New:

Single crystals were picked at room temperature. The data for x y z were collected from shock-cooled crystals at 100 K mounted onto 0.1 mm CryoLoops in perfluoroalkyl ether oil. The data were collected on a Bruker APEXII QUAZAR with an Incoatec microfocus source with mirror optics as monochromator. The diffractometer was equipped with an Oxford Cryosystems 800 low temperature device and used MoKα radiation, = 0.71073 Å. All data were integrated with SAINT,[3] and an empirical absorption correction (SADABS/TWINABS) was applied.[4][5] All structures were solved by intrinsic phasing using SHELXT[lit] and refined by full-matrix least-squares methods against *F*2 with SHELXL.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. The graphical representations were prepared with the Diamond 3.2k3 software.[6]

Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC xyzxyz (XY) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/.

For the X-ray crystal structureof **7d** a single crystal was mounted with inert oil on a glass fiber.17a The data was collected at 100 K on a Bruker Apex II Ultra with mirror optics. Data reduction was done with SAINT,17b and an empirical absorption correction with SADABS17c was applied. The structure was solved by direct methods (SHELXS-97)17d and refined by full-matrix least-squares methods against *F*2 (SHELXL-97).17d The absolute structures was successfully determined by the Flack x parameter (zero within 3 esd's) during the refinement.17e All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*iso values constrained to 1.5 times the *U*eq of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in the supporting information. CCDC 759503 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

The data for **1,3** and **4** were collected from shock-cooled crystals at 100 K.The data for **1** were collected on a Bruker TXS-Mo rotating anode. For the data collections of **3** and **4** a Incoatec microfocus source was used. Both diffrac­tometers were equipped with a low‑temperature device1 and used monochromated MoKα radiation, λ = 0.71073 Å. Both machines used mirror optics as radiation monochromator. The data of **1-3** were integrated with SAINT,2 and an empirical absorption correction (SADABS) was applied.3 All structures were solved by direct methods (SHELXS-97)4 and refined by full-matrix least-squares methods against *F*2 (SHELXL-97).5 All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*iso values constrained to 1.5 times the *U*eq of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and isotropic displacement parameter restraints.6 Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in ??. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

Anderer text:

The data for **2** was collected from shock-cooled crystals at 100 K on a Bruker TXS-Mo rotating anode with INCOATEC Helios mirror optics as radiation monochromator. The diffrac­tometer was equipped with a low‑temperature device1 and used MoKα radiation, λ = 0.71073 Å. The data of **2** was integrated with SAINT,2 and an empirical absorption correction (SADABS) was applied.3 The structure was solved by direct methods (SHELXS-97)4 and refined by full-matrix least-squares methods against *F*2 (SHELXL-97).5 All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*iso values constrained to 1.5 times the *U*eq of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and isotropic displacement parameter restraints.6 Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in ??. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

The data for x y z were collected from shock-cooled crystals at 100 K (except 4). The data were collected on a Bruker APEXII QUAZAR with an Incoatec microfocus source with mirror optics as monochromator. The diffrac¬tometer were equipped with an Oxford Cryosystems 800 low temperature device1 and used MoK radiation, = 0.71073 Å. All data were integrated with SAINT,2 and an empirical absorption correction (SADABS) was applied.3 All structures were solved by intrinsic phasing using SHELXT[lit] and refined by full-matrix least-squares methods against F2 (SHELXL-2016/6).5 All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints.6 Especially the C-F, C-C and C-O distances of the ORF-Anion were restrained to be of equal length each. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1410017 (2), 1547651 (3), 1547664 (4, 153 K), 1547730 (4, 100 K), 1547666 (5), 1547677 (6), xx (7), 1547679 (3a), 1547680 (4a) 1547692 (4b), 1547700 (4c) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: ++44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for DK\_NTD51a.

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| --- | --- |
| CCDC number | p21c |
| Empirical formula | C26H33NO3Si |
| Formula weight | 435.62 |
| T [K] | 100(2) K |
| Wavelength [pm] | 71.073 |
| Crystal system | Monoclinic |
| Space group | P21/c |
| a [pm] | 1064.56(9) |
| b [pm] | 1103.30(9) |
| c [pm] | 1992.14(16) |
|  | 90° |
|  | 98.9380(10)° |
|  | 90° |
| Volume [nm3] | 2.3114(3) nm3 |
| Z | 4 |
| calcd [Mg/m3] | 1.252 |
|  [mm-1] | 0.129 |
| F(000) | 936 |
| Crystal size | 0.25 x 0.2 x 0.1 mm3 |
| θmin,max [°] | 1.94 to 25.35°. |
| Index ranges | -12<=h<=12, 0<=k<=13, 0<=l<=24 |
| Reflections collected | 76055 |
| Independent reflections | 4228 |
| Rint | 0.0384 |
| Data / restraints / parameters | 4228 / 0 / 284 |
| Goodness-of-fit on F2 | 1.055 |
| R1 [I>2(I)] | 0.0326 |
| *w*R2 [I>2(I)] | 0.0850 |
| R1 (all data) | 0.0362 |
| *w*R2 (all data) | 0.0876 |
| Largest diff. peak and hole e[Å-3] | 0.360 and -0.270 |
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