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# Eco-friendly heterogeneous solid acids as novel and recyclable catalysts in ionic medium for tetrahydropyranols

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**Abstract**

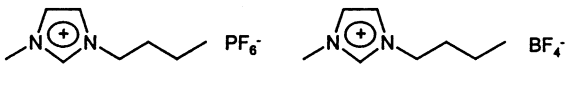
A variety of aldehydes and homoallylic alcohols undergo smoothly Prins-cyclization on the surface of solid acids such as H-ZSM-5 zeolite or Amberlyst-15® ion-exchange resin in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid to afford the corresponding tetrahydropyranols in high yields with *cis*-diastereoselectivity. The recovered ionic liquid containing solid acid was recycled in subsequent runs without loss of activity.


*Keywords:* Solid acids; Homoallyl alcohols; Tetrahydropyranols

## 1. Introduction

The tetrahydropyran ring system is a part of the backbone of various important carbohydrates, polyether antibiotics and marine macrolides [1,2]. Particularly, tetrahydropyranols are found in a number of natural products [3] such as avermectins, aplysiatoxin, oscillatoxins, latrunculins, talaromycins and acutiphycins. Generally, tetrahydropyran derivatives are synthesized by Prins-cyclization reaction using Lewis acid catalysis which often generate a mixture of products [4]. Recently, $InCl_3$ and $Sc(OTf)_3$ and $Ce(OTf)_3$ are found to be useful for this transformation [5]. However, many of these procedures often involve the use of stoichiometric amount of catalysts, longer reaction times and expensive reagents. Furthermore, many of these methods involve the use of more volatile chlorinated solvents and also entail tedious aqueous work-up to isolate the products and thus produce a huge amount of toxic waste. The use of chlorinated hydrocarbons as solvents is undesirable in view of today's environmental consciousness and as results are frequently subject to government restrictions and high waste disposal costs. Consequently methods that successfully minimize their use are the focus of much attention. The recent increased awareness of the potentially detrimental effects of organic solvents on the environment has led to a rapid growth in research into alternative reaction media. In this respect, ionic liquids have recently been shown to be excellent reaction media for various organic transformations.

Ionic liquids have emerged as a set of green solvents with unique properties such as tunable polarity, high thermal stability, and immiscibility with a number of organic solvents, negligible vapor pressure and recyclability [6]. Their high polarity and the ability to solubilise both inorganic and organic compounds can result in enhanced rates of chemical processes and can provide higher selectivities compared to conventional solvents. As a result of their green credentials and potential to enhance rates and selectivities, ionic liquids are finding increasing applications in organic synthesis. Room temperature ionic liquids, especially those based on the 1-*n*-alkyl-3-methylimidazolium cation, have shown great promise as an attractive alternative to conventional solvents. They are particularly promising as solvents for catalysis [7].




[Bmim]$PF_6$ [Bmim]$BF_4$

The use of room temperature ionic liquids has made significant advancement in the development of clean chemical processes in organic synthesis targeted to avoid or at least minimize the use of toxic or waste generating reagents or

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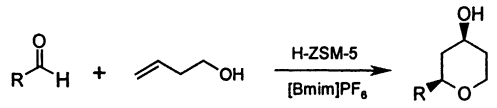



Scheme 1.

solvents. Because of their distinct advantages, ionic liquids can make a great contribution to green chemistry. In recent years, the use of solid acidic catalysts such as clays, ion-exchange resins and zeolites has received considerable attention in different areas of organic synthesis because of their simplicity in operation, environmental compatibility, reusability, greater selectivity, non-corrosiveness and ready availability at low cost [8]. Particularly, acidic zeolites make the reaction processes convenient, more economic, environmentally benign and act as both Bronsted and Lewis acids in their ion-exchanged forms, enabling them to function as efficient catalysts for various transformations [9].

## 2. Results and discussion

In view of the emerging importance of the imidazolium based ionic liquids as novel reaction media, we wish to explore the use of solid acids in ionic liquids as environmentally friendly and recyclable reagent system for the synthesis of tetrahydropyranols (Scheme 1).

4-Hydroxy tetrahydropyrans were formed in high yields when homoallyl alcohols were treated with aldehydes in the presence of acidic zeolite (H-ZSM-5) [9] immobilized in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. For example, the reaction of benzaldehyde with 1-phenyl-3-buten-1-ol on the surface of acidic zeolite in [bmim]$PF_6$ ionic liquid led to the formation of 2,6-diphenyl-4-hydroxy tetrahydropyran **3a** in 90% yield with *cis*-selectivity. The coupling constants of the benzylic hydrogens ($J = 11.5$ Hz) in the $^1$H NMR spectrum of the products as well as hydrogen on the carbon bearing the hydroxyl group ($J = 4.5$ and 11.5 Hz) showed a structure consistent with two phenyl groups and the hydroxyl group being in the *cis*-orientation and equatorial as shown in Fig. 1.

The coupling of aromatic and aliphatic aldehydes with their corresponding homoallylic alcohols on the surface of H-ZSM-5 in [bmim]$PF_6$ produced the corresponding symmetric 2,6-disubstituted-4-hydroxy tetrahydropyrans in high yields. Furthermore, the cross-coupling between aromatic homoallylic alcohols and aliphatic aldehydes or the cross-coupling between aliphatic homoallylic alcohols and

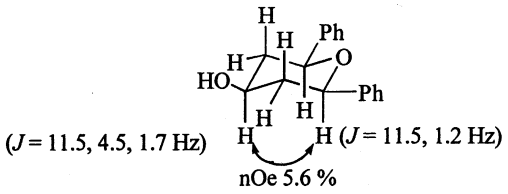
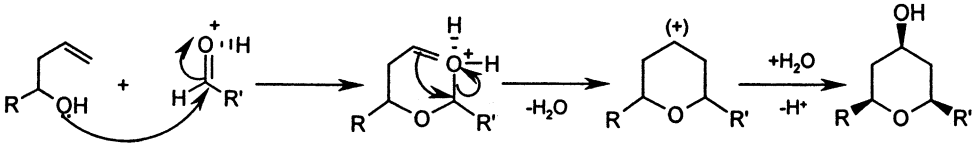



Fig. 1. Coupling constants and NOE spectrum of product **3a**.

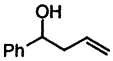
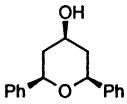
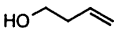
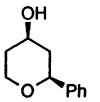
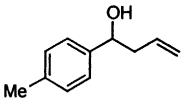
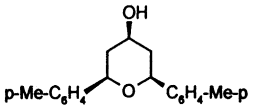
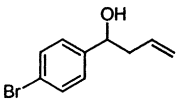
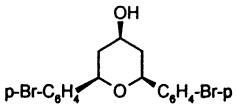
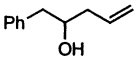
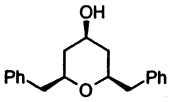
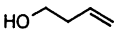
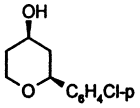
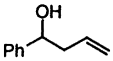
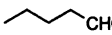
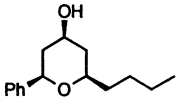
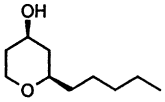
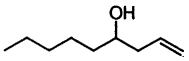
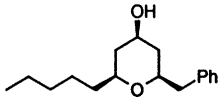
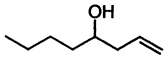
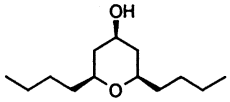
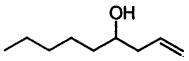
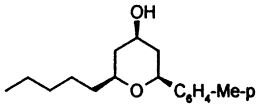
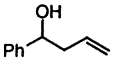
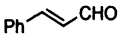
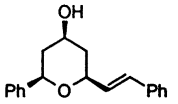
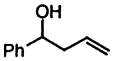
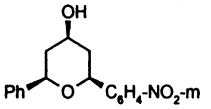
aromatic aldehydes gave the corresponding unsymmetrical tetrahydropyranols. The reactions proceeded efficiently in high yields at ambient temperature under mild conditions. The nature of the substituents on the aromatic rings of the substrates shows some effect on this conversion. It is of interest to note that aliphatic, simple aromatic and moderately activated aromatic aldehydes like chloro and bromo benzaldehyde gave high yields of products compared to strongly activated or deactivated aldehydes. All the products were characterized by $^1$H NMR, IR, and mass spectroscopy and also by comparison with authentic samples [5]. In the all cases, the products were obtained in excellent yields with high *cis*-selectivity. The predominant formation of a single stereoisomer is probably due to thermodynamic factors. The formation of the tetrahydropyranol may be explained by hemi-acetal formation and subsequent Prins-type cyclization (Scheme 2).

The advantage of the use of ionic liquids as novel reaction media for this transformation is that the ease of catalyst/product separation provided by a heterogeneous catalyst. Since the products were weakly soluble in the ionic phase, they were easily separated by simple extraction with ether. The remaining ionic liquid was thoroughly washed with ether and reused in subsequent reactions. However, the products were obtained of the same purity as in the first run, but the yields were gradual decreased in runs carried out using recovered ionic liquid containing solid acid. For example, the reaction of benzaldehyde and 3-buten-1-ol afforded the corresponding 2-phenyl-4-hydroxytetrahydropyran in 90, 85, 82, and 79% yields over four cycles. The decrease in yield using recycled ionic liquid may be attributed to the in situ formation of water in the reaction. However, the activity of ionic liquid was consistent with runs and no decrease in yield was obtained when recycled ionic liquid was activated in each cycle at 80 °C under vacuum. In addition, the reaction did not proceed in wet ionic liquid. This clearly indicates the role of water in this conversion. In further reactions, the efficiency of various quaternary ammonium salts was tested. The Prins-cyclization was not successful




Scheme 2.

Table 1
H-ZSM-5-promoted synthesis of tetrahydropyranols in ionic liquids

| Entry | Allyl alcohol (**1**) | Adehyde (**2**) | Product (**3**)[a] | Reaction time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| **a** |  | PhCHO |  | 4.0 | 90 |
| **b** |  | PhCHO |  | 3.5 | 89 |
| **c** |  | *p*-$MeC_6H_4CHO$ |  | 5.0 | 87 |
| **d** |  | *p*-$BrC_6H_4CHO$ |  | 4.0 | 92 |
| **e** |  | $PhCH_2CHO$ |  | 5.0 | 85 |
| **f** |  | *p*-$ClC_6H_4CHO$ |  | 4.5 | 90 |
| **g** |  |  |  | 4.0 | 89 |
| **h** |  |  |  | 5.0 | 83 |
| **i** |  | $PhCH_2CHO$ |  | 4.0 | 90 |
| **j** |  |  |  | 4.5 | 89 |
| **k** |  | *p*-$MeC_6H_4CHO$ |  | 4.0 | 90 |
| **l** |  |  |  | 5.0 | 85 |
| **m** |  | *m*-$NO_2C_6H_4CHO$ |  | 7.0 | 82 |

[a] All products were characterized by IR, NMR and mass spectroscopy and the characterization data was consistent with authentic compounds.
[b] Isolated and unoptimized yields.

in other molten salts such as tetrabutyl ammonium chloride (*n*-$Bu_4NCl$) or 1-*n*-butyl-3-methylimidazolium chloride ([bmim]Cl). In this reaction, the efficiency of ionic liquid is strongly influenced by the nature of the anion. The products were obtained in low to moderate yields (45–60%) when the reactions were carried out using $H^+$ zeolite in chloroform at refluxing temperature. Among various zeolites such as H-ZSM-5, HY and MCM-41, ZSM-5 is found to be efficient in terms of conversion and reaction rates. Ion-exchange resin, i.e. Amberlyst-15® works equally well for this transformation. Compared to conventional solvents, enhanced reaction rates and improved yields are the features obtained

in ionic liquids. For example, the treatment of benzaldehyde with 1-phenyl-3-buten-1-ol in the presence of solid acid in ionic liquid for 3.0–4.0 h afforded the corresponding product **3a** in 90% yield whereas the same reaction in refluxing chloroform after 7.0 h gave the same product in 60% yield. The simple experimental and product isolation procedures combined with ease of recovery and reuse of this novel reaction media is expected to contribute to the development of green strategy for the synthesis of tetrahydropyranols.

## 3. Conclusion

In this paper, the solid acids such as ZSM-5 and acidic ion-exchange resin in [bmim]$PF_6$ ionic liquid are proved to be a useful and novel reaction catalytic system for Prins-cyclization, avoiding the use of more volatile and chlorinated solvents by playing a dual role of solvent as well as acid catalyst. The substrates show significant increase in reactivity, reducing the reaction times and improving the yields substantially. The notable features of this procedure are mild reaction conditions, simplicity in operation, improved yields and reaction rates, cleaner reaction profiles and recyclability of ionic liquids which make it a simple, convenient and user-friendly process for the synthesis of tetrahydropyranols.

## 4. Experimental

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. $^1$H, $^{13}$C NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim]$BF_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]$PF_6$) ionic liquids were prepared according to the procedures reported in the literature [10].

### 4.1. General procedure

A mixture of aldehyde (1 mmol), homoallylalcohol (1.2 mmol), and H-ZSM-5 zeolite or Amberlyst-15® (0.50 g) in 1-butyl-3-methylimidazolium hexafluorophosphate or 1-butyl-3-methylimidazolium tetrafluoroborate (2 ml) was stirred at ambient temperature for an appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was washed with diethyl ether ($3 \times 10$ ml). The combined ether extracts were concentrated in vacuo and the resulting product was directly charged on small silica gel column and eluted with a mixture of ethyl acetate: *n*-hexane (2:8) to afford pure 2,6-diphenyl-4-hydroxy tetrahydropyranol as a white solid (mp 101–102 °C). The remaining ionic liquid was further washed with ether and recycled in subsequent reactions. Spectral data for products:

- **3a**: solid, mp 102–104 °C, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.55 (br s, 1H), 1.65 (ddd, 2H, $J = 12.5, 11.5, 1.0$ Hz), 2.30 (ddd, 2H, $J = 12.5, 4.5, 1.8$ Hz), 4.18 (m, 1H), 4.60 (dd, 2H, $J = 11.5, 1.0$ Hz), 7.25–7.35 (m, 10H). $^{13}$C NMR (50 MHz, proton decoupled, $CDCl_3$) $\delta$: 43.0, 68.5, 78.5, 126.0, 127.8, 128.5, 142.0. EIMS: *m*/*z*: 254 $M^+$, 236, 136, 104, 77. IR (KBr) $\nu$: 3380, 2950, 2890, 1650, 1490, 1365, 1245, 1135, 1070, 970 $cm^{-1}$.
- **3b**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.55 (m, 1H), 1.62 (m, 1H), 1.95 (m, 1H), 2.09 (br s, 1H), 2.15 (m, 1H), 3.57 (dt, 1H, $J = 12.6, 2.2$ Hz), 3.91 (tt, 1H, $J = 11.0, 4.7, 1.7$ Hz), 4.16 (ddd, 1H, $J = 11.8, 4.7, 1.7$ Hz), 4.31 (dd, 1H, $J = 11.3, 2.2$ Hz), 7.30 (m, 5H) $^{13}$C NMR (50 MHz, proton decoupled, $CDCl_3$) $\delta$: 35.4, 43.2, 66.4, 68.4, 78.4, 126.0, 127.7, 128.5, 141.8. EIMS: *m*/*z*: 179 $M^{1+}$, 178 $M^+$, 177, 161, 160, 159, 145, 131, 105, 91, 77, 44, 43, 39. IR (KBr) $\nu$: 3382, 1494, 1445, 1362, 1244, 1136, 1072, 1023, 979, 954, 881, 802, 753, 694, 636 $cm^{-1}$.
- **3c**: white solid, mp 125–127 °C, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.30 (br s, 1H), 1.55 (dd, 2H, $J = 12.5$ 11.5 Hz), 2.25 (dd, 2H, $J = 12.5, 4.5$ Hz), 2.35 (s, 6H), 4.10 (m, 1H), 4.50 (dd, 2H, $J = 11.5, 1.5$ Hz), 7.15 (d, 4H, $J = 8.0$ Hz), 7.25 (m, 4H, $J = 8.0$ Hz). EIMS: *m*/*z*: 282 $M^+$, 264, 136, 119, 91. IR (KBr) $\nu$: 3380, 2950, 2880, 1610, 1520, 1320, 1150, 950, 780, 720 $cm^{-1}$.
- **3d**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.50 (br s, 1H), 1.55 (dd, 2H, $J = 12.5, 11.5$ Hz), 2.25 (dd, 2H, $J = 12.5$, 4.5 Hz), 4.10 (m, 1H), 4.55 (dd, 2H, $J = 11.5, 1.5$ Hz), 7.35 (d, 4H, $J = 8.4$ Hz), 7.6 (d, 4H, $J = 8.4$ Hz). EIMS: *m*/*z*: 414 $M^{2+}$, 396, 184, 129, 103, 77. IR (KBr) $\nu$: 3395, 3010, 2990, 2850, 1610, 1520, 1450, 1410, 1350, 835, 760 $cm^{-1}$.
- **3e**: liquid, $^1$H NMR (200 MHz, $CDCI_3$) $\delta$: 1.15 (dd, 2H, $J = 12.5, 11.5$ Hz), 1.85 (dd, 2H, $J = 12.5, 4.5$ Hz), 2.65 (dd, 2H, $J = 12.0, 6.0$ Hz), 2.9 (dd, 2H, $J = 12.0$, 6.0 Hz), 3.45 (m, 2H), 3.65 (m, 1H), 7.1–7.3 (m, 10H). EIMS: *m*/*z*: 282 $M^+$, 281, 264, 205, 191, 188, 118, 91, 77. IR (KBr) $\nu$: 3400, 3010, 2990, 2850, 1610, 1550, 1420, 1310, 1150, 1070, 970 $cm^{-1}$.
- **3f**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.47 (m, 1H), 1.62 (m, 1H), 1.97 (m, 1H), 2.14 (m, 1H), 2.30 (br s, 1H), 3.56 (dt, 1H, $J = 12.0, 5.0, 1.8$ Hz), 3.92 (tt, 1H, $J = 11.2, 4.4, 1.8$ Hz), 4.16 (ddd, 1H, $J = 12.0, 5.0, 1.8$ Hz), 4.28 (dd, 1H, $J = 11.4, 2.1$ Hz), 7.26 (d, 2H, $J = 8.8$ Hz), 7.30 (d, 2H, $J = 8.8$ Hz). $^{13}$C NMR (50 MHz, proton decoupled, $CDCl_3$) $\delta$: 35.3, 43.2, 66.3, 68.2, 77.6, 127.3, 128.6, 133.3, 140.4. EIMS: *m*/*z*: 215, 214 $M^{2+}$, 213, 212 $M^+$, 211, 196, 195, 177, 160, 140, 139, 112, 111, 89, 77, 75, 57, 43, 39. IR (KBr) $\nu$: 3382, 2940, 2842, 1489, 1448, 1409, 1364, 1301, 1249, 1163, 1142, 1085, 1015, 987, 691, 885, 823, 717, 689, 594 $cm^{-1}$.
- **3g**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 0.9 (t, 3H, $J = 6.8$ Hz), 1.2–1.45 (m, 6H), 1.5 (m, 1H), 1.65 (m,

1H), 2.0 (dd, 1H, $J = 12.0, 4.5$ Hz), 2.20 (dd, 1H, $J = 12.0, 4.5$ Hz), 3.45 (m, 1H), 3.90 (m, 1H), 4.30 (d, 1H, $J = 11.5$ Hz), 7.20 (m, 5H). EIMS: *m*/*z*: 234 $M^+$, 233, 219, 217, 202, 140, 125, 105, 77, 57. $^{13}$C NMR (50 MHz, proton decoupled, $CDCl_3$) $\delta$: 14.0, 22.5, 28.0, 36.1, 41.0, 43.0, 68.5, 76.2, 77.5, 126.0, 127.5, 128.0, 130.0. IR (KBr) $\nu$: 3380, 3020, 2980, 1600, 1490, 1140, 1080, 760 cm$^{-1}$.

- **3h**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 0.9 (t, 3H, $J = 7.0$ Hz), 1.15–1.57 (m, 10H), 1.71 (br s, 1H), 1.88 (m, 1H), 1.95 (m, 1H), 3.25 (m, 1H), 3.38 (dt, 1H, $J = 12.0, 6.0, 2.1$ Hz), 3.77 (m, 1H), 4.01 (ddd, 1H, $J = 11.7, 4.7, 1.5$ Hz). $^{13}$C NMR (50 MHz, proton decoupled, $CDCl_3$) $\delta$: 14.0, 22.7, 27.7, 35.8, 35.9, 41.6, 65.9, 68.3, 76.3. EIMS: *m*/*z*: 155, 101, 83, 69, 57, 44. IR (KBr) $\nu$: 3380, 2930, 1360, 1250, 1140 cm$^{-1}$.
- **3i**: solid, mp 75–76 °C $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 0.9 (t, 3H, $J = 6.8$ Hz), 1.25 (dd, 2H, $J = 12.0, 11.0$ Hz), 1.30 (m, 6H), 1.50 (br s, 1H), 1.65 (m, 2H), 2.0 (dd, 1H, $J = 12.0, 4.5$ Hz), 2.70 (dd, 1H, $J = 12.0, 6.0$ Hz), 3.30 (m, 1H), 3.50 (m, 2H), 3.80 (m, 1H), 7.25–7.35 (m, 5H). EIMS: *m*/*z*: 262 $M^+$, 228, 171, 127, 109, 91. IR (KBr) $\nu$: 3390, 3010, 2990, 1610, 1490, 1140, 1080, 760 cm$^{-1}$.
- **3j**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 0.9 (t, 6H, $J = 6.8$ Hz), 1.2–1.45 (m, 12H), 1.55 (dd, 2H, $J = 12.5, 11.5$ Hz), 1.90 (dd, 2H, $J = 12.5, 4.5$ Hz), 3.2 (m, 2H), 3.70 (m, 1H). $^{13}$C NMR (50 MHz, proton decoupled, $CDCl_3$) $\delta$: 14.0, 22.5, 27.5, 35.5, 41.0, 68.0, 75.5. ElMS: *m*/*z*: 214 $M^+$, 213, 196, 181, 167, 157, 85, 57, 43. IR (KBr) $\nu$: 3350, 2930, 2860, 1455, 1370, 1245, 1035, 755, 700 cm$^{-1}$.
- **3k**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 0.9 (t, 3H, $J = 6.8$ Hz), 1.25 (m, 6H), 1.40 (dd, 2H, $J = 12.0, 11.0$ Hz), 1.50 (m, 1H), 1.65 (m, 1H), 1.80 (br s, 1H), 2.0 (dd, 1H, $J = 12.0, 4.5$ Hz), 2.20 (dd, 1H, $J = 12.0, 4.5$ Hz), 2.40 (s, 3H), 3.45 (m, 1H), 3.90 (m, 1H), 4.30 (dd, 1H, $J = 11.5, 1.2$ Hz), 7.15 (d, 2H, $J = 8.0$ Hz), 7.25 (d, 2H, $J = 8.0$ Hz). EIMS: *m*/*z*: 262 $M^+$, 244, 173, 121, 119, 91. IR (KBr) $\nu$: 3380, 3020, 2980, 1600, 1490, 1140, 1080, 760 cm$^{-1}$.
- **3l**: solid, mp 102–104 °C, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.45 (dd, 2H, $J = 12.5, 11.5$ Hz), 2.15 (dd, 2H, $J = 12.5, 4.5$ Hz), 4.0 (m, 1H), 4.42 (m, 2H), 6.20 (dd, 1H, $J = 12.0, 2.0$ Hz), 6.55 (d, 1H, $J = 12.0$ Hz), 7.18–7.30 (m, 10H). EIMS: *m*/*z*: 280 $M^+$, 279, 263, 212, 211, 186, 177, 132, 105, 77. IR (KBr) $\nu$: 3390, 2980, 2850, 1660, 1640, 1490, 1365, 1245, 1135, 1070, 970 cm$^{-1}$.
- **3m**: liquid, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.50 (dd, 2H, $J = 12.5, 11.5$ Hz), 2.23 (dd, 2H, $J = 12.5, 4.5$ Hz), 4.02 (m, 1H), 4.5 (dd, 2H, $J = 11.5, 4.5$ Hz), 7.25 (m, 5H), 7.5 (t, 1H, $J = 7.5$ Hz), 7.65 (d, 1H, $J = 7.5$ Hz), 8.0 (dd, 1H, $J = 7.5, 2.0$ Hz), 8.18 (s, 1H). EIMS: *m*/*z*: 300 $M^{1+}$, 299 $M^+$, 298, 281, 204, 181, 177, 105, 77. IR (KBr) $\nu$: 3450, 3150, 3100, 2925, 2855, 1700, 1575, 1530, 1415, 1350, 1287, 1070, 905, 760, 670 cm$^{-1}$.

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## References

[1] D.R. Adams, S.P. Bhatnagar, Synthesis (1977) 661.
[2] K.C. Nicolaou, E.J. Sorensen, Classics in Total Synthesis, VCH, Weinhein, 1996.
[3] F. Perron, K.F. Albizati, J. Org. Chem. 52 (1987) 4130, and references cited therein.
[4] (a) Z.Y. Wei, J.S. Li, D. Wang, Tetrahedron Lett. 28 (1987) 3441;
(b) L. Coppi, A. Ricci, M. Taddei, J. Org. Chem. 53 (1988) 911;
(c) Z.Y. Wei, D. Wang, J.S. Li, T.H. Chan, J. Org. Chem. 54 (1989) 5768.
[5] (a) J. Yang, G.S. Viswanathan, C. Li, J. Tetrahedron Lett. 40 (1999) 1627;
(b) W.C. Zhang, G.S. Viswanathan, C.J. Li, J. Chem. Soc. Chem. Commun. (1999) 291;
(c) W.C. Zhang, C.J. Li, Tetrahedron 56 (2000) 2403;
(d) C.C.K. Keh, V.V. Namboodiri, R.S. Varma, C.J. Li, Tetrahedron Lett. 43 (2002) 4993.
[6] (a) T. Welton, Chem. Rev. 99 (1999) 2071;
(b) P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
[7] R. Sheldon, J. Chem. Soc. Chem. Commun. (2001) 2399.
[8] (a) J.S. Yadav, B.V.S. Reddy, K. Sadashiv, P.S.R. Reddy, Tetrahedron Lett. 43 (2002) 3853;
(b) J.S. Yadav, B.V.S. Reddy, E. Balanarsaiah, S. Raghavendra, Tetrahedron Lett. 43 (2002) 5105;
(c) J.S. Yadav, B.V.S. Reddy, G.M. Kumar, Ch. V.S.R. Murthy, Tetrahedron Lett. 42 (2001) 89.
[9] S.E. Sen, S.M. Smith, K.A. Sullivan, Tetrahedron 55 (1999) 12657.
[10] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.