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Mn(III)-based oxidative tandem free-radical cyclizations of methylenecyclopropanes with substituted dicarbonyl compounds

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Abstract

Manganese(III) acetate-mediated tandem radical cyclization reactions of methylenecyclopropanes with methyl substituted dicarbonyl compounds in acetic acid give dihydronaphthalene derivatives in moderate yields under mild conditions.

Keywords: Radical cyclization; Methylenecyclopropanes; Manganese(III) acetate; Substituted dicarbonyl compounds; Dihydronaphthalene derivatives

1. Introduction

Methylenecyclopropanes (MCPs), highly strained but readily accessible molecules, have been proven to be useful reactivity in organic synthesis because the relief of ring strain provides a potent thermodynamic driving force [1]. In the past several years, more and more attention has been paid to the transition metal-catalyzed reaction of methylenecyclopropanes for construction of complex and interesting organic molecules [2].

Free radical reactions have become increasingly important in organic synthesis in the last decades [3]. Electrophilic radicals produced from the manganese(III) acetate oxidation of various carbonyl compounds undergo efficient addition to a carbon–carbon double bond [4]. These reactions can be performed intermolecularly and intramolecularly. The free radical reaction of methylenecyclopropanes has been well documented [5]. Recently, we and others found that oxidative free radical reactions of MCPs with β-dicarbonyl compounds produced 4,5-dihydrofuran derivatives effectively [6]. In that reaction, the intramolecular attack of the oxygen atom in the carbonyl group gives the oxonium cation and deprotonation to produce the [3+2] annulation products. These results indicate that deprotonation is essential to the annulation of MCPs with $Mn(OAc)_3$. Subsequently, we found that treatment of methyl substituted dicarbonyl compounds, having only one enolizable hydrogen, and MCPs with $Mn(OAc)_3$ provided a concise route to the synthesis of dihydronaphthalene skeleton. The formation of similar oxonium cation is impossible since there is not any hydrogen to deprotonate and is therefore susceptible to rearrangement affording homoallyl radical. In this paper, we wish to describe our results on the reaction between MCPs and methyl substituted dicarbonyl compounds via manganese(III) initiated oxidative free radical reactions (Scheme 1).

Initially, we tested the manganese(III)-mediated reaction of benzylidenecyclopropane **1a** with 2 equiv of $Mn(OAc)_3$ and 1 equiv of 3-methyl-2,4-pentanedione in acetic acid at 80 °C. We were pleased to find that the cyclization product **2a** was isolated in 42% yield after 12 h. Further screening demonstrated that 2.5 equiv of $Mn(OAc)_3$ and 1.2 equiv of 3-methyl-2,4-pentanedione were more suitable for the reaction and the yield of **2a** could be improved to 58% (entry 1, Table 1). With the identification of appropriate reaction conditions for Mn(III)-mediated transformation, we investigated the suitability of this

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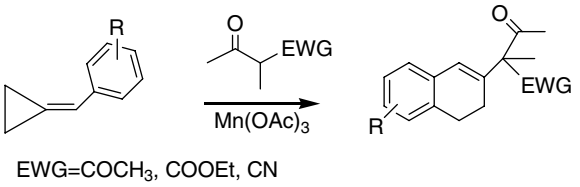
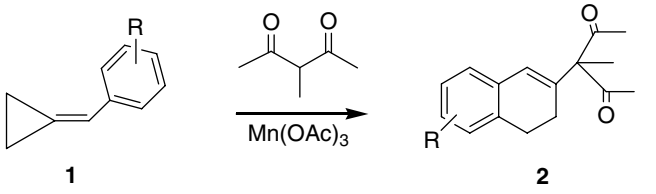


Scheme 1.

Table 1
$Mn(OAc)_3$-mediated reaction of 3-methyl-2,4-pentanedione with various MCPs[a]



Entry	R	Time (h)	Yield (%)[b]
1	H	12	**2a**, 58
2	*p*-Br	12	**2b**, 67
3	*p*-Cl	12	**2c**, 60
4	*p*-CH_3	12	**2d**, 55
5	*p*-OCH_3	12	**2e**, 59
6	*p*-F	12	**2f**, 52
7	*m*-Br	12	**2g**, 61

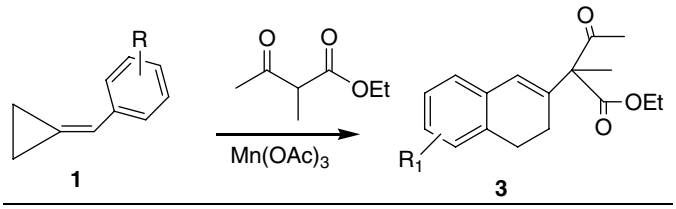
[a] All reactions were carried out using methylenecyclopropanes (1 mmol), 3-methyl-2,4-pentanedione (1.2 mmol) in HOAc (5 mL) at 80 °C for 12 h.
[b] Isolated yields.

approach to a variety of other MCPs. The results are summarized in Table 1. In all cases, the corresponding cyclization products **2a**–**g** were obtained in moderate yields (entries 1–7, Table 1). Electron-donating substituents and electron-withdrawing substituents on the benzene ring of MCPs **1** have little effect to this reaction. For diphenylmethylenecyclopropane no reaction occurred under identical conditions presumably due to the steric hindrance.

Moreover, we examined a similar ring cyclization reaction of MCPs **1** with ethyl 2-methylacetoacetate in the presence of $Mn(OAc)_3$ at 80 °C. However, the dimmer [7] was isolated in 65% yield. We found that when the reaction was carried out at room temperature, the oxidative cyclization product **3a** could be obtained in moderate yield in 24 h. Therefore, we conducted the oxidative cyclization reaction of MCPs **1** with ethyl 2-methylacetoacetate (1.2 equiv) in the presence of $Mn(OAc)_3$ (2.5 equiv) in HOAc at room temperature. The results are summarized in Table 2. As can be seen from Table 2, For MCPs **1a**–**f**, the corresponding cyclization products **3a**–**f** were obtained in moderate yields (entries 1–6, Table 2). For ethyl 2-cyanomethylacetoacetate bearing a cyano group, the cyclization proceeded smoothly under identical conditions (Scheme 2).

The present protocol can also be extended to 2-methyl-3-oxobutanenitrile affording dihydronaphthalene derivatives (Scheme 3). We found that the reactions proceeded smoothly to give the cyclization products in moderate yields in HOAc at 80 °C.

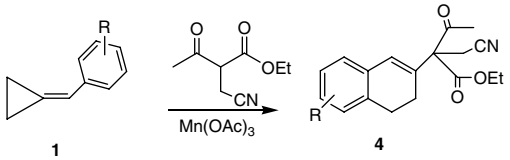
Table 2
$Mn(OAc)_3$-mediated reaction of ethyl 2-methylacetoacetate with various MCPs[a]



Entry	R	Time (h)	Yield (%)[b]
1	H	24	**3a**, 62
2	*p*-Br	24	**3b**, 56
3	*p*-Cl	24	**3c**, 53
4	*p*-CH_3	24	**3d**, 67
5	*o*-Br	24	**3e**, 50
6	*p*-F	24	**3f**, 47

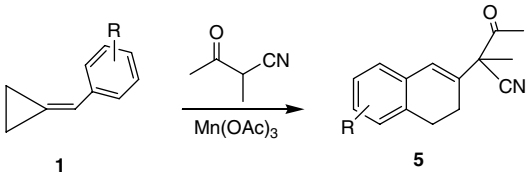
[a] All reactions were carried out using methylenecyclopropanes (1 mmol), ethyl 2-methylacetoacetate (1.2 mmol) in HOAc (5 mL) at room temperature for 24 h.
[b] Isolated yields.

To probe the generality of this reaction, the investigation was extended to a number of substrates and the results are summarized in Table 3. For electron-withdrawing substituents such as ketone, ester, nitrile, the manganese(III)-mediated reaction proceeded smoothly to give the cyclized



4a, R= *p*-Br Yield = 51%
4b, R= *p*-Cl 55%
4c, R= H 66%

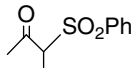
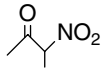
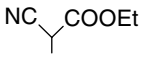
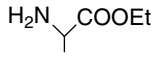
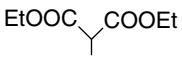
Scheme 2. $Mn(OAc)_3$-mediated reaction of ethyl 2-cyanomethylacetoacetate with MCPs.



5a, R= H Yield=61%
5b, R= *p*-Br 58%
5c, R= *p*-CH_3 53%

Scheme 3. $Mn(OAc)_3$-mediated reaction of 2-methyl-3-oxobutanenitrile with MCPs.

Table 3
$Mn(OAc)_3$-mediated reaction of benzylidenecyclopropane with various substrates[a]

Entry	Substrate	Reaction conditions temperature/solvent/time (h)	Yield (%)
1		80 °C/HOAc/12	Complex
2		80 °C/HOAc/12	Complex
3		80 °C/HOAc/24	NR
4		80 °C/HOAc/24	NR
5		80 °C/HOAc/12	**6**, 55

[a] All reactions were carried out using benzylidenecyclopropane (1 mmol), substrates (1.2 mmol) in HOAc (5 mL).

products in moderate yields (Tables 1 and 2, and Scheme 3). However, other substituents such as sulfone and nitro gave unidentified mixtures (entries 1–2, Table 3). For electron-donating groups, no reaction occurred under identical conditions (entry 4, Table 3). Using diethyl 2-methylmalonate as a substrate in this oxidative reaction, we found that the corresponding cyclization product **6** were obtained in 55% yield (entry 5, Table 3).

A plausible mechanism for the reaction of MCPs **1** with substituted dicarbonyl compounds in the presence of HOAc is shown in Scheme 4. Initiation occurs with the manganese(III) acetate oxidation of substituted dicarbonyl compounds to produce radical **7** [7,8]. The radical intermediate **7** undergoes intermolecular addition to the C=C bond of MCPs to give intermediate **8**. This radical intermediate **8** can be stabilized by nearby aromatic rings [9]. Due to the presence of highly strained three-membered ring, cyclopropyl ring-opened radical rearrangement affords intermediate **9** [10]. The radical carbon attacks the phenyl group intramolecularly to undergo cyclization reaction to produce dihydronaphthalene derivatives with the loss of a proton and oxidation in the presence of another molecule of $Mn(OAc)_3$ [11].

In summary, we have developed a novel radical addition to MCPs **1** mediated by $Mn(OAc)_3$ for the synthesis of dihydronaphthalene skeleton in moderate yields under mild conditions. This result with substituted dicarbonyl compounds as reactants is totally different from previous findings with unsubstituted dicarbonyl compounds as reactants. Further studies, including the reaction mechanism and the scope and limitations of this transformation, are in progress.

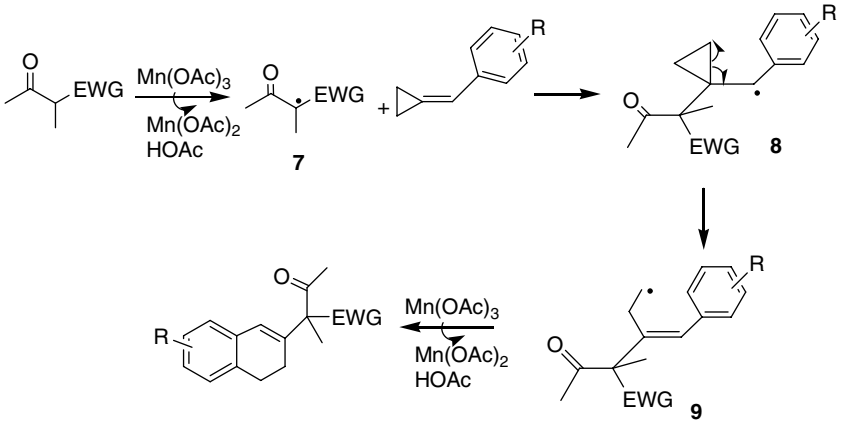
2. Experimental

All ^1H NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 (400 MHz) spectrometer with TMS as the internal standard. ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 (100 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in parts per million and J values are given in hertz. IR spectra were run on a Bruker vector 22 spectrometer. EIMS were determined with a HP5989B mass spectrometer. All the reactions in this paper were performed under nitrogen atmosphere.

2.1. General procedure for the synthesis of *2a–g*

A solution of **1** (1.0 mmol) with $Mn(OAc)_3 \cdot 2H_2O$ (2.5 mmol) and 3-methyl-2,4-pentanedione (1.2 mmol) in HOAc (5 mL) was stirred at 80 °C under N_2 atmosphere for 12 h. The mixture was then diluted with 40 mL of saturated NaCl and extracted three times with EtOAc. The organic phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via chromatography on silica gel with *n*-hexane/EtOAc (9:1) as the eluent to afford **2a–g**.

Compound **2a**: oil: IR (neat) ν_{max}/cm^{-1}: 2930, 1702, 1604. ^1H NMR (400 MHz, $CDCl_3$): 7.05–7.18 (m, 4H),



Scheme 4.

6.38 (s, 1H), 2.83 (t, $J = 9.6$ Hz, 2H), 2.24 (s, 6H), 2.21 (t, $J = 9.6$ Hz, 2H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 207.4, 137.9, 134.8, 133.5, 127.6, 127.2, 126.6, 126.5, 126.4, 71.3, 28.0, 27.4, 25.2, 17.9. MS (EI): *m*/*z*: 242 (M^+, 12.02).

Compound **2b**: oil: IR (neat) ν_{max}/cm^{-1}: 2920, 1715, 1591 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.28–7.30 (m, 2H), 6.91 (m, 1H) 6.33 (s, 1H), 2.80 (t, $J = 7.6$ Hz, 2H), 2.20 (s, 6H), 2.18 (t, $J = 7.6$ Hz, 2H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 207.0, 138.6, 136.9, 132.3, 130.2, 129.5, 127.8, 125.3, 120.9, 71.3, 27.8, 27.3, 25.0, 17.9. MS (EI): *m*/*z*: 320 (M^+, 8.67).

Compound **2c**: oil: IR (neat) ν_{max}/cm^{-1}: 2921, 2935, 1713, 1593. ^{1}H NMR (400 MHz, $CDCl_3$): 7.10-7.15 (m, 2H), 6.97 (m, 1H) 6.34 (s, 1H), 2.80 (t, $J = 7.6$ Hz, 2H), 2.22 (s, 6H), 2.18 (t, $J = 7.6$ Hz, 2H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 207.1, 138.4, 136.7, 132.7, 131.9, 127.5, 127.3, 126.5, 125.3, 71.2, 27.9, 27.3, 24.9, 17.9. MS (EI): *m*/*z*: 276 (M^+, 5.79).

Compound **2d**: oil: IR (neat) ν_{max}/cm^{-1}: 2925, 1701, 1611. ^{1}H NMR (400 MHz, $CDCl_3$): 6.94–6.99 (m, 3H), 6.36 (s, 1H), 2.79 (t, $J = 8$ Hz, 2H), 2.31 (s, 3H), 2.23 (s, 6H), 2.19 (t, $J = 8$ Hz, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 207.6, 137.5, 136.7, 134.8, 130.8, 128.1, 127.2, 126.4, 126.3, 71.2, 28.1, 27.4, 25.3, 21.3, 17.9. MS (EI): *m*/*z*: 256 (M^+, 12.32).

Compound **2e**: oil: IR (neat) ν_{max}/cm^{-1}: 2921, 1724, 1600. ^{1}H NMR (400 MHz, $CDCl_3$): 6.98 (m, 1H), 6.97–6.72 (m, 2H), 6.33 (s, 1H), 3.80 (s, 3H), 2.80 (t, $J = 8.4$ Hz, 2H), 2.23 (s, 6H), 2.18 (t, $J = 8.4$ Hz, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 207.6, 159.2, 136.6, 135.0, 127.6, 126.7, 125.9, 113.4, 111.4, 71.2, 55.3, 28.6, 27.4, 25.0, 17.9. MS (EI): *m*/*z*:272 (M^+, 16.90).

Compound **2f**: oil: IR (neat) ν_{max}/cm^{-1}: 2933, 1705, 1606. ^{1}H NMR (400 MHz, $CDCl_3$): 6.99–7.08 (m, 1H), 6.83–6.87 (m, 2H), 6.35 (s, 1H), 2.81 (t, $J = 8$ Hz, 2H), 2.23 (s, 6H), 2.19 (t, $J = 8$ Hz, 2H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 207.2, 207.1, 162.0 ($J_{C-F} = 251.9$ Hz), 137.6 ($J_{C-F} = 7$ Hz), 137.1, 129.7 ($J_{C-F} = 2.1$ Hz), 127.8 ($J_{C-F} = 8.3$ Hz), 125.3, 113.2 ($J_{C-F} = 22.3$ Hz), 114.5 ($J_{C-F} = 19.6$ Hz), 71.2, 28.2, 27.3, 24.8, 17.9. MS (EI): *m*/*z*: 260 (M^+, 13.23).

Compound **2g**: oil: IR (neat) ν_{max}/cm^{-1} 2919, 1701, 1599. ^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (m 1H), 7.00–7.04 (m, 2H), 6.32 (s, 1H), 2.65 (t, $J = 8$ Hz, 2H), 2.26 (s, 6H), 2.22 (t, $J = 8$ Hz, 2H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 206.9, 138.9, 135.5, 134.3, 131.6, 127.7, 125.8, 125.7, 123.7, 71.1, 27.6, 27.4, 24.9, 18.0. MS (EI): *m*/*z*: 320 (M^+, 9.76).

2.2. General procedure for the synthesis of *3a–f*

A solution of **1** (1.0 mmol) with $Mn(OAc)_3 \cdot 2H_2O$ (2.5 mmol) and ethyl 2-methylacetoacetate (1.2 mmol) in HOAc (5 mL) was stirred at room temperature under N_2 atmosphere for 24 h. The mixture was then diluted with 40 mL of saturated NaCl and extracted three times with EtOAc. The organic phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via chromatography on silica gel with *n*-hexane/EtOAc (5:1) as the eluent to afford **3a–f**.

Compound **3a**: oil: IR (neat) ν_{max}/cm^{-1}: 2984, 2938, 1713, 1618. ^{1}H NMR (400 MHz, $CDCl_3$): 7.12–7.16 (m, 3H), 7.03–7.05 (m, 1H), 6.39 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.82 (t, $J = 8$ Hz, 2H), 2.29 (t, $J = 8$ Hz, 2H), 2.26 (s, 3H), 1.61 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 205.1, 171.5,138.1, 134.9, 133.6, 127.4, 127.1, 126.5, 125.4, 65.8, 65.4, 28.2, 26.9, 25.7, 18.9,13.9. MS (EI): *m*/*z*: 272 (M^+,10.07).

Compound **3b**: oil: IR (neat) ν_{max}/cm^{-1}: 2982, 2940, 1713, 1637. ^{1}H NMR (400 MHz, $CDCl_3$): 7.26–7.29 (m, 2H), 6.90 (m, 1H), 6.35 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.80 (t, $J = 8$ Hz, 2H), 2.27 (t, $J = 8$ Hz, 2H), 2.26 (s, 3H), 1.61 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 204.7, 171.3, 138.7, 137.0, 132.5, 130.0, 129.4, 127.8, 124.5, 120.7, 65.7, 61.5, 27.9, 26.9, 25.4, 18.9,13.9. MS (EI): *m*/*z*: 350 (M^+, 16.08).

Compound **3c**: oil: IR (neat) ν_{max}/cm^{-1}: 2984, 2940, 1713, 1635. ^{1}H NMR (400 MHz, $CDCl_3$): 7.10–7.13 (m, 2H), 6.96 (m,1H), 6.36 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.80 (t, $J = 8$ Hz, 2H), 2.27 (t, $J = 8$ Hz, 2H), 2.26 (s, 3H), 1.61 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 204.7, 171.3, 138.5, 136.7, 132.5, 132.1, 127.5, 127.2, 126.5, 124.4, 65.7, 61.5, 28.0, 26.9, 25.4, 18.9,13.9. MS (EI): *m*/*z*: 307 ($[M+1]^+$, 100).

Compound **3d**: oil: IR (neat) ν_{max}/cm^{-1}: 2983, 2921, 1713, 1611. ^{1}H NMR (400 MHz, $CDCl_3$): 6.94–6.96 (m, 3H), 6.37 (s, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.78 (t, $J = 7.6$ Hz, 2H), 2.30 (s, 3H), 2.27 (t, $J = 7.6$ Hz, 2H), 2.26 (s, 3H), 1.59 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 205.3, 171.6, 137.2, 136.9, 134.9, 130.9, 127.9, 127.1, 126.4, 125.3, 65.7, 61.4, 28.3, 26.9, 25.8, 21.2,19.0, 14.0. MS (EI): *m*/*z*: 286 (M^+,19.57).

Compound **3e**: oil: IR (neat) ν_{max}/cm^{-1}: 2926, 1716, 1633. ^{1}H NMR (400 MHz, $CDCl_3$): 6.96–7.06 (m, 3H), 6.79 (s, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 2.81 (t, $J = 8$ Hz, 2H), 2.28 (s, 3H), 2.26 (t, $J = 8$ Hz, 2H), 2.26 (s, 3H), 1.64 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 204.7, 171.3, 140.6, 137.6, 132.6, 130.8, 128.2, 127.5, 126.3, 124.2, 66.0, 61.6, 29.3, 26.9, 25.4, 18.9, 14.0. MS (EI): *m*/*z*: 350 (M^+, 26.12).

Compound **3f**: oil: IR (neat) ν_{max}/cm^{-1}: 2931, 1714, 1607. ^{1}H NMR (400 MHz, $CDCl_3$): 6.82–6.86 (m, 2H), 6.98–7.02 (m, 1H), 6.36 (s, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.27 (t, $J = 7.6$ Hz, 2H), 2.26 (s, 3H), 1.61 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 204.9, 171.4, 163.1 ($J_{C-F} = 224.7$ Hz), 137.4 ($J_{C-F} = 8.1$ Hz), 137.2 ($J_{C-F} = 2.9$ Hz), 129.8, 127.9 ($J_{C-F} = 8.2$ Hz), 124.4, 114.4 ($J_{C-F} = 22.5$ Hz), 113.1 ($J_{C-F} = 21$ Hz), 65.7, 61.5, 29.6, 26.9, 25.3, 18.9, 13.9. MS (EI): *m*/*z*: 290 (M^+,10.49).

Compound **4a**: oil: IR (neat) ν_{max}/cm^{-1}: 2243, 1715, 1630. ^{1}H NMR (400 MHz, $CDCl_3$): 7.28–7.33 (m, 2H), 6.93–6.95 (m, 1H), 6.36 (s, 1H), 4.36 (q, $J = 7.2$ Hz, 2H),

2.98 (q, $J = 16.8$ Hz, 2H), 2.86 (t, $J = 8$ Hz, 2H), 2.39 (s, 3H), 2.16–2.33 (m, 2H), 1.37 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 200.9, 167.7, 136.5, 134.6, 131.5, 130.2, 129.7, 128.3, 127.5, 121.7, 117.0, 67.9, 62.8, 27.6, 27.4, 24.9, 22.5, 13.8. MS (EI): *m*/*z*: 375 (M^+, 6.88).

Compound **4b**: oil: IR (neat) ν_{max}/cm^{-1}: 2243, 1713, 1633. ^{1}H NMR (400 MHz, $CDCl_3$): 7.13–7.17 (m, 2H), 6.98–7.00 (m, 1H), 6.37 (s, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 2.98 (q, $J = 16.8$ Hz, 2H), 2.84 (t, $J = 8$ Hz, 2H), 2.39 (s, 3H), 2.17–2.36 (m, 2H), 1.37 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 201.0, 167.8, 136.3, 134.6, 133.6, 131.1, 128.1, 127.5, 127.4, 126.8, 117.2, 67.9, 62.9, 27.9, 27.5, 25.0, 22.6, 13.9. MS (EI): *m*/*z*: 331 (M^+, 5.46).

Compound **4c**: oil: IR (neat) ν_{max}/cm^{-1}: 2240, 1718, 1616. ^{1}H NMR (400 MHz, $CDCl_3$): 7.13–7.17 (m, 2H), 7.06–7.20 (m, 4H), 6.40 (s, 1H), 4.37 (q, $J = 7.2$ Hz, 2H), 2.98 (q, $J = 16.8$ Hz, 2H), 2.88 (t, $J = 8$ Hz, 2H), 2.40 (s, 3H), 2.17–2.37 (m, 2H), 1.37 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 201.3, 167.9, 134.4, 134.0, 132.6, 128.6, 128.2, 127.2, 127.0, 126.8, 117.2, 67.9, 62.7, 27.9, 27.5, 25.3, 22.6, 13.9. MS (EI): *m*/*z*: 297 (M^+, 1.67).

2.3. General procedure for the synthesis of **5a–c**

A solution of **1** (1.0 mmol) with $Mn(OAc)_3 \cdot 2H_2O$ (2.5 mmol) and 2-methyl-3-oxobutanenitrile (1.2 mmol) in HOAc (5 mL) was stirred at 80 °C under N_2 atmosphere for 12 h. The mixture was then diluted with 40 mL of saturated NaCl and extracted three times with EtOAc. The organic phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via chromatography on silica gel with *n*-hexane/EtOAc as the eluent to afford **5a–c**.

Compound **5a**: oil: IR (neat) ν_{max}/cm^{-1}: 2250, 1716, 1624. ^{1}H NMR (400 MHz, $CDCl_3$): 7.06–7.20 (m, 4H), 6.39 (s, 1H), 2.83 (t, $J = 8$ Hz, 2H), 2.30 (t, $J = 8$ Hz, 2H), 2.25 (s, 3H), 1.61 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): 201.9, 138.2, 134.7, 133.8, 127.5, 127.1, 126.6, 126.4, 125.4, 117.3, 61.8, 28.1, 27.0, 25.7, 19.4. MS (EI): *m*/*z*: 225 (M^+, 17.15).

Compound **5b**: oil: IR (neat) ν_{max}/cm^{-1}: 2250, 1714, 1632. ^{1}H NMR (400 MHz, $CDCl_3$): 7.28–7.30 (m, 2H), 6.92 (m, 1H), 6.36 (s, 1H), 2.82 (t, $J = 7.6$ Hz, 2H), 2.28 (t, $J = 7.6$ Hz, 2H), 2.27 (s, 3H), 1.61 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): 201.7, 138.8, 137.0, 132.6, 130.0, 129.6, 127.9, 124.8, 120.8, 117.2. 61.8, 27.8, 27.1, 25.5, 19.4. MS (EI): *m*/*z*: 303 (M^+, 10.46).

Compound **5c**: oil: IR (neat) ν_{max}/cm^{-1}: 2249, 1713, 1616. ^{1}H NMR (400 MHz, $CDCl_3$): 6.95–7.00 (m, 3H), 6.39 (s, 1H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.32 (s, 3H), 2.29 (t, $J = 7.6$ Hz, 2H), 2.26 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.0, 137.3, 136.9, 135.0, 130.8, 127.8, 127.2, 126.4, 125.5,117.3, 62.3, 28.2, 27.0, 25.9, 21.3,19.5. MS (EI): *m*/*z*: 239 (M^+, 13.27).

Compound **6**: oil: IR (neat) ν_{max}/cm^{-1}: 1712, 1623.^{1}H NMR (400 MHz, $CDCl_3$): 7.13–7.17 (m, 3H), 7.04–7.06 (m, 1H), 6.42 (s, 1H), 4.26 (q, $J = 7.2$ Hz, 4H), 2.88 (t, $J = 8$ Hz, 2H), 2.45 (t, $J = 8$ Hz, 2H), 1.59 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.5,138.7, 137.8, 134.2, 127.4, 127.1, 126.5, 126.3, 122.3, 61.8, 60.4, 26.9, 25.7, 19.7,13.9. MS (EI): *m*/*z*: 302 (M^+, 16.65).

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