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ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 587–594
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Synthesis of trifluoromethyl-imines by solid acid/superacid catalyzed microwave assisted approach

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Received 6 November 2006; received in revised form 22 January 2007; accepted 24 January 2007
Available online 2 February 2007

Abstract

A new solid acid/superacid catalyzed microwave assisted synthesis of trifluoromethyl-imines is described. Various α,α,α-trifluoromethylketones react readily with primary amines to produce the corresponding imines. Two different strategies have been employed; one is the application of microwave irradiation coupled with solvent-free solid acid catalysis. The other method, for highly deactivated substrates includes the use of a pressure vessel at 175 °C temperature, with solid superacid catalysis. Using the solid acid K-10 montmorillonite or the superacidic perfluorinated resinsulfonic acid Nafion-H, a wide variety of trifluoromethylated imines have been synthesized using the above methods. The products have been isolated in good to excellent yields and high selectivities. This new environmentally friendly synthetic methodology provides significantly higher yields than traditional methods during relatively short reaction times for the preparation of the target compounds.

Keywords: Trifluoromethyl; Imine; Clay; Solid acids; Solid superacid; Catalysis; Microwave irradiation

1. Introduction

Solid acids and solid superacids are among the most important and widely used catalysts in industrial and laboratory practice [1]. Traditionally, acid catalyzed reactions were carried out using mineral acids (e.g. HCl, H_2SO_4, etc.), or Lewis acids ($AlCl_3$, $TiCl_4$, etc.). However, due to the increasing awareness of environmental impact and safety factors in laboratory and industrial processes, solid acid alternatives have been developed [2]. Solid acid catalyzed processes are gradually replacing most industrial acid catalyzed processes. These catalysts are safer than mineral acids, easy to store and handle, the workup procedure, namely the catalyst separation, is easy and they produce no waste. Several different types of solid acid catalysts include: acidic clays, zeolites, silica-occluded heteropoly acids, sulfonated polystyrenes (Dowex, Amberlyst) and polysiloxanes (Deloxane), and various forms of perfluorinated sulfonic acid ion exchange resins, such as Nafion-H® [3].

One particularly important area of their application is the synthesis of organofluorine compounds. Organofluorine chemistry has received extensive attention especially in the pharmaceutical industry and in materials science due to the unique properties of fluorinated compounds [4]. Trifluoromethylated compounds are of particular interest as the strong electron-withdrawing effect of CF_3 group contributes to a number of biologically important molecular properties. For example it results in significant increase in lipophilicity of the molecule, which is a very important feature in drug delivery. The different medicinal applications of fluorinated organic molecules are widespread. Some of the most well known fluorine containing drugs are Prozac® (anti-depressant), Diflucan® (anti-fungal agent), Casodex® (anti-cancer agent) and Desflurane (inhalation anesthetic) [4]. Recent, new

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doi:10.1016/j.jfluchem.2007.01.011

application of organofluorine compounds, include their use as potential therapeutics for HIV, cancer or Alzheimer's disease. Accordingly, the synthesis of these molecules is in great demand [5] and the search for new biologically active fluorinated compounds is in the forefront of organic and medicinal chemistry [6]. Trifluoromethylated imines are particularly important as precursor products or as building blocks for the synthesis of biologically active molecules [7]. Unfortunately the synthesis of these compounds is relatively difficult using traditional methods. One frequently used method is the PTSA catalyzed condensation reaction of trifluoromethyl ketones with various amines, such benzylamines or anilines. The very strong electron withdrawing nature of the trifluoromethyl group stabilizes the tetrahedral hemiaminal intermediate in the target reaction similarly to hemiacetals that can be easily isolated [7e]. The same electron withdrawing effect destabilizes the carbocationic intermediate. Since the thermodynamic stability of the carbocationic intermediate is significantly lower than that of the hemiaminal, the reaction should be reasonably endothermic. To overcome this energy barrier requires the use of high temperature or other non-classical activation methods.

Over the past two decades, microwave assisted organic synthesis has emerged as important area and attracted significant attention as indicated by extensive number of publications [8]. It is a convenient and time saving method, which promotes the application of environmentally benign approaches such as solvent free and heterogeneous catalytic reaction conditions [9].

Herein, we describe a novel, environmentally benign approach for the synthesis of a wide variety of α,α,α-trifluoromethyl-imines. The combination of microwave irradiation and solid acid/superacid catalysis provides high yields while reasonably decreasing the reaction time and also minimizing the formation of undesirable byproducts. The major advantages of this method are short reaction times, high yields and selectivities and ease of work-up and isolation of products.

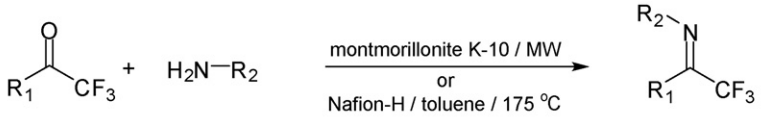
2. Results and discussion

In response to the increasing industrial importance of imines, much research is directed toward the development of catalytic methods for their preparation. Many useful methods have been developed for the synthesis of imines from the corresponding carbonyl compounds and amines using both traditional liquid and contemporary "green" solid acid catalysts [10]. Effective synthesis of trifluoromethylated imines from highly deactivated trifluoromethyl ketones, however, is still an important challenge. Our goal was to develop an efficient and at the same time, environmentally benign method for the synthesis of the target compounds. The condensation of 1,1,1-trifluoroacetophenone with benzylamine has been selected as a model reaction to optimize the process. For comparison, the reaction has been carried out using a traditional synthetic approach. Initially, the reaction was performed in toluene using *p*-toluenesulfonic acid (PTSA) as a catalyst under reflux conditions (110 °C) [11]. This reaction took place extremely slowly providing moderate yield (~70%) after 7 days of reflux (Table 1). To improve the reaction rate we carried out the reaction using the same reactants, catalyst and solvent in a closed pressure tube at 175 °C. Despite the significant increase in temperature the yield was only 25% after 24 h (Table 1). This indicates the need for an alternative approach that provides higher yield in a more reasonable time frame. Our strategy was to apply solid acid catalysis instead of PTSA.

Table 1
Summary of experimental conditions and product yields in condensation of 1,1,1-trifluoroacetophenone with benzylamine

Catalyst	Method of heating	Other	Reaction time (h)	Yield[a] (%)
PTSA	Reflux (110 °C)	Toluene	168	75
PTSA	175 °C	Pressure tube, toluene	24	24
Nafion-H	175 °C	Pressure tube, toluene	48	80
Nafion-H	Microwave irradiation, 175 °C	A/K[b] ratio = 1	0.5	50
K-10	Microwave irradiation, 175 °C	Int. cooling, A/K ratio = 1	1.5	50
K-10	Microwave irradiation, 175 °C	Ar flow, A/K ratio = 1	0.33	5
K-10	Microwave irradiation, 175 °C	A/K ratio = 1.5	0.45	95
–	175 °C	No solvent, pressure tube	24	17
–	Microwave irradiation, 175 °C	A/K ratio = 1.5	0.45	8
PTSA	A/K ratio = 1.5	A/K ratio = 1.5	0.45	22

[a] GC-yield.
[b] A/K—amine/ketone ratio.



R_1 = Ph, CH_2Ph, 1-naphthyl, 2-pyrrolyl, 2-thiophenyl, 3-indolyl, CH_2COOEt, CH_3
R_2 = Ph, substituted-Ph, CH_2Ph, susbtituted-CH_2Ph, 2-naphthyl, *o*-NH_2Ph, *o*-NH_2PhCH_3

Scheme 1. Solid acid catalyzed condensation of various amines and trifluoromethylated ketones.

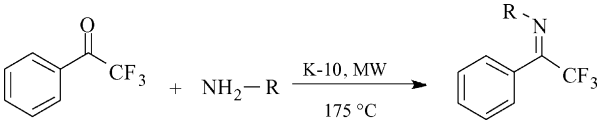
Based on our experience, K-10 montmorillonite and the superacidic perfluorinated resinsulfonic acid Nafion-H were selected as catalysts (Scheme 1).

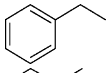
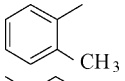
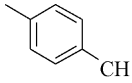
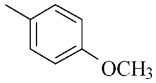
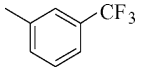
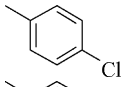
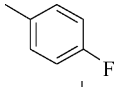
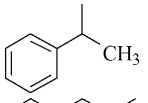
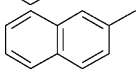
Both catalysts are well-known and widely used in a variety of organic transformations [3,12]. K-10 montmorillonite is a solid acid of moderate acid strength. Its Hammett constant is $H_0 = -8$, which is similar to that of concentrated HNO_3. Its high surface area (250 m^2/g), however, makes it a useful and active catalyst. Both its structural features [13] and synthetic potential [12] have been extensively studied. In contrast, Nafion-H, another widely studied solid acid, possesses very strong acidity [3]. In fact, it is a solid superacid with a Hammett constant of $H_0 = -12.2$ [3]. The above model reaction has been studied using these two catalysts under widely varied experimental conditions. The results are summarized in Table 1.

Beside the catalyst, the use of microwave irradiation and high temperature reaction in a pressure tube vessel were the most significant changes implemented. The microwave assisted reactions have been carried out under solvent-free conditions. The reactants and the catalyst were stirred in ether for 10 min, and then the solvent was removed providing a dry mixture of catalyst with reactants evenly distributed on its surface. This mixture was placed into the microwave cavity and irradiated for a specific time at constant temperature. It was observed that a traditional reaction at 175 °C using Nafion-H as catalyst resulted in only 5% improvement in yield, however, its use significantly reduced reaction times. The Nafion-H catalyzed microwave assisted reaction showed promise, unfortunately, the catalyst formed a dark melt and completely lost activity. Using the thermally stable K-10 as catalysts, the reaction gave nearly quantitative yield (95%) in very short time of irradiation (25 min). It is worth noting that both K-10 and Nafion-H are strong acids; however, the density of the acid centers is relatively low. Depending on the accessibility of the acid center to individual substrates, the amount of available acid centers varies between 1–5 mmol/kg (based on ion-exchange capacities) [3,12,13]. It means, for instance, that the 0.5 g K-10 used had about 5–25 $\times$ 10^{-4} mmol acid centers compare to 1–1.5 mmol reactants. As such, these materials, although used in relatively large amount are still considered as catalysts. Based on the results obtained under optimized reaction conditions, the scope of the microwave-assisted approach has been extended by using 1,1,1-trifluoroacetophenone and wide selection of substituted amines as reaction partners. The results are summarized in Table 2.

The data indicate that trifluoroacetophenone readily undergoes condensation with a wide variety of amines including benzylamine and aniline derivatives providing yields mostly higher than 90%. During the reaction the desired products were formed exclusively, with no byproduct formation. Analysis of the products by both capillary gas chromatography and ^{19}F NMR spectroscopy indicated the formation of a single isomeric product instead of the mixture of two stereoisomers. Many of these products have already been synthesized and described in the literature [14]. We have used this method to synthesize authentic compounds and compare them to our products. Based on this comparison the products have been identified as (*E*)-isomers throughout this study.

Table 2
K-10 catalyzed microwave assisted synthesis of trifluoromethylated imines from 1,1,1-trifluoroacetophenone and various amines at 175 °C



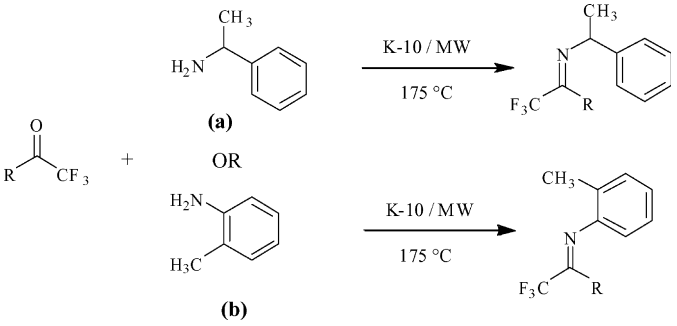
Entry	R	Time (min)	Yield (%)[a]
1		30	90
2		45	95
3		21	95
4		30	60
5		30	95
6		50	90
7		30	95
8		30	91
9		20	95
10		30	92

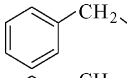
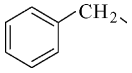
[a] Isolated yields.

These results certainly initiated studies on wide variety of trifluoromethyl ketones and amines, as well. Table 3 summarizes the results obtained in the condensation of aryl-trifluoromethyl ketones with methylbenzylamine and *o*-methylaniline. In Table 4 the scope of the reaction was further widened using aryl- and alkyl-trifluoromethyl ketones, ethyl 3,3,3-trifluoroacetoacetate with *o*-phenylenediamines.

Tables 3 and 4 indicate that the reaction can be carried out effectively with a diverse group of trifluoromethyl ketones and amines. The yields range from good to excellent during short reaction times. Several sensitive substrates such as 2-trifluoroacetylpyrrole and 2-trifluoroacetylthiophene, which tend to polymerize under strongly acidic conditions readily underwent condensation under the relatively mild solid acid/microwave conditions. Ethyl trifluoroacetoacetate and other trifluoromethyl ketones provided the cyclic products in excellent yields and selectivity with two types of phenylenediamines in very short reaction times (Table 4). The cyclization reaction occurred between the second amino and the ethoxy groups. It is also clear that despite the presence of two amino

Table 3
K-10 catalyzed microwave assisted synthesis of trifluoromethylated imines from trifluoromethyl ketones and various amines at 175 °C



Entry	R	Amine	Time (min)	Yield (%)[a]
1		**a**	36	85
2		**b**	30	87
3		**a**	50	95
4		**b**	60	88
5		**a**	78	53
6		**b**	69	90

[a] Isolated yields.

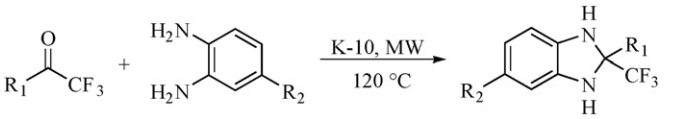
groups in phenylenediamines, only one is able to react to form imine with simple trifluoromethyl ketones, the other amino group becomes highly deactivated. Thus, the first reaction proceeds with high rate, then cyclization takes place, the selectivity is exclusive for the corresponding cyclic product even after extended period of irradiation. Most likely one amino group activates the other one through the continuous conjugation and increases the nucleophilicity of the reacting amino group. Hence, the reaction rates are significantly higher than that of other amines regardless of the ketone used. After the condensation, the strongly electron withdrawing effect of CF_3 will dominate and deactivate the remaining amino group toward condensation.

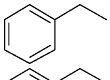
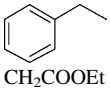
We have also studied the possible reuse of the K-10 montmorillonite. The catalyst appeared to be active even after the fifth consecutive run, although we have observed a gradual decrease in product yields. It is most likely due to the formation of irreversibly adsorbed carbonaceous deposits on the catalyst, which can be removed by high temperature (∼300 °C) aerobic heat treatment.

During these studies we have observed that few CF_3-ketones, such as 9-trifluoroacetyl-anthracene, 1-trifluoroacetylnaphthalene and 3-trifluorocetylindole have shown strong resistance toward reaction. Only 1-trifluoroacetylnaphthalene underwent K-10 catalyzed reaction with a vast excess of amine and much longer irradiation period. The remaining two ketones are so deactivated that they do not show any product formation even after excess amine or extended time of irradiation. The use of the solid superacidic perfluorinated resinsulfonic acid, Nafion-H, partially overcame the problem of reactant deactivation. As Nafion-H appeared to be unstable under microwave irradiation (Table 1), the reactants and Nafion-H were mixed in toluene and heated up in a pressure tube to 175 °C by conventional heating. Nafion-H under these condition provided some product formation but in only low yields in the case of trifluoroacetylnaphthalene and indole, respectively. In the case of trifluoroacetylnaphthalene a subsequent isomerization has also been observed. With 9-trifluoroacetylanthracene the product was obtained in traces only. It is very likely that the presence of an orthogonal C–H bond, e.g. at the naphthyl 8-position interferes with the stabilization of the imine form, leading to an increased stability of the tetrahedral intermediate. The important role of this interaction is clearly supported by the data, that trifluoroacetylnaphthalene with one such interaction gives low yield, while 9-trifluoroacetylanthracene with two such interactions gave the product only in traces.

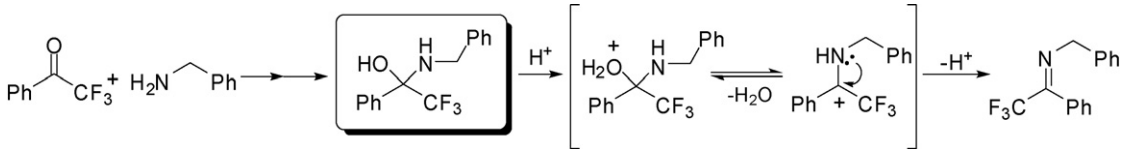
The reaction follows the regular mechanism of acid catalyzed condensation reactions. The CF_3 moiety has a very strong electron withdrawing character, and coupled with the carbonyl oxygen's electron withdrawing nature, the carbonyl C carries a strong partial positive charge that is significantly greater than that of a ketone without α-CF_3 group. This enhanced δ+ charge, in fact, activate the first step in the mechanism, namely the nucleophilic attack on the C providing the highlighted intermediate. However, the subsequent protonation and water elimination of the key intermediate is not favored as the strong electron withdrawing effect of CF_3 destabilizes the carbocationic intermediate (Scheme 2). As a result, the water elimination is the rate-determining step of the condensation reaction in the case of trifluoromethyl ketones.

Table 4
K-10 catalyzed microwave assisted condensation of various trifluoromethyl-ketones and a ketoester with *o*-phenylenediamines at 175 °C



Entry	R_1	R_2	Time (min)	Yield (%)[a]
1		H	1	95
2		CH_3	2	90
3		H	1	92
4		CH_3	2	82
5	CH_2COOEt	H	1	90
6	CH_2COOEt	CH_3	1	92
7	CH_3	H	1	88
8	CH_3	CH_3	3	90

[a] Isolated yields.



Scheme 2. The strongly deactivated dehydration step during the condensation of trifluoromethyl ketones with primary amines.

3. Conclusion

In conclusion, a novel, effective solid acid/superacid catalyzed, economic and environmentally benign method for synthesis of novel trifluoromethylated Schiff bases have been developed. The combination of microwave irradiation and solid acid catalysis greatly reduced reaction time, while improving the yields and making the synthesis of a diverse group of CF_3 imines possible. The short reaction time, mostly solvent-free reaction conditions, ease of product isolation, and the safe nature of the catalysts make the process an attractive alternative for the synthesis of trifluoromethyl-imines in an environmentally benign manner.

4. Experimental

All trifuoromethyl ketones, and amines were purchased from Aldrich and used without further purification. K-10 was a Fluka product. Nafion-H was purchased from Aldrich as a potassium salt and was acidified by successive treatments with HCl and HNO_3 according to the literature [3e]. The $CDCl_3$ used as solvent for NMR studies and the $CFCl_3$, used as reference compound in ^{19}F NMR measurements were obtained form Aldrich. Other solvents used in synthesis were Fisher products with a minimum purity of 99.5%.

The ^{1}H, ^{13}C and ^{19}F spectra were obtained on a 400 MHz superconducting Varian Innova 400 NMR spectrometer, in $CDCl_3$ solvent with tetramethylsilane or the residual solvent signal of $CDCl_3$ as internal standards. $CFCl_3$ was used as internal standard for ^{19}F signals. The temperature was 25 °C (accuracy ±1 °C) and controlled by the Varian control unit. The mass spectrometric identification of the products have been carried out by a Shimadzu QP5050 gas chromatograph-mass spectrometer system (70 eV electron impact ionization) using a 30 m long DB-5 type column (J&W Scientific).

4.1. General procedure for the synthesis of trifluoromethylated imines by microwave assisted K-10 montmorillonite catalyzed condensation of trifluoromethyl ketones with primary amines

Trifluoromethyl ketone (1.0 mmol), amine (1.5 mmol) were dissolved in 3 mL of ether in a round-bottomed flask then K-10 (500 mg) was added. After 5 min stirring the solvent was evaporated under reduced pressure to get the dry mixture of reactants adsorbed on the catalyst's surface. The dry mixture was transferred to a reaction tube and irradiated in the microwave reactor (CEM Discover Benchmate) at 175 °C. During optimization the progress of the reaction was monitored by TLC and GCMS, then the optimized times were used for preparative reactions. After satisfactory conversion, ether was added to the cold mixture, and the product was separated from catalyst by filtration. The products have been isolated as crystals or oils and purified by flash chromatography.

4.2. General procedure for synthesis of trifluoromethylated imines using Nafion-H catalysis in a pressure tube

Trifluoromethylated ketone (1.0 mmol), amine (2.0 mmol) were dissolved with 2 mL of toluene in a Teflon screw-cap pressure tube and then Nafion-H (1 g) was added. The reaction mixture was then immersed into an oil bath preheated to 175 °C. The reaction mixture was stirred by magnetic stirrer and during optimization the progress was monitored by TLC, then the optimized times were used for preparative reactions. After satisfactory conversion, the product was separated from catalyst by filtration. The solvent was removed under vacuum. The oily residue was purified by flash chromatography to obtain the pure product.

4.3. Product characterization

4.3.1. N-[2,2,2-Trifluoro-1-phenylethylidene]aniline (Table 2, Entry-1)

Ref. [7(i)], ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 8.07 (d, $J = 8$ Hz, 1H), 7.54 (t, $J = 8$ Hz, 1H), 7.26 (m, 5H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.72 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 146.1, 130.4, 129.4, 128.9, 128.8, 128.7, 125.5, 120.7; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −70.4 (s, 3F). MS-$C_{14}H_{10}F_3N$ (249), *m/z* (%): 249 (M^+, 25), 180 (100), 77 (60).

4.3.2. 1-Phenyl-N-[2,2,2-trifluoro-1-phenylethylidene]methylamine (Table 2, Entry-2)

Ref. [14(a)], ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 8.07 (d, $J = 8$ Hz, 1H), 7.36 (m, 4H), 7.26 (m, 5H), 4.60 (s, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 138.2, 130.4, 129.1, 128.9, 128.8, 127.8, 127.8, 127.4, 57.0; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −71.3 (s, 3F). MS-$C_{15}H_{12}F_3N$ (263), *m/z* (%): 263 (M^+, 15), 194 (100), 159 (25), 91 (20).

4.3.3. 2-Methyl-N-[2,2,2-trifluoro-1-phenylethylidene]aniline (Table 2, Entry-3)

Ref. [7(j)], ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.18 (m, 5H), 6.92 (t, $J = 3$ Hz, 2H), 6.39 (d, $J = 7.6$ Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 130.3, 130.2, 129.0, 128.4, 128.2, 126.1, 125.1, 118.4, 118.0, 94.4, 17.7; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −69.9 (s, 3F). MS-$C_{15}H_{12}F_3N$ (263), *m/z* (%): 263 (M^+, 30), 194 (100), 91 (50).

4.3.4. 4-Methyl-N-[2,2,2-trifluoro-1-phenylethylidene]aniline (Table 1, Entry-4)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.20 (m, 5H), 6.98 (t, J = 3 Hz, 2H), 6.45 (t, J = 7.6 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 130.9, 130.2, 129.2, 128.2, 128.0, 126.1, 125.5, 118.9, 118.0, 91.3, 19.1, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −70.0 (s, 3F). MS-$C_{15}H_{12}F_3N$ (263), *m/z* (%): 263 (M^+, 40), 194 (100), 91 (30).

4.3.5. 4-Methoxy-N-[2,2,2-trifluoro-1-phenylethylidene]aniline (Table 2, Entry-5)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.29 (m, 5H), 7.22 (m, 2H), 6.71 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 157.9, 139.8, 130.9, 130.2, 128.9, 128.7, 123.5, 114.1, 55.8; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −70.4 (s, 3F). MS-$C_{15}H_{12}F_3NO$ (279), *m/z* (%): 279 (M^+, 30), 210 (100), 195 (15), 167 (15), 105 (10), 77 (20).

4.3.6. 3-(Trifluoromethyl)-N-[2,2,2-trifluoro-1-phenylethylidene]aniline (Table 2, Entry-6)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.30 (m, 5H), 7.02 (s, 1H), 6.86 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 147.7, 131.4, 130.8, 129.6, 129.5, 129.3, 128.9, 128.7, 123.8, 122.2, 122.0, 118.0; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −63.4 (s, 3F), −70.62 (s, 3F). MS-$C_{15}H_8F_6N$ (317), *m/z* (%): 317 (M^+, 20), 248 (100), 145 (40).

4.3.7. 4-Chloro-N-[2,2,2-trifluoro-1-phenylethylidene]aniline (Table 2, Entry-7)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.35 (m, 5H), 7.00 (m, 2H), 6.68 (m, 2H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 130.7, 129.8, 129.2, 128.8, 128.4, 128.3, 122.2; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref); δ (ppm) −70.0 (s, 3F). MS-$C_{14}H_9F_3ClN$ (283), *m/z* (%): 283 (M^+, 30), 214 (100), 111 (30), 75 (25).

4.3.8. 4-Fluoro-N-[2,2,2-trifluoro-1-phenylethylidene]aniline (Table 2, Entry-8)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.35 (m, 5H), 6.91 (m, 2H), 6.65 (m, 2H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 130.5, 128.9, 128.7, 122.8, 122.8, 119.1, 116.3, 115.8, 115.7, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −70.6 (s, 3F). MS-$C_{14}H_9F_4N$ (267), *m/z* (%): 267 (M^+, 25), 198 (100), 95 (40), 75 (15).

4.3.9. 1-Phenyl-N-[2,2,2-trifluoro-1-phenylethylidene]ethylamine (Table 2, Entry-9)

Ref. [7(d)], ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.46 (m, 5H), 7.25 (m, 5H), 4.53 (q, J = 6.4 Hz, 1H), 1.43 (dd, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 143.7, 130.5, 130.0, 128.7, 128.6, 127.6, 127.2, 126.4, 51.9, 24.5; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −71.5 (s, 3F). MS-$C_{16}H_{14}F_3N$ (277), *m/z* (%): 277 (M^+, 10), 193 (5), 105 (100), 77 (20).

4.3.10. N-[2,2,2-Trifluoro-1-phenylethylidene]naphth-2-ylamine (Table 2, Entry-10)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 8.07 (dd, J = 7.6, 0.8 Hz, 2H), 7.67 (m, 5H), 7.41 (m, 3H), 6.87 (dd, J = 2.0, 8.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 144.8, 135.7, 133.7, 131.4, 130.5, 130.3, 130.2, 130.1, 129.3, 128.9, 128.8, 128.0, 127.9, 126.7, 125.7, 120.6, 118.4; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −70.2 (s, 3F). MS-$C_{18}H_{12}F_3N$ (299), *m/z* (%): 299 (M^+, 50), 230 (100), 127 (95).

4.3.11. N-[1-Benzyl-2,2,2-trifluoroethylidene]-1-phenylethylamine (Table 3, Entry-1)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.27 (m, 10H), 5.28 (s, 2H), 4.83 (q, J = 6.4 Hz, 1H), 1.41 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 129.1, 128.7, 128.4, 127.4, 127.2, 126.6, 60.4, 33.3, 24.6; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −72.6 (s, 3F). MS-$C_{17}H_{16}F_3N$ (291), *m/z* (%): 291 (M^+, 10), 187 (25), 105 (100), 77 (10).

4.3.12. N-[1-Benzyl-2,2,2-trifluoroethylidene]-2-methylaniline (Table 3, Entry-2)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.18 (m, 9H), 2.27 (s, 2H), 1.24 (s, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 135.1, 133.5, 130.5, 129.6, 128.8, 128.4, 126.8, 120.7, 114.7, 59.8, 17.8; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −70.5 (s, 3F). MS-$C_{16}H_{14}F_3N$ (277), *m/z* (%): 277 (M^+, 75), 262 (10), 208 (40), 186 (100), 166 (30), 91 (60).

4.3.13. 1-Phenyl-N-[2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethylidene]ethylamine (Table 3, Entry-3)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 8.40 (s, 1H), 7.34 (m, 5H), 6.91 (m, 1H), 6.61 (m, 1H), 6.29 (m, 1H), 5.01 (q, J = 6.4 Hz, 1H), 2.15 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 129.1, 128.7, 127.4, 127.3, 126.6, 126.2, 122.5, 121.7, 115.9, 110.1, 60.1, 24.9; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −69.4 (s, 3F). MS-$C_{14}H_{13}F_3N_2$ (266), *m/z* (%): 266 (M^+, 10), 251 (15), 105 (100), 77 (20).

4.3.14. 2-Methyl-N-[2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethylidene]aniline (Table 3, Entry-4)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.91 (s, 1H), 7.26 (m, 2H), 7.11 (t, J = 7.6 Hz, 2H), 6.78 (t, J = 8 Hz, 1H), 6.70 (q, J = 1.2 Hz, 1H), 6.17 (quin, J = 2.4 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 131.7, 127.7, 126.2, 125.0, 124.4, 117.3, 110.2, 29.8; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −67.6 (s, 3F). MS-$C_{13}H_{11}F_3N_2$ (252), *m/z* (%): 252 (M^+, 30), 237 (100), 183 (50), 91 (60), 65 (45).

4.3.15. 1-Phenyl-N-[2,2,2-trifluoro-1-(2-thiophenyl)ethylidene]ethylamine (Table 3, Entry-5)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.55 (m, 2H), 7.34 (m, 5H), 7.18 (m, 1H), 7.11 (m, 1H), 4.90 (q, J = 6.8 Hz, 1H), 1.55 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 144.1, 136.2, 132.1, 129.5, 128.9, 127.2, 126.5, 121.1, 61.1, 24.5; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ

(ppm) −71.0 (s, 3F). MS-$C_{14}H_{12}F_3NS$ (283), *m/z* (%): 283 (M^+, 10), 199 (20), 105 (100), 77 (15).

4.3.16. 2-Methyl-N-[2,2,2-trifluoro-1-(2-thiophenyl)ethylidene]aniline (Table 3, Entry-6)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.58 (m, 2H), 7.45 (m, 1H), 7.18 (m, 2H), 7.01 (m, 1H), 6.62 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 147.2, 133.5, 133.1, 131.2, 129.5, 127.3, 126.8, 125.4, 119.5, 17.5; ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −68.0 (s, 3F). MS-$C_{13}H_{10}F_3NS$ (269), *m/z* (%): 269 (M^+, 50), 200 (100), 167 (35), 91 (50), 65 (45).

4.3.17. 2-Phenyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-1)

Ref. [7(j)], m.p. 94.3–95.9 °C. ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.59–7.63 (m, 2H), 7.39–7.46 (m, 4H), 6.66–6.98 (m, 3H), 4.42 (bs, 2H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 138.5, 137.8, 135.7, 130.3, 130.1, 129.6, 129.0, 126.1, 121.3, 118.3, 110.2, 110.1, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −82.9 (s, 3F). MS-$C_{14}H_{11}F_3N_2$ (264), *m/z* (%): 264 (M^+, 10), 243 (5), 223 (5), 195 (100), 92 (30), 65 (20).

4.3.18. 5-Methy-2-phenyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-2)

m.p. 95.3–96.8 °C. ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.61 (d, J = 7.6 Hz, 2H), 7.36–7.48 (m, 3H), 6.52–6.62 (m, 3H), 4.42 (bs, 2H) 2.22 (s, 3H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 138.8, 137.9, 135.9, 131.1, 130.1, 129.6, 129.3, 128.8, 125.9, 121.2, 110.9, 110.0, 21.0, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −83.0 (s, 3F). MS-$C_{15}H_{13}F_3N_2$ (278), *m/z* (%): 278 (M^+, 10), 257 (5), 237 (5), 209 (100), 104 (30), 77 (15).

4.3.19. 2-Benzyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-3)

m.p. 44.2–46.0 °C. ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.86–7.92 (m, 1H), 7.25–7.42 (m, 6H), 7.06–7.12 (m, 2H), 5.52 (s, 2H), 4.02 (bs, 2H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 141.4, 135.8, 135.0, 129.8, 129.2, 128.4, 128.1, 126.5, 125.7, 124.0, 121.9, 111.3, 48.6, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −61.9 (s, 3F). MS-$C_{15}H_{13}F_3N_2$ (278), *m/z* (%): 278 (M^+, 5), 209 (10), 187 (100), 167 (30), 116 (10), 91 (75).

4.3.20. 5-Methyl-2-benzyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-4)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 7.84–7.91 (m, 1H), 7.22–7.39 (m, 5H), 7.06–7.12 (m, 2H), 5.49 (s, 2H), 4.10 (bs, 2H), 2.21 (s, 3H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 138.4, 135.6, 135.2, 130.2, 128.2, 127.4, 127.2, 125.2, 121.0, 123.0, 110.4, 110.1, 48.4, 21.1, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −61.7 (s, 3F). MS-$C_{16}H_{15}F_3N_2$ (292), *m/z* (%): 292 (M^+, 10), 273 (5), 251 (5), 223 (15), 201 (100), 181 (15), 91 (50).

4.3.21. 2-Carbetoxymethylene-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-5)

m.p. 68.1–70.2 °C. ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 6.67–6.73 (m, 2H), 6.59–6.64 (m, 2H), 4.62 (bs, 2H), 4.10 (q, J = 7.2 Hz, 2H), 2.84 (s, 2H), 1.14 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 168.6, 137.9, 128.2, 125.4, 122.5, 121.1, 109.8, 81.0, 80.7, 61.8, 39.2, 14.0, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −85.1 (s, 3F). MS-$C_{12}H_{13}F_3N_2O_2$ (274), *m/z* (%): 274 (M^+, 15), 245 (5), 205 (50), 187 (45), 177 (25), 159 (50), 131 (100), 104 (10), 77 (10).

4.3.22. 2-Carbethoxymethylene-5-methyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-6)

m.p. 56.0–58.1 °C. ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 6.42–6.56 (m, 3H), 4.10 (q, J = 7.2 Hz, 2H), 2.83 (s, 2H), 2.19 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 168.4, 138.0, 135.3, 130.7, 130.5, 125.2, 121.0, 110.7, 109.6, 61.6, 38.9, 21.0, 13.8, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −85.2 (s, 3F). MS-$C_{13}H_{15}F_3N_2O_2$ (288), *m/z* (%): 288 (M^+, 40), 259 (10), 219 (100), 201 (70), 191 (40), 181 (15), 145 (90), 104 (10), 77

4.3.23. 2-Methyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-7)

m.p. 110.7–112.3 °C. ^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 6.68–6.74 (m, 2H), 6.58–6.63 (m, 2H), 3.90 (bs, 2H), 1.63 (q, J = 1.2 Hz, 3H). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 138.3, 129.0, 126.1, 123.3, 121.0, 109.8, 79.9, 79.6, 22.4, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −86.4 (s, 3F). MS-$C_9H_9F_3N_2$ (202), *m/z* (%): 202 (M^+, 10), 187 (5), 167 (10), 133 (100), 92 (40), 66 (15).

4.3.24. 2,5-Dimethyl-2-(trifluoromethyl)benzimidazoline (Table 4, Entry-8)

^{1}H NMR (399.81 MHz, $CDCl_3$), δ (ppm) 6.53 (d, J = 0.8 Hz, 2H, Ar), 6.43–6.46 (m, 1H, Ar), 3.78 (bs, 2H, NH_2), 2.21 (s, 3H, CH_3), 1.63 (q, J = 1.2 Hz, 3H, CH_3). ^{13}C NMR (100.53 MHz, $CDCl_3$), δ (ppm) 138.5, 135.7, 130.6, 120.8, 110.6, 109.6, 79.8, 79.5, 21.1, 21.0, ^{19}F NMR (376.19 MHz, $CDCl_3$, $CFCl_3$-Ref), δ (ppm) −86.5 (s, 3F). MS-$C_{10}H_{11}F_3N_2$ (216), *m/z* (%): 216 (M^+, 40), 201 (10), 181 (10), 147 (100), 131 (15), 106 (15), 90 (10).

Acknowledgements

Financial support provided by Michigan Technological University, University of Massachusetts Boston, Loker Hydrocarbon Research Institute (USC), the National Institute of Health (R-15 AG025777-02, B. T.) and the ACS Petroleum Research Fund (B. T.) is gratefully acknowledged.

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