Electronic Supplemantary Information

Synthesis and Coordination Behaviour of Thioether functionalised Gallium and Indium Alkoxides

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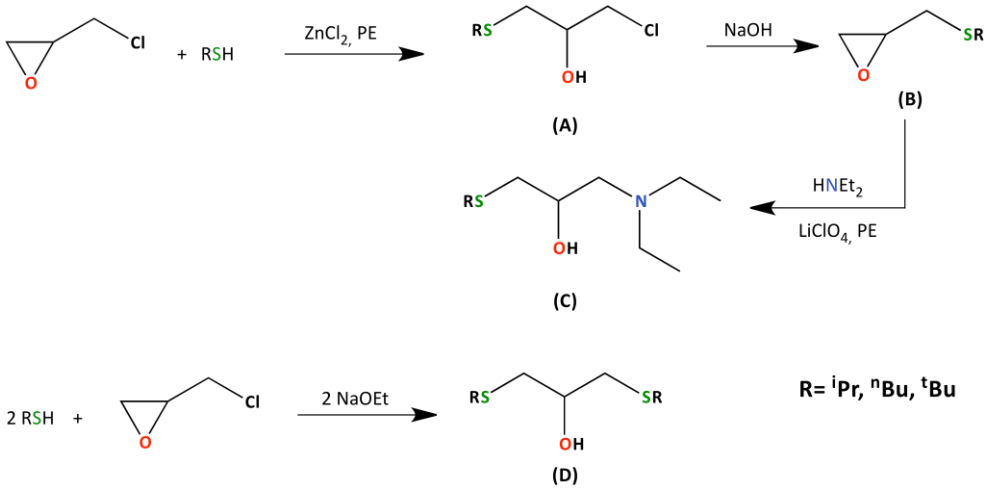
Synthesis of alkanols

Secondary alkanols:



Scheme. S1: Flow chart showing the synthesis procedures for symmetrical and asymmetrical secondary alcohol species.

1st step: 1-Chloro-3-alkylthiopropan-2ol

The reaction was carried out similar to a known procedure reported by Todsen *et al.*.[1] Epichlorhydrin, the respective thiol species and $ZnCl_2$ were mixed and refluxed for 3h. The liquid product was purified by distillation to obtain **A**.

2nd step: Ring closure and oxiran formation to 2-((alkylthio)methyl)oxirane:

Finely ground NaOH was added to the 1-chloro-3-alkylthiopropan-2-ol in 50 ml ether and further refluxed for 2 h. After cooling, saturated brine was added, phases separated and the water phase extracted four times with 50 ml diethyl ether each. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed. Distillation of the crude product yielded the desired oxiranes **B**.

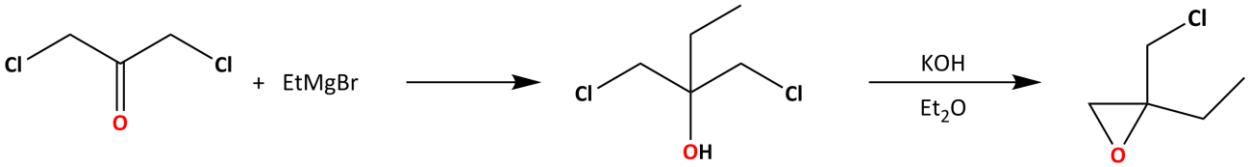
3rd step: Ring opening to gain the desired alcohols.

Asymmetric alkanols: An excess of diethylamine, the respective 2-((alkylthio)methyl)oxirane and 0.25 ml 5 M $LiClO_4$ solution in 20 ml petrol ether were refluxed for 12 h. After cooling, approx. 30 ml saturated brine were added, the phases separated and the water phase extracted 4 times with 50 ml petrol ether. The organic phases were dried over Na_2SO_4 and the solvent was removed. The crude product was purified via distillation to obtain the asymmetrical alcohol **C**.

Symmetric alkanols

a) Similar to the 1st step, the thiol, $ZnCl_2$ and the 2-((alkylthio)methyl)oxirane were mixed and refluxed for 3h. The product was purified by distillation to obtain **D**.
b) 2 equiv. Na were dissolved in absolute ethanol and 2 equiv. of the thiol were added. Subsequently, 1 equiv. epichlorohydrin was added and the mixture was refluxed for 6 h. After cooling to r.t., the mixture was diluted with 50 ml of water and the EtOH removed under reduced pressure. The water phase was then extracted five times with 50 ml petrol ether each. The collected organic phases dried over Na_2SO_4, filtered and the solvent was removed. The crude product was distilled to obtain the respective alcohol **D**.

Tertiary alkanols:



Scheme. S2: Flow chart showing the synthesis of the starting compound before the synthetic steps described below are performed.

1st step: 1-Chloro-3-alkylthiopropan-2-ol

The synthesis was carried out following procedures described by Tanyeli *et al.*.[2]

1 equiv. Mg turnings were covered with dry ether and 1 equiv. ethylbromide was added drop wise until the reaction started. The remaining ethylbromide was diluted with dry ether and added drop wise. After the addition of the ethylbromide, the reaction mixture was refluxed for 3 h until all the Mg was dissolved. 1 equiv. 1,3-dichloroacetone dry ether was slowly added at 0 °C yielding a heterogenic brownish reaction mixture. After adding the ketone, the mixture was further refluxed for 2.5 h and subsequently hydrolysed with saturated NH_4Cl solution and 1 N hydrochloric acid. Phases were separated and the water phase extracted twice with 75 ml ether. The collected organic phases were washed with saturated brine, dried over Na_2SO_4, filtered and the solvent removed to yield a red-brown clear liquid. Fractionated distillation at 74 °C (20 mbar) yielded 1-Chloro-3-alkylthiopropan-2-ol as colourless liquid.

2nd step: 2-Chloromethyl-2-ethyloxirane

The ring closing was based on a well-established procedure. This step is similar to the ring closing for secondary alcohols described above in step 2. The 1-Chloro-2-(chloromethyl)butan-2-ol is mixed with potassium hydroxide and 50 ml ether. The further processing is equivalent to procedure S1 (2nd step).

The further steps are identical with the synthesis of secondary alcohols as described above.

Table S1: Overview of synthesized donor functionalised alcohols and intermediates.

Compound	Abbreviation	Boiling point	Yield
1-^{n}Butylthio-3-chloropropan-2-ol	**(1-1)**	65 °C / 0.1 mbar	44 %
2-((^{n}Butylthio)methyl)oxirane	**(1-2)**	70 °C / 6 mbar	75 %
1,3-Bis(^{n}butylthio)propan-2-ol	**(1)**	144 °C / 4 mbar	93 %
1-^{t}Butylthio-3-chloropropan-2-ol	**(2-1)**	90 °C / 5 mbar	56 %
2-((^{t}Butylthio)methyl)oxirane	**(2-2)**	50 °C / 7 mbar	36 %
1,3-Bis(^{t}butylthio)propan-2-ol	**(2)**	82 °C / 0.3 mbar	80 %
2-((Isopropylthio)methyl)oxirane	**(3-1)**	54 °C / 7 mbar	58 %
1,3-Bis(isopropylthio)propan-2-ol	**(3)**	114 °C / 4 mbar	81 %
1-^{n}Butylthio-3-(diethylamino)propan-2-ol	**(4)**	113 °C / 5 mbar	93 %
1-^{t}Butylthio-3-(diethylamino)propan-2-ol	**(5)**	98 °C / 5 mbar	94 %
1-Diethylamino-3-(isopropylthio)propan-2-ol	**(6)**	62 °C / 0.3 mbar	87 %
1-Chloro-2-(chloromethyl)butan-2-ol	**(7-1)**	74 °C / 20 mbar	81 %
2-Chloromethyl-2-ethyloxirane	**(7-2)**	53 °C / 35 mbar	80 %
1-^{n}Butylthio-2-((^{n}butylthio)methyl)butan-2-ol	**(7)**	109 °C / 0.4 mbar	88 %
1-^{t}Butylthio-2-((^{t}butylthio)methyl)butan-2-ol	**(8)**	80 °C / 0.4 mbar	82 %
1-Isopropylthio-2((isoproyplthio)methyl)butan-2-ol	**(9)**	86 °C / 0.77 mbar	87 %
1-^{n}Butylthio-2-((diethylamino)methyl)butan-2-ol	**(10)**	108 °C / 1.2 mbar	91 %[1]
1-^{t}Butylthio-2-((diethylamino)methyl)butan-2-ol	**(11)**	69 °C / 0.2 mbar	86 %
1-Diethylamino-2((isopropylthio)methyl)butan-2-ol	**(12)**	75 °C / 0.79 mbar	69 %

Characterisation of alkanols and their intermediates

1-^{n}Butylthio-3-chloropropan-2-ol **(1-1)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.92 (t, J=7.28 Hz, 3H, CH_3), 1.41 (m, J=7.34 Hz, 2H,CH_3-CH_2), 1.58 (quint, J=7.28 Hz, 2H, CH_2-CH_2-CH_2), 2.56 (t, J=7.27 Hz, 2H, CH_2-CH_2-S), 2.60-2.85 (m, 3H, S-CH_2-CH, OH), 3.66 (d, J=4.62 Hz, 1H, CH_2-Cl), 3.92 (m, 1H, CH); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 13.4 (s, $CH_3CH_2CH_2$), 21.7 (s, $CH_3CH_2CH_2$), 31. 5 (s, CH_2CH_2-S), 32.1 (CH_2CH_2-S), 36.0 (s, S-CH_2-CH), 47.8 (s, CH_2-Cl), 69.8 (s, CH-OH); IR (ATR, cm^{-1}): v= 3414 (br, OH), 2957 (s, CH), 1041 (s, C-OH); GC-EIMS (m/z) found (calc.): 182.02 (182.05) $[M]^+$, 133.03 (133.07) $[M - CH_2Cl]^+$, 103.03 (103.06) $[^{n}BuSCH_2]^+$

2-((^{n}Butylthio)methyl)oxirane **(1-2)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.89 (t, J=7.32 Hz, 3H, $CH_3CH_2CH_2$), 1.38 (m, J=7.06 Hz, 2H, $CH_3CH_2CH_2$), 1.55 (quint, J=7.12 Hz, 2H, CH_2CH_2-S), 2.50-2.83 (m, 6H, CH_2CH_2-S, S-CH_2-CH, CH_2-O), 3.10 (m, 1H, CH-O); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 13.7 (s, $CH_3CH_2CH_2$), 22.0 (s, $CH_3CH_2CH_2$), 31.8 (s, CH_2CH_2-S), 32.2 (s, CH_2CH_2-S), 34.3 (s, S-CH_2-CH), 47.0 (s, CH_2-O), 52.0 (s, CH-O); IR (ATR, cm^{-1}): v= 2957 (s, CH), 826 (s, Epoxide ringmode); GC-EIMS (m/z) found (calc.): 146.02 (146.07) $[M]^+$, 103.05 (103.06) $[^{n}BuSCH_2]^+$, 61.03 (61.01) $[EtS]^+$

1,3-Bis(^{n}butylthio)propan-2-ol **(1)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.90 (t, J=7.24 Hz, 6H, $CH_3CH_2CH_2$), 1.39 (m, J=7.42 Hz, 4H, $CH_3CH_2CH_2$), 1.56 (quint, J=7.26 Hz, 4H, CH_2CH_2-S), 2.54 (t, J=7.08 Hz, 4H, CH_2CH_2-S), 2.60 (dd, J=7.47 / 13.49 Hz, 2H, S-CH_2-CH), 2.75 (dd, J=4.75 / 13.49 Hz, 2H, S-CH_2-CH), 2.91(d, J=3.02 Hz, 1H, OH), 3.78 (m, 1H, CH); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 13.5 (s, $CH_3CH_2CH_2$), 21.8 (s, $CH_3CH_2CH_2$), 31.7 (s, CH_2CH_2-S), 32.2 (s, CH_2CH_2-S), 38.2 (s, S-CH_2-CH), 68.7 (s, CH-OH); IR (ATR, cm^{-1}): v= 3437 (br, OH), 2966 (s, CH), 1026 (s, C-OH); GC-EIMS (m/z) found (calc.): 236.08 (236.13) $[M]^+$, 218.09 (218.12) $[M - H2O]^+$, 179.02 (179.06) $[M - C4H9]^+$

1-^{t}Butylthio-3-chloropropan-2-ol **(2-1)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 1.33 (s, 9H, $C(CH_3)_3$), 2.61 (s, 1H, OH), 2.72 (dd, J=6.88 / 13.03 Hz, 1H, S-CH_2-CH), 2.81 (dd, J=5.69 / 13.03 Hz, 1H, S-CH_2-CH), 3.57-3.70 (m, 2H, CH_2-Cl), 3.91 (m, J=5.67 Hz, 1H, CH); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 31.1 (s, $C(CH_3)_3$), 32.9 (s, S-CH_2-CH), 42.9 (s, $C(CH_3)_3$), 48.4 (s, CH_2-Cl), 70.4 (CH-OH); IR (ATR, cm^{-1}): v= 3407 (br, OH), 2961 (s, CH), 1043 (s, C-OH); GC-EIMS (m/z) found (calc.): 182.01 (182.05) $[M]^+$, 107.98 (107.98) $[M - {}^{t}BuOH]^+$, 57.08 (57.07) $[^{t}C_4H_9]^+$

2-((^{t}Butylthio)methyl)oxirane **(2-2)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 1.32 (s, 9H, $C(CH_3)_3$), 2.48-2.60 (m, 2H, S-CH_2-CH), 2.74-2.86 (m, 2H, CH_2-O), 3.07 (m, 1H, CH-O); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 30.9 (s, $C(CH_3)_3$), 31.1 (s, S-CH_2), 42.2 (s, $C(CH_3)_3$), 47.6 (s, CH_2-O), 51.6 (s, CH-O); IR (ATR, cm^{-1}): v= 2962 (s, CH), 835 (s, Epoxide ringmode); GC-EIMS (m/z) found (calc.): 146.04 (146.08) $[M]^+$, 90.05 (90.05) $[^{t}BuSH]^+$, 57.08 (57.07) $[^{t}C_4H_9]^+$

1,3-Bis(^{t}butylthio)propan-2-ol **(2)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 1.32 (s, 18H, C(C<u>H</u>$_3$)$_3$), 2.66 (dd, J=7.11/ 12.77 Hz, 2H, S-C<u>H</u>$_2$-CH), 2.75-2.83 (m, 3H, S-C<u>H</u>$_2$-CH, O<u>H</u>), 3.78 (m, 1H, C<u>H</u>); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 31.2 (s, C(<u>C</u>H$_3$)$_3$), 35.2 (s, <u>C</u>H$_2$-S), 42.6 (s, <u>C</u>(CH$_3$)$_3$), 69.9 (<u>C</u>H-OH); IR (ATR, cm^{-1}): ν= 3435 (br, OH), 2960 (s, CH), 1031 (s, C-OH); GC-EIMS (m/z) found (calc.): 179.02 (179.06) [M –^{t}C$_4$H$_9$]$^{+}$, 122.92 (122.99) [M –^{t}C$_4$H$_9$ –C$_4$H$_8$]$^{+}$, 57.04 (57.08) [^{t}C$_4$H$_9$]$^{+}$

2-((Isopropylthio)methyl)oxirane **(3-1)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 1.26 (d, J=6.74 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 2.52-2.84 (m, 4H, S-C<u>H</u>$_2$-CH, C<u>H</u>$_2$-O), 3.02 (m, J=6.67 Hz, 1H, C<u>H</u>(CH$_3$)$_2$), 3.10 (m, 1H, C<u>H</u>-O); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 23.4 (s, CH(<u>C</u>H$_3$)$_2$), 32.8 (s, S-<u>C</u>H$_2$-CH), 35.2 (s, <u>C</u>H(CH$_3$)$_2$), 47.1 (s, <u>C</u>H$_2$-O), 51.9 (<u>C</u>H-O); IR (ATR, cm^{-1}): ν= 2961 (s, CH), 827 (s, Epoxide ringmode); GC-EIMS (m/z) found (calc.): 132.01 (132.06) [M]$^{+}$, 89.03 (89.01) [M –^{i}C$_3$H$_7$]$^{+}$, 74.04 (74.15) [CH$_3$-C(=S)-CH$_3$)$^{+}$

1,3-Bis(isopropylthio)propan-2-ol **(3)**

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 1.26 (d, J=6.77 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 2.63 (dd, J=7.33 / 13.46 Hz, 2H, S-C<u>H</u>$_2$-CH), 2.78 (dd, J=4.94 / 13.46 Hz, 2H, S-C<u>H</u>$_2$-CH), 2.87-3.00 (m, 3H, O<u>H</u>, C<u>H</u>(CH$_3$)$_2$); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 23.6 (s, CH(<u>C</u>H$_3$)$_2$), 35.5 (s, <u>C</u>H(CH$_3$)$_2$), 36.9 (s, S-<u>C</u>H$_2$-CH), 69.3 (s, <u>C</u>H-OH); IR (ATR, cm^{-1}): ν= 3440 (br, OH), 2956 (s, CH), 1025 (s, C-OH); GC-EIMS (m/z) found (calc.): 208.08 (208.10) [M]$^{+}$, 165.99 (165.04) [M –^{i}C$_3$H$_7$]$^{+}$, 122.95 (122.99) [M –2 ^{i}C$_3$H$_7$]$^{+}$

1-^{n}Butylthio-3-(diethylamino)propan-2-ol **(4)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.89 (t, J=7.13 Hz, 3H, C<u>H</u>$_3$CH$_2$CH$_2$), 1.00 (t, J=7.12 Hz, 6H, N(CH$_2$C<u>H</u>$_3$)$_2$), 1.38 (m, J=7.14 Hz, 2H, CH$_3$C<u>H</u>$_2$CH$_2$), 1.56 (quint, J=7.34 Hz, 2H, C<u>H</u>$_2$CH$_2$-S), 2.25-2.70 (m, 10H, CH$_2$C<u>H</u>$_2$-S, S-C<u>H</u>$_2$-CH, N-C<u>H</u>$_2$-CH, N(C<u>H</u>$_2$CH$_3$)$_2$), 3.71 (m, 1H, C<u>H</u>), 3.84 (s, 1H, O<u>H</u>); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 12.0 (s, N(CH$_2$<u>C</u>H$_3$)$_2$), 13.6 (s, <u>C</u>H$_3$CH$_2$CH$_2$), 21.9 (s, CH$_3$<u>C</u>H$_2$CH$_2$), 31.8 (s, <u>C</u>H$_2$CH$_2$-S), 32.7 (s, CH$_2$<u>C</u>H$_2$-S), 37.0 (s, S-<u>C</u>H$_2$-CH), 47.1 (s, N(<u>C</u>H$_2$CH$_3$)$_2$), 58.4 (s, CH-<u>C</u>H$_2$-N), 66.8 (s, <u>C</u>H-OH); IR (ATR, cm^{-1}): ν= 3436 (br, OH), 2963 (s, CH), 1063 (s, C-OH); GC-EIMS (m/z) found (calc.): 116.03 (116.11) [M –^{n}BuSCH$_2$]$^{+}$, 86.06 (86.06) [Et$_2$NCH$_2$]$^{+}$

1-^{t}Butylthio-3-(diethylamino)propan-2-ol **(5)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.99 (t, J=7.12 Hz, 6H, N(CH$_2$C<u>H</u>$_3$)$_2$), 1.31 (s, 9H, C(C<u>H</u>$_3$)$_3$), 2.23-2.76 (m, 8H, N(C<u>H</u>$_2$CH$_3$)$_2$, S-C<u>H</u>$_2$-CH, N-C<u>H</u>$_2$-CH), 3.70 (m, 1H, C<u>H</u>), 3.88 (s, 1H, O<u>H</u>); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 12.1 (s, N(CH$_2$<u>C</u>H$_3$)$_2$), 31.0 (s, C(<u>C</u>H$_3$)$_2$), 33.4 (s, S-<u>C</u>H$_2$-CH), 42.1 (s, <u>C</u>(CH$_3$)$_3$), 47.1 (s, N(<u>C</u>H$_2$CH$_3$)$_2$), 58.8 (s, N-<u>C</u>H$_2$-CH), 68.9 (s, <u>C</u>H-OH); IR (ATR, cm^{-1}): ν= 3433 (br, OH), 2967 (s, CH), 1060 (s, C-OH); GC-EIMS (m/z) found (calc.): 162.05 (162.95) [M –^{t}C$_4$H$_9$]$^{+}$, 116.11 (116.11) [M –^{t}BuSCH$_2$]$^{+}$, 86.07 (86.06) [Et$_2$NCH$_2$]$^{+}$

1-Diethylamino-3-(isopropylthio)propan-2-ol **(6)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.91 (t, J=7.11 Hz, 6H, $N(CH_2C\underline{H}_3)_2$), 1.17 (dd, J=1.57 / 6.76 Hz, 6H, $CH(C\underline{H}_3)_3$), 2.25-2.71 (m, 8H, S-$C\underline{H}_2$-CH, N-$C\underline{H}_2$-CH, $N(C\underline{H}_2CH_3)_2$), 2.97 (quint, 6.72 Hz, 1H, $C\underline{H}(CH_3)_3$), 3.71 (m, 1H, C<u>H</u>), 3.85 (s, 1H, O<u>H</u>); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 12.1 (s, $N(CH_2\underline{C}H_3)_2$), 23.6 (s, $CH(\underline{C}H_3)_2$), 35.5 (s, $\underline{C}H(CH_3)_2$), 35.7 (s, S-$\underline{C}H_2$-CH), 47.3 (s, $N(\underline{C}H_2CH_3)_2$), 58.7 (s, N-$\underline{C}H_2$-CH), 67.0 (s, <u>C</u>H-OH); IR (ATR, cm^{-1}): ν= 3434 (br, OH), 2963 (s, CH), 1063 (s, C-OH); GC-EIMS (m/z) found (calc.): 162.07 (162.10) [M –$^{i}C_3H_7$]$^{+}$, 116.12 (116.11) [M –$^{i}PrSCH_2$]$^{+}$, 86.09 (86.06) [Et_2NCH_2]$^{+}$

1-Chloro-2-(chloromethyl)butan-2-ol **(7-1)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.99 (t, J=7.64 Hz, 3H, $C\underline{H}_3$), 1.71 (q, J=7.52 Hz, 2H, $C\underline{H}_2CH_3$), 2.27 (s, 1H, O<u>H</u>), 3.62 (q, J=11.40 Hz, 4H, $C\underline{H}_2$-Cl); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 7.2 (s, $\underline{C}H_3$), 27.97 (s, $\underline{C}H_2CH_3$), 48.2 (s, $\underline{C}H_2$-Cl), 74.0 (s, <u>C</u>-OH); IR (ATR, cm^{-1}): ν= 3455 (br, OH), 2971 (m, CH), 1741 (m, OH), 739 (m, C-Cl); GC-EIMS (m/z) found (calc.): 126.98 (126.97) [M –C_2H_5]$^{+}$, 107.01 (107.03) [M –CH_2Cl]$^{+}$, 91.01 (91.00) [M –HCl –C_2H_5]$^{+}$

2-Chloromethyl-2-ethyloxirane **(7-2)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.97 (t, J=7.51 Hz, 3H, $C\underline{H}_3$), 1.82 (m, 2H, $C\underline{H}_2CH_3$), 2.77 (s, 2H, $C\underline{H}_2$-O), 3.56 (q, J=11,57 Hz, 2H, $C\underline{H}_2$-Cl); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 8.6 (s $\underline{C}H_3$), 24.5 (s, $\underline{C}H_2CH_3$), 47.6 (s, $\underline{C}H_2$-Cl), 52.3 (s, $\underline{C}H_2$-O), 59.4 (s, CH_2-<u>C</u>-O); IR (ATR, cm^{-1}): ν= 2972 (m, CH), 734 (s, C-Cl); GC-EIMS (m/z) found (calc.): 85.09 (85.06) [M –Cl]$^{+}$, 71.02 (71.05) [M –CH_2Cl]$^{+}$, 55.10 (55.02) [M –HCl –C_2H_5]$^{+}$

1-^{n}Butylthio-2-((^{n}butylthio)methyl)butan-2-ol **(7):**

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.91 (t, J=7.23 Hz, 9H, $C\underline{H}_3CH_2CH_2$, C-$CH_2C\underline{H}_3$), 1.40 (m, J=7.30 Hz, 4H, $CH_3C\underline{H}_2CH_2$), 1.59 (m, 6H, $C\underline{H}_2CH_2$-S, C-$C\underline{H}_2CH_3$), 2.58 (q, J=6.94 Hz, 4H, $CH_2C\underline{H}_2$-S) 2.65 (d, J=13.09 Hz, 1H, S-$C\underline{H}_2$-C), 2.80 (d, J=13.09 Hz, 1H, S-$C\underline{H}_2$-C); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 8.1 (s, C-$CH_2\underline{C}H_3$), 13.8 (s, $\underline{C}H_3CH_2CH_2$), 22.0 (s, $CH_3\underline{C}H_2CH_2$), 31.2 (s, C-$\underline{C}H_2CH_3$), 32.1 (s, $\underline{C}H_2CH_2$-S), 34.0 (s, $CH_2\underline{C}H_2$-S), 41.5 (s, S-$\underline{C}H_2$-C), 74.4 (s, <u>C</u>-OH); IR (ATR, cm^{-1}): ν= 3466 (br, OH), 2958 (s, CH), 1223 (m, OH); GC-EIMS (m/z) found (calc.): 264.14 (264.16) [M]$^{+}$, 161.12 (161.10) [M –$^{n}BuSCH_2$]$^{+}$, 105.06 (105.04) [M –$^{n}BuSCH_2$ –C_4H_9]$^{+}$

1-^{t}Butylthio-2-((^{t}butylthio)methyl)butan-2-ol **(8)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.95 (t, J=7.42 Hz, 3H, C-$CH_2C\underline{H}_3$), 1.32 (s, 18H, $C(C\underline{H}_3)_3$), 1.61 (q, J=7.51 Hz, 2H, C-$C\underline{H}_2CH_3$), 2.63 (d, J=12.09 Hz, 1H, S-$C\underline{H}_2$-C), 2.80 (d, J=12.09 Hz, 1H, S-$C\underline{H}_2$-C), 2.77 (s, 1H, O<u>H</u>); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 8.0 (s, C-$CH_2\underline{C}H_3$), 31.1 (s, $C(\underline{C}H_3)_3$), 31.7 (s, C-$\underline{C}H_2CH_3$), 37.5 (s, S-$\underline{C}H_2$-C), 42.4 (s, $\underline{C}(CH_3)_3$), 72.8 (s, <u>C</u>-OH); IR (ATR, cm^{-1}): ν= 3475 (br, OH), 2961 (s, CH); GC-EIMS (m/z) found (calc.): 207.06 (207.09) [M –$^{t}C_4H_9$]$^{+}$, 132.96 (133.07) [M –$^{t}BuSCH_2$ –C_2H_4]$^{+}$, 57.04 (57.07) [C_4H_9]$^{+}$

1-Isopropylthio-2((isoproyplthio)methyl)butan-2-ol **(9)**

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.92 (t, J=7.54 Hz, 3H, C-$CH_2C\underline{H}_3$), 1.27 (d, J=7.08 Hz, 12H, C($C\underline{H}_3)_2$), 1.62 (q, J=7.47 Hz, 2H, C-$C\underline{H}_2CH_3$), 2.32 (s, br., 1H, O$\underline{H}$), 2.66 (d, J=12.84 Hz, 2H, S-$C\underline{H}_2$-C), 2.81 (d, J=12.84 Hz, 2H, S-$C\underline{H}_2$-C) 2.94 (m, J=6.66 Hz, 2H, C$\underline{H}(CH_3)_2$); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 8.0 (s, C-$CH_2\underline{C}H_3$), 23.7 (s, CH($\underline{C}H_3)_2$), 31.4 (s, C-$\underline{C}H_2CH_3$), 36.8 (s, $\underline{C}H(CH_3)_2$), 39.7 (s, S-$\underline{C}H_2$-C), 73.8 (s, $\underline{C}$-OH); IR (ATR, cm^{-1}): ν= 3475 (br, OH), 2960 (s, CH), 1238 (s, OH); GC-EIMS (m/z) found (calc.): 236.07 (236.13) $[M]^+$, 193.03 (193.07) $[M -{}^{i}C_3H_9]^+$, 132.97 (133.07) $[M -{}^{i}PrS -C_2H_4]^+$, 104.98 (105.04) $[M -{}^{i}C_3H_9 -iPrSCH_2]^+$

1-^{n}Butylthio-2-((diethylamino)methyl)butan-2-ol **(10)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.90 (t, J=7.30 Hz, 6H, C-$CH_2C\underline{H}_3$, $C\underline{H}_3CH_2CH_2$), 1.01 (t, J=7.17 Hz, 6H, N($CH_2C\underline{H}_3)_2$), 1.41 (m, J=7.25 Hz, 2H, $CH_3C\underline{H}_2CH_2$), 1.46-1.64 (m, 4H, $C\underline{H}_2CH_2$-S, C-$C\underline{H}_2CH_3$), 2.33 (d, J=14.04 Hz, 1H, S-$C\underline{H}_2$-C), 2.51-2.66 (m, 9H, $CH_2C\underline{H}_2$-S, S-$C\underline{H}_2$-C, N-$C\underline{H}_2$-C, N($C\underline{H}_2CH_3)_2$), 3.80 (s, 1H, O$\underline{H}$); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 7.9 (s, C-$CH_2\underline{C}H_3$), 12.4 (s, N($CH_2\underline{C}H_3)_2$), 13.8 (s, $\underline{C}H_3CH_2CH_2$), 22.1 (s, $CH_3\underline{C}H_2CH_2$), 30.7 (s, C-$\underline{C}H_2CH_3$), 32.0 (s, $\underline{C}H_2CH_2$-S), 33.6 (s, S-$\underline{C}H_2CH_2$), 40.7 (s, S-$\underline{C}H_2$-C), 49.1 (s, N($\underline{C}H_2CH_3)_2$), 59.8 (s, N-$\underline{C}H_2$-C), 72.7 (s, $\underline{C}$-OH); IR (ATR, cm^{-1}): ν= 3465 (br, OH), 2963 (s, CH), 1063 (s, C-N); GC-EIMS (m/z) found (calc.): 144.08 (144.14) $[M -{}^{n}BuSCH_2)^+$, 86.03 (86.10) $[Et_2NCH_2]^+$, 58.10 (58.04) $[CH_3C(=O)CH_3]^+$

1-^{t}Butylthio-2-((diethylamino)methyl)butan-2-ol **(11)**:

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.93 (t, J=7.34 Hz, 3H, C-$CH_2C\underline{H}_3$), 1.01 (t, J=7.09 Hz, 6H, N($CH_2C\underline{H}_3)_2$), 1.31 (s, 9H, C($C\underline{H}_3)_3$), 1.49 (m, 2H, C-$C\underline{H}_2CH_3$), 2.31 (d, J=14.05 Hz, 1H, S-$C\underline{H}_2$-C) 2.50-2.69 (m, 7H, C-$C\underline{H}_2$-S, N-$C\underline{H}_2$-C, N($C\underline{H}_2CH_3)_2$), 3.89 (s, 1H, O$\underline{H}$); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 7.7 (s, C-$CH_2\underline{C}H_3$), 12.5 (s, N($CH_2\underline{C}H_3)_2$), 30.9 (s, C-$\underline{C}H_2CH_3$), 30.9 (s, C($\underline{C}H_3)_3$), 35.9 (s, S-$\underline{C}H_2$-C), 41.8 (s, $\underline{C}(CH_3)_3$), 49.18 (s, N($\underline{C}H_2CH_3)_2$), 60.3 (s, N-$\underline{C}H_2$-C), 72.1 (s, $\underline{C}$-OH); IR (ATR, cm^{-1}): ν= 3467 (br, OH), 2964 (s, CH), 1064 (s, C-N); GC-EIMS (m/z) found (calc.): 144.10 (144.14) $[M -{}^{t}BuSCH_2)^+$, 86.02 (86.10) $[Et_2NCH_2]^+$, 58.10 (58.04) $[CH_3C(=O)CH_3]^+$

1-Diethylamino-2((isopropylthio)methyl)butan-2-ol **(12)**

^{1}H NMR ($CDCl_3$, 250 MHz, +25 °C, δ [ppm]): 0.91 (t, J=7.41 Hz, 3H, C-$CH_2C\underline{H}_3$), 1.01 (t, J=7.09 Hz, 6H, N($CH_2C\underline{H}_3)_2$), 1.27 (d, J=6.62 Hz, 6H, CH($C\underline{H}_3)_2$), 1.46-1.61 (m, 2H, C-$C\underline{H}_2CH_3$), 2.33 (d, J=14.04 Hz, 1H, S-$C\underline{H}_2$-C), 2.53-2.69 (m, 7H, S-$C\underline{H}_2$-C, N-$C\underline{H}_2$-C, N($C\underline{H}_2CH_3)_2$), 2.90 (m, J=6.67 Hz, 1H, C$\underline{H}(CH_3)_2$), 3.83 (s, 1H, O$\underline{H}$); ^{13}C {^{1}H} NMR ($CDCl_3$, 62.86 MHz, +25 °C, δ [ppm]): 7.8 (s, C-$CH_2\underline{C}H_3$), 12.4 (s, N($CH_2\underline{C}H_3)_2$), 23.6 (s, CH($\underline{C}H_3)_2$), 30.8 (s, C-$\underline{C}H_2CH_3$), 36.3 (s, $\underline{C}H(CH_3)_2$), 38.7 (s, S-$\underline{C}H_2$-C), 49.1 (s, N($CH_3\underline{C}H_2)_2$), 60.0 (s, N-$\underline{C}H_2$-C), 72.5 (s, $\underline{C}$-OH); IR (ATR, cm^{-1}): ν= 3458 (br, OH), 2966 (s, CH), 1063 (s, C-N); GC-EIMS (m/z) found (calc.): 144.15 (144.14) $[M -{}^{t}BuSCH_2)^+$, 86.04 (86.10) $[Et_2NCH_2]^+$, 58.09 (58.09) $[CH_3C(=O)CH_3]^+$

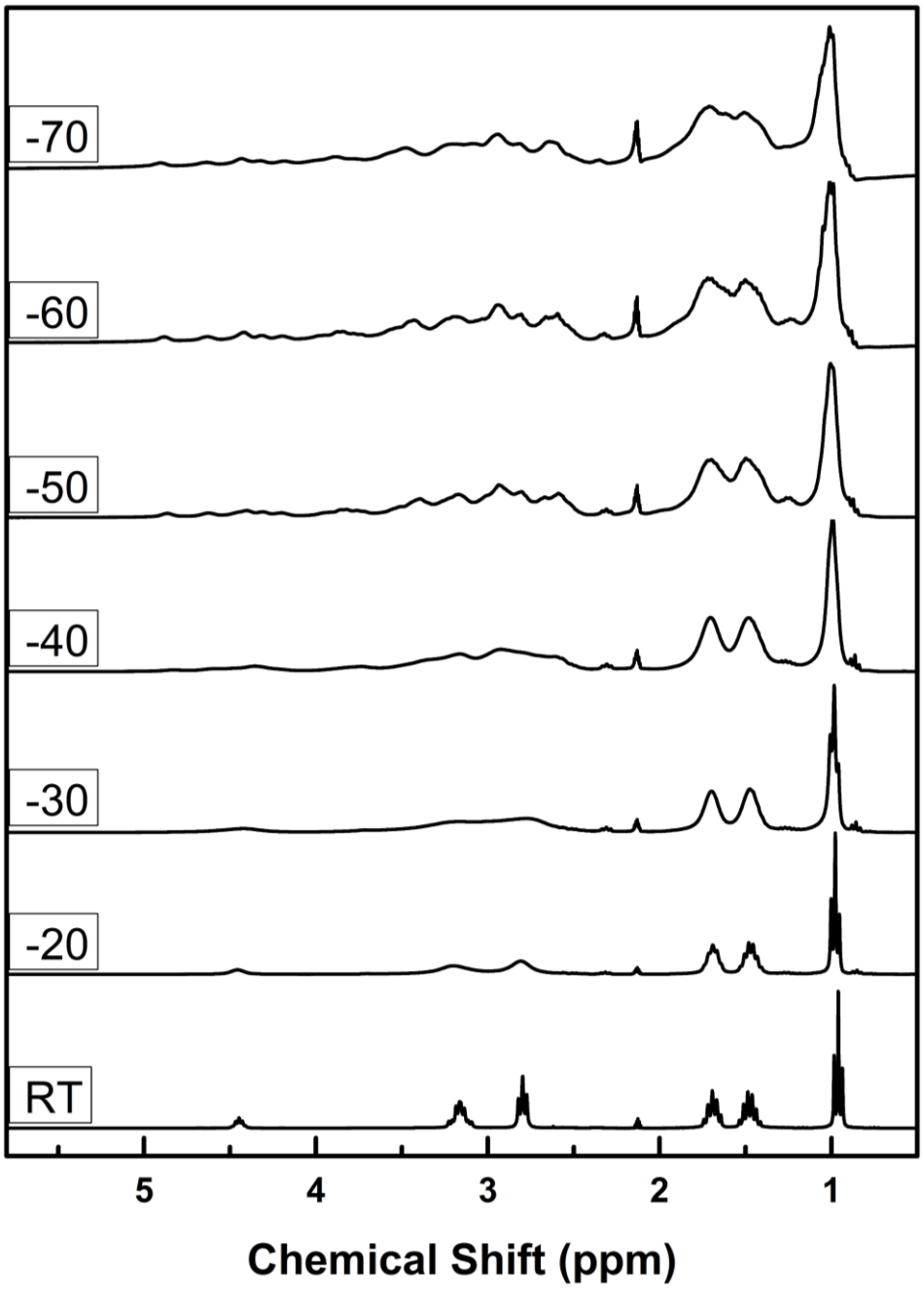


Fig. S1: Variable temperature NMR spectra for **In1** in toluene d^8 at different temperatures down to -70 °C.

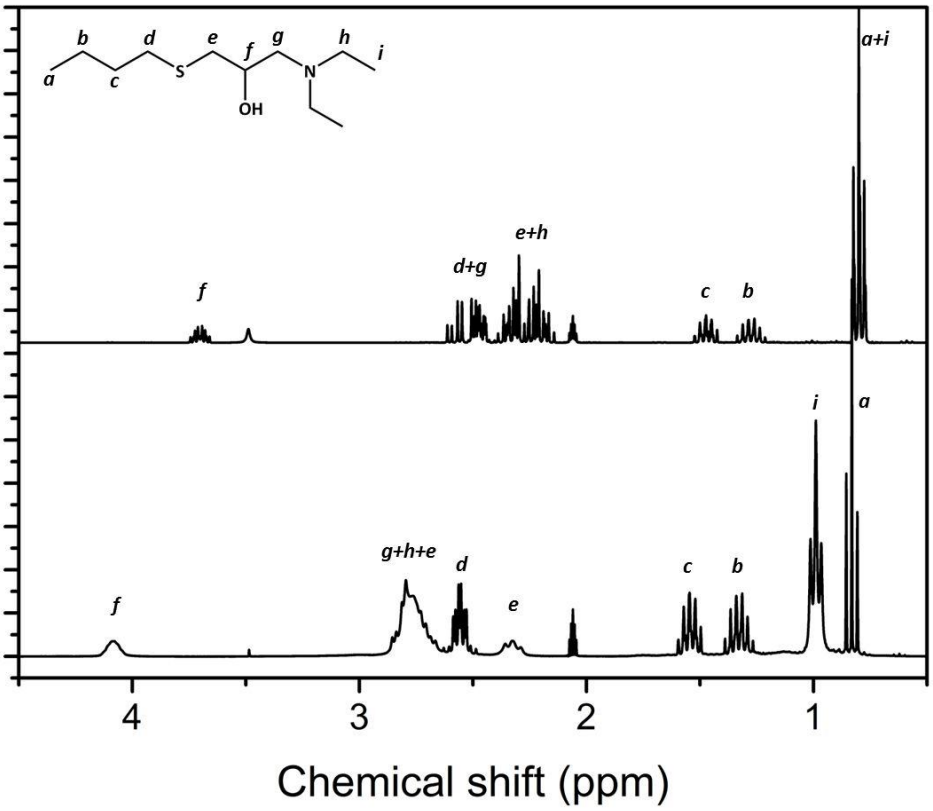


Fig. S2: ^{1}H NMR spectra the alkanol **(4)** in free form in $CDCl_3$ and the respective homoleptic In alkoxide **In4.** It is obvious that the signals related to the amine side chain are shifted strongly downfield due to the coordination to the metal centre. The peaks related to the thioether side chain remain almost unaffected.

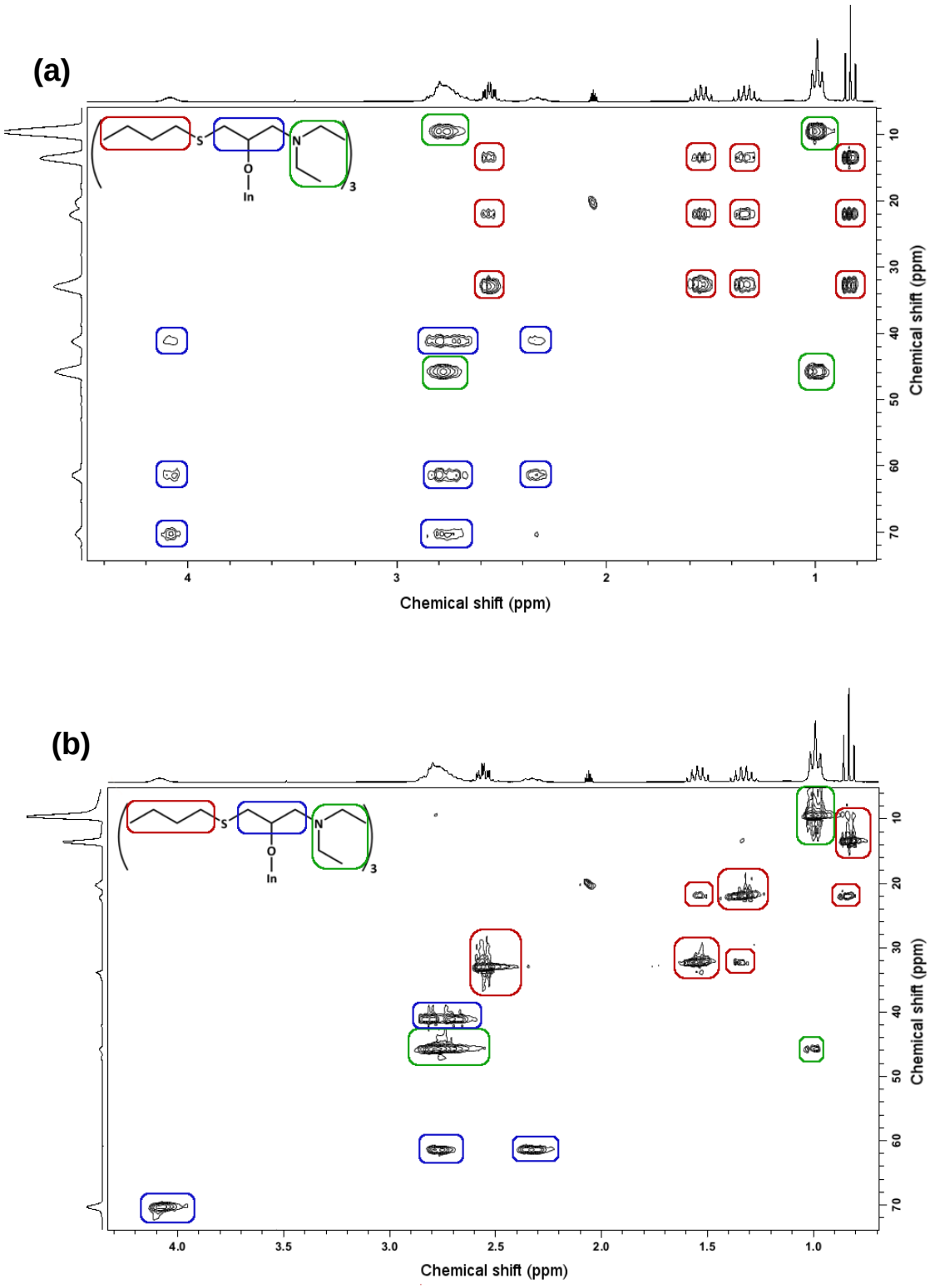


Fig. S 3: 2D NMR spectra of **In4** as illustrated in the images. a) (HSQC-TOCSY) and (b) (HSQC-DEPT) show colour coded the ^{1}H-^{13}C correlations of the different parts of the molecule measured in deuterated toluene.

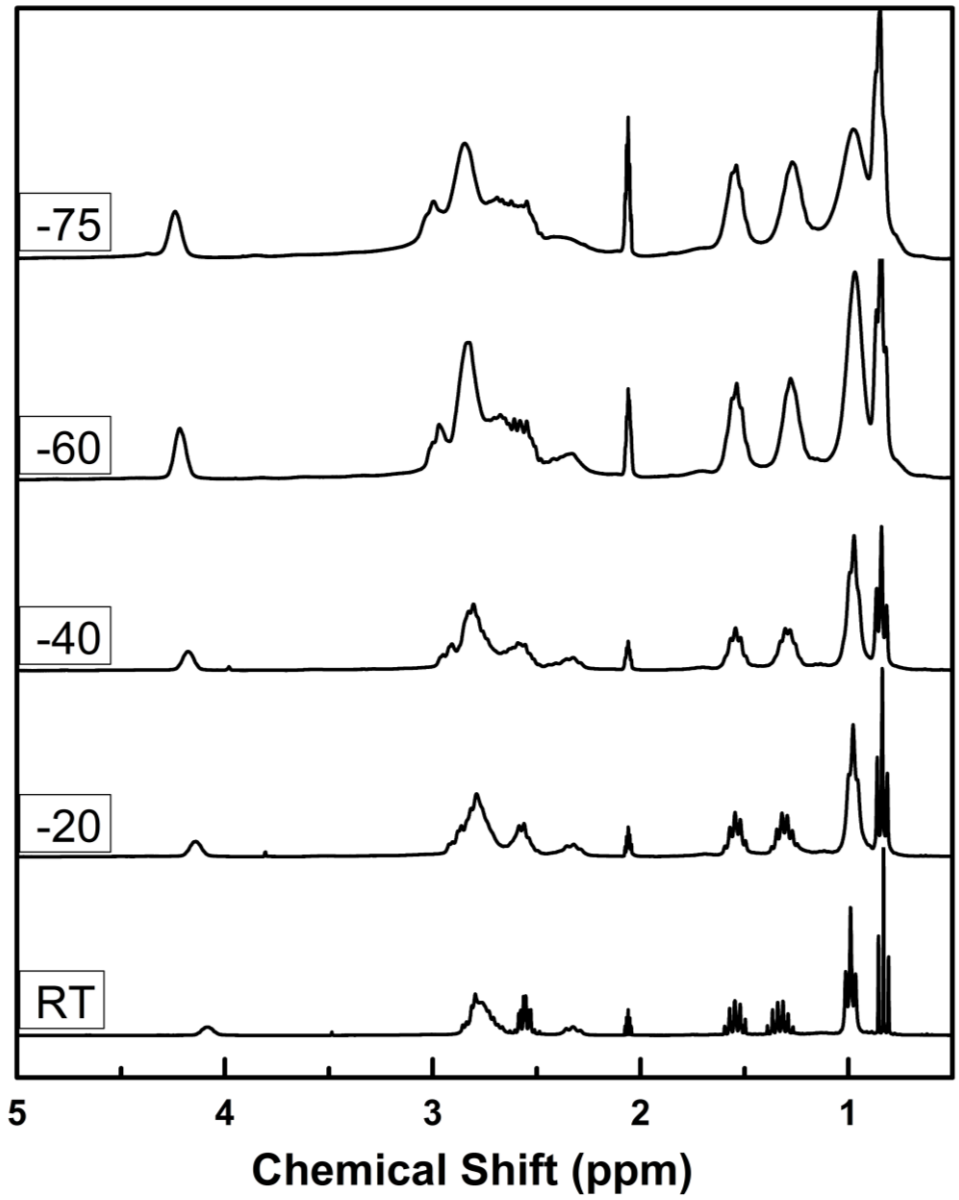


Fig. S 4: Variable temperature ^{1}H spectra of **In4** in deuterated toluene from RT to -70 °C.

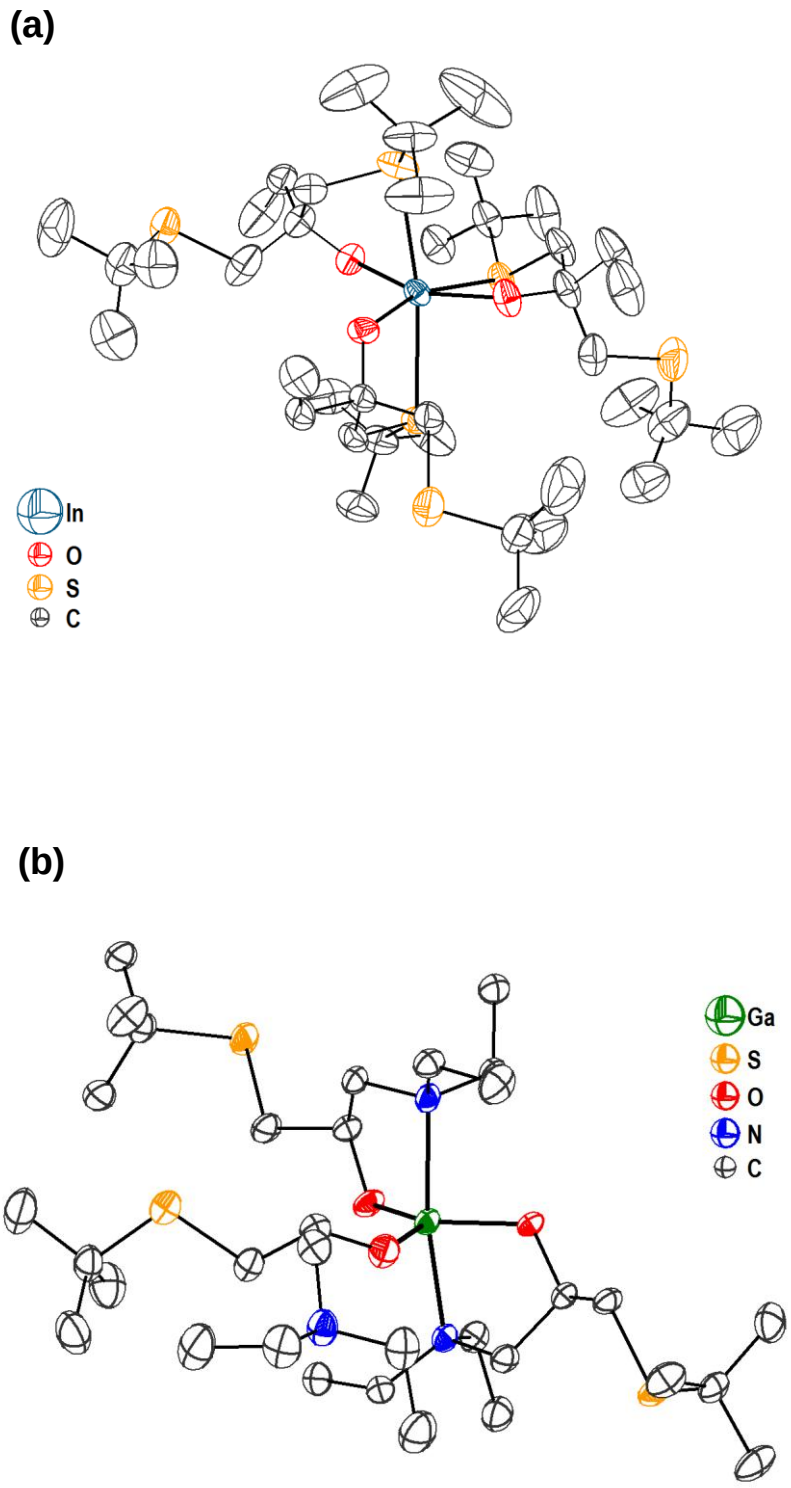


Fig. S5: Thermal ellipsoids with 50% probability of (a) $In(OCEt(CH_2S^tBu)_2)_3$ **In8** and (b) $Ga(OCH(CH_2S^tBu)(CH_2NEt_2))_3$ **Ga5.**

Table S2: Crystal data, data collection parameters and refinement detailsof **In68** and **Ga5.**

	Ga5	**In8** + C_5H_{12}
Chemical formula	$GaO_3N_3S_3C_{33}H_{72}$	$InO_3S_6C_{44}H_{93}$
M [g/mol]	724.84	977.36
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.9239(16)	10.5221(8)
b [Å]	12.8002(12)	14.8955(11)
c [Å]	17.470(4)	18.5318(13)
α [°]	108.527(4)	84.795(2)
β [°]	97.665(4)	83.722(2)
γ [°]	108.690(2)	74.537(2)
V [Å^3]	2117.5(6)	2776.9(4)
Z	2	2
$\rho_{calc.}$ [Mg·m^{-3}]	1.137	1.169
μ [mm^{-1}]	0.83	0.683
Crystal size [mm]	0.10 x 0.16 x 0.40	0.30 x 0.35 x 0.40
Temperature [K]	100(2)	200(2)
No. of measured reflections	11387	144925
No. independent reflections	7385	20301
No. of observed reflections [I > 2·σ(I)]	5897	16308
R_{Int}	0.027	0.030
Θ_{max} [°]	25.0	32.2
Refinement on	F^2	F^2
R[F^2>2σ(F)].ωR(F^2).S	0.048. 0.144. 1.05	0.040, 0.109, 1.13
No. of reflections	7385	20301
No. of parameters	403	667
No. of restraints	0	92
Weighting scheme values *	a = 0.0954. b = 0	a = 0.0348, b = 2.3567
$\Delta\rho_{max}$. $\Delta\rho_{min}$ (e· Å^{-3}]	0.65. -1.43	1.71, -0.97

* $\omega = [\sigma^2(F_o^2) + (a\cdot P)^2 + b\cdot P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$

Table S3: Selected Bond distances and bond angles of **In8** and **Ga5.**

In8	Bond length [Å]		Bond angle (deg)	**Ga5**	Bond length [Å]		Bond angle (deg)
In-O1	2.0504(14)	O1-In-O2	103.25(6)	Ga-O1	1.866(2)	O1-Ga-O2	131.75(10)
In-O2	2.0599(13)	O1-In-O3	156.61(6)	Ga-O2	1.863(2)	O1-Ga-O3	107.91(10)
In-O3	2.0467(15)	O2-In-O3	97.80(6)	Ga-O3	1.842(2)	O2-Ga-O3	120.09(10)
In-S2	2.7210(6)	O1-In-S2	73.30(4)	Ga-N1	2.234(2)	O1-Ga-N1	82.97(9)
In-S4	2.7821(6)	O1-In-S4	101.17(4)	Ga-N2	2.219(3)	O1-Ga-N2	90.67(9)
In-S6	2.8123(5)	O1-In-S6	87.40(4)			O2-Ga-N1	89.19(9)
		O2-In-S2	95.61(4)			O2-Ga-N2	83.56(9)
		O2-In-S4	78.29(4)			O3-Ga-N1	93.58(10)
		O2-In-S6	162.94(4)			O3-Ga-N2	103.06(10)
		O3-In-S2	94.78(5)			N1-Ga-N2	163.32(9)
		O3-In-S4	92.90(5)				
		O3-In-S6	74.75(4)				
		S2-In-S4	170.790(19)				
		S2-In-S6	100.250(19)				
		S4-In-S6	86.662(18)				

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1. T. K. Todsen, C. B. Pollard and E. G. Rietz, *Journal of the American Chemical Society*, 1950, **72**, 4000-4002.
2. C. Tanyeli, A. S. Demir, I. M. Akhmedov, E. Özgül and C. G. Kandemir, *Synth. Commun.*, 1996, **26**, 2967-2980.