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A SYNTHESIS OF SUBSTITUTED 3,6-DIHYDRO-1*H*-BENZO[*C*]OXOCINES *VIA* CLAISEN REARRANGEMENT AND RING-CLOSING METATHESIS

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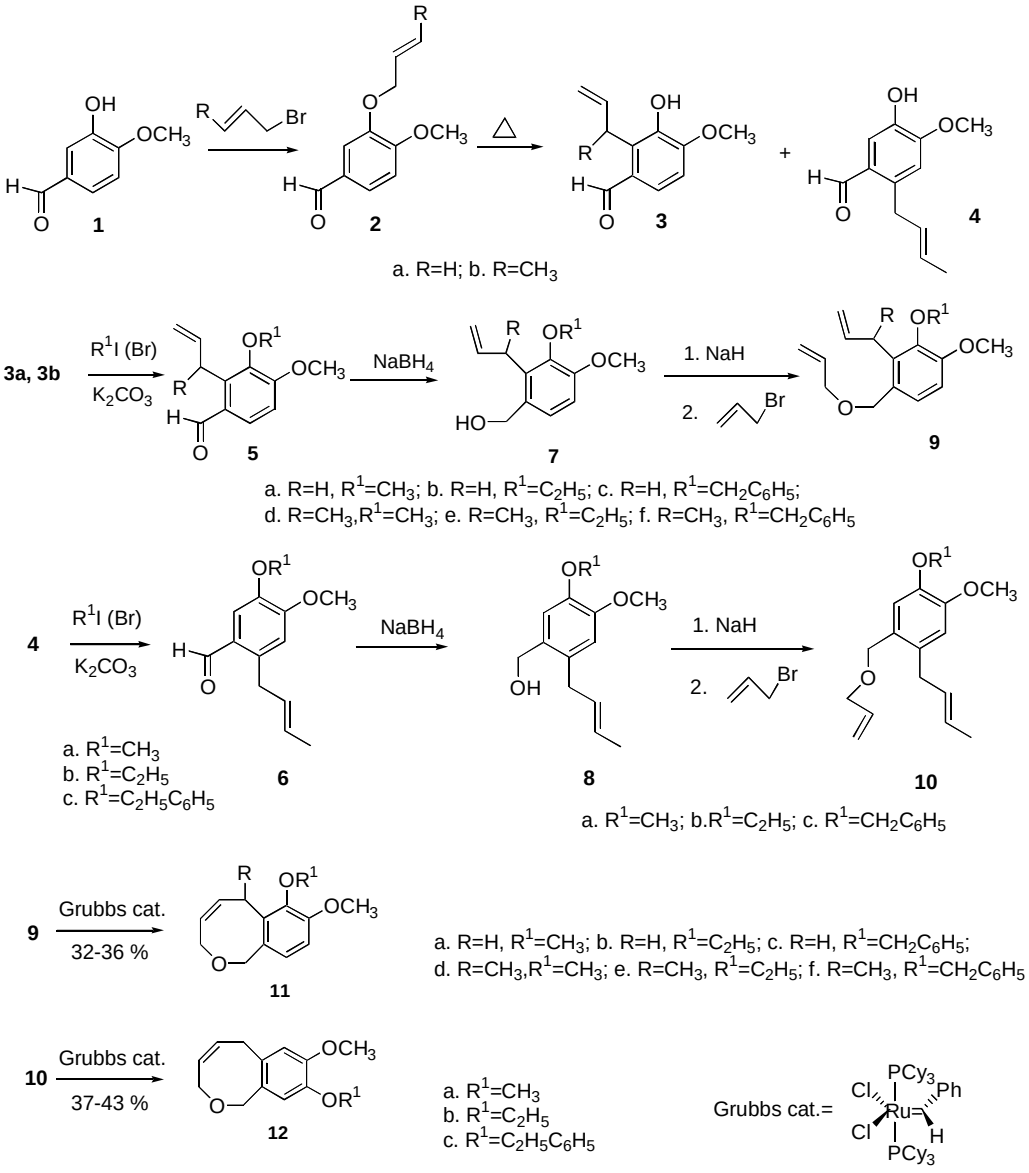
Abstract- Started from isovanillin, based on Claisen rearrangement and ring-closing metathesis (RCM) reaction, a series of substituted 3,6-dihydro-1*H*-benzo[*c*]oxocines were synthesized in moderate yields.

INTRODUCTION

Oxocine, one of structural unit of brevetoxins A and B isolated from marine plants,[1] attract the attention of scientists for their promising neurotoxicity. Many efforts have been made to the construction of structural units for the total synthesis of those bioactive natural polycyclic ethers.[2] Nevertheless, the study on the chemistry of 3,6-dihydro-1*H*-benzo[*c*]oxocine, an oxocine molecule fused with a benzene ring, was quite insufficient. Until present, only few studies have been reported, just as 7,8,9,10-tetraphenyl-3,4,5,6-tatrahydro-1*H*-benzo[*c*]oxocine *via* 1-oxa-3-cyclooctyne was reported by Meier *et al*.,[3] 6-methylene-1,3-dihydro-2-benzo[*c*]oxocine *via* 2-iodobenzyl bromide was reported by Ma *et al*.,[4] and tricyclicfuro[3,2-*c*][2]benzoxocine *via* D-glucose was reported by Chattopadhyay *et al*.[5] Among those methods it suffered from some drawbacks, such as tedious reaction condition, non-commercial available intermediates and multi-synthetic steps. Furthermore, a systematic study of substituted 3,6-dihydro-1*H*-benzo[*c*]oxocines is still lacking. Thus, the development of new and general method for the synthesis of this class of heterocyclic compound is interested, and requisite.

Since 1995 Grubbs *et al*.[6] discovered a novel alkylidene-ruthenium complex as a catalyst for ring-closing metathesis (RCM), it has been widely applied in organic synthesis in many aspects.[7] Based on this chemistry, we have recently reported a new route to *N*-aryl α,β-unsaturated lactams,[8] and substituted naphthalenes.[9] In this continuing studies, we herein report the synthesis of a series of substituted 3,6-dihydro-1*H*-benzo[*c*]oxocines, started from isovanillin, and based on the following sequential reactions such as Claisen rearrangement, *o*-alkylation, reduction, Williamson ether synthesis, and RCM.

The synthetic scheme was shown in **Scheme 1**.



Scheme 1

RESULTS AND DISCUSSION

As our previous study,[9] compounds (**3a-b** and **4**) prepared from the Claisen rearrangement of allylisovanillin (**2a-b**) was reacted with various alkyl halides to give aldehydes (**5a-f, 6a-c**) in good yields. Reduction of aldehydes (**5a-f, 6a-c**) with sodium borohydride in ethanol, afforded the corresponding benzyl alcohols (**7a-f, 8a-c**) in yields of 96-97%. The structural elucidation of **7a-f**, and **8a-c** was supported by their ^{1}H-NMR, ^{13}C-NMR and EI-MS spectral data. For example, the ^{1}H-NMR of **7a** exhibited one proton signal with singlet and D_2O exchangeable at 2.55 ppm, together with two protons signal with singlet at 4.44 ppm indicating benzylic protons, and the formyl proton was no longer observed. IN the ^{13}C-NMR spectrum of **7a** no carbonyl carbon, but benzylic carbon at 62.48 was found instead. Furthermore the molecular ion *m/z* 208 was found in EI-MS spectrum, which is coincident with the

calculated one for **7a**, $C_{12}H_{16}O_3$. Etherification of these benzyl alcohols (**7a-f, 8a-c**) with allyl bromide was carried out by typical Williamson ether synthesis, i.e., by treating these alcohols (**7a-f, 8a-c**) respectively, with sodium hydride, and then reacting with allyl bromide to give corresponding allylbenzyl allyl ethers (**9a-f, 10a-c**) in yields of 71-97%. The structural elucidation of **9a-f, 10a-c** was based on their ^{1}H-NMR, ^{13}C-NMR and EI-MS spectral data. For example, **9b** revealed two sets of allyl protons in ^{1}H-NMR, one at δ 3.52 (ddd, *J* = 5.6 Hz, 1.8 Hz, 1.8 Hz, 2H, ArC$\underline{H}_2$CH=CH_2), δ 4.92 (ddt, *J* = 17.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), δ 4.97 (ddt, *J* = 10.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), and δ 5.95 (ddt, *J* = 17.0 Hz, 10.0 Hz, 5.6 Hz, 1H, $ArCH_2C\underline{H}=CH_2$); the other one at δ 4.01 (ddd, *J* = 5.6 Hz, 1.6 Hz, 1.6 Hz, 2H, OC$\underline{H}_2$CH=CH_2), 5.19 (ddt, *J* = 10.4 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.30 (ddt, *J* =17.2 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), and 5.95 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.6 Hz, 1H, $OCH_2C\underline{H}=CH_2$). In ^{13}C-NMR spectra of **9b**, sixteen lines were found matched the carbon number of **9b**. Furthermore the molecular ion, *m/z* 262 was found which is coincident with the calculated one for **9b**, $C_{16}H_{22}O_3$. Finally cyclization of these allylbenzyl allyl ethers (**9a-f, 10a-c**) with Grubbs catalyst in dichloromethane, afforded a series of title compounds, substituted 3,6-dihydro-1*H*-benzo[*c*]oxocines (**11a-f, 12a-c**) in yields of 31-43%. The structural elucidation of **11a-f, 12a-c** was based on their ^{1}H-NMR, ^{13}C-NMR and EI-MS spectral data. For example, the ^{1}H-NMR spectrum of **11c** exhibited four sets of two-proton signals. Two of them are singlet at δ 4.80 (s, 2H, ArC$\underline{H}_2$O), and 4.96 (s, 2H, OC$\underline{H}_2C_6H_5$), respectively; one of them is doublet at δ 3.69 (d, *J* = 7.4 Hz, 2H, ArC$\underline{H}_2$CH=CH), and the other one is doublet of doublet at δ 4.16 (dd, *J* = 4.8 Hz, 1.2 Hz, 2H, OC$\underline{H}_2$CH=CH). Furthermore it showed two *cis*-oleifinic protons, one at 5.58 (dtt, *J* = 10.8 Hz, 4.8 Hz, 1.2 Hz, 1H, $ArCH_2CH=C\underline{H}CH_2$), and the other one at 5.82 (dtt, *J* = 10.8 Hz, 7.4 Hz, 1.2 Hz, 1H, $ArCH_2C\underline{H}=CHCH_2$). In ^{13}C-NMR spectra of **11c**, seventeen lines were found matched the structure of **11c**. Furthermore the molecular ion, *m/z* 296 was observed, which is coincident with the calculated one for **11c**, $C_{19}H_{20}O_3$.

In conclusion, it disclosed a new synthesis of substituted 3,6-dihydro-1*H*-benzo[*c*]oxocines (**11a-11f** and **12a-12c**).

EXPERIMENTAL

Melting points (Yanaco micro melting-point apparatus) are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Varian Gemini-200 or Varian Unity plus 400 or Bruker Avance 600 Spectrometer. Chemical shifts are measured in parts per million with respect to TMS. Elemental analyses were recorded on a Heraeus CHN-O Rapid analyzer. MS spectra were recorded on Chem/hp/middle instrument, and HRMS were recorded on JEOL, JMSD-200 or on JEOL, JMS-SX. Silica gel (230-400 mesh) for column chromatography and precoated silica gel plates (60F-254) for TLC were purchased from E. Merck. UV light (254 nm) was used to detect spots on TLC plates after development. Grubbs catalyst was purchased from Fluka Company, and isovanillin was purchased from TCI (Japan). Compounds (**2**, **3**, **4, 5,** and **6**) were prepared as our previous studies.[9]

General procedure for the preparation of benzyl alcohols (**7a-f, 8a-c**)

Benzaldehyde (**5a-f, 6a-c**) (10 mmol) dissolved in ethyl alcohol / water (50 mL / 5 mL), was added with

$NaBH_4$ (0.3 g, 8 mmol) in portion, and the mixture was stirred at rt for 30 min. After the reaction was subsided, an additional $NaBH_4$ (0.1 g) was added, and stirring was continued for additional 10 min. The reaction was quenched with ice water (25 mL), and concentrated in *vacuo* to remove ethanol. The residue was extracted with ethyl acetate (50 mL×3). Then the separated organic layer was mixed, and washed with brine (50 mL×1), dried under anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under *vacuo* to give a pale yellow liquid, which was subjected to a silica gel chromatographic column (ethyl acetate / *n*-hexane = 1/3) to afford pure **7a-f**, **8a-c** in yields of 93-98 %.

2-Allyl-3,4-dimethoxybenzyl alcohol (**7a**)[10]

Pure **7a** (2.01 g, 97%) was obtained as pale yellow liquid, R_f 0.24 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.55 (br s, 1H, OH), 3.39 (ddd, *J* = 5.6 Hz, 1.8 Hz, 1.8 Hz, 2H, ArC$\underline{H}_2$CH=CH_2), 3.69 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 4.44 (s, 2H, ArC$\underline{H}_2$OH), 4.80 (ddt, *J* = 17.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH$=C$\underline{H}_2$), 4.89 (ddt, *J* = 10.2 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH$=C$\underline{H}_2$), 5.88 (ddt, *J* = 17.0 Hz, 10.2 Hz, 5.6 Hz, 1H, $ArCH_2C\underline{H}$=CH_2), 6.66 (d, *J* = 8.4 Hz, 1H, Ar$\underline{H}$), 6.95 (d, *J* = 8.4 Hz, 1H, Ar$\underline{H}$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 29.81, 55.38, 60.54, 62.48, 109.94, 114.72, 123.99, 131.52, 132.08, 137.36, 147.04, 152.06; EI-MS (70 eV) *m/z* 208 (M^+, 100), 190 (29), 175 (41), 159 (34), 147 (18), 131 (16), 115 (37), 91 (32), 77 (31), 65 (17), 51 (13); HRMS (EI, *m/z*) calcd for $C_{12}H_{16}O_3$: 208.1099. Found: 208.1096; Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.35; H, 7.68.

2-Allyl-3-ethoxy-4-methoxybenzyl alcohol (**7b**)

Pure **7b** (2.15 g, 97%) was obtained as pale liquid, R_f 0.27 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.99 (br s, 1H, OH), 3.53 (ddd, *J* = 5.8 Hz, 1.8 Hz, 1.8 Hz, 2H, ArC$\underline{H}_2$CH=CH_2), 3.83 (s, 3H, OCH_3), 3.99 (q, *J* = 7.2 Hz, 2H, OC$\underline{H}_2CH_3$), 4.57 (s, 2H, ArC$\underline{H}_2$OH), 4.92 (ddt, *J* = 17.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH$=C$\underline{H}_2$), 4.99 (ddt, *J* = 10.2 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH$=C$\underline{H}_2$), 5.99 (ddt, *J* = 17.0 Hz, 10.2 Hz, 5.8 Hz, 1H, $ArCH_2C\underline{H}$=CH_2), 6.77 (d, *J* = 8.4 Hz, 1H, ArH), 7.05 (d, *J* = 8.4 Hz, 1H, Ar$\underline{H}$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.60, 30.19, 55.55, 63.00, 68.76, 110.05, 114.83, 124.11, 131.91, 132.17, 137.72, 146.52, 152.44 EI-MS (70 eV) *m/z* 222 (M^+, 100), 205 (24), 193 (17), 175 (32), 161 (19), 151 (9), 115 (13), 91 (11); HRMS (EI, *m/z*) calcd for $C_{13}H_{18}O_3$: 222.1256. Found: 222.1264; Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.40; H, 8.01.

2-Allyl-3-benzyloxy-4-methoxybenzyl alcohol (**7c**)

Pure **7c** (2.73 g, 96%) was obtained as colorless crystal mp 59-60 ^{o}C (ethyl acetate + *n*-hexane), R_f 0.24 (ethyl acetate/*n*-hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.53 (ddd, *J* = 5.9 Hz, 1.7 Hz, 1.7 Hz, 2H, ArC$\underline{H}_2$CH=CH_2), 3.88 (s, 3H, OCH_3), 4.61 (s, 2H, $ArCH_2O$), 4.91 (ddt, *J* = 17.0 Hz, 1.7 Hz, 1.7 Hz, 1H, $ArCH_2CH$=C$\underline{H}_2$), 4.99 (s, 2H, OC$\underline{H}_2C_6H_5$), 4.99 (ddt, *J* = 10.0 Hz, 1.7 Hz, 1.7 Hz, 1H, $ArCH_2CH$=C$\underline{H}_2$), 5.98 (ddt, *J* = 17.0 Hz, 10.0 Hz, 5.9 Hz, 1H, $ArCH_2C\underline{H}$=CH_2), 6.84 (d, *J* = 8.4 Hz, 1H, ArH), 7.11 (d, *J* = 8.4 Hz, 1H, ArH), 7.33 (d, *J* = 7.2 Hz, 1H, $OCH_2C_6\underline{H}_5$), 7.37 (t, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$), 7.47 (d, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.33, 55.70, 63.22, 74.69, 110.27, 115.08,

124.63, 127.80, 127.96, 128.34, 132.20, 132.29, 137.81, 137.92, 146.28, 152.59; EI-MS (70eV) *m/z* 284 (M^+, 13), 175 (23), 91 (100), 65 (9); HRMS (EI, *m/z*) calcd for $C_{18}H_{20}O_3$: 284.1412. Found: 284.1411; Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.94; H, 7.14.

3,4-Dimethoxy-2-(1-methylallyl)benzyl alcohol (7d)

Pure **7d** (2.18 g, 98%) was obtained as colorless liquid, R_f 0.32 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 7.2 Hz, 3H, ArCH($C\underline{H}_3$)CH=CH_2), 1.95 (br s, 1H, O$\underline{H}$) , 3.80 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.01 (m, 1H, ArC$\underline{H}$(CH_3)CH=CH_2), 4.59 (d, *J* = 12.0 Hz, 1H, ArC$\underline{H}_2$OH), 4.63 (d, *J* = 12.0 Hz, 1H, ArC$\underline{H}_2$OH), 5.02 (ddd, *J* = 10.4 Hz, 1.7 Hz, 1.7 Hz, 1H, ArCH(CH_3)CH=C$\underline{H}_2$), 5.04 (ddd, *J* = 17.2 Hz, 1.7 Hz, 1.7 Hz, 1H, ArCH(CH_3)CH=C$\underline{H}_2$), 6.22 (ddd, *J* = 17.0 Hz, 10.4 Hz, 5.8 Hz, 1H, ArCH(CH_3)C$\underline{H}$=CH_2), 6.77 (d, *J* = 8.4 Hz, 1H, ArH), 7.04 (d, *J* =8.4 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.38, 36.34, 55.55, 60.58, 63.39, 110.09, 112.88 125.02, 131.55, 137.90, 143.33, 147.70, 152.80; EI-MS (70 eV) *m/z* 222 (M^+, 52), 204 (36), 189 (100), 173 (42), 158 (26), 146 (17), 129 (36), 115 (25), 91 (26), 77 (17); HRMS (EI, *m/z*) calcd for $C_{13}H_{18}O_3$: 222.1256. Found: 222.1254; Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.54; H, 7.95.

3-Ethoxy-4-methoxy-2-(1-methylallyl)benzyl alcohol (**7e**)

Pure **7e** (2.19 g, 93%) was obtained as colorless liquid, R_f 0.34 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.44 (d, *J* = 7.2 Hz, 3H, ArCH($C\underline{H}_3$)CH=CH_2), 3.83 (s, 3H, OCH_3), 4.00 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.04 (m, 1H, ArC$\underline{H}$(CH_3)CH=CH_2), 4.63 (s, 2H, $ArCH_2O$), 5.03 (ddd, *J* = 9.9 Hz, 1.8 Hz, 1.8 Hz, 1H, ArCH(CH_3)CH=C$\underline{H}_2$), 5.04 (ddd, *J* = 17.7 Hz, 1.8 Hz, 1.8 Hz, 1H, ArCH(CH_3)CH=C$\underline{H}_2$), 6.23 (ddd, *J* = 17.7 Hz, 9.9 Hz, 5.3 Hz, 1H, ArCH(CH_3)C$\underline{H}$=CH_2), 6.77 (d, *J* = 8.4 Hz, 1H, ArH), 7.06 (d, *J* =8.4 Hz, 1H, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 15.48, 19.27, 35.93, 55.58, 63.32, 68.42, 110.08, 112.85, 125.07, 131.75, 137.94, 143.42, 146.64, 152.86; EI-MS (70 eV) *m/z* 236 (M^+, 94), 218 (47), 189 (100), 175 (86), 157 (53), 143 (61), 129 (38), 115 (22), 91 (22), 77 (16), 65 (10), 55 (14); HRMS (EI, *m/z*) calcd for $C_{14}H_{20}O_3$: 236.1412. Found: 236.1412; Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.45; H, 8.24.

3-Benzyloxy-4-methoxy-2-(1-methylallyl)benzyl alcohol (7f)

Pure **7f** (2.44 g, 93%) was obtained as colorless liquid, R_f 0.31 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38 [d, *J* = 7.6 Hz, 3H, ArCH($C\underline{H}_3$)CH=CH_2], 2.18 (br s, 1H, OH), 3.82 (s, 3H, OCH_3), 4.09 (m, 1H, ArC$\underline{H}$(CH_3)CH=CH_2), 4.55 (d, *J* = 12.4 Hz, 1H, $ArCH_2O$), 4.61 (d, *J* = 12.4 Hz, 1H, $ArCH_2O$), 4.97 (d, *J* = 11.0 Hz, 1H, $OCH_2C_6H_5$), 4.99 (ddd, *J* = 9.4 Hz, 1.8 Hz, 1.8 Hz, 1H, ArCH(CH_3)CH=C$\underline{H}_2$), 5.00 (ddd, *J* = 18.2 Hz, 1.8 Hz, 1.8 Hz, 1H, ArCH(CH_3)CH=C$\underline{H}_2$), 5.01 (d, *J* = 11.0 Hz, 1H, $OC\underline{H}_2C_6H_5$), 6.15 (ddd, *J* = 18.2 Hz, 9.4 Hz, 5.2 Hz, 1H, ArCH(CH_3)C$\underline{H}$=CH_2), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 7.07 (d, *J* = 8.4 Hz, 1H, ArH), 7.30 (d, *J* = 7.2 Hz, 1H, $OCH_2C_6\underline{H}_5$), 7.36 (t, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$), 7.47 (d, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.12, 35.76, 55.50, 62.94, 74.15, 110.08, 112.91, 125.19, 127.57, 127.77, 128.19, 131.77, 137.83, 137.95, 143.21, 146.08, 152.56; EI-MS (70 eV) *m/z* 298 (M^+, 54), 190 (46), 176 (10), 157 (17), 91 (100), 65 (15); HRMS

(EI, *m/z*) calcd for $C_{19}H_{22}O_3$: 298.1569. Found: 298.1568; Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.67; H, 7.21.

2-(2-Butenyl)-4,5-dimethoxybenzyl alcohol (8a)

Pure **8a** (2.13 g, 96%) was obtained as colorless liquid, R_f 0.20 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.66 (dd, *J* = 6.0 Hz, 1.3 Hz, 3H, $ArCH_2CH=CHC\underline{H}_3$), 3.31 (dd, *J* = 6.0 Hz, 1.4 Hz, 2H, $ArC\underline{H}_2CH=CHCH_3$), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.61 (d, *J* = 4.4 Hz, 2H, $ArC\underline{H}_2OH$), 5.42 (dqt, *J* = 15.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $ArCH_2CH=C\underline{H}CH_3$), 5.58 (1H, dtq, *J* =15.2 Hz, 6.0 Hz, 1.4 Hz, $ArCH_2C\underline{H}=CHCH_3$), 6.69 (1H, s, ArH), 6.92 (1H, s, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 17.74, 35.25, 55.86, 62.66, 111.96, 113.02, 126.08, 130.27, 130.72, 130.96, 147.19, 148.29 EI-MS (70 eV) *m/z* 222 (M^+, 60), 204 (33), 189 (100), 173 (12), 91 (9); HRMS (EI, *m/z*) calcd for $C_{13}H_{18}O_3$: 222.1256. Found: 222.1257; Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.48; H, 7.95.

2-(2-Butenyl)-5-ethoxy-4-methoxybenzyl alcohol (**8b**)

Pure **8b** (2.27 g, 96 %) was obtained as colorless liquid, R_f 0.26 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.63 (d, *J* = 6.2 Hz, 3H, $ArCH_2CH=CHC\underline{H}_3$), 3.23 (d, *J* = 6.2 Hz, 2H, $ArC\underline{H}_2CH=CHCH_3$), 3.49 (br s, 1H, OH), 3.78 (s, 3H, OCH_3), 3.97 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.50 (s, 2H, $ArC\underline{H}_2O$), 5.39 (dq, *J* = 15.0 Hz, 6.2 Hz, 1H, $ArCH_2CH=C\underline{H}CH_3$), 5.52 (dt, *J* = 15.2 Hz, 6.2 Hz, 1H, $ArCH_2C\underline{H}=CHCH_3$), 6.65 (s, 1H, ArH), 6.89 (s, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.29, 17.27, 34.58, 55.35, 61.51, 63.83, 112.67, 112.81, 125.40, 129.59, 130.29, 130.53, 145.91, 147.87; EI-MS (70 eV) *m/z* 236 (M^+, 100), 218 (42), 203 (43), 189 (34), 175 (89), 165 (19), 145 (11), 115 (9), 91 (13), 77 (10), 55 (10); HRMS (EI, *m/z*) calcd for $C_{14}H_{20}O_3$: 236.1412. Found: 236.1414; Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 72.09; H, 8.39.

5-Benzyloxy-2-(2-butenyl)-4-methoxybenzyl alcohol (**8c**)

Pure **8c** (2.80 g, 94%) was obtained as colorless liquid, R_f = 0.27 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.67 (dd, *J* = 6.2 Hz, 1.5 Hz, 3H, $ArCH_2CH=CHC\underline{H}_3$), 3.33 (dd, *J* = 6.4 Hz, 1.5 Hz, 2H, $ArC\underline{H}_2CH=CHCH_3$), 3.88 (s, 3H, OCH_3), 4.57 (d, *J* = 5.6 Hz, 2H, $ArC\underline{H}_2OH$), 5.13 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.44 (dqt, *J* = 15.2 Hz, 6.4 Hz, 1.5 Hz, 1H, $ArCH_2CH=C\underline{H}CH_3$), 5.59 (1H, dtq, *J* = 15.2 Hz, 6.2 Hz, 1.5 Hz, $ArCH_2C\underline{H}=CHCH_3$), 6.73 (1H, s, ArH), 6.95 (1H, s, ArH), 7.30 (d, *J* = 7.4 Hz, 1H, $OCH_2C_6\underline{H}_5$), 7.36 (t, *J* = 7.4 Hz, 2H, $OCH_2C_6\underline{H}_5$), 7.45 (d, *J* = 7.4 Hz, 2H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.84, 35.43, 56.15, 62.91, 71.27, 113.81, 115.01, 126.27, 127.37, 127.80, 128.50, 130.38, 130.80, 131.91, 137.28, 146.57, 149.25 EI-MS (70 eV) *m/z* 298 (M^+, 65), 189 (40), 161 (27), 91 (100), 65 (11); HRMS (EI, *m/z*) calcd for $C_{19}H_{22}O_3$: 298.1569. Found: 298.1570; Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.57; H, 7.19.

General procedure for the preparation of 2-allyl-1-alloxymethylbenzenes (**9a-f, 10a-c**)

Alcohols (**7a-f, 8a-c**) (10 mmol) dissolved in anhydrous THF (35 mL) was added with sodium hydride (60% NaH, 0.26 g, 11 mmol) and the mixture was stirred at rt for 10 min, followed by adding with allyl

bromide (1.0 mL, 11 mmol) in drops. After the reaction mixture was continually stirred for 2 h, until the end of reaction monitored by TLC, it was quenched with saturated ammonium chloride (20 mL). Then the solution was concentrated under *vacuo* to remove THF. The residue was extracted with ethyl acetate (50 mL×3). The extracted organic solution was combined, and washed with brine (50 mL×1), and then dried under anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under *vacuo* to give pale yellow liquid. When subjected to a silica gel chromatographic column (ethyl acetate / hexane = 1/3), it gave pure **9a-f**, **10a-c** in yields of 81-93%.

2-Allyl-1-allyloxymethyl-3,4-dimethoxybenzene (**9a**)

Pure **9a** (2.3 g, 93%) was obtained as pale yellow liquid, R_f 0.61 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.51 (ddd, *J* = 5.6 Hz, 1.8, 1.8 Hz, 2H, $ArC\underline{H}_2CH=CH_2$), 3.81 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.01 (ddd, *J* = 5.6 Hz, 1.5 Hz, 1.5 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 4.44 (s, 2H, $ArC\underline{H}_2O$), 4.92 (ddt, *J* = 17.2 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 4.98 (ddt, *J* = 10.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 5.20 (ddt, *J* = 10.0 Hz, 1.5 Hz, 1.5 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.30 (ddt, *J* = 17.2 Hz, 1.5 Hz, 1.5 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.95 (ddt, *J* = 17.2 Hz, 10.0 Hz, 5.6 Hz, 1H, $ArCH_2C\underline{H}=CH_2$), 5.96 (ddt, *J* = 17.2 Hz, 10.0 Hz, 5.6 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 7.06 (d, *J* = 8.4 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.19, 55.61, 60.72, 69.95, 71.11, 109.86, 114.80, 117.10, 125.04, 129.44, 132.59, 134.84, 137.10, 147.42, 152.50; EI-MS (70 eV) *m/z* 248 (M^+, 38), 191 (78), 190 (100), 175 (59), 159 (79), 147 (25), 115 (51), 91 (31), 77 (18); HRMS (EI, *m/z*) calcd for $C_{15}H_{20}O_3$: 248.1412. Found: 248.1410; Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.79; H, 7.81.

2-Allyl-1-allyloxymethyl-3-ethoxy-4-methoxybenzene (**9b**)

Pure **9b** (2.1 g, 81%) was obtained as pale yellow liquid, R_f 0.64 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 3.52 (ddd, *J* = 5.6 Hz, 1.8 Hz, 1.8 Hz, 2H, $ArC\underline{H}_2CH=CH_2$), 3.83 (s, 3H, OCH_3), 3.99 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.01 (ddd, *J* = 5.6 Hz, 1.6 Hz, 1.6 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 4.44 (s, 2H, $ArC\underline{H}_2O$), 4.92 (ddt, *J* = 17.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 4.97 (ddt, *J* = 10.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 5.19 (ddt, *J* = 10.4 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.30 (ddt, *J* =17.2 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.95 (ddt, *J* = 17.0 Hz, 10.0 Hz, 5.6 Hz, 1H, $ArCH_2C\underline{H}=CH_2$), 5.95 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.6 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.76 (d, *J* = 8.4 Hz, 1H, ArH), 7.05 (d, *J* = 8.4 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.70, 30.38, 55.62, 68.73, 70.01, 71.11, 109.80, 114.69, 117.07, 124.84, 129.42, 132.70, 134.88, 137.13, 146.67, 152.62; EI-MS (70 eV) *m/z* 262 (M^+, 55), 204 (100), 192 (10), 176 (91), 175 (81), 165 (41), 161 (93), 145 (60), 115 (39), 105 (13), 91 (22), 77 (20); HRMS (EI, *m/z*) calcd for $C_{16}H_{22}O_3$: 262.1569. Found: 262.1569; Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.54; H, 8.19.

2-Allyl-1-allyloxymethyl-3-benzyloxy-4-methoxybenzene (**9c**)

Pure **9c** (2.9 g, 89%) was obtained as pale yellow liquid, R_f 0.61 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.50 (ddd, *J* = 5.8 Hz, 1.8 Hz, 1.8 Hz, 2H, $ArC\underline{H}_2CH=CH_2$), 3.87 (s, 3H, OCH_3), 4.00 (ddd, *J* = 5.6 Hz, 1.5 Hz, 1.5 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 4.45 (s, 2H, $ArCH_2O$), 4.89 (ddt, *J* = 17.2 Hz,

1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 4.96 (ddt, *J* = 10.0 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 4.98 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.20 (ddt, *J* = 10.0 Hz, 1.5 Hz, 1.5 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.29 (ddt, *J* = 17.2 Hz, 1.5 Hz, 1.5 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.93 (ddt, *J* = 17.2 Hz, 10.0 Hz, 5.8 Hz, 1H, $ArCH_2C\underline{H}=CH_2$), 5.95 (ddt, *J* = 17.2 Hz, 10.0 Hz, 5.6 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.81 (d, *J* = 8.4 Hz, 1H, ArH), 7.09 (d, *J* = 8.4 Hz, 1H, ArH) 7.32 (d, *J* = 7.2 Hz, 1H, $OCH_2C_6\underline{H}_5$), 7.37 (t, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$), 7.47 (d, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.38, 55.70, 69.96, 71.08, 74.60, 109.97, 114.87, 117.09, 125.17, 127.72, 127.92, 128.31, 129.56, 132.87, 134.87, 137.05, 138.07, 146.32, 152.60; EI-MS (70 eV) *m/z* 324 (M^+, 4), 175 (17), 161 (12), 145 (11), 117 (16), 91 (100); HRMS (EI, *m/z*) calcd for $C_{21}H_{24}O_3$: 324.1725. Found: 324.1724; Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 78.10; H, 7.18.

1-Allyloxymethyl-3,4-dimethoxy-2-(1-methylallyl)benzene (**9d**)

Pure **9d** (2.0 g, 77 %) was obtained as pale yellow liquid, R_f 0.66 (ethyl acetate / hexane = 1/3), ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.42 (d, *J* = 7.2 Hz, 3H, $ArCH(C\underline{H}_3)CH=CH_2$), 3.80 (s, 3H, OCH_3) , 3.84 (s, 3H, OCH_3), 3.94 (m, 1H, $ArC\underline{H}(CH_3)CH=CH_2$), 3.99 (ddd, *J* = 5.4 Hz, 1.6 Hz, 1.6 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 4.45 (d, *J* = 11.2 Hz, 1H, $ArCH_2O$), 4.49 (d, *J* = 11.2 Hz, 1H, $ArCH_2O$), 4.99 (ddd, *J* = 10.2 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH(CH_3)CH=C\underline{H}_2$), 5.03 (ddd, *J* = 17.3 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH(CH_3)CH=C\underline{H}_2$), 5.19 (ddt, *J* = 10.2 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.29 (ddt, *J* = 17.2 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.94 (ddt, *J* =17.2 Hz, 10.2 Hz, 5.4 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.21(ddd, *J* =17.3 Hz, 10.2 Hz, 5.8 Hz, 1H, $ArCH(CH_3)C\underline{H}=CH_2$), 6.75 (d, *J* = 8.4 Hz, 1H, ArH), 7.02 (d, *J* = 8.4 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.21, 36.75, 55.58, 60.57, 70.63, 70.84, 109.82, 112.67, 116.93, 125.58, 128.68, 134.87, 138.63, 143.23, 147.90, 153.00; EI-MS (70 eV) *m/z* 262 (M^+, 11), 204 (69), 189 (100), 174 (44), 129 (12); HRMS (EI, *m/z*) calcd for $C_{16}H_{22}O_3$: 262.1569. Found: 262.1568; Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.60; H, 8.15.

1-Allyloxymethyl-3-ethoxy-4-methoxy-2-(1-methylallyl)benzene (9e)

Pure **9e** (1.96 g, 71%) was obtained as pale yellow liquid, R_f 0.69 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.42 (d, *J* = 7.2 Hz, 3H, $ArCH(C\underline{H}_3)CH=CH_2$), 3.82 (s, 3H, OCH_3), 3.98 (ddd, *J* = 5.8 Hz, 1.6 Hz, 1.6 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 4.01 (m, 1H, $ArC\underline{H}(CH_3)CH=CH_2$), 4.03 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.47 (s, 2H, $ArCH_2O$), 4.99 (ddd, *J* = 10.4 Hz, 2.0 Hz, 2.0 Hz, 1H, $ArCH(CH_3)CH=C\underline{H}_2$), 5.03 (ddd, *J* = 17.5 Hz, 2.0 Hz, 2.0 Hz, 1H, $ArCH(CH_3)CH=C\underline{H}_2$), 5.18 (ddt, *J* = 10.4 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.29 (ddt, *J* = 17.2 Hz, 1.6 Hz, 1.6 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.94 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.8 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.22 (ddd, *J* =17.5 Hz, 10.4 Hz, 5.6 Hz, 1H, $ArCH(CH_3)C\underline{H}=CH_2$), 6.74 (d, *J* =8.4 Hz, 1H, ArH), 7.03 (d, *J* = 8.4 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.43, 19.01, 36.32, 55.52, 68.15, 70.49, 70.81, 109.73, 112.53, 116.84, 125.43, 128.81, 134.85, 138.54, 143.14, 146.76, 152.97; EI-MS (70 eV) *m/z* 276 (M^+, 19), 218 (100), 203 (36), 189 (78), 175 (84), 157 (44), 143 (46), 129 (23), 115 (12), 91 (11); HRMS (EI, *m/z*) calcd for $C_{17}H_{24}O_3$: 276.1725. Found: 276.1723; Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.14; H, 8.43.

1-Allyloxymethyl-3-benzyloxy-4-methoxy-2-(1-methylallyl)benzene (**9f**)

Pure **9f** (2.84 g, 84%) was obtained as pale yellow liquid, R_f 0.65 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 7.2 Hz, 3H, ArCH(C<u>H</u>$_3$)CH=CH$_2$), 3.85 (3H, s, OCH$_3$), 3.99 (ddd, *J* = 5.8 Hz, 1.5 Hz, 1.5 Hz, 2H, OC<u>H</u>$_2$CH=CH$_2$), 4.03 (m, 1H, ArC<u>H</u>(CH$_3$)CH=CH$_2$), 4.48 (s, 2H, ArCH$_2$O), 4.97 (ddd, *J* = 10.2 Hz, 1.6 Hz, 1.6 Hz, 1H, ArCH(CH$_3$)CH=C<u>H</u>$_2$), 4.99 (d, *J* = 11.0 Hz, 1H, OC<u>H</u>$_2$C$_6$H$_5$), 5.01 (ddd, *J* = 17.0 Hz, 1.6 Hz, 1.6 Hz, 1H, ArCH(CH$_3$)CH=C<u>H</u>$_2$), 5.03 (d, *J* = 11.0 Hz, 1H, OC<u>H</u>$_2$C$_6$H$_5$), 5.18 (ddt, *J* = 10.4 Hz, 1.5 Hz, 1.5 Hz, 1H, OCH$_2$CH=C<u>H</u>$_2$), 5.29 (ddt, *J* = 17.2 Hz, 1.5 Hz, 1.5 Hz, 1H, OCH$_2$CH=C<u>H</u>$_2$), 5.94 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.8 Hz, 1H, OCH$_2$C<u>H</u>=CH$_2$), 6.17 (ddd, *J* = 17.0 Hz, 10.2 Hz, 5.3 Hz, 1H, ArCH(CH$_3$)C<u>H</u>=CH$_2$), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 7.08 (d, *J* = 8.4 Hz, 1H, ArH), 7.31 (d, *J* = 7.2 Hz, 1H, OCH$_2$C$_6$<u>H</u>$_5$), 7.37 (d, *J* = 7.2 Hz, 2H, OCH$_2$C$_6$<u>H</u>$_5$), 7.48 (d, *J* = 7.2 Hz, 2H, OCH$_2$C$_6$<u>H</u>$_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.09, 36.32, 55.61, 70.46, 70.87, 74.04, 109.88, 112.85, 116.93, 125.81, 127.56, 127.75, 128.27, 128.95, 134.85, 138.12, 138.81, 143.09, 146.41, 152.88 EI-MS (70 eV) *m/z* 338 (M^+, 4), 189 (37), 175 (11), 157 (12), 131 (11), 91 (100), 65 (85); HRMS (EI, *m/z*) calcd for $C_{22}H_{26}O_3$: 338.1882. Found: 338.1884; Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.23; H, 7.49.

1-Allyloxymethyl-2-(2-butenyl)-4,5-dimethoxybenzene (10a)

Pure **10a** (1.94 g, 74 %) was obtained as pale yellow liquid, R_f = 0.53 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.66 (dd, *J* = 6.0 Hz, 1.3 Hz, 3H, ArCH$_2$CH=CHC<u>H</u>$_3$), 3.30 (dd, *J* = 6.0 Hz, 1.3 Hz, 2H, ArC<u>H</u>$_2$CH=CHCH$_3$), 3.85 (3H, s, OCH$_3$), 3.86 (3H, s, OCH$_3$), 4.02 (ddd, *J* = 5.6 Hz, 1.4 Hz, 1.4 Hz, 2H, OC<u>H</u>$_2$CH=CH$_2$), 4.46 (s, 2H, ArCH$_2$O), 5.20 (ddt, *J* = 10.3 Hz, 1.4 Hz, 1.4 Hz, 1H, OCH$_2$CH=C<u>H</u>$_2$), 5.30 (ddt, *J* = 17.3 Hz, 1.7 Hz, 1.7 Hz, 1H, OCH$_2$CH=C<u>H</u>$_2$), 5.43 (dqt, *J* = 15.2 Hz, 6.0 Hz, 1.3 Hz, 1H, ArCH$_2$CH=C<u>H</u>CH$_3$), 5.56 (dtq, *J* = 15.2 Hz, 6.0 Hz, 1.3 Hz, 1H, ArCH$_2$C<u>H</u>=CHCH$_3$), 5.96 (ddt, *J* = 17.3 Hz, 10.3 Hz, 5.6 Hz, 1H, OCH$_2$C<u>H</u>=CH$_2$), 6.69 (s, 1H, ArH), 6.90 (s, 1H, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 17.72, 35.16, 55.81, 69.51, 71.03, 112.43, 112.84, 116.89, 125.83, 127.95, 129.77, 131.60, 134.79, 146.97, 148.31 EI-MS (70 eV) *m/z* 262 (M^+, 14), 204 (59), 189 (100), 174 (21); HRMS (EI, *m/z*) calcd for $C_{16}H_{22}O_3$: 262.1569. Found: 262.1570; Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.52; H, 8.15.

1-Allyloxymethyl-2-(2-butenyl)-5-ethoxy-4-methoxybenzene (10b)

Pure **10b** (2.68 g, 97%) was obtained as pale yellow liquid R_f 0.60 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.44 (t, *J* = 7.2 Hz, 3H, OCH$_2$C<u>H</u>$_3$), 1.66 (ddt, *J* = 6.2 Hz, 1.4 Hz, 1.4 Hz, 3H, ArCH$_2$CH=CHC<u>H</u>$_3$), 3.30 (ddq, *J* = 6.4 Hz, 1.4 Hz, 1.4 Hz, 2H, ArC<u>H</u>$_2$CH=CHCH$_3$), 3.85 (s, 3H, OCH$_3$), 4.01 (ddd, *J* = 5.8 Hz, 1.5 Hz, 1.5 Hz, 2H, OC<u>H</u>$_2$CH=CH$_2$), 4.09 (q, *J* = 7.2 Hz, 2H, OC<u>H</u>$_2$CH$_3$), 4.45 (s, 2H, ArCH$_2$O), 5.20 (ddt, *J* = 10.2 Hz, 1.5 Hz, 1.5 Hz, 1H, OCH$_2$CH=C<u>H</u>$_2$), 5.30 (ddt, *J* = 17.4 Hz, 1.5 Hz, 1.5 Hz, 1H, OCH$_2$CH=C<u>H</u>$_2$), 5.43 (dqt, *J* = 15.2 Hz, 6.2 Hz, 1.4 Hz, 1H, ArCH$_2$CH=C<u>H</u>CH$_3$), 5.55 (dtq, *J* = 15.2 Hz, 6.4 Hz, 1.4 Hz, 1H, ArCH$_2$C<u>H</u>=CHCH$_3$), 5.96 (ddt, *J* = 17.4 Hz, 10.2 Hz, 5.8 Hz, 1H, OCH$_2$C<u>H</u>=CH$_2$), 6.69 (s, 1H, Ar<u>H</u>), 6.90 (s, 1H, Ar<u>H</u>); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.81, 17.78, 35.22, 55.93, 64.35, 69.58, 71.02, 113.14, 114.10, 116.93, 125.87, 127.95, 129.85, 131.73, 134.87, 146.28,

148.71 EI-MS (70 eV) *m/z* 276 (M^+, 22), 218 (58), 203 (41), 175 (100), 165 (14), 147 (11), 131 (21), 115 (20), 91 (21), 77 (14), 55 (12) HRMS (EI, *m/z*) calcd for $C_{17}H_{24}O_3$: 276.1725. Found: 276.1728; Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.04; H, 8.57.

1-Allyloxymethyl-5-benzyloxy-2-(2-butenyl)-4-methoxybenzene (10c)

Pure **10c** (3.17 g, 94%) was obtained as pale yellow liquid, R_f 0.61 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.66 (dd, *J* = 6.2 Hz, 1.3 Hz, 3H, $ArCH_2CH=CHC\underline{H}_3$), 3.29 (dd, *J* = 6.2 Hz, 1.4 Hz, 2H, $ArC\underline{H}_2CH=CHCH_3$), 3.87 (3H, s, OCH_3), 3.93 (ddd, *J* = 5.8 Hz, 1.5 Hz, 1.5 Hz, 2H, $OC\underline{H}_2CH=CH_2$), 4.41 (s, 2H, $ArCH_2O$), 5.13 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.17 (ddt, *J* = 10.4 Hz, 1.5 Hz, 1.5 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.24 (ddt, *J* = 17.2 Hz, 1.5 Hz, 1.5 Hz, 1H, $OCH_2CH=C\underline{H}_2$), 5.43 (dqt, *J* = 15.2 Hz, 6.2 Hz, 1.3 Hz, 1H, $ArCH_2CH=C\underline{H}CH_3$), 5.54 (dtq, *J* = 15.2 Hz, 6.2 Hz, 1.4 Hz, 1H, $ArCH_2C\underline{H}=CHCH_3$), 5.90 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.8 Hz, 1H, $OCH_2C\underline{H}=CH_2$), 6.71 (s, 1H, ArH), 6.92 (s, 1H, ArH), 7.29 (d, *J* = 7.2 Hz, 1H, $OCH_2C_6\underline{H}_5$), 7.35 (t, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$), 7.44 (d, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.84, 35.28, 56.08, 69.49, 70.90, 71.19, 113.54, 115.45, 116.93, 126.01, 127.36, 127.69, 128.01, 128.44, 129.79, 132.46, 134.84, 137.36, 146.20, 149.13; EI-MS (70 eV) *m/z* 338 (M^+, 9), 189 (74), 161 (27), 146 (14), 131 (18), 91 (100), 65 (12), 55 (42); HRMS (EI, *m/z*) calcd for $C_{22}H_{26}O_3$: 338.1882. Found: 338.1883; Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.43; H, 7.49.

General procedure for the preparation of substituted 3,6-dihydro-1*H*-benzo[*c*]oxocines (11a-f, 12a-c)

Compound (**9a-f, 10a-c**) (1 mmol) dissolved in anhydrous CH_2Cl_2 (15 mL), was added to Grubbs catalyst (0.04 g, 0.05 mmol). The mixture was stirred for 12 h at ambient temperature under dry argon. Finally the solvent was removed under reduced pressure, and the residue was subjected to a silica gel chromatographic column (*n*-hexane/MTBE =1:1) to give **11a-f, 12a-c** in yields of 31-43%.

7, 8-Dimethoxy-3,6-dihydro-1*H*-benzo[c]oxocine (11a)

Pure **11a** (0.08 g, 36%) was obtained as colorless liquid; R_f 0.53 (ethyl acetate/*n*-hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.72 (d, *J* = 7.4 Hz, 2H, $ArC\underline{H}_2CH=CH$), 3.80 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.20 (d, *J* = 4.8 Hz, 2H, $OC\underline{H}_2CH=CH$), 4.81 (s, 2H, $ArCH_2O$), 5.63 (dtt, *J* = 10.8 Hz, 4.8 Hz, 1.2 Hz, 1H, $OCH_2C\underline{H}=CH$), 5.97, (dtt, *J* = 10.8 Hz, 7.4 Hz, 1.2 Hz, 1H, $ArCH_2C\underline{H}=CH$), 6.72 (d, *J* = 8.2 Hz, 1H, $Ar\underline{H}$), 6.85 (d, *J* = 8.2 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.90, 55.55, 60.84, 67.05, 72.95, 109.32, 124.08, 128.59, 130.20, 131.24, 133.09, 146.34, 152.50; EI-MS (70 eV) *m/z* 220 (M^+, 57), 189 (52), 174 (34), 159 (36), 151 (100), 131 (18), 115 (49), 91 (30), 77 (22); HRMS (EI, *m/z*) calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1098; Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.20; H, 7.19.

7-Ethoxy-8-methoxy-3,6-dihydro-*1H*-benzo[c]oxocine (11b)

Pure **11b** (0.08 g, 34%) was obtained as colorless liquid; R_f 0.53 (ethyl acetate/*n*-hexane = 1/3), ^{1}H-NMR

(400 MHz, $CDCl_3$) δ 1.40 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 3.73 (d, *J* = 7.6 Hz, 2H, $ArC\underline{H}_2CH{=}CH$), 3.83 (s, 3H, OCH_3), 3.98 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.19 (dd, *J* = 4.8 Hz, 1.0 Hz, 2H, $OC\underline{H}_2CH{=}CH$), 4.81 (s, 2H, $ArCH_2O$), 5.62 (dtt, *J* = 10.8 Hz, 4.8 Hz, 1.0 Hz, 1H, $ArCH_2CH{=}C\underline{H}$), 5.95 (dtt, *J* = 10.8 Hz, 7.6 Hz, 1.0 Hz, 1H, $ArCH_2C\underline{H}{=}CH$), 6.71 (d, *J* = 7.6 Hz, 1H, $Ar\underline{H}$), 6.83 (d, *J* = 7.6 Hz, 1H, ArH), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.61, 25.25, 55.64, 66.90, 68.99, 72.86, 109.41, 123.96, 128.47, 130.16, 131.45, 133.32, 145.61, 152.68; EI-MS (70eV) *m/z* 234 (M^+, 44), 203 (12), 175 (22), 165 (88), 143 (84), 137 (38), 115 (100), 91 (33), 77 (30), 65 (11); HRMS (EI, *m/z*) calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1257; Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.04; H, 7.58.

7-Benzyloxy-8-methoxy-3,6-dihydro-1*H*-benzo[c]oxocine (11c)

Pure **11c** (0.1 g, 34 %) was obtained as colorless crystal, mp 47-48 ^oC; R_f 0.48 (ethyl acetate/*n*-hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.69 (d, *J* = 7.4 Hz, 2H, $ArC\underline{H}_2CH{=}CH$), 3.86 (s, 3H, OCH_3), 4.16 (dd, *J* = 4.8 Hz, 1.2 Hz, 2H, $OC\underline{H}_2CH{=}CH$), 4.80 (s, 2H, $ArCH_2O$), 4.96 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.58 (dtt, *J* = 10.8 Hz, 4.8 Hz, 1.2 Hz, 1H, $ArCH_2CH{=}C\underline{H}$), 5.82 (dtt, *J* = 10.8 Hz, 7.4 Hz, 1.2 Hz, 1H, $ArCH_2C\underline{H}{=}CH$), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 6.87 (d, *J* = 8.0 Hz, 1H, ArH), 7.33 (d, *J* =7.2 Hz, 1H, $OCH_2C_6\underline{H}_5$), 7.38 (t, *J* =7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$), 7.48 (d, *J* = 7.2 Hz, 2H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.29, 55.71, 66.87, 72.78, 75.03, 109.55, 124.29, 127.86, 128.10, 128.36, 130.26, 131.38, 133.41, 137.77, 145.28, 152.65; EI-MS (70 eV) *m/z* 296 (M^+, 4), 143 (10), 115 (13), 91 (100); HRMS (EI, *m/z*) calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1410; Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.85; H, 6.91.

7,8-Dimethoxy-6-methyl-3,6-dihydro-1*H*-benzo[*c*]oxocine (11d)

Pure **11d** (0.08 g, 35%) was obtained as colorless liquid, R_f 0.50 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.34 (d, *J* = 7.6 Hz, 3H, $ArCH(C\underline{H}_3)CH{=}CH$), 3.64 (dd, *J* = 12.6 Hz, 7.4 Hz, 1H, $OC\underline{H}_2CH{=}CH$), 3.81 (s, 3H, OCH_3), 3.84 (dd, *J* = 12.6 Hz, 7.4 Hz, 1H, $OC\underline{H}_2CH{=}CH$), 3.87 (s, 3H, OCH_3), 4.31 (m, 1H, $ArC\underline{H}(CH_3)CH{=}CH$), 4.45 (d, *J* = 11.6 Hz, 1H, $ArCH_2O$), 4.91 (d, *J* = 11.6 Hz, 1H, $ArCH_2O$), 5.46 (m, 1H, $ArCH(CH_3)CH{=}C\underline{H}$), 6.05 (ddd, *J* = 10.2 Hz, 4.0 Hz, 1.4 Hz, 1H, $ArCH(CH_3)C\underline{H}{=}CH$), 6.83 (d, *J* = 8.2 Hz, 1H, ArH), 7.00 (d, *J* = 8.2 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.97, 33.17, 55.55, 58.14, 60.87, 65.23, 110.43, 118.63, 126.63, 128.04, 139.30, 142.52, 145.40, 152.68; EI-MS (70 eV) *m/z* 234 (M^+, 11), 203 (100), 188 (74), 172 (30), 159 (17), 151 (71), 129 (14), 115 (18), 91 (13), 77 (9); HRMS (EI, *m/z*) calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1254; Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.94; H, 7.59.

7-Ethoxy-8-methoxy-6-methyl-3,6-dihydro-1*H*-benzo[*c*]oxocine (11e)

Pure **11e** (0.08 g, 34%) was obtained as colorless liquid, R_f 0.52 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.32 (d, *J* = 7.6 Hz, 3H, $ArCH(C\underline{H}_3)CH{=}CH$), 1.38 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 3.63 (dd, *J* = 12.3 Hz, 7.9 Hz, 1H, $OC\underline{H}_2CH{=}CH$), 3.84 (dd, *J* = 12.3 Hz, 7.9 Hz, 1H, $OC\underline{H}_2CH{=}CH$), 3.85 (s, 3H, OCH_3), 4.00 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.34 (m, 1H, $ArC\underline{H}(CH_3)CH{=}CH$), 4.44 (d, *J* = 11.6 Hz, 1H, $ArCH_2O$), 4.92 (d, *J* = 11.6 Hz, 1H, $ArCH_2O$), 5.46 (m, 1H, $ArCH(CH_3)CH{=}C\underline{H}$), 6.06 (1H,

ddd, *J* = 11.7 Hz, 3.8 Hz, 1.3 Hz, ArCH(CH_3)C<u>H</u>=CH), 6.82 (d, *J* = 8.0 Hz, 1H, ArH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.57, 24.97, 33.38, 55.56, 57.94, 65.14, 68.99, 110.40, 118.48, 126.48, 127.92, 139.60, 142.70, 144.40, 152.79; EI-MS (70 eV) *m/z* 248 (M^+, 25), 217 (37), 207 (11), 175 (16), 165 (100), 157 (53), 143 (23), 137 (27), 115 (24), 91 (11); HRMS (EI, *m/z*) calcd for $C_{15}H_{20}O_3$: 248.1412. Found: 248.1415; Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.78; H, 7.83.

7-Benzyloxy-8-methoxy-6-methyl-3,6-dihydro-1*H*-benzo[*c*]oxocine (**11f**)

Pure **11f** (0.10 g, 32%) was obtained as colorless liquid, R_f 0.49 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.26 (d, *J* = 7.6 Hz, 3H, ArCH(C<u>H</u>$_3$)CH=CH), 3.56 (dd, *J* = 12.4 Hz, 8.4 Hz, 1H, OC<u>H</u>$_2$CH=CH), 3.69 (dd, *J* = 12.4 Hz, 8.4 Hz, 1H, OC<u>H</u>$_2$CH=CH), 3.90 (s, 3H, OCH_3), 4.27 (m, 1H, ArC<u>H</u>(CH_3)CH=CH), 4.41 (d, *J* = 11.6 Hz, 1H, $ArCH_2O$), 4.89 (d, *J* = 11.6 Hz, 1H, $ArCH_2O$), 5.00 (s, 2H, OC<u>H</u>$_2$C$_6$H$_5$), 5.38 (m, 1H, ArCH(CH_3)CH=C<u>H</u>), 5.94 (1H, ddd, *J* = 11.7 Hz, 4.0 Hz, 1.3 Hz, ArCH(CH_3)C<u>H</u>=CH), 6.85 (d, *J* = 8.2 Hz, 1H, ArH), 7.00 (d, *J* = 8.2 Hz, 1H, ArH), 7.30 (d, *J* = 7.2 Hz, 1H, OCH_2C_6<u>H</u>$_5$), 7.34 (d, *J* = 7.2 Hz, 2H, OCH_2C_6<u>H</u>$_5$), 7.42 (d, *J* = 7.2 Hz, 2H, OCH_2C_6<u>H</u>$_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.97, 33.50, 55.65, 57.88, 65.03, 110.53, 118.33, 126.60, 127.98, 128.25, 128.40, 137.43, 139.84, 142.61, 143.82, 152.80; EI-MS (70 eV) *m/z* 310 (M^+, 4), 219 (19), 191 (10), 157 (18), 131 (15), 91 (100); HRMS (EI, *m/z*) calcd for $C_{20}H_{22}O_3$: 310.1569. Found: 310.1570; Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.61; H, 6.79.

8,9-Dimethoxy-3,6-dihydro-1*H*-benzo[*c*]oxocine (12a)

Pure **12a** (0.09 g, 41%) was obtained as colorless liquid, R_f 0.37 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.58 (d, *J* = 7.2 Hz, 2H, ArC<u>H</u>$_2$CH=CH), 3.85 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 4.19 (d, *J* = 4.8 Hz, 2H, OC<u>H</u>$_2$CH=CH), 4.80 (s, 2H, $ArCH_2O$), 5.62 (dt, *J* = 10.8 Hz, 4.8 Hz, 1H, $ArCH_2CH$=C<u>H</u>), 5.94 (dt, *J* = 10.8 Hz, 7.2 Hz, 1H, $ArCH_2$C<u>H</u>=CH), 6.63 (s, 1H, ArH), 6.64 (s, 1H, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 33.85, 55.88, 55.91, 67.15, 72.40, 111.73, 113.35, 127.60, 128.69, 130.93, 131.27, 147.03, 148.13; EI-MS (70 eV) *m/z* 220 (M^+, 100), 189 (76), 179 (14), 159 (12), 151 (94), 115 (15), 91 (14), 77 (13); HRMS (EI, *m/z*) calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1096; Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.26; H, 7.19;

9-Ethoxy-8-methoxy-3,6-dihydro-1*H*-benzo[*c*]oxocine (12b)

Pure **12b** (0.10 g, 43%) was obtained as colorless liquid, R_f 0.46 (Ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.44 (t, *J* = 7.0 Hz, 3H, OCH_2C<u>H</u>$_3$), 3.57 (d, *J* = 7.2 Hz, 2H, ArC<u>H</u>$_2$CH=CH), 3.86 (s, 3H, OCH_3), 4.06 (q, *J* = 7.0 Hz, 2H, OC<u>H</u>$_2$CH$_3$), 4.19 (d, *J* = 4.8 Hz, 2H, OC<u>H</u>$_2$CH=CH), 4.78 (s, 2H, $ArCH_2O$), 5.62 (dt, *J* = 10.8 Hz, 4.8 Hz, 1H, $ArCH_2CH$=C<u>H</u>), 5.94 (1H, dtt, *J* = 10.8 Hz, 7.2 Hz, $ArCH_2$C<u>H</u>=CH), 6.63 (s, 1H, ArH), 6.64 (s, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.81, 33.88, 55.93, 64.39, 67.12, 72.39, 113.31, 113.63, 127.62, 128.69, 130.92, 131.24, 146.34, 148.46; EI-MS (70 eV) *m/z* 234 (M^+, 98), 220 (24), 205 (55), 190 (40), 175 (85), 165 (100), 147 (37), 131 (31), 115 (33), 103 (29), 91 (49), 77 (35), 65 (20), 55 (14); HRMS (EI, *m/z*) calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1257; Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.54; H, 7.49.

9-Benzyloxy-8-methoxy-3,6-dihydro-1*H*-benzo[*c*]oxocine (12c)

Pure **12c** (0.11 g, 37%) was obtained as colorless liquid, R_f 0.51 (ethyl acetate / hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.56 (d, *J* = 7.2 Hz, 2H, ArC<u>H</u>$_2$CH=CH), 3.87 (s, 3H, OCH_3), 4.17 (d, *J* = 4.8 Hz, 2H, OC<u>H</u>$_2$CH=CH), 4.73 (s, 2H, $ArCH_2O$), 5.09 (s, 2H, OC<u>H</u>$_2$C$_6$CH$_5$), 5.61 (dt, *J* = 10.8 Hz, 4.8 Hz, 1H, $ArCH_2$CH=C<u>H</u>), 5.92 (dt, *J* = 10.8 Hz, 7.2 Hz, 1H, $ArCH_2$C<u>H</u>=CH), 6.66 (s, 2H, ArH), 7.29 (d, *J* = 7.2 Hz, 1H, OCH_2C_6<u>H</u>$_5$), 7.35 (t, *J* = 7.2 Hz, 2H, OCH_2C_6<u>H</u>$_5$), 7.42 (d, *J* = 7.2 Hz, 2H, OCH_2C_6<u>H</u>$_5$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 33.85, 56.03, 67.27, 71.27, 72.36, 114.02, 114.66, 127.28, 127.74, 128.44, 128.80, 130.98, 131.61, 137.17, 146.26, 148.90; EI-MS (70 eV) *m/z* 296 (M^+, 50), 205 (12), 175 (13), 91 (100); HRMS (EI, *m/z*) calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1414; Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.34; H, 6.59.

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