Supporting information for

**Synthesis of fluorous ligand and its application for asymmetric
addition of dimethylzinc to aldehydes**

Yasser S. Sokeirik, Hiroyuki Mori, Masaaki Omote, Kazuyuki Sato, Atsushi Tarui,
Itsumaro Kumadaki, Akira Ando*
Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata,
573-0101 Japan
aando@pharm.setsunan.ac.jp

1. <i>General information</i>	S2
2. <i>Synthesis of ligand (1a)</i>	S3-S4
3. <i>General procedure for addition of dimethylzinc, and recycling of 1a</i>	S5
4. <i>Spectral data of products</i>	S6-S9
5. <i>X-ray analysis of 1a</i>	S10-S34
6. <i>References</i>	S35
7. <i>NMR charts</i>	S36-S5

1. General Information.

^1H NMR spectra were recorded on JNM-GX400 and JEOL-ECA-600SN spectrometers. Chemical Shifts are reported in ppm from tetramethylsilane as the internal standard. Data are reported as follows: chemical shifts, relative integration value, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra for new ligands were too complicated to assign due to coupling with fluorine, and not described. Mass spectra were obtained on JEOL JMS-700T spectrometers. Chromatographic purification was done with 230-400 mesh silica gel column. Analytical gas chromatography (GC) was performed on a Hitachi 3500 gas chromatograph with a flame ionization detector and split mode capillary injection system, using a TC-5 column (0.25 mm, 15 m, GL Sciences Inc.), or chiral column: GAMMA DEX 225TM (Spelco, 0.25 mm, 30 m). Peak areas were calculated on a Hitachi D-2500 Chromato-Integrator. Analytical high performance liquid chromatography (HPLC) was performed on a Jasco TRI-ROTAR-VITM liquid chromatograph equipped with a variable wavelength UV detector (Jasco UVIDEC-100-VI), using a Daicel ChiralcelTM OD-H column (0.46 cm I.D. $\times$ 25 cm) (Daicel Inc.) and HITACHI L-6000 pump system. Peak areas were calculated on a Shidazu C-R1BTM Chromato-Integrator. HPLC grade isopropanol and hexane were used as the eluting solvents. All the reactions were carried out under an argon atmosphere in flame-dried glassware using standard inert techniques for introducing reagents and solvents. All aldehydes were purified before use. Me_2Zn (1M in hexane) was purchased from Kanto. Titanium tetraisopropoxide was purchased from Wako and distilled before use. Hexane was distilled over P_2O_5 and stored over MS 4Å. Diethyl ether and toluene were distilled over benzophenone ketyl sodium just before use.

2. Synthesis of 1a.

1-((4*R*,5*R*)-2,2-dimethyl-5-(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-tetratriacontafluoro-9-hydroxyheptadecan-9-yl)-1,3-dioxolan-4-yl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononan-1-one
(1-((4*R*,5*R*)-2,2-dimethyl-5-(1-hydroxy-1,1-bis(perfluorooctyl)methyl-1,3-dioxolan-4-yl)perfluorononan-1-one (3**))**

To a vigorously stirred solution of EtMgBr (6.67 mL of 3 M solution, 20 mmol) in Et₂O (130 mL) at –65 °C was added slowly a solution of perfluorooctyl iodide (4.90 mL, 20 mmol) in Et₂O (20 mL). After the complete addition, the temperature was raised to –40 °C in 30 min. After the temperature reached –40 °C, a solution of dimethyl (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (**2**, 0.92 mL, 5 mmol) in Et₂O (20 mL) was added. After the temperature was raised further to –30 °C, the mixture was vigorously stirred for 4 h at the same temperature. After the reaction mixture was quenched with saturated NH₄Cl, the organic phase was separated, and the aqueous phase was extracted with Et₂O (3×30 mL). The combined organic phase was dried over anhydrous MgSO₄ and evaporated to give red oil, which was purified by silica gel column chromatography using an eluent system of 15% Et₂O in hexane to yield 5.02 g (71%, average of the best 3 trials) of **3** as a pale yellow solid. M.p. 35–36 °C. [α]_D –1.68 (c 2.6, Et₂O). ¹H NMR (CDCl₃, 600 MHz, 55 °C) δ: 5.31 (1H, d, *J* = 6.3 Hz), 5.16 (1H, d, *J* = 6.3 Hz), 3.72 (1H, s, disappeared with D₂O), 1.54 (3H, s), 1.33 (3H, s). IR (KBr) cm^{–1}: 3600, 1750. MS *m/z*: 1413 (M–1[–]). HRMS Calcd. for C₃₁H₈F₅₁O₄: 1412.9608 (M–1[–]). Found: 1412.9615.

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-tetratriacontaf luoro-9-((4*R*,5*S*)-5-((*S*)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-1-hydroxynonyl)-2,2-di methyl-1,3-dioxolan-4-yl)heptadecan-9-ol
((α'*S*,4*R*,5*S*)-2,2-dimethyl-α,α'-tris(perfluorooctyl)-1,3-dioxolane-4,5-dimethanol (1a**))**

A mixture of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (684 mg, 2 mmol) and compound **3** (1414 mg, 1 mmol) in Et_2O (6 mL) and CH_3OH (12 mL) at 0 °C was stirred for 15 min. To this solution was added NaBH_4 (144 mg, 4 mmol) portion wise, and the mixture was stirred for further 3 h at room temperature. Excess NaBH_4 was decomposed with acetone, and then the reaction mixture was quenched with NH_4Cl , and extracted with Et_2O . The Et_2O layer was dried over anhydrous MgSO_4 , and evaporated to give the crude product as an oily mass, which was crystallized from CHCl_3 to give **1a** (1034 mg, 73%) in a pure form as colorless crystals. Mp 79-81 °C. $[\alpha]_D -7.81$ (c 1.21, Et_2O). ^1H NMR (CDCl_3 , 600 MHz, 55° C) δ : 4.53 (1H, d, $J = 8.0$ Hz), 4.41 (1H, d, $J = 8.0$ Hz), 4.14-4.08 (1H, m), 3.54 (1H, s, disappeared with D_2O), 2.60 (1H, d, $J = 12.6$ Hz, disappeared with D_2O), 1.30 (3H, s) 1.28 (3H, s). IR (KBr) cm^{-1} : 3500. MS m/z : 1417 ($\text{M}+1^+$). HRMS Calcd. for $\text{C}_{31}\text{H}_{12}\text{F}_{51}\text{O}_4$: 1416.9921 ($\text{M}+1^+$). Found: 1416.9928.

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-tetratriacontafluoro-9-((4*R*,5*S*)-5-((*R*)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluoro-1-hydroxynonyl)-2,2-dimethyl-1,3-dioxolan-4-yl)heptadecan-9-ol
 ((α' *R*,4*R*,5*S*)-2,2-dimethyl- α,α,α' -tris(perfluorooctyl)-1,3-dioxolane-4,5-dimethanol (**1b**))

This isomer could not be obtained in pure form. It was obtained by evaporation of solvent from the above filtrate and identified as a mixture with isomer **1a** in 7:3 ratio by GLC. It also contains irremovable 1 equivalent to **1b** of diethylether. ^1H NMR (CDCl_3 , 600 MHz, 55° C) δ : 4.93 (1H, s, disappeared with D_2O), 4.51-4.48 (2H, m, 1H disappeared with D_2O), 4.01-3.97 (1H, m), 3.56-3.51 (1H, m), 1.29 (3H, s) 1.19 (3H, s).

3. General procedure for addition of dimethylzinc to aldehydes:

To a solution of **1a** (100 mg , 0.07 mmol) in dry hexane (10 mL) was added freshly distilled titanium tetrakisopropoxide (415 μ L, 1.40 mmol), and the mixture was stirred for 30 min at room temperature. To this mixture, Me₂Zn (3 mL of 1 M solution in hexane, 3 mmol) was added and the resulting mixture was stirred for additional 15 min. The mixture was cooled to -35 °C and an appropriate aldehyde (1.18 mmol) was added slowly. The mixture was kept stirring at this temperature and checked by GLC. After the peak of the starting aldehyde disappeared, the mixture was quenched with NH₄Cl, then the whole mixture was filtered through a sintered glass. The product was extracted with an appropriate solvent and purified by flash column chromatography. The ee is checked by chiral HPLC. Racemic α -methyl carbinols were prepared by the reaction of methylmagnesium bromide with the corresponding aldehydes and used to confirm the separation of the racemates by hplc. The absolute configuration of each product was estimated by the sign of optical rotation in literature.

Recycling of catalyst **1a**.

General procedure for recycling of ligand **1a** is as follows.

The residue obtained by evaporation of the solvent from the organic phase after work-up of the above reaction using benzaldehyde was treated with 2 mL toluene and cooled to -40 °C. The ligand (**1a**), which was precipitated as a white solid, was separated by filtration. The white solid was washed 2 times with cold toluene (2 mL each) to remove any impurities. After drying the solid, ligand (**1a**) was checked by GLC and ¹H NMR to determine the purity, and the weight was measured to check the yield of recycling. The ligand was used for the next cycle without further purification. The recovery of **1a**, yield and ee of the product were summarized in Table 2.

4. Spectral data of the products.

(*R*)-1-Phenylethanol (Entry 1, Table 1)

E.e. 96%. Yield 99%. $[\alpha]_D +42.92$ (c 1.04, CHCl_3). Lit.¹ (*R*)-1-phenylethanol $[\alpha]_D +45.2$ (c 1.01, CH_2Cl_2). ^1H NMR (CDCl_3) δ : 7.30-7.23 (4H, m), 7.21-7.15 (1H, m), 4.79 (1H, q, $J = 6.3$ Hz), 2.02 (1H, br s, disappeared with D_2O), 1.39 (3H, d, $J = 6.3$ Hz). ^{13}C NMR (CDCl_3) δ : 25.07, 70.26, 125.14, 127.19, 128.21, 145.52. MS m/z : 122 (M^+). HRMS Calcd. for $\text{C}_8\text{H}_{10}\text{O}$: 122.0732 (M^+). Found: 122.0736.

HPLC analysis: Column OD-H, hexane-isopropanol (95:5) 0.5 mL/min, retention time 16.17 min (*R*), 19.50 min (*S*).

(*R*)-1-(4-Methoxyphenyl)ethanol (Entry 2, Table 1)

E.e. 92%. Yield 95%, $[\alpha]_D +40.64$ (c 1.53, CHCl_3). Lit.² (*R*)-1-(4-methoxyphenyl)ethanol $[\alpha]_D +39.80$ (c 2.3, CHCl_3). ^1H NMR (CDCl_3) δ : 7.18(2H, d, $J = 8.3$ Hz), 6.76 (2H, d, $J = 8.3$ Hz), 4.71 (1H, q, $J = 6.3$ Hz), 3.69 (3H, s), 2.27 (1H, s, disappeared with D_2O), 1.36 (3H, d, $J = 6.3$ Hz). ^{13}C NMR (CDCl_3) δ : 24.15, 55.14, 69.92, 113.43, 126.53, 137.83, 158.95. MS m/z : 152 (M^+). HRMS Calcd. for $\text{C}_9\text{H}_{12}\text{O}_2$: 152.0837 (M^+). Found: 152.0840.

HPLC analysis: column OD-H, hexane-isopropanol (96:4) 0.4 mL/m, retention time 37.56 min (*R*), 41.96 min (*S*).

(*R*)-1-(4-(Trifluoromethyl)phenyl)ethanol (Entry 3, Table 1)

E.e. >99% Yield = 96%, $[\alpha]_D +24.14$ (c 1.41, CHCl_3). Lit.³ (*R*)-1-(4-(trifluoromethyl)phenyl)ethanol $[\alpha]_D +20.6$ (c 2.6, CHCl_3). ^1H NMR (CDCl_3) δ : 7.52(2H, d, $J = 8.3$ Hz), 7.40 (2H, d, $J = 8.3$ Hz), 4.87 (1H, q, $J = 6.3$ Hz), 2.11 (1H, br s, disappear with D_2O), 1.42 (3H, d, $J = 6.3$ Hz). ^{13}C NMR (CDCl_3) δ : 25.36, 69.69, 123.85 (q, $J = 271$ Hz), 125.20 (q, $J = 3.8$ Hz), 125.41, 129.3 (q, $J = 32.4$ Hz), 149.45. MS m/z : 190 (M^+). HRMS Calcd. for $\text{C}_9\text{H}_9\text{F}_3\text{O}$: 190.0605 (M^+). Found: 190.0610.

HPLC analysis: column OD-H, hexane-isopropanol (99:1) 1 mL/m, retention time 21.17 min (*R*). (*S*)-isomer was not observed.

(*R*)-1-(Naphthalen-2-yl)ethanol (Entry 4, Table 1)

E.e. = 95% Yield = 99%, $[\alpha]_D +37.77$ (c 1.04, CHCl_3). Lit.² (*R*)-1-(naphthalen-2-yl)ethanol $[\alpha]_D +38.1$ (c 1.5, CHCl_3). ^1H NMR (CDCl_3) δ : 7.84-7.78 (4H, m), 7.51-4.42 (3H, m), 5.05 (1H, q, $J = 6.3$ Hz), 2.00 (1H, s, disappeared with D_2O), 1.57 (3H, d, $J = 6.3$ Hz). ^{13}C NMR (CDCl_3) δ : 25.07, 70.37, 123.54, 123.56, 125.54, 125.89, 127.40, 127.67, 128.05, 132.63, 133.34, 142.87. MS m/z : 172

(M⁺). HRMS Calcd. for C₁₂H₁₂O: 172.0888 (M⁺). Found: 172.0881.

HPLC analysis: column OD-H, hexane-isopropanol (97.5:2.5) 0.6 mL/m, retention time 48.07 min (S), 51.27 min (R).

(R)-1-(2-Fluorophenyl)ethanol (Entry 5, Table 1)

E.e. = 89% Yield = 97%, [α]_D +36.61 (c 1.23, CHCl₃). Lit.⁴ (R)-1-(2-fluorophenyl)ethanol [α]_D +37.00 (c 1.2, CHCl₃), ¹H NMR (CDCl₃) δ : 7.47 (1H, dt, *J* = 7.8, 1.9 Hz), 7.26-7.18 (1H, m), 7.12 (1H, d, *J* = 7.8 Hz), 7.10-6.95 (1H, m), 5.16 (1H, q, *J* = 6.3 Hz), 2.54 (1H, s, disappeared with D₂O), 1.48 (3H, d, *J* = 6.3 Hz). ¹³C NMR (CDCl₃) δ : 23.93, 64.22, 115.01 (d, *J* = 22.0 Hz), 124.04 (d, *J* = 3.3 Hz), 127.07 (d, *J* = 5.0 Hz), 128.46 (d, *J* = 6.3 Hz), 132.43 (d, *J* = 13.3 Hz), 159.39 (d, *J* = 244.2 Hz). MS *m/z*: 140 (M⁺). HRMS Calcd. for C₈H₉FO: 140.0637 (M⁺). Found: 140.0638.

HPLC analysis: column OD-H, hexane-isopropanol, (99:1), 0.5 mL/m, retention time 32.17 min (R), 35.40 min (S).

(R)-1-(2-Chlorophenyl)ethanol (Entry 6, Table 1)

E.e. = 91% Yield = 97%, [α]_D +47.19 (c 1.53, CHCl₃). Lit.⁴ (R)-1-(2-chlorophenyl)ethanol [α]_D +48.6 (c 2.3, CHCl₃), ¹H NMR (CDCl₃) δ : 7.46 (1H, dd, *J* = 8.3, 1.9 Hz), 7.23-7.18 (2H, m), 7.08 (1H, td, *J* = 7.8, 1.9 Hz), 5.16 (1H, q, *J* = 6.3 Hz), 2.59 (1H, s, disappeared with D₂O), 1.36 (3H, d, *J* = 6.3 Hz). ¹³C NMR (CDCl₃) δ : 23.43, 66.75, 126.15, 126.92, 128.09, 129.09, 131.30, 142.78. MS *m/z*: 156 (M⁺). HRMS Calcd. for C₈H₉ClO: 156.0342 (M⁺). Found: 156.0346.

HPLC analysis: column OD-H, hexane-isopropanol (99:1) 0.6 mL/m, retention time 32.83 min (R), 36.50 min (S).

(R)-Nonan-2-ol (Entry 7, Table 1)

E.e. = 91% Yield = 98%, [α]_D -9.69 (c 1.7, CHCl₃). Lit.⁵ (R)-nonan-2-ol [α]_D -6.95 (c 1.1, CHCl₃), ¹H NMR (CDCl₃) δ : 3.71 (1H, sextet, *J* = 5.9 Hz), 1.84 (1H, s, disappeared with D₂O), 1.45-1.14 (12H, m), 1.10 (3H, d, *J* = 6.3 Hz), 0.81 (3H, t, *J* = 6.5 Hz). ¹³C NMR (CDCl₃) δ : 14.08, 22.66, 23.37, 25.79, 29.30, 29.68, 31.87, 39.48, 67.97. MS *m/z* for the dinitrobenzoate derivative: 338 (M⁺). HRMS Calcd. for C₁₆H₂₂N₂O₆: 338.1478 (M⁺). Found: 338.1482.

HPLC analysis performed on 3,5 dinitrobenzoate: column OD-H, hexane-isopropanol, (99:1) 0.5 mL/m, retention time 31.53 min (S), 36.73 min (R).

(R)-4-Phenylbutan-2-ol (Entry 8, Table 1)

334.1164.

HPLC analysis performed on 3,5 dinitrobenzoate: column OD-H, hexane-isopropanol, (95:5) 0.5 mL/min, retention time 43.34 min (*R*), 42.14 min (*S*).

(*R*)-1-(Furan-2-yl)ethanol (Entry 12, Table 1)

E.e. = 97%. Yield = 98%, $[\alpha]_D +7.86$ (c 0.9, CHCl_3). Lit.⁹ (*R*)-1-(furan-2-yl)ethanol $[\alpha]_D +15.5$ (c 2.02, CHCl_3), ^1H NMR (CDCl_3) δ : 7.38-7.35 (1H, m), 6.32 (1H, dd, $J = 3.4, 1.9$ Hz), 6.22 (1H, d, $J = 16.1$ Hz), 4.87 (1H, q, $J = 6.3$), 2.20 (1H, s, disappeared with D_2O), 1.54 (3H, d, $J = 6.3$ Hz), ^{13}C NMR (CDCl_3) δ : 21.35, 63.65, 105.03, 111.04, 141.77, 157.39. MS m/z : 112 (M^+). HRMS Calcd. for $\text{C}_6\text{H}_8\text{O}_2$: 112.0524 (M^+). Found: 112.0516.

HPLC analysis: column OD-H, detector setting is 220 nm, hexane-isopropanol (97.5:2.5) 0.3 mL/min, retention time 42.68 min (*R*), (*S*) not observed.

(*R*)-1-(Benzofuran-2-yl)ethanol (Entry 13, Table 1)

E.e. = 84% Yield = 99%, $[\alpha]_D +16.83$ (c 0.53, CHCl_3). Lit.¹⁰ (*R*)-1-(benzofuran-2-yl)ethanol $[\alpha]_D +19.9$ (c 1.21, CHCl_3), ^1H NMR (CDCl_3) δ : 7.41 (1H, dd, $J = 7.3, 1.4$ Hz), 7.33 (1H, d, $J = 8.3$ Hz), 7.17-7.07 (2H, m), 6.46 (1H, s), 4.87 (1H, q, $J = 6.3$ Hz), 2.20 (1H, s, disappeared with D_2O), 1.46 (3H, d, $J = 6.3$ Hz), ^{13}C NMR (CDCl_3) δ : 21.38, 63.77, 101.61, 111.23, 120.85, 121.07, 122.79, 127.88, 154.70, 160.01. MS m/z : 162 (M^+). HRMS Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_2$: 162.0681 (M^+). Found: 162.0686. MS m/z for the dinitrobenzoate derivative: 356 (M^+). HRMS Calcd. for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_7$: 356.0645 (M^+). Found: 356.0641.

HPLC analysis: column OD-H performed on 3,5 dinitrobenzoate, hexane-isopropanol (99:1) 0.5 mL/min, retention time 44.76 min (*S*), 51.56 min (*R*).

5. X-ray analysis of compound 1a: (This figure shows the relative configuration of **1a**. We started the synthesis from (*R,R*)-tartarate, and this figure shows the enantiomer of **1a**.)

Table 1. Crystal data and structure refinement for takab.

Identification code	takab	
Empirical formula	C31 H11 F51 O4	
Formula weight	1416.40	
Temperature	183(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 19.882(7) Å	α= 90°.
	b = 6.143(2) Å	β= 90.880(6)°.
	c = 36.399(12) Å	γ= 90°.
Volume	4445(3) Å ³	
Z	4	

Density (calculated)	2.116 Mg/m ³
Absorption coefficient	0.281 mm ⁻¹
F(000)	2752
Crystal size	0.30 x 0.08 x 0.05 mm ³
Theta range for data collection	0.56 to 28.22°.
Index ranges	-26<=h<=25, -7<=k<=8, -34<=l<=48
Reflections collected	13962
Independent reflections	5525 [R(int) = 0.0276]
Completeness to theta = 26.22°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9861 and 0.9205
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5525 / 1 / 777
Goodness-of-fit on F ²	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1605
R indices (all data)	R1 = 0.0710, wR2 = 0.1757
Largest diff. peak and hole	0.651 and -0.441 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for takab. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
F(1)	5707(1)	1281(5)	7957(1)	36(1)
F(2)	6088(1)	-602(5)	7498(1)	33(1)
F(3)	5170(1)	-4010(6)	7905(1)	42(1)
F(4)	4653(1)	-913(6)	7970(1)	42(1)
F(5)	4300(2)	-3384(7)	7400(1)	53(1)
F(6)	5292(1)	-3217(5)	7175(1)	40(1)
F(7)	4005(2)	494(7)	7308(1)	54(1)
F(8)	5026(2)	1677(5)	7314(1)	52(1)
F(9)	4276(2)	-1702(6)	6666(1)	57(1)
F(10)	5271(2)	-240(8)	6673(1)	64(1)
F(11)	3765(2)	2605(10)	6707(1)	90(2)
F(12)	4778(3)	3730(7)	6657(1)	85(2)
F(13)	3802(3)	543(9)	6080(1)	86(2)
F(14)	4852(3)	1130(10)	6025(1)	88(2)
F(15)	3602(3)	5059(10)	6099(2)	90(2)
F(16)	4019(4)	3713(11)	5612(1)	115(2)
F(17)	4611(3)	5523(10)	5986(2)	92(2)
F(18)	5468(1)	-1745(6)	8504(1)	43(1)
F(19)	6404(2)	-284(5)	8692(1)	40(1)
F(20)	5908(2)	-5686(5)	8572(1)	40(1)
F(21)	6947(1)	-4722(6)	8646(1)	40(1)
F(22)	5626(2)	-2998(7)	9188(1)	58(1)
F(23)	6710(2)	-2656(6)	9260(1)	56(1)
F(24)	5721(2)	-7350(7)	9230(1)	55(1)
F(25)	6806(2)	-7191(7)	9230(1)	50(1)
F(26)	5722(2)	-4779(8)	9850(1)	70(1)
F(27)	6819(2)	-4895(8)	9858(1)	68(1)
F(28)	5694(3)	-9217(9)	9873(1)	84(2)
F(29)	6760(3)	-9330(9)	9853(1)	80(2)
F(30)	5826(4)	-6604(11)	10495(1)	124(3)
F(31)	6881(3)	-7112(12)	10475(1)	110(2)

F(32)	5645(4)	-10992(16)	10535(2)	145(4)
F(33)	6302(4)	-9789(11)	10939(1)	125(3)
F(34)	6670(4)	-11506(11)	10490(2)	114(2)
F(35)	7013(2)	333(5)	6966(1)	41(1)
F(36)	7977(1)	1954(7)	7041(1)	45(1)
F(37)	6421(2)	4497(10)	7013(1)	82(2)
F(38)	7418(3)	5841(7)	6963(1)	79(2)
F(39)	6507(2)	2358(7)	6393(1)	71(1)
F(40)	7565(2)	3035(8)	6357(1)	64(1)
F(41)	6301(2)	6895(9)	6416(1)	77(2)
F(42)	7340(2)	7277(8)	6275(1)	73(1)
F(43)	6052(3)	4511(10)	5826(1)	95(2)
F(44)	7079(4)	4246(10)	5706(1)	105(2)
F(45)	6245(4)	9117(10)	5792(1)	130(3)
F(46)	7186(3)	8377(14)	5566(2)	126(3)
F(47)	6512(7)	5669(13)	5079(2)	179(5)
F(48)	5609(4)	6890(20)	5281(2)	187(6)
F(49)	5929(4)	8875(13)	4682(1)	134(3)
F(50)	6044(8)	10913(14)	5119(2)	219(7)
F(51)	6838(5)	9680(30)	4892(3)	267(10)
O(1)	7511(1)	-1425(6)	8279(1)	28(1)
O(2)	8064(1)	151(7)	7812(1)	33(1)
O(3)	6512(2)	-3865(6)	7942(1)	29(1)
O(4)	7569(2)	3968(6)	7674(1)	31(1)
C(1)	8151(2)	-516(8)	8184(1)	31(1)
C(2)	7013(2)	-277(8)	8073(1)	26(1)
C(3)	7369(2)	61(8)	7706(1)	25(1)
C(4)	8665(2)	-2308(10)	8203(2)	43(1)
C(5)	8320(3)	1406(11)	8427(2)	43(1)
C(6)	6389(2)	-1799(8)	8085(1)	26(1)
C(7)	5826(2)	-765(8)	7837(1)	27(1)
C(8)	5133(2)	-1951(9)	7782(1)	33(1)
C(9)	4845(2)	-2137(9)	7381(2)	35(1)
C(10)	4626(2)	48(9)	7197(1)	35(1)
C(11)	4629(2)	8(9)	6772(2)	36(1)
C(12)	4361(3)	2085(10)	6581(2)	42(1)

C(13)	4304(3)	1982(13)	6158(2)	54(2)
C(14)	4101(4)	4014(14)	5955(2)	63(2)
C(15)	6150(2)	-1950(8)	8497(1)	29(1)
C(16)	6314(2)	-4115(8)	8699(1)	30(1)
C(17)	6221(2)	-3933(9)	9125(1)	34(1)
C(18)	6254(2)	-6142(9)	9329(1)	34(1)
C(19)	6258(3)	-5931(10)	9755(1)	38(1)
C(20)	6250(3)	-8129(10)	9962(1)	42(1)
C(21)	6283(4)	-7949(12)	10381(2)	56(2)
C(22)	6219(5)	-10078(15)	10590(2)	72(2)
C(23)	7196(2)	2255(7)	7517(1)	24(1)
C(24)	7319(2)	2123(8)	7102(1)	26(1)
C(25)	7039(3)	4096(9)	6891(1)	36(1)
C(26)	6976(2)	3819(9)	6469(1)	34(1)
C(27)	6819(3)	5934(10)	6257(1)	38(1)
C(28)	6629(3)	5566(10)	5849(2)	45(1)
C(29)	6575(3)	7635(11)	5616(2)	50(1)
C(30)	6220(5)	7350(15)	5241(2)	69(2)
C(31)	6259(7)	9210(20)	4971(2)	94(3)

Table 3. Bond lengths [Å] and angles [°] for takab.

F(1)-C(7)	1.352(6)
F(2)-C(7)	1.349(5)
F(3)-C(8)	1.343(6)
F(4)-C(8)	1.345(6)
F(5)-C(9)	1.330(6)
F(6)-C(9)	1.347(6)
F(7)-C(10)	1.333(5)
F(8)-C(10)	1.341(6)
F(9)-C(11)	1.317(7)
F(10)-C(11)	1.340(6)
F(11)-C(12)	1.316(7)
F(12)-C(12)	1.334(8)
F(13)-C(13)	1.361(9)
F(14)-C(13)	1.309(8)
F(15)-C(14)	1.298(9)
F(16)-C(14)	1.272(8)
F(17)-C(14)	1.377(10)
F(18)-C(15)	1.361(5)
F(19)-C(15)	1.339(6)
F(20)-C(16)	1.338(6)
F(21)-C(16)	1.329(5)
F(22)-C(17)	1.339(6)
F(23)-C(17)	1.336(6)
F(24)-C(18)	1.340(6)
F(25)-C(18)	1.327(6)
F(26)-C(19)	1.329(7)
F(27)-C(19)	1.334(7)
F(28)-C(20)	1.328(7)
F(29)-C(20)	1.320(7)
F(30)-C(21)	1.301(9)
F(31)-C(21)	1.334(10)
F(32)-C(22)	1.285(12)
F(33)-C(22)	1.291(8)
F(34)-C(22)	1.310(11)

F(35)-C(24)	1.348(6)
F(36)-C(24)	1.335(5)
F(37)-C(25)	1.336(6)
F(38)-C(25)	1.333(7)
F(39)-C(26)	1.320(7)
F(40)-C(26)	1.337(6)
F(41)-C(27)	1.327(7)
F(42)-C(27)	1.324(7)
F(43)-C(28)	1.319(8)
F(44)-C(28)	1.320(8)
F(45)-C(29)	1.298(9)
F(46)-C(29)	1.312(8)
F(47)-C(30)	1.327(12)
F(48)-C(30)	1.259(11)
F(49)-C(31)	1.250(11)
F(50)-C(31)	1.254(15)
F(51)-C(31)	1.226(14)
O(1)-C(2)	1.421(5)
O(1)-C(1)	1.437(5)
O(2)-C(1)	1.424(6)
O(2)-C(3)	1.430(5)
O(3)-C(6)	1.395(6)
O(4)-C(23)	1.404(5)
C(1)-C(4)	1.503(7)
C(1)-C(5)	1.509(7)
C(2)-C(3)	1.538(6)
C(2)-C(6)	1.554(6)
C(2)-H(2)	1.0000
C(3)-C(23)	1.549(6)
C(3)-H(3)	1.0000
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800

C(6)-C(7)	1.561(6)
C(6)-C(15)	1.585(6)
C(7)-C(8)	1.569(6)
C(8)-C(9)	1.562(7)
C(9)-C(10)	1.559(8)
C(10)-C(11)	1.550(7)
C(11)-C(12)	1.543(8)
C(12)-C(13)	1.541(9)
C(13)-C(14)	1.503(11)
C(15)-C(16)	1.552(7)
C(16)-C(17)	1.569(6)
C(17)-C(18)	1.547(7)
C(18)-C(19)	1.554(7)
C(19)-C(20)	1.547(8)
C(20)-C(21)	1.530(8)
C(21)-C(22)	1.519(11)
C(23)-C(24)	1.535(6)
C(23)-H(23)	1.0000
C(24)-C(25)	1.536(7)
C(25)-C(26)	1.547(7)
C(26)-C(27)	1.540(7)
C(27)-C(28)	1.546(7)
C(28)-C(29)	1.531(9)
C(29)-C(30)	1.536(9)
C(30)-C(31)	1.509(12)

C(2)-O(1)-C(1)	107.0(3)
C(1)-O(2)-C(3)	110.4(3)
O(2)-C(1)-O(1)	104.3(3)
O(2)-C(1)-C(4)	109.0(4)
O(1)-C(1)-C(4)	108.0(4)
O(2)-C(1)-C(5)	110.8(4)
O(1)-C(1)-C(5)	110.6(4)
C(4)-C(1)-C(5)	113.7(4)
O(1)-C(2)-C(3)	101.5(3)
O(1)-C(2)-C(6)	103.8(4)

C(3)-C(2)-C(6)	118.9(4)
O(1)-C(2)-H(2)	110.6
C(3)-C(2)-H(2)	110.6
C(6)-C(2)-H(2)	110.6
O(2)-C(3)-C(2)	103.1(3)
O(2)-C(3)-C(23)	107.1(4)
C(2)-C(3)-C(23)	113.6(4)
O(2)-C(3)-H(3)	110.9
C(2)-C(3)-H(3)	110.9
C(23)-C(3)-H(3)	110.9
C(1)-C(4)-H(4A)	109.5
C(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(1)-C(5)-H(5A)	109.5
C(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
O(3)-C(6)-C(2)	113.2(3)
O(3)-C(6)-C(7)	106.5(4)
C(2)-C(6)-C(7)	107.8(4)
O(3)-C(6)-C(15)	110.9(4)
C(2)-C(6)-C(15)	108.1(4)
C(7)-C(6)-C(15)	110.4(3)
F(2)-C(7)-F(1)	107.3(4)
F(2)-C(7)-C(6)	105.9(3)
F(1)-C(7)-C(6)	108.6(4)
F(2)-C(7)-C(8)	105.5(4)
F(1)-C(7)-C(8)	108.4(4)
C(6)-C(7)-C(8)	120.4(4)
F(3)-C(8)-F(4)	108.1(4)
F(3)-C(8)-C(9)	105.0(4)

F(4)-C(8)-C(9)	105.0(4)
F(3)-C(8)-C(7)	110.6(4)
F(4)-C(8)-C(7)	110.0(4)
C(9)-C(8)-C(7)	117.5(4)
F(5)-C(9)-F(6)	106.9(4)
F(5)-C(9)-C(10)	107.2(4)
F(6)-C(9)-C(10)	111.5(4)
F(5)-C(9)-C(8)	106.3(4)
F(6)-C(9)-C(8)	108.7(4)
C(10)-C(9)-C(8)	115.7(4)
F(7)-C(10)-F(8)	107.3(5)
F(7)-C(10)-C(11)	108.9(4)
F(8)-C(10)-C(11)	108.4(4)
F(7)-C(10)-C(9)	107.5(4)
F(8)-C(10)-C(9)	110.3(4)
C(11)-C(10)-C(9)	114.2(4)
F(9)-C(11)-F(10)	109.7(5)
F(9)-C(11)-C(12)	110.4(4)
F(10)-C(11)-C(12)	107.3(5)
F(9)-C(11)-C(10)	107.1(5)
F(10)-C(11)-C(10)	106.8(4)
C(12)-C(11)-C(10)	115.5(4)
F(11)-C(12)-F(12)	107.7(6)
F(11)-C(12)-C(13)	107.7(5)
F(12)-C(12)-C(13)	106.0(6)
F(11)-C(12)-C(11)	110.5(5)
F(12)-C(12)-C(11)	108.8(4)
C(13)-C(12)-C(11)	115.8(5)
F(14)-C(13)-F(13)	106.0(6)
F(14)-C(13)-C(14)	111.7(6)
F(13)-C(13)-C(14)	104.2(6)
F(14)-C(13)-C(12)	109.6(5)
F(13)-C(13)-C(12)	106.2(5)
C(14)-C(13)-C(12)	118.1(6)
F(16)-C(14)-F(15)	112.5(7)
F(16)-C(14)-F(17)	105.1(7)

F(15)-C(14)-F(17)	101.6(7)
F(16)-C(14)-C(13)	113.1(7)
F(15)-C(14)-C(13)	114.4(6)
F(17)-C(14)-C(13)	109.1(6)
F(19)-C(15)-F(18)	106.7(4)
F(19)-C(15)-C(16)	109.2(4)
F(18)-C(15)-C(16)	105.9(4)
F(19)-C(15)-C(6)	109.9(4)
F(18)-C(15)-C(6)	108.9(4)
C(16)-C(15)-C(6)	115.8(4)
F(21)-C(16)-F(20)	108.4(4)
F(21)-C(16)-C(15)	111.3(4)
F(20)-C(16)-C(15)	109.4(4)
F(21)-C(16)-C(17)	106.9(4)
F(20)-C(16)-C(17)	108.4(4)
C(15)-C(16)-C(17)	112.4(4)
F(23)-C(17)-F(22)	109.0(5)
F(23)-C(17)-C(18)	108.3(4)
F(22)-C(17)-C(18)	109.0(4)
F(23)-C(17)-C(16)	107.9(4)
F(22)-C(17)-C(16)	108.5(4)
C(18)-C(17)-C(16)	114.0(4)
F(25)-C(18)-F(24)	108.1(5)
F(25)-C(18)-C(17)	108.9(4)
F(24)-C(18)-C(17)	109.2(4)
F(25)-C(18)-C(19)	108.7(4)
F(24)-C(18)-C(19)	107.9(4)
C(17)-C(18)-C(19)	113.9(4)
F(26)-C(19)-F(27)	110.0(6)
F(26)-C(19)-C(20)	108.9(4)
F(27)-C(19)-C(20)	107.0(5)
F(26)-C(19)-C(18)	108.2(4)
F(27)-C(19)-C(18)	108.2(4)
C(20)-C(19)-C(18)	114.5(5)
F(29)-C(20)-F(28)	106.6(6)
F(29)-C(20)-C(21)	108.5(5)

F(28)-C(20)-C(21)	107.6(5)
F(29)-C(20)-C(19)	109.1(5)
F(28)-C(20)-C(19)	109.5(5)
C(21)-C(20)-C(19)	115.0(5)
F(30)-C(21)-F(31)	107.3(8)
F(30)-C(21)-C(22)	108.8(7)
F(31)-C(21)-C(22)	106.6(6)
F(30)-C(21)-C(20)	110.1(6)
F(31)-C(21)-C(20)	107.9(6)
C(22)-C(21)-C(20)	115.7(6)
F(32)-C(22)-F(33)	108.3(8)
F(32)-C(22)-F(34)	105.9(9)
F(33)-C(22)-F(34)	106.7(7)
F(32)-C(22)-C(21)	112.3(7)
F(33)-C(22)-C(21)	111.3(7)
F(34)-C(22)-C(21)	112.0(7)
O(4)-C(23)-C(24)	110.4(4)
O(4)-C(23)-C(3)	111.0(3)
C(24)-C(23)-C(3)	110.6(4)
O(4)-C(23)-H(23)	108.2
C(24)-C(23)-H(23)	108.2
C(3)-C(23)-H(23)	108.2
F(36)-C(24)-F(35)	108.3(4)
F(36)-C(24)-C(23)	109.8(3)
F(35)-C(24)-C(23)	109.1(4)
F(36)-C(24)-C(25)	109.1(4)
F(35)-C(24)-C(25)	107.5(4)
C(23)-C(24)-C(25)	112.9(4)
F(38)-C(25)-F(37)	107.8(5)
F(38)-C(25)-C(24)	109.7(4)
F(37)-C(25)-C(24)	107.8(4)
F(38)-C(25)-C(26)	108.7(4)
F(37)-C(25)-C(26)	106.9(4)
C(24)-C(25)-C(26)	115.7(4)
F(39)-C(26)-F(40)	108.0(5)
F(39)-C(26)-C(27)	109.4(4)

F(40)-C(26)-C(27)	108.7(4)
F(39)-C(26)-C(25)	109.2(4)
F(40)-C(26)-C(25)	106.6(4)
C(27)-C(26)-C(25)	114.6(4)
F(42)-C(27)-F(41)	108.3(6)
F(42)-C(27)-C(26)	110.4(4)
F(41)-C(27)-C(26)	108.0(4)
F(42)-C(27)-C(28)	108.5(5)
F(41)-C(27)-C(28)	107.6(5)
C(26)-C(27)-C(28)	113.8(5)
F(44)-C(28)-F(43)	105.5(6)
F(44)-C(28)-C(29)	109.6(5)
F(43)-C(28)-C(29)	108.6(5)
F(44)-C(28)-C(27)	108.2(5)
F(43)-C(28)-C(27)	109.4(5)
C(29)-C(28)-C(27)	115.2(5)
F(45)-C(29)-F(46)	107.5(8)
F(45)-C(29)-C(28)	110.0(5)
F(46)-C(29)-C(28)	107.9(6)
F(45)-C(29)-C(30)	106.8(6)
F(46)-C(29)-C(30)	109.3(6)
C(28)-C(29)-C(30)	115.2(6)
F(48)-C(30)-F(47)	107.8(11)
F(48)-C(30)-C(31)	107.8(9)
F(47)-C(30)-C(31)	105.9(8)
F(48)-C(30)-C(29)	110.7(7)
F(47)-C(30)-C(29)	106.6(7)
C(31)-C(30)-C(29)	117.7(8)
F(51)-C(31)-F(49)	108.7(10)
F(51)-C(31)-F(50)	103.5(14)
F(49)-C(31)-F(50)	108.8(12)
F(51)-C(31)-C(30)	112.9(11)
F(49)-C(31)-C(30)	113.2(10)
F(50)-C(31)-C(30)	109.4(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for takab. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	40(2)	22(1)	45(2)	-3(1)	-7(1)	4(1)
F(2)	28(1)	41(2)	31(1)	3(1)	-1(1)	-9(1)
F(3)	30(1)	30(2)	66(2)	14(2)	-3(1)	-6(1)
F(4)	25(1)	52(2)	49(2)	8(2)	8(1)	8(1)
F(5)	30(1)	54(2)	74(2)	7(2)	-12(1)	-17(2)
F(6)	38(1)	28(2)	53(2)	-11(1)	-5(1)	4(1)
F(7)	41(2)	74(3)	47(2)	8(2)	8(1)	26(2)
F(8)	66(2)	27(2)	61(2)	-3(2)	-27(2)	-1(2)
F(9)	77(2)	38(2)	56(2)	-8(2)	-14(2)	-15(2)
F(10)	46(2)	74(3)	72(2)	15(2)	21(2)	20(2)
F(11)	86(3)	117(5)	66(2)	31(3)	24(2)	67(3)
F(12)	141(4)	35(2)	78(3)	-3(2)	-49(3)	-15(3)
F(13)	121(4)	69(3)	66(3)	0(2)	-28(3)	-30(3)
F(14)	117(4)	96(4)	53(2)	-1(3)	22(2)	48(3)
F(15)	95(3)	78(3)	98(3)	21(3)	4(3)	37(3)
F(16)	217(7)	77(4)	49(2)	3(3)	-19(3)	14(5)
F(17)	108(4)	76(4)	91(3)	18(3)	-6(3)	-16(3)
F(18)	30(1)	57(2)	43(2)	12(2)	11(1)	14(1)
F(19)	64(2)	26(2)	30(1)	-5(1)	10(1)	-1(1)
F(20)	53(2)	32(2)	34(1)	1(1)	0(1)	-9(1)
F(21)	35(1)	41(2)	43(2)	11(1)	11(1)	13(1)
F(22)	68(2)	66(3)	41(2)	15(2)	19(2)	35(2)
F(23)	90(3)	38(2)	41(2)	3(2)	-14(2)	-23(2)
F(24)	66(2)	60(3)	38(2)	7(2)	-6(2)	-28(2)
F(25)	60(2)	48(2)	43(2)	7(2)	13(2)	19(2)
F(26)	98(3)	73(3)	40(2)	10(2)	21(2)	44(3)
F(27)	82(3)	75(3)	45(2)	9(2)	-16(2)	-40(3)
F(28)	107(3)	83(4)	62(2)	32(2)	-26(2)	-54(3)
F(29)	119(4)	72(3)	49(2)	16(2)	19(2)	51(3)
F(30)	228(8)	103(5)	42(2)	22(3)	41(3)	90(5)
F(31)	147(5)	114(5)	67(3)	29(3)	-49(3)	-58(5)

F(32)	122(5)	186(8)	128(5)	101(6)	-17(4)	-65(6)
F(33)	264(8)	79(4)	31(2)	12(2)	-5(3)	23(5)
F(34)	183(7)	79(4)	80(3)	29(3)	14(4)	52(4)
F(35)	65(2)	30(2)	29(1)	-2(1)	-2(1)	-7(2)
F(36)	28(1)	68(2)	39(2)	9(2)	8(1)	14(2)
F(37)	71(2)	130(5)	47(2)	33(2)	22(2)	73(3)
F(38)	156(5)	29(2)	49(2)	5(2)	-34(2)	-20(2)
F(39)	100(3)	57(3)	54(2)	23(2)	-35(2)	-41(2)
F(40)	74(2)	79(3)	39(2)	14(2)	21(2)	45(2)
F(41)	99(3)	89(4)	43(2)	15(2)	12(2)	63(3)
F(42)	100(3)	55(2)	63(2)	24(2)	-32(2)	-32(3)
F(43)	105(3)	108(5)	71(3)	47(3)	-44(2)	-56(3)
F(44)	185(6)	96(4)	33(2)	-1(2)	7(2)	76(4)
F(45)	264(9)	73(4)	53(3)	4(3)	-11(4)	92(5)
F(46)	108(4)	168(7)	103(4)	85(5)	-32(3)	-66(5)
F(47)	380(15)	96(5)	58(3)	-20(3)	-74(5)	77(8)
F(48)	131(5)	293(14)	133(5)	137(8)	-80(5)	-92(8)
F(49)	240(8)	97(5)	63(3)	29(3)	-64(4)	-15(6)
F(50)	490(20)	71(5)	87(5)	20(4)	-80(8)	48(9)
F(51)	170(8)	450(30)	175(9)	223(14)	-33(6)	-99(12)
O(1)	23(1)	30(2)	32(2)	5(1)	-3(1)	-2(1)
O(2)	21(1)	43(2)	34(2)	4(2)	1(1)	2(1)
O(3)	32(2)	22(2)	33(2)	-5(1)	6(1)	0(1)
O(4)	32(2)	24(2)	37(2)	-5(1)	0(1)	-4(1)
C(1)	27(2)	28(2)	37(2)	1(2)	0(2)	-2(2)
C(2)	26(2)	22(2)	29(2)	0(2)	-2(2)	1(2)
C(3)	21(2)	22(2)	32(2)	1(2)	-2(2)	0(2)
C(4)	33(2)	36(3)	58(3)	7(3)	-6(2)	4(2)
C(5)	37(3)	42(3)	49(3)	-7(3)	-4(2)	-10(2)
C(6)	24(2)	24(2)	29(2)	-3(2)	4(2)	0(2)
C(7)	30(2)	21(2)	31(2)	3(2)	3(2)	-1(2)
C(8)	24(2)	27(2)	48(3)	3(2)	3(2)	5(2)
C(9)	21(2)	33(3)	50(3)	-5(2)	-1(2)	-2(2)
C(10)	26(2)	35(3)	43(3)	-5(2)	-5(2)	4(2)
C(11)	34(2)	30(3)	46(3)	-4(2)	-2(2)	5(2)
C(12)	45(3)	35(3)	47(3)	-6(2)	-6(2)	9(2)

C(13)	64(4)	49(4)	49(3)	-4(3)	2(3)	4(3)
C(14)	85(5)	54(4)	50(4)	0(3)	-5(3)	6(4)
C(15)	30(2)	27(2)	30(2)	1(2)	6(2)	6(2)
C(16)	30(2)	31(2)	28(2)	3(2)	4(2)	2(2)
C(17)	37(2)	32(3)	33(2)	-3(2)	4(2)	4(2)
C(18)	37(2)	32(3)	32(2)	-1(2)	1(2)	-3(2)
C(19)	44(3)	34(3)	35(2)	3(2)	3(2)	-2(2)
C(20)	52(3)	41(3)	33(3)	7(2)	-2(2)	3(3)
C(21)	87(5)	51(4)	29(3)	-1(3)	0(3)	13(4)
C(22)	117(7)	60(5)	40(3)	14(3)	0(4)	8(5)
C(23)	21(2)	19(2)	31(2)	-2(2)	-1(2)	-2(2)
C(24)	25(2)	21(2)	32(2)	0(2)	0(2)	5(2)
C(25)	41(3)	31(3)	35(2)	2(2)	4(2)	12(2)
C(26)	34(2)	29(3)	38(2)	3(2)	2(2)	5(2)
C(27)	43(3)	35(3)	34(2)	3(2)	-1(2)	6(2)
C(28)	59(3)	35(3)	39(3)	3(2)	-3(2)	0(3)
C(29)	66(4)	42(3)	42(3)	7(3)	-1(3)	-5(3)
C(30)	98(6)	60(5)	49(4)	7(4)	-17(4)	-3(5)
C(31)	153(10)	80(7)	50(4)	32(5)	-13(5)	-17(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for takab.

	x	y	z	U(eq)
H(2)	6912	1154	8191	31
H(3)	7281	-1188	7535	30
H(4A)	8530	-3485	8035	64
H(4B)	8696	-2870	8454	64
H(4C)	9104	-1737	8130	64
H(5A)	8750	2032	8353	64
H(5B)	8353	927	8683	64
H(5C)	7965	2508	8402	64
H(23)	6707	2559	7554	28

Table 6. Torsion angles [°] for takab.

C(3)-O(2)-C(1)-O(1)	11.1(5)
C(3)-O(2)-C(1)-C(4)	126.2(4)
C(3)-O(2)-C(1)-C(5)	-107.9(4)
C(2)-O(1)-C(1)-O(2)	-31.4(5)
C(2)-O(1)-C(1)-C(4)	-147.3(4)
C(2)-O(1)-C(1)-C(5)	87.7(5)
C(1)-O(1)-C(2)-C(3)	37.6(4)
C(1)-O(1)-C(2)-C(6)	161.5(3)
C(1)-O(2)-C(3)-C(2)	11.3(5)
C(1)-O(2)-C(3)-C(23)	131.4(4)
O(1)-C(2)-C(3)-O(2)	-29.4(4)
C(6)-C(2)-C(3)-O(2)	-142.3(4)
O(1)-C(2)-C(3)-C(23)	-144.9(3)
C(6)-C(2)-C(3)-C(23)	102.2(5)
O(1)-C(2)-C(6)-O(3)	-58.0(4)
C(3)-C(2)-C(6)-O(3)	53.7(5)
O(1)-C(2)-C(6)-C(7)	-175.4(3)
C(3)-C(2)-C(6)-C(7)	-63.8(5)
O(1)-C(2)-C(6)-C(15)	65.2(4)
C(3)-C(2)-C(6)-C(15)	176.9(4)
O(3)-C(6)-C(7)-F(2)	-62.7(4)
C(2)-C(6)-C(7)-F(2)	59.0(4)
C(15)-C(6)-C(7)-F(2)	176.9(4)
O(3)-C(6)-C(7)-F(1)	-177.7(3)
C(2)-C(6)-C(7)-F(1)	-56.0(4)
C(15)-C(6)-C(7)-F(1)	61.9(5)
O(3)-C(6)-C(7)-C(8)	56.6(5)
C(2)-C(6)-C(7)-C(8)	178.3(4)
C(15)-C(6)-C(7)-C(8)	-63.8(5)
F(2)-C(7)-C(8)-F(3)	106.8(4)
F(1)-C(7)-C(8)-F(3)	-138.6(4)
C(6)-C(7)-C(8)-F(3)	-12.7(6)
F(2)-C(7)-C(8)-F(4)	-133.8(4)
F(1)-C(7)-C(8)-F(4)	-19.1(5)

C(6)-C(7)-C(8)-F(4)	106.7(5)
F(2)-C(7)-C(8)-C(9)	-13.8(5)
F(1)-C(7)-C(8)-C(9)	100.9(5)
C(6)-C(7)-C(8)-C(9)	-133.3(4)
F(3)-C(8)-C(9)-F(5)	50.2(5)
F(4)-C(8)-C(9)-F(5)	-63.7(5)
C(7)-C(8)-C(9)-F(5)	173.6(4)
F(3)-C(8)-C(9)-F(6)	-64.5(5)
F(4)-C(8)-C(9)-F(6)	-178.4(4)
C(7)-C(8)-C(9)-F(6)	58.9(6)
F(3)-C(8)-C(9)-C(10)	169.1(4)
F(4)-C(8)-C(9)-C(10)	55.2(5)
C(7)-C(8)-C(9)-C(10)	-67.4(5)
F(5)-C(9)-C(10)-F(7)	35.1(6)
F(6)-C(9)-C(10)-F(7)	151.8(4)
C(8)-C(9)-C(10)-F(7)	-83.3(5)
F(5)-C(9)-C(10)-F(8)	151.8(4)
F(6)-C(9)-C(10)-F(8)	-91.5(5)
C(8)-C(9)-C(10)-F(8)	33.4(6)
F(5)-C(9)-C(10)-C(11)	-85.8(5)
F(6)-C(9)-C(10)-C(11)	30.9(5)
C(8)-C(9)-C(10)-C(11)	155.8(4)
F(7)-C(10)-C(11)-F(9)	-68.2(6)
F(8)-C(10)-C(11)-F(9)	175.3(4)
C(9)-C(10)-C(11)-F(9)	51.9(5)
F(7)-C(10)-C(11)-F(10)	174.3(5)
F(8)-C(10)-C(11)-F(10)	57.9(6)
C(9)-C(10)-C(11)-F(10)	-65.5(6)
F(7)-C(10)-C(11)-C(12)	55.2(6)
F(8)-C(10)-C(11)-C(12)	-61.3(5)
C(9)-C(10)-C(11)-C(12)	175.3(4)
F(9)-C(11)-C(12)-F(11)	69.6(6)
F(10)-C(11)-C(12)-F(11)	-170.9(5)
C(10)-C(11)-C(12)-F(11)	-52.0(7)
F(9)-C(11)-C(12)-F(12)	-172.4(5)
F(10)-C(11)-C(12)-F(12)	-52.9(6)

C(10)-C(11)-C(12)-F(12)	66.0(6)
F(9)-C(11)-C(12)-C(13)	-53.2(7)
F(10)-C(11)-C(12)-C(13)	66.3(6)
C(10)-C(11)-C(12)-C(13)	-174.8(5)
F(11)-C(12)-C(13)-F(14)	-169.8(7)
F(12)-C(12)-C(13)-F(14)	75.2(7)
C(11)-C(12)-C(13)-F(14)	-45.5(8)
F(11)-C(12)-C(13)-F(13)	-55.7(7)
F(12)-C(12)-C(13)-F(13)	-170.7(6)
C(11)-C(12)-C(13)-F(13)	68.6(7)
F(11)-C(12)-C(13)-C(14)	60.7(8)
F(12)-C(12)-C(13)-C(14)	-54.3(8)
C(11)-C(12)-C(13)-C(14)	-175.0(6)
F(14)-C(13)-C(14)-F(16)	56.5(10)
F(13)-C(13)-C(14)-F(16)	-57.5(9)
C(12)-C(13)-C(14)-F(16)	-175.0(7)
F(14)-C(13)-C(14)-F(15)	-173.0(7)
F(13)-C(13)-C(14)-F(15)	73.0(8)
C(12)-C(13)-C(14)-F(15)	-44.5(10)
F(14)-C(13)-C(14)-F(17)	-60.1(8)
F(13)-C(13)-C(14)-F(17)	-174.0(6)
C(12)-C(13)-C(14)-F(17)	68.5(8)
O(3)-C(6)-C(15)-F(19)	143.3(4)
C(2)-C(6)-C(15)-F(19)	18.7(5)
C(7)-C(6)-C(15)-F(19)	-98.9(4)
O(3)-C(6)-C(15)-F(18)	-100.1(4)
C(2)-C(6)-C(15)-F(18)	135.3(4)
C(7)-C(6)-C(15)-F(18)	17.6(5)
O(3)-C(6)-C(15)-C(16)	19.0(5)
C(2)-C(6)-C(15)-C(16)	-105.6(4)
C(7)-C(6)-C(15)-C(16)	136.7(4)
F(19)-C(15)-C(16)-F(21)	-78.4(5)
F(18)-C(15)-C(16)-F(21)	167.1(4)
C(6)-C(15)-C(16)-F(21)	46.3(5)
F(19)-C(15)-C(16)-F(20)	161.9(4)
F(18)-C(15)-C(16)-F(20)	47.4(5)

C(6)-C(15)-C(16)-F(20)	-73.4(5)
F(19)-C(15)-C(16)-C(17)	41.6(5)
F(18)-C(15)-C(16)-C(17)	-73.0(5)
C(6)-C(15)-C(16)-C(17)	166.2(4)
F(21)-C(16)-C(17)-F(23)	52.4(5)
F(20)-C(16)-C(17)-F(23)	169.0(4)
C(15)-C(16)-C(17)-F(23)	-70.1(5)
F(21)-C(16)-C(17)-F(22)	170.4(4)
F(20)-C(16)-C(17)-F(22)	-73.0(5)
C(15)-C(16)-C(17)-F(22)	47.9(6)
F(21)-C(16)-C(17)-C(18)	-68.0(5)
F(20)-C(16)-C(17)-C(18)	48.6(5)
C(15)-C(16)-C(17)-C(18)	169.6(4)
F(23)-C(17)-C(18)-F(25)	-69.4(5)
F(22)-C(17)-C(18)-F(25)	172.1(4)
C(16)-C(17)-C(18)-F(25)	50.8(5)
F(23)-C(17)-C(18)-F(24)	172.7(4)
F(22)-C(17)-C(18)-F(24)	54.2(5)
C(16)-C(17)-C(18)-F(24)	-67.1(5)
F(23)-C(17)-C(18)-C(19)	52.1(6)
F(22)-C(17)-C(18)-C(19)	-66.4(5)
C(16)-C(17)-C(18)-C(19)	172.2(4)
F(25)-C(18)-C(19)-F(26)	176.8(5)
F(24)-C(18)-C(19)-F(26)	-66.2(6)
C(17)-C(18)-C(19)-F(26)	55.1(6)
F(25)-C(18)-C(19)-F(27)	57.6(6)
F(24)-C(18)-C(19)-F(27)	174.6(5)
C(17)-C(18)-C(19)-F(27)	-64.0(6)
F(25)-C(18)-C(19)-C(20)	-61.7(6)
F(24)-C(18)-C(19)-C(20)	55.4(6)
C(17)-C(18)-C(19)-C(20)	176.7(4)
F(26)-C(19)-C(20)-F(29)	176.5(5)
F(27)-C(19)-C(20)-F(29)	-64.6(6)
C(18)-C(19)-C(20)-F(29)	55.3(7)
F(26)-C(19)-C(20)-F(28)	60.1(6)
F(27)-C(19)-C(20)-F(28)	179.0(5)

C(18)-C(19)-C(20)-F(28)	-61.1(6)
F(26)-C(19)-C(20)-C(21)	-61.2(7)
F(27)-C(19)-C(20)-C(21)	57.6(7)
C(18)-C(19)-C(20)-C(21)	177.6(5)
F(29)-C(20)-C(21)-F(30)	173.9(7)
F(28)-C(20)-C(21)-F(30)	-71.1(8)
C(19)-C(20)-C(21)-F(30)	51.3(9)
F(29)-C(20)-C(21)-F(31)	57.0(8)
F(28)-C(20)-C(21)-F(31)	172.1(6)
C(19)-C(20)-C(21)-F(31)	-65.5(8)
F(29)-C(20)-C(21)-C(22)	-62.2(9)
F(28)-C(20)-C(21)-C(22)	52.8(8)
C(19)-C(20)-C(21)-C(22)	175.2(7)
F(30)-C(21)-C(22)-F(32)	61.5(10)
F(31)-C(21)-C(22)-F(32)	176.9(8)
C(20)-C(21)-C(22)-F(32)	-63.1(10)
F(30)-C(21)-C(22)-F(33)	-60.1(11)
F(31)-C(21)-C(22)-F(33)	55.3(10)
C(20)-C(21)-C(22)-F(33)	175.3(7)
F(30)-C(21)-C(22)-F(34)	-179.5(8)
F(31)-C(21)-C(22)-F(34)	-64.1(9)
C(20)-C(21)-C(22)-F(34)	55.9(11)
O(2)-C(3)-C(23)-O(4)	-33.2(5)
C(2)-C(3)-C(23)-O(4)	79.9(4)
O(2)-C(3)-C(23)-C(24)	89.7(4)
C(2)-C(3)-C(23)-C(24)	-157.1(4)
O(4)-C(23)-C(24)-F(36)	55.1(5)
C(3)-C(23)-C(24)-F(36)	-68.3(5)
O(4)-C(23)-C(24)-F(35)	173.5(3)
C(3)-C(23)-C(24)-F(35)	50.2(4)
O(4)-C(23)-C(24)-C(25)	-66.9(5)
C(3)-C(23)-C(24)-C(25)	169.7(4)
F(36)-C(24)-C(25)-F(38)	-50.4(6)
F(35)-C(24)-C(25)-F(38)	-167.6(4)
C(23)-C(24)-C(25)-F(38)	72.0(5)
F(36)-C(24)-C(25)-F(37)	-167.5(4)

F(35)-C(24)-C(25)-F(37)	75.3(5)
C(23)-C(24)-C(25)-F(37)	-45.1(6)
F(36)-C(24)-C(25)-C(26)	72.9(5)
F(35)-C(24)-C(25)-C(26)	-44.3(5)
C(23)-C(24)-C(25)-C(26)	-164.7(4)
F(38)-C(25)-C(26)-F(39)	-168.6(5)
F(37)-C(25)-C(26)-F(39)	-52.5(6)
C(24)-C(25)-C(26)-F(39)	67.5(6)
F(38)-C(25)-C(26)-F(40)	74.9(6)
F(37)-C(25)-C(26)-F(40)	-169.0(5)
C(24)-C(25)-C(26)-F(40)	-49.0(6)
F(38)-C(25)-C(26)-C(27)	-45.5(6)
F(37)-C(25)-C(26)-C(27)	70.6(6)
C(24)-C(25)-C(26)-C(27)	-169.3(4)
F(39)-C(26)-C(27)-F(42)	-168.6(5)
F(40)-C(26)-C(27)-F(42)	-50.8(6)
C(25)-C(26)-C(27)-F(42)	68.4(6)
F(39)-C(26)-C(27)-F(41)	73.1(6)
F(40)-C(26)-C(27)-F(41)	-169.1(5)
C(25)-C(26)-C(27)-F(41)	-49.9(6)
F(39)-C(26)-C(27)-C(28)	-46.3(6)
F(40)-C(26)-C(27)-C(28)	71.5(6)
C(25)-C(26)-C(27)-C(28)	-169.4(5)
F(42)-C(27)-C(28)-F(44)	75.1(7)
F(41)-C(27)-C(28)-F(44)	-167.9(6)
C(26)-C(27)-C(28)-F(44)	-48.2(7)
F(42)-C(27)-C(28)-F(43)	-170.4(6)
F(41)-C(27)-C(28)-F(43)	-53.4(7)
C(26)-C(27)-C(28)-F(43)	66.2(7)
F(42)-C(27)-C(28)-C(29)	-47.8(7)
F(41)-C(27)-C(28)-C(29)	69.2(7)
C(26)-C(27)-C(28)-C(29)	-171.1(5)
F(44)-C(28)-C(29)-F(45)	-166.8(7)
F(43)-C(28)-C(29)-F(45)	78.4(8)
C(27)-C(28)-C(29)-F(45)	-44.6(8)
F(44)-C(28)-C(29)-F(46)	-49.9(8)

F(43)-C(28)-C(29)-F(46)	-164.7(7)
C(27)-C(28)-C(29)-F(46)	72.3(8)
F(44)-C(28)-C(29)-C(30)	72.4(8)
F(43)-C(28)-C(29)-C(30)	-42.3(8)
C(27)-C(28)-C(29)-C(30)	-165.4(6)
F(45)-C(29)-C(30)-F(48)	-56.2(11)
F(46)-C(29)-C(30)-F(48)	-172.2(10)
C(28)-C(29)-C(30)-F(48)	66.2(11)
F(45)-C(29)-C(30)-F(47)	-173.2(8)
F(46)-C(29)-C(30)-F(47)	70.8(10)
C(28)-C(29)-C(30)-F(47)	-50.7(10)
F(45)-C(29)-C(30)-C(31)	68.3(11)
F(46)-C(29)-C(30)-C(31)	-47.7(12)
C(28)-C(29)-C(30)-C(31)	-169.3(8)
F(48)-C(30)-C(31)-F(51)	-174.8(14)
F(47)-C(30)-C(31)-F(51)	-59.7(16)
C(29)-C(30)-C(31)-F(51)	59.2(16)
F(48)-C(30)-C(31)-F(49)	-50.8(14)
F(47)-C(30)-C(31)-F(49)	64.3(14)
C(29)-C(30)-C(31)-F(49)	-176.7(10)
F(48)-C(30)-C(31)-F(50)	70.6(15)
F(47)-C(30)-C(31)-F(50)	-174.2(13)
C(29)-C(30)-C(31)-F(50)	-55.3(15)

Symmetry transformations used to generate equivalent atoms:

6. References

1. Mathre, D. J.; Thompson, A.; Douglas, S. A. W.; Hoogsteen, K.; Carroll, J. D.; Corley, E. G.; Grabowski, E. J. *J. Org. Chem.* **1993**, *58*, 2880-2888.
2. Du, D.; Fang, T.; Zhang, S. *Org. Lett.* **2006**, *7*, 1327-1330.
3. Cozzi P. G.; Krotusz, P. *J. Am. Chem. Soc.* **2006**, *128*, 4940-4941.
4. Liu, P. N.; Deng J. G.; Tu, Y. Q.; Wanga, S. H. *Chem. Cummn.* **2004**, 2070-2071.
5. Cho, B.; Kim, D. *Bull. Korean Chem. Soc.* **2004**, *25*, 1385-1391.
6. Homann, M. J.; Vail, R. B.; Previte, E.; Tamarez, M.; Morgan, B.; Dodds, D. R.; Zaks, A. *Tetrahedron* 2004, *60*, 789-797.
7. Guindon, Y; Oglivie, W.; Bordeleau, J.; Chui, W. Durkin, K. Goris, V.; Yoakim, C. *J. Am. Chem. Soc.* **2002**, *125*, 428-436.
8. Cho, B. T.; Park W. S. *Bull. Korean Chem. Soc.* **1987**, *8*, 257-260
9. Hayashi, M.; Kaneko, T.; Oguni, N.; *J. Chem. Soc., Perkin Trans. 1* **1991**, *1*, 25-28.
10. Kusakabe, M.; Kitano, Y.; Kobayashi, Y.; Sato, F. *J. Org. Chem.* **1989**, *54*, 2085-2091

7, NMR charts