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Regioselectivity in Aromatic Claisen Rearrangements

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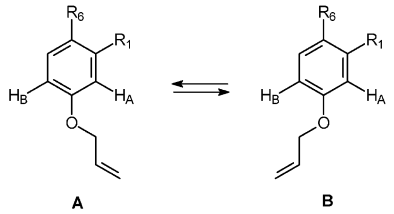
Theoretical calculations and the isomeric product composition for a series of eight meta-substituted allyl aryl ethers confirm the reliability of a new ^{1}H NMR methodology used to predict aromatic Claisen regioselectivity from ground-state conformational preference of the reactant allyloxy group. Frontier HOMO—LUMO intramolecular orbital interactions, a classical approach in predicting reactivity and selectivity for Claisen rearrangements of allyl vinyl ethers, is shown to fail to mimic transition-state orbital interactions for aromatic Claisen rearrangements of meta-substituted allyl aryl ethers. B3LYP/6-31G(d,p) calculations on reactants and transition states are shown, however, to correctly predict the outcome of such aromatic Claisen rearrangements from either the preferential reactant ground-state conformation (theoretical predictions that agree with the NMR measurements) or the less energetic transition state, or both.

Introduction

The recognition that the Claisen rearrangement is the only known 3,3-sigmatropic shift enzyme-catalyzed reaction (chorismate—perphenate rearrangement)[1] has reawakened the interest for this pericyclic transformation of allyl vinyl and allyl aryl ethers, and has further promoted this classic and useful synthetic reaction to an outstanding in vivo biosynthetic transformation.[2] The intramolecular cyclic nature of the Claisen rearrangement is well established, and theoretical calculations have indicated that this exothermic process occurs via a nonsynchronized concerted pathway. There is, however, considerable disagreement over the transition-state structures, which endangers product prediction and the understanding of substituent and solvent effects. Particularly challenging has been to predict the regioselectivity and transition-state structures for aromatic Claisen rearrangements of meta-substituted allyl aryl ethers.[4,5]

Recent theoretical calculations on aromatic and aliphatic Claisen rearrangements were supported by a set of experimental kinetic isotope effects.[4] It was then concluded that the nature of the electronic structure of these transition states is between those calculated at the B3LYP/6-31G* and MP2/6-31G* levels. The main drawback in comparing theoretical and experimental data on Claisen rearrangements lies in the inaccuracy of experimental results, which is often the case for kinetic isotope effects of heavy atoms. This inaccuracy was well observed in the above-mentioned study[4] for which half of the reported experimental data were found to be inaccurate and then remeasured.

SCHEME 1



Probing transition-state structures through the regioselectivity of aromatic Claisen rearrangements should provide therefore a reliable alternative since small differences in transition-state structures lead to significant product changes. It is therefore clear that our ability to predict and explain the products of meta-substituted allyl aryl ether deserves a more extensive theoretical investigation based on a reliable set of experimental data. Toward this end, we have recently developed a new methodology to predict aromatic Claisen regioselectivity based on determining the ground-state conformational preference of the reactant allyloxy moiety (**A** and **B** conformers, Scheme 1) via a collection of ^{1}H NMR data.[6]

From this study[6] we verify that the reactant ground-state conformation closely relates to the ratio of the

(1) Haslam, E. *Shikimic Acid: Metabolism and Metabolites*; Wiley: New York, 1993; see also references therein.

(2) (a) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423. (b) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, 22, 1. (c) Bennett, G. B. *Synthesis* **1977**, 589.

(3) (a) Aviyente, V.; Yoo, H. Y.; Houk, K. M. *J. Org. Chem.* **1997**, *62*, 6121. (b) Yamabe, S.; Okumoto, S.; Hayashi, T. *J. Org. Chem.* **1996**, *61*, 6218. (c) Ganem, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 936. (d) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 2748.

(4) Meyer, M. P.; DelMonte, A. J.; Singleton, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 10865.

(5) (a) Coates, R. M.; Rogers, B. D.; B. D.; Hobbs, S. J.; Peck, D. R.; Curran, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 1160. (b) Brandes, E.; Gricco, P. A.; Gajewski, J. J. *J. Org. Chem.* **1989**, *54*, 515. (c) Gajewski, J. J.; Jurayj, J.; Kimbrough, D. R.; Gande, M. E.; Ganem, B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170.

(6) Rodrigues, D. C.; Fernandes, S. A.; Marsaioli, A. J. *Magn. Reson. Chem.* **2000**, *38*, 970.

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TABLE 1. NOE Differences and Longitudinal Relaxations (T_1) Used To Determine Conformational Preferences from ^{1}H NMR Measurements Using Eq 1 and Then To Predict the Outcome of the Aromatic Claisen Rearrangement for the Allyl Aryl Ethers, and the Observed Experimental Relative Yields of the Two Competitive Products[a]

allyl aryl ether	total yield (%)	%NOE(H_A)[b]/ %NOE(H_B)	T_1(H_B)[c]/ T_1(H_A)	population ratio A:B	product ratio P^A: P^B
1	90	1.1	0.9	1.0:1.0	1.0:1.0
2	96	1.1	0.8	0.9:1.0	0.6:1.0
3	85	1.1	1.3	1.4:1.0	1.2:1.0
4	90	1	0.9	0.9:1.0	0.7:1.0
5	30	2.3	0.8	1.8:1.0	1.8:1.0
6	56	2.6	0.8	2.1:1.0	14:1.0
7	80	1.6	1	1.6:1.0	1.4:1.0
8	90	5.9	1.8	11:1.0	1.0:0

[a] Errors associated with these measurements were found to be less than <5%. [b] Determined at 500 MHz with an NMR spectrometer from $CDCl_3$ or C_5D_5N solutions. [c] Determined by a $180°_{sel}-\tau-90°$ pulse sequence for degassed samples.

competing Claisen rearrangement products. This interesting relationship prompted us to reinvestigate the system both theoretically and experimentally to verify whether the preferential ground-state conformation of aryl allyl ethers bears a correlation with the transition state of lower energy, thus predicting the preferential regiochemistry of aromatic Claisen rearrangements.

Herein we present additional experimental results on a series of asymmetric meta-substituted allyl aryl ethers (**1**−**8**) via which the effectiveness of this new ^{1}H NMR methodology has been further tested. Theoretical calculations on reactants, transition states, and intermediates have also been performed to verify whether the preferential ground-state conformations would indeed correlate with the thermodynamically or kinetically favored reaction pathway for aromatic Claisen rearrangements. Calculations have also been performed to test the ability of frontier HOMO−LUMO orbital interactions to mimic the transition state of aromatic Claisen rearrangements of allyl aryl ethers, a classical approach used to predict reactivity and selectivity for Claisen rearrangements of allyl vinyl ethers.

Results and Discussion

Population of Conformers. Eight meta-substituted allyl aryl ethers (**1**−**8**) were synthezised, and the ratios of their two stable conformers (Table 1) determined at equilibrium conditions by ^{1}H NMR. The Kruse equation[7] (eq 1) was applied to measure the population of conformers **A** and **B** and then to predict the ratio of the two competitive products. Kruse's equation requires the measurement of the NOE enhancements of both hydrogens ortho to the allyloxy residue (H_A and H_B) upon excititation of the methylene group attached to the oxygen of the allyloxy group, and correction of these values by the longitudinal relaxations (T_1) and the correlation times (τ_c) of these two hydrogens. The correlation time ratio was considered close to 1 on the basis of Kruse's results for very similar molecules.[7]

$$\frac{\text{population}(\mathbf{A})}{\text{population}(\mathbf{B})} = \frac{\eta(H_A)}{\eta(H_B)} \frac{T_1(H_B)}{T_1(H_A)} \frac{\tau_c(H_B)}{\tau_c(H_A)} \qquad (1)$$

SCHEME 2

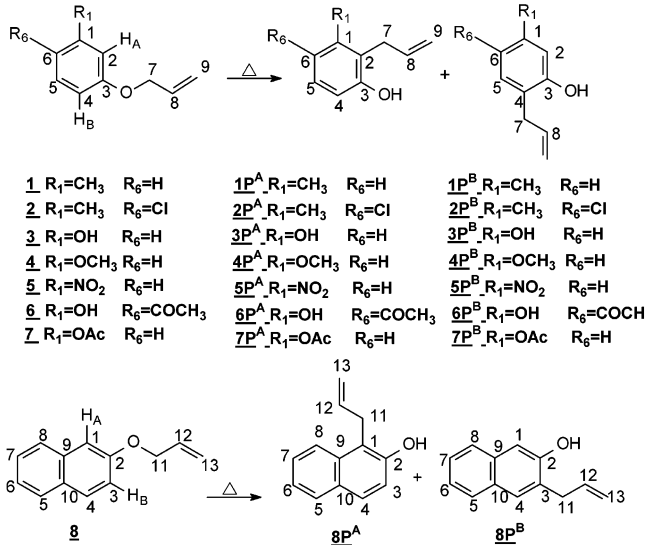


TABLE 2. Electronic and Relative Energies for the Conformers, Transition States, and Intermediates for the Two Competitive Claisen Rearrangements of the Allyl Aryl Ethers 1, 6, 8, and 4 As Calculated by B3LYP DFT/ HF Hybrid Functionals at the 6-31G(d,p) Basis Set

allyl aryl ether	species	electronic energy (hartrees)	rel energy (kcal/mol)
1	**1A**	−463.51630	0
	1B	−463.51634	0
	1I^A	−463.50108	9.6
	1I^B	−463.50277	8.6
	1TS^A	−463.46264	33.7
	1TS^B	−463.46256	33.7
6	**6A**	−652.09238	0
	6B	−652.09162	0.5
	6I^A	−652.08396	5.3
	6I^B	−652.07250	12.5
	6TS^A	−652.04184	31.7
	6TS^B	−652.03507	36.0
8	**8A**	−577.82567	0
	8B	−577.82332	1.5
	8I^A	−577.82253	1.9
	8I^B	−577.79018	22.3
	8TS^A	−577.77651	30.8
	8TS^B	−577.76021	41.1
4	**4A**	−538.70239	0.4
	4B	−538.70312	0
	4I^A	−538.69282	6.5
	4I^B	−538.69460	5.3
	4TS^A	−538.64637	35.6
	4TS^B	−538.64672	35.4

Regioselectivity. Table 1 also summarizes the experimental relative yields of the competitive products ($\mathbf{P}^A$ and $\mathbf{P}^B$) for the aromatic Claisen rearrangements of **1**−**8**. Note that when the population ratios of the two conformers **A** and **B** (Scheme 1) are compared with the product ratios (Scheme 2), a clear correlation between these two ratios is noted: with no exception, the favored conformer **A** or **B** leads to the major product $\mathbf{P}^A$ or $\mathbf{P}^B$ (Table 1). For **1**, for instance, NMR predicts that the populations of conformers **1A** and **1B** are nearly equal (1:1), and accordingly, the observed relative yields of **1P**^{A} and **1P**^{B}

(7) Kruse, L. I.; DeBrosse, C. W.; Kruse, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 5435.

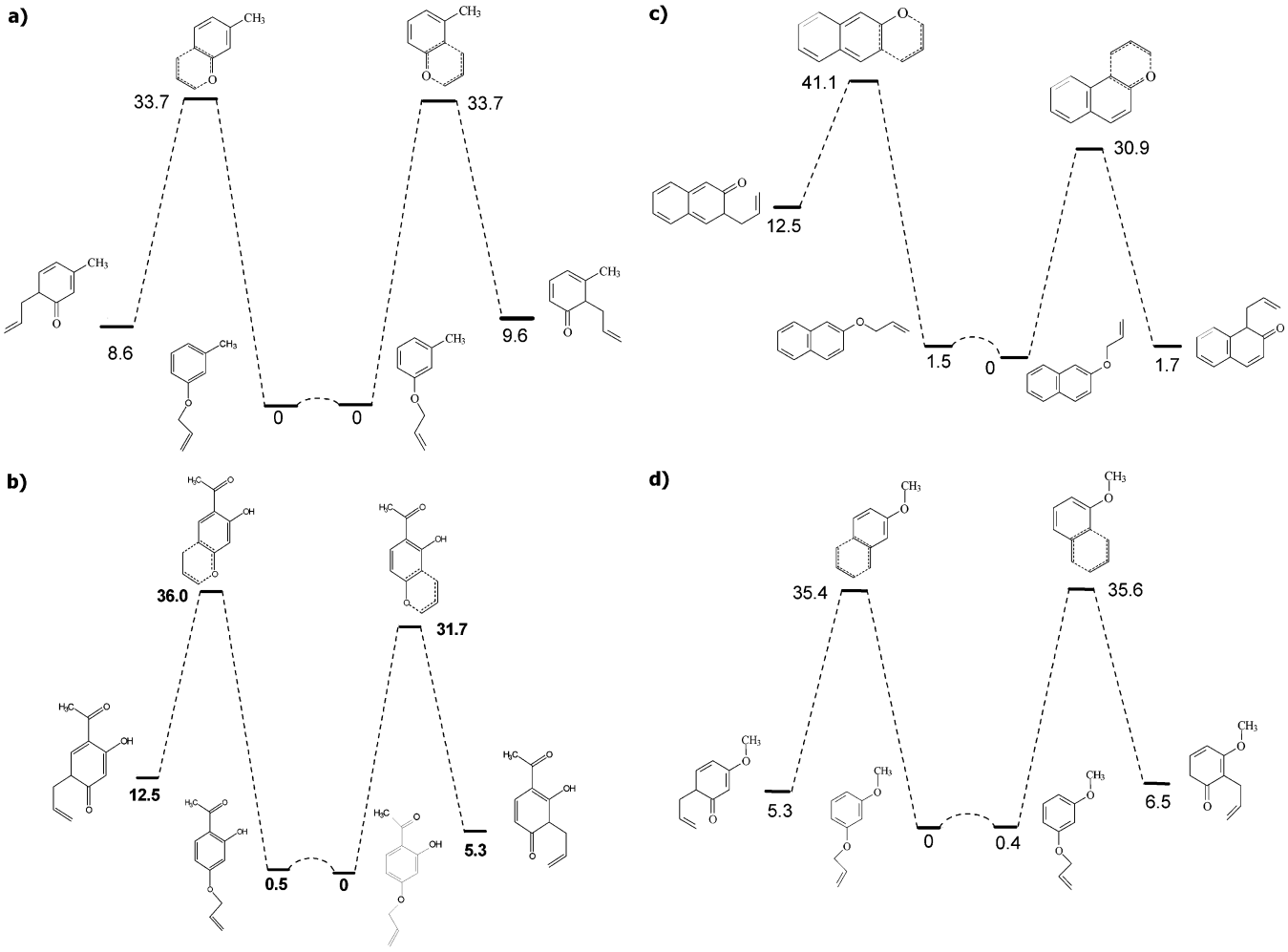


FIGURE 1. B3LYP/6-31G(d,p) potential energy surface diagrams for the competitive aromatic Claisen rearrangements of (a) **1**, (b) **6**, (c) **8**, and (d) **4**.

are nearly the same (1:1). For **8**, NMR indicates that conformer **8A** greatly dominates over **8B**, and indeed, **8P**^{A} is observed as the exclusive product. For **2** and **4**, NMR indicates that conformers **2B** and **4B** are slightly favored, and again, products **2P**^{B} and **4P**^{B} are formed preferentially.

Theoretical Calculations. To verify whether the favored conformer indeed correlates with the kinetically or thermodynamically favored Claisen rearrangement, calculations were performed using the B3LYP DFT/HF hybrid functionals and 6-31G(d,p) basis set. For these calculations, four representative allyl aryl ethers were selected: **1**, **6**, **8**, and **4** (Table 1). Ethers **1**, **6**, and **8** were selected because of increasing preference for conformer **A**, whereas conformer **4B** is slightly predominant over **4**; hence, they provide good test cases to test the accuracy of the theoretical predictions. Table 2 summarizes the electronic and relative energies calculated for conformers **A** and **B**, for the transition states of both competitive Claisen rearrangements (**TS**^{A} and **TS**^{B}), and for their corresponding intermediates (**I**^{A} and **I**^{B}).

Relative Energy of Conformers. For the four allyl aryl ethers tested, conformers **A** and **B** (Scheme 1) are found by the theoretical calculations as the only two local minima, with an energy barrier of 1.3 kcal/mol separating both conformers. Both **1A** and **1B** are found to display nearly the same energy; hence, **1** should show no conformational preference. But **6A** and **8A** are considerably more stable than **6B** (by 0.5 kcal/mol) and **8B** (by 1.5 kcal/mol), whereas the opposite is observed for **4**; that is, **4B** is more stable than **4A** by 0.4 kcal/mol. Therefore, the theoretical predictions on the relative stabilities (hence populations) of the two stable conformers **A** and **B** fully agree with the NMR predictions (Table 1). Note also that the increasing **A**:**B** ratios predicted by NMR with the order **1** < **6** < **8** (Table 1) are also predicted by the B3LYP/6-31G(d,p) calculations as they show, in the same order, increasing energy differences between the corresponding conformers **A** and **B**.

Transition-State and Intermediate Energies. Figure 1 shows potential energy surface diagrams for the two competitive aromatic Claisen rearrengments of **1**, **6**, **8**, and **4**, whereas Figure 2 displays, as a representative example, the optimized structure of **1TS**^{A}. In the diagrams of Figure 1, the energies of the reactant conformers, transition states, and competitive intermediates to final products are all compared. For **1** (Figure 1a), **1TS**^{A} and **1TS**^{B} are both placed 33.7 kcal/mol above the reactants, and are connected to either **1A** or **1B** via intermediates **1I**^{A} and **1I**^{B} of close energies: +9.6 and +8.6 kcal/mol above the reactants. Therefore, as predicted by NMR and as experimentally observed (Table

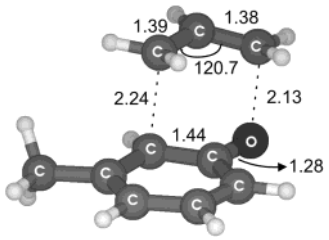
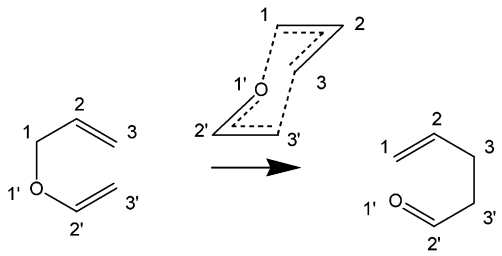


FIGURE 2. B3LYP/6-31G(d,p)-optimized geometry of the transition state for the aromatic Claisen rearrangement of **1**.

SCHEME 3



1), both **1P**^{A} and **1P**^{B} are nearly equally favored, both kinetically and thermodynamically. For **6** and **8**, however, and again as predicted by NMR and observed experimentally (Table 1), the **6P**^{A} and **8P**^{A} products formed via intermediates **6I**^{A} (Figure 1b) and **8I**^{A} (Figure 1c) should be favored since they are connected to the more stable reactants **6A** and **8A** via the less energetic transition states **6TS**^{A} (+31.7 kcal/mol) and **8TS**^{A} (+30.9 kcal/mol). Therefore, aromatic Claisen rearrangements via intermediates **6I**^{A} (+5.3 kcal/mol) and **8I**^{A} (+1.7 kcal/mol) are both thermodynamically and kinetically favored. Note that a greater difference in activation energy (TS energies) in favor of **IA** over **IB** is observed for **8** (−10.3 kcal/mol) than for **6** (−4.3 kcal/mol), which also fully agrees with the observed regioselectivity: a 14:1 mixture of **6P**^{A}/**6P**^{B} is formed, whereas **8P**^{A} is formed exclusively (Table 1).

For **4**, the calculations (Figure 1d) also predict the correct regioselectivity. The more stable conformer **4B** is connected to the thermodynamically favored intermediate **4I**^{B} (+5.3 kcal/mol) via the kinetically favored Claisen rearrangement product, which proceeds via the less energetic transition state **4TS**^{B} (+35.4 kcal/mol) to form the predominant product **4P**^{B} (Table 1). Because all the electronic energies were calculated at 0 K, whereas the reactions were performed at 573 K (200 °C), a quantitative relationship between the reaction product ratios and the calculated transition-state energies is not expected. Considering that the higher the temperature the lower the selectivity, the reaction product ratio should be smaller than the values calculated from the transition-state energy difference.

Electronic Nature of the Aromatic Claisen Rearrangement. Orbital interaction and electronic structure analysis of the reactants and transition states for aromatic Claisen rearrangements of allyl aryl ethers reveals interesting aspects that greatly differ from those of the classical Claisen rearrangement of allyl vinyl ethers (Scheme 3). The transition state of the classical Claisen rearrangement can be described as proceeding through intramolecular HOMO (*O*-vinyl moiety) and LUMO (allyl moiety) orbital interactions within the resonating π-electron system.[9]

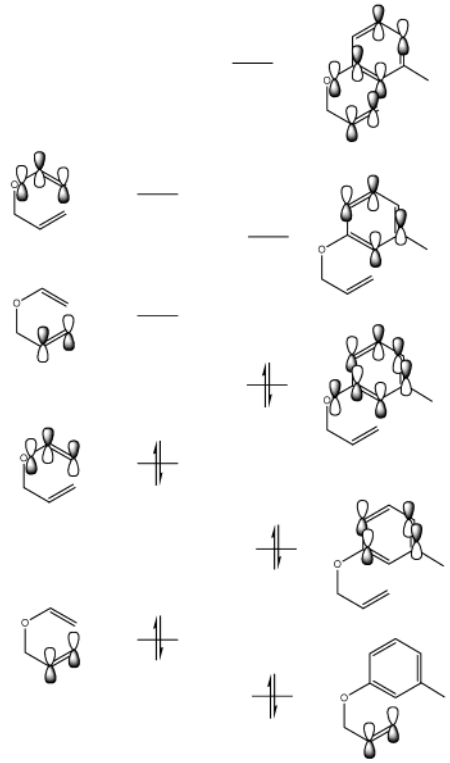


FIGURE 3. Atomic orbitals forming frontier molecular orbitals in the simplest allyl vinyl ether (left) and in allyl aryl ethers (as exemplified for **1**, right), and their relative energies in arbitrary off-scale units.

For aromatic Claisen rearrangements, however, the replacement of a vinyl by an aryl group greatly increases the number and complexity of the molecular π orbitals of the allyl aryl ethers. Hence, simple frontier HOMO−LUMO orbital interactions cannot be used to predict reactivity (and regioselectivity) by mimicking the TS orbital interactions for aromatic Claisen rearrangements. Figure 3 clearly exemplifies this effect; note that for the allyl vinyl ether (left) the LUMO has contributions from the allyl group antibonding π orbital, but for the allyl aryl ether **1** (right) the LUMO has only contributions (coefficients) from the antibonding π orbitals of the aryl group with no coefficients at all at the allyl group. As π-orbital-containing substituents are added to the aryl ring, the π stack becomes more complex, and any resemblance to the allyl vinyl ether HOMO−LUMO interactions disappears completely.

Conclusions

The regioselectivity of aromatic Claisen rearrangements for meta-substituted allyl aryl ethers is correctly predicted by NMR measurements or B3LYP/6-31G(d,p) calculations, or both. NMR reveals the preferred conformation of the reactants, which, with no exception, was found to lead to the major isomeric product. B3LYP/6-

(8) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1994; p 98.

(9) (a) Hammond, G. S.; Hogle, D. H. *J. Am. Chem. Soc.* **1955**, *77*, 338. (b) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111.

31G(d,p) calculations, which accurately describe the energetics of the two competitive Claisen rearrangements, predict correctly the major isomeric product by providing reliable relative energies of competitive conformers, transition states, and intermediates. For all allyl aryl ethers studied herein, the favored product has been shown to arise from the more favored conformer **A** or **B** via both the kinetically and thermodynamically favored reaction pathway. The regioselectivity for the Claisen rearrangement of meta-substituted allyl aryl ethers is mainly influenced, as expected, by the electronic effects of the meta substituent, which governs the relative stability of conformers, transition states, and intermediate to final products.

Because product ratios can be correctly predicted from the population ratios of conformers, it is concluded that the electronic effect of the meta group affects the stability of both conformers and transition states, thus creating a somewhat fortuitous but close and useful relationship between the energies of the ground state of the reactants and transition states for aromatic Claisen rearrangements. However, B3LYP/6-31G(d,p) calculations have shown that, owing to the complex electronic structure of the allyl aryl ethers, simple frontier HOMO−LUMO intramolecular orbital interactions fail to mimic transition-state orbital interactions, and therefore, these interactions cannot be used to predict the reactivity or regioselectivity of the aromatic Claisen rearrangement. Fortunately, however, either NMR data or theoretical calculations on the preferred conformer or competitive transition states, or both, have been demonstrated in this study to be reliable for reactivity and regioselectivity predictions of the outcome of aromatic Claisen rearrangement of allyl aryl ethers.

Experimental Methods

NMR Spectra. These spectra were acquired at 499.883 or 300.069 MHz for 0.2 mol L^{-1} solutions in $CDCl_3$ or d_5-pyridine using TMS as the internal reference. Broad-band decoupled and DEPT ($\theta = 135°$ and 90°) ^{13}C NMR spectra were acquired at 125.696 or 75.452 MHz. 2D NMR data (H,H correlation spectroscopy, gradient COSY, and H,C correlation spectroscopy, HSQC) were taken using pulse sequences applied to the ^1H and ^{13}C NMR signal assignments of all compounds. In the degassed T_1 and NOE relaxation experiments, the samples were submitted four times to a cyclic operation involving rapid vacuum and sonication at 263 K followed by introduction of argon into the evacuated tube equipped with an appropriate septum and a stainless steel syringe needle connected to a vacuum pump via thick-walled silicone-rubber tubing. Argon was introduced via a second stainless steel syringe needle.

^1H T_1 Measurements. After a rapid approximation of the longest ^1H T_1, accurate ^1H T_1 measurements were made at 298 K by applying a standard, 180°−τ−90°−D, sequence. The delay for each sample was 5 times the approximate longest T_1. A minimum of 11 τ values were used, and exponential processing was performed by the appropriate software. The errors for the T_1 measurements were near 2%. Typical data acquisition parameters were spectral width 8000 Hz, acquisition time 2 s, relaxation delay 60 s, and 8 or 16 repetitions or number of transients. Typical data processing parameters were line broadening 1.0 Hz and FT size 65 K.

Nuclear Overhauser Effect (NOE) Enhancement Measurements. NOE difference measurements were performed on the same samples as used to determine ^1H T_1 values. The pulse sequences CYCLENOE, available in the instrument, were employed in different experiments for each sample and produced almost identical NOE difference spectra displaying closely related ratios. The NOE enhancements at positions A and B of the allyl aryl ether Claisen rearrangement products were performed at 298 K on degassed samples prepared as mentioned above.

GC, IR, and MS Measurements. GC−MS analyses were carried out using an instrument equipped with a fused-silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness); the column temperatures were programmed from 373 to 563 K at 15 K min^{-1}. Helium was used as the carrier gas at a flux of 1 mL min^{-1}. Electron ionization mass spectra were acquired at 70 eV. The scanning speed was 0.84 scan s^{-1} from *m*/*z* 40 to *m*/*z* 550.

Computational Methods. Structures of the species investigated were fully optimized by theoretical calculations with no symmetry constraints using B3LYP DFT/HF hybrid functionals and 6-31G(d,p) basis sets[10] as implemented in Gaussian 98.[11] Transition states were characterized by a single negative vibrational frequency. The optimized geometries in Cartesian coordinates of all the species investigated herein are available as Supporting Information.

Preparation of Allyl Aryl Ethers 1−8. General Procedure. Appropriate hydroxybenzene derivatives were dissolved in dry acetone, and both anhydrous K_2CO_3 (2 equiv) and allyl bromide (1.5 equiv) were added. The mixture was refluxed and monitored by thin-layer chromatography (TLC). After completion of the reaction (~8 h), the reaction mixture was filtered and acetone was removed under vacuum. The residue was purified by flash chromatography on silica gel to yield the desired ally aryl ether in an average yield of 90%.

3-(Allyloxy)methylbenzene (1): IR (film) (cm^{-1}) 3031, 2923, 2867, 1602, 1585, 1490, 1457, 1423, 1290, 125.6969, 1159, 1033, 993, 925, 770, 690; ^1H NMR (499.883 MHz, $CDCl_3$) $\delta = 2.32$ (s, 3H), 4.51 (ddd, $^3J = 5.4$ Hz, $^4J = 1.5$ Hz, $^4J = 1.0$ Hz, 2H), 5.27 (ddt, $^3J = 10.5$ Hz, $^2J = 1.5$ Hz, $^4J = 1.0$ Hz, 1H), 5.39 (ddt, $^3J = 17.3$ Hz, $^4J = 1.5$ Hz, $^2J = 1.5$ Hz, 1H), 6.02 (ddt, $^3J = 17.3$ Hz, $^3J = 10.5$ Hz, $^3J = 5.4$ Hz, 1H), 6.72 (dt, $^3J = 8.1$ Hz, $^4J = 2.2$ Hz, 1H), 6.74 (t, $^4J = 2.2$ Hz, 1H), 6.76 (dt, $^3J = 8.1$ Hz, $^4J = 2.2$ Hz, 1H), 7.15 (t, $^3J = 8.1$ Hz, 1H); ^{13}C NMR (125.696 MHz) $\delta = 20.32$, 68.64, 111.55, 115.57, 117.49, 121.65, 129.16, 133.44, 139.45, 158.59; EI-MS *m*/*z* (rel intens) 148 (100) (148.2038 calcd for $C_{10}H_{12}O$, M^+), 133 (72), 105 (36), 91 (15), 77 (16), 41 (12).

3-(Allyloxy)-6-chloromethylbenzene (2): IR (film) (cm^{-1}) 2923, 2863, 1649, 1597, 1577, 1482, 1410, 1381, 1309, 1242, 1171, 1033, 993, 927; ^1H NMR (499.883 MHz, $CDCl_3$) $\delta = 2.32$ (s, 3H), 4.48 (dt, $^3J = 5.4$ Hz, $^4J = 1.2$ Hz, 2H), 5.27 (1H, ddt, $^3J = 10.5$ Hz, $^4J = 1.2$ Hz, $^2J = 1.2$ Hz, 1H), 5.39 (ddt, $^3J = 17.2$ Hz, $^4J = 1.2$ Hz, $^2J = 1.2$ Hz, 1H), 6.02 (ddt, $^3J = 17.2$ Hz, $^3J = 10.5$ Hz, $^3J = 5.4$ Hz, 1H), 6.67 (dd, $^3J = 8.8$ Hz, $^4J = 2.9$ Hz, 1H), 6.73 (d, $^4J = 2.9$ Hz, 1H), 7.20 (d, $^3J = 8.8$ Hz); ^{13}C NMR (125.696 MHz) $\delta = 20.32$, 68.96, 113.29, 117.30, 117.73, 125.696.93, 129.55, 133.05, 136.96, 157.10; EI-MS *m*/*z* (rel intens) 182 (100) (182.6489 calcd for $C_{10}H_{11}OCl$, M^+), 167 (14), 147 (68), 141 (50), 91 (8), 77 (29), 41 (12).

3-(Allyloxy)hydroxybenzene (3): IR (film) (cm^{-1}) 3400, 2872, 1598, 1492, 1461, 1424, 1283, 1172, 1148, 1027, 936, 836, 765, 686; ^1H NMR (499.883 MHz, $CDCl_3$) $\delta = 4.48$ (ddl, $^3J =$

(10) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

5.1 Hz, ^4J = 1.0 Hz, 2H), 5.27 (dl, ^3J = 10.5 Hz, 1H), 5.39 (dl, ^3J = 17.3 Hz, 1H), 5.72 (s, OH, 1H), 6.02 (ddt, ^3J = 17.3 Hz, ^3J = 10.5 Hz, ^3J = 5.1 Hz, 1H), 6.44 (t, ^4J = 1.0 Hz, 1H), 6.50 (dt, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H), 6.51 (dt, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H), 7.11 (t, ^3J = 8.4 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 68.89, 102.37, 107.21, 108.08, 117.88, 130.16, 133.07, 156.66, 159.83; EI-MS *m/z* (rel intens) 150 (100) (150.1760 calcd for $C_9H_{10}O_2$, M^+), 135 (13), 110 (21), 95 (9), 77 (3), 41 (9).

3-(Allyloxy)methoxybenzene (4): IR (film) (cm^{-1}) 3088, 2939, 2836, 1594, 1492, 1454, 1424, 1363, 1334, 1288, 1265, 1201, 1151, 1083, 1044, 992, 927, 836; ^{1}H NMR (499.883 MHz, C_5H_5N) δ = 3.38 (s, 3H), 4.51 (ddd, ^3J = 5.4 Hz, ^4J = 1.5 Hz, ^4J = 1.2 Hz, 2H), 5.28 (ddt, ^3J = 10.5 Hz, ^2J = 1.5 Hz, ^4J = 1.2 Hz, 1H), 5.41 (ddt, ^3J = 17.2 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz), 6.05 (ddt, ^3J = 17.2 Hz, ^3J = 10.5 Hz, ^3J = 5.4 Hz, 1H), 6.49 (t, ^4J = 2.2 Hz, 1H), 6.51 (dt, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1H), 6.52 (dt, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1H), 7.19 (t, ^3J = 8.2 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 55.20, 68.76, 101.16, 106.37, 106.80, 117.66, 129.82, 133.20, 159.79, 160.76; EI-MS *m/z* (rel intens) 164 (100) (164.2028 calcd for $C_{10}H_{12}O_2$, M^+), 149 (18), 137 (45), 121 (20), 91 (27), 77 (46), 41 (15).

3-(Allyloxy)nitrobenzene (5): IR (film) (cm^{-1}) 3098, 2872, 1617, 1582, 1529, 1482, 1425, 1351, 1322, 1286, 1248, 1100, 1024, 994, 931, 861, 818, 729, 738, 672; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 4.62 (dt, ^3J = 5.4 Hz, ^4J = 1.5 Hz, 2H), 5.35 (ddt, ^3J = 10.5 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz, 1H), 5.45 (ddt, ^3J = 17.3 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz, 1H), 6.05 (ddt, ^3J = 17.3 Hz, ^3J = 10.5 Hz, ^3J = 5.4 Hz, 1H), 7.25 (dt, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1H), 7.43 (t, ^3J = 8.3 Hz, 1H), 7.74 (t, ^4J = 2.2 Hz, 1H), 7.82 (dl, ^3J = 8.3 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 69.33, 109.05, 115.88, 118.53, 121.89, 129.95, 132.12, 149.18, 159.09; EI-MS *m/z* (rel intens) 179 (2) (179.1741 calcd for $C_9H_9NO_3$, M^+), 162 (2), 132 (2), 77 (3), 41 (100).

4-(Allyloxy)-2-hydroxyacetophenone (6): IR (film) (cm^{-1}) 3433, 3088, 2928, 1634, 1584, 1506, 1426, 1372, 1332, 125.6963, 1195, 1135, 1068, 1004, 938, 796, 574; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.55 (s, 3H), 4.56 (dt, ^3J = 5.1 Hz, ^4J = 1.6 Hz, 2H), 5.32 (dt, ^3J = 10.5 Hz, ^4J = 1.6 Hz, 1H), 5.42 (dt, ^3J = 17.3 Hz, ^4J = 1.6 Hz, 1H), 6.03 (ddt, ^3J = 17.3 Hz, ^3J = 10.5 Hz, ^3J = 5.1 Hz, 1H), 6.41 (d, ^4J = 2.4 Hz, 1H), 6.46 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H), 7.60 (d, ^3J = 8.8 Hz, 1H), 12.55 (s, 1H); ^{13}C NMR (125.696 MHz) δ = 26.15, 68.88, 101.58, 107.93, 113.90, 118.31, 132.10, 132.26, 164.95, 165.05, 202.53; EI-MS *m/z* (rel intens) 192 (14) (192.2128 calcd for $C_{11}H_{12}O_3$, M^+), 177 (37), 149 (9), 137 (19), 77(11), 41 (100).

2-(Allyloxy)naphthalene (7): IR (film) (cm^{-1}) 3057, 2918, 1630, 1600, 1510, 1470, 1390, 125.6968, 1217, 1183, 1120, 1012, 919, 838, 810, 746, 473; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 4.63 (dt, ^3J = 5.4 Hz, ^4J = 1.5 Hz, 2H), 5.31(ddt, ^3J = 10.5 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz, 1H), 5.46 (ddt, ^3J = 17.2 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz, 1H), 6.11 (ddt, ^3J = 17.2 Hz, ^3J = 10.5 Hz, ^3J = 5.4 Hz, 1H), 7.13 (dl, ^4J = 2.7 Hz, 1H), 7.17 (dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz, 1H), 7.32 (td, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1H), 7.42 (td, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H), 7.71 (dl, ^3J = 7.6 Hz, 1H), 7.73 (d, ^3J = 8.9 Hz, 1H), 7.75.452 (dl, ^3J = 8.6 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 68.75.452, 106.97, 117.70, 118.93, 123.62, 126.31, 126.73, 127.61, 128.99, 129.38, 133.16, 134.48, 156.49; EI-MS *m/z* (rel intens) 184 (20) (184.2368 calcd for $C_{13}H_{12}O$, M^+), 169 (13), 143 (8), 128 (6), 115 (100), 89 (10), 63 (9), 41 (12).

3-(Allyloxy)acetylbenzene (8): IR (film) (cm^{-1}) 3088, 2928, 2872, 1766, 1707, 1488, 1424, 1370, 1313, 1285, 1262, 1210, 1166, 1139, 1019, 900, 867, 783, 688, 529; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.27 (s, 3H), 4.51 (ddd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, ^4J = 1.5 Hz, 2H), 5.28 (ddt, ^3J = 10.5 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz, 1H), 5.40 (ddt, ^3J = 17.3 Hz, ^4J = 1.7 Hz, ^2J = 1.5 Hz, 1H), 6.03 (ddt, ^3J = 17.3 Hz, ^3J = 10.5 Hz, ^3J = 5.1 Hz, 1H), 6.66 (t, ^4J = 2.4 Hz, 1H), 6.68 (dt, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1H), 6.81(dt, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1H), 7.25 (t, ^3J = 8.2 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 21.02, 68.88, 108.40, 112.27, 113.87, 117.72, 129.73, 132.00, 151.54, 159.42, 169.26; EI-MS *m/z* (rel intens) 192 (34) (192.2128 calcd for $C_{11}H_{12}O_3$, M^+), 150 (100), 157 (10), 122 (6), 43 (4).

2-Allyl-3-hydroxymethylbenzene (1P^A) and 4-allyl-3-hydroxymethylbenzene (1P^B): mixture of **1P^A** and **1P^B**; IR (film) (cm^{-1}) 3429, 3078, 2925, 2855, 1708, 1637, 1586, 1508, 1468, 1420, 1272, 1177, 1156, 1111, 996, 956, 913, 816, 776, 747; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.28 (s, 3H), 2.29 (s, 3H), 3.37 (dl, ^3J = 6.1 Hz, 2H), 3.43 (ddd, ^3J = 5.8 Hz, ^4J = 1.5 Hz, ^2J = 1.5 Hz, 2H), 5.02 (ddt, ^3J = 17.1 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.06 (ddt, ^3J = 10.1 Hz, ^4J = 1.8 Hz, ^2J = 1.5 Hz, 1H), 5.13 (ddt, ^3J = 9.9 Hz, ^4J = 1.8 Hz, ^2J = 1.5 Hz, 1H), 5.14 (ddt, ^3J = 17.1 Hz, ^4J = 1.8 Hz, ^2J = 1.5 Hz, 1H), 5.96 (ddt, ^3J = 17.1 Hz, ^3J = 9.9 Hz, ^3J = 5.8 Hz, 1H), 6.00 (ddt, ^3J = 17.1 Hz, ^3J = 10.1 Hz, ^3J = 6.1 Hz, 1H), 6.64 (sl, 1H), 6.66 (d, ^3J = 7.9 Hz, 1H), 6.70 (dl, ^3J = 7.6 Hz, 1H), 6.77 (d, ^3J = 7.6 Hz, 1H), 7.00 (d, ^3J = 7.9 Hz, 1H), 7.01 (t, ^3J = 7.9 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 19.56, 20.98, 30.55, 34.79, 113.35, 115.37, 116.25, 116.50, 121.63, 122.08, 122.78, 123.83, 126.99, 130.20, 135.51, 136.66, 137.92, 138.16, 153.90, 153.97; EI-MS *m/z* (rel intens) 148 (90) (148.2038 calcd for $C_{10}H_{12}O$, M^+), 133 (100), 105 (77), 91 (47), 77 (40), 51 (21), 41 (8).

2-Allyl-6-chloro-3-hydroxymethylbenzene (2P^A): IR (film) (cm^{-1}) 3428, 3080, 2978, 2925, 2855, 1637, 1581, 1493, 1442, 1398, 1379, 1278, 1227, 1193, 1164, 1140, 1106, 1031, 998, 917, 807, 661, 620; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.28 (s, 3H), 3.33 (dl, ^3J = 6.2 Hz, 2H), 4.90 (s, OH, 1H), 5.14 (ddt, ^3J = 16.9 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.16 (ddt, ^3J = 10.1 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.94 (ddt, ^3J = 16.9 Hz, ^3J = 10.1 Hz, ^3J = 6.2 Hz, 1H), 6.61 (d, ^3J = 8.4 Hz, 1H), 7.11 (d, ^3J = 8.4 Hz, 1H); ^{13}C NMR (75.452 MHz) δ = 19.74, 34.51, 116.77, 118.05, 124.07, 125.696.56, 130.21, 135.60, 135.68, 152.30; EI-MS *m/z* (rel intens) 182 (100) (182.6489 calcd for $C_{10}H_{11}OCl$, M^+), 167 (17), 147 (87), 132 (33), 91 (54), 77 (24), 51 (36), 41 (13).

4-Allyl-6-chloro-3-hydroxymethylbenzene (2P^B): IR (film) (cm^{-1}) 3428, 3080, 2978, 2925, 2855, 1637, 1581, 1493, 1442, 1398, 1379, 1278, 1227, 1193, 1164, 1140, 1106, 1031, 998, 917, 807, 661, 620; ^{1}H NMR (300.069 MHz, $CDCl_3$) δ = 2.32 (s, 3H), 3.45 (dt, ^3J = 5.7 Hz, ^4J = 1.8 Hz, 2H), 4.90 (s, OH, 1H), 4.97 (ddt, ^3J = 17.2 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.07 (ddt, ^3J = 10.3 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.92 (ddt, ^3J = 17.2 Hz, ^3J = 10.3 Hz, ^3J = 5.7 Hz, 1H), 6.67 (s, 1H), 7.06 (s, 1H); ^{13}C NMR (75.452 MHz) δ = 16.49, 31.29, 114.07, 115.62, 124.28, 125.696.68, 127.51, 134.78, 135.15, 152.30; EI-MS *m/z* (rel intens) 182 (100) (182.6489 calcd for $C_{10}H_{11}OCl$, M^+), 167 (44), 147 (60), 132 (42), 115 (27), 91 (90), 77 (45), 51 (62), 41 (12).

2-Allyl-1,3-dihydroxybenzene (3P^A): IR (film) (cm^{-1}) 3415, 2918, 1614, 1465, 1370, 1294, 1206, 1106, 1020, 995, 919, 782, 742; ^{1}H NMR (300.069 MHz, $CDCl_3$) δ = 3.47 (ddt, ^3J = 6.0 Hz, ^4J = 1.8 Hz, ^4J = 1.5 Hz, 2H), 5.13 (ddt, ^3J = 10.1 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.15 (ddt, ^3J = 17.2 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.29 (s, 2OH, 2H), 6.01 (ddt, ^3J = 17.2 Hz, ^3J = 10.1 Hz, ^3J = 6.0 Hz, 1H), 6.41 (d, ^3J = 8.4 Hz, 2H), 6.96 (t, ^3J = 8.4 Hz, 1H); ^{13}C NMR (75.452 MHz) δ = 27.46, 108.26, 112.01, 115.93, 127.63, 135.94, 155.02; EI-MS *m/z* (rel intens) 150 (96) (150.1760 calcd for $C_9H_{10}O_2$, M^+), 132 (18), 123 (49), 107 (20), 91 (100), 77 (29), 51 (47).

4-Allyl-1,3-dihydroxybenzene (3P^B): IR (film) (cm^{-1}) 3390, 2976, 2929, 2856, 1723, 1617, 1511, 1464, 1377, 1265, 1225, 1161, 1112, 975.452, 917, 839, 738, 703; ^{1}H NMR (499.883 MHz, $CDCl_3$): δ = 3.34 (dl, ^3J = 6.4 Hz, 2H), 5.12 (s, OH, 2H), 5.14 (dd, ^3J = 9.9 Hz, ^2J = 1.5 Hz, 1H), 5.15 (dd, ^3J = 17.4 Hz, ^2J = 1.5 Hz, 1H), 6.00 (ddt, ^3J = 17.4 Hz, ^3J = 9.9 Hz, ^3J = 6.4 Hz, 1H), 6.36 (sl, 1H); 6.37 (dd, ^3J = 7.6 Hz, ^4J = 2.4 Hz, 1H), 6.94 (d, ^3J = 7.6 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 34.56, 103.30, 107.74, 116.31, 117.35, 131.06, 136.76, 155.16, 155.47; EI-MS *m/z* (rel intens) 150 (100) (150.1760 calcd for $C_9H_{10}O_2$, M^+), 132 (41), 123 (26), 107 (43), 91 (85), 77 (31), 51 (25).

2-Allyl-3-methoxybenzene (4P^A): IR (film) (cm^{-1}) 3443, 3078, 2928, 2838, 1637, 1596, 1499, 1470, 1440, 1326, 1274,

1243, 1211, 1115, 1070, 997, 913, 777, 736, 634; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 3.46 (ddd, ^3J = 5.8 Hz, ^4J = 1.8 Hz, ^4J = 1.5 Hz, 2H), 3.80 (s, 3H), 5.07 (ddt, ^3J = 10.9 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.10 (ddt, ^3J = 17.4 Hz, ^4J = 1.8 Hz, ^2J = 1.8 Hz, 1H), 5.98 (ddt, ^3J = 17.4 Hz, ^3J = 10.9 Hz, ^3J = 5.8 Hz), 6.48 (dl, ^3J = 7.5 Hz, 1H), 6.49 (dl, ^3J = 7.5 Hz, 1H), 7.07 (t, ^3J = 7.5 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 27.32, 55.79, 103.32, 108.79, 113.61, 115.34, 127.51, 136.30, 155.14, 158.22; EI-MS *m/z* (rel intens) 164 (100) (164.2028 calcd for $C_{10}H_{12}O_2$, M^+), 149 (31), 135 (38), 121 (36), 107 (46), 91 (36), 77 (59), 65 (25), 51 (33), 43 (13).

4-Allyl-3-methoxybenzene (4P^B): IR (film) (cm^{-1}) 3417, 3078, 3034, 2928, 2838, 1619, 1596, 1519, 1468, 1434, 1285, 1202, 1162, 1113, 1037, 997, 959, 915, 836, 780, 633, 574; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 3.37 (dl, ^3J = 6.1 Hz, 2H), 3.79 (s, 3H), 5.16 (ddt, ^3J = 9.6 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.17 (ddt, ^3J = 17.6 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.32 (s, OH, 1H), 6.02 (ddt, ^3J = 17.6 Hz, ^3J = 9.6 Hz, ^3J = 6.1 Hz, 1H), 6.46 (d, ^4J = 2.4 Hz, 1H), 6.48 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1H), 7.02 (d, ^3J = 8.2 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 34.43, 55.28, 102.00, 106.22, 116.14, 117.46, 130.81, 136.79, 154.97, 159.49; EI-MS *m/z* (rel intens) 164 (100) (164.2028 calcd for $C_{10}H_{12}O_2$, M^+), 149 (20), 137 (67), 121 (27), 103 (49), 91 (38), 77 (70), 65 (30), 51 (43), 41 (22).

2-Allyl-3-nitrobenzene (5P^A): IR (film) (cm^{-1}) 3402, 2928, 2856, 1637, 1608, 1525, 1452, 1333, 1280, 1206, 1153, 1092, 1000, 960, 919, 839, 807, 736, 668, 587; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 3.61 (dl, ^3J = 6.1 Hz, 2H), 5.15 (ddl, ^3J = 16.2 Hz, ^2J = 1.5 Hz, 1H), 5.16 (ddl, ^3J = 11.0 Hz, ^2J = 1.5 Hz, 1H), 5.83 (s, OH, 1H), 6.01 (ddt, ^3J = 16.2 Hz, ^3J = 11.0 Hz, ^3J = 6.1 Hz, 1H), 7.07 (d, ^3J = 8.2 Hz, 1H), 7.23 (dd, ^3J = 8.2 Hz, ^3J = 7.9 Hz, 1H), 7.42 (d, ^3J = 7.9 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 29.97, 116.65, 116.87, 120.04, 120.50, 127.65, 134.35, 150.99, 155.35; EI-MS *m/z* (rel intens) 179 (8) (179.1741 calcd for $C_9H_9O_3N$, M^+) 162 (44), 150 (42), 145 (47), 131 (33), 116 (16), 103 (40), 89 (17), 77 (100), 65 (31), 51 (69), 43 (18).

4-Allyl-3-nitrobenzene (5P^B): IR (film) (cm^{-1}) 3458, 3088, 2923, 2851, 1640, 1597, 1511, 1427, 1349, 1262, 1117, 1082, 998, 953, 928, 880, 818, 741; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 3.48 (dl, ^3J = 6.4 Hz, 2H), 5.18 (ddl, ^3J = 17.1 Hz, ^4J = 1.5 Hz, 1H), 5.20 (ddl, ^3J = 10.2 Hz, ^2J = 1.5 Hz, 1H), 5.99 (ddt, ^3J = 17.1 Hz, ^3J = 10.2 Hz, ^3J = 6.4 Hz, 1H), 7.27 (d, ^3J = 8.2 Hz, 1H), 7.68 (d, ^4J = 2.1 Hz, 1H), 7.76 (dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 34.69, 110.54, 115.89, 117.62, 130.68, 133.85, 134.61, 147.42, 154.40; EI-MS *m/z* (rel intens) 179 (100) (179.1741 calcd for $C_9H_9O_3N$, M^+), 164 (12), 147 (3), 132 (13), 118 (14), 103 (33), 89 (6), 77 (49), 63 (13), 51 (26), 41 (6).

3-Allyl-2,4-dihydroxyacetophenone (6P^A): IR (film) (cm^{-1}) 3134, 2923, 1625, 1589, 1494, 1373, 1320, 1274, 1211, 1112, 1039, 1001, 924, 794, 611, 563, 444; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.57 (s, 3H), 3.48 (dl, ^3J = 6.1 Hz, 2H), 5.12 (dl, ^3J = 10.3 Hz, 1H), 5.16 (dl, ^3J = 17.1 Hz, 1H), 5.99 (ddt, ^3J = 17.1 Hz, ^3J = 10.3 Hz, ^3J = 6.1 Hz, 1H), 6.24 (s, OH, 1H), 6.41 (d, ^3J = 8.8 Hz, 1H), 7.56 (d, ^3J = 8.8 Hz, 1H), 12.55 (s, OH, 1H); ^{13}C NMR (125.696 MHz) δ = 26.17, 26.61, 107.65, 112.62, 113.84, 116.00, 130.71, 135.45, 161.30, 162.72, 203.08; EI-MS *m/z* (rel intens): 192 (32) (192.2128 calcd for $C_{11}H_{12}O_3$, M^+), 177 (73), 149 (34), 121 (5), 91(14), 77 (20), 65 (14), 43 (100).

5-Allyl-2,4-dihydroxyacetophenone (6P^B): IR (film) (cm^{-1}) 3281, 2923, 1637, 1508, 1434, 1373, 1329, 1238, 1134, 1052, 956, 916, 796, 636, 562; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.56 (s, 3H), 3.36 (dl, ^3J = 6.4 Hz, 2H), 5.16 (ddt, ^3J = 10.3 Hz, ^2J = 1.7 Hz, ^4J = 1.5 Hz, 1H), 5.18 (ddt, ^3J = 17.1 Hz, ^2J = 1.7 Hz, ^4J = 1.5 Hz, 1H), 6.00 (ddt, ^3J = 17.1 Hz, ^3J = 10.3 Hz, ^3J = 6.4 Hz, 1H), 7.26 (s, 1H), 7.46 (s,1H), 12.55 (s, 1H); ^{13}C NMR (125.696 MHz) δ = 26.29, 34.15, 103.70, 114.20, 116.82, 117.49, 132.80, 136.09, 161.21, 163.71, 202.65; EI-MS *m/z* (rel intens): 192 (57) (192.2128 calcd for $C_{11}H_{12}O_3$, M^+), 177 (100), 165 (3), 149 (16), 121 (3), 103 (3), 91 (4), 77 (5), 43 (14).

Allyl-2-naphthol (7P^A): IR (film) (cm^{-1}) 3415, 3074, 2980, 2925, 2656, 1628, 1599, 1515, 1467, 1438, 1395, 1355, 1264, 1144, 1062, 986, 969, 914, 810, 746, 547; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 3.85 (dl, ^3J = 5.9 Hz, 2H), 5.09 (ddl, ^3J = 17.1 Hz, ^2J = 1.7 Hz, 1H), 5.12 (ddl, ^3J = 10.3 Hz, ^2J = 1.7 Hz, 1H), 6.10 (ddt, ^3J = 17.1 Hz, ^3J = 10.3 Hz, ^3J = 5.9 Hz, 1H), 7.11 (d, ^3J = 8,8 Hz, 1H), 7.36 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz 1H), 7.50 (t, ^3J = 7.5 Hz, ^4J = 1.0 Hz 1H), 7.68 (d, ^3J = 8.8 Hz, 1H), 7.80 (d, ^3J = 7.6 Hz, 1H), 7.93 (d, ^3J = 7.6 Hz, 1H); ^{13}C NMR (125.696 MHz) δ = 29.20, 115.84, 116.84, 117.87, 122.98, 123.11, 126.43, 128.25, 128.52, 129.35, 133.20, 135.76, 151.11; EI-MS *m/z* (rel intens) 184 (96) (184.2368 calcd for $C_{13}H_{12}O$, M^+), 169 (100), 152 (11), 141 (29), 128 (21), 115 (27), 102 (5), 91 (9), 76 (13), 63 (19), 51 (2), 43 (1).

2-Allyl-3-hydroxyacetylbenzene (8P^A): IR (film) (cm^{-1}) 3436, 3083, 2923, 1737, 1638, 1607, 1514, 1465, 1430, 1371, 1233, 1151, 1108, 1022, 976, 913, 672, 600; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.28 (s, 3H), 3.35 (dl, ^3J = 6.4 Hz, 2H), 5.12 (ddt, ^3J = 9.8 Hz, ^2J = 1.8 z, ^4J = 1.5 Hz, 1H), 5.13 (ddt, ^3J = 17.4 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.96 (ddt, ^3J = 17.4 Hz, ^3J = 9.8 Hz, ^3J = 6.4 Hz, 1H), 6.64 (dl, ^3J = 8.2 Hz, 1H), 6.66 (dl, ^3J = 8.2 Hz, 1H), 7.08 (t, ^3J = 8.2 Hz, 1H); ^{13}C NMR (75.452 MHz) δ = 21.10, 34.40, 109.28, 113.50, 116.48, 123.39, 130.60, 136.19, 149.87, 154.69, 169.95; EI-MS *m/z* (rel intens) 192 (2) (192.2128 calcd for $C_{11}H_{12}O_3$, M^+) 150 (35), 135 (12), 123 (19), 107 (11), 77 (24), 43 (100).

4-Allyl-3-hydroxyacetylbenzene (8P^B): IR (film) (cm^{-1}) 3436, 3083, 2923, 1737, 1638, 1607, 1514, 1465, 1430, 1371, 1233, 1151, 1108, 1022, 976, 913, 672, 600; ^{1}H NMR (499.883 MHz, $CDCl_3$) δ = 2.30 (s, 3H), 3.32 (dt, ^3J = 6.4 Hz, ^4J = 1.5 Hz, 2H), 5.07 (ddt, ^3J = 10.1 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.09 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.5 Hz, 1H), 5.90 (ddt, ^3J = 17.1 Hz, ^3J = 10.1 Hz, ^3J = 6.4 Hz, 1H), 6.54 (d, ^4J = 2.4 Hz, 1H), 6.59 (dd, ^3J = 8.1 Hz, ^4J = 2.4 Hz, 1H), 7.01 (d, ^3J = 8.1 Hz, 1H); ^{13}C NMR (75.452 MHz) δ = 20.87, 28.46, 113.45, 114.62, 115.99, 118.45, 127.43, 135.30, 149.78, 155.28, 169.73; EI-MS *m/z* (rel intens) 192 (14) (192,2128 calcd for $C_{11}H_{12}O_3$, M^+) 150 (56), 135 (40), 123 (10), 107 (23), 77 (19), 43 (100).

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