

## Supplementary information

The table below reports the crystallographic data of the structure of NaO<sup>t</sup>Bu, as reported to CCDC with #1017545.

Chemical formula	[C <sub>4</sub> H <sub>9</sub> NaO] <sub>6</sub>	
Formula weight	576.61	
Temperature	100(2) K	
Range for data collection	2.2 to 20.8° 2 $\theta$	
Wavelength	0.71073 Å (Mo K $\alpha$ )	
Crystal system	orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 18.1583(16) Å b = 19.2347(17) Å c = 51.548(4) Å	$\alpha$ = 90° $\beta$ = 90° $\gamma$ = 90°
Volume	18004(3) Å <sup>3</sup>	
F(000)		6240.00
Reflections collected		90802
Independent reflections		18808 [R(int) = 0.069]
Goodness-of-fit on F <sup>2</sup>		1.06
$\Delta/\sigma_{\max}$		< 0.001
Final R indices	14462 data; I>2 $\sigma$ (I) all data	R1 = 0.0580, wR2 = 0.1414 R1 = 0.0846, wR2 = 0.1565
Reflections/parameters/restraints		18080/1711/36