Efficient Preparation of 4-Iodofuran-2(5*H*)-ones by Iodolactonisation of 2,3-Allenoates with I_2

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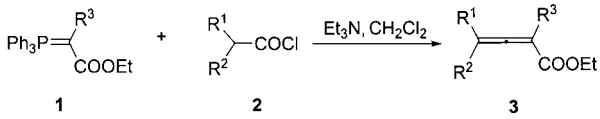
4-Iodofuran-2(5*H*)-ones were prepared, in moderate to high yields, by the facile iodolactonisation of ethyl 2,3-allenoates with I_2 in aqueous MeCN by the direct participation of the carbonyl oxygen atom in the regioselective electrophilic addition of the allene moiety.

Butenolides are a class of compounds with biological interest.[1,2] Recently, we have developed some methodologies for the synthesis of differently substituted butenolides,[3,4] and we have also developed a halolactonisation of 2,3-allenoic acids that affords 3-halobutenolides, which are important precursors for introducing different substituents at the β-position in related coupling reactions.[5] 2,3-Allenoic acids are usually prepared by the hydrolysis of 2,3-allenoates in a process that usually affords 3-alkynoic acids as by-products.[6] Thus, new protocols for the direct synthesis of 4-halobutenolides from 2,3-allenoates are highly desirable. Gill et al. have reported that the reaction of ethyl 4-methyl-2,3-butadienoate with Br_2 in CCl_4 affords the corresponding β-bromobutenolides in 56–58% yields.[7] We have also succeeded in the direct halolactonisation of 2,3-allenoates with $CuBr_2$, which affords 3-bromobutenolides.[8] However, the coupling reaction of a C–Br bond is, in most cases, not as efficient as that of a C–I bond. Marshall et al. have reported the iodolactonisation of methyl, (trimethylsilyl)ethyl, or benzyl esters of some 2,3-allenoic acids with IBr.[6] Herein, we wish to report an efficient iodolactonisation of 2,3-allenoates with I_2, which is cheaper and more readily available.

Results and Discussion

Synthesis of Starting Materials

The starting 2,3-allenoates were prepared according to the Wittig-type reaction of ylides **1** with acyl chlorides **2** (Scheme 1).



1 **2** **3**

1a: R^3 = H **1b**: R^3 = CH_3 **1c**: R^3 = *n*-C_3H_7 **1d**: R^3 = Bn

2a: R^1 = *n*-C_3H_7 R^2 = H **2b**: R^1 = *n*-C_4H_9 R^2 = H **2c**: R^1 = *n*-C_7H_{15} R^2 = H

2d: R^1 = CH_3 R^2 = CH_3 **2e**: R^1 = Ph R^2 = H **2f**: R^1 = *n*-C_7H_{15} R^2 = H

Scheme 1.

Recently, we have observed a highly stereoselective iodohydroxylation of 1,2-allenyl sulfoxides with I_2, in which the sulfinyl group participates in the electrophilic addition process to afford (*Z*)-2-iodo-3-sulfinyl-2-alkenols via five-membered intermediates.[9] Thus, we imagined that we may be able to develop a protocol for the direct iodolactonisation of 2,3-allenoates with the participation of the carbonyl oxygen atom. We tested this protocol with ethyl 2,3-allenoate **3a** as the starting material, and were lucky to observe that the iodolactonisation occurred in an aqueous MeCN (MeCN/H_2O = 4:1) solution to afford the expected product **4a** in 61% yield (Entry 1, Table 1). Through screening, we found that the best MeCN/H_2O ratio is 15:1 (Entry 4, Table 1). It should be noted that the reaction in the absence of H_2O affords **4a** in only 46% yield (Entry 6, Table 1). The reactions in other aqueous organic solvents are not competitive (Entries 7–9, Table 1).

The results of the iodolactonisation of 2,3-allenoates with I_2 under this set of standard reaction conditions are summarised in Table 2. It should be noted that the reaction affords 3-iodobutenolides in good to excellent yields and also that the reaction scope is very wide: R^1 can be alkyl or aryl, R^2 can be H or ethyl, and R^3 can be H, alkyl, or benzyl; 4-monosubstituted, 2,4-disubstituted, or 2,2,4-trisubstituted 2,3-allenoates can be iodolactonized to afford products **4** in moderate to high yields. Even the reaction

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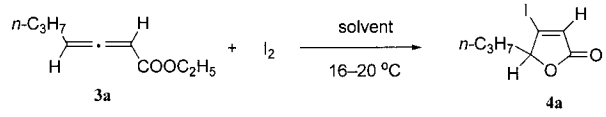
Table 1. Iodolactonisation reaction of **3a** under different conditions.[a]



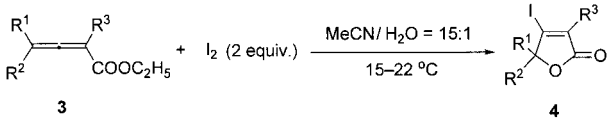
3a **4a**

Entry	Solvent	Time [h]	Yield of **4a** [%][b]
1	CH_3CN/H_2O (4:1)	2	61
2	CH_3CN/H_2O (20:1)	26	67
3	CH_3CN/H_2O (12:1)	10	70
4	CH_3CN/H_2O (15:1)	20	71
5[c]	CH_3CN/H_2O (15:1)	19	63
6	CH_3CN	43	46
7[d]	CH_3CN/EtOH (2:1)	11.5	48
8	Acetone/H_2O (15:1)	18	36
9	THF/H_2O (15:1)	19	39
10[e]	CH_3CN/H_2O (12:1)	21	48

[a] The reaction was conducted with 0.2–0.4 mmol of **3a** and I_2 (2 equiv.). [b] Isolated yield. [c] The reaction was conducted at 30 °C. [d] The reaction was conducted at 0–5 °C. [e] Substrate/I_2 = 1:1.2.

with 4-phenyl-2,3-alkadienoates **3j**–**l**, which react with $CuBr_2$ to give the corresponding 4-bromobutenolides in very low yields and selectivity,[8] afforded **4j**–**l** smoothly.

Table 2. Cyclisation of I_2 with 2,3-allenoates.[a]



3 **4**

Entry	**3** R^1	R^2	R^3	Time [h]	Yield of **4** [%][b]
1	n-C_3H_7	H	H (**3a**)	20	71 (**4a**)
2	n-C_4H_9	H	H (**3b**)	12	65 (**4b**)
3	n-C_7H_{15}	H	H (**3c**)	14	69 (**4c**)
4	n-C_3H_7	H	Bn (**3d**)	11	78 (**4d**)
5	n-C_4H_9	H	Bn (**3e**)	14	72 (**4e**)
6	n-C_3H_7	H	CH_3 (**3f**)	10	88 (**4f**)
7	n-C_4H_9	H	CH_3 (**3g**)	16	89 (**4g**)
8	n-C_7H_{15}	H	CH_3 (**3h**)	3	91 (**4h**)
9	CH_3	CH_3	CH_3 (**3i**)	3	77 (**4i**)
10	Ph	H	CH_3 (**3j**)	3	83 (**4j**)
11	Ph	H	n-C_3H_7 (**3k**)	0.7	94 (**4k**)
12	Ph	H	Bn (**3l**)	0.7	81 (**4l**)
13	CH_3	CH_3	H (**3m**)	12	60 (**4m**)

[a] The reaction was carried out using 0.2–0.4 mmol of the 2,3-allenoate. [b] Isolated yield.

In conclusion, we have developed a convenient method for the efficient synthesis of 4-iodobutenolides by the iodolactonisation of ethyl 2,3-allenoates with I_2 in aqueous MeCN. Further studies in this area are being conducted in our laboratory.

Experimental Section

Starting Materials: Compounds **3a**,[11] **3b**,[12] **3d**,[8] **3f**,[13] **3g**,[13] **3i**,[14] **1j**[13] and **1m**[15] were prepared according to known procedures.[16] Compounds **3c**, **3h**, **3e**, **3k** and **3l** were prepared as follows.

Ethyl Undeca-2,3-dienoate (3c). Typical Procedure: NEt_3 (7.6 mL, 55 mmol) was added at 0 °C to a solution of **1a** (17.4 g, 50 mmol) in dichloromethane (20 mL). After 5 min at 0 °C, a solution of acetyl chloride (**2c**; 11.47 g, 65 mmol) in dichloromethane (15 mL) was added dropwise at 0 °C with stirring, and the solution was stirred at room temp. overnight. After evaporation of the solvent, the residue was treated with 80 mL of diethyl ether and then filtered. This process was repeated until no further $OPPh_3$ precipitated. After concentration, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to afford 7.48 g (71%) of ethyl undeca-2,3-dienoate (**3c**) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53(m, 2 H), 4.16 (q, J = 7.2 Hz, 2 H), 2.10 (dq, J = 7.2 Hz and 3.2 Hz, 2 H), 1.42–1.47 (m, 2 H), 1.22–1.36 (m, 11 H), 0.85 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.3, 166.2, 95.3, 88.2, 60.6, 31.7, 29.0, 28.8, 28.7, 27.4, 22.6, 14.2, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 1961, 1720, 1253, 1158. HRMS: calcd. for $C_{13}H_{22}NaO_2$ [M^+ + Na] 233.1512; found 233.1508 cm^{-1}.

The following compounds were prepared similarly.

Ethyl 2-Benzylocta-2,3-dienoate (3e): The reaction of **1d** (17.5 g, 40 mmol), NEt_3 (6.1 mL, 44 mmol) and **2b** (8.0 g, 60 mmol) afforded 7.11 g (77%) of **3e** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08–7.21 (m, 5 H), 5.35–5.40 (m, 1 H), 4.05–4.14 (m, 2 H), 3.44–3.53 (m, 2 H), 1.94–1.99 (m, 2 H), 1.21–1.26 (m, 4 H), 1.17 (t, J = 7.2 Hz, 3 H), 0.80 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.5, 167.2, 139.4, 128.8, 128.0, 126.0, 100.5, 95.2, 60.7, 35.3, 30.8, 27.5, 21.8, 14.1, 13.7 ppm. IR (neat): $\tilde{\nu}$ = 1958, 1711, 1268, 1094 cm^{-1}. MS (70 eV, EI): m/z (%) = 258 (42.08) [M^+], 91 (100). HRMS: calcd. for $C_{17}H_{22}O_2$ 258.1620; found 258.1616.

Ethyl 2-Methylundeca-2,3-dienoate (3h): The reaction of **1b** (21.7 g, 60 mmol), NEt_3 (9.2 mL, 66 mmol) and **2c** (15.9 g, 90 mmol) afforded 13.19 g (98%) of **3h** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36–5.42 (m, 1 H), 4.10–4.16 (m, 2 H), 2.05 (q, J = 7.2 Hz, 2 H), 1.81 (d, J = 2.8 Hz, 3 H), 1.35–1.43 (m, 2 H), 1.19–1.32 (m, 11 H), 0.84 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.0, 168.0, 95.5, 93.7, 60.6, 31.8, 29.0, 28.81, 28.75, 27.9, 22.6, 15.2, 14.2, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 1960, 1712, 1270, 1121 cm^{-1}. MS (70 eV, EI): m/z (%) = 224 (1.89) [M^+], 112 (100). HRMS: calcd. for $C_{14}H_{24}O_2$ 224.1776; found 224.1774.

Ethyl 4-Phenyl-2-propylbuta-2,3-dienoate (3k): The reaction of **1c** (28.2 g, 60 mmol), NEt_3 (18.4 mL, 132 mmol) and **2e** (13.9 g, 90 mmol) afforded 9.03 g (65%) of **3k** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.26 (m, 5 H), 6.45 (t, J = 3.2 Hz, 1 H), 4.14 (q, J = 7.2 Hz, 2 H), 2.27–2.29 (m, 2 H), 1.45–1.47 (m, 2 H), 1.19 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.0, 166.8, 132.7, 128.7, 127.6, 127.2, 104.4, 98.2, 61.0, 30.9, 21.3, 14.2, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 1943, 1712, 1460, 1251 cm^{-1}. HRMS: calcd. for $C_{15}H_{16}NaO_2$ [M^+ + Na] 253.1197; found 253.1199.

Ethyl 2-Benzyl-4-phenylbuta-2,3-dienoate (3l): The reaction of **1d** (10.38 g, 20 mmol), NEt_3 (6.1 mL, 44 mmol) and **2e** (3.40 g, 22 mmol) afforded 2.52 g (45%) of **3l** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.39 (m, 10 H), 6.57 (s, 1 H), 4.24–4.29 (m, 2 H), 3.78 (s, 2 H), 1.27–1.32 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.9, 166.2, 139.0, 132.1, 128.9, 128.7, 128.2, 127.7, 127.2, 126.3, 104.2, 98.5, 61.1, 35.5, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 1945, 1712, 1600, 1495, 1455 cm^{-1}. HRMS: calcd. for $C_{19}H_{18}NaO_2$ [M^+ + Na] 301.1199; found 301.1191.

4-Iodo-5-propylfuran-2(5*H*)-one (4a). Typical Procedure: A solution of **3a** (81.9 mg, 0.53 mmol) and iodine (254 mg, 1 mmol) in 4 mL of MeCN/H_2O (15:1) was stirred at 16 °C for 12 h. The mixture was then quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. This mixture was extracted with diethyl ether (3 × 25 mL), washed with NaCl and dried with anhydrous Na_2SO_4. Concentration and column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) afforded **4a** (94.9 mg, 71%) as a white solid. M.p. 57–58 °C (petroleum ether/diethyl ether) (ref.[7] 58–59 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (s, 1 H), 4.89–4.92 (m, 1 H), 1.67–1.98 (m, 1 H), 1.50–1.55 (m, 1 H), 1.35–1.42 (m, 2 H), 0.91 (t, J = 6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 129.9, 125.5, 87.9, 34.6, 17.3, 13.7 ppm. MS (70 eV, EI): m/z (%) = 253 (100) [M^+ + 1]. IR (KBr): $\tilde{\nu}$ = 1738, 1582, 1296, 1168 cm^{-1}.

The following compounds were prepared similarly.

5-Butyl-4-iodofuran-2(5*H*)-one (4b): The reaction of **3b** (84.6 mg, 0.5 mmol) and I_2 (256.7 mg, 1 mmol) afforded 86.4 mg (65%) of **4b** as a white solid. M.p. 61–62 °C (petroleum ether/diethyl ether) (ref.[5b] 62–63 °C, *n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (s, 1 H), 4.96–4.98 (m, 1 H), 2.02–2.08 (m, 1 H), 1.58–1.64 (m, 1 H), 1.37–1.42 (m, 4 H), 0.92 (t, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 130.0, 125.5, 88.0, 32.2, 25.7, 22.3, 13.8 ppm.

5-Heptyl-4-iodofuran-2(5*H*)-one (4c): The reaction of **3c** (63.6 mg, 0.3 mmol) and I_2 (152.4 mg, 0.6 mmol) afforded 63.4 mg (69%) of **4c** as a white solid. M.p. 78–79 °C (petroleum ether/diethyl ether) (ref.[5b] 78–79 °C, *n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (s, 1 H), 4.89–4.91 (m, 1 H), 1.70–2.02 (m, 1 H), 1.49–1.56 (m, 1 H), 1.20–1.33 (m, 10 H), 0.82 (t, J = 6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 130.0, 125.5, 88.0, 32.5, 31.7, 29.1, 29.0, 23.7, 22.6, 14.1 ppm.

3-Benzyl-4-iodo-5-propylfuran-2(5*H*)-one (4d): The reaction of **3d** (76.1 mg, 0.31 mmol) and I_2 (156 mg, 0.61 mmol) afforded 82.4 mg (78%) of **4d** as a white solid. M.p. 87–88 °C (petroleum ether/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.25 (m, 5 H), 4.79–4.80 (m, 1 H), 3.53–3.61 (m, 2 H), 1.86–1.99 (m, 1 H), 1.42–1.47 (m, 1 H), 1.30–1.36 (m, 2 H), 0.85 (t, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 138.3, 136.5, 128.8, 128.6, 126.9, 122.6, 85.5, 34.9, 33.1, 17.3, 13.7 ppm. MS (70 eV, EI): m/z (%) = 342 (15.71) [M^+], 129 (100). IR (KBr): $\tilde{\nu}$ = 1739, 1633, 1494, 1451, 1192 cm^{-1}. $C_{14}H_{15}IO_2$ (342.2): calcd. C 49.14, H 4.42; found C 49.19, H 4.52.

3-Benzyl-5-butyl-4-iodofuran-2(5*H*)-one (4e): The reaction of **3e** (79.3 mg, 0.307 mmol) and I_2 (152.6 mg, 0.6 mmol) afforded 78.4 mg (72%) of **4e** as a white solid. M.p. 92–93 °C (petroleum ether/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.34 (m, 5 H), 4.78–4.80 (m, 1 H), 3.59 (d, J = 11.2 Hz, 1 H), 3.56 (d, J = 11.2 Hz, 1 H), 1.96–1.99 (m, 1 H), 1.49–1.53 (m, 1 H), 1.26 (m, 4 H), 0.81 (t, J = 5 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 138.3, 136.5, 128.8, 128.6, 126.9, 122.5, 85.6, 33.1, 32.5, 25.8, 22.3, 13.8 ppm. MS (70eV, EI): m/z (%) = 357 (8.50) [M^+ + 1], 115 (100). IR (KBr): $\tilde{\nu}$ = 3029, 1760, 1635, 1495, 1061 cm^{-1}. HRMS: calcd. for $C_{15}H_{17}IO_2$ 356.02733; found 356.02289.

4-Iodo-3-methyl-5-propylfuran-2(5*H*)-one (4f): The reaction of **3f** (83.5 mg, 0.5 mmol) and I_2 (254.9 mg, 1 mmol) afforded 116.2 mg (88%) of **4f** as a white solid. M.p. 63–65 °C (petroleum ether/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84–4.86 (m, 1 H), 1.96–2.02 (m, 1 H), 1.90 (s, 3 H), 1.50–1.53 (m, 1 H), 1.37–1.47 (m, 2 H), 0.93 (t, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 135.6, 121.6, 85.4, 34.9, 17.3, 13.7, 12.8 ppm. MS (70 eV, EI): m/z (%) = 266 (14.05) [M^+], 139 (100). IR (KBr): $\tilde{\nu}$ = 1740, 1639, 1462, 1275, 1083, 1010 cm^{-1}. $C_8H_{11}IO_2$ (266.1): calcd. C 36.11, H 4.17; found C 36.13, H 4.36.

5-Butyl-4-iodo-3-methylfuran-2(5*H*)-one (4g): The reaction of **3g** (91.9 mg, 0.5 mmol) and I_2 254 mg (1 mmol) afforded 125.3 mg (89%) of **4g** as a white solid. M.p. 68–70 °C (petroleum ether/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.87–4.89 (m, 1 H), 2.04–2.07 (m, 1 H), 1.93 (s, 3 H), 1.56–1.60 (m, 1 H), 1.33 (m, 4 H), 0.88–0.94 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 135.7, 121.6, 85.5, 34.4, 25.8, 22.3, 13.9, 12.8 ppm. IR (KBr): $\tilde{\nu}$ = 1739, 1640, 1466, 1273, 1088, 1039 cm^{-1}. MS (70 eV, EI): m/z (%) = 281 (97.9) [M^+ + 1], 41 (100). $C_9H_{13}IO_2$ (280.1): calcd. C 38.59, H 4.68; found C 38.55, H 4.66.

5-Heptyl-4-iodo-3-methylfuran-2(5*H*)-one (4h): The reaction of **3h** (88.2 mg, 0.4 mmol) and I_2 (203 mg, 0.8 mmol) afforded 115.6 mg (91%) of **4h** as a white solid. M.p. 83–84 °C (petroleum ether/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84–4.88 (m, 1 H), 2.00–2.04 (m, 1 H), 1.91 (s, 3 H), 1.55–1.57 (m, 1 H), 1.25–1.34 (m, 10 H), 0.85–0.91 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 135.7, 121.5, 85.6, 32.8, 31.7, 29.1, 29.0, 23.7, 22.6, 14.1, 12.8 ppm. MS (70 eV, EI): m/z (%) = 322 (5.93) [M^+ + 1], 41 (100). IR (KBr): $\tilde{\nu}$ = 1735, 1640, 1276, 1088 cm^{-1}. $C_{12}H_{19}IO_2$ (322.2): calcd. C 44.74, H 5.94; found C 44.80, H 6.07.

4-Iodo-3,5,5-trimethylfuran-2(5*H*)-one (4i): The reaction of **3i** (79.3 mg, 0.51 mmol) and I_2 254 mg (1 mmol) afforded 99.7 mg (77%) of **4i** as a white solid. M.p 138–140 °C (petroleum ether/diethyl ether) (ref.[7] 140–141 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (s, 3 H), 1.45 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 134.6, 129.5, 88.0, 25.8, 13.1 ppm. IR (KBr): $\tilde{\nu}$ = 1734, 1640, 1288, 1080 cm^{-1}. MS (70 eV, EI): m/z (%) = 252 (14.84) [M^+], 43 (100).

4-Iodo-3-methyl-5-phenylfuran-2(5*H*)-one (4j): The reaction of **3j** (82.5 mg, 0.41 mmol) and I_2 (202 mg, 0.80 mmol) afforded 102.1 mg (83%) of **4j** as a white solid. M.p. 93–94 °C (petroleum ether/diethyl ether) (ref.[10] 93–94 °C, *n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.42 (m, 3 H), 7.24–7.25 (m, 2 H), 5.75 (s, 1 H), 2.02 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 135.5, 133.6, 129.8, 128.9, 127.6, 122.2, 87.6, 13.0 ppm.

4-Iodo-5-phenyl-3-propylfuran-2(5*H*)-one (4k): The reaction of **3k** (94.0 mg, 0.40 mmol) and I_2 206.8 mg (0.80 mmol) afforded 125.5 mg (94%) of **4k** as a white solid. M.p. 102–104 °C (petroleum ether/diethyl ether) (ref.[5b] 104–105 °C, *n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.41 (m, 3 H), 7.22–7.24 (m, 2 H), 5.73 (s, 1 H), 2.40 (t, J = 7.2 Hz, 2 H), 1.63–1.69 (m, 2 H), 0.99 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 138.9, 133.8, 129.7, 128.9, 127.5, 122.0, 87.4, 29.2, 20.6, 13.8 ppm. IR (KBr): $\tilde{\nu}$ = 1758, 1635, 1493, 1454 cm^{-1}. MS (70 eV, EI): m/z (%) = 328 (6.17) [M^+], 105 (100).

3-Benzyl-4-iodo-5-phenylfuran-2(5*H*)-one (4l): The reaction of **3l** (84.2 mg, 0.30 mmol) and I_2 153.9 mg (0.60 mmol) afforded 91.9 mg (81%) of **4l** as a white solid. M.p. 100–102 °C (petroleum ether/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.38 (m, 10 H), 5.72 (s, 1 H), 3.76 (d, J = 14.4 Hz, 1 H), 3.69 (d, J = 14.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 138.1, 136.4, 133.6, 129.9, 129.0, 128.9, 128.7, 127.6, 127.0, 122.9, 87.7, 33.3 ppm. IR (KBr): $\tilde{\nu}$ = 1761, 1633, 1602, 1495, 1455 cm^{-1}. MS (70 eV, EI): m/z (%) = 376 (4.52) [M^+], 203 (100). HRMS: calcd. for $C_{17}H_{13}IO_2$ 375.99603; found 375.99608.

4-Iodo-5,5-dimethylfuran-2(5*H*)-one (4m): The reaction of **3m** (71.2 mg, 0.5 mmol) and I_2 257.4 mg (1.02 mmol) afforded 71.0 mg (60%) of **4m** as a white solid. M.p. 120–122 °C (petroleum ether/

diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.37 (s, 1 H), 1.47 (s, 6 H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 170.4, 133.2, 129.1, 90.5, 25.54 ppm. IR (KBr): $\tilde{\nu}$ = 1735, 1584, 1278, 1246 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 238 (33.73) [M$^+$], 223 (100). HRMS: calcd. for $C_6H_7IO_2$ 237.94908; found 237.94925.

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