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ScienceDirect
Tetrahedron 63 (2007) 4929–4936
Tetrahedron

Synthesis of diaryl ethers based on one-pot [3+3] cyclizations of 1,3-bis(silyl enol ethers)

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Received 19 February 2007; revised 21 March 2007; accepted 22 March 2007
Available online 27 March 2007

Abstract—Functionalized and sterically encumbered diaryl ethers were prepared by [3+3] cyclization of 1,3-bis(silyl enol ethers) with 2-aryloxy-3-(silyloxy)alk-2-en-1-ones.

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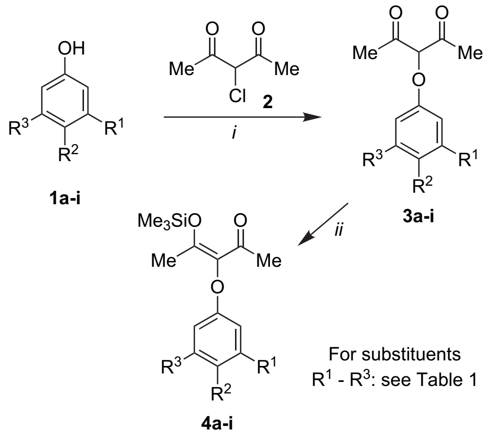
1. Introduction

Diaryl ethers containing an ester or carboxylic acid function constitute an important subgroup of the pharmacologically important substance class of diaryl ethers.[1] They occur in a number of natural products such as geodinhydrate methylester and methyl chloroasterrate,[2a,b] 1-desgalloylsanguiin,[3] dehydrotrigallic acid,[4] epiphorellic acid,[5] jolkianin,[6] remurin A,[7] or micareic acid.[8] Diaryl ethers are available by classic Ullmann reactions and related methods.[9] In recent years, the Buchwald–Hartwig reaction and related transformations proved to be versatile methods for the synthesis of diaryl ethers.[10] Recently, Beller et al. reported the transition metal catalyzed coupling of phenols with aryl chlorides.[11] Despite their great synthetic utility, the scope of all these methods is limited by the availability of the starting materials. In fact, the synthesis of more complex aryl halides or triflates by regioselective functionalization of arenes is often a difficult task. In addition, the transition metal catalyzed formation of diaryl ethers containing a sterically encumbered ether linkage often proceeds in low yield or not at all.

The formal [3+3] cyclization of 1,3-bis(silyl enol ethers)[12] with 3-(siloxy)alk-2-en-1-ones provides a versatile method for the synthesis of functionalized arenes.[13] Recently, we reported the application of this method to the synthesis of functionalized diaryl ethers.[14] Herein, we report full details of these studies. With regard to our preliminary communication,[14] the preparative scope has been significantly extended. Our method relies on assembly of one of the two arene moieties (in contrast to transition metal catalyzed C–O coupling reactions). Notably, functionalized and sterically encumbered diaryl ethers, which are not readily available by other methods, can be prepared.

2. Results and discussion

3-(Phenoxy)pentane-2,4-diones **3a–i** were prepared, following a known procedure,[15] by potassium carbonate mediated reaction of phenols **1a–i** with 3-(chloro)pentane-2,4-dione (**2**). The synthesis of derivatives **3a** and **3d** was previously reported.[15] The silylation[16] of **3a–i** afforded the novel 2-aryloxy-3-(silyloxy)alk-2-en-1-ones **4a–i** (Scheme 1 and Table 1). Only moderate to low yields were obtained for **3a–i**. The silylation proceeded in very good yields.



Scheme 1. Synthesis of **4a–i**. Reagents and conditions: (i) K_2CO_3, acetone, 2 h, reflux; (ii) Me_3SiCl, NEt_3, C_6H_6, 20 °C, 72 h.

Keywords: Arenes; Cyclizations; Diaryl ethers; Silyl enol ethers.

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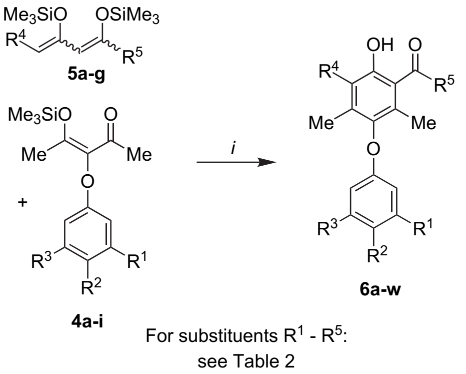
doi:10.1016/j.tet.2007.03.143

Table 1. Synthesis of **3a–i** and **4a–i**

3 and **4**	R^1	R^2	R^3	**3**[a] (%)	**4**[a] (%)
a	H	H	H	—[b]	91
b	Me	H	Me	20	94
c	H	Et	H	35	80
d	H	Cl	H	—[b]	96
e	H	OMe	H	24	95
f	OMe	OMe	H	40	97
g	H	Br	H	25	84
h	H	CN	H	25	82
i	H	CH_2CO_2Me	H	26	87

[a] Yields of isolated products.

[b] Commercially available.



Scheme 2. Synthesis of **6a–w**. Reagents and conditions: (i) $TiCl_4$, CH_2Cl_2, −78 °C→20 °C, 20 h.

The $TiCl_4$ mediated cyclization of 2-aryloxy-3-(silyloxy)-alk-2-en-1-ones **4a–i** with 1,3-bis(silyl enol ethers) **5a–g** afforded the diaryl ethers **6a–w** in moderate to good yields (Scheme 2 and Table 2). The reactions were carried out following a typical procedure previously reported for related [3+3] cyclizations.[13] The best results were obtained when stoichiometric amounts of the starting materials and $TiCl_4$ were used. The latter was added to a dichloromethane solution of the starting materials at −78 °C with subsequent warming of the mixture to 20 °C. The high concentration of the solution (only 2 mL of solvent per 1 mmol of starting material) proved to be a very important parameter. The yields significantly decreased when the reactions were carried out in more dilute solutions. The quality of the starting materials, reagents and solvent also played an important role.

Notably, the presence of functional groups (chloride, bromide, cyano, ester or methoxy groups) proved to be—in principle—compatible with the reaction conditions. A variety of functionalized diaryl ethers (**6h–w**) were successfully prepared without any decrease in yield compared to reactions of non-functionalized substrates. In most of the cyclization reactions, β-ketoester derived 1,3-bis(silyl enol ethers) were employed. However, the use of 1,3-bis(silyl enol ether) **5e**, prepared from acetylacetone, also proved to be successful. In contrast, employment of 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (derived from benzoylacetone) resulted in the formation of complex mixtures. This can be explained by its lower reactivity compared to β-ketoester derived 1,3-bis(silyl enol ethers). The cyclization of 2-aryloxy-3-(silyloxy)alk-2-en-1-ones with 1,3-bis(silyl enol ethers) **5b**, **5c** and **5g**, containing an additional alkyl group attached to carbon atom C-4, afforded heavily substituted diaryl ethers. However, most derivatives (**6b**, **6c**, **6e**, **6g**, **6j**, **6l**, **6n** and **6w**) were obtained in relatively low yield. On the other hand, no decrease in the yield was observed in case of **6i** and **6u**. In conclusion, relatively low yields were obtained for diaryl ethers **6a–c**, **6e**, **6g**, **6l**, **6n** and **6w**. The reason for this remains unclear at present, since considerably better yields were obtained for closely related derivatives. Therefore, the quality of the starting materials employed for each individual experiment seems to play an important role.

Table 2. Synthesis of **6a–w**

4	**5**	**6**	R^1	R^2	R^3	R^4	R^5	**6**[a] (%)
a	**a**	**a**	H	H	H	H	OEt	35
a	**b**	**b**	H	H	H	Me	OEt	30
a	**c**	**c**	H	H	H	Et	OEt	32
b	**a**	**d**	Me	H	Me	H	OEt	58
b	**b**	**e**	Me	H	Me	Me	OEt	39
c	**a**	**f**	H	Et	H	H	OEt	60
c	**b**	**g**	H	Et	H	Me	OEt	36
d	**d**	**h**	H	Cl	H	H	OMe	54
d	**b**	**i**	H	Cl	H	Me	OEt	49
d	**c**	**j**	H	Cl	H	Et	OEt	43
d	**e**	**k**	H	Cl	H	H	Me	35
e	**b**	**l**	H	OMe	H	H	OEt	30
f	**a**	**m**	OMe	OMe	H	H	OEt	58
f	**b**	**n**	OMe	OMe	H	Me	OEt	35
g	**a**	**o**	H	Br	H	H	OEt	58
g	**f**	**p**	H	Br	H	H	OCH_2Ph	59
h	**a**	**q**	H	CN	H	H	OEt	50
h	**f**	**r**	H	CN	H	H	OCH_2Ph	54
i	**a**	**s**	H	CH_2CO_2Me	H	H	OEt	50
i	**f**	**t**	H	CH_2CO_2Me	H	H	OCH_2Ph	65
i	**g**	**u**	H	CH_2CO_2Me	H	*n*-Hex	OEt	54
i	**e**	**v**	H	CH_2CO_2Me	H	H	Me	55
e	**b**	**w**	H	OMe	H	Me	OEt	30

[a] Yields of isolated products.

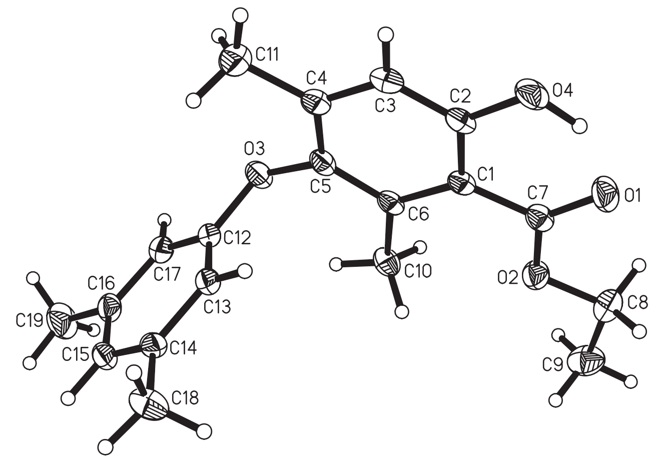


Figure 1. ORTEP plot of **6d**.

The structures of diaryl ethers **6** were proved by spectroscopic methods. The structure of derivative **6d** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[17]

In conclusion, a variety of functionalized and sterically encumbered diaryl ethers were prepared by formal [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 2-aryloxy-3-(silyloxy)alk-2-en-1-ones. A general rule for the influence of a specific substitution pattern of the starting materials on the yield of the reactions could not be observed. In contrast, the quality of the starting materials employed for each individual experiment seems to play an important role.

3. Experimental section

3.1. General

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For the ^{1}H and ^{13}C NMR spectra the deuterated solvents indicated were used. ^{13}C NMR spectral assignments are supported by DEPT analyses. Mass spectral data (MS) were obtained by electron 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.

3.1.1. Synthesis of 3-(aryloxy)pentane-2,4-diones 3a–i. The reactions were carried out according to a known procedure.[15] The synthesis of **3a** and **3d** was previously reported.[15]

3.1.1.1. 3-(3,5-Dimethylphenoxy)pentane-2,4-dione (3b). Starting with **2** (10.00 g, 74.3 mmol), 3,5-dimethylphenol (12.00 g, 104.0 mmol) and K_2CO_3 (25.00 g, 185.7 mmol), **3b** was isolated as a yellow solid (3.00 g, 19%), mp 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02 (s, 6H, CH_3), 2.28 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 6.51 (s, 2H, ArH), 6.66 (s, 1H, ArH), 14.41 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8 (2C), 21.3 (2C, CH_3), 111.9 (2C), 123.9 (CH), 130.9, 139.8 (2C), 158.0, 186.4 (2C, C); IR (KBr): $\tilde{\nu}$ = 3436 (w), 2965 (m), 1739 (m), 1610 (m), 1505 (s), 1298 (m), 1213 (m), 831 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 220 (M^{+}, 100), 178 (25), 122 (88), 107 (29), 91 (28), 77 (31), 43 (64); elemental analysis: calcd (%) for $C_{13}H_{16}O_3$ (220.26): C 70.89, H 7.32; found: C 71.05, H 7.07.

3.1.1.2. 3-(4-Ethylphenoxy)pentane-2,4-dione (3c). Starting with **2** (10.00 g, 74.3 mmol), 4-ethylphenol (12.90 g, 105.5 mmol) and K_2CO_3 (25.60 g, 185.7 mmol), **3c** was isolated as a colourless oil (5.30 g, 35%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.21 (t, 3H, *J*=7.5 Hz, CH_3), 2.03 (s, 6H, CH_3), 2.60 (q, 2H, *J*=7.8 Hz, CH_2), 6.82 (d, 2H, *J*=8.7 Hz, ArH), 7.12 (d, 2H, *J*=8.8 Hz, ArH), 14.42 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.7, 20.8 (2C, CH_3), 27.9 (CH_2), 114.1 (2C), 129.1 (2C, CH), 131.0, 137.9, 156.0, 186.5 (2C, C); IR (KBr): $\tilde{\nu}$ = 3436 (w), 2965 (m), 1739 (m), 1610 (m), 1505 (s), 1298 (m), 1213 (m), 831 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 220.1 (M^{+}, 90), 178.1 (29), 122.1 (61), 107.1 (64), 43.1 (100); HRMS (EI): calcd for $C_{13}H_{16}O_3$ [M]$^{+}$: 220.1091; found: 220.1094.

3.1.1.3. 3-(4-Methoxyphenoxy)pentane-2,4-dione (3e). Starting with **2** (4.00 g, 29.7 mmol), 4-methoxyphenol (5.20 g, 42.2 mmol) and K_2CO_3 (10.20 g, 74.3 mmol), **3e** was isolated as a colourless oil (1.50 g, 24%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02 (s, 6H, CH_3), 3.77 (s, 3H, OCH_3), 6.83 (s, 4H, ArH), 14.39 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8 (2C), 55.6 (CH_3), 114.91 (2C), 114.95 (2C, CH), 131.2, 151.9, 154.7, 186.5 (2C, C); IR (KBr): $\tilde{\nu}$ = 3085 (w), 3003 (m), 2956 (m), 2839 (w), 1607 (s), 1507 (s), 1309 (s), 1262 (s), 1228 (s), 1194 (s), 1166 (s), 1128 (s), 1026 (s), 951 (s), 740 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 222.0 (M^{+}, 100), 151.0 (16), 124.0 (40), 108.0 (22); HRMS (EI): calcd for $C_{12}H_{14}O_4$ [M]$^{+}$: 222.0878; found: 222.0886.

3.1.1.4. 3-(3,4-Dimethoxyphenoxy)pentane-2,4-dione (3f). Starting with **2** (6.00 g, 44.5 mmol), 3,4-dimethoxyphenol (9.70 g, 63.3 mmol) and K_2CO_3 (15.40 g, 111.4 mmol), **3f** was isolated as a pink solid (4.50 g, 40%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.03 (s, 6H, CH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.31 (dd, 1H, *J*=8.7, 2.8 Hz, ArH), 6.55 (d, 1H, *J*=2.8 Hz, ArH), 6.75 (d, 1H, *J*=8.7 Hz, ArH), 14.42 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8 (2C), 55.9, 56.3 (CH_3), 99.9, 103.6, 111.8 (CH), 131.5, 144.3, 150.2, 152.4, 186.5 (2C, C); IR (KBr): $\tilde{\nu}$ = 3085 (w), 3003 (m), 2956 (m), 2839 (w), 1607 (s), 1507 (s), 1309 (s), 1262 (s), 1228 (s), 1194 (s), 1166 (s), 1128 (s), 1026 (s), 951 (s), 740 (m) cm^{-1}; MS (CI): 253.1 (100); elemental analysis: calcd (%) for $C_{13}H_{16}O_5$ (252.26): C 61.90, H 6.39; found: C 61.73, H 6.30.

3.1.1.5. 3-(4-Bromophenoxy)pentane-2,4-dione (3g). Starting with **2** (10.00 g, 74.3 mmol), 4-bromophenol (14.40 g, 105.5 mmol) and K_2CO_3 (25.60 g, 185.7 mmol), **3g** was isolated as a pink oil (5.10 g, 25%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.01 (s, 6H, CH_3), 6.81 (d, 2H, *J*=8.7 Hz, ArH), 7.40 (d, 2H, *J*=8.7 Hz, ArH), 14.39 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.7 (2C, CH_3), 114.4 (C), 116.0 (2C, CH), 130.7 (C), 132.8 (2C, CH), 157.1, 186.3 (2C, C); IR (KBr): $\tilde{\nu}$ = 2925 (w), 1593 (m), 1481 (s), 1303 (m), 1213 (m), 1165 (m), 1070 (m), 825 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 272.0 (M^{+}, 42), 270.0 (43), 230.0 (17), 228.0 (18), 174.0 (39), 172.0 (40), 101.1 (32); HRMS (EI): calcd for $C_{11}H_{11}BrO_3$ [M]$^+$: 269.9890; found: 269.9886.

3.1.1.6. 3-(4-Cyanophenoxy)pentane-2,4-dione (3h). Starting with **2** (10.00 g, 74.3 mmol), 4-cyanophenol (12.50 g, 105.5 mmol) and K_2CO_3 (26.50 g, 185.8 mmol), **3h** was isolated as a colourless oil (4.20 g, 25%), mp 67–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02 (s, 6H, CH_3), 7.02 (d, 2H, *J*=9.0 Hz, ArH), 7.65 (d, 2H, *J*=9.0 Hz, ArH), 14.42 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.7 (CH_3), 106.0 (C), 115.2 (CH_{Ar}), 118.5, 130.4 (C), 134.5 (CH_{Ar}), 161.2, 186.0 (C); IR (KBr): $\tilde{\nu}$ = 3390 (w), 2953 (w), 1738 (s), 1611 (s), 1296 (m), 1223 (s), 1165 (m), 827 (m), 732 (s) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 217 (M$^+$, 69), 175 (25), 101 (30), 43 (100); elemental analysis: calcd (%) for $C_{12}H_{11}O_3N$ (217.23): C 66.34, H 5.11, N 6.45; found: C 65.97, H 4.88, N 6.33.

3.1.1.7. Methyl 2-(4-(2,4-dioxopentane-3-yloxy)-phenyl) acetate (3i). Starting with **2** (10.00 g, 74.3 mmol), methyl 4-hydroxy acetate (17.20 g, 104.0 mmol) and K_2CO_3 (25.60 g, 185.7 mmol), **3i** was isolated as a colourless oil (4.30 g, 26%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 5.29 (s, 2H, CH_2), 6.87 (d, 2H, *J*=8.7 Hz, ArH), 7.22 (d, 2H, *J*=8.7 Hz, ArH), 14.42 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.7 (CH_3), 40.0 (CH_2), 51.9 (OCH_3), 114.3 (CH_{Ar}), 127.6 (C), 130.6 (CH_{Ar}), 130.8, 157.0, 172.0, 186.3 (C); IR (KBr): $\tilde{\nu}$ = 3436 (w), 2965 (m), 1739 (m), 1610 (m), 1505 (s), 1298 (m), 1213 (m), 831 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 264 (M$^+$, 100), 222.1 (36), 205.1 (47), 166.1 (34), 107.1 (87), 43.1 (61); elemental analysis: calcd (%) for $C_{14}H_{16}O_5$ (442.56): C 63.63, H 6.10; found: C 63.26, H 5.88.

3.1.2. Synthesis of 2-aryloxy-3-(silyloxy)alk-2-en-1-ones 4a–i. The reactions were carried out according to a known procedure.[16] Due to their low stability, silyl enol ethers **4a–i** were used directly after their preparation and not characterized by spectroscopy.

3.1.3. General procedure for the synthesis of diaryl ethers 6a–w. To a dichloromethane solution (2 mL/mmol) of **4** (1.0 mmol) and **5** (1.0 mmol) was added $TiCl_4$ (1.0 mmol) at −78 °C. The solution was allowed to warm to ambient temperature within 20 h. To the solution was added a saturated solution of $NaHCO_3$ (10 mL). The organic and the aqueous layers were separated and the latter was extracted with diethyl ether (3×30 mL). The filtrate was concentrated in vacuo and the residue was purified by chromatography (silica gel, EtOAc/*n*-heptane=1:4).

3.1.3.1. Ethyl 3-phenoxy-6-hydroxy-2,4-dimethylbenzoate (6a). Starting with 1,3-bis(silyl enol ether) **5a** (350 mg, 1.2 mmol), 3-(siloxy)alk-2-en-1-one **4a** (342 mg, 1.2 mmol) and $TiCl_4$ (0.14 mL, 1.2 mmol), **6a** was isolated as a colourless solid (125 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.27 (t, 3H, *J*=7.1 Hz, CH_3), 1.96 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 4.28 (q, 2H, *J*=7.1 Hz, OCH_2), 6.59–7.13 (m, 6H, ArH), 11.04 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 15.3, 17.2 (CH_3), 61.6 (CH_2), 111.1 (C), 114.4 (2C), 117.4, 121.4, 129.6 (2C, CH), 133.7, 139.8, 143.8, 157.9, 159.6, 171.3 (C); IR (KBr): $\tilde{\nu}$ = 3432 (w), 2980 (w), 1657 (s), 1474 (s), 1373 (s), 1318 (s), 1226 (s), 1207 (m), 1058 (m), 751 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 286.1 (M$^+$, 24), 240.0 (100), 211.0 (10), 135.0 (10); elemental analysis: calcd (%) for $C_{17}H_{18}O_4$ (286.32): C 71.31, H 6.34; found: C 71.03, H 6.62.

3.1.3.2. Ethyl 3-phenoxy-6-hydroxy-2,4,5-trimethylbenzoate (6b). Starting with 1,3-bis(silyl enol ether) **5b** (400 mg, 1.3 mmol), 3-(siloxy)alk-2-en-1-one **4a** (367 mg, 1.3 mmol) and $TiCl_4$ (0.15 mL, 1.3 mmol), **6b** was isolated as a colourless solid (130 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.40 (t, 3H, *J*=7.1 Hz, CH_3), 2.08 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.42 (q, 2H, *J*=7.1 Hz, OCH_2), 6.72–7.27 (m, 5H, ArH), 11.51 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=10.9, 12.8, 13.1, 14.3 (CH_3), 60.6 (CH_2), 109.4 (C), 113.5 (2C), 120.3 (CH), 123.0 (C), 128.6 (2C, CH), 129.2, 137.1, 142.4, 156.8, 157.2, 170.9 (C); IR (KBr): $\tilde{\nu}$ = 3438 (w), 2937 (w), 1649 (s), 1396 (s), 1293 (s), 1222 (s), 1031 (m), 810 (m), 753 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 300.0 (M$^+$, 88), 254.0 (100), 226.0 (72), 211.0 (17); HRMS (EI): calcd for $C_{18}H_{20}O_4$ [M]$^+$: 300.13563; found: 300.13561.

3.1.3.3. Ethyl 5-ethyl-3-phenoxy-6-hydroxy-2,4-dimethylbenzoate (6c). Starting with 1,3-bis(silyl enol ether) **5c** (400 mg, 1.3 mmol), 3-(siloxy)alk-2-en-1-one **4a** (349 mg, 1.3 mmol) and $TiCl_4$ (0.14 mL, 1.3 mmol), **6c** was isolated as a colourless solid (130 mg, 32%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.10 (t, 3H, *J*=7.5 Hz, CH_3), 1.38 (t, 3H, *J*=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.70 (q, 2H, *J*=7.5 Hz, CH_2), 4.40 (q, 2H, *J*=7.1 Hz, OCH_2), 6.69–7.23 (m, 5H, ArH), 11.44 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.0, 13.3, 14.1, 15.3 (CH_3), 19.7, 61.5 (CH_2), 110.6 (C), 114.5 (2C), 121.2, 129.6 (2C, CH), 130.1, 130.4, 137.4, 143.5, 157.6, 158.2, 171.9 (C); IR (KBr): $\tilde{\nu}$ = 2969 (m), 1651 (s), 1599 (m), 1492 (s), 1394 (s), 1320 (s), 1221 (s), 1052 (m), 748 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 314.1 (M$^+$, 46), 268.1 (100), 240.1 (10), 225.1 (2); elemental analysis: calcd (%) for $C_{19}H_{22}O_4$ (314.37): C 72.59, H 7.05; found: C 72.65, H 6.95.

3.1.3.4. Ethyl 3-(3,5-dimethylphenoxy)-6-hydroxy-2,4-dimethylbenzoate (6d). Starting with 1,3-bis(silyl enol ether) **5a** (500 mg, 1.8 mmol), 3-(siloxy)alk-2-en-1-one **4b** (533 mg, 1.8 mmol) and $TiCl_4$ (0.19 mL, 1.8 mmol), **6d** was isolated as a colourless solid (330 mg, 58%), mp 125–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.41 (t, 3H, *J*=7.1 Hz, CH_3), 2.11 (s, 3H, CH_3), 2.24 (s, 6H, CH_3), 2.34 (s, 3H, CH_3), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 6.35 (s, 2H, ArH), 6.62 (s, 1H, ArH), 6.76 (s, 1H, ArH), 11.19 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 15.4, 17.3, 21.3 (2C, CH_3), 61.6 (CH_2), 111.1 (C), 112.1 (2C), 117.3, 123.3 (CH), 133.7, 139.4 (2C), 139.9, 143.9, 158.0, 159.5, 171.4 (C); IR (KBr): $\tilde{\nu}$ = 3030 (w), 2957 (m), 1660 (s), 1505 (s), 1470 (s), 1397 (s), 1373 (s), 1313 (s), 1241 (s), 1220 (s), 1077 (m), 826 (m), 799 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 314.2 (M$^+$, 34), 268.1 (100); elemental analysis: calcd (%) for $C_{19}H_{22}O_4$ (314.37): C 72.59, H 7.05; found: C 72.18, H 6.88.

3.1.3.5. Ethyl 3-(3,5-dimethylphenoxy)-6-hydroxy-2,4,5-trimethylbenzoate (6e). Starting with 1,3-bis(silyl enol ether) **5b** (500 mg, 1.7 mmol), 3-(siloxy)alk-2-en-1-one **4b** (506 mg, 1.7 mmol) and $TiCl_4$ (0.18 mL, 1.7 mmol), **6e** was isolated as a colourless solid (220 mg, 39%), mp 111–112 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.42 (t, 3H, *J*=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.25 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 4.44 (q, 2H, *J*=7.1 Hz, OCH_2), 6.35 (s, 2H, ArH), 6.62 (s, 1H, ArH), 11.54 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.9, 13.9, 14.1, 15.3, 21.3 (2C, CH_3), 61.5 (CH_2), 110.3 (C), 112.2 (2C), 123.1 (CH), 123.8, 130.3, 138.2, 139.4 (2C), 143.5, 157.7, 158.3, 172.0 (C); IR (KBr): $\tilde{\nu}$ = 3430 (w), 2921 (m), 1647 (s), 1612 (s), 1594 (s), 1400 (s), 1378 (s), 1318 (s), 1289 (s), 1218 (s), 1142 (s), 1032 (m), 834 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 328.2 (M^+, 38), 282.2 (100), 239.2 (14); elemental analysis: calcd (%) for $C_{20}H_{24}O_4$ (328.40): C 73.14, H 7.36; found: C 73.16, H 7.57.

3.1.3.6. Ethyl 3-(4-ethylphenoxy)-6-hydroxy-2,4-dimethylbenzoate (6f). Starting with 1,3-bis(silyl enol ether) **5a** (500 mg, 1.8 mmol), 3-(siloxy)alk-2-en-1-one **4c** (533 mg, 1.8 mmol) and $TiCl_4$ (0.19 mL, 1.8 mmol), **6f** was isolated as a colourless solid (339 mg, 60%), mp 52–53 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.20 (t, 3H, *J*=7.5 Hz, CH_3), 1.40 (t, 3H, *J*=7.1 Hz, CH_3), 2.10 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.58 (q, 2H, *J*=7.5 Hz, CH_2), 4.42 (q, 2H, *J*=7.1 Hz, OCH_2), 6.65 (d, 2H, *J*=8.7 Hz, ArH), 6.75 (s, 1H, ArH), 7.06 (d, 2H, *J*=8.7 Hz, ArH), 11.17 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2, 15.4, 15.7, 13.3 (CH_3), 27.9, 61.7 (CH_2), 111.2 (C), 114.3 (2C), 117.4, 129.9 (2C, CH), 133.8, 137.2, 140.0, 144.1, 156.0, 159.6, 171.5 (C); IR (KBr): $\tilde{\nu}$ = 3030 (w), 2957 (m), 1660 (s), 1505 (s), 1470 (s), 1397 (s), 1373 (s), 1313 (s), 1241 (s), 1220 (s), 1077 (m), 826 (m), 799 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 314.2 (M^+, 29), 268.2 (100); elemental analysis: calcd (%) for $C_{19}H_{22}O_4$ (314.37): C 72.59, H 7.05; found: C 72.42, H 7.11.

3.1.3.7. Ethyl 3-(4-ethylphenoxy)-6-hydroxy-2,4,5-trimethylbenzoate (6g). Starting with 1,3-bis(silyl enol ether) **5b** (500 mg, 1.7 mmol), 3-(siloxy)alk-2-en-1-one **4c** (507 mg, 1.7 mmol) and $TiCl_4$ (0.18 mL, 1.7 mmol), **6g** was isolated as a colourless solid (200 mg, 36%), mp 49–50 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.20 (t, 3H, *J*=7.5 Hz, CH_3), 1.39 (t, 3H, *J*=7.1 Hz, CH_3), 2.08 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.58 (q, 2H, *J*=7.5 Hz, CH_2), 4.41 (q, 2H, *J*=7.1 Hz, OCH_2), 6.63 (d, 2H, *J*=8.7 Hz, ArH), 7.06 (d, 2H, *J*=8.7 Hz, ArH), 11.51 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.9, 13.9, 14.1, 15.3, 15.6 (CH_3), 27.9, 61.6 (CH_2), 110.3 (C), 114.3 (2C, CH), 123.9 (C), 128.8 (2C, CH), 130.3, 136.9, 138.2, 143.6, 156.3, 157.7, 172.0 (C); IR (KBr): $\tilde{\nu}$ = 2969 (m), 1651 (s), 1599 (m), 1492 (s), 1394 (s), 1320 (s), 1221 (s), 1052 (m), 748 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 328.2 (M^+, 31), 282.2 (100), 254.2 (13), 225.1 (8); HRMS (EI): calcd for $C_{20}H_{24}O_4$ $[M]^+$: 328.14543; found: 328.14541.

3.1.3.8. Methyl 3-(4-chlorophenoxy)-6-hydroxy-2,4-dimethylbenzoate (6h). Starting with 1,3-bis(silyl enol ether) **5d** (500 mg, 1.9 mmol), 3-(siloxy)alk-2-en-1-one **4d** (574 mg, 1.9 mmol) and $TiCl_4$ (0.21 mL, 1.9 mmol), **6h** was isolated as a colourless solid (315 mg, 54%), mp 83 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.09 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 6.67 (d, 2H, *J*=9.0 Hz, ArH), 6.76 (s, 1H, ArH), 7.20 (d, 2H, *J*=9.0 Hz, ArH), 11.10 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.2, 17.1, 52.2 (CH_3), 111.1 (C), 115.7 (2C), 117.6 (CH), 126.3 (C), 129.6 (2C, CH), 133.5, 139.7, 143.6, 156.5, 159.7, 171.7 (C); IR (KBr): $\tilde{\nu}$ = 3431 (m), 2959 (w), 1661 (s), 1486 (s), 1442 (m), 1361 (m), 1326 (s), 1318 (s), 1074 (m), 825 (m), 803 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 306 (M^+, 33), 274 (100), 246 (10), 163.1 (8); elemental analysis: calcd (%) for $C_{16}H_{15}ClO_4$ (306.74): C 62.65, H 4.93; found: C 62.42, H 4.68.

3.1.3.9. Ethyl 3-(4-chlorophenoxy)-6-hydroxy-2,4,5-trimethylbenzoate (6i). Starting with 1,3-bis(silyl enol ether) **5b** (662 mg, 2.1 mmol), 3-(siloxy)alk-2-en-1-one **4d** (654 mg, 2.1 mmol) and $TiCl_4$ (0.24 mL, 2.1 mmol), **6i** was isolated as a colourless solid (325 mg, 43%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.40 (t, 3H, *J*=7.1 Hz, CH_3), 2.06 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.42 (q, 2H, *J*=7.1 Hz, OCH_2), 6.66 (d, 2H, *J*=9.0 Hz, ArH), 7.19 (d, 2H, *J*=9.0 Hz, ArH), 11.52 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.8, 13.7, 14.1, 15.2 (CH_3), 61.6 (CH_2), 110.4 (C), 115.8 (2C, CH), 124.2, 126.1 (C), 129.5 (2C, CH), 130.0, 137.7, 143.2, 156.9, 157.9, 171.8 (C); IR (KBr): $\tilde{\nu}$ = 2978 (w), 1650 (s), 1484 (s), 1398 (m), 1316 (s), 1221 (s), 1033 (m), 805 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 334.1 (M^+, 34), 288.1 (100), 260.1 (20); elemental analysis: calcd (%) for $C_{18}H_{19}ClO_4$ (334.79): C 64.57, H 5.72; found: C 64.26, H 5.86.

3.1.3.10. Ethyl 4-ethyl-3-(4-chlorophenoxy)-6-hydroxy-2,4-dimethylbenzoate (6j). Starting with 1,3-bis(silyl enol ether) **5c** (662 mg, 2.1 mmol), 3-(siloxy)alk-2-en-1-one **4d** (654 mg, 2.1 mmol) and $TiCl_4$ (0.24 mL, 2.1 mmol), **6j** was isolated as a colourless solid (325 mg, 43%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.12 (t, 3H, *J*=7.5 Hz, CH_3), 1.40 (t, 3H, *J*=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.72 (q, 2H, *J*=7.5 Hz, CH_2), 4.42 (q, 2H, *J*=7.1 Hz, OCH_2), 6.67 (d, 2H, *J*=9.0 Hz, ArH), 7.20 (d, 2H, *J*=9.0 Hz, ArH), 11.48 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.0, 13.2, 14.1, 15.3 (CH_3), 19.7, 61.6 (CH_2), 110.6 (C), 115.8 (2C, CH), 126.1 (C), 129.5 (2C, CH), 130.2, 130.3, 137.1, 143.3, 156.8, 157.8, 171.8 (C); IR (KBr): $\tilde{\nu}$ = 2978 (w), 1650 (s), 1484 (s), 1398 (m), 1316 (s), 1221 (s), 1033 (m), 805 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 347.9 (M^+, 51), 301.9 (100), 273.9 (38); elemental analysis: calcd (%) for $C_{19}H_{21}ClO_4$ (347.9): C 65.42, H 6.07; found: C 65.80, H 6.22.

3.1.3.11. 1-(3-(4-Chlorophenoxy)-6-hydroxy-2,4-dimethylphenyl)ethanone (6k). Starting with 1,3-bis(silyl enol ether) **5e** (500 mg, 2.0 mmol), 3-(siloxy)alk-2-en-1-one **4d** (609 mg, 2.0 mmol) and $TiCl_4$ (2.04 mL, 2.0 mmol), **6k** was isolated as a yellow solid (205 mg, 35%); ^1H NMR (400 MHz, $CDCl_3$): δ=2.09 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 6.69 (d, 2H, *J*=9.0 Hz, ArH), 6.76 (s, 1H, ArH), 7.22 (d, 2H, *J*=9.0 Hz, ArH), 11.94 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.0, 17.2, 33.0 (CH_3), 115.7 (2C), 118.4 (CH), 120.9, 126.5 (C), 129.7 (2C, CH), 131.7, 140.2, 143.6, 156.4, 159.3, 205.3 (C); IR (KBr): $\tilde{\nu}=3341$ (w), 2925 (w), 1629 (m), 1485 (s), 1296 (m), 1227 (s), 1091 (m), 827 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 290.0 (M^+, 95), 275.0 (100), 165.0 (43); HRMS (EI): calcd for $C_{16}H_{15}ClO_3$ $[M]^+$: 290.07042; found: 290.07056.

3.1.3.12. Ethyl 3-(4-methoxyphenoxy)-6-hydroxy-2,4-dimethylbenzoate (6l). Starting with 1,3-bis(silyl enol ether) **5a** (589 mg, 2.1 mmol), 3-(siloxy)alk-2-en-1-one **4e** (627 mg, 2.1 mmol) and $TiCl_4$ (0.23 mL, 2.1 mmol), **6l** was isolated as a colourless solid (344 mg, 52%), mp 88–89 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=1.41 (t, 3H, *J*=7.1 Hz, CH_3), 2.11 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 6.67 (d, 2H, *J*=9.1 Hz, ArH), 6.76 (s, 1H, ArH), 6.80 (d, 2H, *J*=9.1 Hz, ArH), 11.67 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 15.3, 17.2, 55.6 (CH_3), 61.6 (CH_2), 111.1 (C), 114.7 (2C), 115.0 (2C), 117.4 (CH), 133.8, 139.9, 144.2, 152.0, 154.1, 159.5, 171.3 (C); IR (KBr): $\tilde{\nu}=3423$ (w), 2993 (m), 1659 (s), 1505 (s), 1405 (s), 1374 (m), 1316 (s), 1217 (s), 1075 (m), 824 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 316.2 (M^+, 58), 270.2 (100), 199.1 (5), 135.1 (14); elemental analysis: calcd (%) for $C_{18}H_{20}O_5$ (316.34): C 68.34, H 6.37; found: C 68.13, H 6.67.

3.1.3.13. Ethyl 3-(3,4-dimethoxyphenoxy)-6-hydroxy-2,4-dimethylbenzoate (6m). Starting with 1,3-bis(silyl enol ether) **5a** (500 mg, 1.8 mmol), 3-(siloxy)alk-2-en-1-one **4f** (590 mg, 1.8 mmol) and $TiCl_4$ (0.19 mL, 1.8 mmol), **6m** was isolated as a colourless solid (362 mg, 58%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.41 (t, 3H, *J*=7.1 Hz, CH_3), 2.11 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 6.05 (dd, 1H, *J*=2.8, 8.7 Hz, ArH), 6.52 (d, 1H, *J*=2.8 Hz, ArH), 6.68 (d, 1H, *J*=8.7 Hz, ArH), 6.76 (s, 1H, ArH), 11.17 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 15.3, 17.2, 55.8, 56.3 (CH_3), 61.6 (CH_2), 100.0, 104.0 (CH), 111.1 (C), 111.7, 117.4 (CH), 133.8, 139.9, 143.7, 144.0, 150.0, 152.4, 159.5, 171.3 (C); IR (KBr): $\tilde{\nu}=3426$ (w), 2939 (m), 1659 (s), 1512 (s), 1466 (s), 1450 (s), 1393 (m), 1260 (m), 1211 (s), 1124 (m), 1023 (m), 802 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 346.2 (M^+, 65), 300.2 (100), 285.1 (19), 150.1 (7); elemental analysis: calcd (%) for $C_{19}H_{22}O_6$ (346.37): C 65.88, H 6.40; found: C 66.10, H 6.04.

3.1.3.14. Ethyl 3-(3,4-dimethoxyphenoxy)-6-hydroxy-2,4,5-trimethylbenzoate (6n). Starting with 1,3-bis(silyl enol ether) **5b** (500 mg, 1.7 mmol), 3-(siloxy)alk-2-en-1-one **4f** (562 mg, 1.7 mmol) and $TiCl_4$ (0.18 mL, 1.7 mmol), **6n** was isolated as a colourless solid (215 mg, 35%), mp 110–111 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=1.40 (t, 3H, *J*=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.42 (q, 2H, *J*=7.1 Hz, OCH_2), 6.02 (dd, 1H, *J*=2.8 Hz, 8.7 Hz, ArH), 6.52 (d, 1H, *J*=2.8 Hz, ArH), 6.67 (d, 1H, *J*=8.7 Hz, ArH), 11.51 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.8, 13.8, 14.1, 15.3, 55.8, 56.3 (CH_3), 61.6 (CH_2), 100.1, 104.1 (CH), 110.3 (C), 111.7 (CH), 123.9, 130.3, 138.2, 143.64, 143.69, 150.0, 152.7, 157.7, 171.9 (C); IR (KBr): $\tilde{\nu}=3442$ (w), 2992 (m), 1643 (s), 1510 (s), 1447 (m), 1393 (m), 1312 (s), 1260 (s), 1212 (s), 1192 (s), 1131 (m), 836 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 360.2 (M^+, 49), 314.2 (100), 215.1 (2), 138.1 (6); elemental analysis: calcd (%) for $C_{20}H_{24}O_6$ (360.40): C 66.65, H 6.71; found: C 66.47, H 7.14.

3.1.3.15. Ethyl 3-(4-bromophenoxy)-6-hydroxy-2,4-dimethylbenzoate (6o). Starting with 1,3-bis(silyl enol ether) **5a** (400 mg, 1.4 mmol), 3-(siloxy)alk-2-en-1-one **4g** (497 mg, 1.4 mmol) and $TiCl_4$ (0.16 mL, 1.4 mmol), **6o** was isolated as a yellow solid (305 mg, 58%), mp 50–52 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.41 (t, 3H, *J*=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 4.42 (q, 2H, *J*=7.1 Hz, OCH_2), 6.63 (d, 2H, *J*=9.0 Hz, ArH), 6.76 (s, 1H, ArH), 7.34 (d, 2H, *J*=9.0 Hz, ArH), 11.19 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 15.3, 17.1 (CH_3), 61.7 (OCH_2), 111.2, 113.6 (C), 116.0 (CH_{Ar}), 117.6 (C), 132.5 (CH_{Ar}), 139.5, 143.5, 157.1, 159.7, 171.2 (C); IR (KBr): $\tilde{\nu}=3430$ (w), 2995 (m), 1660 (s), 1483 (s), 1373 (s), 1346 (m), 1316 (s), 1217 (s), 1067 (m), 1058 (m), 1003 (m), 836 (s), 799 (s), 599 (m), 501 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 366 (M^+, ^{81}Br 30), 364 (^{79}Br, 30), 320 (100), 318 (99), 163 (8); elemental analysis: calcd (%) for $C_{17}H_{17}O_4Br$ (365.218): C 55.91, H 4.69; found: C 56.19, H 4.33.

3.1.3.16. Benzyl 3-(4-bromophenoxy)-6-hydroxy-2,4-dimethylbenzoate (6p). Starting with 1,3-bis(silyl enol ether) **5f** (300 mg, 0.89 mmol), 3-(siloxy)alk-2-en-1-one **4g** (306 mg, 0.89 mmol) and $TiCl_4$ (0.09 mL, 0.89 mmol), **6p** was isolated as a yellow solid (220 mg, 59%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.91 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 6.52 (d, 2H, *J*=7.1 Hz, ArH), 6.64 (s, 1H, ArH), 6.71 (d, 2H, *J*=7.1 Hz, ArH), 7.22–7.35 (m, 5H, ArH), 11.21 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.5, 17.2 (CH_3), 67.5 (OCH_2), 111.6, 113.6 (C), 116.0, 116.2, 117.6 (CH_{Ar}), 128.5, 128.6, 132.5, 132.7 (CH_{Ar}), 134.9, 139.8, 143.5, 157.0, 159.9, 171.0, 186.2 (C); IR (KBr): $\tilde{\nu}=3033$ (w), 2959 (w), 1662 (s), 1428 (s), 1385 (m), 1309 (s), 1229 (s), 1162 (m), 1069 (s), 1005 (m), 828 (s), 697 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 428 (M^+, ^{81}Br 93), 426 (^{79}Br, 90), 320 (88), 318 (87), 91 (100); HRMS (EI): calcd for $C_{22}H_{19}BrO_4$ $[M]^+$: 426.045476; found: 426.046612.

3.1.3.17. Ethyl 3-(4-cyanophenoxy)-6-hydroxy-2,4-dimethylbenzoate (6q). Starting with 1,3-bis(silyl enol ether) **5a** (500 mg, 1.82 mmol), 3-(siloxy)alk-2-en-1-one **4h** (530 mg, 1.82 mmol) and $TiCl_4$ (0.20 mL, 1.82 mmol), **6q** was isolated as a colourless solid (284 mg, 50%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.41 (t, 3H, *J*=7.1 Hz, CH_3), 2.08 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.44 (q, 2H, *J*=7.1 Hz, OCH_2), 6.80 (d, 2H, *J*=8.5 Hz, ArH), 6.84 (s, 1H, ArH), 7.57 (d, 2H, *J*=8.5 Hz, ArH), 11.22 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 15.2 (CH_3), 61.8 (OCH_2), 105.1, 111.3 (C), 115.4, 117.8 (CH_{Ar}), 118.8, 133.3 (C), 134.3 (CH_{Ar}), 139.0, 142.8, 143.7, 160.1, 161.3, 171.1 (C); IR (KBr): $\tilde{\nu}=3390$ (w), 2953 (w), 1738 (s), 1611 (s), 1296 (m), 1223 (s), 1165 (m), 827 (m), 732 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 311 (M^+, 26), 265 (100), 135 (4); elemental analysis: calcd (%) for $C_{18}H_{17}O_4N$ (311.34): C 69.44, H 4.49; found: C 69.32, H 4.35.

3.1.3.18. Benzyl 3-(4-cyanophenoxy)-6-hydroxy-2,4-dimethylbenzoate (6r). Starting with 1,3-bis(silyl enol ether) **5f** (400 mg, 1.19 mmol), 3-(siloxy)alk-2-en-1-one **4h** (340 mg, 1.19 mmol) and $TiCl_4$ (0.13 mL, 1.19 mmol), **6r** was isolated as a yellow oil (292 mg, 54%); ^1H NMR (300 MHz, $CDCl_3$): δ=2.02 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 5.35 (s, 2H, OCH_2), 6.76 (d, 2H, J=9.0 Hz, ArH), 7.20 (s, 1H, ArH), 7.30–7.37 (m, 5H, Ph), 7.50 (d, 2H, J=9.0 Hz, ArH), 11.11 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.4, 15.7 (CH_3), 67.5 (CH_2), 105.0, 111.1 (C), 115.3, 118.8 (CH_{Ar}), 118.7 (C), 125.1, 128.1 (CH_{Ar}), 128.6 (C), 133.2 (CH_{Ar}), 134.7, 139.3, 142.7, 160.1, 161.1, 170.8 (C); MS (EI, 70 eV): m/z (%): 373 (M^+, 34), 265 (13), 91 (100); elemental analysis: calcd (%) for $C_{23}H_{19}NO_4$ (373.40): C 73.98, H 5.13, N 3.75; found: C 73.51, H 4.98, N 3.72.

3.1.3.19. Ethyl 3-(4-methylacetatephenoxy)-6-hydroxy-2,4-dimethylbenzoate (6s). Starting with 1,3-bis(silyl enol ether) **5a** (400 mg, 1.45 mmol), 3-(siloxy)alk-2-en-1-one **4i** (480 mg, 1.45 mmol) and $TiCl_4$ (0.16 mL, 1.45 mmol), **6s** was isolated as a colourless solid (259 mg, 50%), mp 72–73 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.40 (t, 3H, J=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.55 (s, 2H, CH_2), 3.68 (s, 3H, OCH_3), 4.42 (q, 2H, J=7.1 Hz, OCH_2), 6.69 (d, 2H, J=8.7 Hz, ArH), 6.75 (s, 1H, ArH), 7.15 (d, 2H, J=8.7 Hz, ArH), 11.17 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 15.3, 17.2 (CH_3), 40.1 (CH_2), 51.9 (OCH_3), 61.6 (OCH_2), 111.1 (C), 114.5, 117.4 (CH_{Ar}), 126.8 (C), 130.4 (CH_{Ar}), 136.6, 139.7, 143.7, 157.6, 159.5, 171.3, 172.1 (C); IR (KBr): $\tilde{\nu}$ = 3438 (w), 2987 (s), 1740 (s), 1605 (s), 1505 (s), 1318 (s), 1216 (s), 1143 (s), 1012 (m), 874 (m), 802 (s), 642 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 358 (M^+, 28), 312 (100), 253 (13); elemental analysis: calcd (%) for $C_{20}H_{22}O_6$ (358.39): C 67.03, H 6.19; found: C 67.38, H 6.37.

3.1.3.20. Benzyl 6-hydroxy 3-(4-(2-methoxy-2-oxoethyl)phenoxy)-2,4-dimethylbenzoate (6t). Starting with 1,3-bis(silyl enol ether) **5f** (500 mg, 1.49 mmol), 3-(siloxy)-alk-2-en-1-one **4i** (500 mg, 1.49 mmol) and $TiCl_4$ (0.16 mL, 1.49 mmol), **6t** was isolated as a yellow solid (292 mg, 54%), mp 66–67 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.09 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.54 (s, 2H, CH_2), 3.68 (s, 3H, OCH_3), 5.39 (s, 2H, OCH_2), 6.67 (d, 2H, J=8.7 Hz, ArH), 6.76 (s, 1H, ArH), 7.25 (d, 2H, J=8.7 Hz, ArH), 7.35–7.43 (m, 5H, Ph), 11.11 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.6, 17.2 (CH_3), 40.1 (CH_2), 67.5 (CH_2), 110.9 (C), 114.4, 114.5, 117.5 (CH_{Ar}), 126.9 (C), 128.3, 128.5, 128.6, 130.5, 130.7 (CH_{Ar}), 133.7, 134.9, 140.1, 143.7, 157.0, 159.7, 171.1, 172.2; IR (KBr): $\tilde{\nu}$ = 3441 (w), 2955 (m), 1736 (s), 1655 (s), 1612 (m), 1509 (s), 1435 (m), 1387 (s), 1313 (s), 1231 (s), 1161 (s), 1055 (m), 908 (m), 803 (s), 751 (s), 695 (s), 585 (m); elemental analysis: calcd (%) for $C_{25}H_{24}O_6$ (420.45): C 71.41, H 5.75; found: C 71.51, H 5.38.

3.1.3.21. Ethyl 3-(4-(2-methoxy-2-oxoethyl)phenoxy)-5-hydroxy-4-*n*-hexyl-2,4-dimethylbenzoate (6u). Starting with 1,3-bis(silyl enol ether) **5g** (500 mg, 1.39 mmol), 3-(siloxy)alk-2-en-1-one **4i** (460 mg, 1.39 mmol) and $TiCl_4$ (0.15 mL, 1.39 mmol), **6u** was isolated as a yellow oil (292 mg, 54%); ^1H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, 3H, J=6.9 Hz, CH_3), 1.28–1.32 (m, 8H, CH_2), 1.39 (t, 3H, J=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.67 (t, 2H, J=8.2 Hz, CH_2), 3.56 (s, 2H, OCH_2), 3.69 (s, 2H, CH_2), 4.11 (q, 2H, J=7.1 Hz, OCH_2), 6.67 (d, 2H, J=8.7 Hz, ArH), 7.15 (d, 2H, J=8.7 Hz, ArH), 11.42 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.3, 14.0, 15.3 (CH_3), 22.6, 26.5, 29.0, 29.6, 31.7, 40.2 (CH_2), 52.0 (OCH_3), 61.5 (CH_2), 110.5 (C), 114.6 (CH_{Ar}), 126.7, 128.9, 130.3 (C), 130.4 (CH_{Ar}), 137.6, 143.4, 157.3, 157.8, 171.9, 172.3 (C); IR (KBr): $\tilde{\nu}$ = 2954 (s), 2928 (s), 1742 (s), 1655 (s), 1609 (m), 1373 (m), 1315 (s), 1222 (s), 1159 (m), 1052 (s), 1014 (m), 806 (s) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 442 (M^+, 100), 396 (63), 367 (46), 353 (34), 326 (90), 233 (33); elemental analysis: calcd (%) for $C_{28}H_{34}O_6$ (442.56): C 70.56, H 7.74; found: C 70.21, H 7.30.

3.1.3.22. Methyl 2-(4-(3-acetyl-4-hydroxy-2,4-dimethyl)phenoxy)phenylacetate (6v). Starting with 1,3-bis(silyl enol ether) **5e** (400 mg, 1.63 mmol), 3-(siloxy)alk-2-en-1-one **4i** (540 mg, 1.63 mmol) and $TiCl_4$ (0.17 mL, 1.6 mmol), **6v** was isolated as a yellow oil (280 mg, 55%); ^1H NMR (300 MHz, $CDCl_3$): δ=2.09 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 3.57 (s, 2H, CH_2), 3.69 (s, 3H, OCH_3), 6.71 (d, 2H, J=8.6 Hz, ArH), 6.75 (s, 1H, ArH), 7.17 (d, 2H, J=8.6 Hz, ArH), 11.91 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.0, 17.2, 33.0 (CH_3), 40.0 (CH_2), 51.9 (OCH_3), 114.4, 118.4 (CH_{Ar}), 120.8, 127.0 (C), 130.5 (CH_{Ar}), 131.7, 140.3, 143.7, 156.8, 157.0, 172.0, 186.3, 205.3 (C); IR (KBr): $\tilde{\nu}$ = 3390 (w), 2953 (w), 1738 (s), 1611 (s), 1296 (m), 1223 (s), 1165 (m), 827 (m), 732 (s) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 311 (M^+, 26), 265 (100), 135 (4); elemental analysis: calcd (%) for $C_{19}H_{22}O_4$ (314.38): C 72.59, H 7.05; found: C 72.23, H 7.06.

3.1.3.23. Ethyl 3-(4-methoxyphenoxy)-6-hydroxy-2,4,5-trimethylbenzoate (6w). Starting with 1,3-bis(silyl enol ether) **5b** (341 mg, 1.2 mmol), 3-(siloxy)alk-2-en-1-one **4e** (353 mg, 1.2 mmol) and $TiCl_4$ (0.13 mL, 1.2 mmol), **6w** was isolated as a colourless solid (120 mg, 30%); ^1H NMR (400 MHz, $CDCl_3$): δ=1.40 (t, 3H, J=7.1 Hz, CH_3), 2.08 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.42 (q, 2H, J=7.1 Hz, OCH_2), 6.65 (d, 2H, J=9.1 Hz, ArH), 6.78 (d, 2H, J=9.1 Hz, ArH), 11.51 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=10.8, 12.8, 13.1, 14.3, 54.6 (CH_3), 60.5 (CH_2), 109.3 (C), 113.7 (2C), 114.1 (2C, CH), 122.9, 129.3, 137.2, 142.8, 151.3, 153.0, 156.7, 170.9 (C); IR (KBr): $\tilde{\nu}$ = 2969 (m), 1651 (s), 1599 (m), 1492 (s), 1394 (s), 1320 (s), 1221 (s), 1052 (m), 748 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 330.2 (M^+, 44), 284.2 (100); HRMS (EI): calcd for $C_{19}H_{22}O_5$ $[M]^+$: 330.14618; found: 330.14616.

Acknowledgements

Financial support by the state of Pakistan (HEC scholarship for M.A.R.) and by the state of Mecklenburg-Vorpommern (Landesgraduiertenstipendium for Z.A.) is gratefully acknowledged.

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