Water-Accelerated Claisen Rearrangements

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Abstract: Allyl aryl ethers undergo accelerated Claisen and [1,3] rearrangements in the presence of a mixture of trialkylalanes and water or aluminoxanes. The ratio of *ortho*-, *meta*-, and *para*-Claisen products depends to a large extent on the presence of water and to a much lesser extent on the nature of the alane.

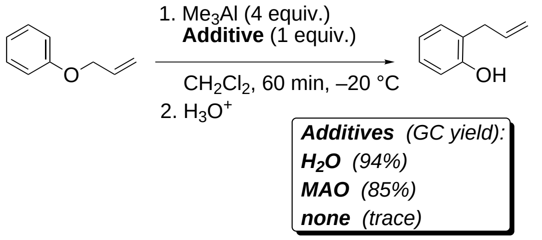
Keywords: alanes; allyl phenyl ethers; Claisen rearrangement; [1,3] rearrangement; water

Introduction

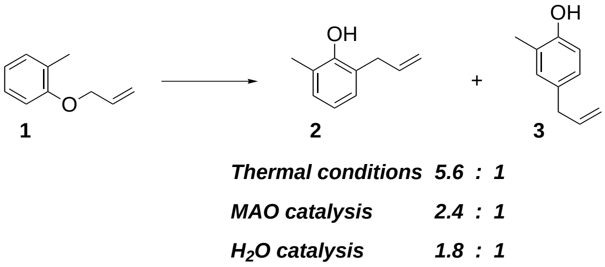
The Claisen rearrangement has proven to be an efficient tool for the selective formation of new carbon-carbon bonds.[1] Since its discovery in 1912,[2] many efforts have focused on the catalysis of this reaction.[3] Several Al(III) derivatives have been used to accelerate the sigmatropic shift, including Et_2AlCl.[4,5] The main drawback of some of these methods can be attributed to side reactions, such as dealkylations, alkene hydrometalations, and/or cyclizations of the *ortho*-products.[3a, e] An attractive procedure without these competitive side reactions was reported by Yamamoto and co-workers,[3c] who used Me_3Al in combination with 4-bromo-2,6-di-*tert*-butylphenol for the rearrangement of allyl phenyl ethers.

The addition of water to organic and organometallic reaction mixtures, including alanes, can lead to surprisingly beneficial effects on the reaction rate, product yield, and regio-, diastereo- and enantioselectivity.[6] A most intriguing aspect of H_2O-promoted transformations is the role that this hard Lewis base can play in providing a source for more highly Lewis acidic species.

Recently, we have found that the addition of stoichiometric quantities of water to the reaction mixture accelerates both the trimethylaluminum-mediated aromatic Claisen reaction and the asymmetric carboalumination of terminal alkenes.[7] Methylaluminoxane (MAO)[8] has a similar effect (Scheme 1). Interestingly, we also observed that in the cases of *ortho*-substituted phenyl ethers a subsequent rearrangement took place giving rise to the *para*-Claisen[9] derivatives (Scheme 2).[7c] While the thermal rearrangement of 1-allyloxy-2-methylbenzene at 190 °C for 24 h provided a 5.6:1 mixture of 2-allyl-6-methylphenol and 4-allyl-2-methylphenol,[10] the corresponding water- and trimethylalane-catalyzed conversions proceeded at 0 °C in a few minutes to give 1.8:1 and 2.4:1 ratios, respectively, of these isomeric phenols. These preliminary results prompted us to pursue a more thorough investigation into the acceleration and selectivity of the Claisen rearrangement of allyl aryl ethers.



Scheme 1.



Scheme 2.

Results and Discussion

In order to evaluate the rate and the regioselectivity of the Claisen rearrangement of allyl aryl ethers in the presence of aluminum-based Lewis acids, the conversion of ether **1** to the *ortho*- and *para*-allylphenols **2** and **3** was studied in detail (Scheme 2, Table 1). After addition of 1 equivalent of H_2O to a solution of 4 equivalents of Me_3Al in CH_2Cl_2, 1 equivalent of substrate was added and the reaction mixture was stirred at – 20 °C. Unless

Table 1. Claisen rearrangement of 1-allyloxy-2-methylbenzene (**1**).[a]

Entry	Alane	Additive	Temperature	Reaction time	*ortho:para* selectivity
1	$EtAlCl_2$	–	-78° C	30 min	1:3.4
2	Et_2AlCl	–	-20° C	2.5 h	3.7:1
3	Me_3Al	–	r.t.	3 d	7.6:1
4	Me_3Al	H_2O	r.t.	1 h	3.2:1
5	Me_3Al	H_2O	-20° C	2 h	1.8:1
6	Me_3Al	H_2O	-78° C	2 d	1.7:1[b]
7	Me_3Al	D_2O	-20° C	5 h	2.9:1
8	Me_3Al	MAO	r.t.	1 h	2.6:1
9	Me_3Al	MAO	-20° C	2 h	2.4:1
10	Me_3Al	MMAO-3A	-20° C	2 h	2.8:1
11	Me_3Al	$PhB(OH)_2$	-20° C	2.5 h	6.8:1
12	Me_3Al	*o*-CF_3-C_6H_4-$B(OH)_2$	-20° C	2 d	6.6:1[b]
13	Me_3Al	4-Br-2,6-*t*-Bu-C_6H_2OH	r.t.	17 h	2.2:1
14	Me_3Al	1,1′-bi-2-naphthol	-20° C	16 h	5.0:1
15	(*i*-Bu)$_3$Al	H_2O	r.t.	15 h	2.6:1
16	(*i*-Bu)$_3$Al	H_2O	-20° C	3 d	1.7:1
17	(*i*-Bu)$_3$Al	MAO	-20° C	2.5 h	2.5:1
18	(*i*-Bu)$_3$Al	MMAO-3A	-20° C	25 h	4.4:1
19	(*n*-Oct)$_3$Al	H_2O	r.t.	1 d	2.7:1
20	HO-IBAO	–	r.t.	4 d	2.2:1[b]
21	MMAO-3A	–	-20° C	2 h	2.9:1
22	MMAO-3A	–	-78° C	2 d	2.9:1[b]
23	TIBDAO	–	r.t.	9 d	2.0:1[a]
24	SMAO	–	r.t.	1 d	5.1:1[a]
25	SMAO	–	r.t.	7 d	9.4:1[a]
26	Et_2Zn	H_2O	r.t.	2 d	–
27	Me_3Al	H_2O	r.t.	1 d	9.1:1[c]
28	Me_3Al	D_2O	r.t.	1 d	9.6:1[c]

[a] Acronyms: MAO (methylaluminoxane), MMAO-3A (modified MAO-type 3A), HO-IBAO (hydroxyisobutylaluminoxane), TIBDAO (tetraisobutyldialuminoxane), SMAO (SiO_2-supported MAO).

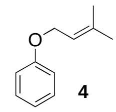
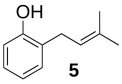
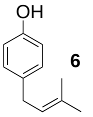
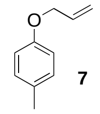
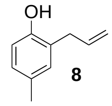
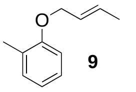
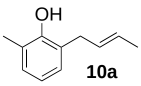
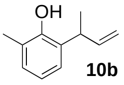
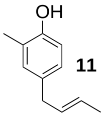
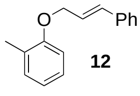
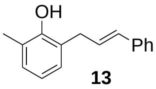
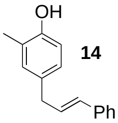
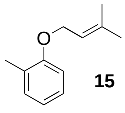
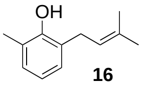
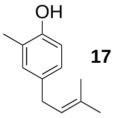
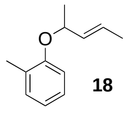
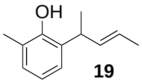
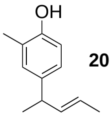
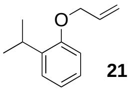
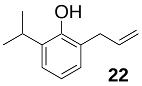
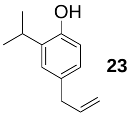
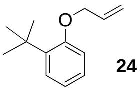
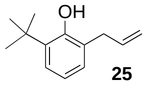
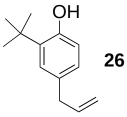
[b] Low conversion of the starting material was detected by GC.

[c] In the presence of 2 equivalents of 2,6-di-*tert*-butyl-4-methylpyridine.

indicated otherwise, reaction times in Table 1 refer to the time necessary for conversions of $> 80\%$.

The largest acceleration factor was achieved with ethylaluminum dichloride (Table 1, Entry 1); however, many side products were obtained and the unusual *para*-selective ratio of **2** to **3** was likely to be strongly influenced by a partially selective product decomposition. The best method in terms of clean conversion, high reaction rate and significant *para*-selectivity was achieved by using Me_3Al in the presence of water at -20 °C (Entry 5). Under these conditions, the *ortho*- and *para*-isomers were obtained in a 1.8:1 ratio after 2 h. At -78 °C, the reaction was extremely sluggish, while only an insignificant change in selectivity resulted (Entry 6). An increase in the reaction temperature accelerated conversion and increased the isomeric ratio in favor of the *ortho*-product (Entry 4). Surprisingly, with D_2O we observed a considerable deuterium isotope effect on the ratio of **2** vs. **3** (Entry 7), and we have currently no conclusive explanation for this interesting phenomenon. It can be speculated that the rate of hydrolysis of Me_3Al with D_2O is significantly different and thus the nature of the activating species is altered vs. H_2O. Alternatively, if the most active species contains an Al-O-D(H) substructure and the accelerating effect on the [3,3] sigmatropic shift is at least partially due to Brønsted acid catalysis,[1c,11,12] a substantial isotope effect would result. The Brønsted acid species could be selectively quenched by a sterically hindered base. Indeed, at -20 °C in the presence of 2 equivalents of 2,6-di-*tert*-butyl-4-methylpyridine, a significant reduction in the rate and the yield of product formation was observed in both the Me_3Al/D_2O and Me_3Al/H_2O reaction mixtures. After 24 h at room temperature, a uniform *ortho*:*para* selectivity of ca. 9:1 was detected (Entries 27 and 28). Benzeneboronic acid also proved to be a good accelerator affording a large amount of the 2-allylphenol **2** (Entry 11); however, the sterically more hindered 2-trifluoromethylbenzeneboronic acid was not as effective (Entry 12). The reaction using Yamamoto's conditions[3c] was initiated at -20 °C, but after 24 h the ratio between starting material **1** and *ortho*-product **2**

Table 2. Me_3Al/H_2O-accelerated Claisen rearrangements.

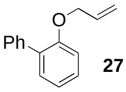
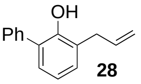
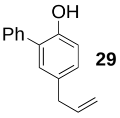
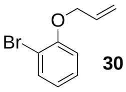
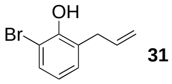
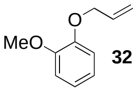
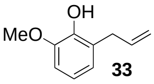
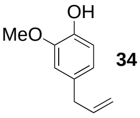
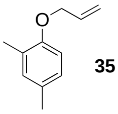
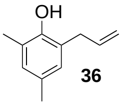
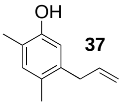
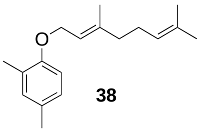
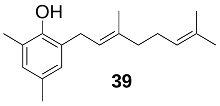
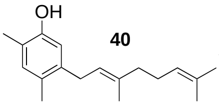
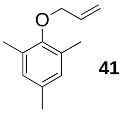
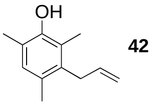
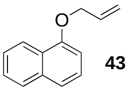
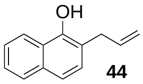
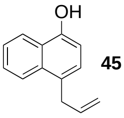
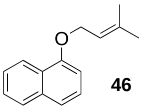
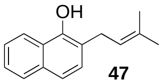
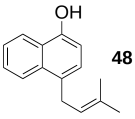
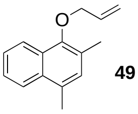
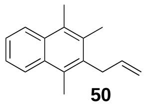
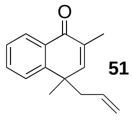
Entry	Allyl ether	Time[a]	Products	Yield (ratio)
1	 **4**	1.25 h	 **5**  **6**	62% (1.2:1)
2	 **7**	1 h	 **8**	84%
3	 **9**	2 h	 **10a**  **10b**  **11**	46% (1:1:2)
4	 **12**	1 h	 **13**  **14**	60% (1.8:1)
5	 **15**	2 h	 **16**  **17**	55% (1:2.1)
6	 **18**	1.5 h	 **19**  **20**	33% (1:2.5)
7	 **21**	24 h (r.t.)	 **22**  **23**	95% (3:1)
8	 **24**	8 h	 **25**  **26**	40% (14:1)

Continued on next page.

was still 9:1. Upon warming this reaction mixture to room temperature and stirring overnight, a final *ortho: para* ratio of 2.2:1 was achieved (Entry 13). In contrast, the use of 1,1′-bi-2-naphthol as an additive afforded a 5.0:1 mixture of both isomers after 16 h at –20 °C (Entry 14). When bulkier trialkylaluminum derivatives were used in combination with water as an additive, the relative amount of the *ortho*-product **2** was constant at –20 °C (Entries 5 and 16), or slightly decreased at r.t. (Entries 4, 15 and 19), but these reactions proceeded at a slower rate than in the presence of Me_3Al. Overall, effects upon use of bulkier alanes were less dramatic than what could have been expected based on the steric interaction of the *ortho*-substituent and the oxygen-complexed alane derivatives in the six-membered chair-like transition state of the Claisen rearrangement leading to product **2.** Using aluminoxanes, including modified and SiO_2-supported MAO, alone or in combination with trialkylalanes did not result in improvements in the product distribution (Entries 8 – 10, 17, 18, 20 – 25). Finally, when other organometallics such as Et_2Zn were used as potential precursors to Lewis acids in the presence of water, no conversion was observed after 2 d at room temperature (Entry 26).

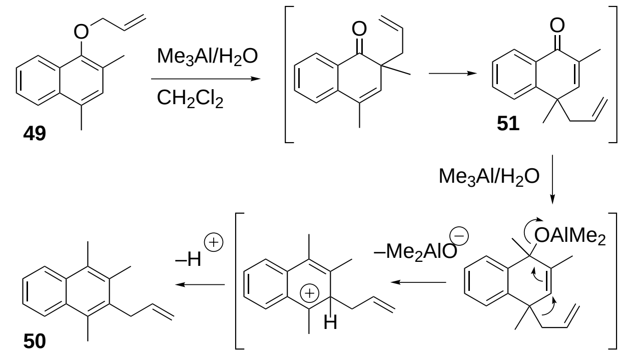
We next examined the influence of substrate structure on the rate and the regioselectivity of the accelerated aromatic Claisen reaction in the presence of Me_3Al and water. Specifically, we probed the substituent effects in the aromatic ring and the allyl ether chain (Table 2). In general, the use of more hindered *ortho*-substituted phenyl ethers resulted in prolonged reaction times as well as higher *ortho*-selectivities (Entries 7 – 9). An *ortho*-bromo or *ortho*-methoxy group led also to strong preference for the *ortho*-Claisen product (Entries 10 and 11). As expected, when the *para*-position was substituted (Entry 2), the *ortho*-isomer was obtained exclusively; however, when both *ortho*- and *para*-positions were substituted, a 3.8 – 2:1 mixture of *ortho*-

Table 2. Continued.

9	 **27**	3.5 h	 **28**	 **29**	89% (13:1)
10	 **30**	1 h		 **31**	[b]
11	 **32**	5 h	 **33**	 **34**	21% (5.5:1)
12	 **35**	5 h	 **36**	 **37**	52% (3.8:1)
13	 **38**	2 h	 **39**	 **40**	50% (2:1)
14	 **41**	2.5 h (r.t.)		 **42**	71%
15	 **43**	21 h	 **44**	 **45**	54% (18:1)
16	 **46**	2 h	 **47**	 **48**	48% (1:4)
17	 **49**	10 h (0 °C)	 **50**	 **51**	58% (1.4:1)

[a] Reactions were performed at $-20\,^{\circ}C$ unless otherwise indicated.
[b] The product decomposed during chromatography on SiO_2.

and *meta*-isomers resulted (Entries 12 and 13). In the case of the 2,4,6-trimethylated phenyl ether **41**, the *meta*-isomer **42** was the sole product (Entry 14). More substituted allylic groups generally favored consecutive [3,3] sigmatropic rearrangements affording larger proportions of the *para*-substituted phenols.[13] With naphthol derivatives, substituent variations in the aryl or allyl subunits provoked more dramatic effects (Entries 15 – 17), affording higher differences in the ratios of the obtained products. While the simple allylated ether **43** reacted almost exclusively to the *ortho*-allylated naphthol **44**, the prenylated **46** provided *para*-product **48** as the major isomer. In general, products of [1,3] sigmatropic (abnormal Claisen) rearrangements[14] formed to a significant extent with more highly substituted allylic ethers (Entries 1, 3, 4, 5, 13, and 16). Products **5**, **10a**, **13**, **16**, **39**, and **47** appear to be derived from intramolecular processes, however, since a crossover experiment with a mixture of **1** and **4** provided only phenols **2**, **3**, and **5**, but no mixed products. In addition, treatment of a mixture of *ortho*-cresol and allylic halides with Me_3Al/H_2O in CH_2Cl_2 provided only minor amounts of *ortho*- and *para*-allylated products after several days at room temperature. A special mention is due for the case of the allyl 2,4-dimethylnaphthyl ether **49** which rearranged to give the 4-allyl-substituted enone **51** as well as the *meta*-allylnaphthalene **50**, which presumably resulted from the methylation of **51** followed by rearrangement and aromatization (Entry 17). A possible mechanism for this sequence of [3,3] sigmatropic shifts and consecutive dienol-benzene rearrangement[15] is presented in Scheme 3.



Scheme 3.

Conclusion

The combined use of Me_3Al and H_2O has proven to be an efficient new method for achieving large rate enhancements in the Claisen rearrangement of allyl aryl ethers along with significant improvements in the regioselectivity in favor of the *para*-Claisen products. The selective preparation of *para*-Claisen products is of particular interest in calixarene chemistry,[16] but the experimental protocols presented in this article should be of general utility for the application of the aromatic Claisen rearrangement in organic synthesis. The mechanistic origin for the large acceleration of the Claisen rearrangement upon use of Me_3Al and H_2O in dichloromethane is very different from the well-known rate enhancement in water as a solvent;[17] the former mixture generates a transient strong Lewis acid related but not identical to MAO,[8] which activates the substrate by complexation to the ether oxygen atom.[6] The actual structure of the highly activated species that is obtained by addition of water to Me_3Al remains to be elucidated, but an interesting isotope effect found for D_2O points toward the potential involvement of Brønsted acid catalysis in the accelerated [3,3] and [1,3] sigmatropic rearrangements.

Experimental Section

General Remarks

All air- and moisture-sensitive reactions were performed under an atmosphere of N_2 and all glassware was dried at 140 °C prior to use. THF was dried by distillation from Na/benzophenone, and dry CH_2Cl_2 was obtained by distillation from CaH_2. 10 wt % solutions of MAO and TIBDAO in toluene were obtained from Aldrich. A 7.7 wt % solution of MMAO-3A in toluene (7.7 wt % Al in toluene) was purchased from Akzo Nobel. $(n\text{-Oct})_3Al$ was obtained from Albemarle as well as the procedures to prepare the HO-IBAO and SMAO. NMR spectra were recorded in $CDCl_3$ at either 300 MHz (^1H) or 75 MHz (^{13}C). Chemical shifts (δ) are reported in parts per million and the residual solvent peak was used as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration and coupling constants. IR spectra were obtained on a Nicolet AVATAR 360 FTIR E. S. P. Spectrometer. Mass spectra were obtained on a VG-70-70 HF instrument. The following starting materials and products are known compounds: **1**,[18] **2**,[18a] **3**,[10] **4**,[19] **5**,[19] **6**,[3c] **7**,[20] **8**,[18a] **9**,[21] **10a**,[22a] **10b**,[22b] **11**,[23] **13**,[24] **14**,[24] **15**,[25] **16**,[25] **17**,[25] **18**,[26] **19**,[26] **20**,[26] **21**,[27] **22**,[28] **23**,[28] **24**,[10,20] **25**,[10] **26**,[10] **27**,[29] **28**,[30] **29**,[31] **30**,[32] **31**,[33] **32**,[34] **33**,[34] **34**,[35] **35**,[3c] **36**,[36] **37**,[36] **38**,[3c] **41**,[37] **42**,[36] **43**,[38] **44**,[38] **45**,[39] **46**,[3c,18b] **47**,[40] **48.**[40]

Representative Procedure for the Preparation of Allyl Aryl Ethers: Preparation of Cinnamyl *o*-Cresyl Ether (12) by the Mitsunobu Reaction

A solution of PPh_3 (2.67 g, 10.2 mmol), cinnamyl alcohol (1.41 g, 10.5 mmol), and *o*-cresol (1.00 g, 9.25 mmol) in THF (10 mL) was treated at 0 °C with DIAD (2.0 mL, 10.1 mmol). The reaction mixture was stirred at 0° for 2.5 h, warmed to room temperature, quenched with 1 M HCl and extracted with Et_2O. The combined organic layers were dried ($MgSO_4$), concentrated, and purified by chromatography on SiO_2 (hexanes/EtOAc, 15:1) to afford **12** as a light yellow oil; yield: 1.45 g (70%); IR: ν = 3081, 3059, 3026, 2915, 2855, 1601, 1494, 1450, 1378, 1241, 1191, 1122, 1016, 966, 751, 692 cm^{-1}; ^1H NMR: δ = 7.44 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.22 – 7.13 (m, 2H), 6.93 – 6.87 (m, 2H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.0, 5.5 Hz, 1H), 4.73 (dd, *J* = 5.5, 1.2 Hz, 2H), 2.31 (s, 3H); ^{13}C-NMR: δ = 156.7, 136.5, 132.2, 130.7, 128.5, 127.7, 126.9, 126.7, 126.5, 126.0, 124.9, 120.5, 111.3, 68.5, 16.3; MS (EI): *m/z* (rel. intensity) = 224 (14), 117 (100); HRMS (EI): *m/z* calcd. for $C_{16}H_{16}O$: 224.1201; found: 224.1199.

1-Allyloxy-2,4-Dimethylnaphthalene (49)

Prepared according to the general procedure. Yellow oil; yield: 82%; IR: ν = 3071, 2923, 2866, 1617, 1597, 1468, 1455, 1386, 1344, 1273, 1245, 1226, 1105, 753 cm^{-1}; ^1H NMR: δ = 7.98 (br t, *J* = 8.6 Hz, 2H), 7.52 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.42 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.12 (s, 1H), 6.14 (ddt, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.48 (ddt, *J* = 17.2,1 1.7, 1.7 Hz, 1H), 5.31 (ddt, *J* = 10.5,1.5, 1.5 Hz, 1H), 4.67 (dt, *J* = 5.1, 1.6 Hz, 1H), 2.70 (s, 3H), 2.58 (s, 3H); ^{13}C NMR: δ = 152.9, 133.9, 133.4, 128.5, 125.8, 124.5, 124.1, 123.3, 118.1, 117.1, 116.6, 70.6, 19.7, 10.6; MS (EI): *m/z* (rel. intensity) = 212 (86), 171 (90), 143 (100), 141 (40), 128 (83), 115 (39); HRMS (EI): *m/z* calcd. for $C_{15}H_{16}O$: 212.1201; found: 212.1202.

Representative Procedure for the Water-Accelerated Claisen Rearrangement: Reaction of the Allyl Aryl Ether 38

A solution of Me_3Al (64 mg, 0.86 mmol) in CH_2Cl_2 (2 mL) was treated with water (4μL, 0.22 mmol) at – 50 °C. The cooling bath was removed and the solution was allowed to warm to room temperature. The reaction mixture was cooled to – 20 °C, treated with a solution of the allyl aryl ether **38** (54 mg, 0.21 mmol) in CH_2Cl_2 (1 mL), and stirred at – 20 °C for 2 h.

The mixture was quenched dropwise with 1 M HCl (1 mL), warmed to room temperature, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), concentrated and purified by chromatography on SiO_2 (hexanes/EtOAc, 10:1) to afford the *ortho*-phenol **39** (yield: 18.1 mg, 33%) and the *meta*-phenol **40** (yield: 9.0 mg, 17%).

ortho-Phenol **39**: Colorless oil; IR: ν = 3475, 2965, 2921, 2856, 1484, 1450, 1377, 1197 cm^{-1}; ^{1}H NMR: δ = 6.83 (s, 1H), 6.77 (s, 1H), 5.31 (br t, *J* = 7.2 Hz, 1H), 5.13 – 5.05 (m, 1H), 5.01 (s, 1H), 3.35 (d, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 2.21 (s, 3H), 2.15 – 2.05 (m, 4H), 1.80 (s, 3H), 1.61 (s, 1H); ^{13}C NMR: δ = 151.0, 138.5, 132.0, 129.6, 129.2, 128.1, 125.9, 124.3, 123.7, 122.0, 39.7, 30.4, 26.3, 25.7, 20.4, 17.7, 16.1, 15.8; MS (EI): *m/z* (rel. intensity) = 258 (19), 173 (100), 135 (27); HRMS (EI): *m/z* calcd. for $C_{18}H_{26}O$: 258.1984; found: 258.1978.

meta-Phenol **40**: Colorless oil; IR: ν = 3417, 2962, 2924, 2857, 1452, 1377, 1276, 1196 cm^{-1}; ^{1}H NMR: δ = 6.89 (s, 1H), 6.60 (s, 1H), 5.23 (br t, *J* = 7.1 Hz, 1H), 5.20 – 5.05 (m, 1H), 4.46 (s, 1H), 3.23 (d, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 2.19 (s, 3H), 2.15 – 2.00 (m, 4H), 1.70 (s, 3H), 1.66 (s, 1H); ^{13}C NMR: δ = 151.7, 138.7, 136.1, 132.5, 131.4, 128.1, 124.3, 122.4, 120.6, 115.2, 39.7, 31.6, 26.6, 25.7, 18.4, 17.7, 16.1, 15.1; MS (EI): *m/z* (rel. intensity) = 258 (23), 189 (26), 135 (22), 123 (20), 88 (33), 86 (87), 84 (100), 69 (29); HRMS: (EI) *m/z* calcd. for $C_{18}H_{26}O$: 258.1984; found: 258.1992.

2-Allyl-1,3,4-trimethylnaphthalene (50)

Yellow oil; yield: 34%; IR: ν = 3075, 3001, 2924, 1637, 1441, 1382, 910, 750 cm^{-1}; ^{1}H NMR: δ = 8.15 – 8.07 (m, 2H), 7.55 – 7.47 (m, 2H), 6.09 (ddt, *J* = 17.2, 10.2, 5.2 Hz, 1H), 5.09 (ddt, *J* = 10.2, 1.9, 1.9 Hz, 1H), 4.89 (ddt, *J* = 17.2, 1.9, 1.9 Hz, 1H), 3.69 (dt, *J* = 5.2, 1.9 Hz, 2H), 2.68 (s, 3H), 2.66 (s, 3H), 2.48 (s, 3H); ^{13}C NMR: δ = 135.9, 134.1, 132.9, 131.7, 131.4, 129.7, 129.3, 124.8, 124.5, 124.4, 124.3, 115.2, 34.8, 16.9, 15.3, 14.9; MS (EI): *m/z* (rel. intensity) = 210 (100), 195 (72), 180 (30), 169 (44), 160 (28); HRMS (EI): *m/z* calcd. for $C_{16}H_{16}$: 210.1409; found: 210.1409.

4-Allyl-2,4-dimethyl-4*H*-naphthalen-1-one (51)

Colorless oil; yield: 24%; IR: ν = 2977, 2927, 1654, 1624, 1450, 1379, 1356, 758 cm^{-1}; ^{1}H NMR: δ = 7.58 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.37 – 7.30 (m, 2H), 6.14 (d, *J* = 1.0 Hz, 1H), 5.29 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1 H), 4.90 – 7.75 (m, 2H), 2.88 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.56 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.38 (s, 3H), 1.47 (s, 3H); ^{13}C NMR: d = 202.9, 152.3, 145.7, 133.2, 130.9, 129.7, 126.7, 126.5, 125.5, 125.2, 117.7, 51.4, 46.6, 27.0, 20.6; MS (EI): *m/z* (rel. intensity) = 212 (57), 171 (75), 143 (100), 141 (40), 128 (83), 127 (26), 115 (55); HRMS (EI): *m/z* calcd. for C_{15} $H_{16}O$: 212.1201; found: 212.1191.

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