$InCl_3$-Catalyzed Regioselective Ring-Opening Reactions of Epoxides to β-Hydroxy Ethers

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By applying a catalytic amount of indium trichloride, regioselective ring-opening of epoxides to β-hydroxy ethers was established. While the alcoholysis of styrene oxides produced S_N1-type product, the alcoholysis of α-heteroatom-substituted epoxides predominantly produced S_N2-type product.

Key Words : Indium trichloride, Ring opening, Epoxide, β-Hydroxy ether

Introduction

The epoxide ring opening reaction with alcohols is an important transformation in the synthesis of β-hydroxy ethers, which are valuable organic solvents, some natural products,[1] and intermediates for α-alkoxy ketones and α-alkoxy acids. Previous attempts to achieve the alcoholysis of epoxides under basic or acidic conditions resulted in polymerization and low regioselectivity because of the need for high temperature.[2] Recently, various approaches have been tried to bring about this transformation under milder conditions.[3] However, the reported procedures still have limitations, such as high reaction temperature,[3c,3i] prolonged reaction time,[3c,3j] low selectivity[3c] and non-catalytic nature of the reagent.[3c]

Lewis acids are some of the most important reagents in synthetic organic reactions, and those mostly encountered in organic synthesis are $ZnCl_2$, $AlCl_3$, $BF_3{\cdot}OEt_2$, $TiCl_4$, $SnCl_4$, etc. Recently, indium trichloride, $InCl_3$, which is stable in aqueous media, has received considerable attention as a mild Lewis acid in various organic transformations such as Friedel-Crafts alkylation with ketones or aldehydes,[4] reduction of acid chlorides with allylic tins,[5] insertion reactions of α-diazo ketones,[6] Biginelli reaction,[7] Mukaiyama aldol reactions,[8] imino Diels-Alder reactions,[8] conjugate addition of indoles with electron-deficient olefins,[9] and bromolysis or iodolysis of α,β-epoxycarboxylic acids.[10] It has also been used as a catalyst for the synthesis of various useful organic compounds.[11] Early attempts for the alcoholysis of epoxides under acidic or basic conditions suffered from a need for high temperature, which consequently resulted in extensive polymerization and low regioselectivity.[2] Thus, it is worth examining $InCl_3$ as a catalyst for the ring opening-reaction of epoxides to β-hydroxy ethers. In this paper, we report a mild and highly efficient procedure for the synthesis of β-hydroxy ethers using $InCl_3$ as a catalyst.

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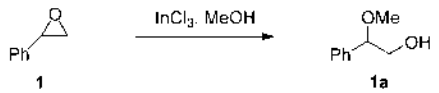
Results and Discussion

In control experiments, various reaction conditions were examined to determine the optimum conditions for $InCl_3$-catalyzed 1,2-epoxide ring-opening reaction to β-hydroxy ether. The results are summarized in Table 1. The reaction of styrene oxide with methanol in the presence of $InCl_3$ proceeds smoothly under mild conditions with excellent conversion in a short reaction time and with a high degree of regioselectivity. All of the reactions examined produced 2-methoxy-2-phenylethanol (**1a**) as a predominant product along with only a trace amount of its regioisomer, 2-methoxy-1-phenylethanol. The reactions of styrene oxide with methanol using a relatively large amount of $InCl_3$ such as 1 equiv (Table 1, entry 1) or 0.5 equiv (entry 2) gave the desired product in low yield, while the reaction using a proper catalytic amount (0.2 equiv) of $InCl_3$ gave the desired product in relatively high yield (entry 3). In addition, the formation of 2-chloro-2-phenylethanol was observed when the amount of $InCl_3$ was increased. When 1 equiv of $InCl_3$ was applied, 2-chloro-2-phenylethanol was obtained as a by-product in 13% yield. When the reaction was performed in

Table 1. $InCl_3$-catalyzed ring-opening reaction of styrene oxide with methanol under various reaction conditions



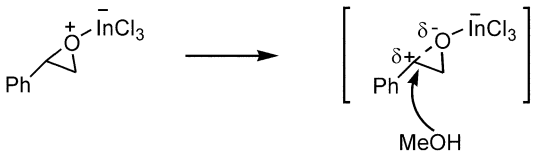
1 **1a**

Entry	Molar ratio **1** : $InCl_3$	MeOH (mL)	Temp. (°C)	Time (h)	Yield (**1a**, %)[a]
1	1 : 1	5	50	2	69[b]
2	1 : 0.5	5	50	2	81[c]
3	1 : 0.2	5	50	2	94
4	1 : 0.1	5	50	2	78
5	1 : 0.2	5	rt	8	72
6	1 : 0.2	5	reflux	40 min	94
7	1 : 0.2	10	50	2	89

[a]GC yield with an internal standard. [b]13% of 2-chloro-2-phenylethanol was obtained. [c]8% of 2-chloro-2-phenylethanol was obtained.

the absence of $InCl_3$, **1** was recovered entirely unreacted.

The results appear to be the obvious consequence of the involvement of a carbocation intermediate that is formed by a Lewis acid-assisted ring-opening reaction.[3e,3h] With $InCl_3$, ring-opening via C-O bond cleavage is catalyzed by $InCl_3$ and the C-O bond is polarized to a greater extent in structure A (eq. 1) due to better stabilization of the positive charge. This consideration can easily explain the high level of regioselectivity. Thus, the benzylic position is the favored site for the nucleophilic attack of methanol, which gives rise to the formation of 2-methoxy-2-phenyl ethanol with essentially complete regioselectivity.



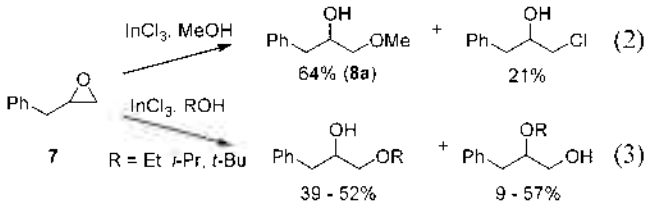
(1)

A

Using the optimized reaction conditions, we investigated the scope of ring-opening reactions of various 1,2-epoxides, and the results are summarized in Table 2. The reaction appears to be generally applicable, since most of the substrates were consumed to give the corresponding β-hydroxy ethers in good to excellent yields. The procedure was applied successfully to various 1,2-epoxides and is expected to be safe for substrates that contain delicate functionalities because of the mild conditions. In general, among the alcohols tested for the ring-opening reaction of epoxides, methanol gave the best yield. As the alkyl group of the alcohol becomes bulkier, the yield of the reaction gradually decreases. The ring opening reaction of epoxides with *t*-BuOH produced β-hydroxy ether in low yields (25-55%) in most cases. Nucleophilic attack of the alcohol towards the benzylic site of the epoxide could be controlled by steric constraints and it is quite clear that a bulky alkyl group of alcohol retards the reaction due to steric hindrance.

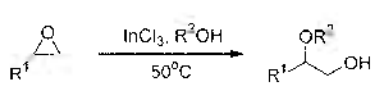
To extend the scope of the ring-opening reaction, alcoholysis of 1,2-epoxy-3-phenylpropane (**7**) in the presence of $InCl_3$ (0.2 equiv) was examined. Surprisingly, when **7** was reacted with MeOH, the regioselectivity of the ring-opening was totally reversed compared to the reactions with the compounds in Table 2. The corresponding 1-methoxyaryl alcohol (**8a**) was obtained in 64% yield along with 21% of unexpected 1-chloro-3-phenyl-2-propanol and a trace amount of 2-methoxy-3-phenyl-1-propanol.

However, as the alkyl group of the alcohol became bulkier, the ring-opening of **7** gave a mixture of two isomers (Table 3). In the case of solvolysis in *t*-BuOH, the amount of **9d** (57%) was greater than the amount of **8d** (39%). The reason for this difference in regioselectivity is not yet clear.



Since we obtained different results regarding stereocontrol between styrene oxide-type epoxide and α-phenyl epoxide, we extended our investigation on the ring-opening reaction to α-heteroatom-substituted epoxides to study the effect of the a-substituent. The results are summarized in Table 4. All of the compounds we examined produced one regioisomer, which was a different regioisomer obtained from styrene oxide-type substrates. While styrene oxide-type substrates produced typical S_N1-type product, α-heteroatom-substituted substrates produced S_N2-type product, *i.e.* the nucleophile attacked a less hindered site. Moreover, the reactivity also seemed to be reversed. While the alcoholysis of styrene oxide type substrates required a longer reaction time with a bulkier alcohol, the alcoholysis of α-heteroatom-substituted epoxide completed faster with bulkier alcohols. In addition, the yield improved when a bulkier alcohol was used. This implies that the reaction proceeds *via* an S_N2-type ring-opening reaction even though the neutral alcohol is a weak

Table 2. Ring-opening reactions of 1,2-epoxides in the presence of $InCl_3$ (0.2 equiv.) in alcohol at 50 °C

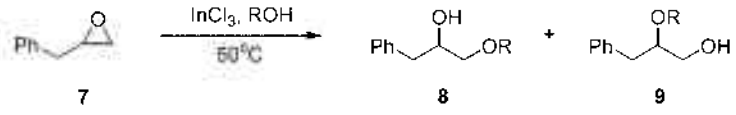


a(R^2 = Me)
b(R^2 = Et)
c(R^2 = *i*-Pr)
d(R^2 = *t*-Bu)

Entry	Substrate	Solvent	Time (h)	Product	Isolated yield (%)
1		MeOH	2	**1a**	92 (94)[a]
2		EtOH	6	**1b**	84
3	Ph (1)	*i*-PrOH	6	**1c**	71
4		*t*-BuOH	13	**1d**	55
5		MeOH	6	**2a**	83
6		EtOH	6	**2b**	78
7	Cl (2)	*i*-PrOH	6	**2c**	73
8		*t*-BuOH	12	**2d**	53
9		MeOH	6	**3a**	86
10		EtOH	6	**3b**	66
11	H_3C (3)	*i*-PrOH	6	**3c**	59
12		*t*-BuOH	12	**3d**	33
13		MeOH	3	**4a**	65
14		EtOH	3	**4b**	71
15	S (4)	*i*-PrOH	18	**4c**	57
16		*t*-BuOH	24	**4d**	25
17		MeOH	12	**5a**	80
18		EtOH	18	**5b**	65
19	(5)	*i*-PrOH	18	**5c**	50
20		*t*-BuOH	12	**5d**	33
21		MeOH	18	**6a**	65[b]
22		EtOH	20	**6b**	43[b]
23	O (6)	*i*-PrOH	24	**6c**	46[b]
24		*t*-BuOH	2	**6d**	45[b]

[a]GC yield with an internal standard. [b]4-6% of 2-chlorocyclohexanol was obtained.

Table 3. Ring-opening reactions of 1,2-epoxy-3-phenylpropane in the presence of $InCl_3$ (0.2 equiv.) in alcohol at 50 °C



Entry	Substrate	Solvent	Time (h)	Product (Isolated yield, %)	
				8	**9**
1	 (**7**)	MeOH	22	**8a** (64)[a]	–
2		EtOH	37	**8b** (52)[b]	**9b** (<9)
3		*i*-PrOH	24	**8c** (48)	**9c** (31)
4		*t*-BuOH	5	**8d** (39)	**9d** (57)

[a]21% of 1-chloro-3-phenyl-2-propanol was obtained. [b]18% of 1-chloro-3-phenyl-2-propanol was obtained.

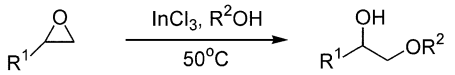
nucleophile.

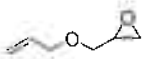
Semiempirical modeling (PM3, closed shell) for representative epoxides *i.e.* styrene oxide (**1**), 1,2-epoxy-3-phenylpropane (**7**) and 1,2-epoxy-3-phenoxypropane (**10**), was examined to perceive the effect of $InCl_3$ in each case even though there would be additional factors such as solvent effect. Modeling revealed somewhat different interaction between $InCl_3$ and the oxygen atom in the substrate, as shown in Figure 1.

In the case of styrene oxide, the indium atom in $InCl_3$ approaches the oxygen atom of the epoxide in the normal position as expected with an In--O distance of 2.710 Å, and this implies that $InCl_3$ effectively facilitates the ring-opening to give more favorable benzylic carbocation formation. In the case of 1,2-epoxy-3-phenylpropane (**7**), the distance between the indium and the oxygen atom (2.820 Å) is greater than that with styrene oxide, which results in less interaction between the oxygen atom and $InCl_3$. In contrast, indium is closer to C1 of the phenyl group: 2.881 Å, which is 0.033 Å shorter than the distance with styrene oxide.

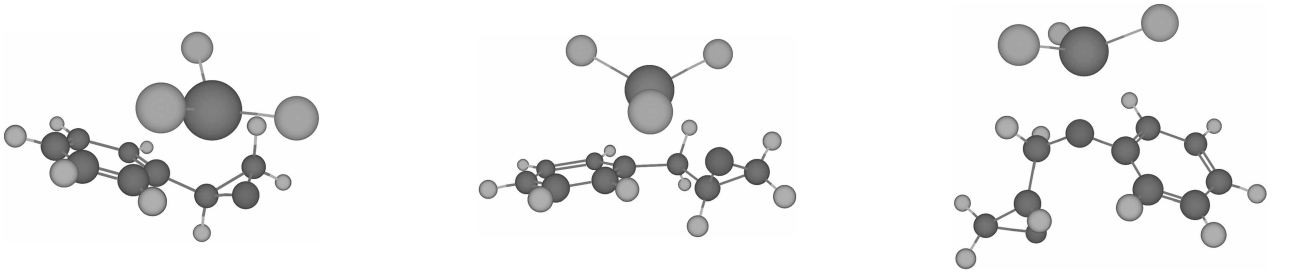
A more dramatic change was observed with 1,2-epoxy-3-phenoxypropane (**10**). For **10**, the most favorable approach of $InCl_3$ is to the phenoxy oxygen atom rather than the oxygen atom in the epoxide ring: the distance between indium and the phenoxy oxygen atom is 2.218 Å, while the

Table 4. Ring-opening reactions of 1,2-epoxides in the presence of $InCl_3$ (0.2 equiv.) in alcohol at 50 °C



Entry	Substrate	Solvent	Time (h)	Product	Isolated yield (%)
1	 (**10**)	MeOH	9	**10a**	74[a]
2		EtOH	18	**10b**	79[b]
3		*i*-PrOH	14	**10c**	90
4		*t*-BuOH	13	**10d**	81
5	 (**11**)	MeOH	18	**11a**	42[c]
6		EtOH	12	**11b**	40[d]
7		*i*-PrOH	6	**11c**	48
8		*t*-BuOH	3	**11d**	65
9	 (**12**)	MeOH	24	**12a**	47[e]
10		EtOH	24	**12b**	57[f]
11		*i*-PrOH	15	**12c**	64
12		*t*-BuOH	4	**12d**	75

[a]19% of 1-chloro-3-phenoxy-2-propanol was obtained. [b]15% of 1-chloro-3-phenoxy-2-propanol was obtained. [c]7% of 1,3-dichloro-2-propanol was obtained. [d]4% of 1,3-dichloro-2-propanol was obtained. [e]22% of 1-allyloxy-3-chloro-2-propanol was obtained. [f]6% of 1-allyloxy-3-chloro-2-propanol was obtained.



A. Styrene oxide with $InCl_3$

In, O : 2.710 Å
In, C(Ph, C1) : 2.914 Å
In, C(Ph, C2) : 2.864 Å

B. 1,2-epoxy-3-phenylpropane with $InCl_3$

In, O : 2.820 Å
In, C(Ph, C1) : 2.881 Å
In, C(Ph, C2) : 2.867 Å

C. 1,2-epoxy-3-phenoxypropane with $InCl_3$

In, O(Phenoxy) : 2.218 Å
In, C(Ph, C1) : 2.924 Å

Figure 1. Semiempirical modeling of the interaction between epoxide and $InCl_3$.

oxygen atom on the epoxide ring is oriented far from the indium atom. It seems that it is difficult for the oxygen atom on epoxide to interact with the indium atom, and instead the epoxide ring is oriented anti to the oncoming $InCl_3$ that is somewhat unexpected. Furthermore, the addition of MeOH molecule to the system shows a favorable move toward the less hindered side of the epoxide while the addition of *t*-BuOH to the system does not show any regioselective move toward the epoxide, which is quite consistent with our experimental results. Due to ineffective interaction between the indium atom and the oxygen atom on the epoxide ring, S_N1-like ring-opening may be impared. Consequently, S_N2-like ring-opening may occur with an alcohol nucleophile. In addition to carbocation stability, it seems that the different approach of $InCl_3$ to the substrate also affects the reactivity and regioselectivity.

In conclusion, the $InCl_3$-catalyzed reaction of epoxides resulted in regioselective ring-opening to β-hydroxy ethers. While alcoholysis occurs at the more substituted carbon of styrene type epoxides, the alcohols attack the less hindered side of the a-heteroatom-substituted epoxides.

Experimental Section

General consideration. Most of chemical reagents were purchased from Aldrich and used without further purification in most cases. Solvents were purchased and dried by a standard method. ^{1}H NMR spectra were recorded on 300 MHz Bruker or Jeol instrument and ^{13}C NMR spectra were recorded on 75 MHz Bruker or Jeol instrument. Chemical shifts are in ppm from tetramethylsilane (TMS). High-resolution MS were recorded on a Jeol JMS-DX 303 mass spectrometer and GC/MS were recorded on a HP6890 mass spectrometer. IR spectra were recorded on a Nicolet 205 FT-IR. Analytical data were obtained with an EA-1110, CHNS-O CEinstruments. Melting points were determined on an Electrothermal apparatus and are uncorrected. Analytical gas chromatography (GC) was performed on a HP 6890 gas chromatograph equipped with a HP-5 column (25 m × 0.2 mm × 0.5 μm). All the major products were isolated by flash column chromatography on silica gel (230-400 mesh ATSM, purchased from Merck) with eluents of mixed solvents (ethyl acetate and hexane).

General procedure for β-hydroxy ether synthesis. To a solution of epoxide (1 mmol) in the appropriate alcohol (5 mL), $InCl_3$ (0.2 mmol) was added and the mixture stirred at 50 °C. The reaction was monitored by TLC. After completion of the reaction, solvent was evaporated under reduced pressure. Saturated $NaHCO_3$ (30 mL) was added and extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was separated and dried with $MgSO_4$. Evaporation of the solvent followed by chromatography on a short column of silica gel gave the corresponding product in 25-92% yield.

2-Methoxy-2-phenylethanol (1a)[12] Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.41 (m, 5H), 4.32 (dd, J = 4.0 Hz, 8.3 Hz, 1H), 3.58-3.72 (m, 2H), 3.31 (s, 3H), 2.37 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.2, 128.5, 128.1, 126.8, 84.6, 67.4, 56.9; IR (KBr) 3420, 3030, 2982, 2933, 1454, 1355, 1112 cm^{-1}; GC-MS m/z (rel. intensity) 152 (1, M$^-$), 121 (100), 105 (16), 91 (41), 77 (44).

2-Ethoxy-2-phenylethanol (1b)[12] Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.39 (m, 5H), 4.42 (dd, J = 4.2 Hz, 8.2 Hz, 1H), 3.56-3.70 (m, 2H), 3.36-3.53 (m, 2H), 2.35 (dd, J = 3.8 Hz, 9.2 Hz, 1H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.9, 128.3, 127.8, 126.6, 82.7, 67.2, 64.3, 15.1; IR (KBr) 3428, 3033, 2979, 2873, 1452, 1347, 1105 cm^{-1}; GC-MS m/z (rel. intensity) 166 (1, M$^-$), 135 (100), 121 (3), 107 (63), 91 (12), 79 (54).

2-(1-Methylethoxy)-2-phenylethanol (1c)[12] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.37 (m, 5H), 4.53 (dd, J = 4.6 Hz, 7.9 Hz, 1H), 3.54-3.64 (m, 3H), 2.55 (dd, J = 4.2 Hz, 8.6 Hz, 1H), 1.19 (d, J = 5.9 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.6, 128.3, 127.8, 126.7, 79.9, 69.4, 67.4, 23.4, 21.2; IR (KBr) 3426, 3033, 2973, 2924, 1453, 1380, 1099 cm^{-1}; GC-MS m/z (rel. intensity) 180 (1, M$^+$), 149 (50), 121 (8), 107 (100), 91 (15), 79 (35).

2-(1,1-Dimethylethoxy)-2-phenylethanol (1d)[12] White solid; mp 76-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.36 (m, 5H), 4.62 (dd, J = 4.4 Hz, 8.2 Hz, 1H), 3.43-3.57 (m, 2H), 2.27 (dd, J = 3.8 Hz, 9.5 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 142.3, 128.2, 127.3, 126.4, 75.2, 74.9, 67.8, 28.8; IR (KBr) 3449, 3031, 2976, 2931, 1453, 1367, 1190 cm^{-1}; GC-MS m/z (rel. intensity) 194 (1, M$^-$), 163 (33), 121 (9), 107 (100), 91 (41), 79 (18).

2-(4-Chlorophenyl)-2-methoxyethanol (2a)[13] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.26 (dd, J = 4.3 Hz, 7.8 Hz, 1H), 3.51-3.65 (m, 2H), 3.28 (s, 3H), 2.36 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 136.8, 133.8, 128.7, 128.2, 84.0, 67.1, 56.9; IR (KBr) 3436, 3004, 2937, 2913, 1454, 1112, 829 cm^{-1}; GC-MS m/z (rel. intensity) 186 (8, M$^+$), 151 (11), 141 (100), 125 (6), 113 (29), 77 (66).

2-(4-Chlorophenyl)-2-ethoxyethanol (2b)[14] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.39 (dd, J = 4.4 Hz, 7.9 Hz, 1H), 3.57-3.65 (m, 2H), 3.35-3.52 (m, 2H), 2.57 (dd, J = 4.2 Hz, 8.4 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.6, 133.7, 128.7, 128.1, 82.0, 67.2, 64.6, 15.2; IR (KBr) 3435, 3031, 2976, 2874, 1491, 1091, 825 cm^{-1}; GC-MS m/z (rel. intensity) 200 (1, M$^-$), 169 (100), 155 (3), 141 (84), 125 (13), 113 (20), 77 (41).

2-(4-Chlorophenyl)-2-(1-methylethoxy)ethanol (2c) Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.35 (m, 4H), 4.50 (t, J = 6.1 Hz, 1H), 3.50-3.63 (m, 3H), 2.41-2.44 (m, 1H), 1.19 (d, J = 6.1 Hz, 3H), 1.12 (d, J = 6.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.3, 133.6, 128.6, 128.1, 79.3, 69.8, 67.3, 23.4, 21.4; IR (KBr) 3436, 3049, 2972, 2925, 1596, 1487, 1379, 1085, 823 cm^{-1}; GC-MS m/z (rel. intensity) 214 (1, M$^+$), 183 (37), 155 (6), 141 (100), 125 (10), 113 (12), 77 (17); HRMS (EI) calcd for $C_{11}H_{15}ClO_2$ 214.0761, found 214.0757. Anal. Calcd for $C_{11}H_{15}ClO_2$: C, 61.54; H, 7.04. Found: C, 61.56; H, 6.71.

2-(4-Chlorophenyl)-2-(1,1-dimethylethoxy)ethanol (2d)

Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 4H), 4.54 (dd, J = 4.3 Hz, 8.1 Hz, 1H), 3.35-3.50 (m, 2H), 2.30 (br s, 1H), 1.11(s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 140.8 133.0, 128.4, 127.7, 75.1, 74.5, 67.7, 28.7; IR (KBr) 3447, 3058, 2977, 2931, 1486, 1360, 1087, 738 cm^{-1}; GC-MS m/z (rel. intensity) 228 (1, M$^-$), 197 (27), 155 (9), 141 (100), 125 (10), 113 (6), 77 (11); HRMS (EI) calcd for $C_{12}H_{17}ClO_2$ 228.0917, found 228.0932; Anal. Calcd for $C_{12}H_{17}ClO_2$: C, 63.02; H, 7.49. Found: C, 63.48; H, 7.62.

2-Methoxy-2-(4-methylphenyl)ethanol (3a)[13] Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.26 (m, 4H), 4.28 (dd, J = 3.9 Hz, 8.4 Hz, 1H), 3.53-3.71 (m, 2H), 3.29 (s, 3H), 2.52 (dd, J = 3.7 Hz, 9.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.7, 135.1, 129.1, 126.7, 84.5, 67.2, 56.6, 21.0; IR (KBr) 3426, 3022, 2929, 2871, 1447, 1351, 1115, 815 cm^{-1}; GC-MS m/z (rel. intensity) 166 (1, M$^-$), 135 (100), 119 (14), 105 (12), 91 (30), 77 (4).

2-Ethoxy-2-(4-methylphenyl)ethanol (3b) Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.43 (dd, J = 3.8 Hz, 8.4 Hz, 1H), 3.59-3.74 (m, 2H), 3.39-3.56 (m, 2H), 2.66 (br s, 1H), 2.39 (s, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.7, 136.0, 129.2, 126.7, 82.7, 67.4, 64.3, 21.1, 15.3; IR (KBr) 3438, 3025, 2977, 2929, 1448, 1339, 1098, 815 cm^{-1}; GC-MS m/z (rel. intensity) 180 (1, M$^-$), 149 (100), 134 (9), 121 (57), 105 (31), 93 (39), 77 (18).; HRMS (EI) calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1151. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.22; H, 9.00.

2-(1-Methylethoxy)-2-(4-methylphenyl)ethanol (3c) Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.50 (dd, J = 4.4 Hz, 8.2 Hz, 1H), 3.54-3.62 (m, 3H), 2.50 (dd, J = 3.6 Hz, 8.9 Hz, 1H), 2.34 (s, 3H), 1.18 (d, J = 6.0 Hz, 3H), 1.12 (d, J = 6.2 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.5, 136.5, 129.1, 126.7, 79.7, 69.3, 67.4, 23.4, 21.2, 21.1; IR (KBr) 3440, 3022, 2974, 2924, 1456, 1382, 1092, 815 cm^{-1}; GC-MS m/z (rel. intensity) 194 (1, M$^+$), 163 (49), 135 (7), 121 (100), 105 (17), 93 (29), 77 (11); HRMS (EI) calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1301. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.15.

2-(1,1-Dimethylethoxy)-2-(4-methylphenyl)ethanol (3d) White solid; mp 61-62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.59 (dd, J = 4.7 Hz, 8.1 Hz, 1H), 3.42-3.55 (m, 2H), 2.33 (s, 3H), 2.27 (dd, J = 4.3 Hz, 8.8 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.2, 136.9, 128.9, 126.3, 75.0, 74.8, 67.9, 28.8, 21.1; IR (KBr) 3459, 3052, 2977, 2930, 1390, 1268, 815 cm^{-1}; GC-MS m/z (rel. intensity) 177 (27, M$^+$-CH_2OH), 135 (9), 121 (100), 105 (25), 93 (16), 77 (9); HRMS (EI) calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1449; Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.97; H, 9.77.

2-Methoxy-2-thiophen-3-ylethanol (4a) Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 3.0 Hz, 5.0 Hz, 1H), 7.24 (dd, J = 1.3 Hz, 3.0 Hz, 1H), 7.04 (dd, J = 1.3 Hz, 5.0 Hz, 1H), 4.42 (dd, J = 4.0 Hz, 8.2 Hz, 1H), 3.61-3.78 (m, 2H), 3.32 (s, 3H), 2.35 (dd, J = 4.1 Hz, 9.0 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.7, 126.2, 125.9, 122.7, 80.5, 66.3, 56.8; IR (KBr) 3422, 3099, 2937, 1458, 1110 cm^{-1}; GC-MS m/z (rel. intensity) 158 (5, M$^-$), 127 (100), 111 (17), 97 (12), 84 (3); HRMS (EI) calcd for $C_7H_{10}O_2S$ 158.0402, found 158.0411. Anal. Calcd for $C_7H_{10}O_2S$: C, 53.14; H, 6.37. Found: C, 53.13; H, 6.56.

2-Ethoxy-2-thiophen-3-ylethanol (4b) Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, J = 2.9 Hz, 5.0 Hz, 1H), 7.21 (d, J = 2.9 Hz, 1H), 7.04 (dd, J = 1.3 Hz, 5.0 Hz, 1H), 4.52 (dd, J = 3.9 Hz, 8.1 Hz, 1H), 3.55-3.75 (m, 2H), 3.37-3.53 (m, 2H), 2.54 (br s, 1H), 1.21 (d, J = 7.1 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 140.5, 126.1, 126.0, 122.4, 78.8, 66.5, 64.5, 15.3; IR (KBr) 3431, 3103, 2976, 2929, 1448, 1325, 1097 cm^{-1}; GC-MS m/z (rel. intensity) 172 (4, M$^+$), 141 (100), 126 (7), 113 (62), 97 (27), 85 (54); HRMS (EI) calcd for $C_8H_{12}O_2S$ 172.0558, found 172.0558. Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02. Found: C, 55.62; H, 7.24.

2-(1-Methylethoxy)-2-thiophen-3-ylethanol (4c) Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.31 (m, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.04 (d, J = 5.0 Hz, 1H), 4.62 (dd, J = 4.2 Hz, 7.9 Hz, 1H), 3.57-3.70 (m, 3H), 2.56 (br s, 1H), 1.18 (d, J = 6.0 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 141.1, 126.0, 125.9, 122.1, 76.0, 69.4, 66.6, 23.3, 21.3; IR (KBr) 3436, 3102, 2972, 2925, 1464, 1381, 1087 cm^{-1}; GC-MS m/z (rel. intensity) 186 (1, M$^-$), 155 (63), 127 (6), 113 (100), 97 (17), 85 (38); HRMS (EI) calcd for $C_9H_{14}O_2S$ 186.0715, found 186.0718. Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.58. Found: C, 58.00; H, 7.55.

2-(1,1-Dimethylethoxy)-2-thiophen-3-ylethanol (4d) Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, J = 2.9 Hz, 4.9 Hz, 1H), 7.15-7.17 (m, 1H), 7.04 (dd, J = 1.3 Hz, 4.9 Hz, 1H), 4.72 (t, J = 6.2 Hz, 1H), 3.54 (t, J = 5.9 Hz, 2H), 2.27 (s, 1H), 1.17 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 143.6, 126.1, 125.6, 121.1, 74.9, 71.5, 67.2, 28.7; IR (KBr) 3434, 3103, 2976, 2931, 1464, 1368, 1086 cm^{-1}; GC-MS m/z (rel. intensity) 200 (1, M$^+$), 169 (34), 127 (9), 113 (100), 97 (6), 85 (18); HRMS (EI) calcd for $C_{10}H_{16}O_2S$ 200.0871, found 200.0868. Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.96; H, 8.05. Found: C, 59.76; H, 8.08.

2-Methoxy-2-naphthalen-2-ylethanol (5a)[15] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.86 (m, 4H), 7.40-7.52 (m, 3H), 4.47 (dd, J = 3.8 Hz, 8.4 Hz, 1H), 3.65-3.82 (m, 2H), 3.35 (s, 3H), 2.56 (dd, J = 3.7 Hz, 9.0 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 135.7, 133.2, 128.3, 127.8, 127.6, 126.2, 126.1, 126.0, 124.3, 84.8, 67.1, 56.9; IR (KBr) 3425, 3060, 2932, 2872, 1445, 1370, 1108 cm^{-1}; GC-MS m/z (rel. intensity) 202 (9, M$^+$), 171 (100), 155 (21), 141 (6), 127 (18).

2-Ethoxy-2-naphthalen-2-ylethanol (5b) Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.85 (m, 4H), 7.42-7.51 (m, 3H), 4.58 (dd, J = 3.9 Hz, 8.3 Hz, 1H), 3.64-3.80 (m, 2H), 3.40-3.59 (m, 2H), 2.54 (br s, 1H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 136.4, 133.2, 133.1, 128.3, 127.8, 127.7, 126.2, 126.0, 124.4, 82.8, 67.3, 64.6, 15.3; IR (KBr) 3428, 3056, 2974, 2931, 1439, 1376,

1095 cm^{-1}; GC-MS m/z (rel. intensity) 216 (7, M^-), 185 (100), 170 (13), 154 (42), 141 (48), 129 (76); HRMS (EI) calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1153; Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.40; H, 7.40.

2-(1-Methylethoxy)-2-naphthalen-2-ylethanol (5c) Pale-yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78-7.85 (m, 4H), 7.45-7.51 (m, 3H), 4.69 (dd, J = 4.2 Hz, 8.2 Hz, 1H), 3.60-3.75 (m, 3H), 2.40 (dd, J = 3.7 Hz, 9.3 Hz, 1H), 1.23 (d, J = 5.9 Hz, 3H), 1.14 (d, J = 6.2 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.1, 133.1, 128.2, 127.7, 127.6, 126.1, 125.9, 125.8, 124.5, 80.1, 69.6, 67.3, 23.4, 21.3; IR (KBr) 3431, 3061, 2975, 2930, 1466, 1379, 1118 cm^{-1}; GC-MS m/z (rel. intensity) 230 (4, M^+), 199 (45), 170 (29), 157 (100), 141 (98), 129 (64), 115 (28); HRMS (EI) calcd for $C_{15}H_{18}O_2$ 230.1307, found 230.1307; Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.17; H, 7.90.

2-(1,1-Dimethylethoxy)-2-naphthalen-2-ylethanol (5d) White solid; mp 104-105 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80-7.84 (m, 4H), 7.42-7.50 (m, 3H), 4.79 (dd, J = 4.9 Hz, 7.7 Hz, 1H), 3.53-3.64 (m, 2H), 2.35 (br s, 1H), 1.20 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.8, 133.2, 133.0, 128.0, 127.8, 127.7, 126.1, 125.7, 125.2, 124.6, 75.3, 75.1, 67.8, 28.9; IR (KBr) 3441, 3058, 2977, 2931, 1468, 1364, 1266, 1078 cm^{-1}; GC-MS m/z (rel. intensity) 244 (1, M^-), 213 (18), 170 (10), 157 (100), 141 (57), 129 (34), 115 (16); HRMS (EI) calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1465; Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.54; H, 8.35.

***trans*-2-Methoxycyclohexanol (6a)**[16] Colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.37-3.44 (m, 1H), 2.90-2.98 (m, 1H), 2.57 (br s, 1H), 1.99-2.15 (m, 2H), 1.69-1.76 (m, 2H), 1.06-1.31 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 85.0, 73.8, 56.3, 32.0, 28.3, 24.1, 23.9; IR (KBr) 3440, 2934, 2862, 1453, 1102 cm^{-1}; GC-MS m/z (rel. intensity) 130 (50, M^-), 112 (13), 98 (32), 84 (46), 71 (100), 58 (23).

***trans*-2-Ethoxycyclohexanol (6b)**[17] Colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (ddd, J = 7.1 Hz, 9.3 Hz, 14.0 Hz, 1H), 3.42 (dq, J = 7.0 Hz, 9.3 Hz, 2H), 3.02 (ddd, J = 4.3 Hz, 8.5 Hz, 10.7 Hz, 1H), 1.99-2.10 (m, 2H), 1.70-1.73 (m, 2H), 1.10-1.30 (m, 4H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 83.5, 73.7, 64.0, 32.0, 29.2, 24.2, 23.9, 15.6; IR (KBr) 3441, 2974, 2934, 2865, 1451, 1107 cm^{-1}; GC-MS m/z (rel. intensity) 144 (16, M^-), 126 (2), 115 (8), 98 (32), 85 (100), 70 (68), 57 (80).

***trans*-2-(1-Methylethoxy)cyclohexanol (6c)**[17] Colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68-3.80 (m, 1H), 3.33-3.41 (m, 1H), 3.04-3.11 (m, 1H), 2.73 (s, 1H), 1.92-2.02 (m, 2H), 1.67-1.71 (m, 2H), 1.10-1.40 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 81.3, 73.7, 69.5, 31.9, 30.3, 24.4, 24.0, 23.7, 22.2; IR (KBr) 3450, 2976, 2937, 2863, 1450, 1076 cm^{-1}; GC-MS m/z (rel. intensity) 158 (2, M^-), 143 (13), 115 (22), 98 (55), 81 (41), 70 (100), 57 (50).

***trans*-2-(1,1-Dimethylethoxy)cyclohexanol (6d)**[17] Colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 3.21-3.29 (m, 1H), 3.11-3.19 (m, 1H), 1.94-2.00 (m, 1H), 1.83-1.89 (m, 1H), 1.57-1.64 (m, 2H), 1.09-1.31 (m, 13H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 76.4, 73.9, 73.8, 33.4, 32.0, 29.0, 24.7, 24.1; IR (KBr) 3440, 2976, 2934, 2861, 1452, 1071 cm^{-1}; GC-MS m/z (rel. intensity) 172 (6, M^+), 157 (13), 116 (85), 97 (69), 79 (75), 69 (43), 57 (100).

1-Methoxy-3-phenyl-2-propanol (8a)[18] Colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.32 (m, 5H), 3.94-4.03 (m, 1H), 3.25-3.40 (m, 2H), 3.35 (s, 3H), 2.71-2.84 (m, 2H), 2.61 (d, J = 3.7 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.9, 129.2, 128.3, 126.3, 75.9, 71.1, 58.9, 39.7; IR (KBr) 3429, 3033, 2922, 2898, 1450, 1125, 1085 cm^{-1}; GC-MS m/z (rel. intensity) 166 (1, M^+), 148 (45), 121 (29), 103 (40), 92 (100), 75 (24).

1-Ethoxy-3-phenyl-2-propanol (8b)[19] Pale-yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.31 (m, 5H), 3.95-4.04 (m, 1H), 3.27-3.56 (m, 4H), 2.72-2.84 (m, 2H), 2.68 (s, 1H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.1, 129.4, 128.4, 126.4, 73.8, 71.3, 66.7, 39.9, 15.1; IR (KBr) 3436, 3032, 2977, 2929, 1450, 1118 cm^{-1}; GC-MS m/z (rel. intensity) 162 (35, $M^- - H_2O$), 133 (35), 121 (26), 103 (35), 92 (100), 77 (12), 61 (42).

1-(1-Methylethoxy)-3-phenyl-2-propanol (8c)[20] Pale-yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18-7.31 (m, 5H), 3.93-4.00 (m, 1H), 3.57 (sep, J = 6.1 Hz, 1H), 3.42 (dd, J = 3.4 Hz, 9.3 Hz, 1H), 3.27 (dd, J = 7.1 Hz, 9.3 Hz, 1H), 2.82 (dd, J = 6.9 Hz, 13.7 Hz, 1H), 2.76 (dd, J = 6.5 Hz, 13.6 Hz, 1H) 2.61-2.63 (m, 1H), 1.15 (d, J = 6.1 Hz, 3H), 1.14 (d, J = 6.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.2, 129.3, 128.4, 126.3, 72.1, 71.5, 71.4, 39.9, 22.1; IR (KBr) 3435, 3028, 2976, 2931, 1456, 1134, 1081 cm^{-1}; GC-MS m/z (rel. intensity) 194 (1, M^+), 176 (39), 134 (17), 121 (59), 103 (62), 91 (100), 77 (14), 61 (40).

1-(1,1-Dimethylethoxy)-3-phenyl-2-propanol (8d) Pale-yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.32 (m, 5H), 3.90-3.99 (m, 1H), 3.37 (dd, J = 3.5 Hz, 8.8 Hz, 1H), 3.23 (dd, J = 7.1 Hz, 8.8 Hz, 1H), 2.74-2.86 (m, 2H), 2.53-2.54 (m, 1H), 1.19 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.3, 129.2, 128.3, 126.2, 73.1, 71.6, 64.9, 39.9, 27.5; IR (KBr) 3439, 3033, 2974, 2924, 1454, 1201, 1078 cm^{-1}; GC-MS m/z (rel. intensity) 190 (3, $M^- - H_2O$), 148 (6), 134 (25), 121 (49), 103 (20), 92 (67), 77 (8), 65 (10), 57 (100); HRMS (EI) calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1471. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.82; H, 9.71.

2-Ethoxy-3-phenyl-1-propanol (9b) Pale-yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.32 (m, 5H), 3.43-3.61 (m, 5H), 2.89 (dd, J = 6.0 Hz, 13.5 Hz, 1H), 2.74 (dd, J = 7.1 Hz, 13.5 Hz, 1H), 2.15 (br s, 1H), 1.18 (t, J = 6.9 Hz, 3H); IR (KBr) 3433, 3028, 2934, 2865, 1454, 1101 cm^{-1}; GC-MS m/z (rel. intensity) 180 (3, M^+), 162 (1), 149 (79), 131 (11), 121 (67), 103 (50), 91 (98), 77 (18), 61 (100); HRMS (EI) calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1145; Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.95; H, 9.00.

2-(1-Methylethoxy)-3-phenyl-1-propanol (9c) Pale-yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18-7.31 (m, 5H), 3.52-3.66 (m, 3H), 3.44-3.46 (m, 1H), 2.82 (dd, J = 6.3 Hz, 13.5 Hz, 1H), 2.74 (dd, J = 6.7 Hz, 13.5 Hz, 1H), 2.26 (br s, 1H), 1.14 (d, J = 6.2 Hz, 3H), 1.05 (d, J = 6.2 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$) δ 138.3, 129.4, 128.3, 126.2, 78.7, 70.6, 64.2, 38.3, 22.8, 22.5; IR (KBr) 3425, 3031, 2970, 2926, 1453, 1124, 1036 cm^{-1}; GC-MS m/z (rel. intensity) 194 (1, M^+), 163 (33), 134 (2), 121 (93), 103 (57), 91 (100), 77 (11), 61 (58); HRMS (EI) calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1324; Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.10; H, 9.48.

2-(1,1-Dimethylethoxy)-3-phenyl-1-propanol (9d) Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.33 (m, 5H), 3.74-3.82 (m, 1H), 3.41-3.58 (m, 2H), 2.84 (d, J = 6.8 Hz, 2H), 2.19 (s, 1H), 1.19 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.6, 129.6, 128.2, 126.1, 74.2, 72.8, 64.6, 39.9, 28.4; IR (KBr) 3446, 3030, 2979, 2934, 1455, 1194, 1074 cm^{-1}; GC-MS m/z (rel. intensity) 208 (1, M^+), 177 (11), 148 (3), 117 (28), 103 (7), 92 (49), 77 (5), 65 (7), 57 (100); HRMS (EI) calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1462. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.96; H, 9.79.

1-Methoxy-3-phenoxy-2-propanol (10a)[21] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.30 (m, 2H), 6.89-6.97 (m, 3H), 4.12-4.18 (m, 1H), 3.99-4.01 (m, 2H), 3.50-3.59 (m, 2H), 3.39 (s, 3H), 3.00 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 158.5, 129.5, 121.0, 114.5, 73.6, 69.0, 68.9, 59.2; IR (KBr) 3424, 3039, 2932, 2886, 1598, 1501, 1458, 1374, 1250, 1113, 1040 cm^{-1}; GC-MS m/z (rel. intensity) 182 (35, M^+), 136 (2), 119 (11), 108 (13), 94 (100), 77 (25).

1-Ethoxy-3-phenoxy-2-propanol (10b)[3f] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.27 (m, 2H), 6.88-6.94 (m, 3H), 4.12-4.21 (m, 1H), 3.93-4.02 (m, 2H), 3.44-3.61 (m, 4H), 3.37-3.39 (m, 1H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 158.6, 129.8, 129.5, 121.0, 114.6, 71.6, 69.0, 66.9, 15.1; IR (KBr) 3428, 3040, 2978, 2933, 1597, 1498, 1458, 1381, 1247, 1115, 1044 cm^{-1}; GC-MS m/z (rel. intensity) 196 (41, M^-), 136 (3), 119 (11), 103 (19), 94 (100), 77 (25).

1-(1-Methylethoxy)-3-phenoxy-2-propanol (10c)[22] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.31 (m, 2H), 6.91-6.98 (m, 3H), 4.07-4.16 (m, 1H), 3.98-4.03 (m, 2H), 3.53-3.68 (m, 3H), 2.65 (d, J = 4.6 Hz, 1H), 1.18 (d, J = 6.0 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 158.6, 129.4, 120.9, 114.5, 72.2, 69.1, 68.9, 68.8, 21.9; IR (KBr) 3433, 3041, 2976, 2932, 1603, 1498, 1461, 1370, 1247, 1129, 1075 cm^{-1}; GC-MS m/z (rel. intensity) 210 (26, M^+), 119 (11), 107 (14), 94 (100), 77 (21).

1-(1,1-Dimethylethoxy)-3-phenoxy-2-propanol (10d)[3e] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.22 (m, 2H), 6.83-6.89 (m, 3H), 3.97-4.04 (m, 1H), 3.89-3.94 (m, 2H), 3.47 (dd, J = 4.6 Hz, 9.2 Hz, 1H), 3.42 (dd, J = 5.7 Hz, 9.2 Hz, 1H), 2.78 (d, J = 4.7 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 158.7, 129.4, 120.9, 114.5, 73.4, 69.3, 68.9, 62.6, 27.5; IR (KBr) 3433, 3041, 2973, 2932, 1600, 1497, 1365, 1239, 1082 cm^{-1}; GC-MS m/z (rel. intensity) 224 (14, M^-), 168 (3), 150 (12), 133 (9), 119 (11), 107 (13), 94 (100), 77 (19).

1-Chloro-3-methoxy-2-propanol (11a)[23] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (sex, J = 5.4 Hz, 1H), 3.64 (dd, J = 5.3 Hz, 11.0 Hz, 1H), 3.58 (dd, J = 5.9 Hz, 11.0 Hz, 1H), 3.51 (d, J = 5.0 Hz, 2H), 3.41 (s, 3H), 2.78 (d, J = 5.7 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 73.3, 70.1, 59.2, 45.2; IR (KBr) 3417, 2930, 2904, 1124, 740 cm^{-1}; GC-MS m/z (rel. intensity) 124 (1, M^-), 88 (43), 75 (100), 58 (6).

1-Chloro-3-ethoxy-2-propanol (11b)[3g] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (sex, J = 5.4 Hz, 1H), 3.50-3.71 (m, 6H), 2.78 (d, J = 5.5 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 71.1, 70.2, 66.9, 46.0, 15.0; IR (KBr) 3409, 2979, 2933, 1114, 746 cm^{-1}; GC-MS m/z (rel. intensity) 138 (1, M^-), 102 (11), 89 (20), 79 (10), 59 (100).

1-Chloro-3-(1-methylethoxy)-2-propanol (11c)[3g] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (sex, J = 5.4 Hz, 1H), 3.40-3.59 (m, 5H), 2.80 (d, J = 5.7 Hz, 1H), 1.17 (d, J = 6.1 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 72.3, 70.3, 68.5, 45.9, 21.9; IR (KBr) 3413, 2972, 2933, 1129, 749 cm^{-1}; GC-MS m/z (rel. intensity) 137 (2, M^+-CH_3), 116 (7), 103 (5), 93 (18), 85 (10), 79 (8), 73 (100), 61 (38).

1-Chloro-3-(1,1-dimethylethoxy)-2-propanol (11d)[3g] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (sex, J = 5.5 Hz, 1H), 3.65 (dd, J = 5.7 Hz, 11.0 Hz, 1H), 3.58 (dd, J = 5.7 Hz, 11.0 Hz, 1H), 3.47 (d, J = 5.1 Hz, 2H), 2.70 (d, J = 5.9 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 73.4, 70.5, 62.2, 45.8, 27.4; IR (KBr) 3421, 2976, 2931, 1368, 1194, 1090, 743 cm^{-1}; GC-MS m/z (rel. intensity) 151 (5, M^+-CH_3), 117 (1), 100 (12), 87 (4), 74 (4), 57 (100).

3-Methoxy-1-(2-propenoxy)-2-propanol (12a)[24] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (ddt, J = 5.7 Hz, 10.4 Hz, 17.2 Hz, 1H), 5.28 (ddd, J = 1.6 Hz, 3.0 Hz, 17.2 Hz, 1H), 5.20 (ddd, J = 1.2 Hz, 3.0 Hz, 10.4 Hz, 1H), 4.03 (dt, J = 1.4 Hz, 5.7 Hz, 2H), 3.95-3.99 (m, 1H), 3.41-3.55 (m, 4H), 3.39 (s, 3H), 2.61 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 134.3, 117.1, 73.7, 72.2, 71.1, 69.2, 59.0; IR (KBr) 3403, 3077, 2931, 1195, 1097 cm^{-1}; GC-MS m/z (rel. intensity) 115 (1, M^+-OCH_3), 105 (1), 101 (25), 89 (95), 83 (23), 75 (100), 71 (80), 59 (49), 55 (17).

3-Ethoxy-1-(2-propenoxy)-2-propanol (12b)[3g] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, J = 2.6 Hz, 10.4 Hz, 17.2 Hz, 1H), 5.27 (ddd, J = 1.7 Hz, 2.6 Hz, 17.2 Hz, 1H), 5.18 (ddd, J = 1.2 Hz, 2.6 Hz 10.4 Hz, 1H), 4.00-4.04 (m, 2H), 3.96-3.98 (m, 1H), 3.41-3.57 (m, 6H), 3.05 (br s, 1H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 134.4, 117.1, 72.2, 71.7, 71.3, 69.3, 66.7, 15.0; IR (KBr) 3410, 3083, 2984, 2875, 1114 cm^{-1}; GC-MS m/z (rel. intensity) 115 (1, M^+-OCH_2CH_3), 103 (38), 89 (39), 71 (33), 61 (100).

3-(1-Methylethoxy)-1-(2-propenoxy)-2-propanol (12c)[3g] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84-5.95 (m, 1H), 5.28 (d, J = 17.2 Hz, 1H), 5.19 (d, J = 10.3 Hz, 1H), 4.02 (d, J = 5.7 Hz, 2H), 3.89-3.97 (m, 1H), 3.41-3.64 (m, 5H), 2.98 (d, J = 4.2 Hz, 1H), 1.16 (d, J = 6.2 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 134.5, 117.0, 72.2, 72.0, 71.3, 69.5, 69.2, 21.9; IR (KBr) 3416, 3086, 2980, 2933, 1129, 1083 cm^{-1}; GC-MS m/z (rel. intensity) 159 (1, M^+-CH_3), 143 (1), 131 (6), 117 (12), 103 (22), 83 (22), 73 (100), 61

(75).

3-(1,1-Dimethylethoxy)-1-(2-propenoxy)-2-propanol (12d)[3g] Pale-yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80-5.91 (m, 1H), 5.13-5.26 (m, 2H), 3.98 (dd, J = 1.3 Hz, 5.7 Hz, 2H), 3.81-3.89 (m, 1H), 3.30-3.50 (m, 4H), 2.62 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 134.6, 117.0, 73.1, 72.2, 71.4, 69.7, 62.9, 27.4; IR (KBr) 3445, 3088, 2976, 2931, 1364, 1197, 1085 cm^{-1}; GC-MS m/z (rel. intensity) 173 (2, M^+-CH_3), 131 (8), 115 (10), 100 (5), 83 (6), 71 (13), 57 (100).

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