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A tandem Baylis–Hillman-singlet oxygen oxidation reaction for facile synthesis of γ-substituted γ-hydroxybutenolides

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ABSTRACT

A series of highly functionalised γ-hydroxyacryl γ-hydroxybutenolides, **2**, were synthesised in 25–50% overall yields in two or three steps from 2-furfural using a tandem Baylis–Hillman-singlet oxygen oxidation reaction.

1. Introduction

The γ-substituted γ-hydroxybutenolide core is a common motif in terpenoid natural products. Some novel examples only recently discovered are shown in Figure 1. Many of these natural products exhibit potent biological activities and serve as interesting leads in drug discovery research.[1–6]

Biogenetically, it has been suggested that these γ-hydroxybutenolide containing natural products may derive from their furanoid precursors by singlet oxygen oxidation.[4d] Recently, singlet oxygen has been used extensively in biomimetic synthesis involving furan oxidation for rapid and efficient construction of many natural products.[7] We have also pursued a singlet oxygen based strategy of efficiently converting functionalised furans derived from 3-furfural and simple acrylates to α- or β-substituted γ-hydroxybutenolides.[8] Herein we report the extension of this tandem Baylis–Hillman-singlet oxygen oxidation strategy to rapidly convert 2-furfural to highly functionalised γ-substituted γ-hydroxybutenolide synthons, **2** (Scheme 1). Currently there are few diversity-oriented methods that can rapidly access highly functionalised γ-substituted γ-hydroxybutenolides from singlet oxygen oxidation of furans. The highly reactive yet chemospecific nature of singlet oxygen oxidation, along with the cost-effectiveness of this class of reactions, was envisioned to enhance the generality of this biomimetic approach and also provide highly functionalised new γ-substituted γ-hydroxybutenolides as useful building blocks.

2. Results and discussion

This sequence initiates with the Baylis–Hillman (BH) reaction, a versatile approach for convergent construction of functionalized molecules from simple and readily accessible starting materials such as aldehydes and enones.[9]

However, the BH reaction can be limitedT:/PGN/ELSEVIER/TET/web/00018514/ in its scope, as reflected by the moderate yields observed for many substrates. Nonetheless, this reaction is amenable to preparative scales, which compensates for the yield efficiency. Several known BH reaction conditions were investigated and optimised for yields of **1** from 2-furfural and various acrylates.[10] The most general method for this reaction was to use DBU in neat condition (Scheme 2).

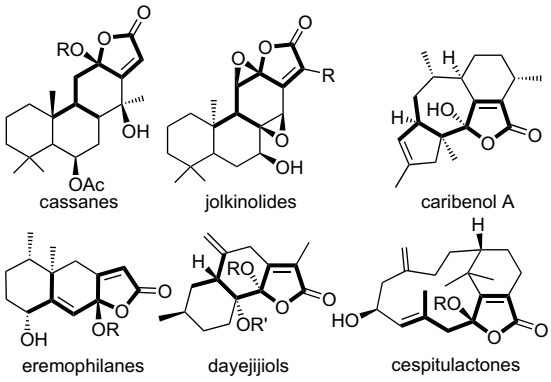

Figure 1. Examples of natural products with a γ-substituted γ-hydroxybutenolide core.

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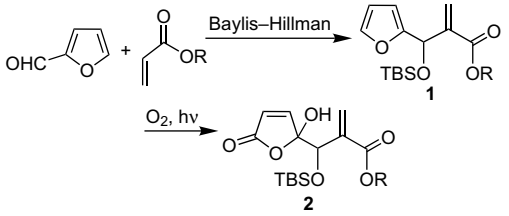
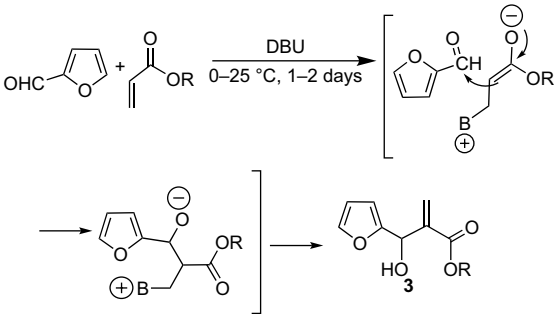
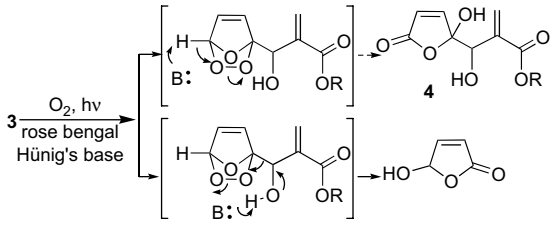


Scheme 1.



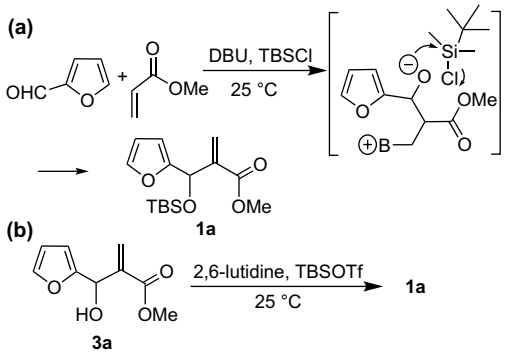
Scheme 2.

It is well known that an alkyl amine base can be used in singlet oxygen oxidation to catalyse the disproportionation of the endoperoxide intermediate (Scheme 3).[11] However, initial attempts on using the BH adducts directly in the singlet oxygen oxidation resulted only in hydroxybutenolide. The presence of a free hydroxy group led to base-promoted fragmentation of the side chain during the oxidation reaction.



Scheme 3.

To circumvent this problem, silyl protection schemes of the secondary alcohol were investigated using the BH adduct **3a** (Scheme 4).



Scheme 4.

Given the mechanism of the BH reaction, which involves an alkoxide intermediate, various silyl protecting groups were first examined for in situ trapping of the alkoxide intermediate. While TMSCl was able to furnish silyl protected BH adducts, the TMS group was too labile for the subsequent singlet oxygen oxidation reaction, and as such the reaction only resulted in complex reaction mixtures. TBSCl was also able to protect the hydroxy group. With in situ trapping of the alkoxide intermediate, this provided **1a** in 36% yield from 2-furfural over two steps in one-pot (Scheme 4a). The hydroxy group could also be protected separately using TBSOTf after the BH reaction for a better yield of 50% over two steps (Scheme 4b). The yields of these two approaches to **1** with various acrylates are summarised in Table 1. For smaller ester substituents, the two-step sequence provided slightly higher yields (entries a & b). However, for larger ester substituents, the much simpler one-pot procedure gave comparable yields.

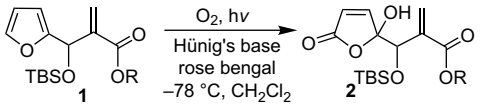
The TBS protected series of functionalised furans was then subjected to singlet oxygen oxidation. Reactions generally proceeded in very good to excellent yields for all substrates (Table 2).

Hünig's base was essential to the formation of butenolides as its absence resulted in complex mixtures. The rate of this conversion, compared to that of the series from 3-furfural under similar conditions,[8a] was slower, but still complete within a few hours. The resulting diastereomeric mixtures of butenolides were in 2:1 ratio. Given the lability of the stereocenter at the acetal carbon, this may be inherently related to the relative stability of the two diastereomeric butenolides. The TBS protection was readily removed under acidic, basic or neutral conditions but the resulting butenolides decomposed rapidly. However, the TBS protected γ-substituted γ-hydroxybutenolides themselves are stable without any sign of intramolecular

Table 1
Preparation of **1** from 2-furfural

Entry	Acrylate	**3a–g** (%)	**1a–g** (from **3**) (%)	**1a–g** (one-pot) (%)
a	Methyl	52	98	36
b	Ethyl	55	97	38
c	Butyl	47	96	43
d	Dodecyl	36	94	31
e	Benzyl	49	86	42
f	Cinnamyl	44	98	40
g	Allyl	33	93	33
h	Chloroethyl	51	84	44

Table 2
Preparation of **2** by singlet oxygen oxidation of **1**



Entry	R	**2a–g** (%)
a	Methyl	88
b	Ethyl	91
c	Butyl	90
d	Dodecyl	78
e	Benzyl	80
f	Cinnamyl	87
g	Allyl	82
h	Chloroethyl	78

cyclisation, even with a free γ-hydroxy group in close proximity to an enone ester.

3. Conclusions

In summary, this sequence allows for the first time the facile synthesis of highly funtionalised γ-hydroxyl acryl γ-hydroxybutenolides from readily available starting materials in two or three steps. These diverse butenolides may be used as building blocks for natural products with a butenolide core, as well as useful synthons for butenolide-based diversity-oriented libraries.

4. Experimental

4.1. General

Unless otherwise stated, all chemicals and reagents were used without further purification. All reactions were performed under a nitrogen atmosphere and monitored by thin-layer chromatography (TLC) using silica gel 60 F_{254} on aluminium pre-coated plates (0.25 mm). Visualisation was accomplished using either a UV lamp (254 nm) or heating with basic $KMnO_4$ solution. Flash column chromatography was performed on silica gel (60 Å, 40–63 μm, 230–400 mesh). ^{1}H NMR spectra were recorded on Bruker DPX400 (400 MHz) and DPX600 (600 MHz) spectrometers and are reported in parts per million using the specified solvent as internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker DPX400 (101 MHz) spectrometer and reported in parts per million using the specified solvent as internal standard ($CDCl_3$ at 77.5 ppm). Infrared spectra were recorded on a Perkin–Elmer PE1000 FTIR spectrometer. HRMS was performed at the mass spectrometry laboratory of the University of Illinois at Urbana–Champaign.

4.2. General procedure for the preparation of Baylis–Hillman adducts 2

DBU (3.12 mmol) was added to a stirred solution of an acrylate (3.75 mmol) and 2-furfural (3.12 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1–2 days. Upon completion, ethyl acetate (15 mL) was added to the reaction and neutralised with 1 N HCl, followed by washing with water and brine. The organic layer thus obtained was dried over $NaSO_4$, filtered and concentrated to provide a crude mixture, which was further purified by column chromatography (petroleum ether/ethyl acetate 2:1) to afford the Baylis–Hillman adduct as a colourless oil.

4.2.1. Methyl-2-(furan-2-yl(hydroxy)methyl)acrylate (**3a**)[10d]

Colourless oil. Yield: 52%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3490 (br), 2953 (w), 1719 (s), 1632 (w), 1441 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (d, J=6.8 Hz, 1H, –OH), 3.77 (s, 3H, $-OCH_3$), 5.59 (d, J=6.8 Hz, 1H, H-1′), 5.94 (m, 1H, H-3), 6.26 (ddd, J=3.2, 0.8, 0.8 Hz, 1H, H-3″), 6.33 (dd, J=3.2, 1.8 Hz, 1H, H-4″), 6.38 (s, 1H, H-3), 7.37 (dd, J=1.8, 0.9 Hz, 1H, H-5″); HRMS (ESI) m/z calcd for $C_9H_{10}O_4Na$ $[M+Na]^+$, 205.0468, found 205.0468.

4.2.2. Ethyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3b**)

Colourless oil. Yield: 55%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3456 (br), 2953 (w), 1711 (s), 1634 (w), 1438 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, J=7.1 Hz, 3H, $-CH_3$), 3.23 (br s, 1H, –OH), 4.20 (q, J=7.1 Hz, 1H, $-OCH_2-$), 5.57 (s, 1H, H-1′), 5.92 (s, 1H, H-3), 6.24 (d, J=3.1 Hz, 1H, H-3″), 6.31–6.32 (m, 1H, H-4″), 6.37 (s, 1H, H-3), 7.39–7.41 (m, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 61.5, 67.9, 107.6, 110.9, 127.0, 140.2, 142.7, 154.7, 166.5; HRMS (ESI) m/z calcd for $C_{10}H_{12}O_4Na$ $[M+Na]^+$, 219.0633, found 219.0626.

4.2.3. Butyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3c**)

Colourless oil. Yield: 47%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3472 (br), 2962 (m), 2935 (m), 2873 (m), 1711 (s), 1632 (m), 1463 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J=7.4 Hz, 3H, $-CH_3$), 1.25–1.41 (m, 2H, CH_2CH_3), 1.54–1.66 (m, 2H, $-OCH_2CH_2-$), 3.09 (br s, 1H, –OH), 4.16 (td, J=6.6, 2.2 Hz, 2H, $-OCH_2-$), 5.58 (s, 1H, H-1′), 5.91 (s, 1H, H-3), 6.26 (d, J=3.2 Hz, 1H, H-3″), 6.32–6.33 (m, 1H, H-4″), 6.38 (s, 1H, H-3), 7.37 (dd, J=1.8, 0.7 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 19.6, 31.0, 65.4, 68.1, 107.6, 110.9, 127.0, 140.2, 142.8, 154.7, 166.6; HRMS (ESI) m/z calcd for $C_{12}H_{16}O_4Na$ $[M+Na]^+$, 247.0946, found 247.0948.

4.2.4. Dodecyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3d**)

Colourless oil. Yield: 36%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3472 (br), 2927 (vs), 2854 (s), 1711 (s), 1632 (w), 1463 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 3H, $-CH_3$), 1.27 (br s, 18H, $-(CH_2)_9CH_3$), 1.54–1.67 (m, 2H, $-OCH_2CH_2-$), 2.59 (br s, 1H, –OH), 4.10–4.18 (m, 2H, $-OCH_2-$), 5.58 (s, 1H, H-1′), 5.92 (s, 1H, H-3), 6.26 (d, J=3.2 Hz, 1H, H-3″), 6.33 (dd, J=3.1, 1.8 Hz, 1H, H-4″), 6.68 (s, 1H, H-3), 7.37 (dd, J=1.8, 0.9 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.6, 23.2, 26.4, 28.9, 29.7, 29.8, 29.9, 30.0, 30.1, 30.1, 32.4, 65.7, 68.1, 107.6, 110.9, 127.0, 140.1, 142.8, 154.7, 166.6; HRMS (ESI) m/z calcd for $C_{20}H_{32}O_4Na$ $[M+Na]^+$, 359.2198, found 359.2201.

4.2.5. Benzyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3e**)

Colourless oil. Yield: 49%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3465 (br), 1718 (s), 1632 (w), 1454 (w), 1383 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (br s, 1H, –OH), 5.19 (m, 2H, $PhCH_2-$), 5.62 (s, 1H, H-1′), 5.98 (s, 1H, H-3), 6.23–6.25 (m, 1H, H-3″), 6.31–6.34 (m, 1H, H-4″), 6.44 (s, 1H, H-3), 7.20–7.40 (m, 6H, Ar-H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 67.1, 67.6, 107.7, 110.9, 127.4, 128.1, 128.5, 128.7, 129.0, 135.9, 142.8, 154.6, 166.2; HRMS (ESI) m/z calcd for $C_{15}H_{14}O_4Na$ $[M+Na]^+$, 281.0790, found 281.0778.

4.2.6. Cinnamyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3f**)

Colourless oil. Yield: 44%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3468 (br), 1715 (s), 1633 (w), 1496 (w), 1450 (w), 1386 (m), 966 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (br s, 1H, –OH), 4.83 (d, J=6.6 Hz, 2H, $-OCH_2-$), 5.63 (s, 1H, H-1′), 5.98 (s, 1H, H-3), 6.23–6.29 (m, 2H, H-3″, PhCH=C*H*–), 6.34 (dd, J=3.1, 1.7 Hz, 1H, H-4″), 6.45 (s, 1H, H-3), 6.63 (d, J=16.1 Hz, 1H, Ph*CH*=CH–), 7.25–7.40 (m, 6H, Ar-H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 66.0, 67.9, 107.7, 110.9, 123.1, 127.1, 127.4, 128.6, 129.1, 134.9, 136.5, 140.0, 142.8, 154.6, 166.2; HRMS (ESI) m/z calcd for $C_{17}H_{16}O_4Na$ $[M+Na]^+$, 307.0936, found 307.0934.

4.2.7. Allyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3g**)

Colourless oil. Yield: 33%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3438 (br), 1717 (s), 1631 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (d, 1H, J=6.7 Hz, –OH), 4.66 (d, J=5.5 Hz, 2H, $-OCH_2-$), 5.20–5.34 (m, 2H, $-CH=CH_2$), 5.60 (d, 1H, J=6.6 Hz, H-1′), 5.85–5.90 (m, 1H, $-CH=CH_2$), 5.95 (s, 1H, H-3), 6.27 (d, J=3.3 Hz, 1H, H-3″), 6.34 (dd, J=3.3, 1.8 Hz, 1H, H-4″), 6.43 (s, 1H, H-3), 7.37 (dd, J=1.8, 0.9 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 66.0, 67.9, 107.7, 110.9, 118.9, 127.4, 132.2, 139.9, 142.9, 154.6, 166.1; HRMS (ESI) m/z calcd for $C_{11}H_{12}O_4Na$ $[M+Na]^+$, 231.0633, found 231.0623.

4.2.8. 2-Chloroethyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**3h**)

Colourless oil. Yield: 51%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3488 (br), 1720 (s), 1632 (w), 1393 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (d, J=6.6 Hz, 1H, –OH), 3.68 (t, J=5.7 Hz, 2H, $-CH_2Cl$), 4.41 (t, J=5.7 Hz, 1H, $-OCH_2-$), 5.61 (d, J=6.4 Hz, 1H, H-1′), 6.01 (s, 1H, H-3), 6.28 (s, 1H, H-3″), 6.34 (dd, J=3.3, 1.8 Hz, 1H, H-4″), 6.47 (s, 1H, H-3), 7.37–7.39 (m, 2H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ 41.8, 64.8, 67.5, 107.7, 110.9, 127.9, 139.6, 142.9, 154.4, 165.9; MS (ESI) m/z

(% relative intensity): 253.0 (100), 255.0 (33); HRMS (ESI) *m*/*z* calcd for $C_{10}H_{11}O_4^{35}ClNa$ $[M+Na]^+$, 253.0244, found 253.0237.

4.3. General procedure for the preparation of silyl protected Baylis–Hillman adducts 1

TBS(OTf) (2.0 mmol) was added to a stirred solution of Baylis–Hillman adduct (1.0 mmol) and 2,6-lutidine (2.0 mmol) in anhydrous CH_2Cl_2 (100 μL) at 0 °C. The reaction mixture was allowed to warm to room temperature and monitored by TLC for disappearance of starting material. Reactions were generally complete after 45 min. On completion, the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate 9:1) to afford the product as a colourless oil.

*4.3.1. Methyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1a**)*

Colourless oil. Yield: 98%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2954 (s), 2932 (s), 2890 (m), 2857 (m), 1719 (s), 1633 (m); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.89 (s, 9H, –$C(CH_3)_3$), 3.71 (s, 3H, –OCH_3), 5.67 (s, 1H, H-1′), 6.13–6.15 (m, 2H, H-3″, H-3), 6.27–6.29 (m, 1H, H-4″), 6.38 (s, 1H, H-3), 7.32–7.34 (m, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 18.7, 26.2, 52.3, 66.6, 107.5, 110.7, 125.9, 141.3, 142.4, 155.3, 166.6; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{24}O_4SiNa$ $[M+Na]^+$, 319.1342, found 319.1344.

*4.3.2. Ethyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1b**)*

Colourless oil. Yield: 97%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2958 (s), 2932 (s), 2859 (m), 1713 (s), 1633 (m), 1466 (m); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.89 (s, 9H, –$C(CH_3)_3$), 1.23 (t, *J*=7.1 Hz, 3H, –CH_2CH_3), 4.23–4.09 (m, 2H, –OCH_2–), 5.67 (s, 1H, H-1′), 6.13 (t, *J*=1.7 Hz, 1H, H-3), 6.14 (d, *J*=3.3 Hz, 1H, H-3″), 6.28 (dd, *J*=3.3, 1.8 Hz, 1H, H-4″), 6.37 (t, *J*=1.6 Hz, 1H, H-3), 7.33 (dd, *J*=1.8, 0.9 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 14.6, 18.7, 26.2, 61.1, 66.6, 107.4, 110.7, 125.6, 141.6, 142.3, 155.5, 166.1; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{27}O_4Si$ $[M+H]^+$, 333.1679, found 311.1678.

*4.3.3. Butyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1c**)*

Colourless oil. Yield: 96%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2959 (s), 2933 (s), 2860 (m), 1717 (s), 1635 (m), 1466 (m); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.90–0.92 (m, 12H, –$C(CH_3)_3$, –CH_2CH_3), 1.28–1.34 (m, 2H, –CH_2CH_3), 1.55–1.59 (m, 2H, –OCH_2CH_2–), 4.04–4.16 (m, 2H, –OCH_2–), 5.67 (s, 1H, H-1′), 6.12–6.13 (m, 2H, H-3, H-3″), 6.27 (dd, *J*=3.2, 1.9 Hz, 1H, H-4″), 6.37 (t, *J*=1.4 Hz, 1H, H-3), 7.32 (dd, *J*=1.8, 0.7 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 14.1, 18.7, 19.6, 26.2, 31.0, 65.0, 66.7, 107.4, 110.7, 125.6, 141.6, 142.3, 155.5, 166.3; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{30}O_4SiNa$ $[M+Na]^+$, 361.1811, found 361.1819.

*4.3.4. Dodecyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1d**)*

Colourless oil. Yield: 94%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2927 (s), 2855 (s), 1717 (s), 1636 (w), 1464 (m); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.86–0.89 (m, 12H, –$C(CH_3)_3$, –CH_2CH_3), 1.25–1.30 (m, 18H, –$(CH_2)_9CH_3$), 1.55–1.59 (m, 2H, –OCH_2CH_2–), 4.06 (dt, *J*=10.8, 6.6 Hz, 1H, –OCH_2–), 4.12 (dt, *J*=10.8, 6.6 Hz, 1H, –OCH_2–), 5.66 (s, 1H, H-1′), 6.12–6.15 (m, 2H, H-3, H-3″), 6.28 (dd, *J*=3.1, 1.8 Hz, 1H, H-4″), 6.38 (t, *J*=1.4 Hz, 1H, H-3), 7.32–7.34 (m, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 14.6, 18.8, 23.2, 26.2, 26.3, 29.0, 29.7, 30.0, 30.05, 30.13, 30.15, 30.2, 32.4, 65.3, 66.6, 107.4, 110.7, 125.7, 141.6, 142.3, 155.5, 166.3; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{47}O_4Si$ $[M+H]^+$, 451.3244, found 451.3244.

*4.3.5. Benzyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1e**)*

Colourless oil. Yield: 86%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2954 (m), 2931 (m), 2890 (m), 2857 (m), 1717 (s), 1633 (w), 1461 (w), 1386 (w); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.89 (s, 9H, –$C(CH_3)_3$), 5.10 (d, *J*=12.6 Hz, 1H, PhCH_2–), 5.21 (d, *J*=13.1 Hz, 1H, PhCH_2–), 5.70 (s, 1H, H-1′), 6.13–6.15 (m, 1H, H-3″), 6.17–6.19 (m, 1H, H-3), 6.27–6.29 (m, 1H, H-4″), 6.43–6.45 (m, 1H, H-3), 7.20–7.37 (m, 6H, H-5″, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 18.7, 26.2, 66.7, 66.8, 107.6, 110.8, 126.2, 128.4, 128.6, 129.0, 136.3, 141.3, 142.4, 155.3, 166.0; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{28}O_4NaSi$ $[M+Na]^+$, 395.1757, found 395.1757.

*4.3.6. Cinnamyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1f**)*

Colourless oil. Yield: 98%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2953 (s), 2931 (s), 2888 (s), 2857 (s), 1721 (s), 1635 (m), 1496 (m), 1465 (m), 963 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3H, –$SiCH_3$), 0.14 (s, 3H, –$SiCH_3$), 0.92 (s, 9H, –$C(CH_3)_3$), 4.74 (ddd, *J*=13.0, 6.2, 1.3 Hz, 1H, –OCH_2–), 4.84 (ddd, *J*=13.0, 6.2, 1.3 Hz, 1H, –OCH_2–), 5.74 (s, 1H, H-1′), 6.18–6.32 (m, 4H, H-3, H-3″, H-4″, PhCH=C*H*–), 6.40 (t, *J*=1.4 Hz, 1H, H-3), 6.60 (d, *J*=15.8 Hz, 1H, Ph*CH*=CH_2–), 7.24–7.40 (m, 6H, H-5″, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 18.7, 26.2, 65.6, 66.6, 107.6, 110.7, 123.4, 126.1, 127.0, 128.5, 129.0, 134.4, 136.7, 141.3, 142.4, 155.3, 165.8; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{30}O_4SiNa$ $[M+Na]^+$, 421.1811, found 421.1805.

*4.3.7. Allyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1g**)*

Colourless oil. Yield: 93%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2954 (s), 2930 (s), 2886 (s), 1715 (s), 1630 (w); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.86 (s, 9H, –$C(CH_3)_3$–), 4.53–4.69 (m, 2H, –OCH_2–), 5.15–5.29 (m, 2H, –CH=CH_2), 5.68 (m, 1H, H-1′), 5.82–5.92 (m, 1H, –*CH*=CH_2), 6.15 (d, *J*=3.2 Hz, 1H, H-3″), 6.17 (dd, *J*=1.6, 1.6 Hz, 1H, H-3), 6.28 (dd, *J*=3.2, 1.8 Hz, 1H, H-4″), 6.42 (dd, *J*=1.4, 1.4 Hz, 1H, H-3), 7.34 (dd, *J*=1.8, 0.9 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 18.7, 26.2, 65.7, 66.6, 107.6, 110.7, 118.5, 126.1, 132.4, 141.3, 142.4, 155.3, 165.8; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{26}O_4SiNa$ $[M+Na]^+$, 345.1498, found 345.1499.

*4.3.8. 2-Chloroethyl 2-((tert-butyldimethylsilyloxy)(furan-2-yl)methyl)acrylate (**1h**)*

Colourless oil. Yield: 84%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2954 (m), 2932 (m), 2889 (m), 2858 (m), 1717 (s), 1635 (w), 1466 (m); ^1H NMR (400 MHz, $CDCl_3$) δ −0.02 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.89 (s, 9H, –$C(CH_3)_3$), 3.64 (t, *J*=5.8 Hz, 2H, –CH_2Cl), 4.27–4.43 (m, 2H, –OCH_2–), 5.67 (s, 1H, H-1′), 6.16 (d, *J*=3.3 Hz, 1H, H-3″), 6.21 (s, 1H, H-3), 6.29 (dd, *J*=3.3, 1.8 Hz, 1H, H-4″), 6.45 (s, 1H, H-3), 7.34 (dd, *J*=1.8, 0.9 Hz, 1H, H-5″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.7, 26.2, 30.2, 41.8, 64.6, 66.6, 107.6, 110.8, 126.8, 140.9, 142.5, 155.2, 165.7; MS (ESI) *m*/*z* (% relative intensity): 345.1 (100), 347.1 (32); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{25}^{35}ClO_4SiH$ $[M+H]^+$, 345.1289, found 345.1287.

4.4. General procedure for the preparation of butenolides 2

To a mixture of a Baylis–Hillman adduct (0.30 mmol) and rose bengal (0.003 mmol) in methanol or CH_2Cl_2 (70 mL) was added Hünig's base (0.36 mmol). The reaction mixture was then exposed to singlet oxygen (generated from air with a 150 W flood light) at −78 °C. The reaction mixture was then monitored for disappearance of starting material by TLC. Upon completion, solvent was evaporated under vacuum at room temperature, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 1:1) to afford the butenolide product as a 2:1 diastereomeric mixture.

*4.4.1. Methyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2a**)*

Colourless oil. Yield: 88%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2954 (s), 2933 (s), 2856 (s), 1764 (s), 1721 (s); major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H, $-SiCH_3$), 0.10 (s, 3H, $-SiCH_3$), 0.86 (s, 9H, $-C(CH_3)_3$), 3.82 (s, 3H, $-OCH_3$), 4.89 (s, 1H, H-1′), 5.27 (br s, 1H, –OH), 6.11 (br s, 1H, H-3), 6.14 (br s, 1H, H-3″), 6.50 (br s, 1H, H-3), 7.09 (d, J=5.1 Hz, 1H, H-4″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9, −4.5, 18.5, 26.1, 53.2, 72.7, 107.9, 125.6, 130.2, 138.9, 151.2, 167.6, 170.6; minor diastereomer: ^1H NMR δ 0.04 (s, 3H, $-SiCH_3$), 0.15 (s, 3H, $-SiCH_3$), 0.89 (s, 9H, $-C(CH_3)_3$), 3.80 (s, 3H, $-OCH_3$), 4.83 (s, 1H, H-1′), 5.27 (br s, 1H, –OH), 6.11 (br s, 1H, H-3), 6.13 (br s, 1H, H-3″), 6.50 (br s, 1H, H-3), 6.93 (d, J=5.1 Hz, 1H, H-4″); ^{13}C NMR δ −4.6, −4.4, 18.6, 26.1, 53.0, 73.0, 107.5, 125.1, 130.7, 138.5, 152.1, 167.6, 170.5; HRMS (ESI) m/z calcd for $C_{15}H_{24}O_6SiNa$ $[M+Na]^+$, 351.1240, found 351.1241.

*4.4.2. Ethyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2b**)*

Colourless oil. Yield: 91%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2958 (s), 2935 (s), 2854 (s), 1762 (s), 1711 (s); major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H, $-SiCH_3$), 0.10 (s, 3H, $-SiCH_3$), 0.87 (s, 9H, $-C(CH_3)_3$), 1.34 (t, J=7.2 Hz, 3H, $-CH_3$), 4.24–4.29 (m, 2H, $-OCH_2-$), 4.87 (d, J=1.1 Hz, 1H, H-1′), 5.37 (br s, 1H, –OH), 6.09 (t, J=1.2 Hz, 1H, H-3), 6.12–6.15 (m, 1H, H-3″), 6.49 (d, J=1.1 Hz, 1H, H-3), 7.09 (d, J=6.8 Hz, 1H, H-4″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9, −4.5, 14.55, 18.5, 26.1, 62.5, 72.8, 107.9, 125.6, 129.9, 139.2, 151.3, 168.4, 170.5; minor diastereomer: ^1H NMR δ 0.05 (s, 3H, $-SiCH_3$), 0.15 (s, 3H, $-SiCH_3$), 0.90 (s, 9H, $-C(CH_3)$), 1.32 (t, J=7.4 Hz, 3H, $-CH_3$), 4.24–4.29 (m, 2H, $-OCH_2-$), 4.82 (d, J=1.1 Hz, 1H, H-1′), 5.31 (br s, 1H, –OH), 6.12–6.15 (m, 2H, H-3, H-3″), 6.51 (d, J=1.1 Hz, 1H, H-3), 6.93 (d, J=5.7 Hz, 1H, H-4″); ^{13}C NMR δ −4.6, −4.4, 14.58, 18.6, 26.1, 62.2, 73.0, 107.5, 125.0, 130.5, 138.8, 152.2, 167.3, 170.6; HRMS (ESI) m/z calcd for $C_{16}H_{27}O_6Si$ $[M+H]^+$, 343.1577, found 343.1574.

*4.4.3. Butyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2c**)*

Colourless oil. Yield: 90%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2958 (s), 2931 (s), 1764 (s), 1708 (s); major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H, $-SiCH_3$), 0.10 (s, 3H, $-SiCH_3$), 0.86 (s, 9H, $-C(CH_3)_3$), 0.96 (t, J=7.3 Hz, 3H, $-CH_2CH_3$), 1.34–1.48 (m, 2H, $-CH_2CH_3$), 1.61–1.73 (m, 2H, $-OCH_2CH_2-$), 4.14–4.24 (m, 2H, $-OCH_2-$), 4.87 (s, 1H, H-1′), 5.41 (br s, 1H, –OH), 6.08 (br s, 1H, H-3), 6.10–6.14 (m, 1H, H-3″), 6.48 (d, J=0.9 Hz, 1H, H-3), 7.09 (d, J=5.6 Hz, 1H, H-4″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9, −4.5, 14.2, 18.5, 19.6, 26.07, 31.0, 66.3, 72.85, 107.9, 125.5, 129.8, 139.2, 151.3, 168.4, 170.6; minor diastereomer: ^1H NMR δ 0.05 (s, 3H, $-SiCH_3$), 0.15 (s, 3H, $-SiCH_3$), 0.90 (s, 9H, $-C(CH_3)_3$), 0.95 (t, J=7.3 Hz, 3H, $-CH_2CH_3$), 1.34–1.48 (m, 2H, $-CH_2CH_3$), 1.61–1.73 (m, 2H, $-OCH_2CH_2-$), 4.14–4.24 (m, 2H, $-OCH_2-$), 4.82 (s, 1H, H-1′), 5.34 (br s, 1H, –OH), 6.06–6.14 (m, 2H, H-3, H-3″), 6.51 (d, J=0.7 Hz, 1H, H-3), 6.93 (d, J=5.6 Hz, 1H, H-4″); ^{13}C NMR δ −4.6, −4.4, 14.2, 18.6, 19.6, 26.12, 31.0, 66.0, 72.94, 107.5, 125.0, 130.5, 138.8, 152.2, 167.4, 170.5; HRMS (ESI) m/z calcd for $C_{18}H_{31}O_6Si$ $[M+H]^+$, 371.1890, found 371.1898.

*4.4.4. Dodecyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2d**)*

Colourless oil. Yield: 78%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2928 (vs), 2856 (s), 1772 (s), 1705 (m), 1462 (m), 1103 (s), 1080 (s); major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 0.0 (s, 3H, $-SiCH_3$), 0.10 (s, 3H, $-SiCH_3$), 0.87 (s, 9H, $-C(CH_3)_3$), 0.88 (m, 3H, $-(CH_2)_9CH_3$), 1.19–1.43 (m, 18H, $-(CH_2)_9CH_3$), 1.63–1.75 (m, 2H, $-OCH_2CH_2-$), 4.15–4.24 (m, 2H, $-OCH_2-$), 4.87 (d, J=0.7 Hz, 1H, H-1′), 5.41 (br s, 1H, –OH), 6.08 (m, 1H, H-3), 6.11–6.15 (m, 1H, H-3″), 6.48 (d, J=1.1 Hz, 1H, H-3), 7.09 (d, J=5.7 Hz, 1H, H-4″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9, −4.5, 14.6, 18.5, 23.2, 26.07, 26.37, 28.9, 29.7, 29.8, 29.99, 30.04, 30.1 (br), 32.4, 66.6, 72.8, 107.9, 125.6, 129.9, 139.2, 151.2, 168.4, 170.6; minor diastereomer: ^1H NMR δ 0.05 (s, 3H, $-SiCH_3$), 0.15 (s, 3H, $-SiCH_3$), 0.88 (m, 3H, $-(CH_2)_9CH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.19–1.43 (m, 18H, $-(CH_2)_9CH_3$), 1.63–1.75 (m, 2H, $-OCH_2CH_2-$), 4.15–4.24 (m, 2H, $-OCH_2-$), 4.81 (d, J=0.7 Hz, 1H, H-1′), 5.33 (br s, 1H, –OH), 6.11–6.15 (m, 2H, H-3, H-3′), 6.51 (d, J=1.2 Hz, 1H, H-3), 6.93 (d, J=5.7 Hz, 1H, H-4″); ^{13}C NMR δ −4.6, −4.4, 14.6, 18.6, 23.2, 26.12, 26.39, 28.98, 29.7, 29.8, 29.99, 30.04, 30.1 (br), 32.4, 66.3, 72.9, 107.5, 125.0, 130.5, 138.8, 152.2, 167.4, 170.5; HRMS (ESI) m/z calcd for $C_{26}H_{47}O_6Si$ $[M+H]^+$, 483.3142, found 483.3139.

*4.4.5. Benzyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2e**)*

Colourless oil. Yield: 80%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2955 (m), 2932 (m), 2890 (m), 2859 (m), 1775 (s), 1711 (s), 1629 (w), 1461 (w), 1391 (m), 1100 (s), 1082 (s); major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ −0.01 (s, 3H, $-SiCH_3$), 0.10 (s, 3H, $-SiCH_3$), 0.86 (s, 9H, $-C(CH_3)_3$), 4.91 (s, 1H, H-1′), 5.25 (s, 2H, $PhCH_2-$), 6.07 (d, J=5.7 Hz, 1H, H-3″), 6.11 (m, 1H, H-3), 6.53 (s, 1H, H-3), 7.06 (d, J=5.7 Hz, 1H, H-4″), 7.31–7.42 (m, 5H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.5 (br), 18.5 (br), 26.1 (br), 68.0, 72.9, 107.8, 125.5, 128.8 (br), 129.2, 130.3, 135.6 (br), 139.0, 151.2, 167.9, 170.5; minor diastereomer: ^1H NMR δ 0.04 (s, 3H, $-SiCH_3$), 0.15 (s, 3H, $-SiCH_3$), 0.90 (s, 9H, $-C(CH_3)_3$), 4.85 (s, 1H, H-1′), 5.23 (s, 2H, $PhCH_2-$), 6.01 (d, J=5.6 Hz, 1H, H-3″), 6.14 (m, 1H, H-3), 6.55 (m, 1H, H-3), 6.83 (d, J=5.6 Hz, 1H, H-4″), 7.31–7.42 (m, 5H, Ar–H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9 (br), 18.5 (br), 26.1 (br), 67.8, 73.0, 107.5, 125.1, 128.8 (br), 129.1, 130.7, 135.6 (br), 138.7, 152.0, 166.8, 170.5; HRMS (ESI) m/z calcd for $C_{21}H_{29}O_6Si$ $[M+H]^+$, 405.1733, found 405.1735.

*4.4.6. Cinnamyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2f**)*

Colourless oil. Yield: 87%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 3365 (br), 2955 (m), 2932 (m), 2889 (m), 2858 (m), 1771 (s), 1712 (s), 1628 (w), 1466 (m), 1097 (s), 967 (m), 840 (s); major diastereomer: ^1H NMR (600 MHz, $CDCl_3$) δ 0.02 (br s, 3H, $-SiCH_3$), 0.12 (br s, 3H, $-SiCH_3$), 0.87 (br s, 9H, $-C(CH_3)_3$), 4.86 (d, J=6.3 Hz, 2H, $-OCH_2-$), 4.91 (br s, 1H, H-1′), 5.36 (br s, 1H, –OH), 6.06–6.18 (m, 2H, H-3, H-3″), 6.30 (dt, J=15.8, 6.6 Hz, 1H, PhCH=C*H*–), 6.56 (s, 1H, H-3), 6.69 (d, J=15.7 Hz, 1H, Ph*CH*=CH–), 7.10 (br s, 1H, H-4″), 7.27–7.43 (m, 5H, Ar–H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.5 (br), 18.4 (br), 26.0 (br), 66.8, 72.6, 108.0, 122.6, 125.5, 127.1, 128.8, 129.1, 130.0 (br), 135.5, 139.2, 151.3, 167.9, 170.6 (br); minor diastereomer: ^1H NMR δ 0.02 (br s, 3H, $-SiCH_3$), 0.12 (br s, 3H, $-SiCH_3$), 0.88 (br s, 9H, $-C(CH_3)_3$), 4.86 (d, 2H, J=6.3 Hz, $-OCH_2-$), 4.91 (br s, 1H, H-1′), 5.36 (br s, 1H, –OH), 6.06–6.18 (m, 2H, H-3, H-3″), 6.30 (dt, J=15.8, 6.6 Hz, 1H, PhCH=C*H*–), 6.56 (s, 1H, H-3), 6.69 (d, J=15.7 Hz, 1H, Ph*CH*=CH–), 6.94 (br s, 1H, H-4″), 7.27–7.43 (m, 5H, Ar–H); ^{13}C NMR δ −5.0 (br), 18.4 (br), 26.0 (br), 66.6, 72.8, 107.6, 122.6, 125.0, 127.1, 128.8, 129.1, 130.6 (br), 136.3, 138.7, 152.2, 166.9, 170.6; HRMS (ESI) m/z calcd for $C_{23}H_{30}O_6SiNa$ $[M+Na]^+$, 453.1709, found 453.1707.

*4.4.7. Allyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2g**)*

Colourless oil. Yield: 78%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2956 (m), 2932 (m), 2891 (m), 2858 (m), 1773 (s), 1711 (s), 1630 (w), 1463 (m), 1389 (s), 1100 (s), 840 (s); major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H, $-SiCH_3$), 0.11 (s, 3H, $-SiCH_3$), 0.86 (s, 9H, $-C(CH_3)_3$), 4.67–4.73 (m, 2H, $-OCH_2-$), 4.90 (d, 1H, J=0.9 Hz, H-1′), 5.18 (br s, 1H, –OH), 5.26–5.39 (m,

2H, –CHg=CH_2), 5.88–6.02 (m, 1H, –CH=CH_2), 6.11–6.13 (m, 2H, H-3, H-3″), 6.54 (d, J=1.1 Hz, 1H, H-3), 7.09 (d, J=5.7 Hz, 1H, H-4″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9, −4.5, 18.5, 26.1, 66.8, 72.8, 107.8, 119.6, 125.6, 130.3, 131.8, 139.0, 151.2, 167.8, 170.6; minor diastereomer: ^{1}H NMR δ 0.05 (s, 3H, –$SiCH_3$), 0.16 (s, 3H, –$SiCH_3$), 0.90 (s, 9H, –C(CH_3)$_3$), 4.67–4.73 (m, 2H, –OCH_2–), 4.83 (d, J=0.9 Hz, 1H, H-1′), 5.18 (br s, 1H, –OH), 5.27–5.39 (m, 2H, –CH=CH_2), 5.88–6.02 (m, 1H, –CH=CH_2), 6.13–6.16 (m, 2H, H-3, H-3′), 6.55 (d, J=0.9 Hz, 1H, H-3), 6.92 (d, J=5.7 Hz, 1H); ^{13}C NMR δ −4.6, −4.4, 18.6, 26.1, 66.6, 73.0, 107.5, 119.5, 125.1, 130.8, 131.9, 138.6, 152.1, 166.8, 170.5; HRMS (ESI) m/z calcd for $C_{17}H_{27}O_6Si$ $[M+H]^+$, 355.1577, found 355.1575.

4.4.8. Chloroethyl 2-((tert-butyldimethylsilyloxy)(2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl)acrylate (**2h**)

Colourless oil. Yield: 82%; IR ($CHCl_3$/NaCl) ν_{max} (cm^{-1}): 2957 (m), 2859 (m), 1766 (s), 1725 (s), 1633 (w), 1395 (w), 1103 (s); major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3H, –$SiCH_3$), 0.11 (s, 3H, –$SiCH_3$), 0.87 (s, 9H, –C(CH_3)$_3$), 3.71–3.77 (m, 2H, –CH_2Cl), 4.32–4.55 (m, 2H, –OCH_2–), 4.91 (s, 1H, H-1′), 4.96 (br s, 1H, –OH), 6.13–6.18 (m, 2H, H-3, H-3″), 6.55–6.57 (m, 1H, H-3), 7.11 (d, J=5.7 Hz, 1H, H-4″); ^{13}C NMR (101 MHz, $CDCl_3$) δ −4.9, −4.5, 18.5, 26.06, 41.8, 65.5, 72.6, 107.7, 125.7, 130.8, 138.7, 151.2, 167.4, 170.5; minor diastereomer: ^{1}H NMR δ 0.06 (s, 3H, –$SiCH_3$), 0.16 (s, 3H, –$SiCH_3$), 0.91 (s, 9H, –C(CH_3)$_3$), 3.71–3.77 (m, 2H, –CH_2Cl), 4.32–4.55 (m, 2H, –OCH_2–), 4.86 (s, 1H, H-1′), 4.99 (br s, 1H, –OH), 6.13–6.18 (m, 2H, H-3, H-3″), 6.55–6.57 (m, 1H, H-3), 6.96 (d, J=5.7 Hz, 1H, H-4″); ^{13}C NMR δ −4.6, −4.4, 18.6, 26.11, 41.9, 65.3, 73.0, 107.5, 125.4, 131.1, 138.4, 151.9, 166.4, 170.4; MS (ESI) m/z (% relative intensity): 377.1 (100), 379.1 (32); HRMS (ESI) m/z calcd for $C_{16}H_{26}^{35}ClO_6Si$ $[M+H]^+$, 377.1187, found 377.1187.

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Supplementary data

Supplementary data for this article (^{1}H and ^{13}C NMR spectra of compounds **1a**–**h** and **2a**–**h**) can be found online. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.019.

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