

Supplementary Information

Inclusion of halobenzene in water-mediated hydrogen-bonded architectures built from a V-shaped host molecule

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General procedure of single crystal X-ray diffraction experiment

A single crystal was immersed in Paratone-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with a CCD detector (APEX II, MoK α : $\lambda = 0.71073$ Å). Absorption correction was performed by an empirical method implemented in SADABS.¹ Structure solution and refinement were performed by using SHELXT-2018/2² and SHELXL-2019/2³.

Single crystal X-ray diffraction experiment for crystal 1a

The colorless plate crystal ($0.300 \times 0.200 \times 0.200$ mm³) was obtained from slow evaporation of a chlorobenzene solution of **1**.

C₃₂H₃₉ClO₇, $M_r = 571.08$; monoclinic, space group $C2/c$, $Z = 4$, $D_{\text{calc}} = 1.298$ g·cm⁻³, $a = 14.904(4)$, $b = 21.449(6)$, $c = 9.772(3)$ Å, $\beta = 110.651(3)^\circ$, $V = 2923.3(13)$ Å³, 13230 observed and 2108 [$I > 2\sigma(I)$], 2711 [all data] independent reflections, 285 parameters, 100 restraints, final $R_1 = 0.0372$, $wR_2 = 0.0935$, $S = 1.056$ [$I > 2\sigma(I)$] and $R_1 = 0.0522$, $wR_2 = 0.1016$, $S = 1.049$ [all data]. CCDC 2356259

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water were assigned from the difference Fourier map and refined isotropically. Another hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. A pair of half chlorobenzene molecules (C15-C20, C11 and C21-C26, Cl2) was closely located on a two folded rotation axis. They were refined with PART -n, SAME, SIMU and SUMP. Each occupancy was as follows. C15-C20, C11: 36.5%, C63-C67, O11: 13.5%. (Fig. S1, 2)

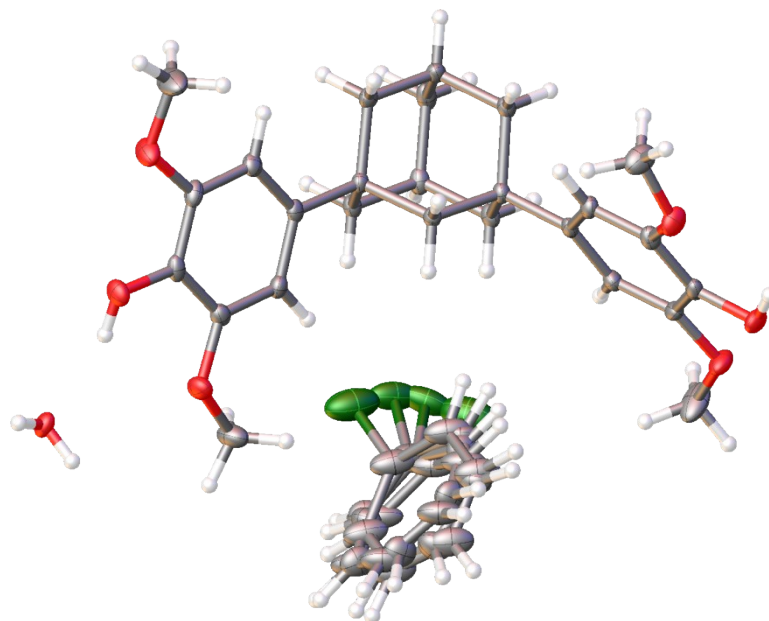


Fig. S1 ORTEP drawing of **1**, water, and chlorobenzene in crystal **1a** (50% probability).

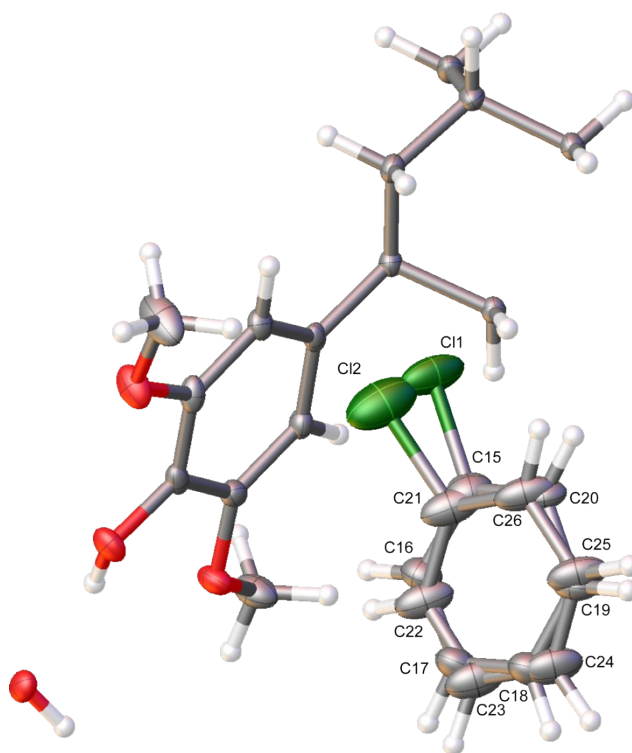


Fig. S2 ORTEP drawing of **1**, water, and chlorobenzene in the asymmetric unit (50% probability).

Single crystal X-ray diffraction experiment for crystal 1b

The low diffracting colorless plate crystal ($0.400 \times 0.300 \times 0.200 \text{ mm}^3$) was obtained from slow evaporation of a bromobenzene solution of **1**.

$\text{C}_{31.69}\text{H}_{38.74}\text{Br}_{0.95}\text{O}_7$, $M_r = 607.53$; monoclinic, space group $C2/c$, $Z = 4$, $D_{\text{calc}} = 1.382 \text{ g}\cdot\text{cm}^{-3}$, $a = 14.823(7)$, $b = 21.293(7)$, $c = 9.842(4) \text{ \AA}$, $\beta = 109.908(6)^\circ$, $V = 2921(2) \text{ \AA}^3$, 8791 observed and 1705 [$I > 2\sigma(I)$], 2348 [all data] independent reflections, 221 parameters, 42 restraints, final $R_1 = 0.0583$, $wR_2 = 0.1449$, $S = 1.007$ [$I > 2\sigma(I)$] and $R_1 = 0.0737$, $wR_2 = 0.1502$, $S = 1.009$ [all data]. CCDC 2356260

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water were assigned from the difference Fourier map and refined isotropically. Another hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The bromobenzene molecules which were symmetrically equivalents were located on a two folded rotation axis. They were refined with PART $-n$ and SIMU. The occupancy of the asymmetric unit was 47.5%. (Fig. S3, 4)

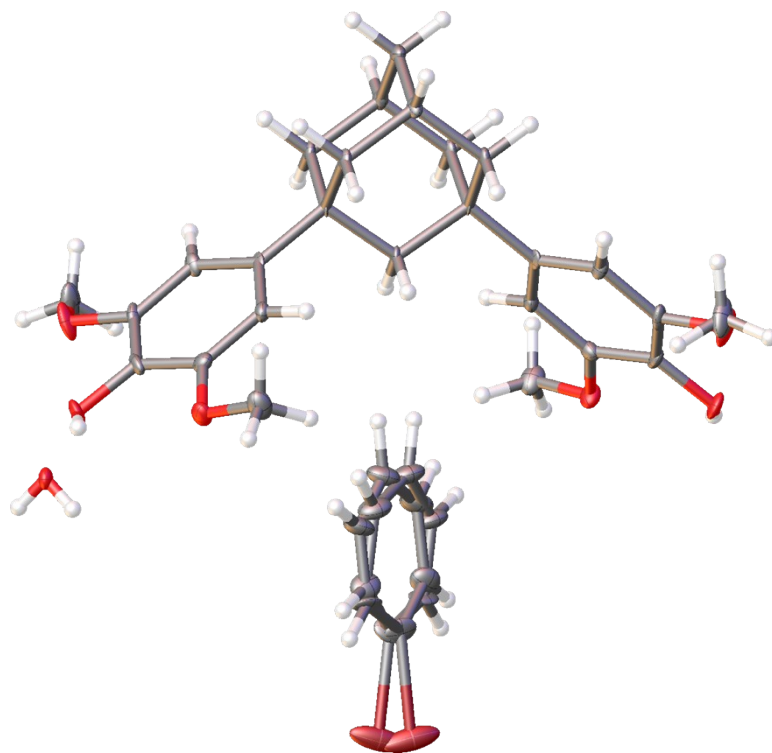


Fig. S3 ORTEP drawing of **1**, water, and bromobenzene in crystal **1b** (50% probability).

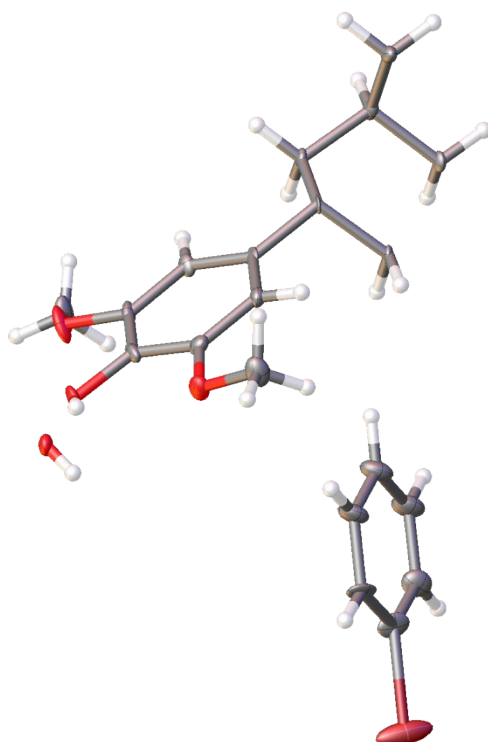


Fig. S4 ORTEP drawing of **1**, water, and bromobenzene in the asymmetric unit (50% probability).

Single crystal X-ray diffraction experiment for **1c**

The colorless plate crystal ($0.400 \times 0.200 \times 0.100 \text{ mm}^3$) was obtained from slow evaporation of an iodobenzene solution of **1**.

$\text{C}_{32}\text{H}_{39}\text{IO}_7$, $M_r = 662.53$; monoclinic, space group $C2/c$, $Z = 4$, $D_{\text{calc}} = 1.493 \text{ g}\cdot\text{cm}^{-3}$, $a = 14.717(3)$, $b = 21.315(5)$, $c = 9.962(2) \text{ \AA}$, $\beta = 109.453(3)^\circ$, $V = 2946.7(12) \text{ \AA}^3$, 13024 observed and 2103 [$I > 2\sigma(I)$], 2669 [all data] independent reflections, 220 parameters, 36 restraints, final $R_1 = 0.0358$, $wR_2 = 0.0761$, $S = 1.074$ [$I > 2\sigma(I)$] and $R_1 = 0.0509$, $wR_2 = 0.0809$, $S = 1.068$ [all data]. CCDC 2356261

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water were assigned from the difference Fourier map and refined isotropically. Another hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The iodobenzene molecules which were symmetrically equivalents were located on a two folded rotation axis. They were refined with PART -n and SIMU. The occupancy of the asymmetric unit was 50%. (Fig. S5, 6)

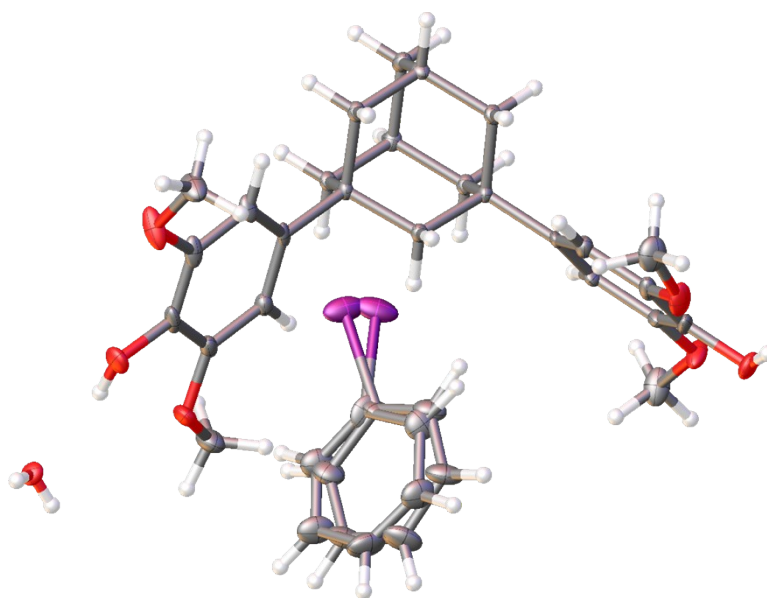


Fig. S5 ORTEP drawing of **1**, water, and iodobenzene in crystal **1c** (50% probability).

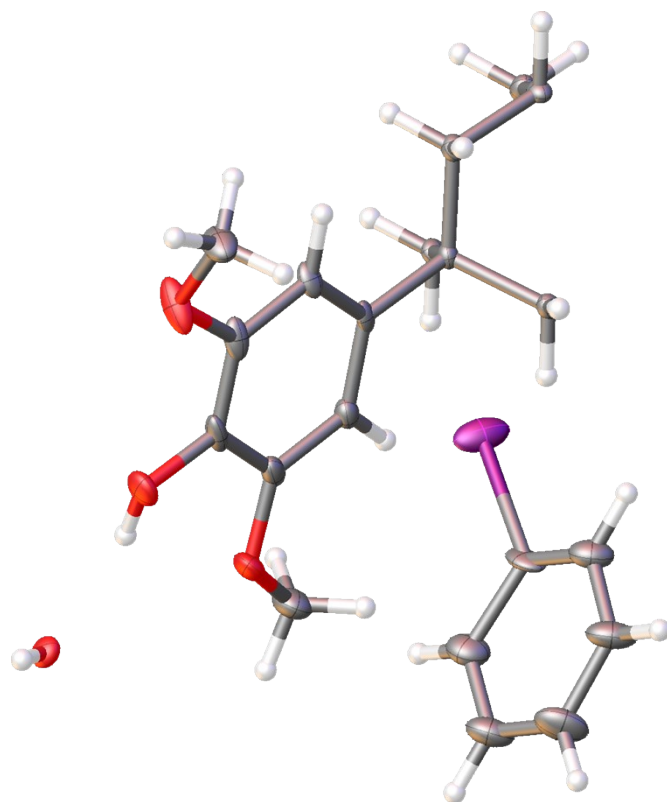


Fig. S6 ORTEP drawing of **1**, water, and iodobenzene in the asymmetric unit (50% probability).

Single crystal X-ray diffraction experiment for **1d**

The bronze prismatic crystal ($0.300 \times 0.300 \times 0.200 \text{ mm}^3$) was obtained from slow evaporation of an *o*-dichlorobenzene solution of **1**.

$\text{C}_{32}\text{H}_{38}\text{Cl}_2\text{O}_7$, $M_r = 605.52$; triclinic, space group $P-1$, $Z = 2$, $D_{\text{calc}} = 1.365 \text{ g}\cdot\text{cm}^{-3}$, $a = 9.710(4)$, $b = 13.163(5)$, $c = 13.202(5) \text{ \AA}$, $\alpha = 111.592(4)$, $\beta = 103.293(4)$, $\gamma = 98.851(4)^\circ$, $V = 1473.0(10) \text{ \AA}^3$, 13482 observed and 3811 [$I > 2\sigma(I)$], 5250 [all data] independent reflections, 382 parameters, final $R_1 = 0.0506$, $wR_2 = 0.1233$, $S = 1.056$ [$I > 2\sigma(I)$] and $R_1 = 0.0758$, $wR_2 = 0.1358$, $S = 1.056$ [all data]. CCDC 2356262

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water were assigned from the difference Fourier map and refined isotropically. Another hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. (Fig. S7)

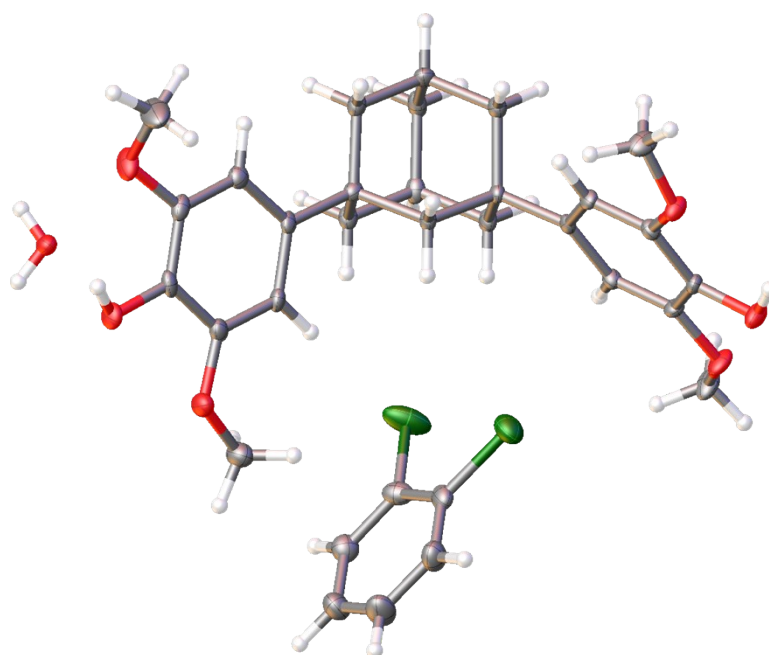


Fig. S7 ORTEP drawing of **1**, water, and *o*-dichlorobenzene in crystal **1d** (50% probability).

Single crystal X-ray diffraction experiment for crystal 3a

The yellow prismatic crystal ($0.300 \times 0.200 \times 0.200 \text{ mm}^3$) was obtained from slow evaporation of a chlorobenzene solution of **3**.

$\text{C}_{62.25}\text{H}_{64.88}\text{Cl}_{3.38}\text{O}_{12}$, $M_r = 1124.68$; triclinic, space group $P-1$, $Z = 2$, $D_{\text{calc}} = 1.313 \text{ g}\cdot\text{cm}^{-3}$, $a = 11.970(2)$, $b = 12.882(2)$, $c = 18.795(3) \text{ \AA}$, $\alpha = 91.412(2)$, $\beta = 100.706(2)$, $\gamma = 91.957(2)^\circ$, $V = 2844.6(9) \text{ \AA}^3$, 26321 observed and 7826 [$I > 2\sigma(I)$], 10153 [all data] independent reflections, 883 parameters, 214 restraints, final $R_1 = 0.0468$, $wR_2 = 0.1134$, $S = 1.026$ [$I > 2\sigma(I)$] and $R_1 = 0.0643$, $wR_2 = 0.1223$, $S = 1.024$ [all data]. CCDC 2356263 All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 147, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

Six disordered chlorobenzene molecules (A , B , C , D , E and F) in the asymmetric unit were successfully refined.

The chlorobenzene molecules A and B were refined with occupancy of 95.2% and 94.4%, respectively. The overlapped chlorobenzene molecules C , D , E and F were fully or partially refined with FLAT, PART (-)n, SAME and SIMU. Each occupancy was as follows. C : 83.6%, D : 39.0%, E : 15.4%, F : 9.8%. The molecule C overlapped with E and F . The molecule D riding on the inversion center overlapped with D^* (symmetry operation: 1-x, -y, -z), E and E^* (symmetry operation: 1-x, -y, -z). The molecule E overlapped with C , D and D^* . The molecule F overlapped with C . (Fig. S8, 9)

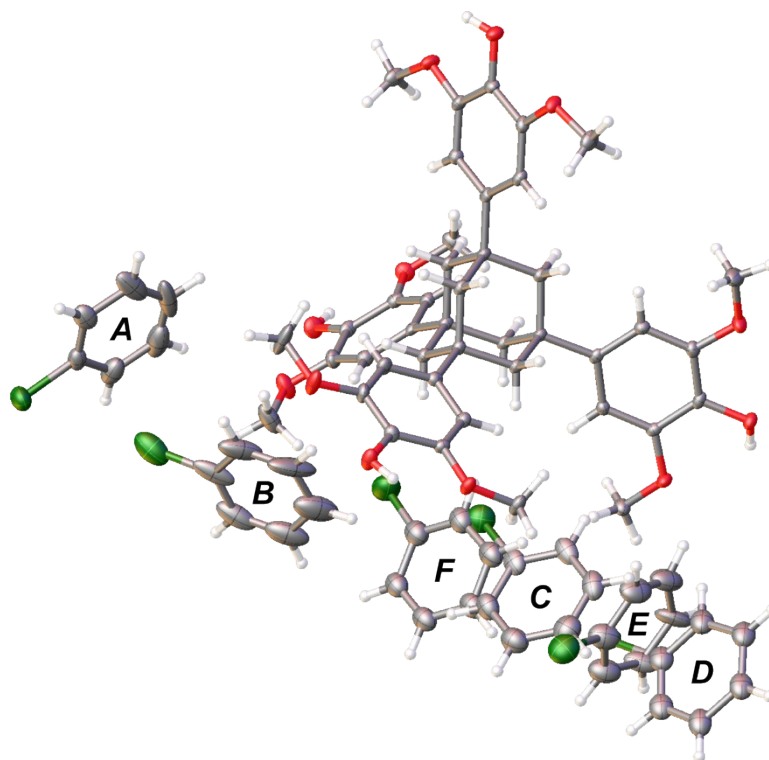


Fig. S8 ORTEP drawing of **3** and chlorobenzene molecules in the asymmetric unit (50% probability).

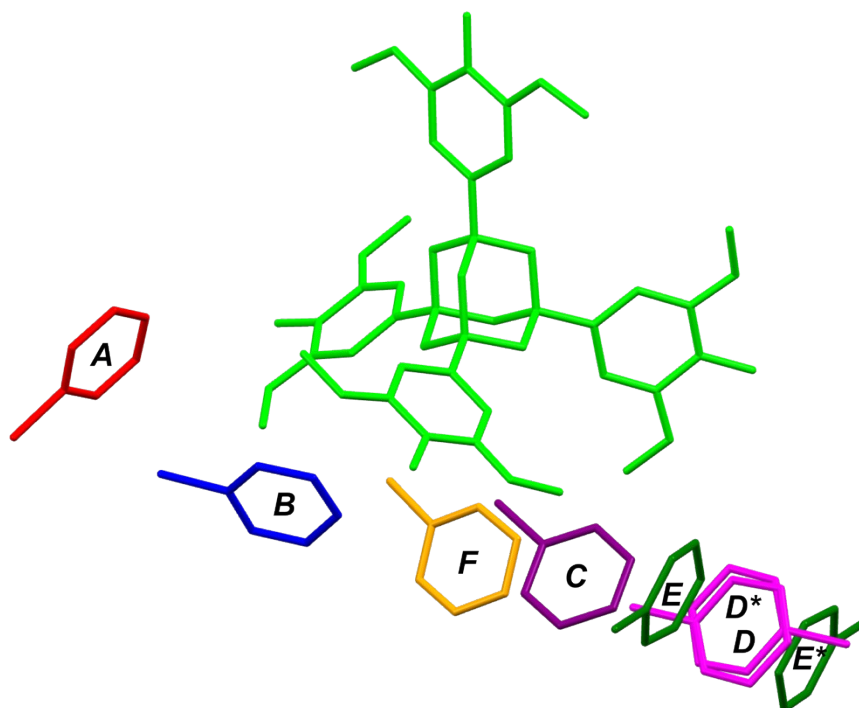


Fig. S9 Crystal structure of **3a** (Hydrogen atoms are omitted for clarity).

References

- (1) G. M. Sheldrick, *SADABS*. University of Göttingen, Germany, 1996.
- (2) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
- (3) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.