Electronic Supplementary Information

Reactivity of a carbonyl moiety in organotin(IV) compounds. Novel Pd(II) and Cu(II) complexes supported by organotin(IV) ligands

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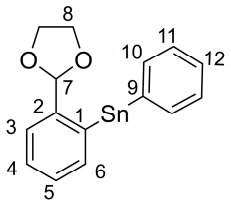
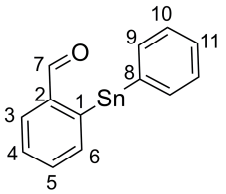
Content

Numbering schemes for NMR resonance assignments



(**1**)



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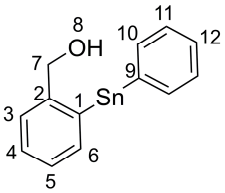

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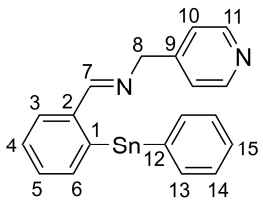
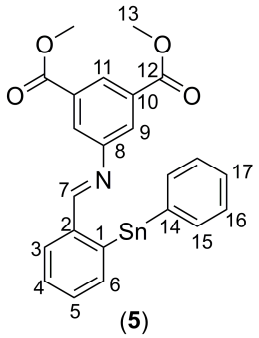


(**4**), (**7**)



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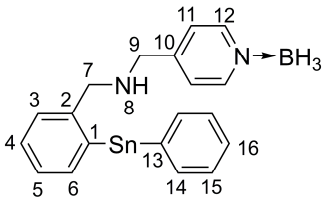

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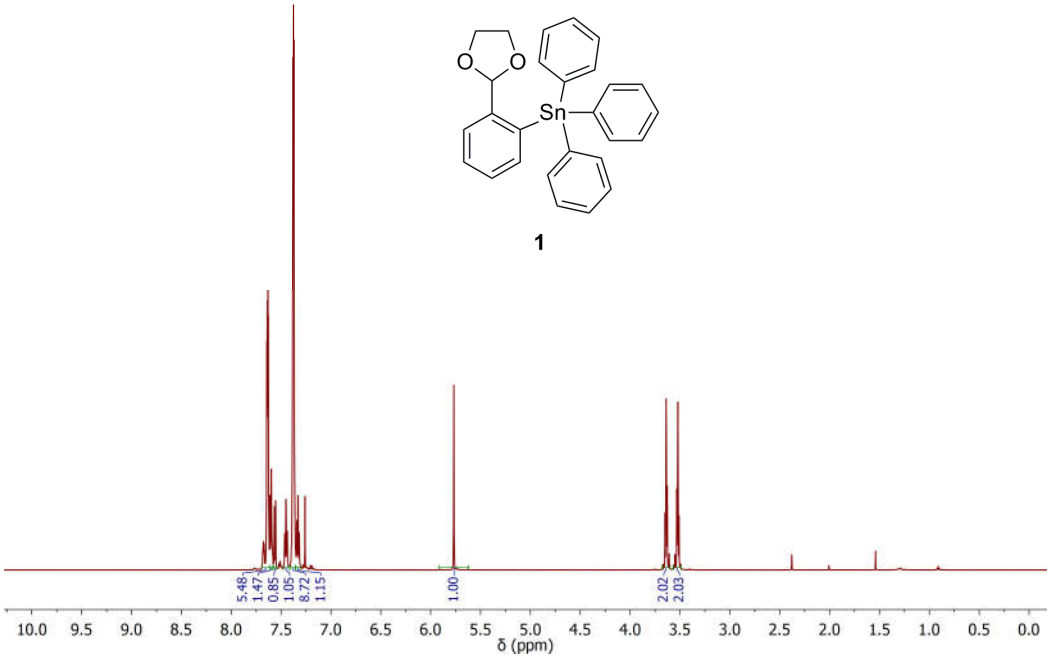

Figure S1. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [2-{$(CH_2O)_2CH$}C_6H_4]$SnPh_3$ (**1**).

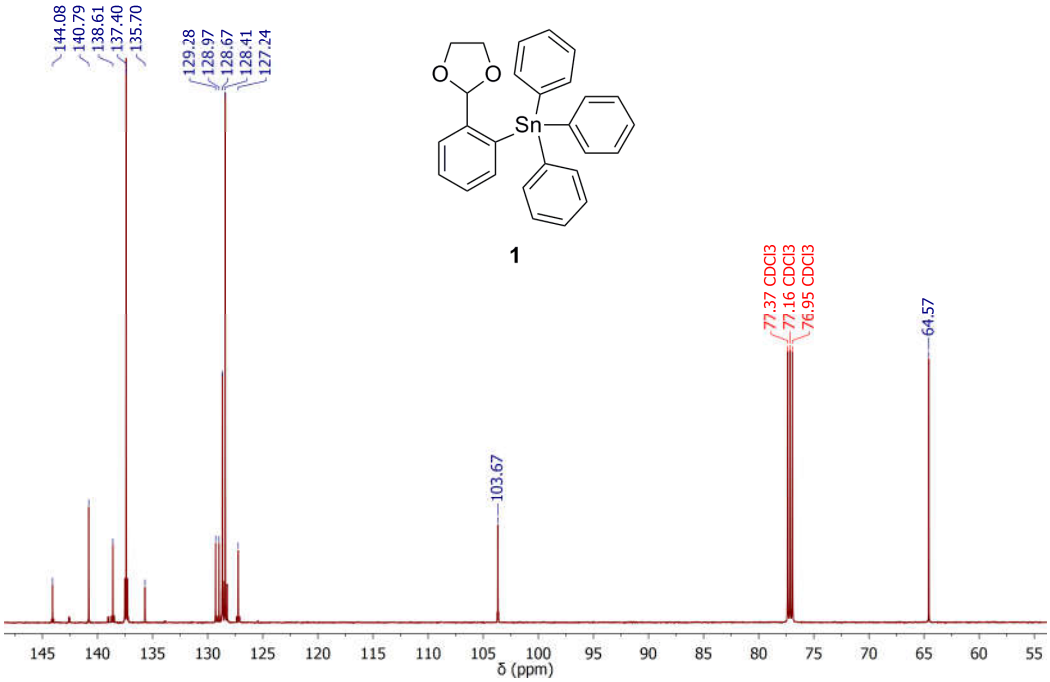

Figure S2. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-{$(CH_2O)_2CH$}C_6H_4]$SnPh_3$ (**1**).

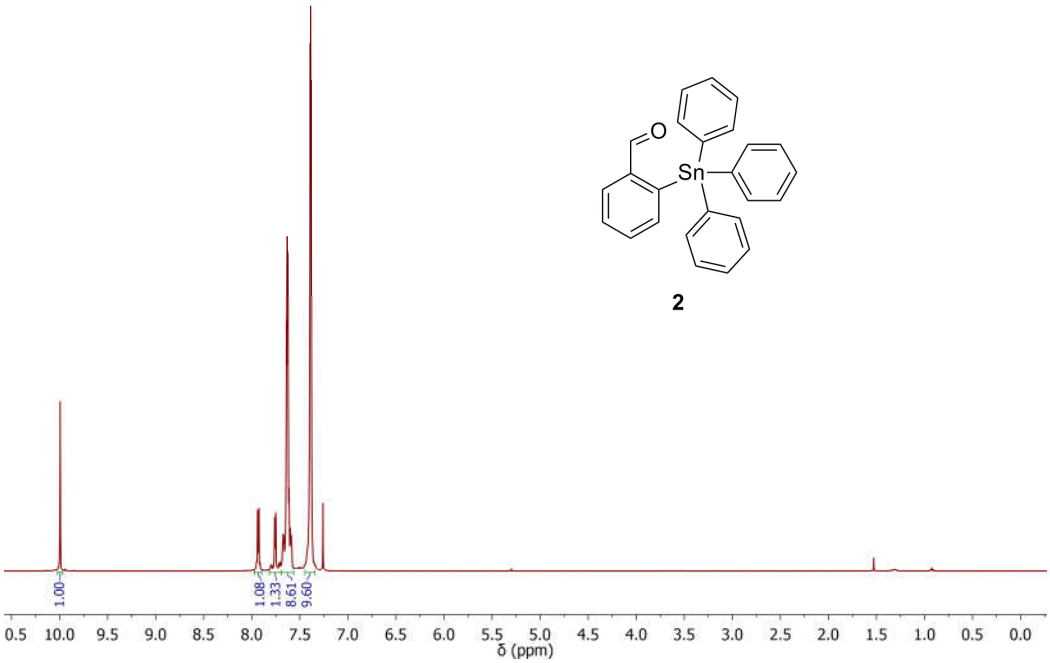

Figure S3. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [2-(O=CH)C_6H_4]$SnPh_3$ (**2**).

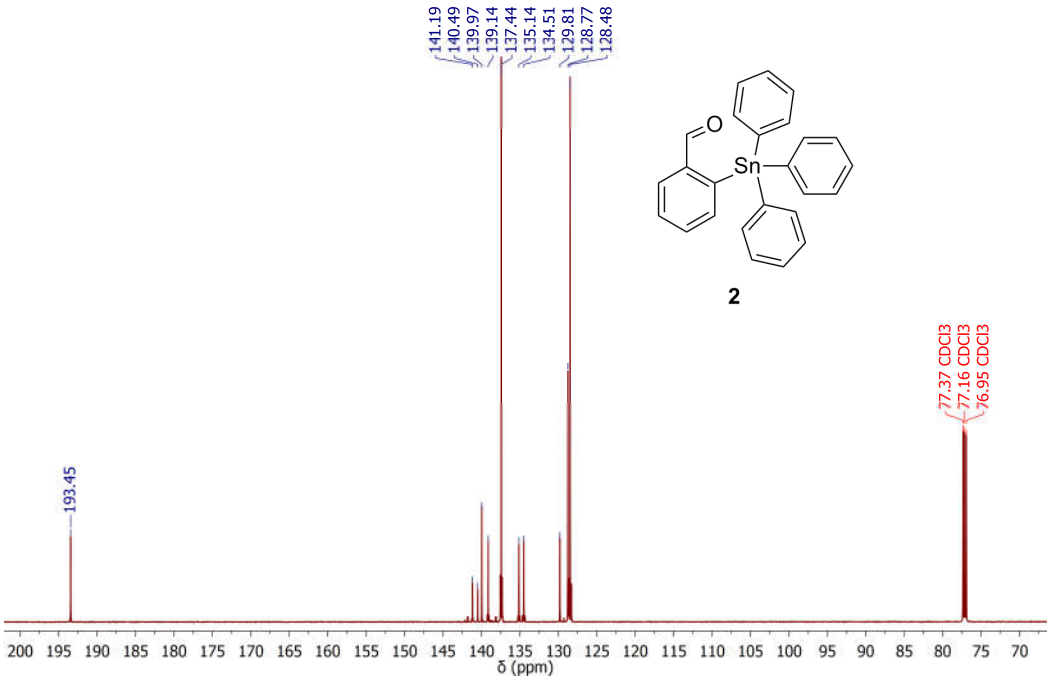

Figure S4. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-(O=CH)C_6H_4]$SnPh_3$ (**2**).

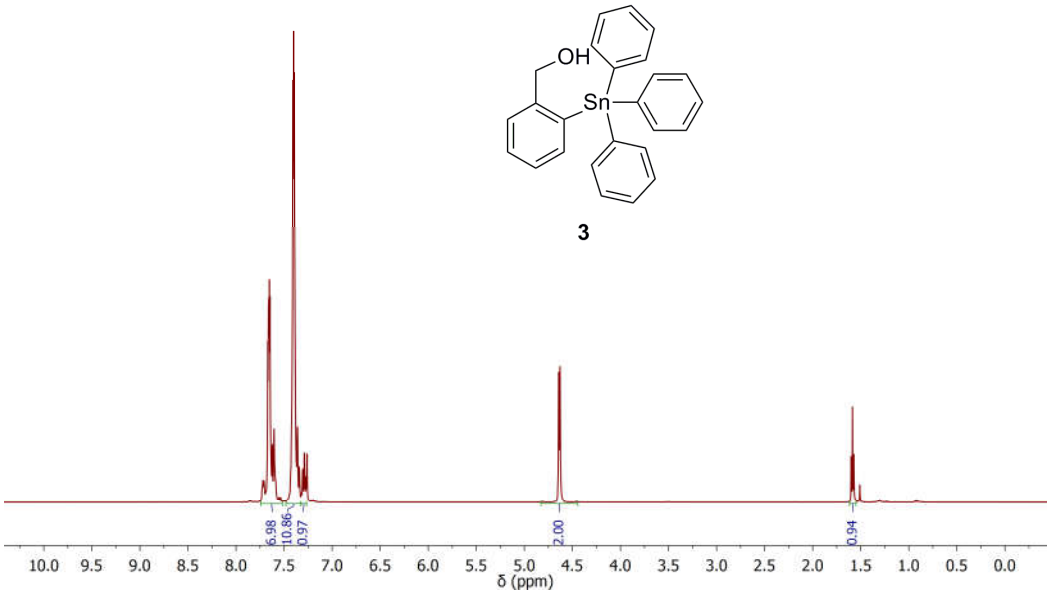

Figure S5. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [2-($HOCH_2$)C_6H_4]$SnPh_3$ (**3**).

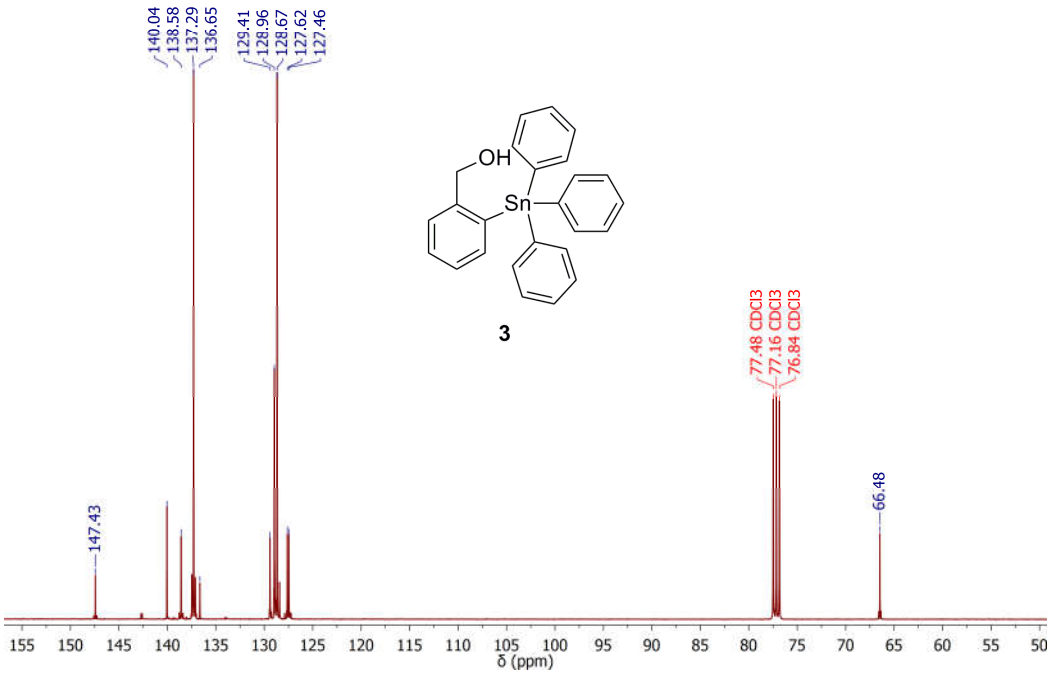

Figure S6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-($HOCH_2$)C_6H_4]$SnPh_3$ (**3**).

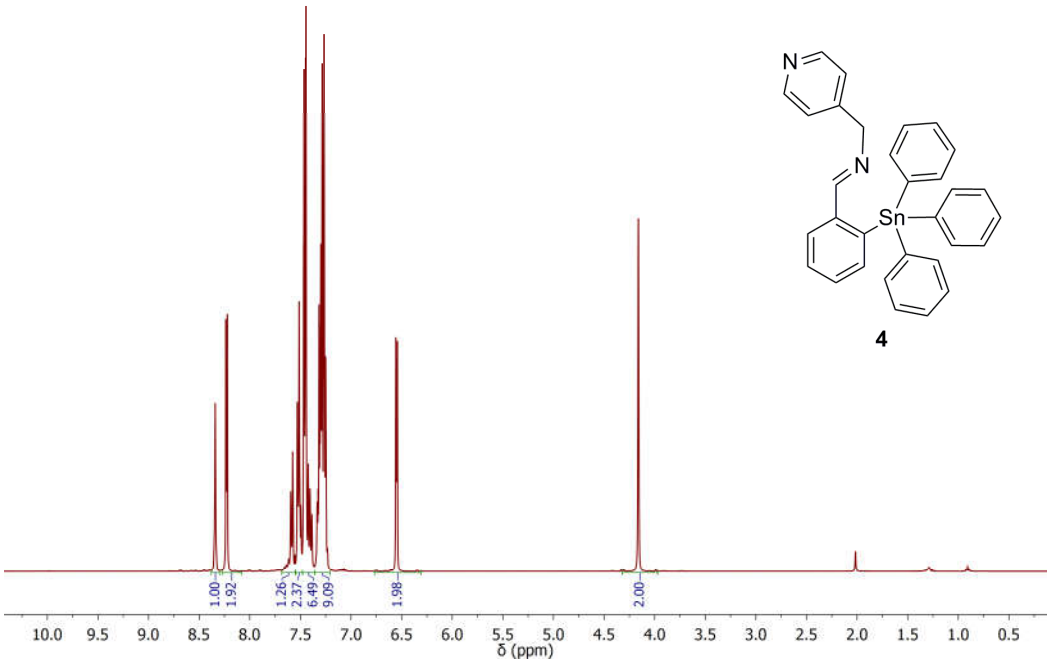

Figure S7. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [2-(4′-$PyCH_2N{=}CH)C_6H_4$]$SnPh_3$ (**4**).

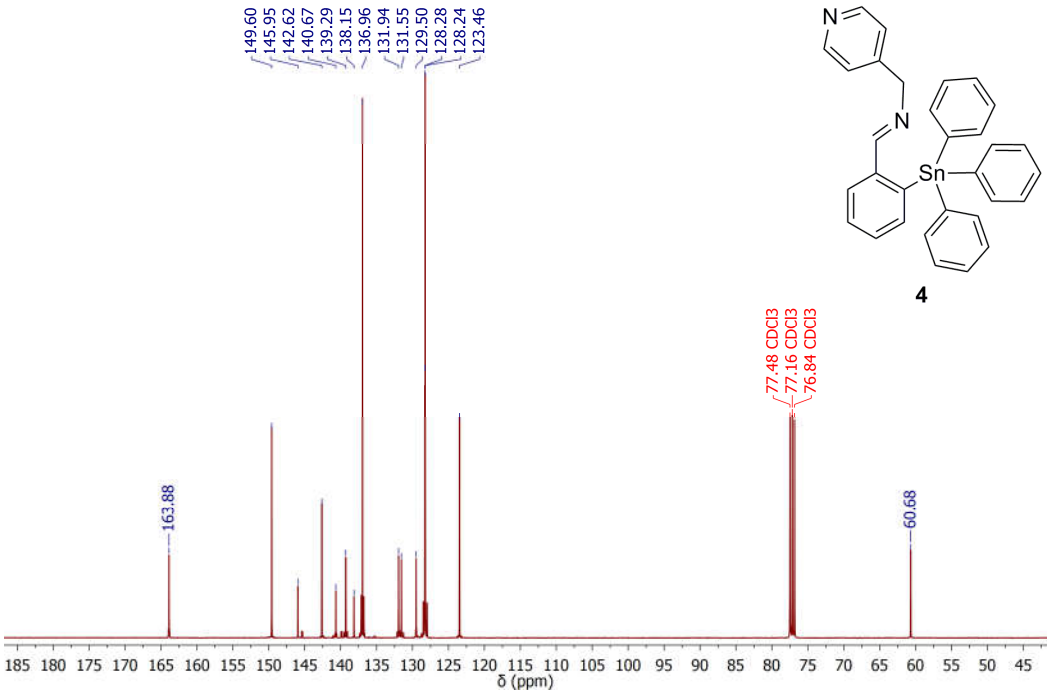

Figure S8. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-(4′-$PyCH_2N{=}CH)C_6H_4$]$SnPh_3$ (**4**).

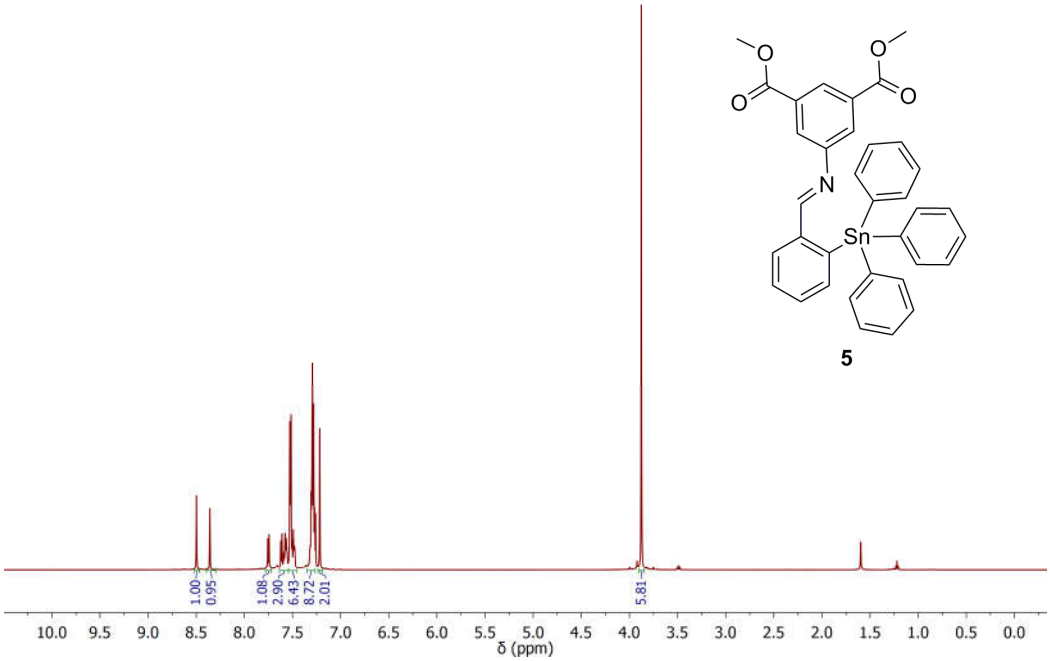

Figure S9. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [2-(3',5'-$(MeOOC)_2$-$C_6H_3N{=}CH)C_6H_4$]$SnPh_3$ (**5**).

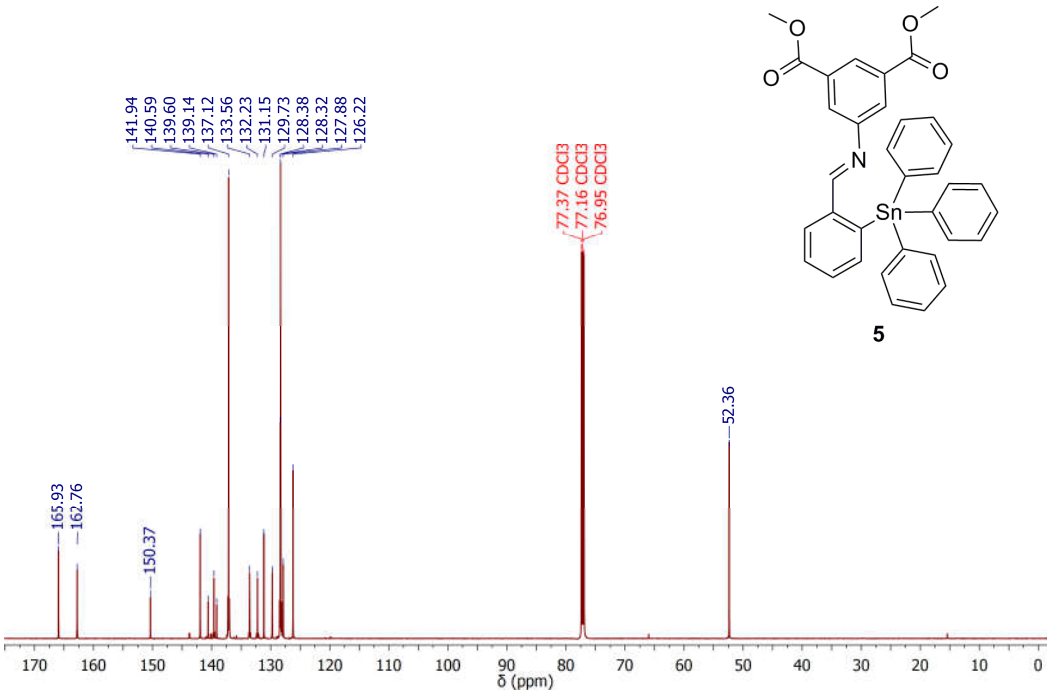

Figure S10. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-(3',5'-$(MeOOC)_2$-$C_6H_3N{=}CH)C_6H_4$]$SnPh_3$ (**5**).

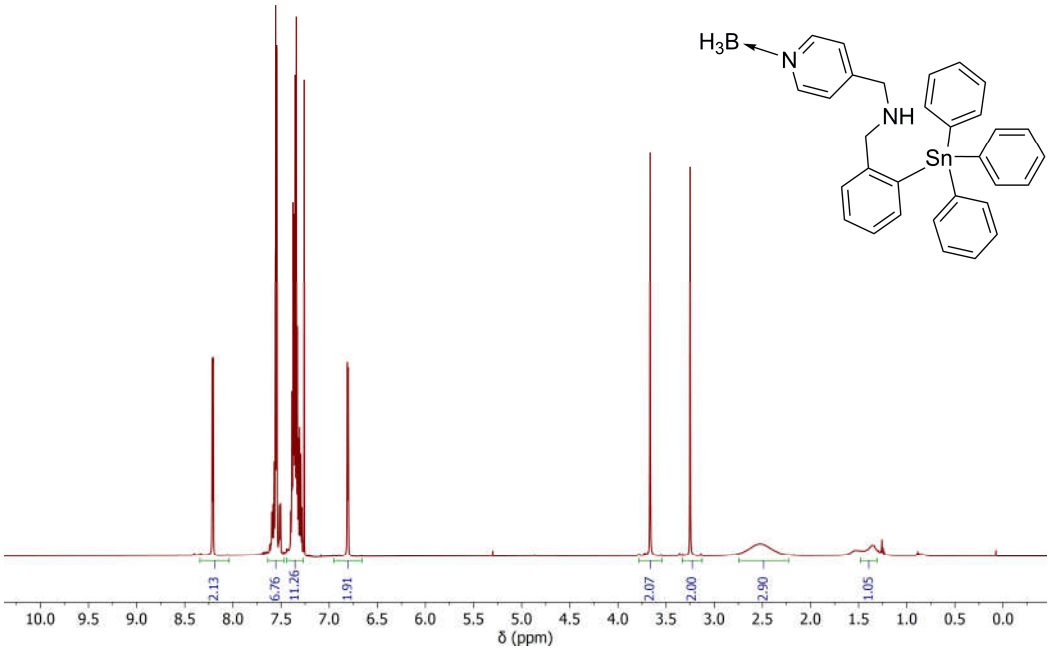

Figure S11. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [2-(4'-$PyCH_2NH$–CH_2)C_6H_4]$SnPh_3 \cdot BH_3$ (**6**).

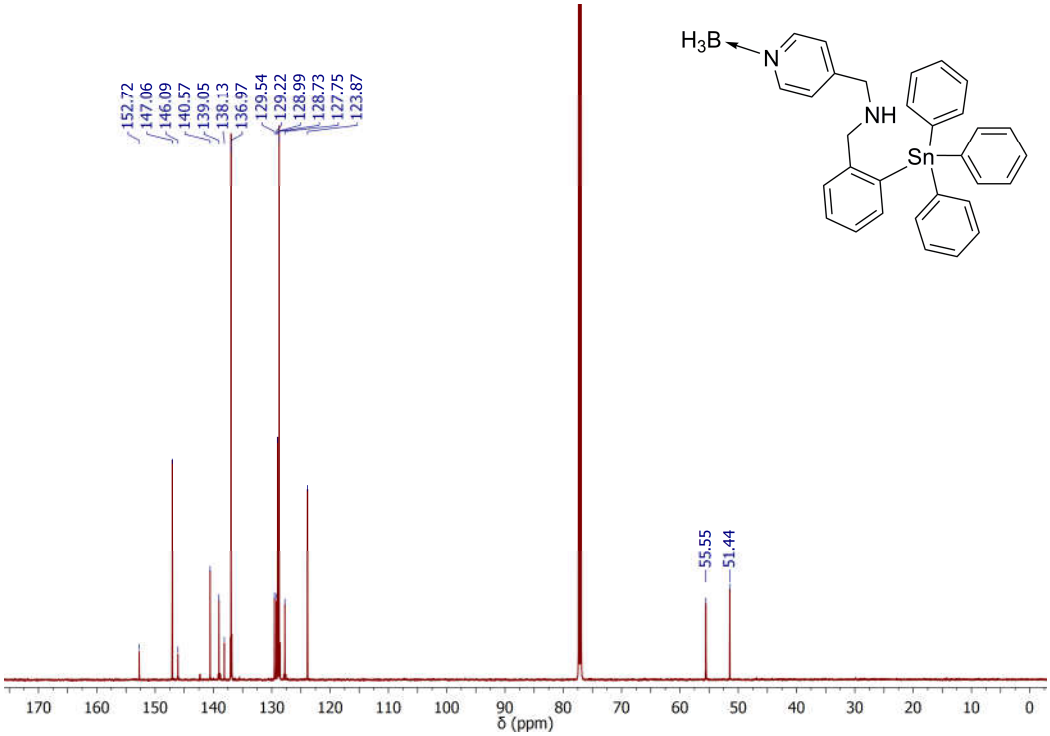

Figure S12. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-(4'-$PyCH_2NH$–CH_2)C_6H_4]$SnPh_3 \cdot BH_3$ (**6**).

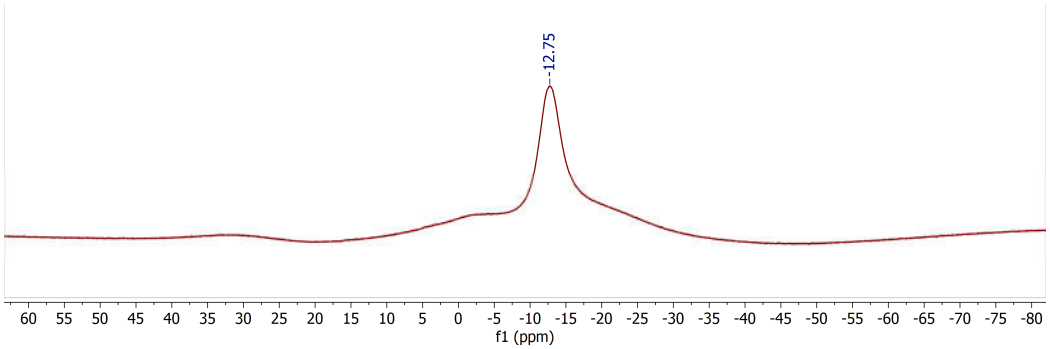

Figure S13. $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 20 °C) spectrum of [2-(4'-$PyCH_2NH$–CH_2)C_6H_4]$SnPh_3 \cdot BH_3$ (**6**).

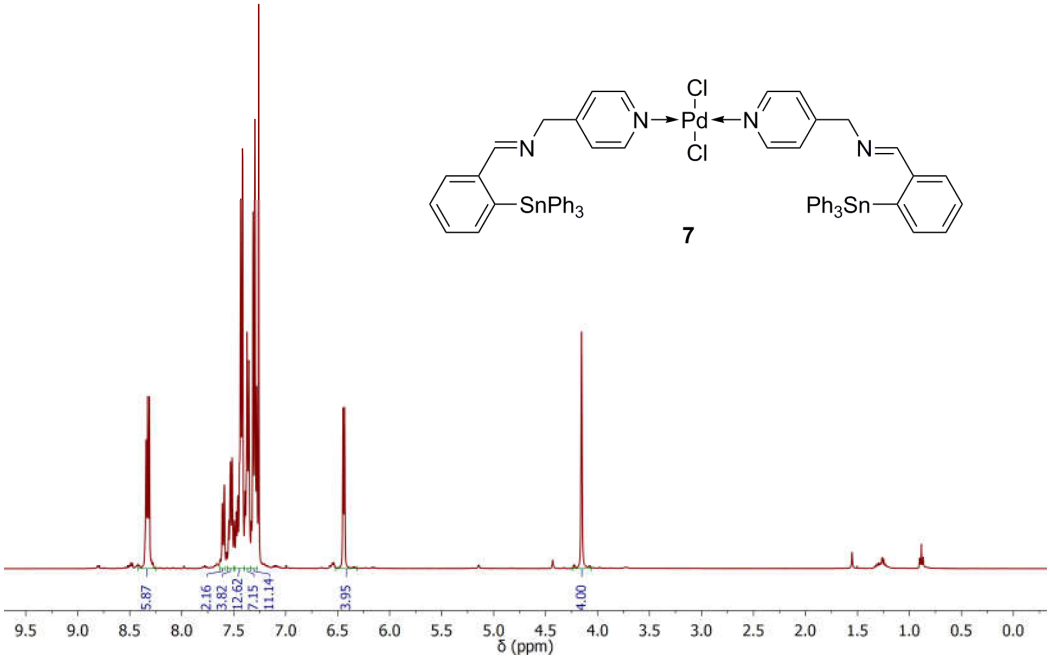

Figure S14. ^{1}H NMR ($CDCl_3$, 20 °C) spectrum of [{2-(4′-$PyCH_2N{=}CH)C_6H_4SnPh_3$}$_2PdCl_2$] (**7**).

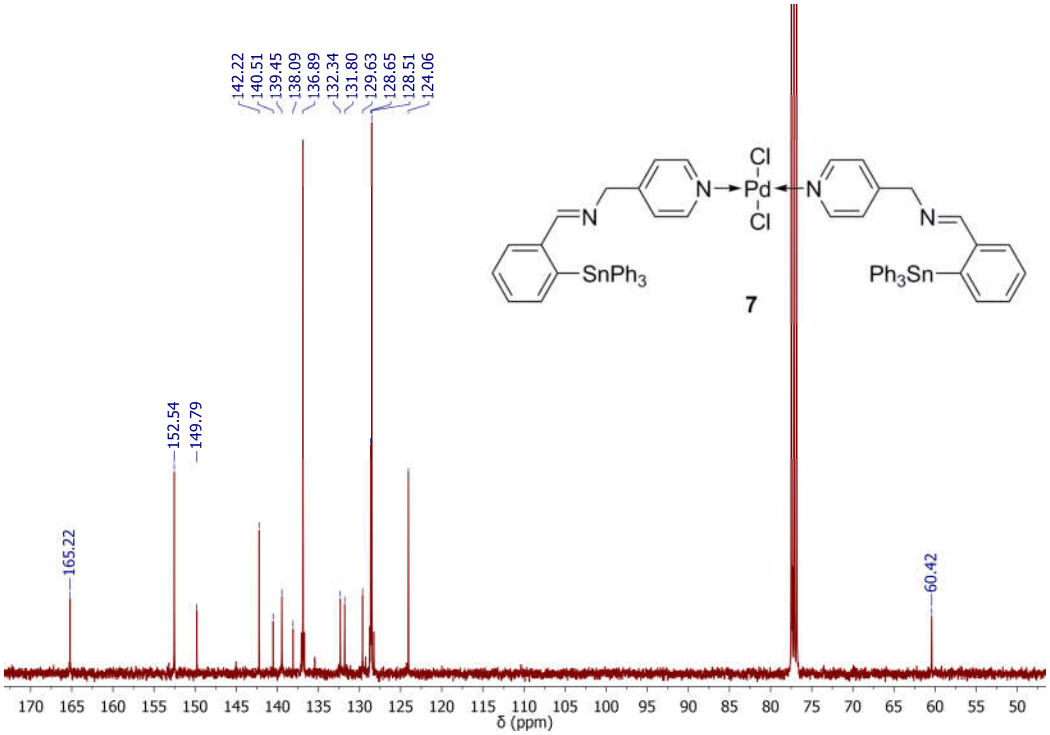

Figure S15. ^{13}C NMR ($CDCl_3$, 20 °C) spectrum of [{2-(4′-$PyCH_2N{=}CH)C_6H_4SnPh_3$}$_2PdCl_2$] (**7**).

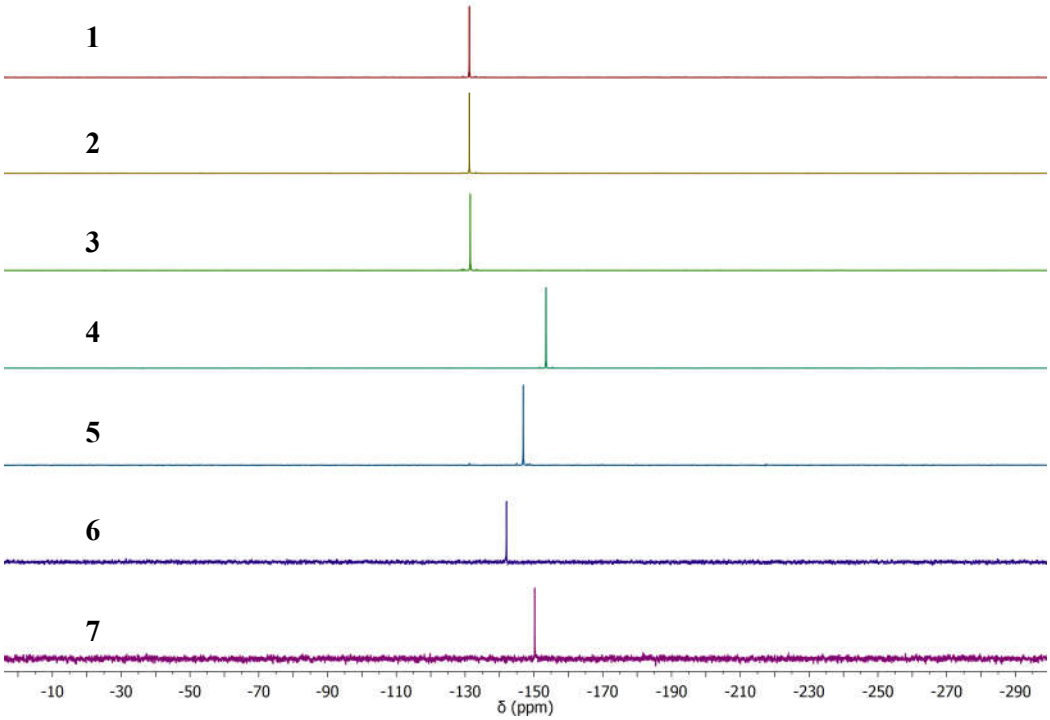

Figure S16. ^{119}Sn NMR ($CDCl_3$, 20 °C) stacked spectra of compounds **1**-**7**.

Table S1. X-ray crystal data and structure refinement for compounds **1**, **2**, **4** and **5**

	1·C$_7$H$_8$	**2**	**4**	**5**
Empirical formula	$C_{61}H_{56}O_4Sn$	$C_{25}H_{20}OSn$	$C_{31}H_{26}N_2Sn$	$C_{35}H_{29}NO_4Sn$
Formula weight	1090.43	455.10	545.23	646.28
Temperature (K)	150(2)	100(2)	297(2)	150(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	$P2_1/n$	$Pna2_1$	P-1	P-1
a (Å)	9.844(2)	16.9881(6)	9.898(16)	10.0636(1)
b (Å)	18.861(4)	15.2425(5)	11.551(2)	11.6223(2)
c (Å)	14.068(3)	7.7375(2)	12.613(3)	14.212(2)
α (º)	90	90	70.529(4)	96.462(2)
β (º)	108.167(4)	90	80.243(4)	97.444(2)
γ (º)	90	90	67.538(3)	113.734(2)
Volume (Å^3)	2481.8(10)	2003.56(11)	1255.0(5)	1483.8(4)
Z	2	4	2	2
D_{calc} (g cm^{-3})	1.459	1.509	1.443	1.447
Absorption coefficient (mm^{-1})	1.055	1.286	1.039	0.900
F(000)	1108	912	552	656
Crystal size (mm)	0.29x0.25x0.22	0.08x0.08x0.11	0.29x0.28x0.26	0.23x0.26x0.33
θ range for data collection (º)	1.867 to 25.099	2.40 to 28.28	1.714 to 24.999	1.469 to 24.999
Reflections collected	24041	28944	11831	14095
Independent reflections	4423	4967	4367	5182
	[R_{int} = 0.0481]	[R_{int} = 0.0333]	[R_{int} = 0.0361]	[R_{int} = 0.0255]
Absorption correction	Multi-Scan[1]	Multi-Scan[1]	Multi-Scan[1]	Multi-Scan[1]
Data / restraints / parameters	4423 / 123 / 335	4967 / 1 / 244	4367 / 0 / 307	5182 / 0 / 372
Goodness-of-fit on F^2	1.095	1.085	1.026	1.088
Final R indices [I>2σ(I)]	R_1 = 0.0385	R_1 = 0.0327	R_1 = 0.0324	R_1 = 0.0252
	wR_2 = 0.0984	wR_2 = 0.0857	wR_2 = 0.0657	wR_2 = 0.0614
R indices (all data)	R_1 = 0.0457	R_1 = 0.0370	R_1 = 0.0402	R_1 = 0.0271
	wR_2 = 0.1031	wR_2 = 0.0885	wR_2 = 0.0690	wR_2 = 0.0623
Largest difference peak and hole (e Å^{-3})	1.421 and −0.477	1.494 and −0.942	0.48 and −0.301	0.55 and −0.21
CCDC No.	2003707	2003708	2003705	2003706

G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

Table S2. X-ray crystal data and structure refinement for compounds **6-8**.

	6	**7**	**8**
Empirical formula	$C_{31}H_{31}BN_2Sn$	$C_{62}H_{52}Cl_2N_4PdSn_2$	$C_{72}H_{54}CuF_{12}N_4O_4Sn$
Formula weight	561.08	1267.75	1568.11
Temperature (K)	297(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*c	$P2_1/n$	$C2/c$
a (Å)	14.6278(17)	8.2544(7)	27.3118(9)
b (Å)	13.3165(15)	17.3898(14)	12.8432(5)
c (Å)	14.9311(17)	18.3621(16)	20.0980(7)
α (º)	90	90	90
β (º)	111.563(2)	95.750(3)	111.2470(1)
γ (º)	90	90	90
Volume (Å^3)	2704.9(5)	2622.5(4)	6570.6(4)
Z	4	2	4
D_{calc} (g cm^{-3})	1.378	1.605	1.585
Absorption coefficient (mm^{-1})	0.966	1.431	1.162
F(000)	1144	1264	3132
Crystal size (mm)	0.20x0.25x0.29	0.05x0.05x0.07	0.06x0.09x0.14
θ range for data collection (º)	2.140 to 25.099	2.23 to 29.48	2.18 to 28.30
Reflections collected	12809	75729	111572
Independent reflections	4780	7288	8170
	[R_{int} = 0.0477]	[R_{int} = 0.0651]	[R_{int} = 0.0366]
Absorption correction	Multi-Scan[1]	Multi-Scan[1]	Multi-Scan[1]
Data / restraints / parameters	4780 / 9 / 332	7288 / 2510 / 651	8170 / 360 / 487
Goodness-of-fit on F^2	1.036	1.006	1.030
Final R indices [I>2σ(I)]	R_1 = 0.0389	R_1 = 0.0477	R_1 = 0.0298
	wR_2 = 0.0904	wR_2 = 0.1071	wR_2 = 0.0702
R indices (all data)	R_1 = 0.0416	R_1 = 0.0951	R_1 = 0.0346
	wR_2 = 0.0919	wR_2 = 0.1335	wR_2 = 0.0735
Largest difference peak and hole (e Å^{-3})	1.068 and −0.317	0.566 and −0.758	2.241 and −1.327
CCDC No.	2003704	2003709	2003710

[1]G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

- the crystal contains a 1:1 mixture of $pS_{O(1)}$-$S_{C(7)}$-**1** and $pR_{O(1)}$-$R_{C(7)}$-**1**

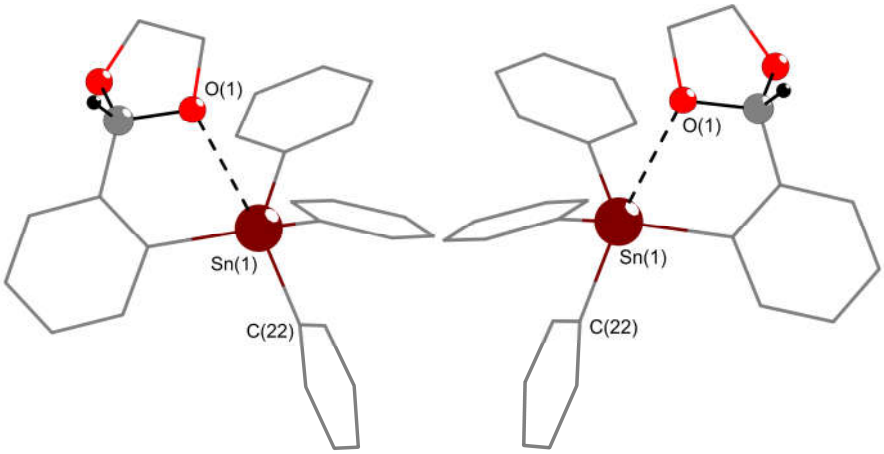

Figure S17. Molecular structure of $pS_{O(1)}$-$S_{C(7)}$-**1** isomer (*left*) and $pR_{O(1)}$-$R_{C(7)}$-**1** isomer (*right*) in the crystal of **1** (only methyne hydrogen is shown).

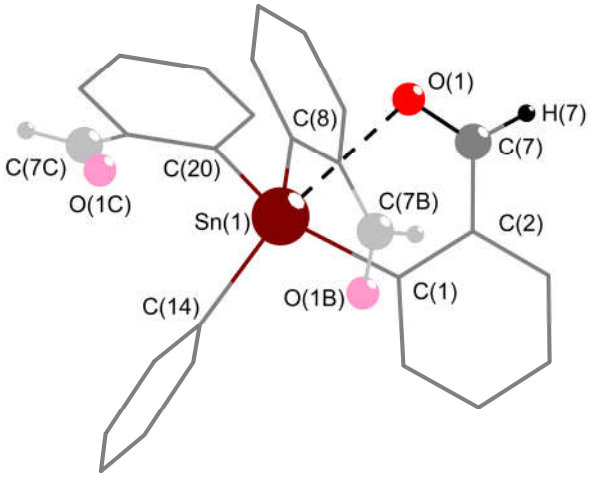

Figure S18. Molecular structure of **3** showing the carbonyl fragment located on three different phenyl rings with a site having preponderant occupancy [0.69 C(7)] over the others [0.18 C(7B) and 0.13 C(7C)] (only carbonyl hydrogen atoms are shown).

- the crystal contains a 1:1 mixture of *pS*$_{N(1)}$-*S*$_{N(1)}$-**6** and *pR*$_{N(1)}$-*R*$_{N(1)}$-**6**

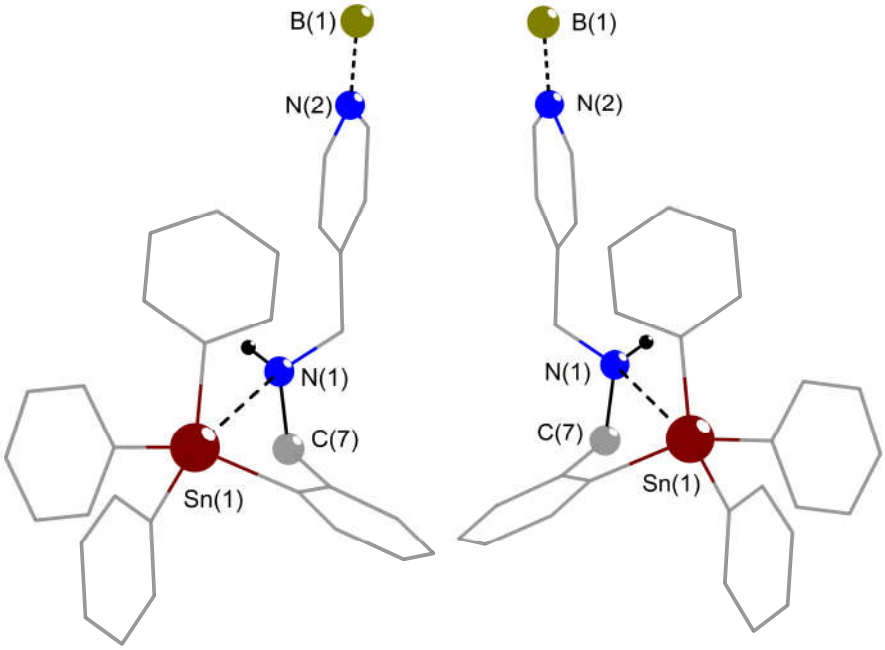

Figure S19. Molecular structure of *pS*$_{N(1)}$-*S*$_{N(1)}$-**6** isomer (*left*) and *pR*$_{N(1)}$-*R*$_{N(1)}$-**6** isomer (*right*) in the crystal of **6** (only amine hydrogen is shown).

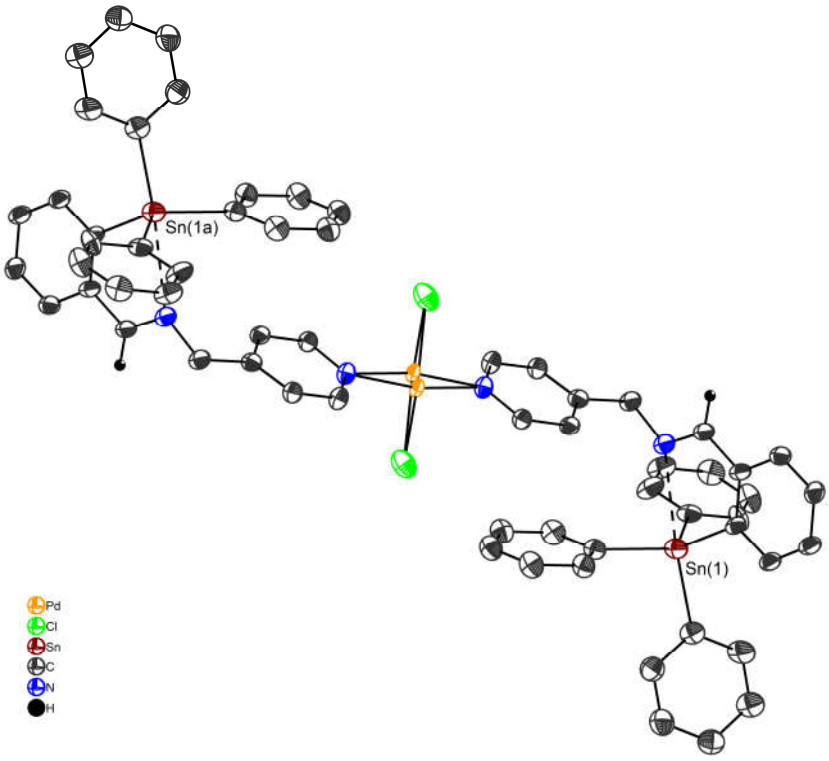

Figure S20. ORTEP representation at 30% probability of **7**, displaying only the major occupancy site of the molecule (68%) (only imine hydrogen atoms are shown). Selected interatomic distances (Å) and bond angles (°): Sn(1)–C distances (Å): 2.192(10), 2.194(11), 2.157(7), 2.154(8), Sn(1)···N distance 2.737(12) (Å), axial angle N–Sn(1)–C = 174.4(4)°.

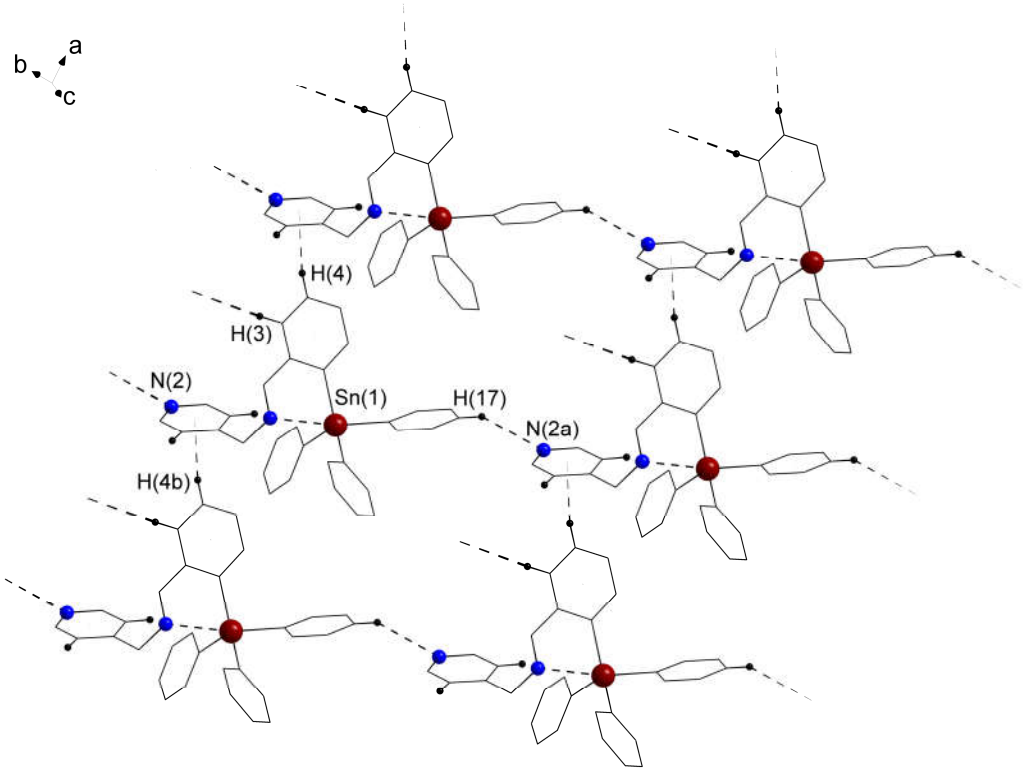

Figure S21. Packing of the molecules in the crystal of **4**, showing the interconnected chains forming a layer (only hydrogen atoms involved in intermolecular contacts are shown). [Symmetry equivalents atom (*1+x, –1+y, 1+z*), (*–1+x, y, z*) are given by "a", "b", respectively].

- intermolecular distance H(17)···N(2a) 2.66 Å $\sum r_{vdW}$(N,H) 2.75 Å
  C(4b)–H(4b)···$Ph_{centroid}${Py} 2.89 Å γ = 12.2°l

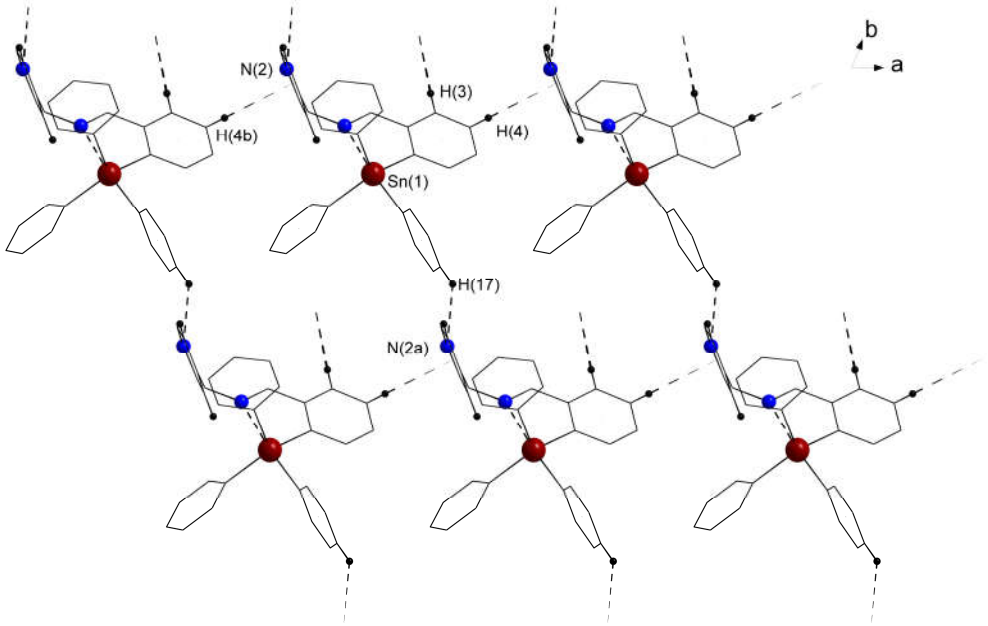

Figure S22. Viewing along c axis of the packing of molecules in the crystal of **4**, showing the interconnected chains forming a layer (only hydrogen atoms involved in intermolecular contacts are shown). [Symmetry equivalents atom (*1+x, –1+y, 1+z*), (*–1+x, y, z*) are given by "a", "b", respectively].

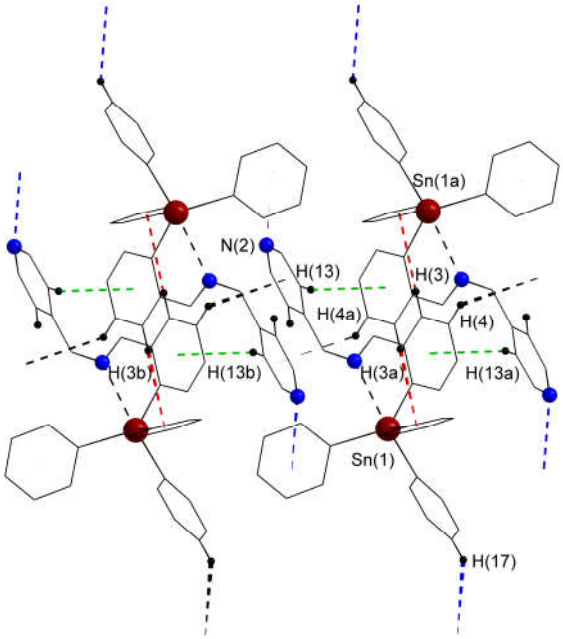

Figure S23. Packing of the molecules in the crystal **4**, showing the interconnected layers forming 3D supramolecular architecture (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, 1–y, –z*), (*–x, 1–y, –z*) are given by "a" and "b" respectively].

C(3)–H(3)···$Ph_{centroid}${C(26)–C(31)}	2.85 Å	γ = 6.4°
C(13b)–H(13b)···$Ph_{centroid}${C(1)–C(6)}	2.95 Å	γ = 18.2°

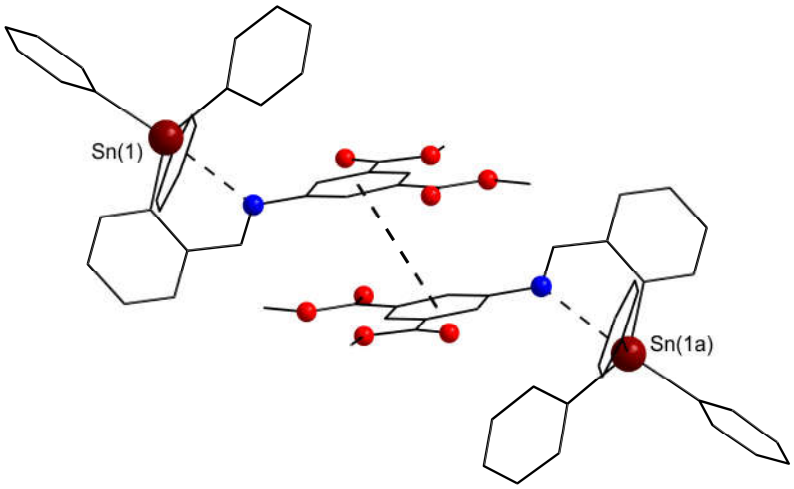

Figure S24. Offset π···π stacking in the crystal of **5** (hydrogen atoms are omitted for clarity) [symmetry equivalent (*2–x*, *1–y*, *2–z*) is corresponding to "a"].

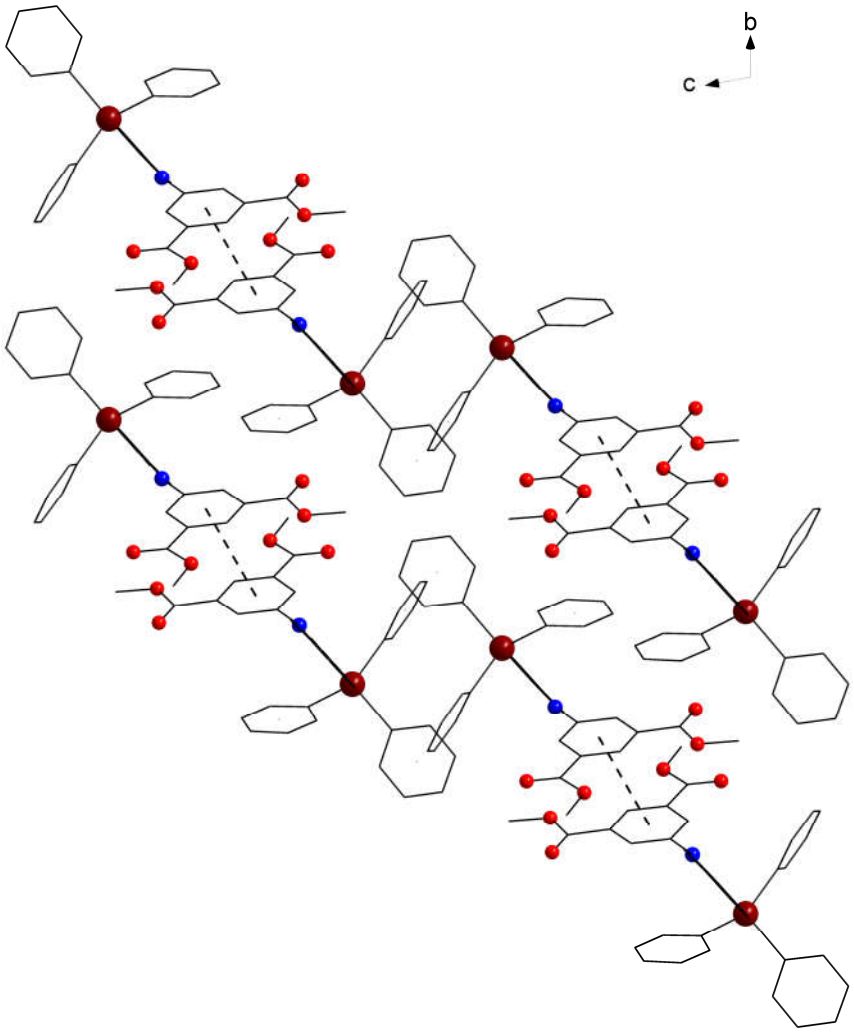

Figure S25. View along *a* axis of the crystal packing of **5** (hydrogen atoms are omitted for clarity).

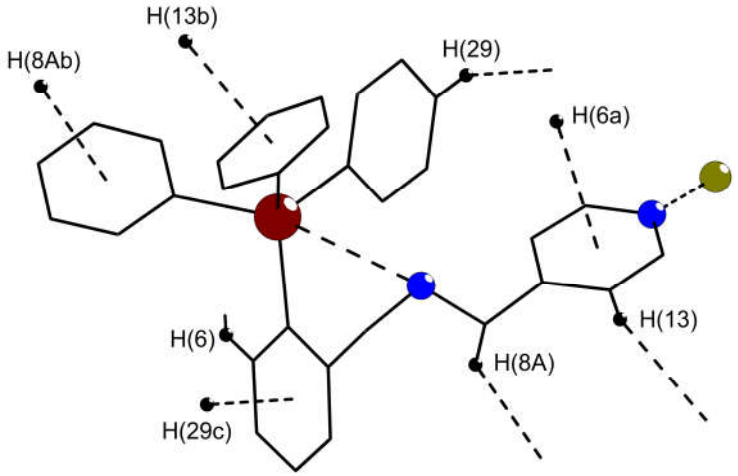

Figure S26. CH···π interactions in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*0.5+x*, *0.5–y*, *0.5+z*), (*–0.5+x*, *0.5+y*, *z*) and (*–0.5+x*, *–0.5+y*, *z*) are given by "a", "b" and "c", respectively].

Intermolecular CH···π interactions		
C(6)–H(6)···$Ph_{centroid}${Py}	3.08 Å	γ = 9.0°
C(8)–H(8A)···$Ph_{centroid}${C(14)–C(19)}	3.06 Å	γ = 18.9°
C(13)–H(13)···$Ph_{centroid}${C(20)–C(25)}	2.79 Å	γ = 5.3°
C(29)–H(29)···$Ph_{centroid}${C(1)–C(6)}	2.83 Å	γ = 18.3°

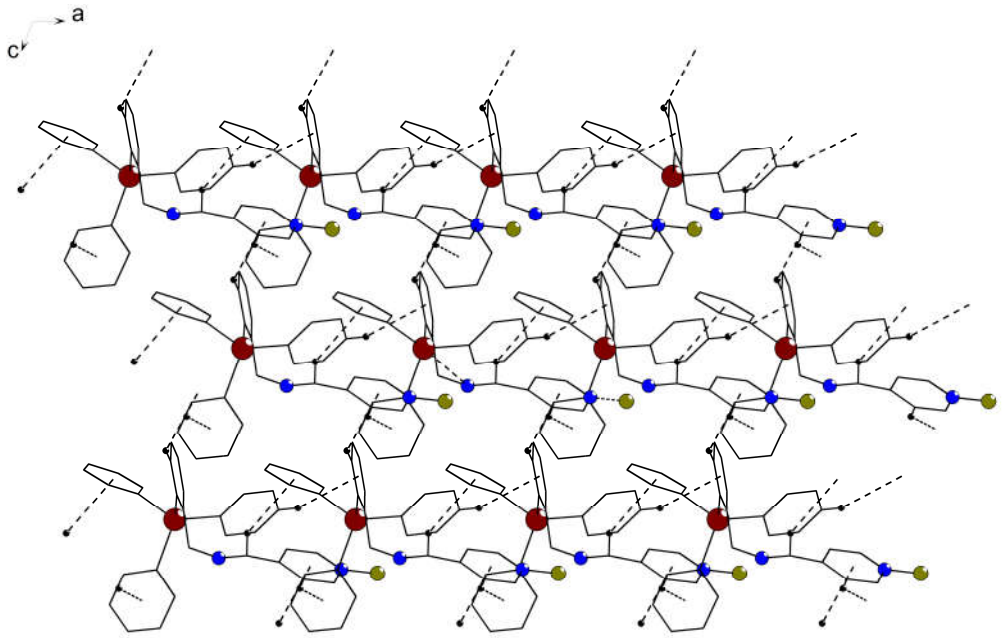

Figure S27. View along *b* axis of the 3D supramolecular architecture in the crystal packing of **6** (only hydrogen atoms involved in intermolecular contacts are shown).

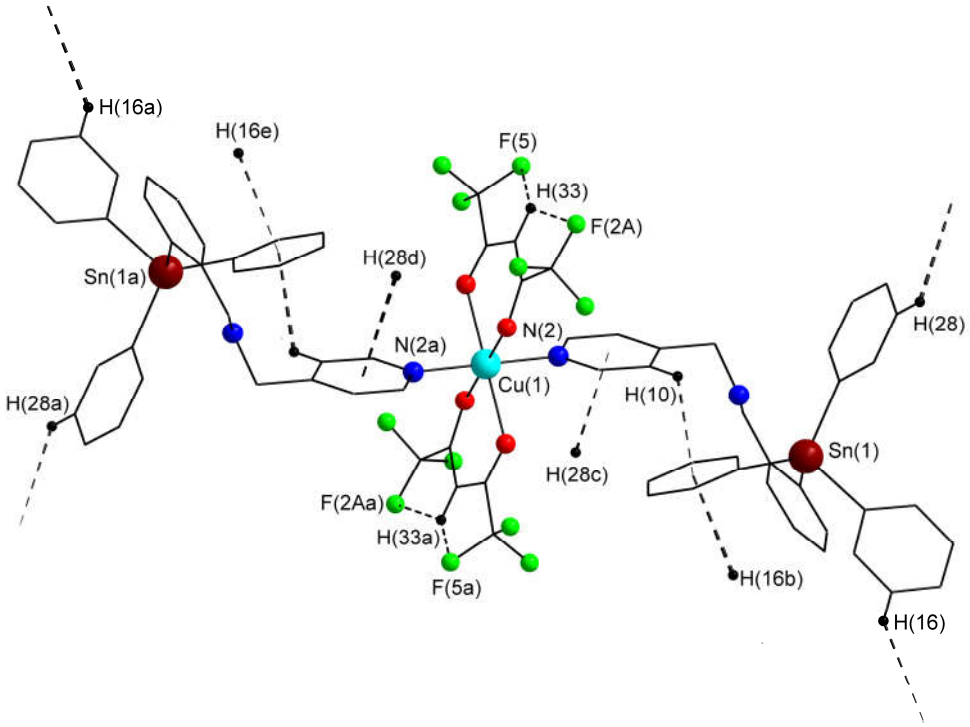

Figure S28. CH···π interactions in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x*, *1–y*, *1–z*), (*1.5–x*, *0.5–y*, *2–z*), (*1.5–x*, *–0.5+y*, *1.5–z*), (*–0.5+x*, *1.5–y*, *–0.5+z*) and (*–0.5+x*, *0.5+y*, *–1+z*) are given by "a", "b", "c", "d" and "e", respectively; only the major occupancy site of the disordered CF_3 fragment is depicted].

Intramolecular H···F interactions

F(5)–(H33)	2.50 Å	$\sum r_{cov}$(F,H) = 0.88 Å
F(2A)–(H33)	2.29 Å	$\sum r_{vdW}$(F,H) = 2.55 Å

Intramolecular CH···π interactions

C(10)–H(10)···$Ph_{centroid}${C(20)–C(25)}	2.77 Å	γ = 10.4°

Intermolecular CH···π interactions

C(16)–H(16)···$Ph_{centroid}${C(20)–C(25)}	2.88 Å	γ = 5.3°
C(28)–H(28)···$Ph_{centroid}${Py}	2.96 Å	γ = 14.1°

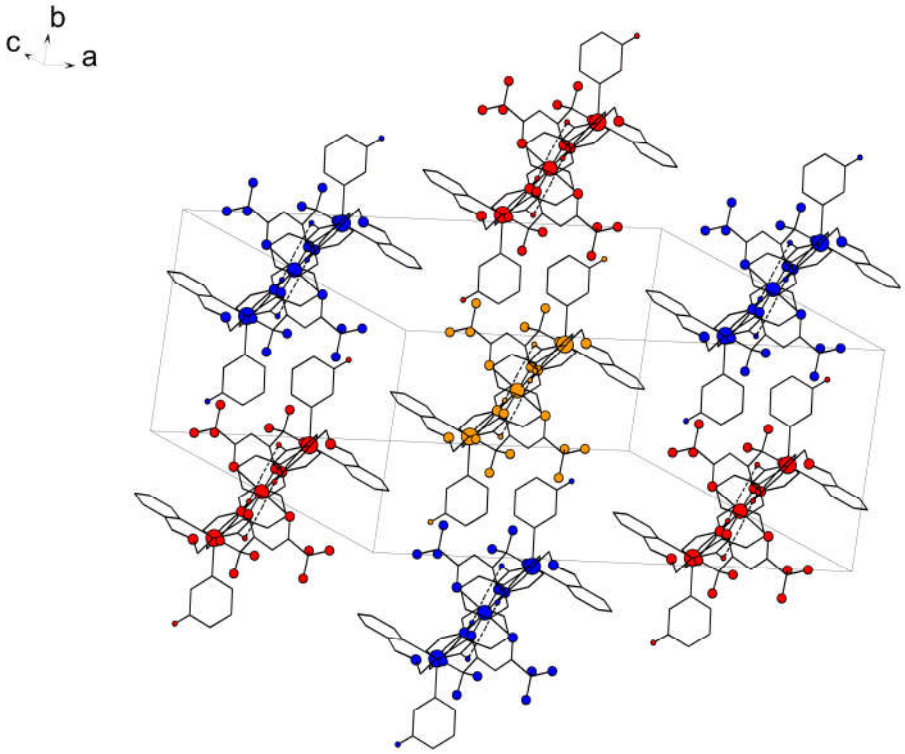

Figure S29. View of the parallel chain-like polymers in the crystal of **8** generated by the CH···π interaction C(16)–H(16)···$Ph_{centroid}${C(20)–C(25)} (only hydrogen atoms involved in intermolecular contacts are shown).

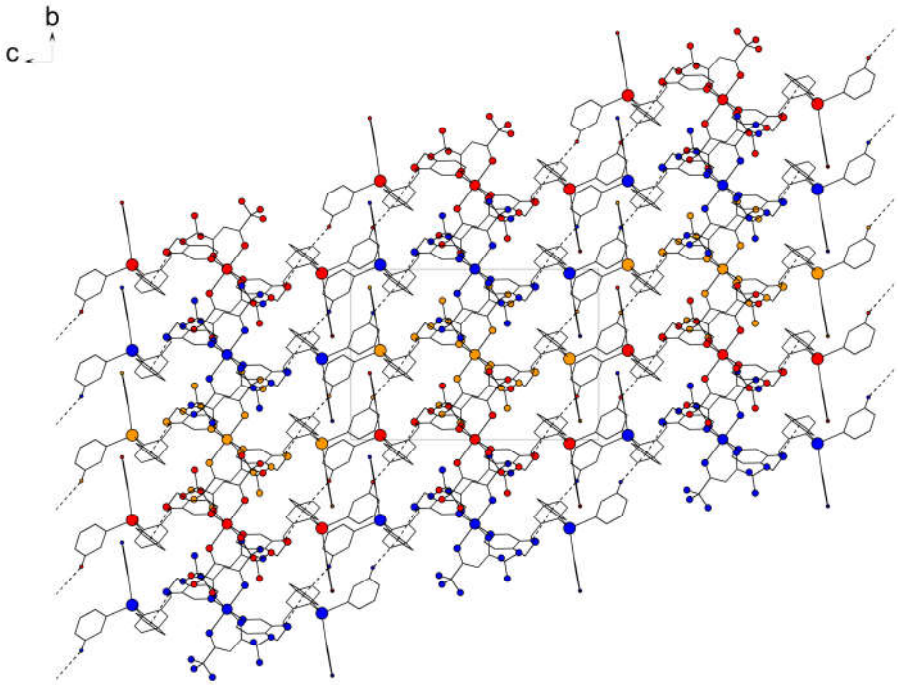

Figure S30. View along *a* axis of the parallel chain-like polymers in the crystal of **8** generated by the CH···π interaction C(16)–H(16)···$Ph_{centroid}${C(20)–C(25)} (only hydrogen atoms involved in intermolecular contacts are shown).

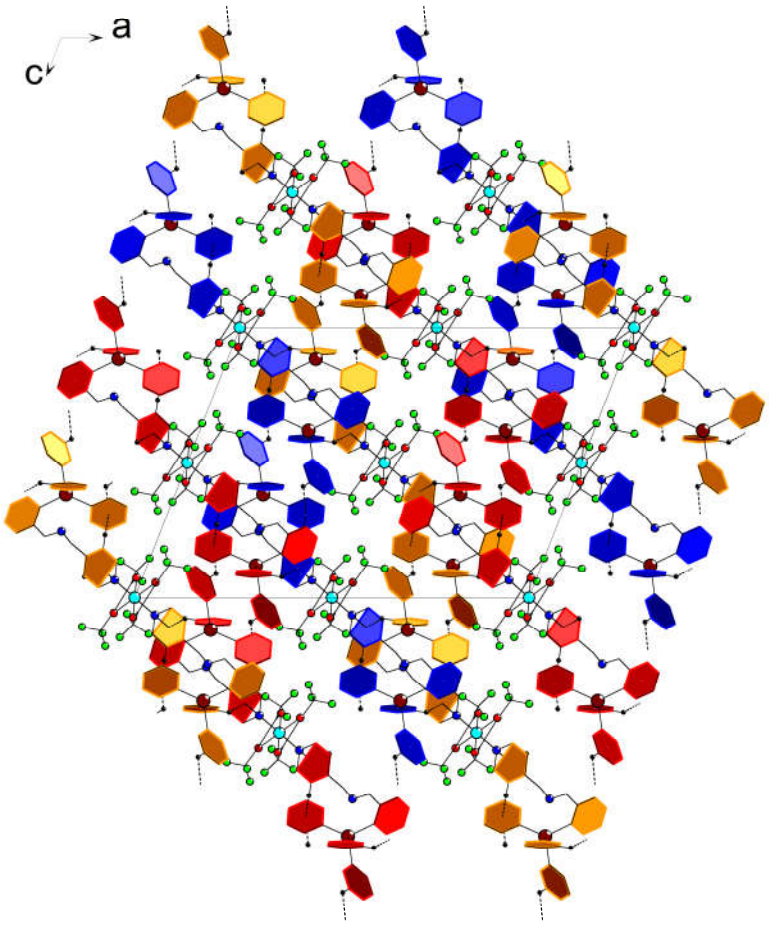

Figure S31. View along *b* axis of the 3D supramolecular architecture in the crystal of **8**. Interconnected chain-like polymers are highlighted in different colours (only hydrogen atoms involved in intermolecular contacts are shown).