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Copper-Mediated [3 + 2] Oxidative Cyclization Reaction of *N*-Tosylhydrazones and *β*-Ketoesters: Synthesis of 2,3,5-Trisubstituted Furans

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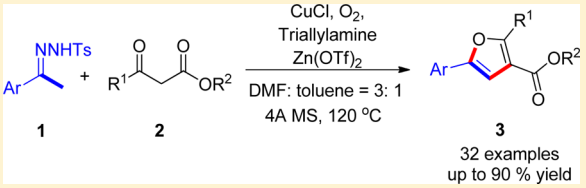
Supporting Information

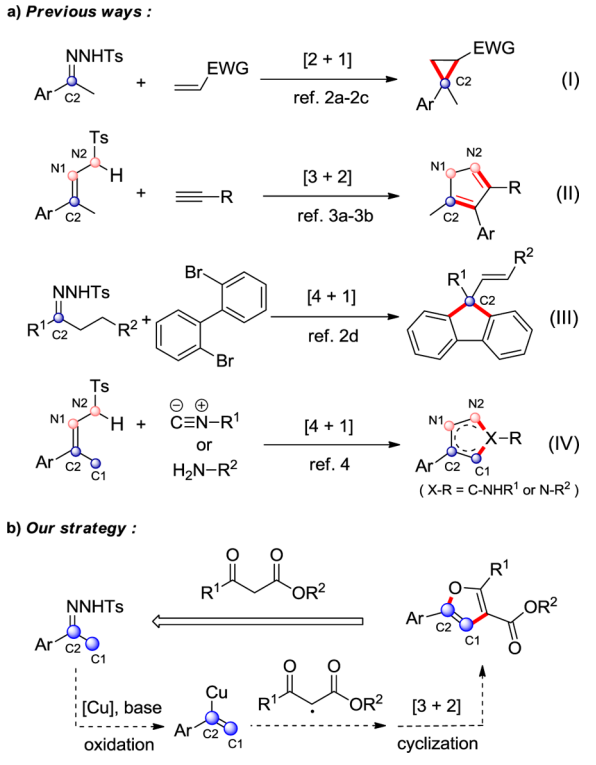
ABSTRACT: The first attempt at utilizing *N*-tosylhydrazones as two-carbon synthons has been successfully achieved, which underwent a copper-mediated [3 + 2] oxidative cyclization reaction to afford 2,3,5-trisubstituted furans in moderate to good yields. The features of this method include inexpensive metal catalyst, readily available substrates, high regioselectivity, and convenient operation. The studies provide important approaches for further exploration of the powerful and diverse reaction abilities of *N*-tosylhydrazones.



INTRODUCTION

N-Tosylhydrazones, derived easily from the corresponding ketones, have been long applied in diverse organic transformations, including Bamford−Stevens and Shapiro reactions. It is well-known that *N*-tosylhydrazones can generate diazo compounds *in situ* in the presence of base and further form metal-carbene species, which have been demonstrated exhibiting excellent synthetic utilities in cross-coupling reactions.[1] Recently, *N*-tosylhydrazones have been widely explored in building various ring products via cyclization reactions, such as [2 + 1], [3 + 2], [4 + 1] cycloadditions, in which *N*-tosylhydrazones are generally used as synthons by providing one or two bonding sites. For example, *N*-tosylhydrazones were utilized as single-carbon synthons to construct cyclopropane-containing products with electron-deficient alkenes[2a−c] (Scheme 1a, I). Valdés[3a,b] reported a [3 + 2] cycloaddition/[1,5]-*δ* rearrangement to prepare substituted pyrazoles from *N*-tosylhydrazones and terminal acetylenes (Scheme 1a, II), in which C2 and N2 were offered as bonding sites. Later, the Valdés group reported a [4 + 1] cyclization reaction to prepare spirofluorene and spiro-acridine derivatives[2d] (Scheme 1a, III). It is noteworthy that *N*-tosylhydrazones were provided C2 as single-carbon synthons. Since 2013, several [4 + 1] cyclization reactions[4] between *N*-tosylhydrazones and nucleophilic substrates, such as isocyanides and anilines, to construct five-membered heterocycles have been reported successively (Scheme 1a, IV), among which nucleophilic reagents were applied to C1 and N2 positions. To the best of our knowledge, there are few reports[3c] on building cyclized products by employing C1 and C2 as bonding sites. As part of our interest in the synthetic applications of *N*-tosylhydrazones, we are particularly interested in exploring novel methods to construct active structural motifs via unprecedented utilization of *N*-tosylhydrazones as C_2 synthons in cyclization reactions, which still is a great challenge.

Scheme 1. Cyclization Reactions of *N*-Tosylhydrazones



Polysubstituted furans, an important class of heterocyclic compounds, are known to be ubiquitous structural motifs and building blocks in natural products,[5] synthetic pharmaceuticals,[6]

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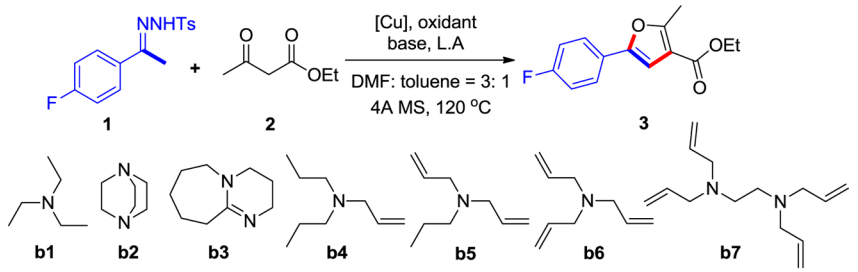
Table 1. Optimization of Reaction Conditions[a]



b1 = Triethylamine; **b2** = 1,4-Diazabicyclo[2.2.2]octane; **b3** = 1,8-Diazabicyclo[5.4.0]undec-7-ene; **b4** = *N*,*N*-dipropylprop-2-en-1-amine; **b5** = *N*-allyl-*N*-propylprop-2-en-1-amine; **b6**= Triallylamine; **b7** = 1,2-Bis(diallylamino)ethane.

entry[a]	[Cu] (equiv)	oxidant	base	yield[b] (%)
1	CuCl (0.5)	air	**b1**	37
2	CuI (0.5)	air	**b1**	19
3	Cu (0.5)	air	**b1**	16
4	$Cu(OAc)_2$ (0.5)	air	**b1**	30
5	CuCl (1)	air	**b1**	61
6	CuCl (1.5)	air	**b1**	57
7	CuCl (1)	O_2	**b1**	71
8	CuCl (1)	BQ	**b1**	74
9	CuCl (1)	$PhI(OAc)_2$	**b1**	36
10	CuCl (1)	O_2	**b2**	46
11	CuCl (1)	O_2	**b3**	42
12	CuCl (1)	O_2	**b4**	72
13	CuCl (1)	O_2	**b5**	77
14	CuCl (1)	O_2	**b6**	85 (81)[c]
15	CuCl (1)	O_2	**b7**	83

[a]Reaction conditions: All reactions were performed with **1** (0.1 mmol), **2** (0.15 mmol), base (0.2 mmol), $Zn(OTf)_2$ (0.1 mmol) in 1.5 mL of solvent (DMF:toluene = 3:1) at 120 °C for 10 h unless otherwise noted. [b]Determined by GC−MS using *n*-dodecane as an internal standard. [c]Isolated yield.

and agrochemicals. In the methods of transition-metal catalysis, including Pd[7]-, Cu[8]-, Ag[9]-, Au[10]-, and Ru[11]-catalyzed organic transformations, 1,3-dicarbonyl compounds are generally used to construct polysubstituted furans from functional olefins, electron-poor alkynes, or terminal alkynes.[12] Very recently, our group[13] disclosed the transformations from ketone-derived *N*-tosylhydrazones to alkynes and diynes via a copper-catalyzed selectively oxidative process. Unlike most of the transition-metal-catalyzed cross-couplings of *N*-tosylhydrazones,[14] the oxidative cross-coupling reactions ultilized C1-positions as binding sites instead of C2-positions. Inspired by this study, we herein disclose a novel approach for the construction of 2,3,5-trisubstituted furans from *N*-tosylhydrazones and *β*-ketoesters via the copper-mediated [3 + 2] oxidative cyclization reactions (Scheme 1b). We supposed that highly activated 1,3-dicarbonyl compounds would first connect to C1-positions of *N*-tosylhydrazones, and then undergo the cyclization process. To our knowledge, it is a rare application that *N*-tosylhydrazones are used as two-carbon synthons to build active cyclic compounds, which would further broaden the synthetic applications of *N*-tosylhydrazones and the methods of constructing polysubstituted furans.

RESULTS AND DISCUSSION

Initially, *N*-tosylhydrazone of 4-fluoroacetophenone (**1**) and ethyl acetoacetate (**2**) were chosen as model substrates, and the optimization results are shown in Table 1. Based on the investigation to various copper catalysts and the corresponding equivalent under simple conditions that Et_3N (0.2 mmol) and $Zn(OTf)_2$ (0.1 mmol) were added in 1.5 mL of solvent (DMF:toluene = 3:1) at 120 °C under an air atmosphere for 10 h (entries 1−6), we found that, when 1.0 equiv of CuCl was added, the best reaction activity was exhibited and the desired product (**3**) was obtained in 61% yield (entry 5). According to our previous work on the oxidative cross-couplings of *N*-tosylhydrazones, the judicious choice of the oxidant and base might be the key to the success of this reaction. Through the examination of various oxidants, such as O_2, BQ, DDQ, $PhI(OAc)_2$, and TBHP, O_2 was considered to be the best choice (entries 7−9). To further improve the yield, we replaced Et_3N with different bases (entries 10−15). To our delight, tertiary amines with an olefins structure could effectively improve the yield of the desired product (entries 12−15), and **b6** displayed the best efficiency and the yield increased to 85% (entry 14). We suspected that triallylamine acted as both base and ligand to facilitate this reaction. Thus, the optimal catalytic system for this copper-mediated [3 + 2] oxidative cyclization reaction was **1** (0.1 mmol), **2** (0.15 mmol), CuCl (0.1 mmol), triallylamine (0.2 mmol), $Zn(OTf)_2$ (0.1 mmol), in 1.5 mL of solvent (DMF:toluene = 3:1) at 120 °C under an O_2 atmosphere for 10 h.

With the optimal reaction conditions in hand, we began to explore the substrate scope of *N*-tosylhydrazones in this Cu-mediated [3 + 2] oxidative cyclization reaction (Table 2). The results indicated that *N*-tosylhydrazones containing electron-withdrawing or electron-donating groups were well tolerated and the desired polysubstituted furans could be afforded in moderate yields. In general, *N*-tosylhydrazones bearing electron-withdrawing groups, including *para*- (**3aa**−**3fa**), *ortho*- (**3na**), *meta*- (**3oa** and **3pa**), and difluoro-substituted positions (**3ra**), gave better results. Electron-donating groups, such as 4-methyl, 4-

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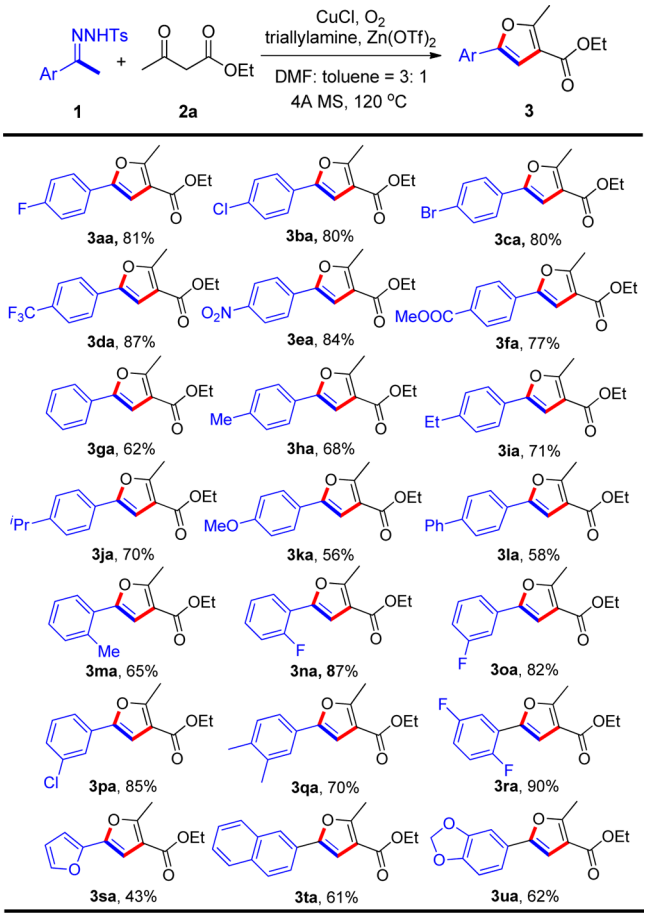
Table 2. Substrate Scope of *N*-Tosylhydrazones[a]



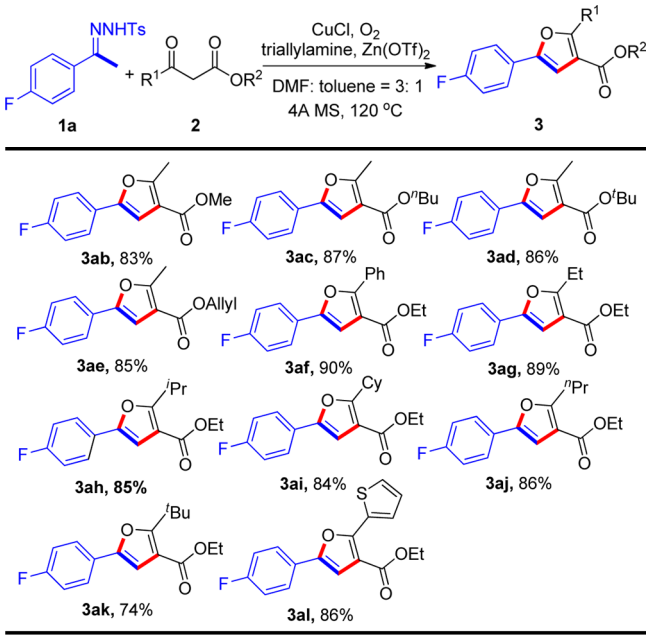
[a]Reaction conditions: All reactions were performed with **1** (0.3 mmol), **2a** (0.45 mmol), CuCl (0.3 mmol), triallylamine (0.6 mmol), $Zn(OTf)_2$ (0.3 mmol), and 2.0 mL of solvent (DMF:toluene = 3:1) at 120 °C under an O_2 atmosphere for 10 h. Yields refer to the isolated yields.

ethyl, 4-isopropyl, 2-methyl, and dimethyl groups, were also well tolerated under the optimized conditions. However, 4-methoxy- and 4-phenyl-substituted substrates (**3ka** and **3la**) gave lower yields. Notably, heterocyclic and naphthone derived *N*-tosylhydrazones are good substrates to deliver the correponding furans in moderate to good yield (**3sa** and **3ta**).

A series of *β*-ketoesters were then examined in this transformation, and the results are shown in Table 3. Methyl, *norm*-butyl, *tert*-butyl, and allyl acetoacetates could be tolerated and converted to the desired furans in good yields (**3ab**−**3ae**). Moreover, when R^1 were alkyl groups, including ethyl, isopropyl, cyclopropyl, *norm*-propyl, and *tert*-butyl, good isolated yields were also obtained (**3ag**−**3ak**). A higher yield was achieved when using ethyl benzoylacetate and ethyl 3-oxo-3-(thiophen-2-yl)propanoate as substrates, and the target furans were produced in 90% (**3af**) and 86% (**3al**) yields, respectively.

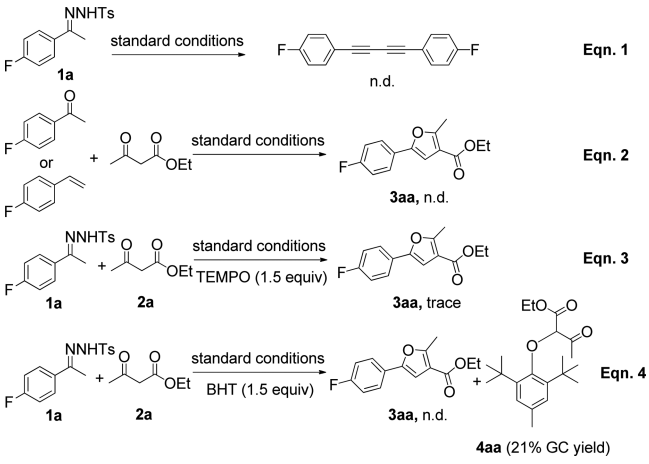
To further verify the mechanism of the oxidative cyclization reaction, a series of control experiments were carried out, and the results are shown in Scheme 2. When *N*-tosylhydrazone **1a** was used as the only substrate to react under the optimal conditions (Scheme 2, eq 1), no internal alkyne product was generated, which indicated that the reactions might not proceed via copper acetylide intermediates.[13] Moreover, when subjecting 4-fluoroacetophenone and 4-fluorostyrene and ethyl acetoacetate under

Table 3. Substrate Scope of *β*-Ketoesters[a]



[a]Reaction conditions: All reactions were performed with **1** (0.3 mmol), **2a** (0.45 mmol), CuCl (0.3 mmol), triallylamine (0.6 mmol), $Zn(OTf)_2$ (0.3 mmol), and 2.0 mL of solvent (DMF:toluene = 3:1) at 120 °C under an O_2 atmosphere for 10 h. Yields refer to the isolated yields.

Scheme 2. Mechanistic Studies



the standard conditions (Scheme 2, eq 2), no desired furan products were detected. This observation suggested that the oxidative cyclization reactions would not occur via the formations of ketones or olefin intermediates. Furthermore, only a trace amount of desired product was detected when 1.5 equiv of TEMPO was introduced into the standard reaction system (Scheme 2, eq 3). When 1.5 equiv of radical trapping reagent BHT was added to the standard reaction system, no desired product was detected. However, to our delight, ethyl acetoacetate radical intermediates could be caught by BHT and **4aa** was generated in 21% yield (Scheme 2, eq 4), which strongly support that the reaction should proceed via a radical cyclization pathway.

Interestingly, when the *N*-tosylhydrazone of 4-phenylacetophenone and 2-acetonaphthone, with large conjugated structures, were utilized as substrates, the olefin byproducts **4la** and

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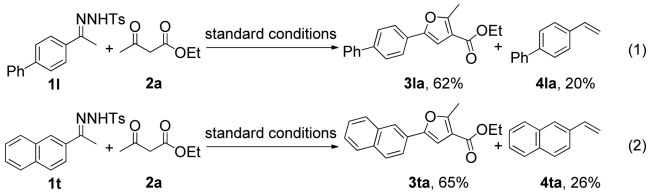
4ta, which were supposed to be generated through the protonation processes of vinyl copper intermediates, could be obtained in 20% and 26% yields, respectively, with the desired furans **3la** and **3ta** (Scheme 3).

Scheme 3. Formation of Olefins[a]



[a]Yields refer to the GC yields.

On the basis of the above experimental results, the plausible reaction mechanism to rationalize this Cu-mediated [3 + 2] oxidative cyclization reaction of *N*-tosylhydrazones and *β*-ketoesters is illustrated in Scheme 4. Initially, the diazo compound **A** is generated *in situ* from *N*-tosylhydrazone **1** in the presence of base,[13] which further reacts with copper(I) catalyst to form the copper(I) carbene species **B**. Then, the oxidation of **B** gives the vinyl copper(II) complex **C**.[15] Meanwhile, single-electron oxidation of *β*-ketoesters yields free radical intermediate **D**,[16] $Zn(OTf)_2$ as a Lewis acid might increase the activity of radical **D**,[17] which could subsequently attack the C1 positon of **C** to generate the radical intermediate **E**. After further oxidation and electronic rearrangement, **E** can convert into the vinyl copper(II) intermediate **F** (*path a*), and the intermediate **G** is subsequently formed through the departure of Lewis acid. Finally, the reductive elimination of **G**[18] releases the desired product **3** and copper(0) under reaction condition. Alternatively, radical intermediate **E** may also convert into heterocyclic intermediates **H** via intramolecular addition[19] (*path b*), and after further oxidation, **H** converts into the final product **3**.

In summary, a copper-mediated [3 + 2] oxidative cyclization reaction to afford 2,3,5-trisubstituted furans from *N*-tosylhydrazones and *β*-ketoesters has been developed, which is the first implementation of utilizing *N*-tosylhydrazones as two-carbon synthons. The formations of a vinyl copper complex and *β*-ketoester free radical intermediates are supposed to be the key steps of this oxidative cyclization process. This transformation provides a novel protocol in cyclization reactions and cross-couplings of hydrazone compounds, and presents potential applications in hydrazine chemistry. Furthermore, the uses of inexpensive metal catalyst, readily available substrates, high regioselectivity, as well as convenient operation make this innovative and practical method particularly attractive.

EXPERIMENTAL SECTION

General Information. Melting points were measured with a melting point instrument and were uncorrected. ^1H and ^{13}C NMR spectra were recorded using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is the solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a spectrometer. GC−MS was obtained using electron ionization. HRMS was obtained with an LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100−400 mesh silica gel plates, and visualization was effected at 254 nm. Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification.

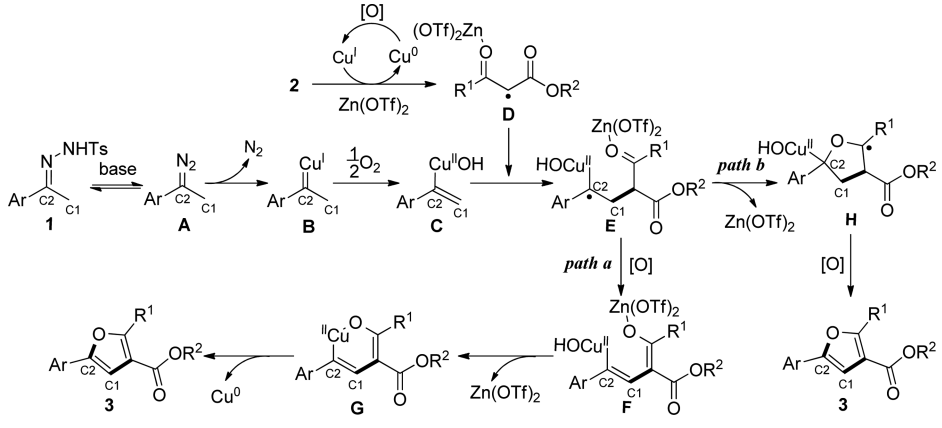
General Procedure for *N*-Tosylhydrazones. A mixture of ketone compounds (5.0 mmol) and *p*-toluenesulfonhydrazide (5.0 mmol) in 7.5 mL of MeOH was stirred at 70 °C for 0.5−3 h to afford the corresponding *N*-tosylhydrazone **1** as a white precipitate. After that, the precipitate was washed and filtered with petroleum ether twice and dried under vacuum to provide the pure compounds.

General Procedure for 2,3,5-Trisubstituted Furans. A mixture of *N*-tosylhydrazone (0.3 mmol), ethyl acetoacetate (0.45 mmol), CuCl (0.3 mmol), triallylamine (0.6 mmol), and $Zn(OTf)_2$ (0.3 mmol) in 2.0 mL of solvent (DMF:toluene = 3:1) was successively added to a Schlenk tube. The mixture was stirred under an O_2 atmosphere at 120 °C for 10 h. After that, water was added to quench the reaciton and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA = 30:1−50:1) as the eluent to afford the corresponding furans.

*Ethyl 5-(4-Fluorophenyl)-2-methylfuran-3-carboxylate (**3aa**).*[12a] Yield: 60 mg (81%), pale white solid, mp: 60−62 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.60 (t, J = 6.0 Hz, 2H), 7.07 (t, J = 8.4 Hz, 2H), 6.81 (s, 1H), 4.31 (q, J = 7.0 Hz, 2H), 2.63 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.0, 162.3 (d, J = 247.5 Hz), 158.6, 150.9, 126.5 (d, J = 3.3 Hz), 125.4 (d, J = 8.1 Hz), 115.8 (d, J = 22.0 Hz), 115.5, 105.2, 60.2, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1714, 1600, 1500, 1428, 1233, 1096, 1042; HRMS (ESI) calc. $C_{14}H_{13}FNaO_3$ $[M + Na]^+$: 271.0741, found: 271.0745.

*Ethyl 5-(4-Chlorophenyl)-2-methylfuran-3-carboxylate (**3ba**).*[12a] Yield: 64 mg (80%), pale white solid, M.p.: 77−79 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 6.87 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 1.37 (t, J = 7.1

Scheme 4. Proposed Mechanism



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Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.9, 158.9, 150.7, 133.3, 128.9, 128.6, 124.9, 115.6, 106.0, 60.3, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1691, 1480, 1430, 1390, 1235, 1089, 1040; HRMS (ESI) calc. $C_{14}H_{13}ClNaO_3$ [M + Na]$^+$: 287.0445, found: 287.0447.

*Ethyl 5-(4-Bromophenyl)-2-methylfuran-3-carboxylate (**3ca**).*[12a] Yield: 73 mg (80%), pale white solid, M.p.: 72−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.48 (s, 4H), 6.87 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.63 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.8, 158.9, 150.6, 131.8, 129.0, 125.1, 121.4, 115.6, 106.1, 60.3, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1698, 1604, 1477, 1425, 1386, 1232, 1094, 1038, 1005; HRMS (ESI) calc. $C_{14}H_{13}BrNaO_3$ [M + Na]$^+$: 330.9940, found: 330.9939.

*Ethyl 2-Methyl-5-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (**3da**).* Yield: 78 mg (87%), yellow solid, M.p.: 60−63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 6.91 (s, 1H), 4.24 (q, J = 6.6 Hz, 2H), 2.57 (s, 3H), 1.29 (t, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.7, 159.6, 150.2, 133.2, 129.2 (q, J = 32.7 Hz), 125.7 (q, J = 3.8 Hz), 124.1 (q, J = 272.0 Hz), 123.6, 115.8, 107.6, 60.4, 14.3, 13.9; IR (KBr, cm^{-1}): ν = 1713, 1616, 1435, 1327, 1245, 1160, 1107, 1067; HRMS (ESI) calc. $C_{15}H_{14}F_3O_3$ [M + H]$^+$: 299.0890, found: 299.0887.

*Ethyl 2-Methyl-5-(4-nitrophenyl)furan-3-carboxylate (**3ea**).* Yield: 69 mg (84%), yellow solid, M.p.: 129−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.11 (s, 1H), 4.34 (q, J = 6.7 Hz, 2H), 2.68 (s, 3H), 1.39 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.4, 160.6, 149.4, 146.6, 135.7, 124.3, 123.8, 116.3, 109.6, 60.5, 14.3, 14.0; IR (KBr, cm^{-1}): ν = 1702, 1602, 1509, 1436, 1332, 1243, 1101, 846; HRMS (ESI) calc. $C_{14}H_{13}NNaO_5$ [M + Na]$^+$: 298.0686, found: 298.0685.

*Ethyl 5-(4-(Methoxycarbonyl)phenyl)-2-methylfuran-3-carboxylate (**3fa**).*[20] Yield: 67 mg (77%), yellow solid, M.p.: 89−91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 6.8 Hz, 2H), 7.59 (d, J = 7.0 Hz, 2H), 6.93 (s, 1H), 4.27 (d, J = 6.0 Hz, 2H), 3.86 (s, 3H), 2.59 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 163.6, 159.5, 150.5, 133.8, 130.0, 128.7, 123.1, 115.7, 107.7, 60.2, 52.0, 14.3, 13.8; IR (KBr, cm^{-1}): ν = 1707, 1610, 1434, 1275, 1245, 1100, 1040; HRMS (ESI) calc. $C_{16}H_{16}NaO_5$ [M + Na]$^+$: 311.0890, found: 311.0898.

*Ethyl 2-Methyl-5-phenylfuran-3-carboxylate (**3ga**).*[12a] Yield: 44 mg (62%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.67 (d, J = 7.7 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 3.2 Hz, 1H), 6.91 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.68 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.1, 158.6, 151.7, 130.1, 128.7, 127.6, 123.7, 115.4, 105.5, 60.2, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1715, 1602, 1444, 1296, 1235, 1094, 1040; HRMS (ESI) calc. $C_{14}H_{14}NaO_3$ [M + Na]$^+$: 253.0835, found: 253.0838.

*Ethyl 2-Methyl-5-(p-tolyl)furan-3-carboxylate (**3ha**).*[12a] Yield: 49 mg (68%), pale white solid, M.p.: 59−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.82 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 2.36 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 158.3, 151.9, 137.5, 129.4, 127.4, 123.6, 115.3, 104.7, 60.2, 21.3, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1703, 1429, 1388, 1236, 1099, 1039; HRMS (ESI) calc. $C_{15}H_{16}NaO_3$ [M + Na]$^+$: 267.0992, found: 267.0986.

*Ethyl 5-(4-Ethylphenyl)-2-methylfuran-3-carboxylate (**3ia**).*[12a] Yield: 54 mg (71%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.83 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.64−2.69 (m, 5H), 1.38 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 158.3, 152.0, 143.9, 128.2, 127.7, 123.7, 115.3, 104.8, 60.2, 28.7, 15.5, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1716, 1606, 1426, 1234, 1095, 1043; HRMS (ESI) calc. $C_{16}H_{18}NaO_3$ [M + Na]$^+$: 281.1148, found: 281.1151.

*Ethyl 5-(4-Isopropylphenyl)-2-methylfuran-3-carboxylate (**3ja**).* Yield: 58 mg (70%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.55 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 4.30 (q, J = 6.5 Hz, 2H), 2.87−2.94 (m, 1H), 2.63 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H), 1.25 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 158.3, 152.0, 148.5, 127.8, 126.8, 123.8, 115.3, 104.8, 60.2, 33.9, 23.9, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1716, 1607, 1422, 1235, 1096, 1050; HRMS (ESI) calc. $C_{17}H_{20}NaO_3$ [M + Na]$^+$: 295.1305, found: 295.1305.

*Ethyl 5-(4-Methoxyphenyl)-2-methylfuran-3-carboxylate (**3ka**).*[12a] Yield: 43 mg (56%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.73 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.63 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 159.2, 158.0, 151.8, 125.1, 123.2, 115.3, 114.2, 103.8, 60.1, 55.3, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1714, 1604, 1502, 1427, 1246, 1176, 1096, 1033; HRMS (ESI) calc. $C_{15}H_{16}NaO_4$ [M + Na]$^+$: 283.0941, found: 283.0947.

*Ethyl 5-([1,1′-Biphenyl]-4-yl)-2-methylfuran-3-carboxylate (**3la**).*[21] Yield: 53 mg (58%), white solid, M.p.: 83−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.74 (d, J = 6.3 Hz, 2H), 7.65 (d, J = 6.7 Hz, 4H), 7.48 (s, 2H), 7.39 (s, 1H), 6.97 (s, 1H), 4.41−4.31 (m, 2H), 2.71 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.0, 158.7, 151.5, 140.5, 140.3, 129.1, 128.8, 127.4, 127.4, 126.9, 124.1, 115.6, 105.7, 60.2, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1715, 1606, 1418, 1235, 1097, 1045; HRMS (ESI) calc. $C_{20}H_{18}NaO_3$ [M + Na]$^+$: 329.1148, found: 329.1153.

*Ethyl 2-Methyl-5-(o-tolyl)furan-3-carboxylate (**3ma**).*[22] Yield: 48 mg (65%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.66 (d, J = 6.2 Hz, 1H), 7.21−7.24 (m, 3H), 6.76 (s, 1H), 4.32 (d, J = 6.3 Hz, 2H), 2.64 (s, 3H), 2.48 (s, 3H), 1.37 (t, J = 5.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 158.2, 151.2, 134.6, 131.2, 129.4, 127.7, 126.8, 126.0, 115.2, 109.1, 60.2, 21.9, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1716, 1609, 1418, 1234, 1092, 1033; HRMS (ESI) calc. $C_{15}H_{16}NaO_3$ [M + Na]$^+$: 267.0992, found: 267.0994.

*Ethyl 5-(2-Fluorophenyl)-2-methylfuran-3-carboxylate (**3na**).* Yield: 65 mg (87%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.76 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 6.2 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 5.6 Hz, 1H), 7.05 (s, 1H), 4.31 (q, J = 7.0 Hz, 2H), 2.65 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.0, 158.6, 158.5 (d, J = 251.1 Hz), 145.8 (d, J = 2.7 Hz), 128.6 (d, J = 8.3 Hz), 125.7 (d, J = 2.9 Hz), 124.2 (d, J = 3.5 Hz), 118.4 (d, J = 12.0 Hz), 116.1, 115.8 (d, J = 13.8 Hz), 115.7 (d, J = 1.4 Hz), 110.6 (d, J = 11.9 Hz), 60.2, 14.4, 13.8; IR (KBr, cm^{-1}): ν = 1717, 1607, 1489, 1421, 1237, 1092, 1039; HRMS (ESI) calc. $C_{14}H_{13}FNaO_3$ [M + Na]$^+$: 271.0741, found: 271.0741.

*Ethyl 5-(3-Fluorophenyl)-2-methylfuran-3-carboxylate (**3oa**).* Yield: 61 mg (82%), pale white solid, M.p.: 53−55 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.39 (d, J = 7.6 Hz, 1H), 7.30−7.34 (m, 2H), 6.94 (t, J = 8.3 Hz, 1H), 6.90 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.8, 163.1 (d, J = 244 Hz), 159.0, 150.5 (d, J = 2.9 Hz), 132.1 (d, J = 8.5 Hz), 130.3 (d, J = 8.5 Hz), 119.2 (d, J = 2.9 Hz), 115.6, 114.4 (d, J = 21.4 Hz), 110.5 (d, J = 23.7 Hz), 106.6, 60.3, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1701, 1611, 1428, 1233, 1185, 1094, 1040; HRMS (ESI) calc. $C_{14}H_{13}FNaO_3$ [M + Na]$^+$: 271.0741, found: 271.0744.

*Ethyl 5-(3-Chlorophenyl)-2-methylfuran-3-carboxylate (**3pa**).* Yield: 67 mg (85%), pale yellow solid, M.p.: 57−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.62 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 6.91 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.8, 159.1, 150.2, 134.8, 131.7, 130.0, 127.5, 123.6, 121.7, 115.6, 106.7, 60.3, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1715, 1608, 1556, 1424, 1236, 1098, 1047; HRMS (ESI) calc. $C_{14}H_{13}ClNaO_3$ [M + Na]$^+$: 287.0445, found: 287.0444.

*Ethyl 5-(3,4-Dimethylphenyl)-2-methylfuran-3-carboxylate (**3qa**).* Yield: 54 mg (70%), yellow solid, M.p.: 102−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.41 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 6.81 (s, 1H), 4.31 (q, J = 6.1 Hz, 2H), 2.63 (s, 3H), 2.27 (d, J = 9.0 Hz, 6H), 1.36 (t, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 158.2, 152.1, 136.9, 136.2, 130.0, 127.8, 124.9, 121.2, 115.3, 104.6, 60.1, 19.8, 19.6, 14.4, 13.9; IR (KBr, cm^{-1}): ν = 1699, 1599, 1427, 1224, 1094, 1020; HRMS (ESI) calc. $C_{16}H_{18}NaO_3$ [M + Na]$^+$: 281.1148, found: 281.1149.

*Ethyl 5-(2,5-Difluorophenyl)-2-methylfuran-3-carboxylate (**3ra**).* Yield: 72 mg (90%), yellow solid, M.p.: 78−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.43 (s, 1H), 7.12−7.00 (m, 2H), 6.89 (s, 1H), 4.32 (q, J = 7.0 Hz, 2H), 2.65 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101

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MHz, $CDCl_3$, ppm): δ = 163.7, 159.0, 158.8 (dd, J = 241.8, 2.1 Hz), 154.4 (dd, J = 247.0, 2.1 Hz), 144.8, 119.5 (dd, J = 14.7, 8.7 Hz), 117.0 (dd, J = 24.3, 8.9 Hz), 115.9 (d, J = 1.2 Hz), 114.7 (dd, J = 24.4, 8.7 Hz), 111.9 (dd, J = 26.5, 3.6 Hz), 111.6 (d, J = 12.5 Hz), 60.3, 14.3, 13.8; IR (KBr, cm^{-1}): ν = 1713, 1614, 1496, 1232, 1103, 1041; HRMS (ESI) calc. $C_{14}H_{12}F_2NaO_3$ $[M + Na]^+$: 289.0647, found: 289.0647.

*Ethyl 5-Methyl-[2,2′-bifuran]-4-carboxylate (**3sa**).* Yield: 28 mg (43%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.44 (s, 1H), 6.79 (s, 1H), 6.56 (s, 1H), 6.47 (d, J = 1.3 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.65 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.8, 158.4, 145.7, 144.3, 142.1, 115.1, 111.3, 105.5, 60.3, 14.3, 13.8; IR (KBr, cm^{-1}): ν = 1719, 1598, 1463, 1251, 1095; HRMS (ESI) calc. $C_{12}H_{12}NaO_4$ $[M + Na]^+$: 243.0628, found: 243.0623.

*Ethyl 2-Methyl-5-(naphthalen-2-yl)furan-3-carboxylate (**3ta**).*[22] Yield: 51 mg (61%), white solid, M.p.: 76−79 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.08 (s, 1H), 7.81 (dd, J = 17.7, 8.2 Hz, 3H), 7.69 (d, J = 8.4 Hz, 1H), 7.41−7.47 (m, 2H), 6.98 (s, 1H), 4.32 (q, J = 6.5 Hz, 2H), 2.67 (s, 3H), 1.37 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.1, 158.9, 151.8, 133.5, 132.8, 128.5, 128.2, 127.8, 127.4, 126.6, 126.1, 122.1, 122.0, 115.6, 106.1, 60.3, 14.4, 14.0; IR (KBr, cm^{-1}): ν = 1713, 1606, 1422, 1232, 1094, 1045; HRMS (ESI) calc. $C_{18}H_{16}NaO_3$ $[M + Na]^+$: 303.0992, found: 303.0985.

*Ethyl 5-(Benzo[d][1,3]dioxol-5-yl)-2-methylfuran-3-carboxylate (**3ua**).* Yield: 51 mg (62%), white solid, M.p.: 122−124 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 7.6 Hz, 1H), 7.09 (s, 1H), 6.82 (d, J = 7.8 Hz, 1H), 6.72 (s, 1H), 5.97 (s, 2H), 4.30 (q, J = 6.3 Hz, 2H), 2.62 (s, 3H), 1.36 (t, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.10, 158.08, 151.53, 148.04, 147.24, 124.52, 117.59, 115.32, 108.61, 104.46, 104.31, 101.20, 60.18, 14.38, 13.86; IR (KBr, cm^{-1}): ν = 1712, 495, 1450, 1270, 1232, 1094, 932; HRMS (ESI) calc. $C_{15}H_{14}NaO_5$ $[M + Na]^+$: 297.0733, found: 297.0731.

*Methyl 5-(4-Fluorophenyl)-2-methylfuran-3-carboxylate (**3ab**).*[23] Yield: 59 mg (83%), brown solid, M.p.: 92−95 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.59 (t, J = 6.2 Hz, 2H), 7.07 (t, J = 8.3 Hz, 2H), 6.80 (s, 1H), 3.84 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.4, 162.3 (d, J = 247.5 Hz), 158.7, 151.0, 126.4 (d, J = 3.3 Hz), 125.4 (d, J = 8.1 Hz), 115.8 (d, J = 22.0 Hz), 115.2, 105.1, 51.4, 13.8; IR (KBr, cm^{-1}): ν = 1702, 1594, 1498, 1443, 1230, 1096, 1039; HRMS (ESI) calc. $C_{13}H_{11}FNaO_3$ $[M + Na]^+$: 257.0584, found: 257.0584.

*Butyl 5-(4-Fluorophenyl)-2-methylfuran-3-carboxylate (**3ac**).* Yield: 72 mg (87%), yellow solid, M.p.: 49−51 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (t, J = 6.6 Hz, 2H), 7.06 (t, J = 8.4 Hz, 2H), 6.80 (s, 1H), 4.26 (t, J = 6.4 Hz, 2H), 2.63 (s, 3H), 1.72 (m, J = 7.0 Hz, 2H), 1.47 (m, J = 3.0 Hz, 2H), 0.98 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.1, 162.3 (d, J = 247.4 Hz), 158.5, 150.9, 126.5 (d, J = 3.3 Hz), 125.4 (d, J = 8.1 Hz), 115.7 (d, J = 22.0 Hz), 115.5, 105.2 (d, J = 1.3 Hz), 64.1, 30.8, 19.3, 13.9, 13.7; IR (KBr, cm^{-1}): ν = 1710, 1565, 1440, 1245, 1161, 1108, 1042; HRMS (ESI) calc. $C_{16}H_{17}FNaO_3$ $[M + Na]^+$: 299.1054, found: 299.1059.

*tert-Butyl 5-(4-Fluorophenyl)-2-methylfuran-3-carboxylate (**3ad**).* Yield: 72 mg (86%), brown oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.52 (t, J = 5.4 Hz, 2H), 6.99 (t, J = 7.7 Hz, 2H), 6.68 (s, 1H), 2.53 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.4, 162.2 (d, J = 247.3 Hz), 157.9, 150.6, 126.6 (d, J = 2.8 Hz), 125.4 (d, J = 8.1 Hz), 116.9, 115.7 (d, J = 21.9 Hz), 105.5, 80.7, 28.3, 13.9; IR (KBr, cm^{-1}): ν = 1709, 1599, 1499, 1401, 1235, 1166, 1096, 1034; HRMS (ESI) calc. $C_{16}H_{17}FNaO_3$ $[M + Na]^+$: 299.1054, found: 299.1057.

*Allyl 5-(4-Fluorophenyl)-2-methylfuran-3-carboxylate (**3ae**).* Yield: 66 mg (85%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.60 (t, J = 5.8 Hz, 2H), 7.07 (t, J = 8.0 Hz, 2H), 6.83 (s, 1H), 6.02 (dq, J = 10.0, 5.3 Hz, 1H), 5.39 (d, J = 17.1 Hz, 1H), 5.28 (d, J = 10.4 Hz, 1H), 4.77 (d, J = 4.8 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 163.6, 162.3 (d, J = 247.7 Hz), 158.9, 151.0, 132.4, 126.4 (d, J = 3.4 Hz), 125.5 (d, J = 8.1 Hz), 118.1, 115.8 (d, J = 22.0 Hz), 115.2, 105.1, 64.9, 13.9; IR (KBr, cm^{-1}): ν = 1716, 1599, 1499, 1404, 1229, 1091, 1038; HRMS (ESI) calc. $C_{15}H_{13}FNaO_3$ $[M + Na]^+$: 283.0741, found: 283.0739.

*Ethyl 5-(4-Fluorophenyl)-2-phenylfuran-3-carboxylate (**3af**).* Yield: 83 mg (90%), white solid, M.p.: 93−95 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.06 (d, J = 7.0 Hz, 2H), 7.70 (s, 2H), 7.45 (t, J = 9.8 Hz, 3H), 7.11 (t, J = 7.7 Hz, 2H), 7.03 (s, 1H), 4.34 (q, J = 6.3 Hz, 2H), 1.37 (t, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.5, 162.6 (d, J = 248.0 Hz), 156.5, 151.5, 129.7, 129.4, 128.4, 128.2, 126.2 (d, J = 2.9 Hz), 125.8 (d, J = 8.2 Hz), 115.9 (d, J = 22.0 Hz), 115.8, 107.6, 60.7, 14.3; IR (KBr, cm^{-1}): ν = 1717, 1593, 1495, 1227, 1094; HRMS (ESI) calc. $C_{19}H_{15}FNaO_3$ $[M + Na]^+$: 333.0897, found: 333.0893.

*Ethyl 2-Ethyl-5-(4-fluorophenyl)furan-3-carboxylate (**3ag**).* Yield: 70 mg (89%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.60 (s, 2H), 7.06 (t, J = 8.0 Hz, 2H), 6.81 (s, 1H), 4.31 (q, J = 6.4 Hz, 2H), 3.06 (q, J = 6.6 Hz, 2H), 1.36 (t, J = 6.6 Hz, 3H), 1.31 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.9, 163.4, 162.3 (d, J = 247.3 Hz), 150.8, 126.5 (d, J = 3.1 Hz), 125.4 (d, J = 8.1 Hz), 115.7 (d, J = 22.0 Hz), 114.6, 105.2, 60.2, 21.3, 14.3, 12.3; IR (KBr, cm^{-1}): ν = 1715, 1598, 1500, 1231, 1101, 1050; HRMS (ESI) calc. $C_{15}H_{15}FNaO_3$ $[M + Na]^+$: 285.0897, found: 285.0899.

*Ethyl 5-(4-Fluorophenyl)-2-isopropylfuran-3-carboxylate (**3ah**).* Yield: 72 mg (85%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.61 (t, J = 6.0 Hz, 2H), 7.08 (t, J = 8.0 Hz, 2H), 6.81 (s, 1H), 4.31 (q, J = 6.6 Hz, 2H), 3.80 (m, J = 6.6 Hz, 1H), 1.33−1.38 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 166.6, 163.9, 162.3 (d, J = 247.0 Hz), 150.5, 126.6 (d, J = 3.4 Hz), 125.4 (d, J = 8.1 Hz), 115.7 (d, J = 22.0 Hz), 113.6, 105.2, 60.2, 27.4, 20.8, 14.4; IR (KBr, cm^{-1}): ν = 1715, 1596, 1500, 1382, 1229, 1060; HRMS (ESI) calc. $C_{16}H_{17}FNaO_3$ $[M + Na]^+$: 299.1054, found: 299.1051.

*Ethyl 2-Cyclopropyl-5-(4-fluorophenyl)furan-3-carboxylate (**3ai**).* Yield: 68 mg (84%), pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50 (t, J = 5.8 Hz, 2H), 7.04 (t, J = 7.8 Hz, 2H), 6.78 (s, 1H), 4.32 (q, J = 6.5 Hz, 2H), 2.82 (m, J = 6.6 Hz,1H), 1.37 (t, J = 6.5 Hz, 3H), 1.07−1.13 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 164.2, 162.6, 162.2 (d, J = 247.3 Hz), 149.5, 126.4 (d, J = 3.3 Hz), 125.2 (d, J = 8.0 Hz), 115.7 (d, J = 22.0 Hz), 115.0, 105.5, 60.2, 14.4, 9.3, 8.9; IR (KBr, cm^{-1}): ν = 1713, 1596, 1501, 1426, 1229, 1065; HRMS (ESI) calc. $C_{16}H_{15}FNaO_3$ $[M + Na]^+$: 297.0897, found: 297.0896.

*Ethyl 5-(4-Fluorophenyl)-2-propylfuran-3-carboxylate (**3aj**).* Yield: 71 mg (86%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, J = 8.2, 5.5 Hz, 2H), 7.07 (t, J = 8.5 Hz, 2H), 6.82 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H), 1.77 (m, J = 7.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.9, 162.5, 162.3 (d, J = 247.5 Hz), 150.8, 126.6 (d, J = 3.2 Hz), 125.5 (d, J = 8.1 Hz), 115.8 (d, J = 22.0 Hz), 115.2, 105.2, 60.2, 29.6, 21.6, 14.4, 13.8; IR (KBr, cm^{-1}): ν = 1716, 1598, 1501, 1428, 1229, 1106, 1054; HRMS (ESI) calc. $C_{16}H_{17}FNaO_3$ $[M + Na]^+$: 299.1054, found: 299.1060.

*Ethyl 2-(tert-Butyl)-5-(4-fluorophenyl)furan-3-carboxylate (**3ak**).* Yield: 64 mg (74%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.60 (t, J = 6.6 Hz, 2H), 7.07 (t, J = 8.0 Hz, 2H), 6.87 (s, 1H), 4.31 (q, J = 6.5 Hz, 2H), 1.49 (s, 9H), 1.38 (t, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 167.6, 163.6, 162.2 (d, J = 247.5 Hz), 148.8, 126.6 (d, J = 3.5 Hz), 125.4 (d, J = 8.1 Hz), 115.8 (d, J = 22.0 Hz), 114.2, 107.2, 60.3, 34.8, 28.2, 14.3; IR (KBr, cm^{-1}): ν = 1722, 1594, 1498, 1377, 1239, 1158, 1067; HRMS (ESI) calc. $C_{17}H_{19}FNaO_3$ $[M + Na]^+$: 313.1210, found: 313.1210.

*Ethyl 5-(4-Fluorophenyl)-2-(thiophen-2-yl)furan-3-carboxylate (**3al**).* Yield: 82 mg (86%), white solid. M.p.: 83−85 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 3.7 Hz, 1H), 7.65 (dd, J = 8.3, 5.5 Hz, 2H), 7.43 (d, J = 5.0 Hz, 1H), 7.06−7.13 (m, 3H), 6.94 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.2, 162.6 (d, J = 248.4 Hz), 152.0, 150.8, 131.6, 128.8, 128.0, 127.5, 125.9 (d, J = 3.4 Hz), 125.8 (d, J = 8.2 Hz), 115.9 (d, J = 22.1 Hz), 114.2, 107.2, 60.7, 14.4; IR (KBr, cm^{-1}): ν = 1712, 1538, 1562, 1497, 1383, 1242, 1096; HRMS (ESI) calc. $C_{17}H_{13}FNaO_3S$ $[M + Na]^+$: 339.0462, found: 339.0465.

■ ASSOCIATED CONTENT

Supporting Information

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Spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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