Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 12562–12575

Regioselective synthesis of 4-chlorophenols, 10-chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-ones, and 4-chloro-1-hydroxy-9*H*-fluoren-9-ones based on [3+3] cyclizations of 1,3-bis(silyloxy)-1,3-dienes with 2-chloro-3-silyloxy-2-en-1-ones

Mirza Arfan Yawer,[a] Ibrar Hussain,[a] Stefanie Reim,[a] Zafar Ahmed,[a,b] Ehsan Ullah,[a,b] Inam Iqbal,[a] Christine Fischer,[b] Helmut Reinke,[a] Helmar Görls[c] and Peter Langer[a,b,*]

[a]*Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany*
[b]*Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany*
[c]*Institut für Anorganische und Analytische Chemie, Universität Jena, August-Bebel-Str. 2, 07740 Jena, Germany*

Received 23 August 2007; revised 1 October 2007; accepted 4 October 2007
Available online 7 October 2007

Abstract—A variety of 4-chlorophenols, 10-chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-ones, and 4-chloro-1-hydroxy-9*H*-fluoren-9-ones were prepared by formal [3+3] cyclizations of 1,3-bis(silyloxy)-1,3-dienes with 2-chloro-3-(silyloxy)alk-2-en-1-ones.

1. Introduction

4-Chlorophenols are of considerable pharmacological relevance and occur in a variety of natural products. This includes dibenzo[*b*,*e*][1,4]dioxepin-11-ones,[1] spirocycles (e.g. aspirochlorins, grisandions, griseofulvins),[2,10] xanthones (austocystin A),[3] tetracyclins,[4] isochromanones (ochratoxin A),[5] terpenes (ascofuranol, ascochlorin),[6] macrocycles (radicicol, bazzanin K),[7] dibenzo[*b*,*d*]pyran-6-ones (graphislactone G),[8] oligosaccharides (flambamycin),[9] benzophenones,[10] polycycles,[11] arenes,[12] and biaryls (ambigol A).[13] Chloroarenes also represent useful starting materials in transition metal catalyzed cross-coupling reactions.[14,15]

Classic syntheses of functionalized chlorophenols, based on chlorination of phenols, often suffer from low regioselectivities and yields. A few syntheses of 4-chlorophenols based on [4+2] cycloadditions of chloro-substituted buta-1,3-dienes have been reported. For example, Brassard and Savard reported the synthesis of a chlorinated anthraquinone by [4+2] cycloaddition of 2-chloro-1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene with 2-chloronaphthoquinone.[16a] A 4-chlorophenol was prepared also by [4+2] cycloaddition of a chlorinated thiophene with dimethyl acetylenedicarboxylate.[16b] Some years ago, Chan and co-workers reported[17] an elegant approach to salicylates based on [3+3] cyclizations of 1,3-bis(silyl enol ethers),[18] which can be regarded as electroneutral equivalents of 1,3-dicarbonyl dianions.[19] Recently, we reported the application of this method to the synthesis of functionalized 4-chlorophenols.[20] Herein, we report full details of these studies. With regard to our preliminary communication, the preparative scope was greatly extended and a variety of novel chlorinated phenols and biaryls were regioselectively prepared. In addition, the synthesis of novel 10-chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-ones (dibenzo[*b*,*d*]pyran-6-ones, biaryl lactones) and 4-chloro-1-hydroxy-9*H*-fluoren-9-ones, based on regioselective [3+3] cyclizations, is reported. Notably, the functionalized chlorinated arenes reported herein are not readily available by other methods.

2. Results and discussion

2.1. 4-Chlorophenols

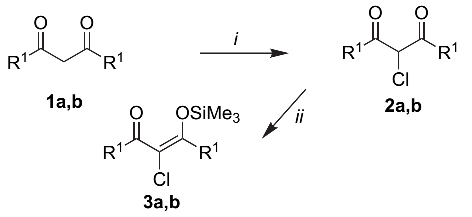
2-Chloro-1,3-diketones **2a**,**b** are readily available by reaction of 1,3-diketones with *N*-chlorosuccinimide (NCS).[21] The reaction of **2a** and **2b** with Me_3SiCl/NEt_3 afforded 2-chloro-3-(silyloxy)alk-2-en-1-ones **3a**[22] and **3b**, respectively (Scheme 1). 1,3-Bis(silyl enol ethers) **4a**–**j** were prepared from the corresponding β-ketoesters as reported.[23,24] The $TiCl_4$ mediated [3+3] cyclization of **3a**,**b** with 1,3-bis(silyl enol ethers) **4a**–**j** afforded the desired 4-chlorophenols **5a**–**l** (Scheme 2, Table 1). The cyclizations were carried

---

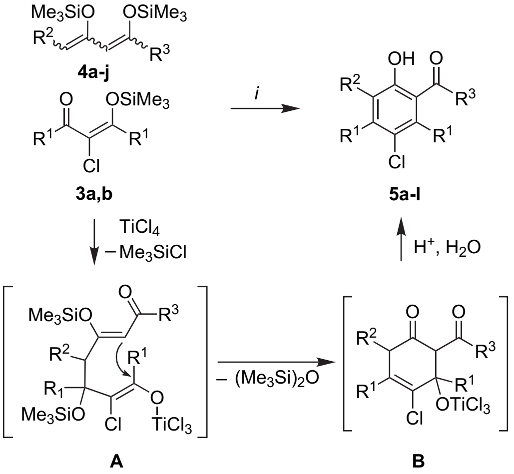
* Corresponding author. Tel.: +49 381 4986410; fax: +49 381 4986412; e-mail: peter.langer@uni-rostock.de

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.10.027

following the general procedure reported for related cyclizations.[17,19] During optimization, the (high) concentration, the stoichiometry, and the temperature proved to be important parameters.



Scheme 1. Synthesis of 2-chloro-3-silyloxy-2-en-1-ones **3a**,**b**. Conditions: (i) NCS (1 equiv), CCl_4, 75–80 °C; (ii) NEt_3 (1.6 equiv), Me_3SiCl (1.8 equiv), C_6H_6, 20 °C.



Scheme 2. Synthesis of 4-chlorophenols **5a**–**l**. Conditions: (i) $TiCl_4$, CH_2Cl_2, −78→20 °C.

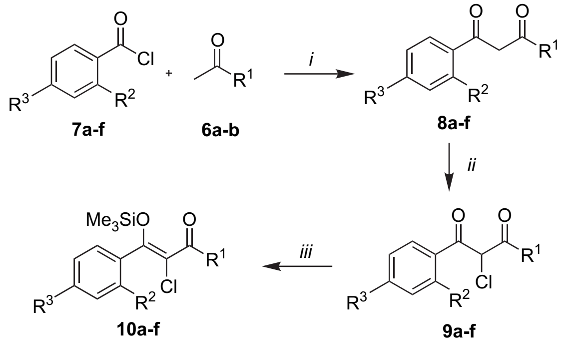
Table 1. Synthesis of chlorinated phenols **5a**–**l**

3	4	5	R^1	R^2	R^3	%[a] (**5**)
a	**a**	**a**	Me	H	OMe	62
a	**b**	**b**	Me	H	Me	50
a	**c**	**c**	Me	H	Ph	44
a	**d**	**d**	Me	Me	OEt	55
a	**e**	**e**	Me	Et	OEt	56
a	**f**	**f**	Me	OMe	OMe	67
a	**g**	**g**	Me	^{n}Bu	OMe	53
a	**h**	**h**	Me	$(CH_2)_3Ph$	OMe	36
a	**i**	**i**	Me	$(CH_2)_6Cl$	OMe	26
a	**j**	**j**	Me	H	$(CH_2)_2OMe$	35
b	**a**	**k**	Et	H	OMe	52
b	**e**	**l**	Et	Et	OEt	54

[a] Isolated yields.

2.2. 3-Aryl-4-chlorophenols

The 2-chloro-3-(silyloxy)alk-2-en-1-ones **10a**–**f** were prepared as follows. The LDA mediated reaction of ketones **6a**,**b** with benzoyl chlorides **7a**–**f** afforded the 1,3-diketones **8a**–**f**. The chlorination of the latter with NCS afforded the products **9a**–**f**, which were transformed into **10a**–**f** by silylation (Scheme 3, Table 2). The $TiCl_4$ mediated cyclization of 1,3-bis(silyl enol ethers) **4a**,**b**,**e**,**k** with 2-chloro-3-(silyloxy)alk-2-en-1-ones **10a**–**f** afforded the chlorinated biaryls **11a**–**r** (Scheme 4, Table 3).



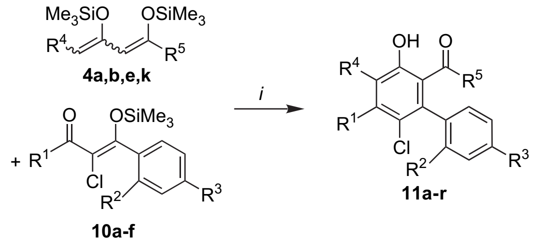
Scheme 3. Synthesis of 2-chloro-3-silyloxy-2-en-1-ones **10a**–**f**. Conditions: (i) LDA (1.5 equiv), THF; (ii) NCS (1 equiv), CCl_4, 75–80 °C; (iii) NEt_3 (1.6 equiv), Me_3SiCl (1.8 equiv), C_6H_6, 20 °C.

Table 2. Synthesis of 2-chloro-3-silyloxy-2-en-1-ones **10a**–**f**

	R^1	R^2	R^3	%[a]		
				8	**9**	**10**
a	Me	H	H	—[b]	95	90
b	Me	H	F	36	66	80
c	Me	H	Cl	38	52	73
d	Me	Me	H	33	44	72
e	Me	OMe	H	37	47	76
f	^{n}Pr	OMe	H	72	81	84

[a] Isolated yields.

[b] Commercially available.



Scheme 4. Synthesis of 3-aryl-4-chlorophenols **11a**–**r**. Conditions: (i) $TiCl_4$, CH_2Cl_2, −78→20 °C.

Table 3. Synthesis of 3-aryl-4-chlorophenols **11a**–**r**

4	10	11	R^1	R^2	R^3	R^4	R^5	%[a] (**11**)
a	**a**	**a**	Me	H	H	H	OMe	49
k	**a**	**b**	Me	H	H	Me	OMe	31
b	**a**	**c**	Me	H	H	H	Me	43
e	**a**	**d**	Me	H	H	Et	OEt	43
a	**b**	**e**	Me	H	F	H	OMe	30
k	**b**	**f**	Me	H	F	Me	OMe	48
e	**b**	**g**	Me	H	F	Et	OEt	44
a	**c**	**h**	Me	H	Cl	H	OMe	44
k	**c**	**i**	Me	H	Cl	Me	OMe	34
e	**c**	**j**	Me	H	Cl	Et	OEt	47
a	**d**	**k**	Me	Me	H	H	OMe	26
k	**d**	**l**	Me	Me	H	Me	OMe	40
a	**e**	**m**	Me	OMe	H	H	OMe	47
k	**e**	**n**	Me	OMe	H	Me	OMe	50
e	**e**	**o**	Me	OMe	H	Et	OEt	42
a	**f**	**p**	^{n}Pr	OMe	H	H	OMe	34
k	**f**	**q**	^{n}Pr	OMe	H	Me	OMe	46
e	**f**	**r**	^{n}Pr	OMe	H	Et	OEt	51

[a] Isolated yields.

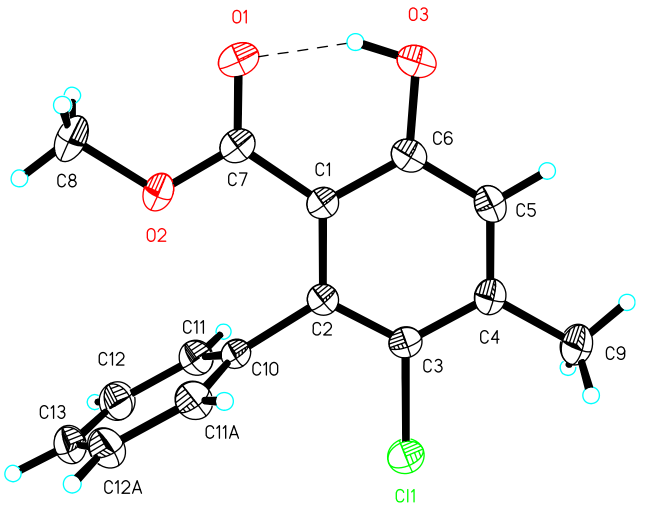


Figure 1. ORTEP of **11a**.

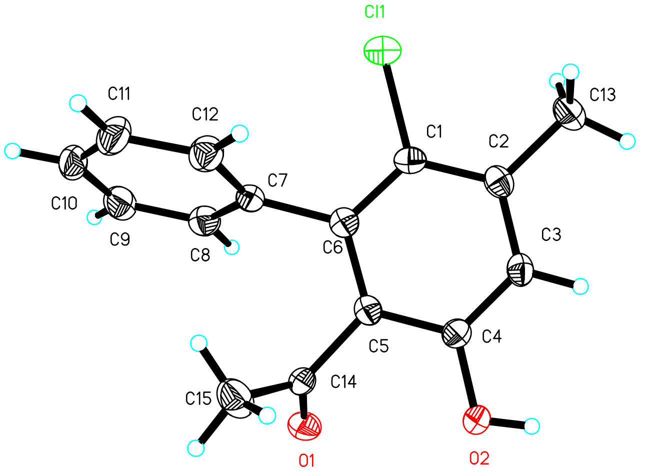


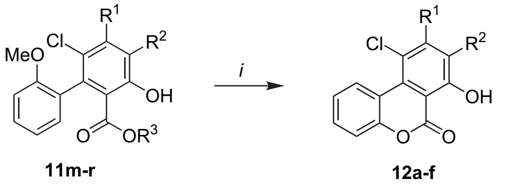
Figure 2. ORTEP of **11c**.

The structures of products **11a**,**c** were independently confirmed by X-ray crystal structure analyses (Figs. 1 and 2).[25]

2.3. 10-Chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-ones

The chlorinated biaryls **11m–r** contain an *ortho*-methoxy group located at one of the aryl groups. Treatment of **11m–r** with borontribromide and subsequent addition of an aqueous solution of potassium *tert*-butanolate, following a protocol recently reported by us,[26] afforded the novel 10-chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **12a–f** (Scheme 5, Table 4).

The structure of **12d** was independently confirmed by X-ray crystal structure analysis (Fig. 3).[25]



Scheme 5. Synthesis of dibenzo[*b*,*d*]pyran-6-ones **12a–f**. Conditions: (i) (1) BBr_3 (4 equiv), CH_2Cl_2, 0→20 °C, 18 h; (2) KO^{t}Bu, H_2O, 15 min, 20 °C.

Table 4. Synthesis of 6*H*-benzo[*c*]chromen-6-ones **12a–f**

11	**12**	R^1	R^2	R^3	%[a] (**12**)
m	**a**	Me	H	Me	73
n	**b**	Me	Me	Me	78
o	**c**	Me	Et	Et	67
p	**d**	^{n}Pr	H	Me	88
q	**e**	^{n}Pr	Me	Me	54
r	**f**	^{n}Pr	Et	Et	48

[a] Isolated yields.

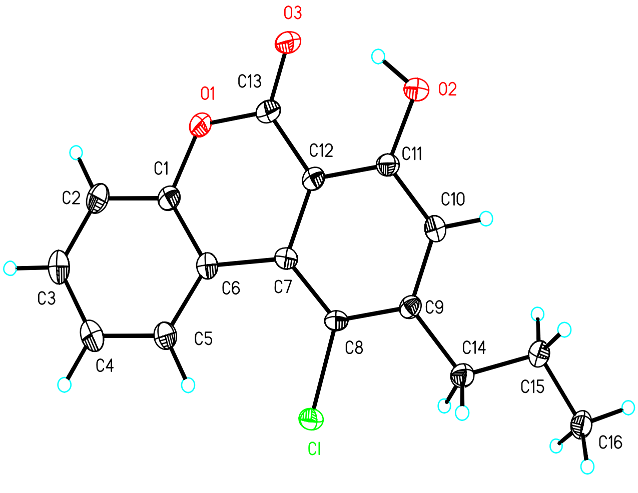
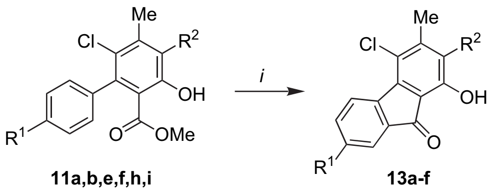


Figure 3. ORTEP of **12d**.

2.4. 4-Chloro-1-hydroxy-9*H*-fluoren-9-ones

The reaction of chlorinated biaryls **11a**,**b**,**e**,**f**,**h**,**i** with concd sulfuric acid, following a protocol recently reported by us,[27] afforded the novel chlorinated fluorenones **13a–f** by an intramolecular Friedel–Crafts acylation (Scheme 6, Table 5). The chloride and the fluoride functions proved to be compatible with the harsh reaction conditions.

In conclusion, a general method for the regioselective synthesis of chlorinated, sterically encumbered phenols and biaryls by formal [3+3] cyclizations of 1,3-bis(silyl enol



Scheme 6. Synthesis of fluorenones **13a–f**. Conditions: (i) concd H_2SO_4, 20 °C, 1 h.

Table 5. Synthesis of fluorenones **13a–f**

11	**13**	R^1	R^2	%[a] (**13**)
a	**a**	H	H	70
b	**b**	H	Me	86
e	**c**	F	H	61
f	**d**	F	Me	55
h	**e**	Cl	H	84
i	**f**	Cl	Me	74

[a] Isolated yields.

ethers) with 2-chloro-3-(silyloxy)alk-2-en-1-ones was reported. 4-Chlorophenols **5a–l** are isolated in moderate to good yields (except for **5i** containing a labile ω-chloroalkyl group). The 3-aryl-4-chlorophenols **11a–r** are formed in moderate yields. The yields mainly depend on the individual quality of the starting materials and on the handling of each individual experiment. The combination of the [3+3] cyclization with BBr_3 or acid mediated cyclization reactions provides a convenient approach to 10-chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **12** and 4-chloro-1-hydroxy-9*H*-fluoren-9-ones **13**. These transformations generally proceed in good yields.

3. Experimental section

3.1. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra, the deuterated solvents indicated were used. Mass spectrometric (MS) data 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. Methyl 3-chloro-6-hydroxy-2,4-dimethylbenzoate (5a). Starting with 1,3-bis-silyl enol ether **4a** (2.00 g, 7.6 mmol), silyl enol ether **3a** (1.58 g, 7.6 mmol), and $TiCl_4$ (0.85 mL, 7.6 mmol), **5a** was isolated as a colorless solid (1.01 g, 62%), mp=59–60 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=2.35 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 6.76 (s, 1H, ArH), 10.83 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.9, 21.9, 52.3 (CH_3), 111.9 (C), 117.4 (CH), 126.8, 137.9, 143.6, 159.9, 171.3 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3426 (w), 3000 (w), 2952 (s), 2874 (m), 1663 (s), 1603 (s), 1564 (s), 1449 (s), 1381 (m), 1358 (s), 1310 (s), 1229 (s), 1190 (s), 1104 (m), 943 (m). MS (EI, 70 eV): *m*/*z* (%)=216 ($[M]^+$, [^{37}Cl], 29), 214 ($[M]^+$, [^{35}Cl], 88), 184 (100), 154 (61), 91 (64). Elemental analysis calcd (%) for $C_{10}H_{11}ClO_3$ (214.65): C 55.95, H 5.16; found: C 55.97, H 5.12.

3.1.2. 1-(3-Chloro-6-hydroxy-2,4-dimethylphenyl)ethanone (5b). Starting with 1,3-bis-silyl enol ether **4b** (1.10 g, 4.5 mmol), silyl enol ether **3a** (930 mg, 4.5 mmol), and $TiCl_4$ (0.50 mL, 4.5 mmol), **5b** was isolated as a colorless solid (432 g, 49%), mp=99 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=2.35 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.61 (s, 3H, OCH), 6.75 (s, 1H, ArH), 11.15 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8, 21.7, 32.7 (CH_3), 117.9 (CH), 122.4, 126.8, 136.1, 143.8, 158.6, 205.4 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3176 (s), 1661 (s), 1606 (m), 1451 (m), 1398 (m), 1358 (m), 1310 (m), 1237 (s), 845 (m). MS (EI, 70 eV): *m*/*z* (%)=200 ($[M]^+$, [^{37}Cl], 12), 198 ($[M]^+$, [^{35}Cl], 36), 183.1 (100), 91.1 (22). Elemental analysis calcd (%) for $C_{10}H_1ClO_2$ (198.64): C 60.46, H 5.58; found: C 60.56, H 5.64.

3.1.3. (3-Chloro-6-hydroxy-2,4-dimethylphenyl)(phenyl)methanone (5c). Starting with 1,3-bis-silyl enol ether **4c** (1.50 g, 4.9 mmol), silyl enol ether **3a** (1.01 g, 4.9 mmol), and $TiCl_4$ (0.53 mL, 4.9 mmol), **5c** was isolated as a yellow solid (560 mg, 44%), mp=199 °C. ^1H NMR (250 MHz, acetone-d_6): δ=2.15 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 6.87 (s, 1H, ArH), 7.52–7.87 (m, 5H, ArH), 8.71 (s, 1H, OH). ^{13}C NMR (75 MHz, acetone-d_6): δ=17.6, 21.0 (CH_3), 116.6 (CH), 126.1, 127.9 (C), 129.6 (2C), 130.0 (2C), 134.3 (CH), 134.5, 138.5, 138.7, 153.3, 196.9 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3355 (s), 1657 (s), 1597 (m), 1578 (m), 1277 (m), 1239 (m), 1107 (m), 921 (m), 712 (w). GC–MS (EI, 70 eV): *m*/*z* (%)=262 ($[M]^+$, [^{37}Cl], 17), 260 ($[M]^+$, [^{35}Cl], 51), 259.1 (100), 242.0 (20), 224.1 (33), 183.0 (30), 105.1 (31), 77.1 (63). Elemental analysis calcd (%) for $C_{15}H_{13}ClO_2$ (260.72): C 69.10, H 5.03; found: C 69.12, H 5.08.

3.1.4. Ethyl 3-chloro-6-hydroxy-2,4,5-trimethylbenzoate (5d). Starting with 1,3-bis-silyl enol ether **4d** (500 mg, 1.7 mmol), silyl enol ether **3a** (359 mg, 1.7 mmol), and $TiCl_4$ (0.19 mL, 1.7 mmol), **5d** was isolated as a yellow oil (230 mg, 55%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.42 (t, 3H, *J*=7.0 Hz, CH_3), 2.20 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 11.60 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.5, 14.1, 18.3, 20.0 (CH_3), 61.8 (CH_2), 111.5, 123.9, 126.9, 134.5, 141.4, 158.0, 171.5 (C). IR (neat, cm^{-1}): $\tilde{\nu}$=2982 (m), 2935 (m), 1654 (s), 1599 (m), 1448 (m), 1381 (s), 1342 (m), 1305 (m), 1284 (s), 1243 (s), 1182 (s), 1099 (m), 1034 (m), 1015 (m), 801 (m). MS (EI, 70 eV): *m*/*z* (%)=244 ($[M]^+$, [^{37}Cl], 8), 242 ($[M]^+$, [^{35}Cl], 26), 196.0 (100), 168.0 (68), 105.0 (28), 77.0 (30). Elemental analysis calcd (%) for $C_{12}H_{15}ClO_3$ (242.70): C 59.38, H 6.22; found: C 59.42, H 5.99.

3.1.5. Ethyl 3-chloro-5-ethyl-6-hydroxy-2,4-dimethylbenzoate (5e). Starting with 1,3-bis-silyl enol ether **4e** (600 mg, 1.9 mmol), silyl enol ether **3a** (410 mg, 1.9 mmol), and $TiCl_4$ (0.21 mL, 1.9 mmol), **5e** was isolated as a yellow oil (285 mg, 56%). ^1H NMR (250 MHz, $CDCl_3$): δ=1.10 (t, 3H, *J*=7.3 Hz, CH_3), 1.42 (t, 3H, *J*=7.3 Hz, CH_3), 2.40 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 2.74 (q, 2H, *J*=7.6 Hz, CH_2), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 11.11 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.2, 14.1, 17.6, 20.0 (CH_3), 20.2, 61.8 (CH_2), 111.8, 127.2, 130.0, 134.6, 140.8, 157.8, 171.4 (C). IR (neat, cm^{-1}): $\tilde{\nu}$=2972 (m), 2935 (w), 2874 (w), 1655 (s), 1598 (m), 1447 (m), 1372 (s), 1306 (s), 1262 (s), 1231 (s), 1180 (s), 1110 (m), 1039 (m), 807 (m). MS (EI, 70 eV): *m*/*z* (%)=258 ($[M]^+$, [^{37}Cl], 12), 256 ($[M]^+$, [^{35}Cl], 35), 210.0 (100), 195.0 (17), 182.0 (99), 167.0 (14). Elemental analysis calcd (%) for $C_{13}H_{17}ClO_3$ (256.72): C 60.82, H 6.67; found: C 61.02, H 6.41.

3.1.6. Methyl 3-chloro-6-hydroxy-5-methoxy-2,4-dimethyl-benzoate (5f). Starting with 1,3-bis-silyl enol ether **4f** (0.436 g, 1.50 mmol), 3-chloro-4-trimethylsilanyloxypent-3-en-2-one (**3a**) (0.310 g, 1.50 mmol), and $TiCl_4$ (0.2 mL, 1.50 mmol) in CH_2Cl_2 (3 mL), **5f** was isolated after column chromatography (silica gel, *n*-heptane/EtOAc 20:1) as a white solid (0.246 g, 67%), mp 62–63 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.36 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 10.63 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.6, 19.5 (CH_3), 52.5, 60.3 (OCH_3), 113.0, 126.6, 132.4, 136.2, 145.1, 153.3 (C), 171.3 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2957 (m), 2944 (m), 2851 (w), 1740 (w), 1700 (w), 1656 (s), 1600 (w), 1560 (w), 1443 (s), 1406 (s), 1362 (s), 1308 (s), 1287 (s), 1257 (s), 1217 (s), 1166 (w), 1119 (w), 1078 (m), 1062 (m), 1037 (w), 1006 (m). MS (EI, 70 eV): *m*/*z* (%)=246 ($[M]^+$, [^{37}Cl], 15), 244 ($[M]^+$, [^{35}Cl], 43), 214 (35), 213 (33), 212 (100), 186 (31), 185 (25), 184 (94), 183 (48), 169 (33). Anal. Calcd for $C_{11}H_{13}ClO_4$ (244.67): C, 54.00; H, 5.36. Found: C, 54.16; H, 5.60.

3.1.7. Methyl 3-butyl-5-chloro-2-hydroxy-4,6-dimethylbenzoate (5g). Starting with 1,3-bis-silyl enol ether **4g** (0.475 g, 1.50 mmol), 3-chloro-4-trimethylsilanyloxy-pent-3-en-2-one (**3a**) (0.310 g, 1.50 mmol), and $TiCl_4$ (0.2 mL, 1.50 mmol) in CH_2Cl_2 (3 mL), **5g** was isolated after column chromatography (silica gel, *n*-heptane/EtOAc 20:1) as a white solid (0.217 g, 53%), mp 72–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92–0.97 (m, 3H, CH_3), 1.35–1.51 (m, 4H, CH_2), 2.39 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.71 (t, *J*=7.6 Hz, 2H, CH_2), 3.96 (s, 3H, OCH_3), 11.05 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 17.9, 20.1 (CH_3), 22.9, 26.8, 31.2 (CH_2), 52.3 (OCH_3), 111.6, 127.3, 128.9, 134.6, 141.3, 158.0 (C), 172.0 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3421 (br, w), 3018 (w), 2961 (s), 2929 (m), 2873 (m), 2860 (m), 1655 (s), 1599 (m), 1558 (w), 1438 (s), 1389 (s), 1363 (s), 1310 (s), 1280 (s), 1243 (s), 1194 (s), 1163 (s), 1117 (m), 1035 (m). MS (GC–MS, 70 eV): *m*/*z* (%)=272 ($[M]^+$, [^{37}Cl], 10), 270 ($[M]^+$, [^{35}Cl], 30), 225 (32), 223 (100), 196 (57), 195 (42). Anal. Calcd for $C_{14}H_{19}ClO_3$ (270.75): C, 62.10; H, 7.07. Found: C, 62.10; H, 7.11.

3.1.8. Methyl 3-chloro-6-hydroxy-2,4-dimethyl-5-(3-phenyl-propyl)-benzoate (5h). Starting with 1,3-bis-silyl enol ether **4h** (0.568 g, 1.50 mmol), 3-chloro-4-trimethylsilanyloxy-pent-3-en-2-one (**3a**) (0.310 g, 1.50 mmol), and $TiCl_4$ (0.2 mL, 1.50 mmol) in CH_2Cl_2 (3 mL), **5h** was isolated after column chromatography (silica gel, *n*-heptane/EtOAc 20:1) as a white solid (0.180 g, 36%), mp 50–52 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.77–1.87 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 2.70–2.79 (m, 4H, CH_2), 3.97 (s, 3H, OCH_3), 7.18–7.24 (s, 3H, CH), 7.27–7.32 (m, 2H, CH), 11.09 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=17.8, 20.0 (CH_3), 26.7, 30.4, 36.0 (CH_2), 52.3 (OCH_3), 111.6 (C), 125.7 (CH), 127.3 (C), 128.2, 128.3, 128.3, 128.4 (CH), 134.8, 141.3, 142.2, 158.1 (C), 171.9 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3421 (br, w), 3083 (w), 3060 (w), 3027 (m), 2951 (m), 2930 (m), 2856 (w), 1659 (s), 1593 (m), 1558 (w), 1495 (w), 1439 (s), 1386 (m), 1347 (s), 1307 (s), 1263 (s), 1230 (s), 1196 (s), 1158 (s), 1142 (s), 1087 (m), 1039 (m), 1030 (m). MS (EI, 70 eV): *m*/*z* (%)=334 ($[M]^+$, [^{37}Cl], 9), 332 ($[M]^+$, [^{35}Cl], 28), 198 (31), 197 (16), 196 (100).

3.1.9. Methyl 3-chloro-5-(6-chloro-hexyl)-6-hydroxy-2,4-dimethyl-benzoate (5i). Starting with 1,3-bis-silyl enol ether **4i** (0.569 g, 1.50 mmol), 3-chloro-4-trimethylsilanyloxy-pent-3-en-2-one (**3a**) (0.310 g, 1.50 mmol), and $TiCl_4$ (0.2 mL, 1.50 mmol) in CH_2Cl_2 (3 mL), **5i** was isolated after column chromatography (silica gel, *n*-heptane/EtOAc 20:1) as a white solid (0.128 g, 26%), mp 51–53 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.44–1.51 (m, 6H, CH_2), 1.78 (q, *J*=6.8 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.71 (t, *J*=6.8 Hz, 2H, CH_2), 3.53 (t, *J*=6.8 Hz, 2H, CH_2), 3.96 (s, 3H, OCH_3), 11.07 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=17.9, 20.1 (CH_3), 26.7, 26.8, 28.8, 29.0, 32.6, 45.1 (CH_2), 52.3 (OCH_3), 111.6, 127.3, 128.6, 134.8, 141.2, 158.0 (C), 172.0 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3422 (br, w), 3015 (w), 2954 (s), 2925 (s), 2854 (m), 1654 (s), 1596 (m), 1558 (w), 1438 (s), 1388 (s), 1361 (s), 1311 (s), 1267 (s), 1251 (s), 1234 (s), 1198 (s), 1163 (s), 1131 (w), 1099 (w), 1033 (w). MS (EI, 70 eV): *m*/*z* (%)=334 ($[M]^+$, [^{37}Cl], 17), 332 ($[M]^+$, [^{35}Cl], 26), 287 (37), 285 (62), 265 (27), 198 (33), 197 (31), 196 (100), 195 (60). Anal. Calcd for $C_{16}H_{22}Cl_2O_3$ (333.25): C, 57.67; H, 6.65. Found: C, 57.57; H, 6.85.

3.1.10. (2-Methoxyethyl) 3-chloro-6-hydroxy-2,4-dimethyl-benzoate (5j). Starting with 1,3-bis-silyl enol ether **4j** (0.457 g, 1.50 mmol), 3-chloro-4-trimethylsilanyloxy-pent-3-en-2-one (**3a**) (0.310 g, 1.50 mmol), and $TiCl_4$ (0.2 mL, 1.50 mmol) in CH_2Cl_2 (3 mL), **5j** was isolated after column chromatography (silica gel, *n*-heptane/EtOAc 20:1) as a yellow oil (0.137 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 3.42 (s, 3H, OCH_3), 3.73 (t, *J*=4.8 Hz, 2H, CH_2), 4.51 (t, *J*=4.8 Hz, 2H, CH_2), 6.77 (s, 1H, CH), 10.47 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.7, 21.8 (CH_3), 58.9 (OCH_3), 64.4, 69.9 (CH_2), 112.5 (C), 117.4 (CH), 126.9, 138.1, 143.4, 159.4 (C), 170.2 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3409 (br, w), 2985 (m), 2956 (m), 2928 (m), 2892 (m), 2821 (w), 1731 (m), 1661 (s), 1610 (s), 1565 (m), 1456 (s), 1375 (s), 1347 (s), 1306 (s), 1229 (s), 1192 (s), 1116 (s), 1065 (m), 1026 (s). MS (EI, 70 eV): *m*/*z* (%)=260 ($[M]^+$, [^{37}Cl], 7), 258 ($[M]^+$, [^{35}Cl], 20), 184 (35), 183 (25), 182 (100). Anal. Calcd for $C_{12}H_{15}ClO_4$ (258.70): C, 55.71; H, 5.84. Found: C, 55.60; H, 5.74.

3.1.11. Methyl 3-chloro-2,4-diethyl-6-hydroxybenzoate (5k). Starting with 1,3-bis-silyl enol ether **4a** (1.00 g, 3.8 mmol), silyl enol ether **3b** (0.90 g, 3.8 mmol), and $TiCl_4$ (0.42 mL, 3.8 mmol), **5k** was isolated as a colorless oil (477 mg, 52%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.20 (t, 3H, *J*=7.3 Hz, CH_3), 1.23 (s, 3H, *J*=7.3 Hz, CH_3), 2.75 (q, 2H, *J*=7.0 Hz, CH_2), 3.08 (q, 2H, *J*=7.3 Hz, CH_2), 3.97 (s, 3H, OCH_3), 6.78 (s, 1H, ArH), 10.81 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.3, 13.7 (CH_3), 26.3, 28.0 (CH_2), 52.4 (CH_3), 111.5 (C), 116.1 (CH), 125.9, 143.7, 149.2, 160.3, 171.2 (C). IR (neat, cm^{-1}): $\tilde{\nu}$=2971 (m), 2938 (m), 2876 (w), 1665 (s), 1602 (m), 1562 (m), 1431 (m), 1354 (m), 1312 (s), 1224 (s), 1189 (m), 1109 (m), 806 (m), 687 (w). GC–MS (EI, 70 eV): *m*/*z* (%): 242.1 ($[M]^+$, 15), 210.0 (100), 167.0 (65), 91.0 (23), 77.0 (28), 77.1 (63). Elemental analysis calcd (%) for $C_{12}H_{15}ClO_3$ (242.70): C 59.39, H 6.23; found: C 59.56, H 6.36.

3.1.12. Ethyl 3-chloro-2,4,5-triethyl-6-hydroxybenzoate (5l). Starting with 1,3-bis-silyl enol ether **4e** (600 mg, 1.9 mmol), silyl enol ether **3b** (466 mg, 1.9 mmol), and $TiCl_4$ (0.21 mL, 1.9 mmol), **5l** was isolated as a colorless oil (305 mg, 54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (t, 3H, *J*=7.3 Hz, CH_3), 1.18 (s, 3H, *J*=7.3 Hz, CH_3), 1.23 (t, 3H, *J*=7.3 Hz, CH_3), 1.43 (t, 3H, *J*=7.0 Hz, CH_3), 2.71

(q, 2H, J=7.3 Hz, CH_2), 2.85 (q, 2H, J=7.3 Hz, CH_2), 3.06 (q, 2H, J=7.3 Hz, CH_2), 4.44 (q, 2H, J=7.3 Hz, OCH_2), 11.11 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.6, 13.8, 13.9, 14.0 (CH_3), 20.0, 24.5, 26.4, 61.8 (CH_2), 111.5, 126.2, 129.8, 140.6, 146.5, 158.3, 171.3 (C). IR (neat, cm^{-1}): $\tilde{\nu}$=2978 (s), 2935 (m), 2875 (m), 1657 (s), 1394 (s), 1372 (s), 1309 (s), 1267 (s), 1244 (m), 1220 (s), 1170 (s), 1151 (m), 1027 (w), 817 (w). GC–MS (EI, 70 eV): m/z (%)=286 ([M]$^+$, [^{37}Cl], 10), 284 ([M]$^+$, [^{35}Cl], 32), 238.0 (100), 210.0 (16), 175.0 (59), 115.0 (18). Elemental analysis calcd (%) for $C_{15}H_{21}ClO_3$ (284.78): C 63.26, H 7.43; found: C 63.19, H 7.43.

3.1.13. Methyl 5-chloro-2-hydroxy-4-methyl-6-phenylbenzoate (11a). Starting with bis-silyl enol ether **4a** (0.429 g, 1.65 mmol), $TiCl_4$ (0.313 g, 1.65 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10a** (0.403 g, 1.5 mmol), **11a** was isolated (0.204 g, 49%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.28 (s, 3H, CH_3), 3.24 (s, 3H, OCH_3), 6.82 (s, 1H, Ar), 6.99 (dd, J=7.4, 1.5 Hz, 2H, Ar), 7.20–7.23 (m, 2H, Ar), 7.25–7.28 (m, 1H, Ar), 10.67 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=20.2 (CH_3), 54.4 (OCH_3), 110.4 (CH), 124.3 (C), 125.5 (CH), 126.1 (2CH), 127.0 (2CH), 139.0, 140.6, 142.2, 158.3 (C), 169.2 (C=O). GC–MS (EI, 70 eV): m/z (%)=278 ([M]$^+$, [^{37}Cl], 10), 276 ([M]$^+$, [^{35}Cl], 30), 246 ([^{37}Cl], 33), 244 ([^{35}Cl], 100), 216 (22), 181 (10), 152 (27), 76 (14). HRMS (EI) calcd for $C_{15}H_{13}ClO_3$ ([M]$^+$, [^{35}Cl]): 276.05477; found: 276.05475.

3.1.14. Methyl 6-chloro-3-hydroxy-4,5-dimethyl[1,1′-biphenyl]-2-carboxylate (11b). Starting with bis-silyl enol ether **4f** (0.452 g, 1.65 mmol), $TiCl_4$ (0.313 g, 1.65 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10a** (0.403 g, 1.5 mmol), **11b** was isolated (0.133 g, 31%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.19 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.25 (s, 3H, OCH_3), 6.99–7.02 (m, 2H, Ar), 7.21–7.24 (m, 2H, Ar), 7.26–7.29 (m, 1H, Ar), 11.03 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.6, 17.1 (CH_3), 50.8 (OCH_3), 110.0, 124.6, 125.0 (C), 125.7 (CH), 126.4 (2CH), 127.6 (2CH), 137.9, 139.5, 140.7, 156.8 (C), 170.2 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3063 (w), 3025 (w), 2951 (m), 1655 (s), 1244 (s), 1200 (s), 1175 (s), 1014 (m), 708 (s). GC–MS (EI, 70 eV): m/z (%)=292 ([M]$^+$, [^{37}Cl], 11), 290 ([M]$^+$, [^{35}Cl], 33), 260 ([^{37}Cl], 19), 258 ([^{35}Cl], 57), 223 (100), 195 (10), 165 (21), 82 (8). HRMS (EI) calcd for $C_{16}H_{15}ClO_3$ ([M]$^+$, [^{35}Cl],): 290.07042; found: 290.07028.

3.1.15. 1-(6-Chloro-3-hydroxy-5-methyl-biphenyl-2-yl)-ethanone (11c). Starting with 3-chloro-4-phenyl-4-(trimethylsilyloxy)but-3-en-2-one (0.748 g, 2.91 mmol), 2,4-bis-(trimethylsilanyloxy)penta-1,3-diene (0.710 g, 2.91 mmol), and $TiCl_4$ (0.550 g, 2.91 mmol), **11c** (0.324 g, 43%) was obtained as yellow crystals, mp 68 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=11.95 (s, 1H, OH), 7.50–7.43 (m, 3H, ArH), 7.30–7.25 (m, 2H, ArH), 6.95 (s, 1H, Ar–H), 2.42 (s, 3H, CH_3), 1.68 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ=206.2 (CO), 159.8, 144.4, 141.7, 139.5 (C), 130.4 (2C), 128.9 (3C) (CH–Ph), 125.2, 121.0 (C), 120.2 (CH), 32.0, 22.1 (CH_3). IR (Nujol, cm^{-1}): $\tilde{\nu}$=3206 (m), 1673 (m), 1330 (s), 1209 (m), 742 (s). MS (EI, 70 eV): m/z (%)=262.0 (M$^+$, [^{37}Cl], 33), 260 (M$^+$, [^{35}Cl], 99), 247 (34), 245 (100), 212 (1), 210 (34), 183 (4), 181 (32), 152 (28). Anal. Calcd for $C_{15}H_{13}O_2Cl$ (260.50): C 69.09, H 5.00; found: C 69.28, H 5.20.

3.1.16. Ethyl 6-chloro-4-ethyl-3-hydroxy-5-methyl[1,1′-biphenyl]-2-carboxylate (11d). Starting with bis-silyl enol ether **4e** (0.452 g, 1.65 mmol), $TiCl_4$ (0.313 g, 1.65 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10a** (0.403 g, 1.5 mmol), **11d** was isolated (0.205 g, 43%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.56 (t, J=7.2 Hz, 3H, CH_3), 1.04 (t, J=7.5 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.71 (q, J=7.4 Hz, 2H, CH_2), 3.77 (q, J=7.2 Hz, 2H, OCH_2), 6.99–7.03 (m, 2H, Ar), 7.19–7.21 (m, 2H, Ar), 7.25–7.28 (m, 1H, Ar), 11.19 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.8, 12.1, 16.3 (CH_3), 19.2 (CH_2), 59.9 (OCH_2), 110.2, 124.9 (C), 125.6 (CH), 126.4 (2CH), 127.7 (2CH), 130.9, 138.1, 140.0, 140.2, 156.9 (C), 169.8 (C=O). GC–MS (EI, 70 eV): m/z (%)=320 ([M]$^+$, [^{37}Cl], 18), 318 ([M]$^+$, [^{35}Cl], 54), 274 ([^{37}Cl], 27), 272 ([^{35}Cl], 79), 259 ([^{37}Cl], 4), 257 ([^{35}Cl], 13), 237 (81), 219 (100), 165 (42), 115 (6), 77 (5). HRMS (EI) calcd for $C_{18}H_{19}ClO_3$ ([M]$^+$, [^{35}Cl]): 318.10172; found: 318.101231.

3.1.17. Methyl 6-chloro-4′-fluoro-3-hydroxy-5-methyl-[1,1′-biphenyl]-2-carboxylate (11e). Starting with bis-silyl enol ether **4a** (0.429 g, 1.65 mmol), $TiCl_4$ (0.313 g, 1.65 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10b** (0.430 g, 1.5 mmol), **11e** was isolated (0.125 g, 28%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=122–124 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.26 (s, 3H, CH_3), 3.28 (s, 3H, OCH_3), 6.81 (s, 1H, Ar), 6.93 (m, 2H, Ar), 6.95 (m, 2H, Ar), 10.70 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=20.6 (CH_3), 50.9 (OCH_3), 110.8 (C), 113.4, 113.7, 118.3 (CH), 124.8 (C), 128.4, 128.6 (CH), 135.3, 139.9, 142.9, 162.5, 162.7 (C), 169.5 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2955 (m), 2853 (w), 1671 (s), 1515 (s), 1362 (s), 1235 (s), 1166 (s), 1014 (m), 809 (s). GC–MS (EI, 70 eV): m/z (%)=296 ([M]$^+$, [^{37}Cl], 12), 294 ([M]$^+$, [^{35}Cl], 36), 262 (100), 234 (36), 199 (14), 170 (31), 85 (13). HRMS (EI) calcd for $C_{15}H_{12}ClFO_3$ ([M]$^+$, [^{35}Cl]): 294.04535; found: 294.045720.

3.1.18. Methyl 6-chloro-4′-fluoro-3-hydroxy-4,5-dimethyl[1,1′-biphenyl]-2-carboxylate (11f). Starting with bis-silyl enol ether **4f** (0.452 g, 1.65 mmol), $TiCl_4$ (0.313 g, 1.65 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10b** (0.430 g, 1.5 mmol), **11f** was isolated (0.224 g, 48%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=65–68 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 6.97 (m, 2H, Ar), 6.99 (m, 2H, Ar), 11.08 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.7, 17.1 (CH_3), 50.9 (OCH_3), 110.0 (C), 113.3, 113.6 (CH), 125.3 (C), 129.2, 129.3 (CH), 135.8, 136.8, 140.9, 157.0, 159.1, 162.4 (C), 170.1 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3054 (w), 2960 (m), 1659 (s), 1511 (s), 1470 (s), 1245 (s), 1015 (s), 806 (w). GC–MS (EI, 70 eV): m/z (%)=310 ([M]$^+$, [^{37}Cl], 10), 308 ([M]$^+$, [^{35}Cl], 32), 276 (59), 241 (100), 213 (13), 183 (21), 91 (5). HRMS (EI) calcd for $C_{16}H_{14}ClFO_3$ ($[M]^+$, $[^{35}Cl]$): 308.06100; found: 308.060892.

3.1.19. Ethyl 5-chloro-3-ethyl-2-hydroxy-4-methyl-6-(4-fluorophenyl)benzoate (11g). Starting with bis-silyl enol ether **4e** (0.499 g, 1.65 mmol), $TiCl_4$ (0.313 g, 1.65 mmol) CH_2Cl_2 (3 mL), and silyl enol ether **10b** (0.430 g, 1.5 mmol), **11g** was isolated (0.219 g, 44%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a light red solid (mp=73–75 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ=0.55 (t, J=7.2 Hz, 3H, CH_3), 0.97 (t, J=7.4 Hz, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.62 (q, J=7.5 Hz, 2H, CH_2), 3.73 (q, J=7.2 Hz, 2H, OCH_2), 6.86 (m, 2H, Ar), 6.88 (m, 2H, Ar), 11.11 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=12.9, 13.1, 17.4 (CH_3), 20.4 (CH_2), 61.2 (OCH_2), 111.3 (C), 114.3, 114.6, 130.3, 130.4 (CH), 132.3, 137.1, 138.0, 141.2, 158.0, 160.3, 163.6 (C), 170.7 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2970 (m), 2927 (m), 1655 (s), 1511 (s), 1376 (s), 1233 (s), 1217 (s), 1187 (s), 810 (w). GC–MS (EI, 70 eV): *m/z* (%)=338 ($[M]^+$, $[^{37}Cl]$, 18), 336 ($[M]^+$, $[^{35}Cl]$, 54), 290 (82), 255 (100), 237 (86), 183 (43), 170 (82), 133 (6), 91 (2), 51 (2). HRMS (EI) calcd for $C_{18}H_{18}ClFO_3$ ($[M]^+$, $[^{35}Cl]$): 336.09230; found: 336.09188.

3.1.20. Methyl 4′,6-dichloro-3-hydroxy-5-methyl[1,1′-biphenyl]-2-carboxylate (11h). Starting with bis-silyl enol ether **4a** (0.567 g, 2.18 mmol), $TiCl_4$ (0.413 g, 2.18 mmol) CH_2Cl_2 (3 mL), and silyl enol ether **10c** (0.606 g, 2.00 mmol), **11h** was isolated (0.275 g, 44%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=80–82 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=2.29 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 6.85 (m, 1H, Ar), 6.93–6.96 (m, 2H, Ar), 7.24–7.27 (m, 2H, Ar), 10.76 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=21.5 (CH_3), 51.9 (OCH_3), 111.5 (C), 119.4 (CH), 125.6 (C), 127.8 (2CH), 129.8 (2CH), 132.8, 138.8, 140.6, 144.0, 159.8 (C), 170.3 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2952 (m), 2923 (w), 1671 (s), 1452 (s), 1229 (s), 1190 (s), 1018 (s), 820 (w). GC–MS (EI, 70 eV): *m/z* (%)=314 ($[M]^+$, $[2\times^{37}Cl]$, 3), 312 ($[M]^+$, $[^{37}Cl]$, $[^{35}Cl]$, 18), 310 ($[M]^+$, $[2\times^{35}Cl]$, 28), 278 (100), 250 (13), 215 (15), 187 (8), 152 (9), 93 (8), 76 (9). HRMS (EI) calcd for $C_{15}H_{12}Cl_2O_3$ ($[M]^+$, $[2\times^{35}Cl]$): 310.01580; found: 310.01625.

3.1.21. Methyl 4′,6-dichloro-3-hydroxy-4,5-dimethyl[1,1′-biphenyl]-2-carboxylate (11i). Starting with bis-silyl enol ether **4f** (0.598 g, 2.18 mmol), $TiCl_4$ (0.413 g, 2.18 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10c** (0.606 g, 2.00 mmol), **11i** was isolated (0.220 g, 34%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a light yellow solid, mp=95–97 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=2.23 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.34 (s, 3H, OCH_3), 6.96–6.99 (m, 2H, Ar), 7.27–7.29 (m, 2H, Ar), 11.12 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.1, 18.6 (CH_3), 52.4 (OCH_3), 111.2, 126.0, 126.9 (C), 128.2 (2CH), 130.5 (2CH), 131.1, 138.0, 139.8, 142.4, 158.5 (C), 171.4 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3053 (w), 2957 (m), 2927 (w), 1660 (s), 1441 (s), 1244 (s), 1202 (s), 1016 (s), 809 (m). GC–MS (EI, 70 eV): *m/z* (%)=328 ($[M]^+$, $[2\times^{37}Cl]$, 4), 326 ($[M]^+$, $[^{37}Cl]$, $[^{35}Cl]$, 17), 324 ($[M]^+$, $[2\times^{35}Cl]$, 27), 292 (53), 257 (100), 229 (11), 165 (25), 99 (5), 82 (12). HRMS (EI) calcd for $C_{16}H_{14}Cl_2O_3$: 324.03145 ($[M]^+$, $[2\times^{35}Cl]$); found: 324.031296.

3.1.22. Ethyl 4′,6-dichloro-4-ethyl-3-hydroxy-5-methyl-[1,1′-biphenyl]-2-carboxylate (11j). Starting with bis-silyl enol ether **4e** (0.659 g, 2.18 mmol), $TiCl_4$ (0.413 g, 2.18 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10c** (0.606 g, 2.00 mmol), **11j** was isolated (0.335 g, 47%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=94–96 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.67 (t, J=7.2 Hz, 3H, CH_3), 1.09 (t, J=7.4 Hz, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.74 (q, J=7.4 Hz, 2H, CH_2), 3.85 (q, J=7.2 Hz, 2H, OCH_2), 6.97–6.99 (m, 2H, Ar), 7.26–7.29 (m, 2H, Ar), 11.25 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=12.8, 13.0, 17.4 (CH_3), 20.3 (CH_2), 61.2 (OCH_2), 110.9, 125.7 (C), 127.7 (2CH), 130.1 (2CH), 132.4, 132.6, 137.7, 139.6, 141.2, 158.0 (C), 170.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3431 (w), 2966 (m), 2929 (m), 1672 (s), 1382 (s), 1305 (s), 1219 (s), 1101 (m), 186 (m). MS (EI, 70 eV): *m/z* (%)=356 ($[M]^+$, $[2\times^{37}Cl]$, 3), 354 ($[M]^+$, $[^{37}Cl]$, $[^{35}Cl]$, 16), 352 ($[M]^+$, $[2\times^{35}Cl]$, 25), 306 (35), 271 (100), 199 (4), 165 (15), 152 (4), 82 (2). HRMS (EI) calcd for $C_{18}H_{18}Cl_2O_3$ ($[M]^+$, $[2\times^{35}Cl]$): 352.06275; found: 352.06340.

3.1.23. Methyl 6-chloro-3-hydroxy-2′,5-dimethyl[1,1′-biphenyl]-2-carboxylate (11k). Starting with bis-silyl enol ether **4a** (0.286 g, 1.10 mmol), $TiCl_4$ (0.208 g, 1.10 mmol), CH_2Cl_2 (2 mL), and silyl enol ether **10d** (0.282 g, 1.00 mmol), **11k** was isolated (0.74 g, 26%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.95 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.30 (s, 3H, OCH_3), 6.82 (d, J=7.3 Hz, 1H, Ar), 6.87 (m, 1H, Ar), 7.09–7.13 (m, 1H, Ar), 7.75–7.77 (m, 2H, Ar), 10.89 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=20.0, 22.0 (CH_3), 52.4 (OCH_3), 111.8 (C), 119.4, 125.6 (CH), 126.1 (C), 127.6, 128.2, 129.5 (CH), 135.8, 140.6, 142.1, 144.5, 160.5 (C), 171.0 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3421 (w), 3064 (w), 2949 (w), 1668 (s), 1441 (s), 1349 (s), 1323 (s), 1228 (s), 1036 (w), 734 (s), 706 (s). GC–MS (EI, 70 eV): *m/z* (%)=292 ($[M]^+$, $[^{37}Cl]$, 13), 290 ($[M]^+$, $[^{35}Cl]$, 38), 258 (100), 223 (14), 195 (22), 165 (26), 152 (24), 82 (11). HRMS (EI) calcd for $C_{16}H_{15}ClO_3$ ($[M]^+$, $[^{35}Cl]$): 290.07042; found: 290.070510.

3.1.24. Methyl 6-chloro-3-hydroxy-2′,4,5-trimethyl[1,1′-biphenyl]-2-carboxylate (11l). Starting with bis-silyl enol ether **4f** (0.302 g, 1.10 mmol), $TiCl_4$ (0.208 g, 1.10 mmol), CH_2Cl_2 (3 mL), and silyl enol ether **10d** (0.282 g, 1.00 mmol), **11l** was isolated (0.123 g, 40%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.95 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.29 (s, 3H, OCH_3), 6.81 (d, J=7.3 Hz, 1H, Ar), 7.08–7.12 (m, 1H, Ar), 7.13–7.17 (m, 2H, Ar), 11.24 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.1, 18.6, 20.0 (CH_3), 52.4 (OCH_3), 111.0 (C), 125.5, 125.6 (CH), 126.1, 126.3 (C), 128.4, 129.5 (CH), 136.0, 139.0, 141.2, 142.4, 158.7 (C), 171.6 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3060 (m), 2951 (s), 2856 (m), 1667 (s), 1439 (s), 1384 (s), 1320 (m), 1202 (s), 1013 (s), 807 (s), 703 (s). GC–MS (EI, 70 eV): *m/z* (%)=306 ($[M]^+$, $[^{37}Cl]$, 14), 304 ($[M]^+$, $[^{35}Cl]$, 44), 272 (72), 257 (100), 237 (29), 165 (32), 115 (5), 89 (11). HRMS (EI) calcd for $C_{17}H_{17}ClO_3$ ($[M]^+$, $[^{35}Cl]$): 304.08607; found: 304.08662.

3.1.25. Methyl 6-chloro-3-hydroxy-2′-methoxy-5-methyl-[1,1′-biphenyl]-2-carboxylate (11m). Starting with bis-silyl enol ether **4a** (0.573 g, 2.20 mmol), $TiCl_4$ (417 g, 2.20 mmol), CH_2Cl_2 (4 mL), and silyl enol ether **10e** (0.597 g, 2.00 mmol), **11m** was isolated (0.285 g, 47%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a slightly yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ=2.28 (s, 3H, CH_3), 3.28 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 6.80 (m, 1H, Ar), 6.81–6.83 (m, 1H, Ar), 6.84 (m, 1H, Ar), 6.85–6.86 (m, 1H, Ar), 7.18–7.24 (m, 1H, Ar), 10.76 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=20.68 (CH_3), 50.8, 54.7 (OCH_3), 109.4 (CH), 111.0 (C), 118.0 (CH), 118.1 (C), 119.1 (CH), 125.1 (C), 127.7, 128.6 (CH), 137.8, 142.8, 155.2, 158.8 (C), 169.6 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=308 ($[M]^+$, $[^{37}Cl]$, 12), 306 ($[M]^+$, $[^{35}Cl]$, 37), 274 (100), 245 (8), 231 (8), 211 (8), 183 (7), 168 (11), 139 (10), 91 (3), 76 (6). HRMS (EI) calcd for $C_{16}H_{15}ClO_4$ ($[M]^+$, $[^{35}Cl]$): 306.06534; found: 306.06620.

3.1.26. Methyl 6-chloro-3-hydroxy-2′-methoxy-4,5-dimethyl[1,1′-biphenyl]-2-carboxylate (11n). Starting with bis-silyl enol ether **4f** (0.604 g, 2.20 mmol), $TiCl_4$ (417 g, 2.20 mmol), CH_2Cl_2 (4 mL), and silyl enol ether **10e** (0.597 g, 2.00 mmol), **11n** was isolated (0.319 g, 50%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=78–80 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=2.16 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.27 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 6.79–6.82 (m, 1H, Ar), 6.83–6.87 (m, 2H, Ar), 7.16–7.22 (m, 1H, Ar), 11.10 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.7, 17.2 (CH_3), 50.8, 54.7 (OCH_3), 109.3 (CH), 110.2 (C), 119.1 (CH), 125.0, 125.1 (C), 127.5, 128.7 (CH), 129.1, 134.7, 140.8, 155.3, 157.0 (C), 170.2 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3063 (w), 2953 (m), 2923 (m), 1668 (s), 1436 (s), 1293 (s), 1200 (s), 1015 (m), 744 (s). GC–MS (EI, 70 eV): *m/z* (%)=322 ($[M]^+$, $[^{37}Cl]$, 17), 320 ($[M]^+$, $[^{35}Cl]$, 56), 288 (100), 273 (32), 257 (97), 181 (19), 165 (13), 152 (13), 115 (5), 76 (7). HRMS (EI) calcd for $C_{17}H_{17}ClO_4$ ($[M]^+$, $[^{35}Cl]$): 320.08099; found: 320.081273.

3.1.27. Ethyl 6-chloro-4-ethyl-3-hydroxy-2′-methoxy-5-methyl[1,1′-biphenyl]-2-carboxylate (11o). Starting with bis-silyl enol ether **4e** (0.665 g, 2.20 mmol), $TiCl_4$ (417 g, 2.20 mmol), CH_2Cl_2 (4 mL), and silyl enol ether **10e** (0.597 g, 2.00 mmol), **11o** was isolated (0.290 g, 42%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=90–92 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.63 (t, *J*=7.1 Hz, 3H, CH_3), 1.09 (t, *J*=7.4 Hz, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.73 (q, *J*=7.4 Hz, 2H, CH_2), 3.66 (m, 3H, OCH_3), 3.83 (q, *J*=7.1 Hz, 2H, OCH_2), 6.82–6.85 (m, 1H, Ar), 6.86–6.88 (m, 2H, Ar), 7.21–7.27 (m, 1H, Ar), 11.24 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.9, 12.1, 16.4 (CH_3), 19.4 (CH_2), 54.6 (OCH_3), 59.9 (OCH_2), 109.3 (CH), 110.5 (C), 119.1 (CH), 125.3 (C), 127.4, 128.7 (CH), 129.4, 130.8, 134.8, 140.0, 155.5, 157.0 (C), 169.9 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2971 (m), 2958 (m), 2871 (m), 1649 (s), 1299 (s), 1233 (s), 1114 (s), 1030 (s), 811 (w). GC–MS (EI 70, eV): *m/z* (%)=350 ($[M]^+$, $[^{37}Cl]$, 15), 348 ($[M]^+$, $[^{35}Cl]$, 46), 302 (74), 287 (19), 271 (100), 249 (16), 224 (7), 181 (11), 165 (12), 115 (4), 77 (2). HRMS (EI) calcd for $C_{19}H_{21}ClO_4$ ($[M]^+$, $[^{35}Cl]$): 348.11229; found: 348.11171.

3.1.28. Methyl 6-chloro-3-hydroxy-2′-methoxy-5-propyl[1,1′-biphenyl]-2-carboxylate (11p). Starting with bis-silyl enol ether **4a** (0.573 g, 2.20 mmol), $TiCl_4$ (417 g, 2.20 mmol), CH_2Cl_2 (4 mL), and silyl enol ether **10f** (0.653 g, 2.00 mmol), **11p** was isolated (0.229 g, 34%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a slightly yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.87 (t, *J*=7.4 Hz, 3H, CH_3), 1.50–1.62 (m, 2H, CH_2), 2.52–2.65 (m, 2H, CH_2), 3.27 (m, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 6.79 (s, 1H, Ar), 6.82 (m, 1H, Ar), 6.83–6.85 (m, 2H, Ar), 7.17–7.23 (m, 1H, Ar), 10.73 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=12.9 (CH_3), 21.2, 35.7 (CH_2), 50.8, 54.7 (OCH_3), 109.4 (CH), 111.1 (C), 117.2 (CH), 117.3 (C), 119.1 (CH), 124.7 (C), 127.6, 128.7 (CH), 138.0, 146.6, 155.3, 158.8 (C), 169.6 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=336 ($[M]^+$, $[^{37}Cl]$, 12), 334 ($[M]^+$, $[^{35}Cl]$, 37), 302 (100), 274 (43), 230 (10), 181 (5), 152 (9), 139 (8). HRMS (EI) calcd for $C_{18}H_{19}ClO_4$ ($[M]^+$, $[^{35}Cl]$): 334.09664; found: 334.09699.

3.1.29. Methyl 6-chloro-3-hydroxy-2′-methoxy-4-methyl-5-propyl[1,1′-biphenyl]-2-carboxylate (11q). Starting with bis-silyl enol ether **4f** (0.604 g, 2.20 mmol), $TiCl_4$ (417 g, 2.20 mmol) CH_2Cl_2 (4 mL), and silyl enol ether **10f** (0.653 g, 2.00 mmol), **11q** was isolated (0.325 g, 47%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a slightly yellow viscous oil. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.90 (t, *J*=7.4 Hz, 3H, CH_3), 1.41–1.49 (m, 2H, CH_2), 2.17 (s, 3H, CH_3), 2.67–2.74 (m, 2H, CH_2), 3.25 (m, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 6.78 (d, *J*=8.1 Hz, 1H, Ar), 6.82–6.83 (m, 2H, Ar), 7.14–7.20 (m, 1H, Ar), 11.07 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=4.8, 14.2 (CH_3), 16.3, 38.0 (CH_2), 53.7, 57.6 (OCH_3), 112.3 (CH), 113.3 (C), 122.0 (CH), 127.6, 127.8 (C), 130.4, 131.7 (CH), 132.1, 137.9, 147.7, 158.3, 160.2 (C), 173.1 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3000 (w), 2958 (s), 2931 (m), 2872 (m), 1663 (s), 1249 (s), 1218 (s), 1104 (m), 1028 (s), 808 (m). MS (EI, 70 eV): *m/z* (%)=350 ($[M]^+$, $[^{37}Cl]$, 13), 348 ($[M]^+$, $[^{35}Cl]$, 37), 316 (100), 301 (15), 285 (14), 257 (21), 181 (11), 165 (7), 69 (13). HRMS (EI) calcd for $C_{19}H_{21}ClO_4$ ($[M]^+$, $[^{35}Cl]$): 348.11229; found: 348.11170.

3.1.30. Ethyl 6-chloro-4-ethyl-3-hydroxy-2′-methoxy-5-propyl[1,1′-biphenyl]-2-carboxylate (11r). Starting with bis-silyl enol ether **4e** (0.665 g, 2.20 mmol), $TiCl_4$ (417 g, 2.20 mmol) CH_2Cl_2 (4 mL), and monosilyl enol ether **10f** (0.654 g, 2.00 mmol), **11r** was isolated (0.384 g, 51%) by column chromatography (silica gel, *n*-heptane/EtOAc=30:1→20:1) as a colorless solid, mp=79–81 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.64 (t, *J*=7.2 Hz, 3H, CH_3), 0.97 (t, *J*=7.4 Hz, 3H, CH_3), 1.13

(t, J=7.4 Hz, 3H, CH$_3$), 1.47–1.54 (m, 2H, CH$_2$), 2.67–2.69 (m, 2H, CH$_2$), 2.72–2.76 (m, 2H, CH$_2$), 3.67 (s, 3H, OCH$_3$), 3.83 (q, J=7.2 Hz, 2H, OCH$_2$), 6.84 (d, J=8.1 Hz, 1H, Ar), 6.87–6.89 (m, 2H, Ar), 7.22–7.28 (m, 1H, Ar), 11.19 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=11.9, 13.2, 13.5 (CH$_3$), 19.3, 21.9, 32.4 (CH$_2$), 54.7 (OCH$_3$), 59.9 (OCH$_2$), 109.4 (CH), 110.7 (C), 119.1 (CH), 124.9 (C), 127.4, 128.8 (CH), 129.5, 130.5, 135.1, 144.1, 155.5, 157.3 (C), 169.8 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3421 (w), 2959 (s), 2932 (s), 2870 (m), 1652 (s), 1392 (s), 1243 (s), 1185 (s), 1049 (m), 801 (w). MS (EI, 70 eV): m/z (%)=378 ([M]$^+$, [^{37}Cl], 14), 376 ([M]$^+$, [^{35}Cl], 42), 330 (100), 299 (84), 287 (7), 271 (8), 181 (9), 165 (6), 131 (8), 69 (19), 43 (12). HRMS (EI) calcd for $C_{21}H_{25}ClO_4$ ([M]$^+$, [^{35}Cl]): 376.14359; found: 376.142978.

3.2. General procedure for synthesis of benzo[*c*]chromen-6-ones 12a–f by lactonization with BBr$_3$

To a CH$_2$Cl$_2$ solution of **6** was added BBr$_3$ at 0 °C. The solution was allowed to warm to 20 °C for 18 h. To the solution was added an aqueous solution of KO^{t}Bu (0.1 M) and the solution was stirred for 15 min. The organic and the aqueous layers were separated and the latter was extracted with CH$_2$Cl$_2$. The combined organic layers were dried (Na$_2$SO$_4$), filtered, and the filtrate was concentrated in vacuo. The product was purified by chromatography (silica gel, *n*-hexane/EtOAc=20:1) as a colorless solid.

3.2.1. 10-Chloro-7-hydroxy-9-methyl-6*H*-benzo[*c*]chromen-6-one (12a). Starting with **11m** (0.104 g, 0.31 mmol) in CH$_2$Cl$_2$ (5 mL), BBr$_3$ (0.339 g, 1.35 mmol), and KO^{t}Bu (10 mL, 0.1 M aqueous solution), **12a** was isolated as a colorless solid (0.063 g, 73%), mp=107–110 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ=2.45 (s, 3H, CH$_3$), 6.96 (s, 1H, Ar), 7.27–7.30 (m, 2H, Ar), 7.41–7.46 (m, 1H, Ar), 9.24–9.27 (m, 1H, Ar), 11.78 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=21.0 (CH$_3$), 104.0 (C), 115.7 (CH), 116.1 (C), 117.2 (CH), 119.1 (C), 122.5, 125.8, 128.8 (CH), 129.3, 147.0, 148.5, 159.1 (C), 163.2 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3026 (w), 2957 (w), 2924 (w), 1667 (s), 1265 (s), 1218 (s), 1102 (s), 1031 (s), 763 (s). GC–MS (EI, 70 eV): m/z (%)=262 ([M]$^+$, [^{35}Cl], 33), 260 ([M]$^+$, [^{35}Cl], 100), 225 (26), 197 (13), 169 (8), 139 (10), 112 (14), 69 (5). HRMS (EI) calcd for $C_{14}H_9ClO_3$ ([M]$^+$, [^{35}Cl]): 260.02347; found: 260.02249.

3.2.2. 10-Chloro-7-hydroxy-8,9-dimethyl-6*H*-benzo[*c*]chromen-6-one (12b). Starting with **11n** (0.129 g, 0.37 mmol) in CH$_2$Cl$_2$ (5 mL), BBr$_3$ (0.374 g, 1.49 mmol), and KO^{t}Bu (10 mL, 0.1 M aqueous solution), **12b** was isolated as a colorless solid (0.080 g, 78%), mp=154–156 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ=2.23 (s, 3H, CH$_3$), 2.41 (s, 3H, CH$_3$), 7.22–7.24 (m, 1H, Ar), 7.26 (m, 1H, Ar), 7.36–7.42 (m, 1H, Ar), 9.17 (dd, J=8.4, 2.1 Hz, 1H, Ar), 12.18 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=10.9, 16.9 (CH$_3$), 102.9 (C), 115.5 (CH), 116.2, 119.3 (C), 123.3 (CH), 124.7 (C), 125.8 (CH), 126.4 (C), 128.2 (CH), 145.1, 148.2, 157.3 (C), 163.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3446 (w), 2925 (m), 2851 (m), 1669 (s), 1597 (s), 1397 (s), 1254 (s), 1168 (s), 1113 (m), 780 (s). GC–MS (EI, 70 eV): m/z (%)=276 ([M]$^+$, [^{37}Cl], 33), 274 ([M]$^+$, [^{35}Cl], 100), 259 (7), 239 (16), 211 (7), 181 (6), 165 (6), 152 (8), 115 (4), 76 (5). HRMS (EI) calcd for $C_{15}H_{11}ClO_3$ ([M]$^+$, [^{35}Cl]): 274.03912; found: 274.03900.

3.2.3. 10-Chloro-8-ethyl-7-hydroxy-9-methyl-6*H*-benzo[*c*]chromen-6-one (12c). Starting with **11o** (0.110 g, 0.31 mmol) in CH$_2$Cl$_2$ (5 mL), BBr$_3$ (0.315 g, 1.26 mmol), and KO^{t}Bu (10 mL, 0.1 M aqueous solution), **12c** was isolated as a colorless solid (0.060 g, 60%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=1.06 (t, J=7.4 Hz, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 2.71 (q, J=7.4 Hz, 2H, CH$_2$), 7.17–7.18 (m, 1H, Ar), 7.21 (m, 1H, Ar), 7.32–7.37 (m, 1H, Ar), 9.08–9.11 (m, 1H, Ar), 12.12 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=13.4, 18.6 (CH$_3$), 20.8 (CH$_2$), 105.4 (C), 117.8 (CH), 118.5, 121.8 (C), 124.6, 128.0 (CH), 128.8 (C), 130.5 (CH), 132.9, 146.8, 150.5, 159.5 (C), 165.9 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2969 (m), 2928 (m), 1663 (s), 1393 (s), 1242 (s), 1166 (s), 1116 (m), 758 (m). GC–MS (EI, 70 eV): m/z (%)=290 ([M]$^+$, [^{37}Cl], 16), 288 ([M]$^+$, [^{35}Cl], 49), 273 (100), 245 (3), 181 (7), 165 (6), 152 (7), 126 (3), 76 (5). HRMS (EI) calcd for $C_{16}H_{13}ClO_3$ ([M]$^+$, [^{35}Cl]): 288.05477; found: 288.05465.

3.2.4. 10-Chloro-7-hydroxy-9-propyl-6*H*-benzo[*c*]chromen-6-one (12d). Starting with **11p** (0.107 g, 0.32 mmol) in CH$_2$Cl$_2$ (5 mL), BBr$_3$ (0.320 g, 1.27 mmol), and KO^{t}Bu (10 mL, 0.1 M aqueous solution), **12d** was isolated as a colorless crystalline (0.078 g, 88%), mp=115–117 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.95 (t, J=7.4 Hz, 3H, CH$_3$), 1.56–1.68 (m, 2H, CH$_2$), 2.69–2.75 (m, 2H, CH$_2$), 6.89 (s, 1H, Ar), 7.21–7.22 (m, 1H, Ar), 7.25 (m, 1H, Ar), 7.36–7.42 (m, 1H, Ar), 9.18–9.21 (m, 1H, Ar), 11.73 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=14.3 (CH$_3$), 22.7, 37.9 (CH$_2$), 106.3 (C), 117.9 (CH), 118.5 (C), 118.9 (CH), 121.0 (C), 124.7, 128.2, 131.1 (CH), 131.8, 150.0, 153.0, 161.4 (C), 165.4 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2965 (m), 2931 (m), 2876 (m), 1675 (s), 1606 (m), 1421 (s), 1232 (s), 1216 (s), 1105 (w), 765 (s). GC–MS (EI, 70 eV): m/z (%)=290 ([M]$^+$, [^{37}Cl], 33), 288 ([M]$^+$, [^{35}Cl], 100), 260 (94), 253 (16), 225 (38), 197 (13), 181 (10), 168 (14), 152 (18), 139 (23), 126 (6), 75 (5). HRMS (EI) calcd for $C_{16}H_{13}ClO_3$ ([M]$^+$, [^{35}Cl]): 288.05477; found: 288.05478.

3.2.5. 10-Chloro-7-hydroxy-8-methyl-9-propyl-6*H*-benzo[*c*]chromen-6-one (12e). Starting with **11q** (0.129 g, 0.37 mmol) in CH$_2$Cl$_2$ (5 mL), BBr$_3$ (0.320 g, 1.27 mmol), and KO^{t}Bu (10 mL, 0.1 M aqueous solution), **12e** was isolated as a light brown solid (0.060 g, 54%), mp=98–100 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ=1.01 (t, J=7.4 Hz, 3H, CH$_3$), 1.49–1.54 (m, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.83–2.89 (m, 2H, CH$_2$), 7.23–7.24 (m, 1H, Ar), 7.27 (m, 1H, Ar), 7.36–7.42 (m, 1H, Ar), 9.20 (d, J=8.9 Hz, 1H, Ar), 12.20 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=11.4, 13.4 (CH$_3$), 20.6, 33.1 (CH$_2$), 104.0 (C), 116.4 (CH), 117.3, 119.8 (C), 123.2, 126.8 (CH), 127.3, 127.7 (C), 129.1 (CH), 149.2, 149.9, 158.6 (C), 164.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2968 (m), 2925 (m), 2861 (m), 1671 (s), 1598 (m), 1394 (s), 1259 (s), 1221 (m), 1166 (s), 774 (s). GC–MS (EI, 70 eV): m/z (%)=304 ([M]$^+$, [^{37}Cl], 33), 302 ([M]$^+$, [^{35}Cl], 100), 274 (52), 267 (22), 239 (44), 181 (16), 152 (17), 115 (5), 76 (5). HRMS (EI) calcd for $C_{17}H_{15}ClO_3$ ([M]$^+$, [^{35}Cl]): 302.07042; found: 302.07123.

3.2.6. 10-Chloro-8-ethyl-7-hydroxy-9-propyl-6*H*-benzo[*c*]chromen-6-one (12f). Starting with **11r** (0.200 g, 0.51 mmol) in CH$_2$Cl$_2$ (5 mL), BBr$_3$ (0.513 g, 2.12 mmol), and KO^{t}Bu (10 mL, 0.1 M aqueous solution), **12f** was isolated as a light red solid (0.080 g, 48%), mp=98–100 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ=1.03 (t, *J*=7.4 Hz, 3H, CH$_3$), 1.13 (t, *J*=7.4 Hz, 3H, CH$_3$), 1.55–1.60 (m, 2H, CH$_2$), 2.75 (q, *J*=7.4 Hz, 2H, CH$_2$), 2.83–2.88 (m, 2H, CH$_2$), 7.24–7.25 (m, 1H, Ar), 7.27–7.28 (m, 1H, Ar), 7.37–7.42 (m, 1H, Ar), 9.20–9.23 (m, 1H, Ar), 12.19 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=14.1, 14.9 (CH$_3$), 20.8, 23.1, 34.1 (CH$_2$), 105.7 (C), 117.8 (CH), 118.7, 121.4 (C), 124.6, 128.3 (CH), 129.4 (C), 130.6 (CH), 132.8, 150.6, 150.8, 160.0 (C), 166.1 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2955 (m), 2928 (m), 2869 (m), 1677 (s), 1597 (w), 1383 (s), 1243 (s), 1215 (s), 1116 (s), 753 (s). GC–MS (EI, 70 eV): *m*/*z* (%)=314 ([M]$^+$, [^{35}Cl], 33), 316 ([M]$^+$, [^{35}Cl], 100), 302 (8), 301 (40), 273.1 (51), 205 (7), 165 (4), 76 (4). HRMS (EI) calcd for C$_{18}$H$_{17}$ClO$_3$ ([M]$^+$, [^{35}Cl]): 316.08607; found: 316.08636.

3.2.7. 3-Chloro-4-phenyl-4-[(trimethylsilyl)oxy]-3-buten-2-one (10a). To a stirred benzene solution (120 mL) of **9a** (9.50 g, 48.3 mmol) was added triethylamine (10.71 mL, 77.3 mmol). After the solution was stirred for 2 h, trimethylchlorosilane (10.98 mL, 86.9 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (75 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give **10a** as a dark yellow oil (10.10 g, 90%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.26 (s, 9H, CH$_3$), 1.99 (s, 3H, CH$_3$), 7.33–7.36 (m, 2H, Ar), 7.40–7.43 (m, 1H, Ar), 7.70–7.73 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=0.5, 0.7, 1.9, 21.4 (CH$_3$), 111.6 (CCl), 128.1 (2CH), 129.1 (2CH), 132.4 (CH), 137.7, 157.4 (C), 191.8 (C=O).

3.2.8. 3-Chloro-4-(4-fluorophenyl)-4-[(trimethylsilyl)-oxy]-3-buten-2-one (10b). To a stirred benzene solution (45 mL) of **9b** (3.25 g, 15.11 mmol) was added triethylamine (3.38 mL, 24.17 mmol). After the solution was stirred for 2 h, trimethylchlorosilane (3.43 mL, 27.2 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (75 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give **10b** as reddish yellow oil (3.50 g, 80%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.24 (s, 9H, CH$_3$), 1.91 (s, 3H, CH$_3$), 7.00–7.03 (m, 2H, Ar), 7.72–7.76 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=0.6, 0.8, 1.9, 21.4 (CH$_3$), 111.4 (C), 115.2, 115.5, 131.9, 132.1 (CH), 157.9, 163.7, 167.3 (C), 188.4 (C=O).

3.2.9. 3-Chloro-4-(4-chlorophenyl)-4-[(trimethylsilyl)-oxy]-3-buten-2-one (10c). To a stirred benzene solution (33 mL) of **9c** (2.607 g, 11.27 mmol) was added triethylamine (2.52 mL, 18.0 mmol). After the solution was stirred for 2 h, trimethylchlorosilane (2.56 mL, 20.3 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (75 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give **10c** as reddish yellow oil (2.51 g, 73%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.24 (s, 9H, CH$_3$), 2.01 (s, 3H, CH$_3$), 7.29 (m, 2H, Ar), 7.62–7.65 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=0.8, 0.9, 2.0, 21.6 (CH$_3$), 111.6 (C), 128.6 (2CH), 130.8 (2CH), 136.3, 138.9, 158.6 (C), 190.9 (C=O).

3.2.10. 3-Chloro-4-(2-methylphenyl)-4-[(trimethylsilyl)-oxy]-3-buten-2-one (10d). To a stirred benzene solution (13.8 mL) of **9d** (1.16 g, 5.5 mmol) was added triethylamine (1.23 mL, 8.84 mmol). After the solution was stirred for 2 h, trimethylchlorosilane (1.25 mL, 9.9 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (50 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give **10d** as reddish yellow oil (1.13 g, 72%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.20 (s, 9H, CH$_3$), 2.14 (s, 3H, CH$_3$), 2.57 (s, 3H, CH$_3$), 728 (m, 1H, Ar), 7.35 (m, 1H, Ar), 7.47 (m, 1H, Ar), 7.48 (m, 1H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=0.4, 1.1, 2.1, 25.7 (CH$_3$), 108.4 (C), 125.6, 127.5, 130.1, 130.5 (CH), 134.8, 135.4, 182.6 (C), 195.3 (C=O).

3.2.11. 3-Chloro-4-(2-methoxyphenyl)-4-[(trimethylsilyl)-oxy]-3-buten-2-one (10e). To a stirred benzene solution (35.3 mL) of **9f** (2.67 g, 11.7 mmol) was added triethylamine (2.64 mL, 18.8 mmol). After the solution was stirred for 2 h, trimethylchlorosilane (2.67 mL, 21.19 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (75 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give **10e** as reddish yellow oil (2.70 g, 76%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.02 (s, 9H, CH$_3$), 1.96 (s, 3H, CH$_3$), 3.72 (s, 3H, OCH$_3$), 6.85–6.88 (m, 1H, Ar), 7.10–7.12 (m, 1H, Ar), 7.30–7.33 (m, 1H, Ar), 7.70–7.81 (m, 1H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=0.2 (3CH$_3$), 28.8 (CH$_3$), 54.9 (OCH$_3$), 110.7 (CH), 117.8 (C), 120.3 (CH), 122.8, 124.9 (C), 129.9, 131.4 (CH), 156.2 (C), 192.8 (C=O).

3.2.12. 2-Chloro-1-(2-methoxyphenyl)-1-[(trimethylsilyl)-oxy]-1-hexen-3-one (10f). To a stirred benzene solution (43.8 mL) of **9f** (3.72 g, 14.6 mmol) was added triethylamine (3.28 mL, 23.4 mmol). After the solution was stirred for 2 h, trimethylchlorosilane (3.32 mL, 26.3 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (75 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give **10f** as reddish yellow oil (4.05 g, 84%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ=0.02 (s, 9H, CH$_3$), 0.74 (t, *J*=7.4 Hz, 3H, CH$_3$), 1.38–1.50 (m, 2H, CH$_2$), 2.38 (t, *J*=7.2 Hz, 2H, CH$_2$), 3.73 (s, 3H, OCH$_3$), 6.86–6.87 (m, 1H, Ar), 6.90–6.92 (m, 1H, Ar), 7.10 (dd, *J*=7.4, 1.7 Hz, 1H, Ar), 7.29–7.31 (m, 1H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ=0.4, 0.8, 0.9, 13.6 (CH$_3$), 17.6, 42.7 (CH$_2$), 55.1 (OCH$_3$), 110.8 (CH), 117.6 (C), 120.4 (CH), 125.8 (C), 130.1, 131.1 (CH), 155.2, 156.3 (C), 196.3 (C=O).

3.2.13. 2-Chloro-1-(4-flourophenyl)butane-1,3-dione (9b). A mixture of **8b** (4.11 g, 22.8 mmol) and NCS (3.09 g, 22.8 mmol) in CCl$_4$ (50 mL) was heated at reflux for 4 h. After cooling, the precipitate of succinimide was filtered off and water was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **9b** as dark yellow oil (3.25 g, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.29 (s, 3H, CH_3), 5.46 (s, 1H, CH), 7.06–7.09 (m, 2H, Ar), 7.92–7.97 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=25.6 (CH_3), 63.2 (CH), 115.1, 115.3, 131.2, 131.3 (CH), 163.7, 167.7 (C), 187.3, 197.6 (C=O). GC–MS (EI 70 eV): *m/z* (%)=216 ([M]$^+$, [^{37}Cl], 12), 214 ([M]$^+$, [^{35}Cl], 4), 199 (4), 172 (114), 123 (100), 95 (39), 75 (13), 43 (19). HRMS (EI) calcd for $C_{10}H_8ClFO_2$ ([M]$^+$, [^{35}Cl]): 214.01914; found: 214.01824.

3.2.14. 3-Chloro-4-(4-chlorophenyl)butane-1,3-dione (9c). A mixture of **8c** (4.38 g, 22.3 mmol) and NCS (3.02 g, 22.3 mmol) in CCl_4 (49 mL) was heated at reflux for 4 h. After cooling, the precipitate of succinimide was filtered off and water was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **9c** as yellowish oil (2.60 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.31 (s, 3H, CH_3), 5.43 (s, 1H, CH), 7.42 (m, 2H, CH_3), 7.84–7.87 (m, 2H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=27.0 (CH_3), 64.5 (CH), 128.7 (C), 129.7 (2CH), 131.1 (2CH), 141.6 (C), 189.1, 198.9 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=234 ([M]$^+$, [2×^{37}Cl], 1), 232 ([M]$^+$, [^{37}Cl], [^{35}Cl], 6), 230 ([M]$^+$, [2×^{35}Cl], 10), 215 (3), 188 (13), 139 (100), 111 (38), 75 (21), 43 (26). HRMS (EI) calcd for $C_{10}H_8Cl_2O_2$ ([M]$^+$, [2×^{35}Cl]): 229.98959; found: 229.98919.

3.2.15. 2-Chloro-1-*o*-tolylbutane-1,3-dione (9d). A mixture of **8d** (2.21 g, 12.5 mmol) and NCS (1.67 g, 12.5 mmol) in CCl_4 (27.6 mL) was heated at reflux for 4 h. After cooling, the precipitate of succinimide was filtered off and water was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **9d** as a yellow oil (1.16 g, 44%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.27 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.16 (m, 1H, Ar), 7.19–7.20 (m, 2H, Ar), 7.24 (m, 1H, Ar), 15.46 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=19.6, 26.0 (CH_3), 108.6 (C), 125.8, 127.7, 130.4 (CH), 135.5, 135.7, 182.9 (C), 195.6 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3389 (w), 3066 (m), 2929 (m), 2870 (m), 1684 (m), 1570 (m), 1201 (m), 1037 (m), 903 (m), 738 (w). GC–MS (EI, 70 eV): *m/z* (%)=212 ([M]$^+$, [^{37}Cl], 3), 210 ([M]$^+$, [^{35}Cl], 7), 195 (100), 175 (6), 160 (11), 119 (92), 103 (15), 77 (12), 65 (19), 43 (21). HRMS (EI) calcd for $C_{11}H_{11}ClO_2$ ([M]$^+$, [^{35}Cl]): 210.04421; found: 210.04370.

3.2.16. 2-Chloro-1-(2-methoxyphenyl)butane-1,3-dione (9e). A mixture of **8e** (4.80 g, 25.0 mmol) and NCS (3.33 g, 25 mmol) in CCl_4 (55 mL) was heated at reflux for 4 h. After cooling, the precipitate of succinimide was filtered off and water was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **9e** as yellow oil (2.67 g, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.26 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 5.56 (s, 1H, CH), 6.88 (d, *J*=8.4 Hz, 1H, Ar), 6.91–6.96 (m, 1H, Ar), 7.40–7.46 (m, 1H, Ar), 7.74 (dd, *J*=7.6, 1.9 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=26.0 (CH_3), 54.5 (OCH_3), 66.9 (CH), 110.8, 120.4 (CH), 123.4 (C), 130.4, 134.3 (CH), 157.4 (C), 189.3, 196.3 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=228 ([M]$^+$, [^{37}Cl], 3), 226 ([M]$^+$, [^{35}Cl], 1), 197 (^{37}Cl, 8), 195 (^{35}Cl, 24), 135 (100), 108 (7), 92 (9), 77 (21), 63 (5). HRMS (EI) calcd for $C_{10}H_9ClO_2$ ([M]$^+$, [^{35}Cl]): 226.03912; found: 226.03926.

3.2.17. 2-Chloro-1-(2-methoxyphenyl)hexane-1,3-dione (9f). A mixture of **8f** (4.00 g, 18 mmol) and NCS (2.41 g, 18 mmol) in CCl_4 (40 mL) was heated at reflux for 4 h. After cooling, the precipitate of succinimide was filtered off and water was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **9f** as yellowish oil (3.72 g, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.80 (t, *J*=7.4 Hz, 3H, CH_3), 1.48–1.58 (m, 2H, CH_2), 2.51–2.58 (m, 2H, CH_2), 3.73 (s, 3H, OCH_3), 5.64 (s, 1H, CH), 6.83–6.86 (m, 1H, Ar), 6.87–6.92 (m, 1H, Ar), 7.36–7.42 (m, 1H, Ar), 7.71 (dd, *J*=7.8, 1.7 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.6 (CH_3), 15.0, 39.5 (CH_2), 55.6 (OCH_3), 65.8, 110.0, 119.3 (CH), 122.6 (C), 129.5, 133.5 (CH), 156.5 (C), 188.5, 197.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=2957 (w), 2926 (w), 1665 (s), 1618 (w), 1440 (s), 1344 (s), 1177 (s), 1094 (m), 805 (s). GC–MS (EI, 70 eV): *m/z* (%)=256 ([M]$^+$, [^{37}Cl], 6), 254 ([M]$^+$, [^{35}Cl], 12), 223 (79), 184 (59), 135 (100), 92 (46), 77 (76), 43 (64). HRMS (EI) calcd for $C_{13}H_{15}ClO_3$ ([M]$^+$, [^{35}Cl]): 254.07042; found: 254.07013.

3.2.18. 4-(4-Fluorophenyl)-4-hydroxy-3-buten-2-one (8b). To a stirred solution of LDA (75 mmol) in THF (62 mL) was added acetone (2.904 g, 50.0 mmol) at −78 °C. After the solution was stirred for 1 h, 4-fluorobenzoyl chloride (9.51 g, 60.0 mmol) was added. The temperature of the solution was allowed to rise to 20 °C for 12 h. A saturated solution of NH_4Cl was added, the layers were separated, and the aqueous layer was extracted with ethylacetate (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc 30:1→20:1) to give **8b** as a colorless solid (3.9 g, 36%), mp=48–49 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.11 (s, 3H, CH_3), 6.04 (s, 1H, CH), 7.04 (m, 2H, CH), 7.81 (m, 2H, CH), 16.07 (br s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.4 (CH_3), 95.3 (CH), 114 (d, ^3J=21.8 Hz, 2CH), 128.4 (d, ^2J=8.9 Hz, 2CH), 130.3 (d, ^4J=2.9 Hz, C), 164.3 (d, ^1J=252.0 Hz, CF), 181.9 (C), 191.8 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=1603 (s), 1507 (s), 1297 (m), 1246 (s), 1159 (m), 1095 (m), 1014 (w), 849 (s), 786 (s), 506 (w). MS (EI, 70 eV): *m/z* (%)=180 ([M]$^+$, 64), 165 (66), 138 (6), 123 (100), 109 (6), 95 (48), 85 (11), 75 (20), 69 (50), 50 (5), 43 (23). HRMS (EI) calcd for $C_{10}H_9FO_2$ ([M]$^+$): 180.05811; found: 180.05765.

3.2.19. 4-(4-Chlorophenyl)-4-hydroxy-3-buten-2-one (8c). To a stirred solution of LDA (75 mmol) in THF (62 mL) was added acetone (2.904 g, 50.0 mmol) at −78 °C. After the solution was stirred for 1 h, 4-chlorobenzoyl chloride (10.5 g, 60.0 mmol) was added. The temperature of the solution was allowed to rise to 20 °C for 12 h. A saturated solution of NH_4Cl was added, the layers were separated, and the aqueous layer was extracted with ethylacetate (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc 30:1→20:1) to give **8c** as a light yellow solid (3.762 g, 38%), mp=66–68 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.12 (s, 3H, CH_3), 6.06 (s, 1H, CH), 7.33 (m, 1H, CH), 7.35 (m, 1H, CH), 7.72 (m, 1H, CH), 7.75 (m, 1H, CH), 16.01 (br s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.1 (CH_3), 96.9 (CH), 128.7 (2CH), 129.3 (2CH), 133.7, 138.9, 182.6 (C), 194.1 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3075 (m), 2847 (m), 1594 (s), 1547 (s), 1486 (s), 1284 (m), 1113 (m), 1093 (s), 1012 (s), 840 (m), 779 (s), 437 (m). MS (EI, 70 eV): *m/z* (%)=198 ([M]$^+$, [^{37}Cl], 34), 196 ([M]$^+$, [^{35}Cl], 69), 181 (87), 161 (26), 154 (8), 139 (100), 111 (44), 101 (5), 89 (13), 85 (25), 75 (36), 69 (79), 63 (6), 50 (11), 43 (36). HRMS (EI) calcd for $C_{10}H_9ClO_2$ ([M]$^+$, [^{35}Cl]): 196.02856; found: 196.02870.

3.2.20. 4-Hydroxy-4-(2-methylphenyl)-3-buten-2-one (8d). To a stirred solution of LDA (75 mmol) in THF (62 mL) was added acetone (2.904 g, 50.0 mmol) at −78 °C. After the solution was stirred for 1 h, 2-methylbenzoyl chloride (9.25 g, 60.0 mmol) was added. The temperature of the solution was allowed to rise to 20 °C for 12 h. A saturated solution of NH_4Cl was added, the layers were separated, and the aqueous layer was extracted with ethylacetate (3×150 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc 30:1→20:1) to give **8d** as a yellowish oil (3.5 g, 33%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.05 (s, 3H, CH_3), 2.39 (s, 3H, CH_{3Ar}), 5.74 (s, 1H, CH), 7.12 (d, ^3J=7.2 Hz, 2H, CH), 7.22 (m, 1H, CH), 7.35 (dd, ^3J=7.4 Hz, ^4J=1.9 Hz, 1H, CH), 15.90 (br s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.0 (CH_3), 25.9 (CH_3), 101.1 (CH), 126.1, 128.6, 131.2, 132.0 (CH), 136.3, 139.7, 188.5 (C), 193.3 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2967 (w), 1717 (m), 1606 (s), 1457 (s), 1264 (s), 1159 (m), 1069 (w), 769 (w), 735 (s), 662 (w). GC–MS (EI, 70 eV): *m/z* (%)=176 ([M]$^+$, 13), 161 (100), 143 (3), 132 (6), 119 (35), 91 (41), 85 (10), 77 (8), 69 (30), 65 (17), 51 (6), 43 (21), 39 (7). HRMS (EI) calcd for $C_{11}H_{12}O_2$ ([M]$^+$): 176.08318; found: 176.08266.

3.2.21. 4-Chloro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (13a). Concd sulfuric acid (8.5 mL) was added to **11a** (195 mg, 0.71 mmol) and the solution was stirred for 1 h. Then water was added and aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **13a** as yellow solid (70 mg, 40%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.27 (s, 3H, CH_3), 6.57 (s, 1H, Ar), 7.18–7.25 (m, 1H, Ar), 7.38–7.44 (m, 1H, Ar), 7.55 (d, *J*=7.2 Hz, 1H, Ar), 8.03 (d, *J*=7.6 Hz, 1H, Ar), 8.43 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.3 (CH_3), 117.5 (C), 120.5 (CH), 122.0 (C), 124.4, 124.8, 129.6 (CH), 135.0 (C), 135.1 (CH), 139.9, 143.3, 147.9, 156.0 (C), 195.2 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=246 ([M]$^+$, [^{37}Cl], 50), 244 ([M]$^+$, [^{35}Cl], 100), 216 (10), 181 (21), 152 (37), 126 (3), 90 (7), 76 (17). HRMS (EI) calcd for $C_{14}H_9ClO_2$ ([M]$^+$, [^{35}Cl]): 244.02856; found: 244.02847.

3.2.22. 4-Chloro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (13b). Concd sulfuric acid (3.1 mL) was added to **11b** (74 mg, 0.27 mmol) and the solution was stirred for 1 h. Then water was added and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **13b** as yellow solid (60 mg, 86%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.07 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 7.11–7.22 (m, 1H, Ar), 7.36–7.42 (m, 1H, Ar), 7.50–7.53 (m, 1H, Ar), 7.96–7.99 (m, 1H, Ar), 8.76 (s, 1H, OH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=11.8, 17.1 (CH_3), 116.0, 122.0 (C), 123.8, 124.1 (CH), 127.9 (C), 128.7 (CH), 134.3 (C), 134.5 (CH), 136.5, 143.3, 144.9, 154.3 (C), 195.5 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=260 ([M]$^+$, [^{37}Cl], 50), 258 ([M]$^+$, [^{35}Cl], 100), 243 (12), 223 (29), 195 (11), 176 (9), 165 (27), 152 (12), 139 (6), 115 (5), 82 (8). HRMS (EI) calcd for $C_{15}H_{11}ClO_2$ ([M]$^+$, [^{35}Cl]): 258.04421; found: 258.04414.

3.2.23. 4-Chloro-7-fluoro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (13c). Concd sulfuric acid (2.31 mL) was added to **11e** (57 mg, 0.19 mmol) and the solution was stirred for 1 h. Then water was added and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **13c** as yellow solid (30 mg, 61%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.29 (s, 3H, CH_3), 6.58 (s, 1H, Ar), 7.06–7.13 (m, 1H, Ar), 7.09 (dd, *J*=7.2, 2.4 Hz, 1H, Ar), 8.01–8.05 (m, 1H, Ar), 8.33 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.9 (CH_3), 110.5 (CH), 116.3, 118.9 (C), 119.7, 120.4, 124.7 (CH), 135.9, 137.6, 137.9, 147.1, 154.7 (C), 162.5 (d, ^1J=251.1 Hz, CF), 192.2 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=264 ([M]$^+$, [^{37}Cl], 50), 262 ([M]$^+$, [^{35}Cl], 100), 234 (15), 199 (13), 152 (7), 132 (7), 110 (8), 99 (11), 84 (11). HRMS (EI) calcd for $C_{14}H_8ClFO_2$ ([M]$^+$, [^{35}Cl]): 262.01914; found: 262.01903.

3.2.24. 4-Chloro-7-fluoro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (13d). Concd sulfuric acid (3.06 mL) was added to **11f** (79 mg, 0.25 mmol) and the solution was stirred for 1 h. Then water was added and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **13d** as yellow solid (38 mg, 55%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.04 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 6.98–7.05 (m, 1H, Ar), 7.13–7.18 (m, 1H, Ar), 7.85–7.89 (m, 1H, Ar), 8.58 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.8, 15.2 (CH_3), 109.6 (CH), 114.3 (C), 118.3 (CH), 119.6 (C), 123.5 (CH), 125.8, 133.9, 134.8, 136.9, 148.4, 152.4 (C), 161.5 (d, ^1J=251.0 Hz, CF), 191.7 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=278 ([M]$^+$, [^{37}Cl], 50), 276 ([M]$^+$, 100), 261 (16), 241 (31), 213 (12), 183 (25), 170 (11), 138 (6), 91 (7). HRMS (EI) calcd for $C_{15}H_{10}ClFO_2$ ([M]$^+$, [^{35}Cl]): 276.03479; found: 276.03433.

3.2.25. 4,7-Dichloro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (13e). Concd sulfuric acid (3.3 mL) was added to **11h** (85 mg, 0.27 mmol) and the solution was stirred for 1 h. Then water was added and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **13e** as yellow solid (65 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.31 (s, 3H, CH_3), 6.63 (s, 1H, Ar), 7.44 (dd, J=8.1, 2.1 Hz, 1H, Ar), 7.53 (m, 1H, Ar), 8.00 (d, J=8.0 Hz, 1H, Ar), 8.35 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.3 (CH_3), 117.4 (C), 120.8 (CH), 122.2 (C), 124.7, 125.8, 135.4 (CH), 135.9, 136.6, 139.2, 141.4, 148.5, 156.2 (C), 193.7 (C=O). GC–MS (EI, 70 eV): *m/z* (%)=282 ([M]$^+$, [2×^{37}Cl], 15), 280 ([M]$^+$, [^{37}Cl], [^{35}Cl], 65), 278 ([M]$^+$, [2×^{35}Cl] 100), 251 (11), 215 (12), 186 (24), 152 (57), 137 (8/), 123 (12), 107 (21), 93 (17), 75 (9). HRMS (EI) calcd for $C_{14}H_8Cl_2O_2$ ([M]$^+$, [2×^{35}Cl]): 277.98959; found: 277.98973.

3.2.26. 4,7-Dichloro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (13f). Concd sulfuric acid (2.76 mL) was added to **11i** (74 mg, 0.23 mmol) and the solution was stirred for 1 h. Then water was added and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1→20:1) to give **13f** as yellow solid (50 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.11 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 7.36 (dd, J=8.1, 2.1 Hz, 1H, Ar), 7.49–7.50 (m, 1H, Ar), 7.94–7.97 (m, 1H, Ar), 8.58 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.3, 17.6 (CH_3), 116.5, 123.1 (C), 124.6, 125.7 (CH), 128.8 (C), 134.4 (C), 135.3, 136.3, 136.5, 141.8, 145.9, 154.9 (C), 194.4 (C=O).GC–MS (EI, 70 eV): *m/z* (%)=296 ([M]$^+$, [2×^{37}Cl], 15), 294 ([M]$^+$, [^{37}Cl], [^{35}Cl], 65), 292 ([M]$^+$, [2×^{35}Cl], 277 (10), 257 (15), 229 (9), 199 (5), 165 (11), 150 (6), 111 (7), 82 (10).

Acknowledgements

Financial support from the state of Pakistan (HEC scholarship for M.A.Y., I.H., and I.I.), and from the state of Mecklenburg-Vorpommern (scholarship for Z.A.) is gratefully acknowledged.

References and notes

1. (a) Sala, T.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1981**, 849; (b) Birkbeck, A. A.; Sargent, M. V.; Elix, J. A. *Aust. J. Chem.* **1990**, *43*, 419; (c) Mahandru, M. M.; Tajbakhsh, A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 413; (d) Elix, J. A.; Jenie, U. A.; Arvidsson, L.; Joergensen, P. M.; James, P. W. *Aust. J. Chem.* **1986**, *39*, 719; (e) Nielsen, J.; Nielsen, P. H.; Frisvad, J. C. *Phytochemistry* **1999**, *50*, 263.
2. (a) Sakata, K.; Masago, H.; Sakurai, A.; Takahashi, N. *Tetrahedron Lett.* **1982**, *23*, 2095; (b) Tomozane, H.; Takeuchi, Y.; Choshi, T.; Kishida, S.; Yamato, M. *Chem. Pharm. Bull.* **1990**, *38*, 925; (c) Belofsky, G. N.; Gloer, K. B.; Gloer, J. B.; Wicklow, D. T.; Dowd, P. F. *J. Nat. Prod.* **1998**, *61*, 1115.
3. Steyn, P.; Vleggaar, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2250.
4. See for example 6-demethylchlortetracyclin: Olack, G.; Morrison, H. *J. Org. Chem.* **1991**, *56*, 4969.
5. Nozawa, K.; Nakajima, S.; Yamada, M.; Kawai, K.-i. *Chem. Pharm. Bull.* **1980**, *28*, 1622.
6. (a) Wei, S.; Chu, J. *Experientia* **1974**, *30*, 174; (b) Sasaki, H.; Hosokawa, T.; Sawada, M.; Ando, K. *J. Antibiot.* **1973**, *26*, 676; (c) Hunter, R.; Mellows, G. *Tetrahedron Lett.* **1978**, *19*, 5051.
7. (a) Kwon, H. J.; Yoshida, M.; Abe, K.; Horinouchi, S.; Beppu, T. *Biosci. Biotechnol. Biochem.* **1992**, *56*, 538; (b) Lampilas, M.; Lett, R. *Tetrahedron Lett.* **1992**, *33*, 777; (c) Elix, J. A.; Barclay, C. E.; Lumbsch, H. T.; Wardlaw, J. H. *Aust. J. Chem.* **1997**, *50*, 971; Bazzanin: (d) Martin, U.; Zapp, J.; Becker, H. *Phytochemistry* **1998**, *47*, 89.
8. Zhang, H.-W.; Huang, W.-Y.; Song, Y.-C.; Chen, J.-R.; Tan, R.-X. *Helv. Chim. Acta* **2005**, *88*, 2861.
9. Flambamycin: (a) Ollis, W. D.; Smith, C.; Wrigth, D. E. *Tetrahedron* **1979**, *35*, 105; Everninomicin: (b) Schering Co., Kenilworth, N.J. (USA). U.S. Patent 3,920,629, 1975; *Chem. Abstr.* **1975**, *84*, 90526.
10. Oda, T.; Yamaguchi, Y.; Sato, Y. *Chem. Pharm. Bull.* **1986**, *34*, 858.
11. 4-*O*-Methylarmillaridin: (a) Donnelly, D. M. X.; Hutchinson, R. M. *Phytochemistry* **1990**, *29*, 179; Melledonal B: (b) Arnone, A.; Cardillo, R.; Nasini, G.; Meille, S. V. *J. Chem. Soc., Perkin Trans. 1* **1988**, 503.
12. (a) Jinno, S.; Hata, K.; Shimidzu, N.; Okita, T. *J. Antibiot.* **1998**, *51*, 508; (b) Jinno, S.; Okita, T. *Chem. Pharm. Bull.* **1998**, *46*, 1688; (c) Papendorf, O.; Koenig, G. M.; Wright, A. D. *Phytochemistry* **1998**, *49*, 2383; (d) Bohlmann, F.; Knauf, W.; Misra, L. N. *Tetrahedron* **1984**, *40*, 4987; Methoxymicareic acid: (e) Elix, J. A.; Jones, A. J.; Lajide, L.; Coppins, B. J.; James, P. W. *Aust. J. Chem.* **1984**, *37*, 2349.
13. Falch, B. S.; Koenig, G. M.; Wright, A. D.; Sticher, O. *J. Org. Chem.* **1993**, *58*, 6570.
14. *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004.
15. (a) Harkal, S.; Kumar, K.; Michalik, D.; Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Beller, M. *Tetrahedron Lett.* **2005**, *46*, 3237 and references cited therein; (b) Harkal, S.; Rataboul, F.; Zapf, A.; Fuhrmann, C.; Riermeier, T. H.; Monsees, A.; Beller, M. *Adv. Synth. Catal.* **2004**, *346*, 1742.
16. (a) Savard, J.; Brassard, P. *Tetrahedron Lett.* **1979**, *20*, 4911; (b) Corral, C.; Lissavetzky, J.; Manzanares, I. *Synthesis* **1997**, 29.
17. (a) Chan, T.-H.; Brownbridge, P. *J. Am. Chem. Soc.* **1980**, *102*, 3534; (b) Brownbridge, P.; Chan, T.-H.; Brook, M. A.; Kang, G. J. *Can. J. Chem.* **1983**, *61*, 688.
18. For a review of 1,3-bis(silyl enol ethers), see: Langer, P. *Synthesis* **2002**, 441.

19. For a review of [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 1,3-dielectrophiles, see: Feist, H.; Langer, P. *Synthesis* **2007**, 327.
20. Ahmed, Z.; Langer, L. *Tetrahedron Lett.* **2006**, *47*, 417.
21. Roshchupkina, G. I.; Gatilov, Y. V.; Rybalova, T. V.; Reznikov, V. A. *Eur. J. Org. Chem.* **2004**, 1765.
22. Tius, M. A.; Kwoka, C. K.; Gu, X. Q.; Zhao, C. *Synth. Commun.* **1994**, *24*, 871.
23. Molander, G. A.; Cameron, K. O. *J. Am. Chem. Soc.* **1993**, *115*, 830.
24. Nguyen, V. T. H.; Bellur, E.; Appel, B.; Langer, P. *Synthesis* **2006**, 1103.
25. CCDC-654466 (**11a**), CCDC-654467 (**11c**), and CCDC-652984 (**12d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
26. Hussain, I.; Nguyen, V. T. H.; Yawer, M. A.; Dang, T. T.; Fischer, C.; Reinke, H.; Langer, P. *J. Org. Chem.* **2007**, *72*, 6255.
27. Reim, S.; Lau, M.; Langer, P. *Tetrahedron Lett.* **2006**, *47*, 6903.