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Direct one-pot synthesis of β-hydroxysulfides from terminal olefins in a mixture of [bmim][BF_4] and water in presence of molecular oxygen

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Abstract

Highly efficient and an environmentally benign method has been developed for the direct one-pot synthesis of β-hydroxysulfides in good yields under mild and neutral conditions from alkenes and thiophenols in the presence of aerial oxygen using a mixture of ionic liquid [bmim][BF_4] and water. This protocol tolerates a wide variety of functional groups or substrates and does not require the use of either acid or base catalysts. Ionic liquid can be recovered and reused for a number of runs with negligible loss of its activity.

Keywords: β-Hydroxysulfides; Ionic liquid; Alkenes

1. Introduction

β-Hydroxysulfides are important building blocks for the synthesis of higher functionalized organic molecules [1]. They exhibit great synthetic utility in the field of pharmaceuticals [2] and natural products, [3] particularly for the synthesis of leukotrienes such as LTC_4 and LTD_4. One of the most straightforward synthetic procedures for the preparation of β-hydroxysulfides is the ring opening of epoxides with thiols in the presence of promoters and/or catalysts [4]. However, most of the reported methods consist of Lewis acid catalysts to perform these reactions under mild conditions, but these methods suffer with various disadvantages such as drastic reaction conditions, poor regioselectivity, lower yields and undesirable side-products by rearrangement of oxiranes and oxidation of thiols [5].

Further, another method commonly used for the straightforward synthesis of β-hydroxysulfides involves the thiol–oxygen co-oxidation reactions (TOCO) of olefins [6]. Generally, TOCO reaction proceeds by free-radical-chain pathway. However, these reactions usually require base catalyst with large excess of thiols and are initiated by UV irradiation or peroxides. This methodology also suffers with regioselectivity, lower yields (upto 50%) and undesirable side-products. Thus, in principle, a direct conversion of alkenes in to β-hydroxysulfides would be a useful contribution to the synthesis of this functional class. The addition of thiols and various nucleophiles onto carbon–carbon double bonds proceeds usually in a Markonikov or anti-Markovnikov manner [7].

There is need for extensively valid approach if possible by means of environmentally benign solvents, which is gaining considerable importance in the present day organic synthesis. Improving the efficiency of organic synthesis, including minimizing the energy cost and chemical waste, is a big target in synthetic chemistry. In this context, performing multistep bond-formation and/or bond-cleavage in one-pot is an attractive strategy [8].

Ionic liquids (ILs) have recently gained recognition as possible environmentally benign alternative solvents in various chemical processes because of their many fascinating and intriguing properties [9]. They are attractive, especially, for the immobilization of transition metal based catalysts, Lewis acids and enzymes [9a,b]. Moreover, ionic liquids are simple, easy to recycle, inexpensive to prepare and their properties can be fine-tuned by changing the anion or the alkyl group attached to cation. The unique property of ionic liquids is that they

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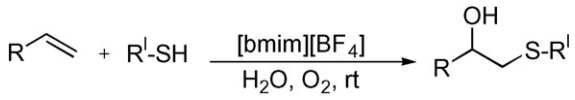
have undetectable vapour pressure, which makes them optimal replacements and practical alternatives to the volatile organic solvents traditionally used as industrial solvents for many important organic transformations. In addition, several ionic liquids enhance the reaction rates and selectivity, compared to organic solvents with the added benefit of the ease of recovery and reuse of these ionic solvents makes a significant contribution to green chemistry. Because of the distinct advantages of room temperature ionic liquids as environmentally benign reaction media for catalytic processes, much attention has been focused on organic reactions in ionic liquids. Several groups have demonstrated the feasibility of ionic liquid supported organic synthesis of small molecules [10] and peptides, [11] in which the excess reagents and by-products in the multistep reactions can be removed easily by simple washing with a solvent. In view of the emerging importance of imidazolium based ionic liquids as novel reaction media and in continuation of our interest on the use of ionic liquids in promoting various organic transformations [12], we have attempted the addition of thiols to alkenes in a mixture of ionic liquid [bmim][BF_4] and water. The ionic liquid [bmim][BF_4] has been selected for these transformations because of its excellent miscibility with water [9f].

2. Results and discussion

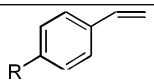
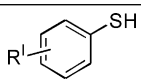
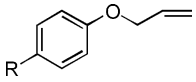
We describe, herein, the remarkable catalytic activity of ionic liquid [bmim][BF_4] in the addition of various thiols to alkenes in water for the exclusive formation of β-hydroxysulfides (Scheme 1).

To the best of our knowledge, this is the first one-pot β-hydroxysulfide synthesis with broad substrate specificity. The yields are impressive with various substituted alkenes and thiols (Table 1), and the regioselectivity of entries 1–15 is a perfect single isomer. In all these cases, the single isomer is derived from the attack of thiols at the terminal carbon. β-Hydroxysulfide could be obtained in 74% yield even from the much less reactive cyclohexene (Table 1, entry 20) and the yields are also encouraging in the case of phenoxy methylalkenes (Table 1, entries 16–19). This is the first practically feasible anti-Markovnikov addition reaction of thiols with a variety of olefins in ionic liquid. The reaction proceeds efficiently at room temperature in a short time (3–5.5 h) without the need of any acid or base catalyst. This methodology is compatible with various substituted alkenes and substituted aromatic thiols with different functionalities such as acetoxy bromo, chloro, methyl and methoxy under mild reaction conditions and no by-product formation is observed. These reactions are highly selective in the generation of β-hydroxysulfide as the only product in excellent yields keeping the other functionalities intact. However, lower yields were observed with alkyl thiols. The ionic liquid [bmim][BF_4] can be easily recovered and reused. The compounds have been characterized by spectroscopy, elemental analysis or otherwise compared with the known compounds [5].



Scheme 1. R = aryl, aryloxy-methylene, alkyl; R^1 = aryl.

Table 1
One-pot synthesis of 3-hydroxysulfides from terminal olefins in a mixture of [bmim][BF_4] and water

Entry	Styrene	Thiol	Time (h)	Yield (%)[a,b]
				
1	R = H	R^1 = H	3.0	85[c]
2	H	*p*-Br	3.0	85
3	H	*o*-Me	4.0	80
4	OAc	H	4.0	80
5	Br	H	3.0	82
6	Br	*p*-Br	3.0	80
7	Br	*p*-MeO	4.5	84
8	Cl	H	3.0	83
9	Cl	*p*-Br	3.0	84
10	Cl	*p*-MeO	4.5	86
11	Me	H	3.5	80
12	Me	*p*-Br	3.0	82
13	Me	*p*-MeO	3.5	83
14	OMe	H	3.5	84
15	OMe	*p*-Br	3.5	80
				
16	R = H	H	5.0	67
17	Cl	H	5.0	64
18	Me	H	5.0	65
19	OMe	H	5.0	66
20		H	5.5	74

[a] All the products were characterized by IR, ^{1}H NMR, mass spectrometry.
[b] Isolated yields.
[c] Catalyst was recovered and reused or five consecutive runs.

The catalytic activity of ionic liquid for this anti-Markonikov addition is established by the fact that no reaction has been observed in the absence of it. In the case of organic solvents such as acetonitrile, dichloromethane, methanol, tetrahydrofuran and aqueous methanol and aqueous acetonitrile, only the formation of thioether (10–12%) is observed and trace of β-hydroxysulfide could be seen. When the reactions are performed in ionic liquid [bmim][BF_4] under argon atmosphere, the addition product i.e., thioether alone is formed. This indicates that aerial oxygen is involved in the formation of β-hydroxysulfides. The operation TOCO reaction can also be ruled out in this case as follows. The fact that the olefin and thiol are taken in equimolar ratio and the yields are always more than 50% in all the compounds studied rules out the TOCO mechanism. In case, thiol acts as the reducing agent, the maxium possible theoretical yield of β-hydroxysulfides cannot exceed more than 50%.

The thiophenol attacks the alkene in an anti-Markonikov manner resulting in the formation of β-hydroxysulfides in a mixture of ionic liquid and water in presence of oxygen. It is further observed that this reaction does not take place with nucleophiles such as amines and phenols even after long reaction times

(∼20 h). Thus, it is observed that the reaction may not be going through the formation of epoxide since epoxides can be opened up with this type of nucleophiles [13].

3. Conclusion

In conclusion, we have demonstrated ionic liquid-catalyzed hydroxysulfide reaction as a new entry to β-hydroxysulfides directly from terminal olefins. These ionic liquid mediated reactions are very useful both from economical and environmental points of view. This reaction is simple and runs under relatively mild conditions with short reaction times and higher selectivities using a recyclable catalyst. Moreover, this green strategy avoids the use of moisture-sensitive and heavy metal Lewis acids and also eliminates routine aqueous workup procedures for the isolation of required products. To our knowledge, this is the first example of an ionic liquid mediated activation of inert alkenes towards nucleophilic addition. This protocol may lead to a new dimension in the terminal olefin functionalization.

4. Experimental

A mixture of alkene (1 mmol), [bmim][BF_4] (2 mL) and water (1 mL) was stirred at room temperature under an oxygen atmosphere. To this stirred suspension thiophenol (1 mmol) was added and the reaction mixture was further stirred at the same temperature under an oxygen atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction (Table 1), the product was extracted with ether. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum and the resulting product though seen as single compound by TLC, was further purified by using silica column chromatography to get the pure product as pale yellow oil. Ionic liquid was recovered and reused.

4.1. 1-Phenyl-2-(phenylsulfanyl)-1-ethanol (Table 1, entry 1)

Pale yellow oil; yield: 85%; ^{1}H NMR ($CDCl_3$) δ: 2.69 (brs, 1H, OH), 2.91–3.00 (m, 1H), 3.21 (dd, 1H, J = 3.0, 13.5 Hz), 4.60 (dd, 1H, J = 3.7, 9.8 Hz), 7.10–7.24 (m, 8H), 7.33 (d, 2H, J = 7.5 Hz); mass: m/z 230 (M^+); IR (KBr): 3420 cm^{-1}; Anal. Calcd for $C_{14}H_{14}OS$: C 73.01, H 6.13, S 13.92. Found: C 72.92, H 6.02, S 13.48.

4.2. 2-[(4-Brmophenyl)sulfanyl]-1-phenyl-1-ethanol (Table 1, entry 2)

Pale yellow oil; yield: 85%; ^{1}H NMR ($CDCl_3$) δ: 2.61 (d, 1H, J = 2.2 Hz), 3.04–3.12 (m, 1H), 3.28 (dd, 1H, J = 3.7, 13.5 Hz), 4.68–4.73 (m, 1H), 7.27–7.35 (m, 7H), 7.44 (d, 2H, J = 9.0 Hz); mass: m/z 309 (M^+); IR (KBr): 3425 cm^{-1}; Anal. Calcd for $C_{14}H_{13}BrOS$: C 54.38, H 4.24, S 10.37. Found: C 54.20, H 4.09, S 10.12.

4.3. 2-[(2-Methylphenyl)sulfanyl)-1-phenyl-1-ethanol (Table 1, entry 3)

Pale yellow oil; yield: 80%; ^{1}H NMR ($CDCl_3$) δ: 2.44 (s, 3H), 2.71 (brs, 1H, OH), 2.97–3.00 (m, 1H), 3.26 (dd, 1H, J = 3.7, 14.1Hz), 4.60 (dd, 1H, J = 1.5, 9.6 Hz), 7.12–7.18 (m, 3H), 7.25–7.40 (m, 6H); mass: m/z 244 (M^+); IR (KBr): 3422 cm^{-1}; Anal. Calcd for $C_{15}H_{16}OS$: C 73.73, H 6.60, S 13.12. Found: C 73.40, H 6.48, S 12.98.

4.4. 4-[1-Hydroxy-2-(phenylsulfanyl)ethyl]phenyl acetate (Table 1, entry 4)

Yellow oil; yield: 80%; ^{1}H NMR ($CDCl_3$) δ: 2.28 (s, 3H), 2.80 (brs, 1H, OH), 2.96–3.04 (m, 1H), 3.28 (dd, 1H, J = 3.7, 14.3 Hz), 4.66 (dd, 1H, J = 3.0, 9.8 Hz), 7.00 (d, 2H, J = 8.3 Hz), 7.18–7.41 (m, 7H); mass: m/z 288 (M^+); IR (KBr): 1752, 3445 cm^{-1}; Anal. Calcd for $C_{16}H_{16}O_3S$: C 66.64; H 5.59, S 11.12. Found: C 66.32, H 5.41, S 11.01.

4.5. 1-(4-Bromophenyl)-2-(phenylsulfanyl)-1-ethanol (Table 1, entry 5)

Pale yellow oil; yield: 82%; ^{1}H NMR ($CDCl_3$) δ: 2.81 (d, 1H, J = 1.5 Hz), 2.92–3.05 (m, 1H), 3.25 (dd, 1H, J = 3.7, 13.5 Hz), 4.60 (d, 1H, J = 9.8 Hz), 7.18–7.33 (m, 5H), 7.37–7.45 (m, 4H); mass: m/z 309 (M^+); IR (KBr): 3425 cm^{-1}; Anal. Calcd for $C_{14}H_{13}BrOS$: C 54.38; H 4.24, S 10.37. Found: C 54.20, H 4.22, S 10.12.

4.6. 1-(4-Bromophenyl)-2-[(4-bromophenyl)sulfanyl]-1-ethanol (Table 1, entry 6)

Yellow oil; yield: 80%; ^{1}H NMR ($CDCl_3$) δ: 2.70 (d, 1H, J = 2.2 Hz), 2.98–3.06 (m, 1H), 3.23 (dd, 1H, J = 3.7, 14.3 Hz), 4.65 (d, 1H, J = 9.0 Hz), 7.22 (d, 2H, J = 8.3 Hz), 7.26–7.30 (m, 2H), 7.45 (t, 4H, J = 7.5 Hz); mass: m/z 388 (M^+); IR (KBr): 3425 cm^{-1}; Anal. Calcd for $C_{14}H_{12}Br_2OS$: C 43.32, H 3.12, S 8.26. Found: C 43.17, H 3.18, S 8.12.

4.7. 1-(4-Bromophenyl)-2-[(4-methoxyphenyl)sulfanyl)-1-ethanol (Table 1, entry 7)

Yellow oil; yield: 84%; ^{1}H NMR ($CDCl_3$) δ: 2.77–2.89 (m, 1H), 2.90 (brs, 1H, OH), 3.10 (dd, 1H, J = 3.7, 14.1Hz), 3.81 (s, 3H), 4.51 (d, 1H, J = 8.0 Hz), 6.81 (d, 2H, J = 8.9 Hz), 7.16 (d, 2H, J = 8.9 Hz), 7.39 (t, 4H, J = 6.6 Hz); mass: m/z 339 (M^+); IR (KBr): 3430 cm^{-1}; Anal. Calcd for $C_{15}H_{15}BrO_2S$: C 53.11, H 4.46, S 9.45. Found: C 52.91, H 4.30, S 9.21.

4.8. 1-(4-Chlorophenyl)-2-(phenylsulfanyl)-1-ethanol (Table 1, entry 8)

Pale yellow oil; yield: 83%; ^{1}H NMR ($CDCl_3$) δ: 2.79 (brs, 1H, OH), 2.90–3.02 (m, 1H), 3.25 (dd, 1H, J = 3.3, 14.2 Hz), 4.63 (d, 1H, J = 8.4 Hz), 7.20–7.49 (m, 9H); mass: m/z 264 (M^+); IR

(KBr): 3424 cm^{-1}; Anal. Calcd for $C_{14}H_{13}ClOS$: C 63.51, H 4.95, S 12.11. Found: C 63.29, H 4.76, S 11.98.

4.9. 2-[(4-Brmophenylsulfanyl)-1-(4-chlorophenyl)-1-ethanol (Table 1, entry 9)

Yellow oil; yield: 84%; ^1H NMR ($CDCl_3$) δ: 2.68 (brs, 1H, OH), 2.94–3.05 (m, 1H), 3.21 (dd, 1H, $J = 3.7$, 12.4 Hz), 4.64 (d, 1H, $J = 8.0$ Hz), 7.21–7.31 (m, 6H), 7.40 (d, 2H, $J = 9.0$ Hz); mass: m/z 343 (M^+); IR (KBr): 3425 cm^{-1}; Anal. Calcd for $C_{14}H_{12}BrClOS$: C 48.93, H 3.52, S 9.33. Found: C 48.77, H 3.42, S 9.06.

4.10. 1-(4-Chlorophenyl)-2-[(4-methoxyphenyl)sulfanyl]-1-ethanol (Table 1, entry 10)

Yellow oil; yield: 86%; ^1H NMR ($CDCl_3$) δ: 2.79–2.89 (m, 1H), 2.94 (brs, 1H, OH), 3.12 (dd, 1H, $J = 2.8$, 13.1Hz), 3.81 (s, 3H), 4.55 (d, 1H, $J = 8.4$ Hz), 6.82 (d, 2H, $J = 8.4$ Hz), 7.18–7.30 (m, 4H), 7.38 (d, 2H, $J = 8.4$ Hz); mass: m/z 294 (M^+); IR (KBr): 3430 cm^{-1}; Anal. Calcd for $C_{15}H_{15}ClO_2S$: C 61.12, H 5.13, S 10.88. Found: C 60.94, H 5.00, S 10.38.

4.11. 1-(4-Methylphenyl)-2-(phenylsulfanyl)-1-ethanol (Table 1, entry 11)

Pale yellow oil; yield: 80%; ^1H NMR ($CDCl_3$) δ: 2.32 (s, 3H), 2.68 (d, 1H, $J = 2.4$ Hz), 2.98–3.08 (m, 1H), 3.28 (dd, 1H, $J = 3.7$, 14.1 Hz), 4.65 (d, 1H, $J = 9.6$ Hz), 7.09 (d, 2H, $J = 8.6$ Hz), 7.18–7.33 (m, 5H), 7.39 (d, 2H, $J = 8.6$ Hz); mass: m/z 244 (M^+); IR (KBr): 3446 cm^{-1}; Anal. Calcd for $C_{15}H_{16}OS$: C 73.73, H, 6.60, S 13.12. Found: C 73.49, H 6.42, S 12.98.

4.12. 2-[(4-Brmophenyl)sulfanyl)-1-(4-methylphenyl)-1-ethanol (Table 1, entry 12)

Yellow oil; yield: 82%; ^1H NMR ($CDCl_3$) δ: 2.34 (s, 3H), 2.52 (brs, 1H, OH), 3.00–3.08 (m, 1H), 3.21 (dd, 1H, $J = 3.7$, 14.3 Hz), 4.64 (dd, 1H, $J = 3.7$, 9.0 Hz), 7.11 (d, 2H, $J = 8.4$ Hz), 7.17–7.25 (m, 4H), 7.40 (d, 2H, $J = 8.4$ Hz); mass: m/z 323 (M^+); IR (KBr): 3430 cm^{-1}; Anal. Calcd for $C_{15}H_{15}BrOS$: C 55.74, H 4.68, S 9.92. Found: C 55.40, H 4.52, S 9.49.

4.13. 2-[(4-Methoxyphenyl)sulfanyl)-1-(4-methylphenyl)-1-ethanol (Table 1, entry 13)

Yellow oil; yield: 83%; ^1H NMR ($CDCl_3$) δ: 2.33 (s, 3H), 2.82–2.94 (m, 1H), 3.13 (dd, 1H, $J = 2.9$, 13.3 Hz), 3.80 (s, 3H), 4.52 (dd, 1H, $J = 2.9$, 9.6 Hz), 6.82 (d, 2H, $J = 8.9$ Hz), 7.10 (q, 4H, $J = 8.1$, 8.9 Hz), 7.38 (d, 2H, $J = 8.1$ Hz); mass: m/z 274 (M^+); IR (KBr): 3446 cm^{-1}; Anal. Calcd for $C_{16}H_{18}O_2S$: C 70.04, H 6.61, S 11.68. Found: C 69.82, H 6.49, S 11.45.

4.14. 1-(4-Methoxyphenyl)-2-(phenylsulfanyl)-1-ethanol (Table 1, entry 14)

Pale yellow oil; yield: 84%; ^1H NMR ($CDCl_3$) δ: 2.66 (brs, 1H, OH), 2.97–3.10 (m, 1H), 3.26 (dd, 1H, $J = 3.6$, 13.3 Hz), 3.80 (s, 3H), 4.64 (d, 1H, $J = 9.7$ Hz), 6.83 (d, 2H, $J = 8.5$ Hz), 7.22–7.34 (m, 5H), 7.40 (d, 2H, $J = 8.5$ Hz); mass: m/z 260 (M^+); IR (KBr): 3430 cm^{-1}; Anal. Calcd for $C_{15}H_{16}O_2S$: C 69.20, H 6.19, S 12.31. Found: C 68.95, H 6.04, S 12.07.

4.15. 2-[(4-Bromophenyl)sulfanyl)-1-(4-methoxyphenyl)-1-ethanol (Table 1, entry 15)

Yellow oil; yield: 80%; ^1H NMR ($CDCl_3$) δ: 2.49 (d, 1H, $J = 2.2$ Hz), 3.00–3.09 (m, 1H), 3.20 (dd, 1H, $J = 3.7$, 13.5 Hz), 3.79 (s, 3H), 4.63 (d, 1H, $J = 8.3$ Hz), 6.81 (d, 2H, $J = 8.3$ Hz), 7.19–7.26 (m, 4H), 7.40 (d, 2H, $J = 8.3$ Hz); mass: m/z 339 (M^+); IR (KBr): 3438 cm^{-1}; Anal. Calcd for $C_{15}H_{15}BrO_2S$: C 53.11, H 4.46, S 9.45. Found: C 52.91, H 4.39, S 9.23.

4.16. 1-phenoxy-3-(phenylsulfanyl)-2-propanol (Table 1, entry 16)

Pale yellow oil; yield: 67%; ^1H NMR ($CDCl_3$, 200 MHz) δ: 3.10 (d, 2H, $J = 6.8$ Hz), 3.80 (d, 2H, $J = 7.0$ Hz), 4.20 (m, 1H), 6.77–7.80 (m, 10H); mass: m/z 260 (M^+); IR (KBr): 3420 cm^{-1}; Anal. Calcd for $C_{15}H_{16}O_2S$: C 69.20, H 6.19, S 12.31. Found: C 69.01, H 5.99, S 12.10.

4.17. 1-(4-Chlorophenoxy)-3-(phenylsulfanyl)-2-propanol (Table 1, entry 17)

Yellow oil; yield: 64%; ^1H NMR ($CDCl_3$) δ: 2.55 (brs, 1H, OH), 3.05–3.30 (m, 2H), 3.90–4.20 (m, 3H), 6.80 (d, 2H, $J = 9.0$ Hz), 7.10–7.35 (m, 7H); mass: m/z 294 (M^+); IR (KBr): 3430 cm^{-1}; Anal. Calcd for $C_{15}H_{15}ClO_2S$: C 61.12, H 5.13, S 10.88. Found: C 60.95, H 4.93, S 10.11.

4.18. 1-(4-Methylphenoxy)-3-(phenylsulfanyl)-2-propanol (Table 1, entry 18)

White solid; yield: 65%; ^1H NMR ($CDCl_3$) δ: 2.30 (s, 3H), 2.60 (brs, 1H, OH), 3.05–3.30 (m, 2H), 3.90–4.20 (m, 3H), 6.75 (d, 2H, $J = 8.2$ Hz), 7.07 (d, 2H, $J = 8.2$ Hz), 7.15–7.50 (m, 5H); mass: m/z 276 (M^{+2}); IR (KBr): 3417 cm^{-1}; Anal. Calcd for $C_{16}H_{18}O_2S$: C 70.04, H 6.61, S 11.68. Found: C 69.92, H 6.34, S 11.38.

4.19. 1-[(4-Methoxyphenoxy)-3-(phenylsulfanyl)-2-propanol (Table 1, entry 19)

Yellow oil; yield: 66%; ^{1}HNMR ($CDCl_3$) δ: 2.60 (brs, 1H, OH), 3.05–3.30 (m, 2H), 3.80 (s, 3H), 3.90–4.15 (m, 3H), 6.80 (s, 4H), 7.10–7.50 (m, 5H); mass: m/z 290 (M^+); IR (KBr): 3406 cm^{-1}; Anal. Calcd for $C_{16}H_{18}O_3S$: C 66.18, H 6.25, S 11.04. Found: C 66.08, H 5.99, S 10.79.

4.20. 2-(Phenylsulfanyl)-1-cyclohexanol (Table 1, entry 20)

Oil; yield: 74%; ^{1}H NMR ($CDCl_3$) δ: 1.20–1.40 (m, 4H), 1.65–1.80 (m, 1H), 2.14–2.43 (m, 2H), 2.78 (ddd, 1H, J = 11.6, 9.8, 4.5 Hz), 3.00 (brs, 1H, OH), 3.30 (ddd, 1H, J = 9.8, 9.8, 4.5 Hz), 7.20–7.30 (m, 5H); mass: m/z 208 (M^+); IR (KBr): 3345 cm^{-1}; Anal. Calcd for $C_{12}H_{16}OS$: C 69.19, H 7.74, S 15.39. Found: C 68.97, H 7.39, S 15.09.

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