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Indium-Mediated, Highly Efficient and Diastereoselective Addition of Cyclic Secondary Allylic Bromides to Carbonyl Compounds

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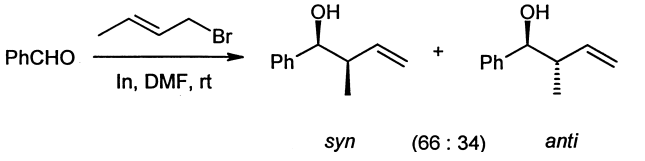
Abstract—Indium-mediated addition of 3-bromocyclohexene and 3-bromocyclooctene to a variety of aromatic aldehydes and cyclohexanone proceeds smoothly with excellent *syn* diastereoselectivity to produce the corresponding cycloalkenyl substituted homoallylic alcohols in good to high yields.

Allylic organometallic compounds have been extensively used for the allylation of carbonyl compounds to obtain homoallylic alcohols.[1] The regio- and diastereoselectivities are highly dependent on the metal used, the geometry of the alkene and the additives (e.g. Lewis acids). In the last few years, indium has emerged as one of the most attractive metals for allyl group transfer.[2] The regio- and stereoselectivities of acyclic allylindium reagents is well studied. For example, indium mediated addition of crotyl bromide to carbonyl compounds is γ-selective, but the diastereoselectivity is poor (Eq. (1)).[3] Recently, modifications such as addition of lithium alkoxide (ligand tuning)[4] or lanthanide triflate[5] to the reaction mixture and careful tailoring of reaction conditions[6] have been shown to improve the diastereoselectivity of addition of acyclic allylindium reagents to carbonyl compounds.



(1)

Cycloalkenes possessing a side chain at the allylic position and adorned with a hydroxyl group at the homoallylic position on the side chain are important intermediates in organic synthesis.[7] They can be obtained by a coupling reaction between cyclic allylic organometallic reagents and carbonyl compounds. Notable among the metals used for such coupling reactions are Sn,[8] Ge,[9] Bi,[10] Ti,[7,11] Zn,[12] etc., which in many cases involve elaborate procedures and activation of the metals before use to generate the corresponding cyclic allylic metal reagent. Further, in the case of certain cyclic 6-membered allylic organometallic reagents their generation from the corresponding bromide was not straightforward and furnished poor yields of the desired product due to the formation of dimeric homocoupling products.[7,8b] In connection with an ongoing project, we became interested in developing simpler procedures for cycloalkenyl group transfer with high stereoselection. Surprisingly, to the best of our knowledge, indium-mediated coupling of cycloalkenyl halides to carbonyl compounds has not been studied so far. We describe herein an efficient and highly diastereoselective addition of cyclohex-2-enyl- and cyclooct-2-enyl indium to a variety of aromatic aldehydes.

Results and Discussion

The indium-mediated coupling reactions were initially performed employing 3-bromocyclohexene and a variety of aromatic aldehydes (Table 1). The reactions were very clean and were complete within a few hours. The reaction of benzaldehyde furnished a mixture of *syn* and *anti* diastereomers in a ratio of 92:8 (Scheme 1 and entry 1, Table 1). Cyclohexenylation of an α,β-unsaturated aldehyde (entry 2) gave solely 1,2-addition product in excellent yield and diastereoselectivity. The results summarized in Table 1 clearly demonstrate that the reactions are equally efficient with both electron donating as well as electron withdrawing substituents on the aromatic aldehyde. Polynuclear aromatic (entry 3) together with biphenylic aldehydes (entry 5) also gave good yields of the product. It is interesting to note that 9-anthraldehyde (entry 3) furnished essentially a single diastereomer. The reaction

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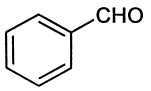
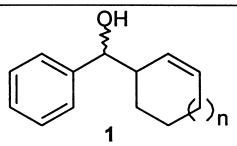
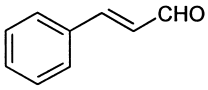
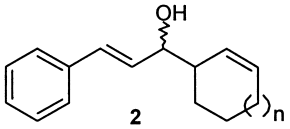
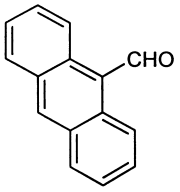
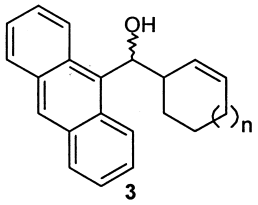
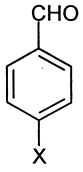
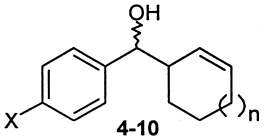
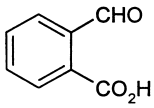
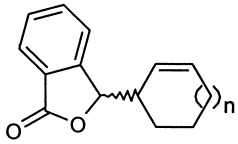
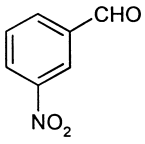
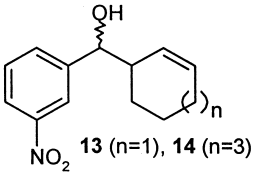
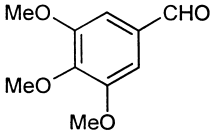
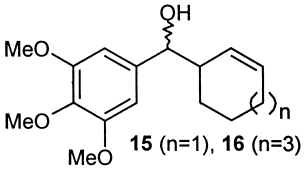
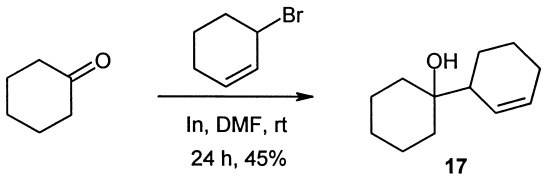
Table 1. Indium-mediated coupling of cycloalkenyl bromides with aromatic aldehydes

Entry	Starting Material	Time (h)	Product	n	Yield (%)	*syn* : *anti*[a]
1		2	 **1**	1	78	92:8
2		4	 **2**	1	95	90:10
3		12	 **3**	1	95[b]	One isomer
4	 (X = OMe)	2	 **4-10**	1	96	90:10
5	(X = Ph)	6		1	96	91:9
6	(X = Ph)	6		3	75	75:25
7	(X = I)	4		1	94	91:9
8	(X = I)	6		3	98	95:5
9	(X = Cl)	16		1	77	92:8
10	(X = Cl)	2		3	94	88:12
11		8	 **11** (n=1), **12** (n=3)	1	78	92:8
12		12		3	85	One isomer
13		8	 **13** (n=1), **14** (n=3)	1	97	88:12
14		18		3	80	88:12
15		1.5	 **15** (n=1), **16** (n=3)	1	98	87:13
16		4.5		3	61	76:24

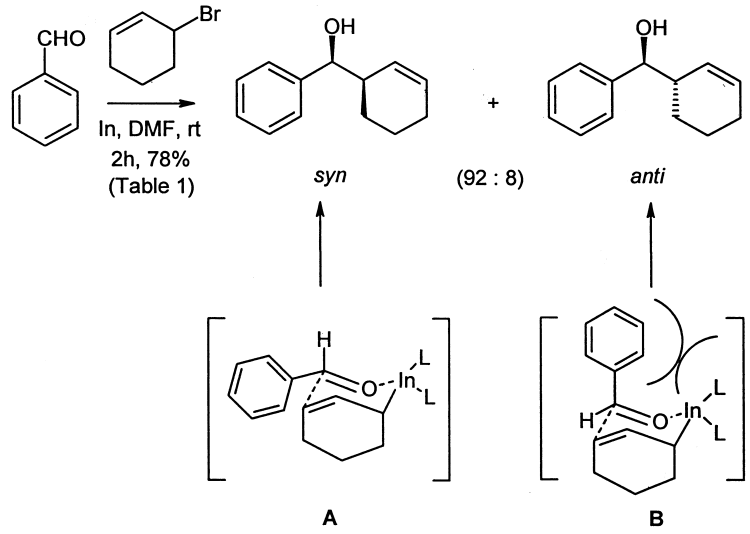
[a] Based on ^{1}H NMR integration of proton on carbinol carbon.
[b] Yield based on recovered starting material (80% conversion).

conditions are compatible with various substituents, including halogens (entries 7–10), on the aromatic ring. The carboxylic acid group is also tolerated in these reactions but when it is *o*-substituted, it gave the corresponding lactone (entry 11). The coupling reactions were also performed using 3-bromocyclooctene with a few aromatic aldehydes under similar conditions in order to check the generality of the reaction (entries 6, 8, 10, 12, 14 and 16). Cyclohexenylation in all the cases showed very high *syn* selectivity, but cyclooctenylation using 3-bromocyclooctene in some cases (entry 6, 16), gave moderate *syn* selectivity. Cyclohexenylation of ketones was also attempted employing cyclohexanone. The reaction was sluggish and gave only 45% yield of the corresponding homoallyl alcohol (Eq. (2)).



(2)

The ratio of *syn* and *anti* isomers was unambiguously assigned in the case of benzaldehyde adducts (Scheme 1) and is based on comparison of ^{1}H NMR values (400 MHz)



Scheme 1.

with those reported in the literature.[8a] The two doublets corresponding to the protons on carbinol carbon for both the isomers are well resolved (*syn*: δ=4.55 ppm and *anti*: δ=4.44 ppm). Another characteristic feature in the ^{1}H NMR is the position of the vinylic protons. Both the vinylic protons of cyclohexenyl moiety are well separated for the *syn* isomer, but in the case of *anti* isomer, they are further deshielded and appear at almost identical position.[8a] The same trend is followed in all the cases studied, and we assigned the ratios based on these consistent values. The transition-states A and B for the formation of *syn* and *anti* isomers, respectively, satisfactorily explains the observed results (Scheme 1). The exclusive formation of only one isomer in the case of 9-anthraldehyde (entry 3), is clearly elucidated based on the overwhelming steric congestion in the transition state when the bulky anthryl group occupies the hindered axial position in the less-favored transition-state B.

In summary, we have reported a simple, preparatively useful indium-mediated coupling of 3-bromocyclohexene and 3-bromocyclooctene with aromatic aldehydes to obtain homoallylic cycloalkenyl alcohol derivatives in good to excellent yields. High diastereoselectivities are observed with *syn* isomer being the major product.

Experimental

Melting points were recorded on a JSGW melting point apparatus and are uncorrected. DMF was dried using standard procedures. IR spectra were recorded either as a KBr pellet or neat on a Perkin-Elmer 1320 infrared spectrophotometer with NaCl optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol 400 spectrometer. The samples were dissolved in $CDCl_3$, using tetramethyl silane as the internal standard and spectra were given in the δ scale. The *syn*/*anti* ratios were determined by the integration of the peaks derived from the carbinol protons of both the isomers. Missing signals of the minor isomers are hidden by signals of the major isomers. CHN analysis was done in Technische Universität Dresden, Sektion Chemie. TLC was performed on glass coated with silica gel (acme). All the products were filtered through a short silica gel (acme; 100–200 mesh) column.

General procedure

(Entry 1): 3-bromocyclohexene (200 mg, 1.24 mmol) was added dropwise to a stirred suspension of indium metal (80 mg, 0.7 mmol) in 0.2 ml of DMF under inert atmosphere at room temperature until all the metal dissolved. Then a solution of benzaldehyde (53 mg, 0.5 mmol) in 1 ml of DMF was added slowly to the reaction mixture and stirring was continued at room temperature until the completion of the starting material (tlc). The reaction mixture was diluted with 5 ml of water and extracted three times with ether. Combined ether layer was washed once with brine and dried over Na_2SO_4, filtered and concentrated. Silica gel column purification gave the pure product in 78% yield. Compound **1** is known.[8a]

(*E*)-1-Cyclohex-2-enyl-3-phenyl-prop-2-en-1-ol (2). Yield: 95%, obtained as viscous liquid; *syn*/*anti*=90:10. ^{1}H NMR: δ 1.41–1.68 (m, 3H), 1.75–1.83 (m, 2H), 1.99 (br s, 2H), 2.36–2.43 (m, 1H), 4.14 (t, *J*=5.6 Hz, 1H, carbinol H of minor isomer), 4.18 (t, *J*=6.8 Hz, 1H, carbinol H of major isomer), 5.64 (dd, *J*=10.0, 2.2 Hz, 1H), 5.81–5.87 (m, 1H), 6.21–6.28 (m, 1H), 6.58 (d, *J*=15.8 Hz, 1H), 7.21–7.39 (m, 5H); ^{13}C NMR: δ 21.08, 24.11, 25.08, 41.59, 75.91, 126.32, 127.40, 127.54, 128.37, 129.65, 130.46, 131.26, 136.61; IR (neat): 3390, 3000, 2910, 1610 cm^{-1}. Anal. calcd for $C_{15}H_{18}O$: C 84.07, H 8.47; found: C 84.99, H 8.28.

1-Anthracen-9-yl-1-cyclohex-2-enyl-methanol (3). Yield: 95%, obtained as solid which was crystallized in CH_2Cl_2/hexane (1:10), mp 96–98°C; *syn*/*anti*=one isomer, ^{1}H NMR: δ 1.58–1.64 (m, 1H), 1.80–2.05 (m, 4H), 2.22–2.29 (m, 1H), 2.40 (br s, 1H), 3.28–3.34 (m, 1H), 4.75 (dd, *J*=10.1, 2.2 Hz, 1H), 5.48–5.53 (m, 1H), 5.89 (d, *J*=10.0 Hz, 1H), 7.38–7.45 (m, 4H), 7.92–7.95 (m, 2H), 8.34 (s, 1H), 8.60 (br s, 2H); ^{13}C NMR: δ 20.81, 25.19, 26.63, 41.79, 74.16, 124.64, 125.33, 127.81, 128.16, 128.95, 129.19, 129.86, 131.55, 133.64, 133.88; IR (KBr):

3400, 3000, 2900 cm^{-1}. Anal. calcd for $C_{21}H_{20}O$: C 87.46, H 6.99; found: C 87.09, H 6.68.

1-Cyclohex-2-enyl-1-(4-methoxy-phenyl)-methanol (4). Yield: 96%, obtained as solid which was crystallized in CH_2Cl_2/hexane (1:10), mp 42–44°C; *syn*/*anti*=90:10, ^1H NMR: δ 1.42–1.55 (m, 2H), 1.69–1.78 (m, 2H), 1.97 (br s, 3H), 2.44 (br s, 1H), 3.78 (s, 3H), 4.36 (d, *J*=7.6 Hz, 1H, carbinol H of minor isomer), 4.46 (d, *J*=7.1 Hz, 1H, carbinol H of major isomer), 5.33 (dd, *J*=10.1, 2.0 Hz, 1H), 5.74–5.79 (m, 1H), 6.88 (d, *J*=8.6 Hz, 2H), 7.23 (d, *J*=8.5 Hz, 1H); ^{13}C NMR: δ 20.96, 24.22, 25.17, 42.89, 55.21, 77.05 (carbinol C of major isomer), 77.66 (carbinol C of minor isomer), 113.50, 127.65, 127.89, 129.92, 135.09, 158.81; IR (neat): 3420, 3000, 2900, 1600 cm^{-1}. Anal. cacld. for $C_{14}H_{18}O_2$: C 77.03, H 8.31; found: C 77.39, H 8.69.

1-Biphenyl-4-yl-1-cyclohex-2-enyl-methanol (5). Yield: 96%, obtained as solid which was crystallized in CH_2Cl_2/hexane (1:10), mp 69–72°C; *syn*/*anti*=91:9, ^1H NMR: δ 1.45–1.60 (m, 2H), 1.69–1.81 (m, 2H), 1.98 (s, 2H), 2.12 (br s, 1H), 2.50 (m, 1H), 4.46 (d, *J*=6.8 Hz, carbinol H of minor isomer), 4.57 (d, *J*=6.6 Hz, carbinol H of major isomer), 5.40 (dd, *J*=10.3, 2.2 Hz, 1H), 5.78–5.85 (m, 1H), 7.30–7.43 (m, 5H), 7.54–7.58 (m, 4H); ^{13}C NMR: δ 20.99, 23.88, 25.17, 42.89, 77.18 (carbinol C of major isomer), 77.78 (carbinol C of minor isomer), 126.82, 126.91, 126.95, 127.13, 127.92, 128.67, 130.29, 140.14, 140.77, 141.90; IR (KBr): 3400, 3000, 1590, 900 cm^{-1}. Anal. calcd for $C_{19}H_{20}O$: C 86.32, H 7.63; found: C 86.64, H 7.98.

1-Biphenyl-4-yl-1-cyclooct-2-enyl-methanol (6). Yield: 75%, obtained as viscous liquid. *syn*/*anti*=75:25, ^1H NMR: δ 1.15–1.67 (m, 8H), 1.91–2.37 (m, 3H), 2.88–2.97 (m, 1H), 4.50 (d, *J*=7.8 Hz, 1H, carbinol H of minor isomer), 4.59 (d, *J*=7.1 Hz, 1H, carbinol H of major isomer), 5.31 (t, *J*=10.0 Hz, 1H), 5.49–5.64 (m, 1H), 7.30–7.44(m, 5H), 7.54–7.60 (m, 4H); ^{13}C NMR: δ 25.45, 26.63, 26.76, 29.30, 31.59, 43.20, 77.78 (carbinol C of major isomer), 78.59 (carbinol C of minor isomer) 126.91, 126.98, 127.00, 127.16, 128.68, 130.19, 130.27, 140.25, 140.77, 142.45; IR (neat): 3400, 3000, 2900, 1660 cm^{-1}. Anal. calcd for $C_{21}H_{24}O$: C 86.26, H 8.27; found: C 87.18, H 8.24.

1-Cyclohex-2-enyl-1-(4-iodo-phenyl)-methanol (7). Yield: 94%, obtained as viscous liquid. *syn*/*anti*=91:9, ^1H NMR: δ 1.42–1.51 (m, 2H), 1.59–1.64 (m, 1H), 1.67–1.73 (m, 1H), 1.96 (m, 2H), 2.29 (s, 1H), 2.39–2.43(m, 1H), 4.34 (d, *J*=6.6 Hz, 1H, carbinol H of minor isomer), 4.47 (d, *J*=6.4 Hz, 1H, carbinol H of major isomer), 5.34 (dd, *J*=10.2, 2.0 Hz, 1H), 5.77–5.82 (m, 1H), 7.04 (d, *J*=6.5 Hz, 2H), 7.63 (d, *J*=6.5 Hz, 2H); ^{13}C NMR: δ 20.83, 23.47, 25.05, 42.80, 76.65 (carbinol C of major isomer), 77.30 (carbinol C of minor isomer), 92.61, 127.50, 128.49, 130.59, 137.11, 142.38; IR (neat): 3400, 3000, 2900, 1580, 720 cm^{-1}. Anal. calcd for $C_{13}H_{15}IO$: C 49.70, H 4.81; found: C 49.52, H 4.35.

1-Cyclooct-2-enyl-1-(4-iodo-phenyl)-methanol (8). Yield: 98%, obtained as viscous liquid. *syn*/*anti*=95:5, ^1H NMR: δ 1.15–1.68 (m, 6H), 1.83–1.89 (m, 1H), 1.97–2.15 (m, 4H), 2.83–2.85 (m, 1H), 4.42 (d, *J*=7.6 Hz, 1H, carbinol H of minor isomer), 4.50 (d, *J*=6.8 Hz, 1H, carbinol H of major isomer), 5.22 (t, *J*=10.0 Hz, 1H), 5.56–5.63 (m, 1H), 7.05 (d, *J*=8.0 Hz, 2H), 7.64 (d, *J*=7.8 Hz, 2H); ^{13}C NMR: δ 23.64, 26.26, 26.69, 29.32, 31.41, 43.17, 77.41 (carbinol C of major isomer), 78.15 (carbinol C of minor isomer), 92.86, 128.74, 129.84, 130.47, 137.21, 142.94; IR (neat): 3400, 3000, 2910, 1570, 730 cm^{-1}. Anal. calcd for $C_{15}H_{19}IO$: C 52.65, H 5.60; found: C 52.66, H 5.26.

1-(4-Chloro-phenyl)-1-cyclohex-2-enyl-methanol (9). Yield: 77%, obtained as viscous liquid. *syn*/*anti*=92:8. Compound **9** is known.[10]

1-(4-Chloro-phenyl)-1-cyclooct-2-enyl-methanol (10). Yield: 94%, obtained as viscous liquid. *syn*/*anti*=88:12, ^1H NMR: δ 1.18–1.66 (m, 7H), 1.85–1.90 (m, 1H)1.99–2.02 (m, 1H), 2.09–2.16 (m, 2H), 2.84–2.86 (m, 1H), 4.46 (d, *J*=7.8 Hz, 1H, carbinol H of minor isomer), 4.53 (d, *J*=7.1 Hz, 1H, carbinol H of major isomer), 5.22 (dd, *J*=10.2, 9.5 Hz, 1H), 5.58–5.60 (m, 1H), 7.23–7.29 (m, 4H); ^{13}C NMR: δ 25.36, 26.59, 26.70, 29.23, 31.48, 43.25, 77.35 (carbinol C of major isomer), 78.05 (carbinol C of minor isomer), 128.05, 128.31, 129.88, 130.42, 133.04, 141.88; IR (neat): 3380, 3000, 2900, 1630, 820 cm^{-1}. Anal. calcd for $C_{15}H_{19}ClO$: C 71.85, H 7.64; found: C 71.42, H 7.98.

3-Cyclohex-2-enyl-3H-isobenzofuran-1-one (11). Yield: 78%, obtained as viscous liquid. *syn*/*anti*=92:8, ^1H NMR: δ 1.41–1.55 (m, 3H), 1.73–1.75 (m, 1H), 1.99–2.02 (m, 2H), 2.70–2.73 (m, 1H), 5.36 (d, *J*=10.3 Hz, 1H, carbinol H of minor isomer), 5.47 (d, *J*=4.9 Hz, 1H, carbinol H of major isomer), 5.70 (dd, *J*=10.1, 2.2 Hz, 1H), 5.87–5.91 (m, 1H), 7.49–7.55 (m, 2H), 7.66–7.70 (m, 1H), 7.90 (m, 1H); ^{13}C NMR: δ 20.66, 22.78, 24.75, 39.68, 83.54, 122.29, 125.54, 125.89, 126.54, 128.95, 130.76, 133.70, 148.44, 170.46; IR (neat): 3000, 2900, 1740, 1600 cm^{-1}. Anal. calcd for $C_{14}H_{14}O_2$: C 78.48, H 6.59; found: C 78.81, H 6.72.

3-Cyclooct-2-enyl-3H-isobenzofuran-1-one (12). Yield: 85%, obtained as viscous liquid. *syn*/*anti*=one isomer, ^1H NMR: δ 1.32–1.37 (m, 3H), 1.50–1.67 (m, 5H), 2.04–2.19 (m, 2H), 2.95–3.03 (m, 1H), 5.42 (d, *J*=5.8 Hz, 1H), 5.55 (m, 1H), 5.81–5.88 (m, 1H), 7.51–7.54 (m, 2H), 7.64–7.68 (m, 1H), 7.89–7.91 (m, 1H); ^{13}C NMR: δ 24.97 (t), 26.53 (2C, t), 29.04 (t), 30.44 (t), 41.09 (d), 83.99 (d), 122.41 (d), 125.47 (d), 126.45 (s), 128.38 (d), 128.98 (d), 132.06 (d), 133.77 (d), 148.99 (s), 170.54 (s); IR (neat): 3000, 2900, 1750, 1600 cm^{-1}. Anal. calcd for $C_{16}H_{18}O_2$: C 79.31, H 7.48; found: C 78.93, H 7.70.

1-Cyclohex-2-enyl-1-(3-nitro-phenyl)-methanol (13). Yield: 97%, obtained as viscous liquid. *syn*/*anti*=88:12, ^1H NMR: δ 1.47–1.60 (m, 3H), 1.71–1.74 (m, 1H), 1.98 (br s, 2H), 2.51 (m, 1H), 2.66 (br s, 1H), 4.61 (d, *J*=6.1 Hz, 1H, carbinol H of minor isomer), 4.74 (d, *J*=5.8 Hz, 1H, carbinol H of major isomer), 5.40 (d, *J*=10.0 Hz, 1H), 5.85–5.88 (m, 1H), 7.48–7.52 (m, 1H), 7.66–7.68 (m, 1H), 8.08–8.11 (m,1H), 8.19 (s, 1H); ^{13}C NMR: δ 20.78, 23.10, 24.97, 42.75, 75.97 (carbinol C of major isomer), 76.70 (carbinol

C of minor isomer), 121.29, 122.09, 126.93, 128.90, 131.32, 132.54, 144.94, 147.98; IR (neat): 3400, 3010, 1510, 1340 cm^{-1}. Anal. calcd for $C_{13}H_{15}NO_3$: C 66.93, H 6.48, N 6.00; found: C 66.35, H 6.04, N 6.09.

1-Cyclooct-2-enyl-1-(3-nitro-phenyl)-methanol (14). Yield: 80%, obtained as viscous liquid. *syn*/*anti*=88:12, ^{1}H NMR: δ 1.22–1.71 (m, 7H), 1.84–1.89 (m, 1H), 2.0–2.03 (m, 1H), 2.09–2.15 (m, 1H), 2.35 (br s, 1H), 2.89–2.91 (m, 1H), 4.68 (d, *J*=6.8 Hz, 1H, carbinol H of minor isomer), 4.71 (d, *J*=6.8 Hz, 1H, carbinol H of major isomer), 5.24–5.29 (m, 1H), 5.56–5.67 (m, 1H), 7.50 (dd, *J*=8.0, 7.8 Hz, 1H), 7.67 (d, *J*=7.6 Hz, 1H), 8.10–8.12 (m, 1H), 8.20 (br s, 1H); ^{13}C NMR: δ 25.28, 26.67 (2C), 29.16, 31.18, 43.47, 76.93, 121.71, 122.44, 129.26, 129.29, 131.23. 132.85, 145.67, 148.14; IR (neat): 3380, 3000, 2900, 1520, 1450 cm^{-1}. Anal. calcd for $C_{15}H_{19}NO_3$: C 68.94, H 7.33, N 5.36; found: C 68.01, H 7.38, N 5.14.

1-Cyclohex-2-enyl-1-(3,4,5-trimethoxy-phenyl)-methanol (15). Yield: 98%, obtained as solid which was crystallized in CH_2Cl_2/hexane (1:10), mp 82–83°C; *syn*/*anti*=87:13, ^{1}H NMR: δ 1.48–1.57 (m, 2H), 1.70–1.80 (m, 2H), 1.99 (s, 2H), 2.18 (s, 1H), 2.45 (br s, 1H), 3.83 (s, 3H), 3.85 (s, 6H), 4.37 (d, *J*=6.6 Hz, 1H, carbinol H of minor isomer), 4.45 (d, *J*=6.8 Hz, 1H, carbinol H of major isomer), 5.36 (dd, *J*=10.2, 2.2 Hz, 1H), 5.81 (m, 1H), 6.55 (s, 2H); ^{13}C NMR: δ 20.97, 23.97, 25.12, 42.88, 55.96, 60.76, 77.53 (carbinol C of major isomer), 78.00 (carbinol C of minor isomer), 103.34, 127.90, 130.18, 136.91, 138.70, 152.97; IR (KBr): 3300, 2800, 1580, 1100 cm^{-1}. Anal. calcd for $C_{16}H_{22}O_4$: C 69.04, H 7.97; found: C 69.18, H 8.27.

1-Cyclooct-2-enyl-1-(3,4,5-trimethoxy-phenyl)-methanol (16). Yield: 61%, obtained as viscous liquid. *syn*/*anti*=76:24, ^{1}H NMR: δ 1.12–2.17 (m, 11H), 2.87 (m, 1H), 3.81 (s, 6H, OMe of minor isomer), 3.82 (s, 3H, OMe of minor isomer), 3.83 (s, 6H, OMe of major isomer), 3.85 (s, 3H, OMe of major isomer), 4.39 (d, *J*=8.1 Hz, 1H, carbinol H of minor isomer), 4.48 (d, *J*=7.1 Hz, 1H, carbinol H of major isomer), 5.26 (t, *J*=10.5 Hz, 1H, olefinic H of major isomer), 5.49 (t, *J*=9.0 Hz, 1H, olefinic H of minor isomer), 5.59 (dt, *J*=8.3, 8.9 Hz, olefinic H of major isomer), 5.85 (dt, *J*=8.5, 9.5 Hz, olefinic H of minor isomer), 6.53 (s, 2H, aromatic H of major isomer), 6.56 (s, 2H, aromatic H of minor isomer); ^{13}C NMR: δ 25.40, 26.64, 26.77, 29.29, 31.56, 43.14, 56.06, 60.78, 78.22 (carbinol C of major isomer), 79.11 (carbinol C of minor isomer), 103.66, 130.07, 130.26, 130.95, 139.15, 153.00; IR (neat): 3400, 2850, 1580, 1220 cm^{-1}; Anal. calc. For $C_{18}H_{26}O_4$: C 70.56, H 8.55; found: C 70.24, H 8.36.

Bicyclohexyl-2′-en-1-ol (17). Yield: 45%, obtained as viscous liquid. Compound **17** is known.[13]

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