Supporting Information

A Molecular-Sized Tunnel-Porous Crystal with a Ratchet Gear Structure and Its One-way Guest-Molecule Transportation Property

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Table of Contents

1. General Methods

NMR: ^{1}H (300 MHz) and ^{19}F NMR (282 MHz) spectra were recorded on a Varian MERCURY 300 instrument. ^{1}H NMR (300 MHz) was recorded by Varian GEMINI 2000 instrument. ^{13}C (50 MHz) NMR was recorded by Varian GEMINI 200 instrument. Chemical shifts were determined with non-deuterated residual $CHCl_3$ (δ 7.26) as an internal standard for ^{1}H NMR, $CDCl_3$ (δ 77.0) as an internal standard for ^{13}C NMR and C_6F_6 (δ 0.00) as a standard for ^{19}F 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 R-AXIS RAPID II diffractometer using filtered Mo-Kα raduation.

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.

Diethyl ether : Merck. Diethyl ether was used without further purification.

Ethyl acetate : Nacalai Tesque.

Dichloromethane : Kanto Chemicals. Dichloromethane was distilled from calcium hydride prior to use.

n-Hexane : Daishin chemicals. *n*-Hexane was distilled from conc. H_2SO_4 (95%).

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

Chloroform ($CHCl_3$) : Nacalai Tesque. $CHCl_3$ was used without further purification.

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

DMF : Kanto Chemicals. DMF was distilled from calcium hydride prior to use.

Reagents

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

2,3-Naphthalene dicarboxylic acid	Wako Pure Chemicals
Anthracene	Kanto Chemicals
Methanol	Nacalai Tesque
Sulfuric acid (96%) :	Kanto Chemicals
Acetic acid (99%) :	Nacalai Tesque.
Nitric acid (60%) :	Kanto Chemicals.
(*S*,*S*)-(-)-*N*-*N*’-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) (salen-Co) :	Aldrich.
2-Thionaphthol :	Kanto Chemicals.
Triethylamine (Et_3N) :	Nacalai Tesque.
Sodium hydrogen carbonate ($NaHCO_3$) :	Kanto Chemicals.
Magnesium sulfate anhydrous ($MgSO_4$) :	Nacalai Tesque.
(*S*)-3,3,3-Trifluoropropene oxide (TFPO) :	gift from Japan Energy Co.

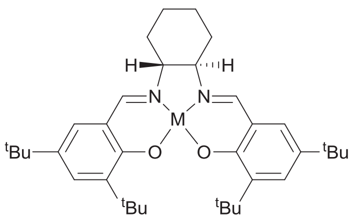
Others

Silica (Silica gel 60 for column chromatography) :	Merck.
$CDCl_3$ (for all NMR analysis) :	Acros Organics.

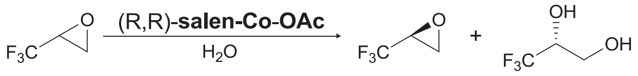
3. Synthesis of Double Headed Trifluorolactate TLFA-2,3-naph

Preparation of Optically Pure (*S*)-Trifluorolactic Acid

Optically pure (*S*)-3,3,3-trifluoropropene oxide (ref. 1s).

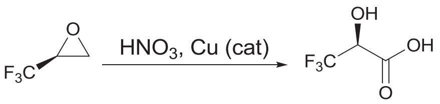


M = Co : (R,R)-**salen-Co**
M = Co(OAc) : (R,R)-**salen-Co-OAc**



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 H_2O (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. N_2. Another optical resolution procedure gave optically pure (>99.5% ee) (*S*)-3,3,3-Trifluoropropene oxide in 60% yield. Optical purity of the (*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. Et_3N in THF.

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

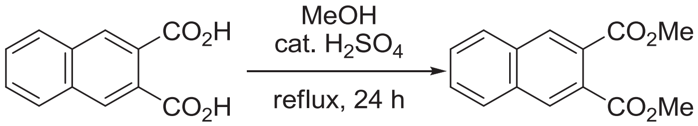


In a two-necked round-bottomed flask equipped with a reflux condenser and an addition funnel, metal Cu powder (0.145 g, 2.2 mmol, 0.01 eq.) was dissolved in 60% nitric acid (d 1.38, 68 ml, 900 mmol, 4.5 eq.) and the solution was stirred. (*S*)-3,3,3-Trifluoropropene oxide (17.3 ml, 200 mmol, >99.5% ee) 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 NO_2 started. The reaction mixture was vigorously stirred at 80 °C for 12 h until stopping of NO_2 generation, then cooled to room temperature. NO_2 was removed to external in fume hood. Saturated Na_2CO_3 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 $CHCl_3$ 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 (NO_2), which are generated during the oxidation, should be taken.

Preparation of Double Headed Trifluorolactate TFLA-2,3-naph

Dimethyl 2,3-naphthalenedicarboxylate (S-1)



S-1
93%

A solution of 2,3-naphthalenedicarboxylic acid (1.074 g, 5 mmol) in MeOH (9.4 ml) and concd H_2SO_4 (0.3 ml, cat.) was stirred under reflux for 18 h. The reaction mixture was cooled in an ice bath and was diluted with H_2O. Extraction with EtOAc, washing with saturated $NaHCO_3$ aq. and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give yellowish white powder. Synthesis of **S-1** was confirmed by comparing to authentic data (ref s3).

1.136 g, 93% yield. Yellowish white powder.

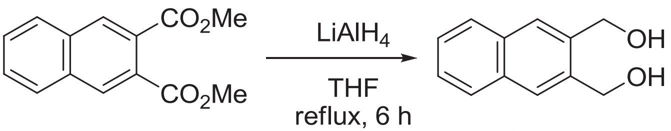
IR(KBr): 1740 cm^{-1}; ^1H NMR ($CDCl_3$): δ8.26 (s, 2H), 7.93 (dd, J = 3.2, 6.2 Hz, 2H), 7.63 (dd, J_1 = 3.2, 6.2 Hz, 2H), 3.96 (s, 6H). MS: m/z 244 (32), 213 (100), 183 (7), 127

(32), 114 (8)

Authentic data (ref s3)

^{1}H NMR ($CDCl_3$): δ8.28 (s, 2H), 7.95-7.93 (m, 2H), 7.66-7.64 (m, 2H), 3.98 (s, 6H).

2,3-Bis(hydroxymethyl)naphthalene (S-2)



S-1 **S-2** 80%

A solution of dimethyl 2,3-naphthalenedicarboxylate (0.734 g, 3.0 mmol) in THF (25 ml) under Ar atmosphere was dropped to a solution of $LiAlH_4$ (0.263 g, 6.9 mmol, 2.3 eq.) in THF (25 ml) under Ar atmosphere and cooled to 0 °C. Then the solution was stirred at 0 °C to 70 °C for 15 h. Water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was recrystallized with THF and hexane to give white powder. Synthesis of **S-2** was confirmed by comparing to authentic data (ref s4).

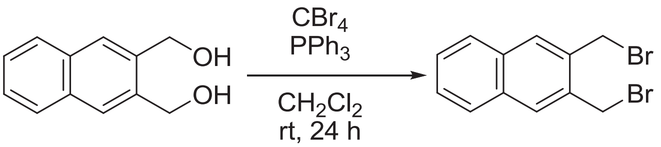
0.452 g, 80% yield. White powder.

IR(KBr): 3050 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ7.83 (dd, *J* = 3, 6 Hz, 2H), 7.82 (s, 2H), 7.50 (dd, *J* = 3, 6 Hz, 2H), 4.91 (s, 4H), 2.2 (br). MS: m/z 188 (27), 170 (90), 169 (73), 141 (100), 128 (34), 115 (47).

Authentic data (ref s4)

^{1}H NMR ($CDCl_3$): δ7.89 (s, 2H), 7.93-7.40 (m, δ7.67, 4H), 4.87 (d, *J* = 5.6 Hz, 4H), 4.44 (t, *J* = 5.6 Hz, 2H).

2,3-Bis(bromomethyl)naphthalene (S-3)



S-2 **S-3** 71%

A solution of diol (0.509 g, 2.7 mmol), triphenylphosphine (1.745 g, 6.7 mmol), tetrabromomethane (2.70 g, 8.1 mmol) in CH_2Cl_2 (5 ml) was stirred at ambient temperature for 12 h. Diethyl ether was added to the mixture then, white solid was precipitated. After filtration of the white solid, remained solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography (diethyl ether) to give white powder. Synthesis of **S-3** was confirmed by comparing to authentic data (ref s4).

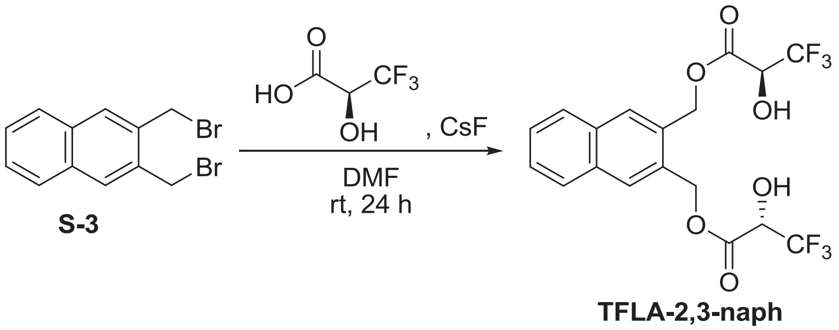
0.599 g, 71% yield. White solid.

IR(KBr): 1260 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ7.87 (s, 2H), 7.81 (dd, *J* = 3, 6 Hz, 2H), 7.51 (dd, J_1 = 3, 6 Hz, 2H), 4.89 (s, 4H). MS: m/z 314 (11), 235 (58), 233 (59), 154 (100), 76 (31).

Authentic data (ref s4)

^{1}H NMR (CDCl$_3$): δ8.05 (s, 2H), 7.98-7.49 (m, δ7.74, 4H), 5.01 (s, 4H).

naphthalene-2,3(*S*,*S*)-bis(methyl-3,3,3-trifluorolactate) TFLA-2,3-naph



TFLA-2,3-naph
77%

CsF (1.0 g, 6.6 mmol) and dibromide (0.828 g, 2.6 mmol) was dissolved in DMF (5 ml). A solution of (*S*)-trifluoroactic acid (1.13 g, 7.9 mmol) in DMF (5 ml) was then added slowly. The reaction mixture was stirred for 24 h at ambient temperature. Water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The crude products were purified by silica gel column chromatography (hexane : ether = 1: 1) and distilled under reduced pressure (1 mmHg) at 180 °C to give white powder.

0.895 g, 77% White powder. Mp 130 - 131 °C. IR(KBr): 3460, 3380, 1770, 1750 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ7.93 (s, 2H), 7.87 (dd, *J* = 3, 6 Hz, 2H), 7.58 (dd, *J* = 3, 6 Hz, 2H), 5.58 (s, 4H), 4.54 (quint, *J* = 8 Hz, 2H), 3.39 (d, *J* = 8 Hz, 2OH). ^{19}F NMR (CDCl$_3$): δ85.9 (d, *J* = 7 Hz, 6F). MS: m/z 440 (4), 297 (8), 197 (17), 170 (100), 141 (41). Anal. Calcd for $C_{18}H_{14}F_6O_6$: C 49.10, H 3.18, Found: C 49.02, H 3.06

Crystalllization of Double Headed Trifluorolactate TFLA-2,3-naph and anthracene

Double-headed trifluorolactate **TFLA-2,3-naph** (0.1 g, 0.2 mmol) was recrystallized from ether/*n*-hexane (0.2 ml; 0.2 ml) solution with anthracene (0.4 g, 2.2 mmol) for UV fluorescence observation (Figure S1). Containing anthracene was confirmed by ^{1}H NMR. ^{1}H NMR indicated that the co-crystal contained 11 mol% amount of anthracene.

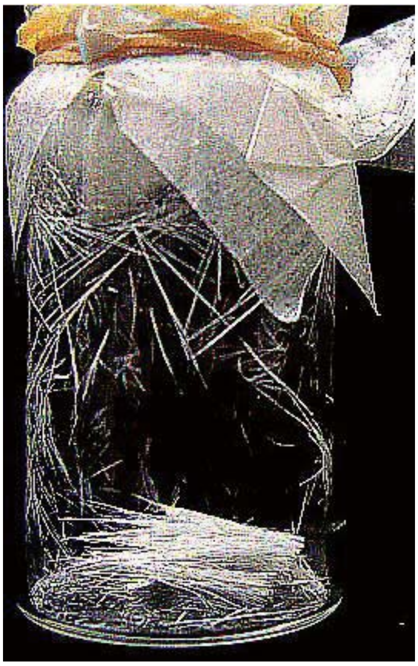
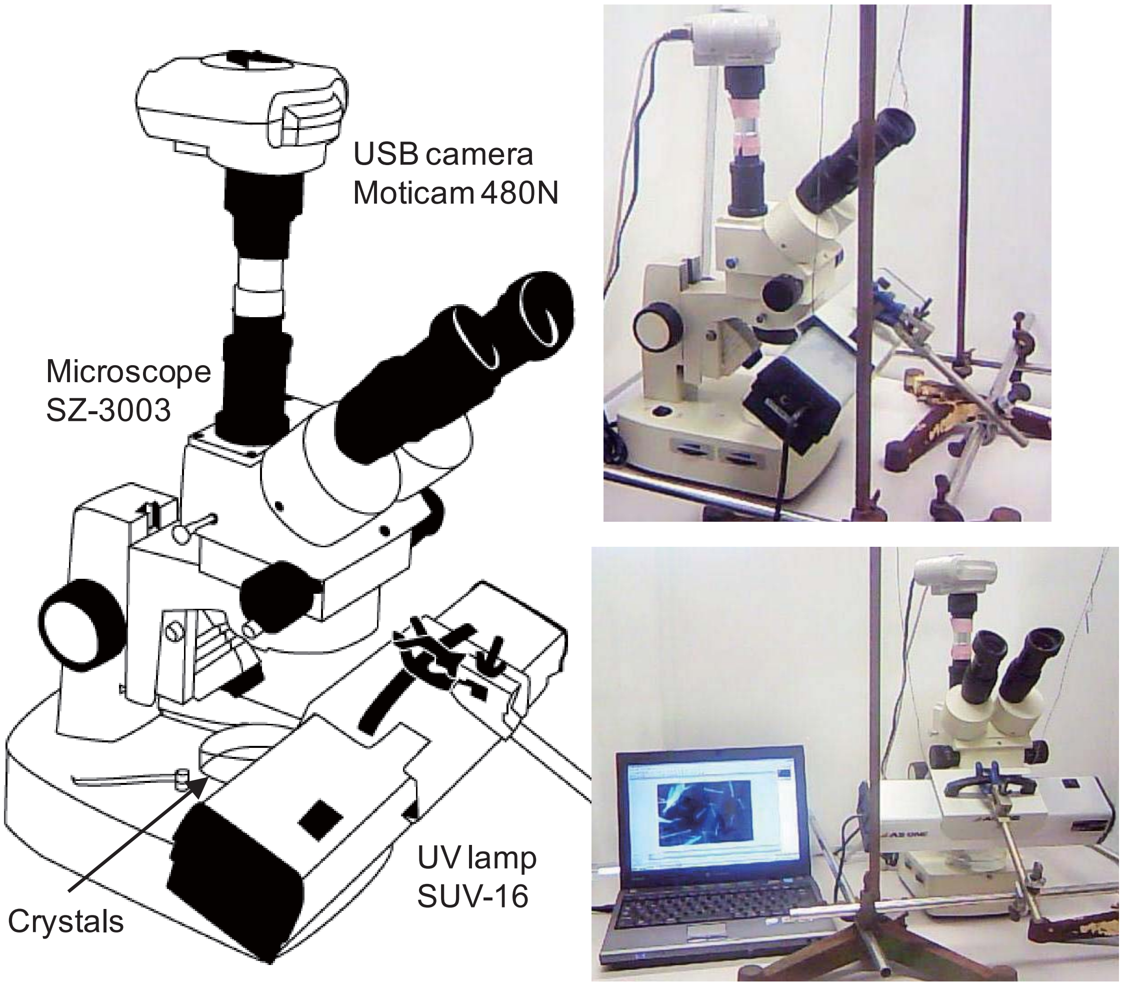


Figure S1. Picture of anthracene containing crystal.

4. Equipment for fluorescence observation

Fluorescence observation apparatus

The fluorescence moving was confirmed by observation of crystals. Fluorescence of crystal was observed by following combination of microscope and UV-lamp (Figure S2).



Fisure S2. Fluorescence observation apparatus.

Microscope type SZ-3003 (ocular lens: 10×, objective lens: 0.7 – 4.5×, observed by 30×) was purchased from AS-ONE. Crystals were radiated every other day by AS-ONE type SUV-16 UV lamp (254 nm, 22.0 W) to observe fluorescence distribution. Shimadzu Moticam 480N USB camera was attached to the microscope to take photos. Photos were processed on Shimadzu Motic Image Plus 2.2S program ver 2.21.

Fluorescence observation for other sample

Figure S3 shows other sample. In this case, anth@**TFLA-2,3-naph** crystal was put on moisten filter paper with hexane. Therefore, moved anthracene was broaden at one terminal of the crystal.

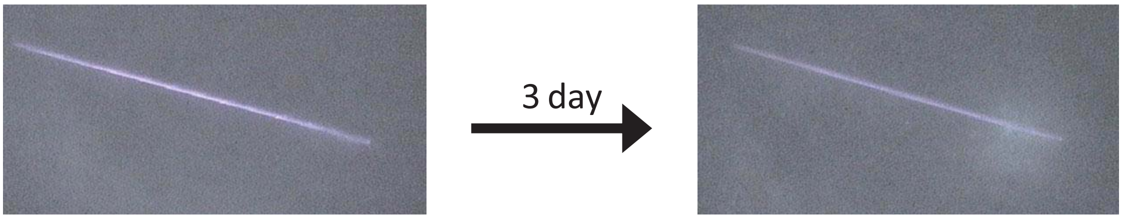


Figure S3. Fluorescence change for other sample.

5. X-ray crystallography of fluorescence part and quenched part

The diffraction measurement was performed on a Rigaku RAXIS RAPID. Detail parameters are summarized in the Table S1.

Table S1. Crystallographic parameters

Compound	**With anthracene**	**No anthracene**
Empirical formula	$C_{21.50}H_{16.5}F_6O_6$	$C_{18}H_{14}F_6O_6$
CCDC number	837539	837540
Crystal size (mm^3)	5.1 x 0.015 x 0.015	5.1 x 0.015 x 0.015
Crystal color	colorless	colorless
Crystal habit	needle	needle
Crystal System	monoclinic	monoclinic
Space group	$P2_1$ (#4)	$P2_1$ (#4)
a (Å)	13.118(1)	13.308(6)
b (Å)	5.1733(1)	5.176(3)
c (Å)	17.135(2)	15.272(7)
β°	112.756(8)	98.75(1)
Dcalc ($g{\cdot}cm^{-3}$)	1.502	1.406
Volume ($Å^3$)	1072.3(2)	1039.7(8)
Z value	2	2
μ (cm^{-1})	12.623	1.382
Temperature (°C)	25 ± 1	25 ± 1
Reflection measured	12752	9888
Unique reflection	3574	2635
R(int)	0.0399	0.1008
$2\theta_{max}$	136.4	55.0
Reflection/parameter Ratio	12.2	9.65
R_1 for [$I>2\sigma(I)$]	0.0583	0.1057
R_1 for all data	0.0603	0.1830
$wR_2(F^2)$ for all data	0.1669	0.3487
Max shift error	0.000	0
Goodness of fit	1.135	1.032
Maximum peak in Final Diff. Map ($e{\cdot}Å^{-3}$)	0.32	0.39
Minimum peak in Final Diff. Map ($e{\cdot}Å^{-3}$)	-0.38	-0.28

Confirmation of crystal direction by plane indices

Plane indices were determined by "Shape" software (Figure S4a). 3D model was prepared by tracing crystal outline in order to connect plane indices with lattice constant. Then, plane indices were determined based on mounted crystal angle and lattice constant. Mounted crystal angle was confirmed by oscillation photograph. Tunnel direction was determined based on lattice constant and naphthalene location (Figure S4b).

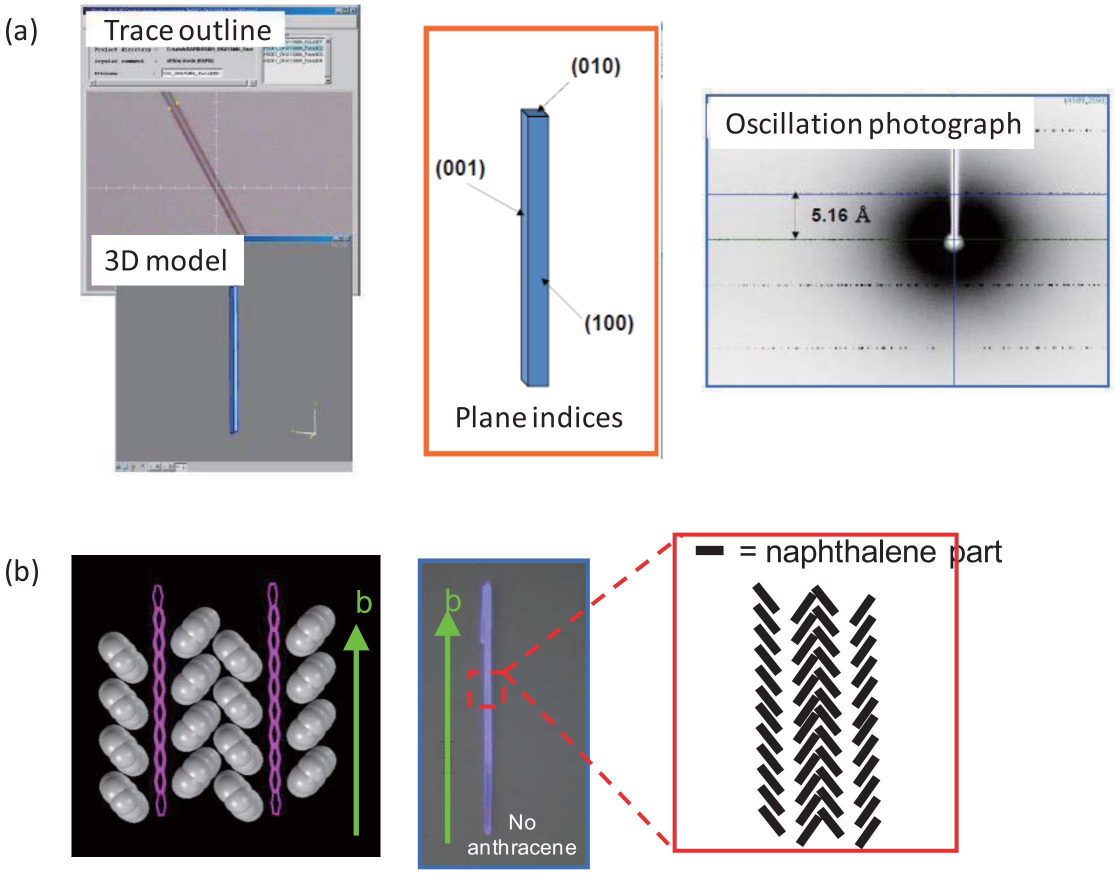


Figure S4. Plane indices and tunnel direction. (a) Determining plane indices. (b) Tunnel direction based on plane indices.

Reference

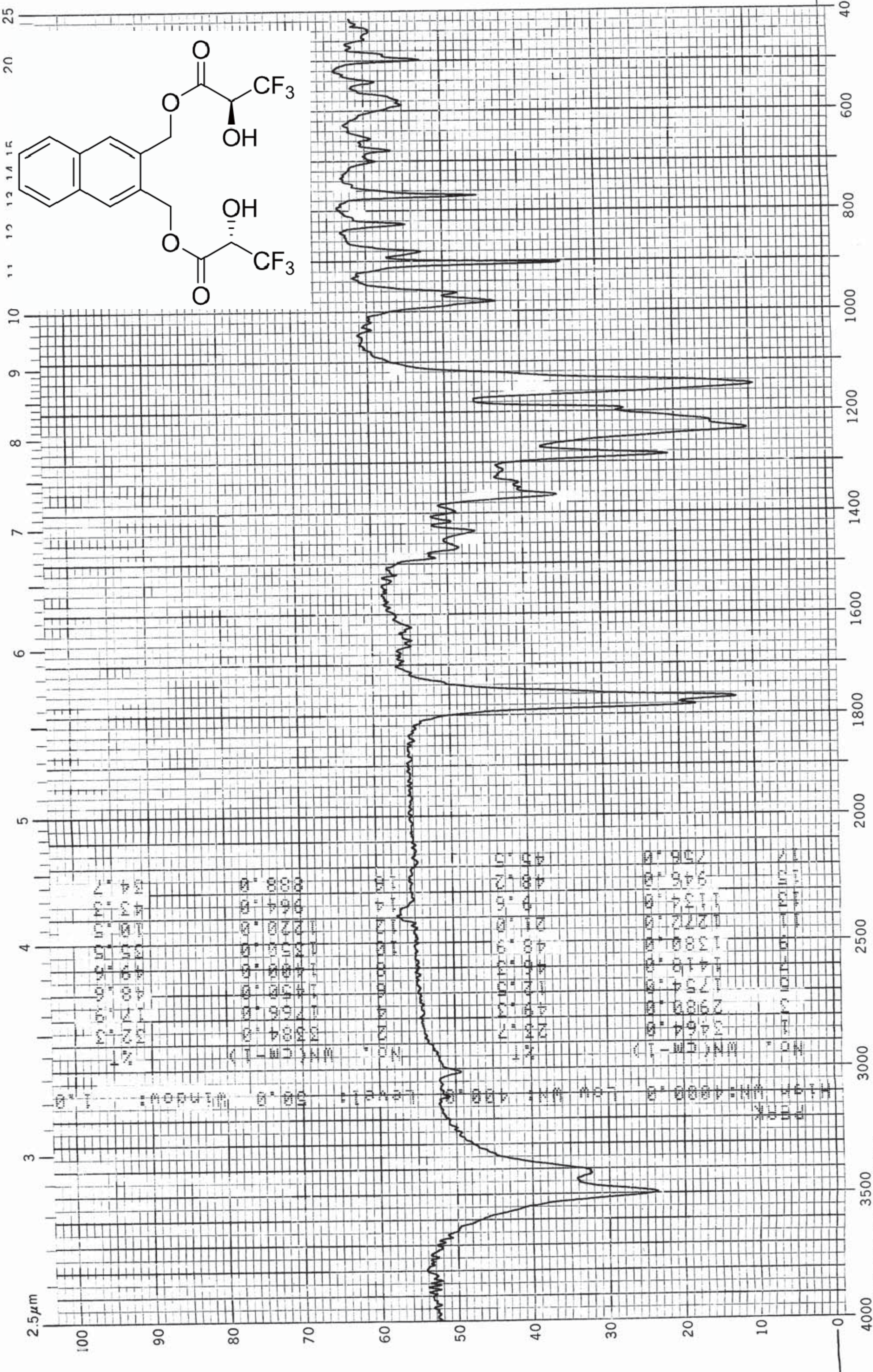
(ref. s1) Schaus, S. E.; Branders, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307.

(ref. s2) Katagiri, T.; Obara, F.; Toda, S.; Furuhashi, K.; *Synlett* **1994**, 507.

(ref. s3) Sanguinet, L.; Willliams, J. C.; Yang, Z.; Twieg, R. J.; Mao, G.; Singer, K. D.; Wiggers, G.; Petschek, R. G. *Chem. Mater.* **2006**, *18*, 4259.

(ref. s4) Wilcox, C. F. Jr.; Webner, K. A. *J. Org. Chem*. **1986**, *51*, 1088.

IR spectrum of naphthalene-2,3(S,S)-bis(methyl-3,3,3-trifluorolactate) TFLA-2,3-naph



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PEAK
High WN:4000.0  Low WN: 400.0  Level:  50.0  Window:   1.0

No.   WN(cm-1)        %T       No.   WN(cm-1)        %T
 1     3464.0        23.7       2     3384.0        32.3
 3     2980.0        49.3       4     1766.0        17.9
 5     1754.0        12.5       6     1450.0        48.6
 7     1416.0        46.3       8     1400.0        49.6
 9     1380.0        48.9      10     1350.0        35.5
11     1272.0        21.0      12     1220.0        10.5
13     1134.0         9.6      14      964.0        43.3
15      946.0        48.2      16      888.0        34.7
17      756.0        45.5
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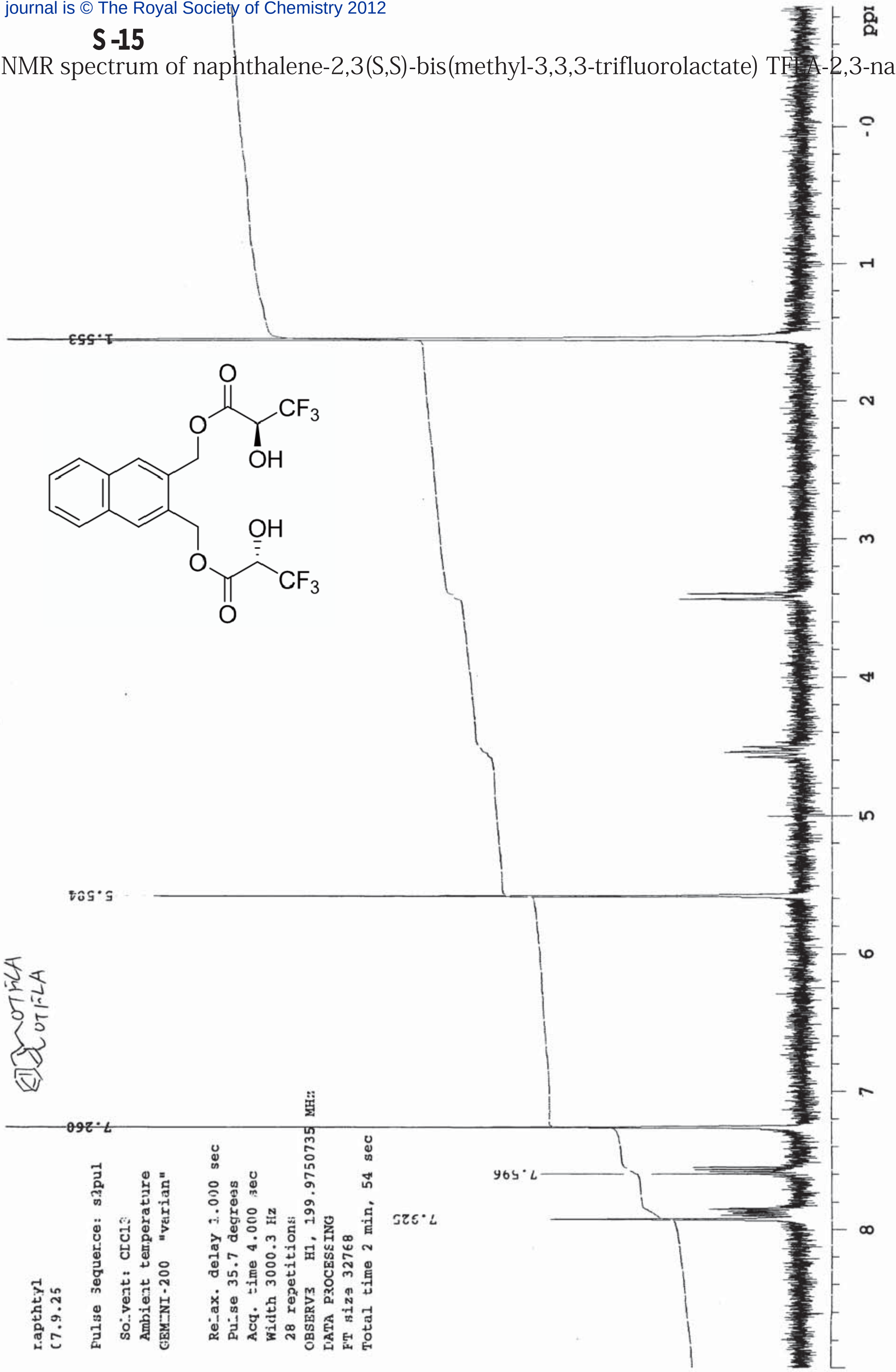
IH NMR spectrum of naphthalene-2,3(S,S)-bis(methyl-3,3,3-trifluorolactate) TFLA-2,3-naph



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07.9.25

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-200 "varian"

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Pulse 35.7 degrees
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Width 3000.3 Hz
28 repetitions
OBSERVE H1, 199.9750735 MHz
DATA PROCESSING
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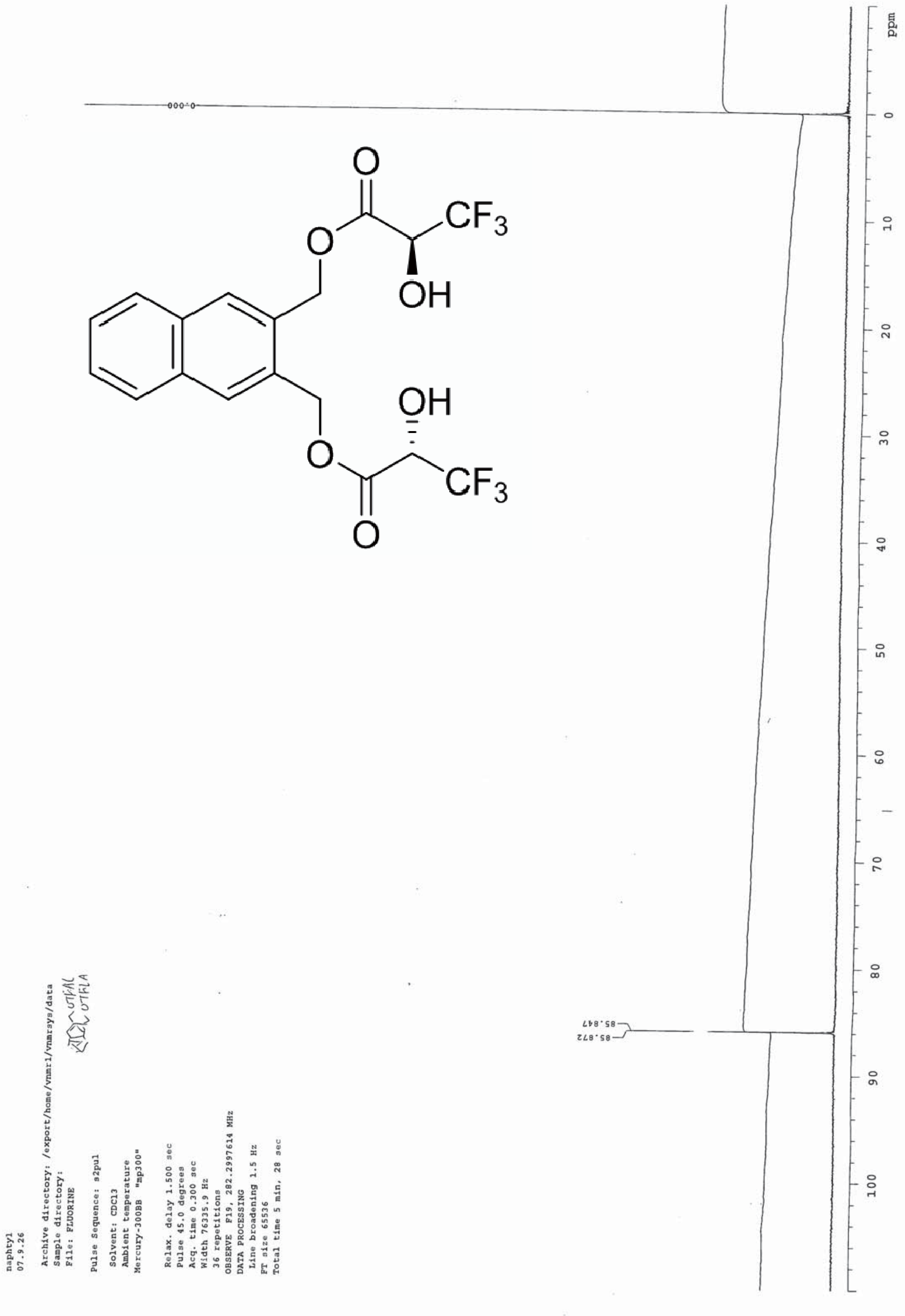
Total time 2 min, 54 sec

19F NMR spectrum of naphthalene-2,3(S,S)-bis(methyl-3,3,3-trifluorolactate) TFLA-2,3-naph



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naphtyl
07.9.26

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Sample directory:
File: FLUORINE

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Solvent: CDCl3
Ambient temperature
Mercury-300BB "mp300"

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Acq. time 0.300 sec
Width 76335.9 Hz
36 repetitions
OBSERVE  F19, 282.2997614 MHz
DATA PROCESSING
  Line broadening 1.5 Hz
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Total time 5 min, 28 sec
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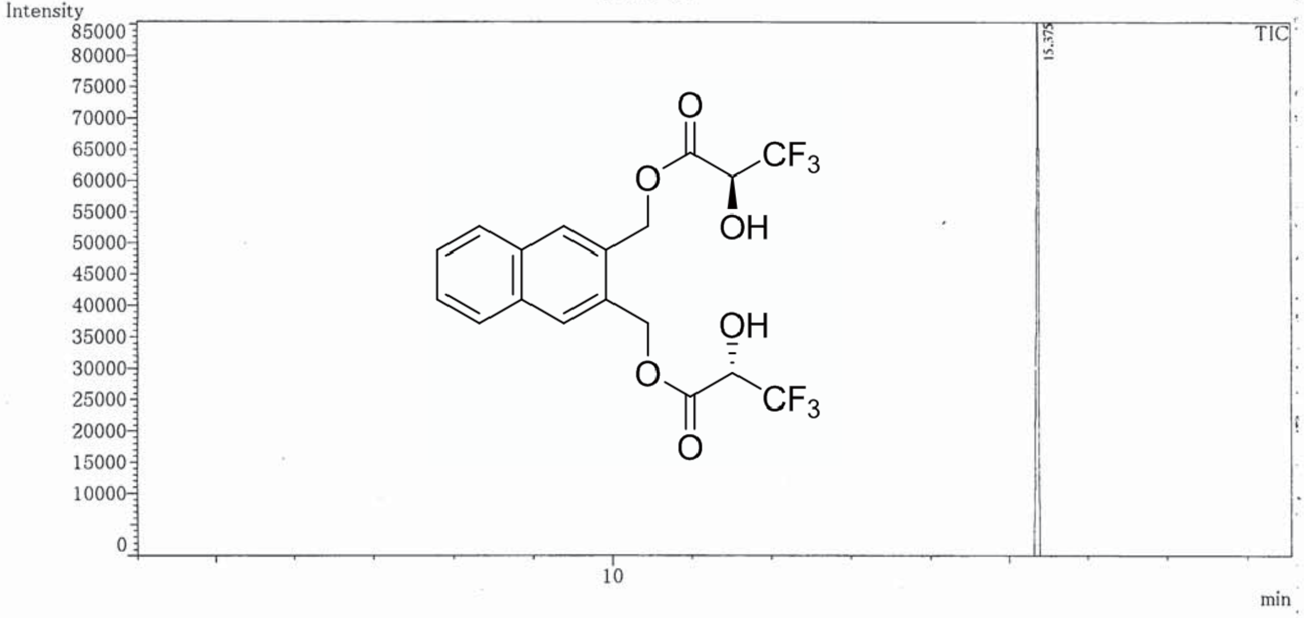
GC-MS of naphthalene-2,3(S,S)-bis(methyl-3,3,3-trifluorolactate) TFLA-2,3-naph

C:¥GCMSsolution¥Data¥yasumoto¥ty-naph.qgd

クロマトグラム



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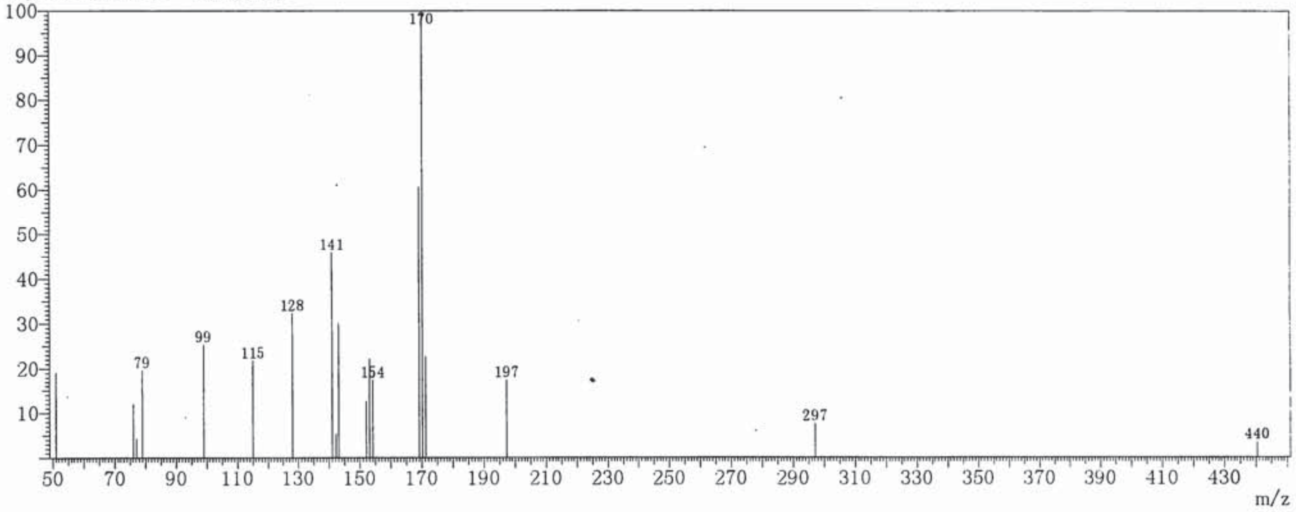

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バックグラウンド: ピークから計算

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77.15	4.35	128.05	32.29	152.10	12.63	170.10	100.00	440.35	3.47
79.05	19.47	141.05	45.92	153.10	22.09	171.15	22.68		

2010/3/29 [illegible]より引きつぎ

S -18

1H NMR spectrum of co-crystal for TFLA-2,3-naph and anthracene