Reaction of Active Methylene Compounds with α-Fluoroalkyl Ketones or Esters: A Convenient Synthesis of 4-Trifluoromethylpyridines and *meta*-Trifluoromethylphenols

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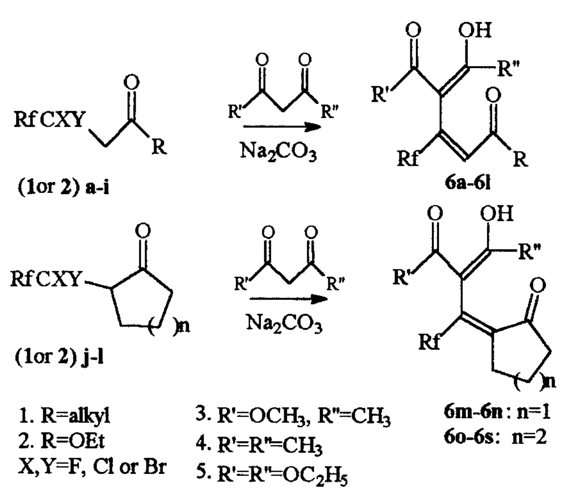
Received 25 December 1995; revised 2 April 1996

The reaction of α-fluoroalkyl ketones **1** or ethyl α-fluoroalkylacetates **2** with active methylene compounds such as methyl acetoacetate (**3**), acetylacetone (**4**) and diethyl malonate (**5**) produced unsaturated fluoroalkyl-containing 1,5-dicarbonyl compounds **6**, from which polyalkyl-substituted 4-trifluoromethylpyridines **7**, 4-trifluoromethylpyrid-2(1*H*)-ones **8** and *meta*-trifluoromethylphenols **9** were synthesized conveniently.

Synthesis of polysubstituted aromatic and heterocyclic compounds are a subject of significant interest. As a special branch of such compounds, fluoro- or trifluoromethylpyridines, pyridones and phenols are filling an increasingly important role in dyes, herbicides, insecticides, fungicides and antipyretics.[1] As a result, considerable efforts have been devoted in recent years to the development of new methodologies for the synthesis of such compounds.[2] Among them, fluorination or trifluoromethylation of aromatic compounds[3] is one of the most widely used methods, which, however, leads to the formation of a mixture of positional isomers. Another useful way is construction of aromatic skeletons via condensation of fluorine-containing building blocks with suitable moieties[4] but usually the procedures are tedious. Owing to the directive action of pyridinic nitrogen and the phenolic hydroxyl group, the 4-site of pyridines or the *meta*-site of phenols is unfavourable for direct substitution. Consequently, very few methods on the regiospecific synthesis of 4-trifluoromethylpyridines or pyrid-2(1*H*)-ones and *meta*-tifluoromethylphenols have been reported,[5] and none concerns their polyalkyl-substituted derivatives.

α-Fluoroalkylcarbonyl compounds have been exploited as fluoroalkyl-containing building blocks in synthesis of fluoroalkylated heterocyclic compounds.[6] In our continuing study, we found that not only heteroatoms but also the carbanions could react with such compounds. When active methylene compounds such as methyl acetoacetate (**3**), acetylacetone (**4**), and diethyl malonate (**5**) were allowed to react with α-fluoroalkyl ketone **1** or ethyl α-fluoroalkylacetates **2** under basic conditions, the stabilized carboanions attacked not the carbonyl carbons but the dihalomethylene at the β-position to them to afford products **6**. Compounds **6** contained three carbonyl groups located as two 1,5-dicarbonyl functions and thus are versatile precursors for annulation by available methods. From **6** which contained a trifluoromethyl group, polyalkyl-substituted 4-trifluoromethylpyridines **7**, 4-trifluoromethylpyrid-2(1*H*)-ones **8** and *meta*-trifluoromethylphenols **9** were produced conveniently. Compounds of such type are useful.[7] Herein, we report the results in detail.

In the presence of sodium carbonate, α-fluoroalkyl ketones **1**[8] or ethyl α-fluoroalkylacetates **2**[9] reacted with active methylene compounds i. e. methyl acetoacetate (**3**), acetylacetone (**4**) and diethyl malonate (**5**) at 60 °C in aprotic dipolar solvents to afford **6** as the main products (Scheme 1). Spectral data of **6** indicated that a reaction at the halogenated β-carbon of the carbonyl group occurred. ^{19}F NMR spectrum revealed a fluoroalkyl group one carbon shorter than that of the starting material **1** or **2**. The IR spectrum with absorption at $\nu = 1760-1710$, 1650, 1600 cm^{-1} and the UV spectrum with absorption at $\lambda_{max} = 240-310$ nm showed the presence of an extensive conjugated carbonyl system, which was also supported by the signal of enolic proton at $\delta = 13.0-17.5$ in ^{1}H NMR. The results obtained are summarized in Table 1.



Scheme 1

The reaction gave *E* isomers stereoselectively. The configuration of the newly formed double bond in products **6** is assigned according to the signals of trifluoromethyl group [at $\delta = (-9.0)$ to (-10.7) in ^{19}F NMR] and the hydrogen linked to this double bond [at $\delta = 6.58$ to 7.25 in ^{1}H NMR].[10]

In the reaction of α-fluoroalkyl ketone **1** with active methylene compounds, minor products were produced which proved to be the direct addition products of activated methylene groups onto ketonic carbonyl functions. This side reaction could be reduced by dropping the active methylene compounds into the mixture of other reactants which had been well stirred in solvent for one hour at 60 °C.

In such a reaction, an aprotic dipolar solvent was necessary and 1,4-dioxane proved to be the most suitable one although tetrahydrofuran and acetonitrile could also be used. Sodium hydride in THF also promoted the reaction well but sodium carbonate was a milder base. Reaction

Table 1. Reaction of **1** or **2** with **3**, **4** or **5** to Prepare Compounds **6**

Entry	Substrate	R_FCXY	R	Reagent	R′	R″	Product[a]	R_F	Yield[b] (%)
1	**1a**	CF_3CF_2	CH_3	**3**	OCH_3	CH_3	**6a**	CF_3	80
2	**1b**	CF_3CCl_2	$C(CH_3)_3$	**4**	CH_3	CH_3	**6b**	CF_3	85
3	**1c**	CF_3CF_2	$C(CH_3)_3$	**3**	OCH_3	CH_3	**6c**	CF_3	84
4	**1d**	CF_3CFBr	$C(CH_3)_3$	**3**	OCH_3	CH_3	**6c**	CF_3	90
5		CF_3CFBr	$C(CH_3)_3$	**5**	OC_2H_5	OC_2H_5	**6d**	CF_3	85
6	**2e**	CF_3CFBr	OC_2H_5	**3**	OCH_3	CH_3	**6e**	CF_3	90
7	**2f**	$ClCF_2CF_2$	OC_2H_5	**3**	OCH_3	CH_3	**6f**	$ClCF_2$	88
8		$Cl(CF_2)_3CF_2$	CH_3	**3**	OCH_3	CH_3	**6g**	$Cl(CF_2)_3$	83
9	**1g**	$Cl(CF_2)_3CF_2$	CH_3	**4**	CH_3	CH_3	**6h**	$Cl(CF_2)_3$	87
10		$Cl(CF_2)_3CF_2$	CH_3	**5**	OC_2H_5	OC_2H_5	**6i**	$Cl(CF_2)_3$	83
11	**1h**	$Cl(CF_2)_3CF_2$	$C(CH_3)_3$	**4**	CH_3	CH_3	**6j**	$Cl(CF_2)_3$	81
12	**2i**	$Cl(CF_2)_3CF_2$	OC_2H_5	**3**	OCH_3	CH_3	**6k**	$Cl(CF_2)_3$	86
13		$Cl(CF_2)_3CF_2$	OC_2H_5	**4**	CH_3	CH_3	**6l**	$Cl(CF_2)_3$	89
			n						$E+Z$[2]
14	**1j**	CF_3CF_2	1	**4**	CH_3	CH_3	**6m**	CF_3	80
15		CF_3CF_2	1	**5**	OC_2H_5	OC_2H_5	**6n**	CF_3	80
16	**1k**	CF_3CF_2	2	**4**	CH_3	CH_3	**6o**	CF_3	82
17		CF_3CF_2	2	**5**	OC_2H_5	OC_2H_5	**6p**	CF_3	85
18		$ClCF_2CF_2$	2	**3**	OCH_3	CH_3	**6q**	$ClCF_2$	88
19	**1l**	$ClCF_2CF_2$	2	**4**	CH_3	CH_3	**6r**	$ClCF_2$	85
20		$ClCF_2CF_2$	2	**5**	OC_2H_5	OC_2H_5	**6s**	$ClCF_2$	80

[a] All new products were fully characterized by ^1H NMR, ^{19}F NMR, IR, MS and elemental analysis.

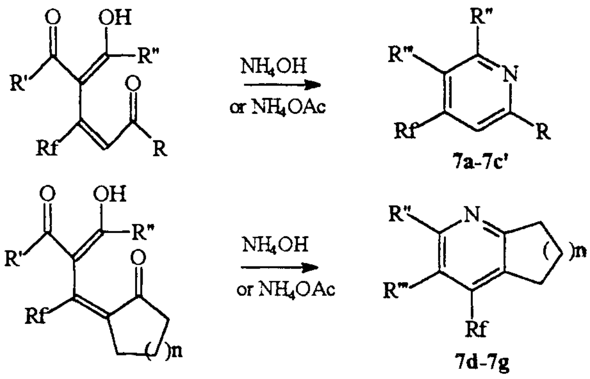
[b] The mixture of E and Z isomers ($E \gg Z$), isolated yield based on **1** or **2**.

temperature, the nature of the fluoroalkyl group and the reagents (**3**, **4** or **5**) did not have much effect on the reaction. The haloatoms on the β-carbons were eliminated during reaction and, therefore, substrates **1a–d** all gave products containing a trifluoromethyl group (entries 1–5).

Based on this reaction, we prepared a series of trifluoromethyl- or chlorodifluoromethyl-containing substrates **6** and synthesized thereof many useful but unavailable trifluoromethylated or chlorodifluoromethylated pyridines, phenols and their derivatives.

Since 1,5-dicarbonyl groups in products **6** are versatile functional groups for cyclization, further transformation of such compounds into 4-trifluoromethylated pyridines **7** and pyrid-2(1*H*)-ones **8** was available. Treatment of **6** which contained at least one ketonic carbonyl group with concentrated ammonium hydroxide (A) in THF afforded the expected products **7** or **8** in good yields. Fluoroalkyls in **6** had little effect on the reaction and remained on the 4-position of the products. Therefore, from different structured substrates **6**, 4-trifluoromethyl-substituted pyridines or pyrid-2(1*H*)-ones and 4-trifluoromethyltetrahydroquinolines or -quinolones were prepared by this convenient method.

Substrates containing two ketonic carbonyl groups in the 1,5-positions could react with the milder reagent ammonium acetate (B) to give the direct condensation products 4-fluoroalkylpyridines **7** in excellent yields. When ammonium hydroxide was used as the reagent, mixtures of compounds **7** and their corresponding deacetylated derivatives **7′** were usually obtained (if **7** contains an acetyl



Substrate	Product	R_f	R	R′	R‴	R″
6c	**7a**	CF_3	$C(CH_3)_3$	OCH_3	CO_2CH_3	CH_3
6g	**7b**	$Cl(CF_2)_3$	CH_3	OCH_3	CO_2CH_3	CH_3
6h	**7c**	$Cl(CF_2)_3$	CH_3	CH_3	$COCH_3$	CH_3
	7c′	$Cl(CF_2)_3$	CH_3	CH_3	H	CH_3
			n			
6m	**7d**	CF_3	1	CH_3	$COCH_3$	CH_3
	7d′	CF_3	1	CH_3	H	CH_3
6o	**7e**	CF_3	2	CH_3	$COCH_3$	CH_3
	7e′	CF_3	2	CH_3	H	CH_3
6r	**7f**	$ClCF_2$	2	CH_3	$COCH_3$	CH_3
	7f′	$ClCF_2$	2	CH_3	H	CH_3
6q	**7g**	$ClCF_3$	2	OCH_3	CO_2CH_3	CH_3

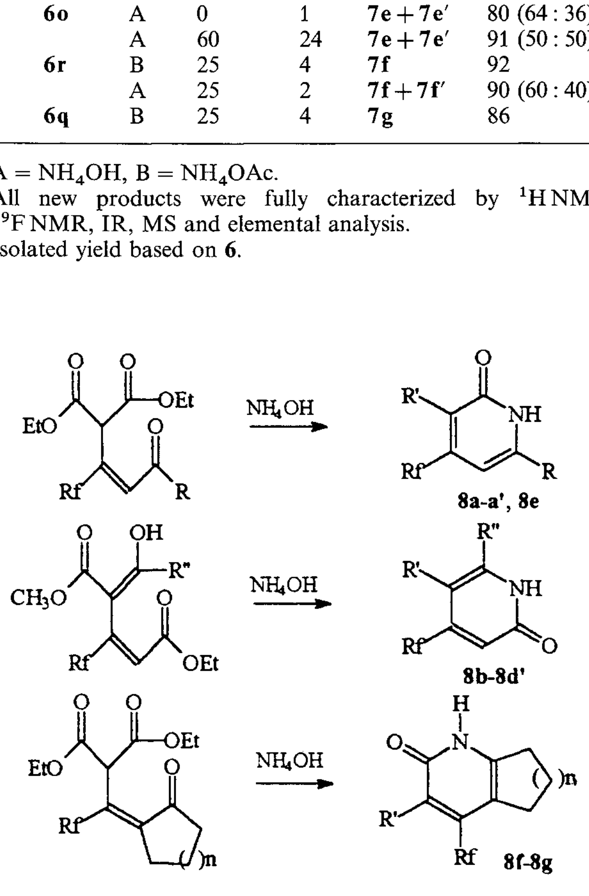
Scheme 2

group linked to the pyridine ring) (Scheme 2). Results for preparation of **7** and **7'** are listed in Table 2.

Table 2. Synthesis of 4-Fluoroalkylpyridines **7**

Entry	Substrate	Reagent	Temperature (°C)	Time (h)	Product	Yield (%)
1	**6c**	A	20	2	**7a**	89
2	**6g**	A	20	2	**7b**	91
3	**6h**	B	25	5	**7c**	95
4		A	20	2	**7c**+**7c'**	90 (63 : 37)
5	**6m**	B	25	4	**7d**	87
6		A	25	2	**7d**+**7d'**	91 (59 : 41)
7		B	25	5	**7e**	87
8	**6o**	A	0	1	**7e**+**7e'**	80 (64 : 36)
9		A	60	24	**7e**+**7e'**	91 (50 : 50)
10	**6r**	B	25	4	**7f**	92
11		A	25	2	**7f**+**7f'**	90 (60 : 40)
12	**6q**	B	25	4	**7g**	86

[a] A = NH_4OH, B = NH_4OAc.
[b] All new products were fully characterized by ^1H NMR, ^{19}F NMR, IR, MS and elemental analysis.
[c] Isolated yield based on **6**.



Substrate	Product	Rf	R	R'	R''
6d	**8a**	CF_3	$C(CH_3)_3$	$CO_2C_5H_5$	
	8a'	CF_3	$C(CH_3)_3$	H	
6e	**8b**	CF_3		CO_2CH_3	CH_3
6f	**8c**	$ClCF_2$		CO_2CH_3	CH_3
6k	**8d**	$Cl(CF_2)_3$		CO_2CH_3	CH_3
	8d'(8e)	$Cl(CF_2)_3$		H	CH_3
6i	**8e(8d')**	$Cl(CF_2)_3$	CH_3	H	
			n		
6n	**8f**	CF_3	1	$CO_2C_2H_5$	
	8f'	CF_3	1	H	
6s	**8g**	$ClCF_2$	2	$CO_2C_2H_5$	
	8g'	$ClCF_2$	2	H	

Scheme 3

As to substrates with one ketonic carbonyl and one esteric carbonyl group for condensation, ammonium hydroxide was the only active reagent and polysubstituted 4-trifluoromethylpyrid-2(1*H*)-ones **8** together with the corresponding dealkoxycarbonylated or deacetylated derivatives **8'** were obtained in moderate to good yields (Scheme 3). Results are listed in Table 3.

Table 3. Synthesis of 4-Fluoroalkylpyridones **8**

Entry	Substrate	Reagent[b]	Temp. (°C)/t (h)	Main Product	Conversion (%)	Yield (%)[c] (X : X')[d]
1	**6d**	A	25/6	**8a**+**8a'**	80	45 (60 : 40)
2	**6d**	B+A	60/24	**8a**+**8a'**	100	60 (55 : 45)
3	**6e**	B+A	25/24	**8b**	100	61 (80 : 20)
4	**6f**	B+A	25/24	**8c**	100	50 (85 : 15)
5	**6k**	A	60/10	**8d**+**8d'**	98	45 (30 : 70)
6	**6i**	A	60/10	**8e(8d')**	100	70 (20 : 80)
7	**6n**	A	60/10	**8f**	100	78 (88 : 12)
8	**6s**	A	25/6	**8g**+**8g'**	80	50 (20 : 80)
9	**6s**	A	70/10	**8g**+**8g'**	100	73 (18 : 82)

[a] A = NH_4OH, B = NH_4OAc; B + A means that A was added after reaction of **6** with B for 2 h.
[b] All new products were fully characterized by ^1H NMR, ^{19}F NMR, IR, MS and elemental analysis.
[c] Overall isolated yield based on **6**.
[d] X : X' = Ratio of the directly condensed product **8** to its corresponding dealkoxycarbonylated or deacetylated derivative **8'**.

It was interesting to notice that on treatment by ammonium hydroxide, deacetylation always occurred at r.t. in the preparation of **7** or **8**. However, dealkoxycarbonylation occurred at r.t. in the preparation of **8** but never did even at reflux in the preparation of **7**. Compounds **7** or **8** did not transform into their corresponding **7'** or **8'** under even more severe conditions. A reasonable explanation is that both dealkoxycarbonylation and deacetylation might occur in the course of and in competition with the condensation reaction but not on the products.

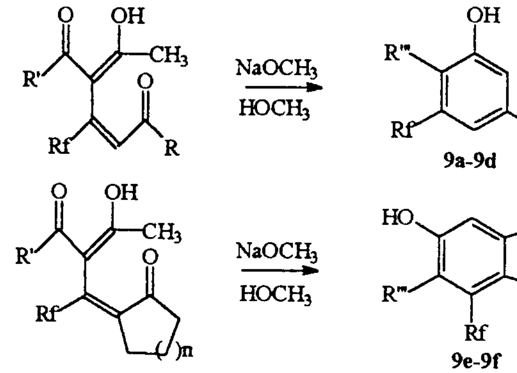
The versatile 1,5-dicarbonyl compounds **6** were also common precursors for the preparation of polyalkyl-substituted *meta*-fluoroalkylphenols on condition that they contained two ketonic carbonyl groups in the 1,5-positions and at least one of which was an acetyl group. When such substrates were treated with 2–3 molecular equivalents of sodium methoxide in anhydrous methanol at r.t. for 10 h, the intramolecular aldol condensation proceeded readily to give annulation products **9** in high yields (Scheme 4). Other reaction systems of choice were NaH in THF or KOH in EtOH, but with less efficiency. Results of the reaction are summarized in Table 4.

Two isomers of the product were expected from substrate **6a**, **6g** or **6h**, because in these cases, both of the functional groups involved in condensation were acetyl groups. However, only one product was identified and its ^1H NMR spectrum revealed definitely a phenol hydroxylic proton involved in a intramolecular hydrogen bond

Table 4. Synthesis of *meta*-Fluoroalkylphenols

Entry	Substrate	Product[b]	Reagent	Rf	R	R'''	Yield (%)[b]
1	**6a**	**9a**	NaOCH$_3$/ HOCH$_3$	CF$_3$	CH$_3$	CO$_2$CH$_3$	87
2	**6b**	**9b**		CF$_3$	C(CH$_3$)$_3$	H	80
3	**6g**	**9c**		Cl(CF$_2$)$_3$	CH$_3$	CO$_2$CH$_3$	85
4	**6h**	**9d**[c]		Cl(CF$_2$)$_3$	CH$_3$	H	88
					n		
5	**6p**	**9e**	NaOCH$_3$/ HOCH$_3$	CF$_3$	1	H	86
6	**6r**	**9f**		CF$_3$	2	H	83

[a] All new products were fully characterized by ^{1}H NMR, ^{19}F NMR, IR, MS and elemental analysis.
[b] Isolated yield based on **6**.
[c] Compound **1g** reacted with acetylacetone in NaH/THF gave **9d** directly.



Scheme 4

by the single resonance at $\delta = 11.6-13.0$. Therefore, the structure for them were assigned as **9a**, **9c** and **9d**, respectively.

In such a reaction, deacetylation usually followed the annulation reaction and in fact, a mixture of starting material, the direct annulation product and its deacetylation derivative could be detected and isolated in the course of reaction. A higher temperature or longer reaction time facilitated the deacetylation. Fluoroalkyl groups and alkyl groups in substrates **6** had little effect on the reaction. Therefore, *meta*-trifluoromethylphenols and 6-hydroxy-4-trifluoromethylindan (**9e**), which were minor products as isomers of fluoroalkylation, were prepared in high yields from **6** containing a trifluoromethyl group.

Mps are uncorrected. IR spectra were recorded as film for liquid samples and KCl plates for solid samples on a Shimadzu IR-440 Spectrometer. ^{1}H NMR spectra were measured using CDCl$_3$ as solvent and internal TMS as standard on a Varian EM-390A spectrometer. ^{19}F NMR spectra were obtained with external CF$_3$COOH as standard with upfield shifts positive on a Varian EM-360L spectrometer at 56.4 MHz. Mass spectra were recorded on a HP5989A mass spectrometer. All chemicals and reagents were of analytical grade and were used without further purification. Light petroleum refers to the fraction boiling in the range 60–90 °C.

1,5-Dicarbonyl Substrates 6; General Procedure:

A mixture of **1** (5 mmol) and sodium carbonate (20 mmol) in 1,4-dioxane (10 mL) was well stirred at 60 °C for 1 h and then active methylene compound (6 mmol) was added dropwise. Stirring was continued under the same conditions for 10–15 h. After the reaction was complete (monitored by TLC and ^{19}F NMR) the mixture was poured into H$_2$O (50 mL) and extracted with Et$_2$O (3 × 20 mL). The combined extracts were washed thoroughly with brine and dried (Na$_2$SO$_4$). The residue which remained after evaporation was purified by flash chromatography on silica gel using light petroleum/EtOAc mixture (20 : 1–10 : 1 by volume) as eluent to give pure products as an oil in high yield.

2-Hydroxy-3-(methoxycarbonyl)-4-(trifluoromethyl)hepta-2,4-dien-6-one (**6a**):

UV: λ_{max} (nm) = 248.

IR: ν_{max} = 2950 (CH, OH), 1720 (C=O), 1650, 1610 (C=C), 1260, 1180 cm^{-1}.

^{1}H NMR: δ = 13.60 (1 H, s), 6.70 (1 H, s), 3.70 (3 H, s), 2.26 (3 H, s), 1.95 (3 H, s).

^{19}F NMR: δ = − 10.50 (3 F, s).

MS: (*m*/*z*) = 252 (M$^+$, 5.28), 235 (40.12), 216 (21.78), 43 (100).

Analysis: Calc. for C$_{10}$H$_{11}$F$_3$O$_4$: C, 47.61; H, 4.37; F, 22.62 Found: C, 47.21; H, 4.00; F, 22.54.

3-Acetyl-2-hydroxy-7,7-dimethyl-4-(trifluoromethyl)octa-2,4-dien-6-one (**6b**):

UV: λ_{max} (nm) = 282.

IR: ν_{max} = 2960, 1700, 1600, 1280, 1180, 1130 cm^{-1}.

^{1}H NMR: δ = 16.70 (1 H, s), 7.25 (1 H, s), 2.06 (6 H, s), 1.20 (9 H, s).

^{19}F NMR: δ = − 10.30 (3 F, s).

MS: (*m*/*z*) = 261 (M$^+$ − OH, 90.73), 235 (29.52), 215 (37.10), 43 (100).

Analysis: Calc. for C$_{13}$H$_{17}$F$_3$O$_3$: C, 56.11; H, 6.12; F, 20.50 Found: C, 55.68; H, 6.12; F, 20.54.

2-Hydroxy-3-(methoxycarbonyl)-7,7-dimethyl-4-(trifluoromethyl)-octa-2,4-dien-6-one (**6c**):

IR: ν_{max} = 2950 (CH, OH), 1710 (C=O), 1660, 1620 (C=C), 1260 cm^{-1}.

^{1}H NMR: δ = 13.05 (1 H, s), 7.10 (1 H, s), 3.70 (3 H, s), 1.95 (3 H, s), 1.18 (9 H, s).

^{19}F NMR: δ = − 10.30 (3 F, s).

MS: (*m*/*z*) = 277 (M$^+$ − OH, 9.65), 259 (9.02), 237 (5.90), 219 (17.76), 57 (100).

HRMS: Calc. for C$_{13}$H$_{17}$F$_3$O$_4$: 294.1080; Found: 294.1064.

Ethyl 5-Hydroxy-4-(methoxycarbonyl)-3-(trifluoromethyl)hexa-2,4-dienecarboxylate (**6e**):

UV: λ_{max} (nm) = 248.

IR: ν_{max} = 2980, 1740, 1660, 1620, 1450, 1260 cm^{-1}.

^{1}H NMR: δ = 13.70 (1 H, s), 6.58 (1 H, s), 4.20 (2 H, q), 3.77 (3 H, s), 1.96 (3 H, s), 1.24 (3 H, t).

^{19}F NMR: δ = − 9.0 (3 F, s).

MS: $(m/z) = 251$ ($M^+ - OCH_3$, 25.70), 250 (49.61), 222 (24.60), 205 (100), 194 (15.39), 177 (51.57), 163 (51.05), 43 (93.15).

Analysis: Calc. for $C_{11}H_{13}F_3O_5$: C, 46.46; H, 4.40; F, 20.21 Found: C, 46.54; H, 4.46; F, 20.08.

Ethyl 3-(Chlorodifluoromethyl)-5-hydroxy-4-(methoxycarbonyl)-hexa-2,4-dienecarboxylate (**6f**):

UV: λ_{max} (nm) = 250.

IR: λ_{max} = 2960, 1710, 1650, 1600, 1250 cm^{-1}.

^{1}H NMR: δ = 13.30 (1 H, s), 6.55 (1 H, s), 4.20 (2 H, q), 3.76 (3 H, s), 2.40 (3 H, s), 1.67 (3 H, t).

^{19}F NMR: δ = − 19.0 (2 F, s).

MS: $(m/z) = 299$ ($M^+ + H$, 13.82), 278 (4.71), 267 (48.36), 225 (44.57), 193 (34.52).

Analysis: Calc. for $C_{11}H_{13}F_2O_5Cl$: C, 44.69; H, 4.10; F, 12.73 Found: C, 43.98; H, 4.24; F, 12.50.

4-(ω-Chlorohexafluoropropyl)-2-hydroxy-3-methoxycarbonylhepta-2,4-dien-6-one (**6g**):

IR: ν_{max} = 2900, 1715, 1660, 1610, 1260, 1180 cm^{-1}.

^{1}H NMR: δ = 13.30 (1 H, s), 6.73 (1 H, s), 3.71 (3 H, s), 2.26 (3 H, s), 1.93 (3 H, s).

^{19}F NMR: δ = − 10.05 (3 F, s), 32.6 (2 F, m), 42.2 (2 F, m).

MS: $(m/z) = 369$ ($M^+ + H$, 2.01), 351 (50.07), 337 (14.46), 325 (17.26), 305 (26.84), 295 (18.85), 293 (25.40), 43 (100).

HRMs: Calc. for $C_{12}H_{11}F_6O_4Cl$: 368.0251; Found: 368.0208.

3-Acetyl-4-(ω-chlorohexafluoropropyl)-2-hydroxyhepta-2,4-dien-6-one (**6h**):

UV: λ_{max} (nm) = 282.

IR: ν_{max} = 2900, 1710, 1660, 1610, 1260 cm^{-1}.

^{1}H NMR: δ = 17.45 (1 H, s), 6.86 (1 H, s), 2.33 (3 H, s), 2.10 (6 H, s).

^{19}F NMR: δ = − 10.0 (3 F, s), 32.0 (2 F, m), 41.3 (2 F, m).

MS: $(m/z) = 335$ ($M^+ - OH$, 5.21), 292 (3.88), 247 (10.07), 223 (14.46), 131 (12.03), 43 (100).

Analysis: Calc. for $C_{12}H_{11}F_6O_3Cl$: C, 40.85; H, 3.12; F, 32.34 Found: C, 40.49; H, 3.17; F, 32.44.

Ethyl 3-(ω-Chlorohexafluoropropyl)-2-(ethoxycarbonyl)-5-hydroxyhexa-2,4-dienecarboxylate (**6i**):

UV: λ_{max} (nm) = 318.

IR: ν_{max} = 1760, 1650, 1580, 1180 cm^{-1}.

^{1}H NMR: δ = 6.10 (1 H, s), 4.40 (4 H, m), 2.40 (3 H, s), 1.40 (6 H, m).

^{19}F NMR: δ = − 8.3 (2 F, m), 36.0 (2 F, m), 43.0 (2 F, m).

MS: $(m/z) = 412$ (M^+, 2.71), 388 (10.97), 335 (13.14), 297 (12.90), 233 (24.84), 149 (100).

Analysis: Calc. for $C_{14}H_{15}F_6O_5Cl$: C, 40.73; H, 3.64; F, 27.64 Found: C, 40.10; H, 2.82; F, 27.30.

Ethyl-3-(ω-Chlorohexafluoropropyl)-5-hydroxy-4-(methoxycarbonyl)hexa-2,4-dienecarboxylate (**6k**):

UV: λ_{max} (nm) = 310.

IR: ν_{max} = 2960, 1740, 1660, 1610, 1440, 1250, 1180 cm^{-1}.

^{1}H NMR: δ = 13.18 (1 H, s), 6.55 (1 H, s), 4.20 (2 H, q), 3.76 (3 H, s), 1.98 (3 H, s), 1.30 (3 H, t).

^{19}F NMR: δ = − 10.06 (2 F, m), 33.2 (2 F, s), 42.6 (2 F, s).

MS: $(m/z) = 398$ (M^+, 13.82), 378 (14.86), 367 (14.17), 337 (12.34), 325 (30.90), 311 (35.97), 293 (91.53), 43 (100).

Analysis: Calc. for $C_{13}H_{13}F_6O_5Cl$: C, 39.15; H, 3.26; F, 28.61. Found: C, 39.00; H, 3.23; F, 28.34

Ethyl 4-Acetyl-3-(ω-chlorohexafluoropropyl)-5-hydroxyhexa-2,4-dienecarboxylate (**6l**):

IR: ν_{max} = 2960, 1730, 1600, 1390, 1180 cm^{-1}.

^{1}H NMR: δ = 16.90 (1 H, s), 6.70 (1 H, s), 4.25 (2 H, q), 2.10 (6 H, s), 1.30 (3 H, t).

^{19}F NMR: δ = − 10.0 (2 F, m), 31.5 (2 F, s), 41.3 (2 F, s).

MS: $(m/z) = 383$ ($M^+ + H$, 60.15), 362 (13.11), 341 (62.40), 321 (11.61), 289 (41.87).

Analysis: Calc. for $C_{13}H_{13}F_6O_4Cl$: C, 40.78; H, 3.40; F, 29.80. Found: C, 40.40; H, 3.15; F, 30.44.

2-[3′-Acetyl-2′-hydroxy-4′-(trifluoromethyl)buten-2′-ylidene]cyclopentanone (**6m**):

UV λ_{max} (nm): 282.

IR: ν_{max} = 2960, 1730, 1600, 1200, 1120 cm^{-1}.

^{1}H NMR: δ = 16.70 (1 H, s), 3.60 (2 H, m), 2.40 (2 H, m), 2.31 (2 H, m), 1.96 (6 H, s).

^{19}F NMR: δ = − 15.3 (2 F, m).

MS: $(m/z) = 244$ ($M^+ - H_2O$, 18.59), 234 (8.85), 213 (22.21), 186 (49.15), 43 (100).

Analysis: Calc. for $C_{12}H_{13}F_3O_3$: C, 54.96; H, 4.96; F, 21.76 Found: C, 54.25; H, 5.00; F, 21.54.

2-[3′-Acetyl-2′-hydroxy-4′-(trifluoromethylbuten)-2′-ylidene]cyclohexanone (**6o**):

UV: λ_{max} (nm): 282.

IR: ν_{max} = 2950, 1715, 1600, 1410, 1130 cm^{-1}.

^{1}H NMR (300 MHz): δ = for one isomer: 17.10 (1 H, s), 2.90 (2 H, m), 2.46 (2 H, m), 2.15 (6 H, s), 1.95 (4 H, m); ^{19}F NMR: δ = − 20.0; for the other: 15.0 (1 H, s), 2.66 (2 H, m), 2.54 (2 H, m), 2.10 (2 H, m), 2.15 (6 H, s), 1.90 (2 H, m); ^{19}F NMR: δ = − 18.0.

MS: $(m/z) = 275$ ($M^+ - H$, 0.94), 259 ($M^+ - OH$, 77.44), 233 (44.04), 213 (100), 171 (15.04).

Analysis: Calc. for $C_{13}H_{15}F_3O_3$: C, 56.52; H, 5.43; F, 20.65 Found: C, 56.16; H, 5.38; F, 20.19.

Condensation of 6 with Ammonia to Produce 4-Fluoroalkylpyridines 7 or 4-Fluoroalkylpyrid-2(1*H*)-ones 8:

To a well-stirred solution of **6** (5 mmol) in THF (5 mL), $NH_3{\cdot}H_2O$ (or NH_4OAc) (15 mmol) was added slowly. Then the mixture was stirred vigorously at r.t. till the reaction was complete (monitored by TLC. About 2 h for preparation of **7** and about 10 h for **8**). The reactant was diluted with H_2O (50 mL) and extracted with Et_2O (3 × 20 mL) (for **8**, extracted with EtOAc). Drying (Na_2SO_4) followed by concentration furnished the crude product which was subjected to flash chromatography to afford **7** as an oil in high yield or **8** as white crystals in moderate to good yield.

6-tert-Butyl-3-(methoxycarbonyl)-2-methyl-4-(trifluoromethyl)pyridine (**7a**):

IR: ν_{max} = 2960 (CH), 1750 (C=O), 1590 (C=C), 1175 cm^{-1}.

^{1}H NMR: δ = 7.37 (1 H, s), 3.93 (3 H, s), 2.60 (3 H, s), 1.40 (9 H, s).

^{19}F NMR: δ = − 16.5 (3 F, s).

MS (m/z): 276 ($M^+ + 1$, 27.58), 261 ($M^+ + 1\text{-}CH_3$, 17.11), 244 ($M^+ - CH_3O$, 100), 229 (19.06), 201 (32.56), 92 (28.25), 91 (25.55).

HRMS: Calc. for $C_{13}H_{16}F_3NO_2$: 275.1133; Found: 275.1110.

4-(ω-Chlorohexafluoropropyl)-2,6-dimethyl-3-(methoxycarbonyl)-pyridine (**7b**):

UV: λ_{max} (nm): 274.

IR: ν_{max} = 2960, 1750, 1600, 1280, 1170 cm^{-1}.

^{1}H NMR: δ = 7.15 (1 H, s), 3.93 (3 H, s), 2.66 (3 H, s), 2.58 (3 H, s).

^{19}F NMR: δ = − 9.6 (2 F, m), 31.0 (2 F, m), 41.5 (2 F, s).

MS: $(m/z) = 349$ (M^+, 28.43), 334 (4.57), 318 ($M^+ - CH_3O$, 100), (7.07), 174 (22.17).

Analysis: Calc. for $C_{12}H_{10}F_6NO_2Cl$: C, 41.20; H, 2.86; N, 4.00; F, 32.63 Found: C, 41.30; H, 2.89; N, 3.40; F 32.64.

3-Acetyl-4-(ω-chlorohexafluoropropyl)-2,6-dimethylpyridine (**7c**):

UV: λ_{max} (nm) = 276.

IR: ν_{max} = 1720, 1595, 1380, 1330, 1180 cm^{-1}.

^{1}H NMR: δ = 7.15 (1 H, s), 2.66 (3 H, s), 2.56 (3 H, s).

^{19}F NMR: δ = − 10.3 (2 F, m), 29.0 (2 F, m), 41.0 (2 F, s).

MS: $(m/z) = 333$ (M^+, 6.17), 318 ($M^+ - CH_3$, 100), 298 ($M^+ - Cl$, 8.89), 255 (4.25), 174 (17.11).

Analysis: Calc. for $C_{12}H_{10}F_6NOCl$: C, 43.18; H, 3.00; N, 4.20. Found: C, 43.21; H, 2.62; N, 3.93.

3-Acetyl-2-methyl-5,6-propylene-4-(trifluoromethyl)pyridine (**7d**):

IR: $\nu_{\max} = 2970, 1720, 1350, 1140\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 3.06$ (4H, m), 2.55 (6H, 2×s), 2.18 (2H, m).

^{19}F NMR: $\delta = -19.2$ (3F, s).

MS (m/z): 243 (M^{+}, 12.46), 228 ($M^{+} - CH_3$, 88.97), 200 ($M^{+} - CH_3CO$, 33.12), 180 (4.01), 43 (100).

Analysis: Calc. for $C_{12}H_{12}F_3NO$: C, 59.26; H, 4.94; N, 5.76; F, 23.45 Found: C, 52.20; H, 5.02; N, 5.62; F, 23.80.

3-Acetyl-2-methyl-4-(trifluoromethyl)-5,6,7,8-tetrahydroquinoline (**7e**):

UV: $\lambda_{\max}$ (nm) = 286.

IR: $\nu_{\max} = 2940, 1720, 1200, 1140\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 2.90$ (4H, m), 2.50 (3H, s), 2.45 (3H, s), 1.82 (4H, m).

^{19}F NMR: $\delta = -21.0$ (3F, s).

MS: (m/z) = 257 (M^{+}, 14.28), 242 ($M^{+} - CH_3$, 100), 214 [$M^{+} - CH_3CO$, 38.92].

HRMS: Calc. for $C_{13}H_{14}F_3NO$: 257.1028; Found: 257.1017.

2-Methyl-4-(trifluoromethyl)-5,6,7,8-tetrahydroquinoline (**7e′**):

UV: $\lambda_{\max}$ (nm) = 282.

IR: $\nu_{\max} = 2910, 1450, 1350, 1140\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 7.17$ (1H, s), 2.91 (4H, m), 2.56 (3H, s), 1.85 (4H, m).

^{19}F NMR: $\delta = -13.8$ (3F, s).

MS: (m/z) = 215 (M^{+}, 100), 200 (26.13), 187 (42.34), 174 (4.09), 146 (17.86).

HRMS: Calc for $C_{11}H_{12}F_3N$: 215.0921; Found: 215.0960.

3-Acetyl-4-(chlorodifluoromethyl)-2-methyl-5,6,7,8-tetrahydroquinoline (**7f**):

IR: $\nu_{\max} = 2950, 1720, 1420, 1120\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 3.0$ (4H, m) 2.55 (3H, s), 2.47 (3H, s), 1.90 (4H, m).

^{19}F NMR: $\delta = -33.0$ (2F, s).

MS (m/z) = 273 (M^{+}, 13.19), 258 ($M^{+} - CH_3$), 100), 238 (258 − HF), 15.23), 230 ($M^{+} - CH_3CO$, 17.18), 215 (9.06).

HRMS: Calc. for $C_{13}H_{14}F_2NOCl$: 273.0723; Found: 273.0723.

4-(Chlorodifluoromethyl)-2-methyl-3-(methoxycarbonyl)-5,6,7,8-tetrahydroquinoline (**7g**):

UV: $\lambda_{\max}$ (nm): 290.

IR: $\nu_{\max} = 2980, 1750, 1440, 1270, 1130\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 3.83$ (3H, s), 2.96 (4H, m), 2.50 (3H, s), 1.84 (4H, m).

^{19}F NMR: $\delta = -31.0$ (2F, s).

MS (m/z): 289 (M^{+}, 73.82), 269 ($M^{+} - HF$ 14.54), 2.58 ($M^{+} - OCH_3$, 100), 254 ($M^{+} - Cl$, 78.44), 238 (258 − HF, 62.31), 218 (37.09), 230 ($M^{+} - CO_2CH_3$, 20.9).

Analysis: Calc. for $C_{13}H_{14}F_2NO_2Cl$: C, 52.26; H, 4.69; N, 4.69; F, 13.13 Found: C, 52.29; H, 4.67; N, 4.54; F, 13.44.

6-tert-Butyl-5-(ethoxycarbonyl)-4-trifluoromethylpyrid-2(1H)-one (**8a**): mp 195–197 °C.

UV: $\lambda_{\max}$ (nm): 328.

IR: $\nu_{\max} = 4200, 2950, 1740, 1650, 1620, 1460\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 6.33$ (1H, s), 4.35 (2H, q), 1.44 (9H, s), 1.30 (3H, t).

^{19}F NMR: $\delta = -15.0$ (3F, s).

MS: (m/z) = 292 ($M^{+} + 1$, 38.68), 276 (2.87), 246 ($M^{+} - OC_2H_5$, 38.49), 230 (100), 219 (14.26).

HRMS: Calc. for $C_{13}H_{16}F_3NO_3$: 291.1083; Found: 291.1113.

6-tert-Butyl-4-trifluoromethylpyrid-2(1H)-one (**8a′**):
mp 173–174 °C.

UV: $\lambda_{\max}$ (nm): 324.

IR: $\nu_{\max} = 4300, 2900, 1740, 1670, 1610, 1460\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 6.72$ (1H, s), 6.29 (1H, s), 1.46 (9H, s).

^{19}F NMR: $\delta = -11.8$ (3F, s).

MS: (m/z) = 219 (M^{+}, 32.82), 204 ($M - CH_3$, 100), 186 (11.55), 177 (12.59).

Analysis: Calc. for $C_{10}H_{12}F_3NO$: C, 54.79; H, 5.48; N, 6.39; F, 26.02 Found: C, 54.47; H, 5.44; N, 6.16; F, 26.23.

5-(Methoxycarbonyl)-6-methyl-4-trifluoromethylpyrid-2(1H)-one (**8b**): mp 200–203 °C.

IR: $\nu_{\max} = 4100, 1730, 1680, 1290, 1160\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 6.76$ (1H, s), 3.90 (3H, s), 2.53 (3H, s).

^{19}F NMR: $\delta = -14.0$ (3F, s).

MS: (m/z) = 235 (M^{+}, 42.10), 216 ($M^{+} - F$, 3.57), 204 ($M^{+} - OCH_3$, 100).

Analysis: Calc. for $C_9H_8F_3NO_3$: C, 45.96; H, 3.40; N, 5.96; F, 24.25 Found: C, 45.98; H, 3.18; N, 5.89; F, 24.23.

4-(Chlorodifluoromethyl)-5-methoxycarbonyl-6-methylpyrid-2(1H)-one (**8c**): mp 190–192 °C.

IR: $\nu_{\max} = 4100, 1730\ (-CO_2)\ 1670\ (-CO-N), 1280, 1120\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 6.73$ (1H, s), 3.83 (3H, s), 2.40 (3H, s).

^{19}F NMR: $\delta = -25.3$ (2F, s).

MS: (m/z) = 251 (M^{+}, 39.0), 231 ($M^{+} - HF$, 11.81), 220 ($M^{+} - OCH_3$, 100), 178 (12.35).

Analysis: Calc. for $C_9H_8F_2NO_3Cl$: C, 42.94; H, 3.18; N, 5.57; F, 15.11; Cl, 14.11. Found: C, 42.81; H, 2.67; N, 5.38; F, 15.23; Cl, 14.04.

4-(*ω-Chlorohexafluoropropyl)-5-methoxycarbonyl-6-methylpyrid-2(1H)-one* (**8d**): mp 145–148 °C.

IR: $\nu_{\max} = 3100, 1740, 1670, 1280\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 13.80$ (1H, br s), 6.74 (1H, s), 3.90 (3H, s), 2.53 (3H, s).

^{19}F NMR: $\delta = -9.60$ (2F, s), 30.0 (2F, s), 40.6 (2F, s)

MS: (m/z) = 351 (M^{+}, 35.63), 320 (100), 279 (2.58), 252 (9.10).

Analysis: Calc. for $C_{11}H_8F_6NO_3Cl$: C, 37.55; H, 2.27; N, 3.98; F, 32.43. Found: C, 37.43; H, 1.90; N, 3.72; F, 32.24.

4-(ω-Chlorohexafluoropropyl)-6-methylpyrid-2(1H)-one (**8d′** or **8e**): mp 103–106 °C.

IR: $\nu_{\max} = 3100, 1670, 1180, 1120\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 6.70$ (1H, s), 6.23 (1H, s), 2.46 (3H, s).

^{19}F NMR: $\delta = -11.0$ (2F, s), 35.4 (2F, s), 42.7 (2F, s).

MS: (m/z) = 293 (M^{+}, 45.43), 258 ($M^{+} - Cl$, 9.74), 238 (3.54), 158 [$M^{+} - Cl(CF_2)_2$, 6.42], 130 (158 − CO, 100).

Analysis: Calc. for $C_9H_6F_6NOCl$: C, 36.80; H, 2.04; N, 4.77; F, 38.84. Found: C, 36.62; H, 2.07; N, 4.35; F, 37.68.

3-(Ethoxycarbonyl)-5,6-propylene-4-(trifluoromethyl)pyrid-2(1H)-one (**8f**): mp 129–131 °C.

IR $\nu_{\max} = 4300, 2900, 1740, 1640, 1610, 1460\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 4.35$ (2H, q), 3.0 (4H, m), 2.5 (2H, m), 2.26 (2H, m), 1.3 (3H, t).

^{19}F NMR: $\delta = -8.5$ (3F, s).

MS: (m/z) = 275 (M^{+}, 54.82), 247 ($M^{+} - CO$, 4.95), 230 ($M^{+} - OC_2H_5$, 100), 201 ($M^{+} - HCO_2C_2H_5$, 85.25), 173 (37.65).

Analysis: Calc. for $C_{12}H_{12}F_3NO_3$: C, 52.36; H, 4.36; N, 5.09; F, 20.73. Found: C, 51.93; H, 4.27; N, 4.98; F, 20.76.

5,6-Propylene-4-(trifluoromethyl)pyrid-2(1H)-one (**8f**):
mp 196–199 °C.

IR: $\nu_{\max} = 4300, 2900, 1670, 1620, 1460\ \mathrm{cm}^{-1}$.

^{1}H NMR: $\delta = 6.37$ (1H, s), 3.10 (2H, m), 2.46 (2H, m), 2.34 (2H, m).

^{19}F NMR: $\delta = -13.0$ (3F, s).

MS: (m/z) = 203 (M^{+}, 100), 175 ($M^{+} - CO$, 100), 161 [$M^{+} - (CH_2)_3$, 51.74.

Analysis: Calc. for $C_9H_8F_3NO$: C, 53.20; H, 3.94; N, 6.90; F, 28.08. Found: C, 52.60; H, 4.12; N, 6.53; F, 28.53.

4-(Chlorodifluoromethyl)-3-(ethoxycarbonyl)-5,6,7,8-tetrahydroquinolin-2-one (**8g**): mp 168–170 °C.

UV: $\lambda_{\max}$ (nm) = 340.

IR: $\nu_{\max} = 4300, 2900, 1720, 1640, 1460\ \mathrm{cm}^{-1}$.

^{1}H NMR: δ = 4.35 (2 H, q), 2.68 (4 H, m), 1.75 (4 H, m).

^{19}F NMR: δ = −9.2 (2 F, s).

MS: (m/z) = 305 (M^+, 54.74), 260 (M^+ $-OC_2H_5$, 100), 233 (M^+ $-CO_2C_2H_5$, 90.72), 255 (47.8), 203 [M^+ $-Cl-(CH_2)_4$, 78.55].

Analysis: Calc. for $C_{13}H_{14}F_2N_3Cl$: C, 51.06; H, 4.58; N, 4.58; F, 12.43. Found: C, 51.54; H, 4.57; N, 4.39; F, 12.44.

4-(Chlorodifluoromethyl)-5,6,7,8-tetrahydroquinolin-2-one (**8 g′**): mp 210–211 °C.

UV: λ_{max} (nm): 332.

IR: ν_{max} = 4200, 2900, 1670, 1620, 1460 cm^{-1}.

^{1}H NMR: δ = 6.66 (1 H, s), 2.70 (4 H, m), 1.77 (4 H, m).

^{19}F NMR: δ = −25.0 (2 F, s).

MS: (m/z) = 233 (M^+, 100), 218 (3.63), 206 (M^+ −CO, 44.59), 198 (30.61), 177 [M^+ $-(CH_2)_4$, 32.0], 170 (M^+ −Cl−CO, 40.31), 142 (28.96).

Analysis: Calc. for $C_{10}H_{10}F_2NOCl$: C, 51.39; H, 4.28; N, 6.00; F, 16.27. Found: C, 51.08; H, 4.16; N, 5.89; F, 16.19.

Intramolecular Aldol Condensation of 6 to Prepare *meta*-Fluoroalkylphenols 9

To a well-stirred solution of **6** (5 mmol) in aq MeOH (10 mL), NaOMe (20 mmol) was added slowly at 0–5 °C. Then the mixture was allowed to stir at r.t. overnight (about 10 h, monitored by TLC). The reactant was diluted with water (50 mL) and extracted with Et_2O (3 × 20 mL). Washing with brine followed by drying (Na_2SO_4), then evaporation of solvents furnished the crude product which was subjected to flash chromatography to afford **9** as an oil in high yields.

2-(Methoxycarbonyl)-5-methyl-3-(trifluoromethyl)phenol (**9 a**):

IR: ν_{max} = 3350 (OH), 1670 (C=O), 1610 (C=C), 1340, 1120 cm^{-1}.

^{1}H NMR: δ = 12.3 (1 H, s), 7.03 (1 H, s), 6.93 (1 H, s), 3.95 (3 H, s), 2.24 (3 H, s).

^{19}F NMR: δ = −13.5 (3 F, s).

MS: (m/z) = 234 (M^+, 33.67), 219 (13.01), 202 (100), 173 (29.24).

HRMS: Calc. for $C_{10}H_9F_3O_3$: 234.0504; Found: 234.0538.

5-tert-Butyl-3-(trifluoromethyl)phenol (**9 b**):

UV: λ_{max} (nm) = 282.

IR: λ_{max} = 3300, 1610, 1350, 1130 cm^{-1}.

^{1}H NMR: δ = 7.20 (1 H, s), 7.03 (1 H, s), 6.90 (1 H, s), 5.64 (1 H, br), 1.30 (9 H, s).

^{19}F NMR: δ = −14.0 (3 F, s).

MS: (m/z) = 218 (M^+, 38.81), 203 (100), 175 (53.84).

Analysis: Calc. for $C_{11}H_{13}F_3O$: C, 60.55; H, 6.00; F, 26.15. Found: C, 59.81, H, 6.61; F, 25.50.

3-(ω-Chlorohexafluoropropyl)-2-(methoxycarbonyl)-5-methylphenyl (**9 c**):

IR: ν_{max} = 3800, 1660, 1600, 1450, 1160 cm^{-1}.

^{1}H NMR: δ = 13.0 (1 H, s), 7.13 (1 H, s), 7.03 (1 H, s), 3.76 (3 H, s), 1.87 (3 H, s).

^{19}F NMR: δ = −11.0 (2 F, s), 34.0 (2 F, m), 41.0 (2 F, s).

MS: (m/z) = 350 (M^+, 23.45), 319 (100), 245 (6.37), 215 (11.28).

Analysis: Calc. for $C_{12}H_9F_6O_3Cl$: C, 41.08; H, 2.56; F, 32.52. Found: C, 40.81; H, 2.39; F, 33.0.

3-(ω-Chlorohexafluoropropyl)-5-methylphenol (**9 d**):

IR: ν_{max} = 3300, 1680, 1640, 1420, 1150 cm^{-1}.

^{1}H NMR: δ = 11.6 (1 H, s), 7.06 (1 H, s), 6.93 (1 H, s), 2.70 (3 H, s), 2.65 (3 H, s).

^{19}F NMR: δ = −11.0 (2 F, s), 33.7 (2 F, m), 42.5 (2 F, s).

MS: (m/z) = 334 (M^+, 21.26), 319 (100), 299 (2.25).

Analysis: Calc. for $C_{12}H_9F_6O_2Cl$: C, 43.11; H, 2.70; F, 34.13. Found: C, 43.66; H, 2.90; F, 34.50.

6-Hydroxy-4-(trifluoromethyl)indan (**9 e**):

UV: λ_{max} (nm): 292.

IR: ν_{max} = 3350, 2970, 1620, 1470, 1360, 1120 cm^{-1}.

^{1}H NMR: δ = 6.92 (2 H, 2 × s), 5.50 (1 H, br), 2.90 (4 H, m), 2.10 (2 H, m).

^{19}F NMR: δ = −15.5 (3 F, s).

MS: (m/z) = 202 (M^+, 89.78), 183 (19.39), 172 (3.42), 133 (M^+ $-CF_3$).

Analysis: Calc. for $C_{10}H_9F_3O$: C, 59.4; H, 4.46; F, 28.22. Found: C, 58.36; H, 4.40; F, 28.90.

9-Hydroxy-7-(trifluoromethyl)tetralin (**9 f**):

UV: λ_{max} (nm): 290.

IR: ν_{max} = 3300, 2900, 1620, 1460, 1110 cm^{-1}.

^{1}H NMR: δ = 6.96 (1 H, s), 6.73 (1 H, s), 5.20 (1 H, br), 2.80 (4 H, m), 1.80 (4 H, m).

^{19}F NMR: δ = −16.5 (3 F, s).

MS: (m/z) = 216 (M^+, 80.01), 197 (5.95), 188 (100), 175 (16.67), 159 (5.84), 147 (73.93).

Analysis: Calc. for $C_{11}H_{11}F_3O$: C, 61.11; H, 5.09; F, 26.39. Found: C, 60.89; H, 5.43; F, 26.38.

We gratefully acknowledge the financial support from the National Natural Science Foundation of China.

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