Electronic Supporting Information

NCN-pincer organopnictogen(III) bis(aryloxides)

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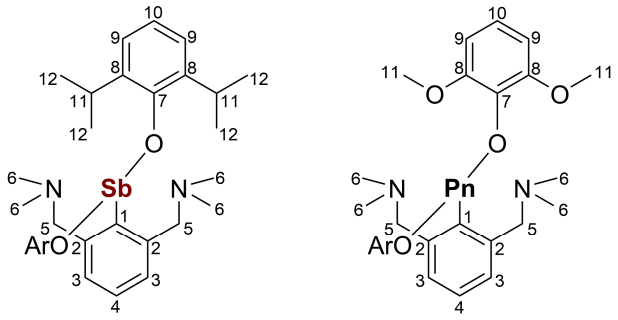

3 **Pn** = **Sb** (**4**), **Bi** (**5**)

Scheme S1. Full numbering scheme for NMR assignments.

Representative NMR spectra

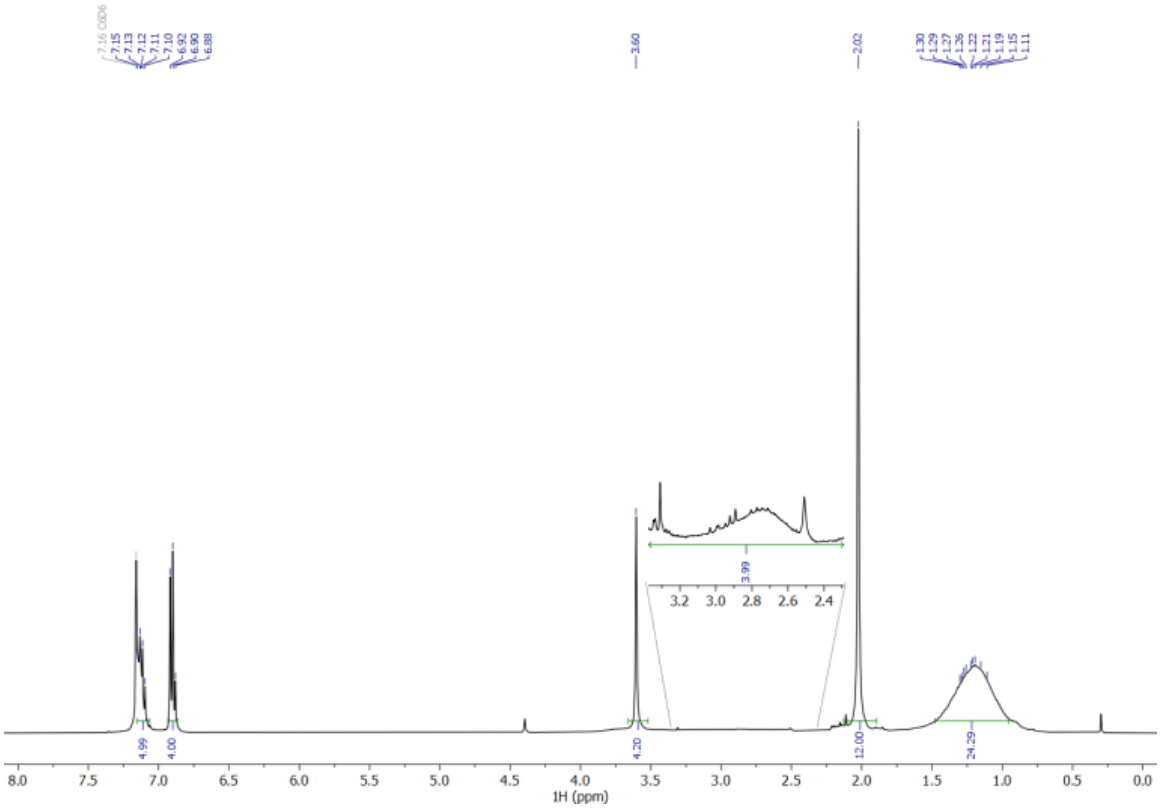

Figure S1. ^{1}H NMR spectrum of **3** (C_6D_6, 400 MHz) at r.t.

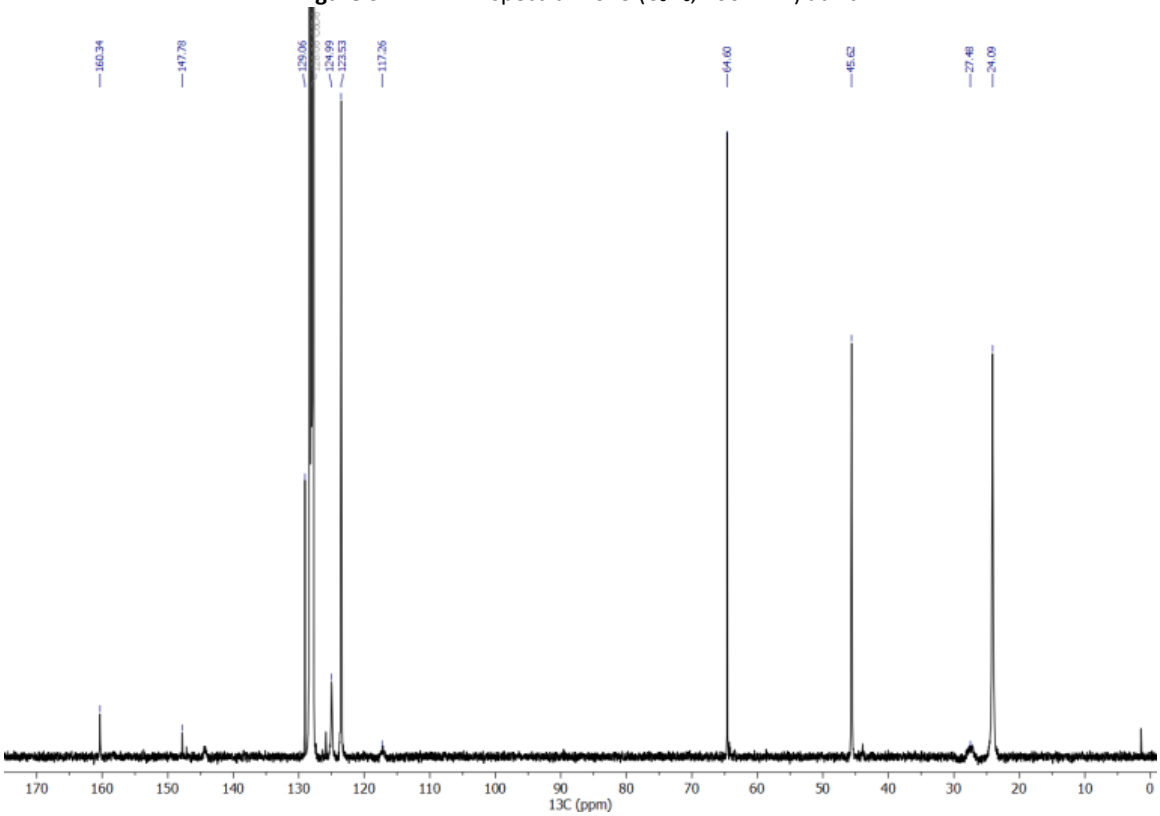

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3** (C_6D_6, 101 MHz) at r.t.

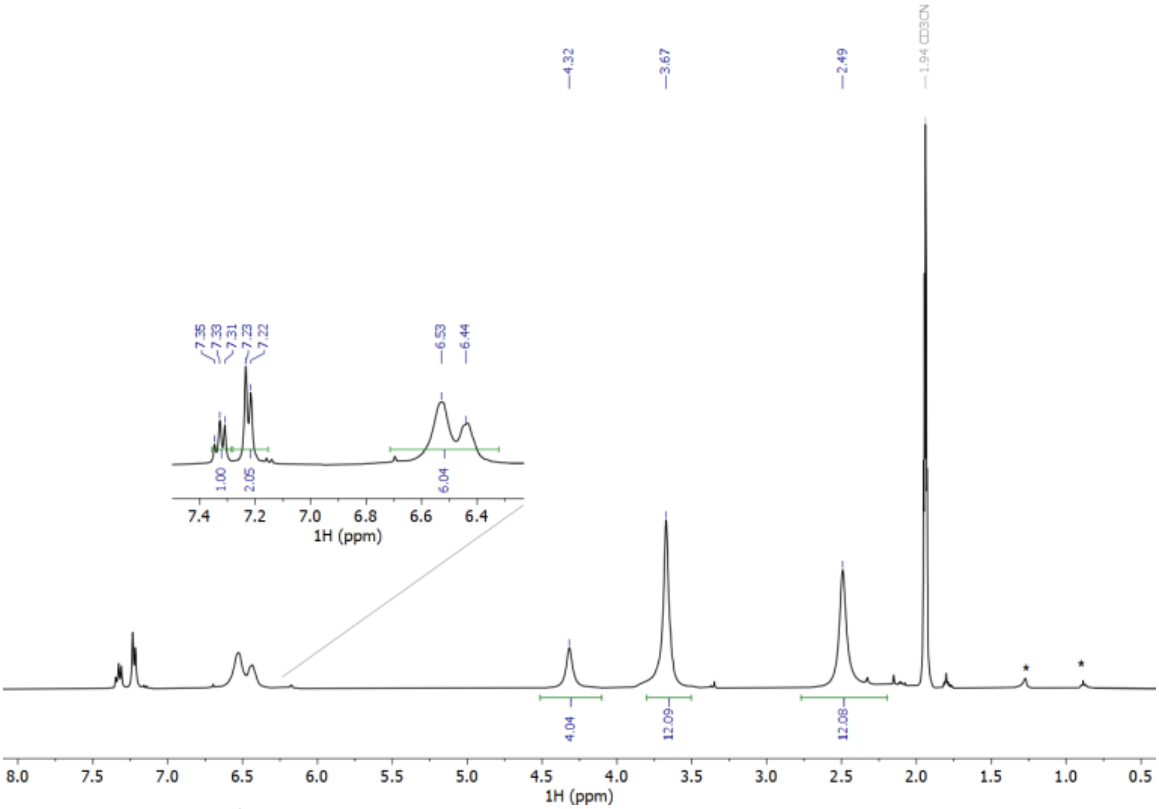

Figure S3. ^{1}H NMR spectrum of **4** (CD_3CN, 400 MHz) at r.t. (* denotes residual *n*-hexane).

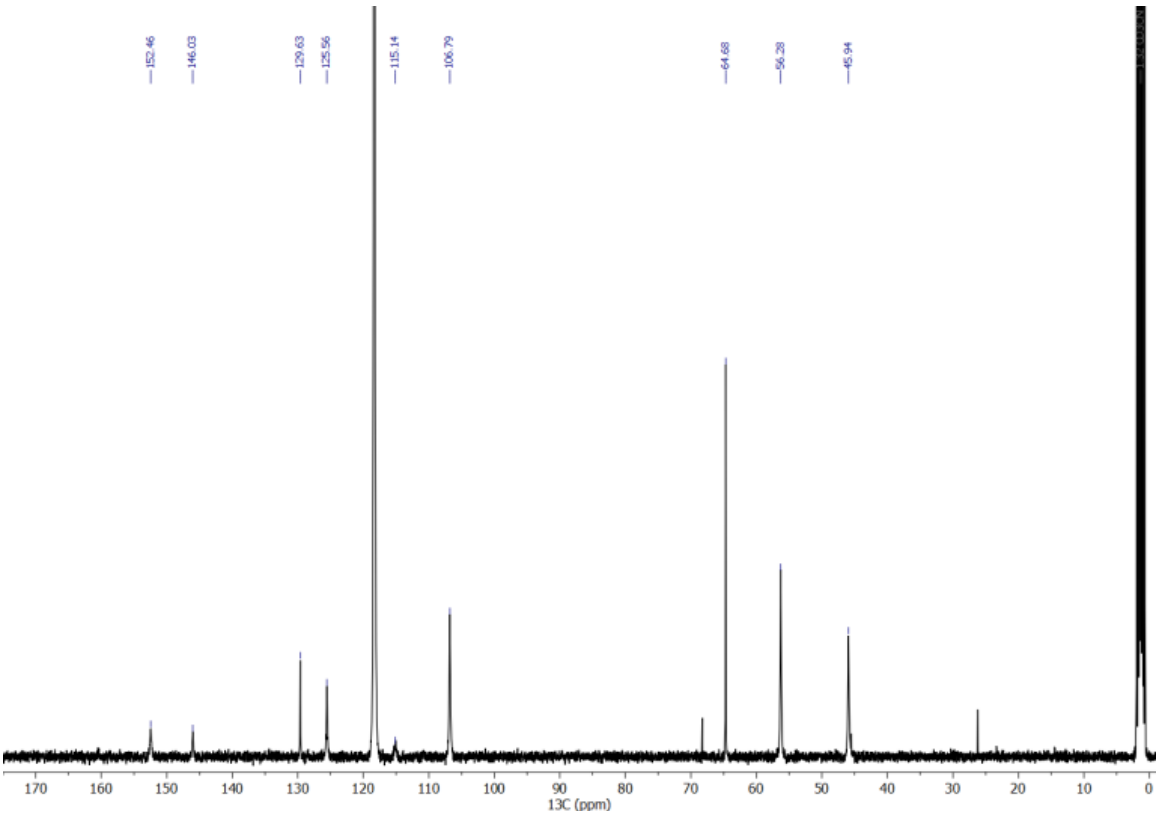

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (CD_3CN, 101 MHz) at r.t.

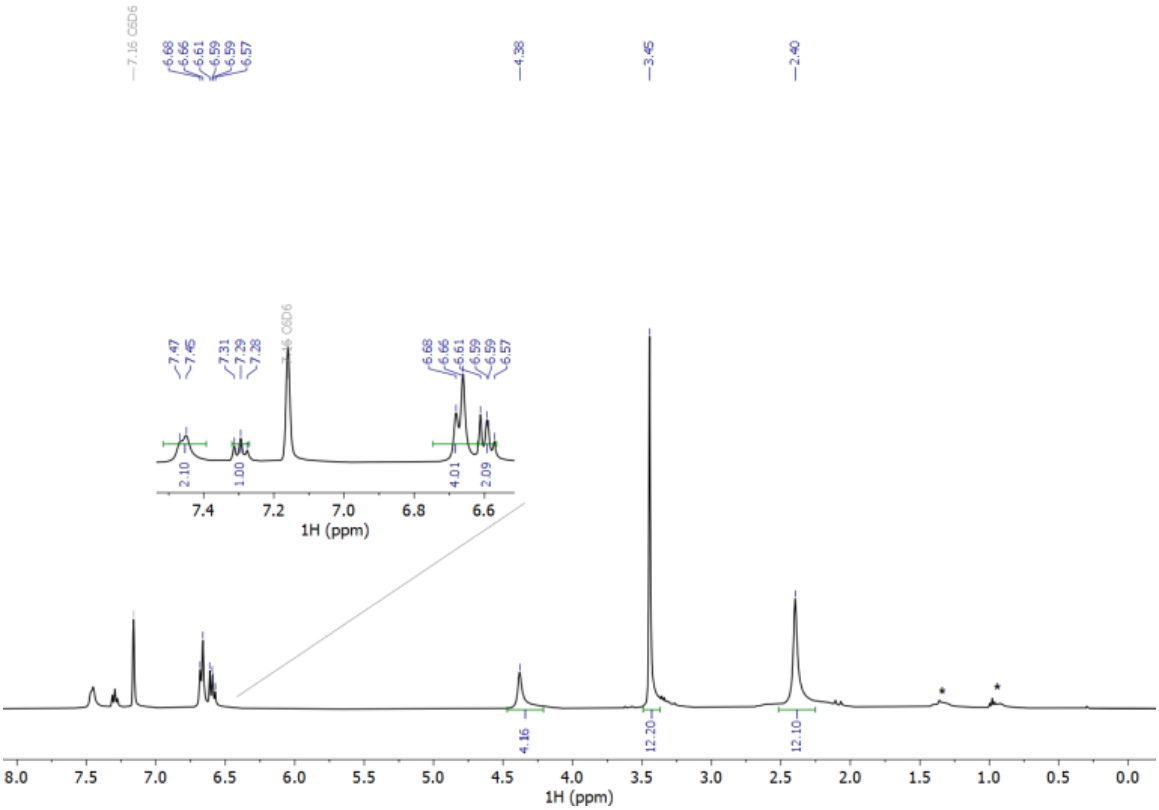

Figure S5. ^{1}H NMR spectrum of **5** (C_6D_6, 400 MHz) at r.t.(* denotes residual *n*-hexane).

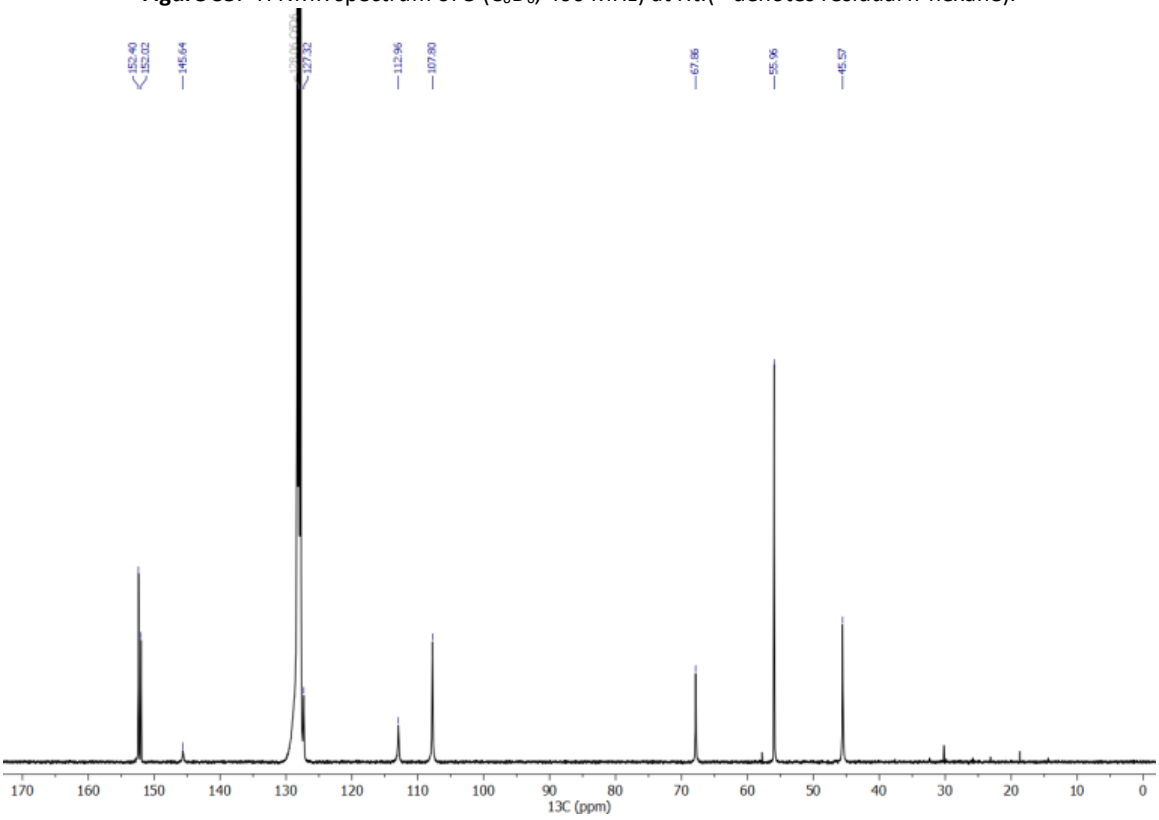

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **5** (C_6D_6, 101 MHz) at r.t.

Crystallographic data

Table S1. Selected X-ray data collection.

Compound	3	5
Empirical formula	$C_{36}H_{53}N_2O_2Sb$	$C_{28}H_{37}N_2O_6Bi$
Formula weight	667.55	706.57
Crystal size /mm	0.090 x 0.070 x 0.060	0.180 x 0.100 x 0.090
Crystal habit	clear colourless	yellow block
Wavelength (Å)	0.71073	0.71073
Temperature (K)	100.(2)	100.(2)
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a (Å)	18.6622(10)	14.6780(9)
b (Å)	10.6493(5)	22.2864(13)
c (Å)	17.3555(9)	9.5439(6)
α (°)	90	90
β (°)	95.402(2)	117.719(2)
γ (°)	90	90
Volume (Å^3)	3433.9(3)	2763.7(3)
Z	4	4
Density (calculated) (g cm^{-1})	1.291	1.698
Absorption coefficient (mm^{-1})	0.835	6.423
F(000)	1400	1400
θ range for data collections (°)	2.19-30.67	3.15-43.19
T_{max} / T_{min}	0.93 / 0.95	0.47 / 0.56
Reflections collected	55025	135024
Independent reflections, R_{int}	3754, 0.0559	10348, 0.0296
Miller indices, h, k, l (min/max)	-23/23, -13/13, -22/22	-28/28, -42/42, -17/18
Completeness to θ	100%	99.8%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3754 / 0 / 193	10348 / 0 / 173
Goodness-of-fit on F^2	1.052	1.140
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0202	R_1 = 0.0121
	wR_2 = 0.0437	wR_2 = 0.0323
R indices (all data)	R_1 = 0.0252	R_1 = 0.0131
	wR_2 = 0.0460	wR_2 = 0.0325
Largest diff. peak and hole, eA^{-3}	0.433, -0.296	1.102, -1.205
CCDC No.	**2176504**	**2176505**

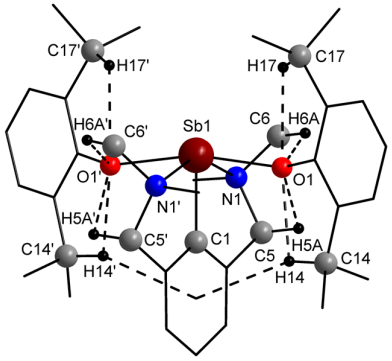

Figure S7. Molecular structure of isomer (pR_{N1},$pR_{N1'}$)-**3** showing the intramolecular C–H···O and C–H···π ($Ar_{centroid}$) contacts (only hydrogen atoms involved in intramolecular contacts are shown) [symmetry equivalent atoms (*1–x, y, 1.5–z*) are given by "prime"].

-	intramolecular distances	C(14)–H(14)$_{methanetriyl}$···O(1)	2.39 Å	
		C(17)–H(17)$_{methanetriyl}$···O(1)	2.44 Å	
		C(6)–H(6a)$_{methyl}$···O(1)	2.55 Å	
		C(5)–H(5a)$_{methylene}$···O(1)	2.63 Å	
		C(14)–H(14)$_{methanetriyl}$···$Ar_{centroid}${C(1)-C(4),C(2'), C(3')}	2.83 Å	(γ = 21.0°)

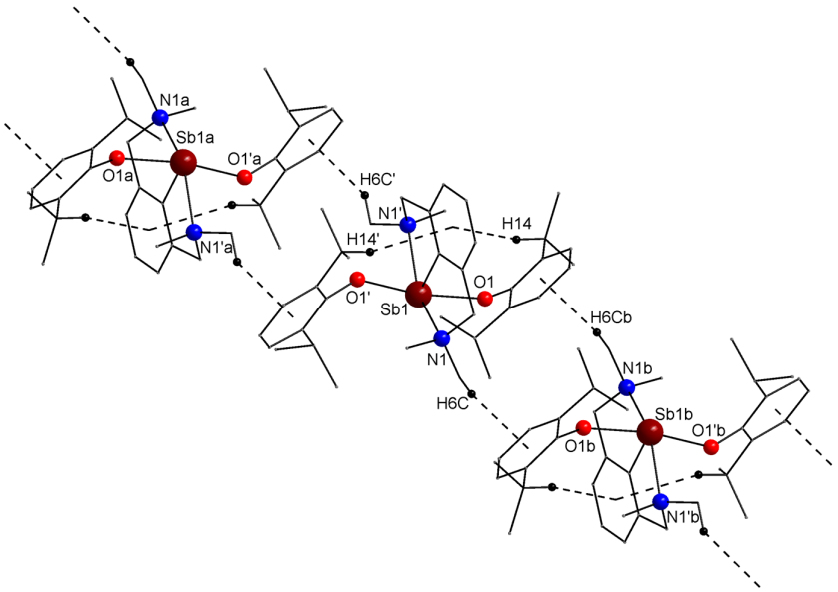

Figure S8. Chain polymer built through intra- and intermolecular C–H···π ($Ar_{centroid}$) contacts between alternating (pR_{N1},$pR_{N1'}$)- and (pS_{N1},$pS_{N1'}$)-**3** isomers in the crystal of **3** (only hydrogen atoms involved in intra- and intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, y, 1.5–z*), (*1–x, 1–y, 2–z*), (*x, 1–y, 0.5+z*), (*1–x, 1–y, 1–z*) and (*x, 1–y, –0.5+z*) are given by "prime", "a", "prime a", "b" and "prime b"].

-	intermolecular distances	C(6b)–H(6Cb)$_{N\text{-}methyl}$···$Ar_{centroid}${C(8)-C(13)}	2.63 Å	(γ = 6.1°)

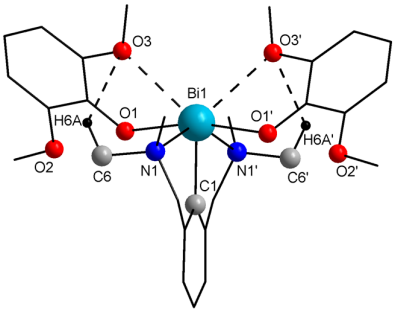

Figure S9. Molecular structure of isomer (pS_{N1},$pS_{N1'}$)-**5** showing the intramolecular C−H···O contacts (only hydrogen atoms involved in intramolecular contacts are shown) [symmetry equivalent atoms (*1–x, y, 0.5–z*) are given by "prime"].

- intramolecular distances C(6)−H(6A)$_{N\text{-methyl}}$ ···O(3) 2.62 Å

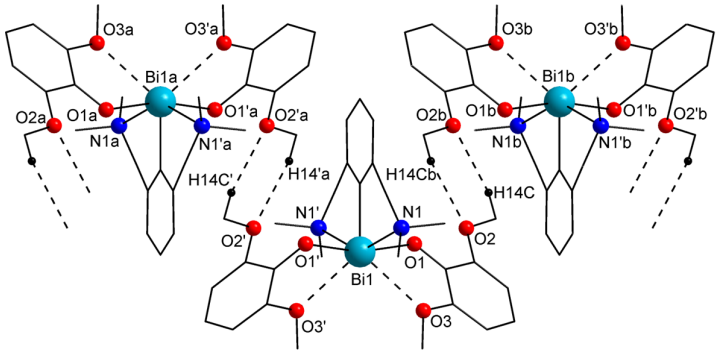

Figure S10. View along axis *c* of the chain polymer built through intermolecular C−H···O contacts between (pS_{N1},$pS_{N1'}$)-**5** isomers in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, y, 0.5–z*), (*0.5–x, 1.5–y, 1–z*), (*–0.5+x, 1.5–y, 0.5+z*), (*1.5–x, 1.5–y, –z*) and (*0.5+x, 1.5–y, –0.5+z*) are given by "prime", "a", "prime a", "b" and "prime b"].

- intermolecular distances C(14)−H(14C)$_{O\text{-methyl}}$···O(2b) 2.48 Å

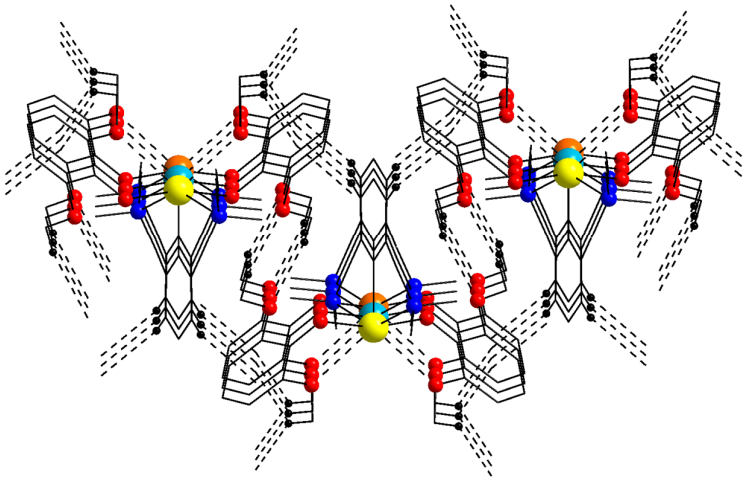

Figure S11. View along axis *c* of a layer built through intermolecular C−H···π ($Ar_{centroid}$) contacts between chain polymers of (pS_{N1},$pS_{N1'}$)-**5** isomers in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1.5–x, 1.5–y, 1–z*) are given by "c"].

- intermolecular distances C(3)−H(3)$_{aryl}$···$Ar_{centroid}${C(8c)-C(13c)}2.75 Å (γ = 2.7°)

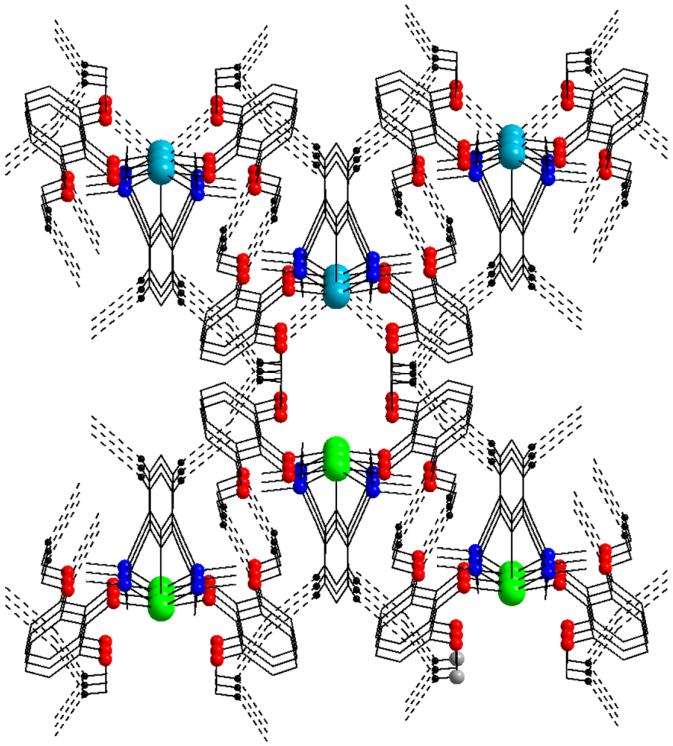

Figure S12. View along axis *c* of a 3D supramolecular association built through intermolecular C−H···π ($Ar_{centroid}$) contacts between alternating layers of (pS_{N1},$pS_{N1'}$)-**5** isomers (Bi atoms in light blue color) and layers of (pR_{N1},$pR_{N1'}$)-**5** isomers (Bi atoms in green color) in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown [symmetry equivalent atoms) (*x, 1–y, –0.5+z*) are given by "d"].

- intermolecular distances C(15c)−H(15Bc)$_{methyl}$···$Ar_{centroid}${C(8)-C(13)} 2.48 Å (γ = 7.3°)