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

Sie-Rong Li,[a,b] Hsing-Ming Chen,[c] Liang-Yeu Chen,[b] Jui-Chi Tsai,[b] Po-Yuan Chen,[a] Sodio Chih-Neng Hsu,[a] and Eng-Chi Wang[a*]

[a]*Faculty of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung City, Taiwan 807*

[b]*Institute of Pharmaceutical Sciences, Kaohsiung Medical University, Kaohsiung City, Taiwan 807*

[c]*School of Medical and Health Sciences, Fooyin University, Kaohsiung County, Taiwan 831*

E-mail: enchwa@kmu.edu.tw

Abstract

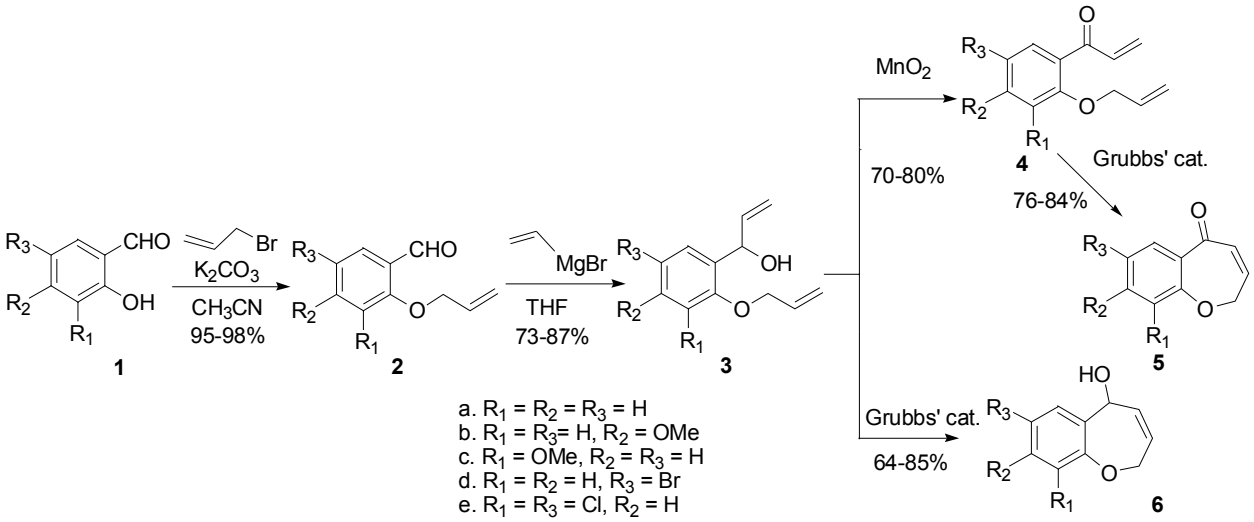
A new synthetic method for 1-benzoxepin-5-ones and 1-benzoxepin-5-ols from salicylaldehydes was described. Based on *O*-allylation, Grignard reaction, oxidation, and ring-closing metathesis in sequence, salicylaldehydes were converted to the target compounds in good yields, respectively.

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

Introduction

The 1-benzoxepine moiety which plays a core structure both in naturally occurring products[1] and in certain synthetic biological molecules,[2] have abstracted the attention of chemists. In addition, benzoxepinone which has been employed as starting material, can be converted to corresponding quinoline by the Friedlander reaction,[3] and can be transformed into benzoxepine by isomerization of double bond, reduction of carbonyl group, and dehydration of giving alcohol in sequence.[4] The major synthetic methods for benzoxepinones which were reported in literatures, include the cyclopropanation 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 benzoxepin-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.[9] 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).



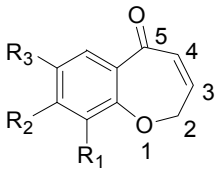
Scheme 1

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.[10] 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 MnO_2 in dichloromethane, (2-allyloxyaryl)-2-propen-1-ones (**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, 2*H*-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, 2*H*-1-benzoxepin-5-ol (**6a-e**) were given in 64-85% yields, respectively. Thus, we have established a new route to both 2*H*-1-benzoxepin-5-ones and 2*H*-1-benzoxepin-5-ols. The structure of **5a-e** and **6a-e** were respectively elucidated by spectral data such as ^{1}H-

NMR, ^{13}C-NMR and mass spectra. The typical signals of ^{1}H-NMR of 2*H*-1-benzoxepin-5-ones **(5a-e)** and 2*H*-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 2*H*-1-benzoxepin-5-one **(5a-e)** and 2*H*-1-benzoxepin-5-ol **(6a-c**)



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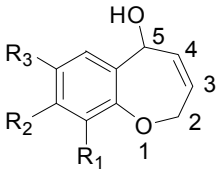

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a. $R_1 = R_2 = R_3 = H$
b. $R_1 = R_3 = H$, $R_2 = OMe$
c. $R_1 = OMe$, $R_2 = R_3 = H$
d. $R_1 = R_2 = H$, $R_3 = Br$
e. $R_1 = R_3 = Cl$, $R_2 = H$

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

[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 α,β-unsaturated carbonyl functionality of benzoxepinones and allyl alcoholic 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 K_2CO_3 (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, R_f = 0.16 (ethyl acetate: *n*-hexane = 1: 15), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.65 (dt, *J* = 5.2, 1.2 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.34 (ddt, *J* = 10.4, 1.2, 1.2 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.45 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 6.01 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.97 (m, 1H, ArH), 7.02 (m, 1H, ArH), 7.52 (m, 1H, ArH), 7.83 (m, 1H, ArH), 10.53 (s, 1H, CHO); ^{13}C-NMR ($CDCl_3$, 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 ($[M+1]^+$, 100), 162 (M^+, 24), 161 (54), 133 (24), 121 (76), 120 (19), 105 (18), 92 (26); HRMS calcd for $C_{10}H_{10}O_2$: 162.0681. Found: 162.0680.

2-Allyloxy-4-methoxybenzaldehyde (2b).[11] (18.24 g, 95%) was obtained as colorless crystal, mp 37-38°C, R_f = 0.33 (ethyl acetate: *n*-hexane = 1: 6), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.85 (s, 3H, OCH_3), 4.62 (dt, *J* = 5.2, 1.4 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.33 (ddt, *J* = 10.6, 1.4, 1.4 Hz, 1H, $OCH_2CH= C\underline{H}_aH_b$), 5.45 (ddt, *J* = 17.4, 1.4, 1.4 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 6.04 (ddt, *J* = 17.4, 10.6, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.43 (d, *J* = 2.0 Hz, 1H, ArH), 6.54 (dd, *J* = 8.8, 2.0 Hz, 1H, ArH), 7.81 (d, *J* = 8.8 Hz, 1H, ArH), 10.35 (s, 1H, CHO); ^{13}C-NMR ($CDCl_3$, 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 ($[M+1]^+$, 30), 192 (M^+, 35), 164 (28), 163 (54), 151 (100), 150 (91), 135 (45), 122 (27), 95 (28); HRMS calcd for $C_{11}H_{12}O_3$: 192.0786. Found: 192.0784.

2-Allyloxy-3-methoxybenzaldehyde (2c).[12] (18.82 g, 98%) was obtained as colorless liquid, R_f = 0.26 (ethyl acetate: *n*-hexane = 1: 6), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.86 (s, 3H, OCH_3), 4.62 (dt, *J* = 6.0, 1.2 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.33 (ddt, *J* = 10.2, 1.2, 1.2 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.45 (ddt, *J* = 17.4, 1.2, 1.2 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 6.04 (ddt, *J* = 17.4, 10.2, 6.0 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 7.10 (m, 2H, ArH), 7.37 (m, 1H, ArH), 10.41 (s, 1H, CHO); ^{13}C-NMR ($CDCl_3$, 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 ($[M+1]^+$, 100), 192 (M^+, 54), 175 (17), 166 (20), 164 (29), 163 (55), 151 (83), 136 (17) , 131 (20), 122 (20); HRMS calcd for $C_{11}H_{12}O_3$: 192.0786. Found: 192.0783.

2-Allyloxy-5-bromobenzaldehyde (2d).[13] (23.03 g, 96%) was obtained as colorless liquid, R_f = 0.50 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.60 (dt, *J* = 5.2, 1.6 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.31 (ddt, *J* = 10.8, 1.6, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.40 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 6.02 (ddt, *J* = 17.2, 10.8, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 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 $C_{10}H_9BrO_2$: 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, $OC\underline{H}_2CH=CH_2$), 5.32 (d, *J* = 10.4 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.39 (dd, *J* = 16.8, 1.2 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 6.07 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 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, 131.7, 135.6, 156.2, 187.9; EI-MS (70eV) *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 $C_{10}H_8Cl_2O_2$: 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_4Cl. The giving 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, $OC\underline{H}_2CH=CH_2$), 5.16 (ddd, *J* = 10.4, 1.2 Hz, 1.2 Hz, 1H, CH(OH)- $CH=C\underline{H}_aH_b$), 5.29 (ddt, *J* = 10.4, 1.2, 1.2 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.32 (ddd, *J* = 17.6, 1.2, 1.2 Hz, 1H, $CH(OH)CH=CH_a\underline{H}_b$), 5.41 (ddt, *J* = 17.6, 1.2, 1.2 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 5.44 (m, 1H, $C\underline{H}(OH)CH=CH_2$), 6.05 (ddt, *J* = 17.6, 10.4, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.13 (ddd, *J* = 17.6, 10.4, 5.6 Hz, 1H, $CH(OH)C\underline{H}=CH_a\underline{H}_b$), 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 = 0.31 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 2.82 (br d, *J* = 5.2 Hz, 1H, OH), 3.77 (s, 3H, OCH_3), 4.53 (dt, *J* = 5.2, 1.2 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.14 (ddd, *J* = 10.4, 1.2, 1.2 Hz, 1H, $CH(OH)CH=C\underline{H}_aH_b$), 5.28 (ddt, *J* = 10.4, 1.4 Hz, 1.4 Hz, 1H,

$OCH_2CH=C\underline{H}_aH_b$), 5.30 (ddd, *J* = 17.2, 1.2, 1.2 Hz, 1H, $CH(OH)CH=CH_a\underline{H}_b$), 5.40 (m, 1H, $C\underline{H}(OH)CH=CH_2$), 5.41 (ddt, *J* = 17.2, 1.4 Hz, 1.4 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 6.04 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.11 (ddd, *J* = 17.2, 10.4, 5.4 Hz, 1H, $CH(OH)C\underline{H}=CH_2$), 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); ^{13}C-NMR ($CDCl_3$, 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 $C_{13}H_{16}O_3$: 220.1099. Found: 220.1099.

1-(2-Allyloxy-3-methoxyphenyl)prop-2-en-1-ol (3c).[15] (5.62 g, 85%) was obtained as colorless liquid, R_f = 0.33 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.93 (br d, *J* = 4.4 Hz, 1H, OH), 3.83 (s, 3H, OCH_3), 4.52 (ddt, *J* = 12.0, 5.6, 1.6 Hz, 1H, $OC\underline{H}_aH_bCH=CH_2$), 4.56 (ddt, *J* = 12.0, 5.6, 1.6 Hz, 1H, $OCH_a\underline{H}_bCH=CH_2$), 5.15 (ddd, *J* = 10.4, 1.6, 1.6 Hz, 1H, $CH(OH)CH=C\underline{H}_aH_b$), 5.23 (ddt, *J* = 10.4, 1.6, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.31 (ddd, *J* = 17.2, 1.6, 1.6 Hz, 1H, $CH(OH)CH=CH_a\underline{H}_b$), 5.36 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 5.47 (m, 1H, $C\underline{H}(OH)CH=CH_2$), 6.07 (ddd, *J* = 17.2, 10.4, 5.2 Hz, 1H, $CH(OH)C\underline{H}=CH_2$), 6.07 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.84 (dd, *J* = 8.0, 1.6 Hz, 1H, ArH), 6.93 (dd, *J* = 8.0, 1.6 Hz, 1H, ArH), 7.04 (t, *J* = 8.0 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 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 $C_{13}H_{16}O_3$: 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, R_f = 0.32 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 2.73 (br s, 1H, OH), 4.54 (dt, *J* = 5.2, 1.6 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.18 (ddd, *J* = 10.4, 1.6, 1.6 Hz, 1H, $CH(OH)CH=C\underline{H}_aH_b$), 5.30 (ddt, *J* = 10.4, 1.6, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.33 (ddd, *J* = 17.2, 1.6, 1.6 Hz, 1H, $CH(OH)CH=CH_a\underline{H}_b$), 5.39 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 5.42 (m, 1H, $C\underline{H}(OH)CH=CH_2$), 6.02 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.06 (ddd, *J* = 17.2, 10.4, 5.4 Hz, 1H, $CH(OH)C\underline{H}=CH_2$), 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); ^{13}C-NMR ($CDCl_3$, 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 $C_{12}H_{13}BrO_2$: 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, R_f = 0.35 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 2.39 (d, *J* = 4.6 Hz, 1H, OH), 4.52 (dt, *J* = 5.6, 1.6 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.24 (ddd, *J* = 10.2, 1.4, 1.4 Hz, 1H, $CH(OH)CH=C\underline{H}_aH_b$), 5.30 (ddt, *J* = 10.2, 1.6, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.37 (ddd, *J* = 17.2, 1.4, 1.4 Hz, 1H, $CH(OH)CH=CH_a\underline{H}_b$), 5.42 (ddt, *J* = 17.0, 1.6, 1.6 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 5.50 (m, 1H, $C\underline{H}(OH)CH=CH_2$), 6.02 (ddd, *J* = 17.2, 10.2, 5.4 Hz, 1H, $CH(OH)C\underline{H}=CH_2$), 6.10 (ddt, *J* = 17.0, 10.2, 5.4 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 7.30 (d, *J* = 2.6 Hz, 1H, ArH), 7.32 (d, *J* = 2.6 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 69.7, 74.6, 115.8, 118.6, 126.3, 128.6,

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 $C_{12}H_{12}Cl_2O_2$: 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 CH_2Cl_2 (85 mL) was added MnO_2 (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-Allyloxyphenyl)-2-propen-1-one (4a). (3.01 g, 80%) was obtained as colorless liquid, R_f = 0.53 (ethyl acetate: *n*-hexane = 1: 10), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.61 (dt, *J* = 5.2, 1.2 Hz, 2H, OC$\underline{H}_2$CH=CH_2), 5.28 (ddt, *J* = 10.4, 1.2, 1.2 Hz, 1H, OCH_2CH=C$\underline{H}_2$), 5.42 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H, OCH_2CH=C$\underline{H}_2$), 5.79 (dd, *J* = 10.4, 1.6 Hz, 1H, COCH=C$\underline{H}_a$H$_b$), 6.03 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, $OCH_2C\underline{H}$=CH_2), 6.28 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H, COCH=CH$_a\underline{H}_b$), 6.95 (m, 1H, ArH), 7.00 (m, 1H, ArH), 7.04 (dd, *J* = 17.2, 10.4 Hz, 1H, COCH=C$\underline{H}_2$), 7.43 (m, 1H, ArH), 7.58 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 69.3, 112.9, 117.6, 120.9, 128.2, 128.9, 130.5, 132.5, 132.9, 136.7, 157.2, 193.3; EI-MS (70 eV) *m/z* (rel. intensity, %) 189 ($[M+1]^+$, 6), 188 (M^+, 2), 170 (16), 169 (26), 147 (38), 131 (24), 121 (100), 91 (22); HRMS calcd for $C_{12}H_{12}O_2$: 188.0837. Found: 188.0839.

1-(2-allyloxy-4-methoxyphenyl)-2-propen-1-one (4b). (3.08 g, 70%) was obtained as colorless liquid, R_f = 0.38 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.83 (s, 3H, OCH_3), 4.59 (dt, *J* = 5.2, 1.6 Hz, 2H, OC$\underline{H}_2$CH=CH_2), 5.30 (ddt, *J* = 10.6, 1.6, 1.6 Hz, 1H, OCH_2CH=C$\underline{H}_a$H$_b$), 5.44 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H, OCH_2CH=CH$_a\underline{H}_b$), 5.70 (dd, *J* = 10.4, 1.8 Hz, 1H, COCH=C$\underline{H}_a$H$_b$), 6.04 (ddt, *J* = 17.2, 10.6, 5.2 Hz, 1H, $OCH_2C\underline{H}$=CH_2), 6.32 (dd, *J* = 17.2, 1.8 Hz, 1H, COCH=CH$_a\underline{H}_b$), 6.45 (d, *J* = 2.2 Hz, 1H, ArH), 6.54 (dd, *J* = 8.8, 2.2 Hz, 1H, ArH), 7.18 (dd, *J* = 17.2, 10.4 Hz, 1H, COC$\underline{H}$=CH_2), 7.71 (d, *J* = 8.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 55.4, 69.3, 99.6, 105.7, 117.7, 121.7, 126.7, 132.3, 132.8, 136.8, 159.4, 164.1, 190.7; EI-MS (70eV) *m/z* (rel. intensity, %) 219 ($[M+1]^+$, 68), 218 (M^+, 48), 217 (29), 188 (32), 163 (40), 151 (100), 121 (42), 91 (42), 77 (38), 63 (38); HRMS calcd for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0945.

1-(2-Allyloxy-3-methoxyphenyl)-2-propen-1-one (4c).[15] (3.24 g, 74%) was obtained as colorless liquid, R_f = 0.38 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.87 (s, 3H, OCH_3), 4.50 (dt, *J* = 5.8, 1.2 Hz, 2H, OC$\underline{H}_2$CH=CH_2), 5.17 (ddt, *J* = 10.2, 1.2, 1.2 Hz, 1H, OCH_2CH=C$\underline{H}_a$H$_b$), 5.28 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H, OCH_2CH=CH$_a\underline{H}_b$), 5.86 (dd, *J* = 10.4, 1.4 Hz, 1H, COCH=C$\underline{H}_a$H$_b$), 6.00 (ddt, *J* = 17.2, 10.2, 5.8 Hz, 1H, $OCH_2C\underline{H}$=CH_2), 6.22 (dd, *J* = 17.6, 1.4 Hz, 1H, COCH=CH$_a\underline{H}_b$), 6.94 (dd, *J* = 17.2, 10.4 Hz, 1H, COC$\underline{H}$=CH_2) 7.07 (m, 3 H, ArH); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 55.8, 74.8, 115.0, 117.7, 120.7, 123.9, 129.2, 133.4, 133.9, 136.5, 146.3, 152.7, 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 $C_{13}H_{14}O_3$: 218.0943. Found: 218.0943.

1-(2-Allyloxy-5-bromophenyl)-2-propen-1-one (4d). (3.79 g, 71%) was obtained as colorless liquid, R_f = 0.50 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 4.59 (dt, *J* = 5.2, 1.4 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.29 (ddt, *J* = 10.6, 1.4, 1.4 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.40 (ddt, *J* = 17.2, 1.4, 1.4 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 5.84 (dd, *J* = 10.2, 1.6 Hz, 1H, $COCH=C\underline{H}_aH_b$), 6.00 (ddt, *J* = 17.2, 10.6, 5.2 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.29 (dd, *J* = 17.2, 1.6 Hz, 1H, $COCH=CH_a\underline{H}_b$), 6.84 (d, *J* = 8.8 Hz, 1H, ArH), 6.99 (dd, *J* = 17.2, 10.2 Hz, 1H, $COC\underline{H}=CH_2$), 7.51 (dd, *J* = 8.8, 2.6 Hz, 1H, ArH), 7.67 (d, *J* = 2.6 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 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), 201 (96), 199 (100), 198 (67), 170 (24) , 169 (31), 131 (24), 119 (25), 90 (35), 89 (31), 63 (62); HRMS calcd for $C_{12}H_{11}BrO_2$: 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, R_f = 0.61 (ethyl acetate: *n*-hexane = 1: 15), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.43 (dt, *J* = 6.0, 1.2 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 5.25 (ddt, *J* = 10.4, 1.2, 1.2 Hz, 1H, $OCH_2CH=C\underline{H}_aH_b$), 5.32 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H, $OCH_2CH=CH_a\underline{H}_b$), 5.98 (dd, *J* = 10.4, 1.2 Hz, 1H, $COCH=C\underline{H}_aH_b$), 5.99 (ddt, *J* = 17.2, 10.4, 6.0 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.29 (dd, *J* = 17.6, 1.2 Hz, 1H, $COCH=CH_a\underline{H}_b$), 6.91 (dd, *J* = 17.6, 10.4 Hz, 1H, $COC\underline{H}=CH_2$), 7.38 (d, *J* = 2.8 Hz, 1H, ArH), 7.52 (d, *J* = 2.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 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 $C_{12}H_{10}Cl_2O_2$: 256.0058. Found: 256.0060.

General procedure for the preparation of 2*H*-1-benzoxepin-5-one (5a-e)

The (2-allyloxyphenyl)-2-propen-1-one (**4a-e**) (10 mmol) dissolved in anhydrous CH_2Cl_2 (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**.

2*H*-1-Benzoxepin-5-one (5a).[4] (1.3 g, 81%) was obtained as colorless liquid, R_f = 0.35 (ethyl acetate: *n*-hexane = 1: 10), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.55 (dd, *J* = 4.8, 1.2 Hz, 2H, $OC\underline{H}_2$-CH=CHCO), 6.43 (dt, *J* = 11.6, 1.2 Hz, 1H, $OCH_2CH=C\underline{H}CO$), 6.75 (dt, *J* = 11.6, 4.8 Hz, 1H, $OCH_2C\underline{H}$=CHCO), 7.09 (m, 1H, ArH), 7.17 (m, 1H, ArH), 7.47 (m, 1H, ArH), 7.95 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 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 $C_{10}H_8O_2$: 160.0519. Found: 160.0521.

8-Methoxy-2*H*-1-benzoxepin-5-one (5b). (1.45 g, 76%) was obtained as colorless liquid, R_f = 0.26 (ethyl acetate: *n*-hexane = 1: 9), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.83 (s, 3H, OCH_3), 4.68 (dd, *J* = 5.2, 1.2 Hz, 2H, $OC\underline{H}_2CH=CHCO$), 6.41 (dt, *J* = 11.6, 1.2 Hz, 1H, $OCH_2CH=C\underline{H}CO$), 6.52 (d, *J* = 2.4 Hz, 1H, ArH), 6.69 (dt, *J* = 11.6, 5.2 Hz, 1H, $OCH_2C\underline{H}$=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, OC<u>H</u>$_2$CH=CHCO), 6.44 (dt, *J* = 11.6, 1.4 Hz, 1H, OCH_2CH=C<u>H</u>CO), 6.76 (dt, *J* = 11.6, 4.4 Hz, 1H, OCH_2C<u>H</u>=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), 76 (12), 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, OC<u>H</u>$_2$CH=CHCO), 6.41 (dt, *J* = 11.6, 1.2 Hz, 1H, OCH_2CH=C<u>H</u>CO), 6.78 (dt, *J* = 11.6, 4.8 Hz, 1H, OCH_2C<u>H</u>=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 $C_{10}H_7BrO_2$: 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, OC<u>H</u>$_2$CH=CHCO), 6.41 (dt, *J* = 11.8, 1.4 Hz, 1H, OCH_2CH=C<u>H</u>CO), 6.80 (dt, *J* = 11.8, 4.6 Hz, 1H, OCH_2C<u>H</u>=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 $C_{10}H_6Cl_2O_2$: 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_2Cl_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).[4] (1.30 g, 80%) was obtained as colorless liquid, R_f = 0.18 (ethyl acetate: *n*-hexane = 1: 10), ^{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, OC<u>H$_a$</u>H$_b$CH=CH), 4.60 (ddd, *J* = 17.2, 4.8, 2.4 Hz, 1H, OCH_a<u>H$_b$</u>CH=CH), 5.48 (m, 1H, OCH_2C<u>H</u>=CHCH(OH)), 5.50 (m, 1H, OCH_2CH=CHC<u>H</u>(OH)), 5.99 (ddt, *J* = 11.6, 4.0, 2.4 Hz, 1H, OCH_2CH=C<u>H</u>CH(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_aH_bCH=CH), 4.57 (ddd, *J* = 17.2, 4.4, 2.2 Hz, 1H, OCH_aH_bCH=CH), 5.38 (m, 1H, OCH_2CH=CHCH(OH)), 5.46 (m, 1H, OCH_2- CH=CHCH(OH)), 5.97 (ddt, *J* = 11.6, 4.2, 2.2 Hz, 1H, OCH_2CH=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 (29), 175 (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: 192.0786.

9-Methoxy-2,5-dihydro-1-benzoxepin-5-ol (6c). (1.22 g, 64%) was obtained as colorless crystal, mp 99-100°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_aH_bCH=CH), 4.59 (ddd, *J* = 17.6, 4.8, 2.4 Hz, 1H, OCH_aH_bCH=CH), 5.47 (m, 1H, OCH_2CH=CHCH(OH)), 5.54 (m, 1H, OCH_2CH=CHCH(OH)), 5.97 (ddt, *J* = 11.6, 4.4, 2.4 Hz, 1H, OCH_2CH=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°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_aH_bCH=CH), 4.63 (ddd, *J* = 17.2, 4.8, 2.4 Hz, 1H, OCH_aH_bCH=CH), 5.48 (m, 1H, OCH_2CH=CHCH(OH)), 5.58 (m, 1H, OCH_2CH=CHCH(OH)), 5.92 (ddt, *J* = 12.0, 3.6, 2.4 Hz, 1H, OCH_2CH=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, 131.4, 131.5, 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 $C_{10}H_9BrO_2$: 239.9786. Found: 239.9788.

7,9-Dichloro-2,5-dihydro-1-benzoxepin-5-ol (6e). (1.95 g, 85%) was obtained as colorless crystal, mp 139-140°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_aH_bCH=CH), 4.70 (ddd, *J* = 17.6, 5.0, 2.4 Hz, 1H, OCH_aH_bCH=CH), 5.46 (m, 1H, OCH_2CH=CHCH(OH)), 5.69 (m, 1H, OCH_2CH=CHCH(OH)), 5.89 (ddt, *J* = 11.6, 3.6, 2.4 Hz, 1H, OCH_2CH=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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