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Phosphane-Mediated Domino Synthesis of Tetrasubstituted Furans from Simple Terminal Activated Olefins

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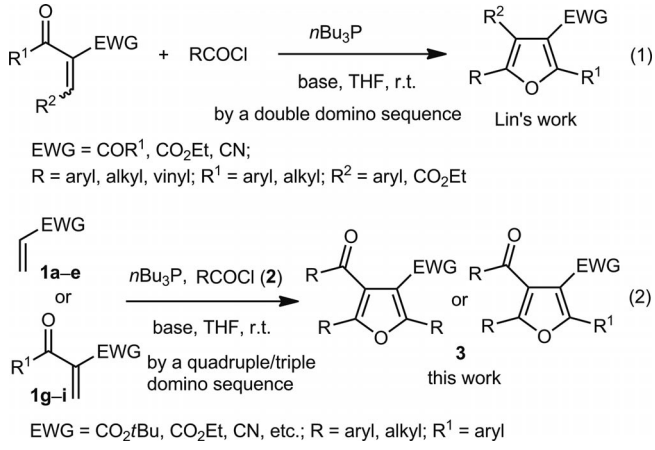
Convenient and highly efficient syntheses of tetrasubstituted furans with flexible substituent patterns from simple and readily available starting materials have been developed. Under very mild conditions, with the mediation of stoichiometric nBu$_3$P, simple terminal activated olefins and acyl chlorides or anhydrides smoothly furnish tetrasubstituted furans in modest to excellent yields. This synthetic strategy features a flexible selection of substituent pattern and a *C*-acylation/*O*-acylation/*C*-acylation/intramolecular Wittig reaction multiple domino assembly sequence.

Introduction

Polysubstituted furans are an important class of heterocyclic compounds. Their importance stems primarily from their ubiquity as structural components in naturally occurring products and artificial pharmaceuticals,[1,2] and also from their usefulness as synthetic building blocks.[3] Although many classical and well-established methods have proven very effective for the synthesis of furan derivatives, efficient synthesis of polysubstituted furans with flexible substituent patterns has long been a challenging goal.[4] During the past decade, many transition-metal-catalyzed annulations of alkynyl, allenyl, or cyclopropyl ketones or other derivatives have provided powerful means of access to diversely substituted furans.[5] Most of them, however, are unable to provide furans with high flexibility in terms of substituent patterns. Most recently, non-metal-mediated – particularly phosphane-enabled – cyclizations have emerged as new and efficient synthetic routes to polysubstituted furans.[6] Remarkably, a stoichiometric phosphane-mediated domino synthetic strategy pioneered by Lin et al. has proven to be highly effective for the synthesis of polysubstituted furans.[6b] Tetrasubstituted furans could be conveniently prepared from activated trisubstituted olefins through an nBu$_3$P-based *O*-acylation/intramolecular Wittig reaction sequence [Scheme 1, Equation (1)]. Although significant progress has been witnessed in the synthesis of polysubstituted furans, the development of new synthetic methods that allow facile assembly of polysubstituted furans under mild conditions from simple and readily available starting materials remains an important objective.



Scheme 1. Phosphane-mediated domino synthesis of tetrasubstituted furans.

As part of our ongoing efforts in exploring stoichiometric phosphane-mediated synthetic reactions, with particular regard to phosphorus ylides generated in situ,[7] and also inspired by a successful sequential synthesis of polysubstituted furans through intramolecular Wittig reactions reported by Lin,[6b] we set out to investigate the feasibility of phosphane-triggered domino assembly of tetrasubstituted furans from simple and readily available terminal activated olefins [Scheme 1, Equation (2)]. The purpose of the utilization of terminal activated olefins was to allow a more flexible selection of substituent pattern in the synthesis of tetrasubstituted furans.

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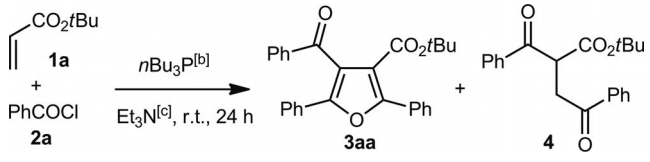
Results and Discussion

Our investigation started with a model reaction between *tert*-butyl acrylate (**1a**, Table 1) and benzoyl chloride (**2a**). Initial results (Entries 1–6) revealed that, under mild conditions and in the presence of NEt_3 in excess (2.25 mmol), tetrasubstituted furan **3aa** bearing 3- and 4-functional groups was smoothly formed in modest yields from acrylate **1a** (1.0 mmol) and benzoyl chloride (**2a**, 1.5 mmol) with mediation by nBu$_3$P (0.6 mmol). The 1,4-dicarbonyl compound **4** was also isolated as a byproduct in low yield in each case (Entries 1–6). Other phosphanes such as PPh_3, Ph_2PMe, and $PhPMe_2$ were totally ineffective for the transformation. Other bases such as DBU, DMAP, and K_2CO_3 were also screened: DBU and DMAP were not as effective as NEt_3, and K_2CO_3 did not work at all. The substrate molar ratio of **1a**/**2a**/phosphane/NEt_3 was found to have a significant impact on the yields both of **3aa** and of **4** (Entries 7–10). When acrylate **1a** was employed in excess with regard to benzoyl chloride (**2a**), byproducts[8] such as **4** were formed in appreciable yields (Entries 1–9). In contrast, the use of benzoyl chloride (**2a**) in 20% excess relative to acrylate **1a** gratifyingly resulted in a 92% yield of **3aa** (Entry 10). A new and efficient phosphane-mediated synthesis of tetrasubstituted furans from acrylates and acyl chlorides had thus been achieved.

Table 1. Brief survey of the model reaction conditions.[a]

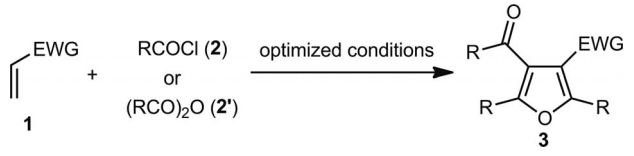


Entry	Solvent	Substrate molar ratio[d]	**3aa** [%][e]	**4** [%][e]
1	THF	1.0:1.5:0.6:2.25	73	14
2	CH_2Cl_2	1.0:1.5:0.6:2.25	54	12
3	toluene	1.0:1.5:0.6:2.25	30	34
4	hexanes	1.0:1.5:0.6:2.25	72	11
5	1,4-dioxane	1.0:1.5:0.6:2.25	55	21
6	CH_3CN	1.0:1.5:0.6:2.25	71	7
7	THF	1.5:1.5:0.6:2.25	47	27
8	THF	1.5:1.5:0.9:2.25	56	34
9[f]	THF	0.5:1.0:0.6:1.5	29	26
10	THF	0.5:1.8:0.6:2.7	92	–

[a] Typical conditions: a mixture of **1a**/**2a**/phosphane/base in the specified molar ratio was stirred in the solvent (2.0 mL) under N_2 at room temp. for 24 h. [b] Other phosphanes such as PPh_3, Ph_2PMe, and $PhPMe_2$ were found ineffective. [c] Bases such as DBU, DMAP, and K_2CO_3 were also screened but gave inferior results. [d] Refers to **1a**/**2a**/phosphane/base. [e] Isolated yield. [f] Byproduct *tert*-butyl 2,5-diphenylfuran-3-carboxylate (**5**) was isolated in 13% yield (see ref.[8]).

Under the optimized conditions, the substrate scopes with respect to terminal activated olefins **1** and acylation agents **2** were examined (Table 2). With use of *tert*-butyl acrylate (**1a**), a series of substituted benzoyl chlorides **2**, with the exception of *o*-chlorobenzoyl chloride (**2d**), readily afforded the corresponding tetrasubstituted furans **3** in high yields (Entries 1–6). The inferior yield in the case of **2d** could be attributed to the significant steric hindrance of the *ortho*-chlorine substituent (Entry 4). Heteroaroyl chlorides such as 2-furoyl chloride (**2g**) and 2-thenoyl chloride (**2h**) were also effective, providing the corresponding polysubstituted furans **3ag** and 3a**h** in modest yields (Entries 7, 8). Variation of the alkyl group in acrylates **1** did not substantially interfere with the formation of furan product. Methyl, ethyl, and *n*-butyl acrylates **1b**–**d** all delivered the expected furan products with selected benzoyl chlorides in excellent yields (Entries 9–14). Acrylonitrile (**1e**) also proved to be a good activated olefin in the reaction. With representative benzoyl chlorides **2**, acrylonitrile (**1e**) smoothly gave the expected furans **3** in very good yields (Entries 15–17). Both aliphatic and aromatic anhydrides **2′** were found to be effective acylation agents, readily delivering alkyl- and aryl-substituted furans **3** in acceptable yields in their reactions with acrylate **1a** (Entries 18–20).

Table 2. Synthesis of tetrasubstituted furans **3** from olefins **1** and acyl chlorides **2** or anhydrides **2′**.[a]

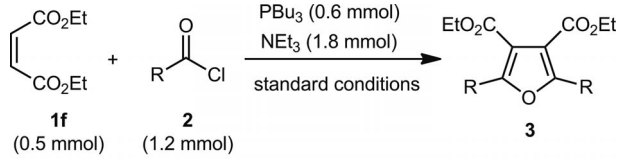


Entry	EWG in **1**	R in **2** or **2′**	**3** (yield [%][b])
1	CO_2tBu (**1a**)	Ph (**2a**)	**3aa** (92)
2	CO_2tBu (**1a**)	4-ClC_6H_4 (**2b**)	**3ab** (99)
3	CO_2tBu (**1a**)	3-ClC_6H_4 (**2c**)	**3ac** (99)
4	CO_2tBu (**1a**)	2-ClC_6H_4 (**2d**)	**3ad** (36)
5	CO_2tBu (**1a**)	4-MeC_6H_4 (**2e**)	**3ae** (97)
6	CO_2tBu (**1a**)	4-$NO_2C_6H_4$ (**2f**)	**3af** (80)
7	CO_2tBu (**1a**)	2-furyl (**2g**)	**3ag** (50)
8	CO_2tBu (**1a**)	2-thienyl (**2h**)	**3ah** (48)
9	CO_2Me (**1b**)	4-ClC_6H_4 (**2b**)	**3bb** (94)
10	CO_2Me (**1b**)	4-MeC_6H_4 (**2e**)	**3be** (90)
11	CO_2Et (**1c**)	4-ClC_6H_4 (**2b**)	**3cb** (98)
12	CO_2Et (**1c**)	4-MeC_6H_4 (**2e**)	**3ce** (96)
13	CO_2nBu (**1d**)	4-ClC_6H_4 (**2b**)	**3db** (96)
14	CO_2nBu (**1d**)	4-MeC_6H_4 (**2e**)	**3de** (92)
15	CN (**1e**)	Ph (**2a**)	**3ea** (96)
16	CN (**1e**)	4-ClC_6H_4 (**2b**)	**3eb** (88)
17	CN (**1e**)	4-MeC_6H_4 (**2e**)	**3ee** (99)
18	CO_2tBu (**1a**)	Me (**2′a**)	**3aa′** (40)
19	CO_2tBu (**1a**)	Et (**2′b**)	**3ab′** (36)
20	CO_2tBu (**1a**)	Ph (**2′c**)	**3aa** (48)

[a] Optimized conditions: alkene **1** (0.5 mmol) and either acyl chloride **2** or anhydride **2′** (1.8 mmol) were added to THF (2.0 mL) under N_2 at room temp., followed by addition of PBu_3 (0.6 mmol) and NEt_3 (2.7 mmol); the resulting mixture was stirred at room temp. for 24 h. [b] Isolated yield based on **1**.

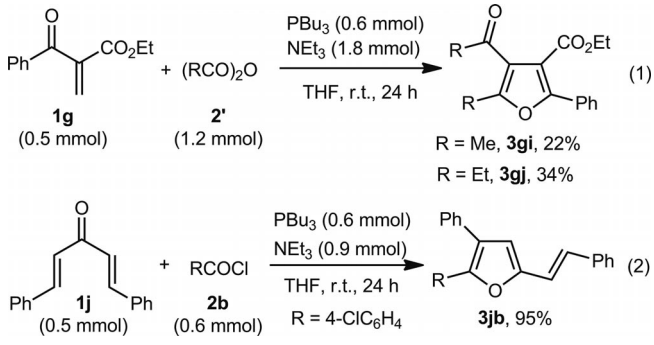
The scope of the activated olefins **1** was further examined. Other electron-deficient olefins were also found to be good candidates in the reaction. Under the standard conditions with a modified substrate molar ratio, both diethyl maleate (**1f**, Scheme 2) and alkyl 2-acylacrylates **1g**–**i** (Scheme 3, Table 3) could produce tetrasubstituted furans in modest to excellent yields in their reactions with various acyl chlorides **2**. With representative benzoyl chlorides **2**,

maleate **1f** afforded symmetric tetrasubstituted furans **3fa**–**fe** in modest yields (Scheme 2). 2-Acylacrylates **1g**–**i** can be regarded as *C*-benzoylation derivatives of the corresponding acrylates. Gratifyingly, the PBu_3-mediated furan-forming reactions between **1g**–**i** and acyl chlorides **2b**–**j** took place smoothly, providing a facile synthetic route to tetrasubstituted furans such as **3gb**–**ie**, bearing four different substituents (Table 3). Other aromatic acyl chlorides **2**, with the exception of *o*-chlorobenzoyl chloride, afforded good yields. With olefin **1g**, both aliphatic acyl chlorides **2i**,**j** and anhydrides **2′a**,**b** readily afforded the corresponding furans **3gi** and **3gj**, but in inferior yields [Table 3, Entries 8 and 9 and Scheme 3, Equation (1)]. Under similar conditions, however, styryl ketone **1j** exclusively delivered trisubstituted furan **3jb** in 95% yield [Scheme 3, Equation (2)].[9] The formation of **3jb** is presumably through an *O*-acylation/intramolecular Wittig reaction sequence, just as disclosed in recent work by Lin.[6c]



R, **2**	Isolated yield, **3**
Ph, **2a**	33%, **3fa**
4-ClC_6H_4, **2b**	50%, **3fb**
3-ClC_6H_4, **2c**	51%, **3fc**
4-MeC_6H_4, **2e**	29%, **3fe**

Scheme 2. Synthesis of tetrasubstituted furans **3** from diethyl maleate (**1f**).

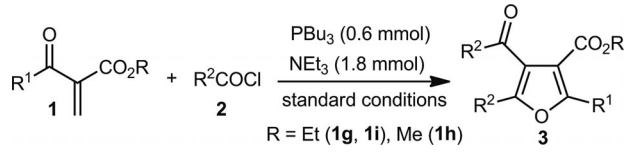


Scheme 3. Polysubstituted furans **3** from other activated olefins.

The structures of compounds **3**, **4**, and **5** were identified by ^1H NMR, ^{13}C NMR, and HRMS (ESI) measurements. Compound **3aa** was further confirmed by X-ray crystallographic analysis.

To allow better understanding of the nature of this nBu_3P-mediated convergent synthesis of tetrasubstituted furans **3**, two control experiments were conducted (Scheme 4). Byproducts **4** and **5**, isolated from the model reaction during the conditions survey (Table 1), were each treated with benzoyl chloride (**2a**) under the standard conditions. Although the cyclocondensation of 1,4-dicarbonyl

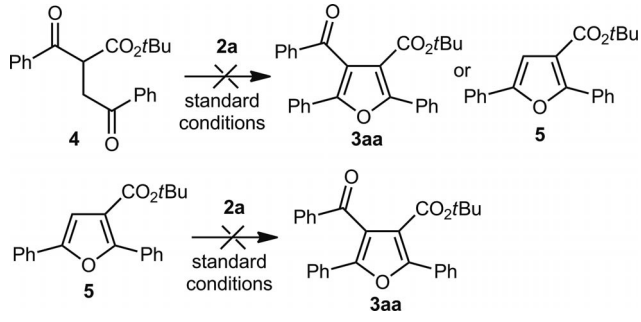
Table 3. Synthesis of tetrasubstituted furans **3** from olefins **1** and acyl chlorides **2**.[a]



Entry	R^1 in **1**	R^2 in **2**	Time [h]	**3** (yield [%] [b])
1	C_6H_5 (**1g**)	4-ClC_6H_4 (**2b**)	24	**3gb** (88)
2	C_6H_5 (**1g**)	3-ClC_6H_4 (**2c**)	13	**3gc** (81)
3	C_6H_5 (**1g**)	2-ClC_6H_4 (**2d**)	22	**3gd** (30)
4	C_6H_5 (**1g**)	4-MeC_6H_4 (**2e**)	13	**3ge** (76)
5	C_6H_5 (**1g**)	4-$NO_2C_6H_4$ (**2f**)	15	**3gf** (69)
6	C_6H_5 (**1g**)	2-furyl (**2g**)	13	**3gg** (80)
7	C_6H_5 (**1g**)	2-thienyl (**2h**)	9	**3gh** (76)
8	C_6H_5 (**1g**)	Me (**2i**)	24	**3gi** (25)
9	C_6H_5 (**1g**)	Et (**2j**)	48	**3gj** (14)
10	4-FC_6H_4 (**1h**)	4-ClC_6H_4 (**2b**)	16	**3hb** (88)
11	4-FC_6H_4 (**1h**)	4-MeC_6H_4 (**2e**)	14	**3he** (94)
12	4-FC_6H_4 (**1h**)	2-furyl (**2g**)	18	**3hg** (86)
13	4-$MeOC_6H_4$ (**1i**)	4-ClC_6H_4 (**2b**)	10	**3ib** (83)
14	4-$MeOC_6H_4$ (**1i**)	4-MeC_6H_4 (**2e**)	12	**3ie** (82)

[a] Conditions: alkene **1** (0.5 mmol) and acyl chloride **2** (1.2 mmol) were added to THF (2.0 mL) under N_2 at room temp., followed by addition of PBu_3 (0.6 mmol) and NEt_3 (1.8 mmol); the resulting mixture was stirred for the time specified. [b] Isolated yield based on **1**.

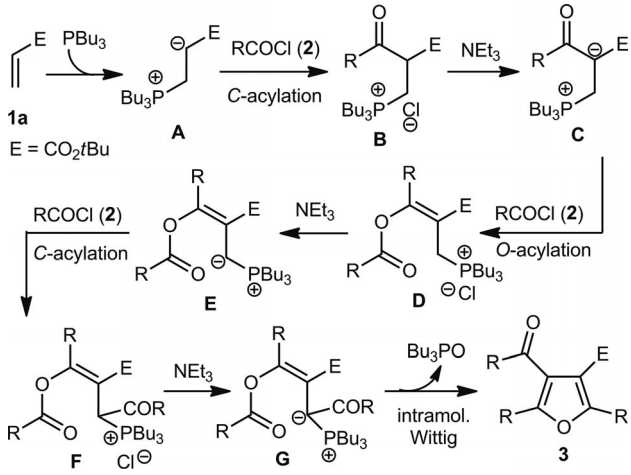
compounds provides effective access to substituted furans by a Paal–Knorr process,[4a] byproduct **4** as a 1,4-dicarbonyl compound failed to give either tetrasubstituted furan **3aa** or trisubstituted furan **5**. In addition, byproduct **5** could not be converted into the tetrasubstituted furan **3aa** under the standard conditions by acylation either. Apparently, compounds **4** and **5** were competitively formed byproducts and not intermediates in the formation of tetrasubstituted furan **3aa**.



Scheme 4. Control experiments.

From the experimental results in this work, a multiple domino process that accounts for the formation of tetrasubstituted furans **3** is proposed. As shown in Scheme 5, nucleophilic addition of PBu_3 to acrylate **1a** could initially generate a zwitterion **A**, which could undergo a *C*-acylation reaction with acyl chloride **2** to give a phosphonium chloride **B**. In the presence of NEt_3 as base, phosphonium salt **B** could be converted into a phosphonium enolate **C**, which could lead to a phosphonium chloride **D** through an *O*-

acylation reaction with acyl chloride **2**. Phosphonium salt **D** could generate a phosphorus ylide **E** through the action of NEt_3. Ylide **E** could undergo another *C*-acylation reaction with **2** to give a phosphonium chloride **F**, which could subsequently be converted into an ylide **G** through the action of NEt_3. Finally, ylide **G** could accomplish the domino assembly of tetrasubstituted furan **3** through an intramolecular Wittig reaction. Formation of the tetrasubstituted furans **3** from acrylate **1a** is therefore presumably through a quadruple domino *C*-acylation/*O*-acylation/*C*-acylation/intramolecular Wittig reaction sequence (Scheme 5).



Scheme 5. Proposed mechanism for the formation of furans **3** from acrylate **1a**.

Although verification of the above mechanism needs more evidence, the formation of tetrasubstituted furans **3** from 2-acylacrylates **1g**–**i** under the standard conditions (Table 3) strongly implies that the *C*-acylation of the activated olefin **1a** should be the first step in the quadruple domino sequence. According to the proposed mechanism, furans **3gb**–**ie** are generated through a triple domino *O*-acylation/*C*-acylation/intramolecular Wittig reaction sequence (Table 3), and furans **3fa**–**fe** from diethyl maleate (**1f**) are presumably formed through another *C*-acylation/*O*-acylation/intramolecular Wittig reaction triple domino process (Scheme 2). The formation of byproducts **4** and **5** (Table 1) could be also explained by this proposed mechanism: **4** could be formed through a water-involving reductive hydrolysis of the phosphonium salt **F**,[10,11] whereas trisubstituted furan **5** could result from a competing intramolecular Wittig reaction of intermediate **E** (Scheme 5).

Conclusions

A general and convenient phosphane-mediated domino synthesis of tetrasubstituted furans from simple terminal activated olefins has been successfully developed. This synthetic method involves a highly efficient multiple domino sequence consisting of *C*-acylation, *O*-acylation, and intramolecular Wittig reaction as key unit steps. As demonstrated in this work, the use of simple terminal activated olefins allows a more flexible selection of substituent pattern in the synthesis of polysubstituted furans. Furthermore, this method provides easy access to 3,4-functionalized furans, which often display important biological activities.[12] The introduction of functional groups at the 3- and 4-positions of furan rings by classical synthetic methods is difficult because of the inherent properties of furans, such as the regiopreference for the 2- and 5-positions in electrophilic substitution.[4e] Future efforts in our laboratory will be directed towards further investigation of the feasibility of this protocol in the construction of other heterocyclic structures.

Experimental Section

General: Unless otherwise noted, all reactions were carried out under nitrogen and under anhydrous conditions. Solvents were purified by standard procedures prior to use. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Column chromatography was performed on silica gel (200–300 mesh) with a mixture of petroleum ether (60–90 °C)/ethyl acetate as the eluent. 2-Acyl acrylates **1g**–**i** were prepared by the reported procedure.[13] CCDC-861370 (for **3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical Procedure for the Synthesis of Tetrasubstituted Furans 3: PBu_3 (150 μL, 0.6 mmol) and Et_3N (375 μL, 2.7 mmol) were sequentially added by microsyringe under N_2 to a solution of the activated olefin **1a** (64 mg, 0.5 mmol) and acylation agent **2a** (253 mg, 1.8 mmol) in THF (2.0 mL). The resulting reaction mixture was stirred at room temperature. After completion of the reaction as monitored by TLC, water (10 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with saturated brine (10 mL) and dried with anhydrous sodium sulfate. After filtration, the solvent was removed in a rotary evaporator under reduced pressure, and the residue was subjected to column chromatographic isolation on silica gel with elution with petroleum ether/ethyl acetate (20:1–40:1) to give furan **3aa** (195 mg) in 92% yield. Other furans **3** were synthesized similarly, under the conditions listed in Tables 2, 3, Schemes 2, 3.

***tert*-Butyl 4-Benzoyl-2,5-diphenylfuran-3-carboxylate (3aa):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and benzoyl chloride (**2a**, 1.8 mmol, 209 μL) were employed in the typical procedure to give the product **3aa** (200 mg, 92%); white solid; m.p. 181–182 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.98 (m, 4 H), 7.55–7.57 (m, 2 H), 7.49 (t, J = 7.4 Hz, 1 H), 7.36–7.43 (m, 5 H), 7.19–7.25 (m, 3 H), 1.08 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 161.8, 155.4, 150.0, 137.6, 133.6, 129.6, 129.6, 129.1, 128.9, 128.8, 128.7, 128.7, 128.40, 128.3, 126.0, 121.9, 117.0, 82.3, 27.4 ppm. HRMS (MALDI): calcd. for $C_{28}H_{24}O_4Na$ $[M + Na]^+$ 447.1567; found 447.1563.

***tert*-Butyl 4-(4-Chlorobenzoyl)-2,5-bis(4-chlorophenyl)furan-3-carboxylate (3ab):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 4-chlorobenzoyl chloride (**2b**, 1.8 mmol, 229 μL) were employed in the typical procedure to give the product **3ab** (260 mg, 96%); yellow solid; m.p. 198–200 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.7 Hz, 2 H), 7.92 (d, J = 8.7 Hz, 2 H), 7.53 (d, J = 8.7 Hz, 2 H), 7.46 (d, J = 8.7 Hz, 2 H), 7.44 (d, J = 8.7 Hz, 2 H), 7.30 (d, J = 8.7 Hz, 2 H), 1.19 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 161.3, 154.7, 149.1, 140.4, 136.0, 135.7, 135.1, 130.9, 129.8, 129.2, 129.1, 128.6, 127.3, 127.2, 127.1, 121.9, 117.3, 82.9,

27.5 ppm. HRMS (MALDI): calcd. for $C_{28}H_{21}Cl_3O_4Na$ [M + Na]$^+$ 549.0398; found 549.0402.

***tert*-Butyl 4-(3-Chlorobenzoyl)-2,5-bis(3-chlorophenyl)furan-3-carboxylate (3ac):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 3-chlorobenzoyl chloride (**2c**, 1.8 mmol, 231 μL) were employed in the typical procedure to give the product **3ac** (261 mg, 99%); yellow solid; m.p. 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.98 (s, 1 H), 7.95 (t, J = 4.4 Hz, 2 H), 7.83 (d, J = 7.8 Hz, 1 H), 7.67 (s, 1 H), 7.55 (d, J = 8.2 Hz, 1 H), 7.38–7.46 (m, 4 H), 7.22–7.29 (m, 2 H), 1.23 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 161.1, 154.0, 149.2, 138.8, 135.1, 134.8, 134.2, 133.7, 130.3, 130.1, 130.1, 130.1, 129.9, 129.6, 129.2, 129.1, 128.4, 127.6, 126.6, 126.0, 124.2, 122.4, 117.9, 83.0, 27.5 ppm. $C_{28}H_{21}Cl_3O_4$ (527.83): calcd. C 63.71, H 4.01; found C 63.41, H 3.67.

***tert*-Butyl 4-(2-Chlorobenzoyl)-2,5-bis(2-chlorophenyl)furan-3-carboxylate (3ad):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 2-chlorobenzoyl chloride (**2d**, 1.8 mmol, 229 μL) were employed in the typical procedure to give the product **3ad** (96 mg, 36%); yellow solid; m.p. 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, J = 7.6, 1.8 Hz, 1 H), 7.61 (dd, J = 7.4, 1.8 Hz, 1 H), 7.61 (td, J = 7.6, 1.8 Hz, 2 H), 7.36–7.42 (m, 2 H), 7.28–7.34 (m, 2 H), 7.25–7.28 (m, 2 H), 7.18–7.24 (m, 2 H), 1.22 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.4, 161.2, 153.4, 152.9, 137.1, 134.2, 134.0, 133.2, 132.5, 132.3, 132.2, 131.5, 131.0, 130.8, 129.7, 129.7, 129.7, 128.8, 128.0, 126.4, 126.3, 126.2, 124.9, 119.1, 81.8, 27.6 ppm. HRMS (MALDI): calcd. for $C_{28}H_{21}Cl_3O_4Na$ [M + Na]$^+$ 549.0398; found 549.0392.

***tert*-Butyl 4-(4-Methylbenzoyl)-2,5-di-*p*-tolylfuran-3-carboxylate (3ae):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 4-toluoyl chloride (**2e**, 1.8 mmol, 238 μL) were employed in the typical procedure to give the product **3ae** (230 mg, 97%); white solid; m.p. 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.2 Hz, 2 H), 7.79 (d, J = 8.1 Hz, 2 H), 7.41 (d, J = 8.2 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 6.97 (d, J = 8.0 Hz, 2 H), 2.27 (s, 3 H), 2.24 (s, 3 H), 2.15 (s, 3 H), 1.06 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 161.8, 155.4, 149.6, 144.3, 139.6, 138.6, 135.2, 129.6, 129.2, 129.2, 128.8, 128.2, 126.4, 126.2, 125.7, 121.4, 116.3, 81.9, 27.4, 21.6, 21.3, 21.1 ppm. HRMS (MALDI): calcd. for $C_{31}H_{30}O_4Na$ [M + Na]$^+$ 489.2036; found 489.2035.

***tert*-Butyl 4-(4-Nitrobenzoyl)-2,5-bis(4-nitrophenyl)furan-3-carboxylate (3af):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 4-nitrobenzoyl chloride (**2f**, 1.8 mmol, 0.334 g) were employed in the typical procedure to give the product **3af** (223 mg, 80%); yellow solid; m.p. 179–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (t, J = 8.6 Hz, 2 H), 8.36 (t, J = 8.6 Hz, 2 H), 8.30 (d, J = 8.6 Hz, 2 H), 8.23 (d, J = 8.6 Hz, 2 H), 8.18 (d, J = 8.6 Hz, 2 H), 7.79 (d, J = 8.6 Hz, 2 H), 1.22 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.3, 160.4, 156.4, 154.3, 150.9, 149.1, 148.4, 147.9, 141.1, 133.9, 133.5, 130.4, 129.5, 126.7, 124.4, 124.2, 123.7, 119.6, 84.2, 27.6 ppm. $C_{28}H_{21}N_3O_{10}$ (559.49): calcd. C 60.11, H 3.78, N 7.51; found C 59.85, H 3.94, N 7.53.

***tert*-Butyl 2,5-Di(furan-2-yl)-4-(furan-2-ylcarbonyl)furan-3-carboxylate (3ag):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 2-furoyl chloride (**2g**, 1.8 mmol, 178 μL) were employed in the typical procedure to give the product **3ag** (100 mg, 50%); oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, J = 16.0, 6.7 Hz, 3 H), 7.45 (s, 1 H), 7.13 (s, 1 H), 6.87 (d, J = 3.1 Hz, 1 H), 6.55–6.58 (m, 2 H), 6.45 (d, J = 1.4 Hz, 1 H), 1.29 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 160.9, 153.3, 147.1, 146.8, 144.0, 143.8, 143.5, 143.4, 143.2, 119.5, 119.1, 114.8, 114.2, 112.51, 112.0, 111.6, 110.4, 82.1, 27.6 ppm. HRMS (MALDI): calcd. for $C_{22}H_{18}O_7Na$ [M + Na]$^+$ 417.0945; found 417.0940.

***tert*-Butyl 2,5-Di(thien-2-yl)-4-(thien-2-ylcarbonyl)furan-3-carboxylate (3ah):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and 2-thenoyl chloride (**2h**, 1.8 mmol, 178 μL) were employed in the typical procedure to give the product **3ah** (106 mg, 48%); oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (dd, J = 3.8, 1.0 Hz, 1 H), 7.70 (dd, J = 4.0, 0.9 Hz, 1 H), 7.60 (dd, J = 3.8, 0.9 Hz, 1 H), 7.49 (dd, J = 5.0, 1.0 Hz, 1 H), 7.45 (dd, J = 4.7, 0.9 Hz, 1 H), 7.33 (dd, J = 5.0, 0.9 Hz, 1 H), 7.16 (dd, J = 5.0, 3.9 Hz, 1 H), 7.09 (dd, J = 4.7, 4.0 Hz, 1 H), 7.02 (dd, J = 5.0, 3.8 Hz, 1 H), 1.25 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.0, 160.6, 149.9, 144.9, 144.2, 133.6, 133.5, 129.4, 129.2, 128.4, 127.6, 127.3, 126.8, 126.6, 126.1, 125.7, 119.3, 113.8, 81.4, 26.5 ppm. HRMS (MALDI): calcd. for $C_{22}H_{18}S_3O_4Na$ [M + Na]$^+$ 465.0529; found 465.0527.

Methyl 4-(4-Chlorobenzoyl)-2,5-bis(4-chlorophenyl)furan-3-carboxylate (3bb): Methyl acrylate (**1b**, 0.5 mmol, 45 μL) and 4-chlorobenzoyl chloride (**2b**, 1.8 mmol, 229 μL) were employed in the typical procedure to give the product **3bb** (227 mg, 94%); yellow solid; m.p. 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.4 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 3.50 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 162.6, 155.1, 149.7, 140.3, 136.2, 135.7, 135.3, 130.4, 129.7, 129.2, 129.1, 128.7, 127.3, 127.0, 126.8, 122.0, 115.6, 51.8 ppm. HRMS (MALDI): calcd. for $C_{25}H_{15}Cl_3O_4Na$ [M + Na]$^+$ 506.9928; found 506.9926.

Methyl 4-(4-Methylbenzoyl)-2,5-di-*p*-tolylfuran-3-carboxylate (3be): Methyl acrylate (**1b**, 0.5 mmol, 45 μL) and *p*-toluoyl chloride (**2e**, 1.8 mmol, 238 μL) were employed in the typical procedure to give the product **3be** (189 mg, 90%); yellow solid; m.p. 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.0 Hz, 2 H), 7.85 (d, J = 7.9 Hz, 2 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 7.9 Hz, 2 H), 7.22 (d, J = 7.9 Hz, 2 H), 7.10 (d, J = 7.9 Hz, 2 H), 3.46 (s, 3 H), 2.41 (s, 3 H), 2.37 (s, 3 H), 2.29 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 163.1, 155.9, 150.1, 144.2, 140.0, 138.8, 135.2, 129.3, 129.3, 129.2, 129.0, 128.2, 126.2, 126.1, 125.8, 121.39, 114.8, 51.4, 21.6, 21.4, 21.2 ppm. HRMS (MALDI): calcd. for $C_{28}H_{24}O_4$ [M]$^+$ 424.1669; found 424.1667.

Ethyl 4-(4-Chlorobenzoyl)-2,5-bis(4-chlorophenyl)furan-3-carboxylate (3cb): Ethyl acrylate (**1c**, 0.5 mmol, 55 μL) and 4-chlorobenzoyl chloride (**2b**, 1.8 mmol, 229 μL) were employed in the typical procedure to give the product **3cb** (243 mg, 98%); white solid; m.p. 177–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.4 Hz, 2 H), 7.90 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.46 (t, J = 8.4 Hz, 2 H), 7.44 (t, J = 8.4 Hz, 2 H),7.31 (d, J = 8.4 Hz, 2 H), 4.00 (q, J = 7.1 Hz, 2 H), 0.93 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 162.1, 155.2, 149.4, 140.3, 136.2, 135.7, 135.2, 130.6, 129.8, 129.2, 129.1, 128.6, 127.2, 127.1, 126.9, 121.9, 115.8, 61.2, 13.4 ppm. HRMS (MALDI): calcd. for $C_{26}H_{17}Cl_3O_4Na$ [M + Na]$^+$ 521.0085; found 521.0078.

Ethyl 4-(4-Methylbenzoyl)-2,5-di-*p*-tolylfuran-3-carboxylate (3ce): Ethyl acrylate (**1c**, 0.5 mmol, 55 μL) and 4-toluoyl chloride (**2e**, 1.8 mmol, 238 μL) were employed in the typical procedure to give the product **3ce** (209 mg, 96%); white solid; m.p. 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.9 Hz, 2 H), 7.88 (d, J = 7.9 Hz, 2 H), 7.53 (d, J = 7.9 Hz, 2 H), 7.28 (d, J = 7.9 Hz, 2 H), 7.23 (d, J = 7.9 Hz, 2 H), 7.10 (d, J = 7.9 Hz, 2 H), 3.97 (q, J = 7.0 Hz, 2 H), 2.41 (s, 3 H), 2.38 (s, 3 H), 2.29 (s, 3 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2, 162.7, 156.0, 149.9, 144.3, 139.9, 138.8, 135.3, 129.4, 129.3, 129.3, 128.9, 128.4, 126.2, 126.1, 125.8, 121.4, 114.9, 60.7, 21.7, 21.4, 21.2,

13.2 ppm. HRMS (MALDI): calcd. for $C_{29}H_{26}O_4Na$ $[M + Na]^+$ 461.1723; found 461.1719.

Butyl 4-(4-Chlorobenzoyl)-2,5-bis(4-chlorophenyl)furan-3-carboxylate (3db): *n*-Butyl acrylate (**1d**, 0.5 mmol, 72 μL) and 4-chlorobenzoyl chloride (**2b**, 1.8 mmol, 229 μL) were employed in the typical procedure to give the product **3db** (254 mg, 96%); yellow solid; m.p. 142–143 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.6 Hz, 2 H), 7.91 (d, J = 8.6 Hz, 2 H), 7.54 (d, J = 8.7 Hz, 2 H), 7.46 (d, J = 8.7 Hz, 2 H), 7.44 (d, J = 8.7 Hz, 2 H),7.31 (d, J = 8.7 Hz, 2 H), 3.96 (t, J = 6.6 Hz, 2 H), 1.23–1.30 (m, 2 H), 1.03–1.12 (m, 2 H), 0.78 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 162.2, 155.3, 149.3, 140.4, 136.2, 135.6, 135.2, 130.7, 129.9, 129.2, 129.2, 128.6, 127.2, 127.1, 126.9, 121.9, 115.8, 65.2, 30.1, 19.0, 13.5 ppm. HRMS (MALDI): calcd. for $C_{28}H_{21}Cl_3O_4Na$ $[M + Na]^+$ 549.0398; found 549.0398.

Butyl 4-(4-Methylbenzoyl)-2,5-di-*p*-tolylfuran-3-carboxylate (3de): *n*-Butyl acrylate (**1d**, 0.5 mmol, 72 μL) and 4-toluoyl chloride (**2e**, 1.8 mmol, 238 μL) were employed in the typical procedure to give the product **3de** (214 mg, 92%); white solid; m.p. 120–121 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.1 Hz, 2 H), 7.88 (d, J = 8.0 Hz, 2 H), 7.51 (d, J = 8.1 Hz, 2 H), 7.27 (d, J = 8.1 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.09 (d, J = 8.1 Hz, 2 H), 3.93 (t, J = 6.5 Hz, 2 H), 2.40 (s, 3 H), 2.37 (s, 3 H), 2.27 (s, 3 H), 1.20–1.27 (m, 2 H), 1.02–1.11 (m, 2 H), 0.74 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 162.8, 156.1, 149.7, 144.3, 139.9, 138.7, 135.1, 129.5, 129.3, 129.3, 128.9, 128.4, 126.3, 126.1, 125.7, 121.3, 115.0, 64.7, 30.0, 21.6, 21.4, 21.2, 18.9, 13.5 ppm. HRMS (MALDI): calcd. for $C_{31}H_{30}O_4Na$ $[M + Na]^+$ 489.2036; found 489.2033.

4-Benzoyl-2,5-diphenylfuran-3-carbonitrile (3ea):[14] Acrylonitrile (**1e**, 0.5 mmol, 33 μL) and benzoyl chloride (**2a**, 1.8 mmol, 209 μL) were employed in the typical procedure to give the product **3ea** (167 mg, 96%); white solid; m.p. 152–154 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.0 Hz, 2 H), 7.88 (d, J = 8.0 Hz, 2 H), 7.52–7.59 (m, 6 H), 7.39 (t, J = 7.5 Hz, 2 H), 7.31 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 159.0, 153.8, 136.3, 134.0, 130.8, 130.0, 129.9, 129.2, 128.7, 128.7, 127.8, 127.4, 127.3, 125.7, 122.1, 113.4, 94.2 ppm.

4-(4-Chlorobenzoyl)-2,5-bis(4-chlorophenyl)furan-3-carbonitrile (3eb): Acrylonitrile (**1e**, 0.5 mmol, 33 μL) and 4-chlorobenzoyl chloride (**2b**, 1.8 mmol, 229 μL) were employed in the typical procedure to give the product **3eb** (198 mg, 88%); yellow solid; m.p. 181–182 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.6 Hz, 2 H), 7.81 (d, J = 8.6 Hz, 2 H), 7.53 (d, J = 8.3, Hz, 2 H), 7.51 (d, J = 8.3, Hz, 2 H), 7.41 (d, J = 8.6 Hz, 2 H), 7.33 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 158.1, 152.9, 141.0, 137.2, 136.6, 134.4, 131.2, 129.7, 129.3, 129.2, 128.6, 127.0, 125.9, 125.4, 122.1, 112.9, 94.5 ppm. HRMS (MALDI): calcd. for $C_{24}H_{12}Cl_3NO_2Na$ $[M + Na]^+$ 473.9826; found 473.9824.

4-(4-Methylbenzoyl)-2,5-di-*p*-tolylfuran-3-carbonitrile (3ee): Acrylonitrile (**1e**, 0.5 mmol, 33 μL) and 4-toluoyl chloride (**2e**, 1.8 mmol, 238 μL) were employed in the typical procedure to give the product **3ee** (195 mg, 99%); yellow solid; m.p. 165–167 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 2 H), 7.71 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.1 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.02 (d, J = 8.0 Hz, 2 H), 2.33 (s, 3 H), 2.29 (s, 3 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.0, 158.8, 153.2, 145.1, 141.1, 140.0, 133.9, 130.1, 129.8, 129.4, 129.3, 127.1, 125.6, 125.2 124.7, 121.5, 113.7, 93.3, 21.7, 21.5, 21.3 ppm. HRMS (MALDI): calcd. for $C_{27}H_{21}NO_2Na$ $[M + Na]^+$ 414.1465; found 414.1460.

***tert*-Butyl 4-Acetyl-2,5-dimethylfuran-3-carboxylate (3aa′):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and acetic anhydride (**2′a**, 1.8 mmol, 171 μL) were employed in the typical procedure to give the product **3aa′** (47 mg, 40%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 2.43 (s, 3 H), 2.34 (s, 3 H), 1.55 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 163.0, 156.1, 152.9, 122.8, 114.2, 81.5, 31.0, 28.1, 13.4, 12.8 ppm. HRMS (MALDI): calcd. for $C_{13}H_{18}O_4Na$ $[M + Na]^+$ 261.1097; found 261.1090.

***tert*-Butyl 2,5-Diethyl-4-propionylfuran-3-carboxylate (3ab′):** *tert*-Butyl acrylate (**1a**, 0.5 mmol, 73 μL) and propionic anhydride (**2′b**, 1.8 mmol, 232 μL) were employed in the typical procedure to give the product **3ab′** (50 mg, 36%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.88 (q, J = 7.6 Hz, 2 H), 2.75 (q, J = 7.3 Hz, 2 H), 2.66 (q, J = 7.5 Hz, 2 H), 1.53 (s, 9 H), 1.23 (t, J = 7.6 Hz, 3 H), 1.20 (t, J = 7.5 Hz, 3 H), 1.13 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 163.0, 161.0, 156.1, 121.7, 113.1, 81.3, 36.8, 28.1, 21.0, 20.4, 12.6, 12.4, 8.2 ppm. HRMS (MALDI): calcd. for $C_{16}H_{25}O_4$ $[M + H]^+$ 281.1747; found 281.1755.

Diethyl 2,5-Diphenylfuran-3,4-dicarboxylate (3fa):[15] Diethyl maleate (**1f**, 0.5 mmol, 81 μL) and benzoyl chloride (**2a**, 1.2 mmol, 140 μL) were employed in the typical procedure to give the product **3fa** (59 mg, 33%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.3 Hz, 4 H), 7.43 (m, 6 H), 4.35 (q, J = 7.1 Hz, 4 H), 1.34 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 153.2, 129.4, 128.9, 128.4, 127.3, 115.5, 61.4, 14.0 ppm.

Diethyl 2,5-Bis(4-chlorophenyl)furan-3,4-dicarboxylate (3fb): Diethyl maleate (**1f**, 0.5 mmol, 81 μL) and 4-chlorobenzoyl chloride (**2b**, 1.2 mmol, 153 μL) were employed in the typical procedure to give the product **3fb** (108 mg, 50%); white solid; m.p. 113–114 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.4 Hz, 2 H), 7.42 (d, J = 8.4 Hz, 2 H), 4.35 (q, J = 7.1 Hz, 2 H), 1.34 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 152.4, 135.7, 128.8, 128.7, 127.2, 116.1, 61.6, 14.0 ppm. HRMS (MALDI): calcd. for $C_{22}H_{18}Cl_2O_5Na$ $[M + Na]^+$ 455.0424; found 455.0423.

Diethyl 2,5-Bis(3-chlorophenyl)furan-3,4-dicarboxylate (3fc): Diethyl maleate (**1f**, 0.5 mmol, 81 μL) and 3-chlorobenzoyl chloride (**2c**, 1.2 mmol, 154 μL) were employed in the typical procedure to give the product **3fc** (110 mg, 51%); white solid; m.p. 72–73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 2 H), 7.75 (m, 2 H), 7.39 (m, 4 H), 4.37 (q, J = 7.1 Hz, 2 H), 1.36 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 151.9, 134.5, 130.2, 129.8, 129.6, 127.3, 125.5, 116.6, 61.7, 14.0 ppm. HRMS (MALDI): calcd. for $C_{22}H_{18}Cl_2O_5Na$ $[M + Na]^+$ 455.0424; found 455.0421.

Diethyl 2,5-Di-*p*-tolylfuran-3,4-dicarboxylate (3fe): Diethyl maleate (**1f**, 0.5 mmol, 81 μL) and 4-toluoyl chloride (**2e**, 1.2 mmol, 259 μL) were employed in the typical procedure to give the product **3fe** (57 mg, 29%); white solid; m.p. 113–115 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.2 Hz, 2 H), 7.25 (d, J = 8.2 Hz, 2 H), 4.34 (q, J = 7.1 Hz, 2 H), 1.34 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 153.3, 139.6, 129.1, 127.3, 126.2, 61.3, 21.4, 14.0 ppm. HRMS (MALDI): calcd. for $C_{24}H_{24}O_5Na$ $[M + Na]^+$ 415.1516; found 415.1523.

Ethyl 4-(4-Chlorobenzoyl)-5-(4-chlorophenyl)-2-phenylfuran-3-carboxylate (3gb): 2-Acyl acrylate **1g** (0.5 mmol, 102 mg) and 4-chlorobenzoyl chloride (**2b**, 1.2 mmol, 153 μL) were employed in the typical procedure to give the product **3gb** (204 mg, 88%); yellow solid; m.p. 135–136 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, J = 7.8, 16.8 Hz, 2 H), 7.84–7.80 (m, 2 H), 7.50–7.44 (m, 2 H), 7.39 (t, J = 6.0 Hz, 3 H), 7.37–7.30 (m, 2 H), 7.25–7.18 (m, 2 H), 3.91 (q, J = 7.1 Hz, 2 H), 0.85 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 162.2, 156.4, 149.2, 140.2, 135.8,

135.0, 130.6, 130.1, 129.1, 129.1, 128.6, 128.5, 128.3, 127.1, 127.1, 121.9, 115.4, 61.1, 13.4 ppm. HRMS (MALDI): calcd. for $C_{26}H_{18}Cl_2O_4$ [M]$^+$ 464.0577; found 464.0583.

Ethyl 4-(3-Chlorobenzoyl)-5-(3-chlorophenyl)-2-phenylfuran-3-carboxylate (3gc): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and 3-chlorobenzoyl chloride (**2c**, 1.2 mmol, 154 μL) were employed in the typical procedure to give the product **3gc** (188 mg, 81%); yellow solid; m.p. 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, J = 7.8, 1.7 Hz, 2 H), 7.97 (t, J = 1.7 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 1 H), 7.68 (d, J = 1.7 Hz, 1 H), 7.62–7.47 (m, 4 H), 7.47–7.36 (m, 2 H), 7.33–7.21 (m, 2 H), 4.01 (q, J = 7.1 Hz, 2 H), 0.94 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 162.1, 156.7, 148.9, 139.0, 135.2, 134.9, 133.6, 130.2, 130.2, 130.1, 130.1, 129.1, 129.0, 128.7, 128.5, 128.3, 127.5, 125.9, 124.1, 122.3, 115.4, 61.2, 13.4 ppm. HRMS (MALDI): calcd. for $C_{26}H_{18}Cl_2O_4Na$ [M + Na]$^+$ 487.0474; found 487.0478.

Ethyl 4-(2-Chlorobenzoyl)-5-(2-chlorophenyl)-2-phenylfuran-3-carboxylate (3gd): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and 2-chlorobenzoyl chloride (**2d**, 1.8 mmol, 153 μL) were employed in the t ypical procedure to give the product **3gd** (70 mg, 30%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 7.2 Hz, 2 H), 7.54 (d, J = 7.6 Hz, 2 H), 7.42–7.46 (m, 4 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.23–7.28 (m, 3 H), 7.12–7.20 (m, 2 H), 4.15 (q, J = 7.1 Hz, 2 H), 1.18 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.2, 163.6, 154.7, 152.9, 137.2, 133.9, 132.6, 132.4, 132.1, 131.1, 130.7, 130.5, 129.7, 128.6, 128.5, 127.8, 127.5, 126.3, 126.3, 126.3, 125.7, 114.7, 61.5, 13.7 ppm. HRMS (MALDI): calcd. for $C_{26}H_{18}Cl_2O_4Na$ [M + Na]$^+$ 487.0474; found 487.0470.

Ethyl 4-(4-Methylbenzoyl)-2-phenyl-5-*p*-tolylfuran-3-carboxylate (3ge): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and 4-toluoyl chloride (**2e**, 1.2 mmol, 259 μL) were employed in the typical procedure to give the product **3ge** (161 mg, 76%); white solid; m.p. 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.2 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H), 7.53 (d, J = 8.1 Hz, 2 H), 7.41–7.49 (m, 3 H), 7.23 (d, J = 7.9 Hz, 2 H), 7.11 (d, J = 8.1 Hz, 2 H), 3.97 (q, J = 7.2 Hz, 2 H), 2.39 (s, 3 H), 2.30 (s, 3 H), 0.90 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 162.6, 155.6, 150.3, 144.4, 138.9, 135.2, 129.7, 129.5, 129.4, 129.4, 129.1, 128.4, 128.2, 126.1, 125.8, 121.4, 115.5, 60.8, 21.7, 21.2, 13.3 ppm. HRMS (MALDI): calcd. for $C_{28}H_{24}O_4Na$ [M + Na]$^+$ 447.1567; found 447.1562.

Ethyl 4-(4-Nitrobenzoyl)-5-(4-nitrophenyl)-2-phenylfuran-3-carboxylate (3gf): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and 4-nitrobenzoyl chloride (**2f**, 1.8 mmol, 223 mg) were employed in the typical procedure to give the product **3gh** (168 mg, 69%); brown solid; m.p. 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 8.7 Hz, 2 H), 8.21 (d, J = 8.8 Hz, 2 H), 8.15 (d, J = 8.7 Hz, 2 H), 8.05 (dd, J = 6.3, 3.1 Hz, 2 H), 7.79 (d, J = 8.8 Hz, 2 H), 7.54 (t, J = 3.1 Hz, 3 H), 4.02 (q, J = 7.1 Hz, 2 H), 0.96 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 161.6, 158.0, 150.7, 148.0, 147.6, 141.5, 134.0, 130.8, 130.1, 128.9, 128.5, 128.0, 126.4, 124.3, 124.2, 124.1, 115.7, 61.5, 13.5 ppm. HRMS (ESI): calcd. for $C_{26}H_{19}N_2O_8$ [M + H]$^+$ 487.1136; found 487.1143.

Ethyl 3-(Furan-2-ylcarbonyl)-5-phenyl-2,2′-bifuran-4-carboxylate (3gg): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and 2-furoyl chloride (**2g**, 1.2 mmol, 119 μL) were employed in the typical procedure to give the product **3gg** (150 mg, 80%); brown solid; m.p. 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, J = 7.9, 1.6 Hz, 2 H), 7.61 (s, 1 H), 7.44–7.50 (m, 4 H), 7.18 (d, J = 3.5 Hz, 2 H), 6.91 (d, J = 3.5 Hz, 2 H), 6.55 (dd, J = 3.5, 1.6 Hz, 1 H), 6.46 (dd, J = 3.5, 1.6 Hz, 1 H), 4.06 (q, J = 7.1 Hz, 2 H), 1.00 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 162.6, 155.5, 153.2, 146.8, 144.1, 143.8, 143.6, 129.9, 128.5, 128.4, 128.3, 120.0, 118.8, 114.9, 112.5, 111.6, 110.5, 61.0, 13.5 ppm. HRMS (MALDI): calcd. for $C_{22}H_{16}O_6Na$ [M + Na]$^+$ 399.0839; found 399.0840.

Ethyl 2-Phenyl-5-(thien-2-yl)-4-(thien-2-ylcarbonyl)furan-3-carboxylate (3gh): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and 2-thenoyl chloride (**2h**, 1.2 mmol, 119 μL) were employed in the typical procedure to give the product **3gh** (155 mg, 76%); brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 6.6 Hz, 2 H), 7.69 (d, J = 4.8 Hz, 1 H), 7.59 (d, J = 3.1 Hz, 1 H), 7.45–7.50 (m, 4 H), 7.33 (d, J = 4.8 Hz, 1 H), 7.09 (t, J = 4.5 Hz, 1 H), 7.02 (t, J = 4.5 Hz, 1 H), 4.02 (q, J = 7.1 Hz, 2 H), 0.97 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.1, 162.5, 155.4, 147.0, 145.0, 134.7, 134.2, 130.3, 129.9, 128.6, 128.4, 128.3, 128.3, 127.8, 127.2, 126.8, 120.5, 115.2, 61.1, 13.3 ppm. HRMS (MALDI): calcd. for $C_{22}H_{16}O_4S_2Na$ [M + Na]$^+$ 431.0382; found 431.0380.

Ethyl 4-Acetyl-5-methyl-2-phenylfuran-3-carboxylate (3gi): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and acetyl chloride (**2i**, 1.2 mmol, 85 μL) were employed in the typical procedure to give the product **3gi** (34 mg, 25%); white solid; m.p. 35–37 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.4 Hz, 2 H), 7.48–7.33 (m, 3 H), 4.35 (q, J = 7.1 Hz, 2 H), 2.57 (s, 3 H), 2.44 (s, 3 H), 1.32 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.3, 164.8, 155.6, 152.1, 129.2, 129.0, 128.4, 126.9, 123.8, 113.9, 61.6, 30.1, 14.0, 13.9 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}O_4$ [M + H]$^+$ 273.1121; found 273.1117.

Ethyl 5-Ethyl-2-phenyl-4-propionylfuran-3-carboxylate (3gj): 2-Acylacrylate **1g** (0.5 mmol, 102 mg) and propionyl chloride (**2j**, 1.2 mmol, 105 μL) were employed in the typical procedure to give the product **3gj** (21 mg, 14%); white solid; m.p. 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.7 Hz, 2 H), 7.48–7.33 (m, 3 H), 4.33 (q, J = 7.1 Hz, 2 H), 2.89 (q, J = 7.5 Hz, 3 H), 2.75 (q, J = 7.2 Hz, 2 H), 1.31 (t, J = 7.5 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H) 1.17 (t, J = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 164.7, 159.08, 152.6, 129.2, 128.4, 128.4, 127.2, 122.8, 113.6, 61.5, 35.8, 21.2, 13.9, 12.5, 8.1 ppm. HRMS (ESI): calcd. for $C_{18}H_{21}O_4$ [M + H]$^+$ 301.1434; found 301.1435.

Methyl 4-(4-Chlorobenzoyl)-5-(4-chlorophenyl)-2-(4-fluorophenyl)-furan-3-carboxylate (3hb): 2-Acylacrylate **1h** (0.5 mmol, 104 mg) and 4-chlorobenzoyl chloride (**2b**, 1.2 mmol, 153 μL) were employed in the typical procedure to give the product **3hb** (206 mg, 88%); yellow solid; m.p. 159–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–8.01 (m, 2 H), 7.88 (d, J = 8.5 Hz, 2 H), 7.56 (d, J = 8.6 Hz, 2 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.31 (d, J = 8.6 Hz, 2 H), 7.19 (t, J = 8.6 Hz, 2 H), 3.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 163.7 (J = 251.7 Hz), 162.6, 155.5, 149.4, 140.2, 135.8, 135.2, 130.7 (J = 8.6 Hz), 130.4, 129.2, 129.1, 127.2, 126.9, 124.8, 121.8, 115.6 (J = 21.9 Hz), 115.1, 51.7 ppm. HRMS (ESI): calcd. for $C_{25}H_{16}Cl_2FO_4$ [M + H]$^+$ 469.0404; found 469.0408.

Methyl 2-(4-Fluorophenyl)-4-(4-methylbenzoyl)-5-*p*-tolylfuran-3-carboxylate (3he): 2-Acyl acrylate **1h** (0.5 mmol, 104 mg) and 4-toluoyl chloride (**2e**, 1.2 mmol, 259 μL) were employed in the typical procedure to give the product **3he** (201 mg, 94%); white solid; m.p. 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.08 (m, 2 H), 7.84 (d, J = 7.9 Hz, 2 H), 7.52 (d, J = 7.9 Hz, 2 H), 7.24 (d, J = 7.9 Hz, 2 H), 7.17 (t, J = 8.6 Hz, 2 H), 7.12 (d, J = 7.9 Hz, 2 H), 2.40 (s, 3 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.00, 163.5 (J = 250.9 Hz), 163.1, 154.7, 150.5, 144.4, 139.1, 135.2, 130.5 (J = 8.4 Hz), 129.4, 129.3, 125.9, 125.3, 125.2, 121.4, 115.4 (J = 21.9 Hz), 115.1, 51.5, 21.7, 21.3 ppm. HRMS (ESI): calcd. for $C_{27}H_{22}FO_4$ [M + H]$^+$ 429.1497; found 429.14.97.

Methyl 5-(4-Fluorophenyl)-3-(furan-2-ylcarbonyl)-2,2′-bifuran-4-carboxylate (3hg): 2-Acylacrylate **1h** (0.5 mmol, 104 mg) and 2-furoyl chloride (**2g**, 1.2 mmol, 119 μL) were employed in the typical procedure to give the product **3hg** (163 mg, 86%); yellow solid; m.p. 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–8.09 (m, 2 H), 7.61 (s, 1 H), 7.45 (s, 1 H), 7.15–7.20 (m, 2 H), 6.91 (d, J = 3.4 Hz, 1 H), 6.56 (dd, J = 3.6, 1.7 Hz, 1 H), 6.46 (dd, J = 3.6, 1.7 Hz, 1 H), 3.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.2 163.6 (J = 251.1 Hz), 163.1, 154.7, 153.2, 146.9, 144.3, 143.9, 143.4, 130.6 (J = 8.6 Hz), 124.8, 119.9, 118.6, 115.5 (J = 21.9 Hz), 114.5, 112.5, 111.7, 110.8, 51.9 ppm. HRMS (ESI): calcd. for $C_{21}H_{13}FO_6$ $[M + H]^+$ 381.0769; found 381.0775.

Ethyl 4-(4-Chlorobenzoyl)-5-(4-chlorophenyl)-2-(4-methoxyphenyl)-furan-3-carboxylate (3ib): 2-Acylacrylate **1i** (0.5 mmol, 117 mg) and 4-chlorobenzoyl chloride (**2b**, 1.2 mmol, 153 μL) were employed in the typical procedure to give the product **3ib** (205 mg, 83%); yellow solid; m.p. 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.8 Hz, 2 H), 7.91 (d, J = 8.5 Hz, 2 H), 7.54 (d, J = 8.6 Hz, 2 H), 7.43 (d, J = 8.6 Hz, 2 H), 7.29 (d, J = 8.6 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 2 H), 3.99 (q, J = 7.1 Hz, 2 H), 3.88 (s, 3 H), 0.92 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 162.3, 161.0, 156.8, 148.5, 140.1, 135.9, 134.8, 130.6, 130.2, 129.1, 129.0, 127.2, 127.0, 121.8, 121.2, 114.1, 113.7, 60.9, 55.3, 13.4 ppm. HRMS (ESI): calcd. for $C_{27}H_{21}Cl_2O_5$ $[M + H]^+$ 495.0761; found 495.0768.

Ethyl 2-(4-Methoxyphenyl)-4-(4-methylbenzoyl)-5-*p*-tolylfuran-3-carboxylate (3ie): 2-Acylacrylate **1i** (0.5 mmol, 117 mg) and 4-toluoyl chloride (**2e**, 1.2 mmol, 259 μL) were employed in the typical procedure to give the product **3ie** (186 mg, 82%); white solid; m.p. 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.8 Hz, 2 H), 7.87 (d, J = 7.8 Hz, 2 H), 7.52 (d, J = 7.8 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 3.96 (q, J = 7.1 Hz, 2 H), 3.87 (s, 3 H), 2.40 (s, 3 H), 2.30 (s, 3 H), 0.89 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 162.8, 160.8, 156.0, 149.6, 144.3, 138.7, 135.3, 130.1, 129.5, 129.4, 129.4, 126.2, 125.8, 121.7, 121.4, 114.2, 113.7, 60.7, 55.3, 21.7, 21.3, 13.3 ppm. HRMS (ESI): calcd. for $C_{29}H_{27}O_5$ $[M + H]^+$ 455.1853; found 455.1855.

(*E*)-2-(4-Chlorophenyl)-3-phenyl-5-styrylfuran (3jb): (1*E*,4*E*)-1,5-Diphenylpenta-1,4-dien-3-one (**1j**, 0.5 mmol, 118 mg) and 4-chlorobenzoyl chloride (**2b**, 0.6 mmol, 77 μL) were employed in the typical procedure to give the product **3jb** (169 mg, 95%); yellow solid; m.p. 131–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.5 Hz, 4 H), 7.33–7.38 (m, 7 H), 7.24 (d, J = 7.0 Hz, 3 H), 7.14 (d, J = 16.2 Hz, 1 H), 6.89 (d, J = 16.2 Hz, 1 H), 6.47 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 146.8, 136.9, 133.9, 133.2, 129.4, 128.8, 128.7, 128.6, 128.6, 127.8, 127.7, 127.5, 127.3, 126.4, 125.1, 115.9, 113.1 ppm. HRMS (MALDI): calcd. for $C_{24}H_{17}ClO$ $[M]^+$ 356.0962; found 356.0968.

***tert*-Butyl 2-Benzoyl-4-oxo-4-phenylbutanoate (4):** Table 1, Entry 8. Yield 34%; m.p. 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 7.5 Hz, 2 H), 8.01 (d, J = 7.5 Hz, 2 H), 7.56–7.62 (m, 2 H), 7.45–7.52 (m, 3 H), 5.04 (dd, J = 7.6, 6.0 Hz, 1 H), 3.79 (dd, J = 18.2, 7.6 Hz, 1 H), 3.67 (dd, J = 18.2, 6.0 Hz, 1 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 195.2, 168.3, 136.4, 136.2, 133.4, 133.3, 128.9, 128.6, 128.5, 128.2, 82.4, 50.0, 37.9, 27.7 ppm. HRMS (MALDI): calcd. for $C_{21}H_{22}O_4Na$ $[M + Na]^+$ 361.1410; found 361.1415.

***tert*-Butyl 2,5-Diphenylfuran-3-carboxylate (5):** Table 1, Entry 9. Yield 13%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.3 Hz, 2 H), 7.73 (d, J = 7.5 Hz, 2 H), 7.38–7.48 (m, 5 H), 7.31 (t, J = 7.4 Hz, 1 H), 7.03 (s, 1 H), 1.56 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 155.9, 152.1, 130.0, 129.9, 129.1, 128.8, 128.5, 128.0, 127.9, 123.9, 117.37, 108.2, 81.2, 28.2 ppm. HRMS (ESI): calcd. for $C_{21}H_{20}O_3Na$ $[M + Na]^+$ 343.1305; found 343.1306.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra for compounds **3**, **4**, and **5** and ORTEP drawing of the crystal structure for **3aa**.

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[8] In some cases (Table 1, Entries 1–9) small amounts of byproduct **5** were observed in the ^{1}H NMR spectra of the crude products, and even isolated (in 13% yield) in one case (Entry 9).

[9] Despite benzoyl chloride **2b** being used in large excess, such as in a **1j/2b**/PBu_3/NEt_3 molar ratio of 0.5:1.2:0.6:1.8, trisubstituted furan **3jb** was still the exclusive product (obtained in 78% yield).

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[11] In another experiment, running the model reaction in water-containing toluene resulted in an increase in the yield of **4**.

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[15] Compound **3fa** is a known compound, see: D. T. Hsu, C. H. Lin, *J. Org. Chem.* **2009**, *74*, 9180.

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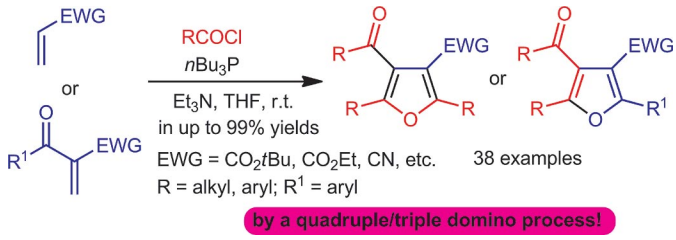
Flexible Furan Substituent Patterns



Simplicity can give rise to flexibility and efficiency. Convenient and highly efficient syntheses of tetrasubstituted furans from simple terminal activated olefins through phosphane-mediated multiple domino assembly sequences (such as *C*-acylation/*O*-acylation/*C*-acylation/intramolecular Wittig reaction) have been achieved.

Keywords: Polysubstituted furans / Activated olefins / Domino reactions / Oxygen heterocycles / Phosphanes

