Base Mediated Aromatization of Carbonyl Condensation Products Derived from 2-(2-Bromoprop-2-enyl)cyclohexanone Derivatives *via* '*Intramolecular Unsaturation Transfer*'

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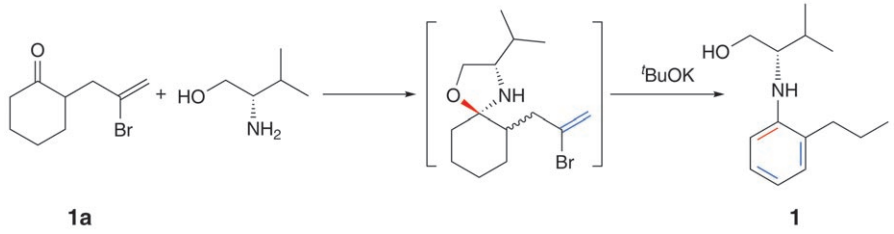
Alkylbenzenes are synthesized for the first time from aliphatic hydrocarbons *via* an one pot, transition metal-free coupling approach under basic conditions. The method consists of two steps: condensation of 2-bromoprop-2-enyl- or 2-propargylcyclohexanone with alcohols, amines, or amino alcohols, followed by base treatment (*Scheme 1*). Phenolic ethers and *N*-phenylated polyalkyl aromatic compounds are shown to be in the scope of the demonstrated reaction (*Table*). The proposed mechanism suggests that the unsaturation in another part of the molecule (propargyl-group equivalent) is transferred into the cyclohexane ring to yield a benzene ring through a series of prototropic shifts.

Introduction. – Despite comprising a major portion of all organic compounds, synthetic procedures for the preparation of molecules containing benzene ring(s) are mainly dependent on modifications of benzene derivatives [1]. Alternative methods described in the literature include oxidative, radical, or transition metal mediated dehydrogenation of cyclohexane derivatives [2], direct construction of a benzene ring *via* intramolecular cyclization or cycloaddition [3], and biotransformations [4]. Recently, in a study on the synthesis of tetrahydroindole derivatives [5a], we discovered that, when treated with ^{t}BuOK, oxazolidines and acetals derived from 2-(2-bromoprop-2-enyl)cyclohexanone [5a][5b] yielded an aromatized product, in which the cyclohexane ring was converted to a benzene ring, whereas the 2-bromoprop-2-enyl moiety was transformed into a Pr group (*Scheme 1*). In this report, we present the preliminary results on our research of the mechanism, synthetic utility, and scope of this particular transformation.

Scheme 1. *Aromatization* via *Intamolecular Unsaturation Transfer*



1a **1**

Results and Discussion. – In the *Table*, a number of aromatization products obtained by the process described above are listed, and it is shown that the method is applicable to 1,2-amino alcohols, diol, primary alcohol, and amine structures to yield *N*-alkyl-2-propylanilines or corresponding phenol ethers and gives important clues about both the scope and mechanism of this reaction.

It is well documented in the literature that chiral 1,2-amino alcohols can act as ligands in catalytic asymmetric organozinc additions [6] and boron-catalyzed reactions, and serve as building blocks in the synthesis of biologically active compounds [7][8]. Moreover, it is very likely that the synthesized compounds may serve as valuable chiral ligands or may be starting materials for biologically active targets. There are also procedures available for different kinds of modifications on Pr groups attached to a phenyl unit [9]. Phenolic ethers, which are available *via* our methodology, may also be used as starting materials for several biologically active products [10].

In *Entries 12* and *13*, it is observed that a Me group present in the starting material **1c** remains in the aromatized product, which clearly indicates that alkyl-substituted benzene derivatives are also available *via* our methodology. The substrates for aromatization products are prepared from readily available, cheap cyclohexanone derivatives; are easily obtained *via* various *Stork*-enamine species; and are converted to valuable *N*-alkylphenylated compounds in one step without the inclusion of any transition metal compounds. All these data together indicate that, under optimized conditions for each target, this aromatization reaction can provide valuable shortcuts in organic synthesis.

The most important information that allows us to propose a mechanism for this reaction is the unsaturation of the cyclohexane moiety to yield a benzene ring and the saturation of the 2-bromoprop-2-enyl group to a propane entity, which strongly indicates an '*intramolecular unsaturation transfer*' from the 2-bromoprop-2-enyl moiety to a cyclohexane ring. *Entry 5* in the *Table*, in which a propargyl unit has replaced the 2-bromoprop-2-enyl unit, also underwent an aromatization reaction and this strongly excludes the possibility of a radical reaction mechanism because there is no reasonable candidate of a radical source in this case. This prompted us to propose a reaction mechanism that proceeded through ionic intermediates. KOH, 4-(dimethylamino)pyridine, and 1,8-diazabicyclo[5.4.0]undec-7-ene were also screened as base instead of ^{t}BuOK with the same stoichiometry, but failed to yield any aromatized product. In *Scheme 2*, the reaction mechanism is outlined, and an imine is selected as a model condensation product[1]). According to our mechanistic model, two C=C bonds of the benzene ring are provided by the unsaturation in the 2-bromoprop-2-enyl moiety, whereas the third C=C bond, which completes the transformation to a benzene ring, is provided by the functional group (oxazolidine, acetal, imine), which has replaced the C=O *O*-atom in the starting ketone. The driving force for this reaction may be the isomerization under these 'forced' reaction conditions, which ultimately gave the final

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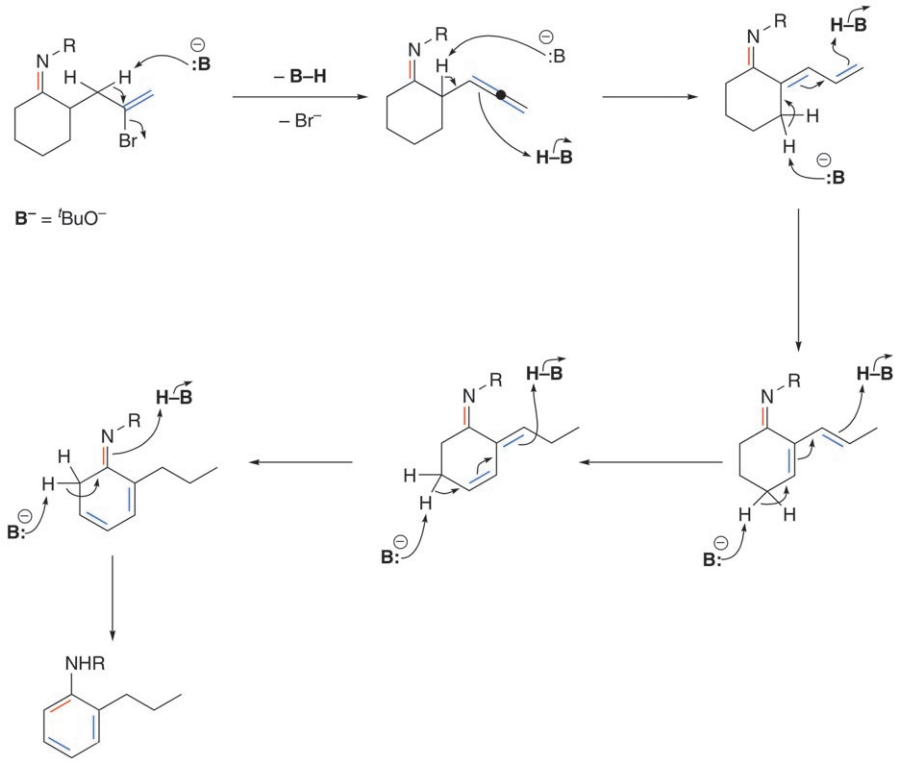
[1]) For amino alcohols, the question of 'which intermediate, imine or oxazolidine yields the aromatized product' may arise at this point. It is reported that these two species are in tautomeric equilibrium with each other for different C=O compounds [11]. Both compounds can be converted to the same enamine species under reaction conditions. Acetals will similarly yield enol ethers under the same conditions and provide the third C=C bond to complete the aromatization.

Scheme 2. *Proposed Reaction Mechanism by Consecutive Prototropic Shifts*

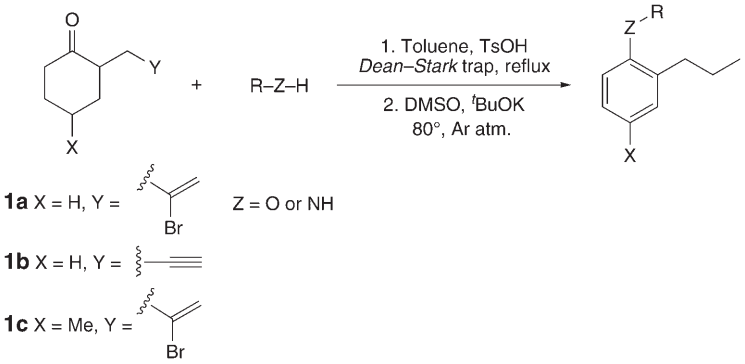


(and probably the most stable under the reaction conditions) aromatized product, which is not further converted to any other product.

Another evidence for the proposed reaction mechanism comes from a designed experiment, in which the cyclohexanone ring was 'blocked' for aromatization by replacing two H-atoms by Me groups (*Scheme 3*). 4,4-Dimethyl-2-(prop-2-yn-1-yl)cyclohexanone **13** was treated with triethyl orthoformate and EtOH to yield 1-ethoxy-4,4-dimethyl-6-(prop-2-yn-1-yl)cyclohexene (**14**). When **14** was subjected to the aromatization conditions, a structure resembling to proposed intermediates, (6*E*)-1-ethoxy-4,4-dimethyl-6-(prop-2-en-1-ylidene)cyclohexene (**15**) was isolated as expected.

In conclusion, we have demonstrated a new coupling method for the synthesis of substituted benzene rings. This study, which concentrated on the establishment of scope and mechanism of the presented aromatization reaction, may be extended to further targets by optimizing the conditions for higher yields, which may provide a new and useful method for synthetic applications. We are planning to use the chiral products obtained as ligands in asymmetric synthesis, to modify the propyl group by alternating the side chain in the starting ketone, and to use our method to synthesize benzolactam V-8 [12].

Table. *Aromatization of Various Condensation Products*



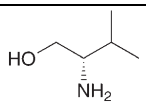
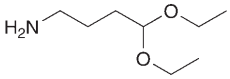
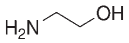
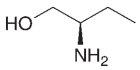
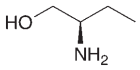
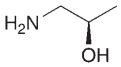
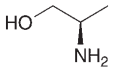
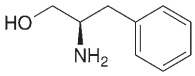
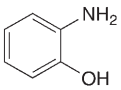
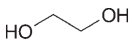
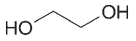
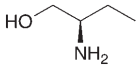
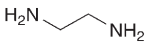
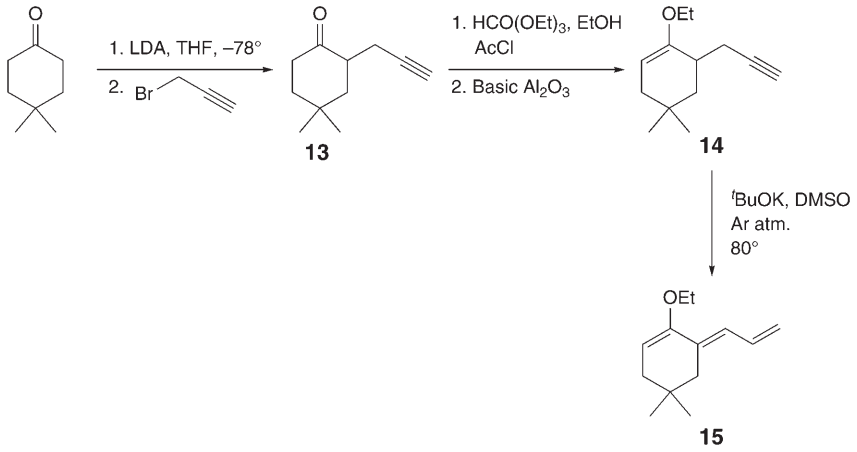
Entry	Substrate	R–Z–H	Product	Yield [%][a])
1	**1a**		**1**	35
2	**1a**		**2**	33
3	**1a**		**3**	22
4	**1a**		**4**	56
5	**1b**[b])		**4**	42
6	**1a**		**5**	30
7	**1a**		**6**	45
8	**1a**		**7**	31
9	**1a**		**8**	12
10	**1a**		**9**	45
11[c])	**1a**	EtOH	**10**	30

Table (cont.)

Entry	Substrate	R–Z–H	Product	Yield [%][a])
12	**1c**		**11**	34
13	**1c**		**12**	37
14	**1a**		No reaction	–

[a]) Yields after chromatography. [b]) For synthesis, see [5c]. [c]) The synthetic procedure is different from outlined above, see *Exper. Part.*

Scheme 3



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Experimental Part

1. *General*. Reactions were monitored by TLC after a 'mini' workup of the reaction mixture, using precoated SiO_2 plates (*Merck* silica gel *60 F-254*), visualized by UV light and phosphomolybdic acid in EtOH. For purification of crude mixtures, flash chromatography (FC) was applied using SiO_2 (*J. T. Baker* 0.063–0.200 mm). Polarimetric measurements: *Rudolph Scientific Autopol III* polarimeter and reported as follows $[\alpha]_D^{20}$ (*c* in g per 100 ml, solvent). IR Spectra: *Digilab Excalibur* Series FT-IR. ^{1}H- and ^{13}C-NMR Spectra: in $CDCl_3$, on a *Bruker Spectrospin Avance DPX 400* spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C); chemical shifts with respect to Me_4Si (^{1}H, 0.00 ppm) or $CDCl_3$ (^{13}C, 77.1 ppm). HR-MS Data: LC-MS analysis: *APCI-Q-TOF II* (*Waters*, Milford, MA, USA) at the Mass Spectrometry Facility Center for Functional Genomics University at Albany.

2. *Starting Materials.* All commercially available chemicals were purchased from *Aldrich Chemicals.* Substrates are distilled prior to use. Dimethyl sulfoxide (DMSO) was dried over CaH_2 prior to use.

3. *Synthesis of Aromatized Products* **1**–**12**. Products **1**–**12** were obtained by the procedure described for **1**. *(2*S*)-3-Methyl-2-[(2-propylphenyl)amino]butan-1-ol* (**1**). 1 equiv. of 2-(2-bromoprop-2-enyl)cy-

clohexanone (0.31 g, 1.43 mmol) was mixed with 1.5 equiv. of (*S*)-valinol (0.22 g, 2.15 mmol) and 10 mg of TsOH in dry toluene (30 ml). The mixture was heated under reflux for 6 h, toluene was evaporated *in vacuo*, and dry DMSO (5 ml) and *t*BuOK (0.32 g, 2.86 mmol) were added. The reaction mixture was immersed in an oil bath at 80° and agitated for a further 3 h with a magnetic stirrer, and purified by FC without workup to yield a yellow-brown oil, **1** (0.11 g, 35% yield). $[\alpha]_D^{25} = -10.03$ ($c = 1.5$, $CHCl_3$). IR (CCl_4): 3424, 2960, 2931, 2873, 1605, 1586, 1507, 1455, 1310, 1251, 1164. ^{1}H-NMR: 0.83–0.96 (*m*, 9 H); 1.59 (*sext*, $J = 7.3$, 2 H); 1.78–1.92 (*m*, 2 H); 2.40 (*t*, $J = 6.2$, 2 H); 3.32 (*t*, $J = 6.2$, 1 H); 3.50–3.54 (*m*, 2 H); 3.70 (*dd*, $J = 6.7, 4.2$, 1 H); 6.58–6.64 (*m*, 2 H); 6.97–7.04 (*m*, 2 H). ^{13}C-NMR: 145.9; 129.8; 127.5; 126.8; 117.5; 111.6; 62.9; 60.7; 37.1; 30.4; 22.2; 19.5; 14.7. HR-CI-MS: 222.1867 ($[M+H]^+$, $C_{14}H_{24}NO^+$; calc. 222.1858).

N-*(4,4-Diethoxybutyl)-2-propylaniline* (**2**): Yellow oil, 33% yield. IR (CCl_4): 3491, 2872, 2358, 1558, 1510, 1133. ^{1}H-NMR: 0.92 (*t*, $J = 7.3$, 3 H); 1.12 (*t*, $J = 8.5$, 6 H); 1.57 (*sext*, $J = 7.6$, 2 H); 1.66 (br. *s*, 4 H); 2.35 (*t*, $J = 7.7$, 2 H); 3.10 (br. *s*, 2 H); 3.39–3.47 (*m*, 2 H); 3.55–3.62 (*m*, 2 H); 4.47 (br. *s*, 1 H); 6.10 (*d*, $J = 8.0$, 1 H); 6.59 (*t*, $J = 7.4$, 1 H); 6.96 (*d*, $J = 7.3$, 1 H); 7.04 (*t*, $J = 7.6$, 1 H). ^{13}C-NMR: 146.2; 129.4; 127.6; 126.5; 117.1; 110.5; 103.1; 61.6; 44.2; 33.7; 31.7; 25.2; 20.0; 15.8; 14.7. HR-CI-MS: 280.2287 ($[M+H]^+$, $C_{17}H_{30}NO_2^+$; calc. 280.2277).

2-[(2-Propylphenyl)amino]ethanol (**3**). Yellow oil, 22% yield. IR (CCl_4): 3413, 2958, 2927, 2873, 2353, 1697, 1605, 1507, 1452, 1310, 1256, 1052. ^{1}H-NMR: 0.92 (*t*, $J = 7.3$, 3 H); 1.56–1.65 (*m*, 2 H); 2.39 (*t*, $J = 7.7$, 2 H); 3.24 (*t*, $J = 5.3$, 2 H); 3.76 (*t*, $J = 5.3$, 2 H); 6.58 (*d*, $J = 8.0$, 1 H); 6.63 (*t*, $J = 7.4$, 1 H); 6.97 (*d*, $J = 7.4$, 1 H); 7.01–7.06 (*m*, 1 H). ^{13}C-NMR: 144.6; 128.2; 126.0; 125.9; 116.6; 109.7; 60.2; 45.2; 32.2; 20.7; 13.2. HR-CI-MS: 180.1383 ($[M+H]^+$, $C_{11}H_{18}NO^+$; calc. 180.1388).

*(2*R*)-2-[(2-Propylphenyl)amino]butan-1-ol* (**4**). Yellow oil, 56% yield. $[\alpha]_D^{25} = +22.05$ ($c = 1.1$, $CHCl_3$). IR (CCl_4): 3425, 2965, 2933, 2874, 2352, 1698, 1605, 1586, 1510, 1454, 1311, 1245, 1058, 913. ^{1}H-NMR: 0.88–0.95 (*m*, 6 H); 1.48–1.65 (*m*, 4 H); 2.39 (*t*, $J = 7.7$, 2 H); 3.37–3.43 (*m*, 1 H); 3.50 (*dd*, $J = 10.9, 5.6$, 1 H); 6.60–6.63 (*m*, 2 H); 6.97–7.05 (*m*, 2 H). ^{13}C-NMR: 145.2; 129.4; 127.1; 126.7; 117.3; 111.2; 64.0; 56.4; 33.3; 25.0; 21.8; 14.3; 10.6. HR-CI-MS: 208.1715 ($[M+H]^+$, $C_{13}H_{22}NO^+$; calc. 208.1701).

*(2*R*)-1-[(2-Propylphenyl)amino]propan-2-ol* (**5**). Brown oil, 30% yield. $[\alpha]_D^{25} = -4.76$ ($c = 0.7$, $CHCl_3$). IR (CCl_4): 3426, 2965, 2932, 2873, 2352, 1698, 1606, 1586, 1510, 1455, 1378, 1311, 1129, 1010, 908. ^{1}H-NMR: 0.93 (*t*, $J = 7.3$, 3 H); 1.20 (*d*, $J = 6.2$, 3 H); 1.58 (*sext*, $J = 7.5$, 2 H); 2.40 (*t*, $J = 7.7$, 2 H); 2.95 (*dd*, $J = 12.8, 4.3$, 1 H); 3.19 (*dd*, $J = 12.8, 3.4$, 1 H); 3.95–4.03 (*m*, 1 H); 6.58 (*d*, $J = 8.1$, 1 H); 6.63 (*t*, $J = 7.4$, 1 H); 6.97 (*d*, $J = 7.4$, 1 H); 7.02–7.06 (*m*, 1 H). ^{13}C-NMR: 144.7; 128.2; 126.0; 125.9; 116.6; 109.7; 65.4; 50.8; 32.3; 20.8; 20.0; 13.2. HR-CI-MS: 194.1550 ($[M+H]^+$, $C_{12}H_{20}NO^+$; calc. 194.1545).

*(2*R*)-2-[(2-Propylphenyl)amino]propan-1-ol* (**6**). Yellow oil, 45% yield. $[\alpha]_D^{25} = -1.99$ ($c = 0.2$, $CHCl_3$). IR (CCl_4): 3420, 2962, 2932, 2873, 1605, 1586, 1507, 1455, 1310, 1165, 998. ^{1}H-NMR: 0.92 (*t*, $J = 7.3$, 3 H); 1.12 (*d*, $J = 6.4$, 3 H); 1.51–1.62 (*m*, 2 H); 2.37 (*t*, $J = 7.7$, 2 H); 3.44–3.49 (*m*, 1 H); 3.57–3.64 (*m*, 2 H); 6.68–6.73 (*m*, 2 H); 6.99–7.21 (*m*, 2 H). ^{13}C-NMR: 143.9; 128.4; 126.0; 116.6; 110.5; 65.2; 49.6; 32.3; 20.8; 16.7; 13.2. HR-CI-MS: 194.154 ($[M+H]^+$, $C_{12}H_{20}NO^+$, calc. 194.1545).

*(2*R*)-3-Phenyl-2-[(2-propylphenyl)amino]propan-1-ol* (**7**). Yellow oil, 31% yield. $[\alpha]_D^{25} = +87.26$ ($c = 0.5$, $CHCl_3$). IR (CCl_4): 3488, 2814, 2359, 1588, 1510, 1257, 1011. ^{1}H-NMR: 0.94 (*t*, $J = 7.4$, 3 H); 1.48–1.58 (*m*, 2 H); 2.36 (*t*, $J = 7.8$, 2 H); 2.89 (*dd*, $J = 13.7, 7.2$, 1 H); 2.95 (*dd*, $J = 13.7, 5.7$, 1 H); 3.55 (*dd*, $J = 10.7, 4.7$, 1 H); 3.71 (*dd*, $J = 10.8, 4.3$, 1 H); 3.76–3.80 (*m*, 1 H); 6.69 (*dt*, $J = 7.5, 1.1$, 1 H); 6.74 (*d*, $J = 8.2$, 1 H); 7.02 (*dd*, $J = 7.4, 1.5$, 1 H); 7.09–7.13 (*m*, 1 H); 7.18–7.21 (*m*, 3 H); 7.25–7.29 (*m*, 2 H). ^{13}C-NMR: 144.6; 138.1; 129.2; 129.0; 128.5; 127.4; 126.5; 117.6; 111.2; 63.2; 55.6; 37.5; 33.3; 21.7; 14.3. HR-CI-MS: 270.1857 ($[M+H]^+$, $C_{18}H_{24}NO^+$; calc. 270.1858).

2-[(2-Propylphenyl)amino]phenol (**8**). The procedure above was applied, at the end of reaction, 15 ml 1% HCl was added. The aq. phase was washed with Et_2O, the org. phase concentrated and the resulting oil purified by SiO_2 chromatography. Yellow oil, 12% yield. IR (CCl_4): 3426, 2964, 2933, 2873, 2352, 1698, 1584, 1495, 1455, 1240, 912. ^{1}H-NMR: 0.94 (*t*, $J = 7.32$, 3 H); 1.64 (*sext*, $J = 7.48$, 2 H); 2.54 (*t*, $J = 7.64$, 2 H); 5.15 (br. *s*, 1 H); 5.60 (br. *s*, 1 H); 6.62 (*d*, $J = 7.82$, 1 H); 6.78–6.81 (*m*, 2 H); 6.88 (*d*, $J = 7.00$, 1 H); 6.95–6.99 (*m*, 3 H); 7.08 (*d*, $J = 7.35$, 1 H). ^{13}C-NMR: 150.4; 142.8; 130.1; 129.9; 129.8; 127.0; 125.3; 123.8; 121.1; 120.8; 116.1; 115.3; 33.4; 22.5; 14.2. HR-CI-MS: 228.1386 ($[M+H]^+$, $C_{15}H_{18}NO^+$; calc. 228.1388).

2-(2-Propylphenoxy)ethanol (**9**): Yellow oil, 45% yield. IR (CCl_4): 3426, 2961, 2934, 2873, 2352, 2250, 1698, 1588, 1493, 1452, 1378, 1291, 1241, 1129, 1047, 908. ^{1}H-NMR: 0.86 (*t*, *J* = 7.4, 3 H); 1.48–1.59 (*m*, 2 H); 2.52 (*t*, *J* = 7.6, 2 H); 3.84–3.87 (*m*, 2 H); 3.95–3.98 (*m*, 2 H); 6.74 (*d*, *J* = 6.7, 1 H); 6.81 (*t*, *J* = 7.4, 1 H); 7.03–7.08 (*m*, 2 H). ^{13}C-NMR: 156.5; 131.3; 130.1; 126.9; 120.9; 111.6; 69.4; 61.7; 32.2; 23.1; 14.1. HR-CI-MS: 181.1220 ($[M+H]^+$, $C_{11}H_{17}O_2^+$; calc. 181.1229).

Synthesis of 1-Ethoxy-2-propylbenzene (**10**) [13]. **1a** (1.00 g, 4.61 mmol) was mixed with 1.3 equiv. of triethyl orthoformate (0.9 g, 6.0 mmol) in 0.5 ml EtOH. Later, 0.05 ml AcCl was added to the mixture, stirred overnight, filtered through a pad of SiO_2 with 20:1 hexane/AcOEt, and concentrated to give *ca.* 0.8 g of a crude oil. To the resulting oil, 1.0 equiv. of ^{t}BuOK (0.77 g, 6.88 mmol) in 5 ml dry DMSO was added, the mixture was immersed in an oil bath at 80° and agitated for 3 h with a magnetic stirrer, and purified by FC without workup to yield **11** (0.23 g, 30% yield).

Synthesis of 2-(2-bromoprop-2-en-1-yl)-4-methylcyclohexanone (**1c**). 1-(4-Methylcyclohex-1-enyl)-pyrrolidine [14] (7.8 g, 0.047 mol) was mixed with 2 equiv. of 2,3-dibromopropene (18.9 g, 0.095 mol) in 30 ml dry dioxane at 0° under Ar and refluxed for 3 h. Later, 15 ml 1% HCl soln. was added, and the mixture was refluxed for another 3 h. The mixture was concentrated *in vacuo*, the aq. phase washed with Et_2O. The Et_2O phase was washed with sat. brine, dried over $MgSO_4$, and concentrated. The resulting oil was purified by vacuum distillation: B.p. 101° (3 Torr): (4.54 g, 42% yield). IR (CCl_4) 1714, 1631, 1133, 890. ^{1}H-NMR: 0.92–2.94 (*m*, 13 H); 5.36 (br. *s*, 1 H); 5.53 (br. *s*, 1 H). HR-CI-MS: 231.0377 ($[M+H]^+$, $C_{10}H_{16}BrO^+$; calc. 231.0385).

2-(4-Methyl-2-propylphenoxy)ethanol (**11**). Yellow oil, 34% yield. IR (CCl_4): 3360, 2960, 2873, 2444, 1715, 1613, 1502, 1457, 1252, 1230, 1079, 1042, 978, 936, 909. ^{1}H-NMR: 0.88 (*t*, *J* = 7.4, 3 H); 1.60–1.67 (*m*, 2 H); 2.26 (*s*, 3 H); 2.50 (*t*, *J* = 7.4, 2 H); 3.92–3.95 (*m*, 2 H); 4.03–4.05 (*m*, 2 H); 6.73 (*d*, *J* = 8.1, 1 H); 6.93–6.95 (*m*, 2 H). ^{13}C-NMR: 153.3; 130.1; 129.9; 129.1; 126.1; 110.7; 68.6; 60.8; 31.2; 22.2; 19.5; 13.1. HR-CI-MS: 195.1377 ($[M+H]^+$, $C_{12}H_{19}O_2^+$; 195.1385).

*(2*R*)-2-[(4-Methyl-2-propylphenyl)amino]butan-1-ol* (**12**). Yellow oil, 37% yield. $[\alpha]_D^{25} = -3.71$ (*c* = 1.2, $CHCl_3$). IR (CCl_4): 3426, 2965, 2932, 2874, 2352, 1698, 1512, 1456, 1261, 1059. ^{1}H-NMR: 0.91 (*t*, *J* = 7.5, 3 H); 0.95 (*t*, *J* = 7.4, 3 H); 1.50–1.67 (*m*, 5 H); 2.18 (*s*, 3 H); 2.37–2.41 (*m*, 2 H); 3.36–3.42 (*m*, 1 H); 3.50 (*dd*, *J* = 10.8, 5.9, 1 H); 3.72 (*dd*, *J* = 10.7, 4.1, 1 H); 6.58 (*d*, *J* = 8.1, 1 H); 6.83–6.87 (*m*, 2 H). ^{13}C-NMR: 141.8; 129.3; 126.4; 126.0; 125.6; 110.7; 63.1; 55.9; 32.4; 24.1; 21.1; 19.4; 13.3; 9.6. HR-CI-MS: 222.1874 ($[M+H]^+$, $C_{14}H_{24}NO^+$; calc. 222.1858).

*(6*E*)-1-Ethoxy-4,4-dimethyl-6-(prop-2-en-1-ylidene)cyclohexene* (**15**). 4,4-Dimethylcyclohexanone (10.0 g, 0.079 mol) was dissolved in 150 ml of dry THF and brought to −78° under Ar atmosphere. At this temp., 1.1 equiv. LDA soln. (87 ml, 2M in THF/heptane/ethylbenzene) was added dropwise within 0.5 h *via* mixing and mixed for another h at this temp. Later, 1.1 equiv. of propargyl bromide (9.36 ml, 80% soln. in toluene) was added dropwise at −78° in 0.5 h and mixed for another h. The reaction was quenched by addition of 50 ml aq. NH_4Cl, 100 ml of Et_2O was added, and the org. phase separated. The aq. phase was washed with 100 ml of Et_2O, the org. phases were combined, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The remaining oil was distilled under vacuum: B.p. 81–110° (3 Torr), yield 4.92 g of *4,4-dimethyl-2-(prop-2-yn-1-yl)cyclohexanone* (**13**) as a yellow oil (38% yield, 0.030 mol) of practical purity. Later, **13** was protected in the same way as **10** to get the corresponding acetal, and an oil was obtained. This oil was purified by chromatography from chromatography grade basic alumina (*Fluka*) using AcOEt/hexanes as eluent to yield 2.87 g of *1-ethoxy-4,4-dimethyl-6-(prop-2-yn-1-yl)cyclohexene* **14** as a colorless oil (47% yield, 0.014 mol). ^{1}H-NMR: 0.92 (*s,* 3 H); 0.97 (*s*, 3 H); 1.26 (*t*, *J* = 6.91, 3 H); 1.34–2.63 (*m*, 8 H); 3.59–3.74 (*m*, 2 H); 4.54 (*d*, *J* = 5.73, 1 H). ^{13}C-NMR: 153.8; 93.8; 83.3; 69.0; 61.9; 42.2; 37.9; 34.7; 31.4; 29.8; 25.0; 22.7; 14.0.

When the general procedure for aromatization was applied to **14**, 244 mg of **15** was obtained by chromatography over SiO_2 (9% yield, 1.27 mmol). ^{1}H-NMR: 0.95 (*s*, 6 H); 1.35 (*t*, *J* = 6.94, 3 H); 2.03 (*d*, *J* = 4.35, 2 H); 2.27 (*s*, 2 H); 3.77 (*q*, *J* = 6.91, 2 H); 4.83 (*t*, *J* = 4.35, 1 H); 5.13 (*d*, *J* = 9.86, 1 H); 5.30 (*d*, *J* = 16.36, 1 H); 6.56–6.72 (*m*, 2 H). ^{13}C-NMR: 151.4; 132.7; 123.2; 117.6; 99.2; 62.6; 39.6; 38.5; 30.5; 29.7; 28.3; 14.8. HR-CI-MS: 193.1586 ($[M+H]^+$, $C_{13}H_{21}O^+$; calc. 193.1592).

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