### Transition-Metal-Catalyzed Domino Reactions: Efficient One-Pot Regiospecific Synthesis of Highly Functionalized Polysubstituted Furans from Electron-Deficient Alkynes and 2-Yn-1-ols

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Abstract: Based on the reactive behavior of different transitionmetal catalysts, three methods for the synthesis of highly functionalized polysubstituted furan derivatives are presented: (i) copper(I) iodide catalyzed regiospecific synthesis of furan aldehydes/ketones from alkynols and diethyl but-2-ynedioate under atmospheric pressure; (ii) nano-Cu<sub>2</sub>O-catalyzed domino process for the regioselective synthesis of  $\alpha$ -carbonylfurans from readily accessible starting materials; (iii) silver-catalyzed one-pot cyclization in toluene at 50 °C for the synthesis of furan derivatives. It was notably that all the domino reactions were smooth under mild conditions with commercially available catalysts, and afforded highly functionalized furans in moderate to good yields. As we know, furans derivatives are extremely useful organic molecules used as synthetic building blocks for the synthesis of more elaborate heterocyclic compounds.

**Key words:** transition-metal-catalyzed domino reaction, functionalized polysubstituted furan, copper(I) iodide, nano-Cu<sub>2</sub>O, silver(I) acetate

### Introduction

Synthetic organic transformations are at the heart of synthetic chemistry and have been developed in a fascinating way over the past few decades.<sup>1</sup> Insofar as one of the fundamental aims of organic synthesis is the preparation of complex and diverse compounds from readily accessible starting materials, the importance of synthetic efficiency becomes immediately apparent and has been well-recognized by organic synthetic chemists. Domino reactions have received attention and have been extensively used as powerful tools in modern organic synthesis for the synthetically efficient construction of various heterocyclic molecules in one sequence without the isolation of intermediates.<sup>2</sup> It was obvious that this type of reaction would allow the minimization of waste and, thus, make waste management unnecessary, since they use dramatically decreased amounts of solvents, reagents, and energy when compared to stepwise reactions.<sup>3</sup> In the past few years, organic chemists have been expected not only to design new chemical reactions but also to improve catalyst systems to maximize resource utilization and decrease waste, especially in terms of environmental health and safety. Transi-

SYNTHESIS 2011, No. 7, pp 1019–1036 Advanced online publication: 03.03.2011 DOI: 10.1055/s-0030-1258461; Art ID: Z53310SS © Georg Thieme Verlag Stuttgart · New York tion-metal-catalyzed domino reactions have dramatically improved and expanded, providing an indispensable, simple methodology for synthetic organic chemistry. Therefore, new strategies and methodologies for the construction of heterocyclic skeletons are required to make the already known domino reactions simpler, less expensive, and greener.<sup>4</sup>

Moreover, copper and silver were among the first metals identified by early humans and they are also important transition-metal catalysts. They are widely used to synthesize various functionalized molecules in organic chemistry. In this paper, we would like to design copper- and silver-catalyzed reactions for the construction of functionalized furan skeletons.

Furans are one of the most important heterocyclic compounds<sup>5</sup> and worthy of our attention as functionalized furan exhibit extensively biological activity<sup>6</sup> and many naturally occurring compounds contain the furan skeleton as a key structural unit.<sup>7</sup> Therefore, organic chemists have been making extensive efforts to construct furan derivatives by developing new and efficient synthetic methodologies.8 Transition-metal-catalyzed domino reactions are one of the most attractive methodologies for the synthesis of furans,9 since transition-metal-catalyzed domino reactions can directly construct polysubstituted furans from accessible starting materials under readily mild conditions<sup>10</sup> (Scheme 1). Although several useful procedures have been developed that allow the preparation of functionalized furan molecule, there is still an intrinsic need to design transition-metal-catalyzed domino reactions for the synthesis of furans under mild conditions and using simple catalytic systems.



Scheme 1 Transition-metal-catalyzed synthesis of furans

Herein, we reported two convenient copper(I)-<sup>11</sup> and silver(I)-catalyzed<sup>12</sup> protocols for the synthesis of highly functionalized polysubstituted furans **3** and **4** by a one-pot cyclization reaction from electron-deficient alkynes **1** and alkynols **2** (Scheme 2 and Figure 1).

### **Results and Discussion**

### Copper(I)-Catalyzed Synthesis of α-Carbonyl Polysubstituted Furans

Initially, 1,5-enyne **3a**, the adduct of diethyl but-2-ynedioate (**1a**) with prop-2-yn-1-ol (**2a**) was treated, in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane<sup>13</sup> (DABCO, 10 mol%), with 2.5 mol% of silver(I) tetrafluoroborate or copper(I) iodide in *N*,*N*-dimethylformamide at 80 °C. Interestingly, different polysubstituted furan rings, **3aa** and **4aa**, were obtained with high regiospecificity (Scheme 2). Subsequently, our efforts focused on searching for potential catalysts and suitable reaction conditions to synthesize  $\alpha$ -carbonyl polysubstituted furans **3aa**, since few general procedures are available for the synthesis of  $\alpha$ -carbonyl polysubstituted furans.

Encouraged by the copper(I) iodide catalyzed synthesis of furan derivatives, the effect of several commercially available copper salts, solvents, and various temperatures on the reactivity and selectivity in the domino reaction of



Scheme 2 Silver(I)- or copper(I)-catalyzed one-pot synthesis of furan derivatives

### **Biographical Sketches**





**Dr. Hua Cao** was born in Hunan, China, in 1981. After receiving his B.S. degree in chemistry at the Hunan Normal University in 2004, he obtained his M.S. degree under the supervision of Prof. Baoan Song in 2007 from Guizhou University.

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my of Sciences. In 2003, he joined South China University of Technology (SCUT). He is currently the leading Professor of Chemistry and Deputy Dean of School of Chemistry and Chemical Jiang. He was awarded the Research Award in 2008. His current research interests are focused on developing new metal-catalyzed system and methodologies for the construction of several functionalized heterocyclic compounds.

Engineering, SCUT. His research interests include synthetic methodology, green chemistry, and carbon dioxide conversion.

Huawen Huang was raised in Hunan, China. He received a B.S. degree from the School of Chemical Engineering at Northwest University (Xi'an, China) in 2009 under the mentorship of Professor Fan Daidi. He is currently a Ph.D. candidate in the laboratory of Professor Huanfeng Jiang in the School of Chemistry and Chemical Engineering, at South China University of Technology (Guangzhou, China). His current research is focused on novel methods for the synthesis of heterocyclic compounds.



1a with 2a were surveyed. In a typical procedure, 1a (0.5 mmol), 2a (0.5 mmol) and DABCO in dichloromethane were stirred for 10 minutes at room temperature; the solution was evaporated to dryness under reduced pressure. Subsequently, 2.5 mol% of the copper salt in N,N-dimethylformamide were added at 50 °C. It was found that the desired product 3aa was formed in the presence of copper(I) catalysts (Table 1), such as copper(I) chloride (entry 1), copper(I) iodide (entry 2), copper(I) bromide (entry 3), and copper(I) oxide (entry 4). On the other hand, it was also confirmed that little reaction took place in the presence of copper(II), such as copper(II) oxide (entry 5) and copper(II) bromide (entry 6), even for prolonged reaction times. With regard to the solvent, only N,N-dimethylformamide was proven to be suitable in the presence of copper(I) iodide and **3aa** was obtained in 71% yield, while other solvents, such as dichloromethane (entry 7), toluene (entry 8), tetrahydrofuran (entry 9), and 1,4-dioxane (entry 10), led to lower yields. Finally, different temperatures were also examined (entries 11-14), and the results showed that the optimal temperature in N,N-dimethylformamide was 80 °C.

To explore the scope of the reaction with diethyl but-2ynedioate (1a), the effects of various 2-yn-1-ols 2 (Figure 1) were examined. First, prop-2-yn-1-ol (2a) was tested and the corresponding furan 3aa was obtained in



Figure 1 Electron-deficient alkynes 1 and alkynols 2 utilized

**Table 1**Screening of Copper Salts in the Synthesis of  $\alpha$ -CarbonylPolysubstituted Furans

CO <sub>2</sub> Et + CO <sub>2</sub> Et	HO	CO cat. I <sub>2</sub> , r.t. r.t. to 100	EtO <sub>2</sub> C EtO <sub>2</sub> C	Н
1a	2a		3a	a
Entry	Catalyst	Solvent	Temp (°C)	Yield <sup>a</sup> (%)
1	CuCl	DMF	50	53
2	CuI	DMF	50	71
3	CuBr	DMF	50	62
4	Cu <sub>2</sub> O	DMF	50	59
5	CuO	DMF	50	19
6	CuBr <sub>2</sub>	DMF	50	23
7	CuI	$CH_2Cl_2$	50	45
8	CuI	toluene	50	44
9	CuI	THF	50	19
10	CuI	1,4-dioxane	50	27
11	CuI	DMF	r.t.	8
12	CuI	DMF	80	78
13	CuI	DMF	30	31
14	CuI	DMF	100	74

<sup>a</sup> Isolated yields.

78% isolated yield (Scheme 3). Other 3-substituted 2-yn-1-ols **2c,d,h-p** were also employed and the corresponding furans 3ac,ad,ah-ap were formed in 45-71% isolated yields. From Scheme 3, these results indicated that aliphatic groups could work well as aryl groups. The presence of either electron-donating aryl groups (e.g., 2i, 2l) or electron-withdrawing groups (e.g., 2j, 2k) on the aromatic ring of the alkynols resulted in the formation of furans (e.g., 3ai, 3al or 3aj, 3ak, respectively) in good yields in this transformation. It was also obvious that substituents presented in the *p*- and *m*-positions of the aromatic group of alkynols, such as 2d and 2l had no negative effects on the reaction and the respective furans 3ad and 3al were formed in good yield. However, if more sterically hindered o-substituted aromatic groups, such as 2i and 2m, were employed in the alkynol, the corresponding products 3ai and 3am were obtained in lower yields. Subsequently, the effect of 1,3-disubstituted 2-yn-ols were examined and the desired furans **3ap-ar** were obtained in 54–59% yields (Scheme 3). Unfortunately, when 1a was exchanged by other alkynoates, such as ethyl propynoate or ethyl but-2-ynoate (1d), the desired products were not detected.



Scheme 3 Copper(I) iodide catalyzed domino reactions for the synthesis of furans

# Nano-Cu<sub>2</sub>O-Catalyzed Domino Reaction Synthesis of Furans

This domino process could not take place when ethyl phenylpropynoate (**1b**) was employed as the substrate, replacing diethyl but-2-ynedioate (**1a**), in the presence of copper(I) iodide catalyst (Table 2, entry 1). Therefore, it was essential to design and develop a new method for the synthesis of  $\alpha$ -carbonyl furans.

Initially, we chose ethyl phenylpropynoate (**1b**) and prop-2-yn-1-ol (**2a**) as the standard substrates to search for potential catalysts and suitable reaction conditions, and the results are summarized in Table 2. In a typical procedure, **1b** (0.5 mmol), **2a** (0.5 mmol) and tributylphosphine<sup>14</sup> were added and the mixture was stirred for 30 minutes in dichloromethane at room temperature. The solution was then evaporated to dryness under reduced pressure. Subsequently, the catalyst was added in *N*,*N*-dimethylformamide at 50 °C.

As shown in Table 2, the corresponding product **3ba** was detected when copper(I) iodide was substituted by cop-



		EtO <sub>2</sub> C		
ļ	+ $H_{2}$ $H_$		СНО	
Ph 1b	HO	2hc		
D	2a	308	1	
Entry	Catalyst	Air or O <sub>2</sub> (atm)	Temp (°C)	Yield <sup>a</sup> (%)
1	5 mol% CuI	air	80	-
2	5 mol% Cu <sub>2</sub> O	air	80	<5
3	5 mol% Cu <sub>2</sub> O	air	120	<5
4	5 mol% Ru <sub>3</sub> (CO) <sub>12</sub>	air	80	-
5	5 mol% PdCl <sub>2</sub>	air	80	-
6	5 mol% Pd(OAc) <sub>2</sub>	air	80	-
7	$5 \text{ mol}\% \text{ Pd}(\text{dba})_2$	air	80	-
8	5 mol% NiSO <sub>4</sub>	air	80	trace
9	5 mol% nano-Cu <sub>2</sub> O	air	80	62
10	5 mol% nano-Cu <sub>2</sub> O	$O_{2}(1)$	80	67
11	5 mol% nano-Cu <sub>2</sub> O	O <sub>2</sub> (3)	80	46
12	5 mol% nano-Cu <sub>2</sub> O	O <sub>2</sub> (5)	80	41
13	10  mol% nano-Cu <sub>2</sub> O	O <sub>2</sub> (5)	80	58
14	10  mol% nano-Cu <sub>2</sub> O	$O_{2}(1)$	80	69
15	10  mol% nano-Cu <sub>2</sub> O	air	80	68
16	10  mol% nano-Cu <sub>2</sub> O	air	100	65
17	10 mol% nano-Cu <sub>2</sub> O	air	50	75
18	10 mol% nano-Cu <sub>2</sub> O	air	r.t.	_

<sup>a</sup> GC yields.

per(I) oxide (entry 2). We assumed that an increase in temperature might influence the formation of **3ba**. However, it was observed that the yield of **3ba** did not change markedly even at 120 °C (entry 3). Other late-transition-metal catalysts, such as  $Ru_3(CO)_{12}$ ,  $PdCl_2$ ,  $Pd(OAc)_2$ , and  $Pd(dba)_2$  (entries 4–7), were also employed; however, no conversion was observed in these cases. Nickel(II) sulfate was also used as the catalyst, and trace of **3ba** was detected by GC-MS (entry 8).

Inspired by the result that copper(I) oxide could catalyze the reaction, we attempted to prepare nano-Cu<sub>2</sub>O. According to previous reports,<sup>15</sup> copper(I) oxide microcrystals were prepared by a simple hydrothermal method. Copper(II) acetate monohydrate and acetic acid (AR grade) were employed as starting materials. First, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (1.548 g) was dissolved in deionized water (50 mL) to form a clear solution. Then, acetic acid (1 mL) was added into the solution under continuous stirring to form the precursor solution. The precursor solution was transferred into Teflon-lined stainless steel autoclave, which was then maintained at 200 °C for 27 hours. The red product collected from the bottom of the container was washed with deionized water several times and dried in a vacuum oven at 60 °C for five hours. The formation of the nano-Cu<sub>2</sub>O was confirmed by XRD (Figure 2) and SEM analysis (Figure 3).



Figure 2 XRD pattern of copper(I) oxide particles



Figure 3 SEM Images of nano-Cu<sub>2</sub>O

As we expected, the reaction yield of **3ba** dramatically increased to 62% (entry 9), when 5 mol% nano-Cu<sub>2</sub>O was employed in *N*,*N*-dimethylformamide under atmospheric pressure. We attempted to improve the yields by substituting air by oxygen and even increasing oxygen pressure (entries 10–12). It was noteworthy that the use of pure oxygen instead of atmospheric oxygen had no significant influence on the yields. However, when a higher pressure of oxygen was used (entries 11 and 12), the yield decreased gradually, which indicated that nano-Cu<sub>2</sub>O was oxidized to copper(II) oxide at high oxygen pressures. Inspired by

the above results, we tried to change the amount of catalyst to improve the yield of **3ba**. The results indicated that the corresponding furan **3ba** was formed in moderate to good yield by using 10 mol% nano-Cu<sub>2</sub>O (entries 13–17). Next, we examined the effect of solvents and temperatures and found that *N*,*N*-dimethylformamide and 50 °C were optimum conditions for this transformation. Balancing all results it was concluded that the optimal conditions for this domino reaction involved the use of 10 mol% nano-Cu<sub>2</sub>O in *N*,*N*-dimethylformamide at 50 °C.

With the optimal reaction conditions in hand, we next explored the scope of this domino reaction. The results are summarized in Scheme 4. It was shown that the reaction conditions are useful for a range of electron-deficient alkynes 1b-e and 3-substituted 2-yn-ols. It was obvious that the reaction between ethyl phenylpropynoate (1b) and differently 3-substituted 2-yn-1-ols  $2\mathbf{a}-\mathbf{h}$  (R<sup>3</sup> = H, Me, Ph, 3-Tol, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, pyridin-2-yl, thiophen-2-yl) had a beneficial effect on the reaction products, and in most cases the corresponding products **3aa-ah** were obtained in moderate to good yields. These results indicated that the substituted 2-yn-1-ol with different substituent groups presented on the aromatic ring could react smoothly, and the corresponding products were obtained in good yields. It was also shown that both electron-rich and electron-withdrawing groups at the aromatic ring had no effect on this domino reaction.

To further expand the scope of this transformation, other electron-deficient alkynes, such as 1,3-bis(4-tolyl)prop-2yn-1-one (1c), ethyl but-2-ynoate (1d), and 1,3-diphenylprop-2-yn-1-one (1e), were employed. The results showed that ethyl but-2-ynoate (1d) and aryl alkynyl ketones 1c,e were also well tolerated under the optimum conditions and afforded the corresponding products in good yields (60–73%). It was noteworthy that no other regioisomers were detected in this transformation, which indicated that this cyclization was regioselective and chemoselective. Finally, the molecular structure of representative product **3cc** was determined by X-ray crystallography (Figure 4).



Figure 4 X-ray crystal structure of compound 3cc

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Scheme 4 Nano-Cu<sub>2</sub>O-catalyzed synthesis of furans

Furthermore, 5-phenylpenta-2,4-diyn-1-ol (**2s**) and 5-(4-tolyl)penta-2,4-diyn-1-ol (**2t**) (Scheme 5) were also surveyed and the desired products **3bs**, **3es**, **3at**, **3hs** were obtained in 42–51% yield. It was especially noteworthy that novel 2,4,5-trisubstituted 3-ynylfurans were obtained in an extremely direct manner without tedious stepwise synthesis.<sup>16</sup>

Finally, the substrates 3-phenyl-1-(thiophen-2-yl)prop-2yn-1-one (**1f**) and 3-phenyl-1-(4-tolyl)prop-2-yn-1-one (**1g**) were also examined as replacements for **1a–e** and the



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Scheme 5 The formation of 2-ynylfurans; isolated yields

corresponding products were obtained (Scheme 6). Notably, it was found that a pair of isomer furans was observed and gave high yields of products under the optimized conditions. This result demonstrated that since two carbonyl groups in complex  $\mathbf{D}$  (Scheme 12) were both active in the following cyclization reaction, regioisomers would be produced.

# Silver(I) Acetate Catalyzed Domino Reaction Synthesis of Furans

From above investigation, two efficient domino reactions were developed for the synthesis of  $\alpha$ -carbonyl furans by copper(I) catalysis. Next, we report a convenient silver-catalyzed domino reaction for the synthesis of polysubstituted furans.

Initially, the reaction of **1a** with **2a** was investigated as a model system to explore potential catalysts and suitable reaction conditions and the results are shown in Table 3. Based on the experience of our previous work, it was obvious that 4aa was obtained in the presence of silver(I) tetrafluoroborate and triphenylphosphine in N,N-dimethylformamide at 80 °C (Scheme 1 and Table 3, entry 1). We next examined the reaction using 5 mol% of silver(I) acetate and 10 mol% triphenylphoshine and the yield of 4aa dramatically increased to 68% (entry 2). Other catalysts, such as 5 mol% AgNO<sub>3</sub>, 5 mol% Ag<sub>2</sub>CO<sub>3</sub>, 5 mol% PdCl<sub>2</sub>, 5 mol% Pd(OAc)<sub>2</sub>, 5 mol% Pd(dba)<sub>2</sub>, 5 mol% Ru<sub>3</sub>(CO)<sub>12</sub>, and 3 mol% AuCl<sub>3</sub>, were employed (entries 3-10). The results indicated that silver(I) acetate was an efficient catalyst for the synthesis of polysubstituted furans. Subsequently, the effects of solvents were examined for this domino reaction. To our surprise, when toluene was used as the solvent, it was found that the yield of 3aa in-



**Scheme 6** The formation of regioisomeric furans (ratio determined by <sup>1</sup>H NMR)

creased to 76% (entry 11). Other solvents, such as 1,2dichloroethane and 1,4-dioxane, were also employed and led to moderate yields (entries 12 and 13). Finally, different temperatures were also tested (entries 7–14), and it was found that 50 °C was the optimum for this transformation.

On the basis of the above optimization of the reaction conditions, it provided possible to synthesize a series of polysubstituted furans by silver(I) acetate catalysis (Scheme 7). The typical results indicated that the reaction was quite general, forming polysubstituted furans with very high regio- and stereoselectivity; In the electron-deficient alkyne 1,  $R^1$  may be aryl, OEt, or OMe;  $R^2$  may be CO<sub>2</sub>Et, aryl, or CO<sub>2</sub>Me. Differently 3-substituted 2-yn-1ols 2 ( $R^3 = H$ , Me, Ph, 3-Tol, 4-MeOC<sub>6</sub>H<sub>4</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, 2-FC<sub>6</sub>H<sub>4</sub>, thiophen-2-yl, 4-EtC<sub>6</sub>H<sub>4</sub>, 2-EtC<sub>6</sub>H<sub>4</sub>) had a beneficial effect on the reaction products, and in most cases the corresponding products 4aa-ht were obtained in moderate to good yields. These results showed that aliphatic groups could work well as aryl groups. Both electron-rich aryl groups and electron-withdrawing groups were obtained good yields in this transformation. Subsequently, ethyl 3-phenylpropynoate (1b) and 1,3-diphenylprop-2yn-1-one (1e) were also examined and the desired products 4be, 4ea, and 4ec were obtained in 70-79% yields. Furthermore, 5-phenylpenta-2,4-diyn-1-ol (2s) and 5-(4tolyl)penta-2,4-diyn-1-ol (2t) were also employed. Inter-

 Table 3
 Optimization of the Synthesis of 4aa

CO2Et				<b>E+O</b> O	
ll -	+ DA	BCO Cl <sub>2</sub> , r.t.			
CO <sub>2</sub> Et	ОН	EtO <sub>2</sub> C	0	EtO <sub>2</sub> C <sup>-</sup>	0
1a	2a		3a		4aa
Entry	Catalyst		Solv	rent Temp (°C)	Yield <sup>a</sup> (%)
1	5 mol% Ag	BF <sub>4</sub> /10% Ph <sub>3</sub> P	DM	F 100	37
2	5 mol% Ag	OAc/10% Ph <sub>3</sub> F	DM	F 100	68
3	5 mol% Ag	NO <sub>3</sub> /10% Ph <sub>3</sub> P	DM	F 100	32
4	5 mol% Ag	CO <sub>3</sub> /10% Ph <sub>3</sub> P	DM	F 100	trace
5	5 mol% Pd	Cl <sub>2</sub> /10% Ph <sub>3</sub> P	$CH_2$	Cl <sub>2</sub> 50	-
6	5 mol% Pd	(OAc) <sub>2</sub> /10% Ph	<sub>3</sub> P DM	F 100	-
7	5 mol% Pd	(dba) <sub>2</sub>	DM	F 100	-
8	5 mol% Ru	<sub>3</sub> (CO) <sub>12</sub>	DM	F 100	_
9	3 mol% Au	Cl <sub>3</sub>	DM	F 100	11
10	3 mol% Au	Cl <sub>3</sub> /5 mol% Ph	<sub>3</sub> P DM	F 100	13
11	5 mol% Ag	OAc/10 mol%	Ph <sub>3</sub> P tolue	ene 100	76
12	5 mol% Ag	OAc/10 mol%	Ph <sub>3</sub> P DCE	E 100	40
13	5 mol% Ag	OAc/10 mol%	Ph <sub>3</sub> P 1,4-0	dioxane 100	46
14	5 mol% Ag	OAc/10 mol%	Ph <sub>3</sub> P tolue	ene 50	79
15	5 mol% Ag	OAc/10 mol%	Ph <sub>3</sub> P tolue	ene r.t.	_

<sup>a</sup> Yield determined by GC.

estingly, the desired products **4cs**, **4es**, **4hs**, and **4ht** were formed in 68–75% yields. No formation of other regioisomers was observed by GC/MS. It was especially noteworthy that novel 2,3,5-trisubstituted 4-ynylfurans were formerly formed in an extremely direct manner without tedious stepwise synthesis.

These promising results encouraged us to extend the scope of the reaction using other electron-deficient alkynes ( $\mathbb{R}^1 \neq \mathbb{R}^2$ ). Interestingly, substrates bearing different substituents gave a pair of regio-isomers. As shown in Scheme 8, electron-deficient alkynes **1f**, **1g**, **1i** were examined and the desired products **4ia–gc** and their regio-isomers **5ia–gc** were obtained in reasonable yields. To our knowledge, this transformation has not been previously reported. The molecular structure of representative product **5ic** was confirmed by an X-ray diffraction study (Figure 5).

### Mechanism

To gain further insight into the mechanism of this novel transformation, we envisioned the possibility to trap the intermediates of the domino reaction. Recently, Hofmann<sup>17</sup> has reported the formation of a carbene dimer







**Scheme 8** Cyclization of alkynyl ketones with 2-yn-1-ols (<sup>a</sup> ratio determined by HPLC; <sup>b</sup> ratio determined by <sup>1</sup>H NMR)



Scheme 9 The formation of compound 6



Scheme 10 The reaction of 3aa with ethyl 2-diazoacetate

via reaction of a copper(I) carbene with nucleophilic diazo compounds. Stimulated by this novel result, we tried to trap a copper carbene in our reactions by using ethyl 2-diazoacetate (Scheme 9). Compounds 1a (0.5 mmol) and 2a (0.5 mmol) with DABCO (0.05 mmol) in dichloromethane were stirred for 10 minutes at room temperature. The solution was evaporated and N,Ndimethylformamide (3 mL) and nano-Cu<sub>2</sub>O (0.3 mmol) were added at 50 °C. Subsequently, ethyl 2-diazoacetate (0.8 mmol) was added; interestingly, the vinylfuran 6 was observed. Compound 6 was not formed (Scheme 10) when 3aa reacted with ethyl 2-diazoacetate under the optimal conditions. These results indicated that a copper carbene complex was likely to be formed during this domino reaction.

To investigate a possible H-migration in the reaction, an experiment was performed using deuterium-labeled prop-2-yn-1-ol (**2aD**) at 50 °C by nano-Cu<sub>2</sub>O catalysis (Scheme 11). Compounds **3aaD** and **4aaD** were not observed as the products, which indicated that the deuterium was eliminated during the rearrangement and cyclization processes.



Figure 5 X-ray crystal structure of compound 5ic



Scheme 11 Deuterium-labeling experiment



Scheme 12 Proposed mechanism

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On the basis of the above experimental results, a plausible reaction mechanism is shown in Scheme 12. DABCO- or tributylphosphine-promoted nucleophilic addition of propargyl alcohol to electron-deficient alkynes formed enyne adduct A. A 6-endo-dig addition of the enol ether onto copper(I)-alkyne complex **B** resulted in the formation of intermediates C or C', which collapsed to give the  $\beta$ -allenic ketones **D** or **D**'.<sup>18</sup> Complex **D** underwent cyclization, 1,3-H shift, and oxidation to form E and E'.<sup>19</sup> Since two carbonyl groups in complex **D** were both active in the following cyclization reaction, carbene complexes E and E'would be produced by different attack direction (paths I and II) in the presence of a copper catalyst and air. Subsequently, carbene complexes E and E' underwent carbene oxidation<sup>20</sup> with an oxygen metathesis to give the desired products  $\alpha$ -carbonyl furans. While complex **D'** underwent cyclization, the desired products were formed by H shift directly.

### Conclusion

In summary, we have reported an unprecedented copper(I)-catalyzed synthesize of  $\alpha$ -carbonyl furans via a cyclization/rearrangement/oxidation sequence of 1,5enynes and also described silver(I) acetate catalyzed, onepot domino reactions for the synthesis of polysubstituted furan under mild conditions. All the catalytic systems were environmentally benign and effective for the formation C–C and C–O bonds. In addition, our findings opened a convenient synthetic route to a variety of  $\alpha$ -carbonyl furans which are useful synthetic intermediates for bioactive and natural compounds. It was noteworthy that these synthesis methods are also attractive because furans are extremely useful organic molecules that are used as synthetic building blocks for the synthesis of more elaborate heterocyclic compounds.

All reactions were performed under an air atmosphere in a roundbottom flask equipped with a magnetic stirrer bar; yields are isolated yields unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer and referenced to  $\delta = 7.26$  and 77.0 for CDCl<sub>3</sub> solvent, respectively, with TMS as internal standard. IR spectra were obtained as KBr pellets or as liquid films between two KBr pellets with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GCMS–QP5050A at an ionization voltage of 70 eV equipped with a DB–WAX capillary column (i.d. = 0.25 mm, length = 30 m). Elemental analysis was performed on a Vario EL elemental analyzer. TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

### Diethyl 5-Formylfuran-2,3-dicarboxylate (3aa); Typical Procedure

Diethyl acetylenedicarboxylate (1a, 0.5 mmol), prop-2-yn-1-ol (2a, 0.5 mmol), and DABCO (0.05 mmol) in  $CH_2Cl_2$  were stirred at r.t. for 10 min. The soln was evaporated to dryness under reduced pressure. Subsequently, 2.5% mmol CuI and DMF were added at 80 °C. After completion of the reaction (TLC monitoring), the soln was evaporated to dryness under reduced pressure and then  $H_2O$  (8 mL)

was added. The aq soln was extracted with  $Et_2O$  (3 × 8 mL) and the combined extracts were dried (anhyd MgSO<sub>4</sub>). The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **3aa**.

### Ethyl 5-Formyl-2-phenylfuran-3-carboxylate (3ba); Typical Procedure

Ethyl phenylpropynoate (**1b**, 0.5 mmol), prop-2-yn-1-ol (**2a**, 0.5 mmol), and Bu<sub>3</sub>P (0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> were stirred at r.t. for 30 min. The soln was evaporated to dryness under reduced pressure. Subsequently, DMF and nano-Cu<sub>2</sub>O were added at 50 °C. After completion of the reaction (TLC monitoring), H<sub>2</sub>O (8 mL) was added. The aq soln was extracted with Et<sub>2</sub>O ( $3 \times 8$  mL) and the combined extracts were dried (anhyd MgSO<sub>4</sub>). The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **3ba**.

### Diethyl 5-Methylfuran-2,3-dicarboxylate (4aa); Typical Procedure

Diethyl acetylenedicarboxylate (1a, 0.5 mmol), prop-2-yn-1-ol (2a, 0.5 mmol), and DABCO (0.05 mmol) in  $CH_2Cl_2$  were stirred at r.t. for 10 min. The soln was evaporated to dryness under reduced pressure. Subsequently, AgOAc/Ph<sub>3</sub>P and toluene were added at 50 °C. After completion of the reaction (TLC monitoring), the soln was evaporated to dryness under reduced pressure and then  $H_2O$  (8 mL) was added. The aq soln was extracted with  $Et_2O$  (3 × 8 mL) and the combined extracts were dried (anhyd MgSO<sub>4</sub>). The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **4aa**.

#### Diethyl 5-Formylfuran-2,3-dicarboxylate (3aa)

IR (KBr): 2978, 1732, 1667, 1574, 1028 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.75 (s, 1 H), 7.45 (s, 1 H), 4.32–4.44 (m, 4 H), 1.22–1.40 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 178.3, 160.9, 157.1, 151.6, 147.0, 124.4, 119.2, 62.4, 61.9, 14.0.

MS (EI): *m*/*z* = 240, 213, 195, 167, 140.

Anal. Calcd for  $C_{11}H_{12}O_6$ : C, 55.00; H, 5.04. Found: C, 55.08; H, 5.02.

#### **Diethyl 5-Formyl-4-phenylfuran-2,3-dicarboxylate (3ac)** IR (KBr): 3069, 2977, 1734, 1680, 1546 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.70 (s, 1 H), 7.47 (s, 5 H), 4.43 (q, *J* = 8.0 Hz, 2 H), 4.28 (q, *J* = 8.0 Hz, 2 H), 1.40 (t, *J* = 8.0 Hz, 3 H), 1.22 (q, *J* = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 178.0, 162.0, 157.1, 147.5, 144.3, 136.1, 129.7, 129.5, 128.7, 127.5, 126.3, 62.3, 62.1, 14.0, 13.7.

MS (EI): *m*/*z* = 316, 288, 225, 213, 170, 115, 77.

Anal. Calcd for  $C_{17}H_{16}O_6$ : C, 64.55; H, 5.10. Found: C, 64.67; H, 5.08.

#### **Diethyl 5-Formyl-4-(3-tolyl)furan-2,3-dicarboxylate (3ad)** IR (KBr): 3052, 2984, 1739, 1580, 1538, 788 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.69 (s, 1 H), 7.26–7.35 (m, 4 H), 4.43 (q, *J* = 8.0 Hz, 2 H), 4.31 (q, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H), 1.40 (t, *J* = 8.0 Hz, 3 H), 1.26 (t, *J* = 8.0 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 178.0, 162.0, 157.1, 147.5, 144.2, 138.5, 136.4, 130.5, 128.6, 127.4, 126.3, 62.3, 62.1, 21.3, 14.0, 13.8.

MS (EI): *m*/*z* = 330, 302, 284, 227, 184, 143, 128, 115, 91, 77.

Anal. Calcd for  $C_{18}H_{18}O_6$ : C, 65.45; H, 5.49. Found: C, 65.58; H, 5.44.

### Diethyl 5-Formyl-4-(thiophen-2-yl)furan-2,3-dicarboxylate (3ah)

IR (KBr): 3067, 2983, 1733, 1717, 1698, 1653, 1558 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.91 (s, 1 H), 7.53 (d, *J* = 5.2 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.15–7.17 (m, 1 H), 4.37–4.47 (m, 4 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 1.34 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 178.0, 162.2, 157.1, 147.5, 144.3, 132.4, 130.5, 129.1, 128.5, 128.0, 127.6, 127.0, 126.3, 62.6, 14.1, 13.9.

MS (EI): *m*/*z* = 322, 294, 220, 148, 121.

Anal. Calcd for  $C_{15}H_{14}O_6S$ : C, 55.89; H, 4.38. Found: C, 55.97; H, 4.36.

### Diethyl 5-Formyl-4-(2-methoxyphenyl)furan-2,3-dicarboxylate (3ai)

IR (KBr): 3054, 2985, 1735, 1718, 1651, 1618, 1057 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.62 (s, 1 H), 7.42–7.44 (m, 1 H), 7.32–7.34 (m, 1 H), 6.97–7.06 (m, 2 H), 4.42 (q, *J* = 7.2 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 3.77 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H), 1.18 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 178.3, 161.9, 157.4, 156.8, 147.8, 144.8, 133.1 131.6, 131.4, 126.6, 120.8, 116.8, 111.0, 62.3, 61.7, 55.3, 14.2, 13.9.

MS (EI): *m*/*z* = 346, 315, 271, 227, 215, 199, 171, 115, 77.

Anal. Calcd for  $C_{18}H_{18}O_7$ : C, 62.42; H, 5.24. Found: C, 62.30; H, 5.26.

### Diethyl 5-Formyl-4-[4-(methoxycarbonyl)phenyl]furan-2,3-dicarboxylate (3aj)

IR (KBr): 3052, 2983, 1734, 1714, 1650, 1609, 1033 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.73 (s, 1 H), 8.12 (d, *J* = 8.0 Hz, 2 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 4.46 (q, *J* = 8.0 Hz, 2 H), 4.30 (q, *J* = 8.0 Hz, 2 H), 3.96 (s, 3 H), 1.39 (t, *J* = 8.0 Hz, 3 H), 1.21 (t, *J* = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 178.0, 166.3, 161.8, 157.1, 147.7, 144.7, 134.4, 132.2, 131.4, 129.9, 129.7, 126.2, 62.6, 62.4, 52.4, 14.1, 13.9.

MS (EI): *m*/*z* = 374, 347, 315, 271, 213, 129, 59.

Anal. Calcd for  $C_{19}H_{18}O_8$ : C, 60.96; H, 4.85. Found: C, 61.04; H, 4.83.

# Diethyl 4-(2-Fluorophenyl)-5-formylfuran-2,3-dicarboxylate (3ak)

IR (KBr): 3071, 2986, 1696, 1621, 1593 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.67 (s, 1 H), 7.37–7.45 (m, 2 H), 7.14–7.23 (m, 2 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 1.17 (t, *J* = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 178.0, 161.5, 161.1, 158.6, 157.2, 147.9, 145.4, 131.9, 131.7, 129.1, 126.0, 124.5, 116.0, 62.6, 62.1, 14.1, 13.8.

MS (EI): *m*/*z* = 344, 241, 213, 169, 141, 128, 115, 91, 77.

Anal. Calcd for  $C_{17}H_{15}FO_6$ : C, 61.08; H, 4.52. Found: C, 61.21; H, 4.49.

# Diethyl 4-(4-Ethylphenyl)-5-formylfuran-2,3-dicarboxylate (3al)

IR (KBr): 3064, 2971, 1738, 1665, 1602, 1477 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.63 (s, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.21 (t, *J* = 8.0 Hz, 2 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 2.64 (q, *J* = 7.6 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.15–1.22 (m, 6 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 178.2, 162.2, 157.2, 147.5, 146.2, 144.2, 136.4, 129.5, 128.3, 126.4, 124.7, 62.4, 62.2, 28.6, 15.2, 14.1, 13.8.

MS (EI): *m*/*z* = 344, 241, 213, 169, 141, 128, 115, 91, 77.

Anal. Calcd for  $C_{19}H_{20}O_6$ : C, 66.27; H, 5.85. Found: C, 66.02; H, 5.90.

### **Diethyl 5-Formyl-4-(2-tolyl)furan-2,3-dicarboxylate (3am)** IR (KBr): 3110, 2984, 1732, 1587, 1444, 718 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.54 (s, 1 H), 7.25–7.40 (m, 4 H), 4.45 (q, *J* = 7.2 Hz, 2 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 2.23 (s, 3 H), 1.44 (t, *J* = 7.2 Hz, 3 H), 1.11 (t, *J* = 7.2 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 178.0, 161.5, 157.4, 147.9, 145.1, 137.2, 136.0, 130.3, 129.7, 127.3, 125.8, 62.5, 61.9, 20.0, 14.2, 13.7.

MS (EI): *m*/*z* = 330, 301, 257, 211, 155, 127, 115, 77.

Anal. Calcd for  $C_{18}H_{18}O_6$ : C, 65.45; H, 5.49. Found: C, 65.34; H, 5.52.

**Diethyl 4-Methyl-5-propanoylfuran-2,3-dicarboxylate (3ap)** IR (KBr): 2984, 1731, 1684, 1586, 1539, 1038 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.38–4.44 (m, 4 H), 2.98 (q, J = 7.2 Hz, 2 H), 2.44 (s, 3 H), 1.37–1.41 (m, 6 H), 1.20 (t, J = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 192.5, 162.5, 157.4, 142.2, 128.7, 126.6, 62.0, 61.7, 28.7, 14.0, 13.77, 9.28, 7.23.

MS (EI): *m*/*z* = 282, 253, 236, 209, 153, 136.

Anal. Calcd for  $C_{14}H_{18}O_6$ : C, 59.57; H, 6.43. Found: C, 59.68; H, 6.37.

## **Diethyl 4-Ethyl-5-propanoylfuran-2,3-dicarboxylate (3aq)** IR (KBr): 2985, 1728. 1684, 1523, 1136 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.40 (q, J = 8.0 Hz, 4 H), 2.96 (q, J = 7.6 Hz, 2 H), 2.87 (q, J = 7.6 Hz, 2 H), 1.36–1.40 (m, 6 H), 1.15–1.21 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 192.5, 162.9, 157.6, 148.1, 142.2, 135.0, 126.5, 62.0, 60.4, 32.8, 21.1, 14.2, 14.1, 7.39.

MS (EI): *m*/*z* = 296, 250, 221, 192, 178, 91, 57, 43.

Anal. Calcd for  $C_{15}H_{20}O_6$ : C, 60.80; H, 6.80. Found: C, 60.95; H, 6.74.

# Diethyl 5-Butanoyl-4-phenylfuran-2,3-dicarboxylate (3ar) IR (KBr): 3059, 2965, 1733, 1695, 1592 $\rm cm^{-1}.$

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40 (s, 5 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 2.84 (q, *J* = 7.2 Hz, 2 H), 1.63–1.72 (m, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 190.6, 162.5, 157.4, 147.7, 141.7, 131.7, 131.4, 129.5, 129.0, 128.3, 127.1, 122.8, 62.8, 62.0, 41.7, 17.0, 14.2, 13.9, 13.7.

MS (EI): *m*/*z* = 358, 330, 284, 241, 184, 129, 43.

Anal. Calcd for  $C_{20}H_{22}O_6$ : C, 67.03; H, 6.19. Found: C, 66.89; H, 6.23.

#### **Ethyl 5-Formyl-2-phenylfuran-3-carboxylate (3ba)** IR (KBr): 2921, 2853, 1683, 1216, 766 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.66 (s, 1 H), 8.06–8.08 (m, 2 H), 7.64 (s, 1 H), 7.45–7.47 (m, 3 H), 4.31 (q, *J* = 7.2 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 177.4, 162.2, 161.5, 150.2, 131.0, 129.1, 128.3, 128.2, 123.8, 116.1, 61.2, 14.1.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>: 244.0736; found: 244.0732.

### **Ethyl 5-Formyl-4-methyl-2-phenylfuran-3-carboxylate (3bb)** IR (KBr): 2927, 1771, 1722, 1599, 1238, 698 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.81 (s, 1 H), 7.81–7.83 (m, 2 H), 7.41–7.43 (m, 3 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 2.55 (s, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 177.7, 163.1, 160.8, 147.4, 135.2, 130.5, 128.9, 128.6, 128.1, 116.6, 60.9, 13.9, 10.1.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>: 258.0892; found: 258.0889.

#### Ethyl 5-Formyl-2,4-diphenylfuran-3-carboxylate (3bc)

IR (KBr): 2983, 1772, 1724, 1677, 1228, 695 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.47 (s, 1 H), 7.93–7.95 (m, 2 H), 7.44 (s, 8 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 177.4, 163.1, 159.3, 146.9, 140.1, 130.8, 129.8, 129.1, 128.5, 128.4, 128.2, 116.4, 61.2, 13.5.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>: 320.1049; found: 320.1044.

### Ethyl 5-Formyl-2-phenyl-4-(3-tolyl)furan-3-carboxylate (3bd)

IR (KBr): 3054, 2973, 2855, 1773, 1724, 1674, 1577, 1276, 782, 693  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.50 (s, 1 H), 7.94–7.97 (m, 2 H), 7.27–7.48 (m, 7 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 2.42 (s, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 176.9, 162.7, 158.6, 146.5, 139.7, 137.4, 130.2, 130.0, 129.3, 128.6, 128.2, 128.1, 128.0, 127.9, 127.7, 126.6, 116.1, 60.7, 20.8, 13.0.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>: 334.1205; found: 334.1201.

#### Ethyl 5-Formyl-4-(4-methoxyphenyl)-2-phenylfuran-3-carboxylate (3be)

IR (KBr): 3053, 2923, 2847, 1724, 1674, 1245, 844 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.50 (s, 1 H), 7.91–7.93 (m, 2 H), 7.39–7.48 (m, 5 H), 6.98–7.00 (m, 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 3.87 (s, 3 H), 1.05 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 177.5, 163.4, 160.5, 147.0, 139.8, 131.5, 131.2, 130.7, 130.3, 128.8, 128.5, 128.4, 121.2, 113.8, 61.2, 55.3, 13.6.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>O<sub>5</sub>: 350.1154; found: 350.1150.

### Ethyl5-Formyl-4-(4-nitrophenyl)-2-phenylfuran-3-carboxylate (3bf)

IR (KBr): 3060, 2977, 2854, 2229, 1773, 1722, 1680, 1227, 695  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.52 (s, 1 H), 7.93–7.95 (m, 2 H), 7.75–7.77 (m, 2 H), 7.48–7.60 (m, 5 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.4, 161.9, 159.7, 146.4, 136.3, 133.9, 131.4, 130.6, 130.2, 128.3, 128.0, 127.5, 117.7, 115.6, 112.5, 60.9, 13.1.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>NO<sub>6</sub>: 365.0899; found: 365.0904.

### Ethyl 5-Formyl-2-phenyl-4-(pyridin-2-yl)furan-3-carboxylate (3bg)

IR (KBr): 2912, 2847, 1763, 1725, 1236, 626 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.75 (s, 1 H), 8.70–8.72 (m, 1 H), 7.35–7.97 (m, 8 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 1.03 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 178.3, 163.2, 158.8, 149.5, 149.2, 147.4, 137.3, 136.2, 130.7, 128.4, 128.3, 124.9, 123.4, 116.3, 61.2, 13.6.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub>: 321.1001; found: 321.006.

## Ethyl 5-Formyl-2-phenyl-4-(thiophen-2-yl)furan-3-carboxylate (3bh)

IR (KBr): 2925, 1765, 1722, 1675, 1236, 704 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.67 (s, 1 H), 7.86–7.89 (m, 2 H), 7.12–7.50 (m, 6 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 1.11 (t, *J* = 7.2 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.2, 163.1, 158.9, 147.9, 135.3, 133.5, 130.8, 130.2, 128.5, 128.4, 128.3, 127.4, 126.9, 125.8, 116.5, 61.5, 13.6.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>S: 326.0613; found: 326.0605.

**4-(4-Methylbenzoyl)-5-(4-tolyl)furan-2-carbaldehyde (3ca)** IR (KBr): 2985, 1772, 1666, 1604, 1145, 830 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.70 (s, 1 H), 7.72–7.77 (m, 4 H), 7.43 (s, 1 H), 7.16–7.27 (m, 4 H), 2.42 (s, 3 H), 2.36 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 190.1, 177.3, 159.7, 150.1, 144.5, 141.2, 134.7, 129.9, 129.3, 128.0, 125.5, 123.7, 122.5, 21.6, 21.4.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>: 304.1099; found: 304.1095.

#### **3-Methyl-4-(4-methylbenzoyl)-5-(4-tolyl)furan-2-carbaldehyde (3cb)**

IR (KBr): 3050, 2929, 1770, 1660, 1603, 1245, 1179, 962, 826  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.83 (s, 1 H), 7.71–7.73 (m, 2 H), 7.45–7.47 (m, 2 H), 7.05–7.18 (m, 4 H), 2.35 (s, 3 H), 2.27 (s, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.8, 177.6, 156.5, 147.3, 145.1, 140.5, 134.6, 129.8, 129.5, 129.4, 129.3, 129.0, 127.3, 127.1, 125.6, 123.7, 21.7, 21.3, 9.33.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>O<sub>3</sub>: 318.1256; found: 318.1253.

### 4-(4-Methylbenzoyl)-3-phenyl-5-(4-tolyl)furan-2-carbaldehyde (3cc)

IR (KBr): 3054, 2920, 1768, 1659, 1607, 1238, 957 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.60 (s, 1 H), 7.59–7.70 (m, 4 H), 7.08–7.37 (m, 9 H), 2.30 (s, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.6, 177.2, 156.0, 146.3, 144.9, 140.7, 140.0, 134.4, 129.8, 129.6, 129.4, 129.3, 129.0, 128.8, 128.5, 127.2, 125.3, 122.5, 21.6, 21.3.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>20</sub>O<sub>3</sub>: 380.1412; found: 380.1409.

#### **Ethyl 5-Formyl-2,4-dimethylfuran-3-carboxylate (3db)** IR (KBr): 2971, 1744, 1715, 1678, 1559 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.69 (s, 1 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 2.62 (s, 3 H), 2.50 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 176.9, 164.5, 163.3, 147.3, 134.9, 116.4, 60.5, 14.7, 14.2, 9.98.

HRMS (EI): m/z [M]<sup>+</sup> calcd for  $C_{10}H_{12}O_4$ : 196.0736; found: 196.0729.

#### 4-Benzoyl-5-phenylfuran-2-carbaldehyde (3ea)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.70 (s, 1 H), 7.78–7.82 (m, 4 H), 7.53–7.57 (m, 1 H), 7.32–7.44 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 190.4, 177.5, 159.8, 150.3, 137.0, 133.5, 130.7, 129.6, 128.6, 128.4, 128.2, 123.7, 122.7.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>12</sub>O<sub>3</sub>: 276.0786; found: 276.0780.

### 4-Benzoyl-3-methyl-5-phenylfuran-2-carbaldehyde (3eb)

IR (KBr): 3027, 2864, 1705, 1663, 1598, 658 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.86 (s, 1 H), 7.79–7.81 (m, 2 H), 7.23–7.55 (m, 8 H), 2.31 (s, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 192.0, 177.7, 156.8, 147.4, 136.8, 133.9, 132.4, 130.1, 129.6, 128.7, 128.6, 128.3, 127.5, 127.1, 123.8, 9.37.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>: 290.0943; found: 290.0933.

### 4-Benzoyl-3,5-diphenylfuran-2-carbaldehyde (3ec)

IR (KBr): 3034, 2968, 2923, 1660, 1593, 1051, 695 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.61 (s, 1 H), 7.69–7.77 (m, 4 H), 7.26–7.45 (m, 11 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.9, 177.4, 156.2, 146.5, 140.1, 136.6, 133.9, 130.4, 129.6, 129.4, 129.2, 128.7, 128.6, 127.9, 127.4, 122.8.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>24</sub>H<sub>16</sub>O<sub>3</sub>: 352.1099; found: 352.1093.

#### 4-Benzoyl-3-(4-methoxyphenyl)-5-phenylfuran-2-carbaldehyde (3ee)

IR (KBr): 3028, 2966, 1754, 1719, 1661 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.61 (s, 1 H), 7.26–7.78 (m, 14 H), 3.73 (m, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 192.1, 177.3, 160.4, 156.0, 146.5, 139.7, 136.8, 133.9, 131.0, 130.3, 129.7, 128.7, 128.6, 128.1, 127.4, 122.9, 120.8, 114.2, 55.2.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>25</sub>H<sub>18</sub>O<sub>3</sub>: 382.1205; found: 382.1199.

### 4-Benzoyl-3-(4-nitrophenyl)-5-phenylfuran-2-carbaldehyde (3ef)

IR (KBr): 3029, 2950, 1761, 1720, 1624 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.66 (s, 1 H), 7.65–7.98 (m, 6 H), 7.29–7.49 (m, 8 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.2, 177.1, 156.8, 146.5, 136.3, 134.3, 132.4, 132.2, 132.1, 130.7, 130.3, 129.6, 128.9, 128.8, 128.6, 127.5, 127.1, 122.6.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>24</sub>H<sub>15</sub>NO<sub>5</sub>: 397.0950; found: 397.0946.

## 4-Benzoyl-5-phenyl-3-(thiophen-2-yl)furan-2-carbaldehyde (3eh)

IR (KBr): 3026, 2937, 1769, 1726, 1650 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.84 (s, 1 H), 7.81–7.83 (m, 2 H), 7.66–7.69 (m, 2 H), 7.32–7.48 (m, 8 H), 7.17–7.18 (m, 1 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.4, 177.1, 155.9, 146.7, 134.1, 133.1, 132.1, 130.4, 130.2, 129.7, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.3, 122.7.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>22</sub>H<sub>14</sub>O<sub>3</sub>S: 358.0664; found: 358.0660.

#### Ethyl 5-Formyl-2-phenyl-4-(phenylethynyl)furan-3-carboxylate (3bs)

IR (KBr): 3067, 2983, 1733, 1717, 1698, 1653, 1558 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.91 (s, 1 H), 7.93–7.95 (m, 2 H), 7.38–7.58 (m, 8 H), 4.37 (q, 2 H), 1.34 (t, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.0, 161.9, 161.0, 151.2, 131.8, 131.1, 129.5, 129.1, 128.6, 128.3, 127.8, 121.9, 121.0, 99.7, 61.4, 14.1.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>22</sub>H<sub>16</sub>O<sub>4</sub>: 344.1049; found: 344.1045.

### 4-Benzoyl-5-phenyl-3-(phenylethynyl)furan-2-carbaldehyde (3es)

IR (KBr): 3067, 2983, 1733, 1717, 1698, 1653, 1558 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.89 (s, 1 H), 7.94–7.95 (m, 2 H), 7.75–7.77 (m, 2 H), 7.57–7.61 (m, 1 H), 7.22–7.48 (m, 8 H), 7.09–7.11 (m, 2 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.3, 175.8, 158.0, 150.5, 136.7, 134.0, 132.4, 131.7, 130.9, 130.0, 129.5, 128.7, 128.6, 128.3, 127.7, 127.5, 127.1, 124.7, 123.6, 121.2, 121.0, 100.6.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>16</sub>O<sub>3</sub>: 376.1099; found: 376.1054.

## Diethyl 5-Formyl-4-(4-tolylethynyl)furan-2,3-dicarboxylate (3at)

IR (KBr): 2977, 1748, 1720, 1609 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.94 (s, 1 H), 7.44–7.45 (m, 2 H), 7.19–7.20 (m, 2 H), 4.22–4.46 (m, 4 H), 2.39 (s, 3 H), 1.39–1.41 (m, 6 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.6, 160.6, 156.8, 151.6, 145.6, 140.3, 131.9, 129.3, 126.1, 118.3, 118.1, 100.5, 62.6, 62.5, 21.6, 14.1, 14.0.

HRMS (EI): m/z [M]<sup>+</sup> calcd for  $C_{20}H_{18}O_6$ : 354.1103; found: 354.1107.

## Dimethyl 5-Formyl-4-(phenylethynyl)furan-2,3-dicarboxylate (3hs)

IR (KBr): 2983, 2874, 1763, 1724, 1642 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.93 (s, 1 H), 7.53–7.55 (m, 2 H), 7.37–7.39 (m, 3 H), 3.97 (s, 3 H), 3.96 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 176.5, 160.9, 157.2, 151.7, 145.5, 132.0, 129.9, 128.5, 125.9, 121.2, 117.8, 100.3, 53.2, 53.0.

HRMS (EI): m/z [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>O<sub>6</sub>: 312.0634; found: 312.0627.

**5-Phenyl-4-(thiophen-2-ylcarbonyl)furan-2-carbaldehyde (3fa)** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.74 (s, 1 H), 7.87–7.89 (m, 2 H), 7.72–7.74 (m, 1 H), 7.56–7.59 (m, 2 H), 7.40–7.41 (m, 3 H), 7.08–7.11 (m, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 181.9, 177.4, 159.1, 150.4, 143.9, 135.3, 134.8, 130.8, 128.7, 128.3, 128.1, 122.8.

#### 4-Benzoyl-5-(thiophen-2-yl)furan-2-carbaldehyde (4fa)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.66 (s, 1 H), 8.08–8.09 (m, 1 H), 7.82–7.84 (m, 2 H), 7.42–7.62 (m, 5 H), 7.12–7.14 (m, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 189.5, 177.2, 155.9, 149.2, 137.8, 133.2, 131.3, 130.9, 129.3, 128.7, 128.0, 123.8, 120.8.

#### 3,5-Diphenyl-4-(thiophen-2-ylcarbonyl)furan-2-carbaldehyde (3fc) and 4-Benzoyl-3-phenyl-5-(thiophen-2-yl)furan-2-carbaldehvde (4fc)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.62 (s, 1 H), 9.58 (s, 0.33 H), 7.75-7.78 (m, 2 H), 7.71-7.74 (m, 0.68 H), 7.60-7.61 (m, 0.35 H), 7.57-7.58 (m, 1 H), 7.41-7.43 (m, 2.62 H), 7.34-7.36 (m, 6.20 H), 7.01-7.03 (m, 0.32 H), 7.34-7.36 (m, 6.20 H), 7.25-7.32 (m, 1.32 H), 7.01-7.03 (m, 0.32 H), 6.88-6.90 (m, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 183.8, 182.8, 177.4, 177.1, 158.6, 158.5, 155.6, 154.9, 146.4, 144.1, 142.4, 140.5, 139.6, 135.8, 135.4, 133.7, 130.4, 129.7, 129.3, 128.8, 128.7, 128.4, 128.3, 127.4, 123.4, 122.9.

#### 4-(4-Methylbenzoyl)-5-phenylfuran-2-carbaldehyde (3ga) and 4-Benzoyl-5-(4-tolyl)furan-2-carbaldehyde (4ga)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.73$  (s, 1 H), 9.71 (s, 0.67 H), 7.82–7.86 (m, 3.37 H), 7.73–7.78 (m, 3.32 H), 7.57–7.60 (m, 0.68 H), 7.60-7.61 (m, 0.35 H), 7.57-7.58 (m, 1 H), 7.41-7.43 (m, 2.62 H), 7.34–7.36 (m, 0.86 H), 7.17–7.47 (m, 9.70 H), 2.42 (s, 3 H), 2.37 (s, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 190.4, 190.0, 177.4, 177.3, 160.1, 159.2, 150.4, 150.2, 144.6, 141.3, 137.3, 134.0, 133.4, 130.6, 130.1, 129.9, 129.6, 129.3, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 126.5, 123.7, 123.4, 123.0, 122.3, 21.6, 21.4.

#### Diethyl (E)-5-(3-Ethoxy-3-oxoprop-1-enyl)furan-2,3-dicarboxvlate (6)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34–7.38 (m, 1 H), 6.86 (s, 1 H), 6.51-6.55 (m, 1 H), 4.20-4.40 (m, 6 H), 1.27-1.38 (m, 9 H).

 $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.9, 161.7, 157.4, 151.7, 144.3,$ 129.1, 125.2, 120.9, 115.0, 61.8, 61.6, 60.8, 14.0.

HRMS (EI): *m*/*z* [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>18</sub>O<sub>7</sub>: 310.1053; found: 310.1049.

### Diethyl 5-Methylfuran-2,3-dicarboxylate (4aa)

Yellowish viscous oil.

IR (KBr): 2980, 1725, 1603, 1581, 1138 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.30 (s, 1 H), 4.25–4.31 (m, 4 H), 2.30 (s, 3 H), 1.26-1.32 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 162.7, 157.8, 155.4, 142.0, 125.1,$ 109.2, 61.2, 14.1, 14.0, 13.5.

MS (EI): *m*/*z* = 226, 198, 181, 153, 126, 109.

Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>5</sub>: C, 58.40; H, 6.24. Found: C, 58.26; H, 6.32.

#### Diethyl 4,5-Dimethylfuran-2,3-dicarboxylate (4ab) Yellowish viscous oil.

IR (KBr): 2983, 1722, 1556, 1092 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 4.27 - 4.35$  (m, 4 H), 2.25 (s, 3 H), 1.96 (s, 3 H), 1.29-1.35 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9, 157.9, 152.0, 140.0, 126.5, 116.57, 61.3, 61.0, 14.2, 14.1, 11.7, 8.50.

MS (EI): *m*/*z* = 240, 229, 194, 166, 137.

Anal. Calcd for C12H16O5: C, 59.99; H, 6.71. Found: C, 60.24; H, 6.63.

### Diethyl 5-Methyl-4-phenylfuran-2,3-dicarboxylate (4ac)

Yellowish viscous oil.

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IR (KBr): 3059, 2984, 1732, 1558, 1177, 700 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.22–7.34 (m, 5 H), 4.29 (q, J = 7.2 Hz, 2 H), 4.21 (q, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9, 157.8, 152.6, 139.5, 131.7, 130.7, 128.8, 128.3, 127.7, 126.6, 122.6, 111.4, 61.6, 61.2, 14.2, 13.9, 12.6.

MS (EI): *m*/*z* = 302, 257, 229, 202, 185, 128, 77.

Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>: C, 67.54; H, 6.00. Found: C, 67.30; H, 6.14.

### Diethyl 5-Methyl-4-(3-tolyl)furan-2,3-dicarboxylate (4ad) Yellowish viscous oil.

IR (KBr): 3052, 2984, 2935, 1733, 1610, 1557, 1096, 789 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.19–7.21 (m, 1 H), 7.02–7.09 (m, 3 H), 4.31 (q, J = 7.2 Hz, 2 H), 4.21 (q, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.30 (s, 3 H), 1.29 (t, *J* = 6.8 Hz, 3 H), 1.16 (t, *J* = 6.8 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 164.0, 157.8, 152.6, 139.4, 138.1, 130.6, 129.4, 128.5, 128.4, 126.7, 125.8, 122.7, 61.6, 61.2, 21.3, 14.1, 13.9, 12.6.

MS (EI): *m*/*z* = 316, 271, 243, 199, 91.

Anal. Calcd for C<sub>18</sub>H<sub>20</sub>O<sub>5</sub>: C, 68.34; H, 6.37. Found: C, 68.13; H, 6.45.

### Diethyl 4-(4-Methoxyphenyl)-5-methylfuran-2,3-dicarboxylate (4ae)

Yellowish viscous oil.

IR (KBr): 3041, 2983, 1737, 1606, 1560, 773 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.22 (d, *J* = 8.0 Hz, 2 H), 6.94 (t, *J* = 9.6 Hz, 2 H), 4.39 (q, *J* = 8.0 Hz, 2 H), 4.27 (q, *J* = 8.0 Hz, 2 H), 3.82 (s, 3 H), 2.39 (s, 3 H), 1.36 (t, J = 7.2 Hz, 3 H), 1.24 (t, J = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 164.0, 159.1, 157.8, 152.4, 139.3, 130.0, 126.7, 122.9, 122.2, 114.0, 61.6, 61.2, 55.2, 14.1, 13.9, 12.5.

MS (EI): *m*/*z* = 332, 304, 287, 259, 232, 187, 115.

Anal. Calcd for  $C_{18}H_{20}O_6$ : C, 65.05; H, 6.07. Found: C, 65.22; H, 5.93.

### Diethyl 5-Methyl-4-(thiophen-2-yl)furan-2,3-dicarboxylate (4ah)

Yellowish viscous oil.

IR (KBr): 3057, 2986, 1732, 1612, 1575, 1027 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33–7.34 (m, 1 H), 7.05–7.06 (m, 2 H), 4.30–4.39 (m, 4 H), 2.49 (s, 3 H), 1.28–1.37 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.7, 157.6, 153.2, 139.5, 132.9, 127.3 126.9, 125.9, 116.1, 111.6, 61.9, 61.4, 14.2, 13.9, 13.0.

MS (EI): *m*/*z* = 308, 263, 235, 208, 163, 135, 91.

Anal. Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>S: C, 58.43; H, 5.23. Found: C, 58.26; H, 5.17.

### Diethyl 4-(2-Methoxyphenyl)-5-methylfuran-2,3-dicarboxylate (4ai)

Yellowish viscous oil.

IR (KBr): 3044, 2971, 1731, 1609, 1561, 1156 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97 (d, *J* = 8.0 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 1 H), 7.22 (d, J = 7.6 Hz, 1 H), 4.36 (q, J = 6.8 Hz, 2 H), 4.09 (q, J = 6.8 Hz, 2 H), 3.72 (s, 3 H), 2.20 (s, 3 H), 1.34 (t, J = 7.2 Hz, 3 H), 1.03 (t, J = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 167.1, 162.8, 158.0, 152.2, 140.4, 131.9, 131.6, 131.1, 130.5, 128.2, 126.1, 122.7, 61.2, 61.1, 52.1, 14.1, 13.6, 12.2.

MS (EI): *m*/*z* = 332, 314, 242, 226.

Anal. Calcd for  $C_{18}H_{20}O_6$ : C, 65.05; H, 6.07. Found: C, 65.20; H, 5.95.

# Diethyl 4-[4-(Methoxycarbonyl)phenyl]-5-methylfuran-2,3-dicarboxylate (4aj)

Yellowish viscous oil.

IR (KBr): 3046, 2983, 1729, 1612, 1573, 1046 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.05 (d, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 4.37 (q, *J* = 8.0 Hz, 2 H), 4.26 (q, *J* = 8.0 Hz, 2 H), 3.90 (s, 3 H), 2.39 (s, 3 H), 1.33 (t, *J* = 8.0 Hz, 3 H), 1.19 (t, *J* = 8.0 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.6, 163.6, 157.6, 153.0, 152.9, 140.0, 135.5, 129.8, 128.8, 126.1, 121.8, 61.8, 61.4, 52.1, 14.1, 13.9, 12.7.

MS (EI): *m*/*z* = 360, 329, 315, 288, 211, 143, 128, 58.

Anal. Calcd for  $C_{19}H_{20}O_7$ : C, 63.33; H, 5.59. Found: C, 63.02; H, 5.63.

# Diethyl 4-(2-Fluorophenyl)-5-methylfuran-2,3-dicarboxylate (4ak)

Yellowish viscous oil.

IR (KBr): 3057, 2986, 1732, 1612, 1575, 1027 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.30–7.33 (m, 2 H), 7.07–7.15 (m, 2 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 4.21 (q, *J* = 8.0 Hz, 2 H), 2.31 (s, 3 H), 1.32 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.1, 157.7, 153.6, 140.5, 131.3, 129.9, 129.8 126.3, 124.1, 118.6, 115.8, 115.6, 61.4, 61.3, 14.1, 13.8, 12.7.

MS (EI): *m*/*z* = 320, 275, 247, 220, 203, 116.

Anal. Calcd for  $C_{17}H_{17}FO_5$ : C, 63.74; H, 5.35. Found: C, 63.56; H, 5.42.

# Diethyl 4-(4-Ethylphenyl)-5-methylfuran-2,3-dicarboxylate (4al)

Yellowish viscous oil.

IR (KBr): 3039, 2975, 1728, 1600, 1577, 765 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.19 (s, 4 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 2.63 (q, *J* = 7.6 Hz, 2 H), 2.38 (s, 3 H), 1.33 (t, *J* = 6.8 Hz, 3 H), 1.18–1.25 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 164.0, 157.8, 152.5, 143.8, 139.4, 128.7, 128.0, 127.9, 126.7, 122.6, 61.6, 61.2, 28.5, 15.3, 14.2, 13.9, 12.6.

MS (EI): *m*/*z* = 330, 315, 285, 258, 77.

Anal. Calcd for  $C_{19}H_{22}O_5$ : C, 69.07; H, 6.71. Found: C, 69.29; H, 6.57.

### Diethyl 5-Methyl-4-(2-tolyl)furan-2,3-dicarboxylate (4am) Yellowish viscous oil.

IR (KBr): 3048, 2983, 1732, 1560, 1450, 1177, 758 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.11–7.26 (m, 4 H), 4.39 (q, *J* = 8.0 Hz, 2 H), 4.14 (q, *J* = 8.0 Hz, 2 H), 2.21 (s, 3 H), 2.15 (s, 3 H), 1.37 (t, *J* = 8.0 Hz, 3 H), 1.08 (t, *J* = 8.0 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.3, 157.9, 152.7, 140.0, 137.4, 130.4, 129.9, 128.3, 126.9, 125.5, 122.4, 111.3, 61.2, 60.6, 19.7, 14.2, 13.7, 12.3.

MS (EI): *m*/*z* = 316, 270, 242, 198, 170, 115, 91.

Anal. Calcd for  $C_{18}H_{20}O_5$ : C, 68.34; H, 6.37. Found: C, 68.25; H, 6.44.

# Diethyl 4-(2-Ethylphenyl)-5-methylfuran-2,3-dicarboxylate (4an)

Yellowish viscous oil.

IR (KBr): 3042, 2985, 1727, 1608, 1562, 763 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.25–7.33 (m, 2 H), 7.06–7.15 (m, 2 H), 4.35 (q, *J* = 8.0 Hz, 2 H), 4.18 (q, *J* = 8.0 Hz, 2 H), 2.50 (q, *J* = 7.6 Hz, 2 H), 2.30 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H), 0.99 (t, *J* = 7.2 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.1, 157.7, 153.6, 140.5, 131.3, 129.9, 126.3, 124.0, 118.6, 116.8, 115.8, 61.4, 61.3, 46.2, 14.1, 13.7, 12.6, 11.5.

MS (EI): *m*/*z* = 330, 315, 285, 257, 77.

Anal. Calcd for  $C_{19}H_{22}O_5$ : C, 69.07; H, 6.71. Found: C, 70.42; H, 6.65.

#### Diethyl 4-Ethyl-5-methylfuran-2,3-dicarboxylate (4ao) Yellowish viscous oil.

IR (KBr): 2981, 1730, 1603, 1528, 1105 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.28–4.36 (m, 4 H), 2.39 (d, J = 7.6 Hz, 2 H), 2.27 (s, 3 H), 1.29–1.36 (m, 6 H), 1.07 (t, J = 7.6 Hz, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl\_3):  $\delta$  = 164.1, 157.9, 151.8, 139.7, 122.8, 110.8, 61.4, 61.0, 16.9, 14.7, 14.1, 14.0, 11.7.

MS (EI): *m*/*z* = 254, 208, 179, 162, 135, 108.

Anal. Calcd for  $C_{13}H_{18}O_5$ : C, 61.40; H, 7.14. Found: C, 61.16; H, 7.20.

## Ethyl 4-(4-Methoxyphenyl)-5-methyl-2-phenylfuran-3-carbox-ylate (3be)

White solid; mp 100.8–102.7 °C.

IR (KBr): 3057, 2986, 1732, 1612, 1575, 1027 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.83 (d, *J* = 7.2 Hz, 2 H), 7.36–7.44 (m, 3 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 6.93 (d, *J* = 7.6 Hz, 2 H), 4.13 (q, *J* = 6.8 Hz, 2 H), 3.85 (s, 3 H), 2.32 (s, 3 H), 1.05 (t, *J* = 6.8 Hz, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 164.6, 158.7, 153.7, 148.2, 130.7, 130.2, 128.5, 128.0, 127.5, 125.2, 122.5, 115.0, 113.4, 60.3, 55.2, 13.6, 11.9.

MS (EI): *m*/*z* = 336, 308, 291, 105, 77.

Anal. Calcd for  $C_{21}H_{20}O_4$ : C, 74.98; H, 5.99. Found: C, 74.76; H, 6.02.

#### (5-Methyl-2-phenylfuran-3-yl)(phenyl)methanone (4ea) Yellowish viscous oil.

IR (KBr): 3037, 1746, 1612, 1582, 1031 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81 (d, *J* = 9.6 Hz, 2 H), 7.64–7.66 (m, 2 H), 7.25–7.49 (m, 6 H), 6.28 (s, 1 H), 2.39 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.9, 154.4, 151.1, 138.2, 132.6, 130.0, 129.6, 128.9, 128.6, 128.5, 128.4, 128.2, 127.2, 121.7, 109.7, 13.3.

MS (EI): *m*/*z* = 262, 185, 105, 77.

Anal. Calcd for  $C_{18}H_{14}O_2$ : C, 82.42; H, 5.38. Found: C, 82.03; H, 5.42.

#### (5-Methyl-2,4-diphenylfuran-3-yl)(phenyl)methanone (4ec) Yellowish viscous oil.

IR (KBr): 3032, 1749, 1604, 1576 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81 (d, *J* = 9.6 Hz, 2 H), 7.55–7.57 (d, *J* = 8.4 Hz, 2 H), 7.35–7.39 (m, 1 H), 7.14–7.27 (m, 10 H), 2.45 (s, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 193.7, 150.8, 148.1, 137.5, 133.1, 132.2, 130.0, 129.8, 129.7, 129.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 128.0, 126.8, 126.2, 123.5, 121.7, 12.2.

MS (EI): *m*/*z* = 262, 141, 105, 77.

Anal. Calcd for  $C_{24}H_{18}O_2$ : C, 85.18; H, 5.36. Found: C, 84.92; H, 5.43.

### [5-Methyl-4-(phenylethynyl)-2-(4-tolyl)furan-3-yl](4-tolyl)methanone (4cs)

White solid; mp 142.5–144.3 °C.

IR (KBr): 3035, 2950, 1742, 1645 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.84 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.06–7.22 (m, 9 H), 2.53 (s, 3 H), 2.38 (s, 3 H), 2.31 (s, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.1, 154.4, 151.8, 143.4, 138.2, 134.8, 130.6, 129.8, 128.6, 128.5, 127.5, 127.4, 126.2, 126.0, 122.7, 121.2, 105.6, 94.5, 79.6, 21.4, 20.7, 12.3.

MS (EI): *m*/*z* = 390, 223, 207, 119, 105, 91, 77.

Anal. Calcd for  $C_{28}H_{22}O_2$ : C, 86.13; H, 5.68. Found: C, 85.90; H, 5.70.

### [5-Methyl-2-phenyl-4-(phenylethynyl)furan-3-yl](phenyl)methanone (4es)

Yellowish viscous oil.

IR (KBr): 3029 1738, 1632 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94 (d, *J* = 7.2 Hz, 2 H), 7.08–7.65 (m, 13 H), 2.54 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.3, 154.8, 151.9, 137.2, 132.7, 130.7, 129.6, 128.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 126.7, 126.1, 122.5, 121.7, 105.7, 94.7, 79.4, 12.3.

MS (EI): *m*/*z* = 390, 223, 207, 119, 105, 91, 77.

Anal. Calcd for  $C_{26}H_{18}O_2$ : C, 86.16; H, 5.01. Found: C, 86.41; H, 4.97.

#### Dimethyl 5-Methyl-4-(2-phenylethynyl)furan-2,3-dicarboxylate (4hs)

IR (KBr): 3051 2969, 1730, 1647, 1582, 1027 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45–7.47 (m, 2 H), 7.31–7.33 (m, 3 H), 3.93 (s, 3 H), 3.89 (s, 3 H), 2.49 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 162.6, 159.4, 157.8, 140.6, 131.6, 128.7, 128.5, 126.4, 122.7, 106.5, 94.9, 52.7, 52.5, 13.2.

MS (EI): *m*/*z* = 298, 267, 211, 152, 59.

Anal. Calcd for  $C_{17}H_{14}O_5$ : C, 68.45; H, 4.73. Found: C, 68.59; H, 4.69.

## Dimethyl 5-Methyl-4-(4-tolylethynyl)furan-2,3-dicarboxylate (4ht)

White solid; mp 123.9–125.4  $^{\circ}\text{C}.$ 

IR (KBr): 3055 2973, 1728, 1650 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.37 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 7.2 Hz, 2 H), 3.95 (s, 3 H), 3.91 (s, 3 H), 2.50 (s, 3 H), 2.36 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.0, 158.5, 157.2, 140.0, 138.3, 130.9, 128.6, 125.9, 119.1, 106.0, 94.5, 52.0, 51.8, 20.9, 12.5.

MS (EI): *m*/*z* = 312, 297, 281, 167, 59.

Anal. Calcd for  $C_{18}H_{16}O_5$ : C, 69.22; H, 5.16. Found: C, 69.43; H, 5.19.

## (2-Chlorophenyl)(5-methyl-2-phenylfuran-3-yl)methanone (4ia)

IR (KBr): 3027, 1723, 1608, 1542 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.76–7.78 (m, 2 H), 7.20–7.36 (m, 7 H), 6.23 (s, 1 H), 2.37 (s, 3 H).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 189.8, 156.9, 151.5, 139.7, 131.3, 130.9, 130.0, 129.7, 129.2, 129.1, 128.9, 128.0, 127.9, 126.3, 122.5, 109.0, 13.3.

MS (EI): *m*/*z* = 296, 185, 139, 77.

Anal. Calcd for  $C_{18}H_{13}CIO_2$ : C, 72.85; H, 4.42. Found: C, 72.73; H, 4.49.

## [5-Methyl-2-(2-chlorophenyl)furan-3-yl](phenyl)methanone (5ia)

Yellowish viscous oil.

IR (KBr): 3029, 1720, 1600, 1537 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.74 (d, *J* = 8.0 Hz, 2 H), 7.37–7.43 (m, 2 H), 7.22–7.33 (m, 3 H), 7.16–7.20 (m, 2 H), 6.46 (s, 1 H), 2.43 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.0, 152.4, 138.0, 133.5, 132.2, 131.9, 130.1, 129.8, 129.7, 129.3, 127.8, 126.3, 124.3, 108.2, 13.4.

MS (EI): *m*/*z* = 296, 261, 130, 77.

Anal. Calcd for  $C_{18}H_{13}CIO_2$ : C, 72.85; H, 4.42. Found: C, 72.42; H, 4.46.

## (2-Chlorophenyl)(5-methyl-2,4-diphenylfuran-3-yl)methanone (4ic)

Yellowish viscous oil.

IR (KBr): 3018, 1732 1609, 1561 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.71–7.73 (m, 2 H), 7.42–7.44 (m, 1 H), 7.14–7.32 (m, 11 H), 2.47 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.9, 150.7, 149.1, 137.6, 133.4, 132.5, 132.1, 132.0, 130.1, 129.8, 129.6, 129.4, 129.3, 128.1, 127.7, 126.8, 126.4, 124.2, 122.8, 12.3.

MS (EI): *m*/*z* = 372, 261, 139, 111, 105, 77.

Anal. Calcd for  $C_{24}H_{17}CIO_2$ : C, 77.31; H, 4.60. Found: C, 77.13; H, 4.68.

### [2-(2-Chlorophenyl)-5-methyl-4-phenylfuran-3-yl](phenyl)methanone (5ic)

White solid; mp 121–123 °C.

IR (KBr): 3021, 1730 1613, 1570 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.70–7.73 (m, 2 H), 7.29–7.35 (m, 5 H), 7.16–7.25 (m, 7 H), 2.37 (s, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.0, 154.5, 148.4, 138.4, 132.6, 132.0, 131.7, 131.0, 129.6, 129.3, 128.9, 128.5, 128.1, 127.9, 127.7, 127.5, 126.8, 125.9, 123.3, 12.0.

MS (EI): *m*/*z* = 372, 337, 105, 77.

Anal. Calcd for  $C_{24}H_{17}CIO_2$ : C, 77.31; H, 4.60. Found: C, 77.54; H, 4.51.

(5-Methyl-2-phenylfuran-3-yl)(thiophen-2-yl)methanone (4fa) Yellowish viscous oil. IR (KBr): 3020, 1728 1610, 1540 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.78–7.80 (m, 2 H), 7.63–7.66 (m, 2 H), 7.30–7.39 (m, 3 H), 7.06–7.08 (m, 1 H), 6.44 (s, 1 H), 2.45 (s, 3 H).

13C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 183.4, 153.6, 151.3, 144.8, 134.2, 133.9, 133.0, 130.8, 130.0, 128.6, 128.3, 127.8, 127.0, 121.6, 109.3, 13.4.

MS (EI): *m*/*z* = 268, 235, 165, 111, 77.

Anal. Calcd for  $C_{16}H_{12}O_2S$ : C, 71.62; H, 4.51. Found: C, 71.84; H, 4.14.

# [5-Methyl-2-(thiophen-2-yl)furan-3-yl](phenyl)methanone (5fa)

IR (KBr): 3025, 1726, 1602, 1530 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.88–7.90 (m, 3 H), 7.48–7.60 (m, 3 H), 7.38–7.40 (m, 1 H), 7.08–7.10 (m, 1 H), 6.29 (s, 1 H), 2.41 (s, 3 H).

13C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.5, 150.4, 138.9, 132.2, 132.0, 129.3, 128.2, 127.6, 127.3, 127.1, 120.3, 109.7, 13.3.

MS (EI): *m*/*z* = 268, 191, 105, 77.

Anal. Calcd for  $C_{16}H_{12}O_2S$ : C, 71.62; H, 4.51. Found: C, 71.76; H, 4.15.

## (5-Methyl-2-phenylfuran-3-yl)(4-tolyl) methanone~(4ga)~and~[5-Methyl-2-(4-tolyl)furan-3-yl](phenyl) methanone~(5ga)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.87 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.38–7.43 (m, 3 H), 7.30–7.32 (m, 3 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.31 (s, 2 H), 2.42 (s, 3 H), 2.41 (s, 3 H), 2.39 (s, 3 H), 2.34 (s, 3 H).

 $^{13}\mathrm{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.9, 191.7, 154.9, 153.9, 151.0, 150.8, 143.5, 138.7, 138.4, 135.8, 132.5, 132.3, 130.1, 129.9, 129.6, 129.4, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 127.3, 127.2, 127.1, 127.1, 121.9, 121.1, 109.8, 109.7, 21.6, 21.3, 13.5, 13.4.

MS (EI): *m*/*z* = 276, 105, 91, 55.

Anal. Calcd for  $C_{19}H_{16}O_2$ : C, 82.58; H, 5.84. Found: C, 82.15; H, 5.90.

#### (5-Methyl-2,4-diphenylfuran-3-yl)(4-tolyl)methanone (4gc) and [5-Methyl-4-phenyl-2-(4-tolyl)furan-3-yl](phenyl)methanone (5gc)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.80 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 7.25–7.32 (m, 16 H), 7.08–9.10 (m, 4 H), 2.50 (s, 3 H), 2.49 (s, 3 H), 2.32 (s, 3 H), 2.31 (s, 3 H).

 $^{13}\mathrm{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 194.0, 193, 8, 148.3, 144.4, 138.3, 133.3, 132.6, 132.5, 130.2, 130.0, 129.4, 129.3, 128.7, 128.5, 128.4, 128.2, 127.1, 126.4, 126.2, 123.7, 21.8, 21.4, 12.6, 12.5.

MS (EI): *m*/*z* = 352, 105, 91, 77, 55.

Anal. Calcd for  $C_{25}H_{20}O_2$ : C, 85.20; H, 5.72. Found: C, 85.77; H, 5.68.

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