Supporting Information

Synthesis and Characterization of Hexa-coordinated Sn(IV) complexes of *Meso*-Aryl Dipyrrins

Ritambhara Sharma,[a] Avijit Ghosh,[a] Benedikt Wolfram,[b] Martin Bröring[b] and Mangalampalli Ravikanth[*a]

[a] Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India

[b] Institute for inorganic and analytical chemistry, Technische Universitat Braunschweig, 38106, Germany

Content

Experimental Section

General synthesis of Sn(IV)(dpm)$_2$Cl$_2$ complexes:

A sample of *meso*-(aryl) dipyrromethane (100 mg) was taken in 15 mL tetrahydrofuran and DDQ (1.2 equivalent) was added to the solution. The reaction mixture was stirred for 45 min. The solvent was removed on rotary evaporator and the crude product was dissolved in 15 mL pyridine. To the pyridine solution, $SnCl_2.2H_2O$ (3 equivalents) was added and the reaction mixture was refluxed for 4 h. The progress of the reaction was monitored by TLC analysis and absorption spectroscopy. After completion of the reaction, the solvent was removed under vacuum on a rotary evaporator. The crude product was dissolved in CH_2Cl_2 and washed thoroughly with aqueous $NaHCO_3$. The organic layer was collected and washed with water, dried over Na_2SO_4, filtered, and evaporated under vacuum. The recrystalization of crude product from CH_2Cl_2-petrolium ether solvent mixture afforded pure compounds as orange solids.

Bis(5(phenyl)dipyrrinato)dichlorotin(IV) (1a)

Yield 55%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 8.8 (pseudo t, 2H, *J*(H,H) = 1.56 Hz), 7.49 (br, 4H, Ar) 7.39 (br, 4H, Ar), 7.20 (br, 2H, Ar), 6.81 (dd, 2H, *J*(H,H) = 4.20, 1.56 Hz), 6.74 (pseudo t, 2H, *J*(H,H) = 1.29 Hz), 6.63 (dd, 2H, *J*(H,H) = 4.20, 1.56 Hz), 6.60 (dd, 2H, *J*(H,H) = 4.28, 1.29 Hz), 6.28 (dd, 2H, *J*(H,H) = 4.28, 1.29 Hz). ^{13}C NMR ($CDCl_3$, 100MHz), δ, ppm: 55.59, 113.06, 116.86, 117.46, 129.63, 132.26, 135.62, 139.63, 147.93, 148.71, 149.95, 160.73. HR-MS calcd. for ($C_{30}H_{22}Cl_2N_4Sn$) [(M-Cl)$^+$]: *m/z* 593.0585 and found *m/z* 593.0555 [(M-Cl)$^+$]. UV-vis ($CHCl_3$), λ_{max} in nm (ε_o): 462 (4.90), 497 (4.76), 342 (4.32).

Bis(5(*p*-tolyl)dipyrrinato)dichlorotin(IV) (2a)

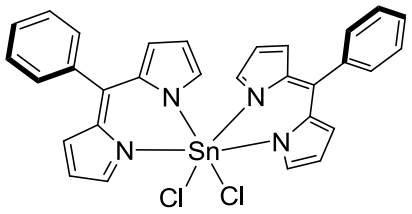
Yield 52%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ(ppm): 8.8 (pseudo t, 2H, *J*(H,H) = 1.34 Hz), 7.37 (br, 2H, Ar) 7.18-7.27 (br, 4H, Ar), 7.12 (br, 2H, Ar), 6.82 (dd, 2H, *J*(H,H) = 4.34, 1.34 Hz), 6.79 (s, 2H, py), 6.63 (m, 2H, py), 6.60 (m, 2H, py), 6.26 (dd, 2H, *J*(H,H) = 4.32, 2.64 Hz), 2.45(S, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100MHz): 150.07, 148.88, 139.54, 139.01, 135.81, 135.73, 135.62, 134.37, 130.61, 128.38, 128.13, 117.50, 116.87, 21.53. HR-MS calcd. for ($C_{32}H_{26}Cl_2N_4Sn$) [(M-Cl)$^+$]: *m/z* 622.0975 and found *m/z* 622.0946 [(M-Cl)$^+$]. UV-vis ($CHCl_3$), $\lambda_{max,}$ nm (ε_o): 461 (4.91), 497 (4.75), 336 (4.37).

Bis(5(4-methoxyphenyl)dipyrrinato)dichlorotin(IV) (3a)

yield 54%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 8.8 (pseudo t, 2H, *J*(H,H) = 1.39 Hz), 6.94 (br, 3H, Ar), 7.1(br, 2H, Ar), 7.4(br, 3H, Ar), 6.87(dd, 2H, *J*(H,H) = 4.20, 1.39 Hz), 6.76 (pseudo t, 2H, *J*(H,H) = 1.92 Hz), 6.66 (dd, 2H, *J*(H,H) = 4.24, 1.39 Hz), 6.63 (dd, 2H, *J*(H,H) = 4.20, 1.92 Hz), 6.27 (dd, 2H, *J*(H,H) = 4.20, 1.92 Hz) 3.91 (s, 6H, OCH3). ^{13}C NMR ($CDCl_3$, 100MHz): 55.59, 113.06, 116.86, 117.46, 129.63, 132.26, 135.62, 139.63, 147.93, 148.71, 149.95, 160.73. HR-MS calcd. for ($C_{32}H_{26}Cl_2N_4O_2Sn$) [(M-Cl)$^+$]: *m/z* 653.0782 and found *m/z* 653.0766 [(M-Cl)$^+$]. UV-vis ($CHCl_3$), $\lambda_{max,}$ nm (ε_o): 462 (4.87), 497 (4.71), 374 (4.29).

Bis(5(4-bromophenyl)dipyrrinato)dichlorotin(IV) (4a)

Yield 49% . ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 8.8 (pseudo t, 2H, *J*(H,H) = 1.58 Hz), 7.62 (d, 2H, *J*(H,H) = 8.1), 7.55 (d, 2H, *J*(H,H) = 8.0), 7.35 (d, 2H, *J* = 8.0), 7.1 (d, 2H, *J* = 8.0), 6.8 (dd, 2H, *J*(H,H) = 4.24, 1.58 Hz), 6.78 (s, 2H, Py), 6.65 (dd, 2H, *J*(H,H) = 4.20, 1.58), 6.57 (dd, 2H, *J*(H,H) = 4.32, 1.33 Hz), 6.3 (dd, 2H, *J*(H,H) = 4.32, 1.33 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): 150.86, 149.33, 146.21, 139.16, 138.60, 136.02, 135.58, 135.52, 132.11, 131.97, 131.12, 130.87, 123.95, 117.91, 117.46. ES-MS calcd. for ($C_{30}H_{20}Cl_2N_4Br_2SnCl$) 785.93 and found 750.61 $(M\text{-}Cl)^+$. UV-vis ($CHCl_3$), $\lambda_{max,}$ nm (ε_o): 463 (4.90), 499 (4.75), 342 (4.36).



Compound 1a

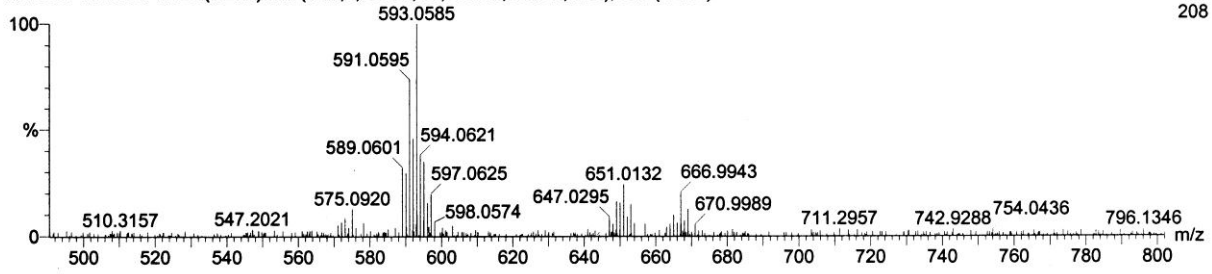
M.Wt. calculated = 628.02; Observed $[M-Cl]^+$: 593.0585

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

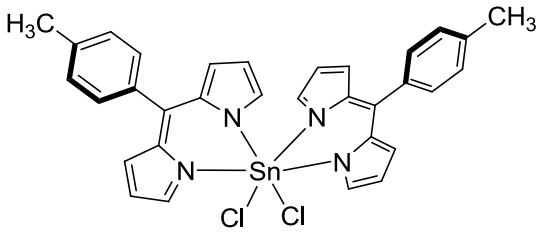
Monoisotopic Mass, Odd and Even Electron Ions
15 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Waters(Micromass) : Q-Tof micro(YA-105) Dept. Of Chemistry - I.I.T.(B) 12-Oct-201218:02:48
C30H22Cl2N4Sn
MRK-RS-PHSNDPM 22 (0.219) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Cm (12:37) TOF MS ES+
208



Minimum:				-1.5		
Maximum:		50.0	10.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
593.0585	593.0555	3.0	5.0	22.5	1	C30 H22 N4 Cl Sn

Figure S1. HR-MS mass spectrum of compound **1a**.



Compound 2a

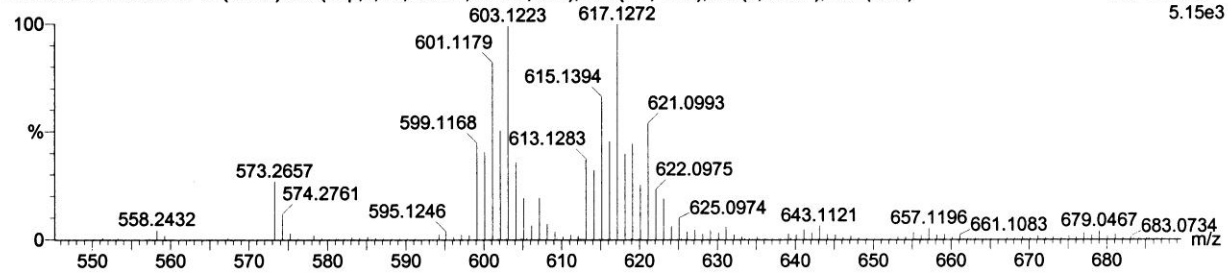
M. Wt. calculated = 656.06; Observed $[M-Cl]^+$: 622.0975

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

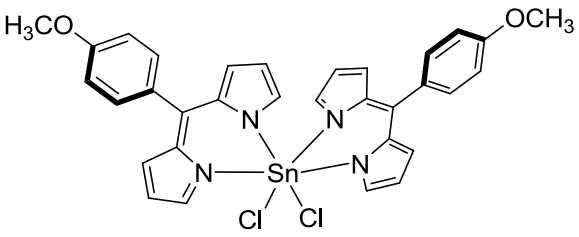
Monoisotopic Mass, Odd and Even Electron Ions
31 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Waters(Micromass) : Q-Tof micro(YA-105) Dept. Of Chemistry - I.I.T.(B) 28-Sep-201218:42:38
C32H26Cl2N4Sn
MRK-RS-TOLSNDPM 12 (0.120) AM (Top,5, Ht,5000.0,556.28,1.00); Sm (Md, 4.00); Sb (5,40.00); Cm (5:35) TOF MS ES+
5.15e3



Minimum:				-1.5		
Maximum:		50.0	50.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
622.0975	622.0946	2.9	4.7	22.0	1	C32 H27 N4 Cl Sn

Figure S2. HR-MS mass spectrum of compound **2a**.



Compound 3a

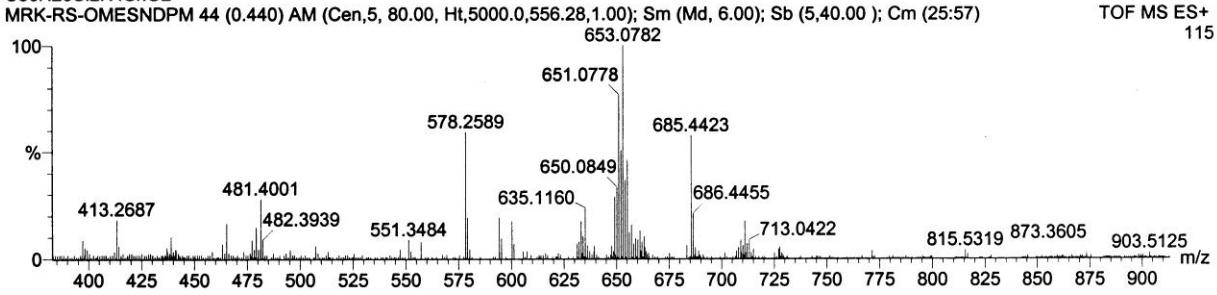
M. Wt. calculated = 688.05; Observed $[M-Cl]^+$: 653.0782

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

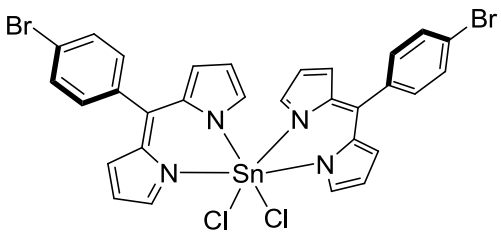
Monoisotopic Mass, Odd and Even Electron Ions
1422 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Waters(Micromass) : Q-Tof micro(YA-105) Dept. Of Chemistry - I.I.T.(B) 12-Oct-201217:50:53
C36H26Cl2N4SnO2
MRK-RS-OMESNDPM 44 (0.440) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sm (Md, 6.00); Sb (5,40.00); Cm (25:57) TOF MS ES+
115



Minimum:				-1.5		
Maximum:		50.0	5.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
653.0782	653.0766	1.6	2.5	22.5	1	C32 H26 N4 O2 Cl Sn

Figure S3. HR-MS mass spectrum of compound **3a**.



Compound 4a

M. Wt. calculated = 785.93; Observed $[M-Cl]^+$: 750.61

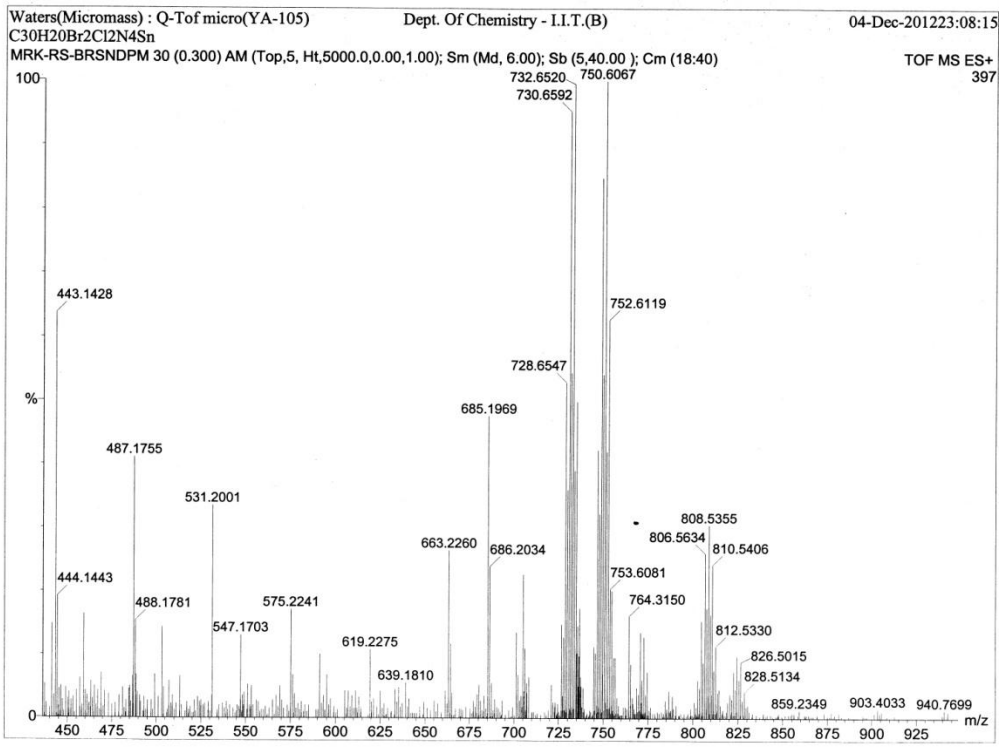


Figure S4. ES-MS mass spectrum of compound **4a**.

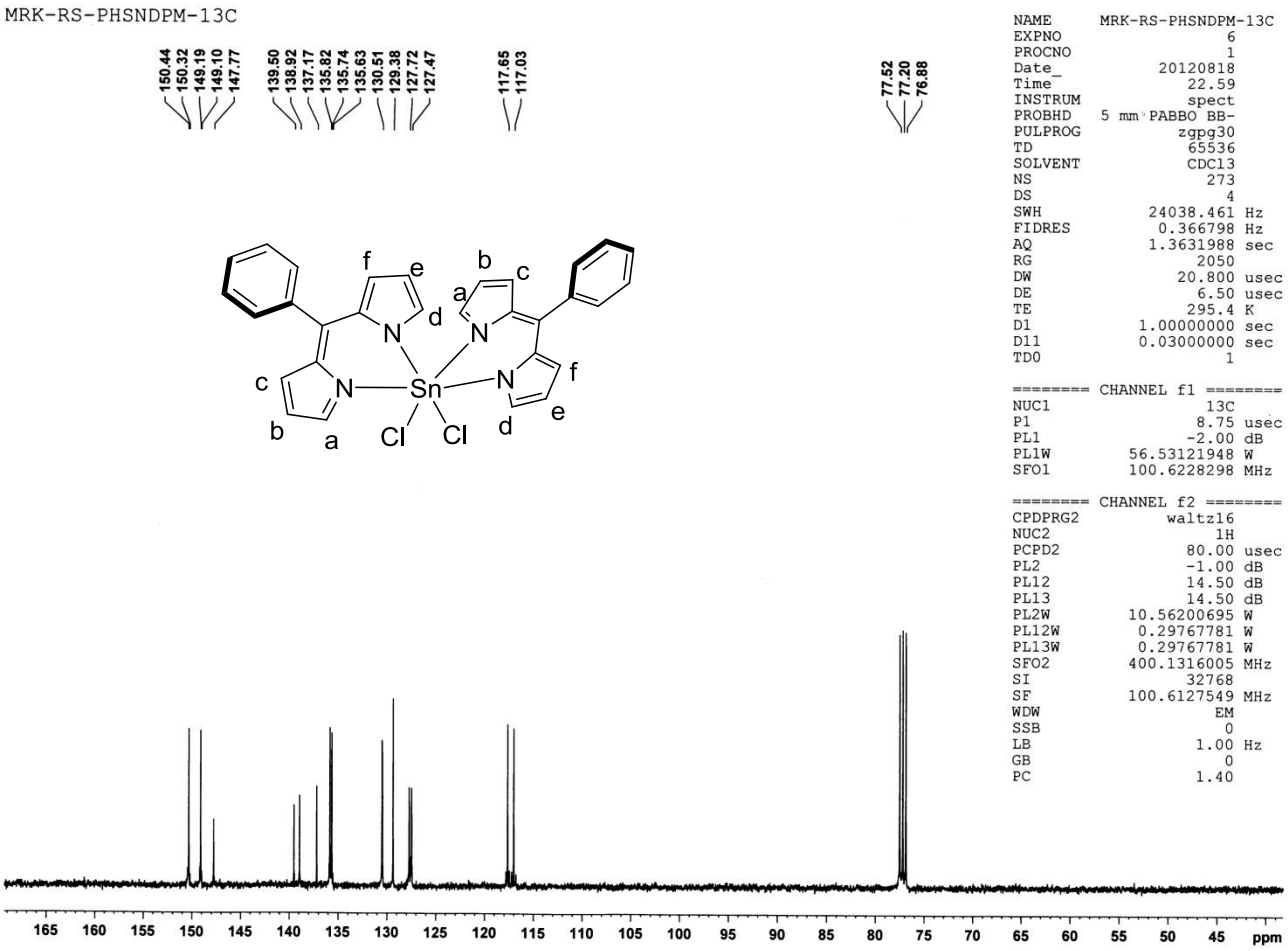


Figure S5. ^{13}C NMR spectrum of compound **1a** recorded in $CDCl_3$ at room temperature.

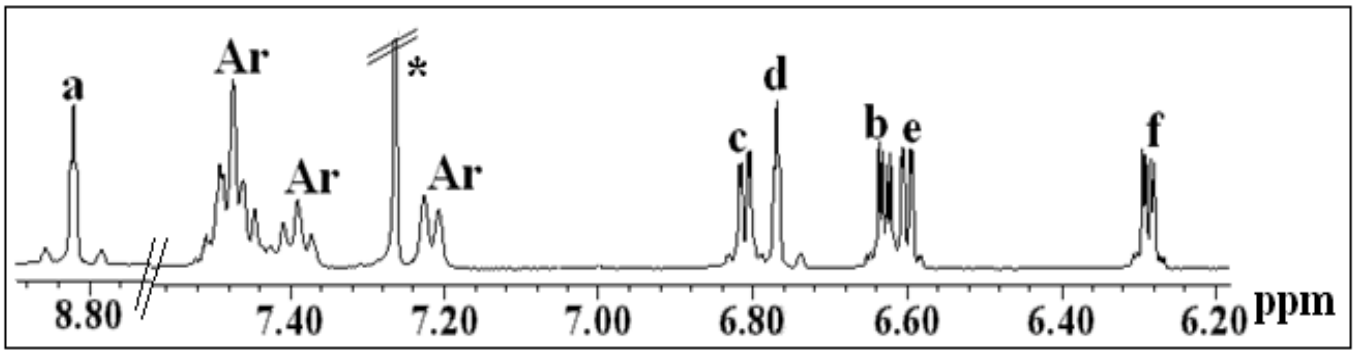


Figure S6. Partial ^{1}H NMR spectrum of compound **1a** recorded in $CDCl_3$ at room temperature.

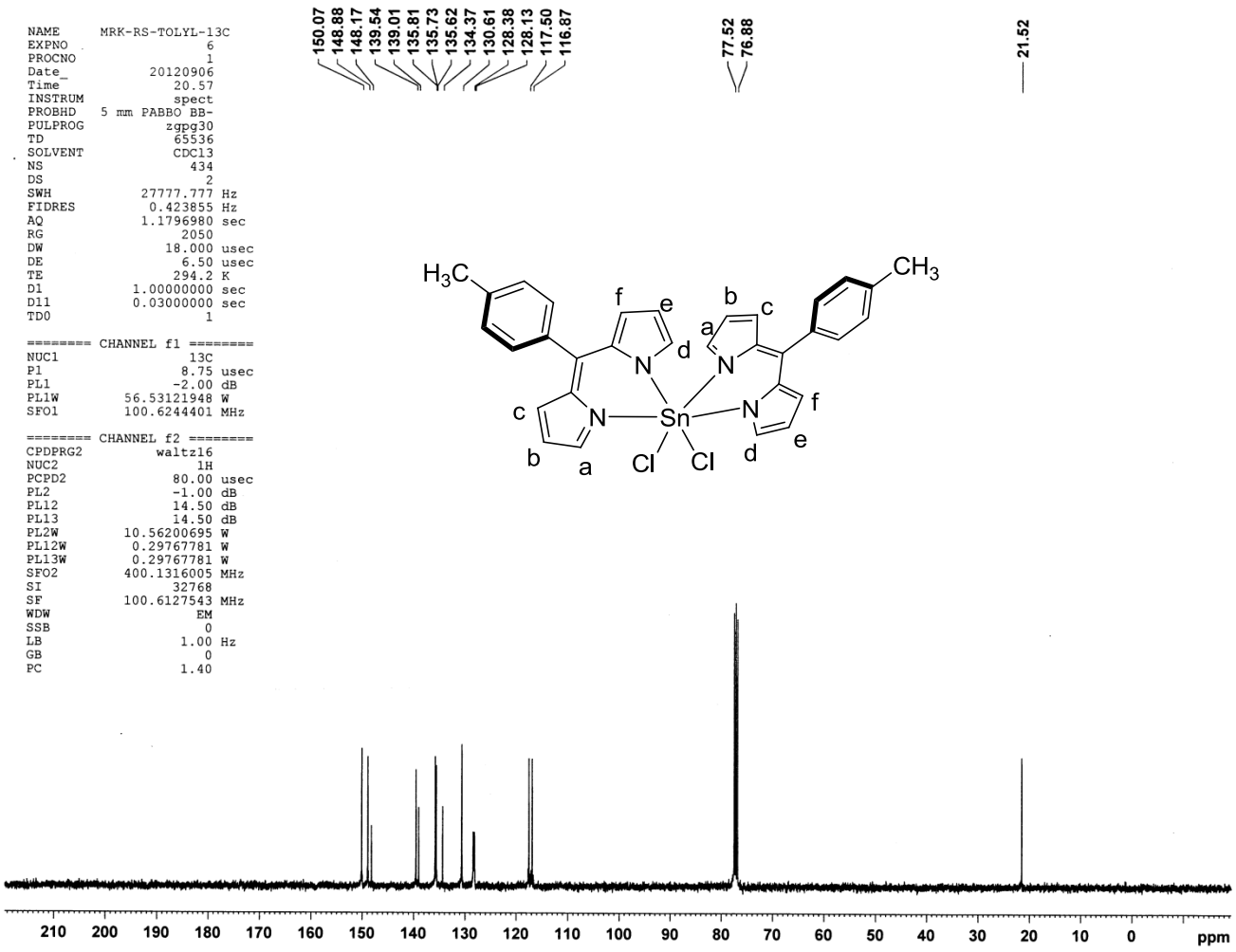


Figure S7. ^{13}C NMR spectrum of compound **2a** recorded in $CDCl_3$ at room temperature.

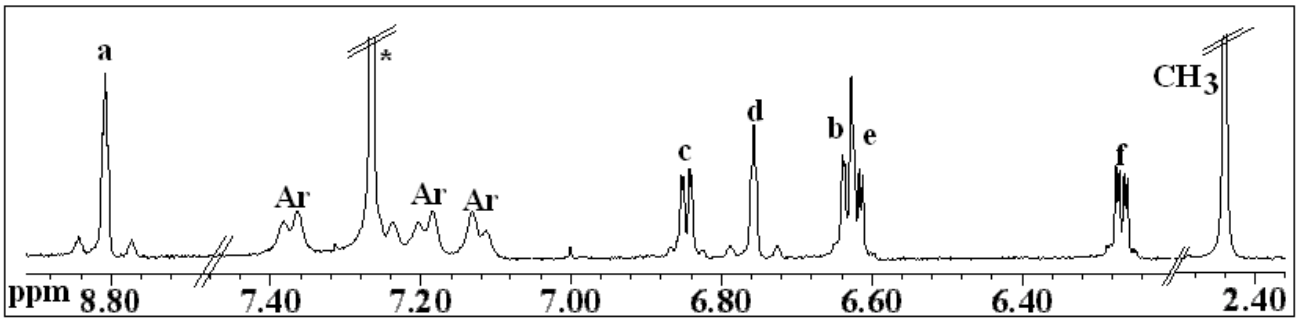


Figure S8. Partial ^{1}H NMR spectrum of compound **2a** recorded in $CDCl_3$ at room temperature.

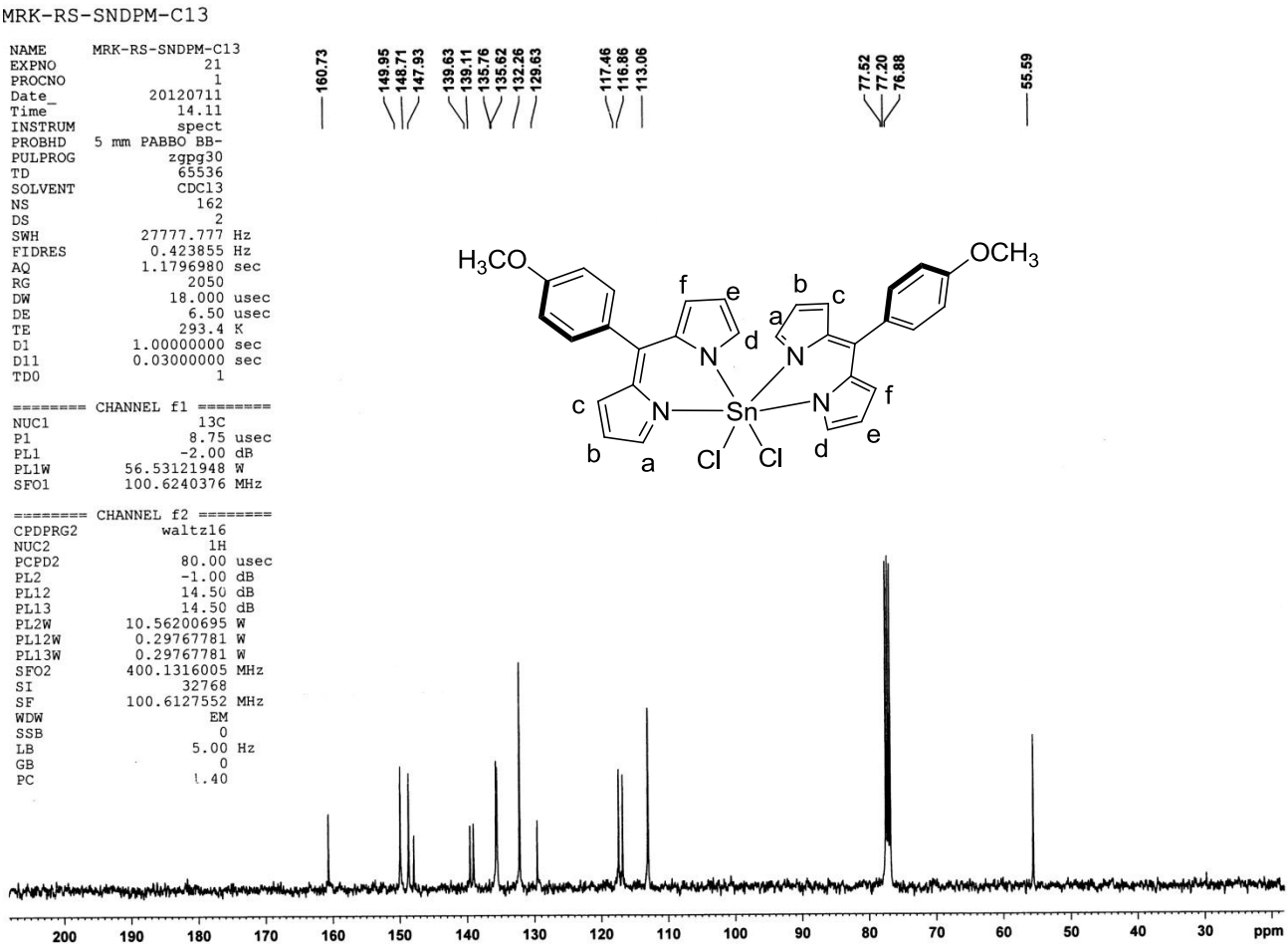


Figure S9. ^{13}C NMR spectrum of compound **3a** recorded in $CDCl_3$ at room temperature.

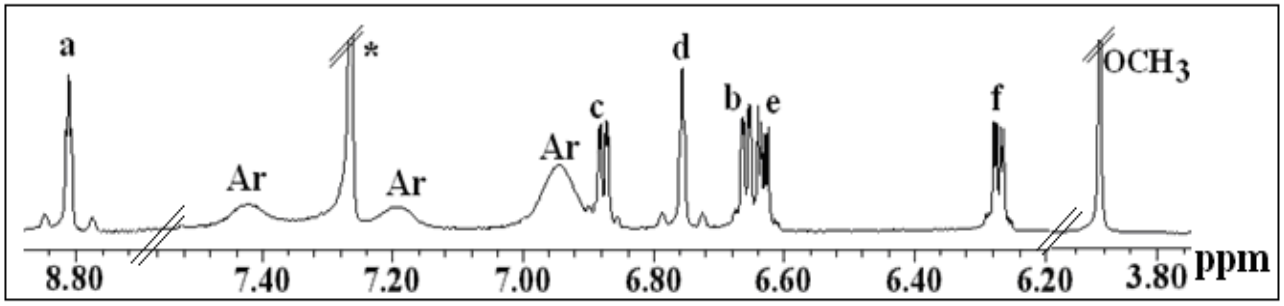


Figure S10. Partial ^{1}H NMR spectrum of compound **3a** recorded in $CDCl_3$ at room temperature.

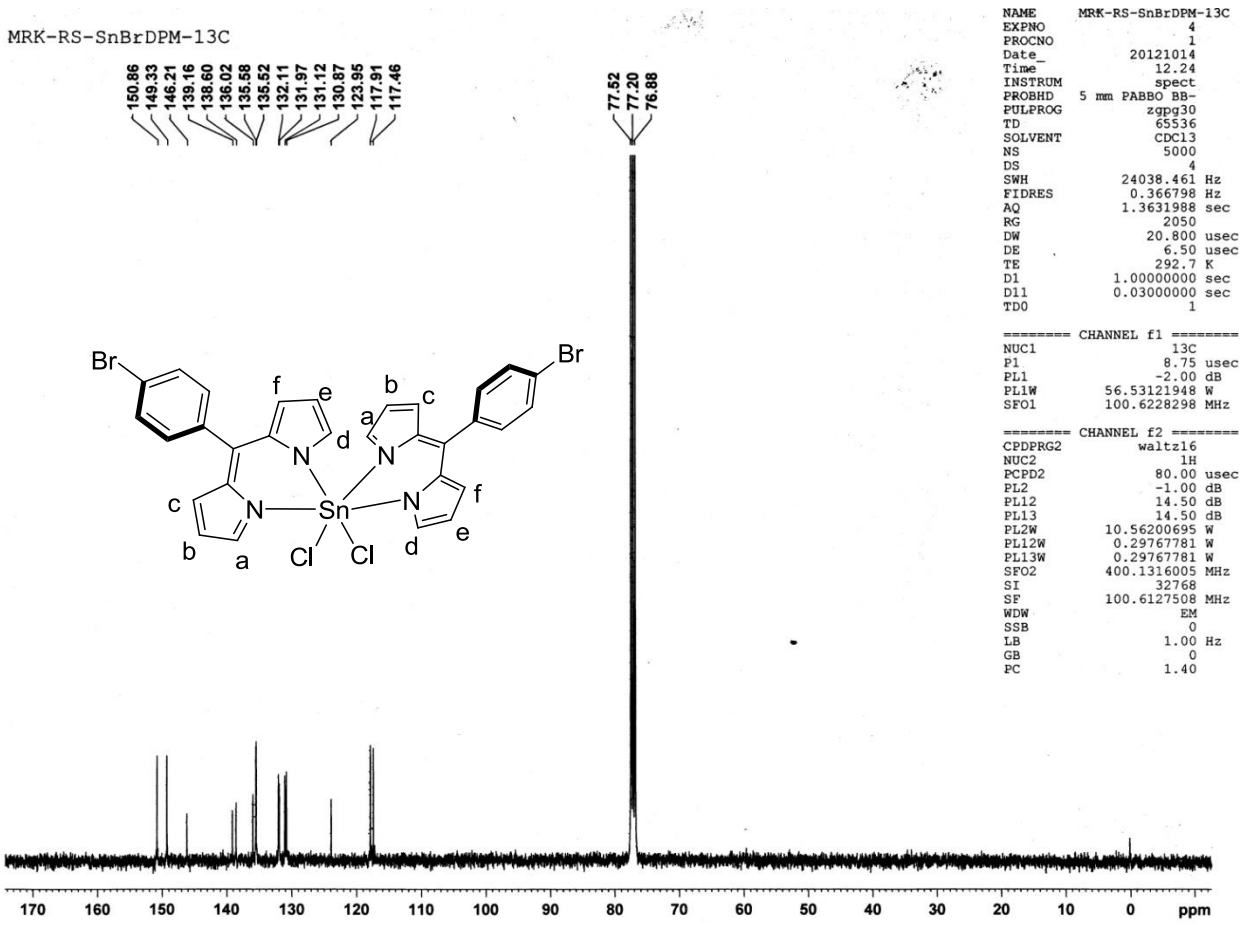


Figure S11. ^{13}C NMR spectrum of compound **4a** recorded in $CDCl_3$ at room temperature.

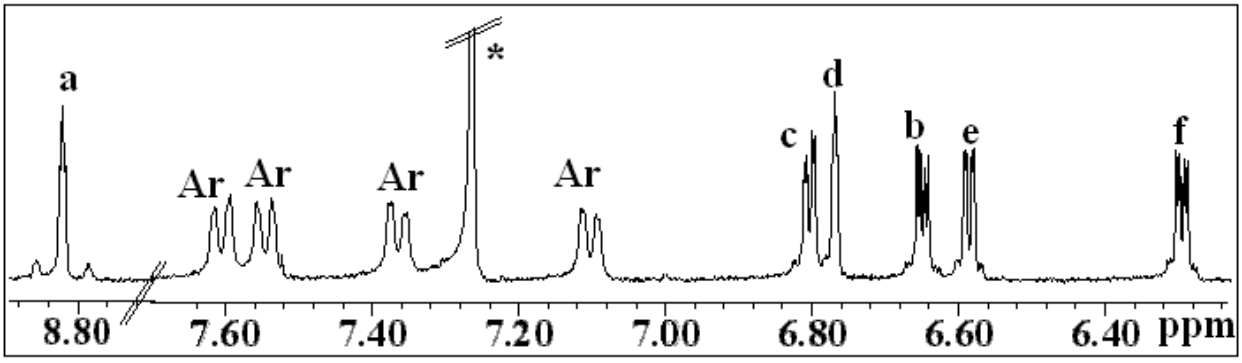


Figure S12. Partial ^{1}H NMR spectrum of compound **4a** recorded in $CDCl_3$ at room temperature.

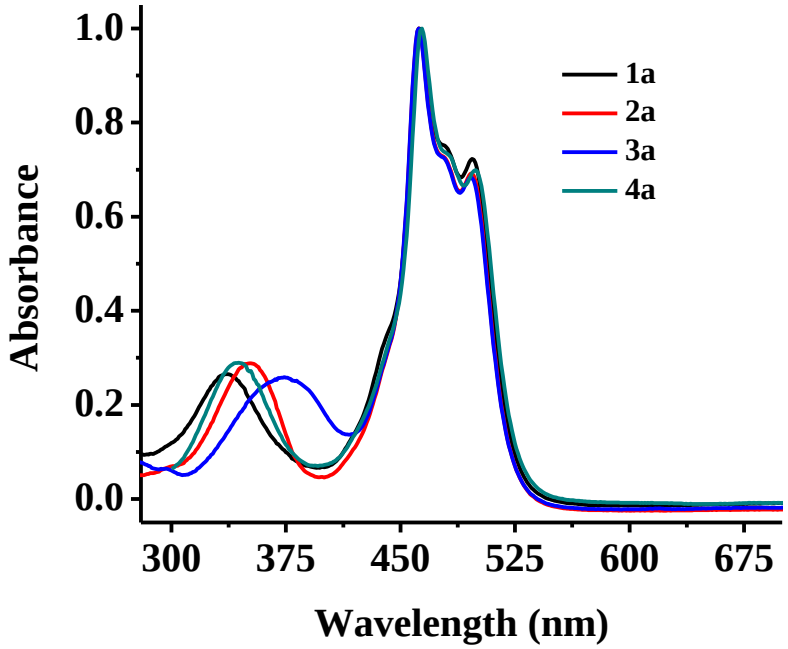


Figure S13. Normalized absorption spectra of compounds **1a-4a** recorded in $CHCl_3$ at room temperature.

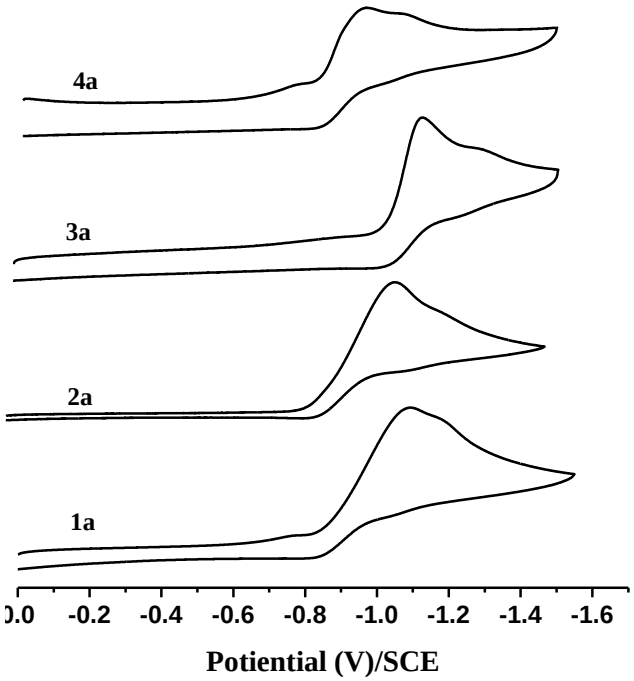


Figure S14. Reduction waves of compounds **1a-4a** recorded in CH_2Cl_2 solvent using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and saturated calomel electrode (SCE) as reference electrode at scan rates of 50 mVs^{-1}.

Table S1. Absorption and redox data of compounds **1a-4a**.

Compound	Absorbance [nm] (log ε)			E_{red} [V]	E_{ox} [V]
1a	462 (4.90)	497 (4.76)	342 (4.32)	-1.09	1.66
2a	461 (4.91)	497 (4.75)	336 (4.37)	-1.08	1.55
3a	462 (4.87)	497 (4.71)	374 (4.29)	-1.39	1.44
4a	463 (4.90)	499 (4.75)	342 (4.36)	-1.02	1.48

X-ray Crystallography

Experimental details relating to the crystallographic characterization are summarized in Table S1. Diffraction data were collected using graphite monochromated Mo Kα radiation on an Agilent diffractometer (Xcalibur, EOS) at 100 K using ω-scans. The structures were solved by direct methods and refined against F^2 by least-squares utilizing the software packages SHELXL-97[1], SIR-92[2], PLATON[3], and WINGX[4]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. CCDC 917693 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References:

(1) G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.

(2) A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

(3) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 1998.

(4) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

Crystalographic data for compound 3a

Empirical formula	$C_{32}H_{26}Cl_2N_4O_2Sn$
Formula weight	688.18
Crystal system	Monoclinic
Space group	P21/c
a (A˚)	8.5375(2) Å
b (A˚)	21.9688(4) Å
c (A˚)	17.2218(3) Å
α (deg)	90°
β (deg)	115.703(2)°
γ (deg).	90°
Volume (*V*)	2910.49(10) $Å^3$
Z	4
Density (calculated)	1.570 Mg/m^3
Absorption coefficient	1.099 mm^{-1}
F (000)	1384
R(int)	0.0243
Completeness to theta	28.99°
R1, wR2	0.0197 , 0.0450
R1 wR2	0.0225, 0.0463
Goodness-of-fit on F^2	1.067
Largest diff. peak and hole	0.428 and -0.388 $e.Å^{-3}$