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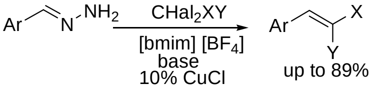

X=F, Cl, Br; Y=Cl, Br, CF$_3$, CO$_2$Et

- -CuCl immobilized in ionic liquid
- -RT
- -no catalyst leaching
- -no loss of catalyst efficiency
- -no contamination of the environment

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ABSTRACT

It was demonstrated that ionic liquids are superb recyclable media for copper catalyzed reactions using catalytic olefination reaction as an example. As a result a novel green access to the halogenoalkenes was elaborated. Possibility to perform up to 5 reaction cycles without catalyst leaching and decreasing of the yield was demonstrated. A number of various ionic liquids was screened and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim] [BF_4]) was found the solvent with highest efficiency. Mild conditions, high atom economy comparing to other known methods, low amounts of wastes and possibility to recover ionic liquid are the advantages of the proposed method.

1. Introduction

Transition metal catalyzed transformations are of increasing importance in modern organic chemistry, having numerous applications in both academia and industry.[1] The importance of such transformations has been well acknowledged by several Nobel prizes obtained during last decade (2010 Richard F. Heck, Ei-ichi Negishi and Akira Suzuki "for palladium-catalyzed cross couplings in organic synthesis"; 2005 Yves Chauvin, Robert H. Grubbs and Richard R. Schrock "for the development of the metathesis method in organic synthesis"; 2001 William S. Knowles and Ryoji Noyori "for their work on chirally catalyzed hydrogenation reactions", K. Barry Sharpless "for his work on chirally catalyzed oxidation reactions"). High universality, chemo-, regio- and stereoselectivity are distinct advantages of these transformations. On the other hand there are some difficulties, restricting more wide industrial use of transition metals catalyzed transformations. First one is a quite high price of most effective noble metals (Pt, Pd, Ir, Rh) as well as some ligands (e.g. phosphorous derivatives), therefore repeatable use of catalysts is highly desirable. In addition the toxicity of these compounds can not be ignored and demands special precautions to prevent or eliminate contamination of reaction products as well as the environment.

Both points lead to noticeable increase in the final price of the products and decrease efficiency, which obstruct industrial applications of such catalysts. Recycling and reusing of the catalyst is a possible solution and efforts have been taken to elaborate corresponding techniques. There are only a few recyclable homogeneous catalysts reported, which can be settle down and recycled by interphase,[2] clathrate-enabled,[3] silyl[4]- or fluorous-tagged,[5] redox,[6] photo[7] and phase-switchable[8] techniques. Switching from homogeneous catalysis mode to heterogeneous catalysis mode (immobilization of catalyst on solid support) is more open to the possibility of repeatable use of catalysts. However, very often immobilized catalyst show lower catalytic efficiencies due to the higher diffusion limit, reduced dispersion degree and unmatchable chemical microenvironment of the active sites.[9] Also many reactions lead to leaching of catalyst even when metals are immobilized on inert surface.

A promising strategy for many catalytic reactions is the application of ionic liquids as a reaction media. Ionic liquids have been shown as a valuable immobilizing media for transition metal catalyst, allowing several repeated reaction cycles without significant decreasing of catalytic activity and catalyst leaching. Another benefit of this strategy is a possibility to recycle transition metal catalyst and prevent both the reaction product and the environment from heavy metal contamination.[10] Due to their low volatility, immiscibility with non-polar organic

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solvents, stability and possibility to be easily recovered ionic liquids (ILs) are very attractive replacement to conventional solvents especially for use in green reactions.[11,12]

Halogenated alkenes are versatile reagents in organic synthesis, which is used for synthesis of various alkenes, alkynes, derivatives of carboxylic acids, carbo- and heterocyclic compounds.[13] In 1999 a novel catalytic olefination reaction (COR) was elaborated in our laboratory. COR is a transformation of *N*-unsubstituted hydrazones into alkenes under treatment with polyhalogenated alkanes (PHAs) in the presence of a base and catalytic amounts of copper salts (Figure 1). Having a wide synthetic scope, the reaction allows to synthesize both alkyl and aryl substituted alkenes, including fluorinated ones and derivatives with functional groups.[14] Simple experimental procedure, which does not require using of organometallics or toxic organophosphorus compounds, affordable price and availability of starting materials, high yields and stereoselectivity are distinct advantages of the reaction. Because of application of hydrazine derivatives is necessary for COR, copper forms soluble complexes. We attempted to use heterogeneous copper catalysts, however highly aggressive leaching of copper has been observed to lead to significant loss of catalyst effectiveness even after first cycle.[15] Therefore, COR is one of the most difficult reaction in terms of control of catalyst leaching and its multiple use.

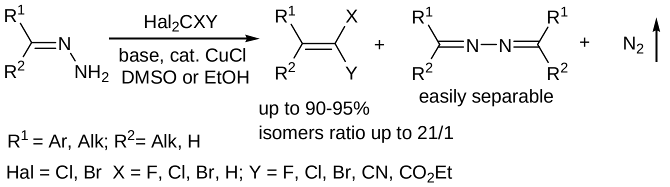


Figure 1. Catalytic olefination reaction (COR).

With green applications of COR in mind, we decided to examine various ILs as a reusable reaction media for the reaction. Here we would like to report a novel green approach towards alkenes based on COR in ILs.

2. Results and discussion

To start our investigation several ILs were tested as solvents for COR. Hydrazone of 4-chlorobenzaldehyde **1a** and $CBrCl_3$ were used as a model system for catalytic olefination (10% of CuCl). It was found that reaction of **1a** with $CBrCl_3$ in ILs leads to target dichloroalkene **2a** in good to high yields (Figure 2). Imidazolium as well as pyrrolidinium ILs show comparable results to give target alkene **2a** in high yields. We tried to track influence of reaction efficiency (yield of model product in multiple runs) from nature of ionic liquids. Several parameters of ionic liquids (nature of cation and anion, dielectric constants, viscosity, electrolytic conductivity, hydrophobicity[16]) were analysed. However, the reaction is appeared to be most sensitive to the anion nature and hydrophobicity of IL as its function. Thus, the yields of alkene **2a** are lower in case of extremely lipophilic (hydrophobic) tris(pentafluoroethyl)trifluorophosphate anion ($P(C_2F_5)_3F_3^-$), never downing lower 40-50% however. The other anions (BF_4^-, $CF_3SO_3^-$, $B(CN)_4^-$, PF_6^-, $CF_3CO_2^-$, $CH_3OSO_3^-$, $(CF_3SO_2)_2N^-$) show yields up to 80% in first run and average yields around 70% for 3-5 runs. Possible explanation can be contributed to the delicate balance of hydrophilic and lipophilic properties of the ILs. The most lipophilic ionic liquids, **IL2** and **IL3,** can not dissolve aqueous ammonia (using as a base), which lead to formation of water-IL two phase system to give lower yields. In contrast, being mixed with aqueous ammonia, most hydrophilic **IL1** lost its ability to dissolve effectively hydrazone **1a**, which also lead to decreasing of the yields. Recently it was demonstrated that water can form complex aggregates with some ILs to change significantly properties of the solvent.[17]

High yields were also obtained then reactions were performed in repeated manner. In some case up to 5 runs were carried out with no significant decrease in the yields. The best results were obtained for ionic liquids IL **6-8, 10, 11**. Among those 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim] [BF_4]) **IL10** showed almost no decrease of the yield and was chosen as a reaction media for further investigations (Figure 2).

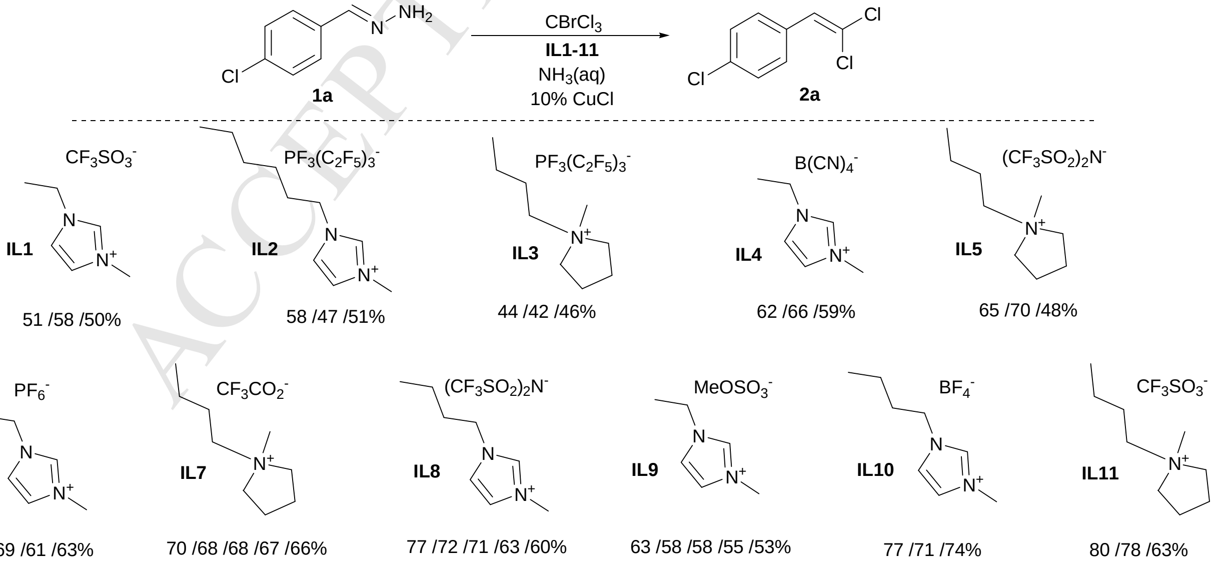
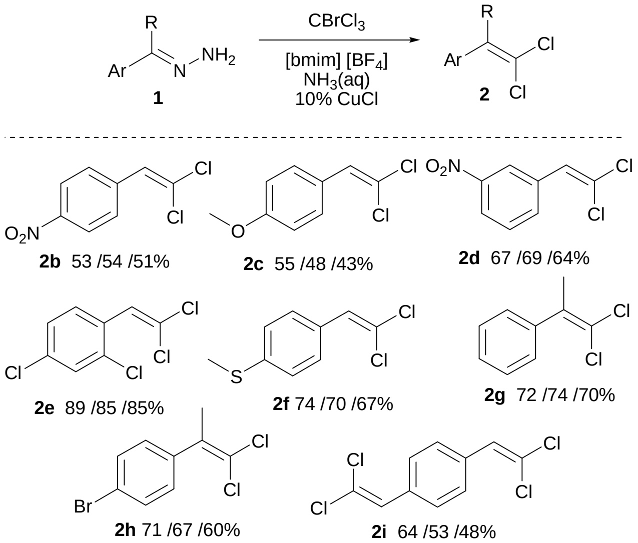


Figure 2. COR of hydrazone **1a** with $CBrCl_3$ in **ILs 1-11**.

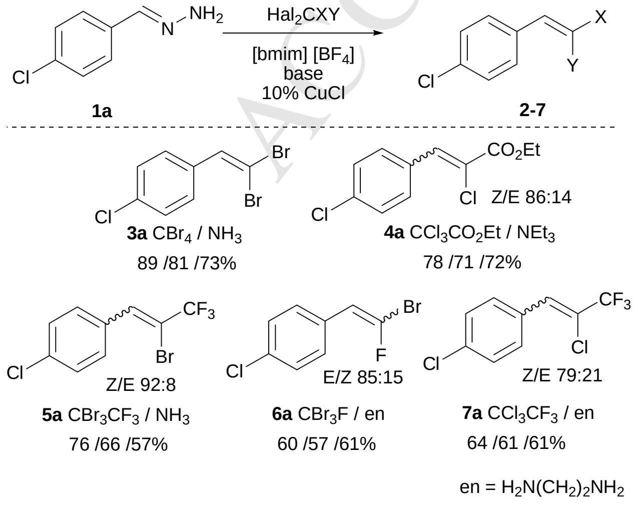
To investigate the synthetic scope of the method, we performed the reaction of various hydrazones with $CBrCl_3$ in **IL10** as a solvent. The corresponding dichloroalkenes with both electron-withdrawing and electron-donating substituents were prepared in good yields. Diene **2i** was also synthesized from bis-hydrazone of terephthalic aldehyde. Hydrazones of some acetophenones were also involved effectively into the reaction to give tetrasubstituted alkenes **2g,2h** in a similar way (Scheme 1). In principle, non-aromatic hydrazones can also be involved in this olefination.[14] However, due to low stability of aliphatic hydrazones the reaction performed in repeated manner is less efficient, therefore we investigated only aromatic derivatives in this study.



Scheme 1. Synthesis of alkenes **2** by COR with $CBrCl_3$ in **IL10**.

Next, the reaction of hydrazone **1a** with a set of polyhalogenated alkanes was also investigated. 1-Butyl-3-methylimidazolium tetrafluoroborate **IL10** has been chosen again as a reaction media. It was found, that other PHAs can be also involved successfully into the COR in 1-butyl-3-methylimidazolium tetrafluoroborate to give the corresponding alkenes **3a** and **4a** in high yields (Scheme 2). The reaction proceeded stereoselectively to afford mostly the less hindered isomer with aryl and most bulky substituent in *trans*-position (in cases, there formation of isomers is possible) and the ratio of E/Z isomers was equal to the usual COR selectivity. Configurations of the isomers were determined by comparison with literature data.

Utilization of freons, which are suspected to be active agents of the ozone layer depletion, is an urgent problem to solve.[14e] One the best possible solutions is to find out simple and environmentally friendly chemical transformations of freons into useful products. Using olefination with freons in ILs corresponding fluorinated styrenes **5a-7a** can be also prepared effectively (Scheme 2). Styrenes **5a-7a** have been shown to be versatile building blocks for the synthesis of various fluorinated molecules.[13,18,19] So, olefination in ILs provides a very convenient way for freons utilization as well.



Scheme 2. Synthesis of alkenes **2-7** in **IL10**.

Several improvements of the experimental technique were also made. Thus, the "conventional COR" is carried out in polar solvent (DMSO, EtOH or ethylene glycol), then diluted with 10-20 fold amount of water and extracted with dichloromethane. After drying of the extract and evaporation of the solvent, the residue obtained is purified by chromatography on silica gel eluting with hexane (or hexane-dichloromethane mixtures). In contrast, COR in ionic liquids does not require quenching of the reaction mixture with water and extraction is carried out by hexane. Since byproducts of the reaction (azines) are poor soluble in hexane, the extract thus obtained contains almost pure target alkene and purification can be carried out using minimal amount of silica gel. Moreover, repeated use of silica gel column as well as recovery of hexane makes the process very simple and economical. Another important advance of this method is the immobilization of copper salts in the IL layer. As a result no waste contaminated water with copper is formed. At the same time, CuCl does not decrease its catalytic activity in up to 5 repeated reaction runs. Very important also is purity of formed alkenes which contain no copper traces after silica gel column (Figure 3).

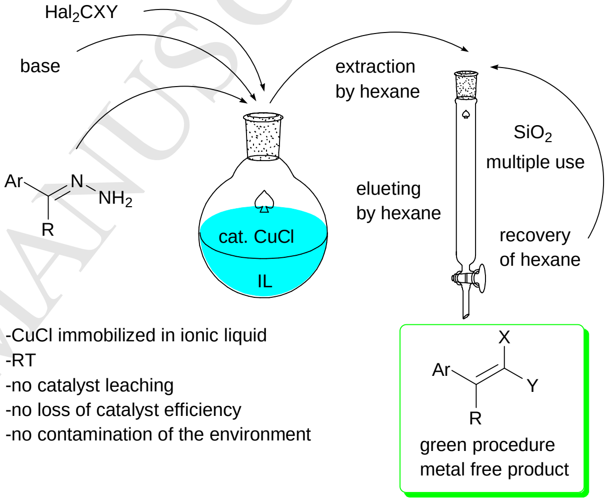


Figure 3. Green access to halogenoalkenes using catalytic olefination reaction (COR)

Comparing to other methods such as Corey-Fuchs[20] or Horner-Wadsworth-Emmons[21] reactions, the method proposed has also several advantages. First of all, simplicity and safety of experimental technique should be mentioned. The reaction is performed at room temperature with no need to exclude air. In contrast to mentioned methods, our method does not produce stoichiometric amounts of toxic phosphorous compounds or zinc salts. Side products of the reaction (azines) are low toxic compounds. Stoichiometrically formed ammonium halogenides are even less toxic and nitrogen gas is not toxic at all. In addition, these products are immobilized in IL phase, which prevent their leaking to the environment. Atom economy of the reaction is 0.53 (in case of dibromide), which is much higher than the corresponding values of Corey-Fuchs reaction (0.23 with PPh_3, 0.29 with PPh_3 and Zn), which is used mostly for synthesis of dibromides from aldehydes. The possibility to recover easily hexane and IL are also benefits of the reaction. Taking all mentioned facts into account, one can conclude, that COR in ILs goes very well with the principals of green chemistry and can be used as a greener alternative to known methods.[11,12]

3. Conclusion

ILs were found to be prospective solvents for COR, providing convenient pathway to a number of substituted alkenes, which are valuable materials for organic synthesis. Effective immobilization of transition metal catalyst in ionic liquid allows performing up to 5 repeated reaction cycles without significant decrease of the yields and prevents contamination of the environment. Simple experimental procedure, low toxicity and low amounts of wastes, higher atom economy comparing to known methods (Corey-Fuchs or Horner-Wadsworth-Emmons reactions) are the advantages of proposed approach.

4. Experimental Section

General details

Ionic liquids **IL1-11** were received from Merck. All solvents and reagents were of reagent grade and used without additional purification. Hydrazones of carbonyl compounds were obtained by reaction with hydrazine hydrate in refluxing ethanol as reported previously.[14a] All reactions were monitored by thin-layer chromatography carried out on Merck silica gel plates (Silufol UV-254). Column chromatography was performed on silica gel (Merck, 63–200 mesh). ^{1}H NMR spectra were recorded at 400 and 600 MHz in $CDCl_3$. ^{13}C NMR spectra were recorded at 150 MHz in $CDCl_3$. HRMS spectra were measured at Orbitrap Elite instrument. ^{1}H NMR spectra of compounds **2a**[22], **2b**[23], **2c**[24], **2d**[25], **2e**[23], **2i**[14d], **2g**[26], **3a**[27], **4a**[28], **5a**[14b], **6a**[19d], **7a**[29] are in agreement with those in the literature.

COR in ILs (general procedure):

First run: 10 mL glass vial was equipped with stirring bar, IL (1 mL), hydrazone of the corresponding carbonyl compound (1 mmol), base (NH_3 or ethylenediamine (2 mmol)), CuCl (0.1 mmol) and stirred at room temperature for 2 min. Next, polyhalogenated alkane (2 mmol) was added under cold water (10-15 °C) bath cooling. Reaction mixture was stirred overnight, then hexane (2 mL) was added and two phase mixture obtained was stirred for 5 min. Hexane layer was separated via suction by pipette, the operation was repeated another 3 times. Combined hexane phases were passed through short silica gel pad using hexane or hexane-CH_2Cl_2 1:1 mixture (**4a**) as eluents.

Second and subsequent runs: To the mixture left from the previous run, hydrazone of aryl aldehyde (1mmol), base (2 mmol) were added and stirred at room temperature for 2 min. Next, polyhalogenated alkane (5 mmol) was added under water bath cooling and stirred overnight. The product was isolated and purified as in the first run.

*4.1. 1-Chloro-4-(2,2-dichlorovinyl)benzene (**2a**)*

Colorless oil; ^{1}H NMR (400 MHz $CDC1_3$) 6.81 (s, 1H, $C\underline{H}=CCl_2$), 7.30 (d, 2H, Ar, *J* = 8.3), 7.49 (d, 2H, Ar, *J* = 8.4). ^{1}H NMR spectra of **2a** are in agreement with literature [22].

*4.2. 1-(2,2-Dichlorovinyl)-4-nitrobenzene (**2b**)*

Yellow solid; mp 88-90 °C (lit.[23] 88-89 °C). ^{1}H NMR (400 MHz $CDC1_3$) 6.93 (s, 1H, $C\underline{H}=CCl_2$), 7.69 (d, 2H, Ar, *J* = 8.8), 8.22 (d, 2H, Ar, *J* = 8.8). ^{1}H NMR spectra of **2b** are in agreement with literature[23].

*4.3. 1-(2,2-Dichlorovinyl)-4-methoxybenzene (**2c**)*

Colorless oil; ^{1}H NMR (400 MHz $CDC1_3$) 3.78 (s, 3H, $OC\underline{H}_3$), 6.80 (s, 1H, $C\underline{H}=CCl_2$), 6.83 (d, 2H, Ar, *J* = 8.5), 7.21 (d, 2H, Ar, *J* = 8.5). ^{1}H NMR spectra of **2c** are in agreement with literature[24].

*4.4. 1-(2,2-Dichlorovinyl)-3-nitrobenzene (**2d**)*

Yellow solid; mp 53-54 °C (lit.[30] 53-55 °C). ^{1}H NMR (600 MHz $CDC1_3$) 6.92 (s, 1H, $C\underline{H}=CCl_2$), 7.55 (t, 1H, Ar, *J* = 8.0), 7.81-7.83 (m, 1H), 8.16 (ddd, 1H, Ar, *J* = 8.0, *J* = 2.2, *J* = 1.0). ^{1}H NMR spectra of **2d** are in agreement with literature[25].

*4.5. 2,4-Dichloro-1-(2,2-dichlorovinyl)benzene (**2e**)*

Colorless crystals; mp 49-50 °C (lit.[23] 47-48 °C), ^{1}H NMR (400 MHz $CDC1_3$) 6.99 (s, 1H, $C\underline{H}=CCl_2$), 7.28 (dd, 1H, Ar, *J* = 8.5, *J* = 2.1), 7.43 (d, 1H, Ar, *J* = 2.1), 7.65 (d, 1H, Ar, *J* = 8.5). ^{1}H NMR spectra of **2e** are in agreement with literature[23].

*4.6. (4-(2,2-Dichlorovinyl)phenyl)(methyl)sulfane (**2f**)*

Brown crystals; mp 57-58 °C; ^{1}H NMR (600 MHz $CDC1_3$) 2.48 (s, 3H, SMe), 6.79 (s, 1H, $C\underline{H}=CCl_2$), 7.22 (d, 2H, Ar, *J* = 8.4), 7.46 (d, 2H, Ar, *J* = 8.4); ^{13}C NMR (150 MHz $CDC1_3$) 15.3, 120.3, 126.0, 128.0, 128.9, 129.9, 139.4; ESI-MS: MH^+, found 218.9790. $C_9H_8Cl_2SH$ requires 218.9797.

*4.7. 1-(1,1-Dichloroprop-1-en-2-yl)benzene (**2g**)*

Colorless oil; ^{1}H NMR (400 MHz $CDC1_3$) 2.21 (s, 3H, Me), 7.26-7.40 (m, 5H, Ar). ^{1}H NMR spectra of compounds **2g** are in agreement with literature[26].

*4.8. 1-Bromo-4-(1,1-dichloroprop-1-en-2-yl)benzene (**2h**)*

Colorless oil; ^{1}H NMR (600 MHz $CDC1_3$) 2.18 (s, 3H, Me), 7.14 (d, 2H, Ar, *J* = 7.9), 7.49 (d, 2H, Ar, *J* = 7.9); ^{13}C NMR (150 MHz $CDC1_3$) 22.8, 117.6, 121.8, 129.5, 131.6, 134.6, 138.9; ESI-MS: MH^+, found 264.9171. $C_9H_7BrCl_2H$ requires 264.9181.

*4.9. 1,4-bis(2,2-Dichlorovinyl)benzene (**2i**)*

Colorless crystals; mp 77-78 °C (lit.[14d] 77-78 °C), ^{1}H NMR (400 MHz $CDC1_3$) 6.86 (s, 2H, $C=C\underline{H}$), 7.57 (s, 4H, Ar). ^{1}H NMR spectra of **2i** are in agreement with literature[14d].

*4.10. 1-(2,2-Dibromovinyl)-4-chlorobenzene (**3a**)*

Colorless crystals; mp 35-37 °C (lit.[27] 35-36 °C), ^{1}H NMR (400 MHz $CDC1_3$) 7.26 (d, 2H, Ar, *J* = 8.7), 7.35 (s, 1H, $C\underline{H}=CBr_2$), 7.39 (d, 2H, Ar, *J* = 8.7). ^{1}H NMR spectra of **3a** are in agreement with literature[27].

*4.11. Ethyl 2-chloro-3-(4-chlorophenyl)acrylate (**4a**)*

Yellow oil; mixture of Z/E isomers in ratio 86:14; ^{1}H NMR (400 MHz $CDC1_3$) 1.31 (t, 3H, CH_3, *J* = 7.1), 4.33 (q, 2H, CH_2, *J* = 7.1), 7.32 (d, 2H, Ar, *J* = 8.7), 7.71 (d, 2H, Ar, *J* = 8.7), 7.77 (s, 1H, $C\underline{H}=CClCO_2Et$). ^{1}H NMR spectra of compounds **4a** are in agreement with literature[28].

*4.12. 1-(2-Bromo-3,3,3-trifluoroprop-1-enyl)-4-chlorobenzene (**5a**)*

Colorless oil; mixture of Z/E isomers in ratio 92:8; ^{1}H NMR (400 MHz $CDC1_3$) *Z*-isomer: 7.40 (d, 2H, Ar, *J* = 8.8), 7.55 (s, 1H, $C\underline{H}=CBrCF_3$), 7.66 (d, 2H, Ar, *J* = 8.8). *E*-isomer: 7.20 (d, 2H, Ar, *J* = 8.5), 7.34 (d, 2H, Ar, *J* = 8.5), 7.45 (s, 1H, $C\underline{H}=CBrCF_3$). ^{1}H NMR spectra of **5a** are in agreement with literature[14b].

*4.13. (2-Bromo-2-fluorovinyl)-4-chlorobenzene (**6a**)*

Colorless oil; mixture of E/Z isomers in ratio 85:15; ^{1}H NMR (400 MHz $CDC1_3$) *E*-isomer: 5.92 (d, 1H, $C\underline{H}=CBrF$, *J* = 32.3), 7.31 (m, 4H, Ar). *Z*-isomer: 6.60 (d, 1H, $C\underline{H}=CBrF$, *J* = 14.9), 7.32 (d, 2H, Ar, *J* = 8.4), 7.40 (d, 2H, Ar, *J* = 8.4). ^{1}H NMR spectra of **6a** are in agreement with literature[19d].

*4.14. 1-(2-Chloro-3,3,3-trifluoroprop-1-enyl)-4-chlorobenzene (**7a**)*

Colorless oil; mixture of Z/E isomers in ratio 79:21; ^{1}H NMR (400 MHz CDC1$_3$) *Z*-isomer: 7.07 (s, 1H, $C\underline{H}=CClCF_3$), 7.20 (d, 2H, Ar, *J* = 8.7), 7.48 (d, 2H, Ar, *J* = 8.7). *E*-isomer: 7.02 (s, 1H, $C\underline{H}=CClCF_3$), 7.03 (d, 2H, Ar, *J* = 8.4), 7.17 (d, 2H, Ar, *J* = 8.4). ^{1}H NMR spectra of **7a** are in agreement with literature[29].

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References and notes

1. (a) Wang, Y.-M.; Lackner, A. D.; Toste, F. D. *Acc. Chem. Res.* **2014**, *47*, 889–901; (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322–5363; (c) Huang, J.-L.; Dai, X.-J.; Li, C.-J. *Eur. J. Org. Chem.* **2013**, 6496–6500; (d) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960–9009.
2. (a) Wu, D. Y.; Marzini, M.; Lindner, E.; Mayer, H. A. *Z. Anorg, Allg. Chem.* **2005**, *631*, 2538–2539; (b) Gelman, F.; Blum, J.; Avnir, D. *J. Am. Chem. Soc.* **2002**, *124*, 14460–14463; (c) Akiyama, R.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2602–2604.
3. Dioumaev, V. K.; Bullock, R. M. *Nature* **2003**, *424*, 530–532.
4. Huang, J.-L.; Wang, J.-Zh.; Li, H.-X.; Guo, H.; O'Doherty, G. A. *Green Chem.* **2015**, *17*, 1473-1478.
5. For a review, see: (a) Gladysz, J. A.; Curran, D. P.; Horvath, I. T. *Handbook of Fluorous Chemistry*, Wiley-VCH, Weinheim, 2004; (b) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72–75; (c) Curran, D. P.; Hadida, S. *J. Am. Chem. Soc.* **1996**, *118*, 2531–2532; (d) Wende, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 5861–5872; (e) Yao, Q.; Zhang, Y. *J. Am. Chem. Soc.* **2004**, *126*, 74–75.
6. (a) Liu, G.; He, H.; Wang, J. *Adv. Synth. Catal.* **2009**, *351*, 1610–1620; (b) Süner, M.; Plenio, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6885–6888.
7. (a) Yang, Y.; Zhang, B.; Wang, Y. Z.; Yue, L.; Li, W.; Wu, L. X. *J. Am. Chem. Soc.* **2013**, *135*, 14500–14503; (b) Liu, G. Y.; Wang, J. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 4425–4429.
8. (a) Xi, Z. W.; Zhou, N.; Sun, Y.; Li, K. L. *Science* **2001**, *292*, 1139–1141; (b) Hourdin, G.; Germain, A.; Moreau C.; Fajula, F. *J. Catal.* **2002**, *209*, 217–224; (c) Desset, S. L.; Cole-Hamilton, D. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 1472–1474; (d) Uk Son, S.; Jang, Y. J.; Park, J. N.; Na, H. B.; Park, H. M.; Yun, H. J.; Lee, J. H.; Hyeon, T. *J. Am. Chem. Soc.* **2004**, *126*, 5026–5027; (e) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852–7872.
9. (a) Lu, J. N.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815–838; (b) Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6786–6801; (c) Sheldon, R. A. *Green Chem.* **2005**, *7*, 267-278; (d) McMorn, P.; Hutchings, G. J. *Chem. Soc. Rev.* **2004**, *33*, 108-122; (e) De Vos, D. E. ; Dams, M. ; Sels, B. F. ; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615-3640; (f) Metivier, P. *Fine Chemicals through Heterogeneous Catalysis*, Wiley, Weinheim, 2001, pp. 211; (g) De Vos, D. E. ; Vankelecom, F. J. ; Jabobs, P. A. *Chiral Catalyst Immobilization and Recycling*, Wiley-VCH, Weinheim, 2000, pp. 640; (h) Corma, A. *Chem. Rev.* **1997**, *97*, 2373-2419.
10. (a) Zhou, Zh.-M.; Li, Zh.-H.; Hao, X.-Y.; Dong, X.; Li, X.; Dai, L.; Liu, Y.-Q.; Zhang, J.; Huang, H.-F.; Li, X.; Wang, J.-L. *Green Chem.* **2011**, *13*, 2963–2971; (b) Cotugno, P.; Monopoli, A.; Ciminale, F.; Milella, A.; Nacci, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 13563–13567; (c) Khan, N.-H.; Prasetyanto, E. A.; Kim, Y.-K.; Ansari, M. B.; Park, S.-E. *Catal. Lett.* **2010**, *140*, 189–196; (d) Park, S. B.; Alper, H. *Chem. Commun.* **2005**, 1315–1317; (e) Sun, H.; Harms, K.; Sundermeyer, J. *J. Am. Chem. Soc.* **2004**, *126*, 9550-9551.
11. (a) Dupont, J.; de Souza, R. F.; Z. Suarez, P. A. *Chem. Rev.* **2002**, *102*, 3667–3692; (b) Pˆarvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615–2665; (c) Liu, S. F.; Xiao, J. L. *J. Mol. Catal. A: Chem.* **2007**, *270*, 1–43; (d) Śledź, P.; Mauduit, M.; Grela, K. *Chem. Soc. Rev.* **2008**, *37*, 2433–2442; (e) Šebesta, R.; Kmentová, I.; Toma, S. *Green Chem.* **2008**, *10*, 484–496; (f) Miao, W.; Chan, T. H. *Acc. Chem. Res.* **2006**, *39*, 897–908.
12. (a) Sheldon, R. A.; Arends, I.; Hanefeld, U. *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, 2007; (b) Green chemistry, in special issue, *Chem. Rev.* **2007**, *107*, 2167-2820.
13. Chelucci, G. *Chem. Rev.* **2012**, *112*, 1344–1462.
14. (a) Nenajdenko, V. G.; Korotchenko, V. N.; Shastin, A. V.; Balenkova, E. S. *Russ. Chem. Bull*. **2004**, *53*, 1034-1064; (b) Nenajdenko, V. G.; Varseev, G. N.; Shastin, A. V.; Balenkova, E. S. *J. Fluorine Chem.* **2005**, *126*, 907-913; (c) Goldberg, A. A.; Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Nenajdenko, V. G. *J. Fluorine Chem.* **2010**, *131*, 384-388; (d) Muzalevskiy, V.M.; Shikhaliev, N. Q.; Magerramov, A.M.; Gurbanova, N.V.; Geydarova, S.D.; Balenkova, E.S.; Shastin, A.V.; Nenajdenko, V.G. *Russ. Chem. Bull.* **2013**, *62*, 678–682; (e) Nenajdenko, V. G.; Muzalevskiy, V. M.; Shastin, A. V. *Chem. Rev.* **2015**, *115*, 973–1050.
15. Nenajdenko, V. G.; Vasil'kov, A. Y.; Goldberg, A. A.; Muzalevskiy, V. M.; Naumkin, A. V.; Podshibikhin, V. L.; Shastin, A. V.; Balenkova, E. S. *Mendeleev Comm.* **2010**, *20*, 200-202.
16. (a) Ignat'ev, N.V.; Finze, M.; Sprenger, J.A.P.; Kerpen, C.; Bernhardt, E.; Willner, H. *J. Fluorine Chem.* **2015**, *177*, 46–54; (b) Ignat'ev, N.V.; Welz-Biermann, U.; Kucheryna, A.; Bissky, G.; Willner, H. *J. Fluorine Chem.* **2005**, *126*, 1150-1159; (c) Ignat'ev, N.V.; Barthen, P.; Kucheryna, A.; Willner, H.; Sartori, P. *Molecules* **2012**, *17*, 5319-5338; (d) Wasserscheid, P.; Welton, T. (Eds.), *Ionic Liquids in Synthesis,* Wiley-VCH Verlag Gmbh, Weinheim, 2008.
17. Kashin, A. S.; Galkin, K. I.; Khokhlova, E. A.; Ananikov, V. P. *Angew. Chem. Int. Ed.* **2016**, *55*, 2161–2166.
18. (a) Mokrushin, M. G.; Shastin, A. V.; Muzalevskiy, V. M.; Balenkova, E. S.; Nenajdenko, V. G. *Mendeleev Comm.* **2008**, 327-328; (b) Nenajdenko, V. G.; Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Kondrashov, E. V.; Ushakov, I. A.; Rulev, A. Y. *J. Org. Chem.* **2010**, *75*, 5679-5688; (c) Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Nenajdenko, V. G. *Russ. Chem. Bull.* **2007**, *56*, 1526-1533; (d) Rulev, A. Y.; Muzalevskiy, V. M.; Kondrashov, E. V.; Ushakov, I. A.; Shastin, A. V.; Balenkova, E. S.; Haufe, G.; Nenajdenko, V. G. *Eur. J. Org. Chem.*, **2010**, 300-310; (e) Wang, C.; Chen, L.-H.; Deng, C.-L.; Zhang, X.-G. *Synthesis* **2014**, *46*, 313-319; (f) Jiang, B.; Zhang, F.; Xiong, W. *Tetrahedron* **2002**, *58*, 261-264; (g) Zhou, H.; Niu, J.-J.; Xu, J.-W.; Hu, S.-J. *Synth. Comm.* **2009**, *39*, 716-732; (h) Sun, L.-L.; Liao, Zh.-Y.; Tang, R.-Y.; Deng, C.-L.; Zhang, X.-G. *J. Org. Chem.* **2012**, *77*, 2850-2856; (i) Sun, L.-L.; Hu, B.-L.; Tang, R.-Y.; Deng, C.-L.; Zhang, X.-G. *Adv. Synth. Catal.* **2013**, *355*, 377-382; (j) Dong, S.-X.; Zhang, X.-G.; Liu, Q.; Tang, R.-Y.; Zhong, P.; Li, J.-H. *Synthesis* **2010**, 1521-1525; (k) Li, C.-L.; Zhang, X.-G.; Tang, R.-Y.; Zhong, P.; Li, J.-H. *J. Org. Chem.* **2010**, *75*, 7037-7040; (l) Shi, S.; Sun, L.-L.; Liao, Z.-Y.; Zhang, X.-G. *Synthesis* **2012**, *44*, 966-972.
19. (a) Nenajdenko, V. G.; Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Haufe, G. *J. Fluorine Chem.* **2007**, *128*, 818-826; (b) Eddarir, S.; Kajjout, M.; Rolando, C. *Tetrahedron* **2012**, *68*, 603-607; (c) Schneider, C.; Masi, D.; Couve-Bonnaire, S.; Pannecoucke, X.; Hoarau, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 3246-3249; (d) Rouse, K.; Schneider, C.; Bouillon, J.-P.; Levacher, V.; Hoarau, C.; Couve-Bonnaire, S.; Pannecoucke, X. *Org. Biomol. Chem.* **2015**, *14*, 353-357.
20. Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769–3772.
21. a) Horner, L.; Hoffmann, H. M. R.; Wippel, H. G.; Klahre, G. *Ber.* **1959**, *92*, 2499–2505; b) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733.
22. Arthuis, M.; Lecup, A.; Roulland, E. *Chem. Comm.* **2010**, *46*, 7810-7812.
23. Newman, S. G.; Bryan, C. S.; Perez, D.; Lautens, M. *Synthesis* **2011**, 342-346.
24. Liron, F.; Fosse, C.; Pernolet, A.; Roulland, E. *J. Org. Chem.* **2007**, *72*, 2220-2223.
25. Ando A.; Miki, T.; Kumadaki, I. *J. Org. Chem.* **1988**, *53*, 3637-3639.

26. Chien, C.-T.; Tsai, C.-C.; Tsai, C.-H.; Chang, T.-Y.; Tsai, P.-K.; Wang, Y.-C.; Yan, T.-H. *J. Org. Chem.* **2006**, *71*, 4324-4327.
27. Sha,Q.; Wei, Y. *Synthesis* **2013**, *45*, 413-420.
28. Huang, Z.; Yu, X.; Huang, X. *J. Org. Chem.* **2002**, *67*, 8261-8264.
29. Fujita, M.; Hiyama, T. *Bull. Chem. Soc.* **1987**, *60*, 4377–4384.
30. Krabbenhoft, H. O. *J. Org. Chem.* **1978**, *43*, 1305-1310.

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