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Experimental Details

General procedures. All starting materials were purchased from Aldrich Chemical Company. Solvents were used without further purification. Melting point tests were carried out on an Electrothermal Mel-Temp apparatus and are uncorrected. Elemental analyses were carried out on a Thermo Finnigan Flash EA 1112 elemental microanalyzer. High resolution mass spectra were acquired by LC/MSD TOF on an Agilent Technologies instrument with APCI as the ionization source. ^{1}H, ^{13}C and ^{119}Sn-NMR spectra were recorded in CD_3OD on a Bruker 400 MHz Advance III HD: ^{1}H (399.78 MHz), ^{13}C (100.52 MHz) and ^{119}Sn (149.4 MHz). Chemical shifts (ppm) are relative to $(CH_3)_4Si$ for ^{1}H and ^{13}C and to $(CH_3)_4Sn$ for ^{119}Sn.

Synthesis of [N-(3-Diethylamino-1-oxidobenzylidene)-11-hydroxybenzyhydrazidato] diphenyltin(IV) 1. A solution of 2-hydroxy-4-(diethylamino)-benzaldehyde (0.19, 1 mmol), 4-hydroxy-benzoylhydrazine (0.15, 1 mmol), and diphenyltin (IV) oxide (0.29, 1 mmol) in acetonitrile (50 ml) was heated to reflux for 20 h in a Dean–Stark trap for the azeotropic removal of water, and allowed to cool to room temperature. Then, all volatiles were removed under vacuum. The residue was extracted with hexane to yield **1** as a yellow solid. Yield: 61%. M. p. 246 ºC. ^{1}H NMR (400.13 MHz, CD_3OD, 298 K) δ: 1.17 (t, 6H, ^{3}J = 7.0 Hz, H-16), 3.60 (m, 3H, H-15), 6.26 (d, 1H, ^{3}J= 2.4 Hz, H-2), 6.29 (dd, 1H, ^{3}J= 8.9 Hz, 2.5 Hz, H-4), 6.85 (d, 2H, ^{3}J = 9.2 Hz, H-11, H-13), 7.07 (d, 1H, ^{3}J= 9.0 Hz, H-5), 7.42 (m, 6H, H-m, H-p), 7.83 (m, 4H, ^{3}J (^{1}H-$^{119/117}Sn$) =83.2/71.2 Hz ,H-o), 7.98 (d, 2H, ^{3}J = 9.2 Hz, H-10, H-14), 8.48 (s, 1H, ^{3}J (^{1}H-^{119}Sn) = 57.6 Hz, H-7). ^{13}C NMR (100.61 MHz, CD_3OD, 298 K) δ: 13.09 (C-16), 45.62 (C-15), 101.87 (C-2), 105.59 (C-4), 108.35 (C-6), 116.02 (C-11,C-13), 125.81 (C-12), 129.85 (C-m), 130.17 (C-10, C-14), 131.39 (C-p), 137.62 (C-5), 140.94 (C-i) 155.50 (C-3), 160.51 (C-7), 161.46 (C-9), 168.56 (C-8), 170.08 (C-1). COSY correlation [δH/δH]: 6.26/6.29 (H-2/H-4),

6.29/7.07 (H-4/H-5), 6.85/7.98 (H-11, H-13/H-10, H-14), 7.42/7.83 (H-m, H-p/H-o). HETCOR correlation [δH/δC]: 1.17/13.09 (H-16/C-16), 3.60/45.62 (H-15/C-15), 6.26/101.87 (H-2/C-2), 6.29/105.59 (H-4/C-4), 6.85/116.02 (H-11, H-13/C-11, C-13), 7.07/137.62 (H-5/C-5), 7.42/129.85 (H-m/C-m), 7.42/131.39 (H-p/C-p), 7.83/137.12 (H-o/C-o), 7.98/130.17 (H-10, H-14/C-10, C-14), 8.48/160.51 (H-7/C-7). ^{119}Sn NMR (149 MHz, CD_3OD, 298 K) δ: - 331.35. Anal. calcd for $C_{30}H_{29}N_3O_3Sn$: C 60.23 %, H 4.89 %, N 7.02 %; found: C 61.63 %, H 5.86 %, N 6.65 %. TOF calc. for [$(C_{30}H_{29}N_3O_3Sn + H)^+$]: 600.130367; found: 600.130531 (error= 0.272333 ppm).

Synthesis of [N-(3-Diethylamino-1-oxidobenzylidene)-11-hydroxybenzyhydrazidato] di-n-butyltin(IV) 2. A solution of 2-hydroxy-4-(diethylamino)-benzaldehyde (0.19, 1 mmol), 4-hydroxy-benzoylhydrazine (0.15, 1 mmol), and dibutyltin (IV) oxide (0.25, 1 mmol) in acetonitrile (50 ml) was heated to reflux for 20 h in a Dean–Stark trap for the azeotropic removal of water, and allowed to cool to room temperature. Then, all volatiles were removed under vacuum. The residue was extracted with hexane to yield **2** as a yellow solid. Yield: 58.5%. M. p. 132ºC. ^{1}H NMR (400.13 MHz, CD_3OD, 298 K) δ: 0.86 (t, 6H, ^{3}J = 7.3 Hz, H-δ), 1.20 (t, 6H, ^{3}J = 7.0 Hz, H-16), 1.36 (m, 4H,H-γ), 1.47 (t, 4H, ^{3}J= 8 Hz, H-α), 1.66 (m, 4H, H-β), 3.43 (m, 3H, H-15), 5.97 (d, 1H, ^{3}J= 2.4 Hz, H-2), 6.25 (dd, 1H, ^{3}J= 9.0 Hz, 2.4 Hz, H-4), 6.80 (d, 2H, ^{3}J = 8.8 Hz, H-11, H-13), 7.03 (d, 1H, ^{3}J= 9.0 Hz, H-5), 7.83 (d, 2H, ^{3}J = 8.8 Hz, H-10, H-14), 8.45 (s, 1H, ^{3}J (^{1}H-^{119}Sn) = 46.8 Hz, H-7). ^{13}C NMR (100.61 MHz, CD_3OD, 298 K) δ: 13.08 (C-16), 13.97 (C-δ), 22.47 (C-α), 27.38 (C-γ), 28.16 (C-β), 45.56 (C-15), 101.13 (C-2), 104.87 (C-4), 112.38 (C-6), 115.58 (C-11,C-13), 125.60 (C-12), 129.81 (C-10, C-14), 137.10 (C-5), 155.27 (C-3), 160.24 (C-7), 161.24 (C-9), 169.34 (C-8), 169.49 (C-1). COSY correlation [δH/δH]: 0.86/1.36 (H-δ/H-γ), 1.20/3.43 (H-16/H-15), 1.36/1.66 (H-γ/H-β), 1.47/1.66 (H-α/H-β), 5.97/6.25 (H-2/H-4), 6.25/7.03 (H-4/H-5), 6.80/7.83 (H-11, H-13/H-10, H-14). HETCOR correlation [δH/δC]: 0.86/13.97 (H-δ/ C-δ), 1.20/13.08 (H-16/H-16), 1.36/27.38 (H-γ/C-γ),

1.47/22.47 (H- α/C-α), 1.66/28.16 (H- β/C-β), 3.43/45.56 (H-15/C-15), 5.97/101.13 (H-2/C-2), 6.25/104.87 (H-4/C-4), 6.80/115.58 (H-11, H-13/C-11, C-13), 7.03/137.10 (H-5/C-5), 7.83/129.81 (H-10, H-14/C-10, C-14), 8.45/160.24 (H-7/C-7). ^{119}Sn NMR (149 MHz, CD_3OD, 298 K) δ: -194.41 ppm. This compound was an oil and elemental analysis was difficult to obtain. TOF calc. for [($C_{26}H_{36}N_3O_3Sn$ + H)$^+$]: 560.193036; found: 560.193036 (error= 0.103742 ppm).

Synthesis of [N-(3-Methoxy-1-oxidobenzylidene)-11-hydroxybenzyhydrazidato] diphenyltin(IV) 3. A solution of 2-hydroxy-4-methoxy benzaldehyde (0.15, 1 mmol), 4-hydroxy-benzoylhydrazine (0.15, 1 mmol), and diphenyltin (IV) oxide (0.29, 1 mmol) in acetonitrile (50 ml) was heated to reflux for 20 h in a Dean–Stark trap for the azeotropic removal of water, and allowed to cool to room temperature. Then, all volatiles were removed under vacuum. The residue was extracted with hexane to yield **3** as a yellow solid. Yield: 55.1%. M. p. 202 ºC. ^{1}H NMR (400.13 MHz, CD_3OD, 298 K) δ: 3.86 (s, 3H, H-15), 6.41 (dd, 1H, ^{3}J = 8.7 Hz, 2.4 Hz, H-4), 6.57 (d, 1H, ^{3}J = 2.4 Hz, H-2), 6.86 (d, 2H, ^{3}J = 8.8 Hz, H-11, H-13), 7.20 (d, 1H, ^{3}J = 8.8 Hz, H-5), 7.42 (m, 6H, H-m, H-p), 7.80 (m, 4H, ^{3}J (^{1}H-$^{119/117}$Sn) =84/72 Hz ,H-o), 8.03 (d, 2H, ^{3}J = 8.8 Hz, H-10, H-14), 8.66 (s, 1H, ^{3}J (^{1}H-^{119}Sn) = 54.7 Hz, H-7).^{13}C NMR (100.61 MHz, CD_3OD, 298 K) δ: 56.23 (C-15), 105.59 (C-2) , 108.59 (C-4), 112.59 (C-6), 116.30 (C-11, C-13), 125.60 (C-12), 130.15 (C-m), 130.71 (C-10, C-14), 131.74 (C-p), 137.24 (C-o), 137.37 (C-5), 140.92 (C-i), 161.55 (C-7), 162.08 (C-9), 168.03 (C-3), 170.07 (C-8), 170.75 (C-1). COSY correlation [δH/δH]: 6.41/6.57 (H-4/H-2), 6.41/7.20 (H-4/H-5), 6.56/8.03 (H-11, H-13/H-10, H-14), 7.42/7.80 (H-m, H-p/H-o). HETCOR correlation [δH/δC]: 3.86/56.23 (H-15/C-15), 6.41/108.59 (H-4/C-4), 6.57/105.59 (H-2/C-2), 6.56/116.30 (H-11, H-13/C-11, C-13), 7.20/137.37 (H-5/C-5), 7.42/130.15 (H-m/C-m), 7.42/131.74 (H-p/C-p), 7.80/137.24 (H-o/C- o), 8.03/130.71 (H-10, H-14/C-10, C-14), 8.66/161.55 (H-7/C-7). ^{119}Sn NMR (149 MHz, CD_3OD, 298 K) δ: - 336.54 ppm. Anal. calcd for $C_{27}H_{22}N_2O_4Sn$: C 58.20 %,

H 3.98 %, N 5.03 %; found: C 60.33 %, H 5.97 %, N 5.38 %. TOF calc. for [($C_{27}H_{22}N_2O_4Sn$ + $H)^+$]: 559.067432; found: 559.067363 (error= -0.125058 ppm).

Synthesis of [N-(3-Methoxy-1-oxidobenzylidene)-11-hydroxybenzyhydrazidato] di-n-butyltin(IV) 4. A solution of 2-hydroxy-4-methoxy benzaldehyde (0.15, 1 mmol), 4-hydroxy-benzoylhydrazine (0.15, 1 mmol), dibutyltin (IV) oxide (0.25, 1 mmol) in acetonitrile (50 ml) was heated to reflux for 20 h in a Dean–Stark trap for the azeotropic removal of water, and allowed to cool to room temperature. Then, all volatiles were removed under vacuum. The residue was extracted with hexane to yield **4** as a yellow solid. Yield: 87.3%. M. p. 120ºC. ^{1}H NMR (400.13 MHz, CD_3OD, 298 K) δ: 0.85 (t, 6H, ^3J = 7.3 Hz, H- δ), 1.34 (m, 4H,H-γ), 1.49 (t, 4H, ^3J = 7.7 Hz, H-α), 1.64 (m, 4H, H-β), 3.79 (s, 3H, H-15), 6.25 (d, 1H, ^3J = 2.4 Hz, H-2), 6.35 (dd, 1H, ^3J = 8.7Hz, 2.4 Hz, H-4), 6.80 (d, 2H, ^3J = 8.8 Hz, H-11, H-13), 7.15 (d, 1H, ^3J = 8.8 Hz, H-5), 7.87 (d, 2H, ^3J = 8.8 Hz, H-10, H-14), 8.62 (s, 1H, ^3J (^{1}H-^{119}Sn) = 40.9 Hz, H-7). ^{13}C NMR (100.61 MHz, CD_3OD, 298 K) δ: 14.07 (C-δ), 22.87 (C-α), 27.37 (C-γ), 28.29 (C-β), 55.85 (C-15),104.72 (C-2), 107.74 (C-4), 112.38 (C-6), 115.92 (C-11,C-13), 125.60 (C-12), 130.38 (C-10, C-14), 136.91 (C-5), 161.26 (C-7), 161.60 (C-9), 167.56 (C-3), 170.27 (C-8), 170.31 (C-1).COSY correlation [δH/δH]: 0.85/1.34 (H-δ/H-γ), 1.34/1.64 (H-γ/H-β), 1.49/1.64 (H-α/H-β), 6.25/6.35 (H-2/H-4), 6.35/7.15 (H-4/H-5), 6.80/7.87 (H-11, H-13/H-10, H-14). HETCOR correlation [δH/δC]: 0.85/14.07 (H-δ/ C-δ), 1.34/27.37 (H-γ/C-γ), 1.49/22.87 (H-α/C-α), 1.64/28.29 (H- β/C-β), 3.79/55.85 (H-15/C-15), 6.25/104.72 (H-2/C-2), 6.35/107.74 (H-4/C-4), 6.80/115.92 (H-11, H-13/C-11, C-13), 7.15/136.91 (H-5/C-5), 7.87/130.38 (H-10, H-14/C-10, C-14), 8.62/161.26 (H-7/C-7). ^{119}Sn NMR (149 MHz, CD_3OD, 298 K) δ: -198.64 ppm. Anal. calcd for $C_{23}H_{30}N_2O_4Sn$: C 53.41 %, H 5.85 %, N 5.42 %; found: C 56.35 %, H 7.50 %, N 6.90 %. TOF calc. for [($C_{23}H_{36}N_2O_4Sn$ + $H)^+$]: 519.130033; found: 519.130063 (error= 0.057334 ppm).

Synthesis of [N-(3-Hydroxy-1-oxidobenzylidene)-11-hydroxybenzyhydrazidato] diphenyltin(IV) 5. A solution of 2,4-dihydroxybenzaldehyde (0.14, 1 mmol), 4-hydroxy-benzoylhydrazine (0.15, 1 mmol), and diphenyltin (IV) oxide (0.29, 1 mmol) in acetonitrile (50 ml) was heated to reflux for 20 h in a Dean–Stark trap for the azeotropic removal of water, and allowed to cool to room temperature. Then, all volatiles were removed under vacuum. The residue was extracted with hexane to yield **5** as a yellow solid. Yield: 95.7%. M. p. 194ºC. ^{1}H NMR (400.13 MHz, CD_3OD, 298 K) δ: 6.31 (dd, 1H, ^{3}J = 8.6 Hz, 2.3 Hz, H-4), 6.43 (d, 1H, ^{3}J = 2.3 Hz, H-2), 6.86 (d, 2H, ^{3}J = 8.8 Hz, H-11, H-13), 7.14 (d, 1H, ^{3}J = 8.7 Hz, H-5), 7.41 (m, 6H, H-m, H-p), 7.81 (m, 4H, ^{3}J (^{1}H-$^{119/117}$Sn) =83.2/72.8 Hz ,H-o), 8.03 (d, 2H, ^{3}J = 8.8 Hz, H-10, H-14), 8.63 (s, 1H, ^{3}J (^{1}H-^{119}Sn) = 54.8 Hz, H-7).^{13}C NMR (100.61 MHz, CD_3OD, 298 K) δ: 107.38 (C-2) , 109.06 (C-4), 111.81 (C-6), 116.06 (C-11,C-13), 125.49 (C-12), 129.91 (C-m), 130.43 (C-10, C-14), 131.50 (C-p), 137.04 (C-o), 137.74 (C-5), 140.68 (C-i), 161.46 (C-7), 161.75 (C-9), 166.40 (C-3), 169.58 (C-8), 170.75 (C-1). COSY correlation [δH/δH]: 6.31/6.43 (H-4/H-2), 6.31/7.14 (H-4/H-5), 6.86/8.03 (H-11, H-13/H-10, H-14), 7.41/7.81 (H-m, H-p/H-o). HETCOR correlation [δH/δC]: 6.31/109.06 (H-4/C-4), 6.43/107.38 (H-2/C-2), 6.86/116.06 (H-11, H-13/C-11, C-13), 7.14/137.74 (H-5/C-5), 7.41/129.91 (H-m/C-m), 7.41/131.50 (H-p/C-p), 7.81/137.04 (H-o/C- o), 8.03/130.43 (H-10, H-14/C-10, C-14), 8.63/161.46 (H-7/C-7). ^{119}Sn NMR (149 MHz, CD_3OD, 298 K) δ: -335.50 ppm. Anal. calcd for $C_{26}H_{20}N_2O_4Sn$: C 57.49 %, H 3.71 %, N 5.16 %; found: C 55.91 %, H 5.97 %, N 5.03 %. TOF calc. for [($C_{26}H_{20}N_2O_4Sn$ + H)$^{+}$]: 545.051782; found: 545.051870 (error= 0.159918 ppm).

Synthesis of [N-(3-Hydroxy-1-oxidobenzylidene)-11-hydroxybenzyhydrazidato] di-n-butyltin(IV) 6. A solution of 2,4-dihydroxybenzaldehyde (0.14, 1 mmol), 4-hydroxy-benzoylhydrazine (0.15, 1 mmol), and dibutyltin (IV) oxide (0.25, 1 mmol) in acetonitrile (50 ml) was heated to reflux for 20 h in a Dean–Stark trap for the azeotropic removal of water, and allowed to cool to room temperature. Then, all volatiles were removed under vacuum. The

residue was extracted with hexane to yield **6** as a yellow solid. Yield: 70.2%. M. p. 180ºC. ^{1}H NMR (400.13 MHz, CD_3OD, 298 K) δ: 0.83 (t, 6H, ^{3}J = 7.3 Hz, H- δ), 1.33 (m, 4H,H-γ), 1.46 (t, 4H, ^{3}J = 7.2 Hz, H-α), 1.61 (m, 4H, H-β), 6.12 (d, 1H, ^{3}J = 2.3 Hz, H-2), 6.24 (dd, 1H, ^{3}J = 8.6Hz, 2.3 Hz, H-4), 6.79 (d, 2H, ^{3}J = 8.8 Hz, H-11, H-13), 7.08 (d, 1H, ^{3}J = 8.7 Hz, H-5), 7.84 (d, 2H, ^{3}J = 8.8 Hz, H-10, H-14), 8.57 (s, 1H, ^{3}J (^{1}H-^{119}Sn) = 43.6 Hz, H-7). ^{13}C NMR (100.61 MHz, CD_3OD, 298 K) δ: 13.94 (C-δ), 22.75 (C-α), 27.37 (C-γ), 28.11 (C-β), 106.83 (C-2), 108.52 (C-4), 111.80 (C-6), 115.89 (C-11,C-13), 125.66 (C-12), 130.33 (C-10, C-14), 137.47 (C-5), 161.38 (C-7), 161.50 (C-9), 166.07 (C-3), 170.11 (C-8), 170.17 (C-1). COSY correlation [δH/δH]: 0.83/1.33 (H-δ/H-γ), 1.33/1.61 (H-γ/H-β), 1.46/1.61 (H- α /H- β), 6.12/6.24 (H-2/H-4), 6.24/7.08 (H-4/H-5), 6.79/7.84 (H-11, H-13/H-10, H-14). HETCOR correlation [δH/δC]: 0.83/13.94 (H-δ/ C-δ), 1.33/27.37 (H-γ/C-γ), 1.46/22.75 (H-α/C-α), 1.61/28.11 (H-β/C-β), 6.12/106.83 (H-2/C-2), 6.24/108.52 (H-4/C-4), 6.79/115.89 (H-11, H-13/C-11, C-13), 7.08/137.47 (H-5/C-5), 7.84/130.33 (H-10, H-14/C-10, C-14), 8.57/161.38 (H-7/C-7). ^{119}Sn NMR (149 MHz, CD_3OD, 298 K) δ: -197.88 ppm. Anal. calcd for $C_{22}H_{28}N_2O_4Sn$: C 52.51 %, H 5.61 %, N 5.57 %; found: C 54.10 %, H 6.76 %, N 5.89 %. TOF calc. for [($C_{22}H_{28}N_2O_4Sn$ + H)$^{+}$]: 505.114383; found: 505.114337 (error= -0.091377 ppm).

X-ray data collection and structure determination. The crystals data of **4** and **5** were recorded on an Enraf Nonius Kappa-CCD (l MoKa = 0.71073, graphite monochromator, T = 293 K-CCD rotating images scan mode). The crystals were mounted on a Lindeman tube. The structures were solved by direct methods using SHELXS-9718 and refined against F2 on all data by full-matrix least-squares with SHELXL-97.[1] All of the software manipulations were done under the WIN-GX environment program set.[2] Heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were found by Fourier map differences and refined isotropically.

One-photon photophysical characterization. Spectroscopic grade methanol, ethanol, DMSO and THF were used. Solutions were studied as prepared, in order to avoid any solvolysis or photodegradation effect. UV-Vis absorbance spectra were measured using an Agilent Cary 60 Spectrophotometer (Agilent technologies, UK), at wavelengths from 200 nm to 700 nm with 0.5 nm intervals. Fluorescence quantum yields of the complexes in solution were measured using xenon arc lamp excitation with a FluoTime 300 spectrometer (Picoquant, Germany) by scanning the emission wavelength from 375 nm to 700 nm, using quinine sulfate in 0.5 M H_2SO_4 as a standard, which has a known quantum yield of 0.546 at 310 nm excitation at 295 K. Lifetimes were recorded using the time-correlated single photon counting (TCSPC) technique. The TCSPC instrument consisted of a pulsed supercontinuum fiber laser (Pulsed Fianium SC-400-4-PP, UK) coupled to a tunable Fianium SuperChrome filter (Fianium, UK) via optical fiber. The output of the SuperChrome system is coupled to the laser entry port on a FluoTime 300 spectrometer (PicoQuant Germany) by optical fiber. Lifetimes were obtained by tail fitting of the decay curves, and the quality of fit was judged by minimization of reduced chi-squared and residuals.

Two-photon photophysical characterization. The excitation source was a broadband Ti:Sapphire laser with a repetition rate of 80 MHz (Vitara UBB, Coherent). The compressed pulses from the oscillator had duration of 15fs. The laser spectrum was filtered with a band pass filter (Thorlabs 800 nm 10nm FWHM) and subsequently attenuated by a combination of 2 neutral density filters at a time (Thorlabs) to obtain different excitation powers. The emission passed through a dichroic mirror (Semrock FF652-Di01) and was focused by an objective (Nikon Plan Fluor 10x) into a cuvette with the sample. The emitted light was collected by the same objective and reflected by the dichroic mirror onto a short-pass filter (Semrock, FF01-650/SP) to filter out any residual laser light. Subsequently it was focussed by a lens (Edmund PCX UV 25x38, coating UV-VIS CTD TS) onto an optical fibre and guided into the

spectrometer (Ocean Optics QE 65000 for recording the shape of the spectra and AvaSpec ULS2048L-USB2 from Avantes for power series). Two different spectrometers were used because the Ocean Optics spectrometer corrects for wavelength dependent sensitivity and displays the spectral shape correctly but has a nonlinear response to different total light intensities. For that reason, a correction factor for each compound was calculated comparing the Avantes spectra with the Ocean Optics spectra. The cross sections where calculated with these corrected values.

The two photon cross section of the sample (σ_2^S) was calculated[3] using a standard with a known cross section σ_2^R :

$$\frac{\sigma_2^S \phi^S}{\sigma_2^R \phi^R} = \frac{\eta^R \left(n_{\lambda emission}^S\right)^2 n_{\lambda excitation}^R C^R F^S \langle P^R \rangle^2}{\eta^S \left(n_{\lambda emission}^R\right)^2 n_{\lambda excitation}^S C^S F^R \langle P^S \rangle^2}$$

where ϕ is the quantum yield of the fluorescence, η accounts for the wavelength dependence of the detection efficiency, n is the refractive index of the solvent C is the concentration, F is the integrated fluorescence signal and P is the excitation power. The superscripts R and S denote reference and sample respectively.

By making the simplifications $n_{\lambda emission} = n_{\lambda excitation} = n$ and $\eta^R = \eta^S$ this can be written as:

$$\frac{\sigma_2^S \phi^S}{\sigma_2^R \phi^R} = \frac{n^S C^R M^S}{n^R C^S M^R}$$

With $M = \frac{F}{\langle P \rangle^2}$, the slope of the area below the fluorescence signal F plotted against the square of the excitation power $\langle P \rangle^2$. The measurements were taken in solution with an absorption lower than 0.1 to avoid reabsorption effects. The used standard was Rhodamine B with a quantum yield[4] $\phi^R = 0.7$ and a two photon cross section of 120±18 GM (at 800nm).[5]

Cell culture and fluorescence microscopy. HeLa cancer cell line was purchased from American Type Culture Collection (ATCC) (Manassas VA, USA). The cells were maintained in Dulbecco´s Modified Eagle Medium: Nutrient Mixture F-12 (DMEM/F12) (Invitrogen, USA), supplemented with 10% fetal bovine serum (FBS) (Invitrogen, USA), and 100 IU/mL penicillin, 100 μg/mL streptomycin, and incubated at 37°C in a controlled humidified atmosphere with 5% CO_2. Cell counting was carried out using Trypan blue (0.4% Sigma-Aldrich), a Neubauer chamber and an optic microscope (Zeiss Primo Star) as proposed by the ATCC's standard protocols. Sterile coverslips were placed inside a twelve-well plate and 1×10^5 cells/mL were seeded and incubated for 24 hours. Then, cells were washed twice with PBS 1X and PFA 4% was added, after 20 min incubation at 4°C cells were washed twice. The organotin compounds **1**-**6** (in DMSO) were added to cells at concentration of 5 mM, cells were incubated for 30 min and washed twice. Finally coverslips where placed on a slide and observed by confocal microscopy (Olympus X70; Olympus, Tokyo, Japan) and a multiphoton confocal microscopy (LSM710NLO, Carl Zeiss with excitation at 842 nm).

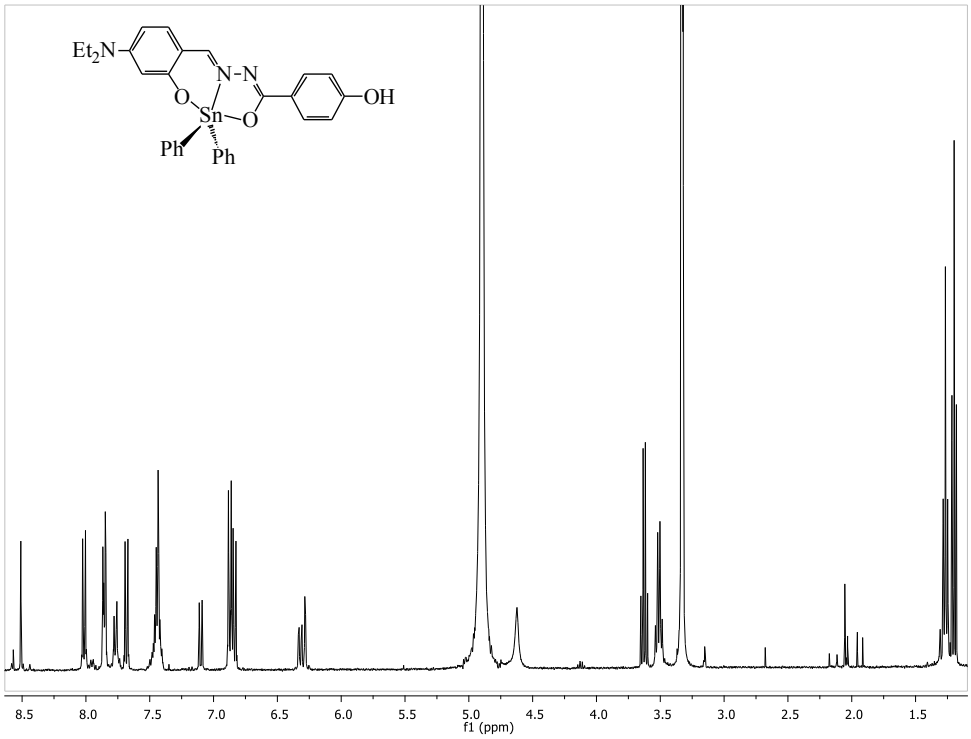

Fig. S1. ^{1}H-NMR (400 MHz, CD_3OD. 298 K) spectrum of compound **1**.

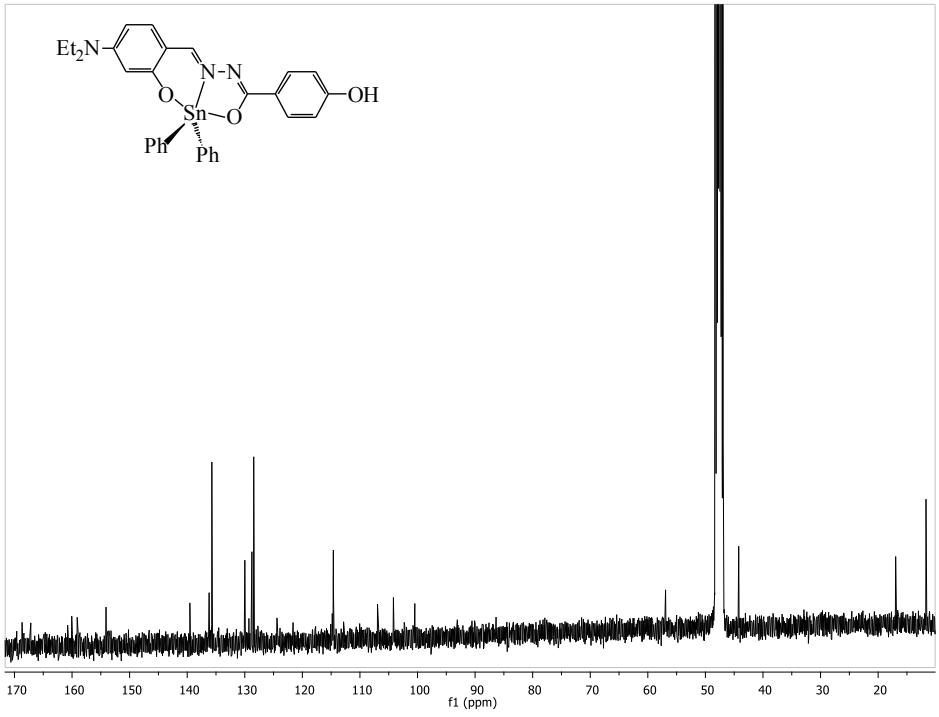

Fig. S2. ^{13}C-NMR (100 MHz, CD_3OD. 298 K) spectrum of compound **1**.

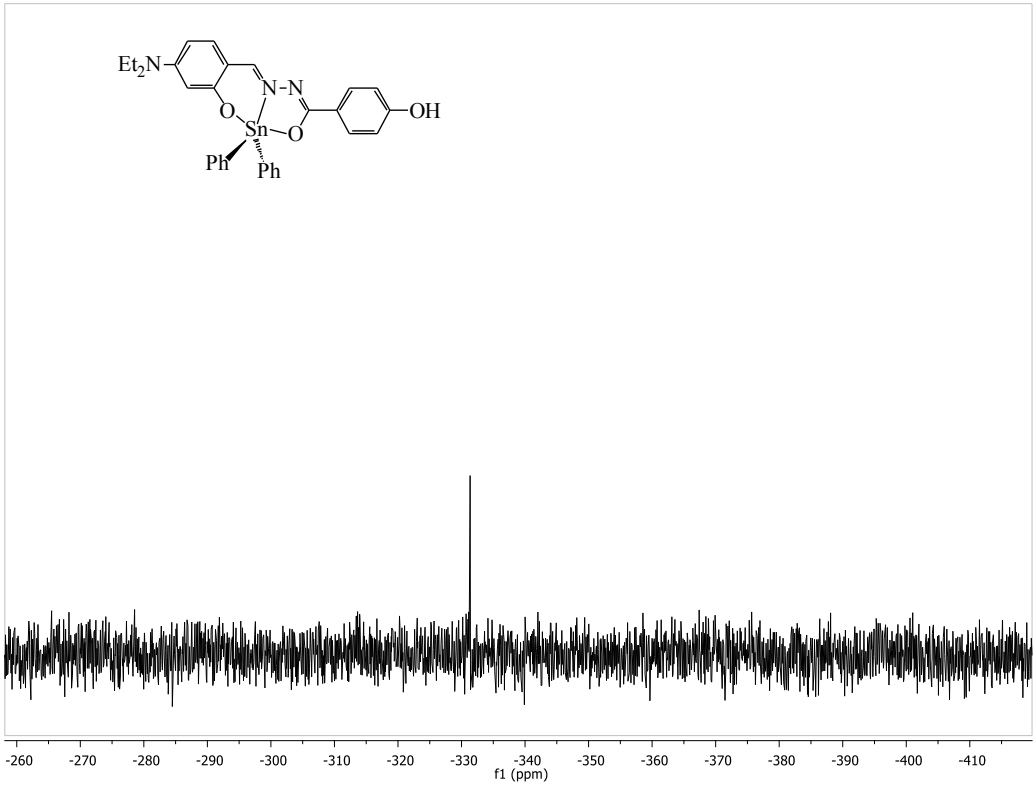

Fig. S3. ^{119}Sn-NMR (149 MHz, CD_3OD. 298 K) spectrum of compound **1**.

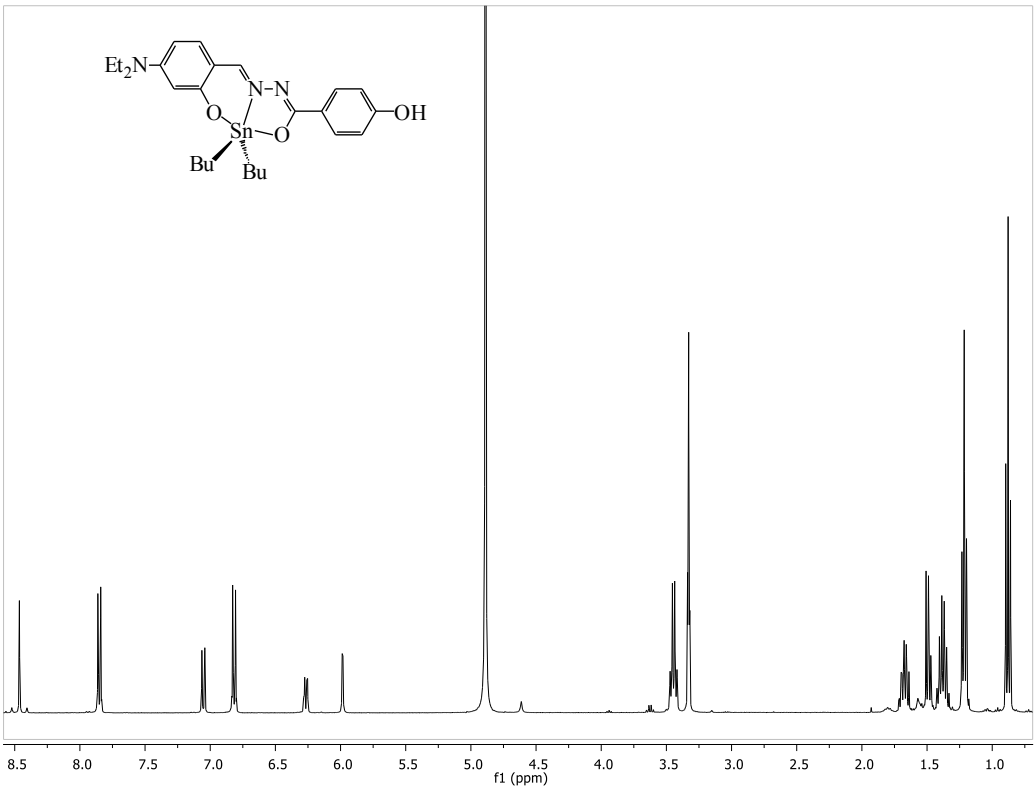

Fig. S4.^{1}H-NMR (400 MHz, CD_3OD. 298 K) spectrum of compound **2**.

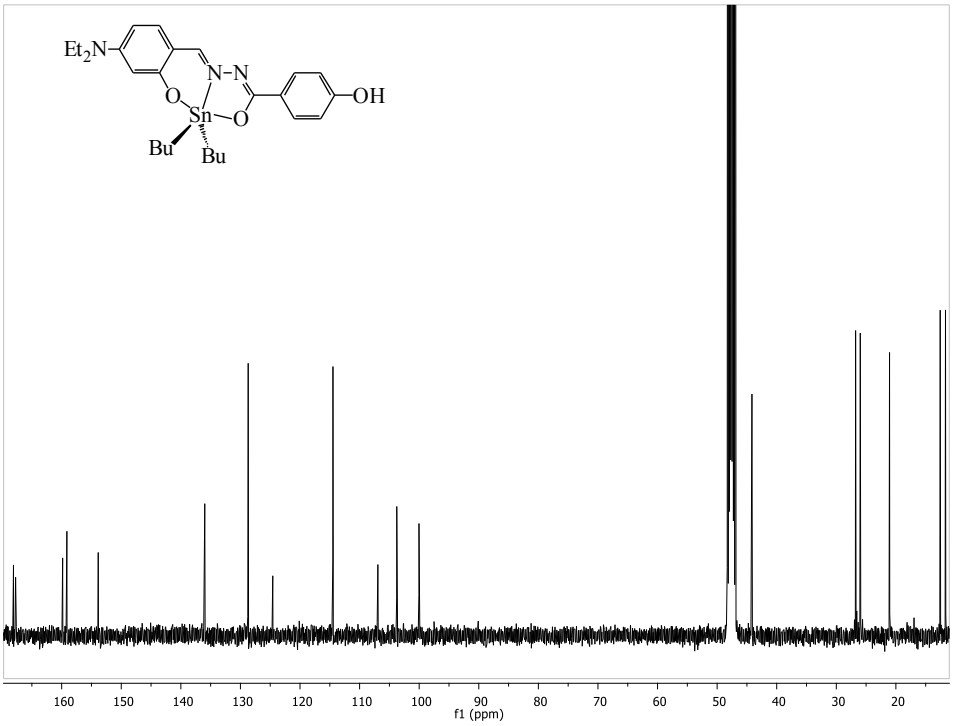

Fig. S5.^{13}C-NMR (100 MHz, CD_3OD. 298 K) spectrum of compound **2**.

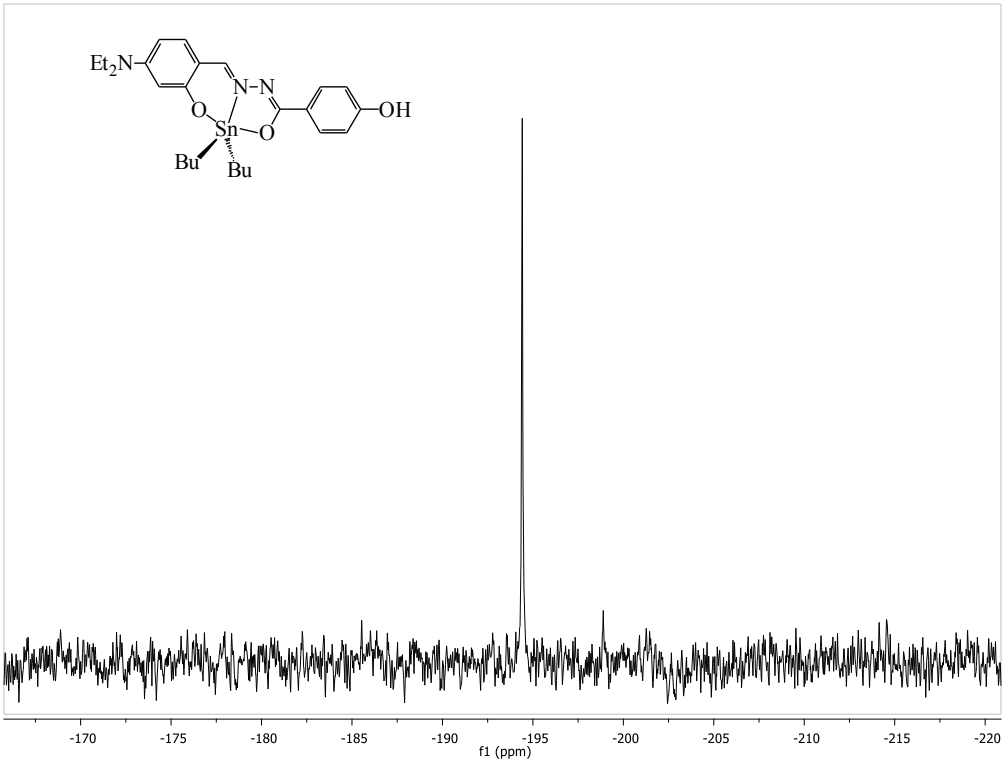

Fig. S6.^{119}Sn-NMR (149 MHz, CD_3OD. 298 K) spectrum of compound **2**.

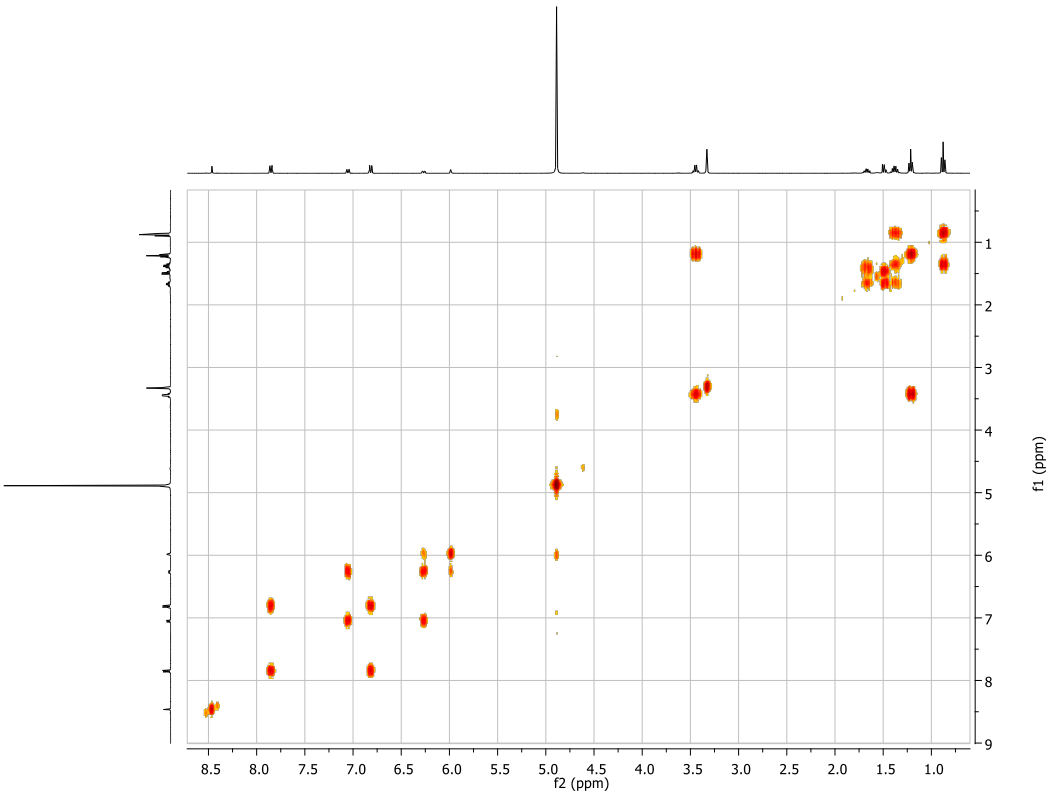

Fig. S7. $^{1}H/^{1}H$ COSY spectrum of compound **2.**

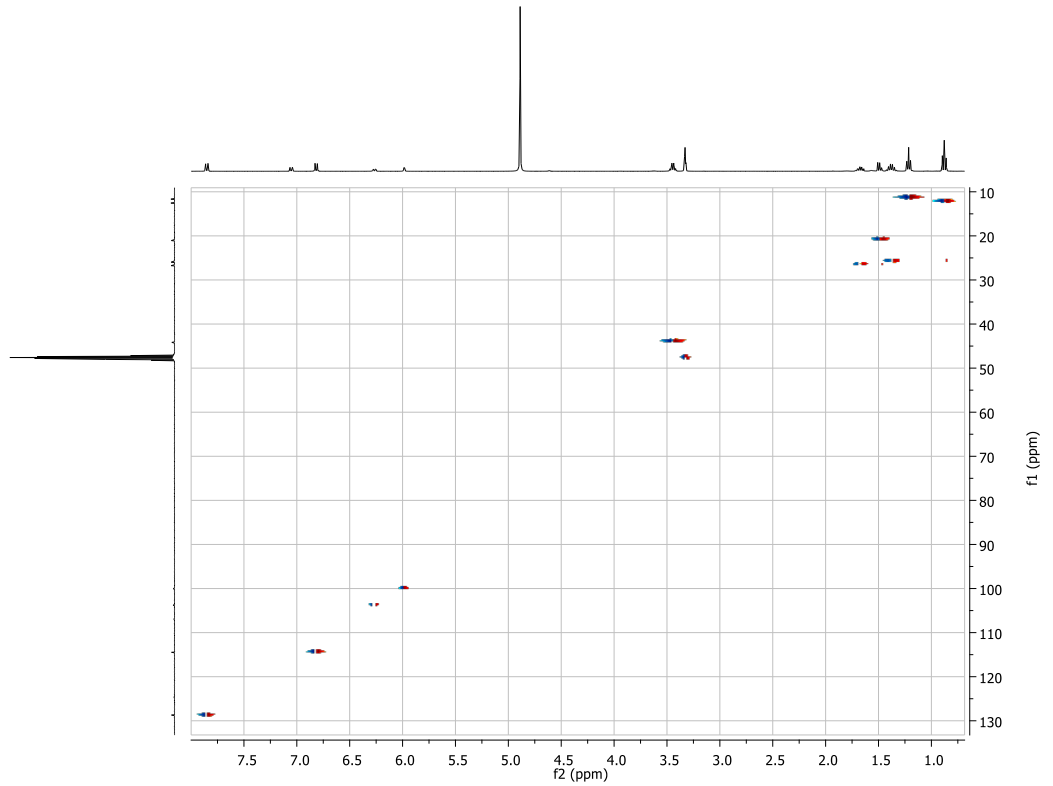

Fig. S8. $^{1}H/^{13}C$ HETCOR spectrum of compound **2.**

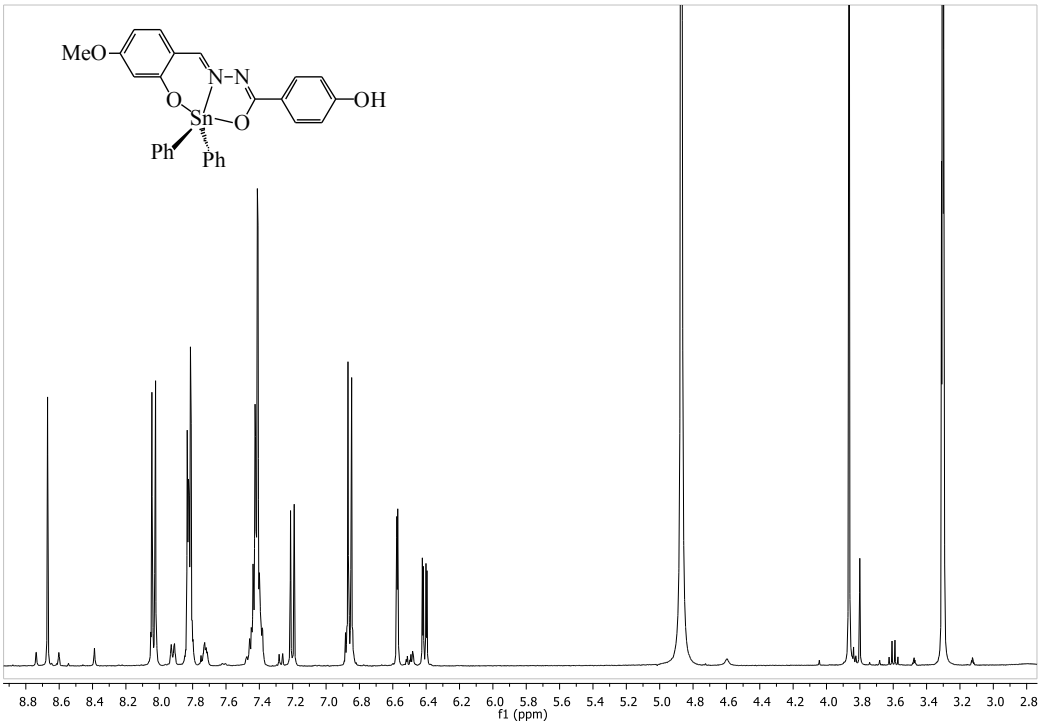

Fig. S9. ^{1}H-NMR (400 MHz, CD_3OD. 298 K) spectrum of compound **3**.

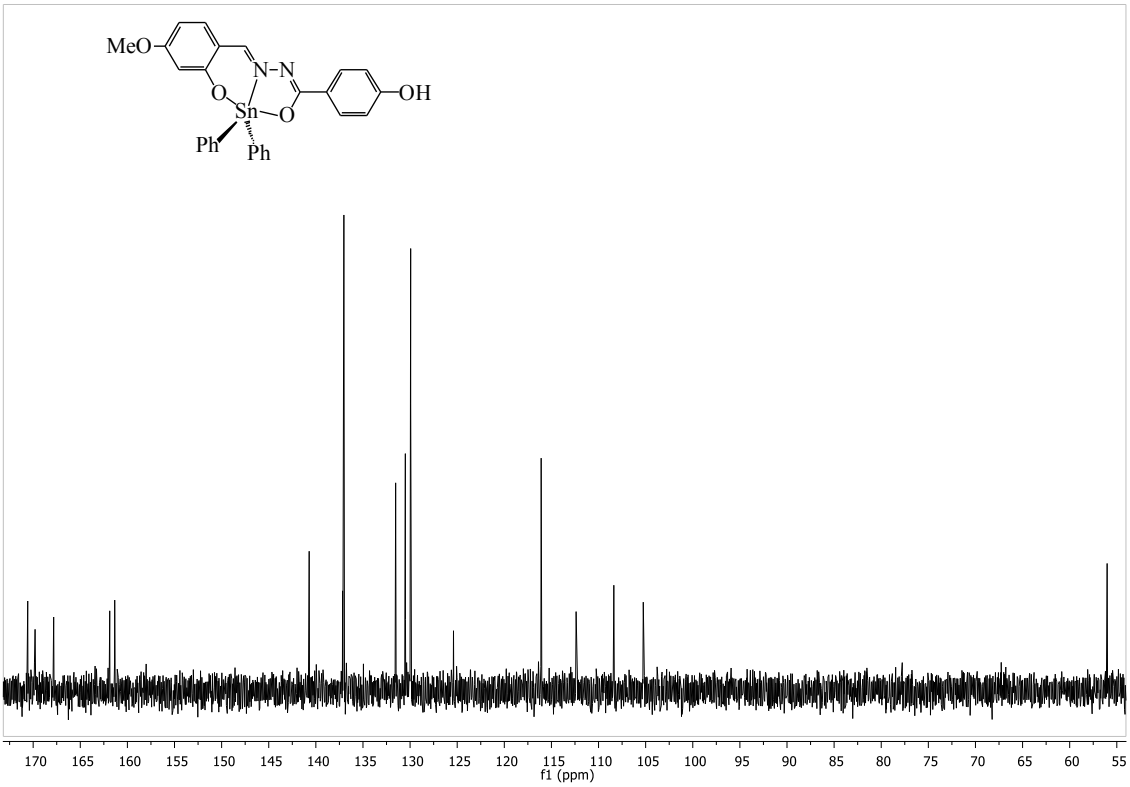

Fig. S10. ^{13}C-NMR (100 MHz, CD_3OD. 298 K) spectrum of compound **3**.

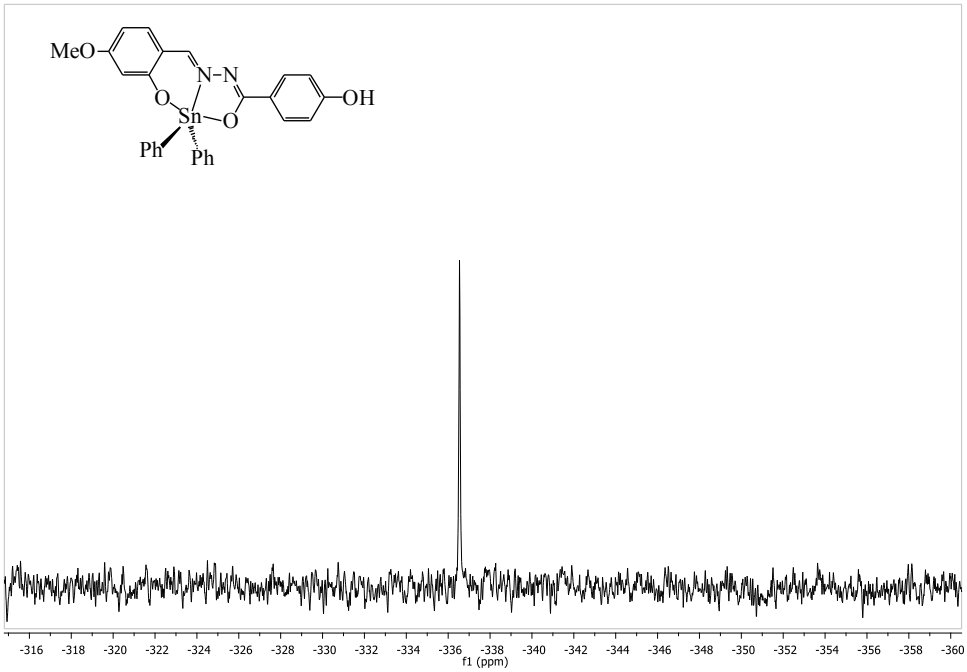

Fig. S11. ^{119}Sn-NMR (149 MHz, CD_3OD. 298 K) spectrum of compound **3**.

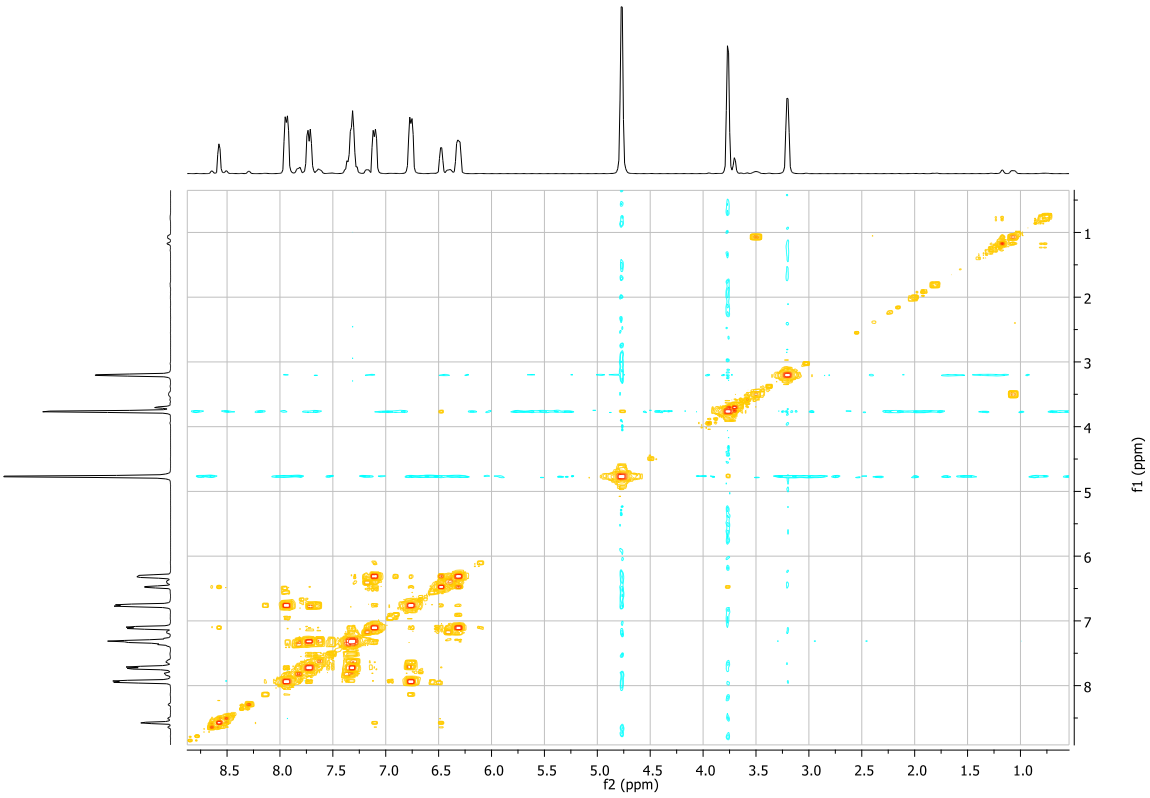

Fig. S12. ^{1}H/^{1}H COSY spectrum of compound **3**

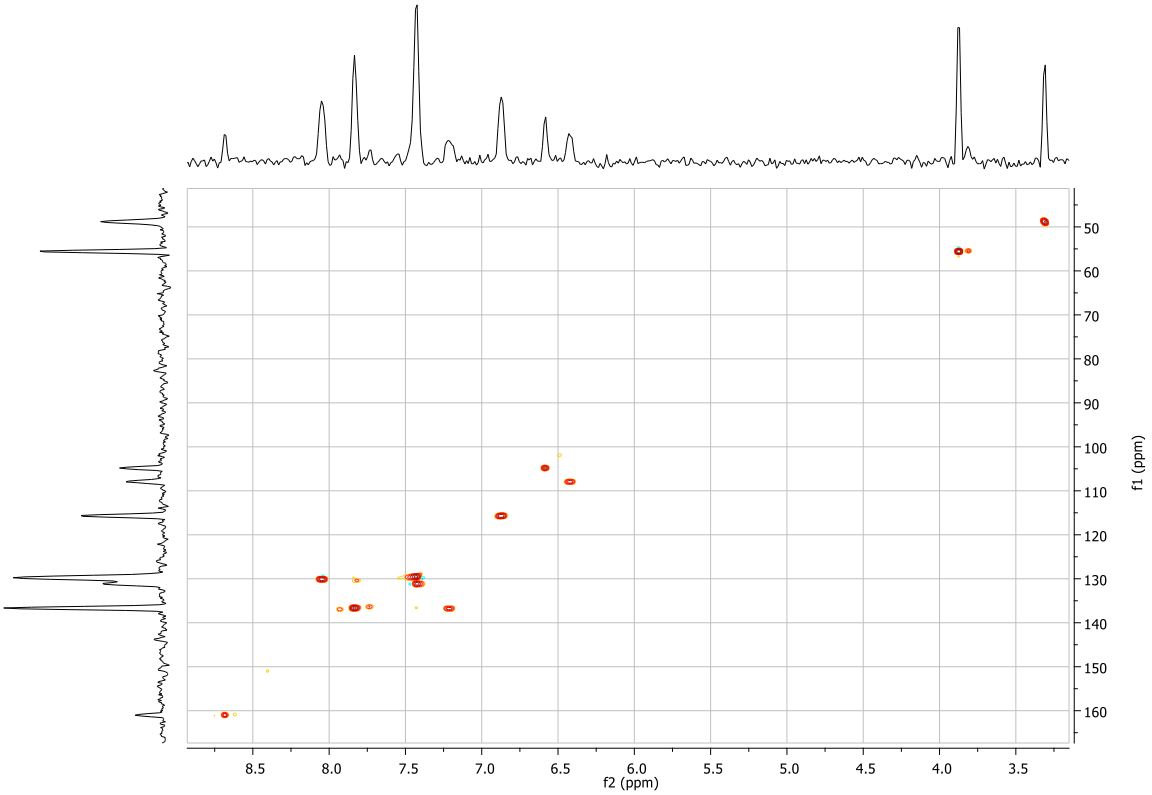

Fig. S13. $^{1}H/^{13}C$ HETCOR spectrum of compound **3**

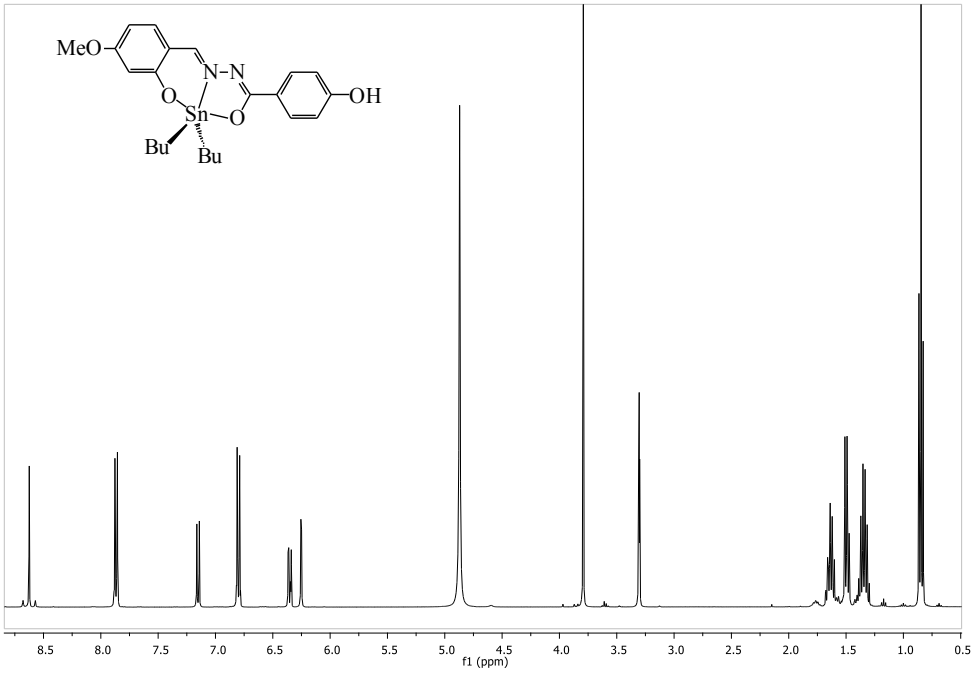

Fig. S14. ^{1}H-NMR (400 MHz, CD_3OD. 298 K) spectrum of compound **4**.

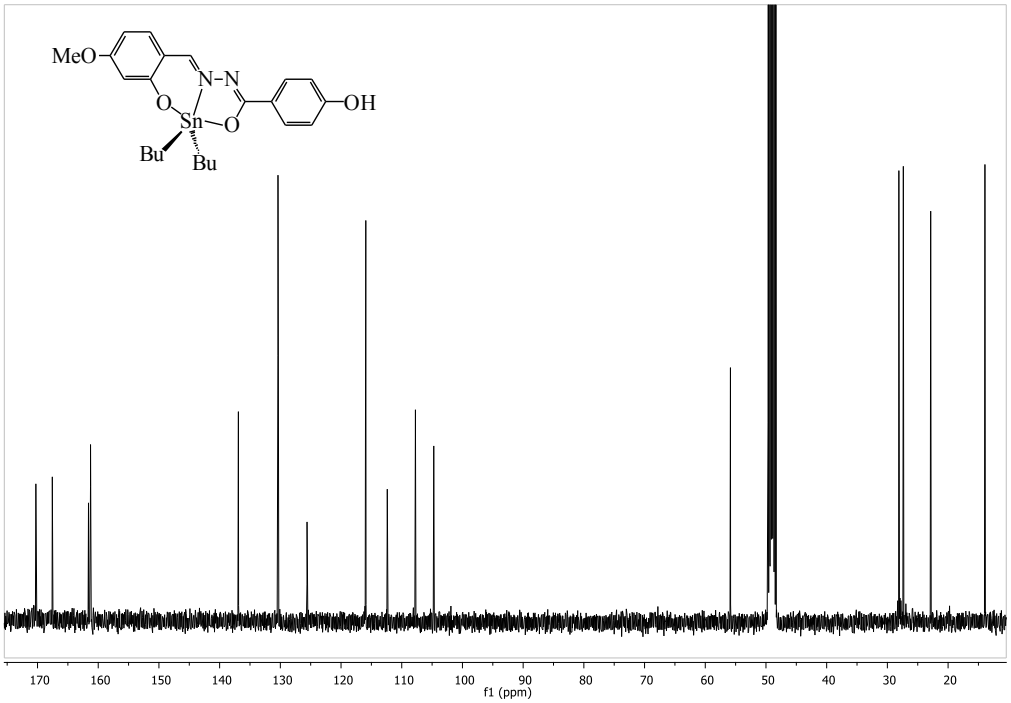

Fig. S15. ^{13}C-NMR (100 MHz, CD_3OD. 298 K) spectrum of compound **4**.

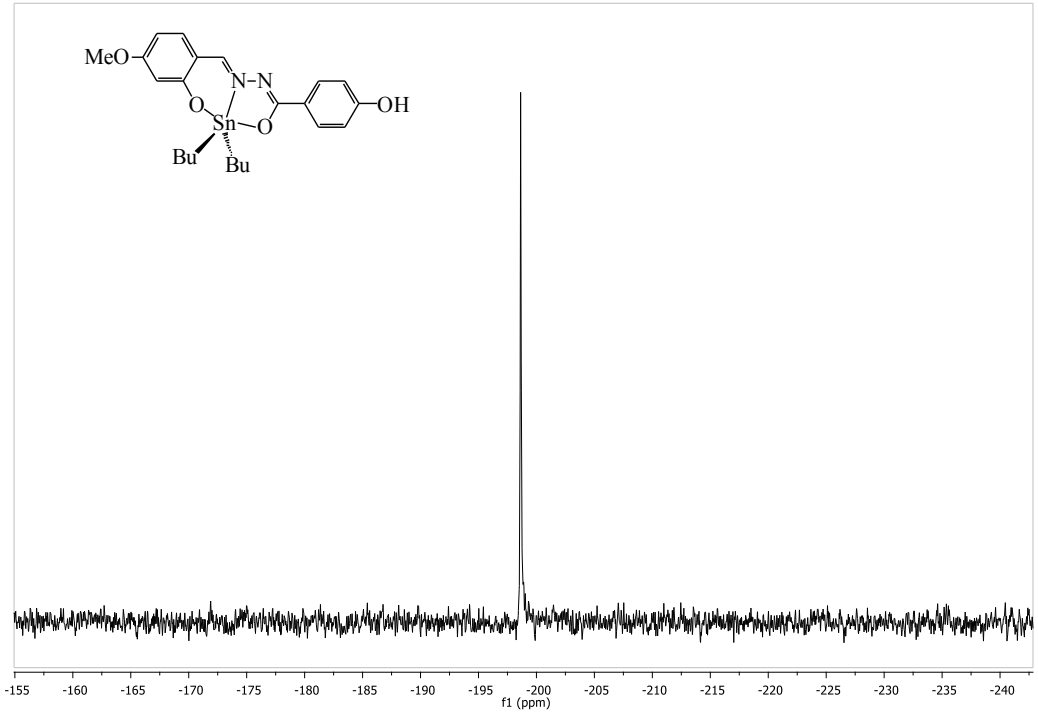

Fig. S16. ^{119}Sn-NMR (149 MHz, CD_3OD. 298 K) spectrum of compound **4**.

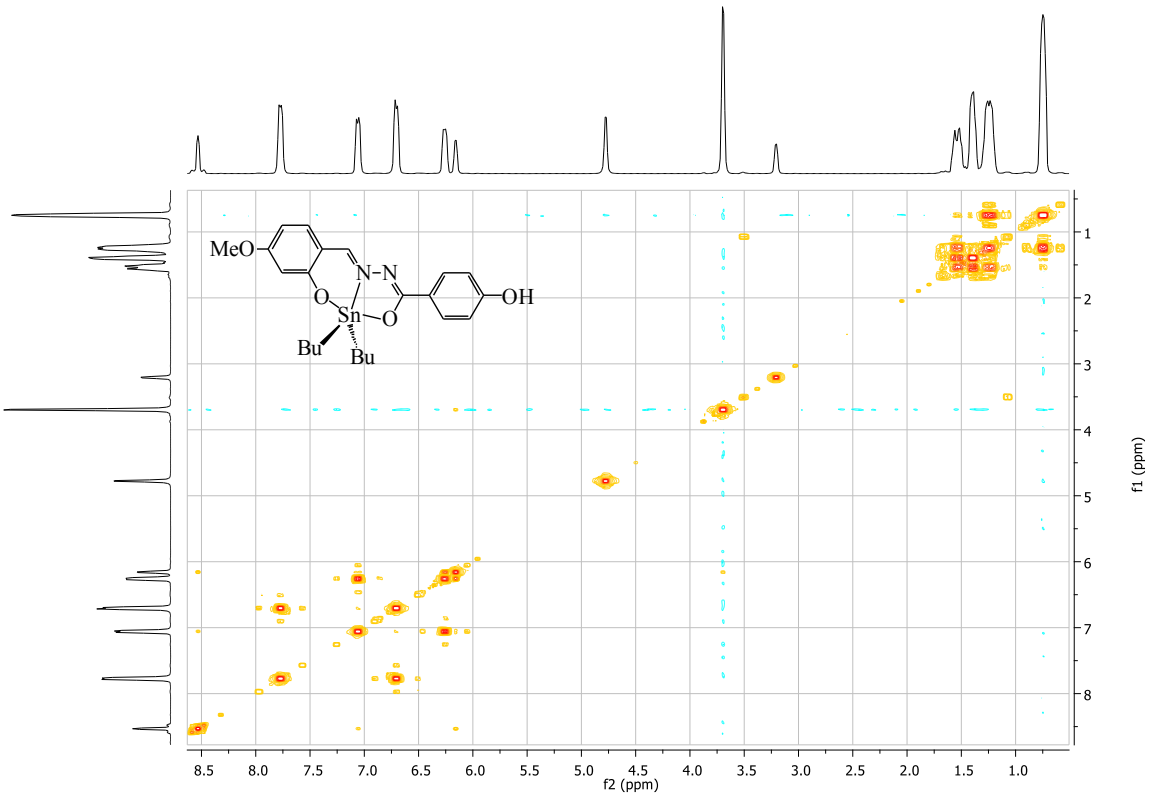

Fig. S17. $^{1}H/^{1}H$ COSY spectrum of compound **4.**

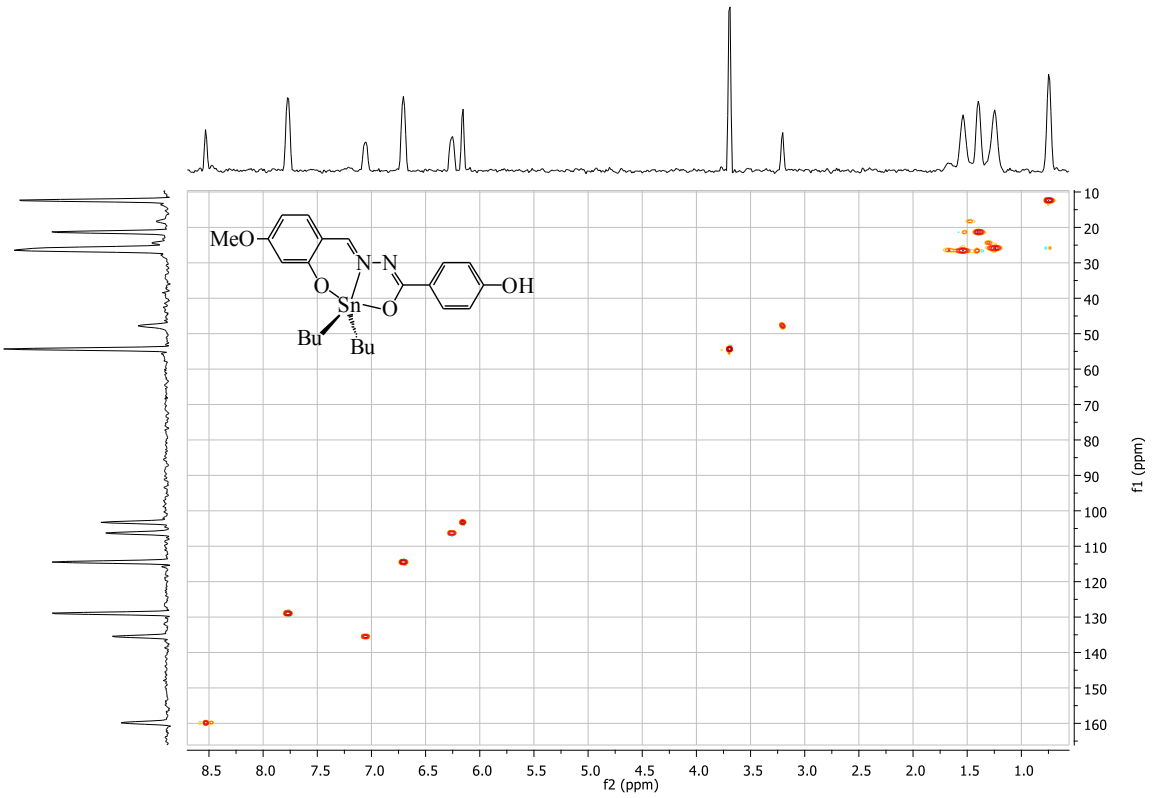

Fig. S18. $^{1}H/^{13}C$ HETCOR spectrum of compound **4.**

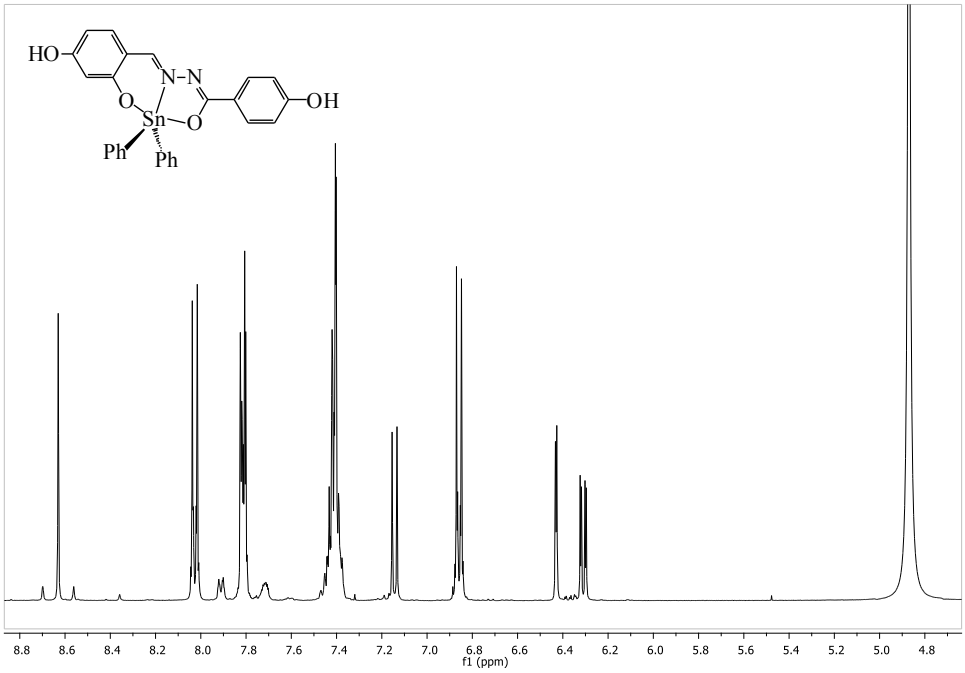

Fig. S19. ^{1}H-NMR (400 MHz, CD_3OD. 298 K) spectrum of compound **5**.

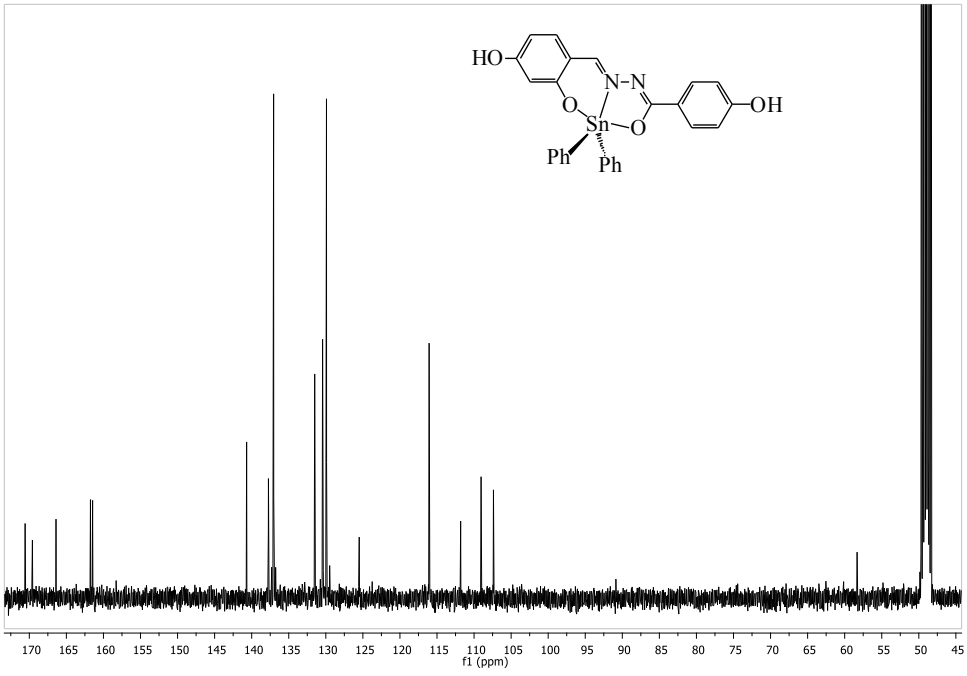

Fig. S20. ^{13}C-NMR (100 MHz, CD_3OD. 298 K) spectrum of compound **5**.

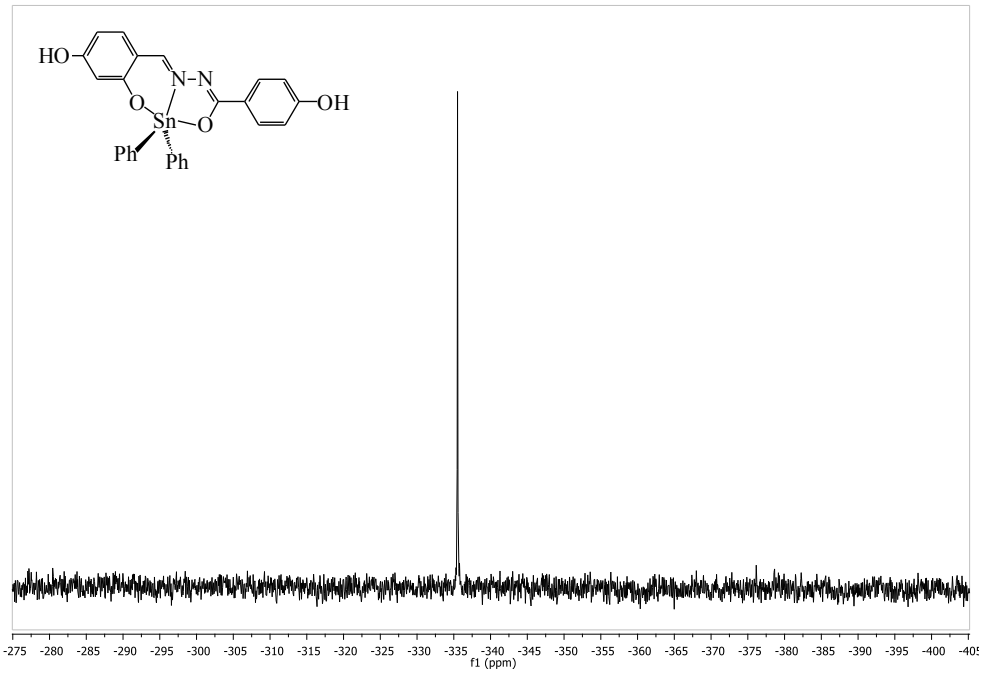

Fig. S21. ^{119}Sn-NMR (149 MHz, CD_3OD. 298 K) spectrum of compound **5**.

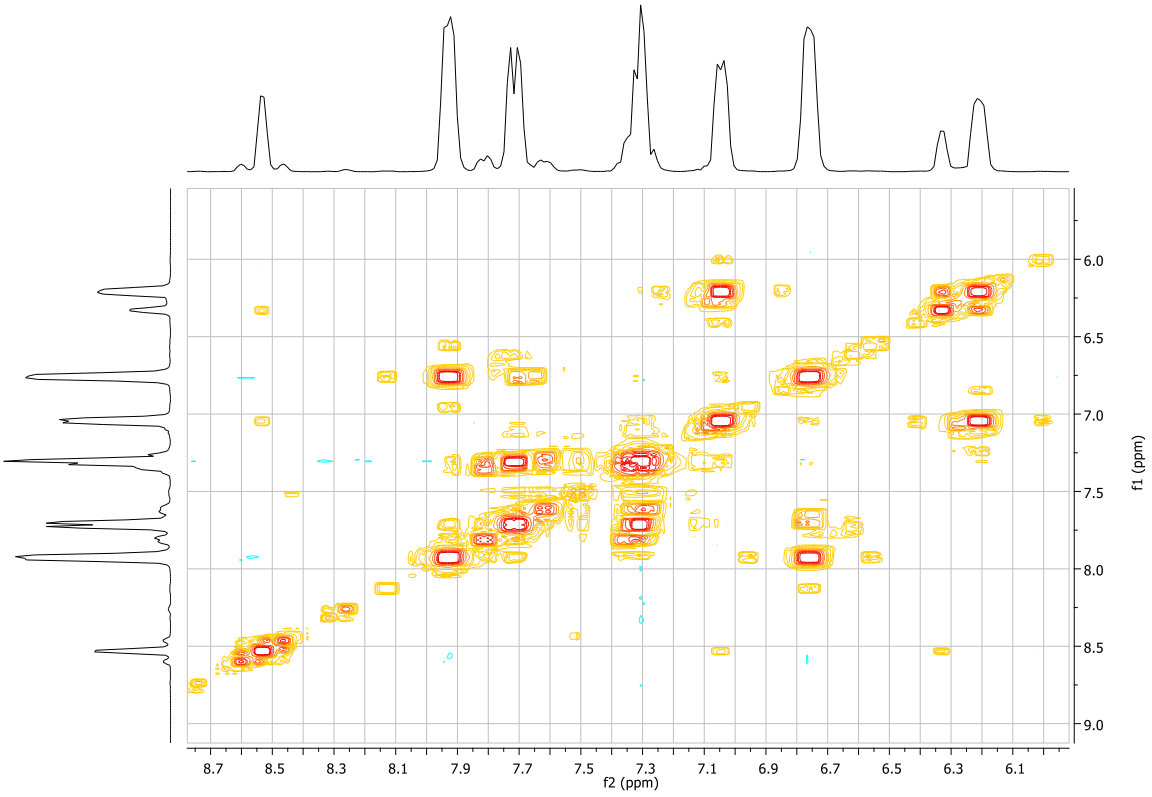

Fig. S22. ^{1}H/^{1}H COSY spectrum of compound **5.**

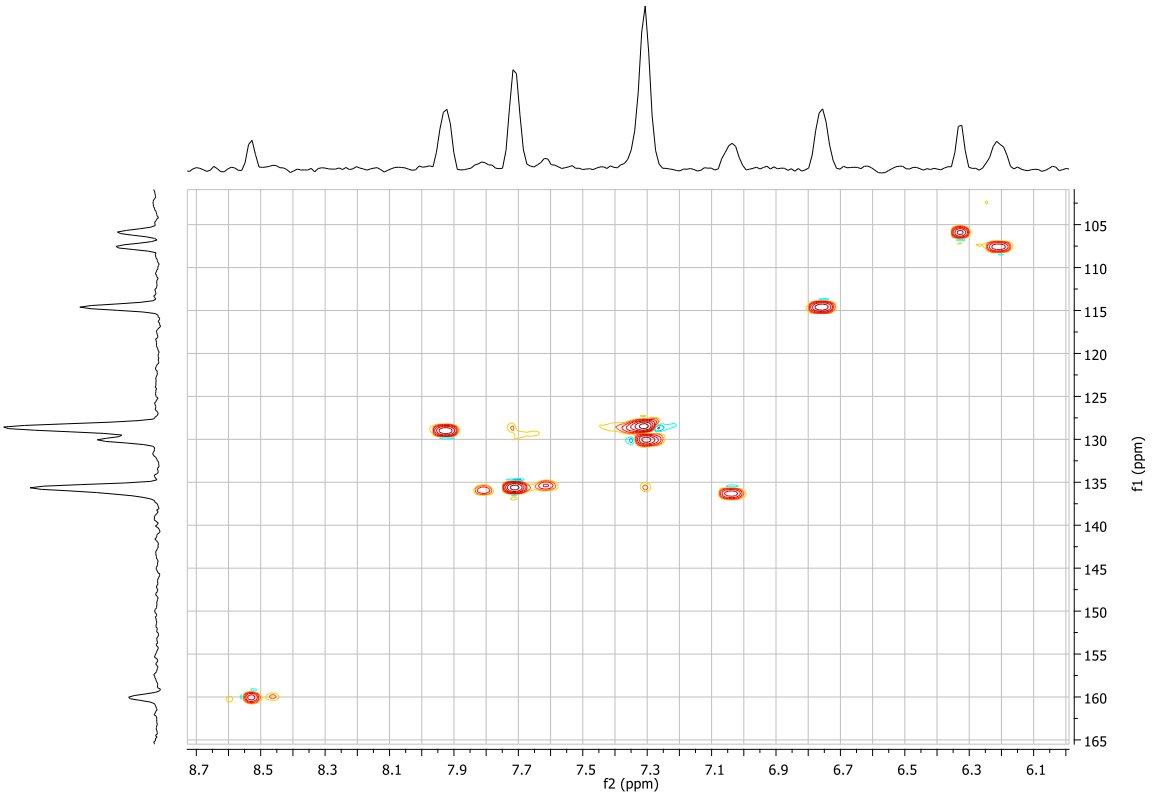

Fig. S23. $^{1}H/^{13}C$ HETCOR spectrum of compound **5.**

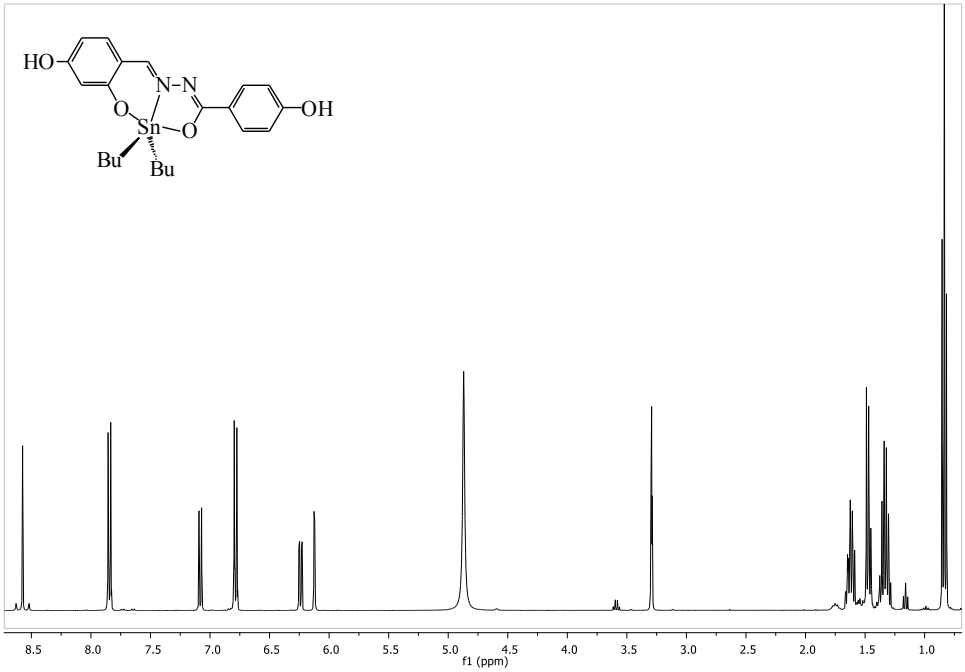

Fig. S24. ^{1}H-NMR (400 MHz, CD_3OD. 298 K) spectrum of compound **6**.

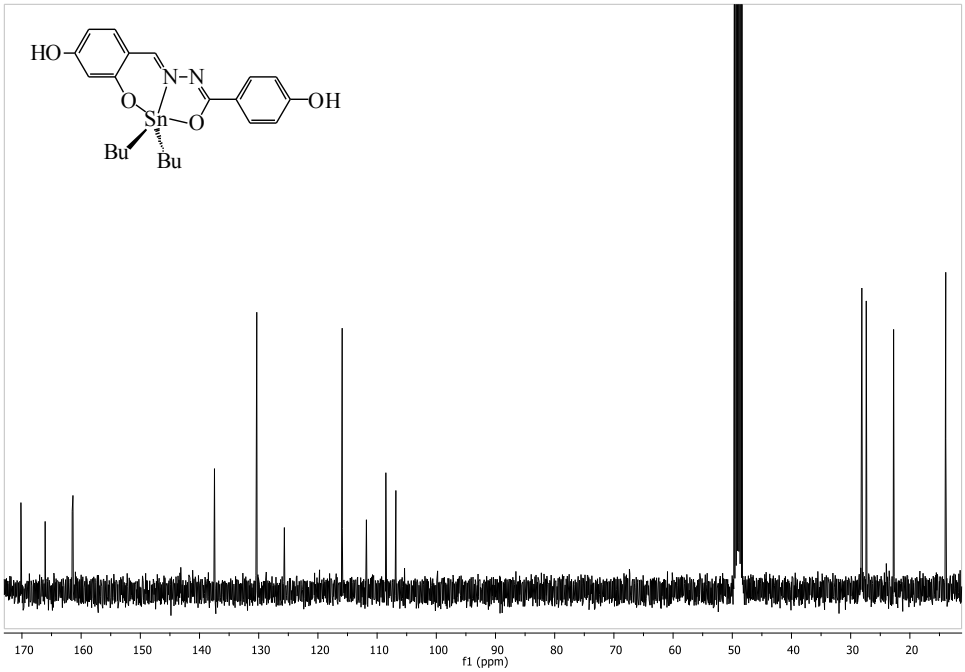

Fig. S25. ^{13}C-NMR (100 MHz, CD_3OD. 298 K) spectrum of compound **6**.

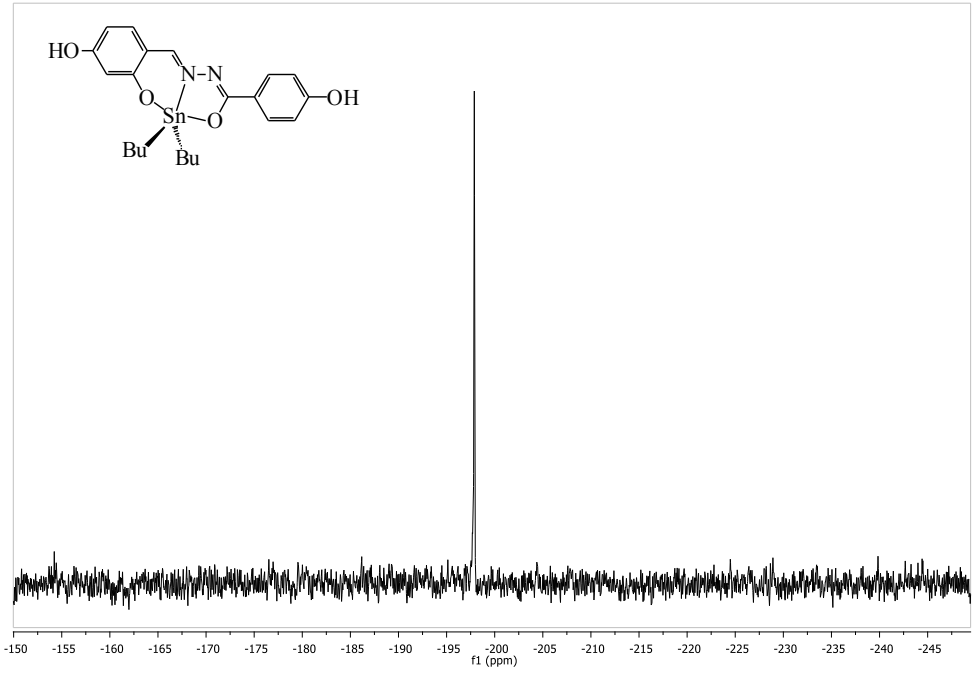

Fig. S26. ^{119}Sn-NMR (149 MHz, CD_3OD. 298 K) spectrum of compound **6**.

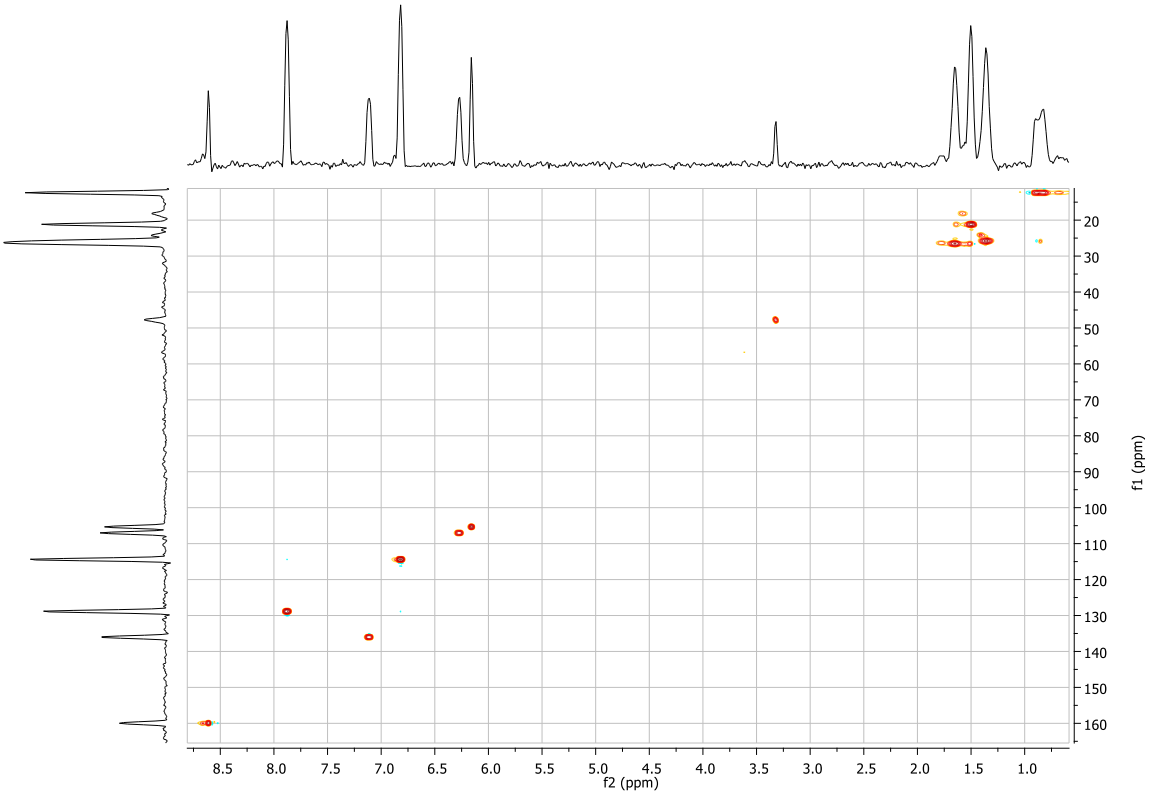

Fig. S27. $^{1}H/^{1}H$ COSY spectrum of compound **6.**

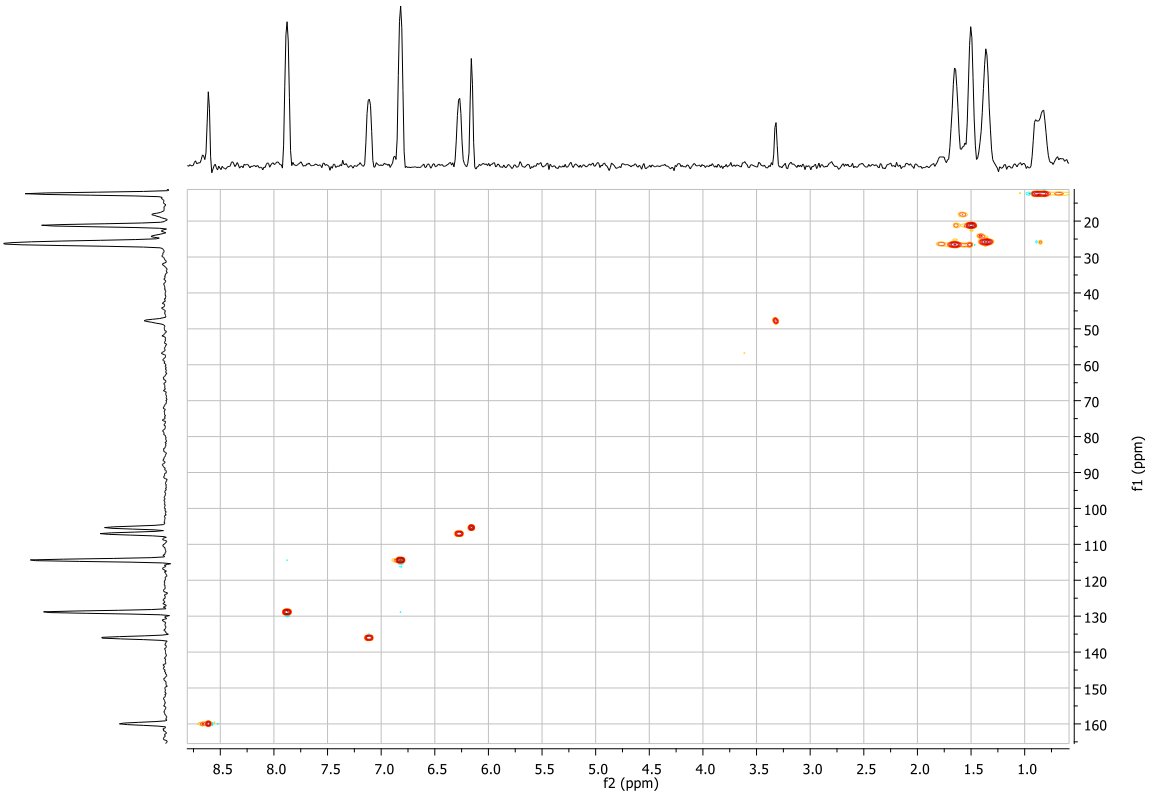

Fig. S28. $^{1}H/^{13}C$ HETCOR spectrum of compound **6.**

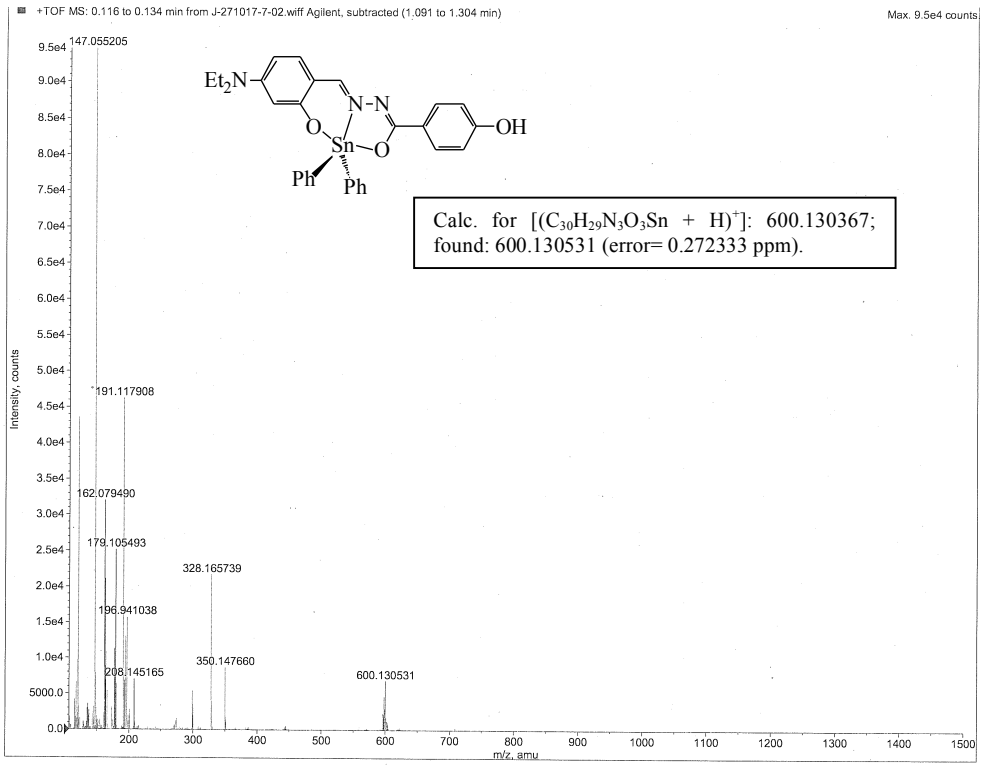

Fig. S29. Mass spectrum of compound **1**.

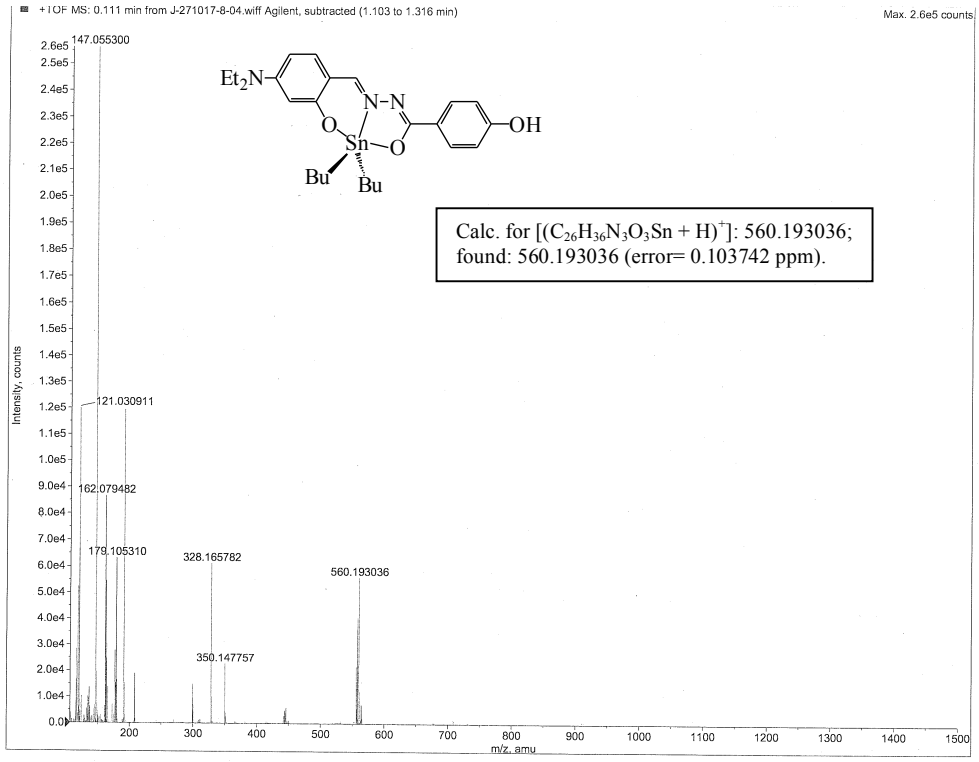

Fig. S30. Mass spectrum of compound **2**.

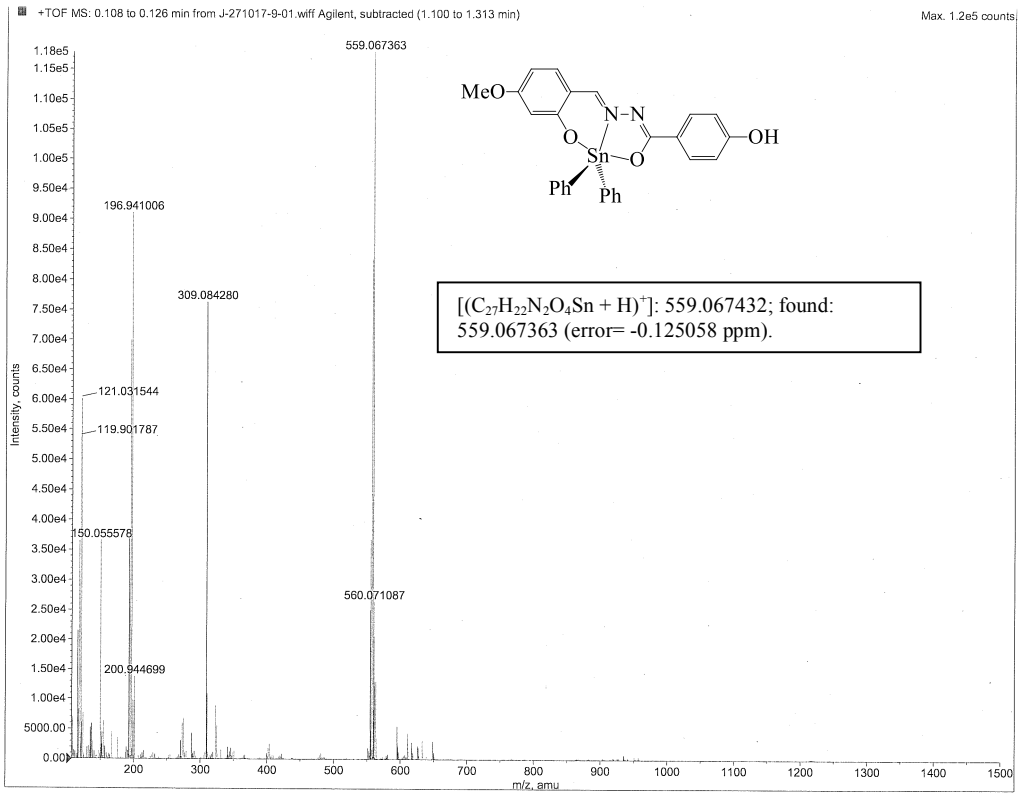

Fig. S31. Mass spectrum of compound **3**.

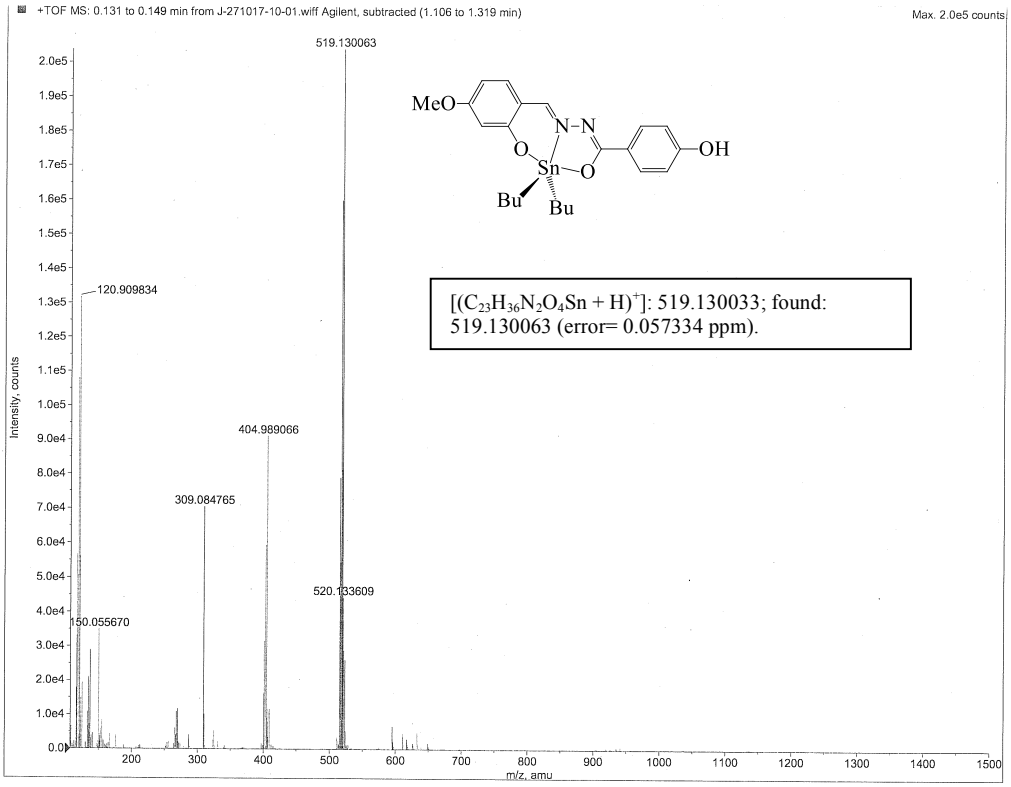

Fig. S32. Mass spectrum of compound **4.**

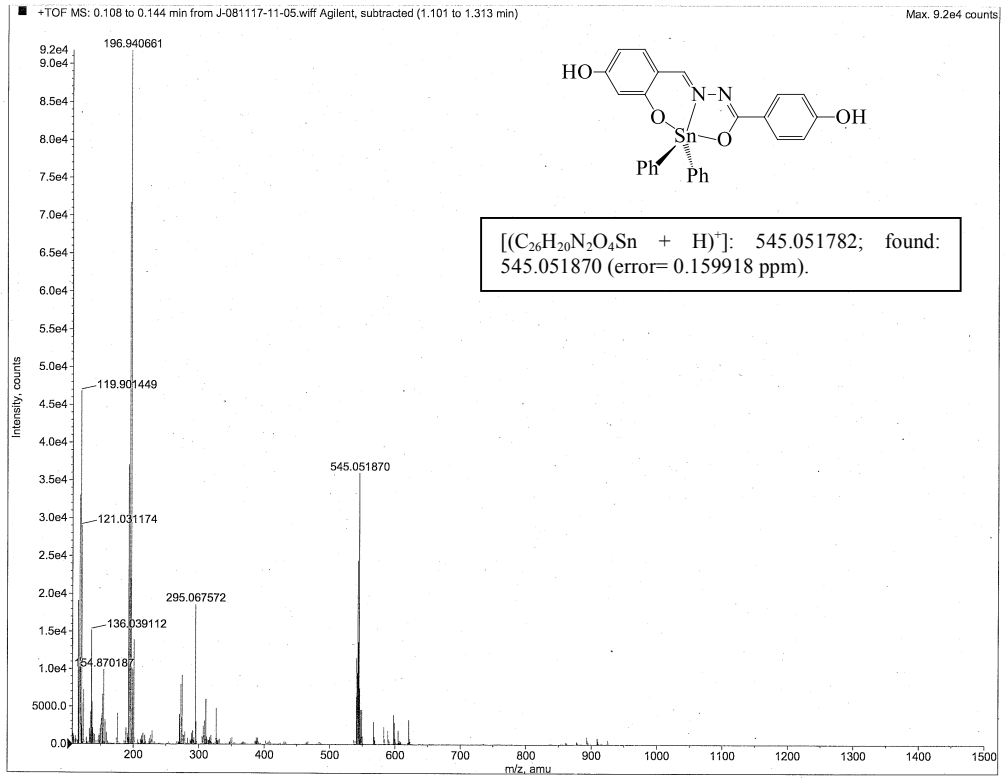

Fig. S33. Mass spectrum of compound **5**.

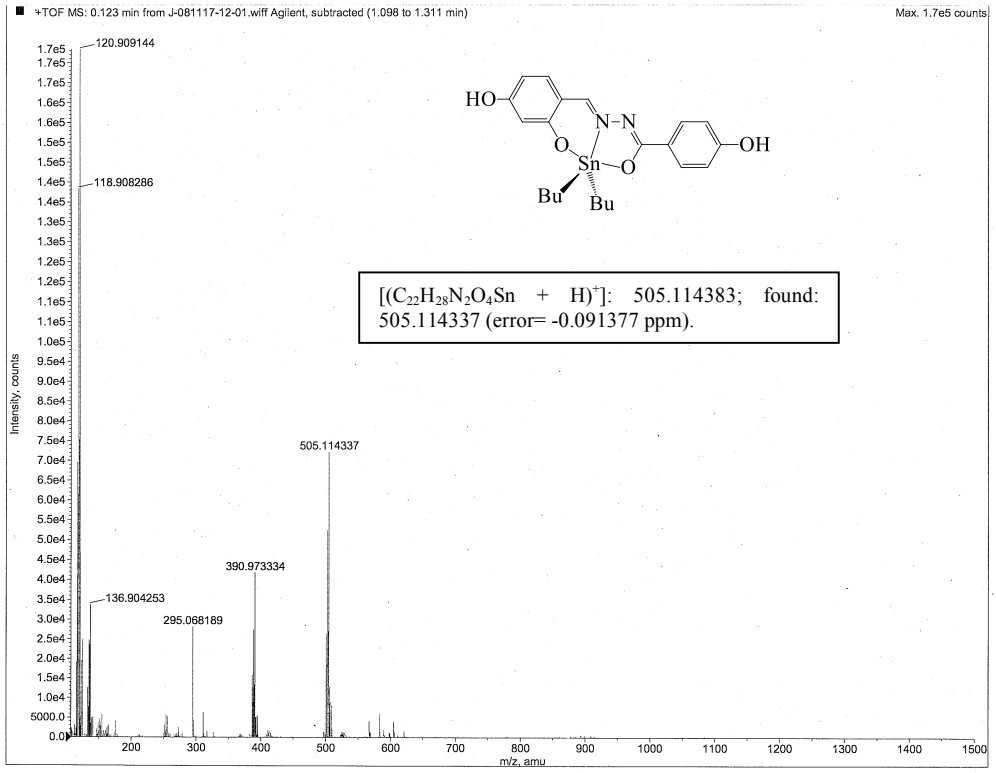

Fig. S34. Mass spectrum of compound **6.**

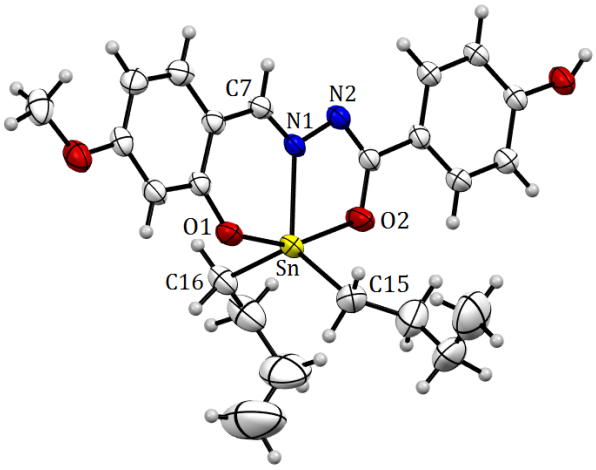

Fig. 35. Crystal structure of **4**. Selected bond distances: Sn-O1 2.134(3), Sn-O2 2.125(3), Sn-N1 2.157(3), Sn-C16 2.106(5), Sn-C20 2.133(4), and N1-C7 1.298(4) Å. Selected angles: O1-Sn-O2 156.91(10), C15-Sn-C16 129.7(2).

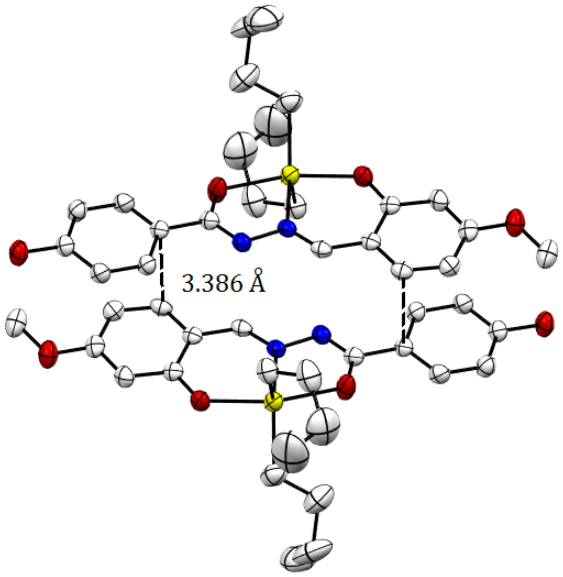

Fig. 36. Crystal structure of **4** with π-π short contacts.

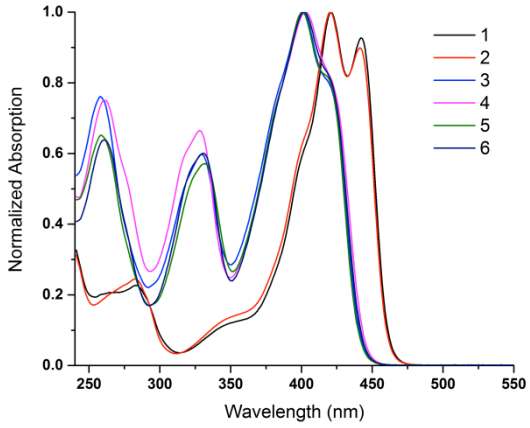

Fig. 37. Electronic absorption spectra of compounds **1-6** in ethanol.

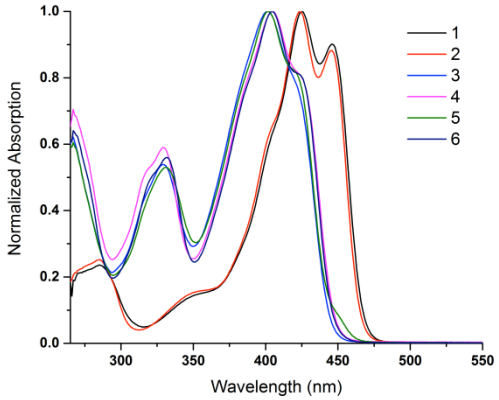

Fig. 38. Electronic absorption spectra of compounds **1-6** in DMF.

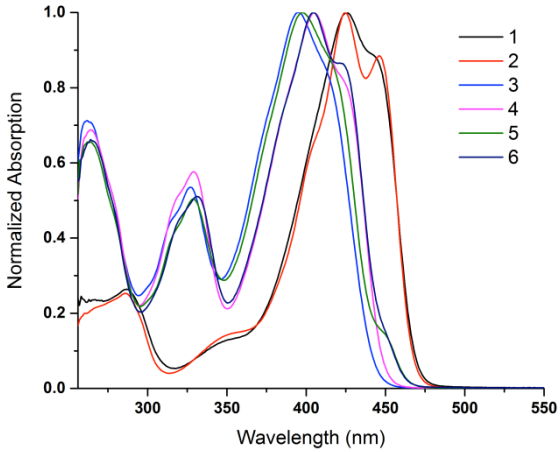

Fig. 39. Electronic absorption spectra of compounds **1-6** in DMSO.

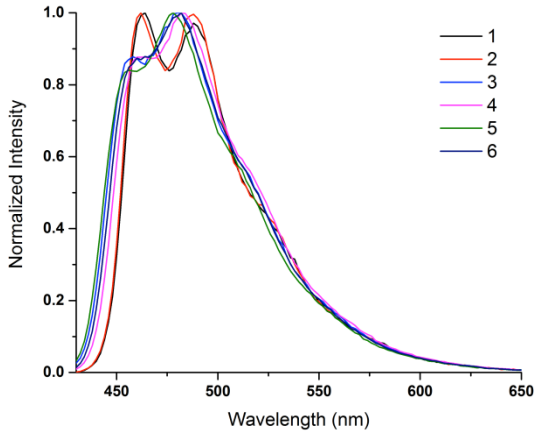

Fig. 40. Emission spectra of compounds **1-6** in ethanol.

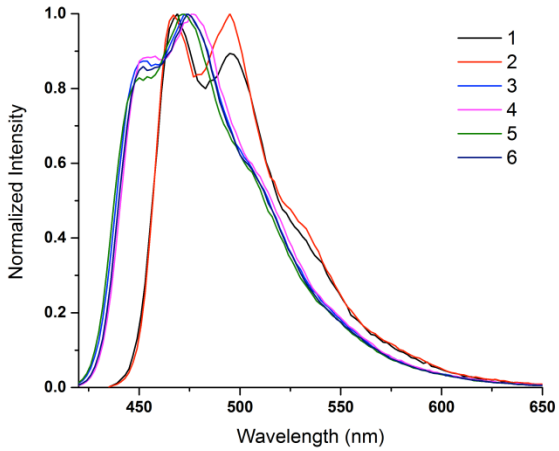

Fig. 41. Emission spectra of compounds **1-6** in DMF.

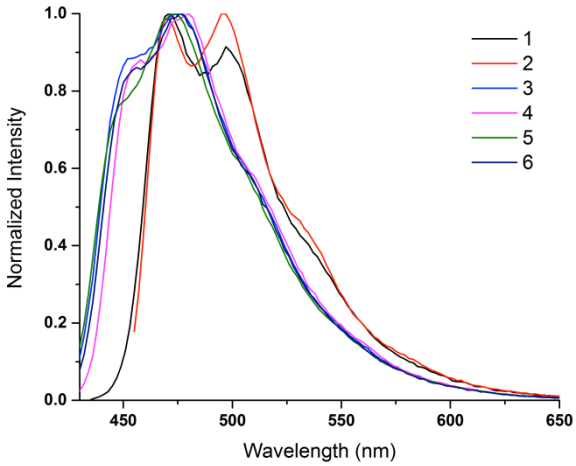

Fig. 42. Emission spectra of compounds **1-6** in DMSO.

Supplementary tables

Table S1. Crystal data for compounds **4** and **5**.

	4	**5**
Empirical formula	$C_{46}H_{56}N_4O_8Sn$	$C_{27}H_{24}N_2O_5Sn$
Formula weight	1030.32	575.17
Temperature, K	293(2)	293(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a, Å	8.297(4)	9.6096(5)
b, Å	14.002(6)	9.8315(6)
c, Å	21.361(11)	14.1654(8)
α	75.003(18) ^{o}	99.520(3)°
β	88.190(15)^{o}	107.064(3)°
γ	81.062(19)^{o}	91.187(3)°
V,Å^3	2368(2)	1258.36(13)
Z	2	2
$\rho_{calc.mg.cm}^{-3}$	1.445	1.518
μ, mm^{-1}	1.108	1.055
2θ range for data collection	2.485-29.629°	2.223-25.075°
Index ranges	-11≤*h*≤11, -19≤*h*≤19, -29≤*h*≤29	-11≤*h*≤11, -11≤*h*≤11, -16≤*h*≤16
No. of reflns collected	173294	22629
No. of indep reflns	13317	4460
[R_{int}]	0.0481	0.0288
Goodness of fit	1.058	1.109
*R*1, w*R*2 (I>2σ(I))	0.0426/0.0934 0.1318	0.0221/0.0549 0.1318
*R*1, w*R*2 (all data)	0.0752/0.1138 0.1387	0.0264/0.0566 0.1387

Table S2. Photophysical properties of compounds **1-6** in ethanol.

Comp.	λmax[a] [nm]	ε [b]	λem [nm][c]	Φ [%][d	τ [ns][e]	χ2[f]
1	421, 442	6.08	464, 488	17	2.00	1.07
2	421, 442	6.59	462, 488	17	1.94	0.98
3	330, 401	2.50	458, 480	28	1.88	0.97
4	328, 403	2.60	462, 482	28	1.91	1.01
5	332, 401	2.69	456, 478	23	1.67	1.07
6	330, 402	3.20	460, 482	23	1.69	1.02

[a] Absorption maxima. [b] Extinction coefficient at longest wavelength in units of 10^4 $M^{-1}cm^{-1}$.[c] Emission maximum. [d] emission quantum yield (366 nm). [e] fluorescence lifetime (430 nm). [f] decay fit parameter.

Table S3. Photophysical properties of compounds **1-6** in DMF.

Comp.	λ_{max}[a] [nm]	ε [b]	λ_{em} [nm][c]	Φ [%][d	τ [ns][e]	χ^2[g]
1	425, 446	4.59	469, 495	13	1.97	0.97
2	424, 446	4.84	467, 495	19	1.96	0.98
3	329, 401	2.42	452, 473	31	1.91	0.99
4	330, 405	3.02	452, 476	25	2.00	0.96
5	331, 402	2.38	450, 472	25	1.71 (0.60)[f] [0.6190] 0.19 (0.40)	0.97
6	332, 405	2.38	452, 474	26	1.83	1.12

[a] Absorption maxima. [b] Extinction coefficient at longest wavelength in units of 10^4 $M^{-1}cm^{-1}$.[c] Emission maximum. [d] emission quantum yield (366 nm). [e] fluorescence lifetime (430 nm). [f] biexponential fit with fractional amplitude in parentheses [g] decay fit parameter

Table S4. Photophysical properties of compounds **1-6** in DMSO.

Comp.	λmax[a] [nm]	ε [b]	λem [nm][c]	Φ [%][	τ [ns][e]	χ2[g]
1	425, 443	4.06	471, 497	20	1.92	1.03
2	424, 446	4.24	469, 495	20	1.92	1.06
3	327, 395	2.51	452, 476	34	1.89	0.97
4	329, 405	3.11	458, 480	27	1.67	1.01
5	329, 398	2.34	472	20	1.71 (0.60)[f] 0.28 (0.40)	0.98
6	331, 405	2.60	456, 476	20	1.67 0.62 (0.16)	0.99

[a] Absorption maxima. [b] Extinction coefficient at longest wavelength in units of 10^4 $M^{-1}cm^{-1}$.[c] Emission maximum. [d] emission quantum yield (366 nm). [e] fluorescence lifetime (430 nm). [f] biexponential fit with amplitude in parentheses [g] decay fit parameter

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