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Journal of Fluorine Chemistry 125 (2004) 705–709
JOURNAL OF FLUORINE CHEMISTRY
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# Reaction of carbonyl compounds with xenon difluoride in the presence of silicon tetrafluoride

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Received 25 September 2003; received in revised form 19 November 2003; accepted 28 November 2003

Available online 13 January 2004

**Abstract**

Reaction of various carbonyl compounds with xenon difluoride in the presence of silicon tetrafluoride was investigated. Aromatic aldehyde, ketones, and α-ketoester react with xenon difluoride to give α,α-difluoroalkyl phenyl ethers. However, acid fluoride, ester, acid cyanide, α-ketocarboxylic acid, or thioester do not afford the corresponding products. In the case of cinnamaldehyde, fluorination was accompanied by intramolecular cyclization to afford fluorinated epoxide.


*Keywords:* Carbonyl compound; Cinnamaldehyde; Fluorination; Rearrangement; Cyclization; Xenon difluoride; Silicon tetrafluoride

## 1. Introduction

Xenon difluoride ($XeF_2$) is well known as a useful reagent for electrophilic fluorinations. A variety of fluorination reactions, such as fluorination to aromatic ring and to unsaturated compound, fluorodeiodination, fluorodecarboxylation, etc. have been developed and applied to prepare organic fluorine compounds [1]. As one of these reactions, fluorination reaction of aromatic aldehydes or ketones with $XeF_2$ was reported [2,3]. When aromatic aldehydes or ketones react with $XeF_2$ in the presence of hydrogen fluoride (HF), fluorination is accompanied by skeletal rearrangement, and α,α-difluoroalkyl aryl ethers are obtained. However, the reaction of the other carbonyl compounds with $XeF_2$ had not been reported.

We have been studying fluorination with $XeF_2$ using silicon tetrafluoride ($SiF_4$) as a promoter. It was reported that $XeF_2$ are activated by acidic catalyst, such as HF, boron trifluoride etherate ($BF_3OEt_2$), etc [4]. And we had demonstrated that $SiF_4$ also activates $XeF_2$ and enhances *vic*-difluorination of phenylalkenes or fluoroalkenes and reaction of benzaldehydes [5,6].

In the course of this study, we investigated the reaction of various kinds of carbonyl compounds with $XeF_2$ in the presence of $SiF_4$, and found that α-ketoester, as well as aromatic aldehyde and ketones, give α,α-difluoroalkyl phenyl ethers. We also found that unprecedented epoxide formation proceeds in the reaction of cinnamaldehydes.

## 2. Results and discussion

Initially, the reaction of aromatic ketones (**1**, $R^2 = CH_3$, $C_2H_5$, Ph) with $XeF_2$ in the presence of $SiF_4$ was investigated (Scheme 1), and the results are summarized in Table 1. α,α-Difluoroalkyl phenyl ethers (**2**) were obtained, and the result was influenced by substituents on the benzene ring. In the case of substrates substituted by an electron-withdrawing group, the product was obtained in relatively high yield (entry 1, 2), but the yield was relatively low (entry 4) when an electron donating group is substituted on the benzene ring. Especially, in the case of *p*-methoxyacetophenone, which has a strong electron donating methoxy group, tarry material was obtained (entry 5). The effect of substituent would be explained by the concept that the more the benzene ring is electron-rich, the more side-reactions such as fluorination on the benzene ring proceed, which is similar to the reaction of benzaldehydes with $XeF_2$ [2,5].

The reaction was examined using various aromatic carbonyl compounds, and the results are summarized in Table 2. In the case of acid fluoride, ester, and acid cyanide, the corresponding α,α-difluoroalkyl phenyl ethers were not obtained, although only fluorination to the benzene ring

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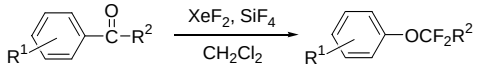
doi:10.1016/j.jfluchem.2003.11.019




$R^1$ = H, *p*-$NO_2$, *p*-Cl, *p*-$CH_3$, *p*-$CH_3O$

$R^2$ = $CH_3$, $C_2H_5$, Ph, H, F, $OC_2H_5$, CN, $COOCH_3$, $SC_2H_5$, COOH

Scheme 1. Reaction of aromatic carbonyl compounds with $XeF_2$ in the presence of $SiF_4$.

Table 1
The reaction of aromatic ketones[a]

| Entry | Substrate | Yield of the product (%)[b] | Recovery of the substrate (%)[b] |
|---|---|---|---|
| 1[c] | *p*-$NO_2C_6H_4C(O)CH_3$ | 91 | 3 |
| 2 | *p*-$ClC_6H_4C(O)CH_3$ | 53 | 21 |
| 3 | $C_6H_5C(O)CH_3$ | 40 | 23 |
| 4 | *p*-$CH_3C_6H_4C(O)CH_3$ | 18 | 34 |
| 5 | *p*-$CH_3OC_6H_4C(O)CH_3$ | –[d] | 42 |
| 6 | $C_6H_5C(O)C_2H_5$ | 27 | 38 |
| 7 | $C_6H_5C(O)C_6H_5$ | 20 | 31 |

[a] Substrate (1 mmol), $XeF_2$ (1.2 mmol), $SiF_4$ (0.5 mmol), and dichloromethane (3 ml) were placed in a reactor (10 ml) and agitated at room temperature for 2–2.5 days.
[b] Determined by $^1H$ and $^{19}F$ NMR of the crude product ($C_6H_5CF_3$ was used as an internal standard).
[c] 8 mmol of $SiF_4$ was used.
[d] Tarry material was obtained.

occurred in the case of ester and acid cyanide (entries 3–5). On the other hand, the reaction of α-ketoester proceeded and afforded the corresponding α,α-difluoroalkyl phenyl ether (entry 6). In the case of α-ketoacid, fluorodecarboxylation [7] proceeded and afforded acid fluoride (entry 7). The reaction of thioester with $XeF_2$ also afforded acid fluoride by desulfurization-fluorination [8] (entry 8).

The mechanism of this reaction from aromatic carbonyl compounds **1** to α,α-difluoroalkyl phenyl ethers **2** has been proposed as shown in Scheme 2 [1c,2,5]. $XeF_2$ would be activated by $SiF_4$ and react with **1** to form alkoxyxenon intermediate (**3**). Migration of the phenyl group to the oxygen atom proceeds with loss of xenon and attack of fluoride anion to afford **2**.

Table 2
The reaction of aromatic carbonyl compounds[a]

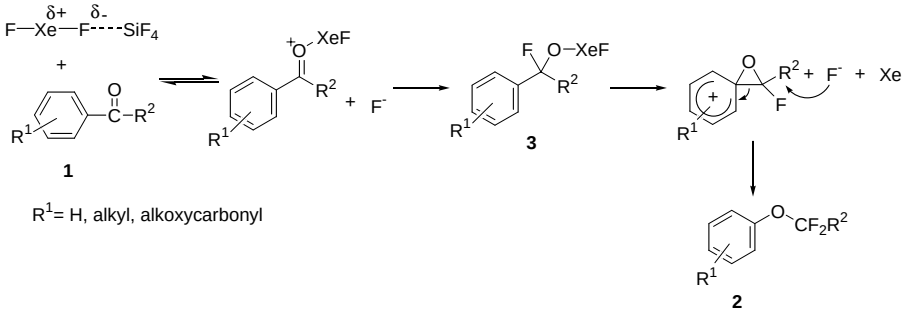
| Entry | Substrate | Yield of $PhOCF_2R$ (%)[b] |
|---|---|---|
| 1[c] | $C_6H_5C(O)CH_3$ | 40 |
| 2[d] | $C_6H_5C(O)H$ | 57 |
| 3[e] | $C_6H_5C(O)F$ | 0 |
| 4[f] | $C_6H_5C(O)OC_2H_5$ | 0 |
| 5[g] | $C_6H_5C(O)CN$ | 0 |
| 6[h] | $C_6H_5C(O)COOC_2H_5$ | 43 |
| 7[i] | $C_6H_5C(O)COOH$ | 0 |
| 8[j] | $C_6H_5C(O)SC_2H_5$ | 0 |

[a] Substrate (1 mmol), $XeF_2$ (1.2 mmol), $SiF_4$ (0.5 mmol), and dichloromethane (3 ml) were placed in a reactor (10 ml) and agitated at room temperature for 16 h to 2.5 days.
[b] Determined by $^{19}F$ NMR of the crude product ($C_6H_5CF_3$ was used as an internal standard).
[c] Recovery of the substrate was 23% (data from Table1, entry 3).
[d] 9 mmol of $SiF_4$ was used (data from [5]).
[e] No reaction.
[f] Fluorination to benzene ring proceeded in 10%.
[g] Fluorination to benzene ring proceeded in 6%.
[h] Recovery of the substrate was 31%.
[i] $C_6H_5C(O)F$ was obtained in 73%.
[j] $C_6H_5C(O)F$ was obtained in 79%.

Next, the reaction of non-aromatic carbonyl compounds was attempted. The reaction of aliphatic carbonyl compounds afforded tarry matters. However, in the case of cinnamaldehyde, fluorination and intramolecular cyclization proceeds to afford fluorinated epoxide (Scheme 3).

This reaction was significantly influenced by the catalyst. As shown in Table 3, the reaction was very slow without a catalyst. When HF or $BF_3OEt_2$, which are representative catalysts in fluorination with $XeF_2$ [4], were used as catalysts, the yield of fluoroepoxide (**5**) was low. On the other hand, **5** was obtained in much higher yield with $SiF_4$. Probably, further undesirable reactions of **5**, such as ring opening, origomerization, etc., would proceed by HF and $BF_3OEt_2$, however, $SiF_4$ afforded good result because not only does it have catalytic activity for $XeF_2$ [5], but also acidity of $SiF_4$ is so weak that **5** was obtained without further reaction [9].

The reactions of several α,β-unsaturated aldehydes are summarized in Table 4. The reaction of β-phenyl cinnamaldehyde was accompanied by *vic*-difluorination to the double

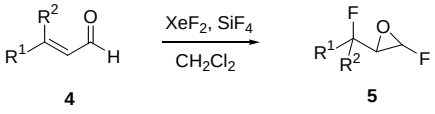



Scheme 2. Postulated mechanism of transformation of aromatic carbonyl compounds to α,α-difluoroalkyl aryl ethers.

Table 3
Effect of catalyst on the reaction of cinnamaldehyde[a]

| Entry | Catalyst | Amount of catalyst (mmol) | Time (h) | Yield (%)[b] | Recovery of the substrates (%)[b] |
|---|---|---|---|---|---|
| 1 | – | | 36 | 3 | 82 |
| 2 | $SiF_4$ | 0.5 | 16 | 60 | 6 |
| 3 | HF | 0.3 | 18 | 3 | 88 |
| 4 | HF | 4 | 1.5 | 38 | 10 |
| 5 | $BF_3O(C_2H_5)_2$ | 0.1 | 2 | 2 | 1 |

[a] Substrate (1 mmol), $XeF_2$ (1.2 mmol), catalyst and dichloromethane (3 ml) were placed in a reactor (10 ml) and agitated at room temperature.
[b] Determined by $^1H$ and $^{19}F$ NMR of the crude product ($C_6H_5CF_3$ was used as an internal standard).




4

5

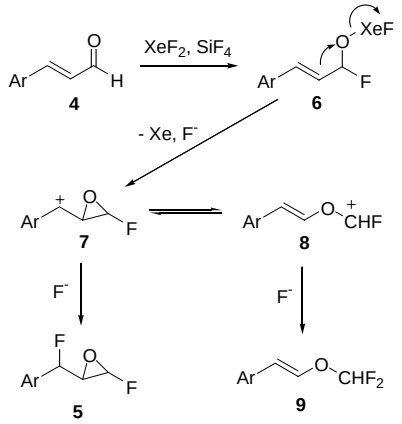
a: $R^1$ = Ph, $R^2$ = H
b: $R^1$ = $R^2$ = Ph
c: $R^1$ = *p*-$NO_2C_6H_4$, $R^2$ = H

Scheme 3. Reaction of cinnamaldehydes with $XeF_2$ in the presence of $SiF_4$.

Table 4
The reaction of α,β-unsaturated aldehydes[a]

| Entry | Substrate | Yield of **5** (%)[b] |
|---|---|---|
| 1[c] | $C_6H_5CH{=}CHCHO$ | 60 |
| 2[d] | $(C_6H_5)_2C{=}CHCHO$ | 44 |
| 3[e] | *p*-$NO_2C_6H_5CH{=}CHCHO$ | 26 |

[a] Substrate (1 mmol), $XeF_2$ (1.2 mmol), $SiF_4$ (0.5 mmol), and dichloromethane (3 ml) were placed in a reactor (10 ml) and agitated at room temperature for 16 h.
[b] Determined by $^{19}F$ NMR of the crude product ($C_6H_5CF_3$ was used as an internal standard).
[c] The substrate was recovered in 6% (data from Table 3, entry 2).
[d] Byproducts, such as $(C_6H_5)_2C{=}CFCHO$ (11%), $(C_6H_5)_2CFCHFCHO$ (4%) etc., was obtained, and the substrate was recovered in 8%.
[e] The products by skeletal rearrangement, *p*-$NO_2C_6H_5CH{=}CHOCHF_2$ and *p*-$NO_2C_6H_5CHFCHFOCHF_2$ were obtained in 17 and 9%, respectively.




4 6 7 8 5 9

Scheme 4. Postulated mechanism of the reaction of cinnamaldehydes.

bond and elimination of HF [5,10] to give α-fluoro-β-phenyl cinnamaldehyde. In the case of 3-(*p*-nitorophenyl)propenal, formation of difluoromethoxy ether (*p*-$NO_2C_6H_5CH{=}CHOCHF_2$) proceeded competitively and its fluorination product (*p*-$NO_2C_6H_5CHFCHFOCHF_2$), was also obtained.

The formation of epoxide **5** would be explained by the reaction mechanism as follows (Scheme 4). By the reaction of **4** with $XeF_2$ in the presence of $SiF_4$, alkoxyfluoroxenon species (**6**) is formed similarly to the above-mentioned reaction of aromatic carbonyl compounds with $XeF_2$. Intramolecular cyclization of **6** proceeds to form intermediate cation (**7**) followed by transformation to **5** by the attack of fluoride anion. In the case of 3-(*p*-nitorophenyl)propenal, it is assumed that ether type cation intermediate (**8**) is formed by C–C bond cleavage to give difluoromethoxy ether (**9**). Probably, the nitro group on the benzene ring would destabilize the cation **7** by its electron withdrawing effect, which drives rearrangement from **7** to **8**.

## 3. Conclusion

We have disclosed the reaction of various carbonyl compounds with $XeF_2$. In the presence of $SiF_4$, α,α-difluoroalkyl aryl ethers were obtained by the reaction of aromatic aldehyde, ketones, or α-ketoester via fluorination accompanied by skeletal rearrangement. However, in the case of aryl acid fluoride, ester, acid cyanide, α-ketocarboxylic acid or thioester, the skeletal rearrangement does not proceed. And especially, α-ketocarboxylic acid or thioester afforded the corresponding acid fluoride.

On the other hand, we have found that fluorination and intramolecular cyclization proceed by the reaction of cinnamaldehyde with $XeF_2$ in the presence of $SiF_4$ to give novel fluorinated epoxide.

## 4. Experimental details

### 4.1. General

All the reagents are commercially available. Reagents and solvents employed were purified prior to use except for $XeF_2$ and $SiF_4$. IR spectra were measured with FT-IR 8900 (Japan Spectroscopic). $^1H$ and $^{19}F$ NMR were measured

with JNM-EX270 (JEOL, 270 MHz) using TMS and $CFCl_3$ as internal standards and $CDCl_3$ as a solvent.

### 4.2. A typical experimental procedure for the reaction

Substrate (1.0 mmol) dissolved in $CH_2Cl_2$ (3 ml) and $XeF_2$ (1.2 mmol) were placed in a stainless-steel reactor equipped with a stop valve (volume, 10 ml). $SiF_4$ (0.5 mmol) was introduced into the reactor at −196 °C from a vacuum line. The reactor was warmed up to ambient temperature and shaken vigorously for the indicated time. The reaction mixture was poured into aqueous saturated $NaHCO_3$. The aqueous phase was extracted with $CH_2Cl_2$ and the combined organic phase was dried with $MgSO_4$. After evaporation of the solvent, the crude product was analyzed by $^1H$ and $^{19}F$ NMR spectroscopy to determine the yield of the product. The product was purified by preparative thin layer chromatography.

All the compounds were characterized by NMR, IR, and/or high-resolution MS analysis. Representative data are as follows.

1-(1,1-Difluoroethoxy)-4-nitrobenzene: $^1H$ $\delta$ 1.99 (3H, $CH_3$, t, $J_3 = 13.4$ Hz), 7.3 (2H aromatic, m), 8.2 (2H aromatic, m); $^{19}F$ $\delta$ −66.1 (q, $J_4 = 13.4$ Hz); IR (KBr, $cm^{-1}$) 1596, 1526, 1494, 1404, 1349, 1270, 1187, 1160, 980, 930, 867, 843, 750; MS calcd 203.03934, obsd 203.0379.

1-Chloro-4-(1,1-difluoroethoxy)benzene: $^1H$ $\delta$ 1.91 (3H, $CH_3$, t, $J_3 = 13.4$ Hz), 7.1 (2H aromatic, m), 7.3 (2H aromatic, m); $^{19}F$ $\delta$ −65.4 (q, $J_4 = 13.4$ Hz); IR (KBr, $cm^{-1}$) 1489, 1404, 1278, 1186, 1151, 1091, 1016, 977, 925; MS calcd 192.0153, obsd 192.0161.

(1,1-Difluoroethoxy)benzene: $^1H$ $\delta$ 1.91 (3H, $CH_3$, t, $J_3 = 13.3$ Hz), 7.1–7.3 (5H aromatic, m); $^{19}F$ $\delta$ −64.9 (q, $J_4 = 13.3$ Hz); IR (KBr, $cm^{-1}$) 1506, 1403, 1276, 1183, 978, 924, 736, which correspond to the authentic sample [3].

1-(1,1-Difluoroethoxy)-4-methylbenzene: $^1H$ $\delta$ 1.90 (3H, $CH_3$, t, $J_3 = 13.3$ Hz), 7.1 (4H aromatic, m); $^{19}F$ $\delta$ −64.9 (q, $J_4 = 13.3$ Hz); IR (KBr, $cm^{-1}$) 1510, 1401, 1280, 1184, 1150, 980, 924; MS calcd 172.0699, obsd 192.0702.

(1,1-Difluoropropoxy)benzene: $^1H$ $\delta$ 1.16 (3H, $CH_3$, t, $J_3 = 7.5$ Hz), 2.15 (2H, $CH_2$, tq, $J_3 = 11.1$ Hz, $J_4 = 7.5$ Hz), 7.1–7.4 (5H aromatic, m); $^{19}F$ $\delta$ −73.2 (t, $J_3 = 11.1$ Hz); IR (KBr, $cm^{-1}$) 2992, 2953, 1592, 1506, 1493, 1470, 1372, 1293, 1255, 1161, 1044, 1015, 974, 752, 693; MS calcd 172.0699, obsd 192.0723.

(Difluorophenoxymethyl)benzene: $^1H$ $\delta$ 7.2–7.5 (8H aromatic, m), 7.7–7.8 (2H aromatic, m); $^{19}F$ $\delta$ −65.9 (s); IR (KBr, $cm^{-1}$) 1505, 1492, 1455, 1321, 1200, 1144, 1046, 764, 695, which correspond to the authentic sample [3].

Methyl difluorophenoxyacetate: $^1H$ $\delta$ 3.94 (3H, $CH_3$, s), 7.2–7.3 (3H aromatic, m), 7.3–7.4 (2H aromatic, m); $^{19}F$ $\delta$ −76.6 (s); IR (KBr, $cm^{-1}$) 1783, 1505, 1492, 1358, 1206, 1138, 738, 690, which correspond to the authentic sample [11].

1,3-Difluoro-3-phenyl-1,2-epoxypropane, which consisted of four isomers, **5-A**, **5-B**, **5-C**, **5-D** (ratio = 41:25:24:10). **5-A**: $^1H$(TMS) $\delta$ 3.55 (C**H** on the epoxide ring, dm, $J_2 = 4.2$ Hz), 5.36–5.4 (PhC**H**F, m), 5.54 (C**H**F on the epoxide ring, m), 7.4 (5H aromatic, m); $^{19}F$($CFCl_3$) $\delta$ −155.2 (CH**F** on the epoxide ring, dd, $J_2 = 85.1$, 1.5 Hz), −186.9 (PhCH**F**, dd, $J_2 = 46.4$, 15.9 Hz); **5-B**: $^1H$ $\delta$ 3.5 (C**H** on the epoxide ring, dm, $J_2 = 2.6$ Hz), 5.44–5.48 (PhC**H**F, m), 5.54 (C**H**F on the epoxide ring, m), 7.4 (5H aromatic, m); $^{19}F$ $\delta$ −155.4 (CH**F** on the epoxide ring, ddd, $J_2 = 85.5$, 3.1, 1.8 Hz), −187.3 (PhCH**F**, dd, $J_2 = 47.6$, 16.5 Hz); **5-C**: $^1H$ $\delta$ 3.2 (C**H** on the epoxide ring, ddm, $J_2 = 8.3$, 2.0 Hz), 5.44–5.48 (PhC**H**F, m), 5.59 (C**H**F on the epoxide ring, dm, $J_2 = 2.0$ Hz), 7.4 (5H aromatic, m); $^{19}F$ $\delta$ −161.5 (CH**F** on the epoxide ring, ddd, $J_2 = 86.1$, 2.4, 1,8 Hz), −187.2 (PhCH**F**, ddd, $J_2 = 47.6$, 7.3, 4.3 Hz); **5-D**: $^1H$ $\delta$ 3.18 (C**H** on the epoxide ring, ddm, $J_2 = 7.5$, 1.4 Hz), 5.36–5.4 (PhC**H**F, m), 5.69 (C**H**F on the epoxide ring, dm, $J_2 = 1.4$ Hz), 7.4 (5H aromatic, m); $^{19}F$ $\delta$ −163.7 (CH**F** on the epoxide ring, ddd, $J_2 = 86.7$, 2.4, 1,8 Hz), −183.9 (PhCH**F**, ddd, $J_2 = 45.8$, 1.8, 1.8 Hz); IR (KBr, $cm^{-1}$) 3038, 1455, 1124, 1047, 757; MS calcd 170.0543, obsd 170.0522.

1,3-Difluoro-3,3-diphenyl-1,2-epoxypropane: $^1H$ $\delta$ 3.91 (C**H**, dd, $J_2 = 17.7$, 1.8 Hz), 5.55 (C**H**F, d, $J_2 = 86.0$ Hz), 7.4 (5H aromatic, m); $^{19}F$ $\delta$ −153.2 (C**F**, d, $J_2 = 17.7$ Hz), −155.6 (CH**F**, d, $J_2 = 86.0$ Hz); IR (KBr, $cm^{-1}$) 3063, 1450, 1259, 1126, 1048, 973, 925, 746, 698; MS calcd 246.0856, obsd 246.0864.

1,3-Difluoro-3-(4-nitrophenyl)-1,2-epoxypropane, which consisted of four isomers, **5-E**, **5-F**, **5-G**, **5-H** (ratio = 24:42:18:16). **5-E**: $^1H$ $\delta$ 3.56 (C**H** on the epoxide ring, ddd, $J_2 = 18.9$, 3.4, 2.0 Hz), 5.63 (C**H**F on the epoxide ring, d, $J_2 = 84.8$ Hz), 5.66 ($NO_2C_6H_4$C**H**F, dd, $J_2 = 45.8$, 3.4 Hz), 7.6 (2H aromatic, m), 8.3 (2H aromatic, m); $^{19}F$ $\delta$ −154.8 (CH**F** on the epoxide ring, d, $J_2$=84.8 Hz), −192.3 ($NO_2C_6H_4$CH**F**, dd, $J_2 = 45.8$, 18.9 Hz); **5-F**: $^1H$ $\delta$ 3.53 (C**H** on the epoxide ring, ddd, $J_2 = 14.4$, 3.2, 2.0 Hz), 5.54 (C**H**F on the epoxide ring, d, $J_2 = 83.6$ Hz), 5.6 ($NO_2$-$C_6H_4$C**H**F, m), 7.6 (2H aromatic, m), 8.3 (2H aromatic, m); $^{19}F$ $\delta$ −155.2 (CH**F** on the epoxide ring, d, $J_2 = 83.6$ Hz), −190.7 ($NO_2C_6H_4$CH**F**, dd, $J_2 = 47.0$, 14.4 Hz); **5-G**: $^1H$ $\delta$ 3.2 (C**H** on the epoxide ring, m), 5.6 ($NO_2C_6H_4$C**H**F, m), 5.69 (C**H**F on the epoxide ring, ddd, $J_2 = 86.1$, 4.6, 2.0 Hz), 7.6 (2H aromatic, m), 8.3 (2H aromatic, m); $^{19}F$ $\delta$ −160.9 (CH**F** on the epoxide ring, d, $J_2 = 86.1$ Hz), −190.5 ($NO_2C_6H_4$CH**F**, ddd, $J_2 = 42.1$, 7.9, 5.5 Hz); **5-H**: $^1H$ $\delta$ 3.2 (C**H** on the epoxide ring, m), 5.5 ($NO_2C_6H_4$C**H**F, dd, $J_2 = 45.2$, 8.3 Hz), 5.8 (C**H**F on the epoxide ring, ddd, $J_2 = 86.7$, 2.0, 2.0), 7.6 (2H aromatic, m), 8.3 (2H aromatic, m); $^{19}F$ $\delta$ −163.3 (CH**F** on the epoxide ring, dd, $J_2 = 86.7$, 3.1 Hz), −189.2 ($NO_2C_6H_4$CH**F**, dd, $J_2 = 45.2$, 3.1 Hz); IR (KBr, $cm^{-1}$) 1527, 1457, 1124, 1043, 944, 857, 833, 716; MS calcd 215.0393, obsd 215.0381.

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