Supporting Information

Synthesis and structures of hypervalent organoantimony and -bismuth chlorides containing asymmetric C,E,C-chelating (E = O, S) ligands

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Fig. S1 ^{1}H NMR spectrum of Compound **1**

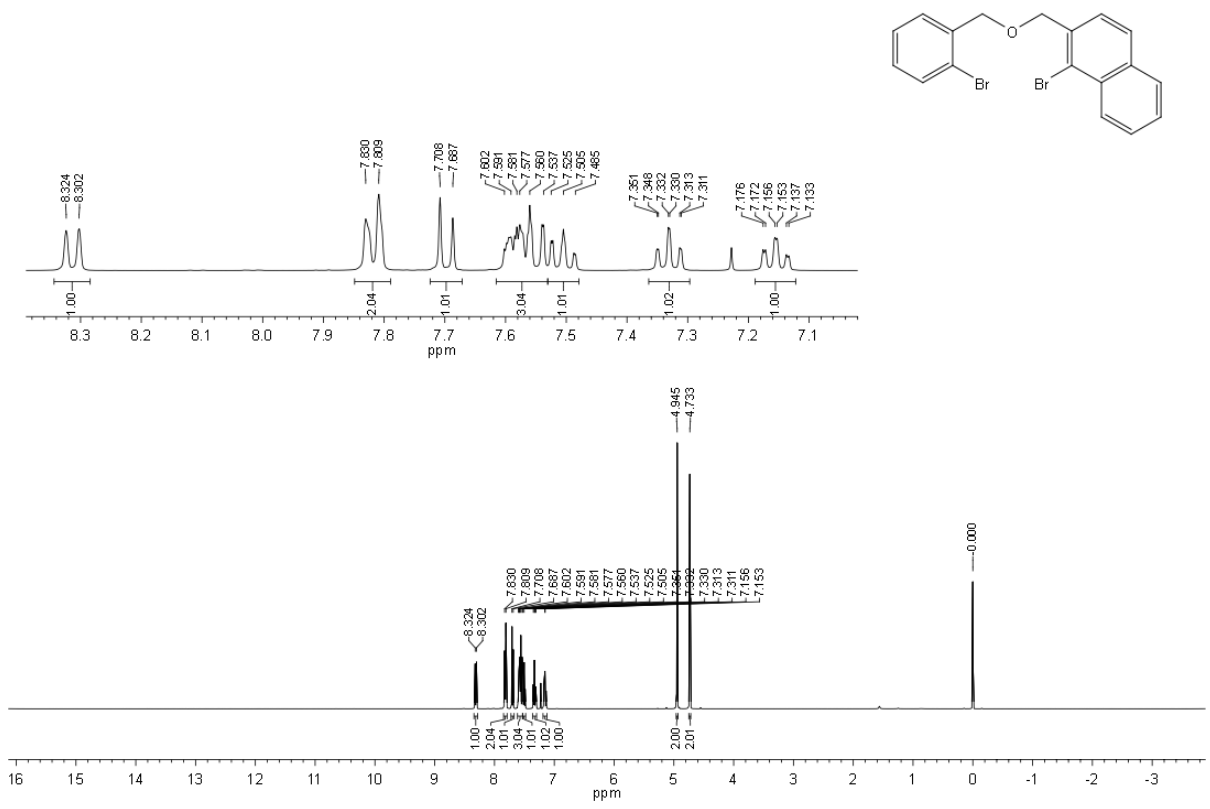

Fig. S2 ^{13}C NMR spectrum of Compound **1**

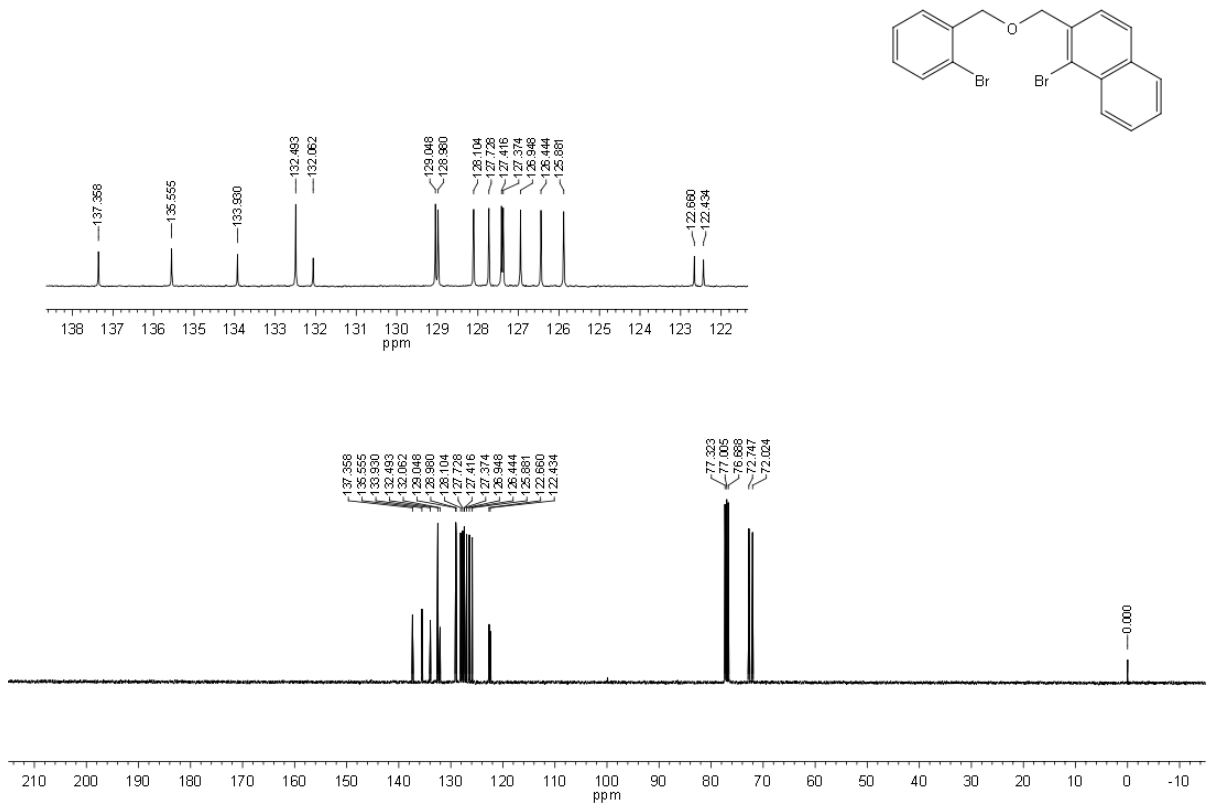

Fig. S3 ^{1}H NMR spectrum of Compound **2**

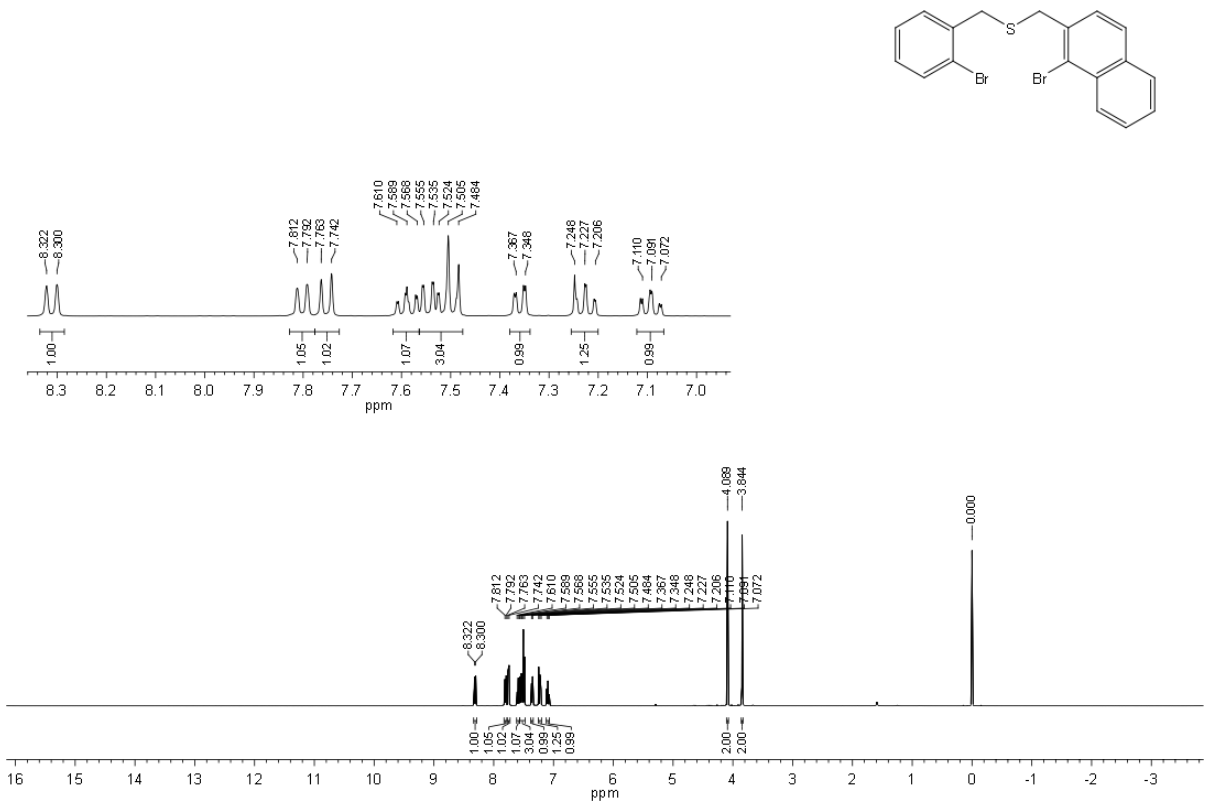

Fig. S4 ^{13}C NMR spectrum of Compound **2**

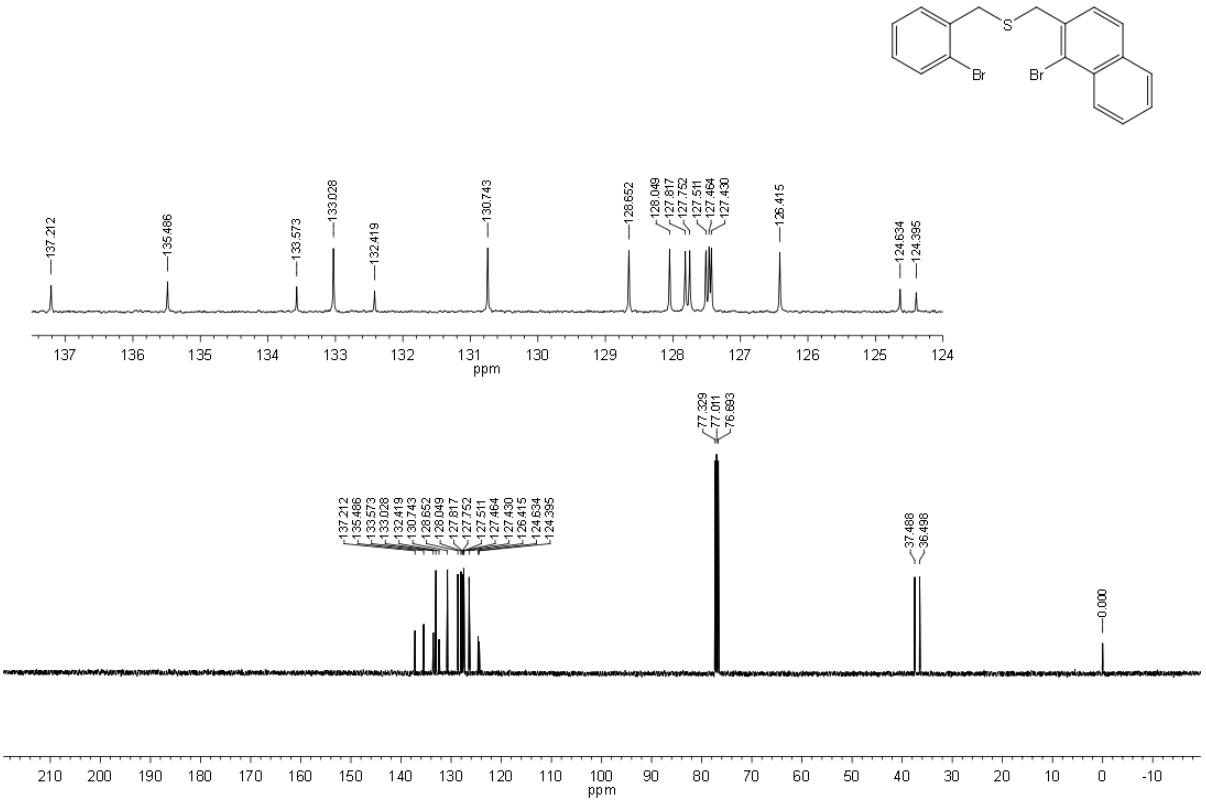

Fig. S5 ^{1}H NMR spectrum of Compound **3**

Fig. S6 ^{13}C NMR spectrum of Compound **3**

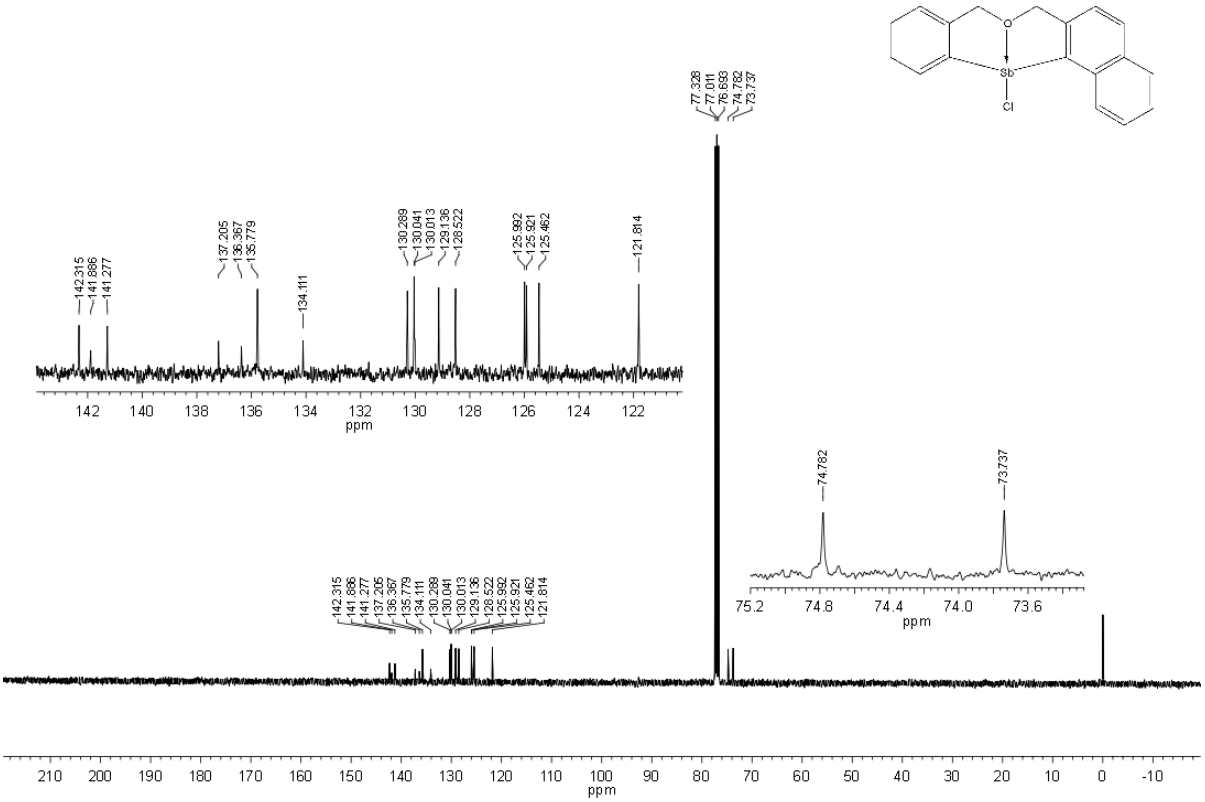

Fig. S7 ^{1}H NMR spectrum of Compound **4**

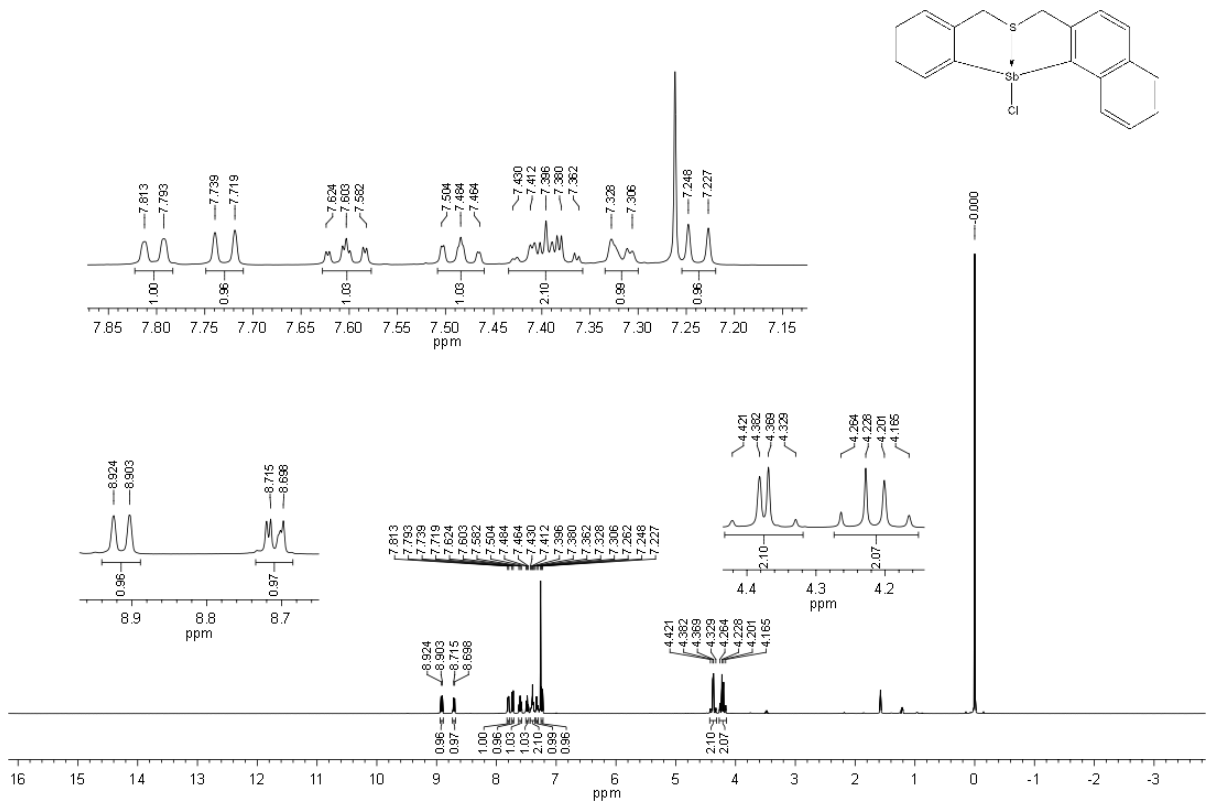

Fig. S8 ^{13}C NMR spectrum of Compound **4**

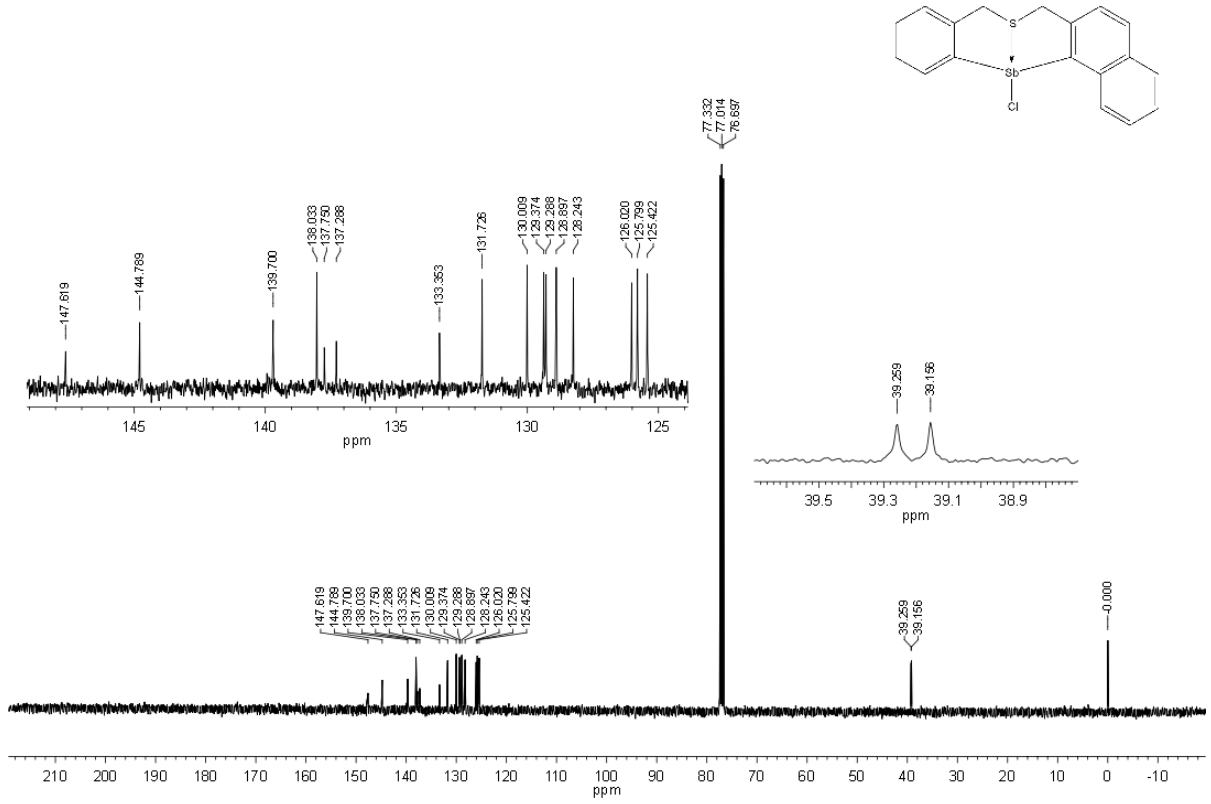

Fig. S9 ^{1}H NMR spectrum of Compound **5**

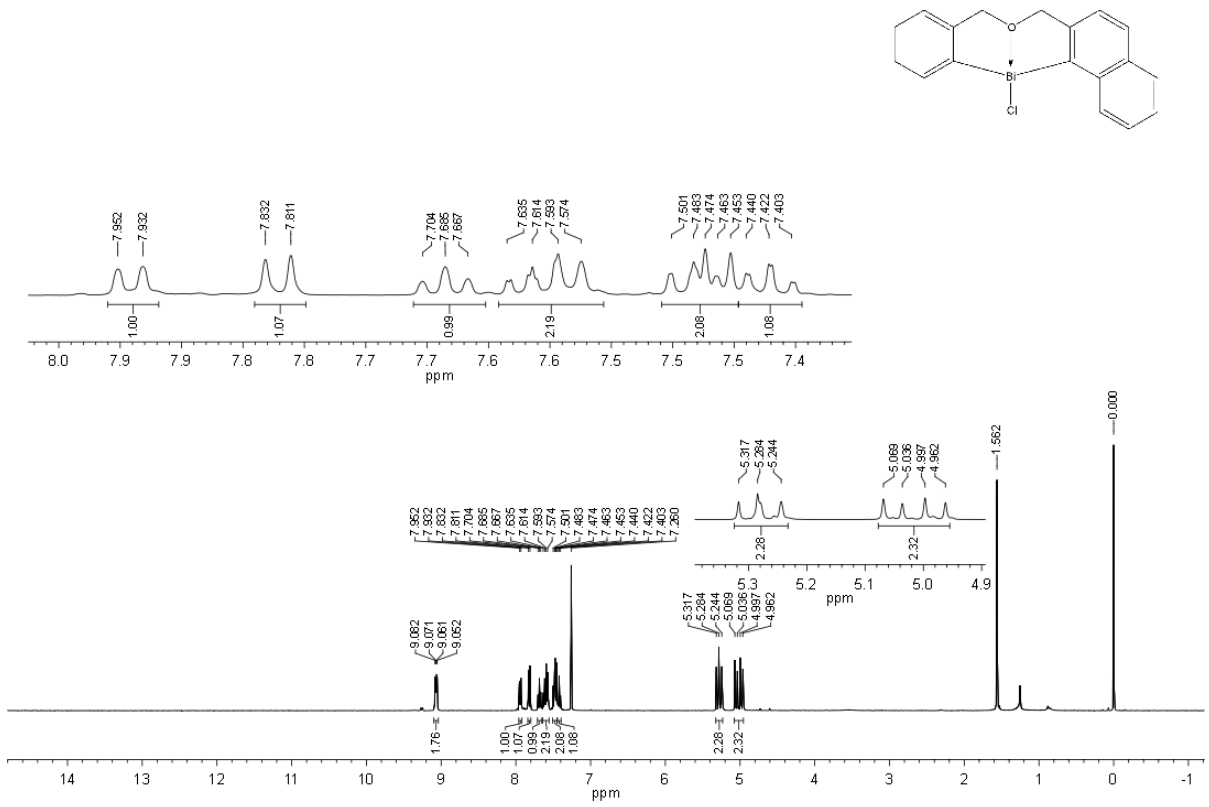

Fig. S10 ^{13}C NMR spectrum of Compound **5**

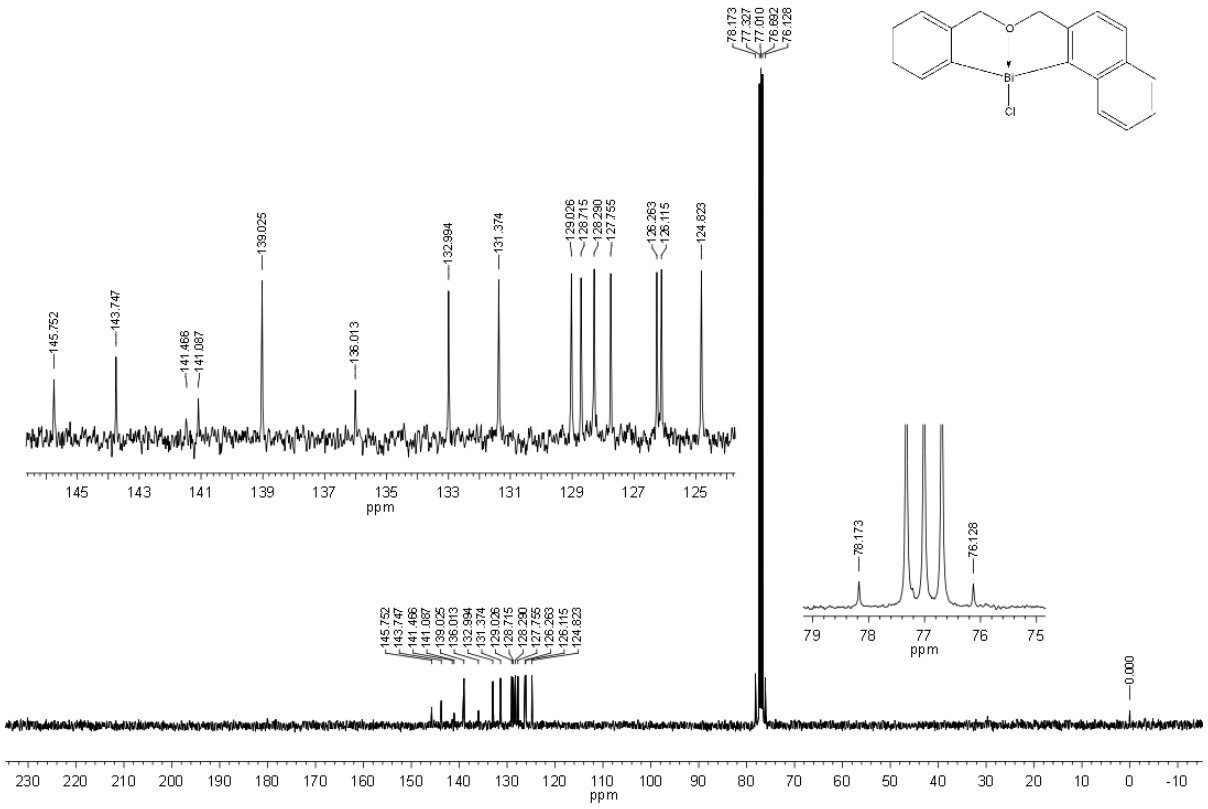

Fig. S11 ^{1}H NMR spectrum of Compound **6**

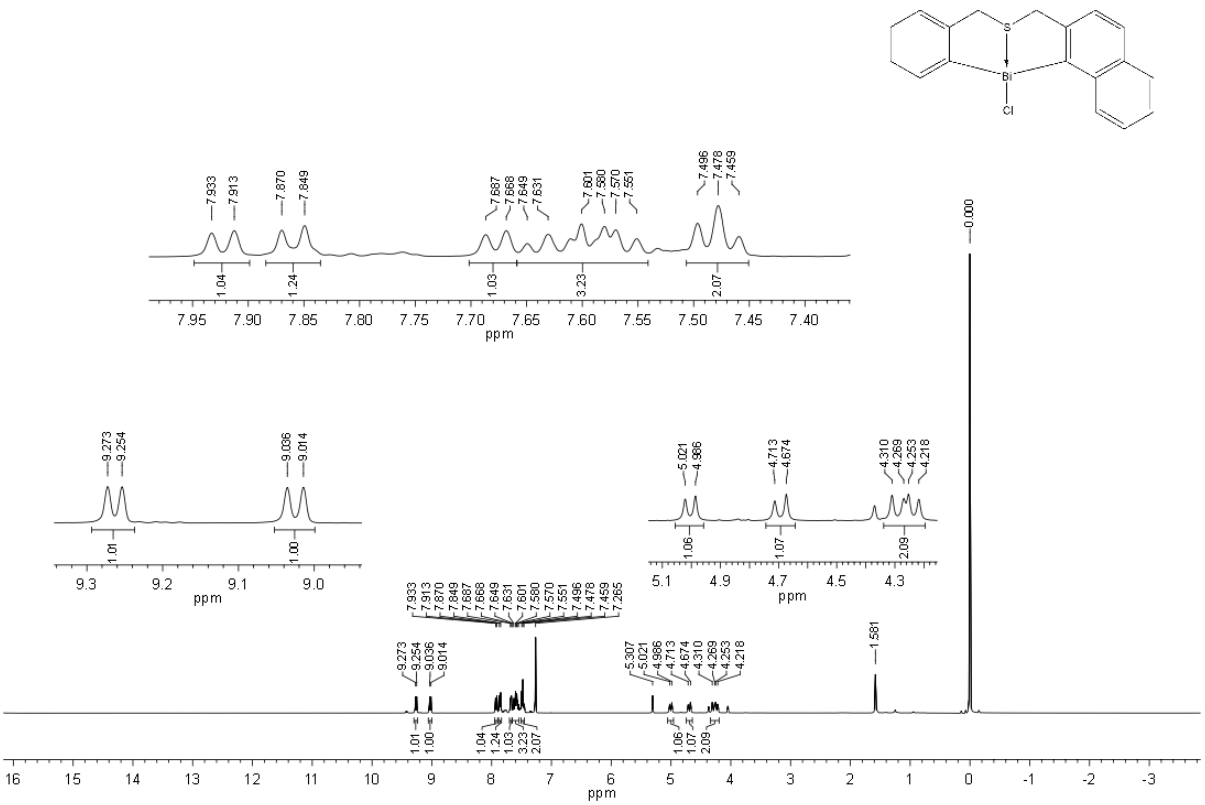

Fig. S12 ^{13}C NMR spectrum of Compound **6**

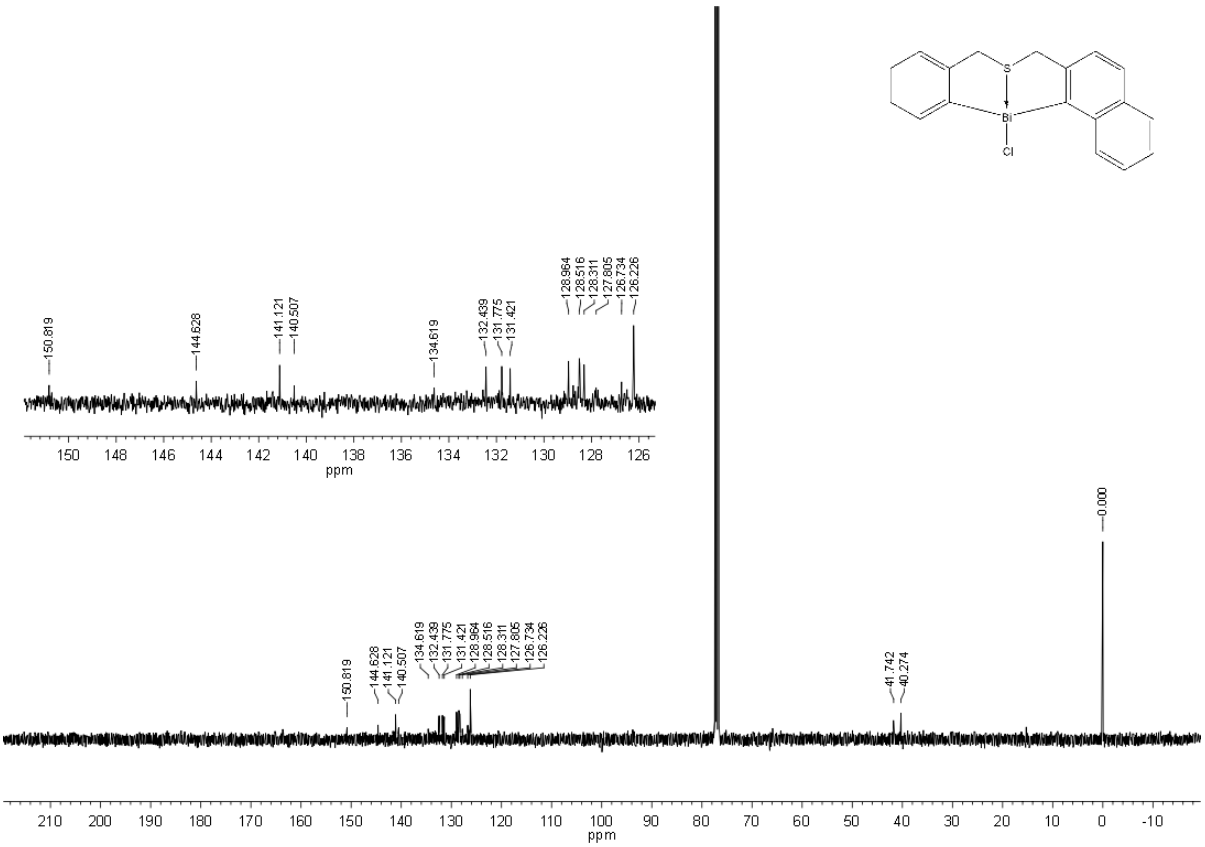

Table S1 Crystal data and structure refinement for compound **3**

Empirical formula	C18 H14 Cl O Sb
Formula weight	403.49
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	P2(1)/c
Unit cell dimensions	a = 11.7504(10) Å α= 90°
	b = 14.4272(12) Å β = 93.251(2)°
	c = 8.9688(8) Å γ = 90°
Volume	1518.0(2) Å ^{3}
Z	4
Density (Calculated)	1.766 Mg/m^3
Absorption coefficient	1.988 mm^{-1}
F(000)	792
Crystal size	0.368 × 0.279× 0.215 mm
Theta range for data collection	2.24 to 27.00 °
Limiting indices	-10<=h<=14, -18<=k<=16, -11<=l<=11
Reflections collected / unique	8803 / 3307 [R(int) = 0.1210]
Completeness to theta = 27.00	99.6 %
Absorption correction	Empirical
Max. and min. transmission	0.8109 and 0.6259
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3307 / 0 / 191
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1079
R indices (all data)	R1 = 0.0455, wR2 = 0.1108
Extinction coefficient	0.0179(11)
Largest diff. peak and hole	1.314 and -1.085 e. Å $^{-3}$

Table S2 Crystal data and structure refinement for compound **4**

Empirical formula	C18 H14 Cl S Sb
Formula weight	419.55
Temperature	293(2) K
Wavelength	0.71073
Crystal system	Monoclinic
space group	P2(1)/n
Unit cell dimensions	a = 11.4234(8) Å α = 90°
	b = 11.2183(8) Å β = 111.4280(10)°
	c = 13.3640(10) Å γ = 90°
Volume	1594.2(2) Å ^{3}
Z	4
Density (Calculated)	1.748 Mg/m^3
Absorption coefficient	2.019 mm^{-1}
F(000)	824
Crystal size	0.265 × 0.156 × 0.132 mm
Theta range for data collection	2.01 to 26.00 °
Limiting indices	-14<=h<=12, -13<=k<=13, -16<=l<=16
Reflections collected / unique	9412 / 3129 [R(int) = 0.0284]
Completeness to theta = 26.00	99.9 %
Absorption correction	Empirical
Max. and min. transmission	0.7765 and 0.6168
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3129 / 0 / 190
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0658
R indices (all data)	R1 = 0.0284, wR2 = 0.0672
Largest diff. peak and hole	1.009 and -0.497 e.Å ^{3}

Table S3 Crystal data and structure refinement for compound **5**

Empirical formula	C18 H14 Bi Cl O
Formula weight	490.72
Temperature	133(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
space group	Pna2(1)
Unit cell dimensions	a = 20.5263(19) Å α = 90°
	b = 15.8560(15) Å β = 90°
	c = 4.5578(4) Å γ = 90°
Volume	1483.4(2) Å ^{3}
Z	4
Density (Calculated)	2.197 Mg/m^3
Absorption coefficient	12.060 mm^{-1}
F(000)	920
Crystal size	0.28 × 0.20 × 0.10 mm
Theta range for data collection	1.62 to 26.99°
Limiting indices	-26<=h<=24, -20<=k<=20, -5<=l<=4
Reflections collected / unique	10320 / 3079 [R(int) = 0.0266]
Completeness to theta = 26.99	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3785 and 0.1332
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3079 / 1 / 190
Goodness-of-fit on F^2	0.965
Final R indices [I>2sigma(I)]	R1 = 0.0154, wR2 = 0.0354
R indices (all data)	R1 = 0.0190, wR2 = 0.0365
Absolute structure parameter	-0.006(6)
Largest diff. peak and hole	0.585 and -0.746 e.Å $^{-3}$

Table S4 Crystal data and structure refinement for compound **6**

Empirical formula	C18 H14 Bi Cl S	
Formula weight	506.78	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
space group	P2(1)/n	
Unit cell dimensions	a = 11.6940(12) Å	α = 90°
	b = 11.4596(12) Å	β = 110.526(2)°
	c = 12.4340(13) Å	γ = 90°
Volume	1560.5(3) $Å^3$	
Z	4	
Density (Calculated)	2.157 Mg/m^3	
Absorption coefficient	11.593 mm^{-1}	
F(000)	952	
Crystal size	0.311 × 0.165 × 0.112 mm	
Theta range for data collection	2.49 to 25.99°	
Limiting indices	-14<=h<=14, -11<=k<=14, -15<=l<=15	
Reflections collected / unique	9015 / 3063 [R(int) = 0.0852]	
Completeness to theta = 25.99	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.00000 and 0.06827	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3063 / 0 / 191	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1084	
R indices (all data)	R1 = 0.0552, wR2 = 0.1118	
Extinction coefficient	0.0004(3)	
Largest diff. peak and hole	2.790 and -2.783 e. .$Å^{-3}$	