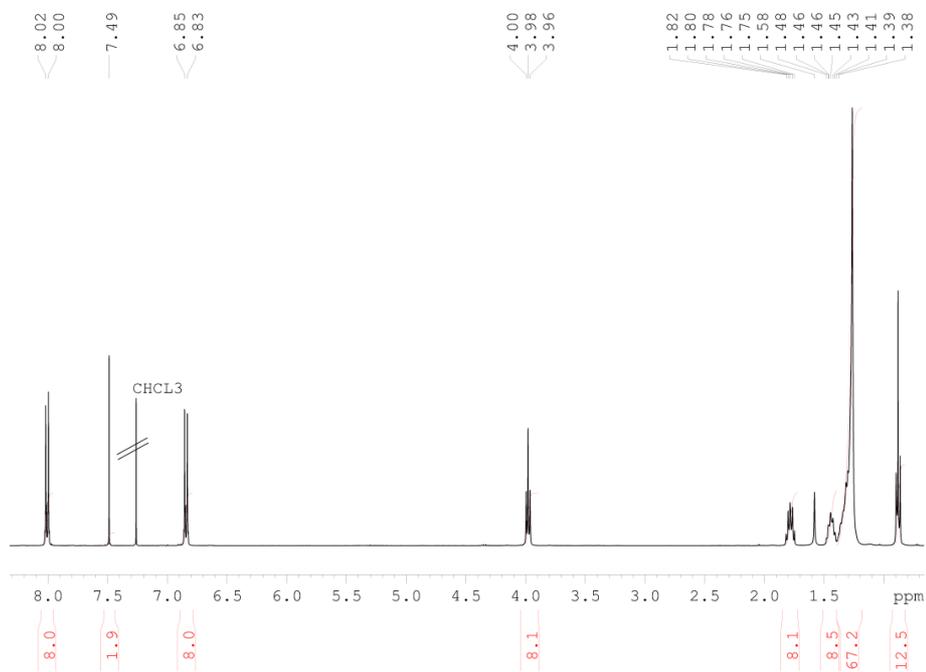


## **Supporting information**

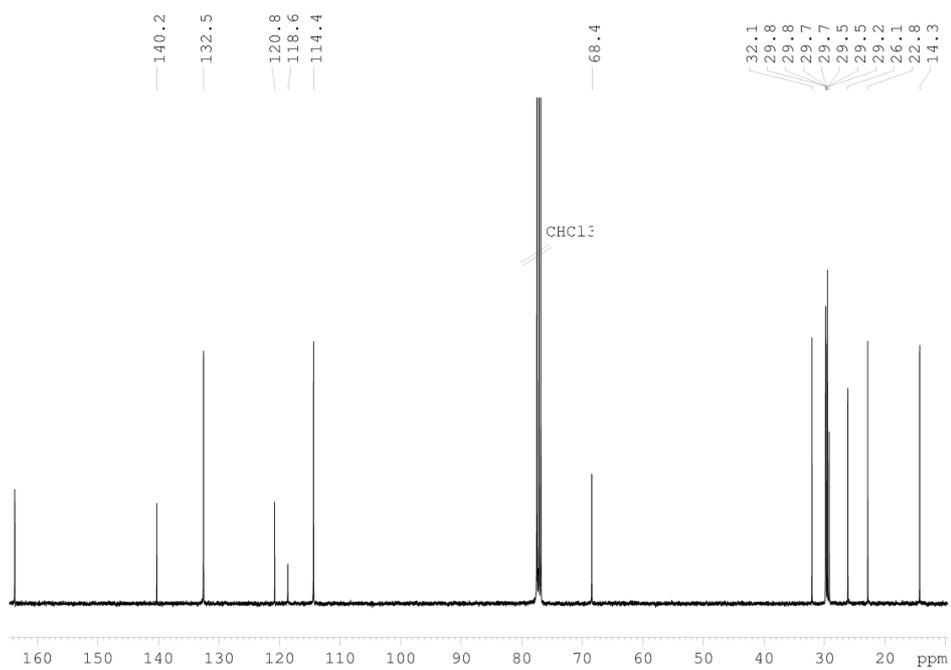
- (1)  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra
- (2) Modeling and X-ray Simulation

# (1) <sup>1</sup>H- and <sup>13</sup>C-NMR spectra

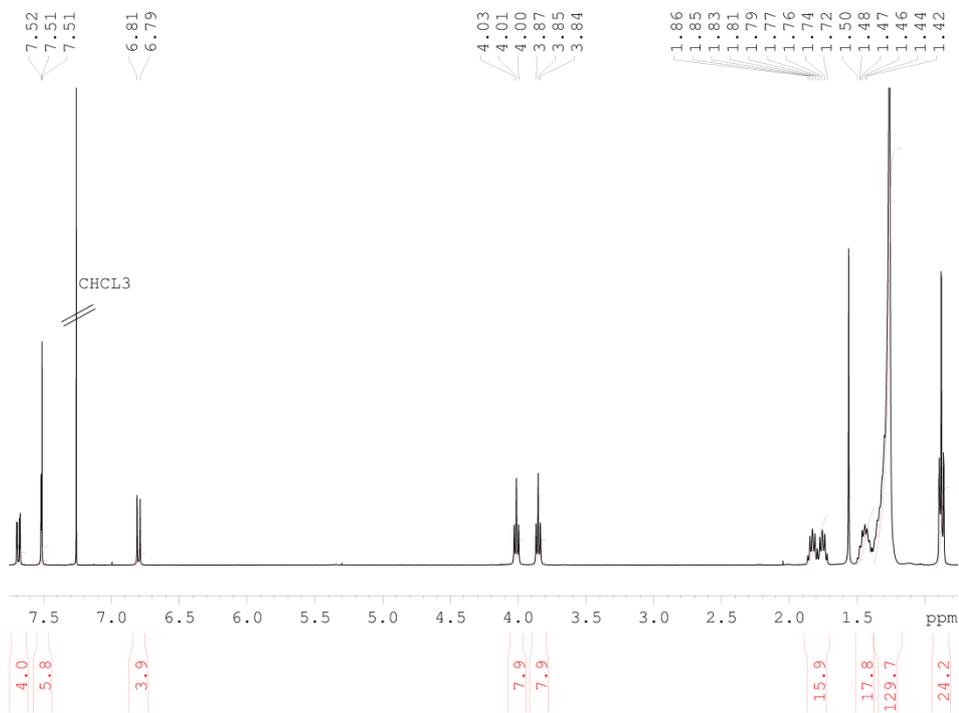
S0a: <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400 MHz)



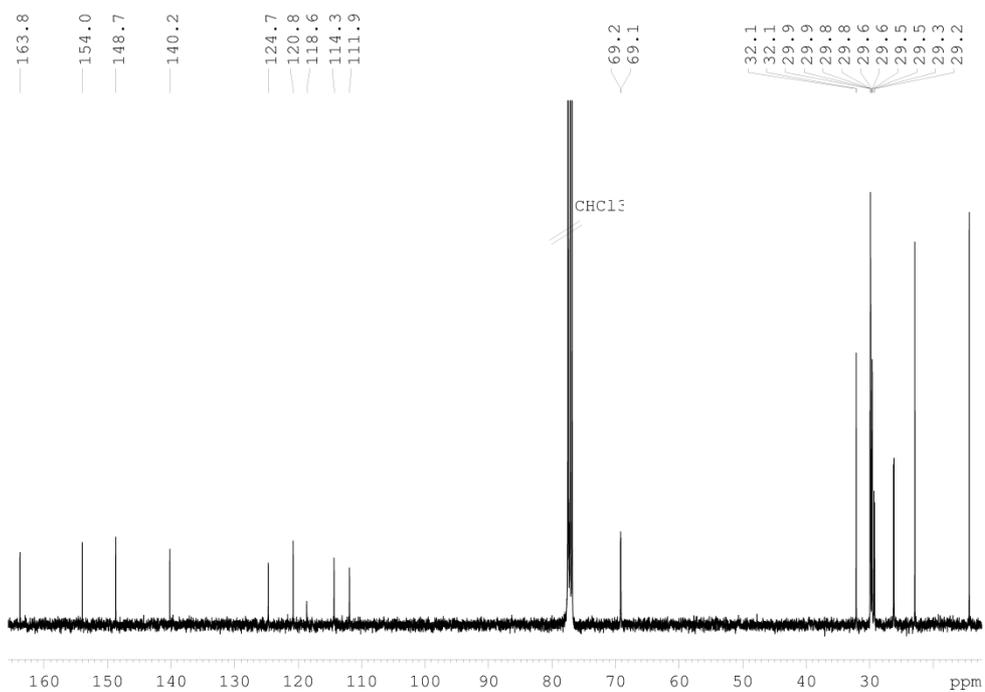
S0a: <sup>13</sup>C-NMR in CDCl<sub>3</sub> (100 MHz)



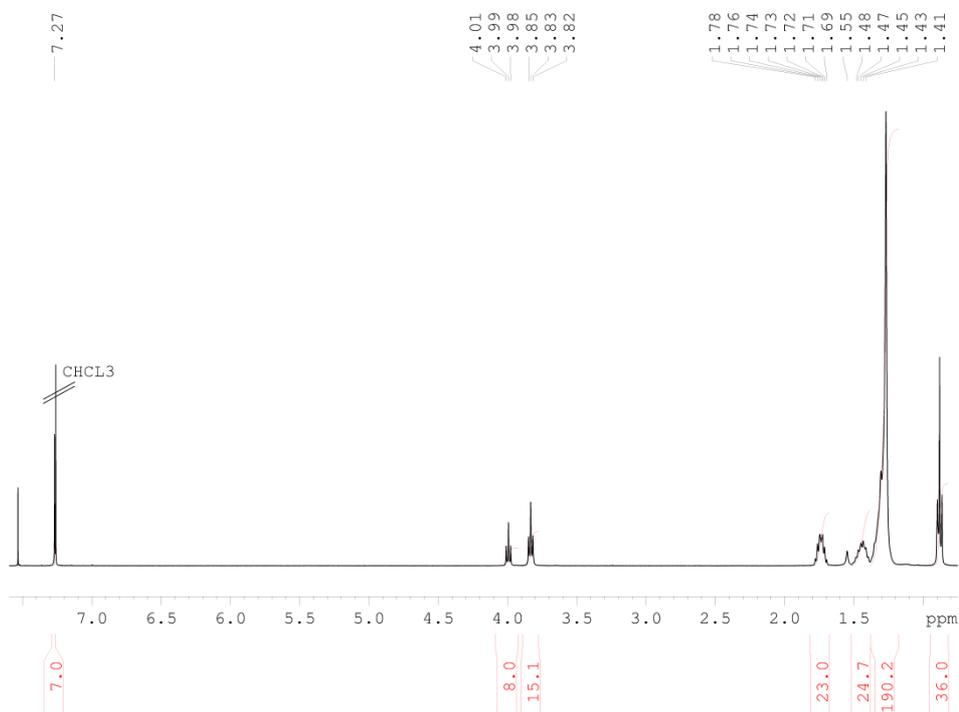
**S0b:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



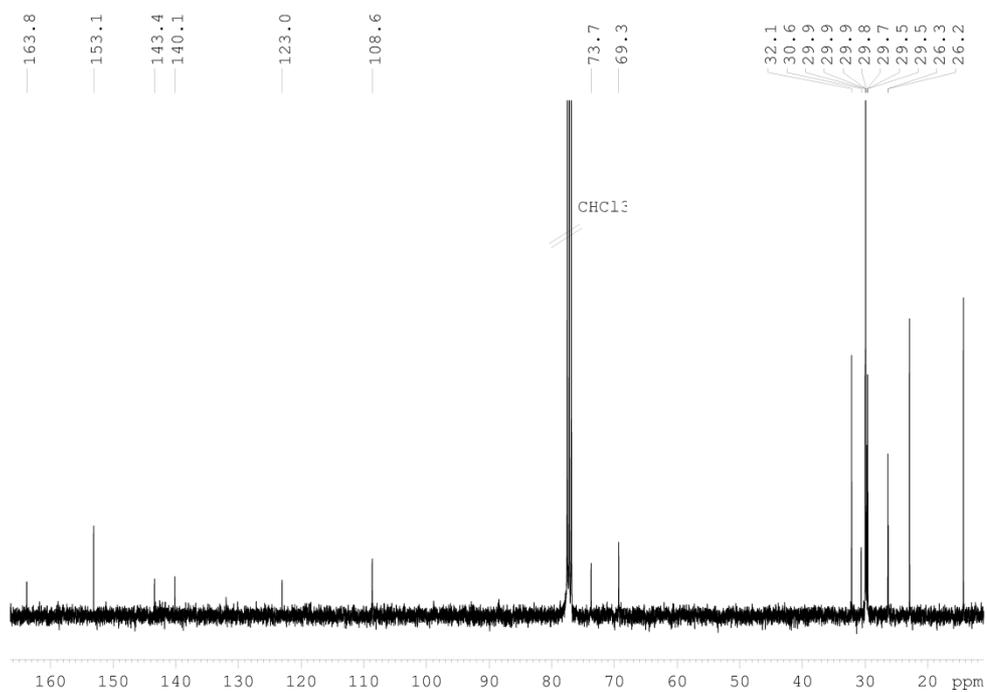
**S0b:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



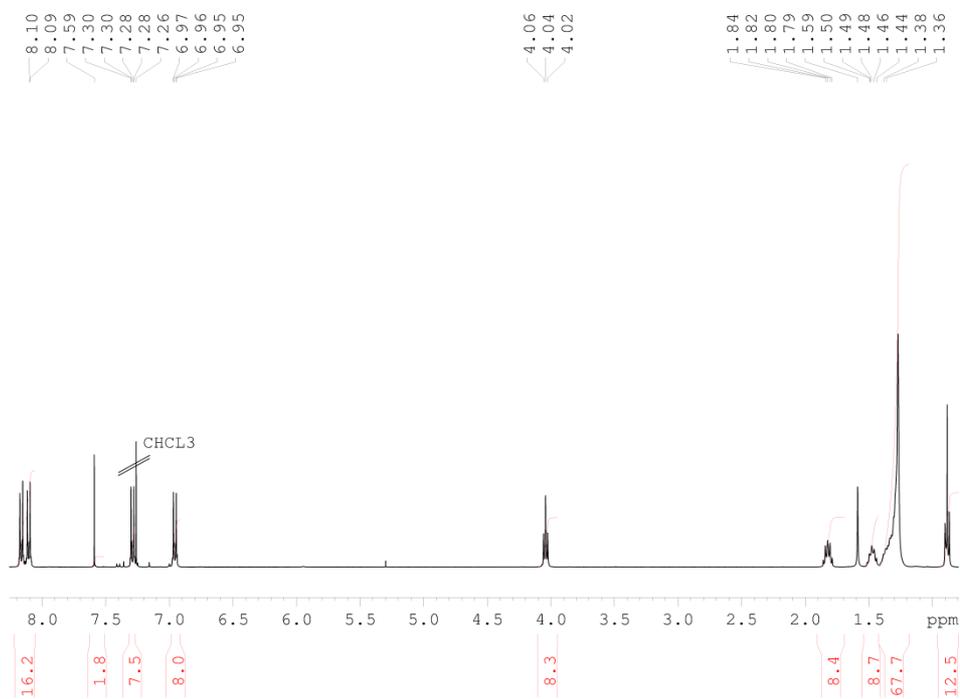
**S0c:**  $^1\text{H}$ -NMR in  $\text{CDCl}_3$  (400 MHz)



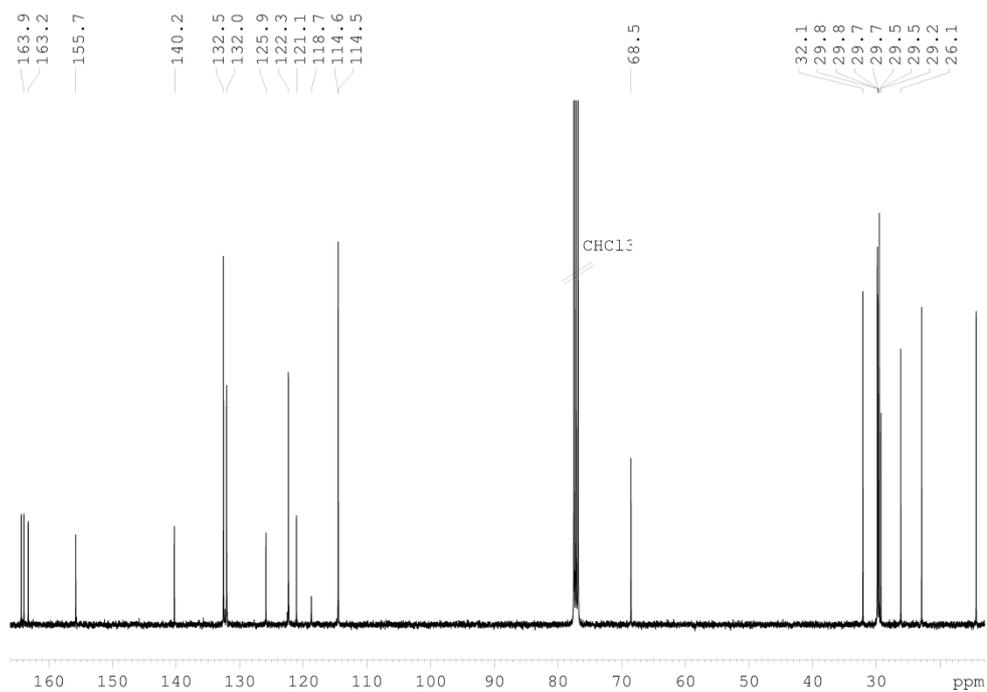
**S0c:**  $^{13}\text{C}$ -NMR in  $\text{CDCl}_3$  (100 MHz)



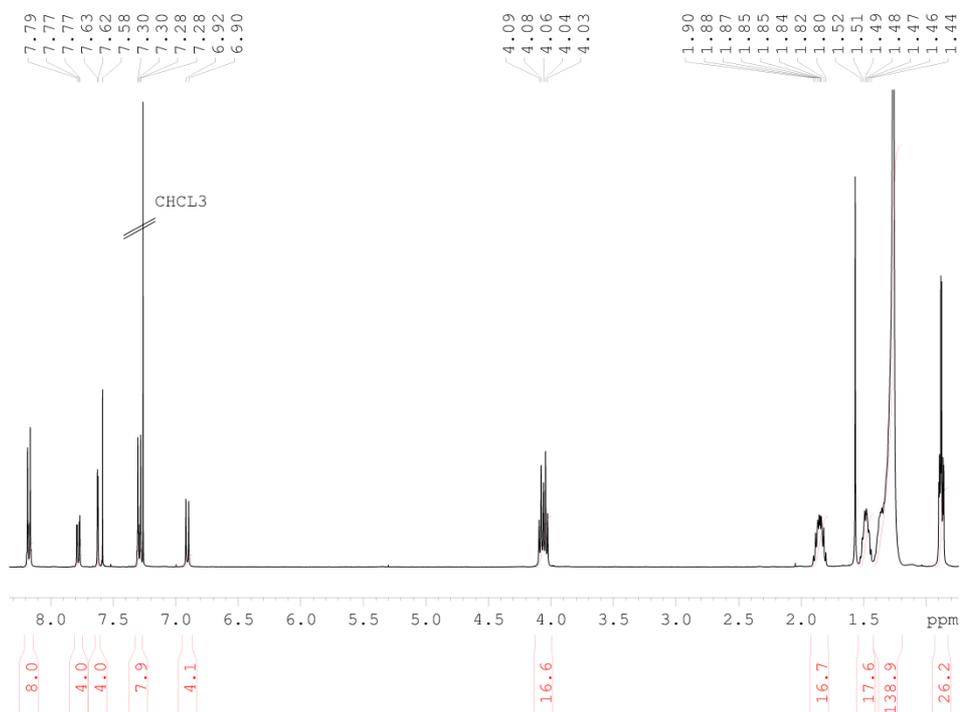
**S1a:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



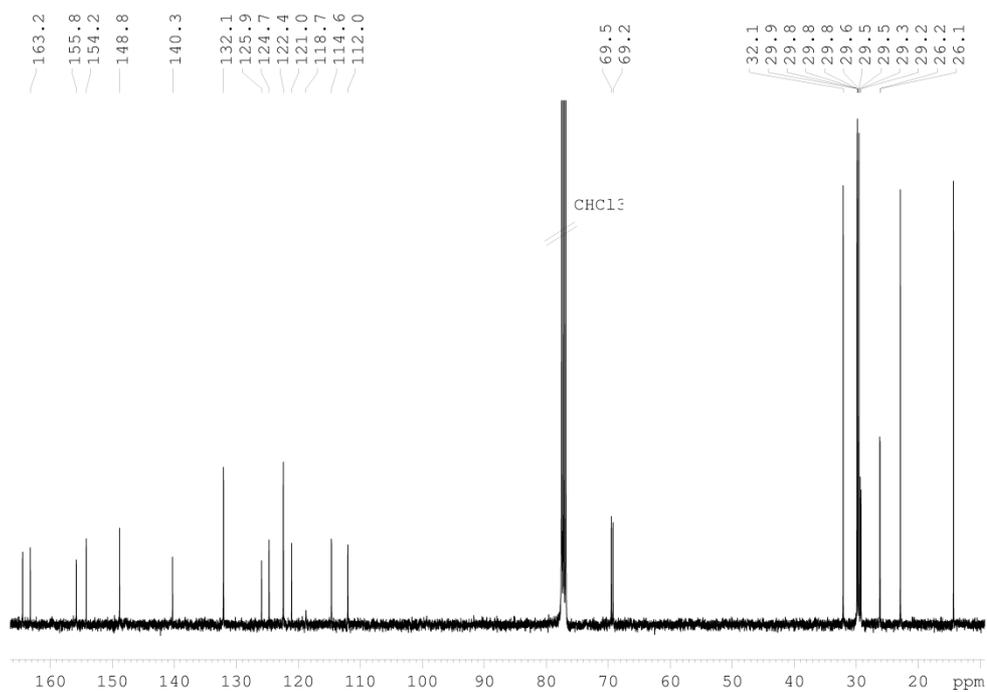
**S1a:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



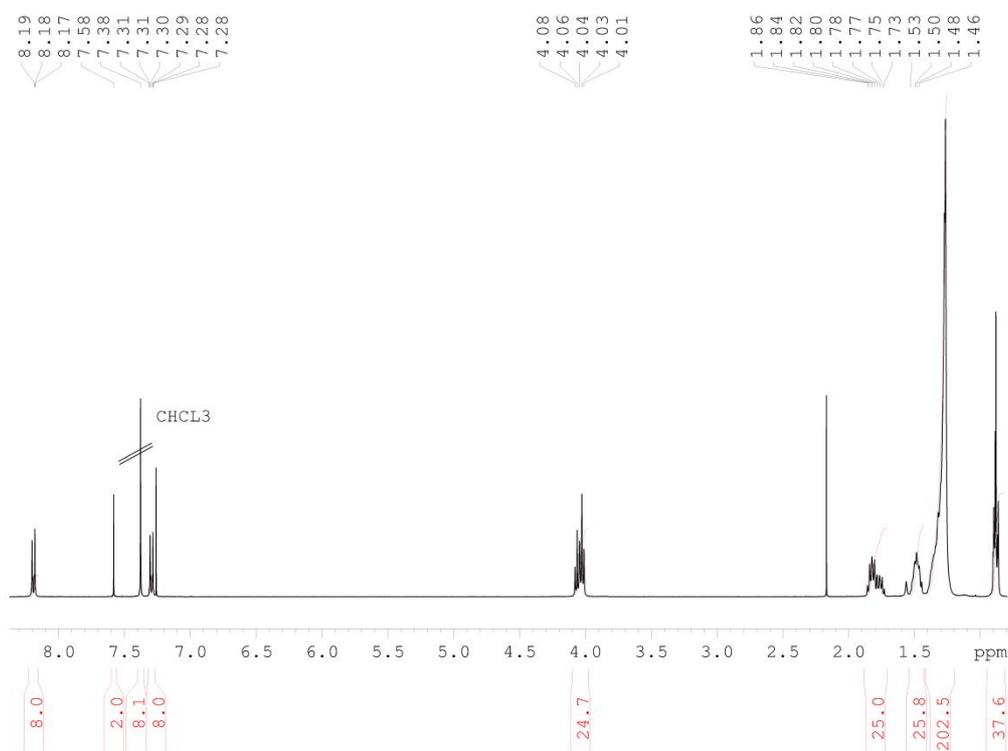
**S1b:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



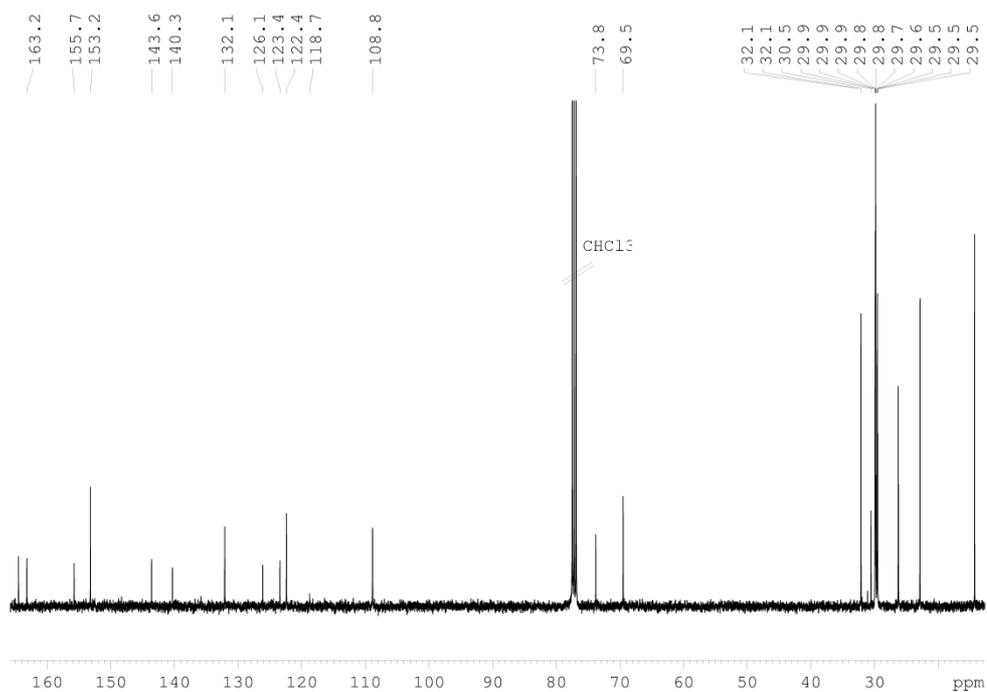
**S1b:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



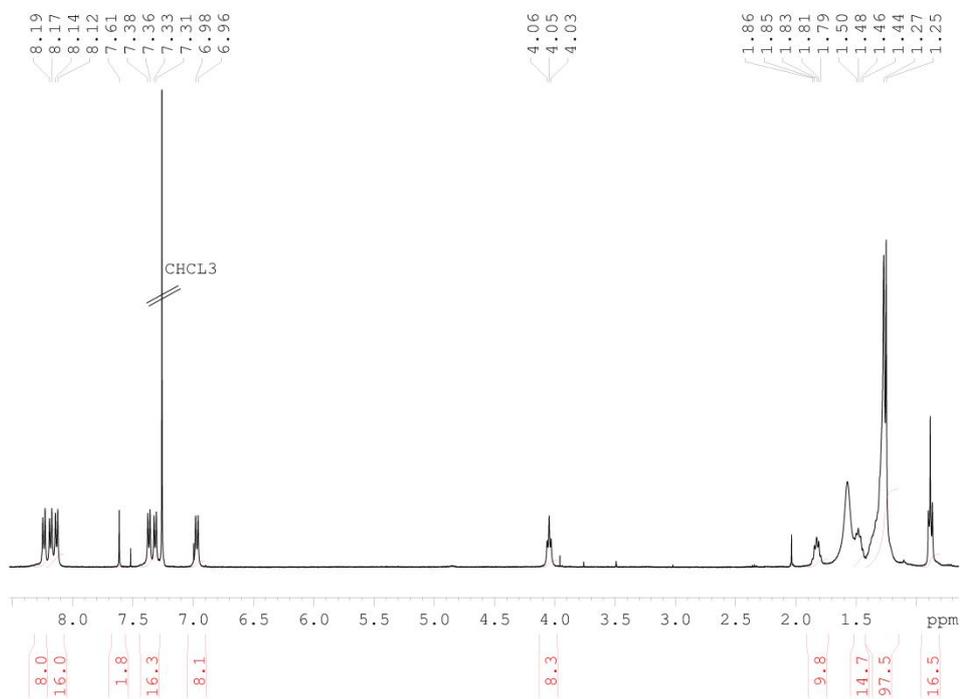
**S1c:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



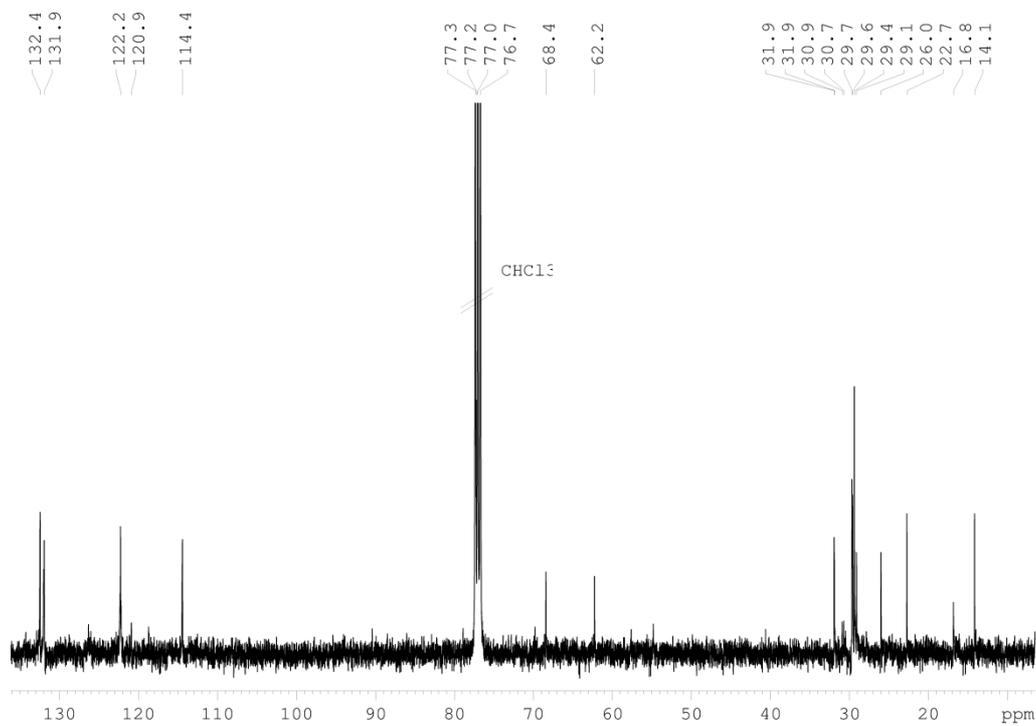
**S1c:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



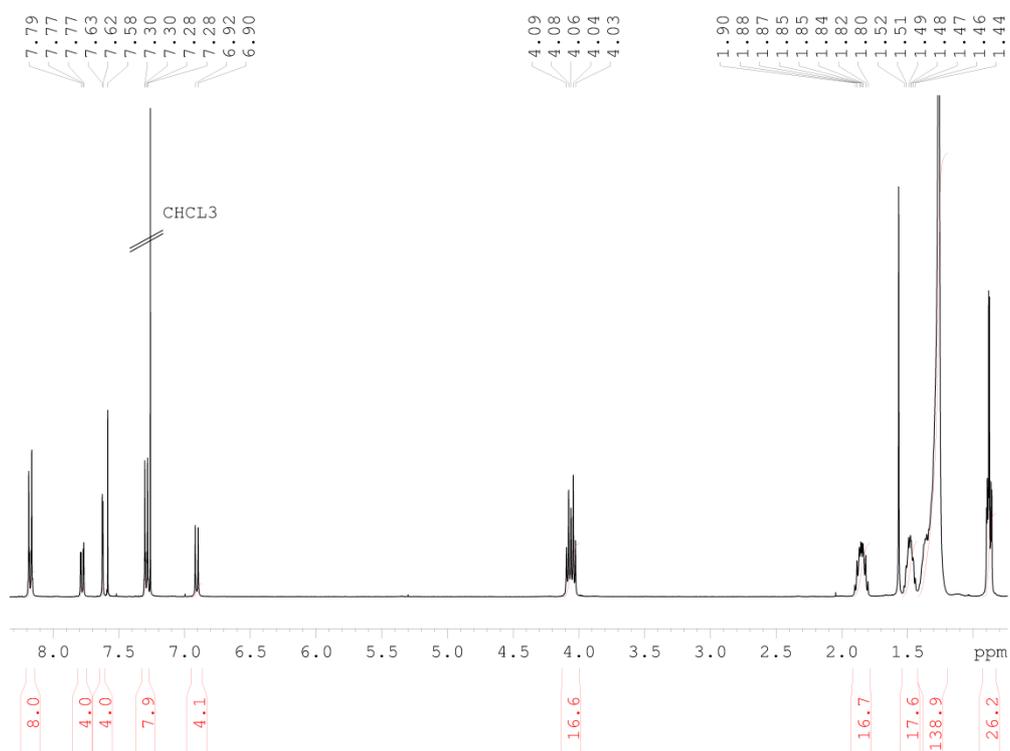
**S2a:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



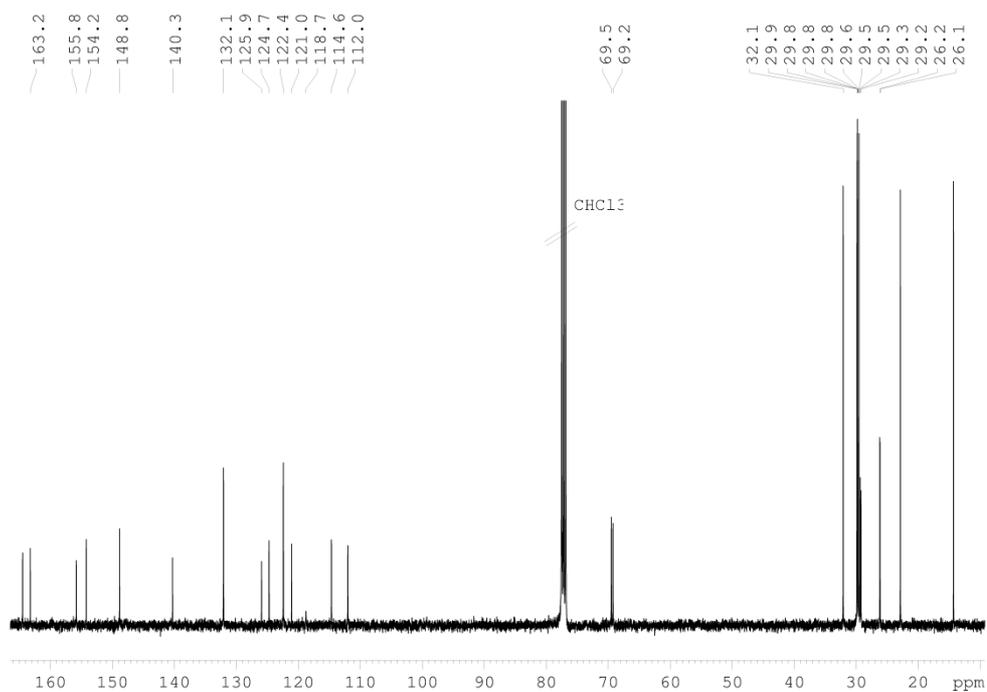
**S2a:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



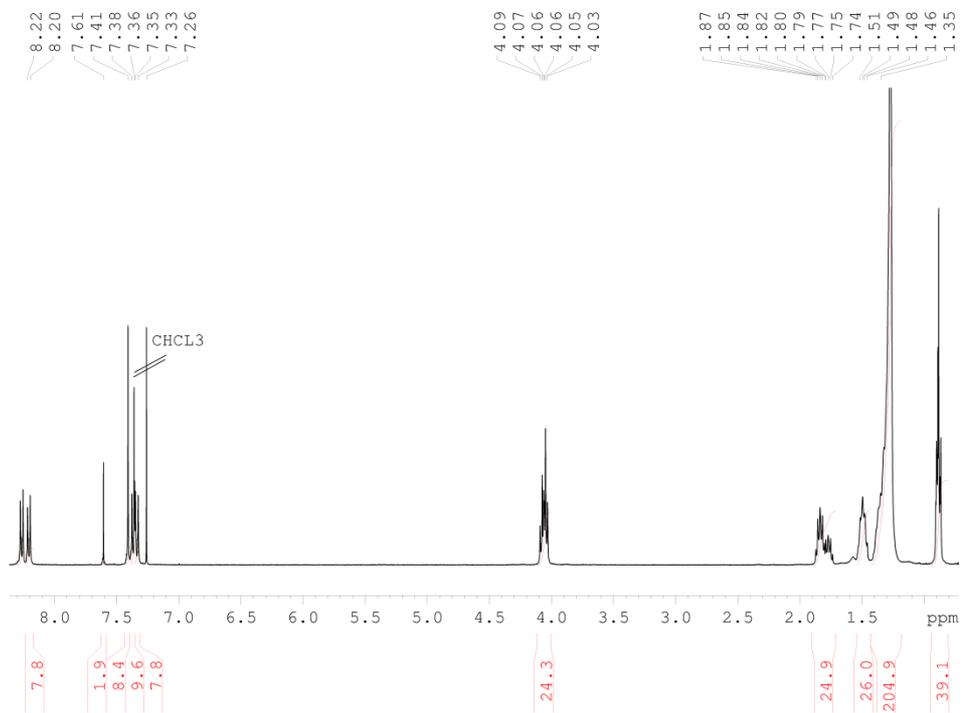
**S2b:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



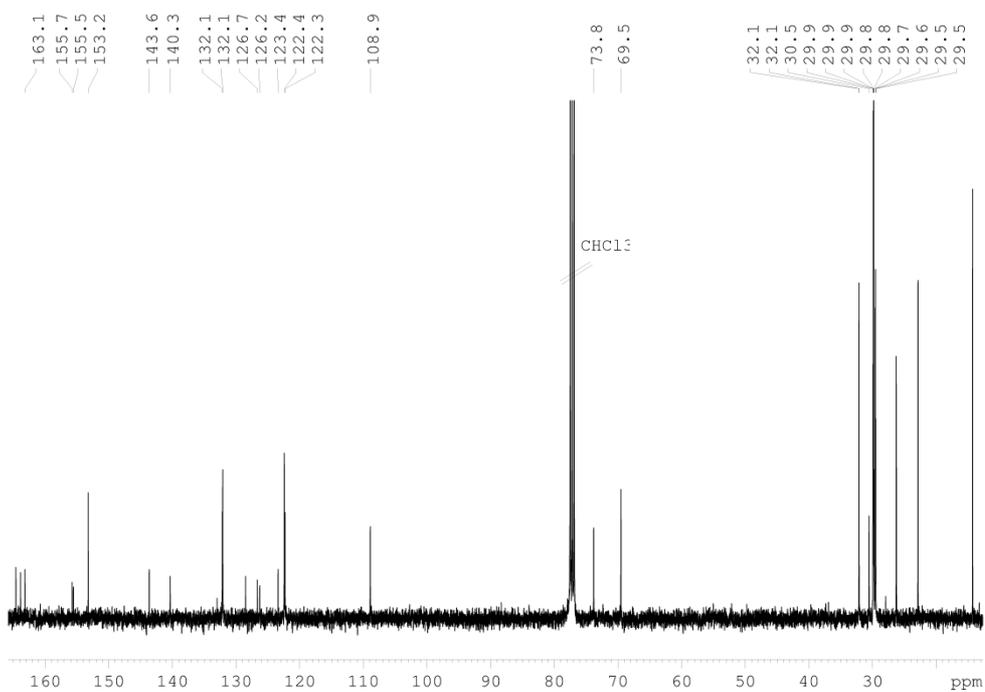
**S2b:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



**S2c:**  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  (400 MHz)



**S2c:**  $^{13}\text{C-NMR}$  in  $\text{CDCl}_3$  (100 MHz)



## (1) Modeling and X-ray Simulation

- a) **Modeling:** All columnar LC phases were modelled with the program Accelrys Materials Studio 4.4.

### *S1c – bowl shaped*

First a bowl-shaped structure was formed, which fits in the hexagonal cell ( $a = b = 42.4 \text{ \AA}$ ). Then the eight molecules were packed in a helix, with a height of  $c = 27.7 \text{ \AA}$ . Subsequent molecules were rotated by  $(360/8)^\circ = 45^\circ$  and shifted along the columnar axis by  $27.7 / 8 \text{ \AA} = 3.46 \text{ \AA}$ . The helix was placed in a hexagonal cell with  $a = b = 42.4 \text{ \AA}$  and  $c = 27.7 \text{ \AA}$ . The density of this model amounts to  $1.00 \text{ g cm}^{-3}$ . This model has been geometry optimized by the force field COMPASS first by an atom based summation and subsequently by an Ewald summation method, until the non-bonding energy was strongly negative.

### *S1c – cone-shaped dimer*

A cone-shaped structure was formed, by folding the arms on one side. Then a dimer was formed to fill the hexagonal cell ( $a = b = 42.4 \text{ \AA}$ ) most efficiently. The four dimers were packed in a helix, with a height of  $c = 27.7 \text{ \AA}$ . The helix was formed by copying the dimer, rotating by  $(360/8)^\circ = 90^\circ$  and shifting along the columnar axis by  $27.7 / 8 \text{ \AA} = 6.92 \text{ \AA}$ . The helix was placed in a hexagonal cell with  $a = b = 42.4 \text{ \AA}$  and  $c = 27.7 \text{ \AA}$ . The density of this model amounts to  $1.00 \text{ g cm}^{-3}$ . This model has been geometry optimized by the force field COMPASS first by an atom based summation and subsequently by an Ewald summation method, until the non-bonding interaction energies were strongly negative.

### *S2c – cone-shaped tetramer*

First a cone-shaped structure was formed, by folding the arms on one side. Then a tilted tetramer was formed to fill the body-centred orthorhombic cell ( $a = 92.1 \text{ \AA}$ ,  $b = 53.8 \text{ \AA}$ ,  $c = 51.0 \text{ \AA}$ ) most efficiently. The first column was assembled by copying the tetramer, rotating by  $(360/5)^\circ = 72^\circ$  and shifting along the columnar axis by  $51.0/5 \text{ \AA} = 10.3 \text{ \AA}$ . The column was then copied and shifted by  $a/2$ ,  $b/2$  and  $c/2$  in order to generate the body-centered orthorhombic unit cell. The unit cell contains two columns with 5 tetramers each, thus 40 mesogens. The density of this model amounts to  $0.98 \text{ g cm}^{-3}$ . This model has been geometry optimized by the force field COMPASS first by an atom based summation and subsequently by an Ewald summation method, until the non-bonding interaction energies were strongly negative.

### ***S2b – bowl shaped***

A bowl-shaped structure was formed, with the arms tilting more than  $45^\circ$  from the normal to the columnar axis. Then the 40 molecules were packed in two helices, with a height of  $c = 71.54 \text{ \AA}$ . The first column was assembled by rotating subsequent molecules by  $(360/5)^\circ = 18^\circ$  and shifting along the columnar axis by  $71.54/20 \text{ \AA} = 3.577 \text{ \AA}$ . The helix was placed in a centred monoclinic cell with  $a = 79.5 \text{ \AA}$ ,  $b = 36.0 \text{ \AA}$ ,  $c = 71.54 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 81.5^\circ$  and was then copied, shifted by  $a/2$ ,  $b/2$  and  $c/2$  in order to generate the centered unit cell. The density of this model amounts to  $0.98 \text{ g cm}^{-3}$ . This model has been geometry optimized by the force field COMPASS first by an atom based summation and subsequently by an Ewald summation method, until the non-bonding energy was strongly negative.

### ***S1b – cluster, hand-shuttlecock***

First the hand-shuttlecock structure was formed, with a tilt of  $26^\circ$  of the aromatic building block and the arms lying orthogonal to the layer. Then a cluster of

2 x 3 molecules with alternated chains was fitted in a small cell with the size of 28 x 28 x 33.3 Å<sup>3</sup> and duplicated to fill a lamella with a layer thickness  $c = 33.3$  Å (given from the SAXS and WAXS investigation). The number of molecules filling this cell was calculated, based on a density of 0.96 gcm<sup>-3</sup>. To verify the space-filling of the model a supercell was built in all directions in space.

### ***S1a, S0a – rod-shaped, tilted***

Both models were built the same way but with different parameters. First the *ortho*-arms were rotated out of the plan of the central aromatic ring, lying parallel to each other on the same side of the molecule. This rod-shaped structure was then tilted (**S0a:** 57 °, **S1a:** 55 °) and the alkyl chains were oriented orthogonal to the smectic layer. The structure was duplicated to fill a cell with the height of the smectic layer (**S0a:** 29.1 Å, **S1a:** 32.6 Å),  $a$  and  $b$  were freely selected. The associated number of molecules was calculated based on a density of 0.96 gcm<sup>-3</sup> for both mesogens. To verify the space-filling of the model a supercell was built in all directions in space.

#### **b) Simulation of the fiber diffraction pattern:**

For the columnar phases of compound **S1c** and **S2c** the fibre diffraction patterns were simulated using the model obtained via Materials Studio. The model has been exported as PDB-File and loaded into the Fibre Diffraction simulation module of Clearer.[1] To fit the pattern the fibre axis was set to (0,0,1) with a “crystallite size” of 150 nm (a), 150 nm (b) and 60 nm (c). The “crystal size” has been adapted to best fit the pattern. The cell dimensions were set to experimental parameters. The fibre disorder parameters  $\sigma(\theta)$  and  $\sigma(\Phi)$  were 0.15 radians and infinite with a sample interval of 1 pixel. The contrast was adjusted to best visualize the signals of the pattern. In the case of **S2b** the pattern was simulated with the program Accelrys Materials Studio 4.4.

- [1] O. S. Makin, P. Sikorski, L. C. Serpell, *J Appl Crystallogr* **2007**, *40*, 966-972.