Supplementary Information

Inclusion crystals of V-shaped host molecules having trialkoxybenzene moieties with carborane or benzoquinone derivative

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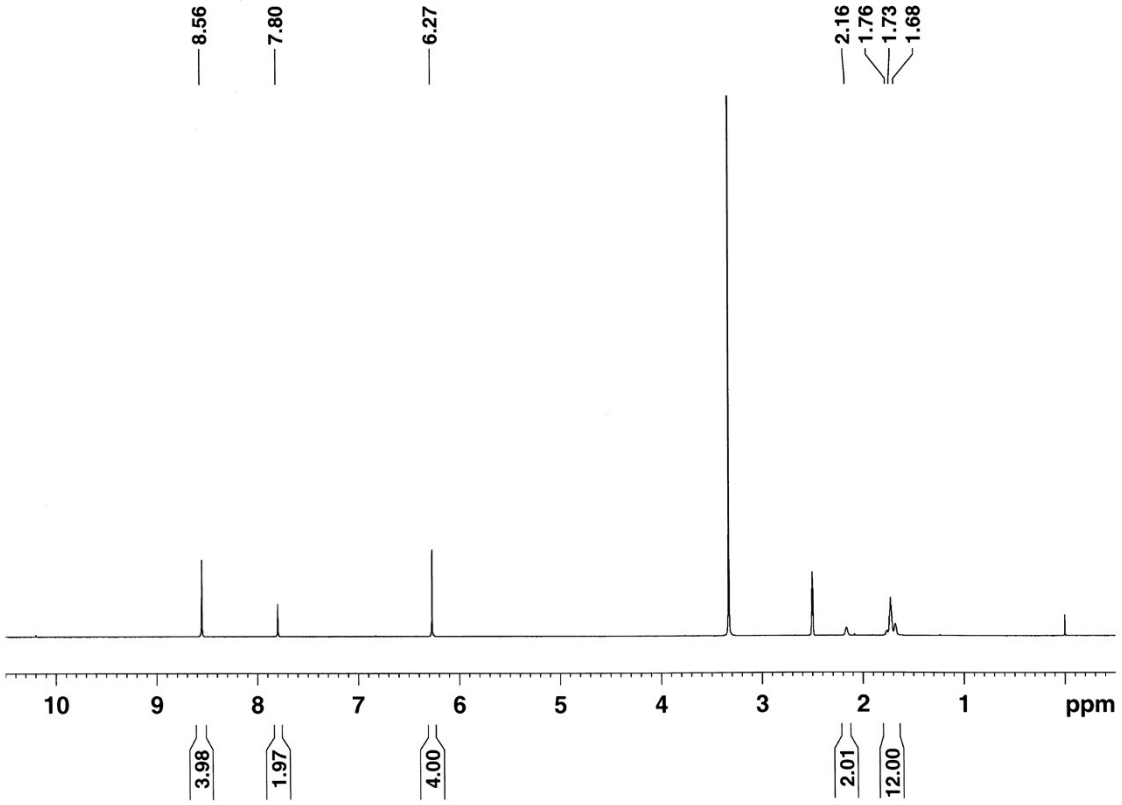
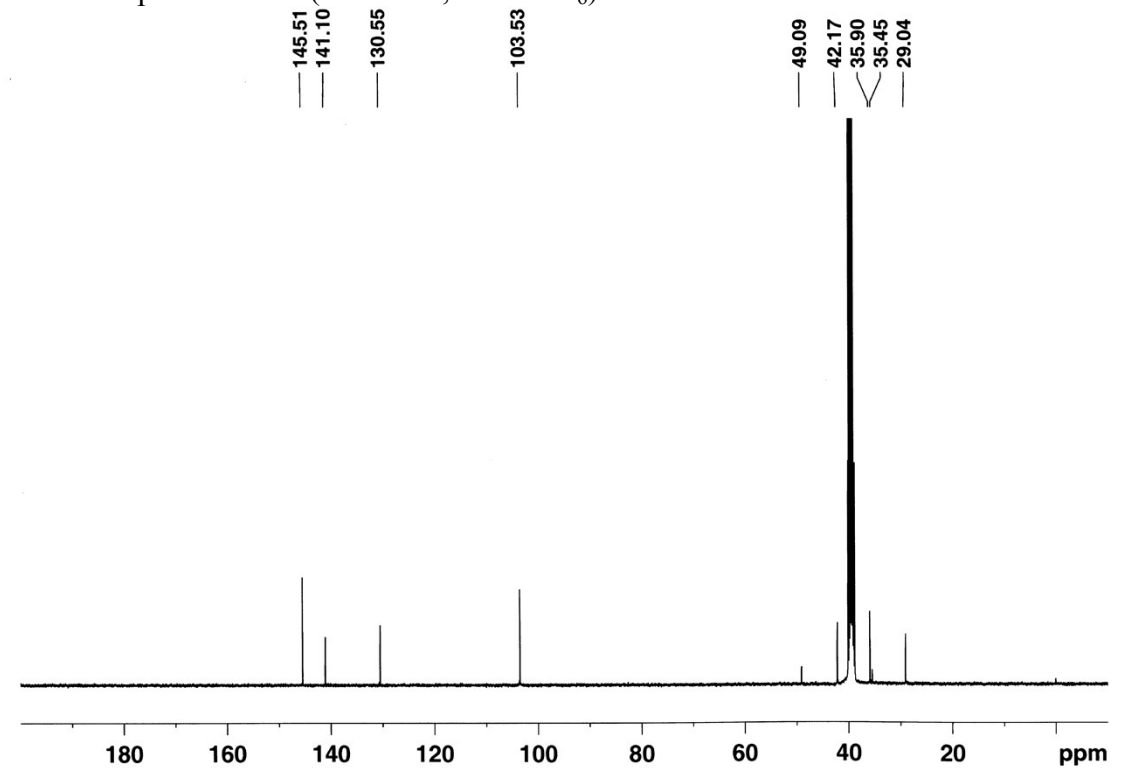
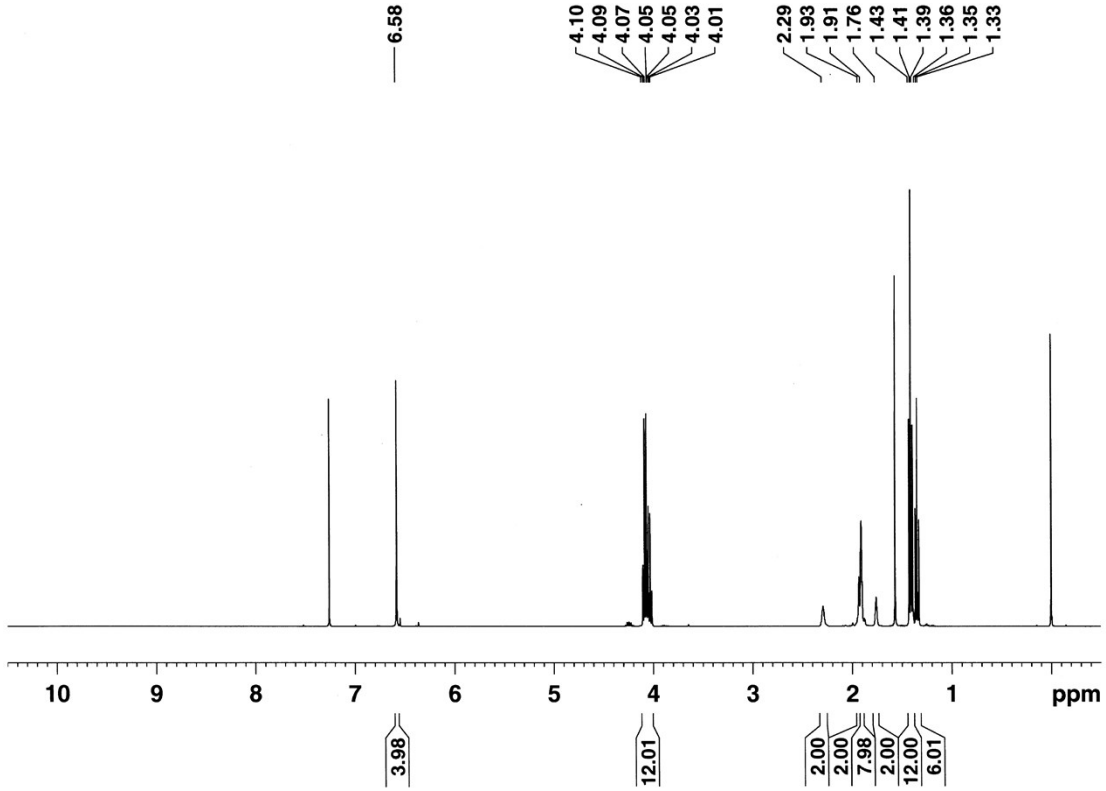
^{1}H NMR spectrum of **3** (400 MHz, DMSO-d_6)



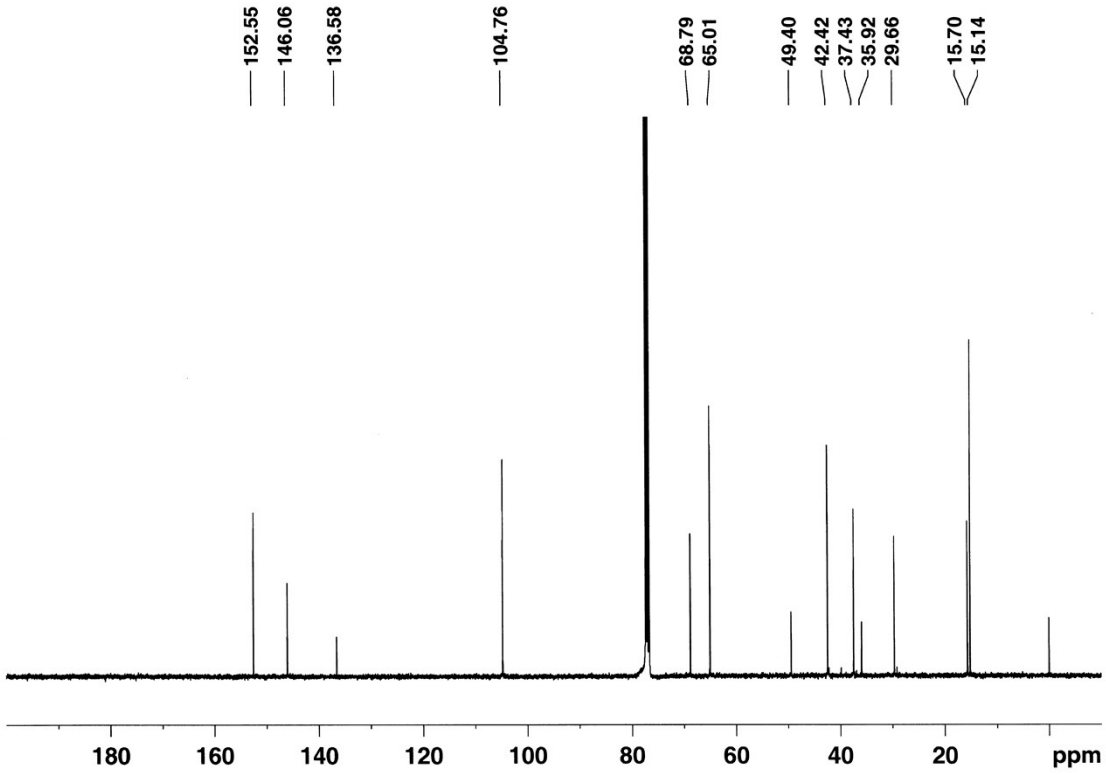
^{13}C NMR spectrum of **3** (100 MHz, DMSO-d_6)



^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$)



Single crystal X-ray diffraction experiment for 1a

The low diffracting colourless plate crystal (0.120 × 0.040 × 0.030 mm^3), which was obtained from toluene, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2018/3[3].

$C_{30}H_{48}B_{10}O_6$, *M*r = 612.78; orthorhombic, space group *Pbca*, *Z* = 8, D_{calc} = 1.217 g·cm^{-3}, *a* = 20.6673(6), *b* = 13.5157(4), *c* = 23.9379(7) Å, *V* = 6686.6(3) $Å^3$, 82781 observed and 4855 independent [$I > 2\sigma(I)$] reflections, 469 parameters, final R_1 = 0.0596, wR_2 = 0.1216, *S* = 1.057 [$I > 2\sigma(I)$]. CCDC 2020083

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms except for the carborane were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The hydrogen atoms of the carborane were found by the Fourier map and refined isotropically.

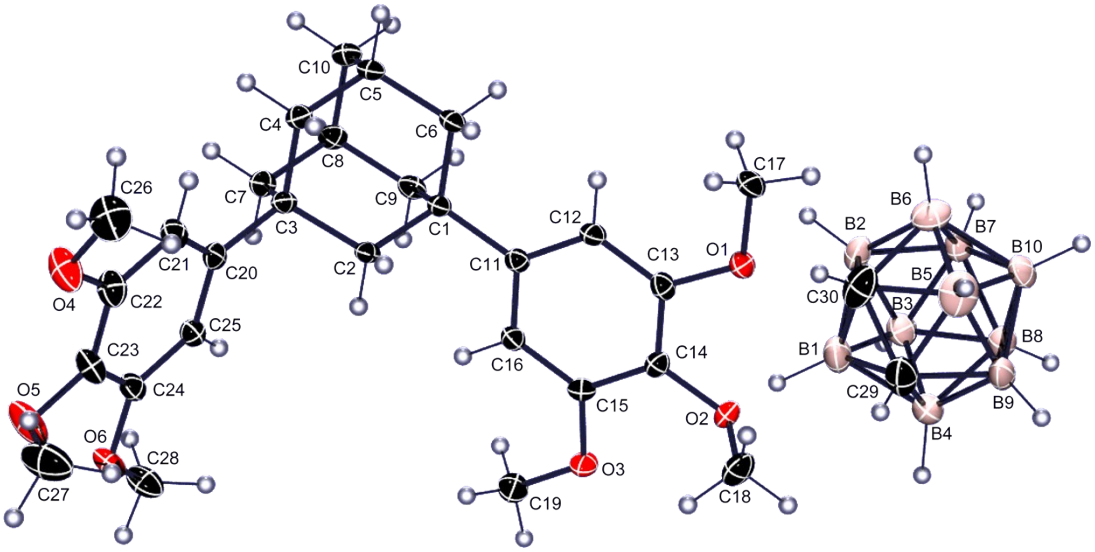


Fig. S1 Ortep drawing of crystal **1a** (50% probability).

Single crystal X-ray diffraction experiment for 1b

The low diffracting reddish prismatic crystal (0.100 × 0.100 × 0.020 mm^3), which was obtained from acetone, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2018/3[3].

$C_{40}H_{36}F_8O_{10}$, *M*r = 828.69; monoclinic, space group $P2_1/n$, $Z = 4$, $D_{calc} = 1.525$ g·cm^{-3}, $a = 12.1831(7)$, $b = 19.5278(11)$, $c = 15.2066(9)$ Å, $\beta = 93.949(3)°$ $V = 3609.2(4)$ $Å^3$, 42756 observed and 5308 independent [$I > 2\sigma(I)$] reflections, 638 parameters, 36 restraints, final $R_1 = 0.0657$, $wR_2 = 0.1309$, $S = 1.160$ [$I > 2\sigma(I)$]. CCDC 2020084

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

Two tetrafluoro-1,4-benzoquinone molecules found were refined as follows. C=O bonds and C–F bonds were discriminated from their initial bond distances of corresponding Q peaks and refined without any restraints related to the bond length. The overlapped and disordered tetrafluoro-1,4-benzoquinone molecules (C35-C40, O9-O10 and F5-F8, and C41-C46, O11-O12 and F9-F12) were refined with PART n, and the occupancy ratio was 0.6 : 0.4. RIGU was applied to C41-C46.

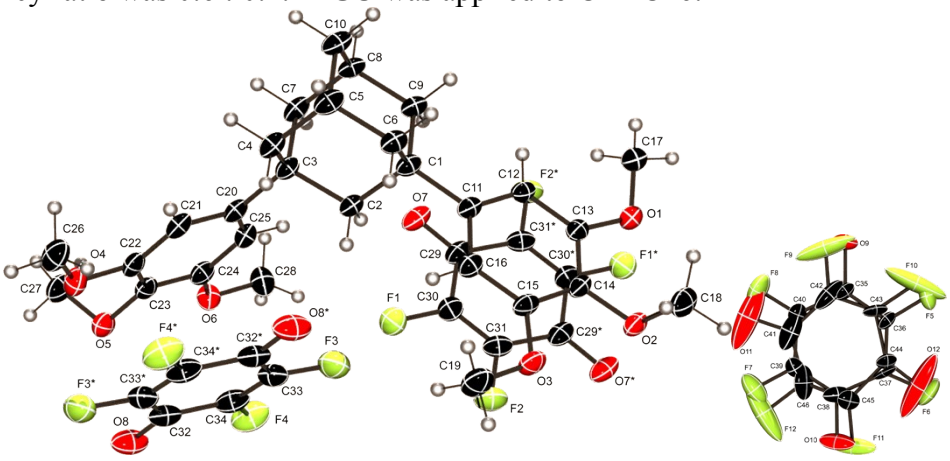


Fig. S2 Ortep drawing of crystal **1b** (50% probability).

Single crystal X-ray diffraction experiment for 2

The low diffracting colourless plate crystal (0.100 × 0.100 × 0.050 mm^3), which was obtained from hexane/dichloromethane, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2018/3[3].

$C_{34}H_{48}O_6$, *M*r = 552.72; monoclinic, space group *C*2/*c*, *Z* = 8, D_{calc} = 1.198 g·cm^{-3}, *a* = 35.013(5), *b* = 6.8212(9), *c* = 25.942(4) Å, *β* = 98.573(9)° *V* = 6126.5(15) $Å^3$, 37477 observed and 3495 independent [$I > 2\sigma(I)$] reflections, 443 parameters, 12 restraints, final R_1 = 0.0907, wR_2 = 0.2018, *S* = 1.175 [$I > 2\sigma(I)$]. CCDC 2020085

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

A couple of disordered moieties (C11-C20, O1, O2, and C11B-C20B, O1B, O2B) refined with PART n were partly applied to SAME and EADP, and occupancy ratio was 62/38.

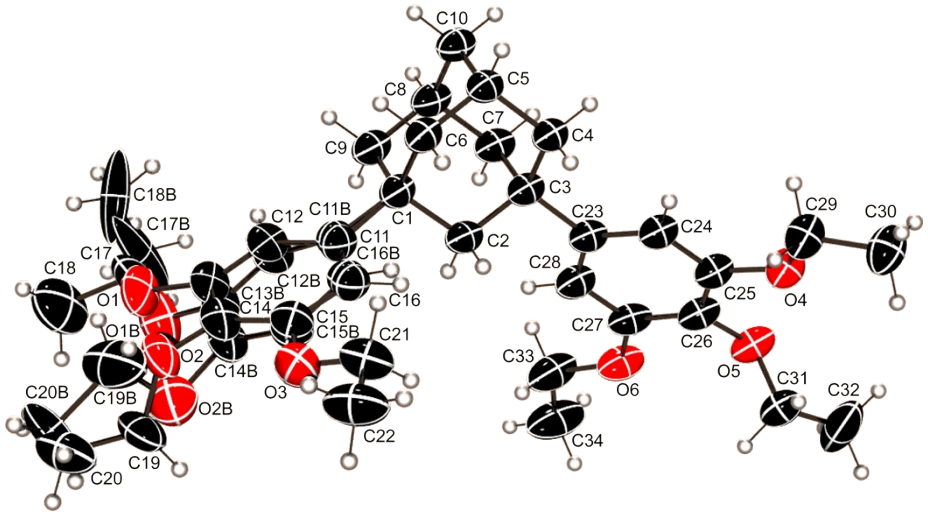


Fig. S3 Ortep drawing of crystal **2** (50% probability).

Single crystal X-ray diffraction experiment for 2b

The low diffracting reddish prismatic crystal (0.100 × 0.080 × 0.080 mm^3), which was obtained from acetone, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2018/3[3].

$C_{40}H_{48}F_4O_8$, *M*r = 732.78; triclinic, space group *P*-1, *Z* = 2, D_{calc} = 1.317 g·cm^{-3}, *a* = 11.4725(5), *b* = 13.0256(5), *c* = 14.4011(6) Å, *α* = 70.066(2), *β* = 78.992(2), *γ* = 66.264(2)° *V* = 1848.36(14) $Å^3$, 25254 observed and 5457 independent [$I > 2\sigma(I)$] reflections, 524 parameters, final R_1 = 0.0510, wR_2 = 0.1204, *S* = 1.014 [$I > 2\sigma(I)$]. CCDC 2020086

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The disordered ethoxy moieties were refined with PART n. Occupancy ratio was 0.66 : 0.34 (C19, C20 / C19B, C20B), and 0.51 : 0.49 (C31, C32, O5 / C31B, C32B, O5B).

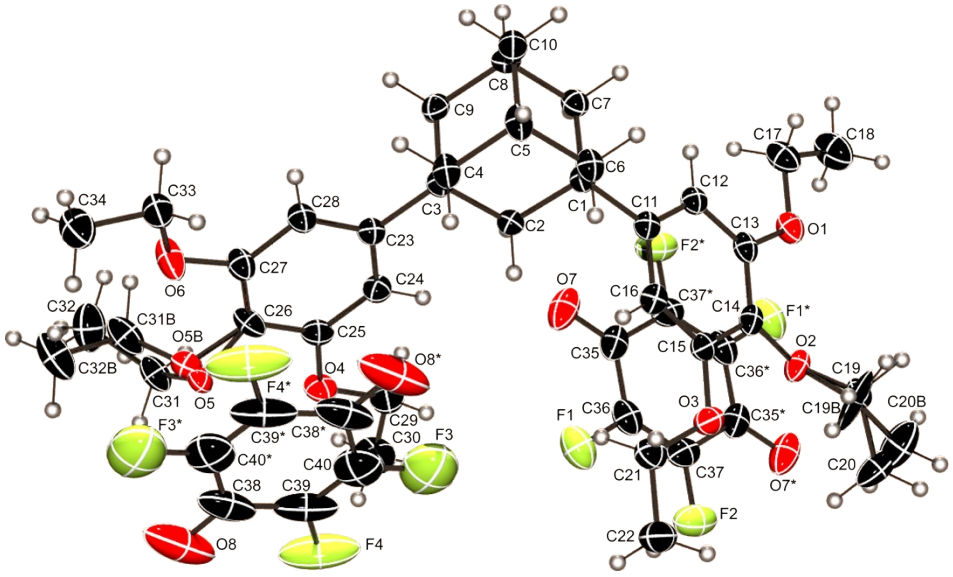


Fig. S4 Ortep drawing of crystal **2b** (50% probability).

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.