Nanoporous organic layerd crystals of double-headed bis(trifluorolactate)s. Hydrogen-bonded systematic crystal structures controlled by the symmetries of molecular components.

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Electronic Supplementary Information (ESI)

(i) Compound data for (*S*,*S*)-**3**

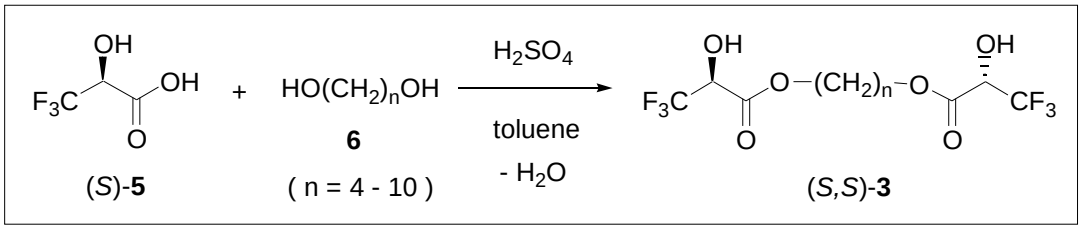
(ii) ORTEP plots for **3**

(iii) Additional figures of **3**

(iv) ^{1}H NMR spectra of dissolved crystals **3f**, **3g**, and **4f** in $CDCl_3$

(v) TG curves of inclusion compounds **3f**, **3g**, and **4f**

Synthesis of double-headed (*S*,*S*)-bis(trifluorolactate)s 3



Typical synthetic procedure for **3** and the compound data for **3a** are described in the experimental section.

Pentamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate) [(*S*,*S*)-3b]: 78% yield. Colourless crystal. Mp 100-101 ºC. IR (KBr): 3432, 2968, 1754, 1742, 1462, 1134 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J = 7.2 Hz, 2H), 4.39 (dt, J_1 = 10.8 Hz, J_2 = 6.6 Hz, 2H), 4.29 (dt, J_1 = 10.8 Hz, J_2 = 6.6 Hz, 2H), 3.47 (d, J = 7.8 Hz, 2OH), 1.71-1.82 (m, 4H), 1.41-1.53 (m, 2H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J = 7.2 Hz, 6F). ^{13}C NMR (CD_3OD): δ 168.2, 124.4 (q, J = 281 Hz), 71.2 (q, J = 32 Hz), 67.1, 28.9, 23.0. MS: m/z 145 (1), 99 (4), 69 (100), 68 (17), 51(5), 41(49); Anal. Calcd for $C_{11}H_{14}F_6O_6$: C 37.09, H, 3.96, Found: C 36.83, H, 4.19. $[\alpha]^{25}_D$ –6.61 (*c* 1.0, acetone).

Hexamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate) [(*S*,*S*)-3c]: 80% yield. Colourless crystal. Mp 113-114 ºC. IR (KBr): 3444, 2980, 1750, 1738, 1228, 1130 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (q, J = 7.2 Hz, 2H), 4.36 (dt, J_1 = 10.8 Hz, J_2 = 6.6 Hz, 2H), 4.30 (dt, J_1 = 10.8 Hz, J_2 = 6.6 Hz, 2H), 1.65-1.80 (m, 4H), 1.35-1.50 (m, 4H), OHs were not observed. ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J = 6.9 Hz, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J = 282 Hz), 69.8 (q, J = 32.5 Hz), 67.3, 28.1, 25.0. MS: m/z 145 (2), 127 (5), 117 (1), 99 (9), 83 (80), 67 (34), 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. $[\alpha]^{25}_D$ –5.80 (*c* 1.1, acetone).

Heptamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate) [(*S*,*S*)-3d]: 92% yield. Colourless crystal. Mp 93-94 ºC. IR (KBr): 3448, 2952, 2872, 1750, 1740, 1270, 1190, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J = 6.6 Hz, 2H), 4.35 (dt, J_1 = 10.8 Hz, J_2 = 6.6 Hz, 2H), 4.29 (dt, J_1 = 10.5 Hz, J_2 = 6.6 Hz, 2H), 3.51 (d, J = 6.9 Hz, 2OH), 1.6-1.8 (m, 4H), 1.25-1.45 (m, 6H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J = 6.9 Hz, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J = 284 Hz), 69.8 (q, J = 32.1 Hz), 67.5, 28.4, 28.1, 25.3. MS: m/z 141 (2), 99 (4), 98 (4), 97 (48), 81 (11), 69 (19), 68 (29), 67 (19), 55

(100), 41 (25); Anal. Calcd for $C_{13}H_{18}F_6O_6$: C 40.63, H, 4.72, Found: C 40.79, H, 5.0. $[\alpha]^{25}_D$ –4.33 (*c* 1.1, acetone).

Octamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate) [(*S*,*S*)-3e]: 90% yield. Colourless crystal. Mp 71-72 ºC. IR (KBr): 3452, 2948, 1750, 1734, 1224, 1198, 1134 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.47 (quintet, J = 7.2 Hz, 2H), 4.36 (dt, J_1 = 10.5 Hz, J_2 = 6.6 Hz, 2H), 4.30 (dt, J_1 = 10.8 Hz, J_2 = 6.6, 2H), 3.41 (d, J = 7.8 Hz, 2OH), 1.71 (quintet, J = 6.6 Hz, 4H), 1.35 (brs, 8H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J = 6.9 Hz, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J = 284 Hz), 69.7 (q, J = 33.3 Hz), 67.6, 28.7, 28.1, 25.3. MS: m/z 145 (1), 129 (1), 111 (21), 110 (12), 98 (8), 95 (7), 83 (10), 82 (41), 81 (22), 69 (100), 68 (31), 67 (42), 56 (10), 55 (84), 54 (37), 43 (16), 42 (16), 41 (62); Anal. Calcd for $C_{14}H_{20}F_6O_6$: C 42.22, H 5.06, Found: C 42.0, H 5.29. $[\alpha]^{25}_D$ –4.38 (*c* 1.1, acetone). The ee was determined to be >99% ee by HPLC analysis of the dibenzoate ester (Daicel Chiralcel® OD-H, 100:1 hexane:*i*-PrOH, 1.0 mL / min, 254 nm, t_{SS}(major) = 13.3 min, t_{RS}(minor) = 15.6 min, t_{RR}(minor) = 19.1 min).

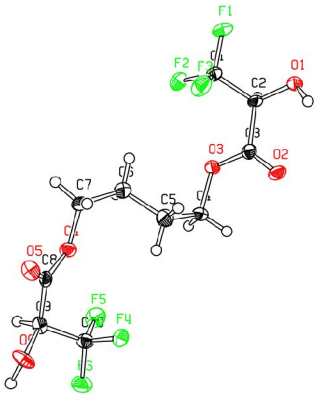
Nonamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate) [(*S*,*S*)-3f]: 71% yield. Colourless crystal. Mp 48-49 ºC. IR (KBr): 3444, 2940, 1752, 1740, 1344, 1280, 1228, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.48 (quintet, J = 7.2 Hz, 2H), 4.35 (dt, J_1 = 10.5 Hz, J_2 = 6.6 Hz, 2H), 4.29 (dt, J_1 = 10.5 Hz, J_2 = 6.6 Hz, 2H), 3.44 (d, J = 7.8 Hz, 2OH), 1.71 (quintet, J = 6.9 Hz, 4H), 1.25-1.40 (brs, 10H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, J = 6.9 Hz, 6F). ^{13}C NMR ($CDCl_3$): δ 167.5, 122.2 (q, J = 281 Hz), 69.8 (q, J = 33.2 Hz), 67.7, 29.1, 28.8, 28.2, 25.4; MS: m/z 145 (1), 125 (5), 124 (6), 96 (23), 95 (15), 83 (41), 82 (34), 81 (23), 69 (100), 68 (37), 67 (34), 57 (19), 56 (13), 55 (84), 54 (26), 43 (15), 42 (11), 41 (45); Anal. Calcd for $C_{15}H_{22}F_6O_6$: C 43.69, H 5.38, Found: C 43.72, H 5.34. $[\alpha]^{25}_D$ –3.93 (*c* 1.1, acetone).

Decamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate) [(*S*,*S*)-3g]: 90% yield. Colourless crystal. Mp 56 ºC. IR (KBr): 3440, 1752, 1748, 1467, 1344, 1224, 1190, 1130 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.47 (q, J = 6.9 Hz, 2H), 4.35 (dt, J_1 = 10.8 Hz, J_2 = 6.6 Hz, 2H), 4.29 (dt, J_1 = 10.5 Hz, J_2 = 6.6 Hz, 2H), 3.41 (d, J = 7.5 Hz, 2OH), 1.71 (quintet, J = 7.2 Hz, 4H), 1.25-1.43 (brs, 12H). ^{19}F NMR

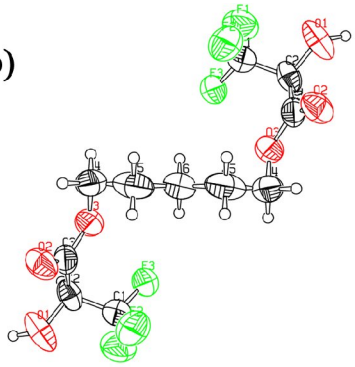
($CDCl_3$): δ 85.0 (d, *J* = 6.9 Hz, 6F). ^{13}C NMR ($CDCl_3$): δ 167.6, 122.3 (q, *J* = 282 Hz), 69.8 (q, *J* = 33.3 Hz), 67.7, 29.2, 28.9, 28.2, 25.4. MS: m/z 145 (2), 138 (4), 110 (14), 97 (22), 96 (22), 95 (17), 83 (60), 82 (37), 81 (25), 69 (57), 68 (36), 67 (32), 57 (22), 56 (15), 55 (100), 54 (28), 43 (21), 42 (13), 41 (53); Anal. Calcd for $C_{16}H_{24}F_6O_6$: C 45.07, H 5.67, Found: C 45.2, H 5.57. $[\alpha]^{25}_D$ –3.78 (*c* 1.1, acetone).

Fig. 1S ORTEP plots for **3** at 50% probability level. Disordered moieties are omitted for clarity.

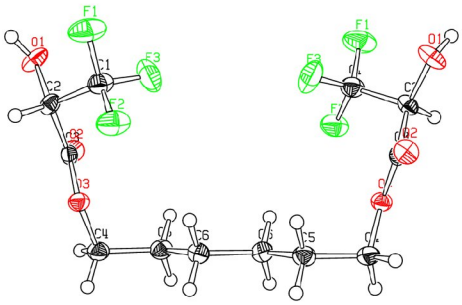
(3a)



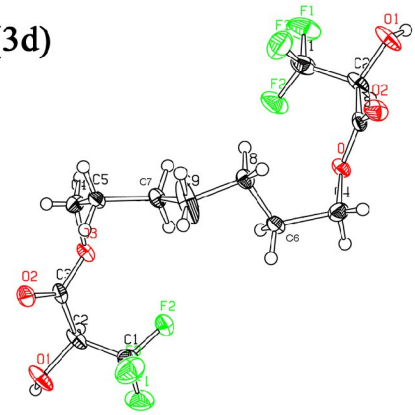
(3b)



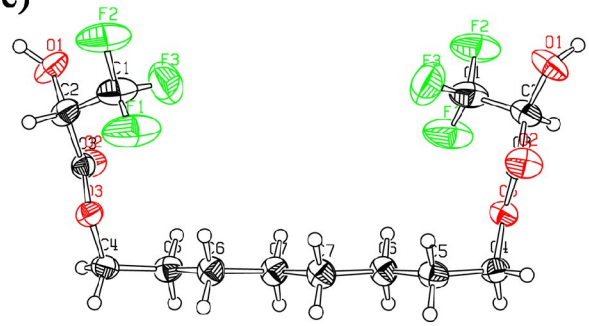
(3c)



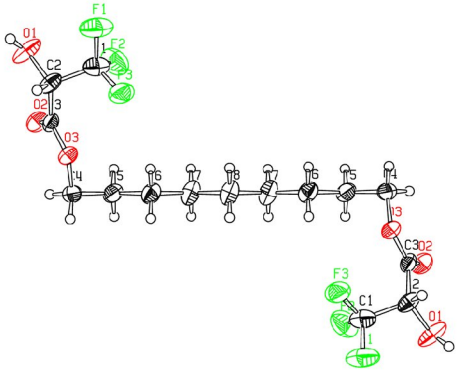
(3d)



(3e)



(3f)



(3g)

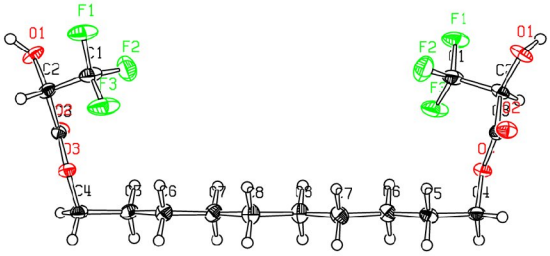


Fig. 2S Crystal structure of **3**. H-atoms of methylene groups and disordered moieties are omitted for clarity. Hash bonds are hydrogen bonds.

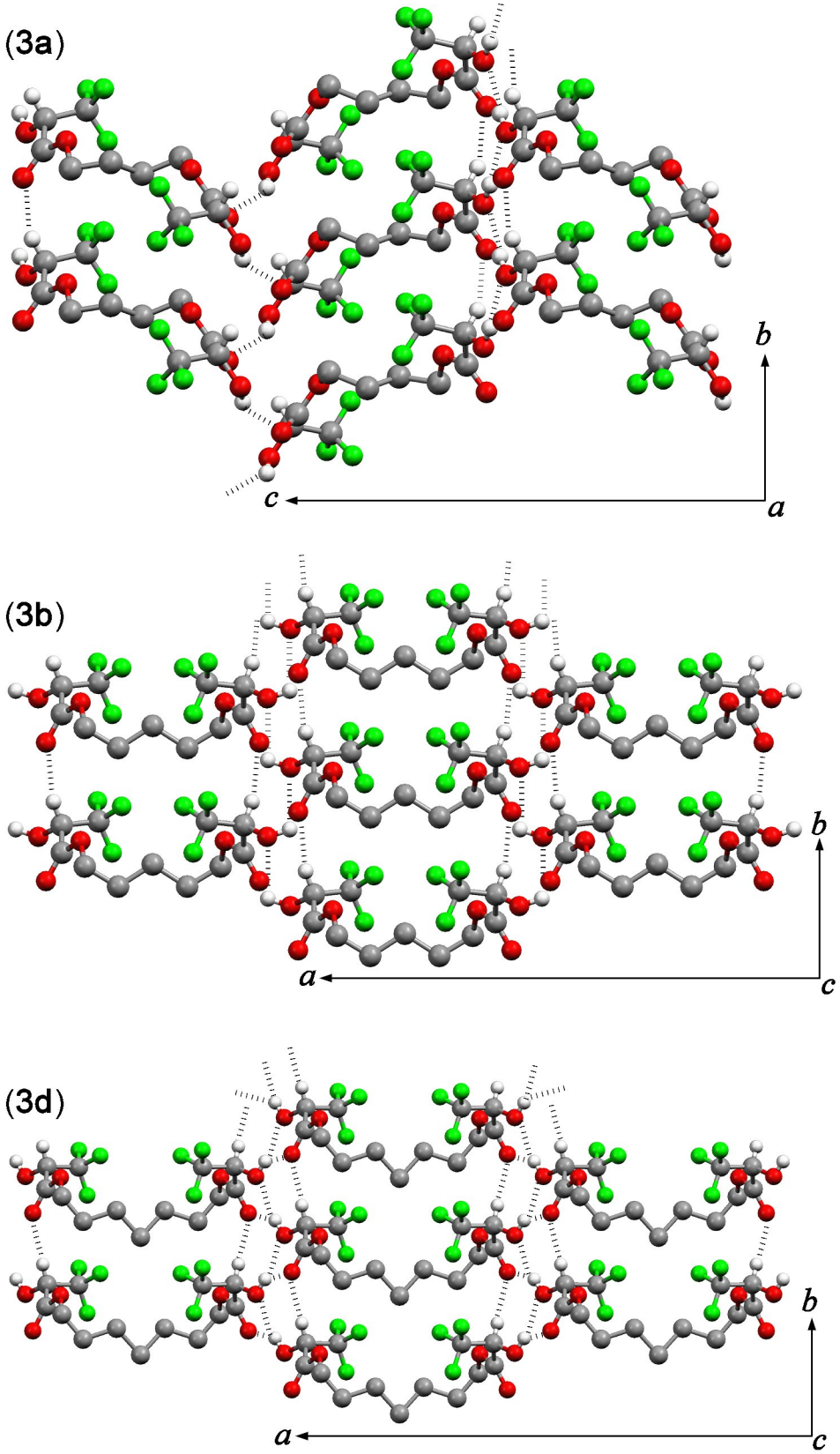


Fig. 2S Crystal structures of **3** (continued).

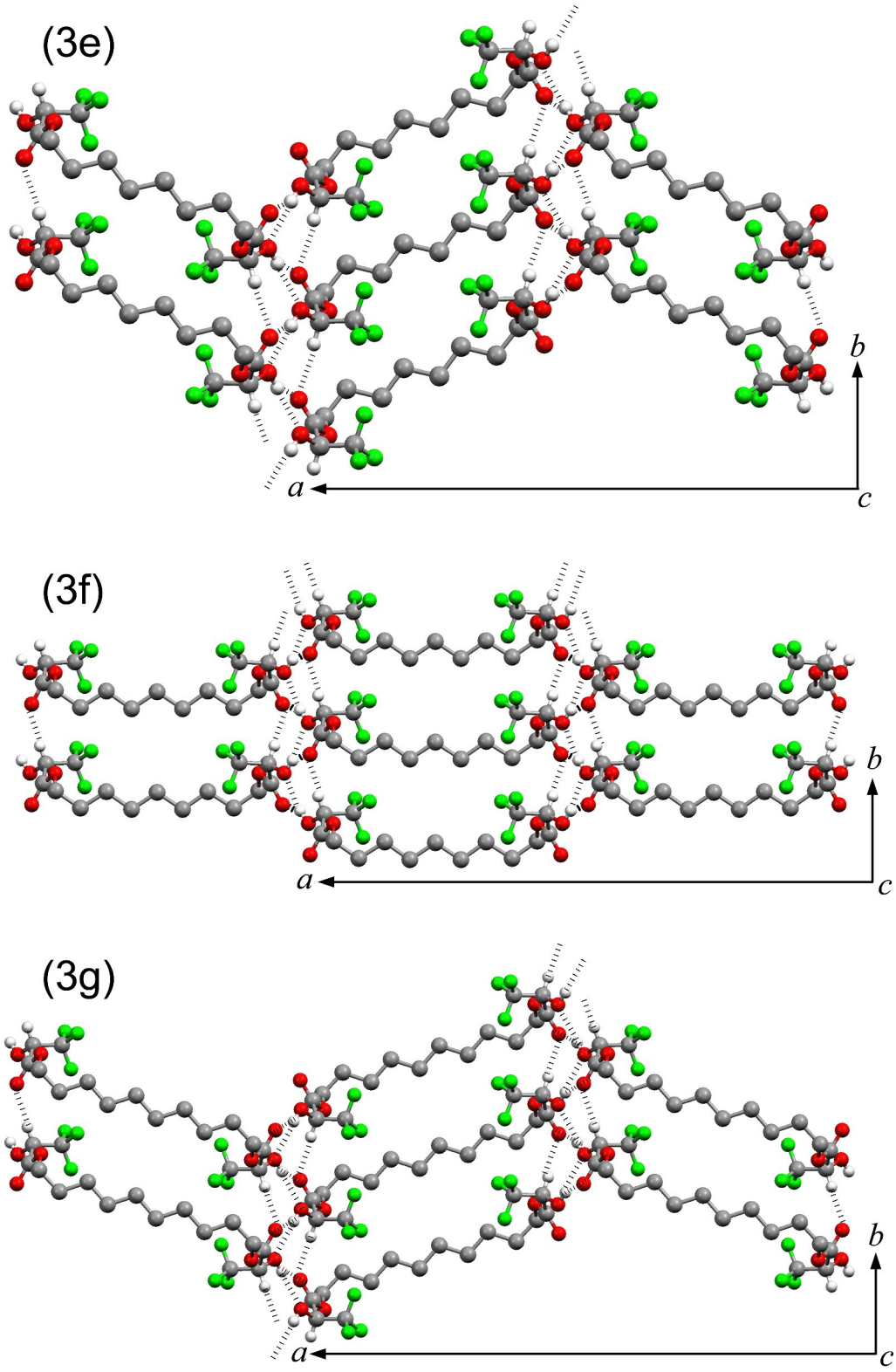


Fig. 3S ^{1}H NMR chart of **3f** which crystallized from octane/THF (in $CDCl_3$)

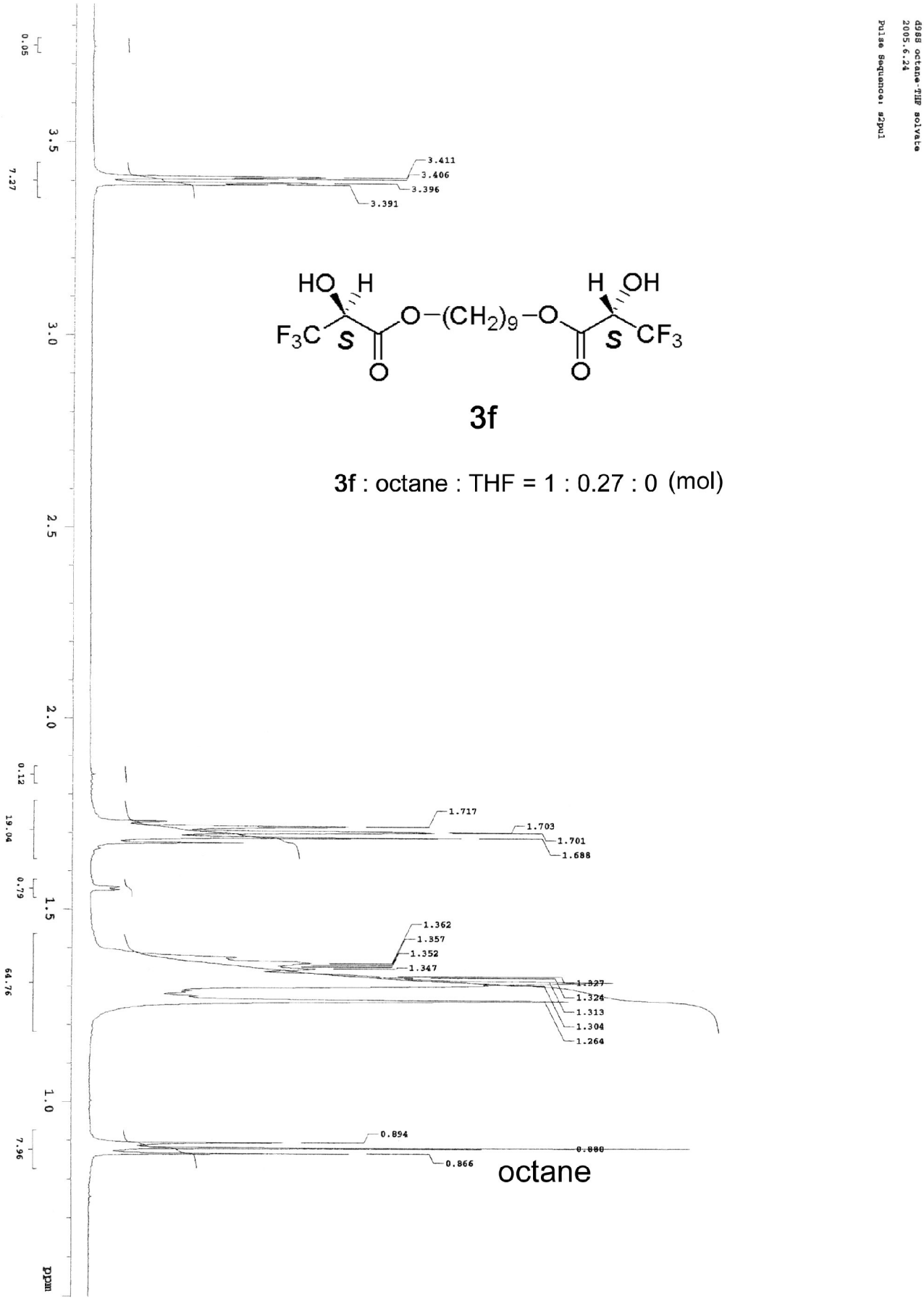


Fig. 4S ^{1}H NMR spectra of **4f** which crystallized from hexane/ether (in $CDCl_3$)

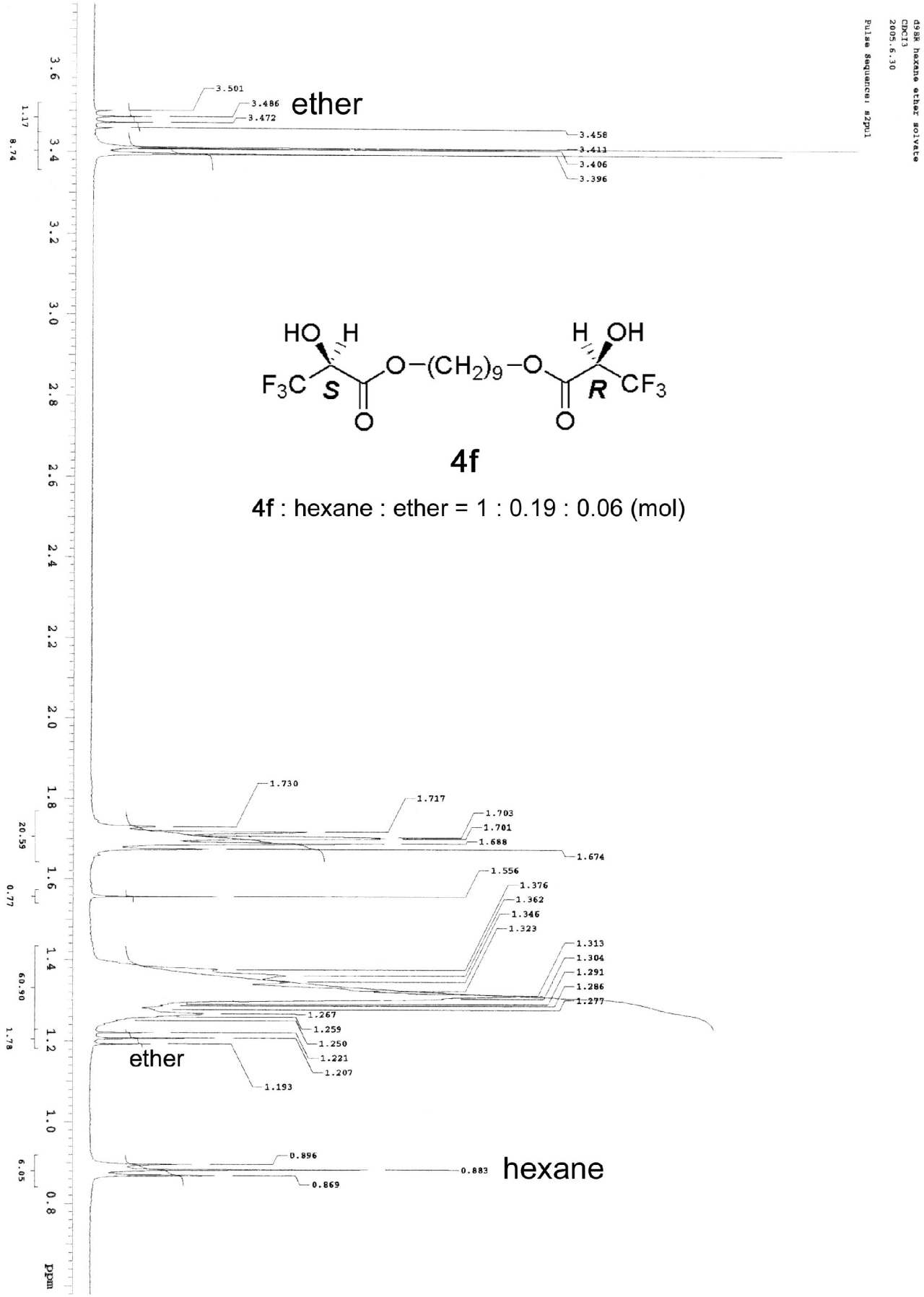


Fig. 5S ^{1}H NMR spectra of **3g** which crystallized from hexane/ether (in $CDCl_3$)

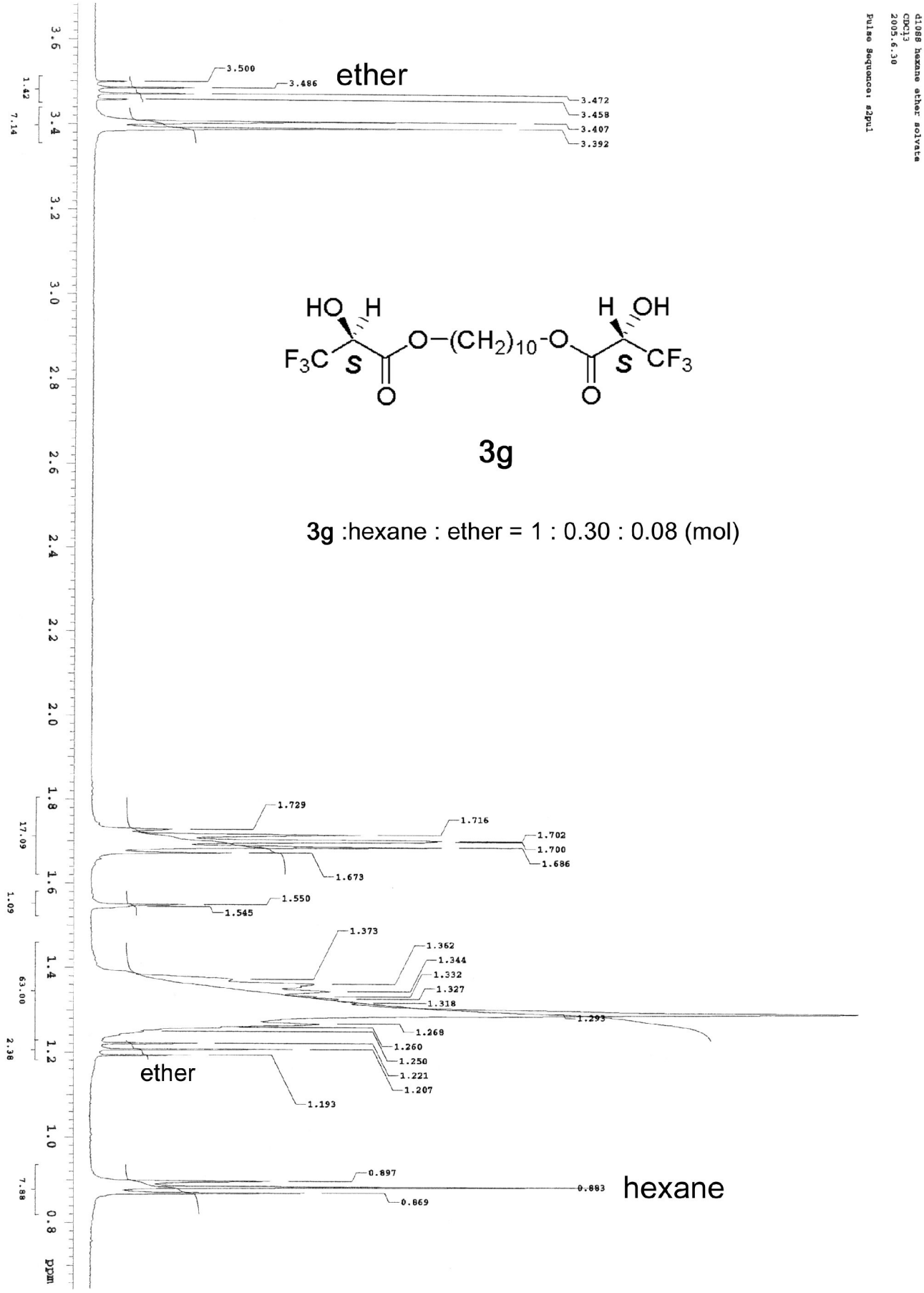
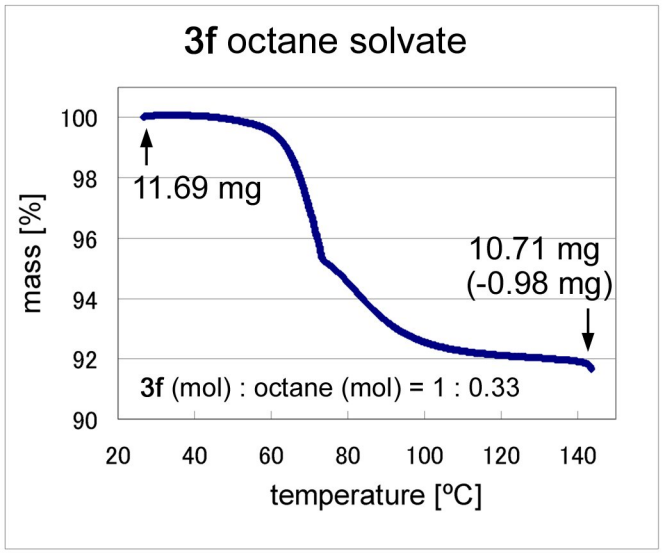
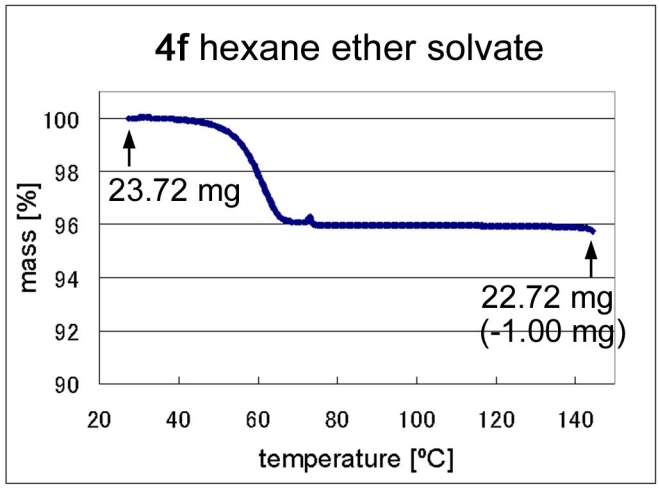
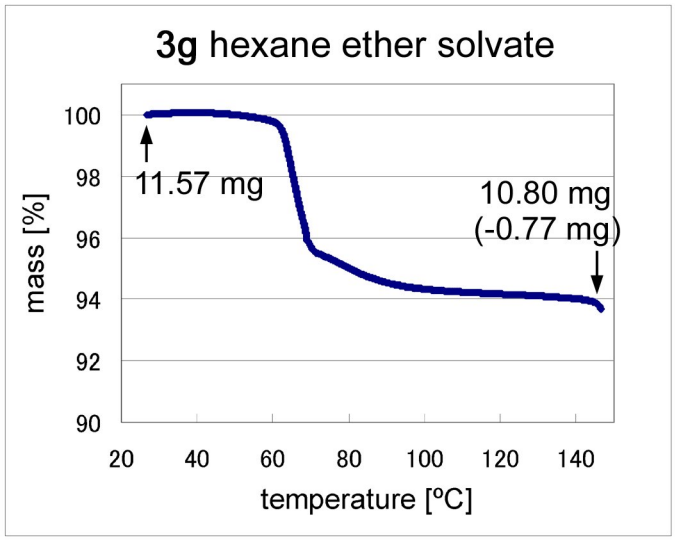


Fig. 6S TG curves for **3f**, **4f** and **3g** crystals which included some crystallization solvents.
Undesirable decomposition of the fluorine compounds with generation of heat was occurred over 140 ºC, so TG analysis was stopped at 145 ºC.





4f (mol) : (hexane+ehter) (mol) = 1 : 0.21~0.25



3g (mol) : (hexane+ehter) (mol) = 1 : 0.35~0.40