Synthesis of 1-benzoxepin-5-ones (ols) from salicylardehydes via ring-closing metathesis

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Abstract
A new synthetic method for 1-benzoxepin-5-ones and 1-benzoxepin-5-ols from salicylardehydes was described. Based on O-allylation, Grignard reaction, oxidation, and ring-closing metathesis in sequence, salicylardehydes were converted to the target compounds in good yields, respectively.

Keywords: Ring-closing metathesis, salicylardehydes, 1-benzoxepin-5-ones, 1-benzoxepin-5-ols

Introduction
The 1-benzoxepine moiety which plays a core structure both in naturally occurring products1 and in certain synthetic biological molecules, 2 have abstracted the attention of chemists. In addition, benzoxyepinone which has been employed as starting material, can be converted to corresponding quinoline by the Friedlander reaction, 3 and can be transformed into benzoxyepine by isomerization of double bond, reduction of carbonyl group, and dehydration of giving alcohol in sequence. 4 The major synthetic methods for benzoxyepinones which were reported in literatures, include the cyclopropagation and sequential reductive cleavage of flavones, 5 the reaction of bromoalkyl ketones through the sequential reduction and oxidation, 6 the reaction of dihydrobenzoxepinone via silylation and following by desilylation with DDQ and collidine. 7 The drawbacks of those reported methods include the lack of conciseness, straightforward, and commercial available starting materials. Furthermore, the synthesis of benzoxyepin-5-ols was paid little attention in reported literatures. 4,8 Therefore, to develop a concise and practical method for the title compounds is requisite and significant. Since Grubbs’ catalyst was developed in 1995,
the ring-closing metathesis (RCM) has been widely applied to the compounds which were
difficulty to be synthesized by the previous reported methods. However, the synthesis of 1-
benzoxepin-5-ols and 1-benzoxepin-5-ones utilized RCM has not been reported in current
publications. Based on the chemistry of RCM, herein we would like to report a concise and
practical method for those compounds (Scheme 1).

Scheme 1

Results and Discussion

By the reaction of salicylaldehydes (1a-e) and allyl bromide in the presence of potassium
carbonate in refluxing acetonitrile for 4h, allyloxybenzaldehydes (2a-e) was obtained in 95-98%
yields. At the same condition if the reaction was carried out in refluxing acetone instead of
acetonitrile, the yield of 2a-e was decreased. Subsequently, 2a-e was reacted with
vinylmagnesium bromide to give (2-allyloxyaryl)-2-propen-1-ols (3a-e) in 73-87% yields,
respectively. The giving 3a-e which are all new compounds except 3c, have satisfactory spectral
data. Followed by oxidation of 3a-e with MnO2 in dichloromethane, (2-allyloxyaryl)-2-propen-1-
one (4a-e) were obtained in 70-80% yields, respectively, together with small amount of
unidentified by-product. The products 4a-e which are all new compounds except 4c, have
satisfactory spectral data. Subsequently, by the treatment of 4a-e with Grubbs catalyst (2nd
generation) in dichloromethane at room temperature for 6 hr, 2H-1-benzoxepin-5-ones (5a-e)
were produced in 76-84% yields, respectively. Furthermore, by the treatment of (2-allyloxyaryl)-
2-propen-1-ol (3a-e) with Grubbs catalyst (2nd generation) in dichloromethane at room
temperature for 6 hr, 2H-1-benzoxepin-5-ol (6a-e) were given in 64-85% yields, respectively.
Thus, we have established a new route to both 2H-1-benzoxepin-5-ones and 2H-1-benzoxepin-5-
ols. The structure of 5a-e and 6a-e were respectively elucidated by spectral data such as 1H-
NMR, $^{13}$C-NMR and mass spectra. The typical signals of $^1$H-NMR of 2H-1-benzoxepin-5-ones (5a-e) and 2H-1-benzoxepin-5-ols (6a-e), such as H-2, H-3, H-4, and H-5, together with typical carbonyl carbon of $^{13}$C-NMR of 5a-e were summarized in Table 1.

Table 1. The typical signals of $^1$H-NMR of 2H-1-benzoxepin-5-one (5a-e) and 2H-1-benzoxepin-5-ol (6a-c)

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-2</th>
<th>H-3</th>
<th>H-4</th>
<th>H-5</th>
<th>C-5$^a$</th>
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<tbody>
<tr>
<td>5a</td>
<td>4.55 (dd)</td>
<td>6.75 (dt)</td>
<td>6.43 (dt)</td>
<td>-</td>
<td>189.86</td>
</tr>
<tr>
<td>5b</td>
<td>4.68 (dd)</td>
<td>6.69 (dt)</td>
<td>6.41 (dt)</td>
<td>-</td>
<td>188.14</td>
</tr>
<tr>
<td>5c</td>
<td>4.78 (dd)</td>
<td>6.76 (dt)</td>
<td>6.44 (dt)</td>
<td>-</td>
<td>190.37</td>
</tr>
<tr>
<td>5d</td>
<td>4.73 (dd)</td>
<td>6.78 (dt)</td>
<td>6.41 (dt)</td>
<td>-</td>
<td>188.22</td>
</tr>
<tr>
<td>5e</td>
<td>4.81 (dd)</td>
<td>6.80 (dt)</td>
<td>6.41 (dt)</td>
<td>-</td>
<td>187.89</td>
</tr>
<tr>
<td>6a</td>
<td>4.52, 4.60 (ddd)</td>
<td>5.48 (m)</td>
<td>5.99 (ddt)</td>
<td>5.50 (m)</td>
<td>-</td>
</tr>
<tr>
<td>6b</td>
<td>4.48, 4.57 (ddd)</td>
<td>5.46 (m)</td>
<td>5.97 (ddt)</td>
<td>5.38 (m)</td>
<td>-</td>
</tr>
<tr>
<td>6c</td>
<td>4.52, 4.59 (ddd)</td>
<td>5.47 (m)</td>
<td>5.97 (ddt)</td>
<td>5.54 (m)</td>
<td>-</td>
</tr>
<tr>
<td>6d</td>
<td>4.46, 4.63 (ddd)</td>
<td>5.48 (m)</td>
<td>5.92 (ddt)</td>
<td>5.58 (m)</td>
<td>-</td>
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<tr>
<td>6e</td>
<td>4.47, 4.70 (ddd)</td>
<td>5.46 (m)</td>
<td>5.89 (ddt)</td>
<td>5.69 (m)</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$The chemical shifts of carbonyl carbon (C-5) of 5a-e in $^{13}$C-NMR spectra.

In conclusion, a new synthetic method for benzoxepinones and benzoxepinols from salicylaldehydes was established. The application of $\alpha,\beta$-unsaturated carbonyl functionality of benzoxepinones and allyl alcholic functionality of benzoxepinols to synthesize some related compounds is in progressive.

**Experimental Section**

**General Procedures.** Melting points (Yanaco micro melting-point apparatus) were uncorrected. $^1$H-NMR and $^{13}$C-NMR spectra were obtained on a Varian Gemini-200 or Varian Unity plus 400 Spectrometer. Chemical shifts were measured in parts per million with respect to TMS. Mass spectra were recorded on a Chem/hp/middle spectrometer connected to a Hewlett Packard series II model gas-liquid chromatograph. HRMS spectra were performed on a JEOL JMS SX/SX 102A instrument. Silica gel (230-400 mesh) for column chromatography and precoated silica gel
plates (60 F-254) for TLC was purchased from E. Merck Company. UV light (254 nm) was used to detect spots on TLC plates after development.

**General procedure for the preparation of 2-allyloxybenzaldehydes (2a-e)**

The 2-hydroxybenzaldehydes (1a-e) (100 mmol) dissolved in anhydrous acetonitrile (150 mL) was added anhydrous K₂CO₃ (120 mmol). The mixture which was obtained was stirred and added allyl bromide (120 mmol) and heated to reflux for 4 hr. Work-up as in the general procedure gave crude 2a-e which was further purified by silica-gel column (ethyl acetate: n-hexane = 1: 15) to give pure 2a-e.

2-Allyloxybenzaldehyde (2a). 10 (15.69 g, 97%) was obtained as colorless liquid, Rᵣ = 0.16 (ethyl acetate: n-hexane = 1: 15), ¹ H-NMR (CDCl₃, 400 MHz) δ 4.65 (dt, J = 5.2, 1.2 Hz, 2H, OCH₂CH=CH₂), 5.34 (ddt, J = 10.4, 1.2, 1.2 Hz, 1H, OCH₂CH=CH₂H₃), 5.45 (ddt, J = 17.2, 1.2, 1.2 Hz, 1H, OCH₂CH=CH₂H₃), 6.01 (ddt, J = 17.2, 10.4, 5.2 Hz, 1H, OCH₂CH=CH₂), 7.02 (m, 1H, ArH), 7.52 (m, 1H, ArH), 7.83 (m, 1H, ArH), 10.53 (s, 1H, CHO); ¹³C-NMR (CDCl₃, 100 MHz) δ 69.0, 112.8, 117.9, 120.7, 125.0, 128.3, 132.3, 135.8, 160.8, 189.6; EI-MS (70 eV) m/z (rel. intensity, %) 163 ([M+1]¹, 100), 162 (M¹, 36), 161 (54), 133 (24), 121 (76), 120 (19), 105 (18), 92 (26); HRMS calcd for C₁₀H₁₀O₂: 162.0681. Found: 162.0680.

2-Allyloxy-4-methoxybenzaldehyde (2b). 11 (18.24 g, 95%) was obtained as colorless crystal, mp 37-38°C, Rᵣ = 0.33 (ethyl acetate: n-hexane = 1: 6), ¹ H-NMR (CDCl₃, 200 MHz) δ 3.85 (s, 3H, OCH₃), 4.62 (dt, J = 5.2, 1.4 Hz, 2H, OCH₂CH=CH₂), 5.33 (ddt, J = 10.6, 1.4, 1.4 Hz, 1H, OCH₂CH=CH₂H₃), 5.45 (ddt, J = 17.4, 1.4, 1.4 Hz, 1H, OCH₂CH=CH₂H₃), 6.04 (ddt, J = 17.4, 10.6, 5.2 Hz, 1H, OCH₂CH=CH₂), 6.43 (d, J = 2.0 Hz, 1H, ArH), 6.54 (dd, J = 8.8, 2.0 Hz, 1H, ArH), 7.85 (d, J = 8.8 Hz, 1H, ArH), 10.35 (s, 1H, CHO); ¹³C-NMR (CDCl₃, 50 MHz) δ 55.6, 69.1, 99.0, 106.0, 118.1, 119.2, 130.4, 132.2, 162.6, 166.0, 188.2; EI-MS (70 eV) m/z (rel. intensity, %) 193 ([M+1]¹, 30), 192 (M¹, 35), 175 (17), 166 (20), 164 (29), 163 (54), 151 (100), 150 (91), 135 (45), 122 (27), 95 (28); HRMS calcd for C₁₁H₁₄O₃: 192.0786. Found: 192.0784.

2-Allyloxy-3-methoxybenzaldehyde (2c). 12 (18.82 g, 98%) was obtained as colorless liquid, Rᵣ = 0.26 (ethyl acetate: n-hexane = 1: 6), ¹ H-NMR (CDCl₃, 200 MHz) δ 3.86 (s, 3H, OCH₃), 4.62 (dt, J = 6.0, 1.2 Hz, 2H, OCH₂CH=CH₂), 5.33 (ddt, J = 10.2, 1.2, 1.2 Hz, 1H, OCH₂CH=CH₂H₃), 5.45 (ddt, J = 17.4, 1.2, 1.2 Hz, 1H, OCH₂CH=CH₂H₃), 6.04 (ddt, J = 17.4, 10.2, 6.0 Hz, 1H, OCH₂CH=CH₂H₃), 7.10 (m, 2H, ArH), 7.37 (m, 1H, ArH), 10.41 (s, 1H, CHO); ¹³C-NMR (CDCl₃, 50 MHz) δ 55.9, 75.0, 113.3, 117.9, 118.9, 124.0, 130.0, 133.0, 151.1, 152.9, 190.2; EI-MS (70 eV) m/z (rel. intensity, %) 193 ([M+1]¹, 100), 192 (M¹, 54), 175 (17), 166 (20), 164 (29), 163 (55), 151 (83), 136 (17), 131 (20), 122 (20); HRMS calcd for C₁₁H₁₂O₃: 192.0786. Found: 192.0784.

2-Allyloxy-5-bromobenzaldehyde (2d). 13 (23.03 g, 96%) was obtained as colorless liquid, Rᵣ = 0.50 (ethyl acetate: n-hexane = 1: 9), ¹ H-NMR (CDCl₃, 400 MHz) δ 4.60 (dt, J = 5.2, 1.6 Hz, 2H, OCH₂CH=CH₂), 5.31 (ddt, J = 10.8, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₂H₃), 5.40 (ddt, J = 17.2, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₂H₃), 6.02 (ddt, J = 17.2, 10.8, 5.2 Hz, 1H, OCH₂CH=CH₂), 6.84 (d, J = 8.8 Hz, 1H, ArH), 7.54 (dd, J = 8.8, 2.8 Hz, 1H, ArH), 7.84 (d, J = 2.8 Hz, 1H, ArH),
10.38 (s, 1H, CHO); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 69.3, 113.4, 114.8, 118.4, 126.1, 130.7, 131.8, 138.1, 159.6, 188.1; EI-MS (70 eV) m/z (rel. intensity, %) 242 ([M+2]$^+$, 20), 240 (M$^+$, 21), 201 (48), 200 (44), 199 (56), 198 (34), 143 (24), 133 (70), 132 (100), 64 (27), 63 (54); HRMS calcd for C$_{10}$H$_9$BrO$_2$: 239.9786. Found: 239.9786.

2-Allyloxy-3,5-dichlorobenzaldehyde (2e). $^{14}$ (21.85 g, 95%) was obtained as colorless crystal, mp 43-44°C, R$_f$ = 0.61 (ethyl acetate: n-hexane = 1: 15), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 4.61 (d, $J = 6.4$ Hz, 2H, OCH$_2$CH=CH$_2$), 5.32 (d, $J = 10.4$ Hz, 1H, OCH$_2$CH=CHH$_b$), 5.39 (dd, $J = 16.8$, 1.2 Hz, 1H, OCH$_2$CH=CHH$_a$H$_b$), 6.07 (ddt, $J = 16.8$, 10.4, 6.4 Hz, 1H, OCH$_2$CH=CH$_2$), 7.61 (d, $J = 2.8$ Hz, 1H, ArH), 7.69 (d, $J = 2.8$ Hz, 1H, ArH), 10.27 (s, 1H, CHO); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 76.6, 120.3, 126.5, 129.9, 130.4, 131.6, 135.6, 156.2, 187.9; EI-MS (70 eV) m/z (rel. intensity, %) 232 ([M+2]$^+$, 5), 230 (M$^+$, 8), 203 (44), 201 (69), 191 (59), 190 (72), 189 (100), 188 (95), 167 (42), 135 (34), 133 (57), 97 (63); HRMS calcd for C$_{10}$H$_8$Cl$_2$O$_2$: 229.9901. Found: 229.9902.

General procedure for the preparation of (2-allyloxyaryl)-2-propen-1-ol (3a-e)
Under N$_2$, the O-allyloxybenzaldehydes (2a-e) (30 mmol) dissolved in anhydrous THF (100 mL) was stirred and cooled to 0°C and was subsequently added vinylmagnesium bromide (1.6 M) (22.5 mL, 36 mmol). The resulting mixture was stirred at 0°C for 0.5 hr and then at room temperature for 2 hr and then, quenched with saturated aq. NH$_4$Cl. The resulting mixture was concentrated in vacuo to remove THF and the resulting residue was extracted with ethyl acetate (20 mL x 5). The organic layer was combined and washed with brine, and then dried over anhydrous MgSO$_4$, and filtered in sequence. The giving filtrate was concentrated in vacuo to remove the solvent. The residue which was obtained was purified by silica gel column chromatography (ethyl acetate: n-hexane = 1: 15) to give pure 3a-e.

1-(2-Allyloxyphenyl)-2-propen-1-ol (3a). (4.60 g, 81%) was obtained as colorless liquid, R$_f$ = 0.38 (ethyl acetate: n-hexane = 1: 10), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.87 (br d, $J = 6.0$ Hz, 1H, OH), 4.57 (dt, $J = 5.2$, 1.2 Hz, 2H, OCH$_2$CH=CH$_2$), 5.16 (ddd, $J = 10.4$, 1.2 Hz, 1H, CH(OH)-CH=CHH$_b$), 5.29 (ddt, $J = 10.4$, 1.2, 1.2 Hz, 1H, OCH$_2$CH=CHH$_b$), 5.32 (ddd, $J = 17.6$, 1.2, 1.2 Hz, 1H, CH(OH)CH=CH$_2$H$_b$), 5.41 (ddt, $J = 17.6$, 1.2, 1.2 Hz, 1H, OCH$_2$CH=CHH$_b$), 5.44 (m, 1H, CH(OH)CH=CH$_2$), 6.05 (ddt, $J = 17.6$, 10.4, 5.2 Hz, 1H, OCH$_2$CH=CH$_2$), 6.13 (ddd, $J = 17.6$, 10.4, 5.6 Hz, 1H, CH(OH)CH=CHH$_b$), 6.87 (m, 1H, ArH), 6.96 (m, 1H, ArH), 7.23 (m, 1H, ArH), 7.31 (m, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 68.9, 71.6, 111.9, 114.5, 117.6, 121.1, 127.5, 128.6, 131.0, 132.0, 139.4, 155.7; EI-MS (70 eV) m/z (rel. intensity, %) 190 (M$^+$, 6), 150 (10), 149 (100), 147 (18), 133 (12), 132 (19), 131 (97), 121 (81), 107 (25), 103 (26), 93 (14), 91 (19); HRMS calcd for C$_{12}$H$_{14}$O$_2$: 190.0988. Found: 190.0986.

1-(2-Allyloxy-4-methoxyphenyl)prop-2-en-1-ol (3b). (5.74 g, 87%) was obtained as colorless liquid, R$_f$ = 0.03 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.82 (br d, $J = 6.0$ Hz, 1H, OH), 3.77 (s, 3H, OCH$_3$), 4.53 (dt, $J = 5.2$, 1.2 Hz, 2H, OCH$_2$CH=CH$_2$), 5.14 (ddd, $J = 10.4$, 1.2, 1.2 Hz, 1H, CH(OH)CH=CHH$_b$), 5.28 (ddt, $J = 10.4$, 1.4 Hz, 1.4 Hz, 1H, CH(OH)CH=CHH$_b$), 5.41 (ddt, $J = 17.6$, 1.2, 1.2 Hz, 1H, OCH$_2$CH=CHH$_b$), 5.44 (m, 1H, CH(OH)CH=CH$_2$), 6.05 (ddt, $J = 17.6$, 10.4, 5.2 Hz, 1H, OCH$_2$CH=CH$_2$), 6.13 (ddd, $J = 17.6$, 10.4, 5.6 Hz, 1H, CH(OH)CH=CHH$_b$), 6.87 (m, 1H, ArH), 6.96 (m, 1H, ArH), 7.23 (m, 1H, ArH), 7.31 (m, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 68.9, 71.6, 111.9, 114.5, 117.6, 121.1, 127.5, 128.6, 131.0, 132.0, 139.4, 155.7; EI-MS (70 eV) m/z (rel. intensity, %) 190 (M$^+$, 6), 150 (10), 149 (100), 147 (18), 133 (12), 132 (19), 131 (97), 121 (81), 107 (25), 103 (26), 93 (14), 91 (19); HRMS calcd for C$_{12}$H$_{14}$O$_2$: 190.0988. Found: 190.0986.
OCH₂CH=CH₃H₆b), 5.30 (ddd, J = 17.2, 1.2, 1.2 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.40 (m, 1H, CH(OH)CH=CH₂), 5.41 (ddt, J = 17.2, 1.4 Hz, 1.4 Hz, 1H, OCH₂CH=CH₃H₆b), 6.04 (ddt, J = 17.2, 10.4, 5.2 Hz, 1H, OCH₂CH=CH₂), 6.11 (dd, J = 17.2, 10.4, 5.4 Hz, 1H, CH(OH)CH=CH₂), 6.44 (d, J = 2.4 Hz, 1H, ArH), 6.47 (dd, J = 8.0, 2.4 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 1H, ArH); ¹³C-NMR (CDCl₃, 50 MHz) δ 55.2, 68.8, 70.8, 99.8, 104.5, 114.1, 117.6, 123.7, 128.0, 132.8, 139.7, 156.6, 160.1; EI-MS (70 eV) m/z (rel. intensity, %) 221 ([M+1]⁺, 4), 220 (M⁺, 21), 203 (100), 202 (50), 201 (13), 164 (15), 161 (13), 151 (11); HRMS calcd for C₁₃H₁₆O₃: 220.1099. Found: 220.1099.

1-(2-Allyloxy-3-methoxyphenyl)prop-2-en-1-ol (3c). (5.62 g, 85%) was obtained as colorless liquid, Rf = 0.33 (ethyl acetate: n-hexane = 1: 9), ¹H-NMR (CDCl₃, 400 MHz) δ 2.93 (br d, J = 4.4 Hz, 1H, OH), 3.83 (s, 3H, OCH₃), 4.52 (dt, J = 12.0, 5.6 Hz, 1H, OCH₂CH=CH₂), 5.15 (ddd, J = 10.4, 1.6, 1.6 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.23 (ddd, J = 10.4, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₃H₆b), 5.31 (dd, J = 17.2, 1.6, 1.6 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.36 (dd, J = 17.2, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₃H₆b), 6.07 (dd, J = 17.2, 10.4, 5.2 Hz, 1H, CH(OH)CH=CH₂), 6.08 (ddd, J = 17.2, 10.4, 5.4 Hz, 1H, CH(OH)CH=CH₂), 6.84 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 6.93 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 1H, ArH); ¹³C-NMR (CDCl₃, 100 MHz) δ 55.6, 70.6, 73.7, 111.6, 114.3, 117.5, 119.1, 124.1, 134.0, 136.4, 139.9, 146.0, 152.4; EI-MS (70 eV) m/z (rel. intensity, %) 220 (M⁺, 19), 204 (17), 203 (100), 202 (59), 201 (11), 164 (23), 163 (11), 162 (20), 161 (32); HRMS calcd for C₁₃H₁₆O₃: 220.1099. Found: 220.1100.

1-(2-Allyloxy-5-bromophenyl)prop-2-en-1-ol (3d). (5.85 g, 73%) was obtained as colorless liquid, Rf = 0.32 (ethyl acetate: n-hexane = 1: 9), ¹H-NMR (CDCl₃, 200 MHz) δ 2.73 (br s, 1H, OH), 4.54 (dt, J = 5.2, 1.6 Hz, 2H, OCH₂CH=CH₂), 5.18 (ddd, J = 10.4, 1.6, 1.6 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.30 (dd, J = 10.4, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₃H₆b), 5.33 (dd, J = 17.2, 1.6, 1.6 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.39 (dd, J = 17.2, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₃H₆b), 5.42 (m, 1H, CH(OH)CH=CH₂), 6.02 (ddd, J = 17.2, 10.4, 5.2 Hz, 1H, OCH₂CH=CH₂), 6.06 (ddd, J = 17.2, 10.4, 5.4 Hz, 1H, CH(OH)CH=CH₂), 6.73 (d, J = 8.8 Hz, 1H, ArH), 7.32 (dd, J = 8.8, 2.6 Hz, 1H, ArH), 7.46 (d, J = 2.6 Hz, 1H, ArH); ¹³C-NMR (CDCl₃, 50 MHz) δ 69.1, 70.5, 113.4, 113.6, 115.1, 117.9, 130.1, 131.1, 132.58, 133.3, 138.7, 154.6; EI-MS (70 eV) m/z (rel. intensity, %) 270 ([M+2]⁺, 17), 268 (M⁺, 17), 211 (71), 209 (72), 148 (57), 132 (41), 131 (100), 120 (72), 103 (62), 91 (56); HRMS calcd for C₁₂H₁₃BrO₂: 268.0099. Found: 268.1100.

1-(2-Allyloxy-3,5-dichlorophenyl)prop-2-en-1-ol (3e). (5.81 g, 75%) was obtained as colorless liquid, Rf = 0.35 (ethyl acetate: n-hexane = 1: 9), ¹H-NMR (CDCl₃, 200 MHz) δ 2.39 (d, J = 4.6 Hz, 1H, OH), 4.54 (dt, J = 5.6, 1.6 Hz, 2H, OCH₂CH=CH₂), 5.18 (ddd, J = 10.2, 1.4, 1.4 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.30 (dd, J = 10.2, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₃H₆b), 5.37 (dd, J = 17.2, 1.4, 1.4 Hz, 1H, CH(OH)CH=CH₃H₆b), 5.42 (dd, J = 17.0, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₃H₆b), 5.50 (m, 1H, CH(OH)CH=CH₂), 6.02 (ddd, J = 17.2, 10.2, 5.4 Hz, 1H, CH(OH)CH=CH₂), 6.10 (dd, J = 17.0, 10.2, 5.4 Hz, 1H, OCH₂CH=CH₂), 7.30 (d, J = 2.6 Hz, 1H, ArH), 7.32 (d, J = 2.6 Hz, 1H, ArH); ¹³C-NMR (CDCl₃, 50 MHz) δ 69.1, 70.5, 113.4, 113.6, 115.1, 117.9, 130.1, 131.1, 132.58, 133.3, 138.7, 154.6; EI-MS (70 eV) m/z (rel. intensity, %) 270 ([M+2]⁺, 17), 268 (M⁺, 17), 211 (71), 209 (72), 148 (57), 132 (41), 131 (100), 120 (72), 103 (62), 91 (56); HRMS calcd for C₁₂H₁₃BrO₂: 268.0099. Found: 268.1100.
129.4, 129.9, 132.8, 138.8, 139.1, 150.9; EI-MS (70 eV) m/z (rel. intensity, %) 260 ([M+2]⁺, 53%), 258 (M⁺, 1), 203 (16), 202 (42), 201 (71), 200 (66), 199 (100), 189 (17), 167 (19), 165 (39), 137 (18); HRMS calcd for C₁₂H₁₂Cl₂O₂: 258.0214. Found: 258.0214.

General procedure for the preparation of (2-allyloxyphenyl)-2-propen-1-one (4a-e)
The (2-allyloxyphenyl)-2-propen-1-ol (3a-e) (20 mmol) which was dissolved in anhydrous CH₂Cl₂ (85 mL) was added MnO₂ (200 mmol). The mixture was stirred at room temperature for 5 hr. After concentration **in vacuo**, the residue which was obtained was purified by silica gel column chromatography (ethyl acetate: n-hexane = 1: 20) to give pure 4a-e.

1-(2-allyloxy-4-methoxyphenyl)-2-propen-1-one (4b). (3.08 g, 70%) was obtained as colorless liquid, Rf = 0.38 (ethyl acetate: n-hexane = 1: 9), ¹H-NMR (CDCl₃, 200 MHz) δ 3.83 (s, 3H, OCH₃), 4.59 (dt, J = 5.2, 1.6 Hz, 2H, OCH₂CH=CH₂), 5.30 (ddt, J = 10.6, 1.6, 1.6 Hz, 1H, OCH₂CH=CH₂), 6.12 (dd, J = 10.6, 5.2 Hz, 1H, OCH₂CH=CH₂), 7.11 (m, 3 H, ArH); ¹³C-NMR (CDCl₃, 50 MHz) δ 55.4, 69.3, 99.6, 105.7, 117.7, 121.7, 126.7, 132.3, 132.8, 136.8, 146.4, 152.2, 193.6; EI-MS (70 eV) m/z (rel. intensity, %) 219 ([M+1]⁺, 68), 218 (M⁺, 48), 217 (29), 188 (32), 163 (40), 151 (100), 121 (42), 77 (38), 63 (38); HRMS calcd for C₁₃H₁₄O₃: 218.0943. Found: 218.0943.

1-(2-Allyloxy-3-methoxyphenyl)-2-propen-1-one (4c). (3.24 g, 74%) was obtained as colorless liquid, Rf = 0.38 (ethyl acetate: n-hexane = 1: 9), ¹H-NMR (CDCl₃, 200 MHz) δ 3.87 (s, 3H, OCH₃), 4.50 (dt, J = 5.8, 1.2 Hz, 2H, OCH₂CH=CH₂), 5.17 (ddt, J = 10.2, 1.2, 1.2 Hz, 1H, OCH₂CH=CH₂), 5.28 (ddt, J = 10.2, 1.2, 1.2 Hz, 1H, OCH₂CH=CH₂), 6.00 (ddt, J = 10.2, 1.2, 5.8 Hz, 1H, OCH₂CH=CH₂), 6.22 (dd, J = 10.6, 5.8 Hz, 1H, OCH₂CH=CH₂), 6.94 (dd, J = 10.6, 5.8 Hz, 1H, OCH₂CH=CH₂), 7.07 (m, 3 H, ArH); ¹³C-NMR (CDCl₃, 50 MHz) δ 55.8, 74.8, 99.6, 105.7, 117.7, 121.7, 126.7, 132.3, 132.8, 136.8, 152.2, 193.6; EI-MS (70eV) m/z (rel. intensity, %) 219 ([M+1]⁺, 100), 218 (M⁺, 34), 177 (22), 164 (13), 162 (15), 151 (52), 150 (20), 122 (21), 121 (35), 91 (22); HRMS calcd for C₁₃H₁₄O₃: 218.0943. Found: 218.0943.
1-(2-Allyloxy-5-bromophenyl)-2-propen-1-one (4d). (3.79 g, 71%) was obtained as colorless liquid, Rf = 0.50 (ethyl acetate: n-hexane = 1: 9). 1H-NMR (CDCl3, 200 MHz) δ 4.59 (dt, J = 5.2, 1.4 Hz, 2H, OCH2CH=CH2), 5.29 (ddt, J = 10.6, 1.4, 1.4 Hz, 1H, OCH2CH=CHHb), 5.40 (ddt, J = 17.2, 1.4, 1.4 Hz, 1H, OCH2CH=CHHb), 5.84 (dd, J = 10.2, 1.6 Hz, 1H, COCH=CHHb), 6.00 (dd, J = 17.2, 10.6, 5.2 Hz, 1H, OCH2CH=CH2), 6.29 (dd, J = 17.2, 1.6 Hz, 1H, COCH=CHHb), 6.84 (d, J = 8.8 Hz, 1H, ArH), 6.99 (dd, J = 17.2, 10.2 Hz, 1H, COCH=CHHb), 7.51 (dd, J = 8.8, 2.6 Hz, 1H, ArH), 7.67 (d, J = 2.6 Hz, 1H, ArH); 13C-NMR (CDCl3, 50 MHz) δ 69.6, 113.3, 114.8, 118.0, 129.0, 130.4, 132.1, 132.9, 135.3, 136.2, 156.2, 191.6; EI-MS (70 eV) m/z (rel. intensity, %) 268 ([M+2] +, 5), 267 ([M+1] +, 10), 266 (M +, 5), 265 ([M-1] +, 9), 227 (33), 225 (36), 198 (67), 170 (24), 169 (31), 131 (24), 90 (35), 89 (31), 63 (62); HRMS calcd for C12H11BrO2: 265.9942. Found: 265.9944.

1-(2-Allyloxy-3,5-dichlorophenyl)-2-propen-1-one (4e). (3.75 g, 73%) was obtained as colorless liquid, Rf = 0.61 (ethyl acetate: n-hexane = 1: 15). 1H-NMR (CDCl3, 400 MHz) δ 4.43 (dt, J = 6.0, 1.2 Hz, 2H, OCH2CH=CH2), 5.25 (ddt, J = 10.4, 1.2, 1.2 Hz, 1H, OCH2CH=CHHb), 5.32 (dd, J = 17.2, 1.2, 1.2 Hz, 1H, OCH2CH=CHHb), 5.98 (dd, J = 10.4, 1.2 Hz, 1H, COCH=CHHb), 5.99 (dd, J = 17.2, 10.4, 6.0 Hz, 1H, OCH2CH=CH2), 6.29 (dd, J = 17.6, 1.2 Hz, 1H, COCH=CHHb), 7.38 (d, J = 2.8 Hz, 1H, ArH), 7.52 (d, J = 2.8 Hz, 1H, ArH); 13C-NMR (CDCl3, 100 MHz) δ 76.3, 119.4, 128.1, 129.8, 129.9, 131.4, 132.3, 132.8, 135.5, 135.7, 152.0, 191.5; EI-MS (70 eV) m/z (rel. intensity, %) 258 ([M+2] +, 1), 257 ([M+1] +, 6), 256 (M +, 2), 255 ([M-1] +, 7), 217 (25), 215 (42), 202 (24), 191 (64), 190 (64), 189 (100), 188 (81), 161 (23), 159 (28), 133 (21), 97 (33); HRMS calcd for C12H10Cl2O2: 256.0058. Found: 256.0060.

General procedure for the preparation of 2H-1-benzoxepin-5-one (5a-e)
The (2-allyloxyphenyl)-2-propen-1-one (4a-e) (10 mmol) dissolved in anhydrous CH2Cl2 (100 mL) was added Grubbs' Catalyst (5 mol %) and the mixture was stirred at room temperature for 6 hr. Then, the mixture was concentrated in vacuo to remove the solvent. The resulting residue was purified by silica gel column chromatography (ethyl acetate: n-hexane = 1: 20) to give pure 5a-e.

2H-1-Benzoxepin-5-one (5a). (1.3 g, 81%) was obtained as colorless liquid, Rf = 0.01 (ethyl acetate: n-hexane = 1: 15). 1H-NMR (CDCl3, 400 MHz) δ 4.55 (dd, J = 4.8, 1.2 Hz, 2H, OCH2CH=CHCO), 6.43 (dt, J = 11.6, 1.2 Hz, 1H, OCH2CH=CHCO), 6.75 (dt, J = 11.6, 4.8 Hz, 1H, OCH2CH=CHCO), 7.09 (m, 1H, ArH), 7.17 (m, 1H, ArH), 7.47 (m, 1H, ArH), 7.95 (m, 1H, ArH), 8.13 (m, 1H, ArH); 13C-NMR (CDCl3, 100 MHz) δ 68.8, 121.4, 123.9, 129.9, 131.2, 134.4, 134.8, 141.6, 159.0, 189.9; EI-MS (70 eV) m/z (rel. intensity, %) 161 ([M+1] +, 11), 160 (M +, 100), 132 (37), 131 (98), 104 (15), 103 (21), 77 (12); HRMS calcd for C10H8O2: 160.0519. Found: 160.0521.

8-Methoxy-2H-1-benzoxepin-5-one (5b). (1.45 g, 76%) was obtained as colorless liquid, Rf = 0.26 (ethyl acetate: n-hexane = 1: 9). 1H-NMR (CDCl3, 200 MHz) δ 3.83 (s, 3H, OCH3), 4.68 (dd, J = 5.2, 1.2 Hz, 2H, OCH2CH=CHCO), 6.41 (dt, J = 11.6, 1.2 Hz, 1H, OCH2CH=CHCO), 6.52 (d, J = 2.4 Hz, 1H, ArH), 6.69 (dt, J = 11.6, 5.2 Hz, 1H, OCH2CH=CHCO), 6.70 (dd, J =
9.0, 2.4 Hz, 1H, ArH), 7.97 (d, J = 9.0 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 50 MHz) δ 55.6, 68.3, 104.7, 111.0, 122.2, 133.2, 135.6, 139.4, 161.4, 164.98, 188.1; EI-MS (70 eV) m/z (rel. intensity, %) 191 ([M+1]$^+$, 34), 190 (M$^+$, 91), 62 (75), 161 (100), 147 (25), 106 (20), 91 (24), 63 (62), 62 (21), 51 (27); HRMS calcd for C$_{11}$H$_{10}$O$_3$: 190.0630. Found: 190.0630.

9-Methoxy-2$H$-1-benzoxepin-5-one (5c). (1.58 g, 83%) was obtained as colorless crystal, mp 81-82°C, R$_f$ = 0.18 (ethyl acetate: n-hexane = 1: 10), $^1$H-NMR (CDCl$_3$, 200 MHz) δ 3.90 (s, 3H, OCH$_3$), 4.78 (dd, J = 4.4, 1.4 Hz, 2H, OCH$_2$CH=CHCO), 6.44 (dt, J = 11.6, 1.4 Hz, 1H, OCH$_2$CH=CHCO), 6.76 (dt, J = 11.6, 4.4 Hz, 1H, OCH$_2$CH=CHCO), 7.11 (m, 2 H, ArH), 7.47 (dd, J = 6.6, 3.2 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 50 MHz) δ 56.3, 69.3, 116.4, 121.9, 123.8, 131.8, 133.7, 141.9, 148.3, 151.4, 190.4; EI-MS (70 eV) m/z (rel. intensity, %) 191 ([M+1]$^+$, 44), 190 (M$^+$, 100), 161 (32), 147 (12), 119 (13), 91 (27), 65 (13), 63 (15), 51 (18); HRMS calcd for C$_{11}$H$_{10}$O$_3$: 190.0630. Found: 190.0631.

7-Bromo-2$H$-1-benzoxepin-5-one (5d). (1.95 g, 82 %) was obtained as colorless crystal, mp 72-73°C, R$_f$ = 0.30 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 4.73 (dd, J = 4.8, 1.2 Hz, 2H, OCH$_2$CH=CHCO), 6.41 (dt, J = 11.6, 1.2 Hz, 1H, OCH$_2$CH=CHCO), 6.98 (d, J = 8.4 Hz, 1H, ArH), 7.54 (dd, J = 8.4, 2.4 Hz, 1H, ArH), 8.05 (d, J = 2.4 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 68.8, 116.7, 123.4, 131.0, 133.6, 133.9, 137.3, 141.8, 157.9, 188.2; EI-MS (70 eV) m/z (rel. intensity, %) 240 ([M+2]$^+$, 57), 238 (M$^+$, 57), 211 (80), 209 (82), 131 (100), 103 (61), 102 (35), 77 (39), 63 (42); HRMS calcd for C$_{10}$H$_7$BrO$_2$: 237.9629. Found: 237.9630.

7,9-Dichloro-2$H$-1-benzoxepin-5-one (5e). (1.91 g, 84%) was obtained as colorless crystal, mp 111-112°C, R$_f$ = 0.39 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 200 MHz) δ 4.81 (dd, J = 4.6, 1.4 Hz, 2H, OCH$_2$CH=CHCO), 6.41 (dt, J = 11.8, 1.4 Hz, 1H, OCH$_2$CH=CHCO), 7.56 (d, J = 2.6 Hz, 1H, ArH), 7.76 (d, J = 2.6 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 50 MHz) δ 69.4, 128.0, 129.1, 129.5, 132.7, 133.0, 134.2, 142.3, 152.9, 187.9; EI-MS (70 eV) m/z (rel. intensity, %) 230 ([M+2]$^+$, 42), 228 (M$^+$, 64), 201 (68), 199 (100), 165 (33), 136 (21), 102 (31); HRMS calcd for C$_{10}$H$_6$Cl$_2$O$_2$: 227.9745. Found: 227.9745.

General procedure for the preparation of 2,5-dihydro-1-benzoxepin-5-ol (6a-e)
The (2-allyloxyphenyl)-2-propen-1-ol (3a-e) (10 mmol) dissolved in anhydrous CH$_2$Cl$_2$ (100 mL) was stirred with added Grubbs' catalyst (5 mol %). The mixture was continually stirred at room temperature for 6 hr. Then, it was concentrated in vacuo to remove the solvent. The residue which was obtained was purified by silica gel column chromatography (ethyl acetate: n-hexane = 1: 15) to give pure 6a-e.

2,5-Dihydro-1-benzoxepin-5-ol (6a). (1.30 g, 80%) was obtained as colorless liquid, R$_f$ = 0.18 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.75 (d, J = 8.0 Hz, 1H, OH), 4.52 (ddd, J = 17.2, 4.8, 2.4 Hz, 1H, OCH$_3$H$_6$CH=CH), 4.60 (ddd, J = 17.2, 4.8, 2.4 Hz, 1H, OCH$_3$H$_6$CH=CH), 5.48 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.50 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.99 (ddt, J = 11.6, 4.0, 2.4 Hz, 1H, OCH$_2$CH=CHCH(OH)), 7.08 (m, 1H, ArH), 7.12 (m, 1H,
ArH), 7.25 (m, 1H, ArH), 7.32 (m, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 68.9, 71.0, 121.6, 124.6, 125.4, 127.8, 128.9, 131.6, 139.2, 156.2; EI-MS (70 eV) m/z (rel. intensity, %) 162 (M$^+$, 11), 145 (13), 144 (25), 133 (18), 132 (16), 131 (100), 115 (27), 105 (23), 77 (13); HRMS calcd for C$_{10}$H$_{10}$O$_2$: 162.0681. Found: 162.0679.

8-Methoxy-2,5-dihydro-1-benzoxepin-5-ol (6b). (1.59 g, 83%) was obtained as colorless liquids, R$_f$ = 0.13 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 200 MHz) δ 3.19 (br s, 1H, OH), 3.76 (s, 3H, OCH$_3$), 4.48 (ddd, J = 17.2, 4.4, 2.2 Hz, 1H, OCH$_2$-CH=CH), 4.57 (ddd, J = 17.2, 4.4, 2.2 Hz, 1H, OCH$_2$-CH=CH), 5.38 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.46 (m, 1H, OCH$_2$-CH=CHCH(OH)), 5.97 (ddt, J = 11.6, 4.2, 2.2 Hz, 1H, OCH$_2$CH=CHCH(OH)), 6.64 (d, J = 2.6 Hz, 1H, ArH), 6.63 (dd, J = 8.8, 2.6 Hz, 1H, ArH), 7.18 (d, J = 8.8 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 50 MHz) δ 55.3, 68.5, 70.7, 107.5, 109.3, 126.4, 127.3, 131.0, 131.8, 157.0, 159.9; EI-MS (70 eV) m/z (rel. intensity, %) 193 ([M+1]$^+$, 13), 192 (M$^+$, 100), 177 (37), 161 (45), 150 (80), 121 (29), 91 (47), 77 (42), 63 (39), 51 (35); HRMS calcd for C$_{11}$H$_{12}$O$_3$: 192.0786. Found: 192.0788.

9-Methoxy-2,5-dihydro-1-benzoxepin-5-ol (6c). (1.22 g, 64%) was obtained as colorless crystal, mp 99-100$^\circ$C, R$_f$ = 0.13 (ethyl acetate: n-hexane = 1: 10), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.81 (br d, J = 8.0 Hz, 1H, OH), 3.86 (s, 3H, OCH$_3$), 4.52 (ddd, J = 17.6, 4.8, 2.4 Hz, 1H, OCH$_2$-CH=CH), 4.59 (ddd, J = 17.6, 4.8, 2.4 Hz, 1H, OCH$_2$-CH=CH), 5.47 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.54 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.97 (ddt, J = 11.6, 4.4, 2.4 Hz, 1H, OCH$_2$CH=CHCH(OH)), 6.88 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 6.93 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 7.07 (t, J = 8.0 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 55.9, 68.6, 70.0, 111.6, 116.8, 124.8, 127.6, 131.6, 141.1, 144.0, 151.9; EI-MS (70 eV) m/z (rel. intensity, %) 193 ([M+1]$^+$, 34), 192 (M$^+$, 86), 175 (27), 177 (19), 163 (34), 131 (36), 103 (100), 91 (49), 77 (38), 51 (24); HRMS calcd for C$_{11}$H$_{12}$O$_3$: 192.0786. Found: 192.0788.

7-Bromo-2,5-dihydro-1-benzoxepin-5-ol (6d). (1.86 g, 78%) was obtained as colorless crystal, mp 111-113$^\circ$C, R$_f$ = 0.20 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.58 (d, J = 7.6 Hz, 1H, OH), 4.46 (ddd, J = 17.2, 4.8, 2.4 Hz, 1H, OCH$_2$H$_2$CH=CH), 4.63 (ddd, J = 17.2, 4.8, 2.4 Hz, 1H, OCH$_2$H$_2$CH=CH), 5.48 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.54 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.92 (dd, J = 12.0, 3.6, 2.4 Hz, 1H, OCH$_2$CH=CHCH(OH)), 6.95 (d, J = 8.4 Hz, 1H, ArH), 7.35 (dd, J = 8.4, 2.4 Hz, 1H, ArH), 7.49 (d, J = 2.4 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 68.1, 71.0, 117.5, 123.4, 127.4, 128.2, 132.1, 131.4, 141.4, 155.0; EI-MS (70 eV) m/z (rel. intensity, %) 242 ([M+2]$^+$, 17), 240 (M$^+$, 17), 211 (46), 209 (44), 161 (24), 133 (45), 132 (100), 131 (33), 115 (59), 105 (23), 63 (22); HRMS calcd for C$_{10}$H$_9$BrO$_2$: 239.9786. Found: 239.9786.

7,9-Dichloro-2,5-dihydro-1-benzoxepin-5-ol (6e). (1.95 g, 85%) was obtained as colorless crystal, mp 139-140$^\circ$C, R$_f$ = 0.26 (ethyl acetate: n-hexane = 1: 9), $^1$H-NMR (CDCl$_3$, 200 MHz) δ 2.53 (d, J = 7.4 Hz, 1H, OH), 4.47 (ddd, J = 17.6, 5.0, 2.4 Hz, 1H, OCH$_2$H$_2$CH=CH), 4.70 (ddd, J = 17.6, 5.0, 2.4 Hz, 1H, OCH$_2$H$_2$CH=CH), 5.46 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.69 (m, 1H, OCH$_2$CH=CHCH(OH)), 5.89 (ddt, J = 11.6, 3.6, 2.4 Hz, 1H, OCH$_2$CH=CHCH(OH)), 7.27 (d, J = 2.4 Hz, 1H, ArH), 7.31 (d, J = 2.4 Hz, 1H, ArH); $^{13}$C-NMR (CDCl$_3$, 50 MHz) δ 67.9, 69.9,
123.5, 126.8, 127.8, 128.5, 123.00, 131.6, 142.7, 149.8; EI-MS (70eV) m/z (rel. intensity, %) 232 ([M+2]+, 26), 230 (M+, 41), 203 (49), 201 (100), 199 (60), 189 (43), 167 (62), 166 (89), 149 (49), 133 (41), 132 (58), 131 (75); HRMS calcd for C_{10}H_8Cl_2O_2: 229.9901. Found: 229.9903.

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References