

# Supporting Information

*For*

## **Synthetic Access to a Hydrocarbon-soluble Trifluorinated Ge(II) Compound and its Sn(II) Congener**

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## S1. $^{19}\text{F}$ Solid-state NMR

Solid-state magic-angle spinning (MAS) NMR spectra were recorded at temperatures of 10-20 °C on a 14.1 T (600 MHz  $^1\text{H}$  Larmor frequency) wide-bore Bruker instrument. Micro-crystals of compounds **3** and **4** were packed under inert atmosphere into 4.0-mm MAS rotors. The spectra were recorded at MAS frequencies of 3 kHz, 4 kHz, 6 kHz and 10.5 kHz for compound **3** and MAS frequencies of 4 kHz, 6 kHz, 10.5 kHz and 11.5 kHz were employed for compound **4**. Initial  $^{19}\text{F}$  magnetization was created by direct  $^{19}\text{F}$  excitation or by  $^1\text{H}$ - $^{19}\text{F}$  cross-polarization (CP) with 50 or 500  $\mu\text{s}$  contact time. The spectra recorded with different initial  $^{19}\text{F}$  magnetization show the same pattern. Proton decoupling was applied during acquisition using the SPINAL-64 scheme with RF field amplitudes in the range of 50-55 kHz. The inter-scan delay was set to 4 s. Chemical shifts were calibrated externally using a  $\text{C}_6\text{F}_6$  sample as a reference for  $^{19}\text{F}$  (-164.9 ppm).

The spectra recorded at slow spinning rates (e.g. Figures S1 B and S1 D) show a number of spinning side bands, reflecting the presence of sizeable anisotropic interactions, namely  $^{19}\text{F}$ - $^{19}\text{F}$  dipolar couplings and chemical shift anisotropy, determined by the anisotropy of the electronic environment of the observed nuclei. Compound **4** exhibits more spinning side bands, which reflects stronger effective anisotropic interactions. This can be due to a larger anisotropy of the electronic environment and/or less molecular mobility, which can average out anisotropic interactions. The line width of the center band at an MAS rate of 10.5 kHz is 243 Hz and 1581 Hz for compounds **3** and **4**, respectively. The broader line width of compound **4** might reflect higher structural heterogeneity and/or the presence of different conformers.

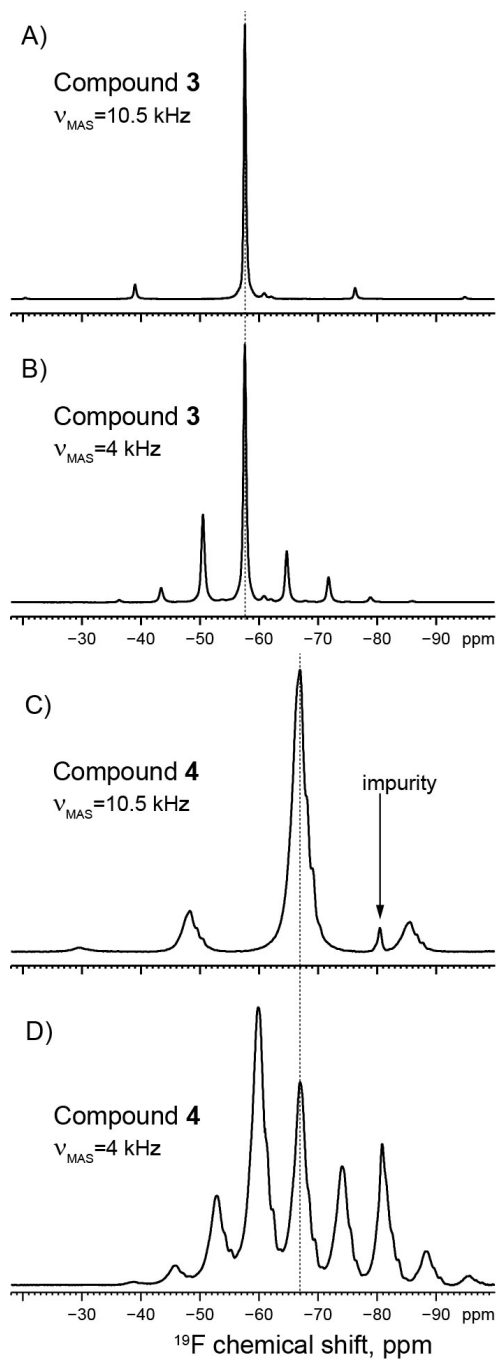


Figure S1.  $^{19}\text{F}$  direct excitation spectra of compound **3** (A and B) and compound **4** (C and D) recorded at MAS frequencies of 10.5 kHz and 4 kHz on a 600 MHz spectrometer.

## S2. Crystallographic Information

**Table S1.** Crystal data and structure refinement parameters for compounds **3**, and **4**.

Parameters	<b>3</b>	<b>4</b>
CCDC No.	965765	965766
Empirical formula	C <sub>15</sub> H <sub>25</sub> N <sub>2</sub> F <sub>3</sub> Ge	C <sub>15</sub> H <sub>25</sub> N <sub>2</sub> F <sub>3</sub> Sn
Formula Weight	362.98	408.84
Crystal system	orthorhombic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	<i>a</i> = 9.3477(11) Å <i>b</i> = 10.5608(12) Å <i>c</i> = 17.8086(19) Å $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$	<i>a</i> = 9.573(5) Å <i>b</i> = 17.473(4) Å <i>c</i> = 11.177(12) Å $\alpha = 90^\circ$ $\beta = 105.99(5)^\circ$ $\gamma = 90^\circ$
Volume, <i>Z</i>	1758.1(3) Å <sup>3</sup> , 4	1797(2) Å <sup>3</sup> , 4
Density (calcd)	1.367 g/cm <sup>3</sup>	1.510 g/cm <sup>3</sup>
Absorption coefficient	1.766 mm <sup>-1</sup>	0.986 mm <sup>-1</sup>
<i>F</i> (000)	752	824
Crystal size/mm	0.98 x 0.49 x 0.21	0.32 x 0.09 x 0.09
$\theta$ range for data collection	2.242 to 27.546 °	1.930 to 21.793 °
Limiting indices	-12 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -23 ≤ <i>l</i> ≤ 21	-11 ≤ <i>h</i> ≤ 11, -20 ≤ <i>k</i> ≤ 20, -13 ≤ <i>l</i> ≤ 12
Reflections collected	15229	9783
Independent reflections	4054 ( <i>R</i> <sub>int</sub> = 0.0402)	3192 ( <i>R</i> <sub>int</sub> = 0.0488)
Completeness to $\theta$	100 % ( $\theta = 25.241^\circ$ )	98.3 % ( $\theta = 21.835^\circ$ )
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full - matrix least - squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4054 / 177 / 256	3192 / 106 / 251
Goodness - of - fit on <i>F</i> <sup>2</sup>	1.041	1.072
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0281, <i>wR</i> 2 = 0.0566	<i>R</i> 1 = 0.0362, <i>wR</i> 2 = 0.0980
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0360, <i>wR</i> 2 = 0.0587	<i>R</i> 1 = 0.0377, <i>wR</i> 2 = 0.0993
Largest diff. peak and hole	0.274 and -0.190 e.Å <sup>-3</sup>	0.410 and -0.457 e.Å <sup>-3</sup>