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Envirocat (K10-MX)-Catalyzed Regioselective Transformation of Alkenes into Iodohydrins and β-Iodo Ethers and Further Conversion of Iodohydrins to Epoxides Using Al_2O_3-Na_2CO_3 Under MWI

Shallu [a], M. L. Sharma [a] & Jasvinder Singh [a]

[a] Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India

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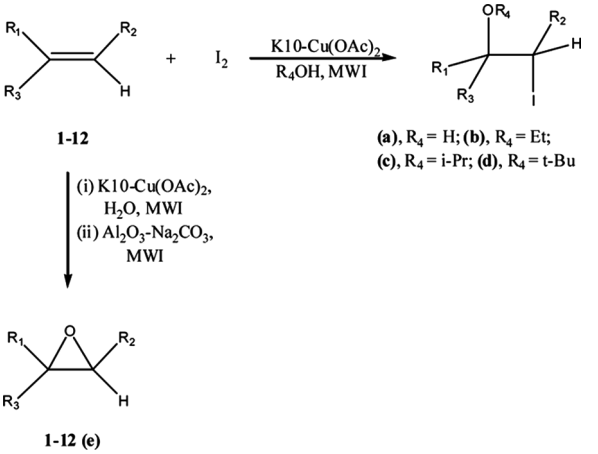
ENVIROCAT (K10-MX)–CATALYZED REGIOSELECTIVE TRANSFORMATION OF ALKENES INTO IODOHYDRINS AND β-IODO ETHERS AND FURTHER CONVERSION OF IODOHYDRINS TO EPOXIDES USING Al_2O_3-Na_2CO_3 UNDER MWI

Shallu, M. L. Sharma, and Jasvinder Singh

Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India

GRAPHICAL ABSTRACT



Abstract *Commercial K10 clay was converted to extremely efficient and environmentally friendly catalyst K10-MX for the preparation of iodohydrins and* β*-iodo ethers from alkenes (terminal as well as internal) using microwave irradiation. This method was further extended for the conversion of alkenes to epoxides via iodohydrin intermediate in a one-pot reaction system.*

Keywords Alkenes; electrophilic addition; β-iodo ethers; iodohydrins; heterogeneous catalysis

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Address correspondence to Jasvinder Singh, Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh 160014, India. E-mail: jsbrar_pu@yahoo.com

INTRODUCTION

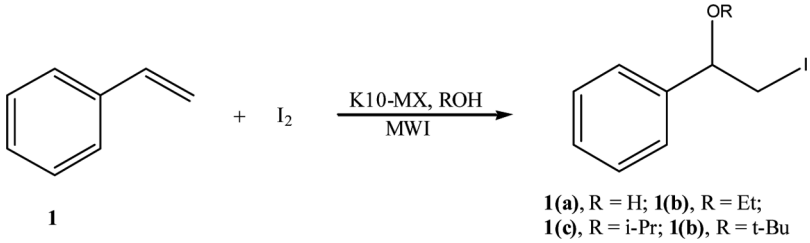
Development of new environmentally friendly synthetic methodologies in organic chemistry has been an important area of research. The functionalization of alkenes has applications in various important transformations. The formation of halohydrins from alkenes is a well-established procedure.[1] Iodohydrins are useful intermediates in organic synthesis for the preparation of epoxides. Though the formation of chlorohydrins and bromohydrins from alkenes and dilute aqueous solutions of the halogens is achieved in good yields,[2] the formation of iodohydrins is usually difficult using the same procedure because of the reversibility of the addition of iodine to the double bond. Indeed, in most cases, the formation of iodohydrins cannot be obtained in satisfactory yields in the absence of an iodide ion scavenger ($AgNO_3$, HgO,[3] $CuO{\cdot}HBF_4$[4] or an oxidizing agent[5]).

β-Iodo ethers are useful intermediates for stereoselective radical reactions[6] and for the synthesis of *E*- or *Z*-alkenes with good to moderate diastereoselectivity.[7] Traditional methods for preparing these compounds include the reactions of alkenes with $HIO_4{\cdot}2H_2O/NaHSO_3$,[8] N-iodoimides,[8] N-iodosaccharin,[8] bis(pyridine)iodine(I) salts,[8] dimethyldioxirene/MeI,[9] triiodide ion in aqueous media,[10] $Fe_2(SO_4)_3/I_2$ in the presence of H_2O/alcohol,[8] N-iodosuccinimide/alcohols,[11,12] and IBX-I_2[13]. Also, epoxides are useful intermediates in synthetic organic chemistry,[14] and the interest in these valuable compounds has increased with the discovery of some biological activities related to the oxirane ring.[15] There are several methodologies for the preparation of epoxides, for example, the reaction of alkenes with peracids/bases,[16] O_2 or H_2O_2 using a metal-based catalytic system[17] or zeolites,[18] H_2O_2/auxiliaries (nitriles, carbodiimides, etc.).[19] On the other hand, halohydrins are widely used in epoxide synthesis in both laboratory and industrial scales.[20]

Growing interest in the catalysis of organic reactions by inorganic reagents supported on high-surface-area inorganic material[21] has led to a new family of supported reagents such as envirocat, which represents a breakthrough in environmentally friendly chemistry.[22] One such commercially available envirocat, EPZ-10, has been employed by Mahajan et al. for the transformation of alkenes into β-iodo ethers and iodohydrins.[23] Some work citing the use of natural Brazilian clays (F-101 and F-117) has also been reported in the literature.[24,25] All these methodologies suffer from limitations such as long reaction times, requirement for inert atmosphere, harsh refluxing conditions, or high costs of commercial catalysts. Moreover, no method so far has reported the conversions of internal alkenes in good yields. The good versatility, reusability, low cost, and enhanced selectivity and yield turn clays into very attractive catalysts in green chemistry.[26,27]

RESULTS AND DISCUSSION

Herein we propose the use of a few envirocats (prepared by treating montmorillonite K10 clay with aqueous solutions of different metal salts, i.e., MX)[28] as a highly efficient and convenient protocol for regioselective synthesis of iodohydrins, β-iodo ethers, and further epoxides from alkenes under microwave irradiation (MWI), promoting both the yields and rates of the reactions greatly. These



Scheme 1.

K10-MX catalysts exhibit both Brønsted as well as Lewis acid characteristics.[29,30] To the best of our knowledge no such technique has been reported so far for iodohydrin, β-iodo ether and epoxide preparation.

In a preliminary experiment, the reaction of styrene and I_2/H_2O with different K10-MX catalysts was explored to determine the optimal conditions (Scheme 1 and Table 1). Applying our methodology, we obtained 1-hydroxy-2-iodo-1-phenylethane **1(a)** in 99% yield in just 4 min while using K10-$Cu(OAc)_2$ catalyst and 0.50 mol. equiv. of I_2 (entry 5, Table 1). When simple K10 clay was used with 2 mol. equiv. of I_2, the yield of **1(a)** did not exceed 37% even up on irradiating up to 16 min (entry 1, Table 1). K10-$Zn(OAc)_2$ and K10-$Fe(NO_3)_3$ catalysts also gave good yields of **1(a)** (96% and 90% respectively) but the irradiation time had to be increased (entries 9 and 10, Table 1). In the case of K10-$Fe(NO_3)_3$, the amount of I_2 also had to be raised along with the time of irradiation.

A kinetic study comparing different K10-MX catalysts and simple K10 clay was performed through coiodination of styrene with H_2O/I_2. Figure 1 demonstrates that the reaction with simple K10 clay is very slow and although all the catalysts (K10-MX) had almost similar activity in 30 min (except K10-MCl_x), K10-$Cu(OAc)_2$ showed a greater catalytic effect in a small reaction time (4 min entry 5, Table 1). Also, the kinetics of the same reaction using K10-$Cu(OAc)_2$ catalyst were studied

Table 1. Microwave-assisted conversion of **1** to **1(a)** using different K10-MX catalysts

No.	MX	Mol. equiv. of I_2	Time (min)	Yield (%)[a]
1	—	2.00	16	37[b]
2	$FeCl_3$	2.00	6	71
3	$ZnSO_4 \cdot 7H_2O$	1.50	8	73
4	$Bi(NO_3)_3$	1.50	8	80
5	$Cu(OAc)_2 \cdot H_2O$	0.50	4	99
6	$NiCl_2 \cdot 6H_2O$	2.00	9	60
7	HgO	1.00	7	87
8	$CuSO_4 \cdot 5H_2O$	1.00	6	83
9	$Zn(OAc)_2 \cdot 2H_2O$	0.50	5	96
10	$Fe(NO_3)_3$	0.75	5	90
11	$CuCl_2$	2.00	9	68

[a]Isolated yields based on **1** (styrene).
[b]Simple K10 clay is used without any doping with MX.

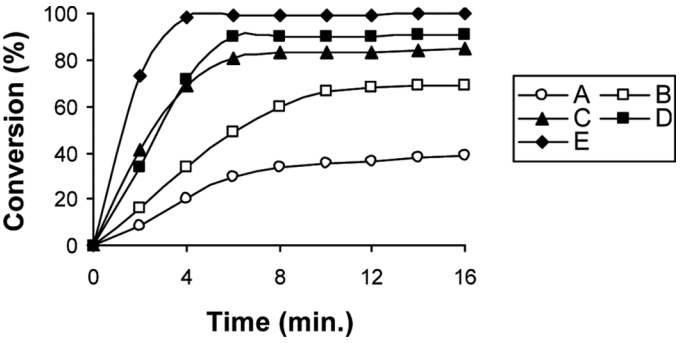


Figure 1. Conversion of **1** to **1(a)** catalyzed by K10-MX catalysts as a function of time. A=K10; B=K10-$CuCl_2$; C=K10-$CuSO_4$; D=K10-$Fe(NO_3)_3$; and E=K10-$Cu(OAc)_2$.

to see the influence of different amounts of iodine. Figure 2 demonstrates that as different catalysts and irradiation time influence the reaction yields, changing the mol. equiv. of I_2 also has a great impact. Here we investigated the conversion of **1** to **1(a)** catalyzed by K10-$Cu(OAc)_2$ using different mol. equiv. amounts of I_2 and found that **1(a)** was formed in 99% yield when 0.50 mol. equiv. of I_2 was used. No further increase in yield occurs with addition of more I_2 (irradiation was done for 4 min). K10-$CuSO_4$ required 1 mol. equiv. of I_2 to give a maximum yield of 83%.

Based on these results, it was decided to demonstrate the generality and utility of this simple methodology to prepare diverse iodohydrins and β-iodo ethers from alkenes (Scheme 2 and Table 2) using cheap and self-prepared envirocat K10-$Cu(OAc)_2$. This catalyst proved to be very efficient even when the reactions were carried out at room temperature (rt) as shown in Table 2. As we have mentioned earlier, with the use of MWI the reaction rates as well as the yields were further enhanced, especially in case of internal alkenes (entries 10 and 11, Table 2). Here we found that the conversions were very efficient for all the substrates except for undec-10-en-1-ol and undec-10-en-1-oic acid (entries 6 and 7 respectively,

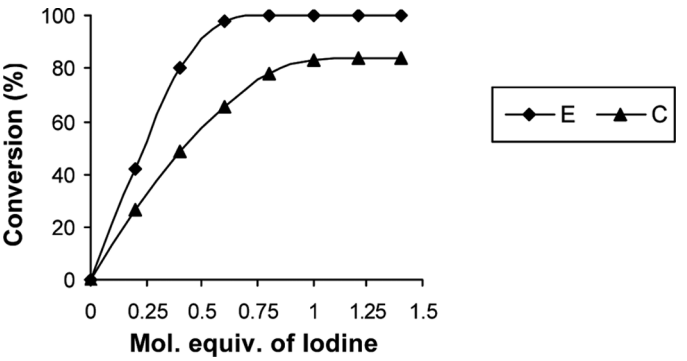
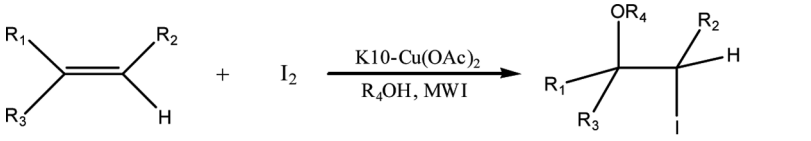


Figure 2. Conversion of **1** to **1(a)** catalyzed by E=K10-$Cu(OAc)_2$ in comparison to C=K10-$CuSO_4$ as a function of mol. equiv. of I_2.

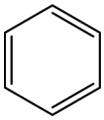
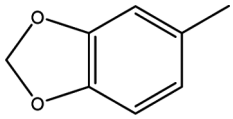
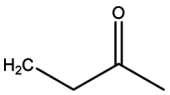
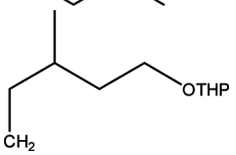


1-12

(a), $R_4 = H$; **(b)**, $R_4 = Et$;
(c), $R_4 = i\text{-}Pr$; **(d)**, $R_4 = t\text{-}Bu$

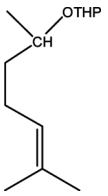
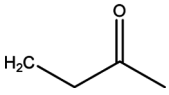
Scheme 2.

Table 2. Microwave assisted conversion of alkenes to iodohydrins and β-iodo ethers catalyzed by $K10\text{-}Cu(OAc)_2 \cdot H_2O$

S. No.[a]	R_1	R_2	R_3	Time (min)[b] R.T.	Time (min)[b] MWI	Yield (%)[c,d] R.T.	Yield (%)[c,d] MWI
1		H	H	40, 30, 35, 40	4, 3, 3, 4	97, 94, 95, 93	99, 99, 98, 98
2	$CH_3-(CH_2)_3-$	H	H	45, 30, 35, 45	5, 4, 4, 4	91, 92, 92, 90	96, 97, 96, 96
3	$CH_3-(CH_2)_7-$	H	H	45, 30, 35, 50	6, 5, 6, 6	90, 91, 91, 89	96, 97, 95, 94
4	$-(CH_2)_4-$		H	40, 30, 35, 45	5, 4, 4, 4	91, 93, 92, 90	97, 98, 96, 95
5		H	H	40, 35, 40, 45	4, 5, 5, 5	91, 94, 94, 91	96, 97, 97, 96
6	$HO-(CH_2)_9-$	H	H	40, 35, 35, 40	5, 5, 6, 6	36, 40, 40, 38	40, 46, 45, 43
7	$HOOC-(CH_2)_8-$	H	H	45, 30, 35, 45	6, 4, 4, 5	80, 42, 45, 40	91, 51, 57, 60
8	$MeOOC-(CH_2)_8-$	H	H	45, 35, 35, 40	7, 5, 5, 5	86, 90, 91, 85	93, 95, 94, 93
9	$EtOOC-(CH_2)_8-$	H	H	45, 35, 35, 40	7, 5, 5, 5	87, 91, 90, 85	94, 95, 94, 94
10	Me		Me	55, 50, 50, 60	8, 7, 7, 8	72, 71, 74, 72	90, 92, 93, 92
11	Me		Me	50, 45, 45, 55	7, 6, 7, 8	74, 75, 76, 73	91, 95, 93, 92

(*Continued*)

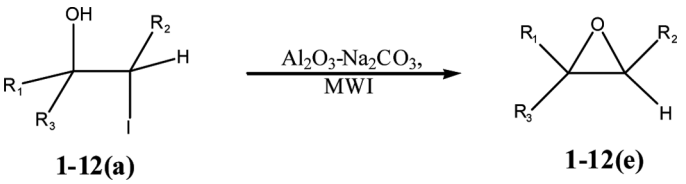
Table 2. Continued

S. No.[a]	R_1	R_2	R_3	Time (min)[b] R.T.	Time (min)[b] MWI	Yield (%)[c,d] R.T.	Yield (%)[c,d] MWI
12		H	H	45, 40, 40, 50	6, 5, 6, 6	69, 70, 72, 71	88, 86, 87, 87
13[e]	$CH_3-(CH_2)_3-$ + Me	H + 	H + Me	45, 30, 35, 45	5, 4, 4, 4	89, 90, 90, 88 + 4, 5, 4, 4	93, 94, 93, 91 + 3, 6, 5, 3

[a]**1–12** = Different substrates.
[b]Time of stirring/irradiation for obtaining products **(a), (b), (c), (d)** respectively.
[c]Isolated yields based on corresponding substrates for products **(a), (b), (c), (d)** respectively.
[d]**1–12(a)**, R_4 = H; **1–12(b)**, R_4 = Et; **1–12(c)**, R_4 = i-Pr; **1–12(d)**, R_4 = t-Bu.
[e]A mixture of substrates **2** and **10** was taken in a 1:1 ratio and the appropriate amounts of I_2 and catalyst were added.

Table 2). This is because the −OH group present in **6** undergoes substitution by the −I group along with the addition reaction across the double bond, thus lowering the yield of required products. In case of **7**, though the iodohydrin **7(a)** is formed in a very good amount, the β-iodoethers **7(b), (c),** and **(d)** are poor in yield because of esterification of −COOH group in **7** as the competing side reaction. Also, comparatively great selectivity of the terminal double bond over the internal has been shown, which corresponds to the steric factors (entries 12 and 13, Table 2).

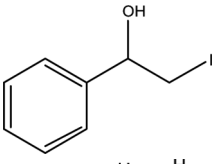
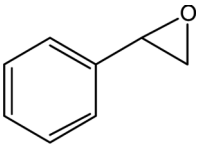
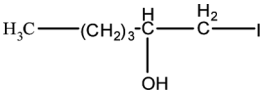
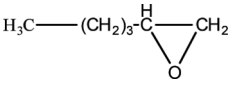
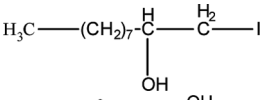
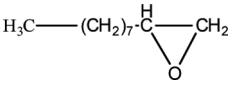
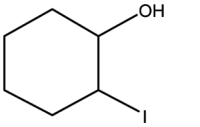
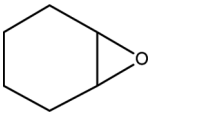
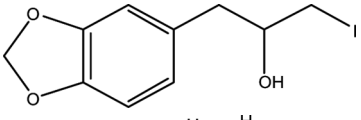
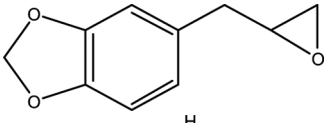
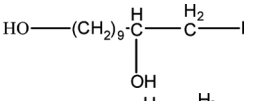
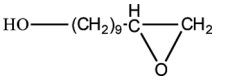
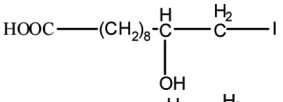
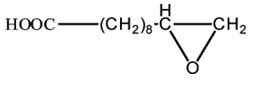
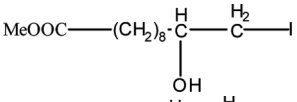
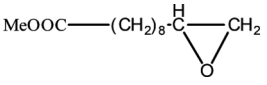
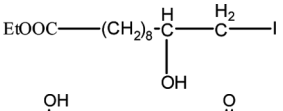
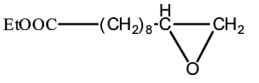
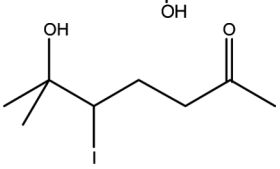
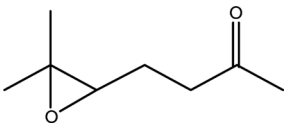
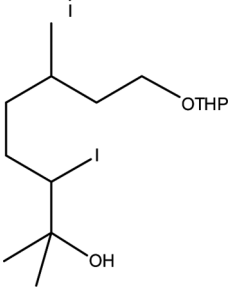
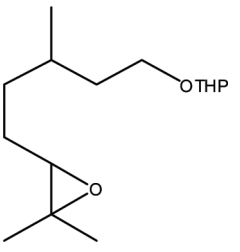
Further, we have converted alkenes to corresponding epoxides via a one-pot reaction using K10-$Cu(OAc)_2$ followed by addition of Al_2O_3-Na_2CO_3 under MWI (Scheme 3, Table 3). Completion of the reaction was monitored with the help of thin-layer chromatography (TLC) in all the cases. Here also the presence of −OH



1-12(a) **1-12(e)**

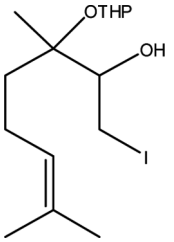
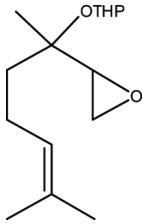
Scheme 3.

Table 3. Microwave-assisted conversion of iodohydrins [prepared by using K10-$Cu(OAc)_2 \cdot H_2O$)] to epoxides catalyzed by Al_2O_3-Na_2CO_3

No.	Reactant	Product (e)	Time (min.)	Yield (%)[a]
1.			0.5	99
2.			0.5	98
3.			1	98
4.			0.5	97
5.			0.75	99
6.			1.5	75
7.			1.5	92
8.			1	96
9.			1	95
10.			1.75	90
11.			1.75	94

(*Continued*)

Table 3. Continued

No.	Reactant	Product (e)	Time (min.)	Yield (%)[a]
12.			1.5	87

[a]Isolated yields based on corresponding substrates.

group in substrate **6** hinders the overall formation of product **6(e)**, though the conversion of **6(a)** to **6(e)** was found to be comparably efficient (Entry 6, Table 3).

CONCLUSION

In conclusion, we have described how these envirocats (K10-MX), prepared by us, serve as efficient catalysts for iodohydrin, β-iodo ether, and epoxide formation in excellent yields under MWI without making use of high-boiling solvents such as 1,4-dioxan (which has trouble isolating pure products) and long reaction times. The reaction has been found to be very efficient in both terminal and internal alkenes. The conversion is very fast, and the advantages of heterogeneous catalyst in terms of easy workup procedures coupled with simple operation and recyclability (7–8 times after reactivation) of catalysts are obvious. Moreover, because I_2 is completely consumed, the reaction represents an example of atom economy that can be explained by oxidative regeneration of I_2 and H_2 because of the dissociation of the hydroiodic acid formed during the addition reaction. Thus, we see that the reaction conditions are mild, and in our opinion the method is simpler than the traditional routes to these compounds from alkenes.[3–20] This simple methodology is also an alternative route for the epoxidation of acid-sensitive alkenes or the epoxidation of alkenes yielding acid-sensitive epoxides.

EXPERIMENTAL

Alkenes were purified by standard methods,[31] and all other chemicals were used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded (δ/ppm) on a Bruker Avance II 400-MHz NMR spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Fourier transform–infrared (FT-IR) spectra were recorded on a Perkin-Elmer model 1430 spectrometer (NaCl films). The isolated products **1–10(a)**, **(b)**, **(c)**, and **(d)** are stable at rt for several hours and can be stored in a freezer for at least 3 months without significant detectable decomposition except for **1–10(e)**.

K10-MX Catalysts: Typical Procedure

K10 clay (10 g) was added to a round-bottom flask having MX (15 g) dissolved in distilled water (60 mL). The solution was stirred for 7–8 h; the catalyst was filtered, washed with distilled water, and heated at 280 °C for 5–6 h before use.

Al_2O_3-Na_2CO_3 Catalyst: Typical Procedure

Al_2O_3 and Na_2CO_3 both were taken in a 1:1 ratio in a pestle mortar and ground together to make a homogeneous powder. Then this powder catalyst was activated by keeping it in an oven at 200 °C overnight before use.

Iodohydrins 1–12(A): Typical Procedure

In a 25-mL Erlenmeyer flask, alkene (5 mmol), water (10 mL), I_2 (0.5 mol. equiv., 2.5 mmol), and K10-$Cu(OAc)_2$ (0.5 g) were taken, and the reaction mixture was irradiated under microwaves with continuous stirring for few minutes (as shown in Table 2), at 40–45 °C. The completion of reaction was monitored using TLC, and then the reaction mixture was filtered. CH_2Cl_2 or Et_2O (25 mL) was added, and the organic layer was washed with 5% $Na_2S_2O_3$ solution (3×5 mL) and brine (5 mL). After drying over anhydrous Na_2SO_4, the organic layer was filtered through a small SiO_2 column, and the solvent was removed under reduced pressure on a rotary evaporator (bath: 50 °C) followed by final concentration at rt to give the corresponding **1–12** (a) as a colorless or light yellow liquid.

β-Iodo Ethers 1–12(B, C, D): Typical Procedure

The procedure is the same, except EtOH, i-PrOH, or t-BuOH (10 mL) were used instead of water to give **1–12** (b), **1–12** (c), or **1–12** (d) respectively.

Epoxides 1–12(E): Typical Procedure

The procedure is the same as for iodohydrins. The reaction mixture containing iodohydrin was further used without any workup. Al_2O_3-Na_2CO_3 (1 g) was added to this reaction mixture and irradiated for the required time (as given in Table 3) at 40–45 °C followed by the workup to give **1–12 (e)**.

Product Characterization Data

1-Hydroxy-2-iodo-1-phenylethane 1(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (bs, 1H, D_2O exchangeable), 3.37–3.50 (m, 2H), 4.83 (dd, 1H, $J1 = 8.8$, $J2 = 3.6$ Hz), 7.34–7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 74.1, 125.8, 128.4, 128.7, 141.1. IR (cm^{-1}, neat) ν 3433 (br), 3027, 2925, 2892, 1173, 1063, 909, 760, 699.

1-Ethoxy-2-iodo-1-phenylethane 1(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, 3H, $J = 7.0$ Hz), 3.20–3.25 (m, 2H), 3.33–3.37 (m, 2H), 4.30 (dd, 1H, $J1 = 5$, $J2 = 8.0$ Hz), 7.20–7.27 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 15.3, 65.1,

81.9, 126.6, 128.4, 128.7, 140.6. IR (cm^{-1}, neat) ν 3060, 2973, 1510, 1492, 1369, 1172, 1094, 762, 700.

2-Iodo-1-isopropoxy-1-phenylethane 1(c). ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (d, 3H, $J = 5.4$ Hz), 1.20 (d, 3H, $J = 5.4$ Hz), 3.29 (d, 2H, $J = 6$ Hz), 3.55 (sept, 1H, $J = 6.1$ Hz), 4.50 (t, 1H, $J = 6.8$ Hz), 7.31–7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 21.4, 23.2, 70.5, 79.6, 126.5, 128.2, 128.6, 141.4. IR (cm^{-1}, neat) ν 3061, 2969, 2882, 1173, 1118, 1089, 1064, 761, 700.

1-*tert*-Butoxy-2-iodo-1-phenylethane 1(d). ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 9H), 3.16 (d, 2H, $J = 7.8$ Hz), 4.55 (dd, 1H, $J1 = 5.3$, $J2 = 7.7$ Hz), 7.18–7.26 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 28.8, 29.1, 74.8, 75.1, 126.3, 127.7, 128.6, 143.7. IR (cm^{-1}, neat) ν 2975, 1600, 1366, 1188, 1173, 1068, 700, 645.

Styrene oxide 1(e). ^1H NMR (400 MHz, $CDCl_3$) δ 2.79 (dd, 1H, $J1 = 5.5$, $J2 = 2.6$ Hz), 3.13 (dd, 1H, $J1 = 5.5$, $J2 = 4.0$ Hz), 3.85 (dd, 1H, $J1 = 2.6$, $J2 = 4.0$ Hz), 7.33-7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 52.4, 125.5, 128.2, 128.8, 137.6. IR (cm^{-1}, neat) ν 3027, 2925, 2892, 1451, 1251, 1071, 790, 760, 699.

1-Iodo-hexan-2-ol 2(a). ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J = 6.6$ Hz), 1.25–1.52 (m, 6H), 2.09 (bs, 1H, D_2O exchangeable), 3.04–3.07 (m, 1H), 3.32–3.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 16.8, 22.5, 27.8, 36.5, 70.9. IR (cm^{-1}, neat) ν 3391 (br), 2956, 2929, 2858, 1182, 763, 621.

2-Ethoxy-1-iodo-hexane 2(b). ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, $J = 6.6$ Hz), 1.11 (t, 3H, $J = 7.0$ Hz), 1.22–1.49 (m, 6H), 2.85–2.94 (m, 1H), 3.19–3.25 (m, 2H), 3.38–3.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 14.0, 15.4, 23.4, 25.4, 36.1, 58.6, 75.9. IR (cm^{-1}, neat) ν 2955, 2865, 1559, 1456, 1367, 1109, 760, 688.

1-Iodo-2-isopropoxy-hexane 2(c). ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.6$ Hz), 1.06 (d, 3H, $J = 5.4$ Hz), 1.18 (d, 3H, $J = 5.4$ Hz), 1.25–1.46 (m, 6H), 2.87–2.97 (m, 1H), 3.19–3.26 (m, 2H), 3.44 (sept, 1H, $J = 6.1$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1, 14.0, 23.3, 25.5, 36.3, 60.6, 76.4. IR (cm^{-1}, neat) ν 2986, 2889, 1570, 1476, 1367, 1135, 761, 685.

2-*tert*-Butoxy-1-iodo-hexane 2(d). ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.6$ Hz), 1.07 (s, 9H), 1.26–1.49 (m, 6H), 2.88–2.99 (m, 1H), 3.20–3.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 15.6, 24.3, 25.8, 30.7, 36.9, 62.3, 73.8. IR (cm^{-1}, neat) ν 2960, 2874, 1440, 1380, 1135, 762, 688.

1-Hexene oxide 2(e). ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J = 6.6$ Hz), 1.24–1.50 (m, 6H), 2.45 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.56 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 2.94–2.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 28.8, 33.2, 47.0, 51.8. IR (cm^{-1}, neat) ν 2956, 2928, 2858, 1426, 1182, 763, 621.

1-Iodo-decan-2-ol 3(a). ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J = 6.6$ Hz), 1.21–1.50 (m, 14H), 2.61 (bs, 1H, D_2O exchangeable), 3.15–3.20 (m, 1H), 3.31–3.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 14.4, 22.9, 23.1,

30.1, 30.3, 30.6, 32.5, 38.6, 75.6. IR (cm^{-1}, neat) ν 3369 (br), 2923, 2852, 1456, 1181, 759, 623.

2-Ethoxy-1-iodo-decane 3(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, $J = 6.6$ Hz), 1.12 (t, 3H, $J = 7.0$), 1.21–1.50 (m, 14H), 2.89–2.96 (m, 1H), 3.16–3.26 (m, 2H), 3.40–3.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 14.0, 22.6, 23.2, 30.0, 30.3, 30.6, 32.5, 36.4, 59.6, 78.6. IR (cm^{-1}, neat) ν 2954, 2867, 1565, 1449, 1367, 1113, 762, 656.

1-Iodo-2-isopropoxy-decane 3(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.6$ Hz), 1.10 (d, 3H, $J = 5.4$ Hz), 1.21 (d, 3H, $J = 5.4$ Hz), 1.27–1.49 (m, 14H), 2.89–2.99 (m, 1H), 3.21–3.29 (m, 2H), 3.56 (sept, 1H, $J = 6.1$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 14.2, 15.0, 23.1, 23.5, 30.1, 30.4, 30.8, 32.9, 36.6, 61.7, 78.4. IR (cm^{-1}, neat) ν 2963, 2892, 1559, 1451, 1323, 1131, 761, 655.

2-*tert*-Butoxy-1-iodo-decane 3(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J = 6.6$ Hz), 1.09 (s, 9H), 1.28–1.51 (m, 14H), 2.90–2.99 (m, 1H), 3.22–3.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 14.0, 23.3, 23.8, 30.0, 30.4, 30.7, 31.2, 37.9, 65.3, 75.8. IR (cm^{-1}, neat) ν 2960, 2894, 1449, 1344, 1135, 762, 656.

1-Decene oxide 3(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J = 6.6$ Hz), 1.25–1.53 (m, 14H), 2.57 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.75 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 2.94–2.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.9, 30.0, 30.5, 32.2, 33.5, 46.9, 49.8. IR (cm^{-1}, neat) ν 2926, 2852, 1456, 1181, 759, 623.

2-Iodo-cyclohexanol 4(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25–1.55 (m, 4H), 1.79–1.81 (m, 2H), 1.99–2.07 (m, 2H), 3.14 (bs, 1H, D_2O exchangeable), 3.53–3.62 (m, 1H), 3.70–3.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 27.4, 33.6, 38.0, 41.9, 75.1. IR (cm^{-1}, neat) ν 3391 (br), 2933, 2856, 1447, 1350, 1160, 1066, 756, 657.

1-Ethoxy-2-iodo-cyclohexane 4(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, 3H, $J = 7.0$), 1.27–1.59 (m, 4H), 1.80–1.85 (m, 2H), 1.99–2.16 (m, 2H), 3.26–3.30 (m, 2H), 3.54–3.60 (m, 1H), 3.78–3.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 20.6, 27.4, 31.0, 33.6, 38.0, 57.9, 78.1. IR (cm^{-1}, neat) ν 2941, 2865, 1455, 1367, 1158, 1031, 781, 662.

1-Iodo-2-isopropoxy-cyclohexane 4(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, 3H, $J = 5.4$ Hz), 1.20 (d, 3H, $J = 5.4$ Hz), 1.29–1.60 (m, 4H), 1.81–1.85 (m, 2H), 2.09–2.15 (m, 2H), 3.57 (sept, 1H, $J = 6.1$ Hz), 3.60–3.74 (m, 1H), 3.79–4.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 25.9, 28.4, 29.9, 33.8, 38.9, 64.3, 76.5. IR (cm^{-1}, neat) ν 2954, 2820, 1187, 1105, 1016, 782, 663.

1-*tert*-Butoxy-2-iodo-cyclohexane 4(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.24–1.51 (m, 4H), 1.73–1.79 (m, 2H), 1.92–2.05 (m, 2H), 3.50–3.59 (m, 1H), 3.67–3.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 26.8, 30.4, 34.1, 38.9, 41.9, 66.7, 76.4. IR (cm^{-1}, neat) ν 2949, 2845, 1439, 1329, 1145, 1037, 759, 659.

Cyclohexene oxide 4(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27–1.56 (m, 4H), 1.81–1.87 (m, 2H), 2.04–2.11 (m, 2H), 3.57–3.64 (m, 1H), 3.73–3.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 28.6, 56.9. IR (cm^{-1}, neat) ν 2924, 2815, 1405, 1036, 756, 657.

1-Iodo-3-[3,4-(methylenedioxy)phenyl]-propan-2-ol 5(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (bs, 1H, D_2O exchangeable), 2.70 (d, 2H, $J = 6.6$ Hz), 3.19–3.24 (m, 2H), 3.52–3.56 (m, 1H), 5.84 (s, 2H), 6.51–6.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 42.3, 71.7, 96.1, 108.4, 109.6, 122.2, 130.7, 146.4, 147.8. IR (cm^{-1}, neat) ν 3427 (br), 2916, 1247, 776, 600.

5-(2-Ethoxy-3-iodo-propyl)-benzo-[1,3]-dioxole 5(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, 3H, $J = 7.0$), 2.68 (d, 2H, $J = 6.6$ Hz), 3.21–3.25 (m, 2H), 3.28–3.33 (m, 2H), 3.41–3.53 (m, 1H), 5.90 (s, 2H), 6.52–6.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 15.3, 44.3, 59.6, 71.7, 96.1, 114.4, 115.6, 121.2, 132.7, 144.4, 148.8. IR (cm^{-1}, neat) ν 2973, 2806, 1515, 1462, 1284, 1094, 762, 640.

5-(3-Iodo-2-isopropoxy-propyl)-benzo-[1,3]-dioxole 5(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, 3H, $J = 5.4$ Hz), 1.19 (d, 3H, $J = 5.4$ Hz), 2.67 (d, 2H, $J = 6.6$ Hz), 3.15–3.19 (m, 2H), 3.45–3.51 (m, 1H), 3.59 (sept, 1H, $J = 6.1$ Hz), 5.93 (s, 2H), 6.67–6.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 23.1, 42.8, 60.5, 77.3, 95.3, 110.4, 114.6, 124.6, 133.7, 148.4, 149.8. IR (cm^{-1}, neat) ν 2981, 2821, 1167, 1036, 775, 602.

5-(2-*tert*-Butoxy-3-iodo-propyl)-benzo[1,3]dioxole 5(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 2.66 (d, 2H, $J = 6.6$ Hz), 3.17–3.21 (m, 2H), 3.49–3.53 (m, 1H), 5.81 (s, 2H), 6.48–6.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 32.9, 44.3, 75.6, 97.8, 109.7, 110.9, 123.2, 132.7, 148.1, 149.4. IR (cm^{-1}, neat) ν 2936, 1255, 780, 610.

Safrole oxide 5(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.79 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 2.99 (d, 2H, $J = 6.6$ Hz), 3.54–3.58 (m, 1H), 5.87 (s, 2H), 6.56–6.63 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 46.7, 51.9, 96.1, 114.1, 118.3, 124.2, 131.9, 147.1, 149.2. IR (cm^{-1}, neat) ν 2916, 1247, 1025, 776, 600.

11-Iodo-undecane-1,10-diol 6(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25–1.29 (m, 14H), 1.52–1.54 (m, 2H), 2.33 (bs, 2H, D_2O exchangeable), 3.24–3.31 (m, 2H), 3.34–3.35 (m, 1H), 3.67–3.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 23.0, 29.1, 33.5, 36.3, 62.4, 68.1. IR (cm^{-1}, neat) ν 3399 (br), 2923, 2845, 1696, 1119, 647, 613.

10-Ethoxy-11-iodo-undecan-1-ol 6(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, 3H, $J = 7.0$), 1.27–1.31 (m, 14H), 1.55–1.59 (m, 2H), 2.15 (bs, 1H, D_2O exchangeable), 3.16–3.26 (m, 2H), 3.28–3.33 (m, 2H), 3.37–3.42 (m, 1H), 3.53–3.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 15.2, 23.2, 26.3, 30.2, 33.2, 36.4, 63.4, 75.1. IR (cm^{-1}, neat) ν 2926, 2852, 1656, 1169, 675, 635.

11-Iodo-10-isopropoxy-undecan-1-ol 6(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, 3H, $J = 5.4$ Hz), 1.20 (d, 3H, $J = 5.4$ Hz), 1.26–1.30 (m, 14H), 1.50–1.56 (m, 2H), 2.17 (bs, 1H, D_2O exchangeable), 3.21–3.28 (m, 2H), 3.31–3.33 (m, 1H), 3.54 (sept, 1H, $J = 6.1$ Hz), 3.64–3.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 23.1, 30.1, 33.7, 36.9, 62.1, 66.1, 76.1. IR (cm^{-1}, neat) ν 2960, 2830, 1122, 1079, 649, 619.

10-*tert*-Butoxy-11-iodo-undecan-1-ol 6(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.27–1.32 (m, 14H), 1.53–1.57 (m, 2H), 2.14 (bs, 1H, D_2O exchangeable), 3.27–3.33 (m, 2H), 3.36–3.41 (m, 1H), 3.70–3.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 22.9, 28.7, 31.0, 33.1, 36.0, 62.1, 67.7. IR (cm^{-1}, neat) ν 2945, 2837, 1689, 1117, 647, 615.

Undecenol oxide 6(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.27 (m, 14H), 1.49–1.53 (m, 2H), 2.20 (bs, 1H, D_2O exchangeable), 2.58 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.66 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 3.02–3.09 (m, 1H), 3.61–3.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 22.8, 29.0, 33.4, 46.1, 49.9, 68.1. IR (cm^{-1}, neat) ν 2925, 2815, 1059, 647, 609.

10-Hydroxy-11-iodo-undecanoic Acid 7(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21–1.30 (m, 12H), 1.56–1.59 (m, 2H), 2.29 (bs, 1H, D_2O exchangeable), 2.31 (t, 2H, $J = 7.4$ Hz), 3.18–3.20 (m, 1H), 3.30–3.34 (m, 2H), 11.0 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 24.5, 25.3, 29.1, 29.2, 29.5, 35.8, 39.9, 70.7, 178.2. IR (cm^{-1}, neat) ν 3392 (br), 2928, 2853, 1712, 1116, 762, 612.

10-Ethoxy-11-iodo-undecanoic Acid 7(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, 3H, $J = 7.0$), 1.19–1.28 (m, 12H), 1.49–1.53 (m, 2H), 2.30 (t, 2H, $J = 7.4$ Hz),), 3.16–3.20 (m, 1H), 3.28–3.34 (m, 2H), 3.36–3.40 (m, 2H), 11.1 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 15.0, 24.7, 25.9, 29.6, 29.9, 29.8, 35.8, 39.8, 59.6, 78.7, 177.2. IR (cm^{-1}, neat) ν 2928, 2853, 1712, 1644, 1118, 771, 614.

11-Iodo-10-isopropoxy-undecanoic Acid 7(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, 3H, $J = 5.4$ Hz), 1.21 (d, 3H, $J = 5.4$ Hz), 1.23–1.31 (m, 12H), 1.57–1.61 (m, 2H), 2.34 (t, 2H, $J = 7.4$ Hz), 3.21–3.27 (m, 1H), 3.34–3.39 (m, 2H), 3.46 (sept, 1H, $J = 6.1$ Hz), 11.1 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 23.1, 24.2, 25.3, 30.1, 30.7, 31.5, 35.8, 39.9, 65.6, 73.1, 178.2. IR (cm^{-1}, neat) ν 2934, 2813, 1712, 1024, 760, 614.

10-*tert*-Butoxy-11-iodo-undecanoic Acid 7(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.23–1.30 (m, 12H), 1.56–1.58 (m, 2H), 2.32 (t, 2H, $J = 7.4$ Hz), 3.16–3.19 (m, 1H), 3.29–3.34 (m, 2H), 11.1 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 24.5, 25.3, 29.1, 29.2, 29.5, 31.9, 35.8, 40.3, 74.4, 179.7. IR (cm^{-1}, neat) ν 2947, 2837, 1740, 1120, 762, 617.

Undecenoic acid oxide 7(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22–1.31 (m, 12H), 1.55–1.59 (m, 2H), 2.35 (t, 2H, $J = 7.4$ Hz), 2.60 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.71 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 3.00–3.06 (m, 1H), 11.0 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 24.5, 25.3, 29.1, 29.2, 29.5, 35.8, 39.9, 70.7, 178.2. IR (cm^{-1}, neat) ν 3392 (br), 2928, 2853, 1712, 1116, 762, 612.

Methyl-10-hydroxy-11-iodoundecanoate 8(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25–1.30 (m, 12H), 1.52–1.60 (m, 2H), 2.00 (bs, 1H, D_2O exchangeable), 2.25 (t, 2H, $J = 7.4$ Hz), 3.18–3.20 (m, 2H), 3.21–3.23 (m, 1H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 22.9, 25.4, 29.7, 30.0, 30.3, 30.6, 33.3, 38.6, 50.4, 75.6, 172.2. IR (cm^{-1}, neat) ν 3470 (br), 2926, 1738, 1173, 762, 613.

10-Ethoxy-11-iodo-undecanoic acid methyl ester 8(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, 3H, $J = 7.0$), 1.27–1.31 (m, 12H), 1.54–1.61 (m, 2H),

2.29 (t, 2H, $J = 7.4$ Hz), 3.16–3.19 (m, 2H), 3.20–3.26 (m, 1H), 3.29–3.35 (m, 2H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 14.0, 23.0, 25.7, 29.7, 30.0, 30.5, 30.8, 33.6, 39.4, 50.6, 78.8, 174.5. IR (cm^{-1}, neat) ν 2929, 2864, 1740, 1173, 765, 614.

11-Iodo-10-isopropoxy-undecanoic acid methyl ester 8(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, 3H, $J = 5.4$ Hz), 1.21 (d, 3H, $J = 5.4$ Hz), 1.25–1.29 (m, 12H), 1.49–1.58 (m, 2H), 2.23 (t, 2H, $J = 7.4$ Hz), 3.15–3.20 (m, 2H), 3.17–3.21 (m, 1H), 3.44 (sept, 1H, $J = 6.1$ Hz), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 20.7, 24.6, 30.1, 30.6, 30.9, 31.6, 33.9, 39.6, 52.4, 66.1, 75.6, 174.7. IR (cm^{-1}, neat) ν 2955, 2811, 1742, 1146, 762, 612.

10-*tert*-Butoxy-11-iodo-undecanoic acid methyl ester 8(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.27–1.31 (m, 12H), 1.54–1.60 (m, 2H), 2.27 (t, 2H, $J = 7.4$ Hz), 3.21–3.26 (m, 2H), 3.27–3.31 (m, 1H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.1, 29.7, 30.0, 30.3, 30.4, 30.9, 33.8, 38.9, 50.4, 67.4, 75.6, 172.2. IR (cm^{-1}, neat) ν 2926, 1738, 1173, 762, 613.

Methyl undecenoate oxide 8(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26–1.31 (m, 12H), 1.53–1.61 (m, 2H), 2.27 (t, 2H, $J = 7.4$ Hz), 2.63 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.75 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 3.01–3.06 (m, 1H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 22.9, 25.4, 29.7, 30.0, 30.3, 30.6, 33.3, 46.1, 49.3, 51.3, 172.0. IR (cm^{-1}, neat) ν 2906, 1742, 1019, 762, 614.

Ethyl-10-hydroxy-11-iodoundecanoate 9(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25–1.30 (m, 12H), 1.31 (t, 3H, $J = 7.0$ Hz), 2.00 (bs, 1H, D_2O exchangeable), 2.25 (t, 2H, $J = 7.4$ Hz), 3.18–3.20 (m, 2H), 3.30–3.35 (m, 1H), 4.10–4.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.4, 22.9, 25.4, 30.2, 33.3, 38.6, 50.4, 59.5, 75.6, 172.2. IR (cm^{-1}, neat) ν 3460 (br), 2820, 1740, 1050, 763, 614.

10-Ethoxy-11-iodo-undecanoic acid ethyl ester 9(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, 3H, $J = 7.0$), 1.24–1.29 (m, 12H), 1.30 (t, 3H, $J = 7.0$ Hz), 2.26 (t, 2H, $J = 7.4$ Hz), 3.17–3.19 (m, 2H), 3.29–3.40 (m, 3H), 4.09–4.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 13.5, 14.5, 23.0, 25.5, 30.3, 33.6, 39.2, 55.4, 59.9, 77.8, 173.5. IR (cm^{-1}, neat) ν 2899, 2820, 1740, 1050, 765, 613.

11-Iodo-10-isopropoxy-undecanoic acid ethyl ester 9(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, 3H, $J = 5.4$ Hz), 1.21 (d, 3H, $J = 5.4$ Hz), 1.25–1.29 (m, 12H), 1.32 (t, 3H, $J = 7.0$ Hz), 2.27 (t, 2H, $J = 7.4$ Hz), 3.19–3.23 (m, 2H), 3.31–3.35 (m, 1H), 3.45 (sept, 1H, $J = 6.1$ Hz), 4.11-4.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.4, 22.9, 23.3, 25.4, 30.2, 33.3, 38.6, 50.4, 59.5, 65.2, 75.6, 172.2. IR (cm^{-1}, neat) ν 2866, 1742, 1065, 763, 614.

10-*tert*-Butoxy-11-iodo-undecanoic acid ethyl ester 9(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.27–1.30 (m, 12H), 1.34 (t, 3H, $J = 7.0$ Hz), 2.27 (t, 2H, $J = 7.4$ Hz), 3.19–3.23 (m, 2H), 3.34–3.38 (m, 1H), 4.13–4.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.4, 22.9, 25.4, 30.2, 30.8, 33.7, 39.6, 52.4, 59.5, 66.4, 73.9, 174.2. IR (cm^{-1}, neat) ν 2831, 1742, 1035, 763, 619.

Ethyl undecenoate oxide 9(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.28 (m, 12H), 1.29 (t, 3H, $J = 7.0$ Hz), 2.21 (t, 2H, $J = 7.4$ Hz), 2.65 (dd, 1H, $J1 = 8.2$, $J2 = 3.9$ Hz), 2.78 (dd, 1H, $J1 = 8.2$, $J2 = 1.1$ Hz), 3.09–3.14 (m, 1H), 4.08–4.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.4, 22.7, 25.4, 30.2, 33.5, 46.1, 49.8, 59.7, 75.6, 174.2. IR (cm^{-1}, neat) ν 2820, 1745, 1046, 763, 615.

6-Hydroxy-5-iodo-6-methyl-heptan-2-one 10(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 6H), 2.05 (s, 3H), 2.08–2.11 (m, 2H), 2.30 (bs, 1H, D_2O exchangeable), 2.40–2.45 (m, 2H), 3.55–3.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7, 24.1, 29.5, 32.3, 49.4, 75.1, 198.4. IR (cm^{-1}, neat) ν 3391 (br), 2850, 1707, 1183, 701, 620.

6-Ethoxy-5-iodo-6-methyl-heptan-2-one 10(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, 3H, $J = 7.0$), 1.27 (s, 6H), 2.09 (s, 3H), 2.10–2.14 (m, 2H), 2.44–2.48 (m, 2H), 3.28–3.35 (m, 2H), 3.61–3.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 23.3, 26.1, 28.9, 37.3, 42.4, 58.1, 78.7, 203.1. IR (cm^{-1}, neat) ν 2879, 2801, 1716, 1189, 745, 631.

5-Iodo-6-isopropoxy-6-methyl-heptan-2-one 10(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, 3H, $J = 5.4$ Hz), 1.18 (d, 3H, $J = 5.4$ Hz), 1.24 (s, 6H), 2.01 (s, 3H), 2.04–2.10 (m, 2H), 2.39–2.43 (m, 2H), 3.41 (sept, 1H, $J = 6.1$ Hz), 3.52–3.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 23.7, 24.5, 30.1, 32.9, 49.9, 66.7, 76.3, 201.7. IR (cm^{-1}, neat) ν 2869, 1720, 1153, 704, 621.

6-*tert*-Butoxy-5-iodo-6-methyl-heptan-2-one 10(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.27 (s, 6H), 2.08 (s, 3H), 2.10–2.14 (m, 2H), 2.41–2.46 (m, 2H), 3.58–3.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7, 24.1, 29.5, 30.7, 32.3, 49.4, 75.1, 201.1. IR (cm^{-1}, neat) ν 2849, 1708, 1186, 707, 619.

Methyl heptenone oxide 10(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 6H), 2.09 (s, 3H), 1.98–2.04 (m, 2H), 2.35–2.41 (m, 2H), 3.01–3.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 23.5, 29.5, 32.3, 55.4, 65.3, 203.7. IR (cm^{-1}, neat) ν 2830, 1720, 1163, 724, 621.

3-Iodo-2,6-dimethyl-8-(tetrahydro-pyran-2-yloxy)-octan-2-ol 11(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.18–1.22 (m, 2H), 1.24 (s, 6H), 1.36–1.40 (m, 2H), 1.57–1.65 (m, 7H), 1.75–1.82 (m, 2H), 2.46 (bs, 1H, D_2O exchangeable), 3.21–3.26 (m, 2H), 3.42–3.55 (m, 3H), 4.89–4.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 20.3, 27.5, 28.7, 33.1, 36.4, 38.2, 43.1, 60.2, 63.8, 75.6, 101.3. IR (cm^{-1}, neat) ν 3454 (br), 2919, 2815, 1444, 1165, 740, 662.

2-(7-Ethoxy-6-iodo-3,7-dimethyl-octyloxy)-tetrahydro-pyran 11(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 3H), 1.11 (t, 3H, $J = 7.0$), 1.19–1.24 (m, 2H), 1.27 (s, 6H), 1.38–1.44 (m, 2H), 1.59–1.67 (m, 7H), 1.76–1.85 (m, 2H), 3.24–3.37 (m, 4H), 3.45–3.57 (m, 3H), 4.93–4.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 19.3, 20.3, 27.5, 28.9, 33.3, 36.4, 38.5, 43.6, 57.1, 60.8, 63.9, 76.4, 103.2. IR (cm^{-1}, neat) ν 2908, 2875, 1434, 1167, 745, 660.

2-(6-Iodo-7-isopropoxy-3,7-dimethyl-octyloxy)-tetrahydro-pyran 11(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.08 (d, 3H, $J = 5.4$ Hz), 1.17 (d, 3H, $J = 5.4$ Hz), 1.20–1.24 (m, 2H), 1.26 (s, 6H), 1.38–1.43 (m, 2H), 1.58–1.66 (m, 7H),

1.79–1.84 (m, 2H), 3.23–3.29 (m, 2H), 3.40 (sept, 1H, $J = 6.1$ Hz), 3.44–3.53 (m, 3H), 4.89–4.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 20.2, 23.7, 27.6, 28.9, 33.5, 36.8, 38.9, 43.8, 61.8, 63.8, 69.1, 75.6, 105.2. IR (cm^{-1}, neat) ν 2936, 2845, 1155, 740, 661.

2-(7-*tert*-Butoxy-6-iodo-3,7-dimethyl-octyloxy)-tetrahydro-pyran 11(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 3H), 1.11 (s, 9H), 1.19–1.23 (m, 2H), 1.26 (s, 6H), 1.37–1.43 (m, 2H), 1.56–1.65 (m, 7H), 1.77–1.83 (m, 2H), 3.23–3.27 (m, 2H), 3.43–3.57 (m, 3H), 4.91–4.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 21.1, 27.9, 29.2, 30.9, 33.6, 36.8, 38.9, 43.5, 61.1, 64.0, 76.7, 103.1. IR (cm^{-1}, neat) ν 2921, 2805, 1441, 1137, 742, 667.

2-(3,7-Dimethyl-oct-6-enyloxy)-tetrahydro-pyran oxide 11(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.16–1.20 (m, 2H), 1.23 (s, 6H), 1.34–1.37 (m, 2H), 1.55–1.61 (m, 7H), 1.72–1.79 (m, 2H), 2.69–2.78 (m, 1H), 3.20–3.26 (m, 2H), 3.39–3.51 (m, 2H), 4.87–4.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 20.3, 27.5, 28.7, 33.1, 36.4, 38.2, 43.1, 54.3, 60.2, 63.8, 65.1, 100.8. IR (cm^{-1}, neat) ν 2919, 2801, 1025, 740, 666.

1-Iodo-3,7-dimethyl-3-(tetrahydro-pyran-2-yloxy)-oct-6-en-2-ol 12(a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 3H), 1.36–1.42 (m, 2H), 1.56–1.62 (m, 4H), 1.68 (s, 6H), 1.75–1.89 (m, 4H), 2.35 (bs, 1H, D_2O exchangeable), 3.16–3.26 (m, 2H), 3.58–3.65 (m, 2H), 4.01 (dd, 1H, $J1 = 8.8$, $J2 = 3.6$ Hz), 4.90–4.96 (m, 1H), 5.18–5.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 18.7, 19.3, 25.3, 28.0, 33.6, 34.8, 62.5, 71.5, 86.1, 93.6, 124.8, 132.4. IR (cm^{-1}, neat) ν 3442 (br), 2951, 1626, 1430, 1157, 758, 612.

2-[1-(1-Ethoxy-2-iodo-ethyl)-1,5-dimethyl-hex-4-enyloxy]-tetrahydro-pyran 12(b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, 3H, $J = 7.0$), 1.28 (s, 3H), 1.34–1.41 (m, 2H), 1.52–1.59 (m, 4H), 1.65 (s, 6H), 1.73–1.84 (m, 4H), 3.14–3.23 (m, 2H), 3.28–3.34 (m, 2H), 3.53–3.61 (m, 2H), 4.00 (dd, 1H, $J1 = 8.8$, $J2 = 3.6$ Hz), 4.88–4.93 (m, 1H), 5.15–5.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1, 15.2, 18.9, 20.3, 26.6, 28.5, 34.6, 35.3, 60.2, 62.9, 72.1, 86.9, 93.8, 125.7, 134.1. IR (cm^{-1}, neat) ν 2989, 2866, 1645, 1442, 1134, 777, 638.

2-[1-(2-Iodo-1-isopropoxy-ethyl)-1,5-dimethyl-hex-4-enyloxy]-tetrahydro-pyran 12(c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, 3H, $J = 5.4$ Hz), 1.19 (d, 3H, $J = 5.4$ Hz), 1.30 (s, 3H), 1.37–1.44 (m, 2H), 1.57–1.63 (m, 4H), 1.70 (s, 6H), 1.76–1.89 (m, 4H), 3.19–3.27 (m, 2H), 3.47 (sept, 1H, $J = 6.1$ Hz), 3.60–3.67 (m, 2H), 4.05 (dd, 1H, $J1 = 8.8$, $J2 = 3.6$ Hz), 4.91–4.96 (m, 1H), 5.20–5.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 18.7, 19.3, 23.0, 25.3, 28.0, 33.6, 34.8, 62.5, 66.7, 71.5, 87.3, 95.4, 125.8, 134.8. IR (cm^{-1}, neat) ν 2956, 1629, 1143, 760, 616.

2-[1-(1-*tert*-Butoxy-2-iodo-ethyl)-1,5-dimethyl-hex-4-enyloxy]-tetrahydro-pyran 12(d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.27 (s, 3H), 1.34–1.40 (m, 2H), 1.53–1.59 (m, 4H), 1.65 (s, 6H), 1.71–1.84 (m, 4H), 3.13–3.21 (m, 2H), 3.53–3.63 (m, 2H), 4.01 (dd, 1H, $J1 = 8.8$, $J2 = 3.6$ Hz), 4.87–4.92 (m, 1H), 5.15–5.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1, 18.7, 19.4, 25.3, 28.1, 30.1, 33.6, 34.8, 62.5, 71.5, 86.1, 95.2, 124.8, 134.1. IR (cm^{-1}, neat) ν 2943, 1631, 1415, 1109, 761, 614.

2-(1,5-Dimethyl-1-vinyl-hex-4-enyloxy)-tetrahydro-pyran oxide 12(e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 3H), 1.35–1.40 (m, 2H), 1.55–1.60 (m, 4H), 1.66 (s, 6H), 1.73–1.84 (m, 4H), 2.66 (dd, 1H, *J1* = 8.2, *J2* = 3.9 Hz), 2.79 (dd, 1H, *J1* = 8.2, *J2* = 1.1 Hz), 3.29 (dd, 1H, *J1* = 8.8, *J2* = 3.6 Hz), 3.55–3.63 (m, 2H), 4.88–4.94 (m, 1H), 5.15–5.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 18.7, 19.3, 25.3, 28.0, 33.6, 34.8, 38.1, 62.4, 64.6, 87.1, 95.6, 125.8, 134.4. IR (cm^{-1}, neat) ν 2951, 1629, 1063, 758, 613.

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REFERENCES

1. Rodriguez, J.; Dulcere, J. P. Cohalogenation in organic synthesis. *Synthesis* **1993**, 1177–1205, and references cited therein.
2. Cornforth, J. W.; Green, D. T. Iodohydrins and epoxides from olefins. *J. Chem. Soc. (C)* **1970**, 846–849.
3. (a) Bougault, J. Oxidation of the anethole and the analogous bodies (isosafrole, isoapitol, etc.), which likewise contain a propenyl side chain. *C. R. Acad. Sci.* **1900**, *130*, 1766–1768; (b) Bougault, J. Effect of iodine and yellow mercury oxide on styrene and safrole. *C. R. Acad. Sci.* **1900**, *131*, 528–530.
4. Barluenga, J.; Rodriguez, M. A.; Campos, P. J.; Asensio, G. A general and useful copper(II)-promoted iodofunctionalization of unsaturated systems. *J. Chem. Soc., Chem. Commun.* **1987**, 1491–1492.
5. (a) Parrilli, M.; Barone, G.; Adinolfi, M.; Mangoni, L. Iodohydrins and iodohydrin esters. V. A novel alkene epoxidation procedure. *Tetrahedron Lett.* **1976**, 207–208; (b) Antonioletti, R.; D'Auria, M.; De Mico, A.; Piancatelli, G.; Scettri, A. A facile route to iodohydrins and epoxides by oxidation of olefin-iodine complexes with pyridinium dichromate. *Tetrahedron* **1983**, *39*, 1765–1768.
6. Guindon, Y.; Guérin, B.; Chabot, C.; Mackintosh, H.; Olgivie, W. W. Stereoselective radical allylation of α -Iodo-β-alkoxy esters: Reversal of facial selectivity by Lewis acid complexation. *Synlett* **1995**, 449–451.
7. Maeda, K.; Shinokubo, H.; Oshima, K. Olefin Inversion: Stereospecific olefin synthesis from *Vicinal* alkoxyiodoalkanes with butyllithium by an E2 *Syn* mechanism. *J. Org. Chem.* **1996**, *61*, 6770–6771.
8. De Mattos, M. C. S.; Sanseverino, A. M. An easy and efficient synthesis of iodohydrins from alkenes. *J. Chem. Res., Synop.* **1994**, 440–441.
9. Sanseverino, A. M.; da Silva, F. M.; Jones, J. Jr.; de Mattos, M. C. S. Coiodination of alkenes with oxygenated nucleophiles: Intramolecular reactions. *Quim. Nova* **2001**, *24*, 637–645.
10. Sanseverino, A. M.; de Mattos, M. C. S. An improved synthesis of β-iodo ethers and iodohydrins from alkenes. *Synthesis* **1998**, 1584–1586.
11. Smietana, M.; Gouverneur, V.; Mioskowski, C. An improved synthesis of iodohydrins from alkenes. *Tetrahedron Lett.* **2000**, *41*, 193–195.
12. Middleton, D. S.; Simpkins, N. S. A mild method for the preparation of functionalised, unsymmetrical ketene acetals. *Synth. Commun.* **1989**, *19*, 21–29

13. Moorthy, J. N.; Senapati, K.; Kumar, S. IBX-I_2 redox couple for facile generation of IOH and I^+: Expedient protocol for iodohydroxylation of olefins and iodination of aromatics. *J. Org. Chem.* **2009**, *74*, 6287–6290
14. (a) Badathala, V. Clay catalysts in organic synthesis. *Synlett.* **2004**, 388–389; (b) Varma, R. S. Clay and clay-supported reagents in organic synthesis. *Tetrahedron* **2002**, *58*, 1235–1255; (c) Vaccari, A. Clays and catalysis: A promising future. *Appl. Clay Sci.* **1999**, *14*, 161–198.
15. Marco-Contelles, J.; Molina, M. T.; Anjum, S. Naturally occurring cyclohexane epoxides: Sources, biological activities, and synthesis. *Chem. Rev.* **2004**, *104*, 2857–2900.
16. (a) Smith, J. G. Synthetically useful reactions of epoxides. *Synthesis* **1984**, 629–656; (b) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. Recent advances in the preparation and synthetic applications of oxiranes. *Tetrahedron* **1983**, *39*, 2323–2367.
17. (a) Liu, S. Y.; Nocera, D. G. A simple and versatile method for alkene epoxidation using aqueous hydrogen peroxide and manganese salophen catalysts. *Tetrahedron Lett.* **2006**, *47*, 1923–1926; (b) Kureshy, R. I.; Singh, S.; Khan, N. H.; Abdi, S. H. R.; Ahmed, I.; Bhatt, A.; Jasra, R. V. Environmentally friendly protocol for enantioselective epoxidation of nonfunctionalized alkenes catalyzed by recyclable homochiral dimeric Mn(III) salen comp1exes with hydrogen peroxide and UHP adduct as oxidants. *Catal. Lett.* **2006**, *107*, 127–130; (c) Rebelo, L. H.; Gonçalves, A. R.; Pereira, M. M.; Simões, M. M. Q.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. Epoxidation reactions with hydrogen peroxide activated by a novel heterogeneous metalloporphyrin catalyst. *J. Mol. Catal. A: Chem.* **2006**, *256*, 321–323.
18. Corma, A. State of the art and future challenges of zeolites as catalysts. *J. Catal.* **2003**, *216*, 298–312.
19. Grigoropoulou, G.; Clark, J. H.; Elings, J. A. Recent developments on the epoxidation of alkenes using hydrogen peroxide as an oxidant. *Green Chem.* **2003**, *5*, 1–7.
20. Weissermel, K. *Industrial Organic Chemistry*; Wiley-VCH: Wienheim, 1997; p. 266–267.
21. Clark, J. H.; Kybett, A. P.; Macquarrie, D. J. *Supported Reagents*; VCH: New York, 1992.
22. Clark, J. H.; Macquarrie, D. J. Environmentally friendly catalytic methods. *Chem. Soc. Rev.* **1996**, *25*, 303–310.
23. Mahajan, V. A.; Shinde, P. D.; Gajare, A. G.; Karthikeyan, M.; Wakharkar, R. D. EPZ-10 catalyzed regioselective transformation of alkenes into β-iodoethers, iodohydrins and 2-iodomethyl-2,3-dihydrobenzofurans. *Green Chem.* **2002**, *4*, 325–327
24. (a) Villegas, R. A. S.; de Aguiar, M. R. M. P.; de Mattos, M. C. S.; Guarino, A. W. S.; Barbosa, L. M.; Assumpção, L. C. F. N. An Environmentally friendly preparation of iodohydrins from alkenes mediated by clay-minerals. *J. Braz. Chem. Soc.* **2004**, *15*, 150–152; (b) Villegas, R. A. S.; do Espirito Santo, Jr., J. L.; de Mattos, M. C. S.; de Aguiar, M. R. M. P.; Guarino, A. W. S. Characterization of natural brazilian clays and their utilization as catalysts in the coiodination of alkenes with water and alcohols. *J. Braz. Chem. Soc.*, **2005**, *16*, 565–570.
25. Correa, K. S. M.; Bernini, R. B.; de Mattos, M. C. S.; de Aguiar, M. R. M. P.; Guarino, A. W. S. A New environmentally friendly clay-catalyst for one-pot coiodination and epoxidation of alkenes. *J. Braz. Chem. Soc.*, **2007**, *18*, 1509–1514.
26. Sheldon, R. A.; Downing, R. S. Heterogeneous catalytic transformations for environmentally friendly production. *Appl. Catal. A* **1999**, *189*, 163–183.
27. (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 2000; (b) Lenardao, E. J.; Freitag, R. A.; Dabdoub, M. J.; Batista, A. C. F.; Silveira, C. C. Green chemistry: the 12 principles of green chemistry and it insertion in the teach and research activities. *Quim. Nova* **2003**, *26*, 123–129.
28. (a) Natekar, R. S.; Samant, S. D. Catalysis of friedel-crafts alkylation using virgin and Lewis acid doped bentonite K-10. *Indian J. Chemistry* **1995**, *34B*, 257–260; (b) Kamath,

C. R.; Shinde, A. B.; Samant, S. D. Diels-Alder reaction of pyran-2(H)-ones, part V: Diels-Alder reaction of 4,6-disubstituted pyran-2(H)-ones with 1,4-naphthoquinone and N-phenylmaleimide under dry state adsorbed condition (DSAC) on montmorillonite K10, filtrol-24, bentonite, pyrophyllite; and Al^{3+}, Zn^{2+}, Fe^{3+} exchanged montmorillonite K10 and bentonite. *Indian J. Chem.* **2000**, *39B*, 270–276; (c) Chalais, S.; Laszlo, P.; Mathy, A. Catalysis of the cyclohexadienone-phenol rearrangement by a Lewis-acidic clay system. *Tetrahedron Lett.* **1986**, *27*, 2627–2630.

29. Gajare, A. S.; Shingare, M. S.; Bandgar, B. P. Selective transdithioacetalization of acetals, ketals, oxathioacetals and oxathioketals catalyzed by envirocat $EPZ10^{R}$. *J. Chem. Res. Synop.* **1998**, 452–453.
30. Clark, J. H.; Cullen, S. R.; Barlow, S. J.; Bastock, T. W. Environmentally friendly chemistry using supported reagent catalysts: Structure–property relationships for clayzic. *J. Chem. Soc. Perkin Trans.* **1994**, *2*, 1117–1130.
31. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1988.