Lewis Acidic Chloroaluminate Ionic Liquids: Novel Reaction Media for the Synthesis of 4-Chloropyrans

Jhillu S. Yadav,*[a] Basi V. S. Reddy,[a] Maddi Sridhar Reddy,[a] Namelikonda Niranjan,[a] and Attaluri R. Prasad[a]

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1-*n*-Butyl-3-methylimidazolium chloroaluminate [bmim]-Cl·$AlCl_3$ (N = 0.56–0.67) ionic liquid has been employed as an alternative reaction medium to conventional acid catalysts for Prins cyclizations, to produce 4-chlorotetrahydropyran derivatives in excellent yields and in short reaction times. The ionic liquid plays a dual role as both catalyst and solvent, providing a rapid and efficient route to the synthesis of chlorotetrahydropyrans.

Introduction

Prins cyclization is a powerful synthetic route for the construction of six-membered tetrahydropyran derivatives.[1−3] The tetrahydropyran ring system is a core unit in a number of natural products,[4] such as avermectins, aplysiatoxins, oscillatoxins, latrunculins, talaromycins and acutiphycins. Generally, tetrahydropyran derivatives are prepared by Prins cyclization under acid catalysis conditions;[5−8] indium halides have also recently been found to be useful for this transformation.[9−10] However, many of these classical methods often involve the use of expensive reagents and extended reaction times, and also generate mixtures of products.[5−8] Furthermore, the use of more volatile organic solvents is environmentally undesirable. There is therefore still scope to develop more general and practical methods for this transformation.

The development of cost-effective and environmentally benign catalytic systems is one of the main themes of contemporary organic synthesis. From the viewpoints of atom economy and green chemistry, the ionic liquids are attracting growing interest as alternative reaction media for various organic transformations.[11−13] In particular, choloroaluminate ionic liquids are fascinating, thanks to their Lewis acidity, which can be varied over a wide range, and their intrinsic ability to solvate a variety of substances. These properties coupled together offer the advantages of homogeneous Lewis acid catalysis that can be exploited in several synthetically useful reactions. These ionic liquids are easily prepared from $AlCl_3$ and 1-butyl-3-methylimidazolium chloride. These chloroaluminate ionic liquids have the advantage of being liquid at room temperature over a considerable composition range of apparent mol fraction of $AlCl_3$ (N = 0.30−0.67) and also have negligible vapour pressures, making them useful alternatives to conventional molecular organic solvents for various synthetically useful transformations.[14−16] Furthermore, chloroaluminate ionic liquids play dual roles both as Lewis acid catalyst and as solvent.

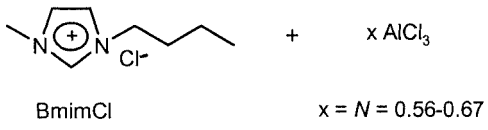


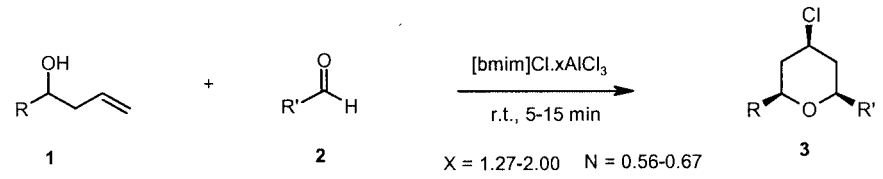
Figure 1. Complexation of $AlCl_3$ with BmimCl

Results and Discussion

In the ever-increasing quest for exploration of newer reactions in chloroaluminate ionic liquids, we report here for the first time on Prins cyclization reactions in ionic liquids. These chloroaluminate ionic liquids have been utilized both as catalyst and as solvent in Prins cyclizations for the rapid synthesis of functionalized tetrahydropyran derivatives.

Treatment of benzaldehyde with 1-phenyl-3-buten-1-ol in the presence of [bmim]Cl·$x$$AlCl_3$ (x = 2 equiv. of $AlCl_3$, N = 0.67) at ambient temperature gave the corresponding 4-chloro-2,4-diphenyltetrahydropyran in 95% yield. Initially, we carried out the Prins cyclization in [bmim]Cl·$AlCl_3$ (N = 0.67). Several reactions with various benzaldehydes gave almost quantitative conversions when the aldehyde, homoallyl alcohol and ionic liquid were used in the molar ratio of 1.0:1.2:0.5, respectively. The Lewis acidic species in such ionic liquids is $Al_2Cl_7^-$, and its concentration in the ionic liquid is a function of the mol fraction (N) of $AlCl_3$. No reactions were observed in the basic

[a] Division of Organic Chemistry, Indian Institute of Chemical Technology,
Hyderabad 500 007, India
Fax: (internat.) + 91-40/27160512
E-mail: yadav@iict.ap.nic.in



Scheme 1

($N < 0.5$) and neutral ($N = 0.5$) ionic liquids, as expected. In ionic liquids of compositions in the range $N = 0.56-0.67$, however, progressive increases in the reaction rates due to the corresponding increases in the concentration of the catalytic species in the liquid were observed. High to quantitative yields and remarkable enhancements in reaction rates were obtained in [bmim]Cl·$AlCl_3$ ($N = 0.67$) ionic liquid (Table 1). Further increases in the mol fraction N of $AlCl_3$ resulted in no significant improvement either in yields or in reaction rates. These results prompted us to explore the use of [bmim]Cl·$AlCl_3$ ($N = 0.67$) ionic liquid for other substrates bearing both electron-rich and electron-deficient substituents on the aromatic ring. Thus, treatment of various homoallyl alcohols with aldehydes produced the corresponding 4-chlorotetrahydropyrans in 85−97% yields (Table 2). The reactions proceeded rapidly at room temperature under mild conditions. The reactions are clean and the products are obtained in excellent yields with high diastereoselectivity. Only a single isomer was obtained in each reaction, its structure being confirmed by ^{1}H NMR and NOE experiments. The assignment of the stereochemistry was based on the coupling constants of the hydrogens at the C^2 and C^4 positions. The coupling constants of the benzylic hydrogens 2-H_c ($\delta = 4.50$ ppm, $J = 11.0$ Hz) and of the hydrogen on the carbon bearing the halide group 4-H_c ($\delta = 4.05$ ppm, $J = 4.5$, 11.0 Hz) in the ^{1}H NMR spectrum showed a structure consistent with two phenyl groups and the halide group being in a *cis* orientation and equatorial position, as shown in Figure 2.

Table 1. Influence of mole fraction (N) of $AlCl_3$ in [bmim]Cl·$x$$AlCl_3$, on the extent of conversion in the reaction of benzaldehyde with 1-phenyl-3-buten-1-ol

N	x	Conversion
0.50	1.00	60
0.56	1.27	79
0.59	1.50	83
0.63	1.75	90
0.67	2.00	95

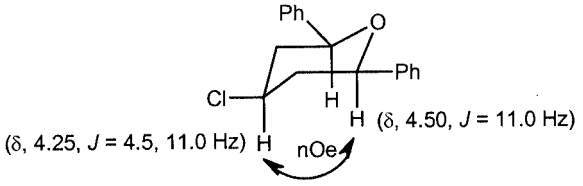
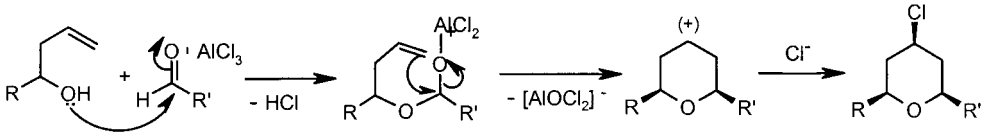


Figure 2. NOE in product **3a**

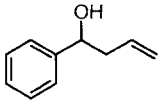
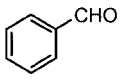
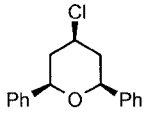
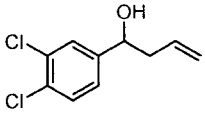
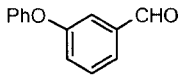
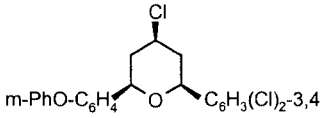
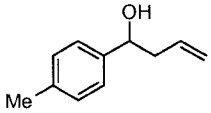
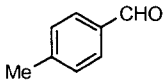
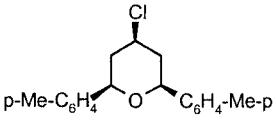
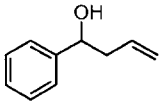
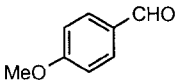
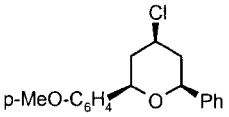
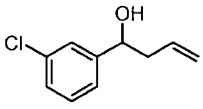
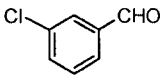
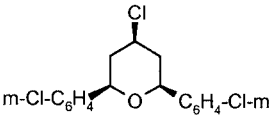
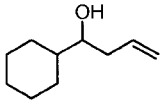
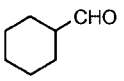
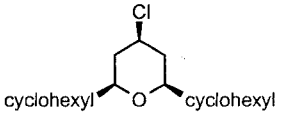
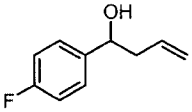
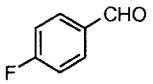
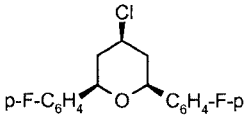
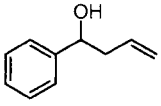
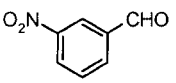
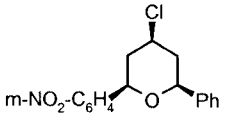
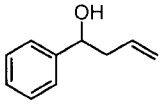
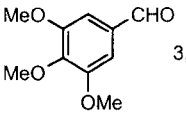
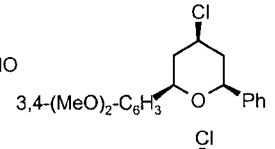
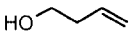
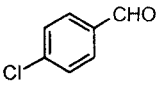
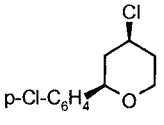
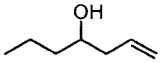
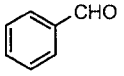
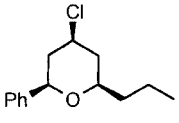
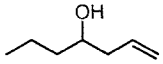
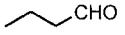
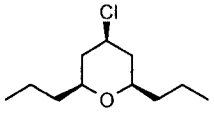
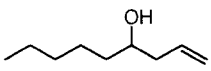
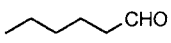
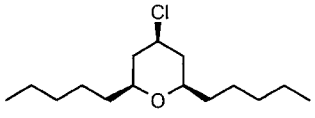
The NOE spectrum of product **3a** indicated that the signal at $\delta = 4.50$ ppm (2-H_c) showed an NOE correlation with the signal at 4.05 (4-H_c). Furthermore, the formation of the products may be explained by hemi-acetal formation and subsequent Prins-type cyclization.

Coupling reactions between aromatic aldehydes and the corresponding homoallylic alcohols in the presence of [bmim]Cl·$AlCl_3$ afforded symmetric 2,6-disubstituted 4-halotetrahydropyrans in high yields. Furthermore, cross-coupling reactions between aromatic homoallyl alcohols and aliphatic aldehydes or between aliphatic homoallyl alcohols and aromatic aldehydes gave the corresponding unsymmetrical chloropyrans. The scope and generality of this process is illustrated with respect to various aldehydes and homoallyl alcohols and the results are summarized in Table 2. The nature of the substituents on the aromatic ring shows some effect on this conversion. It should be noted that aliphatic, simple aromatic and moderately activated aldehydes such as chloro, fluoro and *meta*-phenoxybenzaldehydes gave higher yields of products than strongly activated or deactivated aldehydes. Diverse functional groups (e.g., halogens, methoxy, phenoxy and nitro substituents) were tolerated well under these reaction conditions. To compare the efficiency of [bmim]$AlCl_4$, we also carried out experiments in the ionic liquids [bmim]PF_6, [bmim]BF_4 and [bmim]Cl. However, the reactions did not take place in these ionic liquids in the absence of Lewis acid. The main advantage of the use of chloroaluminate ionic liquids for this transformation is that they are especially inexpensive, easy to prepare on multi-gram scales and easy to handle. Furthermore, they showed significant enhancements in reaction rates and yields. This method is therefore an advanced and attractive strategy for the construction of six-membered chloro-substituted tetrahydropyran systems.



Scheme 2

Table 2. [bmim]$AlCl_4$-promoted synthesis of 4-chloro tetrahydropyrans in ionic liquids

Entry	Allyl alcohol	Aldehyde	Product [a]	Reaction time (min)	Yield [b] (%)
a)				5.0	95
b)				8.0	89
c)				5.0	93
d)				9.0	88
e)				6.0	95
f)				5.0	91
g)				7.0	90
h)				12.0	87
i)				10.0	85
j)				5.0	90
k)				8.0	91
l)				5.0	90
m)				6.0	92

[a] All products were characterized by IR, NMR and mass spectroscopy and the characterization data are consistent with authentic compounds.[3,8] [b] Isolated and unoptimized yields.

Conclusion

The ionic liquid [bmim]Al_2Cl_7 has been shown to be a useful and novel reaction medium for Prins cyclizations, eliminating the need for the use of more volatile chlorinated hydrocarbons such as chloroform or dichloromethane by playing a dual role both as solvent and as Lewis acid catalyst. The substrates show significant increases in reactivity, which reduces the reaction times and improves the yields substantially. The experimental procedure is quite simple and convenient, and the reaction conditions are amenable to scale-up. This method provides easy access to the synthesis of functionalized tetrahydropyrans with diverse chemical structures. This method also showed the reaction rates increasing with corresponding increases in the molar fraction of the $AlCl_3$ in ionic liquid, affording high to quantitative levels of conversion in short reaction times.

Experimental Section

General Remarks: Ionic liquids were prepared as described previously.[17] Preparation of chloroaluminate(iii) ionic liquids: $AlCl_3$ (3 g, 23.1 mmol for X ($AlCl_3$) = 0.52, *mildly acidic ionic liquid*, or 5.6 g, 42 mmol for X ($AlCl_3$) = 0.67, *strongly acidic ionic liquid*) was added slowly over 30 min to 1-butyl-3-methylimidazolium chloride (21 mmol) in a glove box, to afford a clear liquid upon stirring. The round-bottomed flask was sealed with a septum and removed from the glove box.

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 with KBr optics. ^{1}H NMR spectra were recorded on a Gemini 200 spectrometer in $CDCl_3$, with TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyser.

General Procedure: [bmim]Cl·$x$$AlCl_3$ (x = 2.0 equiv., N = 0.67) ionic liquid (2 mL) was added to a mixture of homoallyl alcohol (2 mmol) and aldehyde (2 mmol), and the resulting mixture was stirred for the specified time. After completion of the reaction (as indicated by TLC), the reaction mass was quenched with icecold water and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100−200 mesh, ethyl acetate/hexane, 0.5−9.5) to afford pure 4-chlorotetrahydropyran. The products were characterized by IR and NMR spectroscopy and by their physical constants. The characterization data were found to be consistent with authentic samples.[5−8,18] All the products **3a**−**m** were prepared by the same procedure.

4-Chloro-2,6-diphenyltetrahydro-2*H*-pyran (3a): Liquid (516.8 mg, 95% yield). ^{1}H NMR ($CDCl_3$): δ = 1.90 (dd, J = 11.0, 12.5 Hz, 2 H), 2.45 (dd, J = 4.5, 12.5 Hz, 2 H), 4.25 (tt, J = 2.5, 12.5 Hz, 1 H), 4.50 (dd, J = 4.5, 11.0 Hz, 2 H), 7.2−7.4 (m, 10 H) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$): δ = 44.9, 56.3, 78.7, 126.2, 129.9, 128.7, 142.1. EIMS: m/z = 274 [M+2], 272 [M+], 237, 197, 195, 169, 167, 106, 105, 77. IR (KBr): $\tilde{\nu}$ = 3030, 2960, 2890, 1505, 1460, 1290, 1150, 1030, 760, 690 cm^{-1}. $C_{17}H_{17}ClO$ (272.77): calcd. C 74.86, H 6.28, Cl 13.0; found C 74.90, H 6.30, Cl 13.02.

4-Chloro-2-(3,4-dichlorophenyl)-6-(3-phenoxyphenyl)tetrahydro-2*H*-pyran (3b): Liquid (769 mg, 89% yield). ^{1}H NMR ($CDCl_3$): δ = 1.85 (dd, J = 11.0, 12.6 Hz, 2 H), 2.40 (dd, J = 4.5, 12.6 Hz, 2 H), 4.20 (m, 1 H), 4.45 (dd, J = 4.5, 11.0 Hz, 2 H), 6.85−7.05 (m, 7 H), 7.20−7.40 (m, 5 H). EIMS: m/z = 436 [M+2], 434 [M+], 399, 397, 364, 362, 287, 239, 237, 235, 197, 77. IR (KBr): $\tilde{\nu}$ = 3075, 3050, 2960, 1510, 1455, 1280, 1150, 1025 cm^{-1}. $C_{23}H_{19}Cl_3O_2$ (433.76): calcd. C 63.69, H 4.41, Cl, 24.52; found C 63.70, H 4.43, Cl, 24.56.

4-Chloro-2,6-bis(4-methylphenyl)tetrahydro-2*H*-pyran (3c): Liquid (558 mg, 93% yield).^{1}H NMR ($CDCl_3$): δ = 1.90 (dd, J = 11.0, 12.0 Hz, 2 H), 2.35 (s, 6 H), 2.35 (dd, J = 4.0, 12.0 Hz, 2 H), 4.25 (tt, J = 2.5, 12.0 Hz, 1 H), 4.50 (dd, J = 4.0, 11.0 Hz, 2 H), 7.17 (d, J = 7.8 Hz, 4 H), 7.25 (d, J = 7.8 Hz, 4 H). EIMS: m/z = 302 [M+2], 300 [M+], 287, 285, 265, 250, 119, 92, 91, 77. IR (KBr): $\tilde{\nu}$ = 3040, 2930, 1610, 1515, 1450, 1315, 1160, 1030, 950, 775, 715 cm^{-1}. $C_{19}H_{21}ClO$ (300.82): calcd. C 75.86, H 7.04, Cl, 11.79; found C 75.87, H 7.07, Cl, 11.81.

4-Chloro-2-(4-methoxyphenyl)-6-phenyltetrahydro-2*H*-pyran (3d): Liquid (531.4 mg, 88% yield). ^{1}H NMR ($CDCl_3$): δ = 1.92 (ddd, J = 1.5, 11.0, 12.0 Hz, 2 H), 2.45 (m, 2 H), 3.80 (s, 3 H), 4.30 (m, 1 H), 4.50 (dt, J = 4.0, 11.0 Hz, 2 H), 6.85 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.30 (m, 5 H). EIMS: m/z = 304 [M+2], 302 [M+], 267, 197, 169, 167, 166, 105, 104, 77. IR (KBr): $\tilde{\nu}$ = 3035, 3010, 2950, 1590, 1470, 1420, 1150, 1080, 1050, 830, 760, 695 cm^{-1}. $C_{18}H_{19}ClO_2$ (302.79): calcd. C 71.40, H 6.32, Cl, 11.71; found C 71.42, H 6.35, Cl, 11.73.

4-Chloro-2,6-bis(3-chlorophenyl)tetrahydro-2*H*-pyran (3e): Solid, m.p. 132 °C, (646 mg, 95% yield). ^{1}H NMR ($CDCl_3$): δ = 1.84−1.97 (m, 2 H), 2.43−2.49 (ddd, J = 2.1, 4.2, 12.5 Hz, 2 H), 4.26−4.31 (m, 1 H), 4.53−4.57 (dd, J = 4.0, 11.4 Hz, 2 H), 7.26−7.41 (m, 8 H). EIMS: m/z = 344 [M+2], 342 [M+], 305, 201, 200, 165, 151, 138, 129, 103, 89, 77, 63. IR (KBr): $\tilde{\nu}$ = 3050−2850, 1635, 1590, 1560, 1450, 1410, 1360, 1330, 1180, 1100, 1040, 860, 750, 660 cm^{-1}. $C_{17}H_{15}Cl_3O$ (341.66): calcd. C 59.76, H 4.42, Cl, 31.13; found C 59.78, H 4.45, Cl, 31.15.

4-Chloro-2,6-dicyclohexyltetrahydro-2*H*-pyran (3f): Liquid (517 mg, 91% yield). ^{1}H NMR ($CDCl_3$): δ = 0.90−2.30 (m, 26 H), 2.9 (m, 2 H), 3.9 (tt, 2 H, J = 5.0, 12 Hz). EIMS: m/z = 286 [M+2], 284 [M+], 248, 203, 201, 83, 28. IR (KBr): $\tilde{\nu}$ = 2820, 1150, 1080, 750 cm^{-1}. $C_{17}H_{29}ClO$ (284.86): calcd. C 71.68, H 10.26, Cl 12.45; found C 71.70, H 10.29, Cl 12.47.

4-Chloro-2,6-bis(4-fluorophenyl)tetrahydro-2*H*-pyran (3g): Liquid (550.8 mg, 90% yield). ^{1}H NMR ($CDCl_3$): δ = 1.92 (dd, J = 11.2, 12.5 Hz, 2 H), 2.48 (dd, J = 4.5, 12.5 Hz, 2 H), 4.20 (m, 1 H), 4.45 (dd, J = 4.5, 11.2 Hz, 2 H), 6.85−7.05 (m, 7 H), 7.20−7.40 (m, 5 H). EIMS: m/z = 310 [M+2], 308 [M+], 273, 215, 213, 185, 96, 95. IR (KBr): $\tilde{\nu}$ = 3050, 2920, 2850, 1610, 1515, 1450, 1410, 1350, 1170, 835, 760 cm^{-1}. $C_{17}H_{15}ClF_2O$ (308.75): calcd. C 66.13, H 4.90, Cl 11.48, F 12.31; found C 66.15, H 4.94, Cl 12.33, F 12.34.

4-Chloro-2-(3-nitrophenyl)-6-phenyltetrahydro-2*H*-pyran (3h): Liquid (551.6 mg, 87% yield). ^{1}H NMR ($CDCl_3$): δ = 1.95 (dd, J = 11.2, 12.4 Hz, 2 H), 2.45 (m, 2 H), 4.3 (m, 1 H), 4.60 (ddd, J = 2.0, 6.0, 11.2 Hz, 2 H), 7.35 (m, 5 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.72 (d, J = 7.5 Hz, 1 H), 8.15 (dd, J = 7.5, 2.0 Hz, 1 H), 8.22 (s, 2 H). EIMS: m/z = 319 [[M+2]], 317 [M+], 282, 213, 211, 149, 77. IR (KBr): $\tilde{\nu}$ = 3070, 2930, 1630, 1540, 1125, 1055, 740, 695 cm^{-1}. $C_{17}H_{16}ClNO_3$ (317.77): calcd. C 64.26, H 5.07, Cl 11.16, N 4.41; found C 64.29, H 5.11, Cl 11.17, N 4.43.

4-Chloro-2-(3,4-dimethoxyphenyl)-6-phenyltetrahydro-2*H*-pyran (3i): Solid, m.p. 113 °C, (564.4 mg, 85% yield). ^{1}H NMR ($CDCl_3$): δ = 1.90 (ddd, *J* = 1.5, 11.0, 12.2 Hz, 2 H), 2.42 (m, 2 H), 3.82 (s, 3 H), 3.84 (s, 3 H), 4.24 (m, 1 H), 4.49 (dt, *J* = 1.5, 11.0 Hz, 2 H), 6.78 (d, *J* = 7.5 Hz, 1 H), 6.90 (m, 2 H), 7.30 (m, 5 H). EIMS: *m*/*z* = 334 [M+2], 332 [M+], 297, 229, 228, 227, 105, 104, 77. IR (KBr): ṽ = 3030, 3010, 2950, 2870, 1615, 1590, 1520, 1480, 1430, 1170, 1080, 1050, 755, 690 cm^{-1}. $C_{19}H_{21}ClO_3$ (332.82): calcd. C 68.57, H 6.36, Cl 10.65; found C 68.59, H 6.37, Cl 10.67.

4-Chloro-2-(4-chlorophenyl)tetrahydro-2*H*-pyran (3j): Liquid (414 mg, 90% yield). ^{1}H NMR ($CDCl_3$): δ = 1.80 (m, 1 H), 1.95 (m, 1 H), 2.15 (m, 1 H), 2.35 (m, 1 H), 3.55 (dt, *J* = 4.5, 12.3 Hz, 1 H), 4.0−4.35 (m, 3 H), 7.18−7.40 (m, 4 H) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$): δ = 38.0, 44.2, 56.0, 66.2, 68.2, 127.1, 133.2, 140.4. EIMS: *m*/*z* = 234 [M+2], 232 [M+], 197, 195, 160, 142, 141, 139, 138, 112, 93, 92, 91. IR (KBr): ṽ = 3050, 2960, 2930, 2850, 2730, 1598, 1490, 1450, 1410, 1460, 1250, 1140, 1085, 1025, 825, 760 cm^{-1}. $C_{11}H_{12}Cl_2O$ (231.12): calcd. C 57.17, H 5.23, Cl 30.68; found C 57.2, H 5.25, Cl 30.71.

4-Chloro-2-phenyl-6-propyltetrahydro-2*H*-pyran (3k): Liquid (433.2 mg, 91% yield). ^{1}H NMR ($CDCl_3$): δ = 1.0 (m, 6 H), 1.2−2.3 (m, 18 H), 3.3 (m, 2 H), 4.0 (tt, 1H *J* = 5.0, 12.0 Hz) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$): δ = 14.4, 18.9, 38.3, 42.5, 44.7, 56.2, 77.0, 78.5, 126.0, 127.8, 128.6, 141.9. EIMS: *m*/*z* = 240 [M+2], 238 [M+], 203, 197, 195, 163, 161, 28. IR (KBr): ṽ = 3020, 2980, 1600, 1490, 1142, 1080, 762 cm^{-1}. $C_{14}H_{19}ClO$ (238.75): calcd. C 70.43, H 8.02, Cl 14.85; found C 70.41, H 8.05, Cl 14.87.

4-Chloro-2,6-dipropyltetrahydro-2*H*-pyran (3l): Liquid (367.2 mg, 90% yield). ^{1}H NMR ($CDCl_3$): δ = 0.6−2.3 (m, 18 H), 3.3 (m, 2 H), 4.0 (tt, *J* = 5.0, 12.0 Hz, 1 H) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$): δ = 13.9, 18.7, 37.9, 42.7, 56.0, 76.2. EIMS: *m*/*z* = 206 [M+2], 204 [M+], 169, 161. IR (KBr): ṽ = 2830, 1140, 1080, 760 cm^{-1}. $C_{11}H_{21}ClO$ (204.73): calcd. C 64.53, H 10.34, Cl 17.32; found C 64.52, H 10.37, Cl 17.35.

4-Chloro-2,6-dipentyltetrahydro-2*H*-pyran (3m): Liquid (478.4 mg, 92% yield). ^{1}H NMR ($CDCl_3$): δ = 1.0 (t, *J* = 6.9 Hz, 6 H), 1.2−2.3 (m, 20 H), 3.2 (m, 2 H), 4.0 (tt, *J* = 5.0, 12.0 Hz, 1 H) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$): δ = 14.0, 21.5, 25.6, 30.0, 36.2, 42.7, 56.1, 76.5. EIMS: *m*/*z* = 262 [M+2], 260 [M+], 227, 189. IR (KBr): ṽ = 2820, 1140, 1080, 760 cm^{-1}. $C_{15}H_{29}ClO$ (260.84): calcd. C 69.07, H 11.21, Cl, 13.58; found C 69.07, H 11.23, Cl, 13.60.

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