Supplementary Material

Fischer carbene complexes of cobalt(I): synthesis and structure

Mmushi M. Moeng,[a] Frederick P. Malan,[a] Simon Lotz,[a] and Daniela I. Bezuidenhout*[b]

[a] *Department of Chemistry, University of Pretoria, Private Bag X20, Hatfield 0028, Pretoria, South Africa*
[b] *Laboratory of Inorganic Chemistry, Environmental and Chemical Engineering, University of Oulu, P. O. Box 3000, 90014 Oulu, Finland*
*Email: daniela.bezuidenhout@oulu.fi

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S1. ^{1}H and ^{13}C NMR spectra

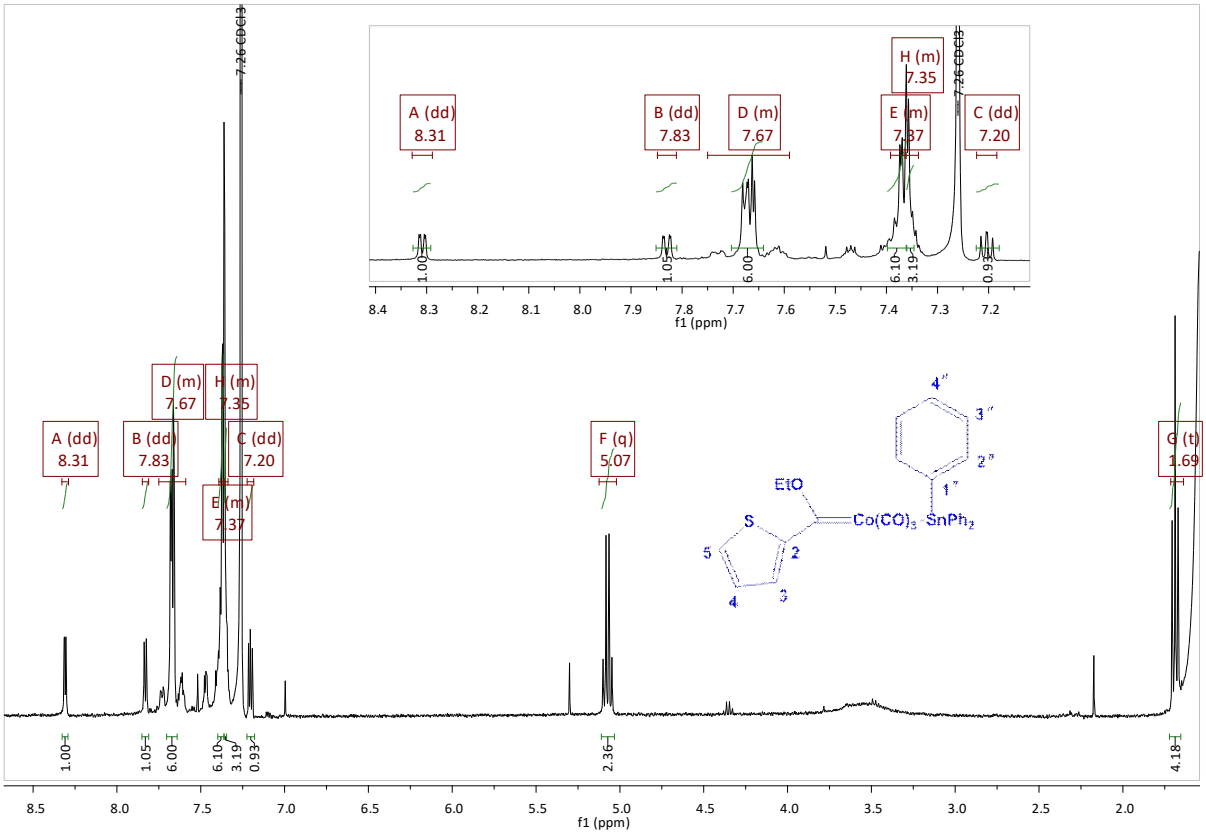

Fig. S1 ^{1}H NMR spectrum of **1** in $CDCl_3$

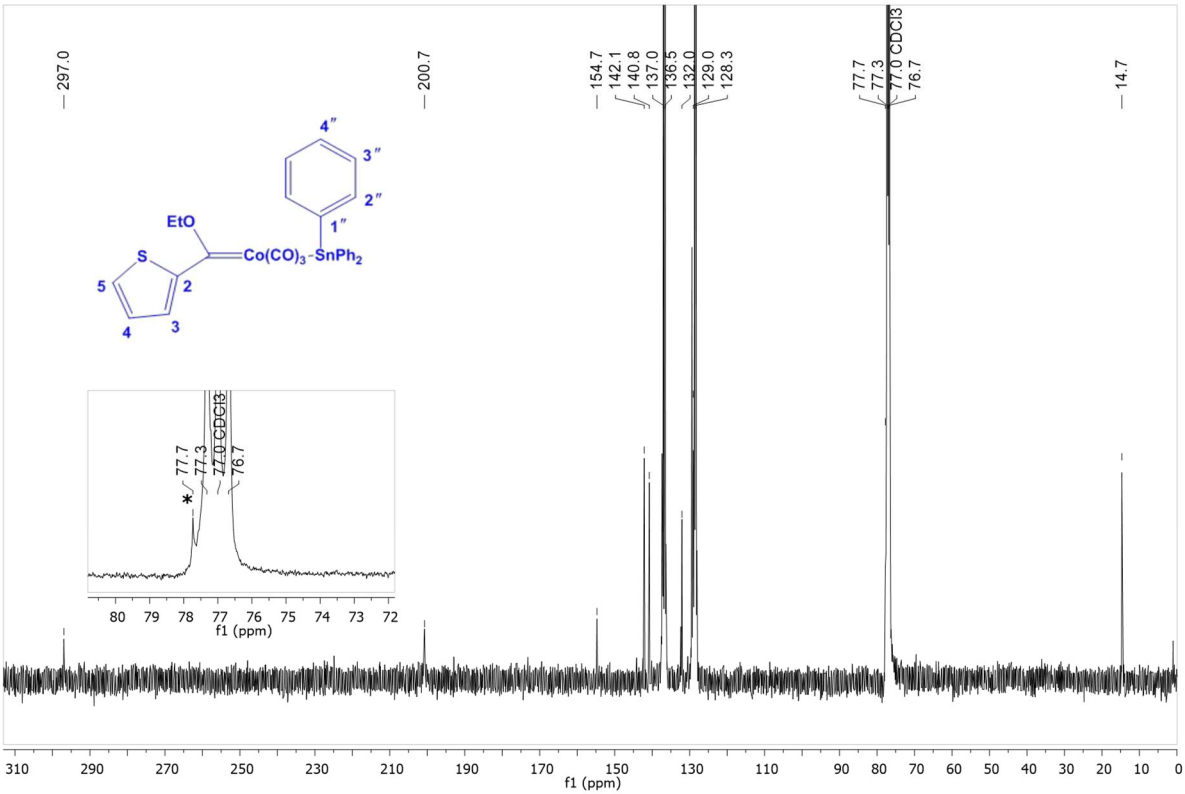

Fig. S2 ^{13}C NMR spectrum of **1** in $CDCl_3$ (*CH_2)

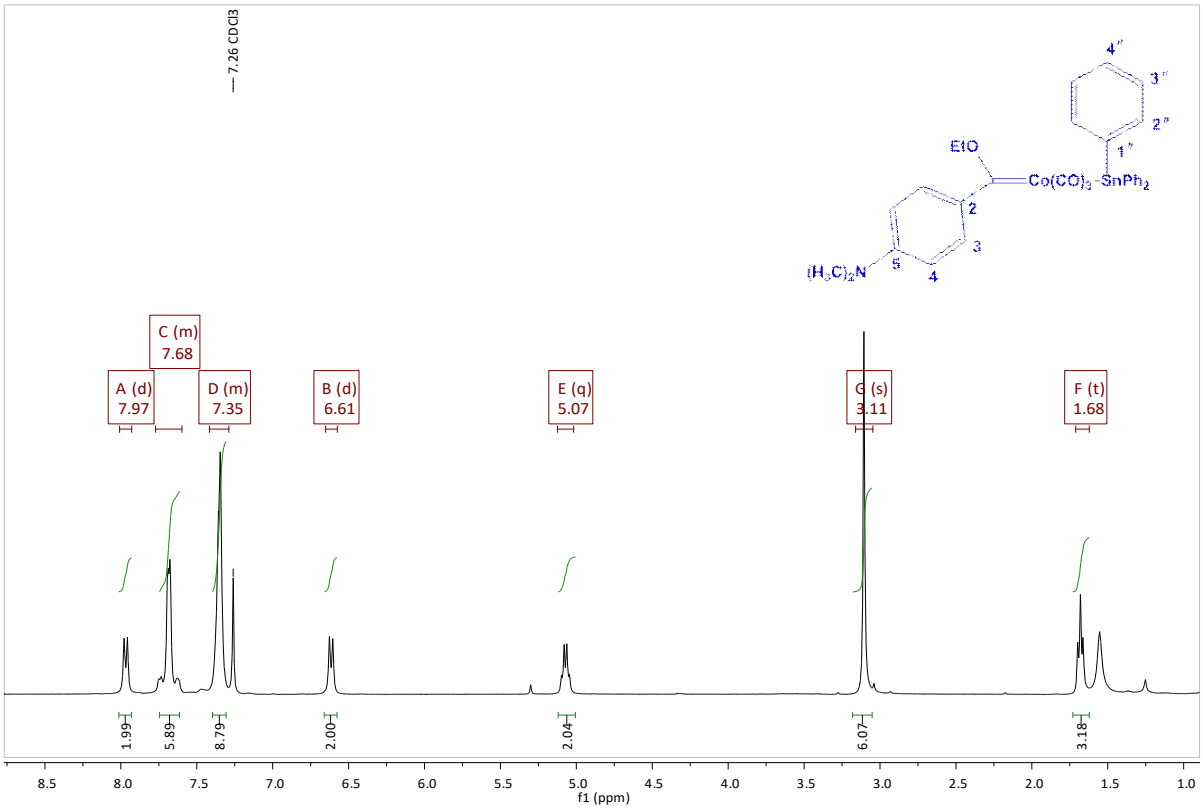

Fig. S3 ^{1}H NMR spectrum of **2** in $CDCl_3$

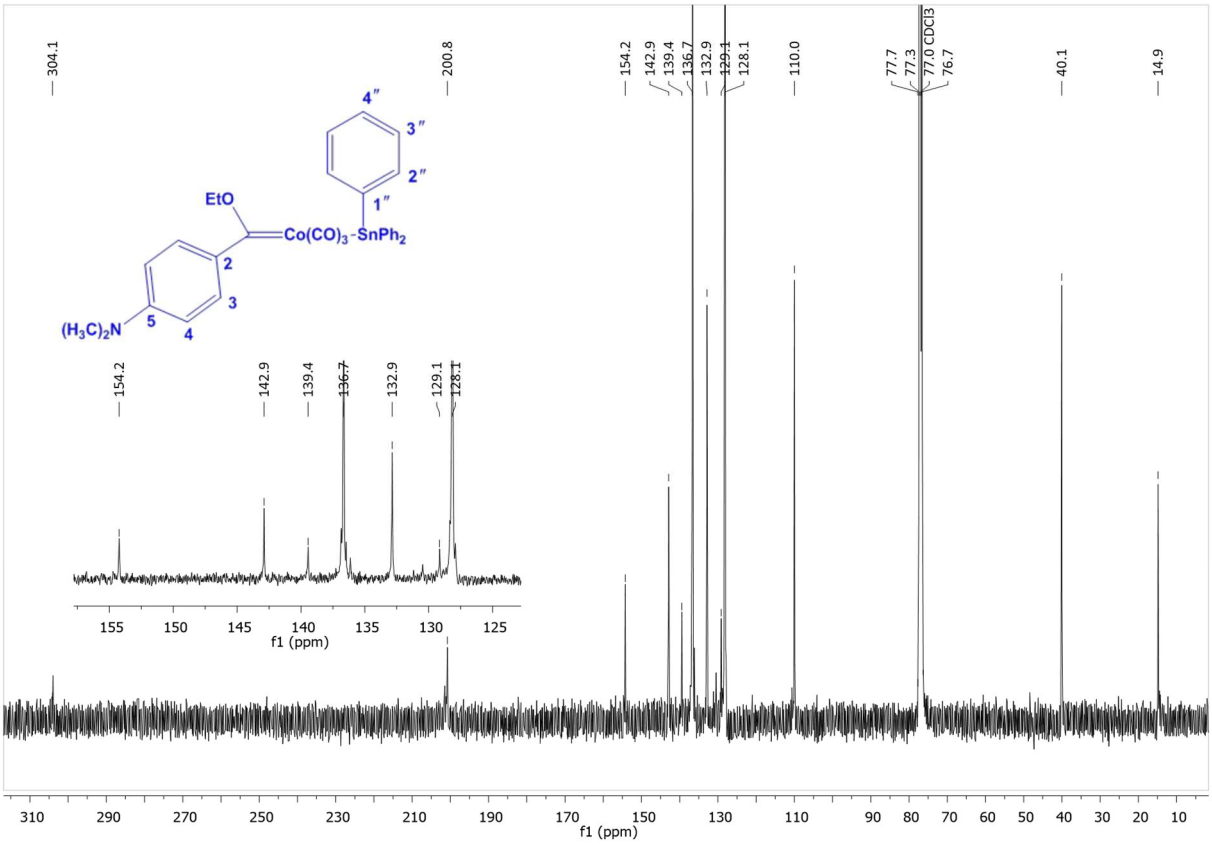

Fig. S4 ^{13}C NMR spectrum of **2** in $CDCl_3$

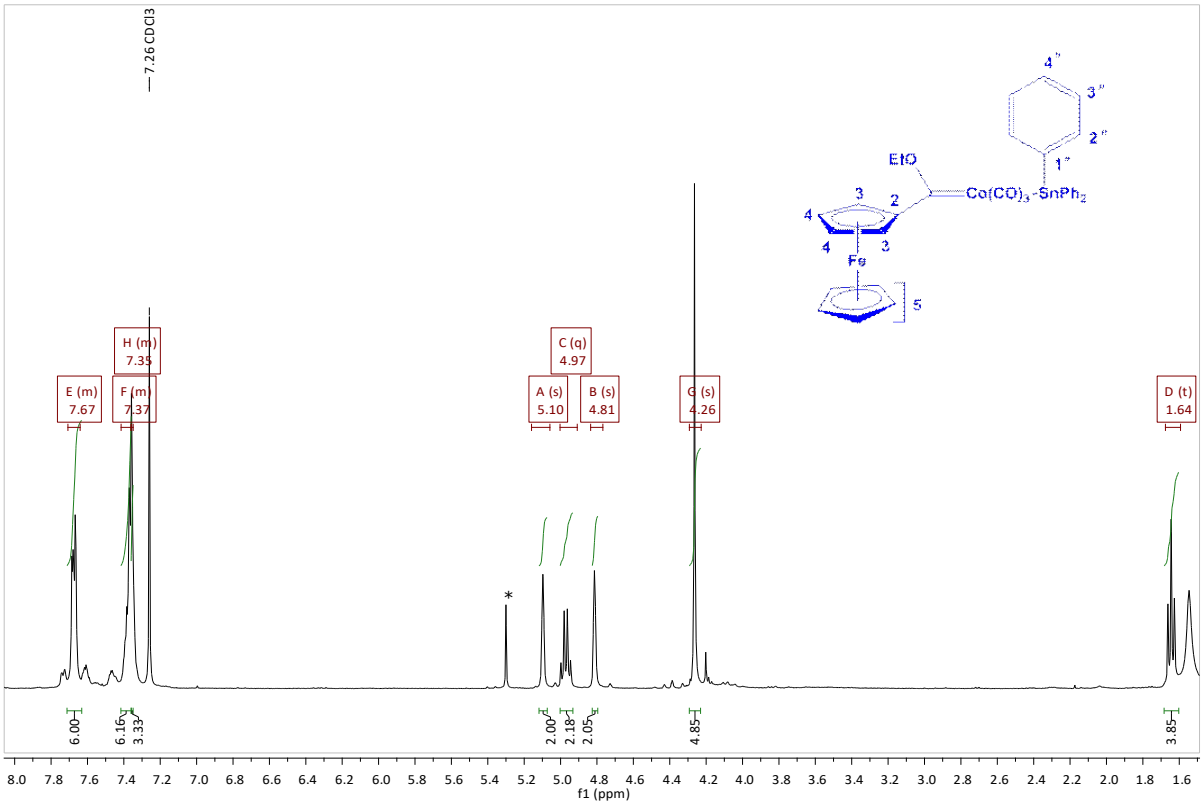

Fig. S5 ^{1}H NMR spectrum of **3** in $CDCl_3$ (* dichloromethane)

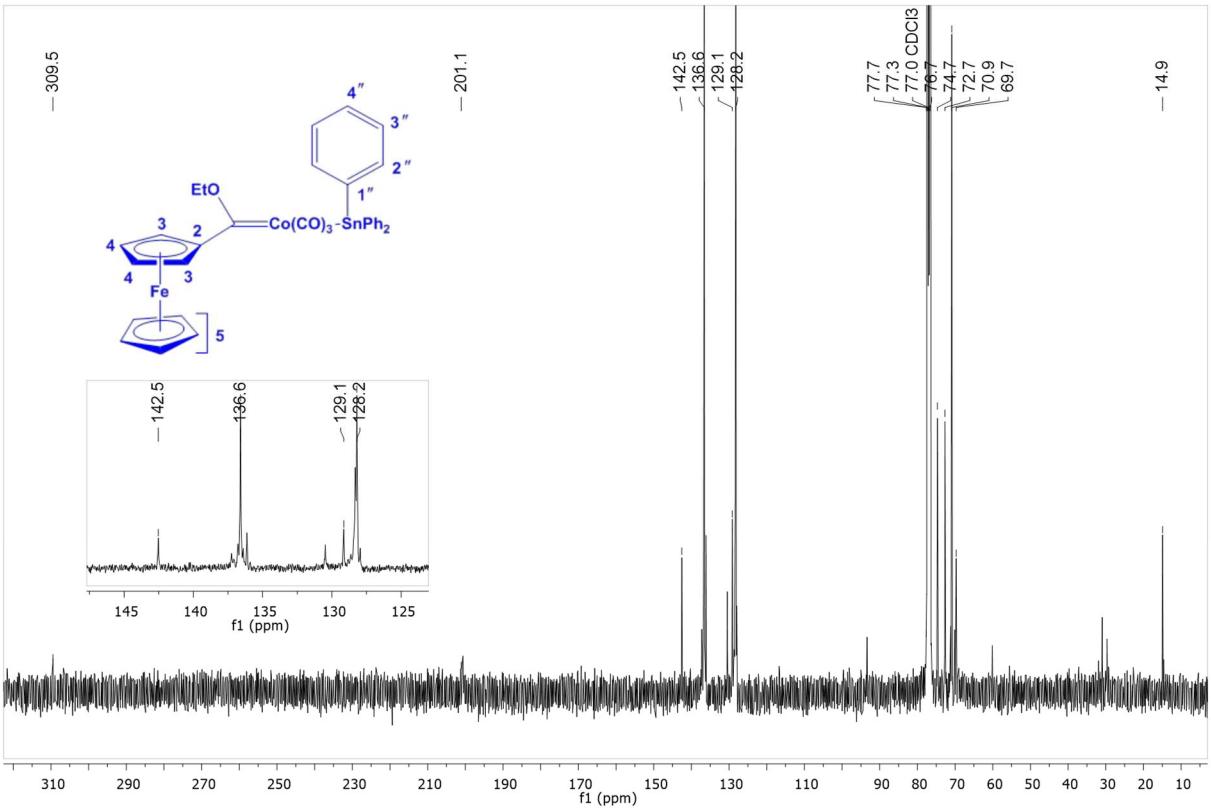

Fig. S6 ^{13}C NMR spectrum of **3** in $CDCl_3$

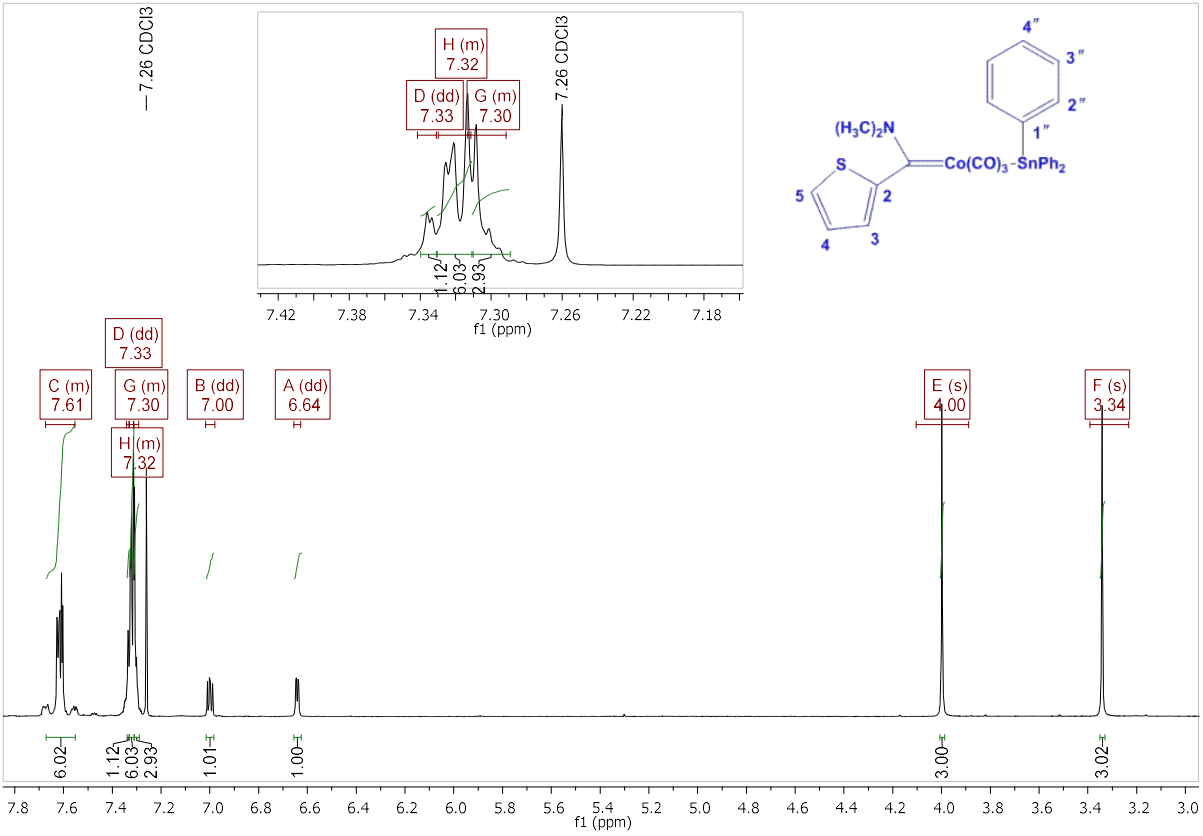

Fig. S7 ^{1}H NMR spectrum of **4** in $CDCl_3$

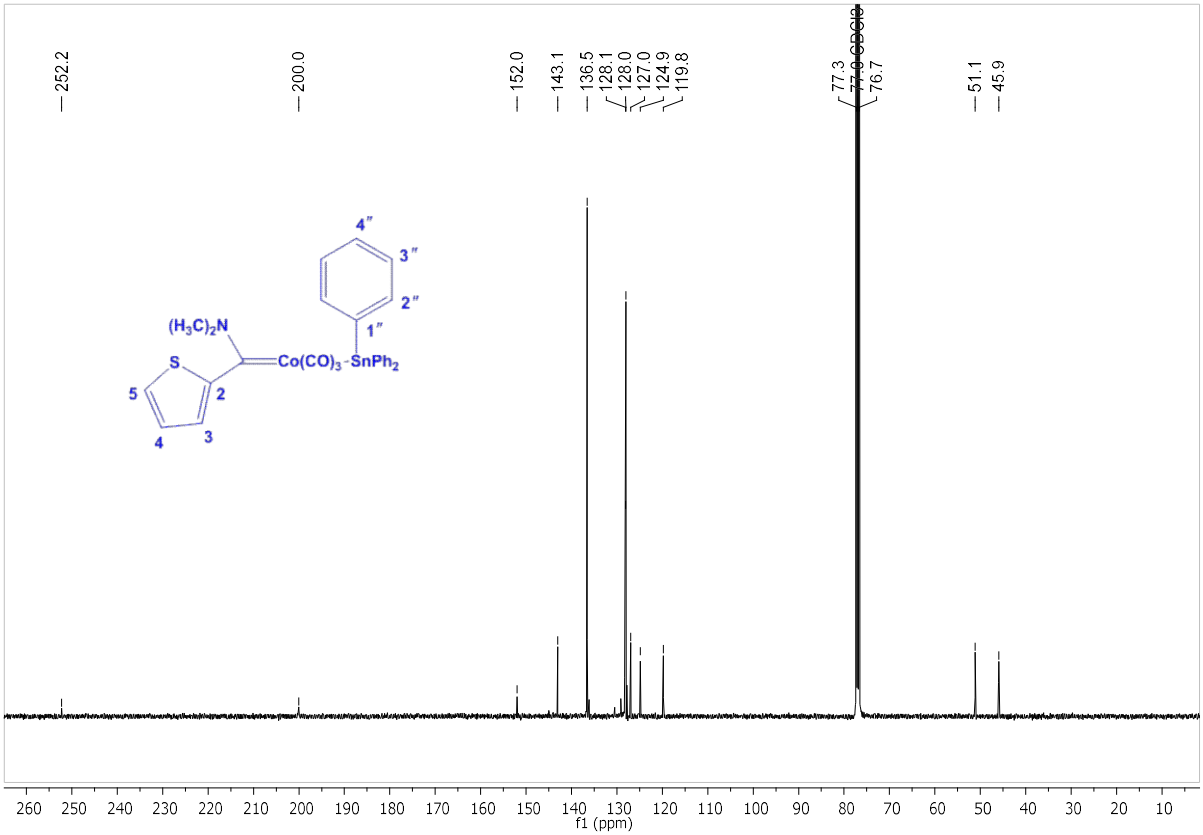

Fig. S8 ^{13}C NMR spectrum of **4** in $CDCl_3$

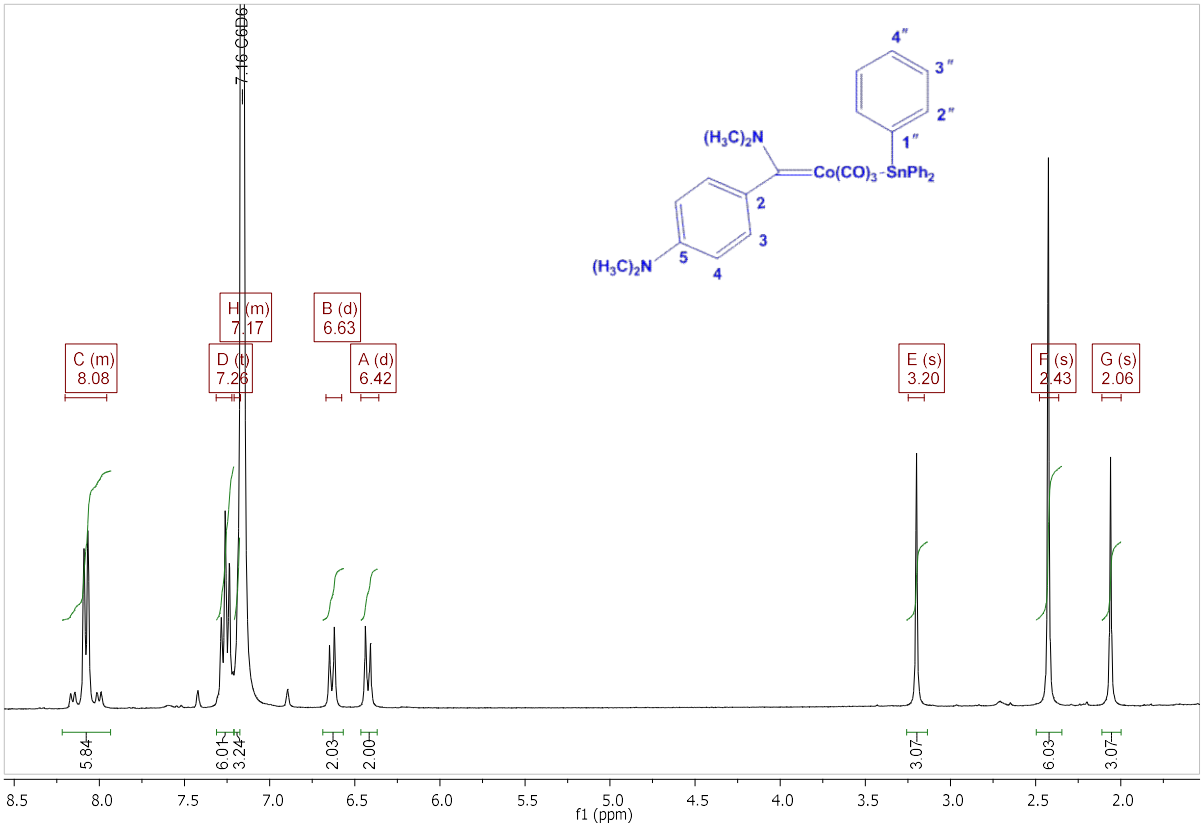

Fig. S9 ^{1}H NMR spectrum of **5** in C_6D_6

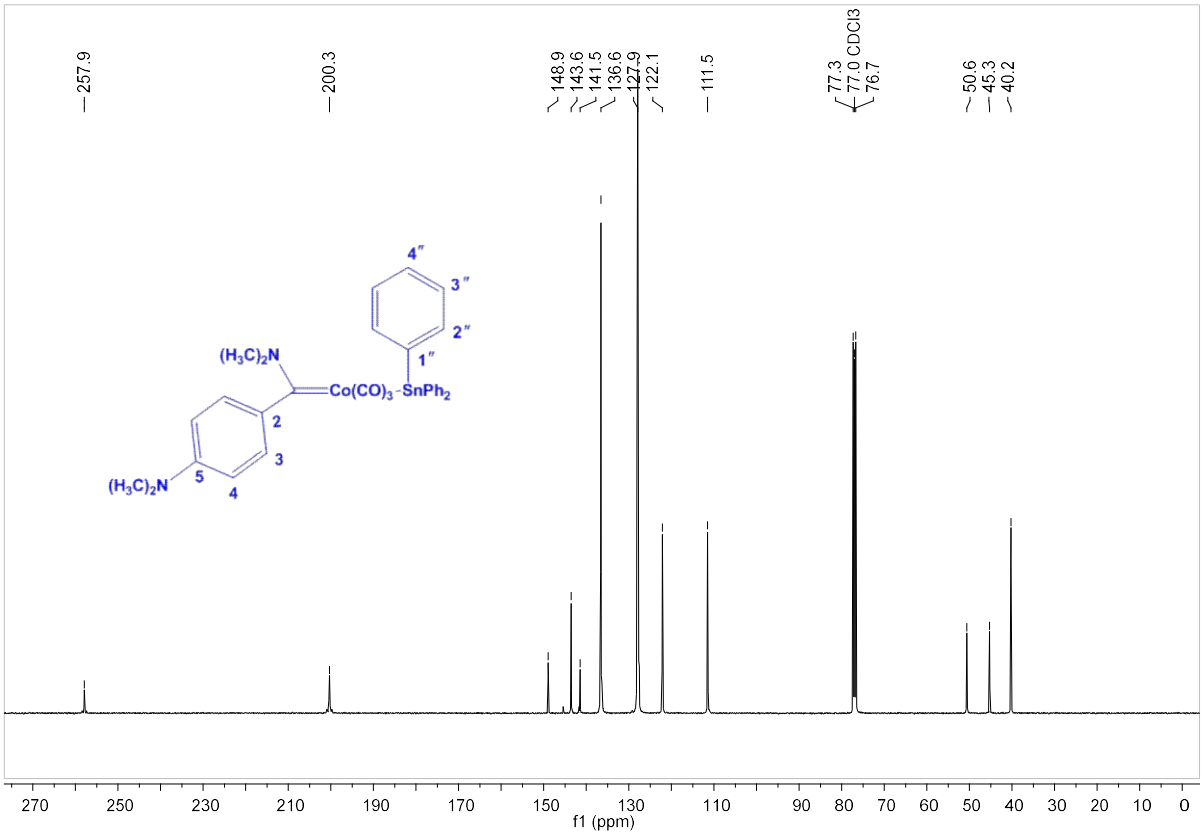

Fig. S10 ^{13}C NMR spectrum of **5** in $CDCl_3$

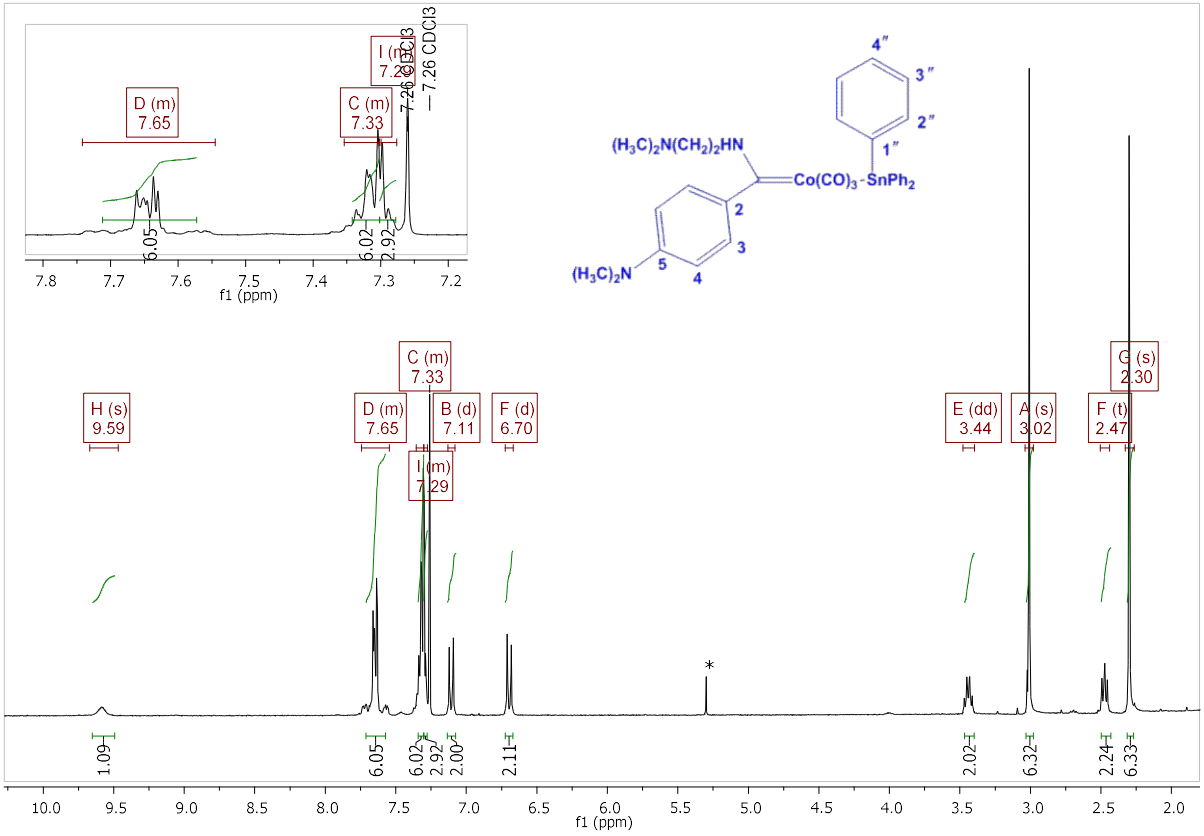

Fig. S11 ^{1}H NMR spectrum of **6** in $CDCl_3$ (*dichloromethane)

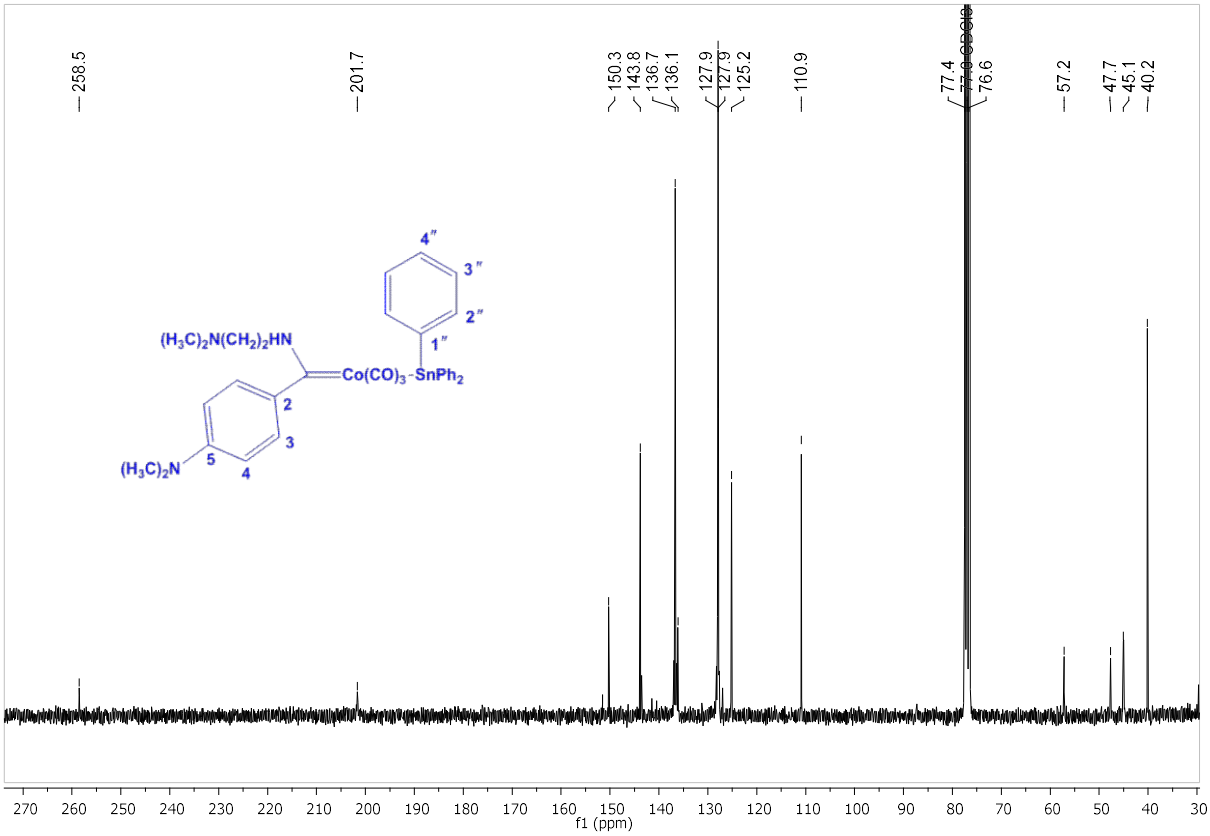

Fig. S12 ^{13}C NMR spectrum of **6** in $CDCl_3$

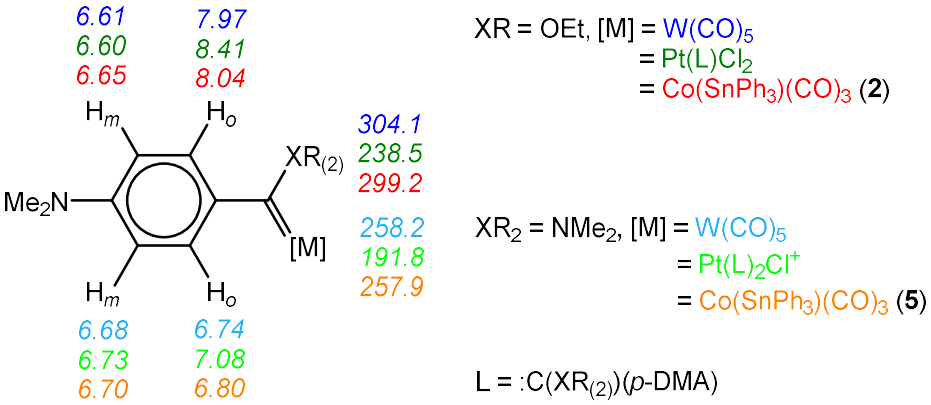

Fig. S13 ^{1}H and ^{13}C chemical shifts (ppm) of the H_o, H_m protons and carbene carbon atom, respectively for *p*-DMA carbene complexes of Co(I) (**2** and **5**), W(0) and Pt(II).

S2. FT-IR Spectra

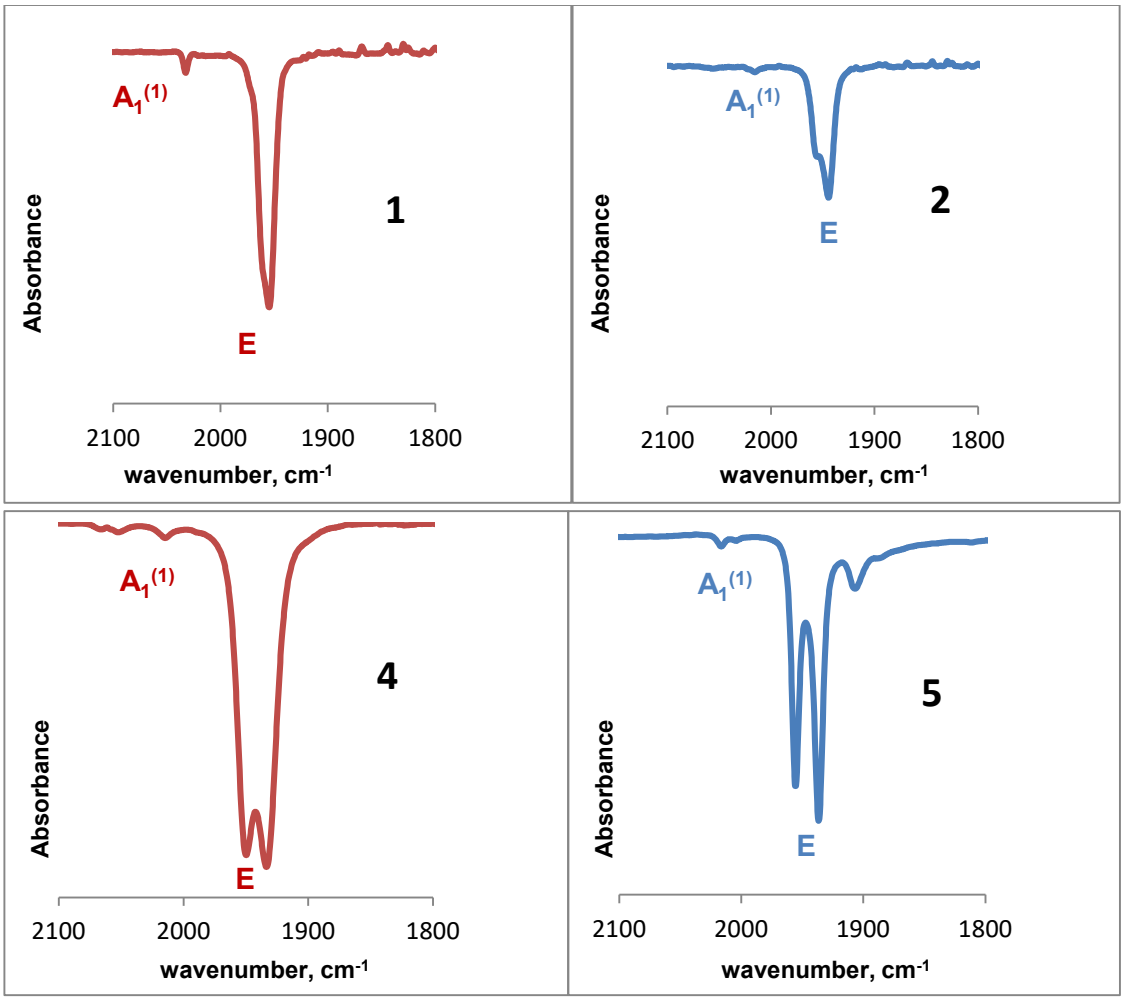

Fig. S14 Selected regions of the FT-IR spectra of **1**, **2**, **4** and **5** showing the carbonyl stretching vibrations

S3. Molecular structures, crystal data collection and structure refinement parameters

Table S1 Crystal data and structure refinement for complexes **1**, **2**, **4**–**6**

	1	**2**	**4**	**5**	**6**
Empirical formula	$C_{28}H_{23}CoO_4SSn$	$C_{28}H_{24}CoNO_3SSn$	$C_{32}H_{30}CoNO_4Sn$	$C_{103.88}H_{109.1}Cl_3Co_3N_{6.11}O_9Sn_3$	$C_{11.33}H_{12}Co_{0.33}INOSSn_{0.33}$
Formula weight	633.14	632.16	670.19	2226.39	237.43
Temperature/K	294(2)	173(2)	294(2)	173(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	P-1	$P2_1/c$	$P2_1/c$	P-1	P-1
a/Å	11.1220(8)	12.0248(4)	17.330(2)	11.4801(6)	11.4488(10)
b/Å	13.0137(9)	12.6795(4)	10.0232(13)	17.7989(9)	12.1620(12)
c/Å	20.5020(16)	17.7219(6)	18.8315(17)	24.9466(13)	12.7391(12)
α/°	102.525(2)	90	90	83.494(2)	81.979(3)
β/°	100.985(2)	102.947(2)	113.688(4)	82.941(2)	67.923(3)
γ/°	102.511(2)	90	90	89.901(2)	84.949(3)
Volume/Å^3	2738.8(3)	2633.34(15)	2995.6(6)	5025.8(5)	1626.4(3)
Z	4	4	4	2	6
ρ_{calc}g/cm^3	1.536	1.595	1.486	1.471	1.454
μ/mm^{-1}	1.624	1.687	1.423	1.356	1.315
F(000)	1264.0	1264.0	1352.0	2258.0	724.0
Crystal size/mm^3	0.484 × 0.099 × 0.078	0.258 × 0.196 × 0.118	0.373 × 0.228 × 0.139	0.372 × 0.184 × 0.098	0.432 × 0.319 × 0.076
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.376 to 52.822	6.108 to 55.998	4.378 to 54.41	4.606 to 52.744	5.022 to 49.424
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -25 ≤ l ≤ 25	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23	-22 ≤ h ≤ 22, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24	-14 ≤ h ≤ 14, -22 ≤ k ≤ 20, -31 ≤ l ≤ 31	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	108267	62985	105128	99671	40131
Independent reflections	11224 [R_{int} = 0.0424, R_{sigma} = 0.0260]	6345 [R_{int} = 0.0451, R_{sigma} = 0.0214]	6669 [R_{int} = 0.0426, R_{sigma} = 0.0166]	20545 [R_{int} = 0.0420, R_{sigma} = 0.0278]	5543 [R_{int} = 0.0318, R_{sigma} = 0.0182]
Data/restraints/	11224/74/696	6345/80/355	6669/0/366	20545/263/1199	5543/0/387

Parameters					
Goodness-of-fit on F^2	1.048	1.120	1.065	1.043	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0604	R_1 = 0.0239, wR_2 = 0.0552	R_1 = 0.0221, wR_2 = 0.0501	R_1 = 0.0490, wR_2 = 0.1197	R_1 = 0.0218, wR_2 = 0.0512
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.0709	R_1 = 0.0337, wR_2 = 0.0582	R_1 = 0.0303, wR_2 = 0.0538	R_1 = 0.0589, wR_2 = 0.1259	R_1 = 0.0253, wR_2 = 0.0530
Largest diff. peak/hole / e $Å^{-3}$	0.56/-0.43	0.34/-0.47	0.26/-0.41	3.07/-1.78	0.47/-0.33

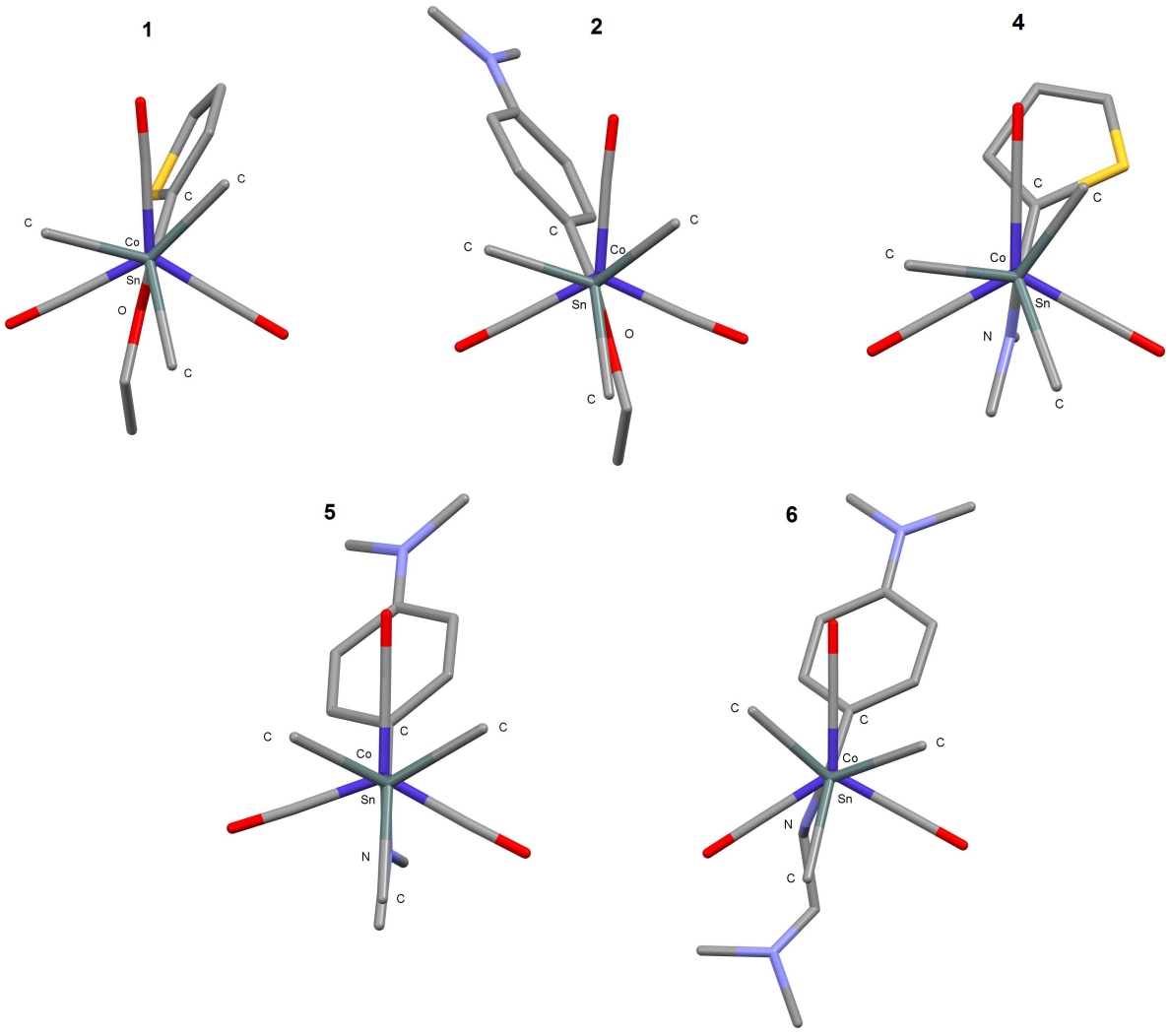

Fig. S15. Capped sticks model of **1**, **2**, **4**–**6** as viewed down the C_{carb}-Co-Sn axial axis showing the ethoxy/amino-, aromatic (hetero)ring-, as well as phenyl Sn substituents in their respective conformations with respect to the trigonal arrangement of the carbonyl ligands. Hydrogen and Sn-phenyl (except C_{ipso}) atoms are omitted for clarity.

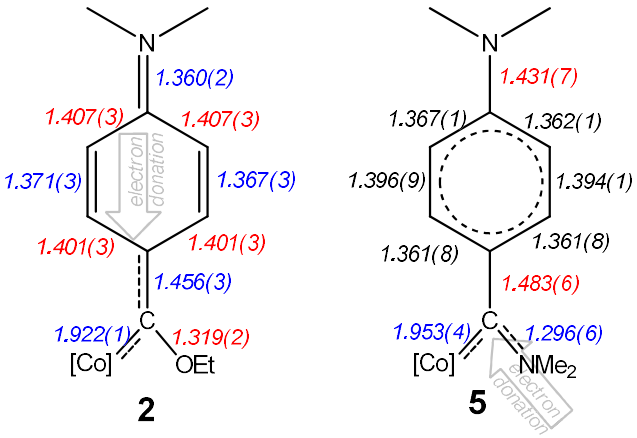

Fig. S16. The role of π-delocalisation in the DMA ring of the FCCs **2** and (long bonds (Å) in red, short bonds (Å) in blue)