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Methylaluminum complexes based on tridentate 2,6-bis(mercaptoalkyl)pyridine S<u>N</u>S-ligands

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Experimental Section

Synthesis of Methylaluminum Complexes (3a-e)
Based on 2,6-Bis(mercaptoalkyl)pyridine *SNS*-Ligands

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 ^{27}Al (104.26 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 external $[Al(H_2O)_6]^{3+}$ (aqueous $Al_2(SO_4)_3$) (for ^{27}Al NMR) standards. In ^{27}Al spectra the broad background signal at 75 ppm is appeared due to NMR tube glass which may be removed using subtracting procedure. 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. Flash chromatography was performed on SiO_2 (0.015-0.040 mm).

Size exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7 column and one precolumn (PL gel 5 μm guard) thermostated at 30 °C. The detection was achieved by differential refractometer. Tetrahydrofuran (THF) was eluted at a flow rate of 1.0 ml min^{-1}. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany).

Solvents were dried using usual procedures. Tetrahydrofuran, diethyl ether were stored over solid KOH and then distilled over sodium/benzophenone. DMSO was refluxed over CaH_2 and then distilled in vacuum. Toluene and *n*-hexane were refluxed and distilled over sodium. Dichloromethane was distilled under CaH_2; $CDCl_3$ was distilled over CaH_2 under argon.

n-BuLi ('Aldrich', 2.5 M solution in hexane), $AlMe_3$ (2.0 M solution in toluene), isobutylene oxide, cycloxene oxide, KSCN were the commercial reagents and were used as received. 2,6-Lutidine ('Aldrich') was distilled from KOH before using. Benzyl alcohol and ε-caprolactone were refluxed and distilled over CaH_2 in vacuum. Dibenzyl ketone was distilled before using.

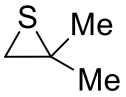
Oxiranes were synthesized by literature procedures (1-oxaspiro[2.5]octane, *cyclo*-$[(CH_2)_5CCH_2O]$[S1]); thiiranes were obtained by known methods (ethylene sulfide, *cyclo*-$[CH_2CH_2S]$;[S2] 2,2-dimethylthiirane, *cyclo*-$[Me_2CCH_2S]$[S3]; 2,2-dibenzylthiirane, *cyclo*-$[CBn_2CH_2S]$[S4]; cycloxene sulfide, *cyclo*-$[(CH_2)_4CHCHS]$[S5]). Known compounds $Me_3SO^+I^-$,[S6] were obtained using literature procedure.

Synthesis of thiiranes

Ethylene sulfide, *cyclo*-$[CH_2CH_2S]$. Obtained using literature procedure from ethylenecarbonate and KSCN.[S2] Yellow liquid; yield 66 %.

^{1}H NMR (δ, ppm, $CDCl_3$): 2.37 (s, 4H, $2CH_2$).

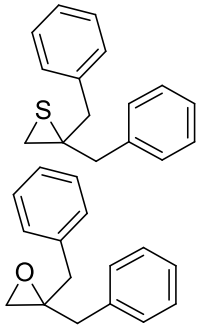
^{13}C NMR (δ, ppm, $CDCl_3$): 18.5 (CH_2).



2,2-Dimethylthiirane, *cyclo*-$[Me_2CCH_2S]$. Obtained using literature procedure from isobutylene oxide and KSCN in water.[S3] Yellowish liquid, b.p. 84-86 °C. Yield 95 %.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.60 (s, 6H, 2Me); 2.38 (s, 2H, CH_2).

^{13}C NMR (δ, ppm, $CDCl_3$): 28.4 (Me); 35.3 (CH_2S); 42.4 (Me_2CS).



2,2-Dibenzylthiirane, *cyclo*-$[Bn_2CCH_2S]$.

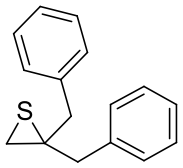
1) Stage 1. **Synthesis of 2,2-dibenzyloxirane, *cyclo*-$[Bn_2CCH_2O]$.** The procedure of Corey-Chaykovsky was used.[S1, 6]

Under argon atmosphere, solid $Me_3SO^+I^-$ (7.39 g, 33.30 mmol) was added portionwise to the suspension of NaH (0.62 g, 26.00 mmol) in DMSO (50 mL) (*Warning! Hydrogen gas evolution is observed!*). The mixture was stirred for 30 min, then solution of dibenzyl ketone (5.05 g, 24.00 mmol) in DMSO was added dropwise for 5 min. The mixture was stirred for 15 min, then it was heated at 60 °C. After cooling to room temperature water (300 mL) was added, the mixture was extracted with ether (3x50 ml). The organic phase was washed with brine (10x50 ml), water (2x50 ml), dried over $MgSO_4$. Then all volatile materials were removed at reduced pressure at room temperature giving 2,2-dibenzyloxirane (5.02 g, 93 %) as orange oil.

^{1}H NMR (δ, ppm, $CDCl_3$): 2.60 (s, 2H, CH_2O); 2.83, 2.89 (2d, $^{2}J_{H\text{-}H}$ = 14.4 Hz, each 2H, CH_2Ph); 7.19-7.24 (m, 4H, Ph_H), 7.26-7.34 (m, 6H, Ph_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 40.2 (CH_2Ph); 51.2 (CH_2O); 59.9 (Bn_2C); 126.6 (p-Ph_C), 128.3, 129.7 (m- and o-Ph_C), 136.8 (*ipso*-Ph_C).

Anal. Calcd. for $C_{16}H_{16}O$ (M_w 224.2976): C 85.68, H 7.19. Found: C 85.54, H 7.04.



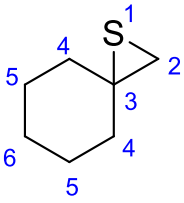
2) Stage 2. **Synthesis of 2,2-dibenzylthiirane, *cyclo*-[Bn_2CCH_2S].** Detailed procedure is given.

2,2-Dibenzyloxirane (4.46 g, 20.00 mmol) was added to a solution of KSCN (3.50 g, 36.00 mmol) in EtOH/water (20:5 ml). The mixture was heated at 60 °C for 20 h. Then all volatile materials were removed under reduced pressure, water (20 ml) was added, and the mixture was extracted with CH_2Cl_2 (3x10 ml). The organic phase was dried over $MgSO_4$, the solvent was removed in vacuum. After flash-chromatography (SiO_2, petroleum ether/EtOAc 20:1, R_f 0.4) *cyclo*-[Bn_2CCH_2S] (3.14 g, 65 %) was isolated as yellow viscous oil.

^{1}H NMR (δ, ppm, $CDCl_3$): 2.54 (s, 2H, CH_2S); 2.93, 3.03 (2d, $^2J_{H\text{-}H}$ = 14.5 Hz, each 2H, CH_2Ph); 7.20-7.25 (m, 4H, Ph_H), 7.26-7.33 (m, 6H, Ph_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 31.8 (CH_2S); 43.9 (CH_2Ph); 49.6 (Bn_2CS); 126.7 (p-Ph_C), 128.2, 129.7 (m- and o-Ph_C), 138.0 (*ipso*-Ph_C).

NMR spectra correspond to literature data.[S4]



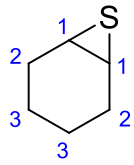
1-Thiaspiro[2.5]octane, *cyclo*-[$(CH_2)_5CCH_2S$].

1-Oxaspiro[2.5]octane, *cyclo*-[$(CH_2)_5CCH_2O$] (8.04 g, 72.00 mmol), was added to a solution of KSCN (16.00 g, 165.00 mmol) in water (15 ml). The two-phase mixture obtained was heated at 50 °C for 30 h. Then the aqueous phase was extracted with ether (4x20 ml), the organic phase was dried over $MgSO_4$, all volatile materials were removed under reduced pressure. The residue was distilled giving *cyclo*-[$(CH_2)_5CCH_2S$] (6.07 g, 66 %) as colorless liquid with typical smell, b.p. 107-108°C/40 Torr.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.37-1.43 (m, 1H, CH(H)), 1.51-1.57 (m, 2H, CH_2), 1.61-1.71 (m, 5H, CH(H), $2CH_2$); 1.84-1.92 (m, 2H, CH_2); 2.36 (s, 2H, CH_2S).

^{13}C NMR (δ, ppm, $CDCl_3$): 25.3 (6-*cyclo*-$[CH_2]_5$); 26.5 (5,5-*cyclo*-$[CH_2]_5$); 33.7 (CH_2S); 38.2 (4,4-*cyclo*-$[CH_2]_5$); 50.7 (3-*cyclo*-$[CH_2]_5$).

Anal. Calcd. for $C_7H_{12}S$ (M_w 128.2352): C 65.56, H 9.43. Found: C 65.48, H 9.56.



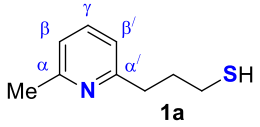
Cycloxene sulfide, *cyclo*-[$(CH_2)_4CHCHS$]. Obtained using literature procedure from cycloxene oxide and KSCN in water/ethanol mixture.[S5]

^{1}H NMR (δ, ppm, $CDCl_3$): 1.19-1.30, 1.48-1.59 (2m, each 2H, 3-CH_2); 2.12-2.19 (m, 4H, 2-CH_2); 3.18-3.21 (m, 2H, 2CHS).

^{13}C NMR (δ, ppm, $CDCl_3$): 19.4 (3,3-*cyclo*-$[CH_2]_4$); 25.8 (2,2-*cyclo*-$[CH_2]_4$); 37.0 (CH).

Synthesis of *SNS*-ligands by thiirane ring-opening by nucleophiles

Stage 1. Synthesis of substituted 2,6-methylpyridines, 2,6-MePy($CH_2CHR^1CR^2R^3SH$) (1a-e). General procedure. At -40 °C, a solution of *n*-BuLi (2.5 M solution in hexane, 10.00 ml, 25.00 mmol, 1.05 eq.) was added dropwise to a solution of 2,6-lutidine (2.57 g, 24.00 mmol) in THF (50 ml). The mixture was slowly warmed to room temperature for 1 h, then it was cooled to -40 °C, and the corresponding thiirane (25.00 mmol, 1.05 eq.), was added dropwise. The reaction mixture was slowly warmed to room temperature and was stirred overnight. Saturated aq. solution of NH_4Cl (50 ml) was added, the aqueous phase was extracted with CH_2Cl_2 (3x20 ml), the organic phase was dried over $MgSO_4$, then all volatile materials were removed under reduced pressure.



2-(3-Mercaptopropyl)-6-methylpyridine, 2,6-MePy($CH_2CH_2CH_2SH$) (1a) was obtained using *General Procedure* from 2,6-lutidine (2.57 g, 24.00 mmol), *n*-BuLi (2.5 M solution in hexane, 10.00 mL, 25.00 mmol), ethylenesulfide, *cyclo*-[CH_2CH_2S] (1.50 g, 25.00 mmol) giving **1a** as colorless oil (1.88 g, 47 %) after vacuum distillation, b. p. 95-100 °C/3 mbar.

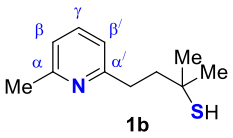
^{1}H NMR (δ, ppm, $CDCl_3$): 1.37 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H, SH); 1.99 (quint, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, C$H_2$$CH_2$SH); 2.48 (s, 3H, Py*Me*); 2.50-2.56 (m, 2H, CH_2SH); 2.81 (t, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, PyCH_2); 6.88-6.94 (m, 2H, β,β'-Py_H); 7.40-7.46 (m, 1H, γ-Py_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 24.1 (CH_2SH); 24.4 (Py*Me*); 34.1 (CH_2CH_2SH); 36.8 (PyCH_2); 119.6, 120.6 (β,β'-Py_C); 136.5 (γ-Py_C); 157.8, 160.3 (α,α'-Py_C).

MS (EI, %): 167 ([M]$^+$, 1); 134 ([M-SH]$^+$, 15); 120 ([M-CH_2SH]$^+$, 85); 107 ([M-CH_2CH_2S]$^+$, 100); 92 ([PyMe]$^+$, 8).

Anal. Calcd. for $C_9H_{13}NS$ (M_w 167.2712): C 64.62, H 7.83. Found: C 64.73, H 7.92.

2-(3-Mercapto-3-methylbutyl)-6-methylpyridine, 2,6-MePy($CH_2CH_2CMe_2SH$) (1b) was obtained in ether using *General Procedure* from 2,6-lutidine (2.57 g, 24.00 mmol), *n*-BuLi (2.5 M solution in hexane, 10.00 mL, 25.00 mmol) and 2,2-dimethylthiirane, *cyclo*-[CMe_2CH_2S] (2.20 g, 25.00 mmol) giving **1b** as yellow oil (2.17 g, 89 %) after flash chromatography (silica gel, petroleum ether/EtOAc 10:1, R_f 0.2).

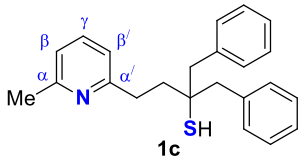


^{1}H NMR (δ, ppm, $CDCl_3$): 1.42 (s, 6H, 2Me); 1.73 (s, 1H, SH); 1.92-1.98 (m, 2H, CH_2C); 2.49 (s, 3H, Py*Me*); 2.85-2.91 (m, 2H, PyCH_2); 6.90-6.96 (m, 2H, β,β'-Py_H); 7.44 (pt, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 24.5 (Py*Me*); 32.7 (Me_2C(SH)); 34.5 (PyCH_2); 44.6 (Me_2C(SH)); 46.5 (CH_2CMe_2); 119.4, 120.4 (β,β'-Py_C); 136.5 (γ-Py_C); 157.7, 161.2 (α,α'-Py_C).

Anal. Calcd. for $C_{11}H_{17}NS$ (M_w 195.3244): C 67.64, H 8.77. Found: C 67.74, H 8.90.

2-(3-Benzyl-3-mercapto-4-phenylbutyl)-6-methylpyridine, 2,6-MePy($CH_2CH_2CBn_2SH$) (1c) was obtained in ether using *General Procedure* from 2,6-lutidine (0.81 g, 7.52 mmol), *n*-BuLi (2.5 M solution in hexane, 3.16 ml, 7.90 mmol) and 2,2-dibenzylthiirane, *cyclo*-[Bn_2CCH_2S] (1.90 g, 7.90 mmol), giving **1c** as brownish oil (2.51 g, 96 %).



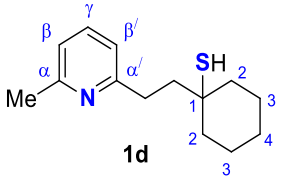
^{1}H NMR (δ, ppm, $CDCl_3$): 1.44 (s, 1H, SH); 1.96-2.02 (m, 2H, CH_2C); 2.55 (s, 3H, Py*Me*); 3.04 (br d, $^2J_{H\text{-}H}$ = 4.4 Hz, 4H, 2CCH_2Ph), 3.07-3.13 (m, 2H, PyCH_2); 6.90, 6.96 (2d, $^3J_{H\text{-}H}$ = 7.6 Hz, each 1H, β,β'-Py_H); 7.25-7.37 (m, 10H, Ph_H); 7.49 (pt, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 24.5 (Py*Me*); 33.8 (PyCH_2); 40.7 (CH_2C(SH)); 47.7 (PhCH_2); 52.1 (Bn_2C(SH)); 119.3, 120.5 (β,β'-Py_C); 126.6 (p-Ph_C); 127.8, 131.3 (m- and o-Ph_C); 136.6 (γ-Py_C); 137.0 (*ipso*-Ph_C); 157.7, 161.0 (α,α'-Py_C).

MS (EI, %): 347 ([M-H]$^+$, 2); 314 ([M-SH]$^+$, 48); 256 ([M-Bn]$^+$, 100); 222 ([M-Bn-H_2S]$^+$, 50); 120 ([M-Bn_2CSH]$^+$, 67); 107 ([Me_2Py]$^+$, 8); 91 ([Bn]$^+$, 45).

Anal. Calcd. for $C_{23}H_{25}NS$ (M_w 347.5163): C 79.49, H 7.25, N 4.03. Found: C 79.32, H 7.25, N 3.96.

2-[2-(1-Mercaptocyclohexyl)ethyl]-6-methylpyridine, 2,6-MePy($CH_2CH_2C[CH_2]_5SH$) (1d) was obtained using *General Procedure* from 2,6-lutidine (0.78 g, 7.26 mmol), *n*-BuLi (2.5 M solution in hexane, 3.05 mL, 7.62 mmol) and 1-thiaspiro[2.5]octane, *cyclo*-[$(CH_2)_5CCH_2S$] (0.98 g, 7.62 mmol), giving **1d** as yellowish viscous oil (1.23 g, 72 %) after flash chromatography (SiO_2, petroleum ether/EtOAc 10:1, R_f 0.3).



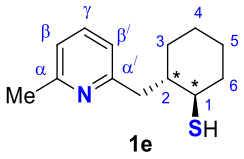
^{1}H NMR (δ, ppm, $CDCl_3$): 1.50 (s, 1H, SH); 1.53-1.58 (m, 5H), 1.60-1.74 (m, 5H) (*cyclo*-$[CH_2]_5$); 1.93-2.00 (m, 2H, CH_2C); 2.50 (s, 3H, Py*Me*); 2.90-2.96 (m, 2H, PyCH_2); 6.93, 6.96 (2d, $^3J_{H\text{-}H}$ = 7.6 Hz, each 1H, β,β'-Py_H); 7.45 (pt, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 22.4 (3,3-*cyclo*-$[CH_2]_5$); 24.4 (Py*Me*); 25.9 (4-*cyclo*-$[CH_2]_5$); 33.0 (PyCH_2); 36.3 (PyCH_2CH_2); 40.0 (2,2-*cyclo*-$[CH_2]_5$); 49.5 (1-*cyclo*-$[CH_2]_5$); 119.5, 120.4 (β,β'-Py_C); 136.6 (γ-Py_C); 157.6, 161.5 (α,α'-Py_C).

MS (EI, %): 202 ([M-SH]$^+$, 7); 201 ([M-H_2S]$^+$, 2); 120 ([M-CySH]$^+$, 100); 106 ([M-HSCyCH_2]$^+$, 30).

Anal. Calcd. for $C_{14}H_{21}NS$ (M_w 235.3882): C 71.44, H 8.99, N 5.95. Found: C 71.34, H 9.12, N 5.83.

trans-2-[(2-Mercaptocyclohexyl)methyl]-6-methylpyridine, trans-2,6-MePy(CH_2-1,2-$CH[CH_2]_4CHSH$) (1e) was obtained using *General Procedure* from 2,6-lutidine (2.69 g, 25.06 mmol), *n*-BuLi (2.5 M solution in hexane, 10.53 mL, 26.31 mmol, 1.05 eq.) and cycloxene sulfide, *cyclo*-[$(CH_2)_4CHCHS$] (3.00 g, 26.31 mmol, 1.05 eq.), giving **1e** as yellowish viscous oil (2.33 g, 42 %) after flash chromatography (SiO_2, petroleum ether/EtOAc 10:1, R_f 0.3).



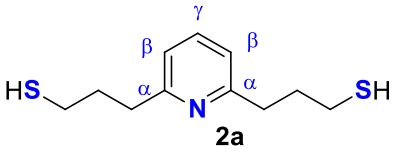
^{1}H NMR (δ, ppm, $CDCl_3$): 0.96-1.06 (m, 1H), 1.14-1.29 (m, 2H), 1.41-1.47 (m, 1H), 1.58-1.67 (m, 2H), 1.68-1.75 (m, 2H) (*cyclo*-$[CH_2]_4$); 1.70 (d, $^2J_{H\text{-}H}$ = 7.0 Hz, 1H, SH); 2.08-2.16 (m, 1H, CH); 2.50 (s, 3H, Py*Me*); 2.47-2.59 (m, 2H, PyC*H*(H), CH); 3.38 (dd, $^3J_{H\text{-}H}$ = 13.3 Hz, $^2J_{H\text{-}H}$ = 3.9 Hz, 1H, PyC*H*(H)); 6.92, 6.94 (2d, $^3J_{H\text{-}H}$ = 7.7 Hz, each 1H, β,β'-Py_H); 7.44 (pt, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py_H).

^{13}C NMR (δ, ppm, $CDCl_3$): 24.6 (Py*Me*); 25.6, 26.9 (4,5-*cyclo*-$[CH_2]_4$); 31.6 (3-*cyclo*-$[CH_2]_4$); 43.1 (6-*cyclo*-$[CH_2]_4$); 38.6 (PyCH_2); 44.4 (CH); 46.7 (CHS); 120.4, 120.5 (β,β'-Py_C); 136.2 (γ-Py_C); 157.6, 161.1 (α,α'-Py_C).

Anal. Calcd. for $C_{13}H_{19}NS$ (M_w 221.3617): C 70.54, H 8.65, N 6.33. Found: C 70.39, H 8.54, N 6.22.

Stage 2. ***Synthesis of SNS-ligands, 2,6-Py(CH$_2$CHR^{1}CR^{2}R^{3}SH)$_2$ (2a-e). General procedure.*** At -40 °C, a solution of *n*-BuLi (2.5 M solution in hexane, 24.43 ml, 61.07 mmol, 2.1 eq.) was added dropwise to a solution of 2,6-MePy(CH$_2$CHR^{1}CR^{2}R^{3}SH) (29.08 mmol) in THF (50 ml). The mixture was slowly warmed and stirred for 4 h, then it was cooled to -40 °C, and the solution of the corresponding thiirane (32.00 mmol, 1.1 eq.) in THF (20 ml) was added dropwise The mixture was slowly warmed to room temperature and was stirred overnight. Saturated aq. solution of NH_4Cl (50 ml) was added, the aqueous phase was extracted with CH_2Cl_2 (3x20 ml), the organic phase was dried over $MgSO_4$, then all volatile materials were removed under reduced pressure.

2,6-Bis(3-mercaptopropyl)pyridine, 2,6-Py(CH$_2$CH$_2$CH$_2$SH)$_2$ (2a) was obtained using *General Procedure* from 2,6-MePy(CH$_2$CH$_2$CH$_2$SH) (**1**) (4.86 g, 29.08 mmol), *n*-BuLi (2.5 M, 24.43 ml, 61.07 mmol, 2.1 eq.) ethylenesulfide, *cyclo*-[CH$_2$CH$_2$S] (2.10 g, 34.90 mmol, 1.2 eq.), giving ligand **2a** as yellowish oil (4.10 g, 62 %) after vacuum distillation, bp 150-160 °C/1 Torr



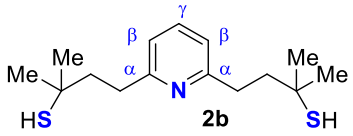
^{1}H NMR (δ, ppm, $CDCl_3$): 1.41 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, 2SH); 2.01 (quint, $^3J_{H\text{-}H}$ = 7.4 Hz, 4H, 2C*H*$_2$CH$_2$SH); 2.50-2.57 (m, 4H, 2CH$_2$SH); 2.84 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, 2CH$_2$Py); 6.95 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, 2β-Py$_H$); 7.47 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 24.0 (*C*H$_2$SH); 33.9 (*C*H$_2$CH$_2$SH); 36.6 (Py*C*H$_2$); 120.1 (β-Py$_C$); 136.6 (γ-Py$_C$); 160.4 (α-Py$_C$).

MS (EI, %): 227 ([M]$^+$, 1); 194 ([M-SH]$^+$, 12); 180 ([M-CH$_2$SH]$^+$, 83); 160 ([M-SH-H$_2$S]$^+$, 10); 146 ([M-CH$_2$SH-H$_2$S]$^+$, 43); 133 ([M-2CH$_2$SH]$^+$, 28); 120 (([M-C$_2$H$_4$S-CH$_2$SH]$^+$, 100); 107 ([Me$_2$Py]$^+$, 24).

Anal. Calcd. for $C_{11}H_{17}NS_2$ (M_w 227.3894): C 58.10, H 7.54, N 6.16. Found: C 57.96, H 7.58, N 6.02.

2,6-Bis(3-mercapto-3-methylbutyl)pyridine, 2,6-Py(CH$_2$CH$_2$CMe$_2$SH)$_2$ (2b) was obtained using *General Procedure* from 2,6-MePy(CH$_2$CH$_2$CMe$_2$SH) (**1b**) (2.10 g, 10.73 mmol), *n*-BuLi (2.5 M solution in hexane, 9.00 ml, 22.53 mmol, 2.1 eq.) and 2,2-dimethylthiirane, *cyclo*-[Me$_2$CCH$_2$S] (0.95 g, 10.73 mmol), giving ligand **2b** as viscous yellow oil (2.83 g, 93 %).



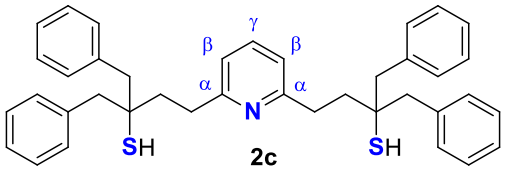
^{1}H NMR (δ, ppm, $CDCl_3$): 1.43 (s, 12H, 2*Me*$_2$C); 1.75 (s, 2H, 2SH); 1.94-2.00 (m, 4H, 2C*H*$_2$C); 2.87-2.93 (m, 4H, 2PyC*H*$_2$); 6.96 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, 2β-Py$_H$); 7.48 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 32.7 (*Me*$_2$C); 34.5 (Py*C*H$_2$); 44.6 (Me$_2$*C*); 46.4 (*C*H$_2$C); 119.7 (β-Py$_C$); 136.6 (γ-Py$_C$); 161.3 (α-Py$_C$).

MS (EI, %): 283 ([M]$^+$, 2); 250 ([M-SH]$^+$, 30); 216 ([M-SH-H$_2$S]$^+$, 41); 208 ([M-Me$_2$CSH]$^+$, 100); 174 ([M-Me$_2$CSH-H$_2$S]$^+$, 80); 107 ([Me$_2$Py]$^+$, 6).

Anal. Calcd. for $C_{15}H_{25}NS_2$ (M_w 283.4957): C 63.55, H 8.89. Found: C 63.55, H 8.98.

2,6-Bis(3-benzyl-3-mercapto-4-phenylbutyl)pyridine, 2,6-Py(CH$_2$CH$_2$CBn$_2$SH)$_2$ (2c) was obtained using *General Procedure* from 2,6-MePy(CH$_2$CH$_2$CBn$_2$SH) (**1c**) (1.84 g, 5.30 mmol), *n*-BuLi (2.5 M solution in hexane, 4.45 mL, 11.13 mmol, 2.1 eq.) and 2,2-dibenzylthiirane, *cyclo*-[Bn$_2$CCH$_2$S] (1.27 g, 5.30 mmol). The crude product was crystallized after treatment with *n*-hexane/ether mixture; the solid obtained was recrystallized from minimal amount of hot *n*-hexane/CH_2Cl_2 mixture giving 2,6-Py(CH$_2$CH$_2$CBn$_2$SH)$_2$ (**2c**) (1.59 g, 51 %) as yellow powder, m. p. 132-134 °C.

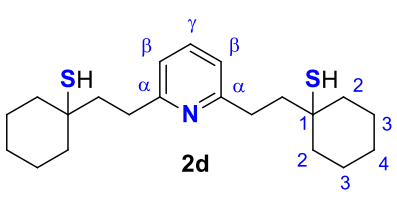


^{1}H NMR (δ, ppm, $CDCl_3$): 1.45 (s, 2H, 2SH); 1.98-2.04 (m, 4H, 2C*H*$_2$C); 3.06 (br d, $^2J_{H\text{-}H}$ = 2.2 Hz, 8H, 4CH$_2$Ph); 3.08-3.14 (m, 4H, 2PyC*H*$_2$); 6.92 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, 2β-Py$_H$); 7.22-7.35 (m, 20H, Ph$_H$); 7.46 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 33.8 (Py*C*H$_2$); 40.4 (*C*H$_2$C); 47.8 (Ph*C*H$_2$); 52.2 (Bn$_2$*C*(SH)); 119.8 (β-Py$_C$); 126.7 (*p*-Ph$_C$); 127.9, 131.3 (*m*- and *o*-Ph$_C$); 136.6 (γ-Py$_C$); 137.0 (*ipso*-Ph$_C$); 161.0 (α-Py$_C$).

Anal. Calcd. for $C_{39}H_{41}NS_2$ (M_w 587.8795): C 79.68, H 7.03, N 2.38. Found: C 79.54, H 6.91, N 2.44.

2,6-Bis[2-(1-mercaptocyclohexyl)ethyl]pyridine, 2,6-Py(CH$_2$CH$_2$C[CH$_2$]$_5$SH)$_2$ (2d) was obtained using *General Procedure* from 2,6-MePy(CH$_2$CH$_2$C[CH$_2$]$_5$SH) (**1d**) (1.18 g, 5.00 mmol), *n*-BuLi (2.5 M, 4.20 ml, 10.50 mmol, 2.1 eq.) and 1-thiaspiro[2.5]octane, *cyclo*-[(CH$_2$)$_5$CCH$_2$S] (0.64 g, 5.00 mmol), giving ligand **2d** (1.55 g, 85 %) as viscous colorless oil after flash-chromatography (SiO_2, petroleum ether/EtOAc 40:1, R_f 0.2).

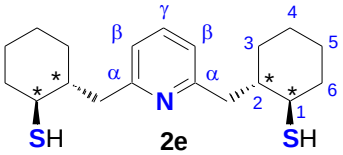


^{1}H NMR (δ, ppm, $CDCl_3$): 1.52 (s, 2H, 2SH); 1.53-1.59 (m, 10H), 1.61-1.76 (m, 10H) (*cyclo*-[$(CH_2)_5$]); 1.95-2.01 (m, 4H, 2PyCH$_2$C*H$_2$*); 2.91-2.97 (m, 4H, PyC*H$_2$*CH$_2$); 6.97 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, 2β-Py$_H$); 7.47 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 22.4 (3,3-*cyclo*-[$(CH_2)_5$]); 25.9 (4-*cyclo*-[$(CH_2)_5$]); 33.0 (Py*C*H$_2$); 36.3 (PyCH$_2$*C*H$_2$); 40.1 (2,2-*cyclo*-[$(CH_2)_5$]); 49.6 (1-*cyclo*-[$(CH_2)_5$]); 119.8 (β-Py$_C$); 136.6 (γ-Py$_C$); 161.5 (α-Py$_C$).

MS (EI, %): 364 ([M]$^+$, 1); 330 ([M-H$_2$S]$^+$, 30); 296 ([M-2H$_2$S]$^+$, 33); 248 ([M-CySH]$^+$, 100); 214 ([M-CySH-H$_2$S]$^+$, 75); 107 ([Me$_2$Py]$^+$, 22).

Anal. Calcd. for $C_{21}H_{33}NS_2$ (M_w 363.6234): C 69.36, H 9.15, N 3.85. Found: C 69.38, H 9.08, N 3.77.



trans,trans-2,6-Bis[(2-mercaptocyclohexyl)methyl]pyridine, trans,trans-2,6-Py(CH$_2$-1,2-CH[CH$_2$]$_4$CHSH)$_2$ (2e) was obtained using *General Procedure* from 2,6-MePy(CH$_2$-1,2-CH[CH$_2$]$_4$CHSH) (**1e**) (1.11 g, 5.03 mmol), *n*-BuLi (2.5 M solution in hexane, 4.23 mL, 10.55 mmol, 2.1 eq.) and cycloxene sulfide, *cyclo*-[$(CH_2)_4$CHCHS] (0.57 g, 5.03 mmol), giving ligand **2e** as viscous colorless oil (1.35 g, 80 %) after chromatography (SiO_2, petroleum ether/EtOAc 9:1, R_f 0.4). Compound represents a mixture of two diastereomers A, B ((*R**,*S**), (*R**,*S**)/(*R**,*S**), (*S**,*R**)) in 2:1 ratio.

^{1}H NMR (δ, ppm, $CDCl_3$): 0.93-1.02 (m, 2H), 1.13-1.28 (m, 4H), 1.41-1.49 (m, 2H), 1.56-1.72 (m, 8H) (*cyclo*-[CH_2]$_4$); 1.75 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, diastereomer B), 1.80 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, diastereomer A) (2H, SH); 2.07-2.13 (m, 2H, PyCH$_2$C*H*); 2.50-2.64 (m, 4H, C*H*S, PyC(H)*H*); 3.26-3.34 (m, 2H, PyC(H)*H*); 6.91 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, diastereomer A), 6.93 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, diastereomer B) (2H, 2β-Py$_H$); 7.45 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, γ-Py$_H$).

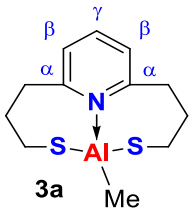
^{13}C NMR (δ, ppm, $CDCl_3$): 25.7, *26.8*, 26.9 (4,5-*cyclo*-[CH_2]$_4$); 31.7 (3-*cyclo*-[CH_2]$_4$); 42.7, *42.8* (6-*cyclo*-[CH_2]$_4$); 38.4, *38.5* (Py*C*H$_2$); 44.0, *44.1* (PyCH$_2$*C*H); *46.5*, 46.6 (CSH); *120.8*, 120.9 (β-Py$_C$); 135.8 (γ-Py$_C$); 159.8 (α-Py$_C$). Signals corresponding to the minor diastereomer B are italicized.

Anal. Calcd. for $C_{19}H_{29}NS_2$ (M_w 335.5703): C 68.00, H 8.71, N 4.7. Found: C 67.62, H 8.68, N 4.26.

Synthesis of Methylaluminum Complexes Based on 2,6-Bis(mercaptoalkyl)pyridine *SNS*-Ligands.

General Procedure

At -50 °C the solution of $AlMe_3$ (2.0 M in toluene, 1.00 ml, 2.00 mmol) was added dropwise to the solution of *SNS*-polydentate ligand (2.00 mmol) in toluene (20 ml). The mixture was slowly warmed to room temperature and was stirred overnight. All volatile materials were removed under reduced pressure.

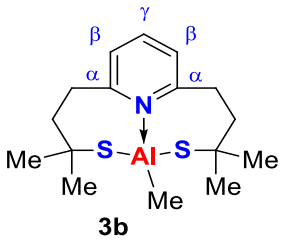


[2,6-Bis(3-sulfidopropyl)pyridine]methylaluminum, [2,6-Py(CH$_2$CH$_2$CH$_2$S)$_2$]AlMe (3a) was obtained using *General Procedure* from $AlMe_3$ (2.0 M in toluene, 1.00 ml, 2.00 mmol) and ligand 2,6-Py(CH$_2$CH$_2$CH$_2$SH)$_2$ (**2a**) (0.4548 g, 2.00 mmol) giving complex **3a** as yellow powder (0.5134 g, 96 %).

^{1}H NMR (δ, ppm, $CDCl_3$): -0.18 (s, 3H, AlMe); 2.03-2.08 (m, 4H, 2PyCH$_2$C*H$_2$*); 2.32-2.38, 2.78-2.84 (2m, each 2H, SC*H*(H)); 3.00-3.06, 3.73-3.81 (2m, each 2H, 2PyC*H*(H)); 7.30 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, 2β-Py$_H$); 7.92 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 25.2 (*C*H$_2$SAl); 31.6 (*C*H$_2$); 33.8 (Py*C*H$_2$); 125.0 (β-Py$_C$); 142.0 (γ-Py$_C$); 162.8 (α-Py$_C$). The signal of Al-*Me* was not found.

Anal. Calcd. for $C_{12}H_{18}AlNS_2$ (M_w 267.3896): C 53.90, H 6.79, N 5.24. Found: C 52.72, H 6.44, N 4.88.



[2,6-Bis(3-methyl-3-sulfidobutyl)pyridine]methylaluminum, [2,6-Py(CH$_2$CH$_2$CMe$_2$S)$_2$]AlMe (3b) was obtained using *General Procedure* from $AlMe_3$ (2.0 M in toluene, 1.00 ml, 2.00 mmol) and ligand 2,6-Py(CH$_2$CH$_2$CMe$_2$SH)$_2$ (**2b**) (0.5670 g, 2.00 mmol) giving complex **3b** as yellow foam (0.6082 g, 94 %).

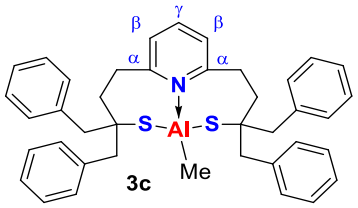
^{1}H NMR (δ, ppm, $CDCl_3$): -0.16 (s, 3H, AlMe); 1.29, 1.43 (2s, each 6H, 4Me); 1.92-1.98, 2.08-2.12 (2m, each 2H, 2PyCH$_2$C*H$_2$*); 3.25-3.31, 3.59-3.67 (2m, each 2H, 2PyC*H$_2$*); 7.25 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, 2β-Py$_H$); 7.84 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, γ-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 33.5, 34.0 (2Me); 35.2 (Py*C*H$_2$); 45.4 (PyCH$_2$*C*H$_2$); 45.8 (Me$_2$*C*); 124.5 (β-Py$_C$); 141.8 (γ-Py$_C$); 164.0 (α-Py$_C$). The signal of Al-*Me* was not found.

^{27}Al NMR (δ, ppm, $CDCl_3$): 153 ($\omega_{1/2}$ = 3100 Hz).

Anal. Calcd. for $C_{16}H_{26}AlNS_2$ (M_w 323.4959): C 59.40, H 8.10, N 4.33. Found: C 58.62, H 7.78, N 4.12.

[2,6-Bis(3-benzyl-3-sulfido-4-phenylbutyl)pyridine]methylaluminum, [2,6-Py(CH$_2$CH$_2$CBn$_2$S)$_2$]AlMe (3c) was obtained using *General Procedure* from $AlMe_3$ (2.0 M in toluene, 1.00 ml, 2.00 mmol) and ligand 2,6-Py($CH_2CH_2CBn_2SH$)$_2$ (**2c**) (1.1758 g, 2.00 mmol) giving complex **3c** as white powder (0.5274 g, 42 %) after recrystallization from minimal amount of *n*-hexane/CH_2Cl_2 mixture.



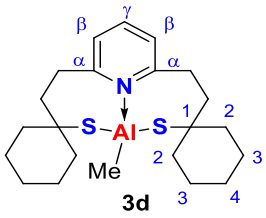
^{1}H NMR (δ, ppm, $CDCl_3$): -0.13 (s, 3H, AlMe); 1.69-1.76, 2.04-2.12 (2m, each 2H, 2PyCH$_2$C*H$_2$*); 2.82-2.90 (m, 2H, PyC(*H*)H); 3.01, 3.16 (2br s, each 4H, 2PhC*H$_2$*); 3.46-3.52 (m, 2H, PyC(*H*)H); 6.76 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, *β*-Py$_H$); 7.24-7.37 (m, 20H, Ph$_H$); 7.59 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, *γ*-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 32.8 (Py*C*H$_2$); 39.7 (PyCH$_2$*C*H$_2$); 49.7, 50.0 (*C*H$_2$Ph); 54.1 (Bn$_2$*C*); 124.3 (β-Py$_C$); 125.9, 126.3 (*p*-Ph$_C$); 127.4, 127.9, 131.0, 131.6 (*m*- and *o*-Ph$_C$); 138.3, 138.4 (*ipso*-Ph$_C$); 141.9 (γ-Py$_C$); 163.5 (α-Py$_C$). The signal of Al-*Me* was not found.

^{27}Al NMR (δ, ppm, $CDCl_3$): 154 ($\omega_{1/2}$ = 5900 Hz).

Anal. Calcd. for $C_{40}H_{42}AlNS_2$ (M_w 627.8797): C 76.52, H 6.74, N 2.23. Found: C 75.83, H 6.49, N 1.92.

[2,6-Bis[2-(1-sulfidocyclohexyl)ethyl]pyridine]methylaluminum, [2,6-Py(CH$_2$CH$_2$C(CH$_2$)$_5$S)$_2$]AlMe (3d) was obtained using *General Procedure* from $AlMe_3$ (2.0 M in toluene, 1.00 ml, 2.00 mmol) and ligand 2,6-Py($CH_2CH_2C[CH_2]_5SH$)$_2$ (**2d**) (0.7272 g, 2.00 mmol) giving complex **3d** as white powder (0.5247 g, 65 %) after hot recrystallization from the minimal amount of *n*-hexane/toluene mixture.

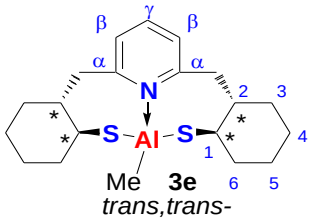


^{1}H NMR (δ, ppm, $CDCl_3$): -0.22 (s, 3H, AlMe); 1.16-1.28 (m, 4H), 1.34-1.47 (m, 6H), 1.52-1.64 (m, 6H), 1.79-1.87 (m, 4H) (*cyclo*-[CH_2]$_5$); 1.89-1.94, 2.10-2.17 (2m, each 2H, 2CCH$_2$); 3.23-3.30, 3.59-3.66 (2m, each 2H, 2PyC*H$_2$*); 7.22 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, 2*β*-Py$_H$); 7.80 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, *γ*-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): 22.6 (3,3-*cyclo*-[CH_2]$_5$); 26.2 (4-*cyclo*-[CH_2]$_5$); 32.3 (PyCH_2); 41.2 (PyCH$_2$*C*H$_2$); 42.5 (2,2-*cyclo*-[CH_2]$_5$); 51.0 (1-*cyclo*-[CH_2]$_5$); 124.3 (β-Py$_C$); 141.6 (γ-Py$_C$); 164.3 (α-Py$_C$). The signal of Al-*Me* was not found.

Anal. Calcd. for $C_{22}H_{34}AlNS_2$ (M_w 403.6236): C 65.47, H 8.49, N 3.47. Found: C 64.33, H 8.18, N 3.42.

[trans,trans-2,6-Bis[(2-sulfidocyclohexyl)methyl]pyridine]methylaluminum, [trans,trans-2,6-Py(CH$_2$-1,2-CH(CH$_2$)$_4$CHS)$_2$]AlMe (3e) was obtained using *General Procedure* from $AlMe_3$ (2.0 M in toluene, 1.00 ml, 2.00 mmol) and ligand 2,6-Py(CH_2-1,2-CH[CH_2]$_4$CHSH)$_2$ (**2e**) (0.6711 g, 2.00 mmol) giving complex **3e** as white powder (0.7126 g, 95 %). Complex **3e** was isolated as a mixture of two diastereomers *A* and *B* ((*R**,*S**), (*R**,*S**)/(*R**,*S**), (*S**,*R**)) in 2:1 ratio.



^{1}H NMR (δ, ppm, $CDCl_3$): -0.23, -0.19 (2s, 3H, AlMe; *A* and *B* diastereoisomers); 1.10-1.74 (m, 16H, *cyclo*-[CH_2]$_4$); 1.78-2.24 (m, 4H), 2.68-3.20 (m, 2H) (2CH, 2PyC*H*(H)); 3.44-3.52, 3.85-4.23 (2m, each 1H, 2SCH); 7.20-7.30 (m, 2H, 2*β*-Py$_H$); 7.81-7.88 (m, 1H, *γ*-Py$_H$).

^{13}C NMR (δ, ppm, $CDCl_3$): *26.3*, 26.4, 26.5, 26.8, 27.0, *27.1* (4,5-*cyclo*-[CH_2]$_4$, *A* and *B* diastereomers); 31.3, 32.7, *37.0* (3-*cyclo*-[CH_2]$_4$, *A* and *B* diastereomers); 38.1, *38.2*, 38.5 (PyCH_2, *A* and *B* diastereomers); 41.6, 42.0, *42.1* (6-*cyclo*-[CH_2]$_4$, *A* and *B* diastereomers); *43.9*, 45.0, 47.9 (CH, *A* and *B* diastereomers); 48.0, *48.2*, 48.7 (SCH, *A* and *B* diastereomers); 125.2, *125.5*, 126.1 (β-Py$_C$, *A* and *B* diastereomers); *140.4*, 140.8 (γ-Py$_C$, *A* and *B* diastereomers); 159.0, 161.0, *164.7* (α-Py$_C$, *A* and *B* diastereomers). Signals corresponding to the minor diastereomer B are italicized. The signals of Al-*Me* were not found.

^{27}Al NMR (δ, ppm, $CDCl_3$): 156 ($\omega_{1/2}$ = 3400 Hz).

Anal. Calcd. for $C_{20}H_{30}AlNS_2$ (M_w 375.5704): C 63.96, H 8.05, N 3.73. Found: C 63.07, H 7.82, N 3.62.

Ring-opening polymerization of ε-caprolactone

Ring-opening polymerization in toluene solution

A toluene solution of benzyl alcohol (0.01 mmol, 1.00 M) was added to the initiator (0.01 mmol), then ε-caprolactone in toluene (1.00 M) was added. The mixture was heated in oil bath at specified temperature and time. Then MeOH (5 ml) was added, all volatile materials were removed under reduced pressure.

Ring-opening polymerization in bulk

ε-Caprolactone and benzyl alcohol were added to the initiator (0.01 mmol). The mixture was heated in oil bath at the specified temperature and time. The material thus obtained was dissolved in THF (10 ml) and poured into MeOH (50 ml). The polymer obtained was filtered off.

Crystallographic Data

Experimental Details. Experimental intensities were collected on a Bruker Smart Apex II diffractometer (graphite monochromatized Mo-*K*α radiation, λ=0.71073 Å) using ω-scan mode. Absorption correction based on measurements of equivalent reflections (SADABS) was applied. The structure was solved by direct methods and refined by full matrix least-squares on F^2 (Shelxtl) with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were found from difference Fourier synthesis and refined isotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2088271.

Table S1. Crystallographic Data for Compound 2,6-Py($CH_2CH_2CBn_2SH)_2$ (**2c**).

empirical formula	$C_{39}H_{41}NS_2$
M_w	587.85
temperature (K)	120(2)
size (mm)	0.40 x 0.25 x 0.20
cryst. system	orthorhombic
space group	*Pbcn*
a (Å)	6.4574(6)
b (Å)	17.4109(16)
c (Å)	28.481(3)
V (Å^3)	3202.1(5)
Z	4
ρ_{cald}(g cm^{-3})	1.219
abs coeff. (mm^{-1})	0.195
F(000)	1256
θ range (deg)	2.34– 27.00
no. of collected/unique rflns.	3504 / 2848
R_{int}	0.0506
data/restraints/params.	2848 / 0 / 273
goodness of fit on F^2	1.027
final *R* indices ($I> 2\sigma(I)$)	R_1 = 0.0364, wR_2 = 0.0859
R indices (all data)	R_1 = 0.0491, wR_2 = 0.0933
largest diff. peak/hole (e/Å^3)	0.332 / -0.232

Action of methyl aluminum complexes 3c and 3d as initiators in ring-opening polymerization of ε-caprolactone (CL)

Table S2. Catalytic activity of methyl aliuminum complexes **3c** and **3d** in ROP of CL.

initiator [a]	[CL]/[Al]	solvent	conversion, % [c]	M_n (NMR), Da [d]	M_n (calc.), Da [e]	M_n, Da [f]	M_w/M_n [f]
3c	300	- [b]	100	26000	34300	20800	1.202
3d	300	- [b]	18	3100	7900	3200	1.086
3c	200	$PhCH_3$	6	600	1500	-	-
3d	200	$PhCH_3$	6	800	1500	-	-

[a] 100 °C; 12 h; 1 eq. of BnOH ([Al] = [BnOH]) was used
[b] in bulk (without solvent)
[c] obtained based on ^{1}H NMR spectroscopy data of crude reaction mixture
[d] M_n (NMR) = $I(\underline{C}H_2Ph)_{PCL} \times M_w(CL) + M_w(BnOH)$
[e] $M_n(calc.) = M_w(CL) \times [CL]_o/[BnOH] \times (conversion) + M_w(BnOH)$
[f] SEC data, THF as an eluent; $M_n = 0.56 \times M_n(experimental)$

NMR spectra of the compounds obtained

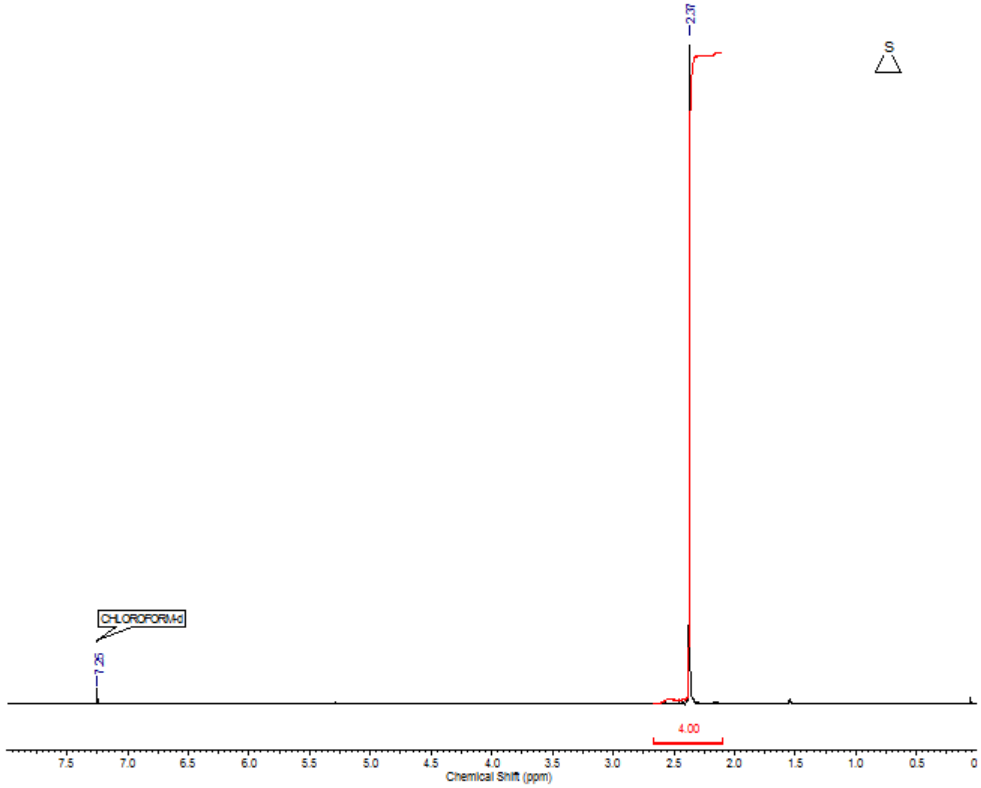


Fig. S1. ^{1}H NMR spectrum ($CDCl_3$, RT) of ethylenesulfide, *cyclo*-[CH_2CH_2S].

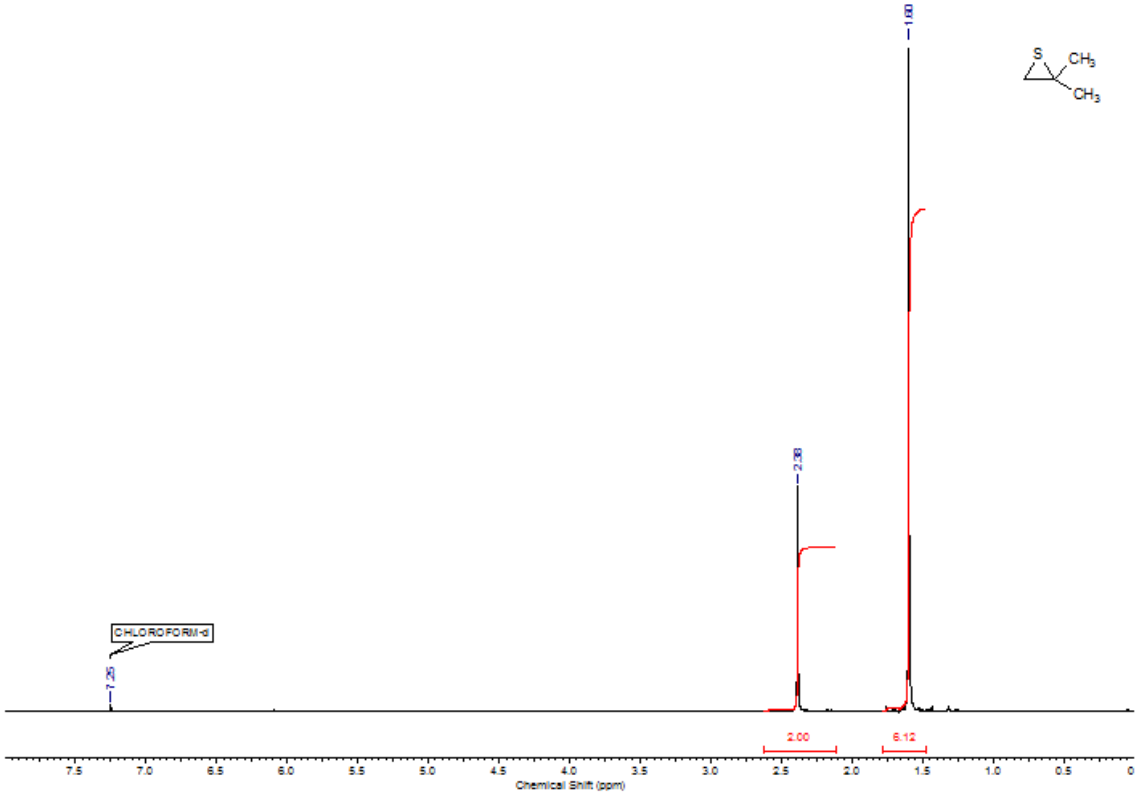


Fig. S2. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,2-dimethylthiirane, *cyclo*-[Me_2CCH_2S].

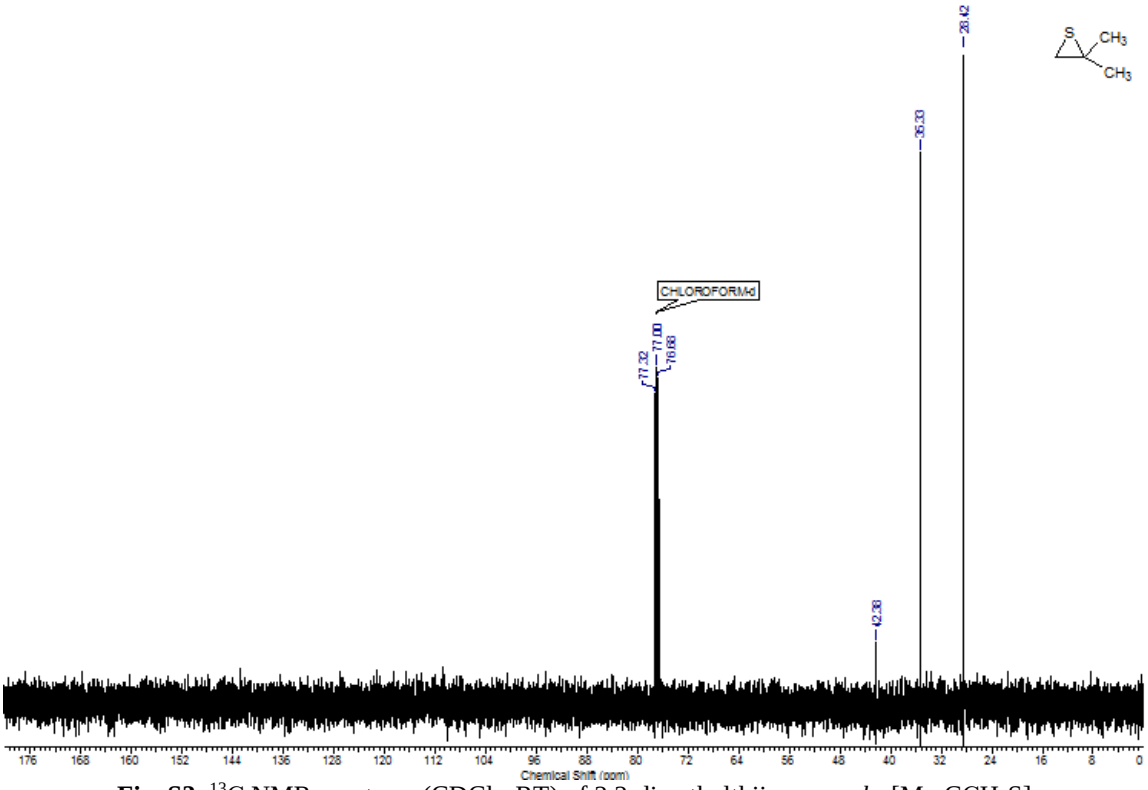


Fig. S3. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,2-dimethylthiirane, *cyclo*-[Me_2CCH_2S].

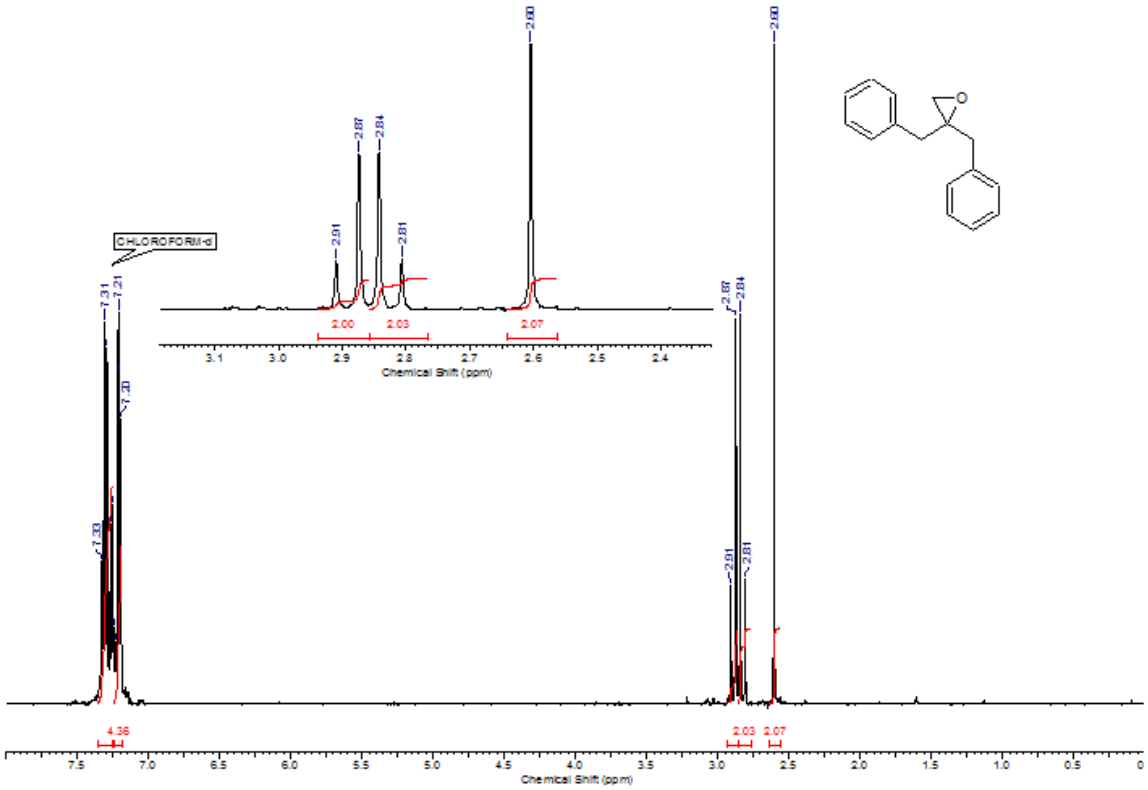


Fig. S4. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,2-dibenzyloxirane, *cyclo*-[Bn_2CCH_2O].

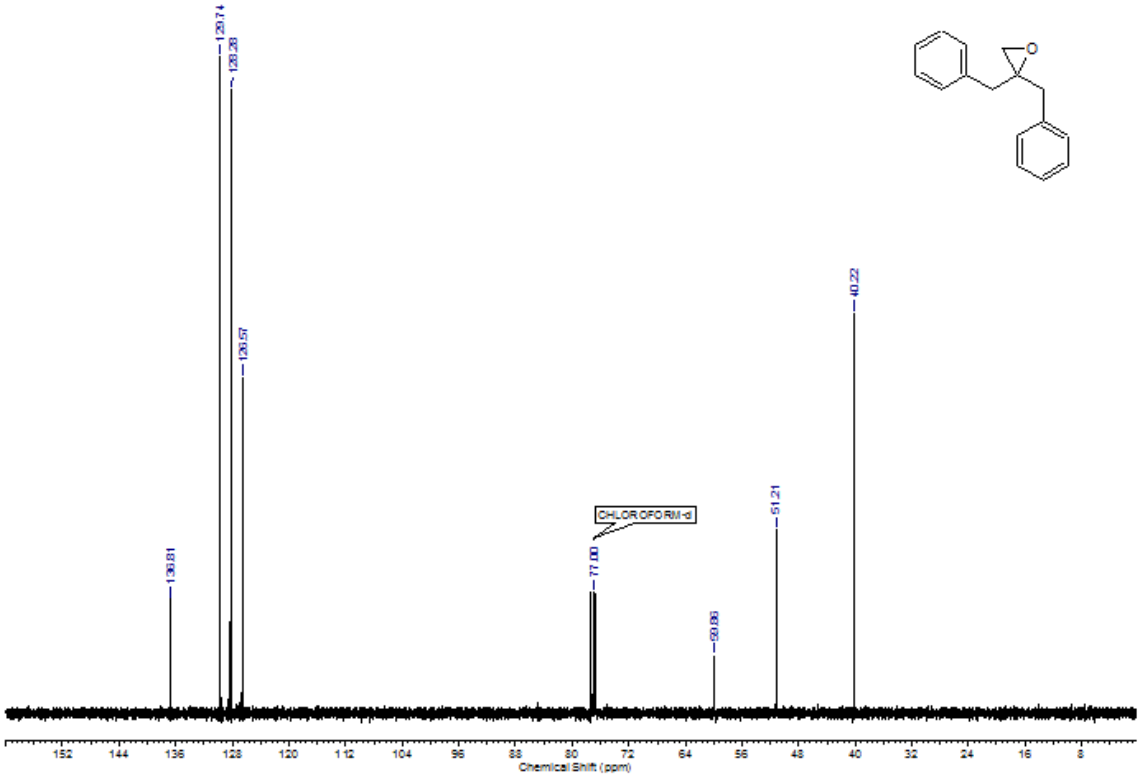


Fig. S5. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,2-dibenzyloxirane, *cyclo*-[Bn_2CCH_2O].

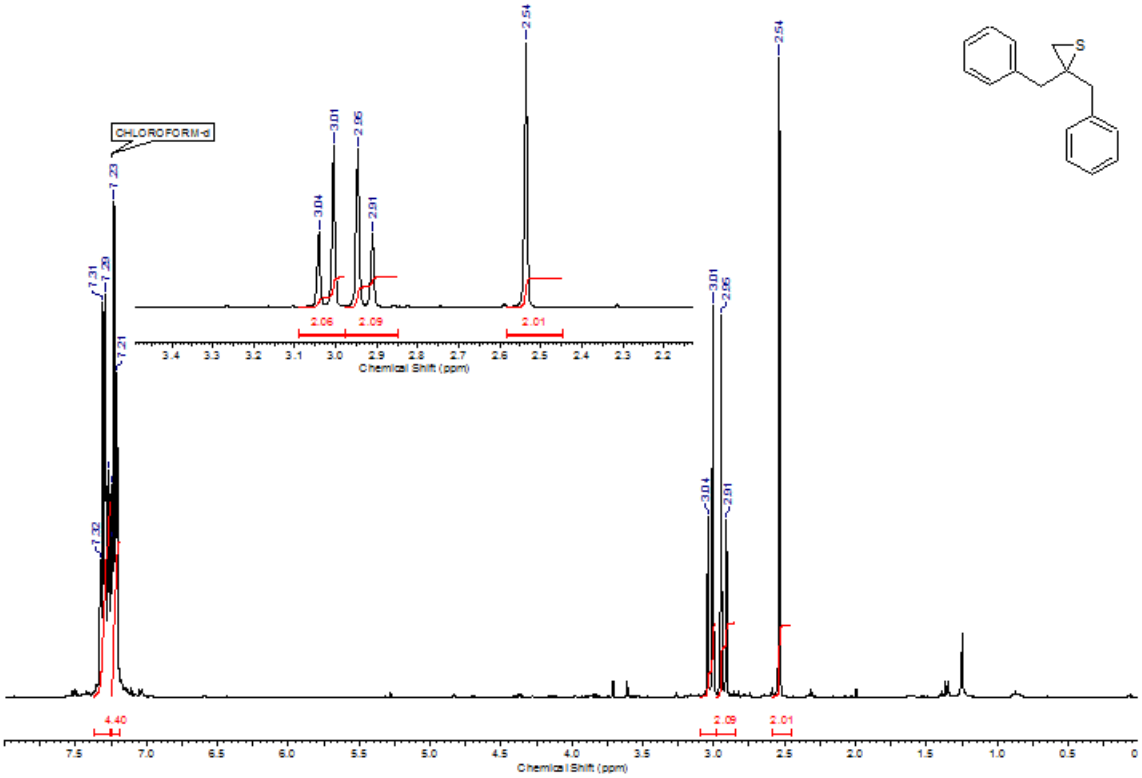


Fig. S6. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,2-dibenzylthiirane, *cyclo*-[Bn_2CCH_2S].

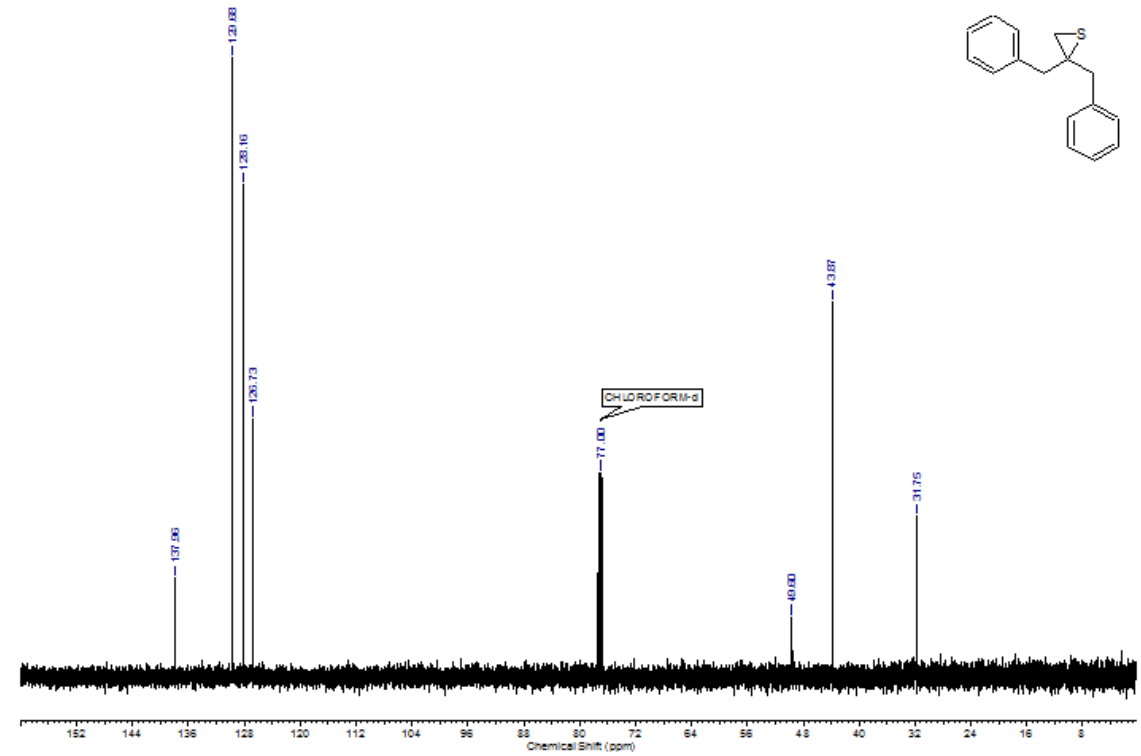


Fig. S7. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,2-dibenzylthiirane, *cyclo*-[Bn_2CCH_2S].

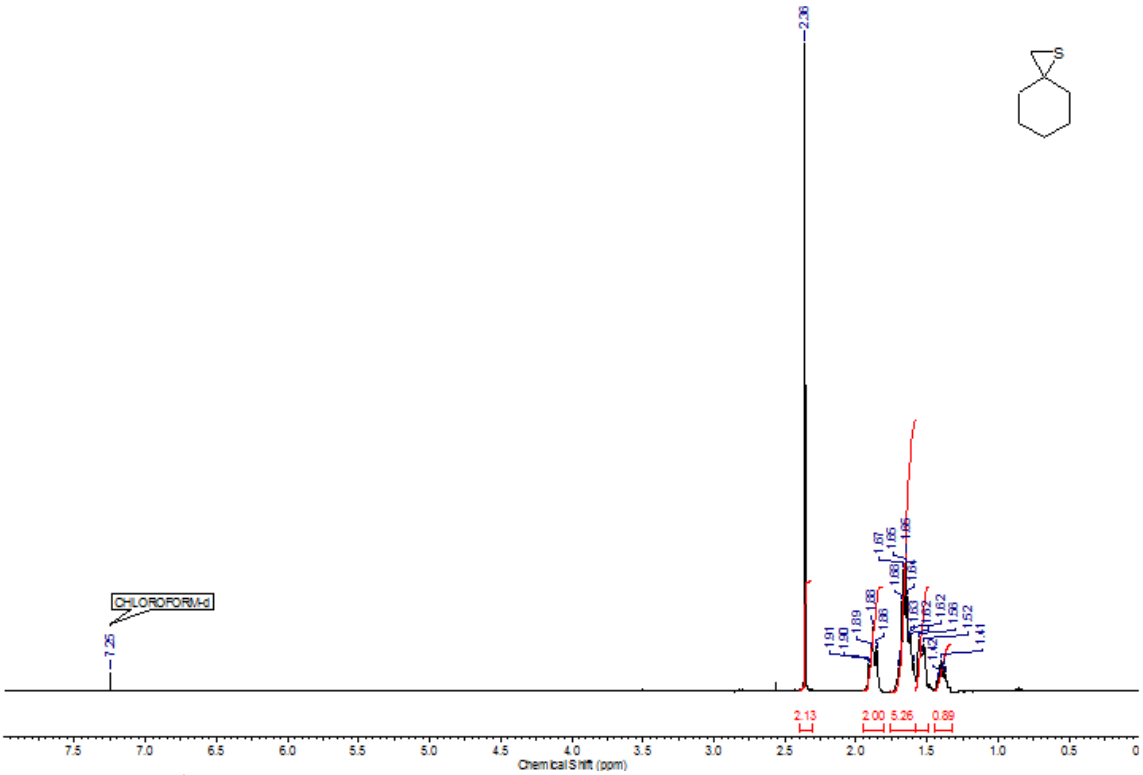


Fig. S8. ^{1}H NMR spectrum ($CDCl_3$, RT) of 1-thiaspiro[2.5]octane, *cyclo*-[$(CH_2)_5CCH_2S$].

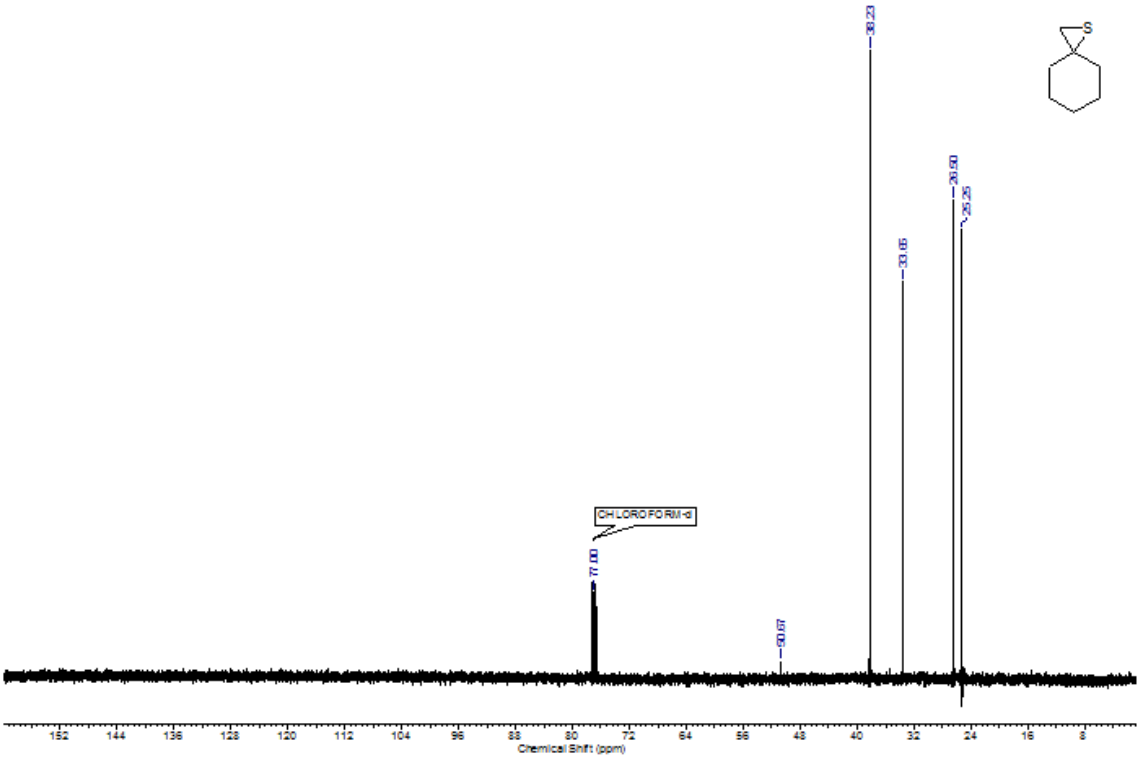


Fig. S9. ^{13}C NMR spectrum ($CDCl_3$, RT) of 1-thiaspiro[2.5]octane, *cyclo*-[$(CH_2)_5CCH_2S$].

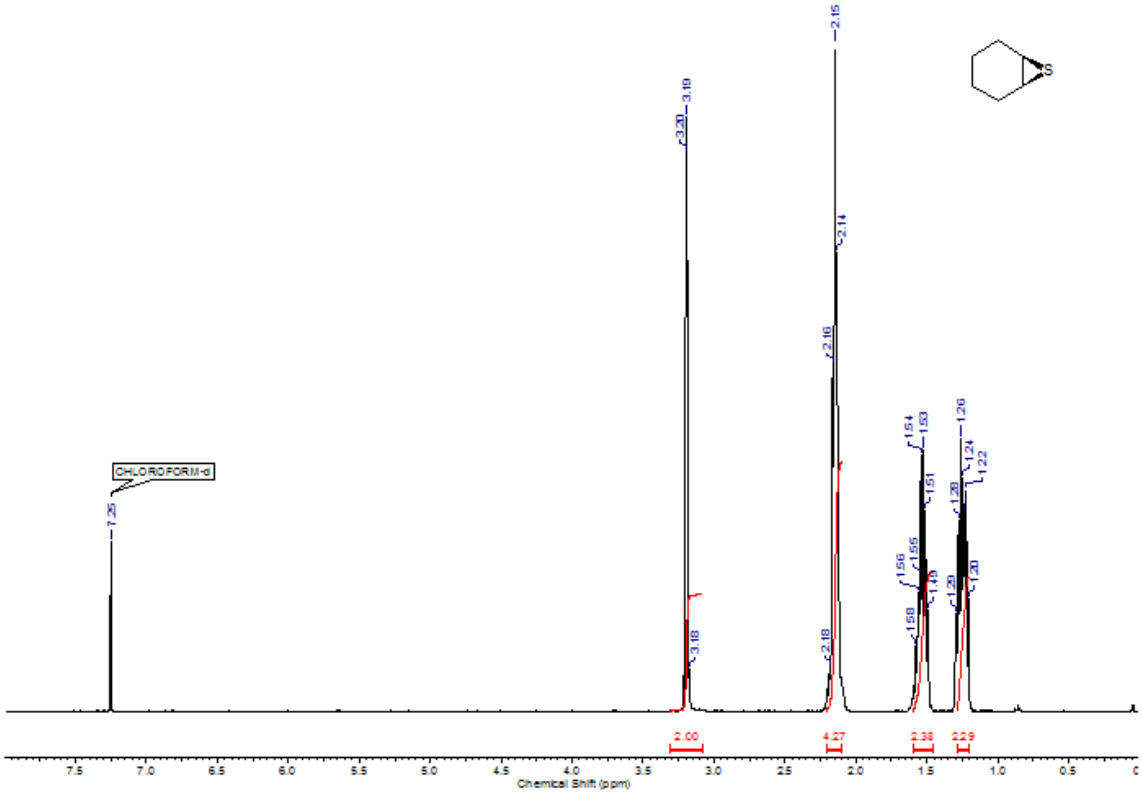


Fig. S10. ^{1}H NMR spectrum ($CDCl_3$, RT) of cycloxene sulfide, *cyclo*-[$(CH_2)_4CHCHS$].

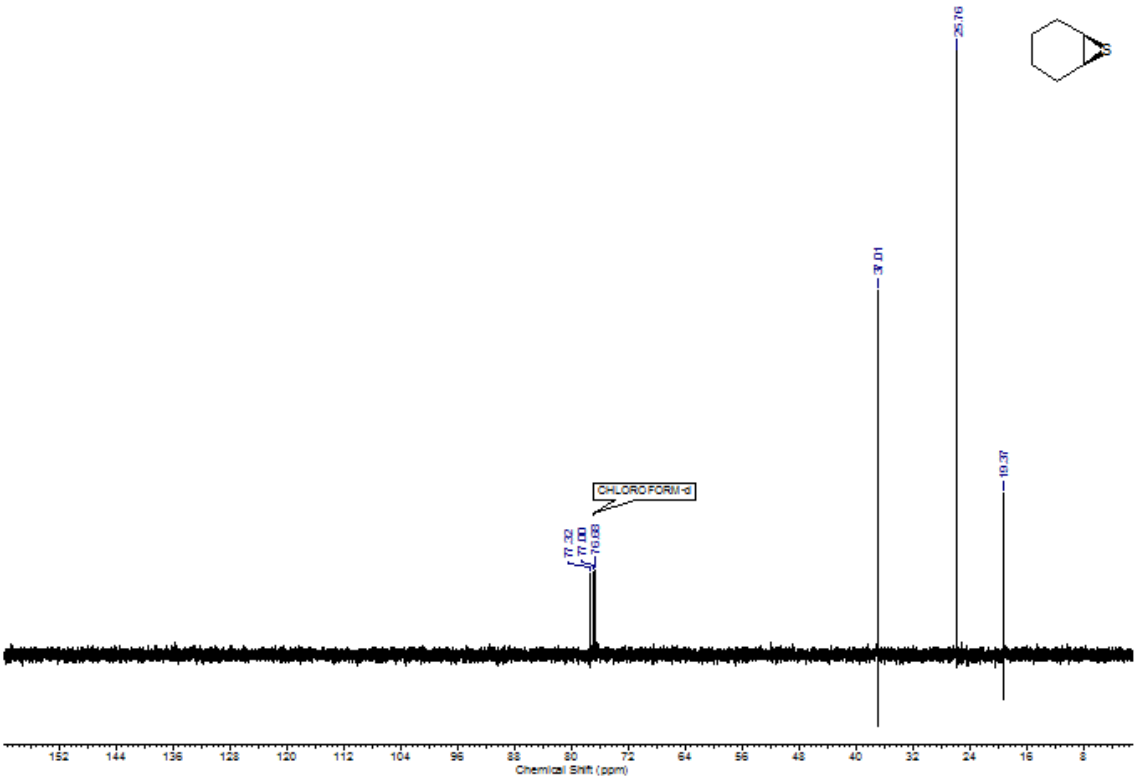


Fig. S11. ^{13}C NMR spectrum ($CDCl_3$, RT) of cycloxene sulfide, *cyclo*-[$(CH_2)_4CHCHS$].

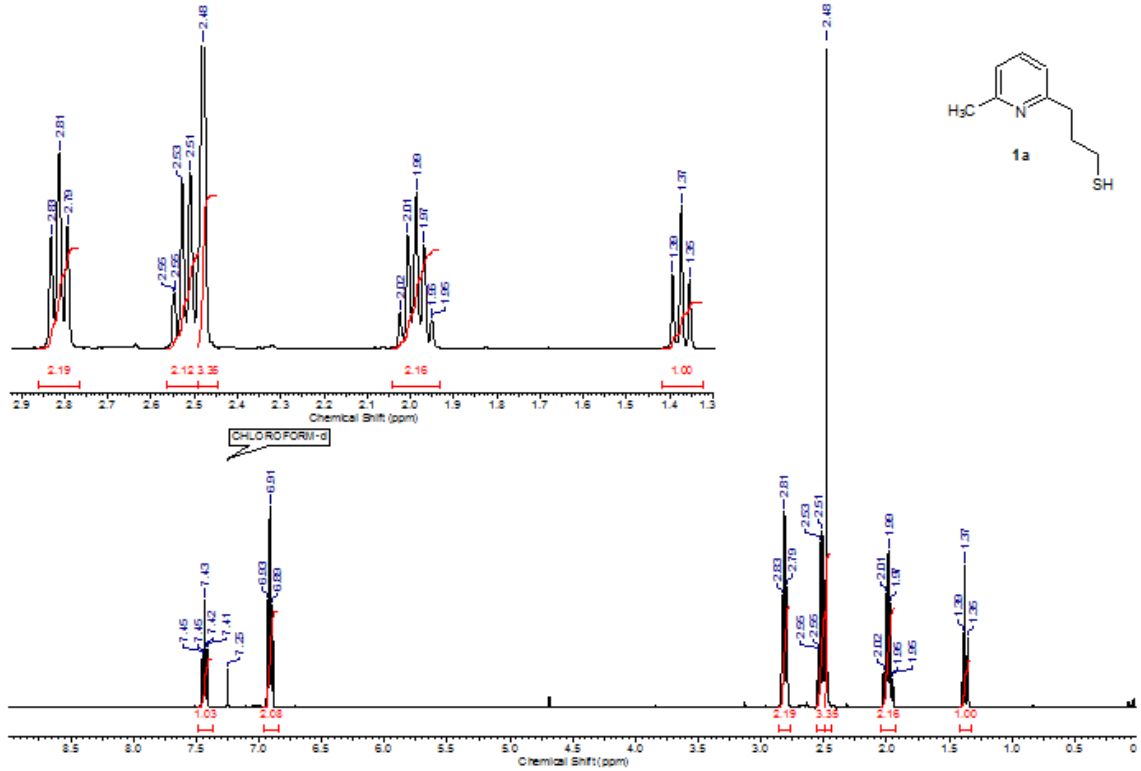


Fig. S12. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2CH_2SH$) (**1a**).

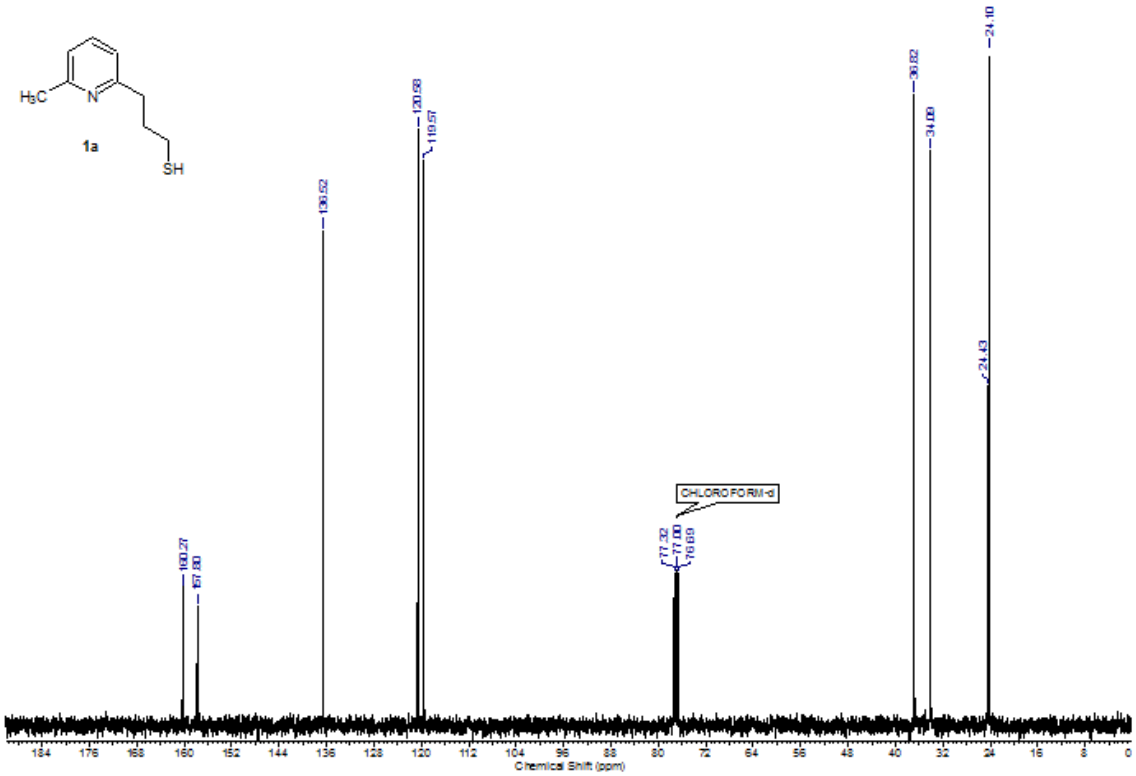


Fig. S13. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2CH_2SH$) (**1a**).

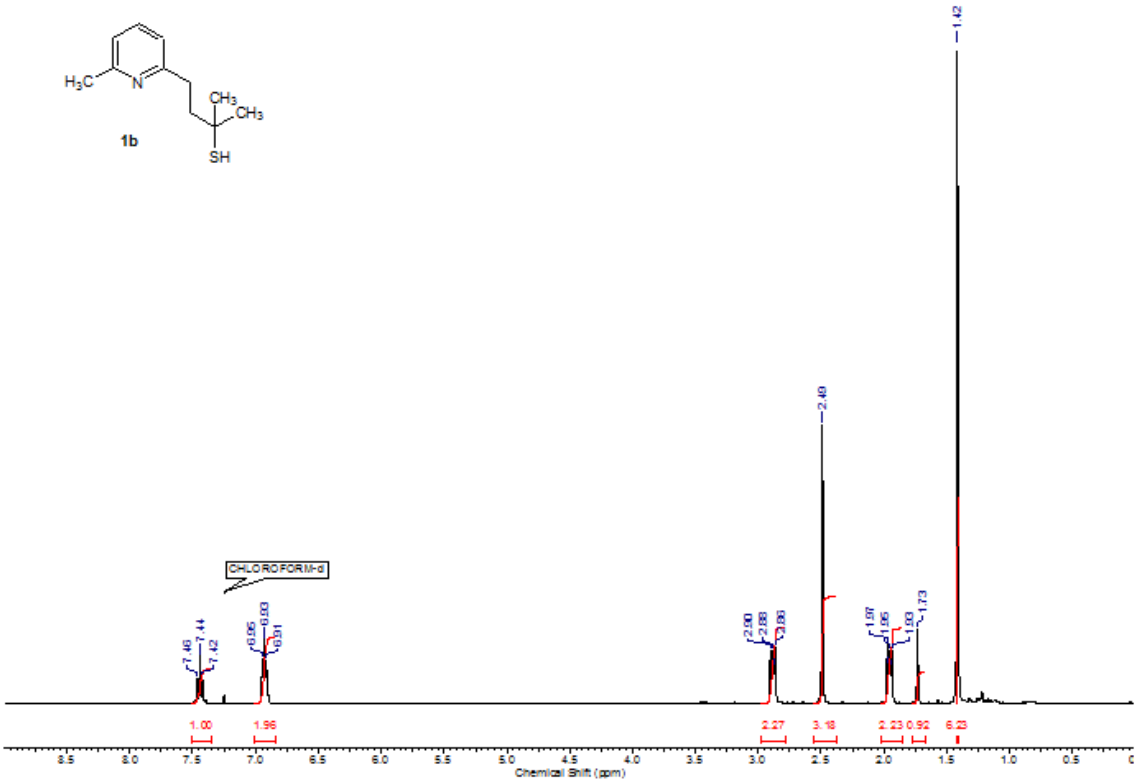


Fig. S14. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2CMe_2SH$) (**1b**).

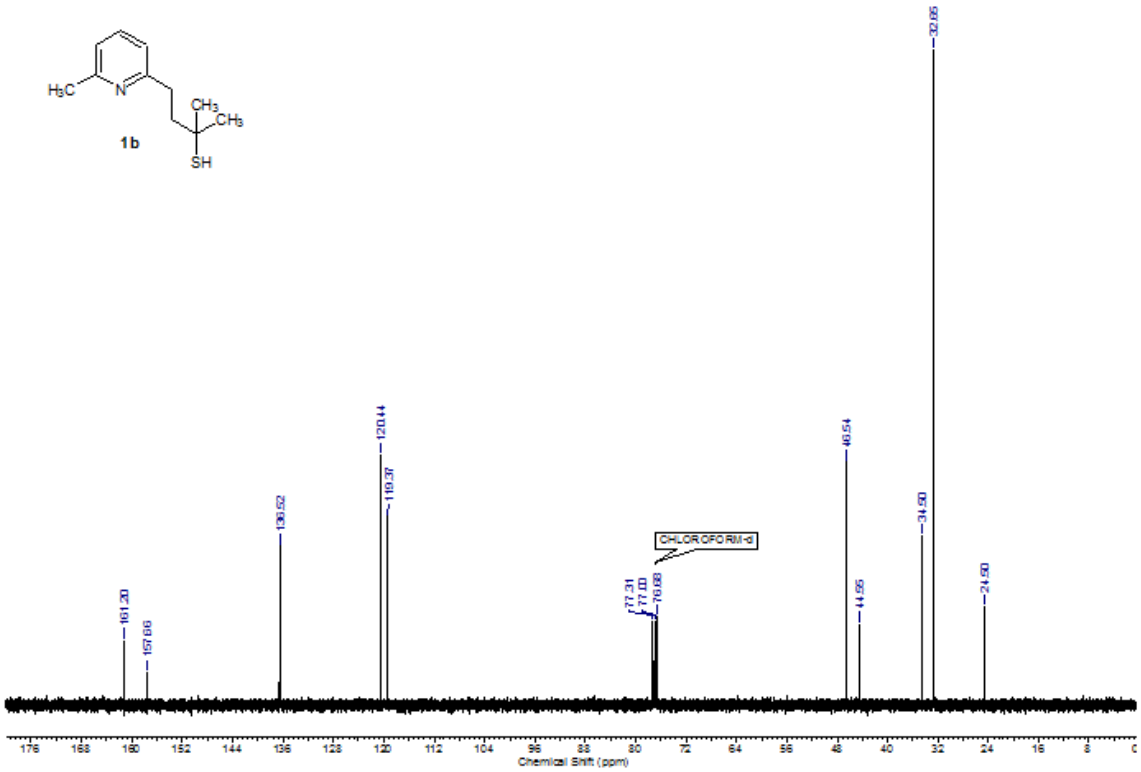


Fig. S15. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2CMe_2SH$) (**1b**).

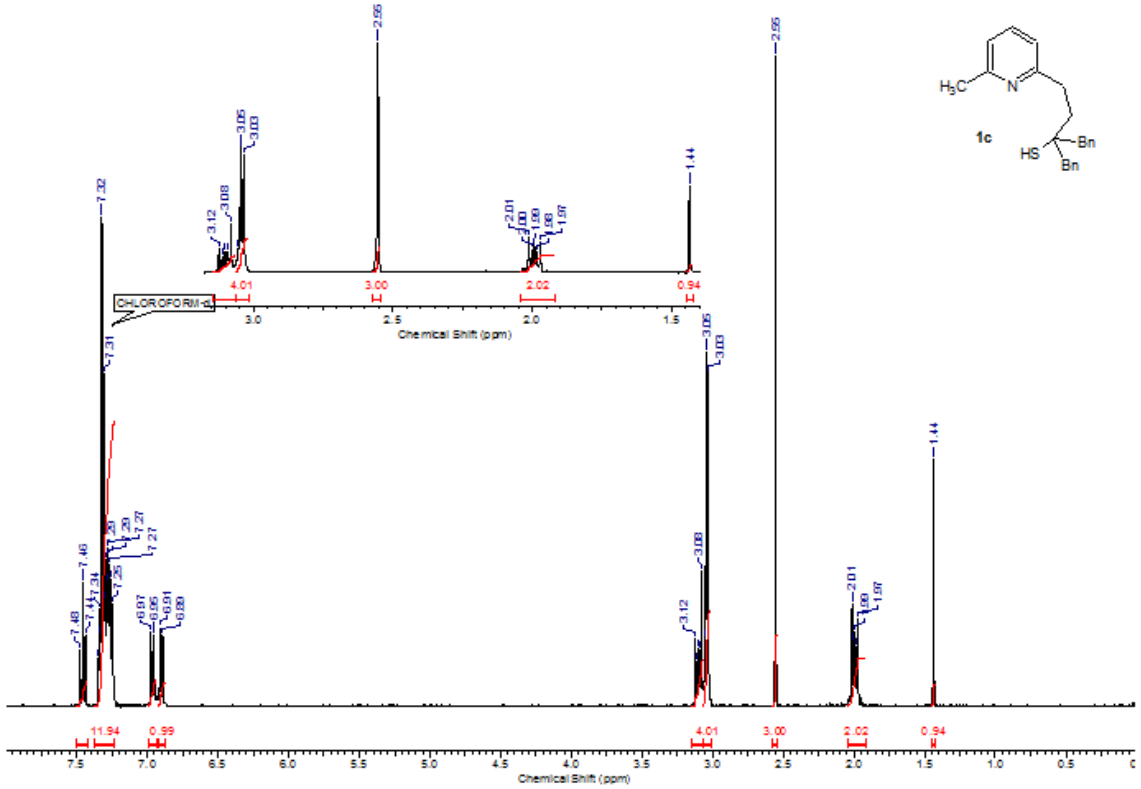


Fig. S16. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2CBn_2SH$) (**1c**).

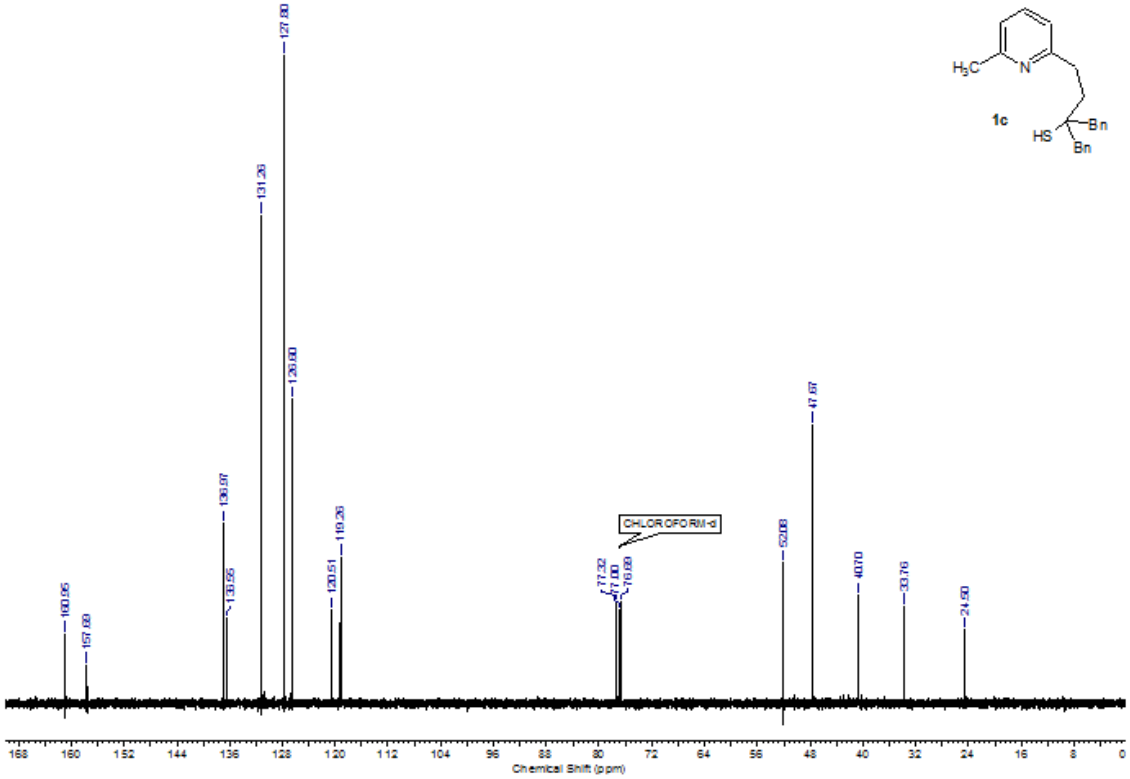


Fig. S17. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2CBn_2SH$) (**1c**).

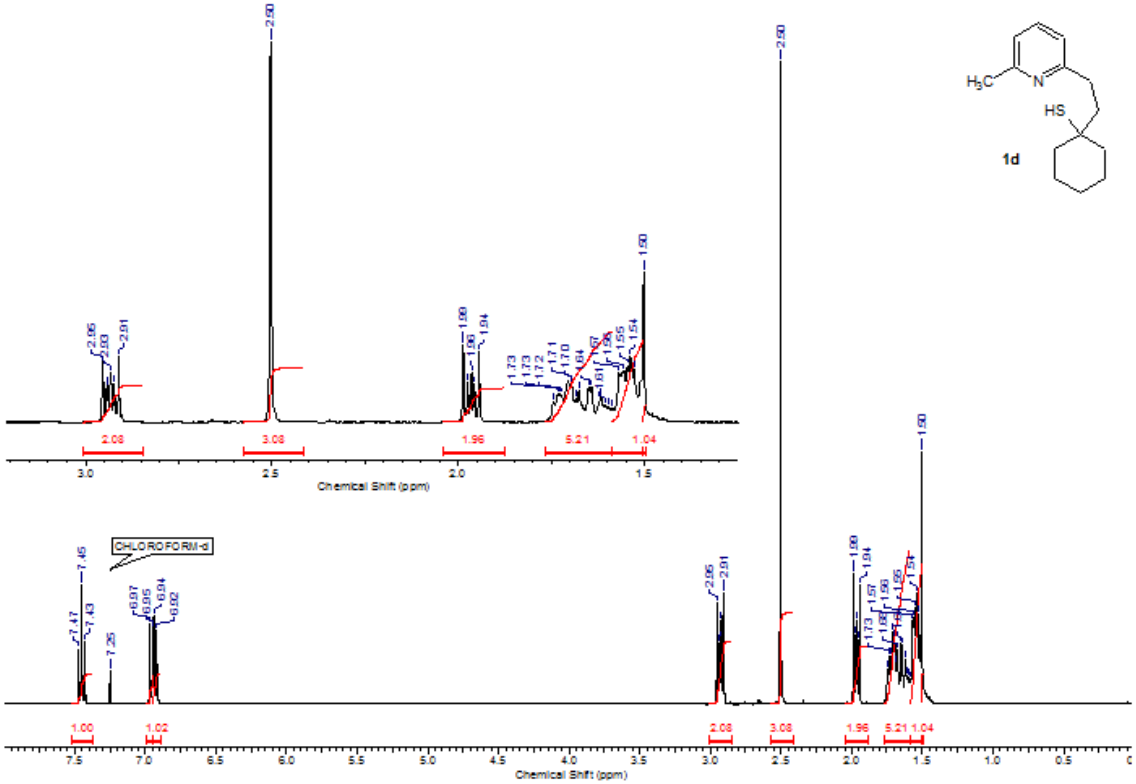


Fig. S18. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2C[CH_2]_5SH$) (**1d**).

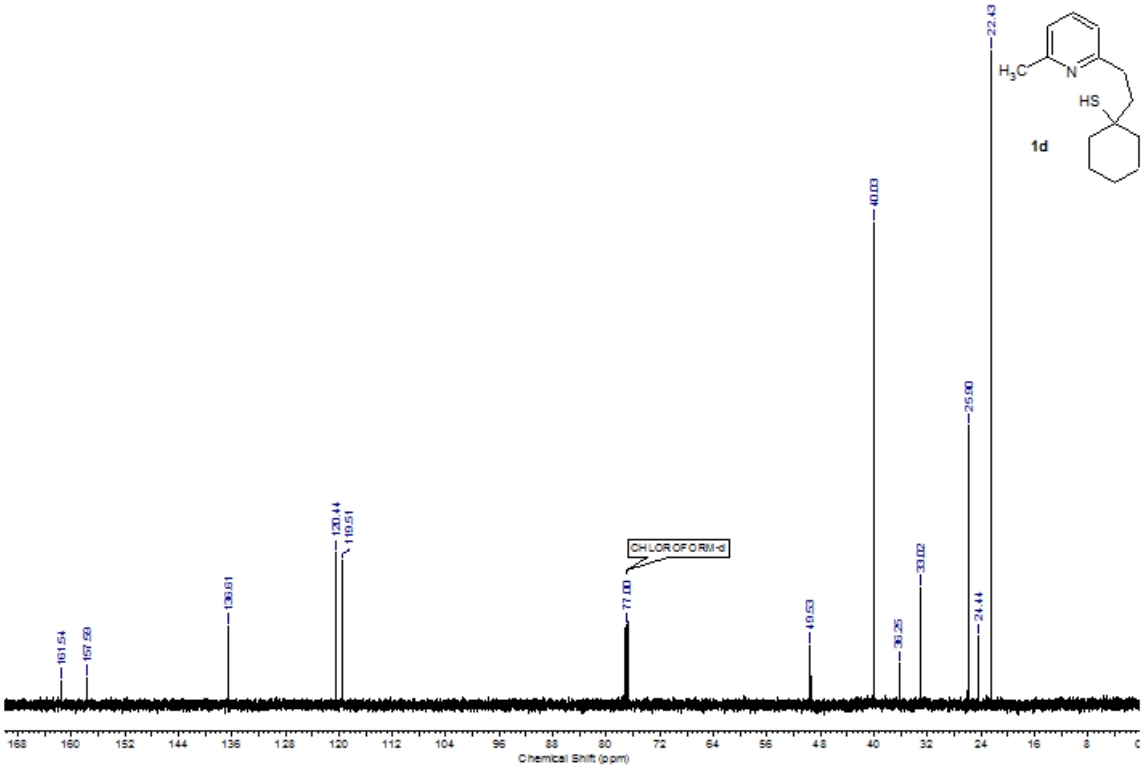


Fig. S19. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-MePy($CH_2CH_2C[CH_2]_5SH$) (**1d**).

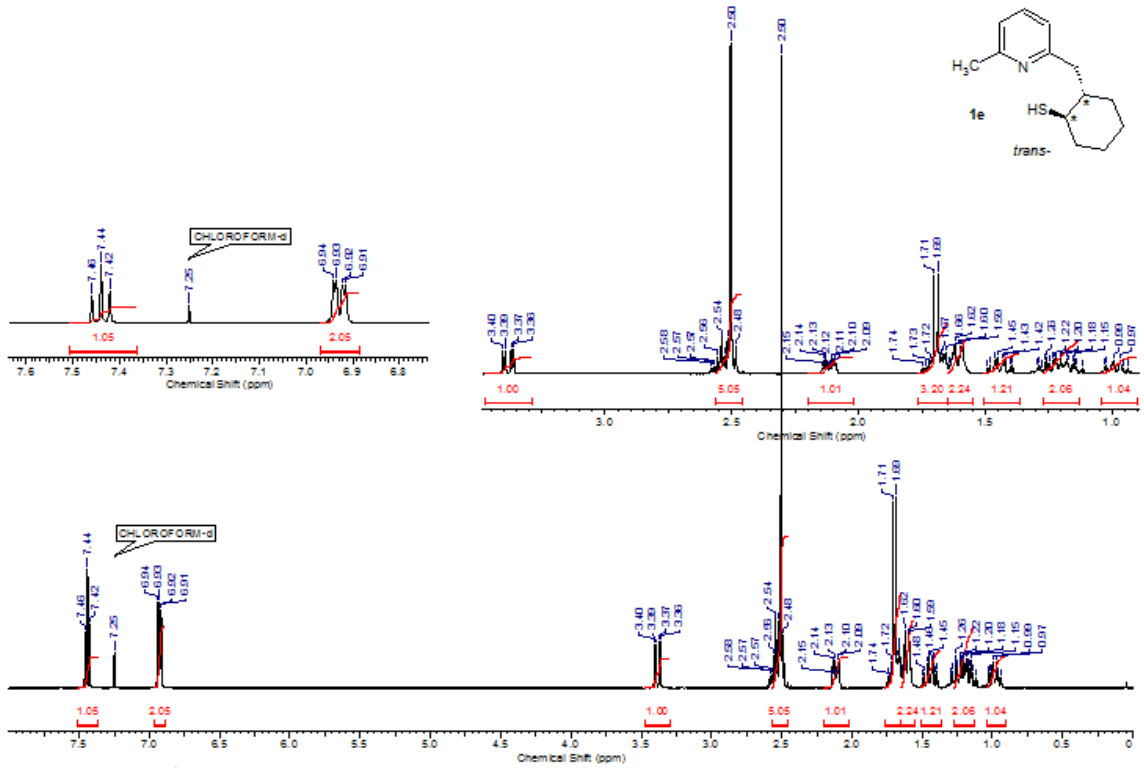


Fig. S20. ^{1}H NMR spectrum ($CDCl_3$, RT) of *trans*-2,6-MePy(CH_2-1,2-CH$[CH_2]_4$CHSH) (**1e**).

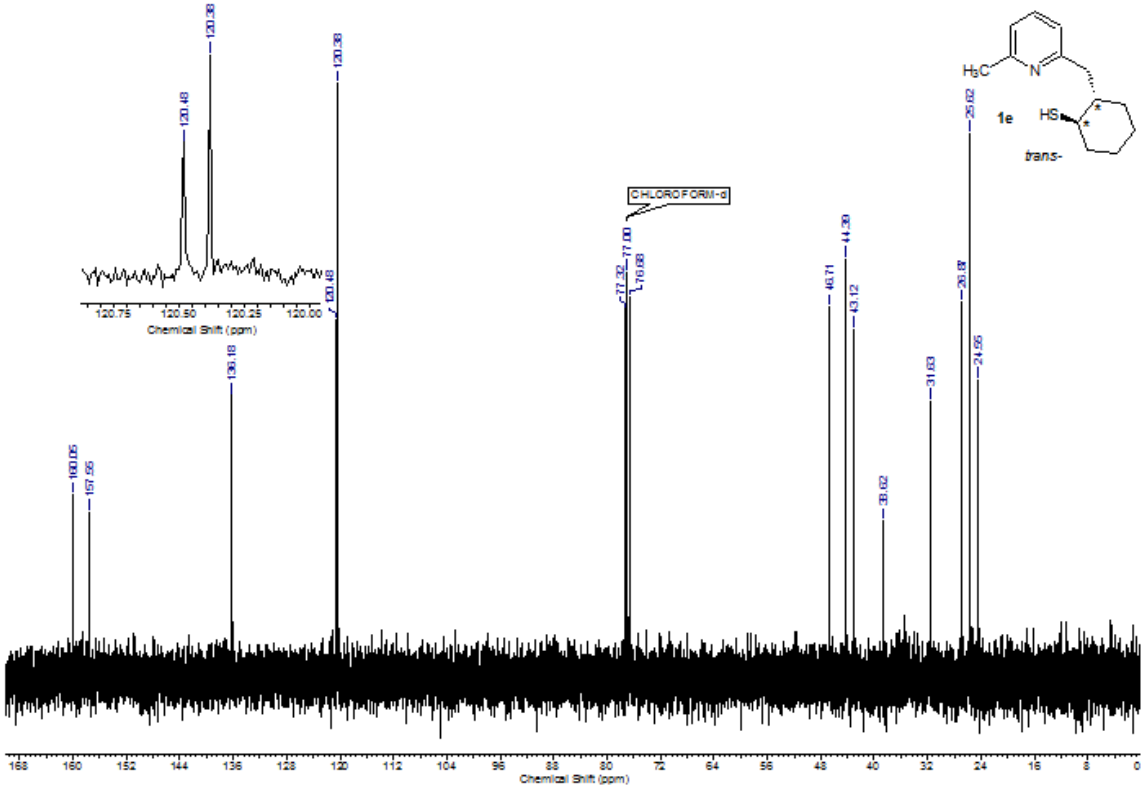


Fig. S21. ^{13}C NMR spectrum ($CDCl_3$, RT) of *trans*-2,6-MePy(CH_2-1,2-CH[CH_2]$_4$CHSH) (**1e**).

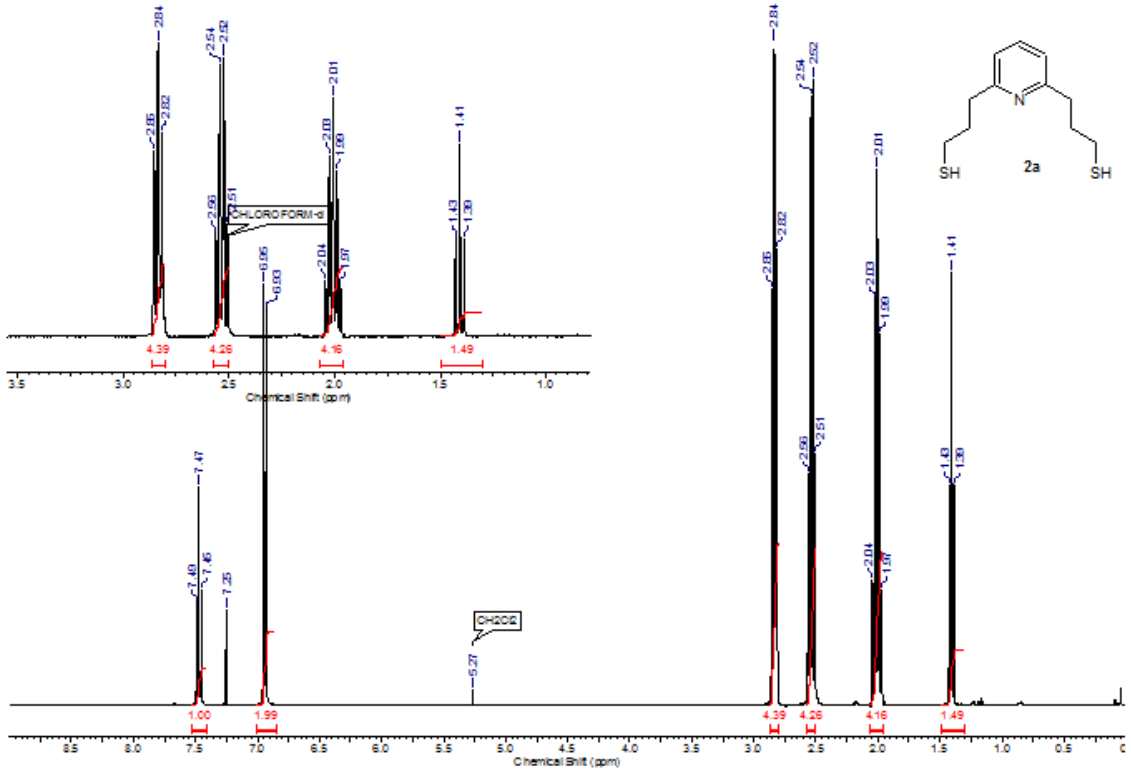


Fig. S22. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CH_2SH$)$_2$ (**2a**).

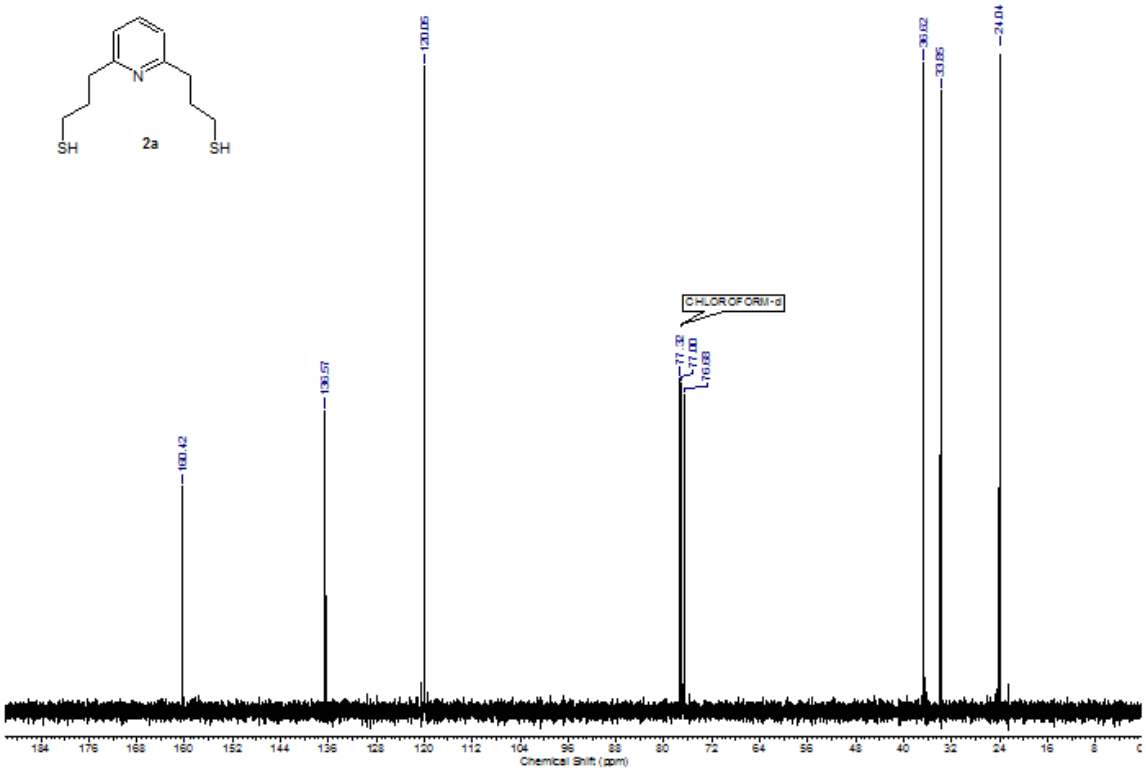


Fig. S23. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CH_2SH)_2$ (**2a**).

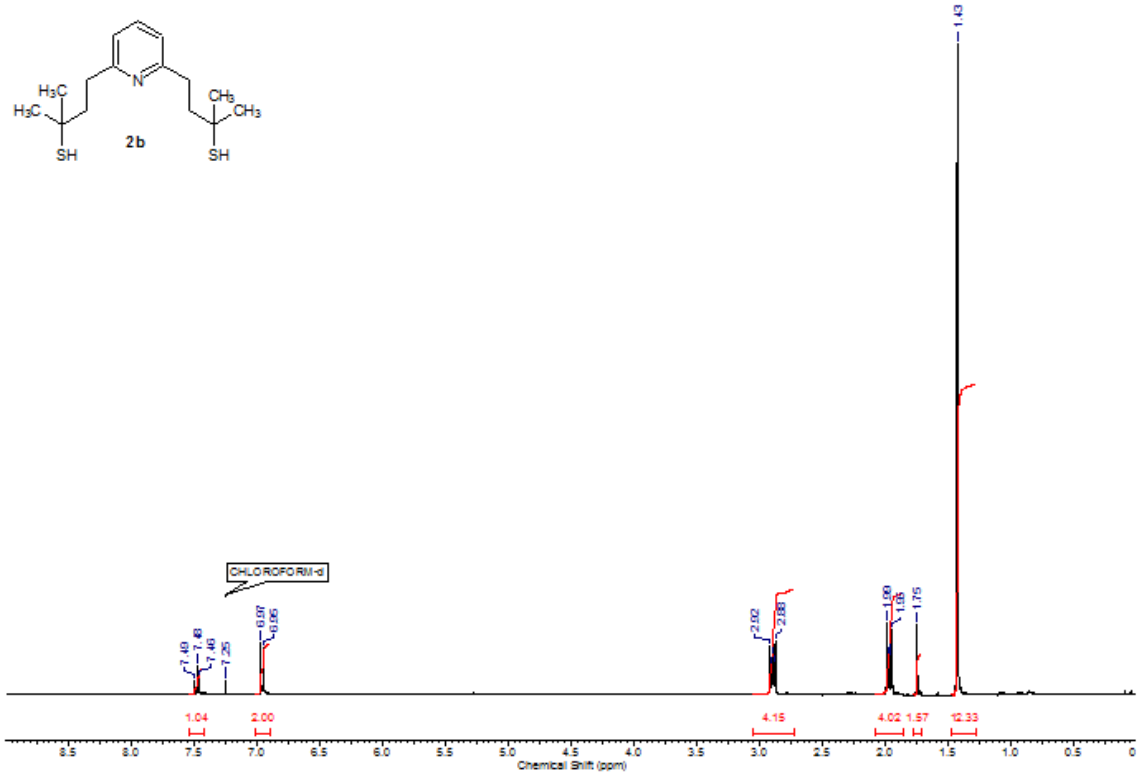


Fig. S24. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CMe_2SH)_2$ (**2b**).

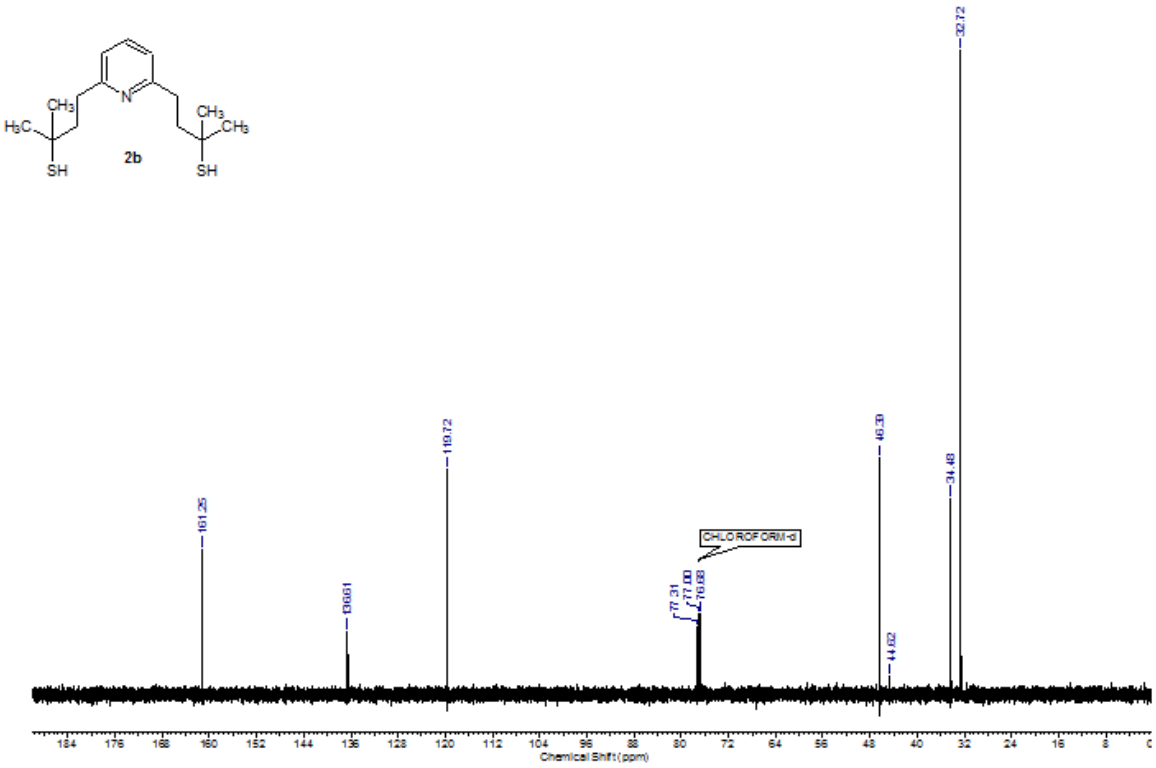


Fig. S25. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CMe_2SH)_2$ (**2b**).

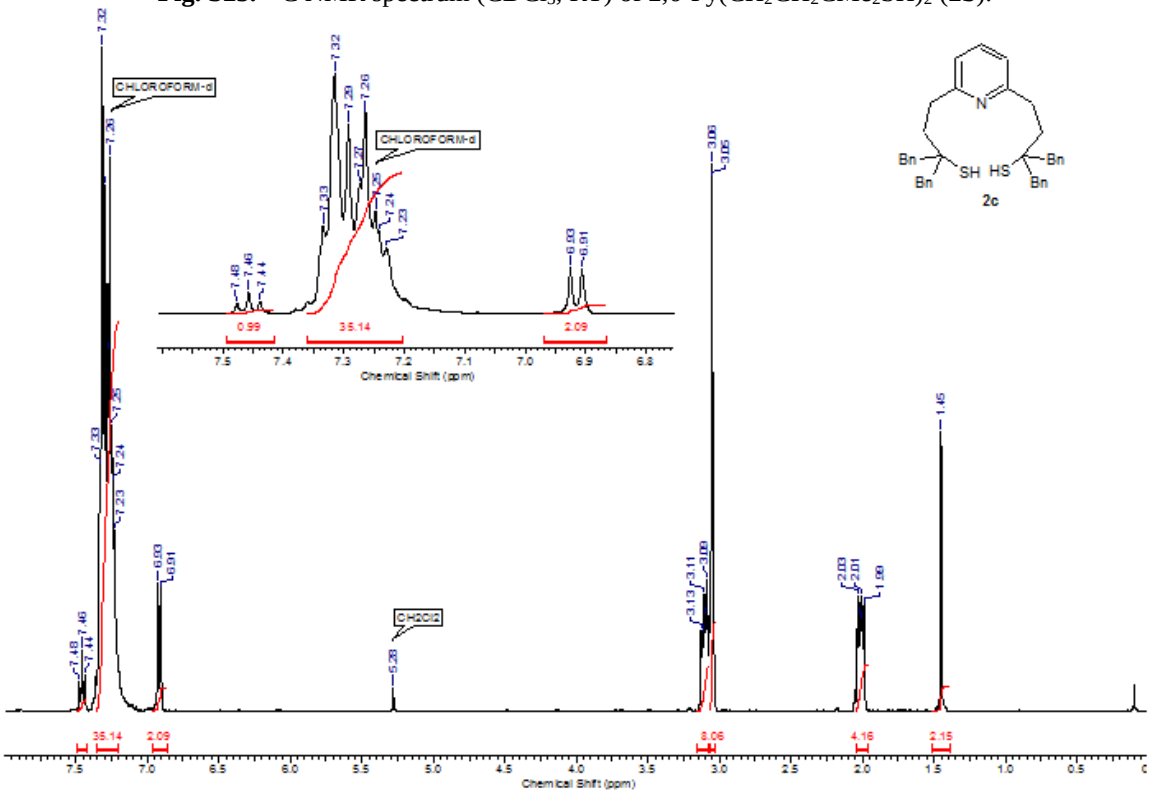


Fig. S26. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CBn_2SH)_2$ (**2c**).

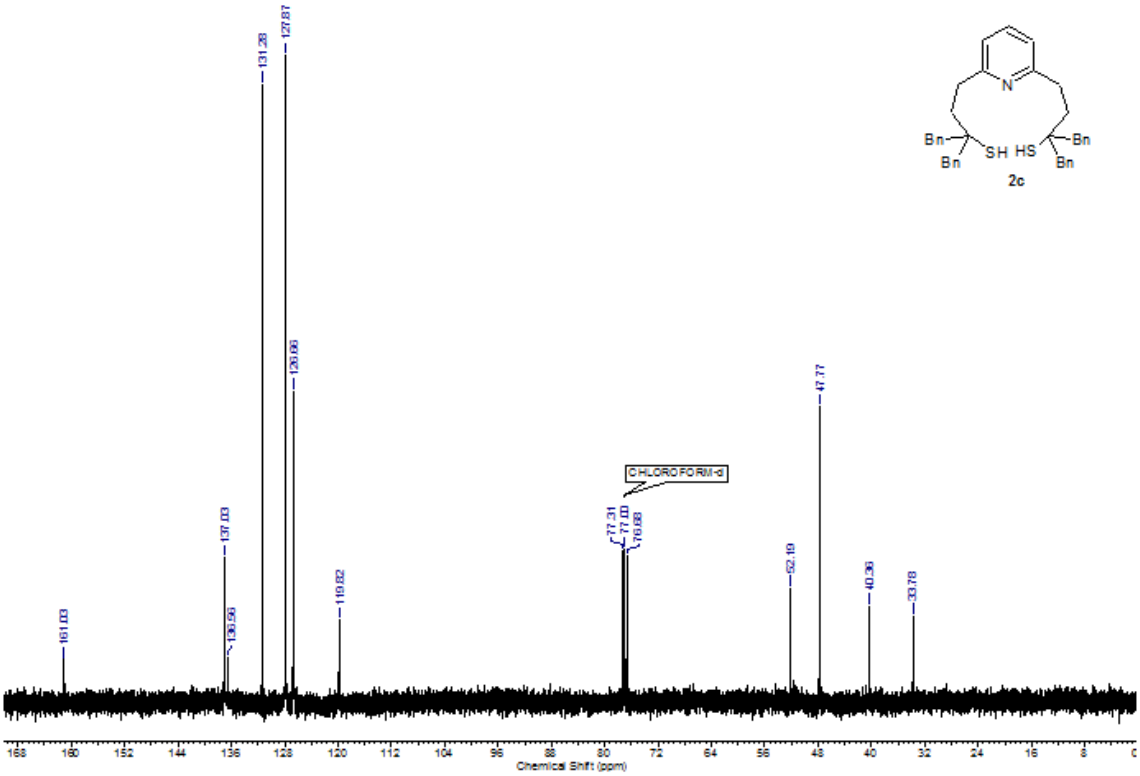


Fig. S27. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2CBn_2SH$)$_2$ (**2c**).

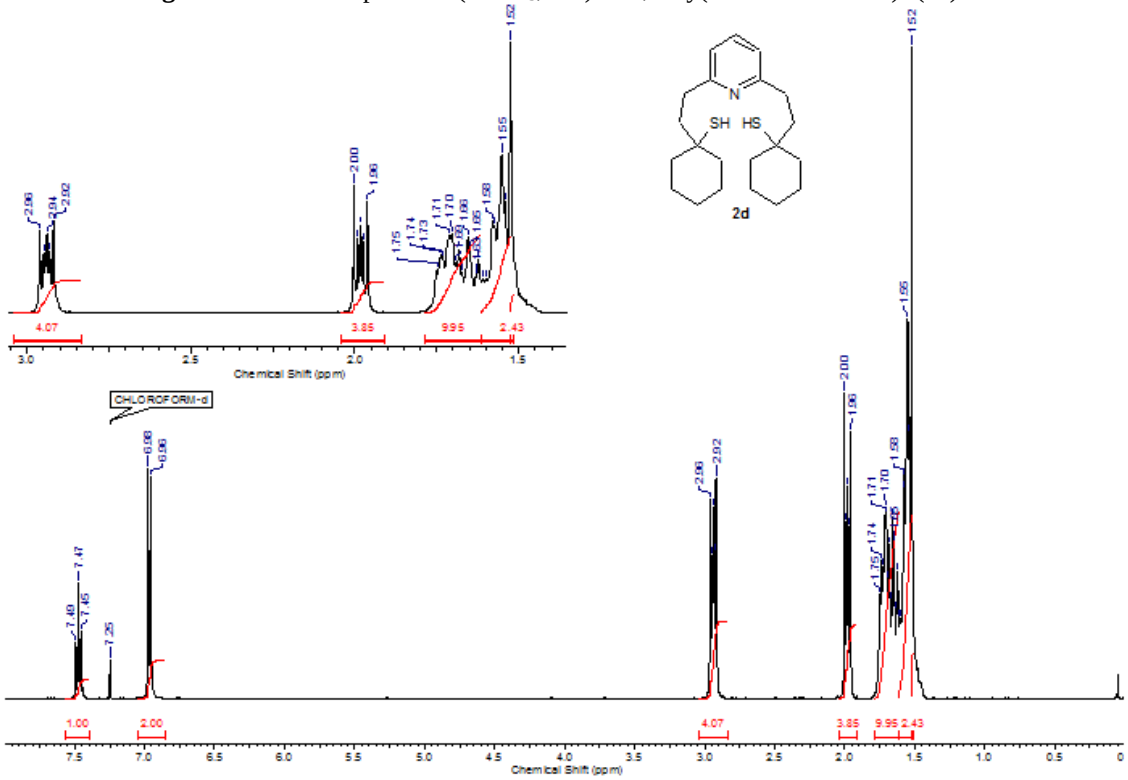


Fig. S28. ^{1}H NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2C(CH_2)_5SH$)$_2$ (**2d**).

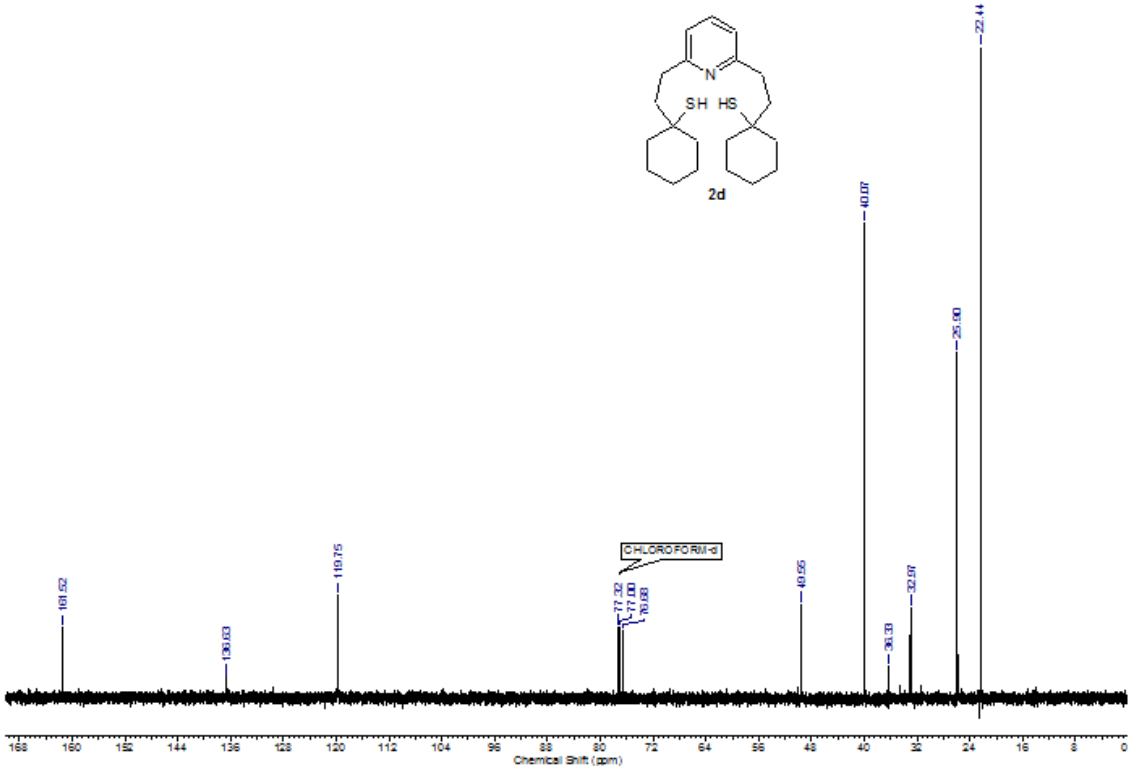


Fig. S29. ^{13}C NMR spectrum ($CDCl_3$, RT) of 2,6-Py($CH_2CH_2C(CH_2)_5SH)_2$ (**2d**).

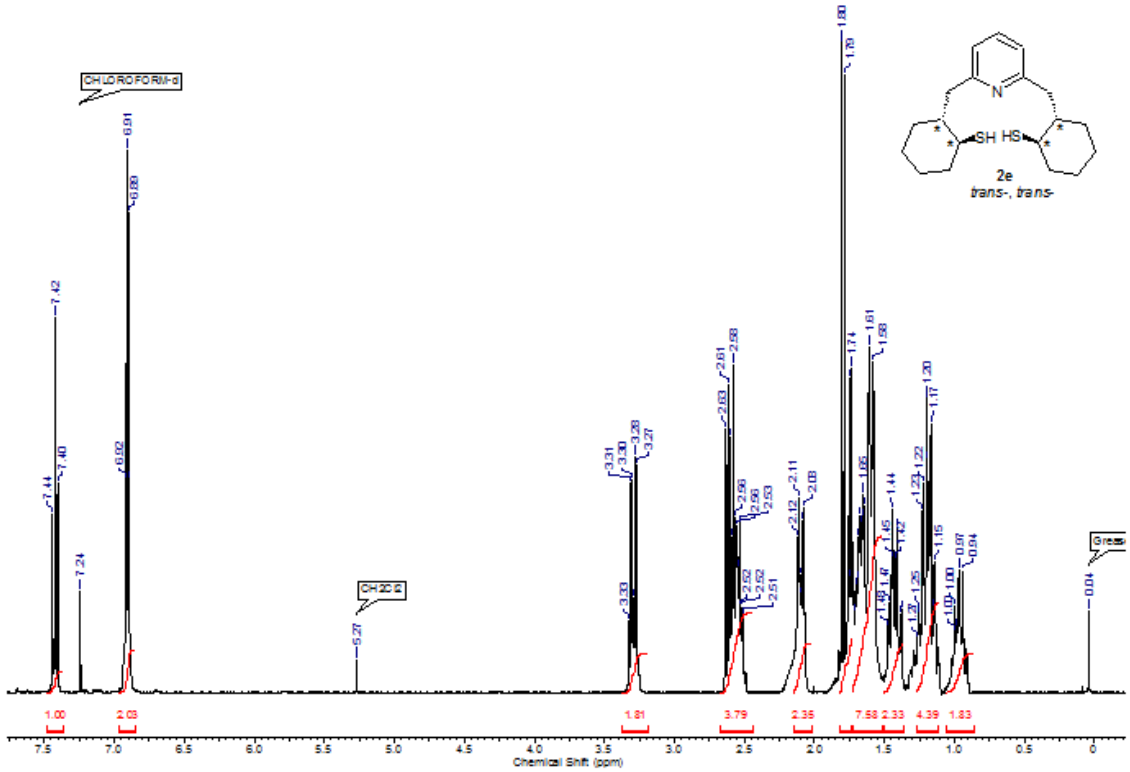


Fig. S30. ^{1}H NMR spectrum ($CDCl_3$, RT) of *trans*-, *trans*-2,6-Py(CH_2-1,2-CH[CH_2]$_4$CHSH)$_2$ (**2e**).

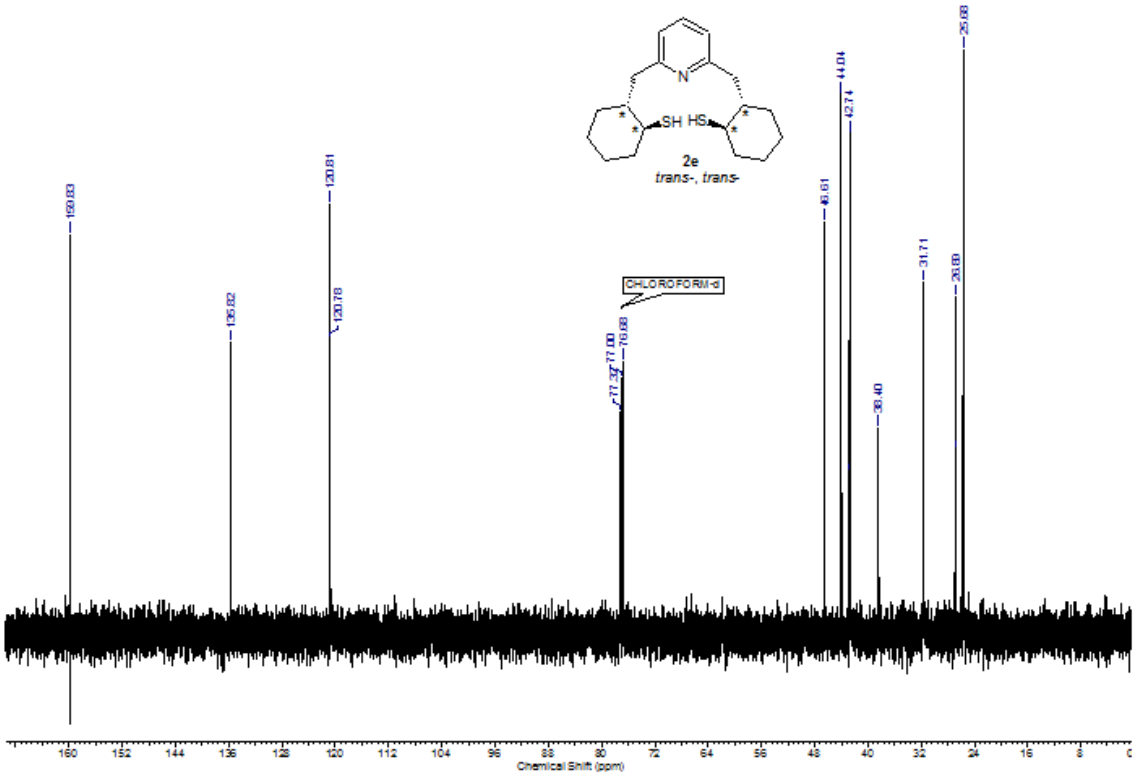


Fig. S31. ^{13}C NMR spectrum ($CDCl_3$, RT) of *trans*-, *trans*-2,6-Py(CH_2-1,2-CH[CH_2]$_4$CHSH)$_2$ (**2e**).

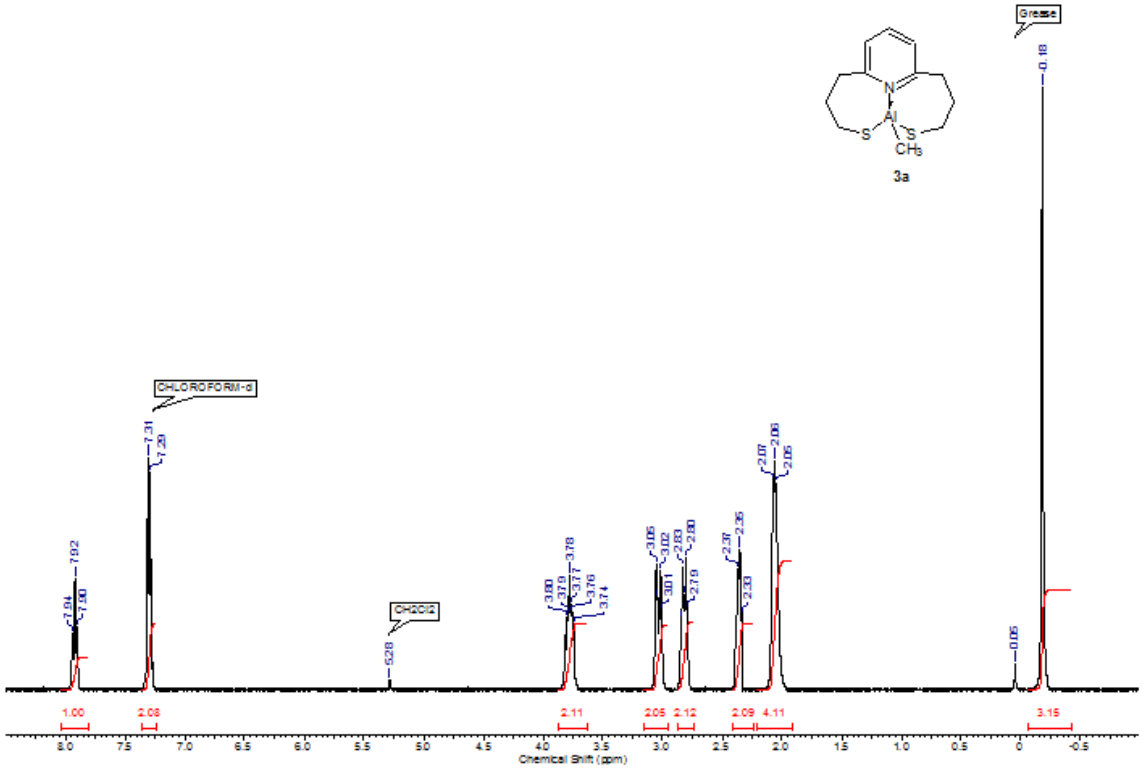


Fig. S32. ^{1}H NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CH_2S$)$_2$]AlMe (**3a**).

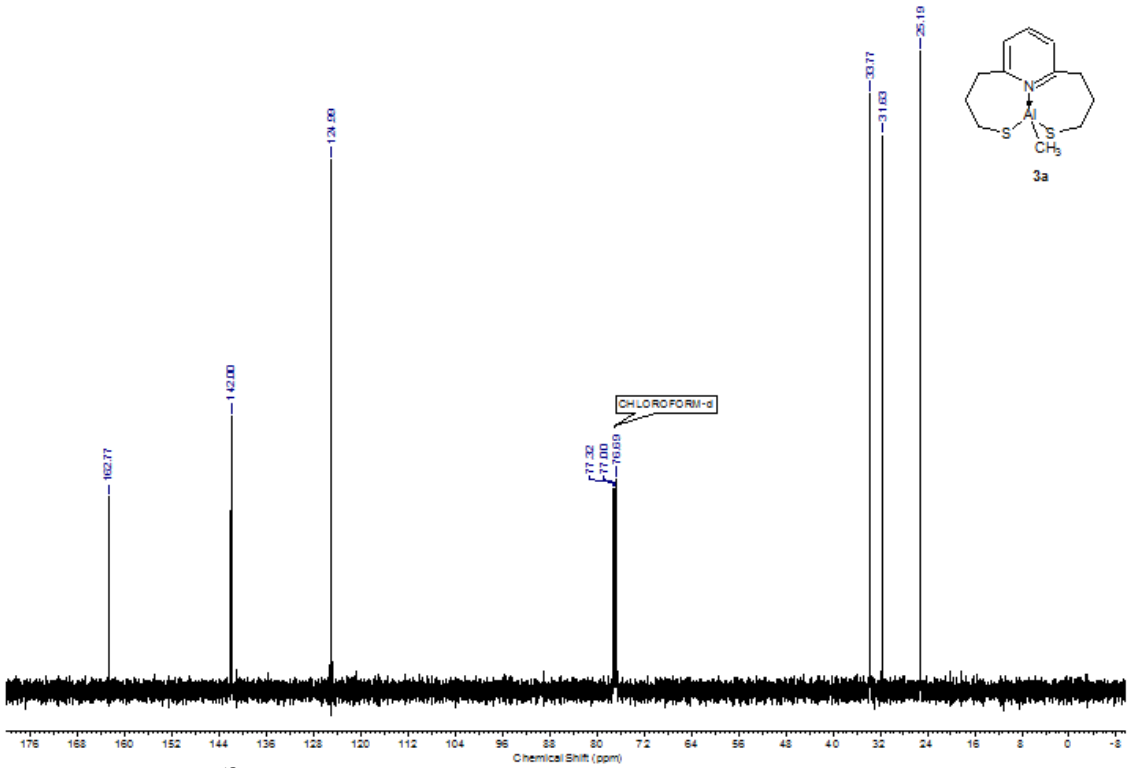


Fig. S33. ^{13}C NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CH_2S)_2$]AlMe (**3a**).

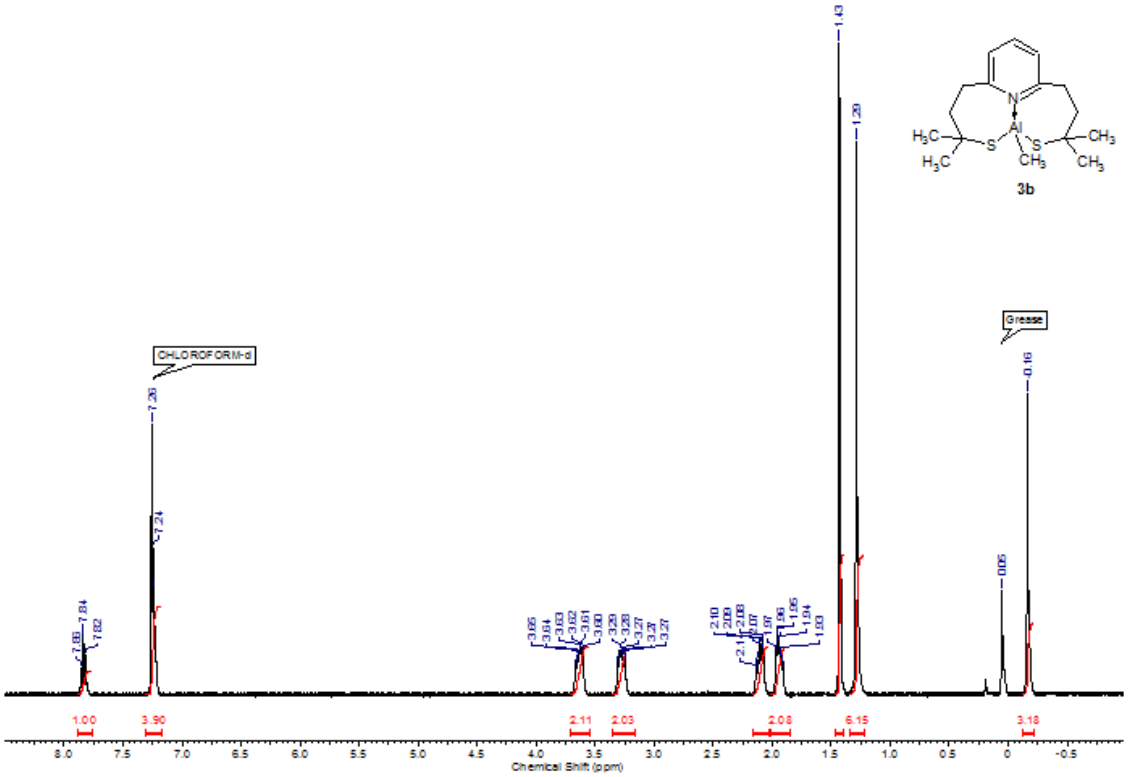


Fig. S34. ^{1}H NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CMe_2S)_2$]AlMe (**3b**).

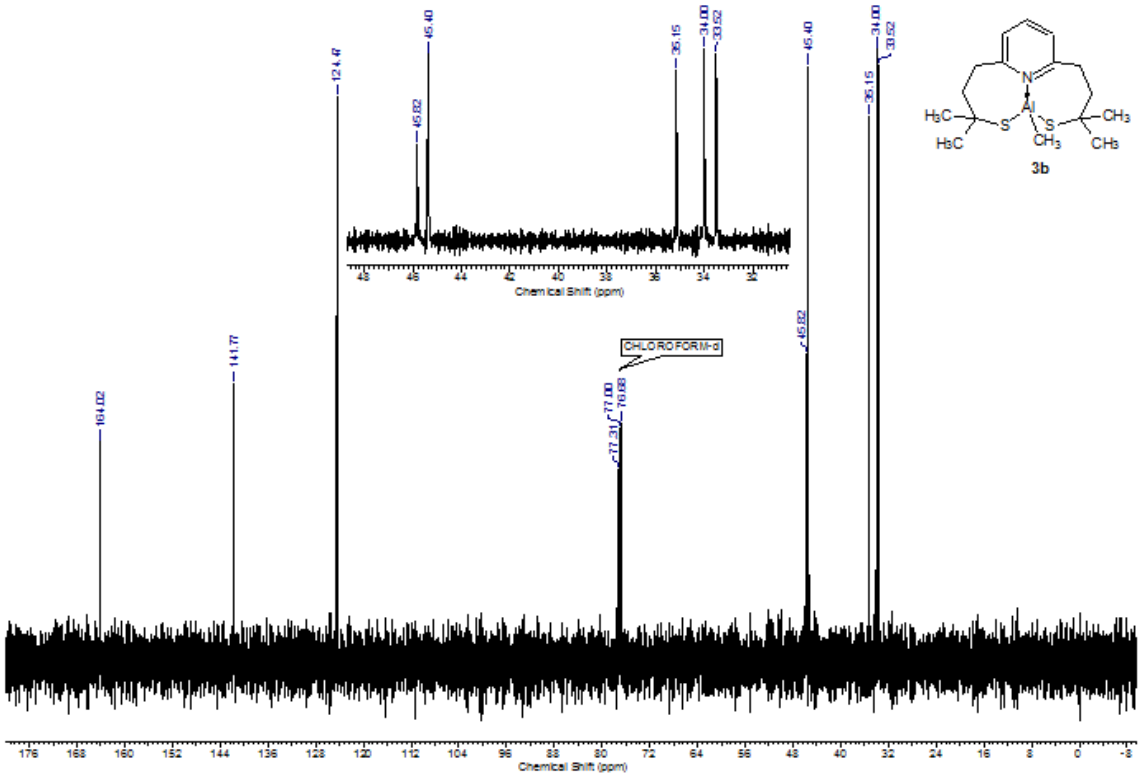


Fig. S35. ^{13}C NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CMe_2S)_2$]AlMe (**3b**).

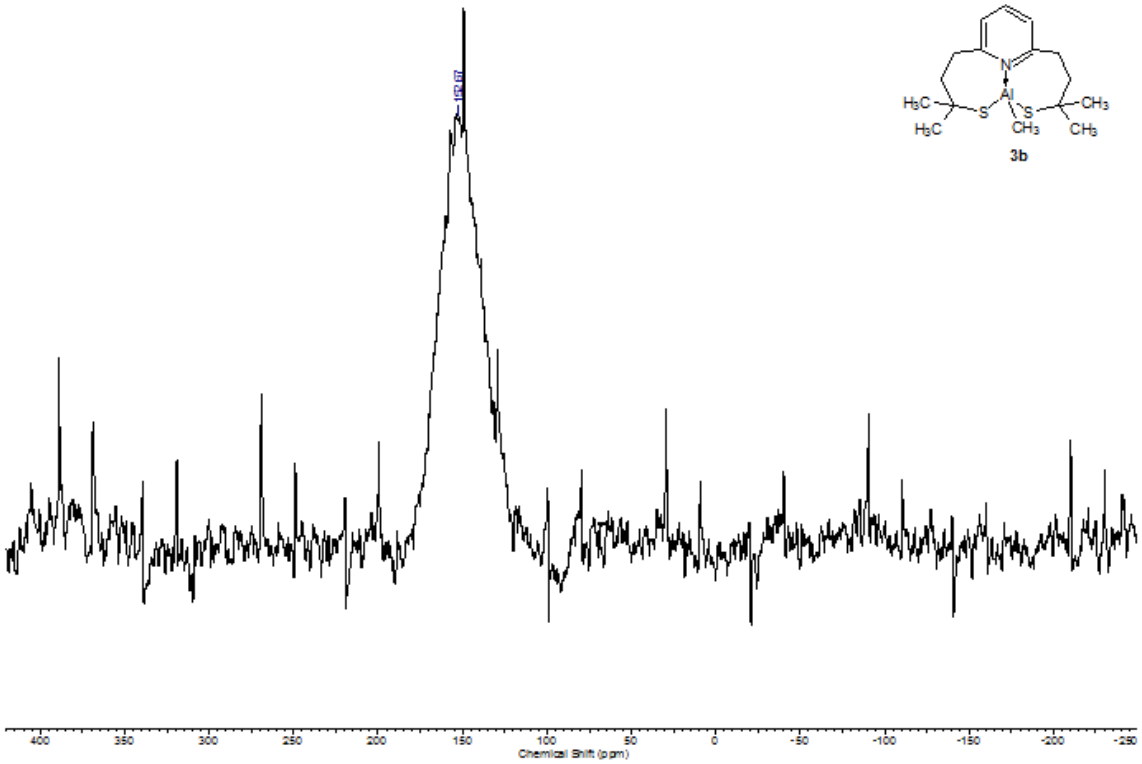


Fig. S36. ^{27}Al NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CMe_2S)_2$]AlMe (**3b**).

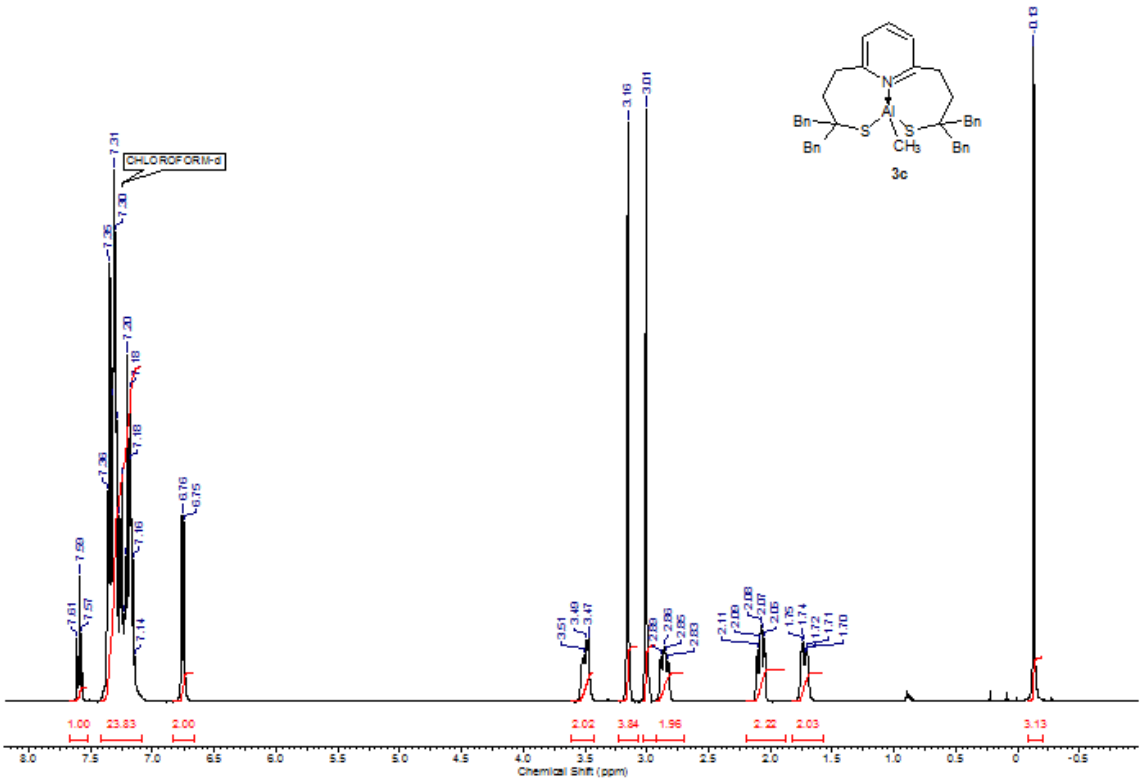


Fig. S37. ^{1}H NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CBn_2S$)$_2$]AlMe (**3c**).

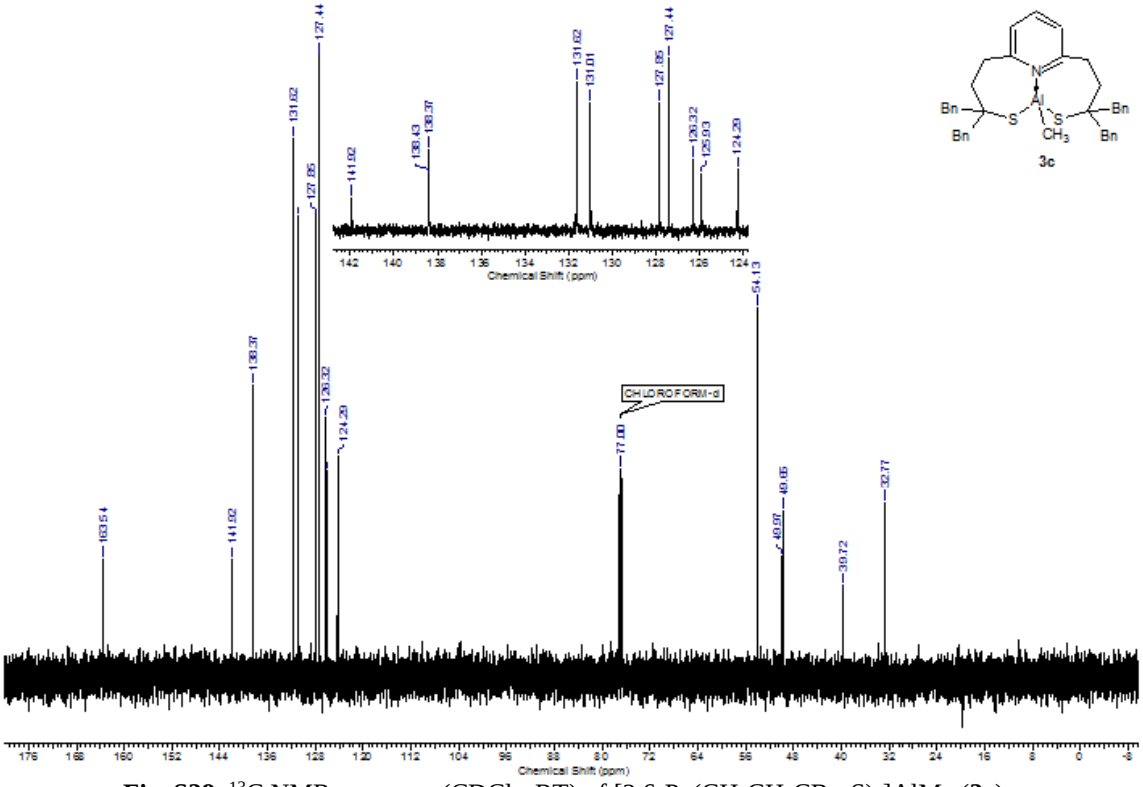


Fig. S38. ^{13}C NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CBn_2S$)$_2$]AlMe (**3c**).

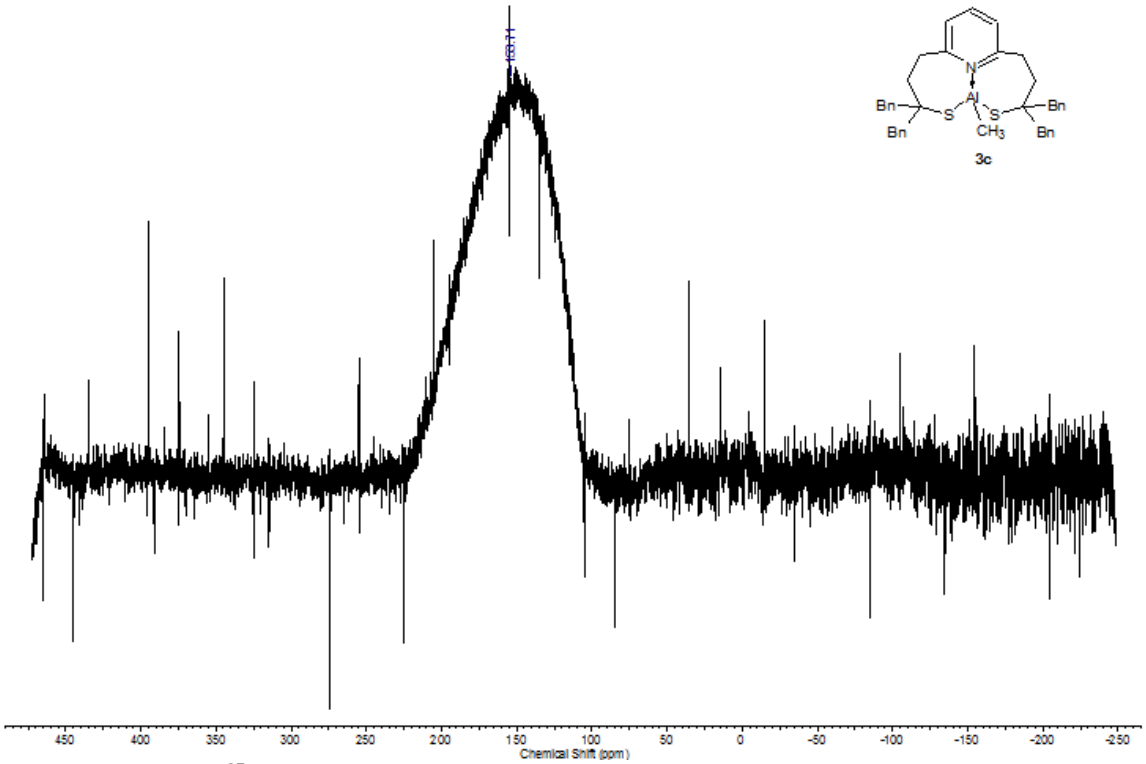


Fig. S39. ^{27}Al NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2CBn_2S)_2$]AlMe (**3c**).

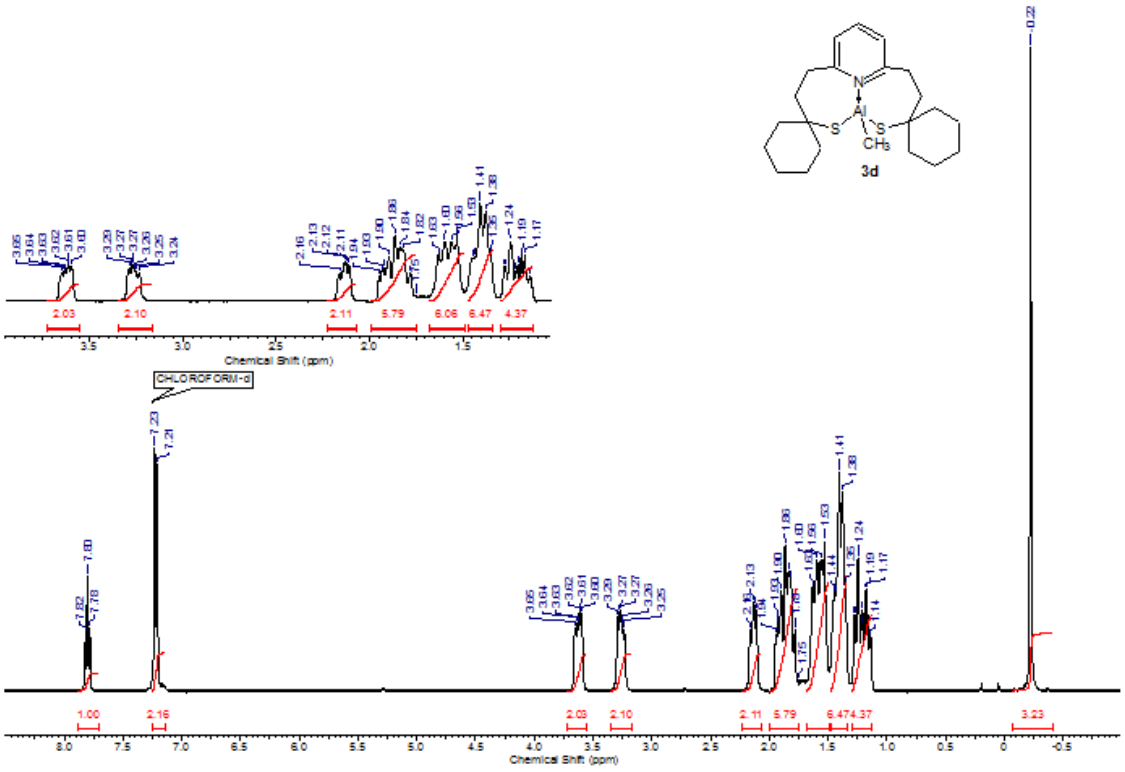


Fig. S40. ^{1}H NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2C(CH_2)_5S)_2$]AlMe (**3d**).

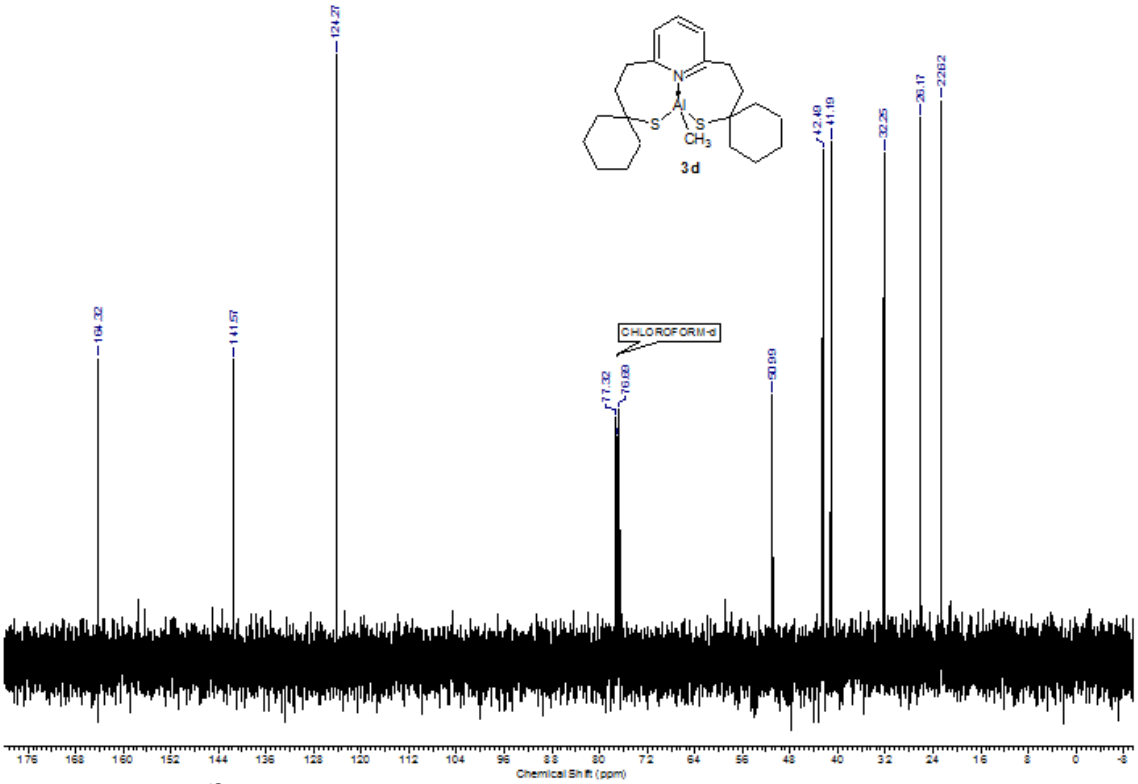


Fig. S41. ^{13}C NMR spectrum ($CDCl_3$, RT) of [2,6-Py($CH_2CH_2C(CH_2)_5S)_2$]AlMe (**3d**).

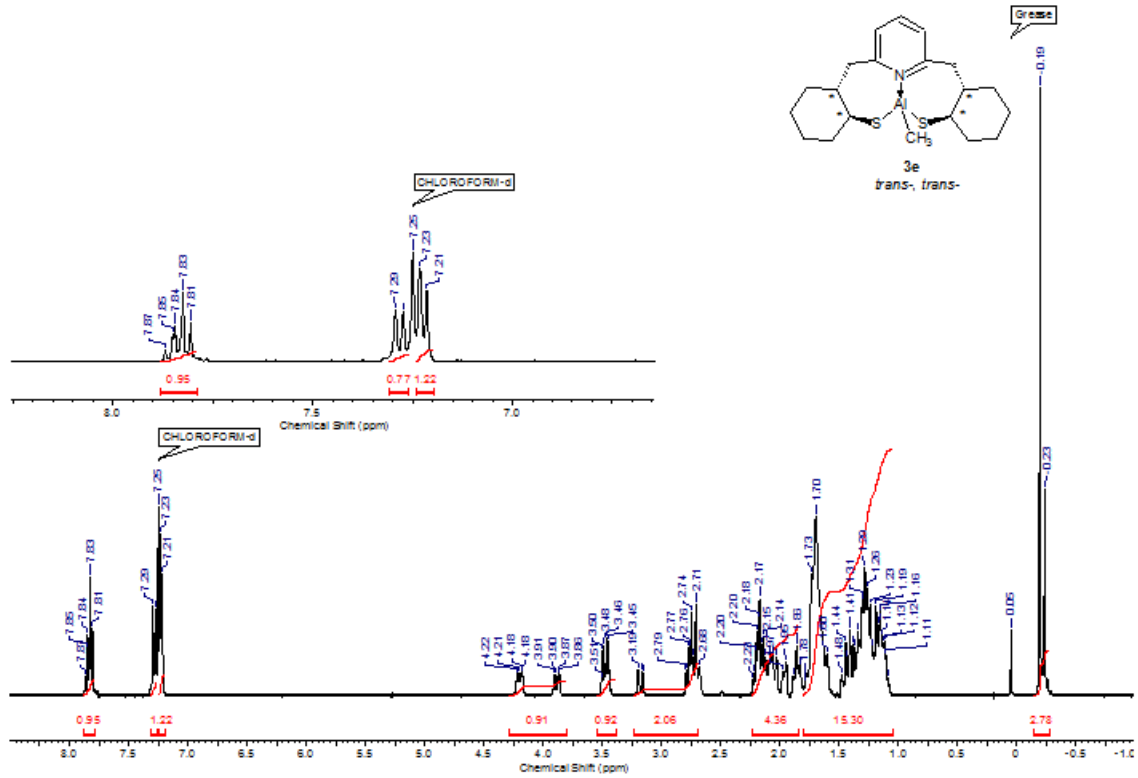


Fig. S42. ^{1}H NMR spectrum ($CDCl_3$, RT) of [*trans*-,*trans*-2,6-Py(CH_2-1,2-$CH(CH_2)_4CHS)_2$]AlMe (**3e**).

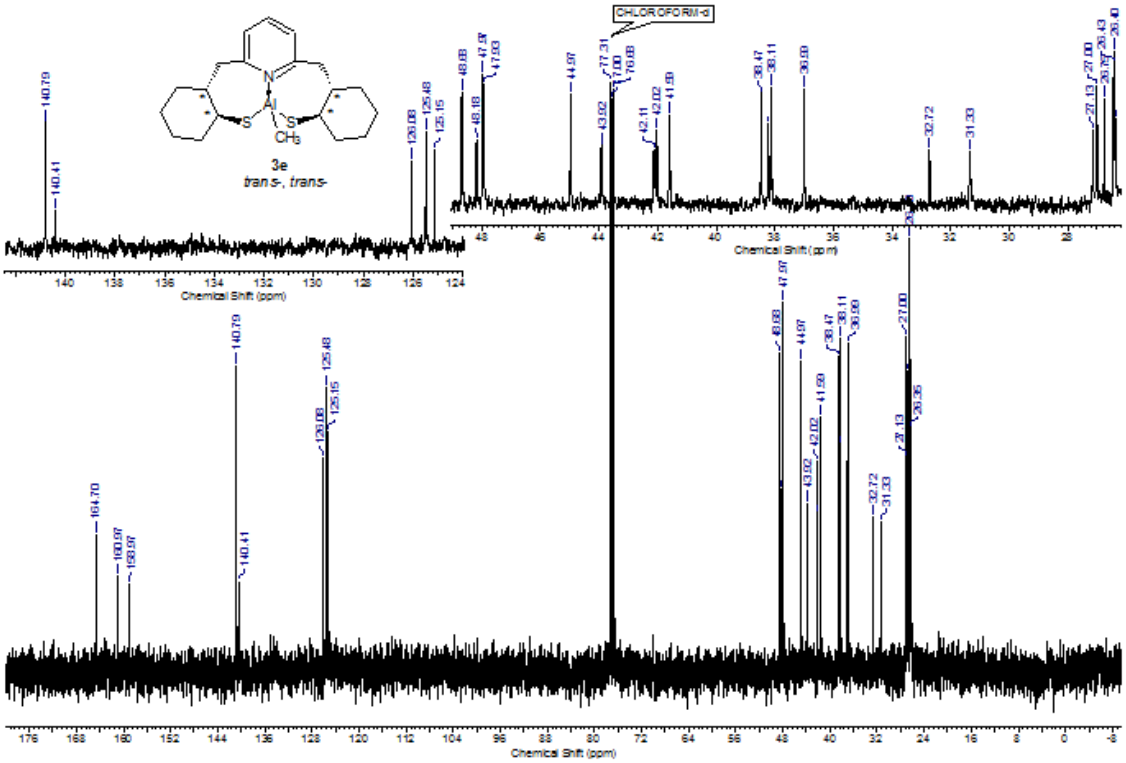


Fig. S43. ^{13}C NMR spectrum ($CDCl_3$, RT) of [*trans*-,*trans*-2,6-Py(CH_2-1,2-CH(CH_2)$_4$CHS)$_2$]AlMe (**3e**).

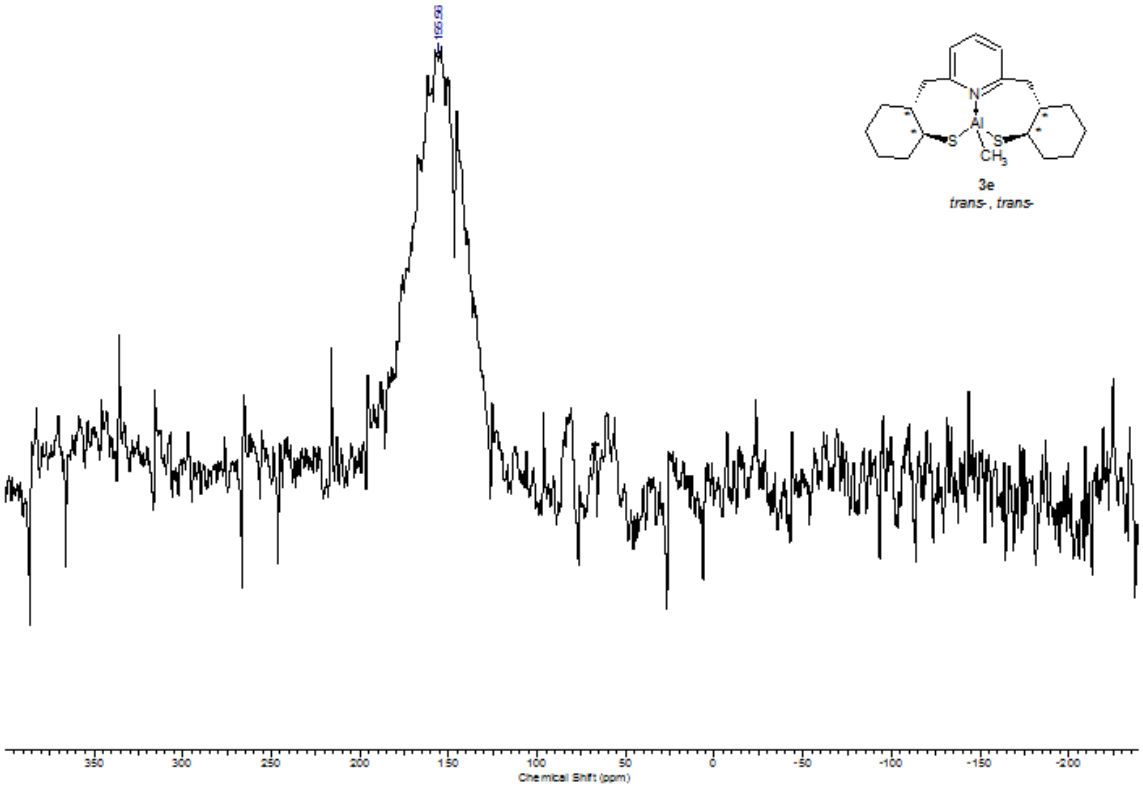


Fig. S44. ^{27}Al NMR spectrum ($CDCl_3$, RT) of [*trans*-,*trans*-2,6-Py(CH_2-1,2-CH(CH_2)$_4$CHS)$_2$]AlMe (**3e**).

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