Supplementary Material (ESI) for Chemical Communications

A binary hydrogen bonding motif based on homochiral recognition: Crystal structures and hydrogen bonding networks of *meso*-(*R,S*)-bis(trifluorolactate)s

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Electronic Supplementary Information (ESI)

(i) Experimental procedures.

(ii) Crystallographic parameter table for **1a-1f'**.

(iii) ORTEP plots for **1a-1f'** at 50% probability level.

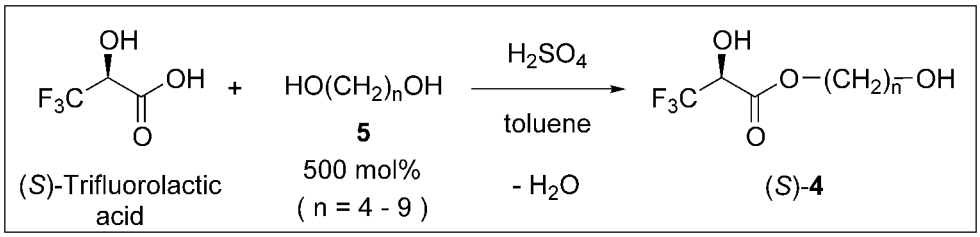
(iv) Additional figures for **1a-1e**.

(v) ^{1}H NMR spectra of crystal **1f** and **1f'** dissolved in $CDCl_3$.

General Methods. IR spectra were measured on Hitachi Model 270-30 Infrared Spectrophotometer. ^{1}H (300 MHz) and ^{19}F (288 MHz) NMR spectra were recorded by Varian MERCURY 300 and the chemical shifts are reported in δ (ppm) values relative to TMS (δ 0 ppm for ^{1}H NMR in $CDCl_3$), C_6F_6 (δ 0 ppm for ^{19}F NMR in $CDCl_3$). ^{13}C (150 MHz) NMR spectra were recorded by Varian UNITY INOBA 600 and the chemical shifts are reported in δ (ppm) values relative to $CDCl_3$ or CD_3OD (δ 77 ppm or δ 49 ppm for ^{13}C NMR, respectively). Coupling constants are reported in hertz (Hz). Elemental analyses were performed on Perkin Elmer series II CHNS/O Analyzer 2400. GC/MS analyses were performed on a Shimadzu GCMS-QP5050A. Melting points were performed on a Yanako MP-S3 melting point measurement apparatus. Optical rotation were measured by Horiba SEPA-300 digital polarimeter with a sodium (λ = 589 nm) lamp, and reported as follows: $[\alpha]^{T(^{o}C)}_{D}$ (*c* g/100 mL, solvent). Toluene was distilled from CaH_2. All other reagents and solvents were employed without further purification. E. Merck silica gel (Kieselgel 60, 230-400 mesh) was employed for the column chromatography.

Supplementary Material (ESI) for Chemical Communications

Preparation of single-headed (*S*)-trifluorolactate (4)



1,4-butanediol mono-(*S*)-3,3,3-trifluorolactate [(*S*)-4a]: Typical procedure of acid catalyzed monoesterification of α,ω-alkanediol with (*S*)-3,3,3-trifluorolactic acid[1]. Two-necked round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a Dean-Stark apparatus surmounted by reflux condenser was charged with 1,4-butanediol **5a** (9.01 g, 100 mmol), a (*S*)-trifluorolactic acid (2.88 g, 20 mmol) and 0.03 g of sulfuric acid as a catalyst in toluene (20 ml). The mixture was brought to reflux with the removal of water. After 1 h, the resulting mixture was cooled to ambient temperature and water was added to the mixture, which was extracted with ether. The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtrated, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (hexane/AcOEt = 1/1) to give the monoester **4a** (2.90 g, 13.4 mmol, 67% yield). White solid. Mp 52-53 ºC. IR (KBr): 3468, 3108, 2972, 1752, 1340, 1268, 1224, 1180, 1132, 1042 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (q, J 7.2, 1H), 4.43 (dt, J_1 10.8, J_2 6.6, J_3 4.5, 1H), 4.34 (dt, J_1 10.8, J_2 6.6, J_3 4.5, 1H), 3.71 (t, J 6, 2H), 3.44 (brs, OH), 1.83 (quintet, J 6, 2H), 1.66 (quintet, J 6, 2H), terminal OH was not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 3F). ^{13}C NMR ($CDCl_3$): δ 167.3, 122.3 (q, J 282), 70.0 (q, J 32.6), 64.2, 58.6, 28.2, 24.6; MS: m/z 185 (2), 145 (15), 117 (8), 99 (8), 87 (5), 79 (7), 71 (11). 55 (100). Anal. Calcd for $C_7H_{11}F_3O_4$: C 38.90, H 5.13. Found: C 39.19, H, 5.27. $[\alpha]^{25}_D$ –6.21 (*c* 1.0, acetone).

1,5-pentanediol mono-(*S*)-3,3,3-trifluorolactate [(*S*)-4b]: 75% yield. White solid. Mp 59-60 ºC. IR (KBr): 3508, 2968, 1746, 1270, 1234, 1146, 1128 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J 6.9, 1H), 4.37 (dt, J_1 10.5, J_2 6.6, 1H), 4.32 (dt, J_1 10.8, J_2 6.6, 1H), 3.67 (t, J = 6.3, 2H), 3.47 (brs, OH), 1.35-1.80 (m, 6H), terminal OH was not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 6.9, 3F). ^{13}C NMR ($CDCl_3$): δ 167.4, 122.3 (q, J 282), 69.9 (q, J 32.7), 67.2, 62.4, 31.8, 28.0, 21.8; MS: m/z 172 (0.4), 145 (3), 144 (1), 117 (2), 101 (27), 86 (6), 79 (8), 69 (100). 68 (49), 67 (33), 57 (43), 56 (89), 55 (36), 51 (13). Anal. Calcd for $C_8H_{13}F_3O_4$: C 41.74, H 5.69. Found: C 41.58, H 5.85. $[\alpha]^{25}_D$ –4.77 (*c* 1.1, acetone).

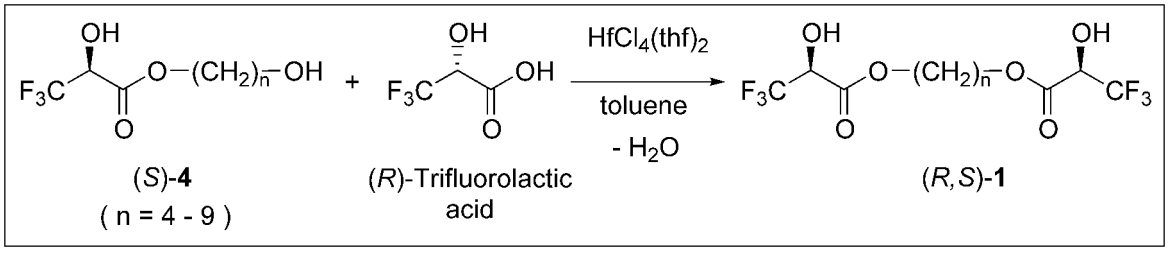
1,6-hexanediol mono-(*S*)-3,3,3-trifluorolactate [(*S*)-4c]: 75% yield. White solid. Mp 57-58 ºC. IR (KBr): 3488, 2952, 1742, 1358, 1272, 1250, 1220, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (q, J 6.9, 1H), 4.36 (dt, J_1 10.5, J_2 6.6, 1H), 4.31 (dt, J_1 10.8, J_2 6.6, 1H), 3.66 (t, J 6.3, 2H), 1.3-1.8 (m, 8H), OHs were not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 6.9, 3F). ^{13}C NMR ($CDCl_3$): δ 167.4, 122.4 (q, J 282), 70.0 (q, J 32.7), 67.2, 62.6, 32.1, 28.1, 25.3, 25.1. MS: m/z 145 (47), 117 (13), 99 (6), 83 (24), 82 (18), 67 (55), 55 (100). Anal. Calcd for $C_9H_{15}F_3O_4$: C 44.26, H 6.19. Found: C 44.38, H 6.43. $[\alpha]^{25}_D$ –3.82 (*c* 1.1, acetone).

1,7-heptanediol mono-(*S*)-3,3,3-trifluorolactate [(*S*)-4d]: White solid. Mp 50-51 ºC. IR (KBr): 3508, 2940, 1746, 1270, 1238, 1146, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (q, J 6.9, 1H), 4.37 (dt, J_1 10.8, J_2 6.6, 1H), 4.28 (dt, J_1 10.5, J_2 6.6, 1H), 3.65 (t, J 6.6, 2H), 3.46 (brs, OH), 1.3-1.8 (m, 10H), terminal OH was not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 3F). ^{13}C NMR ($CDCl_3$): δ 167.3, 122.4 (q, J 282), 69.9 (q, J 32.0), 67.1, 62.6, 32.2, 28.6, 28.0, 25.3. MS: m/z 145 (9), 117 (2), 97 (10), 84 (30), 81 (22), 71 (16), 69 (23), 68 (51), 67 (55), 56 (41), 55 (100). Anal. Calcd for $C_{10}H_{17}F_3O_4$: C 46.51, H 6.64. Found: C 46.47, H 6.53. $[\alpha]^{25}_D$ –4.07 (*c* 1.1, acetone).

1,8-octanediol mono-(*S*)-3,3,3-trifluorolactate [(*S*)-4e]: 80% yield. White solid. Mp 47-48 ºC. IR (KBr): 3476, 2948, 2868, 1750, 1336, 1212, 1184, 1128 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.47 (quintet, J 6.9, 1H), 4.36 (dt, J_1 10.8, J_2 6.6, 1H), 4.27 (dt, J_1 10.5, J_2 6.6, 1H), 3.65 (t, J 6.6, 2H), 3.53 (brs, OH), 1.3-1.75 (m, 12H), terminal OH was not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 6.9, 3F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.3 (q, J 281), 69.9 (q, J 32.7), 67.5, 62.9, 32.5, 29.1, 28.9, 28.2, 25.5, 25.4. MS: m/z 145 (12), 110 (5), 99 (11), 98 (15), 83 (12), 82 (54), 81 (34), 70 (36), 69 (99), 68 (47), 67 (78), 57 (25), 56 (30), 55 (100), 54 (54). Anal. Calcd for $C_{11}H_{19}F_3O_4$: C 48.53, H 7.03. Found: C 48.53, H, 6.82. $[\alpha]^{25}_D$ –3.24 (*c* 1.0, acetone).

1,9-nonanediol mono-(*S*)-3,3,3-trifluorolactate [(*S*)-4f]: 82% yield. White solid. Mp 48-49 ºC. IR (KBr): 3512, 3172, 2932, 2864, 1746, 1342, 1268, 1246, 1176, 1146, 1128 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J 6.9, 1H), 4.37 (dt, J_1 10.8, J_2 6.6, 1H), 4.28 (dt, J_1 10.8, J_2 6.6, 1H), 3.65 (t, J 6.6, 2H), 3.47 (d, J 7.5, OH), 1.25-1.75 (m, 14H), terminal OH was not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 3F). ^{13}C NMR ($CDCl_3$): δ 167.4, 122.4 (q, J 282), 69.9 (q, J 32.7), 67.4, 62.8, 32.5, 29.2, 29.1, 28.8, 28.2, 25.5, 25.4. MS: m/z 145 (3), 144 (2), 112 (7), 96 (26), 95 (24), 84 (18), 83 (46), 82 (49), 81 (46), 71 (16), 70 (18), 69 (81), 68 (60), 67 (70), 57 (26), 56 (32), 55 (100), 54 (49). Anal. Calcd for $C_{12}H_{21}F_3O_4$: C 50.34, H 7.39. Found: C 50.43, H, 7.33. $[\alpha]^{25}_D$ –3.14 (*c* 1.0, acetone).

Preparation of double-headed (*R,S*)-trifluorolactates (1)



Tetramethylene-(*R,S*)-bis(3,3,3-trifluorolactate) (1a): Typical procedure of hafnium(IV) catalyzed esterification[2] of (*S*)-**4** with (*R*)-3,3,3-trifluorolactic acid[3]. Two-necked round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a Dean-Stark apparatus surmounted by a reflux condenser was charged with a compound (*S*)-**4a** (0.324 g, 1.50 mmol), a (*R*)-trifluorolactic acid (0.324 g, 2.25 mmol) and $HfCl_4 \cdot (thf)_2$ (0.0069 g, 0.015 mmol) as a catalyst in toluene (5 ml). The mixture was brought to reflux under Ar atmosphere with the removal of water. After 15 h, the resulting mixture was cooled to

ambient temperature and water (ca. 0.1 ml) was added. After being stirred for 10 min, the resultant mixture was dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (hexane:AcOEt = 5:1) to give the diester **1a** (0.428 g, 1.25 mmol, 83% yield). Colorless crystal. Mp 92-93 ºC. IR (KBr): 3508, 3436, 2988, 2952, 1752, 1350, 1307, 1274, 1228, 1181, 1133 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.25-4.57 (m, 6H), 3.38 (d, J 7.8, 2OH), 1.82 (m, 4H); ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 6F); ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J 282), 69.8 (q, J 33.2), 66.7, 24.7; MS: m/z 199 (2), 145 (1), 129 (1), 99 (5), 79 (5), 73 (12), 56 (5), 55 (100). Anal. Calcd for $C_{10}H_{12}F_6O_6$: C 35.10, H 3.53. Found: C 34.9, H 3.86. $[\alpha]^{25}_D$ = ±0.0, σ(N-1) = 0.07 (*c* 1.0, acetone).

Pentamethylene-(*R,S*)-bis(3,3,3-trifluorolactate) (1b): 82% yield. Colorless crystal. Mp 71-72 ºC. IR (KBr): 3448, 2968, 1743, 1272, 1135 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J 7.5, 2H), 4.39 (dt, J_1 10.8, J_2 6.6, 2H), 4.29 (dt, J_1 10.8, J_2 6.3, 1H), 3.40 (d, J 7.8, 2OH), 1.70-1.80 (m, 4H), 1.40-1.55 (m, 2H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J 282), 69.8 (q, J 32.6), 67.1, 27.8, 21.8; MS: m/z 145 (2), 99 (4), 78 (4), 69 (100), 55 (6). Anal. Calcd for $C_{11}H_{14}F_6O_6$: C 37.09, H 3.96. Found: C 37.0, H 4.16. $[\alpha]^{25}_D$ = ±0, σ(N-1) = 0.10 (*c* 1.1, acetone).

Hexamethylene-(*R,S*)-bis(3,3,3-trifluorolactate) (1c): 67% yield. Colorless crystal. Mp 112-113 ºC. IR (KBr): 3440, 1746, 1468, 1414, 1343, 1294, 1270, 1241, 1220, 1187, 1135, 964 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J 7.2, 2H), 4.39 (dt, J_1 10.8, J_2 6.6, 2H), 4.28 (dt, J_1 10.8, J_2 6.3, 2H), 3.41 (d, J 7.5, 2OH), 1.74 (quintet, J 7, 4H), 1.41 (quintet, J 3, 4H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J 282), 69.8 (q, J 33.2), 67.3, 28.1, 25.0. MS: m/z 145 (2), 127 (5), 117 (1), 99 (9), 83 (80), 82 (22), 79 (11), 67 (34), 56 (14), 55 (100). Anal. Calcd for $C_{12}H_{16}F_6O_6$: C 38.93, H 4.36. Found: C 38.8, H 4.5. $[\alpha]^{25}_D$ = ±0, σ(N-1) = 0.16 (*c* 1.1, acetone).

Heptamethylene-(*R,S*)-bis(3,3,3-trifluorolactate) (1d): 75% yield. Colorless crystal. Mp 94-95 ºC. IR (KBr): 3450, 2952, 1746, 1344, 1268, 1246, 1228, 1194, 1135 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J 7.2, 2H), 4.38 (dt, J_1 10.5, J_2 6.6, 2H), 4.27 (dt, J_1 10.8, J_2 6.6, 2H), 1.71 (quintet, J 7, 4H), 1.25-1.45 (m, 6H), OHs were not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J 282), 69.8 (q, J 32.7), 67.5, 28.4, 28.1, 25.3. MS: m/z 141 (1), 97 (44), 81 (11), 69 (18), 68 (27), 67 (21), 55 (100). Anal. Calcd for $C_{13}H_{18}F_6O_6$: C 40.63, H 4.72. Found: C 40.86, H 4.98. $[\alpha]^{25}_D$ = ±0, σ(N-1) = 0.08 (*c* 1.0, acetone).

Octamethylene-(*R,S*)-bis(3,3,3-trifluorolactate) (1e): 85% yield. Colorless crystal. Mp 84-85 ºC. IR (KBr): 3456, 2972, 2944, 1749, 1342, 1272, 1232, 1188, 1136 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.47 (q, J 7.2, 2H), 4.37 (dt, J_1 10.8, J_2 6.9, 2H), 4.27 (dt, J_1 10.5, J_2 6.6, 2H), 3.43 (d, J 7.5, 2OH), 1.72 (quintet, J 7, 4H), 1.35-1.5 (m, 8H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 7.2, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J 282), 69.8 (q, J 33.2), 67.6, 28.7, 28.1, 25.3. MS: m/z 145 (4), 127 (4), 110 (8), 109 (9), 97 (18), 96 (18), 95 (22), 83 (42), 82 (47), 81 (41), 71 (13), 70 (15), 69 (54), 68 (50), 67 (56), 57 (21), 56 (27), 55 (100), 54 (40). Anal. Calcd for $C_{14}H_{20}F_6O_6$: C 42.22, H 5.06. Found: C 41.86, H 5.32. $[\alpha]^{25}_D$ = ±0, σ(N-1) = 0.11 (*c* 1.2, acetone).

Nonamethylene-(*R,S*)-bis(3,3,3-trifluorolactate) (1f): 78% yield. Colorless crystal. Mp 67-68 ºC. IR (KBr): 3588, 1750, 1226, 1134 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.48 (q, J 7.2, 2H), 4.37 (dt, J_1 10.8, J_2 6.6, 2H), 4.28 (dt, J_1 10.5, J_2 6.6, 2H), 3.43 (d, J 7.5, 2OH), 1.71 (quintet, J 7, 4H), 1.25-1.45 (m, 10H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J 6.9, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J 282), 69.8 (q, J 33.3), 67.7, 29.2, 28.9, 28.2, 25.5. MS: m/z 145 (1), 125 (6), 124 (9), 96 (26), 95 (20), 83 (48), 82 (42), 81 (31), 69 (100), 68 (40), 67 (42), 57 (18), 56 (14), 55 (85), 54 (35). Anal. Calcd for $C_{15}H_{22}F_6O_6$: C 43.69, H 5.38. Found: C 43.87, H 5.31. $[\alpha]^{25}_D = \pm 0$, σ(N-1) = 0.07 (*c* 1.2, acetone).

Preparation of single crystal. Crystallizations of **1a-1f** were performed by slow evaporation of solvents from hexane/ether solutions. Crystal **1f'** was obtained by slow evaporation of solvents from isooctane/THF solutions of compound **1f**.

X-ray crystallographic studies. X-ray diffraction data were collected with a Rigaku RAXIS-IV diffractometer, Mo-Kα radiation [λ = 0.71073 Å]. The temperature was controlled by a low temperature device. The data were collected to a maximam 2θ value of 55.0 °. All structures were solved by direct methods using SIR97[4] or SAPI91[5]. All structures were refined by full-matrix least-squares on F^2 using SIR97 or SHELXL97[6] program. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from Fourier difference maps or placed in calculated positions, and refined isotropically or treated as riding atoms using the SHELXL default parameters, or fixed. In case of the single crystal **1f**, the SQUEEZE[7] option of the program PLATON[8] was used to eliminate the contribution of solvent molecules that were highly disordered, thereby giving final models based only on the ordered part of the crystal structure. The calculations were performed with the teXsan[9] and WinGX[10] crystallographic software package.

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Table 1S Crystallographic parameter table for **1a-1f'**

Compound	**1a**	**1b**	**1c**	**1d**	**1e**	**1f** (as hexane solvate)	**1f '**
CCDC number	246911	246912	246913	246914	246915	246916	264877
Formula	$C_{10}H_{12}F_6O_6$	$C_{11}H_{14}F_6O_6$	$C_{12}H_{16}F_6O_6$	$C_{13}H_{18}F_6O_6$	$C_{14}H_{20}F_6O_6$	$C_{15}H_{22}F_6O_6(C_6H_{14})_n$	$C_{15}H_{22}F_6O_6$
Formula weight	342.19	356.22	370.24	384.27	398.30	498.5[c]	412.32
Crystal size (mm^3)	0.4x0.1x0.1	1.0x0.06x0.02	0.5x0.25x0.05	0.1x0.1x0.03	0.4x0.2x0.1	0.4x0.2x0.2	1.0x0.2x0.2
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal System	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$(#14)	$Pna2_1$(#33)	C2/c(#15)	Pnma(#62)	P-1(#2)	Pnma(#62)	$P2_1/c$ (#14)
a (Å)	7.1113(8)	15.40(1)	19.891(2)	15.613(3)	5.120(1)	15.7479(5)	5.3266(7)
b (Å)	5.0864(3)	18.79(2)	5.1138(2)	21.793(4)	10.895(3)	27.135(1)	20.331(5)
c (Å)	18.142(2)	5.045(3)	15.605(1)	5.0901(5)	17.165(4)	5.0309(1)	16.967(4)
α (º)	90	90	90	90	72.489(8)	90	90
β (º)	98.398(2)	90	100.918(1)	90	89.58(2)	90	94.52(1)
γ (º)	90	90	90	90	85.41(2)	90	90
Volume ($Å^3$)	649.17(10)	1460(6)	1558.6(2)	1731(1)	910.0(4)	2149.8(5)	1831.8(7)
Z value	2	4	4	4	2	4	4
D_{calc} ($g \cdot cm^{-3}$)	1.75	1.62	1.58	1.47	1.45	1.54[c]	1.5
μ (mm^{-1})	0.193	0.175	0.167	0.153	0.149	0.143[c]	0.075
Temperature (K)	120	120	120	120	120	100	115
Reflection collected	2819	6719	5843	10363	4258	4499	6930
Unique reflection	1487	2218	1679	1888	2601	1900	4035
R (int)	0.022	0.073	0.012	0.037	0.03	0.013	0.02
Transmission factor range	0.70-0.98	0.51-1.00	0.78-0.99	0.87-1.00	0.64-0.99	0.64-0.98	0.57-0.97
Max theta (º)	25.85	25.5	25.4	25.4	25.5	25.0	25.75
Data completeness	0.9912	0.887	0.953	0.948	0.769	0.987	0.946
Data / restraints / parameters	1247/0/124	2218/1/209	1371/0/137	1541/0/149	2601/0/236	1900/0/126	3330/0/332
Reflections used [I>2σ(I)]	1043	1002	1283	836	2135	1707	3034
R 1 for [I>2σ(I)][a]	0.0448	0.0567	0.0356	0.0506	0.0851	0.0432	0.0451
R 1 for all data	0.0536	0.1391	0.0375	0.0976	0.0963	0.0465	0.0494
wR 2 for all data[b]	0.116	0.132	0.1273	0.1395	0.269	0.1167	0.1559
Max shift/error	0.0005	0.003	0.0004	0.0001	0	0.000	0.0003
Goodness of fit	1.397	0.869	1.251	1.185	1.111	1.124	1.65
Largest diff. peak ($e \cdot Å^{-3}$)	0.24	0.32	0.25	0.54	0.55	0.33	0.17
Largest diff. hole ($e \cdot Å^{-3}$)	-0.36	-0.36	-0.26	-0.54	-0.43	-0.22	-0.26

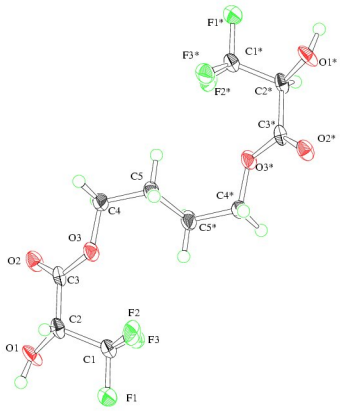
a) $R1 = \sum | Fo - Fc | / \sum | Fo |$

b) $wR2 = [\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2]^{1/2}$

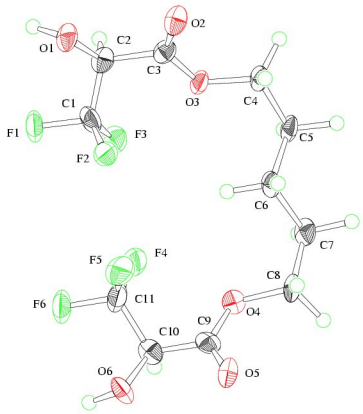
c) calculated as hexane solvate

Figure 1S ORTEP plots for **1a-1f'** at 50% probability level.

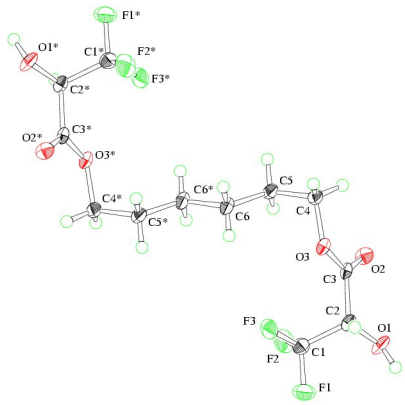
(1a)



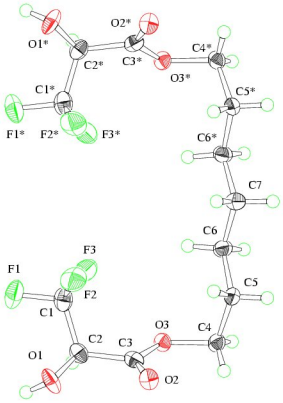
(1b)



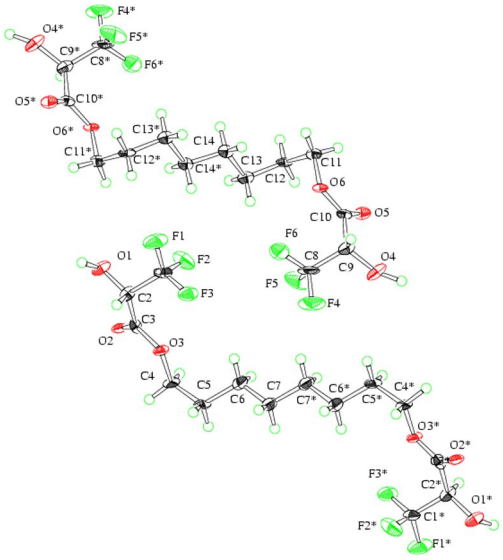
(1c)



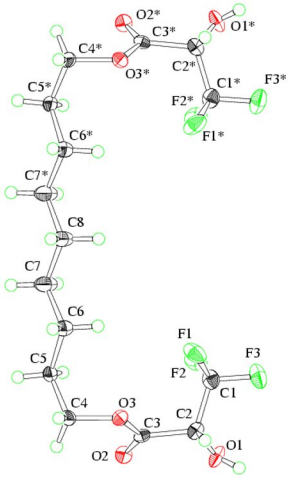
(1d)



(1e)



(1f)



(1f')

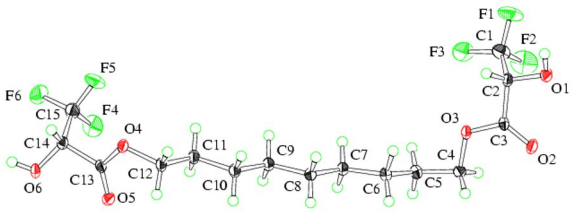


Figure 2S Crystal structure of **1a** viewed down *a* axis.

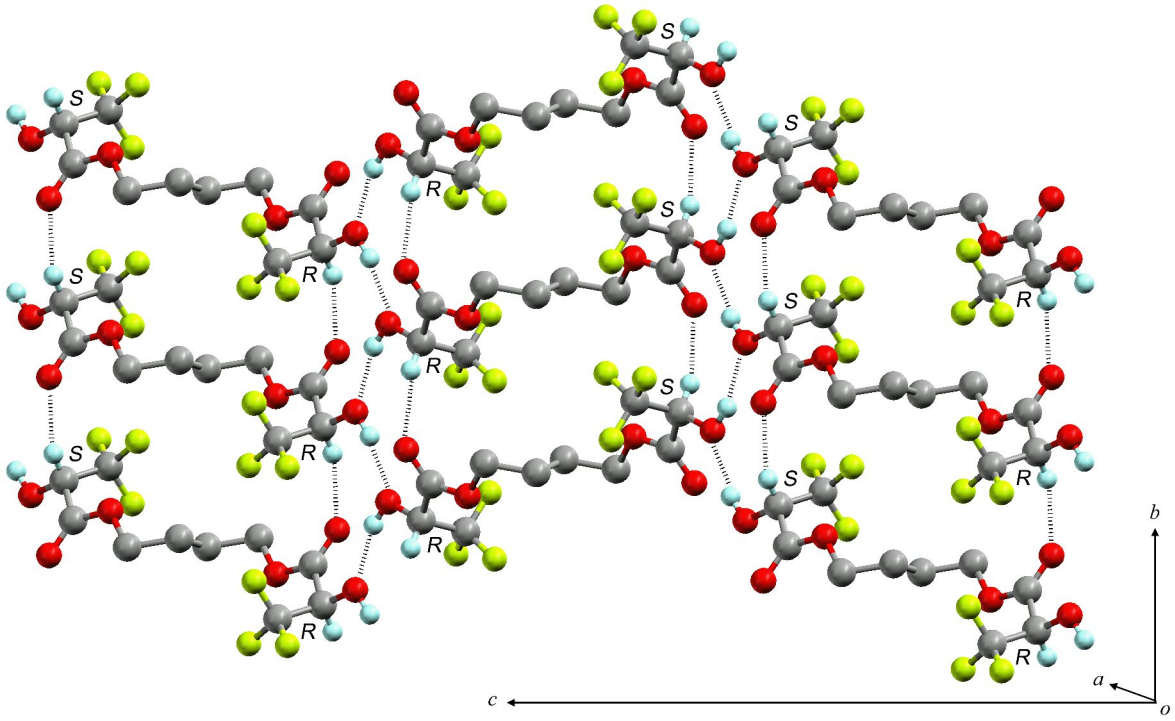


Figure 3S Crystal structure of **1b** viewed down *a* axis.

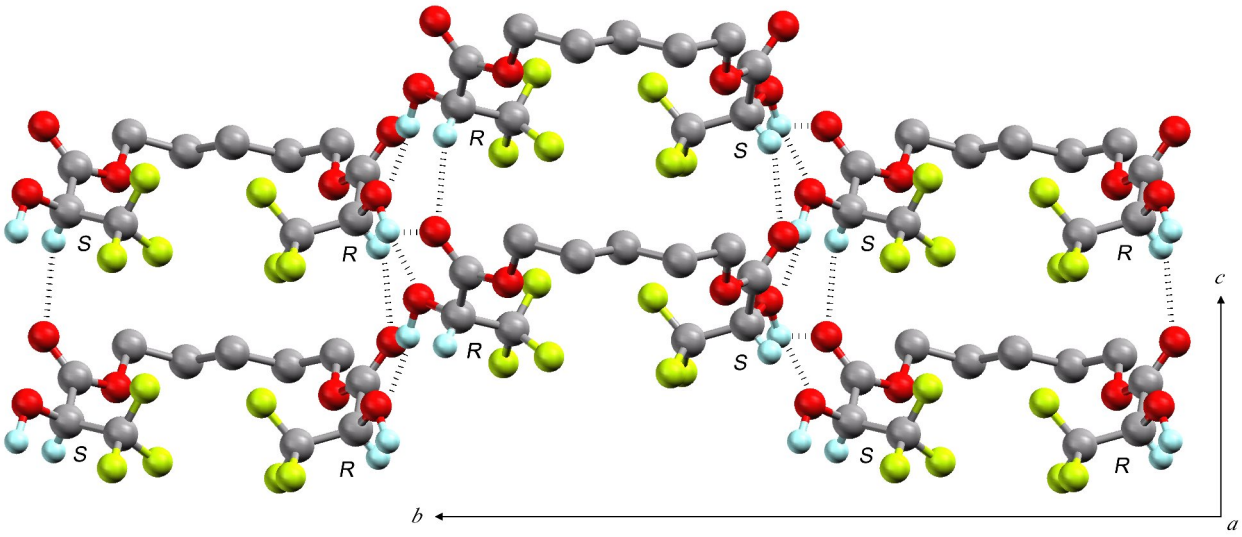


Figure 4S Crystal structure of **1c** viewed down *c* axis.

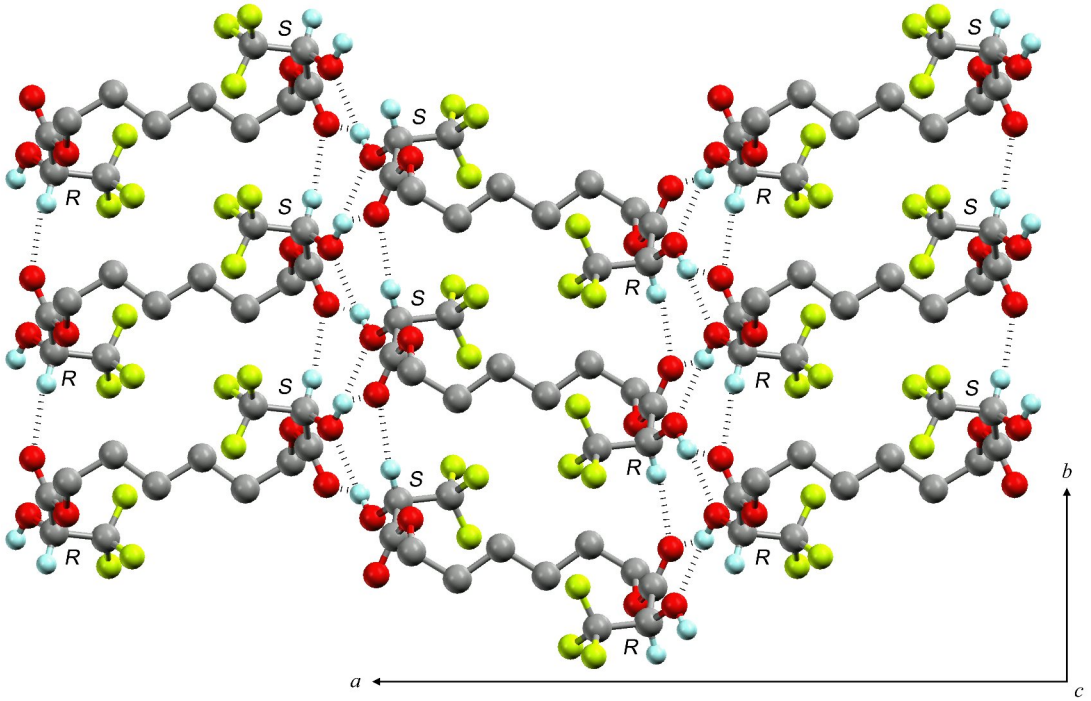


Figure 5S Crystal structure of **1d** viewed down *a* axis.

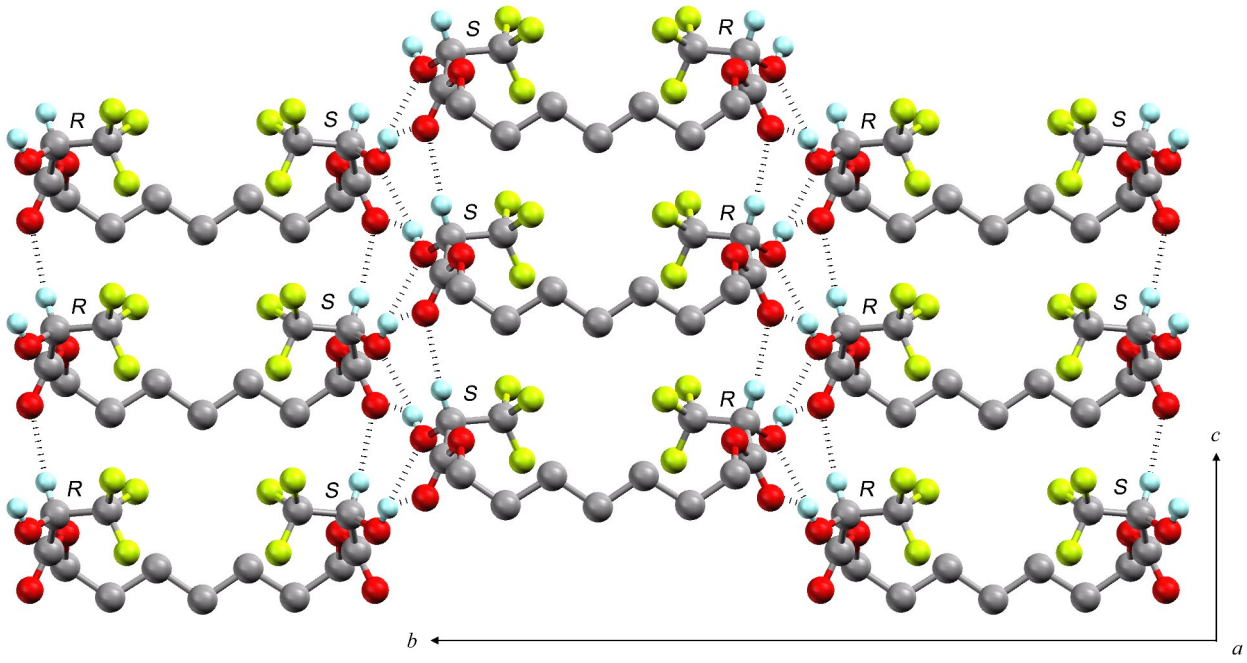


Figure 6S Crystal structure of **1e** viewed down *c* axis.

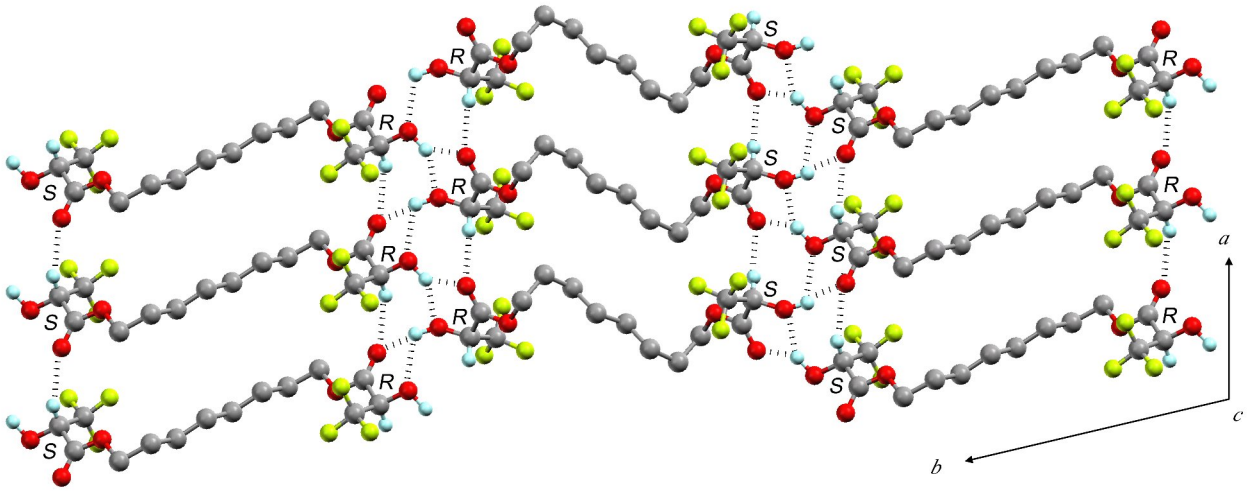


Figure 7S ^{1}H NMR spectrum of crystal **1f** dissolved in $CDCl_3$

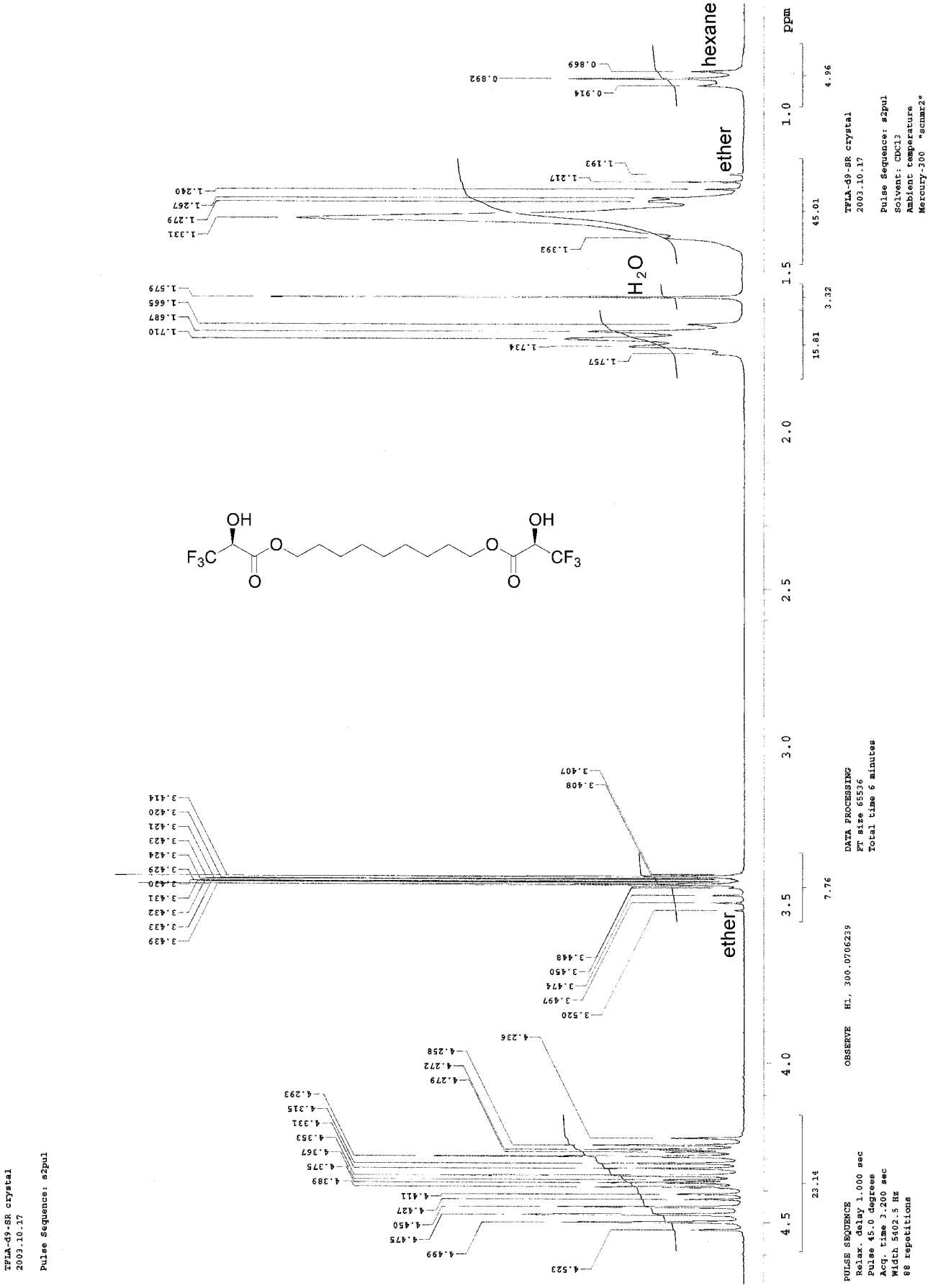


Figure 8S ^{1}H NMR spectrum of crystal **1f'** dissolved in $CDCl_3$ (without guest molecules)