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Syntheses of Substituted Naphthalenes and Naphthols

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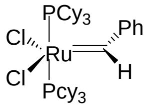
Syntheses of substituted naphthalenes and naphthols are described. Based on Claisen rearrangement, ring-closing metathesis (RCM), and related reactions, isovanillin was successfully transformed into a series of substituted naphthalenes and naphthols with good overall yields.

Keywords: Naphthalenes; Naphthols; RCM.

INTRODUCTION

Naphthalenes found in naturally occurring or synthetic compounds often have various biological activities. For example, michellamines A-C have anti-HIV activities,[1] korupensamines A-D have antimalarial activities,[2,3] and (*S*)-gossypol has antifertility, anti-HIV, and anti-cancer activities.[4] Furthermore, 1-naphthol, used as a starting material for the construction of propranolol,[5] has been widely used in clinics as beta blocker until today. Apart from their interesting biological activities, biaryl naphthalene or naphthol compounds have also found application as chiral reagents.[6] (1,1′-Binaphthyl)-2,2′-diol and its derivatives, for example, are widely used in asymmetric synthesis, either as ligands or as chiral auxiliaries.[7] However, only a few naphthalenes and naphthols with functional substituents have been described.[8-10] Major synthetic strategies include the following: (i) Diels-Alder reaction of *o*-quinodimethanes with dienophiles,[10a] (ii) cyclization of 2-allylacetophenone with potassium *tert*-butoxide,[8f] (iii) anionic cyclization of 2-(1-propenyl)benzamides with base,[8f] and (iv) intramolecular cyclizations of 4-phenylbutyric acid with Lewis acid-catalysed.[10b] However, these methods have certain drawbacks, such as low yields, slow reaction times, and commercial unavailability of starting materials. Thus, the development of an efficient method of constructing naphthalenes with functional substituents is necessary. In 1995, Grubbs, et al.[11] discovered a novel ruthenium- benzylidine carbene complex (Grubbs cat.) catalyzed ring closing olefin metathesis (RCM), which has received a wide and rapid application in organic synthesis.[12,13] Recently we preliminarily reported a novel method of synthesizing substituted naphthalenes[14] based on this RCM chemistry. The results and full experimental details, in addition to a concise synthesis of substituted naphthols, are disclosed herein. The synthetic strategy is based on the following protocol: (i) various allylisovanillins (**2a-d**) undergo [3,3] sigmatropic (Claisen) rearrangement to give 2-allyl-3-hydroxy-4-methoxybenzaldehydes (**3a-b**), and 2-allyl-5-hydroxy- 4-methoxy-benzaldehydes (**4b-d**), respectively (Scheme I), followed by *O*-alkylation with various alkyl halides to furnish *ortho* and (or) *para*-derivatives as key intermediates (**5a-f**, **6a-c**); (ii) subsequently, the key intermediates are allowed to react with vinyl magnesium bromide to give corresponding alcohols (**7a-f**, **8a-c**), respectively; (iii) the resulting alcohols are subjected to RCM reaction to undergo cyclization together with dehydration spontaneously *in situ* to produce various substituted naphthalenes (**9a-f**, **10a-c**), respectively (Scheme II); (iv) the resulting alcohols (**7a-f**, **8a-c**) obtained from ii were oxidized with pyridinium chlorochromate (PCC) or Dess-Martin periodinane (dMP) to afford the corresponding ketones (**11a-f**, **12a-c**), respectively; (v) finally, these ketone derivatives were treated with Grubbs catalyst to undergo RCM and furnish benzocyclohexenones (**13a-f**, **14a-c**), which were then tautomerized *in situ* to give a series of substituted naphthols (**15a-f**, **16a-c**), respectively (Scheme III). Thus, a practical,

Grubbs' cat.=



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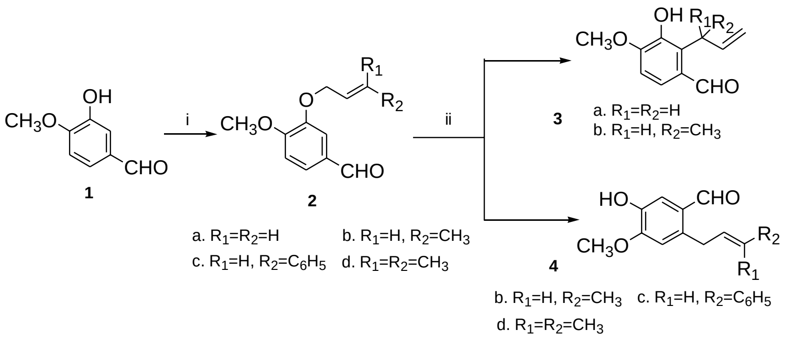
versatile, and straightforward method for synthesizing these title compounds was established based on the Claisen rearrangement, RCM, and related reactions from isovanillin.

RESULTS AND DISCUSSION

As a general procedure and in accordance with our previous report,[14] isovanillin (**1**) was alkylated with various allylic halides such as allyl bromide, 1-bromo-2-butene, *trans*-cinnamyl chloride, and 1-bromo-3-methyl-2-butene in anhydrous acetone in the presence of potassium carbonate to give various allylisovanillins (**2a-d**) in yields of 86-92%, respectively (Scheme I). The Claisen rearrangement of these various allylisovanillins (**2a-d**) was respectively carried out under three different conditions: (A) by heating in neat, (B) on the reflux in decalin, and (C) in *N,N*-diethylaniline to give the different ratio of *ortho* and *para* products. We found a simple allylisovanillin (**2a**) was heated in neat, in decalin or in *N,N*-diethylaniline to furnish an exclusively *ortho* product, 2-allyl-3-hydroxy-4-methoxybenzaldehyde (**3a**) in 92-95% yields, and no *para* product **4a** was observed. On the other hand, when **2b** was treated under the same conditions, reaction time was longer; 16 hrs was needed accomplish the reaction, and to give both *ortho* (**3b**) and *para* product (**4b**) in various ratios with **3b**/**4b**: 48/36, 71/10, and 67/20. The bulky allylisovanillin (**2c**) or (**2d**), when treated under the same conditions of Claisen rearrangement for **2a**, furnished almost always *para* product **4c** or **4d**. The results of our previous study, with extended entries, are summarized in Table 1.

The identification of *ortho* or *para* products for this Claisen rearrangement could be easily confirmed by examining the coupling constants of two aromatic protons in ^{1}H NMR spectra. In the case of double doublet split, it belonged

Scheme I



^{a} Conditions: (i) allyl bromide, or 1-bromo-2-butene, or *trans*-cinnamyl chloride, or 1-bromo-3-methyl-2-butene, K_2CO_3, Acetone, reflux 8h; (ii) A. heated in neat at gently boiling 170 °C; or B. heated in decalin under the 180 °C reflux; or C. heated in *N,N*-diethylanilline under the 217 °C reflux.

Table 1. Conditions and % Yields of **3a-b**, **4b-d** after the Claisen Rearrangement of **2a-d**

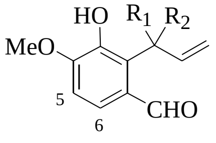
Compounds	Conditions (°C/solvent)	Reaction time (hr)	Products (% yields)	
2a	170-180/neat	3	**3a** (92)	**4a** (--)
	180/decalin	5	**3a** (95)	**4a** (--)
	217/diethylaniline	1	**3a** (95)	**4a** (--)
2b	170-180/neat	16	**3b** (48)	**4b** (36)
	180/decalin	16	**3b** (71)	**4b** (10)
	217/diethylaniline	16	**3b** (67)	**4b** (20)
2c	170-180/neat	--	**3c** (--)	**4c** (--)
	180/decalin	12	**3c** (--)	**4c** (65)
	217/diethylaniline	1	**3c** (--)	**4c** (76)
2d	170-180/neat	6	**3d** (--)	**4d** (79)
	180/decalin	6	**3d** (--)	**4d** (58)
	217/diethylaniline	6	**3d** (--)	**4d** (80)

to *ortho* product, but if singlet, it belonged to *para* product in the structure of **3** or **4**. For example, **4c** showed two singlet one-proton signals at 6.76 and 7.43 ppm, indicating the allyl group located at the *para* position to the hydroxyl group in the structure. A broad one-proton signal at 5.79 ppm presented in the ^{1}H NMR spectrum of **4c**, disappeared after addition of D_2O, indicating the existence of an OH group. To gather further evidence to support formation of **4c**, high-resolution mass spectroscopy showed the desired molecular formula $C_{17}H_{16}O_3$. The NOESY experiments of **4c** revealed the following correlations: (a) CHO ↔ H-1′, H-6, H-2′, H-3′; (b) H-3 ↔ OCH_3, H-2′, H-3′. The ^{13}C NMR spectra showed 15 lines (carbons) were found, which matched the structure of **4c**. The aromatic protons of compounds **3a-b** and **4b-d** in ^{1}H NMR spectra are compiled in Table 2.

Synthesis of naphthalenes[14]

Subsequently, the products of Claisen rearrangement, **3a**, **3b**, and **4b** were alkylated as a general procedure with various alkyl halides such as methyl iodide, ethyl iodide, and benzyl bromide in anhydrous acetone in the presence of potassium carbonate to give **5a-f** and **6a-c** in yields of 80-98% (Scheme II). The structures of **5a-f** and **6a-c** are supported by their ^{1}H and ^{13}C NMR spectra. The ^{1}H-NMR spectra exhibited a new methoxy signal at 3.85 ppm in **5a**, a new ethoxy signal at 1.36 ppm (t, J = 7.0 Hz, 3H), and at 3.96 ppm (q, J = 7.0 Hz, 2H) in **5b**, and two benzylic protons at 4.99 ppm (s, 2H), and one additional five-aromatic proton at 7.3-7.5 ppm

Table 2. ^{1}H NMR of Aromatic Protons Presented in **3a-b** and **4b-d**



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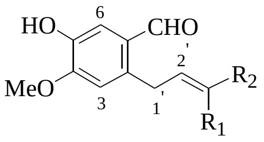

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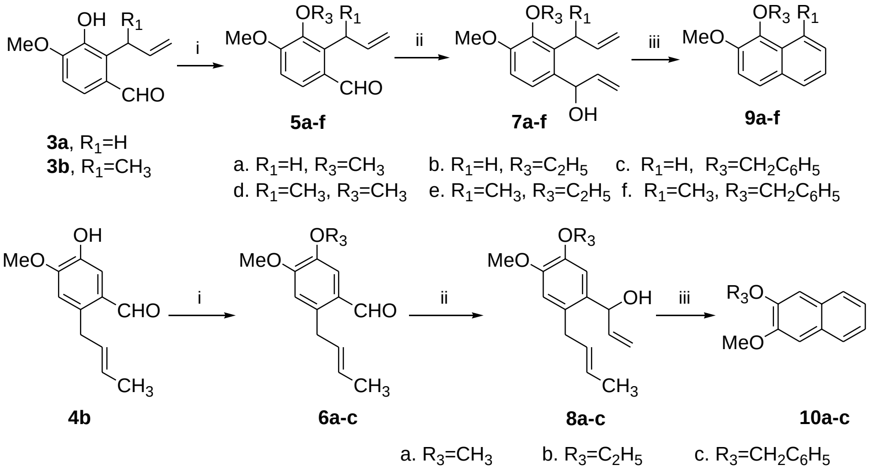
Enrty	R_1	R_2	Compound **3**		Compound **4**	
			H-5	H-6	H-3	H-6
3a	H	H	6.71 (d, J = 8.4 Hz)	7.27 (d, J = 8.4 Hz)		
3b	H	CH_3	6.86 (d, J = 8.5 Hz)	7.46 (d, J = 8.5 Hz)		
4b	H	CH_3			6.70 (s)	7.41 (s)
4c	H	C_6H_5			6.76 (s)	7.43 (s)
4d	CH_3	CH_3			6.71 (s)	7.40 (s)

Scheme II



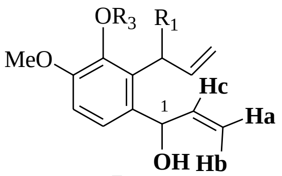
[a] Conditions: (i) methyl iodide, or ethyl iodide, or benzyl bromide, K_2CO_3, Acetone, reflux 8h; (ii) vinyl magnesium bromide, THF, 0 °C, 2h; (iii) 5 % Grubbs cat., 0.05 M CH_2Cl_2, rt.

in **5c**, in comparision with starting materials, **3a-b** and **4b**. This was followed by the addition of Grignard reagent (vinyl magnesium bromide) to compounds **5a-f** or **6a-c**, which gave the 1,2-addition product, 1-(2-allyl-3-alkoxy-4-methoxyphenyl)-2-propen-1-ols (**7a-c**), 1-[3-alkoxy-4-methoxy-2-(1-methylallyl)-phenyl]-2-propen-1-ols (**7d-f**), and 1-[5-alkoxy-2-(2-butenyl)-4-methoxyphenyl]-2-propen-1-ols (**8a-c**) in good yields, respectively.

Evidence of the formation of the propen-1-ols **7a-f** and **8a-c** was confirmed by examining the presence of a new formation of secondary alcohol group or the disappearance of formyl group in ^{1}H or ^{13}C-NMR spectra, in comparison with starting materials. For example, the ^{1}H-NMR spectrum of **8a**, showed the hydroxy signal at δ 2.31, and the disappearance of formyl proton at δ 10.19 in comparision with starting material **6a**, was observed. The ^{13}C-NMR spectrum also confirmed the assignment, as the characteristic signal for carbonyl (δ 189.6) carbon of **6a** had disappeared. In addition, high-resolution mass spectroscopy showed the expected molecular ion of **6a** at *m/z* 248.1412 ($C_{15}H_{20}O_3$ requires *M*, 248.1412). The addition of vinyl Grignard reagent to compounds **5d-f** afforded two diastereomers **7d-f** in a ratio of 3:2 which were determined by the integrated values of ^{13}C-NMR. Their structures are depicted in the experimental section together with some characteristic chemical shifts. Whereas the OH signal of one of the diastereomers appears at δ = 1.90, the corresponding OH signal of the other isomer is shifted to a higher field (δ = 1.81) in **7e**. Some characteristic protons and ^{13}C-NMR data of compounds **7a-f** and **8a-c** are summarized in Table 3.

Finally, by treating these dienes **7a-c** and **8a-c** with 5% mole of Grubbs catalyst in 0.05 M anhydrous CH_2Cl_2 to undergo RCM, followed by dehydration *in situ*, a series of disubstituted naphthalenes (**9a-c**, **10a-c**) were produced in good yields. If the diastereomeric mixture (**7d-f**) were treated with Grubbs catalyst to undergo RCM, the corresponding trisubstituted naphthalenes (**9d-f**) were produced. The structures of naphthalenes **9a-f** and **10a-c** were assigned by their ^{1}H, ^{13}C, and 2D-NMR. For example, the ^{1}H-NMR spectrum of **9a** showed signals from the two *ortho*-coupled protons H-3 and H-4 on the more electron-rich ring at δ 7.31 and 7.60 (*J* = 9.0 Hz), respectively. Signals from two other aromatic protons H-6 and H-7 appeared as triplets at δ 7.36 and 7.48 (*J* = 7.5 Hz), respectively. Signals from the remaining two aromatic protons H-5 and H-8 appeared as doublets at δ 7.81 and 8.13 (*J* = 8.5 Hz), respectively. Finally, the two methoxy groups generated signals in their characteristic regions of δ 4.03 and 4.10. In addition, COSY cross-peaks indicated sequences of (a) H-3 to H-4; and (b) H-6 to H-7, H-5 and H-8. ^{13}C-NMR spectra showed 12 carbons with the presence of two methoxy carbons, six sp^2 tertiary, and four sp^2 quaternary carbons. High-resolution mass spectroscopy showed the desired molecular ion at *m/z* 188.0839 ($C_{12}H_{12}O_2$ requires *M*, 188.0837). Further structural proof for the naphthalenes sub-

Table 3. Characteristic Spectroscopic Data of the Propen-1-ols (**7a-f**, **8a-c**)



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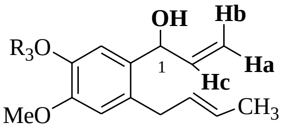

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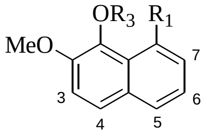
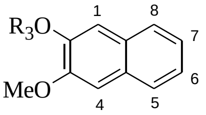
Substrate		^{1}H NMR (CDCl$_3$)			^{13}C	Formula	HRMS	
	OH (br s)	Ha	Hb	Hc	NMR C-1		*calcd*	*found*
7a	2.15	4.90	5.01	5.31	70.50	$C_{14}H_{18}O_3$	234.1256	234.1249
7b	2.11	4.91	5.01	5.31	70.58	$C_{15}H_{20}O_3$	248.1409	248.1409
7c	2.09	4.79	4.87	5.20	70.76	$C_{20}H_{22}O_3$	310.1569	310.1562
7d*	2.13	5.00	5.05	5.31	70.95	$C_{15}H_{20}O_3$	248.1412	248.1410
7e*	1.90	5.04	5.06	5.33	70.75	$C_{16}H_{22}O_3$	262.1569	262.1577
7f*	1.98	4.99	5.03	5.33	70.70	$C_{21}H_{24}O_3$	324.1725	324.1720
8a	2.31	5.31	5.18	6.01	70.67	$C_{15}H_{20}O_3$	248.1414	248.1412
8b	2.11	5.30	5.17	6.00	70.70	$C_{16}H_{22}O_3$	262.1569	262.1567
8c	1.84	5.27	5.14	5.94	70.67	$C_{21}H_{24}O_3$	324.1725	324.1726

*The selected data of the major diastereomer.

Table 4. The Selected ^{1}H NMR Spectra of Substituted Naphthalenes (**9a-f**, **10a-c**)



9a-f



10a-c

	H-1	H-3	H-4	H-5	H-6	H-7	H-8
9a	-	7.31(d)	7.60(d)	7.81(d)	7.36(t)	7.48(t)	8.13(d)
9b	-	7.03(d)	7.35(d)	7.57(d)	7.15(t)	7.28(t)	8.02(d)
9c	-	7.37(d)	7.68(d)	7.50(d)	7.42(t)	7.52(t)	8.24(d)
9d	-	7.29(d)	7.60(d)	7.23(d)	7.62(t)	7.22(d)	-
9e	-	7.21(d)	7.53(d)	7.18(d)	7.56(t)	7.16(d)	-
9f	-	7.31(d)	7.62(d)	7.21(d)	7.61(t)	7.20(d)	-
10a	7.13(s)	-	7.13(s)	7.70(d)	7.35(t)	7.35(t)	7.70(d)
10b	7.13(s)	-	7.13(s)	7.68(d)	7.33(t)	7.35(t)	7.68(d)
10c	7.14(s)	-	7.16(s)	7.62(d)	7.32(t)	7.33(t)	7.68(d)

structure came from the 2D-NMR spectroscopy. The NOESY experiments of **9a-f** and **10a-c** exhibited the following correlations: (a) the spectrum of **9a** showed $OC\underline{H}_3$-2 ↔ H-3, $OC\underline{H}_3$-1; H-4 ↔ H-3, H-5; and H-7 ↔ H-8, H-6; (b) the spectrum of **9e** showed $OC\underline{H}_3$-2 ↔ H-3, OEt-1; H-7 ↔ H-6, Me-8; and H-5 ↔ H-6, H-4; (c) the remaining spectrum of **10c** showed $OC\underline{H}_3$-2 ↔ H-1, $OCH_2C_6\underline{H}_5$-3; H-8 ↔ H-7, H-1; and H-5 ↔ H-6, H-4. The selected ^{1}H-NMR spectral data of compounds **9a-f** and **10a-c** are summarized in Table 4.

Furthermore, this transformation was of particular value because the naphthalenes (**9f**, **10c**) formed crystals suitable for X-ray analysis. The structure of **9f** was firmly established by a single-crystal X-ray structure identification as 1-benzyloxy-2-methoxy-8-methylnaphthalene, and the ORTEP view showed the trisubstituted naphthalene at C-1, C-2, and C-8 in Fig. 1. The disubstituted naphthalene **10c** was also confirmed by X-ray analysis as 2-benzyloxy-3-methoxy-naphthalene. The ORTEP diagram of **10c** is presented in Fig. 2. Selected bond distances and bond angles for **9f** and **10c** are given in the experimental section Table 5 and Table 6, respectively.

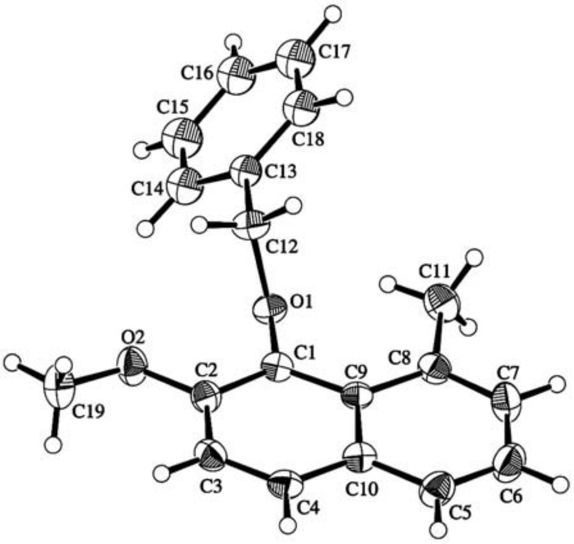


Fig. 1. X-ray crystal structure of naphthalene (**9f**).

Synthesis of naphthols

Oxidation of propen-1-ols **7a-f** and **8a-c** carried out by either PCC or dMP (dess Martin periodinane), gave compound **11a-f** or **12a-c** in 60-69% yields (Scheme III), together with other undesired byproducts in yields of 28-32%.

The chemical elucidation of vinyl ketone **11a-f** and **12a-c** could be confirmed by examining the new formation of

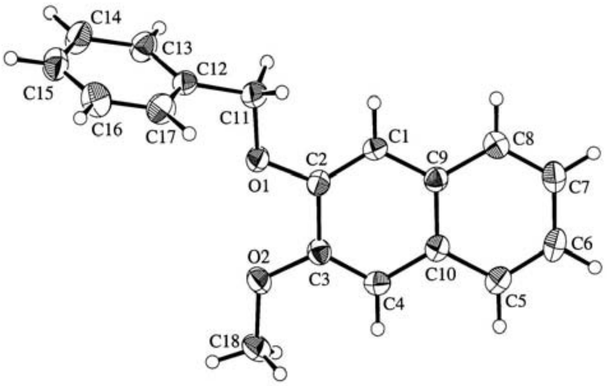


Fig. 2. X-ray crystal structure of naphthalene (**10c**).

Table 5. Selected Crystallographic Bond Distances (Å) for Compounds **9f** and **10c**

atom-atom	distance	atom-atom	distance	atom-atom	distance
		9f[a]			
O(1)-C(1)	1.385(5)	O(1)-C(12)	1.452(5)	O(2)-C(2)	1.376(5)
O(2)-C(19)	1.412(6)	C(1)-C(2)	1.379(6)	C(1)-C(9)	1.418(6)
C(2)-C(3)	1.403(6)	C(3)-C(4)	1.351(7)	C(4)-C(10)	1.403(7)
C(5)-C(6)	1.354(7)	C(5)-C(10)	1.419(6)	C(6)-C(7)	1.407(7)
C(7)-C(8)	1.361(7)	C(8)-C(9)	1.434(6)	C(8)-C(11)	1.516(6)
C(9)-C(10)	1.436(6)	C(12)-C(13)	1.475(6)	C(13)-C(14)	1.400(7)
C(13)-C(18)	1.379(7)	C(14)-C(15)	1.392(8)	C(15)-C(16)	1.359(8)
C(16)-C(17)	1.357(8)	C(17)-C(18)	1.407(8)		
		10c[a]			
O(1)-C(2)	1.368(2)	O(1)-C(11)	1.433(3)	O(2)-C(3)	1.364(2)
O(2)-C(18)	1.427(3)	C(1)-C(2)	1.359(3)	C(1)-C(9)	1.414(3)
C(2)-C(3)	1.429(3)	C(3)-C(4)	1.359(3)	C(4)-C(10)	1.415(3)
C(5)-C(6)	1.363(3)	C(5)-C(10)	1.411(3)	C(6)-C(7)	1.389(4)
C(7)-C(8)	1.365(3)	C(8)-C(9)	1.415(3)	C(9)-C(10)	1.407(3)
C(11)-C(12)	1.501(3)	C(12)-C(13)	1.371(3)	C(12)-C(17)	1.378(3)
C(13)-C(14)	1.383(3)	C(14)-C(15)	1.365(4)	C(15)-C(16)	1.361(4)
C(16)-C(17)	1.385(3)				

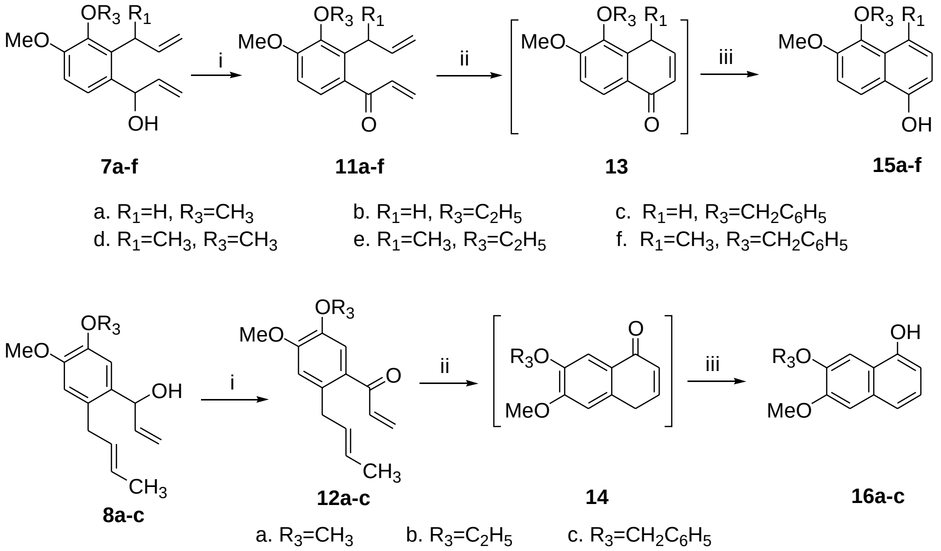
[a] All C-H bond distances are 0.95 Å.

Table 6. Selected Crystallographic Bond Angles (deg) for Compounds **9f** and **10c**

Atom	angle	atom	angle	atom	angle
		9f			
C(2)-O(1)-C(11)	116.9(2)	C(3)-O(2)-C(18)	116.9(2)	C(2)-C(1)-C(9)	121.0(2)
O(1)-C(2)-C(1)	126.0(2)	O(1)-C(2)-C(3)	113.9(2)	C(1)-C(2)-C(3)	120.1(2)
O(2)-C(3)-C(2)	114.4(2)	O(2)-C(3)-C(4)	126.1(2)	C(2)-C(3)-C(4)	119.6(2)
C(3)-C(4)-C(10)	121.1(2)	C(6)-C(5)-C(10)	120.6(2)	C(5)-C(6)-C(7)	120.7(2)
C(6)-C(7)-C(8)	120.1(2)	C(7)-C(8)-C(9)	121.1(2)	C(1)-C(9)-C(8)	122.7(2)
C(1)-C(9)-C(10)	119.0(2)	C(8)-C(9)-C(10)	118.3(2)	C(4)-C(10)-C(5)	121.7(2)
C(4)-C(10)-C(9)	119.1(2)	C(5)-C(10)-C(9)	119.2(2)	C(1)-C(11)-C(12)	107.7(2)
C(11)-C(12)-C(13)	120.7(2)	C(11)-C(12)-C(17)	120.8(2)	C(13)-C(12)-C(17)	118.5(2)
C(12)-C(13)-C(14)	120.6(2)	C(13)-C(14)-C(15)	120.2(2)	C(14)-C(15)-C(16)	119.9(2)
C(15)-C(16)-C(17)	120.0(2)	C(12)-C(17)-C(16)	120.7(2)		
		10c			
C(1)-O(1)-C(12)	114.2(3)	C(2)-O(2)-C(19)	116.9(4)	O(1)-C(1)-C(2)	118.5(4)
O(1)-C(1)-C(9)	119.8(4)	C(2)-C(1)-C(9)	121.7(4)	O(2)-C(2)-C(1)	116.4(4)
O(2)-C(2)-C(3)	123.2(4)	C(1)-C(2)-C(3)	120.4(4)	C(2)-C(3)-C(4)	119.3(4)
C(3)-C(4)-C(10)	122.3(4)	C(6)-C(5)-C(10)	120.3(5)	C(5)-C(6)-C(7)	119.1(5)
C(6)-C(7)-C(8)	123.8(5)	C(7)-C(8)-C(9)	118.5(4)	C(7)-C(8)-C(11)	117.4(4)
C(9)-C(8)-C(11)	124.2(4)	C(1)-C(9)-C(8)	125.4(4)	C(1)-C(9)-C(10)	116.7(4)
C(8)-C(9)-C(10)	117.9(4)	C(4)-C(10)-C(5)	120.1(4)	C(4)-C(10)-C(9)	119.5(2)
C(5)-C(10)-C(9)	120.4(4)	C(1)-C(12)-C(13)	108.1(4)	C(12)-C(13)-C(14)	120.1(4)
C(12)-C(13)-C(18)	122.2(4)	C(14)-C(13)-C(18)	117.7(2)	C(13)-C(14)-C(15)	120.7(5)
C(14)-C(15)-C(16)	120.5(6)	C(15)-C(16)-C(17)	120.1(6)	C(16)-C(17)-C(18)	120.4(5)
C(13)-C(18)-C(17)	120.6(5)				

a carbonyl group or the disappearance of a hydroxy group in ^{1}H or ^{13}C-NMR spectra in comparison with starting materials. For example, compounds **11a-f** and **12a-c** showed one new typical signal at δ 194.10-197.79 ($\underline{C}$=O) in ^{13}C-NMR indicating the effect of oxidation. The molecular formula of compounds **11a-f** and **12a-c** were demonstrated on the basis of HREIMS. Moreover, ^{13}C-NMR and DEPT spectra of **11d** showed 15 carbons and the presence of one methyl, two

Scheme III



[a] Conditions: (i) PCC or dMP, CH_2Cl_2, rt, 1h; (ii) 5 % Grubbs cat., 0.05 M CH_2Cl_2, rt. (iii) tautomerization

methoxy, four sp^2 olefinic, two sp^2 tertiary, one sp^3 tertiary, four sp^2 quaternary, and one carbonyl carbon. COSY cross-peaks indicated sequences of (a) $C\underline{H}_3$-1′ to H-1′; (b) H-3′ to H-2′; and (c) H-5 to H-6. Thus, the phenyl vinyl ketonen skeleton **11d** could be determined. The undesired product from the oxidation of **7a** was identified as 3-(2-allyl-3,4-dimethoxyphenyl)-1-propenal (**11a-un**), which was assigned by ^{1}H, ^{13}C-NMR, and EI-MS. The detailed studies of oxidation of **7a-f** or **8a-c** with other different oxidizing agents are currently in progress in our laboratory, with results forthcoming. Finally, using 5% mol Grubbs catalyst in 0.05 M anhydrous CH_2Cl_2 to undergo ring-closing olefin metathesis, followed by tautomerization *in situ*, gave naphthols (**15a-f**, **16a-c**) instead of benzocyclohexenones (**13**, **14**). The evidence of this transformation can be easily observed in either ^{1}H or ^{13}C-NMR spectra. For example, compound **15a** was found to have the molecular formula $C_{12}H_{12}O_3$ on the basis of high-resolution mass measurement. In addition, it showed two signals of the methoxy group at δ 3.98, and 3.99, and one broad hydroxyl signal at δ 5.65 (D_2O exchangeable), but no olefin proton in ^{1}H-NMR. COSY cross-peaks indicated sequences of (a) H-7 to H-8; and (b) H-3 to H-2 and H-4. ^{13}C-NMR spectra demonstrated 12 carbons and the presence of two methyls, five sp^2 methines, and five sp^2 quaternary carbons. Notably, no carbonyl carbon was observed in the ^{13}C-NMR spectrum. Apparently, compound **15a** was aromatized to lead a naphthol ring *in situ* during cylization. The selected ^{1}H-NMR spectral data of naphthols are summarized in Table 7. The results of percentage yield are summarized in Table 8. The results are of some interest because naphthalenes and naphthols may be useful precursors for the synthesis of potential medicinal agents.

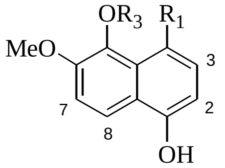
In conclusion, based on Claisen rearrangement, ring-closing olefin metathesis, and related reactions such as Grignard reagents, and PCC or dMP oxidation, we have established a straightforward, versatile, and novel method of transforming isovanillin into a number of substituted naphthalenes (**9a-f** and **10a-c**) and naphthols (**15a-f** and **16a-c**). The application of our synthetic strategy to various potential compounds is currently in progress in our laboratory.

EXPERIMENTAL

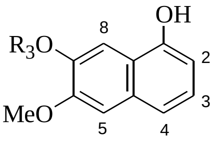
General remarks

Melting points (Yanaco micro melting-point apparatus) are uncorrected. ^{1}H and ^{13}C-NMR spectra were obtained on a Varian Gemini-200, Varian Unity plus 400 or Bruker Advance 600 Spectrometer. NOESY spectra experiments were recorded on a Varian VXR-500. Chemical shifts were measured in parts per million with respect to TMS. Mass spectra were recorded on a Chem/hp/middle instrument. High-resolution mass spectra were performed on JEOL JMS SX/SX 102A. X-ray crystallographic analysis was performed using a Rigaku AFC7S diffractometer. Silica gel (70-230 mesh) for column chromatography and the precoated silica gel plate (60

Table 7. The Selected ^{1}H NMR Spectra of Substituted Naphthols (**15a-f**, **16a-c**)



15a-f



16a-c

	OH	H-2	H-3	H-4	H-5	H-7	H-8
15a	5.45(br s)	6.68(d)	7.28(t)	7.26(d)	-	7.68(d)	7.96(d)
15b	5.67(br s)	6.67(d)	7.27(t)	7.25(d)	-	7.70(d)	7.94(d)
15c	5.45(br s)	6.66(d)	7.29(t)	7.70(d)	-	7.33(d)	7.96(d)
15d	5.35(br s)	6.54(d)	6.95(d)	-	-	7.22(d)	8.02(d)
15e	5.27(br s)	6.55(d)	6.99(d)	-	-	7.26(d)	7.99(d)
15f	5.64(br s)	6.40(d)	6.91(d)	-	-	7.09(d)	8.01(d)
16a	5.37(br s)	6.70(d)	7.16(t)	7.29(d)	7.10(s)	-	7.48(s)
16b	5.47(br s)	6.68(d)	7.15(t)	7.28(d)	7.10(s)	-	7.48(s)
16c	5.50(br s)	6.65(d)	7.13(t)	7.27(d)	7.11(s)	-	7.54(s)

Table 8. Yields (%) for Compounds **11**, **12**, **15**, and **16** in Scheme III

Substituents	Vinyl ketones **11**[a]	Vinyl ketones **12**[a]	Naphthols **15**[a]	Naphthols **16**[a]
a R_1 = H, R_3 = Me	65		62[19]	
b R_1 = H, R_3 = Et	65		61	
c R_1 = H, R_3 = Bn	60		63	
d R_1 = Me, R_3 = Me	58		46	
e R_1 = Me, R_3 = Et	63		53	
f R_1 = Me, R_3 = Bn	60		40	
a R_3 = Me		69		60[19]
b R_3 = Et		72		68
c R_3 = Bn		69		62

[a] Except for **15a**[19] and **16a**[19], all vinyl ketones (**11**, **12**) and naphthols (**15**, **16**) are new compounds, whose structures were confirmed by spectral data such as ^{1}H NMR, ^{13}C NMR, MS, and HRMS.

F-254) for TLC were purchased from E. Merck Co. UV light (254 nm) was used to detect spots on TLC plates after development. 3-Hydroxy-4-methoxybenzaldehyde (isovanillin) (**1**) purchased from TCI (Tokyo Kasei Industry) was directly used without purification. Grubbs catalyst (first generation) was purchased from Fluca Company.

General procedure for preparing 3-allyloxy-4-methoxybenzaldehydes (2a-d)

As a general procedure, isovanillin (**1**) (31 g, 0.2 mol) dissolved in anhydrous acetone (250 mL) was respectively reacted with allyl bromide (18.6 mL, 0.22 mol), 1-bromo-2-butene (23.5 mL, 0.23 mol), *trans* cinnamyl chloride (32.3 mL, 0.23 mol), and 1-bromo-3-methyl-2-butane (23.0 mL, 0.23 mol) in the presence of K_2CO_3 (34.7 g, 0.25 mol) under reflux for 8 hr to give the corresponding 3-allyloxy-4-alkoxybenzaldehydes (**2a-d**), respectively. Work up as typical procedure and purification by chromatographic column (silica gel, ethyl acetate/n-hexane = 1/5) gave various allyloxyisovanillins (**2a-d**), respectively, in good yields.

3-Allyloxy-4-methoxybenzaldehyde (2a)[15a]

Pure **2a** (35.2 g, 92%) was obtained as pale yellow liquid, R_f 0.36 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.96 (s, 3H, $OC\underline{H}_3$), 4.67 (ddd, *J* = 5.2 Hz, 1.2 Hz, 1.2 Hz, 2H, $OC\underline{H}_2CH{=}CH_2$), 5.32 (ddt, *J* = 10.4 Hz, 1.2 Hz, 1.2 Hz, 1H, $OCH_2CH{=}C\underline{H}_2$), 5.45 (ddt, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $OCH_2CH{=}C\underline{H}_2$), 6.09 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.6 Hz, 1H, $OCH_2C\underline{H}{=}CH_2$), 6.99, 7.46 (each d, *J* = 8.0 Hz, 1H, $Ar\underline{H}$), 7.41 (s, 1H, $Ar\underline{H}$), 9.83 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 56.08, 69.64, 110.62, 110.82, 118.51, 126.72, 129.94, 132.44, 148.45, 154.77, 190.76; (70 eV) *m/z* (rel. intensity, %) 192 (M^+, 46), 188 (100), 173 (85), 151 (84), 145 (60), 127 (71), 95 (58).

3-(2-Butenoxy)-4-methoxybenzaldehyde (2b)[15b]

Pure **2b** (36.2 g, 88%) was obtained as pale yellow liquid; R_f 0.37 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.74 (dd, J = 6.2 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CH\text{-}CH_2$), 3.93 (s, 3H, $OC\underline{H}_3$), 4.56 (dd, J = 6.0 Hz, 1.0 Hz, 2H, $CH_3CH=CHC\underline{H}_2$), 5.77 (dtd, J = 15.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2$), 5.89 (dqt, J = 15.2 Hz, 6.2 Hz, 1.0 Hz, 1H, $CH_3C\underline{H}=CHCH_2$), 6.97 (d, J = 8.4 Hz, 1H, $Ar\underline{H}$), 7.40 (d, J = 2.0 Hz, 1H, $Ar\underline{H}$), 7.43 (dd, J = 8.4 Hz, 2.0 Hz, 1H, $Ar\underline{H}$), 9.83 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.45 ($\underline{C}H_3$), 55.70 ($O\underline{C}H_3$), 69.11 ($CH_3CH=CH\underline{C}H_2$), 110.23, 125.01, 126.20, 126.31, 129.63, 130.95, 148.27, 154.41, 190.40 ($\underline{C}HO$); (70 eV) *m/z* (rel. intensity, %) 206 (M^+, 5), 153 (10), 152 (100), 151 (69), 123 (7), 109 (5), 95 (6); HRMS calcd for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0940.

3-(3-Phenyl-2-propenoxy)-4-methoxybenzaldehyde (2c)[15b]

Pure **2c** (46.1 g, 86%) was obtained as pale yellow liquid; R_f 0.40 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 3.96 (s, 3H, $OC\underline{H}_3$), 4.81 (dd, J = 6.0 Hz, 1.0 Hz, 2H, $C_6H_5CH=CHC\underline{H}_2O$), 5.53 (dt, J = 15.2 Hz, 6.0 Hz, 1H, $C_6H_5CH=C\underline{H}CH_2O$), 6.75 (d, J = 15.2 Hz, 1H, $C_6H_5C\underline{H}=CHCH_2O$), 6.98 (d, J = 8.8 Hz, 1H, $Ar\underline{H}$), 7.25-7.40 (m, 5H, $C_6\underline{H}_5$), 7.42 (d, J = 2.0 Hz, 1H, $Ar\underline{H}$), 7.45 (dd, J = 8.8 Hz, 2.0 Hz, 1H, $Ar\underline{H}$), 9.84 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 56.08 ($O\underline{C}H_3$), 69.49 ($O\underline{C}H_2$), 110.59, 110.69, 123.40, 126.60, 126.79, 127.93, 128.47, 129.93, 133.96, 136.13, 148.45, 154.74, 190.76 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 268 (M^+, 27), 178 (19), 177 (90), 165 (22), 164 (100), 162 (20), 149 (21), 136 (68), 135 (31), 115 (17), 93 (20), 91 (38).

3-(3-Methyl-2-butenoxy)-4-methoxybenzaldehyde (2d)

Pure **2d** (35.2 g, 92%) was obtained as pale yellow liquid; R_f 0.39 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.77, 1.79 [each s, 3H, $(C\underline{H}_3)_2C=CHCH_2$], 3.95 (s, 3H, $OC\underline{H}_3$), 4.64 [d, J = 6.0 Hz, 2H, $(CH_3)_2C=CHC\underline{H}_2$], 5.53 [t, J = 6.0 Hz, 1H, $(CH_3)_2C=C\underline{H}CH_2$], 6.98 (d, J = 8.5 Hz, 1H, $Ar\underline{H}$), 7.42 (d, J = 2.0 Hz, 1H, $Ar\underline{H}$), 7.49 (dd, J = 8.5 Hz, 2.0 Hz, 1H, $Ar\underline{H}$), 9.84 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 18.09, 25.70 (each $\underline{C}H_3$), 55.96 ($O\underline{C}H_3$), 65.56 [$(CH_3)_2C=CH\underline{C}H_2$], 110.21, 110.32, 118.93, 126.51, 129.83, 138.39, 148.65, 154.67, 190.78 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 220 (M^+, 0.7), 153 (11), 152 (100), 151 (57), 137 (2), 123 (6), 119 (3), 95 (2); HRMS calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1097.

General procedure for the preparation of 3a-b and 4b-d

Method A, **2a-d** (0.15 mol) was gently boiled and strongly stirred in neat; method B, **2a-d** (0.15 mol) was gently boiled and strongly stirred in decalin; method C, **2a-d** (0.15 mol) was gently boiled and strongly stirred in *N,N*-diethylaniline. All of the above methods were carried out under argon. After the end of each reaction, which was monitored by TLC, (except method A), the giving solution was concentrated *in vacuo* to remove decalin or *N,N*-diethylaniline. And the resulting residue was subjected to chromatographic column (*n*-hexane/EA = 3/1) to give pure **3a-b**, and **4b-d**. The percentage yield was calculated according to the highest percentage yield among the three methods.

2-Allyl-3-hydroxy-4-methoxybenzaldehyde (3a)[16]

Pure **3a** (26.5 g, 92%) was obtained as pale yellow liquid; R_f 0.47 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.75 (ddd, J = 6.0 Hz, 1.6 Hz, 1.6 Hz, 2H, $CH_2=CHC\underline{H}_2Ar$), 3.77 (s, 3H, $OC\underline{H}_3$), 4.84 (ddd, J = 17.5 Hz, 1.6 Hz, 1.6 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 4.88 (ddd, J = 6.0 Hz, 1.6 Hz, 1.6 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.89 (ddt, J = 17.5 Hz, 10.6 Hz, 6.0 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.28 (br s, 1H, $O\underline{H}$), 6.71 (d, J = 8.4 Hz, 1H, $Ar\underline{H}$), 7.27 (d, J = 8.4 Hz, 1H, $Ar\underline{H}$), 9.90 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 28.08 ($CH_2=CH\underline{C}H_2Ar$), 55.76 ($O\underline{C}H_3$), 107.91, 114.96, 125.28, 127.31, 127.74, 136.07, 143.61, 150.80, 191.40 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 192 (M^+, 54), 177 (100), 159 (23), 149 (22), 143 (18), 131 (29), 115 (18), 103 (28), 91 (19); HRMS calcd for $C_{11}H_{12}O_3$: 192.0786. Found: 192.0779.

3-Hydroxy-4-methoxy-2-(1-methyl-2-propenyl)benzaldehyde (3b)[16]

Pure **3b** (14.8 g, 48%) was obtained as pale yellow liquid; R_f 0.42 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.50 (d, J = 7.2 Hz, 3H, $CH_2=CHCHC\underline{H}_3Ar$), 3.98 (s, 3H, $OC\underline{H}_3$), 4.72 (m, 1H, $CH_2=CHC\underline{H}CH_3Ar$), 5.08 (dd, J = 17.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCHCH_3Ar$), 5.12 (dd, J = 10.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_3CHAr$), 5.93 (br s, 1H, $O\underline{H}$), 6.32 (ddd, J = 17.3 Hz, 10.3 Hz, 5.4 Hz, 1H, $CH_2=C\underline{H}CHCH_3Ar$), 6.86 (d, J = 8.5 Hz, 1H, $Ar\underline{H}$), 7.46 (d, J = 8.5 Hz, 1H, $Ar\underline{H}$), 10.21 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 19.11 ($CH_2=CHCH\underline{C}H_3Ar$), 33.95 ($CH_2=CH\underline{C}HCH_3Ar$), 56.13 ($O\underline{C}H_3$), 108.08, 113.75, 125.01, 128.28, 132.90, 142.21, 143.85, 150.90, 191.76 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 206 (M^+, 16), 191 (100), 177 (20), 176 (19), 163 (26), 145 (16), 131 (21), 103 (19), 91 (18); HRMS calcd for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0935.

2-[2-(*E*)-Butenyl]-5-hydroxy-4-methoxybenzaldehyde (4b)[16]

Pure **4b** (11.1 g, 36%) was obtained as pale yellow liquid; R_f 0.34 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.66 (dd, *J* = 6.2 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CHCH_2Ar$), 3.67 (dd, *J* = 6.0 Hz, 1.3 Hz, 2H, $CH_3CH=CHC\underline{H}_2Ar$), 3.96 (s, 3H, $OC\underline{H}_3$), 5.41 (dqd, *J* = 13.2 Hz, 6.2 Hz, 1.3 Hz, 1H, $CH_3C\underline{H}=CHCH_2Ar$), 5.61 (dtd, *J* = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2Ar$), 5.68 (br s, 1H, $O\underline{H}$), 6.70, 7.41 (each s, 1H, $Ar\underline{H}$), 10.13 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 17.85 ($\underline{C}H_3$), 34.84 ($CH_3CH=CH\underline{C}H_2Ar$), 56.03 ($O\underline{C}H_3$), 112.29, 115.59, 126.85, 127.39, 129.94, 137.55, 144.18, 151.22, 190.54 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 206 (M^+, 36), 191 (29), 177 (100), 164 (17), 145 (17), 136 (63), 131 (19), 117 (13), 115 (12), 103 (10), 91 (14); HRMS calcd for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0948.

5-Hydroxy-4-methoxy-2-[3-(*E*)-phenyl-2-propenyl]benzaldehyde (4c)

Pure **4c** was obtained (65% in method B, and 76% in method C) as colorless liquid, R_f 0.24 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.90 (d, *J* = 2.4 Hz, 2H, $C_6H_5CH=CHC\underline{H}_2$), 3.94 (s, 3H, $OC\underline{H}_3$), 5.79 (br s, 1H, OH), 6.36 (m, 1H, $C_6H_5CH=C\underline{H}$), 6.37 (m, 1H, $C_6H_5C\underline{H}=CH$), 6.76, 7.43 (each s, 1H, $Ar\underline{H}$), 7.19-7.30 (m, 5H, $C_6\underline{H}_5$), 10.13 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 35.20, 56.08, 112.56, 116.54, 126.08, 127.24, 127.46, 128.47, 128.91, 131.26, 136.48, 137.11, 144.38, 151.25, 190.61 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 268 (M^+, 18), 178 (17), 177 (100), 165 (10), 164 (39), 162 (12), 136 (50), 91 (15); HRMS calcd for $C_{17}H_{16}O_3$: 268.1099. Found: 268.1098.

5-Hydroxy-4-methoxy-2-(3-methyl-2-butenyl)benzaldehyde (4d)

Pure **4d** was obtained (79% by method A, 58% by method B, and 80% by method C) as colorless liquid, R_f 0.34 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.73, 1.74 (each s, 3H, $(C\underline{H}_3)_2C=CHCH_2$), 3.69 (d, *J* = 7.0 Hz, 2H, $(CH_3)_2C=CHC\underline{H}_2$), 3.95 (s, 3H, $OC\underline{H}_3$), 5.24 (t, *J* = 7.0 Hz, 1H, $(CH_3)_2C=C\underline{H}CH_2$), 5.57 (br s, 1H, OH), 6.71, 7.40 (each s, 1H, $Ar\underline{H}$), 10.13 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.95, 25.63, 30.62, 55.97, 111.91, 115.68, 123.08, 127.30, 132.73, 138.75, 144.02, 151.24, 190.64; EI-MS (70 eV) *m/z* (rel. intensity, %) 220 (M^+, 52), 205 (59), 190 (12), 187 (10), 177 (64), 165 (12), 164 (46), 162 (16), 145 (16), 137 (20), 136 (100), 131 (12), 117 (10), 115 (15), 91 (14); HRMS calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1100.

General procedure for preparing of 5a-f and 6a-c

As the general procedure described, **3a** (1.92 g, 0.01 mol), **3b** (2.06 g, 0.01 mol), and **4b** (2.06 g, 0.01 mol) were respectively alkylated with corresponding methyl iodide, ethyl iodide, and benzyl bromide. After work up and chromatographic purification (*n*-hexane/EA = 5/1), pure compounds **5a-f** and **6a-c** were produced.

2-Allyl-3,4-dimethoxybenzaldehyde (5a)[17a]

Pure **5a** (1.81 g, 88%) was obtained as pale yellow liquid, R_f 0.62 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.73, 3.85 (each s, 3H, $OC\underline{H}_3$), 3.78 (ddd, *J* = 5.8 Hz, 1.8 Hz, 1.8 Hz, 2H, $CH_2=CHC\underline{H}_2Ar$), 4.84 (ddd, *J* = 17.0 Hz, 3.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 4.93 (ddd, *J* = 10.3 Hz, 3.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.94 (ddt, *J* = 17.0 Hz, 10.3 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.85 (d, *J* = 8.6 Hz, 1H, $Ar\underline{H}$), 7.54 (d, *J* = 8.6 Hz, 1H, $Ar\underline{H}$), 9.95 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 28.41 ($CH_2=CH\underline{C}H_2Ar$), 55.50, 60.60 (each, $O\underline{C}H_3$), 109.64, 115.24, 127.62, 128.88, 135.72, 136.91, 146.98, 157.22, 190.59 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 206 (M^+, 58), 191 (100), 175 (38), 174 (19), 163 (21), 147 (22), 131 (27), 103 (33), 91 (32); HRMS calcd for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0935.

2-Allyl-3-ethoxy-4-methoxybenzaldehyde (5b)

Pure **5b** (1.76 g, 80%) was obtained as pale yellow liquid; R_f 0.55 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.36 (t, *J* = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 3.84 (ddd, *J* = 5.8 Hz, 1.8 Hz, 1.8 Hz, 2H, $CH_2=CHC\underline{H}_2Ar$), 3.89 (s, 3H, $OC\underline{H}_3$), 3.96 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 4.88 (ddd, *J* = 17.0 Hz, 3.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 4.98 (ddd, *J* = 10.3 Hz, 3.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.99 (ddt, *J* = 17.0 Hz, 10.3 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.88 (d, *J* = 8.5 Hz, 1H, $Ar\underline{H}$), 7.57 (d, *J* = 8.5 Hz, 1H, $Ar\underline{H}$), 10.02 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 16.09 ($OCH_2\underline{C}H_3$), 29.33 ($CH_2=CH\underline{C}H_2Ar$), 56.27 ($O\underline{C}H_3$), 69.57 ($O\underline{C}H_2CH_3$), 110.26, 115.98, 128.43, 129.34, 136.69, 137.68, 146.96, 158.11, 191.47 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 220 (M^+, 67), 205 (100), 192 (32), 191 (37), 177 (98), 164 (31), 159 (38), 143 (34), 135 (46), 131 (57), 103 (73), 91 (52); HRMS calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1104.

2-Allyl-3-benzyloxy-4-methoxybenzaldehyde (5c)[17b]

Pure **5c** (2.76 g, 98%) was obtained as pale yellow liquid, R_f 0.56 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.88 (ddd, *J* = 5.8 Hz, 1.8 Hz, 1.8 Hz, 2H,

$CH_2=CHC\underline{H}_2Ar$), 3.92 (s, 3H, $OC\underline{H}_3$), 4.91 (ddd, J = 17.0 Hz, 3.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 4.99 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.02 (ddd, J = 10.3 Hz, 3.3 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 6.01 (ddt, J = 17.0 Hz, 10.3 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.94 (d, J = 8.5 Hz, 1H, $Ar\underline{H}$), 7.34-7.48 (m, 5H, $OCH_2C_6\underline{H}_5$), 7.67 (d, J = 8.5 Hz, 1H, $Ar\underline{H}$), 10.06 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 29.41 ($CH_2=CH\underline{C}H_2Ar$), 56.37 ($O\underline{C}H_3$), 75.41 ($O\underline{C}H_2C_6H_5$), 110.49, 116.21, 128.57, 128.72, 128.85, 128.96, 129.69, 136.90, 137.71, 137.96, 146.59, 158.12, 191.42 ($\underline{C}HO$); (70 eV) *m/z* (rel. intensity, %) 282 (M^+, 0.2), 192 (2), 191 (20), 177 (8), 163 (2), 159 (2), 135 (3), 131 (2), 105 (2), 103 (4), 92 (10), 91 (100); HRMS calcd for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1259.

3,4-Dimethoxy-2-(1-methyl-2-propenyl)benzaldehyde (5d)

Pure **5d** (2.02 g, 92%) was obtained as pale yellow liquid, R_f 0.64 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.48 (d, J = 7.3 Hz, 3H, $CH_2=CHC\underline{H}_3CHAr$), 3.78, 3.91 (each s, 3H, $OC\underline{H}_3$), 4.56 (m, 1H, $CH_2=CHCH_3C\underline{H}Ar$), 4.99 (ddd, J = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH_3CHAr$), 5.06 (ddd, J = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH_3CHAr$), 6.22 (ddd, J = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2=C\underline{H}CH_3CHAr$), 6.88 (d, J = 8.6 Hz, 1H, $Ar\underline{H}$), 7.68 (d, J = 8.6 Hz, 1H, $Ar\underline{H}$), 10.23 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 20.62 ($CH_2=CH\underline{C}H_3CH$), 33.68 ($CH_2=CHCH_3\underline{C}H$), 55.72, 60.87 (each, $O\underline{C}H_3$), 109.88, 113.57, 127.82, 128.06, 141.91, 143.06, 146.99, 157.42, 191.02 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 220 (M^+, 15), 205 (100), 191 (19), 177 (23), 161 (15), 115 (14), 91 (14); HRMS calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1105.

3-Ethoxy-4-methoxy-2-(1-methyl-2-propenyl)benzaldehyde (5e)

Pure **5e** (1.87 g, 80%) was obtained as pale yellow liquid, R_f 0.71 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.39 (t, J = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.51 (d, J = 7.2 Hz, 3H, $CH_2=CHC\underline{H}_3CHAr$), 3.92 (s, 3H, $OC\underline{H}_3$), 4.03 (q, J = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.59 (m, 1H, $CH_2=CHCH_3C\underline{H}Ar$), 5.03 (ddd, J = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH_3CHAr$), 5.08 (ddd, J = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCHAr$), 6.25 (ddd, J = 17.3 Hz, 10.3 Hz, 4.4 Hz, 1H, $CH_2=C\underline{H}CH_3CHAr$), 6.90 (d, J = 8.6 Hz, 1H, $Ar\underline{H}$), 7.72 (d, J = 8.6 Hz, 1H, $Ar\underline{H}$), 10.28 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 15.40 ($OCH_2\underline{C}H_3$), 20.73 ($CH_2=CHCH\underline{C}H_3$), 33.50 ($CH_2=CH\underline{C}HAr$), 55.67 ($O\underline{C}H_3$), 68.93 ($O\underline{C}H_2CH_3$), 109.72, 113.51, 127.27, 128.10, 141.95, 143.14, 145.87, 157.44, 191.00 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 234 (M^+, 25), 219 (100), 205 (30), 191 (62), 177 (36), 163(25), 145 (35), 117 (34), 115 (27), 91 (31); HRMS calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1252.

3-Benzyloxy-4-methoxy-2-(1-methyl-2-propenyl)benzaldehyde (5f)

Pure **5f** (2.87 g, 97%) was obtained as pale yellow liquid, R_f 0.67 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.43 (d, J = 7.2 Hz, 3H, $CH_2=CHC\underline{H}_3CHAr$), 3.96 (s, 3H, $OC\underline{H}_3$), 4.55 (m, 1H, $CH_2=CHCH_3C\underline{H}Ar$), 4.98 (ddd, J = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH_3CHAr$), 4.99 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.06 (ddd, J = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH_3CHAr$), 6.26 (ddd, J = 17.3 Hz, 10.3 Hz, 4.4 Hz, 1H, $CH_2=C\underline{H}CH_3CHAr$), 6.94 (d, J = 8.6 Hz, 1H, $Ar\underline{H}$), 7.35-7.44 (m, 5H, $OCH_2C_6\underline{H}_5$), 7.77 (d, J = 8.6 Hz, 1H, $Ar\underline{H}$), 10.29 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 20.81 ($CH_2=CH\underline{C}H_3CHAr$), 33.62 ($CH_2=CHCH_3\underline{C}HAr$), 55.81 ($O\underline{C}H_3$), 74.90 ($O\underline{C}H_2C_6H_5$), 109.95, 113.67, 127.42, 128.04, 128.17, 128.41, 128.70, 137.20, 142.31, 143.13, 145.39, 157.41, 191.06 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 296 (M^+, 0.2), 278 (0.7), 206 (2), 205 (20), 191 (5), 188 (2), 177 (6), 174 (2), 173 (2), 161 (1), 145 (6), 117 (4), 92 (9), 91 (100); HRMS calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1408.

2-(2-Butenyl)-4,5-dimethoxybenzaldehyde (6a)

Pure **6a** (1.83 g, 83%) was obtained as pale yellow liquid; R_f 0.63 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.66 (dd, J = 6.2 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CHCH_2Ar$), 3.67 (d, J = 6.0 Hz, 2H, $CH_3CH=CHC\underline{H}_2Ar$), 3.91, 3.95 (each s, 3H, $OC\underline{H}_3$), 5.43 (dq, J = 13.2 Hz, 6.2 Hz, 1H, $CH_3C\underline{H}=CHCH_2Ar$), 5.64 (dtd, J = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2Ar$), 6.72, 7.39 (each s, 1H, $Ar\underline{H}$), 10.19 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 17.58 ($\underline{C}H_3$), 34.24 ($CH_3CH=CH\underline{C}H_2Ar$), 55.68, 55.76 (each, $O\underline{C}H_3$), 110.36, 112.55, 126.48, 126.68, 129.74, 138.44, 147.49, 153.63, 189.64 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 220 (M^+, 65), 205 (35), 191 (100), 178 (21), 150 (91), 91 (22); HRMS calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1099.

2-(2-Butenyl)-5-ethoxy-4-methoxybenzaldehyde (6b)

Pure **6b** (1.97 g, 84%) was obtained as pale yellow liquid; R_f 0.70 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.48 (t, J = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 1.66 (dd, J = 6.2 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CHCH_2$), 3.67 (d, J = 6.0 Hz, 2H, $CH_3CH=CHC\underline{H}_2$), 3.94 (s, 3H, $OC\underline{H}_3$), 4.15 (q, J = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 5.44 (dq, J = 13.2 Hz, 6.2 Hz, 1H, $CH_3C\underline{H}=CHCH_2Ar$), 5.63 (dtd, J = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2Ar$), 6.70, 7.38 (each s, 1H, $Ar\underline{H}$), 10.18 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 60 MHz) δ 14.63 ($OCH_2\underline{C}H_3$), 17.83 ($\underline{C}H_3$), 34.59 ($CH_3CH=CH\underline{C}H_2Ar$), 56.04, 64.39 ($O\underline{C}H_2CH_3$), 111.84, 112.89, 126.69, 126.95, 129.95, 138.54, 147.01, 154.13, 190.05 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %): 234 (M^+, 71), 205 (100), 191 (40), 177 (68), 164 (51), 145 (25), 136 (61), 131 (31), 115 (25), 103 (16), 91 (27); HRMS calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1256.

5-Benzyloxy-2-(2-butenyl)-4-methoxybenzaldehyde (6c)

Pure **6c** (2.58 g, 87%) was obtained as pale yellow liquid; R_f 0.70 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.66 (dd, *J* = 6.2 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CHCH_2Ar$), 3.66 (d, *J* = 6.0 Hz, 2H, $CH_3CH=CHC\underline{H}_2Ar$), 3.94 (s, 3H, $OC\underline{H}_3$), 5.16 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.42 (dq, *J* = 13.2 Hz, 6.2 Hz, 1H, $CH_3C\underline{H}=CHCH_2Ar$), 5.60 (dtd, *J* = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2Ar$), 6.72, 7.44 (each s, 1H, $Ar\underline{H}$), 7.33-7.46 (m, 5H, $OCH_2C_6\underline{H}_5$), 10.15 (s, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 17.85 ($\underline{C}H_3$), 34.62 ($CH_3CH=CH\underline{C}H_2Ar$), 56.06 ($O\underline{C}H_3$), 70.92 ($O\underline{C}H_2C_6H_5$), 113.13, 113.20, 126.65, 127.01, 127.48, 128.01, 128.57, 129.87, 136.51, 139.01, 146.83, 154.48, 189.99 ($\underline{C}HO$); EI-MS (70 eV) *m/z* (rel. intensity, %) 296 (M^+, 2), 205 (11), 177 (8), 149 (2), 131 (3), 117 (2), 115 (2), 91 (100); HRMS calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1410.

General procedure for preparing 7a-f and 8a-c

Each of the compounds **5a-f** and **6a-c** (5 mmol) dissolved in anhydrous THF (30 mL) was added with vinyl magnesium bromide (1.0 M, 5.5 mL), and the mixture was stirred at room temperature for 2 h. The solution was then quenched with saturated $NH_4Cl_{(aq)}$ solution and extracted with ethyl acetate (15 mL × 5). The extracted solution was washed with brine (10 mL × 2), and dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*, and the given residue was subjected to chromatographic column (silica gel, *n*-hexane/EA = 3/1) to give the pure **7a-f** and **8a-c**.

1-(2-Allyl-3,4-dimethoxyphenyl)-2-propen-1-ol (7a)

Pure **7a** (1.12 g, 96%) was obtained as colorless liquid, R_f = 0.54 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.15 (br s, 1H, OH, D_2O exchangeable), 3.53 (ddd, *J* = 5.4 Hz, 1.8 Hz, 1.8 Hz, 2H, $CH_2=CHC\underline{H}_2Ar$), 3.78, 3.83 (each s, 3H, $OC\underline{H}_3$), 4.90 (ddt, *J* = 17.4 Hz, 2.0 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.01 (ddt, *J* = 10.4 Hz, 2.0 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.16 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)Ar$), 5.31 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)\ Ar$), 5.33 (br s, 1H, $CH_2=CHC\underline{H}(OH)Ar$), 5.94 (ddt, *J* = 17.4 Hz, 10.4 Hz, 5.4 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.02 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH(OH)Ar$), 6.81, 7.14 (each d, *J* = 8.4 Hz, 1H, H-5 and H-6); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 29.63 ($CH_2=CH\underline{C}H_2$), 55.35, 60.64 ($O\underline{C}H_3$), 70.50 ($\underline{C}HOH$), 110.43, 114.29, 115.01, 122.43, 131.26, 133.91, 137.49, 139.95, 146.96, 152.01; EI-MS (70 eV) *m/z* (rel. intensity, %) 234 (M^+, 82), 207 (100), 205 (55), 191 (66), 185 (66), 176 (55), 175 (95), 174 (66), 161 (52), 159 (52), 158 (56), 131 (56), 115 (90), 91 (72); HRMS: calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1249.

1-(2-Allyl-3-ethoxy-4-methoxyphenyl)-2-propen-1-ol (7b)

Pure **7b** (1.13 g, 91%) was obtained as colorless liquid, R_f = 0.53 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 1.36 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 2.11 (br s, 1H, OH, D_2O exchangeable), 3.50 (ddd, *J* = 5.4 Hz, 1.8 Hz, 1.8 Hz, 2H, $CH_2=CHC\underline{H}_2Ar$), 3.82 (s, 3H, $OC\underline{H}_3$), 3.98 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.91 (ddt, *J* = 16.8 Hz, 2.0 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.01 (ddt, *J* = 9.9 Hz, 2.0 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.17 (ddd, *J* = 10.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH\text{-}(OH)Ar$), 5.31 (ddd, *J* = 16.8 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)Ar$), 5.35 (br s, 1H, $CH_2=CHC\underline{H}(OH)Ar$), 5.97 (ddt, *J* = 16.8 Hz, 9.9 Hz, 5.4 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.03 (ddd, *J* = 16.8 Hz, 10.2 Hz, 6.0 Hz, 1H, $CH_2=C\underline{H}CH(OH)Ar$), 6.80, 7.13 (each d, *J* = 8.4 Hz, 1H, H-5 and H-6); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 15.43 ($OCH_2\underline{C}H_3$), 29.69 ($CH_2=CH\underline{C}H_2$), 55.35 ($O\underline{C}H_3$), 68.58 ($O\underline{C}H_2CH_3$), 70.58 ($\underline{C}HOH$), 110.23, 114.07, 115.11, 122.17, 131.23, 133.33, 137.43, 139.95, 146.05, 151.97; EI-MS (70 eV) *m/z* (rel. intensity, %) 248 (M^+, 70), 221 (60), 177 (43), 175 (43), 173 (44), 161 (54), 159 (80), 147 (41), 145 (42), 143 (80), 141 (43), 131 (84), 115 (90), 103 (65), 91 (63); HRMS: calcd for $C_{15}H_{20}O_3$: 248.1412. Found: 248.1409.

1-(2-Allyl-3-benzyloxy-4-methoxyphenyl)-2-propen-1-ol (7c)

Pure **7c** (1.47 g, 95%) was obtained as colorless liquid, R_f = 0.45 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.09 (br s, 1H, OH, D_2O exchangeable), 3.37 (ddd, *J* = 5.4 Hz, 1.8 Hz, 1.8 Hz, 2H, $CH_2=CHC\underline{H}_2Ar$), 3.75 (s, 3H, $OC\underline{H}_3$), 4.79 (ddt, *J* = 17.4 Hz, 2.0 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 4.87 (s, 2H, $OC\underline{H}_2C_6H_5$), 4.90 (ddt, *J* = 10.4 Hz, 2.0 Hz, 1.8 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.07 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)Ar$), 5.20 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH\text{-}CH(OH)Ar$), 5.24 (br s, 1H, $CH_2=CHC\underline{H}(OH)Ar$), 5.91 (ddt, *J* = 17.4 Hz, 10.4 Hz, 5.4 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.02 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH(OH)Ar$), 6.74, 7.07 (each d, *J* = 8.4 Hz, 1H, H-5 and H-6), 7.21-7.36 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 29.84 ($CH_2=CH\underline{C}H_2$), 55.58 ($O\underline{C}H_3$), 70.76 ($\underline{C}HOH$), 74.57 ($O\underline{C}H_2C_6H_5$), 110.52, 114.37, 115.11, 122.61, 127.68, 127.86, 128.18, 128.21, 131.55, 133.96, 137.49, 139.92, 145.88, 152.18; EI-MS (70 eV) *m/z* (rel. intensity, %) 310 (M^+, 3), 201 (6), 177 (5), 175 (4), 169 (4), 161 (5), 160 (7), 159 (5), 145 (4), 143 (5), 141 (5), 131 (10), 129 (4), 128 (4), 115 (9), 103 (6), 92 (8), 91 (100); HRMS: calcd. for $C_{20}H_{22}O_3$: 310.1569. Found: 310.1562.

1-[3,4-Dimethoxy-2-(1-methylallyl)phenyl]-2-propen-1-ol (7d)

7d (0.97 g, 78%) was isolated as pale yellow liquid in a 3:2 mixture of diastereomers, $R_f = 0.55$ (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, major diastereomer 400 MHz) δ 1.44 (d, *J* = 7.2 Hz, 3H, $CH_2=CH(C\underline{H}_3)CH$), 2.13 (br s, 1H, OH, D_2O exchangeable), 3.79, 3.83 (each s, 3H, $OC\underline{H}_3$), 4.10 (m, 1H, $CH_2=CH(CH_3)C\underline{H}$), 5.00 (ddd, *J* = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH(CH_3)CH$), 5.05 (ddd, *J* = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH(CH_3)CH$), 5.18 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH\text{-}(OH)Ar$), 5.31 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)Ar$), 5.47 (br s, 1H, $CH_2=CHC\underline{H}(OH)Ar$), 6.06 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH\text{-}(OH)Ar$), 6.21 (ddd, *J* = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2=C\underline{H}(CH_3)CH$), 6.80, 7.12 (each d, *J* = 8.8 Hz, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, major diastereomer 100 MHz) δ 19.28 ($CH_2=CH(\underline{C}H_3)CHAr$), 35.26 ($CH_2=CH(CH_3)\underline{C}HAr$), 55.52, 60.61 (each, $O\underline{C}H_3$), 70.95, 110.41, 112.79, 114.22, 123.11, 133.38, 137.52, 140.21, 143.35, 147.40, 152.35; ^{1}H-NMR ($CDCl_3$, minor diastereomer 400 MHz) δ 1.41 (d, *J* = 7.2 Hz, 3H, $CH_2=CH(C\underline{H}_3)CH$), 2.08 (br s, 1H, OH, D_2O exchangeable), 3.79, 3.83 (each s, 3H, $OC\underline{H}_3$), 4.10 (m, 1H, $CH_2=CH(CH_3)C\underline{H}$), 4.99 (ddd, *J* = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH(CH_3)CH$), 5.03 (ddd, *J* = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH\text{-}(CH_3)CH$), 5.18 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)Ar$), 5.28 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH(OH)Ar$), 5.47 (br s, 1H, $CH_2=CH\text{-}C\underline{H}(OH)Ar$), 6.02 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH(OH)Ar$), 6.16 (ddd, *J* = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2=C\underline{H}(CH_3)CHAr$), 6.80, 7.12 (each d, *J* = 8.8 Hz, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, minor diastereomer 100 MHz) δ 19.69 ($CH_2=CH(\underline{C}H_3)CH$), 35.36 ($CH_2=CH(CH_3)\underline{C}H$), 55.52, 60.61 (each, $O\underline{C}H_3$), 70.95, 110.45, 112.85, 114.37, 123.38, 133.36, 137.32, 140.25, 143.46, 147.40, 152.39; EI-MS (70 eV) *m/z* (rel. intensity, %) 248 (M^+, 40), 221 (50), 215 (41), 205 (41), 199 (40), 189 (100), 188 (51), 174 (41), 115 (61); HRMS: calcd. for $C_{15}H_{20}O_3$: 248.1412. Found: 248.1410.

1-[3-Ethoxy-4-methoxy-2-(1-methylallyl)phenyl]-2-propen-1-ol (7e)

7e (1.07 g, 82%) was isolated as pale yellow liquid in a 3:2 mixture of diastereomers, $R_f = 0.64$ (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, major diastereomer 400 MHz) δ: 1.37 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.47 (d, *J* = 7.2 Hz, 3H, $CH_2=CHC\underline{H}_3CHAr$), 1.90 (br s, 1H, OH, D_2O exchangeable), 3.83 (s, 3H, $OC\underline{H}_3$), 4.00 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.19 (m, 1H, $CH_2=CH(CH_3)C\underline{H}Ar$), 5.04 (ddd, *J* = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH(CH_3)CH$), 5.06 (ddd, *J* = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH(CH_3)CH$), 5.18 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH$), 5.33 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH$), 5.51 (br s, 1H, $CH_2=CHC\underline{H}$), 6.08 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH$), 6.22 (ddd, *J* = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2=C\underline{H}CH_3CHAr$), 6.82, 7.11 (each d, *J* = 8.8 Hz, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, major diastereomer 100 MHz) δ 15.49 ($OCH_2\underline{C}H_3$), 19.33 ($CH_2=CH\underline{C}H_3CHAr$), 34.84 ($CH_2=CHCH_3\underline{C}HAr$), 55.59 ($O\underline{C}H_3$), 68.52 ($O\underline{C}H_2CH_3$), 70.75, 110.46, 112.82, 114.10, 123.23, 133.64, 137.52, 140.24, 143.47, 146.23, 152.45; ^{1}H-NMR ($CDCl_3$, minor diastereomer 400 MHz) δ 1.42 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.42 (d, *J* = 7.2 Hz, 3H, $CH_2=CHC\underline{H}_3CHAr$), 1.81 (br s, 1H, OH, D_2O exchangeable), 3.83 (s, 3H, $OC\underline{H}_3$), 3.98 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.19 (m, 1H, $CH_2=CH(CH_3)C\underline{H}Ar$), 5.00 (ddd, *J* = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH(CH_3)CH$), 5.03 (ddd, *J* = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CH\text{-}(CH_3)CH$), 5.18 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH$), 5.30 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2=CHCH$), 5.51 (br s, 1H, $CH_2=CHC\underline{H}$), 6.04 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.8 Hz, 1H, $CH_2=C\underline{H}CH$), 6.18 (ddd, *J* = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2=C\underline{H}CH_3CHAr$), 6.80, 7.13 (each d, *J* = 8.8 Hz, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, minor diastereomer 100 MHz) δ 15.49 ($OCH_2\underline{C}H_3$), 19.79 ($CH_2=CH\underline{C}H_3CH$), 35.00 ($CH_2=CHCH_3\underline{C}H$), 55.59 ($O\underline{C}H_3$), 68.56 ($O\underline{C}H_2CH_3$), 70.75, 110.51, 112.88, 114.32, 123.56, 133.75, 137.60, 140.28, 143.64, 146.35, 152.54; EI-MS (70 eV) *m/z* (rel. intensity, %) 262 (M^+, 72), 235 (60), 203 (77), 175 (58), 173 (70), 169 (51), 159 (71), 157 (80), 145 (61), 143 (51), 131 (70), 129 (68), 128 (57), 115 (100), 91 (60); HRMS: calcd. for $C_{16}H_{22}O_3$: 262.1569. Found: 262.1577.

1-[3-Benzloxy-4-methoxy-2-(1-methylallyl)phenyl]-2-propen-1-ol (7f)

7f (1.30 g, 80%) was isolated as pale yellow liquid in a 3:2 mixture of diastereomers, $R_f = 0.60$ (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, major diastereomer 400 MHz) δ 1.42 (d, *J* = 7.2 Hz, 3H, $CH_2=CH(C\underline{H}_3)CHAr$), 1.98 (br s, 1H, OH), 3.86 (s, 3H, $OC\underline{H}_3$), 4.11 (m, 1H, $CH_2{=}CH(CH_3)C\underline{H}Ar$), 4.99 (ddd, *J* = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CH(CH_3)CH$), 4.97 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.03 (ddd, *J* = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CH(CH_3)CH$), 5.19 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH$), 5.33 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH$), 5.51 (br s, 1H, $CH_2{=}CHC\underline{H}$), 6.07 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.6 Hz, 1H, $CH_2{=}C\underline{H}CH$), 6.18 (ddd, *J* = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2{=}C\underline{H}CH_3CHAr$), 6.85, 7.15 (each d, *J* = 8.8 Hz, 1H, $Ar\underline{H}$), 7.31-7.47 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, major diastereomer 100 MHz) δ 19.35 ($CH_2{=}CH(\underline{C}H_3)CH$), 34.84 ($CH_2{=}CH(CH_3)\underline{C}H$), 55.67 ($O\underline{C}H_3$), 70.70, 74.42 ($O\underline{C}H_2C_6H_5$), 110.62, 112.99, 114.14, 123.66, 127.71, 127.92, 128.31, 133.78, 133.90, 137.71, 140.24, 143.41, 145.84, 152.38; ^{1}H-NMR ($CDCl_3$, minor diastereomer 400 MHz) δ 1.36 (d, *J* = 7.2 Hz, 3H, $CH_2{=}CH(C\underline{H}_3)CHAr$), 1.94 (br s, 1H, OH), 3.86 (s, 3H, $OC\underline{H}_3$), 4.11 (m, 1H, $CH_2{=}CH(CH_3)C\underline{H}Ar$), 4.97 (ddd, *J* = 10.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CH(CH_3)CH$), 4.99 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.01 (ddd, *J* = 17.3 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CH(CH_3)CH$), 5.19 (ddd, *J* = 10.6 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH$), 5.31 (ddd, *J* = 17.2 Hz, 1.2 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH$), 5.51 (br s, 1H, $CH_2{=}CHC\underline{H}$), 6.03 (ddd, *J* = 17.2 Hz, 10.6 Hz, 5.6 Hz, 1H, $CH_2{=}C\underline{H}CH$), 6.15 (ddd, *J* = 17.3 Hz, 10.3 Hz, 4.8 Hz, 1H, $CH_2{=}C\underline{H}CH_3CHAr$), 6.84, 7.17 (each d, *J* = 8.8 Hz, 1H, $Ar\underline{H}$), 7.31-7.47 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, minor diastereomer 100 MHz) δ 19.80 ($CH_2{=}CH(\underline{C}H_3)CH$), 35.00 ($CH_2{=}CH(CH_3)\underline{C}H$), 55.67 ($O\underline{C}H_3$), 70.70, 74.46 ($O\underline{C}H_2C_6H_5$), 110.83, 113.05, 114.38, 123.97, 127.71, 127.92, 128.31, 133.78, 133.90, 137.81, 140.29, 143.59, 146.00, 152.48; EI-MS (70 eV) *m/z* (rel. intensity, %) 324 (M^+, 0.4), 233 (8), 191 (3), 173 (3), 161 (2), 159 (3), 131 (5), 151 (7), 103 (3), 92 (9), 91 (100); HRMS: calcd. for $C_{21}H_{24}O_3$: 324.1725. Found: 324.1720.

1-(2-Butenyl-4,5-dimethoxyphenyl)-2-propen-1-ols (8a)

Pure **8a** (1.03 g, 83%) was obtained as pale yellow liquid, R_f = 0.40 (EA/*n*-hexane = 1/3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.66 (dd, *J* = 6.4 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH{=}CH{-}CH_2Ar$), 2.31 (br s, 1H, OH), 3.32 (d, *J* = 6.0 Hz, 2H, $CH_3CH{=}CHC\underline{H}_2Ar$), 3.84, 3.85 (each s, 3H, $OC\underline{H}_3$), 5.18 (ddd, *J* = 10.4 Hz, 1.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCHOH$), 5.31 (ddd, *J* = 17.2 Hz, 1.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCHOH$), 5.40 (br s, 1H, $CH_2{=}CHC\underline{H}OH$), 5.42 (dq, *J* = 13.2 Hz, 6.4 Hz, 1H, $CH_3C\underline{H}{=}CHCH_2Ar$), 5.56 (dtq, *J* = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH{=}C\underline{H}CH_2Ar$), 6.01 (ddd, *J* = 17.2 Hz, 10.4 Hz, 4.4 Hz, 1H, $CH_2{=}C\underline{H}CHOH$), 6.65, 6.96 (each s, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.68 ($\underline{C}H_3$), 35.05 ($CH_3CH{=}CH{-}\underline{C}H_2Ar$), 55.71, 55.71 (each, $O\underline{C}H_3$), 70.67, 109.68, 112.75, 114.39, 126.11, 130.07, 130.16, 132.36, 139.86, 147.40, 148.11; EI-MS (70 eV) *m/z* (rel. intensity, %) 248 (M^+, 94), 230 (66), 215 (76), 206 (55), 205 (51), 191 (74), 189 (72), 188 (70), 175 (81), 151 (54), 115 (84), 91 (59); HRMS: calcd. for $C_{15}H_{20}O_3$: 248.1412. Found: 248.1411.

1-(2-Butenyl-5-ethoxy-4-methoxyphenyl)-2-propen-1-ols (8b)

Pure **8b** (1.10 g, 84%) was obtained as pale yellow liquid, R_f = 0.50 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.43 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.67 (dd, *J* = 6.4 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH{=}CHCH_2Ar$), 2.11 (br s, 1H, OH), 3.32 (d, *J* = 6.0 Hz, 2H, $CH_3CH{=}CHC\underline{H}_2Ar$), 3.84 (s, 3H, $OC\underline{H}_3$), 4.07 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 5.17 (ddd, *J* = 10.4 Hz, 1.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCHOH$), 5.30 (ddd, *J* = 17.2 Hz, 1.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCHOH$), 5.39 (br s, 1H, $CH_2{=}CHC\underline{H}OH$), 5.43 (dq, *J* = 13.2 Hz, 6.2 Hz, 1H, $CH_3C\underline{H}{=}CHCH_2Ar$), 5.56 (dtq, *J* = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH{=}C\underline{H}CH_2Ar$), 6.00 (ddd, *J* = 17.2 Hz, 10.4 Hz, 4.6 Hz, 1H, $CH_2{=}C\underline{H}CHOH$), 6.65, 6.96 (each s, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.70 ($OCH_2\underline{C}H_3$), 17.71 ($\underline{C}H_3$), 35.11 ($CH_3CH{=}CH\underline{C}H_2Ar$), 55.82 ($O\underline{C}H_3$), 64.26 ($O\underline{C}H_2CH_3$), 70.70, 111.35, 113.08, 114.37, 126.11, 130.16, 130.26, 132.40, 139.92, 146.75, 148.51; EI-MS (70 eV) *m/z* (rel. intensity, %) 262 (M^+, 72), 244 (47), 201 (44), 191 (53), 189 (42), 177 (49), 175 (69), 174 (51), 161 (46), 145 (63), 131 (58), 128 (47), 115 (75); HRMS: calcd. for $C_{16}H_{22}O_3$: 262.1569. Found: 262.1567.

1-(5-Benzyloxy-2-butenyl-4-methoxyphenyl)-2-propen-1-ols (8c)

Pure **8c** (1.49 g, 92%) was obtained as pale yellow liquid, R_f = 0.60 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.66 (dd, *J* = 6.4 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH{=}CH{-}CH_2Ar$), 1.84 (br s, 1H, OH), 3.32 (d, *J* = 6.0 Hz, 2H, $CH_3CH{=}CH{-}C\underline{H}_2Ar$), 3.86 (s, 3H, $OC\underline{H}_3$), 5.07 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.14 (ddd, *J* = 10.4 Hz, 1.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCHOH$), 5.27 (ddd, *J* = 17.2 Hz, 1.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCHOH$), 5.33 (br s, 1H, $CH_2{=}CHC\underline{H}OH$), 5.42 (dq, *J* = 13.2 Hz, 6.2 Hz, 1H, $CH_3C\underline{H}{=}CHCH_2Ar$), 5.56 (dtq, *J* = 13.2 Hz, 6.0 Hz, 1.3 Hz, 1H, $CH_3CH{=}C\underline{H}CH_2Ar$), 5.94 (ddd, *J* =17.2 Hz, 10.4 Hz, 4.4 Hz, 1H, $CH_2{=}C\underline{H}CHOH$), 6.68, 7.00 (each s, 1H, $Ar\underline{H}$), 7.27-7.43 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.81 ($\underline{C}H_3$), 35.52 ($CH_3CH{=}CH\underline{C}H_2$), 56.08 ($O\underline{C}H_3$), 70.67, 71.16 ($O\underline{C}H_2C_6H_5$), 112.87, 113.54, 114.55, 126.78, 127.54, 127.75, 128.40, 130.18, 131.09, 132.44, 137.20, 139.80, 146.70, 149.07; EI-MS (70 eV) *m/z* (rel. intensity, %) 324 (M^+, 2), 215 (12), 187 (3), 183 (6), 157

(3), 155 (14), 145 (3), 131 (10), 129 (8), 117 (5), 115 (9), 105 (4), 103 (6), 92 (7), 91(100); HRMS: calcd. for $C_{21}H_{24}O_3$: 324.1725. Found: 324.1726.

General procedure for the preparation of naphthalenes 9a-f and 10a-c

Compounds **7a-f** or **8a-c** (1 mmol) dissolved in anhydrous CH_2Cl_2 (20 mL), and mixed with Grubbs catalyst (5% mol). The mixture was stirred for 2 h at ambient temperature under dry argon. Finally, the solvent was removed under reduced pressure, and the residue was subjected to a silica gel column (3:1 hexane/MTBE) or distilled under vacuum to give **9a-f** and **10a-c**, respectively.

1,2-Dimethoxynaphthalene (9a)[18a]

Pure **9a** (0.16 g, 86%) was obtained as colorless liquid, bp 80-81 °C (3 mmHg); R_f = 0.74 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 4.03, 4.10 (each s, 3H, 2-OC$\underline{H}_3$ and 1-OC$\underline{H}_3$), 7.31, 7.60 (each d, *J* = 9.0 Hz, 1H, 3-H and 4-H), 7.36, 7.48 (each t, *J* = 7.5 Hz, 1H, 6-H and 7-H), 7.81, 8.13 (each d, *J* = 8.5 Hz, 1H, 5-H and 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.37 (O$\underline{C}$H$_3$), 60.64 (O$\underline{C}$H$_3$), 114.92, 120.97, 123.73, 123.87, 125.78, 127.39, 128.77, 129.42, 142.59, 148.01; EI-MS (70 eV) *m/z* (rel. intensity, %) 188 (M$^+$, 100), 173 (73), 145 (58), 130 (29), 127 (64), 117 (31), 115 (32), 102 (31); HRMS: calcd. for $C_{12}H_{12}O_2$: 188.0837. Found: 188.0839.

1-Ethoxy-2-methoxynaphthalene (9b)

Pure **9b** (0.19 g, 89%) was obtained as colorless liquid, bp 90-91 °C (3 mmHg); R_f = 0.81 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.31 (t, *J* = 6.8 Hz, 3H, OCH$_2$C$\underline{H}_3$), 3.72 (s, 3H, OC$\underline{H}_3$), 4.03 (q, *J* = 6.8 Hz, 2H, OC$\underline{H}_2$CH$_3$), 7.03, 7.35 (each d, *J* = 9.0 Hz, 1H, 3-H and 4-H), 7.15, 7.28 (each t, *J* = 7.5 Hz, 1H, 6-H and 7-H), 7.57, 8.02 (each d, *J* = 8.5 Hz, 1H, 5-H and 8-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 15.64 (OCH$_2\underline{C}$H$_3$), 56.59 (O$\underline{C}$H$_3$), 68.96 (O$\underline{C}$H$_2$CH$_3$), 115.13, 121.39, 123.81, 123.85, 125.76, 127.42, 129.41, 129.54, 141.83, 148.25; EI-MS (70 eV) *m/z* (rel. intensity, %) 202 (M$^+$, 100), 174 (58), 173 (77), 159 (91), 145 (58), 131 (39), 130 (23), 127 (60), 117 (29), 115 (40), 103 (18), 102 (38); HRMS: calcd. for $C_{13}H_{14}O_2$: 202.0994 Found: 202.0993.

1-Benzyloxy-2-methoxynaphthalene (9c)

Pure **9c** (0.23 g, 83%) was obtained as colorless liquid, bp 145-146 °C (3 mmHg); R_f = 0.86 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 4.05 (s, 3H, OC$\underline{H}_3$), 5.27 (s, 2H, OC$\underline{H}_2$C$_6$H$_5$), 7.37, 7.68 (each d, *J* = 9.0 Hz, 1H, 3-H and 4-H), 7.42, 7.52 (each t, *J* = 7.5 Hz, 1H, 6-H and 7-H), 7.43-7.43 (m, 5H, OCH$_2$C$_6\underline{H}_5$), 7.50, 8.24 (each d, *J* = 8.5 Hz, 1H, 5-H and 8-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 56.75 (O$\underline{C}$H$_3$), 75.10 (O$\underline{C}$H$_2$C$_6$H$_5$), 115.16, 121.43, 123.94, 124.17, 125.95, 127.48, 127.78, 128.06, 128.28, 129.21, 129.57, 137.83, 141.76, 148.33; EI-MS (70 eV) *m/z* (rel. intensity, %) 264 (M$^+$, 100), 231 (37), 203 (33), 202 (35), 143 (16), 116 (14), 115 (42), 105 (28), 101 (32), 91(23); HRMS: calcd. for $C_{18}H_{16}O_2$: 264.1150. Found: 264.1158.

1,2-Dimethoxy-8-methylnaphthalene (9d)[18b,c]

Pure **9d** (0.18 g, 89%) was obtained as colorless liquid, bp 95-96 °C (3 mmHg); R_f = 0.83 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 2.93 (s, 3H, C$\underline{H}_3$), 3.93, 4.00 (each s, 3H, 2-OC$\underline{H}_3$ and 1-OC$\underline{H}_3$), 7.22, 7.23 (each d, *J* = 4.7 Hz, 1H, 7-H and 5-H), 7.29, 7.60 (each d, *J* = 9.0 Hz, 1H, 3-H and 4-H), 7.62 (t, *J* = 4.7 Hz, 1H, 6-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 23.47 ($\underline{C}$H$_3$), 56.58 (O$\underline{C}$H$_3$), 60.92 (O$\underline{C}$H$_3$), 114.39, 123.55, 124.90, 126.36, 128.25, 128.95, 130.77, 133.18, 145.20, 149.66; EI-MS (70 eV) *m/z* (rel. intensity, %) 202 (M$^+$, 96), 187 (100), 172 (26), 159 (81), 144 (59), 141 (24), 131 (17), 128 (16), 116 (27), 115 (58); HRMS: calcd. for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0992.

1-Ethoxy-2-methoxy-8-methylnaphthalene (9e)

Pure **9e** (0.19 g, 89%) was obtained as colorless liquid, bp 100-101 °C (3 mmHg); R_f = 0.87 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.45 (t, *J* = 7.2 Hz, 3H, OCH$_2$C$\underline{H}_3$), 2.90 (s, 3H, C$\underline{H}_3$), 3.92 (s, 3H, OC$\underline{H}_3$), 4.06 (q, *J* = 7.2 Hz, 2H, OC$\underline{H}_2$CH$_3$), 7.16, 7.18 (each d, *J* = 4.8 Hz, 1H, 7-H and 5-H), 7.21, 7.53 (each d, *J* = 9.0 Hz, 1H, 3-H and 4-H), 7.56 (t, *J* = 4.8 Hz, 1H, 6-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 15.37 (OCH$_2\underline{C}$H$_3$), 23.76 ($\underline{C}$H$_3$), 56.71 (O$\underline{C}$H$_3$), 69.25 (O$\underline{C}$H$_2$CH$_3$), 114.49, 123.49, 124.84, 126.42, 126.65, 128.95, 130.88, 133.35, 144.15, 149.81; EI-MS (70 eV) *m/z* (rel. intensity, %) 216 (M$^+$, 79), 188 (34), 187 (100), 173 (52), 172 (20), 159 (54), 145 (27), 144 (37), 116 (20), 115 (46); HRMS: calcd. for $C_{14}H_{16}O_2$: 216.1150. Found: 216.1153.

1-Benzyloxy-2-methoxy-8-methylnaphthalene (9f)

Pure **9f** (0.22 g, 80%) was obtained as colorless crystals, mp 67-68 °C, bp 120-121 °C (3 mmHg); R_f = 0.88 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 2.89 (s, 3H, C$\underline{H}_3$), 3.99 (s, 3H, OC$\underline{H}_3$), 5.07 (s, 2H, OC$\underline{H}_2$C$_6$H$_5$), 7.20, 7.21 (each d, *J* = 5.2 Hz, 1H, 7-H and 5-H), 7.31, 7.62 (each d,

J = 9.0 Hz, 1H, 3-H and 4-H), 7.61 (t, J = 5.2 Hz, 1H, 6-H), 7.35-7.57 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 24.05 ($\underline{C}H_3$), 56.85 ($O\underline{C}H_3$), 75.56 ($O\underline{C}H_2C_6H_5$), 114.61, 123.64, 125.26, 126.49, 127.71, 127.93, 128.36, 128.65, 129.10, 130.92, 133.35, 137.92, 144.12, 149.81; EI-MS (70 eV) *m/z* (rel. intensity, %) 278 (M^+, 100), 263 (23), 245 (21), 235 (12), 202 (28), 145 (25), 129 (14), 115 (22), 91 (20); HRMS: calcd. for $C_{19}H_{18}O_2$: 278.1307. Found: 278.1307.

2,3-Dimethoxynaphthalene (10a)[18d]

Pure **10a** (0.15 g, 82%) was obtained as colorless crystals, mp 67-68 °C; R_f = 0.72 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 4.00 (s, 6H, 2-$OC\underline{H}_3$ and 3-$OC\underline{H}_3$), 7.13 (s, 2H, 1-H and 4-H), 7.35 (t, J = 7.5 Hz, 2H, 6-H and 7-H), 7.70 (d, J = 8.5 Hz, 2H, 5-H and 8-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 55.82 (2-$O\underline{C}H_3$ and 3-$O\underline{C}H_3$), 106.31, 124.17, 126.28, 129.18, 149.45 (2-C and 3-C); EI-MS (70 eV) *m/z* (rel. intensity, %) 188 (M^+, 100), 173 (20), 145 (40), 130 (10), 127 (22), 117 (26), 115 (47), 102 (34); HRMS: calcd. for $C_{12}H_{12}O_2$: 188.0837. Found: 188.0831.

2-Ethoxy-3-methoxynaphthalene (10b)

Pure **10b** (0.17 g, 84%) was obtained as colorless crystals, mp 77-78 °C; R_f = 0.74 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.56 (t, J = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 4.00 (s, 3H, $OC\underline{H}_3$), 4.23 (q, J = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 7.13 (s, 2H, 1-H and 4-H), 7.33, 7.35 (each t, J = 7.5 Hz, 1H, 6-H and 7-H), 7.68 (d, J = 8.5 Hz, 2H, 5-H and 8-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.61 ($OCH_2\underline{C}H_3$), 55.80 ($O\underline{C}H_3$), 64.09 ($O\underline{C}H_2CH_3$), 106.36, 107.27, 124.04, 127.30, 127.90, 126.20, 129.07, 129.19, 148.72, 149.65; EI-MS (70 eV) *m/z* (rel. intensity, %) 202 (M^+, 79), 174 (100), 159 (58), 131 (91), 115 (31), 102 (33); HRMS: calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0992.

2-Benzyloxy-3-methoxynaphthalene (10c)[18e]

Pure **10c** (0.23 g, 89%) was obtained as colorless crystals, mp 137-138 °C; R_f = 0.77 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 4.00 (s, 3H, $OC\underline{H}_3$), 5.27 (s, 2H, $OC\underline{H}_2C_6H_5$), 7.14, 7.16 (each s, 1H, 1-H and 4-H), 7.32, 7.33 (each t, J = 7.5 Hz, 1H, 6-H and 7-H), 7.32-7.50 (m, 5H, $OCH_2C_6\underline{H}_5$), 7.62, 7.68 (each d, J = 8.5 Hz, 1H, 5-H and 8-H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 55.88 ($O\underline{C}H_3$), 7.32 ($O\underline{C}H_2C_6H_5$), 106.63, 108.89, 124.07, 124.26, 126.24, 126.34, 127.30, 127.90, 128.59, 129.06, 129.36, 136.81, 148.58, 149.92; EI-MS (70 eV) *m/z* (rel. intensity, %) 264 (M^+, 15), 145(3), 115(8), 102(9), 91(100); HRMS: calcd. for $C_{18}H_{16}O_2$: 264.1150. Found: 264.1142.

General procedure for preparing 11a-f and 12a-c

Each compound of **7a-f** and **8a-c** (3 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL), added to oxidizing agent PCC (3.5 mmol) or dMP (3.5 mmol), and stirred for 1 h at room temperature. After the end of reaction, the reaction mixture was extracted with ethyl acetate (15 mL × 5). The extracted solution was washed with brine (10 mL × 2), dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum, and the given residue was subjected to chromatographic column (silica gel, *n*-hexane/EA = 5/1) to furnish the pure **11a-f** and **12a-c**.

1-(2-Ally-3,4-dimethoxy)phenyl vinyl ketone (11a)

Pure **11a** (0.45 g, 65%) was obtained as colorless liquid, R_f = 0.61 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.65 (ddd, J = 6.0 Hz, 1.6 Hz, 1.6 Hz, 2H, $ArC\underline{H}_2CH=CH_2$), 3.82, 3.91 (each s, 3H, $OC\underline{H}_3$), 4.97 (ddt, J = 17.4 Hz, 2.0 Hz, 1.6 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.00 (ddt, J = 10.4 Hz, 2.0 Hz, 1.6 Hz, 1H, $C\underline{H}_2=CHCH_2Ar$), 5.92 (dd, $J_{cis\text{-}gem}$ = 10.5 Hz, 1.5 Hz, 1H, $ArCOCH=C\underline{H}_2$), 5.94 (ddt, J = 17.4 Hz, 10.4 Hz, 6.0 Hz, 1H, $CH_2=C\underline{H}CH_2Ar$), 6.15 (dd, $J_{trans\text{-}gem}$ = 17.3 Hz, 1.5 Hz, 1H, $ArCOCH=C\underline{H}_2$), 6.79 (dd, $J_{trans\text{-}cis}$ = 17.3 Hz, 10.5 Hz, 1H, $ArCOC\underline{H}=C\underline{H}_2$), 6.82, 7.28 (each d, J = 8.5 Hz, 1H, H-5 and H-6); ^{13}C-NMR ($CDCl_3$, 50 MHz), δ 30.45, 55.66, 60.75, 109.01, 115.09, 125.86, 130.30, 131.39, 134.32, 136.50, 137.29, 147.79, 155.05, 194.72; EI-MS (70 eV) *m/z* (rel. intensity, %) 232 (M^+, 36), 217 (43), 201 (20), 191 (100), 190 (24), 189 (26), 175 (15), 174 (22), 131 (15), 115 (16); HRMS: calcd. for $C_{14}H_{16}O_3$: 232.1099. Found: 232.1098.

3-(2-Allyl-3,4-dimethoxyphenyl)-1-propenal (11a-un)

Pure **11a-un** (0.26 g, 33%) was obtained as pale yellow crystals, mp 35-36 °C, R_f = 0.66 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.63 (dt, J = 5.6 Hz, 1.8 Hz, 2H, $ArC\underline{H}_2CH=CH_2$), 3.82, 3.92 (each s, 3H, $OC\underline{H}_3$), 4.89 (ddt, J = 17.4 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 5.08 (ddt, J = 10.2 Hz, 1.8 Hz, 1.8 Hz, 1H, $ArCH_2CH=C\underline{H}_2$), 5.99 (ddt, J = 17.4 Hz, 10.2 Hz, 5.6 Hz, 1H, $ArCH_2C\underline{H}=CH_2$), 6.59 (dd, J = 15.8 Hz, 8.0 Hz, 1H, $ArCH=C\underline{H}CHO$), 6.88, 7.44 (each d, J = 8.8 Hz, 1H, $Ar\underline{H}$), 7.65 (d, J = 15.8 Hz, 1H, $ArC\underline{H}=CHCHO$), 9.65 (d, J = 8.0 Hz, 1H, $C\underline{H}O$); ^{13}C-NMR ($CDCl_3$, 50 MHz), δ 29.81, 55.74, 60.96, 110.67, 115.98, 123.39, 126.45, 128.15, 133.81, 136.39, 147.42, 150.35, 154.99, 193.76 (C=O); EI-MS (70 eV) *m/z* (rel. intensity, %) 232 (M^+, 29), 201 (15), 191 (100), 189 (23), 188 (21), 176 (23), 174 (14), 172 (15), 158 (21), 115 (25).

1-(2-Allyl-3-ethoxy-4-methoxy)phenyl vinyl ketone (11b)

Pure **11b** (0.48 g, 65%) was obtained as colorless liquid, R_f = 0.59 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.44 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 3.65 (ddd, *J* = 5.8 Hz, 1.6 Hz, 1.6 Hz, 2H, $ArC\underline{H}_2CH{=}CH_2$), 3.94 (s, 3H, $OC\underline{H}_3$), 4.07 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.99 (ddt, *J* = 17.4 Hz, 2.0 Hz, 1.6 Hz, 1H, $C\underline{H}_2{=}CHCH_2Ar$), 5.09 (ddt, *J* = 10.4 Hz, 2.0 Hz, 1.6 Hz, 1H, $C\underline{H}_2{=}CHCH_2Ar$), 5.97 (dd, $J_{cis\text{-}gem}$ = 10.3 Hz, 1.4 Hz, 1H, $ArCOCH{=}C\underline{H}_2$), 5.96 (ddt, *J* = 17.4 Hz, 10.4 Hz, 5.8 Hz, 1H, $CH_2{=}C\underline{H}CH_2Ar$), 6.20 (dd, $J_{trans\text{-}gem}$ = 17.3 Hz, 1.4 Hz, 1H, $ArCOCH{=}C\underline{H}_2$), 6.85 (dd, $J_{trans\text{-}cis}$ = 17.3 Hz, 10.3 Hz, 1H, $ArCOC\underline{H}{=}CH_2$), 6.86, 7.32 (each d, *J* = 8.5 Hz, 1H, H-5 and H-6); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 15.55, 30.53, 55.74, 68.78, 108.84, 114.94, 125.72, 128.07, 131.31, 134.38, 136.48, 145.33, 146.93, 155.13, 194.77; EI-MS (70 eV) *m/z* (rel. intensity, %) 246 (M^+, 43), 231 (50), 217 (33), 205 (100), 203 (31), 190 (25), 189 (32), 185 (20), 177 (22), 175 (37), 159 (27), 157 (25), 131 (24), 91 (24); HRMS: calcd. for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1257.

1-(2-Allyl-3-benzyloxy-4-methoxy)phenyl vinyl ketone (11c)

Pure **11c** (0.55 g, 60%) was obtained as colorless liquid, R_f = 0.56 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.65 (ddd, *J* = 5.8 Hz, 1.6 Hz, 1.6 Hz, 2H, $C\underline{H}_2CH{=}CH_2$), 3.91 (s, 3H, $OC\underline{H}_3$), 4.90 (ddt, *J* = 17.4 Hz, 2.0 Hz, 1.6 Hz, 1H, $C\underline{H}_2{=}CHCH_2Ar$), 4.95 (ddt, *J* = 10.4 Hz, 2.0 Hz, 1.6 Hz, 1H, $C\underline{H}_2{=}CHCH_2Ar$), 4.99 (s, 2H, $OC\underline{H}_2Ph$), 5.91 (dd, $J_{cis\text{-}gem}$ = 10.5 Hz, 1.5 Hz, 1H, $ArCOCH{=}C\underline{H}_2$), 5.92 (ddt, *J* = 17.4 Hz, 10.4 Hz, 5.8 Hz, 1H, $CH_2{=}C\underline{H}CH_2Ar$), 6.14 (dd, $J_{trans\text{-}gem}$ = 17.4 Hz, 1.5 Hz, 1H, $ArCOCH{=}C\underline{H}_2$), 6.78 (dd, $J_{trans\text{-}cis}$ = 17.4 Hz, 10.5 Hz, 1H, $ArCOC\underline{H}{=}CH_2$), 6.84, 7.30 (each d, *J* = 8.5 Hz, 1H, H-5 and H-6), 7.32-7.48 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 50 MHz), δ 30.61, 55.71, 74.64, 109.06, 115.20, 126.02, 127.86, 127.92, 128.33, 130.32, 131.48, 134.59, 136.53, 137.22, 137.62, 146.59, 155.13, 194.79; EI-MS (70 eV) *m/z* (rel. intensity, %) 308 (M^+, 1), 219 (1), 218 (7), 217 (47), 203 (10), 189 (4), 185 (7), 175 (3), 157 (3), 115 (3), 92 (8), 91 (100); HRMS: calcd. for $C_{20}H_{20}O_3$: 308.1412. Found: 308.1412.

1-[3,4-Dimethoxyl-2-(1-methyallyl)]phenyl vinyl ketone (11d)

Pure **11d** (0.43 g, 58%) was obtained as colorless liquid, R_f = 0.59 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.48 (d, *J* = 6.8 Hz, 3H, $CH_2{=}CHCH(C\underline{H}_3)Ar$), 3.87 (m, 1H, $CH_2{=}CHC\underline{H}(CH_3)Ar$), 3.90, 3.94 (each s, 3H, $OC\underline{H}_3$), 4.96 (ddd, *J* = 10.4 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH(CH_3)Ar$), 4.98 (ddd, *J* = 17.4 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH(CH_3)Ar$), 5.98 (dd, *J* = 10.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCOAr$), 6.07 (dd, *J* = 17.5 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCOAr$), 6.16 (ddd, *J* = 17.4 Hz, 10.4 Hz, 6.4 Hz, 1H, $CH_2{=}C\underline{H}CH(CH_3)Ar$), 6.68 (dd, *J* = 17.5 Hz, 10.6 Hz, 1H, $CH_2{=}C\underline{H}COAr$), 6.79, 7.04 (each d, *J* = 8.5 Hz, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 19.52, 38.10, 55.60, 60.52, 109.38, 113.30, 124.18, 131.33, 132.03, 136.66, 137.65, 142.59, 148.09, 154.65, 197.10; EI-MS (70 eV) *m/z* (rel. intensity, %) 246 (M^+, 20), 231 (100), 218 (38), 216 (27), 205 (95), 204 (26), 203 (75), 201 (21), 189 (26), 188 (28), 187 (28), 175 (26), 115 (21); HRMS: calcd. for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1255.

1-[3-Ethoxy-4-methoxyl-2-(1-methyallyl)]phenyl vinyl ketone (11e)

Pure **11e** (0.49 g, 63%) was obtained as colorless liquid, R_f = 0.61 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.45 (d, *J* = 7.2 Hz, 3H, $CH_2{=}CHCH(C\underline{H}_3)Ar$), 1.46 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 3.89 (m, 1H, $CH_2{=}CHC\underline{H}(CH_3)Ar$), 3.90 (s, 3H, $OC\underline{H}_3$), 4.13 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 5.00 (ddd, *J* = 10.4 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH(CH_3)Ar$), 5.05 (ddd, *J* = 16.4 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH(CH_3)Ar$), 6.04 (dd, *J* = 10.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCOAr$), 6.10 (dd, *J* = 17.5 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCOAr$), 6.22 (ddd, *J* = 16.4 Hz, 10.4 Hz, 5.8 Hz, 1H, $CH_2{=}C\underline{H}CH(CH_3)Ar$), 6.73 (dd, *J* = 17.5 Hz, 10.6 Hz, 1H, $CH_2{=}C\underline{H}COAr$), 6.84, 7.08 (each d, *J* = 8.5 Hz, 1H, $Ar\underline{H}$); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 15.33, 19.41, 37.81, 55.53, 68.09, 109.19, 113.20, 124.04, 131.21, 132.07, 137.67, 138.62, 142.52, 147.03, 154.67, 197.17; EI-MS (70 eV) *m/z* (rel. intensity, %) 260 (M^+, 28), 245 (89), 232 (32), 219 (100), 217 (29), 216 (21), 204 (28), 203 (77), 189 (41), 187 (23), 175 (28), 173 (22), 115 (29); HRMS: calcd. for $C_{16}H_{20}O_3$: 260.1412. Found: 260.1414.

1-[3-Benzyloxy-4-methoxyl-2-(1-methyallyl)]phenyl vinyl ketone (11f)

Pure **11f** (0.58 g, 60%) was obtained as colorless liquid, R_f = 0.57 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.50 (d, *J* = 7.2 Hz, 3H, $CH_2{=}CHCH(C\underline{H}_3)Ar$), 3.96 (m, 1H, $CH_2{=}CHC\underline{H}(CH_3)Ar$), 3.98 (s, 3H, $OC\underline{H}_3$), 5.03 (ddd, *J* = 10.4 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH(CH_3)Ar$), 5.06 (ddd, *J* = 16.4 Hz, 2.4 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCH(CH_3)Ar$), 5.15 (s, 2H, $OC\underline{H}_2C_6H_5$), 6.09 (dd, *J* = 10.6 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCOAr$), 6.15 (dd, *J* = 17.5 Hz, 1.2 Hz, 1H, $C\underline{H}_2{=}CHCOAr$), 6.22 (ddd, *J* = 16.4 Hz, 10.4 Hz, 5.8 Hz, 1H,

$CH_2=C\underline{H}CH(CH_3)Ar$), 6.77 (dd, *J* = 17.5 Hz, 10.6 Hz, 1H, $CH_2=C\underline{H}COAr$), 6.92, 7.15 (each d, *J* = 8.5 Hz, 1H, $Ar\underline{H}$), 7.35-7.58 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 19.57, 37.82, 55.66, 73.88, 109.37, 113.63, 124.45, 127.83, 128.08, 128.27, 129.33, 131.38, 132.20, 137.83, 139.01, 142.52, 146.72, 154.62, 197.24; EI-MS (70 eV) *m/z* (rel. intensity, %) 322 (M^+, 2), 231 (11), 213 (5), 203 (5), 115 (6), 92 (9), 91 (100); HRMS: calcd. for $C_{21}H_{22}O_3$: 322.1569. Found: 322.1567.

1-[(2-Butenyl)-4,5-dimethoxy]phenyl vinyl ketone (12a)

Pure **12a** (0.51 g, 69%) was obtained as colorless liquid, R_f = 0.42 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.64 (dd, *J* = 5.7 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CHCH_2Ar$), 3.46 (d, *J* = 6.2 Hz, 2H, $CH_3CH=CHC\underline{H}_2Ar$), 3.88, 3.92 (each s, 3H, $OC\underline{H}_3$), 5.42 (dq, *J* = 13.2 Hz, 5.7 Hz, 1H, $CH_3C\underline{H}=CHCH_2Ar$), 5.56 (dtq, *J* = 13.2 Hz, 6.2 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2Ar$), 5.93 (dd, *J* = 10.4 Hz, 1.3 Hz, 1H, $ArCOCH=C\underline{H}_2$), 6.18 (dd, *J* = 17.5 Hz, 1.3 Hz, 1H, $ArCOCH=C\underline{H}_2$), 6.76, 7.00 (each s, 1H, H-3 and H-6), 6.81 (dd, *J* = 17.5 Hz, 10.4 Hz, 1H, $ArCOC\underline{H}=CH_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz), δ 17.77, 36.19, 55.84, 56.03, 112.14, 113.23, 126.42, 129.90, 129.96, 130.07, 134.63, 136.54, 146.45, 151.06, 194.88; EI-MS (70 eV) *m/z* (rel. intensity, %) 246 (M^+, 82), 231 (76), 217 (95), 205 (45), 204 (60), 191 (100), 161 (41), 145 (32), 133 (34), 131 (40), 128 (34), 115 (39); HRMS: calcd. for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1256.

1-[(2-Butenyl)-5-ethoxy-4-methoxy]phenyl vinyl ketone (12b)

Pure **12b** (0.56 g, 72%) was obtained as colorless liquid, R_f = 0.40 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.69 (t, *J* = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 1.89 (dd, *J* = 5.6 Hz, 1.3 Hz, 3H, $C\underline{H}_3CH=CHCH_2$), 3.69 (d, *J* = 6.3 Hz, 2H, $CH_3CH=CHC\underline{H}_2$), 4.15 (s, 3H, $OC\underline{H}_3$), 4.33 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 5.71 (dq, *J* = 13.2 Hz, 5.6 Hz, 1H, $CH_3C\underline{H}=CHCH_2$), 5.76 (dtq, *J* = 13.2 Hz, 6.3 Hz, 1.3 Hz, 1H, $CH_3CH=C\underline{H}CH_2$), 6.17 (dd, *J* = 10.3 Hz, 1.3 Hz, 1H, $ArCOCH=C\underline{H}_2$), 6.42 (dd, *J* = 17.0 Hz, 1.3 Hz, 1H, $ArCOCH=C\underline{H}_2$), 7.00, 7.26 (each s, 1H, H-3 and H-6), 7.04 (dd, *J* = 17.0 Hz, 10.3 Hz, 1H, $ArCOC\underline{H}=CH_2$); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 14.66, 17.76, 36.17, 55.82, 64.58, 113.41, 113.80, 126.33, 129.74, 129.92, 130.11, 134.69, 136.51, 145.61, 151.41, 194.83; EI-MS (70 eV) *m/z* (rel. intensity, %) 260 (M^+, 100), 245 (65), 231 (56), 219 (31), 217 (40), 205 (80), 203 (39), 191 (38), 190 (64), 177 (26), 175 (28), 145 (29), 115 (29); HRMS: calcd. for $C_{16}H_{20}O_3$: 260.1412. Found: 260.1412.

1-[5-Benzyloxy-(2-butenyl)-4-methoxy]phenyl vinyl ketone (12c)

Pure **12c** (0.66 g, 69%) was obtained as colorless liquid, R_f = 0.41 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.65 (dd, *J* = 5.7 Hz, 1.2 Hz, 3H, $C\underline{H}_3CH=CHCH_2Ar$), 3.44 (d, *J* = 6.2 Hz, 2H, $CH_3CH=CHC\underline{H}_2Ar$), 3.93 (s, 3H, $OC\underline{H}_3$), 5.13 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.46 (dq, *J* = 13.2 Hz, 5.7 Hz, 1H, $CH_3C\underline{H}=CHCH_2Ar$), 5.49 (dtq, *J* = 13.2 Hz, 6.2 Hz, 1.2 Hz, 1H, $CH_3CH=C\underline{H}CH_2Ar$), 5.84 (dd, *J* = 10.4 Hz, 1.3 Hz, 1H, $ArCOCH_2=C\underline{H}_2$), 6.00 (dd, *J* = 17.5 Hz, 1.3 Hz, 1H, $ArCOCH_2=C\underline{H}_2$), 6.67 (dd, *J* = 17.5 Hz, 10.4 Hz, 1H, $ArCOC\underline{H}=CH_2$), 6.78, 7.02 (each s, 1H, H-3 and H-6), 7.35-7.46 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 17.85, 36.25, 55.96, 71.36, 113.75, 115.63, 126.47, 127.40, 127.95, 128.56, 128.88, 129.50, 130.22, 135.57, 136.49, 136.81, 145.23, 151.89, 194.83; EI-MS (70 eV) *m/z* (rel. intensity, %) 322 (M^+, 2), 232 (2), 231 (11), 213 (5), 203 (5), 189 (3), 181 (2), 175 (3), 115 (6), 92 (9), 91 (100); HRMS: calcd. for $C_{21}H_{22}O_3$: 322.1569. Found: 322.1569.

General procedure for the preparation of naphthols 15a-f and 16a-c

Compound **11a-f** or **12a-c** (1 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) and then mixed with Grubbs catalyst (5% mol). Under dry argon, the mixture, stirred at ambient temperature for 12 h, was concentrated under reduced pressure. The resulting residue was subjected to a silica gel column (3:1 hexane/MTBE) or distilled under vacuum to give **15a-f** and **16a-c**, respectively.

5,6-Dimethoxy-1-naphthol (15a)[19]

Pure **15a** (0.13 g, 62%) was obtained as colorless crystals, mp 149-150 °C; R_f = 0.34 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.98, 3.99 (each s, 3H, $OC\underline{H}_3$), 5.45 (br s, 1H, $O\underline{H}$), 6.68, 7.26 (each d, *J* = 7.6 Hz, 1H, H-2 and H-4), 7.28 (t, *J* = 7.6 Hz, 1H, H-3), 7.68, 7.96 (each d, *J* = 9.2 Hz, 1H, H-7 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 55.76, 60.13, 105.78, 112.93, 114.55, 117.42, 119.73, 125.40, 129.68, 141.67, 147.93, 150.77; EI-MS (70 eV) *m/z* (rel. intensity, %) 204 (M^+, 100), 190 (10), 189 (79), 161 (44), 146 (17), 143 (14), 133 (29), 118 (17), 115 (20); HRMS: calcd. for $C_{12}H_{12}O_3$: 204.0786. Found: 204.0786.

5-Ethoxy-6-methoxy-1-naphthol (15b)

Pure **15b** (0.13 g, 61%) was obtained as colorless crystals, mp 120-121 °C; R_f = 0.34 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.47 (t, *J* = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 3.97 (s, 3H, $OC\underline{H}_3$), 4.19 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 5.67

(br s, 1H, $O\underline{H}$), 6.67, 7.25 (each d, *J* = 7.2 Hz, 1H, H-2 and H-4), 7.27 (t, *J* = 7.2 Hz, 1H, H-3), 7.70, 7.94 (each d, *J* = 8.8 Hz, 1H, H-7 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 15.75, 56.78, 69.32, 106.74, 114.11, 114.26, 118.16, 120.71, 126.20, 129.88, 141.74, 149.05, 151.65; (70 eV) *m/z* (rel. intensity, %) 219 (M^{+1}, 10), 218 (83), 191 (10), 190 (100), 175 (21), 161 (16), 147 (58), 146 (13), 131 (10), 118 (14); HRMS: calcd. for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0944.

5-Benzyloxy-6-methoxy-1-naphthol (15c)

Pure **15c** (0.16 g, 63%) was obtained as colorless crystals, mp 122-123 °C; R_f = 0.33 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.99 (s, 3H, $OC\underline{H}_3$), 5.15 (s, 2H, $OC\underline{H}_2Ph$), 5.45 (br s, 1H, $O\underline{H}$), 6.66, 7.70 (each d, *J* = 8.0 Hz, 1H, H-2 and H-4), 7.29 (t, *J* = 8.0 Hz, 1H, H-3), 7.33, 7.96 (each d, *J* = 9.2 Hz, 1H, H-7 and H-8), 7.25-7.56 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 56.85, 75.27, 106.78, 114.17, 118.38, 120.68, 126.27, 127.90, 128.22, 128.37, 129.86, 130.98, 137.86, 141.74, 149.10, 151.56; (70 eV) *m/z* (rel. intensity, %) 280 (M^+, 43), 202 (9), 189 (12), 161 (10), 131 (9), 118 (10), 91 (100); HRMS: calcd. for $C_{18}H_{16}O_3$: 280.1099. Found: 280.1099.

5,6-Dimethoxy-4-methyl-1-naphthol (15d)

Pure **15d** (0.10 g, 46%) was obtained as yellow liquid, R_f = 0.31 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.78 (s, 3H, $ArC\underline{H}_3$), 3.87, 3.95 (each s, 3H, $OC\underline{H}_3$), 5.35 (br s, 1H, $O\underline{H}$), 6.54, 6.95 (each d, *J* = 10.4 Hz, 1H, H-2 and H-3), 7.22, 8.02 (each d, *J* = 8.8 Hz, 1H, H-7 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 22.97, 56.53, 61.16, 106.16, 113.22, 119.01, 121.79, 124.96, 128.81, 129.36, 144.84, 150.15, 150.25; (70 eV) *m/z* (rel. intensity, %) 219 (M^{+1}, 100), 218 (27), 205 (18), 204 (29), 203 (28), 175 (16), 115 (11); HRMS: calcd. for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0943.

5-Ethoxy-6-methoxy-4-methyl-1-naphthol (15e)

Pure **15e** (0.13 g, 62%) was obtained as colorless crystals, mp 112-113 °C; R_f = 0.27 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.46 (t, *J* = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 2.81 (s, 3H, $ArC\underline{H}_3$), 3.98 (s, 3H, $OC\underline{H}_3$), 4.06 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 5.27 (br s, 1H, $O\underline{H}$), 6.55, 6.99 (each d, *J* = 7.2 Hz, 1H, H-2 and H-3), 7.26, 7.99 (each d, *J* = 9.2 Hz, 1H, H-7 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 15.37, 23.31, 56.70, 69.37, 106.07, 113.57, 118.56, 121.70, 125.75, 128.56, 129.88, 144.09, 149.78, 150.54; (70 eV) *m/z* (rel. intensity, %) 232 (M^+, 56), 204 (21), 203 (100), 189 (24), 175 (17), 160 (20), 131 (20), 115 (21); HRMS: calcd. for $C_{14}H_{16}O_3$: 232.1099. Found: 232.1099.

5-Benzyloxy-6-methoxy-4-methyl-1-naphthol (15f)

Pure **15f** (0.12 g, 40%) was obtained as yellow liquid, R_f = 0.25 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.76 (s, 3H, $C\underline{H}_3$), 3.99 (s, 3H, $OC\underline{H}_3$), 5.17 (s, 2H, $OC\underline{H}_2C_6H_5$), 5.64 (br s, 1H, $O\underline{H}$), 6.40, 6.91 (each d, *J* = 10.4 Hz, 1H, H-2 and H-3), 7.09, 8.01 (each d, *J* = 8.8 Hz, 1H, H-7 and H-8), 7.36-7.59 (m, 5H, $OCH_2C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 23.46, 55.94, 74.77, 112.11, 124.55, 126.04, 127.50, 127.98, 128.18, 128.39, 128.45, 128.75, 128.92, 137.78, 145.78, 149.93, 151.59; (70 eV) *m/z* (rel. intensity, %) 294 (M^+, 11), 204 (13), 203 (100), 91 (73); HRMS: calcd. for $C_{19}H_{18}O_3$: 294.1256. Found: 294.1250.

6,7-Dimethoxy-1-naphthol (16a)[19]

Pure **16a** (0.12 g, 60%) was obtained as colorless crystals, mp 149-150 °C; R_f = 0.17 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.00, 4.02 (each s, 3H, $OC\underline{H}_3$), 5.37 (br s, 1H, $O\underline{H}$), 6.70, 7.29 (each d, *J* = 8.4 Hz, 1H, H-2 and H-4), 7.16 (t, *J* = 8.4 Hz, 1H, H-3), 7.10, 7.48 (each s, 1H, H-5 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 55.79, 55.88, 100.67, 106.25, 107.33, 119.15, 119.51, 124.19, 130.77, 149.01, 149.89, 150.45; EI-MS (70 eV) *m/z* (rel. intensity, %) 204 (M^+, 100), 161 (38), 146 (13), 133 (17), 131 (20), 118 (19), 115 (11); HRMS: calcd. for $C_{12}H_{12}O_3$: 204.0786. Found: 204.0786.

7-Ethoxy-6-methoxy-1-naphthol (16b)

Pure **16b** (0.15 g, 68%) was obtained as colorless crystals, mp 161-162 °C; R_f = 0.16 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.53 (t, *J* = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 3.98 (s, 3H, $OC\underline{H}_3$), 4.25 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 5.47 (br s, 1H, $O\underline{H}$), 6.68, 7.28 (each d, *J* = 8.4 Hz, 1H, H-2 and H-4), 7.15 (t, *J* = 8.4 Hz, 1H, H-3), 7.10, 7.48 (each s, 1H, H-5 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 14.60, 55.80, 64.19, 101.63, 106.34, 107.25, 119.07, 119.60, 124.10, 130.68, 148.27, 150.06, 150.48; (70 eV) *m/z* (rel. intensity, %) 219 (M^{+1}, 13), 218 (91), 191 (12), 190 (100), 175 (20), 161 (14), 147 (48), 146 (13), 131 (11), 118 (12); HRMS: calcd. for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0945.

7-Benzyloxy-6-methoxy-1-naphthol (16c)

Pure **16c** (0.17 g, 62%) was obtained as colorless crystals, mp 156-157 °C; R_f = 0.19 (EA/*n*-hexane = 1/4); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.97 (s, 3H, $OC\underline{H}_3$), 5.24 (s, 2H, $OC\underline{H}_2Ph$), 5.50 (br s, 1H, $O\underline{H}$), 6.65, 7.27 (each d, *J* = 9.0 Hz, 1H, H-2 and H-4), 7.13 (t, $J = 9.0$ Hz, 1H, H-3), 7.29-7.49 (m, 5H, $OCH_2C_6\underline{H_5}$), 7.11, 7.54 (each s, 1H, H-5 and H-8); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 55.83, 70.66, 102.75, 106.56, 107.30, 119.04, 119.50, 124.29, 127.57, 127.89, 128.51, 130.91, 136.72, 148.11, 150.25, 150.51; EI-MS (70 eV) *m/z* (rel. intensity, %) 280 (M^+, 43), 189 (12), 161 (10), 131 (9), 118 (10), 91 (100); HRMS: calcd. for $C_{18}H_{16}O_3$: 280.1099. Found: 280.1100.

X-ray Crystal Structure Determination of Naphthalenes (9f)

A colorless plate crystal of $C_{19}H_{18}O_2$ (**9f**) was obtained by recrystallization from ethylacetate. Data collection was performed at 293 ± 1 K. The crystal (0.20 × 0.60 × 0.80 mm) belongs to the orthorhombic system, space group $P2_12_12_1$, with $a = 5.148(2)$ Å, $b = 9.910(2)$ Å, $c = 28.892(2)$ Å, $V = 1474.1(6)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.254$ g/cm^3, λ(Mo-Kα) = 0.71069 Å. Intensity data were measured on a Rigaku AFC7S diffractometer 2θ of 52.0°. A total of 1757 reflections were collected. The structure was solved by direct methods (SIR92) and refined by a full-matrix least-squares procedure. The non-hydrogen atoms were given anisotropic thermal parameters. The refinement converged to a final $R = 0.062$, $R_w = 0.094$ for 1276 observed reflections [$I > 3.00\ \sigma(I)$] and 160 variable parameters.

X-ray Crystal Structure Determination of Naphthalenes (10c)

A colorless prism crystal of $C_{18}H_{16}O_2$ (**10c**) was obtained by recrystallization from ethylacetate. Data collection was performed at 293 ± 1 K. The crystal (0.26 × 0.58 × 0.80 mm) belongs to the monoclinic system, space group $P2_1/c$, with $a = 12.896(2)$ Å, $b = 5.648(4)$ Å, $c = 20.275(2)$ Å, $\beta = 108.53(1)°$, $V = 1400.1(7)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.254$ g/cm^3, λ(Mo-Kα) = 0.71069 Å. Intensity data were measured on a Rigaku AFC7S diffractometer 2θ of 52.0°. A total of 3127 reflections were collected. The structure was solved by direct methods (SIR92) and refined by a full-matrix least-squares procedure. The non-hydrogen atoms were refined anisotropically. The refinement converged to a final $R = 0.037$, $R_w = 0.046$ for 1378 observed reflections [$I > 3.00\ \sigma(I)$] and 181 variable parameters.

Supporting Information Available

Crystallographic data for the structures **9f** (CCDC 207314) and **10c** (CCDC 207232) is available free of charge via the Internet at http://www.ccdc.cam.ac.uk

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