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Mild and Tunable Benzoic Acid Catalysts for Rearrangement Reactions of Allylic Alcohols

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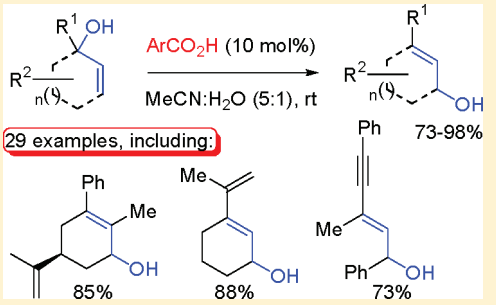
Supporting Information

ABSTRACT: An efficient and simple catalytic method for the isomerization of readily prepared allylic alcohols is described. We focus particularly on cyclic examples and the synthesis of unusual enyne and dienols. The benzoic acid catalysts employed are commercially available and very inexpensive and can be tuned for reactivity and substrate sensitivity.



Rearrangement reactions, whereby a functional group is transposed from one position to another, constitute important supplements to bond-forming reactions in the synthesis of complex molecules.[1] In this context, the 1,3-rearrangement of allylic alcohols is particularly useful because of their high synthetic utility[2] and the common case that one isomer is typically easier to synthesize than the other.[3] Classical methods to perform this transformation typically involve superstoichiometric quantities of strong acids under harsh conditions.[4] For example, a recently reported method requires a full 2 equiv of $MeSO_3H$ to mediate this rearrangement.[5] Such conditions often result in poor yields, particularly with sensitive substrates, due a myriad of competing reactions, including skeletal rearrangements, eliminations, and formation of oligomeric byproducts.[6] Dramatic improvements in terms of scope and selectivity have been reported recently, either through stoichiometric activation of the alcohol functionality[7] or with the use of transition-metal oxo complexes.[8,9] However, it would be ideal to avoid the waste generated from stoichiometric activation and the cost and toxicity associated with transition-metal catalysts.

Our interest in this reaction began with attempts to rearrange alcohol **1a** to **2a** using perfluorinated phenylboronic acid **3** (Figure 1).[10] Even after extensive screening of reaction conditions, we achieved only poor yields of **2a** along with significant formation of elimination products.[11]

Additional screening of acid catalysts and reaction conditions identified 10 mol % of salicylic acid (**4a**, $pK_a = 2.97$) in MeCN at ambient temperature to be most effective in terms of reaction rate, although with significant formation of dimerized ether dehydration products. Addition of small amounts of water improved the yield of desired product, although the time required for complete conversion increased. A 5:1 mixture of MeCN/water proved to be the best compromise for these

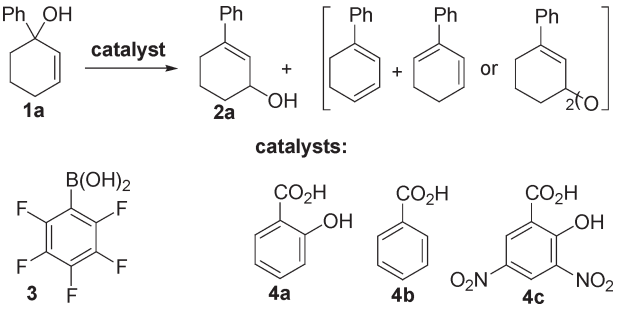


Figure 1. Metal-free rearrangement catalysts.

competing factors. Under these reaction conditions, **2a** was isolated in near-quantitative yield (Table 1, entry 1). We next investigated the scope of this reaction on a variety of cyclic allylic alcohols. Cycloheptanol analogue **1b** afforded the product **2b** in similarly high yield as for **2a** (entry 2). For most of the cylclic allylic alcohols tested, salicylic acid (**4a**) proved to be the optimal catalyst in terms of reaction time and substrate sensitivity. However, cyclopentenol **1c** proved to be substantially more sensitive than **1a** or **1c**, and the molecule decomposed when treated with catalyst **4a** (entry 3). We reasoned that a less acidic catalyst would be more appropriate for this substrate and were pleased to observe formation of the desired product (**2c**) in high yield upon treatment with benzoic acid (**4b**, $pK_a = 4.19$) under otherwise identical conditions (entry 4). Aliphatic substrates **1d**−**f** showed a moderate increase in yield of products **2d**−**f** with increasing bulk of the ring substituent. Electron-rich aromatic ring substituents also proved suitable (entry 8), whereas electron-poor

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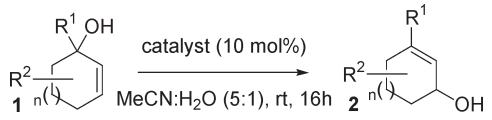
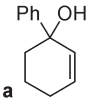
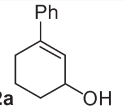
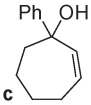
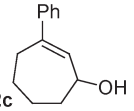
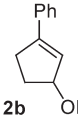
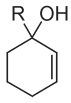
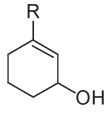
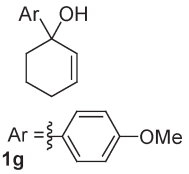
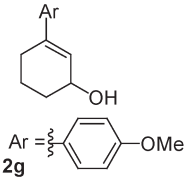
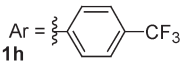
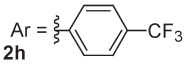
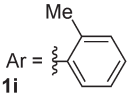
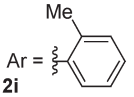
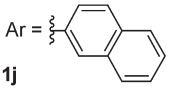
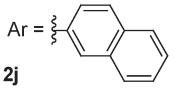
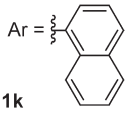
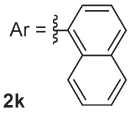
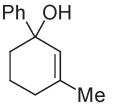
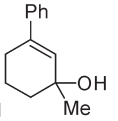
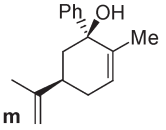
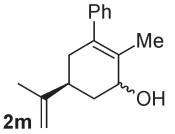
Table 1. Rearrangement of Cyclic Allylic Alcohols

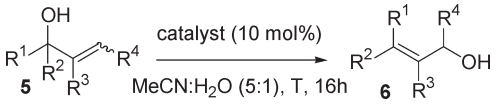


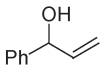
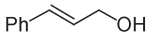
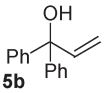
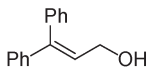
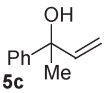
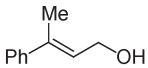
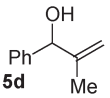
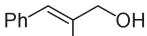
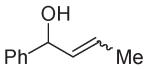
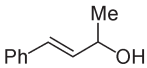
entry	1	catalyst	2, yield (%)[a]
1	 **1a**	**4a**	 **2a**	97
2	 **1c**	**4a**	 **2c**	94
3	 **1b**	**4a**		0[b]
4		**4b**	**2b**	86
5	 **1d**: R = *n*-Bu	**4a**	 **2d**: R = *n*-Bu	84
6	**1e**: R = *s*-Bu	**4a**	**2e**: R = *s*-Bu	87
7	**1f**: R = *t*-Bu	**4a**	**2f**: R = *t*-Bu	91
8	 **1g**	**4a**	 **2g**	86
9		**4a**		63
10	**1h**	**4c**	**2h**	95
11	 **1i**	**4a**	 **2i**	93
12	 **1j**	**4a**	 **2j**	89
13	 **1k**	**4a**	 **2k**	76
14	 **1l**	**4a**	 **2l**	84
15		**4a**		0
16	**1m**	**4c**	**2m**	85[c]

[a] Isolated yields. [b] complete decomposition of starting material. [c] 1:2 mixture of *cis*/*trans* isomers.

derivatives reacted sluggishly in the presence of **4a** (entry 9) with significant recovery of starting material. However, increasing the acidity of the catalyst by using **4c** (pK_a = 1.53) afforded the product

Table 2. Rearrangement of Acyclic Allylic Alcohols



entry	5	catalyst, T	6, yield (%)[a]
1			
2	**5a**	**4a**, rt		0[b]
		4a, reflux	**6a**	90
3		**4a**, rt		5
4		**4a**, reflux		81
5	**5b**	**4c**, rt	**6b**	93
6		**4a**, rt		0[b]
7	**5c**	**4a**, reflux	**6c**	77
8		**4a**, rt		0[b]
9		**4a**, reflux		27
10	**5d**	**4c**, reflux	**6d** 	74
11	 **5e**	**4a**, reflux	 **6e**	85

[a] Isolated yields. [b] Complete recovery of unreacted starting material.

in excellent yield (entry 10). Bulky aromatic substituents in substrates **1i** and **1j** had little effect on the reaction, whereas the very bulky 1-naphthyl-substituted **1k** had a moderate effect on product yield (entry 13). Vinyl substitution appears to have some effect on substrate reactivity. γ-Substituted **1l** reacted cleanly to afford tertiary alcohol **2l** with **4a**, whereas no reaction was observed with the same catalyst and **1m**. Similarly to entry 10, the use of **4c** resulted in much improved conversion of **1m** to **2m**.

Having established the scope of the rearrangement reaction for cyclic allylic alcohols, we turned our attention to acyclic alcohols (Table 2). The use of salicylic acid at room temperature proved ineffective at catalyzing the rearrangement of **5a**−**e**, with (at best) only trace amounts of product isolated (entry 3).

However, heating the same mixtures resulted in good to excellent yields of **6a**−**c** and **6e** (entries 2, 4, 7, and 11). Alternatively, the more acidic catalyst **4c** can be employed at room temperature for the rearrangement of **5b** to **6b** (entry 5). Similarly to **1m**, β-substituted substrate **5d** (entry 9) was substantially less reactive than unsubstituted analogues. Rearrangement was found to occur upon heating with **4c**, which resulted in an isolated yield of 74% for **6d**.

We attribute this limited reactivity to the increased steric crowding at the alcohol, which may limit access of the catalyst. In all cases, complete selectivity for the *E*-isomer was observed, a significant result given the modest selectivities observed for similar substrates with alternative catalysts.[8,11] Furthermore, no dimerization products were observed for these less sterically hindered substrates, even at elevated temperatures.

The efficiency of these catalysts in promoting the rearrangement of allylic alcohols and particularly those with a propensity to form highly stabilized carbocations, suggested that they might be well suited to the rearrangement of bis-allylic and allylic−propargylic alcohols. The potential conjugated products are found in

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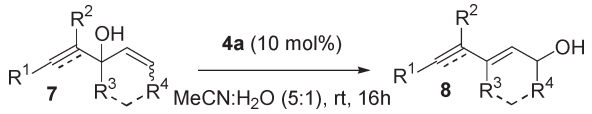
Table 3. Conjugated Dienes and Enynes



entry	7	8	yield[a]
1	**7a**	**8a**	96
2	**7b**	**8b**	97
3	**7c**	**8c**	89
4	**7d**	**8d**	73
5	**7e**	**8e**	93
6	**7f**	**8f**	88
7	**7g**	**8g**	75

[a] Isolated yields.

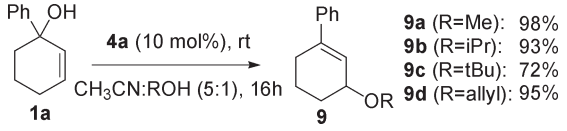
natural products[12] and are substrates of high synthetic utility in Diels–Alder[13] and related cycloaddition reactions.[14] A scalable route to such products would therefore be highly desirable.[15]

Indeed, we observed excellent yields for the conversion of aryl-, alkyl-, and silyl-substituted cyclic allylic–propargylic alcohols **7a–c** to conjugated enynes **8a–c** (Table 3). Acyclic substrate **7d** also performed well under these conditions, affording **8d** in good yield and with complete selectivity with respect to the geometry of the rearranged alkene. Remarkably, all substrates showed complete selectivity for alkene rearrangement, despite the propensity for acid catalysts to promote the related Meyer–Schuster rearrangement.[16]

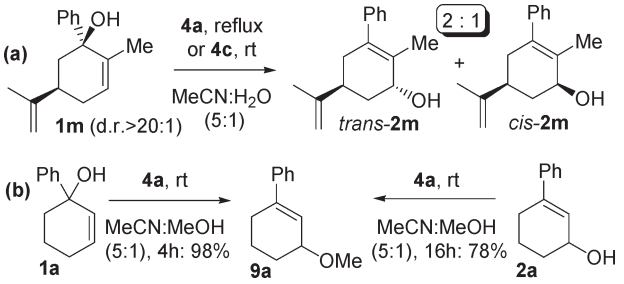
Similarly high selectivities were observed in the bis-allylic alcohol series. Rearrangement of vinyl-substituted cyclohexenols **7e** and **7f** occurs exclusively over the endocyclic double bond to form **8e** and **8f**, respectively, in high yields. This result is in contrast to our observation of exclusive exocyclic double bond selectivity in the Friedel–Crafts arylation of similar substrates.[10] Acyclic bis-allylic substrate **7g** rearranged to form **8g** as the exclusive product in good yield and with complete *E*-selectivity.

The necessity for addition of an external nucleophile prompted us to examine the use of other oxygen-based nucleophiles in this reaction. Simple alcohols, when used in place of water as an additive, result in the formation of allylic ethers in good to near-quantitative yields (Scheme 1). A decrease in yield is observed as the steric hindrance of the alcohol increases (cf. **9a–c**), with significant formation of ether dimerization products

Scheme 1. Reaction with Alcohols



Scheme 2. Mechanistic Probes



observed in the case of **9c**.[17] When allyl alcohol is used, the resulting diene **9d** is isolated in excellent yield.

Two preliminary experiments shed light on a possible mechanism for this transformation. Subjecting homochiral carvone-derived substrate **1m** to either catalyst **4a** at reflux or **4c** at room temperature results in an identical 2:1 mixture of *trans*/*cis* diastereomeric products (Scheme 2 (a)). This suggests an ionic mechanism involving formation of an allylic carbocation followed by preferred attack of water from the least hindered face. Formation of such a carbocation is consistent with our observation that electron-rich substrates (e.g., **1g**) rearrange efficiently under these conditions, whereas electron-poor derivatives (e.g., **1h**) require more forcing conditions. Furthermore, increasing the acidity of the catalysts (e.g., from **4a** to **4c**) results in increased reactivity for substrates that react via poorly stabilized carbocations. Such results are also consistent with an ionic mechanism.

In a second experiment (Scheme 2 (b)), reaction times for conversion of **1a** and **2a** to **9a** were compared. Compound **1a** reacts rapidly, whereas **2a** requires longer reaction times and results in lower yield of **9a**, with starting material recovered. This suggests a common carbocation intermediate and that the regiochemistry of the rearrangement is governed by product stability.

In summary, we have developed a mild, catalytic system for the rearrangement of allylic alcohols and preparation of allylic ethers. The acidity (and thus the reactivity) of the catalysts can be tuned for substrate sensitivity/reactivity; they are very inexpensive and nontoxic. The products, including synthetically useful conjugated dienes and enynes, are produced in high yields and with excellent selectivity for the *E*-isomers. Preliminary mechanistic investigations suggest an ionic mechanism. Further expansion of the scope of this reaction and mechanistic experiments are ongoing in our laboratory and will be reported in due course.

EXPERIMENTAL SECTION

Allylic alcohol substrates (**1**, **5**, **7**) were prepared according to previously reported procedures.[10]

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1-*sec*-Butyl-cyclohex-2-enol (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81−5.75 (m, 1H), 5.53−5.48 (d, J = 10.0 Hz, 1H), 2.02−1.97 (m, 1H), 1.97−1.93 (m, 1H), 1.89−1.79 (m, 1H), 1.74−1.70 (m, 2H), 1.63−1.58 (m, 2H), 1.55−1.45 (m, 2H), 1.36−1.29 (m, 1H), 0.89−0.77 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 132.7, 130.5, 130.1, 72.0, 71.9, 45.2, 45.0, 30.7, 30.3, 25.3, 25.2, 24.6, 22.9, 18.54, 18.52, 13.9, 12.8, 12.7, 12.6; FTIR (neat) υ 3449, 3016, 2832, 1708, 1460, 1380, 1172, 1069, 850, 736 cm^{-1}; HRMS (m/z) calcd for $C_{10}H_{17}$ (MALDI-TOF, (M − OH)$^+$) 137.1331, found 137.1330.

1-naphthalen-1-yl-cyclohex-2-enol (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84−8.81 (d, J = 7.5 Hz, 1H), 7.99−7.95 (d, J = 7.3 Hz, 1H), 7.90−7.86 (m, 2H), 7.61−7.57 (m, 2H), 7.56−7.51 (dd, J = 7.5 Hz, J = 7.8 Hz, 1H), 6.16−6.11 (dt, J = 10.0 Hz, J = 3.5 Hz, 1H), 6.06−6.02 (d, J = 10.0 Hz, 1H), 2.73 (s, br, 1H), 2.61−2.53 (m, 1H), 2.29−2.25 (m, 2H), 2.22−2.15 (m, 1H), 2.01−1.91 (m, 1H), 1.72−1.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 135.0, 134.0, 130.7, 129.8, 129.2, 128.6, 126.8, 125.3, 125.2, 125.0, 124.9, 73.7, 37.3, 25.1, 19.6; FTIR (neat) υ 3419, 2924, 2855, 1458, 1377, 1167, 966, 904, 739 cm^{-1}; HRMS (m/z) calcd for $C_{16}H_{15}$ (MALDI-TOF, (M − OH)$^+$) 207.1174, found 207.1179.

1-Oct-1-ynyl-cyclohex-2-enol (7b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60−5.58 (m, 2H), 2.07−2.02 (t, J = 7.3 Hz, 2H), 1.88−1.80 (m, 3H), 1.77−1.71 (m, 1H), 1.65−1.56 (m, 2H), 1.39−1.31 (m, 2H), 1.27−1.18 (m, 2H), 1.19−1.11 (m, 4H), 0.77−0.72 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.4, 128.2, 84.1, 83.8, 65.0, 38.0, 31.2, 28.5, 28.4, 24.6, 22.4, 19.2, 18.6, 13.9; FTIR (neat) ν 3367. 2932, 2859, 2232, 1456, 1322, 1182, 1054, 959, 737 cm^{-1}; HRMS (m/z) calcd for $C_{14}H_{21}$ (MALDI-TOF, (M − OH)$^+$) 189.1644, found 189.1638.

3-Methyl-1-phenyl-hexa-1,4-dien-3-ol (7g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.38 (m, 2H), 7.34−7.29 (m, 2H), 7.25−7.21 (m, 1H), 6.67−6.59 (m, 1H), 6.43−6.38 (d, J = 16.1 Hz, 0.5 H), 6.35−6.30 (d, J = 16.1 Hz, 0.5H), 5.73−5.57 (m, 2H), 2.19 (s, br, 1H), 1.83−1.80 (d, J = 5.5 Hz, 1.5H), 1.75−1.73 (d, J = 5.0 Hz, 1.5H), 1.54 (s, 1.5H), 1.48 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 137.0, 136.9, 135.89, 135.87, 135.8, 128.6, 128.5, 127.41, 127.39, 127.1, 126.81, 126.77, 126.5, 124.0, 73.4, 72.9, 30.0, 28.4, 17.8, 14.4; FTIR (neat) ν 3419, 3026, 2972, 2928, 1710, 1494, 1448, 1367, 969, 749, 694 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{15}$ (MALDI-TOF, (M − OH)$^+$) 171.1174, found 171.1181.

General Procedure A for the rearrangement of allylic Alcohols. To a 10 mL round-bottom flask containing the substrate (**1**, **5**, or **7**, 1.0 mmol) in CH_3CN (5 mL) and H_2O (1 mL) was added catalyst **4a**, **b**, or **c** (0.1 mmol). The flask was either loosely capped with a septum and the resulting mixture allowed to stir at room temperature for 16 h or fitted with a condensor and heated to reflux for 16 h and cooled to room temperature. A saturated solution of $NaHCO_3$ (20 mL) was added and the mixture extracted with Et_2O (2 × 25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. Purification (if necessary) of the residue by flash chromatography (EtOAc/hexanes) afforded the products **2**, **6**, and **8**.

3-Phenylcyclohept-2-enol (2b). Prepared according to general procedure A with **1b** (188 mg) and **4a** (14 mg) at room temperature to afford **2b** (177 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.32 (m, 4H), 7.15−7.21 (m, 1H), 5.96−6.01 (m, 1H), 4.52−4.57 (m, 1H), 2.72−2.82 (s, br, 1H), 2.58−2.62 (dd, J = 15.1 Hz, J = 6.5 Hz, 1H), 2.38−2.49 (m, 1H), 1.92−2.10 (m, 1H), 1.82−1.88 (m, 1H), 1.72−1.81 (m, 1H), 1.64−1.72 (m, 2H), 1.35−1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.5, 136.0, 128.1, 126.0, 125.6, 71.8, 36.3, 32.5, 28.0, 26.1; FTIR (neat) ν 3387, 3079, 3056, 3027, 2927, 2851, 1948, 1879, 1804, 1687, 1645, 1598, 1493, 1080, 761 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{15}$ (MALDI-TOF, (M − OH)$^+$) 171.1174, found 171.1166.

3-Phenylcyclopent-2-enol (2c). Prepared according to general procedure A with **1c** (160 mg) and **4b** (12 mg) at room temperature to afford **2c** (138 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.50 (d, J = 7.0 Hz, 2H), 7.21−7.33 (m, 3H), 6.20−6.23 (s, 1H), 4.97−5.02 (m, 1H), 2.81−2.84 (m, 1H), 2.60−2.63 (m, 1H), 2.40−2.42 (m, 1H), 1.81−1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 135.7, 128.5, 127.9, 127.3, 126.0, 77.0, 33.8, 31.4; FTIR (neat) ν 3406, 3079, 3055, 2935, 2246, 1947, 1877, 1802, 1737, 1598, 1493, 1069, 757 cm^{-1}; HRMS (m/z) calcd for $C_{11}H_{11}$ (MALDI-TOF, (M − OH)$^+$) 143.0861, found 143.0868.

3-*sec*-Butylcyclohex-2-enol (2e). Prepared according to general procedure A with **1e** (154 mg) and **4a** (14 mg) at room temperature to afford **2e** (134 mg, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46−5.49 (m, 1H), 4.16−4.21 (m, 1H), 2.10−2.13 (br, 1H), 1.92−2.00 (m, 2H), 1.70−1.85 (m, 2H), 1.52−1.60 (m, 2H), 1.34−1.42 (m, 1H), 1.26−1.32 (m, 1H), 0.96−1.00 (d, J = 7.0 Hz, 3H), 0.85−0.90 (m, 1H), 0.79−0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 123.4, 65.8, 42.5, 32.2, 27.6, 25.2, 19.2, 18.9, 11.8; FTIR (neat) ν 3360, 2660, 1709, 1662, 1456, 1059, 1023, 909, 759 cm^{-1}; HRMS (m/z) calcd for $C_{10}H_{17}$ (MALDI-TOF, (M − OH)$^+$) 137.1331, found 137.1326.

3-*tert*-Butylcyclohex-2-enol (2f). Prepared according to general procedure A with **1f** (154 mg) and **4a** (14 mg) at room temperature to afford **2f** (140 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53−5.55 (m, 1H), 4.18−4.23 (m, 1H), 1.90−2.10 (m, 2H), 1.76−1.84 (m, 1H), 1.66−1.59 (m, 1H), 1.52−1.58 (m, 2H), 1.48−1.51 (m, 1H), 1.01−1.04 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 120.3, 66.5, 35.3, 31.9, 28.8, 24.6, 19.9, 14.4; FTIR (neat) ν 3405, 3050, 2960, 2866, 1712, 1395, 1367, 1280, 1073, 1027, 999 cm^{-1}; HRMS (m/z) calcd for $C_{10}H_{17}$ (MALDI-TOF, (M − OH)$^+$) 137.1331, found 137.1330.

3-(4-Methoxyphenyl)cyclohex-2-enol (2g). Prepared according to general procedure A with **1g** (204 mg) and **4a** (14 mg) at room temperature to afford **2g** (175 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.35 (d, J = 8.8 Hz, 2H), 6.83−6.86 (d, J = 8.8 Hz, 2H), 6.05−6.07 (m, 1H), 4.34−4.38 (m, 1H), 3.77 (s, 3H), 2.25−2.45 (m, 3H), 1.86−1.92 (m, 2H), 1.64−1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 138.7, 133.7, 126.1, 124.9, 113.4, 65.9, 54.9, 31.5, 27.2, 19.2; FTIR (Nujol) ν 3336, 3034, 2723, 2052, 1902, 1640, 1607, 1031, 966 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{15}O$ (MALDI-TOF, (M − OH)$^+$) 187.1123, found 187.1143.

3-(4-Trifluoromethylphenyl)cyclohex-2-enol (2h). Prepared according to general procedure A with **1h** (242 mg) and **4c** (23 mg) at room temperature to afford **2h** (230 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.56 (d, J = 8.0 Hz, 2H), 7.45−7.49 (d, J = 8.2 Hz, 2H), 6.17−6.21 (s, 1H), 4.36−4.41 (s, 1H), 2.75−2.83 (s, 1H), 2.26−2.46 (m, 2H), 1.87−1.96 (m, 2H), 1.87−1.96 (m, 2H), 1.55−1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.8, 127.4, 124.0, 123.5, 64.5, 29.8, 25.7, 17.8; FTIR (neat) ν 3350, 3025, 2936, 2865, 1921, 1616, 1410, 1071, 1016, 738 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{12}F_3$ (MALDI-TOF, (M − OH)$^+$) 225.0891, found 225.0907.

3-*o*-Tolylcyclohex-2-enol (2i). Prepared according to general procedure A with **1i** (188 mg) and **4a** (14 mg) at room temperature to afford **2i** (175 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02−7.15 (m, 5H), 4.31−4.35 (m, 1H), 2.10−2.34 (m, 6H), 1.82−1.95 (m, 2H), 1.66−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.3, 134.6, 129.9, 128.2, 127.9, 126.7, 124.5, 65.7, 31.5, 30.2, 19.4, 19.5; FTIR (neat) ν 3342, 3059, 3016, 2929, 2860, 1945, 1911, 1801, 1702, 1660, 1601, 1485, 1052, 756 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{16}$ (MALDI-TOF, (M − OH)$^+$) 171.1174, found 171.1189.

3-Naphthalen-2-ylcyclohex-2-enol (2j). Prepared according to general procedure A with **1j** (224 mg) and **4a** (14 mg) at room temperature to afford **2j** (170 mg, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.76 (dd, J = 6.3 Hz, J = 3.5 Hz, 1H), 7.75−7.71 (m, 4H), 7.70−7.66 (d, J = 8.5 Hz, 1H), 6.22−6.24 (m, 1H), 3.35−4.40 (m, 1H), 2.30−2.50 (m, 3H), 1.80−1.98 (m, 3H), 1.60−1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.3, 133.3, 132.6, 127.9, 127.6, 127.3,

125.9, 125.6, 123.8, 123.6, 66.1, 31.5, 27.2, 19.4; FTIR (Nujol) ν 3310, 3052, 1627, 1594, 1376, 1054, 976, 782, 744 cm^{-1}; HRMS (m/z) calcd for $C_{16}H_{15}$ (MALDI-TOF, $(M - OH)^+$) 207.1174, found 207.1176.

3-Naphthalen-1-ylcyclohex-2-enol (2k). Prepared according to general procedure A with **1k** (224 mg) and **4a** (14 mg) at room temperature to afford **2k** (199 mg, 89%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.96 (dd, J = 4.5 Hz, J = 3.3 Hz, 2H), 7.75−7.80 (dd, J = 6.0 Hz, J = 3.8 Hz, 2H), 7.67−7.71 (d, J = 8.3 Hz, 1H), 7.33−7.43 (m, 4H), 7.19−7.23 (m, 1H), 2.17−2.41 (m, 2H), 1.85−2.01 (m, 2H), 1.65−1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 141.1, 133.6, 130.9, 129.7, 128.2, 127.1, 125.7, 125.5, 125.4, 125.2, 124.6, 65.7, 31.6, 31.1, 19.6; FTIR (neat) ν 3359, 3055, 2929, 2859, 1929, 1812, 1662, 1449, 1057, 735 cm^{-1}; HRMS (m/z) calcd for $C_{16}H_{15}$ (MALDI-TOF, $(M - OH)^+$) 207.1174, found 207.1173.

1-Methyl-3-phenylcyclohex-2-enol (2l). Prepared according to general procedure A with **1l** (188 mg) and **4a** (14 mg) at room temperature to afford **2l** (158 mg, 84%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.44 (m, 2H), 7.26−7.29 (m, 3H), 6.04−6.06 (s, 1H), 2.00−2.39 (m, 4H), 1.59−1.80 (m, 5H), 1.31−1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 131.2, 128.4, 123.1, 122.5, 68.1, 36.8, 29.4, 28.9, 19.5; FTIR (neat) ν 3388, 3080, 3055, 2964, 2866, 2204, 1950, 1880, 1714, 1626, 1488, 1070, 1017, 755 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{15}$ (MALDI-TOF, $(M - OH)^+$) 171.1174, found 171.1166.

3-Phenylethynylcyclohex-2-enol (8a). Prepared according to general procedure A with **7a** (198 mg) and **4a** (14 mg) at room temperature to afford **8a** (190 mg, 96%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.42 (dd, J = 7.3 Hz J = 3.8 Hz, 2H), 7.23−7.27 (m, 3H), 6.15−6.18 (m, 1H), 4.23−4.28 (m, 1H), 2.60−2.70 (s, br, 1H), 2.10−2.28 (m, 2H), 1.72−1.90 (m, 2H), 1.52−1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 131.3, 127.9, 123.6, 123.4, 123.1, 89.8, 88.5, 65.3, 30.8, 29.2, 18.9; FTIR (neat) ν 3358, 3079, 3055, 2934, 2204, 1950, 1880, 1804, 1664, 1627, 1596, 1488, 1069, 755 cm^{-1}; HRMS (m/z) calcd for $C_{14}H_{13}O$ (MALDI-TOF, $(M - H)^+$) 197.0967, found 197.0958.

3-Oct-1-ynylcyclohex-2-enol (8b). Prepared according to general procedure A with **7b** (206 mg) and **4a** (14 mg) at room temperature to afford **8b** (200 mg, 97%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.96−5.90 (m, 1H), 4.18−4.22 (m, 1H), 2.53−2.58 (s, br, 1H), 2.56−2.30 (t, J = 7.0 Hz, J = 14.3 Hz, 2H), 2.00−2.16 (m, 2H), 1.70−1.86 (m, 2H), 1.46−1.60 (m, 4H), 1.24−1.42 (m, 6H), 0.86−0.92 (t, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 123.9, 89.4, 80.9, 64.9, 36.8, 31.5, 30.9, 29.4, 28.3, 22.2, 18.8, 13.6; FTIR (neat) ν 3350, 3030, 2953, 2221, 1666, 1630, 1432, 1063, 969, 725 cm^{-1}; HRMS (m/z) calcd for $C_{14}H_{21}$ (MALDI-TOF, $(M - OH)^+$) 189.1644, found 189.1642.

3-Methyl-1,5-diphenylpent-2-en-4-yn-1-ol (8d). Prepared according to general procedure A with **7d** (248 mg) and **4a** (14 mg) at room temperature to afford **8d** (181 mg, 73%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.52 (m, 4H), 7.34−7.40 (m, 5H), 7.26−7.32 (m, 1H), 5.91−5.95 (d, J = 9.0, 1H), 5.85−5.88 (d, J = 9.0 Hz, 1H), 2.22−2.25 (s, 1H), 1.98−2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.3, 128.4, 127.6, 125.8, 124.1, 110.5, 67.9, 14.8; FTIR (neat) ν 3353, 3060, 3027, 2930, 2316, 1600, 1494, 1449, 1020, 967, 743 cm^{-1}; HRMS (m/z) calcd for $C_{18}H_{15}O$ (MALDI-TOF, $(M - H)^+$) 247.1123, found 247.1107.

3-Isopropenylcyclohex-2-enol (8f). Prepared according to general procedure A with **7f** (138 mg) and **4a** (14 mg) at room temperature to afford **8f** (123 mg, 89%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.85−5.87 (s, 1H), 5.04−5.06 (s, 1H), 4.92−4.94 (s, 1H), 4.28−4.36 (s, br, 1H), 2.39−2.42 (m, 1H), 2.18−2.22 (m, 2H), 1.89−1.91 (m, 4H), 1.50−1.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.9, 126.9, 111.8, 66.3, 31.5, 25.1, 20.0, 19.2; FTIR (neat) ν 3416, 3022, 2939, 2834, 1708, 1438, 1168, 1056, 967, 901, 740 cm^{-1}; HRMS (m/z) calcd for C_9H_{13} (MALDI-TOF, $(M - OH)^+$) 121.1018, found 121.1022.

4-Methyl-6-phenylhexa-3,5-dien-2-ol (8g). Prepared according to general procedure A with **7g** (188 mg) and **4a** (14 mg) at room temperature to afford **8g** (141 mg, 75%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.45 (d, J = 7.3 Hz, 2H), 7.31−7.36 (dd, J = 7.3 Hz, J = 15.1 Hz, 3H), 7.22−7.26 (d, J = 7.3 Hz, 1H), 6.76−6.82 (d, J = 16.3 Hz, 1H), 6.54−6.59 (d, J = 16.1 Hz, 1H), 5.63−5.66 (d, J = 16.1 Hz, 1H), 5.63−5.66 (d, J = 8.5 Hz, 1H), 4.73−4.80 (m, 1H), 1.93−1.94 (s, 3H), 1.31−1.33 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.5, 134.5, 133.0, 128.6, 128.6, 128.0, 127.3, 126.4, 64.7, 23.5, 12.7; FTIR (neat) ν 3417, 3060, 3027, 2972, 2928, 2247, 1950, 1880, 1805, 1708, 1599, 1493 cm^{-1}; HRMS (m/z) calcd for $C_{13}H_{15}$ (MALDI-TOF, $(M - OH)^+$) 171.1174, found 171.1165.

General Procedure B for the Preparation of Allylic Ethers. To a vial containing **1a** (174 mg, 1.0 mmol) in CH_3CN (5 mL) and the alcohol (1 mL) was added catalyst **4a** (0.1 mmol, 14 mg). The vial was capped and the mixture allowed to stir at room temperature for 16 h. A saturated solution of $NaHCO_3$ (20 mL) was added and the mixture extracted with Et_2O (2 × 25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. Purification (if necessary) of the residue by flash chromatography (EtOAc/hexanes) afforded the products **5**.

1-(3-Methoxycyclohex-1-enyl)benzene (9a). Prepared according to general procedure B with methanol to afford **9a** (184 mg, 98%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.41 (d, J = 7.0 Hz, 2H), 7.20−7.31 (m, 2H), 6.15−6.17 (m, 1H), 3.82−3.89 (m, 1H), 3.40 (s, 1H), 2.35−2.45 (m, 1H), 1.87−1.91 (m, 4H), 1.66−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.0, 127.9, 126.9, 125.0, 124.0, 74.6, 55.5, 27.4, 19.3; FTIR (neat) ν 3371, 2935, 1668, 1446, 1348. 1258, 1190, 1095, 945, 758, 694 cm^{-1}; HRMS (m/z) calcd for $C_{12}H_{13}$ (MALDI-TOF, $(M - OMe)^+$) 157.1017, found 157.1006.

1-(3-Isopropoxycyclohex-1-enyl)benzene (9b). Prepared according to general procedure B with 2-propanol to afford **9b** (201 mg, 93%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.43 (m, 2H), 7.28−7.33 (m, 2H), 7.23−7.25 (m, 1H), 6.08−6.10 (m, 1H), 4.08−4.12 (s, 1H), 2.30−2.50 (m, 3H), 1.94−1.96 (s, 3H), 1.66−1.70 (m, 2H), 1.18−1.22 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 139.3, 127.8, 126.8, 125.4, 125.0, 70.7, 68.8, 28.7, 27.2, 22.8, 22.4, 19.5; FTIR (neat) ν 3453, 3082, 3057, 3031, 2968, 2934, 2863, 1944, 1884, 1806, 1711, 1676, 1643, 1598, 1577 cm^{-1}; HRMS (m/z) calcd for $C_{12}H_{13}$ (MALDI-TOF, $(M - O^iPr)^+$) 157.1017, found 157.1000.

1-(3-*tert*-Butoxycyclohex-1-enyl)benzene (9c). Prepared according to general procedure B with *tert*-butyl alcohol to afford **9c** (166 mg, 72%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.44 (m, 2H), 7.28−7.33 (m, 2H), 7.21−7.27 (m, 1H), 5.98−6.00 (m, 1H), 4.18−4.22 (s, 1H), 2.29−2.47 (m, 2H), 1.87−1.88 (s, 2H), 1.64−1.76 (m, 3H), 1.27−1.29 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.4, 127.6, 127.4, 126.5, 124.8, 73.1, 65.7, 30.9, 27.9, 26.7, 20.1; FTIR (neat) ν 3504, 3027, 2958, 2870, 1390, 1366, 1270, 1221, 1164, 1123, 1086, 1044, 1015, 958 cm^{-1}; HRMS (m/z) calcd for $C_{12}H_{13}$ (MALDI-TOF, $(M - O^tBu)^+$) 157.1017, found 157.1019.

1-(3-Allyloxycyclohex-1-enyl)benzene (9d). Prepared according to general procedure B with allyl alcohol to afford **9d** (203 mg, 95%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.46 (d, J = 7.2 Hz, 2H), 7.31−7.36 (t, J = 7.2 Hz, J = 14.8 Hz, 2H), 7.24−7.26 (t, J = 7.2 Hz, J = 14.5 Hz, 1H), 6.19−6.21 (s, 1H), 5.93−6.03 (m, 1H), 5.32−5.39 (dd, J =15.3 Hz, J = 17.1 Hz, 1H), 5.20−5.24 (dd, J = 8.7 Hz, J = 10.5 Hz, 1H), 4.08−4.18 (m, 3H), 2.45−2.54 (m, 1H), 2.34−2.43 (m, 1H), 1.89−2.01 (m, 2H), 1.68−1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.6, 134.8, 127.6, 126.6, 124.7, 124.1, 115.9, 72.4, 68.6, 27.4, 27.0, 19.1; FTIR (neat) ν 33131, 3081, 3057, 3031, 2936, 2861, 2663, 1947, 1873, 1804, 1712 cm^{-1}; HRMS (m/z) calcd for $C_{12}H_{13}$ (MALDI-TOF, $(M - O\text{-allyl})^+$) 157.1017, found 157.1016.

■ ASSOCIATED CONTENT

Supporting Information. General experimental methods and ^1H and ^{13}C NMR spectra for all new compounds and

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known compounds prepared by new methods. This material is available free of charge via the Internet at http://pubs.acs.org/.

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