

Electronic Supporting Information

NCN-pincer organopnictogen(III) bis(aryloxides)

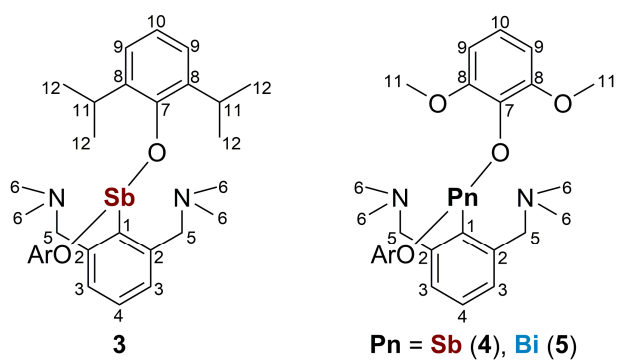
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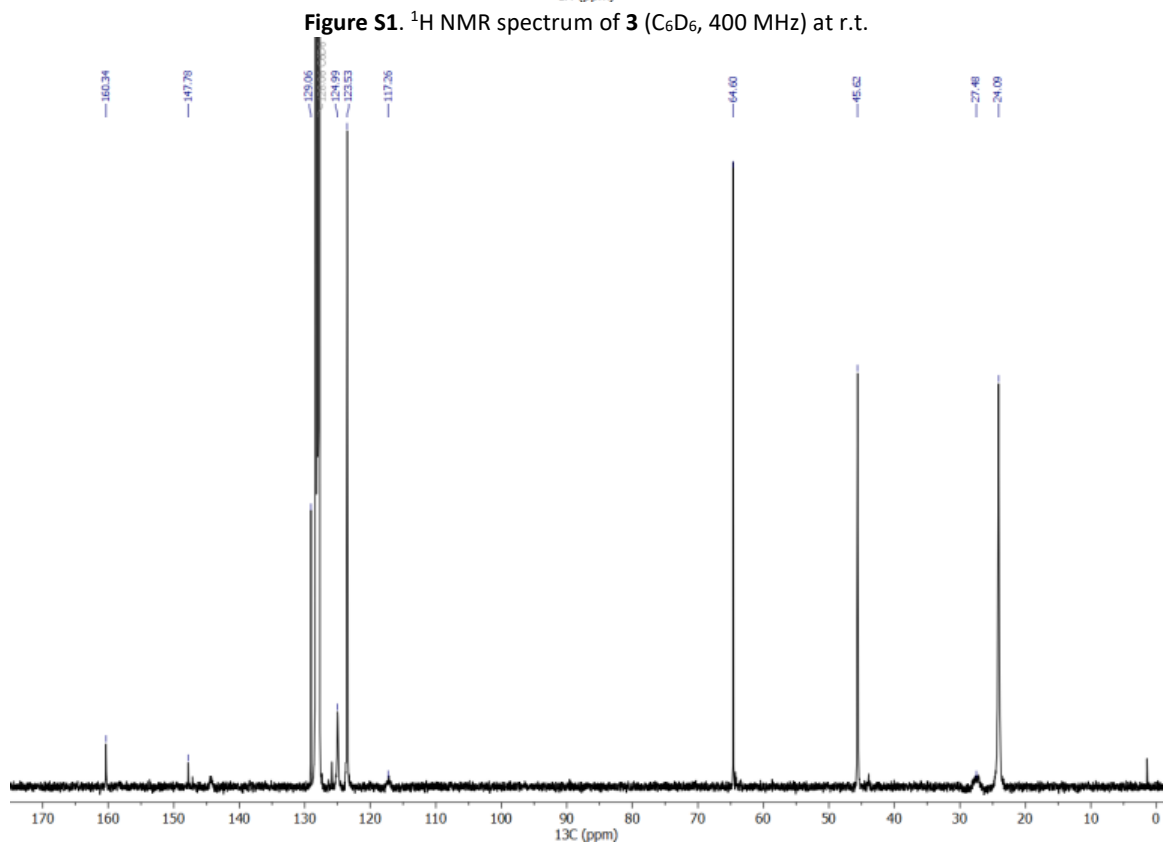
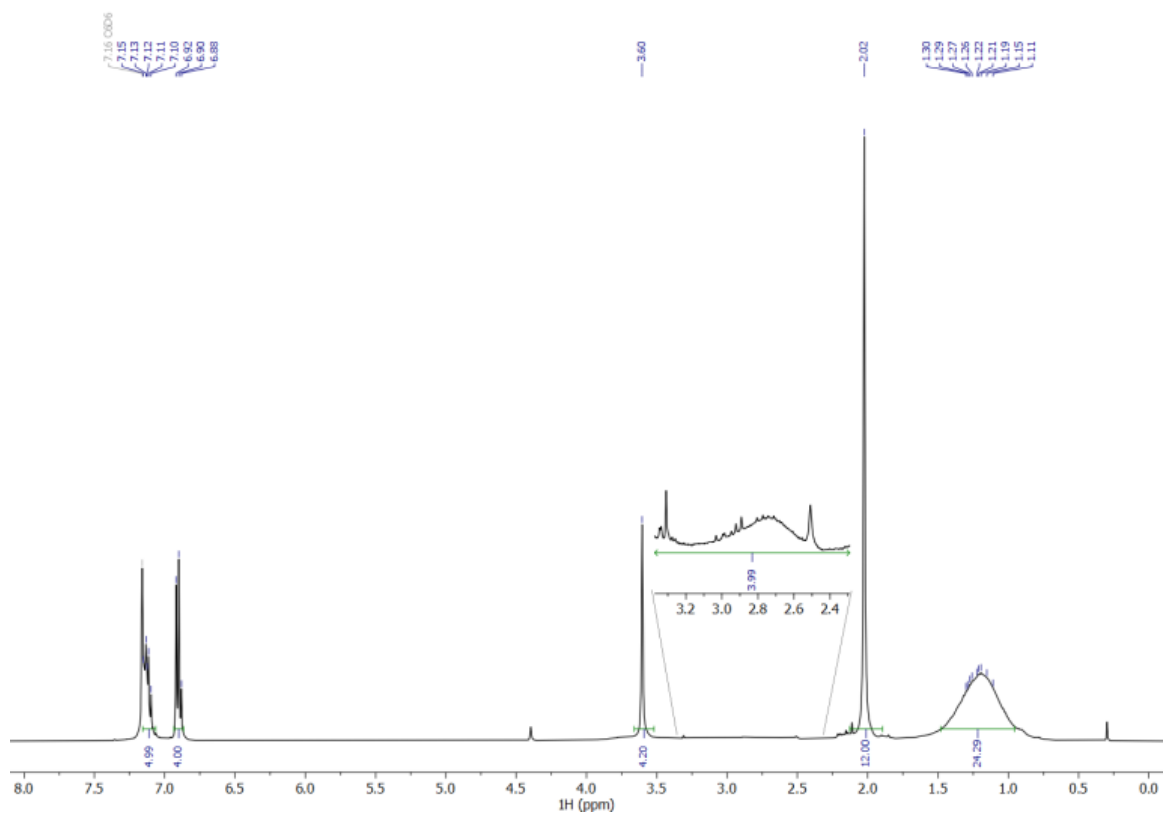
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Scheme S1. Full numbering scheme for NMR assignments.

Representative NMR spectra



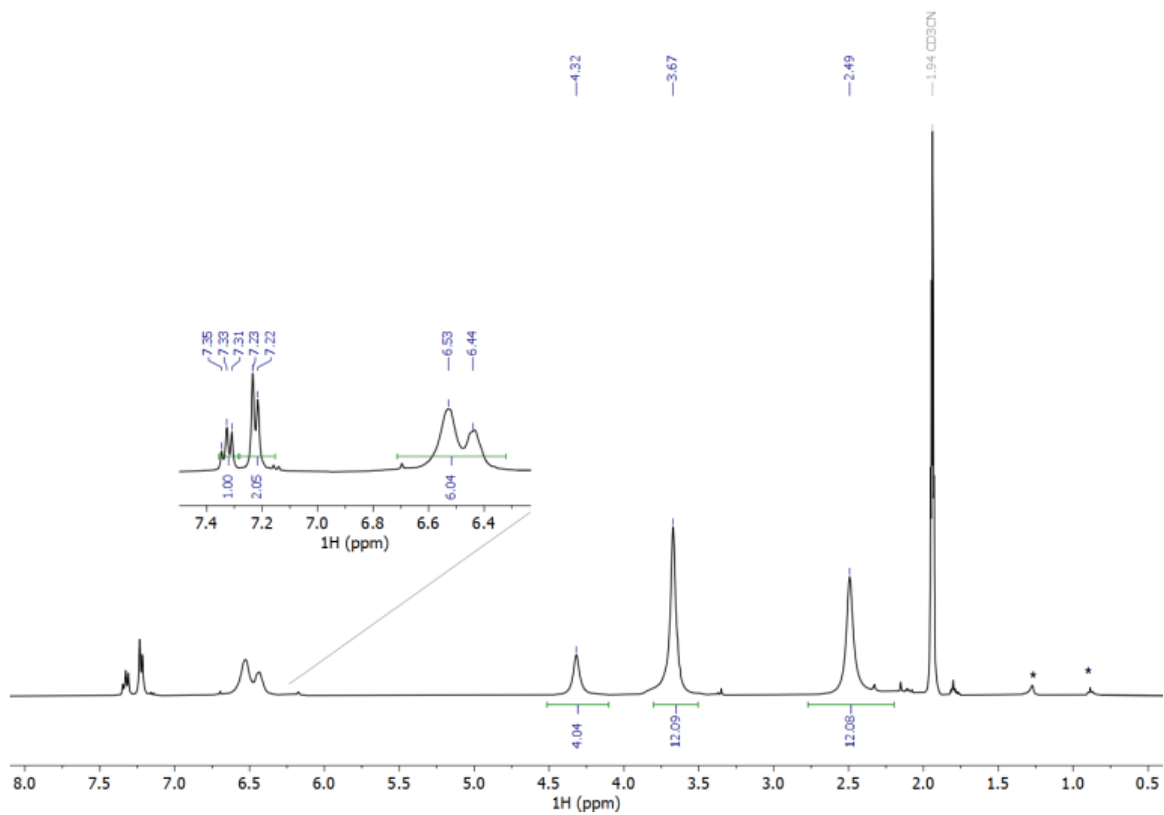


Figure S3. ^1H NMR spectrum of **4** (CD_3CN , 400 MHz) at r.t. (* denotes residual *n*-hexane).

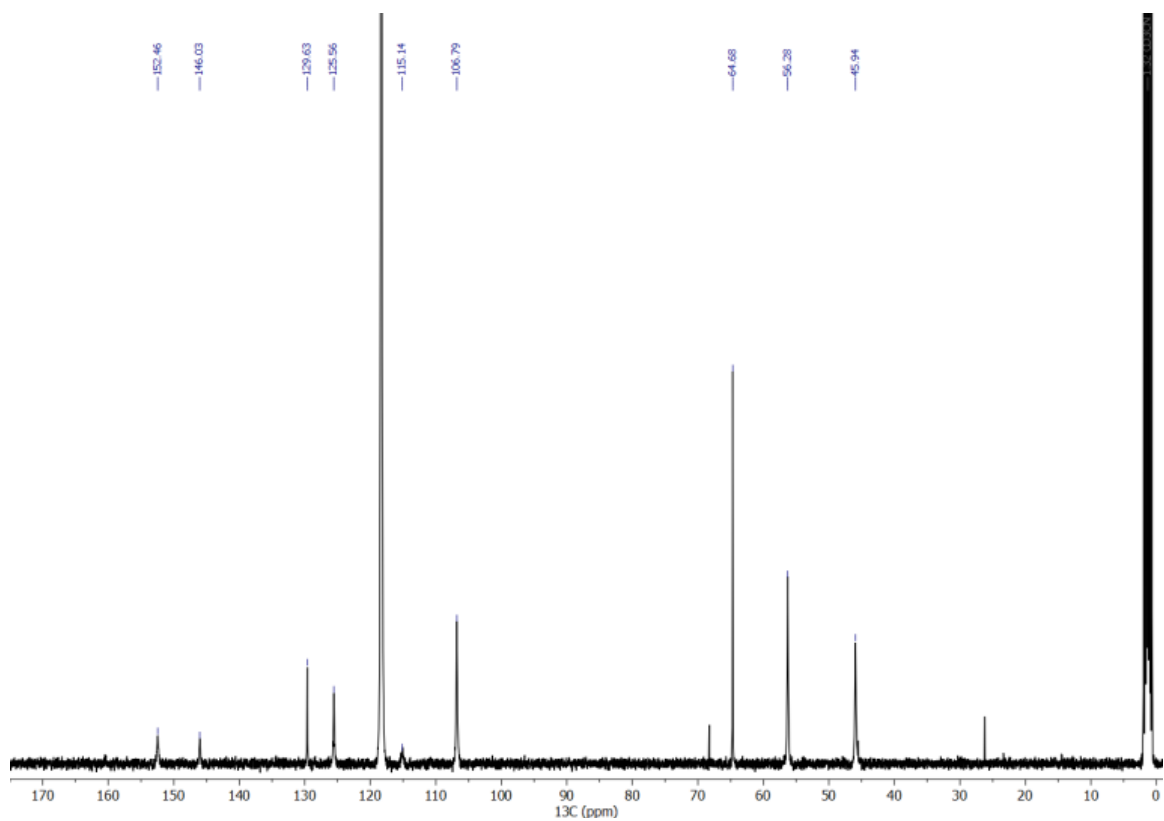
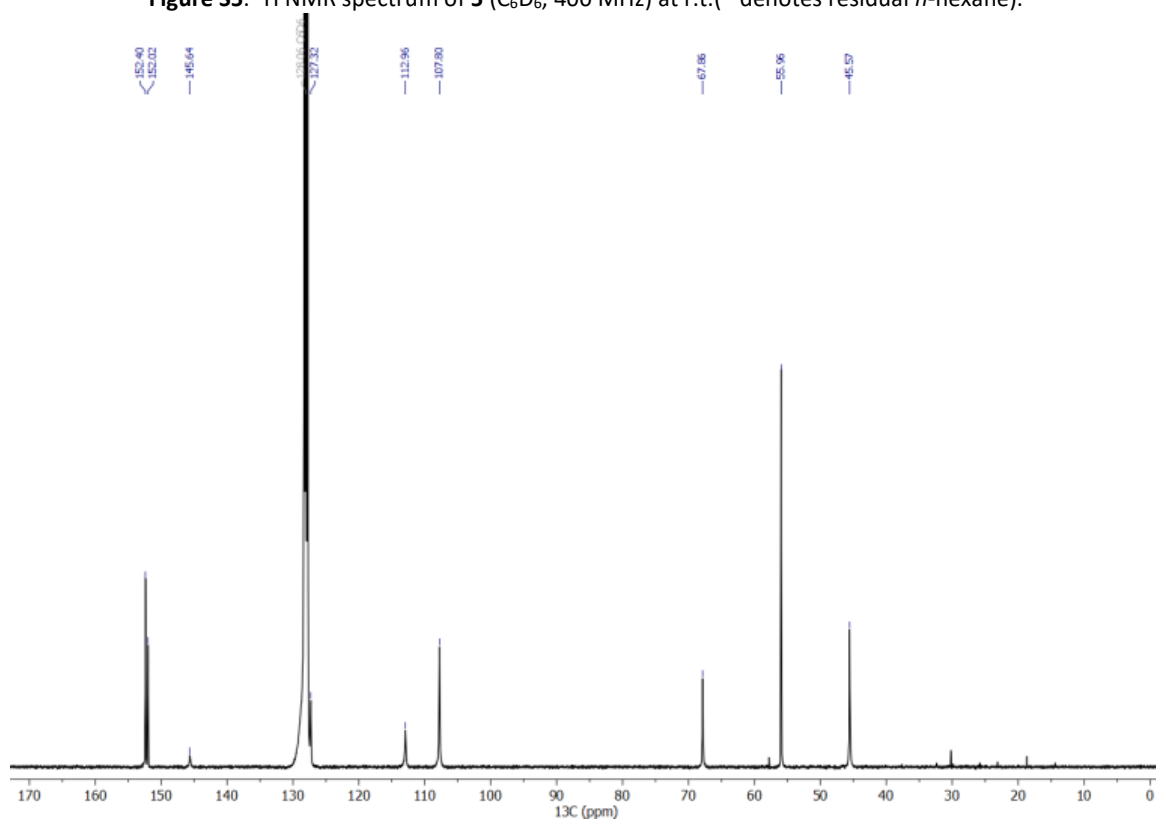
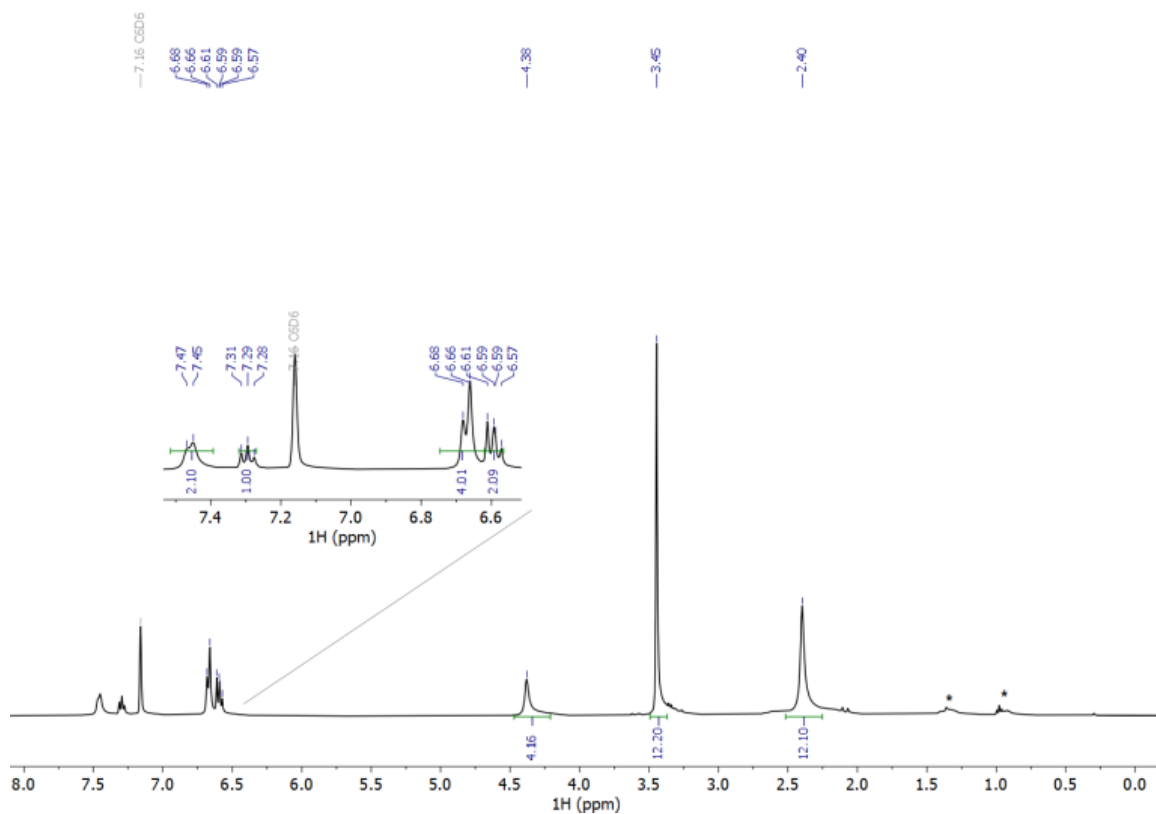


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (CD_3CN , 101 MHz) at r.t.



Crystallographic data

Table S1. Selected X-ray data collection.

Compound	3	5
Empirical formula	C ₃₆ H ₅₃ N ₂ O ₂ Sb	C ₂₈ H ₃₇ N ₂ O ₆ Bi
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 ⁻³)	1.291	1.698
Absorption coefficient (mm ⁻¹)	0.835	6.423
<i>F</i> (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, <i>R</i> _{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 <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3754 / 0 / 193	10348 / 0 / 173
Goodness-of-fit on <i>F</i> ²	1.052	1.140
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0202 <i>wR</i> ₂ = 0.0437	<i>R</i> ₁ = 0.0121 <i>wR</i> ₂ = 0.0323
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0252 <i>wR</i> ₂ = 0.0460	<i>R</i> ₁ = 0.0131 <i>wR</i> ₂ = 0.0325
Largest diff. peak and hole, eÅ ⁻³	0.433, -0.296	1.102, -1.205
CCDC No.	2176504	2176505

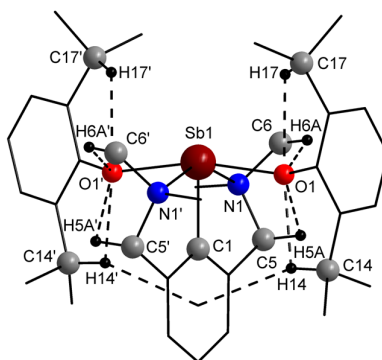


Figure S7. Molecular structure of isomer ($pR_{N1}, pR_{N1'}$)-**3** showing the intramolecular C–H \cdots O and C–H \cdots π (Ar_{centroid}) contacts (only hydrogen atoms involved in intramolecular contacts are shown) [symmetry equivalent atoms ($1-x, y, 1.5-z$) are given by “prime”].

- intramolecular distances	C(14)–H(14) _{methanetriyl} \cdots O(1)	2.39 Å	
	C(17)–H(17) _{methanetriyl} \cdots O(1)	2.44 Å	
	C(6)–H(6a) _{methyl} \cdots O(1)	2.55 Å	
	C(5)–H(5a) _{methylene} \cdots O(1)	2.63 Å	
	C(14)–H(14) _{methanetriyl} \cdots Ar _{centroid} {C(1)–C(4), C(2'), C(3')}	2.83 Å	($\gamma = 21.0^\circ$)

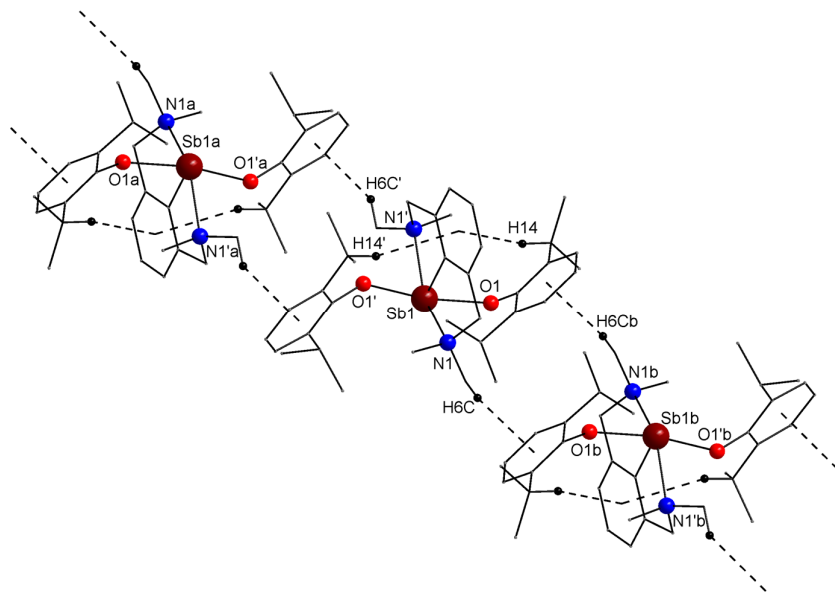


Figure S8. Chain polymer built through intra- and intermolecular C–H \cdots π (Ar_{centroid}) contacts between alternating ($pR_{N1}, pR_{N1'}$)- and ($pS_{N1}, pS_{N1'}$)-**3** isomers in the crystal of **3** (only hydrogen atoms involved in intra- and intermolecular contacts are shown) [symmetry equivalent 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-methyl} \cdots Ar _{centroid} {C(8)–C(13)}	2.63 Å	($\gamma = 6.1^\circ$)
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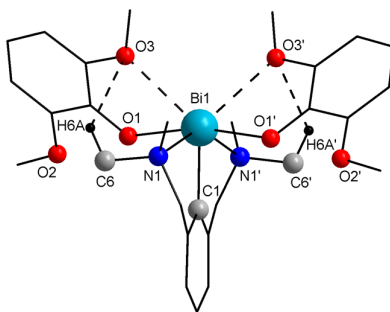


Figure S9. Molecular structure of isomer ($pS_{N1}, pS_{N1'}$)-**5** showing the intramolecular C–H...O contacts (only hydrogen atoms involved in intramolecular contacts are shown) [symmetry equivalent atoms ($1-x, y, 0.5-z$) are given by “prime”].

- intramolecular distances C(6)–H(6A)_{N-methyl}...O(3) 2.62 Å

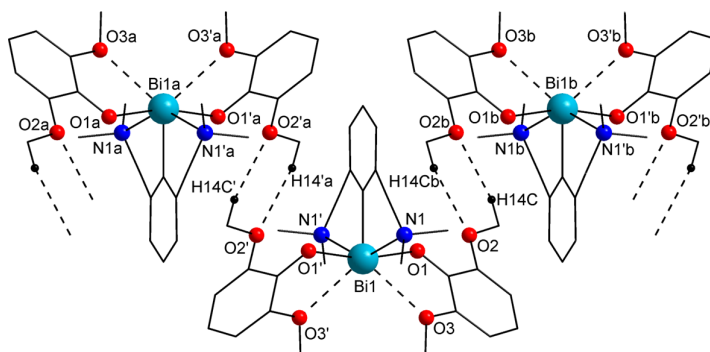


Figure S10. View along axis *c* of the chain polymer built through intermolecular C–H...O contacts between ($pS_{N1}, pS_{N1'}$)-**5** isomers in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms ($1-x, y, 0.5-z$), ($0.5-x, 1.5-y, 1-z$), ($-0.5+x, 1.5-y, 0.5+z$), ($1.5-x, 1.5-y, -z$) 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-methyl}...O(2b) 2.48 Å

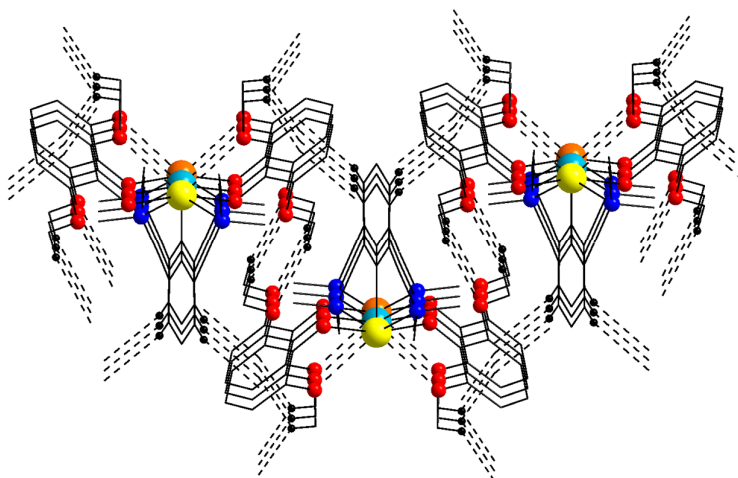


Figure S11. View along axis *c* of a layer built through intermolecular C–H... π (Ar_{centroid}) contacts between chain polymers of ($pS_{N1}, pS_{N1'}$)-**5** isomers in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms ($1.5-x, 1.5-y,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

- intermolecular distances C(3)–H(3)_{aryl}... $Ar_{\text{centroid}}\{C(8c)-C(13c)\}$ 2.75 Å ($\gamma = 2.7^\circ$)

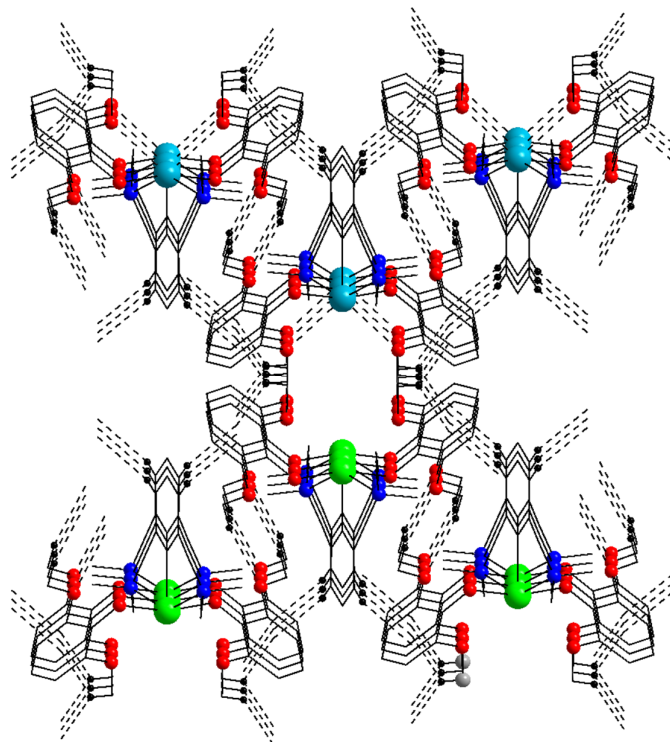


Figure S12. View along axis *c* of a 3D supramolecular association built through intermolecular C–H⋯π (A_{centroid}) contacts between alternating layers of ($pS_{N1}, pS_{N1'}$)-**5** isomers (Bi atoms in light blue color) and layers of ($pR_{N1}, pR_{N1'}$)-**5** isomers (Bi atoms in green color) in 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}⋯ A_{centroid} {C(8)–C(13)} 2.48 Å ($\gamma = 7.3^\circ$)