Journal of Fluorine Chemistry 132 (2011) 367–372

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Short communication

A facile tandem reaction to access β-hydroxy-α,α-difluoroketone derivatives catalyzed by titanocene dichloride/magnesium

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ARTICLE INFO

Article history:
Received 12 February 2011
Received in revised form 5 March 2011
Accepted 19 March 2011
Available online 25 March 2011

Keywords:
Tandem reaction
Barbier-type allylation
Brook rearrangement
Fluoride-promoted aldol reaction

ABSTRACT

Tandem reactions of Barbier-type allylation, Brook rearrangement and fluoride-promoted aldol reaction were developed, which afforded a facile, "one-pot" process to β-hydroxy-α,α-difluoroketone derivatives with good to excellent yields.

1. Introduction

Traditionally designed organometallic catalysts are synthesized and optimized to facilitate a single particular reaction [1]. However, the increasing demand for expedient synthetic processes requires the development of more efficient organometallic catalysts that are utilized for catalyzing multiple, mechanistically distinct reactions directly or by simple modifications [2]. From another point of view, the demands for environmentally benign and economical synthetic process also accelerate the development of effective sequential multiple catalytic transformations. We can easily anticipate that this strategy would minimize the production of residual metal pollution, and processing time. Some efforts and successes have been made to realize the sequential catalysis of two (or more) distinct reactions, notably in asymmetric catalysis [3]. Despite the significant developments achieved, the integration of two or more reactions in one-pot with the promotion of a catalytic species is still a great challenge for chemists.

Acylsilanes are the synthetic equivalents of aldehydes due to the facile cleavage of carbon–silicon bonds, which have been explored extensively for several decades [4]. As a very important milestone of the silicon chemistry, the Brook rearrangement, a unique transformation of acylsilanes that involves 1, 2 or 1, n-silyl group migration from the carbonyl carbon atom to oxygen atom, has been widely utilized for making useful building blocks and complicated natural products [5]. In 2004, Welch reported a novel method for synthesis of trifluoroacetyltrialkyl(aryl)silanes, which further reacted with allylic Grignard reagents to access difluoro enol silyl ethers via the Brook rearrangement [6]. Although difluoro enol silyl ethers are very useful synthons of difluoro compounds, which provide a wide reservoir for bioactive fluorinated compounds. The methods to access difluoro enol silyl ethers are rather limited, sometimes their preparations can be rather air-sensitive, tenuous or under harsh conditions [7], furthermore, there are several reports about using this adduct *in situ* for further transformations, notably, by adding extra Lewis acid catalysts [8]. As an effort to expand the strategy mentioned above in this fluorine chemistry, herein, we demonstrate a tandem reaction of Barbier-type allylation, Brook rearrangement and fluoride-promoted aldol reaction from the starting acylsilane, allylbromide and arylaldehyde catalyzed by titanocene dichloride/magnesium, as the result, β-hydroxy-α,α-difluoroketone derivatives were formed in one-pot process.

2. Results and discussion

The titanocene-catalyzed method for generation of organometallic reagents *in situ* for further transformations has been explored for almost 20 years, such as the Cp_2TiCl_2(cat.)/Zn system accelerated the reaction of aldehydes or ketones with allylic bromides [9]. The Ti^{4+} species were reduced by Zn^0 to Ti^{3+} species, which eventually accelerated the generation of allylzinc bromides. Comparing the chemical potentials of $Zn^0 \rightarrow Zn^{2+}$ (+0.7618 V) with $Mg^0 \rightarrow Mg^{2+}$ (+2.372 V) [10], we hypothesized that Grignard reagents could be generated with the same procedure by mixing the magnesium powder with catalytic amount of Cp_2TiCl_2 in the

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doi:10.1016/j.jfluchem.2011.03.014

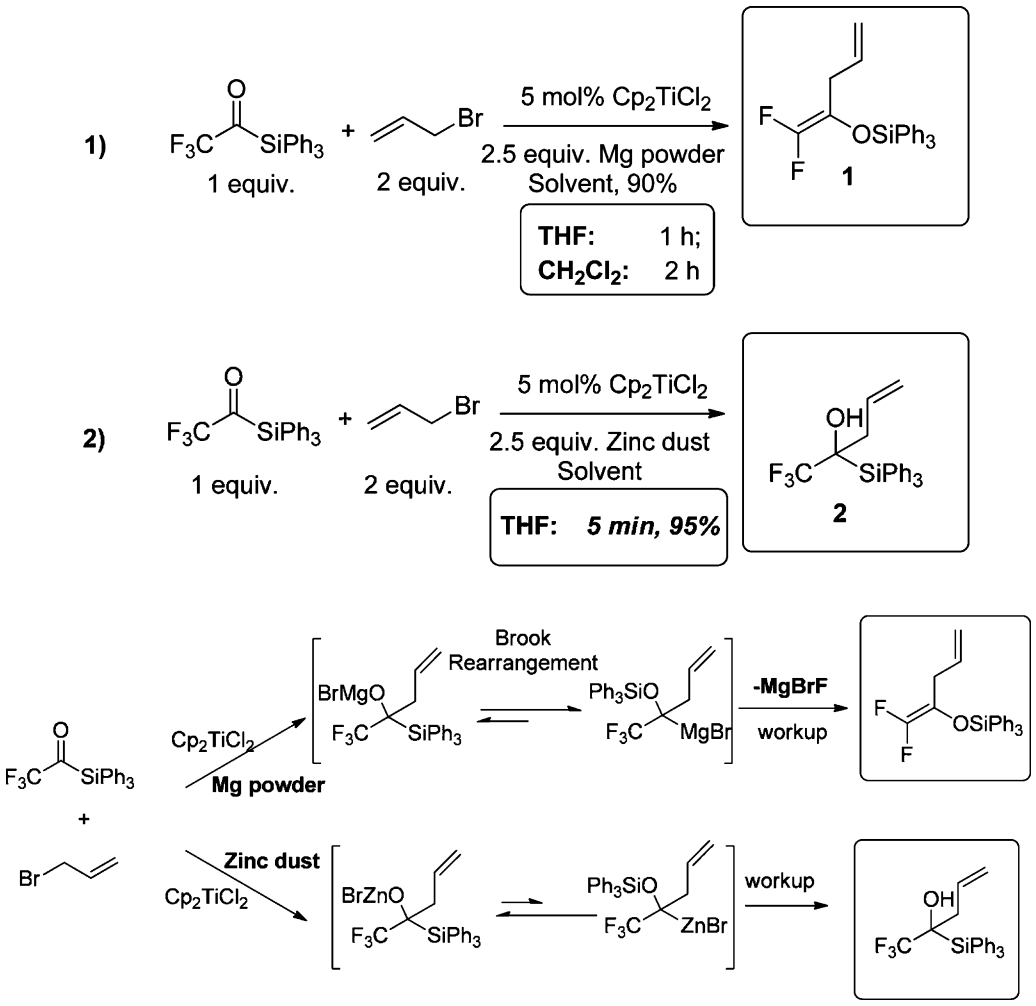


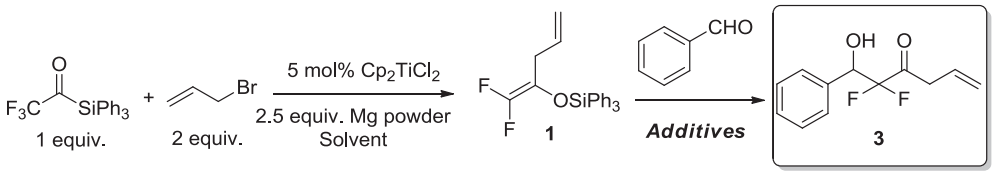
Fig. 1. Cp_2TiCl_2/M(Mg or Zn)accelerated the allylation of trifluoroacylsilane.

presence of allylbromides, and then the *in situ* generated allylmagnesium bromides could react with carbonyl compounds. With the trifluoroacetyltriphenylsilane in hand [11], we began by examining the allylation with allyl bromide in the presence of 5 mol% Cp_2TiCl_2 and 2.5 equiv. magnesium powder or zinc dust. As expected, different adducts were formed: difluoro enol silyl ether (**1**) was isolated with 90% yield for Cp_2TiCl_2/Mg system. Although the reaction rate varied with different solvents, THF was proved to be the best solvent for this allylation–Brook rearrangement, as shown in (Fig. 1, Eq. (1)). By contrast, the allylation underwent very fast for Cp_2TiCl_2/Zn system, but Brook rearrangement did not take place in the process, only Barbier-type allylation product (**2**) was isolated with 95% yield (Eq. (2)) [12].

Based on our empirical results and previous mechanistic study on the Cp_2TiCl_2/M system, we deduced that 2 equiv. of MgBrX (X = F, or Br) could generate *in situ* after the above reaction, which might be an efficient Lewis acid catalyst [13]. Notably, difluoro enol silyl ether (**1**) is an ideal substrate for the fluoride-promoted aldol reaction. We, therefore, attempted to realize the tandem reactions by adding aldehydes right after the adduct **1** completely formed. At the outset, the allylation of trifluoroacetyltriphenylsilane, allylbromide in the presence of 5 mol% Cp_2TiCl_2 and magnesium powder was chosen as model reaction; benzaldehyde was added after the acylsilane consumed (equation in Table 1). Unfortunately, without any additive with benzaldehyde, very low yield of aldol adduct **3** was observed (entry 1). As fluoride additives have been reported as effective activators for the Mukaiyama-aldol reaction [14], various fluoride sources were screened. In spite of the fact that KF or TBAF (tetrabutylammonium fluoride) did not enhance the yield, TBAT (tetrabutylammonium triphenyldifluorosilicate) as the well-known anhydrous fluoride source did improve the result dramatically, 73% yield of adduct **3** was isolated (entry 4). Regardless of that dichloromethane slowed down the earlier allylation and Brook rearrangement, it improved the aldol addition yield to 86% with the sacrifice of a few more time (entry 5). The aldol reaction did not proceed when only TBAT or other fluorine sources were used as a catalyst, indicating the essential role of the magnesium atom for the success of this reaction. Moreover, the Ti^{3+} species were necessary to achieve good yield for the tandem reaction. For control experiments using trifluoroacetyltriphenylsilane, allylmagnesium bromide without Cp_2TiCl_2, only 45% yield of adduct **3** was isolated (entry 6).

In an effort to explore the scope and versatility of the tandem reactions, various aldehydes were firstly examined on the basis of the optimized conditions. As shown in Table 2, arylaldehydes with electron-withdrawing substituents were found to give excellent yield (entries 5–8). Reactions between the intermediate **1** with a variety of electron-rich substrates like 4-methyl-, 2-methyl-, 4-methoxy-, 4-dimethylamino-substituted arylaldehydes, also proceed smoothly, giving the aldol adducts in good yields (entries 1–4). α,β-Unsaturated aldehyde underwent the tandem reaction to yield the corresponding β-hydroxy-α,α-difluoroketone adduct

Table 1
The optimization of the tandem reaction.[a]



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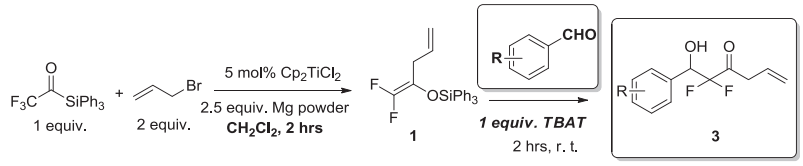
Entry	Solvent	Additive	Yield[b]
1	THF	–	<10%
2	THF	TBAF	15%
3	THF	KF	<10%
4	THF	TBAT	73%
5[c]	CH_2Cl_2	TBAT	86%
6[d]	CH_2Cl_2	TBAT	45%

[a] 1 h for first step, 2 h for aldol addition.
[b] Isolated yield.
[c] 2 h for first step.
[d] Allylmagnesium bromide was used directly without Cp_2TiCl_2.

Table 2
The aldehydes scope of the tandem reaction.



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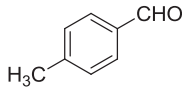
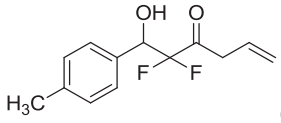
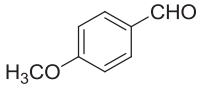
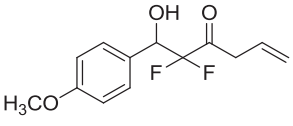
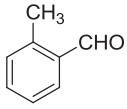
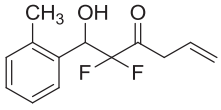
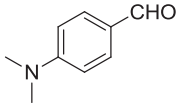
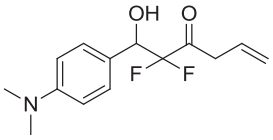
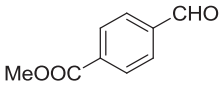
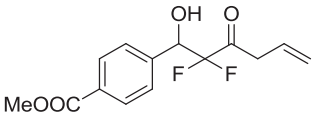
Entry	Aldehyde	Product	Yield (%)
1		 (3-1)	87
2		 (3-2)	73
3		 (3-3)	82
4		 (3-4)	80
5		 (3-5)	86

Table 2 (*Continued*)

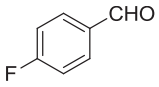
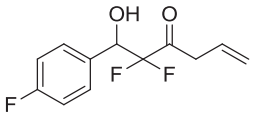
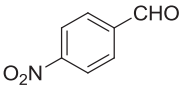
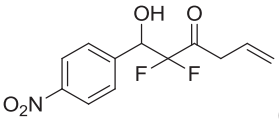
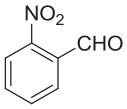
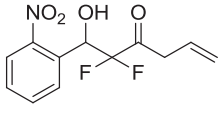
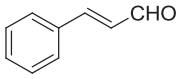
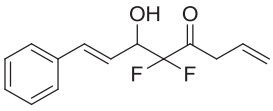
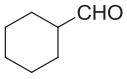
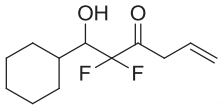
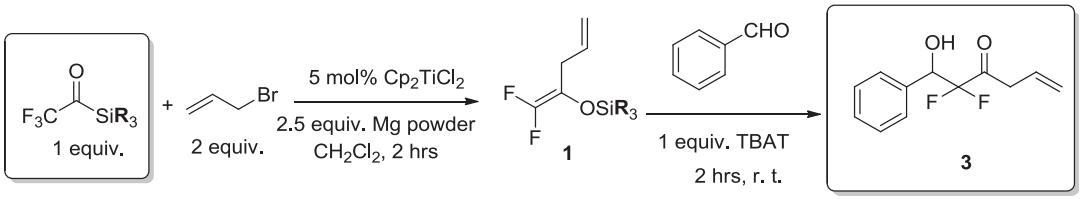
Entry	Aldehyde	Product	Yield (%)
6		 **(3-6)**	90
7		 **(3-7)**	96
8		 **(3-8)**	93
9		 **(3-9)**	80
10		 **(3-10)**	65

Table 3
The acylsilanes scope of the tandem reaction.



Entry	Trifluoroacylsilane	Isolated yield (%)
1	R = Ph, Ph, Ph (**5**)	86
2	R = Me, Me, Me (**6**)	95
3	R = Et, Et, Et (7)	92
4	R = *i*-Pr, *i*-Pr, *i*-Pr (**8**)	85
5	R = Me, Me, *t*-Bu (**9**)	90
6	R = *t*-Bu, Ph, Ph (**10**)	81

with 80% yield, and aliphatic aldehyde also proved to be viable substrate (entries 9 and 10).

To gain more insight into the substrate scope of the tandem reaction, we prepared a series of trifluoroacylsilanes according to Welch's method [11], and then examined the size effect of R group to the reaction. In each case a good to excellent yield of the aldol adduct was observed. As shown in Table 3, the sterically hindered substrates afforded lower yields compared with less bulky substrates (entries 4 and 6). The differentiated yields could be deduced from two factors: (1) the sterically hindered R groups on silicon atom would make the carbonyl moiety become less susceptible to the nucleophilic attack of allylmagnesium bromide; (2) the approaching difficulty of fluoride source to silicon atom for substrates with sterically hindered R groups would increase substantially, which eventually affected the activation efficiency of the oxygen–silicon bond in aldol addition step.

3. Conclusion

We have demonstrated that the allylation–Brook rearrangement products of trifluoroacylsilanes, allylbromides in the presence of catalytic amount of Cp_2TiCl_2 and magnesium powder, *in situ* reacted with aldehydes without adding extra Lewis acid catalyst. Notably, TBAT was a vital additive to the aldol step. The viable tandem reaction underwent Barbier-type allylation, Brook

rearrangement and fluoride-promoted aldol addition, which afforded a facile, "one-pot" process to β-hydroxy-α,α-difluoroketone derivatives with good to excellent yields. We are presently investigating the application of this tandem reaction to a novel intermolecular cyclization.

4. Experimental

4.1. General experimental procedures

Solvents and reagents were reagent grade and used without purification unless otherwise noted. Tetrahydrofuran (THF) was distilled over sodium and benzophenone and stored under argon. CH_2Cl_2 was distilled over CaH_2 and stored with molecular sieves. Trifluoroethanol, chlorosilanes, aldehydes were distilled under vacuum and stored under nitrogen. LDA was prepared from fresh distilled $(i\text{-Pr})_2NH$ with commercial n-BuLi (2.5 M hexane solution). Magnesium powder and zinc dust obtained from Aldrich Corp. were used without further activation. All reactions were carried out in oven dried glassware under nitrogen or argon unless otherwise specified. All ^1H NMR (400 MHz) spectra were recorded on a Bruker-DMX 400 using $CDCl_3$ solution in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). ^{19}F NMR spectra are given in ppm upfiled with CCl_3F as the internal standard and $CDCl_3$ as the solvent. Coupling constants are reported in hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. High and low resolution fast atom bombardment (FAB) measurements were made with a JEOL JMS-AX505HA mass spectrometer.

4.2. Preparation of trifluoroacetyltriphenylsilane (5)

To a round-bottom flask (flame-dried, three-neck with a septum cap, 100 mL) under an argon atmosphere, containing THF (5 mL), 2,2,2-trifluoroethanol (500 mg, 5 mmol), chlorotriphenylsilane (1.47 g, 5 mmol), and HMPA (0.5 mL) in a dry ice/acetone bath, was added dropwise a freshly prepared solution of LDA (17.5 mmol, 3.5 equiv., in 100 mL of THF). After the addition was complete, the solution was kept at −78 °C for 4 h, then warmed up and stirred at r.t. overnight. 1.5 equiv. of TMSCl was injected slowly into the above solution via syringe at 0 °C. After being stirred for 4 h at room temperature, the reaction was terminated by addition of distilled water and extracted with hexanes. The organic layer was separated, washed with saturated brine, and dried over anhydrous Na_2SO_4. After the removal of the drying agent by filtration, the solvent was evaporated and the residue was purified by flash column chromatography (100% hexanes) to afford the difluorovinylsilyenolate intermediate **4** with 75% yield.

To a solution of Selectfluor® (266 mg, 0.75 mmol) in 5 mL of acetonitrile was added a solution of compound **4** (0.5 mmol) in 2 mL of dichloromethane at 0 °C. The resulting mixture was stirred at room temperature for 24 h. The reaction was quenched by the addition of 5 mL water, and then extracted with dichloromethane (5 mL ×2). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The product trifluoroacetyltriphenylsilane (**5**) was purified by silica gel column chromatography using 100% hexane to afford white solids as 86% yield. Substrates **6**, **7**, **8**, **9**, **10** were synthesized with the similar procedure. All these NMR data were consistent with the literature reported values [11].

4.3. General procedure for the tandem reaction

A flame dried 15 mL vial under argon atmosphere, containing 6 mg Cp_2TiCl_2 (5 mol%) and 30 mg magnesium powder (2.5 equiv., 1.25 mmol), was added 2 mL freshly distilled CH_2Cl_2. The dark-red heterogeneous solution was stirred for 10 min at r.t. before the solution of 178 mg trifluoroacetyltriphenylsilane (**5**), 86 μL allylbromide in 3 mL CH_2Cl_2 was injected. When the dark-red solution faded to colorless, and the magnesium powder disappeared (about 2 h), the solution of 53 mg benzaldehyde, 540 mg TBAT (0.5 mmol) in 5 mL CH_2Cl_2 was dropwisely added at 0 °C. After the addition was complete, the solution was kept at room temperature for another 2 h. The reaction was terminated by addition of aqueous NH_4Cl and extracted with ethyl acetate. Further purification was achieved by column chromatography (with ethyl acetate: hexanes = 1:5 as eluent), which afforded aldol adduct **3** as colorless oil with 86% yield.

4.3.1. 2,2-Difluoro-1-hyroxy-1-phenylhex-5-en-3-one (3)

As colorless oil in 86% yield, ^{1}HNMR ($CDCl_3$) δ 2.75 (brs, 1H), 3.76 (d, J = 6.5 Hz, 2H), 5.18–5.25 (m, 1H), 5.77–5.91 (m, 1H), 6.16 (d, J = 16.2 Hz, 1H), 6.54 (d, J = 16.2 Hz, 1H), 7.36–7.50 (m, 5H). ^{19}F NMR ($CDCl_3$) δ 116.15 (dd, J = 271, 7.5 Hz, 1F), 125. 65 (dd, J = 271, 16.7 Hz, 1F). HRMS (FAB$^+$): Calc'd for $C_{12}H_{12}F_2O_2$: 226.0805; found: 226.0816.

4.3.2. 2,2-Difluoro-1-hyroxy-1-(p-tolyl)hex-5-en-3-one (3-1)

As colorless oil in 87% yield, ^{1}HNMR ($CDCl_3$) δ 2.35 (s, 3H), 2.74 (brs, 1H), 3.77 (d, J = 6.5 Hz, 2H), 5.16–5.23 (m, 1H), 5.75–5.90 (m, 1H), 6.16 (d, J = 16.3 Hz, 1H), 6.54 (d, J = 16.3 Hz, 1H), 7.18 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ 115.75 (dd, J = 271, 7.5 Hz, 1F), 124.60 (dd, J = 271, 16.7 Hz, 1F). HRMS (FAB$^+$): Calc'd for $C_{13}H_{14}F_2O_2$: 240.0962; found: 240.0965.

4.3.3. 2,2-Difluoro-1-hyroxy-1-(4-methoxyphenyl)hex-5-en-3-one (3-2)

As colorless oil in 73% yield, ^{1}HNMR ($CDCl_3$) δ 2.74 (brs, 1H), 3.76 (d, J = 6.5 Hz, 2H), 3.84 (s, 3H), 5.20–5.31 (m, 1H), 5.78–5.95 (m, 1H), 6.18 (d, J = 16 Hz, 1H), 6.50 (d, J = 16 Hz, 1H), 6.89 (d, J = 7.2 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ 110 (dd, J = 271, 7.5 Hz, 1F), 121. 3 (dd, J = 271, 16.7 Hz, 1F). HRMS (FAB$^+$): Calc'd for $C_{13}H_{14}F_2O_3$: 256.0911; found: 256.0920.

4.3.4. 2,2-Difluoro-1-hyroxy-1-(o-tolyl)hex-5-en-3-one (3-3)

As colorless oil in 82% yield, ^{1}HNMR ($CDCl_3$) δ 2.36 (s, 3H), 2.75 (brs, 1H), 3.76 (d, J = 6.5 Hz, 2H), 5.16–5.23 (m, 1H), 5.75–5.90 (m, 1H), 6.16 (d, J = 16.3 Hz, 1H), 6.54 (d, J = 16.3 Hz, 1H), 7.19–7.39 (m, 4H). ^{19}F NMR ($CDCl_3$) δ 115.73 (dd, J = 271, 7.5 Hz, 1F), 124.61 (dd, J = 271, 16.7 Hz, 1F). HRMS (FAB$^+$): Calc'd for $C_{13}H_{14}F_2O_2$: 240.0962; found: 240.0968.

4.3.5. 2,2-Difluoro-1-hyroxy-1-(4-(dimethylamino)phenyl)hex-5-en-3-one (3-4)

As colorless oil in 80% yield, ^{1}HNMR ($CDCl_3$) δ 2.76 (brs, 1H), 3.10 (s, 6H), 3.77 (d, J = 6.5 Hz, 2H), 5.19–5.28 (m, 1H), 5.76–5.93 (m, 1H), 6.20 (d, J = 16.2 Hz, 1H), 6.45 (d, J = 16.2 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ 113.26 (dd, J = 271, 7.5 Hz, 1F), 123.1 (dd, J = 271, 16.6 Hz, 1F). HRMS (FAB$^+$): Calc'd for $C_{14}H_{17}F_2NO_2$: 269.1227; found: 269.1219.

4.3.6. Methyl 4-(2,2-difluoro-1-hydroxy-3-oxohex-5-en-1-yl)benzoate (3-5)

As colorless oil in 86% yield, ^{1}HNMR ($CDCl_3$) δ 2.77 (brs, 1H), 3.76 (d, J = 6.5 Hz, 2H), 3.90 (s, 3H), 5.23–5.35 (m, 1H), 5.76–5.93 (m, 1H), 6.23 (d, J = 16.1 Hz, 1H), 6.54 (d, J = 16.1 Hz, 1H), 7.29 (d, J = 7.3 Hz, 2H), 7.95 (d, J = 7.3 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ 118.62 (dd, J = 271, 7.5 Hz, 1F), 127.6 (dd, J = 271, 16.6 Hz, 1F). HRMS (FAB$^+$): Calc'd for $C_{14}H_{14}F_2O_4$: 284.0860; found: 284.0871.

4.3.7. 2,2-Difluoro-1-(4-fluorophenyl)-1-hydroxyhex-5-en-3-one (3-6)

As colorless oil in 90% yield, ^{1}HNMR ($CDCl_3$) δ 2.77 (brs, 1H), 3.77 (d, J = 6.5 Hz, 2H), 5.20–5.35 (m, 1H), 5.73–5.90 (m, 1H), 6.13 (d, J = 16.1 Hz, 1H), 6.45 (d, J = 16.1 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ −115.3, 117 (dd, J = 271, 7.5 Hz, 1F), 125.6 (dd, J = 271, 16.6 Hz, 1F). HRMS (FAB^+): Calc'd for $C_{12}H_{11}F_3O_2$: 244.0711; found: 244.0723.

4.3.8. 2,2-Difluoro-1-hydroxy-1-(4-nitrophenyl)hex-5-en-3-one (3-7)

As pale yellow oil in 96% yield, ^{1}HNMR ($CDCl_3$) δ 2.77 (brs, 1H), 3.78 (d, J = 6.5 Hz, 2H), 5.65–5.90 (m, 2H), 6.31 (d, J = 16.1 Hz, 1H), 6.54 (d, J = 16.1 Hz, 1H), 7.72 (d, J = 7.2 Hz, 2H), 8.30 (d, J = 7.2 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ 122.76 (dd, J = 285, 8.6 Hz, 1F), 132.8 (dd, J = 285, 21 Hz, 1F). HRMS (FAB^+): Calc'd for $C_{12}H_{11}F_2NO_4$: 271.0656; found: 271.0660.

4.3.9. 2,2-Difluoro-1-hydroxy-1-(2-nitrophenyl)hex-5-en-3-one (3-8)

As pale yellow oil in 93% yield, ^{1}HNMR ($CDCl_3$) δ 2.77 (brs, 1H), 3.77 (d, J = 6.5 Hz, 2H), 5.67–5.91 (m, 2H), 6.30 (d, J = 16.1 Hz, 1H), 6.52 (d, J = 16.1 Hz, 1H), 7.72–8.07 (m, 4H). ^{19}F NMR ($CDCl_3$) δ 122.70 (dd, J = 285, 8.3 Hz, 1F), 131.6 (dd, J = 285, 20.5 Hz, 1F). HRMS (FAB^+): Calc'd for $C_{12}H_{11}F_2NO_4$: 271.0656; found: 271.0663.

4.3.10. (E)-5,5-Difluoro-6-hydroxy-8-phenylocta-1,7-dien-4-one (3-9)

As colorless oil in 80% yield, ^{1}HNMR ($CDCl_3$) δ 2.77 (brs, 1H), 3.75 (d, J = 6.5 Hz, 2H), 5.23–5.89 (m, 3H), 6.03 (m, J = 17.4 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 7.23–7.41 (m, 5H). ^{19}F NMR ($CDCl_3$) δ 108.05 (dd, J = 278, 6.8 Hz, 1F), 119.3 (dd, J = 278, 23.2 Hz, 1F). HRMS (FAB^+): Calc'd for $C_{14}H_{14}F_2O_2$: 252.0962; found: 252.0966.

4.3.11. 1-Cyclohexyl-2,2-difluoro-1-hydroxyhex-5-en-3-one (3-10)

As colorless oil in 65% yield, ^{1}HNMR ($CDCl_3$) δ 1.03–2.50 (m, 12H), 3.74 (d, J = 6.5 Hz, 2H), 3.96–4.15 (m, 1H), 5.25-5.30 (m, 1H), 6.09 (d, J = 16.2 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ 105.75 (dd, J = 290, 6.6 Hz, 1F), 116.03 (dd, J = 290, 20.1 Hz, 1F). HRMS (FAB^+): Calc'd for $C_{12}H_{18}F_2O_2$: 232.1275; found: 232.1281.

Acknowledgements

This project is supported by *National Natural Science Foundation of China* (NSFC, Grant No. 21002019), and L. W. also thanks the *Harbin Institute of Technology* for startup financial support.

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