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Triflic Acid-Catalyzed Cycloisomerization Reactions of Donor–Acceptor Cyclopropanes: Access to Alkyl 5-Arylfuran-2-carboxylates

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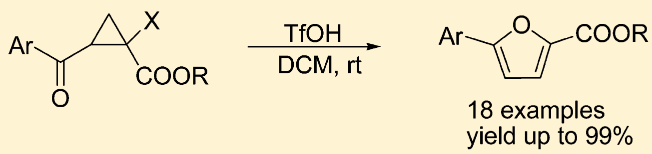
Supporting Information

ABSTRACT: A direct synthetic strategy starting from alkyl 1-alkoxy-2-aroylcyclopropanecarboxylates was developed for the construction of alkyl 5-arylfuran-2-carboxylates. These donor–acceptor cyclopropanes smoothly undergo a simple ring-opening reaction or/and cycloisomerization reaction in the presence of acid at room temperature, which greatly depends on the properties of the acid used in the experiment. Alkyl 5-arylfuran-2-carboxylates were afforded in high yields in triflic acid, whereas alkyl 2,5-dioxo-5-phenylpentanoate became the major product in other protic acids and Lewis acids.



One of the most important kinds of polysubstituted furans are 2,5-disubstituted. This feature structure is not only widely present in many natural products[1] and pharmaceuticals[2] but can also be utilized as a versatile synthetic building block.[3] Although some synthetic methods for substituted furans have already been reported,[4] the main approaches to 2,5-disubstituted furans involve the introduction of designated groups in existing furan precursors[5] and the generation of a furan ring by metal-catalyzed cyclization of unsaturated alcohols, unsaturated ketones, and haloalkynes or 1, 3-diynes with ketones or aldehydes.[6] These methods, however, suffer from different disadvantages, such as limitations of substrates, harsh reaction conditions, or poor chemoselectivity. Therefore, it is still of great importance to develop new and efficient synthetic strategies for various 2,5-disubstituted furans.

As useful three-carbon synthons, cyclopropanes with donor and acceptor substituents in the vicinal positions (donor–acceptor cyclopropanes) have attracted much attention from synthetic chemists for their successful application in the construction of natural products.[7] Because of the high polarization of one of three C–C bonds of the ring, donor–acceptor cyclopropanes are readily transformed into useful 1,3-dipoles via a ring-opening reaction by treatment with Lewis acids or bases. These 1,3-dipoles easily participate in formal $[3 + n]$ ($n = 2, 3, 4$) cycloaddition reactions with various suitable dipolarophiles to yield carbocyclic or heterocyclic compounds.[8] In addition, donor–acceptor cyclopropanes as appropriate candidates can also undergo cyclodimerization in the absence of dipolarophiles or other reagents.[9] Recently, we reported a cycloisomerization between alkyl 2-acyl-1-chlorocyclopropanecarboxylates with aliphatic amines under basic conditions, which mainly gave 2-pyrone derivatives.[10] The key intermediate was assigned to be alkyl 2-acyl-1-aminocyclopropanecarboxylates generated in situ in the above reaction. The analogous alkyl 2-acyl-1-alkoxycyclopropanecarboxylates **1**, however, could not undergo spontaneous cycloisomerization under the above conditions. Interestingly, a cycloisomerization product, ethyl 5-phenylfuran-2-carboxylate **2a**, was obtained when substrate **1a** was treated with triflic acid. In fact, the cycloisomerization of donor–acceptor cyclopropanes to substituted furans was scarcely reported.[11] To our knowledge, this is the first transition metal-free example for the direct construction of 2,5-disubstituted furans from donor–acceptor cyclopropanes. Therefore, the reaction details were carefully investigated and depicted as follows.

At the beginning of our study, the reaction of substrate **1a**, prepared easily by treatment of alkyl 2-acyl-1-chlorocyclopropanecarboxylates with phenol in the presence of Cs_2CO_3 in acetonitrile, was used as a probe for evaluating the effect of the properties of acids and solvents on the reaction. The observed results are summarized in Table 1. Treatment of **1a** with one equivalent amount of concentrated H_2SO_4, CH_3SO_3H, or $BF_3 \cdot Et_2O$ in dichloromethane (DCM) at room temperature mainly afforded ethyl 2,5-dioxo-5-phenylpentanoate **3a** in 72, 98, or 69% yields, respectively, within 10 h as well as a small amount of desired product **2a** (Table 1, entries 1–3). Typical Lewis acids such as anhydrous $FeCl_3$ and $AlCl_3$ were also tested, and besides the main product **3a**, cycloisomerization product **2a** was also isolated in 19 and 14% yields, respectively (Table 1, entries 4 and 5). For assessing the effect of acid strength on the reaction, triflic acid (TfOH) as the strongest protic acid was also employed to promote the above reaction. An unexpected result was observed in this case, where **2a** was isolated in 75% yield as the main product without any **3a** (Table 1, entry 6). A detectable decline in the yield of **2a** appeared when the loading of TfOH was decreased from 1.0 to 0.5 equiv. (Table 1, entry 7). On the contrary, increasing the loading of TfOH from 1.0 to 1.5 or 2.0 equiv can markedly accelerate the reaction, and a satisfying yield of **2a** was obtained in the case of 2.0 equiv (Table 1, entries 8 and 9). These observations clearly indicate that the properties of the acid play an important role in this transformation.

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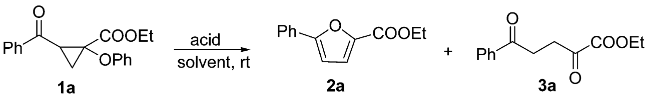
Table 1. Optimization of the Reaction Parameters[a]



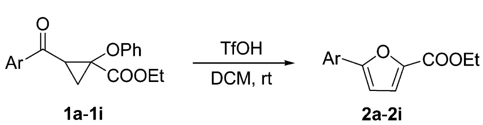
entry	catalyst	solvent	T (h)	yield (%)[b] 2a	3a
1	H_2SO_4 (1 equiv)	DCM	10	trace	72
2	CH_3SO_3H (1 equiv)	DCM	10	trace	98
3	$BF_3.Et_2O$ (1 equiv)	DCM	10	trace	69
4	$FeCl_3$ (1 equiv)	DCM	10	19	64
5	$AlCl_3$ (1 equiv)	DCM	10	14	64
6	CF_3SO_3H (1 equiv)	DCM	10	75	
7	CF_3SO_3H (0.5 equiv)	DCM	10	55	
8	CF_3SO_3H (1.5 equiv)	DCM	3	76	
9	CF_3SO_3H (2 equiv)	DCM	2	80	
10	CF_3SO_3H (2 equiv)	toluene	1	76	
11	CF_3SO_3H (2 equiv)	CH_3CN	1	70	
12	CF_3SO_3H (2 equiv)	DMF	24		

[a]General conditions: **1a** (0.2 mmol), catalyst, and solvent (3.0 mL) at rt. [b]Isolated yield.

Next, the influence of solvent on the reaction was estimated using TfOH as the promoter. Some common solvents such as toluene, CH_3CN, and DMF were chosen for this purpose. As shown in Table 1, the yield observed in toluene was slightly lower than that in DCM (entry 10), and a further decline appeared in CH_3CN (entry 11). To our surprise, almost no reaction occurred when the reaction was conducted in DMF, a well-known aprotic polar solvent with certain alkalinity, even with extending the reaction time to 24 h (Table 1, entry 12). Therefore, we believe that the property of solvent also has a marked influence on the reaction, and nonpolar and weakly polar solvents favored this tandem process. On the basis of these observations, 2.0 equiv of TfOH and DCM were employed as the suitable acid and solvent in the following experiments.

With the optimal conditions in hand, various donor−acceptor cyclopropanes were examined next. All of the observed results are listed in Table 2. It is clear that the electronic property of the 2-aroyl group exerts a definite influence on both the reaction time and product yield. Substrates **1b** and **c** with electron-donating Me and MeO groups showed a relatively lower reactivity in comparison with substrates **1d−f** with electron-withdrawing Cl and Br groups (Table 2, entries 4−6). For example, the reaction of **1c** bearing a 4-MeO group was completed after 3 h, whereas that of **1f** with a 2-Br group finished within 0.5 h. In the case of **1g** with a 4-biphenyl group, the reaction proceeded quickly, giving desired product **2g** in an excellent yield of 91% (entry 7). In addition, the reaction of substrate **1h** with a 2-furanyl group gave a complicated mixture (Table 2, entry 8), whereas that of substrate **1i** with the 2-thienyl group gave desired product **2i** in 63% yield (Table 2, entry 9). The big difference in product distribution may be due to the facile polymerization of the furan derivative caused by the strong acid TfOH.

Table 2. Effect of Ar Group on the Cycloisomerization Reactions of Donor−Acceptor Cyclopropanes[a]

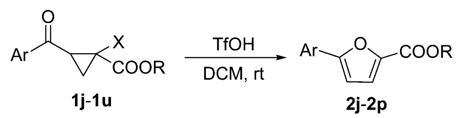


entry	1	Ar	T (h)	product	yield (%)[b]
1	**1a**	C_6H_5	2	**2a**	80
2	**1b**	$4\text{-}MeC_6H_4$	2	**2b**	87
3	**1c**	$4\text{-}MeOC_6H_4$	3	**2c**	83
4	**1d**	$4\text{-}ClC_6H_4$	1	**2d**	84
5	**1e**	$4\text{-}BrC_6H_4$	1	**2e**	78
6	**1f**	$2\text{-}BrC_6H_4$	0.5	**2f**	97
7	**1g**	$4\text{-}PhC_6H_4$	1	**2g**	91
8	**1h**	2-furyl	0.5	[c]	
9	**1i**	2-thienyl	1	**2i**	63

[a]General conditions: **1** (0.2 mmol) and TfOH (0.4 mmol) in DCM (3.0 mL) at room temperature. [b]Isolated yield. [c]Complicated mixture.

Moreover, steric effects of the ester group on the reaction were also investigated. The results listed in Table 3 clearly show that the methyl ester **1j−m** provided the highest yields (Table 3, entries 1−4), and the bulky *t*-butyl ester **1n** gave a complicated mixture owing to its chemical instability ($t\text{-}Bu^+$) (Table 3, entry 5). When R was $(CH_2)_2Cl$ and benzyl, this reaction could also occur under the same conditions in moderate yields (Table 3, entries 6 and 7). Next, substrates with different substituted phenoxy groups were explored under the optimized conditions. In fact, the leaving phenoxy group scarcely had an effect on the reaction (Table 3, entries 8 and 9). The presence of 2-propynyloxy or morpholinyl groups instead of a phenoxy group led to the formation of a small amount of hydrolysis product **3a** in addition to the expected product **2a** (Table 3, entries 10 and 11). The reaction did not proceed when X is Cl because of its electronic property (Table 3, entry 12). Obviously, the electronic property of the leaving group has a big effect on the cycloisomerization of this reaction.

Table 3. Effect of Ester group and X Group on Cycloisomerization Reactions of Donor−Acceptor Cyclopropanes[a]



entry	substrate **1**	T (h)	product	yield (%)[b]
1	Ar = C_6H_5, R = Me, X = OPh **1j**	1	**2j**	80
2	Ar = $4\text{-}MeOC_6H_4$, R = Me, X = OPh **1k**	1	**2k**	78
3	Ar = $4\text{-}ClC_6H_4$, R = Me, X = OPh **1l**	1	**2l**	94
4	Ar = $4\text{-}PhC_6H_4$, R = Me, X = OPh **1m**	0.5	**2m**	99
5[c]	Ar = C_6H_5, R = *t*-Bu, X = OPh **1n**	1		
6	Ar = C_6H_5, R = $(CH_2)_2Cl$, X = OPh **1o**	1	**2o**	60
7	Ar = C_6H_5, R = Bn, X = OPh **1p**	1	**2p**	36
8	Ar = C_6H_5, R = Me, X = $4\text{-}MeOC_6H_4O$ **1q**	1	**2j**	85
9	Ar = C_6H_5, R = Me, X = $4\text{-}ClC_6H_4O$ **1r**	1	**2j**	84
10	Ar = C_6H_5, R = Et, X = $OCH_2C{\equiv}CH$ **1s**	12	**2a**	54(21)[d]
11	Ar = C_6H_5, R = Et, X = morpholinyl **1t**	12	**2a**	57(36)[d]
12[e]	Ar = C_6H_5, R = Et, X = Cl **1u**	24		

[a]General conditions: **1** (0.2 mmol) and TfOH (0.4 mmol) in DCM (3.0 mL) at room temperature. [b]Isolated yield. [c]Complex mixture. [d]Yield of **3a** in parentheses. [e]No reaction.

For the mechanistic details of this tandem reaction to be understood, some control experiments were also performed (Scheme 1). In the presence of 50% aqueous TfOH, substrate **1a** can also be converted to **3a** completely in 80% yield, almost without the formation of desired product **2a** (Scheme 1a).

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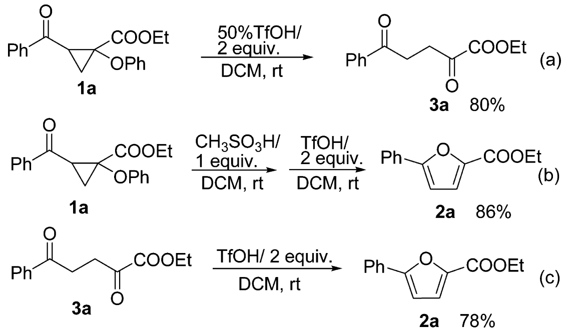
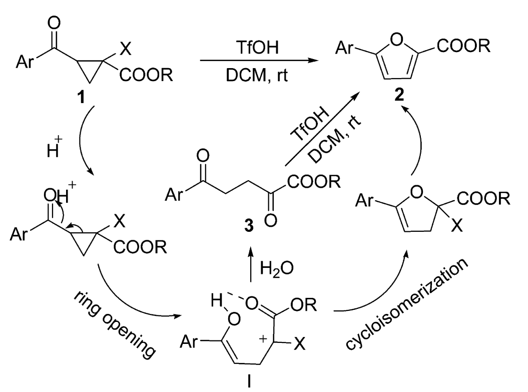
Scheme 1. Mechanistic Study for the Cycloisomerization



Moreover, when an additional 2 equiv of TfOH was added to the untreated reaction mixture obtained by treatment of **1a** with 1 equiv of CH_3SO_3H in DCM at room temperature, the reaction continued and gave expected product **2a** in 86% yield (Scheme 1b). Furthermore, 2-ketoester **3a** isolated from the reaction mixture can directly turn into ethyl 5-phenylfuran-2-carboxylate **2a** in the presence of 2 equiv of TfOH at room temperature in DCM in 78% yield (Scheme 1c). From the above observations, we believe that the acid strength has a crucial role in the tandem reaction, and 2-ketoester **3** could be the key intermediate of this reaction.

On the basis of our findings described above, we proposed a possible mechanism for this tandem process to rationalize the formation of substituted furans (Scheme 2). At the beginning, the donor−acceptor cyclopropane was protonated in the presence of TfOH, and the protonation weakened the C1−C2 bond of donor−acceptor cyclopropanes by polarization. The presence of an electron-donating group at the C1 site prompted the ring-opening reaction to furnish reactive intermediate **I**. The latter was smoothly transformed into the product 5-phenylfuran-2-carboxylates through the cycloisomerization and removal of phenol. Simultaneously, the presence of water caused the competitive hydrolysis of intermediate **I** to afford 2-ketoester **3**. Actually, in the presence of TfOH, 2-ketoeste **3** can be directly converted into alkyl 5-phenylfuran-2-carboxylates via continuous cycloisomerization and dehydration.

Scheme 2. Proposed Mechanism for Cycloisomerization



In conclusion, we have developed a simple and direct approach for the synthesis of alkyl 5-phenylfuran-2-carboxylates from donor−acceptor cyclopropanes under transition metal-free conditions. The operational simplicity, ready availability of starting materials, and good chemical yields make this novel synthetic method appealing in diversity-oriented synthesis. This protocol is expected to find considerable applications in the synthesis of functionized furans, a structural motif for a large number of pharmaceuticals and functional materials.

■ EXPERIMENTAL SECTION

General Methods. All reagents and solvents were of commercial grade and purified prior to use when necessary. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates. Flash column chromatography was performed on silica gel 60 Å, 10−40 μm. All ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer with solvent resonances as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet q = quartet, m = multiplet, and br s = broad signal. All coupling constants (*J*) are given in Hz. IR spectra were recorded on an infrared spectrometer. Melting points were recorded on a melting point detector. HRMS was measured on a TOF-Q mass spectrometer equipped with an ESI technique.

*Typical Procedure for Synthesis of Ethyl 2-Benzoyl-1-phenoxycyclopropanecarboxylate (**1a**).* Ethyl 2-benzoyl-1-chlorocyclopropanecarboxylate (10 mmol) was added to a solution of phenol (10 mmol) and Cs_2CO_3 (22 mmol) in 20 mL of CH_3CN, and the mixture was stirred at room temperature. The reaction was monitored by TLC until the ethyl 2-benzoyl-1-chlorocyclopropanecarboxylate disappeared completely. The mixture was quenched with water and extracted with CH_2Cl_2. Combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as eluent to afford the corresponding product **1a** in 97% yield. Unless otherwise specified, all other products **1** were synthesized according to this typical procedure.

*Typical Procedure for the Preparation of 5-Phenylfuran-2-carboxylate (**2a**).* To a solution of TfOH (0.034 mL; 0.4 mmol) in anhydrous dichloromethane (3 mL) was slowly added donor−acceptor cyclopropane **1a** (0.2 mmol). The reaction mixture was stirred at room temperature and followed by TLC until all of substrate **1a** disappeared. The mixture was quenched with water, and the organic layer was separated. The layer was washed with water and dried (anhydrous Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, petroleum ether-EtOAc, 30:1) to afford product **2a**. Unless otherwise specified, all other products **2** were obtained according to this typical procedure.

*Typical Experimental Procedure for Product **3a**.* Compounds **1a** (0.2 mmol) and CH_3SO_3H (0.2 mmol) were added to 3 mL of anhydrous DCM, and the mixture was stirred at room temperature. The reaction was followed by TLC until all of substrate **1a** disappeared. The mixture was quenched with water, and the organic layer was separated. The layer was washed with water and dried (anhydrous Na_2SO_4), and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as eluent to afford product **3a**.

*Ethyl 2-Benzoyl-1-phenoxycyclopropanecarboxylate (**1a**).* Colorless viscous liquid (total of 3.0 g, 97% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.94 (m, 2H), 7.51−7.42 (m, 3H), 7.20−7.13 (m, 2H), 6.94−6.89 (m, 1H), 6.85−6.80 (m, 2H), 4.35−4.27 (m, 2H), 3.64 (dd, *J* = 8.9, 7.8 Hz, 1H), 2.27 (dd, *J* = 7.7, 5.4 Hz, 1H), 2.02 (dd, *J* = 9.0, 5.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 170.7, 157.2, 137.7, 133.3, 129.2, 128.7, 128.4, 122.0, 115.8, 63.9, 62.3, 33.8, 20.0, 14.2. HRMS (ESI) *m/z*: calcd for $C_{19}H_{18}O_4Na$ $[M + Na]^+$, 333.1103; found, 333.1112.

*Ethyl 2-(4-Methylbenzoyl)-1-phenoxycyclopropanecarboxylate (**1b**).* Yellowish viscous liquid (total of 3.2 g, 98% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.77 (dd, *J* = 14.1, 6.8 Hz, 1H), 6.70 (t, *J* = 8.2 Hz, 2H), 4.21−4.11 (m, 2H), 3.51 (dd, *J* = 8.8, 7.9 Hz, 1H), 2.26 (s, 3H), 2.13 (dt, *J* = 11.0, 5.5 Hz, 1H), 1.88 (dd, *J* = 9.0, 5.4 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 170.6, 157.3, 144.1, 135.3, 129.4, 129.2, 128.5, 121.9, 115.8, 63.8, 62.2, 33.7,

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21.7, 19.8, 14.2. HRMS (ESI) m/z: calcd for $C_{20}H_{20}O_4Na$ [M + Na]$^+$, 347.1259; found, 347.1264.

*Ethyl 2-(4-Methoxybenzoyl)-1-phenoxycyclopropanecarboxylate (**1c**).* Yellowish viscous liquid (total of 2.8 g, 81% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, J = 9.2 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 6.90 (dd, J = 13.0, 7.0 Hz, 2H), 6.85−6.78 (m, 3H), 4.27 (qd, J = 7.1, 2.7 Hz, 2H), 3.80 (s, 3H), 3.64−3.57 (m, 1H), 2.24 (dd, J = 7.7, 5.4 Hz, 1H), 1.98 (dd, J = 9.0, 5.4 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 170.7, 163.7, 157.3, 130.7, 129.2, 121.9, 115.8, 113.9, 63.7, 62.3, 55.5, 33.5, 19.8, 14.2. HRMS (ESI) m/z: calcd for $C_{20}H_{20}O_5Na$ [M + Na]$^+$, 363.1208; found, 363.1211.

*Ethyl 2-(4-Chlorobenzoyl)-1-phenoxycyclopropanecarboxylate (**1d**).* Yellowish viscous liquid (total of 3.1 g, 89% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, J = 8.4 Hz, 2H), 7.30 (t, J = 5.2 Hz, 2H), 7.04 (ddd, J = 12.3, 6.6, 4.9 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.69 (dd, J = 7.6, 4.1 Hz, 2H), 4.21−4.12 (m, 2H), 3.49 (dd, J = 8.9, 7.8 Hz, 1H), 2.20−2.12 (m, 1H), 1.90 (dt, J = 17.2, 8.6 Hz, 1H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 170.5, 157.2, 139.7, 136.0, 129.8, 129.2, 129.0, 122.1, 115.8, 64.0, 62.4, 33.6, 20.1, 14.1. HRMS (ESI) m/z: calcd for $C_{19}H_{17}ClO_4Na$ [M + Na]$^+$, 367.0713; found, 367.0719.

*Ethyl 2-(4-Bromobenzoyl)-1-phenoxycyclopropanecarboxylate (**1e**).* Yellow solid (total of 3.4 g, 88% yield); mp 44−46 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.78 (m, 2H), 7.64−7.58 (m, 2H), 7.20−7.13 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.80 (dd, J = 8.7, 0.9 Hz, 2H), 4.30 (qd, J = 7.1, 2.1 Hz, 2H), 3.58 (dd, J = 8.9, 7.8 Hz, 1H), 2.26 (dd, J = 7.7, 5.5 Hz, 1H), 2.02 (dd, J = 9.0, 5.5 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 170.5, 157.1, 136.4, 132.0, 129.8, 129.2, 128.5, 122.1, 115.8, 63.9, 62.4, 33.6, 20.1, 14.1. HRMS (ESI) m/z: calcd for $C_{19}H_{17}BrO_4Na$ [M + Na]$^+$, 411.0208; found, 411.0217.

*Ethyl 2-(2-Bromobenzoyl)-1-phenoxycyclopropanecarboxylate (**1f**).* Yellowish viscous liquid (total of 3.8 g, 98% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 4.1 Hz, 2H), 7.30−7.27 (m, 1H), 7.23 (dd, J = 8.5, 7.5 Hz, 2H), 6.99 (dd, J = 9.1, 5.7 Hz, 1H), 6.89 (d, J = 7.8 Hz, 2H), 4.28−4.22 (m, 2H), 3.53 (dd, J = 8.8, 7.8 Hz, 1H), 2.24 (dd, J = 7.7, 5.5 Hz, 1H), 2.09 (dd, J = 8.9, 5.5 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 170.1, 157.4, 141.2, 133.8, 132.2, 129.9, 129.3, 127.5, 122.2, 119.6, 116.0, 65.1, 62.3, 37.3, 21.4, 14.2. HRMS (ESI) m/z: calcd for $C_{19}H_{17}BrO_4Na$ [M + Na]$^+$, 411.0208; found, 411.0201.

*Ethyl 2-(Biphenylcarbonyl)-1-phenoxycyclopropanecarboxylate (**1g**).* Yellowish viscous liquid (total of 3.8 g, 99% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.66−7.61 (m, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 7.17 (dd, J = 11.3, 4.7 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 4.36−4.26 (m, 2H), 3.67 (dd, J = 8.8, 7.9 Hz, 1H), 2.29 (dd, J = 7.7, 5.5 Hz, 1H), 2.03 (dt, J = 13.1, 6.5 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 170.7, 157.3, 145.9, 139.9, 136.4, 129.2, 129.0, 129.0, 128.3, 127.3, 122.0, 115.6, 63.9, 62.3, 33.9, 20.0, 14.2. HRMS (ESI) m/z: calcd for $C_{25}H_{22}O_4Na$ [M + Na]$^+$, 409.1416; found, 409.1409.

*Ethyl 2-(Furan-2-carbonyl)-1-phenoxycyclopropanecarboxylate (**1h**).* White solid (total of 2.6 g, 86% yield); mp 46−49 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 0.9 Hz, 1H), 7.23−7.12 (m, 3H), 6.90 (dd, J = 14.8, 7.4 Hz, 1H), 6.88−6.80 (m, 2H), 6.53 (dd, J = 3.6, 1.7 Hz, 1H), 4.35−4.22 (m, 2H), 3.65 (dd, J = 9.0, 7.9 Hz, 1H), 2.27 (dd, J = 7.8, 5.4 Hz, 1H), 1.98 (dd, J = 9.1, 5.4 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 170.4, 157.2, 153.4, 146.5, 129.1, 121.9, 117.2, 115.6, 112.6, 63.9, 62.3, 33.3, 19.8, 14.1. HRMS (ESI) m/z: calcd for $C_{17}H_{16}O_5Na$ [M + Na]$^+$, 323.0895; found, 323.0902.

*Ethyl 1-Phenoxy-2-(thiophene-2-carbonyl)cyclopropanecarboxylate (**1i**).* White solid (total of 3.1 g, 99% yield); mp 44−47 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 3.8, 0.9 Hz, 1H), 7.62 (dd, J = 4.9, 0.9 Hz, 1H), 7.15 (ddd, J = 17.0, 6.2, 2.9 Hz, 3H), 6.91 (t, J = 7.4 Hz, 1H), 6.87−6.82 (m, 2H), 4.35−4.22 (m, 2H), 3.57 (dd, J = 9.0, 7.7 Hz, 1H), 2.24 (dd, J = 7.6, 5.5 Hz, 1H), 2.00 (dd, J = 9.1, 5.5 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 170.5, 157.2, 144.9, 134.1, 132.3, 129.2, 128.2, 122.0, 115.8, 63.8, 62.3, 34.3, 20.1, 14.1. HRMS (ESI) m/z: calcd for $C_{17}H_{16}O_4SNa$ [M + Na]$^+$, 339.0667; found, 339.0659.

*Methyl 2-Benzoyl-1-phenoxycyclopropanecarboxylate (**1j**).* Colorless viscous liquid (total of 2.7 g, 92% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.89 (m, 2H), 7.57 (dd, J = 14.8, 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 8.0 Hz, 2H), 6.90 (dd, J = 16.6, 9.3 Hz, 1H), 6.81 (d, J = 8.5 Hz, 2H), 3.81 (s, 3H), 3.65 (t, J = 8.4 Hz, 1H), 2.27 (dd, J = 7.7, 5.5 Hz, 1H), 2.02 (dd, J = 9.0, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 171.2, 157.2, 137.6, 133.3, 129.3, 128.7, 128.3, 122.1, 115.8, 63.7, 53.2, 33.9, 20.1. HRMS (ESI) m/z: calcd for $C_{18}H_{16}O_4Na$ [M + Na]$^+$, 319.0946; found, 319.0939.

*Methyl 2-(4-Methoxybenzoyl)-1-phenoxycyclopropanecarboxylate (**1k**).* White solid (total of 2.9 g, 90% yield); mp 73−75 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.7 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 9.0 Hz, 2H), 6.92 (t, J = 7.4 Hz, 2H), 6.81 (d, J = 8.0 Hz, 1H), 3.81 (s, 3H), 3.49 (s, 3H), 3.17 (t, J = 9.4 Hz, 1H), 2.45 (dd, J = 8.1, 6.3 Hz, 1H), 1.68 (dt, J = 16.6, 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 168.9, 163.9, 156.7, 130.9, 129.6, 122.1, 115.7, 115.5, 113.9, 63.5, 63.4, 55.5, 52.5, 35.5, 19.8. HRMS (ESI) m/z: calcd for $C_{19}H_{18}O_5Na$ [M + Na]$^+$, 349.1054; found, 349.1049.

*Methyl 2-(4-Chlorobenzoyl)-1-phenoxycyclopropanecarboxylate (**1l**).* Yellowish viscous liquid (total of 3.0 g, 91% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H), 3.61 (dd, J = 15.3, 6.6 Hz, 1H), 2.27 (dd, J = 7.6, 5.6 Hz, 1H), 2.03 (dd, J = 9.0, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 171.1, 157.1, 139.8, 135.9, 129.7, 129.3, 129.0, 122.2, 115.7, 63.8, 53.3, 33.7, 20.2. HRMS (ESI) m/z: calcd for $C_{18}H_{15}ClO_4Na$ [M + Na]$^+$, 353.0557; found, 353.0548.

*Methyl 2-(Biphenylcarbonyl)-1-phenoxycyclopropanecarboxylate (**1m**).* White solid (total of 3.2 g, 85% yield); mp 95−97 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.65−7.60 (m, 2H), 7.49−7.42 (m, 2H), 7.39 (dd, J = 13.4, 6.1 Hz, 1H), 7.17 (t, J = 8.0 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.68 (t, J = 8.4 Hz, 1H), 2.29 (dd, J = 7.6, 5.5 Hz, 1H), 2.04 (dd, J = 9.0, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 171.3, 157.2, 146.0, 139.8, 136.4, 129.3, 129.0, 129.0, 128.3, 127.3, 122.1, 115.8, 63.7, 53.3, 34.0, 20.1. HRMS (ESI) m/z: calcd for $C_{24}H_{20}O_4Na$ [M + Na]$^+$, 395.1259; found, 395.1248.

*t-Butyl 2-Benzoyl-1-phenoxycyclopropanecarboxylate (**1n**).* Yellowish viscous liquid (total of 3.3 g, 99% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.88 (m, 2H), 7.56 (dd, J = 14.6, 7.3 Hz, 1H), 7.51−7.41 (m, 2H), 7.17−7.11 (m, 2H), 6.88 (dd, J = 13.9, 6.6 Hz, 1H), 6.83 (t, J = 9.7 Hz, 2H), 3.61 (t, J = 8.3 Hz, 1H), 2.29−2.21 (m, 1H), 2.03−1.90 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 169.4, 157.4, 137.8, 133.2, 129.1, 128.7, 128.3, 121.8, 115.7, 83.1, 64.4, 33.2, 27.9, 19.8. HRMS (ESI) m/z: calcd for $C_{21}H_{22}O_4Na$ [M + Na]$^+$, 361.1416; found, 361.1411.

*2-Chloroethyl 2-Benzoyl-1-phenoxycyclopropanecarboxylate (**1o**).* Yellowish viscous liquid (total of 2.9 g, 83% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 11.8, 4.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.17 (dt, J = 10.0, 5.0 Hz, 2H), 6.96−6.90 (m, 1H), 6.84 (d, J = 7.9 Hz, 2H), 4.58−4.42 (m, 2H), 3.72−3.63 (m, 3H), 2.29 (dt, J = 9.3, 4.6 Hz, 1H), 2.11−1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 170.3, 157.1, 137.6, 133.3, 129.3, 128.7, 128.4, 122.2, 115.9, 65.2, 63.5, 41.3, 34.1, 19.9. HRMS (ESI) m/z: calcd for $C_{19}H_{17}ClO_4Na$ [M + Na]$^+$, 367.0713; found, 367.0708.

*Benzyl 2-Benzoyl-1-phenoxycyclopropanecarboxylate (**1p**).* Yellowish viscous liquid (total of 3.3 g, 90% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.45−7.36 (m, 2H), 7.27 (dd, J = 8.4, 5.1 Hz, 2H), 7.19 (dd, J = 6.4, 2.6 Hz, 3H), 7.16−7.10 (m, 2H), 6.89 (dd, J = 10.8, 3.9 Hz, 1H), 6.83−6.78 (m, 2H), 5.25 (d, J = 2.8 Hz, 2H), 3.63−3.54 (m, 1H), 2.30−2.22 (m, 1H), 2.02 (dd, J = 9.0, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 170.5, 157.2, 137.6, 135.3, 133.3, 129.3, 128.7, 128.6, 128.5, 128.4, 128.1, 122.1, 115.9, 67.8, 63.8, 33.9, 19.8. HRMS (ESI) m/z: calcd for $C_{24}H_{20}O_4Na$ [M + Na]$^+$, 395.1259; found, 395.1251.

*Methyl 2-Benzoyl-1-(4-methoxyphenoxy)cyclopropanecarboxylate (**1q**).* White solid (total of 3.2 g, 97% yield); mp 118−119 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4

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Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.50−7.42 (m, 2H), 6.76 (t, J = 8.4 Hz, 2H), 6.70 (d, J = 9.1 Hz, 2H), 3.84 (s, 3H), 3.70 (s, 3H), 3.66−3.58 (m, 1H), 2.25 (dd, J = 7.6, 5.5 Hz, 1H), 1.97 (dd, J = 9.0, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 171.4, 154.8, 151.2, 137.7, 133.2, 128.7, 128.3, 116.9, 114.4, 64.4, 55.6, 53.2, 34.2, 20.0. HRMS (ESI) m/z: calcd for $C_{19}H_{18}O_5Na$ [M + Na]$^+$, 349.1052; found, 349.1046.

Methyl 2-Benzoyl-1-(4-chlorophenoxy)cyclopropanecarboxylate (1r). Yellowish viscous liquid (total of 3.0 g, 92% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.87 (m, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.15−7.09 (m, 2H), 6.79−6.73 (m, 2H), 3.82 (s, 3H), 3.65 (dt, J = 19.1, 9.5 Hz, 1H), 2.26 (dd, J = 7.7, 5.5 Hz, 1H), 2.01 (dd, J = 9.1, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 170.8, 155.8, 137.5, 133.4, 129.2, 128.7, 128.3, 127.1, 117.1, 63.9, 53.3, 33.7, 20.0. HRMS (ESI) m/z: calcd for $C_{18}H_{15}ClO_4Na$ [M + Na]$^+$, 353.0557; found, 353.0548.

Ethyl 2-Benzoyl-1-(prop-2-ynyloxy)cyclopropanecarboxylate (1s). Yellowish viscous liquid (total of 2.1 g, 77% yield). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.37−4.29 (m, 2H), 4.21−4.10 (m, 1H), 3.44−3.36 (m, 1H), 2.44−2.37 (m, 2H), 1.75 (dd, J = 8.9, 5.3 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H), 0.99 (q, J = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 171.0, 137.5, 133.3, 128.7, 128.3, 78.7, 75.3, 66.3, 62.1, 58.5, 33.7, 18.9, 14.2. HRMS (ESI) m/z: calcd for $C_{16}H_{16}O_4Na$ [M + Na]$^+$, 295.0946; found, 295.0937.

Ethyl 2-Benzoyl-1-morpholinocyclopropanecarboxylate (1t). Yellow solid (total of 2.7 g, 88% yield); mp 209−211 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 8.1, 1.4 Hz, 2H), 7.41−7.29 (m, 3H), 5.22 (t, J = 2.7 Hz, 1H), 4.36−4.29 (m, 2H), 3.84−3.69 (m, 4H), 3.10 (qd, J = 18.0, 2.7 Hz, 2H), 2.97−2.84 (m, 2H), 2.68−2.55 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 155.2, 130.1, 128.6, 128.3, 125.2, 101.2, 92.4, 66.8, 61.9, 46.3, 38.2, 14.2. HRMS (ESI) m/z: calcd for $C_{17}H_{21}NO_4Na$ [M + Na]$^+$, 326.1368; found, 326.1357.

Ethyl 5-Phenylfuran-2-carboxylate (2a).[12a] Yellow liquid (35 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.71 (m, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 6.73 (d, J = 3.6 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.5, 143.9, 129.6, 128.9, 128.8, 124.8, 119.8, 106.8, 60.9, 14.4. IR (neat): ν 2982, 2931, 1717, 1530, 1481, 1450, 1374, 1302, 1272, 1217, 1141, 1019, 763 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{12}O_3Na$ [M + Na]$^+$, 239.0684; found, 239.0681.

Ethyl 5-p-Tolylfuran-2-carboxylate (2b).[12a] Yellow liquid (40 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.23−7.17 (m, 3H), 6.67 (d, J = 3.6 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.8, 143.5, 139.0, 129.5, 126.9, 124.8, 119.9, 106.2, 60.8, 21.4, 14.4. IR (neat): ν 2982, 2924, 1721, 1537, 1488, 1373, 1302, 1272, 1215, 1140, 1019, 798, 760 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{14}H_{14}O_3Na$ [M + Na]$^+$, 253.0841; found, 253.0837.

Ethyl 5-(4-Methoxyphenyl)furan-2-carboxylate (2c).[12a] Yellow liquid (41 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.52 (m, 2H), 7.22 (d, J = 3.6 Hz, 1H), 6.94 (t, J = 5.8 Hz, 2H), 6.60 (d, J = 3.6 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 159.0, 157.7, 143.3, 126.4, 122.5, 120.0, 114.3, 105.4, 60.8, 55.4, 14.4. IR (neat): ν 2981, 2939, 2838, 1719, 1613, 1591, 1538, 1488, 1373, 1303, 1256, 1139, 1065, 1021, 960, 922, 835, 796, 759 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{14}H_{14}O_4Na$ [M + Na]$^+$, 269.0790; found, 269.0783.

Ethyl 5-(4-Chlorophenyl)furan-2-carboxylate (2d).[12a] Yellow solid (40 mg, 84% yield); mp 72−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.66 (m, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 3.6 Hz, 1H), 6.71 (d, J = 3.6 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 156.3, 144.1, 134.7, 129.1, 128.0, 126.0, 119.8, 107.2, 61.0, 14.4. IR (neat): ν 2984, 2937, 1724, 1586, 1529, 1477, 1411, 1371, 1301, 1276, 1217, 1142, 1095, 1018, 962, 833, 800, 760 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{11}ClO_3Na$ [M + Na]$^+$, 273.0294; found, 273.0293.

Ethyl 5-(4-Bromophenyl)furan-2-carboxylate (2e).[12b] Yellow solid (46 mg, 78% yield); mp 84−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 3.6 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 156.3, 144.2, 132.0, 128.5, 126.3, 123.0, 119.8, 107.3, 61.0, 14.4. IR (neat): ν 2987, 2908, 1723, 1579, 1519, 1470, 1368, 1297, 1214, 1145, 1110, 1020, 1007, 922, 864, 802, 763 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{11}BrO_3Na$ [M + Na]$^+$, 316.9789; found, 316.9784.

Ethyl 5-(2-Bromophenyl)furan-2-carboxylate (2f). Yellow liquid (57 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.9, 1.6 Hz, 1H), 7.72−7.60 (m, 1H), 7.44−7.34 (m, 1H), 7.26 (d, J = 3.7 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.18 (td, J = 8.0, 1.7 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 154.7, 143.9, 134.2, 130.1, 129.8, 129.7, 127.6, 120.4, 119.1, 112.3, 61.0, 14.4. IR (neat): ν 2981, 2932, 1725, 1581, 1560, 1519, 1465, 1432, 1372, 1300, 1246, 1214, 1145, 1020, 963, 923, 808, 760 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{11}BrO_3Na$ [M + Na]$^+$, 316.9789; found, 316.9781.

Ethyl 5-(4-Diphenyl)furan-2-carboxylate (2g).[12c] White solid (53 mg, 91% yield); mp 99−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, J = 10.6 Hz, 2H), 7.69−7.55 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 3.6 Hz, 1H), 6.74 (d, J = 3.6 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.3, 144.0, 141.6, 140.3, 128.9, 128.5, 127.70, 127.5, 127.0, 125.3, 119.9, 107.0, 60.9, 14.4. IR (neat): ν 2985, 2925, 1723, 1535, 1502, 1411, 1372, 1303, 1216, 1154, 1021, 919, 838, 800, 760 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{16}O_3Na$ [M + Na]$^+$, 315.0997; found, 315.0993.

Ethyl 5-(Thiophen-2-yl)furan-2-carboxylate (2i).[12d] Yellow liquid (28 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 3.6, 0.9 Hz, 1H), 7.33 (dd, J = 5.0, 1.0 Hz, 1H), 7.20 (d, J = 3.6 Hz, 1H), 7.07 (dd, J = 5.0, 3.7 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 152.9, 143.4, 132.3, 127.9, 126.2, 125.1, 119.9, 106.7, 60.9, 14.4. IR (neat): ν 3115, 2982, 1721, 1595, 1543, 1494, 1486, 1420, 1379, 1347, 1301, 1259, 1223, 1206, 1139, 1016, 957, 893, 849, 797, 759 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{11}H_{10}O_3SNa$ [M + Na]$^+$, 245.0248; found, 245.0243.

Methyl 5-Phenylfuran-2-carboxylate (2j).[12a] White solid (32 mg, 80% yield); mp 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.75 (m, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.35 (dd, J = 8.4, 6.3 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 6.74 (d, J = 3.6 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 157.6, 143.6, 129.5, 129.0, 128.8, 124.9, 120.1, 106.9, 51.9. IR (neat): ν 292844, 1712, 1529, 1481, 1450, 1371, 1305, 1273, 1219, 1192, 1139, 1066, 1027, 991, 921, 797, 763 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{12}H_{10}O_3Na$ [M + Na]$^+$, 225.0630; found, 225.0623.

Methyl 5-(4-Methoxyphenyl)furan-2-carboxylate (2k).[12e] White solid (36 mg, 78% yield); mp 83−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.59 (m, 2H), 7.23 (d, J = 3.6 Hz, 1H), 7.00−6.87 (m, 2H), 6.60 (d, J = 3.6 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 159.3, 157.8, 142.9, 126.4, 122.5, 120.3, 114.3, 105.4, 55.4, 51.8. IR (neat): ν 2942, 2843, 1730, 1614, 1588, 1489, 1432, 1368, 1318, 1256, 1187, 1146, 1065, 985, 919, 829, 789, 754 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{12}O_4Na$ [M + Na]$^+$, 255.0633; found, 255.0627.

Methyl 5-(4-Chlorophenyl)furan-2-carboxylate (2l).[12e] White solid (44 mg, 94% yield); mp 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.58 (m, 2H), 7.44−7.34 (m, 2H), 7.23 (d, J = 3.6 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.4, 143.8, 134.8, 129.1, 128.0, 126.1, 120.0, 107.2, 51.9. IR (neat): ν 3134, 2948, 1730, 1583, 1565, 1529, 1474, 1408, 1364, 1299, 1213, 1105, 1090, 1025, 987, 911, 805, 756 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{12}H_9ClO_3Na$ [M + Na]$^+$, 259.0138; found, 259.0132.

Methyl 5-(4-Diphenyl)furan-2-carboxylate (2m). White solid (55 mg, 99% yield); mp 159−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.58−7.48 (m, 4H), 7.35 (t, J = 7.5 Hz, 2H), 7.29−7.24 (m, 1H), 7.16 (d, J = 3.6 Hz, 1H), 6.65 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 157.4, 143.6, 141.6, 140.2, 128.9, 128.4, 127.7, 127.5, 127.0, 125.3, 120.2, 107.0, 51.9. IR (neat): ν 2925, 2375, 1707, 1584, 1539, 1504, 1434, 1411, 1366, 1303, 1220,

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1189, 1072, 1029, 987, 919, 805, 760 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}O_3Na$ $[M + Na]^+$, 301.0841; found, 301.0837.

2-Chloroethyl 5-Phenylfuran-2-carboxylate (2o). Yellow liquid (30 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.73 (m, 2H), 7.43 (dd, J = 10.3, 4.6 Hz, 2H), 7.39−7.32 (m, 1H), 7.30 (d, J = 3.6 Hz, 1H), 6.75 (d, J = 3.6 Hz, 1H), 4.57 (t, J = 5.8 Hz, 2H), 3.80 (t, J = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 158.1, 143.0, 129.4, 129.1, 128.9, 124.9, 120.8, 107.0, 64.2, 41.5. IR (neat): ν 3125, 2960, 1723, 1573, 1528, 1478, 1450, 1384, 1309, 1271, 1217, 1140, 1014, 961, 921, 804, 762 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{11}ClO_3Na$ $[M + Na]^+$, 273.0294; found, 273.0286.

Benzyl 5-Phenylfuran-2-carboxylate (2p). Yellow liquid (20 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.4 Hz, 2H), 7.45 (t, J = 7.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 3H), 7.38−7.31 (m, 2H), 7.27 (d, J = 3.6 Hz, 1H), 7.24−7.15 (m, 1H), 6.73 (d, J = 3.6 Hz, 1H), 5.37 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 157.8, 143.5, 135.8, 129.5, 129.0, 128.8, 128.7, 128.6, 128.4, 124.9, 120.3, 106.9, 66.4. IR (neat): ν 3033, 2956, 2926, 1720, 1573, 1528, 1478, 1451, 1379, 1298, 1271, 1216, 1135, 1066, 1026, 970, 921, 804, 783, 762 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}O_3Na$ $[M + Na]^+$, 301.0841; found, 301.0839.

Ethyl 2,5-Dioxo-5-phenylpentanoate (3a).[10] Yellow liquid (46 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.97 (m, 2H), 7.63−7.57 (m, 1H), 7.49 (dd, J = 10.5, 4.7 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 3.42 (t, J = 6.1 Hz, 2H), 3.29 (dd, J = 7.0, 5.6 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 193.2, 160.8, 136.3, 133.4, 128.6, 128.1, 62.5, 33.1, 32.6, 14.0. IR (KBr): ν 2963, 2909, 1725, 1666, 1604, 1447, 1405, 1369, 1254, 1088, 1022, 865, 800 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{14}O_4Na$ $[M + Na]^+$ 257.0790, found 257.0786.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00161.

Copies of ^{1}H and ^{13}C NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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