Nucleophilic Fluoroalkylation of α,β-Unsaturated Carbonyl Compounds with α-Fluorinated Sulfones: Investigation of the Reversibility of 1,2-Additions and the Formation of 1,4-Adducts

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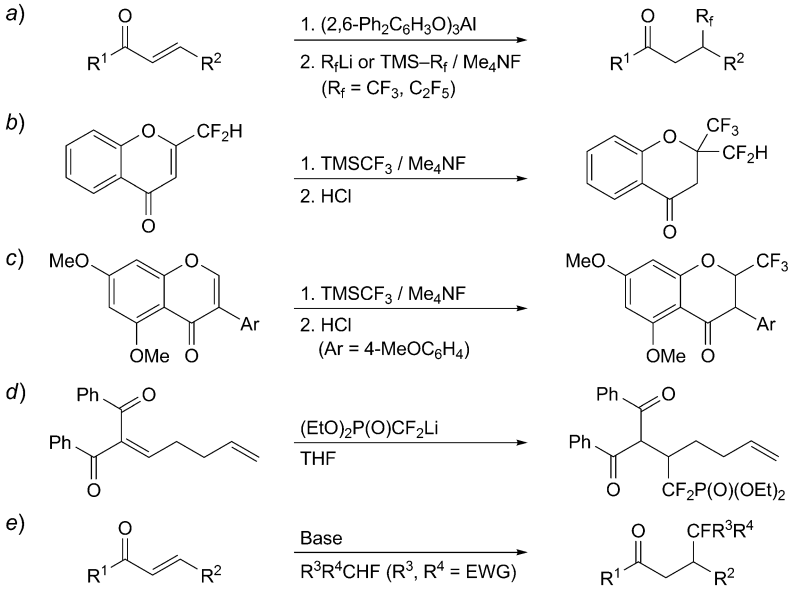
Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

A detailed investigation of the reactions of $PhSO_2CF_2H$ and $PhSO_2CH_2F$ with (*E*)-chalcone (=(*E*)-1,3-diphenylprop-2-en-1-one) at low temperatures revealed that these two reactions were kinetically controlled, and the ratios of 1,2- *vs.* 1,4-adducts, which did not change much over time at these temperatures, reflect the relative rates of the two reaction pathways. The controlled experiments of converting the $PhSO_2CF_2$- and $PhSO_2CHF$-substituted 1,2-adducts to 1,4-adducts showed that these isomerizations are not favored due to the low stability and hard-soft nature of $PhSO_2CF_2^-$ and $PhSO_2CHF^-$ anions. Moreover, taking advantage of the remarkable stability and softness of $(PhSO_2)_2CF^-$ anion, an efficient thermodynamically controlled isomerization of $(PhSO_2)_2CF$-substituted 1,2-adduct to 1,4-adduct was achieved for the first time.

Introduction. – Nucleophilic fluoroalkylation, typically involving the transfer of an α-fluoro carbanion to an electrophile, represents one of the major synthetic methods to synthesize organofluorine compounds [1–7]. α,β-Unsaturated carbonyls (such as α,β-enones) are ambident electrophiles, which have been extensively used in organic synthesis [8][9]. However, the addition chemistry to α,β-unsaturated CO compounds can be of practical synthetic utility only if one of the two regioisomers is generated selectively [10]. Therefore, regioselective incorporation of a fluoroalkyl into the C(1) or C(3) position of α,β-unsaturated carbonyls has attracted much attention these years [11–18].

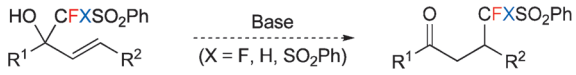
Due to the high electronegativity of the F-atom, many α-fluoro carbanions such as F_3C^- are considered as hard nucleophiles and thus usually undergo 1,2-addition reactions with α,β-unsaturated carbonyl compounds [11][16]. On the contrary, the high regioselective nucleophilic introduction of a fluoroalkyl group in C(3) position of α,β-unsaturated carbonyl compounds (1,4-addition) is a challenging task, which is usually attributed to the intrinsic unmatched hard/soft nature between the fluorinated nucleophiles and the C(3) position of α,β-unsaturated carbonyl compounds [16]. Reported methods for 1,4-addition of a fluoroalkyl group in α,β-enones and α,β-enals include: *1*) *in situ* protection of the CO group with a sterically hindered *Lewis* acid such as aluminum tris(2,6-diphenylphenoxide) (*Scheme 1,a*) [12]; *2*) activation of the β-position with an electron-withdrawing group (EWG) or an aryl group (*Scheme 1*, *b*

Scheme 1. *Reprentative Examples for the Regioselective Nucleophilic Introduction of a Fluoroalkyl Group* (R_f) *in the β-Position of Enones*



and *c*) [13–15]; and *3*) modification of the fluoroalkyl moiety with EWGs that can soften the corresponding α-fluorinated carbanion (*Scheme 1*,*d* and *e*) [16][17]. However, all these methods focus on the direct 1,4-addition reactions. It is known that 1,4-adducts are usually thermodynamically more stable than the 1,2-adducts, and thus the 1,2-adducts could be transformed to 1,4-adducts especially when the 1,2-addition reaction is reversible [9][19]. The isomerization of 1,2- to 1,4-adducts in aldol reaction of enones to ketones has been reported previously [19]. In this article, we discuss the reversibility of the 1,2-addition in nucleophilic fluoroalkylation of α,β-enones and α,β-enals with α-fluorinated sulfones and the isomerization of 1,2- to 1,4-adducts at different temperatures (*Scheme 2*).

Scheme 2. *Proposed Conversion of 1,2- to 1,4-Adducts*

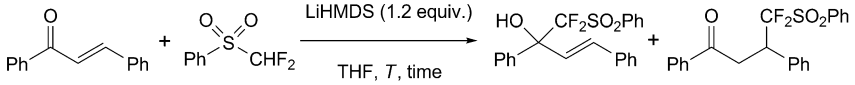


Results and Discussion. – Sulfur stabilization plays an important role in selective nucleophilic di- and monofluoromethylation, and by this strategy, CF_2H and CH_2F have been introduced in various electrophiles containing C–X (X = leaving groups), C=O, C=N, C=C, and C≡C bonds [3–7]. Among various S-based fluoroalkylation reagents, α-fluorinated sulfones represent the ideal reagents due to the versatile transformation of the sulfone functionality [3][4]. In recent years, with the aid of sulfonyl substituent, fluoroalkylation of α,β-enones and α,β-enals with bis(benzene-

sulfonyl)fluoromethane ($(PhSO_2)_2CHF$; **1**) in 1,4-addition manner has been achieved by us and others [16][17][20–22]. We also examined the nucleophilic fluoroalkylation of chalcones with difluoromethyl phenyl sulfone ($PhSO_2CF_2H$; **2**) and fluoromethyl phenyl sulfone ($PhSO_2CH_2F$; **3**), and, in all cases, the full control of C(3) regioselectivity was difficult to achieve [16]. However, by comparing the fluoroalkylation of a series of chalcones, it was found that the reaction with $PhSO_2CF_2H$ (**2**) favored 1,2-adducts, while the reaction with $PhSO_2CH_2F$ preferred the 1,4-adducts. This indicates that the number of F-substituents affects the hard/soft nature of the carbanions [3][4][16]. According to the product ratios 1,4-/1,2-adduct, the order of softness of α-fluoro carbanions was repored *approximately* as: $(PhSO_2)_2CF^- > PhSO_2CHF^- > PhSO_2CF_2^-$ [16].

For a better understanding of the reaction, we carried out a further study of the nucleophilic addition of $PhSO_2CF_2H$ (**2**) and $PhSO_2CH_2F$ (**3**) to chalcone (=(*E*)-1,3-diphenylprop-2-en-1-one; **4**) at different temperatures. Lithium hexamethyldisilazide (LiHMDS) was chosen as the base with THF as the solvent, and no additive was used. The results for the reaction between $PhSO_2CF_2H$ (**2**) and chalcone **4** are compiled in *Table 1*. When the reaction was conducted at $-78°$ and quenched after 30 min, 1,2- and 1,4-adducts were obtained in 90% total yield with a 81:19 ratio (*Entry 1*). Prolonged reaction time (8 h) did not influence the product ratio and overall yield (*Entry 2*). It is interesting to observe that the product ratio was also not significantly affected by increasing the temperature (-50 to $0°$), albeit the total yield decreased (*Entries 3*, *5*, and *7*). Moreover, at a given temperature (-50, -25, or $0°$), the total yield did not change much over time (*Entries 4*, *6*, and *8*).

Table 1. *Reaction of $PhSO_2CHF_2$* (**2**) *with (*E*)-Chalcone* (**4**)



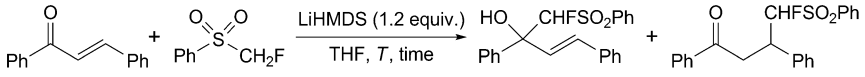
4 (1 equiv.) **2** (1 equiv.) **5** **6**

Entry	*T* [°]	Time [h]	Ratio **5**/**6**[a])	Total yield [%] **5** + **6**[a])
1	−78	0.5	81:19	90 (73 + 17)
2	−78	8	82:18	90 (74 + 16)
3	−50	0.5	81:19	72 (58 + 14)
4	−50	8	81:19	74 (60 + 14)
5	−25	0.5	83:17	46 (38 + 8)
6	−25	7	85:15	44 (37 + 7)
7	0	0.5	83:17	24 (20 + 4)
8	0	7	80:20	20 (16 + 4)
9	r.t.	0.5	67:33	6 (4 + 2)
10	r.t.	7	n.d.[b])	trace

[a]) The ratios and yields were determined by ^{19}F-NMR with $PhCF_3$ as an internal standard. [b]) n.d. = Not determined.

The results for the reaction between $PhSO_2CH_2F$ (**3**) and chalcone **4** are collected in *Table 2*. When the reaction was conducted at $-78°$ and quenched after 0.1 h, 1,2- and

Table 2. *Reaction of $PhSO_2CH_2F$* (**3**) *with (*E*)-Chalcone* (**4**)



4 (1 equiv.) **3** (1 equiv.) **7** **8**

Entry	*T* [°]	Time [h]	Ratio of **7**/**8**[a])	Total yield [%] **7** + **8**[a])
1	– 78	0.1	43 : 57	96 (41 + 55)
2	– 78	0.5	42 : 58	96 (40 + 56)
3	– 78	7	43 : 57	96 (41 + 55)
4	– 50	0.5	52 : 48	97 (50 + 47)
5	– 50	7	54 : 46	97 (52 + 45)
6	– 25	0.5	64 : 36	96 (61 + 35)
7	– 25	7	64 : 36	97 (62 + 35)
8	0	0.5	71 : 29	94 (67 + 27)
9	0	7	70 : 30	90 (63 + 27)
10	r.t.	0.5	71 : 29	94 (67 + 27)
11	r.t.	7	15 : 85	39 (6 + 33)

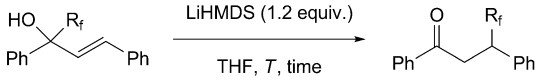
[a]) The ratios and yields were determined by ^{19}F-NMR with $PhCF_3$ as an internal standard.

1,4-adducts were obtained in 96% total yield with a 43 : 57 ratio (*Entry 1*). Similar to the reaction with $PhSO_2CF_2H$ (**2**), prolonged reaction time (0.5 or 7 h) did not significantly influence the product ratio and overall yield (*Entries 2* and *3*). At the temperatures tested (– 50, – 25, and 0°), the total yield and product ratio did not change over time (*Entries 5*, *7*, and *9*). Different from the reaction with $PhSO_2CF_2H$, the product ratio of this reaction was temperature-dependent, and the yield of 1,2-adduct increased gradually with the elevation of temperature (*Entries 2*, *4*, *6*, and *8*). When the reaction was performed at r.t., due to the relative higher stability of $PhSO_2CHFLi$ compared to that of $PhSO_2CF_2Li$, $PhSO_2CHFLi$ could react with **1** smoothly to give the 1,2- and 1,4-adducts in 94% total yield with a 71 : 29 ratio (*Entry 10*). However, at this temperature, the 1,2-adduct gradually decomposed over time, and, therefore, only a small amount of 1,2-adduct isomerized into the 1,4-adduct (*Entry 11*).

The data compiled in *Tables 1* and *2* indicate that the nucleophilic fluoroalkylation of chalcone **4** with $PhSO_2CF_2Li$ and $PhSO_2CHFLi$ is kinetically controlled, and both the lithium alcoholate (1,2-adduct) and the lithium enolate (1,4-adduct) are stable at temperatures below 0°. Therefore, the product ratios can reflect the relative rates of the 1,2- and 1,4-addition reactions. These data also suggest that the 1,4-addition reaction between $PhSO_2CH_2F$ and **4** is kinetically more favored than that between $PhSO_2CF_2H$ and **4**.

To get more insights into the reversibility of the 1,2-addition reaction and the kinetic preference of the formation of the 1,4-adducts, we examined the isomerization of the 1,2-adducts **5**, **7**, and **9** under basic conditions (*Table 3*). When alcohol **5** was treated with 1.2 equiv. of LiHMDS at – 78°, and the reaction mixture was stirred at the same temperature for 12 h, no 1,4-adduct **6** was detected by ^{19}F-NMR spectroscopy after quenching the reaction with saturated aqueous solution of NH_4Cl (*Entry 1*). Similar results were obtained for alcohols **7** and **9** (*Entries 2 and 3*). It is worthy of

Table 3. *Conversion of 1,2-Adducts to 1,4-Adducts*



5, **7**, and **9** → **6**, **8**, and **10**

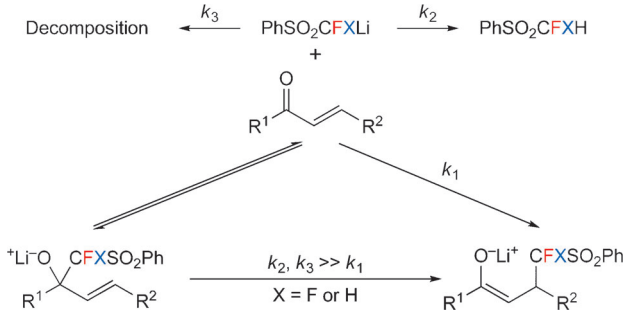
Entry	R_f	*T* [°]	Time [h]	Conversion [%][a])	Yield [%][a])[b])
1	$PhSO_2CF_2$	−78	12	**5**: <1	**6**: 0
2	$PhSO_2CHF$	−78	10	**7**: <1	**8**: 0
3	CF_3	−78	10	**9**: <1	**10**: 0
4	$PhSO_2CF_2$	r.t.	8	**5**: >99	**6**: 0 (**2**: 60)
5	$PhSO_2CHF$	r.t.	10	**7**: >99	**8**: 9 (**3**: 73)
6	CF_3	r.t.	11	**9**: <1	**10**: 0

[a]) The conversion and yields were determined by ^{19}F-NMR using $PhCF_3$ as an internal standard. [b]) Yields of R_f–H were given in parentheses.

noting that the diastereomer ratio (4.3:1) of **7** was maintained during the reaction. These results suggest that the 1,2- adducts **5**, **7**, and **9** are relatively stable at −78°, and the *retro*-1,2-addition can hardly take place under the above conditions.

Subsequently, we carried out the reactions under conditions such that the *retro*-1,2-addition is favored (*Table 3*, *Entries 4–6*). After the addition of 1.2 equiv. of LiHMDS to the THF solution of **5** at −78°, the solution was allowed to warm to room temperature and stirred for 8 h. Although the 1,2-adduct **5** was consumed completely, no 1,4-adduct **6** was detected (only **2** was formed in 60% yield; *Entry 4*). When 1,2-adduct **7** was used as a substrate, 1,4-adduct **8** was obtained in only 9 % yield (*Entry 5*), which is much lower than the kinetically controlled formation of **8** (27% yield, see *Table 2*, *Entry 10*). These results demonstrate that, in our cases, although the 1,4-adduct is thermodynamically more stable than the 1,2-adduct, the *retro*-1,2-addition reaction results in the protonation and partial decomposition of the fluoroalkyl anions rather than their 1,4-addition to chalcones under such conditions (*Scheme 3*). As a result, it is difficult to isomerize the fluoroalkylated 1,2-adduct **5** and **7** to the 1,4-adducts **6** and **8**, respectively, under thermodynamically controlled conditions. Different from **5** and **7**,

Scheme 3. *Possible Competive Pathways That Influence the Formation of 1,4-Adduct under Thermodynamically Controlled Conditions*

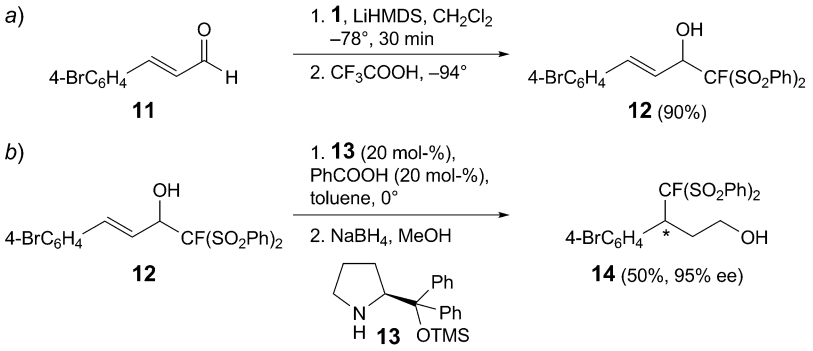


compound **9** is stable even at room temperature, and its *retro*-1,2-addition was not observed (*Entry 6*).

Based on aforementioned results and discussion, a successful isomerization of 1,2- to 1,4-adduct should fulfill two prerequisites: one is the reversibility of the 1,2-addition, the other is the stability of the fluoroalkyl anion. To the best of our knowledge, there has been no report on the effective conversion of 1,2-adduct, which was generated by the reaction of an α,β-unsaturated carbonyl compound with an α-fluoro carbanion, to 1,4-adduct. In 2011, we reported a successful addition reaction of $(PhSO_2)_2CHF$ (**1**) with an aldehyde at $-94°$ promoted by Li–O interaction, which was previously assumed to be unattainable [23][24]. The reaction was proved to be general, and only the kinetically controlled 1,2-adduct was observed in the case of (*E*)-cinnamaldehyde [23]. The excellent 1,2-addition selectivity probably results from the higher reactivity and the less steric hindrance of the α-C-atom. In 2009, *Rios* and co-workers, *Cordova* and co-workers, and *Wang* and co-workers independently reported the catalytic enantioselective conjugate addition of **1** to α,β-unsaturated aldehydes [20–22]. Based on the above achievements of us and others, we envisioned that the 1,2-adduct of $(PhSO_2)_2CHF$ (**1**) with an α,β-unsaturated aldehyde might be converted to 1,4-adduct under the activation of an organocatalyst.

The 1,2-adduct **12** was synthesized from **1** and aldehyde **11** in 90% yield according to the procedure described in [23] (*Scheme 4,a*). It was found that, with **13** as a catalyst, PhCOOH as an additive, and toluene as a solvent, **12** could be successfully isomerized to the 1,4-adduct in a moderate yield (50%) and excellent enantiomeric excess (95% ee) after the reduction with $NaBH_4$ (*Scheme 4,b*).

Scheme 4. *Synthesis of Alcohol* **12** *and Its Isomerization to* **14**



Conclusions. – In summary, an investigation of the reactions of $PhSO_2CF_2H$ (**2**) and $PhSO_2CH_2F$ (**3**) with (*E*)-chalcone (**4**) at low temperatures revealed that these two reactions were kinetically controlled, and the ratios of 1,2- *vs.* 1,4-adducts at these temperatures did not change much over time. The controlled experiments of converting the isolated $PhSO_2CF_2$- and $PhSO_2CHF$-substituted 1,2-adducts to 1,4-adducts showed that the relatively low thermal stability and/or hard/soft nature of α-fluoro carbanions, such as $PhSO_2CF_2^-$ and $PhSO_2CHF^-$, hampered the formation of the thermodynamically more favorable 1,4-adducts *via* reversible 1,2-additions under thermodynamically

controlled conditions. Eventually, taking advantage of the remarkable stability and softness of $(PhSO_2)_2CF^-$ anion, an efficient and thermodynamically controlled isomerization of $(PhSO_2)_2CF$-substituted 1,2-adduct to 1,4-adduct was achieved for the first time.

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Experimental Part

General. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Toluene, THF, and CH_2Cl_2 were distilled over Na. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra: *Bruker AM300*, *DPX-400*, or *Avance-500*; ^{1}H-NMR chemical shifts were determined relative to internal TMS (δ(H) 0.0 ppm) or to the signal of a residual protonated solvent ($CDCl_3$ δ(H) 7.26 ppm); ^{13}C-NMR chemical shifts were determined relative to internal TMS (δ(C) 0.0 ppm), and ^{19}F-NMR chemical shifts were determined relative to $CFCl_3$ (δ(F) 0.0 ppm) or $PhCF_3$ (δ(F) -63.7 ppm). MS: *Ionspec 4.7 T* mass spectrometer. HR-ESI-MS: *FTMS-7* mass spectrometer.

Reactions of Difluoromethyl Phenyl Sulfone (**2**) *and Fluoromethyl Phenyl Sulfone* (**3**) *with* (E)*-Chalcone* (=*(2*E*)-1,3-Diphenylprop-2-en-1-one*; **4**). *General Procedure.* Under N_2, to a stirred mixture of **2** or **3** (0.5 mmol), and **4** (0.5 mmol) in dry THF (2.5 ml) at temps. as indicated in *Tables 1* and *2*, was added lithium hexamethyldisilazide (LiHMDS; 1.0M in THF, 0.6 ml, 0.6 mmol). After the corresponding reaction time, the reaction was quenched by an adding excess amount of sat. aq. soln. of NH_4Cl (1 ml). The org. layer was subjected to ^{19}F-NMR analysis with $PhCF_3$ as an internal standard, and the yield of the products were calculated from the ^{19}F-NMR integrals.

*(3*E*)-1,1-Difluoro-2,4-diphenyl-1-(phenylsulfonyl)but-3-en-2-ol* (**5**). ^{19}F-NMR (282 MHz, THF): -104.3 (*d*, *J* = 239, 1 F); -106.3 (*d*, *J* = 239, 1 F).

4,4-Difluoro-1,3-diphenyl-4-(phenylsulfonyl)butan-1-one (**6**). ^{19}F-NMR (282 MHz, THF): -99.3 (*dd*, *J* = 233, 11.4, 1 F); -106.0 (*dd*, *J* = 233, 22.7, 1 F).

*(3*E*)-1-Fluoro-2,4-diphenyl-1-(phenylsulfonyl)but-3-en-2-ol* (**7**). ^{19}F-NMR (282 MHz, THF): -179.9 (*d*, *J* = 44, 1 F, isomer 1); -181.9 (*d*, *J* = 44, 1 F, isomer 2).

4-Fluoro-1,3-diphenyl-4-(phenylsulfonyl)butan-1-one (**8**). ^{19}F-NMR (282 MHz, THF): -180.3 (*dd*, *J* = 48, 18, 1 F, minor isomer); -185.6 (*dd*, *J* = 48, 28, 1 F, major isomer).

1,2-Addition of Bis(benzenesulfonyl)fluoromethane (=*1,1′-[(Fluoromethanediyl)disulfonyl]dibenzene*; **1**) *to* (E)*-3-(4-Bromophenyl)acrylaldehyde* (=*(2*E*)-3-(4-Bromophenyl)prop-2-enal*; **11**) *for the Syntheses of Alcohol* **12**. Under N_2, to a stirred mixture of **1** (157 mg, 0.5 mmol) and **11** (158 mg, 0.75 mmol) in dry CH_2Cl_2 (5 ml) at $-78°$ was added LiHMDS (1.0M in THF, 0.6 ml, 0.6 mmol). After 0.5 h, the reaction was quenched by adding excess amount of TFA (1 ml) at $-94°$, followed by extraction of the mixture with CH_2Cl_2 and H_2O. The org. layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was subjected to CC (SiO_2 (acidified with 1% TFA in petroleum ether before use)) to give product **12** (236 mg, 90%).

*Data of (3*E*)-4-(4-Bromophenyl)-1-fluoro-1,1-bis(phenylsulfonyl)but-3-en-2-ol* (**12**). IR (film): 3514, 3063, 1584, 1487, 1448, 1349, 1168, 1136, 1077, 998, 978, 849, 800, 708. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01 (*d*, *J* = 7.6, 2 H); 7.89 (*d*, *J* = 7.7, 2 H); 7.74 (*d*, *J* = 7.4, 1 H); 7.69–7.54 (*m*, 3 H); 7.49–7.40 (*m*, 4 H); 7.09 (*d*, *J* = 8.3, 2 H); 6.53 (*d*, *J* = 15.9, 1 H); 6.06 (*dd*, *J* = 15.9, 5.1, 1 H); 5.01 (*s*, 1 H); 3.61 (*s*, 1 H). ^{19}F-NMR (282 MHz, $CDCl_3$): -137.67 (*s*). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.2; 135.6; 135.5; 135.0; 134.7; 132.7; 131.7; 131.2; 129.1; 129.0; 128.4; 122.8; 122.2; 112.1 (*d*, *J* = 273.5); 72.2 (*d*, *J* = 21.3). MALDI-MS: 547 ($[M+Na]^+$). HR-ESI-MS: 546.9664 ($[M+Na]^+$, $C_{22}H_{18}BrFNaO_5S_2^+$; calc. 546.9661).

Isomerization of 1,2-Addition Product **12** *to 1,4-Addition Product* **14**. Under N_2, **12** (131 mg, 0.25 mmol) and *(2*S*)-2-{diphenyl[(trimethylsilyl)oxy]methyl}pyrrolidine* (**13**; 16 mg, 0.05 mmol) were dissolved in dry toluene (0.8 ml), and then PhCOOH (6 mg, 0.05 mmol) was added to the mixture. The soln. was stirred at 0° for 90 h. The mixture was then directly purified by CC (SiO_2) to give a mixture of **1** and **14**. The mixture was dissolved in MeOH (2 ml), and then the soln. was cooled to 0°. $NaBH_4$ (72 mg,

1.9 mmol) was added in three portions, and the resulting mixture was stirred at 0° for 60 min. After the addition of H_2O (2 ml), the mixture was extracted with Et_2O (15 ml × 3). The combined org. layers were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by CC (SiO_2; petroleum ether/AcOEt 5:1) to give **14** (63 mg, 50 % yield).

Data of 3-(4-Bromophenyl)-4-fluoro-4,4-bis(phenylsulfonyl)butan-1-ol (**14**) [21]. ee 95% (*SINO-AD*; 4.6 mm × 250 mm), hexanes/IPA 50:50, 1.0 ml/min, λ 214 nm, t_R (major) 7.27 min, t_R (minor) 11.33 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.86 (*d*, *J* = 7.5, 2 H); 7.79 (*d*, *J* = 7.7, 2 H); 7.73 (*d*, *J* = 7.5, 1 H); 7.65 (*t*, *J* = 7.5, 1 H); 7.55 (*t*, *J* = 7.8, 2 H); 7.46 (*t*, *J* = 7.8, 2 H); 7.32 (*d*, *J* = 8.5, 2 H); 6.94 (*d*, *J* = 8.3, 2 H); 4.18 (*d*, *J* = 11.5, 1 H); 3.80 (*s*, 1 H); 3.29–3.21 (*m*, 1 H); 3.11–2.97 (*m*, 1 H); 2.75 (*t*, *J* = 13.0, 1 H). The ^{1}H-NMR data are consistent with those given in [21].

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