### SUPPORTING INFORMATION

# Synthesis of 2-Acetyl Trisubstituted Furans via Copper-Mediated Deacylation Cleavage of Unstrained C(sp<sup>3</sup>)-C(sp<sup>2</sup>) Bonds

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### **Table of Contents:**

1. General methods	S2
2. General procedure for the synthesis of 2-acyl trisubstituted furans	3 and spectral
data for <b>3</b>	S2~S10
3. GC-MS analysis for the by-product	S10~S12
3. References	
4. Copies of <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of compounds <b>3</b> and <b>A</b>	S13~S33
5. Crystal Structure of <b>3a</b>	S34
6. Crystal Structure of A2	S35

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**General methods.** All solid products were recrystallized from ethyl acetate and hexane, and the melting points are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a BRUKER AVANCE-300 or a BRUKER AVANCE-500 in CDCl<sub>3</sub> with TMS as the internal standard. The starting material acetylenic ketones were prepared according to previously reported procedure.<sup>1</sup>

#### General procedure for the synthesis of 2-acyl trisubstituted furans 3

To a stirring mixture of 0.5 mmol (0.11 g) 3-phenyl-1-*p*-tolylprop-2-yn-1-one (**1a**) and 1.0 mmol (0.1 mL) acetylacetone in 2.0 mL DMSO were added successively 0.5 mmol (0.95 g) CuI and 0.1 mmol (0.015 mL) DBU. The reaction mixture was stirred at 80 °C for 15 h. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with saturated NH<sub>4</sub>Cl and extracted with ethyl acetate ( $3 \times 10$  mL). The combined organics were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate /petroleum ether = 1/80) to afford products **3a**.

#### 1-(3-phenyl-5-(p-tolyl)furan-2-yl)ethanone (3a)



White solid; mp: 101-102 °C; yield: 72%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.72-7.67(m, 4H), 7.46-7.38 (m, 3H), 7.28-7.26 (m, 2H), 6.85 (s, 1H), 2.53 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.8, 156.2, 146.5, 139.9, 136.0, 132.5, 130.1, 129.6, 129.0, 128.6, 127.0, 125.3, 109.8, 28.0, 21.8; IR (KBr, *v*, cm<sup>-1</sup>): 1668, 1598, 1493, 1451, 1332, 921, 836; HRMS *m/z* (ESI) calcd for C<sub>19</sub>H<sub>17</sub>O<sub>2</sub> (M+H)<sup>+</sup> 277.1229, found 277.1223.

#### 1-(3-(4-methoxyphenyl)-5-(p-tolyl)furan-2-yl)ethanone (3b)



White solid; mp: 87-88 °C; yield: 73%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.71-7.67 (m, 4H), 7.28-7.25 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.84 (s, 1H), 3.85 (s, 3H), 2.55 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  187.5, 159.9, 155.7, 145.9, 139.5, 135. 5, 130.6, 129.6, 126.7, 124.9, 124.3, 113.6, 109.2, 55.3, 27.6, 21.4; IR (KBr, *v*, cm<sup>-1</sup>): 1670, 1588, 1473, 1451, 1336, 925, 819; HRMS *m/z* (ESI) calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 307.1334, found 307.1332.

1-(5-(4-chlorophenyl)-3-(4-methoxyphenyl)furan-2-yl)ethanone (3c)



White solid; mp: 147-148 °C; yield: 65%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.74-7.65 (m, 4H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.87 (s, 1H), 3.85 (s, 3H), 2.54 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.9, 160.4, 154.6, 146.6, 135.7, 135.5, 131.0, 129.6, 128.2, 126.5, 124.3, 114.1, 110.6, 55.7, 28.1; IR (KBr, *v*, cm<sup>-1</sup>): 1675, 1579, 1493, 1450, 1352, 971, 856; HRMS *m/z* (ESI) calcd for C<sub>19</sub>H<sub>16</sub>ClO<sub>3</sub> (<sup>35</sup>Cl, M+H)<sup>+</sup> 327.0788, found 327.0786.

#### 1-(3-(4-methoxyphenyl)-5-phenylfuran-2-yl)ethanone (3d)



White solid; mp: 98-99 °C; yield: 68%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, J = 7.0 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.48-7.36 (m, 3H), 6.96 (d, J = 8.8 Hz, 2H), 6.89 (s, 1H), 3.85 (s, 3H), 2.56 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.0, 160.4, 155.7, 146.5, 135.7, 131.0, 129.6, 129.3, 125.3, 124.5, 114.0, 110.2, 105.4, 55.7, 28.0; IR (KBr, v, cm<sup>-1</sup>): 1668, 1581, 1491, 1351, 1332, 951, 847; HRMS m/z (ESI) calcd for C<sub>19</sub>H<sub>17</sub>O<sub>3</sub> (M+H)<sup>+</sup> 293.1178, found 293.1172.

1-(3,5-di-*p*-tolylfuran-2-yl)ethanone (3e)



White solid; mp: 52-53 °C; yield: 74%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 4H), 6.83 (s, 1H), 2.53 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.8, 156.1, 146.4, 139.9, 139.0, 136.1, 130.0, 129.5, 129.3, 127.0, 125.3, 109.8, 28.0, 21.8, 21.7; IR (KBr, *v*, cm<sup>-1</sup>): 1678, 1560, 1493, 1455, 1334, 952, 866; HRMS *m/z* (ESI) calcd for C<sub>20</sub>H<sub>19</sub>O<sub>2</sub> (M+H)<sup>+</sup> 291.1385, found 291.1380

#### 1-(5-(4-nitrophenyl)-3-(p-tolyl)furan-2-yl)ethanone (3f)



White solid; mp: 146-147 °C; yield: 65%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.08 (s, 1H), 2.55 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.0, 152.9, 148.1, 147.8, 139.5, 135.9, 135.3, 129.5, 128.7, 125.7, 124.8, 113.5, 28.2, 21.8; IR (KBr, *v*, cm<sup>-1</sup>): 1665, 1523, 1493, 1451, 1353, 1332, 921, 836; HRMS *m/z* (ESI) calcd for C<sub>19</sub>H<sub>16</sub>NO<sub>4</sub> (M+H)<sup>+</sup> 322.1079, found 322.1074.

#### 1-(5-(4-methoxyphenyl)-3-(p-tolyl)furan-2-yl)ethanone (3g)



White solid; mp: 65-66 °C; yield: 71%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 3.85 (s, 3H), 2.51 (s, 3H), 2.39 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.7, 160.9, 156.0, 146.3, 139.0, 136.3, 129.6, 129.5, 129.3, 126.9, 122.6, 114.8, 109.0, 55.8, 28.0, 21.7; IR (KBr, *v*, cm<sup>-1</sup>): 1681, 1564, 1463, 1421, 1362, 921, 851; HRMS *m/z* (ESI) calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 307.1334, found 307.1332.





White solid; mp: 81-82 °C; yield: 58%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.75-7.66 (m, 4H), 7.44 (d, J = 8.6 Hz, 2H), 7.11 (t, J = 8.7 Hz, 2H), 6.87 (s, 1H), 2.56 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.0, 163.3 (d, J = 247.2 Hz), 154.7, 146.7, 135.7, 134.8, 131.5 (d, J = 8.2 Hz), 129.7, 128.0, 126.5, 115.6 (d, J = 21.5 Hz), 110.6, 28.0; IR (KBr, v, cm<sup>-1</sup>): 1676, 1530, 1483, 1448, 1352, 971, 841; HRMS *m/z* (ESI) calcd for C<sub>18</sub>H<sub>13</sub>ClFO<sub>2</sub> (<sup>35</sup>Cl , M+H)<sup>+</sup> 315.0588, found 315.0583.

#### 1-(3-(4-fluorophenyl)-5-(4-nitrophenyl)furan-2-yl)ethanone (3i)



White solid; mp: 180-181 °C; yield: 63%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H), 7.71-7.68 (m, 2H), 7.14 (t, J = 8.6 Hz, 2H), 7.08 (s, 1H), 2.60 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.0, 162.5, 153.0, 148.2, 147.7, 135.1, 134.7, 131.5 (d, J = 8.8 Hz), 127.5 (d, J = 3.8 Hz), 125.7, 124.9, 115.7 (d, J = 21.3 Hz), 113.3, 28.1; IR (KBr, v, cm<sup>-1</sup>): 1654, 1598, 1512, 1493, 1461, 1335, 940, 830; HRMS m/z (ESI) calcd for C<sub>18</sub>H<sub>13</sub>FNO<sub>4</sub> (M+H)<sup>+</sup> 326.0829, found 326.0823. 1-(5-(2-bromophenyl)-3-(p-tolyl)furan-2-yl)ethanone (3j)



White solid; mp: 62-63 °C; yield: 51%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 9.2 Hz, 1H), 7.71 (d, J = 7.9 Hz,1H), 7.61 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.6 Hz,1H), 7.35 (s, 1H), 7.26-7.22 (m, 3H), 2.55 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  187.8, 152.7, 146.1, 138.7, 134.8, 134.4, 130.1, 130.0, 129.6, 129.2, 129.0, 128.9,127.7, 120.7, 115.1, 27.8, 21.4; IR (KBr, v, cm<sup>-1</sup>): 1661, 1559, 1473, 1448, 1332, 920, 849, 808; HRMS *m/z* (ESI) calcd for C<sub>19</sub>H<sub>16</sub>BrO<sub>2</sub> (<sup>79</sup>Br, M+H)<sup>+</sup> 355.0334, found 355.0328.

#### 1-(3-(4-methoxyphenyl)-5-(o-tolyl)furan-2-yl)ethanone (3k)



White solid; mp: 61-62 °C; yield: 75%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.78-7.70 (m, 3H), 7.30-7.25 (m, 3H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 3.85 (s, 3H), 2.60 (s, 3H), 2.55 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.1, 160.3, 155.8, 146.2, 136.1, 135.2, 132.0, 131.0, 129.5, 129.2, 128.3, 126.7, 124.6, 114.0, 113.5, 55.7, 28.2, 22.3; IR (KBr, *v*, cm<sup>-1</sup>): 1701, 1532, 1473, 1466, 1331, 921, 836; HRMS *m/z* (ESI) calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 307.1334, found 307.1329.

#### 1-(3-(4-chlorophenyl)-5-(o-tolyl)furan-2-yl)ethanone (3l)



White solid; mp: 80-81 °C; yield: 72%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.69-7.66 (m, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.24-7.22 (m, 3H), 6.70 (s, 1H), 2.51 (s, 3H), 2.49 (s,

3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.2, 156.1, 146.4, 136.2, 134.9, 134.0, 132.0, 131.0, 130.7, 129.7, 128.9, 128.8, 128.3, 126.7, 113.3, 28.1, 22.3; IR (KBr, *v*, cm<sup>-1</sup>): 1678, 1522, 1496, 1441, 1374, 944, 867; HRMS *m/z* (ESI) calcd for C<sub>19</sub>H<sub>16</sub>ClO<sub>2</sub> (<sup>35</sup>Cl, M+H)<sup>+</sup> 311.0839, found 311.0833.

#### 1-(3,5-diphenylfuran-2-yl)ethanone (3m)



Yellow solid; mp: 64-65 °C; yield: 52%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.82-7.81 (m, 2H), 7.70-7.68 (m, 2H), 7.48-7.37 (m, 6H), 6.91 (s, 1H), 2.54 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.0, 155.8, 146.7, 135.9, 132.4, 129.7, 129.67, 129.6, 129.4, 129.0, 128.6, 125.3, 110.5, 28.1; IR (KBr, v, cm<sup>-1</sup>): 1640, 1605, 1507, 1448, 1255, 1368, 1177, 1027, 890; HRMS *m/z* (APCI) calcd for C<sub>18</sub>H<sub>15</sub>O<sub>2</sub> (M+H)<sup>+</sup> 263.1066 found 263.1064.

#### 1-(4-(*p*-tolyl)-[2,2'-bifuran]-5-yl)ethanone (3n)



White solid; mp: 56-57 °C; yield: 75%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d, J = 8.1 Hz, 2H), 7.51-7.50 (m, 1H), 7.24-7.23 (m, 2H), 6.84-6.83 (m, 1H), 6.78 (s, 1H), 6.54-6.53 (m, 1H), 2.49 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.8, 148.0, 146.2, 145.6, 143.9, 139.2, 135.9, 129.5, 129.3, 129.1, 112.3, 110.2, 108.9, 28.0, 21.8; IR (KBr, v, cm<sup>-1</sup>): 1667, 1546, 1472, 1455, 1377, 921, 834; HRMS *m/z* (ESI) calcd for C<sub>17</sub>H<sub>15</sub>O<sub>3</sub> (M+H)<sup>+</sup> 267.1021, found 267.1016.

#### 1-(3-phenyl-5-(thiophen-2-yl)furan-2-yl)ethanone (30)



White solid; mp: 60-61 °C; yield: 60%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.68-7.66 (m, 2H), 7.49-7.48 (m, 1H), 7.44-7.37 (m, 4H), 7.12-7.10 (m, 1H), 6.74 (s, 1H), 2.51 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.7, 151.4, 146.1, 136.0, 132.5, 132.1, 129.6, 129.1, 128.6, 128.5, 127.2, 125.8, 110.2, 28.0; IR (KBr, *v*, cm<sup>-1</sup>): 1670, 1550, 1472, 1456, 1375, 921, 830; HRMS *m/z* (APCI) calcd for C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>S (M+H)<sup>+</sup> 269.0630, found 269.0632.

#### 1-(3-phenyl-5-(pyridin-2-yl)furan-2-yl)ethanone (3p)



White solid; mp: 59-60 °C; yield: 40%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.68-8.66 (m, 1H), 7.92-7.90 (m, 1H), 7.84-7.80 (m, 1H), 7.72-7.70 (m, 2H), 7.46-7.40 (m, 3H), 7.34 (s, 1H), 7.31-7.29 (m, 1H), 2.56 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.1, 154.9, 150.3, 148.4, 147.2, 137.3, 135.8, 132.0, 129.6, 129.1, 128.6, 123.9, 119.9, 113.4, 28.1; IR (KBr, *v*, cm<sup>-1</sup>): 1665, 1546, 1468, 1451, 1380, 921, 837; HRMS *m/z* (APCI) calcd for C<sub>17</sub>H<sub>14</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 264.1019, found 267.1016.

#### 1-(3-(thiophen-2-yl)-5-(p-tolyl)furan-2-yl)ethanone (3q)



White solid; mp: 55-56 °C; yield: 62%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.32-8.31 (m, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.57-7.56 (m, 1H), 7.36-7.35 (m, 1H), 7.27 (d, J = 8.3 Hz, 2H), 6.96 (s, 1H), 2.62 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.2, 156.1, 146.4, 140.0, 132.2, 130.1, 130.1, 128.8, 127.1, 126.9, 125.5, 125.2, 108.8, 28.1, 21.9; IR (KBr, v, cm<sup>-1</sup>): 1667, 1546, 1472, 1455, 1377, 921, 834; HRMS *m/z* (APCI) calcd for C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>S (M+H)<sup>+</sup> 283.0787, found 283.0784.

#### 1-(3-(*tert*-butyl)-5-(4-methoxyphenyl)furan-2-yl)ethanone (3r)



Yellow solid; mp: 100-101 °C; yield: 50%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.65 (s, 1H), 3.86 (s, 3H), 2.58 (s, 3H), 1.4 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.8, 160.7, 154.7, 147.3, 147.1, 126.6, 122.9, 114.7, 107.5, 55.8, 129.6, 31.9, 29.6(2C), 28.3; IR (KBr, v, cm<sup>-1</sup>): 1653, 1609, 1525, 1474, 1252, 1172, 1032, 928, 835; HRMS m/z (APCI) calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub> (M+H)<sup>+</sup> 273.1485, found 273.1479.

#### 1-(3-cyclopropyl-5-(p-tolyl)furan-2-yl)ethanone (3s)



Yellow solid; mp: 98-99 °C; yield: 42%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.25 (s, 1H), 2.82-2.77 (m, 1H), 2.56 (s, 3H), 2.38 (s, 3H), 1.11-1.07 (m, 2H), 0.73-0.70 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.9, 156.4, 148.6, 141.0, 139.7, 129.9, 127.2, 125.1, 104.3, 27.4, 21.8, 10.1, 7.8; IR (KBr, v, cm<sup>-1</sup>): 1653, 1592, 1538, 1486, 1262, 1184, 1037, 927, 817; HRMS *m/z* (APCI) calcd for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub> (M+H)<sup>+</sup> 241.1223, found 241.1222.

#### (2Z, 4E)-4-(1-hydroxyethylidene)-3-phenyl-1-(p-tolyl)hex-2-ene-1,5-dione (A1)



Yellow solid; mp: 94-95 °C; yield: 76%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, J = 8.2 Hz, 2H), 7.62-7.60 (m, 2H), 7.54 (s, 1H), 7.45-7.44 (m, 3H), 7.28 (t, J = 4.8 Hz, 2H), 2.43 (s, 3H), 1.92 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  190.7, 190.6, 149.1, 144.4, 140.1, 136.1, 130.5, 129.9, 129.6, 128.8, 127.5, 125.8, 111.4, 24.0 (2 C), 22.1; IR (KBr, v, cm<sup>-1</sup>): 3501, 1658, 1654, 1607, 1558, 1370, 1184, 1018, 826; HRMS m/z (APCI) calcd for C<sub>21</sub>H<sub>21</sub>O<sub>3</sub> (M+H)<sup>+</sup> 321.1485, found 321.1483.

#### (2Z,4E)-4-(1-hydroxyethylidene)-1,3-diphenylhex-2-ene-1,5-dione (A2)



Yellow solid; mp: 103-104 °C; yield: 80%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.98-7.97 (m, 2H), 7.63-7.61 (m, 2H), 760-7.58 (m, 1H), 7.55 (s, 1H), 7.50-7.47 (m, 2H), 7.45 (t, J = 3.4 Hz, 3H), 1.92 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  191.7, 190.6, 149.7, 140.0, 138.7, 133.4, 130.6, 129.6, 129.2, 128.6, 127.6, 125.5, 111.3, 24.0 (2 C); IR (KBr, v, cm<sup>-1</sup>): 3505, 1654, 1654, 1607, 1560, 1370, 1184, 1019, 828; HRMS *m/z* (APCI) calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 307.1328 found 307.1325.

### **GC-MS Analysis for the By-product**

To a stirring mixture of 0.5 mmol (0.11 g) 3-phenyl-1-*p*-tolylprop-2-yn-1-one (**1a**) and 1.0 mmol (0.1 mL) acetylacetone in 2.0 mL DMSO were added successively 0.5 mmol (0.95 g) CuI and 0.1 mmol (0.015 mL) DBU. The reaction mixture was stirred at 80 °C for 15 h. After the completion of the reaction (monitored by TLC), the reaction mixture was used directly for GC-MS analysis.





11/19/18 22:38:59



**References:** 

1. (a) Stork, G.; Tomasz, M. J. Am. Chem. Soc. **1962**, 84, 310; (b) Goldman, I. M. J. Org. Chem. **1969**, 34, 1979.

# Copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compounds 3 and A



1-(3-phenyl-5-(*p*-tolyl)furan-2-yl)ethanone (3a)

120

160

1-(3-(4-methoxyphenyl)-5-(*p*-tolyl)furan-2-yl)ethanone (3b)



1-(5-(4-chlorophenyl)-3-(4-methoxyphenyl)furan-2-yl)ethanone (3c)





1-(3-(4-methoxyphenyl)-5-phenylfuran-2-yl)ethanone (3d)



# 1-(3,5-di-*p*-tolylfuran-2-yl)ethanone (3e)







1-(5-(4-nitrophenyl)-3-(*p*-tolyl)furan-2-yl)ethanone (3f)















1-(3-(4-fluorophenyl)-5-(4-nitrophenyl)furan-2-yl)ethanone (3i)

1-(5-(2-bromophenyl)-3-(p-tolyl)furan-2-yl)ethanone (3j)





1-(3-(4-methoxyphenyl)-5-(*o*-tolyl)furan-2-yl)ethanone (3k)



1-(3-(4-chlorophenyl)-5-(*o*-tolyl)furan-2-yl)ethanone (3l)





# 1-(3,5-diphenylfuran-2-yl)ethanone (3m)





1-(4-(*p*-tolyl)-[2,2'-bifuran]-5-yl)ethanone (3n)







#### 1-(3-phenyl-5-(pyridin-2-yl)furan-2-yl)ethanone (3p)





1-(3-(thiophen-2-yl)-5-(p-tolyl)furan-2-yl)ethanone (3q)

![](_page_29_Figure_0.jpeg)

![](_page_29_Figure_1.jpeg)

![](_page_30_Figure_0.jpeg)

![](_page_30_Figure_1.jpeg)

![](_page_31_Figure_0.jpeg)

(2Z, 4E)-4-(1-hydroxyethylidene)-3-phenyl-1-(*p*-tolyl)hex-2-ene-1,5-dione (A1)

![](_page_31_Figure_2.jpeg)

![](_page_32_Figure_0.jpeg)

(2Z,4E)-4-(1-hydroxyethylidene)-1,3-diphenylhex-2-ene-1,5-dione (A2)

![](_page_32_Figure_2.jpeg)

# Crystal Structure of 3a (CCDC 1847632)

![](_page_33_Figure_1.jpeg)

![](_page_33_Figure_2.jpeg)

# Crystal Structure of A2 (CCDC 1873152)

![](_page_34_Picture_1.jpeg)

![](_page_34_Picture_2.jpeg)