3-Bromopropenyl Methyl Carbonate: A New Reagent for the α-Hydroxy Allylation Reaction of Aldehydes in Water

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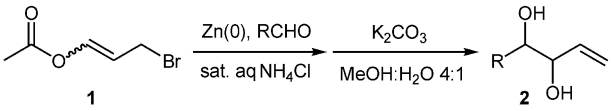
Abstract: 3-Bromopropenyl methyl carbonate reacts smoothly with aldehydes in the presence of zinc in a mixture of saturated aqueous NH_4Cl and THF (9:1). Monoprotected alk-1-en-3,4-diols are formed in high yields and in short reaction times. The reaction is diastereoselective, saturated aldehydes afford *anti*-adducts, while α,β-unsaturated and aromatic aldehydes preferentially give the *syn*-isomers. Very simple conditions for the conversion of intermediate monocarbonate derivatives of alk-1-en-3,4-diols to cyclic carbonates are also reported.

Key words: zinc, 3-bromopropenyl carbonates, heterosubstituted allyl zinc complexes, water as solvent, monoprotected alk-1-en-3,4-diols

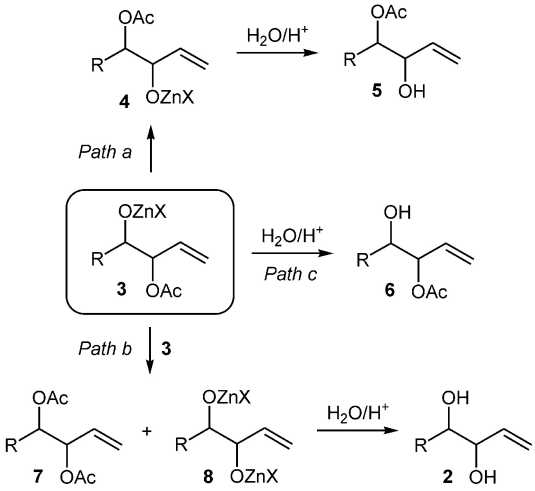
Twenty years have passed since the seminal work of Pétrier and Luche on the allylation of aldehydes in aqueous media using organozinc reagents formed in situ. Allylic bromides were reacted in a Barbier-type protocol, using a mixture of saturated aqueous NH_4Cl and THF as the solvent and zinc as the metal, to give homoallylic alcohols in almost quantitative yields (> 95%) and short reaction times (30–45 min).[1] In 2001 the Presidential Green Chemistry Challenge Award (academic category) was won by Li for his important contribution in the field of Grignard/Barbier reactions using allylic halides and indium in water and in air.[2] In recent times water as a solvent or co-solvent for organometallic chemistry has been thoroughly investigated[3] and expanded, for example, in palladium-catalyzed cross-coupling reactions[4] and in Lewis acid promoted processes.[5] Water, the archetypical green solvent, is not only low cost, non-toxic, and a safer solvent, compared with commonly used organic solvents,[6] but often affords different results such as increased reactions rates, for example in pericyclic cycloadditions, or modified selectivities.[7]

We recently proposed a new protocol for the α-hydroxy allylation of carbonyl compounds in aqueous solvents, using 3-bromopropenyl acetate **1** as the precursor of a heterosubstituted allylic organometallic species, thus opening a route to alk-1-en-3,4-diols **2** (Scheme 1).[8] The diastereochemical outcome of this reaction was unprecedented among alternative hydroxyallylation reagents;[9] indeed, saturated aldehydes mainly afforded *anti*-adducts while aromatic or α,β-unsaturated aldehydes led to *syn*-adducts.



Scheme 1

The reaction of **1** with metallic zinc in saturated aqueous ammonium chloride solutions is very rapid at room temperature, and if an aldehyde is present, the corresponding diols **2** are obtained in very good yields (60–90%) after hydrolysis and purification by flash chromatography. Hydrolysis of the intermediate ester functionality to free alk-1-en-3,4-diols **2** is advisable, owing to the occurrence of both intramolecular (Path a, Scheme 2) and intermolecular (Path b, Scheme 2) transesterification reactions involving the intermediate alkoxide **3**, leading to a number of adducts, as outlined in Scheme 2.



Scheme 2

In principle, the desired monoprotected product **6** could be obtained in high yields if quenching of the intermediate zinc alkoxide **3** with water (Path c) is faster than the transesterification processes (Paths b and c). The idea of lowering the carbonyl electrophilicity led us to explore the reactivity of 3-bromopropenyl carbonate **10** as a new precursor of heterosubstituted allylic organometallic species. 3-Bromopropenyl methyl carbonate (**10**) can be obtained

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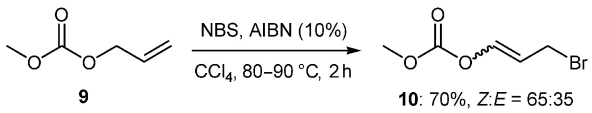
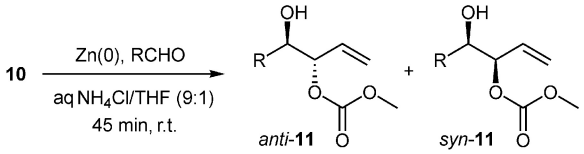
in good yield, as a 65:35 mixture of *Z*/*E*-isomers, by radical bromination[10] of allyl methyl carbonate (**9**)[11] (Scheme 3).



Scheme 3

We were delighted by the observation that the reaction of **10** (1.2 equiv) with aldehydes in saturated aqueous NH_4Cl and THF (9:1) using a slight excess of zinc (1.5 equiv) proceeded smoothly affording the monoprotected adducts **11** in high yields as the sole products, after 45 minutes at room temperature (Scheme 4, Table 1).



Scheme 4

Table 1 Zinc Mediated α-Hydroxy Allylation of Aldehydes with **10**

Entry	R in RCHO	**11**, Yield (%)[a]	*anti*-**11**/*syn*-**11**[b]
1	Cyclohexyl-	**11a**, 92[c]	95:5
2	1-Methylethyl-	**11b**, 92[c]	95:5
3	2-Methypropyl-	**11c**, 86	70:30
4	2-Phenylethyl-	**11d**, 85	75:25
5	Nonyl-	**11e**, 95	90:10
6	Phenyl-	**11f**, 95	30:70
7	1-Naphthyl-	**11g**, 93	40:60
8	4-Methoxyphenyl-	**11h**, 98	12:88
9	4-Fluorophenyl-	**11i**, 91	30:70
10	(*E*)-2-Phenylethenyl-	**11j**, 88	25:75

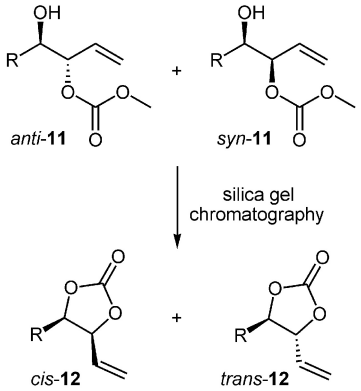
[a] Yields determined by ^{1}H NMR spectroscopy and GC-MS of the crude reaction mixtures.
[b] Diastereomeric ratio determined by ^{1}H spectroscopy and GC-MS of the crude reaction mixtures.
[c] Isolated yields.

Diasteroselectivity was determined by ^{1}H NMR spectroscopy after conversion of **11** into the corresponding diols **2** by basic hydrolysis (K_2CO_3, MeOH–H_2O, 4:1). As reported by Jiang et al.[12] and later on confirmed by us,[8b] the chemical shift of the homoallylic proton (H-4) in *syn*-**2** always resonates 0.1–0.3 ppm upfield from that of *anti*-**2**. Moreover, we observed that GC retention times of *syn*-**11** are always less than those of *anti*-**11**.

Further trends in chromatographic properties were observed in this work, which are useful for anticipating *syn*/*anti* or *cis*/*trans* stereorelationships in **11** and **12**, respectively. For example, *trans*-**12** has a higher R_f on silica with respect to *cis*-**12** and GC retention times of *trans*-**12** are always lower than retention times of *cis*-**12**.

As reported in Table 1, the same stereochemical preference displayed by 3-bromopropenyl acetate (**1**) was observed using carbonate **10**. Again, while aliphatic aldehydes give *anti*-adducts with good diastereoselectivity, aromatic and α,β-unsaturated aldehydes furnished *syn*-adducts, generally with lower levels of diastereoselctivity. This behavior, peculiar to 3-halopropenyl esters and carbonates, is ascribed to the presence of a C=O group on the oxygen substituent; a theoretical study on the reaction mechanism will be published in due course.

When we tried to purify **11** by flash-chromatography on silica we observed the cyclization of **12** to 1,3-dioxolanones, to variable extents, depending on the nature of the R group (Scheme 5).



Scheme 5

In particular: i) when R is a secondary aliphatic alkyl group (Table 1, entries 1, 2), compounds **11** are quite stable on silica gel and can be isolated in high yields simply by flash chromatography; ii) when R is a primary aliphatic alkyl group (Table 1, entries 3–5) only partial cyclization to **12** is observed; and iii) extensive cyclization occurs when R is aromatic or unsaturated (Table 1, entries 6–10). This general trend can be easily explained considering: i) the relative bulkiness of R group and ii) the fact that cyclization of *anti*-**11** affords sterically crowded *cis*-**12**, while *syn*-**11** gives the less sterically congested *trans*-**12**.

A frequently used trick to purify products sensitive to the acidity of silica gel involves the addition of a small amount of Et_3N (1–3%) to the eluent. To our surprise, the presence of Et_3N increased the rate of cyclization, independently of the nature of the R group. So we developed a very easy procedure for the complete cyclization of **11** to **12**, promoted by Et_3N adsorbed onto SiO_2: the crude reaction mixture containing **11** was stirred with Et_3N/SiO_2 in Et_2O for two hours at room temperature, the solvent was removed, and the solid residue was chromatographed (Table 2).

Table 2 Cyclization to 1,3-Dioxolanones **12** Promoted by Et_3N/SiO_2

Entry	**11**	*trans*-**12**, Yield (%)[a]	*cis*-**12**, Yield (%)[a]
1	**11a**	*trans*-**12a**, 5	*cis*-**12a**, 88
2	**11b**	*trans*-**12b**, 5	*cis*-**12b**, 82
3	**11c**	*trans*-**12c**, 21	*cis*-**12c**, 56
4	**11d**	*trans*-**12d**, 22	*cis*-**12d**, 59
5	**11e**	*trans*-**12e**, 10	*cis*-**12e**, 72
6	**11f**	*trans*-**12f**, 61	*cis*-**12f**, 32
7	**11g**	*trans*-**12g**, 50	*cis*-**12g**, 35
8	**11h**	*trans*-**12h**, 83	*cis*-**12h**, 15
9	**11i**	*trans*-**12i**, 62	*cis*-**12i**, 26
10	**11j**	*trans*-**12j**, 58	*cis*-**12j**, 24

[a] Yields, determined after purification by flash-chromatography on silica gel, refer to the two-step sequence – formation of **11** and cyclization to **12**.

In conclusion, we have reported a simple and very efficient procedure for the synthesis of monoprotected alk-1-en-3,4-diols **11** in an aqueous medium. The most important advantages of this procedure with respect to that previously reported, based on ester **1**, are: i) the preparation of **10** does not require the use of highly toxic acrolein; ii) **10** is noticeably more stable and easier to store than **1**; e.g., **10** can be stored under an inert atmosphere at room temperature for several months without appreciable decomposition; and iii) the organozinc complex derived from **10** proved to be more reactive than the corresponding organometallic species derived from **1**, as confirmed on the one hand as the isolated yields (Table 2) are systematically 5–15% higher than those previously reported using **1**,[8b] and on the other hand by the successful α-hydroxyallylation of 4-fluorobenzaldehyde (Table 2, entry 9), which conversely undergoes decomposition under the same experimental conditions, using **1**.[8b]

Finally, the use of the carbonate functionality could in principle allow us to modulate the reactivity of 3-bromopropenyl carbonates, as well as the stability of the final adducts; for example the stability of open chain adducts **11** can be increased by using *tert*-butyl carbonates instead of a methyl carbonate, or, conversely, the spontaneous in situ formation of cyclic carbonates **12** could be achieved by using an RO group which is a better leaving group than the methoxy group. Work aimed at exploring the further potential of carbonates is in progress.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300 and on a Varian Gemini 2000; chemical shifts are reported in ppm relative to TMS. GC analyses were performed with a HP5890 II instrument (HP-5MS cross-linked 5% phenylmethyl silicone glass capillary column, 0.25–μm film thickness) coupled to a HP5971 quadrupole mass detector. Melting points are uncorrected. All reagents were commercially available and were used without further purification, unless otherwise stated.

3-Bromopropenyl Methyl Carbonate (10)

AIBN (0.328 g, 2 mmol) was added to a mixture of freshly purified NBS[10] (3.56 g, 20 mmol) and allyl methyl carbonate (2.73 mL, 24 mmol) in CCl_4 (100 mL). The heterogeneous solution was rapidly brought to reflux (2–3 min) and stirred for 2 h at 80–90 °C. After cooling to r.t., the solution was filtered, and the organic solvent was evaporated at reduced pressure. The residue was rapidly chromatographed through a short pad of silica (cyclohexane–EtOAc, 9:1) and **10** was further purified by distillation under vacuum (bp 45–55 °C, ca. 3×10^{-2} mmHg) to afford 2.73 g (14 mmol, 70%) of the title compound as a 65:35 mixture of *Z* and *E* isomers.

(*Z*)-10

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 4.07 (dt, *J* = 1.0, 8.6 Hz, 2 H), 5.24 (dt, *J* = 6.1, 8.6 Hz, 1 H), 7.00 (dt, *J* = 1.0, 6.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9, 55.4, 111.4, 138.4, 152.8.

GC-MS (70 eV): *m*/*z* (%) = 55 (19), 59 (61), 71 (69), 115 (100), 119 (3), 121 (3), 194 (1), 196 (1).

(*E*)-10

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 3.98 (dt, *J* = 1.0, 8.6 Hz, 2 H), 5.73 (dt, *J* = 8.6, 12.2 Hz, 1 H), 7.24 (dt, *J* = 1.2, 12.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.8, 55.1, 109.6, 140.6, 152.6.

GC-MS (70 eV): *m*/*z* (%) = 55 (16), 59 (80), 71 (68), 115 (100), 119 (3), 121 (3), 194 (1), 196 (1).

4-Hydroxy-3-propenyl Methyl Carbonates (11); General Procedure

3-Bromopropenyl methyl carbonate (**10**; 0.145 mL, 1.2 mmol) and Zn (0.098 g, 1.5 mmol) were sequentially added to a solution of the aldehyde (1 mmol) in sat. aq NH_4Cl–THF (9:1, 5 mL); the heterogeneous solution was vigorously stirred at 20 ± 3 °C for 45 min. The aqueous phase was extracted with Et_2O, the combined organic phases were dried (Na_2SO_4), and concentrated at reduced pressure. The crude mixture so obtained was analyzed by ^{1}H NMR and GC-MS. Both **11a** and **11b** can be purified by flash chromatography on silica without significant decomposition; all other products were subjected to cyclization to **12** without prior purification.

***anti*-1-Cyclohexyl-1-hydroxybut-3-en-2-yl Methyl Carbonate (*anti*-11a)**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94–1.32 (m, 6 H), 1.51–2.05 (m, 5 H), 3.56 (br dd, *J* = ca. 4.0, 7.6 Hz, 1 H), 3.80 (s, 3 H), 5.18 (ddt, *J* = 0.9, 4.0, 7.4 Hz, 1 H), 5.40 (ddd, *J* = 0.9, 1.5, 10.5 Hz, 1 H), 5.45 (ddd, *J* = 0.9, 1.5, 17.4 Hz, 1 H), 5.95 (ddd, *J* = 7.4, 10.5, 17.4 Hz, 1 H).

GC-MS (70 eV): *m*/*z* (%) = 55 (100), 65 (44), 81 (30), 119 (3), 134 (2), 197 (1).

Anal. calcd for $C_{12}H_{20}O_4$ (228.14): C, 63.14; H, 8.83. Found: C, 63.75; H, 8.77.

***anti*-4-Hydroxy-5-methylhex-1-en-3-yl Methyl Carbonate (*anti*-11b)**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.6 Hz, 3 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 1.59–1.86 (m, 1 H), 3.51 (dd, *J* = 4.3, 7.3 Hz, 1 H), 3.80 (s, 3 H), 5.15 (dd, *J* = 4.3, 7.4 Hz, 1 H), 5.40 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.45 (dt, *J* = 1.0, 17.5 Hz, 1 H), 5.95 (ddd, *J* = 7.4, 10.3, 17.5 Hz, 1 H).

GC-MS (70 eV): *m*/*z* (%) = 55 (100), 69 (30), 79 (6), 97 (2), 157 (1).

Anal. calcd for $C_9H_{16}O_4$ (188.12): C, 57.43; H, 8.57. Found: C, 57.94; H, 8.61.

1,3-Dioxolan-2-ones (12); General Procedure

Et_3N/SiO_2 was prepared by simply stirring silica gel (25 g) with Et_3N (5 mL, 3.6 g, 36 mmol) in Et_2O at r.t. for 1 h. The solvent was completely removed under reduced pressure to give 27.5 g of silica (ca. 0.9 mmol Et_3N/1 g SiO_2). The crude reaction mixture containing **11** was stirred with Et_3N/SiO_2 (1.5 g) in Et_2O (10 mL) for 2 h at r.t., the solvent was evaporated under reduced pressure and products were purified by flash chromatography on silica (cyclohexane–EtOAc, 9:1).

4,5-*trans*-4-Cyclohexyl-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12a)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.77–1.43 (m, 6 H), 1.52–1.99 (m, 5 H), 4.09 (t, *J* = 6.6 Hz, 1 H), 4.79 (br tt, *J* = ca. 1.0, 6.8 Hz, 1 H), 5.38 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.44 (dt, *J* = 1.0, 17.2 Hz, 1 H), 5.87 (ddd, *J* = 7.0, 10.3, 17.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.2, 25.4, 26.0, 27.6, 27.7, 41.0, 80.3, 85.5, 120.6, 133.1, 154.4.

GC-MS (70 eV): *m*/*z* (%) = 55 (64), 67 (31), 79 (12), 81 (42), 95 (100), 109 (3), 119 (10), 134 (8), 196 (1).

Anal. calcd for $C_{11}H_{16}O_3$ (196.24): C, 67.32; H, 8.22. Found: C, 66.93; H, 8.15.

4,5-*cis*-4-Cyclohexyl-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12a)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88–1.43 (m, 5 H), 1.48–1.88 (m, 6 H), 4.38 (dd, *J* = 7.2, 8.9 Hz, 1 H), 5.05 (br tt, *J* = ca. 0.7, 7.3 Hz, 1 H), 5.48 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.49 (dt, *J* = 1.0, 17.2 Hz, 1 H), 5.94 (ddd, *J* = 7.4, 10.3, 17.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 25.0, 25.8, 27.9, 28.6, 37.1, 80.1, 83.8, 121.8, 129.1, 154.5.

GC-MS (70 eV): *m*/*z* (%) = 55 (67), 79 (15), 81 (44), 95 (100), 109 (6), 134 (5).

Anal. calcd for $C_{11}H_{16}O_3$ (196.24): C, 67.32; H, 8.22. Found: C, 66.86; H, 8.28.

4,5-*trans*-4-(1-Methylethyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12b)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.8 Hz, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 1.99 (dhept, *J* = 6.8 Hz, 1 H), 4.09 (t, *J* = 6.7 Hz, 1 H), 4.76 (tt, *J* = 1.0, 6.8 Hz, 1 H), 5.40 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.47 (dt, *J* = 1.0, 17.2 Hz, 1 H), 5.88 (ddd, *J* = 6.9, 10.3, 17.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2, 17.3, 31.5, 80.3, 86.1, 120.7, 133.1, 154.3.

GC-MS (70 eV): *m*/*z* (%) = 56 (100), 69 (54), 73 (48), 79 (10), 84 (9), 97 (4), 101 (3).

Anal. calcd for $C_8H_{12}O_3$ (156.18): C, 61.52; H, 7.74. Found: C, 61.39; H, 7.69.

4,5-*cis*-4-(1-Methylethyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12b)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.7 Hz, 3 H), 1.09 (d, *J* = 6.7 Hz, 3 H), 1.96 (dhept, *J* = 6.7, 8.7 Hz, 1 H), 4.32 (dd, *J* = 7.2, 8.7 Hz, 1 H), 5.05 (br tt, *J* = ca. 1.0, 7.2 Hz, 1 H), 5.48 (dt, *J* = 1.0, 10.5 Hz, 1 H), 5.52 (dt, *J* = 1.0, 17.7 Hz, 1 H), 5.93 (ddd, *J* = 7.1, 10.5, 17.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8, 18.6, 27.8, 80.1, 84.9, 121.9, 129.1, 154.4.

GC-MS (70 eV): *m*/*z* (%) = 56 (100), 69 (46), 73 (44), 79 (7), 84 (7), 97 (3), 101 (2).

Anal. calcd for $C_8H_{12}O_3$ (156.18): C, 61.52; H, 7.74. Found: C, 60.91, H, 7.80.

4,5-*trans*-4-(2-Methylpropyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12c)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.6 Hz, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H), 1.40–1.60 (m, 1 H), 1.66–1.98 (m, 2 H), 4.37 (ddd, *J* = 4.0, 7.7, 9.2 Hz, 1 H), 4.60 (br tt, *J* = ca. 1.0, 7.7 Hz, 1 H), 5.44 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.50 (dt, *J* = 1.0, 17.3 Hz, 1 H), 5.89 (ddd, *J* = 7.0, 10.3, 17.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9, 22.8, 24.8, 80.6, 83.1, 121.4, 131.9, 154.3.

GC-MS (70 eV): *m*/*z* (%) = 55 (61), 57 (30), 69 (100), 93 (4), 98 (5), 111 (2), 115 (1).

Anal. calcd for $C_9H_{14}O_3$ (170.21): C, 63.51; H, 8.29. Found: C, 63.50; H, 8.23.

4,5-*cis*-4-(2-Methylpropyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12c)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.6 Hz, 3 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 1.29 (ddd, *J* = 3.4, 8.4, 14.4 Hz, 1 H), 1.64 (ddd, *J* = 5.1, 10.5, 14.4 Hz, 1 H), 1.77–1.88 (m, 1 H), 4.80 (ddd, *J* = 3.4, 7.6, 10.5 Hz, 1 H), 5.08 (br tt, *J* = ca. 1.0, 7.4 Hz, 1 H), 5.46 (dt, *J* = 1.0, 10.5 Hz, 1 H), 5.49 (dt, *J* = 1.0, 17.4 Hz, 1 H), 5.84 (ddd, *J* = 7.1, 10.5, 17.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 23.0, 24.7, 38.5, 78.3, 80.0, 121.3, 129.5, 154.4.

GC-MS (70 eV): *m*/*z* (%) = 55 (68), 57 (30), 69 (100), 93 (5), 98 (5), 111 (4), 115 (1).

Anal. calcd for $C_9H_{14}O_3$ (170.21): C, 63.51; H, 8.29. Found: C, 63.22; H, 8.22.

4,5-*trans*-4-(2-Phenylethyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12d)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97–2.07 (m, 1 H), 2.07–2.19 (m, 1 H), 2.75 (dt, *J* = 8.3, 14.1 Hz, 1 H), 2.89 (ddd, *J* = 5.6, 9.3, 14.1 Hz, 1 H), 4.31 (ddd, *J* = 4.4, 7.6, 12.0 Hz, 1 H), 4.66 (br dt, *J* = ca. 1.0, 7.3 Hz, 1 H), 5.42 (dt, *J* = 1.0, 10.6 Hz, 1 H), 5.47 (dt, *J* = 1.0, 17.4 Hz, 1 H), 5.84 (ddd, *J* = 7.4, 10.6, 17.4 Hz, 1 H), 7.17–7.37 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.9, 34.6, 80.8, 82.6, 121.4, 126.4, 128.3, 128.6, 131.8, 139.7, 154.1.

GC-MS (70 eV): *m*/*z* (%) = 55 (15), 65 (15), 70 (18), 77 (12) 83 (35), 91 (100), 105 (13), 117 (15), 141 (5), 149 (7), 156 (28), 218 (1).

Anal. calcd for $C_{13}H_{14}O_3$ (218.25): C, 71.54; H, 6.47. Found: C, 71.75; H, 6.41.

4,5-*cis*-4-(2-Phenylethyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12d)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75–1.88 (m, 1 H), 1.94–2.09 (m, 1 H), 2.71 (dt, *J* = 8.2, 13.9 Hz, 1 H), 2.90 (ddd, *J* = 4.8, 9.1, 13.9 Hz, 1 H), 4.69 (ddd, *J* = 3.7, 7.8, 10.5 Hz, 1 H), 5.08 (br dt, *J* = ca. 1.0, 7.3 Hz, 1 H), 5.46 (dt, *J* = 1.0, 10.5 Hz, 1 H), 5.50 (dt, *J* = 1.0, 17.1 Hz, 1 H), 5.84 (ddd, *J* = 7.0, 10.5, 17.1 Hz, 1 H), 7.17–7.37 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.4, 31.8, 78.6, 79.8, 121.5, 126.4, 128.4, 128.6, 129.2, 139.9, 154.2.

GC-MS (70 eV): *m*/*z* (%) = 55 (10), 65 (19), 70 (36), 91 (100), 105 (24), 117 (19), 141 (5), 156 (14), 218 (22).

Anal. calcd for $C_{13}H_{14}O_3$ (218.25): C, 71.54; H, 6.47. Found: C, 71.13; H, 6.44.

4,5-*trans*-4-nonyl-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12e)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3 H), 1.20–1.42 (m, 14 H), 1.63–1.86 (m, 2 H), 4.31 (dt, *J* = 5.0, 7.6 Hz, 1 H), 4.64 (br dt, *J* = ca. 1.0, 7.4 Hz, 1 H), 5.43 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.50 (dt, *J* = 1.0, 17.4 Hz, 1 H), 5.88 (ddd, *J* = 7.2, 10.3, 17.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 22.6, 24.6, 29.1, 29.2, 29.26, 29.3, 31.8, 32.9, 81.9, 82.6, 121.1, 132.2, 154.3.

GC-MS (70 eV): *m*/*z* (%) = 55 (100), 69 (86), 80 (87), 83 (84), 93 (33), 95 (33), 97 (41), 107 (18), 121 (25), 135 (24), 149 (14), 163 (3), 178 (1), 196 (1).

Anal. calcd for $C_{14}H_{24}O_3$ (240.34): C, 69.96; H, 10.07. Found: C, 69.71; H, 9.99.

4,5-*cis*-4-Nonyl-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12e)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3 H), 1.22–1.40 (m, 14 H), 1.48–1.75 (m, 2 H), 4.70 (ddd, *J* = 3.9, 7.6, 9.8 Hz, 1 H), 5.08 (br dt, *J* = ca. 1.0, 7.6 Hz, 1 H), 5.47 (dt, *J* = 1.0, 10.5 Hz, 1 H), 5.51 (dt, *J* = 1.0, 17.6 Hz, 1 H), 5.85 (ddd, *J* = 7.3, 10.5, 17.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.5, 25.3, 29.0, 29.1, 29.2, 29.3, 29.8, 31.7, 79.9 (2C), 121.2, 129.4, 154.3.

GC-MS (70 eV): *m*/*z* (%) = 55 (100), 69 (92), 80 (75), 83 (98), 93 (29), 95 (31), 97 (49), 107 (17), 121 (23), 135 (21), 149 (14), 163 (3), 178 (1), 196 (1).

Anal. calcd for $C_{14}H_{24}O_3$ (240.34): C; 69.96, H, 10.07. Found: C, 69.33; H, 10.12.

4,5-*trans*-4-Phenyl-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12f)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.89 (ddt, *J* = 1.0, 7.0, 8.1 Hz, 1 H), 5.29 (d, *J* = 8.9 Hz, 1 H), 5.47 (dt, *J* = 1.0, 16.5 Hz, 1 H), 5.49 (dt, *J* = 1.0, 10.6 Hz, 1 H), 6.00 (ddd, *J* = 7.0, 10.6, 16.5 Hz, 1 H), 7.32–7.54 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 82.8, 84.5, 121.8, 125.8, 129.0, 129.5, 131.1, 134.6, 153.8.

GC-MS (70 eV): *m*/*z* (%) = 51 (48), 55 (18), 63 (24), 77 (73), 91 (41), 105 (77), 117 (100), 131 (14), 145 (35), 190 (17).

Anal. calcd for $C_{11}H_{10}O_3$ (190.20); C, 69.46, H, 5.30. Found: C, 70.09; H, 5.25.

4,5-*cis*-4-Phenyl-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12f)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.18–5.53 (m, 4 H), 5.78 (d, *J* = 7.5 Hz, 1 H), 7.20–7.30 (m, 2 H), 7.36–7.46 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.6, 81.1, 121.2, 126.1, 128.7, 129.2, 130.1, 133.0, 154.4.

GC-MS (70 eV): *m*/*z* (%) = 51 (49), 55 (15), 63 (26), 77 (71), 91 (34), 105 (74), 117 (100), 131 (13), 145 (36), 190 (18).

Anal. calcd for $C_{11}H_{10}O_3$ (190.20): C, 69.46; H, 5.30. Found: C, 69.77; H, 5.28.

4,5-*trans*-4-(1-Naphthyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12g)
Mp 95–98 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.04 (ddt, *J* = 1.0, 6.2, 7.2 Hz, 1 H), 5.53 (dt, *J* = 1.0, 17.9 Hz, 1 H), 5.56 (dt, *J* = 1.0, 10.5 Hz, 1 H), 6.07 (d, *J* = 6.2 Hz, 1 H), 6.18 (ddd, *J* = 7.2, 10.5, 17.9 Hz, 1 H), 7.52–7.61 (m, 3 H), 7.66 (dt, *J* = 1.0, 7.1 Hz, 1 H), 7.73–7.80 (m, 1 H), 7.91–7.99 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.3, 83.8, 122.0, 122.2, 123.2, 125.3, 126.2, 126.9, 129.3, 129.5, 129.9, 130.8, 131.9, 133.8, 154.2.

GC-MS (70 eV): *m*/*z* (%) = 51 (11), 63 (11), 77 (11), 127 (32), 128 (42), 140 (100), 155 (31), 167 (26), 195 (14), 240 (36).

Anal. calcd for $C_{15}H_{12}O_3$ (240.25): C, 74.99; H, 5.03. Found: C, 74.43; H, 5.06.

4,5-*cis*-4-(1-Naphthyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12g)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.97 (dt, *J* = 1.0, 10.3 Hz, 1 H), 5.16 (ddd, *J* = 6.7, 10.3, 17.0 Hz, 1 H), 5.32 (dt, *J* = 1.0, 17.0 Hz, 1 H), 5.63 (ddt, *J* = 1.0, 6.7, 8.1 Hz, 1 H), 6.57 (d, *J* = 8.1 Hz, 1 H), 7.51–7.68 (m, 5 H), 7.86–7.98 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 78.3, 80.6, 120.9, 121.8, 123.2, 125.4, 126.2, 126.9, 128.8, 129.30, 129.34, 129.41, 129.43, 133.4, 154.2.

GC-MS (70 eV): *m*/*z* (%) = 51 (5), 63 (8), 77 (7), 127 (32), 128 (46), 140 (100), 155 (29), 167 (25), 195 (13), 240 (42).

Anal. calcd for $C_{15}H_{12}O_3$ (240.25): C, 74.99; H, 5.03. Found: C, 74.45; H, 4.99.

4,5-*trans*-4-(4-Methoxyphenyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12h)
Mp 98–99 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 4.89 (ddt, *J* = 1.0, 7.1, 8.3 Hz, 1 H), 5.22 (d, *J* = 8.3 Hz, 1 H), 5.44 (dt, *J* = 1.0, 17.7 Hz, 1 H), 5.45 (dt, *J* = 1.0, 10.6 Hz, 1 H), 5.96 (ddd, *J* = 7.1, 10.6, 17.7 Hz, 1 H), 6.96 (d, *J* = 9.1 Hz, 2 H), 7.40 (d, *J* = 9.1 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 83.1, 84.6, 114.6, 121.7, 126.4, 127.7, 131.3, 160.7.

GC-MS (70 eV): *m*/*z* (%) = 51 (23), 63 (15), 65 (11), 77 (38), 91 (40), 105 (11), 115 (12), 120 (76), 135 (100), 147 (37), 159 (5), 176 (4), 220 (45).

Anal. calcd for $C_{12}H_{12}O_4$ (220.07): C, 65.45; H, 5.49. Found: C, 64.87; H,5.45.

4,5-*cis*-4-(4-methoxyphenyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12h)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 5.18–5.52 (m, 4 H), 5.74 (d, *J* = 7.2 Hz, 1 H), 6.93 (d, *J* = 9.1 Hz, 2 H), 7.17 (d, *J* = 9.1 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3, 80.7, 81.2, 114.2, 121.1, 125.0, 127.7, 130.4, 160.3.

GC-MS (70 eV): *m*/*z* (%) = 51 (22), 63 (15), 65 (11), 77 (39), 91 (37), 105 (12), 115 (11), 120 (71), 135 (100), 147 (30), 159 (6), 176 (4), 220 (38).

Anal. calcd for $C_{12}H_{12}O_4$ (220.07): C, 65.45; H, 5.49. Found: C, 65.14; H, 5.52.

4,5-*trans*-4-(4-Fluorophenyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12i)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.85 (ddt, *J* = 0.7, 7.1, 8.0 Hz, 1 H), 5.26 (d, *J* = 8.0 Hz, 1 H), 5.46 (dt, *J* = 0.7, 17.4 Hz, 1 H), 5.50 (dt, *J* = 0.7, 10.5 Hz, 1 H), 5.98 (ddd, *J* = 7.1, 10.5, 17.4 Hz, 1 H), 7.10–7.19 (m, 2 H), 7.32–7.40 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 82.3, 84.7, 116.2 (d, $J_{C\text{-}F}$ = 22 Hz), 122.3, 127.9 (d, $J_{C\text{-}F}$ = 8.5 Hz), 130.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.9, 153.7, 163.3 (d, $J_{C\text{-}F}$ = 250 Hz).

GC-MS (70 eV): *m*/*z* (%) = 55 (17), 57 (18), 75 (24), 95 (42), 97 (38), 108 (100), 123 (80), 125 (80), 135 (86), 147 (9), 163 (21), 164 (16), 208 (17).

Anal. calcd for $C_{11}H_9FO_3$ (208.19): C, 63.46; H, 4.36. Found: C, 63.75; H, 4.40.

4,5-*cis*-4-(4-Fluorophenyl)-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12i)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.22–5.49 (m, 4 H), 5.77 (d, *J* = 7.9 Hz, 1 H), 7.06–7.16 (m, 2 H), 7.19–7.26 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.0, 81.0, 115.9 (d, J_{C-F} = 22 Hz), 121.4, 128.1 (d, J_{C-F} = 8.6 Hz), 128.9 (d, J_{C-F} = 3.7 Hz), 130.0, 154.2, 163.0 (d, J_{C-F} = 248 Hz).

GC-MS (70 eV): *m*/*z* (%) = 55 (15), 57 (20), 75 (28), 95 (50), 97 (45), 108 (100), 123 (88), 125 (77), 135 (81), 147 (12), 163 (21), 164 (14), 208 (20).

Anal. calcd for $C_{11}H_9FO_3$ (208.19): C, 63.46; H, 4.36. Found: C, 64.01; H, 4.33.

4,5-*trans*-4-[(*E*)-2-Phenylethenyl]-5-ethenyl-1,3-dioxolan-2-one (4,5-*trans*-12i)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.82 (ddt, *J* = 0.7, 6.8, 8.1 Hz, 1 H), 4.90 (br dt, *J* = ca. 1.0, 8.0 Hz, 1 H), 5.48 (dt, *J* = 0.7, 10.5 Hz, 1 H), 5.53 (dt, *J* = 0.7, 17.4 Hz, 1 H), 5.97 (ddd, *J* = 6.8, 10.5, 17.4 Hz, 1 H), 6.18 (dd, *J* = 7.5, 15.9 Hz, 1 H), 6.78 (dd, *J* = 1.0, 15.9 Hz, 1 H), 7.30–7.48 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 82.5, 82.8, 121.2, 121.6, 126.9, 128.7, 129.0, 131.0, 134.7, 136.9, 153.9.

GC-MS (70 eV): *m*/*z* (%) = 51 (10), 55 (7), 68 (14), 77 (15), 91 (8), 104 (17), 115 (100), 131 (22), 143 (5), 154 (3), 172 (1), 216 (1).

Anal. calcd for $C_{13}H_{12}O_2$ (216.23): C, 72.21; H, 5.59. Found: C, 71.50; H,5.60.

4,5-*cis*-4-[(*E*)-2-Phenylethenyl]-5-ethenyl-1,3-dioxolan-2-one (4,5-*cis*-12i)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23 (ddt, *J* = 1.0, 6.8, 7.8 Hz, 1 H), 5.34 (dt, *J* = 1.0, 7.8 Hz, 1 H), 5.47 (dt, *J* = 1.0, 10.5 Hz, 1 H), 5.54 (dt, *J* = 0.7, 17.4 Hz, 1 H), 5.85 (ddd, *J* = 6.8, 10.5, 17.4 Hz, 1 H), 6.09 (dd, *J* = 7.8, 15.9 Hz, 1 H), 6.76 (dd, *J* = 1.0, 15.9 Hz, 1 H), 7.30–7.48 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.2, 80.4, 120.2, 121.2, 126.9, 128.7, 128.9, 129.8, 135.0, 136.5, 154.1.

GC-MS (70 eV): *m*/*z* (%) = 51 (8), 55 (6), 68 (12), 77 (14), 91 (9), 104 (16), 115 (100), 131 (22), 143 (6), 154 (3), 172 (1), 216 (1).

Anal. calcd for $C_{13}H_{12}O_2$ (216.23): C,72.21; H, 5.59. Found: C, 72.00; H, 5.56.

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