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Journal of Organometallic Chemistry 662 (2002) 77–82

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Regioselective, stereospecific, and chemoselective fluorination of epoxy alcohols: development of fluorinating hybrid reagents, associated with Lewis acid metal fluoride/ammonium hydrogen fluoride

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Received 28 March 2002; accepted 5 September 2002

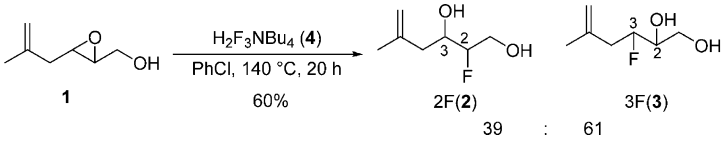
Abstract

A new type of fluorinating reagent of Lewis acid metal fluoride/ammonium hydrogen fluoride is developed for regio-, stereo-, and chemoselective ring opening fluorination of epoxy alcohols.

Keywords: Regioselective fluorination; Epoxy alcohols; Fluorinating hybrid reagents

1. Introduction

Several methods have recently been developed to give chiral organo-fluorine compounds [1], as recent examples of enantioselective electrophilic fluorination. One of the simplest methods for asymmetric introduction of a fluorine substituent into a molecule involves the Sharpless–Katsuki asymmetric epoxidation [2] followed by ring opening fluorination leading to enantio-enriched fluorohydrine. Epoxides undergo a ring-opening fluorination by HF/amine complex such as HF/pyridine [3] to react, however, also with olefin [4]. Potassium hydrogen fluoride or potassium difluoride, KHF_2 also serve as fluorinating reagents and react with epoxides to give fluorohydrins [5]. Ring-opening fluorination of epoxides can also be carried out with tetrabutylammonium dihydrogen trifluoride ($Bu_4N^+H_2F_3^-$; $TBAH_2F_3$) [6,7]. The coproduced reagent $TBAHF_2^-$ is reported to be readily converted back to $TBAH_2F_3$ by KHF_2 [7]. The order of nucleophilicity and selectivity of a fluoride ion is reported: nucleophilicity [8]: TBAF > $TBAHF_2$ > $TBAPh_3SnF_2$, $TBAPh_3SiF_2$; selectivity: $TBAHF_2$ ~ $TBAPh_3SiF_2$ > anhydrous TBAF. However, even by using $TBAH_2F_3$, ring opening fluorination of epoxy alcohols generally provides the regioisomeric mixture with 3-fluorinated 1,2-diols as the major one (Eq. (1)) [6,9]. Thus, the high regio- and stereocontrol in ring-opening fluorination of epoxide to give 2-fluorinated 1,3-diols has remained as a challenging problem. Herein reported are fluorinating hybrid reagents of Lewis acid



1 → 2F(2) 39 : 3F(3) 61 (1)

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0022-328X/02/$ - see front matter
PII: S0022-328X(02)01888-0

Table 1
Ring opening fluorination with Lewis acidic metal salts and ammonium hydrogen fluoride

Entry	MF_n	Reagent	Temperature (°C)	Time (h)	2F + 3F [a]	2F:3F [a]
1	–	HF/Py	0	1	Complex mixture	–
2	–	$H_2F_3NBu_4$	140	20	60%	39:61
3	ScF_3	$H_2F_3NBu_4$	r.t.	24	No reaction	–
4	TiF_4	$H_2F_3NBu_4$	r.t.	8	86% [b]	66:34
5	FeF_3	$H_2F_3NBu_4$	r.t.	24	No reaction	–
6	CuF_2	$H_2F_3NBu_4$	r.t.	24	No reaction	–
7	SnF_2 [c]	$H_2F_3NBu_4$	r.t.	72	20%	65:35

[a] % Yield and ratio were determined by ^{19}F-NMR.
[b] Isolated yield.
[c] CH_2Cl_2 was used.

metal fluoride/ammonium hydrogen fluoride for regio-, stereo-, and chemoselective ring opening fluorination of epoxy alcohols.

2. Results and discussion

In the presence of a variety of metal fluorides, chemo- and regioselectivities in ring opening fluorination of epoxyalcohol (**1**) as a highly functionalized substrate were examined. The results with the combined use of Lewis acidic metal salts and ammonium hydrogen fluoride are shown in Table 1. Titanium tetrafluoride assisted the fluorination reaction under mild conditions to give fluorohydrins in high yields. The reaction in chlorobenzene was completed within 8 h at room temperature and the expected fluorohydrins (**2**, **3**) were obtained in 86% yield. C-2-fluorinated product (**2**) was obtained as the major product (entry 4). The structures of the fluorohydrins (**2**, **3**) were determined to show the stereospecific S_N2 inversion process by the decoupling of the allylic proton in ^{1}H-NMR and also confirmed by C–F coupling constant of ^{13}C-NMR (see Section 3).

Thus, we focused our attention on the regioselectivity of fluorination by changing Group 4 transition metal fluorides (Table 2). Group 4 transition metal fluorides mediated the fluorination reaction under mild conditions to give fluorohydrins in high yields. The regioselectivity depends on the combination of metals and solvents employed. Therefore, the C-2- or C-3-fluorinated products can be obtained selectively. The highest C-2-regioselectivity was obtained when HfF_4 was used with TBA·H_2F_3 (**4**) in THF (entry 8).

Table 2
Ring opening fluorination using Group 4 transition metals

Entry	MF_n	Solvent	Time (h)	2F + 3F [a] (%)	2F:3F[a]
1	TiF_4	CH_2Cl_2	8	58	42:58
2		THF	24	67	59:41
3	TiF_3	CH_2CI_2	19	78	60:40
4		THF	48	77	63:37
5	ZrF_4	CH_2Cl_2	8	65	60:40
6		THF	8	67	74:26
7	HIF_4	CH_2Cl_2	4	83	63:37
8		THF	4	81	74:26

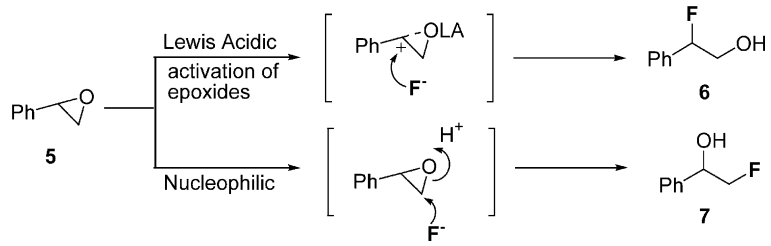
[a] % Yield and ratio were determined by ^{19}F-NMR.

Then we examined the characteristic feature of Group 4 transition metal fluorides by the ring opening fluorination of styrene oxide. When metal fluorides activate epoxides as Lewis acids, the reaction will proceed via stable carbenium ion intermediate to give the secondary fluoride product. On the other hand, when metal fluorides/ammonium fluoride hybride reagents are nucleophilic rather than Lewis acidic, the fluoride will attack the less hindered side to give the primary fluorinated product (Scheme 1).

The results of the ring opening fluorination of styrene oxide (**5**) are shown in Table 3. In the reaction of **5** with **4** without metal fluoride, primary fluorinated product (**7**) was obtained predominantly (entry 1). While in the presence of metal fluorides, only secondary fluorinated product (**6**) was obtained and the aldehyde (**8**) was also obtained as a by-product (entry 2). The formation of the aldehyde (**8**) suggests that the reaction proceeds via benzylic carbenium ion intermediate and hydride shift takes place to give aldehyde **8** (Scheme 2). Therefore, the metal fluorides are likely to activate the epoxides as Lewis acid metal complexes.

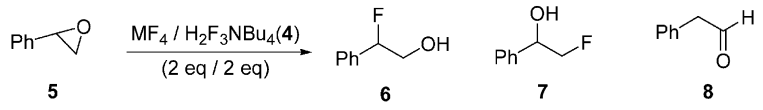
In the reaction of 2,3-epoxyhexanol (**9**) with **4** and metal fluorides, C-3-fluorinated product was obtained predominantly (Table 4). The highest C-3-regioselectivity (89% selective) was obtained when TiF_4 was used with **4** in CH_2Cl_2 (Entry 2).

Next, the effect of steric bulkiness around the epoxide ring was examined on the regioselectivity of fluorination of **12** (Table 5). The C-3-regioselectivity was decreased as compared with **9**. Interestingly, in comparison with **1**, C-2-regioselectivity of **12** was lower than that of **1**. It



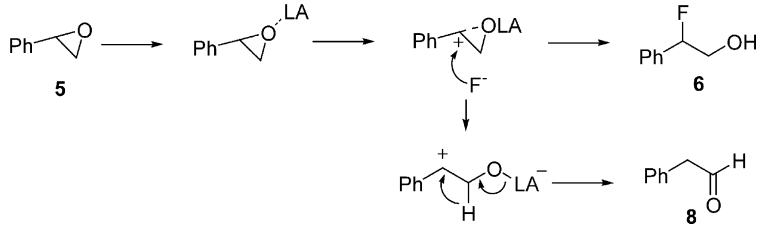
Scheme 1.

Table 3
Ring opening fluorination of styrene oxide



Entry	MF_4	Solvent	Temperature (°C)	Time (h)	**6**+**7** [a] (%)	**6**:**7** [a]	**8** [b] (%)
1	–	PhCl	140	5	84	35:65	–
2	TIF_4	THF	r.t.	1	46	100:0	10
3	HfF_4	THF	r.t.	3	40	100:0	15

[a] % Yield and ratio were determined by ^{19}F-NMR.
[b] % Yield was determined by ^{1}H-NMR.



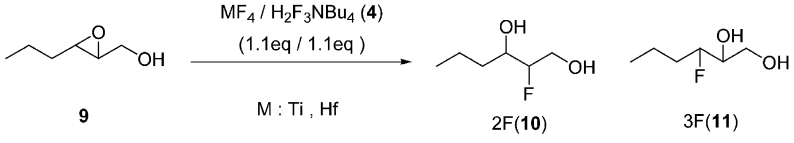
Scheme 2.

suggests that olefin functionality has significant effect in increasing the C-2-regioselectivity, presumably because of the electron withdrawing effect.

Then, the effect of the olefin was examined by fluorination of **15** obtained via hydrogenation of **1** (Table 6). The regioselectivity was almost the same as **9**. It is clear that the olefin functionality is necessary to increase the C-2 regioselectivity.

The plausible mechanism is shown in Scheme 3. The regioselectivity largely depends on the ionic radii of

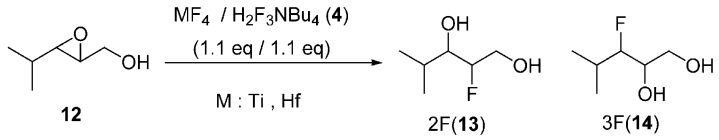
Table 4
Ring opening fluorination of 2,3-epoxyhexanol



Entry	MF_n	Solvent	Temperature (°C)	Time (h)	2F+3F [a]	2F:3F[a]
1	– [b]	PhCl	140	18	90	21:79
2	TiF_4	CH_2Cl_2	r.t.	4	92	11:89
3	HfF_4	THF	r.t.	4	74	39:61

[a] % Yield and ratio were determined by ^{19}F-NMR.
[b] Two equivalents of $H_2F_3NBu_4$ was used.

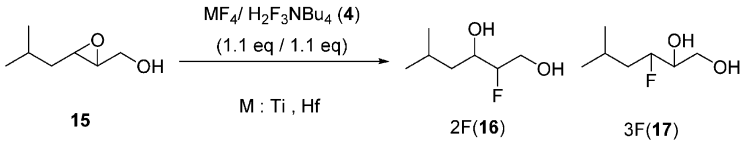
Table 5
Ring opening fluorination of 2,3-epoxy-4-methylpentanol



Entry	MF_n	Solvent	Temperature (°C)	Time (h)	2F+3F [a]	2F:3F [a]
1	– [b]	PhCl	140	24	69	33:67
2	TiF_4	CH_2Cl_2	r.t.	4	74	20:80
3	HfF_4	THF	r.t.	24	76	63:37

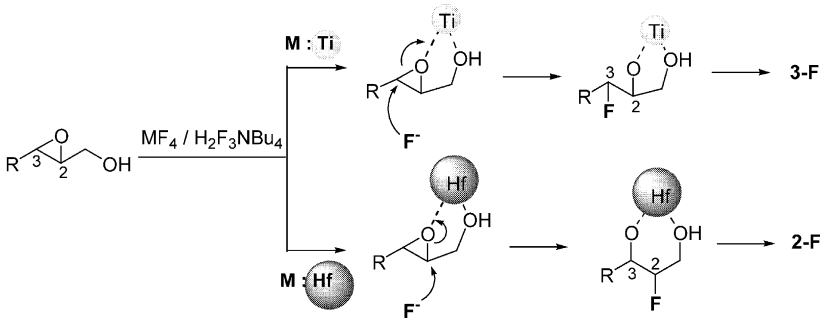
[a] % Yield and ratio were determined by ^{19}F-NMR.
[b] Two equivalents of $H_2F_3NBu_4$ was used.

Table 6
Ring opening fluorination of 2,3-epoxy-5-methylhexanol



Entry	MF_n	Solvent	Temperature (°C)	Time (h)	2F+3F [a]	2F:3F [a]
1 [b]	–	PhCl	140	24	57	13:87
2	TiF_4	CH_2Cl_2	r.t.	6	56	14:86
3	HfF_4	THF	r.t.	6	71	39:61

[a] % Yield and ratio were determined by ^{19}F-NMR.
[b] Two equivalents of $H_2F_3NBu_4$ was used.



Scheme 3.

Group 4 transition metals. The smallest Ti leads to the small five-membered dioxametallacycle via C-3-fluorination. By contrast, the largest Hf affords the large six-membered ring with a coordinating and bulky solvent (THF) via C-2-fluorination.

In summary, we have thus developed the fluorinating hybrid reagents associated with Lewis acid metal fluorides/ammonium hydrogen fluoride for regioselective, stereospecific, and chemoselective ring opening fluorination of epoxy alcohols. The highly regio-, stereo-, and chemoselective ring opening fluorination of epoxy alcohol 1 can be employed in the synthesis of 2α- and 2β-fluorinated A-ring analogs of 19-nor-1α,25(OH)$_2$D$_3$ which are useful for the analysis of the VDR-binding conformation of the A-rings on the basis of the ^{19}F-NMR analysis [11].

3. Experimental

3.1. General

^{1}H-NMR and ^{13}C-NMR spectra were measured on a Varian GEMINI 300 (300 MHz) and a Varian GEMINI

400 (400 MHz) spectrometers, ^{19}F-NMR spectra were measured on a Varian GEMINI 400 (400 MHz) spectrometer. Chemical shifts of ^{1}H-NMR were expressed in parts per million downfield from Me_4Si as an internal standard ($\delta = 0$) in $CDCl_3$. Chemical shifts of ^{13}C-NMR were expressed in parts per million in $CDCl_3$ as an internal standard ($\delta = 77.1$). Chemical shifts of ^{19}F-NMR were expressed in parts per million downfield from BTF as an internal standard ($\delta = -63.24$) in $CDCl_3$.

3.2. General procedure for fluorohydrin synthesis: (2R,3S)-2-fluoro-5-methyl-5-hexene-1,3-diol (2) and (2R,3S)-3-fluoro-5-methyl-5-hexene-1,2-diol (3)

A 10-ml test tube with Ar inlet was charged with hafnium (IV) tetrafluoride (133 mg, 0.52 mmol) and THF (2.0 ml) at 0 °C. To the suspension was added tetrabutylammonium dihydrogentrifluoride (H_2F_3-NBu_4) (**4**) [10] (166 mg, 0.55 mmol) in THF (0.5 ml) and stirred for 10 min at that temperature. (2*R*,3*S*)-5-Methyl-2,3-epoxyhex-5-en-1-ol (**1**) (60 mg, 0.47 mmol) was added dropwise and, after 10 min of stirring, the reaction mixture was warmed up to room temperature. After stirring for 8 h at that temperature, the reaction mixture was quenched with a saturated aqueous solution of sodium hydrogencarbonate. The aqueous layer was extracted three times with ether, and the combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. After evaporation under reduced pressure, the resultant residue was purified by silica-gel chromatography to give (2*R*,3*S*)-2-fluoro-5-methyl-5-hexene-1,3-diol (**2**) and (2*R*,3*S*)-3-fluoro-5-methyl-5-hexene-1,2-diol (**3**). The regioselectivity and yield were determined by ^{19}F-NMR by using BTF as an internal standard; **2**:**3** = 74:26 (74% yield).

3.2.1. (2R,3S)-2-Fluoro-5-methyl-5-hexene-1,3-diol (2)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −197.7 (dtd, J = 46.6, 25.2, 9.0 Hz, 1F). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.18 (dd, J = 14.1, 10.2 Hz, 1H), 2.41 (bd, J = 14.1 Hz, 1H), 2.56 (bs, 2H), 3.93 (dd, J = 25.2, 4.2 Hz, 2H), 4.00 (dddd, J = 10.2, 9.3, 6.3, 3.3 Hz, 1H), 4.26–4.46 (ddd, J = 47.1, 6.3, 4.2 Hz, 1H), 4.84 (s, 1H), 4.92 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 22.3, 41.7 (d, ^{3}J = 3.7 Hz), 62.2 (d, ^{2}J = 20.6 Hz), 68.0 (d, ^{2}J = 25.4 Hz), 95.0 (d, ^{1}J = 171.1 Hz), 114.4, 141.5.

3.2.2. (2R,3S)-3-Fluoro-5-methyl-5-hexene-1,2-diol (3)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −191.0 (dddd, J = 58.3, 37.6, 19.2, 10.2 Hz, 1F). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3H), 2.36–2.48 (m, 2H), 2.52 (bs, 2H), 3.71–3.80 (m, 3H), 4.52–4.74 (dddd, J = 48.3, 8.7, 4.8, 3.0 Hz, 1H), 4.84 (s, 1H), 4.87 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 22.8, 39.6 (d, ^{2}J = 20.6 Hz), 62.7 (d, ^{3}J = 4.9 Hz), 72.9 (d, ^{2}J = 23.0 Hz), 92.1 (d, ^{1}J = 172.3 Hz), 113.5, 141.2.

3.2.3. 2-Fluoro-2-phenylethanol (6)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −186.0 (ddd, J = 49.3, 29.7, 20.7 Hz, 1F). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.67–3.78 (ddd, J = 30.8, 12.4, 3.2 Hz, 1H), 3.80–3.89 (ddd, J = 19.2, 12.4, 8.0 Hz, 1H), 5.41–5.56 (ddd, J = 49.32, 8.0, 3.2 Hz, 1H), 7.26–7.37 (m, 5H).

3.2.4. 2-Fluoro-1-phenylethanol (7)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −221.4 (td, J = 48.1, 15.0 Hz, 1F). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.30–4.47 (ddd, J = 48.4, 9.6, 7.6 Hz, 1H), 4.35–4.50 (ddd, J = 48.4, 9.6, 4.0 Hz, 1H), 4.89–4.95 (ddd, J = 14.0, 7.6, 4.0 Hz, 1H), 7.26–7.32 (m, 5H).

3.2.5. 2-Fluoro-hexane-1,3-diol (10)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −195.9 (dtd, J = 47.4, 25.8, 11.0 Hz, 1F). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.39–1.51 (m, 2H), 1.52–1.63 (m, 2H), 3.35 (brs, 2H), 3.80–3.93 (m, 3H), 4.26–4.41 (dtd, J = 47.2, 4.8, 3.2 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 13.9, 18.7, 34.8 (d, ^{3}J = 3.8 Hz), 61.7 (d, ^{2}J = 21.4 Hz), 70.5 (d, ^{2}J = 23.7 Hz), 95.3 (d, ^{1}J = 173.8 Hz).

3.2.6. 3-Fluoro-hexane-1,2-diol (11)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −193.6 (dddd, J = 48.9, 34.2, 20.3, 12.4 Hz, 1F). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.35–1.44 (m, 1H), 1.50–1.59 (m, 2H), 1.61–1.69 (m, 1H), 3.46 (brs, 2H), 3.62–3.76 (m, 3H), 4.36–4.52 (dtd, J = 48.0, 6.8, 5.2 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 13.8, 18.4 (d, ^{3}J = 3.0 Hz), 33.2 (d, ^{3}J = 20.6 Hz), 62.7 (d, ^{3}J = 5.4 Hz), 73.1 (d, ^{2}J = 23.7 Hz), 93.7 (d, ^{1}J = 170.8 Hz).

3.2.7. 2-Fluoro-4-methyl-pentane-1,3-diol (13)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −197.2 (dtd, J = 47.0, 26.3, 7.9 Hz, 1F). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 6H), 1.88 (q, J = 6.8 Hz, 1H), 3.01 (bs, 1H), 3.23 (bs, 1H), 3.66–3.70 (m, 1H), 3.88 (d, J = 3.2 Hz, 1H), 3.94 (d, J = 2.4 Hz, 1H), 4.40–4.55 (ddt, J = 47.2, 6.8, 3.6 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 18.7, 19.1, 29.7 (d, ^{3}J = 3.8 Hz), 62.2 (d, ^{2}J = 22.2 Hz), 74.9 (d, ^{2}J = 22.9 Hz), 93.2 (d, ^{1}J = 171.5 Hz).

3.2.8. 3-Fluoro-4-methyl-pentane-1,2-diol (14)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −204.3 (dddd, J = 49.3, 26.3, 13.9 Hz, 1F). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.97 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.94–2.05 (dqd, J = 25.6, 6.8, 2.0 Hz, 1H), 3.23 (bs, 1H), 3.53 (bs, 1H), 3.66–3.70 (m, 1H), 3.76 (d, J = 10.4 Hz, 1H), 3.79 (d, J = 10.4 Hz, 1H), 4.14–4.29 (ddd, J = 48.0, 6.0, 5.2 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 16.1 (d, ^{3}J = 5.4 Hz), 18.9 (d, ^{3}J = 5.4 Hz), 28.8 (d, ^{2}J = 20.0

Hz), 63.0 (d, $^3J = 4.5$ Hz), 70.8 (d, $^2J = 25.3$ Hz), 94.5 (d, $^1J = 173.9$ Hz).

3.2.9. (2R,3S)-2-Fluoro-5-methyl-hexane-1,3-diol (**16**)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −195.2 (bddd, J = 46.6, 26.3, 9.0 Hz, 1F). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.90 (d, $J = 6.8$ Hz, 6H), 1.77–1.86 (m, 3H), 3.54 (bs, 1H), 3.87 (dd, $J = 14.8$, 5.2 Hz, 1H), 3.93 (dd, $J = 14.8$, 5.2 Hz, 1H), 3.92–4.00 (m, 2H), 4.25–4.28 (dtd, J = 47.2, 5.2, 3.2 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 21.5, 23.6, 24.4, 41.6, 61.7 (d, $^2J = 22.1$ Hz), 69.0 (d, $^2J = 23.0$ Hz), 95.7 (d, $^1J = 173.1$ Hz).

3.2.10. (2R,3S)-3-Fluoro-5-methyl-hexane-1,2-diol (17)

^{19}F-NMR (376 MHz, $CDCl_3$) δ −192.9 (bddd, J = 47.0, 28.2, 14.7 Hz, 1F). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.93, (d, $J = 6.8$ Hz, 3H), 0.95 (d, $J = 6.8$ Hz, 3H), 1.32–1.38 (ddd, $J = 14.4$, 9.2, 2.4 Hz, 1H), 1.42–1.49 (ddd, $J = 14.4$, 9.2, 2.4 Hz, 1H), 1.57–1.68 (m, 1H), 3.47 (bs, 1H), 3.63–3.76 (m, 4H), 4.45–4.62 (dddd, $J = 48.8$, 10.4, 5.2, 2.4 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 21.7, 23.4, 24.5, 40.0 (d, $^2J = 19.9$ Hz), 62.6 (d, $^3J = 6.1$ Hz), 73.5 (d, $^2J = 23.0$ Hz), 92.5 (d, $^1J = 170.1$ Hz).

Acknowledgements

We are grateful to Professor Masahiro Terada of Tohoku University for his useful discussion.

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