

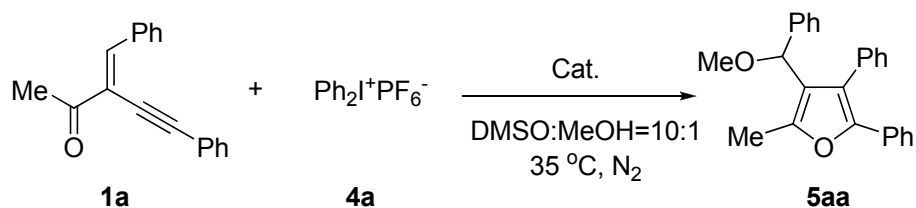
## Supporting information

### **Tetrasubstituted Furans by Pd<sup>II</sup>/Cu<sup>I</sup>-Cocatalyzed Three- Component Domino Reactions of 2-(1-Alkynyl) -2-alken- 1-ones, Nucleophiles and Diaryliodonium Salts.**

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### Optimization of the reaction conditions <sup>a</sup>

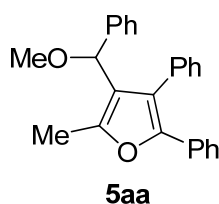


Entry	Catalyst (5 mol%)	Additives (equiv)	NMR Yield of <b>5aa</b> (%)
1 <sup>b</sup>	Pd(OAc) <sub>2</sub>	none	38
2	[PdCl <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub> ]	none	15
3 <sup>c</sup>	Pd(OAc) <sub>2</sub>	none	0
4 <sup>b</sup>	Pd(OAc) <sub>2</sub>	CuCl <sub>2</sub> (0.1)	59
5	Pd(OAc) <sub>2</sub>	CuCl <sub>2</sub> (0.1)	62
6	Pd(OAc) <sub>2</sub>	Cu(OTf) <sub>2</sub> (0.1)	45
7	Pd(OAc) <sub>2</sub>	CuBr <sub>2</sub> (0.1)	61
8	Pd(OAc) <sub>2</sub>	Cu(OAc) <sub>2</sub> (0.1)	21
9	Pd(OAc) <sub>2</sub>	CuCl (0.1)	68
<b>10</b>	<b>Pd(OAc)<sub>2</sub></b>	<b>CuI (0.1)</b>	<b>77</b>
11	Pd(OAc) <sub>2</sub>	CuI (0.2)	61
12	Pd(OAc) <sub>2</sub>	Ag <sub>2</sub> O (0.1)	53
13	Pd(OAc) <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub> (0.1)	58
14 <sup>d</sup>	Pd(OAc) <sub>2</sub>	CuI (0.1)	62
15 <sup>e</sup>	[( $\pi$ -allyl)PdCl] <sub>2</sub>	CuI (0.1)	70
16 <sup>f</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>	CuI (0.1)	0
<b>17<sup>g</sup></b>	<b>none</b>	<b>CuI (0.1)</b>	<b>0</b>

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **4a** (0.6 mmol) and catalyst (5 mol%) in DMSO (3 mL)/MeOH (0.3 mL) at 35 °C for 10-20 h, NMR yields were determined by <sup>1</sup>H NMR spectroscopy using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>b</sup> **4a** (0.33 mmol). <sup>c</sup> K<sub>2</sub>CO<sub>3</sub> (1 equiv) was added. <sup>d</sup> K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O (0.1 equiv) was added. <sup>e</sup> 0.5 equiv of Et<sub>3</sub>N was added. <sup>f</sup> 1.2 equiv. of K<sub>2</sub>CO<sub>3</sub>, 1,2-allenyl ketone was isolated in 56% yield. <sup>g</sup> N.R. = no reaction.

## The characterization data for the newly synthesized compounds.

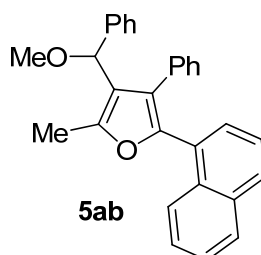
### 1. 3-(Methoxy(phenyl)methyl)-2-methyl-4,5-diphenylfuran (**5aa**)



A solution of yne-enone **1a** (73.8 mg, 0.3 mmol),  $\text{Ph}_2\text{I}^+\text{PF}_6^-$  **4a** (255.6 mg, 0.6 mmol),  $\text{Pd}(\text{OAc})_2$  (3.4 mg, 0.015 mmol) and  $\text{CuI}$  (5.7 mg, 0.03 mmol) in DMSO (3 mL)/MeOH (0.3 mL) was stirred at 35 °C under  $\text{N}_2$ . After completion of the reaction (monitored by TLC), water (5 mL) was added. The aqueous solution was extracted with diethyl ether (3×5 mL) and then the combined organic layer was washed with brine (20 mL). After drying ( $\text{MgSO}_4$ ) and filtration, the organic layer was concentrated. The crude product was purified by column chromatography (petroleum ether: diethyl ether = 60: 1) to give **5aa** (76.4 mg, 72%).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.37 ~ 7.31 (m, 5 H), 7.27 ~ 7.23 (m, 2 H), 7.21 ~ 7.15 (m, 7 H), 7.11 (t,  $J$  = 7.2 Hz, 1 H), 5.05 (s, 1 H), 3.32 (s, 3 H), 2.29 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.75, 146.37, 141.31, 133.71, 131.04, 130.35, 128.57, 128.19, 128.04, 127.37, 127.02, 126.58, 126.52, 124.92, 123.76, 121.75, 77.17, 56.63, 12.91 ppm. MS (70 eV):  $m/z$  (%): 354 ( $\text{M}^+$ , 13.40), 77 (100). HRMS calcd for  $\text{C}_{25}\text{H}_{22}\text{O}_2$ : 354.1620, found: 354.1617. IR (neat): 3059, 3029, 1603, 1502, 1445, 1245, 1089, 1072, 693  $\text{cm}^{-1}$ .

### 2. 3-(Methoxy(phenyl)methyl)-2-methyl-5-(naphthalen-1-yl)-4-phenylfuran (**5ab**)

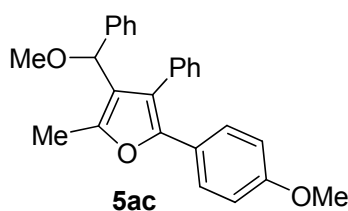


The reaction of **1b** (88.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/

MeOH (0.3 mL) for 40 h at 35 °C gave **5ab** (103.5 mg, 85%).

Colorless oil:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.05 ~ 8.00 (m, 1 H), 7.83 ~ 7.72 (m, 2 H), 7.46 ~ 7.37 (m, 2 H), 7.33 ~ 7.23 (m, 7 H), 7.17 ~ 7.09 (m, 5 H), 5.30 (s, 1 H), 3.40 (s, 3 H), 2.32 (s, 3 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.72, 147.20, 141.20, 133.75, 133.25, 131.77, 130.07, (130.07), 128.64, 128.54, 128.42, 128.18, 128.13, (128.13), 127.17, 126.77, (126.77), 126.19, 126.09, 125.75, 125.05, 120.31, 77.43, 56.79, 13.16 ppm. MS (70 eV):  $m/z$  (%): 404 ( $\text{M}^+$ , 9.61), 84 (100). HRMS calcd for  $\text{C}_{29}\text{H}_{24}\text{O}_2$ : 404.1776, found: 404.1776. IR (neat): 2987, 2901, 1604, 1508, 1493, 1449, 1083, 1073, 730, 698  $\text{cm}^{-1}$ .

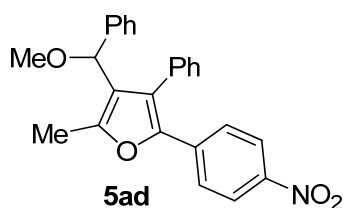
### 3. 3-(Methoxy(phenyl)methyl)-5-(4-methoxyphenyl)-2-methyl-4-phenylfuran (**5ac**)



The reaction of **1c** (82.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/MeOH (0.3 mL) for 11 h at 35 °C gave **5ac** (86.6 mg, 75%).

Colorless oil:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.33 ~ 7.31 (m, 3 H), 7.27 ~ 7.16 (m, 9 H), 6.72 (d,  $J$  = 9.0 Hz, 2 H), 5.05 (s, 1 H), 3.72 (s, 3 H), 3.31 (s, 3 H), 2.28 (s, 3 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.33, 148.01, 146.46, 141.36, 133.87, 130.43, 128.51, 128.00, 127.21, 126.96, 126.50, 126.39, 123.99, 122.12, 121.43, 113.65, 77.20, 56.59, 55.10, 12.84 ppm. MS (70 eV):  $m/z$  (%): 384 ( $\text{M}^+$ , 10.63), 43 (100). HRMS calcd for  $\text{C}_{26}\text{H}_{24}\text{O}_3$ : 384.1725, found: 384.1725. IR (neat): 2930, 1605, 1510, 1249, 1076, 772  $\text{cm}^{-1}$ .

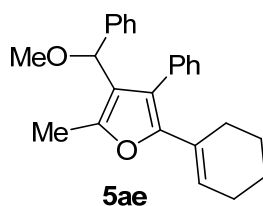
### 4. 3-(Methoxy(phenyl)methyl)-2-methyl-5-(4-nitrophenyl)-4-phenylfuran (**5ad**)



The reaction of **1d** (87.3 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/MeOH (0.3 mL) for 60 h at 35 °C gave **5ad** (63.6 mg, 53%).

Yellow oil:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01 (d,  $J$  = 9.0 Hz, 2 H), 7.50 ~ 7.38 (m, 5 H), 7.30 ~ 7.14 (m, 7 H), 5.04 (s, 1 H), 3.31 (s, 3 H), 2.34 (s, 3 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.12, 145.52, 144.37, 140.78, 136.79, 132.68, 129.87, 128.94, 128.10, 128.10, 127.85, 127.19, 126.39, 124.54, 123.75, 123.09, 77.00, 56.67, 13.04 ppm. MS (70 eV):  $m/z$  (%): 399 ( $\text{M}^+$ , 2.51), 121 (100). HRMS calcd for  $\text{C}_{25}\text{H}_{21}\text{NO}_4$ : 399.1471, found: 399.1468. IR (neat): 2925, 1592, 1562, 1510, 1332, 1076, 700  $\text{cm}^{-1}$ .

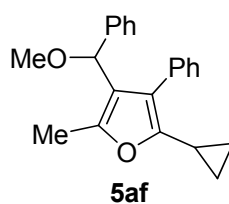
#### 5. 2-Cyclohexenyl-4-(methoxy(phenyl)methyl)-5-methyl-3-phenylfuran (**5ae**)



The reaction of **1e** (75.0 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/MeOH (0.3 mL) for 14 h at 35 °C gave **5ae** (73.7 mg, 69%).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.30 ~ 7.10 (m, 10 H), 6.03 (s, 1 H), 4.94 (s, 1 H), 3.27 (s, 3 H), 2.20 (s, 3 H), 2.06 (bs, 2 H), 1.91 (bs, 2 H), 1.51 (bs, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.28, 147.06, 141.50, 134.25, 130.55, 128.21, 127.92, 127.83, 126.90, 126.86, 126.49, 124.06, 122.08, 121.12, 77.14, 56.49, 26.04, 25.36, 22.54, 21.98, 12.73 ppm. MS (70 eV):  $m/z$  (%): 358 ( $\text{M}^+$ , 3.11), 84 (100). HRMS calcd for  $\text{C}_{25}\text{H}_{26}\text{O}_2$ : 358.1933, found: 358.1935. IR (neat): 3029, 2932, 1722, 1604, 1492, 1448, 1087, 1073, 729, 698  $\text{cm}^{-1}$ .

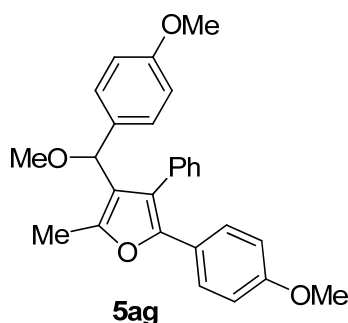
#### 6. 2-Cyclopropyl-4-(methoxy(phenyl)methyl)-5-methyl-3-phenylfuran (**5af**)



The reaction of **1f** (63.0 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/MeOH (0.3 mL) for 27 h at 35 °C gave **5af** (73.7 mg, 54%).

Yellow oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.34 ~ 7.30 (m, 2 H), 7.26 ~ 7.16 (m, 8 H), 5.15 (s, 1 H), 3.32 (s, 3 H), 2.12 (s, 3 H), 1.85 ~ 1.77 (m, 1 H), 0.82 ~ 0.72 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.58, 146.50, 141.38, 133.47, 130.14, 128.02, 127.99, 126.92, 126.60, 126.52, 122.05, 119.30, 77.31, 56.59, 12.66, 7.73, 6.65, 6.47 ppm. MS (70 eV): m/z (%): 318 (M<sup>+</sup>, 14.58), 105 (100). HRMS calcd for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>: 318.1620, found: 318.1620. IR (neat): 2927, 2818, 2361, 2341, 1605, 1492, 1442, 1266, 1087, 698 cm<sup>-1</sup>.

### 7. 3-(Methoxy(4-methoxyphenyl)methyl)-5-(4-methoxyphenyl)-2-methyl-4-phenylfuran (**5ag**)

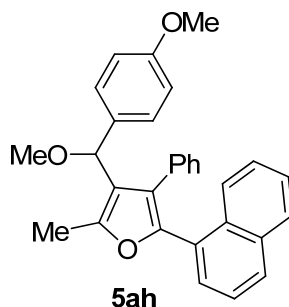


The reaction of **1g** (91.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/MeOH (0.3 mL) for 10 h at 35 °C gave **5ag** (84.3 mg, 69%).

Yellow oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.33 ~ 7.30 (m, 3 H), 7.25 (d, *J* = 8.8 Hz, 2 H), 7.18 ~ 7.16 (m, 2 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 6.79 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 4.99 (s, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.29 (s, 3 H), 2.31 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.62, 158.33, 147.79, 146.45, 133.90, 133.54, 130.40, 128.48, 127.87, 127.18, 126.39, 124.03, 122.09, 121.49, 113.65, 113.40, 77.09, 56.48, 55.17, 55.10, 12.92 ppm. MS (70 eV): m/z (%): 414 (M<sup>+</sup>, 9.61), 43 (100). HRMS calcd for C<sub>27</sub>H<sub>26</sub>O<sub>4</sub>: 414.1831, found: 414.1831. IR (neat): 2933, 2835,

1608, 1510, 1462, 1442, 1246, 1171, 1032, 731  $\text{cm}^{-1}$ .

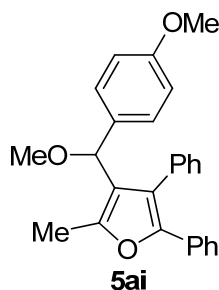
**8. 3-(Methoxy(4-methoxyphenyl)methyl)-2-methyl-5-(naphthalen-1-yl)-4-phenyl furan (5ah)**



The reaction of **1h** (97.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/ MeOH (0.3 mL) for 28 h at 35 °C gave **5ah** (85.2 mg, 65%).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.03 (d,  $J$  = 8.0 Hz, 1 H), 7.79 (d,  $J$  = 7.2 Hz, 1 H), 7.73 (dd,  $J$  = 7.2 Hz, 2.0 Hz, 1 H), 7.42 ~ 7.38 (m, 2 H), 7.31 ~ 7.23 (m, 4 H), 7.14 ~ 7.12 (m, 3 H), 7.09 ~ 7.07 (m, 2 H), 6.86 (d,  $J$  = 8.8 Hz, 2 H), 5.24 (s, 1 H), 3.77 (s, 3 H), 3.36 (s, 3 H), 2.36 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.75, 149.49, 133.74, 133.37, 133.28, 131.76, 130.02, 128.60, 128.51, 128.47, 128.07, 126.73, 126.18, 126.06, 125.72, 125.03, 120.37, 113.56, 77.31, 56.62, 55.18, 13.23 ppm. MS (70 eV):  $m/z$  (%): 434 ( $\text{M}^+$ , 11.35), 43 (100). HRMS calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_3$ : 434.1882, found: 434.1880. IR (neat): 3055, 2931, 1608, 1510, 1443, 1246, 1170, 1081, 730  $\text{cm}^{-1}$ .

**9. 3-(Methoxy(4-methoxyphenyl)methyl)-2-methyl-4,5-diphenylfuran (5ai)**

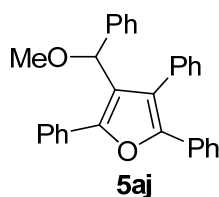


The reaction of **1i** (82.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/ MeOH (0.3 mL) for 11 h at 35 °C gave **5ai** (78.2 mg, 68%).

Colorless oil:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.34 ~ 7.31 (m, 5 H), 7.22 ~ 7.09 (m,

7 H), 6.79 (d,  $J = 8.7$  Hz, 2 H), 4.99 (s, 1 H), 3.76 (s, 3 H), 3.29 (s, 3 H), 2.33 (s, 3 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.65, 148.50, 146.34, 133.72, 133.47, 131.05, 130.29, 128.54, 128.17, 127.86, 127.33, 126.55, 124.89, 123.70, 121.80, 113.43, 77.03, 56.50, 55.18, 12.98$  ppm. MS (70 eV):  $m/z$  (%): 384 ( $\text{M}^+$ , 13.40), 84 (100). HRMS calcd for  $\text{C}_{26}\text{H}_{24}\text{O}_3$ : 384.1725, found: 384.1726. IR (neat): 2931, 1606, 1510, 1443, 1246, 1083, 693  $\text{cm}^{-1}$ .

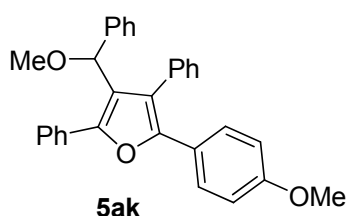
### 10. 3-(Methoxy(phenyl)methyl)-2,4,5-triphenylfuran (5aj)



A solution of **1j** (92.4 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol),  $[(\pi\text{-allyl})\text{PdCl}]_2$  (5.5 mg, 0.015 mmol), CuI (5.7 mg, 0.03 mmol) and  $\text{Et}_3\text{N}$  (15.2 mg, 0.15 mmol) in DMSO (3 mL)/MeOH (0.3 mL) was stirred at 35 °C for 30 h to give **5aj** (65.8 mg, 53%).

Yellow oil:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.84 \sim 7.81$  (m, 2 H), 7.43 ~ 7.10 (m, 18 H), 5.43 (s, 1 H), 3.34 (s, 3 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta = 150.27, 147.70, 140.73, 133.40, 130.71, 130.61, 130.38, 128.52, 128.30, 128.25, 128.04, 127.85, 127.73, 127.52, 127.12, 126.90, 126.51, 125.52, 125.31, 122.50, 76.70, 56.61$  ppm. MS (70 eV):  $m/z$  (%): 416 ( $\text{M}^+$ , 20.01), 105 (100). HRMS calcd for  $\text{C}_{30}\text{H}_{24}\text{O}_2$ : 416.1776, found: 416.1777. IR (neat): 3059, 2926, 1683, 1597, 1492, 1448, 1073, 692  $\text{cm}^{-1}$ .

### 11. 3-(Methoxy(phenyl)methyl)-5-(4-methoxyphenyl)-2,4-diphenylfuran (5ak)

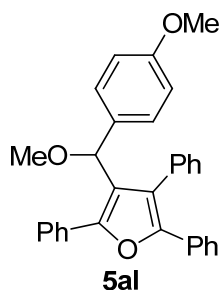


The reaction of **1k** (101.4 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/MeOH (0.3 mL) for 12 h at 35 °C gave **5ak** (75.9 mg, 57%).



Yellow solid: m.p.: 108 ~ 109 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81 (d,  $J$  = 7.2 Hz, 2 H), 7.36 ~ 7.33 (m, 4 H), 7.32 ~ 7.23 (m, 6 H), 7.19 ~ 7.13 (m, 5 H), 6.75 (d,  $J$  = 8.8 Hz, 2 H), 5.43 (s, 1 H), 3.73 (s, 3 H), 3.33 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.75, 149.66, 147.89, 140.80, 133.60, 130.75, 130.50, 128.46, 128.21, 127.82, 127.52, 127.37, 126.99, 126.86, 126.80, 126.52, 123.92, 123.64, 122.35, 113.77, 76.77, 56.56, 55.14 ppm. MS (70 eV):  $m/z$  (%): 446 ( $\text{M}^+$ , 23.66), 105 (100). HRMS calcd for  $\text{C}_{31}\text{H}_{26}\text{O}_3$ : 446.1882, found: 446.1880. IR (neat): 2988, 2929, 2901, 1603, 1569, 1510, 1491, 1254, 1177, 1075, 690  $\text{cm}^{-1}$ .

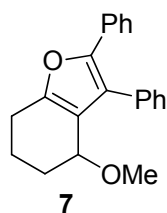
### 12. 3-(Methoxy(4-methoxyphenyl)methyl)-2,4,5-triphenylfuran (5al)



A solution of **11** (101.4 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol),  $[(\pi\text{-allyl})\text{PdCl}]_2$  (5.5 mg, 0.015 mmol), CuI (5.7 mg, 0.03 mmol) and  $\text{Et}_3\text{N}$  (15.2 mg, 0.15 mmol) in DMSO (3 mL)/MeOH (0.3 mL) was stirred at 35 °C for 23 h to give **5al** (81.3 mg, 61%).

White solid: m.p.: 44 ~ 45 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.84 (d,  $J$  = 7.6 Hz, 2 H), 7.42 (d,  $J$  = 7.6 Hz, 2 H), 7.38 ~ 7.29 (m, 6 H), 7.27 ~ 7.15 (m, 7 H), 6.73 (d,  $J$  = 8.8 Hz, 2 H), 5.35 (s, 1 H), 3.75 (s, 3 H), 3.30 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.59, 150.03, 147.68, 133.48, 132.94, 130.76, 130.71, 130.37, 128.53, 128.30, 128.24, 127.93, 127.66, 127.53, 127.11, 125.54, 125.34, 122.54, 113.32, 76.68, 56.52, 55.19 ppm. MS (70 eV):  $m/z$  (%): 446 ( $\text{M}^+$ , 19.10), 105 (100). HRMS calcd for  $\text{C}_{31}\text{H}_{26}\text{O}_3$ : 446.1882, found: 446.1877. IR: 3058, 2931, 2835, 1606, 1510, 1443, 1246, 1083, 764, 693  $\text{cm}^{-1}$ .

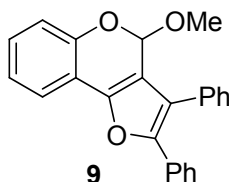
### 13. 4-Methoxy-2,3-diphenyl-4,5,6,7-tetrahydrobenzofuran (7)



The reaction of **6** (58.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (14.0 mg, 0.015 mmol), CuI (5.7 mg, 0.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (49.7 mg, 0.36 mmol) in DMSO (3 mL)/ MeOH (0.3 mL) for 10 h at 35 °C gave **7** (63.0 mg, 69%).

Colorless oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.46 ~ 7.40 (m, 4 H), 7.38 ~ 7.33 (m, 2 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 7.22 ~ 7.17 (m, 2 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 4.07 (d, *J* = 2.4 Hz, 1 H), 3.20 (s, 3 H), 2.82 ~ 2.74 (m, 1 H), 2.65 ~ 2.54 (m, 1 H), 2.16 ~ 2.02 (m, 2 H), 1.89 ~ 1.83 (m, 1 H), 1.56 ~ 1.47 (m, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.61, 147.24, 133.71, 131.26, 129.72, 128.43, 128.15, 126.98, 126.81, 125.78, 122.08, 120.42, 70.62, 56.04, 26.62, 23.22, 17.58 ppm. MS (70 eV): *m/z* (%): 304 (M<sup>+</sup>, 74.45), 77 (100). HRMS calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>: 304.1463, found: 304.1464. IR (neat): 3058, 2939, 1603, 1502, 1443, 1074, 907, 731, 694 cm<sup>-1</sup>.

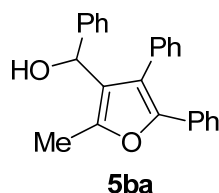
#### 14. 4-Methoxy-2,3-diphenyl-4H-furo[3,2-c]chromene (**9**)<sup>[21]</sup>



The reaction of **8** (50.1 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/ MeOH (0.3 mL) for 9 h at 35 °C gave **9** (50.6 mg, 47%).

Colorless oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.67 (d, *J* = 7.6 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.46 (d, *J* = 7.2 Hz, 2 H), 7.42 ~ 7.35 (m, 3 H), 7.30 ~ 7.11 (m, 4 H), 7.10 ~ 7.06 (m, 2 H), 6.05 (s, 1 H), 3.52 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 150.89, 149.28, 146.09, 132.18, 130.57, 129.33, 128.82, 128.67, 128.39, 127.72, 127.68, 126.22, 121.90, 120.60, 120.10, 117.01, 116.06, 115.28, 97.49, 55.06 ppm. MS (70 eV): *m/z* (%): 354 (M<sup>+</sup>, 0.62), 84 (100). IR (neat): 3058, 2928, 1644, 1602, 1504, 1450, 1067, 951, 733 cm<sup>-1</sup>.

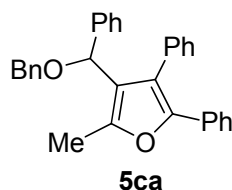
### 15. (2-Methyl-4,5-diphenylfuran-3-yl)(phenyl)methanol (**5ba**)



The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) and H<sub>2</sub>O (10.8 mg, 2 equiv) in DMSO (3 mL) for 12 h at 35 °C gave **5ba** (55.8 mg, 56%).

Yellow oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.32 ~ 7.27 (m, 5 H), 7.25 ~ 7.08 (m, 10 H), 5.63 (s, 1 H), 2.26 (s, 3 H), 2.06 (bs, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.56, 146.55, 143.06, 133.49, 130.90, 130.27, 128.69, 128.19, 128.09, 127.47, 126.96, 126.69, 125.85, 124.98, 124.09, 122.82, 68.13, 12.85 ppm. MS (70 eV): m/z (%): 340 (M<sup>+</sup>, 31.18), 43 (100). HRMS calcd for C<sub>24</sub>H<sub>20</sub>O<sub>2</sub>: 340.1463, found: 340.1464. IR (neat): 3377, 3059, 3029, 1602, 1502, 1446, 1014, 693 cm<sup>-1</sup>.

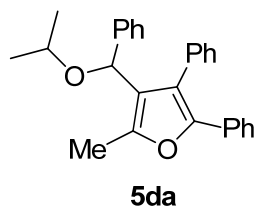
### 16. 3-(Benzyloxy(phenyl)methyl)-2-methyl-4,5-diphenylfuran (**5ca**)



The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/BnOH (0.3 mL) for 19 h at 35 °C gave **5ca** (73.6 mg, 57%).

Yellow oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.34 ~ 7.19 (m, 15 H), 7.17 ~ 7.09 (m, 5 H), 5.29 (s, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.43 (d, *J* = 12.0 Hz, 1 H), 2.30 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.09, 146.42, 141.48, 138.35, 133.67, 131.06, 130.35, 128.56, 128.26, 128.20, 128.04, 127.75, 127.43, 127.34, 127.01, 126.66, 126.61, 124.97, 123.76, 121.82, 74.53, 70.41, 13.00 ppm. MS (70 eV): m/z (%): 430 (M<sup>+</sup>, 4.86), 43 (100). HRMS calcd for C<sub>31</sub>H<sub>26</sub>O<sub>2</sub>: 430.1933, found: 430.1932. IR (neat): 3061, 3029, 2918, 2859, 1602, 1562, 1495, 1448, 1065, 730, 693 cm<sup>-1</sup>.

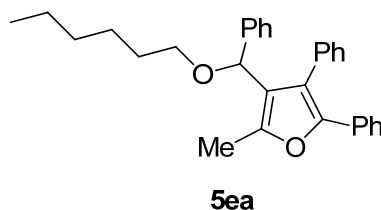
### 17. 3-(Isopropoxy(phenyl)methyl)-2-methyl-4,5-diphenylfuran (**5da**)



The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/*i*PrOH (0.3 mL) for 12 h at 35 °C gave **5da** (60.6 mg, 53%).

Yellow oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.37 ~ 7.27 (m, 5 H), 7.26 ~ 7.15 (m, 9 H), 7.12 ~ 7.08 (m, 1 H), 5.29 (s, 1 H), 3.67 ~ 3.57 (m, 1 H), 2.29 (s, 3 H), 1.10 (d, *J* = 6.0 Hz, 3 H), 1.04 (d, *J* = 6.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.92, 146.15, 142.21, 133.88, 131.13, 130.40, 128.60, 128.18, 128.00, 127.39, 126.83, 126.67, 126.50, 124.86, 123.72, 122.71, 71.92, 68.55, 22.24, 21.82, 13.09 ppm. MS (70 eV): *m/z* (%): 382 (M<sup>+</sup>, 8.62), 43 (100). HRMS calcd for C<sub>27</sub>H<sub>26</sub>O<sub>2</sub>: 382.1933, found: 382.1932. IR (neat): 3029, 2970, 1603, 1502, 1446, 1373, 1048, 693 cm<sup>-1</sup>.

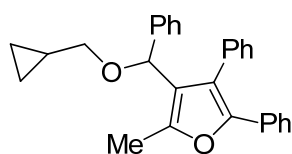
### 18. 3-(Hexyloxy(phenyl)methyl)-2-methyl-4,5-diphenylfuran (**5ea**)



The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/*n*-C<sub>6</sub>H<sub>13</sub>OH (0.3 mL) for 13 h at 35 °C gave **5ea** (81.0 mg, 64%).

Yellow oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35 ~ 7.30 (m, 5 H), 7.27 ~ 7.15 (m, 9 H), 7.13 ~ 7.09 (m, 1 H), 5.14 (s, 1 H), 3.42 ~ 3.29 (m, 2 H), 2.26 (s, 3 H), 1.59 ~ 1.51 (m, 2 H), 1.37 ~ 1.22 (m, 6 H), 0.89 ~ 0.85 (m, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.75, 146.29, 141.85, 133.89, 131.17, 130.45, 128.64, 128.27, 128.09, 127.42, 126.99, 126.67, 126.61, 124.98, 123.83, 122.43, 75.42, 69.07, 31.77, 29.88, 26.08, 22.70, 14.16, 13.06 ppm. MS (70 eV): *m/z* (%): 424 (M<sup>+</sup>, 4.18), 43 (100). HRMS calcd for C<sub>30</sub>H<sub>32</sub>O<sub>2</sub>: 424.2402, found: 424.2404. IR (neat): 2929, 2857, 1603, 1502, 1447, 1092, 1071, 729, 694 cm<sup>-1</sup>.

### 19. 3-((Cyclopropylmethoxy)(phenyl)methyl)-2-methyl-4,5-diphenylfuran (5fa)

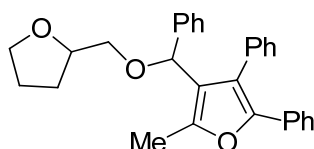


**5fa**

The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/cyclopropylmethanol (0.3 mL) for 20 h at 35 °C gave **5fa** (81.5 mg, 69%).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.36 ~ 7.31 (m, 5 H), 7.28 ~ 7.13 (m, 9 H), 7.11 ~ 7.06 (m, 1 H), 5.19 (s, 1 H), 3.24 ~ 3.16 (m, 2 H), 2.24 (s, 3 H), 1.07 ~ 0.96 (m, 1 H), 0.47 ~ 0.45 (m, 2 H), 0.15 ~ 0.08 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.74, 146.25, 141.47, 133.79, 131.05, 130.33, 128.54, 128.15, 128.04, 127.33, 126.98, 126.70, 126.53, 124.91, 123.73, 122.12, 75.00, 73.37, 12.97, 10.65, 3.00, 2.96 ppm. MS (70 eV):  $m/z$  (%): 394 ( $\text{M}^+$ , 12.52), 43 (100). HRMS calcd for  $\text{C}_{28}\text{H}_{26}\text{O}_2$ : 394.1933, found: 394.1933. IR: 3061, 3028, 1603, 1563, 1502, 1446, 1066, 908, 754, 694  $\text{cm}^{-1}$ . IR (neat): 3061, 3028, 2857, 1603, 1502, 1446, 1066, 694  $\text{cm}^{-1}$ .

### 20. 2-Methyl-4,5-diphenyl-3-(phenyl((tetrahydrofuran-2-yl)methoxy)methyl)furan (5ga)



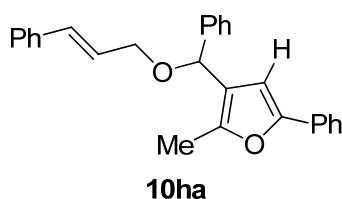
**5ga**

The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/tetrahydro-furfuryl methanol (0.3 mL) for 20 h at 35 °C gave **5ga** (71.9 mg, 57%, dr = 1.0/1.0).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.33 ~ 7.29 (m, 5 H); 7.27 ~ 7.14 (m, 9 H); 7.11 ~ 7.07 (m, 1 H); [5.23 (s, 0.5 H), 5.21 (s, 0.5 H)]; 4.09 ~ 4.03 (m, 1 H); 3.86 ~ 3.79 (m, 1 H); 3.77 ~ 3.72 (m, 1 H); 3.49 ~ 3.30 (m, 2 H); [2.30 (s, 1.5 H), 2.29 (s, 1.5 H)]; 1.98 ~ 1.79 (m, 3 H); 1.68 ~ 1.57 (m, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.85, 146.24, 141.43, 133.66, 131.01, (130.34, 130.31), 128.52, 128.15, 127.94,

127.31, (126.92, 126.88), (126.56, 126.52), (124.88, 124.87), 123.68, 123.65, 121.92, (77.82, 77.63), (75.73, 75.64), (71.36, 71.32), (68.27, 68.24), 28.37, (25.67, 25.61), (12.96, 12.93) ppm. MS (70 eV):  $m/z$  (%): 424 ( $M^+$ , 3.48), 43 (100). HRMS calcd for  $C_{29}H_{28}O_3$ : 424.2038, found: 424.2032. IR (neat): 2940, 2860, 1602, 1563, 1502, 1447, 1070, 730, 694  $cm^{-1}$ .

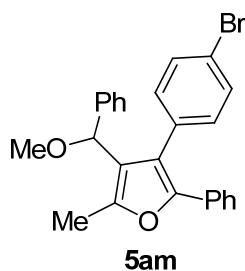
### 21. 3-(Cinnamyloxy(phenyl)methyl)-2-methyl-5-phenylfuran (10ha)



The reaction of **1a** (73.8 mg, 0.3 mmol), **4a** (255.6 mg, 0.6 mmol) in DMSO (3 mL)/ cinnamyl alcohol (0.3 mL) for 20 h at 35 °C gave **10ha** (86.0 mg, 75%).

Yellow oil:  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.59 (d,  $J$  = 7.6 Hz, 2 H), 7.45 ~ 7.33 (m, 6 H), 7.32 ~ 7.27 (m, 5 H), 7.25 ~ 7.16 (m, 2 H), 6.60 (d,  $J$  = 16.0 Hz, 1 H), 6.54 (s, 1 H), 6.39 ~ 6.30 (m, 1 H), 5.44 (s, 1 H), 4.24 ~ 4.13 (m, 2 H), 2.37 (s, 3 H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 151.84, 148.63, 141.64, 136.65, 132.49, 130.79, 128.53, 128.50, 128.43, 127.64, 127.46, 126.87, 126.59, 126.44, 126.09, 123.30, 122.34, 105.34, 74.94, 68.96, 12.21 ppm. MS (70 eV):  $m/z$  (%): 380 ( $M^+$ , 2.47), 43 (100). HRMS calcd for  $C_{27}H_{24}O_2$ : 380.1776, found: 380.1778. IR (neat): 3028, 2853, 1698, 1663, 1600, 1555, 1491, 1449, 1056, 734  $cm^{-1}$ .

### 22. 3-(4-Bromophenyl)-4-(methoxy(phenyl)methyl)-5-methyl-2-phenylfuran (5am)

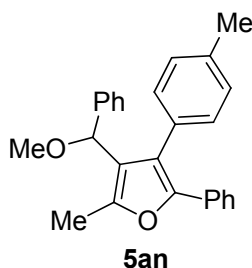


The reaction of **1a** (73.8 mg, 0.3 mmol), (4- $BrC_6H_4$ ) $_2I^+OTf^-$  (352.0 mg, 0.6 mmol)

in DMSO (3 mL)/ MeOH (0.3 mL) for 18 h at 35 °C gave **5am** (86.6 mg, 69%).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 (d,  $J$  = 8.0 Hz, 2 H), 7.30 (d,  $J$  = 8.0 Hz, 2 H), 7.27 ~ 7.11 (m, 8 H), 7.03 (d,  $J$  = 7.6 Hz, 2 H), 5.05 (s, 1 H), 3.32 (s, 3 H), 2.31 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.03, 146.64, 140.94, 132.71, 132.04, 131.69, 130.67, 128.29, 128.07, 127.13, 126.87, 126.47, 125.01, 122.21, 121.49, 121.41, 77.18, 56.62, 12.79 ppm. MS (70 eV):  $m/z$  (%): 432 ( $\text{M}^+$ , 9.81), 434 ( $\text{M}^++2$ , 10.13), 43 (100). HRMS calcd for  $\text{C}_{25}\text{H}_{21}\text{O}_2\text{Br}[\text{M}+2]$ : 434.0704, found: 434.0704. IR (neat): 2923, 1600, 1562, 1495, 1447, 1071, 693  $\text{cm}^{-1}$ .

### 23. 3-(Methoxy(phenyl)methyl)-2-methyl-5-phenyl-4-p-tolylfuran (**5an**)



A solution of **1a** (73.8 mg, 0.3 mmol),  $(4\text{-MeC}_6\text{H}_4)_2\text{I}^+\text{OTf}^-$  (274.8 mg, 0.6 mmol),  $[(\pi\text{-allyl})\text{PdCl}]_2$  (5.5 mg, 0.015 mmol), CuI (5.7 mg, 0.03 mmol) and  $\text{Et}_3\text{N}$  (15.2 mg, 0.5 equiv) in DMSO (3 mL)/MeOH (0.3 mL) was stirred at 35 °C for 10 h to give **5an** (82.1 mg, 74%).

Yellow oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.35 (d,  $J$  = 8.0 Hz, 2 H), 7.28 ~ 7.24 (m, 2 H), 7.22 ~ 7.15 (m, 7 H), 7.12 ~ 7.08 (m, 3 H), 5.04 (s, 1 H), 3.32 (s, 3 H), 2.39 (s, 3 H), 2.27 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.66, 146.22, 141.37, 136.99, 131.11, 130.49, 130.10, 129.35, 128.16, 128.04, 126.99, 126.51, 126.47, 124.82, 123.76, 121.76, 77.04, 56.62, 21.30, 12.94 ppm. MS (70 eV):  $m/z$  (%): 368 ( $\text{M}^+$ , 18.59), 43 (100). HRMS calcd for  $\text{C}_{26}\text{H}_{24}\text{O}_2$ : 368.1776, found: 368.1774. IR (neat): 2920, 1601, 1561, 1492, 1448, 1095, 758  $\text{cm}^{-1}$ .

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[3] M. Bielawski, M. Zhu and B. Olfsson, *Adv. Synth. Catal.*, 2007, **349**, 2610.