Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 850-852

Tetrylenes based on polydentate sulfur-containing ligands

Andrey I. Fedulin, Yurii F. Oprunenko, Sergey S. Karlov,
Galina S. Zaitseva and Kirill V. Zaitsev

Table of contents

Experimental Section

Experimental Details…..…….…….....S3

Ligand synthesis…….……..……....S3

Synthesis of SNO-ligands

*2,6-Py(CH₂CMe₂SH)CH₂CMe₂OH (**3**)*..……..……..…….…….…….....S3
a) Stage 1; synthesis of 2,6-MePy(CH₂CMe₂OH)
b) Stage 2; synthesis of 2,6-Py(CH₂CMe₂OH)₂
c) Stage 3; synthesis of 2,6-Py(CH=CMe₂)CH₂CMe₂OH (**2**)
Compound 2,6-Py(CH=CMe₂)CH₂CMe₂OH, compound 2,6-Py[CH=CMe₂]₂
d) Stage 4; synthesis of 2,6-Py(CH₂CMe₂OH)CH₂CMe₂SC(O)Me
e) Stage 5; synthesis of 2,6-Py(CH₂CMe₂SH)CH₂CMe₂OH (**3**)

*2,6-Py(CH₂CH₂CMe₂OH)CH₂CH₂CMe₂SH (**4**)*..……..…….…….……...…….....S5
a) Stage 1; synthesis of 2,6-MePy(CH₂CH₂CMe₂SH)
b) Stage 2; synthesis of 2,6-Py(CH₂CH₂CMe₂OH)CH₂CH₂CMe₂SH (**4**)

Tetrylene synthesis

General procedure…….……S6

*Germylene ([2,6-Py(CH₂CH₂CH₂S)₂]Ge)ₙ (**6a**)*..……...…….……S6
*Germylene ([2,6-Py(CH₂CH₂CMe₂S)₂]Ge)ₙ (**6b**)*..…….…….……S6
*Stannylene ([2,6-Py(CH₂CH₂CH₂S)₂]Sn)ₙ (**6c**)*...……...…….…….……S6
*Stannylene ([2,6-Py(CH₂CH₂CMe₂S)₂]Sn)ₙ (**6d**)*...……..……S7
*Germylene [2,6-Py(CH₂CMe₂S)CH₂CMe₂O]Ge (**7a**)*…….……S7
*Stannylene ([2,6-Py(CH₂CMe₂S)CH₂CMe₂O]Sn)₂ (**7b**)*……..……S7
*Stannylene [2,6-Py(CH₂CH₂CMe₂O)CH₂CH₂CMe₂S]Sn (**7c**)*...…….……S8
*Stannylene (O[2-C₆H₄S]₂Sn)₂ (**8**)*....…….…….……..S8

Bromination of germylene ([2,6-Py(CH₂CH₂CH₂S)₂]Ge)ₙ (6a)…...…….……..S8

NMR spectra of the compounds obtained

Fig. S1. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-MePy(CH₂CMe₂OH).……..…….....S9

Fig. S2. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-$MePy(CH_2CMe_2OH)$..S9
Fig. S3. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CMe_2OH)_2$…..S10
Fig. S4. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CMe_2OH)_2$…..S10
Fig. S5. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH{=}CMe_2)CH_2CMe_2OH$ (**2**)..S11
Fig. S6. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH{=}CMe_2)CH_2CMe_2OH$ (**2**)..S11
Fig. S7. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-$Py[CH{=}CMe_2]_2$……..S12
Fig. S8. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-$Py[CH{=}CMe_2]_2$...S12
Fig. S9. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CMe_2OH)CH_2CMe_2SC(O)Me$……...S13
Fig. S10. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CMe_2OH)CH_2CMe_2SH$ (**3**)……..S13
Fig. S11. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CMe_2OH)CH_2CMe_2SH$ (**3**)……..S14
Fig. S12. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CH_2CMe_2OH)CH_2CH_2CMe_2SH$ (**4**)..S14
Fig. S13. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-$Py(CH_2CH_2CMe_2OH)CH_2CH_2CMe_2SH$ (**4**)..S15
Fig. S14. ^{1}H NMR spectrum (C_6D_6, RT) of [2,6-$Py(CH_2CMe_2S)CH_2CMe_2O$]Ge (**7a**)……..S15
Fig. S15. ^{13}C NMR spectrum (C_6D_6, RT) of [2,6-$Py(CH_2CMe_2S)CH_2CMe_2O$]Ge (**7a**)…….S16
Fig. S16. ^{1}H NMR spectrum (C_6D_6, RT) of ([2,6-$Py(CH_2CMe_2S)CH_2CMe_2O$]$Sn)_2$ (**7b**)..S16
Fig. S17. ^{13}C NMR spectrum (C_6D_6, RT) of ([2,6-$Py(CH_2CMe_2S)CH_2CMe_2O$]$Sn)_2$ (**7b**)……..S17
Fig. S18. ^{119}Sn NMR spectrum (C_6D_6, RT) of ([2,6-$Py(CH_2CMe_2S)CH_2CMe_2O$]$Sn)_2$ (**7b**)……..S17
Fig. S19. ^{1}H NMR spectrum ($CDCl_3$, RT) of [2,6-$Py(CH_2CH_2CMe_2O)CH_2CH_2CMe_2S$]Sn (**7c**)..S18
Fig. S20. ^{13}C NMR spectrum ($CDCl_3$, RT) of [2,6-$Py(CH_2CH_2CMe_2O)CH_2CH_2CMe_2S$]Sn (**7c**)..S18
Fig. S21. ^{119}Sn NMR spectrum ($CDCl_3$, RT) of [2,6-$Py(CH_2CH_2CMe_2O)CH_2CH_2CMe_2S$]Sn (**7c**)..S19
Fig. S22. ^{1}H NMR spectrum (DMSO-d_6, RT) of ($O[2\text{-}C_6H_4S]_2Sn)_2$ (**8**)...S19
Fig. S23. ^{13}C NMR spectrum (DMSO-d_6, RT) of ($O[2\text{-}C_6H_4S]_2Sn)_2$ (**8**)...S20
Fig. S24. ^{1}H NMR spectrum (DMSO-d_6, RT) of ($O[2\text{-}C_6H_4S]_2Sn)_2$ (**8**)...S20

Table S1. Selected stannylenes studied by ^{119}Sn NMR spectroscopy……..S21

References..S24

Experimental Section

Experimental Details. All operations were conducted in a dry argon atmosphere using standard Schlenk techniques. NMR spectra, ^{1}H NMR (400.130 MHz), ^{13}C NMR (100.613 MHz) and ^{119}Sn NMR (149.211 MHz) spectra were recorded on Bruker 400 or Agilent 400 spectrometers at 295 K. Chemical shifts in the spectra are given in ppm relative to internal Me_4Si (for ^{1}H, ^{13}C NMR) or Me_4Sn (for ^{119}Sn NMR). Elemental analyses were carried out using PerkinElmer® 2400 Series II CHN Elemental Analyzer in N. D. Zelinsky IOC RAS (Moscow, Russia) or Heraeus Vario Elementar EL apparatus in Graz University of Technology (Graz, Austria). Mass spectra (EI-MS, 70 eV) were recorded on a quadrupole mass spectrometer FINNIGAN MAT INCOS 50 with direct insertion; all assignments were made with reference to the most abundant isotopes. Matrix-assisted laser-desorption-ionization time-off flight mass spectrometry (MALDI-TOF-MS) analyses were performed on a Microflex (Bruker Daltonics) time-of-flight mass spectrometers; spectra were recorded in positive linear mode. Flash chromatography was performed on SiO_2 (0.015-0.040 mm).

Solvents were dried using standard procedures. Tetrahydrofuran and diethyl ether were stored over solid KOH and then distilled over sodium/benzophenone. Toluene and *n*-hexane were refluxed and distilled over sodium. Acetone was refluxed and distilled over P_4O_{10}, then over K_2CO_3, after over $KMnO_4$. Ethanol was refluxed and distilled over CaH_2 and stored over molecular sieves 3 Å. Dichloromethane was distilled from CaH_2; C_6D_6 was distilled over sodium under argon; $CDCl_3$ was distilled over CaH_2 under argon; DMSO-d_6 was refluxed and distilled over CaH_2 under argon, and stored over molecular sieves 3 Å.

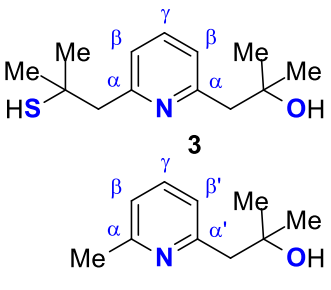
Commercial *n*-BuLi ("Aldrich") was used as received. 2,6-Lutidine ("Aldrich") was distilled from KOH before using.

Compounds 2,6-MePy($CH_2CH_2CMe_2SH$),[S1] ligands 2,6-Py($CH_2CH_2CH_2SH$)$_2$ (**1a**),[S1] 2,6-Py($CH_2CH_2CH_2SH$)$_2$ (**1b**),[S1] O[2-C_6H_4SH]$_2$ (**5**)[S2] were obtained using literature procedures.

Ligand synthesis

Synthesis of SNO-ligands

2,6-Py(CH_2CMe_2SH)CH_2CMe_2OH (3)



a) Stage 1; synthesis of 2-(2-hydroxy-2-methylpropyl)-6-methylpyridine, 2,6-MePy(CH_2CMe_2OH). At -40 °C, a solution of BuLi (2.5 M solution in hexane, 38.00 mL, 95.00 mmol) was added dropwise to a solution of 2,6-lutidine (10.00 g, 93.30 mmol) in ether (200 mL). The mixture was slowly warmed to room temperature for 1 h, then cooled to -40 °C, and acetone (5.52 g, 95.00 mmol) was added dropwise. The mixture was slowly warmed to room temperature and was stirred overnight. Saturated aq. solution of NH_4Cl (100 mL) was added, the aqueous phase was extracted with CH_2Cl_2 (3x50 mL), the organic phase was dried over $MgSO_4$, then the volatiles were removed under reduced pressure. After distillation 2,6-MePy(CH_2CMe_2OH) (29.40 g, 95 %) was obtained as colorless oil, b.p. 96-98 °C (7 Torr).

^{1}H NMR (δ, ppm, $CDCl_3$): 1.16 (s, 6H, CMe_2); 2.46 (s, 3H, *Me*Py); 2.82 (s, 2H, CH_2); 6.14 (br s, 1H, OH); 6.87, 6.97 (2d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, each 1H, β,β'-Py_H); 7.46 (pt, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 24.2 (*Me*Py); 29.4 (C*Me*$_2$); 48.2 (CH_2); 70.5 (CMe$_2$); 120.9, 121.2 (β,β'-Py_C); 136.9 (γ-Py_C); 157.1, 159.1 (α,α'-Py_C).

Anal. Calcd. for $C_{10}H_{15}NO$ (M_w 165.2322): C 72.69, H 9.15, N 8.48. Found: C 72.76, H 9.07, N 8.56.

b) Stage 2; synthesis of 2,6-bis(2-hydroxy-2-methylpropyl)pyridine, 2,6-Py(CH$_2$CMe$_2$OH)$_2$. Compound was obtained analogously to 2,6-Py(CH$_2$CH$_2$CH$_2$SH)$_2$ (**1a**) in ether (150 mL) from MePyCH$_2$CMe$_2$OH (11.11 g, 67.20 mmol), *n*-BuLi (2.5 M solution in hexane, 54.00 mL, 134.40 mmol) and acetone (4.68 g, 80.60 mmol). To terminate the reaction, 2 M aq. solution of HCl (100 mL) was added, the mixture was stirred for 30 min and then neutralized with 2 M aq. solution of NaOH. The aqueous phase was extracted with CH_2Cl_2 (3x50 mL), the combined organic phases were dried over $MgSO_4$, and the volatiles were removed under reduced pressure. The residue was distilled collecting fraction with b.p. 110-160 °C (1 Torr), then it was treated with *n*-hexane (20 mL) and stored at -20 °C. The crystals formed were washed with *n*-hexane (5 mL) to afford 2,6-Py(CH$_2$CMe$_2$OH)$_2$ (2.10 g, 14 %) as white powder.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.19 (s, 12H, 4CH$_3$); 2.88 (s, 4H, 2CH$_2$); 4.25 (br s, 2H, 2OH); 7.04 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, 2β-Py$_H$); 7.56 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py$_H$). ^{1}H NMR spectrum parameters correspond to those given in the literature.[S3]

^{13}C NMR (δ, ppm, $CDCl_3$): 29.5 (Me); 49.7 (Py*C*H$_2$); 70.7 (*C*Me$_2$); 122.4 (β,β'-Py$_C$); 137.1 (γ-Py$_C$); 158.3 (α-Py$_C$).

c) Stage 3; synthesis of 2-(2-hydroxy-2-methylpropyl)-6-(2-methylprop-1-en-1-yl)pyridine, 2,6-Py(CH=CMe$_2$)CH$_2$CMe$_2$OH (2). A mixture of 2,6-Py(CH$_2$CMe$_2$OH)$_2$ (2.10 g, 9.40 mmol) and concentrated orthophosphoric acid (85 %, 45 mL) was heated at 130 °C for 12 h. Then it was neutralized with 2 M aq. solution of NaOH, extracted with $CHCl_3$ (3x20 mL), and dried over $MgSO_4$. The volatiles were removed under reduced pressure. The residue was subjected to column chromatography to afford two compounds, 2,6-Py(CH=CMe$_2$)CH$_2$CMe$_2$OH (**2**) and 2,6-Py[CH=CMe$_2$]$_2$.

2

Compound ***2,6-Py(CH=CMe$_2$)CH$_2$CMe$_2$OH (2)*** (0.63 g, 36 %) (silica gel, petroleum ether/EtOAc 9:1; R$_f$ 0.2) was isolated as yellowish oil.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.19 (s, 6H, *Me*$_2$C(OH)); 1.91, 2.04 (2s, each 3H, *Me*$_2$C=); 2.87 (s, 2H, CH$_2$); 6.15 (br s, 1H, OH); 6.26 (s, 1H, =C*H*); 6.87, 7.02 (2d, $^3J_{H\text{-}H}$ = 7.7 Hz, each 1H, β,β'-Py$_H$); 7.53 (pt, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 20.0, 27.6 (*Me*$_2$C=); 29.5 (*Me*$_2$C(OH)); 48.4 (Py*C*H$_2$); 70.6 (Me$_2$*C*(OH)); 121.1, 121.6 (β,β'-Py$_C$); 124.3 (*C*=); 136.8 (γ-Py$_C$); 155.9, 158.9 (α,α'-Py$_C$). Signal H*C*= not found due to overlapping with other signals.

Anal. Calcd. for $C_{13}H_{19}NO$ (M$_w$ 205.2961): C 76.06, H 9.33, N 6.82. Found: C 75.86, H 9.14, N 6.72.

2,6-Bis(2-methylprop-1-en-1-yl)pyridine, 2,6-Py[CH=CMe$_2$]$_2$, (0.21 g, 12%) (silica gel, petroleum ether/EtOAc 200:3; R$_f$ 0.2) was isolated as yellow oil.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.92, 2.05 (2s, each 12H, 4Me); 6.33 (br s, 2H, 2C*H*=); 6.95 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, 2β-Py$_H$); 7.52 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, γ-Py$_H$). ^{1}H NMR spectrum parameters correspond to those given in the literature.[S3]

^{13}C NMR (δ, ppm, $CDCl_3$): 19.8, 27.3 (*Me*$_2$C=); 120.5 (β-Py$_C$); 125.4 (Me$_2$*C*=); 135.7 (γ-Py$_C$); 139.8 (=*C*H); 156.5 (α-Py$_C$).

d) Stage 4; synthesis of 2-(2-hydroxy-2-methylpropyl)-6-[2-methyl-2-(S-ethanethioato)propyl]pyridine, 2,6-Py(CH₂CMe₂OH)CH₂CMe₂SC(O)Me. Alkene 2,6-Py(CH=CMe$_2$)CH$_2$CMe$_2$OH **2** (2.22 g, 10.80 mmol) and thioacetic acid (1.95 mL, 27.00 mmol, 2.5 eq.) were dissolved in toluene (10 mL), and this was refluxed for 5 h. The volatiles were removed under reduced pressure giving 2,6-Py(CH$_2$CMe$_2$OH)CH$_2$CMe$_2$SC(O)Me (2.92 g, 96 %) as viscous yellow oil.

^{1}H NMR (δ, ppm, CDCl$_3$): 1.20 (s, 6H, *Me*$_2$C(OH)); 1.45 (s, 6H, *Me*$_2$C(SAc)); 2.24 (s, 3H, *Me*C(O)); 2.87 (s, 2H, C*H*$_2$C(OH)); 3.25 (s, 2H, C*H*$_2$CS); 6.28 (br s, 1H, OH); 6.95-7.03 (m, 2H, β,β'-Py$_H$); 7.52-7.56 (m, 1H, γ-Py$_H$).

MALDI TOF MS, *m/z* (rel. %): 281 ([M]$^+$, 100).

Anal. Calcd. for C$_{15}$H$_{23}$NO$_2$S (M$_w$ 281.4136): C 64.02, H 8.24, N 4.98. Found: C 64.17, H 8.38, N 5.12.

e) Stage 5; synthesis of 2-(2-mercapto-2-methylpropyl)-6-(2-hydroxy-2-methylpropyl)pyridine, 2,6-Py(CH₂CMe₂SH)CH₂CMe₂OH (3). Compound 2,6-Py(CH$_2$CMe$_2$OH)CH$_2$CMe$_2$SC(O)Me (2.33 g, 8.28 mmol) and KOH (2.78 g, 49.68 mmol, 6.0 eq.) were dissolved in ethanol (30 mL). After 1 h, the mixture was carefully neutralized with glacial AcOH (2.90 mL, 52.16 mmol, 6.3 eq.). The volatiles were removed under reduced pressure, the residue was dissolved in CH$_2$Cl$_2$ (50 mL), dried over MgSO$_4$, and then evaporated giving 2,6-Py(CH$_2$CMe$_2$SH)CH$_2$CMe$_2$OH (**3**) (1.74 g, 88 %) as viscous brown oil with typical mercaptane smell.

3

^{1}H NMR (δ, ppm, CDCl$_3$): 1.20 (s, 6H, *Me*$_2$C(OH)); 1.41 (s, 6H, *Me*$_2$C(SH)); 2.88 (s, 2H, C*H*$_2$C(Me$_2$)OH); 3.02 (s, 2H, C*H*$_2$C(Me$_2$)SH); 6.98, 7.13 (2d, $^3J_{H\text{-}H}$ = 7.7 Hz, each 1H, β,β'-Py$_H$); 7.56 (pt, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py$_H$). The signals O*H* and S*H* were not found.

^{13}C NMR (δ, ppm, CDCl$_3$): 29.5 (*Me*$_2$COH); 32.9 (2*Me*$_2$CSH); 44.5, 53.9 (*C*H$_2$C(Me$_2$)); 48.2 (Me$_2$*C*(SH)); 70.8 (Me$_2$*C*(OH)); 122.3, 123.0 (β,β'-Py$_C$); 136.7 (γ-Py$_C$); 157.0, 159.3 (α,α'-Py$_C$).

MS (EI, %): 206 ([M-SH]$^+$, 42), 188 ([M-SH-H$_2$O]$^+$, 74), 165 ([M-Me$_2$CS]$^+$, 55), ([M-H$_2$O-Me$_2$CS]$^+$, 100).

Anal. Calcd. for C$_{13}$H$_{21}$NOS (M$_w$ 239.3769): C 65.23, H 8.84, N 5.85. Found: C 65.11, H 8.92, N 5.77.

2,6-Py(CH₂CH₂CMe₂OH)CH₂CH₂CMe₂SH (4)

a) Stage 1; synthesis of 2-methyl-6-(3-mercapto-3-methylbutyl)pyridine, 2,6-MePy(CH₂CH₂CMe₂SH). Compound was obtained using our original procedure comprising ring-opening of 2,2-dimethylthiirane with lutidinyllithium.[S1]

4

b) Stage 2; synthesis of 2-(3-mercapto-3-methylbutyl)-6-(3-hydroxy-3-methylbutyl)pyridine, 2,6-Py(CH₂CH₂CMe₂OH)CH₂CH₂CMe₂SH (4).

At -40 °C, a solution of *n*-BuLi (2.5 M solution in hexane, 3.29 mL, 8.23 mmol, 2.1 eq.) was added dropwise to a solution of 2,6-MePy(CH$_2$CH$_2$CMe$_2$SH) (0.75 g, 3.84 mmol) in ether (50 mL). The mixture was slowly warmed to room temperature within 1 h. Then it was cooled to -40 °C, and 2,2-dimethyloxirane (0.28 g, 3.90 mmol) was added dropwise. The mixture was slowly warmed to room temperature and was stirred overnight. Saturated aq. solution of NH$_4$Cl (50 mL) was added, the aqueous phase was extracted with CH$_2$Cl$_2$ (3x20 mL), the organic phase was dried over MgSO$_4$, then the volatiles were removed under reduced pressure. The residue was subjected to column

chromatography to afford product **4** (1.23 g, 56 %) as viscous colorless oil (silica gel, petroleum ether/EtOAc 3:1, R_f 0.2).

^{1}H NMR (δ, ppm, $CDCl_3$): 1.26 (s, 6H, 2*Me*$_2$COH); 1.41 (s, 6H, 2*Me*$_2$CSH); 1.74 (s, 1H, SH); 1.89 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, C*H*$_2$C(OH)); 1.94-1.98, 2.87-2.91 (2m, each 2H, 2PyC*H*$_2$); 2.93 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, C*H*$_2$C(SH)); 4.63 (br s, 1H, OH); 6.97 (pd, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, β,β'-Py$_H$); 7.48 (pt, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py$_H$).

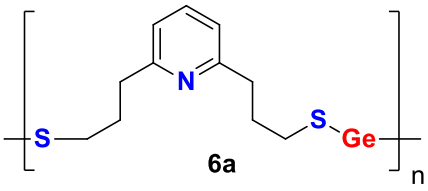
^{13}C NMR (δ, ppm, $CDCl_3$): 29.8 (*Me*$_2$COH); 32.6 (*Me*$_2$CSH); 32.8, 34.1, 41.9, 46.3 (4*C*H$_2$); 44.6 (Me$_2$*C*(SH)); 69.7 (Me$_2$*C*(OH)); 119.8, 120.3 (β,β'-Py$_C$); 137.0 (γ-Py$_C$); 160.9, 161.5 (α,α'-Py$_C$).

Anal. Calcd. for $C_{15}H_{25}NOS$ (M_w 267.4301): C 67.37, H 9.42. Found: C 67.23, H 9.69.

Tetrylene synthesis

General procedure. At -40 °C, a solution of polydentate *SNS*- or *SNO*-ligand (1.00 mmol, 1.0 eq.) in toluene (20 mL) was added dropwise to a solution of Lappert's tetrylene, E[N(SiMe$_3$)$_2$]$_2$ (E = Ge, Sn), (1.00 mmol, 1.0 eq.) in toluene (5 mL). The mixture was slowly warmed to room temperature and stirred overnight.

Poly[(2,6-bis(3-sulfidopropyl)pyridine)germylene], ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]Ge)$_n$ (6a)

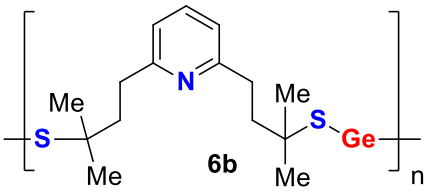


Germylene **6a** was obtained using general procedure from Ge[N(SiMe$_3$)$_2$]$_2$ (0.1967 g, 0.50 mmol) and ligand 2,6-Py(CH$_2$CH$_2$CH$_2$SH)$_2$ (**1**) (0.1137 g, 0.50 mmol). The precipitate formed was filtered off, washed with toluene (2x5 mL) giving ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]Ge)$_n$ (**6a**) (0.1405 g, 94 %) as yellowish powder.

Due to low solubility in common organic solvents ($CDCl_3$, THF-d$_8$, DMSO-d$_6$) NMR spectra of material **6a** could not be registered.

Anal. Calcd. for $C_{11}H_{15}GeNS_2$ (M_w 298.0135): C 44.33, H 5.07, N 4.70. Found: C 43.84, H 5.19, N 4.78.

Poly[(2,6-bis(3-sulfido-3-methylbutyl)pyridine)germylene], ([2,6-Py(CH$_2$CH$_2$CMe$_2$S)$_2$]Ge)$_n$ (6b)

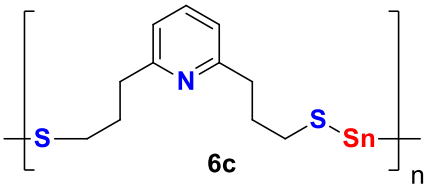


Germylene **6b** was obtained using general procedure from Ge[N(SiMe$_3$)$_2$]$_2$ (0.1652 g, 0.42 mmol) and ligand 2,6-Py(CH$_2$CH$_2$CMe$_2$SH)$_2$ (**1b**) (0.1191 g, 0.42 mmol). The precipitate formed was filtered off, washed with toluene (2x5 mL) giving ([2,6-Py(CH$_2$CH$_2$CMe$_2$S)$_2$]Ge)$_n$ (**6b**) (0.1353 g, 91 %) as yellowish powder.

Due to low solubility in common organic solvents ($CDCl_3$, THF-d$_8$, DMSO-d$_6$) NMR spectra of material **6b** could not be registered.

Anal. Calcd. for $C_{15}H_{23}GeNS_2$ (M_w 354.1198): C 50.88, H 6.55, N 3.96. Found: C 50.43, H 6.38, N 4.12.

Poly[(2,6-bis(3-sulfidopropyl)pyridine)stannylene], ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]Sn)$_n$ (6c)



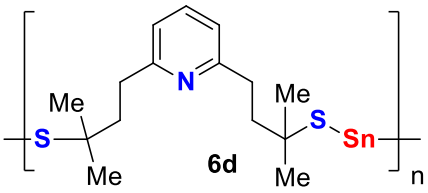
Stannylene **6c** was obtained using general procedure from Sn[N(SiMe$_3$)$_2$]$_2$ (0.2461 g, 0.56 mmol) and ligand 2,6-Py(CH$_2$CH$_2$CH$_2$SH)$_2$ (**1a**) (0.1273 g, 0.56 mmol). The

precipitate formed was filtered off, washed with toluene (2x5 mL) giving ([2,6-Py($CH_2CH_2CH_2S)_2$]Sn)$_n$ (**6c**) (0.1851 g, 96 %) as white powder.

Due to low solubility in common organic solvents ($CDCl_3$, THF-d_8, DMSO-d_6) NMR spectra of material **6c** were not registered.

Anal. Calcd. for $C_{11}H_{15}NS_2Sn$ (M_w 344.0835): C 38.40, H 4.39, N 4.07. Found: C 38.23, H 4.24, N 3.89.

Poly[(2,6-bis(3-sulfido-3-methylbutyl)pyridine)stannylene], ([2,6-Py($CH_2CH_2CMe_2S)_2$]Sn)$_n$ (6d)

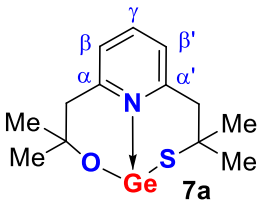


Stannylene **6d** was obtained using general procedure from Sn[$N(SiMe_3)_2$]$_2$ (0.5889 g, 1.34 mmol) and ligand 2,6-Py($CH_2CH_2CMe_2SH)_2$ (**1b**) (0.3799 g, 1.34 mmol). The precipitate formed was filtered off, washed with toluene (2x5 mL) giving ([2,6-Py($CH_2CH_2CMe_2S)_2$]Sn)$_n$ (**6d**) (0.4934 g, 92 %) as yellowish powder.

Due to low solubility in common organic solvents ($CDCl_3$, THF-d_8, DMSO-d_6) NMR spectra of material **6d** were not registered.

Anal. Calcd. for $C_{15}H_{23}NS_2Sn$ (M_w 400.1898): C 45.02 H 5.79, N 3.50. Found: C 44.63, H 5.64, N 3.43.

[2-(2-Sulfido-2-methylpropyl)-6-(2-oxido-2-methylpropyl)pyridine]germylene, [2,6-Py($CH_2CMe_2S)CH_2CMe_2O$]Ge (7a)



Germylene **7a** was obtained using general procedure from Ge[$N(SiMe_3)_2$]$_2$ (0.3952 g, 1.00 mmol) and ligand 2,6-Py($CH_2CMe_2SH)CH_2CMe_2OH$ (**3**) (0.2403 g, 1.00 mmol). The volatiles were removed under reduced pressure giving germylene [2,6-Py($CH_2CMe_2S)CH_2CMe_2O$]Ge (**7a**) (0.2982 g, 96 %) as yellow powder.

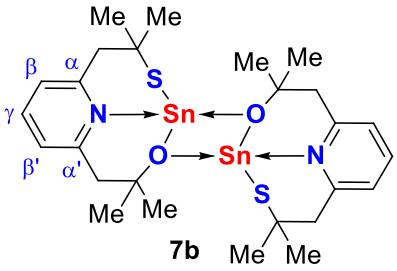
^{1}H NMR (δ, ppm, C_6D_6): 1.05, 1.16, 1.50, 1.74 (4s, each 3H, 4Me); 2.32, 2.40 (2d, $^2J_{H\text{-}H}$ = 14.1 Hz, each 1H, CH_2C(Me_2)O); 2.74, 3.14 (2d, $^2J_{H\text{-}H}$ = 13.9 Hz, each 1H, CH_2C(Me_2)S); 6.25, 6.35 (2d, $^3J_{H\text{-}H}$ = 7.7 Hz, each 1H, β,β'-Py$_H$); 6.84 (br s, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, C_6D_6): 28.3, 34.1, 35.0, 37.3 (2Me_2C); 44.5 (Me_2C(S)); 47.2, 49.0 (2CH_2); 69.7 (Me_2C(O)); 123.5, 124.9 (β,β'-Py$_C$); 138.4 (γ-Py$_C$); 157.4, 157.9 (α,α'-Py$_C$).

MALDI TOF MS, *m/z* (rel. %): 309 ([M-1]$^+$, 100).

Anal. Calcd. for $C_{13}H_{19}GeNOS$ (M_w 310.0011): C 50.37, H 6.18, N 4.52. Found: C 49.84, H 5.93, N 4.24.

[2-(2-Sulfido-2-methylpropyl)-6-(2-oxido-2-methylpropyl)pyridine]stannylene, ([2,6-Py($CH_2CMe_2S)CH_2CMe_2O$]Sn)$_2$ (7b)



Stannylene **7b** was obtained using general procedure from Sn[$N(SiMe_3)_2$]$_2$ (0.3682 g, 0.84 mmol) and ligand 2,6-Py($CH_2CMe_2SH)CH_2CMe_2OH$ (**3**) (0.2002 g, 0.84 mmol). The volatiles were removed under reduced pressure giving stannylene ([2,6-Py($CH_2CMe_2S)CH_2CMe_2O$]Sn)$_2$ (**7b**) (0.2852 g, 95 %) as white powder.

^{1}H NMR (δ, ppm, C_6D_6): 1.21, 1.40, 1.82, 2.08 (4s, each 6H, 8Me); 2.42-2.47 (m, 4H, 2CH_2); 3.30 (d, $^2J_{H\text{-}H}$ = 12.5 Hz, 2H, 2CH(H)); 3.40-3.43 (m, 2H, 2CH(H)); 6.36, 6.44 (2d, $^3J_{H\text{-}H}$ = 7.8 Hz, each 2H, 2β,β'-Py$_H$); 6.95 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, 2γ-Py$_H$).

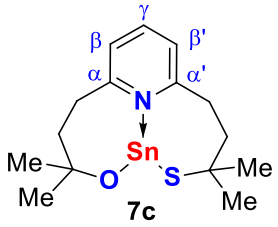
^{13}C NMR (δ, ppm, C_6D_6): 29.6, 34.9, 35.0, 39.6 (2*Me*$_2$C); 45.8 (Me$_2$*C*(S)); 49.8, 52.2 (2*C*H$_2$); 75.6 (Me$_2$*C*(O)); 122.5, 123.7 (β,β'-Py$_C$); 137.0 (γ-Py$_C$); 158.4, 158.6 (α,α'-Py$_C$).

^{119}Sn NMR (δ, ppm, C_6D_6): -228.0 (br s).

MALDI TOF MS, *m/z* (rel. %): 711 ([M-1]$^+$, 100).

Anal. Calcd. for $C_{26}H_{38}N_2O_2S_2Sn_2$ (M_w 712.1399): C 43.85, H 5.38, N 3.93. Found: C 43.56, H 5.22, N 3.78.

[2-(3-Sulfido-3-methylbutyl)-6-(3-oxido-3-methylbutyl)pyridine]stannylene, [2,6-Py(CH$_2$CH$_2$CMe$_2$O)CH$_2$CH$_2$CMe$_2$S]Sn (7c)



7c

Stannylene **7c** was obtained using general procedure from Sn[N(SiMe$_3$)$_2$]$_2$ (0.2032 g, 0.46 mmol) and ligand 2,6-Py(CH$_2$CH$_2$CMe$_2$OH)CH$_2$CH$_2$CMe$_2$SH (**4**) (0.1232 g, 0.46 mmol). The volatiles were removed under reduced pressure giving stannylene [2,6-Py(CH$_2$CH$_2$CMe$_2$O)CH$_2$CH$_2$CMe$_2$S]Sn (**7c**) (0.1691 g, 96 %) as white powder.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.26, 1.65 (2s, each 6H, *Me*$_2$C); 1.80-1.84, 2.12-2.17, 2.78-2.82, 2.92-2.96 (4m, each 2H, 4CH$_2$); 6.91, 7.00 (2d, $^3J_{H\text{-}H}$ = 7.4 Hz, each 1H, β,β'-Py$_H$); 7.42 (pt, $^3J_{H\text{-}H}$ = 7.4 Hz, 1H, γ-Py$_H$).

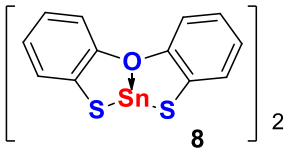
^{13}C NMR (δ, ppm, $CDCl_3$): 29.9, 33.4 (2*Me*$_2$C); 34.0, 34.6, 44.6, 53.2 (4*C*H$_2$); 47.1 (Me$_2$*C*(S)); 73.7 (Me$_2$*C*(O)); 119.6, 128.2 (β,β'-Py$_C$); 136.4 (γ-Py$_C$); 161.2, 162.0 (α,α'-Py$_C$).

^{119}Sn NMR (δ, ppm, $CDCl_3$): 26.3.

MALDI TOF MS, *m/z* (rel. %): 383 ([M-1]$^+$, 100).

Anal. Calcd. for $C_{15}H_{23}NOSSn$ (M_w 384.1242): C 46.90, H 6.04, N 3.65. Found: C 46.52, H 6.12, N 3.48.

[2,2'-Oxybis(benzenethiolato)]stannylene, (O[2-C$_6$H$_4$S]$_2$Sn)$_2$ (8)



8

Stannylene **8** was obtained using general procedure from Sn[N(SiMe$_3$)$_2$]$_2$ (0.5712 g, 0.84 mmol) and ligand O[2-C$_6$H$_4$SH]$_2$ (**5**) (0.1242 g, 0.84 mmol). The precipitate formed was filtered off, washed with toluene (2x5 mL) giving stannylene (O[2-C$_6$H$_4$S]$_2$Sn)$_2$ (**8**) (0.2813 g, 95 %) as white powder.

Stannylene **8** is almost insoluble in common organic solvents (PhMe, $CHCl_3$), sparingly soluble in DMSO.

^{1}H NMR (δ, ppm, DMSO-d$_6$): 6.94-7.03 (m, 12H, Ar$_H$); 7.37-7.41 (m, 4H, Ar$_H$).

^{13}C NMR (δ, ppm, DMSO-d$_6$): 119.8, 123.9, 124.7, 134.0, 155.1 (Ar$_C$). Signal of one quaternary Ar$_C$ was not found.

^{119}Sn NMR (δ, ppm, DMSO-d$_6$): 51.3.

MALDI TOF MS, *m/z* (rel. %): 701 ([M-1]$^+$, 100).

Anal. Calcd. for $C_{24}H_{16}O_2S_4Sn_2$ (M_w 702.0604): C 41.06, H 2.30. Found: C 41.22, H 2.11.

Bromination of germylene ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]Ge)$_n$ (6a)

At 0 ^{o}C, bromine (0.06 g, 20 µL, 0.37 mmol) was added to a suspension of ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]Ge)$_n$ (**6a**) (0.1012 g, 0.34 mmol) in ether (20 mL). The mixture was discolored. After stirring for 2 days, the volatiles were removed under reduced pressure giving ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]GeBr$_2$)$_n$ as grey powder.

Due to low solubility in common organic solvents ($CDCl_3$, THF-d$_8$, DMSO-d$_6$) NMR spectra of dibromide ([2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]GeBr$_2$)$_n$ could not be registered.

Anal. Calcd. for $C_{11}H_{15}Br_2GeNS_2$ (M_w 457.8215): C 28.86, H 3.30, N 3.06. Found: C 27.44, H 3.02, N 2.74.

NMR spectra of the compounds obtained

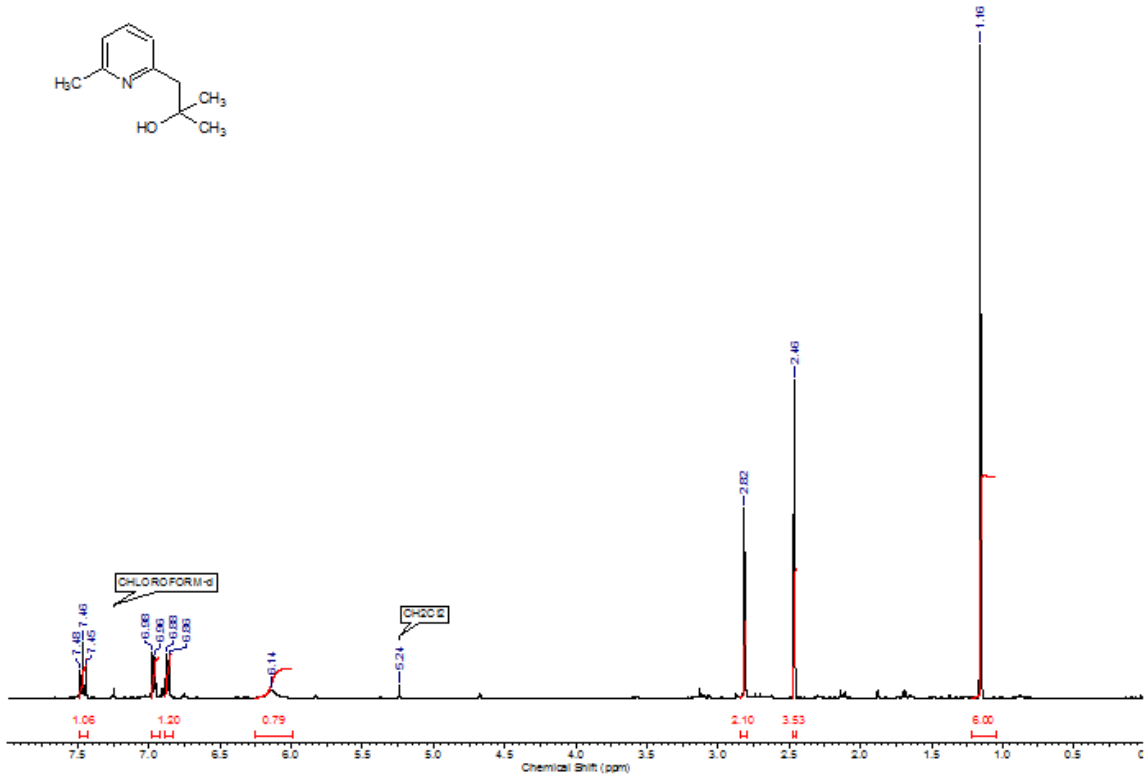


Fig. S1. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-MePy(CH_2CMe_2OH).

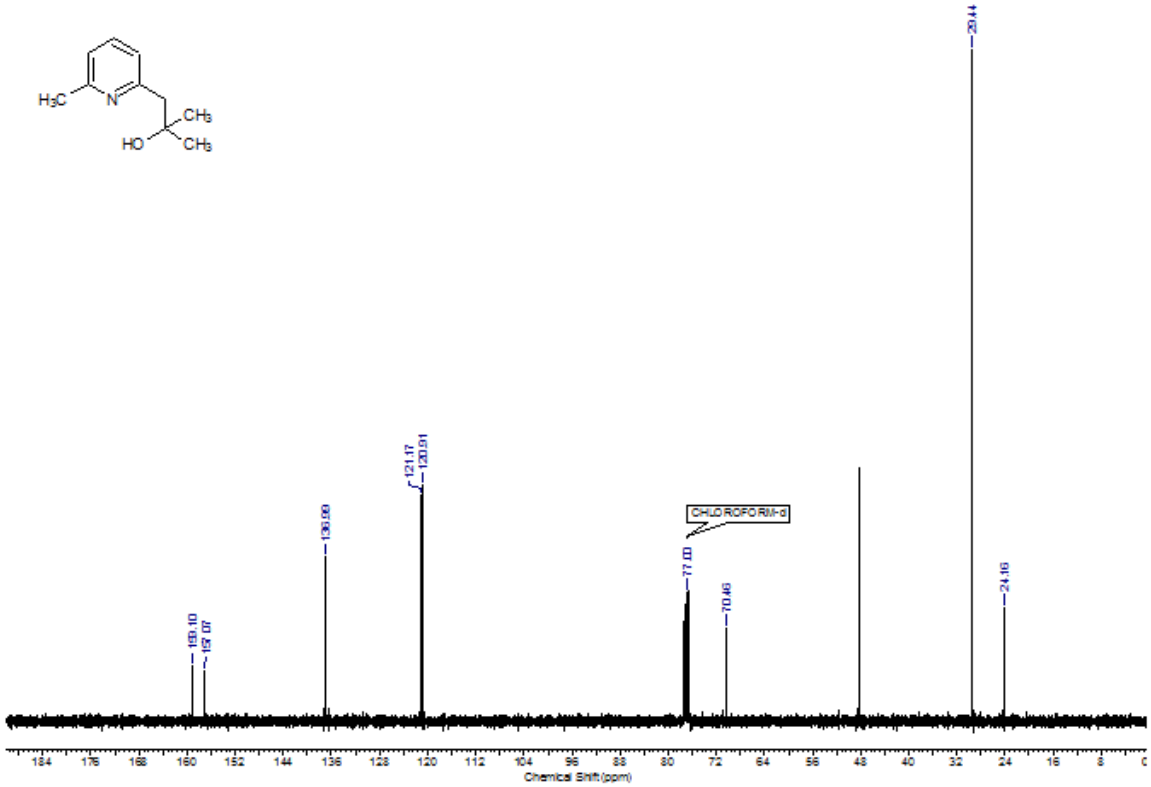


Fig. S2. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-MePy(CH_2CMe_2OH).

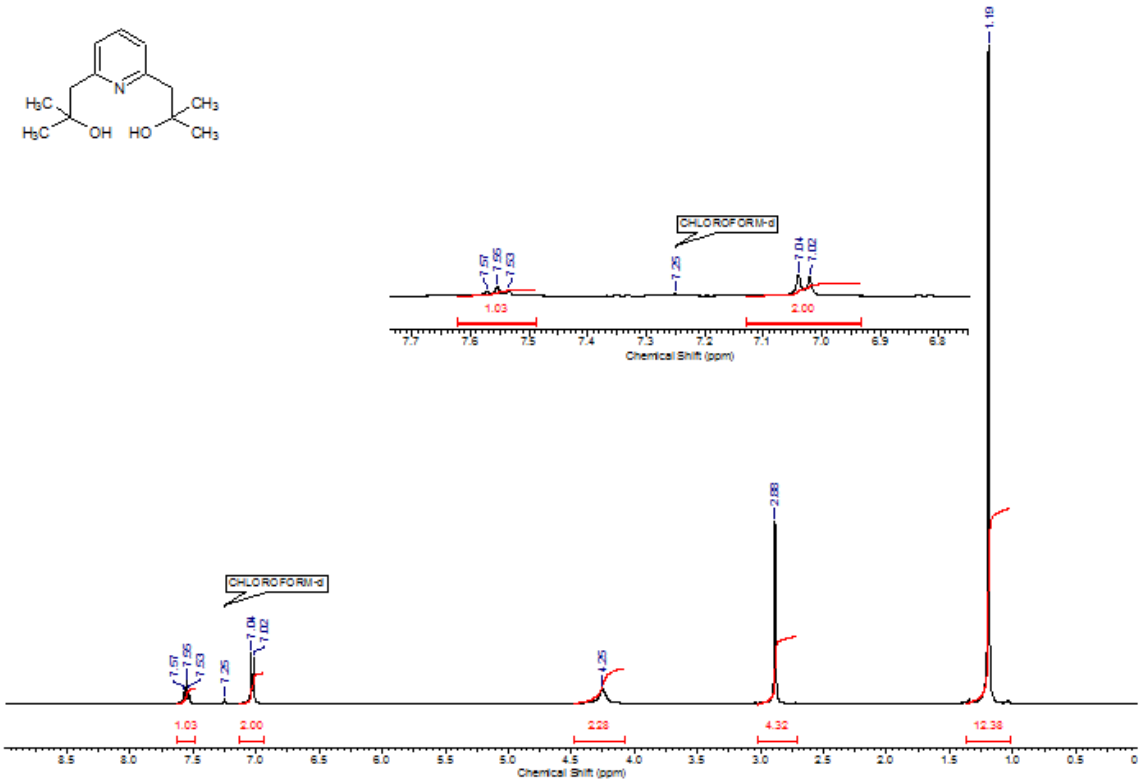


Fig. S3. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH_2CMe_2OH)$_2$.

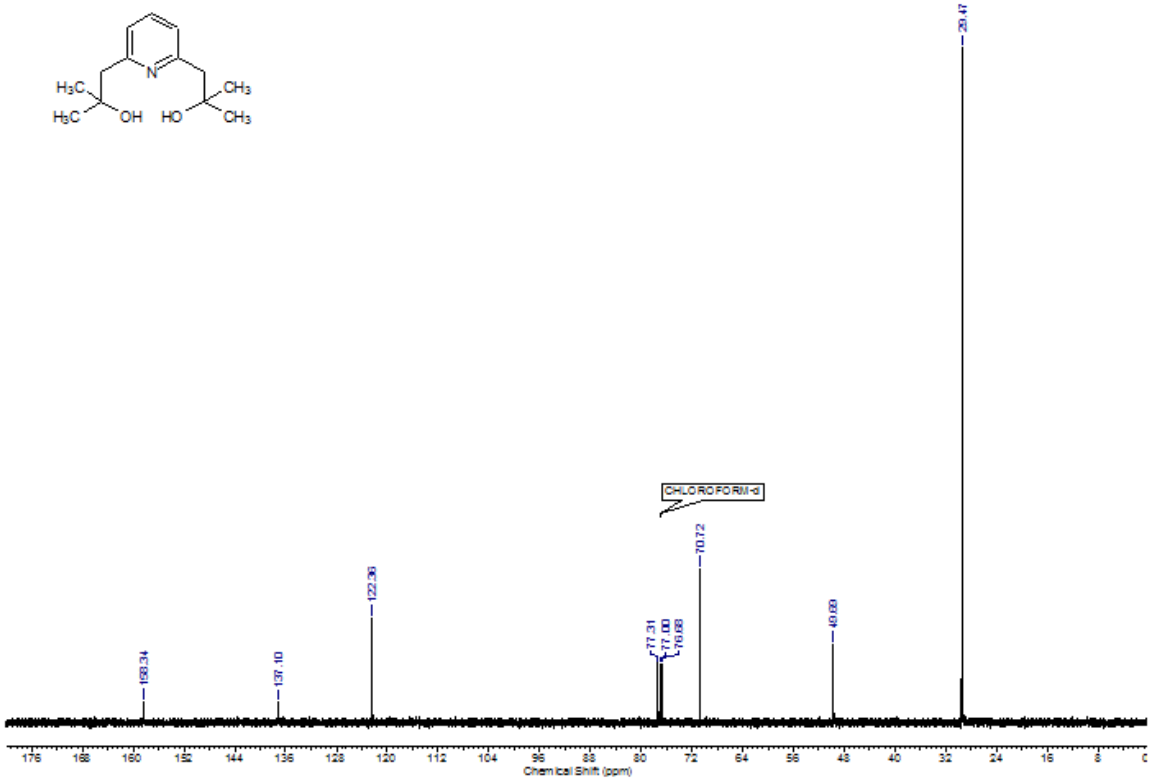


Fig. S4. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH_2CMe_2OH)$_2$.

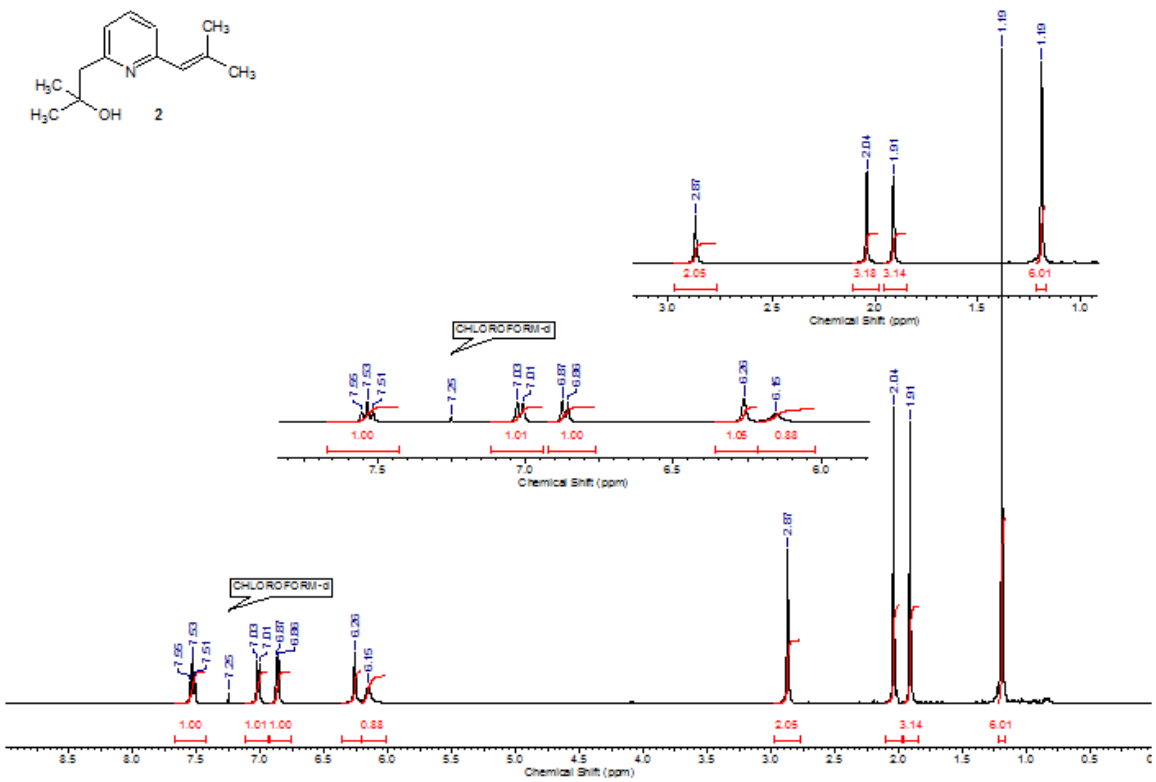


Fig. S5. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH=CMe_2)CH_2CMe_2OH (**2**).

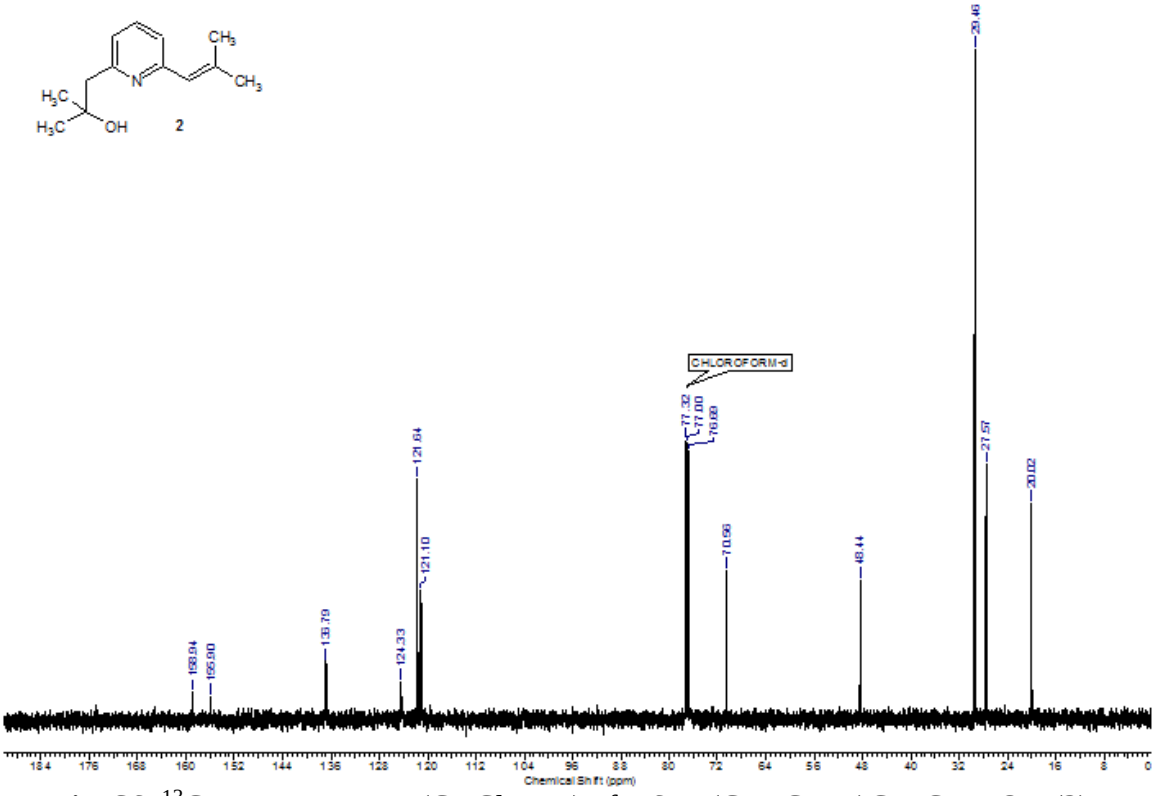


Fig. S6. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH=CMe_2)CH_2CMe_2OH (**2**).

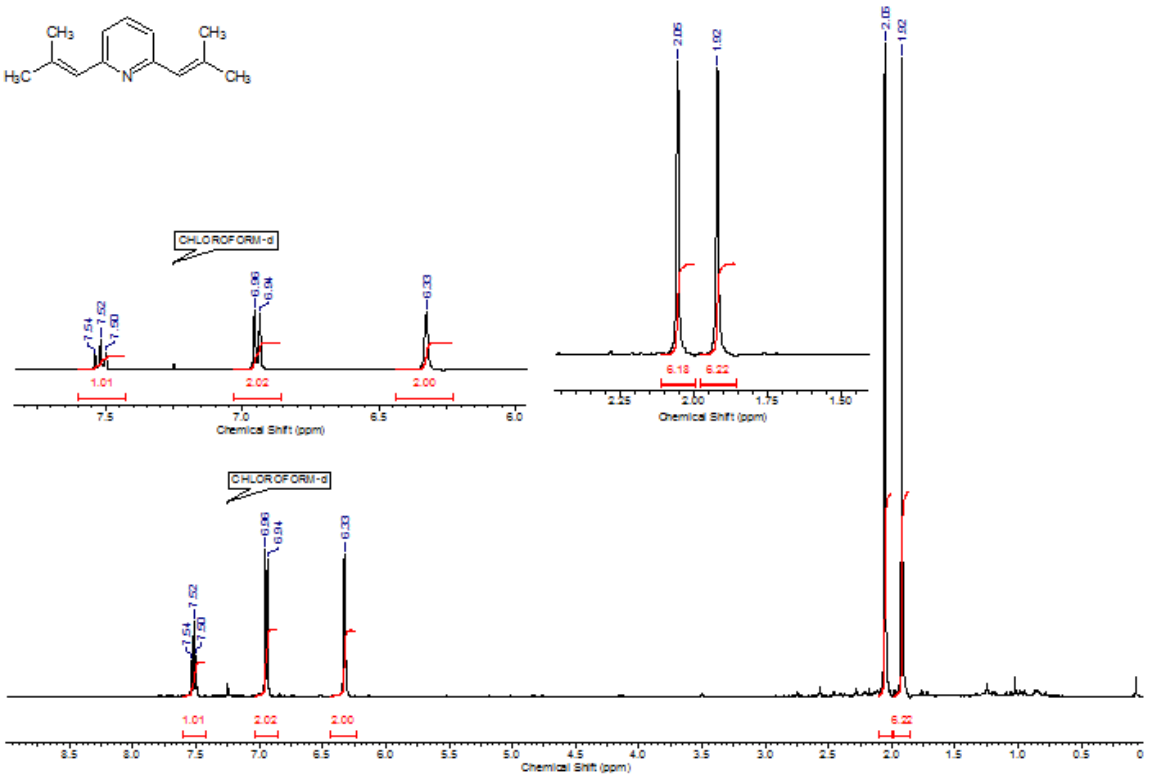


Fig. S7. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py[CH=CMe$_2$]$_2$.

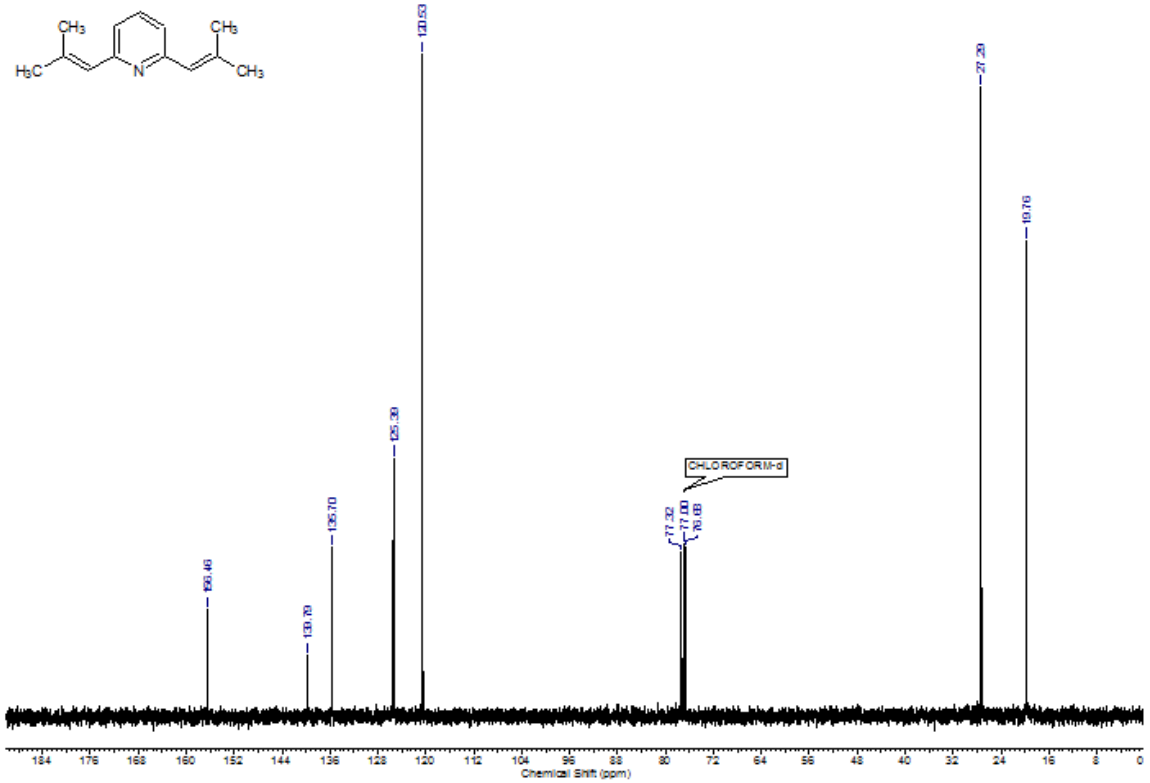


Fig. S8. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py[CH=CMe$_2$]$_2$.

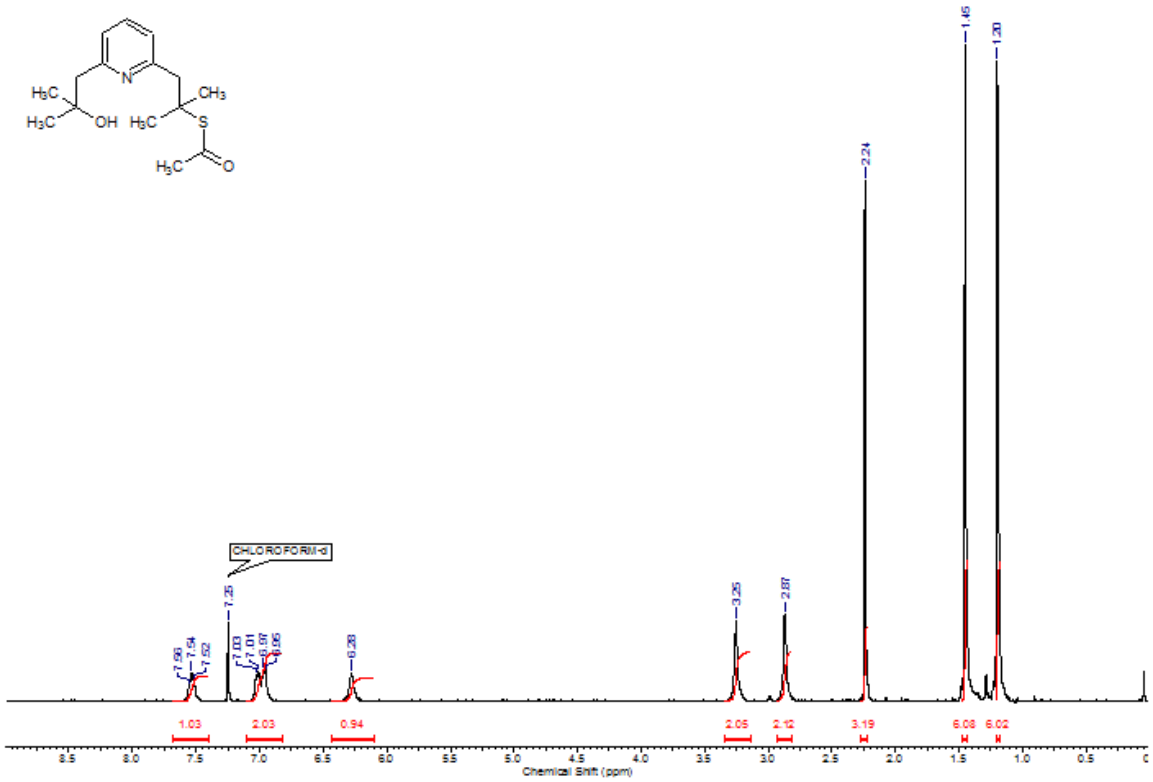


Fig. S9. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH_2CMe_2OH)$CH_2CMe_2SC(O)Me$.

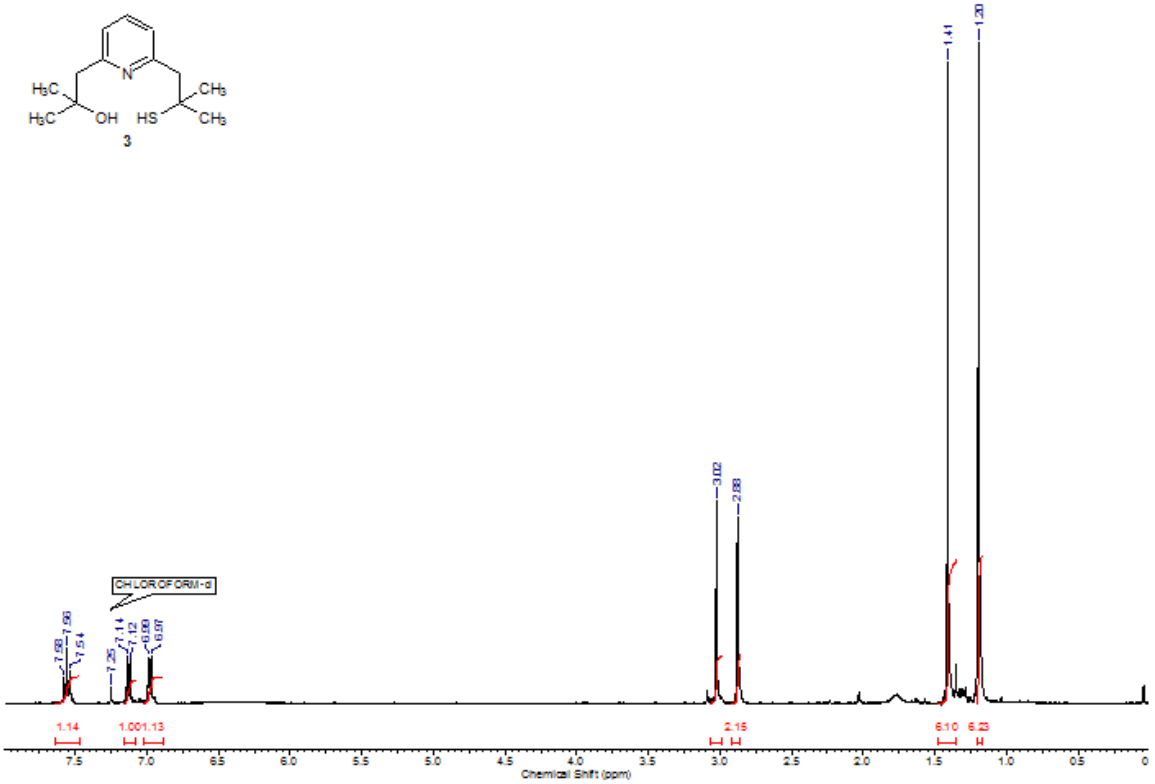


Fig. S10. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH_2CMe_2OH)CH_2CMe_2SH (**3**).

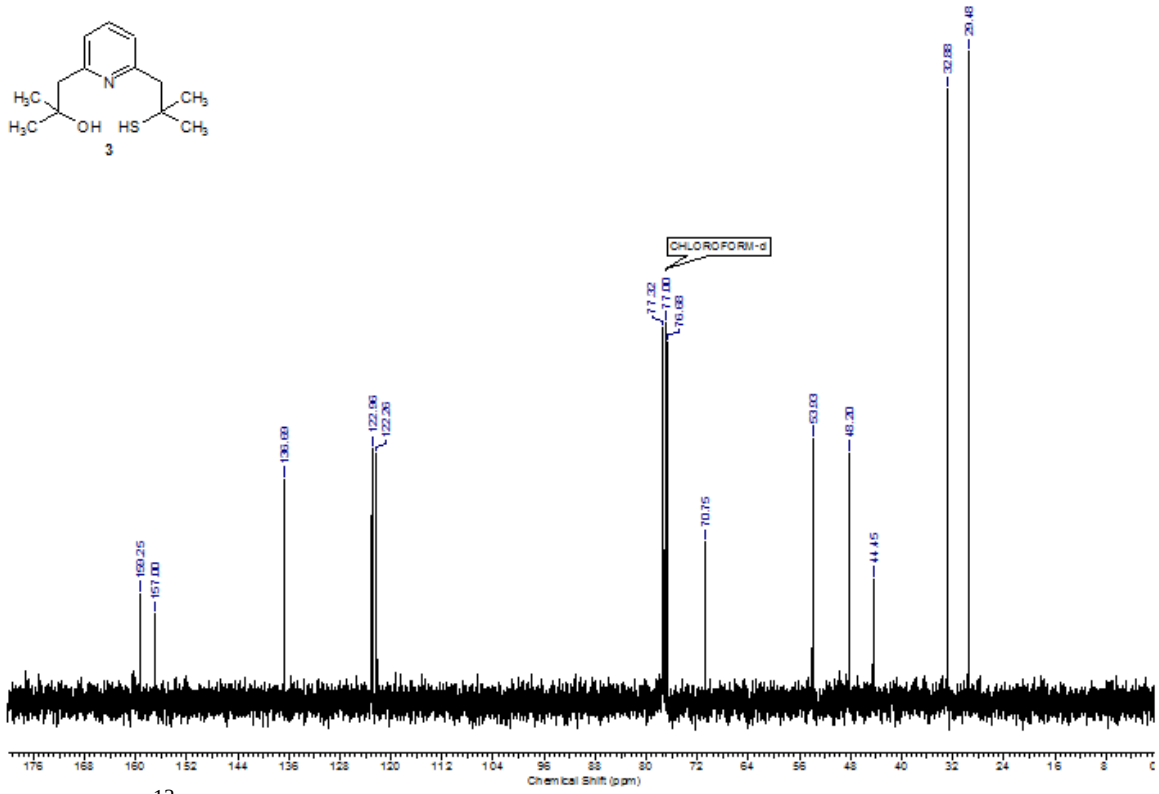


Fig. S11. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py(CH_2CMe_2OH)CH_2CMe_2SH (**3**).

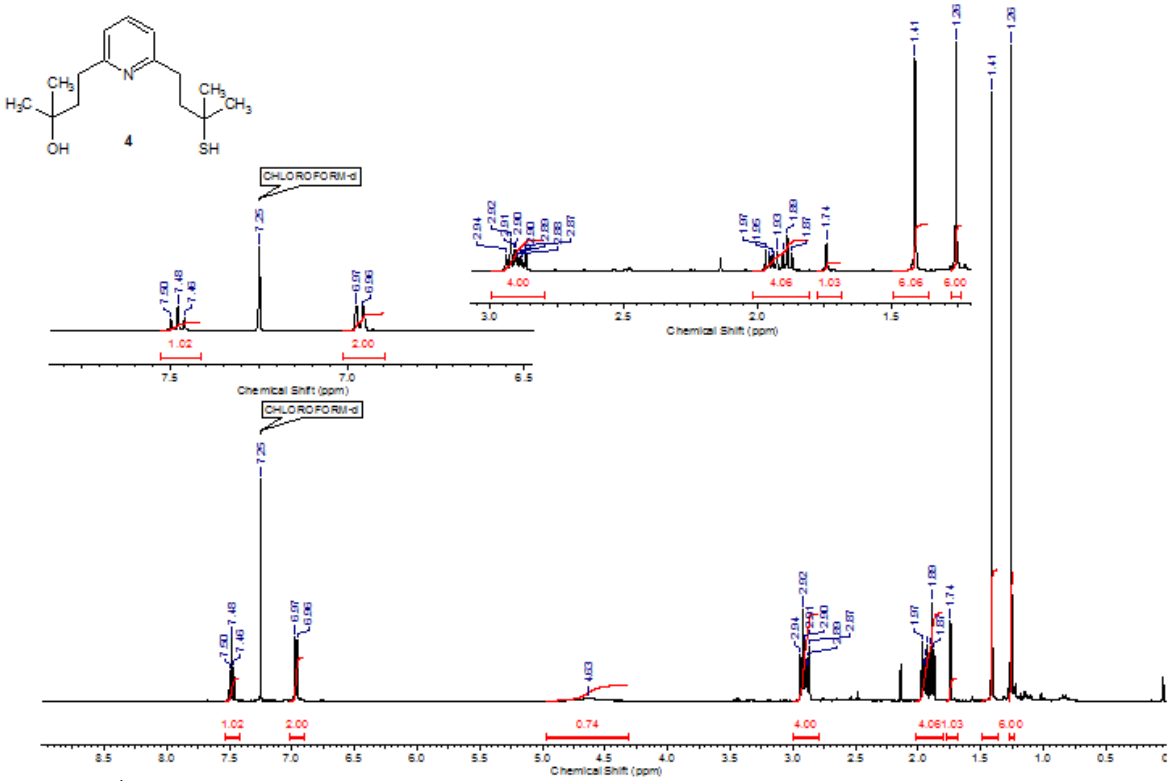


Fig. S12. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CMe_2OH$)$CH_2CH_2CMe_2SH$ (**4**).

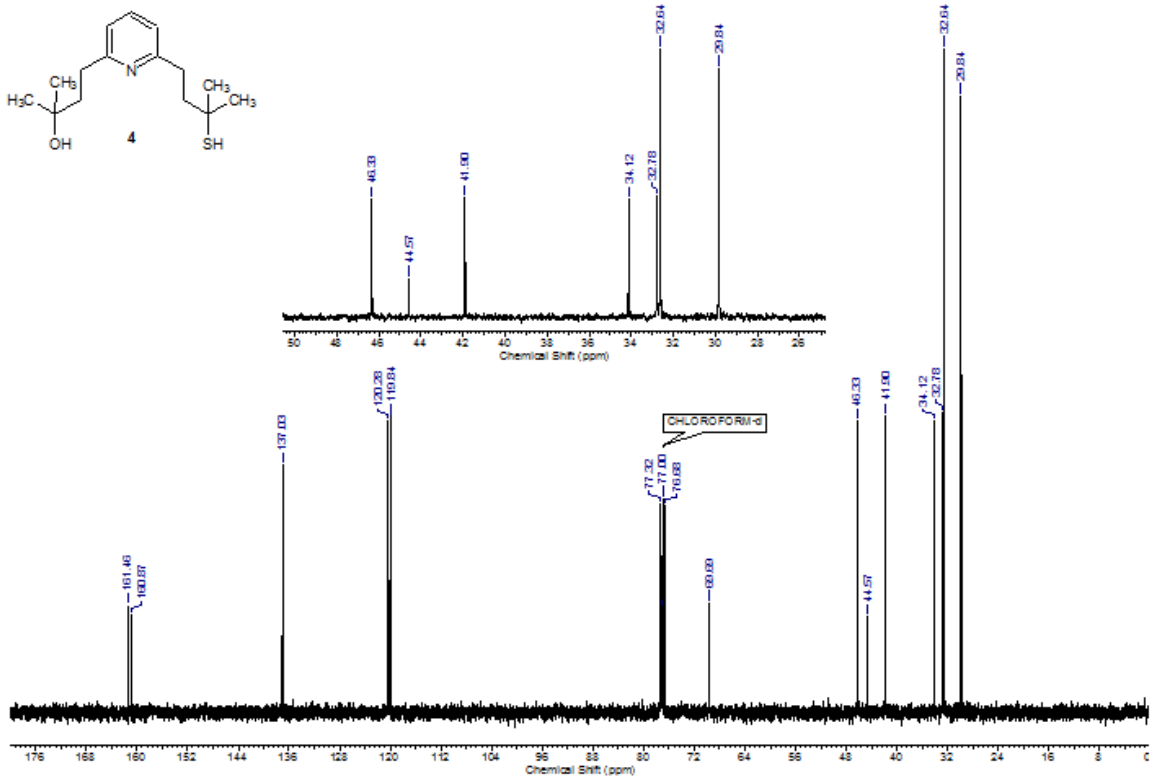


Fig. S13. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CMe_2OH$)$CH_2CH_2CMe_2SH$ (**4**).

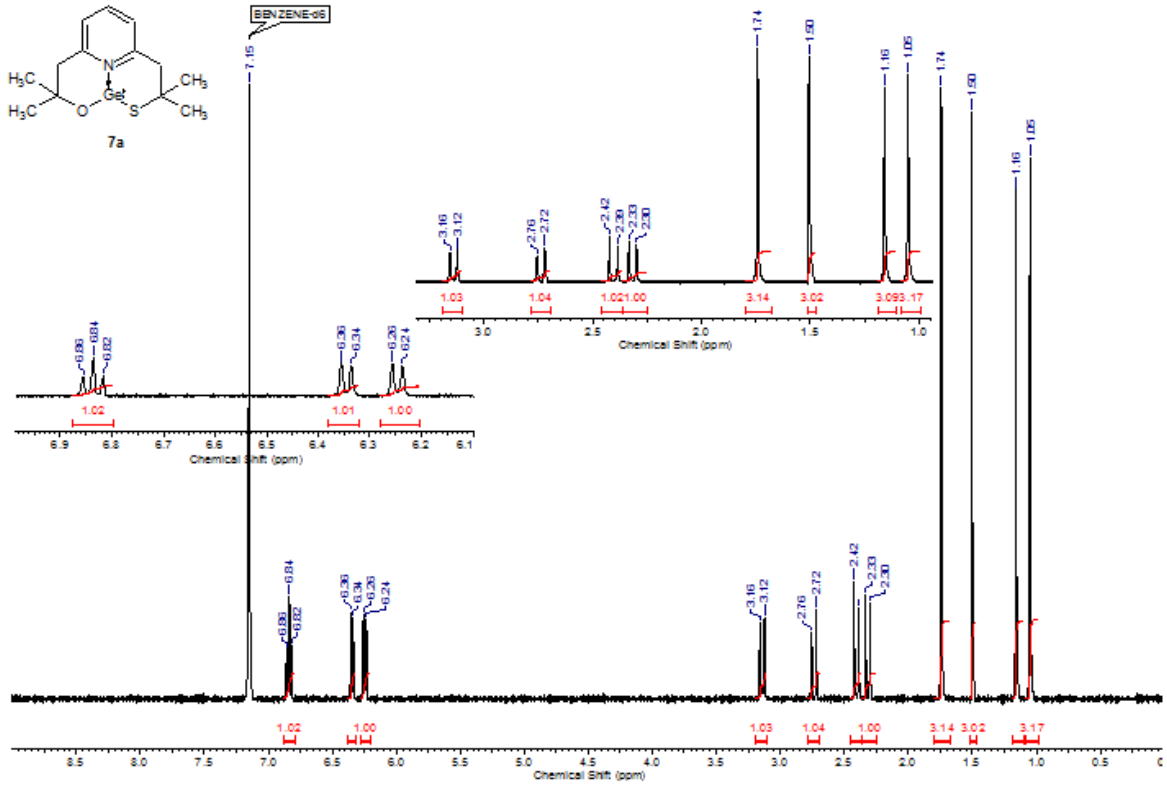


Fig. S14. ^{1}H NMR spectrum (C_6D_6, RT) of [2,6-Py(CH_2CMe_2S)CH_2CMe_2O]Ge (**7a**).

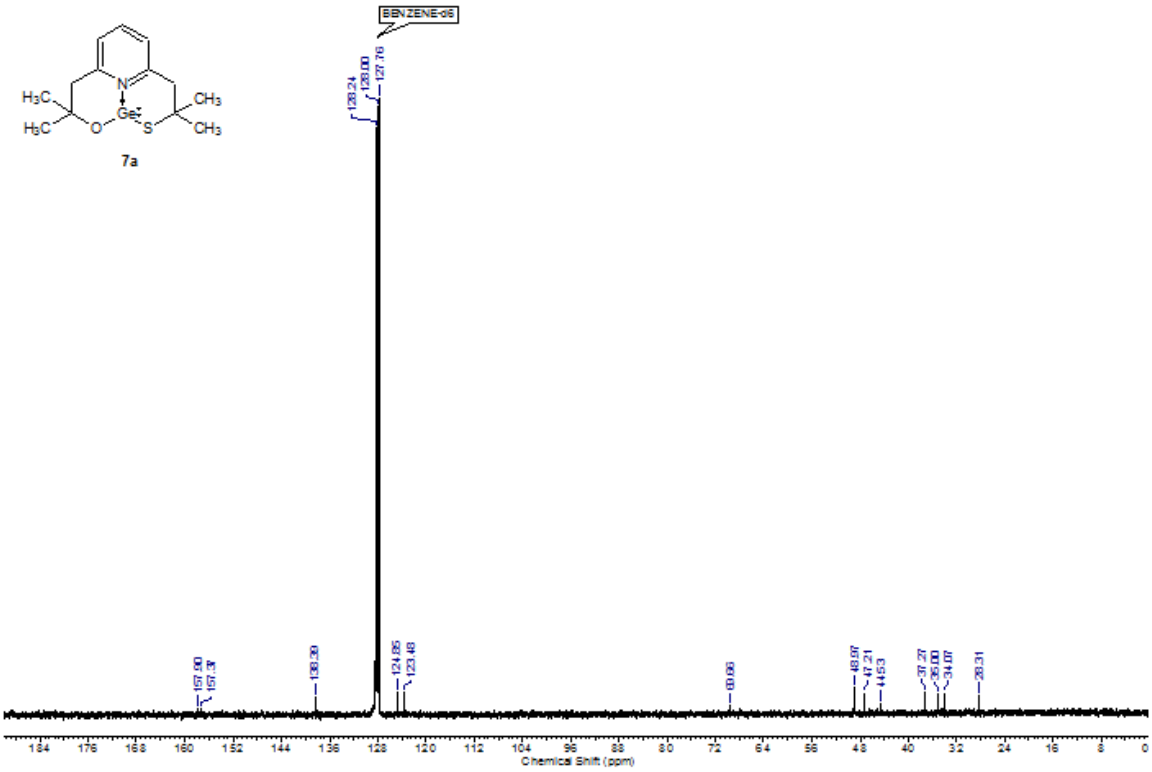


Fig. S15. ^{13}C NMR spectrum (C_6D_6, RT) of [2,6-Py(CH_2CMe_2S)CH_2CMe_2O]Ge (**7a**).

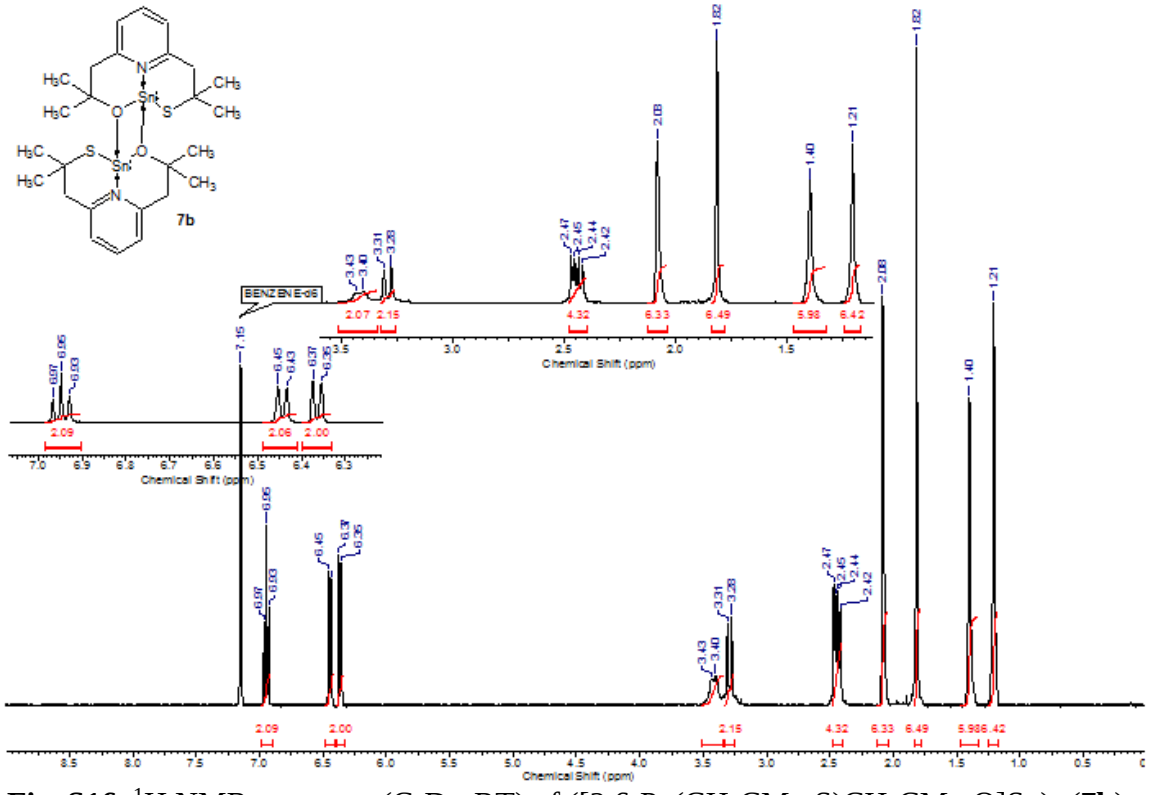


Fig. S16. ^{1}H NMR spectrum (C_6D_6, RT) of ([2,6-Py(CH_2CMe_2S)CH_2CMe_2O]Sn)$_2$ (**7b**).

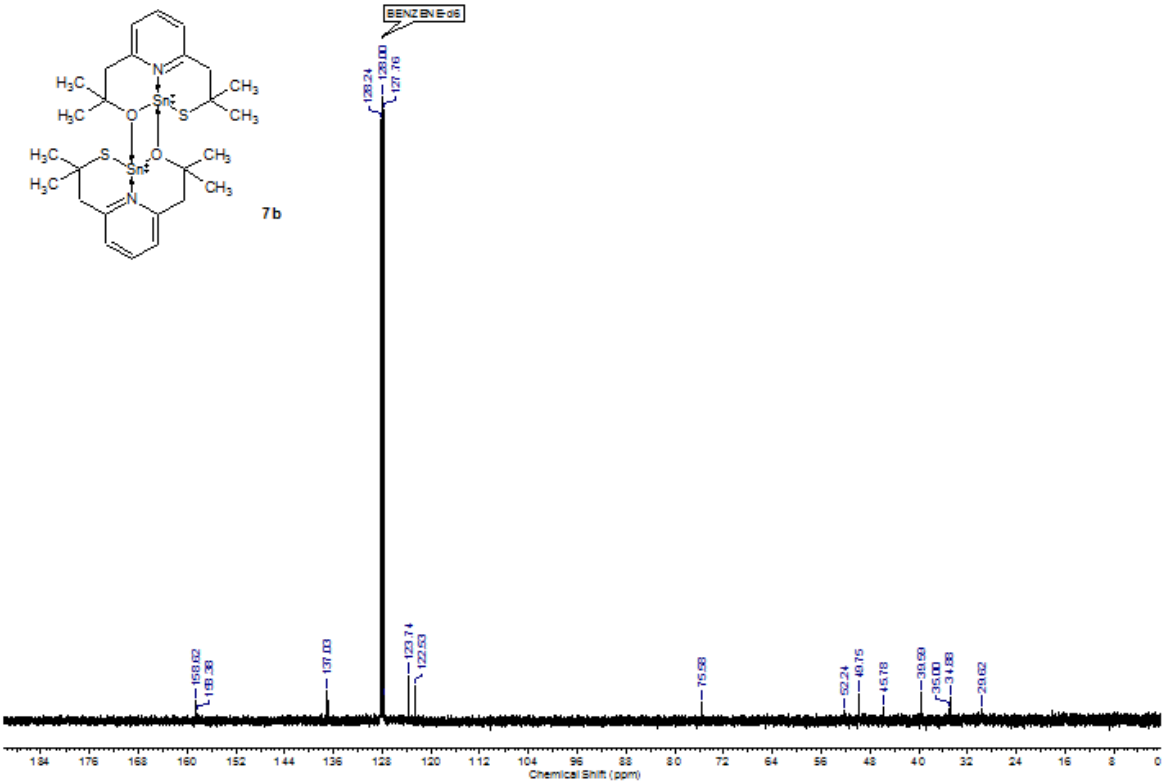


Fig. S17. ^{13}C NMR spectrum (C_6D_6, RT) of ([2,6-Py(CH_2CMe_2S)CH_2CMe_2O]Sn)$_2$ (**7b**).

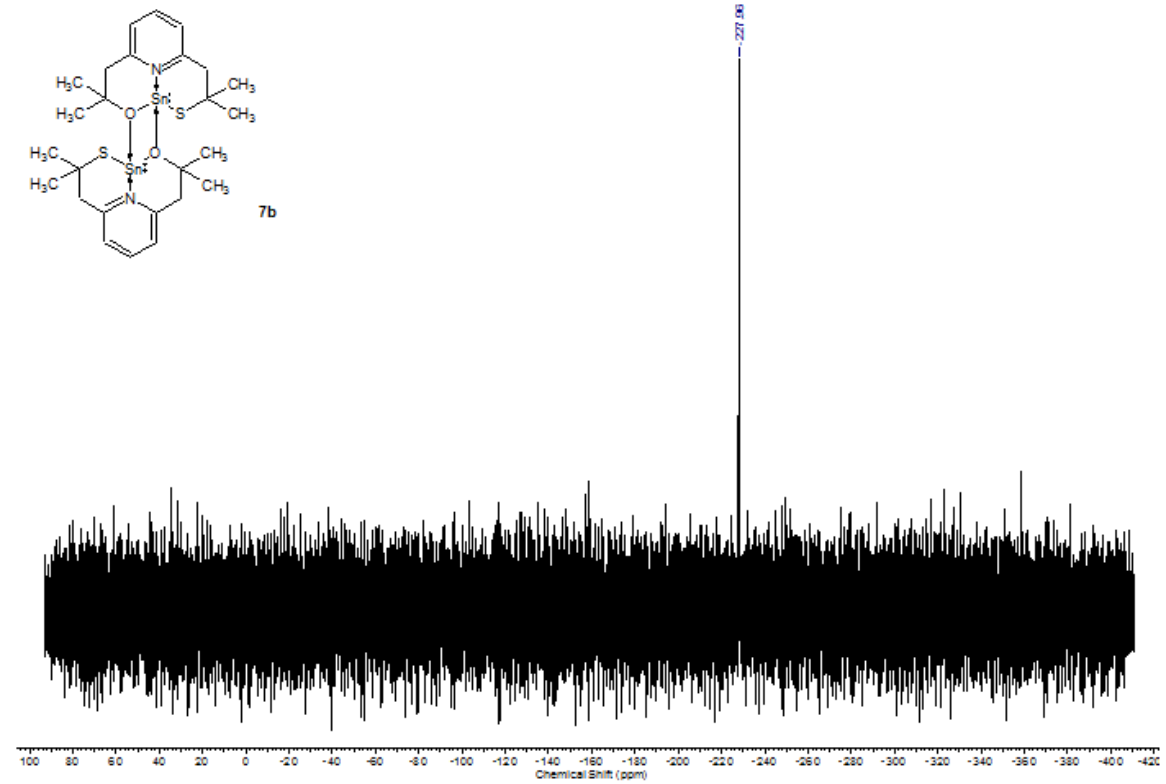


Fig. S18. ^{119}Sn NMR spectrum (C_6D_6, RT) of ([2,6-Py(CH_2CMe_2S)CH_2CMe_2O]Sn)$_2$ (**7b**).

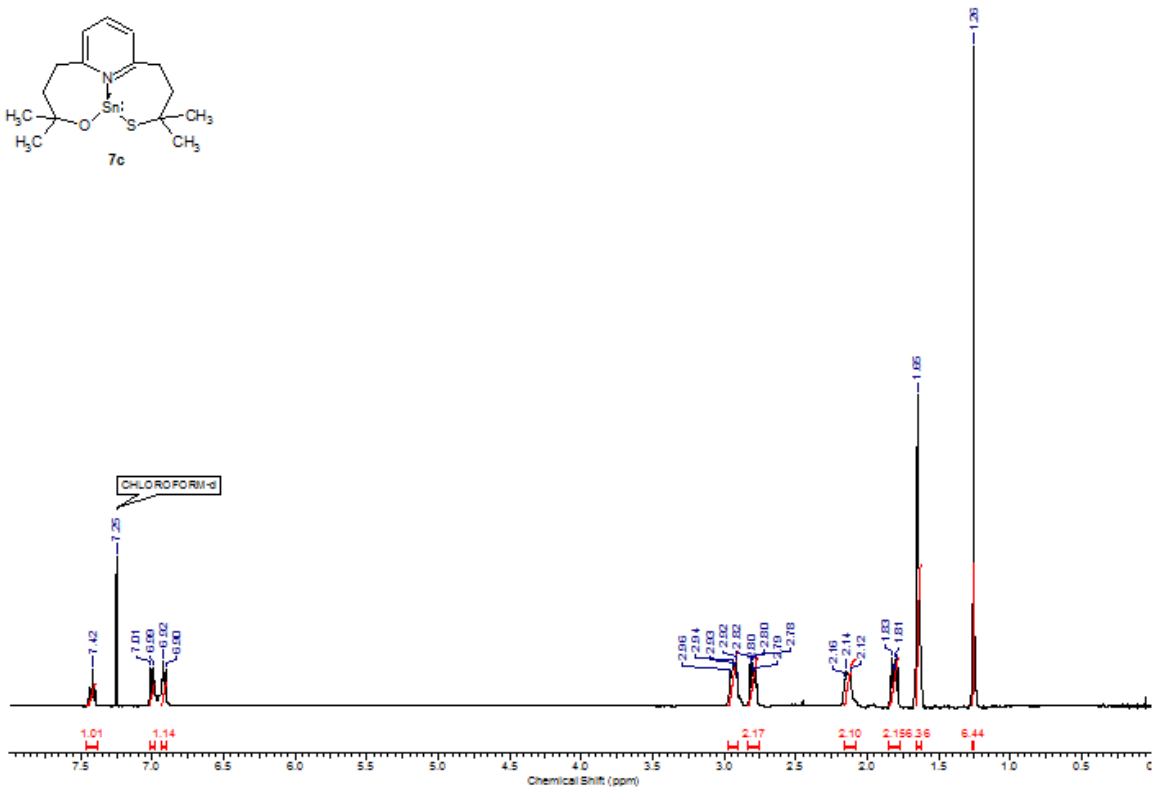


Fig. S19. ^{1}H NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CMe_2O$)$CH_2CH_2CMe_2S$]Sn (**7c**).

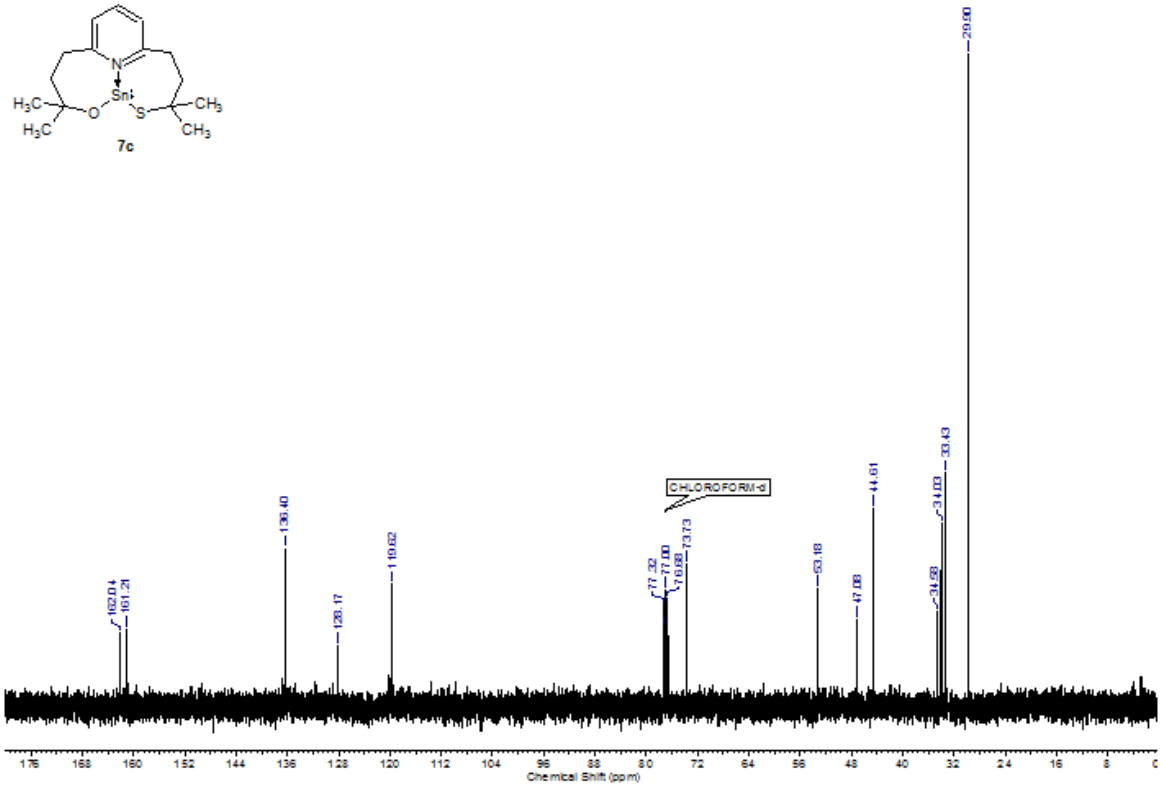


Fig. S20. ^{13}C NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CMe_2O$)$CH_2CH_2CMe_2S$]Sn (**7c**).

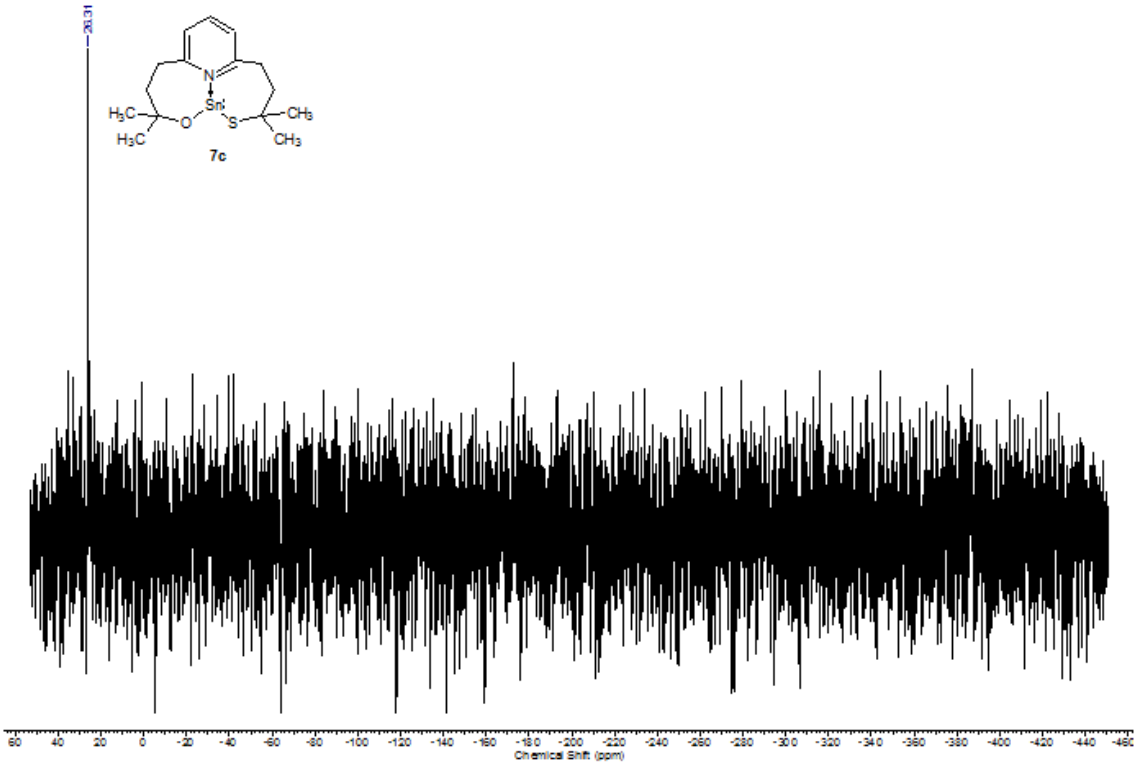


Fig. S21. ^{119}Sn NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CMe_2O$)$CH_2CH_2CMe_2S$]Sn (**7c**).

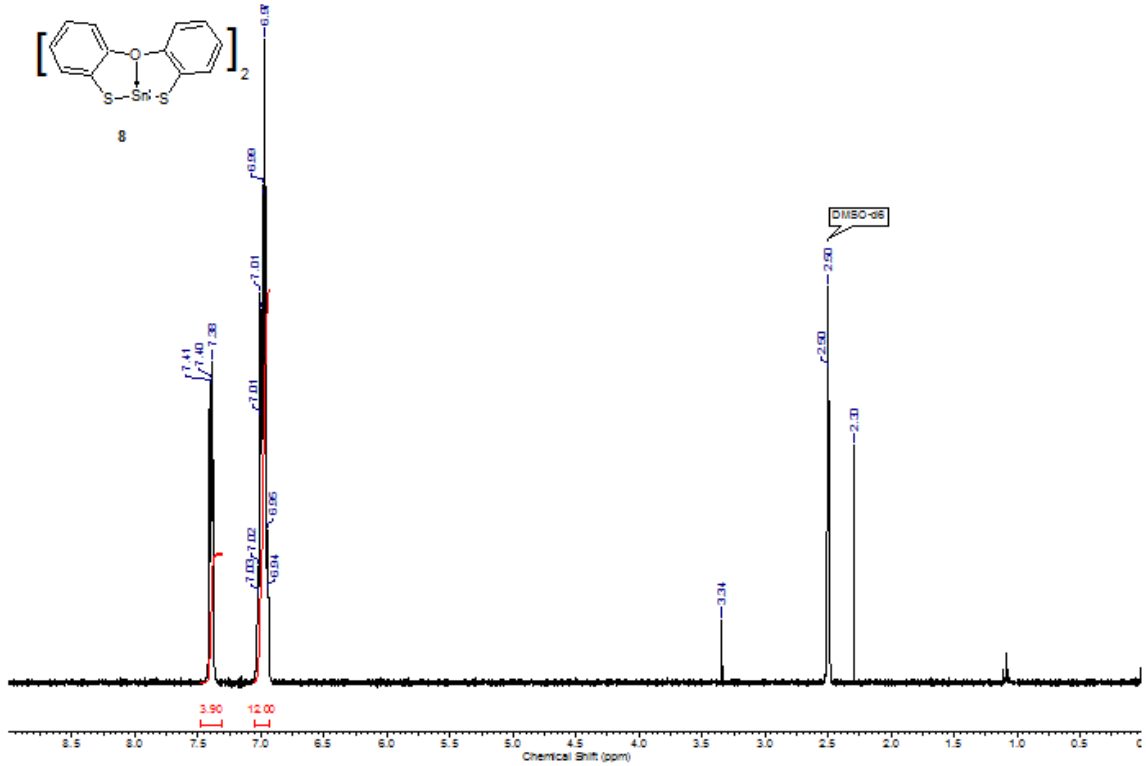


Fig. S22. ^{1}H NMR spectrum (DMSO-d6, RT) of $(O[2\text{-}C_6H_4S]_2Sn)_2$ (**8**).

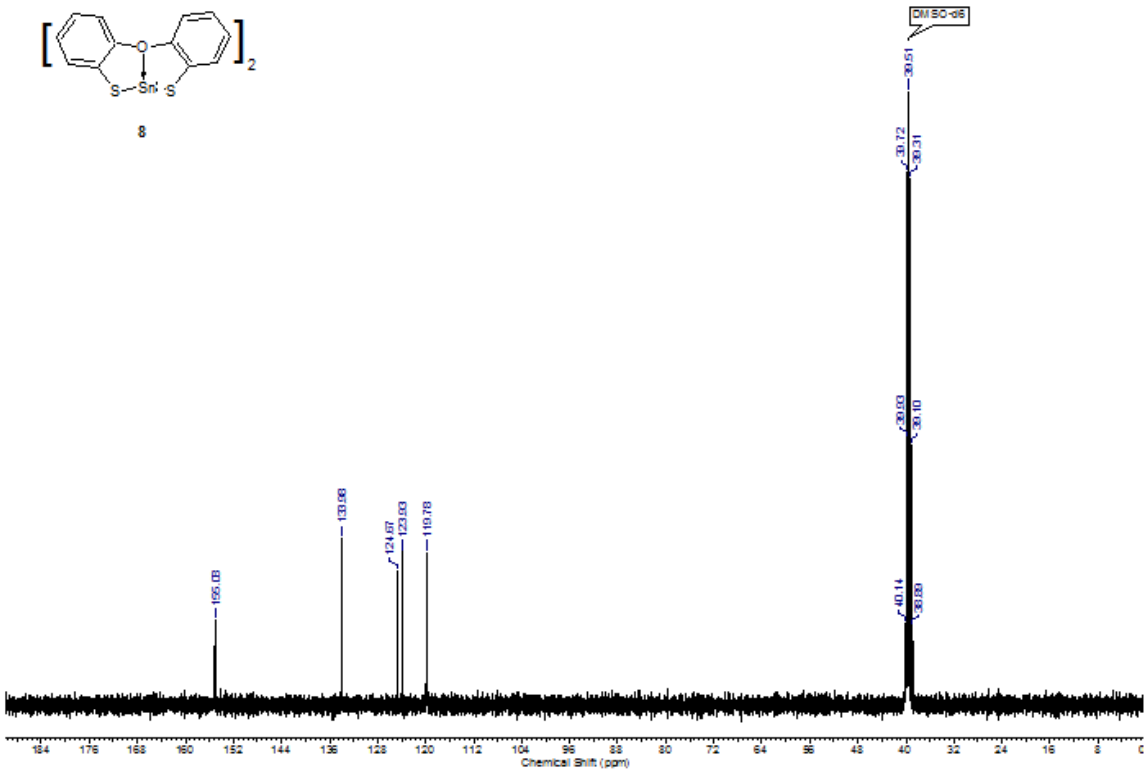


Fig. S23. ^{13}C NMR spectrum (DMSO-d6, RT) of (O[2-C_6H_4S]$_2$Sn)$_2$ (**8**).

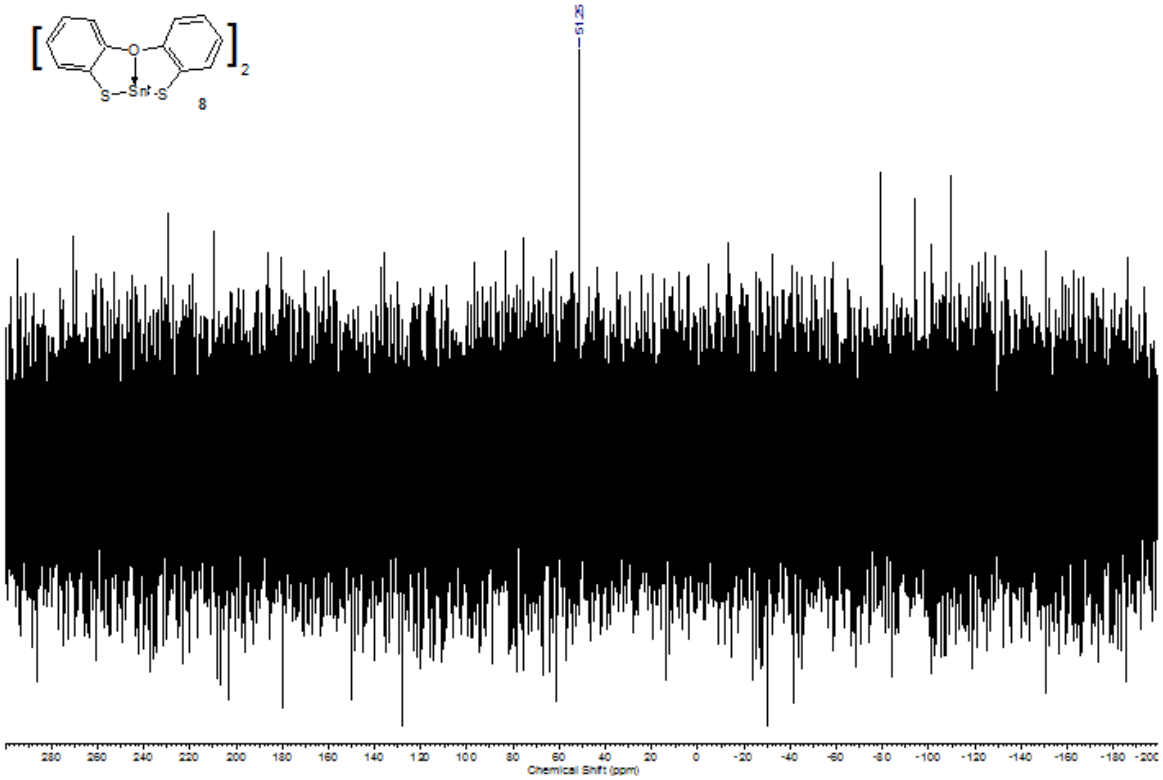
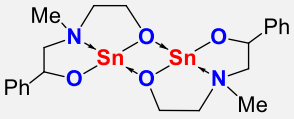
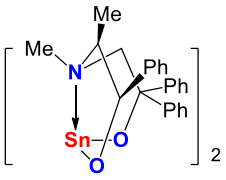
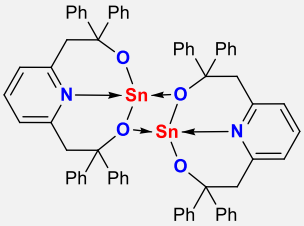
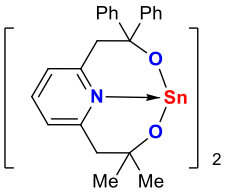
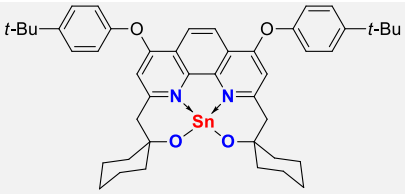
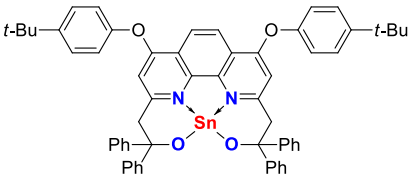
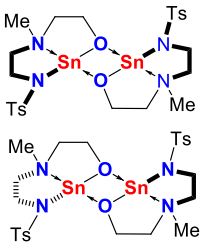
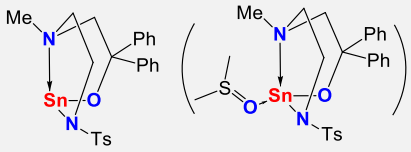
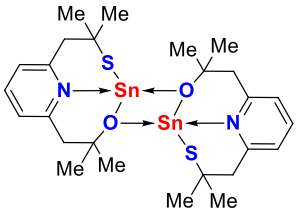
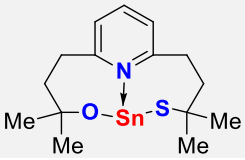
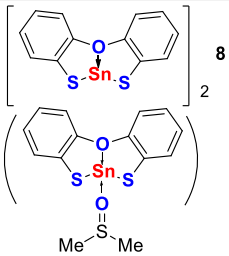


Fig. S24. ^{1}H NMR spectrum (DMSO-d6, RT) of (O[2-C_6H_4S]$_2$Sn)$_2$ (**8**).

Table S1. Selected stannylenes studied by ^{119}Sn NMR spectroscopy.

stannylene [a]	coordination type[b]	structure in solid state (XRD), reference	chemical shift ^{119}Sn NMR, δ, ppm	conditions (solvent, temperature)	reference (NMR)
t-BuN(CH$_2$CH$_2$S)$_2$Sn	*SNS*, monomer	*SNSS*, dimer[S4]	198.7	C_6D_6, 301 K	S5
			140.1	Py-d5, 301 K	
			188.3	CD_2Cl_2, 301 K	
			55.1, -30.3	CD_2Cl_2, 193 K	
MeN(CH$_2$CH$_2$S)$_2$Sn	*SNS*, monomer		91.2	Py-d5, 301 K	S5
			45.4	CD_2Cl_2, 301 K	
			-20.5	CD_2Cl_2, 193 K	
O(CH$_2$CH$_2$S)$_2$Sn	*SOS*, monomer		82.2	Py-d5, 301 K	S5
S(CH$_2$CH$_2$S)$_2$Sn	*SSS*, monomer		65.8	Py-d5, 301 K	S5
t-BuP(CH$_2$CH$_2$S)$_2$Sn	*SPS*, monomer		-238	C_6D_6	S6
PhP(CH$_2$CH$_2$S)$_2$Sn	*SPS*, monomer	*SPS*, monomer[S7]	-113.6	Py-d5, 30 °C	S7
MeN(CH$_2$CH$_2$CH$_2$S)$_2$Sn	*SNS*, monomer		216.0	C_6D_6	S8
	SNNS, monomer [c]		111.0 [c]	Py-d5	
(Me$_2$NCHCMe$_2$S)$_2$Sn	*SNS*, monomer [d]	*SNNS*, monomer[S9]	177.6	C_6D_6	S9
[*t*-BuN(CH$_2$CH$_2$O)$_2$Sn]$_2$	*ONOO*, dimer		-271	$CDCl_3$	S10
[MeN(CH$_2$CH$_2$O)$_2$Sn]$_2$	*ONOO*, dimer	*ONOO*, dimer[S11; S12]	-303	CD_2Cl_2	S10
(Me$_2$NCH$_2$CH$_2$O)$_2$Sn	*ONNO*, monomer	*ONNO*, monomer[S22]	-309.9	$C_6D_5CD_3$	S13
	*ONOO*, dimer		-304.9 (br)	C_6D_6	S12

	*ONNO*, dimer		-254.3 (br)	C_6D_6	S12
	*ONNO*, dimer	*ONNO*, dimer[S23]	-485.9 (br)	C_6D_6	S14
	*ONNO*, dimer		-443.6 (br)	THF-d8	S14
	*ONNO*, monomer		-320.1	$CDCl_3$	S15
	*ONNO*, monomer		-448.0	C_6D_6	S15
S(CH_2CH_2NBu-*t*)$_2$Sn	*NSN*, monomer		77.6	$C_6D_5CD_3$	S16
	*NNOO*, dimer		-363.0, -379.0	$CDCl_3$	S17

		*NNOO*, monomer[c]	-310.0	DMSO-d6	S17
	**7b**	*SNOO*, dimer	-228.0	C_6D_6	**this work**
	**7c**	*SNO*, monomer	26.3	$CDCl_3$	**this work**
	**8**	*SOOS*, monomer [c]	51.3	DMSO-d6	**this work**

[a] NMR spectra were recorded at room temperature (RT, 298 K), unless otherwise stated;
[b] donor coordinated atom is underlined;
[c] coordination with a solvent;
[d] Sn←N coordination bond cleavage and recoordination is observed

References

S1. A. I. Fedulin, A. V. Churakov and K. V. Zaitsev, *Mendeleev Commun.*, 2021, **31**, 847.

S2. J. G. Alvarado-Rodríguez, N. Andrade-López, S. González-Montiel, G. Merino and A. Vela, *Eur. J. Inorg. Chem.*, 2003, **2003**, 3554-3562; doi: 10.1002/ejic.200300199

S3. B. Kaptein, G. Barf, R. M. Kellogg and F. Van Bolhuis, *J. Org. Chem.*, 1990, **55**, 1890-1901; doi: 10.1021/jo00293a039

S4. K. Jurkschat, M. Scheer, A. Tzschach, J. Meunier-Piret and M. Van Meerssche, *J. Organomet. Chem.*, 1985, **281**, 173-180; doi: 10.1016/0022-328X(85)87106-0

S5. A. Tzschach, M. Scheer, K. Jurkschat, A. Zschunke and C. Mügge, *Z. Anorg. Allg. Chem.*, 1983, **502**, 158-164; doi: 10.1002/zaac.19835020720

S6. A. Tzschach and W. Uhlig, *Z. Anorg. Allg. Chem.*, 1981, **475**, 251-255; doi: 10.1002/zaac.19814750427

S7. U. Baumeister, H. Hartung, K. Jurkschat and A. Tzschach, *J. Organomet. Chem.*, 1986, **304**, 107-114; doi: https://doi.org/10.1016/S0022-328X(00)99679-7

S8. A. Tzschach, K. Jurkschat and M. Scheer, *Z. Anorg. Allg. Chem.*, 1983, **507**, 196-198; doi: 10.1002/zaac.19835071224

S9. J.-H. Park, S. G. Kang, Y. K. Lee, T.-M. Chung, B. K. Park and C. G. Kim, *Inorg. Chem.*, 2020, **59**, 3513-3517; doi: 10.1021/acs.inorgchem.9b03369

S10. A. Zschunke, C. Mügge, M. Scheer, K. Jurkschat and A. Tzschach, *J. Crystallogr. Spectrosc. Res.*, 1983, **13**, 201-210; doi: 10.1007/BF01161514

S11. T. Berends, L. Iovkova, G. Bradtmöller, I. Oppel, M. Schürmann and K. Jurkschat, *Z. Anorg. Allg. Chem.*, 2009, **635**, 369-374; doi: 10.1002/zaac.200800434

S12. M. Huang, M. M. Kireenko, E. K. Lermontova, A. V. Churakov, Y. F. Oprunenko, K. V. Zaitsev, C. C. Karlov, D. A. Lemenocskii and G. S. Zaitseva, *Butlerov Commun. (in Russ.)*, 2011, **24**, 26-38; doi:

S13. N. N. Zemlyansky, I. V. Borisova, M. G. Kuznetsova, V. N. Khrustalev, Y. A. Ustynyuk, M. S. Nechaev, V. V. Lunin, J. Barrau and G. Rima, *Organometallics*, 2003, **22**, 1675-1681; doi: 10.1021/om020719a

S14. M. Huang, E. K. Lermontova, K. V. Zaitsev, A. V. Churakov, Y. F. Oprunenko, J. A. K. Howard, S. S. Karlov and G. S. Zaitseva, *J. Organomet. Chem.*, 2009, **694**, 3828-3832; doi: 10.1016/j.jorganchem.2009.06.039

S15. B. N. Mankaev, K. V. Zaitsev, G. S. Zaitseva, A. V. Churakov, M. P. Egorov and S. C. Karlov, *Russ. Chem. Bull.*, 2019 **68**, 380-388 doi: 10.1007/s11172-019-2396-4

S16. A. Tzschach, M. Scheer and K. Jurkschat, *Z. Anorg. Allg. Chem.*, 1984, **515**, 147-150; doi: 10.1002/zaac.19845150817

S17. K. V. Zaitsev, V. S. Cherepakhin, A. V. Churakov, A. S. Peregudov, B. N. Tarasevich, M. P. Egorov, G. S. Zaitseva and S. S. Karlov, *Inorg. Chim. Acta*, 2016, **443**, 91-100; doi: 10.1016/j.ica.2015.12.025