3.91 mmol) in THF (20 mL) at 0 °C, was added 60% NaH (0.18 g, 4.56 mmol). The mixture was stirred at 0 °C for 1 h, and a solution of 4-bromo-3-phenyl-2-butenyl acetate (**10a**; 0.88 g, 3.26 mmol) in THF (5 mL) was added. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The resulting mixture was diluted with EtOAc, washed with 1 M HCl solution, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give **8c** (0.90 g, 2.82 mmol, 86%, 5:1 mixture of *E*/*Z* isomers) as a light-yellow oil. Data for (*E*)-**8c**: ^{1}H NMR: δ = 1.22 (t, J = 7.2 Hz, 3 H), 2.07 (s, 3 H), 2.11 (s, 3 H), 2.96–3.17 (m, 2 H), 3.42 (t, J = 7.2 Hz, 3 H), 4.06–4.18 (m, 2 H), 4.80 (dd, J = 6.8, 2.4 Hz, 2 H), 5.79 (t, J = 6.8 Hz, 1 H), 7.27–7.36 (m, 5 H) ppm. ^{13}C NMR: δ = 14.0, 20.8, 28.3, 29.4, 57.7, 61.3, 61.5, 125.2, 126.7, 128.0, 128.6, 140.6, 141.2, 169.0, 170.7, 201.9 ppm. IR (KBr): $\tilde{\nu}$ = 2982, 1736, 1647, 1443, 1366, 1227, 1150, 1022, 957, 856, 764, 698 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{18}H_{22}O_5$ 318.1467; found 318.1474.

COSY and NOESY spectra of **8c** are included in the Supporting Information.

Ethyl 5-(Acetoxymethyl)-4-phenylfuran-2-carboxylate (14c): To a stirred solution of **8c** (0.11 g, 0.35 mmol) in 94% EtOH (10 mL), was added $Mn(OAc)_3{\cdot}2H_2O$ (0.29 g, 1.04 mmol). The reaction mixture was heated at 50 °C for 5 h, then cooled to room temperature. The resulting mixture was diluted with CH_2Cl_2, washed with 1 M HCl solution, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give **14c** (0.076 g, 0.26 mmol, 74%) as a light-yellow oil. ^{1}H NMR: δ = 1.40 (t, J = 7.2 Hz, 3 H), 2.12 (s, 3 H), 4.40 (q, J = 7.2 Hz, 2 H), 5.17 (s, 2 H), 7.27 (s, 1 H), 7.34–7.46 (m, 5 H) ppm. ^{13}C NMR: δ = 14.4, 20.8, 57.3, 61.3, 118.8, 128.0, 128.1, 128.5, 129.0, 131.4, 144.6, 148.3, 158.6, 170.5 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 2924, 2851, 1721, 1616, 1539, 1497, 1451, 1370, 1315, 1223, 1153, 1107, 1022, 964, 910, 760, 729, 698 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{16}H_{16}O_5$ 288.0997; found 288.0992.

Ethyl 3-(2-Acetoxyethylidene)-1-acetyl-2,3-dihydro-1*H*-indene-1-carboxylate (15c): A solution of **8c** (0.24 g, 0.75 mmol) in 99.9% EtOH (15 mL) was degassed by the freeze-thaw method, and then charged with Ar. $Mn(OAc)_3{\cdot}2H_2O$ (0.63 g, 2.26 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.15 g, 0.75 mmol) were added under an Ar atmosphere and the reaction mixture was heated at 80 °C for 5 h under Ar. After cooling to room temperature, the resulting mixture was diluted with CH_2Cl_2, washed with 1 M HCl, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give **15c** (0.13 g, 0.40 mmol, 53%) as a light-yellow oil. ^{1}H NMR: δ = 1.30 (t, J = 7.2 Hz, 3 H), 2.09 (s, 3 H), 2.13 (s, 3 H), 3.29 (d of A of ABq, J_{AB} = 17.6, J_d = 2.4 Hz, 1 H), 3.54 (d of B of ABq, J_{AB} = 17.6, J_d = 2.4 Hz, 1 H), 4.26 (dq, J_d = 1.6, J_q = 7.2 Hz, 2 H), 4.78 (d of A of ABq, J_{AB} = 12.8, J_d = 7.2 Hz, 1 H), 4.81 (d of B of ABq, J_{AB} = 12.8, J_d = 7.6 Hz, 1 H), 6.12 (tt, J = 7.2, 2.4 Hz, 1 H), 7.30–7.37 (m, 2 H), 7.49–7.54 (m, 1 H), 7.58–7.63 (m, 1 H) ppm. ^{13}C NMR: δ = 14.0, 20.9, 26.1, 36.0, 61.9, 62.0, 70.2, 114.1, 120.9, 127.1, 129.0, 129.2, 140.8, 141.3, 142.7, 170.3, 170.9, 202.5 ppm. IR (KBr): $\tilde{\nu}$ = 2982, 2936, 1736, 1715, 1599, 1447, 1364, 1221, 1153, 1022, 955 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{18}H_{20}O_5$ 316.1310; found 316.1313.

Ethyl 1-Hydroxy-4-oxo-3-phenylcyclopent-2-enecarboxylate (18): To a stirred solution of **8c** (0.24 g, 0.75 mmol) in 94% EtOH (15 mL) was added $Mn(OAc)_3{\cdot}2H_2O$ (0.63 g, 2.26 mmol). The reaction mixture was heated at 80 °C for 5 h, and cooled to room temperature. The resulting mixture was diluted with CH_2Cl_2, washed with 1 M HCl, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give furan **14c** (0.033 g, 0.11 mmol, 15%) and cyclopentenone **18** (0.072 g, 0.29 mmol, 39%) as light-yellow oils. Data for **18**: ^{1}H NMR: δ = 1.28 (t, J = 7.2 Hz, 3 H), 2.81 (d, J = 18.0 Hz, 1 H), 3.10 (d, J = 18.0 Hz, 1 H), 3.89 (s, 1 H), 4.22–4.37 (m, 2 H), 7.41 (s, 1 H), 7.37–7.45 (m, 3 H), 7.70–7.76 (m, 2 H) ppm. ^{13}C NMR: δ = 14.0, 48.7, 63.3, 76.4, 127.7, 128.5, 129.5, 129.9, 144.6, 153.4, 173.9, 203.1 ppm. IR (KBr): $\tilde{\nu}$ = 3453, 2982, 1717, 1493, 1447, 1343, 1261, 1180, 1030, 961, 860, 764, 694 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{14}H_{15}O_4$ 247.0970; found 247.0966.

Ethyl 2-Acetyl-2-hydroxy-4-oxo-4-phenylbutanoate (19): To a stirred solution of **8c** (0.24 g, 0.75 mmol) in 94% EtOH (15 mL) was added $Mn(OAc)_3{\cdot}2H_2O$ (0.63 g, 2.26 mmol). The reaction mixture was stirred at 15 °C for 24 h under an O_2 atmosphere. The resulting mixture was diluted with CH_2Cl_2, washed with 1 M HCl, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give the furan **14c** (0.070 g, 0.23 mmol, 31%) and **19** (0.032 g, 0.12 mmol, 16%) as light-yellow oils. Data for **19**: ^{1}H NMR: δ = 1.28 (t, J = 7.2 Hz, 3 H), 2.36 (s, 3 H), 3.70 (d, J = 18.0 Hz, 1 H), 3.93 (d, J = 18.0 Hz, 1 H), 4.22–4.34 (m, 2 H), 4.61 (s, 1 H), 7.43–7.51 (m, 2 H), 7.57–7.63 (m, 1 H), 7.90–7.98 (m, 2 H) ppm. ^{13}C NMR: δ = 13.9 (OCH_2CH_3), 24.6 ($O{=}CCH_3$), 43.7, 62.9, 82.3, 128.2, 128.7, 133.8, 136.1, 170.2, 197.4, 204.3 ppm. IR (KBr): $\tilde{\nu}$ = 3462, 2982, 2930, 1720, 1686, 1597, 1449, 1354, 1219, 1136, 1072, 1013, 856, 756, 689 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{14}H_{17}O_5$ 265.1076; found 265.1078.

Ethyl 6-Acetoxy-2-acetyl-4-methylhex-4-enoate (8a): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (8.66 g, 65.24 mmol) with 60% NaH (3.05 g, 76.12 mmol) and 4-bromo-3-methyl-2-butenyl acetate (11.26 g, 54.37 mmol) in THF (40 mL) at 0 °C for 1 h and then at room temperature for 12 h, produced **8a** (11.15 g, 43.83 mmol, 80%, *E*/*Z* = 3:1) as a light-yellow oil after purification by SiO_2 flash chromatography. Data for (*E*)-**8a**: ^{1}H NMR: δ = 1.27 (t, J = 6.8 Hz, 3 H), 1.71 (s, 3 H), 2.04 (s, 3 H), 2.23 (s, 3 H), 2.59 (dd, J = 7.6, 2.4 Hz, 2 H), 3.64 (t, J = 7.6 Hz, 1 H), 4.19 (q, J = 6.8 Hz, 2 H), 4.54 (d, J = 6.8 Hz, 2 H), 5.36 (dt, J_d = 1.2, J_t = 6.8 Hz, 1 H) ppm. ^{13}C NMR: δ = 13.8, 16.1, 20.6, 28.6, 37.2, 57.7, 60.6, 61.2, 120.9, 137.6, 169.0, 170.6, 201.7 ppm. IR (KBr): $\tilde{\nu}$ = 3028, 1740, 1601, 1493, 1450, 1076, 1030, 964 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{13}H_{19}O_5$ 255.1232; found 255.1231.

Ethyl 2-Acetyl-6-methoxy-4-methyl-4-hexenoate (8b): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (0.53 g, 3.97 mmol) with 60% NaH (0.17 g, 4.31 mmol) and 1-bromo-4-methoxy-2-methyl-2-butene (0.59 g, 3.31 mmol) in THF (20 mL) at 0 °C for 1 h and then at room temperature for 12 h, produced **8b** (0.41 g, 1.77 mmol, 54%, *E*/*Z* = 4:1) as a light-yellow oil. Data for (*E*)-**8b**: ^{1}H NMR: δ = 1.27 (t, J = 7.2 Hz, 3 H), 1.68 (s, 3 H), 2.23 (s, 3 H), 2.59 (dd, J = 7.6, 3.2 Hz, 2 H), 3.29 (s, 3 H),

3.65 (t, J = 7.6 Hz, 1 H), 3.90 (d, J = 6.8 Hz, 2 H), 4.19 (q, J = 7.2 Hz, 2 H), 5.36 (tq, J_t = 6.8, J_q = 1.2 Hz, 1 H) ppm. ^{13}C NMR: δ = 14.0, 16.3, 28.8, 37.5, 57.7, 58.1, 61.4, 68.6, 123.5, 136.0, 169.3, 202.4 ppm. IR (KBr): $\tilde{\nu}$ = 3012, 1740, 1443, 1366, 1231, 1150, 1099, 1022, 961 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{12}H_{19}O_4$ 227.1283; found 227.1284.

(*E*)-5-Acetyl-6-oxo-3-phenylhept-2-en-1-yl Acetate (8d): To a stirred solution of acetylacetone (0.33 g, 3.25 mmol) in acetone (35 mL) was added anhydrous K_2CO_3 (0.45 g, 3.25 mmol). The mixture was stirred at 20 °C for 1 h, and 4-bromo-3-phenyl-2-butenyl acetate (**10a**; 0.88 g, 3.25 mmol) was added. The mixture was stirred at 20 °C for 12 h, diluted with EtOAc, washed with 1 M HCl, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give **8d** (0.38 g, 1.25 mmol, 40%, a 10:1 mixture of *E*/*Z* isomers) as a light-yellow oil. Data for (*E*)-**8d**: ^{1}H NMR: δ = 2.07 (s, 9 H), 3.10 (d, J = 7.2 Hz, 2 H), 3.65 (t, J = 7.2 Hz, 1 H), 4.80 (d, J = 6.8 Hz, 2 H), 5.80 (t, J = 6.8 Hz, 1 H), 7.25–7.37 (m, 5 H) ppm. ^{13}C NMR: δ = 20.6, 28.2, 29.6, 29.6, 60.9, 65.3, 124.8, 126.3, 127.8, 128.4, 140.1, 140.9, 170.5, 203.0, 203.0 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 1728, 1315, 1234, 1188, 1153, 1096 cm^{-1}. HRMS (FAB$^+$): calcd. for $C_{17}H_{21}O_4$ 289.1440; found 289.1435.

5-(Diethylcarbamoyl)-6-oxo-3-phenylhept-2-en-1-yl Acetate (8e): Following the standard procedure for **8c**, the reaction of *N*,*N*-diethylacetoacetamide (0.39 g, 2.48 mmol) with 60% NaH (0.12 g, 2.90 mmol) and 4-bromo-3-phenyl-2-butenyl acetate (**10a**; 0.56 g, 2.07 mmol) in THF (20 mL) at 0 °C for 1 h and then at room temperature for 12 h under an Ar atmosphere, produced **8e** (0.58 g, 1.69 mmol, 68%, 3:1 mixture of *E*/*Z* isomers) as a light-yellow oil after purification by SiO_2 flash chromatography. Data for (*E*)-**8e**: ^{1}H NMR: δ = 0.86 (t, J = 7.2 Hz, 3 H), 1.03 (t, J = 7.2 Hz, 3 H), 2.07 (s, 3 H), 2.15 (s, 3 H), 2.86–3.20 (m, 4 H), 3.23–3.38 (m, 2 H), 3.46–3.53 (m, 1 H), 4.81 (d of A of ABq, J_{AB} = 13.2, J_d = 6.4 Hz, 1 H), 4.92 (d of B of ABq, J_{AB} = 13.2, J_d = 7.6 Hz, 1 H), 5.83 (t, J = 7.2 Hz, 1 H), 7.26–7.40 (m, 5 H) ppm. ^{13}C NMR: δ = 12.7, 14.0, 20.9, 27.2, 29.2, 40.7, 42.0, 55.4, 61.5, 123.4, 125.1, 126.4, 127.8, 128.5, 140.9, 167.7, 170.7, 203.9 ppm. IR (KBr): $\tilde{\nu}$ = 2974, 1736, 1634, 1433, 1362, 1229, 1134, 1022, 959 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{20}H_{27}NO_4$ 345.1940; found 345.1945.

(*E*)-Ethyl 6-Acetoxy-2-acetyl-4-(4-chlorophenyl)-4-hexenoate (8f): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (0.24 g, 1.87 mmol) with 60% NaH (0.09 g, 2.19 mmol) and 4-bromo-3-(4-chlorophenyl)-2-buten-1-yl acetate (**10b**; 0.47 g, 1.56 mmol) in THF (10 mL) at 0 °C for 1 h and then at room temperature for 12 h under an Ar atmosphere, produced **8f** (0.43 g, 1.22 mmol, 78%, 5.9:1 mixture of *E*/*Z* isomers) as a light-yellow oil after purification by SiO_2 flash chromatography. Data for (*E*)-**8f**: ^{1}H NMR: δ = 1.22 (t, J = 7.2 Hz, 3 H), 2.07 (s, 3 H), 2.12 (s, 3 H), 3.07 (d of A of ABq, J_{AB} = 14.8, J_d = 8.0 Hz, 1 H), 3.09 (d of B of ABq, J_{AB} = 14.8, J_d = 6.8 Hz, 1 H), 3.38 (dd, J = 8.0, 6.8 Hz, 1 H), 4.06–4.18 (m, 2 H), 4.78 (d of A of ABq, J_{AB} = 13.2, J_d = 6.8 Hz, 1 H), 4.80 (d of B of ABq, J_{AB} = 13.2, J_d = 6.8 Hz, 1 H), 5.78 (t, J = 6.8 Hz, 1 H), 7.20–7.34 (m, 4 H) ppm. ^{13}C NMR: δ = 13.8, 20.8, 28.0, 29.3, 57.5, 61.1, 61.5, 125.7, 127.8, 128.6, 133.7, 138.8, 139.9, 168.8, 170.6, 201.5 ppm. IR (KBr): $\tilde{\nu}$ = 2982, 1736, 1715, 1643, 1491, 1443, 1364, 1227, 1150, 1092, 1013, 959, 824, 766 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{18}H_{21}ClO_5$ 352.1078; found 352.1083.

(*E*)-Ethyl 6-Acetoxy-2-acetyl-4-(4-methoxyphenyl)-4-hexenoate (8g): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (0.74 g, 2.47 mmol) with 60% NaH (0.14 g, 3.45 mmol) and 4-bromo-3-(4-methoxyphenyl)-2-buten-1-yl acetate (**10c**; 0.74 g, 2.47 mmol) in THF (20 mL) at 0 °C for 1 h and then at room temperature for 12 h under an Ar atmosphere, produced **8g** (0.69 g, 1.98 mmol, 81%, 8:1 mixture of *E*/*Z* isomers) as a light-yellow oil after purification by SiO_2 flash chromatography. Data for (*E*)-**8g**: ^{1}H NMR: δ = 1.22 (t, J = 7.2 Hz, 3 H), 2.07 (s, 3 H), 2.11 (s, 3 H), 3.04–3.15 (m, 2 H), 3.43 (t, J = 7.2 Hz, 1 H), 3.81 (s, 3 H), 4.05–4.16 (m, 2 H), 4.78 (dd, J = 7.6, 2.8 Hz, 2 H), 5.74 (t, J = 7.2 Hz, 1 H), 7.86 (d, J = 8.8 Hz, 2 H), 7.23 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 13.9, 14.1, 20.8, 28.1, 29.4, 55.1, 57.6, 61.3, 113.8, 123.6, 127.7, 132.6, 140.6, 159.4, 169.0, 170.7, 202.0 ppm. IR (KBr): $\tilde{\nu}$ = 1734, 1717, 1607, 1510, 1443, 1364, 1229, 1179, 1026, 955, 833 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{19}H_{24}O_6$ 348.1573; found 348.1573.

Ethyl 6-Acetoxy-2-acetyl-4-(naphthalene-2-yl)-4-hexenoate (8h): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (0.49 g, 3.76 mmol) with 60% NaH (0.18 g, 4.39 mmol) and 4-bromo-3-(naphthalen-2-yl)-2-buten-1-yl acetate (**10d**; 1.00 g, 3.13 mmol) in THF (10 mL) at 0 °C for 1 h and then at room temperature under an Ar atmosphere, produced **8h** (1.14 g, 3.09 mmol, 98%, 9:1 mixture of *E*/*Z* isomers) as a light-yellow oil after purification by SiO_2 flash chromatography. Data for (*E*)-**8h**: ^{1}H NMR: δ = 1.20 (t, J = 6.8 Hz, 3 H), 2.10 (s, 3 H), 2.11 (s, 3 H), 3.20 (d of A of ABq, J_{AB} = 14.4, J_d = 8.0 Hz, 1 H), 3.24 (d of B of ABq, J_{AB} = 14.4, J_d = 6.8 Hz, 1 H), 3.47 (dd, J = 8.0, 6.8 Hz, 1 H), 4.04–4.14 (m, 2 H), 4.85 (d of A of ABq, J_{AB} = 13.2, J_d = 6.8 Hz, 1 H), 4.88 (d of B of ABq, J_{AB} = 13.2, J_d = 6.8 Hz, 1 H), 5.94 (t, J = 6.8 Hz, 1 H), 7.40 (dd, J = 8.4, 1.6 Hz, 1 H), 7.46–7.53 (m, 2 H), 7.74 (d, J = 1.6 Hz, 1 H), 7.80–7.86 (m, 3 H) ppm. ^{13}C NMR: δ = 14.0, 21.0, 28.2, 29.7, 57.6, 61.5, 61.6, 124.7, 125.5, 125.7, 126.2, 126.4, 127.6, 128.1, 128.3, 132.9, 133.3, 137.8, 141.0, 169.1, 170.9, 202.1 ppm. IR (KBr): $\tilde{\nu}$ = 1734, 1715, 1366, 1229, 1022, 818, 627, 467 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{22}H_{24}O_5$ 368.1622; found 368.1623.

Ethyl 6-Acetoxy-2-acetyl-4-cyclopropyl-4-hexenoate (8i): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (0.32 g, 2.46 mmol) with 60% NaH (0.12 g, 2.86 mmol) and 4-bromo-3-cyclopropyl-2-buten-1-yl acetate (**10e**; 0.48 g, 2.05 mmol) in THF (10 mL) at 0 °C for 1 h and then at room temperature for 12 h under an Ar atmosphere, produced **8i** (0.49 g, 1.74 mmol, 85%, 2:1 mixture of stereoisomers) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 0.43 (dd, J = 5.6, 1.6 Hz, 2 H), 0.67 (ddd, J = 8.8, 8.4, 1.6 Hz, 2 H), 1.18–1.25 (m, 1 H), 1.28 (t, J = 7.2 Hz, 3 H), 2.04 (s, 3 H), 2.26 (s, 3 H), 2.70 (d of A of ABq, J_{AB} = 14.0, J_d = 6.4 Hz, 1 H), 2.78 (d of B of ABq, J_{AB} = 14.0, J_d = 8.0 Hz, 1 H),3.70 (t, J = 7.2 Hz, 1 H),* 3.83 (dd, J = 8.4, 6.8 Hz, 1 H), 4.12–4.25 (m, 2 H), 4.58 (d of A of ABq, J_{AB} = 12.8, J_d = 7.2 Hz, 1 H), 4.63 (d of B of ABq, J_{AB} = 12.8, J_d = 7.2 Hz, 1 H), 4.71 (d of A of ABq, J_{AB} = 13.6, J_d = 7.2 Hz, 1 H),* 4.73 (d of B of ABq, J_{AB} = 13.6, J_d = 6.8 Hz, 1 H),* 5.27 (t, J = 7.2 Hz, 1 H), 5.39 (t, J = 6.4 Hz, 1 H) ppm. ^{13}C NMR: δ = 4.86,* 5.19,* 5.67, 6.41, 11.2,* 13.9, 14.0,* 16.0, 20.8,* 20.9, 29.0,* 29.1, 30.1, 32.1,* 58.1, 60.7, 60.8,* 61.3,* 61.4, 118.6, 122.5,* 141.1,* 142.3, 169.1, 170.7, 202.1, 202.2* ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1736, 1717, 1447, 1362, 1231, 1146, 1022, 995 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{15}H_{23}O_5$ 283.1545; found 283.1551; * denotes peaks from the minor *Z* isomer.

Ethyl 6-Acetoxy-2-acetyl-4-cyclohexyl-4-hexenoate (8j): Following the standard procedure for **8c**, the reaction of ethyl acetoacetate (0.32 g, 2.46 mmol) with 60% NaH (0.12 g, 2.86 mmol) and 4-bromo-3-cyclopropyl-2-buten-1-yl acetate (**10f**; 0.48 g, 2.05 mmol) in THF (10 mL) at 0 °C for 1 h and then at room temperature for 12 h under an Ar atmosphere, produced **8j** (0.49 g, 1.74 mmol,

85%, 2.5:1 mixture of stereoisomers) as a light-yellow oil after purification by SiO_2 flash chromatography. Data for **8j**: ^{1}H NMR: δ = 1.04–1.24 (m, 5 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.64–1.82 (m, 6 H), 2.05 (s, 3 H), 2.24 (s, 3 H), 2.62 (d of A of ABq, J_{AB} = 14.0, J_d = 6.8 Hz, 1 H), 2.64 (d of B of ABq, J_{AB} = 14.0, J_d = 6.8 Hz, 1 H), 2.67 (d of A of ABq, J_{AB} = 14.0, J_d = 8.8 Hz, 1 H),* 2.67 (d of B of ABq, J_{AB} = 14.0, J_d = 8.8 Hz, 1 H),* 3.46 (t, J = 6.4 Hz, 1 H),* 3.57 (dd, J = 8.0, 6.8 Hz, 1 H), 4.11–4.25 (m, 2 H), 4.59 (d of A of ABq, J_{AB} = 12.8, J_d = 7.6 Hz, 1 H), 4.63 (d of B of ABq, J_{AB} = 12.8, J_d = 7.2 Hz, 1 H), 5.34 (t, J = 7.6 Hz, 1 H),* 5.39 (t, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR: δ = 14.0, 21.1, 26.2, 26.7, 26.8, 28.6, 29.3, 32.6, 32.9, 43.3, 58.4, 61.2, 61.6, 119.9, 146.5, 169.3, 171.0, 202.3 ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2853, 1736, 1717, 1449, 1371, 1229, 1148, 1022 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{16}H_{24}O_3$ [$C_{18}H_{28}O_5$ – $C_2H_4O_2$] 264.1725; found 264.1728; * denotes peaks from the minor *Z* isomer.

Ethyl 5-(Acetoxymethyl)-4-methylfuran-2-carboxylate (14a): Following the standard procedure for **14c**, the reaction of β-keto ester **8a** (0.20 g, 0.78 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.68 g, 2.34 mmol) in 94% EtOH (20 mL) at 50 °C for 5 h, produced **14a** (0.10 g, 0.44 mmol, 57%) as a light-yellow oil after purification by SiO_2 flash column chromatography. ^{1}H NMR: δ = 1.37 (t, J = 7.2 Hz, 3 H), 2.08 (s, 3 H), 2.10 (s, 3 H), 4.36 (q, J = 7.2 Hz, 2 H), 5.06 (s, 2 H), 7.00 (s, 1 H) ppm. ^{13}C NMR: δ = 9.7, 14.3, 20.7, 56.0, 61.0, 120.5, 122.2, 144.0, 149.0, 158.7, 170.5 ppm. IR (KBr): $\tilde{\nu}$ = 2986, 1736, 1543, 1443, 1373, 1319, 1196, 1103, 1026, 949 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{11}H_{14}O_5$ 226.0841; found 226.0846.

Ethyl 5-(Methoxymethyl)-4-methylfuran-2-carboxylate (14b): Following the standard procedure for **14c**, the reaction of β-keto ester **8b** (0.10 g, 0.44 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.37 g, 1.31 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, gave **14b** (0.05 g, 0.25 mmol, 60%) as a light-yellow oil after purification by SiO_2 flash column chromatography. ^{1}H NMR: δ = 1.36 (t, J = 7.2 Hz, 3 H), 2.09 (s, 3 H), 3.36 (s, 3 H), 4.34 (q, J = 7.2 Hz, 2 H), 4.42 (s, 2 H), 7.00 (s, 1 H) ppm. ^{13}C NMR: δ = 9.6, 14.3, 58.1, 60.8, 64.4, 120.7, 121.0, 143.4, 151.6, 158.8 ppm. IR (KBr): $\tilde{\nu}$ = 2970, 1728, 1535, 1450, 1369, 1319, 1196, 1096, 1022, 952 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{10}H_{15}O_4$ 199.0970; found 199.0973.

(5-Acetyl-3-phenylfuran-2-yl)methyl Acetate (14d): Following the standard procedure for **14c**, the reaction of β-keto ester **8d** (0.10 g, 0.35 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.29 g, 1.04 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, gave **14d** (0.04 g, 0.16 mmol, 47%) as a light-yellow oil after purification by SiO_2 flash column chromatography. ^{1}H NMR: δ = 2.13 (s, 3 H), 2.53 (s, 3 H), 5.19 (s, 2 H), 7.32 (s, 1 H), 7.36–7.47 (m, 5 H) ppm. ^{13}C NMR: δ = 20.7, 29.6, 57.2, 117.9, 127.9, 128.1, 128.8, 129.0, 131.8, 148.4, 152.1, 170.4, 187.0 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 1744, 1678, 1532, 1493, 1451, 1370, 1323, 1223, 1146, 1026, 914, 768, 729 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{15}H_{14}O_4$ 258.0892; found 258.0892.

[5-(Diethylcarbamoyl)-3-phenylfuran-2-yl]methyl Acetate (14e): Following the standard procedure for **14c**, the reaction of **8e** (0.34 g, 0.97 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.80 g, 2.91 mmol) in 94% EtOH (15 mL) at 50 °C for 5 h, produced **14e** (0.13 g, 0.40 mmol, 41%) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 1.17–1.37 (br. m, 6 H), 2.13 (s, 3 H), 3.59 (br. d, J = 25.2 Hz, 4 H), 5.18 (s, 2 H), 7.18 (s, 1 H), 7.34–7.46 (m, 5 H) ppm. ^{13}C NMR: δ = 20.8, 57.1, 57.1, 64.3, 116.9, 127.1, 127.9, 128.9, 129.4, 131.7, 145.6, 148.3, 159.1, 170.5 ppm. IR (KBr): $\tilde{\nu}$ = 1744, 1626, 1449, 1371, 1223, 1026, 939, 854, 768, 700 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{18}H_{21}O_4N$ 315.1470; found 315.1471.

Ethyl 5-(Acetoxymethyl)-4-(4-chlorophenyl)furan-2-carboxylate (14f): Following the standard procedure for **14c**, the reaction of **8f** (0.27 g, 0.78 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.64 g, 2.33 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, produced **14f** (0.16 g, 0.50 mmol, 65%) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 1.40 (t, J = 7.2 Hz, 3 H), 2.12 (s, 3 H), 4.40 (q, J = 7.2 Hz, 2 H), 5.15 (s, 2 H), 7.29 (s, 1 H), 7.31–7.43 (m, 4 H) ppm. ^{13}C NMR: δ = 14.3, 20.7, 57.0, 61.3, 118.4, 127.2, 129.1, 129.1, 129.7, 134.1, 144.6, 148.3, 158.4, 170.3 ppm. IR (KBr): $\tilde{\nu}$ = 2972, 2930, 1746, 1711, 1595, 1551, 1493, 1441, 1366, 1312, 1223, 1150, 1090, 1020, 955, 912, 826, 762, 727 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{16}H_{15}ClO_5$ 322.0608; found 322.0605.

Ethyl 5-(Acetoxymethyl)-4-(4-methoxyphenyl)furan-2-carboxylate (14g): Following the standard procedure for **14c**, the reaction of **8g** (0.30 g, 0.85 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.68 g, 2.55 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, produced **14g** (0.14 g, 0.44 mmol, 52%) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 1.40 (t, J = 7.2 Hz, 3 H), 2.13 (s, 3 H), 3.85 (s, 3 H), 4.40 (q, J = 7.2 Hz, 2 H), 5.16 (s, 2 H), 6.97 (d, J = 8.4 Hz, 2 H), 7.30 (s, 1 H), 7.33 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 14.3, 20.8, 55.3, 57.2, 61.2, 114.3, 118.7, 123.5, 128.1, 129.0, 144.3, 147.6, 158.6, 159.4, 170.5 ppm. IR (KBr): $\tilde{\nu}$ = 1717, 1605, 1510, 1369, 1221, 1022, 833, 604 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{17}H_{18}O_6$ 318.1103; found 318.1107.

Ethyl 5-(Acetoxymethyl)-4-(naphthalen-2-yl)furan-2-carboxylate (14h): Following the standard procedure for **14c**, the reaction of **8h** (0.20 g, 0.53 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.44 g, 1.59 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, produced **14h** (0.11 g, 0.34 mmol, 64%) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 1.42 (t, J = 7.2 Hz, 3 H), 2.15 (s, 3 H), 4.42 (q, J = 7.2 Hz, 2 H), 5.25 (s, 1 H), 7.44 (s, 1 H), 7.50–7.56 (m, 2 H), 7.83–7.94 (m, 4 H) ppm. ^{13}C NMR: δ = 14.3, 20.8, 57.3, 61.3, 118.8, 125.7, 126.5, 126.6, 127.0, 127.7, 128.0, 128.4, 128.6, 128.7, 132.7, 133.3, 144.6, 148.4, 158.5, 170.4 ppm. IR (KBr): $\tilde{\nu}$ = 1724, 1541, 1445, 1369, 1314, 1219, 1152, 1022, 939, 820, 750 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{20}H_{18}O_5$ 338.1154; found 338.1154.

Ethyl 5-(Acetoxymethyl)-4-cyclopropylfuran-2-carboxylate (14i): Following the standard procedure for **14c**, the reaction of **8i** (0.23 g, 0.80 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.64 g, 2.40 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, produced **14i** (0.13 g, 0.50 mmol, 63%) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 0.58 (dt, J_d = 6.4, J_t = 4.8 Hz, 2 H), 0.95 (dt, J_d = 8.4, J_t = 6.4 Hz, 2 H), 1.36 (t, J = 7.2 Hz, 3 H), 1.79 (tt, J = 8.4, 4.8 Hz, 1 H), 2.10 (s, 3 H), 4.35 (q, J = 7.2 Hz, 2 H), 5.16 (s, 2 H), 6.75 (s, 1 H) ppm. ^{13}C NMR: δ = 5.52, 7.60, 7.60, 14.3, 20.8, 56.2, 61.0, 116.1, 129.6, 144.1, 149.1, 158.5, 170.6 ppm. IR (KBr): $\tilde{\nu}$ = 1717, 1541, 1373, 1215, 1022, 669 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{13}H_{16}O_5$ 252.0998; found 252.1001.

Ethyl 5-(Acetoxymethyl)-4-cyclohexylfuran-2-carboxylate (14j): Following the standard procedure for **14c**, the reaction of **8j** (0.17 g, 0.52 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (0.44 g, 1.57 mmol) in 94% EtOH (10 mL) at 50 °C for 5 h, produced **14j** (0.08 g, 0.29 mmol, 55%) as a light-yellow oil after purification by SiO_2 flash chromatography. ^{1}H NMR: δ = 1.18–1.52 (m, 4 H), 1.37 (t, J = 7.2 Hz, 3 H), 1.70–1.86 (m, 6 H), 2.09 (s, 3 H), 2.54 (tt, J = 11.6, 3.2 Hz, 1 H), 4.36 (q, J = 7.2 Hz, 2 H), 5.07 (s, 2 H), 7.08 (s, 1 H) ppm. ^{13}C NMR: δ = 14.3, 20.8, 25.3, 25.8, 26.3, 28.7, 34.0, 34.1, 56.2, 61.0, 117.6, 133.0, 144.1, 147.6, 158.7, 170.6 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1715, 1539, 1315, 1188, 1022, 764 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{16}H_{22}O_5$ 294.1467; found 294.1467.

General Procedure for the Mn^{III}-Initiated Oxidation of Ethyl 2-Acetyloctanoate (20). Ethyl 2-Acetyl-2-hydroxyoctanoate (21) and Ethyl 2-Oxooctanoate (22)

Method 1 (Thermal Reaction): To a stirred solution of ethyl 2-acetyloctanoate (**20**; 0.15 g, 0.70 mmol) in 94% EtOH (10 mL) was added $Mn(OAc)_3 \cdot H_2O$ (0.19 g, 0.70 mmol). The reaction mixture was heated at 50 °C for 6 h, cooled to room temperature, and quenched with 1 M HCl (5 mL). The mixture was extracted with CH_2Cl_2, washed with brine and H_2O, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give ethyl 2-acetyl-2-hydroxyoctanoate (**21**; 0.025 g, 0.11 mmol, 16%) and ethyl 2-oxooctanoate (**22**; 0.060 g, 0.32 mmol, 46%) as light-yellow oils.

Method 2 (Ultrasonic Irradiation): To a stirred solution of ethyl 2-acetyloctanoate (**20**; 0.16 g, 0.75 mmol) in glacial AcOH (10 mL) was added $Mn(OAc)_3 \cdot H_2O$ (0.02 g, 0.075 mmol). The reaction mixture was stirred at 15 °C under ultrasonic irradiation (20% intensity of 130 W, 20 kHz) for 1 h, and quenched with 1 M HCl (5 mL). The mixture was extracted with CH_2Cl_2, washed with brine and H_2O, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give ethyl 2-oxooctanoate (**22**; 0.088 g, 0.47 mmol, 63%) as a light-yellow oil.

Ethyl 2-(4-Chlorobenzoyl)octanoate (23a)

Step 1: To a stirred suspension of 60% NaH (1.50 g, 36.0 mmol) in toluene (40 mL) was added diethyl carbonate (3.10 g, 26.0 mmol). While the mixture was heated at reflux, a solution of 4-chloroacetophenone (2.00 g, 13.0 mmol) in toluene (10 mL) was added over 15 min. The resulting mixture was then heated at reflux for 15–20 min until the evolution of H_2 ceased. The mixture was cooled to room temperature and quenched by glacial acetic acid (4 mL). Ice-water was added to the above mixture until the solid was completely dissolved. The reaction mixture was extracted with EtOAc, washed with brine and H_2O, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give ethyl 3-(4-chlorophenyl)-3-oxopropanoate (2.23 g, 9.88 mmol, 76%) as a light-yellow oil.

Step 2: To a stirred suspension of 60% NaH (0.40 g, 10. 67 mmol) in THF (10 mL) at 0 °C was added ethyl 3-(4-chlorophenyl)-3-oxopropanoate (2.20 g, 9.73 mmol). The mixture was stirred at 0 °C for 1 h, and a solution of iodohexane (2.90 g, 13.67 mmol) in THF (2 mL) was added. The mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with 1 M HCl, extracted with EtOAc, washed with brine and H_2O, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography to give ethyl 2-(4-chlorobenzoyl)octanoate (**23a**; 1.03 g, 3.04 mmol, 31%) as a light-yellow oil. ^{1}H NMR: δ = 0.87 (t, J = 7.2 Hz, 3 H), 1.18 (t, J = 7.2 Hz, 3 H), 1.22–1.40 (m, 8 H), 1.93–2.06 (m, 2 H), 4.14 (dq, J_d = 0.8, J_q = 7.2 Hz, 2 H), 4.22 (t, J = 7.2 Hz, 1 H), 7.45 (d, J = 8.8 Hz, 2 H), 7.93 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 14.0, 14.0, 22.5, 27.5, 28.8, 29.0, 31.5, 54.4, 61.4, 129.0, 129.9, 134.6, 139.9, 169.8, 194.0 ppm.

Ethyl 2-Benzoyloctanoate (23b): Following the standard procedure for **23a**, the reaction of acetophenone (1.00 g, 8.30 mmol), with 60% NaH (0.90 g, 23.3 mol) and diethyl carbonate (2.00 g, 16.6 mol) in refluxing toluene (20 mL) for 30 min produced ethyl 3-oxo-3-phenylpropanoate (1.24 g, 6.43 mmol, 78%) as a light-yellow oil after purification by SiO_2 flash column chromatography.

The reaction of ethyl 3-oxo-3-phenylpropanoate (1.40 g, 7.28 mmol) with 60% NaH (0.32 g, 8.00 mol) and iodohexane (2.10 g, 9.91 mmol) in THF (10 mL) at 0 °C to room temperature, overnight, produced ethyl 2-benzoyloctanoate (0.95 g, 3.12 mmol, 43%) as a light-yellow oil after purification by SiO_2 flash column chromatography. ^{1}H NMR: δ = 0.87 (t, J = 6.8 Hz, 3 H), 1.17 (t, J = 7.2 Hz, 3 H), 1.20–1.40 (m, 8 H), 1.93–2.07 (m, 2 H), 4.14 (dq, J_d = 0.8, J_q = 6.8 Hz, 2 H), 4.28 (t, J = 7.2 Hz, 1 H), 7.45–7.51 (m, 2 H), 7.56–7.62 (m, 1 H), 7.97–8.02 (m, 2 H) ppm. ^{13}C NMR: δ = 13.9, 14.0, 22.5, 27.5, 28.9, 29.0, 31.5, 54.3, 61.2, 128.5, 128.7, 133.4, 136.3, 170.0, 195.2 ppm.

Ethyl 2-(4-Methylbenzoyl)octanoate (23c): Following the standard procedure for **23a**, the reaction of 4-methylacetophenone (2.00 g, 14.92 mmol) with 60% NaH (1.70 g, 41.78 mol) and diethyl carbonate (3.50 g, 29.84 mol) in refluxing toluene (40 mL) for 30 min produced ethyl 3-oxo-3-(4-tolyl)propanoate (2.50 g, 12.34 mmol, 83%) as a light-yellow oil after purification by SiO_2 flash column chromatography.

The reaction of ethyl 3-oxo-3-(4-tolyl)propanoate (2.40 g, 11.65 mmol) with 60% NaH (0.50 g, 12.76 mol) and iodohexane (3.40 g, 16.24 mmol) in THF (10 mL) at 0 °C to room temperature, overnight, produced **23c** (1.80 g, 5.77 mmol, 50%) as a light-yellow oil after purification by SiO_2 flash column chromatography. ^{1}H NMR: δ = 0.86 (t, J = 7.2 Hz, 3 H), 1.18 (t, J = 7.2 Hz, 3 H), 1.22–1.38 (m, 8 H), 1.93–2.06 (m, 2 H), 2.42 (s, 3 H), 4.14 (dq, J_d = 1.2, J_q = 7.2 Hz, 2 H), 4.26 (t, J = 7.2 Hz, 1 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.89 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR: δ = 14.0, 14.0, 21.6, 22.5, 27.5, 29.0, 29.0, 31.5, 54.2, 61.2, 128.7, 129.3, 133.8, 144.3, 170.2, 194.9 ppm.

Ethyl 2-(4-Methoxybenzoyl)octanoate (23d): Following the standard procedure for **23a**, the reaction of 4-methoxyacetophenone (2.00 g, 13.33 mmol) with 60% NaH (1.50 g, 37.24 mol) and diethyl carbonate (3.20 g, 27.07 mol) in refluxing toluene (40 mL) for 30 min produced ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (2.48 g, 11.16 mmol, 84%) as a light-yellow oil after purification by SiO_2 flash column chromatography.

The reaction of ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (2.50 g, 11.26 mmol) with 60% NaH (0.50 g, 12.39 mol) and iodohexane (3.30 g, 15.76 mmol) in THF (10 mL) at 0 °C to room temperature, overnight, produced **23d** (1.98 g, 5.93 mmol, 53%) as a light-yellow oil after purification by SiO_2 flash column chromatography. ^{1}H NMR: δ = 0.86 (t, J = 7.2 Hz, 3 H), 1.18 (t, J = 7.2 Hz, 3 H), 1.22–1.37 (m, 8 H), 1.91–2.04 (m, 2 H), 3.88 (s, 3 H), 4.14 (dq, J_d = 1.6, J_q = 7.2 Hz, 2 H), 4.24 (t, J = 7.2 Hz, 1 H), 6.95 (d, J = 8.8 Hz, 2 H), 7.99 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 13.9, 13.9, 22.4, 27.4, 28.9, 29.0, 31.4, 53.9, 55.3, 61.0, 113.7, 129.1, 130.8, 163.6, 170.1, 193.5 ppm.

Ethyl 2-(4-Chlorobenzoyl)-2-hydroxyoctanoate (24a), Ethyl 2-Oxooctanoate (22) and 4-Chlorobenzoic Acid (25a): Following the standard procedure for **14c**, the reaction of ethyl 2-(4-chlorobenzoyl)octanoate (**23a**; 0.21 g, 0.68 mmol) and $Mn(OAc)_3 \cdot H_2O$ (0.57 g, 2.04 mmol) in 94% EtOH (10 mL) at 50 °C for 6 h, produced **24a** (0.024 g, 0.07 mmol, 11%), **22** (0.040 g, 0.22 mmol, 32%), and **25a** (0.035 g, 0.16 mmol, 24) after purification by SiO_2 flash column chromatography. Data for **24a**: ^{1}H NMR: δ = 0.85 (t, J = 6.8 Hz, 3 H), 1.19 (t, J = 7.2 Hz, 3 H), 1.17–1.34 (m, 8 H), 2.06–2.22 (m, 2 H), 4.18–4.30 (m, 2 H), 4.31 (s, 1 H), 4.22 (t, J = 7.2 Hz, 1 H), 7.42 (d, J = 8.8 Hz, 2 H), 7.95 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 14.0, 14.1, 21.0, 22.5, 29.2, 31.4, 35.9, 60.4, 82.5, 128.9, 130.8, 140.0, 171.1, 172.0, 194.8 ppm. IR (KBr): $\tilde{\nu}$ = 3478, 2928, 2858, 1730, 1693, 1587, 1468, 1400, 1223, 1150, 1092, 1013, 845 cm^{-1}. HRMS (CI^+): calcd. for $C_{17}H_{24}ClO_4$ 327.1363; found 327.1364.

Ethyl 2-Benzoyl-2-hydroxyoctanoate (24b), Ethyl 2-Oxooctanoate (22) and Benzoic Acid (25b): Following the standard procedure for **14c**, the reaction of ethyl 2-benzoyloctanoate (**23b**; 0.27 g, 0.98 mmol) and $Mn(OAc)_3 \cdot H_2O$ (0.82 g, 2.94 mmol) in 94% EtOH (10 mL) at 50 °C for 6 h, produced **24b** (0.033 g, 0.11 mmol, 12%), **22** (0.040 g, 0.22 mmol, 21%) and **25b** (0.015 g, 0.13 mmol, 13%) after purification by SiO_2 flash column chromatography. Data for **24b**: ^{1}H NMR: δ = 0.83 (t, J = 6.4 Hz, 3 H), 1.17 (t, J = 7.2 Hz, 3 H), 1.15–1.37 (m, 8 H), 2.10–2.26 (m, 2 H), 4.17–4.28 (m, 2 H), 4.44 (s, 1 H), 4.22 (t, J = 7.2 Hz, 1 H), 7.42–7.50 (m, 2 H), 7.55–7.62 (m, 1 H), 7.94–8.02 (m, 2 H) ppm. ^{13}C NMR: δ = 13.8, 14.0, 22.4, 22.4, 29.2, 31.4, 35.9, 62.4, 82.3, 128.6, 129.2, 130.2, 133.6, 171.9, 196.1 ppm. IR (KBr): $\tilde{\nu}$ = 3451, 2957, 1726, 1682, 1584, 1454, 1325, 1290, 1186, 1026, 934, 804 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{17}H_{25}O_4$ 293.1753; found 293.1752.

Ethyl 2-Hydroxy-2-(4-methylbenzoyl)octanoate (24c), Ethyl 2-Oxooctanoate (22) and 4-Methylbenzoic Acid (25c): Following the standard procedure for **14c**, the reaction of ethyl 2-(4-methylbenzoyl)octanoate (**23c**; 0.36 g, 1.24 mmol) and $Mn(OAc)_3 \cdot H_2O$ (1.04 g, 3.72 mmol) in 94% EtOH (10 mL) at 50 °C for 6 h, produced **24c** (0.117 g, 0.38 mmol, 31%), **22** (0.062 g, 0.33 mmol, 27%) and **25c** (0.020 g, 0.15 mmol, 12%) after purification by SiO_2 flash column chromatography. Data for **24c**: ^{1}H NMR: δ = 0.82 (t, J = 6.8 Hz, 3 H), 1.16 (t, J = 7.2 Hz, 3 H), 1.15–1.36 (m, 8 H), 2.10–2.25 (m, 2 H), 2.41 (s, 3 H), 4.21 (dq, J_d = 2.8, J_q = 7.2 Hz, 2 H), 4.55 (s, 1 H), 7.25 (d, J = 8.4 Hz, 2 H), 7.89 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 13.8, 14.0, 21.7, 22.4, 22.4, 29.2, 31.4, 36.0, 62.3, 82.1, 129.3, 129.4, 130.8, 144.7, 171.9, 195.7 ppm. IR (KBr): $\tilde{\nu}$ = 3478, 2928, 2858, 1738, 1678, 1607, 1462, 1368, 1225, 1184, 1059, 922, 837 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{18}H_{27}O_4$ 307.1909; found 307.1915.

Ethyl 2-Hydroxy-2-(4-methoxybenzoyl)octanoate (24d), Ethyl 2-Oxooctanoate (22) and 4-Methoxybenzoic Acid (25d): Following the standard procedure **14c**, the reaction of ethyl 2-(4-methoxybenzoyl)octanoate (0.25 g, 0.81 mmol) and $Mn(OAc)_3 \cdot H_2O$ (0.65 g, 2.43 mmol) in 94% EtOH (10 mL) at 50 °C for 16 h, produced **24d** (0.038 g, 0.11 mmol, 14%), **22** (0.010 g, 0.05 mmol, 6%) and **25d** (0.006 g, 0.04 mmol, 5%) after purification by SiO_2 flash column chromatography. Data for **24d**: ^{1}H NMR: δ = 0.83 (t, J = 6.8 Hz, 3 H), 1.17 (t, J = 7.2 Hz, 3 H), 1.13–1.37 (m, 8 H), 2.10–2.25 (m, 2 H), 3.88 (s, 3 H), 4.16–4.27 (m, 2 H), 4.61 (s, 1 H), 6.93 (d, J = 8.8 Hz, 2 H), 8.01 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 13.9, 13.9, 22.4, 22.5, 29.3, 31.5, 36.2, 55.5, 62.3, 82.0, 113.8, 126.0, 131.8, 163.9, 172.0, 194.4 ppm. IR (KBr): $\tilde{\nu}$ = 3426, 2926, 2857, 1732, 1672, 1599, 1462, 1368, 1224, 1173, 1026, 845 cm^{-1}. HRMS (CI$^+$): calcd. for $C_{18}H_{27}O_5$ 323.1858; found 323.1860.

Supporting Information (see footnote on the first page of this article): Experimental procedures for the intermediate compounds, analytical data, and ^{1}H and ^{13}C NMR spectra for all new compounds.

Acknowledgments

This research was supported by the Ministry of Education, Science and Technology (MEST), National Research Foundation of Korea (Basic Science Research Program, grant numbers 2009-0072552, 2012-000702 and Priority Research Centres Program, grant number 2012-0006693).

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Received: September 6, 2012
Published Online: October 29, 2012

