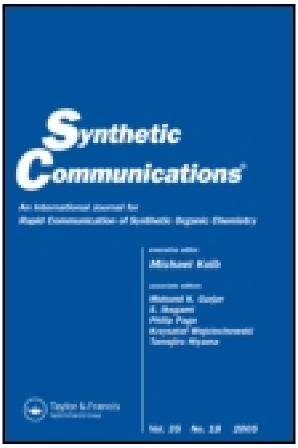

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Facile Strategy for the Synthesis of Furans Utilizing Silver(I)-Promoted Addition/Oxidative Cyclization of 1,3-Dicarbonyl Compounds and Alkynoates

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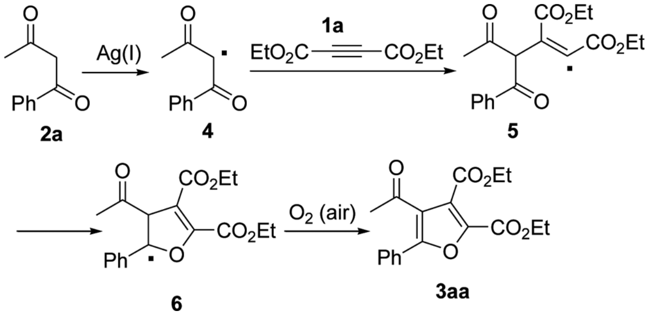
FACILE STRATEGY FOR THE SYNTHESIS OF FURANS UTILIZING SILVER(I)-PROMOTED ADDITION/OXIDATIVE CYCLIZATION OF 1,3-DICARBONYL COMPOUNDS AND ALKYNOATES

Wei-Bing Liu, Cui Chen, and Qing Zhang
School of Chemistry and Life Science, Guangdong University of Petrochemical Technology, Maoming, China

GRAPHICAL ABSTRACT



Abstract *The addition/oxidative cyclization of alkynoates with 1,3-dicarbonyl compounds in the presence of Ag(I) leads to polysubstituted furans. The reaction corresponds to the construction of a furan fragment, which also provides a new way to form the C-O bond.*

Keywords Addition/oxidative cyclization; furan; silver

INTRODUCTION

Over the past few decades, transition metal–catalyzed reactions have emerged as powerful and general methods for the synthesis of organic compounds.[1] Especially late transition metals, the so-called coinage metals, have been widely used for various organic transformations in organic synthesis.[2] In the coinage metal series, silver and gold exhibit special properties because of the availability of the orbitals and relativistic contraction of their electron cloud. The applications of silver salts, mainly Ag (I), in organic synthesis today can be classified into two well-defined

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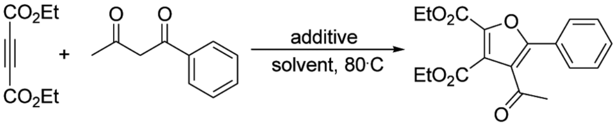
areas: silver-promoted oxidation processes[3] and homogeneous silver-mediated catalyzed reactions.[4] In this article, we disclose an expeditious method in which the Ag(I) is used not only as the catalyst but also as the oxidant to construct furan derivatives.[5] As we all know, furans are some of the most important heteroaromatic compounds with widespread occurrence in nature[6] and are frequently found in many natural products arising from plants and marine organisms.[7] In addition, many of the naturally occurring furans have shown interesting biological activities, such as antiallergic and antiasthamatic activities,[8] as well as cytotoxic and antitumor properties,[9] antidiabetic activity,[10] and several other potentially useful activities.[11]

RESULTS AND DISCUSSION

Our preliminary investigations were focused on the systematic evaluation of different silver catalysts for the desired addition/oxidative cyclization of diethyl but-2-ynedioate (**1a**) and 1-phenylbutane-1,3-dione (**2a**) (Table 1). As shown in

Table 1. Optimization of reaction conditions[a]



1a **2a** **3aa**

Entry	Additive	Solvent	Time (h)	Yield (%)[b]
1	AgOAc	DCE	5	45
2	Ag_2CO_3	DCE	5	23
3	$AgBF_4$	DCE	5	Np
4	AgOTf	DCE	5	Np
5	Ag_2O	DCE	5	Trace
6	$AgNO_3$	DCE	5	Np
7	$AgClO_4$	DCE	5	Trace
8	AgOAc	CH_3CN	5	52
9	AgOAc	DMSO	5	57
10	AgOAc	DMA	5	71
11	AgOAc	Dioxane	5	48
12	AgOAc	Benzene	5	37
13	AgOAc	DMA	5	Trace
14	AgOAc	DMA	5	78
15[c]	CH_3CO_2Na	DMA	2	70
16[d]	AgOAc	DMA	2	79
17[d]	AgOAc	DMA	3	84
18[d]	AgOAc	DMA	4	84

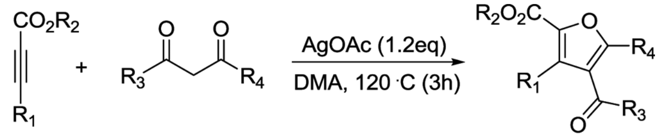
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), additive (1.2 equiv.), in 2 mL solvent at 80 °C for 5 h.

[b] Isolated yields.

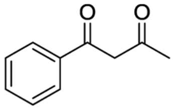
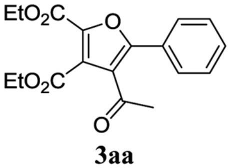
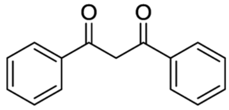
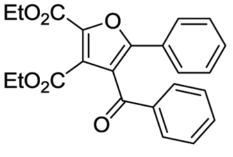
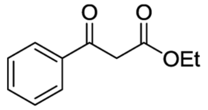
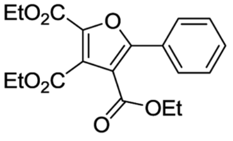
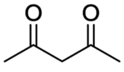
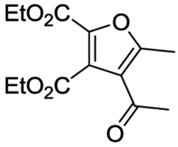
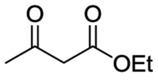
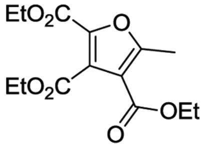
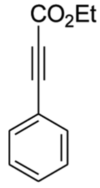
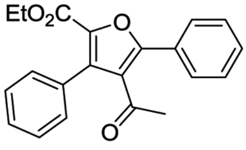
[c] 100 °C.

[d] 120 °C.

Table 2. Synthesis of polyfunctional furans from alkynoates and 1,3-dicarbonyl compounds[a]

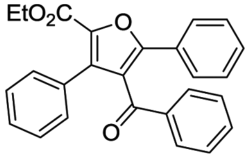
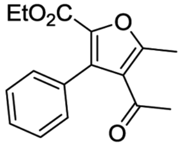
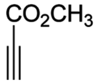
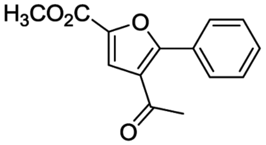
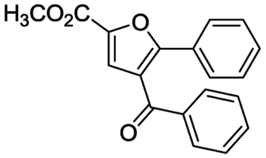
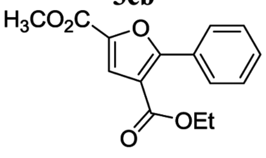
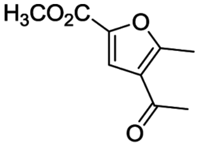
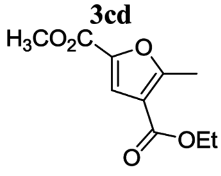


1 **2** **3**

Entry	1	2	Product	Yield[b] (%)
1	 **1a**	 **2a**	 **3aa**	81
2	**1a**	 **2b**	 **3ab**	77
3	**1a**	 **2c**	 **3ac**	80
4	**1a**	 **2d**	 **3ad**	82
5	**1a**	 **1e**	 **3ae**	88
6	 **1b**	**2a**	 **3ba**	50

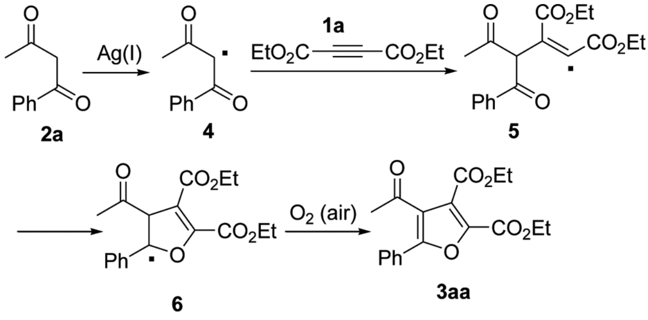
(*Continued*)

Table 2. Continued

Entry	**1**	**2**	Product	Yield[b] (%)
7	**1b**	**2b**	 **3bb**	65
8	**1b**	**2d**	 **3bd**	53
9	 **1c**	**2a**	 **3ca**	78
10	**1c**	**2b**	 **3cb**	71
11	**1c**	**2c**	 **3cc**	73
12	**1c**	**2d**	 **3cd**	76
13	**1c**	**2e**	 **3ce**	75

[a] All the reactions are carried out using 1.0 mmol of **1**, 1.0 mmol of **2**, 1.2 equivalence of AgOAc in DMA (2.0 mL) at 120 °C for 3 h.

[b] Isolated yield.



Scheme 1. Plausible reaction mechanism.

Table 1, the AgOAc showed the greatest activity and afforded the best result in 1,2-dichloroethane (DCE) (entries 1–7). By changing the reaction solvents (entries 8–12), we found that the reaction was not sensitive to the solvent medium and that N,N-dimethylacetamide (DMA) led to the best result (entry 10). We next investigated the dosage of AgOAc (entries 13 and 14), the results showed that 1.2 equivalents of AgOAc was the preferable dosage. Finally, it was interesting to find that when increasing the reaction temperature of this transformation, a significant increase of the yield was observed (entries 14–16) and the practical reaction temperature was 120 °C (entry 16). The optimum reaction time was 3 h (entry 17).

Under the optimized conditions, we explored the scope of the reaction, and the results are summarized in Table 2. A wide variety of 1,3-dicarbonyl compounds could successfully react with alkynoates to afford the corresponding furan derivatives (Table 2). However, the electronic property of the substituents on the alkynes has an obvious influence on the reaction. This reaction proceeded smoothly and afforded the desired product in good to excellent yields for those alkynes substituted with two electron-withdrawing groups. For example, the diethyl but-2-ynedioate (**1a**) reacted with **2a–2e** and led to **3aa–3ae** in good isolated yield, whereas ethyl 3-phenylpropiolate led to inferior result or even traces of the desired product. Methyl propiolate (**1c**) was a desirable partner of **1a**, and when it was employed in the reaction with 1,3-dicarbonyl compounds, it would produce the products in reasonable isolated yield.

A plausible mechanism for the described addition/oxidative cyclization, exemplified by the formation of diethyl 4-acetyl-5-phenylfuran-2, 3-dicarboxylate **3aa**, can be rationalized as shown in Scheme 1. The 1,3-dicarbonyl compound **2a** is first oxidized by silver(I)[12] metal to generate the α -oxoalkyl radical **4**, which then attacks the C-C triple bond of diethyl but-2-ynedioate to give the radical **5**. The nucleophilic adduct **5** now undergoes fast nucleophilic attack by carbonyl oxygen to a benzylic radical **6**, which oxidizes to the desired furan product **3aa** by oxygen of air.

CONCLUSION

In conclusion, a facile and expeditious addition/oxidative cyclization method to construct a furan framework was developed from alkynoates and

1,3-diketones/β-ketoesters. The silver(I) plays a dual role in the reaction, in which Ag (I) is used not only as the catalyst but also as the oxidant. The scope, mechanism, and synthetic applications of this protocol are currently under investigation.

EXPERIMENTAL

All the reactions were carried out at 120 °C in a Schlenk tube equipped with magnetic stir bar. Solvents and all reagents were used as received. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz, and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz. GC–MS was obtained using electron ionization (EI). Infrared (IR) spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. Thin-layer chromatography (TLC) was performed using commercially prepared 100- to 400-mesh silica-gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

General Procedure for the Synthesis of Diethyl 4-Acetyl-5-phenylfuran-2,3-dicarboxylate 3aa

To a stirring mixture of diethyl but-2-ynedioate (**1a**, 170 mg, 1.0 mmol) and 1-phenylbutane-1,3-dione (**2a**, 162 mg, 1.0 mmol), 2 mL DMA and AgOAc (200.4 mg, 1.2 mmol) were added successively. The mixture was stirred at 120 °C for 3 h in a Schlenk tube. After cooling, the solution was directly subjected to isolation by PTLC (GF254) and eluted with a 10:2 petroleum ether–diethyl ether mixture to furnish the desired product **3aa** (300.1 mg, 91%) as a pale yellow viscous oil.

Diethyl 4-Acetyl-5-phenylfuran-2,3-dicarboxylate (3aa)[13]

Pale yellow viscous oil: IR vmax (KBr): 3065, 2996, 2938, 1724, 1659, 1597, 1410, 1252, 1171, 1060, 942, 910, 864, 772, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.41 (m, 2H), 4.36 (q, 2H, $J = 7.2$ Hz), 3.94 (q, 2H, $J = 7.2$ Hz), 2.41 (s, 3H), 1.34 (t, 3H, $J = 7.2$ Hz), 1.05 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 262.2, 159.3, 157.4, 140.4, 137.8, 133.2, 128.8, 128.5, 125.5, 122.1, 67.8, 61.7, 14.0, 13.9, 13.5; GC–MS *m*/*z* (% rel. inten.): 330.07 (M+, 69.67), 240.92 (100).

Diethyl 4-Benzoyl-5-phenylfuran-2,3-dicarboxylate (3ab)[13]

Pale yellow viscous oil: IR vmax (KBr): 3053, 2964, 2935, 1725, 1667, 1596, 1234, 1078, 1038, 903, 860, 812, 771, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.79 (m, 2H), 7.61–7.59 (m, 2H), 7.50–7.48 (m, 1H), 7.38–7.24 (m, 5H), 4.41 (q, 2H, $J = 7.2$ Hz), 4.06 (q, 2H, $J = 7.2$ Hz), 1.38 (t, 3H, $J = 7.2$ Hz), 1.07 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 161.6, 157.5, 155.2, 141,4, 136.9, 133.7, 130.2, 129.0, 128.8, 128.6, 127.8, 127.4, 126.2, 121.5, 61.8, 14.1, 13.6; GC–MS m/z (% rel. inten.): 392.08 (M+, 100).

Triethyl 5-Phenylfuran-2,3,4-tricarboxlate (3ac)

Yellow viscous oil: IR vmax (KBr): 3066, 2964, 1937, 1723, 1606, 1548, 1388, 1371, 1283, 1164, 1071, 938, 847, 771, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.90 (m, 2H), 7.46–7.43 (m, 3H), 4.43–4.34 (m, 4H), 4.26 (q, 2H, $J = 7.2$ Hz), 1.41–1.33 (m, 3H), 1.25 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 161.4, 159.5, 157.3, 139.7, 130.8, 129.2, 128.2, 128.0, 127.7, 127.4, 62.2, 61.8, 61.4, 14.1, 14.0, 13.9; GC–MS m/z (% rel inten.): 359.95 (M+, 100). Anal. calcd. for $C_{19}H_{20}O_7$: C, 63.33; H, 5.59. Found: C, 63.58; H, 5.40.

Diethyl 4-Acetyl-5-methylfuran-2,3-dicarboxylate (3ad)[13,14]

Pale yellow viscous oil: IR vmax (KBr): 2965, 2936, 1709, 1675, 1547, 1411, 1295, 1207, 1156, 1055, 1020, 958, 896, 860, 774, 682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.40 (q, 2H, $J = 7.2$ Hz), 4.33 (q, 2H, $J = 7.2$ Hz), 2.64 (s, 3H), 2.38 (s, 3H), 1.37 (t, 3H, $J = 7.2$ Hz), 1.33 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 163.8, 160.9, 157.3, 139.2, 125.5, 122.3, 62.3, 61.7, 29.4, 15.0, 14.1, 13.9; GC–MS m/z (% rel. inten.): 368.04 (M+, 18.14), 221.96 (100).

Triethyl 5-Methylfuran-2,3,4-tricarboxylate (3ae)[13]

Yellow viscous oil: IR vmax (KBr): 2985, 2938, 1722, 1609, 1566, 1373, 1251, 1175, 1058, 1022, 982, 908, 860, 786, 705, 684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39–4.23 (m, 6H), 2.62 (s, 3H), 1.37–1.27 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 162.2, 161.6, 157.2, 139.0, 126.1, 114.0, 62.0, 61.6, 60.9, 14.1, 14.0; GC–MS m/z (% rel. inten.): 297.98 (M+, 21.74), 251.84 (100).

Ethyl 4-Benzoyl-3,5-diphenylfuran-2-carboxylate (3bb)

Yellow solid, mp: 109–110 °C; IR vmax (KBr): 2961, 2896, 1815, 1710, 1659, 1401, 1270, 1236, 1173, 1029, 973, 900, 863, 765, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.72 (m, 1H), 7.66–7.65 (m, 1H), 7.30–7.28 (m, 1H), 7.24–7.18 (m, 7H), 4.27 (q, 2H, $J = 7.2$ Hz), 1.23 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 158.7, 154.1, 138.6, 136.9, 135.3, 133.6, 130.2, 129.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.0, 123.4, 61.0, 14.0; GC–MS m/z (% rel. inten.): 396.14 (M+, 73.45), 104.98 (100). Anal. calcd. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.60; H, 4.89.

Ethyl 4-Acetyl-5-methyl-3-phenylfuran-2-carboxylate (3bd)

Yellow viscous oil: IR vmax (KBr): 3061, 2983, 2931, 1725, 1674, 1366, 1355, 1292, 1228, 1095, 1040, 976, 918, 867, 804, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.67 (m, 2H), 7.40–7.35 (m, 3H), 4.32 (q, 2H, $J = 7.2$ Hz), 2.54 (s, 3H), 2.42 (s, 3H), 1.29 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 164.8, 155.6, 152.0, 129.5, 128.9, 128.4, 126.9, 123.8, 113.9, 61.6, 30.1, 14.0, 13.9; GC–MS m/z (% rel inten.): 271.95 (M+, 35.64), 225.68 (100). Anal. calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.69; H, 5.98.

Methyl 4-Acetyl-5-phenylfuran-2-carboxylate (3ca)

Yellow solid; mp: 68–70 °C; IR vmax (KBr): 1710, 1682, 1585, 1265, 1173, 1080, 996, 884, 840, 798, 710, 683 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95–7.93 (m, 2H), 7.52 (s, 1H), 7.45–7.44 (m, 3H), 3.91 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.0, 163.0, 158.7, 141.8, 138.1, 132.6, 128.7, 128.3, 122.0, 119.4, 52.0, 14.4; GC–MS *m/z* (% rel inten.): 244.03 (M+, 62.76), 228.86 (100). Anal. calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 70.10; H, 4.88.

Methyl 4-Benzoyl-5-phenylfuran-2-carboxylate (3cb)

Yellow solid; mp: 87–89 °C; IR vmax (KBr): 1722, 1650, 1441, 1385, 1023, 921, 885, 770, 688 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82–7.76 (m, 4H), 7.55–7.53 (m, 1H), 7.41–7.32 (m, 6H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.6, 158.8, 158.5, 142.3, 137.3, 133.3, 130.2, 129.7, 128.5, 128.0, 122.2, 121.0, 52.2; GC–MS *m/z* (% rel. inten.): 306.07 (M+, 100). Anal. calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.50; H, 4.66.

4-Ethyl 2-Methyl 5-Phenylfuran-2,4-dicarboxylate (3cc)

Colorless solid; mp: 72–73 °C; IR vmax (KBr): 2983, 2930, 1732, 1660, 1428, 1327, 1191, 1084, 997, 865, 765, 691 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.04–8.02 (m, 2H), 7.56 (s, 1H), 7.44–7.42 (m, 3H), 4.29 (q, 2H, $J = 7.2$ Hz), 3.90 (s, 3H), 1.32 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.2, 160.1, 158.7, 142.4, 130.4, 128.9, 128.5, 120.6, 115.5, 60.9, 52.1, 14.1; GC–MS *m/z* (% rel. inten.): 273.90 (M+, 100). Anal. calcd. for $C_{15}H_{14}O_4$: C, 65.69; H, 5.15. Found: C, 65.60; H, 5.31.

Methyl 4-Acetyl-5-methylfuran-2-carboxylate (3cd)

Yellow solid; mp: 86–88 °C; IR vmax (KBr): 1726, 1647, 1540, 1362, 1172, 1121, 1020, 995, 764, 706 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 (s, 1H), 3.88 (s, 3H), 2.64 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 193.2, 162.1, 158.6, 142.0, 122.8, 118.2, 52.1, 29.0, 14.7; GC–MS *m/z* (% rel inten.): 181.97 (M+, 38.35), 166.95 (100). Anal. calcd. for $C_9H_{10}O_4$: C, 59.34; H, 5.53. Found: C, 59.55; H, 5.62.

4-Ethyl 2-Methyl 5-Methylfuran-2,4-dicarboxylate (3ce)

Pale yellow viscous oil; IR vmax (KBr): 2987, 2958, 1727, 1637, 1442, 1095, 1032, 963, 896, 805, 714 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (s, 1H), 4.29 (q, 2H, $J = 7.2$ Hz), 3.80 (s, 3H), 2.48 (s, 3H), 1.32 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 163.1, 162.7, 159.1, 145.3, 118.8, 113.5, 60.7, 51.8, 14.1, 13.4; GC–MS *m/z* (% rel. inten.): 212.02 (M+, 17.62), 165.99 (100). Anal. calcd. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.61; H, 5.77.

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