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Anionic 5-*endo-trig* Cyclization of Terminally Difluorinated Homoallylic Alkoxides

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The anionic 5-*endo-trig* cyclization, a disfavored process according to the well-accepted Baldwin's rules, was facilitated by the introduction of two fluorine atoms at the terminal carbon atom. Extensive ab initio calculations of the reaction paths both by Gaussian 94 and Mulliken successfully revealed the role of two fluorine atoms as a stabilization of both transition states and product by their strong electronegative character.

Introduction

Cyclization of organic materials has been recognized as one of the most important class of reactions and thus intensively investigated thus far. More than 20 years ago, Baldwin proposed[1a] the generalized rules on the intramolecular cyclization, and he especially explained the 5-*endo-trig* mode as being "a disfavored ring closure" in a separate article.[1b] This argument was based on the fact that the nucleophilic site or center cannot be located properly at the required position in an intramolecular manner without severe distortion. Since then, exceptional examples of 5-*endo-trig* cyclization via radical species have been disclosed[2] and theoretically studied in detail,[3] while the corresponding anionic version is extremely rare in the literature.[4,5]

One of the most interesting results has been described by Ichikawa and co-workers on the cyclization of 2-(1,1-difluorohex-1-en-2-yl)phenol (**1**) by way of its alkoxide, smoothly converted to the corresponding benzofurane **2** in 80% yield through addition−elimination mechanism.[4a] During the course of our recent research on the preparation of fluorinated aldol structures using D-glucose as the chiral template,[6] we have also encountered an interesting cyclization of **3** as shown in Scheme 2, which might be explained as the result of the intramolecular attack of oxygen at the 6 position activated by fluoride.[7] Although we do not have any definite mechanistic proof for the present reaction proceeding in a 5-*endo-trig* mode, in connection with the above report by Ichikawa, our interest was focused on this special "disfavored" cyclization mode. Then, we planned to perform extensive ab initio calculations on the model cyclization of alkoxide **6b** (derived from 4,4-difluorobut-3-en-1-ol) to investigate the course of this interesting 5-*endo-trig* reaction (**6b** → **7b** → **8b** → **9b** → **10b**) as well as the possibly competing 4-*exo-trig* cyclization (**6b** → **12b** → **13b** → **14b** → **15b**) in detail (Figure 1). Moreover, the corresponding nonfluorinated materials (series **a** of **6**−**11**) were similarly subjected to calculation for gaining clearer understanding of the role of fluorine in this pathway.

Computational Methods

All structures were fully optimized with the ab initio software Mulliken implemented in CAChe Worksystem (SONY/Tektronix Corporation) on an IBM RS-6000-3CT workstation at the HF/6-31G* level of theory. Energy minima and saddle points were confirmed by vibrational frequency analysis furnishing the all positive and only one imaginary frequencies, respectively. Furthermore, single-point calculations (MP2/6-31+G*) were performed by using the conformations obtained by the HF/6-31G* basis set.

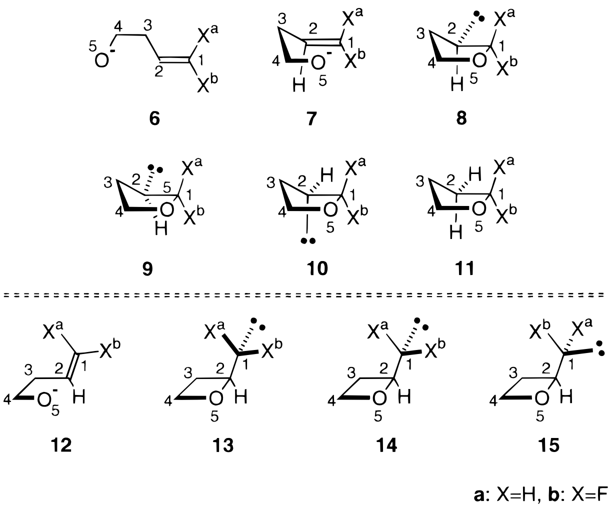
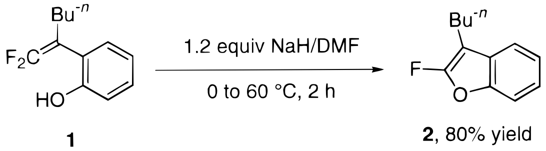


Figure 1. Calculated structures.

SCHEME 1



SCHEME 2

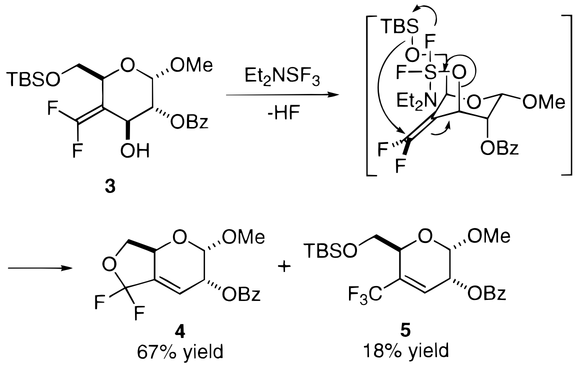


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TABLE 1: Calculated Energy Differences

	energy difference (ΔE, kcal/mol)	
	Gaussian 94[a,b]	Mulliken[b,c]
6a	0.00 (0.00)	0.00 (0.00)
7a	35.79 (20.61)	34.40 (20.78)
8a	25.12 (19.27)	23.57 (21.44)
9a	36.48 (28.31)	37.34 (31.85)
10a	29.41 (24.86)	28.00 (27.64)
6b	0.00 (0.00) [0.00]	0.00 (0.00) [0.00]
7b	21.48 (8.29) [−14.31]	17.68 (8.70) [−16.72]
8b	−6.89 (−8.11) [−32.01]	−7.47 (−7.41) [−31.04]
9b	−3.92 (−7.42) [−40.40]	−6.70 (−7.29) [−44.04]
10b	−8.80 (−10.33) [−38.21]	−11.55 (−9.98) [−39.55]
12b	35.22 (26.23)	35.22 (23.41)
13b	23.93 (24.57)	24.80 (20.92)
14b	34.45 (35.79)	34.74 (31.93)
15b	24.67 (25.91)	24.16 (20.92)

[a] Calculated at the HF/6-311++G** (MP2/6-311++G**//HF/6-311++G**) level of theory. [b] In the bracket was shown $\Delta\Delta E$ ($=\Delta E_{\mathbf{b}\text{-series}} - \Delta E_{\mathbf{a}\text{ series}}$) in kcal/mol. [c] Calculated at the HF/6-31G* (MP2/6-31+G*//HF/6-31G*) level of theory.

The stationary points thus obtained were reoptimized by Gaussian 94[8] on a CRAY C916/12256 supercomputer at Tokyo Institute of Technology computer center at the HF/6-311++G** level of theory, and their confirmation was carried out similarly along with the natural bond orbital analysis.[9] Zero-point vibrational energies (ZPVEs) were also determined through the vibrational frequency analysis, and single-point calculations (MP2/6-311++G**//HF/6-311++G**) were performed in a similar manner.

Conformers thus obtained were visualized by using software Chem3D Pro version 4.0 purchased from Cambridge Software Corporation.

Results and Discussions

Table 1 summarizes the energy differences between the most stable substrates **6** and the transition states (TSs) for cyclization **7** or the final products **10** of 5-*endo-trig* processes for the both non- (**a**) and difluorinated (**b**) series by Gaussian 94 at the HF/6-311++G** level of theory as well as by Mulliken at the HF/6-31G* level of theory. Compound **9** expresses the TSs on the ring conformation change along the reaction coordinate from the intermediates **8** to the final products **10**. The protonated (neutral) material **11** was also calculated for comparison. The possibly competing 4-*exo-trig* reaction pathways were evaluated and the ring formation TS **12b**, the intermediate **13b**, the rotational TS of a CF_2^- group **14b**, and the final product **15b** are shown in the same table for the difluorinated materials. On the other hand, despite the extensive calculation of nonfluorinated 4-*exo-trig* series, we could not locate any conformers from **12a** to **15a** by any computational means tried.

In Table 2 are shown such representative physical properties as NBO charges, bond lengths, bond angles, and dihedral angles by Gaussian 94. The same parameters obtained by Mulliken software as well as detailed energetic data by both softwares are included as Supporting Information.

As summarized in Table 1, from the energetic point of view, cyclization of the nonfluorinated series **a** was found to require an activation energy of 35.8 [34.4] kcal/mol when the calculation was carried out by Gaussian 94 [Mulliken] at the HF/6-311++G** [HF/6-31G*] level of theory, respectively. Further computation indicated that the following inversion at C^2 was not likely to proceed in a smooth manner because both the TS **9a** and the final product **10a** were energetically less favorable than the first TS **7a** and the intermediate **8a**, respectively. This result in regard to the 5-*endo-trig* process, as well as the fact that the corresponding conformers along the 4-*exo-trig* pathway were not obtained, allowed us to conclude that neither path was favorable for the nonfluorinated substrates in the absence of any additional factors.[4b,d,e]

On the other hand, the situation was drastically altered by the entry of two fluorine atoms. Thus, the substrate **6b** passed through the 14.3 kcal/mol lower energy barrier (see $\Delta\Delta E$ values denoted with brackets in Table 1) than the nonfluorinated case to reach to the intermediate **8b**, approximately 7 kcal/mol more stable than the starting material **6b**. Moreover, flip at the C^2 anionic center occurred by way of the TS **9b** with a shallow barrier of only about 3 kcal/mol (Gaussian) or even less than 1 kcal/mol (Mulliken), and the final product was obtained as the global minimum along the reaction coordinate (8.8 or 11.6 kcal/mol energetically preferred to **6b** by Gaussian or Mulliken, respectively). It is worthwhile noting that fluorine introduction gave rise to the enormous stabilization for conformers **8b** to **10b** in a range of 31−44 kcal/mol ($\Delta\Delta E$) when compared to the nonfluorinated system **a**, which, in addition to the electrostatic effect discussed below, is mainly attributed to the hybridization change of the fluorine-attached carbon atom from the thermodynamically less stable sp^2 to the energetically more favorable saturated sp^3 type.[10]

TABLE 2: Representative Physical Properties Obtained by Gaussian 94 (HF/6-311++G)**

	charge[a]			bond length (Å)				bond angle (deg)	dihedral angle (deg)
	C^1	C^2	O^5	C^1-C^2	C^1-X^a	C^1-X^b	C^1-O^5	$O^5-C^1-C^2$	$X^a-C^1-C^2-H^2$
6a	−0.467	−0.065	−1.047	1.3269	1.0799	1.0788			179.0
7a	−0.028	−0.597	−0.899	1.3911	1.0767	1.0804	1.8955	100.5	174.9
8a	0.018	−0.738	−0.731	1.5028	1.0934	1.0886	1.4650	108.8	162.6
9a	0.050	−0.794	−0.715	1.4785	1.1109	1.0922	1.4482	105.4	94.8
10a	0.056	−0.753	−0.704	1.5195	1.1114	1.0896	1.4313	106.0	37.7
11a	0.067	−0.364	−0.665	1.5272	1.0879	1.0838	1.4093	106.0	33.9 (154.9)
6b	0.794	−0.291	−1.047	1.3005	1.3201	1.3226			180.0
7b	1.074	−0.620	−0.948	1.3492	1.3105	1.3082	2.0488	96.2	169.6
8b	1.080	−0.784	−0.694	1.4826	1.3689	1.3659	1.3829	111.3	136.5
9b	1.067	−0.794	−0.682	1.4296	1.3940	1.3928	1.3742	108.8	73.8
10b	1.075	−0.775	−0.684	1.4659	1.4000	1.3628	1.3693	109.5	30.9
11b	1.111	−0.405	−0.648	1.5168	1.3417	1.3311	1.3485	108.2	30.5 (150.5)
12b	0.434	0.036	−0.874	1.3907	1.3697	1.3728	1.8221[b]	124.4[c]	47.3[d]
13b	0.278	0.102	−0.696	1.5031	1.4248	1.4177	1.4609[b]	119.6[c]	59.4[d]
14b	0.263	0.122	−0.676	1.5603	1.4398	1.4060	1.4476[b]	118.2[c]	−3.2[d]
15b	0.278	0.102	−0.696	1.5178	1.4404	1.4282	1.4399[b]	113.5[c]	−68.2[d]

[a] Charges obtained by natural bond orbital analysis. [b] The corresponding C^2-O^5 distance. [c] The corresponding $O^5-C^2-C^1$ angle. [d] The corresponding $X^a-C^1-C^2-C^3$ angle.

As already pointed out, the possibly competing 4-*exo-trig* process was computationally accessible only for the difluorinated series **b**, but the energy profile obtained proved that this process was considerably energy demanding than the corresponding 5-*endo-trig* pathway. The transition state **12b** was 13.7 [17.5] kcal/mol higher in energy than **7b**, and the difference proved to be more pronounced when conformers after cyclization were compared (30.8−38.4 [32.3−41.4] kcal/mol by Gaussian [Mulliken]). Such energetic contrast would stem from the destabilizing electronic interaction of carbanion with fluorine lone pair at the C^1 atom in **13b**−**15b** as well as from the situation that the ring oxygen is inevitably exposed to ample electron density of fluorine or carbanion no matter how the C^1−C^2 bond is rotated.

The inclusion of electron correlation (MP2) resulted in the effective stabilization of **8a** to **10a** relative to **6a** (up to 8.2 kcal/mol), but only a little variation was noticed for the corresponding difluorinated species **8b**−**10b** (up to 3.5 kcal/mol). The most remarkable effect was found for the TS energies for ring formations to lower the energy barrier of 5-*endo-trig* cyclization at **7** to 15.2 (series **a**) and 8.3 (series **b**) kcal/mol or of 4-*exo-trig* process at **12b** to 26.2 kcal/mol.

On the basis of these energetic data, it has been clearly demonstrated that although the anionic 5-*endo-trig* cyclization should not be an easy process in general based on the original concept by Baldwin, this is not the case for the terminally difluorinated compounds, and because of the lower activation energy and formation of the more stable final product, the conversion of **6b** to **10b** is expected to occur in a more feasible fashion than the nonfluorinated case both from the thermodynamic and kinetic points of view.

Close examination of physical property changes disclosed one sharp difference in charge at C^1 during the course of **6**→**7**. As shown in Table 2, the reaction sites C^1 and O^5 in **6a** with the charges of −0.467 and −1.047, respectively, approached each other and the electron density at the former carbon has kept decreasing until the energy maximum **7a**, where C^1 was still weakly anionic (−0.028). On the other hand, the carbon−carbon double bond of **6b** was intrinsically highly polarized to render the C^1 terminus with two fluorine atoms charged in a strongly positive manner (*about +0.8 for the neutral carbon atom*). As the reaction proceeded to the direction of the TS **7b**, the charge separation between the two reaction centers C^1 and O^5 became maximized to such an extent as if they were a pair of "usual" cation and anion. Considering the fact that the Coulombic attraction is proportional to the product of two charges and inversely proportional to the square of their distance, it is not difficult to reach to assumption that the TS **7b** should be in a much earlier stage than the corresponding nonfluorinated TS **7a**. This is actually the case, and the interesting C^1−O^5 atom distance variation (**7b**→**8b**) and the C^1−C^2 bond elongation (**6b**→**7b**) of 0.666 and 0.049 Å, respectively (0.431 and 0.064 Å for the series **a**), apparently supported our hypothesis. 6-31G* calculation by Mulliken anticipated further earlier conditions for both TSs **7** judging from the following values: ΔC^1−O^5 of 0.442 (**7a**) and 0.687 (**7b**) Å and ΔC^1−C^2 of 0.060 (**7a**) and 0.044 (**7b**) Å. The C^1 atom was constantly charged like the usual cation along the reaction coordinate (except for the starting material **6b**, but as described above, the calculated NBO charge is +0.80 at this stage), in quite a sharp contrast to the case of the nonfluorinated counterparts with the virtually neutral C^1 site. In consequence, the early TS **7b** successfully reduces the unfavorable steric interaction as well as the distortion arising from the 13° deviation from the ideal O^5−C^1−C^2 angle of 109° proposed by Baldwin. Thus, such strong electrostatic attraction is concluded as being one of the major factors responsible for effective reduction of the activation energy, leading to the 14−17 kcal/mol energy barrier difference at the TS **7** between series **a** and **b**.

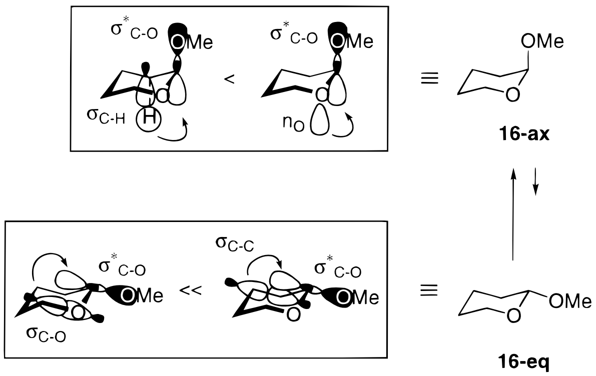
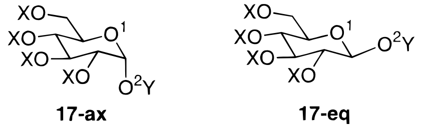


Figure 2. Anomeric Effect.



X: H, Y: Me $r_{O\ 2\text{-}C}$=0.032 Å, $r_{O1\text{-}C}$ =-0.019 Å

X: H, Y: Ph $r_{O2\text{-}C}$ =0.025 Å, $r_{O1\text{-}C}$ =-0.027 Å

X: Ac, Y: Ac $r_{O2\text{-}C}$ =0.023 Å, $r_{O1\text{-}C}$ =-0.023 Å

$r=r_{ax}-r_{eq}$

Figure 3. The representative bond length differences of glucose derivatives.

In every instance C^1−C^2 bonds are longer, but the C^1−O^5 distances are shorter in series **a** than series **b** by up to 0.05 and 0.08 Å, respectively, whose tendency was conveniently elucidated by the well-documented anomeric effect.[11,12] 2-Methoxytetrahydropyran is the representative example whose conformational equilibrium was reported to prefer **16-ax** to **16-eq**, although the ratio is highly dependent on the solvent employed for measurement (Figure 2).[13] Despite the axially disposed methoxy group in the former isomer exerting the more repulsive steric interaction, advantageous orbital interaction of the lower lying σ^*_{C-O} orbital with the adjacent electron-donating n_O, σ_{C-H}, or σ_{C-C} orbitals affected the not overwhelming but clear conformational preference. Taking the electron-donating ability in the order of $n_O > \sigma_{C-H} > \sigma_{C-C} \gg \sigma_{C-O}$ into account,[14] the orbital overlap between σ^*_{C-O} and n_O as well as σ_{C-H} in **16-ax** was expected to be more effective than the case of **16-eq**. As a result, the stronger such electrostatic interaction is, the longer and shorter the Me*O*−*C* and ring C−O bonds become by accepting and releasing electrons, respectively. This type of trend can be found in the crystallographically analyzed glucose derivatives.[15] As depicted in Figure 3, it is explicitly observed that **17-ax** showed 0.02−0.03 Å elongation of the O^2−C bond as well as up to 0.027 Å decrease in the O^1−C bond length when compared with these bond lengths of the isomeric **17-eq**.[16]

With this basic information on the anomeric effect hand,[17] the intermediates **8** were compared with the final products **10** in detail. Because the anion is the most powerful electron donor of all orbitals considered here,[11b] the occupied n_C orbital at C^2 in **8** would strongly interact with the empty σ^* orbital of the newly formed C^1−O bond, while the favorable $n_C\text{-}\cdots\sigma^*_{C-F}$a overlap would be observed in **10b**. Because of the lower energy

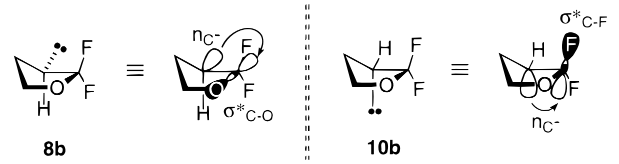


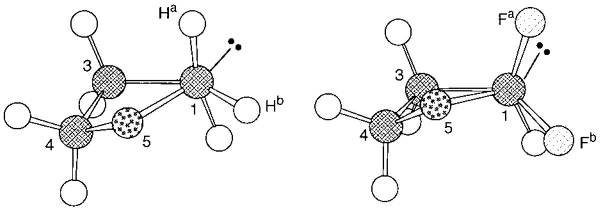
Figure 4. Extended anomeric effect in **8b** and **10b**.

level of the σ^*_{C-F} orbital than the one of the σ^*_{C-O} orbital, **10b** should be electrostatically more stabilized than **8b** (Figure 4). This phenomenon led to not only the decrease in the C^1-C^2 bond length of **10b** by about 0.017 Å, but the significant $C-F^a$ bond elongation of 0.037 or 0.058 Å, in comparison with the $C-F^b$ bond in **10b** or the $C-F^a$ bond in the neutral material (**11b**), respectively (Table 2). However, on the contrary to the case of difluorinated materials, the intermediate **8a** is approximately 4 kcal/mol more stable than the final product **10a**. This discrepancy is attributable to the smaller energy gap between n_{C^-} and σ^*_{C-O} in **8a** than that in the case of n_{C^-} and σ^*_{C-H} in **10a**, the former enhancing the attractive interaction and resulting in 0.17 Å reduction of the C^1-C^2 bond length.

The similar trend was also detected for the 4-*exo-trig* cyclization of difluorinated materials. Thus, the C^2-O^5 bond in **13b** and the C^2-C^3 bond in **15b** bisected the $F^a-C^1-F^b$ angles ($C^2-O^5-C^1-F^a$: 46.0°. $C^2-O^5-C^1-F^b$: 59.9° for **13b**. $C^2-C^3-C^1-F^a$: 68.0°. $C^2-C^3-C^1-F^b$: 35.2° for **15b**.) and the orbital overlap of $n_{C^-}\cdots\sigma^*_{C-O}$ or $n_{C^-}\cdots\sigma^*_{C-C}$ was predicted, respectively. In fact, the C^2-O^5 and C^2-C^3 bond lengths of **13b** were 0.02 and 0.01 Å shorter and longer than the ones of **15b**, respectively. Smaller C^2-C^3 bond length variations between **13b** and **15b** would reflect the lower electron acceptance ability of σ^*_{C-C} orbital than the corresponding σ^*_{C-O} orbital, which also affected their C^1-C^2 bond lengths (1.5031 and 1.5178 Å).

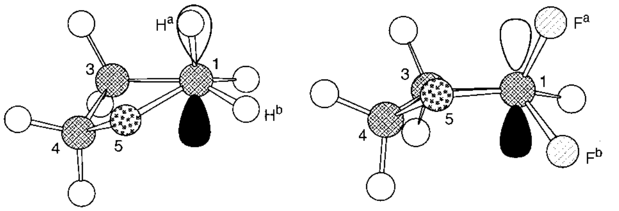
From the conformational point of view, the five-membered rings obtained via the present computational study possessed such a common three-dimensional structure that the C^3 atom deviated from the plane constituted by $C^1-C^2-C^4-O^5$ atoms, while **8b** and **9b** were the exception and it was C^4 that was not to be accommodated in the $C^1-C^2-C^3-O^5$ plane. In Figure 5 were described the Chem3D models of **8b** and **9b**, along with the corresponding nonfluorinated materials **8a** and **9a** as references, which were adequately rotated so as to superpose C^1 on the C^2 atom. Dihedral angles between lone pair (lp) and two hydrogen atoms H^a and H^b were roughly estimated for **8a** as being 40.6 and 87.6° for the $H^a-C^1-C^2-$lp and $H^b-C^1-C^2-$lp angles, respectively. If **8b** possessed a similar conformation to **8a**, electrostatic repulsive interaction of lp would be operated for both F^a and F^b atoms, while a subtle change in shape successfully produced the 20° wider dihedral angle of $F^b-C^1-C^2-$lp and would render electronic repulsion between F^b and lp weaker. On the other hand, dihedral angles of 26.3° or 35.9° between lp and F^a or F^b in **9b** would offer a good chance for the strongly electron-donating anionic robe n_{C^-}, allowing it to almost equally interact with the two empty σ^*_{C-F} orbitals at the same instance, which was distinctly demonstrated in their close bond lengths of 1.3940 or 1.3928 Å, respectively. Although the nonfluorinated **9a** possessed almost ideal location for one hydrogen, the other hydrogen H^b showed about 60° dihedral angle lp−C2−C1−H^b, which would enable only weak interaction to result in the overall disadvantage even when H^a and H^b were substituted by fluorine.

As shown above, our calculation of the alkoxide from 4,4-difluorobut-3-en-1-ol **6b** as the model for the anionic 5-*endo-trig* cyclization unambiguously demonstrated that this process occurs easily over the corresponding 4-*exo-trig* pathway in contrast to the Baldwin's prediction, where the strong polarization and the extended anomeric effect play significantly important roles for stabilization of the cyclization TS **9b** and the final product **10b**, respectively. Further calculation upon monofluorinated materials, as well as the possibility to "violate" of the Baldwin's rules by different fluorinated compounds,[3a] is being studied.



8a
H^a-C^1-C^2-lp: 40.6°
H^b-C^1-C^2-lp: 87.6°

8b
F^a-C^1-C^2-lp: 17.1°
F^b-C^1-C^2-lp: 106.9°



9a
H^a-C^1-C^2-lp: 5.5°
H^b-C^1-C^2-lp: 59.7°

9b
F^a-C^1-C^2-lp: 26.3°
F^b-C^1-C^2-lp: 35.9°

Figure 5. Conformational difference between series **a** and **b** in **8** and **9**.

Supporting Information Available: Calculated energy differences, representative physical properties by Mulliken (HF/6-31G*), energetic details obtained by Gaussian and Mulliken (Tables 3S−5S), and experimental procedure for the preparation of compounds **4** and **5** including their physical properties. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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