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Synthesis of Amino Chalcones in Presence of Ionic Liquid as Soluble Support

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A microwave-assisted liquid phase synthesis of aminochalcones was developed by using aldehyde-functionalized ionic liquid as soluble support. Ionic liquid bound aminoacetophenone was treated with aromatic aldehyde to give supported chalcone derivatives. After cleavage, the target compounds were obtained in 83-92 % yields and ≥ 95 % purities without column chromatographic purification. The recovered aldehyde-functionalized ionic liquid could be reused for several times without affecting its activity and the yields of desired compounds were between 86-89 %. These results indicated that the presented method could be applied efficiently to the liquid phase combinatorial chemistry based on aldol condensation.

Key Words: Functionalized ionic liquid, Support, Amino chalcones, Aldol condensation, Liquid phase synthesis.

INTRODUCTION

Combinatorial chemistry is now widely used to generate vast libraries of compounds for the screening of functionalized molecules. Solid phase organic synthesis plays an important role in combinatorial chemistry due to its advantages such as the use of excess reagents and easy isolation of products[1-7]. Despite its great success, solid phase synthesis still exhibits several shortcomings such as the nature of heterogeneous reaction and low loading capacity of the supports. Therefore, soluble supports such as soluble polymers[8-10] and fluorous phase tags[11-15] have been employed to achieve homogeneous reactions. Unfortunately, there is a main limitation about the use of soluble polymer supports, namely, low loading capacity. And the expense of perfluoroalkane solvents, limitation in solvent selection and the need for specialized reagents may limit general applications of the fluorous phase tags chemistry. More recently, it was found that functionalized ionic liquids might be more compatible soluble supports comparing with soluble polymers and fluorous phase tags[16,17].

Functionalized ionic liquids have been successfully introduced as soluble supports in liquid-phase organic synthesis[18-25]. We also reported the synthesis of 4*H*-pyran derivatives, dihydropyridones derivatives and amino aryl ether derivatives using functionalized ionic liquids as soluble supports[26-29]. It has the advantages of the nature of homogeneous reaction, high loading capacity, wide range of solvents, simple monitoring technology and low cost. In addition, microwave-assisted reactions have become an established tool in organic synthesis[30-32]. Owing to the high polarity of ionic liquids, organic synthesis involving ionic liquids are readily accelerated by microwave irradiation[33,34]. We report herein the microwave-assisted efficient liquid phase synthesis of amino chalcones with aldehyde-functionalized ionic liquid as a soluble support.

Generally, there will be more by-products with imine between the reaction of amino acetophenone and aromatic aldehyde owing amino activity[35]. Therefore according to liquid phase synthesis technology, amino chalcone derivatives were synthesized by using aldehyde-functionalized ionic liquid as a soluble support and imine as linker. Here, we report our results about the application of aldehyde-functionalized ionic liquid as soluble support in the liquid phase synthesis of amino chalcone derivatives (Fig. 1).

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer with TMS as an internal. ESI-MS spectra were recorded on a Micromass LCT KC317 spectrometer. GC-MS spectra were recorded on an Agilent 6890 instrument equipped with Agilent 5973 mass selective detector. FT-IR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer (KBr pellet). HPLC spectra were recorded on HP 1100 high pressure liquid chromatographic instrument. Melting points were determined on a BÜCHI B-540 apparatus and were uncorrected. Reagents (AR Grade) were purchased from

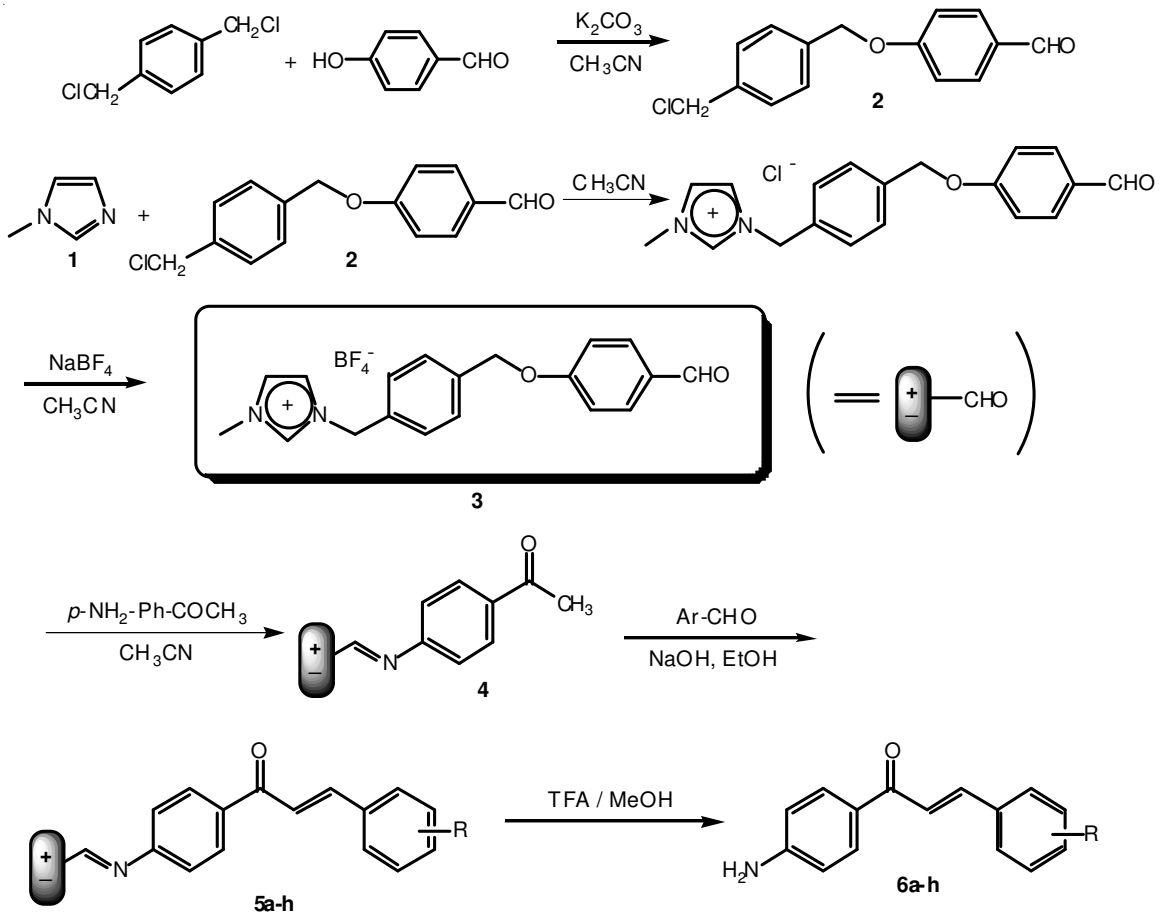

Fig. 1. Synthesis of amino chalcone derivatives using [fmmim][BF_4] as soluble support

commercial resource and used without further purification. All final products **6a-h** are known compounds. Their physical and spectroscopic data were compared with those reported in the literatures and found to be identical.

Synthesis of 1-[4-(*p*-formylphenoxy methylene)benzyl]-3-methylimidazolium tetrafluoroborate (3): A flame-dried flask with a reflux condenser was charged with *p*-xylene dichloride (6.96 g, 40 mmol) and potassium carbonate (3.31 g, 24 mmol) in acetonitrile and then the mixture of *p*-hydroxybenzaldehyde (2.44 g, 20 mmol) and acetonitrile was dropped and refluxed. On completion of the reaction (monitored by TLC), the reaction mixture was separated *via* filtration. The residue was evaporated *in vacuo* and the intermediate **2** was obtained by column chromatography (3.96 g, 76 % yield). The yellow fluid aldehyde-functionalized ionic liquid **3**, 1-[4-(*p*-formylphenoxy methylene) benzyl]-3-methylimidazolium tetrafluoroborate (abbreviated as [fmmim][BF_4]), was obtained in high yield (87 %) by reacting intermediate **2** (2.61 g, 10 mmol) with 1.5-fold excess of 1-methylimidazole **1** (1.23 g, 15 mmol) followed by standard anion metathesis and isolated by acetonitrile.

Grafted IL-bound *p*-aminoacetophenone intermediate (4): The [fmmim][BF_4] (3.94 g, 10 mmol) reacted with *p*-amino acetophenone (2.03 g, 15 mmol) in absolute acetonitrile assisted with microwave radiation for 12 min to yield IL-supported substrate **4**. The isolation procedures for it involved cooling, evaporation and a simple extraction of the excess reagent with dichloromethane. The IL-bound *p*-amino acetophenone **4** was then obtained in 85 % yield.

General procedure for product cleavage: To a solution of IL-bound *p*-amino acetophenone **4** (2.56 g, 5.0 mmol) and aromatic aldehydes (7.5 mmol) in ethanol (10 mL) was added NaOH (0.20 g, 5.0 mmol). The mixture was then refluxed for 5-10 min under microwave irradiation. After filtration and evaporation, the residue was washed with ethyl ether (30 mL × 2 mL), dichloromethane (30 mL × 2 mL) and some water to give **5a-h**. To a solution of as-synthesized **5a-h** in methanol (10 mL) was added trifluoroacetic acid (2 mL). The mixture was stirred for 2-3 h at room temperature. Upon completion, methanol was removed by rotary evaporation and the residue was neutralized with saturated aqueous NaOH. The aqueous phase was extracted with chloroform (10 mL × 2 mL) and the organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to afford the products **6a-e**.

RESULTS AND DISCUSSION

Our starting point was to prepare aldehyde-functionalized ionic liquid **3**, 1-[4-(*p*-formylphenoxy methylene)benzyl]-3-methylimidazolium tetrafluoroborate (abbreviated as [fmmim][BF_4]), from the commercially available 1-methylimidazole **1**. Intermediate **2** was prepared *via* *p*-hydroxybenzaldehyde and 2-fold excess of *p*-xylene dichloride in acetonitrile catalyzed by potassium carbonate. And then intermediate **2** was reacted with 1.5-fold excess of 1-methylimidazole **1** to generate the corresponding imidazolium cation. The solid [fmmim][Cl] was treated through standard

anion metathesis and isolated by acetonitrile, affording yellow fluid [fmmim][BF_4] **3** in high yield (87 %). Selected spectral data of **3** ([fmmim][BF_4]): ^{1}H NMR (500 MHz, D_2O) δ: 3.73 (s, 3H), 4.89 (s, 2H), 5.24 (s, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 7.29-7.30 (m, 6H), 7.52 (d, *J* = 8.8 Hz, 2H), 9.43 (s, 1H); IR (KBr, ν_{max}, cm^{-1}): 3392, 3111, 1681, 1599, 1575, 1509, 1233, 1162, 1082; ESIMS m/z: 307.1 $[M]^+$.

To further evaluate its efficiency in parallel synthesis, [fmmim][BF_4] was utilized in the construction of a small library of amino chalcones. Subsequent transformation of **3** into **4** was performed in one-pot fashion under microwave. The [fmmim][BF_4] reacted with excess *p*-amino acetophenone in absolute acetonitrile to yield IL-supported substrate **4**. The isolation procedures for it involved cooling, evaporation and a simple extraction of the excess reagent with dichloromethane to afford the IL-bound *p*-amino acetophenone **4** in 85 % yield. Spectral data of intermediate **4**: ^{1}H NMR (500 MHz, methanol-d_4) δ: 2.58 (s, 3H), 3.65 (s, 3H), 5.02 (s, 2H), 5.24 (s, 2H), 6.90-7.61 (m, 8H), 6.87-6.89 (m, 2H), 7.36 (s, 1H), 7.48-7.91 (m, 4H), 8.41 (s, 1H); IR (KBr, ν_{max}, cm^{-1}): 1804, 1782, 1625, 1546, 1439, 1360, 1318, 1254, 1183, 1061; ESIMS m/z: 424.2 $[M]^+$.

The next step was the formation of amino chalcones grafted on ionic liquid **5a-h** *via* aldol condensation. And microwave heating was also used in the transition of **4** to **5a-h**. IL-Bound *p*-aminoacetophenone **4** was reacted with different aromatic aldehydes in ethanol in the presence of NaOH under microwave irradiation for 5-10 min. A 1.5-fold excess of aromatic aldehyde relative to **4** was adapted. HPLC analysis was used to monitor the transformations. After the reaction was completed, the product remained covalently bounded to the support and could be easily purified by extraction with ethyl ether, dichloromethane and some water. Following solvent washes, immobilized IL-bound **5a-h** were then subjected to cleavage of aldehyde-functionalized ionic liquid [fmmim][BF_4] with trifluoro acetic acid (TFA) in methanol for 2-3 h at room temperature to provide the desired compounds **6a-h** in 83-92 % yield based on the loading of **4**.

The isolation procedures of products **6a-h** involved neutralization, extraction of the excess reagent with chloroform and evaporation. Each crude product was then characterized by IR, GC-MS, ^{1}H NMR and gave 95-98 % in purity without further column chromatographic purification (Table-1).

From Table-1, the yields of target compounds changed with the substituent group on the aromatic ring. It was observed that electron-withdrawing group could raise the yield of target compounds and the electron-donating group could reduce the yield of target compounds.

4'-Amino chalcone (6a): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.35 (s, 2H), 6.32 (d, *J* = 15.2 Hz, 1H), 6.46-6.56 (m, 2H), 6.64 (d, *J* = 15.2 Hz, 1H), 7.54 (t, *J* = 6.0 Hz, 3H) , 7.58-7.67 (m, 2H), 7.71-7.81 (m, 2H); IR (KBr, ν_{max}, cm^{-1}): 3341, 3198 (NH_2), 3041 (Ar-H), 1675 (C=O), 1651 (Ar-C=C), 1600, 1572, 1560 (C=C); EIMS m/z: 223, 195, 120, 103, 92, 77, 65.

4-Chloro-4'-amino chalcone (6b): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.28 (s, 2H), 6.33 (d, *J* = 14.8 Hz, 1H), 6.47-6.57 (m, 2H), 6.60 (d, *J* = 14.8 Hz, 1H), 7.53-7.67 (m, 2H), 7.68-7.83 (m, 2H), 7.83-7.93 (m, 2H); IR (KBr, ν_{max}, cm^{-1}): 3446, 3328 (NH_2), 3210 (Ar-H), 1645 (C=O), 1632 (Ar-C=C), 1603, 1578, 1510 (C=C); EIMS m/z: 257, 229, 193, 165, 120, 102, 92, 75, 65.

4-Methyl-4'-amino chalcone (6c): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.46 (s, 3H), 5.33 (s, 2H) , 6.35 (d, *J* = 15.6 Hz, 1H), 6.48-6.54 (m, 2H), 6.67(d, *J* = 15.6 Hz, 1H), 7.45-7.61 (m, 4H), 7.66-7.80 (m, 2H); IR (KBr, ν_{max}, cm^{-1}): 3462, 3340 (NH_2), 3235 (Ar-H), 1652 (C=O), 1624 (Ar-C=C), 1608, 1579, 1567 (C=C); EIMS m/z: 237, 222, 209, 194, 165, 145, 120, 92, 77, 65.

4-Methoxy-4'-amino chalcone (6d): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.87 (s, 3H), 5.33 (s, 2H), 6.32 (d, *J* = 14.8 Hz, 1H), 6.49-6.58 (m, 2H), 6.65 (d, *J* = 14.8 Hz, 1H), 7.14-7.28 (m, 2H), 7.54-7.69 (m, 2H), 7.77-7.91 (m, 2H); IR (KBr, ν_{max}, cm^{-1}): 3461, 3352 (NH_2), 3233 (Ar-H), 1678 (C=O), 1652 (Ar-C=C), 1628, 1602, 1518 (C=C); EIMS m/z: 253, 238, 210, 145, 120, 92, 77, 65.

3-Nitro-4'-amino chalcone (6e): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.24 (s, 2H), 6.41 (d, *J* = 15.2 Hz, 1H), 6.43-6.58 (m, 3H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.50-7.63 (m, 1H), 7.84 (s, 1H), 8.11 (s, 1H), 8.31 (s, 1H), 8.52 (s, 1H); IR (KBr, ν_{max}, cm^{-1}): 3422, 3325 (NH_2), 3218 (Ar-H), 1655 (C=O), 1630 (Ar-C=C), 1602, 1550, 1526 (C=C); EIMS m/z: 268, 240, 193, 178, 165, 152, 120, 92, 76, 65.

3-Cyano-4'-amino chalcone (6f): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.27 (s, 2H), 6.32 (d, *J* = 15.6 Hz, 1H), 6.44-6.58 (m, 2H), 6.64 (d, *J* = 15.6 Hz, 1H), 7.52-7.66 (m, 2H), 7.78 (s, 1H), 8.02-8.08 (m, 2H), 8.17 (s, 1H); IR (KBr, ν_{max}, cm^{-1}): 3422, 3337 (NH_2), 3212 (Ar-H), 1653 (C=O), 1630 (Ar-C=C), 1600, 1572, 1512 (C=C); EIMS m/z: 248, 220, 120, 92, 65.

3-Bromo-4'-amino chalcone (6g): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.59 (s, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* =7.9 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 15.5 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 8.03 (s, 1H); IR (KBr, ν_{max}, cm^{-1}): 3422, 3334 (NH_2), 3208 (Ar-H), 1651 (C=O), 1626 (Ar-C=C), 1600, 1578,

TABLE-1
LIQUID PHASE PARALLEL SYNTHESIS OF AMINOCHALCONES USING [fmmim][BF_4] AS SUPPORT

Entry	Product	R	Yield[a] (%)	Purity[b] (%)	m.p. (ºC, Obs.)	m.p. (ºC, Lit.)
1	**6a**	H	87	97	103-104	105-106[36]
2	**6b**	4-Cl	91	98	190-191	193-195[37]
3	**6c**	4-CH_3	85	95	181-182	179-180[38]
4	**6d**	4-OCH_3	86	96	149-150	148-150[38]
5	**6e**	3-NO_2	92	98	214-215	212-214[38]
6	**6f**	3-CN	92	98	231-232	231-233[38]
7	**6g**	3-Br	90	98	186-187	186-187[39]
8	**6h**	4-$N(CH_3)_2$	83	95	189-190	187-188[40]

[a]Isolated yields based on loading of **4**. [b]Determinated by HPLC.

1557 (C=C); EIMS m/z: 303, 302, 301, 275, 273, 222, 146, 120, 92.

4-Dimethylamino-4'-amino chalcone (6h): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.06 (s, 6H), 5.33 (s, 2H), 6.35 (d, *J* = 14.8 Hz, 1H), 6.46-6.54 (m, 2H), 6.67 (d, *J* = 14.8 Hz, 1H), 6.84-6.98 (m, 2H), 7.47-7.61 (m, 2H), 7.71-7.85 (m, 2H); IR (KBr, ν_{max}, cm^{-1}): 3410, 3338 (NH_2), 3221 (Ar-H), 1652 (C=O), 1603 (Ar-C=C), 1566, 1548, 1528 (C=C); EIMS m/z: 266, 265, 120, 92, 77, 65.

In the preparation IL-bound products **5a-h** *via* IL-supported substrate **4** and aromatic aldehyde, catalytic activity of different catalysts was studied, such as pyridine, piperidine, sodium methoxide and sodium hydroxide. For example the preparation of **6a**, the results were shown in Table-2. It was shown that alkalinity was very important to the synhesis of amino chalcone. As the enhancing of the catalyst alkalinity, the yield of target compound was raised. In consideration of economy, sodium hydroxide was used as the base catalyst in this reaction.

TABLE-2
INFLUENCING ON THE PREPARATION OF 4'-AMINOCHALCONE (**6a**) BY DIFFERENT CATALYSTS

Entry	Catalysts	Yield of 4'-aminochalcone (**6a**) (%)
1	Pyridine	0
2	Piperidine	10
3	Sodium methoxide	88
4	Sodium hydroxide	87

At the same time, molar ratio of **4** to different aromatic aldehyde was investigated in the preparation IL-bound products **5a-h**. Take the preparation of **6a** for example, the results were shown in Table-3. It was shown that the yield of 4'-amino chalcone (**6a**) was increasing with the amount aromatic aldehyde, the appropriate molar ratio of **4** to aromatic aldehyde was 1.0:1.5 in the reactions.

TABLE-3
INFLUENCING ON THE PREPARATION OF 4'-AMINOCHALCONE (**6a**) BY DIFFERENT MOLAR RATIO

Entry	Molar ratio of **4** to benzaldehyde	Yield of 4'-aminochalcone (**6a**) (%)
1	1: 1.0	10
2	1: 1.2	50
3	1: 1.3	75
4	1: 1.5	87
5	1: 1.8	87
6	1: 2.0	87

Meanwhile, in order to demonstrate the repeatability of the aldehyde-functionalized ionic liquid [fmmim][BF_4] **3**, the recycle of soluble support [fmmim][BF_4] **3** was also investigated by using the preparation of **6a** as a model. To recover the aldehyde-functionalized ionic liquid [fmmim][BF_4], the residue after neutralization and extraction was washed twice with dichloromethane and then acetone was added. The precipitate CF_3COONa was removed and the filtrate was concentrated *in vacuo* to give regenerated soluble support **3** ([fmmim][BF_4]). Then the IL-bound *p*-amino acetophenone **4** was synthesized in the same way as described previously using recovered [fmmim][BF_4] and applied in the next step. The yield of **6a** maintained at 86-89 % in the first 6 cycles (Table-4). It demonstrated that the recovered aldehyde-functionalized ionic liquid [fmmim][BF_4] could be reused for several times without affecting its activity.

TABLE-4
RECYCLABILITY OF THE ALDEHYDE-FUNCTIONALIZED IONIC LIQUID [fmmim][BF_4]

Entry	Reaction cycles (times)	Recovered yield of **3** (%)	Loading of **4** (%)	Yield of **6a** (%)
1	1	96	85	87
2	2	96	86	89
3	3	95	84	88
4	4	95	85	86
5	5	95	84	87
6	6	95	84	86

Conclusion

In summary, we report herein the synthesis of an aldehyde-functionalized ionic liquids 1-[4-(*p*-formylphenoxy methylene)-benzyl]-3-methylimidazolium tetrafluoroborate (abbreviated as [fmmim][BF_4]) and the regioselective synthesis of 8 amino chalcone derivatives with 83-92 % yields and ≥ 95 % purity through aldol condensation using [fmmim][BF_4] as a soluble support. Every product was identified by ^{1}H NMR, IR and MS. The support could be recovered by simple work-up after removal of product, CF_3COONa, H_2O and solvents. The results of recycle experiments showed that the recovered functionalized ionic liquid could be reused at least 6 times without affecting the yields of desired compound which was fluctuated between 86-89 %. These results indicated that the presented method could be applied efficiently in the liquid phase combinatorial chemistry based on aldol condensation. It offers considerable advantages: the reaction in homogeneous solution, higher loading capacity to lower molecular weight of functionalized ionic liquid and the simple after-treatment. This strategy has advantages including ready product isolation and reusability of the ionic liquid support.

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REFERENCES

1. L.A. Thompson and J.A. Ellman, *Chem. Rev*., **96**, 555 (1996).
2. K.S. Lam, M. Lebl and V. Krchnák, *Chem. Rev*., **97**, 411 (1997).
3. A. Nefzi, J.M. Ostresh and R.A. Houghten, *Chem. Rev*., **97**, 449 (1997).
4. M.C. Pirrung, *Chem. Rev*., **97**, 473 (1997).
5. H. An and P.D. Cook, *Chem. Rev*., **100**, 3311 (2000).
6. D.B. Kassel, *Chem. Rev*., **101**, 255 (2001).
7. D.A. Horton, G.T. Bourne and M.L. Smythe, *Chem. Rev*., **103**, 893 (2003).
8. D.J. Gravert and K.D. Janda, *Chem. Rev*., **97**, 489 (1997).
9. P. Wentworth Jr. and K.D. Janda, *Chem. Commun*., 1917 (1999).
10. P.H. Toy and K.D. Janda, *Acc. Chem. Res*., **33**, 546 (2000).
11. B. Cornils, *Angew. Chem. Int. Ed*., **36**, 2057 (1997).
12. D.P. Curran, *Angew. Chem. Int. Ed*., **37**, 1174 (1998).
13. I.T. Horváth, *Acc. Chem. Res*., **31**, 641 (1998).
14. A. Studer and D.P. Curran, *Tetrahedron*, **53**, 6681 (1997).

15. D.M. Lemal, *J. Org. Chem*., **69**, 1 (2004).
16. J.H. Davis Jr., *Chem. Lett*., **33**, 1072 (2004).
17. W. Miao and T.H. Chan, *Acc. Chem. Res*., **39**, 897 (2006).
18. J. Fraga-Dubreuil and J.P. Bazureau, *Tetrahedron Lett*., **42**, 6097 (2001).
19. J. Fraga-Dubreuil and J.P. Bazureau, *Tetrahedron*, **59**, 6121 (2003).
20. W. Miao and T.H. Chan, *Org. Lett*., **5**, 5003 (2003).
21. S. Anjaiah, S. Chandrasekhar and R. Grée, *Tetrahedron Lett*., **45**, 569 (2004).
22. M. de Kort, A.W. Tuin, S. Kuiper, H.S. Overkleeft, G.A. van der Marelb and R.C. Buijsmana, *Tetrahedron Lett*., **45**, 2171 (2004).
23. H. Hakkou, J.J.V. Eynde, J. Hamelina and J.P. Bazureau, *Tetrahedron*, **60**, 3745 (2004).
24. H. Hakkou, J.J.V. Eynde, J. Hamelina and J.P. Bazureau, *Synthesis*, 1793 (2004).
25. J.Y. Huang, M. Lei and Y.G. Wang, *Tetrahedron Lett*., **47**, 3047 (2006).
26. F.P. Yi, Y.Q. Peng and G.H. Song, *Tetrahedron Lett*., **46**, 3931 (2005).
27. F.P. Yi, Y.Q. Peng and G.H. Song, *Acta Chim. Sin.*, **64**, 1145 (2006) in Chinese.
28. Y.Q. Peng, F.P. Yi and G.H. Song and Y. Zhang, *Monatsh Chem*., **136**, 1751 (2005).
29. F.P. Yi, H.Y. Sun and X.H. Pan, *Acta Chim. Sin.*, **67**, 1237 (2009) in Chinese.
30. M. Larhed, C. Moberg and A. Hallberg, *Acc. Chem. Res*., **35**, 717 (2002).
31. B. Wathey, J. Tiemey, P. Lidstrom and J. Westman, *Drug Discov. Today*, **7**, 373 (2002).
32. A. Lew, P.O. Krutzik, M.E. Hart and A.R. Chamberlin, *J. Comb. Chem*., **4**, 95 (2002).
33. M. Deetlefs and K.R. Seddon, *Green Chem*., **5**, 181 (2003).
34. J. Hoffmann, M. Nüchter, B. Ondruschka and P. Wasserscheid, *Green Chem*., **5**, 296 (2003).
35. A. Frentes, J.M. Marinas and J.V. Sinisterra, *Tetrahedron Lett*., **28**, 4541 (1987).
36. D.H. Marrian, P.B. Russell and A.R. Todd, *J. Chem. Soc*., 1419 (1947).
37. M.R. Mahmoud, A.Y. Soliman and H.M. Bakeer, *Indian J. Chem*., **29B**, 830 (1990).
38. M. Dzurilla and P. Kristian, *Collect Czech. Chem. Commun*., **35**, 417 (1970).
39. F.P. Yi, Y.Q. Peng and G.H. Song, *J. Chem. Res*., **5**, 311 (2005).
40. K. Nakaya, K. Funabidi and K. Shibata, *Bull. Chem. Soc. (Japan)*, **69**, 2961 (1996).