4-*tert*-Butoxy-1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene. A New Diene and its Application to the Synthesis of γ-Alkylidenetetronic Acids

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Z. Naturforsch. **2013**, *68b*, 836 – 840 / DOI: 10.5560/ZNB.2013-3060
Received February 20, 2013

A new approach to γ-alkylidenetetronic acids is reported which is based on Me_3SiOTf-catalyzed [3 + 2] cyclization of 4-*tert*-butoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene with oxalyl chloride, orthogonal protection of the α-hydroxy group by benzylation and subsequent deprotection of the β-hydroxy group.

Key words: Butenolides, Cyclizations, *O*-Heterocycles, Oxalic Acid, Silyl Enol Ethers

Introduction

γ-Alkylidenetetronic acids occur in a number of pharmacologically relevant natural products, such as pulvinic acids [1 – 10]. These heterocycles have also been used as building blocks during the synthesis of natural products [11, 12]. γ-Alkylidenetetronic acids are available, for example, from ascorbic acid. However, the scope of this approach is limited by the fact that derivatives containing substituents located at the exocyclic double bond or at the butenolide moiety are not available [13]. An additional problem arises from the requirement to regioselectively protect the two hydroxy groups [14, 15]. Some years ago, we reported [16, 17] the synthesis of γ-alkylidenebutenolides by [3 + 2] cyclization of 1,3-bis-silyl enol ethers – electroneutral 1,3-dicarbonyl dianion equivalents [18] – with oxalyl chloride. Herein, we wish to report the application of this method to the synthesis of γ-alkylidenetetronic acids based on the synthesis of what is, to the best of our knowledge, the first *tert*-butoxy substituted 1,3-bis-silyl enol ether.

Results and Discussion

We reported earlier the synthesis of β-methoxy- and β-benzyloxy-γ-alkylidenebutenolides **5a** and **5c** from alkyl 4-chloroacetoacetates **1a**, **b** [19]. In the present study we report, for the first time, the synthesis of β-ethoxy- and β-(*tert*-butoxy)-γ-alkylidenebutenolides **5b** and **5d** (Scheme 1, Table 1): the reaction of ethyl 4-chloroacetoacetate (**1b**) with EtOH and *t*BuOH, in the presence of NaH, afforded, in analogy to the known synthesis of **2c**, the ethyl 4-alkoxyacetoacetates **2b** and **2d**, respectively. The latter were transformed, according to a known procedure [20, 21], into the novel 1,3-bis-silyl enol ethers **4b**, **d** [20, 21]. The Me_3SiOTf-catalyzed cyclization of **4b**, **d** with oxalyl chloride afforded the *Z*-configurated butenolides **5b**, **d**.

We have previously reported the synthesis of γ-alkylidenebutenolide **6**, containing two orthogonal protective groups, by [3 + 2] cyclization and subsequent protection of the free hydroxy group with benzoyl chloride (Scheme 2). The deprotection of the benzyl group by hydrogenation afforded, as reported earlier, the desired γ-alkylidenebutenolide **7**. However, the reaction is difficult to carry out, since the exocyclic double bond was, to some extent, hydrogenated to give the γ-lactone **8**. The product ratio strongly depended on the reaction conditions and, thus, tlc control was mandatory; unfortunately, the separation of **7** from **8** proved to be difficult. In addition, all attempts to remove the benzoyl group of **7** (*e. g.* by K_2CO_3/MeOH) resulted in decomposition, due to attack of the methanolate onto the exocyclic double bond and cleavage of the butenolide moiety.

Table 1. Synthesis of γ-alkylidenebutenolides.

2–5	R^1	R^2	% (2) [a]	% (3) [a]	% (4) [a]	% (5) [a]	δ (ppm) [c]
a[b]	Me	Me	70	86	91	75	5.40
b	Et	Et	60	93	83	46	5.61
c[b]	Bn	Et	32	80	72	44	5.64
d	*t*Bu	Et	49	84	92	47	5.63

[a] Yields of isolated products; [b] ref. [19]; [c] chemical shift (^{1}H NMR, $CDCl_3$) of the proton located at the exocyclic double bond.

A solution of this problem was developed based on the use of the *tert*-butyl protective group. The benzylation of butenolide **5d** afforded γ-alkylidenebutenolide **9** containing the orthogonal benzyl and *tert*-butyl protective groups (Scheme 3). Treatment of **9** with TFA resulted in selective cleavage of the *tert*-butyl ether to give the desired γ-alkylidenetetronic acid **10**. The synthesis of **10** proved to be reliable and easy to carry out. Compound **10** represents an important building block for further transformations. Treatment of **5d** with triflic anhydride resulted in cleavage of the *tert*-butyl ether and formation of triflate **11**. While Suzuki reactions of the triflate of **5a** and **5c** were successful [22, 23], the corresponding reactions of **1**, containing an unprotected hydroxyl group, failed.

In conclusion, we have reported the synthesis of γ-alkylidenetetronic acids by Me_3SiOTf-catalyzed cyclization of a 4-*tert*-butoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene with oxalyl chloride, orthogonal protection of the α-hydroxy group and subsequent deprotection of the β-hydroxy group.

Experimental Section

General comments

All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron impact ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60 – 200 mesh) was used. Melting points are uncorrected.

*Procedure for the synthesis of **2***

To a benzene suspension of NaH was slowly added the corresponding alcohol within 30 min. After stirring for 1 h, methyl 4-chloroacetoacetate (**1a**) or ethyl 4-chloroacetoacetate (**1b**) was added slowly by syringe, and the solution was allowed to stirr for 8 – 12 h. An aqueous solution of HCl (10 %, 200 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-hexane-EtOAc= 20 : 1) to give **2**.

*Ethyl 4-ethoxy-3-oxobutanoate (**2b**)*

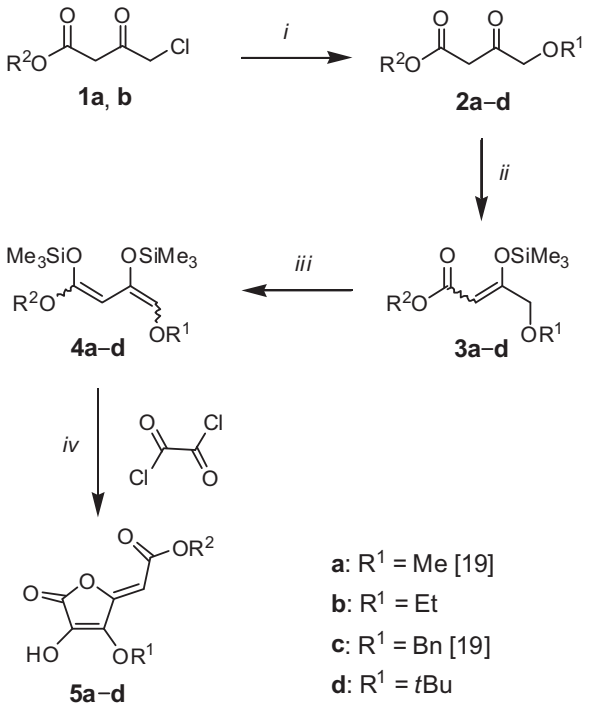
Starting with ethanol (260.0 mmol, 15.2 mL), ethyl 4-chloroacetoacetate (145.0 mmol, 19.7 mL) and NaH (330.0 mmol, 8.00 g) in benzene (200 mL), **2b** was isolated as a yellow oil (15.0 g, 60 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.31 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 3.52 (s, 2 H, CH_2), 3.57 (q, J = 7.2 Hz, 2 H, $CH_2OCH_2CH_3$), 4.11 (s, 2 H, OCH_2CO), 4.23 (q, J = 7.2 Hz, 2 H, OCH_2CH_3).

*Ethyl 4-(tert-butoxy)-3-oxobutanoate (**2d**)*

Starting with *tert*-butanol (135.0 mmol, 9.9 g), ethyl 4-chloroacetoacetate (75.0 mmol, 10.2 mL) and NaH (172.0 mmol, 4.14 g) in benzene (140 mL), **2d** was isolated as a yellow oil (6.80 g, 49 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9 H, CH_3, *t*Bu), 1.28 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 3.54 (s, 2 H, CH_2), 4.01 (s, 2 H, *t*BuOCH_2), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3), 27.3 (CH_3, *t*Bu), 46.3, 61.3, 68.1 (CH_2), 74.3 (C), 167.5, 203.6 (CO). – MS (EI, 70 eV): m/z(%) = 203 (1) $[M]^+$, 157 (3), 114 (15), 87 (12), 57 (100), 41 (30), 20 (29). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2978 (s), 2361 (m), 1746 (s), 1726 (s), 1657 (m), 1369 (s), 1320 (s), 1233 (s), 1195 (s), 1103 (s), 1036 (m). – UV/Vis (CH_3CN, nm): $\lambda_{max}(\log\varepsilon) = 244.8\ (2.56)$.

*General procedure for the synthesis of silyl enol ethers **3***

To a benzene solution of β-ketoester **2** (1.0 equiv.) was added NEt_3 (1.5 equiv.). After stirring for 1 h at 20 °C, Me_3SiCl l (1.5 equiv.) was added dropwise at 20 °C. After stirring for 48 h, the precipitated salts were filtered, and the filtrate was concentrated *in vacuo* to give the silyl enol ether **3**. Due to the unstable nature of the products, only ^{1}H NMR spectra were recorded. The synthesis of **3a** and **3c** has been previously reported [19].



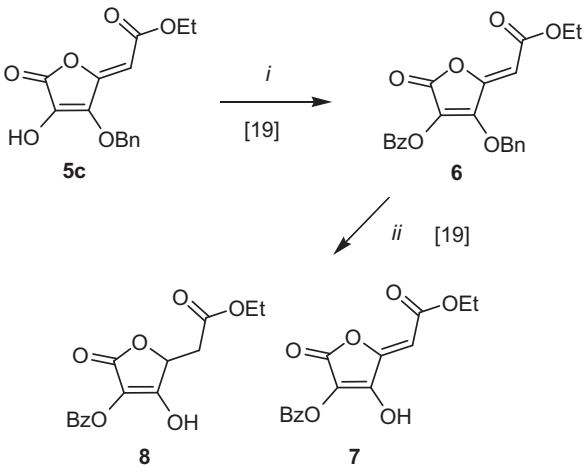
Scheme 1. Synthesis of butenolides **5a**–**d**; *i*: 1) R^1OH, NaH, C_6H_6, 20 °C, 1 h; 2) 20 °C, 12 h; *ii*: Me_3SiCl, NEt_3, C_6H_6, 20 °C, 48 h; *iii*: 1) LDA, THF, −78 °C, 1 h; 2) Me_3SiCl, 20 °C, −78 → 20 °C; *iv*: oxalyl chloride (1.2 equiv.), Me_3SiOTf (0.5 equiv.), CH_2Cl_2, −78 → 20 °C, 12 h.

*1,4-Diethoxy-3-(trimethylsilyloxy)but-2-ene (**3b**)*

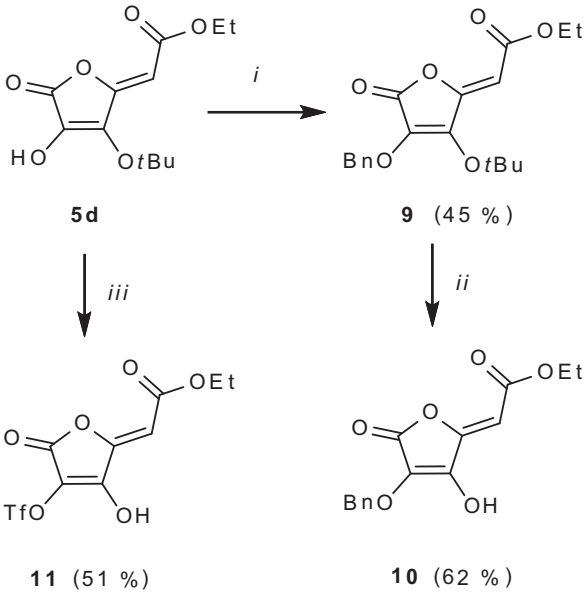
Starting with **2b** (79.1 mmol, 13.78 g) in benzene (300 mL), NEt_3 (118.7 mmol, 16.68 mL) and Me_3SiCl (118.7 mmol, 15.0 mL), **3b** was isolated as a yellow oil (19.5 g, 93 %, $E/Z = 1:1$). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.15$ (s, 9 H, CH_3 of TMS), 1.07 (t, $J = 7.2$ Hz, 3 H, OCH_2CH_3), 1.14 (t, $J = 7.2$ Hz, 3 H, OCH_2CH_3), 3.37 (q, $J = 7.2$ Hz, 2 H, OCH_2CH_3), 3.67 (s, 2 H, OCH_2CO), 3.99 (E/Z, q, $J = 7.2$ Hz, 2 H, OCH_2CH_3), 4.40, 5.27 (E/Z, s, 1 H, CH).

*1-Ethoxy-4-tert-butoxy-3-(trimethylsilyloxy)but-2-ene (**3d**)*

Starting with **2d** (32.5 mmol, 6.50 g) in benzene (100 mL), NEt_3 (48.7 mmol, 6.75 mL) and Me_3SiCl (48.7 mmol, 6.15 g), **3d** was isolated as yellow oil (7.52 g, 84 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.21$ (s, 9 H, CH_3 of TMS), 1.16 (s, 9 H, CH_3, *t*Bu), 1.21 (t, $J = 7.2$ Hz, 3 H, OCH_2CH_3), 3.69 (s, 2 H, OCH_2CO), 4.04 (q, $J = 7.2$ Hz, 2 H, OCH_2CH_3), 5.40 (s, 1 H, CH).



Scheme 2. Synthesis and hydrogenation of butenolide **6** [19]; *i*: BzCl, NEt_3, THF; *ii*: H_2, Pd/C, CH_2Cl_2.



Scheme 3. Synthesis of butenolide **10**; *i*: BnOH, PPh_3, DEAD, THF, 20 °C, 12 h; *ii*: TFA, CH_2Cl_2; *iii*: Tf_2O (1.5 equiv.), pyridine (2.0 equiv.), CH_2Cl_2, −78 → 0 °C, 4 h.

*General procedure for the synthesis of 1,3-bis-silyl enol ethers **4***

A THF solution of LDA was prepared by addition of *n*BuLi (1.5 equiv., 2.5 M or 15 % solution in hexanes) to a THF solution of diisopropylamine (1.5 equiv.) at 0 °C and subsequent stirring for 20 min. To this solution was added a THF solution of **3** (1.0 equiv.) at −78 °C. After stirring for 1 h at −78 °C, Me_3SiCl (1.5 equiv.) was added. The

temperature of the solution was allowed to rise to ambient temperature during 2 h, and the solution was stirred for 1 h at 20 °C. The solvent was removed *in vacuo*, and *n*-hexane was added to the residue. The precipitated lithium chloride was removed by filtration under inert conditions, and the solvent of the filtrate was removed *in vacuo* to give **4**. The product was stored at −20 °C and used without further purification. Due to the unstable nature of the products, only ^{1}H NMR spectra were recorded (except for **4d** which proved to be relatively stable). The synthesis of **4a** and **4c** has been previously reported [19].

*1,4-Diethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**4b**)*

Starting with diisopropylamine (105.0 mmol, 14.76 mL), *n*BuLi (15 % in *n*-hexane, 105.0 mmol, 65.63 mL) in 200 mL of THF, **3b** (70.0 mmol, 17.20 g) and Me_3SiCl (105.0 mmol, 13.26 mL), **4b** was isolated as a yellow oil (18.50 g, 83 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.13$ (s, 9 H, CH_3 of TMS), 0.25 (s, 9 H, CH_3 of TMS), 1.14 (t, $J = 7.2$ Hz, 3 H, OCH_2CH_3), 1.25 (t, $J = 7.0$ Hz, 3 H, OCH_2CH_3), 3.59 (q, $J = 7.1$ Hz, OCH_2CH_3), 4.07 (q, $J = 7.2$ Hz, 2 H, OCH_2CH_3), 4.80 (s, 1 H, CH), 5.42 (s, 1 H, CH).

*1-Ethoxy-4-(tert-butoxy)-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**4d**)*

Starting with diisopropylamine (35.6 mmol, 5.0 mL), *n*BuLi (15 % in *n*-hexane, 35.6 mmol, 22.26 mL) in 100 mL of THF, **3d** (23.7 mmol, 6.51 g) and Me_3SiCl (35.6 mmol, 4.50 mL), **4d** was isolated as a yellow oil (7.52 g, 92 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.18$ (s, 9 H, CH_3 of TMS), 0.27 (s, 9 H, CH_3 of TMS), 1.21 (t, $J = 7.2$ Hz, 3 H, OCH_2CH_3), 1.27 (s, 9 H, CH_3, *t*Bu), 3.79, 4.03 (*E*/*Z*, q, $J = 7.1$ Hz, OCH_2CH_3), 4.52, 5.41 (*E*/*Z*, s, 1 H, CH), 5.64, 5.77 (*E*/*Z*, s, 1 H, CH). – IR (KBr, cm^{-1}): $\tilde{\nu} = 2976$ (s), 1670 (m), 1610 (s), 1367 (m), 1250 (s), 1193 (m), 1136 (s), 1075 (m), 847 (s).UV/Vis (CH_3CN, nm): $\lambda_{max}(\log\varepsilon) =$ 205.9 (3.61), 293.0 (2.93). – MS (EI, 70 eV): $m/z(\%) = 346$ (7) $[M]^+$, 289 (28), 243 (29), 171 (59), 147 (52), 74 (100), 57 (56), 28 (57). – Anal. for $C_{16}H_{34}O_4Si_2$ (346.45): calcd. C 55.47, H 9.89; found C 55.07, H 9.27.

*Procedure for the synthesis of butenolides **5a–d***

To a CH_2Cl_2 solution of Me_3SiOTf (0.5 equiv.) was added a CH_2Cl_2 solution of **4** (1.0 equiv.) at −78 °C. Subsequently, oxalyl chloride (1.2 equiv.) was added at −78 °C. The temperature of the solution was allowed to rise to 20 °C over 12 h. A 4 : 1 mixture of a saturated solution of brine and of hydrochloric acid (10 %) was added. The organic layer was separated, and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and filtered. The solvent of the filtrate was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, *n*-hexane- EtOAc). The synthesis of **5a** and **5c** has been previously reported [19].

*(2Z)-Ethyl 2-(3-ethoxy-4-hydroxy-5-oxofuran-2(5H)-ylidene)acetate (**5b**)*

Starting with **4b** (12.0 mmol, 3.82 g) in 240 mL of CH_2Cl_2, oxalyl chloride (14.4 mmol, 1.83 g) and Me_3SiOTf (6.0 mmol, 1.330 g), **5b** was isolated by column chromatography (*n*-hexane-EtOAc = 5 : 1) as a yellow solid (1.25 g, 46 %), m. p. = 103 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.31$ (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 1.40 (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 4.26 (q, $J = 7.0$ Hz, 2 H, OCH_2CH_3), 4.54 (q, $J = 7.0$ Hz, 2 H, OCH_2CH_3), 5.61 (s, 1 H, CH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.4$, 15.5 (CH_3), 61.2, 68.3 (CH_2), 96.6 (CH), 122.9, 141.4, 151.8, 163.7, 165.9 (C). – MS (EI, 70 eV): $m/z(\%) = 228$ (24) $[M]^+$, 200 (9), 183 (38), 154 (100), 127 (19), 98 (30), 70 (27), 29 (89). – IR (KBr, cm^{-1}): $\tilde{\nu} = 3231$ (br, s), 2985 (m), 1798 (s), 1686 (s), 1656 (s), 1376 (s), 1344 (s), 1318 (s), 1196 (s), 1120 (s), 1035 (s), 995 (m), 837 (m), 755 (m). – UV/Vis (CH_3CN, nm): $\lambda_{max}(log\varepsilon) = 215.8$ (3.74), 259.9 (3.95), 309.9 (3.79). – Anal. for $C_{10}H_{12}O_6$: calcd. C 52.64, H 5.30; found C 52.43, H 6.12.

*(2Z)-Ethyl 2-(3-tert-butoxy-4-hydroxy-5-oxofuran-2(5H)-ylidene)acetate (**5d**)*

Starting with **4d** (10.0 mmol, 3.46 g) in 200 mL of CH_2Cl_2, oxalyl chloride (12.0 mmol, 1.52 g) and Me_3SiOTf (5.0 mmol, 1.11 g), **5d** was isolated by column chromatography (*n*-hexane-EtOAc = 5 : 1) as a yellow solid (1.20 g, 47 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.32$ (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 1.51 (s, 9 H, CH_3, *t*Bu), 4.26 (q, $J = 7.0$ Hz, 2 H, OCH_2CH_3), 5.30 (s, 1 H, OH), 5.63 (s, 1 H, CH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.4$ (CH_3), 26.6 (3 CH_3, *t*Bu), 61.4 (CH_2), 70.8, (C), 95.7 (CH), 123.6, 138.2, 163.8, 165.8, 167.6 (C). – MS (EI, 70 eV): $m/z(\%) = 257$ (1) $[M]^+$, 200 (20), 144 (21), 116 (24), 99 (19), 70 (20), 57 (100), 41 (45), 29 (57). – IR (KBr, cm^{-1}): $\tilde{\nu} = 3352$ (s), 2986 (m), 1768 (s), 1678 (s), 1382 (s), 1328 (s), 1285 (s), 1171 (s), 1126 (s), 846 (m), 753 (m). – UV/Vis (CH_3CN, nm): $\lambda_{max}(\log\varepsilon) = 213.1$ (3.77), 260.7 (3.89), 404.9 (2.83). – Anal. for $C_{12}H_{16}O_6$: calcd.: C 56.24, H 6.29; found C 56.43, H 7.08.

*(2Z)-Ethyl 2-(3-tert-butoxy-4-benzyloxy-5-oxofuran-2(5H)-ylidene)acetate (**9**)*

To a solution of **5d** (0.357 g, 1.4 mmol) in 6 mL of THF was added DEAD (0.293 g, 1.7 mmol, dissolved in 2 mL of THF), benzylic alcohol (0.184 g, 1.7 mmol) and PPh_3 (0.446 g, 1.7 mmol, dissolved in 2 mL of THF). The mixture was stirred at 20 °C for 12 h. The solvent (THF) was evaporated

in vacuo. The residue was purified by column chromatography (silicagel; *n*-hexane-EtOAc = 25 : 1) to give **9** as a colorless oil (0.205 mg, 45 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.32$ (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 1.43 (s, 9 H, CH_3, *t*Bu), 4.24 (q, $J = 7.1$ Hz, 2 H, OCH_2CH_3), 5.29 (s, 1 H, CH), 5.54 (s, 2 H, CH_2, Bn), 7.35 – 7.41 (m, 5 H, Ar). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$ (CH_3), 28.7 (CH_3, *t*Bu), 60.8, 73.1 (CH_2), 73.8 (C), 95.8 (CH), 126.1 (C), 128.6 (2 CH, Ph), 128.7 (CH, Ph), 128.9 (2 CH, Ph), 135.5, 147.7, 153.3, 163.5, 163.8 (C). – MS (EI, 70 eV): $m/z(\%) = 336$ (1) $[M]^+$, 290 (10), 114 (10), 91 (100), 57 (18), 29 (7). – IR (KBr, cm^{-1}): $\tilde{\nu} = 2982$ (s), 1786 (s), 1723 (s), 1706 (s), 1693 (s), 1460 (m), 1393 (s), 1278 (s), 1181 (s), 1098 (s), 1036 (s), 843 (m), 751 (m). – UV/Vis: $\lambda_{max}(\log\varepsilon) = 205.3$ (4.20), 263.8 (4.13).

*(2Z)-Ethyl 2-(4-(benzyloxy)-3-hydroxy-5-oxofuran-2(5H)-ylidene)acetate (**10**)*

To a CH_2Cl_2 solution (1.5 mL) of **9** (0.100 g, 0.343 mmol) was added trifluoroacetic acid (0.395 g, 3.43 mmol). The reaction mixture was stirred for 36 h at 20 °C. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel; *n*-hexane-EtOAc = 20 : 1) to give **10** as a colorless oil (0.062 g, 62 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 4.33 (q, $J = 7.1$ Hz, 2 H, OCH_2CH_3), 5.30 (s, 2 H, CH_2, Bn), 5.54 (s, 1 H, CH), 7.35 – 7.37 (m, 5 H, Ar). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$ (CH_3), 60.8, 73.9 (CH_2), 96.1 (CH), 123.8 (C), 128.7 (2 CH, Ph), 128.8 (CH, Ph), 128.9 (2 CH, Ph), 135.4, 147.7, 150.9, 163.2, 163.5 (C). – MS (EI, 70 eV): $m/z(\%) = 290$ (8) $[M]^+$, 165 (2), 91 (100), 70 (7), 66 (7), 29 (6).

*(2Z)-Ethyl 2-(3-(hydroxy)-4-(trifluoromethylsulfonyloxy)-5-oxofuran-2(5H)-ylidene)acetate (**11**)*

To a CH_2Cl_2 solution (18 mL) of **5d** (0.454 g, 1.8 mmol) was added pyridine (0.285 g, 3.6 mmol) at −78 °C. After stirring for 10 min, triflic anhydride (0.600 g, 2.13 mmol) was added. The mixture was allowed to warm to 0 °C and was stirred for 4 h. The reaction mixture was directly purified by column chromatography (silicagel, CH_2Cl_2) to give **11** as a colorless oil (0.302 g, 51 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.35$ (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 4.22 (q, $J = 7.1$ Hz, 2 H, OCH_2CH_3), 5.94 (s, 1 H, CH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.9$ (CH_3), 62.4 (CH_2), 99.5 (CH), 115.1, 120.4, 149.7, 155.5, 159.9, 164.2 (C). – MS (EI, 70 eV): $m/z(\%) = 332$ (9) $[M]^+$, 287 (35), 199 (45), 154 (19), 114 (189, 70 (100), 29 (30). – IR (KBr, cm^{-1}): $\tilde{\nu} = 3435$ (br, m), 2992 (w), 1802 (s), 1672 (s), 1635 (s), 1433 (s), 1243 (s), 1220 (s), 1031 (s), 645 (m). – UV/Vis: $\lambda_{max}(\log\varepsilon) = 204.3$ (4.02), 261.8 (4.02).

Acknowledgement

Financial support from the Ministry of Education of Vietnam (scholarship for V. T. H. N.), the State of Mecklenburg-Vorpommern (Landesgraduiertenstipendium for Z. A. and Landesforschungsschwerpunkt 'Neue Wirkstoffe und Screeningverfahren') and from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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