Electronic Supplementary Material for publication

‘Helical self-assembly of molecules in pseudopolymorphs of racemic 2,6-di-*O*-(4-halobenzoyl)-*myo*-inositol 1,3,5-orthoformates: Clues for the construction of molecular assemblies for intermolecular acyl transfer reaction’

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Structure Refinement of Inclusion Complexes.

The guest solvents in **2·$CHCl_3$, 2·CH_3COCH_3, 2·CH_3SOCH_3**, **3·$CHCl_3$, 3·CH_3COCH_3**, **3·CH_3SOCH_3**, **3·CH_3CN**, and **3·*p*-$C_6H_4(CH_3)_2$** were ordered whereas in other solvates the solvent molecules exhibited rotational disorder over two-three positions.

2·$CHCl_3$

The Br atom of the axial benzoate group showed orientational disorder due to its close proximity to the edge of the cavity containing disordered solvent molecules. A reasonable model was obtained by splitting the bromine into two components Br2 and Br2' with site occupancies 0.95 and 0.05 respectively, thus the site occupancy factor for the disordered Br atom was constrained to unity. The geometry of the less occupied Br2' atom was refined with the C-Br distance restrained to 1.853(10) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008).

All the H-atoms (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7, inositol ring H atoms and H atom bonded to chloroform molecule, C-H = 0.95 Å for phenyl H atoms) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.803(19) Å. The Cl3 atom of the included CHCl3 molecule revealed larger ADP's indicating orientational disorder. A reasonable model was obtained by splitting the positions of chlorine Cl3 into two components (Cl3 and Cl3') with site occupancies 0.9 and 0.1, thus the sum of the site-occupancy factor was constrained to unity for the disordered atom. The major component of the Cl atom (Cl3) was refined anisotropically while the minor component refined isotropically. The C22-Cl3’ distance was restrained to 1.616(8) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008).

$2 \cdot CH_3COCH_3$

All the H-atoms (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.98 Å for methyl H-atoms of acetone solvate) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(methyl C). The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.81(3) Å. The included acetone molecule has regular geometry and did not reveal any sign of disorder.

$2 \cdot CH_2Cl_2$

The Br atom of the axial benzoate group showed orientational disorder over two positions. A reasonable model was obtained by splitting the bromine into two components Br2 and Br2’ with site occupancies 0.8 and 0.2 respectively, thus the site occupancy factor for the disordered Br atom was constrained to unity. The geometry of the less occupied Br2’ atom was refined with the C-Br distance restrained to 1.937(5) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008).

The H-atom (H4A) bonded to hydroxyl oxygen atom O4 was found in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.805(18) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). Other H-atoms bonded to the host molecule were placed in idealized position (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

The included CH_2Cl_2 molecules also revealed rotational disorder. The disorder was well resolved by splitting the CH_2Cl_2 molecule into three components with site occupancies 0.4, 0.4 and 0.2, thus the site occupancy factor constrained to unity. The C-Cl distances at the three occupancy sites of CH_2Cl_2 molecule were restrained to C22-Cl1 = 1.720(12) Å, C22-Cl2 = 1.776(9) Å, C23-Cl3 = 1.738(13) Å, C23-Cl4 = 1.760(14) Å, C24-Cl5 = 1.731(18) Å, C24-Cl6 = 1.74(3) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). The H-atoms bonded to CH_2Cl_2 molecule were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.99. The displacement parameters of the H-atoms were constrained to ride on their parent atom with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$.

2·CH_3NO_2

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.98 Å for methyl H-atoms of nitromethane solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and $1.5U_{\mathrm{eq}}$(methyl C). The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.812(19) Å.

The included nitromethane molecule showed orientational disorder. The disorder was well resolved by splitting the nitromethane molecule into two components with site occupancies 0.8 and 0.2, thus the site occupancy factor constrained to unity. The bond lengths of the less occupancy nitromethane molecule were restrained to C22’-N1’ = 1.485(19) Å, N1’-O9’ = 1.204(15) Å and N1’-O10’ = 1.179(16) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). The geometry of the minor occupancy conformation of the nitrobenzene molecule was restrained to be similar to the major occupancy conformation using the FLAT instructions in SHELXL97 (Sheldrick, 2008).

$2\cdot C_4H_8O$

The Br atom of the axial benzoate group showed orientational disorder due to its freedom of libration and its proximity to the edge of the cavity containing disordered solvent molecules. A reasonable model was obtained by splitting the bromine into two components Br2 and Br2' with equal site occupancies (0.5), thus the site occupancy factor for the disordered Br atom was constrained to unity. All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.99 Å for methylene H-atoms of THF solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.82(7) Å.

The two carbon atoms C23 and C24 (not bonded to O-atom) of the included THF molecule showed flipping disorder. The disorder was well resolved by splitting the positions of the two carbons into three components with site occupancies 0.4, 0.4 and 0.2, thus the site occupancy factor constrained to unity for these two atoms. The position of other two carbons C22, C25 and oxygen O9 was kept unchanged. The thermal anisotropies of the atoms C23, C23', C23" and C24, C24', C24" were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008).

$2\cdot C_4H_8O_2$

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms,

C-H = 0.95 Å for phenyl H atoms and C-H = 0.99 Å for methylene H-atoms of dioxane solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.86(4) Å.

The included dioxane molecule showed orientational disorder due to its freedom of libration in the cavity created by the host molecules. The disorder was well resolved by splitting the dioxane molecule into two components with site occupancies 0.7 and 0.3, thus the site occupancy factor constrained to unity. The geometry of the dioxane molecules at both the sites was restrained to be in an ideal chair conformation using DFIX and DANG instructions, keeping all, 1-2, 1-3 and 1-4 distances respectively equal for chair conformation. The thermal anisotropies of the atoms of dioxane molecule were constrained using EADP instructions and restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008).

2·CH_3SOCH_3

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.98 Å for methyl H-atoms of DMSO solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and $1.5U_{\mathrm{eq}}$(methyl C). The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.83(7) Å. The included DMSO molecule has regular geometry and did not reveal any sign of disorder.

2·ClCH$_2$CH$_2$Cl

The H-atom (H4A) bonded to hydroxyl oxygen atom O4 was found in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.812(19) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). Other H-atoms bonded to the host molecule were placed in idealized position (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.99 Å for methylene H-atoms of 1,2-dichloroethane solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

The trapped dichloroethane molecule displayed disorder over two positions (occupancies 0.75 and 0.25) with the position of one of the chlorine atoms (Cl1) common. The thermal anisotropies of the disordered atoms were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008). The C-Cl and C-C distances at the two different occupancy sites of ClCH$_2$CH$_2$Cl molecule were restrained using DFIX instruction in SHELXL97 (Sheldrick, 2008).

3·CHCl$_3$

All the H-atoms (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7, inositol ring H atoms and H atom bonded to chloroform molecule, C-H = 0.95 Å for phenyl H atoms) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The O-bound H atom was located in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.804(18) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). The included CHCl$_3$ molecule has regular geometry and did not indicate any sign of disorder.

3·CH_3COCH_3

All the H-atoms (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.98 Å for methyl H-atoms of acetone solvate) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(methyl C). The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.84(3) Å. The included acetone molecule has regular geometry and did not reveal any sign of disorder.

3·CH_2Cl_2(F)

The H-atom (H4A) bonded to hydroxyl oxygen atom O4 was found in difference Fourier map and refined isotropically with refined O-H distance 0.81(3) Å.Other H-atoms bonded to the host molecule were placed in idealized position (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and and C-H = 0.99 Å for methylene H-atoms of DCM solvate) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

The included CH_2Cl_2 molecules also revealed rotational disorder. The disorder was well resolved by splitting the DCM molecule into two components with site occupancies 0.75 and 0.25, thus the site occupancy factor constrained to unity. The geometries of the CH_2Cl_2 molecule were restrained using DFIX and DANG instruction in SHELXL97 (Sheldrick, 2008) to a regular model.

3·CH_3NO_2

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms,

C-H = 0.95 Å for phenyl H atoms and C-H = 0.98 Å for methyl H-atoms of nitromethane solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and $1.5U_{\mathrm{eq}}$(methyl C). The O-bound H atom was located in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.791(15) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008).

The included nitromethane molecule showed orientational disorder. The disorder was well resolved by splitting the nitromethane molecule into two components with site occupancies 0.75 and 0.25, thus the site occupancy factor constrained to unity. The C-N bond lengths of the nitromethane molecules at two different sites were restrained to C22-N1 = 1.524(17) Å and C22'-N1' = 1.552(6) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). The geometry of nitromethane molecules at two different sites was restrained to be planar using the FLAT instruction in SHELXL97 (Sheldrick, 2008). Further the thermal anisotropies of the atoms in nitromethane molecules were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008).

3·C_4H_8O

The Cl atom of the axial benzoate group showed orientational disorder due to its freedom of libration and its proximity to the edge of the cavity containing disordered solvent molecules. A reasonable model was obtained by splitting the chlorine into two components Cl2 and Cl2' with site occupancies 0.85 and 0.15, thus the site occupancy factor for the disordered Cl atom was constrained to unity. The C19-Cl2' bond length was also restrained using DFIX instruction in SHELXL97 (Sheldrick, 2008).

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms,

C-H = 0.95 Å for phenyl H atoms and C-H = 0.99 Å for methylene H-atoms of THF solvate) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H atom was located in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.838(19) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008).

The two carbon atoms C23 and C24 (not bonded to O-atom) of the included THF molecule showed flipping disorder. The disorder was well resolved by splitting the positions of the two carbons into two components with site occupancies 0.8 and 0.2, thus the site occupancy factor constrained to unity for these two atoms. The position of other two carbons C22, C25 and oxygen O9 were kept unchanged. The thermal anisotropies of the atoms C23, C23' and C24, C24' were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008). Further the C-C bond lengths of the carbons C22-C23', C23'-C24' and C24'-C25 were restrained using DFIX instruction in SHELXL97 (Sheldrick, 2008).

3·$C_4H_8O_2$

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.99 Å for methylene H-atoms of dioxane solvate) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H atom was located in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.815(19) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008).

The included dioxane molecule showed orientational disorder due to its freedom of libration in the cavity created by the host molecules. The disorder was well resolved by splitting the dioxane molecule into two components with equal site occupancies 0.5, thus the site occupancy factor constrained to unity. The geometry of the dioxane molecules at both the sites was restrained to an ideal chair conformation using DFIX and DANG instructions, keeping all, 1-2, 1-3 and 1-4 distances respectively equal for chair conformation. The thermal anisotropies of the atoms of dioxane molecule were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008).

3·CH_3SOCH_3

All the H-atoms bonded to the host molecule were located in difference Fourier map and refined isotropically. The O-H distance of the hydroxyl group was restrained to 0.831(18) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). The included DMSO molecule has regular geometry and did not reveal any sign of disorder. H-atoms bonded to the methyl group of the guest DMSO molecule were placed in geometrically idealized positions (C-H = 0.98 Å) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$.

3·$ClCH_2CH_2Cl$

The H-atom (H4A) bonded to hydroxyl oxygen atom O4 was found in difference Fourier map and its parameter was refined with the O-H distance restrained to 0.812(19) Å using DFIX instruction in SHELXL97 (Sheldrick, 2008). Other H-atoms bonded to the host molecule were placed in idealized position (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and C-H = 0.99 Å for methylene H-atoms of

1,2-dichloroethane solvate) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

The trapped dichloroethane molecule displayed disorder over three positions (occupancies 0.2, 0.4 and 0.4) with the position of one of the chlorine atoms (Cl3) common. The thermal anisotropies of the disordered atoms were constrained using EADP instructions and restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008). The C-Cl and C-C distances at the three different occupancy sites of $ClCH_2CH_2Cl$ molecule were restrained using DFIX instruction in SHELXL97 (Sheldrick, 2008).

3·CH_3CN

All the H-atoms bonded to the host molecule were located in difference Fourier map and refined isotropically. The included acetonitrile molecule has regular geometry and did not reveal any sign of disorder. H-atoms bonded to the methyl group of the guest CH_3CN molecule were placed in geometrically idealized positions (C-H = 0.98 Å) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$.

3·*p*-$C_6H_4(CH_3)_2$

All the H-atoms bonded to the host molecule (except hydroxyl H atom) were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms and C-H = 0.95 Å for phenyl H atoms) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The O-bound H atom was located in difference Fourier map and refined isotropically with refined O-H distance 0.83(2) Å. The included xylene molecule occupies the crystallographic inversion center of the space group $P2_1/c$. Only half the xylene molecule is present in the asymmetric unit and other half is generated by centrosymmetric operation across the inversion center. The H-atoms bonded to the xylene were placed in geometrically idealized positions (C-H = 0.95 Å for phenyl H atoms and C-H = 0.98 Å for methyl H atoms) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(methyl C).

$3\cdot C_6H_6$

All the non-hydrogen atoms were refined anisotropically. All the H-atoms bonded to the host molecule were placed in geometrically idealized positions (C-H = 1.00 Å for atom H7 and inositol ring H atoms, C-H = 0.95 Å for phenyl H atoms and O-H = 0.84 Å for hydroxyl H atom) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(OH O).

In **$3\cdot C_6H_6$**, two molecules of benzene were present in the crystal lattice with equal occupancies (0.5). Thus the host guest ratio was 1:1. Both the benzene molecules occupy the crystallographic 2-fold axis. Only half of one benzene molecule is present in the asymmetric unit and other half is generated by two-fold operation. The second benzene molecule in the asymmetric unit (with half occupancy) exhibited statistical disorder across the two-fold axis. The thermal anisotropies of the atoms of both benzene molecules were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008). The geometries of both the benzene molecules were restrained to be planar using the FLAT instructions in SHELXL97. Further the bond distances of the one of the benzene molecules (for half benzene molecule in AU) were restrained using DFIX instructions in SHELXL97.

$3\cdot CH_2Cl_2$(T)

Crystal structure of **$3\cdot CH_2Cl_2$(T)** was determined after a month of its crystallization at room temperature 297(2) K. All the non-H atoms of the host molecules refined anisotropically. The anisotropic displacement parameters for the carbonyl oxygen O8 were too large, indicating orientational disorder. However, a reasonable model was obtained by splitting the positions of carbonyl oxygen O8 into two components (O8 and O8') with equal occupancy (0.5), thus the sum of the site-occupancy factor was constrained to unity for the disordered atom. The anisotropic displacement parameters of these disordered atoms were restrained using ISOR and SIMU instructions. Furthermore the anisotropic displacement parameter for the atom Cl2 was also more being at the vicinity of the edge of the guest inclusion cavity. The ADP's of these atoms were also restrained using DELU and SIMU instructions in SHELXL97 (Sheldrick, 2008).

The H-atom (H4A) bonded to hydroxyl oxygen atom O4, orthoformate H atom H7 and H-atoms bonded to the equatorial benzoyl group (H10, H11, H13 and H14) were found in difference Fourier map and refined isotropically. Other H-atoms bonded to the host molecule were placed in idealized positions (C-H = 0.98 Å for inositol ring H atoms, C-H = 0.93 Å for axial phenyl H atoms) and constrained to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Interestingly, the occupancy of included dichloromethane was as low as 0.06 and revealed rotational disorder over two positions similar to the fully occupied dichloromethane molecule in **$3{\cdot}CH_2Cl_2$(F)** but with trace occupancy. The disorder was well resolved by splitting the dichloromethane molecule into two components with equal site occupancies 0.03. The geometry of the CH_2Cl_2 molecule was restrained using DFIX and DANG instruction and ADPs of the atoms were restrained using ISOR and SIMU instructions in SHELXL97 (Sheldrick, 2008).

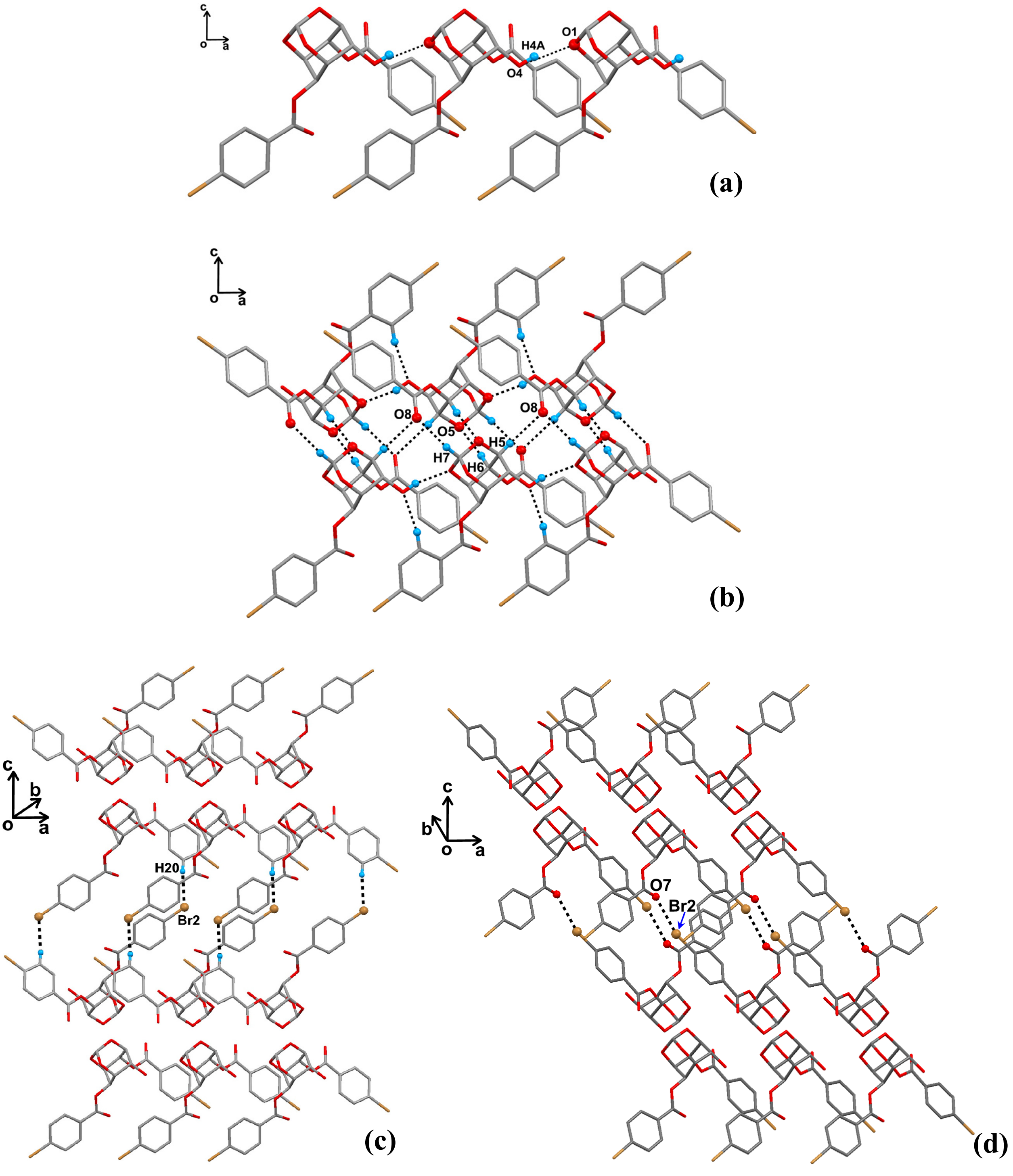


Fig. S1. (a) Molecular strings and (b) subsequent bilayers formed by O-H…O and C-H…O interactions in Forms I and II. Linkage of bilayers in **2** (c) through C-H…Br contacts in Form I crystals and (d) through C-Br…O contacts in Form II crystals.

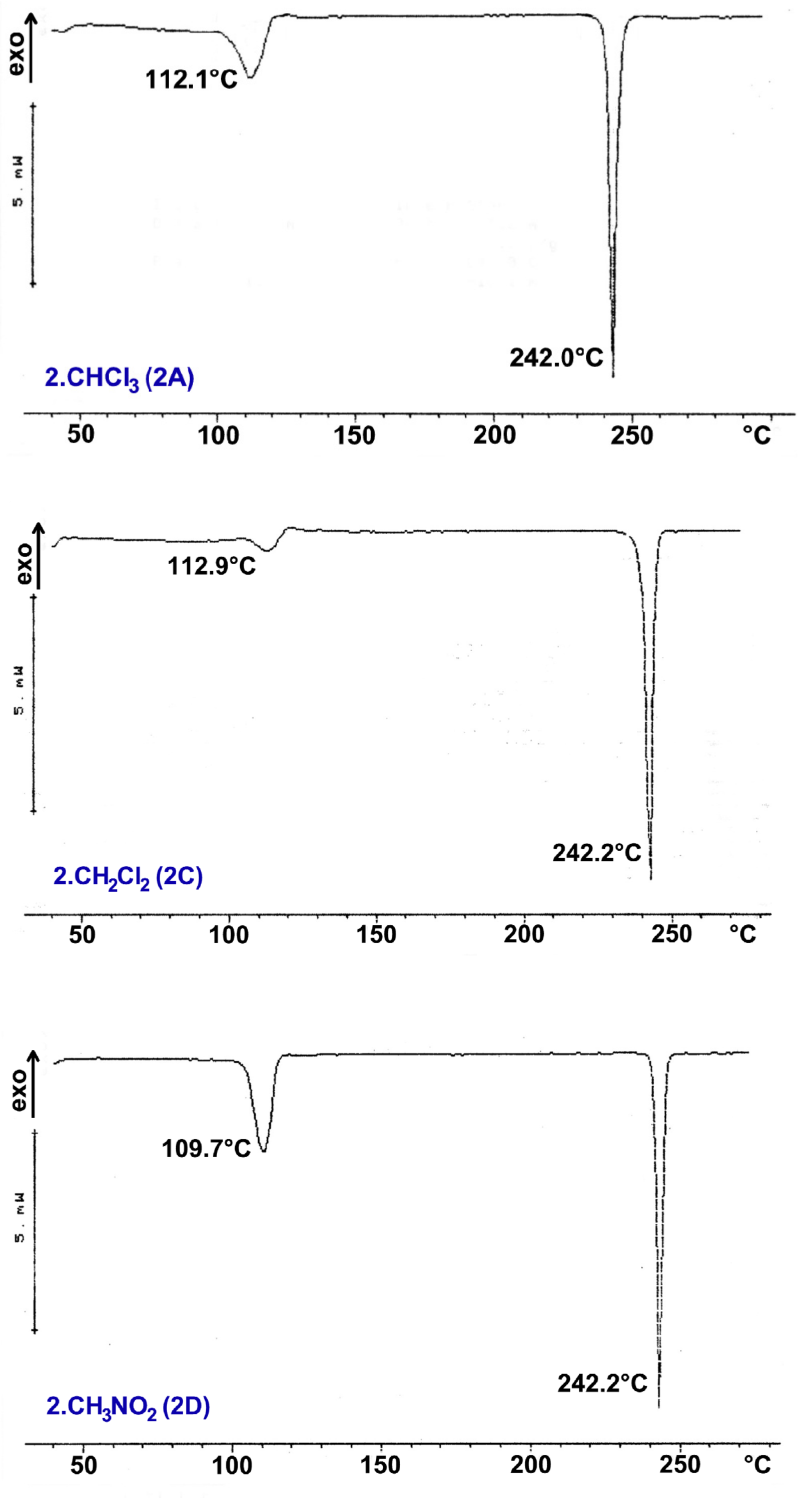
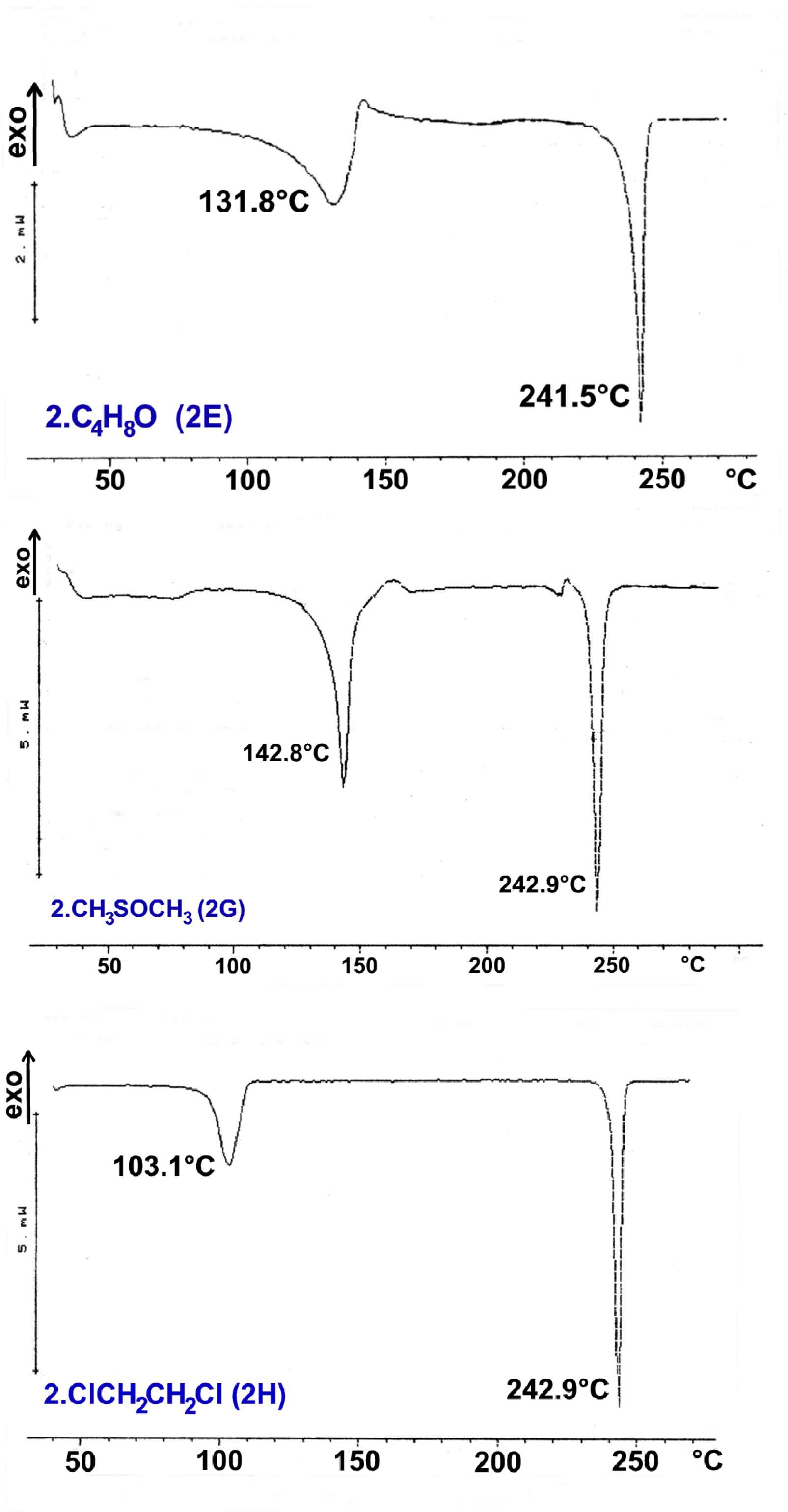


Fig. S2. DSC curves for solvatomorphs of **2**.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241.5°C
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100
150
200
250
°C
exo
5 . mW
142.8°C
242.9°C
2.CH$_3$SOCH$_3$ (2G)
50
100
150
200
250
°C
exo
5 . mW
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100
150
200
250
°C

Fig. S2. Contd…

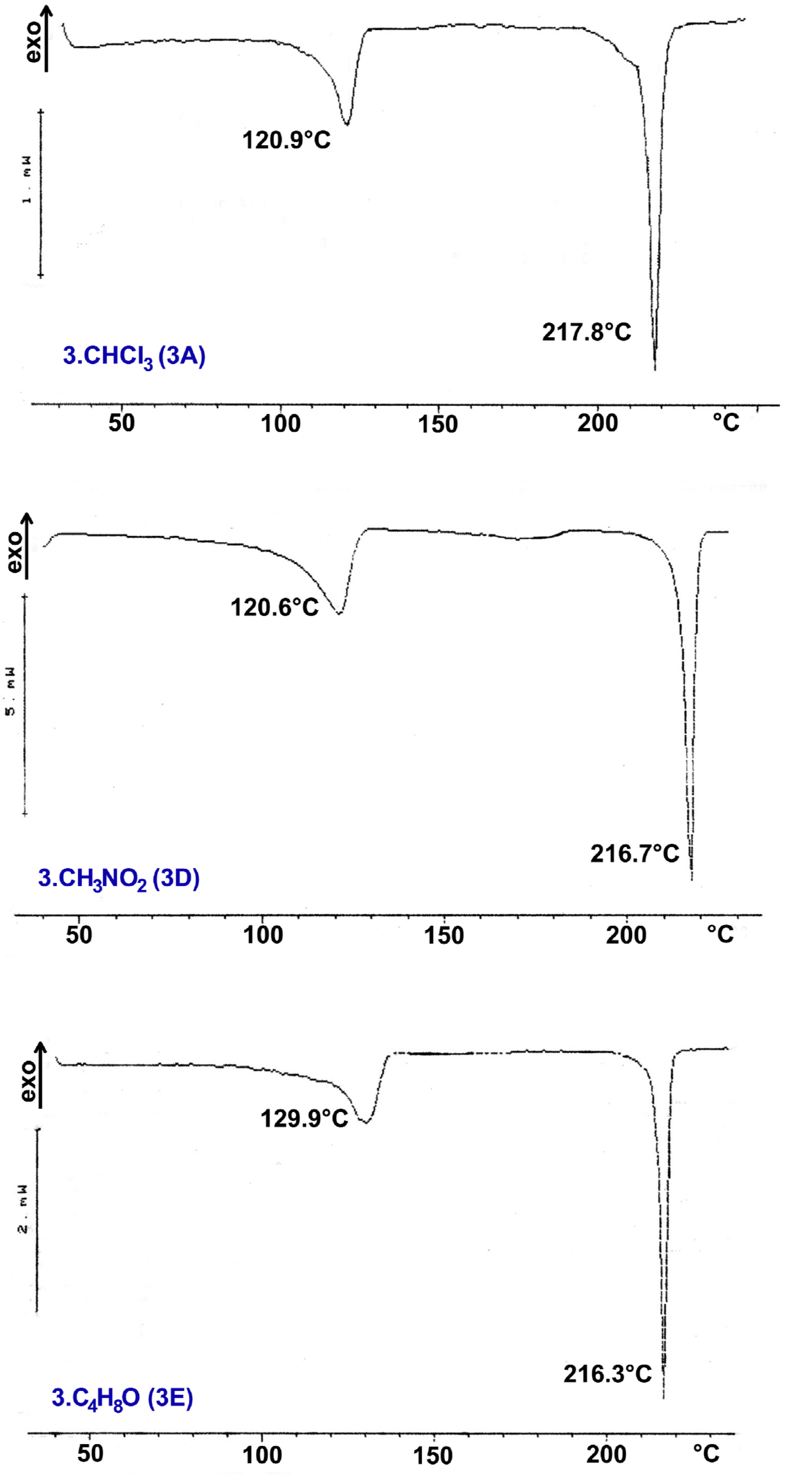
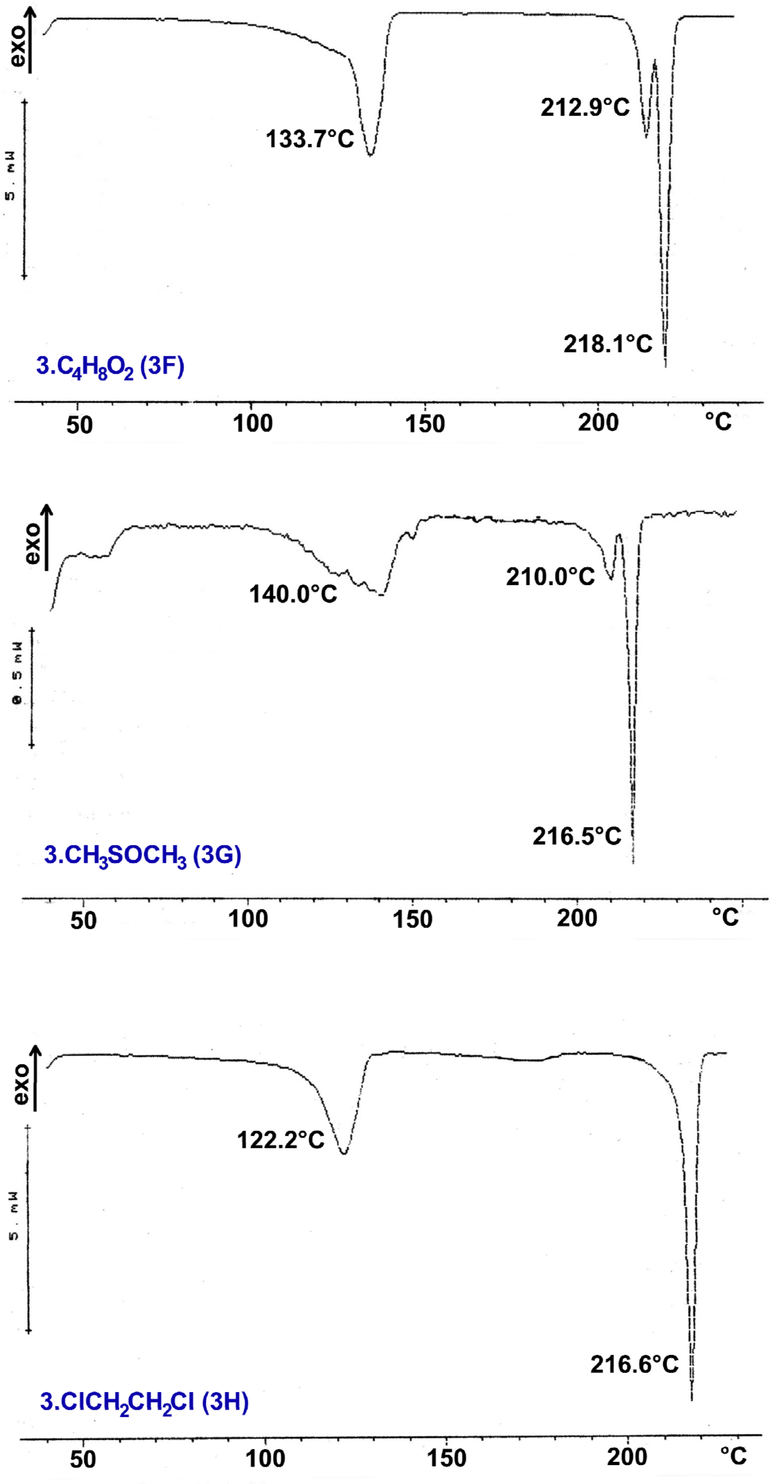


Fig. S3. DSC curves for solvatomorphs of **3**.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218.1°C
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100
150
200
°C
exo
0.5 mW
140.0°C
210.0°C
216.5°C
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50
100
150
200
°C
exo
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100
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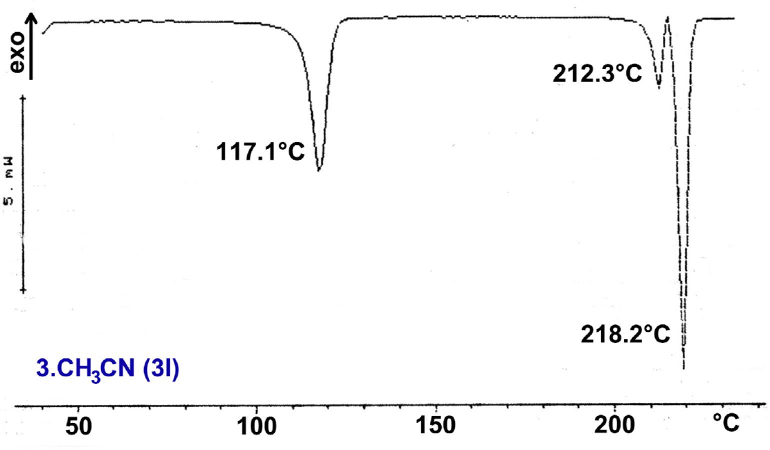
200
°C

Fig. S3. Contd…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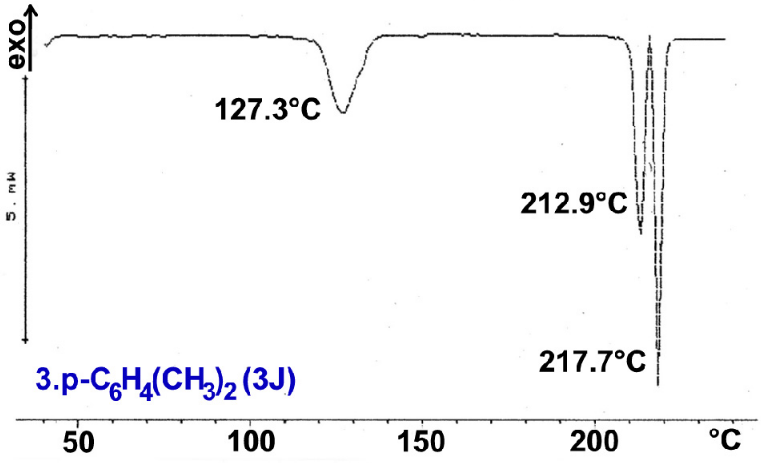
50
100
150
200
°C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212.9°C
217.7°C
3.p-C6H4(CH3)2 (3J)
50
100
150
200
°C

Fig. S3. Contd…

Table S1: Supporting intermolecular hydrogen bonding interactions along helical assembly in solvates of **2** and **3**.

	D-H···A^{a}	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
2.CHCl$_3$	C5-H5···O4^{i}	1.00	2.56	3.296(3)	131
	C5-H5···O7^{i}	1.00	2.65	3.345(3)	127
	C11-H11···O1^{ii}	0.95	2.70	3.524(4)	146
2.CH$_3$COCH$_3$	C5-H5···O4^{iii}	1.00	2.52	3.231(3)	128
	C5-H5···O7^{iii}	1.00	2.59	3.297(3)	127
	C11-H11···O1^{ii}	0.95	2.66	3.489(3)	146
2.CH$_2$Cl$_2$	C5-H5···O4^{iv}	1.00	2.60	3.337(3)	131
	C11-H11···O1^{ii}	0.95	2.59	3.435(3)	149
2.CH$_3$NO$_2$	C5-H5···O4^{i}	1.00	2.45	3.160(3)	127
	C5-H5···O7^{i}	1.00	2.60	3.303(3)	128
2.C$_4$H$_8$O	C5-H5···O4^{iii}	1.00	2.54	3.261(5)	129
	C11-H11···O1^{ii}	0.95	2.57	3.387(5)	144
2.C$_4$H$_8$O$_2$	C5-H5···O4^{i}	1.00	2.69	3.381(4)	126
	C5-H5···O7^{i}	1.00	2.64	3.339(4)	127
	C11-H11···O1^{ii}	0.95	2.64	3.491(4)	149
2.CH$_3$SOCH$_3$	C5-H5···O4^{v}	1.00	2.55	3.277(5)	129
	C5-H5···O7^{v}	1.00	2.59	3.298(4)	127
	C11-H11···O1^{ii}	0.95	2.58	3.437(5)	151
2.ClCH$_2$CH$_2$Cl	C5-H5···O4^{vi}	1.00	2.64	3.348(5)	128
	C11-H11···O1^{ii}	0.95	2.50	3.315(4)	144
3.CHCl$_3$	C5-H5···O4^{i}	1.00	2.58	3.336(3)	132
	C5-H5···O7^{i}	1.00	2.67	3.369(3)	127
	C11-H11···O1^{ii}	0.95	2.51	3.385(3)	153
3.CH$_3$COCH$_3$	C5-H5···O4^{iii}	1.00	2.53	3.240(2)	128
	C5-H5···O7^{iii}	1.00	2.59	3.294(2)	128
	C11-H11···O1^{ii}	0.95	2.61	3.450(2)	148
3.CH$_2$Cl$_2$	C5-H5···O4^{i}	1.00	2.58	3.316(3)	131
	C11-H11···O1^{ii}	0.95	2.53	3.371(3)	148
3.CH$_3$NO$_2$	C5-H5···O4^{v}	1.00	2.58	3.287(2)	128
	C5-H5···O7^{v}	1.00	2.69	3.373(2)	125
	C11-H11···O1^{ii}	0.95	2.56	3.381(2)	145

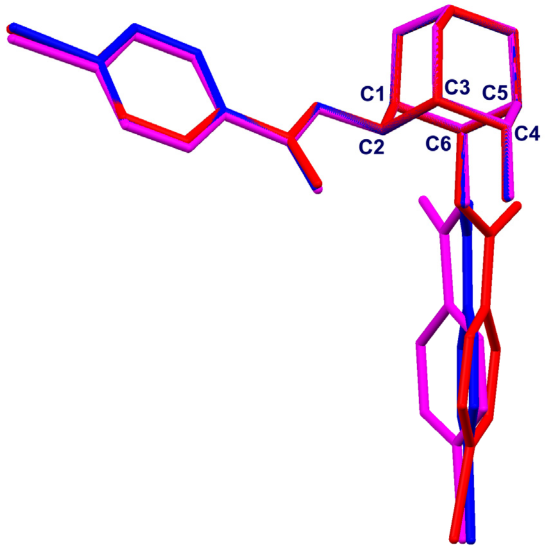
	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
3.C_4H_8O	C5-H5···O4^{iii}	1.00	2.61	3.338(4)	130
	C11-H11···O1^{ii}	0.95	2.55	3.397(4)	148
3.$C_4H_8O_2$	C5-H5···O4^{iii}	1.00	2.61	3.294(4)	126
	C5-H5···O7^{iii}	1.00	2.64	3.337(3)	127
	C11-H11···O1^{ii}	0.95	2.66	3.474(4)	145
3.CH_3SOCH_3	C5-H5···O4^{iii}	0.91(3)	2.55(3)	3.263(3)	135(2)
	C5-H5···O7^{iii}	0.91(3)	2.69(3)	3.292(3)	124(2)
	C11-H11···O1^{ii}	0.89(3)	2.60(3)	3.411(3)	151(2)
3.$ClCH_2CH_2Cl$	C5-H5···O4^{vii}	1.00	2.56	3.265(5)	127
	C11-H11···O1^{ii}	0.95	2.50	3.294(5)	141
3.CH_3CN	C5-H5···O4^{vii}	0.93(2)	2.61(2)	3.332(3)	134(2)
	C11-H11···O1^{ii}	0.96(3)	2.52(3)	3.307(3)	139(2)
3.*p*-$C_6H_4(CH_3)_2$	C11-H11···O1^{viii}	0.95	2.51	3.237(2)	134
3.C_6H_6	C11-H11···O1^{ii}	0.95	2.49	3.227(8)	135

[a]Symmetry codes: (i) $-x + 3/2, y - 1/2, -z + 3/2$; (ii) $x, y + 1, z$;

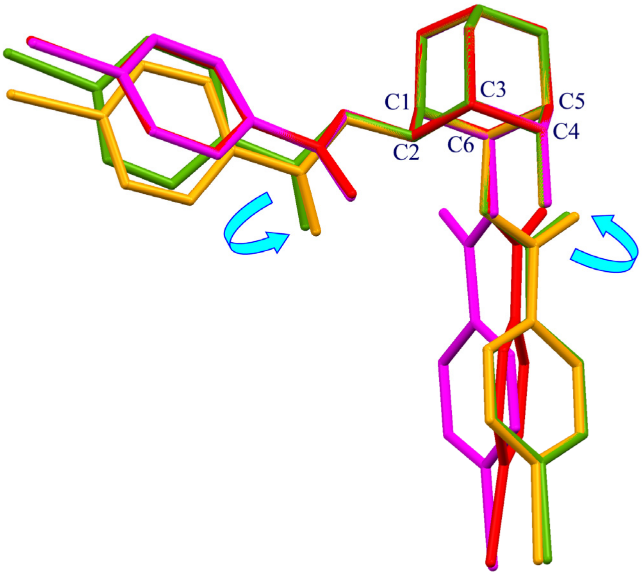
(iii) $-x + 1/2, y - 1/2, -z + 1/2$; (iv) $-x + 3/2, y - 1/2, -z + 1/2$;

(v) $-x + 1/2, y - 1/2, -z + 3/2$; (vi) $-x + 1, y - 1/2, -z + 3/2$; (vii) $-x + 2, y - 1/2, -z + 1/2$;

(viii) $-x + 1, y + 1/2, -z + 3/2$.



(a)



(b)

Fig. S4 Molecular overlap of (a) host molecules in inclusion crystals of **$2 \cdot CHCl_3$** (red), **$2 \cdot CH_2Cl_2$** (blue), **$2 \cdot C_4H_8O_2$** (magenta) and (b) overlap of solvent free polymorphs of **2** (orange and green) and host molecules in **$2 \cdot CHCl_3$** (red) and **$2 \cdot C_4H_8O_2$** (magenta) showing relative orientation of benzoyl groups.

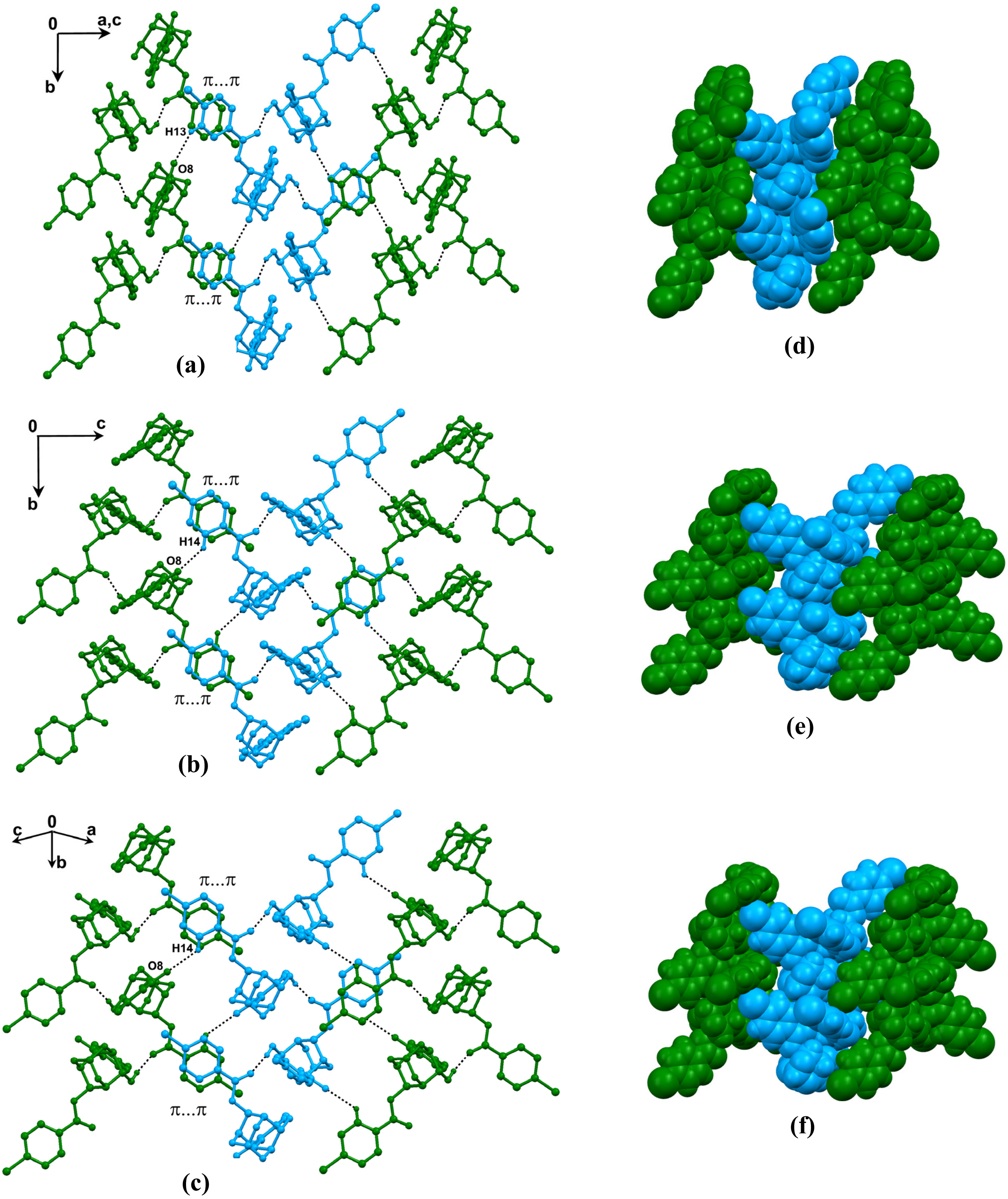
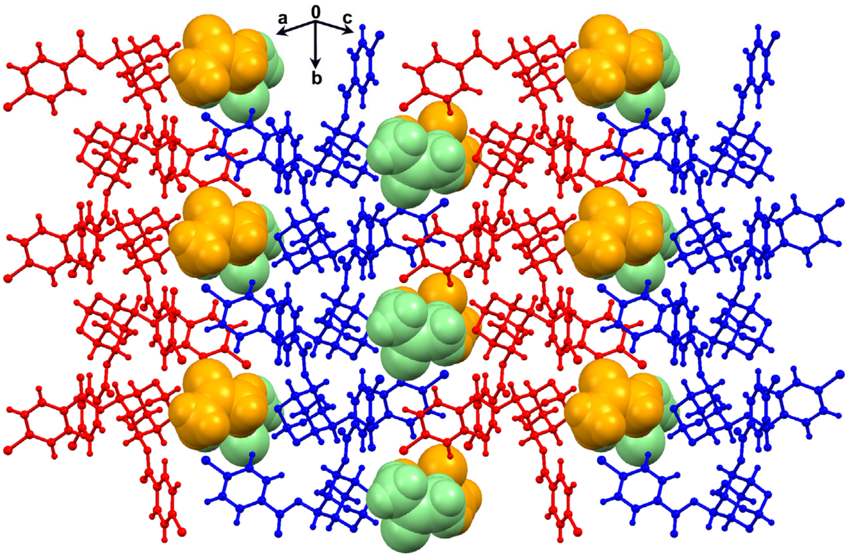
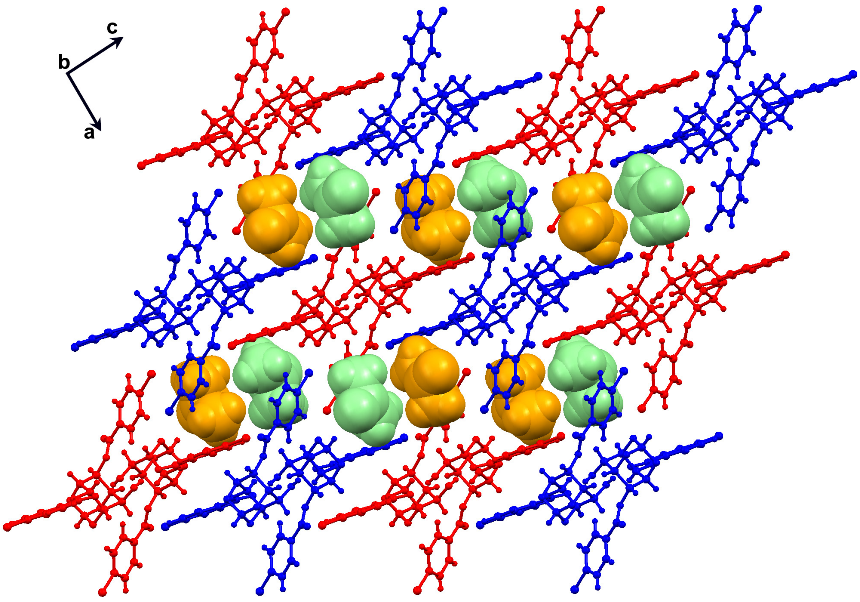


Fig. S5 Interlinking of helices in inclusion crystals of group I (a), group II (b) and group III (c). Space filling models (d), (e) and (f) show the compact packing of helices.

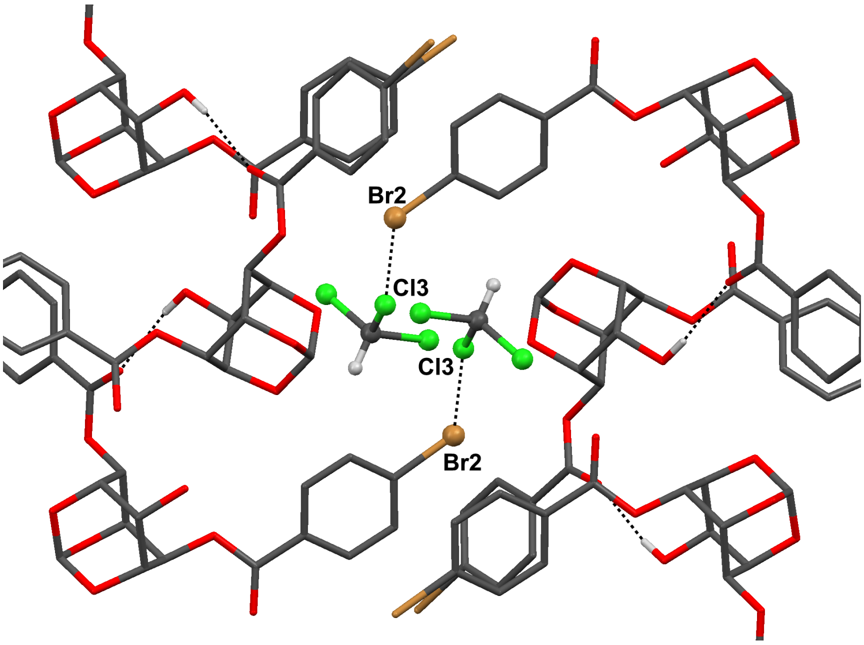


(a)

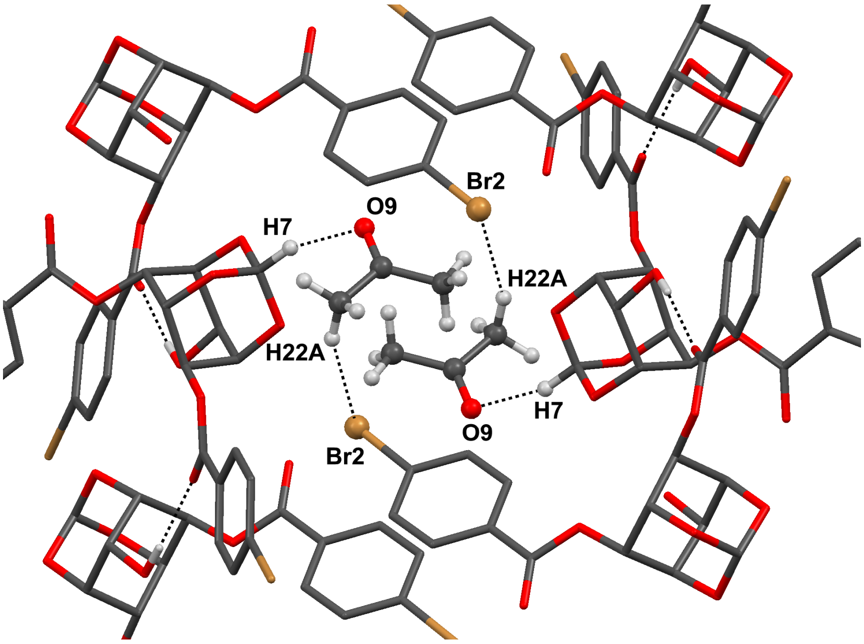


(b)

Fig. S6 Representative CPK view of the host-guest assembly in **3B**; (a) viewed along *ab*-plane and (b) viewed down *b*-axis.

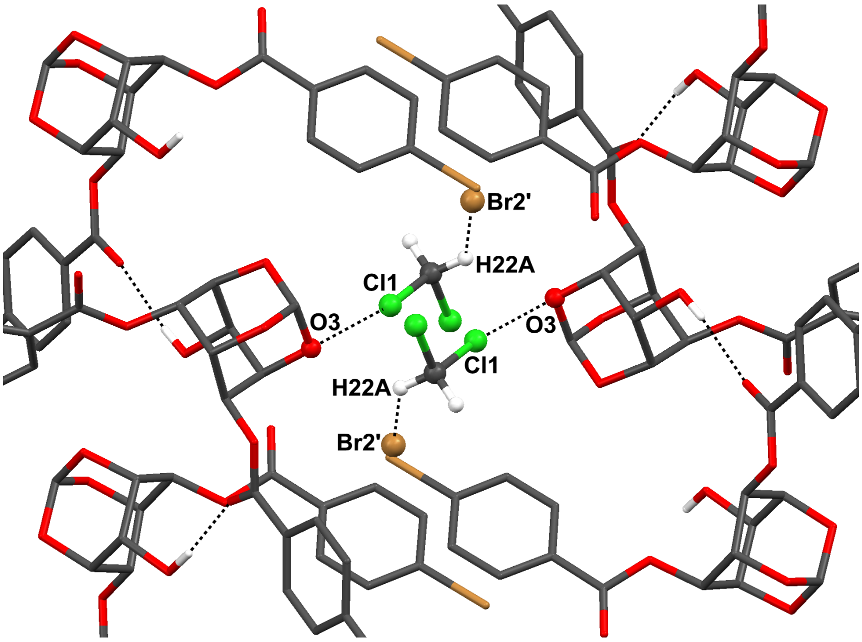


(a) Host-guest interactions in **2·CHCl$_3$**.

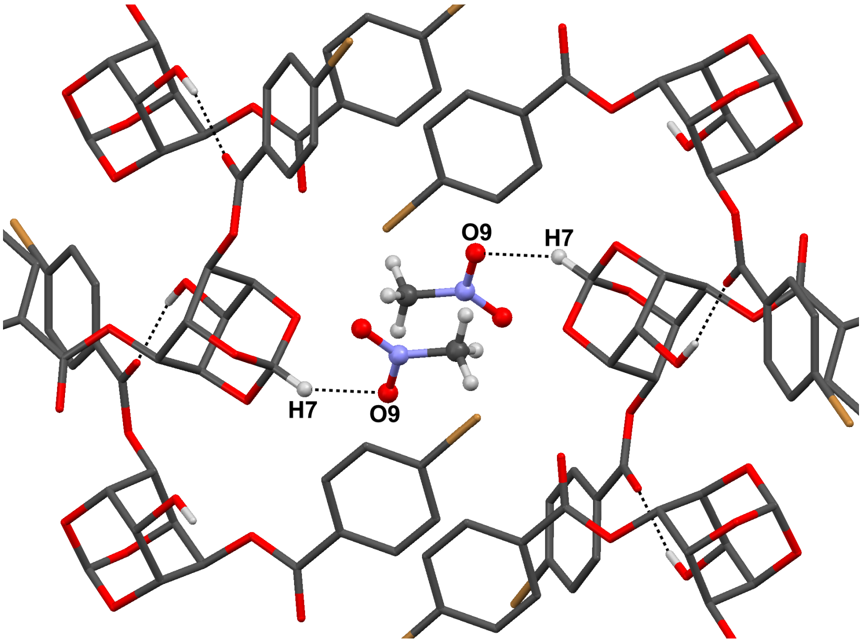


(b) Host-guest interactions in **2·CH$_3$COCH$_3$**.

Fig. S7 Host – guest interactions in solvates of **2**.

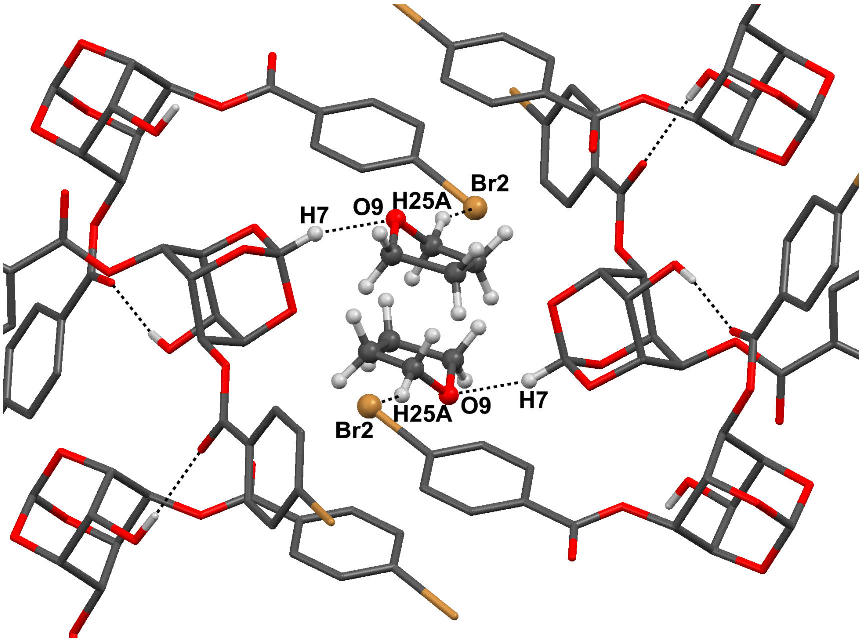


(c) Host-guest interactions in **2·CH_2Cl_2**.

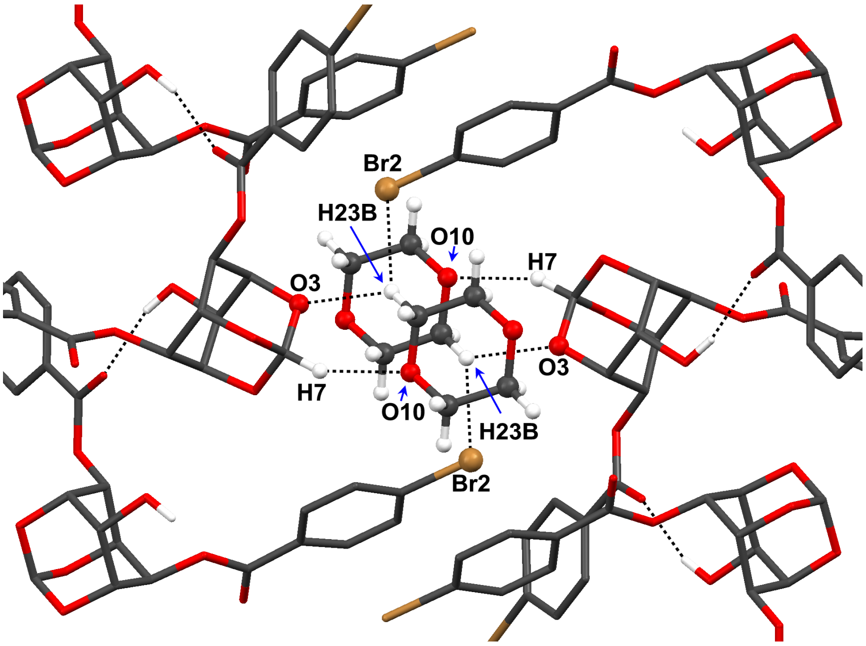


(c) Host-guest interactions in **2·CH_3NO_2**.

Fig. S7 Contd…

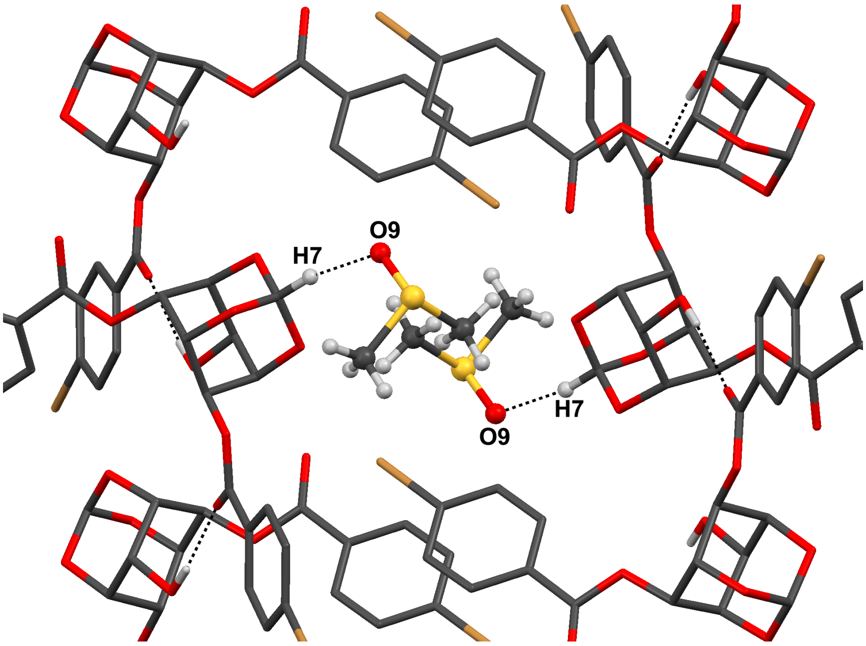


(e) Host-guest interactions in **$2 \cdot C_4H_8O$**.

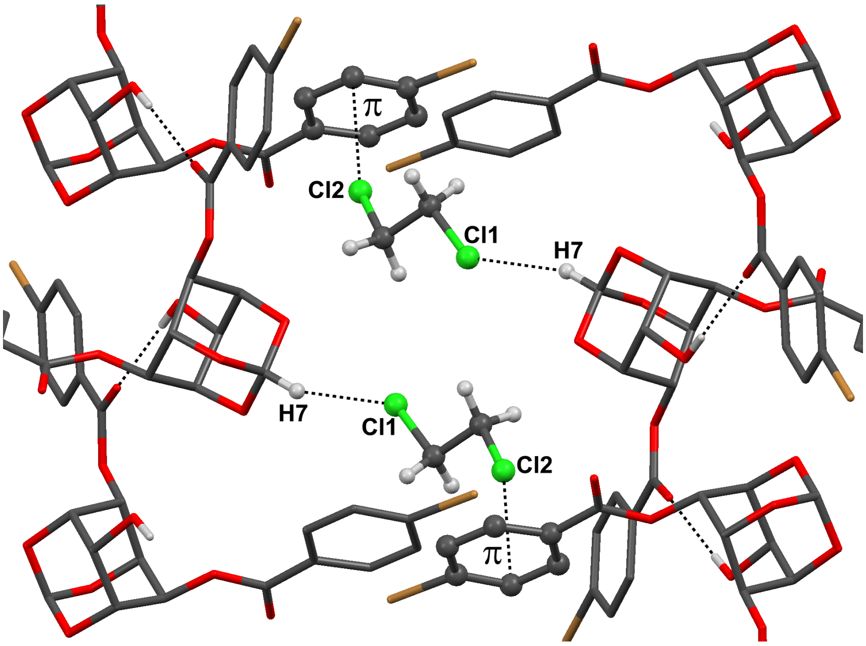


(f) Host-guest interactions in **$2 \cdot C_4H_8O_2$**.

Fig. S7 Contd…



(g) Host-guest interactions in **2·CH_3SOCH_3**.



(h) Host-guest interactions in **2·$C_2H_4Cl_2$**.

Fig. S7 Contd…