Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 2098

www.rsc.org/obc

PAPER

A facile approach to highly functional trisubstituted furans *via* intramolecular Wittig reactions†

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Received 21st October 2010, Accepted 6th December 2010
DOI: 10.1039/c0ob00912a

An efficient and mild synthesis of trisubstituted furans, starting from α,β-unsaturated ketones, tributylphosphine, and acyl chlorides, is described. The strategy employs the intramolecular Wittig protocol as a key step to install the crucial furan ring, leading to a wide variety of highly functional furans in one step.

Introduction

The preparation of multi-substituted furans is of importance in organic synthesis because such a heterocyclic ring is found in numerous interesting compounds, which exhibit a wide array of activities and are also useful building blocks.[1,2] Accordingly, many powerful synthetic routes toward furan rings with specific substitution patterns have been designed and well applied,[1c,3] the majority of which include direct functionalization of furan rings,[4] cyclocondensation of 1,4-dicarbonyl compounds (Paal–Knorr synthesis),[5] Feist-Bénary synthesis,[6] and transition metal-catalyzed cycloisomerization of alkynyl or allenyl substrates.[3a,7] Still, of these developed strategies,[1–7,8] general and efficient methodologies for the syntheses of trisubstituted furans from simple and readily available precursors are of great value.[7a,9]

Recently, we have developed efficient syntheses of tetrasubstituted furans *via* intramolecular Wittig reactions.[10] The zwitterion intermediates, which resulted from the Michael additions of PBu_3 to the corresponding Michael acceptors, are very stable and can be formed effectively. The stabilities of the zwitterions were attributed to the delocalization of the negative charge with a ketone functionality and an electron-withdrawing group (Fig. 1).

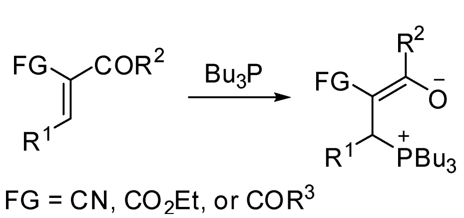

Fig. 1 Stable zwitterion intermediates generated from Michael additions of PBu_3 toward the corresponding Michael acceptors.

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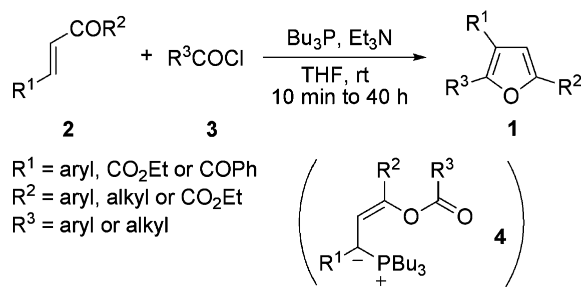
† Electronic supplementary information (ESI) available: General experimental procedures, compound characterization data, and NMR spectra. CCDC reference numbers 792216–792218. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00912a

Our interest in this area is stimulated by the prospect of designing a complementary entry to this class of polysubstituted furans, which cannot be easily acquired by other known protocols, based on our previous report on an intramolecular Wittig reaction. Inspired by our previous work, we herein report a novel preparation of trisubstituted furans **1** starting from Bu_3P, α,β-unsaturated ketones **2**, and acid chlorides **3** in the presence of Et_3N in one step, which is *via* the phosphorus ylides **4** as intermediates (Scheme 1). Different kinds of **2** in combination with various acid chlorides **3** should make this methodology an attractive approach toward a wide diversity of substitution patterns in the furan rings.



Scheme 1 Syntheses of highly functionalized furans **1** from **2**, acid chlorides **3** and Bu_3P in the presence of Et_3N.

Results and discussion

At the outset of our investigations, chalcone (**2a**), Bu_3P, Et_3N, and benzoyl chloride (**3a**) were chosen as a model study to optimize the reaction conditions (Fig. 2). However, pilot studies disclosed that our previously reported addition sequence of reactants proved unsatisfactory and unsuccessful in constructing these series of polysubstituted furans, being frustrated by the formation of messy byproducts and much lower yields (Fig. 2, equations a and b). In contrast to our previous report, the addition sequence of reactants is critical for the success of these designed reactions, because α,β-unsaturated ketones **2** are prone to undergo polymerization in the presence of Bu_3P.[10] Therefore, developing a different protocol was

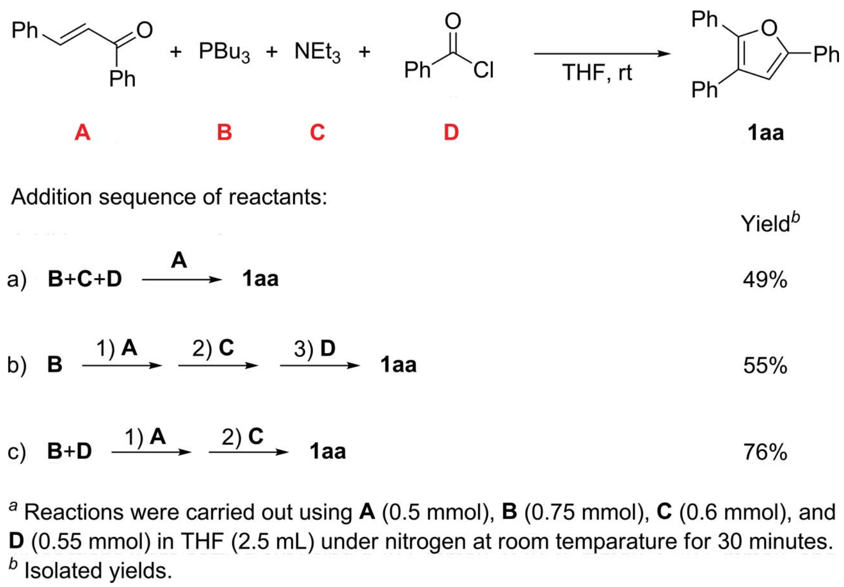
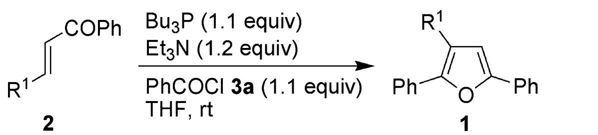


Fig. 2 Optimization of the addition sequence of reactants in the synthesis of **1aa**.[a]

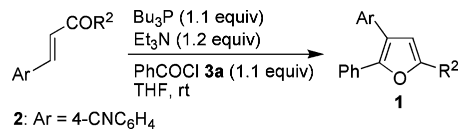
Table 1 Syntheses of furans **1** from **2** and benzoyl chloride (**3a**)[a]



Entry	R^1 (**2**)	Time/min	Yield of **1** (%)[b]
1	C_6H_5 (**2a**)	30	**1aa**, 76
2	4-$NO_2C_6H_4$ (**2b**)	10	**1ba**, 82
3	4-CN_6H_4 (**2c**)	10	**1ca**, 93
4	4-BrC_6H_4 (**2d**)	10	**1da**, 73[c]
5	4-$CF_3C_6H_4$ (**2e**)	10	**1ea**, 93
6	3-$NO_2C_6H_4$ (**2f**)	10	**1fa**, 84
7	3-ClC_6H_4 (**2g**)	10	**1ga**, 78
8	2-$NO_2C_6H_4$ (**2h**)	60	**1ha**, 70
9	4-$CH_3OC_6H_4$ (**2i**)	240	**1ia**, 41[d]
10	2-furyl (**2j**)	10	**1ja**, 60
11	2-thienyl (**2k**)	20	**1ka**, 68

[a] Reactions were carried out using **2** (0.5 mmol) in THF (2.5 mL) under nitrogen at rt. [b] Yields of isolated products. [c] The structure of **1da** was confirmed by X-ray analysis (CCDC number: 792217).† [d] 1.5 equiv of Bu_3P was used.

Table 2 Syntheses of furans **1** from **2** and benzoyl chloride (**3a**)[a]



Entry	R^2 (**2**)	Time/min	Yield of **1** (%)[b]
1	4-$NO_2C_6H_4$ (**2l**)	10	**1la**, 55
2	4-BrC_6H_4 (**2m**)	10	**1ma**, 83
3	3-$NO_2C_6H_4$ (**2n**)	10	**1na**, 68[c]
4	2-BrC_6H_4 (**2o**)	10	**1oa**, 67[d]
5	4-$CH_3OC_6H_4$ (**2p**)	10	**1pa**, 69
6	*t*-butyl (**2q**)	60	**1qa**, 52
7	cyclohexyl (**2r**)	60	**1ra**, 51
8	CO_2Et (**2s**)[e]	30	**1sa**, 55

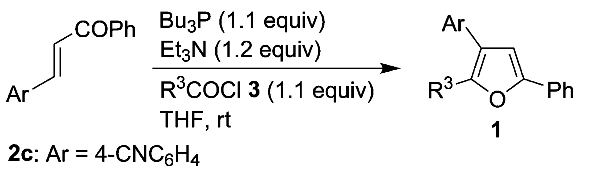
[a] Reactions were carried out using **2** (0.5 mmol) in THF (2.5 mL) under nitrogen at rt. [b] Yields of isolated products. [c] The reaction was carried out in CH_2Cl_2 due to the poor solubility of **2n** in THF. [d] The structure of **1oa** was confirmed by X-ray analysis (CCDC number: 792218).† [e] Ar = 2-furyl

necessary so that adducts between **2** and Bu_3P would not react further before trapping by acid chloride **3** to achieve **4**. After the optimization of the reaction conditions, we found that the best results were given when the reactions were carried out by the dropwise addition of **2** into the reaction mixture of Bu_3P and **3**, and then followed by the addition of Et_3N (Fig. 2, equation c).

Thus, chalcone (**2a**, 1.0 equiv), Bu_3P (1.1 equiv), Et_3N (1.2 equiv), and benzoyl chloride (**3a**, 1.1 equiv) reacted smoothly at room temperature within 30 min, furnishing the highly substituted furan **1aa** in 76% yield (Table 1, entry 1). Other β-aryl-subsituted α,β-unsaturated ketones, such as **2b–k** (R^1 = 4-$NO_2C_6H_4$, 4-CNC_6H_4, 4-BrC_6H_4, 4-$CF_3C_6H_4$, 3-$NO_2C_6H_4$, 3-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$, 2-furyl, or 2-thienyl), reacted successfully with **3a** within 10–240 min, leading to the corresponding products **1** in 41–93% yields (entries 2–11). The electronic effects have a strong influence on the reactivity.[11] The β-aryl-substituted α,β-unsaturated ketones **2b–g**, which bear an electron-withdrawing group on the aromatic ring, reacted with Bu_3P, Et_3N, and **3a** efficiently within 10 min (entries 2–7). However, the reaction of Michael acceptor **2a**, Bu_3P, Et_3N, and **3a** took place in a prolonged time (30 min) to lead to **1aa** (entry 1). It took an even longer time to proceed when **2i** (R^1 = 4-$CH_3OC_6H_4$) was used (4 h, entry 9). In addition, the steric effect of α,β-unsaturated ketones **2** was observed. For example, the Michael acceptor **2b** (R^1 = 4-$NO_2C_6H_4$) reacted with Bu_3P, Et_3N, and **3a** efficiently to furnish **1ba** within 10 min (entry 2). However, in the same reaction conditions, a longer time was necessary for **2h** (R^1 = 2-$NO_2C_6H_4$) to afford **1ha** (70% yield, 1 h) (entry 8).

The broad reaction scope of our protocol was demonstrated by further studies disclosed in Table 2. It showed that in the presence of Bu_3P (1.1 equiv) and Et_3N (1.2 equiv), the reactions of Michael acceptors bearing a ketone function with different substituents,

Table 3 Syntheses of furans **1** from **2c** and acid chloride **3**[a]



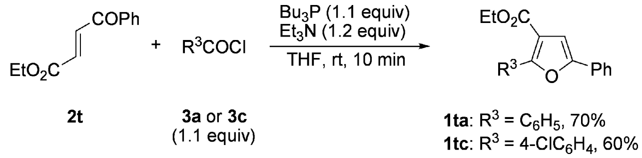
Entry	R^3(**3**)	Time/min	Yield of **1** (%)[b]
1	C_6H_5 (**3a**)	10	**1ca**, 93
2	4-$NO_2C_6H_4$ (**3b**)	10	**1ca**, 64
3	4-ClC_6H_4 (**3c**)	10	**1cc**, 77
4	4-$CH_3OC_6H_4$ (**3d**)	10	**1cd**, 80
5	4-$CH_3C_6H_4$ (**3e**)	10	**1ce**, 87
6	3-ClC_6H_4 (**3f**)	10	**1cf**, 67
7	2-$NO_2C_6H_4$ (**3g**)	—	**1cg**, —
8	2-ClC_6H_4 (**3h**)	10	**1ch**, 72
9	2-BrC_6H_4 (**3i**)	10	**1ci**, 67
10	2-furyl (**3j**)	60	**1cj**, 62
11	2-thienyl (**3k**)	10	**1ck**, 72
12	CH_3 (**3l**)	1800	**1cl**, 24[c]
13	*i*-propyl (**3m**)	60	**1cm**, 52
14	CO_2Et (**3n**)	—	**1cn**, —

[a] Reactions were carried out using **2c** (0.5 mmol) in THF (2.5 mL) under nitrogen at rt. [b] Yields of isolated products. [c] 1.5 equiv of Bu_3P was used.

like **2l–s** (R^2 = 4-$NO_2C_6H_4$, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 2-BrC_6H_4, 4-$CH_3OC_6H_4$, *t*-butyl, cyclohexyl, or CO_2Et), and **3a** (1.1 equiv), took place in 10–60 min, leading to the corresponding adducts **1** in 51–83% yields (Table 2, entries 1–8). Remarkably, electronic and steric effects of the R^2 (R^2 = Ar) group of **2** were hardly observed because the conversion of **2l–p** was complete within 10 min (entries 1–5). Furthermore, when the R^2 group is an aliphatic substituent, such as a *t*-butyl or cyclohexyl group, **2q** or **2r** worked smoothly with **3a**, Bu_3P and Et_3N within 60 min, giving rise to the corresponding furan **1qa** or **1ra** in 52 or 51% yield, respectively (entries 6 and 7). When the R^2 group is an ester functionality (Ar = 2-furyl), **2s** also reacted successfully with **3a** in the same reaction conditions, leading to **1sa** in 55% yield (entry 8).

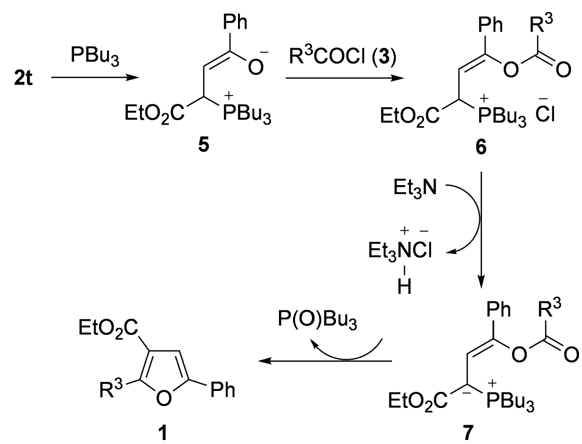
Next, we investigated the reaction scope of our protocol with different kinds of acyl chlorides **3** (Table 3). All the aryl-substituted acid chlorides **3a–f** and **3h–k** (R^3 = C_6H_5, 4-$NO_2C_6H_4$, 4-ClC_6H_4, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, 3-ClC_6H_4, 2-ClC_6H_4, 2-BrC_6H_4, 2-furyl, and 2-thienyl) were applied nicely in our designed reaction with **2c** in the presence of Bu_3P and Et_3N within 10 or 60 min, providing the corresponding furans **1** (62–93% yield) (entries 1–6 and 8–11). Interestingly, when **3g** (R^3 = 2-$NO_2C_6H_4$) was used, no desired reaction took place probably due to the steric hindrance of the nitro group, which retarded the occurrence of the intramolecular Wittig reaction. Besides, under the same reaction conditions, **2c** reacted effectively with an alkyl-substituted acid chloride **3m** (R^3 = *i*-propyl) within 60 min, furnishing **1cm** in 52% yield (entry 13). However, a poor result (**1cl**, 24% yield) was given when acetyl chloride (**3l**) was used even with a prolonged time (30 h, entry 12). Ethyl oxalyl chloride (**3n**) was also examined in our protocol (entry 14). However, no reaction was observed.

Instead of using the Michael acceptor with a ketone functionality (Tables 1–3), a substrate bearing both ketone and ester functions, such as **2t**, was also studied (Scheme 2). The reaction of **2t** and **3a** or **3c** in the presence of Bu_3P and Et_3N proceeded smoothly within 10 min at room temperature, giving rise to the fully functionalized furans **1ta** or **1tc** in 70 or 60% yield.



Scheme 2 Preparation of highly functionalized furans **1ta** and **1tc**.

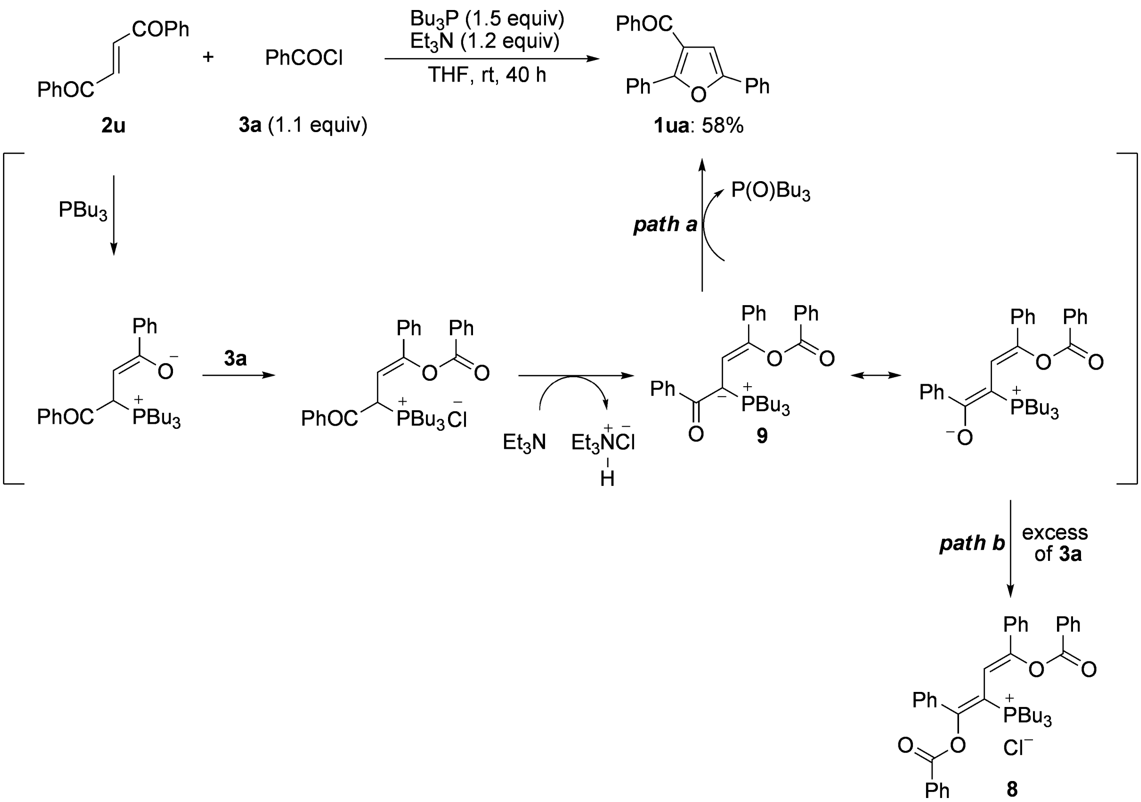
On the basis of the experimental results, a plausible reaction mechanism was proposed (Scheme 3). First, the regioselective Michael addition of Bu_3P toward **2t** took place, providing the corresponding zwitterion **5**. The intermediate **5** was *in situ* acylated with an acid chloride **3**, leading to the formation of **6**. Then deprotonation of **6** by Et_3N occurred, and the resulting ylide **7** underwent an intramolecular Wittig reaction, affording the corresponding furan **1**.



Scheme 3 A proposed mechanism for the formation of **1ta** or **1tc**.

Surprisingly, the more electron-deficient alkene **2u**, which was expected to work efficiently in our protocol, reacted with Bu_3P and benzoyl chloride (**3a**) in the presence of Et_3N in a relatively long time (40 h) in comparison to that of the other alkenes **2a–t** (10 min to 4 h) (Scheme 4). In addition, the interesting compound **8**, which resulted from the trapping of the intermediate **9** with excess **3a**, was observed in our crude mixture and can be confirmed by X-ray analysis.[12] All these phenomena showed that delocalization of the negative charge of **9** can account for the competitive formation of **8** and the relatively weak reactivity for the formation of **1ua**.

In conclusion, our strategy based on an intramolecular Wittig reaction represents a facile and versatile method for a poly-substituted installation at the 2-, 3-, and 5-positions in furans. Furthermore, the easy access to acid chlorides **3** as well as β-aryl-substituted α,β-unsaturated ketones **2**, makes our protocol an efficient approach toward a wide diversity of substitution patterns in the furan rings. Further studies and the extensions of this concept in the preparation of other heterocycles are currently underway in our laboratory.



Scheme 4 Preparation of highly functionalized furans **1ua** and the possible reaction mechanism.

Experimental section

Typical procedure for syntheses of furans 1 from 2 and acid chlorides 3 in the presence of Bu_3P and Et_3N. (TP for Tables 1–3, Schemes 2 and 4)

A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of acid chloride **3** (1.1 equiv) and Bu_3P (137.0 µL, 1.1 equiv) in dry THF (0.5 mL). A solution of **2** (0.5 mmol) in dry THF (2.0 mL) was added, which was followed by the addition of Et_3N (84.0 µL, 1.2 equiv). The reaction mixture was stirred for the indicated time at room temperature. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by flash chromatography furnished **1**.

2,3,5-Triphenylfuran (1aa)[7a]**.** Prepared according to TP from **2a** (104.3 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 30 min]. Purification by flash chromatography (hexanes; R_f: 0.56) yielded **1aa** as white solid (112.4 mg, 76%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.77 (d, 2H, J = 7.7 Hz), 7.61 (d, 2H, J = 7.3 Hz), 7.50–7.26 (m, 11H), 6.82 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.5, 147.9, 134.27, 131.1, 130.5, 128.8, 128.7, 128.6, 127.5, 127.4, 127.3, 126.1, 124.5, 123.8, 109.4. MS (20 eV, EI) m/z (%): 296 [M]$^+$ (100).

3-(4-Nitrophenyl)-2,5-diphenylfuran (1ba). Prepared according to TP from **2b** (126.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.41) yielded **1ba** as yellow solid (139.0 mg, 82%). mp.: 126.5–126.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.23 (d, 2H, J = 8.8 Hz), 7.81–7.74 (m, 2H), 7.64–7.54 (m, 4H), 7.44 (t, 2H, J = 8.0 Hz), 7.40–7.30 (m, 4H), 6.84 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.4, 149.3, 146.7, 141.1, 130.2, 129.9, 129.0, 128.8, 128.6, 128.4, 127.9, 126.6, 123.9, 123.8, 122.2, 108.2. MS (20 eV, EI) m/z (%): 342 [M+1]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 1598 (m), 1517 (s), 1344 (s). HRMS (ESI) for $C_{22}H_{16}NO_3$, [M+H]$^+$ (342.1130) found: 342.1133.

4-(2,5-Diphenylfuran-3-yl)benzonitrile (1ca)[9]**.** Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.41) yielded **1ca** as white solid (149.4 mg, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.79–7.74 (m, 2H), 7.65 (d, 2H, J = 8.4 Hz), 7.57 (d, 4H, J = 4.2 Hz), 7.42 (t, 2H, J = 7.8 Hz), 7.40–7.29 (m, 4H), 6.82 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.3, 149.0, 139.1, 132.4, 130.3, 130.0, 129.0, 128.8, 128.6, 128.3, 127.9, 126.5, 123.8, 122.6, 118.8, 110.7, 108.2. MS (20 eV, EI) m/z (%): 321[M]$^+$ (100).

3-(4-Bromophenyl)-2,5-diphenylfuran (1da). Prepared according to TP from **2d** (143.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes; R_f: 0.58) yielded **1da** as white solid (136.5 mg, 73%). mp.: 127.3–127.5 °C. ^{1}H-NMR (400 MHz,

$CDCl_3$, 25 °C) δ (ppm): 7.78 (d, 2H, J = 7.6 Hz), 7.62 (d, 2H, J = 7.3 Hz), 7.53 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 7.6 Hz), 7.40–7.27 (m, 6H), 6.80 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.8, 148.0, 133.2, 131.8, 130.8, 130.3, 130.2, 128.7, 128.5, 127.7, 127.6, 126.2, 123.8, 123.2, 121.2, 108.9. MS (20 eV, EI) m/z (%): 376 $[M+2]^+$ (100), 374 (64). IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3055 (m), 3033 (m), 1547 (m), 1488 (s), 691 (m), 595 (m). HRMS (ESI) for $C_{22}H_{16}BrO$, $[M+H]^+$ (375.0385) found: 375.0380.

2,5-Diphenyl-3-(4-(trifluoromethyl)phenyl)furan (1ea). Prepared according to TP from **2e** (138.1 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes; R_f: 0.40) yielded **1ea** as white solid (152.1 mg, 93%). mp.: 103.1–103.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.79 (d, 2H, J = 7.6 Hz), 7.70–7.55 (m, 6H), 7.45 (t, 2H, J = 7.5 Hz), 7.41–7.29 (m, 4H), 6.84 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.1, 148.6, 138.1, 130.6, 130.2, 129.4 (quartet, J = 32.0 Hz), 128.8, 128.7, 128.6, 128.0, 127.8, 126.4, 125.6 (quartet, J = 4.0 Hz), 124.2 (quartet, J = 270.0 Hz), 123.9, 123.0, 108.8. MS (20 eV, EI) m/z (%): 364 $[M]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 1617 (w), 1594 (w), 1495 (m), 1325 (s), 1167 (m), 1123 (m), 1067 (s). HRMS (ESI) for $C_{23}H_{16}F_3O$, $[M+H]^+$ (365.1153) found: 365.1156.

3-(3-Nitrophenyl)-2,5-diphenylfuran (1fa). Prepared according to TP from **2f** (126.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.38) yielded **1fa** as yellow solid (143.5 mg, 84%). mp.: 126.6–126.8 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.36–8.34 (m, 1H), 8.21–8.15 (m, 1H), 7.81–7.75 (m, 3H), 7.60–7.50 (m, 3H), 7.44 (t, 2H, J = 7.3 Hz), 7.39–7.29 (m, 4H), 6.86 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.2, 148.8, 148.5, 136.0, 134.5, 130.2, 130.0, 129.5, 128.7, 128.6, 128.2, 127.8, 126.3, 123.8, 123.2, 122.0, 121.9, 108.4. MS (20 eV, EI) m/z (%): 341 $[M]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 1528 (s), 1488 (m), 1440 (w), 1351 (s). HRMS (EI) for $C_{22}H_{16}NO_3$, $[M+H]^+$ (342.1130) found: 342.1139.

3-(3-Chlorophenyl)-2,5-diphenylfuran (1ga). Prepared according to TP from **2g** (121.4 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes; R_f: 0.5) yielded **1ga** as yellow oil (128.8 mg, 78%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25°°C) δ (ppm): 7.69 (d, 2H, J = 7.4 Hz), 7.55–7.50 (m, 2H), 7.40 (s, 1H), 7.35 (t, 2H, J = 7.7 Hz), 7.30–7.16 (m, 7H), 6.72 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.8, 148.3, 136.2, 134.5, 130.7, 130.3, 129.9, 128.8, 128.6, 128.5, 127.8, 127.7, 127.4, 126.9, 126.2, 123.8, 128.1, 109,0. MS (20 eV, EI) m/z (%): 333$[(M+2)+1]^+$ (15), 331 $[M+1]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 1591 (m), 1561 (m), 1488 (s), 1148 (s), 765 (s), 695 (s). HRMS (EI) for $C_{22}H_{15}ClO$, $[M]^+$ (330.0811) found: 330.0811.

3-(2-Nitrophenyl)-2,5-diphenylfuran (1ha). Prepared according to TP from **2h** (126.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 60 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.24) yielded **1ha** as orange solid (119.1 mg, 70%). mp.: 127.0–127.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.99 (d, 1H, J = 8.0 Hz), 7.76 (d, 2H, J = 7.4 Hz), 7.63–7.50 (m, 2H), 7.50–7.39 (m, 5H), 7.35–7.21 (m, 4H), 6.71 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.8, 149.5, 148.7, 132.8, 130.1, 129.2, 128.8, 128.7, 128.5, 127.8, 127.7, 125.5, 124.5, 123.9, 119.3, 109.1. MS (20 eV, EI) m/z (%): 342 $[M+1]^+$ (32), 105 (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 1524 (s), 1488 (m), 1457(m), 1347 (m). HRMS (EI) for $C_{22}H_{16}NO_3$, $[M+H]^+$ (342.1130) found: 342.1139.

3-(4-Methoxyphenyl)-2,5-diphenylfuran (1ia)[13a]**.** Prepared according to TP from **1ia** (119.1 mg, 0.5 mmol), Bu_3P (187.0 µL, 1.5 equiv), Et_3N (90.6 µL, 1.3 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 2 h]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.44) yielded **2ia** as yellow oil (67.1 mg, 41%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.79–7.74 (m, 2H), 7.65–7.61 (m, 2H), 7.45–7.21(m, 8H), 6.96–6.90 (m, 2H), 6.78 (s, 1H), 3.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 158.9, 152.4, 147.5, 131.2, 130.6, 129.8, 128.7, 128.4, 127.4, 127.3, 126.6, 126.0, 124.2, 123.8, 114.1, 109.6, 55.2. MS (20 eV, EI) m/z (%): 327 $[M+1]^+$ (100), 312 (11), 221 (9), 105 (11).

2′,5′-Diphenyl-2,3′-bifuran (1ja). Prepared according to TP from **2j** (99.8 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (63.8 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes; R_f: 0.30) yielded **1ja** as red solid (86.4 mg, 60%). mp.: 70.8–72.4 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.87(d, 2H, J = 7.6 Hz), 7.81 (d, 2H, J = 7.6 Hz), 7.55–7.42 (m, 5H), 7.42–7.30 (m, 2H), 6.99 (s, 1H), 6.58 (d, 1H, J = 3 Hz), 6.54–6.47 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.8, 148.3, 147.9, 141.5, 130.9, 130.2, 128.7, 128.4, 128.0, 127.7, 126.7, 123.9, 114.8, 111.2, 107.1, 107.0. MS (20 eV, EI) m/z (%): 286 $[M]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3114 (w), 3055 (m), 3033 (w), 1606 (m), 1484 (s), 1359 (w), 1148 (s). HRMS (EI) for $C_{20}H_{14}O_2$, $[M]^+$ (286.0994) found: 286.0987.

2,5-Diphenyl-3-(thiophen-2-yl)furan (1ka)[13b]**.** Prepared according to TP from **2k** (107.0 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 20 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.41) yielded **1ka** as yellow solid (103.0 mg, 68%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.78 (t, 4H, J = 7.5 Hz), 7.50–7.28 (m, 7H), 7.19 (d, 1H, J = 3.2 Hz), 7.13–7.06 (m, 1H), 6.86 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.5, 148.5, 135.5, 130.7, 130.2, 128.7, 128.4, 127.9, 127.7, 127.4, 126.4, 126.0, 125.1, 123.8, 117.5, 109.6. MS (20 eV, EI) m/z (%): 302 $[M]^+$ (100).

4-(5-(4-Nitrophenyl)-2-phenylfuran-3-yl)benzonitrile (1la). Prepared according to TP from **2l** (139.1 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 20/1; R_f: 0.50) yielded **1la** as yellow oil (100.9 mg, 55%). mp.: 210.5–212.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.29 (d, 2H, J = 8.2 Hz), 7.87 (d, 2H, J = 8.6 Hz), 7.68 (d, 2H, J = 7.8 Hz), 7.56 (d, 4H, J = 7.4 Hz), 7.38 (s, 3H), 7.05 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 151.2, 150.9, 146.7, 138.3, 135.6, 132.6, 129.6, 129.1, 129.0, 128.8, 126.8, 124.4, 124.0, 123.2, 118.6, 112.1, 111.3. MS (20 eV, EI) *m/z* (%): 367 $[M+1]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3107 (w), 2221 (m), 1598 (s), 1543 (m), 1510 (s), 1443 (m), 1333 (s), 1100 (s). HRMS (EI) for $C_{23}H_{14}N_2O_3$, $[M]^+$ (366.1004) found: 366.0999.

4-(5-(4-Bromophenyl)-2-phenylfuran-3-yl)benzonitrile (1ma). Prepared according to TP from **2m** (156.1 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.25) yielded **1ma** as white solid (165.8 mg, 83%). mp.: 145.0–146.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.69–7.44 (m, 10H), 7.41–7.28 (m, 3H), 6.78 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.1, 149.2, 138.7, 132.4, 131.8, 130.0, 128.9, 128.8, 128.6, 128.4, 126.5, 125.2, 122.6, 121.6, 118.7, 110.8, 108.7. MS (20 eV, EI) *m/z* (%): 401 $[M+2]^+$ (100), 399$[M]^+$ (72). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2229 (s), 1609 (s), 1488 (s), 1148 (m), 1008 (m), 695 (s). HRMS (EI) for $C_{23}H_{14}BrNO$, $[M]^+$ (399.0251) found: 399.0259.

4-(5-(3-Nitrophenyl)-2-phenylfuran-3-yl)benzonitrile (1na). Prepared according to TP from **2n** (139.1 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry CH_2Cl_2 (4.0 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 10/1; R_f: 0.27) yielded **1na** as yellow solid (124.4 mg, 68%). mp.: 185.5–187.3 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.53 (s, 1H), 8.12 (dd, 2H, J = 8.1, 1.7 Hz), 7.66 (d, 2H, J = 8.2 Hz), 7.63–7.51 (m, 5H), 7.41–7.32 (m, 3H), 6.98 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 150.7, 150.3, 148.7, 138.4, 132.5, 131.5, 129.8, 129.7, 129.1, 129.0, 128.8, 128.7, 126.7, 122.8, 122.1, 118.6, 118.4, 111.1, 110.4. MS (20 eV, EI) *m/z* (%): 367 $[M+1]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3048 (s), 2303 (m), 2229 (s), 1558 (m), 1532 (m). HRMS (ESI) for $C_{23}H_{14}N_2NaO$, $[M+Na]^+$ (389.0902) found: 389.0910.

4-(5-(2-Bromophenyl)-2-phenylfuran-3-yl)benzonitrile (1oa). Prepared according to TP from **2o** (156.1 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.39) yielded **1oa** as lemon yellow solid (133.9 mg, 67%). mp.: 124.5–126.1 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.95–7.86 (m, 1H), 7.73–7.50 (m, 7H), 7.45–7.29 (m, 5H), 7.22–7.11 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 150.6, 149.2, 138.9, 134.3, 132.4, 130.4, 130.1, 129.1, 128.8, 128.7, 128.6, 128.5, 127.5, 126.7, 122.3, 119.6, 118.8, 113.7, 110.8. MS (20 eV, EI) *m/z* (%): 402 $[(M+2)+1]^+$ (59), 400 $[M+1]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (m), 2229 (s), 1613 (s), 1469 (s), 1156 (m), 1023 (s), 694 (s). HRMS (ESI) for $C_{23}H_{15}BrNO$, $[M+H]^+$ (400.0337) found: 400.0341.

4-(5-(4-Methoxyphenyl)-2-phenylfuran-3-yl)benzonitrile (1pa). Prepared according to TP from **2p** (131.7 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 20/1; R_f: 0.30) yielded **1pa** as lemon yellow solid (121.2 mg, 69%). mp.: 121.5–123.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.68 (d, 2H, J = 8.6 Hz), 7.63 (d, 2H, J = 8.1 Hz), 7.54 (d, 4H, J = 8.3 Hz), 7.39–7.27 (m, 3H), 6.96 (d, 2H, J = 8.6 Hz), 6.67 (s, 1H), 3.85 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 159.4, 153.4, 148.3, 139.2, 132.4, 130.4, 130.0, 128.6, 128.0, 126.4, 125.3, 123.0, 122.5, 118.8, 114.2, 110.5, 106.7, 55.3. MS (20 eV, EI) *m/z* (%): 351 $[M]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 2229 (s), 1609 (s), 1502 (s), 1303 (m), 1252 (s). HRMS (MALDI) for $C_{24}H_{18}NO_2$, $[M+H]^+$ (352.1337) found: 352.1341.

4-(5-*tert*-Butyl-2-phenylfuran-3-yl)benzonitrile (1qa). Prepared according to TP from **2q** (106.5 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 60 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.27) yielded **1qa** as white solid (78.1 mg, 52%). mp.: 152.8–153.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.58 (d, 2H, J = 8.1 Hz), 7.52–7.42 (m, 4H), 7.36–7.26 (m, 3H), 6.14 (s, 1H), 1.35 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 164.1, 147.7, 139.8, 132.3, 131.0, 128.9, 128.5, 127.8, 126.4, 120.9, 119.0, 110.2, 105.6, 32.7, 29.0. MS (20 eV, EI) *m/z* (%): 302 $[M+1]^+$ (100), 286 (73). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2229 (s), 1609 (m), 1558 (m), 1510 (m). HRMS (EI) for $C_{21}H_{19}NO$, $[M]^+$ (301.1467) found: 301.1469.

4-(5-Cyclohexyl-2-phenylfuran-3-yl)benzonitrile (1ra). Prepared according to TP from **2r** (83.1 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 60 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.38) yielded **1ra** as white solid (83.1 mg, 51%). mp.: 161.3–162.1 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.54 (d, 2H, J = 8.2 Hz), 7.48–7.37 (m, 4H), 7.29–7.18 (m, 3H), 6.09 (s, 1H), 2.70–2.60 (m, 1H), 2.10–2.01 (m, 2H), 1.83–1.64 (m, 3H), 1.44–1.16 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 160.9, 147.6, 139.8, 132.3, 130.9, 128.9, 128.5, 127.8, 126.4, 120.9, 118.9, 110.2, 106.4, 37.2, 31.4, 26.0, 25.8. MS (20 eV, EI) *m/z* (%): 327 $[M]^+$ (100), 285 (21). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (m), 2221 (s), 1602 (s), 1558 (s), 1448 (s), 1255 (m). HRMS (MALDI) for $C_{23}H_{22}NO$, $[M+H]^+$ (328.1711) found: 328.1701.

Ethyl-2′-phenyl-2,3′-bifuran-5′-carboxylate (1sa). Prepared according to TP from **2s** (179.0 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 0.5 h]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.30) yielded **1sa** as colorless oil (132.0 mg, 55%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.78 (d, 2H, J = 6.5 Hz), 7.44–7.40 (m, 5H), 6.50–6.49 (m, 1H), 6.45–6.44 (m, 1H), 4.40 (quartet, 2H, J = 7.0 Hz), 1.40 (t, 3H, J = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 158.7, 152.2, 146.6, 143.4, 142.0, 129.8, 129.3, 128.4, 127.5, 119.1, 114.7, 111.3, 107.7, 61.1, 14.4. MS (20 eV, EI) *m/z* (%): 282 $[M]^+$ (100), 254 (39), 181 (10). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 2988 (w), 1723 (s), 1476 (s), 1321 (s), 1177 (m). HRMS (MALDI) for $C_{17}H_{15}O_4$, $[M+H]^+$ (283.0970) found: 283.0979.

4-(2-(4-Nitrophenyl)-5-phenylfuran-3-yl)benzonitrile (1cb). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv), and **3b** (74.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 10/1; R_f: 0.32) yielded **1cb** as yellow solid (119.6 mg, 65%). mp.: 197.2-199.2 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.16 (d, 2H, J = 7.9 Hz), 7.88–7.30 (m, 11H), 6.84 (s, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 155.0, 146.6, 146.1, 138.3, 136.1, 132.8, 129.3, 129.3, 129.0, 128.7, 126.4, 126.1, 124.1, 124.2, 118.4, 111.9, 109.4. MS (20 eV, EI) m/z (%): 367 [M+1]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3113 (w), 3061 (w), 2227 (s), 1598 (s), 1544 (m), 1515 (s), 1338 (s), 1110 (m). HRMS (MALDI) for $C_{23}H_{15}N_2O_3$, [M+H]$^+$ (367.1077) found: 367.1093.

4-(2-(4-Chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (1cc). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3c** (70.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 20/1; R_f: 0.32) yielded **1cc** as white solid (137.3 mg, 77%). mp.: 138.1–139.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.74 (d, 2H, J = 7.4 Hz), 7.65 (d, 2H, J = 8.3 Hz), 7.52–7.40 (m, 6H), 7.37–7.28 (m, 3H), 6.79 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.5, 147.7, 138.7, 134.0, 132.5, 129.7, 129.0, 128.9, 128.8, 128.7, 128.1, 127.6, 123.8, 123.1, 118.7, 111.0, 108.4. MS (20 eV, EI) m/z (%): 357 [M+2]$^+$ (74), 355 [M]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 2229 (s), 1609 (s), 1491 (s), 1266 (m), 1097 (m), 957 (m), 821 (s), 761 (m), 691 (m). HRMS (MALDI) for $C_{23}H_{15}ClNO$, [M+H]$^+$ (356.0842) found: 356.0851.

4-(2-(4-Methoxyphenyl)-5-phenylfuran-3-yl)benzonitrile (1cd). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3d** (78.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 20/1; R_f: 0.32) yielded **1cd** as yellow solid (139.4 mg, 80%). mp.: 145.0–147.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.74 (d, 2H, J = 7.6 Hz), 7.63 (d, 2H, J = 8.2 Hz), 7.54 (d, 2H, J = 8.2 Hz), 7.49 (d, 2H, J = 8.7 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.35–7.27 (m, 1H), 6.90 (d, 2H, J = 8.7 Hz), 6.80 (s, 1H), 3.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 159.7, 152.8, 149.2, 139.2, 132.3, 130.1, 128.8, 128.7, 128.1, 127.7, 123.7, 123.0, 121.2, 118.9, 114.1, 110.4, 108.0, 55.2. MS (20 eV, EI) m/z (%): 352 [M+1]$^+$ (100), 336 (10). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3113 (w), 3061 (m), 3002 (m), 2962 (m), 2939 (m), 2906 (m), 2227 (s), 1608 (s), 1570 (m), 1516 (s), 1492 (s), 1385 (m), 1301 (m), 1254 (s), 1177 (s), 1028 (s). HRMS (MALDI) for $C_{24}H_{17}NO_2$, [M+H]$^+$ (352.1337) found: 352.1345.

4-(5-Phenyl-2-*p*-tolylfuran-3-yl)benzonitrile (1ce). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3e** (74.0 µ L, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1 R_f: 0.42) yielded **1ce** as lemon yellow solid (145.5 mg, 87%). mp.: 169.5–170.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.76 (d, 2H, J = 7.6 Hz), 7.63 (d, 2H, J = 8.1 Hz), 7.55 (d, 2H, J = 8.2 Hz), 7.50–7.39 (m, 4H), 7.36–7.29 (m, 1H), 7.18 (d, 2H, J = 7.9 Hz), 6.81 (s, 1H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.1, 149.4, 139.3, 138.5, 132.5, 130.2, 129.5, 129.1, 128.9, 127.9, 127.6, 126.7, 123.9, 122.1, 119.0, 110.6, 108.2, 21.3. MS (20 eV, EI) m/z (%): 336 [M+1]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3061 (w), 3031 (w), 2923 (w), 2867 (w), 2227 (s), 1608 (s), 1516 (m), 1493 (s), 1384 (w), 1148 (m), 1051 (m). HRMS (MALDI) for $C_{24}H_{18}NO$, [M+H]$^+$ (336.1388) found: 336.1395.

4-(2-(3-Chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (1cf). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3f** (72.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.28) yielded **1cf** as lemon yellow solid (118.4 mg, 67%). mp.: 105.5–107.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.73 (d, 2H, J = 7.4 Hz), 7.65 (d, 2H, J = 8.3 Hz), 7.58–7.56 (m, 1H), 7.52 (d, 2H, J = 8.3 Hz), 7.42 (t, 2H, J = 7.8 Hz), 7.36–7.29 (m, 2H), 7.28–7.19 (m, 2H), 6.78 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.8, 147.2, 138.6, 134.7, 132.5, 132.0, 129.8, 129.7, 129.1, 128.8, 128.2, 128.1, 126.2, 124.3, 123.9, 123.6, 118.7, 111.1, 108.5. MS (20 eV, EI) m/z (%): 357 [M+2]$^+$ (34), 356 [M+1]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3120 (w), 3064 (m), 2227 (s), 1608 (s), 1592 (s), 1254 (m), 1149 (s), 762 (s). HRMS (MALDI) for $C_{23}H_{14}ClNO$, [M+H]$^+$ (356.0842) found: 356.0851.

4-(2-(2-Chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (1ch). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3h** (70.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.25) yielded **1ch** as white solid (118.1 mg, 72%). mp.: 118.8–119.4 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.77 (d, 2H, J = 7.8 Hz), 7.56 (d, 2H, J = 8.2 Hz), 7.53–7.29 (m, 9H), 6.98 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 154.3, 147.0, 138.2, 133.9, 132.3, 132.1, 130.6, 130.4, 129.9, 129.8, 128.7, 128.0, 127.6, 126.9, 124.5, 123.9, 118.8, 110.3, 106.0. MS (20 eV, EI) m/z (%): 357 [M+2]$^+$ (34), 356 [M+1]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3117 (w), 3064 (m), 2227 (s), 1610 (s), 1557 (m), 1384 (m), 1182 (s), 1151 (s), 762 (s). HRMS (MALDI) for $C_{23}H_{15}ClNO$, [M+H]$^+$ (356.0842) found: 356.0854.

4-(2-(2-Bromophenyl)-5-phenylfuran-3-yl)benzonitrile (1ci). Prepared according to TP from **2c** (116.6 mg 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3i** (74.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.25) yielded **1ci** as white solid (122.0 mg, 67%). mp.: 122.2–123.2 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.80–7.75 (m, 2H), 7.74–7.69 (m, 1H), 7.59–7.53 (m, 2H), 7.47–7.29 (m, 8H), 6.98 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 154.3, 148.6, 138.1, 133.8, 132.5, 132.4, 132.1, 131.0, 130.0, 128.9, 128.2, 127.8, 127.6, 124.2, 124.1, 124.0, 118.9, 110.4, 105.9. MS (20 eV, EI) m/z (%): 401 [M+2]$^+$ (93), 400 [M+1]$^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3120 (w), 3064 (m), 2227 (s), 1607 (s), 1487 (s), 1462 (m), 1267 (m), 1241 (m), 1147 (s), 1028 (s), 689 (s). HRMS (MALDI) for $C_{23}H_{15}BrNO$, [M+H]$^+$ (400.0337) found: 400.0348.

4-(5-Phenyl-2,2′-bifuran-3-yl)benzonitrile (1cj)[9]. Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3j** (55.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 60 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.28) yielded **1cj** as red solid (79.0 mg, 62%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.74 (d, 2H, J = 7.5 Hz), 7.70–7.63 (m, 4H), 7.48–7.38 (m, 3H), 7.41 (t, 1H, J = 7.4 Hz), 6.81 (s, 1H), 6.69 (d, 1H, J = 3.4 Hz), 6.53–6.47 (m, 1H). ^{13}C-NMR (100 MHz,

$CDCl_3$, 25 °C) δ (ppm): 153.4, 145.6, 142.4, 141.1, 137.9, 132.0, 129.7, 129.1, 128.8, 128.1, 123.9, 122.7, 118.9, 111.5, 110.7, 108.3, 107.7. MS (20 eV, EI) m/z (%): 312 $[M+1]^+$ (100).

4-(5-Phenyl-2-(thiophen-2-yl)furan-3-yl)benzonitrile (1ck). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3k** (62.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.32) yielded **1ck** as green solid (117.9 mg, 72%). mp.: 115.1–115.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.74–7.64 (m, 6H), 7.43 (t, 2H, J = 7.4 Hz), 7.37–7.27 (m, 2H), 7.25–7.19 (m, 1H), 7.06–6.98 (m, 1H), 6.78 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.1, 144.4, 138.4, 132.4, 132.2, 129.7, 129.2, 128.8, 128.0, 127.5, 125.7, 125.0, 123.8, 122.4, 118.8, 111.0, 108.1. MS (20 eV, EI) m/z (%): 327 $[M]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3110 (w), 3071 (w), 2227 (s), 1608 (s), 1556 (w), 1525 (w), 1495 (m), 1248 (w), 1146 (m). HRMS (MALDI) for $C_{21}H_{14}NOS$, $[M+H]^+$ (328.0796) found: 328.0801.

4-(2-Methyl-5-phenylfuran-3-yl)benzonitrile (1cl). Prepared according to TP from **2c** (126.6 mg, 0.5 mmol), Bu_3P (187.0 µL, 1.5 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3l** (40.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 30 h]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.25) yielded **1cl** as white solid (28.0 mg, 24%). mp.: 134.9–136.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.72–7.63 (m, 4H), 7.52 (d, 2H, J = 8.2 Hz), 7.39 (t, 2H, J = 7.6 Hz), 7.30–7.23 (m, 1H), 6.77 (s, 1H), 2.53 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 152.4, 148.9, 138.9, 132.4, 130.3, 128.7, 127.7, 127.5, 123.5, 121.7, 119.0, 109.8, 105.5, 13.5. MS (20 eV, EI) m/z (%): 260 $[M+1]^+$ (19), 259 [M] (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 1598 (m), 1517 (s), 1344 (s). HRMS (EI) for $C_{18}H_{13}NO$, $[M]^+$ (259.0997) found: 259.0993.

4-(2-Isopropyl-5-phenylfuran-3-yl)benzonitrile (1cm). Prepared according to TP from **2c** (116.6 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3m** (60.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 60 min]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.29) yielded **1cm** as white solid (75.0 mg, 52%). mp.: 112.1–122.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.67 (d, 4H, J = 7.9 Hz), 7.48 (d, 2H, J = 8.1 Hz), 7.39 (t, 2H, 7.6 Hz), 7.26 (t, 1H, J = 7.4 Hz), 6.71 (s, 1H), 3.24 (septet, 1H, J = 6.8 Hz), 1.37 (d, 6H, J = 6.8 Hz). ^{13}C–NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 157.0, 152.0, 139.1, 132.4, 130.4, 128.7, 128.3, 127.4, 123.5, 120.1, 119.0, 110.0, 105.7, 26.8, 21.6. MS (20 eV, EI) m/z (%): 287 $[M]^+$ (100), 272 (77). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2229 (s), 1609 (s), 1488 (s), 1075 (m), 761 (m). HRMS (EI) for $C_{20}H_{17}NO$, $[M]^+$ (287.1310) found: 287.1307.

Ethyl-2,5-diphenylfuran-3-carboxylate (1ta)[13c]**.** Prepared according to TP from **2t** (92.0 µL, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash chromatography (hexanes/ethyl acetate: 50/1; R_f: 0.38) yielded **1ta** as white solid (101.3 mg, 70%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.12 (d, 2H, J = 7.2 Hz), 7.76 (d, 2H, J = 7.5 Hz), 7.53–7.40 (m, 5H), 7.37–7.30 (m, 1H), 7.11(s, 1H), 4.36 (quartet, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 163.4, 156.4, 152.3, 129.7, 129.2, 128.7, 128.3, 128.0, 127.9, 123.9, 115.7, 107.9, 60.5, 14.2. MS (20 eV, EI) m/z (%): 292 $[M]^+$ (100).

Ethyl-2-(4-chlorophenyl)-5-phenylfuran-3-carboxylate (1tc)[13c]**.** Prepared according to TP from **2t** (92.0 µL, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **3c** (70.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 10 min]. Purification by flash-chromatography (hexanes/ethyl acetate: 20/1; R_f: 0.54) yielded **1tc** as white solid (98.0 mg, 60%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.06 (d, 2H, J = 8.6 Hz), 7.73 (d, 2H, J = 7.6 Hz), 7.50–7.37 (m, 4H), 7.36–7.28 (m, 1H), 7.08 (s, 1H), 4.34 (quartet, 2H, J = 7.1 Hz), 1.38 (t, 3H, J = 7.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 163.4, 155.1, 152.5, 135.2, 129.5, 128.8, 128.4, 128.2, 124.0, 116.2, 108.0, 67.7, 14.2. MS (20 eV, EI) m/z (%): 328 $[M+2]^+$ (28), 326 (100).

(2,5-Diphenylfuran-3-yl)(phenyl)methanone (1ua)[13d]**.** Prepared according to TP from **2u** (118.1 mg, 0.5 mmol), Bu_3P (137.0 µL, 1.1 equiv), Et_3N (84.0 µL, 1.2 equiv), and **1a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction conditions: rt for 40 h]. Purification by flash chromatography (hexanes/ethyl acetate: 40/1; R_f: 0.33) yielded **1ua** as yellow liquid (94.6 mg, 58%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.92 (d, 2H, J = 7.5 Hz), 7.86–7.74 (m, 4H), 7.59–7.28 (m, 9H), 6.95 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 191.6, 154.8, 152.4, 137.9, 132.8, 129.7, 128.9, 128.8, 128.3, 128.2, 128.1, 127.3, 124.0, 122.7, 108.6. MS (20 eV, EI) m/z (%): 324 $[M]^+$ (100), 247 (78), 105 (71).

(*E*)-4-(3-(4-Nitrophenyl)-3-oxoprop-1-enyl)benzonitrile (2l)[13e]**.** The compound **2l** was yielded as orange solid (1.15 g, 35%) according to the procedure of the reported literature. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.37 (d, 2H, J = 8.8 Hz), 8.16 (d, 2H, J = 8.8 Hz), 7.83 (d, 1H, J = 15.7 Hz), 7.75 (s, 4H), 7.40 (d, 1H, J = 15.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 188.3, 150.3, 143.9, 142.3, 138.5, 132.8, 129.5, 128.9, 124.2, 124.0, 118.2, 114.1. MS (20 eV, EI) m/z (%): 277 $[M-1]^+$ (100), 260 (7), 231 (15), 156 (7). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3047 (w), 2221 (s), 1731(w), 1672 (s), 1609 (s), 1524 (s), 1333 (s). HRMS (EI) for $C_{16}H_{10}N_2O_3$, $[M]^+$ (278.0691) found: 278.0695.

(*E*)-4-(3-(3-Nitrophenyl)-3-oxoprop-1-enyl)benzonitrile (2n)[13e]**.** The compound **2n** was yielded as brown solid (0.79 g, 56%) according to the procedure of the reported literature. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.84 (s, 1H), 8.51–8.44 (m, 1H), 8.37 (d, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 15.7 Hz), 7.80–7.70 (m, 5H), 7.61 (d, 1H, J = 15.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 187.4, 148.5, 143.9, 138.9, 138.5, 134.1, 132.8, 130.1, 129.0, 127.5, 123.6, 123.3, 118.2, 114.2. MS (20 eV, EI) m/z (%): 277 $[M-1]^+$ (100). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3092 (w), 3041 (w), 2229 (s), 1668 (s), 1609 (s), 1528 (s), 1432 (m), 1347 (s), 1336 (s). HRMS (MALDI) for $C_{16}H_{11}N_2O_3$, $[M+H]^+$ (279.07769) found: 279.0775.

(*E*)-4-(3-(2-Bromophenyl)-3-oxoprop-1-enyl)benzonitrile (2o)[13e]**.** The compound **2o** was yielded as yellow solid (2.08 g, 67%) according to the procedure of the reported literature. mp.: 130.2–131.1 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.70–7.60 (m, 5H), 7.47–7.31 (m, 4H), 7.17 (d, 1H, J = 16.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 193.6, 143.0, 140.5, 138.6, 133.4, 132.6, 131.8, 129.3, 128.7, 127.4, 119.4, 118.2, 113.6. MS (20 eV, EI) m/z (%): 313 $[M+2]^+$ (92), 311 $[M]^+$ (100), 232(51), 156

(30). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 2221 (s), 1668 (s), 1602 (s), 1333 (s), 665 (m), 629 (m). HRMS (MALDI) for $C_{16}H_{11}BrNO$, $[M+H]^+$ (312.0024) found: 312.0032.

(*E*)-4-(3-(4-Methoxyphenyl)-3-oxoprop-1-enyl)benzonitrile (2p)[13e]. The compound **2p** was yielded as lemon yellow solid (1.96 g, 75%) according to the procedure of the reported literature. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.06–8.01 (m, 2H), 7.78–7.67 (m, 5H), 7.61 (d, 1H, J = 15.6 Hz), 7.02–6.97 (m, 2H), 3.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 187.8, 163.8, 141.2, 139.4, 132.6, 130.9, 130.5, 128.6, 125.0, 118.4, 114.0, 113.2, 55.5. MS (20 eV, EI) m/z (%): 263 $[M]^+$ (100), 135 (49), 108 (7).

(*E*)-4-(3-Cyclohexyl-3-oxoprop-1-enyl)benzonitrile (2r)[13e]. The compound **2r** was yielded as white solid (0.21 g, 20%) according to the procedure of the reported literature. mp.: 93.8–94.6 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.69–7.61 (m, 4H), 7.55 (d, 1H, J = 16.0 Hz), 6.88 (d, 1H, J = 16.0 Hz), 2.68–2.58 (m, 1H), 1.95–1.78 (m, 4H), 1.75–1.66 (m, 1H), 1.49–1.17 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 202.32, 139.6, 139.1, 132.6, 128.5, 127.5, 118.3, 113.3, 48.8, 28.5, 25.8, 25.6. MS (20 eV, EI) m/z (%): 240 $[M+1]^+$ (100), 184 (14), 171 (35), 156 (58), 130 (11), 83 (5). IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 2982 (w), 2944 (w), 2223 (m), 1661 (s), 1613 (s), 1510 (m). HRMS (EI) for $C_{16}H_{18}NO$, $[M+H]^+$ (240.1388) found: 240.1398.

((1*Z*,3*E*)-1,4-Bis(benzoyloxy)-1,4-diphenylbuta-1,3-dien-2-yl)-tributylphosphonium chloride (8). A dry and nitrogen-flushed 10-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **3a** (128.0 μL, 2.2 equiv), Bu_3P (137.0 μL, 1.1 equiv), Et_3N (84.0 μL, 1.2 equiv) and **2u** (118.1 mg, 0.5 mmol) in dry THF (2.5 mL). The reaction mixture was stirred for 10 min at rt. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by simply washing with pentane and ethyl acetate, then recrystallization (dichloromethane/hexanes) furnishes the adduct **8** and NEt_3·HCl. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.81 (d, 2H, J = 7.9 Hz), 7.74 (d, 2H, J = 7.9 Hz), 7.61 (quartet, 2H, J = 7.3 Hz), 7.49–7.34 (m, 9 Hz), 7.30–7.21 (m, 5H), 6.81 (d, 1H, 4.5 Hz), 2.68–2.54 (m, 6H), 1.32–1.27 (m, 12H), 0.75 (t, 9H, 7.2 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C) δ (ppm): 163.4, 162.8, 162.2, 150.9 (d, J = 8 Hz), 135.2, 134.3, 133.2 (d, J = 7 Hz), 132.9, 131.1, 129.9, 129.7, 129.4, 129.2, 128.6 (d, J = 3 Hz), 128.5, 127.7, 127.5, 126.7, 124.9, 107.9 (d, J = 3 Hz), 103.8 (d, J = 58 Hz), 24.0 (d, J = 3 Hz), 23.9 (d, J = 5 Hz), 21.1 (d, J = 38 Hz), 13.1. ^{31}P-NMR (200 MHz, $CDCl_3$, 25 °C) δ (ppm): 32.7. MS (20 eV, ESI) m/z (%): 648 $[M-34]^+$ (37), 647 $[M-35]^+$ (100). HRMS (FAB) for $C_{42}H_{48}O_4P$, $[M-Cl]^+$ (647.3285) found: 647.3290. X-Ray analysis: CCDC 792216.

Acknowledgements

We thank the National Science Council of the Republic of China (NSC Grant No. 99-2113-M-003-004-MY2) and National Taiwan Normal University (99T3030-6) for financial support.

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12 The formation of the compound **8** was clearly observed without the formation of **1ua** when excess of **3a** (2.2 equiv) was used according to our protocol. Notably, it is the first time that the formation of compound **8**, in addition to that of **1ua**, can confirm the existence of the Wittig intermediate **9**. (CCDC number of the compound **8**: 792216).

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