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Supplementary Information

for the article

A New Stable Monomeric Lead(II) Dithiolate $Pb(SCH_2CH_2NMe_2)_2$: An Interplay Between Dynamic "*Flip-Flop*" Process in Solution and Conformational Isomerism in the Solid-State

Victor N. Khrustalev,[a,] Rinat R. Aysin,[a] Irina V. Borisova,[b] Alexander S. Peregudov,[a] Larissa A. Leites,[a] and Nikolai N. Zemlyansky[b]*

[a] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

[b] Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

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Table S1. Crystal data and structure refinement for **4_*LT***.

Identification code	**$Pb(SCH_2CH_2NMe_2)_2$**	
Empirical formula	C8 H20 N2 Pb S2	
Formula weight	415.57	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.3938(5) Å	α = 90°.
	b = 10.7759(5) Å	β = 90°.
	c = 11.4619(6) Å	γ = 90°.
Volume	1283.76(11) $Å^3$	
Z	4	
Density (calculated)	2.150 Mg/m^3	
Absorption coefficient	13.432 mm^{-1}	
F(000)	784	
Crystal size	0.15 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.72 to 30.61°.	
Index ranges	-14<=h<=14, -15<=k<=15, -16<=l<=16	
Reflections collected	16634	
Independent reflections	3889 [R(int) = 0.0284]	
Completeness to theta = 30.61°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.347 and 0.238	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3889 / 0 / 122	
Goodness-of-fit on F^2	0.936	
Final R indices [for 3417 rflns with I>2σ(I)]	R1 = 0.0185, wR2 = 0.0365	
R indices (all data)	R1 = 0.0239, wR2 = 0.0379	
Absolute structure parameter	0.004(5)	
Largest diff. peak and hole	1.412 and -0.877 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4_*LT***. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Pb(1)	4100(1)	4964(1)	7480(1)	15(1)
S(1)	3875(1)	3467(1)	5681(1)	18(1)
S(2)	4194(1)	6980(1)	6179(1)	19(1)
N(1)	1627(2)	5047(3)	7025(2)	17(1)
N(2)	6550(3)	5182(3)	7043(2)	16(1)
C(1)	2129(3)	3514(3)	5456(3)	20(1)
C(2)	1486(3)	4732(3)	5790(3)	19(1)
C(3)	990(3)	4124(3)	7800(3)	24(1)
C(4)	1073(3)	6287(3)	7265(3)	20(1)
C(5)	5769(3)	6657(3)	5531(3)	21(1)
C(6)	6774(3)	6379(3)	6433(3)	18(1)
C(7)	7175(3)	5187(3)	8184(3)	20(1)
C(8)	7008(3)	4127(3)	6332(3)	21(1)

Table S3. Bond lengths [Å] and angles [°] for **4_*LT***.

Pb(1)-N(2)	2.607(3)	C(3)-H(3A)	0.9800
Pb(1)-N(1)	2.623(2)	C(3)-H(3B)	0.9800
Pb(1)-S(1)	2.6283(8)	C(3)-H(3C)	0.9800
Pb(1)-S(2)	2.6370(8)	C(4)-H(4A)	0.9800
S(1)-C(1)	1.834(4)	C(4)-H(4B)	0.9800
S(2)-C(5)	1.831(3)	C(4)-H(4C)	0.9800
N(1)-C(2)	1.464(4)	C(5)-C(6)	1.499(4)
N(1)-C(4)	1.481(4)	C(5)-H(5A)	0.9900
N(1)-C(3)	1.489(4)	C(5)-H(5B)	0.9900
N(2)-C(7)	1.460(4)	C(6)-H(6A)	0.9900
N(2)-C(8)	1.478(4)	C(6)-H(6B)	0.9900
N(2)-C(6)	1.485(4)	C(7)-H(7A)	0.9800
C(1)-C(2)	1.522(4)	C(7)-H(7B)	0.9800
C(1)-H(1A)	0.9900	C(7)-H(7C)	0.9800
C(1)-H(1B)	0.9900	C(8)-H(8A)	0.9800
C(2)-H(2A)	0.9900	C(8)-H(8B)	0.9800
C(2)-H(2B)	0.9900	C(8)-H(8C)	0.9800
N(2)-Pb(1)-N(1)	156.33(8)	C(6)-N(2)-Pb(1)	108.77(18)
N(2)-Pb(1)-S(1)	89.49(6)	C(2)-C(1)-S(1)	115.0(2)
N(1)-Pb(1)-S(1)	77.18(6)	C(2)-C(1)-H(1A)	108.5
N(2)-Pb(1)-S(2)	77.33(6)	S(1)-C(1)-H(1A)	108.5
N(1)-Pb(1)-S(2)	84.03(6)	C(2)-C(1)-H(1B)	108.5
S(1)-Pb(1)-S(2)	93.73(2)	S(1)-C(1)-H(1B)	108.5
C(1)-S(1)-Pb(1)	100.44(11)	H(1A)-C(1)-H(1B)	107.5
C(5)-S(2)-Pb(1)	96.08(10)	N(1)-C(2)-C(1)	113.5(3)
C(2)-N(1)-C(4)	110.4(2)	N(1)-C(2)-H(2A)	108.9
C(2)-N(1)-C(3)	112.2(3)	C(1)-C(2)-H(2A)	108.9
C(4)-N(1)-C(3)	108.6(2)	N(1)-C(2)-H(2B)	108.9
C(2)-N(1)-Pb(1)	106.41(18)	C(1)-C(2)-H(2B)	108.9
C(4)-N(1)-Pb(1)	112.0(2)	H(2A)-C(2)-H(2B)	107.7
C(3)-N(1)-Pb(1)	107.15(18)	N(1)-C(3)-H(3A)	109.5
C(7)-N(2)-C(8)	110.7(3)	N(1)-C(3)-H(3B)	109.5
C(7)-N(2)-C(6)	110.4(3)	H(3A)-C(3)-H(3B)	109.5
C(8)-N(2)-C(6)	111.0(3)	N(1)-C(3)-H(3C)	109.5
C(7)-N(2)-Pb(1)	105.22(18)	H(3A)-C(3)-H(3C)	109.5
C(8)-N(2)-Pb(1)	110.59(19)	H(3B)-C(3)-H(3C)	109.5

N(1)-C(4)-H(4A)	109.5	N(2)-C(6)-H(6B)	109.0
N(1)-C(4)-H(4B)	109.5	C(5)-C(6)-H(6B)	109.0
H(4A)-C(4)-H(4B)	109.5	H(6A)-C(6)-H(6B)	107.8
N(1)-C(4)-H(4C)	109.5	N(2)-C(7)-H(7A)	109.5
H(4A)-C(4)-H(4C)	109.5	N(2)-C(7)-H(7B)	109.5
H(4B)-C(4)-H(4C)	109.5	H(7A)-C(7)-H(7B)	109.5
C(6)-C(5)-S(2)	112.4(2)	N(2)-C(7)-H(7C)	109.5
C(6)-C(5)-H(5A)	109.1	H(7A)-C(7)-H(7C)	109.5
S(2)-C(5)-H(5A)	109.1	H(7B)-C(7)-H(7C)	109.5
C(6)-C(5)-H(5B)	109.1	N(2)-C(8)-H(8A)	109.5
S(2)-C(5)-H(5B)	109.1	N(2)-C(8)-H(8B)	109.5
H(5A)-C(5)-H(5B)	107.9	H(8A)-C(8)-H(8B)	109.5
N(2)-C(6)-C(5)	112.9(3)	N(2)-C(8)-H(8C)	109.5
N(2)-C(6)-H(6A)	109.0	H(8A)-C(8)-H(8C)	109.5
C(5)-C(6)-H(6A)	109.0	H(8B)-C(8)-H(8C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4_*LT***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb(1)	14(1)	19(1)	11(1)	0(1)	1(1)	0(1)
S(1)	19(1)	19(1)	16(1)	-3(1)	-1(1)	1(1)
S(2)	20(1)	17(1)	19(1)	2(1)	0(1)	2(1)
N(1)	15(1)	21(1)	13(1)	2(1)	2(1)	2(1)
N(2)	17(1)	15(1)	17(1)	-1(1)	2(1)	-3(1)
C(1)	21(2)	22(2)	18(2)	-3(1)	-6(1)	1(1)
C(2)	18(2)	21(2)	18(2)	0(1)	-6(1)	4(1)
C(3)	16(2)	27(2)	27(2)	8(1)	0(1)	3(1)
C(4)	18(2)	23(1)	20(2)	-1(1)	1(1)	5(1)
C(5)	23(2)	21(2)	20(2)	3(1)	3(1)	-2(1)
C(6)	15(2)	21(2)	18(2)	2(1)	3(1)	-4(1)
C(7)	20(2)	19(2)	19(1)	-3(1)	-6(1)	-2(1)
C(8)	20(2)	22(2)	19(2)	-6(1)	1(1)	2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4_*LT***.

Atom	x	y	z	U(iso)
H(1A)	1949	3345	4623	24
H(1B)	1732	2838	5917	24
H(2A)	1862	5408	5314	23
H(2B)	559	4680	5600	23
H(3A)	76	4064	7596	35
H(3B)	1074	4390	8614	35
H(3C)	1399	3312	7700	35
H(4A)	204	6333	6938	30
H(4B)	1615	6926	6906	30
H(4C)	1035	6423	8110	30
H(5A)	5692	5939	4996	25
H(5B)	6046	7383	5065	25
H(6A)	7628	6355	6052	22
H(6B)	6785	7057	7015	22
H(7A)	8102	5312	8085	29
H(7B)	7021	4392	8575	29
H(7C)	6820	5861	8659	29
H(8A)	7943	4184	6236	31
H(8B)	6594	4151	5564	31
H(8C)	6792	3346	6724	31

Table S6. Torsion angles [°] for **4_*LT***.

N(2)-Pb(1)-S(1)-C(1)	-162.76(13)	S(2)-Pb(1)-N(2)-C(7)	125.4(2)
N(1)-Pb(1)-S(1)-C(1)	-2.48(13)	N(1)-Pb(1)-N(2)-C(8)	-76.2(3)
S(2)-Pb(1)-S(1)-C(1)	-85.49(11)	S(1)-Pb(1)-N(2)-C(8)	-21.1(2)
N(2)-Pb(1)-S(2)-C(5)	20.06(12)	S(2)-Pb(1)-N(2)-C(8)	-115.1(2)
N(1)-Pb(1)-S(2)-C(5)	-145.26(12)	N(1)-Pb(1)-N(2)-C(6)	45.9(3)
S(1)-Pb(1)-S(2)-C(5)	-68.58(11)	S(1)-Pb(1)-N(2)-C(6)	100.98(18)
N(2)-Pb(1)-N(1)-C(2)	32.2(3)	S(2)-Pb(1)-N(2)-C(6)	7.04(18)
S(1)-Pb(1)-N(1)-C(2)	-25.04(19)	Pb(1)-S(1)-C(1)-C(2)	31.0(2)
S(2)-Pb(1)-N(1)-C(2)	70.2(2)	C(4)-N(1)-C(2)-C(1)	175.4(3)
N(2)-Pb(1)-N(1)-C(4)	-88.6(3)	C(3)-N(1)-C(2)-C(1)	-63.3(3)
S(1)-Pb(1)-N(1)-C(4)	-145.82(19)	Pb(1)-N(1)-C(2)-C(1)	53.6(3)
S(2)-Pb(1)-N(1)-C(4)	-50.60(18)	S(1)-C(1)-C(2)-N(1)	-61.4(3)
N(2)-Pb(1)-N(1)-C(3)	152.4(2)	Pb(1)-S(2)-C(5)-C(6)	-51.8(2)
S(1)-Pb(1)-N(1)-C(3)	95.18(19)	C(7)-N(2)-C(6)-C(5)	-156.3(3)
S(2)-Pb(1)-N(1)-C(3)	-169.60(19)	C(8)-N(2)-C(6)-C(5)	80.5(3)
N(1)-Pb(1)-N(2)-C(7)	164.2(2)	Pb(1)-N(2)-C(6)-C(5)	-41.3(3)
S(1)-Pb(1)-N(2)-C(7)	-140.7(2)	S(2)-C(5)-C(6)-N(2)	68.4(3)

Table S7. Crystal data and structure refinement for **4_*RT***.

Identification code	**$Pb(SCH_2CH_2NMe_2)_2$**	
Empirical formula	C8 H20 N2 Pb S2	
Formula weight	415.57	
Temperature	290(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.4854(8) Å	α = 90°.
	b = 11.0707(8) Å	β = 90°.
	c = 11.5937(8) Å	γ = 90°.
Volume	1345.80(17) $Å^3$	
Z	4	
Density (calculated)	2.051 Mg/m^3	
Absorption coefficient	12.812 mm^{-1}	
F(000)	784	
Crystal size	0.15 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.68 to 30.55°.	
Index ranges	-14<=h<=15, -15<=k<=15, -16<=l<=16	
Reflections collected	17566	
Independent reflections	4077 [R(int) = 0.0384]	
Completeness to theta = 30.55°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.361 and 0.250	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4077 / 21 / 118	
Goodness-of-fit on F^2	1.006	
Final R indices [for 2828 rflns with I>2σ(I)]	R1 = 0.0297, wR2 = 0.0545	
R indices (all data)	R1 = 0.0582, wR2 = 0.0613	
Absolute structure parameter	0.007(9)	
Largest diff. peak and hole	0.775 and -1.166 $e.Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4_*RT***. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Pb(1)	9055(1)	4970(1)	7379(1)	57(1)
S(1)	8808(2)	3485(1)	5638(1)	69(1)
S(2)	9164(2)	6955(1)	6135(2)	75(1)
N(1)	6584(4)	5016(4)	6981(3)	65(1)
N(2)	11499(3)	5177(3)	6933(3)	62(1)
C(1)	7093(3)	3550(5)	5422(6)	84(1)
C(2)	6419(7)	4718(5)	5755(4)	84(1)
C(3)	6017(6)	4159(6)	7807(6)	84(2)
C(4)	6023(6)	6215(5)	7197(6)	78(2)
C(5)	10732(4)	6649(8)	5525(5)	71(2)
C(6)	11755(7)	6375(4)	6421(5)	71(2)
C(5')	10874(4)	7222(12)	6095(18)	71(2)
C(6')	11614(17)	6046(9)	5972(8)	71(2)
C(7)	12069(8)	5114(6)	8101(4)	68(2)
C(8)	12022(10)	4210(5)	6197(6)	68(2)
C(7')	12318(19)	5539(16)	7906(12)	68(2)
C(8')	11850(20)	3951(6)	6532(12)	68(2)

Table S9. Bond lengths [Å] and angles [°] for **4_*RT***.

Pb(1)-S(1)	2.6164(14)	C(4)-H(4B)	0.9600
Pb(1)-N(2)	2.624(3)	C(4)-H(4C)	0.9600
Pb(1)-S(2)	2.6311(16)	C(5)-C(6)	1.523(8)
Pb(1)-N(1)	2.632(4)	C(5)-H(5A)	0.9700
S(1)-C(1)	1.817(3)	C(5)-H(5B)	0.9700
S(2)-C(5')	1.818(5)	C(6)-H(6A)	0.9700
S(2)-C(5)	1.821(5)	C(6)-H(6B)	0.9700
N(1)-C(2)	1.469(7)	C(5')-C(6')	1.522(8)
N(1)-C(4)	1.473(7)	C(5')-H(5C)	0.9700
N(1)-C(3)	1.474(8)	C(5')-H(5D)	0.9700
N(2)-C(7')	1.473(8)	C(6')-H(6C)	0.9700
N(2)-C(8)	1.474(7)	C(6')-H(6D)	0.9700
N(2)-C(6)	1.477(7)	C(7)-H(7A)	0.9600
N(2)-C(6')	1.477(8)	C(7)-H(7B)	0.9600
N(2)-C(8')	1.480(8)	C(7)-H(7C)	0.9600
N(2)-C(7)	1.481(7)	C(8)-H(8A)	0.9600
C(1)-C(2)	1.523(8)	C(8)-H(8B)	0.9600
C(1)-H(1A)	0.9700	C(8)-H(8C)	0.9600
C(1)-H(1B)	0.9700	C(7')-H(7D)	0.9600
C(2)-H(2A)	0.9700	C(7')-H(7E)	0.9600
C(2)-H(2B)	0.9700	C(7')-H(7F)	0.9600
C(3)-H(3A)	0.9600	C(8')-H(8D)	0.9600
C(3)-H(3B)	0.9600	C(8')-H(8E)	0.9600
C(3)-H(3C)	0.9600	C(8')-H(8F)	0.9600
C(4)-H(4A)	0.9600		

S(1)-Pb(1)-N(2)	89.97(9)	C(4)-N(1)-C(3)	108.0(5)
S(1)-Pb(1)-S(2)	96.08(5)	C(2)-N(1)-Pb(1)	106.4(3)
N(2)-Pb(1)-S(2)	77.09(8)	C(4)-N(1)-Pb(1)	112.4(4)
S(1)-Pb(1)-N(1)	77.26(10)	C(3)-N(1)-Pb(1)	105.7(3)
N(2)-Pb(1)-N(1)	157.66(11)	C(8)-N(2)-C(6)	110.6(3)
S(2)-Pb(1)-N(1)	86.01(11)	C(7')-N(2)-C(6')	110.7(3)
C(1)-S(1)-Pb(1)	100.33(19)	C(7')-N(2)-C(8')	110.3(3)
C(5')-S(2)-Pb(1)	101.1(5)	C(6')-N(2)-C(8')	109.9(3)
C(5)-S(2)-Pb(1)	95.5(2)	C(8)-N(2)-C(7)	110.2(3)
C(2)-N(1)-C(4)	108.6(4)	C(6)-N(2)-C(7)	109.7(3)
C(2)-N(1)-C(3)	115.9(5)	C(7')-N(2)-Pb(1)	116.2(9)

C(8)-N(2)-Pb(1)	114.4(4)	N(2)-C(6)-H(6A)	109.9
C(6)-N(2)-Pb(1)	109.6(3)	C(5)-C(6)-H(6A)	109.9
C(6')-N(2)-Pb(1)	106.6(7)	N(2)-C(6)-H(6B)	109.9
C(8')-N(2)-Pb(1)	102.8(9)	C(5)-C(6)-H(6B)	109.9
C(7)-N(2)-Pb(1)	102.1(4)	H(6A)-C(6)-H(6B)	108.3
C(2)-C(1)-S(1)	117.2(4)	C(6')-C(5')-S(2)	111.5(10)
C(2)-C(1)-H(1A)	108.0	C(6')-C(5')-H(5C)	109.3
S(1)-C(1)-H(1A)	108.0	S(2)-C(5')-H(5C)	109.3
C(2)-C(1)-H(1B)	108.0	C(6')-C(5')-H(5D)	109.3
S(1)-C(1)-H(1B)	108.0	S(2)-C(5')-H(5D)	109.3
H(1A)-C(1)-H(1B)	107.2	H(5C)-C(5')-H(5D)	108.0
N(1)-C(2)-C(1)	112.4(4)	N(2)-C(6')-C(5')	116.4(11)
N(1)-C(2)-H(2A)	109.1	N(2)-C(6')-H(6C)	108.2
C(1)-C(2)-H(2A)	109.1	C(5')-C(6')-H(6C)	108.2
N(1)-C(2)-H(2B)	109.1	N(2)-C(6')-H(6D)	108.2
C(1)-C(2)-H(2B)	109.1	C(5')-C(6')-H(6D)	108.2
H(2A)-C(2)-H(2B)	107.9	H(6C)-C(6')-H(6D)	107.3
N(1)-C(3)-H(3A)	109.5	N(2)-C(7)-H(7A)	109.5
N(1)-C(3)-H(3B)	109.5	N(2)-C(7)-H(7B)	109.5
H(3A)-C(3)-H(3B)	109.5	N(2)-C(7)-H(7C)	109.5
N(1)-C(3)-H(3C)	109.5	N(2)-C(8)-H(8A)	109.5
H(3A)-C(3)-H(3C)	109.5	N(2)-C(8)-H(8B)	109.5
H(3B)-C(3)-H(3C)	109.5	N(2)-C(8)-H(8C)	109.5
N(1)-C(4)-H(4A)	109.5	N(2)-C(7')-H(7D)	109.5
N(1)-C(4)-H(4B)	109.5	N(2)-C(7')-H(7E)	109.5
H(4A)-C(4)-H(4B)	109.5	H(7D)-C(7')-H(7E)	109.5
N(1)-C(4)-H(4C)	109.5	N(2)-C(7')-H(7F)	109.5
H(4A)-C(4)-H(4C)	109.5	H(7D)-C(7')-H(7F)	109.5
H(4B)-C(4)-H(4C)	109.5	H(7E)-C(7')-H(7F)	109.5
C(6)-C(5)-S(2)	114.1(5)	N(2)-C(8')-H(8D)	109.5
C(6)-C(5)-H(5A)	108.7	N(2)-C(8')-H(8E)	109.5
S(2)-C(5)-H(5A)	108.7	H(8D)-C(8')-H(8E)	109.5
C(6)-C(5)-H(5B)	108.7	N(2)-C(8')-H(8F)	109.5
S(2)-C(5)-H(5B)	108.7	H(8D)-C(8')-H(8F)	109.5
H(5A)-C(5)-H(5B)	107.6	H(8E)-C(8')-H(8F)	109.5
N(2)-C(6)-C(5)	109.0(5)		

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4_*RT***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb(1)	53(1)	78(1)	41(1)	1(1)	2(1)	2(1)
S(1)	83(1)	64(1)	59(1)	-5(1)	0(1)	5(1)
S(2)	81(1)	58(1)	85(1)	2(1)	-6(1)	12(1)
N(1)	54(2)	91(3)	51(2)	11(4)	0(2)	6(3)
N(2)	56(2)	47(3)	82(3)	9(2)	14(2)	4(2)
C(1)	98(4)	76(3)	79(3)	-6(2)	-27(3)	4(3)
C(2)	98(4)	76(3)	79(3)	-6(2)	-27(3)	4(3)
C(3)	65(4)	103(5)	85(5)	27(4)	10(4)	9(4)
C(4)	72(4)	80(4)	83(4)	12(3)	1(4)	18(3)
C(5)	78(4)	65(4)	70(4)	13(3)	5(3)	-18(3)
C(6)	78(4)	65(4)	70(4)	13(3)	5(3)	-18(3)
C(5')	78(4)	65(4)	70(4)	13(3)	5(3)	-18(3)
C(6')	78(4)	65(4)	70(4)	13(3)	5(3)	-18(3)
C(7)	56(4)	68(3)	82(3)	0(3)	11(3)	-9(3)
C(8)	56(4)	68(3)	82(3)	0(3)	11(3)	-9(3)
C(7')	56(4)	68(3)	82(3)	0(3)	11(3)	-9(3)
C(8')	56(4)	68(3)	82(3)	0(3)	11(3)	-9(3)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4_*RT***.

Atom	x	y	z	U(iso)
H(1A)	6922	3395	4613	101
H(1B)	6710	2896	5859	101
H(2A)	6752	5374	5290	101
H(2B)	5516	4641	5589	101
H(3A)	5155	3986	7585	126
H(3B)	6025	4507	8566	126
H(3C)	6504	3424	7810	126
H(4A)	5133	6200	7003	117
H(4B)	6450	6807	6731	117
H(4C)	6120	6419	7997	117
H(5A)	10664	5967	5004	85
H(5B)	10998	7343	5076	85
H(6A)	12589	6377	6059	85
H(6B)	11747	6989	7018	85
H(5C)	11074	7749	5451	85
H(5D)	11134	7628	6799	85
H(6C)	11334	5649	5271	85
H(6D)	12509	6243	5876	85
H(7A)	12982	5120	8039	102
H(7B)	11799	4382	8474	102
H(7C)	11794	5796	8546	102
H(8A)	12930	4301	6139	102
H(8B)	11650	4262	5442	102
H(8C)	11826	3439	6531	102
H(7D)	12950	6101	7641	102
H(7E)	12731	4839	8220	102
H(7F)	11806	5914	8492	102
H(8D)	12757	3875	6508	102
H(8E)	11502	3821	5774	102
H(8F)	11501	3362	7053	102

Table S12. Torsion angles [°] for **4_*RT***.

N(2)-Pb(1)-S(1)-C(1)	-162.1(2)	N(1)-Pb(1)-N(2)-C(6)	52.3(4)
S(2)-Pb(1)-S(1)-C(1)	-85.1(2)	S(1)-Pb(1)-N(2)-C(6')	80.1(6)
N(1)-Pb(1)-S(1)-C(1)	-0.6(2)	S(2)-Pb(1)-N(2)-C(6')	-16.1(6)
S(1)-Pb(1)-S(2)-C(5')	-99.4(6)	N(1)-Pb(1)-N(2)-C(6')	25.6(7)
N(2)-Pb(1)-S(2)-C(5')	-10.9(6)	S(1)-Pb(1)-N(2)-C(8')	-35.4(6)
N(1)-Pb(1)-S(2)-C(5')	-176.2(6)	S(2)-Pb(1)-N(2)-C(8')	-131.7(6)
S(1)-Pb(1)-S(2)-C(5)	-70.1(3)	N(1)-Pb(1)-N(2)-C(8')	-89.9(7)
N(2)-Pb(1)-S(2)-C(5)	18.5(3)	S(1)-Pb(1)-N(2)-C(7)	-137.0(3)
N(1)-Pb(1)-S(2)-C(5)	-146.8(3)	S(2)-Pb(1)-N(2)-C(7)	126.7(3)
S(1)-Pb(1)-N(1)-C(2)	-26.6(3)	N(1)-Pb(1)-N(2)-C(7)	168.5(4)
N(2)-Pb(1)-N(1)-C(2)	30.0(6)	Pb(1)-S(1)-C(1)-C(2)	29.0(5)
S(2)-Pb(1)-N(1)-C(2)	70.6(3)	C(4)-N(1)-C(2)-C(1)	174.0(5)
S(1)-Pb(1)-N(1)-C(4)	-145.3(3)	C(3)-N(1)-C(2)-C(1)	-64.3(7)
N(2)-Pb(1)-N(1)-C(4)	-88.7(4)	Pb(1)-N(1)-C(2)-C(1)	52.8(6)
S(2)-Pb(1)-N(1)-C(4)	-48.1(3)	S(1)-C(1)-C(2)-N(1)	-59.6(7)
S(1)-Pb(1)-N(1)-C(3)	97.1(4)	Pb(1)-S(2)-C(5)-C(6)	-52.8(5)
N(2)-Pb(1)-N(1)-C(3)	153.7(4)	C(8)-N(2)-C(6)-C(5)	83.4(7)
S(2)-Pb(1)-N(1)-C(3)	-165.7(4)	C(7)-N(2)-C(6)-C(5)	-154.9(5)
S(1)-Pb(1)-N(2)-C(7')	-156.0(8)	Pb(1)-N(2)-C(6)-C(5)	-43.6(5)
S(2)-Pb(1)-N(2)-C(7')	107.7(8)	S(2)-C(5)-C(6)-N(2)	70.7(7)
N(1)-Pb(1)-N(2)-C(7')	149.5(8)	Pb(1)-S(2)-C(5')-C(6')	38.8(13)
S(1)-Pb(1)-N(2)-C(8)	-18.1(3)	C(7')-N(2)-C(6')-C(5')	-78.7(15)
S(2)-Pb(1)-N(2)-C(8)	-114.3(3)	C(8')-N(2)-C(6')-C(5')	159.2(15)
N(1)-Pb(1)-N(2)-C(8)	-72.5(4)	Pb(1)-N(2)-C(6')-C(5')	48.5(13)
S(1)-Pb(1)-N(2)-C(6)	106.7(3)	S(2)-C(5')-C(6')-N(2)	-63.8(17)
S(2)-Pb(1)-N(2)-C(6)	10.5(3)		

Table S13. Crystal data and structure refinement for ***4_HT***

CSD deposition number	**CCDC 780360**	
Identification code	**$Pb(SCH_2CH_2NMe_2)_2$**	
Empirical formula	C8 H20 N2 Pb S2	
Formula weight	415.57	
Temperature	333(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.541(11) Å	a = 90°.
	b = 11.148(12) Å	b = 90°.
	c = 11.645(12) Å	g = 90°.
Volume	1368(2) $Å^3$	
Z	4	
Density (calculated)	2.018 Mg/m^3	
Absorption coefficient	12.605 mm^{-1}	
F(000)	784	
Crystal size	0.15 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.61 to 30.71°.	
Index ranges	-15<=h<=14, -15<=k<=15, -16<=l<=16	
Reflections collected	17933	
Independent reflections	4204 [R(int) = 0.0361]	
Completeness to theta = 30.71°	98.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.383 and 0.264	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4204 / 21 / 124	
Goodness-of-fit on F^2	1.005	
Final R indices [for 2346 rflns with I>2σ(I)]	R1 = 0.0452, wR2 = 0.1011	
R indices (all data)	R1 = 0.0862, wR2 = 0.1192	
Absolute structure parameter	0.066(16)	
Largest diff. peak and hole	0.909 and -1.188 $e.Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ***4_HT***. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Pb(1)	9031(1)	4967(1)	7344(1)	89(1)
S(1)	8786(3)	3494(2)	5618(3)	105(1)
S(2)	9145(3)	6943(2)	6126(3)	116(1)
N(1)	6555(6)	4996(8)	6956(5)	101(2)
N(2)	11474(5)	5169(6)	6890(5)	94(2)
C(1)	7089(5)	3579(9)	5406(13)	136(4)
C(2)	6397(10)	4731(9)	5729(6)	118(4)
C(3)	5987(11)	4178(11)	7803(11)	121(4)
C(4)	5992(11)	6179(9)	7179(11)	118(4)
C(5)	10701(7)	6674(17)	5524(12)	110(4)
C(6)	11701(15)	6378(7)	6427(10)	110(4)
C(5')	10837(5)	7212(17)	6150(30)	110(4)
C(6')	11590(20)	6063(13)	5968(12)	110(4)
C(7)	11999(18)	5057(12)	8055(8)	101(3)
C(8)	11990(20)	4244(10)	6124(11)	101(3)
C(7')	12170(30)	5540(20)	7923(15)	101(3)
C(8')	11890(30)	3980(10)	6495(17)	101(3)

Table S15. Bond lengths [Å] and angles [°] for ***4_HT***.

Pb(1)-S(1)	2.608(3)	C(4)-H(4B)	0.9600
Pb(1)-S(2)	2.623(4)	C(4)-H(4C)	0.9600
Pb(1)-N(2)	2.638(6)	C(5)-C(6)	1.524(12)
Pb(1)-N(1)	2.649(7)	C(5)-H(5A)	0.9700
S(1)-C(1)	1.809(8)	C(5)-H(5B)	0.9700
S(2)-C(5')	1.809(9)	C(6)-H(6A)	0.9700
S(2)-C(5)	1.809(11)	C(6)-H(6B)	0.9700
N(1)-C(2)	1.468(12)	C(5')-C(6')	1.524(12)
N(1)-C(4)	1.470(13)	C(5')-H(5C)	0.9700
N(1)-C(3)	1.471(12)	C(5')-H(5D)	0.9700
N(2)-C(7')	1.468(14)	C(6')-H(6C)	0.9700
N(2)-C(6')	1.469(13)	C(6')-H(6D)	0.9700
N(2)-C(8)	1.470(11)	C(7)-H(7A)	0.9600
N(2)-C(7)	1.471(12)	C(7)-H(7B)	0.9600
N(2)-C(6)	1.471(11)	C(7)-H(7C)	0.9600
N(2)-C(8')	1.472(13)	C(8)-H(8A)	0.9600
C(1)-C(2)	1.524(10)	C(8)-H(8B)	0.9600
C(1)-H(1A)	0.9700	C(8)-H(8C)	0.9600
C(1)-H(1B)	0.9700	C(7')-H(7D)	0.9600
C(2)-H(2A)	0.9700	C(7')-H(7E)	0.9600
C(2)-H(2B)	0.9700	C(7')-H(7F)	0.9600
C(3)-H(3A)	0.9600	C(8')-H(8D)	0.9600
C(3)-H(3B)	0.9600	C(8')-H(8E)	0.9600
C(3)-H(3C)	0.9600	C(8')-H(8F)	0.9600
C(4)-H(4A)	0.9600		

S(1)-Pb(1)-S(2)	96.71(13)	C(4)-N(1)-C(3)	105.9(9)
S(1)-Pb(1)-N(2)	89.76(17)	C(2)-N(1)-Pb(1)	106.0(5)
S(2)-Pb(1)-N(2)	77.00(15)	C(4)-N(1)-Pb(1)	112.2(6)
S(1)-Pb(1)-N(1)	77.22(18)	C(3)-N(1)-Pb(1)	106.2(6)
S(2)-Pb(1)-N(1)	86.71(19)	C(7')-N(2)-C(6')	111.3(3)
N(2)-Pb(1)-N(1)	157.9(2)	C(7')-N(2)-C(8)	120.7(19)
C(1)-S(1)-Pb(1)	99.8(4)	C(6')-N(2)-C(8)	90.0(9)
C(5')-S(2)-Pb(1)	100.1(8)	C(6')-N(2)-C(7)	134.3(10)
C(5)-S(2)-Pb(1)	96.4(5)	C(8)-N(2)-C(7)	111.1(3)
C(2)-N(1)-C(4)	107.8(8)	C(7')-N(2)-C(6)	87.7(9)
C(2)-N(1)-C(3)	118.8(10)	C(8)-N(2)-C(6)	111.1(3)

C(7)-N(2)-C(6)	110.8(3)	S(2)-C(5)-H(5B)	108.9
C(7')-N(2)-C(8')	111.2(3)	H(5A)-C(5)-H(5B)	107.7
C(6')-N(2)-C(8')	110.9(3)	N(2)-C(6)-C(5)	109.7(10)
C(7)-N(2)-C(8')	95.6(13)	N(2)-C(6)-H(6A)	109.7
C(6)-N(2)-C(8')	131.5(11)	C(5)-C(6)-H(6A)	109.7
C(7')-N(2)-Pb(1)	110.2(13)	N(2)-C(6)-H(6B)	109.7
C(6')-N(2)-Pb(1)	106.8(10)	C(5)-C(6)-H(6B)	109.7
C(8)-N(2)-Pb(1)	115.2(10)	H(6A)-C(6)-H(6B)	108.2
C(7)-N(2)-Pb(1)	100.1(8)	C(6')-C(5')-S(2)	112.0(14)
C(6)-N(2)-Pb(1)	108.1(7)	C(6')-C(5')-H(5C)	109.2
C(8')-N(2)-Pb(1)	106.2(13)	S(2)-C(5')-H(5C)	109.2
C(2)-C(1)-S(1)	118.9(7)	C(6')-C(5')-H(5D)	109.2
C(2)-C(1)-H(1A)	107.6	S(2)-C(5')-H(5D)	109.2
S(1)-C(1)-H(1A)	107.6	H(5C)-C(5')-H(5D)	107.9
C(2)-C(1)-H(1B)	107.6	N(2)-C(6')-C(5')	115.1(16)
S(1)-C(1)-H(1B)	107.6	N(2)-C(6')-H(6C)	108.5
H(1A)-C(1)-H(1B)	107.0	C(5')-C(6')-H(6C)	108.5
N(1)-C(2)-C(1)	110.9(9)	N(2)-C(6')-H(6D)	108.5
N(1)-C(2)-H(2A)	109.5	C(5')-C(6')-H(6D)	108.5
C(1)-C(2)-H(2A)	109.5	H(6C)-C(6')-H(6D)	107.5
N(1)-C(2)-H(2B)	109.5	N(2)-C(7)-H(7A)	109.5
C(1)-C(2)-H(2B)	109.5	N(2)-C(7)-H(7B)	109.5
H(2A)-C(2)-H(2B)	108.1	N(2)-C(7)-H(7C)	109.5
N(1)-C(3)-H(3A)	109.5	N(2)-C(8)-H(8A)	109.5
N(1)-C(3)-H(3B)	109.5	N(2)-C(8)-H(8B)	109.5
H(3A)-C(3)-H(3B)	109.5	N(2)-C(8)-H(8C)	109.5
N(1)-C(3)-H(3C)	109.5	N(2)-C(7')-H(7D)	109.5
H(3A)-C(3)-H(3C)	109.5	N(2)-C(7')-H(7E)	109.5
H(3B)-C(3)-H(3C)	109.5	H(7D)-C(7')-H(7E)	109.5
N(1)-C(4)-H(4A)	109.5	N(2)-C(7')-H(7F)	109.5
N(1)-C(4)-H(4B)	109.5	H(7D)-C(7')-H(7F)	109.5
H(4A)-C(4)-H(4B)	109.5	H(7E)-C(7')-H(7F)	109.5
N(1)-C(4)-H(4C)	109.5	N(2)-C(8')-H(8D)	109.5
H(4A)-C(4)-H(4C)	109.5	N(2)-C(8')-H(8E)	109.5
H(4B)-C(4)-H(4C)	109.5	H(8D)-C(8')-H(8E)	109.5
C(6)-C(5)-S(2)	113.3(10)	N(2)-C(8')-H(8F)	109.5
C(6)-C(5)-H(5A)	108.9	H(8D)-C(8')-H(8F)	109.5
S(2)-C(5)-H(5A)	108.9	H(8E)-C(8')-H(8F)	109.5
C(6)-C(5)-H(5B)	108.9		

Table S16. Anisotropic displacement parameters ($Å^2 \times 10^3$) for ***4_HT***. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb(1)	88(1)	108(1)	71(1)	0(1)	3(1)	2(1)
S(1)	122(2)	93(2)	100(2)	-8(1)	0(2)	3(2)
S(2)	125(2)	90(2)	134(2)	2(2)	-8(2)	16(2)
N(1)	83(4)	133(6)	88(4)	23(7)	-2(3)	14(6)
N(2)	88(4)	79(5)	115(5)	10(5)	12(4)	1(4)
C(1)	152(10)	103(8)	152(10)	0(7)	-54(9)	-17(8)
C(2)	112(7)	132(10)	108(7)	-4(6)	-27(5)	21(7)
C(3)	99(8)	147(10)	116(9)	34(7)	14(7)	-7(7)
C(4)	96(7)	138(9)	119(9)	12(7)	10(7)	28(6)
C(5)	118(8)	99(8)	112(10)	12(6)	12(7)	-23(6)
C(6)	118(8)	99(8)	112(10)	12(6)	12(7)	-23(6)
C(5')	118(8)	99(8)	112(10)	12(6)	12(7)	-23(6)
C(6')	118(8)	99(8)	112(10)	12(6)	12(7)	-23(6)
C(7)	100(6)	89(7)	115(7)	-9(7)	9(6)	-16(7)
C(8)	100(6)	89(7)	115(7)	-9(7)	9(6)	-16(7)
C(7')	100(6)	89(7)	115(7)	-9(7)	9(6)	-16(7)
C(8')	100(6)	89(7)	115(7)	-9(7)	9(6)	-16(7)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for ***4_HT***.

Atom	x	y	z	U(iso)
H(1A)	6922	3425	4600	163
H(1B)	6705	2929	5837	163
H(2A)	6729	5392	5279	141
H(2B)	5502	4648	5555	141
H(3A)	5104	4368	7897	181
H(3B)	6414	4266	8526	181
H(3C)	6070	3366	7541	181
H(4A)	5109	6165	6976	177
H(4B)	6421	6774	6727	177
H(4C)	6078	6371	7979	177
H(5A)	10647	6014	4984	132
H(5B)	10968	7381	5103	132
H(6A)	12539	6415	6084	132
H(6B)	11665	6963	7043	132
H(5C)	11053	7782	5551	132
H(5D)	11069	7563	6882	132
H(6C)	11323	5698	5253	132
H(6D)	12483	6272	5887	132
H(7A)	12900	5179	8031	152
H(7B)	11820	4271	8349	152
H(7C)	11618	5649	8545	152
H(8A)	12856	4441	5933	152
H(8B)	11497	4208	5434	152
H(8C)	11970	3480	6503	152
H(7D)	12423	6364	7846	152
H(7E)	12904	5045	8016	152
H(7F)	11627	5458	8582	152
H(8D)	12740	4036	6197	152
H(8E)	11334	3699	5903	152
H(8F)	11880	3428	7128	152

Table S18. Torsion angles [°] for ***4_HT***.

S(2)-Pb(1)-S(1)-C(1)	-84.5(5)	S(1)-Pb(1)-N(2)-C(6)	109.2(5)
N(2)-Pb(1)-S(1)-C(1)	-161.4(5)	S(2)-Pb(1)-N(2)-C(6)	12.2(5)
N(1)-Pb(1)-S(1)-C(1)	0.5(5)	N(1)-Pb(1)-N(2)-C(6)	55.9(8)
S(1)-Pb(1)-S(2)-C(5')	-101.4(9)	S(1)-Pb(1)-N(2)-C(8')	-36.0(8)
N(2)-Pb(1)-S(2)-C(5')	-13.2(9)	S(2)-Pb(1)-N(2)-C(8')	-132.9(8)
N(1)-Pb(1)-S(2)-C(5')	-178.1(9)	N(1)-Pb(1)-N(2)-C(8')	-89.3(10)
S(1)-Pb(1)-S(2)-C(5)	-70.7(6)	Pb(1)-S(1)-C(1)-C(2)	28.7(11)
N(2)-Pb(1)-S(2)-C(5)	17.5(6)	C(4)-N(1)-C(2)-C(1)	173.7(9)
N(1)-Pb(1)-S(2)-C(5)	-147.4(6)	C(3)-N(1)-C(2)-C(1)	-66.0(12)
S(1)-Pb(1)-N(1)-C(2)	-28.2(6)	Pb(1)-N(1)-C(2)-C(1)	53.3(10)
S(2)-Pb(1)-N(1)-C(2)	69.5(7)	S(1)-C(1)-C(2)-N(1)	-60.2(14)
N(2)-Pb(1)-N(1)-C(2)	27.1(10)	C(5')-S(2)-C(5)-C(6)	47.5(17)
S(1)-Pb(1)-N(1)-C(4)	-145.6(7)	Pb(1)-S(2)-C(5)-C(6)	-51.6(11)
S(2)-Pb(1)-N(1)-C(4)	-48.0(6)	C(7')-N(2)-C(6)-C(5)	-156.4(17)
N(2)-Pb(1)-N(1)-C(4)	-90.3(8)	C(6')-N(2)-C(6)-C(5)	45(2)
S(1)-Pb(1)-N(1)-C(3)	99.1(8)	C(8)-N(2)-C(6)-C(5)	81.5(12)
S(2)-Pb(1)-N(1)-C(3)	-163.3(7)	C(7)-N(2)-C(6)-C(5)	-154.6(11)
N(2)-Pb(1)-N(1)-C(3)	154.4(8)	C(8')-N(2)-C(6)-C(5)	87(2)
S(1)-Pb(1)-N(2)-C(7')	-156.5(9)	Pb(1)-N(2)-C(6)-C(5)	-45.8(10)
S(2)-Pb(1)-N(2)-C(7')	106.6(9)	S(2)-C(5)-C(6)-N(2)	71.7(14)
N(1)-Pb(1)-N(2)-C(7')	150.2(11)	C(5)-S(2)-C(5')-C(6')	-43.0(12)
S(1)-Pb(1)-N(2)-C(6')	82.4(8)	Pb(1)-S(2)-C(5')-C(6')	42.4(19)
S(2)-Pb(1)-N(2)-C(6')	-14.5(8)	C(7')-N(2)-C(6')-C(5')	-73(2)
N(1)-Pb(1)-N(2)-C(6')	29.1(10)	C(8)-N(2)-C(6')-C(5')	163.6(19)
S(1)-Pb(1)-N(2)-C(8)	-15.7(6)	C(7)-N(2)-C(6')-C(5')	-76(2)
S(2)-Pb(1)-N(2)-C(8)	-112.7(6)	C(6)-N(2)-C(6')-C(5')	-49.8(19)
N(1)-Pb(1)-N(2)-C(8)	-69.0(8)	C(8')-N(2)-C(6')-C(5')	162(2)
S(1)-Pb(1)-N(2)-C(7)	-134.9(6)	Pb(1)-N(2)-C(6')-C(5')	47.2(18)
S(2)-Pb(1)-N(2)-C(7)	128.1(6)	S(2)-C(5')-C(6')-N(2)	-66(2)
N(1)-Pb(1)-N(2)-C(7)	171.8(8)		

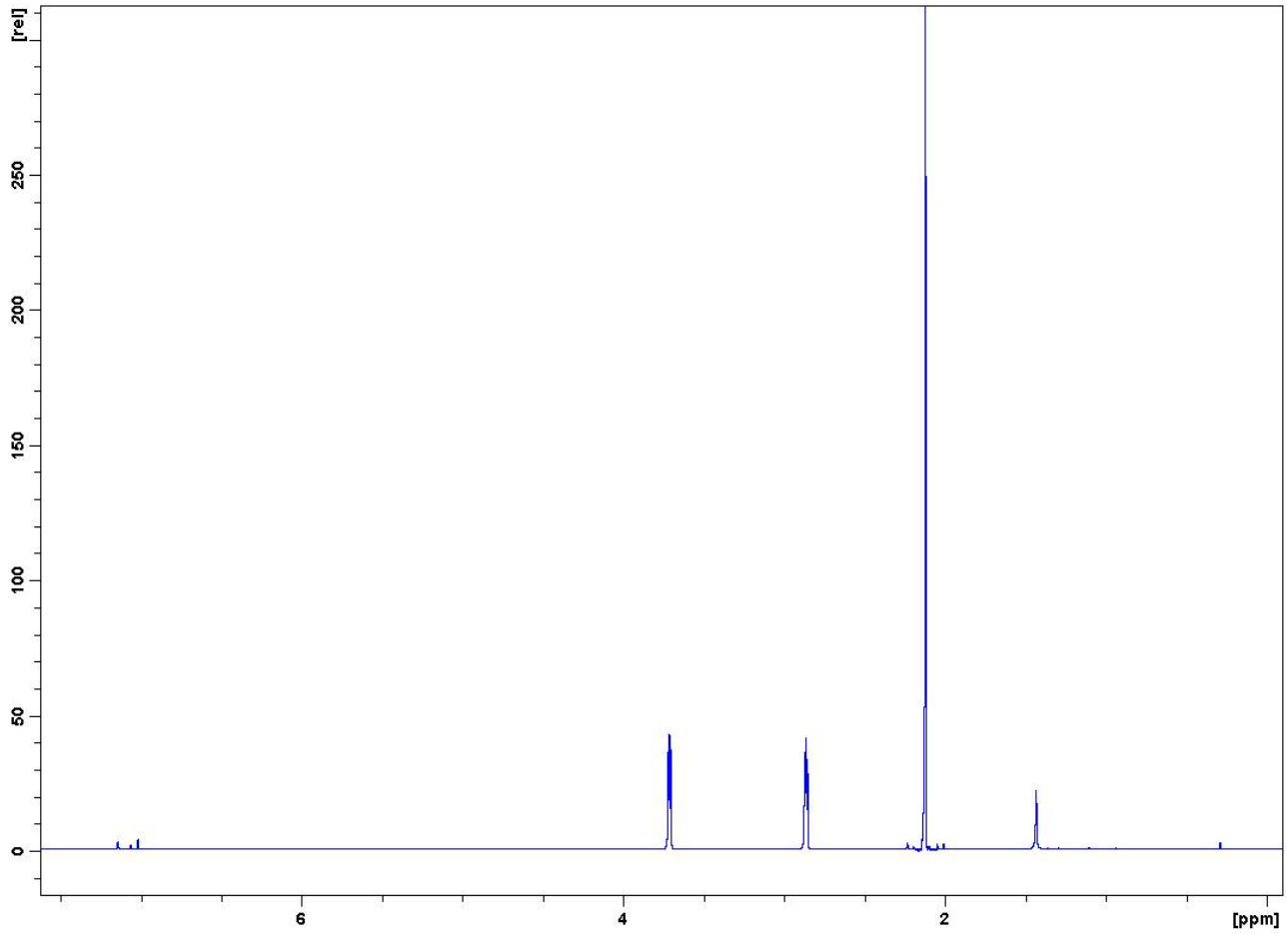

Fig. S1. 600.2 MHz ^{1}H NMR spectrum of **4** at 298 K.

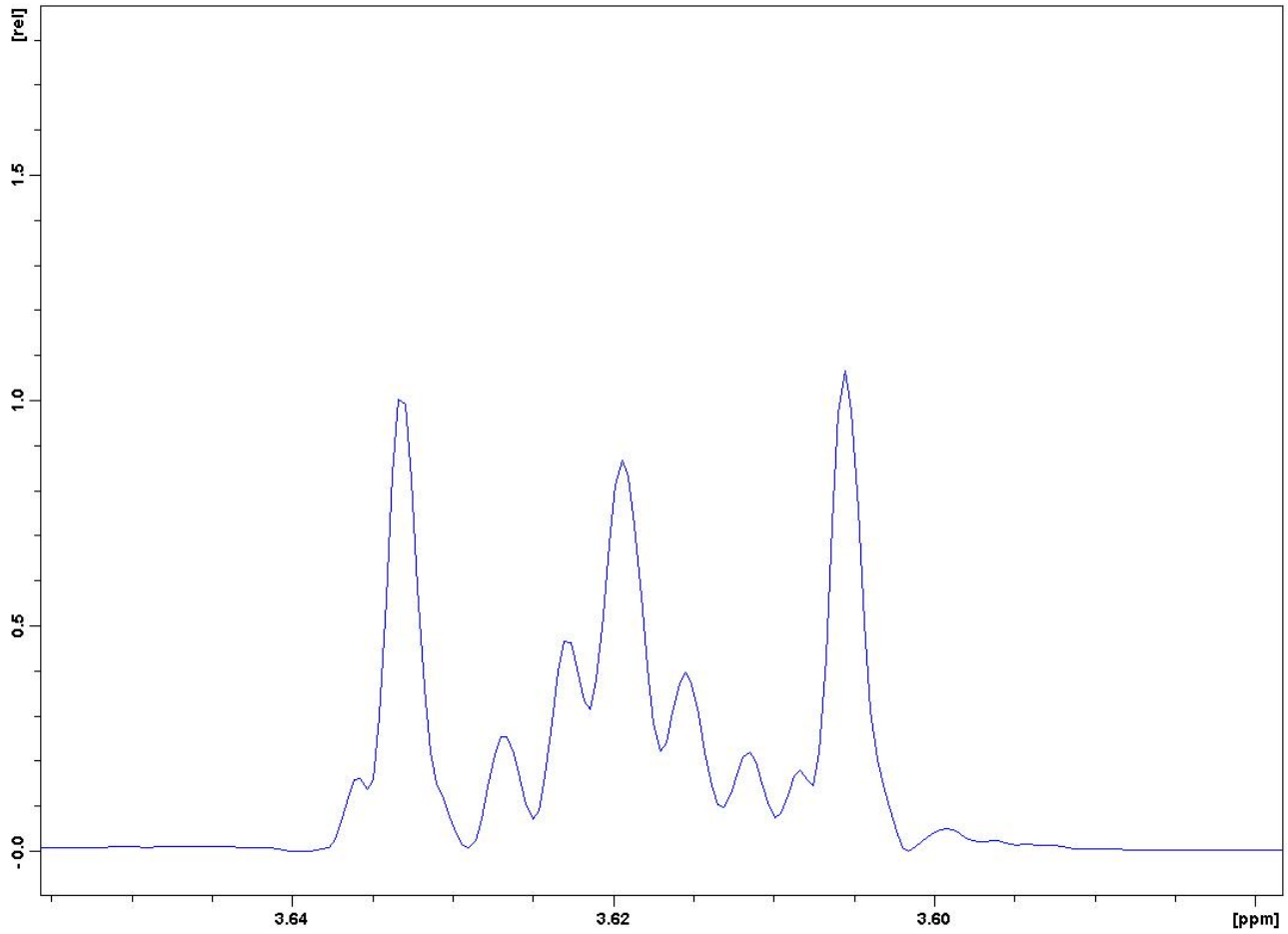

Fig. S2. A portion of 400.1 MHz ^{1}H NMR spectrum of **4** - the SCH_2CH_2N multiplet (*pseudotriplet*).

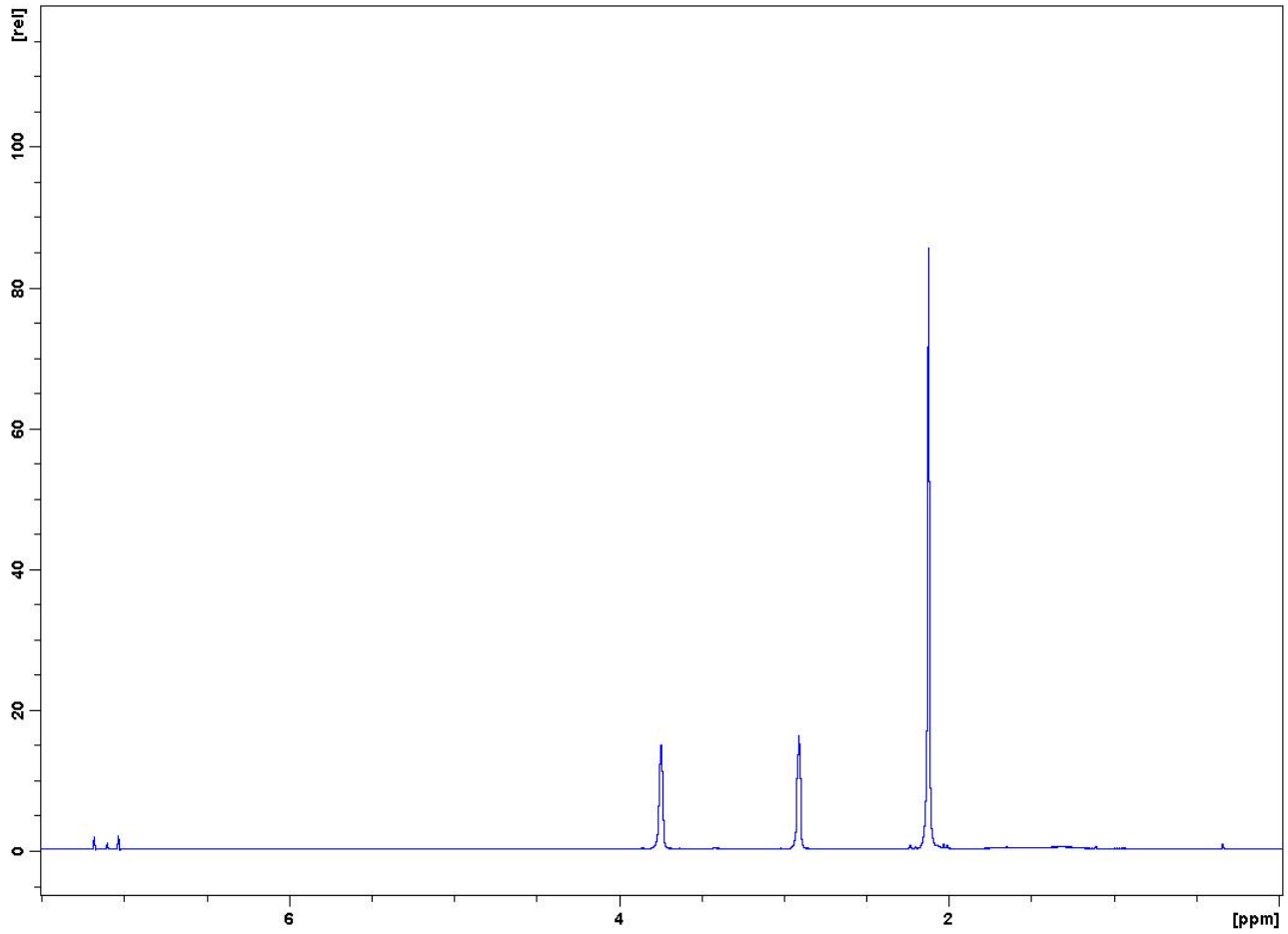

Fig. S3. 600.2 MHz ^{1}H NMR spectrum of **4** at 233 K.

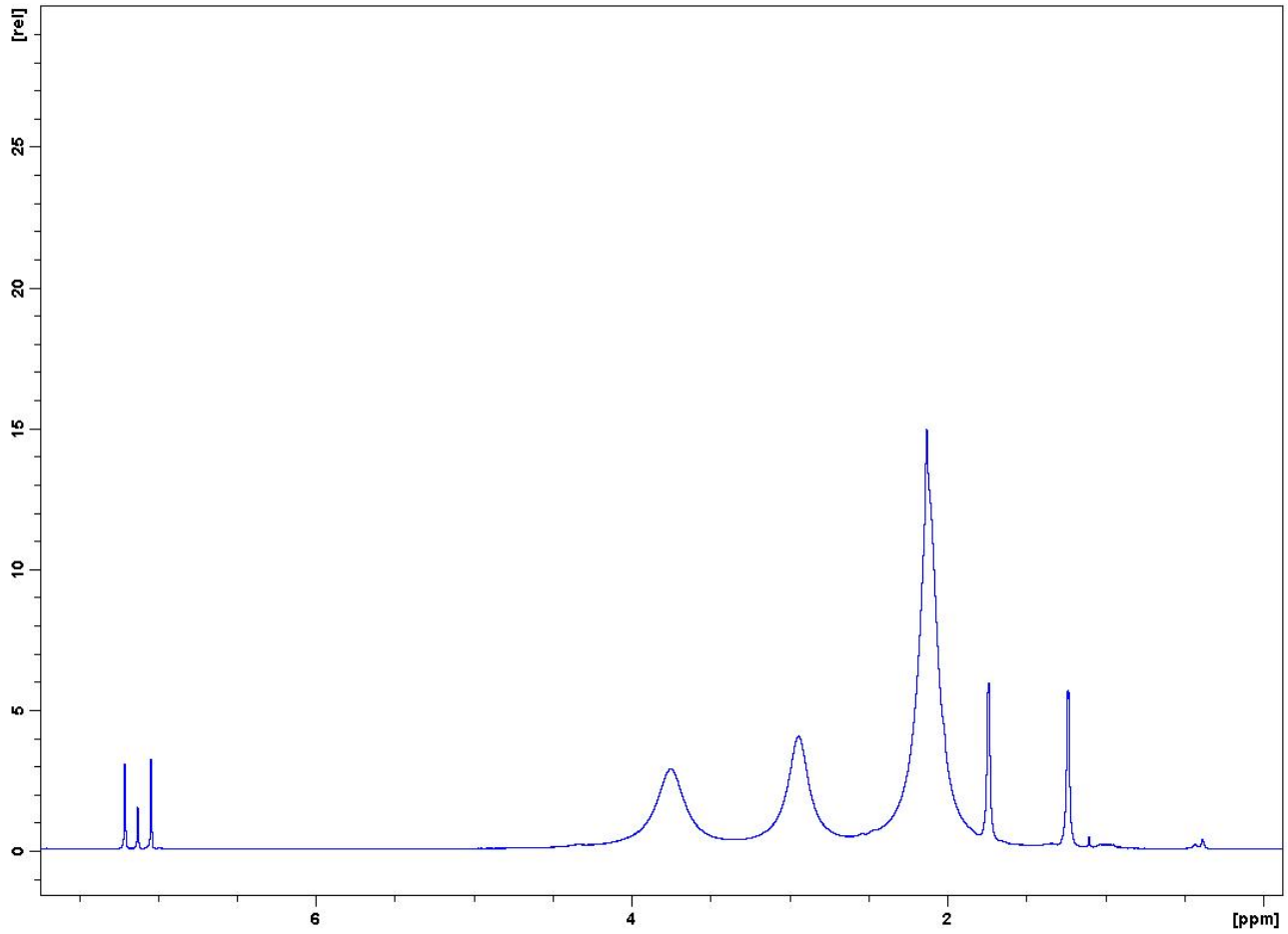

Fig. S4. 600.2 MHz ^{1}H NMR spectrum of **4** at 203 K.

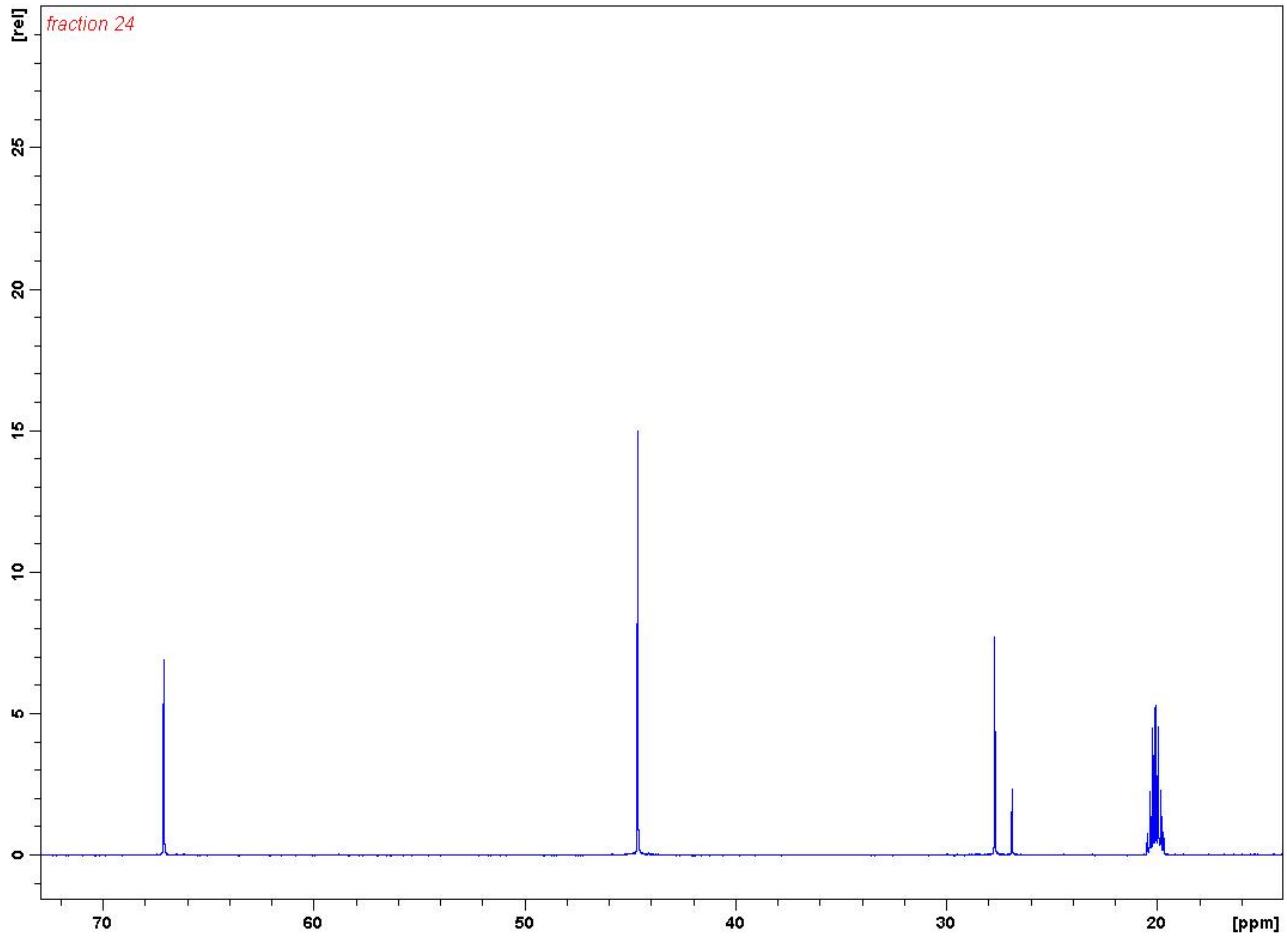

Fig. S5. 150.9 MHz ^{13}C NMR spectrum of **4** at 298 K.

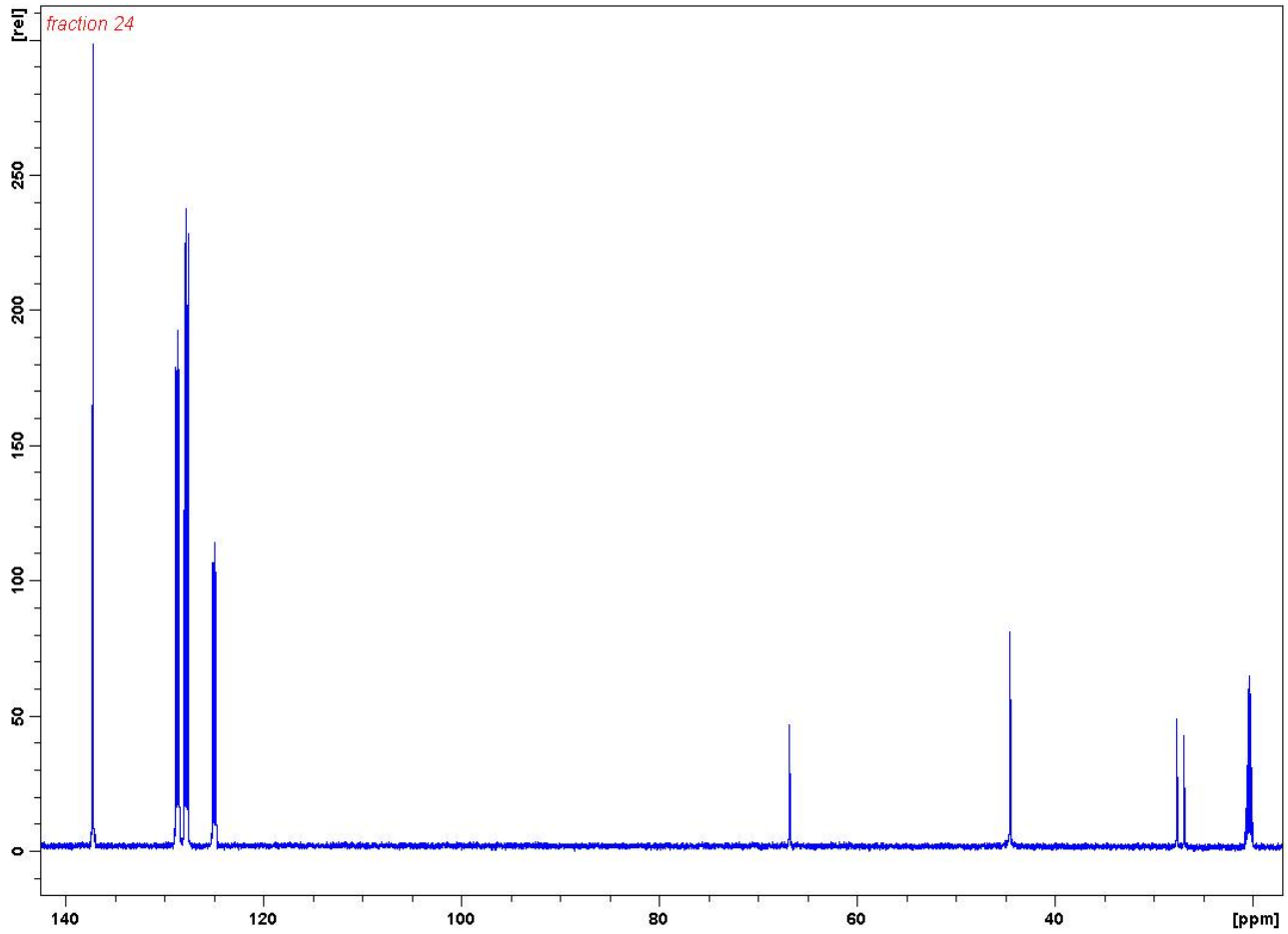

Fig. S6. 150.9 MHz ^{13}C NMR spectrum of **4** at 233 K.

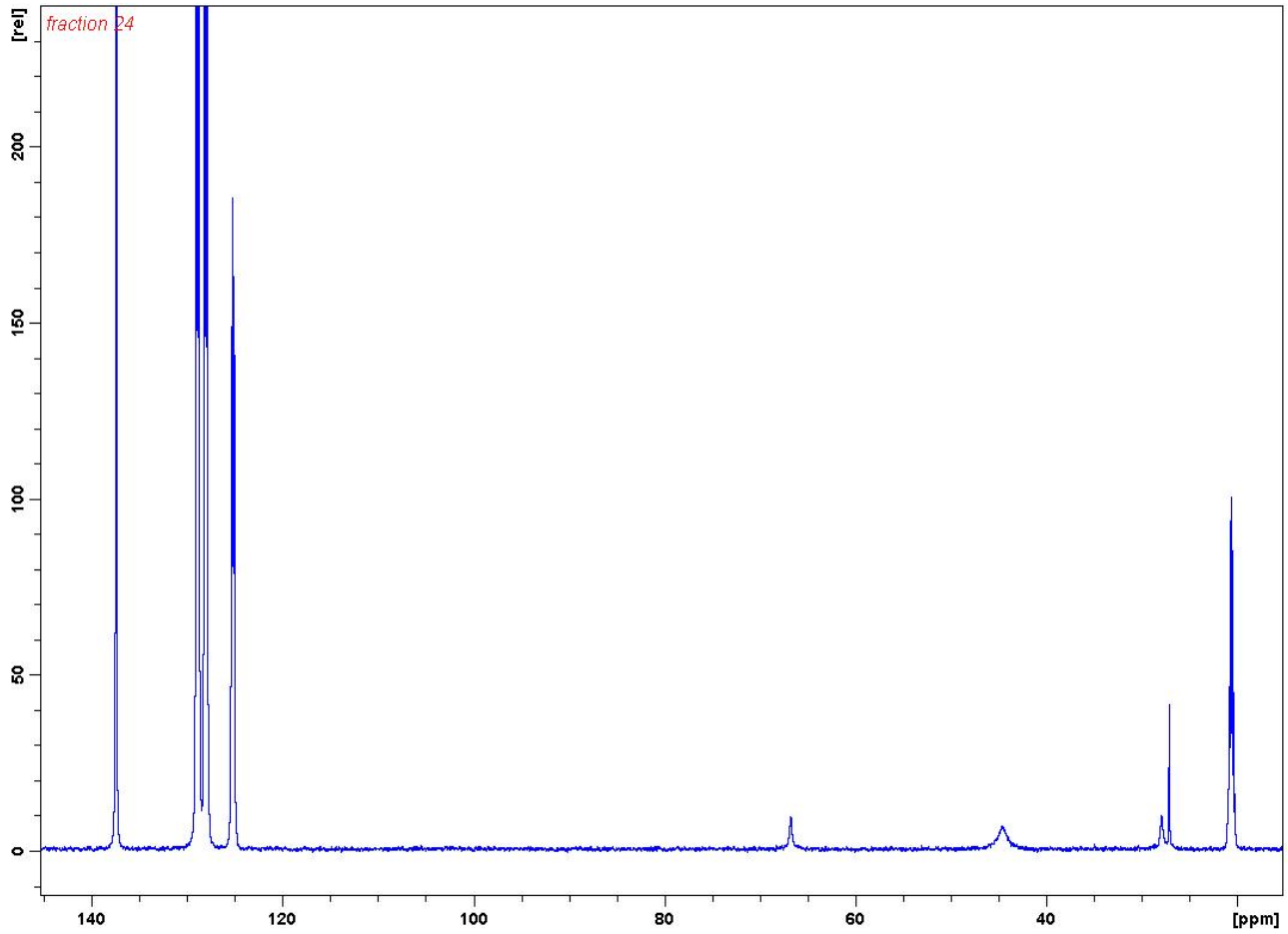

Fig. S7. 150.9 MHz ^{13}C NMR spectrum of **4** at 203 K.

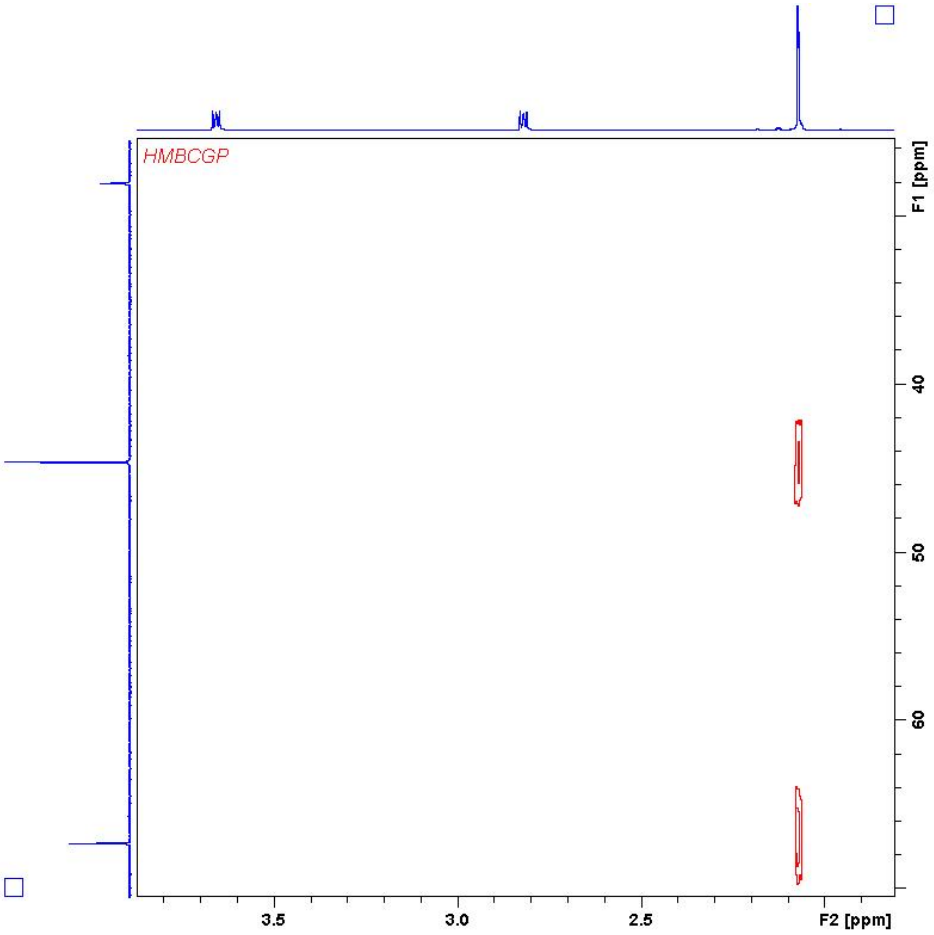

Fig. S8. 600.2 MHz HMBC spectrum of **4** at 298 K.

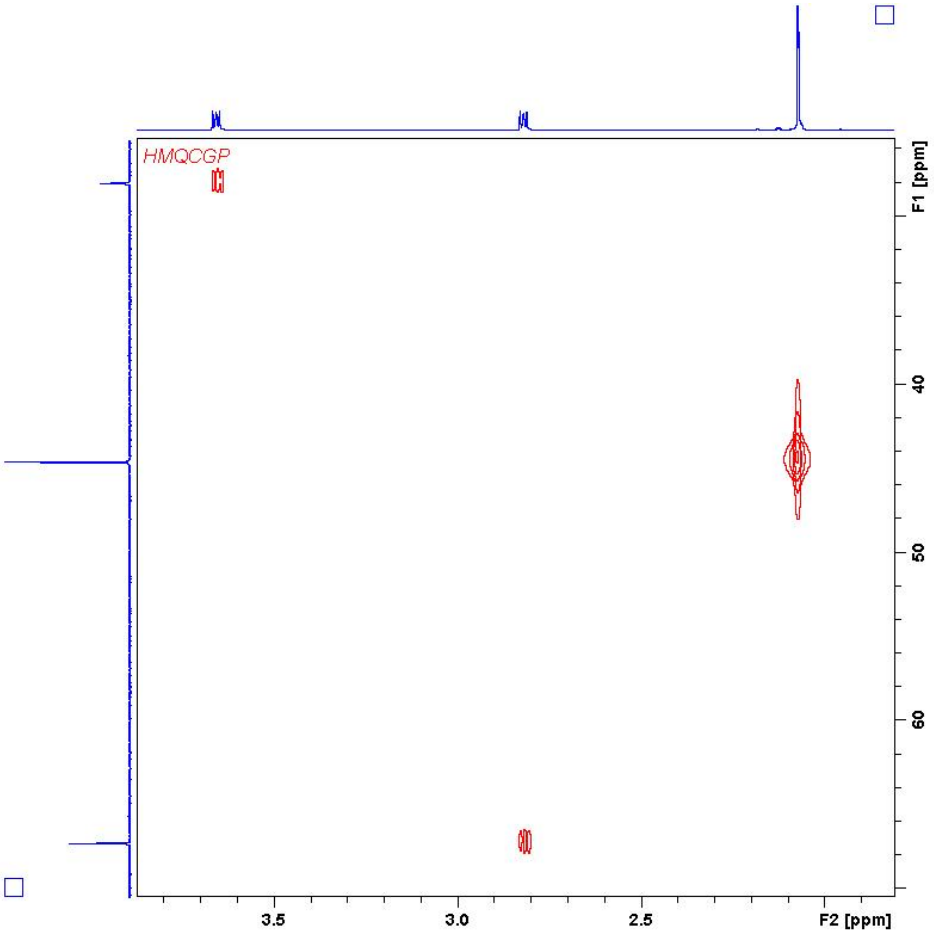

Fig. S9. 600.2 MHz HMQC spectrum of **4** at 298 K.

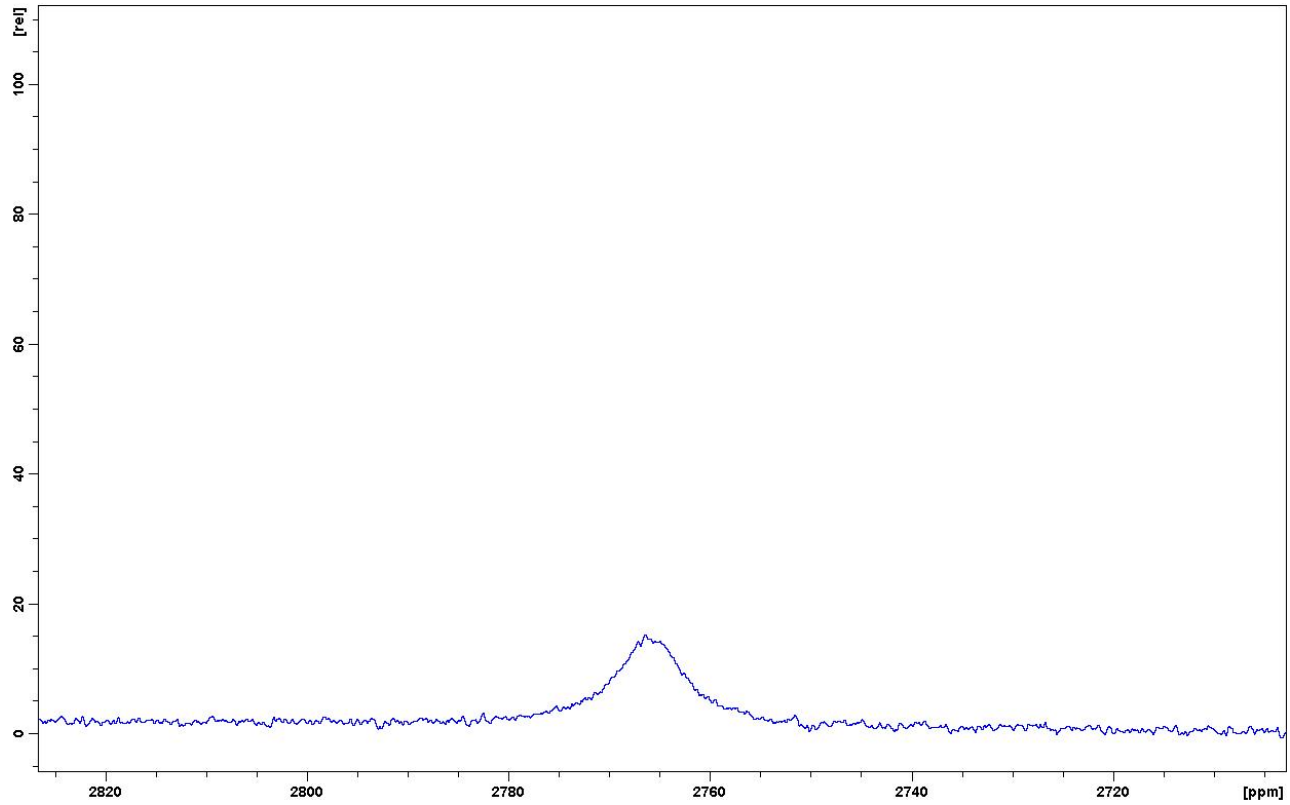

Fig. S10. 83.7 MHz ^{207}Pb spectrum of **4** at 298 K.

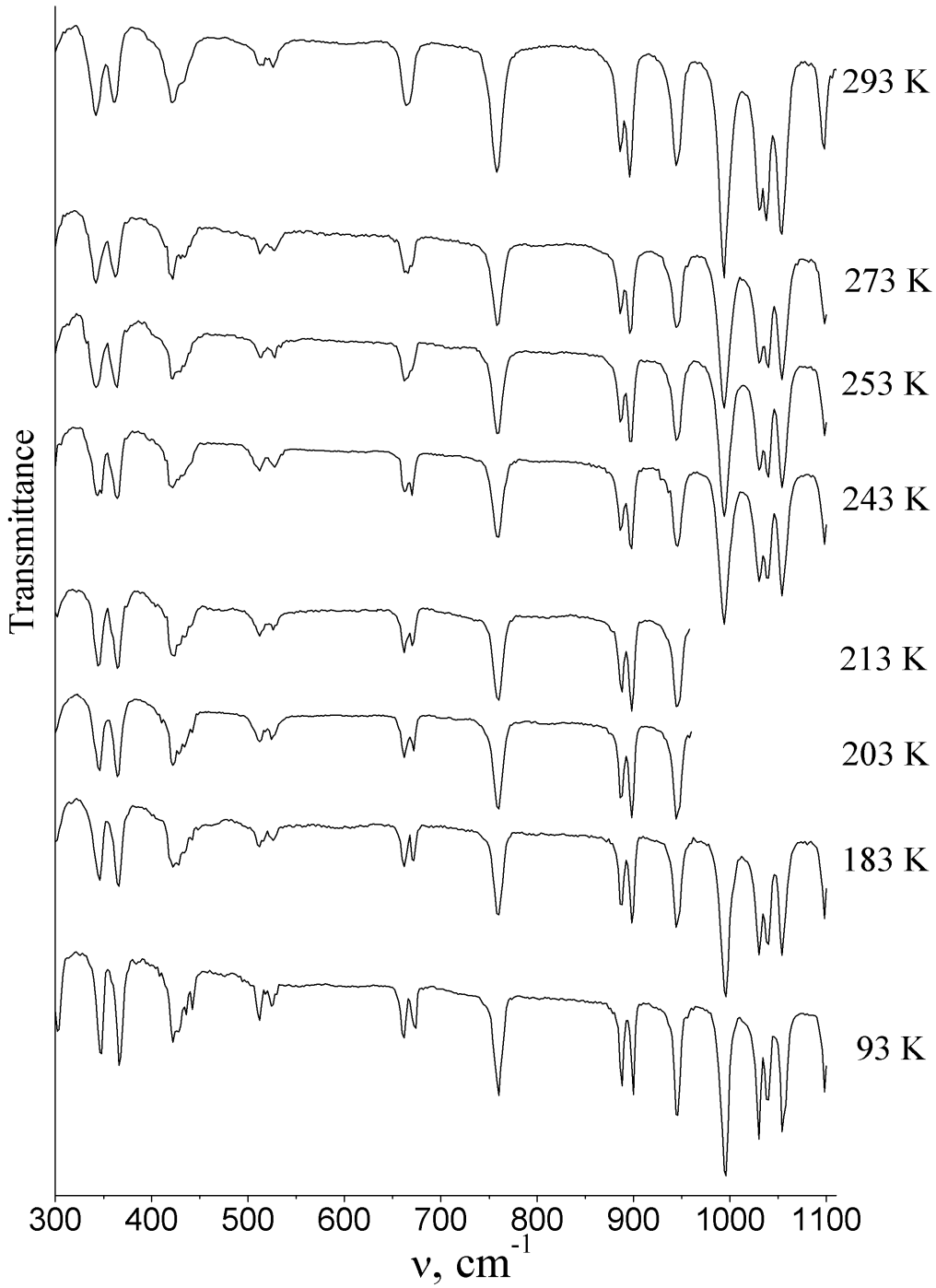

Fig S11. Variable-temperature IR spectra of **4** crystalline film on CsI plate.

DFT calculations

All theoretical calculations of the geometry and normal coordinate analysis (NCA) for both ***AA*** and ***AB*** conformers of **4** were performed in Gaussian 03 [S1] program at the MP2 [S2] and DFT level of theory using the PBE [S3], PBE0 [S4], M05-2X [S5] and B3LYP [S6] functionals. 6-311G(d,p) [S7] valence basis set for C, N and S atoms and cc-pVTZ-pp [S8] effective core potentials for Pb atom were utilized. Calculation of potential energy distribution (PED) were carried out with using NCA99 program [S9].

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Table S19. Experimental and calculated (PBE) frequencies of conformers ***AA*** and ***AB***.

Experimental		Calculated				Forms of vibration modes and PEDs
Raman, cm^{-1}	IR, cm^{-1}	***AB***		***AA***		
344	342	336	A>	325	A-A	
363	360	352	B>	337	A+A	
514	510	496	B	519	A+A	
525	526	518	A	520	A-A	
655	664	649	A	650	A-A	νC–S 75%
		651	B	650	A+A	
	758	747	A-B	749	A-A	ν^{s}C–N 32% + δX-C-H 28%
764		752	A+B	754	A+A	
888	886	878	A	875	A-A	ν^{s}C–N 30% + δX-C-H 41%
898	896	888	B	877	A+A	
948	944	921	B	938	A+A	δCH_2 72% + νC–N 11%
		937	A	938	A-A	
996	994	980	B	984	A-A	ν^{as}C–N 40% + δX-C-H 42%
		983	A	985	A+A	
1209		1200	B	1208	A-A	
1215	1214	1209	A	1209	A+A	

Table S20. Calculated structural parameters (Å and deg.) for conformers ***AA*** and ***AB*** using PBE0 fuctional.

	AA	***AB***
$Pb–S_1$	2.633	2.614
$Pb–S_2$	2.633	2.627
$Pb–N_1$	2.641	2.731
$Pb–N_2$	2.641	2.640
$S_1–Pb–S_2$	101.4	97.35
$N_1–Pb–N_2$	146.65	152.54

Table S21. Calculated energetic parameters (ΔE, ΔH and ΔG, kcal/mol) for **4** (T = 298 K, ***TS*** – transition state from ***AA*** to ***AB***)

Conformer	ΔE	ΔH	ΔG
PBE			
AA	0	0	0
AB	1.51	0.27	2.75
TS	3.49	3.11	3.8
PBE0			
AA	0	0	0
AB	-0.10	-0.09	-0.12
TS	3.72	3.33	4.11
B3LYP			
AA	0	0	0
AB	-0.37	-0.36	-0.37
TS	3.81	3.41	4.32
M05-2X			
AA	0	0	0
AB	0.24	0.22	0.24
TS	3.98	3.57	4.56
MP2			
AA	0	0	0
AB	-0.39		