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PAPER

Selective synthesis of 2,5-disubstituted furan-3-carboxylates and the isomeric 2,4-disubstituted furan-3-carboxylates†

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An unprecedented Ag_2CO_3 and DBU mediated cyclization of 3-substituted 2-(2-bromoallyl)-3-oxo-1-carboxylates leading to the formation of 2,5-disubstituted furan-3-carboxylates has been reported. In the absence of a silver salt, the isomeric 2,4-disubstituted furan-3-carboxylates are obtained.

Introduction

Furans are a fundamental class of five-membered heterocycles. Especially, functionalized furans play an important role as structural elements of many natural products (*e.g.* pochonin G **I**,[1] sarcofuranocembrenolide B **II**,[2] and the sesquiterpenoid **III**[3] isolated from the mycelia of the edible mushroom *Pleurotus cornucopiae* fermented on rice, Fig. 1) which have shown diverse biological properties, such as hair-growth stimulation,[1] anti-allergic,[2] antiapoptotic,[2] and anticancer activities.[3] Moreover, they are important building blocks in organic synthesis.[4] Therefore, the synthesis of furans has attracted a great deal of attention from synthetic organic chemists. Generally, there are two strategies to construct the furan ring: (i) Paal–Knorr synthesis,[5] *i.e.* cyclization of 1,4-dicarbonyl compounds; (ii) cyclization of propargyl/allyl dicarbonyl compounds,[6] allenyl ketones,[7] enynols,[8] alkynyl epoxides[9] or propargyl ethers.[10] Transition metals, $PhI(O_2CCF_3)_2$, PhSeSePh, NBS and even iodine could be used as catalysts for these transformations to obtain highly substituted furans.

Over the last decades, silver-mediated cyclization for the construction of heterocyclic compounds has received considerable attention.[11] Recently, Lei and co-worker have developed useful silver-mediated oxidative cross-coupling/cyclization strategies between 2-aminopyridines,[12] 1,3-dicarbonyl compounds,[13] β-enamino esters[14] and terminal alkynes to create polysubstituted imidazole[1,2-*a*]pyridines, furans, and pyrroles,

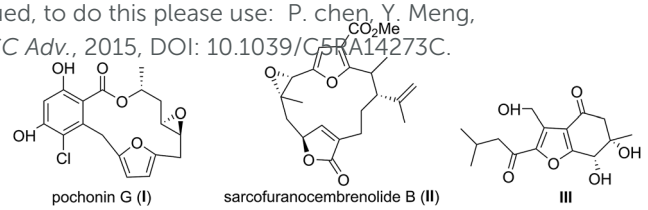
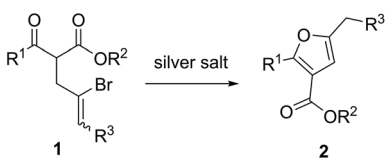


Fig. 1 Representative furan natural products.



Scheme 1 Proposed silver-mediated cyclization to form 2,5-disubstituted furan-3-carboxylates.

respectively. Silver-mediated intramolecular addition of heteroatoms to acetylene,[15] alkene,[16] and allenic intermediates[17] has also been widely applied in the assembly of bioactive heterocycles. Given that 3-substituted 2-(2-bromoallyl)-3-oxo-1-carboxylates **1** could be easily accessed through nucleophilic substitution of 2,3-dibromo-1-propene with 3-oxo-1-propanoates,[6j,18] we wonder a silver-mediated cyclization would lead to the formation of furan-3-carboxylates **2** (Scheme 1). To the best of our knowledge, this demonstration represents the first silver-mediated cyclization of 3-substituted 2-(2-bromoallyl)-3-oxo-1-carboxylates to poly-substituted furans.

Results and discussion

Initial study was carried out with methyl 2-benzoyl-4-bromopent-4-enoate **1a**, which was treated with 2 equivalent

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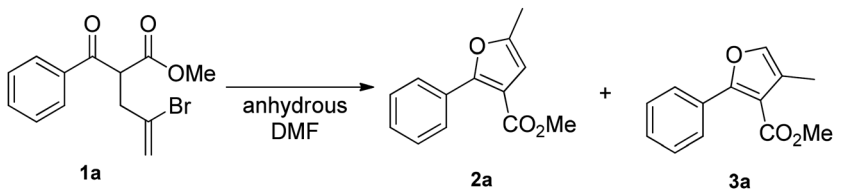
of DBU and a catalytic amount of Ag_2CO_3 (0.05 eq.) at 60 °C (entry 1, Table 1). When the reaction was complete (6 h), two main spots appeared on the TLC plate. After being separated by column chromatography, the two products were found to be the desired furan **2a** and the isomerized product **3a**, respectively. Inspired by the results, we then optimized the reaction conditions in order to obtain either regioisomer selectively.

In the presence of 2 equivalent of DBU, the ratio of **2a** : **3a** improved with increased loading of Ag_2CO_3 (entries 1 and 3–6, Table 1). When 0.5 equivalent of Ag_2CO_3 was used, **2a** was isolated as the sole product in 83% yield (entry 6). The ratio of **2a** : **3a** decreased either changing the base from DBU to Cs_2CO_3 (entry 7 *vs.* 6), or changing the silver salt from Ag_2CO_3 to $AgNO_3$/silica gel (entry 2 *vs.* 1). In the absence of a base, no reaction occurred at all (entry 8). When silver salt was removed from the reaction system, isomer **3a** was the only product obtained although the reaction proceeded slowly and only moderate yield was obtained (entry 9). Inspired by the findings and in order to obtain **3a** selectively, we then explored other bases. Similar to DBU, when conducted in the presence of K_3PO_4 or $NaHCO_3$, the reaction was sluggish and **3a** was isolated in a moderate yield (entries 10 and 11). To our delight, when K_2CO_3 was applied, the reaction was complete in much shorter time and **3a** was isolated in good yield (entry 12). Even better result was obtained when Cs_2CO_3 was used (entry 13). With Cs_2CO_3 as our optimized base, we next investigated the effect of the reaction temperature. The reaction proceeded slowly at temperatures below 60 °C while the yield of **3a** was moderate (entries 14 and 15). By contrast, at temperatures above 60 °C, the reaction proceeded much faster and the product yield was higher (entries 16–18). When the reaction was conducted at 80 °C, **3a** was isolated in the highest yield (92%) (entry 17). Slightly less satisfactory result was obtained when the reaction temperature was raised to 90 °C (entry 18). Finally, we inspected the effect of the quantities of Cs_2CO_3 to the reaction (entries 17 and 19–21) and found that the reaction could work equally well when as low as 0.75 equivalent of the base was applied (entry 20). Further reduction of the amount of Cs_2CO_3 resulted in reduced yield of the product (entry 21).

Having the optimized reaction conditions in hand, we then tested the generality and scope of the present 2,5-disubstituted furan-3-carboxylates and 2,4-disubstituted furan-3-carboxylates, and the results were collected in Table 2. In the presence of 0.5 equivalent of Ag_2CO_3 and 2 equivalent of DBU, the reactions of 3-aryl substituted substrates **1** bearing either an electron-donating group (entries 2 and 3) or electron-withdrawing

Table 1 Optimization of the reaction conditions for the selective formation of **2a** or **3a**, respectively[a]



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

Entry	Base	Silver salt	Temperature (°C)	Reaction time (h)	Ratio of **2a** : **3a**	Yield (%)
1	DBU (2)[b]	Ag_2CO_3 (0.05)[b]	60	6	1 : 3[c]	
2	DBU (2)[b]	$AgNO_3$/silica gel (0.05)[b]	60	6	1 : 8[c]	
3	DBU (2)[b]	Ag_2CO_3 (0.25)[b]	60	5.5	1 : 0.15[c]	
4	DBU (2)[b]	Ag_2CO_3 (0.35)[b]	60	4	1 : 0.03[c]	
5	DBU (2)[b]	Ag_2CO_3 (0.4)[b]	60	3.5	1 : 0.02[c]	
6	**DBU** (2)[b]	**Ag_2CO_3** (0.5)[b]	**60**	**1**	**1 : 0**	**83**[e]
7	Cs_2CO_3 (2)[b]	Ag_2CO_3 (0.5)[b]	60	1	1 : 0.14[c]	
8	—	Ag_2CO_3 (0.5)[b]	60	20	—[d]	
9	DBU (2)[b]	—	60	12	0 : 1	45[e]
10	K_3PO_4 (2)[b]	—	60	25	0 : 1	60[e]
11	$NaHCO_3$ (2)[b]	—	60	22	0 : 1	40[e]
12	K_2CO_3 (2)[b]	—	60	4	0 : 1	74[e]
13	Cs_2CO_3 (2)[b]	—	60	3	0 : 1	78[e]
14	Cs_2CO_3 (2)[b]	—	40	9	0 : 1	46[e]
15	Cs_2CO_3 (2)[b]	—	50	8	0 : 1	70[e]
16	Cs_2CO_3 (2)[b]	—	70	1	0 : 1	85[e]
17	Cs_2CO_3 (2)[b]	—	80	0.7	0 : 1	92[e]
18	Cs_2CO_3 (2)[b]	—	90	0.6	0 : 1	89[e]
19	Cs_2CO_3 (1)[b]	—	80	0.7	0 : 1	92[e]
20	**Cs_2CO_3** (0.75)[b]	—	**80**	**0.7**	**0 : 1**	**92**[e]
21	Cs_2CO_3 (0.5)[b]	—	80	0.7	0 : 1	70[e]

[a] Anhydrous DMF was found to be the most appropriate solvent through screening. [b] Numbers in parenthesis indicated the equivalents of reagents used. [c] Ratio determined on the basis of ^{1}H NMR integration of the crude reaction mixture. [d] No reaction. [e] Isolated yields.

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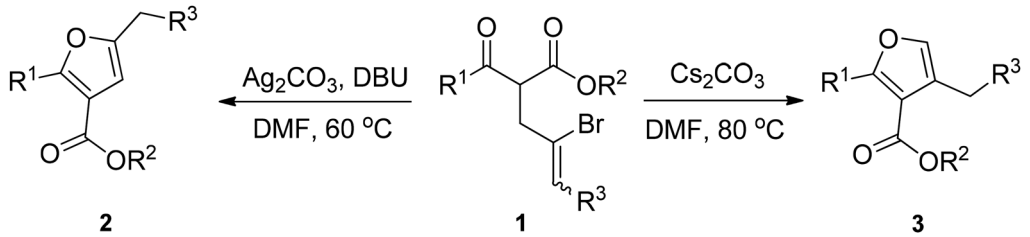
Table 2 Substrate scope for the selective formation of 2,5-disubstituted furan-3-carboxylates **2** or 2,4-disubstituted furan-3-carboxylates **3**, respectively



2 **1** **3**

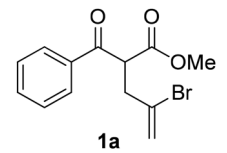
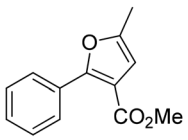
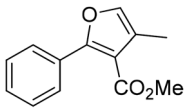
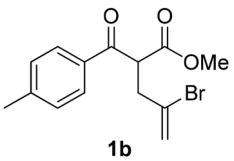
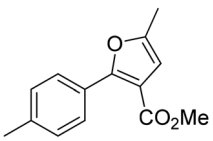
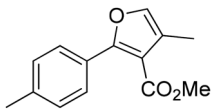
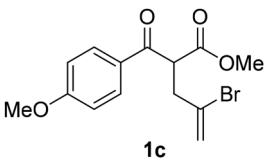
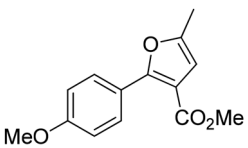
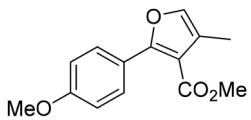
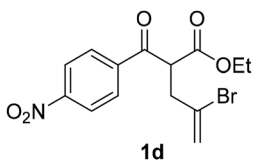
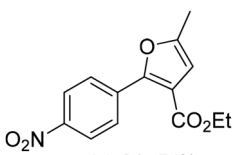
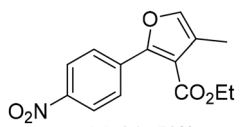
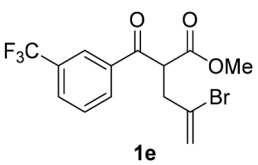
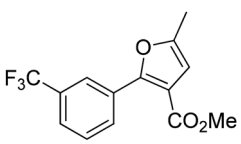
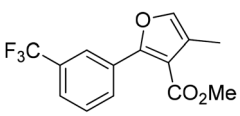
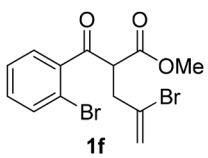
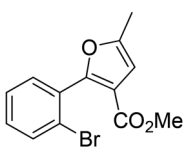
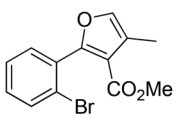
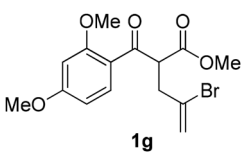
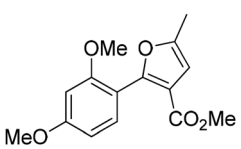
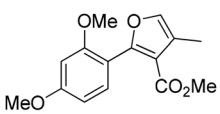
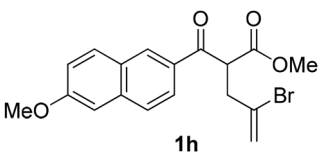
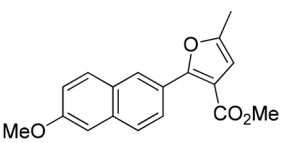
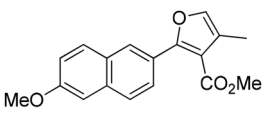
Entry	Substrate	2,5-Disubstituted furan-3-carboxylates	2,4-Disubstituted furan-3-carboxylates
1	 **1a**	 **2a**, 1 h, 83%	 **3a**, 0.7 h, 92%
2	 **1b**	 **2b**, 1 h, 70%	 **3b**, 1 h, 90%
3	 **1c**	 **2c**, 0.8 h, 75%	 **3c**, 1 h, 85%
4	 **1d**	 **2d**, 2 h, 74%	 **3d**, 3 h, 58%
5	 **1e**	 **2e**, 4 h, 69%	 **3e**, 2 h, 65%
6	 **1f**	 **2f**, 1 h, 85%	 **3f**, 3 h, 80%
7	 **1g**	 **2g**, 0.8 h, 38%	 **3g**, 0.8 h, 82%
8	 **1h**	 **2h**, 1 h, 65%	 **3h**, 0.8 h, 80%

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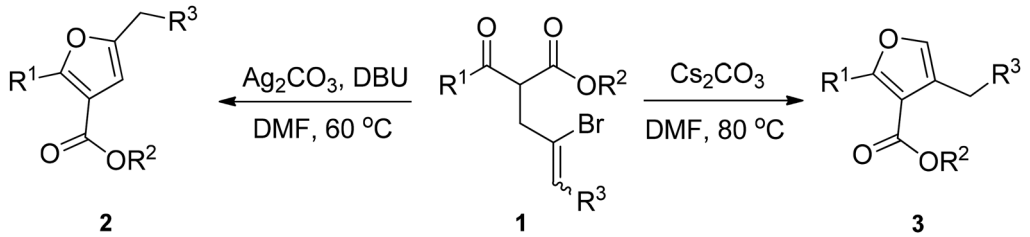
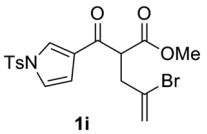
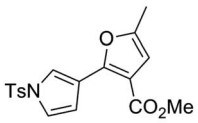
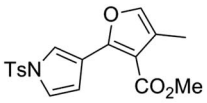
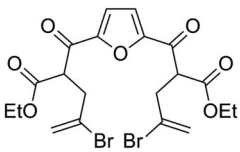
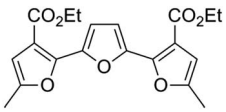
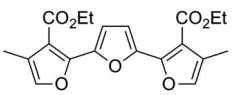
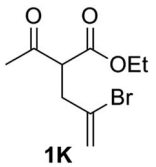
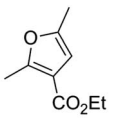
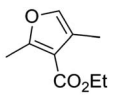
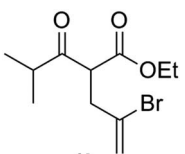
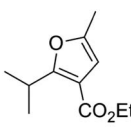
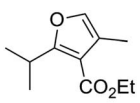
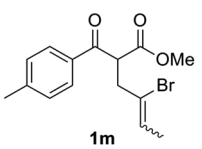
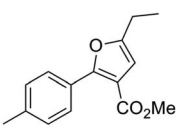
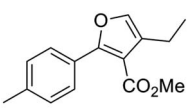
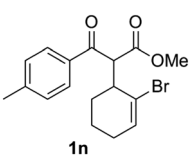
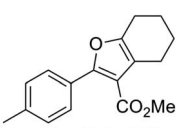
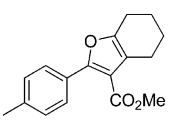
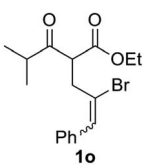
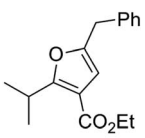
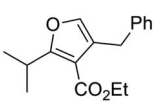
Table 2 (*Contd.*)



2 1 3

Entry	Substrate	2,5-Disubstituted furan-3-carboxylates	2,4-Disubstituted furan-3-carboxylates
9	 **1i**	 **2i**, 1 h, 68%	 **3i**, 0.8 h, 78%
10	 **1j**	 **2j**, 1h, 64%	 **3j**, 1 h, 60%
11	 **1K**	 **2K**, 0.8 h, 88%	 **3K**, 1 h, 85%
12	 **1l**	 **2l**, 0.8 h, 55%	 **3l**, 1 h, 76%
13	 **1m**	 **2m**, 6 h, 80%	 **3m**, 5 h, 60%
14	 **1n**	 **2n**, 15 h, 52%	 **2n**, 25 h, 11%[a]
15	 **1o**	 **2o**, 5 h, 89%	 **3o**, 1 h, 71%

[a] 75% of the unreacted **1n** was recovered.

group (entries 4–6) at the phenyl ring proceeded smoothly to give 2,5-disubstituted furan-3-carboxylates **2b–f** in good yields. However, reaction of substrate **1g** having a 2,4-dimethoxyphenyl ring gave **2g** in poor yield (entry 7). Under the reaction conditions, both substrates bearing naphthalyl and protected pyrrolyl group (**1h** and **1i**) could cyclize to afford good yields of the

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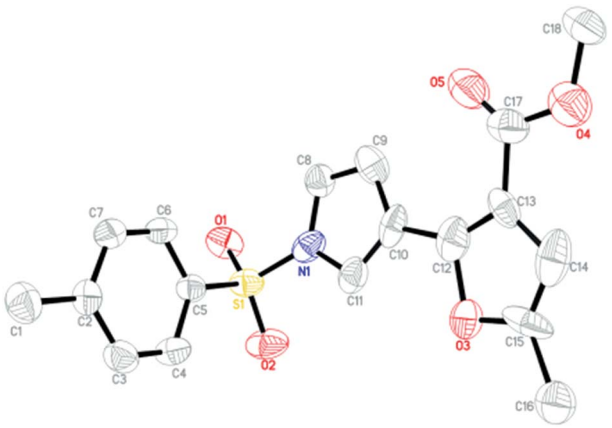


Fig. 2 X-ray single crystal structure of **2i**.

expected products **2h** and **2i**, respectively (entries 8 and 9). The structure of **2i** was unambiguously confirmed by X-ray single crystal diffraction (Fig. 2).[19] Aliphatic β-keto esters **1k** and **1l** (entries 11 and 12), as well as substrates with a substituted 2-bromoallyl moiety **1m–o** (entries 13–15) could also be converted into the corresponding furan-3-carboxylates **2k–o** in good to excellent isolated yield. To our delight, trifuran **2j** was obtained in good yield starting from **1j** (entry 10). On the other hand, in the presence of 0.75 equivalent of Cs_2CO_3, most substrates reacted smoothly to give 2,4-disubstituted furan-3-carboxylates in good to excellent isolated yield (entries 1–13 and 15). In general, substrates bearing electron-donating groups at the phenyl ring (entries 2, 3 and 7) gave higher yields than those bearing electron-withdrawing groups (entries 4 and 5). Quite unexpectedly, reaction of substrate **1n** was sluggish. After 25 h, the desired product **2n** was isolated in 11% yield together with substantial amount (75%) of the unreacted starting material recovered.

Based on the above results and literature reports, plausible mechanisms for the regioselective formation of 2,5-disubstituted furan-3-carboxylates **2** and 2,4-disubstituted furan-3-carboxylates **3** were proposed in Scheme 2. Base promoted elimination of **1** generated the allenic intermediate **I**. Intramolecular attack of the allene function with the enolate carbon gave methylenecyclopropane **III**.[20] Activation of the double bond in **III** with silver[7b,21] (path a) followed by concomitant cyclopropane ring opening and cyclization would generate **V**.[22] β-Elimination of **V** gave **VI**, which aromatized to produce furan **2** by tautomerization. On the other hand, in the absence of silver salt, cyclopropane ring opening and subsequent intramolecular nucleophilic attack at the less sterically hindered carbon atom in the cyclopropane ring[20,23] (path b) would generate **VII**, which tautomerized to produce 2,4-disubstituted furan-3-carboxylates **3**.

Conclusion

In summary, we have developed a valuable approach towards the synthesis of 2,5-disubstituted furan-3-carboxylates and the isomeric 2,4-disubstituted furan-3-carboxylates. The former was accessed by treatment of 3-substituted 2-(2-bromoallyl)-3-oxo-1-carboxylates with Ag_2CO_3/DBU, while the latter could be easily obtained by treatment of the same substrates with Cs_2CO_3.

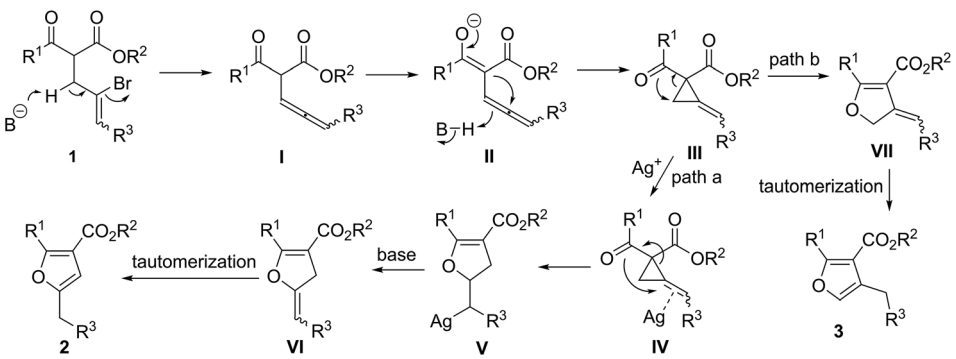
Experimental section

General information

Melting points were determined on a XT4A hot-stage apparatus and are uncorrected. IR spectra were obtained using an IFS25 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Agilent AV400 instrument. High-resolution mass spectra were recorded on a Micromass Q-TOF mass spectrometer. Flash column chromatography was performed over silica gel 200–300 mesh.

General procedure for the synthesis of 2,5-disubstituted furan-3-carboxylates (2a–o)

DBU (2.0 mmol) and silver carbonate (0.5 mmol) were added to a solution of 3-substituted 2-(2-bromoallyl)-3-oxo-1-carboxylates (**1a–o**) (1.0 mmol) in anhydrous DMF (15 mL). The resulting mixture was stirred at 60 °C until the substrate was consumed (monitored by TLC). After being cooled to ambient temperature, the mixture was treated with 1 M HCl (5 mL) and filtered. The filtrate was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were washed with brine (10 mL), then dried over anhydrous sodium sulphate, filtered and



Scheme 2 Proposed mechanism for the regioselective formation of 2,5-disubstituted furan-3-carboxylates **2** and 2,4-disubstituted furan-3-carboxylates **3**.

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concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford 2,3,5-trisubstituted furans **2a–o**.

Methyl 5-methyl-2-phenylfuran-3-carboxylate (2a).[6a] The crude product was purified by column chromatography on silica gel (1% ethyl acetate in petroleum ether) to give **2a** as a colorless oil; yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H), 7.44–7.35 (m, 3H), 6.43 (s, 1H), 3.81 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 156.2, 151.3, 130.1, 129.1, 128.1, 114.2, 108.8, 51.6, 51.4, 13.5; IR (neat): ν_{max}/cm^{-1} 1721, 1559, 1492, 1435, 1378, 1274, 1212, 1097, 1016; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{13}O_3$: 217.0859 $[M + H]^+$; found 217.0859.

Methyl 5-methyl-2-(4′-methylphenyl)furan-3-carboxylate (2b).[6a] The crude product was purified by column chromatography on silica gel (0.5% ethyl acetate in petroleum ether) to give **2b** as an orange oil; yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.41 (s, 1H), 3.80 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 156.6, 150.9, 139.2, 128.9, 128.1, 127.3, 113.6, 108.7, 51.6, 21.5, 13.5; IR (neat): ν_{max}/cm^{-1} 1719, 1587, 1480, 1381, 1223, 1086; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{15}O_3$: 231.1016 $[M + H]^+$; found 231.1016.

Methyl 2-(4′-methoxyphenyl)-5-methylfuran-3-carboxylate (2c). The crude product was purified by column chromatography on silica gel (5% ethyl acetate in petroleum ether) to give **2c** as an orange oil; yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.94 (m, 2H), 6.99–6.95 (m, 2H), 6.41 (q, J = 1.0 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.35 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 160.2, 156.4, 150.5, 129.6, 122.7, 113.5, 112.8, 108.5, 55.3, 51.4, 13.3; IR (neat): ν_{max}/cm^{-1} 1717, 1609, 1580, 1504, 1440, 1378, 1303, 1210; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{15}O_4$: 247.0965 $[M + H]^+$; found 247.0962.

Ethyl 5-methyl-2-(4′-nitrophenyl)furan-3-carboxylate (2d). The crude product was purified by column chromatography on silica gel (3% ethyl acetate in petroleum ether) to give **2d** as a yellow solid; yield 74%; mp 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.20 (m, 4H), 6.50 (q, J = 1.0 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 2.38 (d, J = 1.0 Hz, 1H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 153.0, 152.8, 147.3, 135.8, 128.4, 123.5, 117.7, 110.0, 61.0, 14.3, 13.5; IR (KBr): ν_{max}/cm^{-1} 1724, 1598, 1569, 1516, 1354, 1313, 1300, 1281, 1260, 1215, 1095, 1028; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{14}NO_5$: 276.0866 $[M + H]^+$; found 276.0865.

Methyl 5-methyl-2-(3′-trifluoromethylphenyl)furan-3-carboxylate (2e). The crude product was purified by column chromatography on silica gel (0.5% ethyl acetate in petroleum ether) to give **2e** as an orange oil; yield 69%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 6.46 (s, 1H), 3.83 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 154.1, 151.9, 131.1 (q, J_{F-C} = 1.2 Hz), 130.6, 130.5 (q, J_{F-C} = 32.3 Hz), 128.5, 125.3 (q, J_{F-C} = 3.7 Hz), 124.8 (q, J_{F-C} = 4.0 Hz), 124.0 (q, J_{F-C} = 270.8 Hz), 115.3, 109.1, 51.7, 13.4; IR (neat): ν_{max}/cm^{-1} 1722, 1558, 1439, 1380, 1330, 1268, 1215, 1168, 1127, 1102, 1030; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{12}F_3O_3$: 285.0733 $[M + H]^+$; found 285.0723.

Methyl 2-(2′-bromophenyl)-5-methylfuran-3-carboxylate (2f). The crude product was purified by column chromatography on silica gel (2% ethyl acetate in petroleum ether) to give **2f** as a colorless oil; yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 1H), 7.37 (m, 1H), 7.29 (m, 1H), 7.20 (m, 1H), 6.36 (q, J = 1.0 Hz, 1H), 3.62 (s, 3H), 2.28 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 155.0, 152.3, 132.9, 132.3, 132.1, 130.8, 126.9, 124.0, 116.7, 107.2, 51.6, 13.6; IR (neat): ν_{max}/cm^{-1} 1723, 1570, 1467, 1438, 1383, 1275, 1209, 1102, 1058; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{12}{}^{79}BrO_3$: 294.9964 $[M + H]^+$; found 294.9963.

Methyl 2-(2′,4′-dimethoxyphenyl)-5-methylfuran-3-carboxylate (2g). The crude product was purified by column chromatography on silica gel (7% ethyl acetate in petroleum ether) to give **2g** as a colorless oil; yield 38%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 1H), 6.56–6.49 (m, 2H), 6.37 (q, J = 1.0 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 2.32 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 161.9, 158.5, 153.5, 151.1, 138.8, 131.9, 115.5, 107.2, 104.3, 98.7, 55.6, 55.4, 51.2, 13.4; IR (neat): ν_{max}/cm^{-1} 1719, 1623, 1582, 1504, 1438, 1280, 1209, 1090, 1032; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{17}O_5$: 277.1071 $[M + H]^+$; found 277.1073.

Methyl 2-(6′-methoxynaphthalen-2′-yl)-5-methylfuran-3-carboxylate (2h). The crude product was purified by column chromatography on silica gel (10% ethyl acetate in petroleum ether) to give **2h** as a yellow solid; yield 65%; mp 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (m, 1H), 8.03 (m, 2H), 7.81 (m, 1H), 7.76 (m, 1H), 7.17–7.13 (m, 2H), 6.45 (q, J = 1.0 Hz, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 2.38 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 158.4, 156.4, 151.0, 134.7, 130.3, 128.4, 127.6, 126.4, 125.9, 119.1, 113.8, 108.8, 105.6, 55.3, 51.5, 29.7, 13.4; IR (KBr): ν_{max}/cm^{-1} 1714, 1626, 1602, 1548, 1496, 1392, 1278, 1259, 1202, 1164, 1092, 1031; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{16}NaO_4$: 319.0941 $[M + Na]^+$; found 319.0943.

Methyl 5-methyl-2-(*N*-tosyl-1*H*-pyrrol-3′-yl)furan-3-carboxylate (2i). The crude product was purified by column chromatography on silica gel (10% ethyl acetate in petroleum ether) to give **2i** as a colorless solid; yield 68%; mp 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (m, 1H), 7.84–7.82 (m, 2H), 7.31 (m, 2H), 7.18 (m, 1H), 6.94 (m, 1H), 6.33 (q, J = 1.2 Hz, 1H), 3.85 (s, 3H), 2.41 (s, 3H), 2.31 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 151.6, 150.4, 145.3, 135.9, 130.2, 127.2, 120.8, 119.1, 113.0, 112.8, 108.1, 51.5, 21.8, 13.4; IR (KBr): ν_{max}/cm^{-1} 1713, 1649, 1620, 1594, 1439, 1366, 1293, 1266, 1258, 1189, 1173, 1086; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{17}NNaO_5S$: 382.0720 $[M + Na]^+$; found 382.0729.

Diethyl 5,5″-dimethyl-[2,2′:5′,2″-terfuran]-3,3″-dicarboxylate (2j). The crude product was purified by column chromatography on silica gel (2% ethyl acetate in petroleum ether) to give **2j** as a yellow solid; yield 64%; mp 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H), 6.43 (q, J = 1.2 Hz, 2H), 4.33 (q, J = 7.1 Hz, 4H), 2.40 (d, J = 1.2 Hz, 6H), 1.37 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 151.8, 147.0, 144.8, 144.7, 114.6, 108.7, 60.6, 14.5, 13.7; IR (KBr): ν_{max}/cm^{-1} 1713, 1607, 1538, 1378, 1261, 1215, 1100, 1052, 1024; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}NaO_7$: 395.1101 $[M + Na]^+$; found 395.1100.

Ethyl 2,5-dimethylfuran-3-carboxylate (2k). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **2k** as a yellow oil; yield 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20 (q, J = 0.8 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 2.23 (d, J = 0.8 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 157.7, 150.0, 114.1, 106.3, 60.0, 14.5, 13.8, 13.3; IR (neat): ν_{max}/cm^{-1} 1716, 1624, 1590,

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1406, 1283, 1231, 1206, 1083; HRMS (ESI): *m*/*z* calcd for $C_9H_{13}O_3$: 169.0859 $[M + H]^+$; found 169.0858.

Ethyl 2-isopropyl-5-methylfuran-3-carboxylate (2l). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **2k** as a colorless oil; yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (q, J = 1.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.71 (heptet, J = 7.0 Hz, 1H), 2.24 (d, J = 1.0 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H), 1.24 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 164.4, 149.8, 112.1, 106.2, 60.0, 27.2, 21.0, 14.5, 13.4; IR (neat): ν_{max}/cm^{-1} 1724, 1469, 1250, 1214, 1069, 1025; HRMS (ESI): *m*/*z* calcd for $C_{11}H_{17}O_3$: 197.1172 $[M + H]^+$; found 197.1173.

Methyl 5-ethyl-2-(4′-methylphenyl)furan-3-carboxylate (2m). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **2m** as a yellow oil; yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.41 (t, J = 0.9 Hz, 1H), 3.81 (s, 3H), 2.69 (qd, J = 7.6, 0.9 Hz, 2H), 2.39 (s, 3H), 1.28 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 156.5, 156.4, 139.2, 128.9, 128.2, 127.4, 113.5, 107.2, 51.6, 21.6, 21.3, 12.0; IR (neat): ν_{max}/cm^{-1} 1721, 1504, 1290, 1233, 1099; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{17}O_3$: 245.1172 $[M + H]^+$; found 245.1172.

Methyl 2-(4′-methylphenyl)-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (2n). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **2n** as a colorless oil; yield 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 3.79 (s, 3H), 2.66–2.61 (m, 4H), 2.38 (s, 3H), 1.88–1.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 156.3, 150.7, 138.9, 128.8, 128.3, 127.9, 119.1, 112.8, 51.3, 23.2, 23.0, 22.8, 22.7, 21.6; IR (neat): ν_{max}/cm^{-1} 1720, 1557, 1501, 1438, 1283, 1217, 1095, 1037; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}O_3$: 271.1329 $[M + H]^+$; found 271.1328.

Ethyl 5-benzyl-2-isopropylfuran-3-carboxylate (2o). The crude product was purified by column chromatography on silica gel (0.3% ethyl acetate in petroleum ether) to give **2o** as a colorless oil; yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.22 (m, 5H), 6.18 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.91 (s, 1H), 3.72 (heptet, J = 7.0 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.25 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 164.2, 152.3, 137.7, 128.8, 128.6, 126.7, 112.2, 107.0, 60.0, 34.3, 27.3, 20.9, 14.5; IR (neat): ν_{max}/cm^{-1} 1715, 1576, 1496, 1468, 1455, 1380, 1208, 1059; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{21}O_3$: 273.1485 $[M + H]^+$; found 273.1484.

General procedure for the synthesis of 2,4-disubstituted furan-3-carboxylates (3a–o)

Cesium carbonate (0.75 mmol, 244 mg) was added to a solution of 3-substituted 2-(2-bromoallyl)-3-oxo-1-carboxylates (**1a–o**) (1.0 mmol) in anhydrous DMF (15 mL). The resulting mixture was stirred at 80 °C until the substrate was consumed (monitored by TLC). After being cooled to ambient temperature, the mixture was treated with 1 M HCl (5 mL) and filtered. The filtrate was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were washed with brine (10 mL), then dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford 2,3,4-trisubstituted furans **3a–o**.

Methyl 4-methyl-2-phenylfuran-3-carboxylate (3a).[24] The crude product was purified by column chromatography on silica gel (0.5% ethyl acetate in petroleum ether) to give **3a** as a colorless oil; yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.76 (m, 2H), 7.43–7.37 (m, 3H), 7.24 (s, 1H), 3.80 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 158.1, 139.3, 130.5, 129.2, 128.5, 128.1, 122.6, 114.1, 51.4, 10.3; IR (neat): ν_{max}/cm^{-1} 1717, 1490, 1436, 1290, 1066; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{13}O_3$: 217.0859 $[M + H]^+$; found 217.0859.

Methyl 4-methyl-2-(4′-methylphenyl)furan-3-carboxylate (3b).[24] The crude product was purified by column chromatography on silica gel (0.5% ethyl acetate in petroleum ether) to give **3b** as an orange oil; yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (m, 2H), 7.24–7.22 (m, 3H), 3.81 (s, 3H), 2.39 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 158.4, 139.2, 138.9, 128.8, 128.3, 127.6, 122.5, 113.5, 51.3, 21.5, 10.3; IR (neat): ν_{max}/cm^{-1} 1722, 1590, 1480, 1377, 1223, 1090; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{15}O_3$: 231.1016 $[M + H]^+$; found 231.1018.

Methyl 2-(4′-methoxyphenyl)-4-methylfuran-3-carboxylate (3c). The crude product was purified by column chromatography on silica gel (1% ethyl acetate in petroleum ether) to give **3c** as a yellow solid; yield 85%; mp 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.73 (m, 2H), 6.41 (q, J = 1.0 Hz, 1H), 6.96–6.92 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.18 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 160.3, 158.5, 138.7, 130.0, 123.1, 122.5, 113.6, 113.0, 55.4, 51.3, 10.4; IR (KBr): ν_{max}/cm^{-1} 1717, 1608, 1501, 1438, 1254, 1177, 1074, 1028; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{14}NaO_4$: 269.0784 $[M + Na]^+$; found 269.0784.

Ethyl 4-methyl-2-(4′-nitrophenyl)furan-3-carboxylate (3d). The crude product was purified by column chromatography on silica gel (3% ethyl acetate in petroleum ether) to give **3d** as a yellow solid; yield 58%; mp 83 °C; ^{1}H NMR (400 MHz, CD_3OD): δ 8.28 (m, 2H), 8.04 (m, 2H), 7.53 (s, 1H), 4.33 (q, J = 6.8 Hz, 2H), 2.22 (s, 3H), 1.33 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 165.3, 155.9, 149.0, 142.4, 137.4, 130.0, 124.5, 124.3, 117.9, 61.9, 14.4, 10.1; IR (neat): ν_{max}/cm^{-1} 1712, 1616, 1591, 1545, 1520, 1488, 1474, 1382, 1348, 1297, 1280, 1100, 1072, 1024; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}NNaO_5$: 298.0686 $[M + Na]^+$; found 298.0688.

Methyl 4-methyl-2-(3′-trifluoromethylphenyl)furan-3-carboxylate (3e). The crude product was purified by column chromatography on silica gel (1% ethyl acetate in petroleum ether) to give **3e** as an orange oil; yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.29 (s, 1H), 3.82 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 156.2, 140.0, 131.6 (q, J_{F-C} = 1.2 Hz), 131.2, 130.6 (q, J_{F-C} = 32.3 Hz), 128.6, 125.6 (q, J_{F-C} = 3.8 Hz), 125.4 (q, J_{F-C} = 4.0 Hz), 124.1 (q, J_{F-C} = 271.0 Hz), 123.0, 115.1, 51.5, 10.2; IR (neat): ν_{max}/cm^{-1} 1720, 1604, 1547, 1479, 1439, 1381, 1331, 1283, 1213, 1168, 1128, 1073, 1001; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{11}F_3NaO_3$: 307.0553 $[M + Na]^+$; found 307.0558.

Methyl 2-(2′-bromophenyl)-4-methylfuran-3-carboxylate (3f). The crude product was purified by column chromatography on silica gel (0.5% ethyl acetate in petroleum ether) to give **3f** as a colorless oil; yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (m,

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1H), 7.45 (m, 1H), 7.37 (m, 1H), 7.28 (m, 1H), 6.44 (q, J = 1.0 Hz, 1H), 3.70 (s, 3H), 2.36 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 155.0, 152.3, 133.0, 132.3, 132.1, 130.8, 126.9, 124.1, 116.8, 107.2, 51.6, 13.6; IR (neat): ν_{max}/cm^{-1} 1722, 1570, 1467, 1438, 1383, 1276, 1209, 1102, 1058, 1012; HRMS (ESI): m/z calcd for $C_{13}H_{12}{}^{79}BrO_3$: 294.9964 $[M + H]^+$; found 294.9965.

Methyl 2-(2′,4′-dimethoxyphenyl)-4-methylfuran-3-carboxylate (3g). The crude product was purified by column chromatography on silica gel (2% ethyl acetate in petroleum ether) to give **3g** as an orange oil; yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 1H), 7.22 (q, J = 1.0 Hz, 1H), 6.54 (dd, J = 8.4, 2.3 Hz, 1H), 6.49 (d, J = 2.3 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.69 (s, 3H), 2.18 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 161.9, 158.2, 154.9, 138.9, 131.4, 121.6, 115.4, 113.0, 104.4, 98.6, 55.5, 55.4, 51.1, 9.7; IR (neat): ν_{max}/cm^{-1} 1717, 1618, 1504, 1438, 1292, 1211, 1161, 1090, 1032; HRMS (ESI): m/z calcd for $C_{15}H_{17}O_5$: 277.1071 $[M + H]^+$; found 277.1071.

Methyl 2-(6′-methoxynaphthalen-2′-yl)-4-methylfuran-3-carboxylate (3h). The crude product was purified by column chromatography on silica gel (1% ethyl acetate in petroleum ether) to give **3h** as a colorless solid; yield 80%; mp 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.84–7.73 (m, 3H), 7.28 (q, J = 1.0 Hz, 1H), 7.17–7.13 (m, 2H), 3.93 (s, 3H), 3.82 (s, 3H), 2.22 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 158.6, 158.5, 139.2, 134.9, 130.0, 128.4, 128.0, 126.4, 126.3, 125.7, 122.7, 119.3, 113.8, 105.7, 55.5, 51.4, 10.4; IR (neat): ν_{max}/cm^{-1} 1713, 1627, 1592, 1537, 1504, 1479, 1458, 1392, 1378, 1302, 1287, 1273, 1258, 1202, 1164, 1119, 1093, 1069, 1029; HRMS (ESI): m/z calcd for $C_{18}H_{16}NaO_4$: 319.0946 $[M + Na]^+$; found 319.0943.

Methyl 4-methyl-2-(*N*-tosyl-1*H*-pyrrol-3′-yl)furan-3-carboxylate (3i). The crude product was purified by column chromatography on silica gel (7% ethyl acetate in petroleum ether) to give **3i** as an orange oil; yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (m, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.16 (m, 1H), 7.11 (q, J = 1.0 Hz, 1H), 6.84 (m, 1H), 3.85 (s, 3H), 2.40 (s, 3H), 2.15 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 153.7, 145.4, 138.3, 135.9, 130.3, 127.2, 122.3, 121.1, 120.7, 119.3, 113.1, 112.9, 51.4, 21.8, 10.6; IR (neat): ν_{max}/cm^{-1} 1713, 1606, 1538, 1494, 1474, 1454, 1438, 1373, 1303, 1231, 1214, 1174, 1117, 1018; HRMS (ESI): m/z calcd for $C_{18}H_{17}NNaO_5S$: 382.0720 $[M + Na]^+$; found 382.0723.

Diethyl 4,4″-dimethyl-[2,2′:5′,2″-terfuran]-3,3″-dicarboxylate (3j). The crude product was purified by column chromatography on silica gel (5% ethyl acetate in petroleum ether) to give **3j** as a yellow solid; yield 60%; mp 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H), 7.27 (q, J = 1.2 Hz, 2H), 4.37 (q, J = 3.6 Hz, 4H), 2.21 (d, J = 1.2 Hz, 6H), 1.39 (t, J = 3.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 149.1, 145.1, 139.7, 122.7, 114.8, 114.2, 60.6, 14.4, 10.5; IR (KBr): ν_{max}/cm^{-1} 1701, 1600, 1523, 1307, 1231, 1122, 1101, 1024; HRMS (ESI): m/z calcd for $C_{20}H_{20}NaO_7$: 395.1101 $[M + Na]^+$; found 395.1098.

Ethyl 2,4-dimethylfuran-3-carboxylate (3k). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **3k** as a colorless oil; yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (q, J = 1.1 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.52 (s, 3H), 2.12 (d, J = 1.1 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 160.2, 137.7, 121.3, 113.6, 59.9, 14.5, 14.5, 10.2; IR (neat): ν_{max}/cm^{-1} 1716, 1611, 1563, 1418, 1385, 1298, 1272, 1099; HRMS (ESI): m/z calcd for $C_9H_{13}O_3$: 169.0859 $[M + H]^+$; found 169.0858.

Ethyl 2-isopropyl-4-methylfuran-3-carboxylate (3l). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **3l** as a colorless oil; yield 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (q, J = 1.2 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.71 (heptet, J = 7.0 Hz, 1H), 2.12 (d, J = 1.2 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.23 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 164.9, 137.7, 121.0, 111.8, 59.9, 27.7, 20.8, 14.4, 10.2; IR (neat): ν_{max}/cm^{-1} 1718, 1560, 1282, 1210, 1065; HRMS (ESI): m/z calcd for $C_{11}H_{17}O_3$: 197.1172 $[M + H]^+$; found 197.1173.

Methyl 4-ethyl-2-(4′-methylphenyl)furan-3-carboxylate (3m). The crude product was purified by column chromatography on silica gel (0.3% ethyl acetate in petroleum ether) to give **3m** as a yellow oil; yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.2 Hz, 2H), 7.24–7.22 (m, 3H), 3.80 (s, 3H), 2.67 (qd, J = 7.4, 1.0 Hz, 2H), 2.39 (s, 3H), 1.23 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 158.5, 139.2, 138.3, 129.3, 128.9, 128.4, 127.8, 112.9, 51.4, 21.5, 18.5, 13.8; IR (neat): ν_{max}/cm^{-1} 1716, 1500, 1437, 1293, 1208, 1077; HRMS (ESI): m/z calcd for $C_{15}H_{17}O_3$: 245.1172 $[M + H]^+$; found 245.1170.

Methyl 2-(4′-methylphenyl)-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (2n). The crude product was purified by column chromatography on silica gel (petroleum ether) to give **2n** as a colorless oil; yield 11%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 3.79 (s, 3H), 2.66–2.61 (m, 4H), 2.38 (s, 3H), 1.88–1.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 156.3, 150.7, 138.9, 128.8, 128.3, 127.9, 119.1, 112.8, 51.3, 23.2, 23.0, 22.8, 22.7, 21.6; IR (neat): ν_{max}/cm^{-1} 1720, 1557, 1501, 1438, 1283, 1217, 1095, 1037; HRMS (ESI): m/z calcd for $C_{17}H_{19}O_3$: 271.1329 $[M + H]^+$; found 271.1328.

Ethyl 4-benzyl-2-isopropylfuran-3-carboxylate (3o). The crude product was purified by column chromatography on silica gel (0.5% ethyl acetate in petroleum ether) to give **3o** as a colorless oil; yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.21 (m, 5H), 6.18 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.91 (s, 1H), 3.73 (heptet, J = 7.0 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.25 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 164.2, 152.3, 137.6, 128.8, 128.6, 126.7, 112.2, 107.0, 60.0, 34.3, 27.3, 20.9, 14.4; IR (neat): ν_{max}/cm^{-1} 1715, 1576, 1497, 1468, 1455, 1381, 1208, 1059; HRMS (ESI): m/z calcd for $C_{17}H_{21}O_3$: 273.1485 $[M + H]^+$; found 273.1483.

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