Supporting Information

A Crystal Engineering Weaving of Half-Spiral Molecules by Hydrogen Bonding Chains into Tube Structures

Keisuke Kataoka, Masato Yanagi, and Toshimasa Katagiri*

Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushimanaka 3-1-1, Kita-ku, Okayama 700-8530, Japan

Table of Contents

1. General Methods	S-2
2. Materials	S-3
3. Synthesis of Double-Headed Trifluorolactate 1	S-5
4. X-ray Crystallography of Double-Headed Trifluorolactate 1	S-9
5. DSC-XRD analysis of Double-Headed Trifluorolactate 1	S-11
6. Spectroscopic data	S-13

1. General Methods

NMR: ¹H (300 MHz) and ¹⁹F NMR (282 MHz) spectra were recorded on a Varian MERCURY 300 instrument. ¹H NMR (300 MHz) was recorded by Varian GEMINI 2000 instrument. ¹³C (50 MHz) NMR was recorded by Varian GEMINI 200 instrument. Chemical shifts were determined with non-deuterated residual CHCl₃ (δ 7.26) as an internal standard for ¹H NMR, CDCl₃ (δ 77.0) as an internal standard for ¹³C NMR and C₆F₆(δ 0.00) as a standard for ¹⁹F NMR.

IR: IR spectra were recorded on a Hitachi Model 270-40 Infrared Spectrophotometer.

MS: GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A.

- Elemental Analysis: Elemental analyses were performed on a Perkin Elmer series II CHNS/O Analyzer 2400.
- Single crystal X-ray Diffraction: Single crystal X-ray diffraction was performed on Rigaku VariMax + Saturn724. X-ray data were collected using a Rigaku CCD detector (Saturn 724) mounted on a Rigaku rotating anode X-ray generator (MicroMax-007HF) and Mo-Ka radiation from a corresponding confocal optics.
- DSC-XRD: DSC-XRD was performed on Rigaku RINT-TTR III, XRD-DSC with D/teXUltra.

2. Materials

Solvents:

THF : Wako pure Chemicals. THF was distilled from sodium-benzophenone ketyl prior to use.

Toluene : Nacalai Tesque. Toluene was used without further purification.

Diglyme : Wako pure chemicals. Diglyme was distilled from sodium-benzophenone ketyl prior to use.

Diethyl ether : Merck. Diethyl ether was distilled from sodium-benzophenone ketyl prior to use.

tert-Butyl methyl ether : Wako pure Chemicals. *tert*-Butyl methyl ether was used without further purification.

n-Octane : Nacalai Tesque. *n*-Octane was used without further purification.

n-Hexane : Daishin chemicals. *n*-Hexane was distilled from conc. H₂SO₄ (95%).

2-Propanol : Nacalai Tesque. 2-Propanol was used without further purification.

Chloroform (CHCl₃) : Nacalai Tesque. CHCl₃ was used without further

purification.

Benzene : Nacalai Tesque. Benzene was used without further purification.

Reagents

All reagents were purchased from following suppliers and used without further purification.

Boron trifluoride diethyl etherate (BF ₃ OEt ₂) :	Nacalai Tesque.	
Sodium borohydride (NaBH ₄) :	Nacalai Tesque.	
Hydrogen peroxide (H ₂ O ₂) 35% :	Kanto Chemicals.	
Sodium hydroxide (NaOH) :	Nacalai Tesque.	
Allyl bromide :	TCI.	
Magnesium turnings (Mg) :	Nacalai Tesque.	
α, α '-dichloro- <i>m</i> -xylene :	TCI.	
Sulfuric acid (96%) :	Kanto Chemicals.	
Hydrochloric acid (35%) :	Kanto Chemicals.	
Acetic acid (99%):	Nacalai Tesque.	
Nitric acid (60%) :	Kanto Chemicals.	
(S,S)-(-)- N - N '-Bis(3,5-di- <i>tert</i> -butylsalicylidene)-1,2-cyclohexanediaminocobalt(II)		
(salen-Co):	Aldrich.	
2-Thionaphthol :	Kanto Chemicals.	
Triethylamine (Et ₃ N) :	Nacalai Tesque.	

Sodium hydrogen carbonate (NaHCO3) :Kanto CMagnesium sulfate anhydrous (MgSO4) :Nacalai(S)-3,3,3-Trifluoropropene oxide (TFPO) :gift from

Kanto Chemicals. Nacalai Tesque. gift from Japan Energy Co.

Others

Silica (Silica gel 60 for column chromatography) :	Merck.
CDCl ₃ (for all NMR analysis) :	Acros Organics.

3. Synthesis of Double Headed Trifluorolactate 1 Preparation of Optically Pure (*S*)-Trifluorolactic Acid 2 Optically pure (*S*)-3,3,3-trifluoropropene oxide (ref. 1s).



A solution of the salen-Co catalyst (0.381 g, 0.63 mmol, 0.25 mol%) in toluene (5 ml) was treated with 0.3 ml AcOH for 1 h. Then, a residual solid which obtained after evaporation was allowed to react with (*S*)-3,3,3-trifluoropropene oxide (25.8 ml, 300 mmol with ca. 75% ee). The solution was cooled to 0 °C and treated with H₂O (0.68 ml, 37.5 mmol, 11 mol%). The reaction mixture was warmed up to room temperature and stirred for more 16 h. Then, (*S*)-3,3,3-trifluoropropene oxide was isolated by vacuum distillation (30 mmHg) from the reaction mixture into vessel cooled by liq. N₂. Another optical resolution procedure gave optically pure (>99.5% ee) (*S*)-3,3,3-Trifluoropropene oxide was determined by chiral HPLC analysis with Daicel Chiralcel[®] OD-H column (eluent: *n*-hexane : 2-propanol (20 : 1), flow rate: 1 ml / min, retention time: t_R(minor) = 11.9 min, t_S(major) = 14.2 min) of its 2-napthylesulfide derivative, which obtained by ring opening reaction with 2-napthalenethiol with 1 eq. Et₃N in THF.

(S)-3,3,3-Trifluorolactic acid 2 (ref. s2)

$$F_{3}C \xrightarrow{OH} F_{3}C \xrightarrow{OH} F_{3}C \xrightarrow{OH} OH$$

In a two-necked round-bottomed flask equipped with a reflux condenser and an addition funnel, metal Cu powder (0.145 g, 2.2 mmol, 0.01 eq.) was dissolved in 60% nitric acid (d 1.38, 68 ml, 900 mmol, 4.5 eq.) and the solution was stirred. (*S*)-3,3,3-Trifluoropropene oxide (17.3 ml, 200 mmol, >99.5% ee) was added dropwise to the green colored solution at 0 °C. The reaction mixture was slowly warmed up to 80 °C. Soon the first vigorous generation of NO₂ started. The reaction mixture was

vigorously stirred at 80 °C for 12 h until stopping of NO₂ generation, then cooled to room temperature. NO₂ was removed to external in fume hood. Saturated Na₂CO₃ solution was added to the cooled solution to make the solution basic, then the reaction mixture was stirred for at least 2 h to completely decompose any possible nitric ester. Just prior to the work up, one should ascertain that the solution is basic. The solution was again acidified with an appropriate amount of concentrated HCl to make the solution to be pH 2. The acidic solution was repeatedly extracted with ether (6×50 ml), with keeping pH 2. The combined organic phase was dried by anhydrous sodium sulfate, filtered, and concentrated. If the residue was not solid, azeotropic dehydration with benzene was performed using Dean-Stark apparatus. The resulted solid was recrystallized from CHCl₃ solution at -18 °C. (*S*)-3,3,3-Trifluorolactic acid **2** was isolated in 53% yield as a hydroscopic solid. The filtrate was concentrated, and the residue was distilled under a reduced pressure (110 °C / 20 mmHg), to give (*S*)-3,3,3-trifluorolactic acid **2** in 31% yield.

Caution! The reaction is an exothermic oxidation reaction. Thus, all **safety precautions** should be taken. Do not carry out these reactions on a large scale (<200 mmol scale). Also, precautions against the generation of vigorous amounts of obnoxious fumes (NO₂), which are generated during the oxidation, should be taken.

Preparation of diol 3

1,3-di(3-butenyl)benzene (ref. s3)



In a two-necked round-bottomed flask, magnesium (6.74 g, 288 mmol, 7.2 eq.) was added to Et₂O (40 ml). A solution of allyl bromide (11.6 g, 96 mmol, 2.4 eq.) in Et₂O (40 ml) was added dropwise and allylmagnesium was prepared. The reagent was placed in another flask equipped with a flask condenser by cannulation to remove magnesium residue and a solution of corresponding α , α -dichloro-*m*-xylene (7.0 g, 40 mmol) in Et₂O was added dropwise. Then the reaction mixture was refluxed for 12 h. Sequent to hydrolysis with water phase was extracted with three portions of Et₂O (40 ml). The organic fractions were combined and washed with water and a saturated solution of NaHCO₃ until no acidic reaction was detected, dried over MgSO₄, and filtered. Distillation under reduced pressure (1 mmHg / 60 °C) afforded the product, 1,3-di(3-butenyl)benzene in 89% yield.

1,3-di(3-butenyl)benzene

89% yield. Colorless liquid.

IR(neat): 3080, 2930, 1640, 1610, 1450, 1420, 1000, 910 cm⁻¹. ¹H NMR (CDCl₃; 300 MHz; 20 °C): δ 7.21 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 2.7 Hz, 2H) 5.94-5.81 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 2H), 5.09-5.02 (dq, *J* = 19.2, 1.8 Hz, 2H), 5.01-4.96 (ddt, *J* = 10.2, 1.8, 1.2 Hz, 2H), 2.70 (dd, *J* = 8.1, 7.5 Hz, 4H), 2.41-2.32 (m, 4H) ppm. (lit.(ref. s3): δ 7.49-7.27 (m, 4H), 6.22-6.06 (m, 2H), 5.36-5.24 (m, 4H), 2.99-2.93 (m, 4H), 2.69-2.63 (m, 4H) ppm)

MS: m/z 186 (M⁺: 9), 145 (100), 130 (23), 117 (45), 105 (21), 91 (29).

1,3-benzenedibutanol (ref. s4)



 BF_3OEt_2 (1.02 g, 7.19 mmol) was dropped to a solution of NaBH₄ (0.19 g, 5.03 mmol) and corresponding diallylbenzene (1.14 g, 7.19 mmol) in diglyme (70 ml), then stirring under an Ar atmosphere and cooled to 0 °C for 2.5 h. Then the solution was stirred for further 1 h. A 3 N NaOH aq. (1.5 ml) and 30% H₂O₂ aq. (1.5 ml) was added to the mixture, then decomposed with water, and extract with ether. The combined organic layers was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude obtained was distilled under reduced pressure (1 mmHg / 160 °C) afforded the product, 1,3-benzenedibutanol in 82% yield.

1,3-benzenedibutanol

82% yield. Colorless liquid.
IR(neat): 3320, cm⁻¹.
¹H NMR (CDCl₃; 300 MHz; 20 °C; ppm) δ 7.19 (t, *J* = 7 Hz, 1H), 7.01 (s, 1H), 7.00 (d, *J* = 7 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 4H), 1.2-1.8 (m, 9H) ppm.
MS: m/z 222(M⁺: 8), 204 (9), 186 (20), 158(42), 145 (78), 131 (76), 117 (78), 105 (41), 91 (100).

Preparation of Double-Headed Trifluorolactate 1 (ref. s5)



Round-bottomed flask equipped with a Dean-Stark apparatus surmounted by reflux condenser was charged with 1,3-benzenedibutanol (3.81 g, 23 mmol), (*S*)-trifluorolactic acid (8.26 g, 57.3 mmol), and one drop of H₂SO₄ as a catalyst in toluene (40 mm). The reaction mixture was brought to reflux with the removal of water for 15 h. The resulting mixture was cooled to room temperature and water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated under a reduced pressure. The crude products were purified by silica gel column chromatography (*n*-hexane : ether = 1 : 1) and distilled under reduced pressure (1 mmHg / 150 °C) afforded the product, double-headed trifluorolactate **1** in 53% yield.

benzene-1,3-(*S*,*S*)-bis(butyl-3,3,3-trifluorolactate) 1.

53% yield. Colorless powder. Mp 79 - 80 °C.

IR(KBr): 3460, 1760 cm⁻¹.

¹H NMR (CDCl₃; 300 MHz; 20 °C) δ 7.21 (t, *J* = 7 Hz, 1H), 7.00 (d, *J* = 7.2 Hz 1H), 6.97 (s, 1H), 4.52-4.25 (m, 6H), 3.45 (d, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 4H), 1.80-1.69 (m, 8H) ppm.

¹⁹F NMR (CDCl₃; 282 MHz; 20 °C) δ 85.7 (d, J = 7.1 Hz, 6F) ppm.

¹³C NMR (CDCl₃; 50 MHz; 20 °C) δ 167.5, 141.7, 128.4(2), 128.3(8), 125.9, 122.2 (q, *J* = 282 Hz), 69.8 (q, *J* = 33 Hz), 67.5, 35.2, 27.9, 27.3 ppm.

MS: m/z 302 (12), 247 (30), 186 (37), 171 (13), 158 (56), 145 (100), 130 (78), 117 (65), 104 (27), 91 (46), 79 (23).

Anal. Calcd for C₁₈H₂₀F₆O₆: C 50.63, H 5.06, N 0.00, Found: C 50.71, H 5.10, N 0.00

4. X-ray Crystallography of Double-Headed Trifluorolactate 1

X-ray crystallographic analysis was performed at The Center Labolatory of Rigaku, Tokyo, by Dr. Hasegawa and Dr. Yamasaki.

A single crystal of double-headed trifluorolactate 1 (Figure S1), appropriate for single X-ray diffraction measurement, was obtained by slow evapolation of $^{t}BuOMe/n$ -octane solvents at room temperature. The diffraction measurement was performed on a Rigaku VariMax + Saturn724. Detail parameters are summarized in the Table s1.



Figure s1. Photograph of mounted single ctystal.

Table s1. Crystallographic parameters

Compound	1
Empirical formula	$C_{20}H_{24}F_6O_6$
Formula weight	474.4
Crystal size (mm ³)	0.10 x 0.09 x 0.05
Crystal color	colorless
Crystal habit	block
Crystal System	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁ (#19)
a (Å)	5.3232(10)
b (Å)	15.896(3)
c (Å)	25.664(5)
Dcalc $(g \cdot cm^{-3})$	1.451
Volume (Å ³)	2171.6
Z value	4
$m (cm^{-1})$	1.377
Temperature (°C)	-180 ± 1
Reflection measured	17639
Unique reflection	2859
R(int)	0.034
Max theta (°)	27.5
Data completeness	0.999
Reflection/parameter Ratio	8.74
Reflections used	2859
R_1 for $[I > 2\sigma(I)]$	0.0334
R ₁ for all data	0.0393
$\omega R_2(F^2)$ for all data	0.0814
Max shift error	0.001
Goodness of fit	1.049
Largest diff. Peak (e [.] Å ⁻³)	0.32
Largest diff. Hole (e·Å ⁻³)	-0.38

5. DSC-XRD analysis of Double-Headed Trifluorolactate 1

DSC-XRD measurement was performed at The Center Labolatory of Rigaku, Tokyo, Rigaku, by Dr. Ohbuchi.

A simultaneous powder XRD (RINT-TTRIII and D/teX Ultra, Rigaku)-differential scanning calorimetry (DSC, Rigaku) was carried out with using CuK α (50 kV, 300 mA) radiation at a scanning rate of 80 deg/min over a range of 3–35 deg (2 theta). The heating rate of the DSC measurement was 2 °C/min from room temperature up to 150 °C, and the measurement was performed in flow of air (100 ml/min). Detailed conditions are summarized in Table s2.

 Table s2. Measurement parameters

voltage and current	50 kV-300 mA
scanning axis	$2\theta/ heta$
scanning mode	continuous scan
scanning range	5-35°/20
scanning speed	80°/min
sampling interval	0.02°/step
temperature	rt - 150 °C
heating rate	2 °C /min
condition	air flow (100 ml/min)



Figure s2. DSC-XRD profiles of double-headed trifluorolactate 1.

Reference

- [ref. s1] S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow & E. N. Jacobsen J. Am. Chem. Soc. 2002, 124, 1307-1315
- [ref. s2] T. Katagiri, F. Obara, S. Toda & K. Furuhashi Synlett 1994, 507-508
- [ref. s3] H. Ekkehard, S. A. Christoph, E. Klaus & S. Manfred Organometallics 2002, 21, 4217-4225
- [ref. s4] K. Murayama, Y. Kato, & S. Morimoto Bull. Chem. Soc. Jpn. 1967, 60, 2645-2647

[ref. s5] S. Takahashi, T. Katagiri, & K. Uneyama CrystEngComm 2006, 8, 132-139

Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-13 IR spectrum of double-headed trifluorolactate 1

(-1, -1, -1)





ppm

C4-m 2008/3/6



.



Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-17 GC-MS of double-headed trifluorolactate 1





Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-18 IR spectrum of 1,3-di(3-butenyl)benzene



Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-19 1H NMR spectrum of 1,3-di(3-butenyl)benzene



Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-20 GC-MS of 1,3-di(3-butenyl)benzene



^{#:1} 保持時間:8.9(スキャン#:586) ピーク数:38 ベースピーク:145(66503) スペクトル:平均 8.9-8.9(585-587) バックグラウンド: ピークから計算

55.30

63.10

64.95

0.60

3.38

5.03

91.05

92.20

29.11

2.45

115.00

116.90

44.69



12.03 2.50

2.93

 $146.05 \\ 157.25$

158.05

10.52

1.13

1 / 1

131.05

132.25

Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-21 IR spectrum of 1,3-benzenedibutanol



24-m-dio1

Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-22 1H NMR spectrum of 1,3-benzenedibutanol



Electronic Supplementary Material (ESI) for CrystEngComm This journal is © The Royal Society of Chemistry 2011 S-23 GC-MS of 1,3-benzenedibutanol





1 / 1