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Cu(I)-catalyzed reaction of diazo compounds with terminal alkynes: a direct synthesis of trisubstituted furans

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ABSTRACT

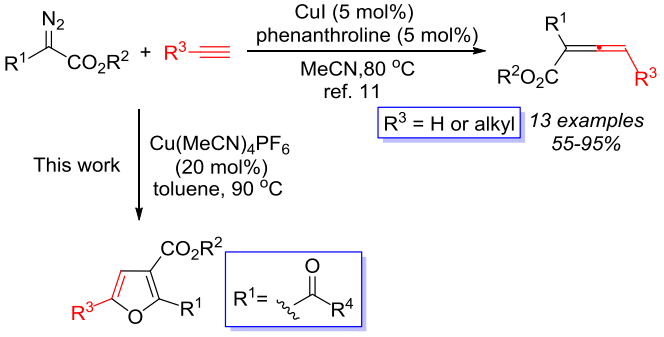
A method for the synthesis of tri-substituted furans has been developed based on Cu(I)-catalyzed reaction of terminal alkynes with β-keto α-diazoesters. This method for the synthesis of 2,3,5-trisubstituted furans is operationally simple and applicable to wide substrate scope. Moreover, this synthesis employs cheap $Cu(MeCN)_4PF_6$ as the catalyst and no additional ligand is needed. Similar reaction has also been applied to ethyl (*E*)-2-diazo-3-(methoxyimino)butanoate for the synthesis of 2,3,5-trisubstituted *N*-methoxypyrroles with limited success.

1. Introduction

Poly-substituted furans constitute an important class of five-membered *O*-heterocycles and broadly found in many natural products, pharmaceuticals and agrochemicals.[1] Furans and their derivatives are also very useful building blocks for organic synthesis.[2] For these reasons, over the past few decades, many chemists have devoted their efforts to the development of novel and efficient methods for the synthesis of mono-, di-, tri-, and poly-substituted furans.[3] Of various methods established over the years, the transition metal-catalyzed cycloaddition of α-diazocarbonyl compounds with alkynes is considered as one of the most versatile and direct approaches for the construction of poly-substituted furans.[4] Davies and Romines in 1988 reported the $Rh_2(OAc)_4$-catalyzed reaction of β-keto α-diazoesters, which gives 2,3,5-trisubstituted furans.[5] Similar Rh(II)-catalyzed reactions have later reported by several other groups.[6]

In addition to the traditional Rh(II) catalysts, other transition metal catalysts have also been explored for this type of transformations. Very recently, Zhang and co-workers reported the use of Co(II)–porphyrin complexes as catalysts for furan synthesis from alkynes and α-diazocarbonyl compounds.[7] Lee and co-workers, on the other hand, employed Ru(II) complex as catalyst in furan synthesis.[8]

Through the literature survey it has been noticed that Cu(I) complexes, as another popular catalysts in carbene transfer reactions,[4,9] have much less explored for the furan synthesis. Recently, Coleman and co-workers have reported a Cu(I)-catalyzed reaction of α-diazoesters with internal alkynes to give tetra-substituted furans.[10] We have recently studied the Cu(I)-catalyzed reaction of terminal alkynes with donor–acceptor diazoacetates. The reaction gives tri-substituted allenes as the major products, instead of furans (Scheme 1).[11] Similar results have also been observed by Fox and co-



Scheme 1. Cu(I)-catalyzed reaction of α-diazoesters and terminal alkynes.

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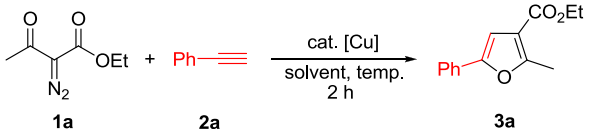
workers.[12] On the other hand, Fu and Saurez in 2004 reported the CuI-catalyzed cross-coupling of terminal alkynes with diazoester, yielding 3-alkynoate derivatives and in some cases 2,3-allenoates as minor products.[13] These results indicate that the reaction pathway for Cu(I)-catalyzed reaction of alkyne with diazo compounds is largely affected by the catalyst system and the structure of the diazo substrates.

Although various methodologies have been reported for furan synthesis based on transition metal-catalyzed reaction of α-diazocarbonyl compounds and alkynes, these methods still suffer from one or more limitations such as lower yields, poor regioselectivity, low efficiency, and complicated catalytic system, etc. In particular, expensive metal catalysts such as $Rh_2(OAc)_4$ are used in most cases. Therefore, it is highly desirable to further develop efficient and simple strategy for substituted furans synthesis with cheap catalysts. Herein we wish to report a $Cu(MeCN)_4PF_6$-catalyzed synthesis of 2,3,5-trisubstituted furan from β-keto α-diazoesters with terminal alkynes. The reaction proceeds with moderate to good yields with excellent regioselectivity. Moreover, the reaction has also been applied to ethyl (*E*)-2-diazo-3-(methoxyimino)butanoate for the synthesis of 2,3,5-trisubstituted *N*-methoxypyrroles.

2. Results and discussion

Initially, we chose β-keto α-diazoester **1a** and phenylacetylene **2a** as model substrates and began our studies with copper catalysts (Table 1). To our delight, $Cu(MeCN)_4PF_6$ led to the expected furan product **3a** with 40% yield at 80 °C in toluene (entry 1). Raising the reaction temperature to 90 °C slightly improved the yield to 60% (entry 2). Further investigation into solvent systems revealed that DCE and dioxane resulted in diminished yield whereas reaction failed to give the desired product in polar solvent MeCN (entries 3–5). With the preliminary results, we next evaluated a series of Cu catalysts and among them, $Cu(OTf)_2$, $Cu(O_2CCF_3)_2$, CuI, $Cu(OEt)_2$ showed less effective, giving 1,3-diynes as the major product (entries 6–10). Then, the ratio of the substrates was examined and it was found that the 1.2:1 ratio of **1a** and **2a** led to improved yield (entry 11). Under this condition, further raising the reaction temperature to 110 °C resulted in diminished yield while at 40 °C the reaction did not occur (entries 12 and 13). Phosphine ligand and base additive were found not effective (entries 14 and 15). Finally, control experiment indicated the reaction did not occur in the absence of Cu(I) catalyst (entry 16).

Table 1
Optimization of the reaction conditions[a]

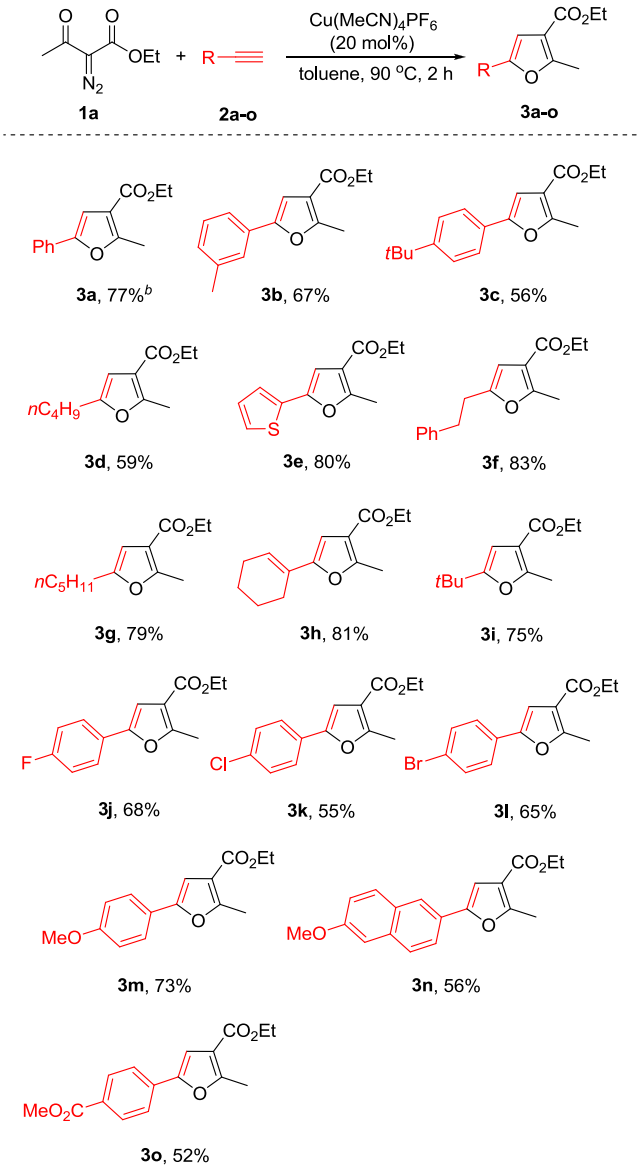


1a **2a** **3a**

Entry	Cat. (20 mol %)	Solvent	**1a**/**2a**	*T* (°C)	**3a**,[a] %
1	$Cu(MeCN)_4PF_6$	Toluene	1:1	80	40
2	$Cu(MeCN)_4PF_6$	Toluene	1:1	90	60
3	$Cu(MeCN)_4PF_6$	DCE	1:1	90	45
4[b]	$Cu(MeCN)_4PF_6$	Dioxane	1:1	90	20
5	$Cu(MeCN)_4PF_6$	MeCN	1:1	90	0
6	$Cu(OTf)_2$	Toluene	1:1	90	37
7	$Cu(O_2CCF_3)_2$	Toluene	1:1	90	46
8	CuI	Toluene	1:1	90	Trace
9	$Cu(OAc)_2$	Toluene	1:1	90	0
10	$Cu(OEt)_2$	Toluene	1:1	90	Trace
11	$Cu(MeCN)_4PF_6$	Toluene	1.2:1	90	77
12	$Cu(MeCN)_4PF_6$	Toluene	1.2:1	110	40
13	$Cu(MeCN)_4PF_6$	Toluene	1.2:1	40	0
14	$Cu(MeCN)_4PF_6$/(2-furyl)$_3$P	Toluene	1.2:1	90	20
15	$Cu(MeCN)_4PF_6$/K_2CO_3 (100 mol %)	Toluene	1.2:1	90	Trace
16	None	Toluene	1.2:1	90	0

[a] Reaction conditions: A mixture of Cu catalyst (20 mol %), **1a** (0.36 mmol), **2a** (0.3 mmol) in 2 mL toluene was stirred at the indicated temperature for 2 h.
[b] Isolated yield by alumina column chromatographic purification method.

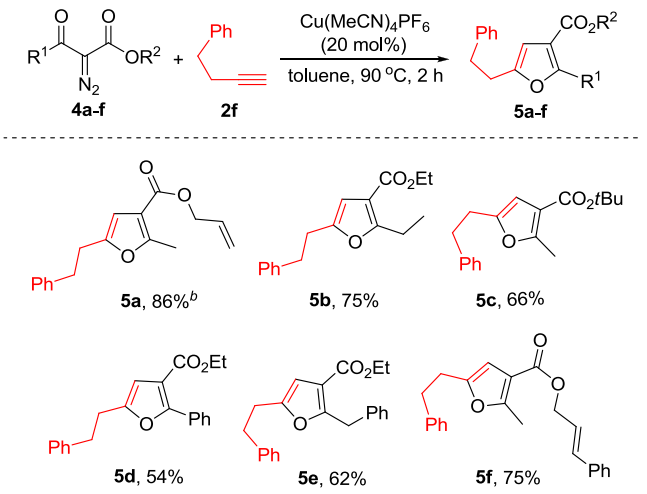
With the best reaction conditions in hand, we investigated the scope of the reaction by screening a variety of terminal alkynes (**2a**–**o**) with ethyl 2-diazo-3-oxobutanoate (**1a**). As shown in Scheme 2, the reaction affords the corresponding furans (**3a**–**o**) in moderate to good yields. Notably, the reaction was not significantly affected by the substituents on the aromatic ring of terminal alkynes. Both electron-rich (**2b**, **2c**, **2m**) and electron-deficient aryl substituted alkynes (**2j**, **2k**, **2o**) were compatible, and alkoxy, acetoxy, fluoro, chloro, bromo groups were tolerated in the reaction. In addition, this approach also worked well with aliphatic alkynes (**2d**, **2f**, **2g**, **3i**), affording the corresponding furans in higher yields. The reaction also worked well with 2-thiophenyl- and β-naphthyl-substituted alkynes (**2e** and **3n**) (Scheme 2).



[a]Reaction conditions: a mixture of Cu catalyst (20 mol%), diazoester **1a** (0.36 mmol), alkynes **2a-o** (0.3 mmol) in 2 mL toluene was stirred at 90 °C for 2 h.
[b]Isolated yield by alumina column chromatographic purification.

Scheme 2. Substrate scope of terminal alkynes.[a]

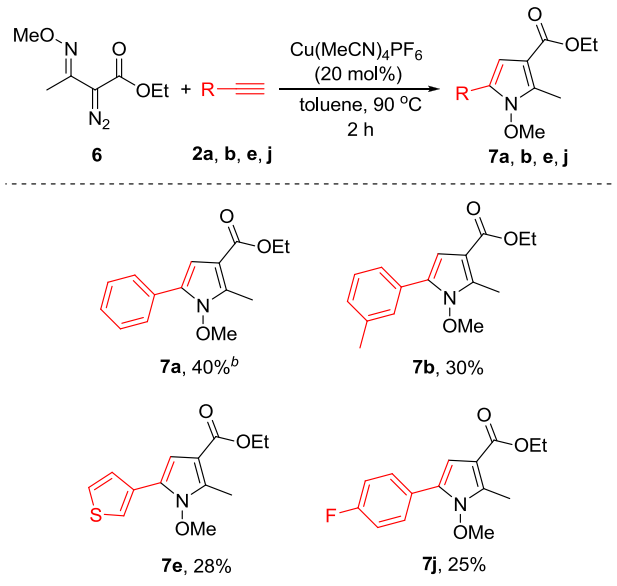
Subsequently, the scope of β-keto α-diazoesters was studied (Scheme 3). The reaction was examined for several β-keto α-diazoesters **4a**–**f** with 4-phenylbutylene **2f** under the optimized reaction conditions. In all the cases the reaction also worked smoothly, giving the corresponding poly-substituted furans in moderate to good yields with good functional group tolerance.



[a] Reaction conditions: a mixture of Cu catalyst (20 mol%), diazoesters **4a-f** (0.36 mmol), alkyne **2f** (0.3 mmol) in 2 mL toluene was stirred at 90 °C for 2 h. [b]Isolated yield by alumina column chromatographic purification.

Scheme 3. Substrate scope of β-keto α-diazoesters.[a]

Encouraged by the above success, we then turned our attention to apply this methodology to synthesize *N*-methoxypyrroles using α-diazoesters bearing C=N bond in the β position. Thus, we chose ethyl (*E*)-2-diazo-3-(methoxyimino)butanoate **6** as the α-diazoester partner and carried out the reaction with terminal alkynes under the optimized reaction conditions. We were pleased to find that under the same reaction conditions, α-diazooximes undergo cyclization reaction with terminal alkynes (**2a**, **b**, **e**, **j**), giving the corresponding *N*-methoxypyrroles (**7a**, **b**, **e**, **j**) (Scheme 4).

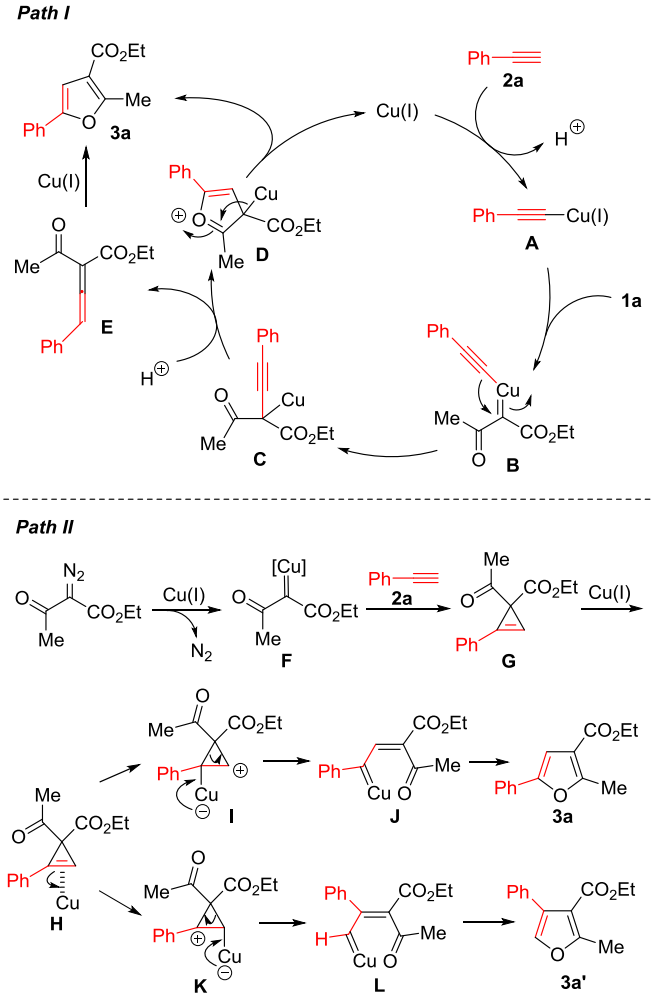


[a] Reaction conditions: a mixture of Cu catalyst (20 mol%), α-diazooxime **6** (0.33 mmol), alkynes **2a, 2b, 2e, 2j** (0.3 mmol) in 2 mL toluene was stirred at 90 °C for 2 h. [b]Isolated yield by silica gel column chromatographic purification.

Scheme 4. Synthesis of *N*-methoxypyrroles from α-diazooxime and terminal alkynes.[a]

However, the yields are low in all the cases, presumably attributed to the instability of ethyl (*E*)-2-diazo-3-(methoxyimino)butanoate under the reaction conditions.

We proposed plausible mechanism to account for the Cu-catalyzed reaction of diazoester and terminal alkyne as shown in Scheme 5. In path I, copper acetylide **A** is firstly formed from phenylacetylene and Cu(I) catalyst, which reacts with diazoester to generate copper-carbene species **B**. The alkynyl migratory insertion of carbene species **B** to the carbenic carbon gives the intermediate **C**, which then produces 2,3-allenoate **E** by the direct protonation. The allene **E** may undergo cyclization to afford the furan product under the Cu(I)-catalyzed reaction conditions. Alternatively, from intermediate **C** intramolecular nucleophilic attack of the carbonyl group to the triple bond produces the intermediate **D**, which later undergoes a subsequent proton transfer to afford furan **3a** with simultaneous regeneration of the Cu(I) catalyst.



Scheme 5. Proposed reaction mechanism.

Alternatively, the reaction may also follow path II. In this case, Cu-catalyzed cyclopropenation occurs to produce cyclopropene **G**. Under the Cu(I) catalysis, the cyclopropene **G** undergoes ring-opening rearrangement to generate Cu carbene intermediate **J** or **L**.[19] From **J**, the furan **3a** is generated through cyclization of the Cu carbene with the carbonyl oxygen, while from **L**, 2,3,4-trisubstituted furan **3a′** is generated.[15] In this study furan **3a′** was not observed, which indicates path II may be less likely compared to path I. However, rigorous investigations are needed to unambiguously establish the reaction mechanism.

3. Summary

In conclusion, we have explored the copper-catalyzed reaction of β-keto α-diazoester with terminal alkynes, resulting in the formation of tri-substituted furans with good efficiency and selectivity. This furan synthesis method use readily available starting materials and in particular use cheap Cu(I) complex as the catalyst. The reaction is highly efficient and shows wide substrate scope. It is thus expected that this method may find applications in organic synthesis.

4. Experimental section

4.1. General

All reactions were performed under nitrogen atmosphere in a 10 mL microwave tube. All solvents were dried before use. For chromatographic purification, 200–300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 MHz and Brucker ARX 400 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). β-Keto α-diazoesters were prepared according to the literature procedure.[14] Unless otherwise noted, materials obtained from commercial suppliers were used without further purifications.

4.2. Typical procedure for the copper-catalyzed cross-coupling of β-keto diazoester and terminal alkynes

Under a nitrogen atmosphere, ethynylbenzene **2a** (30.6 mg, 0.3 mmol) was added in a suspension of $Cu(MeCN)_4PF_6$ (22.3 mg, 0.05 mmol) and β-keto diazoester **1a** (56.16 mg, 0.36 mmol) in toluene (2 mL). The solution was stirred at 90 °C for 2 h and the progress of the reaction was monitored by TLC. After completion of the reaction, it was cooled down to room temperature and the reaction solution was filtered through a short path of silica gel by using EtOAc as eluent. The solvent was removed in vacuum to leave a crude mixture, which was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure product **3a**.

*4.2.1. Ethyl 2-methyl-5-phenylfuran-3-carboxylate (**3a**).*[15] Colorless oil (53 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J=7.2 Hz, 2H), 7.38 (t, J=7.6 Hz, 2H), 7.29–7.26 (m, 1H), 6.88 (s, 1H), 4.31 (q, J=7.1 Hz, 2H), 2.65 (s, 3H), 1.37 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.6, 151.7, 130.0, 128.7, 127.6, 123.6, 115.4, 105.5, 60.2, 14.4, 13.9.

*4.2.2. Ethyl 2-methyl-5-m-tolylfuran-3-carboxylate (**3b**).*[16] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3b** as colorless oil (49 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.27 (t, J=7.6 Hz, 1H), 7.08 (d, J=7.6 Hz, 1H), 6.89 (s, 1H), 4.31 (q, J=7.1 Hz, 2H), 2.65 (s, 3H), 2.38 (s, 3H), 1.37 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.5, 151.8, 138.3, 130.0, 128.6, 128.4, 124.2, 120.8, 115.2, 105.3, 60.2, 21.4, 14.4, 13.9.

*4.2.3. Ethyl 5-(4-tert-butylphenyl)-2-methylfuran-3-carboxylate (**3c**).*[17] Following the typical procedure above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3c** as colorless oil (48 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J=8.8 Hz, 2H), 7.40 (d, J=8.4 Hz, 2H), 6.83 (s, 1H), 4.31 (q, J=7.1 Hz, 2H), 2.64 (s, 3H), 1.37 (t, J=7.2 Hz, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.3, 151.9, 150.7, 127.4, 125.6, 123.4, 115.3, 104.8, 60.1, 34.6, 31.2, 14.4, 13.9.

*4.2.4. Ethyl 5-butyl-2-methylfuran-3-carboxylate (**3d**).*[15] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 100:1, petroleum ether/EtOAc) to afford pure **3d** as colorless oil (37 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (s, 1H), 4.26 (q, J=7.2 Hz, 2H), 2.55 (t, J=7.2 Hz, 2H) one peak was missed because of overlap, 2.53 (br, 3H), 1.63–1.57 (m, 2H), 1.41–1.32 (m, 5H), 0.92 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.4, 154.3, 113.7, 105.3, 59.9, 29.9, 27.3, 22.1, 14.4, 13.8, 13.7.

*4.2.5. Ethyl 2-methyl-5-(thiophen-2-yl) furan-3-carboxylate (**3e**).*[17] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3e** as white powder (57 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.45 (m, 1H), 7.35–7.33 (m, 1H), 7.29–7.26 (m, 1H), 6.70 (s, 1H), 4.31 (q, J=7.2 Hz, 2H), 2.63 (s, 3H), 1.37 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.0, 148.8, 131.7, 126.4, 124.4, 119.1, 115.0, 105.1, 60.2, 14.4, 13.8; IR (film, cm^{-1}) 2927, 1716, 1230, 1097, 1049, 856, 774, 672, 658; EIMS (m/z, relative intensity): 236 (M^+, 74), 207 (100), 191 (17), 163 (10), 121 (10), 111 (23); HRMS (ESI) calcd for $C_{12}H_{13}O_3S$ [$(M+H)^+$]: 237.0580, found: 237.0581.

*4.2.6. Ethyl 2-methyl-5-phenethylfuran-3-carboxylate (**3f**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3f** as a light yellow oil (64 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.22–7.17 (m, 3H), 6.24 (s, 1H), 4.26 (q, J=7.2 Hz, 2H), 2.96–2.91 (m, 2H), 2.88–2.84 (m, 2H), 2.54 (s, 3H), 1.33 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 157.6, 153.1, 140.9, 128.4, 128.3, 126.1, 113.8, 105.9, 59.9, 34.1, 29.6, 14.3, 13.7; IR (film, cm^{-1}) 2924, 1714, 1230, 1209, 1080, 778, 699, 668; EIMS (m/z, relative intensity): 258 (M^+, 19), 213 (11), 167 (100), 139 (18), 121 (28), 91.1 (14), 65.1 (6); HRMS (ESI) calcd for $C_{16}H_{19}O_3$ [$(M+H)^+$]: 259.1329, found: 259.1329.

*4.2.7. Ethyl 2-methyl-5-pentylfuran-3-carboxylate (**3g**).*[18] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 100:1, petroleum ether/EtOAc) to afford pure **3g** as colorless oil (53 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (s, 1H), 4.26 (q, J=7.1 Hz, 2H), 2.56–2.54 (m, 2H), 2.53 (s, 3H), 1.35–1.32 (m, 9H), 0.90 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.4, 154.3, 113.8, 105.3,59.9, 31.2, 27.6, 27.4, 22.4, 14.4, 13.9, 13.7.

*4.2.8. Ethyl 5-cyclohexenyl-2-methylfuran-3-carboxylate (**3h**).*[7] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 100:1, petroleum ether/EtOAc) to afford pure **3h** as yellow oil (57 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 6.28–6.26 (m, 1H), 4.28 (q, J=7.1 Hz, 2H), 2.56 (s, 3H), 2.24–2.23 (m, 2H), 2.20–2.18 (m, 2H), 1.73–1.71 (m, 2H), 1.65–1.62 (m, 2H), 1.34 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 157.7, 153.2, 126.5, 122.7, 114.5, 103.9, 60.0, 25.0, 24.6, 22.2, 22.1, 14.3, 13.8.

*4.2.9. Ethyl 5-tert-butyl-2-methylfuran-3-carboxylate (**3i**).*[15,16] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3i** as colorless oil (47 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (s, 1H), 4.27 (q, J=7.1 Hz, 2H), 2.54 (s, 3H), 1.34 (t, J=7.2 Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.1, 157.4, 113.5, 102.6, 59.9, 32.3, 28.8, 14.4, 13.7.

*4.2.10. Ethyl 5-(4-fluorophenyl)-2-methylfuran-3-carboxylate (**3j**).*[17] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3j** as colorless oil (51 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 2H), 7.07 (t, J=8.8 Hz, 2H), 6.81 (s, 1H), 4.31 (q, J=7.2 Hz, 2H), 2.64 (s, 3H), 1.37 (t,

J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 162.2 (d, J=246.0 Hz), 158.5, 150.8, 126.4 (d, J=3.0 Hz), 125.4 (d, J=8.0 Hz), 115.8 (d, J=21.0 Hz), 115.4, 105.1, 60.2, 14.3, 13.8.

*4.2.11. Ethyl 5-(4-chlorophenyl)-2-methylfuran-3-carboxylate (**3k**).*[17] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3k** as colorless oil (44 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J=8.4 Hz, 2H), 7.33 (d, J=8.4 Hz, 2H), 6.86 (s, 1H), 4.31 (q, J=6.9 Hz, 2H), 2.63 (s, 3H), 1.37 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 158.8, 150.6, 133.2, 128.9, 128.5, 124.8, 116.5, 105.9, 60.2, 14.3, 13.8.

*4.2.12. Ethyl 5-(4-bromophenyl)-2-methylfuran-3-carboxylate (**3l**).*[17] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 100:1, petroleum ether/EtOAc) to afford pure **3l** as colorless oil (60 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 4H), 6.87 (s, 1H), 4.31 (q, J=7.2 Hz, 2H), 2.63 (s, 3H), 1.36 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 158.8, 150.5, 131.8, 128.9, 125.0, 121.3, 115.5, 106.0, 60.2, 14.3, 13.8.

*4.2.13. Ethyl 5-(4-methoxyphenyl)-2-methylfuran-3-carboxylate (**3m**).*[17] Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3m** as light yellow oil (57 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J=8.8 Hz, 2H), 6.95 (d, J=8.8 Hz, 2H), 6.74 (s, 1H), 4.30 (q, J=7.1 Hz, 2H), 3.81 (s, 3H), 2.62 (s, 3H), 1.36 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 159.1, 157.9, 151.7, 125.0, 123.0, 115.2, 114.1, 103.7, 60.0, 55.2, 14.3, 13.8.

*4.2.14. Ethyl 5-(2-methoxynaphthalen-6-yl)-2-methylfuran-3-carboxylate (**3n**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3n** as light yellow oil (52 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.75 (m, 4H), 7.16–7.14 (m, 2H), 7.10 (d, J=2.0 Hz, 1H), 6.93 (s, 1H), 4.32 (q, J=7.1 Hz, 2H), 3.91 (s, 3H), 2.68 (s, 3H), 1.38 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.5, 151.9, 133.9, 130.9, 129.6, 128.8, 127.2, 125.3, 1225, 121.0, 119.3, 115.4, 105.8, 105.2, 60.2, 55.3, 14.4, 13.9; IR (film, cm^{-1}) 2960, 2925, 1729, 1260, 1074, 1018, 799; EIMS (m/z, relative intensity): 310 (M^+, 100), 281 (63), 267 (8), 239 (10), 185 (7), 132 (5); HRMS (ESI) calcd for $C_{19}H_{19}O_4$ [$(M+H)^+$]: 311.1278, found: 311.1286.

*4.2.15. Ethyl 5-(4-(methoxycarbonyl) phenyl)-2-methylfuran-3-carboxylate (**3o**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **3o** as light yellow oil (45 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J=8.4 Hz, 2H), 7.69 (d, J=8.4 Hz, 2H), 7.02 (s, 1H), 4.32 (q, J=7.2 Hz, 2H), 3.92 (s, 3H), 2.66 (s, 3H), 1.38 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.7, 159.6, 150.6, 132.4, 130.1, 129.5, 123.2, 115.8, 107.8, 60.3, 52.3, 52.1, 14.3, 13.9; IR (film, cm^{-1}) 2957, 2925, 1720, 1277, 1248, 1232, 1096, 1044, 1016, 800, 770; EIMS (m/z, relative intensity): 288 (M^+, 71), 259 (100), 243 (14), 229 (14), 163 (9); HRMS (ESI) calcd for $C_{16}H_{17}O_5$ [$(M+H)^+$]: 289.1071, found: 289.1075.

*4.2.16. Allyl 2-methyl-5-phenethylfuran-3-carboxylate (**5a**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **5a** as colorless oil (70 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.30 (m, 2H), 7.22–7.17 (m, 3H), 6.25 (s, 1H), 6.03–5.94 (m, 1H), 5.35 (dd, J=19.2, 1.2 Hz, 1H), 5.25 (dd, J=10.2, 1.6 Hz, 1H), 4.71 (dt, J=5.6, 1.4 Hz, 2H), 2.95–2.91 (m, 2H), 2.88–2.84 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 158.0, 153.2, 140.8, 132.5, 128.4, 128.2, 126.1, 117.8, 113.5, 105.9, 64.6, 34.0, 29.6, 13.7; IR (film, cm^{-1}) 2926, 1715, 1228, 1205, 1076, 777, 699; EIMS (m/z, relative intensity): 270 (M^+, 25), 213 (19), 179 (100), 161 (12), 133 (9), 121 (12), 105 (6), 91 (27), 65 (9); HRMS (ESI) calcd for $C_{17}H_{19}O_3$ [$(M+H)^+$]: 271.1329, found: 271.1330.

*4.2.17. Ethyl 2-ethyl-5-phenethylfuran-3-carboxylate (**5b**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **5b** as colorless oil (61 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.21–7.16 (m, 3H), 6.24 (s, 1H), 4.25 (q, J=7.2 Hz, 2H), 2.97 (q, J=7.5 Hz, 2H), 2.94–2.92 (m, 2H), 2.89–2.85 (m, 2H), 1.32 (t, J=7.2 Hz, 3H), 1.23 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 162.6, 153.1, 140.9, 128.4, 128.3, 126.1, 112.9, 105.9, 59.8, 34.1, 29.6, 21.1, 14.3, 12.4; IR (film, cm^{-1}) 2978, 2931, 1713, 1580, 1209, 1087, 1042, 780, 699; EIMS (m/z, relative intensity): 272 (M^+, 19), 227 (12), 181 (100), 153 (13), 135 (29), 107 (5), 91 (19), 65 (7); HRMS (ESI) calcd for $C_{17}H_{21}O_3$ [$(M+H)^+$]: 273.1485, found: 273.1483.

*4.2.18. tert-Butyl 2-methyl-5-phenethylfuran-3-carboxylate (**5c**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **5c** as light yellow oil (57 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.22–7.17 (m, 3H), 6.20 (s, 1H), 2.94–2.90 (m, 2H), 2.86–2.82 (m, 2H), 2.51 (s, 3H), 1.53 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 156.9, 152.8, 140.9, 128.4, 128.2, 126.1, 115.3, 106.2, 80.2, 34.2, 29.6, 28.3, 13.7; IR (film, cm^{-1}) 2927, 1708, 1367, 1230, 1170, 1081, 779, 699; EIMS (m/z, relative intensity): 286 (M^+, 15), 230 (6), 213 (15), 195 (16), 139 (100), 121 (10), 91 (12), 79 (5); HRMS (ESI) calcd for $C_{18}H_{22}NaO_3$ [$(M+Na)^+$]: 309.1461, found: 309.1468.

*4.2.19. Ethyl 5-phenethyl-2-phenylfuran-3-carboxylate (**5d**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **5d** as light yellow oil (52 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J=6.8 Hz, 2H), 7.44–7.36 (m, 3H), 7.32–7.28 (m, 2H), 7.24–7.20 (m, 3H), 6.45 (s, 1H), 4.27 (q, J=7.2 Hz, 2H), 3.04–2.95 (m, 4H), 1.31 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 156.0, 154.2, 140.7, 130.0, 129.0, 128.4, 128.3, 128.2, 128.0, 126.2, 114.3, 108.5, 60.4, 34.1, 29.6, 14.2; IR (film, cm^{-1}) 2960, 2925, 1718, 1210, 1092, 1073, 1038, 1024, 797, 763, 695; EIMS (m/z, relative intensity): 320 (M^+, 24), 275 (7), 229 (100), 201 (28), 128 (8), 105 (17), 91 (9), 77 (12); HRMS (ESI) calcd for $C_{21}H_{21}O_3$ [$(M+H)^+$]: 321.1485, found: 321.1494.

*4.2.20. Ethyl 2-benzyl-5-phenethylfuran-3-carboxylate (**5e**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **5e** as light yellow oil (62 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.18 (m, 8H), 7.12–7.11 (m, 2H), 6.26 (s, 1H), 4.31 (br, 2H), 4.27 (q, J=7.2 Hz, 2H) one peak was missed because of overlap, 2.93–2.89 (m, 2H), 2.88–2.84 (m, 2H), 1.32 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.8, 154.0, 140.7, 137.8, 128.7, 128.5, 128.4, 128.3, 126.4, 126.1, 114.2, 105.2, 60.1, 34.0, 33.5, 29.6, 14.3; IR (film, cm^{-1}) 2960, 2924, 1713, 1260, 1078, 1063, 1018, 799, 698; EIMS (m/z, relative intensity): 334 (M^+, 40), 305 (19), 289 (9), 243 (100), 214 (15), 197 (56), 167 (8), 152 (6), 141 (18), 115 (13), 105 (20), 91 (64), 65 (13); HRMS (ESI) calcd for $C_{22}H_{23}O_3$ [$(M+H)^+$]: 335.1642, found: 335.1644.

*4.2.21. Cinnamyl 2-methyl-5-phenethylfuran-3-carboxylate (**5f**).* Following the typical procedure described above, the crude residue was purified by alumina column chromatography (eluted with 60:1, petroleum ether/EtOAc) to afford pure **5f** as light yellow oil (78 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.34–7.30 (m,

3H), 7.28–7.25 (m, 2H), 7.20–7.17 (m, 3H), 6.68 (d, J=16.0 Hz, 1H), 6.35 (dt, J=15.6, 6.4 Hz, 1H), 6.27 (s, 1H), 4.87 (dd, J=6.4, 0.8 Hz, 2H), 2.96–2.93 (m, 2H), 2.88–2.84 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.8, 154.0, 140.7, 137.8, 128.7, 128.5, 128.4, 128.3, 126.4, 126.1, 114.2, 108.2, 60.1, 34.0, 33.5, 29.6, 14.3; IR (film, cm^{-1}) 2961, 2925, 1713, 1260, 1073, 1019, 798, 777, 694; EIMS (m/z, relative intensity): 346 (M^+, 11), 255 (28), 213 (63), 139 (20), 117 (100), 91 (27), 65 (5); HRMS (ESI) calcd for $C_{23}H_{22}NaO_3$ [(M+Na)$^+$]: 369.1461, found: 369.1494.

4.3. Typical procedure for the Cu(MeCN)$_4$PF$_6$-catalyzed cross-coupling of (*E*)-2-diazo-3-(methoxyimino)butanoate 6 and terminal alkynes

Under a nitrogen atmosphere, ethynylbenzene **2a** (30.6 mg, 0.3 mmol) was added to a suspension of $Cu(MeCN)_4PF_6$ (22.3 mg, 0.05 mmol) and α-diazooximes **6** (61 mg, 0.33 mmol) in toluene (2 mL). The solution was stirred at 90 °C for 2 h and the progress of the reaction was monitored by TLC. After completion of the reaction, it was cooled down to room temperature and the reaction solution was filtered through a short path of silica gel by using EtOAc as eluent. The solvent was removed in vacuum to leave a crude mixture, which was purified by silica column chromatography (eluted with 20:1, petroleum ether/EtOAc) to afford pure product **7a**.

*4.3.1. Ethyl 1-methoxy-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (**7a**).* Colorless oil (31 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=7.2 Hz, 2H), 7.39 (m, 2H), 7.28 (m, 1H), 6.65 (s, 1H), 4.29 (q, J=7.1 Hz, 2H), 3.71 (s, 3H), 2.60 (s, 3H), 1.36 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 132.4, 130.4, 128.6, 127.05, 127.01, 126.4, 107.9, 105.2, 65.6, 59.5, 14.5, 9.8; IR (film, cm^{-1}); 2976, 1702, 1240, 1065, 971, 757, 695; EIMS (m/z, relative intensity): 259 (M^+, 100), 244 (5), 30 (20), 214 (18), 200 (95), 182 (55), 154 (8), 104 (25), 77 (6), 55 (5); HRMS (ESI) calcd for $C_{15}H_{18}NO_3$ [(M+H)$^+$]: 260.1281, found: 260.1279.

*4.3.2. Ethyl 1-methoxy-2-methyl-5-(m-tolyl)-1H-pyrrole-3-carboxylate (**7b**).* Following the typical procedure described above, the crude residue was purified by silica column chromatography (eluted with 10:1, petroleum ether/EtOAc) to afford pure **7b** as light yellow oil (25 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J=7.6 Hz, 2H), 7.28 (m, 1H), 7.10 (d, J=7.5 Hz, 1H), 6.63 (s, 1H), 4.29 (q, J=7.1 Hz, 2H), 3.71 (s, 3H), 2.59 (s, 3H), 2.39 (s, 3H), 1.36 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 138.2, 132.3, 130.3, 128.5, 127.8, 127.2, 123.5, 107.9, 105.2, 65.6, 59.5, 21.5, 14.5, 9.9; IR (film, cm^{-1}); 2974, 1703, 1608, 1440, 1253, 1217, 1066, 918, 768, 696; EIMS (m/z, relative intensity): 273 (M^+, 90), 258 (10), 244 (15), 228 (18), 214 (100), 196 (35), 168 (10), 128 (8), 118 (18); HRMS (ESI) calcd for $C_{16}H_{20}NO_3$ [(M+H)$^+$]: 274.1438, found: 274.1439.

*4.3.3. Ethyl 1-methoxy-2-methyl-5-(thiophen-3-yl)-1H-pyrrole-3-carboxylate (**7e**).* Following the typical procedure described above, the crude residue was purified by silica column chromatography (eluted with 30:1, petroleum ether/EtOAc) to afford pure **7e** as yellow oil (22 mg, 28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J=1.4, 2.7 Hz, 1H), 7.32–7.36 (m, 2H), 6.62 (s, 1H), 4.29 (q, J=7.1 Hz, 2H), 3.83 (s, 3H), 2.59 (s, 3H), 1.36 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 131.8, 130.6, 126.3, 125.5, 123.3, 119.3, 107.7, 104.3, 65.5, 59.5, 14.5, 9.8; IR (film, cm^{-1}); 2987, 2901, 1702, 1440, 1237, 1066, 769; EIMS (m/z, relative intensity): 265 (M^+, 100), 234 (20), 220 (15), 206 (90), 188 (40), 160 (12), 110 (10); HRMS (ESI) calcd for $C_{13}H_{16}NO_3S$ [(M+H)$^+$]: 266.0845, found: 266.0848.

*4.3.4. Ethyl 5-(4-fluorophenyl)-1-methoxy-2-methyl-1H-pyrrole-3-carboxylate (**7j**).* Following the typical procedure described above, the crude residue was purified by silica column chromatography (eluted with 20:1, petroleum ether/EtOAc) to afford pure **7j** as light yellow oil (21 mg, 25%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J=5.4, 8.6 Hz, 2H), 7.09 (t, J=8.7 Hz, 2H), 6.59 (s, 1H), 4.29 (q, J=7.1 Hz, 2H), 3.70 (s, 3H), 2.59 (s, 3H), 1.36 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 132.3, 128.3, 128.2, 126.2, 115.7, 115.5, 107.9, 105.1, 65.6, 59.6, 14.5, 9.9; IR (film, cm^{-1}); 2928, 1702, 1572, 1489, 1242, 1157, 1065, 810, 771; EIMS (m/z, relative intensity): 277 (M^+, 95), 262 (5), 248 (20), 232 (20), 218 (100), 200 (55), 188 (5), 172 (10), 122 (25), 52 (10); HRMS (ESI) calcd for $C_{15}H_{17}FNO_3$ [(M+H)$^+$]: 278.1187, found: 278.1190.

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Supplementary data

Copies of ^{1}H and/or ^{13}C spectra for isolated products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.07.086.

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