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A multicomponent approach to substituted benzenes involving sequential nickel-catalyzed reactions

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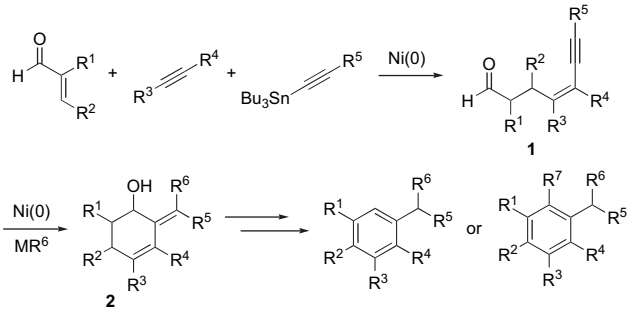
Abstract—Two sequential nickel-catalyzed reactions allow the preparation of highly functionalized alkylidene cyclohexenols. Dehydration of the resulting cycloadducts allows the preparation of densely functionalized aromatic ring systems, whereas a simple sequence involving oxidation followed by carbonyl addition or enolization allows additional diversity incorporation.

1. Introduction

Many approaches to substituted benzene derivatives have been developed, and most strategies involve functionalization of an existing benzene ring. For example, electrophilic and nucleophilic aromatic substitution,[1] directed metallation,[2] and metal-catalyzed cross-couplings of haloaromatics or aryl triflates[3] are very commonly employed. Strategies that involve preparation of the aromatic six-membered ring from non-aromatic precursors are often complementary to the types of substitution patterns that are most easily accessed by conventional approaches.[4] A recent report from our laboratory described the synthesis of substituted alkylidene cyclohexenol derivatives by two related nickel-catalyzed reactions performed in succession.[5] The first step of the sequence involves the three-component nickel-catalyzed coupling of enones, alkynes, and acetylenic stannanes to generate functionalized enynes **1** bearing an aldehyde functional group, and the second step involves a nickel-catalyzed reductive coupling to generate a product alkylidene cyclohexenol **2**. We envisioned that aromatization of the structures obtained by this sequence would provide an unusual and diverse entry to highly substituted benzene derivatives. The overall strategy has the potential to provide access to a very broad range of aromatics since up to five different widely available starting materials each introduce functionality into the aromatic products. Herein we describe the realization of this strategy (Scheme 1).



Scheme 1.

2. Results and discussion

Our previous report describing sequential nickel-catalyzed couplings for the preparation of alkylidene cyclohexenols provided easy access to the precursors of aromatic ring systems.[5] Whereas a broad range of substrates were reported in our original communication detailing the two-step entry to alkylidene cyclohexenols, eight examples of the three-component couplings of enals, alkynes, and acetylenic tin reagents were selected for the proposed aromatization sequence (Scheme 2). The typical coupling procedure involved coupling of an enal, alkyne, and acetylenic tin reagent in THF in the presence of TMSCl and a catalyst derived from in situ reduction of $Ni(acac)_2$ with DIBAL-H. This initial step of our entry to aromatic structures is based upon earlier studies from Ikeda that demonstrated related three-component couplings.[6] As these eight examples (**1a**–**h**) illustrate, variation of all three components is tolerated. The enal component can be as simple as acrolein, or substitution at the α- or β-carbon is allowed. Additionally, couplings of a cyclic enal (cyclohexene carboxaldehyde) also proceed in modest yield. In the alkyne component, internal and terminal alkynes participate with aromatic, aliphatic, or ether-containing groups. Finally, the acetylenic tin reagent may possess

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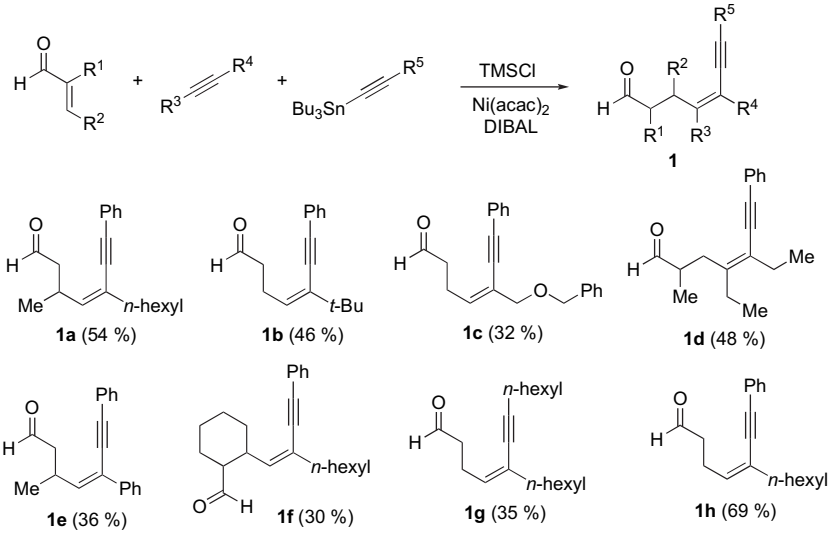


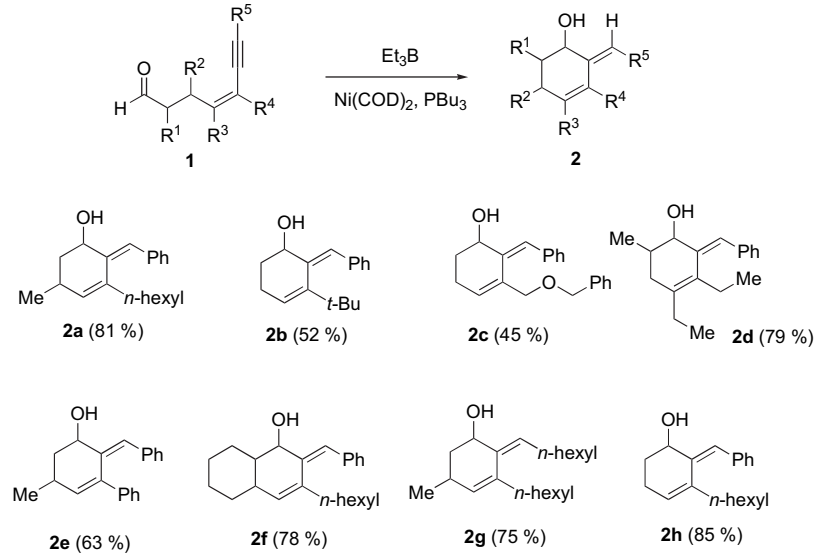
Scheme 2.

aromatic or aliphatic functional groups. While the chemical yields of this initial coupling step are disappointing, it should be noted that many side reactions are possible, including homo- or heterotrimerization of the two alkyne components or homodimerization of the alkynyl stannane.[4,7]

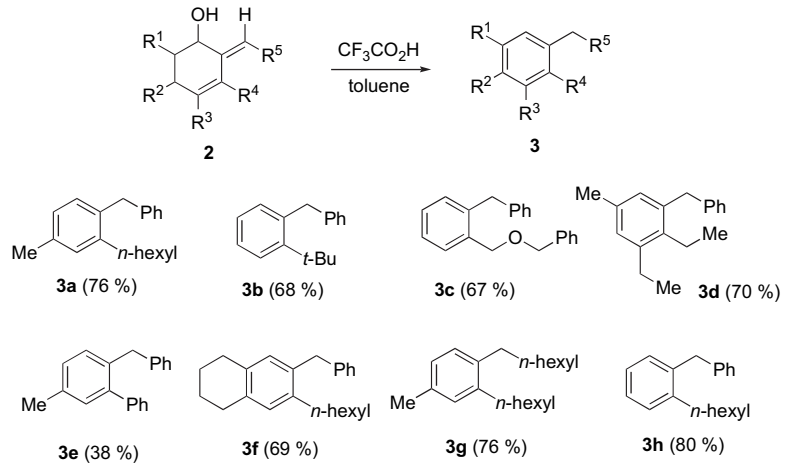
With these eight substrates in hand, nickel-catalyzed reductive cyclizations of enynals **1a–h** involving $Ni(COD)_2/PBu_3$ as catalyst and Et_3B as reducing agent provided access to the corresponding alkylidene cyclohexenols **2a–h** (Scheme 3). The corresponding alkylative cyclizations involving introduction of an alkyl group are also successful, but the products derived from Et_3B-mediated cyclizations were the focus of this study.[8] The reductive cyclization products that bear two or more stereocenters were typically generated as diastereomeric mixtures, which is inconsequential for the purpose of preparing aromatic structures.

Treatment of the alkylidene cyclohexenols **2a–h** with trifluoroacetic acid in toluene directly afforded the aromatic structures **3a–h** via dehydration (Scheme 4). This simple sequence affords access to a broad array of substitution patterns in aromatic ring systems, and should be amenable to many other substitution patterns not explicitly examined in this study.

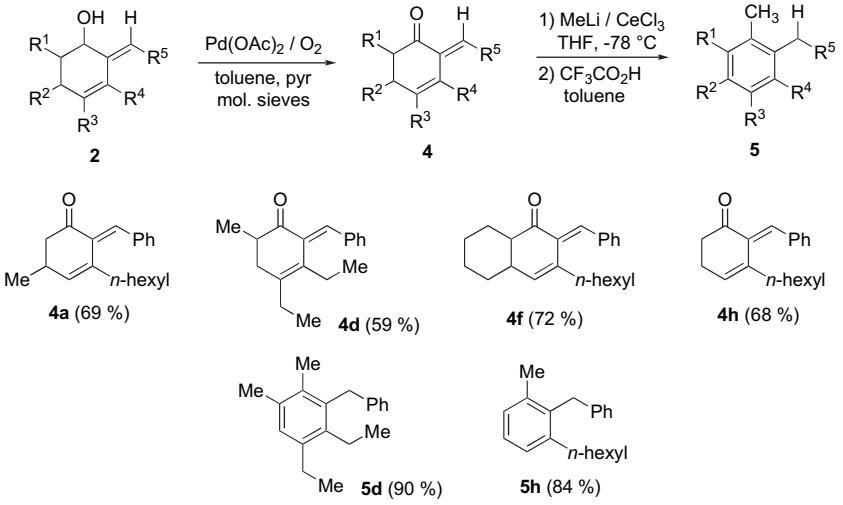
Alternatively, oxidation[9] of the alkylidene cyclohexenols with $Pd(OAc)_2/O_2$ provides alkylidene cyclohexenones **4** that resist aromatization via tautomerization (Scheme 5).[10] These substrates may be functionalized via organocerium reagent addition to the carbonyl, followed by acid-catalyzed dehydration to afford substituted benzenes **5** that now possess substituents derived from four different starting materials. The production of **4d** and **4h** and their conversion to aromatic structures **5d** and **5h** by $MeLi/CeCl_3$ addition[11] followed by trifluoroacetic acid-mediated dehydration illustrates the sequence (Scheme 5). As the various substrate combinations selected for this study illustrate, the following aromatic substitution patterns may be accessed: 1,2-disubstituted, 1,2,3-trisubstituted, 1,2,4-trisubstituted, 1,2,3,5-



Scheme 3.



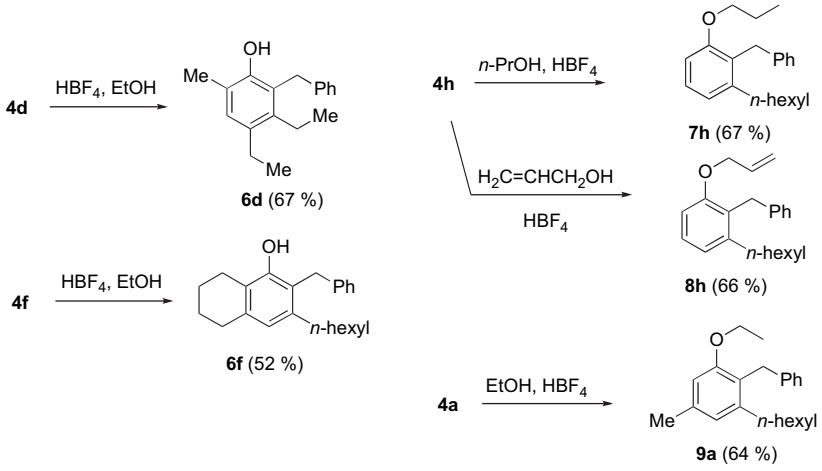
Scheme 4.



Scheme 5.

tetrasubstituted, and 1,2,3,4,5-pentasubstituted. Selection of alternative starting material combinations would allow many other regiochemical substitution patterns to be accessed.

We also considered the production of phenols and aryl ethers by a strategy that retains the oxygenation present in cyclohexenone **4**.[12,13] Direct aromatization of **4d** and **4f** to the corresponding phenol by tautomerization proceeded under forcing conditions to produce phenols **6d** and **6f** in modest yield (Scheme 6). Alkylidene cyclohexenone substrates **4a** and **4h** that possess a simple unsubstituted methylene α to the carbonyl resisted tautomerization, but were converted to



Scheme 6.

aryl ethers **7h**, **8h**, and **9a** in alcohol solvents with strong acids. Control experiments illustrated that the aryl ether products were not produced from O-alkylation of the corresponding phenol derivatives under the reaction conditions.

3. Conclusions

In summary, a variety of highly substituted aromatic structures may be obtained by two sequential nickel-catalyzed couplings, followed by aromatization. Depending on the aromatization sequence chosen, the products may be benzene derivatives, phenols, or aryl ethers. A wide array of substitution patterns are accessible by these procedures, which complement the patterns that are accessible by conventional procedures for the preparation of polysubstituted aromatic compounds.

4. Experimental

4.1. General

Unless otherwise noted, reagents were commercially available and were used without purification. Trimethylsilyl chloride and tributylphosphine were freshly distilled. Tetrahydrofuran (THF) was purified by alumina filtration under nitrogen using a solvent purification system (Innovative Technology, Inc., Model 3 SPS-400-3). All reactions were conducted in a flame-dried glassware under an atmosphere of nitrogen or argon. $Ni(COD)_2$ and $Ni(acac)_2$ were stored in a glove box under argon. ^1H and ^{13}C NMR spectra were obtained at room temperature on a Varian Mercury 400 or Varian Unity 500 MHz instruments. High-resolution mass spectra (HRMS) were obtained from the Central Instrument Facility at Wayne State University and at the University of Michigan.

4.2. General procedure for three-component couplings of α,β-unsaturated aldehydes, alkynes, and alkynyltins

A 0.02 M solution of $Ni(acac)_2$ (0.1 equiv) in THF was stirred at 0 °C, and a solution of DIBAL (0.1 equiv, 1.0 M in hexanes) was added dropwise, followed by the addition of the alkynyltin reagent (1.1 equiv). The alkyne (1.2 equiv), the α,β-unsaturated aldehyde (1.0 equiv), and TMSCl (1.2 equiv) were then added neat, and the reaction mixture was allowed to warm to room temperature and was stirred for 2.5 h (unless otherwise noted). The mixture was quenched by the addition of concd HCl (12 equiv, 2.0 M in acetone), stirred for 15 min, and was poured into concd NH_4F solution (four times the volume of the reaction mixture before quench). The two-phase mixture was vigorously stirred for 30 min and then filtered through Celite and washed with diethyl ether. The aqueous layer was extracted with diethyl ether; the combined organic layers were washed with satd $NaHCO_3$, brine, and dried over $MgSO_4$. The product was purified by flash chromatography on SiO_2 using hexane and CH_2Cl_2 as a solvent system.

4.2.1. (*Z*)-5-Hexyl-3-methyl-7-phenyl-hept-4-en-6-ynal (1a). Following the general procedure in Section 4.2, crotonaldehyde (0.66 mL, 8.0 mmol), 1-octyne (1.41 mL, 9.6 mmol), tributyl(phenylethynyl)tin (3.08 mL, 8.8 mmol), $Ni(acac)_2$ (206 mg, 0.80 mmol), DIBAL (0.80 mL, 0.80 mmol in 1.0 M solution), and TMSCl (1.22 mL, 9.60 mmol) were employed to produce, after flash chromatography (3:1 hexane/CH_2Cl_2), 1.22 g (54%) of product as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.75 (t, J=2.5 Hz, 1H), 7.43–7.45 (m, 2H), 7.28–7.34 (m, 3H), 5.56 (d, J=9.0 Hz, 1H), 3.35–3.44 (m, 1H), 2.42–2.44 (m, 2H), 2.18 (t, J=7.0 Hz, 2H), 1.54–1.60 (m, 2H), 1.28–1.35 (m, 6H), 1.13 (d, J=6.5 Hz, 3H), 0.88–0.92 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 140.8, 131.7, 128.5, 128.4, 123.8, 123.7, 94.7, 87.8, 50.9, 37.2, 31.9, 30.7, 28.8, 28.6, 22.8, 20.8, 14.3; IR (film, cm^{-1}) 2926, 2855, 1724, 1489, 1457, 755, 690; HRMS (EI) *m/e* calcd for $C_{20}H_{26}O$ 282.1984, found 282.1978 (M^+).

4.2.2. (*Z*)-5-*tert*-Butyl-7-phenyl-hept-4-en-6-ynal (1b). Following the general procedure in Section 4.2, acrolein (0.13 mL, 2.0 mmol), *tert*-butyl acetylene (0.30 mL, 2.4 mmol), tributyl(phenylethynyl)tin (0.77 mL, 2.2 mmol), $Ni(acac)_2$ (51 mg, 0.2 mmol), DIBAL (0.2 mL, 0.2 mmol in 1 M solution), and TMSCl (0.3 mL, 2.4 mmol) were employed to produce, after flash chromatography (3:1 hexane/CH_2Cl_2), 220 mg (46%) of a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.44–7.46 (m, 2H), 7.29–7.33 (m, 3H), 5.77 (t, J=7.5 Hz, 1H), 2.7 (q, J=7.0 Hz, 2H), 2.58 (t, J=7.0 Hz, 2H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.4, 135.2, 131.6, 130.8, 128.6, 128.3, 123.9, 96.1, 87.1, 59.7, 43.7, 29.6, 23.8; IR (film, cm^{-1}) 2964, 2868, 1724, 1669, 1596, 1489, 1448, 1392, 1363, 1245, 908, 757, 691; HRMS (EI) *m/e* calcd for $C_{17}H_{20}O$ 240.1514, found 240.1513 (M^+).

4.2.3. (*Z*)-5-Benzyloxymethyl-7-phenyl-hept-4-ene-6-ynal (1c). Following the general procedure in Section 4.2, acrolein (0.17 mL, 2.5 mmol), benzyl propargyl ether (438 mg, 3.0 mmol), tributyl(phenylethynyl)tin (0.96 mL, 2.8 mmol), $Ni(acac)_2$ (64 mg, 0.25 mmol), DIBAL (0.25 mL, 0.25 mmol in 1.0 M solution), and TMSCl (0.38 mL, 3.0 mmol) were employed to produce, after flash chromatography (3:1 CH_2Cl_2/hexane), 240 mg (32%) of a dark brown oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.82 (br s, 1H), 7.44–7.48 (m, 2H), 7.28–7.39 (m, 8H), 6.06 (t, J=7.5 Hz, 1H), 4.59 (s, 2H), 4.10 (s, 2H), 3.49 (q, J=7.5 Hz, 2H), 2.61–2.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.8, 138.3, 137.1, 131.8, 128.64, 128.61, 128.6, 128.0, 127.9, 123.3, 122.3, 95.4, 85.9, 72.6, 72.4, 43.2, 23.3; IR (film, cm^{-1}) 2948, 2914, 2851, 2725, 1723, 1596, 1572, 1490, 1454, 1443, 913; HRMS (EI) *m/e* calcd for $C_{21}H_{20}O_2$ 304.1463, found 304.1468 (M^+).

4.2.4. (*Z*)-4,5-Diethyl-2-methyl-7-phenyl-hept-4-en-6-ynal (1d). Following the general procedure in Section 4.2, methacrolein (0.17 mL, 2.0 mmol), 3-hexyne (0.27 mL, 2.4 mmol), tributyl(phenylethynyl)tin (0.77 mL, 2.2 mmol), $Ni(acac)_2$ (51 mg, 0.2 mmol), DIBAL (0.2 mL, 0.2 mmol in 1.0 M solution), and TMSCl (0.3 mL, 2.4 mmol) were employed to produce, after flash chromatography (3:1 hexane/CH_2Cl_2), 243 mg (48%) of a light yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, J=2.0 Hz, 1H), 7.39–7.41 (m, 2H), 7.28–7.32 (m, 3H), 2.79 (dd, J=13.0, 7.0 Hz, 1H), 2.59–2.66 (m, 1H), 2.5 (dd, J=13.5, 8.0 Hz, 1H), 2.27 (q, J=15.3, 2H), 2.18 (m, 2H), 1.14–1.17 (m, 6H), 1.04 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 145.6, 131.4, 128.5, 128.0, 124.1, 122.3, 93.2, 90.1, 46.1,

35.9, 25.3, 24.8, 14.0, 13.7, 13.4; IR (film, cm^{-1}) 3058, 2956, 2856, 1726, 1662, 1597, 1490, 1456, 756, 691; HRMS (EI) *m/e* calcd for $C_{18}H_{22}O$ 254.1671, found 254.1669 (M^+).

4.2.5. (*Z*)-3-Methyl-5,8-diphenyl-oct-4-en-7-ynal (1e). Following the general procedure in Section 4.2, crotonaldehyde (0.16 mL, 2.0 mmol), phenyl acetylene (0.26 mL, 2.4 mmol), tributyl(phenylethynyl)tin (0.77 mL, 2.2 mmol), $Ni(acac)_2$ (52 mg, 0.2 mmol), DIBAL (0.2 mL, 0.2 mmol in 1.0 M solution), and TMSCl (0.3 mL, 2.4 mmol) were employed to produce, after flash chromatography (3:1 hexane/CH_2Cl_2), 197 mg (36%) of a yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 9.83 (t, J=2.4 Hz, 1H), 7.65–7.68 (m, 2H), 7.53–7.56 (m, 2H), 7.29–7.39 (m, 6H), 6.30 (d, J=6.0 Hz, 1H), 3.56–3.71 (m, 1H), 2.59 (dd, J=2.4, 6.0 Hz, 2H), 1.26 (d, J=6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.1, 141.4, 137.8, 131.8, 128.8, 128.7, 128.5, 128.2, 126.4, 123.8, 123.3, 96.5, 86.4, 50.8, 31.3, 20.6; IR (film, cm^{-1}) 3058, 2958, 2870, 2722, 1723, 1597, 1490, 1446, 1362, 1072, 1027, 908, 756, 691; HRMS (EI) *m/e* calcd for $C_{20}H_{18}O$ 274.1358, found 274.1357 (M^+).

4.2.6. (*Z*)-2-(2-Hexyl-4-phenyl-but-1-en-3-ynyl)cyclohexanecarbaldehyde (1f). Following the general procedure in Section 4.2, cyclohexanecarbaldehyde (0.11 mL, 1.0 mmol), 1-octyne (0.18 mL, 1.2 mmol), tributyl(phenylethynyl)tin (0.39 mL, 1.1 mmol), $Ni(COD)_2$ (28 mg, 0.1 mmol), and TMSCl (0.15 mL, 1.2 mmol) were employed to produce, after flash chromatography (3:1 hexane/CH_2Cl_2), 95 mg (30%) of a brown oil product of two inseparable diastereomers (2:1). ^1H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 0.33H), 9.6 (d, J=3.5 Hz, 0.67H), 7.42–7.45 (m, 2H), 7.29–7.35 (m, 3H), 5.95 (d, J=9.5 Hz, 0.33H), 5.55 (d, J=9.5 Hz, 0.67H), 3.36–3.39 (m, 0.33H), 2.88 (qd, J=10.0, 3.8 Hz, 0.67H), 2.63 (dt, J=8.0, 4.0 Hz, 0.33H), 2.15–2.20 (m, 2H), 2.08 (tt, J=11.3, 3.5 Hz, 0.67H), 1.2–1.87 (m, 16H), 0.89–0.90 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for two isomers δ 205.4, 205.1, 139.6, 137.1, 131.7, 128.5, 128.3, 124.7, 124.4, 123.7, 94.8, 94.4, 88.1, 88.0, 55.5, 53.3, 40.0, 37.6, 37.4, 37.2, 31.9, 31.8, 30.8, 28.8, 28.7, 28.6, 25.8, 25.3, 24.6, 24.2, 23.3, 23.2, 22.8, 14.3; IR (film, cm^{-1}) 2925, 2865, 2845, 2725, 1720, 1599, 1489, 1443, 755, 690; HRMS (EI) *m/e* calcd for $C_{23}H_{30}O$ 322.2297, found 322.2303 (M^+).

4.2.7. (*Z*)-5-Hexyl-3-methyl-tridec-4-en-6-ynal (1g). Following the general procedure in Section 4.2, crotonaldehyde (0.33 mL, 4.0 mmol), 1-octyne (0.65 mL, 4.8 mmol), tributyl(octynyl)tin (1.76 g, 4.4 mmol), $Ni(acac)_2$ (103 mg, 0.4 mmol), DIBAL (0.4 mL, 0.4 mmol in 1.0 M solution), and TMSCl (0.61 mL, 4.8 mmol) were employed to produce, after flash chromatography (4:1 hexane/CH_2Cl_2), 405 mg (35%) of a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.64 (t, J=2.5 Hz, 1H), 5.38 (d, J=9.0 Hz, 1H), 3.21–3.30 (m, 1H), 2.30–2.36 (m, 4H), 2.03 (t, J=7.30 Hz, 2H), 1.52 (quintet, J=7.0 Hz, 2H), 1.35–1.48 (m, 4H), 1.23–1.33 (m, 10H), 1.05 (d, J=7.0 Hz, 3H), 0.85–0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 138.9, 124.2, 95.7, 78.9, 50.9, 37.6, 31.9, 31.5, 30.5, 29.1, 28.8, 28.5, 22.8, 20.8, 19.7, 14.3, 14.25; IR (film, cm^{-1}) 2955, 2928, 2856, 1726, 1627, 1457, 1378, 1350, 1326, 1261, 1108, 1077, 907, 850, 729, 668, 650; HRMS (EI) *m/e* calcd for $C_{20}H_{34}O$ 290.2610, found 290.2607 (M^+).

4.2.8. (*Z*)-5-Hexyl-7-phenyl-hept-4-en-6-ynal (1h). Following the general procedure in Section 4.2, acrolein (0.13 mL, 2.0 mmol), 1-octyne (0.35 mL, 2.4 mmol), tributyl(phenylethynyl)tin (0.77 mL, 2.2 mmol), $Ni(acac)_2$ (51 mg, 0.2 mmol), DIBAL (0.2 mL, 0.2 mmol of 1.0 M solution), and TMSCl (0.3 mL, 2.4 mmol) were employed to produce, after flash chromatography (2:1 hexanes/CH_2Cl_2), 370 mg (69%) of product as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (t, J=1.2 Hz, 1H), 7.43 (m, 2H), 7.32 (m, 3H), 5.72 (t, J=7.5 Hz, 1H), 2.67 (q, J=7.0 Hz, 2H), 2.57 (m, 2H), 2.18 (t, J=7.7 Hz, 2H), 1.55 (m, 2H), 1.30 (m, 6H), 0.89 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 202.3, 134.7, 131.7, 128.5, 128.3, 125.3, 123.7, 94.7, 87.8, 43.6, 37.2, 31.9, 28.8, 28.6, 23.6, 22.8, 14.3; IR (film, cm^{-1}) 3029, 2854, 2722, 2253, 2200, 1724, 1596, 1489, 755, 732; HRMS (EI) *m/e* calcd for $C_{19}H_{24}O$ 268.1827, found 268.1822 (M^+).

4.3. General procedure for the reductive cyclizations of enynals

To a 0.01 M solution of $Ni(COD)_2$ (0.1 equiv) in toluene at room temperature was added Bu_3P (0.2 equiv) followed by Et_3B (2.0 equiv, 1.0 M solution in THF). A 0.2 M solution of the enynal (1.0 equiv) in toluene was then transferred to this mixture at room temperature, and the reaction mixture was stirred until starting material was consumed as judged by TLC analysis. The mixture was quenched with satd NH_4Cl solution followed by 1.0 M HCl solution. After being stirred for 5 min, the mixture was poured into water and extracted with Et_2O, washed with brine, and then dried over $MgSO_4$. The product was purified by flash chromatography on SiO_2.

4.3.1. (*E*)-2-Benzylidene-3-hexyl-5-methyl-cyclohex-3-enol (2a). Following the general procedure in Section 4.3, compound **1a** (181 mg, 0.64 mmol), $Ni(COD)_2$ (18.2 mg, 0.064 mmol) tributylphosphine (0.035 mL, 0.13 mmol), and triethylborane (1.28 mL, 1.28 mmol in 1.0 M solution) were employed to produce, after column chromatography (10:1 hexane/ethyl acetate), 129 mg (81%) of a yellow oil (two inseparable diastereomers, dr 1.2:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.17–7.29 (m, 5H), 6.69 (s, 0.45H), 6.57 (s, 0.55H), 5.56 (br d, J=1.5 Hz, 0.55H), 5.47 (br d, J=1.5 Hz, 0.45H), 4.40 (br d, J=3.0 Hz, 0.55H), 4.29 (d, J=10.5 Hz, 0.45H), 2.61 (m, 0.55H), 2.54 (m, 0.45H), 2.26 (ddd, J=11.5, 6.0, 4.0 Hz, 0.45H), 2.12 (dt, J=14.0, 5.5 Hz, 0.55H), 1.87–1.97 (m, 1H), 1.73–1.83 (m, 2H), 1.59 (ddd, J=15.0, 8.3, 2.8 Hz, 0.55H), 1.41 (dt, J=11.0, 9.0 Hz, 0.45H), 1.26–1.31 (m, 1H), 0.82–1.17 (m, 10H), 0.79 (t, J=7.0 Hz, 1.35H), 0.78 (t, J=7.0 Hz, 1.65H); ^{13}C NMR (125 MHz, $CDCl_3$) for two isomers δ 141.3, 139.8, 139.3, 138.7, 135.9, 135.4, 134.5, 129.32, 129.26, 127.93, 127.91, 126.9, 126.6, 124.7, 120.6, 73.5, 72.0, 42.1, 39.6, 34.6, 34.3, 31.8, 31.73, 31.69, 31.6, 29.1, 29.05, 29.0, 28.96, 28.4, 22.9, 22.7, 22.6, 22.1, 14.4, 14.3; IR (film, cm^{-1}) 3328, 2955, 2925, 2856, 1491, 1454, 698; HRMS (EI) *m/e* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2141 (M^+).

4.3.2. (*E*)-2-Benzylidene-3-*tert*-butyl-cyclohex-3-enol (2b). Following the general procedure in Section 4.3, compound **1b** (72 mg, 0.23 mmol), $Ni(COD)_2$ (8.3 mg 0.03 mmol) tributylphosphine (0.016 mL, 0.06 mmol), and triethylborane (0.6 mL, 0.6 mmol in 1.0 M solution) were employed to produce, after column chromatography (10:1 hexane/ethyl acetate), 38 mg (52%) of a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.28 (m, 4H), 7.16–7.19 (m, 1H), 6.51 (s, 1H), 5.97 (t, J=5.0 Hz, 1H), 4.42 (br s, 1H), 2.25–2.31 (m, 1H), 2.15–2.22 (m, 1H), 2.04–2.12 (m, 1H), 1.69 (br s, 1H), 1.53–1.61 (m, 1H), 0.91 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 142.5, 139.8, 129.2, 128.2, 127.1, 126.6, 122.6, 74.8, 35.9, 32.9, 31.7, 22.5; IR (film, cm^{-1}) 3364, 3024, 2958, 2866, 1297, 1492, 1476, 1446, 1392, 1364, 1249, 927, 738, 697; HRMS (EI) *m/e* calcd for $C_{17}H_{22}O$ 242.1671, found 242.1670 (M^+).

4.3.3. (*E*)-2-Benzylidene-3-benzyloxymethyl-cyclohex-3-enol (2c). Following the general procedure in Section 4.3, compound **1c** (105 mg, 0.345 mmol), $Ni(COD)_2$ (4.2 mg, 0.035 mmol) tributylphosphine (0.018 mL, 0.069 mmol), and triethylborane (0.69 mL, 0.69 mmol in 1 M solution) were employed to produce, after column chromatography (2:1 hexane/ethyl acetate), 48 mg (45%) of a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.29 (m, 8H), 7.15–7.16 (m, 2H), 6.66 (s, 1H), 6.05 (m, 1H), 4.41 (m, 1H), 4.08 (s, 2H), 3.66–3.72 (m, 2H), 2.46–2.50 (m, 1H), 2.34–2.4 (m, 1H), 2.07 (m, 1H), 1.93–2.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.7, 138.5, 132.3, 131.7, 129.2, 128.4, 128.1, 127.9, 127.6, 127.1, 124.4, 72.4, 71.3, 31.0, 23.4; IR (film, cm^{-1}) 3398, 3056, 3026, 2923, 2862, 1596, 1492, 1453, 1360, 1259, 1208, 1118, 1070, 1028, 920, 844, 803, 734, 697; HRMS (EI) *m/e* calcd for $C_{21}H_{22}O_2$ 306.1620, found 306.1619 (M^+).

4.3.4. (*E*)-2-Benzylidene-3,4-diethyl-6-methyl-cyclohex-3-enol (2d). Following the general procedure in Section 4.3, compound **1d** (412 mg, 1.62 mmol), $Ni(COD)_2$ (45 mg, 0.16 mmol) tributylphosphine (0.085 mL, 0.32 mmol), and triethylborane (3.24 mL, 3.24 mmol in 1 M solution) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 326 mg (79%) of two separable diastereomers (2:1) of a light yellow oil. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.28 (m, 2H), 7.17–7.22 (m, 3H), 6.41 (s, 1H), 4.09 (d, J=4.5 Hz, 1H), 2.36 (dd, J=19.0, 6.8 Hz, 1H), 2.16–2.24 (m, 1H), 2.08–2.14 (m, 2H), 2.00–2.08 (m, 1H), 1.85–1.97 (m, 2H), 1.44 (d, J=6.5 Hz, 1H), 1.04–1.07 (m, 6H), 0.70 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 140.3, 138.9, 130.2, 129.3, 128.0, 126.7, 123.1, 77.9, 35.3, 34.9, 26.2, 22.1, 17.7, 14.5, 13.5; IR (film, cm^{-1}) 3336, 2960, 2929, 2872, 1598, 1490, 1456, 749, 698; HRMS (EI) *m/e* calcd for $C_{18}H_{24}O$ 256.1827, found 256.1829 (M^+). Minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–7.31 (m, 5H), 6.48 (s, 1H), 3.94 (d, J=5.5 Hz, 1H), 2.55 (dd, J=18.5, 6.5 Hz, 1H), 1.90–2.21 (m, 6H), 1.72 (br s, 1H), 1.07 (t, J=14.5 Hz, 3H), 1.03 (d, J=7.0 Hz, 3H), 0.74 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 138.9, 138.6, 131.1, 129.3, 128.1, 126.6, 122.7, 78.7, 35.8, 35.7, 26.2, 22.4, 19.5, 14.6, 13.5; IR (film, cm^{-1}) 3409, 2961, 2928, 2871, 1597, 1491, 1456, 850, 758, 697; HRMS (EI) *m/e* calcd for $C_{18}H_{24}O$ 256.1827, found 256.1827 (M^+).

4.3.5. (*E*)-2-Benzylidene-5-methyl-3-phenyl-cyclohex-3-enol (2e). Following the general procedure in Section 4.3, compound **1e** (78 mg, 0.28 mmol), $Ni(COD)_2$ (8.0 mg, 0.028 mmol) tributylphosphine (0.015 mL, 0.05 mmol), and triethylborane (0.57 mL, 0.57 mmol in 1.0 M solution) were employed to produce, after column chromatography (8:1 hexane/ethyl acetate), two separable diastereomers (1.4:1) (49 mg, 63% yield). Major isomer (light yellow thick gum): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04–7.06 (m, 2H), 6.83–6.95 (m, 9H), 5.86 (d, J=3.5 Hz, 1H), 4.57 (dd, J=10.5, 2.5 Hz, 1H), 2.73–2.81 (m, 1H), 2.35–2.40 (ddd, J=11.0, 6.8, 4.5 Hz, 1H), 1.86 (br s, 1H), 1.58 (ddd, J=13.0, 11.0, 9.5 Hz, 1H), 1.23 (d, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.3, 138.6, 137.4, 136.7, 129.5, 127.67, 127.65, 127.1, 126.4, 126.1, 123.0, 72.3, 41.8, 31.9, 22.4; IR (film, cm^{-1}) 3328, 3078, 3055, 3021, 2955, 2925, 2867, 1599, 1575, 1491, 1444, 1347, 1322, 1264, 1196, 1125, 1078, 1028, 758, 734, 696; HRMS (EI) *m/e* calcd for $C_{20}H_{20}O$ 276.1514, found 276.1516 (M^+). Minor isomer (light yellow oil): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04–7.06 (m, 2H), 6.87–6.95 (m, 8H), 6.72 (s, 1H), 5.93 (d, J=3.0 Hz, 1H), 4.62 (br d, J=4.0 Hz, 1H), 2.79–2.87 (m, 1H), 2.24 (dt, J=13.5, 6.5 Hz, 1H), 1.93 (br s, 1H), 1.74 (ddd, J=13.5, 8.5, 2.5 Hz, 1H), 1.24 (d, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 139.3, 138.1, 137.0, 135.6, 129.5, 127.7, 127.65, 127.1, 126.5, 126.4, 126.3, 73.5, 39.6, 29.1, 21.8; IR (film, cm^{-1}) 3336, 3078, 3056, 3021, 2955, 2925, 2868, 1599, 1492, 1444, 1373, 126, 1203, 1128, 1076, 1030, 989, 958, 917, 863, 760, 740, 696; HRMS (EI) *m/e* calcd for $C_{20}H_{20}O$ 276.1514, found 276.1517 (M^+).

4.3.6. (*E*)-2-Benzylidene-3-hexyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-1-ol (2f). Following the general procedure in Section 4.3, compound **1f** (80 mg, 0.25 mmol), $Ni(COD)_2$ (14 mg, 0.0496 mmol) tributylphosphine (0.026 mL, 0.099 mmol), and triethylborane (0.50 mL, 0.50 mmol in 1.0 M solution) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 146 mg (75%) of partially separable diastereomers of light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) for mixture of all diastereomers δ 7.29–7.17 (m, 5H), 6.75, 6.67, 6.54 (s, 1H each isomer), 5.50, 5.40, 5.33 (s, 1H), 4.37, 4.08, 4.02 (s, s, d, J=9.5 Hz, 1H), 2.717 (s, 1H), 0.76–2.14 (m, 23H); ^{13}C NMR (125 MHz, $CDCl_3$) for mixture of all isomers δ 141.1, 139.5, 138.5, 136.1, 134.7, 133.4, 129.04, 129.0, 127.6, 126.4, 126.3, 121.8, 121.0, 75.4, 75.3, 49.8, 43.2, 42.4, 37.3, 34.4, 34.3, 32.5, 31.5, 31.47, 29.2, 29.0, 28.7, 28.5, 26.4, 26.1, 24.7, 22.6, 22.5, 21.1, 14.1; IR (film, cm^{-1}) 3354, 3019, 2923, 2853, 1491, 1446, 1377, 1018, 846, 698; HRMS (EI) *m/e* calcd for $C_{23}H_{32}O$ 324.2453, found 324.2455 (M^+).

4.3.7. (*E*)-2-Heptylidene-3-hexyl-5-methylcyclohex-3-enol (2g). Following the general procedure in Section 4.3, compound **1g** (194 mg, 0.669 mmol), $Ni(COD)_2$ (18 mg, 0.067 mmol) tributylphosphine (0.035 mL, 0.13 mmol), and triethylborane (1.34 mL, 1.34 mmol in 1.0 M solution) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 146 mg (75%) of two inseparable diastereomers (2.4:1) of light yellow oil. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45–5.49 (m, 1H),

5.35–5.37 (m, 1H), 4.19 (br d, J=2.0 Hz, 1H), 2.51–2.53 (m, 1H), 2.35–2.43 (m, 1H), 2.14–2.23 (m, 3H), 1.99 (dt, J=13.5, 5.0 Hz, 1H), 1.55 (br s, 1H), 1.26–1.43 (m, 17H), 1.02 (d, 7.0 Hz, 3H), 0.86–0.89 (m, 6H), diagnostic chemical shifts for minor isomer: δ 4.12 (br d, J=9.5 Hz, 1H), 2.06–2.11 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) for the two diastereomers: δ 137.6, 136.6, 135.7, 134.0, 133.1, 132.2, 129.2, 122.9, 75.2, 72.3, 41.5, 39.0, 36.4, 36.2, 32.1, 31.9, 31.0, 30.7, 30.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.3, 22.9, 22.8, 22.4, 21.7, 14.3; IR (film, cm^{-1}) 3330, 2953, 2922, 2854, 1606, 1456, 1377, 1092, 1035, 972, 840, 725; HRMS (EI) *m/e* calcd for $C_{20}H_{36}O$ 292.2766, found 292.2767 (M^+).

4.3.8. (*E*)-2-Benzylidene-3-hexylcyclohex-3-enol (2h). Following the general procedure in Section 4.3, compound **1h** (804 mg, 3.0 mmol), $Ni(COD)_2$ (83 mg, 0.3 mmol), tributylphosphine (0.15 mL, 0.6 mmol), and triethylborane (6.0 mL, 6.0 mmol of 1.0 M solution), were combined to produce, after flash chromatography (3:1 hexanes/Et_2O), 689 mg (85%) of product as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 5H), 6.59 (s, 1H), 5.64 (m, 1H), 4.36 (dd, J=7.0, 3.0 Hz, 1H), 2.27–2.44 (m, 2H), 2.02 (m, 1H), 1.94 (m, 1H), 1.85 (m, 2H), 1.71 (br s, 1H), 1.11 (m, 4H), 0.99 (m, 2H), 0.89 (m, 2H), 0.78 (t, J=7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 140.1, 138.8, 136.1, 129.3, 128.7, 127.9, 126.8, 123.6, 73.0, 34.6, 31.7, 31.3, 29.05, 28.99, 23.4, 22.7, 14.2; IR (film, cm^{-1}) 3324, 3022, 1590, 1492, 1105, 698; HRMS (EI) *m/e* calcd for $C_{19}H_{26}O$ 270.1984, found 270.1985 (M^+).

4.4. General procedure for the aromatization of alkylidene cyclohexenols

To a 0.05 M solution of the alcohol in toluene, trifluoroacetic acid (2.0 equiv) was added, the reaction was heated to reflux until starting material was consumed as judged by TLC (typically 2–3 h, unless otherwise noted). The reaction mixture was then concentrated under vacuum and purified via column with pure hexanes (unless otherwise noted).

4.4.1. Benzyl-2-hexyl-4-methylbenzene (3a). Following the general procedure in Section 4.4, compound **2a** (51 mg, 0.18 mmol) and trifluoroacetic acid (TFA) (0.026 mL, 0.36 mmol) were employed to produce, after column chromatography (pure hexane), 36 mg (76%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.20 (t, J=7.3 Hz, 1H), 7.15 (d, J=7.5 Hz, 2H), 6.97–7.03 (m, 3H), 4.01 (s, 2H), 2.56 (m, 2H), 2.35 (s, 3H), 1.47–1.54 (m, 2H), 1.26–1.37 (m, 6H), 0.91 (t, J=6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 141.4, 136.1, 135.5, 130.6, 130.4, 129.0, 128.6, 126.8, 126.1, 38.7, 33.3, 32.0, 31.3, 29.7, 22.9, 21.3, 14.4; IR (film, cm^{-1}) 3026, 2999, 2954, 2925, 2856, 1602, 1494, 1453, 1377, 831, 724, 696; HRMS (EI) *m/e* calcd for $C_{20}H_{26}$ 266.2035, found 266.2033 (M^+).

4.4.2. 1-Benzyl-2-*tert*-butylbenzene (3b). Following the general procedure in Section 4.4, compound **2b** (59 mg, 0.24 mmol) and trifluoroacetic acid (TFA) (0.036 mL, 0.49 mmol) were employed to produce, after column chromatography (pure hexane), 40 mg (73%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J=8.0 Hz, 1H), 7.25–7.28 (m, 2H), 7.16–7.20 (m, 2H), 7.10–7.13 (t, J=7.5 Hz, 1H), 7.08 (d, J=7.5 Hz, 2H), 7.02 (d, J=7.5 Hz, 1H), 4.33 (s, 2H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 142.6, 139.0, 133.4, 129.3, 128.5, 126.3, 126.2, 126.0, 40.2, 36.0, 32.0; IR (film, cm^{-1}) 3060, 3025, 2957, 2872, 1601, 1492, 1452, 1395, 1364, 760, 728, 697; HRMS (EI) *m/e* calcd for $C_{17}H_{20}$ 224.1565, found 224.1567 (M^+).

4.4.3. 1-Benzyl-(benzyloxymethyl)benzene (3c). Following the general procedure in Section 4.4, compound **2c** (30 mg, 0.098 mmol) and trifluoroacetic acid (TFA) (0.015 mL, 0.20 mmol) were employed to produce, after column chromatography (6:1 hexane/CH_2Cl_2), 19 mg (67%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.42 (m, 1H), 7.32–7.37 (m, 4H), 7.23–7.31 (m, 5H), 7.13–7.19 (m, 2H), 7.08–7.10 (m, 2H), 4.52 (s, 2H), 4.51 (s, 2H), 4.07 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 139.5, 138.5, 136.5, 130.7, 129.5, 129.0, 128.6, 128.3, 128.1, 127.9, 126.7, 126.2, 72.6, 70.5, 38.6; IR (film, cm^{-1}) 2921, 2851, 1493, 1452, 1360, 732, 696; HRMS (ESI) *m/e* calcd for $C_{21}H_{20}ONa$ 311.1412, found 311.1411 $[M+Na]^+$.

4.4.4. 1-Benzyl-2,3-diethyl-5-methylbenzene (3d). Following the general procedure in Section 4.4, compound **2d** (17 mg, 0.066 mmol, mixture of isomers) and trifluoroacetic acid (TFA) (0.010 mL, 0.132 mmol) were employed to produce, after column chromatography (15:1 hexane/CH_2Cl_2), 11 mg (70%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J=7.0 Hz, 2H), 7.19 (t, J=7.5 Hz, 1H), 7.14 (d, J=7.0 Hz, 2H), 6.93 (s, 1H), 6.79 (s, 1H), 4.01 (s, 2H), 2.60–2.67 (m, 4H), 2.27 (s, 3H), 1.24 (t, J=7.8 Hz, 3H), 1.05 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 141.7, 138.5, 137.5, 135.3, 129.4, 129.0, 128.55, 128.0, 126.0, 39.3, 25.9, 21.7, 21.3, 16.0, 15.3; IR (film, cm^{-1}) 3062, 3025, 2964, 2927, 2872, 1603, 1578, 1494, 1451, 1375, 862, 733, 698; HRMS (EI) *m/e* calcd for $C_{18}H_{22}$ 238.1722, found 238.1725 (M^+).

4.4.5. 2-Benzyl-5-methylbiphenyl (3e). Following the general procedure in Section 4.4, compound **2e** (29 mg, 0.11 mmol) and trifluoroacetic acid (TFA) (0.016 mL, 0.21 mmol) were employed to produce, after column chromatography (pure hexane), 10 mg (38%) of a thick colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.37 (m, 3H), 7.24–7.26 (m, 1H), 7.17–7.22 (m, 3H), 7.11–7.15 (m, 3H), 7.09 (s, 1H), 6.98 (d, J=7.0 Hz, 2H), 3.93 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 142.0, 141.95, 135.9, 135.4, 131.1, 130.5, 129.5, 129.0, 128.4, 128.2, 127.0, 125.9, 38.8, 21.2; IR (film, cm^{-1}) 3026, 2917, 1600, 1488, 1452, 906, 835, 762, 728, 700; HRMS (EI) *m/e* calcd for $C_{20}H_{18}$ 258.1409, found 258.1409 (M^+).

4.4.6. 6-Benzyl-7-hexyl-1,2,3,4-tetrahydronaphthalene (3f). Following the general procedure in Section 4.4, compound **2f** (10.5 mg, 0.0324 mmol) and trifluoroacetic acid (TFA) (0.007 mL, 0.097 mmol) were employed to produce, after column chromatography (pure hexane), 6.8 mg (69%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.28 (m, 2H), 7.13–7.19 (m, 3H), 6.88 (s, 1H), 6.79 (s, 1H), 3.95 (s, 2H), 2.73 (m, 2H), 2.68 (m, 2H), 2.49 (m, 2H), 1.77 (quintet, J=3.3 Hz, 4H), 1.46 (m, 2H), 1.20–1.34

(m, 6H), 0.87 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 138.6, 135.7, 135.3, 134.7, 131.2, 130.2, 129.0, 128.5, 126.0, 38.7, 32.9, 32.0, 31.4, 29.7, 29.2, 29.16, 23.6, 22.8, 14.3; IR (film, cm^{-1}) 3025, 2924, 2855, 1602, 1494, 1452, 1436, 920, 870, 725, 696; HRMS (EI) *m/e* calcd for $C_{23}H_{30}$ 306.2348, found 306.2350 (M^+).

4.4.7. 1-Heptyl-2-hexyl-4-methylbenzene (3g). Following the general procedure in Section 4.4, compound **2g** (52 mg, 0.17 mmol, mixture of isomers) and trifluoroacetic acid (TFA) (0.060 mL, 0.34 mmol) were employed to produce, after column chromatography (pure hexane), 39 mg (80%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, J=7.5 Hz, 1H), 6.98 (s, 1H), 6.95 (d, J=8.0 Hz, 1H), 2.58 (t, J=8.3 Hz, 4H), 2.31 (s, 3H), 1.54–1.61 (m, 4H), 1.31–1.44 (m, 14H), 0.86–0.94 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 137.8, 135.3, 130.1, 129.3, 126.7, 33.0, 32.6, 32.1, 32.0, 31.8, 31.7, 30.0, 29.8, 29.5, 23.0, 22.9, 21.2, 14.4; IR (film, cm^{-1}) 2954, 2923, 2855, 1615, 1501, 1465, 1377, 817, 723; HRMS (EI) *m/e* calcd for $C_{20}H_{34}$ 274.2661, found 274.2660 (M^+).

4.4.8. 1-Benzyl-2-hexylbenzene (3h). Following the general procedure in Section 4.4, compound **2h** (58 mg, 0.19 mmol) and trifluoroacetic acid (TFA) (0.028 mL, 0.37 mmol) were employed to produce, after column chromatography (pure hexane), 43 mg (80%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.3 (t, J=7.5 Hz, 2H), 7.12–7.23 (m, 7H), 4.06 (s, 2H), 2.61 (m, 2H), 1.53 (quintet, J=7.8 Hz, 2H), 1.27–1.38 (m, 6H), 0.91 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 141.3, 138.6, 130.6, 129.6, 129.0, 128.6, 126.7, 126.2, 126.1, 39.1, 33.2, 32.0, 31.1, 29.7, 22.9, 14.4; IR (film, cm^{-1}) 3062, 3025, 2955, 2924, 2851, 1601, 1494, 1452, 751, 729, 670; HRMS (EI) *m/e* calcd for $C_{19}H_{24}$ 252.1878, found 252.1882 (M^+).

4.5. General procedure for the palladium acetate oxidation of alkylidene cyclohexenols

To a toluene solution of palladium acetate (10 mol %) and MS 3 Å, pyridine was added (1.0 equiv) and the solution was heated to 80 °C for 10 min under a balloon of oxygen. After that, a toluene solution of the alcohol (1.0 equiv) (total concentration is 0.1 M with respect to the alcohol) was added dropwise and the reaction was stirred at 80 °C under oxygen until starting material was completely consumed as judged by TLC analysis. Then, the reaction mixture was filtered, the solvent was removed under vacuum, and the crude product was purified by column chromatography on SiO_2.

4.5.1. (*E*)-Benzylidene-3-hexyl-5-methylcyclohex-3-enone (4a). Following the general procedure in Section 4.5, compound **2a** (44 mg, 0.155 mmol), $Pd(OAc)_2$ (7.0 mg, 0.031 mmol), pyridine (0.025 mL, 0.31 mmol), and MS 3 Å (78 mg) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 30 mg (69%) of a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.26–7.34 (m, 5H), 5.98 (d, J=3.5 Hz, 1H), 2.65–2.76 (m, 1H), 2.58 (dd, J=16.5, 5.0 Hz, 1H), 2.16 (dd, J=16.5, 9.0 Hz, 1H), 1.95–2.07 (m, 2H), 1.17 (d, J=7.0 Hz, 3H), 1.08–1.14 (m, 4H), 0.87–1.04 (m, 4H), 0.78 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 138.3, 136.6, 136.1, 134.3, 133.1, 129.6, 128.5, 128.2, 44.8, 33.6, 31.6, 29.0, 28.8, 28.5, 22.6, 20.9, 14.2; IR (film, cm^{-1}) 3056, 3024, 2957, 2925, 2855, 1695, 1623, 1587, 1571, 1516, 1492, 1454, 1406, 1376, 1336, 1241, 1158, 1072, 1029, 830, 739, 698; HRMS (EI) *m/e* calcd for $C_{20}H_{26}O$ 282.1984, found 282.1982 (M^+).

4.5.2. (*E*)-2-Benzylidene-3,4-diethyl-6-methylcyclohex-3-enone (4d). Following the general procedure in Section 4.5, compound **2d** (42 mg, 0.16 mmol), $Pd(OAc)_2$ (7.3 mg, 0.033 mmol), pyridine (0.014 mL, 0.16 mmol), and MS 3 Å (82 mg) were employed to produce, after column chromatography (15:1 hexane/ethyl acetate), 24.5 mg (59%) of a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.35 (m, 6H), 2.41 (dd, J=14.5, 5.0 Hz, 1H), 2.19–2.36 (m, 5H), 2.05 (sextet, J=7.0 Hz, 1H), 1.20 (d, J=6.5 Hz, 3H), 1.10 (t, J=7.3 Hz, 3H), 0.72 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.7, 141.1, 136.7, 135.9, 132.7, 131.2, 129.9, 128.4, 128.2, 39.8, 34.7, 26.9, 22.7, 16.3, 15.2, 12.8; IR (film, cm^{-1}) 2986, 2976, 2925, 2885, 1689, 1599, 1588, 1448, 1181, 1026, 929, 758, 697; HRMS (EI) *m/e* calcd for $C_{18}H_{22}O$ 254.1671, found 254.1671 (M^+).

4.5.3. (*E*)-2-Benzylidine-3-hexyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(2*H*)-one (4f). Following the general procedure in Section 4.5, compound **2f** (35 mg, 0.108 mmol), $Pd(OAc)_2$ (5.0 mg, 0.022 mmol), pyridine (0.0093 mL, 0.108 mmol), and MS 3 Å (70 mg) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 25 mg (72%) of a light yellow oil (inseparable diastereomers). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 0.6H), 7.55 (s, 0.3H), 7.28–7.35 (m, 5H), 6.64 (s, 0.1H), 6.00 (d, J=5.5 Hz, 0.3H), 5.75 (s, 0.6H), 5.60 (s, 0.1H), 2.65 (m, 0.3H), 2.45–2.50 (m, 0.4H), 2.27–2.32 (m, 0.9H), 2.16 (m, 0.7H), 1.91–2.11 (m, 3H), 1.83–1.88 (m, 0.9H), 1.78–1.80 (m, 0.9H), 1.28–1.44 (m, 4.6H), 1.17–1.21 (m, 0.6H), 1.13 (m, 3.6H), 0.87–1.04 (m, 4.1H), 0.78 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) all isomers: δ 204.9, 203.7, 198.6, 137.6, 137.5, 136.7, 136.6, 135.1, 134.2, 133.9, 133.3, 133.1, 132.2, 130.1, 129.4, 129.34, 129.2, 128.2, 128.1, 127.9, 127.85, 127.7, 55.3, 50.1, 46.1, 43.1, 37.6, 33.5, 33.3, 32.8, 32.5, 31.7, 31.4, 30.2, 29.3, 28.84, 28.79, 28.64, 28.56, 28.2, 26.3, 25.9, 25.8, 25.7, 25.1, 24.5, 24.0, 23.5, 22.6, 22.4, 14.1, 14.0; IR (film, cm^{-1}) 2923, 2852, 1690, 1583, 149, 1455, 1383, 1152, 1067, 696; HRMS (EI) *m/e* calcd for $C_{23}H_{30}O$ 322.2297, found 322.2296 (M^+).

4.5.4. (*E*)-Benzylidene-3-hexylcyclohex-3-enone (4h). Following the general procedure in Section 4.5, compound **2h** (25 mg, 0.093 mmol), $Pd(OAc)_2$ (2.1 mg, 0.0093 mmol), pyridine (0.008 mL, 0.093 mmol), and MS 3 Å (46 mg) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 17 mg (68%) of a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.26–7.34 (m, 5H), 6.06 (m, 1H), 2.42–2.49 (m, 4H), 2.03 (t, J=7.3 Hz, 2H), 1.09–1.15 (m, 4H), 0.92–1.04 (m, 4H), 0.77 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 139.5, 136.5, 134.8, 133.0, 129.6, 129.2, 128.5, 128.1, 36.2, 33.7, 31.6, 29.0, 28.8, 22.7, 22.2, 14.2; IR (film, cm^{-1}) 3060, 3027, 2955, 2854, 1694, 1625, 1586, 1492, 1446, 1339, 1252, 1171, 1015, 919, 758, 725, 697;

HRMS (EI) *m/e* calcd for $C_{19}H_{24}O$ 268.1827, found 268.1826 (M^+).

4.6. General procedure for the addition of alkyl lithium reagents to alkylidene cyclohexenones

A 0.05 M THF solution of anhydrous cerium chloride (5.0 equiv) was stirred for 3 h at room temperature. The slurry was cooled to −78 °C and the alkyl lithium (2.0 equiv) was added, the solution was stirred for an additional 1 h at −78 °C. Then, a THF solution of the ketone (1.0 equiv) was added dropwise, and the reaction mixture was stirred at −78 °C for 1 h. The reaction mixture was allowed to warm to 0 °C, quenched with a 1 M HCl solution, stirred for 10 min at 0 °C, extracted with diethyl ether, and dried over $MgSO_4$, evaporated under vacuum and purified by column chromatography.

4.6.1. (*E*)-2-Benzylidene-3,4-diethyl-1,6-dimethylcyclohex-3-enol (alcohol precursor of 5d). Following the general procedure in Section 4.6, $CeCl_3$ (233 mg, 0.945 mmol), CH_3Li (0.24 mL, 0.38 mmol), and compound **4d** (48 mg, 0.19 mmol) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 44 mg (86% yield) of a light yellow oil (single diastereomer). ^1H NMR (500 MHz, $CDCl_3$) δ 7.22–7.28 (m, 4H), 7.16–7.19 (m, 1H), 6.57 (s, 1H), 2.45 (dd, J=18.0, 6.0 Hz, 1H), 2.10 (q, J=7.5 Hz, 2H), 1.87–2.04 (m, 4H), 1.69 (s, 1H), 1.40 (s, 3H), 1.05 (t, J=7.3 Hz, 3H), 0.94 (d, J=6.5 Hz, 3H), 0.71 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 139.6, 137.5, 132.2, 129.2, 128.1, 126.4, 120.4, 74.7, 39.7, 37.2, 26.1, 25.3, 23.1, 16.2, 14.6, 13.3; IR (film, cm^{-1}) 3470, 3075, 3055, 3020, 2962, 2929, 2871, 2832, 1632, 1596, 1490, 1445, 1373, 1317, 1216, 1153, 1108, 1072, 920, 859, 748, 697, 650; HRMS (EI) *m/e* calcd for $C_{19}H_{26}O$ 270.1984, found 270.1984 (M^+).

4.6.2. 1-Benzyl-2,3-diethyl-5,6-dimethylbenzene (5d). Following the general procedure in Section 4.4, the alcohol precursor above (34 mg, 0.13 mmol) and trifluoroacetic acid (TFA) (0.019 mL, 0.25 mmol) were employed to produce, after column chromatography (pure hexane), 28.5 mg (90%), of a light yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25–7.28 (m, 2H), 7.16–7.19 (m, J=7.5 Hz, 2H), 7.05 (d, J=7.0 Hz, 1H), 7.00 (s, 1H), 4.15 (s, 2H), 2.68 (q, J=7.8 Hz, 2H), 2.63 (q, J=7.8 Hz, 2H), 2.29 (s, 3H), 2.10 (s, 3H), 1.28 (t, J=7.5 Hz, 3H), 1.11 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 139.5, 138.7, 136.3, 134.6, 133.8, 129.1, 128.6, 128.2, 125.6, 35.4, 26.00, 22.6, 21.0, 16.2, 16.1, 15.7; IR (film, cm^{-1}) 3060, 3024, 2870, 1603, 1494, 1446, 1451, 1374, 1322, 1264, 1208, 1067, 1030, 1010, 946, 875, 843, 792, 728, 698; HRMS (EI) *m/e* calcd for $C_{19}H_{24}$ 252.1878, found 252.1876 (M^+).

4.6.3. (*E*)-2-Benzylidene-3-hexyl-1-methylcyclohex-3-enol (alcohol precursor of 5h). Following the general procedure in Section 4.6, $CeCl_3$ (138 mg, 0.56 mmol), CH_3Li (0.14 mL, 0.22 mmol), and compound **4h** (30 mg, 0.11 mmol) were employed to produce, after column chromatography (8:1 hexane/ethyl acetate), 25.7 mg (81% yield) of a light yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25–7.28 (m, 2H), 7.17–7.22 (m, 3H), 6.78 (s, 1H), 5.58 (m, 1H), 2.36–2.40 (m, 1H), 2.22–2.29 (m, 1H), 1.80–1.91 (m, 3H), 1.71–1.77 (m, 1H), 1.68 (s, 1H), 1.39 (s, 3H), 0.82–1.17 (m, 8H), 0.78 (t, J=7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 139.5, 137.4, 129.2, 127.9, 127.74, 126.6, 120.8, 72.7, 38.4, 35.0, 31.7, 29.3, 29.1, 25.5, 24.9, 22.7, 14.3; IR (film, cm^{-1}) 3370, 3076, 3054, 3021, 2954, 2925, 2855, 1596, 1492, 1456, 1444, 1367, 1324, 1147, 1096, 1072, 982, 922, 831, 758, 698; HRMS (EI) *m/e* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2139 (M^+).

4.6.4. 1-Benzyl-2-hexyl-6-methylbenzene (5h). Following the general procedure in Section 4.4, the alcohol precursor above (23 mg, 0.082 mmol) and trifluoroacetic acid (TFA) (0.012 mL, 0.16 mmol) were employed to produce, after column chromatography (pure hexane), 18 mg (84%) of a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.23–7.28 (m, 2H), 7.12–7.18 (m, 2H), 7.09 (d, J=6.5 Hz, 1H), 7.06 (d, J=7.0 Hz, 1H), 7.01 (d, J=7.5 Hz, 2H), 4.09 (s, 2H), 2.57 (m, 2H), 2.22 (s, 3H), 1.49 (quintet, J=7.6 Hz, 2H), 1.22–1.33 (m, 6H), 0.87 (t, J=6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 140.6, 137.7, 136.4, 128.6, 128.3, 128.2, 127.5, 126.6, 125.9, 34.8, 33.9, 31.9, 31.6, 29.6, 22.8, 20.6, 14.3; IR (film, cm^{-1}) 3063, 3025, 2955, 2927, 2857, 1603, 1587, 1494, 1467, 1452, 1378, 780, 755, 726; HRMS (EI) *m/e* calcd for $C_{20}H_{26}$ 266.2035, found 266.2035 (M^+).

4.7. General procedure for the synthesis of aryl alkyl ethers and phenols

To a 0.05 M solution of the cyclohexenone in the corresponding alcohol, tetrafluoroboric acid (HBF_4) (5.0 equiv, unless otherwise noted) was added at room temperature, the reaction was refluxed for 10–12 h (unless otherwise noted), quenched with ammonium chloride, extracted with diethyl ether, dried over $MgSO_4$, and purified by column chromatography (hexane/ethyl acetate) to yield the corresponding aryl alkyl ether and/or phenol.

4.7.1. 2-Benzyl-3,4-diethyl-6-methylphenol (6d). Following the general procedure in Section 4.7, compound **4f** (22 mg, 0.087 mmol), HBF_4 (0.11 mL, 0.87 mmol, 10.0 equiv, 48%, 7.87 M), and ethanol (1.7 mL) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 14.5 mg (67%) of a thick yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25–7.28 (m, 2H), 7.15–7.20 (m, 3H), 6.91 (s, 1H), 4.44 (s, 1H), 4.11 (s, 2H), 2.63 (m, 4H), 2.22 (s, 3H), 1.23 (t, J=7.5 Hz, 3H), 1.09 (t, J=7.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 140.5, 139.7, 134.2, 129.5, 128.8, 128.3, 126.4, 124.3, 121.2, 32.3, 25.6, 22.5, 16.3, 16.1, 15.6; IR (film, cm^{-1}) 3568, 3082, 3060, 3024, 2963, 2928, 2870, 1603, 1579, 1493, 1474, 1451, 1375, 1315, 1240, 1209, 947, 878, 730, 698; HRMS (EI) *m/e* calcd for $C_{18}H_{22}O$ 254.1671, found 254.1669 (M^+).

4.7.2. 2-Benzyl-3-hexyl-5,6,7,8-tetrahydronaphthalen-1-ol (6f). Following the general procedure in Section 4.7, compound **4f** (21 mg, 0.065 mmol), HBF_4 (0.17 mL, 1.3 mmol, 20.0 equiv, 48%, 7.87 M), and ethanol (1.3 mL) were employed to produce, after column chromatography (3:1 hexane/CH_2Cl_2), 11 mg (52%) of white solid. Mp 50–52 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24–7.27 (m, 2H), 7.16–7.19 (m, 3H), 6.59 (s, 1H), 4.58 (s, 1H), 4.04 (s, 2H),

2.74 (t, J=6.3 Hz, 2H), 2.53–2.57 (m, 4H), 1.81–1.86 (m, 2H), 1.74–1.79 (m, 2H), 1.45–1.51 (m, 2H), 1.23–1.3 (m, 6H), 0.87 (t, J=6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 140.6, 139.9, 136.6, 128.8, 128.3, 126.3, 122.4, 122.2, 120.8, 33.6, 31.92, 31.88, 31.7, 29.67, 29.66, 23.1, 23.1, 22.8, 14.3; IR (film, cm^{-1}) 3558, 3024, 1620, 1602, 1572, 1493, 1452, 1423, 1339, 1238, 1180, 1075, 1030, 947, 908, 727, 696; HRMS (EI) *m/e* calcd for $C_{23}H_{30}O$ 322.2297, found 322.2293 (M^+).

4.7.3. 2-Benzyl-3-hexyl-phenyl-*n*-propyl ether (7h). Following the general procedure in Section 4.7, compound **4h** (21 mg, 0.078 mmol), HBF_4 (0.055 mL, 0.39 mmol, 48%, 7.87 M), and *n*-propanol (1.6 mL) were employed to produce, after column chromatography (20:1 hexane/ethyl acetate), 16.3 mg (67%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–7.23 (m, 2H), 7.11–7.16 (m, 4H), 6.80 (d, J=7.5 Hz, 1H), 6.74 (d, J=7.5 Hz, 1H), 4.09 (s, 2H), 3.88 (t, J=6.3 Hz, 2H), 2.58 (m, 2H), 1.71 (sextet, J=7.0 Hz, 2H), 1.46 (m, 2H), 1.20–1.33 (m, 6H), 0.92 (t, J=7.5 Hz, 3H), 0.87 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 143.2, 141.9, 128.4, 128.3, 127.4, 127.1, 125.6, 121.7, 109.1, 69.9, 33.5, 31.9, 31.6, 31.4, 29.7, 22.9, 22.8, 14.3, 10.9; IR (film, cm^{-1}) 3062, 3026, 2958, 2927, 2857, 1602, 1584, 1494, 1460, 1390, 1316, 1259, 775, 727, 696, 626, 613; HRMS (EI) *m/e* calcd for $C_{22}H_{30}O$ 310.2297, found 310.2301 (M^+).

4.7.4. 2-Benzyl-3-hexyl-phenyl-allyl ether (8h). Following the general procedure in Section 4.7, compound **4h** (25 mg, 0.093 mmol), HBF_4 (0.059 mL, 0.47 mmol, 48%, 7.87 M), and allyl alcohol (1.0 mL) were employed to produce, after column chromatography (20:1 hexane/CH_2Cl_2, then 10:1 hexane/CH_2Cl_2), 18.9 mg (66%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–7.23 (m, 2H), 7.11–7.16 (m, 4H), 6.82 (d, J=8.0 Hz, 1H), 6.75 (d, J=8.0 Hz, 1H), 5.95 (m, 1H), 5.30 (dq, J=17.8, 1.8 Hz, 1H), 5.18 (dq, J=10.5, 1.5 Hz, 1H), 4.49 (d, J=4.5 Hz, 2H), 4.11 (s, 2H), 2.58 (m, 2H), 1.46 (quintet, J=7.6 Hz, 2H), 1.22–1.33 (m, 6H), 0.86 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 143.4, 141.7, 133.9, 128.4, 128.3, 127.6, 127.1, 125.6, 122.2, 116.9, 109.7, 69.2, 33.5, 31.9, 31.6, 31.3, 29.6, 22.8, 14.3; IR (film, cm^{-1}) 3062, 3026, 2954, 2927, 2857, 1602, 1582, 1494, 1452, 1423, 1379, 1315, 1258, 778, 727, 696, 640; HRMS (EI) *m/e* calcd for $C_{22}H_{28}O$ 308.2140, found 308.2142 (M^+).

4.7.5. 2-Benzyl-3-hexyl-5-methyl-phenyl-ethyl ether (9a). Following the general procedure in Section 4.7, compound **4a** (27 mg, 0.096 mmol), HBF_4 (0.06 mL, 0.48 mmol, 10.0 equiv, 48%, 7.87 M), and ethanol (1.9 mL) were employed to produce, after column chromatography (25:1 hexane/ethyl acetate), 19.0 mg (64%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–7.22 (m, 3H), 7.10–7.13 (m, 2H), 6.63 (s, 1H), 6.57 (s, 1H), 4.03 (s, 2H), 3.97 (q, J=6.8 Hz, 2H), 2.53 (m, 2H), 2.32 (s, 3H), 1.44 (quintet, J=8.0 Hz, 2H), 1.22–1.33 (m, 9H), 0.87 (t, J=6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 142.9, 142.2, 136.8, 128.5, 128.2, 125.5, 124.5, 122.5, 110.4, 63.9, 33.5, 31.9, 31.5, 31.4, 29.7, 22.8, 21.8, 15.2, 14.3; IR (film, cm^{-1}) 3023, 2954, 2925, 2857, 1610, 1580, 1493, 1453, 1290, 1181, 725, 696; HRMS (EI) *m/e* calcd for $C_{22}H_{30}O$ 310.2297, found 310.2297 (M^+).

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