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An ionic liquid as reaction medium for the synthesis of halo-containing β-enaminones at room temperature

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Abstract A series of twenty halomethylated β-enaminones [RC(O)CH=C(R^1)NR^3R^4, where $R = CF_3$, CCl_3, $CHCl_2$; $R^1 = H$, *Me*, *Ph*; $R^3 = H$, *Me*, *Bu*, *Et*; $R^4 = Me$, *Et*, *Bu*, allyl, *tert*-amyl, CH_2CH_2OH, *Bn*, *Ph*] were synthesized using the ionic liquid [bmim]BF_4 at room temperature. It is demonstrated that this ionic liquid is a reaction medium suitable for the amination of β-alkoxyvinyl halomethyl ketones. The advantages of this method are the absence of solvents, short reaction times, and good yields.

Keywords Amines; β-Enaminones; β-Alkoxyvinyl halomethylated ketones; Homogeneous catalysis; Ionic liquids.

Introduction

Recently, much attention has been paid to the development of new methodologies for the synthesis of many kinds of fluorine[chlorine]-containing heterocycles [1]. These compounds are now widely recognized as important materials, having interesting functionalities for use in medicinal and agricultural science [2, 3]. The chemistry and potential utility of β-enaminones in organic synthesis are widely described and several synthesis methods have been reported in literature [4]. However, the synthesis of halomethylated β-enaminones, which may be expected to be a useful building block for the synthesis of fluorine[chlorine]-containing heterocycles, has scarcely been reported so far [5, 6]. One of the most effective methods used to synthesize enaminones containing a halomethyl group is the amination of β-alkoxyvinyl halomethyl ketones [6]. Unfortunately, in general, many of these processes suffer major or minor limitations, such as long reactions times, tedious work-up, unsatisfactory yields, and hazardous or expensive solvents and catalysts [5a].

Our research group has studied exhaustively the chemistry of trihalomethyl enaminones, and we have described methods to faster synthesize trihalomethyl enaminones with good yields, under solvent-free conditions [7]. On the other hand, recently, our research group has explored the effect of ionic liquids in organic reactions involving trihalomethylated compounds. We have reported a practical and efficient procedure for the acylation of enol ethers with trifluoroacetic anhydride and trichloroacetyl chloride in the ionic liquids 1-buthyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and hexafluorophosphate ([bmim]PF_6) [8]. We have also demonstrated that ionic liquids are an excellent medium for condensation reactions between β-alkoxyvinyl halomethyl ketones and cyanoacethydrazide to pyrazoles [9]. In recent years, ionic liquids have attracted a great deal of interest as a possible replacement of traditional solvents for organic reactions, particularly

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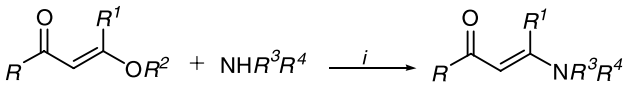
in the area of green chemistry, due to their advantageous properties, including negligible vapor pressure and high thermal and chemical stability. In addition, ionic liquids have been related to allow chemoselectivety to some organic reactions [10].

Thus, as part of our ongoing studies aimed to explore the utility and the effect of ionic liquids in the chemoselectivety of important reactions, we decided to investigate the use of [bmim]BF_4 as a medium to prepare of halomethylated β-enaminones by amination of β-alkoxyvinyl halomethyl ketones.

Results and discussion

A variety of amines, including aliphatic and aromatic amines, were used to substitute the alkoxyde group of six β-alkoxyvinyl halomethyl ketones (Scheme 1). The results are recorded in Table 1. In all the cases, the reactants and products were soluble in [bmim]BF_4 All the isolated products were well characterized by their melting points, ^{1}H and ^{13}C NMR, and GC/MS data.



1, 2, 3, 4, 5, 6 **7a–7m** **8, 9, 10, 11, 12, 13**

i: [BMIM] BF_4, rt, 10 – 30 min (see Table 1)

Scheme 1

The reaction was carried out at room temperature for 30 min using commercially available amines **7** (1 mmol) and β-alkoxyvinyl halomethyl ketones **1–6** (1 mmol) in presence of [bmim]BF_4 as the reaction medium (1 mmol). After the reaction time, the ionic liquid was separated from the products by adding water and chloroform. The desired products **8–13** were obtained after evaporation of chloroform. The ionic liquid was recuperated after the evaporation of water. The results are summarized in Table 1 and show that primary and secondary amines, both aromatic and aliphatic, with linear and branched N-substituents react without any significant difference to give the corresponding halomethylated β-enaminones in good yields. The stereochemistry of halomethylated β-enaminones was determined from their ^{1}H NMR spectra. The formation of the (*Z*)-isomer is proved by the coupling constants of the hydrogen

Table 1 [bmim]BF_4 catalyzed formation of β-enaminones

Reagent (enone)	R	R^1	R^2	Reagent (amine)	R^3	R^4	Product (enaminone)	Reaction time/min	Yield/ %[a]
1	CF_3	*Me*	*Me*	**7a**	H	*Bn*	**8a**	20	80
1	CF_3	*Me*	*Me*	**7b**	H	*Ph*	**8b**	10	92
1	CF_3	*Me*	*Me*	**7c**	*Me*	*Bu*	**8c**	20	70
1	CF_3	*Me*	*Me*	**7d**	*Me*	*Ph*	**8d**	30	70
1	CF_3	*Me*	*Me*	**7e**	*Bu*	*Bu*	**8e**	20	95
1	CF_3	*Me*	*Me*	**7f**	H	*Me*	**8f**	30	70
1	CF_3	*Me*	*Me*	**7g**	H	*tert*-amyl	**8g**	20	68
1	CF_3	*Me*	*Me*	**7h**	H	allyl	**8h**	20	55
1	CF_3	*Me*	*Me*	**7i**	H	CH_2CH_2OH	**8i**	30	67
1	CF_3	*Me*	*Me*	**7j**	H	*Et*	**8j**	10	70
2	CF_3	H	*Et*	**7b**	H	*Ph*	**9b**	20	76
2	CF_3	H	*Et*	**7k**	*Et*	*Et*	**9k**	20	70
3	CF_3	*Ph*	*Me*	**7k**	*Et*	*Et*	**10k**	30	70
4	CCl_3	*Me*	*Me*	**7a**	H	*Bn*	**11a**	30	>99
4	CCl_3	*Me*	*Me*	**7b**	H	*Ph*	**11b**	20	91
4	CCl_3	*Me*	*Me*	**7k**	*Et*	*Et*	**11k**	20	75
4	CCl_3	*Me*	*Me*	**7i**		$-(CH_2)_4-$	**11l**	20	79
5	CCl_3	H	*Et*	**7a**	H	*Bn*	**12a**	30	92
5	CCl_3	H	*Et*	**7b**	H	*Ph*	**12b**	30	95
5	CCl_3	H	*Et*	**7c**	*Me*	*Bu*	**12c**	20	88
6	$CHCl_2$	*Me*	*Me*	**7a**	H	*Bn*	**13a**	20	88
6	$CHCl_2$	*Me*	*Me*	**7c**	*Me*	*Bu*	**13c**	20	91
6	$CHCl_2$	*Me*	*Me*	**7m**		$-(CH_2)_2-O-(CH_2)_2-$	**13m**	30	81

[a] Yields of isolated products

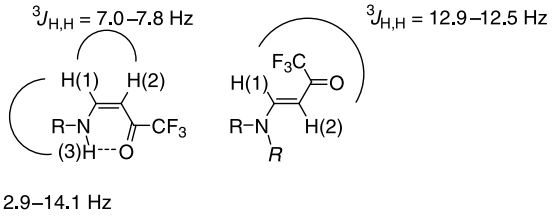


Fig. 1 Coupling constants of the hydrogen atoms at the double bond of (*Z*)- and (*E*)-isomers

atoms at the double bond ($J = 7.0$–7.8 Hz) and by a distinct splitting of the H(1) atom (Fig. 1) on the amino group H(3) atom ($J = 12.9$–14.1 Hz) (Fig. 1) fixed *via* an intramolecular hydrogen bond. In the case of the (*E*)-isomer, $J = 12.0$–12.5 Hz (Fig. 1).

Moreover, the stereochemistry of the enaminones obtained depends on the structure of the starting amine, regardless of the ratio of the (*E*)/(*Z*)-isomers in the starting β-alkoxyvinyl halomethyl ketones. The proposed structures were confirmed by X-ray diffraction for **13a** and **13m** (Fig. 2).

Furthermore, it is proposed that the ionic liquid does not interfere with the stereochemistry of the β-enaminones obtained. This fact is reasonably based on data related to literature, where primary aliphatic amines are described to react with β-alkoxyvinyl halomethyl ketones to give only (*Z*)-isomers, due to the formation of an intramolecular hydrogen bond [11], while the reactions of secondary amines afford (*E*)-isomers [12].

Finally, to demonstrate the generality of this method we investigated the scope of this reaction under optimized conditions and the results are summarized in Table 1. Thus, a variety of β-alkoxyvinyl halomethyl ketones, including 4-H, 4-methyl, and 4-aryl substituted ones, reacted with aliphatic amines, and all the β-alkoxyvinyl halomethyl ketones gave good yields. These reactions were very clean and free from side reactions. However, the 4-aryl substituted β-alkoxyvinyl halomethyl ketones do not undergo substitution with amines, such as diphenylamine.

Although the ionic liquids did not provide higher yields than when the reaction was carried out under solvent-free conditions, it was demonstrated that they are better than other molecular solvents for amination (nucleophilic substitution). The effect of the ionic liquid on the nucleophilic substitution reaction has been investigated and, currently, the authors agree that "the data on the properties such as dielectric constants and polarity are not sufficient to explain the solvent/catalyst effect of ionic liquids in organic transformations". For example, some studies indicate that ionic liquids have polarities similar to those of short-chain alcohols and other polar, aprotic solvents (*DMSO or DMF*) and their polarity is intermediate between water and chlorinated organic solvents, varying in accordance with the nature of the ionic liquid components [13, 14]. Contrarily, others report that they exhibit solvent strengths as great as or greater than the most polar aprotic solvent (acetonitrile) [15]. Moreover, attempts have been made to develop empirical solvent polarity scales as a means to help explain differences in solvent-mediated reaction pathways, reaction yields, synthesis product ratios, chromatographic retention, and extraction coefficients. Clearly, a single parameter of "polarity"/"solvent strength"/"interaction" is not sufficient to explain the variation in experimental results in many solvent-mediated processes. Ionic liquids are among the most complex solvents. Given their structure and diversity of functionality, they are capable of most types of interactions (*e.g.*, dispersive, π-π, *n*-π, hydrogen bonding, dipolar, and ionic/charge–charge). In every solution, there may be a number of different (in terms of type and strength) and often simultaneous solute–solvent interactions. Also, the well-established scenarios for describing dipolar interactions in molecular liquids are not easily transferred to ionic liquids

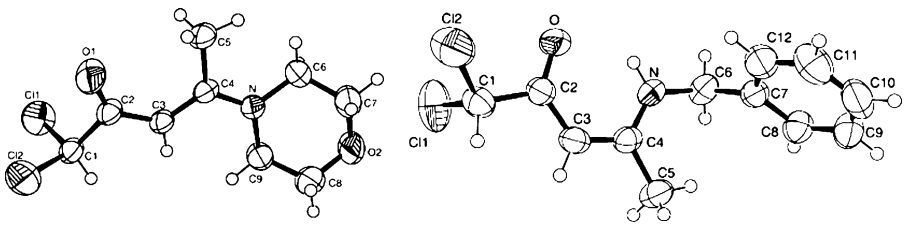


Fig. 2 ORTEP plof of (*E*)-1,1-dichloro-4-morpholin-4-yl-3-penten-2-one (**13m**) and (*Z*)-4-benzylamino-1,1-dichloro-3-penten-2-one (**13a**)

because the net charges of the ions create a fundamentally different environment with partial charge-ordering and screening of dipole–dipole interactions by the sea of surrounding ions. The presence of charged species adds new degrees of freedom in the mix of interactions. In this case, the concept of polarity may even require a careful rethinking of the fundamental nature of solvation [16]. A probable effect of the ionic liquids on activated complexes is that they could become more stable and long-lived in these media [10]. A comparison of the results of this paper with the results described for molecular solvents [6] show that this method allows a relatively short reaction time. All the reactions proceeded to completion under ambient conditions at room temperature in ionic liquid without any other catalyst. For every reaction, the ionic liquid was recovered by the evaporation of water and washed successively with dichloromethane, dried with Na_2SO_4, and then the solvent was evaporated. Recycled, the ionic liquid could be reused several times without any loss of activity.

In conclusion, we disclosed an easy and environmentally sound method for the synthesis of halomethylated β-enaminones starting from differently substituted β-alkoxyvinyl halomethyl ketones with a variety of substituents and amines in the ionic liquid [bmim]BF_4. The simple work-up procedure, mild reaction conditions, short reaction times, and good yields make our methodology a valid contribution to the existing process in the field of β-enaminone synthesis.

Experimental

Unless indicated otherwise, all common reagents and solvents were used as obtained from commercial supplies without further purifications. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) in 5 mm sample tubes at 298 K (digital resolution $\pm$0.01 ppm) in $CDCl_3$/*TMS* solutions. Mass spectra were registered in a HP 5973 MSD connected to a HP 6890 GC and interfaced by a Pentium PC. The CG was equipped with a split–splitless injector, autosampler, cross-linked to a HP-5 capillary column (30 m length, 0.32 mm internal diameter), and He was used as the carrier gas. All melting points were determined on a Reichert Thermovar apparatus. X-Ray data were collected on a Bruker SMART CCD diffractometer. The wavelength of diffractometer is 0.71073 Å and the crystals sizes are $0.44 \times 0.35 \times 0.15\,mm^3$ for **13a** and $0.51 \times 0.39 \times 0.32\,mm^3$ for **13m**. The crystallographic structure was solved by direct methods (SHELXS-97) [17]. Refinements were carried out with the SHELXL-97 [18] package. The ORTEP [19] diagram of the molecules indicating atom numbering scheme with thermal ellipsoids at 50% probability is illustrated in Fig. 2. The ionic liquid [bmim]BF_4 was synthesized according to Ref. [20].

Synthesis of β-enaminones

A mixture of 1 mmol **1–6** and 225 mg [bmim]BF_4 (1 mmol) was stirred until a homogeneous mixture was formed. Then, 1 mmol **7** was added slowly to this mixture. After this, the mixture was stirred at room temperature for 10–30 min. Water ($3\,cm^3$) was added, and the crude products **8–13** were extracted with $3 \times 20\,cm^3$ $CHCl_3$. The organic phases were dried (Na_2SO_4) and the solvent was evaporated. The β-enaminone products were obtained in a pure form, without further purification.

(Z)-4-Benzylamino-1,1,1-trifluoro-3-pent-2-one
(**8a**, $C_{12}H_{12}F_3NO$)
Mp 59–61°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.02$ (s, CH_3), 4.56 (d, CH_2), 5.40 (s, CH) 7.26–7.35 (m, 5H, arom), 11.61 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 19.4$ (CH_3), 47.5 (CH_2), 89.7 (CH), 117.2 (q, CF_3, $J = 288$ Hz), 126.9 (CH), 128.0 (2CH), 129.0 (2CH), 135.9 (CH), 169.6 (C), 175.5 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 243 (M^+, 45), 91 (100), 174 (81), 65 (52), 146 (13); IR (KBr): $\bar{\nu} = 1585$, 1302, 1225, 887, 835, 738, 724 cm^{-1}.

(Z)-1,1,1-Trifluoro-4-phenylamino-3-penten-2-one
(**8b**, $C_{11}H_{10}F_3NO$)
Mp 55–57°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.11$ (s, CH_3), 5.54 (s, CH), 7.15–7.42 (m, 5H, arom), 10.89 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 20.1$ (CH_3), 90.7 (CH), 117.4 (q, CF_3, $J = 288$ Hz), 125.1 (C), 127.3 (2CH), 129.4 (2CH), 136.8, (CH), 167.9 (C), 176.4 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 229 (M^+, 18), 160 (100), 77 (35), 51 (20), 117 (17); IR (KBr): $\bar{\nu} = 3448$, 1578, 1253, 1126, 756, 728 cm^{-1}.

(E)-4-(Butylmethylamino)-1,1,1-trifluoro-3-penten-2-one
(**8c**, $C_{10}H_{16}F_3NO$)
Oil; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.97$ (t, CH_3), 1.34 (sex, CH_2), 1.58 (qui, CH_2), 2.61 (s, CH_3), 3.03 (s, CH_3), 3.40 (t, CH_2), 5.19 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 13.7$ (CH_3), 16.7 (CH_2), 19.8 (CH_3), 30.3 (CH_2), 39.0 (N–CH_2), 52.21 (N–CH_3), 86.9 (CH), 117.0 (q, CF_3, $J =$ 288 Hz), 167.7 (CH), 175.1 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 223 (M^+, 13), 56 (100), 154 (57), 112 (46), 126 (26), 180 (20); IR (KBr): $\bar{\nu} = 1645$, 1552, 1358, 1281, 1111, 866, 777 cm^{-1}.

(E)-1,1,1-Trifluoro-4-(methylphenylamino)-3-penten-2-one
(**8d**, $C_{12}H_{12}F_3NO$)
Oil; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.83$ (s, CH_3), 3.36 (s, CH_3), 5.42 (s, CH), 7.14–7.46 (5H arom) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 30.8$ (CH_3), 41.7 (CH_3), 88.6 (CH), 123.0 (q, CF_3, $J = 292$ Hz), 122.6 (C), 126.4 (CH), 128.2

(CH), 129.1(CH), 129.9 (CH), 144.5 (CH), 168.0 (C), 181.6 (q, C=O, $J = 30$ Hz) ppm; MS: m/z (%) = 243 (M^+, 45), 174 (100), 56 (96), 77 (80), 131 (62), 146 (47), 104 (17); IR (KBr): $\bar{\nu} = 1675$, 1538, 1497, 1202, 1134, 835, 721, 695, 565 cm^{-1}.

(E)-4-Dibutylamino-1,1,1-trifluoro-3-penten-2-one
(**8e**, $C_{13}H_{22}F_3NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.97$ (t, $2CH_3$), 1.36 (sex, $2CH_2$), 1.59 (qui, $2CH_2$), 2.60 (s, CH_3), 3.32 (t, CH_2), 5.25 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 13.5$ ($2CH_3$), 16.9 (CH_3), 18.0 ($2CH_3$), 19.9 ($2CH_2$), 27.9 (CH_2), 30.4 (CH_2), 51.4 ($2CH_2$) 86.4 (CH), 118.1 (q, CF_3, $J =$ 292 Hz), 167.2 (C), 174.7 (q, C = O, $J = 32$ Hz) ppm; MS: m/z (%) = 265 (M^+, 24), 98 (100), 154 (81), 196 (79), 222 (70), 168 (65), 57 (63), 126 (17); IR (KBr): $\bar{\nu} = 2961$, 2933, 1550, 1280, 1236, 1046, 960, 737 cm^{-1}.

(Z)-1,1,1-Trifluoro-4-methylamino-3-penten-2-one
(**8f**, $C_6H_8F_3NO$)
Mp 49–52°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.08$ (s, CH_3), 3.06 (d, CH_3), 5.35 (s, CH), 11.07 (s, CH), 11.08 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 19.1$ (CH_3), 30.1 (CH_3), 19.9 (CH_2), 89.2 (CH), 117.6 (q, CF_3, $J =$ 287 Hz), 170.5 (C), 175.1 (q, C=O, $J = 31$ Hz) ppm; MS: m/z (%) = 167 (M^+, 20), 98 (100), 56 (72), 69 (23), 82 (13); IR (KBr): $\bar{\nu} = 1621$, 1436, 1281, 1244, 1183, 1116, 884, 737 cm^{-1}.

(Z)-4-(1,1-Dimethylpropylamino)-1,1,1-trifluoro-3-penten-2-one (**8g**, $C_{10}H_{16}F_3NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.97$ (t, CH_3), 1.41 (s, $2CH_3$), 1.73 (q, CH_2), 2.19 (s, CH_3), 5.26 (s, CH), 11.59 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 8.1$ (CH_3), 20.7 (CH_3), 27.8 ($2CH_3$), 35.2 ($2CH_2$), 56.7 (C), 90.4 (CH), 117.0 (q, CF_3, $J = 287$ Hz), 169.7 (C), 174.2 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 223 (M^+, 20), 84 (100), 154 (86), 71 (42), 194 (36), 55 (24); IR (KBr): $\bar{\nu} = 2976$, 1608, 1252, 1181, 1122, 871, 739 cm^{-1}.

(Z)-4-Allylamino-1,1,1-trifluoro-3-penten-2-one
(**8h**, $C_8H_{10}F_3NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.08$ (s, CH_3), 3.98 (t, CH_2), 5.23 (d, CH), 5.31 (d, CH), 5.36 (s, CH), 5.84 (m, CH), 11.15 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 19.1$ (CH_3), 45.7 (CH_2), 89.6 (CH), 116.6 (CH_2), 117.7 (q, CF_3, $J = 288$ Hz), 132 (CH), 169.7 (CH), 175.5 (q, C=O, $J =$ 32 Hz) ppm; MS: m/z (%) = 197 (M^+, 34), 128 (100), 154 (50), 166 (48), 69 (48), 81 (30), 54 (27), 96 (21); IR (KBr): $\bar{\nu} = 3367$, 1568, 1255, 1191, 1128, 851, 726 cm^{-1}.

(Z)-1,1,1-Trifluoro-4-(2-hydroxyethylamino)-3-penten-2-one
(**8i**, $C_7H_{10}F_3NO_2$)
Mp 74–76°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.11$ (s, $2CH_2$), 2.90 (s, O–H), 3.52 (q, CH_2), 3.83 (q, CH_2), 5.34 (s, CH), 11.26 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 19.5$ (CH_3), 46.0 (CH_2), 60.5 (CH_2), 89.7 (CH), 117.7 (q, CF_3, $J = 288$ Hz), 170.4 (C), 174.8 (q, C=O, $J = 33$ Hz) ppm; MS: m/z (%) = 197 (M^+, 34), 128 (100), 154 (50), 166 (48), 69 (48), 81 (30), 54 (27), 96 (21); IR (KBr): $\bar{\nu} = 3367$, 1568, 1255, 1191, 1128, 851, 726 cm^{-1}.

(Z)-4-Ethylamino-1,1,1-trifluoro-3-penten-2-one
(**8j**, $C_7H_{10}F_3NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.30$ (t, CH_3), 2.08 (s, CH_3), 3.38 (qui, CH_2), 5.31 (s, CH), 11.09 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 14.6$ (CH_3), 18.9 (CH_3), 38.5 (CH_2), 89.0 (CH), 117.6 (q, CF_3, $J = 287$ Hz), 169.3 (C), 172.2 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 181 (M^+, 49), 112 (100), 94 (50), 69 (27), 138 (8); IR (KBr): $\bar{\nu} = 1614$, 1441, 1298, 1242, 1189, 1117, 881, 741 cm^{-1}.

(E)-4-Diethylamino-1,1,1-trifluoro-3-buten-2-one
(**9b**, $C_8H_{12}F_3NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.26$ (t, $2CH_3$), 3.38 (q, $2CH_2$), 5.32 (d, $J = 12$ Hz, CH), 7.88 (d, $J = 12$ Hz, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 11.4$ (CH_3), 14.4 (CH_3), 43.3 (CH_2), 51.1 (CH_2), 86.8 (CH), 117.7 (q, CF_3, $J =$ 290 Hz), 154.8 (C), 176.9 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 195 (M^+, 28), 126 (100), 56 (47), 69 (32), 195 (28), 108 (28), 82 (28); IR (KBr): $\bar{\nu} = 2983$, 1576, 1262, 1133, 1083, 880, 709 cm^{-1}.

(Z)-1,1,1-Trifluoro-4-Phenylamino-3-buten-2-one
(**9k**, $C_{10}H_8F_3NO$)
Mp 90–92°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 5.65$ (d, $J = 7$ Hz, CH), 6.83 (d, $J = 7$ Hz, CH), 7.12–7.11 (m, 5H, arom), 11.48 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 89.9$ (CH), 119.2 (q, CF_3, $J = 288$ Hz), 117.3 (C), 125.7 (CH), 129.9 (2CH), 138.7 (2CH), 149.7 (CH), 179.3 (q, C=O, $J = 34$ Hz) ppm; MS: m/z (%) = 215 (M^+, 30), 146 (100), 77 (30), 91 (20), 51 (20), 117 (14); IR (KBr): $\bar{\nu} = 3250$, 1601, 1555, 1280, 894, 757 cm^{-1}.

(E)-4-Diethylamino-1,1,1-trifluoro-4-phenyl-3-buten-2-one
(**10k**, $C_{14}H_{16}F_3NO$)
Mp 87–89°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.05$ (t, CH_3), 1.36 (t, CH_3), 3.10 (q, CH_2), 3.52 (q, CH_2), 5.42 (s, CH), 7.17–7.43 (5H, arom) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 11.3$ (CH_3), 13.3 (CH_3), 44.2 (CH_2), 44.6 (CH_2), 86.8 (CH), 109.6 (CH), 109.5 (C), 117.5 (q, CF_3, $J = 288$ Hz), 126.2 (2C), 127.2 (2C), 135.5 (C), 167.2 (C), 174.7 (q, C=O, $J = 32$ Hz) ppm; MS: m/z (%) = 270 (M^+, 25), 202 (100), 104 (68), 77 (34), 149 (19), 56 (17); IR (KBr): $\bar{\nu} = 2977$, 1654, 1522, 1293, 1132, 900, 786 cm^{-1}.

(Z)-4-Benzylamino-1,1,1-trichloro-3-penten-2-one
(**11a**, $C_{11}H_{10}Cl_3NO$)
Mp 87–90°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.51$ (s, CH_2), 7.14 (d, $J = 7$ Hz, 1H), 7.26–7.39 (m, 5H, arom), 10.95 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 19.8$ (CH_3), 86.9 (CH), 97.2 (CCl_3), 126.9 (C), 128 (2CH), 128.9 (2CH), 136 (CH), 168.8 (C), 180.5 (C=O) ppm; MS: m/z (%) = 291

(M^+, 8), 228 (30), 174 (100), 91 (96), 65 (60); IR (KBr): $\bar{\nu} = 1596$, 1310, 1224, 885, 835, 741, 718 cm^{-1}.

(Z)-1,1,1-Trichloro-4-phenylamino-3-penten-2-one
(**11b**, $C_{11}H_{10}Cl_3NO$)
Mp 83–84°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.15$ (s, CH_3), 5.88 (s, CH), 7.17–7.41 (m, 5H arom), 12.14 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 20.6$ (CH_3), 88.3 (CH), 96.9 (CCl_3), 125.1(C), 127.0 (2CH) 129.4 (2CH), 137.3 (CH), 167.0 (CH), 180.2 (C=O) ppm; MS: m/z (%) = 278 (M^+, 5), 160 (100), 77 (26), 51 (16), 117 (11), 214 (10), 178 (8); IR (KBr): $\bar{\nu} = 3196$, 1616, 1320, 1259, 1200, 1154, 738, 556 cm^{-1}.

(E)-1,1,1-Trichloro-4-diethylamino-3-penten-2-one
(**11k**, $C_9H_{14}Cl_3NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.25$ (t, $2CH_3$), 2.58 (s, CH_3), 3.42 (qua, $2CH_2$), 5.69 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 16.3$ ($2CH_3$), 45.2 ($2CH_2$), 84.1 (CH), 99.9 (CCl_3), 166.5 (C), 178.5 (C=O) ppm; MS: m/z (%) = 258 (M^+, 2), 140 (100), 194 (19), 122 (15); IR (KBr): $\bar{\nu} = 2977$, 1652, 1542, 1354, 1129, 1043, 804, 774, 682, 661 cm^{-1}.

(E)-1,1,1-Trichloro-4-pyrrolidin-1-yl-3-penten-2-one
(**11l**, $C_9H_{12}Cl_3NO$)
Mp 108–110°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.02$ (qui, $2CH_2$), 2.59 (s, CH_3), 3.42 (t, CH_2), 3.56 (t, CH_2), 5.58 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 18.2$ (CH_3), 24.7 (CH_2), 25.1 (CH_2), 48.8 (CH_2), 49.0 (CH_2), 85.0 (CH), 99.7 (CCl_3), 165.8 (C), 178.6 (C=O) ppm; MS: m/z (%) = 256 (M^+, 3), 138 (100), 192 (14), 120 (9); IR (KBr): $\bar{\nu} = 1642$, 1544, 1302, 1162, 1028, 817, 801, 660 cm^{-1}.

(Z)-4-Benzylamino-1,1,1-trichloro-3-buten-2-one
(**12a**, $C_{11}H_{10}Cl_3N$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.50$ (s, CH_2), 5.73 (d, $J = 7$ Hz, CH), 7.02 (d, $J = 7$ Hz, CH), 7.14–7.39 (m, 5H arom), 10.97 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 53.1$ (CH_2), 85.1 (C), 96.6 (CCl_3), 127.4 (C), 128.2 (2CH), 129.0 (2CH), 136.1 (CH), 157.2 (CH), 182.2 (C=O) ppm; MS: m/z (%) = 277 (M^+, 4), 91 (100), 160 (53), 65 (18); IR (KBr): $\bar{\nu} = 2927$, 1646, 1580, 1292, 813, 738 cm^{-1}.

(Z)-1,1,1-Trichloro-4-phenylamino-3-buten-2-one
(**12b**, $C_{10}H_8Cl_3NO$)
Mp 102–104°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 5.97$ (d, $J = 7$ Hz, CH), 7.11 (d, $J = 7$ Hz, CH), 7.17–7.68 (m, 5H arom), 11.35 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 88.0$ (CH), 116.9 (CCl_3), 125.1 (2CH), 129.8 (2CH), 138.9 (CH), 148.9 (CH), 182.8 (C=O) ppm; MS: m/z (%) = 263 (M^+, 5), 146 (100), 77 (29), 51 (20), 117 (18), 200 (14), 91 (13); IR (KBr): $\bar{\nu} = 1667$, 1539, 1480, 1302, 818, 759, 718 cm^{-1}.

(E)-4-(Butylmethylamino)-1,1,1-trichloro-3-buten-2-one
(**12c**, $C_9H_{14}Cl_3NO$)
Mp 55–57°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.95$ (t, CH_3), 1.33 (sex, CH_2), 1.61 (qui, $2CH_2$), 2.94 (s, CH_3), 3.35 (t, CH_2), 5.59 (d, $J = 12$ Hz, CH), 7.83 (d, $J = 12$ Hz, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 13.5$ (CH_3), 19.5 (CH_2), 27.8 (CH_2), 35.7 (CH_3), 58.5 (CH_2), 84.7 (CH), 98.0 (CCl_3), 156.8 (CH), 180.7 (C=O) ppm; MS: m/z (%) = 257 (M^+, 28), 140 (100), 84 (24), 55 (19), 194 (17); IR (KBr): $\bar{\nu} = 2959$, 2931, 2872, 1656, 1557, 1278, 1117, 806, 764, 701, 665 cm^{-1}.

(Z)-4-Benzylamino-1,1-dichloro-3-penten-2-one
(**13a**, $C_{12}H_{13}Cl_2NO$)
Mp 74–77°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.08$ (s, CH_3), 4.52 (s, CH_2), 5.41 (s, CH), 5.85 (s, CH) 7.26–7.33 (m, 5H arom), 11.11 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 19.4$ (CH_3), 47.3 (CH_2), 89.7 (CH), 92.0 (CCl_3), 126.9 (C), 127.8 (2CH), 128.9 (2CH), 136.3 (C), 168.2 (C), 184.0 (C=O) ppm; MS: m/z (%) = 257 (M^+, 5), 91 (100), 174 (52), 65 (17); IR (KBr): $\bar{\nu} = 1605$, 1307, 1225, 888, 831, 737, 723 cm^{-1}. Crystallographic data for **13a** were deposited at the Cambridge Crystallographic Data Center (CCDC 649397). Copies of the data can be obtained, free of charge, on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

(E)-4-(Butylmethylamino)-1,1-dichloro-3-penten-2-one
(**13c**, $C_{10}H_{17}Cl_2NO$)
Oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.97$ (t, CH_3), 1.35 (sex, CH_2), 1.59 (qui, CH_2), 2.57 (s, CH_3), 3.04 (s, CH_3), 3.36 (t, CH_2), 5.42 (s, CH), 5.80 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 13.7$ (CH_3), 19.83 (CH_3), 19.86 (CH_2), 30.4 (CH_2), 38.7 (CH_3), 51.9 (CH_2), 72.7 (C), 87.5 (CH), 166.4 (CH), 183.3 (C=O) ppm; MS: m/z (%) = 237 (M^+, 3), 154 (100), 56 (72), 112 (17), 82 (17), 136 (11), 174 (10); IR (KBr): $\bar{\nu} = 2977$, 1652, 1542, 1354, 1129, 1043, 804, 774, 682, 661 cm^{-1}.

(E)-1,1-Dichloro-4-morpholin-4-yl-3-penten-2-one
(**13m**, $C_9H_{13}Cl_2NO_2$)
Mp 96–98°C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.56$ (s, CH_3), 3.51 (qua, $2CH_2$), 3.76 (qua, $2CH_2$), 5.53 (s, CH), 5.79 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 16.1$ (CH_3), 46.5 (CH_2), 66.1 (CH_2), 72.4 (C), 88.7 (CH), 165.9 (CH), 184.4 (C=O) ppm; MS: m/z (%) = 237 (M^+, 6), 154 (100), 55 (33), 96 (22), 174 (12), 126 (7), 202 (5); IR (KBr): $\bar{\nu} = 3012$, 2866, 1633, 1260, 1114, 1002, 782, 690 cm^{-1}. Crystallographic data for **13m** were deposited at the Cambridge Crystallographic Data Center (CCDC 649396). Copies of the data can be obtained, free of charge, on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

1. a) Martins MAP, Cunico W, Pereira CMP, Flores AFC, Bonacorso HG, Zanatta N (2004) Curr Org Synthesis 1:391, and references therein; b) Laurent A, Diab J, Dréan IL (1997) J Fluorine Chem 84:145; c) Sloop JC, Bumgardner CL, Loehle WD (2002) J Fluorine Chem 118:135
2. Bonacorso HG, Wentz AP, Lourega RV, Cechinel CA, Moraes TS, Coelho HS, Zanatta N, Martins MAP, Hörner M, Alves SH (2006) J Fluorine Chem 12:1066
3. Chroust K, Pavlová M, Prokop Z, Mendel J, Božková K, Kubát Z, Zajičková V, Damborský J (2007) Chemosphere 67:152
4. Lyle FR (1985) US Patent 5 973 257; Chem Abstr 65:2870
5. a) Epifano F, Genovese S, Curini M (2007) Tetrahedron Lett 48:2717; b) Lin J, Zhang L-F (2007) Monatsh Chem 138:77; c) Gholap AR, Chakor NS, Daniel T, Lahoti RJ, Srinivasan KV (2006) J Mol Catal A: Chem 245:37; d) Zhang Z-H, Hu J-Y (2006) J Braz Chem Soc 17:1447; e) Lyutenko NV, Gerus II, Kacharov AD, Kukhar VP (2003) Tetrahedron 59:1731; f) Liu J-T, Yang X-J, Zhao F-L (2004) J Fluorine Chem 125:415; g) Das B, Venkateswarlu K, Majhi A, Reddy MR, Reddy KN, Rao YK, Ravikumar K, Sridhar B (2006) J Mol Catal A: Chem 246:276
6. a) Hojo M, Masuda R, Okada SS, Narumiya H, Marimoto K (1989) Tetrahedron Lett 30:6173; b) Zanatta N, Flores DC, Amaral SS, Bonacorso HG, Martins MAP, Flores AFC (2005) Synlett 20:3079; c) Zanatta N, Squizani AMC, Fantinel L, Nachtigall FM, Bonacorso HB, Martins MAP (2002) Synthesis:2409
7. a) Martins MAP, Peres RL, Fiss GF, Dimer FA, Mayer R, Frizzo CP, Marzari MRB, Zanatta N, Bonacorso HG (2007) J Braz Chem Soc 18:1486; b) Martins MAP, Pereira CMP, Cunico W, Moura S, Rosa FA, Peres RL, Machado P, Zanatta N, Bonacorso HG (2006) Ultrason Sonochem 13:364; c) Martins MAP, Cunico W, Brondani S, Peres RL, Zimmermann N, Rosa FA, Fiss GF, Zanatta N, Bonacorso HG (2006) Synthesis 9:1485; d) Martins MAP, Frizzo CP, Moreira DN, Rosa FA, Marzari MRB, Zanatta N, Bonacorso HG (2007) Catal Commun, doi: 10.1016/j.catcom.2007.11.037
8. Martins MAP, Guarda EA, Frizzo CP, Scapin E, Beck P, Costa AC, Zanatta N, Bonacorso HG (2006) J Mol Catal A: Chem 266:100
9. Moreira DN, Longhi K, Frizzo CP, Zanatta N, Bonacorso HG, Martins MAP (2007) Monatsh Chem, doi: 10.1007/s00706-008-0874-8
10. Olivier-Bourbigou H, Magna L (2002) J Mol Catal A: Chem 182–183:419
11. a) Wasserscheid P, Welton T (eds) (2002) Ionic Liquids in Synthesis, Wiley-VCH Verlag, Stuttgart; b) Xiao Y, Sanjay VM (2005) J Organomet Chem 690:3609
12. Gerus II, Gorbunova MG, Vdovenko SI, Yagupolskii YL (1990) Zh Org Khim 26:1877 [J Org Chem USSR, 1990:26, (Engl. Transl.)]
13. Pazenok SV, Gerus II, Chaika EA, Yagupolskii YL (1989) Zh Org Khim 25:379 [J Org Chem USSR, 1989: 25 (Engl. Transl.)
14. Mali KS, Dutt GB, Mukherjee T (2005) J Chem Phys 123:174504
15. Aki SNVK, Brennecke JF, Samanta A (2001) Chem Commun:413
16. a) Wakai C, Oleinikova A, Ott M, Weingärtner HJ (2005) Phys Chem B 109:17028; b) Wakai C, Oleinikova A, Weingärtner HJ (2006) J Phys Chem B 110:5824
17. Sheldrick GM, SHELXS-97 (1997) Program for Crystal Structure Solution, University of Göttingen, Germany
18. Sheldrick GM, SHELXL-97 (1997) Program for Crystal Structure Refinement, University of Göttingen, Germany
19. Farrugia LJ, ORTEP-III for *Windows* (1997) J Appl Crystallogr 30:565
20. Souza R, Suarez PAZ, Consorti CS, Dupont J (2002) Org Synth 79:236