Supporting Information

For

Bismuth Allyloxides

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Experimental Details for the Syntheses of the Used Sodium Salts

All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of dry and oxygen-free argon atmosphere.

[Na(OCH(CH$_3$)CH=CH$_2$]. At 0 °C 4.5 mL 3-butene-2-ol (3.74 g, 52 mmol) were added to a stirred suspension of NaH (1.51 g, 63 mmol) in 50 mL thf. After addition of the first drop a heavy gas evolution could be observed. After 10 minutes the ice-bath was removed and the reaction mixture was allowed to warm up to ambient temperature. After stirring the suspension for 3 h at ambient temperature, the colorless solution was filtered off of unconverted NaH. Removal of all volatile components and drying in vacuum yielded [Na(OCH(CH$_3$)CH=CH$_2$] (4.11 g, 44 mmol, 84 %) in form of a white microcrystalline solid. ^{1}H NMR (C$_6$D$_6$): δ = 6.06 (m, 1H, CH=CH$_2$), 5.19 (dd, 1H, CH$_2$), 4.95 (dd, 1H, CH$_2$), 4.45 (m, 1H, C<u>H</u>(CH$_3$)), 1.32 (d, 3H, CH$_3$); ^{1}H NMR (CD$_3$CN): δ = 5.92 (m, 1H, CH=CH$_2$), 4.96 (dd, 1H, CH$_2$), 4.67 (dd, 1H, CH$_2$), 4.23 (m, 1H, C<u>H</u>(CH$_3$)), 1.00 (d, 3H, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 150.6 (<u>C</u>H=CH$_2$), 110.6 (CH$_2$), 70.6 (<u>C</u>H(CH$_3$)), 28.5 (CH$_3$); ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 153.9 (<u>C</u>H=CH$_2$), 107.8 (CH$_2$), 71.7 (<u>C</u>H(CH$_3$)), 29.5 (CH$_3$).

[Na(OC(CH$_3$)$_2$CH=CH$_2$]. At 0 °C 4.2 mL 2-methyl-3-butene-2-ol (3.4 g, 40 mmol) were added to a stirred suspension of NaH (1.0 g, 42 mmol) in 80 mL thf. After addition of the first drop a heavy gas evolution could be observed. After 10 minutes the ice-bath was removed and the reaction mixture was allowed to warm up to ambient temperature. After stirring the suspension for 3 h at ambient temperature, the colorless solution was filtered off of excess NaH. Removal of all volatile components and drying in vacuum yielded [Na(OC(CH$_3$)$_2$CH=CH$_2$] (3.66 g, 34 mmol, 85 %) in form of a white beige microcrystalline solid. ^{1}H NMR (C$_6$D$_6$): δ = 6.22 (q, 1H, CH), 5.14 (dd, 1H, CH$_2$), 4.82 (dd, 1H, CH$_2$), 1.24 (d, 6H, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 155.7 (CH), 106.5 (CH$_2$), 68.7 (C), 34.5 (CH$_3$). IR (KBr): ν [cm^{-1}] = 3077, 2959, 2919, 2853, 1636, 1465, 1411, 1366, 1351, 1238, 1171, 1158, 1039, 1007, 978, 962, 915, 888, 694, 541, 506, 469, 430. Anal. Calcd for C$_5$H$_9$ONa (M = 108.11 gmol^{-1}): C 55.55, H 8.39 %. Found: C 55.18, H 8.39.

Results of the Structure Refinement of 2

Evaporation of the solvent from a saturated solution of [Bi(OCH(CH$_3$)CH=CH$_2$)$_3$], **2** in toluene led to colorless crystals that were suitable for an X-ray diffraction analyses. The crystal data were collected on a Stoe IPDS 2T diffractometer using Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. Relevant crystallographic data are collected in the Table S1.

Table S1. Crystal data and experimental parameters for the crystal structure analyses of **2**.

	2
Formula	$C_3Bi_2O_5$
temp, K	100(2)
crystal system	monoclinic
space group	P 1 1 2_1/a
a, Å	21.122(3)
b, Å	21.122(3)
c, Å	7.3630(10)
α, deg	90
β, deg	90
γ, deg	120
V, Å^3	2844.3(7)
density, g cm^{-3}	1.972
μ(Mo$_{K\alpha}$), mm^{-1}	12.390
F(000)	1600
GoF	1.034
R_1 [I>2σ(I)]	0.0791
wR_2 [all data]	0.2200
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	4.449/ -1.778

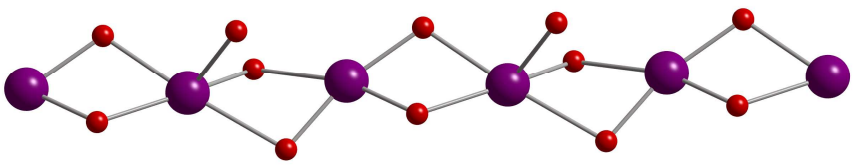

Figure S1. Incomplete molecular structure of **2** showing the identified bismuth and oxygen atom

positions. (Determined carbon atoms of the allyloxide residues were omitted.)

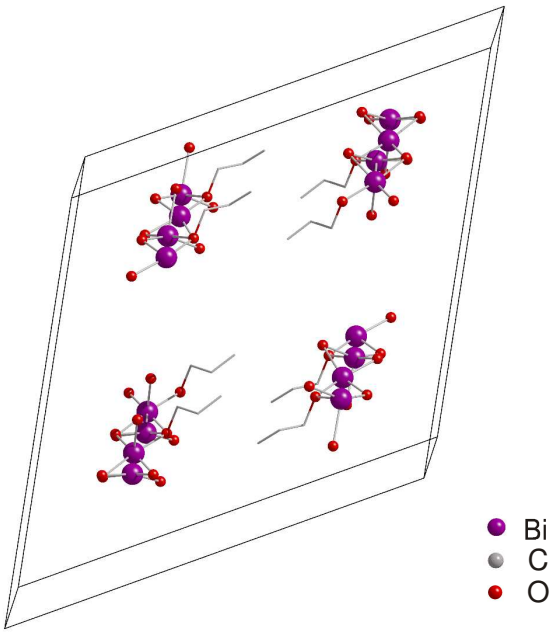

Figure S2. View showing the isolated chains of **2** along the c axes.

Variable Temperature NMR Spectra Recorded in Toluene-d_8

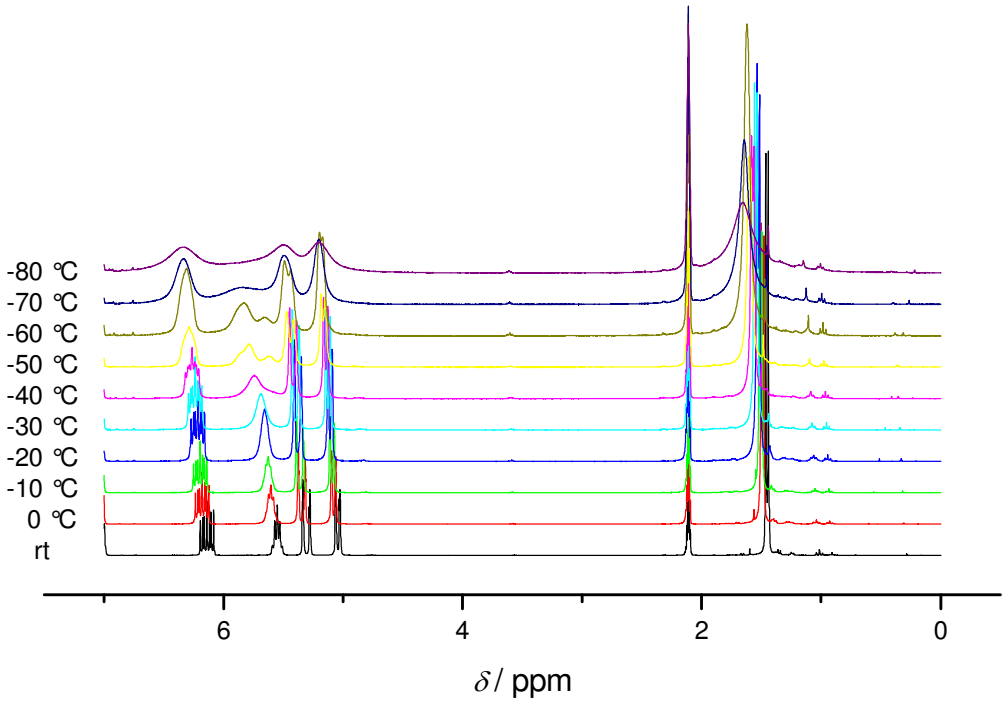

Figure S3. Variable temperature NMR spectra of [Bi(OCH(CH_3)CH=CH_2)$_3$], **2**, in toluene-d_8.

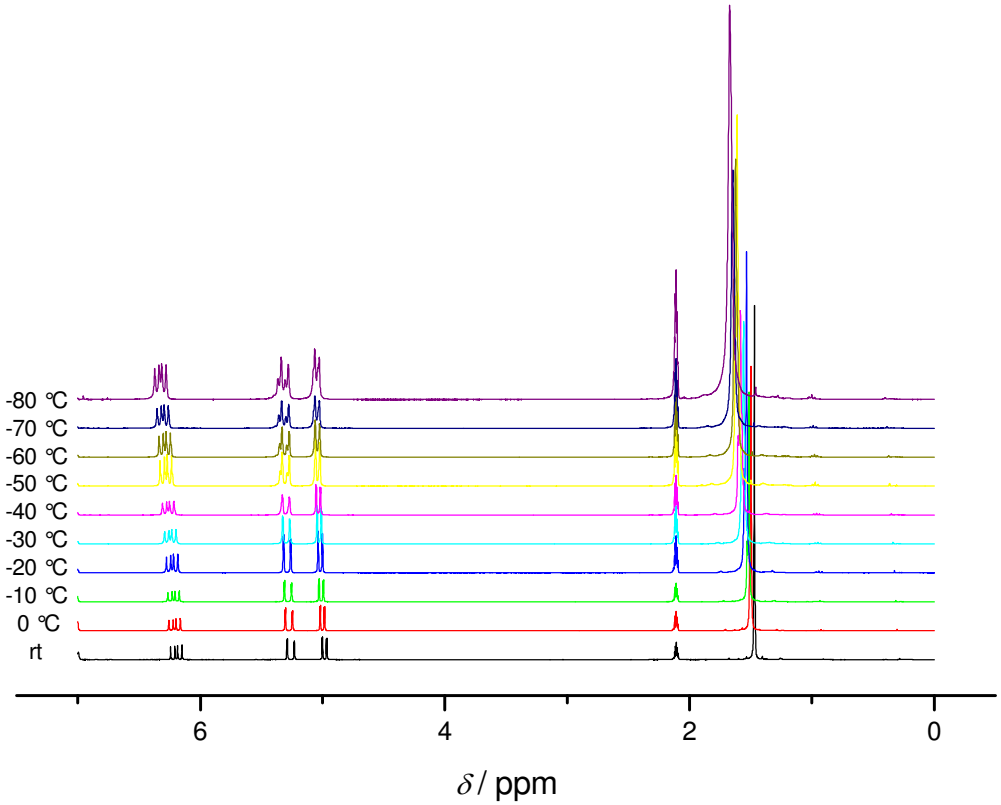

Figure S4. Variable temperature NMR spectra of [Bi(OC(CH$_3$)$_2$CH=CH$_2$)$_3$], **3**, in toluene-d_8.