Use of 1,3-Dioxin-4-ones and Related Compounds in Synthesis. XXXVIII.[1] Use of 1,3-Dioxin-4-ones Having a Fluorine or Trifluoromethyl Group at the 5-Position as $_{\pi}2$ Components in [2+2]-Photocycloaddition and Diels–Alder Reactions[2]

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1,3-Dioxin-4-ones having fluorine or a trifluoromethyl group at the 5-position were used as the $_{\pi}2$ components in Diels–Alder reactions with 1-oxygenated dienes. Use of high-pressure conditions was the essential requisite. While the 5-fluorodioxinones were photolabile, the corresponding trifluoromethyl derivatives participated as the enone components in [2+2]photocycloaddition to alkenes, Ring-opening reactions of these adducts by acetal bond cleavage gave cyclobutanes and cyclohexanes. Diels–Alder reactions of the fluorinated homochiral dioxinones having *l*-menthone at the acetal position with Danishefsky diene proceeded in a completely diastereoselective manner to give single adducts.

Keywords 5-fluoro-1,3-dioxin-4-one; 5-trifluoromethyl-1,3-dioxin-4-one; [2+2]photocycloaddition; high-pressure Diels–Alder reaction; asymmetric Diels–Alder reaction; Danishefsky diene

Due to ready manipulations, as depicted in Chart 1, utilization of 1,3-dioxin-4-ones (A) is convenient for the synthesis of a variety of organic molecules (Chart 1). Thus, in addition to the transformation (path a) *via* acylketene species (B) formed simply by heating in an aprotic solvent, use of these dioxinones as $_{\pi}2$ components in Diels–Alder (path b) and [2+2]photocycloaddition reactions (path c) has provided an alternatives to using the enol form of masked acylacetic acids (Chart 1).[3]

Recently, we reported the synthesis of both 5-trifluoromethyl-[4] and 5-fluoro-1,3-dioxin-4-ones[5] (**1** and **2**) and their transformation to a variety of compounds *via* the corresponding formyl- and acylketene species. In this paper, we report the use of these dioxinones as $_{\pi}2$ components in percyclic reactions. Such work would provide useful means for the preparation of fluorinated organic molecules, which have recently gained much attention in medicinal chemistry.[6]

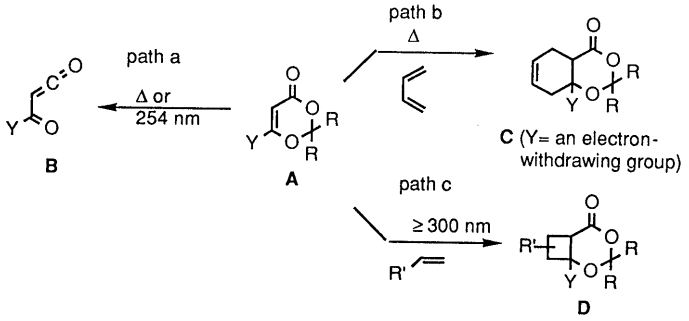
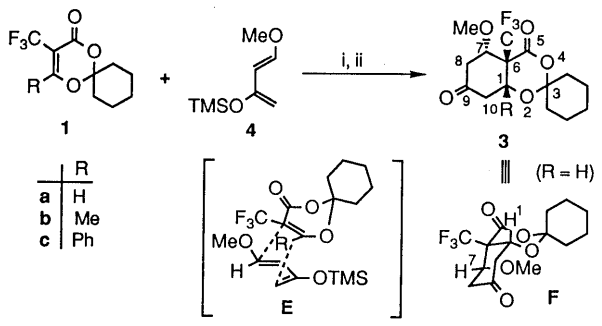


Chart 1



i) toluene, 10 kbar, r. t.; ii) KF, THF

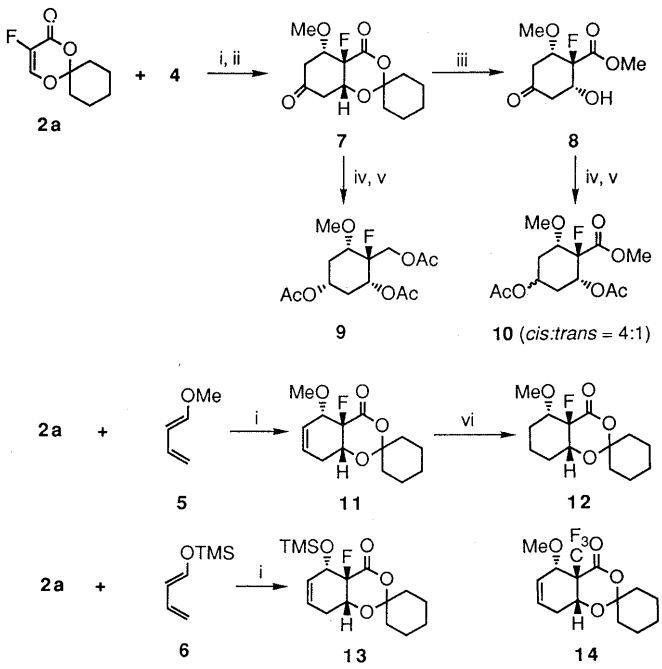
Chart 2

Use of the Dioxinones as $_{\pi}2$ Components in Diels–Alder Reaction Our preliminary result[1] using the 5-trifluoromethyldioxinone (**1a**) in Diels–Alder reaction with *trans*-1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**4**: Danishefsky diene)[7] showed clearly that such dioxinones could participate in this reaction as the $_{\pi}2$ components. Thus, compound **1a** was allowed to react with the diene to give the single adduct **3a** after desilylation of the [4+2]adduct. On the basis of a long-range coupling (2 Hz) due to a W-conformation between C_1-H and C_7-H in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **3a**,[8] its conformation was assigned as F. Obviously, the reaction had proceeded *via* the *endo*-COO transition state (E).

Though this reaction proceeded only under high pressure conditions (10 kbar at room temperature), the same high-pressure reaction using the 5,6-unsubstituted dioxinone did not proceed even at an elevated temperature (75 °C). This fact indicated that attachment of a trifluoromethyl group at the 5-position of the dioxinone ring enhanced the reactivity of the dioxinone (A) as the dienophile.[9] Encouraged by this preliminary result, other dioxinones (**1**) were also reacted with **4** under the high-pressure conditions (10 kbar). In order to compare the reactivities of **1a**—**c**, each reaction was conducted at 75 °C and the products were isolated as the cyclohexanones (**3**) obtained by *in situ* desilylation of the crude [4+2]adducts[10]

TABLE I. Diels–Alder Reactions of Dioxinones (**1** and **2**) with Danishefsky Diene

Entry	Compd.	R	Conditions			Adducts (%)	
			Pressure (kbar)	Temp. (°C)	Time		
1	**1a**	H	10	20	40 h	**3a**	82
2	**1a**	H	10	75	40 h	**3a**	78
3	**1b**	Me	10	75	5 d	**3b**	50
4	**1c**	Ph	10	75	40 h	None	
5	**2a**	H	10	20	40 h	None	
6	**2a**	H	10	75	40 h	**7**	72
7	**2b**	Me	10	75	40 h	None	
8	**2c**	Ph	10	75	40 h	None	

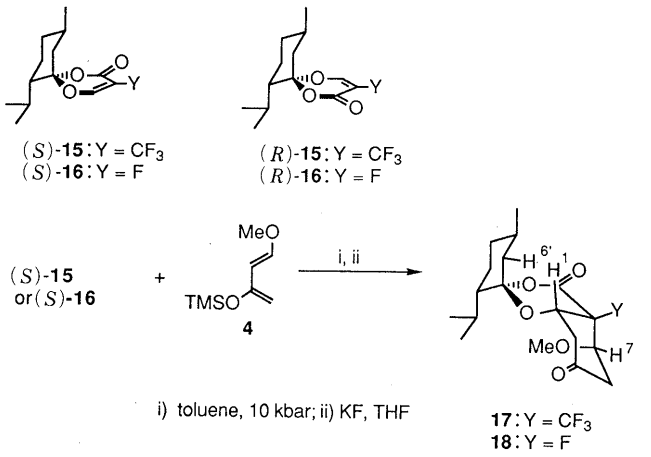


i) toluene, 10 kbar, 75 °C; ii) KF, THF; iii) THF/H_2O, reflux, then CH_2N_2, ether; iv) $NaBH_4$, EtOH; v) Ac_2O, 4-dimethylaminopyridine, CH_2Cl_2; vi) H_2/Pd-C, AcOEt

Chart 3

TABLE II. Diels–Alder Reactions of Dioxinones (**1** and **2**) with 1-Oxygenated Dienes (**5** and **6**)

Entry	Compd.	R	Dienes (eq)		Time	Adducts (%)		Recovered **1** or **2** (%)
1	**1a**	H	**5**	(2)	40 h	**14**	11	34
2	**1a**	H	**5**	(5)	40 h	**14**	62	13
3	**2a**	H	**5**	(2)	40 h	**11**	18	49
4	**2a**	H	**5**	(5)	40 h	**11**	31	13
5	**2a**	H	**6**	(5)	5 d	**13**	59	None



i) toluene, 10 kbar; ii) KF, THF

Chart 4

with potassium fluoride. The results are shown in Table I.

The reaction of the 6-methyldioxinone (**1b**) with **4** also gave the adduct (**3b**) as a single isomer. By analogy with the stereoselective formation of **3a**, it seems reasonable to assume that it has the structure fitted to the product derived from the *endo*-COO-transition state (*cf.* E).

Next, we used the corresponding 5-fluorodioxinone[5] (**2a**) in the same reactions (Chart 3). The expected *endo* adduct (**7**), described later, was obtained as a sole product (Table I).

The fact that the reaction of **2b** with Danishefsky diene (**4**) did not proceed under the same conditions indicated that the reactivity of the 5-fluorinated dioxinones (**2**) was less than that of the corresponding trifluoromethyl derivatives (**1**). In both series of compounds, the 6-phenyl derivatives (**1c** and **2c**) did not afford the cycloadducts.

In order to examine how the structure of dienes affects the reactivity, **4** and five other dienes [cyclopentadiene, and 2,3-dimethyl-, 2,3-dimethoxy-, 1-methoxy- (**5**), and 1-trimethylsilyloxy-butadienes (**6**)] were allowed to react with **2a**. As shown in Table II, only the 1-oxygenated butadienes (**4**, **5** and **6**) afforded the [4+2]adducts (**7**, **11**, **13** and **14**).

The long-range coupling between C_1- and C_7-H observed in the ^{1}H-NMR spectra of **7** and the dihydro derivative (**12**)[11] of **11** showed again that the addition proceeded *via* the *endo*-transition state.

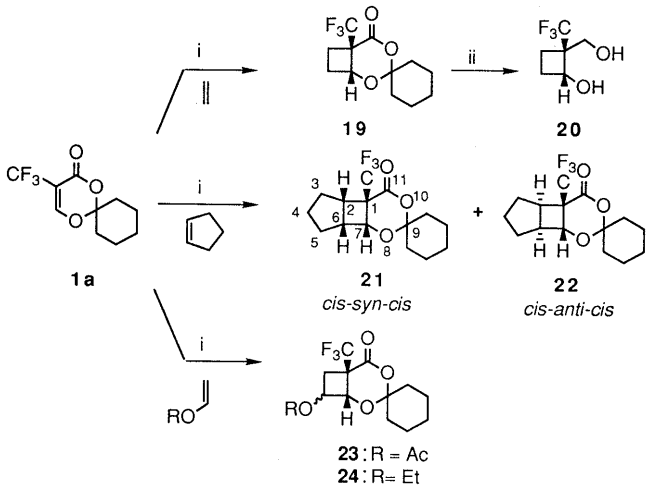
It should be noted that, when **7** was reduced by sodium borohydride in ethanol, the ring-opened primary alcohol (isolated as the triacetate: **9**) was obtained as a sole product in satisfactory yield. On the contrary, the reduction of **8** derived from **7** gave two esters (again isolated as the diacetates: **10**-*cis* and **10**-*trans*)[12] in *ca.* 4:1 ratio. The following two characteristic features of the reduction of **7** to **9** as compared to that of **8** to **10** seem to be noteworthy. These are 1) ready reaction of the lactone group to the primary alcohol and 2) high diastereoselectivity in the reduction of the keto group into the secondary alcohol. Concerning the former characteristic, the presence of a fluorine atom (an electronegative atom) at the neighboring position and the intrinsic ring strain of the *cis*-decalin ring system of **7** result in enhanced reactivity of the lactone carbonyl. Since the presence of the long-range coupling between C_1-H and C_7-H suggests that **7** has a similar conformation to F, the latter characteristic is best explained by assuming that the reagent attacks the keto group from the more exposed convex side of **7**.

As shown in Table II, **1a** also reacted with **5** to give a single product (**14**), whose structure could be assigned as the *endo*-adduct by analogy.

Finally, successful extension of these reactions to the synthesis of enantiomerically pure compounds seems to deserve comment. Thus, utilizing the methodology already established in our[3,13] and other's laboratories,[14] chiral spirocyclic dioxinones [(*S*)- and (*R*)-**15** and -**16**] were synthesized. When the (*S*)-isomer (**15**) was reacted with **4** (Danishefsky diene), a single adduct (**17**) was obtained in 74% yield as the sole isolable product.

The nuclear Overhauser effect (NOE) enhancement[15] observed in the adduct (**17**) (*cf.* **17** in Chart 4) showed clearly that the addition had occurred from the expected isopropyl side. The same isopropyl side preference was also observed for (*S*)-**16**, from which **18** was obtained as a sole product. The long-range coupling (*ca.* 2 Hz) of C_1-H and C_7-H due to a W-conformation suggests further that **17** and **18** have the conformation as depicted in Chart 4.

Use of the Dioxinones as $_\pi$2 (the Enone) Components in [2+2]Photocycloaddition Photocycloaddition of the dioxinone (**1a**) to a variety of olefins was then examined. By using ethylene as the alkene, the [2+2] adduct (**19**) was



i) AcOEt, 254 nm; ii) $LiAlH_4$, THF, -30 °C

Chart 5

obtained in 44% yield; it was treated with lithium aluminum hydride to give the cyclobutanol (**20**). The photocycloaddition of **1a** to cyclopentene afforded the expected adduct in 68% yield as a mixture of *cis–syn–cis* (**21**) and *cis–anti–cis* isomers (**22**). Two isomers could be separated by medium-pressure liquid chromatography (MPLC: Lobar column) to give a less polar adduct (**21**) and a more polar adduct (**22**) in *ca.* 2 : 1 ratio. By analysis of the 500 MHz ^{1}H-NMR spectra, the major adduct (**21**) was assigned *cis–syn–cis* configuration [C_7-H (δ 4.70) as dd (J 7.5 and 1.5 Hz: the latter was obviously due to a long-range coupling between C_7-H and C_2-H: *cis*-relationship in a W-conformation of the cyclobutane ring)].[16] The corresponding signal of **22** appeared at δ 4.47 as a doublet (J 3.0 Hz) without any such coupling. In order to examine the regioselectivity of the reaction, the photoadditions to oxygenated alkenes (vinyl acetate and ethyl vinyl ether) were examined. Only the head-to-tail adducts (**23** and **24**) were identified as mixtures of the *endo*- and *exo*-isomers.[17]

On the contrary, when **2b** was used as the enone component in these reactions, no adduct was obtained at all. Since none of the starting materials was recovered in these reactions, it is obvious that **2b** was decomposed by irradiation (300 nm) *via* the excited states at a much faster rate than their addition to the alkenes.

In conclusion, the result presented in this paper seem to indicate the usefulness of the dioxinone as a $_\pi$2 component in these two pericyclic reactions, which offer flexible methods for preparation of a variety of fluorinated and trifluoromethylated compounds either in racemic or enantiomerically pure forms.

Experimental

All melting points were determined on a micro-hot stage (Yanagimoto) and are uncorrected. Infrared (IR) spectra were measured on a JASCO A-102 spectrometer. ^{1}H-NMR spectra at 500 MHz were recorded with a JNM-FX500 spectrometer using tetramethylsilane (TMS) as an internal standard, respectively. High-resolution mass spectra (MS) were recorded on a JEOL JMS-01SG-2 system. Wakogel (C-200) was employed for silica gel column chromatography. Merck Kieselgel 60F 254 was employed for TLC. Medium-pressure liquid chromatography (MPLC) was performed with a Merck Lobar column (LiChroprep Si 60). The ratios of mixtures of solvents for chromatography are shown as volume/volume. High-pressure reactions were carried out by using a piston-cylinder apparatus equipped with a PK. 15. B pump (Hikari Koatsu Kiki Co., Ltd.). Photolyses were carried out at room temperature either under condition a or b. a) Photoaddition to ethylene was carried out in a quartz immersion apparatus equipped with an Ushio 450 W high-pressure mercury lamp (Vycor filter) and b) for other photoaddition reactions, a Rayonet photochemical reactor lamp (Cat. No. RPR-2537 Å) was used as the light source.

Compounds **1a—c**,[1] **2a**[5a] and **2b, c**[5b] were prepared according to the literature procedures. Dienes were commercial products.

Diels–Alder Reaction of 1 or 2 with *trans*-1-Methoxy-3-trimethylsilyloxybuta-1,3-diene (4: Danishefsky Diene) (General Procedure) A solution of **1** or **2** and **4** in toluene (2 ml) was treated under 10 kbar. The residue obtained after evaporation of the solvent was dissolved in tetrahydrofuran (THF) (5 ml). Then KF (2 eq of **4**) was added to the solution and the mixture was stirred at room temperature for 19 h. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with water and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–AcOEt (3 : 1)] to give the adduct.

***rel*-(1*R*,6*R*,7*S*)-7-Methoxy-5,9-dioxo-6-trifluoromethyl-2,4-dioxabicyclo[4.4.0]decane-3-spirocyclohexane (3a)** A solution of **1a** (71 mg, 0.3 mmol) and **4** (103 mg, 0.6 mmol) in toluene (2 ml) was treated under 10 kbar at room temperature for 40 h. Treatment with KF gave **3a** (82 mg, 82%) as colorless prisms, mp 83—84.5 °C (Et_2O–hexane). *Anal.* Calcd for $C_{15}H_{19}F_3O_5$: C, 53.57; H, 5.69. Found: C, 53.32; H, 5.80. IR ($CHCl_3$): 2960, 1740, 1735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20—2.00 (10 H, m, $CH_2 \times 5$), 2.62 (1H, dd, J=3, 16 Hz, C_8-H), 2.77 (1H, d, J=16 Hz, C_{10}-H), 2.88 (1H, d, J=16 Hz, C_8-H), 2.92 (1H, dd, J=6,16 Hz, C_{10}-H), 3.33 (3H, s, OMe), 4.41 (1H, dt, J=2, 3 Hz, C_7-H), 4.88 (1H, ddd, J=2,3,6 Hz, C_1-H).

***rel*-(1*R*,6*S*,7*S*)-7-Methoxy-1-methyl-5,9-dioxo-6-trifluoromethyl-2,4-dioxabicyclo[4.4.0]decane-3-spirocyclohexane (3b)** A solution of **1b** (75 mg, 0.3 mmol) and **4** (258 mg, 1.5 mmol) in toluene (2 ml) was treated under 10 kbar at 75 °C for 5 d. Treatment with KF gave **3b** (53 mg, 50%) as colorless needles, mp 104—105 °C (Et_2O–hexane). *Anal.* Calcd for $C_{16}H_{21}F_3O_5$: C, 54.86; H, 6.04. Found: C, 54.84; H, 6.30. IR ($CHCl_3$): 2960, 1740, 1735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20—2.00 (10H, m, $CH_2 \times 5$), 1.66 (3H, q, J=2 Hz, C_1-Me), 2.64 (1H, d, J=16 Hz, C_{10}-H), 2.67 (1H, dd, J=4.5, 15 Hz, C_8-H), 2.73 (1H, d, J=16 Hz, C_{10}-H), 2.86 (1H, dd, J=4.5, 15 Hz, C_8-H), 3.33 (3H, s, OMe), 4.40 (1H, t, J=4.5 Hz, C_7-H).

***rel*-(1*R*,6*R*,7*S*)-6-Fluoro-7-methoxy-5,9-dioxo-2,4-dioxabicyclo[4.4.0]decane-3-spirocyclohexane (7)** A solution of **2a** (186 mg, 1.0 mmol) and **4** (344 mg, 2.0 mmol) in toluene (2 ml) was treated under 10 kbar at 75 °C for 40 h. Treatment with KF gave **7** (206 mg, 72%) as colorless prisms, mp 134.5—135.5 °C (AcOEt–hexane). *Anal.* Calcd for $C_{14}H_{19}FO_5$: C, 58.73; H, 6.69. Found: C, 58.80; H, 6.73. IR ($CHCl_3$): 2960, 1740, 1110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20—2.00 (10H, m, $CH_2 \times 5$), 2.68 (1H, ddd, J=2, 4, 16 Hz, C_{10}-H), 2.72 (1H, ddd, J=2, 4.5, 16 Hz, C_8-H), 2.81 (1H, ddd, J=2, 3, 16 Hz, C_8-H), 2.85 (1H, dd, J=5, 16 Hz, C_{10}-H), 3.36 (3H, s, OMe), 4.22 (1H, dddd, J=2, 3, 4.5, 11 Hz, C_7-H), 4.74 (1H, dddd, J=2, 4, 5, 9 Hz, C_1-H).

***rel*-(1*R*,6*S*,7*S*)-6-Fluoro-7-methoxy-5-oxo-2,4-dioxabicyclo[4.4.0]dec-8-ene-3-spirocyclohexane (11)** A solution of **1a** (93 mg, 0.5 mmol) and **5** (210 mg, 2.5 mmol) in toluene (2 ml) was treated under 10 kbar at 75 °C for 40 h. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–AcOEt (10 : 1)] to give **11** (42 mg, 31%) as colorless needles, mp 85—85.5 °C (Et_2O–hexane). *Anal.* Calcd for $C_{14}H_{19}FO_4$: C, 62.21; H, 7.09. Found: C, 61.98; H, 7.31. IR ($CHCl_3$): 2950, 1750, 1305, 1195 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20—2.00 (10 H, m, $CH_2 \times 5$), 2.40 (1H, br dd, J=5, 19 Hz, C_{10}-H), 2.55 (1H, br d, J=19 Hz, C_{10}-H), 3.44 (3H, s, OMe), 3.87 (1H, br d, J=20 Hz, C_7-H), 4.46 (1H, t, J=4.5 Hz, C_1-H), 5.92 (1H, br d, J=10 Hz, C_9-H), 5.99 (1H, br d, J=10 Hz, C_8-H).

***rel*-(1*R*,6*S*,7*S*)-6-Fluoro-5-oxo-7-trimethylsilyloxy-2,4-dioxabicyclo[4.4.0]dec-8-ene-3-spirocyclohexane (13)** A solution of **2a** (558 mg, 3 mmol) and **6** (2.13 g, 15 mmol) in toluene (10 ml) was treated under 10 kbar at 75 °C for 5 d. The residue obtained after evaporation of the solvent was purified by flash chromatography on silica gel [hexane–AcOEt (10 : 1)] to give **13** (546 mg, 59%) as a colorless oil. High-resolution MS *m/z*: Calcd for $C_{16}H_{25}FO_4Si$ (M^+): 328.1506. Found: 328.1511. IR ($CHCl_3$): 2960, 1750, 1250, 1100, 885, 840 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.15 (9H, s, SiMe × 3), 1.40—2.10 (10H, m, $CH_2 \times 5$), 2.39 (1H, dd, J=5, 19 Hz, C_{10}-H), 2.87 (1H, br d, J=19 Hz, C_{10}-H), 4.31 (1H, br d, J=20 Hz, C_7-H), 4.48 (1H, t, J=5 Hz, C_1-H), 5.77 (1H, br d, J=10 Hz, C_9-H), 5.85

(1H, br d, $J=10$ Hz, C_8-H).

***rel*-(1*R*,6*S*,7*S*)-7-Methoxy-5-oxo-6-trifluoromethyl-2,4-dioxabicyclo-[4.4.0]dec-8-ene-3-spirocyclohexane (14)** A solution of **1a** (118 mg, 0.5 mmol) and **5** (210 mg, 2.5 mmol) *in toluene* (2 ml) was treated under 10 kbar at 75 °C for 40 h. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–AcOEt (10 : 1)] to give **14** (99 mg, 62%) as a colorless oil. High-resolution MS *m/z*: Calcd for $C_{15}H_{19}F_3O_4$ (M^+): 320.1235. Found: 320.1211. IR ($CHCl_3$): 2950, 1740, 1270, 1165, 1180 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20—2.10 (10H, m, $CH_2\times5$), 2.44 (1H, br d, $J=19$ Hz, C_{10}-H), 2.63 (1H, br d, $J=19$ Hz, C_{10}-H), 3.42 (3H, s, OMe), 4.08 (1H, d, $J=5$ Hz, C_7-H), 4.64 (1H, d, $J=6$ Hz, C_1-H), 5.95 (1H, ddd, $J=3$, 4.5, 10.5 Hz, C_9-H), 6.05 (1H, ddt, $J=5$, 10.5, 2.2 Hz, C_8-H).

Diels–Alder Adduct of 1a with 4 (Entry 2 in Table I) *rel*-(1*R*,6*S*,7*S*)-7-Methoxy-5-oxo-6-trifluoromethyl-9-trimethylsilyloxy-2,4-dioxabicyclo-[4.4.0]dec-8-ene-3-spirocyclohexane A solution of **1a** (23.6 mg, 0.1 mmol) and **4** (34 mg, 0.2 mmol) in toluene (2 ml) was treated under 10 kbar at 75 °C for 40 h. The residue obtained after evaporation of the solvent was purified by chromatography on a short silica gel column [hexane–AcOEt (1 : 1)] to give the adduct (33 mg, 81%) as a colorless oil. High-resolution MS *m/z*: Calcd for $C_{18}H_{27}F_3O_5Si$ (M^+): 408.1580. Found: 408.1584. IR ($CHCl_3$): 2960, 1740, 1270, 1170 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.10 (9H, s, SiMe × 3), 1.20—2.00 (10H, m, $CH_2\times5$), 2.38 (1H, d, $J=19$ Hz, C_{10}-H), 2.61 (1H, dd, $J=7$, 19 Hz, C_{10}-H), 3.33 (3H, s, OMe), 4.29 (1H, d, $J=5.5$ Hz, C_7-H), 4.68 (1H, d, $J=7$ Hz, C_1-H), 5.16 (1H, dt, $J=5.5$, 2 Hz, C_8-H).

Methyl *rel*-(1*S*,2*R*,6*S*)-1-Fluoro-2-hydroxy-6-methoxy-4-oxocyclohexane-carboxylate (8) A solution of **7** (57.2 mg, 0.2 mmol) in THF (1 ml) and H_2O (0.1 ml) was refluxed for 2.5 h. The residue obtained after evaporation of the solvent was dissolved in Et_2O (1 ml) and treated with excess diazomethane in Et_2O. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–AcOEt (3 : 1)]to give **8** (37 mg, 84%) as colorless needles, mp 86—86.5 °C (AcOEt–hexane). *Anal.* Calcd for $C_9H_{13}FO_5$: C, 49.09; H, 5.95. Found: C, 49.09; H, 5.81. IR ($CHCl_3$): 3610, 1730, 1260 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.76 (1H, m, C_5-H), 2.79 (1H, br d, $J=4$ Hz, OH), 2.82 (1H, m, C_3-H), 2.99 (1H, dd, $J=10$, 15 Hz, C_3-H), 3.03 (1H, dd, $J=10$, 15 Hz, C_5-H), 3.47 (3H, s, OMe), 3.92 (3H, s, COOMe), 3.84 (1H, ddd, $J=6$, 10, 13 Hz, C_6-H), 4.25 (1H, m, C_2-H).

***rel*-(1*R*,2*R*,4*R*,6*S*)-1-Fluoro-2,4-dihydroxy-6-methoxy-cyclohexane-methanol Triacetate (9)** $NaBH_4$ (22.8 mg, 0.6 mmol) was added portionwise to a solution of **7** (57.2 mg, 0.2 mmol) in EtOH (0.5 ml), over 30 min at below 5 °C. After stirring at room temperature for 2 h, 10% HCl was added. The reaction mixture was extracted with AcOEt and the organic layer was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was dissolved in CH_2Cl_2 (1 ml). 4-Dimethylaminopyridine (122.2 mg, 1.0 mmol) and acetic anhydride (204 mg, 2.0 mmol) were added to the solution at below 5 °C. After stirring for 30 min, the reaction mixture was washed with 1% HCl, saturated $NaHCO_3$ and saturated NaCl and then dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–AcOEt (3 : 1)] to give **9** (43 mg, 70%) as a colorless oil. High-resolution MS *m/z*: Calcd for $C_{14}H_{22}FO_7$ [$(M+H)^+$]: 321.1350. Found: 321.1351. IR ($CHCl_3$): 1745, 1365, 1230, 1060 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.76 (1H, q, $J=12$ Hz, C_5-H), 1.87 (1H, q, $J=12$ Hz, C_3-H), 2.04 (3H, s, MeCO), 2.09 (3H, s, MeCO), 2.13 (3H, s, MeCO), 2.21 (1H, m, C_3-H), 2.32 (1H, m, C_5-H), 3.47 (3H, s, OMe), 3.49 (1H, ddd, $J=5$, 12, 13 Hz, C_6-H), 4.56 (1H, dd, $J=12.5$, 14 Hz, CH_2O), 4.59 (1H, dd, $J=12.5$, 15 Hz, CH_2O), 4.90 (1H, tt, $J=5$, 12 Hz, C_4-H), 5.08 (1H, ddd, $J=5$, 12, 13 Hz, C_2-H).

Methyl *rel*-(1*R*,2*R*,4*R*,6*S*)- and (1*R*,2*R*,4*S*,6*S*)-2,4-Diacetoxy-1-fluoro-6-methoxy-cyclohexanecarboxylate (10-*cis* and 10-*trans*) Compound **8** (66 mg, 0.3 mmol) was treated with $NaBH_4$ (5.7 mg, 0.15 mmol) at below 5 °C for 30 min and then with acetic anhydride in a similar manner to that described for preparation of **9** to give **10** as an inseparable mixture of the *cis* and *trans* isomers (68 mg, 74%) in the form of a colorless oil (*cis* : *trans* = *ca.* 4 : 1). High-resolution MS *m/z*: Calcd for $C_{13}H_{19}FO_7$ [$(M+H)^+$]: 307.1193. Found: 307.1206.

10-*cis*: ^{1}H-NMR ($CDCl_3$) δ: 2.07 (6H, s, MeCO × 2), 2.1—2.4 (4H, m, $CH_2\times2$), 3.46 (3H, s, OMe), 3.55 (1H, ddd, $J=5$, 12, 15 Hz, C_6-H), 3.88 (3H, s, COOMe), 4.87 (1H, tt, $J=5$, 12 Hz, C_4-H), 5.11 (1H, ddd, $J=5$, 12, 15 Hz, C_2-H).

10-*trans*: ^{1}H-NMR ($CDCl_3$) δ: 2.07 (6H, s, MeCO × 2), 2.1—2.4 (4H, m, $CH_2\times2$), 3.49 (3H, s, OMe), 3.80 (1H, ddd, $J=5$, 12, 15 Hz, C_6-H), 3.88 (3H, s, COOMe), 5.28 (1H, m, C_4-H), 5.40 (1H, ddd, $J=6.5$, 11.5, 16 Hz, C_2-H).

***rel*-(1*R*,6*R*,7*S*)-6-Fluoro-7-methoxy-5-oxo-2,4-dioxabicyclo[4.4.0]-decane-3-spirocyclohexane (12)** Compound **11** (32 mg, 0.12 mmol) was hydrogenated with 10% Pd/C (10 mg) in AcOEt (5 ml) at room temperature under 1 atm of hydrogen for 30 min. After the removal of the catalyst by filtration, the filtrate was evaporated *in vacuo*. The residue was crystallized from hexane to give **12** (30 mg, 93%) as colorless prisms, mp 94—94.5 °C. *Anal.* Calcd for $C_{14}H_{21}FO_4$: C, 61.75; H, 7.77. Found: C, 61.56; H, 7.86. IR ($CHCl_3$): 2950, 1745, 1305, 1090 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.1 (16H, m, $CH_2\times8$), 3.30 (3H, s, OMe), 3.70 (1H, br d, $J=13$ Hz, C_1-H), 4.28 (1H, m, C_7-H). A decoupling experiment of C_1-H and C_7-H showed long-range coupling between these two protons.

(2*S*,2′*S*,5′*R*)- and (2*R*,2′*S*,5′*R*)-4-Oxo-5-trifluoromethyl-4*H*-1,3-dioxine-2-spiro(2′-isopropyl-5′-methyl)-cyclohexane [(*S*)-15 and (*R*)-15] A solution of a mixture of (2*S*,2′*S*,5′*R*)- and (2*R*,2′*S*,5′*R*)-4-oxo-4*H*-1,3-dioxine-2-spiro(2′-isopropyl-5′-methyl)cyclohexane[18] (1.12 g, 5 mmol) and *N*-iodosuccinimide (1.58 g, 7 mmol) in acetic acid (10 ml) was stirred for 13 h at room temperature in the dark. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–AcOEt (10 : 1)] to give a mixture of (2*S*,2′*S*,5′*R*)- and (2*R*,2′*S*,5′*R*)-5-iodo-4-oxo-4*H*-1,3-dioxine-2-spiro(2′-isopropyl-5′-methyl)cyclohexane (1.00 g, 57%) as a pale yellow oil. High-resolution MS *m/z*: Calcd for $C_{13}H_{19}IO_3$ (M^+): 350.0381. Found: 350.0371.

A suspension of trifluoromethyl iodide (2.53 g, 12.9 mmol), copper powder (1.31 g, 20.6 mmol) and hexamethylphosphoric triamide (5 ml) was stirred at 120—125 °C in a sealed tube for 3 h under an Ar atmosphere.[19] To the mixture was added the iodinated product (1.00 g, 2.86 mmol) obtained above, and whole was stirred at 55 °C for 1.5 h. The reaction mixture was cooled and poured into ice-water. Insoluble material was removed by filtration through Celite. After the extraction of the filtrate with ether, the organic layer was washed with water and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–Et_2O (50 : 1)] and on a Lobar column [hexane–Et_2O (50 : 1)] to give (*S*)-**15** (179 mg, 21%, less polar) as colorless prisms, mp 59—61 °C (pentane) and (*R*)-**15** (218 mg, 26%, more polar) as colorless prisms, mp 69—70 °C (pentane).

(*S*)-**15**: $[\alpha]_D^{24}$ −51.6° (*c* = 0.98, $CHCl_3$). *Anal.* Calcd for $C_{14}H_{19}F_3O_3$: C, 57.53; H, 6.55. Found: C, 57.72; H, 6.79. IR ($CHCl_3$): 2960, 1750, 1640, 1395, 1150, 1105 cm^{-1}. ^{1}H-NMR ($CDCl_3$) *inter alia* δ: 0.92 (3H, d, $J=7$ Hz, isopropyl-Me), 0.93 (3H, d, $J=7$ Hz, $C_{5'}$-Me), 0.97 (3H, d, $J=7$ Hz, isopropyl-Me), 1.17 (1H, t, $J=13$ Hz, $C_{6'}$-axial-H), 2.17 (1H, m, isopropyl-H), 2.53 (1H, ddd, $J=2.5$, 3.5, 13 Hz, $C_{6'}$-equatorial-H), 7.68 (1H, s, C_2-H).

(*R*)-**15**: $[\alpha]_D^{24}$ 3.6° (*c* = 1.07, $CHCl_3$). *Anal.* Calcd for $C_{14}H_{19}F_3O_3$: C, 57.53; H, 6.55. Found: C, 57.30; H, 6.64. IR ($CHCl_3$): 2960, 1750, 1640, 1395, 1150, 1105 cm^{-1}. ^{1}H-NMR ($CDCl_3$) *inter alia* δ: 0.87 (3H, d, $J=7$ Hz, isopropyl-Me), 0.93 (3H, d, $J=7$ Hz, $C_{5'}$-Me), 0.97 (3H, d, $J=7$ Hz, isopropyl-Me), 1.23 (1H, t, $J=13$ Hz, $C_{6'}$-axial-H), 2.29 (1H, m, isopropyl-H), 2.54 (1H, ddd, $J=2.5$, 3.5, 13 Hz, $C_{6'}$-equatorial-H), 7.69 (1H, s, C_2-H).

(2*S*,2′*S*,5′*R*)- and (2*R*,2′*S*,5′*R*)-5-Fluoro-4-oxo-4*H*-1,3-dioxine-2-spiro-(2′-isopropyl-5′-methyl)cyclohexane [(*S*)-16 and (*R*)-16] Fluorine gas (4 mmol) diluted with nitrogen to 5% concentration was bubbled into a solution of a mixture of (2*S*,2′*S*,5′*R*)- and (2*R*,2′*S*,5′*R*)-4-oxo-4*H*-1,3-dioxine-2-spiro(2′-isopropyl-5′-methyl)cyclohexane[18] (672 mg, 3 mmol) in acetonitrile (60 ml) at −20 °C. After nitrogen had been bubbled through to purge excess fluorine, the reaction mixture was diluted with CH_2Cl_2 (60 ml) and washed with saturated $NaHCO_3$. The organic layer was washed with water and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was dissolved in CH_2Cl_2 (60 ml). 1,8-Diazabicyclo[5.4.0]-undec-7-ene (608 mg, 4 mmol) was added portionwise over 5 min to the solution at room temperature. After stirring for 30 min, the reaction mixture was washed with water and the organic layer was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on silica gel [hexane–Et_2O (50 : 1)] to give at first (*S*)-**16** (113 mg, 16%, less polar) as colorless prisms, mp 107—108 °C (pentane) and then (*R*)-**16** (109 mg, 15%, more polar) as colorless prisms, mp 84—86 °C (pentane).

(*S*)-**16**: $[\alpha]_D^{20}$ −72.7° (*c* = 0.66, $CHCl_3$). *Anal.* Calcd for $C_{13}H_{19}FO_3$: C, 64.44; H, 7.90. Found: C, 64.36; H, 7.93. IR ($CHCl_3$): 2970, 1755, 1665, 1160 cm^{-1}. ^{1}H-NMR ($CDCl_3$) *inter alia* δ: 0.91 (3H, d, $J=7$ Hz, isopropyl-Me), 0.92 (3H, d, $J=7$ Hz, $C_{5'}$-Me), 0.96 (3H, d, $J=7$ Hz, isopropyl-Me), 1.08 (1H, t, $J=13$ Hz, $C_{6'}$-axial-H), 2.24 (1H, m, isopropyl-H), 2.76 (1H, ddd, $J=2.5$, 3.5, 13 Hz, $C_{6'}$-equatorial-H), 7.27

(1H, d, J=2.5 Hz, C_2-H).

(*R*)-**16**: $[\alpha]_D^{23}$ −3.0° (c=1.00, $CHCl_3$). *Anal.* Calcd for $C_{13}H_{19}FO_3$: C, 64.44; H, 7.90. Found: C, 64.31; H, 8.04. IR ($CHCl_3$): 2970, 1755, 1665, 1160 cm^{-1}. ^{1}H-NMR ($CDCl_3$) *inter alia* δ: 0.88 (3H, d, J=7 Hz, isopropyl-Me), 0.92 (3H, d, J=7 Hz, $C_{5'}$-Me), 0.96 (3H, d, J=7 Hz, isopropyl-Me), 1.13 (1H, t, J=13 Hz, $C_{6'}$-axial-H), 2.30 (1H, m, isopropyl-H), 2.76 (1H, ddd, J=2.5, 3.5, 13 Hz, $C_{6'}$-equatorial-H), 7.27 (1H, d, J=2.5 Hz, C_2-H).

(1*S*,2′*S*,3*S*,5′*R*,6*S*,7*R*)-7-Methoxy-5,9-dioxo-6-trifluoromethyl-2,4-dioxabicyclo[4.4.0]decane-3-spiro(2′-isopropyl-5′-methyl)cyclohexane (17) A solution of (*S*)-**15** (58.4 mg, 0.2 mmol) and **4** (68.8 mg, 0.4 mmol) in toluene (1.2 ml) was treated under 10 kbar at room temperature for 4 d. Treatment of crude product with KF as described in the general procedure gave **17** (56 mg, 72%) as colorless prisms, mp 154—155 °C (AcOEt–hexane). $[\alpha]_D^{25}$ 22.9° (c=0.34, $CHCl_3$). *Anal.* Calcd for $C_{19}H_{27}F_3O_5$: C, 58.16; H, 6.94. Found: C, 58.15; H, 7.14. IR ($CHCl_3$): 2960, 1735, 1255, 1165 cm^{-1}. ^{1}H-NMR ($CDCl_3$) *inter alia* δ: 0.81 (3H, d, J=7 Hz, isopropyl-Me), 0.89 (3H, d, J=7 Hz, isopropyl-Me), 0.93 (3H, d, J=7 Hz, $C_{5'}$-Me), 1.12 (1H, t, J=13 Hz, $C_{6'}$-axial-H), 1.35 (1H, ddd, J=2, 4, 13 Hz, $C_{2'}$-H), 2.29 (1H, br d, J=13 Hz, $C_{6'}$-equatorial-H), 2.42 (1H, m, isopropyl-H), 2.59 (1H, dd, J=3, 16 Hz, C_8-H), 2.76 (1H, br d, J=16 Hz, C_{10}-H), 2.86 (1H, br d, J=16 Hz, C_8-H), 2.89 (1H, dd, J=7, 16 Hz, C_{10}-H), 3.30 (3H, s, OMe), 4.44 (1H, m, C_7-H), 5.05 (1H, ddd, J=2, 3, 7 Hz, C_1-H).

(1*S*,2′*S*,3*S*,5′*R*,6*S*,7*R*)-6-Fluoro-7-methoxy-5,9-dioxo-2,4-dioxabicyclo-[4.4.0]decane-3-spiro(2′-isopropyl-5′-methyl)cyclohexane (18) A solution of (*S*)-**16** (61 mg, 0.25 mmol) and **4** (86 mg, 0.5 mmol) in toluene (1.2 ml) was treated under 10 kbar at 75 °C for 5 d. Treatment of crude product with KF as described in the general procedure gave **18** (63 mg, 74%) as colorless needles, mp 142—144 °C (AcOEt–hexane). $[\alpha]_D^{23}$ 12.2° (c=0.97, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{27}FO_5$: C, 63.14; H, 7.95. Found: C, 63.18; H, 8.07. IR ($CHCl_3$): 2960, 1740, 1320, 1255, 1100 cm^{-1}. ^{1}H-NMR ($CDCl_3$) *inter alia* δ: 0.80 (3H, d, J=7 Hz, isopropyl-Me), 0.88 (3H, d, J=7 Hz, isopropyl-Me), 0.94 (3H, d, J=7 Hz, $C_{5'}$-Me), 1.15 (1H, t, J=13 Hz, $C_{6'}$-axial-H), 1.35 (1H, ddd, J=2, 4, 13 Hz, $C_{2'}$-H), 2.35 (1H, ddd, J=2, 4, 13 Hz, $C_{6'}$-equatorial-H), 2.43 (1H, m, isopropyl-H), 2.70 (1H, br d, J=16 Hz, C_8-H), 2.71 (1H, br d, J=16 Hz, C_{10}-H), 2.81 (1H, br d, J=16 Hz, C_8-H), 2.85 (1H, dd, J=6.5, 16 Hz, C_{10}-H), 3.33 (3H, s, OMe), 4.27 1H, ddt, J=2, 10, 4 Hz, C_7-H), 4.91 (1H, m, C_1-H). 12.6% NOE at $C_{6'}$-equatorial-H (2.35 ppm) was observed upon irradiation of C_1-H (4.91 ppm).

***rel*-(1*R*,6*R*)-5-Oxo-6-trifluoromethyl-2,4-dioxabicyclo[4.2.0]octane-3-spirocyclohexane (19)** Ethylene gas was bubbled into a solution of **1a** (236 mg, 1 mmol) in AcOEt (160 ml) for 5 min at −40 °C. The solution was irradiated under bubbling of ethylene for 20 min with a high-pressure Hg lamp. The residue obtained after evaporation of the solvent was chromatographed [hexane–AcOEt (5 : 1)] on silica gel to give **19** (117 mg, 44%) as colorless prisms, mp 43—44 °C (pentane). *Anal.* Calcd for $C_{12}H_{15}F_3O_3$: C, 54.55; H, 5.72. Found; C, 54.64; H, 5.90. IR ($CHCl_3$): 2950, 1740, 1355, 1310, 1185, 1170, 1150, 1115 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.0 (10H, m, CH_2 × 5, cyclohexyl), 2.04 (1H, m, CH_2), 2.54 (1H, m, CH_2), 2.64—2.77 (2H, m, CH_2), 4.72 (1H, ddd, J=1.5, 2.5, 6 Hz, C_1-H).

***rel*-(1*R*,2*R*)-2-Hydroxymethyl-2-trifluoromethyl-cyclobutan-1-ol (20)** Ethylene gas was bubbled into a solution of **1a** (236 mg, 1 mmol) in AcOEt (160 ml) for 5 min at −40 °C. The solution was irradiated under bubbling of ethylene for 20 min with a high-pressure Hg lamp. The residue obtained after evaporation of the solvent was dissolved in THF (4 ml). The solution was dropped into the mixture of $LiAlH_4$ (84 mg, 2.2 mmol) in THF (5 ml) at −30 °C over 30 min. The mixture was stirred for 30 min, then 5 drops of 50% NaOH and saturated NaCl were added and the whole was stirred at room temperature for 1 h. The solution was extracted with AcOEt and the organic layer was washed with saturated NaCl and dried over $MgSO_4$. Evaporation of the solvent *in vacuo* gave **20** (126 mg, 74%) as a colorless oil. High-resolution MS m/z: Calcd for $C_6H_9F_3O_2$[$(M+H)^+$]: 171.0633. Found: 171.0648. IR ($CHCl_3$): 3650, 3450, 2950, 2850, 1260, 1050 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.80 (1H, m, CH_2), 1.89 (1H, m, CH_2), 2.08 (1H, m, CH_2), 2.53 (1H, m, CH_2), 2.5 (1H, br s, OH), 2.7 (1H, br s, OH), 4.07 (1H, d, J=12 Hz, CH_2O), 4.10 (1H, d, J=12 Hz, CH_2O), 4.63 (1H, t, J=8 Hz, C_2-H).

[2+2]Photocycloaddition of 1a to Olefins (General Procedure) Argon was bubbled for 5 min into a solution of compound **1a** (71 mg, 0.3 mmol) and olefin (6 mmol) in a mixture of AcOEt (12 ml) and benzene (3 ml) and the solution was irradiated under condition b for 2 h. The residue obtained after evaporation of the solvent was purified by silica gel chromatography to give the adducts.

***rel*-(1*R*,2*S*,6*R*,7*R*)- and (1*R*,2*R*,6*S*,7*R*)-11-Oxo-1-trifluoromethyl-8,10-dioxa-tricyclo[5.4.0.0^{2,6}]undecane-9-spirocyclohexane (21 and 22)** The reaction mixture of **1a** and cyclopentene was chromatographed on silica gel [hexane–AcOEt (20 : 1)] to give a mixture of the two adducts (62 mg, 68%) (**21** : **22** = *ca.* 2 : 1). Separation of this mixture by MPLC [hexane–Et_2O (100 : 1)] gave first **21** (less polar; 38 mg, 42%) and then **22** (more polar; 14 mg, 15%) both as oils.

21: High-resolution MS m/z: Calcd for $C_{15}H_{20}F_3O_3$ [$(M+H)^+$]: 305.1364. Found: 305.1380. IR ($CHCl_3$): 2960, 1740, 1270, 1190, 1155 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.1 (16H, m, CH_2 × 8), 3.08 (1H, q, J=7.5 Hz, C_6-H), 3.18 (1H, br t, J=7.5 Hz, C_2-H), 4.70 (1H, dd, J=1.5, 7.5 Hz, C_7-H).

22: High-resolution MS m/z: Calcd for $C_{15}H_{20}F_3O_3$ [$(M+H)^+$]: 305.1364. Found: 305.1343. IR ($CHCl_3$): 2960, 1740, 1270, 1190 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.2 (16H, m, CH_2 × 8), 2.73 (1H, m, C_6-H), 3.31 (1H, br t, J=8 Hz, C_2-H), 4.47 (1H, d, J=3 Hz, C_7-H).

***rel*-(1*R*,6*R*,8*R*)- and (1*R*,6*R*,8*S*)-8-Acetoxy-5-oxo-6-trifluoromethyl-2,4-dioxabicyclo[4.2.0]octane-3-spirocyclohexane (*endo*-23 and *exo*-23)** The reaction mixture of **1a** and vinyl acetate was chromatographed [hexane–AcOEt (10 : 1)] on silica gel to give a mixture of adducts (73 mg, 76%) (the ratio of adducts was *ca.* 3 : 2 as judged from the ^{1}H-NMR spectrum). The mixture was crystallized from pentane to give *endo*-**23** as colorless prisms, mp 100—101 °C. The ^{1}H-NMR spectrum of the crude product obtained after the mother liquid showed the signals due to *exo*-**23** as the major component.

endo-**23**: *Anal.* Calcd for $C_{14}H_{17}F_3O_5$: C, 52.18; H, 5.32. Found: C, 52.42; H, 5.48. IR ($CHCl_3$): 2960, 1750, 1315, 1230 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.0 (10H, m, CH_2 × 5), 2.10 (3H, s, MeCO), 2.87 (1H, dd, J=8.5, 13.5 Hz, C_7-H), 3.08 (1H, ddd, J=3.5, 8.5, 13.5 Hz, C_7-H), 4.95 (1H, dd, J=3.5, 5 Hz, C_1-H), 5.07 (1H, m, C_8-H).

exo-**23**: ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.0 (10H, m, CH_2 × 5), 2.12 (3H, s, MeCO), 2.65 (1H, ddd, J=2.5, 4, 15 Hz, C_7-H), 3.10 (1H, dd, J=8.5, 15 Hz, C_7-H), 4.74 (1H, m, C_1-H), 4.91 (1H, ddd, J=15, 4, 8.5 Hz, C_8-H).

***rel*-(1*R*,6*R*,8*R*)- and (1*R*,6*R*,8*S*)-8-Ethoxy-5-oxo-6-trifluoromethyl-2,4-dioxabicyclo[4.2.0]octane-3-spirocyclohexane (*endo*-24 and *exo*-24)** The reaction mixture of **1a** and ethyl vinyl ether was chromatographed [hexane–AcOEt (20 : 1)] on silica gel to give first *exo*-**24** (21 mg, 23%, less polar) and then *endo*-**24** (30 mg, 32%, more polar), both as oils.

endo-**24**: High-resolution MS m/z: Calcd for $C_{14}H_{20}F_3O_4$ [$(M+H)^+$]: 309.1313. Found: 309.1290. IR ($CHCl_3$): 2960, 1745, 1310, 1190 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, J=7.5 Hz, $\underline{CH_3}CH_2$), 1.3—2.1 (10H, m, CH_2 × 5), 2.75 (1H, dd, J=9, 13 Hz, C_7-H), 3.01 (1H, ddd, J=3.5, 8, 13 Hz, C_7-H), 3.52 (1H, dq, J=10, 7.5 Hz, $CH_3\underline{CH_2}$), 3.57 (1H, dq, J=10, 7.5 Hz, $CH_3\underline{CH_2}$), 4.17 (1H, m, C_8-H), 4.82 (1H, t, J=3.5 Hz, C_1-H).

exo-**24**: High-resolution MS m/z: Calcd for $C_{14}H_{20}F_3O_4$ [$(M+H)^+$]: 309.1313. Found: 309.1307. IR ($CHCl_3$): 2960, 1750, 1310, 1160, 1120 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, J=7.5 Hz, $\underline{CH_3}CH_2$), 1.3—2.1 (10H, m, CH_2 × 5), 2.54 (1H, ddd, J=2.5, 5, 14 Hz, C_7-H), 2.91 (1H, dd, J=8, 14 Hz, C_7-H), 3.46—3.54 (2H, m, $CH_3\underline{CH_2}$), 3.89 (1H, ddd, J=2.5, 5, 8 Hz, C_8-H), 4.63 (1H, m, C_1-H).

References and Notes

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