

## Supporting Information

### Iodoxolone based Hypervalent Iodine Reagents

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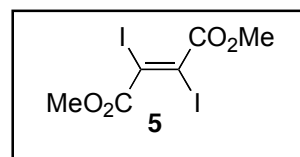
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Experimental procedures for the synthesis of compounds **5**, **6**, (**Z**)-**8a**, (**E**)-**8b**, (**Z**)-**8b**, **9**, **11**, **12**, **13**, **15**, **17a**, **17b**, **19**, **21** and **23**.

#### 2,3-Diiodofumaric acid dimethyl ester (**5**):<sup>1</sup>

The synthesis of 2,3-diiodofumaric acid dimethyl ester (**5**) was performed according to the literature protocol.<sup>1</sup> A solution of dimethyl acetylene dicarboxylate (10.0 mmol, 1.22 mL) and iodine (12.0 mmol, 3.04 g) in 1,2-dichlorobenzene (30 mL) was heated to reflux and stirred until all starting acetylene was consumed, as evidenced by <sup>1</sup>H NMR analysis. After cooling to r. t. the reaction mixture was washed with 20% aq. sodium thiosulfate solution (40 mL), dried over MgSO<sub>4</sub>, filtered and concentrated under reduce pressure. The residue was dissolved in ethanol (15 mL) and the product precipitated by the addition of water (15 mL). Recrystallization from methanol/water furnished colourless crystals (10.0 mmol, 3.96 g, quant.). The spectroscopic data were in agreement with the literature.<sup>1</sup>

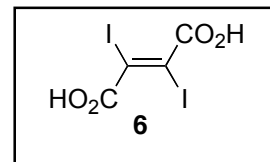


(1) Hollins, R. A.; Campos, M. P. A. *J. Org. Chem.* **1979**, *44*, 3931–3934.

$^1\text{H}$  NMR (acetone- $d_6$ , 500 MHz):  $\delta$  = 3.90 (s, 6H) ppm.  $^{13}\text{C}$  NMR (acetone- $d_6$ , 126 MHz):  $\delta$  = 166.6 (s, 2C), 89.2 (s, 2C), 53.9 (s, 2C) ppm.

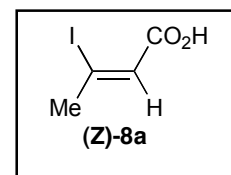
### 2,3-Diiodofumaric acid (**6**):

2,3-Diiodofumaric acid dimethyl ester (**5**) (10.0 mmol, 3.96 g) was dissolved in MeOH (30 mL) followed by addition of aq. 0.5 M KOH solution (60 mL). The reaction mixture was stirred at 40 °C for 6 h. It was cooled to r. t. and acidified by adding an aq. 0.5 M HCl solution. The phases were separated and the aq. phase was extracted with ethyl acetate (100 mL). The combined organic phases were washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure to afford 2,3-diiodofumaric acid (**6**) (9.50 mmol, 3.52 g, 97%).  $^1\text{H}$  NMR and IR data were already reported in the literature.<sup>2</sup>  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 126 MHz):  $\delta$  = 168.9 (s, 2C), 88.8 (s, 2C) ppm. LR-EI  $m/z$  (%): 389 (36), 345 (24), 322 (40), 283 (65), 255 (100), 196 (50), 183 (68). HRMS: calc. for  $[\text{C}_4\text{I}_2\text{NaO}_4]^-$ : 388.7789, found: 388.7786.



### (*Z*)-3-Iodobut-2-enoic acid ((*Z*)-**8a**):<sup>2</sup>

The synthesis of (*Z*)-3-iodobut-2-enoic acid ((*Z*)-**8a**) was performed according to the literature protocol. A 47% aq. hydroiodic acid solution (45.6 mmol, 7.30 mL) was added dropwise to 2-butyric acid **7a** (25.0 mmol, 2.10 g). After stirring for 2 h at 90 °C, 5% aq.  $\text{Na}_2\text{S}_2\text{O}_3$  solution (8 mL) was added. The phases were separated and the organic phase extracted with  $\text{Et}_2\text{O}$  (15 mL). The combined organic phases were washed with brine (15 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure to afford (*Z*)-3-iodobut-2-enoic acid ((*Z*)-**8a**) (4.20 mmol, 900 mg, 17%). The spectroscopic data were in agreement with the literature.<sup>2</sup>



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 2.72 (s, 3H), 6.30 (s, 1H), 9.00-10.50 (s, br, 1H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz):  $\delta$  = 169.1 (s), 125.2 (d), 116.6 (s), 37.1 (q) ppm.

### 3-Iodo-3-phenyl-2-propenoic acid (**8b**):<sup>2</sup>

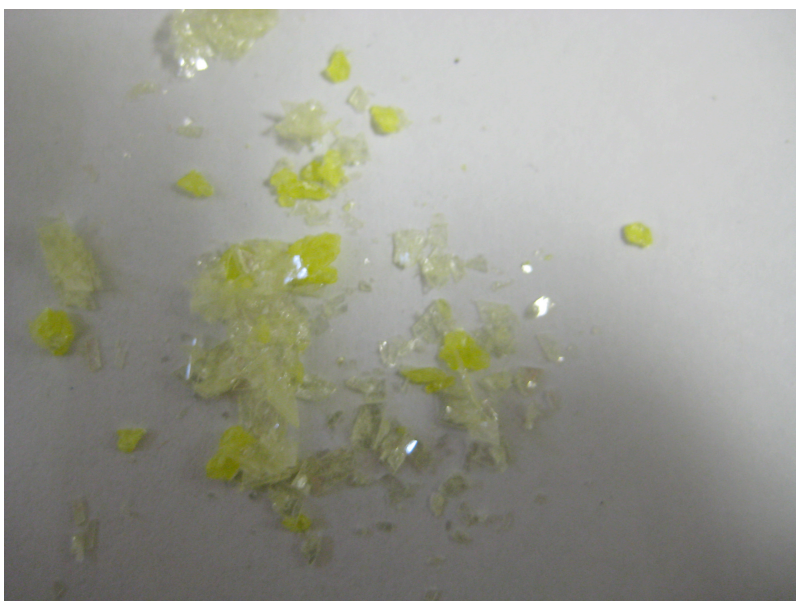
A 57% aq. solution of hydroiodic acid (24.0 mmol, 3.23 mL) was added dropwise to phenylpropionic acid (**7b**) (16.7 mmol, 2.45 g). The reaction mixture was stirred at 70 °C overnight. During the

(2) Abarbri, M.; Thibonnet, J.; Parrain, J.-L.; Duchene, A. *Synthesis* **2002**, 543-551.

reaction, a yellow solid was formed. A 5% aq.  $\text{Na}_2\text{S}_2\text{O}_3$  solution (8 mL) was then added. The phases were separated and the aq. phase extracted with diethyl ether (2 x 50 mL). The combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. Under these reaction conditions, 3-iodo-3-phenyl-2-propenoic acid (**8b**) (12.6 mmol, 3.46 g, 75%) was isolated and the ratio of (*E*)- to (*Z*)-stereoisomer was determined to 1:4 and not, as reported in literature,<sup>2</sup> 0:100. Under different reaction conditions, such as higher temperatures or shorter reaction times, the (*E*)- to (*Z*)-ratio of the product was approximately 1:1.

To separate the two isomers, the product was recrystallized from diethyl ether/petroleum ether. The (*E*)-isomer crystallized first, leaving the (*Z*)-isomer in solution. Pure (*Z*)-isomer could thus be obtained in 10% yield. The structures of the (*Z*)-isomer and the (*E*)-isomer were both verified by X-ray analysis.<sup>3</sup>

The (*E*)-isomer formed bright yellow crystals, whereas the (*Z*)-isomer formed dark yellow crystals (see figure 1). These two different types of crystals were separated manually.



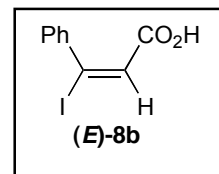
**Figure 1.** Crystals of (*E*)-**8b** (bright yellow) and (*Z*)-**8b** (dark yellow).

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(3) CCDC 718610 ((*E*)-**8b**) and CCDC 718612 ((*Z*)-**8b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**(E)-3-Iodo-3-phenyl-2-propenoic acid ((E)-8b):**<sup>3,4</sup>

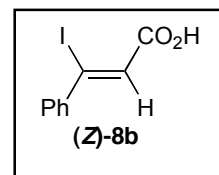
m.p. = 183-184 °C. <sup>1</sup>H NMR (acetone-d<sub>6</sub>, 500 MHz): δ = 6.91 (s, 1H), 7.16-7.23 (m, 5H), 9.50-11.0 (s, br, 1H) ppm. <sup>13</sup>C NMR (acetone-d<sub>6</sub>, 126 MHz): δ = 164.6 (s), 143.5 (s), 133.8 (d), 129.8 (d), 128.8 (d, 2C), 128.6 (d, 2C), 117.2 (s) ppm.



**(Z)- 3-Iodo-3-phenyl-2-propenoic acid ((Z)-8b):**<sup>4,5</sup>

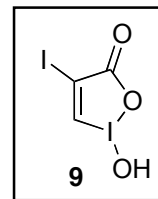
In a Schlenk flask under an atmosphere of nitrogen phenylpropionic acid (**7b**) (17.1 mmol, 2.50 g) was dissolved in acetic acid (10 mL). Sodium iodide (27.1 mmol, 4.06 g, 1.6 eq.) was added under stirring. The mixture was stirred for 4 days at 115 °C. The reaction was then quenched by adding water and ethyl acetate. After separation of the phases, the aq. phase was extracted with ethyl acetate (2 x 10 mL). The combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to give (Z)-3-iodo-3-phenylpropenoic acid ((Z)-8b) which was confirmed by a combination of X-ray structure analysis and <sup>1</sup>H NMR spectroscopy. Recrystallisation from ethyl acetate/ hexane at -28°C afforded the title compound as dark yellow crystals (11.1 mmol, 3.03 g, 65%).

m.p. = 185-186 °C. <sup>1</sup>H NMR (acetone-d<sub>6</sub>, 500 MHz): δ = 6.75 (s, 1H), 7.40-7.46 (m, 3H), 7.59-7.63 (m, 2H) 10.00-12.00 (s, br, 1H) ppm. <sup>13</sup>C NMR (acetone-d<sub>6</sub>, 126 MHz): δ = 166.6 (s), 145.3 (s), 131.8 (d), 130.5 (d, 2C), 130.4 (d, 2C), 129.5 (d), 116.7 (s) ppm.



**1-Hydroxy-4-iodoiodoxol-3(1H)-one (9):**<sup>6</sup>

The synthesis of **9** was performed according to a literature protocol.<sup>7</sup> Diiodofumaric acid (5.0 mmol, 1.84 g) was dissolved in acetic anhydride (2.0 mL), cooled to 0 °C and then treated with 30% aq. peracetic acid solution (3.0 mL) at such a rate that the reaction temperature remained between 0 and 50 °C. After the addition was completed, the mixture was stirred and kept at 0 °C for 5 h, then stirred at r. t. overnight. The colourless precipitate formed after that period of time was filtered off and washed with cold water and acetone and afterwards dried under reduced pressure to afford **9** (4.0 mmol, 1.37 g, 81%).



(4) Xu, W.; Chen, Q.-Y. *J. Org. Chem.* **2002**, 67, 9421-9427.

(5) Piers, E.; Wong, T.; Coish, P. D.; Rogers, C. *Can. J. Chem.* **1994**, 72, 1816-1819.

(6) Willgerodt, C. in *Die organischen Verbindungen mit mehrwertigem Iod*, Enke, Stuttgart, **1914**.

(7) Moss, R. A.; Wilk, B.; Krogh-Jespersen, K.; Blair, J. T.; Westbrook, J. D. *J. Am. Chem. Soc.* **1989**, 111, 250-258.



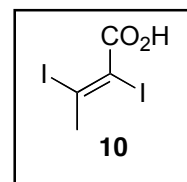
By a second method<sup>8</sup> NaIO<sub>4</sub> (4.50 mmol, 900 mg) and 2,3-diiodofumaric acid (2.0 mmol, 736 mg) in 30% aq. acetic acid (3.0 mL) were vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with ice cold water (10 mL) and kept at r. t. for 2 h. The crude product was collected by filtration, washed with cold water and acetone and was finally air-dried in the dark to afford compound **9** (1.46 mmol, 497 mg, 73%).

By a third method<sup>9</sup> potassium bromate (1.80 mmol, 300 mg) was added over 0.5 h to a vigorously stirred mixture of 2,3-diiodofumaric acid (1.36 mmol, 500 mg) and 1 M aq. H<sub>2</sub>SO<sub>4</sub> solution (4 mL) at 55 °C. The mixture was stirred for additional 3.6 h at 68 °C and then cooled with an ice bath. The colourless precipitate was filtered off and washed with cold water and acetone and finally dried under reduced pressure to afford compound **9** (1.20 mmol, 402 mg, 87%). The structure was verified by X-ray analysis.<sup>10</sup>

Colourless solid; m.p. = 156 °C (lit. 169-170 °C).<sup>6</sup> <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ = 8.43 (s, 1H), 8.05 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz): δ = 166.3 (s), 126.4 (d), 99.1 (s) ppm. IR:  $\tilde{\nu}$  = 3284, 2995, 1610, 1311 cm<sup>-1</sup>. LR-EI *m/z* (%): 362 (53), 340 (23), 274 (20), 179 (100). HRMS: calc. for [C<sub>3</sub>H<sub>2</sub>I<sub>2</sub>O<sub>3</sub>Na]<sup>+</sup>: 362.7986, found: 362.7982.

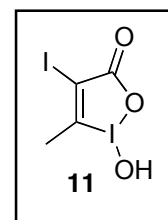
#### (*E*)-2,3-Diiodobut-2-enoic acid (**10**):<sup>11</sup>

Compound **10** was synthesized from 2-butyric acid **7a** according to the literature protocol.<sup>11</sup> The spectroscopic data were in agreement with the literature.<sup>11</sup>



#### 1-Hydroxy-4-iodo-5-methyloxol-3(1*H*)-one (**11**):

Acetic anhydride (9.60 mL), and 30% aq. H<sub>2</sub>O<sub>2</sub> (2.40 mL) were stirred at 40 °C for 4 h. (*E*)-2,3-Diiodobut-2-enoic acid (**10**) (4.80 mmol, 1.62 g) was added in one portion and the mixture was stirred at 40 °C. After 20 h the reaction mixture was diluted with water (50 mL). The mixture was stirred at r. t. for 1 h. After filtration the colourless



(8) Kraszkievicz, L.; Skulski, L. *ARKIVOC* **2003**, 6, 120-125.

(9) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, 113, 7277-7287.

(10) CCDC 718611 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

(11) Langle, S.; Ngi, S. I.; Anselmi, E.; Abarbri, M.; Thibonnet, J.; Duchene, A. *Synthesis* **2007**, 1724-1728.

crystalline solid was washed with water and dried under reduced pressure to afford compound **11** (2.88 mmol, 1.02 g, 60%).<sup>12</sup>

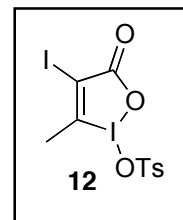
By a second method<sup>13</sup> (*E*)-2,3-diiodobut-2-enoic acid (**10**) (2.0 mmol, 708 mg) was added to a solution of oxone® (2.60 mmol, 1.60 g) in deionized water (6.50 mL). The reaction mixture was heated to 70 °C over 20 min and stirred for 3.5 h at this temperature. The reaction mixture was then cooled to 5 °C and left at this temperature for 1.5 h with slow stirring. The mixture was filtered and the solid was repeatedly rinsed with water (50 mL) and acetone (50 mL) to afford **11** (1.19 mmol, 424 mg, 60%).

Colourless solid; m.p. = 136-137 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ = 2.48 (s, 3H), 8.08 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 126 MHz): δ = 166.6 (s), 132.4 (s) 97.8 (s), 21.7 (q) ppm. IR:  $\tilde{\nu}$  = 3458, 2972, 1613, 1304 cm<sup>-1</sup>. HRMS: calc. for [C<sub>4</sub>H<sub>5</sub>I<sub>2</sub>O<sub>3</sub>]<sup>+</sup>: 354. 8323, found: 354.8331.

#### 1-Tosyloxy-4-iodo-5-methyliodoxol-3(1*H*)-one (**12**):

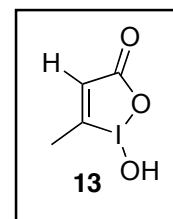
To a stirred mixture of compound **11** (1.20 mmol, 424 mg) in acetic anhydride (600 μL), *p*-TsOH • H<sub>2</sub>O (2.40 mmol, 457 mg) was added at r. t. After 5 min of stirring a slightly exothermic reaction was observed while the suspension turned into a clear solution. The solution was stirred for additional 30 min until a colourless microcrystalline precipitate was formed. Then the reaction mixture was diluted with dry diethyl ether (20 mL). The precipitate was filtered off, washed with diethyl ether (3 x 20 mL) and dried under reduced pressure to afford **12** (750 μmol, 384 mg, 63%).

Colourless solid; m.p. = 154-155 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ = 7.49 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H) 2.47 (s, 3H), 2.29 (s, 3H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 126 MHz): δ = 166.6 (s), 145.3 (s), 137.9 (s), 132.4 (s) 128.1 (d, 2C), 125.5 (d, 2C), 97.8 (s), 21.7 (q), 20.7 (q) ppm. IR:  $\tilde{\nu}$  = 3445, 2972, 1609, 1300, 1179 cm<sup>-1</sup>.



#### 1-Hydroxy-5-methyliodoxol-3(1*H*)-one (**13**):

(*Z*)-3-Iodobut-2-enoic acid ((*Z*)-**8a**) (2.0 mmol, 424 mg) was oxidized by peracetic acid following the above-mentioned method for compound **9** to give compound **13**



(12) Panetta, C. A.; Garlick, S. M.; Durst, H. D.; Longo, F. R.; Ward, J. R. *J. Org. Chem.* **1990**, *55*, 5202-5205.

(13) Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537-4538.

(500  $\mu$ mol, 114 mg, 25% yield). The yield could be doubled (1.0 mmol, 228 mg, 50%) when peracetic acid was replaced by *m*CPBA. The structure was verified by X-ray analysis.<sup>14</sup>

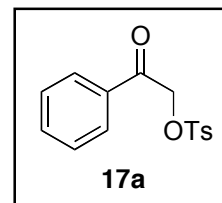
Colourless solid; m.p. = 130-131 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 7.42 (s, 1H), 7.28 (s, 1H), 2.32 (s, 3H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 168.9 (s), 140.3 (s), 126.1 (d), 17.6 (q) ppm. IR:  $\tilde{\nu}$  = 3379, 2920, 1612, 1317 cm<sup>-1</sup>.

### Benzaldehyde (15):

A mixture of benzyl alcohol (1.0 mmol, 108 mg) and hypervalent iodine compound (1.20 mmol each; **1**, **9**, **11** or **13**) was refluxed in acetone (10 mL) for 3 h. The mixture was then subjected directly to column chromatography (silica gel; hexane/ethyl acetate; 9:1 v/v) to afford benzaldehyde (for **1**: 4  $\mu$ mol, 42 mg, 40%), (for **9**: 600  $\mu$ mol, 63 mg, 60%), (for **11**: 400  $\mu$ mol, 42 mg 40%) and (for **13**: 520  $\mu$ mol, 55 mg, 52%).

### $\alpha$ -Tosyloxyacetophenone (**17a**):<sup>15</sup>

A mixture of acetophenone (1.0 mmol, 120 mg), *p*-TsOH • H<sub>2</sub>O (1.0 mmol, 190 mg) and hypervalent iodine compound (1.20 mmol each; **1**, **9**, **11** or **13**) was refluxed in CH<sub>3</sub>CN (10 mL) for 3 h. After completion of the reaction as confirmed by TLC, the mixture was treated with sat. aq. sodium bicarbonate solution (10 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure and subsequently purified by column chromatography (silica gel; petroleum ether/ethyl acetate; 4:1 v/v) to afford **17a** (for **1**: 570  $\mu$ mol, 166 mg, 57%), (for **9**: 730  $\mu$ mol, 212 mg, 73%), (for **11**: 550  $\mu$ mol, 160 mg, 55%) and (for **13**: 630  $\mu$ mol, 183 mg, 63%). The spectroscopic data were in agreement with the literature.<sup>15</sup>



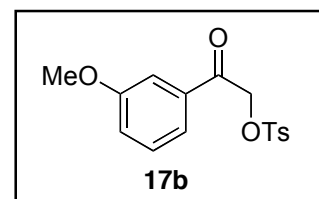
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 7.75-7.80 (m, 4H), 7.55-7.59 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.20 (s, 2H), 2.40 (s, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz):  $\delta$  = 190.3 (s), 145.3 (s), 134.2 (d), 133.8 (s), 132.7 (s), 129.9 (d, 2C), 128.9 (d, 2C), 128.1 (d, 2C), 128.0 (d, 2C), 69.9 (t), 21.7 (q) ppm.

(14) CCDC 718613 (**13**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

(15) Karade, N. N.; Tiwari, G. B.; Shinde, S. V.; Gampawar, S. V.; Kondre, J. M. *Tetrahedron Lett.* **2008**, 49, 3441-3443.

### $\alpha$ -Tosyloxy-3-methoxyacetophenone (**17b**):<sup>16</sup>

Similarly the reaction was performed with 3-methoxyacetophenone **16b** (1.0 mmol, 150 mg) using the same reaction conditions as described above for **16a**.  $\alpha$ -Tosyloxy-3-methoxyacetophenone (**17b**) was obtained (for **1**:

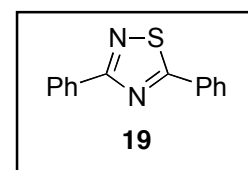


410  $\mu$ mol, 131 mg, 41%), (for **9**: 600  $\mu$ mol, 192 mg, 60%), (for **11**: 500  $\mu$ mol, 160 mg, 50%) and (for **13**: 530  $\mu$ mol, 170 mg, 53%). The spectroscopic data were in agreement with the literature.<sup>16</sup>

Yellow amorphous solid; m.p. = 54-55 °C (lit. 52-54 °C).<sup>16</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 7.78 (m, 2H), 7.29 (m, 5H), 7.07 (m, 1H), 5.18 (s, 2H), 3.76 (s, 3H), 2.40 (s, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz):  $\delta$  = 190.1 (s), 160.0 (s), 145.3 (s), 135.1 (s), 132.7 (s), 130.0 (d, 2C), 128.2 (d, 2C), 121.0 (d), 120.4 (d), 112.3 (d), 70.0 (t), 55.5 (q), 21.7 (q). One carbon signal not detected.

### 3,5-Diphenyl-1,2,4-thiadiazole (**19**):<sup>17</sup>

Thiobenzamide (2.0 mmol, 274 mg) and hypervalent iodine compound (2.0 mmol each; **1**, **9**, **11** or **13**) in CH<sub>3</sub>CN (10 mL) was heated to reflux for 1 h. After completion of the reaction, the mixture was filtered, washed with water



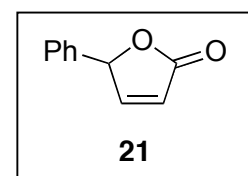
(10 mL) and dried over MgSO<sub>4</sub> and filtered. The solvent was distilled off and the residue obtained was subjected directly to column chromatography (silica gel; hexane/ethyl acetate; 6:1 v/v) to afford 3,5-diphenyl-1,2,4-thiadiazole (**19**) (for **1**: 430  $\mu$ mol, 102 mg, 43%), (for **9**: 820  $\mu$ mol, 195 mg, 82%), (for **11**: 800  $\mu$ mol, 191 mg, 80%) and (for **13**: 710  $\mu$ mol, 169 mg, 71%). The spectroscopic data were in agreement with the literature.<sup>17</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 8.35-8.41 (m, 2H), 7.95-8.01 (m, 2H), 7.39-7.55 (m, 6H) ppm.

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz):  $\delta$  = 188.1 (s), 173.8 (s), 132.9 (s), 131.9 (d), 130.8 (s), 130.4 (d), 129.3 (d, 2C), 128.7 (d, 2C), 128.4 (d, 2C), 127.5 (d, 2C) ppm.

### 5-Phenylfuran-2(5H)-one (**21**):<sup>18</sup>

In a Schlenk flask under an atmosphere of nitrogen (*E*)-3-butenic acid (**20**) (310  $\mu$ mol, 50 mg), the hypervalent iodine compound (326  $\mu$ mol, 1.05 equiv.,



(16) Sakurai, N.; Mukaiyama, T. *Chem. Lett.* **2008**, 37, 388-389.

(17) Cheng, D.; Chen, Z. *Synth. Commun.* **2002**, 32, 2155-2159.

(18) (a) Renard, M.; Ghosez, L. A. *Tetrahedron* **2001**, 57, 2597-2608. (b) Browne, D. M.; Niyomura, O.; Wirth, T. *Org. Lett.* **2007**, 9, 3169-3171.

86 mg **1**; 55 mg **9**; 58 mg **11**; 70 mg **13**) and diphenyl diselenide (15.5  $\mu\text{mol}$ , 5 mol%, 4.8 mg) were dissolved in  $\text{CH}_3\text{CN}$  (4 mL). After adding  $(\text{F}_3\text{CCO})_2\text{O}$  (310  $\mu\text{mol}$ , 65 mg, 1.0 equiv.) the resulting mixture was stirred overnight at 40 °C. The crude reaction mixture was then concentrated under reduced pressure and subjected to column chromatography (silica gel; petrol ether/diethyl ether; 4:1 v/v) to give 5-phenylfuran-2(5*H*)-one **21** (for **1**: 38 mg, 236  $\mu\text{mol}$ , 76%; for **9**: 24 mg, 149  $\mu\text{mol}$ , 48%; for **11**: 7 mg, 43  $\mu\text{mol}$ , 14%; for **13**: 12 mg, 78  $\mu\text{mol}$ , 25%). The spectroscopic data were in agreement with the literature.<sup>18</sup>

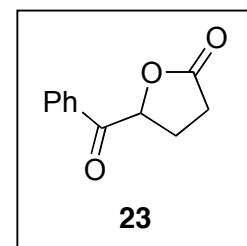
<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.53 (dd,  $J$  = 5.5, 1.6 Hz, 1H), 7.40–7.35 (m, 3H), 7.30–7.25 (m, 2H), 6.23 (dd,  $J$  = 5.5, 2.0 Hz, 1H), 6.01 (dd,  $J$  = 2.0, 1.6 Hz, 1H) ppm.

Procedure for the conversion of **20** to **21** with *in situ* formation of the hypervalent iodine compound **9**:

In a Schlenk flask under an atmosphere of nitrogen **6** (136  $\mu\text{mol}$ , 50 mg) and *m*CPBA (300  $\mu\text{mol}$ , 52 mg, 2.2 equiv.) were dissolved in  $\text{CH}_3\text{CN}$  (4 mL) and stirred at rt for 2 hours. Afterwards **20** (136  $\mu\text{mol}$ , 22 mg), diphenyl diselenide (7  $\mu\text{mol}$ , 2 mg, 5 mol%) and  $(\text{F}_3\text{CCO})_2\text{O}$  (136  $\mu\text{mol}$ , 29 mg, 1.0 equiv.) were added and the resulting mixture stirred overnight at 40 °C. The crude reaction mixture was then concentrated under reduced pressure and subjected to column chromatography (silica gel; petrol ether/diethyl ether; 4:1 v/v) to give 5-phenylfuran-2(5*H*)-one (**21**) (16 mg, 102  $\mu\text{mol}$ , 75%).

#### 5-(Phenylcarbonyl)dihydrofuran-2(3*H*)-one (**23**)<sup>19</sup>

In a Schlenk flask under an atmosphere of nitrogen 5-oxo-5-phenylpentanoic acid (**22**) (96 mg, 0.5 mmol), the iodine containing compound (50  $\mu\text{mol}$ , 10 mol%, 18 mg **6**; 11 mg (**Z**)-**8a**; 14 mg (**Z**)-**8b**; 17 mg **10**), *p*-TsOH·H<sub>2</sub>O (0.1 mmol, 19 mg, 20 mol%) and *m*CPBA (0.6 mmol, 103 mg, 1.2 equiv.) were dissolved in  $\text{CH}_3\text{CN}$  (2.5 mL). The mixture was heated to 50°C and stirred overnight [for (**Z**)-**8a** the reaction time was 4 days at 50°C]. The crude reaction mixture was then concentrated under reduced pressure and subjected to column chromatography (silica gel; petrol ether/diethyl ether; 2:1 v/v) to give 5-(phenylcarbonyl)dihydrofuran-2(3*H*)-one (**23**) (for **6**: 30 mg, 160  $\mu\text{mol}$ ,



(19) (a) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, 31, 201–204. (b) Uyanik, M.; Yasui, T.; Ishihara, K. *Bioorg. Med. Chem. Lett.* **2009**, doi: 10.1016/j.bmcl.2009.03.148.

32%; for **(Z)-8a**: 30 mg, 160  $\mu\text{mol}$ , 32%; for **(Z)-8b**: 38 mg, 200  $\mu\text{mol}$ , 40%; for **10**: 76 mg, 401  $\mu\text{mol}$ , 80%). The spectroscopic data were in agreement with the literature.<sup>19</sup>

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.99 (dd,  $J$  = 8.4 Hz, 1.3 Hz, 2H), 7.62-7.67 (m, 1H), 7.52 (dd,  $J$  = 8.4 Hz, 7.5 Hz, 2H), 5.78-5.82 (m, 1H), 2.42-2.67 (m, 4H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz):  $\delta$  = 194.3 (s), 176.1 (s), 134.3 (d), 134.3 (s), 129.0 (d, 2 C), 128.8 (d, 2 C), 78.2 (d), 26.8 (t), 24.9 (t) ppm.

