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Sodium dithionite initiated reaction of pent-4-en-1-amines with fluoroalkyl iodides for the synthesis of 2-fluoroalkyl pyrrolidine derivatives

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ABSTRACT

Pent-4-en-1-amines are reactive to fluoroalkyl iodides with respect to sodium dithionite initiated free radical addition reactions. We report here the development of a novel and efficient synthesis of 2-fluoroalkyl pyrrolidine derivatives by sodium dithionite initiated one-pot reaction of pent-4-en-1-amines bearing various protecting groups with fluoroalkyl iodides. Among which, the *N*-benzyl-pent-4-en-1-amine exhibited the best tolerance toward the reaction condition in the present study, affording the desired adducts **3** in moderate to good yields of 65–85%.

1. Introduction

Because of the acknowledged effect of fluorine on the physical and chemical properties of organic compounds,[1,2] and in particular its potential influence on the biological activity of pharmaceutical and agrochemical compounds,[3–5] the synthesis of fluorine-containing compounds has fueled great interest among the academia. The addition of fluoroalkyl halide with unsaturated functional groups has provided a convenient method for the introduction of fluoroalkyl group into organic molecules. Such synthetic method has been used for the reaction of various fluoroalkyl halides with different alkenes and alkynes to afford the corresponding versatile adducts that simultaneously bear synthetically useful C–X bond that could be further converted to other fluorine-containing derivatives.[6]

Recently, on a continuing program in the chemistry of fluoroalkyl iodides, we have demonstrated sodium dithionite was effective as an initiator toward the addition–lactonization of 4-pentenoic acids with fluoroalkyl iodides, easily affording fluoroalkyl lactones.[7] On the basis of these results, we envisioned that the reaction of pent-4-en-1-amines with fluoroalkyl iodides would result in a series of novel 2-fluoroalkyl pyrrolidines via a tandem radical addition-intramolecular nucleophilic substitution process. However, many factors including the nucleophilicity of the amino group, spatial hindrance of the substrate and basicity of the acid-absorbed reagent might impact such reaction greatly, therefore problems, such as incomplete conversion of starting materials, termination at the addition stage or unsatisfactory side reactions may occur during this reaction process. To address the issues above, we report here a novel one-pot reaction of pent-4-en-1-amines with fluoroalkyl iodides initiated by sodium dithionite to afford 2-fluoroalkyl pyrrolidine derivatives.

2. Results and discussion

We began our investigation with the $Na_2S_2O_4$-mediated one-pot addition-intramolecular amination reaction of pent-4-en-1-amines with fluoroalkyl iodide according to the conditions in our previous reports.[7] Upon the addition of 3,3-dimethyl-pent-4-en-1-amine (**1a**) and ClC_2F_4I (**2a**) into the solution of CH_3CN/H_2O (3:1) at 25 °C, followed by introduction of the mixture of 1.4 equiv of $Na_2S_2O_4$ and 1.4 equiv of base ($NaHCO_3$ or NaOH) portion wise, a complicated mixture was afforded. To optimize the reaction condition for the formation of 2-fluoroalkyl pyrrolidines, a combination of N-protecting groups, fluoroalkyl iodides, and bases was then attempted.

2.1. Reaction of *N*-acyl-3,3-dimethyl-pent-4-en-1-amine (1b, 1c, 1d) with fluoroalkyl iodide

As shown in Table 1, by investigating the addition of *N*-acyl-3,3-dimethyl-pent-4-en-1-amine **1** (**1b**, **1c**, **1d**) with **2**, we found

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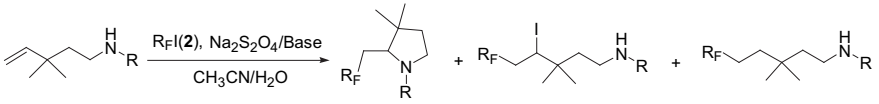
out that the electron-withdrawing *N*-acyl groups were unsatisfactory as a *N*-protecting group toward this reaction. However, there are still some notable points: (1) In the reaction of *N*-acetyl-3,3-dimethyl-pent-4-en-1-amine (**1b**) with **2a**, addition–reduction reaction occurred advantageously (entries 1, 2), giving **5** as the major product, whereas the reaction of **1b** with **2c** led to predominantly proceed addition reaction (entry 3), which gave **4** as the major product. (2) In the case of *N*-Cbz-3,3-dimethyl-pent-4-en-1-amine (**1c**) with **2**, the major adduct **4** was obtained with no desired product **3** and very few addition–reduction product **5** (entries 4–9), whereas addition between *N*-$PhSO_2$-3,3-dimethyl-pent-4-en-1-amine (**1d**) and **2** gave adduct **4** as major products with the minor generation of the desired 2-fluoroalkyl pyrrolidines (entries 10–15). (**3**) Although the product **4** was similarly given in the presence of both bases, however, the use of $NaHCO_3$ or NaOH was inclined to lead to the concomitant generation of product **5** or **3**, respectively.

2.2. Reaction of *N*-phenyl-3,3-dimethyl-pent-4-en-1-amine (1e) with fluoroalkyl iodide

We then attempted to prepare 2-fluoroalkyl pyrrolidines by using *N*-phenyl-3,3-dimethyl-pent-4-en-1-amine (**1e**) as a starting material. However, as shown in Table 2, the reaction unsatisfactorily led to major addition–reduction product **5** and aromatic substitution product **6** without the formation of the desired 2-fluoroalkyl pyrrolidines. In addition, GC analysis indicated **1e** was not converted thoroughly even by prolonged reaction time in the presence of either NaOH or $NaHCO_3$. We speculated the nucleophilicity of amino group was decreased due to the electron-withdrawing effect of phenyl group, thus preventing the desired intramolecular substitution, whereas the addition–reduction product **5** was generated by free radical addition of R_f to C=C and direct subsequent H-abstraction from the solvent. Meanwhile, the aromatic substitution product **6** was presumably produced via free radical aromatic substitution reaction promoted by electron-donating amino group.

Table 1
Reaction of *N*-acyl-3,3-dimethyl-pent-4-en-1-amines with fluoroalkyl iodides



1
R=CH_3CO, 1b; $PhCH_2OCO$, 1c; $PhSO_2$, 1d;

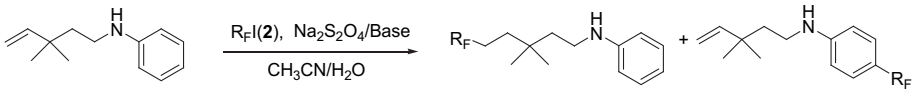
R_F=ClC_2F_4, 2a; C_6F_{13}, 2b, $PhSCF_2$, 2c

3 **4** **5**

Entry	1	2	Base	Reaction results[a](%)		
				3	4	5
1	**1b**	**2a**	$NaHCO_3$	—[b]	**4ba** (41)	**5ba** (59)
2	**1b**	**2a**	NaOH	—	**4ba** (23)	**5ba** (77)
3	**1b**	**2c**	NaOH	—	**4bc** (85)	—
4	**1c**	**2a**	NaOH	—	**4ca** (68)	**5ca** (32)
5	**1c**	**2a**	$NaHCO_3$	—	**4ca** (85)	**5ca** (15)
6	**1c**	**2b**	NaOH	—	**4cb** (73)	**5cb** (27)
7	**1c**	**2b**	$NaHCO_3$	—	**4cb** (78)	**5cb** (12)
8	**1c**	**2c**	NaOH	—	**4cc** (83)	**5cc** (17)
9	**1c**	**2c**	$NaHCO_3$	—	**4cc** (90)	**5cc** (10)
10	**1d**	**2a**	NaOH	**3ca** (32)	**4da** (68)	—
11	**1d**	**2a**	$NaHCO_3$	—	**4da** (87)	—
12	**1d**	**2b**	NaOH	**3cb** (22)	**4db** (78)	—
13	**1d**	**2b**	$NaHCO_3$	—	**4db** (88)	—
14	**1d**	**2c**	NaOH	—	**4dc** (86)	—
15	**1d**	**2c**	$NaHCO_3$	—	**4dc** (85)	—

[a] The yields were determined by GC analysis of the crude reaction mixture.
[b] The symbol '–' means that the corresponding product was not detected by GC analysis of the crude reaction mixture.

Table 2
Reaction of *N*-phenyl-3,3-dimethyl-pent-4-en-1-amine with fluoroalkyl iodides



1e **5ea, 5eb** **6ea, 6eb**

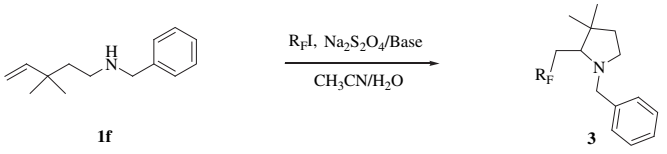
Entry	2	Conditions	Reaction results[a](%)		
			1e	5	6
1	**2a**	NaOH, 5h	51.2	16.3	24.1
2	**2a**	NaOH, 7h	51.0	16.6	24.0
3	**2a**	NaOH, 10h	49.0	16.3	24.1
4	**2a**	$NaHCO_3$, 5h	30.8	31.7	25.4
5	**2b**	$NaHCO_3$, 5h	20.7	20.4	55.7

[a] The reaction results were determined by GC analysis of the crude reaction mixture.

2.3. Reaction of *N*-benzyl-3,3-dimethyl-pent-4-en-1-amine (1f) with fluoroalkyl iodide

To our delight, when substrate **1f** was used as the starting material with the electron-donating benzyl substitution on amino group of 3,3-dimethyl-pent-4-en-1-amine, the desired 2-fluoroalkyl pyrrolidine products were favorably obtained. As revealed in Table 3, the reaction of **1f** with **2a** in the presence of $NaHCO_3$ afforded 2-fluoroalkyl pyrrolidine **3fa** in 57% GC yield together with adduct **4fa** in 24% GC yield (entry 1 in Table 3). We then found out that replacement of $NaHCO_3$ by NaOH led to considerably higher GC yield of **3fa** (79%, entry 2 in Table 3). This might be ascribable to the strong neutralization ability of relatively stronger base toward certain acidic byproducts during the reaction process (i.e., SO_2, H_2SO_3, etc.), therefore facilitating the intramolecular nucleophilic substitution to form pyrrolidine derivatives. With the optimized reaction condition in hand, several other R_FI reactants were employed to explore the scope of the one-pot preparation of 2-fluoroalkyl pyrrolidines. As summarized in Table 3, all the reactions went smoothly, affording the corresponding 2-fluoroalkyl pyrrolidines in moderate to good yields.

Table 3
The reaction of *N*-benzyl-3,3-dimethyl-pent-4-en-1-amine (**1f**) with fluoroalkyl iodides



1f **3**

R_F = ClC_2F_4, **2a**; C_6F_{13}, **2b**; $PhSCF_2$, **2c**

Entry	1	2	Base	3	Yiled[a](%)
1	**1f**	**2a**	$NaHCO_3$	**3fa**	57[b]
2	**1f**	**2a**	NaOH	**3fa**	79
3	**1f**	**2b**	NaOH	**3fb**	65
4	**1f**	**2c**	NaOH	**3fc**	85

[a] The yields were determined by GC analysis of the crude reaction mixture.
[b] Meanwhile, **4fa** was afforded in 24% GC yield.

On the basis of these results observed, the rationale of the formation of 2-fluoroalkyl pyrrolidine products upon the change of *N*-protecting group from acyl and phenyl to benzyl moiety may be explained via S_N2 mechanism. The *N*-acyl in **1b**, **1c**, **1d** and *N*-phenyl in **1e** withdrew electron from nitrogen atom, whereas the *N*-benzyl in **1f** donated electron to nitrogen. Therefore, the nitrogen atom in the latter case held stronger nucleophilicity to facilitate the intramolecular S_N2 procedure, forming the 2-fluoroalkyl pyrrolidine derivatives in good yields.

Since the development of potent synthetic method for the preparation of chiral fluoroalkyl pyrrolidine derivatives remains challenging and valuable, we envision that the chiral carbon generated during the reaction process on pyrrolidine scaffold in the present case would potentially lead to a pair of diastereoisomers by introducing another chiral auxiliary into the substrate. Chiral 2-fluoroalkyl pyrrolidine would then be obtained by the subsequent removal of the chiral auxiliary. The reaction of compound **1g**, (*S*)-*N*-(1-phenylethyl)-3,3-dimethyl-pent-4-en-1-amine, which is synthesized by Scheme 1, with $PhSCF_2I$ was initiated, affording the 2-fluoroalkyl pyrrolidine **3gc** in 86% yield with 1.27:1 dr.

3. Conclusions

In conclusion, the reaction of fluoroalkyl iodides with pent-4-en-1-amines bearing different protecting groups in the presence of $Na_2S_2O_4$ and base ($NaHCO_3$ or NaOH) in aqueous acetonitrile at room temperature was investigated. The protecting group effect was found crucial toward such reaction as the electron-withdrawing acyl- or phenyl-groups led to the major formation of byproducts, whereas the electron-donating benzyl group favorably furnished the desired 2-fluoroalkyl pyrrolidine products in good yields. Our one-pot synthesis of 2-fluoroalkyl pyrrolidines from the reaction of fluoroalkyl iodides with pent-4-en-1-amines using $Na_2S_2O_4$ as the initiator may provide new insights toward the further development of novel fluoroalkyl pyrrolidine derivatives that are of wide applications in organic chemistry. Further studies on the generality and applicability of this method toward the preparation of fluoroalkyl-containing natural product analogues are in progress in our laboratory.

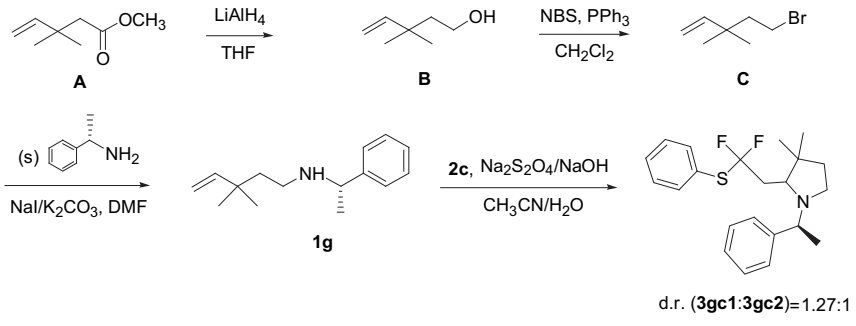
4. Experimental

4.1. General

Melting points were uncorrected. IR spectra were taken on a Perkin–Elmer Jeol 983 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM500 (500 MHz) spectrometer with TMS as internal standard. ^{19}F NMR spectra were recorded on a Bruker AM500 (470 MHz) spectrometer with $CFCl_3$ as external standard. ^{13}C NMR spectra were recorded on a Bruker AM500 (125 MHz) spectrometer. Mass spectra were taken on an HP 5989A spectrometer. High-resolution mass data were obtained on a Finnigan MAT 8430 spectrometer. Column chromatography was performed using silica gel H, particle size 10–40 μm.

4.2. General reaction procedure for the preparation of substrate 1

*4.2.1. The preparation of 3,3-dimethyl-pent-4-en-1-amine (**1a**).* To a NaOH solution (300 mL, 10 M) was added 3,3-dimethyl-pent-4-



Scheme 1.

enoic acid methyl ester (**A**) (113.6 g, 0.8 mol). The mixture was stirred at reflux for 5 h. After the reaction was completed, diluted HCl solution was added to acidify the solution. The mixture was abstracted with methyl *tert*-butyl ether (30 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$. The mixture was filtered through a plug of Celite. After the solvent was removed, 92.8 g 3,3-dimethyl-pent-4-enoic acid (**D**) was obtained, yield 90.6%.

Compound **D** (51.2 g, 0.4 mol) in anhydrous CH_2Cl_2 (300 mL) in an ice bath was added $SOCl_2$ (95.2 g, 0.8 mol) in 30 min. Five drops of DMF was added into the mixture. The mixture was refluxed for 5 h. After the removal of volatile solvents under vacuum, a yellow oil 3,3-Dimethyl-pent-4-enoyl chloride (*E*) was obtained. The oil was added dropwise into 25% ammonia aqueous solution. The mixture was stirred at room temperature for 10 h. After the reaction was completed, two layers were afforded. The water layer was abstracted with methyl *tert*-butyl ether (100 mL×3). The combined organic layer was washed with saturated brine and dried over anhydrous $MgSO_4$. The mixture was filtered, the filtrate was concentrated to afford 32.3 g crude product **F**, yield 63.6%. The crude product could be further purified by recrystallization in petroleum ether, mp: 98 °C.

Under the N_2 atmosphere, to the mixture of $LiAlH_4$ (2.3 g, 0.06 mol) and anhydrous Et_2O (20 mL) in an ice bath was added compound **F** (3.8 g, 0.03 mol) in Et_2O (30 mL) solution. The mixture was stirred at room temperature for 20 h. Water (6 mL) was added to quench the reaction. Methyl *tert*-butyl ether (30 mL) was added to dilute the mixture. The mixture was filtered, and the filtrate was dried over anhydrous $MgSO_4$. After the removal of volatile solvents under vacuum, 2.8 g crude product **1a** was obtained, yield 82.5%. Crude product **1a** could be further purified by distillation, bp: 106 °C.

*4.2.1.1. 3,3-Dimethyl-pent-4-enoic acid methyl ester (**A**).* Colorless oil, bp: 59 °C, 33 mmHg, ^{1}H NMR ($CDCl_3$) δ 5.93–5.87 (1H, m, CH_2=C*H*), 5.00–4.94 (2H, m, CH_2=CH), 3.65 (3H, s, OCH_3), 2.31 (2H, s, CH_2CO), 1.14 (6H, s, C(CH_3)$_2$).

*4.2.1.2. 3,3-Dimethyl-pent-4-enoic amide (**F**).* White solid, mp: 97.3–98.1 °C, ^{1}H NMR ($CDCl_3$) δ 5.97–5.91 (1H, m, CH_2=C*H*), 5.86 (1H, s, NH_2), 5.59 (1H, s, NH_2), 5.08–5.03 (2H, m, CH_2=CH), 2.23 (2H, s, CH_2CO), 1.14 (6H, s, C(CH_3)$_2$).

*4.2.1.3. 3,3-Dimethyl-pent-4-enoic amine (**1a**).* Colorless oil, bp: 160 °C, 760 mmHg, ^{1}H NMR ($CDCl_3$) δ 5.82–5.76 (1H, m, CH_2=C*H*), 4.93–4.89 (2H, m, CH_2=CH), 2.66–2.62 (2H, m, CH_2CH_2NH_2), 1.60 (2H, s, CH_2NH_2), 1.48–1.45 (2H, m, C$H_2$$CH_2NH_2$), 1.00 (6H, s, C(C$H_3$)$_2$).

*4.2.2. The preparation of N-acetyl-3,3-dimethyl-pent-4-en-1-amine (**1b**).* To the mixture of **1a** (4.5 g, 40 mmol) and diethyl ether (200 mL) was added Ac_2O (11.2 g, 110 mmol). The mixture was stirred at room temperature for 8 h. After the reaction was completed, NaOH solution (1 M, 200 mL) was added and stirred for 10 h. The organic layer was separated. The water layer was abstracted with EtOAc (100 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. The mixture was filtered through a plug of Celite. After the solvent was removed, 5.0 g **1b** was obtained, yield 80.3%.

*4.2.2.1. N-acetyl-3,3-dimethyl-pent-4-en-1-amine (**1b**).* Colorless oil, ^{1}H NMR ($CDCl_3$) δ 5.82–5.76 (1H, m, CH_2=C*H*), 5.58 (1H, s, N*H*), 4.98–4.94 (2H, m, CH_2=CH), 3.24–3.19 (2H, m, CH_2NH), 1.96 (3H, s, COCH_3), 1.53–1.50 (2H, m, C$H_2$$CH_2$NH), 1.03 (6H, s, C(C$H_3$)$_2$).

*4.2.3. The preparation of N-Cbz-3,3-dimethyl-pent-4-en-1-amine (**1c**).* To the mixture of **1a** (2.3 g, 20 mmol), K_2CO_3 (6.1 g, 44 mmol), 1,4-dioxane (50 mL), and water (80 mL) was added CbzCl (3.7 g, 22 mmol). The mixture was stirred at room temperature for 1 h. After the reaction was completed, the mixture was abstracted with methyl *tert*-butyl ether (50 mL×3). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The mixture was filtered through a plug of Celite. After the solvent was removed, 5.6 g crude product **1c** was obtained, yield 80.6%. The crude product could be further purified by distillation under vacuum (2.5 mmHg, 168–171 °C).

*4.2.3.1. N-Cbz-3,3-dimethyl-pent-4-en-1-amine (**1c**).* Colorless oil, bp: 168–171 °C, 0.1 mmHg, ^{1}H NMR ($CDCl_3$) δ 7.29–7.23 (5H, m, C_6H_5), 5.74–5.68 (1H, m, CH_2=C*H*), 5.02 (2H, s, CH_2Ph), 4.89–4.86 (2H, m, CH_2=CH), 4.61(1H, s, N*H*), 3.11–3.07 (2H, m, CH_2CH_2NH), 1.47–1.44 (2H, m, C$H_2$$CH_2$NH), 0.95 (6H, s, C(C$H_3$)$_2$).

*4.2.4. The preparation of N-phenylsulfonyl-3,3-dimethyl-pent-4-en-1-amine (**1d**).* To the mixture of **D** (1.1 g, 10 mmol), pyridine (1.2 g, 15 mmol), and NaOH solution (30 mL, pH=11) was added phenylsulfonyl chloride (1.8 g, 10 mmol). The mixture was stirred at room temperature for 3 h. After the reaction was completed, the mixture was abstracted with methyl *tert*-butyl ether (20 mL×3). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The mixture was filtered through a plug of Celite. After the solvent was removed, 2.4 g crude product **1d** was obtained, yield 95.1%. The crude product could be further purified by column chromatography with eluent PE/EA=10:1.

*4.2.4.1. N-Phenylsulfonyl-3,3-dimethyl-pent-4-en-1-amine (**1d**).* Light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.87–7.53 (5H, m, C_6H_5), 5.71–5.66 (1H, m, CH_2=C*H*), 4.94–4.86 (2H, m, CH_2=CH), 4.42 (1H, s, N*H*), 2.89–2.93 (2H, m, CH_2NH), 1.49–1.46 (2H, m, C$H_2$$CH_2$NH), 0.94 (6H, s, C(C$H_3$)$_2$).

*4.2.5. The preparation of N-phenyl-3,3-dimethyl-pent-4-en-1-amine (**1e**).* To a mixture of 3,3-dimethyl-pent-4-enoic acid (**D**) (13.7 g, 0.11 mol) and benzene (50 mL) in an ice bath was added $SOCl_2$ (15.5 mL, 0.21 mol) in 30 min. The mixture was refluxed for 6 h. After the removal of volatile solvents under vacuum, a yellow crude product (*E*) was obtained.

To a mixture of phenylamine (9.9 g, 0.11 mol), Et_3N (10.8 g, 0.11 mol), and methyl *tert*-butyl ether (50 mL) in an ice bath was added crude sample **E** in 30 min, and then stirred at room temperature for 10 h. Diluted HCl aqueous solution was added dropwise into the solution to adjust pH to 2–3, a brown solution was obtained. After the reaction was completed, two layers was obtained, the water layer was abstracted with CH_2Cl_2 (30 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. The mixture was filtered through a plug of Celite. The filtrate was concentrated under vacuum to obtain brown crude product 3,3-dimethyl-pent-4-enoic acid phenylamide (**G**) 19.0 g, yield 87.6%.

Under the N_2 atmosphere, to the mixture of $LiAlH_4$ (1.5 g, 0.04 mol) and anhydrous THF (40 mL) in a bath was added compound **G** (4.1 g, 0.02 mol) in THF (40 mL) solution. The mixture was stirred at room temperature for 20 h. Water (10 mL) was added to quench the reaction, and methyl *tert*-butyl ether (50 mL) was added to dilute the mixture. The mixture was filtered, the filtrate was dried over anhydrous $MgSO_4$, After the removal of volatile solvents under vacuum, 2.3 g crude product **1e** was obtained, yield 61.7%. Crude product **1e** could be further purified by distillation under vacuum. Bp: 105–106 °C, 0.1 mmHg.

*4.2.5.1. N-phenyl-3,3-dimethyl-pent-4-en-1-amine (**1e**).* Yellow oil, bp: 105–106 °C, 0.1 mmHg, ^{1}H NMR ($CDCl_3$) δ 7.21–6.60 (5H, m, C_6H_5), 5.89–5.83 (1H, m, CH_2=C*H*), 5.02–4.98 (2H, m, CH_2=CH),

3.11–3.08 (2H, m, CH_2CH_2NH), 1.66–1.63 (2H, m, CH_2CH_2NH), 1.09 (6H, s, $C(CH_3)_2$).

*4.2.5.2. The preparation of N-benzyl-3,3-dimethyl-pent-4-en-1-amine (**1f**).* To a mixture of $LiAlH_4$ (8.1 g, 0.21 mol) and THF (100 mL) in an ice bath was added 3,3-dimethyl-pent-4-enoic acid methyl ester (**A**) (20.2 g, 0.14 mol) in THF (100 mL) and then stirred at room temperature for 20 h. After the reaction was completed, water (30 mL) was added and the mixture was diluted with methyl *tert*-butyl ether (30 mL). The resulting suspension was filtered. The filtrate was dried over anhydrous $MgSO_4$. After the removal of volatile solvents under vacuum, 13.9 g crude product 3,3-dimethyl-pent-4-en-1-OH (**B**) was obtained, yield 87.0%. Compound **B** could be further purified by distillation under reduced pressure (65–66 °C, 15 mmHg).

To a mixture of NBS (1.0 g, 5.7 mmol), PPh_3 (1.6 g, 6.1 mmol), and CH_2Cl_2 (5 mL) in an ice bath was added **B** (0.5 g, 4.3 mmol) and then stirred at room temperature for 2 h. After the reaction was completed, the solvent was removed under vacuum. The residue was washed with *n*-hexane (15 mL×4). The suspension was filtered, the filtrate was concentrated under vacuum, then 0.6 g 5-bromo-3,3-dimethyl-pent-1-ene (**C**) was obtained, yield 76.2%.

A mixture of compound **C** (3.5 g, 20 mmol), benzylamine (2.4 g, 20 mmol), K_2CO_3 (7.7 g, 60 mmol), NaI (9.0 g, 60 mmol), and DMF (100 mL) was stirred at 100 °C for 20 h. After the reaction was completed, The mixture was cooled to room temperature and abstracted with methyl *tert*-butyl ether (60 mL×3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$. The mixture was filtered through a plug of Celite. After the solvent was removed, 3.2 g **1f** was obtained, yield 79.5%. The crude product could be further purified by distillation under vacuum (2.5 mmHg, 108–109 °C).

*4.2.5.3. N-Benzyl-3,3-dimethyl-pent-4-en-1-amine (**1f**).* Yellow oil, bp: 108–109 °C, 2.5 mmHg, ^{1}H NMR ($CDCl_3$) δ 7.33–7.26 (5H, m, C_6H_5), 5.82–5.77 (1H, m, CH_2=CH), 4.93–4.90 (2H, m, CH_2=CH), 3.77 (2H, s, CH_2Ph), 2.62–2.59 (2H, m, CH_2CH_2NH), 1.55–1.52 (2H, m, CH_2CH_2NH), 1.00 (6H, s, $C(CH_3)_2$).

In the similar way, with (*s*)-1-phenyl-ethylamine instead of benzylamine, **1g** was obtained in 82.0% yield.

*4.2.5.4. N-(1-phenyl-ethyl)-3,3-dimethyl-pent-4-en-1-amine (**1g**).* Light yellow oil, bp: 97–98 °C, 0.1 mmHg, ^{1}H NMR ($CDCl_3$) δ 7.35–7.22 (5H, m, C_6H_5), 5.78–5.72 (1H, m, CH_2=C*H*), 4.88–4.85 (2H, m, CH_2=CH), 3.76–3.72 (1H, m, C*H*(CH_3)Ph), 2.49–2.38 (2H, m, CH_2CH_2NH), 1.55–1.39 (2H, m, CH_2CH_2NH), 1.34–1.33 (3H, m, CHCH_3(Ph)), 0.95 (6H, s, $C(CH_3)_2$).

4.3. General reaction procedure for the preparation for compound 3, 4, 5, 6

To a mixture of **1** (1.0 mmol), **2** (1.1 mmol), acetonitrile (9 mL), and water (3 mL), was added a mixture of sodium dithionite (244 mg, 1.4 mmol) and sodium hydroxide (56 mg, 1.4 mmol) or sodium dicarbonate (56 mg, 1.4 mmol) in portions under stirring at room temperature for 5 h. After the reaction was completed, the mixture was extracted with methyl *tert*-butyl ether (3×30 mL). The combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography to give the products **3**, **4**, **5**, **6**.

*4.3.1. 2-(3-Chloro-2,2,3,3-tetrafluoropropyl)-3,3-dimethyl-1-phenylsulfonyl-pyrrolidine (**3da**).* Light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.81–7.48 (m, 5H, C_6H_5), 3.43–3.38 (m, 2H, CH_2), 3.20–3.15 (m, 1H, CH), 2.84–2.72 (m, 1H, 1/2CH_2), 2.46–2.34 (m, 1H, 1/2CH_2), 1.60–1.55 (m, 1H, 1/2CH_2), 1.28–1.24 (m, 1H, 1/2CH_2), 0.95 (s, 3H, CH_3), 0.51 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −72.58 (2F, d, *J*=35.3 Hz), 111.81 (2F, m). ^{13}C NMR ($CDCl_3$) δ 137.4, 133.6, 129.9, 128.1, 62.9, 47.1, 42.5, 38.9, 34.8, 26.9, 23.4. IR (cm^{-1}, KBr) 2960, 1465, 1445, 1348, 1160, 1095, 935. HRMS calcd for $C_{15}H_{18}ClF_4NO_2S$: 387.0683, found: 387.0680.

*4.3.2. 3,3-Dimethyl-1-phenylsulfonyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-pyrrolidine (**3db**).* Light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.88–7.55 (m, 5H, C_6H_5), 3.51–3.46 (m, 2H, CH_2), 3.28–3.22 (m, 1H, CH), 2.90–2.78 (m, 1H, 1/2CH_2), 2.53–2.40 (m, 1H, 1/2CH_2), 1.72–1.57 (m, 1H, 1/2CH_2), 1.36–1.31 (m, 1H, 1/2CH_2), 1.02 (s, 3H, CH_3), 0.58 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −81.67 (3F, t, *J*=9.9 Hz), −112.11 (2F, m), −122.60 (2F, s), −123.74 (2F, s), −124.47 (2F, s), −127.03 (2F, s). ^{13}C NMR ($CDCl_3$) δ 137.4, 133.7, 129.8, 128.2, 62.6, 47.2, 42.5, 39.0, 35.1, 26.9, 23.5. IR (cm^{-1}, KBr) 2966, 2929, 1471, 1447, 1352, 1238, 1095. HRMS calcd for $C_{19}H_{18}F_{13}NO_2S$: 571.0851, found: 571.0854.

*4.3.3. 1-Benzyl-2-(3-chloro-2,2,3,3-tetrafluoropropyl)-3,3-dimethyl-pyrrolidine (**3fa**).* Light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.26–7.15 (m, 5H, C_6H_5), 4.01 (d, 1H, *J*=13.43 Hz, 1/2CH_2), 3.23 (d, 1H, *J*=13.43 Hz, 1/2CH_2), 2.83 (m, 1H, 1/2CH_2), 2.55 (m, 1H, 1/2CH_2), 2.37–2.28 (m, 2H, CH_2), 2.16–2.08 (m, 2H, CH_2), 1.51 (t, 2H, *J*=7.07 Hz, CH_2), 0.97 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −72.19 (2F, d, *J*=9.4 Hz), −112.21 (2F, m). ^{13}C NMR ($CDCl_3$) δ 138.6, 127.6, 127.5, 125.8, 65.4, 57.7, 49.9, 39.7, 38.1, 30.1, 26.4, 23.3. IR (cm^{-1}, KBr) 3315, 2961, 2924, 1788, 1689, 1467, 1261. HRMS calcd for $C_{16}H_{20}ClF_4N$: 337.1220, found: 337.1216.

*4.3.4. 1-Benzyl-3,3-dimethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)pyrrolidine (**3fb**).* Light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.32–7.24 (m, 5H, C_6H_5), 4.06 (d, 1H, *J*=13.38 Hz, 1/2CH_2), 3.28 (d, 1H, *J*=13.38 Hz, 1/2CH_2), 2.87 (m, 1H, 1/2CH_2), 2.62 (m, 1H, 1/2CH_2), 2.40–2.21 (m, 3H, CH+CH_2), 2.22 (m, 2H), 1.59 (m, 2H, CH_2), 1.04 (s, 3H, CH_3), 1.03 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −81.69 (3F, t, *J*=11.8 Hz), −112.35 (2F, m), −122.63 (2F, s), −123.78 (2F, s), −124.27 (2F, s), −127.05 (2F, s). ^{13}C NMR ($CDCl_3$) δ 138.7, 127.4, 127.2, 125.8, 66.0, 57.7, 49.9, 39.7, 38.1, 28.7, 26.4, 23.4. IR (cm^{-1}, KBr) 2960, 2928, 1659, 1463, 1240, 1204, 1144, 807. HRMS calcd for $C_{20}H_{20}F_{13}N$: 521.1388, found: 521.1390.

*4.3.5. 1-Benzyl-2-(2,2-difluoro-2-phenylthioethyl)-3,3-dimethyl-pyrrolidine (**3fc**).* Light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.61–7.25 (m, 10H, 2C_6H_5), 4.09 (d, 1H, *J*=13.4 Hz, 1/2CH_2), 3.23 (d, 1H, *J*=13.4 Hz, 1/2CH_2), 2.83 (m, 1H, 1/2CH_2), 2.59 (m, 1H, 1/2CH_2), 2.49 (m, 1H, 1/2CH_2), 2.31 (m, 1H, 1/2CH_2), 2.17 (m, 1H, CH), 1.25 (m, 2H, CH_2), 1.01 (s, 3H, CH_3), 0.97 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ 71.37 (ABXY, *J*=202.1, 22.1, 11.8 Hz), 71.77 (ABXY, *J*=202.1, 16.7, 12.2 Hz). ^{13}C NMR ($CDCl_3$) δ 24.5, 27.7, 39.3, 50.9, 58.9, 67.8, 126.6, 128.1, 128.5, 129.0, 129.7, 136.2. IR (cm^{-1}, KBr) 3061, 2955, 1667, 1453, 1369, 1170, 1045, 905. HRMS calcd for $C_{21}H_{25}F_2NS$: 361.1676, found: 361.1678.

*4.3.6. 2-(2,2-Difluoro-2-phenylthioethyl)-3,3-dimethyl-1-((S)-1-phenylethyl)-pyrrolidine (**3gc**).* Compound **3gc1**: light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.66–7.25 (m, 10H, 2C_6H_5), 3.98–3.97 (m, 1H, CH), 2.85–2.84 (m, 2H, CH_2), 2.56–2.53 (m, 1H, CH), 2.43–2.29 (m, 2H, CH_2), 1.45–1.44 (m, 3H, CH_3), 1.32–1.19 (m, 2H, CH_2), 0.91 (s, 3H, CH_3), 0.61 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ 71.19 (ABXY, *J*=202.1, 23.0, 9.4 Hz), 71.34 (ABXY, *J*=202.1, 23.0, 11.8 Hz). ^{13}C NMR ($CDCl_3$) δ 135.4, 129.1, 128.8, 128.1, 127.1, 124.7, 38.1, 36.1, 30.9, 28.7, 28.4, 22.0, 13.1. IR (cm^{-1}, KBr) 3062, 2959, 2926, 1661, 1446, 1374, 1256. HRMS calcd for $C_{22}H_{27}F_2NS$: 375.1832, found: 375.1834.

Compound **3gc2**: light yellow oil, ^{1}H NMR ($CDCl_3$) δ 7.62–7.19 (m, 10H, 2C_6H_5), 4.08–4.04 (m, 1H, CH), 2.96–2.94 (m, 1H, 1/2CH_2), 2.54–2.43 (m, 4H, CH+1/2CH_2+CH_2), 1.52–1.46 (m, 2H, CH_2),

1.36–1.34 (d, 3H, CH_3), 1.04(s, 3H, CH_3), 0.97(s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −70.49 (1F, ABXY, *J*=201.6 Hz, 23.6, 11.5 Hz), −71.67 (1F, ABXY, *J*=201.6, 22.2, 11.5 Hz). ^{13}C NMR ($CDCl_3$) δ 136.1, 129.7, 129.0, 128.0, 127.4, 126.3, 63.5, 54.7, 42.7, 39.6, 29.7, 27.3, 23.7, 11.0. IR (cm^{-1}, KBr) 3061, 2963, 2929, 1685, 1441, 1375, 1260. HRMS calcd for $C_{22}H_{27}F_2NS$: 375.1832, found: 375.1833.

*4.3.7. N-(6,6-difluoro-4-iodo-3,3-dimethyl-6-(phenylthio)hexyl) acetamide (**4bc**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 7.63–7.27 (m, 5H, C_6H_5), 5.53 (s, 1H, NH), 4.20–4.18 (m, 1H, CH), 3.34–3.19 (m, 2H, CH_2), 2.95–2.85 (m, 2H, CH_2), 1.99 (s, 3H, CH_3), 1.73–1.52 (m, 2H, CH_2), 1.09 (s, 3H, CH_3), 1.05 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −71.95 (1F, ABX, *J*=203.5, 13.4, 13.4 Hz), −73.65 (1F, ABX, *J*=203.5, 14.6, 14.6 Hz). ^{13}C NMR ($CDCl_3$) δ 170.0, 136.2, 130.0, 129.1, 128.9, 126.3, 45.7, 40.8, 38.1, 37.7, 35.6, 25.2, 24.2, 23.4. IR (cm^{-1}, KBr) 3285, 3080, 2967, 1648, 1554, 1473, 1369, 1287, 1172, 1043. HRMS calcd for $C_{16}H_{22}F_2INOS$: 441.0435, found: 441.0446.

*4.3.8. Benzyl-7-chloro-6,6,7,7-tetrafluoro-4-iodo-3,3-dimethylheptylcarbamate (**4ca**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 7.36–7.30 (m, 5H, C_6H_5), 5.10 (s, 2H, CH_2), 4.76 (s, 1H, NH), 4.16 (d, 1H, *J*=8.48Hz, CH), 3.25–3.17 (m, 2H, CH_2), 2.89–2.73 (m, 2H, CH_2), 1.75–1.69 (m, 1H, 1/2CH_2), 1.63–1.55 (m, 1H, 1/2CH_2), 1.12 (s, 3H, CH_3), 1.08 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −72.59 (2F, d, *J*=20.7 Hz), 115.57 (2F, m). ^{13}C NMR ($CDCl_3$) δ 158.0, 138.2, 130.2, 129.8, 68.4, 42.6, 39.4, 39.2, 39.1, 38.7, 35.6, 28.0, 26.7, 26.0. IR (cm^{-1}, KBr) 3400, 3300, 3059, 2930, 1723, 1531. HRMS calcd for $C_{17}H_{21}ClF_4INO_2$: 509.0242, found: 509.0244.

*4.3.9. Benzyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-iodo-3,3-dimethyl-undecylcarbamate (**4cb**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 7.35–7.30 (m, 5H, C_6H_5), 5.10 (m, 2H, CH_2), 4.73 (s, 1H, NH), 4.18–4.16 (m, 1H, CH), 3.28–3.13 (m, 2H, CH_2), 2.96–2.74 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.12 (s, 3H, CH_3), 1.08 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −81.68 (3F, t, *J*=9.4 Hz), −115.94 (2F, m), −122.70 (2F, s), −123.76 (2F, s), −124.51 (2F, s), −127.04 (2F, s). ^{13}C NMR ($CDCl_3$) δ 156.9, 137.1, 129.2, 128.8, 128.7, 67.4, 41.6, 38.4, 38.1, 37.7, 33.7, 30.3, 27.5, 27.2, 26.9, 25.6, 25.0, 24.9. IR (cm^{-1}, KBr) 3335, 3067, 3034, 2968, 1699, 1533, 1239, 1143. HRMS calcd for $C_{21}H_{21}F_{13}INO_2$: 693.0409, found: 693.0411.

*4.3.10. Benzyl-6,6-difluoro-4-iodo-3,3-dimethyl-6-(phenylthio)-hexylcarbamate (**4cc**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 7.62–7.61 (m, 2H, C_6H_5), 7.47–7.30 (m, 8H, C_6H_5), 5.15 (s, 2H, CH_2), 4.70 (s, 1H, NH), 4.18 (d, 1H, *J*=7.70 Hz, CH), 3.26–3.17 (m, 2H, CH_2), 2.97–2.81 (m, 2H, CH_2), 1.73–1.67 (m, 1H, 1/2CH_2), 1.57–1.51 (m, 1H, 1/2CH_2), 1.07 (s, 3H, CH_3), 1.04 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −71.97 (1F, ABX, *J*=203.7, 13.2, 13.2 Hz), −73.62 (1F, ABX, *J*=203.7, 14.6, 14.6 Hz). ^{13}C NMR ($CDCl_3$) δ 156.9, 137.2, 136.8, 130.6, 129.8, 129.5, 129.2, 128.8, 127.0, 67.4, 46.3, 41.7, 38.6, 38.1, 37.7, 26.0, 25.0. IR (cm^{-1}, KBr) 3418, 3336, 3062, 3032, 2966, 1885, 1721, 1441. HRMS calcd for $C_{22}H_{26}F_2INO_2S$: 533.0679, found: 406.1668 (lost I).

*4.3.11. N-(7-chloro-6,6,7,7-tetrafluoro-4-iodo-3,3-dimethylheptyl)-benzenesulfonamide (**4da**).* Yellow oil, ^1H NMR ($CDCl_3$) δ 7.90–7.53 (m, 5H, C_6H_5), 4.72 (t, *J*=5.6 Hz, 1H, NH), 4.06–4.04 (m, 1H, CH), 3.02–2.97 (m, 2H, CH_2), 2.87–2.67 (m, 2H, CH_2), 1.72–1.50 (m, 2H, CH_2), 1.04 (s, 3H, CH_3), 1.00 (s, 3H, CH_3). ^{19}F NMR (MHz, $CDCl_3$) δ −72.63 (2F, d, *J*=20.7 Hz), −115.62 (2F, m). ^{13}C NMR ($CDCl_3$) δ 140.5, 133.5, 129.9, 127.7, 39.8, 38.1, 33.9, 30.4, 26.9, 25.6. IR (cm^{-1}, KBr): 3282, 2926, 1668, 1448, 1327, 1257, 1158, 1092. HRMS calcd for $C_{15}H_{19}ClF_4INO_2S$: 514.9806, found: 388.0737 (lost I).

*4.3.12. N-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-iodo-3,3-dimethylundecyl)benzenesulfonamide (**4db**).* Yellow oil, ^1H NMR ($CDCl_3$) δ 7.90–7.52 (m, 5H, C_6H_5), 4.67 (t, *J*=7.1 Hz, 1H, NH), 4.06–4.04 (m, 1H, CH), 3.05–2.99 (m, 2H, CH_2), 2.88–2.70 (m, 2H, CH_2), 1.72–1.39 (m, 2H, CH_2), 1.04 (s, 3H, CH_3), 1.00 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −81.71 (3F, t, *J*=9.6 Hz), −115.98 (2F, m), −122.72 (2F, s), −123.80 (2F, s), −124.53 (2F, s), −127.07 (2F, s). ^{13}C NMR ($CDCl_3$) δ 139.8, 132.8, 129.3, 127.1, 40.9, 39.2, 37.4, 32.4, 26.5, 24.9. IR (cm^{-1}, KBr) 3255, 2980, 1448, 1423, 1322, 1207, 1142, 1064. HRMS calcd for $C_{19}H_{19}F_{13}INO_2S$: 698.9974, found: 572.0947, lost I (127).

*4.3.13. N-(6,6-difluoro-4-iodo-3,3-dimethyl-6-(phenylthio)-hexyl)-benzenesulfonamide (**4dc**).* Light yellow solid, ^1H NMR ($CDCl_3$) δ 7.90–7.38 (m, 10H, 2C_6H_5), 4.33 (t, *J*=37.6 Hz, 1H, NH), 4.08–4.06 (m, 1H, CH), 3.02–2.97 (m, 2H, CH_2), 2.85–2.78 (m, 2H, CH_2), 1.69–1.47 (m, 2H, CH_2), 1.00 (s, 3H, CH_3), 0.97 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ −72.27 (1F, ABX, *J*=204.5, 13.4, 13.4 Hz), −73.74 (1F, ABX, *J*=204.5, 14.8, 14.8 Hz). ^{13}C NMR ($CDCl_3$) δ 140.5, 136.8, 133.4, 130.6, 129.8, 129.7, 127.7, 126.9, 46.2, 41.6, 39.8, 38.1, 37.7, 25.9, 24.8, 23.3. IR (cm^{-1}, KBr) 3284, 2968, 1584, 1474, 1445, 1327, 1160, 1045. HRMS calcd for $C_{20}H_{24}F_2INO_2S_2$: 539.0261, found: 412.1218, lost I (127).

*4.3.14. N-(7-chloro-6,6,7,7-tetrafluoro-3,3-dimethyl-heptyl)-acetamide (**5ba**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 5.53 (s, 1H, NH), 3.28–3.23 (m, 2H, CH_2), 2.06–1.95 (m, 2H, CH_2), 1.97 (s, 3H, CH_3), 1.54–1.50 (m, 2H, CH_2), 1.46–1.43 (m, 2H, CH_2), 0.95 (s, 6H, 2CH_3). ^{19}F NMR ($CDCl_3$) δ −71.81 (2F, s), −115.46 (2F, t, *J*=18.8 Hz). ^{13}C NMR ($CDCl_3$) δ 170.8, 41.5, 36.3, 32.6, 32.3, 27.2, 26.3, 23.9. IR (cm^{-1}, KBr) 3287, 2963, 1653, 1558, 1474, 1370, 1262, 1151. HRMS calcd for $C_{11}H_{18}ClF_4NO$: 291.1013, found: 291.1015.

*4.3.15. N-(7-chloro-6,6,7,7-tetrafluoro-3,3-dimethyl-heptyl)-benzenamine (**5ea**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 7.20–6.59 (m, 5H, C_6H_5), 3.14–3.11 (m, 2H, CH_2), 2.06–2.03 (m, 2H, CH_2), 1.58–1.53 (m, 4H, CH_2+CH_2), 0.99 (s, 6H, 2CH_3). ^{19}F NMR ($CDCl_3$) δ −71.75 (2F, s), −115.39 (2F, t, *J*=16.5 Hz). ^{13}C NMR ($CDCl_3$) δ 148.9, 130.0, 118.1, 113.5, 41.8, 40.3, 32.7, 32.5, 27.5, 26.4. IR (cm^{-1}, KBr) 2957, 2926, 1603, 1506, 1465, 1151, 1088. HRMS calcd for $C_{15}H_{20}ClF_4N$: 325.1220, found: 325.1221.

*4.3.16. N-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-3,3-dimethyl-undecyl)-benzenamine (**5eb**).* Light yellow oil, ^1H NMR ($CDCl_3$) δ 7.21–6.63 (m, 5H, C_6H_5), 3.15–3.12 (m, 2H, CH_2), 2.06–2.02 (m, 2H, CH_2), 1.58–1.50 (m, 3H, CH+CH_2), 0.99 (s, 6H, 2CH_3). ^{19}F NMR (MHz, $CDCl_3$) δ −81.70 (3F, t, *J*=9.4 Hz), −115.51 (2F, t, *J*=16.5 Hz), −122.85 (2F, s), −123.80 (2F, s), −124.19 (2F, s), −127.06 (2F, q, *J*=14.1, 9.4 Hz). ^{13}C NMR ($CDCl_3$) δ 153.1, 136.8, 128.3, 127.8, 39.8, 30.7, 30.5, 28.7, 25.7, 25.1. IR (cm^{-1}, KBr) 2960, 2928, 1602, 1505, 1474, 1240, 1143. HRMS calcd for $C_{19}H_{20}F_{13}N$: 509.1388, found: 509.1389.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.11.090. These data include MOL files and InChiKeys of the most important compounds described in this article.

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