

# A Facile Approach to Highly Functional Trisubstituted Furans via Intramolecular Wittig Reactions

Ko-Wei Chen, Siang-en Syu, Yeong-Jiunn Jang, and Wenwei Lin\*

Department of Chemistry, National Taiwan Normal University  
No. 88, Section 4, Tingchow Road, Taipei 116, Taiwan, ROC  
Fax: (+886) 02 29354249  
e-mail: wenweilin@ntnu.edu.tw

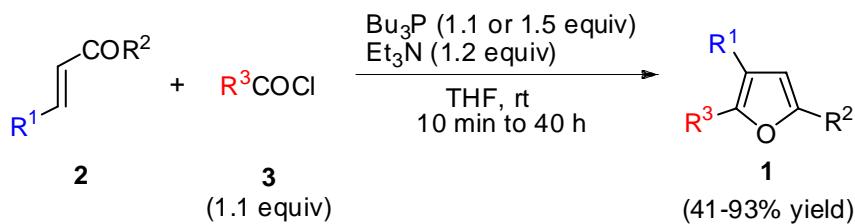
## Supplementary Information

### Index

<b>I. General Information</b>	<b>S2</b>
<b>II. Typical procedure for syntheses of furans 1 from 2 and acid chlorides 3 in the presence of Bu<sub>3</sub>P and Et<sub>3</sub>N. (TP for Tables 1-3, Schemes 2 and 4)</b>	<b>S2</b>
<b>III. Spectra data of compounds 1, 2 and 8</b>	<b>S2</b>
<b>IV. Spectra of X-ray crystallography (1da, 1oa, 2l, 2n, 2o, 2p, 2r, and 8)</b>	<b>S28</b>
<b>V. Spectra of <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR</b>	<b>S30</b>

**I. General Information:** All reactions were carried out under a nitrogen atmosphere in dried glassware. All starting materials were purchased from commercial sources, and used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by  $^1\text{H-NMR}$ . Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60. The temperature of our RT condition ranges from 27 to 30 °C. Majority of  $\beta$ -aryl-substituted  $\alpha,\beta$ -unsaturated ketones are commercial available, except **2l**, **2n**, **2o**, **2p**, and **2r**, which are prepared according to the procedure of the reported literature<sup>1</sup>.

**II. Typical procedure for syntheses of furans **1** from **2** and acid chlorides **3** in the presence of  $\text{Bu}_3\text{P}$  and  $\text{Et}_3\text{N}$ . (TP for Tables 1-3, Schemes 2 and 4)**



R<sup>1</sup> = aryl, CO<sub>2</sub>Eт or COPh

R<sup>2</sup> = aryl, alkyl or CO<sub>2</sub>Eт

R<sup>3</sup> = aryl or alkyl

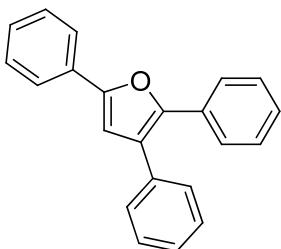
A dry and nitrogen-flushed 10-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of acid chloride **3** (1.1 equiv) and  $\text{Bu}_3\text{P}$  (137.0  $\mu\text{L}$ , 1.1 equiv) in dry THF (0.5 mL). A solution of **2** (0.5 mmol) in dry THF (2.0 mL) was added, which was followed by the addition of  $\text{Et}_3\text{N}$  (84.0  $\mu\text{L}$ , 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**.

**III. Spectra data of compounds **1**, **2** and **8**:**

**Synthesis of 2,3,5-triphenylfuran (**1aa**)<sup>2</sup>:**

<sup>1</sup> Choudary, B. M.; Kantam, M. L.; Ranganath, K. V. S.; Mahendar, K.; Sreedhar, B. *J. Am. Chem. Soc.* **2004**, 126, 3396-3397

<sup>2</sup> Dudnik, Alexander S.; Gevorgyan, Vladimir. *Angew. Chem., Int. Ed.* **2007**, 46, 5195-5197



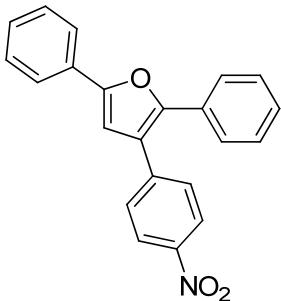
Prepared according to **TP** from **2a** (104.3 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 30 min]. Purification by *flash*-chromatography (hexanes; R<sub>f</sub>: 0.56) yielded **1aa** as white solids (112.4 mg, 76%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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]<sup>+</sup> (100).

### Synthesis of 3-(4-nitrophenyl)-2,5-diphenylfuran (**1ba**):



Prepared according to **TP** from **2b** (126.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.41) yielded **1ba** as yellow solids (139.0 mg, 82%).

mp.: 126.5-126.7 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

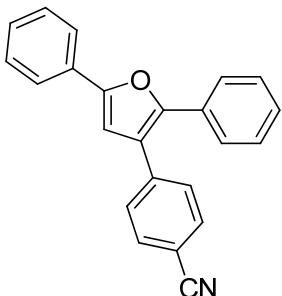
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.4, 149.3, 146.7, 141.1, 130.2, 129.9, 129.0, 128.8, 128.6, 128.4, 127.9, 126.6, 123.9, 123.8, 122.2, 108.2.

**MS** (20 eV, EI)  $m/z$  (%): 342 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3062 (w), 1598 (m), 1517 (s), 1344 (s).

**HRMS** (ESI) for C<sub>22</sub>H<sub>16</sub>NO<sub>3</sub>, [M+H]<sup>+</sup> (342.1130) found: 342.1133.

**Synthesis of 4-(2,5-diphenylfuran-3-yl)benzonitrile (1ca)<sup>3</sup>:**



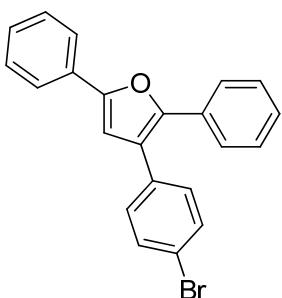
Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0  $\mu$ L, 1.1 equiv), Et<sub>3</sub>N (84.0  $\mu$ L, 1.2 equiv), and **3a** (64.0  $\mu$ L, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ ethyl acetate: 40/1;  $R_f$ : 0.41) yielded **1ca** as white solids (149.4 mg, 93%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /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).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /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]<sup>+</sup> (100).

**Synthesis of 3-(4-bromophenyl)-2,5-diphenylfuran (1da):**



Prepared according to **TP** from **2d** (143.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0  $\mu$ L, 1.1 equiv), Et<sub>3</sub>N (84.0  $\mu$ L, 1.2 equiv), and **3a** (64.0  $\mu$ L, 1.1 equiv) in dry THF (2.5 mL) [reaction

<sup>3</sup> Braun, R. U.; Mueller, T. J. *J. Synthesis* **2004**, 2391-2406.

condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes;  $R_f$  : 0.58) yielded **1da** as white solids (136.5 mg, 73%).

mp.: 127.3-127.5 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

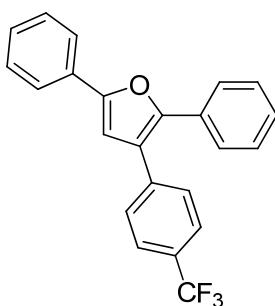
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 152.8, 148.0, 133.2, 131.8, 130.8, 130.3, 130.2, 128.7, 128.5, 127.7, 127.6, 126.2, 123.8, 123.2, 121.2, 108.9.

**MS** (20 eV, EI) *m/z* (%): 376 [M+2]<sup>+</sup> (100), 374 (64).

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055 (m), 3033 (m), 1547 (m), 1488 (s), 691 (m), 595 (m).

**HRMS** (ESI) for C<sub>22</sub>H<sub>16</sub>BrO, [M+H]<sup>+</sup> (375.0385) found: 375.0380.

### Synthesis of 2,5-diphenyl-3-(4-(trifluoromethyl)phenyl)furan (**1ea**):



Prepared according to **TP** from **2e** (138.1 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: 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

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

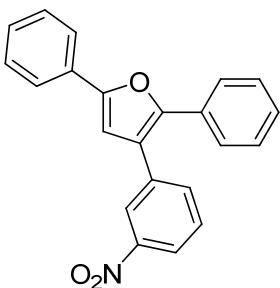
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.1, 148.6, 138.1, 130.6, 130.2, 129.4 (quartet,  $J$  = 32.0 Hz), 128.8, 128.7, 128.6, 128.0, 127.8, 126.4, 125.6 (quartet,  $J$  = 4.0 Hz), 124.2 (quartet,  $J$  = 270.0 Hz), 123.9, 123.0, 108.8.

**MS** (20 eV, EI) *m/z* (%): 364 [M]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3063 (w), 1617 (w), 1594 (w), 1495 (m), 1325 (s), 1167 (m), 1123 (m), 1067 (s).

**HRMS** (ESI) for C<sub>23</sub>H<sub>16</sub>F<sub>3</sub>O, [M+H]<sup>+</sup> (365.1153) found: 365.1156.

**Synthesis of 3-(3-nitrophenyl)-2,5-diphenylfuran (1fa):**



Prepared according to **TP** from **2f** (126.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.38) yielded **1fa** as yellow solid (143.5 mg, 84%).

mp.: 126.6-126.8 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

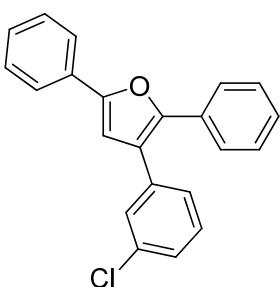
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.2, 148.8, 148.5, 136.0, 134.5, 130.2, 130.0, 129.5, 128.7, 128.6, 128.2, 127.8, 126.3, 123.8, 123.2, 122.0, 121.9, 108.4.

**MS** (20 eV, EI) *m/z* (%): 341 [M]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055 (w), 1528 (s), 1488 (m), 1440 (w), 1351 (s).

**HRMS** (EI) for C<sub>22</sub>H<sub>16</sub>NO<sub>3</sub>, [M+H]<sup>+</sup> (342.1130) found: 342.1139.

**Synthesis of 3-(3-chlorophenyl)-2,5-diphenylfuran (1ga):**



Prepared according to **TP** from **2g** (121.4 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes; R<sub>f</sub>: 0.5) yielded **1ga** as yellow oil (128.8 mg, 78%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

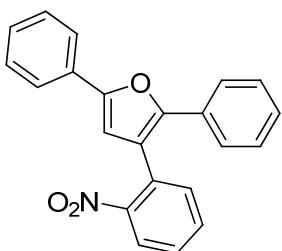
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 152.8, 148.3, 136.2, 134.5, 130.7, 130.3, 129.9, 128.8, 128.6, 128.5, 127.8, 127.7, 127.4, 126.9, 126.2, 123.8, 128.1, 109.0.

**MS** (20 eV, EI) *m/z* (%): 333[(M+2)+1]<sup>+</sup> (15), 331 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055 (w), 1591 (m), 1561 (m), 1488 (s), 1148 (s), 765 (s), 695 (s).

**HRMS** (EI) for C<sub>22</sub>H<sub>15</sub>ClO, [M]<sup>+</sup> (330.0811) found: 330.0811.

### Synthesis of 3-(2-nitrophenyl)-2,5-diphenylfuran (**1ha**):



Prepared according to **TP** from **2h** (126.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 60 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.24) yielded **1ha** as orange solid (119.1 mg, 70%).

mp.: 127.0-127.5 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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.

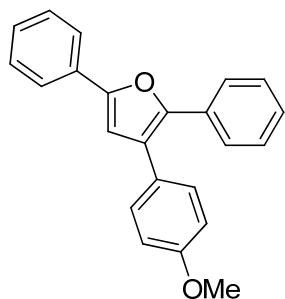
**MS** (20 eV, EI) *m/z* (%): 342 [M+1]<sup>+</sup> (32), 105 (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3063 (w), 1524 (s), 1488 (m), 1457(m), 1347 (m).

**HRMS** (EI) for C<sub>22</sub>H<sub>16</sub>NO<sub>3</sub>, [M+H]<sup>+</sup> (342.1130) found: 342.1139.

### Synthesis of 3-(4-methoxyphenyl)-2,5-diphenylfuran<sup>4</sup> (**1ia**):

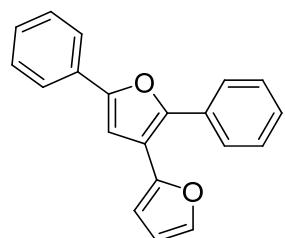
<sup>4</sup> Gopidas, K. R.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, 52, 5505 - 5511



Prepared according to **TP** from **1ia** (119.1 mg, 0.5 mmol), Bu<sub>3</sub>P (187.0 µL, 1.5 equiv), Et<sub>3</sub>N (90.6 µL, 1.3 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 2 h]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.44) yielded **2ia** as yellow oil (67.1 mg, 41%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).  
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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]<sup>+</sup> (100), 312 (11), 221 (9), 105 (11).

### Synthesis of 2',5'-diphenyl-2,3'-bifuran (**1ja**):



Prepared according to **TP** from **2j** (99.8 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3a** (63.8 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes; R<sub>f</sub>: 0.30) yielded **1ja** as red solid (86.4 mg, 60%).

mp.: 70.8-72.4 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.87(d, 2H, *J* = 7.6 Hz), 7.81 (d, 2H, *J* = 7.6Hz), 7.55-7.42 (m, 5H), 7.42-7.30 (m, 2H), 6.99 (s, 1H), 6.58 (d, 1H, *J* = 3Hz), 6.54-6.47 (m, 1H).

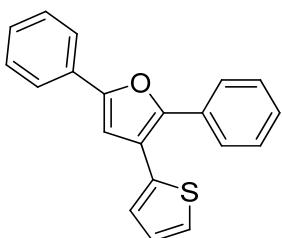
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 152.8, 148.3, 147.9, 141.5, 130.9, 130.2, 128.7, 128.4, 128.0, 127.7, 126.7, 123.9, 114.8, 111.2, 107.1, 107.0.

**MS** (20 eV, EI) *m/z* (%): 286 [M]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3114 (w), 3055 (m), 3033 (w), 1606 (m), 1484 (s), 1359 (w), 1148 (s).

**HRMS** (EI) for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>, [M]<sup>+</sup> (286.0994) found: 286.0987

**Synthesis of 2,5-diphenyl-3-(thiophen-2-yl)furan (1ka)<sup>5</sup>:**



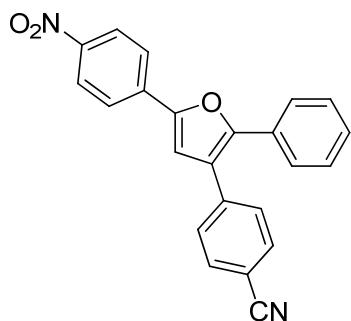
Prepared according to **TP** from **2k** (107.0 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 20 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.41) yielded **1ka** as yellow solid (103.0 mg, 68%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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]<sup>+</sup> (100).

**Synthesis of 4-(5-(4-nitrophenyl)-2-phenylfuran-3-yl)benzonitrile (1la):**



<sup>5</sup> Morrison, B. J.; Musgrave, Oliver C. *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1944–1947.

Prepared according to **TP** from **2l** (139.1 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 20/1; R<sub>f</sub>: 0.50) yielded **1la** as yellow oil (100.9 mg, 55%).

mp.: 210.5-212.5 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

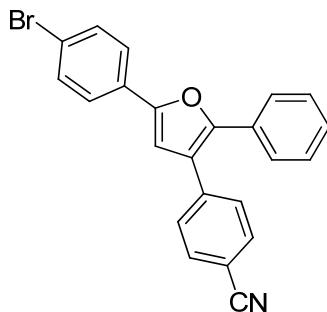
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 151.2, 150.9, 146.7, 138.3, 135.6, 132.6, 129.6, 129.1, 129.0, 128.8, 126.8, 124.4, 124.0, 123.2, 118.6, 112.1, 111.3.

**MS** (20 eV, EI) m/z (%): 367 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3107 (w), 2221 (m), 1598 (s), 1543 (m), 1510 (s), 1443 (m), 1333 (s), 1100 (s).

**HRMS** (EI) for C<sub>23</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>, [M]<sup>+</sup> (366.1004) found: 366.0999.

### Synthesis of 4-(5-(4-bromophenyl)-2-phenylfuran-3-yl)benzonitrile (**1ma**):



Prepared according to **TP** from **2m** (156.1 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.25) yielded **1ma** as white solid (165.8 mg, 83%).

mp.: 145.0-146.5 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.69-7.44 (m, 10H), 7.41-7.28 (m, 3H), 6.78 (s, 1H).

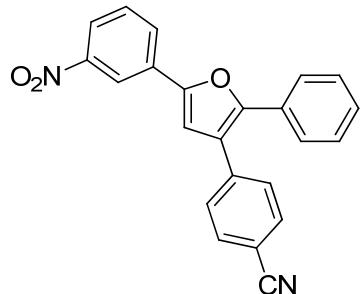
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 152.1, 149.2, 138.7, 132.4, 131.8, 130.0, 128.9, 128.8, 128.6, 128.4, 126.5, 125.2, 122.6, 121.6, 118.7, 110.8, 108.7.

**MS** (20 eV, EI) m/z (%): 401 [M+2]<sup>+</sup> (100), 399[M]<sup>+</sup> (72).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055 (w), 2229 (s), 1609 (s), 1488 (s), 1148(m), 1008(m), 695(s).

**HRMS** (EI) for **C<sub>23</sub>H<sub>14</sub>BrNO, [M]<sup>+</sup>** (399.0251) found: 399.0259.

**Synthesis of 4-(5-(3-nitrophenyl)-2-phenylfuran-3-yl)benzonitrile (1na):**



Prepared according to **TP** from **2n** (139.1mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 10/1; R<sub>f</sub>: 0.27) yielded **1na** as yellow solid (124.4 mg, 68%).

mp.: 185.5-187.3 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

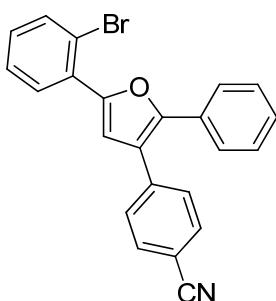
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 150.7, 150.3, 148.7, 138.4, 132.5, 131.5, 129.8, 129.7, 129.1, 129.0, 128.8, 128.7, 126.7, 122.8, 122.1, 118.6, 118.4, 111.1, 110.4.

**MS** (20 eV, EI) *m/z* (%): 367 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3048 (s), 2303 (m), 2229 (s), 1558 (m), 1532 (m).

**HRMS** (ESI) for **C<sub>23</sub>H<sub>14</sub>N<sub>2</sub>NaO, [M+Na]<sup>+</sup>** (389.0902) found: 389.0910.

**Synthesis of 4-(5-(2-bromophenyl)-2-phenylfuran-3-yl)benzonitrile (1oa):**



Prepared according to **TP** from **2o** (156.1 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.39) yielded **1oa** as lemon yellow solid (133.9 mg, 67%).

mp.: 124.5-126.1 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

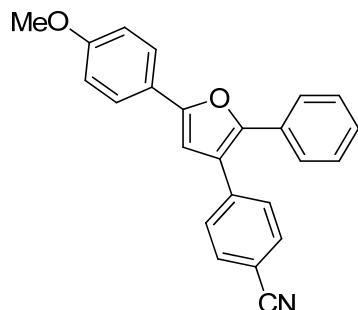
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 150.6, 149.2, 138.9, 134.3, 132.4, 130.4, 130.1, 129.1, 128.8, 128.7, 128.6, 128.5, 127.5, 126.7, 122.3, 119.6, 118.8, 113.7, 110.8.

**MS** (20 eV, EI) m/z (%): 402 [(M+2)+1]<sup>+</sup> (59), 400 [M+1]<sup>+</sup> (100),.

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3063 (m), 2229 (s), 1613 (s), 1469 (s), 1156 (m), 1023 (s), 694 (s).

**HRMS** (ESI) for C<sub>23</sub>H<sub>15</sub>BrNO, [M+H]<sup>+</sup> (400.0337) found: 400.0341.

#### Synthesis of 4-(5-(4-methoxyphenyl)-2-phenylfuran-3-yl)benzonitrile (**1pa**):



Prepared according to **TP** from **2p** (131.7 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3a** (64.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 20/1; R<sub>f</sub>: 0.30) yielded **1pa** as lemon yellow solid (121.2 mg, 69%).

mp.: 121.5-123.5 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

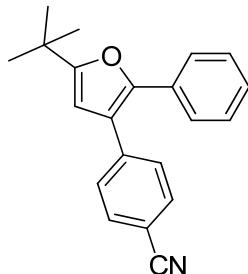
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 159.4, 153.4, 148.3, 139.2, 132.4, 130.4, 130.0, 128.6, 128.0, 126.4, 125.3, 123.0, 122.5, 118.8, 114.2, 110.5, 106.7, 55.3.

**MS** (20 eV, EI) m/z (%): 351 [M]<sup>+</sup> (100).

**IR** ( $\text{CH}_2\text{Cl}_2$ )  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3063 (w), 2229 (s), 1609 (s), 1502 (s), 1303 (m), 1252 (s).

**HRMS** (MALDI) for  $\text{C}_{24}\text{H}_{18}\text{NO}_2$ ,  $[\text{M}+\text{H}]^+$  (352.1337) found: 352.1341.

**Synthesis of 4-(5-tert-butyl-2-phenylfuran-3-yl)benzonitrile (1qa):**



Prepared according to **TP** from **2q** (106.5 mg, 0.5 mmol),  $\text{Bu}_3\text{P}$  (137.0  $\mu\text{L}$ , 1.1 equiv),  $\text{Et}_3\text{N}$  (84.0  $\mu\text{L}$ , 1.2 equiv), and **3a** (64.0  $\mu\text{L}$ , 1.1 equiv) in dry THF (2.5 mL) [reaction condition: 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

**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 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).

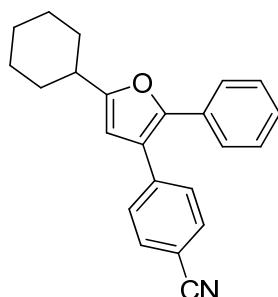
**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 164.1, 147.7, 139.8, 132.3, 131.0, 128.9, 128.5, 127.8, 126.4, 120.9, 119.0, 110.2, 105.6, 32.7, 29.0.

**MS** (20 eV, EI)  $m/z$  (%): 302  $[\text{M}+1]^+$  (100), 286 (73).

**IR** ( $\text{CH}_2\text{Cl}_2$ )  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3055 (w), 2229 (s), 1609 (m), 1558 (m), 1510 (m).

**HRMS** (EI) for  $\text{C}_{21}\text{H}_{19}\text{NO}$ ,  $[\text{M}]^+$  (301.1467) found: 301.1469.

**Synthesis of 4-(5-cyclohexyl-2-phenylfuran-3-yl)benzonitrile (1ra):**



Prepared according to **TP** from **2r** (83.1 mg, 0.5 mmol), tributylphosphine (137.0  $\mu\text{L}$ , 1.1 equiv), triethylamine (84.0  $\mu\text{L}$ , 1.2 equiv), and **3a** (64.0  $\mu\text{L}$ , 1.1 equiv) in dry THF

(2.5 mL) [reaction condition: 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

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

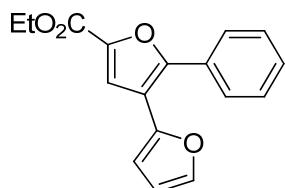
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 160.9, 147.6, 139.8, 132.3, 130.9, 128.9, 128.5, 127.8, 126.4, 120.9, 118.9, 110.2, 106.4, 37.2, 31.4, 26.0, 25.8.

**MS** (20 eV, EI)  $m/z$  (%): 327 [M]<sup>+</sup> (100), 285 (21).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055 (m), 2221 (s), 1602 (s), 1558 (s), 1448 (s), 1255 (m).

**HRMS** (MALDI) for C<sub>23</sub>H<sub>22</sub>NO, [M+H]<sup>+</sup> (328.1711) found: 328.1701.

### Synthesis of ethyl 2'-phenyl-2,3'-bifuran-5'-carboxylate (**1sa**):



Prepared according to **TP** from **2s** (179.0 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: 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%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

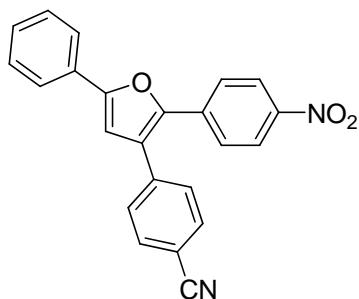
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 158.7, 152.2, 146.6, 143.4, 142.0, 129.8, 129.3, 128.4, 127.5, 119.1, 114.7, 111.3, 107.7, 61.1, 14.4.

**MS** (20 eV, EI)  $m/z$  (%): 282 [M]<sup>+</sup> (100), 254 (39), 181 (10).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2988 (w), 1723 (s), 1476 (s), 1321 (s), 1177 (m).

**HRMS** (MALDI) for C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>, [M+H]<sup>+</sup> (283.0970) found: 283.0979.

### Synthesis of 4-(2-(4-nitrophenyl)-5-phenylfuran-3-yl)benzonitrile (**1cb**):



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3b** (74.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 10/1; R<sub>f</sub>: 0.32) yielded **1cb** as yellow solid (119.6 mg, 65%).

mp.: 197.2-199.2 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.16 (d, 2H, J = 7.9 Hz), 7.88-7.30 (m, 11H), 6.84 (s, 1H).

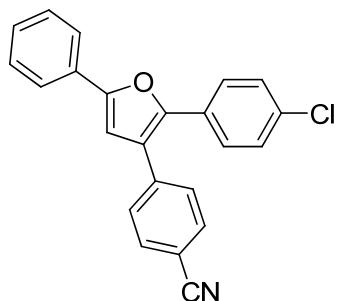
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 155.0, 146.6, 146.1, 138.3, 136.1, 132.8, 129.3, 129.3, 129.0, 128.7, 126.4, 126.1, 124.1, 124.2, 118.4, 111.9, 109.4.

**MS** (20 eV, EI) m/z (%): 367 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3113 (w), 3061 (w), 2227 (s), 1598 (s), 1544 (m), 1515 (s), 1338 (s), 1110 (m).

**HRMS** (MALDI) for C<sub>23</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>, [M+H]<sup>+</sup> (367.1077) found: 367.1093.

#### Synthesis of 4-(2-(4-chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (**1cc**):



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3c** (70.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 20/1; R<sub>f</sub>: 0.32) yielded **1cc** as white solid (137.3 mg, 77%).

mp.: 138.1-139.0 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

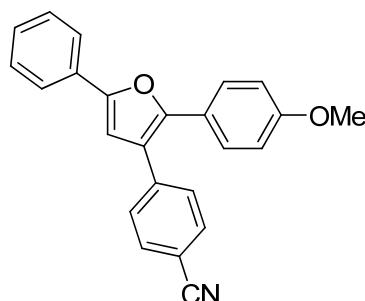
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.5, 147.7, 138.7, 134.0, 132.5, 129.7, 129.0, 128.9, 128.8, 128.7, 128.1, 127.6, 123.8, 123.1, 118.7, 111.0, 108.4.

**MS** (20 eV, EI) *m/z* (%): 357 [M+2]<sup>+</sup> (74), 355 [M]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3063 (w), 2229 (s), 1609 (s), 1491 (s), 1266 (m), 1097 (m), 957 (m), 821 (s), 761 (m), 691 (m).

**HRMS** (MALDI) for C<sub>23</sub>H<sub>15</sub>CINO, [M+H]<sup>+</sup> (356.0842) found: 356.0851.

**Synthesis of 4-(2-(4-methoxyphenyl)-5-phenylfuran-3-yl)benzonitrile (1cd):**



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3d** (78.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 20/1; R<sub>f</sub>: 0.32) yielded **1cd** as yellow solid (139.4 mg, 80%).

mp.: 145.0-147.0 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

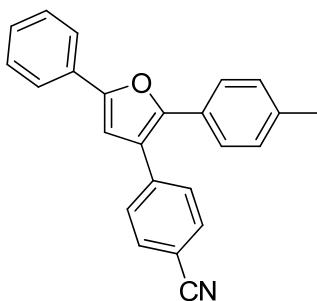
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 159.7, 152.8, 149.2, 139.2, 132.3, 130.1, 128.8, 128.7, 128.1, 127.7, 123.7, 123.0, 121.2, 118.9, 114.1, 110.4, 108.0, 55.2.

**MS** (20 eV, EI) *m/z* (%): 352 [M+1]<sup>+</sup> (100), 336 (10).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 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<sub>24</sub>H<sub>17</sub>NO<sub>2</sub>, [M+H]<sup>+</sup> (352.1337) found: 352.1345.

**Synthesis of 4-(5-phenyl-2-p-tolylfuran-3-yl)benzonitrile (1ce):**



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3e** (74.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1: 0.42) yielded **1ce** as lemon yellow solid (145.5 mg, 87%).

mp.: 169.5-170.9 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

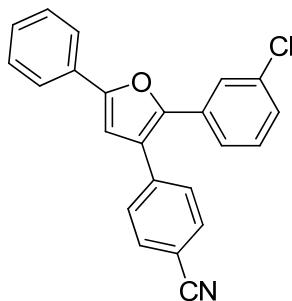
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.1, 149.4, 139.3, 138.5, 132.5, 130.2, 129.5, 129.1, 128.9, 127.9, 127.6, 126.7, 123.9, 122.1, 119.0, 110.6, 108.2, 21.3.

**MS** (20 eV, EI) *m/z* (%): 336 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 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<sub>24</sub>H<sub>18</sub>NO, [M+H]<sup>+</sup> (336.1388) found: 336.1395.

#### Synthesis of 4-(2-(3-chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (1cf):



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3f** (72.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.28) yielded **1cf** as lemon yellow solid (118.4 mg, 67%).

mp.: 105.5-107.5 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

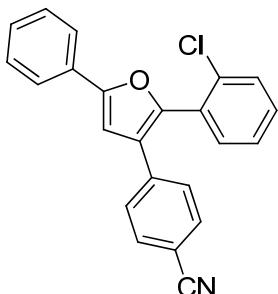
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.8, 147.2, 138.6, 134.7, 132.5, 132.0, 129.8, 129.7, 129.1, 128.8, 128.2, 128.1, 126.2, 124.3, 123.9, 123.6, 118.7, 111.1, 108.5.

**MS** (20 eV, EI) *m/z* (%): 357 [M+2]<sup>+</sup> (34), 356 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3120 (w), 3064 (m), 2227 (s), 1608 (s), 1592 (s), 1254 (m), 1149 (s), 762 (s).

**HRMS** (MALDI) for C<sub>23</sub>H<sub>14</sub>ClNO, [M+H]<sup>+</sup> (356.0842) found: 356.0851.

### Synthesis of 4-(2-(2-chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (**1ch**):



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3h** (70.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.25) yielded **1ch** as white solid (118.1 mg, 72%).

mp.: 118.8-119.4 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

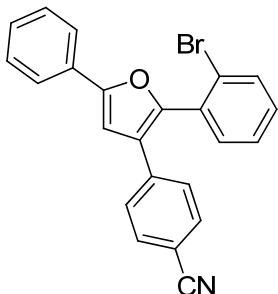
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 154.3, 147.0, 138.2, 133.9, 132.3, 132.1, 130.6, 130.4, 129.9, 129.8, 128.7, 128.0, 127.6, 126.9, 124.5, 123.9, 118.8, 110.3, 106.0.

**MS** (20 eV, EI) *m/z* (%): 357 [M+2]<sup>+</sup> (34), 356 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3117 (w), 3064 (m), 2227 (s), 1610 (s), 1557 (m), 1384 (m), 1182 (s), 1151 (s), 762 (s).

**HRMS** (MALDI) for C<sub>23</sub>H<sub>15</sub>ClNO, [M+H]<sup>+</sup> (356.0842) found: 356.0854.

**Synthesis of 4-(2-(2-chlorophenyl)-5-phenylfuran-3-yl)benzonitrile (1ci):**



Prepared according to **TP** from **2c** (116.6 mg 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3i** (74.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.25) yielded **1ci** as white solid (122.0 mg, 67%).

mp.: 122.2-123.2 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

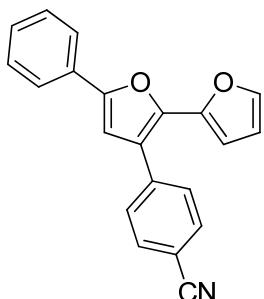
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 154.3, 148.6, 138.1, 133.8, 132.5, 132.4, 132.1, 131.0, 130.0, 128.9, 128.2, 127.8, 127.6, 124.2, 124.1, 124.0, 118.9, 110.4, 105.9.

**MS** (20 eV, EI) *m/z* (%): 401 [M+2]<sup>+</sup> (93), 400 [M+1]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 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<sub>23</sub>H<sub>15</sub>BrNO, [M+H]<sup>+</sup> (400.0337) found: 400.0348.

**Synthesis of 4-(5-phenyl-2,2'-bifuran-3-yl)benzonitrile<sup>3</sup> (1cj):**



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3j** (55.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction

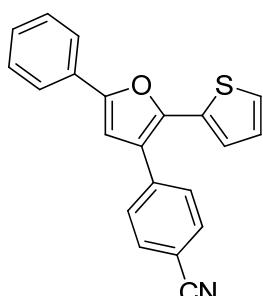
condition: RT for 60 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1;  $R_f$ : 0.28) yielded **1cj** as red solid (79.0 mg, 62%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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]<sup>+</sup> (100).

**Synthesis of 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<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3k** (62.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: 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

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

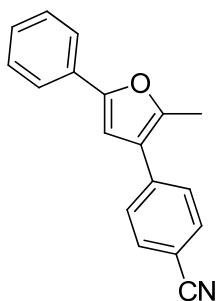
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 153.1, 144.4, 138.4, 132.4, 132.2, 129.7, 129.2, 128.8, 128.0, 127.5, 125.7, 125.0, 123.8, 122.4, 118.8, 111.0, 108.1.

**MS** (20 eV, EI)  $m/z$  (%): 327 [M]<sup>+</sup> (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3110 (w), 3071 (w), 2227 (s), 1608 (s), 1556 (w), 1525 (w), 1495 (m), 1248 (w), 1146 (m).

**HRMS** (MALDI) for C<sub>21</sub>H<sub>14</sub>NOS, [M+H]<sup>+</sup> (328.0796) found: 328.0801.

**Synthesis of 4-(2-methyl-5-phenylfuran-3-yl)benzonitrile (1cl):**



Prepared according to **TP** from **2c** (126.6 mg, 0.5 mmol), Bu<sub>3</sub>P (187.0 µL, 1.5 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3l** (40.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 1800 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.25) yielded **1cl** as white solids (28.0 mg, 24%).

mp.: 134.9-136.0 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

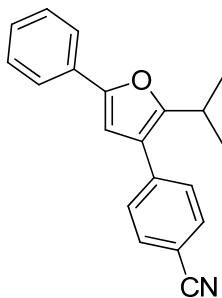
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ ppm: 152.4, 148.9, 138.9, 132.4, 130.3, 128.7, 127.7, 127.5, 123.5, 121.7, 119.0, 109.8, 105.5, 13.5.

**MS** (20 eV, EI) m/z (%): 260 [M+1]<sup>+</sup> (19), 259 [M] (100).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3057 (w), 2921 (w), 2220 (s), 1606 (s), 1560 (m), 1504 (m), 1486 (m), 1443 (m), 1223 (m), 1181 (m), 1060 (m).

**HRMS** (EI) for C<sub>18</sub>H<sub>13</sub>NO, [M]<sup>+</sup> (259.0997) found: 259.0993.

#### Synthesis of 4-(2-isopropyl-5-phenylfuran-3-yl)benzonitrile (**1cm**):



Prepared according to **TP** from **2c** (116.6 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0 µL, 1.1 equiv), Et<sub>3</sub>N (84.0 µL, 1.2 equiv), and **3l** (60.0 µL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 60 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.29) yielded **1cl** as white solid (75.0 mg, 52%).

mp.: 112.1-122.9 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.67 (d, 4H, J = 7.9 Hz), 7.48 (d, 2H, J = 8.1 Hz), 7.39 (t, 2H, 7.6Hz), 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).

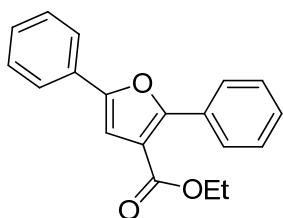
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 157.0, 152.0, 139.1, 132.4, 130.4, 128.7, 128.3, 127.4, 123.5, 120.1, 119.0, 110.0, 105.7, 26.8, 21.6.

**MS** (20 eV, EI) *m/z* (%): 287 [M]<sup>+</sup> (100), 272 (77).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055 (w), 2229 (s), 1609 (s), 1488 (s), 1075 (m), 761 (m).

**HRMS** (EI) for C<sub>20</sub>H<sub>17</sub>NO, [M]<sup>+</sup> (287.1310) found: 287.1307.

### Synthesis of ethyl 2,5-diphenylfuran-3-carboxylate<sup>6</sup> (**1ta**):



Prepared according to **TP** from **2t** (92.0 μL, 0.5 mmol), Bu<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (84.0 μL, 1.2 equiv), and **3a** (64.0 μL, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 50/1; R<sub>f</sub>: 0.38) yielded **1ta** as white solid (101.3 mg, 70%).

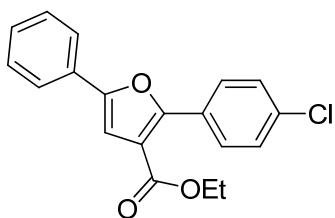
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.12 (d, 2H, J = 7.2 Hz), 7.76 (d, 2H, J = 7.5 Hz), 7.53-7.40 (m, 5H), 7.37-7.30 (m, 1H), 7.11(s, 1H), 4.36 (quartet, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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]<sup>+</sup> (100).

### Synthesis of ethyl 2-(4-chlorophenyl)-5-phenylfuran-3-carboxylate<sup>6</sup> (**1tc**):

<sup>6</sup> Kajikawa, S.; Noiri, Y.; Shudo, H.; Nishino, H.; Kurosawa, K. *Synthesis*, **1998**, 1457-1462



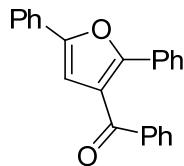
Prepared according to **TP** from **2t** (92.0  $\mu$ L, 0.5 mmol), Bu<sub>3</sub>P (137.0  $\mu$ L, 1.1 equiv), Et<sub>3</sub>N (84.0  $\mu$ L, 1.2 equiv), and **3c** (70.0  $\mu$ L, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 10 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 20/1; R<sub>f</sub>: 0.54) yielded **1tc** as white solid (98.0 mg, 60%).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /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).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /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]<sup>+</sup> (28), 326 (100).

#### Synthesis of (2,5-diphenylfuran-3-yl)(phenyl)methanone<sup>7</sup> (**1ua**):



Prepared according to **TP** from **2u** (118.1 mg, 0.5 mmol), Bu<sub>3</sub>P (137.0  $\mu$ L, 1.1 equiv), Et<sub>3</sub>N (84.0  $\mu$ L, 1.2 equiv), and **1a** (64.0  $\mu$ L, 1.1 equiv) in dry THF (2.5 mL) [reaction condition: RT for 2400 min]. Purification by *flash*-chromatography (hexanes/ethyl acetate: 40/1; R<sub>f</sub>: 0.33) yielded **1ua** as yellow liquid (94.6 mg, 58%).

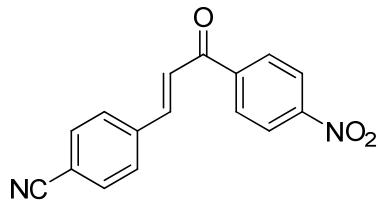
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 7.92 (d, 2H, *J* = 7.5 Hz), 7.86-7.74 (m, 4H), 7.59-7.28 (m, 9H), 6.95 (s, 1H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /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]<sup>+</sup> (100), 247 (78), 105 (71).

<sup>7</sup> Perrier, H.; Bayly, C.; Laliberte, F.; Huang, Z.; Rasori, R.; Robichaud, A.; Girard, Y.; Macdonald, D. *Bio. Med. Chem. Lett.* **1999**, 9, 323-326.

**Synthesis of (E)-4-(3-(4-nitrophenyl)-3-oxoprop-1-enyl)benzonitrile<sup>8</sup> (2l):**



The compound **2l** was yielded as orange solid (1.15 g, 35%) according to the procedure of the reported literature<sup>1</sup>.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

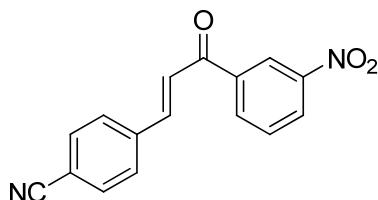
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 188.3, 150.3, 143.9, 142.3, 138.5, 132.8, 129.5, 128.9, 124.2, 124.0, 118.2, 114.1.

**MS** (20 eV, EI) *m/z* (%): 277 [M-1]<sup>+</sup> (100), 260 (7), 231 (15), 156 (7).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>) *ν* (cm<sup>-1</sup>): 3047 (w), 2221 (s), 1731(w), 1672 (s), 1609 (s), 1524 (s), 1333 (s).

**HRMS** (EI) for C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>, [M]<sup>+</sup> (278.0691) found: 278.0695.

**Synthesis of (E)-4-(3-(3-nitrophenyl)-3-oxoprop-1-enyl)benzonitrile<sup>8</sup> (2n):**



The compound **2n** was yielded as brown solid (0.79 g, 56%) according to the procedure of the reported literature<sup>1</sup>.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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* = 15.7Hz), 7.80-7.70 (m, 5H), 7.61 (d, 1H, *J* = 15.6 Hz).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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.

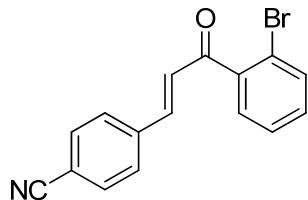
**MS** (20 eV, EI) *m/z* (%): 277 [M-1]<sup>+</sup> (100).

<sup>8</sup> Dzurilla,M.; Kristian,P. *Collect. Czech. Chem. Commun.* **1970**, 35, 417 - 429

**IR** ( $\text{CH}_2\text{Cl}_2$ )  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3092 (w), 3041 (w), 2229 (s), 1668 (s), 1609 (s), 1528 (s), 1432 (m), 1347 (s), 1336 (s).

**HRMS** (MALDI) for  $\mathbf{C}_{16}\mathbf{H}_{11}\mathbf{N}_2\mathbf{O}_3$ ,  $[\mathbf{M}+\mathbf{H}]^+$  (279.07769) found: 279.0775.

**Synthesis of (E)-4-(3-(2-bromophenyl)-3-oxoprop-1-enyl)benzonitrile (2o):**



The compound **2o** was yielded as yellow solid (2.0784 g, 67%) according to the procedure of the reported literature<sup>1</sup>.

mp.: 130.2-131.1 °C

**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 7.70-7.60 (m, 5H), 7.47-7.31 (m, 4H), 7.17 (d, 1H,  $J$  = 16.1 Hz).

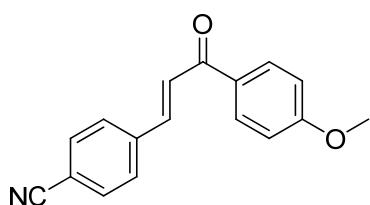
**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 193.6, 143.0, 140.5, 138.6, 133.4, 132.6, 131.8, 129.3, 128.7, 127.4, 119.4, 118.2, 113.6.

**MS** (20 eV, EI)  $m/z$  (%): 313  $[\mathbf{M}+2]^+$  (92), 311  $[\mathbf{M}]^+$  (100), 232(51), 156 (30).

**IR** ( $\text{CH}_2\text{Cl}_2$ )  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3063 (w), 2221 (s), 1668 (s), 1602 (s), 1333 (s), 665 (m), 629 (m).

**HRMS** (MALDI) for  $\mathbf{C}_{16}\mathbf{H}_{11}\mathbf{BrNO}$ ,  $[\mathbf{M}+\mathbf{H}]^+$  (312.0024) found: 312.0032.

**Synthesis of (E)-4-(3-(4-methoxyphenyl)-3-oxoprop-1-enyl)benzonitrile<sup>9</sup> (2p):**



The compound **2r** was yielded as lemon yellow solid (1.96 g, 75%) according to the procedure of the reported literature<sup>1</sup>.

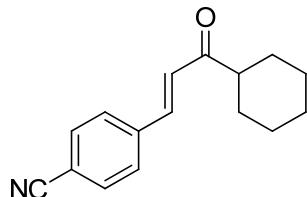
**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.06-8.01 (m, 2H), 7.78-7.67 (m, 5H), 7.61 (d, 1H,  $J$  = 15.6 Hz), 7.02-6.97 (m, 2H), 3.90 (s, 3H).

<sup>9</sup> Schramm; Oana G.; Mueller, Thomas J. *J. Synlett.* **2006**, 1841-1846

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 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]<sup>+</sup> (100), 135 (49), 108 (7).

**Synthesis of (E)-4-(3-cyclohexyl-3-oxoprop-1-enyl)benzonitrile (2r):**



The compound **2p** was yielded as white solid (0.21 g, 20%) according to the procedure of the reported literature<sup>1</sup>.

mp.: 93.8-94.6 °C

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, 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).

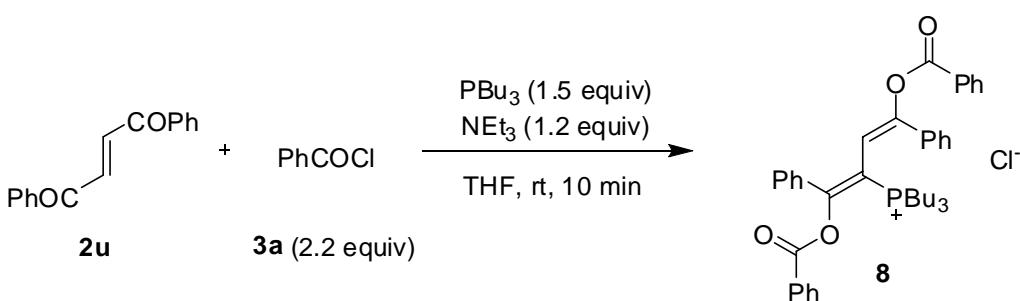
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 202.32, 139.6, 139.1, 132.6, 128.5, 127.5, 118.3, 113.3, 48.8, 28.5, 25.8, 25.6.

**MS** (20 eV, EI) *m/z* (%): 240 [M+1]<sup>+</sup> (100), 184 (14), 171 (35), 156 (58), 130 (11), 83 (5).

**IR** (CH<sub>2</sub>Cl<sub>2</sub>)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3063 (w), 2982 (w), 2944 (w), 2223 (m), 1661 (s), 1613 (s), 1510 (m).

**HRMS** (EI) for C<sub>16</sub>H<sub>18</sub>NO, [M+H]<sup>+</sup> (240.1388) found: 240.1398.

**Synthesis of ((1Z,3E)-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<sub>3</sub>P (137.0 μL, 1.1 equiv), Et<sub>3</sub>N (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 room temperature.

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<sub>3</sub>·HCl**.

**<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>, 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).

**<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>, 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.

**<sup>31</sup>P-NMR** (200 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 32.7.

**MS** (20 eV, ESI) *m/z* (%): 648 [M-34]<sup>+</sup> (37), 647 [M-35]<sup>+</sup> (100).

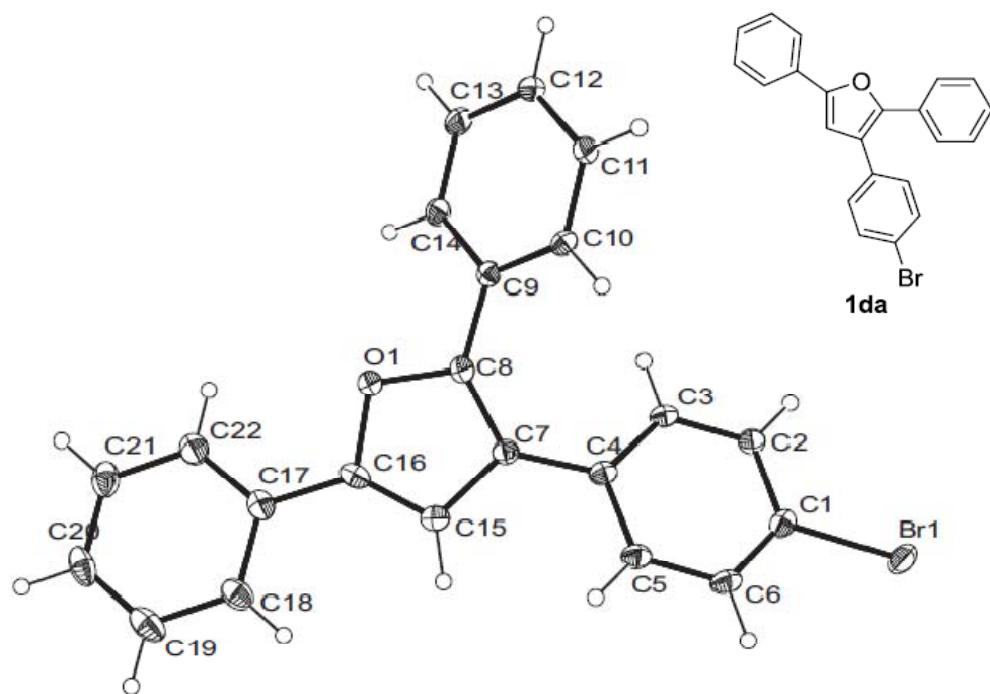
**HRMS** (FAB) for **C<sub>42</sub>H<sub>48</sub>O<sub>4</sub>P, [M-Cl]<sup>+</sup>** (647.3285) found: 647.3290.

X-ray analysis: CCDC 792216

## VI. Spectra of X-ray crystallography (**1da**, **1oa**, and **8**)

**1da:**

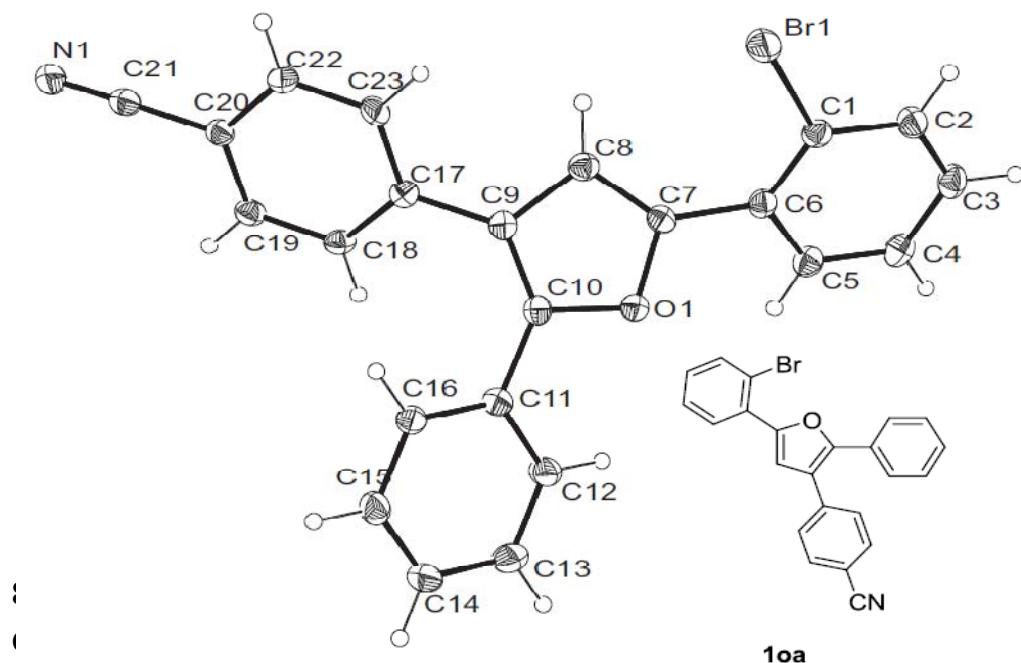
CCDC 792217



**1da**

**1oa:**

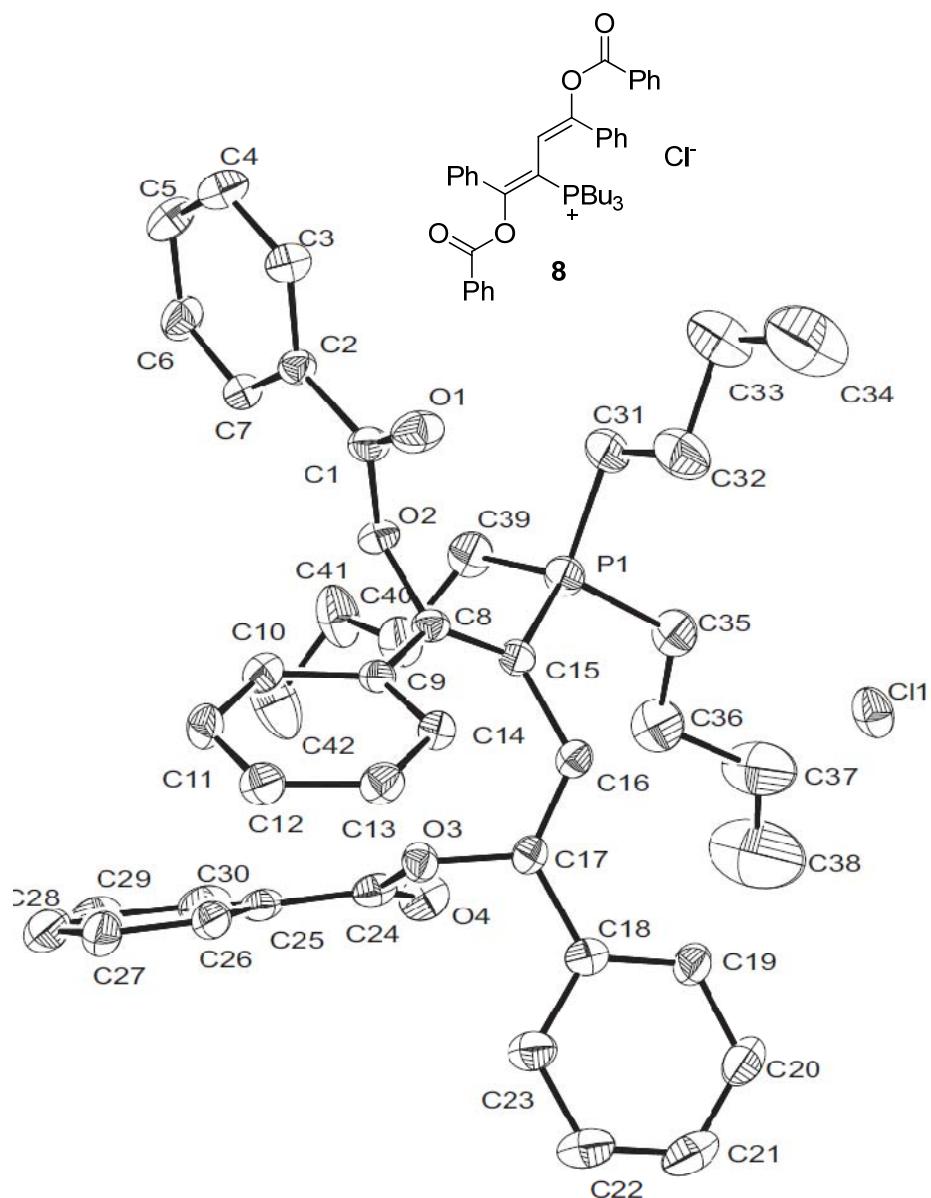
CCDC 792218



**1oa**

8:

CCDC 792216



V. Spectra of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR

