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Investigation of deuterated FOX-7 –

changes in structural behavior and energetic characteristics after deuteration under ambient conditions

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1 Experimental information

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^1H, ^2D, ^{13}C and ^{14}N NMR spectra were recorded at ambient temperature using a Bruker TR 400 instrument. The chemical shifts quoted in ppm in the text refer to tetramethylsilane, D_2O or nitromethane. Dehydration, melting and decomposition temperatures of the described compounds were measured through differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument. The samples were measured in a range of 25–400°C at a heating rate of 5 °C min^{-1}. The activation energies of the compounds were determines by thermal gravimetric analysis (TGA) with a PerkinElmer TGA4000 and usage of the NETZSCH Kinetics Neo software (version 2.5.0.1)[S1]. Infrared spectra were measured with pure samples on a Perkin-Elmer BXII FT-IR system with a Smith DuraSampler IR II diamond ATR.

FOX-7-D_4

For the preparation of NaOD, elemental sodium (1.84 g, 0.08 mol) was carefully dissolved in D_2O (75 mL) under ice cooling. FOX-7 (6.00 g, 0.04 mol) was then added to this solution and stirred for 1 h at room temperature. The mixture was acidified with conc. D_2SO_4 (5 mL) until a pH of about 3 was reached. The precipitate which formed was filtered and washed with a small amount of D_2O and acetone-D_6. To achieve the highest possible isotopic content, these steps were iteratively repeated four times. FOX-7-D_4 (5.23 g, 85%) with a deuteration level of 95.7% was obtained as a light-yellow solid in good yield. Crystals of FOX-7-D_4 were obtained by slow crystallization of the D_2SO_4 solution.

^2D NMR (61 MHz, DMSO-H_6): δ (ppm) 8.62 (s, 4D, ND2); ^{13}C NMR (101 MHz, DMSO-D_6): δ (ppm) 128.4 (C2, C(NO2)2), 158.0 (C1, C(ND2)2); ^{14}N NMR (28.9 MHz, DMSO-D_6): δ (ppm) −25 (2N, C(NO2)2);; IR (ATR): ν = 2579 (s), 2564 (s), 2427 (s), 2405 (s), 1574 (s), 1487 (vs), 1463 (s), 1457 (s), 1406 (vs), 1345 (s), 1256 (vs), 1219 (vs), 1140 (vs), 1079 (vs), 954 (m), 905 (m), 850 (m), 817 (s), 769 (s), 747 (vs), 735 (vs), 692(s) cm^{-1}; DTA (5° min^{-1}) = T(endo): 114°C; T(exo): 255 °C.

2 IR spectroscopy

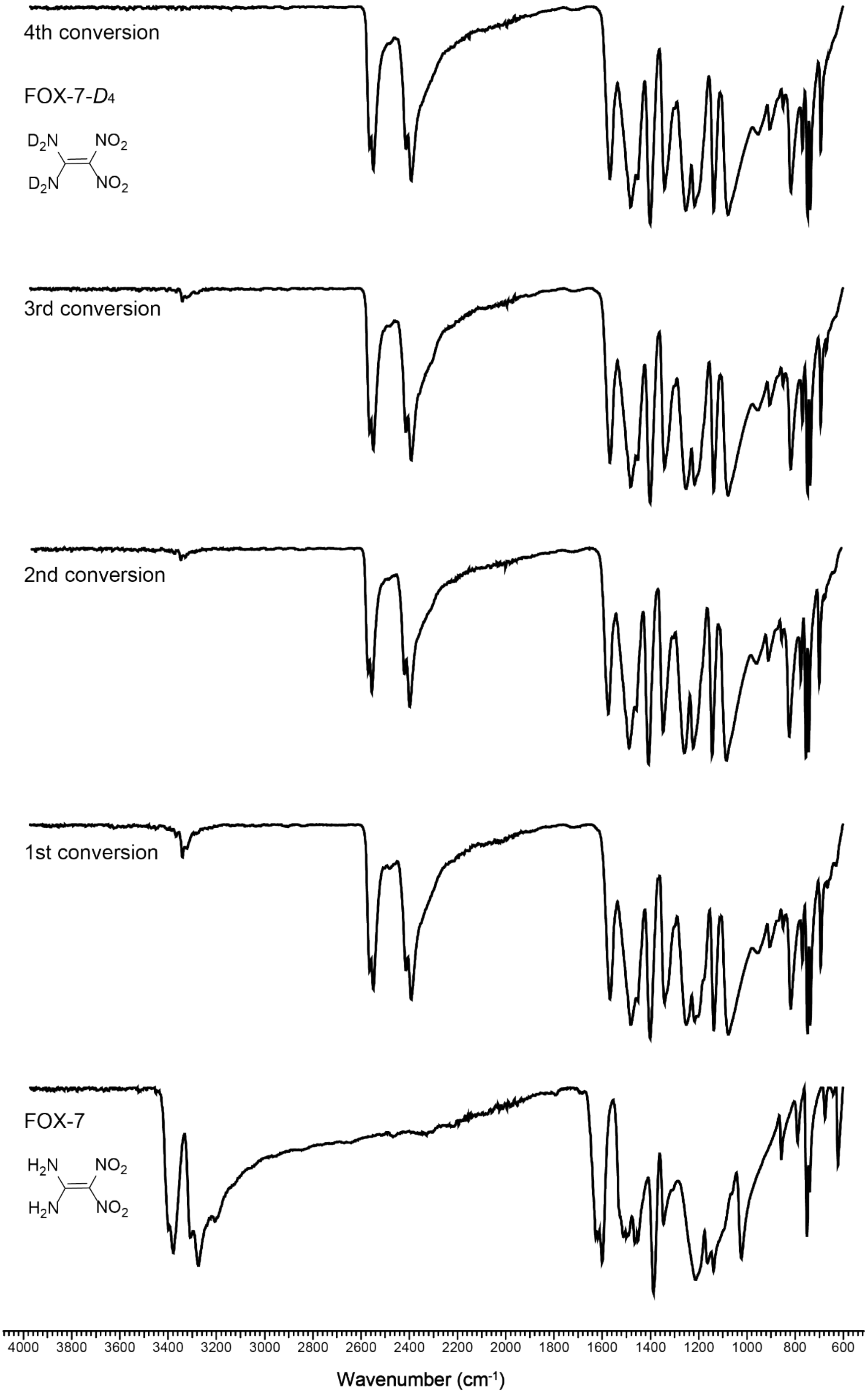

Figure S1. IR spectra of al conversion steps from FOX-7 to FOX-7-D_4.

3 ^{1}H q-NMR measurements

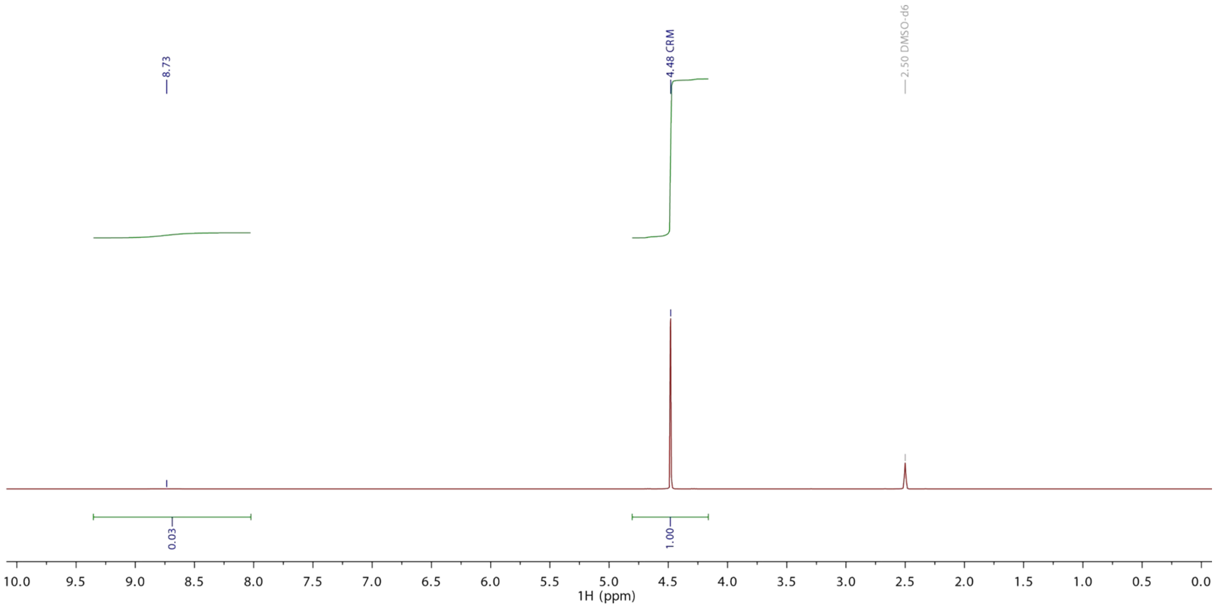

Figure S2. ^{1}H q-NMR of FOX-7-D_4.

Certified Reference Materials (CRM): Ethylene carbonate

$$P_{sample} = \frac{S_{sample}}{S_{standard}} \times \frac{N_{standard}}{N_{sample}} \times \frac{m_{standard}}{m_{sample}} \times \frac{M_{sample}}{M_{standard}} \times P_{standard}$$

$$= \frac{212896.86}{6744429.09} \times \frac{4}{4} \times \frac{10.412}{12.434} \times \frac{148.08}{88.06} \times 0.9992$$

$$= 0.043$$

S = integrated area of the peak

N = number of protons

m = prepared mass

M = molecular weight

P = purity

→ deuteration level: 95.7 %

4 TGA measurements

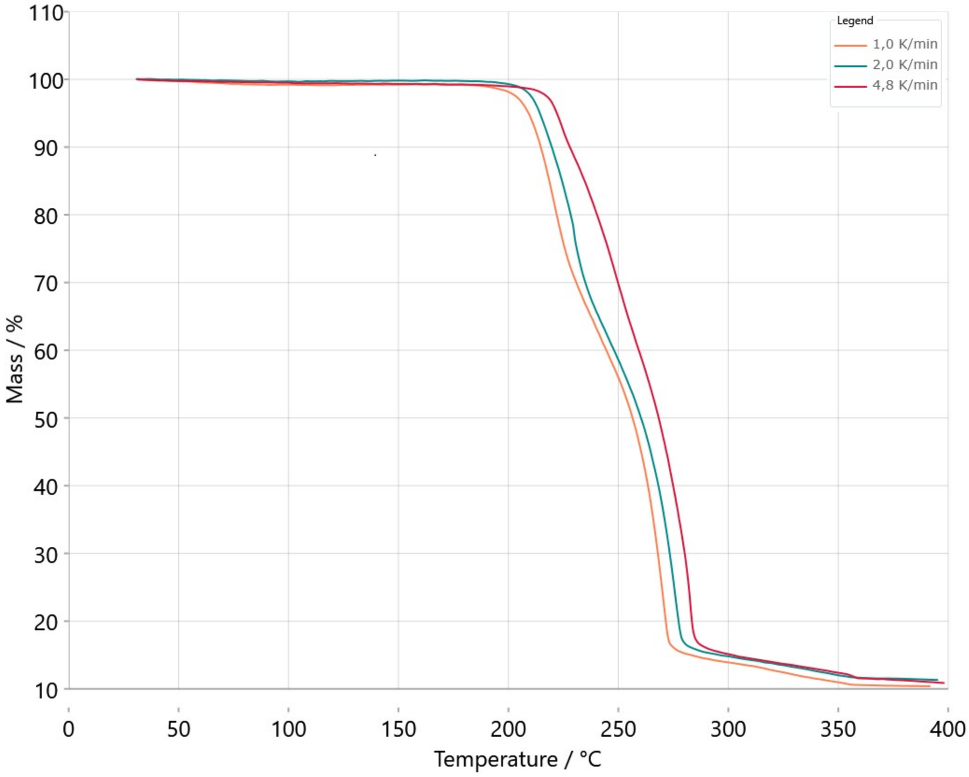

Figure S3. TGA measurement of FOX-7-D_4.

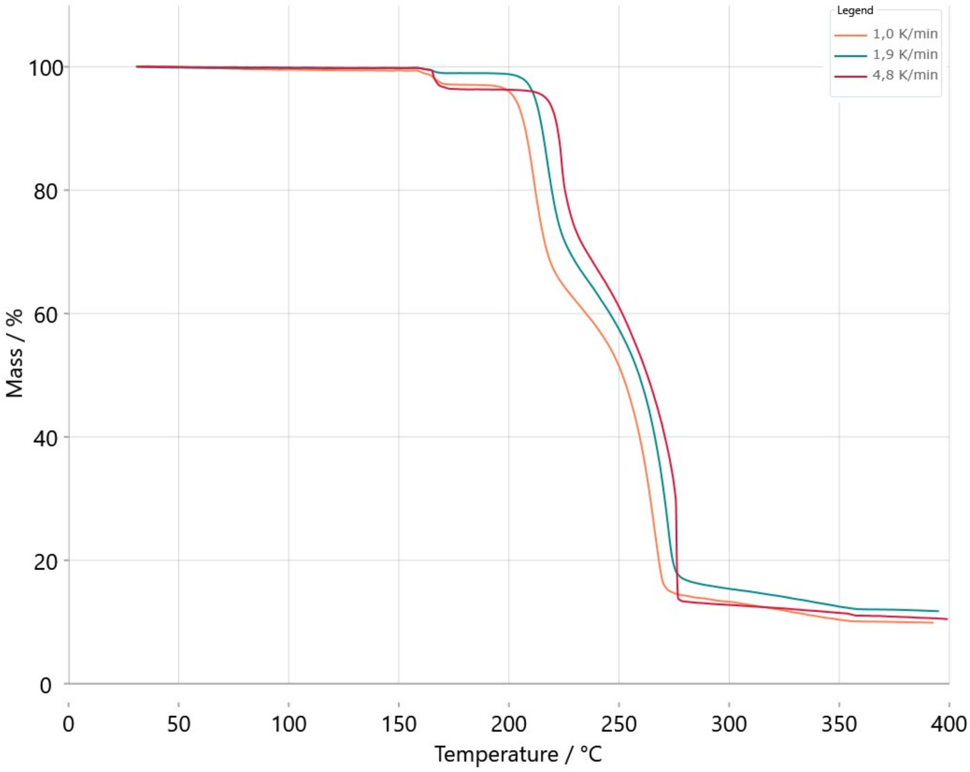

Figure S4. TGA measurement of FOX-7.

5 Activation energy

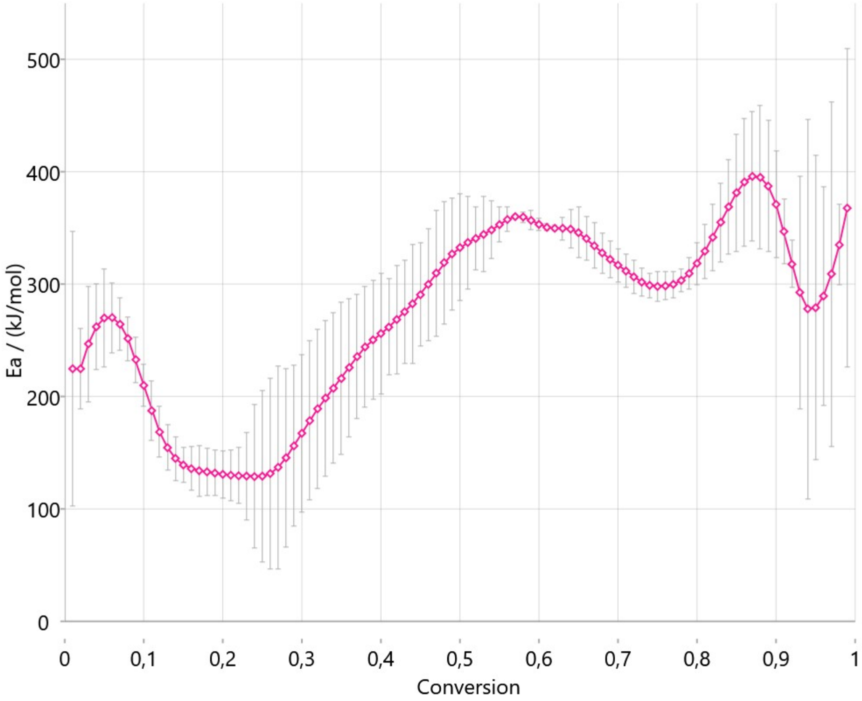

Figure S5. TGA measurement of FOX-7-D_4.

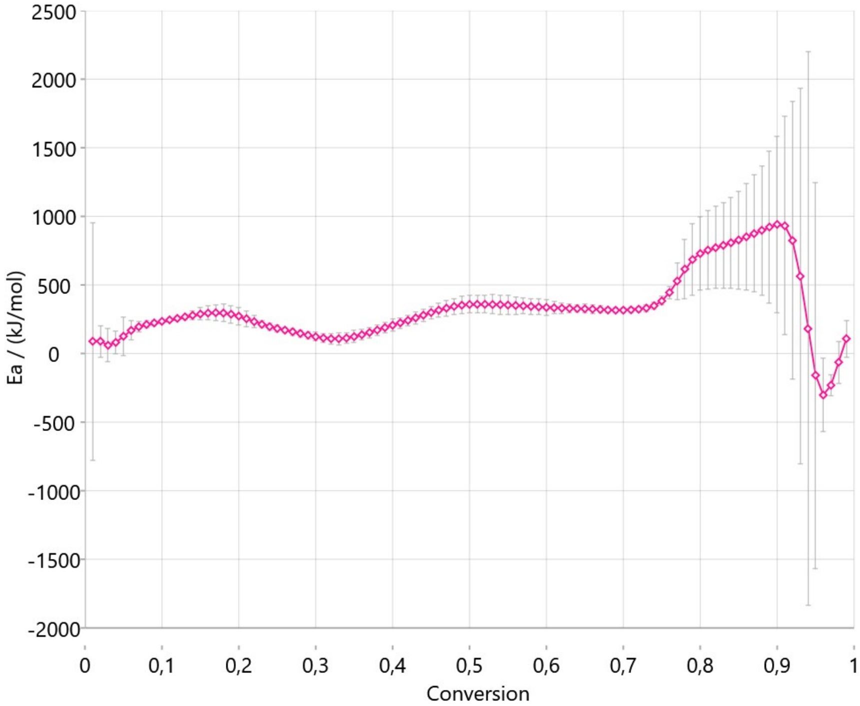

Figure S6. TGA measurement of FOX-7.

6 X-Ray diffraction

For the crystalline compound FOX-7-D_4, an Oxford Xcalibur3 diffractometer with a CCD area detector with a multilayer monochromator, a Photon 2 detector and a rotating-anode generator were employed for data collection using Mo-$K\alpha$ radiation (λ = 0.71073 Å). On the Oxford device, data collection and reduction were carried out using the CRYSALISPRO software.[S2]. The structures were solved by direct methods (SIR-92[S3], SIR-97[S4] or SHELXT[S5]) and refined by full-matrix least-squares on *F*2 (SHELXL[S5]) and finally checked using the PLATON software[S6] integrated in the WinGX[S7] software suite. The absorptions were corrected by a SCALE3 ABSPACK or SADABS Bruker APEX3 multiscan method.[S8,9] All DIAMOND2 plots are shown with thermal ellipsoids at the 50 % probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

Table S1. Crystallographic data and structure refinement details of FOX-7-*D*$_4$.

	FOX-7-*D*$_4$
Formula	$C_2D_4N_4O_4$
FW [g mol^{-1}]	152.12
Crystal system	orthorhombic
Space group	$Pna2_1$
Color / Habit	pale yellow block
Size [mm]	0.05 x 0.25 x 0.50
a [Å]	6.5238(13)
b [Å]	6.9618(8)
c [Å]	11.3592(9)
α [°]	90
β [°]	90
γ [°]	90
***V* [Å^3]**	515.91(13)
Z	4
$\rho_{calc.}$ [g cm^{-3}]	1.958
μ [mm^{-1}]	0.181
F(000)	304
$\lambda_{MoK\alpha}$ [Å]	0.71073
T [K]	101
θ Min-Max [°]	3.4, 28.3
Dataset	-8: 8 ; -9: 9 ; -15: 15
Reflections collected	8171
Independent refl.	1279
R_{int}	0.063
Observed reflections	1090
Parameters	107
R_1 (obs)[a]	0.0442
wR_2 (all data)[b]	0.0937
S [c]	1.07
Resd. dens [e Å^{-3}]	-0.22, 0.27
Device type	Xcalibur, Sapphire3
Solution	SIR-92
Refinement	SHELXL-2018/3
Absorption correction	multi-scan
CCDC	2150220

[a]R1 = Σ||F0|−|Fc||/Σ|F0|; [b]wR2 = [Σ[w(F02−Fc2)2]/Σ[w(F0)2]]1/2; w = [σc2(F02)+(xP)2+yP]−1 and P=(F02+2Fc2)/3; [c]S = {Σ[w(Fo2−Fc2)2]/(n−p)}1/2 (n = number of reflections; p = total number of parameters).

7 Heat of formation calculations

All quantum chemical calculations were carried out using the Gaussian G09 program.[S10] The enthalpies (H) and zero-point energies (ZPE) were calculated using the complete basis set (CBS) method and the W1 method of *Petersson et al*.[S11] assuming a C_2 symmetry.

Heats of formation (HOF) were calculated using the atomization method (Equation S1) using room temperature enthalpies.[S12]

$$\Delta_f H°_{(g,\,M,\,298)} = H_{(\text{Molecule},\,298)} - \sum H°_{(\text{Atoms},\,298)} + \sum \Delta_f H°_{(\text{Atoms},\,298)} \quad \text{(S1)}$$

Table S2. Enthalpies for atoms C, H, N, O and D and their literature values for atomic $\Delta_f H°^{298}$.[S12]

	H^{298K} CBS-4M [a.u.]	H^{298K} CBS-QB3 [a.u.]	H^{298K} W1BD [a.u.]	$\Delta_f H°$(atoms) [kJ mol^{-1}]
C	-37.786153	-37.783015	-37.850513	218.0
H	-0.500991	-0.497457	-0.497634	716.7
N	-54.522456	-54.518173	-54.608828	472.7
O	-74.991184	-74.985259	-75.108878	249.2
D	-0.500991	-0.497457	-0.497634	221.7

The standard molar enthalpy of formation of the FOX-7 derivatives were calculated using $\Delta_f H(g)$ subtracting the enthalpy of sublimation estimated by applying Trouton´s rule.[S13]

8 Calculation of density at 298 K

The room temperature density was recalculated from the corresponding crystal densities by Equation S2 (a_v = 1.5x10^{-4} K).

$$d_{298K} = \frac{d_T}{1 + \alpha_v(298 - T_0)} \quad \text{(S2)}$$

d_T = insert X-ray density in g cm^{-3}

T_0 = insert X-Ray temperatur in K

α_v = correction factor

Table S3. X-Ray and recalculated densities of FOX-7 and FOX-7-*D*$_4$.

	X-Ray density [g cm-3]	Density recalculated to 298K [g cm^{-3}]
FOX-7-*D*$_4$	(@ 101K) 1.958	1.902
FOX-7[S14]	(@ 173K) 1.907	1.872

9 References

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[S2] CrysAlisPro, Oxford Diffraction Ltd., version 171.33.41, **2009**.

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[S8] Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (CrysAlisPro Oxford Diffraction Ltd., Version 171.33.41, 2009).

[S9] APEX3. Bruker AXS Inc., Madison, Wisconsin, USA.

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