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Synthesis of fluoromethylated materials in ionic liquids

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Abstract

Syntheses of fluoromethylated materials via Michael additions with the Baylis–Hillman type reaction and the reaction of fluoromethylated imines with enamines in ionic liquid are described.

Keywords: Micael addition; Ionic liquid; Enamine; Baylis–Hillman reaction

1. Introduction

Extensive research has already been carried out on incorporation of fluorine into molecules which can lead to profound and unexpected results on biological activities and/or physical properties [1,2]. Recent investigations in this field have opened up the possibility for synthesis by employing biocatalysts [3], along with conventional chemical methods [4,5]. They are, however, commonly associated with two major sources of waste: organic solvents and catalysts (such as, enzyme or chemical catalyst). In synthetic chemistry, the research regarding reusable media such as fluorous fluids [6,7] and molten salts (ionic liquids) [8,9] is focused on the reaction media. Especially, the study of reusable media such as molten salts (ionic liquids) is an important for organic synthesis [8,9]. Recently, we have reported the design and utility of a reusable reaction system derived from an ionic liquid and trifluoromethane sulfonic acid or rare earth salts for carbon–carbon bond forming reactions, and we demonstrated the affinity between the ionic liquids and the catalysts [10].

For our continuous studies on the reusable reaction system, we would like to describe the utility of ionic liquid as a reusable medium for the synthesis of fluoromethylated materials based on the Michael addition via Baylis–Hillman reaction, and the reaction of fluoromethylated imines with acetone derivatives in the L–proline–Lewis acid–ionic liquid system.

2. Results and discussion

2.1. Michael addition reaction in ionic liquid

While it is well known that the Baylis–Hillman reaction [11] is a valuable synthetic reaction to obtain the functionalized materials, this reaction system is limited in its practicality by poor reaction rates. Based on the several attempts made to increase the rate of this reaction through either physical or chemical means [12], reaction solvents [13] such as water or fluorinated solvents result in increased rates as a result of hydrophobic and fluorophobic effects, respectively. Further, it is reported that the formation of Lewis acids–1,4-diaza-bicyclo-[2,2,2]-octane (DABCO) complex accelerates the Baylis–Hillman reaction via the metal complex with the reaction intermediate [14]. Therefore, we examined the first example of the Michael additions via the Baylis–Hillman type reaction using activated olefins towards α,β-unsaturated ketones as a chiral auxiliary in the DABCO–ionic liquid system. In this reaction system, the reaction of (4*S*)-3-[(*E*)-4,4,4-trifluorobut-2-enoyl]-4-isopropyl-2-oxazolidinone with activated vinyl moiety proceeded at 80 °C, giving the corresponding material as shown in Table 1. The generally accepted mechanism [11] shown in Scheme 1 involves the Michael addition of DABCO to the activated carbon–carbon bond, followed by an addition to the α,β-unsaturated ketone. Subsequent elimination releases the catalyst, and the cycle continues. Unfortunately, these addition reactions provide low diastereoface selectivity in the reusable ionic liquid–DABCO system. The diastereomers **1b** derived from entry 6 were separated by column chromatography, affording one diastereomer ($[\alpha]^{29}D + 85.1$

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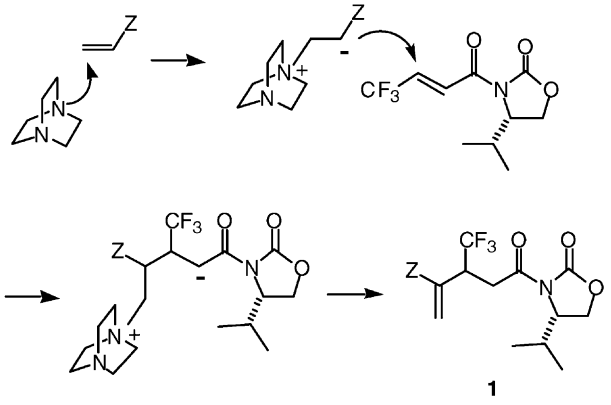
Table 1
Michael addition reaction

Entry	Z (compound number)	Ionic liquid[a]	Yield (%)	dr[b]
1	CN (**1a**)	[emim][OTf]	37	1:1
2		[emim][OTf]	25[c]	1:1
3		[emim][OTf]	30[d]	1:1
4		[bmim][BF_4]	46	1:1
5		[bmim][PF_6]	23	1:1
6	CO_2Me (**1b**)	[emim][OTf]	27	1:1
7	COMe (**1c**)	[emim][OTf]	42	55:45

[a] Ionic liquids: [emim][OTf]; 1-ethyl-3-methyl-1*H*-imidazolium trifluoromethane-sulfonate: [bmim[[BF_4]; 1-butyl-3-methyl-1*H*-imidazoIium tetrafluoro-borate: [bmim][PF_6]; 1-butyl-3-methyl-1*H*-imidazolium hexafluoro-phosphonate.
[b] Diastereomeric ratio.
[c] Second cycle.
[d] Third cycle.



Scheme 1. Mechanism for addition reaction.

(c 0.853, $CHCl_3$)) and another ($[\alpha]^{29}D + 23.9$ (c 0.942, $CHCl_3$)). The structure of compounds **1** was confirmed by ^1H, ^{19}F and ^{13}C NMR spectra and coupling constants (J_{H-H}). In the case of compound **1b** (Z = CO_2Me, $[\alpha]^{29}D + 85.1$ (c 0.853, $CHCl_3$)), the coupling pattern of fluorine (doublet, $J = 9.48$ Hz) supports the interaction of protons with the CF_3CHXY group, and the coupling patterns of protons $C(CF_3)CH_aH_bCO$ (doublet doublet, $J_{Ha-Hb} = 18.4$ Hz, $J_{Ha-Hc} = 4.67$ Hz at 3.41 ppm; $J_{Ha-Hb} = 18.4$ Hz, $J_{Hb-Hc} = 10.4$ Hz at 3.60 ppm) support the interaction of proton with $CH_c(CF_3)$ group. ^{13}C NMR spectra have 15 signals containing two alkenyl carbon atoms (δ 114–130 ppm), CF_3 carbon atom (δ 125.856 ppm, quartet, $J = 279.1$ Hz) and carbonyl carbon atoms (δ 153.830, 165.837, 168.819 ppm). From the results of ^1H, ^{19}F and ^{13}C NMR spectra, we have determined that the structure of the obtained material is the Michael adduct.

In view of 'green chemistry', reuse of the catalyst and solvent are preferable [15]. From the results shown in Table 1 (entries 1–3), successive reuse of the recovered ionic liquid 1-ethyl-3-methyl-1*H*-imidozolium trifluoromethane-sulfonate ([emim][OTf]) in the same reaction yielded amounts of product as high as in the first cycle.

2.2. The reaction using L-proline–Lewis acid–ionic liquid system

In the next step, we have carried out the reaction of fluoromethylated imines with enamines generated from acetone derivatives and L-proline in an ionic liquid. In this reaction system, the reaction did not proceed in the absence of Lewis acid. In the presence of $Sc(OTf)_3$, the reaction smoothly proceeded, giving a fluoromethylated carbinol. Proposed reaction mechanism is shown in Fig. 1. At first, enamine **3** and H_2O were produced from the reaction of corresponding ketone and L-proline, and then the produced H_2O attacked on imine to produce the *N*,*O*-hemiacetal in the presence of Lewis acid ($Sc(OTf)_3$). The *N*,*O*-hemiacetal reacted with enamine **3** in the presence of Lewis acid, giving the reaction intermediate **5**. This intermediate **5** was converted to the β-hydroxyketone **6** with small amount of water contained in ionic liquids Table 2.

In the case of methyl ethyl ketone, the compound **6** (X = Me) was not isolated. Based on the main product

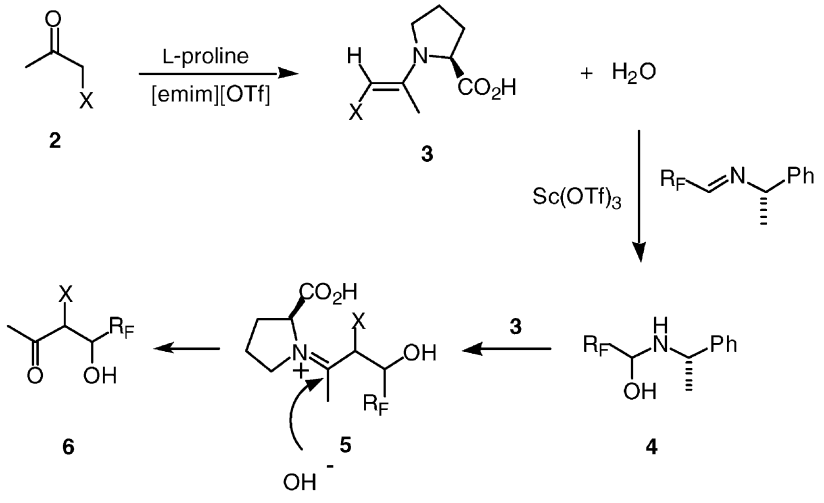


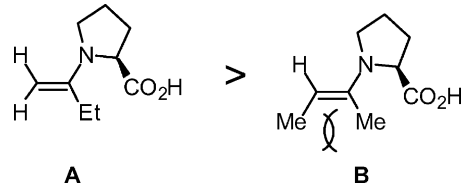
Fig. 1. Proposed reaction mechanism.

Table 2
Synthesis of fluoromethylated carbinols **6**

Entry	R_F	X	Yield (%)	Diastereomeric ratio
1	CF_3	H	37	
2	CHF_2	H	66	
3	CF_3	Me	25[a]	
4	CF_3	OH	18	90:10
5	CHF_2	OH	27	83:17
6	CF_3	Cl	65	63:37

[a] Yield of $EtCOCH_2CH(OH)CF_3$.

($EtCOCH_2CH(OH)CF_3$), it seems that the regioselectivity depends on the stability of produced enamines (enamine **A** is stable more than enamine **B**).



A **B**

The structure of carbinols **6** was confirmed by ^1H, ^{19}F and ^{13}C NMR spectra and coupling constants ($J_{H–H}$). In the case of carbinol **6** ($R_F = CF_3$, X = H), the coupling pattern of proton Y–$CH(CF_3)$ (doublet of quartet of doublet, $J = 9.16$, 6.84, 2.93 Hz) supports the interaction of protons with Y–$CH(CF_3)CH_aH_b$ group. ^{13}C NMR spectra have five signals containing three alkyl carbon atoms (δ 25–75 ppm), CF_3 carbon atoms (δ 124.467 ppm, quartet, $J = 280.0$ Hz) and carbonyl carbon atom (δ 206.274 ppm). From the results of ^{13}C NMR and ^1H NMR spectra, we have determined that the structure of the obtained material is carbinol with CF_3 group.

In conclusion, we have shown that ionic liquids are proved to be good alternative reaction media for the synthesis of the fluorinated materials.

3. Experimental

3.1. General

All commercially available reagents were used without further purification. Chemical shifts of ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in ppm (δ) downfield from the following internal standard (Me4Si, δ 0.00) in $CDCl_3$. The ^{19}F (282 MHz) NMR spectra were recorded in ppm downfield from internal standard C_6F_6 in $CDCl_3$ using a VXR 300 instrument.

3.2. Preparation of (4S)-3-[3-(trifluoromethyl)-4-cyano-4-pentenoyl]-4-isopropyl-2-oxazolidinone (*1a*)

3.2.1. First cycle

In the [emim][OTf] (4 g), (4*S*)-3-[(*E*)-4,4,4-trifluorobut-2-enoyl]-4-isopropyl-2-oxazolidinone (756 mg, 3 mmol), DABCO (329 mg, 3 mmol) and acrylnitrile (0.4 ml, 318 mg, 6 mmol) were added, and then the whole was stirred at 60 °C. After 4 h of stirring at that temperature, the product was extracted with diethyl ether (5× 15 ml) and then ionic liquid [emim][OTf] was recovered. The organic layer was dried over anhydrous $MgSO_4$, and then the solvent was removed. Products were purified by column chromatography on silica gel using a mixture of hexane-ethyl acetate (3:1) as an eluent, giving (4*S*)-3-[3-(trifluoromethyl)-4-cyano-4-pentenoyl]-4-isopropyl-2-oxazolidinone **1a** in 37% yield with diastereomeric ratio (1:1).

3.2.2. Second cycle

Into the recovered ionic liquid, (4*S*)-3-[(*E*)-4,4,4-trifluorobut-2-enoyl]-4-isopropyl-2-oxazolidinone (756 mg, 3 mmol), DABCO (329 mg, 3 mmol) and acrylnitrile (0.4 ml, 318 mg, 6 mmol) were added, and worked-up similarly. Compound **1a** was obtained in 25% yield and ionic liquid was recovered.

Diastereomer mixture: ^1H NMR ($CDCl_3$): δ 0.89 (3H, d, $J = 6.86$ Hz), 0.90 (3H, d, $J = 6.86$ Hz), 2.36 (1H, heptd., $J = 7.14$, 3.58 Hz), 3.38–3.71 (3H, m), 4.24–4.63 (3H, m), 6.17 (1H, d, $J = 2.47$ Hz), 6.26 (1H, d, $J = 2.47$ Hz). ^{19}F NMR ($CDCl_3$): δ 91.40 (d, $J = 7.76$ Hz), 91.45 (d, $J = 8.61$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.569, 14.592, 17.798, 17.881, 28.265, 33.384 (q, $J = 2.0$ Hz), 33.480 (q, $J = 2.0$ Hz), 43.684 (q, $J = 28.63$ Hz), 43.802 (q, $J = 28.63$ Hz), 58.427, 58.621, 63.735, 115.868, 115.937, 116.608, 116.635, 124.805 (q, $J = 279.7$ Hz), 137.282, 137.486, 153.603, 167.975, 168.013. Anal. Calc. for $C1_{13}H_{15}F_3N_2O_3$: C, 51.32; H, 4.97; N, 9.21. Found: C, 51.63; H, 4.71; N, 9.08. IR (KBr): 1794, 1686 cm^{-1} (C=O).

3.3. Preparation of (4S)-3-[3-(trifluoromethyl)-4-methoxycarbonyl-4-pentenoyl]-4-isopropyl-2-oxazolidinone (*1b*)

In the above reaction, (4*S*)-3-[(*E*)-4,4,4-trifluorobut-2-enoyl]-4-isopropyl-2-oxazolidinone (756 mg, 3 mmol), DABCO (329 mg, 3 mmol) and methyl acrylate (6 mmol) were used in ionic liquid [emim][OTf] (4 g), and then worked-up similarly, giving (4*S*)-3-[3-(trifluoromethyl)-4-methyloxocarbonyl-4-pentenoyl]-4-isopropyl-2-oxazolidinone (diastereomers) in 27% yield.

Diasteeomer A 12%: $[\alpha]^{29}D + 85.1$ (*c* 0.853, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.82 (3H, d, $J = 6.86$ Hz), 0.88 (3H, d, $J = 6.87$ Hz), 2.30 (1H, m), 3.41 (1H, dd, $J = 18.4$, 4.67 Hz), 3.60 (1H, dd, $J = 18.4$, 10.4 Hz), 3.84 (3H, s), 4.20–4.31 (4H, m), 5.94 (1H, s), 6.55 (1H, s). ^{19}F NMR ($CDCl_3$): δ 91.25 (d, $J = 9.48$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.639, 17.944, 28.293, 35.364, 38.801 (q, $J = 28.06$ Hz), 52.614, 58.559, 63.658, 114.231, 115.246 (d, $J = 12.31$ Hz), 125.856 (q, $J = 279.1$ Hz), 128.439, 153.830, 165.837, 168.819. IR (KBr): 1789, 1721 cm^{-1} (C=O).

Diastereomer B 15%: $[\alpha]^{29}D + 23.9$ (*c* 0.942, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.87 (3H, d, $J = 7.14$ Hz), 0.90 (3H, d, $J = 7.14$ Hz), 2.37 (1H, m), 3.48–3.51 (2H, m), 3.84 (3H, s),

4.24–4.42 (4H, m), 5.95 (1H, s), 6.57 (1H, s). ^{19}F NMR ($CDCl_3$): δ 91.21 (d, $J = 9.47$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.522, 17.993, 28.137, 35.505, 38.655 (q, $J = 28.06$ Hz), 52.618, 58.487, 63.551, 114.873 (d, $J = 6.87$ Hz), 115.634 (d, $J = 12.6$ Hz), 125.873 (q, $J = 279.1$ Hz), 128.617, 153.781, 165.856, 168.804. IR (KBr): 1779, 1718 cm^{-1} (C=O).

3.4. (4S)-3-[3-(Trifluoromethyl)-4-acetyl-4-pentenoyl]-4-isopropyl-2-oxazolidinone (**1c**)

In the above reaction, (4*S*)-3-[(*E*)-4,4,4-trifluorobut-2-enoyl]-4-isopropyl-2-oxazolidinone (756 mg, 3 mmol), DABCO (329 mg, 3 mmol) and methyl vinyl ketone (6 mmol) were used in ionic liquid [emim][OTf] (4 g), was used, and then worked-up similarly, giving (4*S*)-3-[3-(trifluoromethyl)-4-acetyl-4-pentenoyl]-4-isopropyl-2-oxazolidinone in 42% yield.

^{1}H NMR ($CDCl_3$): δ 0.83 (3H, d, $J = 6.90$ Hz), 0.88 (3H, d, $J = 7.20$ Hz), 2.25 (1H, m), 2.28–2.39 (1H, m), 2.40 (3H, s), 3.44 (2H, d, $J = 7.50$ Hz), 4.22 (1H, dd, $J = 8.55$, 2.70 Hz), 4.28–4.43 (1H, m), 4.36 (1H, dd, $J = 7.80$, 3.60 Hz), 6.15 (1H, s), 6.37 (1H, s). ^{19}F NMR ($CDCl_3$): δ 91.61 (d, $J = 9.31$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.579, 17.712, 25.220, 28.281, 35.273, 36.425 (q, $J = 27.6$ Hz), 58.396, 63.616, 125.797 (q, $J = 277.1$ Hz), 127.452, 143.211, 153.739, 168.641, 196.486. IR (KBr): 1786, 1715, 1683 cm^{-1} (C=O).

3.5. Preparation of 1,1,1-trifluoro-2-hydroxypentan-4-one (**6a**)

A mixture of acetone (10 mmol), imine ($R_F = CF_3$, 1.01 g, 5 mmol), L-proline (0.230 g, 0.25 mmol) and [emim][OTf] (3 g) was stirred at room temperature. After stirring of 48 h at that temperature, organic materials were extracted with diethyl ether (10× 4 ml), and ionic liquid containing L-proline was recovered. The organic layer was dried over anhydrous $MgSO_4$, and then the solvent was removed. The resultant crude product was decomposed to produce the title material by chromatography on silica gel.

^{1}H NMR ($CDCl_3$): δ 2.26 (3H, s), 2.79 (1H, dd, $J = 17.8$, 2.81 Hz), 2.87 (1H, dd, $J = 17.8$, 9.27 Hz), 3.64 (OH), 4.89 (CH, dqd, $J = 9.16$, 6.84, 2.93 Hz). ^{19}F NMR ($CDCl_3$): δ, 82.2 (d $J = 6.09$ Hz) from C_6F_6. ^{13}C NMR ($CDCl_3$): δ 30.770, 42.796, 66.425 (q, $J = 32.35$ Hz), 124.467 (q, $J = 280.0$ Hz), 206.274. IR: 3423 (OH), 1719 cm^{-1} (C=O).

3.6. Preparation of 1,1-difluoro-2-hydroxypentan-4-one (**6b**)

In the above reaction, imine ($R_F = CHF_2$, 5 mmol) was used, and worked-up similarly, giving 1,1-difluoro-2-hydroxypentan-4-one in 66% yield.^{1}H NMR ($CDCl_3$): δ 2.06 (3H, s), 2.60 (2H, d, $J = 6.04$ Hz), 3.25 (1H), 4.25 (1H, m),5.78 (1H, td, $J = 55.8$, 3.57 Hz). ^{19}F NMR ($CDCl_3$): δ 32.96 (ddd, $J = 288.7$, 55.2, 9.18 Hz), 29.90 (ddd, $J = 288.7$, 56.0, 10.3 Hz). ^{13}C NMR ($CDCl_3$): δ 30.467, 42.637 (t, $J = 2.58$ Hz), 66.715 (t, $J = 24.3$ Hz), 115.294 (t, $J = 243.3$ Hz), 207.177.

3.7. Preparation of 1,1,1-trifluoro-2-hydroxyhexan-4-one (**6c**)

In the above reaction, imine ($R_F = CF_3$, 5 mmol), L-proline (0.25 mmol) and ethyl methyl ketone (10 mmol) in ionic liquid ([emim][OTf], 3 g) were used, and then worked-up similarly, giving 1,1,1-trifluoro-2-hydroxyhexan-4-one in 25% yield. ^{1}H NMR ($CDCl_3$): δ 1.09 (3H, t, $J = 7.15$ Hz), 2.54 (2H, q, $J = 7.15$ Hz), 2.75 (1H, dd, $J = 17.58$, 3.29 Hz), 2.83 (1H, $J = 17.58$, 9.07 Hz), 3.85 (OH), 4.51 (1H, m). ^{19}F NMR ($CDCl_3$): δ 82.2 (d, $J = 6.90$ Hz). ^{13}C NMR ($CDCl_3$): δ 7.526, 36.984, 41.408, 66.785 (q, $J = 32.35$ Hz), 124.480 (q, $J = 220.28$ Hz), 208.979.

3.8. Preparation of 1,1,1-trifluoro-2,3-dihydroxypentan-4-one (**6d**)

In the above reaction, imine ($R_F = CF_3$, 5 mmol) and hydroxyacetone (10 mmol) were used, and then worked-up similarly, giving 1,1,1-trifluoro-2,3-dihydroxypentan-4-one in 18% yield.^{1}H NMR ($CDCl_3$): δ 2.35 (3H, s), 4.35 (1H, qd, $J = 6.84$, 1.23 Hz), 4.43 (1H, d, $J = 1.23$ Hz). ^{19}F NMR ($CDCl_3$): δ 84.9 (d, $J = 6.10$ Hz). ^{13}C NMR ($CDCl_3$): δ 25.068, 69.273 (q, $J = 31.5$ Hz), 74.423 (q, $J = 1.43$ Hz), 123.788 (q, $J = 282.9$ Hz), 205.075. IR: 3418 (OH), 1719 cm^{-1} (C=O).

3.9. Preparation of 1,1-difluoro-2,3-dihydroxypentan-4-one (**6e**)

In the above reaction, imine ($R_F = CHF_2$, 5 mmol) and hydroxyacetone (10 mmol) were used, and then worked-up similarly, giving 1,1-difluoro-2,3-dihydroxypentan-4-one in 27% yield. Main: ^{1}H NMR ($CDCl_3$): δ 2.38 (3H, s), 4.18 (1H, m), 4.40 (1H, d) 5.85 (1H, td, $J = 56.3$, 6.04 Hz). ^{19}F NMR ($CDCl_3$): δ 30.85 (ddd, $J = 292.1$, 57.7, 10.3 Hz), 33.59 (ddd, $J = 292.1$, 55.2, 10.3 Hz). ^{13}C NMR ($CDCl_3$): δ 25.220, 70.747 (dd, $J = 27.49$, 23.19 Hz), 75.532, 114.724 (t, $J = 243.3$ Hz), 207.000.

Minor: ^{1}H NMR ($CDCl_3$): δ 2.39 (3H, s), 4.18 (1H, m), 4.38 (1H, d), 5.90 (1H, td, $J = 55.8$, 4.39 Hz). ^{19}F NMR ($CDCl_3$): δ 33.53 (ddd, $J = 291.3$, 54.3, 5.17 Hz), 28.23 (ddd, $J = 291.3$, 56.0, 14.7 Hz). ^{13}C NMR ($CDCl_3$): δ 26.620, 71.317 (dd, $J = 25.19$, 22.62 Hz), 75.612, 114.450 (t, $J = 243.3$ Hz), 207.100.

3.10. Preparation of 1,1,1-trifluoro-2-hydroxy-3-chloropentan-4-one (**6f**)

In the above reaction, imine ($R_F = CF_3$, 5 mmol) and chloroacetone (10 mmol) were used, and then worked-up

similarly, giving 1,1,1-trifluoro-2-hydroxy-3-chloropentan-4-one in 65% yield.

Diastereomer mixture: ^{1}H NMR ($CDCl_3$): δ 2.43 (3H, s), 2.45 (3H, s), 3.01, 3.49 (OH), 4.39 (1H, d, $J = 6.04$ Hz), 4.54 (1H, d, $J = 2.19$ Hz). ^{19}F NMR ($CDCl_3$): δ 85.7 (d, $J = 6.11$ Hz), 86.7 (d, $J = 6.10$ Hz). ^{13}C NMR ($CDCl_3$): δ 27.678, 28.050, 55.907, 60.892, 69.034 (q, $J = 32.1$ Hz), 71.755 (q, $J = 31.2$ Hz), 123.310 (q, $J = 282.3$ Hz), 123.452 (q, $J = 282.6$ Hz), 201.217, 201.262. IR: 3431 (OH), 1723 cm^{-1} (C=O).

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